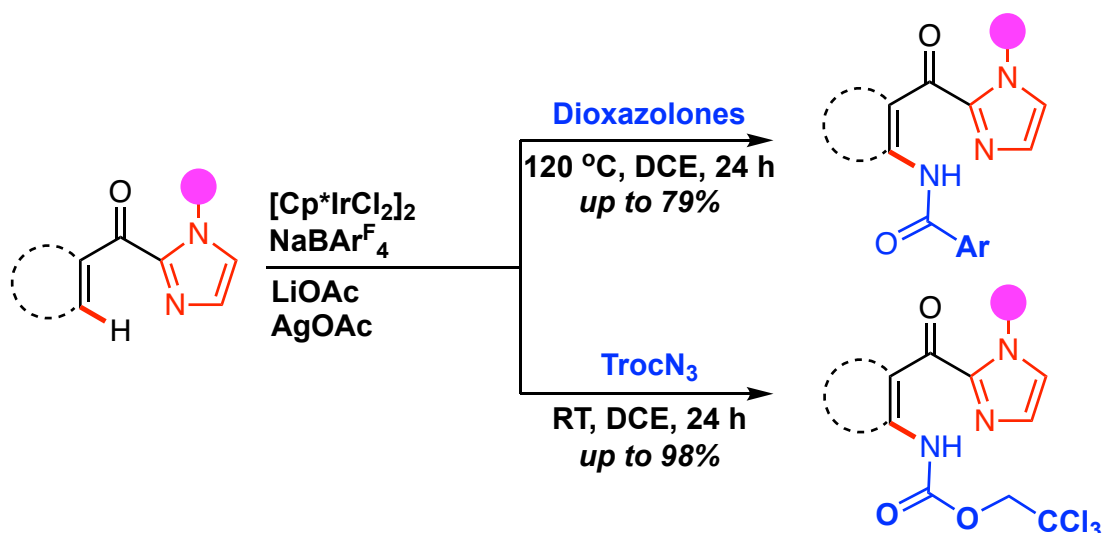


The Iridium (III)-Catalyzed C(sp²)-H Bond Amidation of 2-Aroylimidazoles: A Direct Observations of Kinetic and Thermodynamic Mechanistic Tunability

(Graduate School of Engineering, Osaka University) ○Sanjit Kumar Mahato, Naoto Chatani

Keywords: Carbon-Hydrogen Bond Cleavage; Nitrene Intermediate; Iridium Catalyst; Amidation; Thermodynamic and Kinetic Control

The transition metal catalyzed direct C-N bond formation *via* nitrene insertion plays crucial role to easily access to highly functionalized amides, which are encountered in many natural products and have key factors in screening preclinical drug candidates.¹ Thus, metal catalyzed direct C-H amidation has attracted much attention by organic chemists due to its atom- and step-economical process as it does not require any preactivation of the reactants.^{1b-c} Here, we report an Ir(III)-catalyzed direct C(sp²)-H amidation of 2-arylimidazoles² with dioxazolones and 2,2,2-trichloroethyl azides (TrocN₃) as nitrene sources. Although these two nitrene precursors differ greatly in reactivity and react through different mechanism only by changing the temperature under the same reaction conditions. This methodology is applicable for a wide of substituted aromatic and heterocyclic substrates to produce amido aroylimidazoles in good yields.



1) (a) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400. (b) Ju, M.; Schomaker, J. M. *Nat. Rev. Chem.* **2021**, *5*, 580. (c) Hong, S.Y.; Kim, D.; Chang, S. *Nat. Catal.* **2021**, *4*, 79.

2) (a) Mahato, S. K.; Chatani, N. *ACS Catal.*, **2020**, *10*, 5173. (b) Mahato, S. K.; Ohara, N.; Khake, S. M.; Chatani, N. *ACS Catal.*, **2021**, *11*, 7126. (c) Ohara, N.; Das, A.; Mahato, S. K.; Chatani, N. *Chem. Lett.* **2021**, *50*, 1722.