A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201802847
Angew. Chem. 10.1002/ange.201802847

Link to VoR: http://dx.doi.org/10.1002/anie.201802847
http://dx.doi.org/10.1002/ange.201802847

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10.1002/anie.201802847

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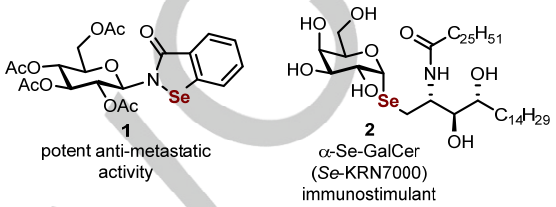
Stereoretentive Manipulations of Anomeric Nucleophiles: Applications in the Synthesis of Selenoglycosides

Feng Zhu, Sloane O'Neill, Jacob Rodriguez, and Maciej A. Walczak*[a]

Abstract: We report a stereospecific cross-coupling of anomeric stannanes with symmetrical diselenides that results in the synthesis of selenoglycosides with exclusive anomeric control and without directing groups. The reaction is compatible with free hydroxyl groups and is demonstrated in the preparation of glycoconjugates derived from mono-, di- and trisaccharides and peptides (35 examples). Given its generality and broad substrate scope, the glycosyl cross-coupling method presented herein can find use in the synthesis of selenium-containing glycomimetics and glycoconjugates.

Carbohydrate mimetics that retain the functional and structural properties of natural saccharides while demonstrating enhanced *in vivo* stabilities constitute a privileged class of molecules.[1] This includes, but is not limited to, their use as tools to decipher the biological roles of glycans and as candidates in drug development. Selenoglycosides comprise a subset of selenium-containing compounds and are known to possess a diverse set of useful biological activities (Figure 1). Their potential application in the development of novel carbohydrate-based therapeutics is suggested by their anti-metastatic (**1**),[2] immunostimulatory (**2**),[3] and anti-tumor[2, 4] activities; additionally, selenoglycosides demonstrate their utility as probes for studying carbohydrate-protein interactions.[5] Furthermore, selenoglycosides function as glycosyl donors with unique reactivities.[6] Under photo-[7] and electrochemical[8] conditions, the C-Se bond readily ionizes, generating cationic or radical-cationic species. Despite demonstrating numerous valuable properties, inherent limitations in their methods of preparation thwart the practical utilization of selenoglycosides as glycomimetics. Herein we report a direct and programmable synthesis of selenoglycosides derived from small molecules and peptides that operates under standardized conditions and results in exclusive anomeric selectivities in a broad range of substrates.

Figure 1. Selected bioactive selenium-containing glycosides.



In general, the methods employed in the preparation of *Se*-glycosides focus on nucleophilic selenium sources that displace anomeric halides (Br, Cl),[9] Lewis-acid catalyzed anomerization of *Se*-glycosides,[3] azidophenylselenation of glycals,[10] and nucleophilic opening of 1,2-*anhydro* sugars (Scheme 1A).[11] In the case of a participating group at C2, high anomeric selectivities are possible but only provide access to the β anomer. Furthermore, the incompatibility of free hydroxyl groups with the conditions necessary for generating oxonium intermediates limit the scope of viable substrates to protected saccharides. A method that allows for the stereoretentive preparation of both anomers of selenoglycosides with simple substrates that require minimal protective group manipulations opens a pathway toward their use in oligosaccharide synthesis, medicinal chemistry, and chemical biology.

We hypothesized that a stereoretentive transfer of glycosides from anomeric nucleophiles to diselenide substrates offers a possible solution (Scheme 1B). Anomeric stannanes of mono- and oligosaccharides are a source of configurationally stable nucleophiles that can be stored and manipulated under ambient conditions without loss of stereochemical integrity.[12] Both anomers of C1 stannanes can be prepared *via* straightforward manipulations of glycal substrates affording 1,2-*cis*- and 1,2-*trans* isomers, and both anomers of 2-deoxysugars.[12] Methods that promote the formation of C(sp^2)-Se bonds are well-established using Ag,[13] Cu,[14] Fe,[15] Ni,[16] and Pd[17] complexes and provide precedent for the reasonable extension of these technologies to the stereoselective synthesis of C(sp^3)-selenides. Investigation into this approach presents an opportunity to fill the knowledge gaps within this underdeveloped area in glycoside synthesis.[14a, 18]

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10.1002/anie.201802847

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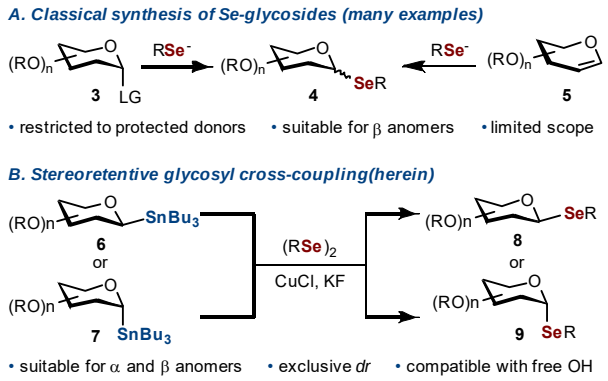
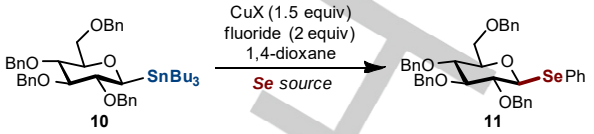
Scheme 1. Selected methods for the preparation of *Se*-glycosides.



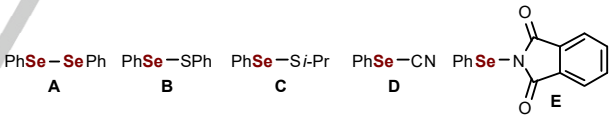
To optimize conditions for installing anomeric selenides, we first tested reactions of β-stannane **10** with various phenylselenide donors (Table 1). From the screening studies, the combination of CuCl (1.5 equiv) and KF (2 equiv) resulted in the best isolated yield (entry 1, 91%) while other copper (I) salts afforded selenide **11** in diminished yields (entries 2 and 3). With respect to the source of fluoride ion, TBAF (entry 5) proved to be the least effective additive resulting only in the formation of D-glucal as by-product. The use of heterogeneous inorganic salts (KF or CsF, entry 4) offered the optimal compromise between fluoride ion reactivity and solubility in 1,4-dioxane. Fluoride, however, is not necessary for the reaction to take place (entry 6) whereas exclusion of copper (entry 7) resulted in trace amounts of **11**. Further modifications of the conditions such as decreased amounts of CuCl (entry 8), shortened reaction times (entry 9), or lower temperatures (entry 10) had only detrimental effects on the reaction yields.

Table 1. Optimization of glycosyl cross-coupling.[a]



Entry	Cu	Fluoride	Se	Temp.	Time	Yield[b,c]
1	CuCl	KF	**A**	110 °C	24 h	91%
2	CuBr	KF	**A**	110 °C	24 h	25%
3	CuI	KF	**A**	110 °C	24 h	7%
4	CuCl	CsF	**A**	110 °C	24 h	58%
5	CuCl	TBAF	**A**	110 °C	24 h	<5%
6	CuCl	None	**A**	110 °C	24 h	70%
7	None	KF	**A**	110 °C	24 h	<5%
8[d]	CuCl	KF	**A**	110 °C	24 h	69%
9	CuCl	KF	**A**	110 °C	12 h	74%
10	CuCl	KF	**A**	90 °C	24 h	55%
11	CuCl	KF	**B**	110 °C	24 h	79%
12	CuCl	KF	**C**	110 °C	48 h	88%
13	CuCl	KF	**D**	110 °C	24 h	44%
14	CuCl	KF	**E**	110 °C	24 h	62%

[a] Reaction conditions: selenide **A**-**E** (0.100 mmol, 1.0 equiv), **10** (1.1 equiv), fluoride (2 equiv), CuX (1.5 equiv), and dry 1,4-dioxane (2 mL) under N_2, 110 °C; [b] Isolated yield; [c] Only β anomer formed; [d] 1 Equiv of CuCl.



The use of symmetrical diselenides (e.g., **A**) suffers from inherent inefficiencies due to the inevitable loss of one-half of the substrate. Using a selenide donor with a competent leaving group such as a thiolate (entries 11 and 12), a cyanide (entry 13), or a phthalimidate (entry 14) resolves this issue. All of these types of reagents are compatible with the optimized conditions (entry 1) and furnish selenoglycoside **11** in 44-88% yield. The facile preparation and excellent yield with selenothiols indicated *i*-propylthiol **C** to be the best substitute for symmetrical selenides. An alternative solution capitalizes on external oxidants that result in regeneration of the diselenide. Based on the proposed mechanism (*vide infra*), the selenol by-product could be recycled and converted back into a diselenide if a proper oxidant (e.g., oxygen, air) that does not interfere with the copper salt, is present. Thus, when the reaction was attempted in a flask open to air, we observed a full conversion of diphenyl diselenide **A** (1 equiv) and stannane **10** (2 equiv) into **11** in 70% yield. This modification eliminates unnecessary forfeiture of selenium material and, in the case of large symmetrical molecules (e.g., peptides, *vide infra*), ensures optimal conversions.

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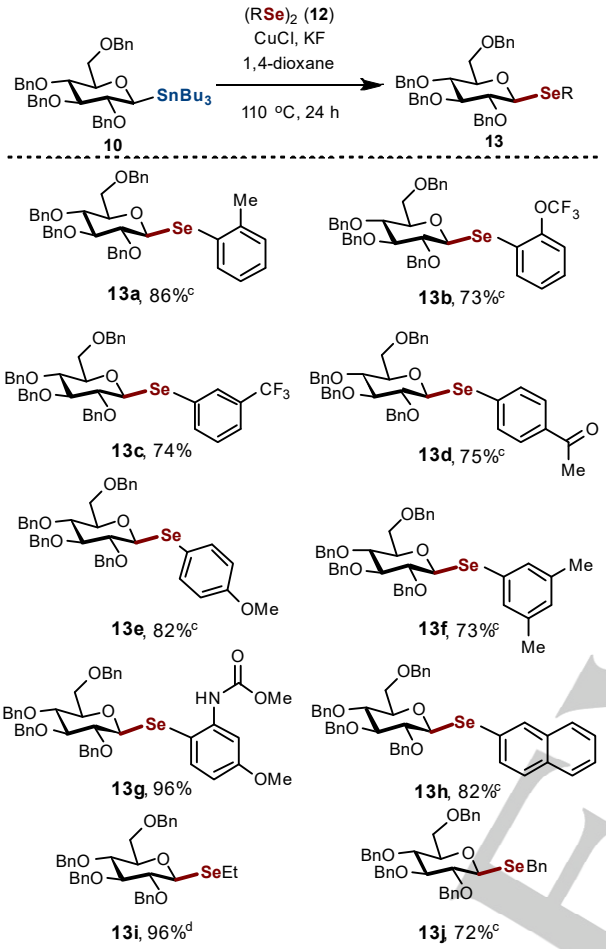
Scheme 2. Scope of cross-coupling with symmetrical diselenides **12**.[a,b]

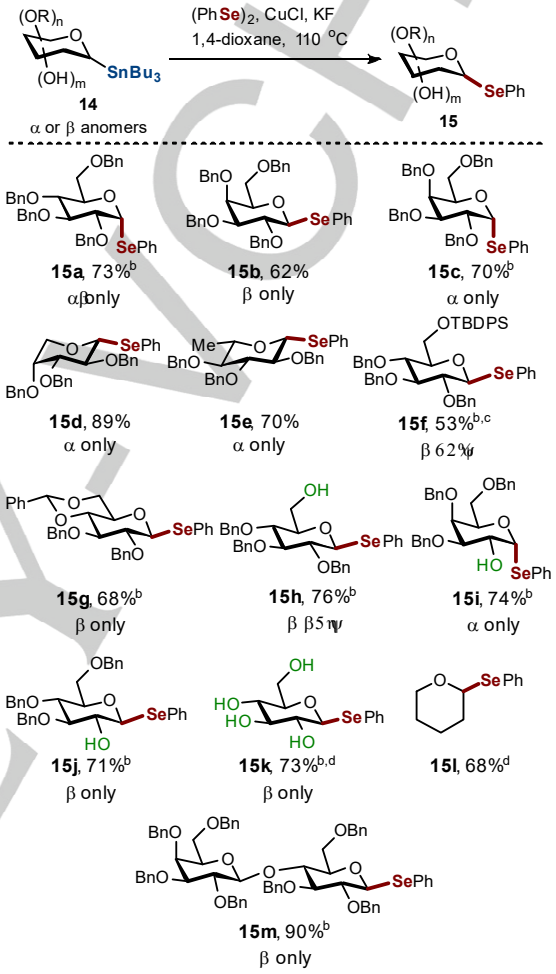


[a] General reaction conditions adopted from Table 1, entry 1. [b] Only β anomer formed (based on ^{1}H NMR of the unpurified reaction mixtures). [c] Reaction time: 48 h. [d] 2 Equiv. of $(EtSe)_2$.

The optimized conditions from Table 1 were first applied to reactions with aryl and alkyl selenides (Scheme 2). Thus, aryl selenides containing substituents at the *ortho*- (**13a** and **13b**), *meta*- (**13c**), and *para*-positions (**13d** and **13e**), as well as di-substituted (**13f** and **13g**), and polycyclic (**13h**) substrates merged efficiently with D-glucose **10** in 73-96% isolated yields. Similarly, symmetrical alkyl selenides afforded products **13i** and **13j** in excellent yields. For all examples presented in Scheme 2, the exclusive formation of the β anomer was observed (^{1}H NMR).

Second, we probed the scope of the cross-coupling reaction using various mono- and disaccharides (Scheme 3). We found that α-D-glucose and both anomers of D-galactose gave their corresponding *Se*-glycosides with very good anomeric selectivities (**15a-c**). Deoxy-sugars such as D-arabinose **15d** and D-quivinose **15e**, silicon- **15f** and benzylidene-protected D-glucose **15g**, and D-lactose **15m** afforded *Se*-glycosides in consistently high yields. We were also pleased to find that the optimized conditions tolerated hydroxyl groups at C6 (**15h**) and C2 (**15i** and **15j**) without detrimental effects to the anomeric selectivities.

Scheme 3. Scope of *Se*-glycoside synthesis.[a,b]



[a] General reaction conditions adopted from Table 1, entry 1. [b] Reaction time: 48 h. [c] Reaction run without KF. [d] 1.5 Equiv of stannane **14**.

An impressive example demonstrating the generality of the cross-coupling method is the conversion of unprotected D-glucose into selenide **15k** in 73% isolated yield and β-selectivity. Traditional nucleophilic methods require extensive protecting group manipulations, and, to the best of our knowledge, no other current method provides direct access to selenoglycosides using carbohydrates with unprotected hydroxyl groups. We also demonstrated that all benzyl groups in **11** could be removed with BCl_3 without cleavage of the sensitive C-Se bond affording **15k** in 79% yield (for details, see the SI).

Next, we tested the scope of the cross-coupling reaction in the preparation of 1,1-selenosaccharides (Scheme 4). In pursuing this aim, we were inspired by the prior work on unnatural D-trehalose analogs that show improved hydrolytic stability.[19] D-trehalose is a disaccharide essential to mycobacterial cell wall synthesis, energy storage, and cellular stress protection.[20]

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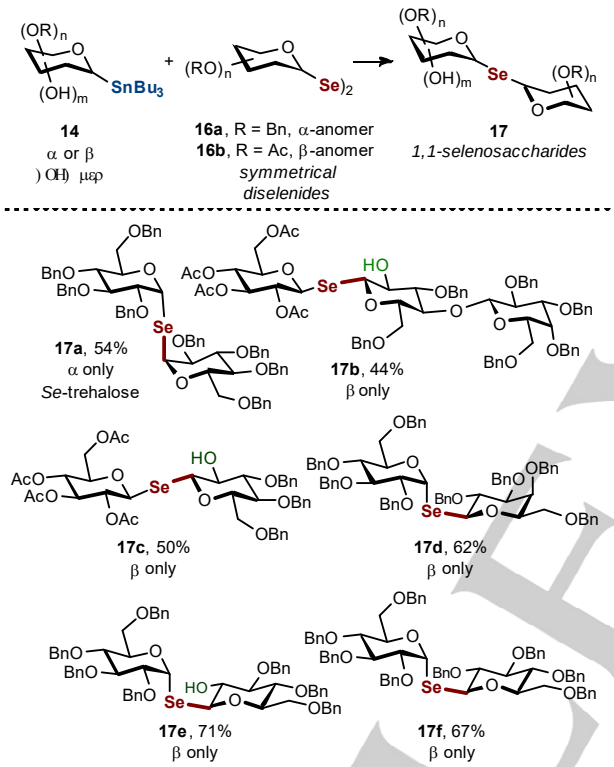
However, a practical and high-yielding method for the synthesis of this important reporter molecule is needed.[21] Thus, direct cross-coupling of α-stannane with α-diselenide **16a** furnished α,α-1,1-linked disaccharide **17a** in excellent yield and exclusive selectivity. We next expanded the scope of the selenoglycoside synthesis to the preparation of β,β-1,1-saccharides **17b-c** and α,β-1,1-saccharides **17d-f** by using the corresponding anomers of the diselenide substrates **16**. This method allows for a programmed introduction of any anomeric configuration of the selenides by a selection of the corresponding coupling partners.

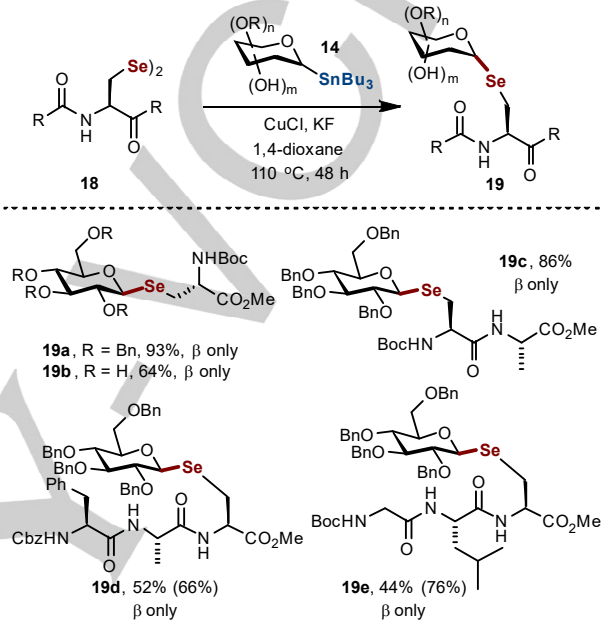
Scheme 4. Synthesis of 1,1-selenoglycosides.[a]



[a] **17a** was prepared using **16a**; **17b-f** were prepared using **16b**.

Finally, we investigated reactions of anomeric stannanes with selenium-containing peptides (Scheme 5). Protein glycosylation is a common post-translational modification and the attachment of glycans through serine and threonine is known to modulate cellular localization, stability, and folding.[22] Selenocysteine, a proteinogenic amino acid, has been used as a handle in site-selective modifications of proteins and peptides via alkylative methods that capitalize on high nucleophilicity of selenols.[23] However, direct glycosylation of selenocysteine has only been reported using classical nucleophilic displacement methods.[9d, 24] To this end, we tested the cross-coupling conditions with seleno-L-cystine using protected and free D-glucose stannanes resulting in high yields of selenocysteine glycoconjugates (**19a-b**). Along the same lines, peptides modified with selenocysteine at the *N*-(**19c**) or *C*-terminus (**19d-e**) were smoothly converted into the corresponding glycoconjugates. The cross-coupling reactions were conducted under oxidative conditions (air) assuring full conversion into selenoglycosides **19**. These results represent the first example of stereospecific glycodiversification of selenopeptides with exclusive control of anomeric configuration and unprecedented functional group tolerance.

Scheme 5. Scope of Se-glycosylation of amino acids and peptides.[a]



[a] General reaction conditions adopted from Table 1, entry 1 using 0.5 equiv of **18** and 1 equiv of **14** under air. Yields in parentheses are based on **14** and refer to reactions with 1 equiv of **18** and 1 equiv of **14** under N_2.

The proposed mechanism of cross-coupling of anomeric nucleophiles with symmetrical diselenides is depicted in Scheme 6. A stereoretentive transmetalation from anomeric nucleophiles **20** to copper is likely facilitated by a fluoride ion that activates the anomeric stannanes towards transfer to copper(I) forming insoluble Bu_3SnF by-product. The configurationally stable C1-copper intermediate **21** undergoes a nucleophilic reaction with diselenide **22** with retention of configuration at C1 and the formation of the selenocopper by-product **24**. Under the oxidative conditions, **24** is converted into diselenide $(RSe)_2$ that enters the cycle and effectively results in a full consumption of the substrate. In the case of the unsymmetrical substrates, where the leaving group is a thiol or a cyanide (Table 1), the regioselectivity of the transfer of anomeric nucleophile to selenium can be explained by the greater electronegative character of the leaving group; we were unable to detect any thioglycosides formed under the optimized conditions. An alternative mechanism in which the copper(I) salt acts as a Lewis acid activating the diselenide towards stereoretentive addition cannot be completely excluded at this point. However, reluctance of anomeric stannanes to undergo a transfer with diselenides in the presence of a Lewis acid additive ($Zn(OTf)_2$, $Sc(OTf)_3$, and BF_3, fluoride excluded) suggests that this pathway plays only a minor role.

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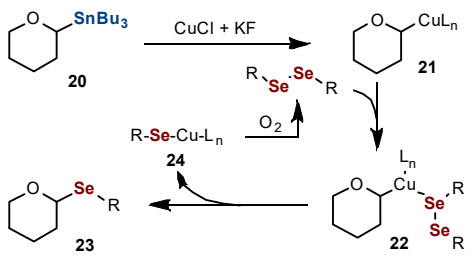
Scheme 6. Proposed mechanism of stereoretentive Se-glycosylation.



In summary, we described here the first example of stereoretentive synthesis of anomeric selenides enabling access to selenoglycomimetics. This method demonstrates unprecedented selectivity and functional group tolerance, including reactions with saccharides containing free hydroxyl groups, peptides, and small molecules without directing groups. Further studies on the applications of anomeric nucleophiles in the synthesis of glycosides and glycomimetics are ongoing.

Acknowledgements

This work was supported by the University of Colorado Boulder and the National Science Foundation (CAREER Award No. CHE-1753225). Mass spectral analyses were recorded at the University of Colorado Boulder Central Analytical Laboratory Mass Spectrometry Core Facility (partially funded by the NIH, RR026641).

Keywords: carbohydrates • stereoretentive cross-coupling • anomeric nucleophiles • selenides • copper

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