

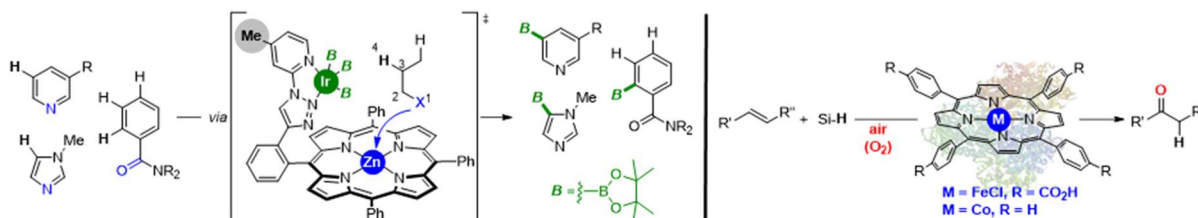
# Homogeneous Metal Catalysis: from Sustainable Transformations to Supramolecular Approaches

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The generation of more efficient, atom- and step-economy transformations is of primary importance to meet the societal challenges associated the 21<sup>st</sup> century. In this context, transition metal catalysis is an enabling technology and, in our laboratories, we have developed a number of sustainable approaches dealing with C-H bond functionalizations, one-pot multi-step sequences, direct reductive aminations, amongst others.<sup>1</sup> They aim at minimizing chemical wastes while controlling metal's reactivity. On another hand, we have developed metal-catalysed transformations which are controlled by remote, kinetically labile interactions taking place in the secondary coordination sphere of the metal catalyst.<sup>2</sup> In particular, we have exploited the reversible coordination bonds between nitrogen- or oxygen-containing substrates and metalloporphyrins as a tool for the design of supramolecular catalysts.<sup>2</sup> These supramolecular catalysts feature unique atom-precise selectivities for C-H bond functionalization besides displaying enzyme-like behaviours.<sup>2</sup> Lastly, the C-H oxidase behaviour of iron- and cobalt-porphyrin catalysts for the industrially-relevant Wacker-type oxidation of olefins into ketones will be shown,<sup>3</sup> which is important for replacing Pd catalysts.



## References:

1. a) *Adv. Synth. Catal.* **2016**, 358, 3847. b) *Org. Lett.* **2017**, 19, 6404. c) *Catal. Sci. Technol.* **2019**, 9, 4711. d) *Catal. Sci. Technol.* **2020**, 10, 180. e) *Catal. Sci. Technol.* **2021**, 11, 5772. f) *Chem. Eur. J.* **2022**, 28, e202201078. g) *Org. Chem. Front.* **2023**, 10, 42. h) *Catal. Sci. Technol.* **2024**, 14, 3984.
2. a) *Chem. Soc. Rev.* **2021**, 50, 3565. b) *Chem. Eur. J.* **2019**, 25, 627. c) *Angew. Chem. Int. Ed.* **2021**, 60, 18006. d) *Chem. Eur. J.* **2022**, 28, e202201970; e) *Faraday Discuss.* **2023**, 244, 186. f) *ACS Catal.* **2023**, 13, 7715. g) *Chem. Sci.* **2024**, 15, 11794.
3. a) *Angew. Chem. Int. Ed.* **2022**, 61, e202211016. b) *ACS Catal.* **2023**, 13, 4421. c) *Angew. Chem. Int. Ed.* **2024**, 63, e202316825. d) *ChemCatChem* **2024**, 16, e202400333. e) Patent EP 22 306 742.2, PCT/EP2023/082988. f) *Chem. Commun.* **2025**, 61, 8471.