Aza-Annulation by C–H Arene Amination with O-Sulfonylhydroxyamines

**Significance:** Primary and N-alkyl arylamines are ubiquitous motifs in nature, pharmaceuticals, and functional materials. Falck and co-workers describe a dirhodium-catalyzed C–H amination using O-sulfonylhydroxyamines as both aminating agents and internal oxidants to give free primary or N-alkyl arylamines. Under these conditions, C–H amination was achieved in moderate to good yields and with good regioselectivity, without the need for arene prefunctionalization or directing groups, for example conversion of 1 into 2. The amination reaction provided the basis for an efficient two-step protocol for converting readily available aryl alcohols into annulated azaarenes through a Mitsunobu and intramolecular C–H amination sequence. The suitability of this method for late-stage amination of complex molecules was also demonstrated.

**Comment:** Despite recent advances in C–H activation methods, the development of a mild and practical arene amination method to form free arylamines without arene prefunctionalization still presents a challenge. This report provides a mild protocol to generate primary or N-alkyl arylamines by using readily available O-sulfonylhydroxyamines. [Another noteworthy method in this area is a photoredox-based C–H amination using an ammonium salt to form anilines (N. A. Romero, K. A. Margrey, N. E. Tay, D. A. Nicewicz Science 2015, 349, 1326)]. In cases of intermolecular C–H amination, the ortho/para-directing effect suggests an electrophilic aromatic substitution mechanism, which limits the arene substrate scope to electron-neutral or electron-rich arenes. The electronic effect is less pronounced in the intramolecular cases, where electron-deficient arenes are still capable of forming annulated azaarenes. Owing to the mild conditions of the protocol, complex drug-like substrates, such as estrone, have been functionalized at a late stage to install amine functionalities, providing a valuable transformation for the pharmaceutical industry.