Asymmetric Allylation of Stereogenic Nitrogen Centers

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Within the last decades, much attention from the chemical community has been directed at the development of asymmetric reactions.[1] Just as a carbon atom, having a tetrahedral configuration, nitrogen with three different substituents can be a stereogenic centre too. Such tertiary amines, however, usually do not show optical activity due to a low energy of the nitrogen inversion, which results in a rapid equilibrium between the enantiomers (Fig. 1). This inversion can be stopped by a conformational strain such as the one observed in Tröger's base[2], or by a quaternization of the nitrogen atom.[3]

Figure 1. Nitrogen (or "umbrella") inversion vs. conformationally stable salt.

Chiral ammonium salts are widely used as phase-transfer catalysts[4] and stereo-controlling cations[5]; they can be found in nature[6] and some exhibit pharmacological activity.[7] Current strategies for the synthesis of such compounds are based on the resolution techniques of diastereoselective adducts[8] or salts.[9] Surprisingly, no asymmetric catalytic transformation has been reported so far.

In this project, we focus on the asymmetric catalytic conversion of amines to ammonium ions. We explored the transition metal-catalyzed allylation of tertiary amines and could realize excellent conversions and significant stereoselectivities (Fig. 2).

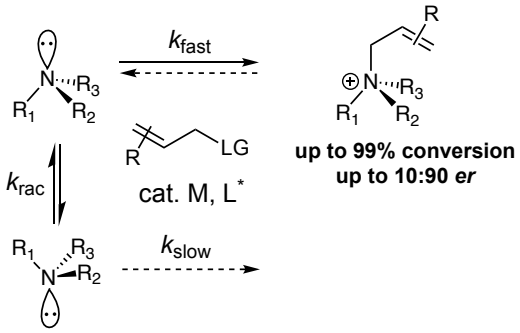

Figure 2. Dynamic kinetic resolution of tertiary amines by asymmetric allylation.

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