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A One-Pot Assembly of Unsymmetrical Biaryl Thioglycosides Through Chemoselective Palladium-Catalyzed Three-Component Tandem Reaction

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ABSTRACT: A range of unsymmetrical biaryls bearing thiosugars could be synthesized in a one-pot multicomponent approach using one catalytic palladium system that permitted the C–S and C–C bonds forming. The reaction showed a high selectivity and was applied to a broad variety of substrates giving access to novel glycosylated bi-aryl structures in good yields.

Functionalized unsymmetrical biaryls are of great prevalence in Nature¹ and are found in many important medicinal compounds (Telmizartan, Boscalid). In addition, they are used in materials chemistry as semiconductors² or as ligands for asymmetric catalysis.³ Biaryl platforms bearing donor and acceptor moieties have important optical properties and have been studied for photolability as two-photon sensitive photoremovable protecting groups for biologically-active molecules delivery⁴. Interestingly, unsymmetrical biaryls functionalized with sugar groups are less reported in the literature. Several pharmacologically important biphenyl glycosides have been described (Figure 1). Lysilactone A is used in traditional Chinese folk medicine.⁵ Biphenylglycosides **2** and **3** have significant antioxidant activity.⁷ Mannoside **4** is a highly efficient FimH antagonist⁸ used for the treatment of urinary tract infections (UTIs). Moreover, several diphenylmethyl- β -C-glycosides such as dapagliflozin have been synthesized as potent inhibitors of SGLT2.⁹

Usually, unsymmetrical biaryls are prepared from haloarenes or triflates,¹⁰ either by palladium¹¹ or by nickel¹² catalyzed cross couplings. They can also be obtained by coupling of two aryls with hypervalent silicon reagents,¹³ or

by C–H bond activation.¹⁴ However, few examples of "one pot"¹⁵ sequential procedures have been reported in the literature. Among these are the Diels-Alder cycloaddition or the reaction of arylhalides with bis(pinacolato)diboron followed by coupling with

Figure 1. Example of Natural and Synthetic Biaryl Glycosides another arylhalide.¹⁶ Nevertheless, structures of biaryls bearing thiosugars and synthetic methods leading to their formation are non-existent.¹⁷ Thiosugars can be used as

sugar surrogates; therefore, their introduction into biaryls is highly relevant since biarylthioglycosides can be investigated as mimetics of biologically relevant *O*-glycosides. *S*-Glycosides are much more stable than *O*-glycosides to both chemical and enzymatic degradation and have been utilized as enzyme inhibitors in various biochemical studies.¹⁸ Owing to the significant importance of biphenylglycosides, there is a strong impetus to discover new chemical transformations for their efficient synthesis and functionalization.

As part of our continuing effort to provide the chemistry community with more efficient ways to produce high value thioglycosides,¹⁹ we became interested in extending our recently disclosed PdG₃-catalyzed arylation of thiosugars at room temperature with aryl iodides²⁰ into a tandem multicomponent reaction (MCR) involving iodo-bromoarenes, thiosugars and arylboronic acids. The procedure consists on using one Pd-catalyst which, under the same catalytic cycle, will promote the catalysis of two individual steps; i) the first is the selective creation of the S–C bond between β -thiosugars and dihalogenated arenes (iodo-bromoarenes); ii) the second is based on C–C bond formation between the monohalogenated thioglycoside intermediate and diverse arylboronic acids. We could assume that in the presence of a nonselective catalyst, the reaction could statistically generate a complex mixture of up to three possible products (Table 1). In this regard, we wished to take advantages of the selectivity of oxidative addition of a C–I bond to Pd (0) species followed by the insertion of a thiol function at room temperature and to then perform a Suzuki-Miyaura coupling reaction at the remaining C–Br bond. We have focused our objective to find one catalytic system that will be highly selective toward the formation of the desired biarylthioglycoside product **4a**. From a synthetic viewpoint, this procedure would offer the shortest and the most efficient route to biarylthioglycosides for the purpose of medicinal chemistry screening program. Herein, we report our success in the development of such protocol.

Initial selectivity tests were performed using PdG₃ XantPhos (10 mol %) as a catalyst, which was reported previously by our group to be effective for the arylation of thiosugars.²⁰ The selectivity was first examined in a model three-component reaction that utilized the tetraacetylated β -thiogalactose **1a** (1 equiv), 1-bromo-3-iodobenzene **2a** (1 equiv) and (4-methoxyphenyl)boronic acid **3a** (1.5 equiv) (Table 1). Gratifyingly, by running the reaction in wet THF for 15 min at room temperature and 3 h at 100 °C using a combination of two bases NEt₃ and K₂CO₃ (4 equiv), we were able to achieve a complete selectivity toward the C–I and C–Br bonds. Under these conditions, compound **4a** was isolated in 48% yield without any side products (Table 1, entry 1). Then we attempted to omit NEt₃ and to our satisfaction, by adding K₂CO₃ (4 equiv) and heating overnight at 80 °C, **4a** was obtained in 55% yield (Table 1, entry 2). Since the latter conditions were superior, we settled on these, using K₂CO₃ as a base. Stirring the mixture at 100 °C in the presence of two equivalents of arylboronic for 12 h, decreased the yield to 42% and led to by-product formation (Table 1, entry 3). Surprisingly, by shortening the reaction time from 12 h to 5 h, the biphenyl β -thioglycoside (*J*_{1,2} = 9.9 Hz) **4a** was isolated in 83% yield when 1.2 equiv of thiogalactose **1a** were used (Table 1, entry 4). Fortunately,

reducing the catalyst loading to 5 mol % gave **4a** in a similar yield (82%, Table 1, entry 5). A second part of this optimization focused upon investigating the feasibility of the reaction at the same temperature (100 °C). Simple mixing of the three components **1a** (1.2 equiv), **2a** (1 equiv) and **3a** (2 equiv) at 100 °C furnished product **4a** in a good 81% yield and with a perfect control of the anomeric configuration (*J*_{1,2} = 9.9 Hz). One can be noted that in all cases, the monohalogenated thioglycoside intermediate has never been observed during the process.

Motivated by these exciting results, we subsequently investigated the substrate scope for this tandem catalytic process by systematically varying the boronic acids **3**, iodo-bromoarenes **2a-e** and the thiosugar substrates **1a-g** (Scheme 1).

Table 1 Optimization of the Coupling Reaction of Tetraacetylated β -thiogalactose **1a**, 1-Bromo-3-iodobenzene **2a** and (4-Methoxyphenyl)boronic acid **3a**^a

entry	base	<i>t</i> (°C)	time (h)	4a (%) ^b	5a/6a (%)
1	Et ₃ N/K ₂ CO ₃	rt then 100	3	48	o/o
2	K ₂ CO ₃	rt then 80	12	55	o/o
3	K ₂ CO ₃	rt then 100	12	42	o/o
4	K ₂ CO ₃	rt then 100	5	83	o/o
5	K ₂ CO ₃	rt then 100	5	82 ^{c,d}	o/o
6	K ₂ CO ₃	100	5	81 ^{c,d,e}	o/o

^aA sealable tube was charged with thiosugar **1a** (1 equiv), 1-bromo-3-iodobenzene **2a** (1 equiv), 4-methoxyphenylboronic acid **3a** (1.5 equiv), PdG₃ XantPhos (10 mol %), base (4 equiv) in THF(wet) (0.22 M) at rt (15 min) then 5 h at 100 °C. ^bYield of isolated product. ^c5 mol % of PdG₃ XantPhos. ^d1.2 equiv of **1a** were used. ^eThe reaction was performed at the same temperature (100 °C).

Gratifyingly, all the tandem S- and C-arylations proceeded cleanly and selectively in good yields. As illustrated in Scheme 1, a variety of electron-rich and electron-deficient, *para* and *meta* substituted arylboronic acids effectively underwent reaction with 1-bromo-3-iodobenzene **2a** and tetra-*O*-acetylated 1-thio- β -D-glucopyranose **1a** in yields up to 80% (products **4a-f**, **4h**, and **4i-k**). In addition, the sterically demanding *ortho* substitution pattern engaged in the tandem coupling reaction of **1a**, furnishing compounds **4g** and **4l,m** having an *ortho* substituent group. Interestingly, heteroarene boronic acids such as pyridyl-4-ylboronic acid and quinoleinyl-6-boronic acid were good substrates in this reaction (compounds **4n,o**). In addition this tandem process was successfully expanded to the coupling of styryl boronic acid providing thioglycosylated stilbene **4p** in an acceptable 56% yield (Scheme 1).

The reaction of unsubstituted *para*-iodo-bromobenzene **2b** with thiogalactose **1a** and boronic acids resulted also in selective formation of biphenyl *para*- β -thioglycoside **4q** in a good yield, while the *ortho*-dihalogenated substrate **2c** gave only a moderate yield of **4r** (32% yield), probably due to steric hindrance. The same product was obtained in

68% yield over two steps when PdCl₂.dppf was used as the catalyst for the Suzuki-Miyaura coupling. Interestingly, the tri-halogenated substrate **2d** was used successfully in this MCR coupling leading selectively to thioglycoside **4s** in 51% yield without affecting the remaining C–Cl bond.

Finally, extending this method to dihalopyridine-based substrate where the catalyst could be deactivated via Pd-pyridine coordination, also proved to be successful. Thus,

3-bromo-5-iodopyridine **2e** was a good partner with **1a** and **3a** under our optimized conditions, furnishing the desired product **4t** in 54% yield.

Of note that in all the studied cases, compounds **4a-t** were isolated as single anomers, clearly indicating that the tandem process is stereoretentive with report to the anomeric configuration of the sugar moiety.

Scheme 1 Scope of One-Pot Boronic Acids **2** Coupling with Thiogalactose **1a** and Iodo-bromoarenes **3a-d**

Regarding the sugar partners, this coupling reaction tolerates a large variety of glycosylthiols **1a-g** (Scheme 2): O-acetylated 1-thio-β-D-galactopyranose **1a**, O-acetylated 1-thio-β-D-glycopyranose **1b**, O-benzoylated 1-thio-β-D-glucopyranose **1c** and O-acetylated *N*-Ac-1-thio-β-D-glucopyranose **1d** all coupled with the dihalobenzenes **2a-b** to give biphenylthioglycosides **5a-e** in respectable yields. Importantly, this procedure is not limited to only protected β-glycosyl thiols, but it also worked successfully with unprotected 1-thiogluco-**1e** without any loss of reactivity. In this cases products **5f,g** were obtained in 63% and 50% yields, respectively. Moreover, the reaction is not limited to monosaccharides, but can be applied to more complex

di- and trisaccharide derivatives. Thus, 1-thio-β-D-cellobiose **1f** and 1-thio-β-D-maltotriose **1g** were efficiently reacted with 1-bromo-3-iodobenzene **2a** to give original biphenyl structures **5h,i** featuring di- and trisaccharides. Importantly, the stereochemistry of the β-1,4'-O-glycosidic bond in the disaccharides **5h** and the α-1,4' in β-trisaccharide **5i** remained intact.

In summary, we have developed an efficient and versatile protocol for the one-pot multicomponent preparation of biphenylthioglycosides. The method tolerates a wide range of functional groups and a variety of protected and unprotected glycosylthiols could be used. We expect this simple

and general method to be of broad utility for the synthesis and development of new medicinal agents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, spectroscopic data and NMR spectra of new compounds.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

Scheme 2 Scope of One-Pot Thiosugars **1b-g** Coupling With Boronic Acid **2a** Iodo-bromoarenes **3a-d**

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