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Tris(4-bromophenyl)aminium hexachloroantimonate-mediated glycosylations of selenoglycosides and thioglycosides. Evidence for single electron transfer?†

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Abstract

Radical cation-initiated glycosylation reactions of phenyl selenoglycosides are described. Glycosylations of phenyl selenoglycosides effected by the single-electron-transfer (SET) reagent, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA), are examined with primary and secondary hydroxyl acceptors. The corresponding reaction of an ethyl thioglycoside with a primary hydroxyl acceptor is also examined. Reactions are performed in the presence of the SET quenching reagent, 1,2,4,5-tetramethoxybenzene, to assess whether BAHA-mediated glycosylation reactions involve SET. These experiments indicate that the reactions are completely quenched in dichloromethane but only partially in acetonitrile. The results provide support for the SET mechanism but an alternative mechanism involving electrophilic activation cannot be discounted. The oxidation potentials of various selenoglycosides are determined by cyclic voltammetry.

1. Introduction

In contrast to conventional Lewis acid-mediated glycosylations that are two-electron processes, radical cation-initiated glycosylations involve single-electron-transfer (SET). Radical-cation initiated (RCI) glycosylations can be represented as shown in Scheme 1. These reactions require the initial generation of a radical cation by the transfer of a single electron from the aglyconic chalcogen to a suitable single-electron acceptor. Subsequent cleavage of the C_1–X bond results in the formation of the oxocarbenium ion which undergoes nucleophilic attack by an alcohol to generate a new glycosidic linkage. The single electron transfer from the glycosyl donor can be effected either electrochemically [1], photochemically [2], or chemically [3].

The electrochemical glycosylation method was introduced by Noyori and Kurimoto [1a] with aryl *O*-glycosides. This novel concept was extended by Balavoine et al. [1b] and Amatore et al. [1c], independently, to phenyl *S*-glycosides. The lower oxidation potentials of the phenyl *S*-glycosides

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† This paper is dedicated, with respect and gratitude, to the memory of Margaret A. Clark.

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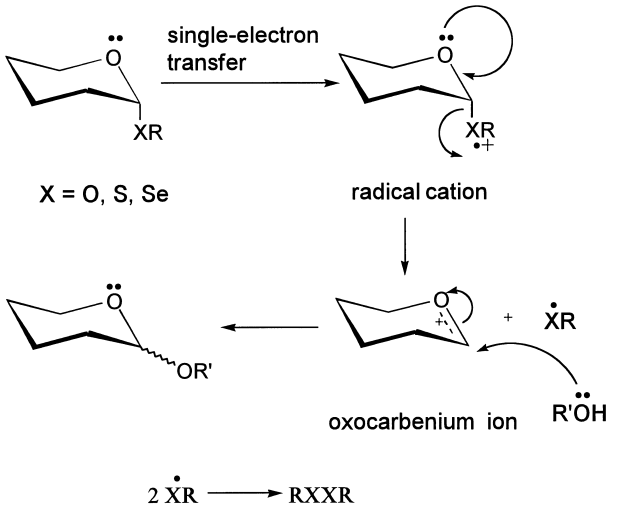


Scheme 1. Radical cation-initiated glycosylation.

compared to those of the corresponding phenyl *O*-glycosides offered the advantage of conducting glycosylations at a lower oxidation potential, providing compatibility with a wider variety of protecting groups.

We and others have demonstrated the versatility of phenyl selenoglycosides in selective activation strategies for oligosaccharide synthesis [4–7]. Activation has been achieved with various promoters such as silver triflate, methyl triflate, phenylselenenyl triflate, and NIS/triflic acid. We now describe full details of the chemically-induced, radical cation-initiated glycosylation reactions with phenyl selenoglycosides, a novel method of effecting selenoglycoside activation, using tris(4-bromophenyl)aminium hexachloroantimonate, $(p\text{-}BrC_6H_4)_3N^{+\cdot}$ (BAHA), as the single electron transfer reagent [8]. Marra et al. [3a] have reported similar glycosylations with ethyl thioglycosides and this group has subsequently applied the method to the synthesis of oligosaccharides [3b,c]. We also provide evidence to support the existence of single electron transfer in BAHA-mediated glycosylation reactions.

2. Results and discussion

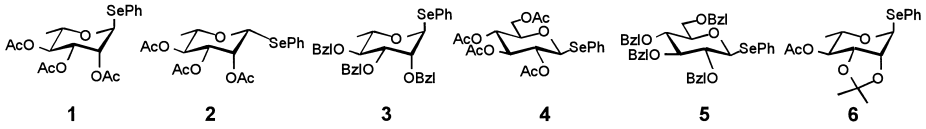
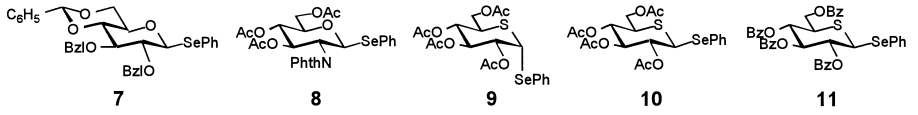
In order to determine a suitable single electron transfer reagent to effect radical cation-initiated glycosylations, the oxidation potentials of various selenoglycosides [4b,9] were determined by cyclic voltammetry [10]. The voltage was scanned from 0 to 2 V in the anodic direction at which point the direction of the scan was reversed. The forward scan showed one anodic wave having a peak potential corresponding to the oxidation potential of the substrate. The reverse scan did not show any cathodic peaks. This result is typical of an 'EC type' mechanism in which the initial electrochemical reaction is followed by a chemical reaction, and is consistent with the disproportionation of the radical-cation to the oxocarbocenium ion (see Scheme 1). The oxidation potentials of the selenoglycosides investigated fall in the range of 1.35–1.5 V (Table 1). These values are lower than those of *S*-glycosides and *O*-glycosides [10] and are reflective of the ionization potentials of oxygen, sulfur, and selenium lone pairs that decrease in the same order [11].

The SET reagent chosen for RCI glycosylations of selenoglycosides was tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) whose reduction potential is reported to be 1.05 V versus SCE [12]. Since the oxidation potentials of the selenoglycosides are higher than that of the aminium salt, one might have expected that the oxidation of selenoglycosides by BAHA would be thermodynamically unfavorable. However, Kamata et al. [13] had reported the radical-cation-mediated desulfurization of thiiranes with BAHA as the SET reagent, although the oxidation potentials of their substrates were in the range of 1.44–1.84 V versus SCE in acetonitrile. Thereafter, Marra et al. [3] claimed to effect RCI glycosylations of thioglycosides with BAHA, in spite of the higher oxidation potentials of the thioglycosides. The results described in the following section establish the validity of the SET mechanism in BAHA-mediated glycosylation reactions.

RCI glycosylations of primary and secondary hydroxyl acceptors with armed and disarmed selenoglycosides were investigated with BAHA as the SET reagent. The glycosylation of the methyl glycoside **12** [14] with the selenoglycoside **1** yielded the disaccharide **13** [4b] in 76% yield (Table 2, entry 1). Glycosylation of the above acceptor with a more reactive armed selenoglycoside donor **5** proceeded in 94% yield producing an $\alpha:\beta$ mixture of disaccharides **14** [15] and **15** [16] in a 1.7:1 ratio (Table 2, entry 2). These glycosylations were effected at ambient temperature.

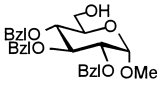
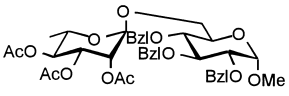
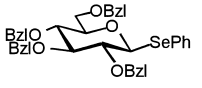
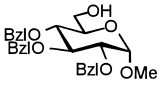
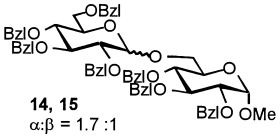
Initial attempts to extend this methodology to secondary alcohol acceptors proved only partly successful. Glycosylation of the methyl glycoside **16** [16] with the selenoglycoside **1** afforded a mixture of products. In addition to a mixture of

Table 1
Oxidation potentials[a] of selenoglycosides

Selenoglycoside						
	1	**2**	**3**	**4**	**5**	**6**
Oxidation potential (V)	1.35	1.41	1.42	1.50	1.33	1.35
Selenoglycoside						
	7	**8**	**9**	**10**	**11**	
Oxidation potential (V)	1.39	1.41	1.52	1.47	1.48	

[a] Oxidation potentials measured versus a standard saturated calomel electrode in dry acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte at a scan rate of 200 mV/s.

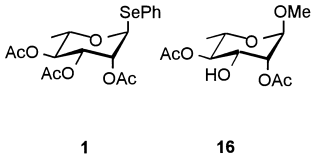
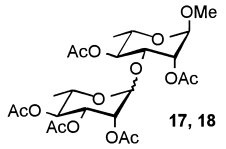
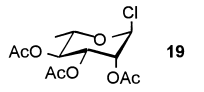
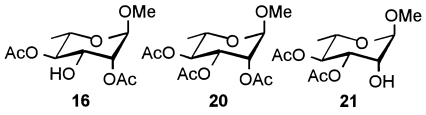
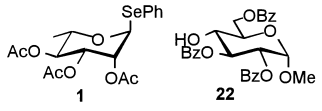
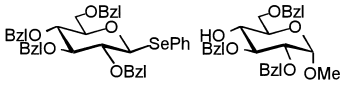
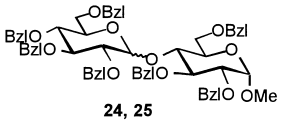
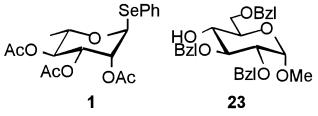
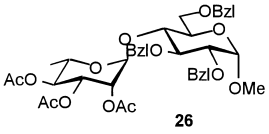
Table 2
BAHA-Mediated glycosylations of a primary hydroxyl acceptor with selenoglycoside donors

Entry	Donor	Acceptor	Molar ratio[a]	Time (h)	Product	Yield (%)
1	**1**	 **12**	2 : 1 : 3	2	 **13**	76%
2	 **5**	 **12**	1 : 0.8 : 1.5	3	 **14, 15** α:β = 1.7 :1	94%

[a] Donor : acceptor : BAHA.

disaccharides **17** [16] and **18** [16], obtained in 52% yield, 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl chloride **19** [17], formed by the reaction of the donor **1** with chloride ions in solution, was also isolated in 36% yield (Table 3, entry 1). The recovered acceptor **16** and trans-esterification products **20** [17] and **21** [18] were also isolated. A similar glycosylation of the unreactive, tribenzoyl acceptor **22** [19] did not provide any of the desired disaccharide. Although the selenoglycoside activation had been effected, as suggested by the isolation of the chloride **19**, 90% of the glycosyl acceptor **22** was recovered from the reaction mixture (Table 3, entry 2). We surmised that modulation of the reactivity of the acceptor was required. Hence, the reaction of the benzylated acceptor **23** was examined. Glycosylation of the methyl glycoside acceptor **23** [20] with the selenoglycoside **5** afforded an α/β mixture of the disaccharides **24** [21] and **25** [21] in a yield of 50% (Table 3, entry 3). The reaction did not reach completion and the unreacted acceptor was recovered. The yield of the reaction based on the recovered acceptor was 90%. Based on these results, we deduced that glycosylations of acceptors containing secondary hydroxyl groups were not very efficient and might require additional amounts of the promoter to reach completion. In the following glycosylation of the same acceptor with the selenoglycoside **1**, the concentration of the promoter BAHA was increased from 1.5 to 3 mol equiv with respect to the selenoglycoside. As observed in earlier experiments, this glycosyl donor had a tendency to form the corresponding chloride under the reaction conditions. Therefore, a twofold excess of the donor **1** was used to ensure that rhamnopyranosyl chloride formation did not

Table 3
BAHA-Mediated glycosylations of secondary hydroxyl acceptors with selenogylcoside donors

Entry	Donor	Acceptor	Molar ratio[a]	Time (h)	Product	Yield (%)
1			1 : 1 : 1	1		52% α:β = 6:1
						36%
						45%
2			1 : 0.8 : 1.5	1		90%
						60%
3			1 : 0.8 : 1.5	2		90%[b]
4			2 : 1 : 6	2		91%[b]

[a] Donor : acceptor : BAHA.
[b] Yield based on acceptor recovered.

reduce the yield of the reaction. The disaccharide **26** was obtained in 73% yield (Table 3, entry 4) and 20% of the acceptor remained unreacted.

RCI Glycosylations or alternative mechanisms?— We realized that the aminium salt BAHA had the potential of effecting glycosylations via four possible mechanisms. The first mechanism, as discussed thus far, involved the intermediacy of radical-cations generated via single electron transfer from the selenoglycoside to the aminium radical cation. Owing to the strongly acidic nature of the reaction medium, a second possibility of acid catalysis was also considered. A third possibility involves direct electrophilic activation of the selenium or sulfur atom, or direct polar reaction of the aminium ion at the *p*-position of the phenyl moiety of the phenyl selenoglycosides. A final possibility involves the intermediacy of glycosyl chlorides.

An effective method of establishing the existence of electron-transfer reactions is by the use of SET quenching reagents. 1,2,4,5-Tetramethoxybenzene (TMB) has been used as an effective SET quenching reagent for the evaluation of BAHA-mediated SET reactions [13,22]. Since the oxidation potential of TMB (0.81 V) [23] is lower than the oxidation potentials of the selenoglycosides, it should be capable of interfering with the BAHA-mediated glycosylations if SET was the dominant mechanism. In the case of acid catalysis, the use of TMB as a quencher should produce little or no change in the outcome of the reaction. The possibility of electrophilic activation is difficult to assess since the addition of quencher will consume the aminium radical cation and will quench the reaction. Thus, proof that the aminium salt is required for the reaction does not necessarily give clear evidence of the mechanism of the reaction.

The BAHA-mediated glycosylations of the methyl glycoside acceptor **12** and the selenoglycoside **5** were performed in dichloromethane and in

acetonitrile as the solvents, in the absence and presence of the quencher, TMB (Table 4, entries 1–4). The reactions in a given solvent were performed simultaneously under identical conditions and concentrations of reactants. The reactions were closely monitored by TLC. A TLC comparison of the reactions with and without quencher in acetonitrile (Table 4, entries 4 and 3) revealed that, after 1 h, the glycosyl acceptor **12** had completely reacted in the latter reaction but was still detectable in the former reaction. The yield of the disaccharides isolated in the reaction with quencher (78%) was lower than for the reaction conducted in the absence of the quencher (89%). The reaction in the presence of TMB conducted in dichloromethane (Table 4, entries 1, 2) was completely quenched and the reactants were recovered almost quantitatively.

The results of a similar investigation performed for the glycosylation of the acceptor **12** with the selenoglycoside **1** indicate that, as in the above case, the reaction was completely quenched in the presence of the quencher TMB when dichloromethane was used as the solvent, and the reactants were recovered quantitatively (Table 4, entries 5 and 6). In acetonitrile, the disaccharide **13** was obtained in 60% yield in the absence of the quencher (Table 4, entry 7). No unreacted acceptor was present at the completion of the reaction. A TLC comparison of this reaction after 1 h with an analogous reaction in the presence of TMB indicated that the reaction had been suppressed in the presence of the quencher (Table 4, entry 8). In the latter case, a substantial amount of the unreacted acceptor was detected by TLC in addition to the expected disaccharide. The unreacted acceptor was recovered from the reaction in a yield of 25%.

We also decided to probe the nature of the BAHA-mediated glycosylations with the ethyl thioglycoside **27** [24] (Table 4). The glycosylation in dichloromethane afforded an α/β mixture of the disaccharides **14** and **15** (Table 4, entry 9). This result contrasts with that of Marra et al. [3] who reported that no reaction occurs in dichloromethane. An analogous reaction in the presence of the quencher was completely quenched (Table 4, entry 10). In acetonitrile, the quencher was effective in suppressing the reaction (Table 4, entries 11 and 12); the disaccharides were isolated in a low yield of 28% and the unreacted acceptor was isolated in a yield of 63% (Table 4, entry 12).

Analysis of these results suggests that, in dichloromethane, SET may be the dominant pathway, since the reactions were completely quenched in the presence of TMB in all three cases investigated. In acetonitrile, however, the reactions continued to proceed in spite of the presence of TMB. We speculated that, in spite of having quenched the SET (or electrophilically activated) reaction, an alternative acid-catalyzed pathway was available to the reactants. The acid-catalyzed

Table 4
Quenching experiments

Entry	Reaction	Conditions[a,b,c]	Results
1	**5** + **12**	3 h, CH_2Cl_2, without quencher	Disaccharides **14, 15**, 94%; $\alpha:\beta = 1.8:1$
2	**5** + **12**	3 h, CH_2Cl_2, with quencher	Acceptor **12** recovered, 96%
3	**5** + **12**	1 h, CH_3CN, without quencher	Disaccharides **14, 15**, 89%; $\alpha:\beta = 1.7:1$
4	**5** + **12**	1 h, CH_3CN, with quencher	Disaccharides **14, 15**, 78%; $\alpha:\beta = 1:7$
5	**1** + **12**	2 h, CH_2Cl_2, without quencher	Disaccharide **13**, 76%
6	**1** + **12**	2 h, CH_2Cl_2, with quencher	Acceptor **12** recovered, 96% Donor **1** recovered, 95%
7	**1** + **12**	1 h, CH_3CN, without quencher	Disaccharide **13**, 60%
8	**1** + **12**	1 h, CH_3CN, with quencher	Disaccharide **13**, 51% Acceptor **12** recovered, 25%
9	**27**[d] + **12**	2 h, CH_2Cl_2, without quencher	Disaccharides **14, 15**, 88%; $\alpha:\beta = 1.5:1$
10	**27**[d] + **12**	2 h, CH_2Cl_2, with quencher	Acceptor **12** recovered, 94% Donor **27** recovered, 96%
11	**27**[d] + **12**	0.5 h, CH_3CN, without quencher	Disaccharides **14, 15**, 81%; $\alpha:\beta = 1:1$
12	**27**[d] + **12**	0.5 h, CH_3CN, with quencher	Disaccharides **14, 15**, 28%; $\alpha:\beta = 1:4.5$ Acceptor **12** recovered, 63%

[a] Donor : acceptor : BAHA = 1 : 0.8 : 1.5.
[b] Quencher = 1,2,4,5-tetramethoxybenzene.
[c] Donor : acceptor : BAHA : quencher = 1 : 0.8 : 1.5 : 6.
[d] Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside **27**.

reaction was less efficient than the RCI reaction, and, therefore, an incomplete reaction was observed. However, this reasoning did not explain why a similar result was not observed in dichloromethane, since Lewis acid-catalyzed glycosylations are generally conducted in the latter solvent.

We suggest, therefore, the following explanation for our observations. Since the oxidation potential of BAHA is lower than that of the selenoglycosides, the direct oxidation of the selenoglycosides by BAHA is thermodynamically unfavorable. We postulate that the oxidation is preceded by the formation of a complex between the selenium atom of the selenoglycoside and the aminium radical-cation. This adduct has a modified oxidation potential and is amenable to oxidation. Similar adducts have been proposed by Gilbert and Marriott [25] for the reaction of NH_3^+ with various sulfides and sulfoxides. We propose that the polarity of acetonitrile facilitates the initial ion-pair dissociation of BAHA and, in turn, the complexation of the selenium and the aminium radical-cation. If trapping of the aminium radical cation by TMB is slower than the electron transfer from selenium, this would lead to a more facile SET (or electrophilically activated) reaction and to an incomplete quenching of the glycosylations by TMB in acetonitrile. Hence, SET (or elecrophilic activation) appears to be the dominant mechanism of the reaction in both dichloromethane and acetonitrile and the acid-catalyzed pathway is of lesser importance. This conclusion is further corroborated by the result of a glycosylation reaction in the presence of anisole as the SET quenching reagent. The oxidation potential of anisole is $+1.76$ V [22]. Since this value is higher than those of the substrates, the quencher should have no appreciable effect on the SET glycosylations. As predicted, the reaction of the methyl glycoside acceptor **12** and the selenoglycoside **1** in the presence of anisole, with BAHA as the promoter, was not quenched, and the disaccharide **13** was isolated in 79% yield.

The question of the stereochemical outcome of the reactions remains to be addressed. The glycosylations with the phenyl selenorhamnoside **1** proceed in a 1,2-trans fashion, as expected due to the anchimeric assistance provided by the acetate substituent at the C-2 position of the glycosyl donor. The glycosylation with the perbenzylated phenyl selenoglucoside **5** in dichloromethane favors the formation of the thermodynamically more stable α-disaccharide **14**. The stereoselectivity of the reactions in acetonitrile is noteworthy. Glycosylations in acetonitrile are reported to occur via the intermediacy of a glycosyl-acetonitrilium ion. Several workers have proposed that the acetonitrilium ion forms at the α-face [26]. This intermediate then undergoes an inversion of configuration in the presence of a glycosyl acceptor. Thus, acetonitrile has been the solvent of choice to promote β-glycosylations with substrates possessing a non-participating substituent at the C-2 position. However, other workers have proposed an equatorial orientation for the acetonitrilium ion [27], whose stability was attributed to the reverse anomeric effect. Subsequent inversion by the acceptor was postulated to account for the preferential formation of the α-disaccharide in these cases.

In our glycosylations with selenoglycoside **5**, the results in dichloromethane and acetonitrile are comparable and the α-disaccharide **14** is only slightly favored. These results are inconsistent, therefore, with either of the above proposals. We suggest that the reaction is under thermodynamic control.

In contrast to the lack of stereoselectivity of this glycosylation reaction in acetonitrile in the absence of the quencher TMB, reactions in the presence of TMB afforded predominantly the β-disaccharide **15**. We speculate that this is due to the formation of an encounter complex of the TMB and the oxocarbenium ion in which the α-face is shielded; nucleophilic attack then occurs at the β-face.

3. Conclusions

O-Substituted phenyl selenoglycosides are amenable to radical-cation-initiated glycosylations effected by the single electron transfer reagent, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA). The glycosylations of reactive primary alcohol acceptors are promising, although the glycosylations of unreactive acceptors are less efficient. Acceptors of moderate reactivity require a greater concentration of the promoter to achieve high yielding reactions.

The oxidation potentials of various phenyl selenoglycosides have been determined. The oxidation potentials of BAHA (1.05 V) and the phenyl selenoglycosides (1.35–1.5 V) indicate that the direct oxidation of the selenoglycosides via single-electron transfer by BAHA is not probable. We suggest a prior complexation of the selenoglycoside and BAHA that produces a complex of modified

oxidation potential, which then undergoes a single-electron-transfer reaction. Results based on quenching experiments are consistent with the existence of the SET mechanism in dichloromethane and acetonitrile, although the possibility of electrophilic activation of the selenoglycosides cannot be discounted.

4. Experimental

General methods.—Melting points were determined on a Fisher–Johns melting-point apparatus and are uncorrected. Optical rotations were measured with a Rudolph Research Autopol II automatic polarimeter. Analytical thin-layer chromatography (TLC) was performed on aluminum plates precoated with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, exposed to UV light, and/or sprayed with 5% sulfuric acid in ethanol and heated at 150 °C. All compounds were purified by medium-pressure column chromatography on Kieselgel 60 (230–400 mesh) according to a published procedure. Solvents were distilled before use and were dried, as necessary, by literature procedures. Solvents were evaporated under reduced pressure and below 40 °C. Reactions performed under nitrogen were also carried out in deoxygenated solvents. Transfers under nitrogen were effected by means of standard Schlenk-tube techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer at 400.13 and 100.6 MHz, for proton and carbon, respectively. The spectra were recorded in deuterochloroform. All new compounds were characterized by either microanalysis or electrospray mass spectrometry. The microanalyses were performed by Mr. Mickey Yang at Simon Fraser University.

Cyclic voltammetry.—Cyclic voltammetry was performed on 1 mM solutions of the substrates in dry acetonitrile. Tetraethylammonium perchlorate (0.1 M) was used as the supporting electrolyte. The cyclic voltammograms were measured at a platinum electrode with reference to a standard saturated calomel electrode. The instrument was calibrated with ferrocene as the standard.

Typical procedure for BAHA-mediated glycosylations with phenyl 2,3,4-tri-O-*acetyl-1-seleno*-α-L-*rhamnopyranoside* (**1**) *in dichloromethane or acetonitrile*.—A mixture of phenyl 2,3,4-tri-*O*-acetyl-1-seleno-α-L-rhamnopyranoside (**1**) (87 mg, 0.2 mmol), the acceptor, and 4 Å molecular sieves was stirred in anhydrous solvent (4 mL) under N_2 for 1 h. BAHA was added and the reaction mixture was stirred until the reaction was complete. The reaction mixture was cooled to 0 °C and neutralized with Et_3N. The mixture was filtered through Celite with dichloromethane, the filtrate was concentrated, and the residue was purified by column chromatography with hexane-ethyl acetate as eluant.

Typical procedure for BAHA-mediated glycosylations with phenyl 2,3,4,6-tetra-O-*benzyl-1-seleno*-β-D-*glucopyranoside* (**5**) *and ethyl 2,3,4,6-tetra*-O-*benzyl-1-thio*-β-D-*glucopyranoside* (**27**) *in dichloromethane or acetonitrile*.—A mixture of phenyl 2,3,4,6-tetra-*O*-benzyl-1-seleno-*β*-D-glucopyranoside (**5**) or ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-*β*-D-glucopyranoside (**27**) (0.1 mmol), the acceptor (0.08 mmol), and 4 Å molecular sieves was stirred in anhydrous solvent (2 mL) under N_2 for 1 h. BAHA (0.15 mmol) was added and the reaction mixture was stirred until the reaction was complete. The reaction mixture was cooled to 0 °C and neutralized with Et_3N. The mixture was filtered through Celite with dichloromethane, the filtrate was concentrated, and the residue was purified by column chromatography with hexane-ethyl acetate as eluant.

Methyl 2,3,4-tri-O-*benzyl-6*-O-*(2,3,4-tri*-O-*acetyl*-α-L-*rhamnopyranosyl)*-α-D-*glucopyranoside* (**13**) *[4b]*.—The product was purified by column chromatography with hexane-ethyl acetate (2.5:1) as eluant, $R_f = 0.37$. The NMR spectral data were identical to the literature data.

Methyl 2,3,4-tri-O-*benzyl-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-α/β-D-*glucopyranosyl)*-β-D-*glucopyranoside* (**14, 15**) *[15]*.—The product was purified by column chromatography with hexane–ethyl acetate (3:1) as eluant, [$R_f = 0.4$] to give an α/β mixture of disaccharides. The NMR spectral data were identical to the literature data.

Methyl 2,3,6-tri-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl*-α, β-D-*glucopyranosyl)*-α-D-*glucopyranoside* (**24, 25**) *[21]*.—The products were purified by column chromatography with hexane–ethyl acetate (4.5:1) as eluant, [R_f of **24** and **25** = 0.4, R_f of recovered **23** = 0.2], to give a 1:1 α/β mixture of disaccharides (43 mg, 50%), and **23** (18 mg, 43%). The NMR spectral data were identical to the literature data.

Methyl 2,3,6-tri-O-*benzyl-4*-O-*(2,3,4-tri*-O-*acetyl*-α-L-*rhamnopyranosyl)*-α-D-*glucopyranoside* (**26**).—The product was purified by column chromatography with hexane–ethyl acetate (2:1) as eluant,

[R_f of disaccharide **26** = 0.25, R_f of acceptor **23** = 0.33], to give the disaccharide **26** as a syrup (53 mg, 73%), and **23** (10 mg, 20%). The yield based on reacted **23** is 91%. $[\alpha]_D^{22}$ +32° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 17.0 (C-6′), 20.6, 20.7 ($3COCH_3$), 55.2 (OCH_3), 66.7 (C-5′), 68.6 (C-5), 69.1 (C-6), 69.9 (C-3′), 70.2 (C-2′), 71.1 (C-4), 73.2 ($2CH_2C_6H_5$), 75.1 (C-3), 75.3 ($CH_2C_6H_5$), 79.8 (C-3), 80.5 (C-2), 97.2 (C-1′), 97.9 (C-1), 127.2–137.9 (Ar); ^1H NMR ($CDCl_3$): δ 1.17 (3H, d, $J_{5',6'}$ = 6.0 Hz, H-6′), 1.98, 1.99, 2.06 (9H, 3s, $3COCH_3$), 3.36 (3H, s, OCH_3), 3.58 (1H, dd, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.2 Hz, H-2), 3.65 (1H, dd, $J_{5,6a}$ = 2.8 Hz, $J_{6a,6b}$ = 9.2 Hz, H-6a), 3.70–3.77 (2H, m, H-4, H-6), 3.82–3.94 (2H, m, H-3, H-5), 4.04 (1H, m, H-5′), 4.51 (2H, AB pattern, $CH_2C_6H_5$), 4.58 (1H, d, $J_{1,2}$ = 3.8 Hz, H-1), 4.60 (1H, d, *J* = 12.0 Hz, $CHHC_6H_5$), 4.69–4.76 (2H, $CHHC_6H_5$), 4.95 (1H, d, $J_{1',2'}$ = 1.8 Hz, H-1′), 4.98 (1H, t, $J_{3',4'+4',5'}$ = 20.0 Hz, H-4′), 5.11 (1H, d, *J* = 11.0 Hz, $CHHC_6H_5$), 5.15 (1H, dd, $J_{1',2'}$ = 1.8 Hz, $J_{2',3'}$ = 3.3 Hz, H-2′), 5.25 (1H, dd, $J_{2',3'}$ = 3.3 Hz, $J_{3',4'}$ = 10.1 Hz, H-3′), 7.30–7.50 (15H, Ar); Anal. Calcd for $C_{40}H_{48}O_{13}$: C, 65.21; H, 6.57; Found: C, 65.11; H, 6.69.

Typical procedure for BAHA-mediated glycosylations with phenyl 2,3,4-tri-O-*acetyl-1-seleno*-α-L-*rhamnopyranoside* (**1**) *in dichloromethane or acetonitrile in the presence of the quencher*.—A mixture of phenyl 2,3,4-tri-*O*-acetyl-1-seleno-α-L-rhamnopyranoside (**1**) (87 mg, 0.2 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**12**) (46 mg, 0.1 mmol), 1,2,4,5-tetramethoxybenzene (240 mg, 1.2 mmol), and 4 Å molecular sieves was stirred in anhydrous solvent (4 mL) under N_2 for 1 h. BAHA (245 mg, 0.3 mmol) was added and the reaction mixture was stirred under N_2 for as long as the corresponding experiment in the absence of the quencher. The reaction mixture was cooled to 0 °C and neutralized with Et_3N. The mixture was filtered through Celite with dichloromethane, the filtrate was concentrated, and the residue was purified by column chromatography with hexane-ethyl acetate as eluant.

Typical procedure for BAHA-mediated glycosylations with phenyl 2,3,4,6-tetra-O-*benzyl-1-seleno*-β-D-*glucopyranoside* (**5**) *and ethyl 2,3,4,6-tetra*-O-*benzyl-1-thio*-β-D-*glucopyranoside* (**27**) *[24] in dichloromethane or acetonitrile in the presence of the quencher*.—A mixture of phenyl 2,3,4,6-tetra-*O*-benzyl-1-seleno-β-D-glucopyranoside (**5**) or ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**27**) [24] (0.1 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**12**) (40 mg, 0.08 mmol), 1,2,4,5-tetramethoxybenzene (115 mg, 0.6 mmol) and 4 Å molecular sieves was stirred in anhydrous solvent (2 mL) under N_2 for 1 h. BAHA (115 mg, 0.15 mmol) was added and the reaction mixture was stirred under N_2 for as long as the corresponding experiment in the absence of the quencher. The reaction mixture was cooled to 0 °C and neutralized with Et_3N. The mixture was filtered through Celite with dichloromethane. The filtrate was concentrated, and the residue was purified by column chromatography with hexane-ethyl acetate as eluant.

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