

Stereoselective Synthesis of C-Glycosides using Potassium Aryltrifluoroborates

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INTRODUCTION

O-Glycosidic compounds are the most abundant and important among all types of glycosides, whereas C-glycosides have attracted considerable interest due to their interesting structures and higher stability toward glycosidases and hydrolytic conditions. Organotrifluoroborates have proven to be a good option to replace boronic acids and boronate esters in many reactions involving the formation of a new C-C bond.¹

Herein, we wish to describe the reaction of potassium aryl trifluoroborates and a sugar oxocarbenium ion to promote the direct C-glycosylation.

RESULTS AND DISCUSSION

Our initial studies focused on the development of an optimum set of reaction conditions. For this purpose, glucal **1** and potassium naphthalen-1-yl trifluoroborate **2a** were used as standard substrates. Initially, the reaction was carried out using different catalysts and conditions. The results are summarized in Table 1.

Table 1. C-glycosilation using different conditions

	conditions	Time (h)	Yield(%) ^a
1	MeCN, 25°C	12	-
2	K-10, MeCN, 25°C	12	-
3	MeCN, BF ₃ •Et ₂ O, 0°C	0.25	75
4	MeCN, BF ₃ •Et ₂ O, 25°C	0.25	69
5	CH ₂ Cl ₂ , BF ₃ •Et ₂ O, 0°C	0.25	10

^a isolated yield

In order to demonstrate the efficiency of the reaction, we explored the generality of our method extending the conditions to other potassium organotrifluoroborates. The results are summarized in Table 2.

Table 2. Arylation of **1** with Potassium aryltrifluoroborates

	Ar	Product	Yield (%) ^a
1			75
2			79
3			80
4			76

^a isolated yield

The potassium organotrifluoroborates **2a-d** were prepared from the corresponding boronic acids using KHF₂ in MeOH:H₂O in good yields and its structure was confirmed by ¹H, ¹³C, ¹¹B, and ¹⁹F NMR analysis.² The reaction gave the desired products in good yields and with α-anomeric selectivity in all cases, being the stereochemistry of the products confirmed by the NOe experiment.

CONCLUSION

In summary, we have demonstrated the use of BF₃•Et₂O as the Lewis acid choice to promote the C-glycosylation of glucals. The glycosides were synthesized under mild conditions, good yields and α-anomeric selectivity.

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CNPq, CAPES, INCT-INAMI

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