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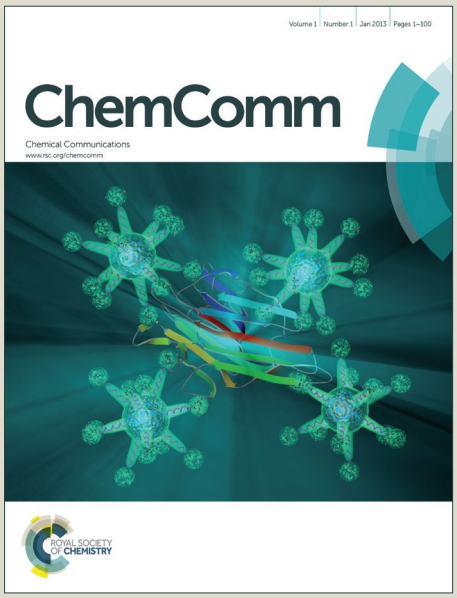

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Gold(I)-Catalyzed *C*-Glycosylation of Glycosyl *ortho*-Alkynylbenzoates, a Role of the Moisture Sequestered by Molecular Sieves

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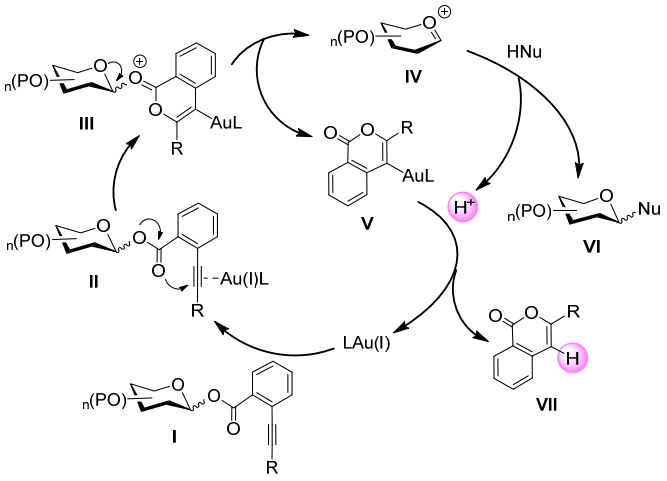
***C*-Glycosylation of glycosyl *ortho*-hexynylbenzoates with allyltrimethylsilane or silyl enol ethers could proceed smoothly under the catalysis of $Ph_3PAuNTf_2$ to provide the corresponding *C*-glycosides in high yields and stereoselectivity, wherein the moisture sequestered by the molecular sieves were disclosed to play a critical role in the gold(I)-catalytic cycle.**

Replacement of the glycosidic C-O acetal linkage in a native glycan or glycoside with a C-C linkage has become a common strategy to attain carbohydrate mimics which are metabolically stable and thus of therapeutic promise.[1] On the other hand, *C*-glycosides occur widely as natural metabolites, which show a great structural diversity in association with a wide spectrum of biological activities.[2] Therefore, synthesis of *C*-glycosides has long been a topic of intensive research.[1,3] Among the various approaches developed for the *C*-glycosides synthesis, *C*-glycosylation adopting modification of the *O*-glycosylation protocols, in that *C*-nucleophiles are used as coupling partners to condense with the conventional glycosyl donors, constitute a straightforward alternative.[3,4]

Recently, we developed a new glycosylation protocol that uses glycosyl *ortho*-alkynylbenzoates as donors and a gold(I) complex (e.g., $Ph_3PAuOTf$ or $Ph_3PAuNTf_2$) as catalyst (Scheme 1).[5] The mild reaction conditions ensure the successful application of this method in the synthesis of extremely complex *O*- and *N*-glycosides.[6,7] Mechanistic studies[8] show that activation of the *ortho*-alkynylbenzoate donor **I** by a gold(I) species LAu(I) leads to formation of glycosyloxypyrylium gold(I) intermediate **III**,[9b,c] which may collapse into sugar oxocarbenium **IV** and isochromen-4-yl-gold(I) complex **V**.[9a] Gold(I) complex **V** is found stable, however, it can be protonated to re-generate the catalytic gold(I) species. Therefore, the proton, which is released from the glycosidic coupling of oxocarbenium **IV** with nucleophile HNu, plays a critical role in the catalytic cycle of the glycosylation (**I** + HNu → **VI** + **VII**).



Scheme 1. The gold(I)-catalyzed *O*- and *N*-glycosylation reaction with a glycosyl *ortho*-alkynylbenzoate **I** as donor (the counter anion is omitted).

Based on this mechanistic rationale, the feasibility of a *C*-glycosylation with such commonly used *C*-nucleophiles as allyltrimethylsilane or silyl enol ethers is not affirmative, because the regeneration of the gold(I) species via protodeauration (i.e., **V** + H^+ → **VII** + LAu(I)) is no longer valid.[10-13] This mechanistic query together with the practical importance of the *C*-glycosylation reaction prompted us to explore the *C*-glycosidic coupling of glycosyl *ortho*-alkynylbenzoates with allyltrimethylsilane/silyl enol ethers under the action of a gold(I) complex.

We first tried the *C*-glycosylation of perbenzoyl and perbenzyl glucopyranosyl *ortho*-hexynylbenzoates (**1a** and **1b**), two reliable *O*-glycosylation donors,[5] with allyltrimethylsilane (**2a**) under the conventional *O*-glycosylation conditions (Table 1). Indeed, treatment of **1a** or **2a** in the presence of $Ph_3PAuOTf$ or $Ph_3PAuNTf_2$ (0.1 equiv) (CH_2Cl_2, 4Å MS, RT) led to complex mixtures, wherein the desired allyl *C*-glycoside **3a** was not detected at all (entries 1 and 2). Treatment of **1b** and **2a** in the presence of $Ph_3PAuOTf$ (0.1 equiv) also led to a complex mixture, however, the desired *C*-glycoside **3b** was detectable on TLC (entry 3). Interestingly, when $Ph_3PAuNTf_2$ (0.1 equiv) was used as the catalyst, the *C*-allylation of

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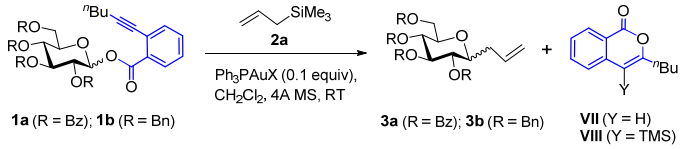
[b] † Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

1b proceeded smoothly, leading to *C*-glycoside **3b** in 85% yield with complete α-selectivity (entry 4).[4]

Table 1. Attempted *C*-glycosylation of glucopyranosyl *ortho*-hexynylbenzoates **1a** and **1b** with allyltrimethylsilane (**2a**).



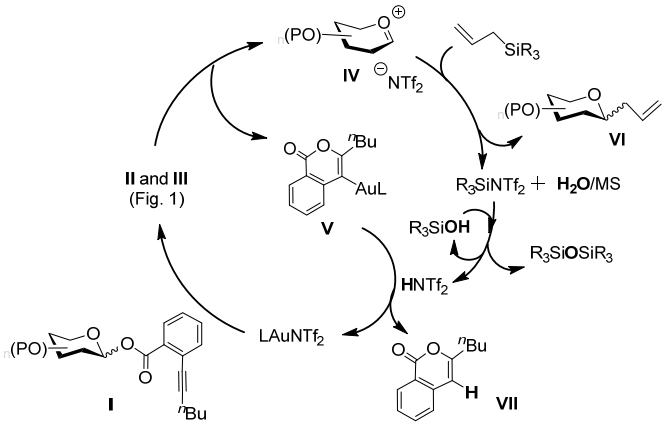
Entry	Donor	Ph_3PAuX	Results[a]
1	**1a**	$Ph_3PAuOTf$	Complex, **3a** not detectable
2		$Ph_3PAuNTf_2$	Complex, **3a** not detectable
3	**1b**	$Ph_3PAuOTf$	Complex, **3b** detectable
4		$Ph_3PAuNTf_2$	**3b** (85%, α only)

[a]Isocoumarin **VII** was identified as a side product, but not the trimethylsilyl derivative **VIII**.

It was reported that allyltrimethylsilane (**2a**) was vulnerable toward $Ph_3PAuOTf$,[14] this might explain the failure of the present *C*-glycosylation with $Ph_3PAuOTf$ as the catalyst. Indeed, NMR analysis showed that **2a** was completely decomposed (mainly into propene) in the presence of $Ph_3PAuOTf$ (0.1 equiv) (CD_2Cl_2, RT) within 10 min, whereas it remained largely intact within 30 min in the presence of $Ph_3PAuNTf_2$ (0.1 equiv) (See SI for details). The failure of perbenzoyl donor **1a** (a disarmed donor) in the present *C*-glycosylation might be attributed to its low reactivity; decomposition of the sugar oxocarbenium intermediates (e.g., **IV**) competed favorably to the *C*-allylation reaction.

What surprised us most was in the successful *C*-glycosylation of the armed donor **1b** that isocoumarin **VII** was produced but not the trimethylsilyl derivative **VIII**, which was known to be stable and isolable.[15] Indeed, treatment of the purified isochromen-4-yl-gold(I) complex **V** with TMSOTf did not lead to **VIII**. Therefore, there must be a proton source, most likely the moisture, which enabled the regeneration of the catalytic Au(I) species (from **V**) in the present *C*-glycosylation.[10]

A conventional glycosylation reaction is always performed under anhydrous conditions, wherein the dried reaction mixture is charged with molecular sieves (MS) to sequester the trace amount of moisture which might be remained or introduced during the experiment even with the protection of argon or nitrogen. We suspected that it was the moisture sequestered by the molecular sieves (namely H_2O/MS) that took part in the in situ protodeauration reaction. Thus, we dried the CH_2Cl_2 solution of the reactants **1b** and **2a** and the CH_2Cl_2 solution of $Ph_3PAuNTf_2$ with 4Å MS, respectively, and took only the supernatants for reaction. The reaction stopped at ~13% conversion of donor **1b** into *C*-glycoside **3b**. This result supported the proposed role of the H_2O/MS in the present *C*-glycosylation reaction. In addition, the resulting ^-OH might consume the Me_3Si^+ derived from the allylation of **2a** to provide Me_3SiOH. To identify the silyl derivatives, we replaced the allyltrimethylsilane with allyldiphenylmethylsilane (**2b**) in the reaction with **1b**. Disiloxane $(Ph_2MeSi)_2O$ was easily isolated as the product (~93% yield based on the starting **2b**), which might be derived from the condensation of $Ph_2MeSiOH$ and Ph_2MeSi^+, while condensation of $Ph_2MeSiOH$ under the action of the gold(I) catalyst was also possible.[16] On the basis of these data, the mechanism of the present *C*-glycosylation was proposed as shown in Scheme 2.

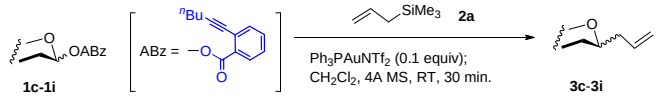


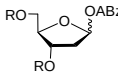
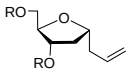
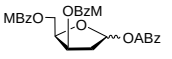
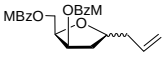
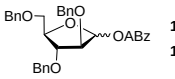
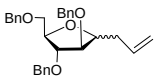
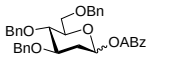
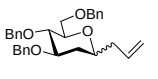
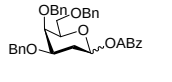
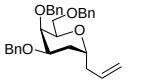
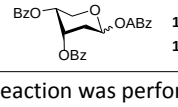
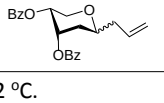
Scheme 2. The mechanistic rationale of the gold(I)-catalyzed *C*-glycosylation of glycosyl *ortho*-alkynylbenzoate **I** with allylsilane.

To testify the scope of the present gold(I)-catalyzed *C*-glycosylation, we first examined the reaction of a panel of the *ortho*-hexynylbenzoate donors (**1c**-**1i**) with allyltrimethylsilane **2a** (Table 2). All the donors were consumed within 30 min in the presence of **2a** (1.2 equiv), $Ph_3PAuNTf_2$ (0.1 equiv), and 4Å MS in CH_2Cl_2 at RT. The allylation reactions of 2-deoxy-ribofuranosyl donors **1c** and **1d** led to the allyl α-*C*-glycoside **3c** (80%) and **3d** (99%), respectively, in a complete stereoselective manner, although much higher yield was attained with the more reactive benzyl protected donor **1d** (entries 1 and 2). Using 2-deoxy-xylofuranosyl *ortho*-hexynylbenzoate **1e** as donor, the reaction at RT gave a complex mixture (partly due to the migration of the methoxybenzoyl group). Nevertheless, the *C*-allylation proceeded cleanly at -72 °C, furnishing allyl *C*-glycoside **3e** in good yield (88%, α/β = 1:3) (entry 3). The 1,3-*cis*-selectivity in the *C*-glycosylation of furanosyl donors have been well studied by Woerpel et al.,[17a,b] and was accounted by the preferred inside attack on the lowest energy conformers of the intermediate oxocarbenium ions displaying the C-3 alkoxy group in a pseudoaxial orientation to maximize electrostatic effects.[17] Subjection of 2,3,5-tri-*O*-benzyl-D-arabinofuranosyl donors **1fα** or **1fβ** to the present reaction led to allyl *C*-glycoside **3f** in 80% and 87% yield, respectively, with an identical stereoselectivity (α/β = 1:2.5) (entries 4 and 5). The slight difference in yields testified that the β-*ortho*-hexynylbenzoate donor (**1fβ**) was slightly more reactive than its α-counterpart (**1fα**).[9b] And the moderate α/β selectivity is in accordance with that attained from the *C*-allylation of the corresponding arabinofuranosyl acetate and fluoride donors.[4d,e] *C*-Glycosylation with 3,4,6-tri-*O*-benzyl-2-deoxy-glucopyranosyl donor **1g** furnished the desired allyl *C*-glycoside **3g** in excellent yield (87%) and α selectivity (α/β = 13:1) (entry 6). In comparison, the 2-deoxy-galactopyranosyl donors **1h** were more reactive; the reactivity

difference between the α- and β-anomers **1hα** and **1hβ** was not discerned in the glycosylation, both led to allyl *C*-glycoside **3h** in quantitative yield and complete α selectivity (entries 7 and 8).[18] The glycosylation of the α- and β-anomer of 3,4-di-*O*-benzoyl-2-deoxy-ribopyranosyl *ortho*-hexynylbenzoate (**1iα** and **1iβ**) led to allyl *C*-glycoside **3i** in a similar yield of 87% with high α selectivity (entries 9 and 10).[4f,h] However, the reaction with the β-anomer as donor resulted in a higher α/β ratio (20:1) than that with the α-counterpart **1iα** (α/β = 7:1), this result implied the involvement of an early intermediate,[19] such as the glycosyloxypyrylium gold(I) complex **III**, in the *C*-glycosylation step.

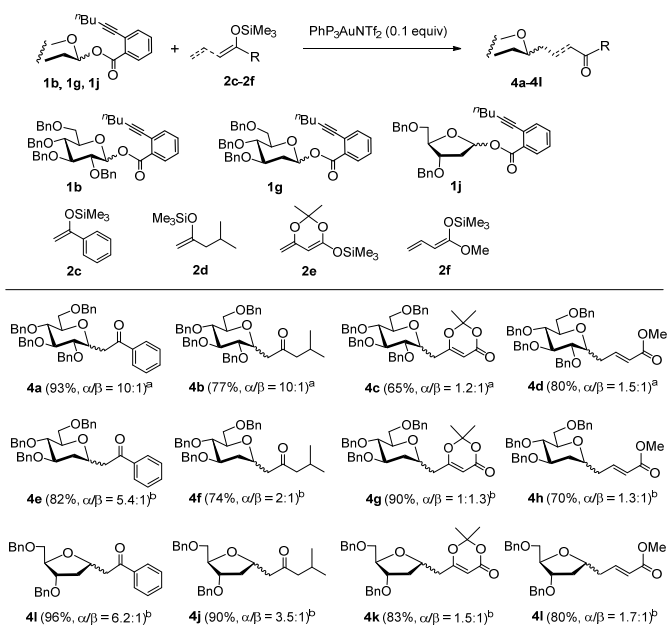
Table 2. *C*-Glycosylation of armed glycosyl *ortho*-hexynylbenzoates (**1c-1i**) with allyltrimethylsilane (**2a**) under the catalysis of $Ph_3PAuNTf_2$.



entry	donor		product (yield, α/β ratio)
1		**1c** (R = MBz)	 **3c** (R = MBz) (80%, α only)
2		**1d** (R = Tol)	**3d** (R = Tol) (99%, α only)
3		**1e**	 **3e** (33%, α/β = 1:2) **3e** (88%, α/β = 1:3)[a]
4		**1fα**	 **3f** (80%, α/β = 1:2.5)
5		**1fβ**	**3f** (87%, α/β = 1:2.5)
6		**1g**	 **3g** (87%, α/β = 13:1)
7		**1hα**	 **3h** (99%, α only)
8		**1hβ**	**3h** (99%, α only)
9		**1iα**	 **3i** (87%, α/β = 7:1)
10		**1iβ**	**3i** (87%, α/β = 20:1)

[a]The reaction was performed at -72 °C.

Next, we explored the gold(I)-catalyzed glycosylation with a panel of the silyl enol ethers (**2c**-**2f**)[20] as *C*-nucleophiles (Scheme 3). Subjection of perbenzyl glucopyranosyl donor **1b** and 1-styrenyloxytrimethylsilane **2c** (1.2 equiv) to the previous allylation conditions (0.1 equiv $Ph_3PAuNTf_2$, 4Å MS, CH_2Cl_2, RT, 30 min) led to the desired *C*-glycoside **4a** in only moderate yield (37%) and stereoselectivity (α/β = 2.5:1). Nevertheless, replacing the solvent CH_2Cl_2 with toluene and 4Å MS with 5Å MS, the reaction of **1b** (1.5 equiv) with **2c** proceeded smoothly to provide **4a** in excellent yield (93%) and α selectivity (α/β = 10:1). Under this modified condition, the glycosylation of **1b** with 4-methyl-2-trimethylsilyloxy-1-pentene **2d** remained the high α selectivity (α/β = 10:1) in affording *C*-glycoside **4b** in 77% yield. However, the similar reactions with (2,2-dimethyl-6-methylene-6H-1,3-dioxin-4-yloxy)trimethylsilane (**2e**) and 1-(trimethylsiloxy)-1-methoxy-1,3-butadiene (**2f**) were found to be poorly stereoselective, providing the coupled *C*-glycosides **4c** (65%) and **4d** (80%) with α/β ratio of 1.2:1 and 1.5:1, respectively. The glycosylation of these silyl enol ethers (**2c**-**2f**) with perbenzyl 2-deoxy-glucopyranosyl donor **1g** and 2-deoxy-ribofuranosyl donor **1j**, which are more reactive than **1b**, proceeded smoothly under the previous *C*-allylation conditions. All the reactions provided the desired *C*-glycosides (**4e**-**4l**) in high yields (70%-96%), however, with high stereoselectivity being only attained with 1-styrenyloxytrimethylsilane (**2c**) (α/β = 5.4:1 and 6.2:1 for **4e** and **4l**, respectively), which is more nucleophilic than **2d**-**2f**.[20c]



Scheme 3. *C*-Glycosylation of armed glycosyl *ortho*-hexynylbenzoates (**1b**, **1g**, and **1j**) with silyl enol ethers (**2c**-**2f**) under the catalysis of $Ph_3PAuNTf_2$. [a] Reaction conditions: donor **1** (1.5 equiv), silyl enol ether **2** (1.0 equiv), $Ph_3PAuNTf_2$ (0.1 equiv), toluene, 5Å MS, argon, RT, 30 min. [b] Reaction conditions: donor **1** (1.0 equiv), silyl enol ether **2** (1.2 equiv), $Ph_3PAuNTf_2$ (0.1 equiv), CH_2Cl_2, 4Å MS, argon, RT, 30 min.

In conclusion, *C*-glycosylation of glycosyl *ortho*-hexynylbenzoates with allyltrimethylsilane or silyl enol ethers could proceed smoothly under the catalysis of $Ph_3PAuNTf_2$. Depending on the coupling partners, the *C*-glycosylation could be highly stereoselective to provide in high yields the corresponding allyl, 2-carbonyl, or enonyl-*C*-glycosides, which are versatile building blocks for the synthesis of various *C*-glycosides of biological significance.[21] The mechanism of the present gold(I)-catalyzed *C*-glycosylation reaction has been proposed on the basis of a series of control experiments. It is disclosed that the moisture which is sequestered by the molecular sieves plays a key role in the re-generation of the catalytic gold(I) species. This finding shall be valuable in understanding the mechanism underlining other glycosylation protocols, wherein the moisture, which is previously thought to be removed by the molecular sieves, might be released to play an important role.

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