

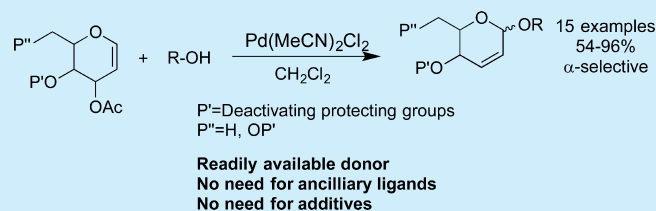
Palladium-Catalyzed α -Stereoselective O-Glycosylation of O(3)-Acylated Glycals

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Supporting Information

ABSTRACT: Pd(MeCN)₂Cl₂ enables the α -stereoselective catalytic synthesis of 2,3-unsaturated O-glycosides from O(3)-acylated glycals without the requirement for additives to preactivate either donor or nucleophile. Mechanistic studies suggest that, unlike traditional (η^3 -allyl)palladium-mediated processes, the reaction proceeds via an alkoxy-palladium intermediate that increases the proton acidity and oxygen nucleophilicity of the alcohol. The method is exemplified with the synthesis of a range of glycosides and glycoconjugates of synthetic utility.



Interest in the synthesis of oligosaccharides and glycoconjugates continues, because of their involvement in many biological processes, some of which are disease-related¹ and because there is a need to efficiently access glycan-based tools to study these processes.^{2,3} The chemical synthesis of complex carbohydrates generally involves the coupling of a fully protected glycosyl donor with a suitably protected glycosyl acceptor (R-OH).⁴⁻⁷ In many instances, these reactions lead to a mixture of two stereoisomers. Thus, having the ability to direct the stereoselective formation of glycosidic linkages with specific reagents in a catalytic manner is highly desirable.

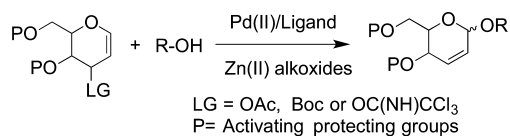
The Ferrier glycosylation reaction involves the allylic coupling of a nucleophile to a glycal bearing a leaving group at C3, which leads to the corresponding 2,3-unsaturated glycoside.⁸⁻¹² The products of this transformation are versatile chiral intermediates in the synthesis of a variety of important compounds from nucleosides and antibiotics to several biologically active natural products.¹³⁻¹⁷ Traditionally, a stoichiometric Lewis acid is required to facilitate the allylic rearrangement,¹⁷ which has limited the utility of this very attractive transformation. More recently, transition metal catalysis has been successfully applied to oligosaccharide synthesis as an improved alternative to traditional glycosylation promoters, including examples involving glycal starting materials where the allylic feature is typically exploited for activation using a metal catalyst.¹⁸⁻³⁰ In this context, palladium(II)-catalysis has been used for the direct activation of 1,2-unsaturated glycals to yield the corresponding 2,3-unsaturated products with good-to-excellent selectivities and yields, and the reaction is thought to proceed via π -allyl intermediates.^{19,26} However, despite employing activated glycals as the starting materials to facilitate the reaction, the poor reactivity of both the glycal donors and alcohol acceptors for an η^3 -metal-mediated reaction has been a major challenge to this approach.³¹⁻³³ Elegant efforts from Lee et al.³⁴ to overcome this issue employ zinc(II) alkoxides, in addition to Pd(OAc)₂ and ancillary ligands, to activate both the acceptor,

for the nucleophilic addition, and the leaving group, for the ionization. More recently, the Nguyen group reported a palladium-catalyzed Ferrier-type glycosylation using glycal donors with a trichloroacetimidate leaving group at C-3. Similarly, prior activation of the glycoside acceptor is required via a zinc alkoxide for the reaction to proceed.³⁵

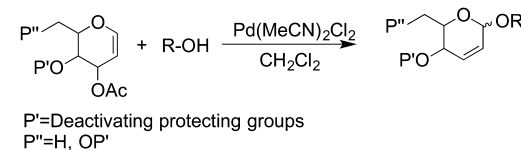
Prompted by our interest in the development of catalytic methods for the synthesis of O-glycosides from glycal starting materials,³⁶⁻³⁹ we undertook synthetic studies toward the palladium catalyzed stereoselective synthesis of 2,3-unsaturated O-glycosides (Scheme 1). Herein we report an additive-free Pd(II) stereoselective synthesis of O-glycosides from “disarmed” glycals that employs only Pd(MeCN)₂Cl₂; a reaction that we propose proceeds via an alkoxy-palladation-type mechanism to yield the glycoside products with high α -stereocontrol.

Scheme 1. Palladium-Catalyzed Synthesis of 2,3-Unsaturated Glycosides

Previous work



Present Work

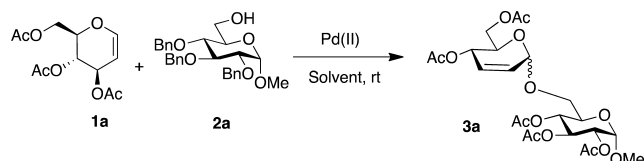


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The ligand and counterion in a transition metal catalyzed reaction plays a key role in stabilizing and activating the central metal atom and fine-tuning the selectivity of the transformation.⁴⁰ Thus, our initial studies began by screening a series of commercial palladium(II) catalysts for their ability to promote the Ferrier-type stereoselective glycosylation of peracetylated glucal **1a** with glucoside acceptor **2a**¹² in the presence of different catalyst loadings and solvents at room temperature. As summarized in Table 1, 10 mol % proved to be

Table 1. Initial Catalyst Screen in the Glycosylation of Glucal 1a



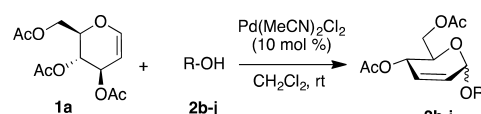
| entry | catalyst (loading mol %) | solvent | time (h) | yield ^d (%) | α : β ^e |
|-------|--|---------------------------------|----------|------------------------|---------------------------------|
| 1 | Pd(MeCN) ₂ Cl ₂ (2.5) | CH ₂ Cl ₂ | 24 | 40 | 5:1 |
| 2 | Pd(MeCN) ₂ Cl ₂ (5) | CH ₂ Cl ₂ | 24 | 52 | 5:1 |
| 3 | Pd(MeCN) ₂ Cl ₂ (10) | CH ₂ Cl ₂ | 5 | 88 ^c | 6:1 |
| 4 | Pd(CH ₃ CN) ₂ (OTf) ₂ (10) | CH ₂ Cl ₂ | 17 | 88 | 3:1 |
| 5 | Pd(CH ₃ CN) ₄ (OTf) ₂ (10) | CH ₂ Cl ₂ | 5 | N/A | N/A ^b |
| 6 | Pd(CH ₃ CN) ₄ (BF ₄) ₂ (10) | CH ₂ Cl ₂ | 5 | 90 | 2.3:1 |
| 7 | Pd(OAc) ₂ (10) | CH ₂ Cl ₂ | 5 | N/A | — |
| 8 | Pd(MeCN) ₂ Cl ₂ (10) | PhMe | 24 | 18 | — |
| 9 | Pd(MeCN) ₂ Cl ₂ (10) | CH ₃ CN | 15 | traces | — |
| 10 | Pd(MeCN) ₂ Cl ₂ (10) | CH ₂ Cl ₂ | 5 | N/A ^d | N/A |
| 11 | Pd(MeCN) ₂ Cl ₂ (10) | CH ₂ Cl ₂ | 5 | N/A ^e | N/A |
| 12 | Pd(MeCN) ₂ Cl ₂ (10) | CH ₂ Cl ₂ | 5 | N/A ^f | N/A |

^aDetermined by crude ¹H NMR. ^bInseparable mixture of products. ^cIsolated yield. ^dAddition of *N*-phenyl-2-(di-*tert*-butylphosphino)pyrrole (0.2 equiv). ^eAddition of tricyclohexylphosphine (0.2 equiv). ^fAddition of Cu(OTf)₂ (0.1 equiv). N/A = not applicable.

the optimum catalyst loading for reactions that used Pd(MeCN)₂Cl₂ in CH₂Cl₂ (88% of **3a**, entry 3), with reactions being much slower when lower catalyst loadings were used (entries 1 and 2). To further investigate the effect of the catalyst, a series of different Pd(II) catalysts (10 mol %) in CH₂Cl₂ were also screened in the glycosylation reaction (Table 1, entries 4–7). It was found that removing or replacing the Cl counterion by a *p*-toluenesulfonate was detrimental to the reaction rate and stereocontrol, while use of tetrafluoroborate eroded the α -selectivity. The use of trifluoromethanesulfonate led to an inseparable complex mixture of products. Moreover, no reaction occurred when Pd(OAc)₂ was employed, demonstrating that Pd(MeCN)₂Cl₂ was the optimal catalyst. Next, we decided to explore solvent effects and the addition of ancillary additives. The use of acetonitrile or toluene as the solvent at room temperature was detrimental to yield (entries 8 and 9), as was the addition of phosphine ligands (*N*-phenyl-2-(di-*tert*-butylphosphino)pyrrole or tricyclohexylphosphine) or Cu(OTf)₂ to the reaction (entries 10–12).

Having established the optimum reaction conditions, our attention turned to exploring the substrate scope of the coupling reaction between **1a** and a range of other OH nucleophiles **2b–j** (Table 2). In all cases, the reactions

Table 2. Acceptor Scope in Glycosylation Reactions with Glucal 1a



| entry | ROH | | time (h) | yield (%) ^[a] | α : β ^[b] |
|-------|---|-----------|-------------------|--------------------------|-----------------------------------|
| 1 | HO(CH ₂) ₃ Br | 2b | 3 | 97 | 9:1 |
| 2 | BnOH | 2c | 3 | 97 | 9:1 |
| 3 | BzO(CH ₂) ₂ OH | 2d | 7 | 90 | 9:1 |
| 4 | HO(CH ₂) ₂ OMe | 2e | 16 | 68 | 9:1 |
| 5 | HO(CH ₂) ₂ OTIPS | 2f | 17 | 65 | 20:1 |
| 6 | HO(CH ₂) ₂ OMe | 2g | 17 | 70 | 4:1 |
| 7 | BocHN(CH ₂) ₂ OH | 2h | 17 ^[c] | 68 | 3:1 |
| 8 | BocHN(CH ₂) ₂ OH | 2i | 17 ^[c] | 64 | >99:1 |
| 9 | N-hydroxysuccinimide | 2j | 15 ^[c] | 90 | >99:1 |

^aYield of isolated product. ^bDetermined by crude ¹H NMR. ^cReaction carried out at 50 °C

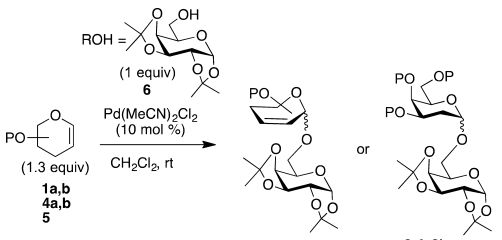
proceeded smoothly within 3–17 h and in good to excellent yield and a clear preference for the α -products. These successes demonstrate that the catalytic system tolerates the presence of common alcohol and amine protecting groups such as acetals, ethers, esters, and carbamates. Glycosylations with primary alcohols **2b–d** afforded the corresponding 2,3-unsaturated glycosides in 90–97% yield within 3–7 h and with a 9:1 α : β ratio (entries 1–3). Reactions with secondary alcohols such as glycosides **2e–g** (Table 2, entries 4–6) prove to be more challenging and required longer reactions times (15–17 h). Moreover, in the case of Boc-protected serine **2h**, threonine **2i**, or *N*-hydroxysuccinimide **2j**, besides longer reaction times, a 50 °C reaction temperature was required (entries 7–9). Under these conditions, the desired products were isolated with similarly high α selectivity (>99:1 to 3:1, α : β ratio) and yields of 64–90%, with the lower yields being attributable to the more hindered nature of the secondary OH nucleophiles.

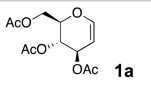
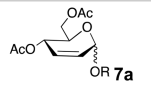
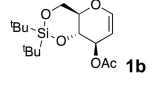
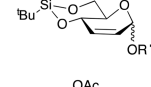
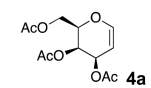
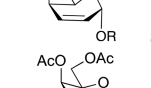
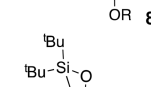
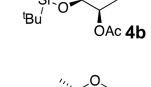
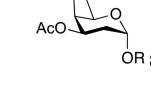
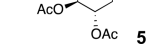
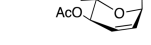
Our attention next turned to exploring the scope of the glycal donor. It has been shown that glycal conformation can modulate both the reactivity and stereoselectivity of these reactions.¹⁷ It has been proposed that the conformational equilibria of glycals (⁴H₅ vs ⁵H₄) are influenced by several contributing factors such as the vinylogous anomeric effect (VAE),⁴¹ which dictates a preferred pseudoaxial orientation of the acyloxy group at C-3, and thus favors a ⁵H₄ conformation; also important are 1,3-diaxial interactions, which compete with

the VAE and are influenced by the substituents at C-5, and the orientation of the C-4 substituent. In the case of galactal, where C-4 is axial, as opposed to equatorial as in glucals, the equilibrium is shifted toward the 4H_5 form. Glycal substrates that favor a bigger shift toward 5H_4 conformations (e.g., glucals) undergo rearrangement/substitution more readily than their corresponding counterparts (e.g., galactals).^{42,43} Furthermore, the use of conformationally constraining protecting groups can also affect both the reactivity and stereocontrol of reactions involving glycal donors.^{38,44,45}

To that end, a series of differentially protected deactivated glycols were prepared. They included peracetylated glucal **1a**, galactal **4a**, and L-rhamnol **5**, conformationally constrained **1b** and **4b**, and all were reacted with **6** as the model acceptor (Table 3). In general, moderate-to-good yields and α -

Table 3. Reaction of Glycals **1b**, **4a**, **4b**, and **5** with Model Glycoside Acceptor **6**



| entry | donor | product | time (h) | yield (%) ^[a] | α : β ^[b] |
|-------|---|---|----------|--------------------------|-----------------------------------|
| 1 |  |  | 6 | 85 | 9:1 |
| 2 |  |  | 18 | 54 | 9:1 |
| 3 |  |  | 15 | 65 | >99:1 |
| | |  | 20 | | |
| 4 |  |  | 18 | 90 | >99:1 |
| 5 |  |  | 7 | 76 | >99:1 |

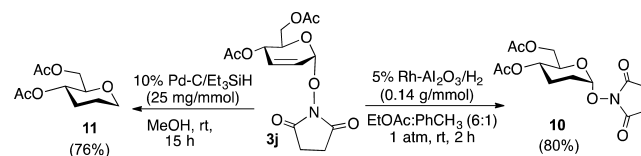
^aIsolated yield. ^bDetermined by ${}^1\text{H}$ NMR.

selectivities were obtained in most examples leading to the formation of 2-deoxy and 2,6-dideoxy Ferrier-type products (entries 1, 2, 3, and 5), with peracetylated glucal **1a** affording the best yields (85%) for the formation of **7a** as a 9:1 α : β mixture, while the 4,6-*O*-constrained glucal **7b** afforded the product in a lower yield of 54%, with stereoselectivity unchanged. As predicted, the reaction with galactal **4a** was less selective toward Ferrier rearrangement and gave a mixture of 2,3-unsaturated product **8a** (65%) and 2-deoxyglycoside **8a'** (20%) with almost complete α -stereocontrol (>99:1). Unexpectedly 4,6-*O*-siloxane protected galactal **4b** yielded only the

2-deoxyglycoside **8b** in 90% yield with high α -selectivity, which we attribute to the additional constraint imposed by the siloxane protecting group, which reduces the reactivity of the glycal toward allylic rearrangement in favor of direct glycosylation.

To demonstrate the synthetic utility of 2,3-unsaturated glycosides, reduction of *O*-linked-*N*-hydroxysuccinimide **3j** was carried out with 5% Rh–Al₂O₃/H₂ to yield the corresponding 2,3-deoxyglycoside **10** in 80% yield, while treatment of **3j** with Et₃SiH and catalytic amounts of 10% Pd/C afforded hydro-pyran **11** in 76% yield (Scheme 2), which gives access to a chiral scaffold that can be further developed as a medically active compound.^{46,47}

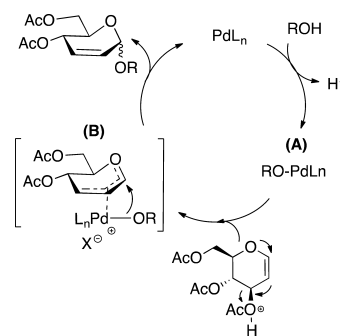
Scheme 2. Synthesis of **11** and **10** from Intermediate **3j**



To probe the mechanism of the palladium-catalyzed Ferrier reaction, ${}^1\text{H}$ NMR spectroscopy studies of glucal **1a** and Pd(MeCN)₂Cl₂ in CD₂Cl₂ did not show any changes in the spectra (Figure S1, SI), suggesting that the palladium catalyst does not interact with the alkene functionality in “disarmed” glycal donors. Indeed, previous results from our group have shown that mixtures of Pd(MeCN)₂Cl₂ and perbenzylated galactal (an “armed” or activated donor) clearly showed downfield H-shifts associated with alkene protons in the glycal (from δ 6.37 ppm to 6.20 and 6.03 ppm).⁴⁰ NMR studies of acceptor **2a** and Pd(MeCN)₂Cl₂ showed upfield shifts corresponding to the OH signal in **2a** (from 1.86 to 1.75 ppm) (Figure S2, SI), while ${}^1\text{H}$ NMR spectra of a mixture containing **1a**, **2a**, and Pd(MeCN)₂Cl₂ in CD₂Cl₂, collected after 10 min and 1 h, showed the disappearance of the OH proton from **1a** and the appearance of new signals corresponding to the Ferrier product (see SI, Figure S4 for details). These results suggest that the reaction proceeds via alkoxypalladation of the OH nucleophile.

As proposed in Scheme 3, palladium-catalyzed allylic rearrangement of deactivated glycals with alcohol nucleophiles

Scheme 3. Proposed Mechanism



involves an initial insertion of Pd into the RO-H bond, rather than the traditional pathway of palladium-mediated alkene activation,^{19,26} to produce alkoxypalladium species (A) with concomitant H⁺ release from the OH nucleophile.⁴⁸ Proton catalyzed allylic rearrangement can now take place, which leads

to the formation of a transient oxocarbenium ion that can undergo reversible coordination with complex (A) from the α -face preferentially, likely due to sterics and a favorable anomeric effect,^{49,50} and formation of a short-lived intermediate (B). Concomitant deoxypalladation and nucleophilic addition of the activated oxygen in a stereoselective manner then yields the 2,3-unsaturated glycosides.⁵¹

In summary, we have described a practical and stereoselective method for the preparation of 2,3-unsaturated glycosides using commercial Pd(MeCN)₂Cl₂ in CH₂Cl₂ from O(3)-acylated glycals. This mechanistically interesting and unprecedented reaction is mild and proceeds with good-to-excellent yields and high selectivity for the α -anomer. The method utilizes commercial starting materials and is widely applicable to a range of nucleophile acceptors. We exemplify the utility of this approach in the stereoselective synthesis of a series of disaccharides, glycosyl-amino acids, and other glycoconjugates including saturated chiral scaffolds of medicinal relevance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01092.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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