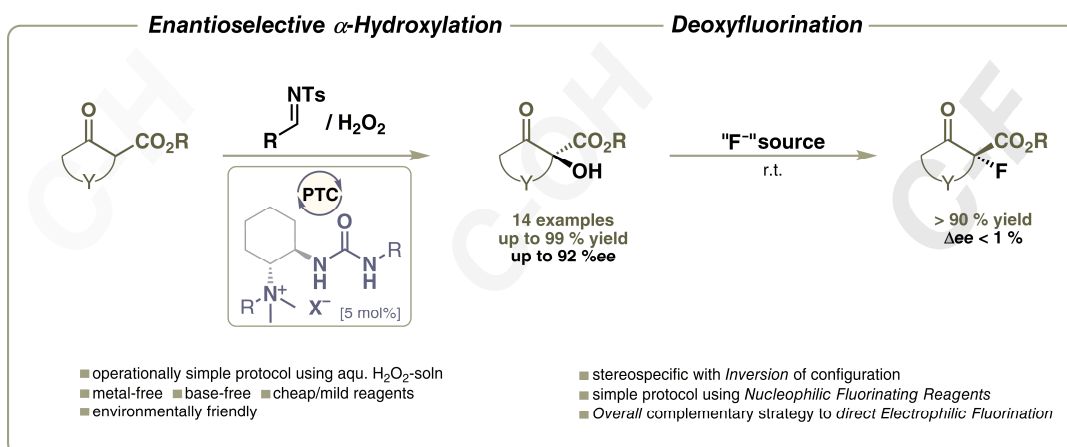


DACH-BASED BIFUNCTIONAL UREA/AMMONIUM SALT CATALYZED ASYMMETRIC α -HYDROXYLATION OF β -KETOESTERS

Christopher Mairhofer and Mario Waser

Institute of Organic Chemistry, Johannes Kepler University, 4040 Linz, Austria

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, an operationally simple, stereospecific (with *inversion*) deoxyfluorination protocol of enantioenriched α -hydroxy- β -ketoesters using nucleophilic NCF-reagents (DAST, diethylaminosulfur trifluoride) was developed.



[1] Christoffers, J.; Baro, A.; Werner, T., *Adv. Synth. Catal.* (2004) 346, 143

[2] Govender, T.; Arvidsson, P. I.; Maguire, G. E. M.; Kruger, H. G.; Naicker, T., *Chem. Rev.* (2016) 116, 9375

[3] (a) Lian, M.; Li, Z.; Gai, Y.; Meng, Q.; Gao, Z. *Chem. – Asian J.* (2012) 7, 2019; (b) Wang, Y.; Yin, H.; Tang, X.; Wu, Y.; Meng, Q.; Gao, Z. *J. Org. Chem.* (2016) 81, 7042; (c) Tang, X.-f.; Feng, S.-h.; Wang, Y.-k.; Yang, F.; Zheng, Z.-h.; Zhao, J.-n.; Wu, Y.-f.; Yin, H.; Liu, G.-z.; Meng, Q.-w., *Tetrahedron* (2018) 74, 3624

[4] (a) Li, Z.; Lian, M.; Yang, F.; Meng, Q.; Gao, Z., *Eur. J. Org. Chem.* (2014) 16, 3491; (b) Ohmatsu, K.; Ando, Y.; Ooi, T., *Synlett* (2017) 28, 1291