Iron(II)-Catalyzed 1,2-Diamination of Styrenes Installing a Terminal Primary Amine Alongside Unprotected Amines

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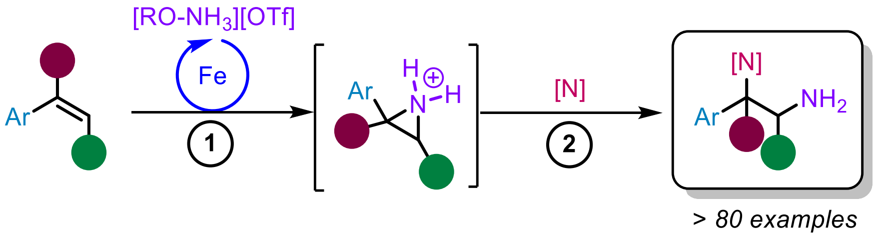

- differentiated vicinal diamines - free terminal NH_2 group
- [N] scope: aliphatic amines, anilines, sulfoximines and NH-heterocycles

1,2-Diamination of alkenes represents an attractive way to generate differentiated vicinal diamines, which are prevalent motifs in biologically active compounds and catalysts.[1,2] However, existing methods are usually limited in scope and produce diamines where one or both nitrogens are protected, adding synthetic steps for deprotection and further N-functionalization to reach a desired target.[3-5] Furthermore, the range of amino groups that can be introduced at the internal position is fairly limited. Here we describe a 1,2-diamination of structurally varied styrenes that directly installs a free amino group at the terminal position and a wide variety of unprotected nitrogen nucleophiles (primary or secondary alkyl or aromatic amines, sulfoximines, N-heterocycles, and ammonia surrogate) at the benzylic position.[6] Two complementary sets of conditions encompass electronically activated and deactivated alkenes with diverse substitution patterns and functional groups.

[1] D. Lucet, T. L. Le Gall, C. Mioskowski, *Angew. Chem. Int. Ed.* **1998**, *37*, 2580-2627
[2] S. R. S. S. Kotti, C. Timmons, G. Li, *Chem. Biol. Drug Des.* **2006**, *67*, 101-114
[3] G. Tan, M. Das, R. Kleinmans, F. Katzenburg, C. Daniliuc, F. Glorius, *Nat. Catal.* **2022**, *5*, 1120-1130
[4] C. Martínez, K. Muñiz, *Angew. Chem. Int. Ed.* **2012**, *51*, 7031-7034
[5] D. E. Holst, C. Dorval, C. K. Winter, I. L. Guzei, Z. K. Wickens, *J. Am. Chem. Soc.* **2023**, *145*, 8299-8307
[6] V. Pozhydaiev, A. Paparesta, J. Moran, D. Lebœuf, *Angew. Chem. Int. Ed.* **2024**, e202411992