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Copper mediated iodoacetoxylation and glycosylation: effective and convenient approaches for the stereoselective synthesis of 2-deoxy-2-iodo glycosides

Suresh Kumar Battina [a], Sudhir Kashyap [a,b,*]

[a] Discovery Laboratory, Organic and Biomolecular Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India
[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India

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ABSTRACT

Copper(II) triflate catalyzed stereoselective glycosylation of 2-iodo-glycosyl acetate donor is reported. Anomeric activation of 2-deoxy-1-*O*-acetyl sugar employing $Cu(OTf)_2$ found to be an attractive as well effective alternative reagent to the most frequently used triflic acid (TfOH) source such as TMSOTf or TBSOTf. Scope of the reaction was explored for various aglycones. This protocol involves simple reaction operation, employs less expensive and non-toxic reagent system, and enables the stereoselective preparation of 2-deoxy-2-iodo-glycosides. Furthermore, $CuI/NaIO_4$ in the presence of AcOH at ambient temperature promoted the regioselective iodoacetoxylation of various glycals to access 2-iodo-glycosyl acetates.

2-Deoxy sugars and their derivatives have been recognized as important synthetic intermediates for constructing several valuable glycoconjugates[1] and natural products.[2] The presence of α or β linkage in 2-deoxy glycosides plays a crucial role in molecular recognition, reactivity, and adhesion of glycosubstances and linked to several cellular processes.[1,2] In this context, stereoselective glycosylation strategies serve as an important chemical tool for assembling venerable sugar molecules and related natural products to probe their biological activities. In view of their pharmacological properties, the stereoselective preparation of 2-deoxy sugars has gained considerable attention and remains a challenging task.[3–5]

The most common and reliable method for the preparation of 2-deoxy glycosides involves glycosylation of 2-deoxy-2-halo-glycosyl acetate donor[6,7] with aglycones using Brønsted acid such as triflic acid (TfOH). In addition, the oxidative iodoglycosylation of glycals using NIS,[8a–c] IDCP[8d,e] or molecular iodine[8f,g] as electrophilic iodonium ion equivalent provide 2-iodoglycosides. Subsequent reductive elimination or deiodonation from C-2 position would generate the 2-deoxy glycoside.[7c] The C-2 substituent in 2-halo-glycosyl acetate play a crucial role in chemical glycosylation as the stereodirecting group and induced anchimeric assistance to control the stereoselectivity.[7] Although promoters such as TMS-OTf and TBS-OTf were found to be suitable reagents for anomeric activation of 2-deoxy-1-*O*-acetyl donors,[6a] strong acidic behavior and excessive loading of catalyst, low reaction temperature, and need of additives such as molecular sieves have remained as the associated disadvantages. Therefore, developing an efficient and convenient glycosylation method by employing economical and non-toxic catalyst for incorporating glycosidic linkage in deoxy sugars in a stereocontrolled manner is highly desirable.

Owing to the inherent moisture/air stability and unique characteristic, Cu(II) triflate and its analogous catalysts have shown remarkable applicability in synthetic organic chemistry.[9] Recent studies on the comparison of metal triflates and strong Brønsted acids reveal that copper(II) triflate is the most effective and promising catalytic system to generate in situ TfOH in highly efficient green transformations.[10] Inspired by this fact and considering the versatile reactivity of $Cu(OTf)_2$ as an inexpensive and moisture stable catalyst, we focused to investigate the glycosylation of 2-deoxy-2-iodo-α-mannopyranosyl acetate donor under mild reaction conditions.

We recently demonstrated the efficiency of $Cu(OTf)_2$ as Lewis acid catalyst in stereoselective glycosylation of glycals to generate various functionalized 2,3-unsaturated glycosides.[11a] In continuation of our research in glycochemistry,[11] herein we report Cu(II) triflate as an alternative and effective catalyst for the anomeric activation of 2-iodo-glycosyl acetate enabling the

* Corresponding author. Tel.: +91 402 716 1649; fax: +91 402 716 0387.
E-mail address: skashyap@iict.res.in (S. Kashyap).

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stereoselective preparation of 2-deoxy-2-iodoglycosides. Furthermore, the regioselective iodoacetoxylation of several glycals was achieved by employing copper(I) iodide as the halide source and stoichiometric $NaIO_4$ as the oxidant in acetic acid at room temperature. We believe that copper mediated glycosylation and preceding oxidative iodoacetoxylation transformations would find its applicability in glycochemistry for synthesizing biologically important deoxy-sugar derivatives.

The iodoacetoxylation of glycals to access 2-deoxy-2-iodo-glycopyranosyl acetate donor is an important transformation in carbohydrate chemistry.[8,12] We envisioned that $NaIO_4$ oxidant would efficiently promote the *umpolung* of copper halide in the presence of acetic acid to generate the electrophilic I-OAc intermediate. Subsequent reaction with an electron-rich double bond following intrinsic regioselective opening of resulting iodonium ion intermediate with a nucleophile, OAc in this case, would provide the 1–2-*trans*-iodo-acetate.

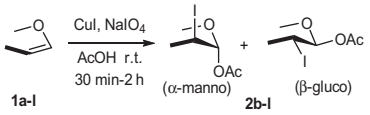
To test this hypothesis, the 3,4,6-tri-*O*-acetyl-D-glucal (**1a**) was subjected to iodoacetoxylation using equimolar amount of CuI and $NaIO_4$ in acetic acid as the solvent (Table 1). To our delight, reaction was completed in utmost 1 h at room temperature to afford the desired glycosyl acetate **2a** in 97% yield (entry 1). An improved diastereoselectivity in favor of α-manno isomer (dr; 87:13) was observed when compared with our previous report (dr; 80:20).[11k] Other oxidants such as H_2O_2, oxone, and CuO in combination with CuI were unsuccessful, however the use of stoichiometric PIDA (phenyliodonium diacetate) as the oxidant resulted in 56% yield albeit with lower dr, 76:24 (entry 2). Notably, the iodoacetoxylation of **1a** with NH_4I/H_2O_2 in Ac_2O/AcOH gives **2a** in 85% with dr 83:17.[12c] On the other hand, molecular iodine in combination with $Cu(OAc)_2{\cdot}6H_2O$ produces **2a** with selectivity upto 92 and a decreased yield (88%) albeit at high temperature.[8f]

The generality and scope of reaction was further illustrated with substrate comprising various protecting groups in glucals. Thus, the iodoacetoxylation of glucals **1b**–**1d** underwent smoothly to access the corresponding 2-deoxy-2-iodo-glycosyl-1-*O*-acetates **2b**–**2d** in good yields (Table 1, entries 3–5). Furthermore, D-galactal (**1e**) and various 6-deoxy sugar derived glycals **1f**–**1j** conveniently underwent regioselective iodoacetoxylation to deliver the desired 2-deoxy glycosyl acetates **2f**–**2j** (entries 6–11). In contrast, the reaction of D-glucal (**1a**) and D-galactal (**1e**) with stoichiometric CAN (2.6 equiv) and NaI/AcOH gives the corresponding glycosyl acetates **2a** and **2e** in 75% and 80% yield, respectively, with a slight variation in dr.[6a] Indeed, the iodoglycosylation of **1e** using NIS in AcOH at 110 °C gives **2e** in a moderate yield 64%.[12d] Further comparison of iodoacetoxylation reactions of **1a** and **1f** using polymer-bound iodate reagent (~4 equiv) highlights the advantage of the present protocol in terms of selectivity and yields.[12e,f] The synthetic utility of this method was further highlighted for disaccharide substrates such as D-lactal (**1k**) and D-maltal (**1l**) to generate the 2-deoxy-disacchaides 1-*O*-acetates **2k**–**2l** in satisfactory yields with a good dr (entries 12 and 13). However, D-lactal (**1k**) gives **2k** in 75% yield by employing I_2/Cu $(OAc)_2{\cdot}6H_2O$ in AcOH at 80 °C.[12g]

Having identified a mild and facile method for the synthesis of 2-deoxy-2-iodo-glycosyl acetates, we next considered the possibility of copper triflate catalyzed glycosylation of 2-iodo-glycosyl acetate donor. Accordingly, the chemical glycosylation of 2-deoxy-2-iodo-α-mannopyranosyl acetate donor (**2a**) with menthol (**3a**) as the acceptor was performed using 10 mol % of $Cu(OTf)_2$ as the promoter. The initial experiment using DCM as the solvent resulted only 30% conversion of the starting material at room temperature in 20 h (Table 2, entry 1). Preliminary optimization employing common organic solvents such as CH_3CN, toluene, and 1,4-dioxane resulted in poor to moderate conversion (entries 2–4). Switching the solvent to 1,2-dichloroethane afforded the desired product **4a** in 68% yields in 20 h (entry 5). However, significant improvement in the rate was realized when the reaction was performed at 60 °C for 1 h, furnishing the glycoside **4a** in 82% yield (entry 6).

Although 5 mol % of $Cu(OTf)_2$ was effective and optimal catalytic amount in the glycosylation of **2a** with **3a** and 2-deoxy-glycoside **4a** was similarly isolated in 86% yield (Table 2, entry 7). Further decreasing the quantity of $Cu(OTf)_2$ resulted in poor conversion albeit at a longer reaction time (entries 8 and 9). No further improvement was observed when the reaction was performed in the presence of molecular sieves (4 Å MS). Importantly, the reaction proceeded with complete selectivity furnishing the single diastereomer, menthyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranoside (**4a**).[13] The spectroscopic data correlated with that of literature report, was found consistent in accordance with the assigned structure.[8g]

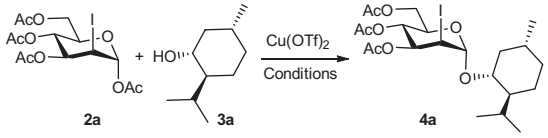
Table 1
CuI/$NaIO_4$ promoted iodoacetoxylation of glycals[a]



Entry	Glycal	Product	Yield[b] (%)	dr[c]
1	3,4,6-Tri-*O*-acetyl-D-glucal (**1a**)	**2a**	97	87:13
2[d]	**1a**	**2a**	56	76:24
3	3,4,6-Tri-*O*-methyl-D-glucal (**1b**)	**2b**	87	60:40
4	3,4,6-Tri-*O*-benzyl-D-glucal (**1c**)	**2c**	92	48:52
5	3,4,6-Tri-*O*-benzoyl-D-glucal (**1d**)	**2d**	98	91:09
6	3,4,6-Tri-*O*-acetyl-D-galactal (**1e**)	**2e**	95	95:05
7	3,4-Di-*O*-acetyl-D-rhamnal (**1f**)	**2f**	88	73:27
8	3,4-Di-*O*-acetyl-L-rhamnal (**1g**)	**2g**	86	65:35
9	3,4-Di-*O*-acetyl-D-xylal (**1h**)	**2h**	84	42:58
10	3,4-Di-*O*-acetyl-D-arabinal (**1i**)	**2i**	93	79:21
11	3,4-Di-*O*-acetyl-L-arabinal (**1j**)	**2j**	86	79:21
12	Per-*O*-acetyl-D-lactal (**1k**)	**2k**	92	94:06
13	Per-*O*-acetyl-D-maltal (**1l**)	**2l**	96	90:10

[a] Reaction conditions: Glycal (1.0 equiv), CuI (1.1 equiv), $NaIO_4$ (1.1 equiv), acetic acid (0.5 mL), room temperature.
[b] Isolated yields.
[c] Based on relative integration of anomeric proton in ^1H NMR spectrum.
[d] Reaction was performed with $PhI(OAc)_2$ (1.1 equiv) instead of $NaIO_4$.

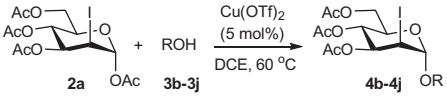
Table 2
Optimization of $Cu(OTf)_2$ catalyzed glycosylation[a]

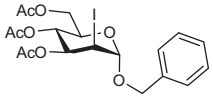
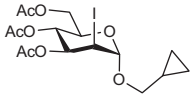
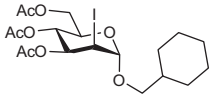
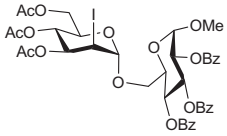
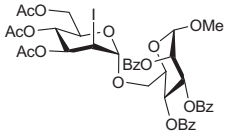
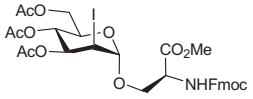
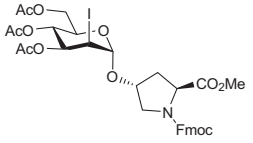
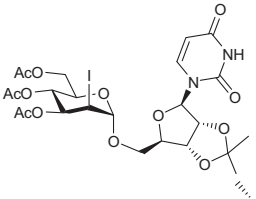
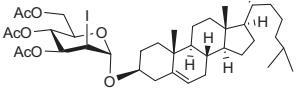


Entry	Catalyst (mol %)	Solvent	Temp (°C)	Time (h)	Yield[b] (%) (Conv[c])
1	10	Dichloromethane	rt	20	NR (30%)
2	10	Acetonitrile	rt	20	38
3	10	Toluene	rt	16	NR (20%)
4	10	1,4-Dioxane	rt	20	NR (20%)
5	10	1,2-Dichloroethane	rt	20	57
6	10	1,2-Dichloroethane	60	1	82
7	**5**	**1,2-Dichloroethane**	**60**	**1**	**86**
8	2	1,2-Dichloroethane	60	8	45
9	1	1,2-Dichloroethane	60	10	NR (20%)

[a] Reaction conditions: **2a** (0.37 mmol), menthol (**3a**) (0.40 mmol).
[b] Isolated yields, NR = not recorded.
[c] Progress of reaction was monitored by TLC analysis at given time.

Table 3
Cu(OTf)$_2$ catalyzed synthesis of 2-deoxy-2-iodo-α-glycosides[a]

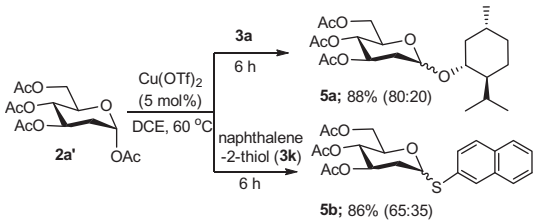


Entry	ROH	2-Deoxy-2-iodo-glycosides		*t* (h)	Yield[b] (%)
1	**3b**		**4b**	1	89
2	**3c**		**4c**	1.5	87
3	**3d**		**4d**	2	92
4	**3e**		**4e**	0.5	82
5	**3f**		**4f**	0.5	84
6	**3g**		**4g**	2	86
7	**3h**		**4h**	0.5	88
8	**3i**		**4i**	6	79
9	**3j**		**4j**	1	82

[a] All reactions were performed with **2a** (1 equiv), ROH (1.2 equiv), 5 mol % Cu(OTf)$_2$ in 1,2-dichloroethane at 60 °C.
[b] Isolated and un-optimized yields.

With the optimal protocol, we next probed the scope of glycosylation reaction with a wide range of acceptors to generate structurally diverse 2-deoxy glycosides. As summarized in Table 3, the glycosylation of **2a** with benzyl alcohol (**3b**) and alicyclic substrate bearing cyclopropyl (**3c**) and cyclohexyl (**3d**) ring proceeded smoothly, allowing the facile synthesis of corresponding 2-deoxy-glycosides **4b**–**4d** in good yields (entries 1–3). Encouraged by these results, we next attempted the glycosylation of carbohydrate derived alcohols to access the disaccharides containing 2-deoxy-sugars. Thus, glucose (**3e**) and mannose (**3f**) derived glycosyl acceptors were successfully incorporated in 2-deoxy-2-iodo-α-mannosides **4e**–**4f** in good yields (entries 4 and 5).

Owing to the distinct biological importance of glycoconjugates containing mannose scaffolds, we next investigated the



Scheme 1. Cu(II) triflate-catalyzed glycosylation of 2-deoxy glycosyl acetate.

glycosylation of amino acid derived aglycones. Thus, glycosylation reaction of **2a** with Fmoc-Ser-OMe (**3g**) in the presence of catalytic Cu(OTf)$_2$ resulted in the corresponding glycoconjugate **4g** in a good yield (Table 3, entry 6). Likewise, N-Fmoc-*trans*-4-hydroxy-L-proline (**3h**) was incorporated in 2-deoxy-mannopyranoside to generate the venerable α-linked mannosylated peptide glycoconjugate **4h** in satisfactory yield (entry 7). In addition, a nucleoside base, uridine derivative (**3i**) and a natural product for instance cholesterol (**3j**) were reacted smoothly affording the corresponding 2-deoxy glycoconjugates **4i**–**4j** in good yields (entries 8 and 9). Notably, all the reactions were proceeded with complete selectivity providing α-mannosides, endorsed to the participation of axially oriented C-2 iodo group in stabilization and controlling the stereochemistry at anomeric position.

We further examined the reactivity of 1-*O*-acetyl donor without any substituent at C-2 position and stereochemical outcome in present protocol. Thus, glycosylation of 2-deoxy glycosyl acetate donor **2a′**, readily prepared from **2a** using deiodonation method, with **3a** in the presence of Cu(OTf)$_2$ (5 mol %) afforded the corresponding 2-deoxy glycoside **5a** in good yield with an α/β ratio of 80:20 in favor of α-anomer (Scheme 1). The feasibility of sulfur nucleophile was also tested under similar conditions. Accordingly, naphthalene-2-thiol (**3k**) was allowed to react with glycosyl donor **2a′**, furnishing the corresponding 2-deoxy thioglycoside **5b** in a good yield albeit as a mixture with α/β ratio of 65:35.

In summary, we have demonstrated an operationally simple glycosylation for the stereoselective synthesis of 2-deoxy-2-iodo-glycosides utilizing solid, moisture tolerant, ease to handle and non-toxic catalytic system. The Cu(OTf)$_2$ catalyzed protocol is convenient and amenable to a wide range structurally diverse acceptors. Moreover, copper(I) iodide in combination with $NaIO_4$ efficiently promoted the iodoacetoxylation of several glycals. Further studies utilizing these protocols to access deoxy saccharides bearing different linkages at anomeric center are currently undergoing in our laboratory.

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Supplementary data

Supplementary data (general synthesis information, procedures, characterization data and ^{1}H, ^{13}C NMR spectra of glycosides) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.01.035.

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13. See Supporting information.