

## Synthesis of C1-alkyl- and acylglycals from glycals using a B-alkyl Suzuki–Miyaura cross coupling approach<sup>☆</sup>

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**Abstract**—A B-alkyl Suzuki–Miyaura cross coupling approach provides a flexible, efficient means to convert glycals to C1-alkylglycals and C1-acylglycals that are versatile synthetic intermediates. This approach uses readily available glycal starting materials and overcomes major limitations associated with direct alkylation or acylation of glycals. Further, a commonly observed side reaction involving reduction of the halide coupling partner is suppressed by preincubation of the borane coupling partner with aqueous base, providing new mechanistic insights into the side reaction.

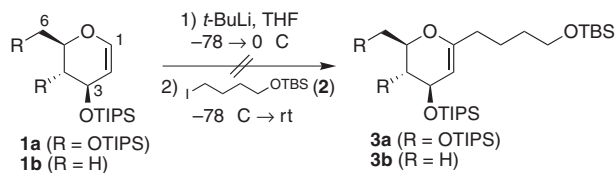
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Glycals are versatile, readily available synthetic intermediates with a wide range of applications in the synthesis of carbohydrates,<sup>1</sup> C-linked carbohydrate analogs,<sup>2</sup> C-aryl glycosides,<sup>3</sup> and a variety of other natural products.<sup>4,5</sup> In the course of a diversity-oriented synthesis project, we required a flexible, efficient method to convert glycals to C1-alkylglycals and C1-acylglycals.<sup>6</sup> Herein we report a B-alkyl Suzuki–Miyaura cross coupling approach to this overall transformation that overcomes major limitations associated with direct alkylation or acylation of glycals. Furthermore, we demonstrate that a commonly observed side reaction involving reduction of the halide coupling partner is effectively suppressed by preincubation of the borane coupling partner with aqueous base. Consequently, we propose a new alternative mechanism for this side reaction.

The seminal studies of Boeckman demonstrated that dihydropyrans can be lithiated at the C1-position (glycal numbering) with *t*-BuLi, then trapped with electrophiles to yield C1-substituted products.<sup>7,8</sup> Glycals have also

been deprotonated with the Schlosser base<sup>9</sup> (*n*-BuLi, KO*t*-Bu), then trapped with Bu<sub>3</sub>SnCl to form isolable C1-tributylstannylglycals.<sup>10</sup> Subsequent tin–lithium exchange using *n*-BuLi regenerates the C1-lithioglycal nucleophile for reaction with electrophiles.<sup>11</sup> Despite the straightforward nature of these approaches, several limitations have emerged. C1-Lithioglycals are relatively weak nucleophiles whose reactivity is attenuated further by the presence of oxygen substituents on the glycal ring.<sup>12</sup> Consequently, alkylation reactions are particularly challenging, generally requiring the use of alkyl iodides, often with HMPA cosolvent and an excess of the C1-lithioglycal.<sup>13</sup> The competing reactivity of C1-lithioglycals as bases can also lead to undesired side reactions.<sup>7b</sup> These considerations significantly limit the flexibility of this approach, an issue of paramount importance in diversity-oriented synthesis.<sup>14</sup>

These concerns were borne out in our initial efforts to alkylate glycals having an oxygen substituent at the C3-position (Scheme 1). TIPS-protected glycals **1a** and

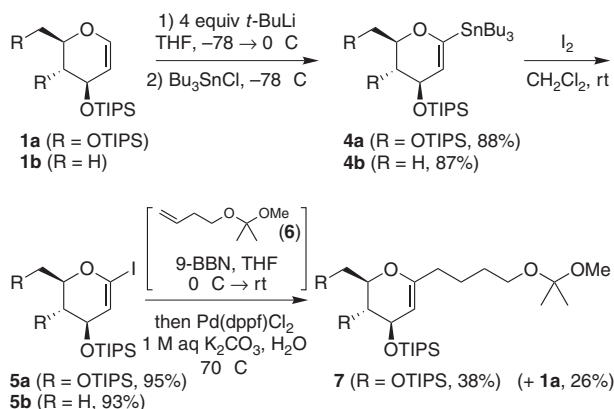


Scheme 1. Attempted direct alkylation of C1-lithioglycals.

**Keywords:** Glycal; Cross coupling; B-Alkyl Suzuki–Miyaura; C-glycoside.

<sup>☆</sup>Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2003.12.006](https://doi.org/10.1016/j.tetlet.2003.12.006)

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**Scheme 2.** Synthesis of C1-iodoglycals and first cross coupling reaction.

**1b** were prepared from D-glucal and 4,6-dideoxy-DL-glucal<sup>15</sup> under standard conditions (TIPSCl, imidazole, DMF, rt).<sup>16</sup> Lithiation of **1a** with *t*-BuLi was accomplished using Friesen's modified protocol.<sup>17,18</sup> However, the resulting C1-lithioglycal was completely unreactive with alkyl iodide **2**, even in the presence of HMPA.<sup>19</sup> The C1-lithioglycal derived from the corresponding stannane (**4a**, Scheme 2) by tin–lithium exchange was likewise unreactive. Deprotonation of **1a** with the Schlosser base,<sup>18</sup> followed by direct addition of excess alkyl iodide **2** did afford partial conversion to the desired C1-alkylglycal **3a**. However, a significant amount of iodide elimination was observed, suggesting competing basicity of the C1-lithioglycal–KO*t*-Bu complex. Alkylations involving the typical transmetalated species (*t*-BuLi then MgBr<sub>2</sub>,<sup>20</sup> MgI<sub>2</sub>, CuI,<sup>12a</sup> MgBr<sub>2</sub>/CuI,<sup>21</sup> MgBr<sub>2</sub>/Li<sub>2</sub>CuCl<sub>4</sub>,<sup>22</sup> or MgBr<sub>2</sub>/Pd(dppf)Cl<sub>2</sub>)<sup>23</sup> failed to afford any coupling product at all. Reactions in the 4,6-dideoxy-DL-glucal series (**1b** and **4b**) yielded similar results.

Thus, we elected to pursue an alternative strategy involving conversion of the parent glycals **1a** and **1b** to C1-iodoglycals followed by a *B*-alkyl Suzuki–Miyaura cross coupling reaction with alkylborane coupling partners.<sup>24,25</sup> We envisioned that this approach would provide flexible access to a variety of C1-alkylglycals

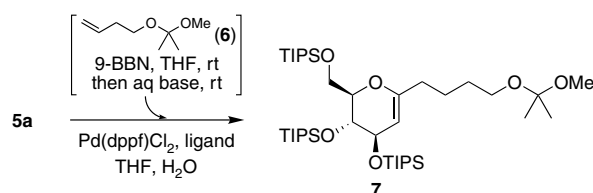
from readily available glycals and olefins. We were also encouraged by previous reports of related cross couplings.<sup>17,26</sup>

C1-iodoglycal substrates **5a** and **5b** were prepared according to Friesen's two-step protocol (Scheme 2).<sup>17,27</sup> In accordance with literature precedent, we found that these compounds, especially **5b**, exhibited capricious stability that varied from batch to batch. Nonetheless, degassing of all solvents with argon and protection from light allowed purification of the iodides by column chromatography for immediate use in cross coupling reactions. In early attempts, we had some success at effecting the desired coupling of iodide **5a** with the alkylborane derived from olefin **6** to yield C1-alkylglycal **7**. However, under a number of reaction conditions, including those of the original Suzuki–Miyaura procedure (shown in Scheme 2),<sup>24</sup> a substantial amount of reduction back to the parent glycal **1a** was also observed. This problematic reduction side reaction has also been observed with other halide substrates.<sup>24,28,29</sup>

We next set out to optimize the cross coupling reaction. After extensive experimentation, we observed a major improvement when we preincubated the hydroboration product with aqueous base for 30 min before addition to the C1-iodoglycal and palladium catalyst. This protocol reduced the amount of reduction to ≤ 5% based upon NMR analysis of the crude product (Table 1, entry 1). Subsequent experiments identified NaOH as the optimal base (entries 1, 2, and 4) with the addition of AsPh<sub>3</sub> proving detrimental to both selectivity and yield (entries 3 and 5).<sup>28</sup> At this fairly high catalyst loading level (20 mol%), selected in consideration of anticipated future applications to solid phase synthesis, the reaction also proceeds rapidly and effectively at room temperature (entry 6).

Only a handful of groups have used base preincubation protocols in Suzuki–Miyaura cross couplings.<sup>26,30</sup> Moreover, to our knowledge, the striking impact of this protocol upon the reduction side reaction has not been recognized previously. This side reaction is generally attributed to reductive elimination of a palladium

**Table 1.** Optimization of the *B*-alkyl Suzuki–Miyaura cross coupling reaction<sup>a</sup>

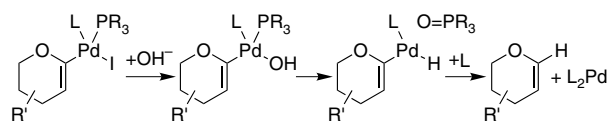


Entry	Temperature (°C)	Base	Ligand	<b>7:1a</b>	Yield (%)
1	70	K <sub>2</sub> CO <sub>3</sub>	None	96:4	63
2	70	Cs <sub>2</sub> CO <sub>3</sub>	None	96:4	71
3	70	Cs <sub>2</sub> CO <sub>3</sub>	AsPh <sub>3</sub>	90:10	59
4	70	NaOH	None	99:1	87
5	70	NaOH	AsPh <sub>3</sub>	98:2	78
6	rt	NaOH	None	98:2	91

<sup>a</sup> 1.5 equiv olefin, 3.0 equiv 9-BBN, 1 h; then 3.0 equiv base (1 M aq), 30 min; then add mixture to **5a** and 20 mol% Pd(dppf)Cl<sub>2</sub>, ±20 mol% AsPh<sub>3</sub>.

hydride species formed by (1)  $\beta$ -hydride elimination of the alkylpalladium intermediate<sup>24,28</sup> or (2) hydride transfer from the excess 9-BBN usually used to drive the hydroboration reaction to completion.<sup>29</sup> However, in a control experiment with C1-iodoglycal **5a**, Pd(dppf)Cl<sub>2</sub>, and aq NaOH, we observed 23% reduction to glycal **1a** (remainder unreacted **5a**). Notably, the two sources of hydride above—alkylborane and 9-BBN—were absent from this reaction. Further investigations revealed a direct correlation between the extent of reduction and the amount of Pd(dppf)Cl<sub>2</sub> used in this control reaction. Concurrent oxidation of the dppf ligand to the corresponding bis(phosphine oxide)<sup>31</sup> was detected by NMR and MS analysis and was evidenced by Pd(0) plating out of the reaction. Inclusion of PPh<sub>3</sub> in the control reaction resulted in a commensurate increase in conversion of **5a** to **1a**, with triphenylphosphine oxide generated as a byproduct.

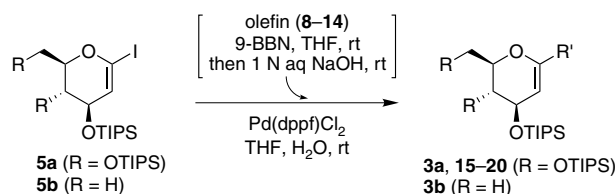
In view of these results, we propose that preincubation of aqueous base with the hydroboration reaction mix-



Scheme 3. Proposed mechanism for hydroxide-mediated reduction.

ture is critical for fully engaging hydroxide as the boron 'ate' complex. If this preincubation protocol is not used and the C1-iodoglycal is exposed to residual free hydroxide in the presence of the palladium catalyst, a competing reaction manifold leads to C1-iodoglycal reduction. This may occur via a mechanism analogous to the known hydroxide-induced disproportionation of (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> to triphenylphosphine oxide and Pd(0).<sup>32</sup> Thus, oxidative insertion of Pd(0) into the C1-iodoglycal would be followed by displacement of iodide by hydroxide (Scheme 3). Oxygen transfer from Pd to phosphine would generate a phosphine oxide and a glycalpalladium hydride species that would undergo reductive elimination to yield the parent glycal. This

Table 2. Scope of the *B*-alkyl Suzuki–Miyaura cross coupling route to C1-alkylglycals<sup>a</sup>



Entry	Iodide	Olefin	Product: R' =	Yield (%) <sup>b</sup>
1	<b>5a</b>	<b>8</b>	<b>3a</b>	88
2	<b>5b</b>	<b>8</b>	<b>3b</b>	81
3	<b>5a</b>	<b>9</b>	<b>15</b>	89
4	<b>5a</b>	<b>10</b>	<b>16</b>	95
5	<b>5a</b>	<b>11</b>	<b>17</b>	85
6	<b>5a</b>	<b>12</b>	<b>18</b>	86
7	<b>5a</b>	<b>13</b>	<b>19</b>	97
8	<b>5a</b>	<b>14</b>	<b>20</b>	95

<sup>a</sup> (i) 1.5 equiv olefin, 3.0 equiv 9-BBN, THF, rt, 3 h; (ii) 3.0 equiv 1 N aq NaOH, rt, 30 min; (iii) add to iodide and 20 mol% Pd(dppf)Cl<sub>2</sub>, THF/H<sub>2</sub>O (6.25:1 final ratio), rt, 1 h.

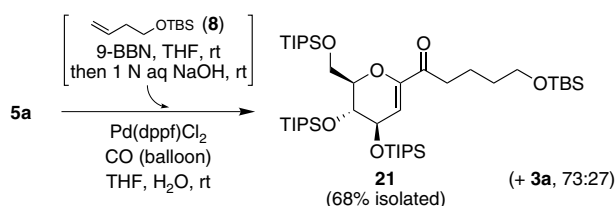
<sup>b</sup> All purified products exhibited satisfactory NMR, IR, and mass spectral data.

proposal is consistent with the observed correlation between the amount of phosphine present and the extent of C1-iodoglycal reduction. Notably, in their detailed mechanistic investigations of the *B*-alkyl Suzuki–Miyaura cross coupling reaction, Matos and Soderquist also observed an analogous reduction of bromobenzene to benzene with concomitant triphenylphosphine oxidation.<sup>33</sup> However, the significance of this additional alternative mechanism for the reduction side reaction in cross couplings has apparently not been fully appreciated until now.

With optimized reaction conditions in hand, we next set out to explore the scope of the *B*-alkyl Suzuki–Miyaura cross coupling reaction.<sup>34</sup> A variety of primary alkylboranes can be coupled with C1-iodoglycals rapidly and efficiently at room temperature (Table 2). Although, as anticipated, cyclohexene-derived secondary alkylboranes are ineffective coupling partners (not shown), steric hindrance is well tolerated at the  $\alpha$ - and  $\beta$ -positions (entries 3–6). Sugar- and amino acid-derived substrates can also be coupled (entries 7 and 8),<sup>35</sup> highlighting the potential utility of this approach for the synthesis of C-linked oligosaccharides and glycopeptides via subsequent stereoselective double bond transformations.<sup>6c,d,36</sup>

Finally, we note that direct acylation of C1-lithiodihydropyrans is also a highly problematic reaction that is ineffective using acid chlorides, anhydrides, and esters.<sup>7b</sup> Limited success has been achieved with DMF, *N,N*-dimethylacetamide,<sup>7b</sup> and  $\gamma$ -butyrolactone.<sup>37</sup> Thus, we were gratified to find that our *B*-alkyl Suzuki–Miyaura cross coupling approach can also be applied under carbonylative conditions to provide C1-acylglycal **21** (Scheme 4).<sup>38</sup> While this reaction merits further optimization, it extends the scope of our approach to provide access to a variety of C1-acylglycals using readily available olefin coupling partners.

In conclusion, we have developed a flexible, efficient method to convert glycals to C1-substituted glycals using a *B*-alkyl Suzuki–Miyaura cross coupling approach. This method provides access to C1-substituted glycals that are not available by direct alkylation or acylation of C1-lithioglycals. Furthermore, a wide range of both the glycal<sup>1,39</sup> and olefin coupling partners are readily available. We have also developed new insights into the problematic reduction side reaction that often occurs during *B*-alkyl Suzuki–Miyaura couplings.



**Scheme 4.** Synthesis of a C1-acylglycal using a carbonylative *B*-alkyl Suzuki–Miyaura cross coupling reaction.

We have demonstrated that aq NaOH alone can effect palladium-mediated reduction of C1-iodoglycals and that this side reaction is essentially eliminated in cross couplings by preincubation of the aq NaOH with the alkylborane prior to addition of the mixture to the C1-iodoglycal and palladium catalyst. Our current efforts are directed toward further improvement of this synthetic approach, translation to solid phase synthesis, and elaboration of both solution and solid phase coupling products in diversity-oriented synthesis.

**Supplementary material.** Experimental procedures and spectral data for compounds **1b**, **3–7**, **15–21** are available at doi:10.1016/j.tetlet.2003.12.006.

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