AZA-PIANCATELLI REACTION FOR THE SYNTHESIS OF NEW SPIROCYCLES

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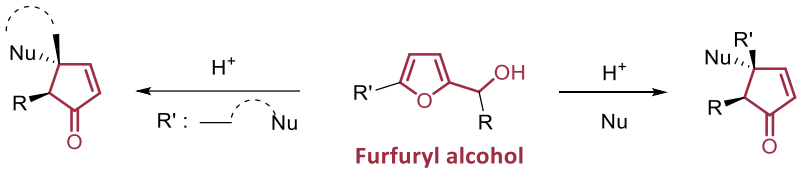
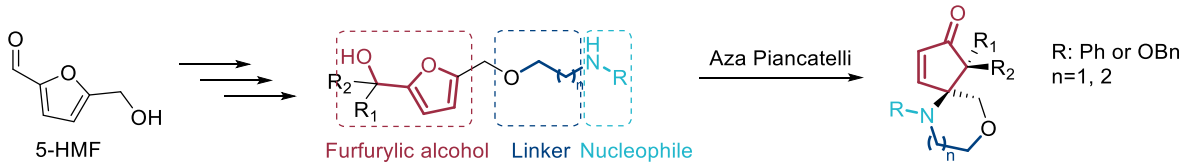
In 1977, Giovanni Piancatelli gave his name to a reaction that provides the formation of cyclopentenone starting from a furfurylic alcohol and a nucleophile.[1] Since then, numerous groups have shown interest for the development of this reaction, using different nucleophiles (oxygenated, nitrogenated or carbonated) and validating an intramolecular version including few enantioselective versions (*Scheme 1*).[2,3]



Scheme 1: The Piancatelli reaction, intra and inter-molecular version

Anilines, benzylhydroxylamines and recently sulfoximines are the most common nitrogenated nucleophiles used in the aza-Piancatelli reaction.[4,5] Moreover, the intramolecular version of the aza-Piancatelli reaction has been investigated by the groups of Read de Alaniz, Tang and Xu, mainly forming 5,5-spirocycles.[6–8]

Engaging a biomass molecule such as 5-HMF (hydroxymethylfurfural) through a multi-step synthesis to access an intramolecular aza-Piancatelli precursor targets an original series of spirocycles: it provides molecular diversity by increasing the spirocycle length (5,6- and 5,7-spirocycles) and bringing a heteroatom on the usually carbonated cycle (*Scheme 2*).[9]



Scheme 2: Synthesis of spirocycles by transforming 5-HMF in a multi-step synthesis

We also studied the opening of substituted aziridines to modify the linker part, thus accessing substituted spirocycles.

References

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