

Recent advances in asymmetric synthesis with chiral imide auxiliaries

David A. Evans and Jared T. Shaw

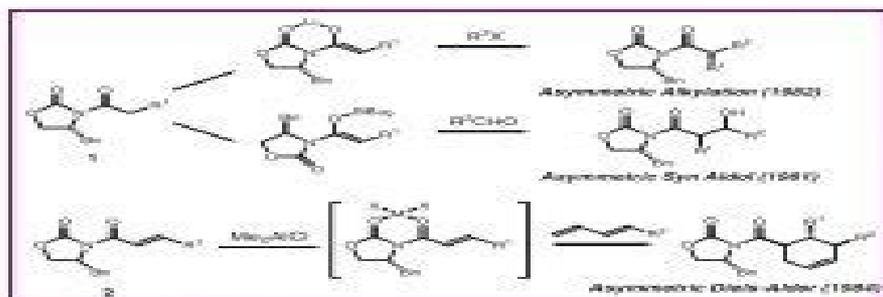
Résumé

Progrès en synthèse asymétrique : utilisation d'imides comme auxiliaires chiraux

Les oxazolidinones chirales et leur dérivés sont des auxiliaires efficaces en synthèse asymétrique. De nouvelles méthodologies ont été développées, notamment des alkylations de composés glycoliques et des réactions d'aldol utilisant une quantité catalytique de métal, produisant les diastéréoisomères anti. Quelques exemples récents et innovateurs d'utilisations de ce type d'auxiliaires en synthèse totale sont aussi abordés.

Mots-clés Key-words

**Auxiliaires chiraux, oxazolidinones, thiazolinethiones, synthèse totale, diastéréosélectivité.
Chiral auxiliaries, oxazolidinones, thiazolinethiones, total synthesis, diastereoselectivity.**



Scheme 1 - Initial reports of asymmetric induction from chiral imides.

The use of chiral *N*-acyloxazolidinone auxiliaries to control absolute stereoinduction has found wide application in a variety of reactions over the last two decades [1]. Despite extensive development by our group and complementary studies by others, new reactions continue to evolve from this useful family of chiral controllers. The most widely employed reactions of these ester surrogates are the asymmetric alkylation, aldol and Diels-Alder reactions (scheme 1). This review covers significant contributions to these areas of development during the last five-year period.

The majority of our work with chiral imides has employed the basic structural elements of oxazolidinone **1** with few exceptions over the last 20 years. Subsequent to our initial reports, many structural variants of **1** have appeared (figure 1). These modified imides have been developed to exhibit different cleavage reactivity or complimentary diastereoselectivity compared

to **1**. The most notable imide analog is the thiazolidine thione developed by Nagao and Fujita, then later used by Crimmins and our group [2]. This auxiliary, unlike many others that have been developed, reacts through different modes of metal binding and thus affords a useful complement to imide **1** (vide infra).

Stereoselective glycolate alkylation

The alkylation of lithium, sodium, and potassium enolates derived from *N*-acyloxazolidinones have proven useful for the preparation of many chiral building blocks. The reaction is generally limited to reactive alkylating agents such as allyl and benzyl halides. The Crimmins group has recently extended the alkylations reaction for use with glycolic acid equivalents such as **3** in the preparation of chiral substrates for a ring-closing metathesis approach to macrocyclic ethers from *Laurencia* Sp (scheme 2) [3].

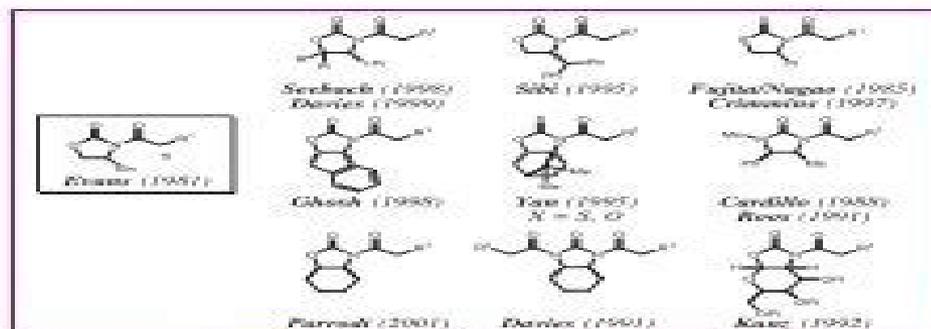


Figure 1 - Selected structural variants of chiral imide **1**.

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