

A Highly Chemoselective Intramolecular Allylic C—H Amination under Iron Catalysis

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Development of a highly chemo- and site-selective C—H amination reaction will be presented. This novel method, which employs an inexpensive, non-toxic [Fe^{III}Pc] catalyst (typically used as an industrial dye), represents the first general C—H amination under iron catalysis. [Fe^{III}Pc] displays a strong preference for allylic C—H amination over aziridination and amination of all other C—H bond types (i.e. allylic > benzylic > etheral > 3° > 2° >> 1°), with the highest chemoselectivities reported to date for nitrene-based C—H aminations. Further, observed reactivity trends are orthogonal to those observed under rhodium catalysis. In polyolefinic substrates, site selectivities for [Fe^{III}Pc]-catalyzed C—H amination can be controlled by the electronic and steric character of the allylic C—H bond. Although this reaction is shown to proceed via a stepwise mechanism, the stereoretentive nature of C—H amination for 3° aliphatic C—H bonds suggests a very rapid radical rebound step.

