Oxidative functionalizations and oxa-Cope rearrangement studies towards naturally occurring diketopiperazine and oxepine series

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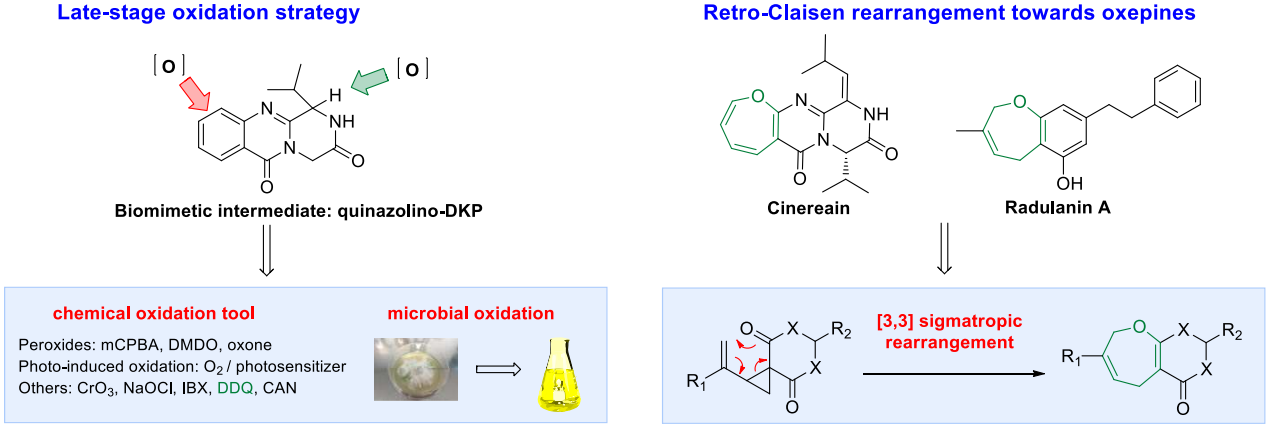
Biomimetic synthesis, inspired by direct and fast biosynthetic processes, is an efficient way to produce complex natural products. This thesis doctoral work focused firstly on the development of collective strategies, from biomimetic intermediates, to get a quick access to three families of diketopiperazines (DKPs), especially oxepino-DKP family. After investigations of the late-stage chemical oxidation reactions and microbial transformations on the quinazolino-DKP, a regioselective late-stage oxidation operated by DDQ was discovered, giving the first insights about the possibility of their collective total synthesis.

In the same time, an alternative methodology to synthesize oxepino-DKPs was explored. A temperature-controlled tandem cyclopropanation/oxa-Cope rearrangement was developed successfully to prepare 2,5-dihydrooxepines. This method was afterwards elucidated by experimental and computational (DFT) studies and further applied as the key step to finish the intractable total synthesis of radulanins.[1] Besides, the radulanin A was proved for the first time as strong herbicide compound, which may lead to good applications in agrochemical uses. Moreover, this oxa-Cope rearrangement approach also led to achieve the installation of 2,5-dihydrooxepine DKP, getting close to the accomplishment of the total synthesis of cinereain.



Short Biography

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[1] Zhang Wei, Baudouin Emmanuel, Cordier Marie, Frison Gilles, Nay Bastien, *Chem. Eur. J.* **2019**, 25, 8643-8648.