HIGHLY ENANTIOSELECTIVE DEAROMATIZATION OF PYRYLIUM DERIVATIVES WITH A HELICAL MULTIDENTATE ANION-BINDING CATALYST

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Asymmetric anion-binding catalysis,[1] which relies on the activation of the ionic substrates by the catalyst binding to their counter-anions and formation of a chiral contact ion pair, has become a powerful synthetic tool, offering new possibilities in the area of enantioselective catalysis. To contribute to the development of new multicoordination anion-binding catalysis, the C-H bond-based chiral tetrais triazole 1 with distinct confined anion-binding pockets was designed to carry out the nucleophilic dearomatization[2] reaction of in situ generated pyrylium derivatives, which present intrinsic reactivity and selectivity issues;[3] i) the nucleophilic reactions to pyrylium salts lead, in most cases, to decomposition or ring-opening adducts, ii) they are less reactive than non-conjugated oxonium ions, iii) it is not easy to fine-tune the stereoelectronic properties on the substrate, making enantio-differentiation difficult to be realized.

Herein, we are pleased to present a new anion-binding organocatalytic approach using low catalytic loadings (1-5 mol) for the highly enantioselective functionalization of chromenones and the more challenging 4H-pyran-4-ones with silyl ketene acetics as nucleophiles (up to 98:2 e.r.).[4]