## SYNLETT Spotlight 180

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## BINOL: A Versatile Chiral Reagent

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## Introduction

The aim of enantioselective synthesis or catalysis is to produce chiral products starting from achiral substrates by exploiting the presence of chiral reagents. The enantiomeric atropisomers of $1,1^{\prime}$-binaphthyl-2,2'-diol (BINOL) are the best-known representatives of axially chiral molecules and were first prepared as racemate in 1873 by von Richter. ${ }^{1}$ BINOL is used for both stoichiometric and catalytic asymmetric reactions. ${ }^{2}$ The chiral atropisomers $(R)-\mathbf{1}\left([\alpha]^{20}{ }_{\mathrm{D}}+35.5 \mathrm{THF}, c 1\right), \mathrm{mp} 205-211^{\circ} \mathrm{C}$ and $(S)-\mathbf{1}$ $\left([\alpha]^{20}{ }_{\mathrm{D}}-34.5\right.$, THF, $\left.c 1\right), \mathrm{mp} 205-211^{\circ} \mathrm{C}$ are stable at high temperature and allow numerous asymmetric reactions under various experimental conditions (Figure 1). ${ }^{3}$ BINOL-mediated asymmetric oxidation, reduction and $\mathrm{C}-\mathrm{C}$ bond-forming reactions are well-established reactions in organic synthesis. BINOL (1) can be easily prepared from 2-naphthol using Cu -amine complexes to give racemic BINOL which can be converted into $(R)$-BINOL $[(R)-\mathbf{1}]$ or $(S)$-BINOL $[(S)-1]$ by enzymatic resolution ${ }^{4}$ or via chemical resolution (Scheme 1). ${ }^{5}$


Figure 1


Scheme 1

## Abstracts

(A) The catalytic asymmetric reduction of different ketones with transient hypervalent trialkoxy silanes in the presence of a small amount of a chiral nucleophile such as BINOL (1) underwent addition to the carbonyl group, forming the corresponding silylprotected alcohols, which were cleaved during the work-up to give enantiomerically enriched alcohols. ${ }^{6}$

(B) Hosomi et al. reported an optically active lithium alkoxide which catalysed asymmetric reduction of imines with trimethoxysilanes affording the expected amines in moderate ee (up to $72 \%$ ). ${ }^{7}$


$63 \%$ yield, $59 \%$ ee
(C) Shibasaki et al. used lanthanum- or ytterbium-modified BINOL derivatives as catalysts in the asymmetric epoxidation of enones with tert-butyl hydroperoxide (TBHP). ${ }^{8}$

(D) Yamamoto et al. reported the first successful example of asymmetric induction which deals with a cyclisation in the presence of a BINOL-Al catalyst. Indeed, a catalyst prepared in situ from dimethyl zinc and optically pure $(R)-(-)$-BINOL promoted the cyclisation of 3-methylcitronellal to methylisopulegol as a single isomer with $90 \%$ ee. ${ }^{9}$

(E) Olsson et al. reported the Diels-Alder reaction between 'noncompatible' dienes and dienophiles by means of a temporary Al or Zr tethering. ${ }^{10}$

(F) Very recently, $\mathrm{Pu}, \mathrm{Yu}$ and coworkers reported the highly enantioselective reaction of an alkynoate with aromatic and $\alpha, \beta$-unsaturated aldehydes for the synthesis of optically active $\gamma$-hydroxy$\alpha, \beta$-acetylenic esters containing three adjacent and structurally very different functional groups which are very useful in the synthesis of highly functionalized organic molecules. ${ }^{11}$


## References

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