DACH-BASED BIFUNCTIONAL UREA/AMMONIUM SALT CATALYZED ASYMMETRIC α-HYDROXYLATION OF β-KETOESTERS

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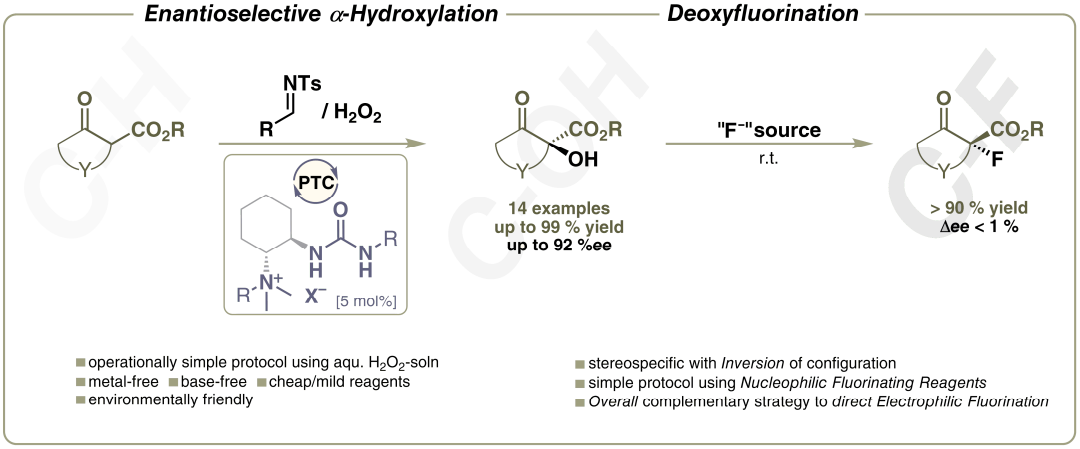
The α-hydroxy-β-oxo ester functionality is a common structural motif found in a variety of natural products, agrochemicals and pharmaceuticals, such as kjellmanianone, vindoline, indoxacarb, and doxycycline.[1] The enantioselective construction of α-hydroxy-β-dicarbonyl structures by means of direct α-oxidation of prochiral 1,3-dicarbonyls with electrophilic oxygen-transfer reagents has emerged as an important synthesis strategy.[2] However, organocatalytic approaches using cheap and environmentally benign oxidants, like oxygen[3] or hydrogen peroxide[4] remain scarce. Herein, we present a novel enantioselective bifunctional organocatalyzed tosylimine-mediated α-hydroxylation of 1-indanone-derived β-ketoesters under base-free conditions using hydrogen peroxide as oxidant. Furthermore, we developed an operationally simple, stereospecific (with *inversion*) deoxyfluorination protocol of enantioenriched α-hydroxy-β-ketoesters using nucleophilic NSF-reagents (DAST, diethylaminosulfur trifluoride).



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