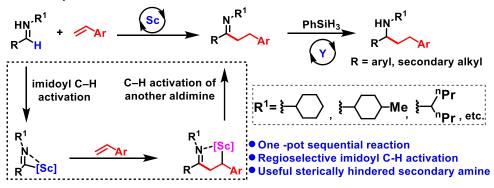
## Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

(¹Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, ²Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako, Saitama 351-0198) OZhou Sun¹, Masayoshi Nishiura ¹,², Xuefeng Cong¹, Zhaomin Hou ¹,²

Keywords: C-H alkylation, aldimines, rare-earth catalyst, hydrosilylation

Sterically hindered secondary amines are an important class of compounds that constitute the major body of bioactive natural products and pharmaceuticals. Therefore, the development of efficient and selective methods for the synthesis of such bulky secondary amines is of great interest and much importance. In principle, the imidoyl C-H alkylation of readily available aldimines with alkenes, which involves the insertion of an alkene into the imidoyl C-H bond, would constitute a straightforward and atom-efficient way for the synthesis of bulky ketimines which after reduction can convert to corresponding secondary amines. However, the related reports of such reactions are limited to specially designed functional group to facilitate chelation-assisted imidoyl C-H activation. Here we report for the first time sequential imidoyl C-H alkylation of aldimines with alkenes followed by hydrosilylation of ketimines catalyzed by half-sandwich rare-earth catalysts.

This protocol offers a straightforward and step-economical route for the synthesis a series of sterically hindered secondary amines from easily accessible aldimines, alkenes and silanes. The imidoyl C-H alkylation of aldimines with styrenes selectively gave the corresponding ketimines by a scandium catalyst and then successive yttrium-catalyzed hydrosilylation can convert to sterically hindered secondary amines, featuring good yields, broad substrate scope, high chemo- and regioselectivity and simple reaction conditions. The reaction mechanism for the imidoyl C-H alkylation was clarified by DFT calculation.



[1] R. N. Salvatore, C. H. Yoon, K. W. Jung, *Tetrahedron* **2001**, *57*, 7785 – 7811.

[2] X. Cong, Q. Zhuo, N. Hao, Z. Mo, G. Zhan, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202115996.

[3] C. Jun, H. Lee, J. Hong. J. Org. Chem. 1997, 62, 1200-1201.