Enantioselective [3+2] Annulation of Aromatic Aldimines with Alkynes via C−H Activation by Half-Sandwich Scandium Catalyst

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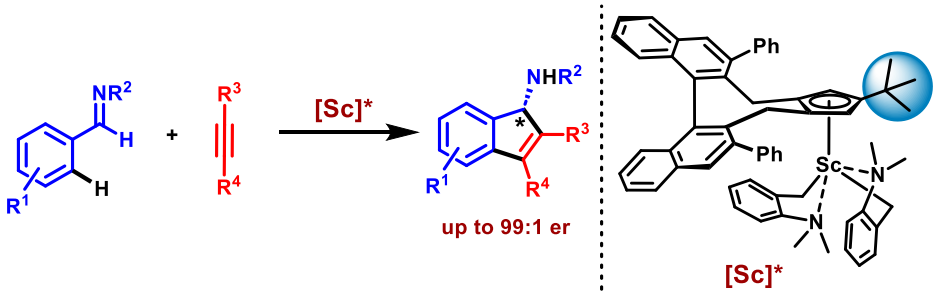
Chiral 1-aminoindenes and its derivatives are important components in a wide array of natural products, pharmaceuticals, bioactive molecules, and functional materials. Therefore, the development of efficient protocols for the asymmetric synthesis of chiral 1-aminoindenes bearing a stereodefined amino functionality is of great interest and much importance. Ideally, formal asymmetric [3+2] annulation of aldimines with alkynes *via* the catalytic C–H activation represents the most straightforward and 100% atom-efficient route for the construction of densely functionalized chiral 1-aminoindenes. However, such an 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 of aldimines with alkynes by using chiral half-sandwich rare-earth-alkyl catalyst.

Herein, we report for the first time the enantioselective [3+2] annulation of a wide range of aldimines with internal alkynes via *ortho*- aryl C(sp^2)–H activation by a novel chiral half-sandwich scandium complex derived from a *tert*-butyl substituted chiral binaphthyl-bearing Cp. This protocol offers an efficient and selective route for the synthesis of a new family of chiral 1-aminoindenes in high yields with high regio- and enantioselectivity. Intriguingly, attractive noncovalent interaction such as C–H···π interaction plays a crucial role for determining the high level of enantioselectivity in an unprecedented manner, established by the DFT studies.



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