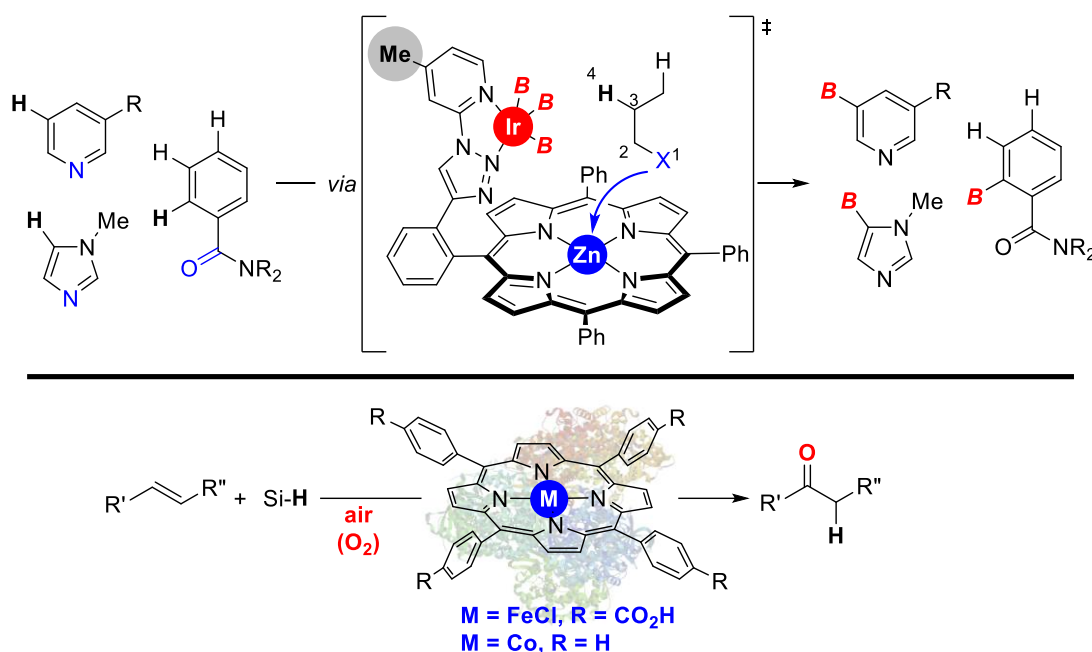


Re-purposing Metalloporphyrins

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Inspired by the hydroxylase activity of cytochromes P-450, exploiting the metal embedded in metalloporphyrins for catalysis has led to unique breakthroughs.¹ On the other hand, metalloporphyrins, typically those derived from zinc, are known to engage in weak coordination chemistry with polar organic compounds, usually nitrogen-containing ones.² We have exploited this behaviour by engineering catalytically productive iridium active sites in the periphery of the porphyrin whilst the embedded zinc centre serves for substrate-binding via remote Zn...N or Zn...O=C interactions.³ The precise distance between the active site and the substrate binding site dictates the selective C-H functionalization for challenging substrates.³ The enzyme-like behaviour of these supramolecular catalysts will be discussed.³ Lastly, the oxidase behaviour of iron- and cobalt-porphyrin catalysts for the industrially-relevant Wacker-type oxidation of olefins into ketones will be shown,⁴ which is important for replacing the scarce, expensive and toxic palladium catalysts.⁵ The oxidation reactions, which involve a complex mechanistic scenario, occur at ambient pressure and temperature with high activity and Markovnikov-selectivity in the presence of an hydrosilane.⁴



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