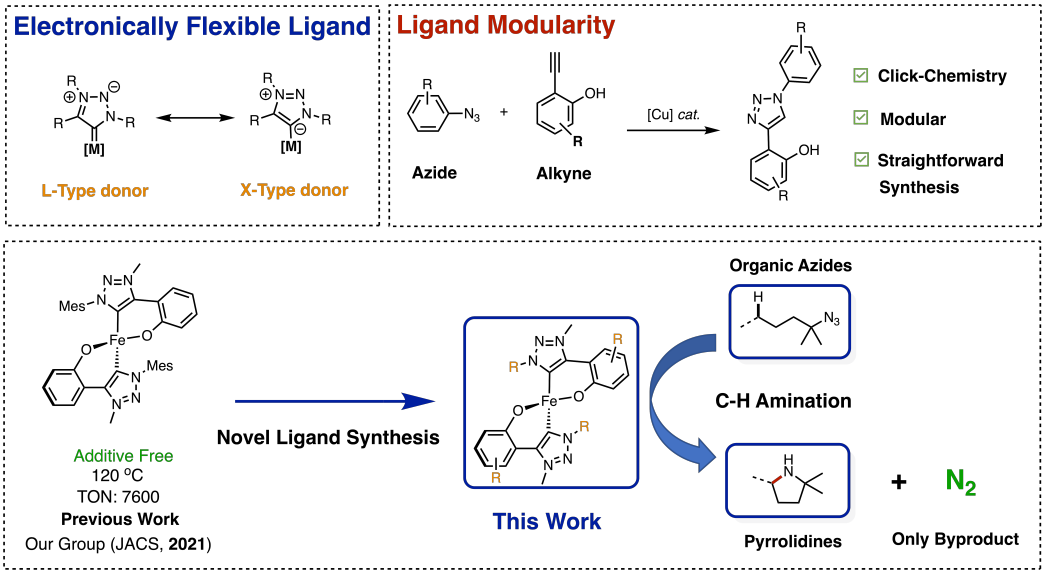
Iron-mesoionic carbene complexes for catalytic intramolecular C-H amination: novel ligand synthesis

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Nitrogen containing heterocycles are ubiquitous across nature and industry with C-N bonds being found in numerous natural products and pharmaceutically relevant molecules.[1,2] Therefore carbon-nitrogen bond formation is of utmost importance with catalytic and atom economical syntheses being particularly attractive. In this context, Betley in 2013 reported and iron-catalysed direct C-H bond amination using an iron-dipyrrinato catalyst to yield a range of pyrrolidines.[3] However, the activity was limited to only single digit TONs requiring 20 mol% catalyst loading and an equivalent of Boc_2O to prevent product inhibition. More recently, Betley also reported the additive-free C-H amination of nickel-dipyrrin complexes.[4] In 2021, our group disclosed a highly efficient iron(II) mesoionic carbene complex, which afforded a range of C-H aminated pyrrolidine products in excellent yield with no need of additives, generating only N_2 as the sole side product with TONs exceeding the state of the art by an order of magnitude.[5]

Herein, we aim to better understand the influence of the ligand and to improve the catalytic performance of the iron complex by designing and synthesising novel ligands. Our data shows that appropriate ligand substitution enhances both the activity and selectivity of C-H amination.



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