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ARTICLE TYPE

Electrochemical nickel-catalyzed Migita cross-coupling of 1-thiosugars with aryl, alkenyl and alkynyl bromides

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Here we report a simple route towards the synthesis of thioglycosides, in which electrochemical cross-coupling is used to form the S–C glycosidic bond from protected and unprotected thiosugars with functionalized aryl bromides under base free conditions. The reaction manifold that we report here demonstrates the power of electrochemistry to access highly complex glycosides under mild conditions.

1-Thioglycosides have emerged as a privileged class of glycosides with a diverse range of potential applications.¹ These glycomimetics are known to be more robust towards enzymatic cleavage under biological conditions.² Representative active glycosides with a thioether linkage are disclosed in Figure 1, including hSGLT1 inhibitor, ligand of lectine A, cytotoxic Hsp90 inhibitor, antimicrobial agent as well as galactin-3-inhibitors. Moreover, thioglycosides are well known to be useful and versatile reactive intermediates in organic synthesis.³

At present, for the functionalization of glycosyl thiols, various catalytic systems based on palladium,⁴ nickel⁵ and copper⁶ have been reported (Figure 1,a-b).⁷ Despite their high interest, these methods require the use of basic conditions with high catalyst loadings (30 mol% in the case of Ni-catalysis) or precious metals such as Pd-catalyst with specially designed ligands.⁸ In addition, an elevated reaction temperature (up to 120 °C cases of Pd- or Cu-catalysis), and long reaction times often limit the practicability or the scope of substrates. Moreover, in all these cases the coupling is effective with only aryl iodides, however the cross-coupling with aryl bromides is rather unexplored. To address these issues, we have reported recently a Ni/Ru dual photocatalyzed arylation of thiosugars with aryl iodides under base-free conditions (Figure 1,c).⁹ However, the more available and less expensive aryl bromides are still unreactive under these photoredox conditions. Only few examples were reported with yield never exceeded 43% yield. Moreover, this method was limited to only protected thiosugars. This set of limitations clearly indicates that glycosyl thiols often behave as a rather special and challenging class of thiol nucleophiles for transition-metal-catalyzed thio-functionalization.

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Figure 1. Examples of natural products, bioactive thioglycosides, and catalytic strategies to access to thioglycosides 3.

Because of the high importance of thioglycosides, the development of a general method for the coupling of both aryl bromides and iodides to protected and unprotected thiosugars under room temperature and without an external base remains a challenging task.

In recent years, electrosynthesis¹⁰ has emerged as a remarkably efficient tool for organic cross-coupling reactions through the use of less precious catalysts, waste-free and inexpensive electric current, thereby avoiding stoichiometric amounts of toxic and costly chemical reagents limiting our impact on the environment. Usually, this method was used successfully in C–H activation process for the formation of C–C and C–heteroatom bonds (C–O, C–P, and C–N) through the directing group strategy.¹¹ However, electrochemical C–heteroatom bond formation *via* cross coupling of nucleophiles with aryl (pseudo)halides was less explored.¹² In particular, methods which use electrosynthesis to form C–S bonds are rare. To the best of our knowledges, only one study from Mei *et al.* reported the cross-coupling reaction of thiophenols with aryl halides.¹³ The authors showed elegantly that this approach allows thiolation of aryl halides. However, this method exhibited several limitations with regards to potential applications: *i*) the use of a large excess of the thiophenol partner (3 equiv) which can be prohibitive for larger scale reactions; *ii*) the scope with respect to the thiols was limited to unfunctionalized thiophenols, thus precluding many synthetic applications. Moreover, the S-arylation of functionalized and complex alkyl thiols bearing free hydroxyl or amino groups such as thiosugars under electrochemistry has never been studied, probably because of the polyhydroxylated complexity of carbohydrates. Herein, we became interested in whether the S-(hetero)arylation of 1-thiosugars could be performed by the electrochemical process. The present study is presented (Figure 1).

To initiate this study, we conducted this electrochemical thioglycosylation by coupling of tetra-*O*-acetylated 1-thio- β -D-glucopyranose **1a** with 4-bromobenzotrifluoride **2a** as a model study under various reaction conditions. Representative results from this study are summarized in Table 1. The reaction of **1a** (1 equiv) with **2a** (3 equiv) was first investigated by using constant-current electrolysis at 4.0 mA in the presence of NiBr₂.diglyme (10 mol%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (di-*t*Bubpy) (10 mol%), LiBr (4 equiv) in DMF at room temperature for 6 h within an undivided cell (Table 1, entry 2). Pleasingly, these conditions afforded the **3a** in a moderate 54% yield as a single β -anomer ($J_{1,2} = 9$ Hz) (See ESI). Interestingly, decreasing the amount of the bromide partner **2a** from 3 equiv to 1 equiv furnished the thioglycoside **3a** in a good 74% yield (entry 1). Using other anodes such as Zn was not effective (entry 9). In addition, reaction with DMA instead DMF was less efficient and gave product **3a** in only 47% yield (entry 11). Interestingly, when the current was increased up to 8mA, the reaction time was shortened to 3h and **3a** was isolated in 74% yield (entry 5). Finally, performing the coupling reaction with 20 mol% of NiBr₂.diglyme and 20 mol% of di-*t*Bubpy furnished **3a** in 80% yield (entry 10). Negative controlling experiments demonstrated the catalyst, the LiBr and the current are necessary (entries 6–8).

Table 1. Optimization of the coupling reaction of **1a**^[a]

Entry	Deviation from the standard conditions	Yield (%) ^b
1	none	74
2	0.3 mmol of 1a and 0.9 mmol of 2a	54
3	0.6 mmol of 1a and 0.3 mmol of 2a	73
4	2 mA, 12 h	71
5	8 mA, 3 h	74
6	No LiBr	0
7	No catalyst	trace
8	No electric current	0
9	Zn instead of Mg	28
10	20 mol% Ni.cat and 20 mol% Dttbpy	80
11	DMA instead of DMF	47

^a Reactions conditions: Mg anode, Ni foam cathode, **1a** (0.3 mmol), **2** (0.3 mmol), NiBr₂.diglyme (10 mol%), di-*t*Bubpy (10 mol%), LiBr (1.2 mmol), DMF (0.3 M), undivided cell, constant current = 4 mA, (Ar) room temperature, 6 h. ^b Isolated yield.

With these encouraging results, we investigated next, the scope and limitations for this electrochemical process by systematically varying the nature of the bromide electrophile **2**. As showed in Table 2, all the S-arylations of tetra-*O*-acetylated 1-thio- β -D-glucopyranose **1a** proceeded cleanly and selectively in good yields. Cross-coupling of **1a** with aryl bromides bearing various functions (–CN, –Cl, –F, –CF₃, –CHO and –OMe) have been successfully achieved under room temperature to afford the corresponding thioglycosides (**3a–m**) in yields up to 87%. In addition, the presence of an *ortho* substitution at the aromatic ring of the coupling partner do not affect the coupling process as compounds **3h** and **3k** were obtained in 80% and 77% yields, respectively. It is noteworthy that a selectivity was observed when a tribromobenzene was used, and only a di-glycosylated product **3m** was obtained in 70% yield even after running the coupling with longer reaction time (6h) and using 6 equiv of **1a**. One can be noted that, 3-bromonaphthalene is less reactive at current conditions than 2-bromonaphthalene giving the desired S-naphthylglycoside **3j** in only 22% yield (*vs* 77% with 2-bromonaphthalene). However this yield could be increased significantly (73% yield) when 3-iodonaphthalene. The same low reactivity was observed with *p*-bromoanisole *vs* *p*-iodoanisole (compound **3l**, 15% *vs* 83%). Interestingly, couplings with heteroaryl bromides derived from quinoline and pyridine have also been successful, furnishing **3n,o** in 46% and 86% yields, respectively. Next, we moved on to investigate the reactivity of a series of alkene and alkyne bromides. Pleasantly, both aryl- and alkyl- substituted alkene bromides ((*E*)-1-(2-bromovinyl)-4-methoxybenzene, *E*- β -styryliodide, (*E*)-1-bromooct-1-ene)) and 2-bromo-1H-indene were transformed efficiently into alkenyl thioglycosides **3p–s** in excellent yields. Finally, alkynyl-thioglycosides **3t–u** were also easily prepared in good yields from corresponding 1-(bromoethynyl)-4-methoxybenzene and 3-

Table 2 Scope of Coupling of Thioglucose **1a** with Halo(hetero)arenes, Alkenyl Halides and Alkynyl Bromides **2**

^a Reactions conditions: Mg anode, Ni foam cathode, **1a** (0.3 mmol), **2** (0.3 mmol), $\text{NiBr}_2 \cdot \text{diglyme}$ (10 mol%), di-tBuppy (10 mol%), LiBr (1.2 mmol), DMF (0.3 M), undivided cell, constant current = 8 mA, N_2 protection, room temperature, 3 h. ^bIsolated yield.

(bromoethynyl)thiophene by this electrochemical method.

The successful synthesis of thioglucosides **3a-u** from tetra-*O*-acetylated 1-thio- β -D-glucopyranose **1a** and various aryl bromides under our optimized electrochemical conditions encouraged us to investigate other glycosyl thiols. As depicted in Table 3, this coupling reaction tolerates different sugars such as *O*-benzoylated 1-thio- β -D-glucopyranose, thio- β -D-galactopyranose and 1-thio- β -D-fucopyranose which furnished the thioglucosides **4a-c** in yields up to 95%. In addition, this coupling could be applied successfully to the more complex and biologically relevant saccharide derivatives thio- β -D-cellobiose and thio- β -D-maltotriose delivering **4d** and **4e** in 90% and 88% yields, respectively.

Table 3. Scope of 1 thio- β -glycosyls **1b-g**^a

^a Reactions conditions: Mg anode, Ni foam cathode, **1b-f** (0.3 mmol), **2** (0.3 mmol), $\text{NiBr}_2 \cdot \text{diglyme}$ (10 mol%), di-tBuppy (10 mol%), LiBr (1.2 mmol), DMF (0.3 M), undivided cell, constant current = 8 mA, N_2 protection, room temperature, 3 h. ^bIsolated yield.

One of the most important task in this area of organometallic chemistry is to discover mild and general methods for easy functionalization of polyhydroxylated compounds with high selectivity without using any protection/deprotection sequence. To further show the synthetic use of our protocol, we evaluated whether the S-arylation of unprotected thiosugars could be realized by this electrochemical method. To our delight, the reaction of unprotected thio- β -D-glucose and thio- β -D-cellobiose yielded the respective products **5a** and **5b** in good yields, and no side products arising from the *O*-arylation were observed (Scheme 1).

Scheme 1. Unprotected thiosugars and cysteine-aminoacid as thiols

^a Reactions conditions: Mg anode, Ni foam cathode, **1g-i** (0.3 mmol), **2a** (0.3 mmol), $\text{NiBr}_2 \cdot \text{diglyme}$ (10 mol%), di-tBuppy (10 mol%), LiBr (1.2 mmol), DMF (0.3 M), undivided cell, constant current = 8 mA, N_2 protection, room temperature, 3 h. ^bIsolated yield.

Finally, as part of our interest in developing new methods to peptide and protein bioconjugation, we considered it worthwhile to investigate the reaction of cysteine aminoacid with aryl bromides (Scheme 1). Direct arylation of cysteine-containing peptides has only been reported using the precious Pd-catalysis.¹⁴

To this end, we tested the reaction of L-cysteine with *p*-cyanophenyl bromide and we were pleased to observe the formation of the S-arylated cysteine **5c** in 67% yield (Scheme 1). This result represent the first example of diversification of cysteine under electrochemical approach and may open new way to the bioconjugation of peptides and protein through this methodology.

In summary, we described here the first electrochemical method of coupling of various anomeric glycosyl thiols with aryl bromides. This method demonstrates unprecedented reactivity in regard to bromide partners (heteroaryl, alkenynyl and alkenyl bromides) and selectivity, including reactions with unprotected thiosugars, and cysteine aminoacid. Further studies on the applications of this method on the S-arylation of more complex polysaccharides and cysteine containing peptides are ongoing.

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