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Efficient Diastereoselective Intermolecular Rhodium-Catalyzed C–H Amination
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Rhodium-Catalyzed Diastereoselective Intermolecular C–H Amination

Significance: Over the last few years, metal-catalyzed C–H functionalization has been an area of intense research. In particular, intramolecular amination reactions of saturated C–H bonds represented a powerful tool for the synthesis of chiral nitrogen-containing compounds (for recent examples, see: J.-S. Liang et al. *J. Org. Chem.* **2004**, *69*, 3610–3619; M. Kim et al. *Org. Lett.* **2006**, *8*, 1073–1076). Herein the first efficient intermolecular version of this reaction is described, using catalytic amounts of chiral rhodium complex [Rh₂((S)-nttl)₄], substoichiometric amounts of alkane and a combination of PhI(OCOt-Bu)₂ and (S)-N-(p-toluenesulfonyl)-p-toluenesulfonimidamide to afford the chiral iminoiodane in situ.

Comment: This methodology proved to be superior in many different aspects to the preexisting catalytic methods reported to date. Indeed, both electron-rich and electron-poor C–H bonds as well as allylic substrates (to a smaller extent) are readily and diastereoselectively functionalized. Of particular synthetic utility is the selectivity in the reaction with 2-methoxyindane which gives selectively the *trans* isomer whereas an intramolecular reaction would have led to the *syn* compound. The high selectivity can be explained by a matched effect between the catalyst system and the sulfonimidamide. Interestingly enough, the cleavage of the sulfonimidoyl group could be carried out without loss of the chiral information.