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

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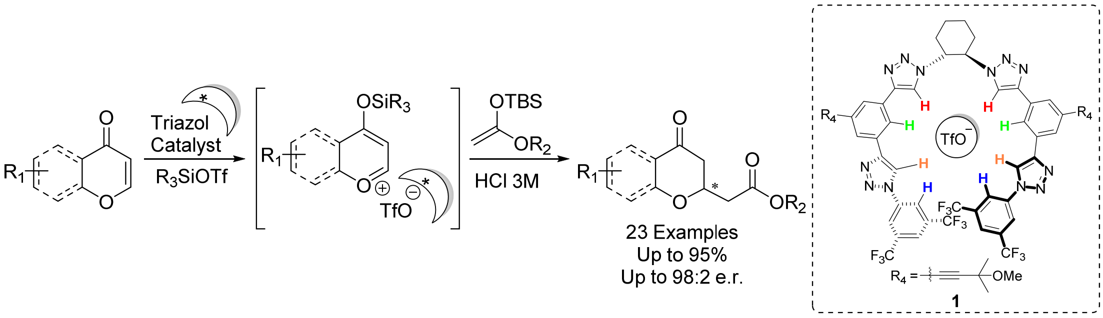
Asymmetric anion-binding catalysis,[1] which relies on the activation of the ionic substrates by the catalyst binding to their counter-anions and formation of a chiral contact ion pair, has become a powerful synthetic tool, offering new possibilities in the area of enantioselective catalysis. To contribute to the development of new multicoordination anion-binding catalysis, the C-H bond-based chiral tetrakis 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.



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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 4*H*-pyran-4-ones with silyl ketene acetals as nucleophiles (up to 98:2 e.r.).[4]

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[2] Zurro, M.; Asmus, S.; Beckendorf, S.; Mück-Lichtenfeld, C.; García Mancheño, O. *J. Am. Chem. Soc.* **2014**, *136*, 13999.

[3] Yang, Z.; He, Y.; Toste, F. D. *J. Am. Chem. Soc.* **2016**, *138*, 9775.

[4] Fischer, T.; Bamberger, J.; Gómez-Martínez, M.; Piekarski, D. G.; García Mancheño, O. *Angew. Chem. Int. Ed.* **2019**, *58*, 3217.