RSC Advances

PAPER

Cite this: *RSC Adv.*, 2021, **11**, 10902

On-water synthesis of glycosyl selenocyanate derivatives and their application in the metal free organocatalytic preparation of nonglycosidic selenium linked pseudodisaccharide derivatives†

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Received 27th January 2021
Accepted 2nd March 2021

DOI: 10.1039/d1ra00711d

rsc.li/rsc-advances

Glycosyl selenocyanate derivatives were prepared in very good yield by the treatment of glycosyl halide or triflate derivatives with potassium selenocyanate in water. A variety of selenium linked pseudodisaccharide derivatives were prepared in excellent yield using glycosyl selenocyanates as stable building blocks in the presence of hydrazine hydrate under metal-free organocatalytic reaction conditions.

Introduction

In order to support the increasing interest in glycobiology research for the development of novel carbohydrate based therapeutics, a large number of oligo- and polysaccharides as well as a diverse range of glycomimetics have been synthesized in the recent past.[1–6] Pseudosugar derivatives (*e.g.* pseudodisaccharides) have been considered as useful glycomimetics for their use as stable enzyme inhibitors.[7] One of the important techniques for the preparation of glycomimetics is to exchange the interglycosidic oxygen atom with other heteroatoms such as nitrogen, sulphur, selenium, *etc.*[8–10] Due to their increased stability towards hydrolysis, a variety of thiosugars and thioglycosides have been prepared for their use in the biochemical investigations of the carbohydrate processing enzymes.[11–15] Organoselenium chemistry has become an important topic of research due to the unique chemical behaviour of Se-containing compounds and their pharmacological potential.[16–20] Although, selenium has been incorporated in different classes of molecules to improve their therapeutic index,[21] the introduction of selenium within the carbohydrate framework has received less attention except for a few reports which include the synthesis of anomeric selenoglycosides[22–27] and their application in the preparation of oligosaccharides,[28–30] glycal derivatives,[31] glycosyl fluorides,[32] C-glycosides[33] and medicinally useful compounds.[34] The synthesis of some cyclic sugar intermediates containing selenium in the ring has also been pursued.[35] In addition, some reports also appeared on the synthesis of non-glycosidically selenium linked pseudodisaccharide derivatives.[18a,21c,36,37] In most of the cases, elemental selenium, selenium oxide, selenourea or aryl selenol has been used as the source of selenium for its incorporation in the carbohydrate intermediates.[22–37] Dialkyl or diaryldiselenides have also been used under reductive reaction conditions to furnish selenoglycosides.[26,29] Obviously, there are several shortcomings associated with the above-mentioned reaction conditions such as use of obnoxious reagents, incompatibility of the base labile protecting groups, hazardous and special reaction conditions *etc.* Therefore, it is quite pertinent to develop reaction conditions avoiding earlier mentioned drawbacks. In the recent past, potassium *p*-methylselenobenzoate (KSeBz) has been successfully used as the selenium source in the preparation of several selenium containing carbohydrate derivatives.[22,27,37] KSeBz has been prepared using a multistep reaction sequence starting from elemental selenium.[22a] As an alternative, a straightforward reaction condition has been reported for the synthesis of selenium linked glycosides using glycosyl selenoacetate as stable building blocks, prepared by the treatment of glycosyl halides with commercially available potassium selenocyanate (KSeCN) in acetonitrile avoiding the prerequisite preparation of the selenating agent.[38] In a separate report, KSeCN has also been used as selenating agent for the preparation of unsymmetrical organoselenide and selenoglycosides.[27b] KSeCN has also been used as the selenating agent for the aqueous medium preparation di-alkyldiselenides.[39] In order to extend the use of KSeCN in the preparation of selenium incorporated carbohydrate derivatives, attempts were made to prepare stable glycosyl selenocyanate derivatives and their utilization in the preparation of selenium linked pseudodisaccharides. Cumpstey and co-worker reported the synthesis of several non-glycosidically selenoether linked pseudodisaccharide derivatives using KSeBz as selenating agent, involving multistep reaction sequence *via* the formation of diselenide derivatives.[37] Lüdtke and co-workers synthesized selenium linked neoglycoconjugates and pseudodisaccharides using lithium

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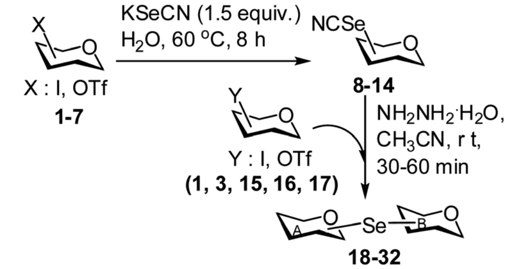
† Electronic supplementary information (ESI) available: Detailed analytical data of compounds **8–14** and **18–32**, copies of the NMR spectra. See DOI: 10.1039/d1ra00711d



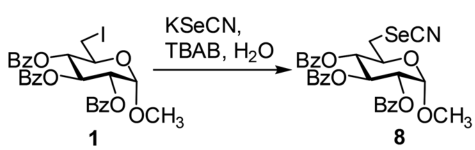
Scheme 1 Synthesis of glycosyl selenocyanate derivatives in aqueous medium and their utilization in the organocatalytic preparation of selenium linked pseudodisaccharide derivatives.

diselenide using multistep reaction sequence.[36a,b] Expensive selenourea has been used as selenating agent in some studies.[27b,36d] In this context, it would be beneficial to develop an environmentally benign aqueous reaction condition in the "Green chemistry" perspective for the preparation of glycosyl selenocyanate derivatives and their direct use in the synthesis of non-glycosidically selenoether linked pseudodisaccharide derivatives by the treatment of suitable glycosyl electrophiles. Inspired by the earlier studies[38,39] on the use of KSeCN as efficient selenylating agent, a straightforward on-water synthesis of stable glycosyl selenocyanate derivatives and their application in the selenoether linked pseudodisaccharide derivatives under a metal-free organocatalytic reaction condition is reported herein (Scheme 1).

Results and discussion

In order to optimize the reaction condition for the preparation of glycosyl selenocyanate derivative, methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-iodo-α-D-glucopyranoside (**1**) was treated with a varied quantity of KSeCN in the presence of tetrabutylammonium bromide (TBAB), a phase transfer catalyst (PTC) in water. The best yield of methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-selenato-α-D-glucopyranoside (**8**) was obtained in 76% by using 1.5 equiv. KSeCN and 0.1 equiv. TBAB in H_2O at 60 °C in 8 h. Reduction of the quantity of KSeCN and TBAB led to the incomplete reaction with low yield of product formation (Table 1). The reaction became sluggish at room temperature. The reaction did not proceed well in absence of TBAB and starting material decomposed under the reaction condition. Following the similar

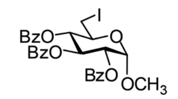
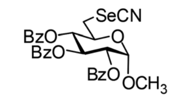
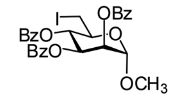
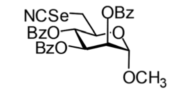
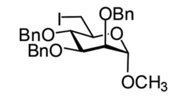
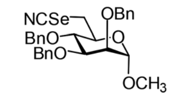
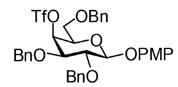
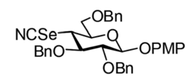
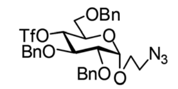
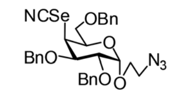
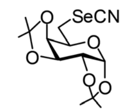
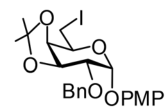
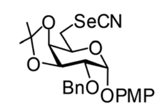
Table 1 Optimization of the formation of glycosyl selenocyanate derivatives in H_2O



Sl no.	KSeCN (equiv.)	TBAB (equiv.)	Time (h)	Temp. (°C)	Yield (%)
1	1.2	0.1	10	60	60
2	1.5	0.1	8	60	76
3	1.5	0.1	8	80	70
4	1.5	0.05	12	60	66
5	1.5	—	24	60	20[a]
6	1.5	0.1	24	RT	40

[a] Starting material decomposed.

Table 2 Synthesis of glycosyl selenocyanate derivatives using potassium selenocyanate and TBAB in H_2O at 60 °C

Sl no.	Starting material	Product	Time (h)	Yield (%)
1	 **1**	 **8**	8	76
2	 **2**	 **9**	8	72
3	 **3**	 **10**	8	78
4	 **4**	 **11**	6	65
5	 **5**	 **12**	6	62
6	 **6**	 **13**	8	78
7	 **7**	 **14**	8	72

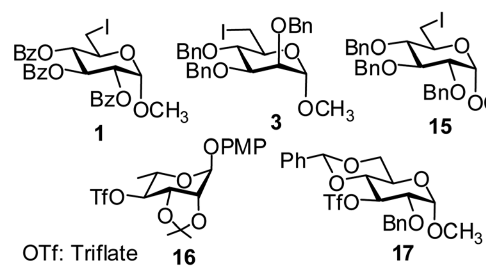
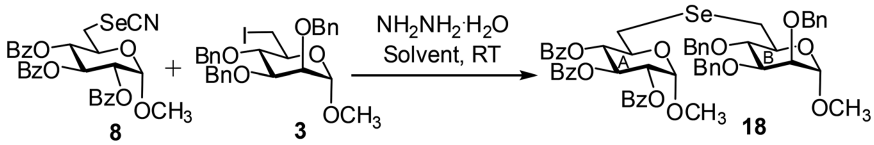


Fig. 1 Glycosyl iodide and triflate derivatives used as electrophiles for the preparation of non-glycosidically selenium linked pseudodisaccharide derivatives.

Table 3 Optimization of the reaction of glycosyl selenocyanate with sugar electrophile at room temperature



Sl no.	Comp. **8** (equiv.)	Comp. **3** (equiv.)	Base (equiv.)	Solvent	Time (min)	Yield (%)
1	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	DMF	45	74
2	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	DMF	60	75
3	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	CH_3CN	60	77
4	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	CH_3CN	45	70
5	1.0	1.2	$NH_2NH_2\cdot H_2O$ (3.0)	CH_3CN	60	70
6	1.0	1.2	$NH_2NH_2\cdot H_2O$ (2.0)	CH_3CN	60	68
7	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	THF	60	45
8	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	CH_3OH	60	25
9	1.0	1.2	$NH_2NH_2\cdot H_2O$ (4.0)	CH_2Cl_2	60	20
10	1.0	1.2	$NaBH_4$ (2.0)	CH_3CN	60	72
11	1.0	1.2	K_2CO_3 (2.0)	CH_3CN	60	—
12	1.0	1.2	Pyrrolidine (4.0)	CH_3CN	120	20
13	1.0	1.2	Pyrrolidine (4.0)	DMF	120	20
14	1.0	1.2	Diethylamine (4.0)	CH_3CN	120	10

reaction condition, a series of glycosyl selenocyanate derivatives (**8–14**) has been prepared in satisfactory yield under aqueous reaction conditions (Table 2). The products were characterized using NMR and mass spectral analysis.

Having a set of stable glycosyl selenocyanate derivatives, it was decided to develop a reaction condition for the preparation of nonglycosidically selenoether linked pseudodisaccharide derivatives by the reaction of glycosyl selenocyanate derivatives with appropriate electrophiles in the presence of an organocatalyst. For this purpose, a panel of sugar electrophiles have been selected, which are presented in Fig. 1.

Compound **8** was allowed to react with compound **3** in the presence of a number of base such as $NaBH_4$, K_2CO_3, hydrazine monohydrate, diethyl amine, piperidine in several organic solvents such as DMF, CH_3CN, THF, CH_3OH, CH_2Cl_2. After a number of experimentation it was observed that required pseudodisaccharide derivative **18** was formed in 77% yield using 1.0 equiv. of compound **8** and 1.2 equiv. of compound **3** in the presence of hydrazine monohydrate (4.0 equiv.) in CH_3CN at room temperature (Table 3). Use of less quantity of electrophile and hydrazine monohydrate resulted in the incomplete consumption of the selenocyanate derivative. Although the use of DMF and CH_3CN as reaction solvents comparable yields of the product **18** was obtained, CH_3CN has been chosen as the solvent in the generalized reaction condition. Among several bases used in the reaction, best yield of the product was obtained in the presence of hydrazine monohydrate as an organic base. Earlier, $NaBH_4$ has been used for the hydrolysis of the *in situ* generated organic selenocyanate derivatives followed by reduction of the diselenide derivatives for the preparation of unsymmetrical selenides.[40] Very recently, hydrazine hydrate has been used as a base cum reducing agent in the preparation unsymmetrical glycosyl disulfide derivatives.[41] In this study, similar reaction condition has been applied for the preparation of a series of nonglycosidically selenoether linked pseudodisaccharide derivatives (**18–32**) in excellent yield (Table 4). The products were unambiguously characterized using NMR and mass spectral analysis.

Experimental

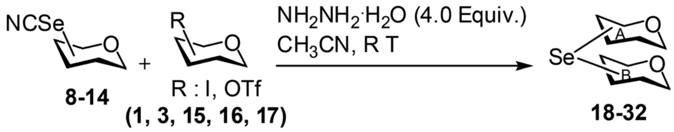
General methods

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

General procedure for the preparation of glycosyl selenocyanate derivatives (8–14). To a solution of glycosyl halide or triflate derivative (**1–7**) (1 mmol) in H_2O (5 mL) was added KSeCN (1.5 mmol) and the reaction mixture was allowed to stir at 60 °C for appropriate time mentioned in Table 1. After complete consumption of the starting material, the reaction mixture was diluted with H_2O (25 mL) and extracted with EtOAc (2 × 20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane–EtOAc as eluant to furnish pure product (**8–14**).

NMR spectral data of glycosyl selenocyanate derivatives (**8–14**):

Table 4 Preparation of selenium linked pseudodisaccharide derivatives using glycosyl selenocyanates in the presence of $NH_2NH_2 \cdot H_2O$ in CH_3CN at room temperature



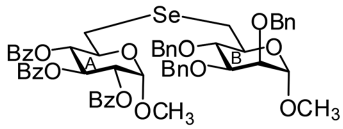
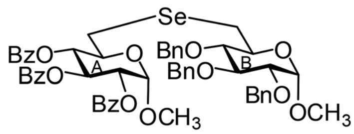
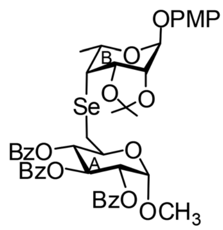
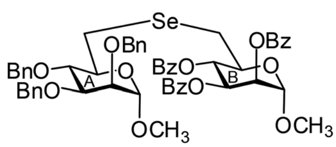
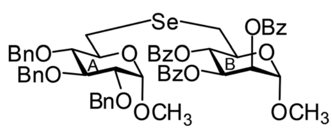
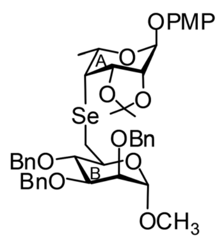
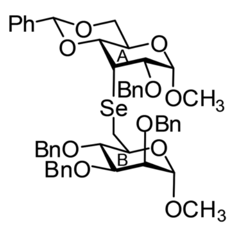
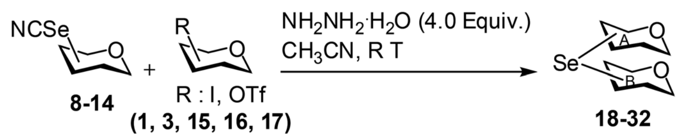
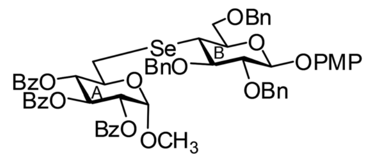
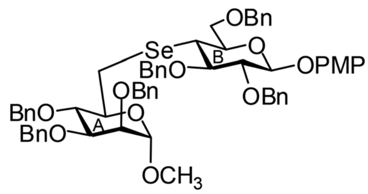
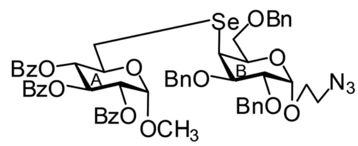
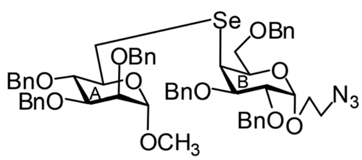
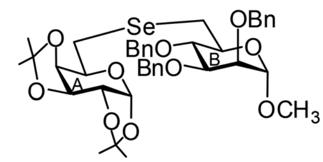
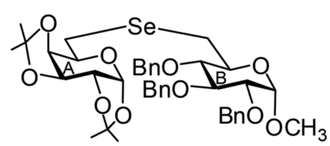
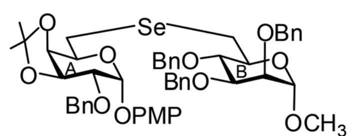
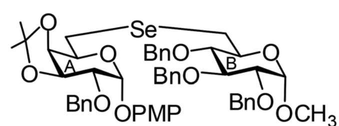
Sl no.	Glycosyl selenocyanate	Glycosyl electrophile	Se-linked pseudodisaccharide derivative	Time (h)	Yield (%)
1	**8**	**3**	 **18**	60	77
2	**8**	**15**	 **19**	60	74
3	**8**	**16**	 **20**	60	65
4	**9**	**3**	 **21**	60	72
5	**9**	**15**	 **22**	60	76
6	**10**	**16**	 **23**	45	68
7	**10**	**17**	 **24**	45	70

Table 4 (*Contd.*)



Sl no.	Glycosyl selenocyanate	Glycosyl electrophile	Se-linked pseudodisaccharide derivative	Time (h)	Yield (%)
8	**11**	**1**	 **25**	60	72
9	**11**	**3**	 **26**	60	70
10	**12**	**1**	 **27**	80	66
11	**12**	**3**	 **28**	80	68
12	**13**	**3**	 **29**	60	76
13	**13**	**15**	 **30**	60	78
14	**14**	**3**	 **31**	60	72
15	**14**	**15**	 **32**	60	70

*Methyl 2,3,4-tri-O-benzoyl-6-deoxy-6-selenocyanato-α-D-glucopyranoside (**8**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98–7.21 (m, 15H, Ar-H), 6.18 (t, J = 9.5 Hz, 1H, H-2), 5.41 (t, J = 10.0 Hz, 1H, H-3), 5.30–5.26 (m, 2H, H-1, H-4), 4.41–4.37 (m, 1H, H-5), 3.57 (s, 3H, OCH_3), 3.42 (dd, J = 12.5 Hz, 3.0 Hz, 1H, H-6$_a$), 3.31 (dd, J = 12.5 Hz, 8.0 Hz, 1H, H-6$_b$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 165.5 (3 PhCO), 133.8–128.3 (Ar-C), 101.3 (SeCN), 97.2 (C-1), 72.5 (C-5), 71.7 (C-2), 69.5 (C-3), 68.2 (C-4), 56.0 (OCH_3), 31.0 (C-6); HRMS for $C_{29}H_{25}NO_8Se$ $[M + H]^+$: calcd 596.0823; found: 596.0802.

*Methyl 2,3,4-tri-O-benzoyl-6-deoxy-6-selenocyanato-α-D-mannopyranoside (**9**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.16 (m, 15H, Ar-H), 5.85 (dd, J = 10.0 Hz, 3.0 Hz, 1H, H-3), 5.68 (t, J = 10.0 Hz, 1H, H-4), 5.58 (br s, 1H, H-2), 4.91 (s, 1H, H-1), 4.32–4.29 (m, 1H, H-5), 3.51 (s, 3H, OCH_3), 3.40 (dd, J = 12.5 Hz, 5.0 Hz, 1H, H-6$_a$), 3.28 (dd, J = 12.5 Hz, 8.0 Hz, 1H, H-6$_b$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 165.2, 165.1 (3 PhCO), 133.8–128.3 (Ar-C), 101.4 (SeCN), 98.8 (C-1), 70.3 (C-2), 70.2 (C-5), 69.1 (C-3), 69.0 (C-4), 55.9 (OCH_3), 31.4 (C-6); HRMS for $C_{29}H_{25}NO_8Se$ $[M + H]^+$: calcd 596.0823; found: 596.0805.

*Methyl 2,3,4-tri-O-benzyl-6-deoxy-6-selenocyanato-α-D-mannopyranoside (**10**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.14 (m, 15H, Ar-H), 4.85 (d, J = 11.5 Hz, 1H, PhCH), 4.60 (d, J = 12.0 Hz, 1H, PhCH), 4.54–4.50 (m, 3H, H-1, 2 PhCH), 4.46 (br s, 2H, 2 PhCH), 3.75 (dd, J = 8.5 Hz, 2.5 Hz, 1H, H-3), 3.70–3.66 (m, 2H, H-4, H-5), 3.64 (br s, 1H, H-2), 3.33 (dd, J = 11.5 Hz, 3.0 Hz, 1H, H-6$_a$), 3.19 (s, 3H, OCH_3), 3.03 (dd, J = 11.5 Hz, 7.0 Hz, 1H, H-6$_b$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–127.7 (Ar-C), 102.1 (SeCN), 99.3 (C-1), 80.0 (C-5), 77.4 (C-2), 75.2 ($PhCH_2$), 74.6 (C-3), 73.0, 72.1 (2 $PhCH_2$), 70.5 (C-4), 55.2 (OCH_3), 31.9 (C-6); HRMS for $C_{29}H_{31}NO_5Se$ $[M + H]^+$: calcd 554.1445; found: 554.1430.

*p-Methoxyphenyl-2,3,6-tri-O-benzyl-4-deoxy-4-selenocyanato-β-D-glucopyranoside (**11**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.31 (m, 15H, Ar-H), 7.04 (d, J = 9.0 Hz, 2H, Ar-H), 6.85 (d, J = 9.0 Hz, 2H, Ar-H), 5.13 (d, J = 11.0 Hz, 1H, PhCH), 5.04 (d, J = 10.0 Hz, 1H, PhCH), 4.95 (d, J = 8.0 Hz, 1H, H-1), 4.87–4.84 (m, 2H, 2 PhCH), 4.69 (d, J = 12.0 Hz, 1H, PhCH), 4.53 (d, J = 12.0 Hz, 1H, PhCH), 4.03 (dd, J = 11.5 Hz, 4.0 Hz, 1H, H-6$_a$), 3.92 (dd, J = 11.5 Hz, 7.0 Hz, 1H, H-6$_b$), 3.87–3.84 (m, 2H, H-2, H-5), 3.81 (s, 3H, OCH_3), 3.78 (t, J = 8.0 Hz, 1H, H-3), 3.41 (t, J = 10.5 Hz, 1H, H-4); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6–114.6 (Ar-C), 102.7 (C-1), 99.1 (SeCN), 83.4 (C-3), 81.2 (C-5), 76.4, 75.1 (2 $PhCH_2$), 75.0 (C-2), 73.6 ($PhCH_2$), 69.0 (C-6), 55.5 (OCH_3), 46.3 (C-4); HRMS for $C_{35}H_{35}NO_6Se$ $[M + H]^+$: calcd 646.1708; found: 646.1690.

*2-Azidoethyl-2,3,6-tri-O-benzyl-4-deoxy-4-selenocyanato-β-D-galactopyranoside (**12**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.24 (m, 15H, Ar-H), 4.79 (d, J = 12.0 Hz, 2H, 2 PhCH), 4.65 (d, J = 4.0 Hz, 1H, H-1), 4.61 (d, J = 12.0 Hz, 1H, PhCH), 4.59 (d, J = 12.0 Hz, 1H, PhCH), 4.56 (d, J = 12.0 Hz, 1H, PhCH), 4.51 (d, J = 12.0 Hz, 1H, PhCH), 4.27–4.23 (m, 2H, H-4, H-5), 4.04 (dd, J = 9.5 Hz, 4.0 Hz, 1H, H-2), 3.75–3.70 (m, 1H, OCH), 3.61 (d, J = 6.0 Hz, 2H, H-6$_{ab}$), 3.57 (dd, J = 9.5 Hz, 3.0 Hz, 1H, H-3), 3.52–3.48 (m, 1H, OCH), 3.45–3.41 (m, 1H, NCH), 3.34–3.32 (m, 1H, NCH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–127.9 (Ar-C), 101.5 (SeCN), 98.0 (C-1), 76.8 (C-3), 76.1 (C-2), 73.7, 73.6, 72.4 (3 $PhCH_2$), 70.5 (C-6), 67.8 (C-5), 67.2 (OCH_2), 54.8 (C-4), 50.5 (NCH_2); HRMS for $C_{30}H_{32}N_4O_5Se$ $[M + H]^+$: calcd 609.1616; found: 609.1597.

*1,2:3,4-Di-O-isopropylidene-6-deoxy-6-selenocyanato-α-D-galactopyranose (**13**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44 (d, J = 5.0 Hz, 1H, H-1), 4.58 (dd, J = 8.0 Hz, 2.5 Hz, 1H, H-3), 4.26–4.25 (m, 1H, H-4), 4.20 (dd, J = 8.0 Hz, 1.5 Hz, 1H, H-2), 4.01–3.99 (m, 1H, H-5), 3.30 (dd, J = 12.0 Hz, 8.0 Hz, 1H, H-6$_a$), 3.17 (dd, J = 12.0 Hz, 5.0 Hz, 1H, H-6$_b$), 1.15 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.27 (s, 6H, 2 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 109 8, 109.1 (2 $C(CH_3)_2$), 102 0 (SeCN), 96.4 (C-1), 72.0 (C-3), 70.9 (C-4), 70.3 (C-2), 66.6 (C-5), 29.2 (C-6), 26.0, 25.9, 24.9, 24.3 (4 CH_3); HRMS for $C_{13}H_{19}NO_5Se$ $[M + H]^+$: calcd 350.0506; found: 350.0487.

*p-Methoxyphenyl-2-O-benzyl-3,4-O-isopropylidene-6-deoxy-6-selenocyanato-α-D-galactopyranoside (**14**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.15 (m, 5H, Ar-H), 6.91 (d, J = 8.5 Hz, 2H, Ar-H), 6.73 (d, J = 8.5 Hz, 2H, Ar-H), 5.26 (d, J = 3.5 Hz, 1H, H-1), 4.70 (d, J = 10 Hz, 1H, PhCH), 4.66 (d, J = 12.5 Hz, 1H, PhCH), 4.43 (t, J = 6.0 Hz, 1H, H-2), 4.29–4.28 (m, 1H, H-5), 4.15–4.14 (m, 1H, H-4), 3.65 (s, 3H, OCH_3), 3.54–3.52 (m, 1H, H-3), 3.36 (dd, J = 12.0 Hz, 8.5 Hz, 1H, H-6$_a$), 3.14 (dd, J = 12.5 Hz, 5.0 Hz, 1H, H-6$_b$), 1.31 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3–114.6 (Ar-C), 109 7 ($C(CH_3)_2$), 102 0 (SeCN), 96.5 (C-1), 75.7 (C-3), 75.6 (C-4), 74.2 (C-5), 72.5 ($PhCH_2$), 67.2 (C-2), 55.5 (OCH_3), 29.6 (C-6), 27.9, 26.3 (2 CH_3); HRMS for $C_{24}H_{27}NO_6Se$ $[M + H]^+$: calcd 506.1082; found: 506.1065.

General reaction condition for the preparation of non-glycosidically Se-linked pseudodisaccharides (18–32). To a solution of glycosyl selenocyanate derivative (**8–14**; 1.0 mmol) in anhydrous CH_3CN (5 mL) was added glycosyl halide/triflate derivate (1.2 mmol) followed by $NH_2NH_2 \cdot H_2O$ (4.0 mmol) and allowed to stir the reaction mixture at room temperature for appropriate time as mentioned in Table 2. The reaction mixture was diluted with H_2O (25 mL) and extracted with EtOAc (2 × 20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane–EtOAc as eluant to furnish pure product (**18–32**).

NMR spectral data of Se-linked pseudodisaccharide derivatives (**18–32**):

*(Methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-glucopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl) selenide (**18**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.28 (m, 30H, Ar-H), 6.16 (t, J = 10 Hz, 1H, H-4$_A$), 5.48 (t, J = 10.0 Hz, 1H, H-3$_A$), 5.28 (dd, J = 10.5 Hz, 3.5 Hz, 1H, H-2$_A$), 5.17 (d, J = 3.5 Hz, 1H, H-1$_A$), 4.99 (d, J = 11.0 Hz, 1H, PhCH), 4.68–4.65 (m, 3H, 3 PhCH), 4.61 (s, 2H, 2 PhCH), 4.59 (br s, 1H, H-1$_B$), 4.30–4.26 (m, 1H, H-5$_A$), 3.83–3.75 (m, 3H, H-3$_B$, H-4$_B$, H-5$_B$), 3.57 (d, J = 5.0 Hz, 1H, H-2$_B$), 3.50 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.11 (d, J = 11.5 Hz, 1H, H-6$_{aA}$), 2.98–2.91 (m, 2H, H-6$_{bA}$, H-6$_{aB}$), 2.89–2.82 (m, 1H, H-6$_{bB}$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 165.6, 165.3 (3 PhCO), 138.5–127.5 (Ar-C), 98.7 (C-1$_B$), 96.7 (C-1$_A$), 80.1 (C-5$_B$), 78.5 (C-2$_B$), 75.2 ($PhCH_2$), 74.5 (C-5$_A$), 73.1 (C-2$_A$), 73.0 (C-3$_A$), 72.5 ($PhCH_2$), 72.2 (C-3$_B$), 72.0 ($PhCH_2$), 70.5 (C-4$_A$), 70.3 (C-4$_B$), 55.5, 54.6 (2 OCH_3), 26.8 (C-6$_B$), 25.4 (C-

6_A); HRMS for $C_{56}H_{56}O_{13}Se$ [M + H]$^+$: calcd 1017.2964; found: 1017.2946.

*(Methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-glucopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-glucopyranosid-6-yl) selenide (**19**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.25 (m, 30H, Ar-H), 6.13 (t, J = 10.0 Hz, 1H, H-4_A), 5.45 (t, J = 10.0 Hz, 1H, H-3_A), 5.27 (dd, J = 10.5 Hz, 3.5 Hz, 1H, H-2_A), 5.14 (d, J = 3.5 Hz, 1H, H-1_A), 4.98 (d, J = 11.0 Hz, 1H, PhC*H*), 4.92 (d, J = 11.0 Hz, 1H, PhC*H*), 4.81 (d, J = 11.0 Hz, 1H, PhC*H*), 4.73 (d, J = 12.0 Hz, 1H, PhC*H*), 4.64 (d, J = 12.5 Hz, 2H, 2 PhC*H*), 4.48 (d, J = 3.5 Hz, 1H, H-1_B), 4.26–4.22 (m, 1H, H-5_A), 3.95 (t, J = 9.0 Hz, 1H, H-4_B), 3.83–3.80 (m, 1H, H-5_B), 3.49 (s, 3H, OC*H*$_3$), 3.47–3.45 (m, 1H, H-2_B), 3.36 (s, 3H, OC*H*$_3$), 3.34 (t, J = 9.0 Hz, H-3_B), 3.03 (d, J = 12.5 Hz, 1H, H-6_{aA}), 2.86 (d, J = 5.5 Hz, 2H, H-6_{abB}), 2.73 (dd, J = 12.5 Hz, 5.0 Hz, 1H, H-6_{bA}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 165.6, 165.3 (3 Ph*C*O), 138.7–127.5 (Ar-C), 97.6 (C-1_A), 96.8 (C-1_B), 81.8 (C-3_A), 81.4 (C-4_A), 80.1 (C-2_B), 75.6, 75.1, 73.1 (3 Ph*C*H$_2$), 72.9 (C-5_B), 72.1 (C-2_A), 71.5 (C-5_A), 70.6 (C-3_B), 70.2 (C-4_B), 55.5, 55.0 (2 O*C*H$_3$), 26.8 (C-6_A), 25.6 (C-6_B); HRMS for $C_{56}H_{56}O_{13}Se$ [M + H]$^+$: calcd 1017.2964; found: 1017.2945.

*(Methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-glucopyranosid-6-yl)-(p-methoxyphenyl 2,3-O-isopropylidene-4,6-di-deoxy-α-L-talopyranosid-4-yl)selenide (**20**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.11 (m, 15H, Ar-H), 6.87 (d, J = 6.5 Hz, 2H, Ar-H), 6.79 (d, J = 6.5 Hz, 2H, Ar-H), 5.93 (t, J = 7.0 Hz, 1H, H-3_B), 5.55 (s, 1H, H-1_A), 5.09 (t, J = 7.0 Hz, 1H, H-4_B), 5.03 (d, J = 1.5 Hz, 1H, H-1_B), 5.01 (d, J = 2.5 Hz, 1H, H-2_B), 4.71 (d, J = 4.0 Hz, 1H, H-2_A), 4.69 (dd, J = 4.0 Hz, 1.0 Hz, 1H, H-3_A), 4.21 (dd, J = 6.0 Hz, 1.5 Hz, 1H, H-4_A), 4.04–4.00 (m, 1H, H-5_B), 3.70 (s, 3H, OC*H*$_3$), 3.37 (s, 3H, OC*H*$_3$), 3.18–3.16 (m, 1H, H-5_A), 2.78 (dd, J = 9.5 Hz, 6.5 Hz, 1H, H-6_{aB}), 2.63 (d, J = 9.5 Hz, 1.5 Hz, 1H, H-6_{bB}), 1.46 (s, 3H, C*H*$_3$), 1.34 (d, J = 7.0 Hz, 3H, CC*H*$_3$), 1.29 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 165.2 (3 Ph*C*O), 154.7–112.9 (Ar-C), 106.5 (*C*(CH$_3$)$_2$), 96.6 (C-1_B), 93.1 (C-1_A), 85.7 (C-3_B, C-5_A), 81.8 (C-5_B), 72.9 (C-2_B), 72.1 (C-4_B), 70.9 (C-2_A), 70.2 (C-3_A), 55.4, 55.3 (2 O*C*H$_3$), 38.0 (C-4_A), 29.7 (C-6_B), 26.8, 25.3 (2 *C*H$_3$), 17.9 (C*C*H$_3$); HRMS for $C_{44}H_{46}O_{13}Se$ [M + H]$^+$: calcd 863.2182; found: 863.2165.

*(Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-mannopyranosid-6-yl)selenide (**21**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.11 (m, 30H, Ar-H), 5.74–5.68 (m, 2H, H-3_B, H-4_B), 5.54 (s, 1H, H-2_B), 4.81 (d, J = 11.0 Hz, 1H, PhC*H*), 4.76 (s, 1H, H-1_B), 4.53 (s, 2H, 2 PhC*H*), 4.50 (d, J = 11.0 Hz, 1H, PhC*H*), 4.45 (s, 2H, 2 PhC*H*), 4.44 (s, 1H, H-1_A), 4.17–4.14 (m, 1H, H-5_A), 3.68–3.61 (m, 4H, H-2_A, H-3_A, H-4_A, H-5_B), 3.40 (s, 3H, OC*H*$_3$), 3.17 (s, 3H, OC*H*$_3$), 3.00 (d, J = 7.5 Hz, 1H, H-6_{aA}), 2.91–2.81 (m, 2H, H-6_{aB}, H-6_{bA}), 2.70–2.66 (m, 1H, H-6_{bB}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 165.4, 165.3 (3 Ph*C*O), 138.5–127.5 (Ar-C), 98.7 (C-1_A), 98.5 (C-1_B), 80.1 (C-5_A), 78.5 (C-2_A), 75.1 (Ph*C*H$_2$), 74.6 (C-3_A), 73.0 (C-2_B), 72.5, 72.0 (2 Ph*C*H$_2$), 71.4 (C-5_B), 70.8 (C-3_B), 70.6 (C-4_B), 69.9 (C-4_A), 55.4, 54.6 (2 O*C*H$_3$), 26.7 (C-6_A), 25.7 (C-6_B); HRMS for $C_{56}H_{56}O_{13}Se$ [M + H]$^+$: calcd 1017.2964; found: 1017.2945.

*(Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-glucopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-mannopyranosid-6-yl) selenide (**22**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.10 (m, 30H, Ar-H), 5.72–5.67 (m, 2H, H-3_B, H-4_B), 5.54 (s, 1H, H-2_B), 4.86 (d, J = 11.0 Hz, 1H, PhC*H*), 4.76–4.74 (m, 2H, H-1_B, PhC*H*), 4.68 (d, J = 11.0 Hz, 1H, PhC*H*), 4.61 (d, J = 11.0 Hz, 1H, PhC*H*), 4.51 (t, J = 11.5 Hz, 2H, 2 PhC*H*), 4.36 (d, J = 3.0 Hz, 1H, H-1_A), 4.16–4.13 (m, 1H, H-5_B), 3.83 (t, J = 9.0 Hz, 1H, H-4_A), 3.71–3.68 (m, 1H, H-5_A), 3.41 (s, 3H, OC*H*$_3$), 3.35 (dd, J = 9.5 Hz, 3.0 Hz, 1H, H-2_A), 3.21 (s, 3H, OC*H*$_3$), 3.19 (t, J = 9.0 Hz, 1H, H-3_A), 2.94 (dd, J = 12.5 Hz, 2.0 Hz, 1H, H-6_{aB}), 2.82–2.80 (m, 2H, H-6_{abA}), 2.59 (dd, J = 12.5 Hz, 8.5 Hz, 1H, H-6_{bB}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 165.4, 165.3 (3 Ph*C*O), 138.7–127.5 (Ar-C), 98.4 (C-1_A), 97.6 (C-1_B), 81.8 (C-3_A), 81.4 (C-5_A), 80.1 (C-2_A), 75.6, 75.0, 73.2 (3 Ph*C*H$_2$), 71.4 (C-2_B), 71.3 (C-5_B), 70.7 (C-3_B), 70.5 (C-4_B), 69.8 (C-4_A), 55.4, 55.1 (2 O*C*H$_3$), 26.7 (C-6_B), 26.0 (C-6_A); HRMS for $C_{56}H_{56}O_{13}Se$ [M + H]$^+$: calcd 1017.2964; found: 1017.2946.

*(Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl)-(p-methoxyphenyl 2,3-O-isopropylidene-4,6-di-deoxy-α-L-talopyranosid-4-yl)selenide (**23**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.19 (m, 15H, Ar-H), 6.91 (d, J = 9.0 Hz, 2H, Ar-H), 6.70 (d, J = 9.0 Hz, 2H, Ar-H), 5.57 (s, 1H, H-1_A), 4.75–4.72 (m, 2H, 2 PhC*H*), 4.69–4.63 (m, 2H, 2 PhC*H*), 4.54–4.52 (m, 3H, H-1_B, 2 PhC*H*), 3.79–3.69 (m, 5H, H-3_A, H-4_A, H-3_B, H-4_B, H-5_B), 3.62 (s, 3H, OC*H*$_3$), 3.60–3.58 (m, 2H, H-2_A, H-2_B), 3.23 (s, 3H, OC*H*$_3$), 3.15–3.13 (m, 1H, H-5_A), 2.87 (d, J = 13.0 Hz, 1H, H-6_{aB}), 2.64–2.60 (m, 1H, H-6_{bB}), 1.47 (s, 3H, C*H*$_3$), 1.38 (d, J = 7.0 Hz, 3H, CC*H*$_3$), 1.30 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6–112.8 (Ar-C), 107.0 (*C*(CH$_3$)$_2$), 98.8 (C-1_B), 92.1 (C-1_A), 86.0 (C-3_B), 81.9 (C-5_B), 80.2 (C-2_B, C-5_A), 78.7 (C-4_B), 75.1 (Ph*C*H$_2$), 74.8 (C-2_A), 72.9 (C-3_A), 72.7 (Ph*C*H$_2$), 72.0 (Ph*C*H$_2$), 55.4, 54.7 (2 O*C*H$_3$), 37.8 (C-4_A), 26.9, 25.4 (2 *C*H$_3$), 25.3 (C-6_B), 18.4 (C*C*H$_3$); HRMS for $C_{44}H_{52}O_{10}Se$ [M + H]$^+$: calcd 821.2804; found: 821.2785.

*(Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl)-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-allopyranosid-3-yl)selenide (**24**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.10 (m, 25H, Ar-H), 5.43 (s, 1H, PhC*H*), 4.75 (d, J = 8.0 Hz, 1H, PhC*H*), 4.69 (d, J = 8.0 Hz, 1H, PhC*H*), 4.65 (d, J = 8.0 Hz, 1H, PhC*H*), 4.60 (d, J = 8.0 Hz, 1H, PhC*H*), 4.54 (s, 1H, H-1_B), 4.54 (d, J = 8.0 Hz, 1H, PhC*H*), 4.50 (d, J = 2.0 Hz, 1H, H-1_A), 4.46 (s, 2H, 2 PhC*H*), 4.27 (d, J = 8.0 Hz, 1H, PhC*H*), 4.19–4.15 (m, 2H, H-4_A, H-5_B), 3.83–3.82 (m, 1H, H-5_A), 3.66–3.57 (m, 5H, H-2_A, H-2_B, H-3_B, H-6_{abA}), 3.51–3.46 (m, 2H, H-3_A, H-4_B), 3.31 (s, 3H, OC*H*$_3$), 3.18 (s, 3H, OC*H*$_3$), 2.99 (dd, J = 9.0 Hz, 1.5 Hz, 1H, H-6_{aB}), 2.82–2.75 (dd, J = 9.0 Hz, 3.5 Hz, 1H, H-6_{bB}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8–126.3 (Ar-C), 101.4 (Ph*C*H), 98.8 (C-1_A), 98.3 (C-1_B), 80.0 (C-5_B), 79.7 (C-2_B), 79.4 (C-2_A), 75.1 (Ph*C*H$_2$), 75.0 (C-4_A), 74.1 (C-4_B), 72.8 (Ph*C*H$_2$), 72.7 (C-3_B), 72.1 (Ph*C*H$_2$), 70.1 (Ph*C*H$_2$), 69.0 (C-6_A), 59.9 (C-5_A), 55.0, 54.8 (2 O*C*H$_3$), 43.6 (C-3_A), 28.6 (C-6_B); HRMS for $C_{49}H_{54}O_{10}Se$ [M + H]$^+$: calcd 883.2960; found: 883.2943.

*(Methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-glucopyranosid-6-yl)-(p-methoxyphenyl 2,3,6-tri-O-benzyl-4-deoxy-β-D-glucopyranosid-4-yl) selenide (**25**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–6.79 (m, 34H, Ar-H), 6.12 (t, J = 10.0 Hz, 1H, H-4_B), 5.43 (t, J = 10.0 Hz, 1H, H-3_B), 5.21 (dd, J = 10.0 Hz, 3.5 Hz, 1H, H-2_B), 5.16 (d, J = 3.0 Hz, 1H, H-1_B), 5.05 (d, J = 10.5 Hz, 1H, PhC*H*), 4.94 (d, J = 10.5 Hz, 1H, PhC*H*), 4.89 (d, J = 10.5 Hz, 1H, PhC*H*), 4.81 (d, J = 7.0 Hz, 1H, H-1_A), 4.78 (d, J = 10.5 Hz, 1H, PhC*H*), 4.62 (s, 2H, 2 PhC*H*), 4.25–4.23 (m, 1H, H-5_A), 4.20 (d, J = 10.5 Hz, 1H, H-

6_{aA}), 3.92–3.89 (m, 1H, H-6_{bA}), 3.79 (s, 3H, OCH_3), 3.65–3.59 (m, 3H, H-2_A, H-3_A, H-5_B), 3.42 (s, 3H, OCH_3), 3.10 (t, J = 10.5 Hz, 1H, H-4_A), 2.98 (d, J = 5.5 Hz, 2H, H-6_{abB}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 165.2 (3 Ph*C*O), 155.2–114.5 (Ar-C), 102.6 (C-1_A), 96.9 (C-1_B), 84.0 (C-3_A), 83.3 (C-5_A), 76.1 (Ph*C*H_2), 76.0 (C-2_A), 74.9, 73.4 (2 Ph*C*H_2), 72.7 (C-2_B), 72.1 (C-3_B), 70.7 (C-6_A), 70.1 (C-4_B), 69.9 (C-5_B), 55.7, 55.5 (2 O*C*H_3), 43.3 (C-4_A), 26.0 (C-6_B); HRMS for $C_{63}H_{62}O_{13}Se$ [M + H]$^+$: calcd 1107.3434; found: 1107.3420.

*(Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl)-(p-methoxyphenyl 2,3,6-tri-O-benzyl-4-deoxy-β-D-glucopyranosid-4-yl) selenide (**26**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–6.78 (m, 34H, Ar-H), 5.10 (d, J = 11.0 Hz, 1H, PhC*H*), 4.95 (d, J = 11.0 Hz, 1H, PhC*H*), 4.91 (d, J = 10.0 Hz, 1H, PhC*H*), 4.86–4.82 (m, 3H, H-1_A, 2 PhC*H*), 4.72 (s, 2H, 2 PhC*H*), 4.66 (s, 1H, H-1_B), 4.59 (s, 2H, 2 PhC*H*), 4.59–4.51 (m, 2H, 2 PhC*H*), 4.48 (d, J = 11.0 Hz, 1H, PhC*H*), 4.20 (d, J = 9.5 Hz, 1H, H-6_{aA}), 3.82–3.79 (m, 5H, H-3_A, H-6_{bA}, OCH_3), 3.76–3.72 (m, 3H, H-3_A, H-5_A, H-2_B), 3.65–3.63 (m, 2H, H-2_A, H-5_B), 3.28 (s, 3H, OCH_3), 3.09 (dd, J = 12.5 Hz, 2.0 Hz, 1H, H-6_{aB}), 2.97–2.93 (m, 2H, H-4_A, H-6_1); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2–114.5 (Ar-C), 102.6 (C-1_A), 99.0 (C-1_B), 84.0 (C-5_B), 83.3 (C-2_B), 80.1 (C-5_A), 78.4 (C-2_A), 76.3 (Ph*C*H_2), 75.9 (C-3_B), 75.1, 75.0 (2 Ph*C*H_2), 74.7 (C-3_A), 73.3, 72.7 (2 Ph*C*H_2), 72.2 (C-4_B), 72.1 (Ph*C*H_2), 71.0 (C-6_A), 55.5, 54.8 (2 O*C*H_3), 42.7 (C-4_A), 26.6 (C-6_B); HRMS for $C_{63}H_{68}O_{10}Se$ [M + H]$^+$: calcd 1065.4056; found: 1065.4040.

*(Methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-glucopyranosid-6-yl)-(2-azidoethyl 2,3,6-tri-O-benzyl-4-deoxy-α-D-galactopyranosid-4-yl) selenide (**27**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47–7.15 (m, 30H, Ar-H), 6.00 (t, J = 10 Hz, 1H, H-4_B), 5.28 (t, J = 10.0 Hz, 1H, H-3_B), 5.12 (dd, J = 10.0 Hz, 3.5 Hz, 1H, H-2_B), 5.01 (d, J = 2.5 Hz, 1H, H-1_B), 4.71 (d, J = 12.0 Hz, 1H, PhC*H*), 4.65–4.62 (m, 2H, H-1_A, PhC*H*), 4.58 (d, J = 12.0 Hz, 1H, PhC*H*), 4.55 (d, J = 12.0 Hz, 1H, PhC*H*), 4.45 (d, J = 12.0 Hz, 1H, PhC*H*), 4.00 (d, J = 12.0 Hz, 1H, PhC*H*), 4.17–4.16 (m, 1H, H-5_B), 4.07–4.05 (m, 1H, H-5_A), 3.91 (dd, J = 9.5 Hz, 3.5 Hz, 1H, H-2_A), 3.85 (dd, J = 9.5 Hz, 3.5 Hz, 1H, H-3_A), 3.71–3.69 (m, 1H, OC*H*), 3.62 (d, J = 6.0 Hz, 2H, H-6_{abA}), 3.46–3.42 (m, 2H, OC*H*, NC*H*), 3.35–3.32 (m, 4H, H-4_A, OCH_3), 3.30–3.28 (m, 1H, NC*H*), 2.88–2.80 (m, 2H, H-6_{abB}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 165.6, 165.3 (3 Ph*C*O), 147.4–125.2 (Ar-C), 98.0 (C-1_B), 96.8 (C-1_A), 78.5 (C-3_A), 77.7 (C-2_A), 73.3, 73.3, 73.2 (3 Ph*C*H_2), 73.0 (C-5_A), 72.3 (C-2_B), 72.2 (C-6_A), 70.3 (C-3_B), 70.2 (C-5_B), 69.9 (C-4_B), 66.7 (O*C*H_2), 55.5 (O*C*H_3), 50.6 (N*C*H_2), 48.4 (C-4_A), 26.3 (C-6_B); HRMS for $C_{57}H_{57}N_3O_{13}Se$ [M + H]$^+$: calcd 1072.3135; found: 1072.3118.

*(Methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl)-(2-azidoethyl 2,3,6-tri-O-benzyl-4-deoxy-α-D-galactopyranosid-4-yl) selenide (**28**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.13 (m, 30H, Ar-H), 4.81 (d, J = 2.5 Hz, 1H, H-1_A), 4.79 (s, 1H, H-1_B), 4.70–4.36 (m, 12H, 12 PhC*H*), 4.17–4.12 (m, 1H, H-5_A), 3.93–3.92 (m, 2H, H-6_{abA}), 3.77–3.75 (m, 1H, OC*H*), 3.73–3.64 (m, 5H, H-2_A, H-2_B, H-3_A, H-4_B, H-5_B), 3.58–3.54 (m, 2H, H-3_B, H-4_A), 3.53–3.49 (m, 1H, OC*H*), 3.44–3.41 (m, 1H, NC*H*), 3.37–3.35 (m, 1H, NC*H*), 3.18 (s, 3H, OCH_3), 3.00 (dd, J = 12.5 Hz, 1.5 Hz, 1H, H-6_{aB}), 2.89 (dd, J = 12.5 Hz, 3.0 Hz, 1H, H-6_{bB}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7–127.4 (Ar-C), 98.8 (C-1_B), 98.2 (C-1_A), 80.1 (C-5_B), 79.2 (C-2_B), 78.3 (C-3_A), 78.2 (C-2_A), 75.2 (Ph*C*H_2), 74.9 (C-5_A), 73.5 (Ph*C*H_2), 73.3 (C-3_B), 73.2, 72.8, 72.7, 72.5 (4 Ph*C*H_2), 72.1 (O*C*H_2), 70.2 (C-4_B), 66.7 (C-6_A), 54.7 (O*C*H_3), 50.6 (N*C*H_2), 47.2 (C-4_A), 27.0 (C-6_B); HRMS for $C_{57}H_{63}N_3O_{10}Se$ [M + H]$^+$: calcd 1030.3757; found: 1030.3739.

*(1,2:3,4-Di-O-isopropylidene-6-deoxy-α-D-galactopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl) selenide (**29**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.18 (m, 15H, Ar-H), 5.42 (d, J = 5.0 Hz, 1H, H-1_A), 4.87 (d, J = 11.0 Hz, 1H, PhC*H*), 4.67–4.62 (m, 2H, 2 PhC*H*), 4.59 (s, 1H, H-1_B), 4.57 (d, J = 11.0 Hz, 1H, PhC*H*), 4.51 (s, 2H, 2 PhC*H*), 4.50 (dd, J = 13.0 Hz, 5.5 Hz 1H, H-3_A), 4.26 (d, J = 7.5 Hz, 1H, H-2_A), 4.19–4.18 (m, 1H, H-4_A), 3.85–3.81 (m, 1H, H-5_A), 3.75–3.74 (m, 1H, H-5_B), 3.71–3.67 (m, 3H, H-2_B, H-3_B, H-4_B), 3.27 (s, 3H, OCH_3), 2.96 (d, J = 12.5 Hz, 1H, H-6_{aA}), 2.76–2.75 (m, 3H, H-6_{bA}, H-6_{abB}), 1.41, 1.33, 1.23, 1.22 (s, 12H, 4 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5–127.5 (Ar-C), 109.0, 108.4 (2 *C*(CH_3)$_2$), 98.8 (C-1_B), 96.6 (C-1_A), 80.1 (C-5_B), 78.7 (C-2_B), 75.1 (Ph*C*H_2), 74.7 (C-3_B), 72.7 (C-4_B), 72.7, 72.0 (2 Ph*C*H_2), 71.8 (C-3_A), 71.0 (C-4_A), 70.5 (C-2_A), 68.3 (C-5_A), 54.7 (O*C*H_3), 26.6 (C-6_A), 26.1, 26.0, 24.9, 24.5 (4 *C*H_3), 24.0 (C-6_B); HRMS for $C_{40}H_{50}O_{10}Se$ [M + H]$^+$: calcd 771.2647; found: 771.2629.

*(1,2:3,4-Di-O-isopropylidene-6-deoxy-α-D-galactopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-glucopyranosid-6-yl)selenide (**30**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.17 (m, 15H, Ar-H), 5.40 (d, J = 4.5 Hz, 1H, H-1_A), 4.89 (d, J = 11.0 Hz, 1H, PhC*H*), 4.81 (d, J = 11.0 Hz, 1H, PhC*H*), 4.71 (d, J = 11.0 Hz, 1H, PhC*H*), 4.69 (d, J = 11.0 Hz, 1H, PhC*H*), 4.58 (t, J = 11.5 Hz, 2H, 2 PhC*H*), 4.47 (d, J = 2.5 Hz, 2H, H-1_B, H-3_A), 4.22 (d, J = 7.5 Hz, 1H, H-2_A), 4.18–4.16 (m, 1H, H-4_A), 3.88 (t, J = 9.5 Hz, 1H, H-3_B), 3.80–3.73 (m, 2H, H-5_A, H-5_B), 3.42 (dd, J = 9.5 Hz, 3.5 Hz, 1H, H-2_B), 3.33 (s, 3H, OCH_3), 3.26 (t, J = 9.5 Hz, 1H, H-4_B), 2.91 (dd, J = 12.5 Hz, 2.0 Hz, 1H, H-6_{aA}), 2.72–2.69 (m, 2H, H-6_{abB}), 2.65 (dd, J = 12.5 Hz, 8.5 Hz, 1H, H-6_{bA}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7–127.5 (Ar-C), 109.1, 108.4 (2 *C*(CH_3)$_2$), 97.8 (C-1_B), 96.6 (C-1_A), 81.8 (C-5_B), 81.6 (C-3_B), 80.1 (C-4_B), 75.6, 75.1, 73.2 (3 Ph*C*H_2), 71.7 (C-3_A), 71.1 (C-2_B), 71.0 (C-4_A), 70.5 (C-2_A), 68.4 (C-5_A), 55.2 (O*C*H_3), 26.5 (C-6_A), 26.1, 26.0, 24.9, 24.5 (4 *C*H_3), 24.0 (C-6_B); HRMS for $C_{40}H_{50}O_{10}Se$ [M + H]$^+$: calcd 771.2647; found: 771.2629.

*(p-Methoxyphenyl-2-O-benzyl-3,4-O-isopropylidene-6-deoxy-α-D-galactopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-mannopyranosid-6-yl)selenide (**31**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.13 (m, 20H, Ar-H), 6.96 (d, J = 8.5 Hz, 2H, Ar-H), 6.70 (d, J = 8.5 Hz, 2H, Ar-H), 5.18 (d, J = 3.0 Hz, 1H, H-1_A), 4.83 (d, J = 11.0 Hz, 1H, PhC*H*), 4.69 (d, J = 12.5 Hz, 1H, PhC*H*), 4.63 (d, J = 12.5 Hz, 1H, PhC*H*), 4.60–4.59 (m, 2H, 2 PhC*H*), 4.47–4.44 (m, 4H, H-1_B, 3 PhC*H*), 4.32 (t, J = 7.0 Hz, 1H, H-4_B), 4.23–4.18 (m, 2H, H-2_B, H-5_B), 3.69–3.68 (m, 2H, H-4_A, H-5_A), 3.62–3.58 (m, 5H, H-3_A, H-3_B, OCH_3), 3.50 (dd, J = 8.0 Hz, 3.5 Hz, 1H, H-2_A), 3.12 (s, 3H, OCH_3), 2.83–2.75 (m, 3H, H-6_{abA}, H-6_{aB}), 2.70 (dd, J = 12.5 Hz, 8.0 Hz, 1H, H-6_{bB}), 1.29, 1.24 (s, 6H, 2 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0–114.5 (Ar-C), 108.9 (*C*(CH_3)$_2$), 98.8 (C-1_B), 96.8 (C-1_A), 80.1 (C-5_B), 78.2 (C-2_B), 76.2 (C-3_B), 75.9 (C-4_B), 75.1 (Ph*C*H_2), 74.6 (C-4_A), 74.3 (C-3_A), 72.6 (Ph*C*H_2), 72.3 (C-5_A), 72.1, 72.0 (2 Ph*C*H_2), 68.6 (C-2_A), 55.4, 54.6 (2 O*C*H_3), 28.2 (*C*H_3), 27.1 (C-6_B), 26.4 (*C*H_3), 24.8 (C-6_A); HRMS for $C_{51}H_{58}O_{11}Se$ [M + H]$^+$: calcd 927.3222; found: 927.3205.

*(p-Methoxyphenyl-2-O-benzyl-3,4-O-isopropylidene-6-deoxy-α-D-galactopyranosid-6-yl)-(methyl 2,3,4-tri-O-benzyl-6-deoxy-α-D-glucopyranosid-6-yl)selenide (**32**).* Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.12 (m, 20H, Ar-H), 6.95 (d, J = 8.5 Hz, 2H, Ar-H), 6.71 (d, J = 8.5 Hz, 2H, Ar-H), 5.19 (d, J = 3.0 Hz, 1H, H-1_A), 4.87 (d, J = 11.0 Hz, 1H, PhC*H*), 4.79 (d, J = 11.0 Hz, 1H, PhC*H*), 4.71–4.63 (m, 4H, H-1_B, 3 PhC*H*), 4.55 (d, J = 12.0 Hz, 1H, PhC*H*), 4.46 (d, J = 11.0 Hz, 1H, PhC*H*), 4.39–4.36 (m, 2H, H-5_A, PhC*H*), 4.21–4.20 (m, 1H, H-4_A), 4.12–4.10 (m, 1H, H-5_B), 3.85 (t, J = 9.0 Hz, 1H, H-3_B), 3.65 (s, 3H, OCH_3), 3.52 (dd, J = 7.5 Hz, 3.5 Hz, 1H, H-3_A), 3.38 (dd, J = 9.5 Hz, 3.5 Hz, 1H, H-2_B), 3.30 (d, J = 7.5 Hz, 1H, H-2_A), 3.24 (s, 3H, OCH_3), 3.21 (t, J = 9.0 Hz, 1H, H-4_B), 2.80 (dd, J = 12.5 Hz, 2.0 Hz, 1H, H-6_{aA}), 2.74 (d, J = 7.5 Hz, 2H, H-6_{abB}), 2.54 (dd, J = 12.5 Hz, 8.0 Hz, 1H, H-6_{bA}), 1.30, 1.26 (s, 6H, 2 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0–114.5 (Ar-C), 109.0 ($C(CH_3)_2$), 97.7 (C-1_B), 96.7 (C-1_A), 81.8 (C-5_B), 81.3 (C-2_B), 80.1 (C-3_B), 76.0 (C-3_A), 75.8 (C-4_A), 75.6, 75.0 (2 PhCH_2), 74.2 (C-4_B), 73.2, 72.2 (2 PhCH_2), 70.8 (C-5_A), 68.5 (C-2_A), 55.4, 55.0 (2 OCH_3), 28.1 (CH_3), 26.7 (C-6_B), 26.4 (CH_3), 24.6 (C-6_A); HRMS for $C_{51}H_{58}O_{11}Se$ $[M + H]^+$: calcd 927.3222; found: 927.3205.

Conclusions

In summary, an "on-water" reaction condition has been developed for the preparation of stable glycosyl selenocyanate derivatives using readily available KSeCN as selenium source under eco-friendly reaction condition. Furthermore, the glycosyl selenocyanate derivatives have been used as stable building blocks for the stereoselective preparation of nonglycosidically selenoether linked pseudodisaccharide derivatives in excellent yield under a meta-free organocatalytic reaction condition. This approach may be considered as a better alternative to those reported earlier for the preparation of selenoether linked sugars because of its simplicity and yield efficiency. To the best of our knowledge this is the maiden report on the synthesis and characterization of glycosyl selenocyanate derivatives and their application in the metal-free organocatalytic synthesis of selenoether linked disaccharide derivatives.

Author contributions

AKM conceived and designed the experiments; TM performed the experiments; AKM and TM analyzed the data; AKM and TM wrote the paper. All authors read and approved the final manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Tapasi Manna thanks UGC, New Delhi for providing senior research fellowship. This work was supported by SERB, New Delhi (Project No. CRG/2019/000352 dated 23.01.2020) (AKM).

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