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Light-Mediated Cross-Coupling of Anomeric Trifluoroborates

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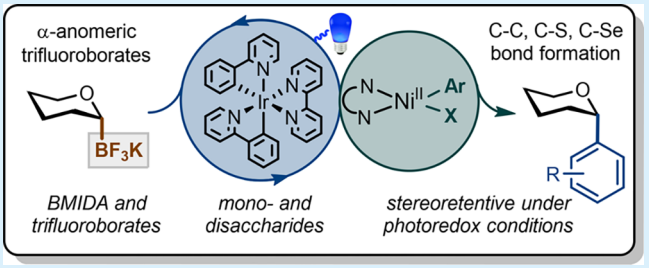
ABSTRACT: Stereoselective reactions at the anomeric carbon constitute the cornerstone of preparative carbohydrate chemistry. Here, we report stereoselective C-arylation and etherification reactions of anomeric trifluoroborates derived from BMIDA esters. These reactions are characterized by high anomeric selectivities for 2-deoxysugars and broad substrate scope (24 examples), including disaccharides and trifluoroborates with free hydroxyl groups. Taken together, this new class of carbohydrate reagents adds the palette of anomeric nucleophile reagents suitable for efficient installation of C−C bonds.



Carbohydrates are critical encoders of biological information because of their extensive structural complexity.[1] Saccharides are also involved in a number of important biological processes.[2−4] Among bioactive glycoconjugates, *C*-aryl glycosides have recently been targeted due to antitumor[5] (e.g., antibiotics **1**[6] and **2**) and antidiabetic activities exemplified by dapagliflozin **3**[7] and *C*-mannosyl proteins (**4**)[8] (Scheme 1A). Recent progress in the chemical synthesis of *C*-glycosides revealed an array of new transformations to rapidly assemble diverse structures.[9] Current methods featuring transition metal-catalyzed synthesis of *C*-aryl glycosides use Co,[10] Fe,[11] Ni,[12] and Zn[13] complexes (Scheme 1B), engaging anomeric halides as viable coupling partners. Alternatively, redox-active esters emerged as the source of anomeric radicals[14] and, when coupled with a Ni catalyst, can produce *C*-aryl glycosides.[15] These methods are characterized by variable selectivities, poor functional group tolerance, and a narrow scope. In an effort to address these obstacles, we recently showed high control of selectivity through a stereoretentive oxidative addition/reductive elimination Pd-catalyzed processes allowing for a complete control of stereochemistry using C1 stannanes.[9b,16] To further expand the scope of anomeric nucleophiles, we hypothesized that C1 trifluoroborates could give rise to air-stable glycosyl donors and could be engaged in $C(sp^3)-C(sp^2)$ cross-coupling reactions. Trifluoroborates have found widespread use as a nucleophilic component in various cross-couplings due to their stability, low toxicity, and compatibility with numerous functional groups.[17] These reagents have been shown to partake in light-mediated reactions with aryl halides using nickel and photoredox catalysts engaged in a dual catalytic system.[17c,18] On the basis of this literature precedent, we further hypothesized that with a proper control of the electronic effects either through the modulation of the protective groups or ligands on the high-valent nickel center, axial trifluoroborates could effectively undergo a stereoretentive coupling with electrophilic partners. This proposal was supported by a recent study from the Hirai group[19] featuring the synthesis of stable silicon-protected potassium trifluoroborates of 2-deoxy-β-D-glucose and β-D-galactose. Here, we report the synthesis and stereoretentive C−C cross-coupling reactions of α-anomeric trifluoroborates **11** of common mono- and disaccharides under the photoredox conditions (Scheme 1C).[20] These reagents are a reliable source of anomeric radicals and can be merged with Ni(II) cocatalyst to form *C*-glycosides in excellent anomeric selectivities.

On the basis of the perceived stability of methyliminodiacetic acid boronate (BMIDA) esters,[21] we attempted the synthesis of C1 boronates derived from 2-deoxysugars and fully oxygenated monosaccharides (for details, see the Supporting Information). Using MIDA proved vital, as it allowed for the synthesis of stable anomers that could be successfully purified on silica. With a diverse group of monosaccharides in hand, we attempted to increase structural diversity of anomeric MIDA boronates by chemical glycosylation with commonly used glycosyl donors (Scheme 2). To this end, two BMIDA glycosyl acceptors **12h** and **12f** were tested. We found that trichloroacetimidates, such as **14** and **16**, could be activated with TMSOTf (5 mol %) and produced disaccharides **18a** and **18b** excellent yields. To test more electrophilic conditions, we employed thioglycoside **15** and prepared BMIDA disaccharide **18b** in 81% using NIS as the activator. We were also interested to test milder, transition metal-catalyzed reactions to expand

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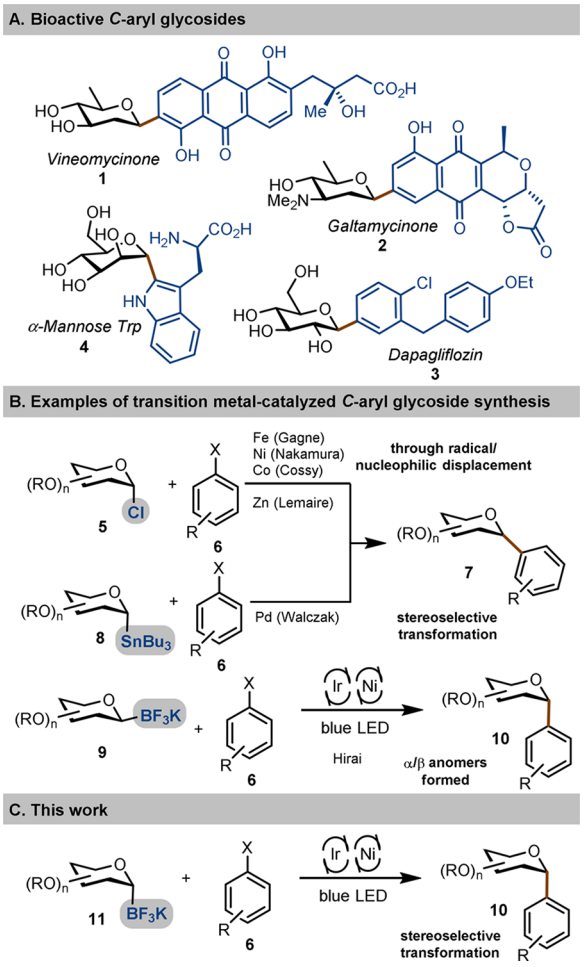
Scheme 1. C-Glycosides and Selected Synthetic Methods

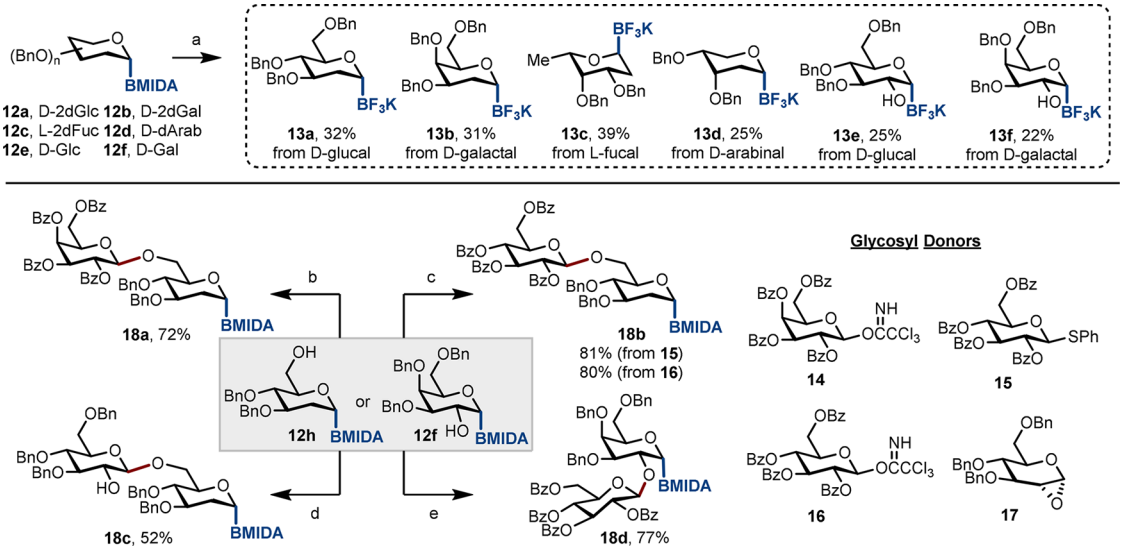


the scope of glycosyl donors. To this end, acceptor **12h** was treated with 1,2-*anhydro* sugar **17** in the presence of a gold catalyst previously reported by Yu.[22] Although this reaction was slow (~30 h at 23 °C), we were able to produce disaccharide **18c** in 52% yield with exclusive β-selectivity. On the basis of these preliminary studies, we conclude that BMIDA esters are compatible with Lewis acid activators and can be considered as a mildly deactivating group when located at the anomeric carbon in a glycosyl acceptor. These results also highlight the utility of BMIDA esters as convenient surrogates of more active boron donors such as boronic acids and trifluoroborates that may not survive electrophilic activation.

Next, we engaged anomeric boronates in C−C cross-coupling reactions. Initially, we tested reactions with MIDA boronates but these reagents proved to be too stable under slow-release Pd-catalyzed cross-coupling conditions.[21a] To overcome this problem, potassium trifluoroborates were studied and 2-deoxy-α-D-glucose **13a** and iodobenzene were selected as the model system (Table 1). Evaluation of several established photocatalyst revealed that PC3 significantly outperformed other Ir- and Ru-based complexes (entries 1−7). Inspired by the prior work for the Molander group, we focused on PC3 as our initial photocatalyst, Cs_2CO_3 (1.5 equiv) as a base in 1,4-dioxane and combination of 5 mol % $NiCl_2$·DME (DME = dimethoxyethane) with 5 mol % dtbpy (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine).[18d] After stirring for 24 h, we isolated 67% of **19** was formed exclusively as the α-anomer and 12% of β-hydride elimination glucal **20** (entry 3). Interestingly, PC6 (entry 6) showed encouraging yield of **19** (69%) but significantly suppressed elimination.

Furthermore, we looked at the role of base focusing on PC3 as the catalyst of choice. We found that the base proved to be essential in increasing the overall yield and reducing the extent of elimination product with CsF as the best additive furnishing **19** in 83% (entry 7). Sodium carbonate (entry 8), potassium *tert*-butoxide (entry 9), and potassium phosphate (entry 10)

Scheme 2. Transformations of Anomeric MIDA Boronates[a]



[a]Reagents and conditions: (a) KHF_2 (5.0 equiv), MeOH, 70 °C, 18 h; (b) **14** (1.2 equiv), **12h** (1.0 equiv), TMSOTf (0.05 equiv), 4 Å MS, CH_2Cl_2, −20 °C, 2 h; (c) **15** (1.2 equiv), **12h** (1.0 equiv), NIS (1.2 equiv), AgOTf (0.2 equiv), 4 Å MS, CH_2Cl_2, −45 °C, 2 h; (d) AgOTf (0.10 equiv), $Au(PPh_3)Cl$ (0.10 equiv), **12h** (1.0 equiv), **17** (1.5 equiv), 4 A° MS, CH_2Cl_2, −78 to 23 °C, 30 h; (e) **14** (1.2 equiv), **12f** (1.0 equiv), TMSOTf (0.05 equiv), 4 Å MS, CH_2Cl_2, −20 °C, 2 h.

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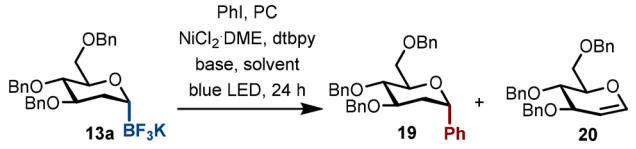
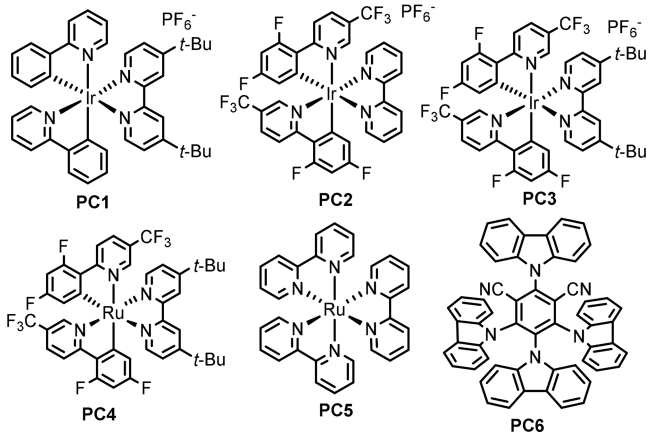
Table 1. Optimization of C−C Cross-Coupling[a]



Entry	Catalyst	Base	Solvent	**19** [%]	**20** [%]
1	PC1	Cs_2CO_3	dioxane	20	2
2	PC2	Cs_2CO_3	dioxane	57	14
3	PC3	Cs_2CO_3	dioxane	67	12
4	PC4	Cs_2CO_3	dioxane	26	5
5	PC5	Cs_2CO_3	dioxane	-	-
6	PC3	CsF	dioxane	83	3
7	PC6	CsF	dioxane	69	6
8	PC3	Na_2CO_3	dioxane	15	20
9	PC3	*t*BuOK	dioxane	-	-
10	PC3	K_3PO_4	dioxane	22	20
11	PC3	KF	dioxane	10	15
12	PC3	LiF	dioxane	9	19
13	PC3	CsF	acetone	73	28
14	PC3	CsF	THF	72	18

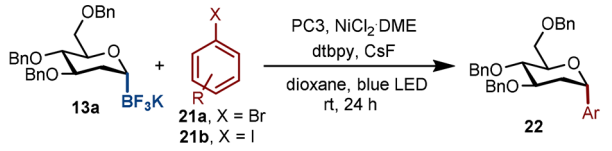


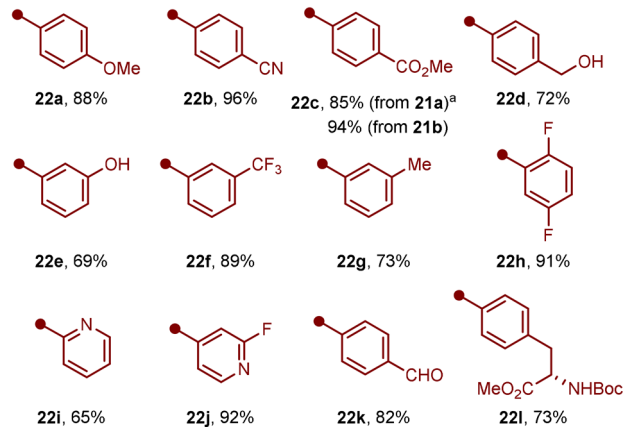
[a]General conditions: **13a** (0.15 mmol), (Ph-I) (0.10 mmol), PC3 (0.025 equiv), $NiCl_2$·DME (0.05 equiv), dtbpy (0.05 equiv), CsF (1.5 equiv), 1,4-dioxane (2.0 mL), blue LED (40W), 23 °C, 24 h, N_2.

showed reduced yields with an increase in elimination. Although additional studies on the role of the base in photoredox reactions is needed, we also established that the counterion combination is essential, and fluoride ion itself is not sufficient to suppress elimination, as demonstrated by the results with KF and LiF (entries 11 and 12, respectively). Finally, we explored solvents other than 1,4-dioxane−acetone (entry 13) and tetrahydrofuran (entry 14) produced comparable although slightly diminished yields. For all conditions shown in Table 1, a single anomer (α) was observed.

With suitable conditions in hand (Table 1, entry 6), our focus was to determine the extent of functional group tolerance (Scheme 3). Electron-rich 4-iodoanisole afforded **22a** in 88% with no loss of stereoselectivity. Electron-deficient cyano (**22b**) and ester (**22c**) groups gave almost quantitative yields (96% and 94%, respectively). These results suggest that electron withdrawing groups furnish better yields likely because of increasing the rate of reductive elimination and the ability to stabilize generated aryl radical.[23] Unprotected 4-iodobenzyl alcohol produced **22d** cleanly in 72% yield signifying that fully deprotected saccharides could be tolerated with these reaction conditions (vide infra). The meta-

Scheme 3. Scope of C-Arylation[b]





[a]87% isolated yield with 0.15 mmol of **13a**. [b]For all compounds tested, only one anomer (α: β > 99: 1) was observed by ^{1}H NMR in crude reaction mixtures. Reagents and conditions taken from Table 1, entry 6. Aryl iodides used for all entries unless stated otherwise.

substituted phenol gave the corresponding glycoside **22e** in an acceptable 69% yield similar to electron-poor (**22f**, **22h**) and electron-rich (**22g**) meta-substituted functional groups, which provided clean conversion into products in 73−91%. These results led us to the investigate more difficult pyridine-based couplings, such as 2-iodopyridine (**22i**) and 2-fluoro-4-iodopyridine (**22j**), which gave the expected products establishing a simple one-step protocol for the synthesis of pyridine glycals. Following these results, we focused on more challenging substrates such as the ones with a formyl group (**22k**, 82%) and 4-iodophenylalanine (**22l**, 73%). For all compounds shown in Scheme 3, exclusive α selectivity was observed (>99:1 α:β, ^{1}H NMR).

After uncovering the broad functional-group tolerance of an assortment of iodoarenes, we proceeded to apply our conditions to incorporate other sugars (Scheme 4). D-Glucose with a free hydroxyl group (**24a**) or protected as an acetate (**24b**) is a viable substrate for photoredox C(sp^3)−C(sp^2) cross-coupling. Similarly, 2-deoxy-D-galactose (**24c**) and dideoxysugars derived from D-arabinose (**24e**) and L-fucose (**24f**) furnished high selectivities in modest to high yields. To our delight, disaccharides are also competent reagents in photocatalytic *C*-arylation and afforded **24d** in 63%. Both, D-galactose (**24g**) and D-glucose (**24h**, **24i**) regardless of the nature of the protective group located at C2 resulted in a mixture of α:β products, with the smaller hydroxyl groups resulting in slightly improved axial preference (2.3−3.7:1). Because the proposed activation method proceeds through a radical species, we also wondered if C1 trifluoroborates can be enaged in C−S[24] and C−Se[25] bond-forming reactions (Scheme 5). To our delight, the formation of both ethers **26** and **28** proceeded smoothly from **13a** and eletrophilic sulfur (**25**) or selenium (**27**) sources without a nickel cocatalyst.

In summary, we introduced here a new class of C1-trifluoroborates that are competent reagents for the formation

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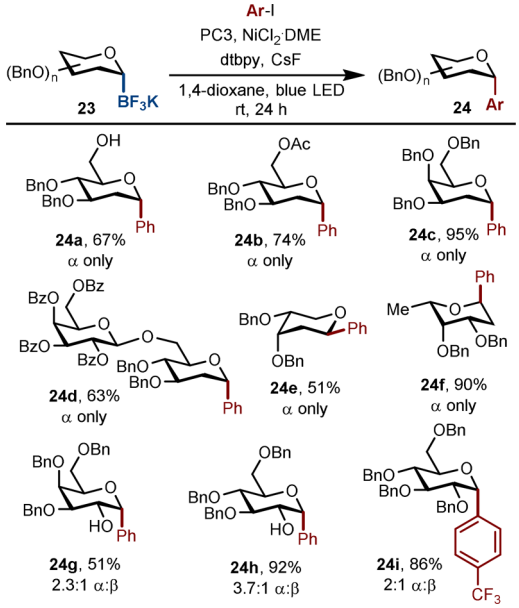
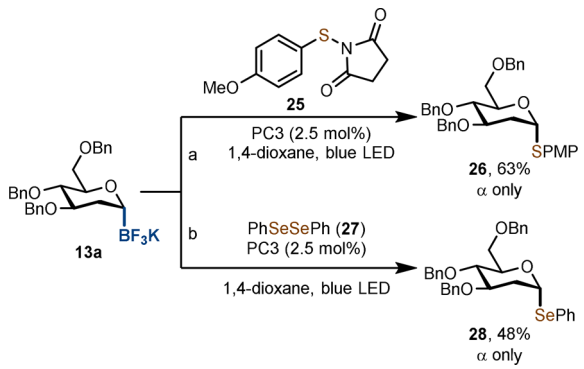
Scheme 4. Scope of Photoredox C-Arylation with Pyranosyl Trifluoroborates



Scheme 5. Scope of Photoredox Etherification of 2-Deoxy-D-glucose Trifluoroborate[a]



[a]Reagents and conditions: (a) **13a** (0.15 mmol), **25** (0.10 mmol), **PC3** (0.025 equiv), 1,4-dioxane (2.0 mL), 23 °C, 24 h, N_2; (b) **13a** (0.10 mmol), **27** (0.10 mmol), **PC3** (0.025 equiv), 1,4-dioxane (2.0 mL), 23 °C, 24 h, N_2.

of C−C and C−chalcogen bonds in 2-deoxy and fully substituted saccharides under the photoredox conditions. Although the overall transformation proceeds via single-electron transfer mechanism, the observed selectivities result in the net stereoretention and complement other C−C cross-coupling technologies with anomeric nucleophiles. Our results are also supportive of the growing importance of stereoelectronic effects such as the metallo-anomeric effect[26] in designing stereoselective glycosylation reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01035.

Copies of NMR spectra, detailed experimental procedures, and computation data (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor Samuel J. Danishefsky on the occasion of his 85th birthday.

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