

Communication

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Iridium-Catalyzed Intermolecular Amidation of sp³ C–H Bonds: Late-Stage Functionalization of an Unactivated Methyl Group

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Direct sp³ C–H Amination



Nishioka, Y.; Uchida, T.; Katsuki, T. Angew. Chem., Int. Ed. **2013**, *52*, 1739.

NHR'

Previous Work on sp² C–H Amination



Kim, J.; Chang, S. Angew. Chem., Int. Ed. 2014, 53, 2203.

Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110.

Optimization of the Reaction Conditions



Some Interesting Substrates



 Sp² C–H amidation is more favorable than sp³ C–H amidation



• Acyl azides can be applied to the current Ir-catalyzed conditions to afford acylamido products

Late-stage Functionalization



C–H Amidation To Form Synthetic Building Units



The first example of the use of dioxazines as a directing group in C–H amination reactions



 The reaction can proceed efficiently at room temperature with a higher catalyst loading



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Double C(sp³)–H Bond Functionalization Mediated by Sequential Hydride Shift/Cyclization Process: Diastereoselective Construction of Polyheterocycles

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C(sp³)-H Functionalization by Internal Redox Process



• Key Feature:

- a) the [1,5]-hydride shift of the C(sp³)–H bond α to the heteroatom
- b) Subsequent 6-endo cyclization to a cationic species affords heterocycle 2



Two Types Of Sequential Hydride Shift



three contiguous stereogenic centers in 4aa and 6ab were completely controlled 10

Effect Of α-substituent Of α,β-unsaturated Trifluoroacetyl Group



bulkiness of the α -substituent controlled the reaction course



Substrate Scope



benzyl

nitrogen

1,5-hydride shift didn't occur

Thank You!