



Copper(I)-Catalyzed Asymmetric C–C Bond Formations

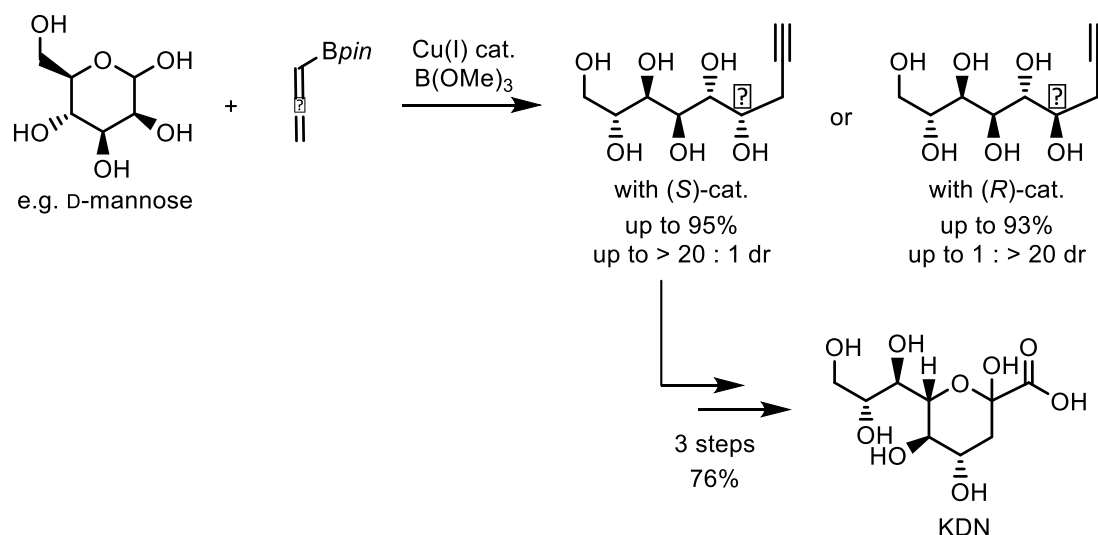
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Abstract: To achieve an efficient and scalable synthesis of wide variety of natural and unnatural sialic acid analogues, we developed a copper(I)-catalyzed asymmetric propargylation of unprotected aldoses. The soft allenylcopper species, catalytically generated from allenylboronate, exhibited high nucleophilicity in the presence of multiple hard protic functional groups of unprotected sugars. The addition of $B(OMe)_3$ was critical for the high reactivity by increasing the concentration of reactive aldehyde forms of aldoses. The propargylation reaction proceeded in high yield and diastereoselectivity in a gram-scale using as little as 0.2 mol % copper(I) catalyst. The diastereoselectivity of the reaction was switched by changing the chirality of the catalyst. The propargylation products were converted to natural and unnatural sialic acid derivatives through a simple three-step sequence [1].

In addition, copper(I)-catalyzed asymmetric iterative aldol reaction will be presented [2].



References:

- [1] X.-F. Wei, Y. Shimizu, M. Kanai, *ACS. Cent. Sci.* **2016**, *2*, 21.
 [2] L. Lin, K. Yamamoto, H. Mitsunuma, Y. Kanzaki, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2015**, *137*, 15418.