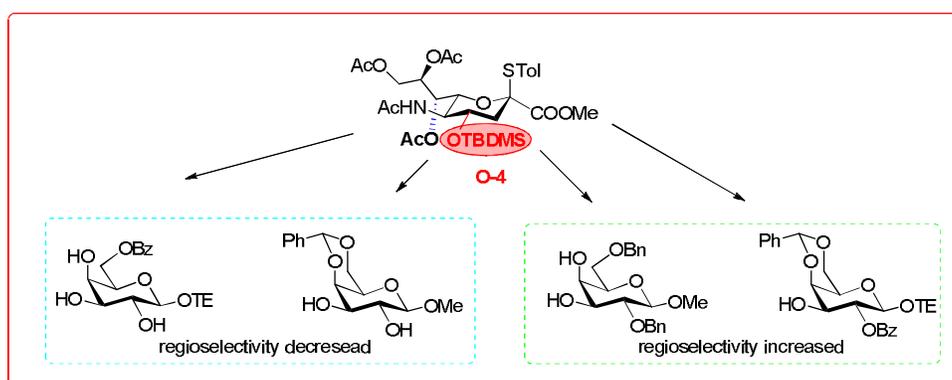


TOWARDS A BETTER REGIOCONTROL IN SIALYLATION REACTIONS

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Sialic acid-containing glycoconjugates are natural products that, in the last two decades, have become extremely important synthetic targets, due to their direct involvement in numerous biological phenomena, ranging from cell-cell adhesion and mobility, to oncogenesis and recognition by viruses and bacteria. Overexpression of sialic acids in carcinomas has been associated with an increment of the cell mobility, facilitating metastasis. Therefore, the synthesis and biomedical investigations of sialic acids and their bioconjugates is an extremely important tool for a better understanding of their biological properties and medicinal relevance, as well as for designing of sialotherapeutics. One major drawback in the field is obtaining a full control (yield and stereoselectivity) in the synthesis of sialic acid-conjugates as well as in their unnatural derivatives. Recently, we observed a strong influence of O-substituents when placed on the glycerol chain (C7-9) and C-4.¹ Thus, testing several benzoylated sialyl donors lead us to a discovery that S-tolyl donor bearing a TBDMS group at C-4 provides complete stereoselectivity in high yields when coupled with primary galactosyl acceptors. Herein we report the data when we applied the same methodology for the coupling with secondary acceptors. Indeed, we observed loss of regioselectivity that can be avoided by the synthesis of monohydroxy-galactosyl acceptors.



¹Premathilake, H. D.; Gobble, C. P.; Pornsuriyasak, P.; Hardimon, T.; Demchenko, A. V.; De Meo, C. How O-substitution of sialyl donors affects their stereoselectivity. *Org. Lett.* **2012**, *14*, 1126-1129.

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