Cp*Ir(III) CATALYZED BRANCH SELECTIVE ALLYLIC AMIDATION OF UNACTIAVTED OLEFINS

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Nitrogen-containing functionalities are among the most importrant motifs in both natural and synthetic bioactive molecules. The methods of construction of C–N bonds, such as reductive amination or direct condensation of carboxylic acids and amines, require prefunctionalization and often cause superstoichiometric amouonts of waste.[1] Modern approaches like direct amination of C−H bonds can dramatically simplify the synthetic routes, providing greener and more straightforward disconnections for amine synthesis. However, most of the transition metal catalyzed allylic C–H amination reactions have in common are aminating in a linear fashion for terminal olefins and requiring stoichiometric amounts of oxidants to regenerate the metal catalyst.[2]

We present a highly branch-selective and redox-neutral allylic C–H amidation protocol enabled by Cp^*Ir^{III} catalysis.[3] Abundant carboxylic acids were simply activated to their corresponding dioxazolones and efficiently coupled with terminal and internal olefins in high efficiency and selectivities. The synthetic value of this protocol is demonstrated by showing a broad substrate scope including complex, bioactive compounds. Mechanistic experiments suggested the formation of Iridium–allyl species by $C(sp^3)$–H activation, which can undergo oxidative addition into the N–O bond of the dioxazolone to form corresponding allyl–Ir–nitrenoid species.

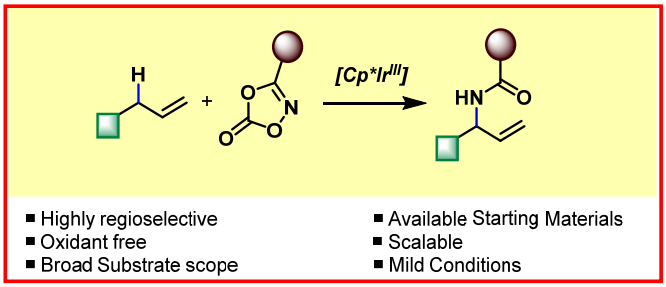

Fig 1. Branch Selective Allylic Amidation

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