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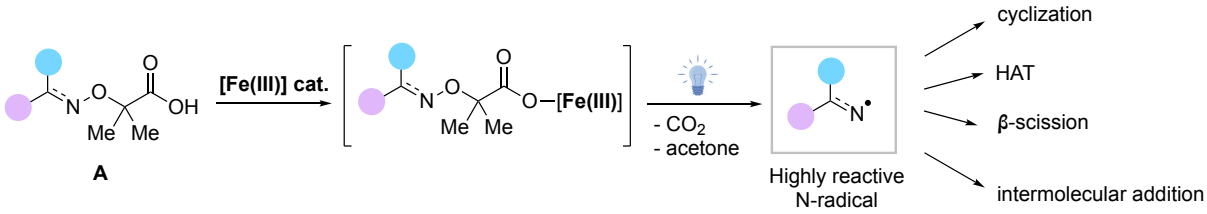
Iron photocatalysis.

Generation and reactivity of nitrogen-centered radicals by ligand-to-metal charge transfer

Visible-light photocatalysis offers a mild and sustainable entry to radical chemistry.[1] Particularly, light excitation can highly modulate Ru(II)- and Ir(III)- photocatalysts redox properties allowing outer-sphere electron transfers to occur. However, the scarcity of Ir and Ru, associated to high cost of the complexes and negative environmental impact of the extraction process, stimulated the evaluation of earth-abundant metal-based photocatalysts. To tackle the ultra-short excited lifetimes of the latter, alternative approaches based on an inner-sphere ligand-to-metal charge transfer have been designed.[2] In particular, iron carboxylates have been identified as photoactive species that could be activated through a visible-light induced homolytic cleavage leading, after CO_2 extrusion, to a carbon-centered radical.[3] These reactions have garnered an exponential attention over the last 5 years and a wide range of transformations have been developed to convert available, stable carboxylic acids into valuable compounds.
The objective of this thesis project is to harness visible light-induced activation of iron carboxylates to form nitrogen-centered radicals, that can be considered as highly versatile reactive intermediates.[4] The transient formation of iminyl and amidyl radicals through carboxylic acid derivatives of type **A** will be investigated and their reactivity in aza-cyclization, hydrogen-atom transfer, β-scissions or intermolecular addition reactions will be explored. This project would significantly broaden the scope if iron photocatalysis enabling to generate molecular diversity in a sustainable fashion.



The thesis project will therefore revolve around organic synthesis and photocatalysis using earth-abundant metals. The PhD student will be involved in substrate design and synthesis, reaction optimization, scope evaluation, product characterization as well as mechanistic investigations.

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[2] a) Y. Abderrazak, A. Bhattacharyya, O. Reiser *Angew. Chem. Int. Ed.* **2021**, *60*, 2. b) F. Juliá *ChemCatChem* **2022**, e202200916. c) A. M. May, J. L. Dempsey *Chem. Sci.* **2024**, *15*, 6661.
[3] S. Gavelle, M. Innocent, T. Aubineau, A. Guérinot *Adv. Synth. Catal.* **2022**, *364*, 4189.
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