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Rhodium-Catalyzed Denitrogenative Transannulation of *N*-Sulfonyl-1,2,3-triazoles with Glycals Giving Pyrroline-Fused *N*-Glycosides

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Cite This: https://doi.org/10.1021/acs.orglett.1c02141 Read Online

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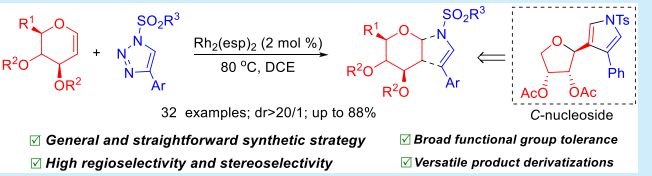
ABSTRACT: Described here is a selective synthesis of 2,3-dihydropyrrole-fused *N*-glycosides through rhodium-catalyzed denitrogenative transannulation of *N*-sulfonyl-1,2,3-triazoles with glycals. A series of pyrroline-fused *N*-glycosides are afforded in moderate to excellent yields with exclusive regioselectivity and stereoselectivity. Functional application of such a resultant product by oxidative addition and epoxidation is also explored. Notably, the treatment of a pyrroline-fused *N*-glycoside (**3a**) with TMSOTf efficiently leads to an interesting unexpected *C*-nucleoside (**9**) via a TMSOTf-inducing ring opening/acetyl migration/ring closing reaction sequence.



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N-Heterocyclic glycosides, widely present in many natural products and bioactive compounds, make up a very significant class of compounds.[1] Nucleosides,[2] glycoproteins, and glycopeptides[3] are the three important categories of *N*-glycosides, which serve as clinical drugs and essential components of DNA/RNA, enzymes, and antibodies in living systems. With the development of glycobiology, more and more structures containing pyrroline or *N*-glycosylated heterocycles have been discovered, such as perinadine A,[4] (±)-aspidophylline A,[5] and *β*-glucosidase inhibitor[6] (Figure 1). They exhibit importantly physiological activities such as antiviral, anticancer, antibacterial, and antifungal activities or inhibition against several glycosidases.[7]

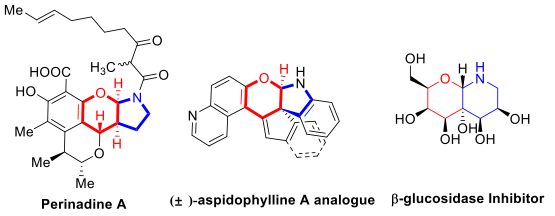

Figure 1. Biologically important DPPs and *N*-glycosylated heterocycles.

Moreover, compared with *O*-glycosides, most *N*-glycosides show stronger biological activities because they are less likely to be hydrolyzed under physiological conditions.[8] The introduction of a sugar moiety through the *N*-glycosidic bonds can significantly improve the activities of certain biologically active natural products.[9] Therefore, the efficient and stereoselective synthesis of *N*-glycosides has attracted a great deal of attention. Dihydropyrro[2,3-*b*]pyrans (DPPs) have two distinct heterocycles of dihydropyrroles and pyrans, which showed prominent antibacterial activities and interleukin inhibitory activity.[5,10] As a consequence, various methods have been developed to synthesize such structural motifs.[11] However, the synthesis of multisubstituted and chiral DPPs has rarely been studied. Therefore, the development of new methodologies for synthesizing *N*-glycosylated heterocycles is desirable.

As special chiral DPPs analogues, 2,3-pyrroline-fused *N*-glycosides (PFGs) containing two biologically important *N*-glycoside and five-membered azaheterocycle[12] motifs might possess valuable biological activities (Scheme 1a). Furthermore, PFG compounds can be further modified through the opening of the pyranose ring and hydrogenation,[11a] cycloaddition,[13] dihydroxylation,[14] or epoxidation[15] of the double bond in the pyrrole ring. However, to the best of our knowledge, there has not been a general and concise method for synthesizing structurally diverse PFGs. To date, a sole synthetic method for the preparation of PFGs through six reaction steps from glucal was reported by Rainier et al. (Scheme 1b).[16] Therefore, a direct and concise methodology for the selective synthesis of structure-diverse PFGs will greatly accelerate the development of new PFG functional molecules and pharmaceuticals. In view of the versatile synthons of glycals[17] and *N*-sulfonyl-1,2,3-triazoles,[18] we envisaged that the direct denitrogenative transannulation of glycals with *N*-sulfonyl-1,2,3-triazoles would provide a direct and reliable method for constructing various PFGs (Scheme 1a). Herein, we present an efficient and straightforward method for the

Received: June 25, 2021

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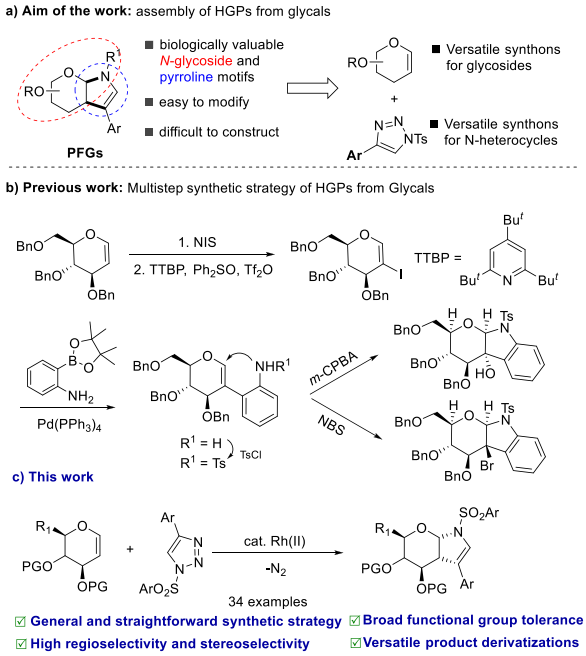
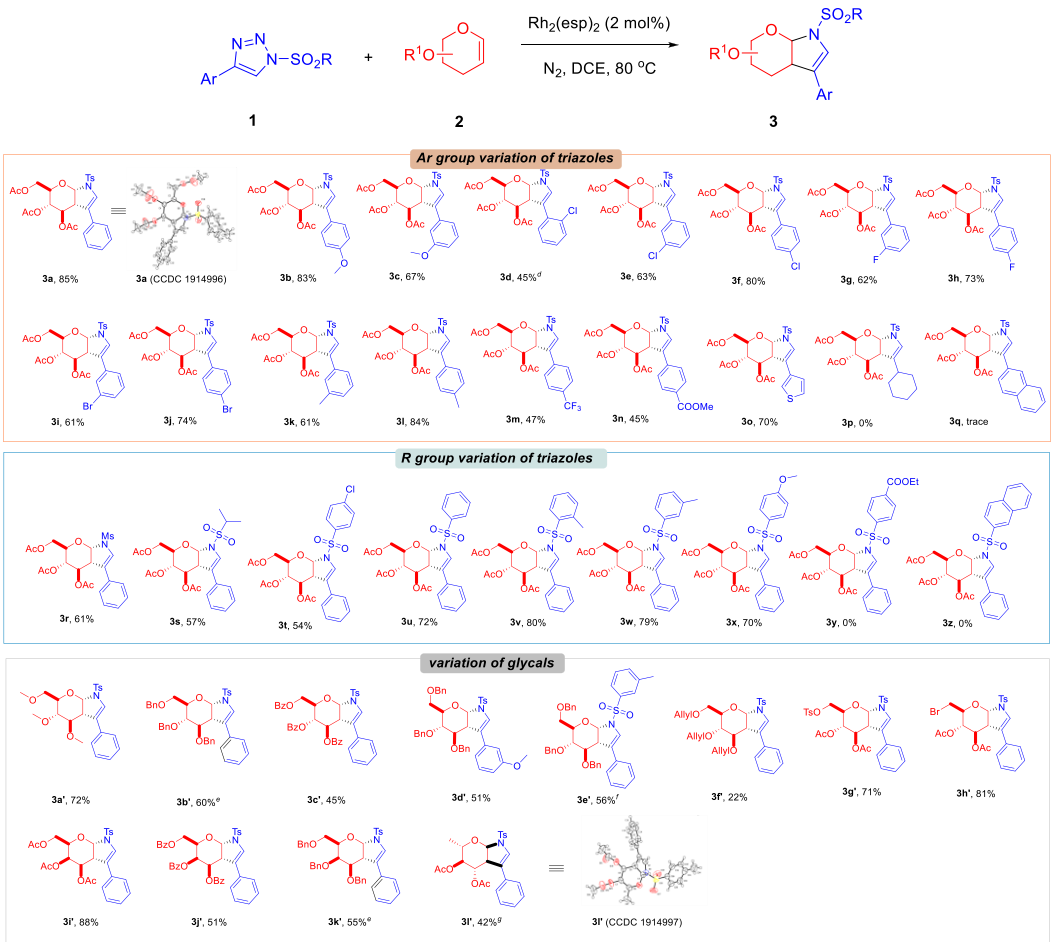
Scheme 1. Synthesis of Pyrroline-Fused *N*-Glycosides



stereoselective preparation of PFGs through a Rh-catalyzed denitrogenative transannulation of commercially available glycals and *N*-sulfonyl-1,2,3-triazoles (Scheme 1c). Various desired PFG compounds were obtained in moderate to excellent yields, and high regioselectivity and stereoselectivity via control of the substrate, instead of using chiral ligands.

Our initial investigation of the reaction condition was conducted using the 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1a**) and commercially available 3,4,6-*O*-acetyl-D-glucal (**2a**) as the model substrates (Tables S1−S5). After evaluating the catalytic capacities of different Rh salts, we found that when the reaction mixture was treated with 1.0 equiv of **1a** and 1.2 equiv of **2a** by using $Rh_2(esp)_2$ (2 mol %) in 1,2-dichloroethane (DCE) at 80 °C for 0.5 h, the desired product **3a** could be obtained in 44% yield as a single diastereomer (Table S2). When $Rh_2(oct)_4$, $Rh_2(OAc)_4$, $Rh_2(TFA)_4$, or $Rh_2(TPA)_4$ was used, **3a** was obtained in lower yields (entries 2−5, Table S1). The change in temperature did not improve the efficiency of the reaction (Table S2). By screening other solvents such as toluene, *m*-xylene, C_6H_5Cl, and CH_3CN, we found DCE was still the best solvent for the process (entries 6−9, respectively, Table S1). Meanwhile, we found that **1a** was consumed rapidly and 3,4,6-tri-*O*-acetyl-D-glucal (**2a**) was consumed slowly. Therefore, we change the charging sequence for **2a** and $Rh_2(esp)_4$ in DCE

Scheme 2. Substrate Scope Evaluation for the Rh-Catalyzed Transannulation of 1,2,3-Triazoles with D-Glycal[a−c]



[a]Reaction conditions: **2a** (0.2 mmol) and $Rh_2(esp)_2$ (0.004 mmol) dissolved in DCE (0.5 mL) at 80 °C, **1** (0.4 mmol) in DCE (3 mL) added dropwise for 1 h, and reacted for an additional 0.5 h. [b]Products formed in >20:1 dr as determined by the crude ^{1}H NMR. [c]Isolation yield. [d]At 90 °C for 1 h. [e]At 90 °C for 1.5 h. [f]For 50 min. [g]At 90 °C for 2 h.

https://doi.org/10.1021/acs.orglett.1c02141
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(0.5 mL) by adding **1a** dropwise to the reaction mixture. To our delight, the yield of **3a** was increased to 51% (entry 10, Table S1). To further explore the optimal conditions, different **1a**:**2a** ratios from 1.2:1 to 4:1 in the presence of $Rh_2(esp)_2$ (2 mol %) were screened (entries 11−14, Table S1), and we found that the desired product **3a** was afforded in 85% yield with a **1a**:**2a** ratio of 2:1 (entry 14, Table S1). However, changing the gas atmosphere to O_2 or air furnished **3a** in 64−65% yield (Table S5). According to the screening of conditions presented above, we determined that the reaction should be conducted at 80 °C in DCE with the catalyst $Rh_2(esp)_2$ (2 mol %). The structure of **3a** was unambiguously determined by X-ray crystallography.

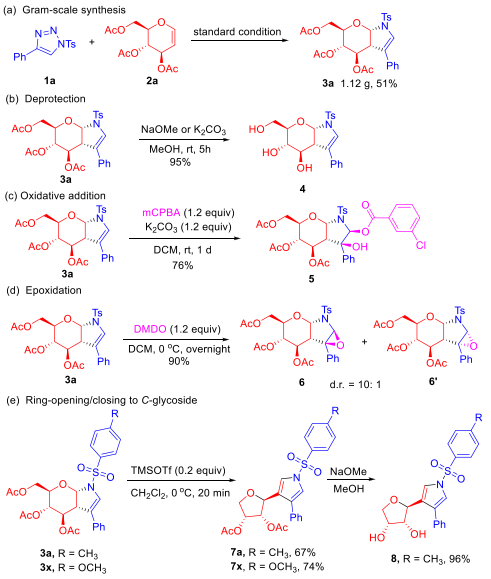
With the optimized reaction conditions in hand, we explored the scope and generality of this methodology (Scheme 2). Using 3,4,6-tri-*O*-acetyl-D-glucal (**2a**) as a model glycal, the modified aryl groups of the triazoles (**1**) were first examined in the Rh-catalyzed cycloaddition. Both electron-donating functional groups (EDGs) and electron-withdrawing functional groups (EWGs) on the benzene ring of 4-aryl-1-tosyl-1,2,3-triazoles **1** with **2a** could work well to form the desired products **3a**−**3o** in yields of 45−85%. The substituent position and electronic effects obviously affected the reaction yields. The products carrying EDGs (**3b** and **3l**) and weak EWGs (**3f**, **3h**, and **3j**) were obtained in higher yields of 73−84% compared to the moderate yields of those carrying strong EWGs (**3m** and **3n**). The products carrying the substituents at the *para* position of the phenyl ring (**3b**, **3f**, **3h**, **3j**, and **3l**) showed higher yields of 73−84% compared to the 61−67% yields of those bearing the substituents at the *meta* position (**3c**, **3e**, **3g**, **3i**, and **3k**). The substituent at the *ortho* position of the phenyl ring (**1d**) afforded the product **3d** in a much lower yield of 45%. It was gratifying that the reaction of a thienyl triazole (**1o**) also proceeded smoothly to produce the desired **3o** in a yield of 70%. However, when the substituent was cyclohexyl, no desired product **3p** was produced with the consumption of triazole. A possible reason is that the stability of cyclohexyl rhodium carbenoid was poor. Meanwhile, the substituent was 1-naphthyl, the reaction also hardly occurred, and a trace of product **3q** was found.

At the same time, the *N*-sulfonyl groups of the triazole substrates were also examined (**3r**−**3z**). When the substrates with less reactive groups such as methanesulfonyl, isopropanesulfonyl, and *p*-chlorobenzenesulfonyl groups were subjected to the Rh-catalyzed cycloaddition, the desired products (**3r**−**3t**) were produced in 61%, 57%, and 54% yields, respectively. The reactions of *N*-phenylsulfonyl triazole (**1u**) and methyl- and methoxyl-substituted phenylsulfonyl triazoles (**1v**−**1x**) proceeded well in high yields of 70−80%. Unfortunately, we did not obtain the desired product **3y** when the phenyl ring had a strong electron-withdrawing ester group. In addition, when the aromatic ring is a naphthalene ring on the sulfonyl group, the reaction hardly occurred.

Finally, the scope of glycal substrates was examined. The Rh-catalyzed cycloaddition of D-glycals containing various protecting groups, such as methyl, benzyl (Bn), and benzoyl (Bz), proceeded smoothly, forming the corresponding products **3a′**−**3e′** in moderate to high yields (45−72%). Notably, the allyl group could be tolerated, though the desired *N*-glycoside **3f′** was afforded in 22% yield. The low yield of **3f′** might be attributed to the reactivity of the allyl group with triazole. The glycal-containing Br or Ts groups were also able to give the target products in high yields (**3g′**, 71%; **3h′**, 80%). In addition, D-galactals with Ac, Bz, and Bn protecting groups were also good substrates for obtaining the desired PFGs (**3i′**, 88%; **3j′**, 51%; **3k′**, 55%). For L-rhamnal (**3l′**), the cycloaddition could also successfully occur, and the structure of **3l′** was unambiguously confirmed by X-ray crystallographic analyses.

To demonstrate the potential of this chemistry, a gram scale study was performed, and **3a** was afforded in 51% yield (Scheme 3a).

Scheme 3. Gram Scale Preparation and Synthetic Applications of 3a



Subsequently, diverse synthetic transformations from **3a** were carried out as illustrated in Scheme 3b−e. The deprotection of **3a** was attempted under alkaline conditions with K_2CO_3 or NaOMe to afford **4** in 95% yield (Scheme 3b), which constitutes the backbone of important biologically active substances.[7] Furthermore, oxidative addition of **3a** with mCPBA directly formed monoprotected diol **5** as a sole stereoisomer in good yield,[19] which was confirmed by HSQC, HMBC NMR spectra, and a selective excitation experiment. Then, the epoxidation of **3a** with DMDO[15] could yield **6** and **6′** in 90% yield with high diastereoselectivity (10/1 dr).

Next, we had a try to open the cyclic *N*,*O*-acetal moiety of **3** into polyhydroxy alkylpyrroles that possess potential biological activities[10,11] through an acid-catalyzed ring opening reaction. When 10% TfOH,[11] $BF_3{\cdot}Et_2O$,[20] or BCl_3,[21] was used in the acid-catalyzed ring opening reactions, complex mixtures were obtained, even at low temperatures. To our surprise, when **3a** was treated with TMSOTf,[22] an unexpected product *C*-nucleoside **7a** was obtained in 67% yield instead of the ring opening product polyhydroxy alkylpyrrole (Scheme 3e). The structure of **7a** was confirmed by mass spectra, HSQC, HMBC NMR spectra, and a selective excitation experiment. Similarly, **7x** can be obtained with a yield of 74% by treating **3x** with TMSOTf. *C*-Glycoside is an important structural unit with a wide range of biological activities, such as cytotoxic and antifungal activities.[23] This unexpected transformation might go by a three-step mechanism, including ring opening of the epoxy, acetyl group migration,[24] and nucleophilic substitution, and provide a new alternative approach to such *C*-nucleosides

https://doi.org/10.1021/acs.orglett.1c02141
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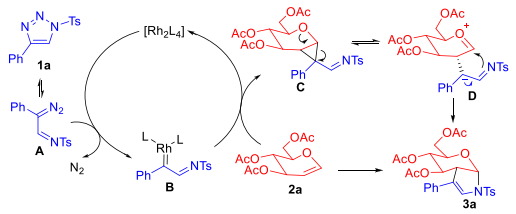
(Figure S1). Subsequently, the removal of the acetyl group of *C*-nucleoside **7a** under the alkaline condition gave compound **8** in quantitative yield.

On the basis of the observations presented above and previous reports,[11] a possible mechanism of the Rh-catalyzed denitrogenative transannulation is depicted in Scheme 4. First,

Scheme 4. Proposed Mechanism



N-sulfonyl-1,2,3-triazole **1a** provides α-diazoimine **A** by the reversible ring-chain tautomerization. Then α-diazoimine **A** interacts with rhodium(II) to yield α-imino rhodium(II) carbenoid **B** through an irreversible process, along with the release of nitrogen gas. The following electrophilic addition of **B** to the double bond of glycal **2a** produces cyclopropyl imine **C** by neighboring group participation of 3-OAc.[25] Then ring opening of the cyclopropane occurred in the effect of the electron-donating cycloalkoxy group to provide intermediate **D**. Finally, the desired *N*-glycosides can be afforded by a nucleophilic attack of the nitrogen atom of **D** by a cationic oxocarbenium from the β face.[25,26] In addition, the addition of carbenoid **B** to the double bond of glycal **2a** to afford the desired *N*-glycoside by a [3+2] cycloaddition is another pathway.

In summary, we have reported an efficient Rh-catalyzed *N*-glycosylation approach for the stereoselective synthesis of pyrroline-fused *N*-glycosides from commercially available glycals and *N*-sulfonyl-1,2,3-triazoles. A mass of *N*-heterocyclic glycosides could be afforded on the basis of the Rh-catalyzed denitrogenative cycloaddition in good yields and exclusive stereoselectivity without the use of chiral ligands or reagents. Moreover, further functionalization of pyrroline-fused *N*-glycosides by oxidative addition, epoxidation, and ring opening also has been successfully applied. Further studies with respect to the biological evaluations of pyrroline-fused *N*-glycosides and the synthesis of complex *N*-heterocyclic glycosides using our approach are ongoing in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02141.

Experimental details, characterization data of compounds, NMR spectra, and X-ray crystallographic data (PDF)

Accession Codes

CCDC 1914996−1914997 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was financially supported by the National Natural Science Foundation of China (21877206, 21702051, and U1604285), the Postdoctoral Science Foundation of Henan Province (001802033), the Henan Science and Technology Program (212102311022), and the Henan Key Laboratory of Organic Functional Molecules and Drug Innovation.

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