Triplet Sensitization with Ring-Contracted Flavins

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Our group has recently shown the enhanced triplet sensitization and hydrogen atom transfer (HAT) capabilities of imidazolonequinoxalines, ring-contracted analogues of flavins (RCF).[1] When compared to their flavin counterpart **1**, RCF **2** exhibits a significantly higher triplet energy ($E(S_0 \leftarrow T_1)$ = 244 kJ mol^{-1}) *vs.* $E(S_0 \leftarrow T_1)$ = 205 kJ mol^{-1}) rivaling commonly used Ir-complexes such as (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ ($E(S_0 \leftarrow T_1)$ = 251 kJ mol^{-1}).[1,2] Our initial work has been focused on using RCF **2** as a catalyst for reaction sequences starting from α-tropolone.[1] We have now expanded the application of RCFs to other transformations that require triplet energy transfer, *inter alia* for the activation of *N*-phenoxy-benzimidates **3** to yield oxazolines (**4**) via *N*-centered radical intermediates **Int I**.[3]

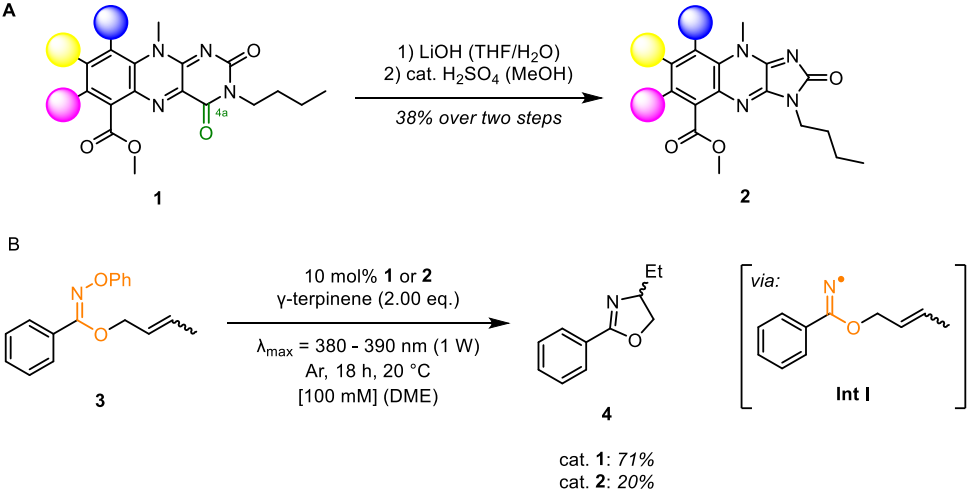

Figure 1: A Synthetic access to ring-contracted flavins (RCF) ***via*** hydroxide attack at the C4a-position followed by decarboxylation and ring closure. **B** Triplet sensitization of *N*-phenoxy-benzimidate **3** by RCF **2**.

[1] A. Rehpenn *et al.*, Angew. Chem., Int. Ed., 2024, **63**, e202318590. [2] Koenig *et al.*, Org. Lett. 2020, **22**, 5035−5040. [3] Prusinowski *et al.*, ACS Catal., 2022,**12** (8), 4327-4332, doi: 10.1021/acscatal.2c00804.