Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

rhodium

C–H amination

diastereoselectivity

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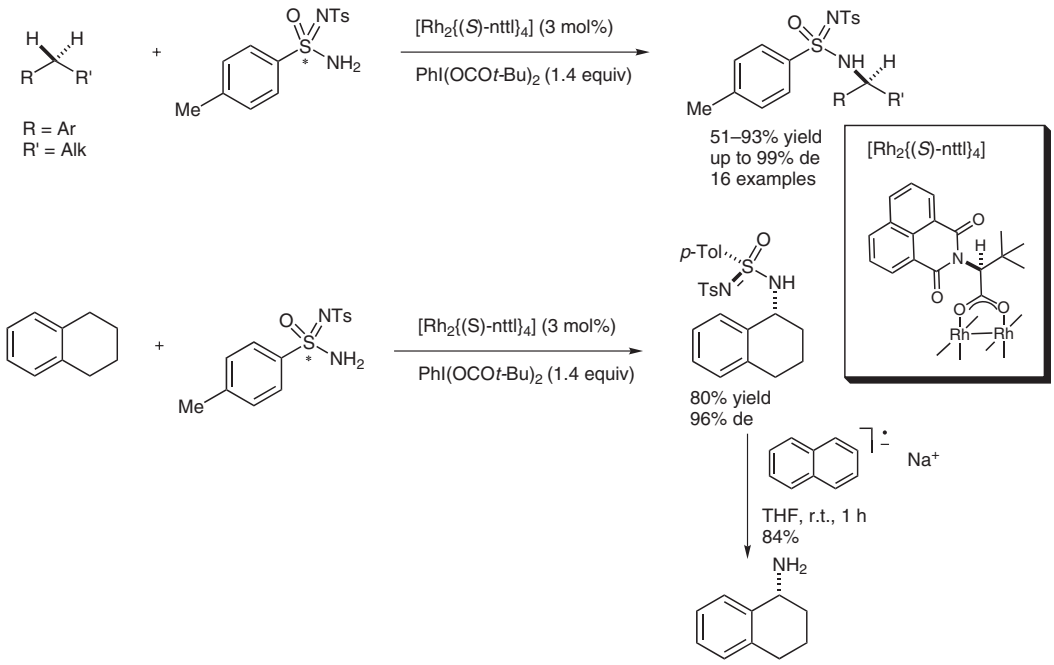
Rhodium-Catalyzed Diastereoselective Intermolecular C–H Amination



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 $[Rh_2\{(S)\text{-nttl}\}_4]$, substoichiometric amounts of alkane and a combination of $PhI(OCOt\text{-}Bu)_2$ 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 lead 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.

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