Z. LI, D. A. CAPRETTO, R. RAHAMAN, C. HE (UNIVERSITY OF CHICAGO, USA)

Silver-Catalyzed Intermolecular Amination of C-H Groups

Angew. Chem. Int. Ed. 2007, 46, 5184-5186.

Silver-Catalyzed Amination of C-H Groups

Significance: New methods for the introduction of C-N functionality by a direct C-H activation are quite valuable, considering the importance of nitrogen-containing functionalities in various synthetic targets. The simple complex of commercially available bathophenanthroline and AgOTf was found to catalyze efficiently the inter- and intramolecular amination of saturated C-H bonds, including non-activated cycloalkanes. This method is now the easiest for the introduction of an amine group into a non-activated alkane or a benzylic position of an arene.

Comment: The intramolecular reaction of carbamates with PhI(OAc)₂ proceeds highly selectively, leading to five-membered heterocycles (oxazolones). For the intermolecular process, PhI=NNs (Ns = p-nitrophenylsulfonyl) as a nitrene source is used. The resulting nosylamides can be readily hydrolyzed to amines. The consideration of the catalyst structure indicates the necessity of a dinuclear core for the Ag-catalyzed nitrene transfer, which is realized in the case of bathophenanthroline-Ag(I) complex by a ligand π -stacking.