

SESSION I: SPEAKER ABSTRACTS

A Highly Reactive and Chemoselective Manganese Catalyst for Intramolecular C(sp³)—H Amination

Jennifer R. Griffin & Shauna M. Paradine, Jinpeng Zhao, Aaron L. Petronico, Shannon M. Miller, and M. Christina White

C—H bond oxidation reactions underscore the existing paradigm wherein high reactivity and high selectivity are inversely correlated. The development of catalysts capable of oxidizing strong aliphatic C(sp³)—H bonds while tolerating more oxidizable functionality remains an unsolved problem. We have developed a novel base metal catalyst, manganese *tert*-butylphthalocyanine [Mn(^tBuPc)], that lies outside of this typical reactivity-selectivity paradigm. [Mn(^tBuPc)] intramolecularly aminates all types of C(sp³)—H bonds without oxidizing more reactive π -functionality, demonstrating an unprecedented balance between reactivity and chemoselectivity for a C—H oxidation reaction. Previous rhodium and iron catalysts developed for this transformation have demonstrated either high reactivity (i.e. capable of aminating strong aliphatic C—H bonds) or high chemoselectivity (i.e. capable of aminating at allylic C—H bonds without competing aziridination), respectively, but never both. Mechanistic studies suggest that the unique reactivity and selectivity of [Mn(^tBuPc)] can be attributed to its mechanism of metallonitrene C—H insertion that lies between stepwise, observed with chemoselective base metals like iron, and concerted, observed with reactive noble metals like rhodium. Rather than achieving a blending of effects, [Mn(^tBuPc)] aminates even 1° aliphatic and propargylic C—H bonds, reactivity and selectivity unusual for previously known catalysts.

