Enantioselective [3+2] Annulation of Aromatic aldimines with Alkenes via C−H Activation by Half-Sandwich Scandium Catalysts

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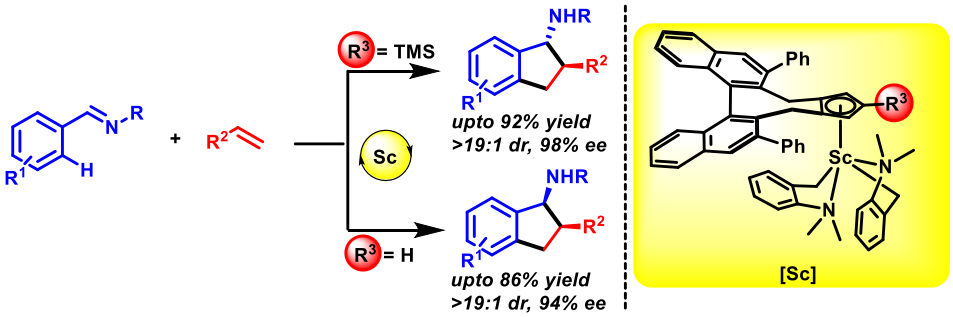
Chiral aminoindanes are valuable structural motifs found in numerous drugs and bioactive molecules. Therefore, the development of a selective and efficient route for the synthesis of densely functionalized chiral aminoindanes is of high interest and importance. In principle, enantioselective formal [3+2] annulation of aromatic aldimines with alkenes via *ortho* aryl C–H bond activation is among the most straightforward and atom-efficient approach for the synthesis of multisubstituted chiral aminoindanes. However, such approach has remained unsuccessful, presumably due to the lack of suitable chiral catalysts. Recently, we have found that half-sandwich rare-earth-alkyl complexes can serve as efficient catalysts for the [3+2] annulation of aldimines and alkenes via C–H activation.[1] These studies invoked us to examine the feasibility of the asymmetric annulation by using chiral half-sandwich rare-earth-alkyl catalyst.

Herein, we demonstrate the first diastereodivergent asymmetric [3+2] annulation of aromatic aldimines with styrenes via C–H bond activation by chiral half-sandwich scandium catalysts. This protocol offers the atom-efficient synthesis of both the *trans* and *cis* diastereoisomers of multisubstituted chiral aminoindanes in high yield along with excellent diastereo- and enantioselectivity by fine-tuning the sterics around the metal-center. Apart from styrenes, aliphatic α-olefins, norbornene, 1,3-dienes were all suitable for the asymmetric transformation.



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