

Chiral Polyols as Catalysts of Asymmetric C-C Bond Formation Reactions

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The creation of a chain of intramolecular hydrogen bonded hydroxyl groups could be expected to facilitate the proton transfer, accompanying the C-C bond formation. According to this hypothesis we have synthesized the series of polyols shown in Figure 1 to investigate their catalytic activity in corresponding reactions.

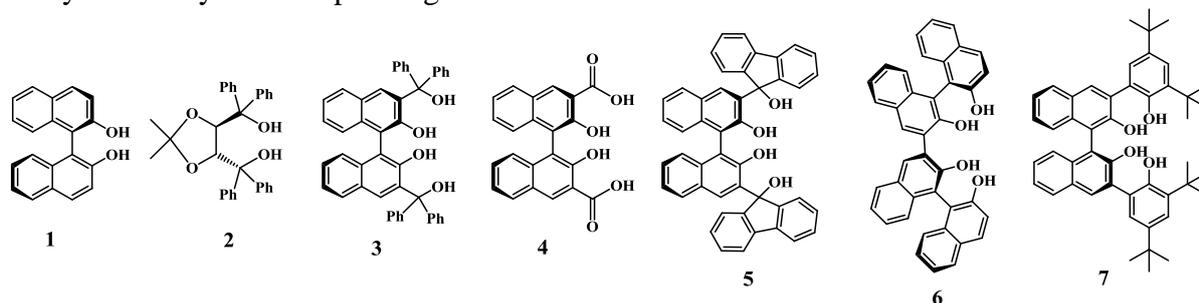


Figure 1. Series of synthesized polyols with a chain of intramolecular hydrogen bonded hydroxyl groups.

We have chosen Li, Na and K salts of (*S*)- or (*R*)-3,3'-bis[bis-(phenyl)hydroxymethyl]-2,2'-dihydroxy-dinaphthalene-1,1' (**3**) as catalysts of a model reaction of asymmetric Michael addition of malonic ester and other nucleophiles to cyclohex-2-enone.

Among other alcohols and phenols it was only BIMBOL that was an efficient catalyst of the reaction producing Michael adducts with 90% ee.

Other reactions tested with BIMBOL as a catalyst include PTC alkylations of amino acid precursors as shown in Fig. 2 and enantioselective epoxide ring opening with anilines (Fig. 3).

The asymmetric alkylation was conducted in CH₂Cl₂ in the presence of KOH and furnished different amino acids in high yield and reasonably high ee (up to 88%).

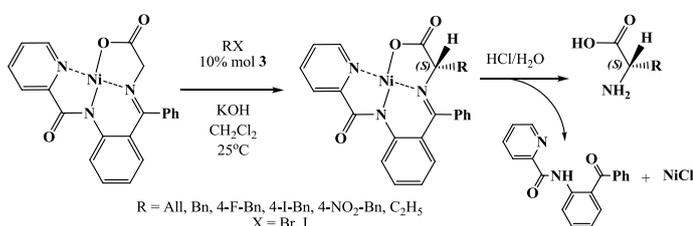


Figure 2. BIMBOL promoted asymmetric alkylation of a glycine

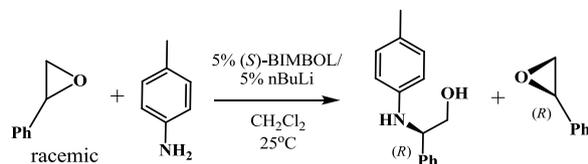


Figure 3. Styrene oxide ring opening catalyzed by mono-lithium salt of BIMBOL.

The ring opening of styrene oxide with anilines was almost not catalyzed by BIMBOL at room temperature. However, mono-lithium salt of BIMBOL showed significant catalytic activity. The reaction was stereoselective furnishing only one isomer. Kinetic resolution was observed and the asymmetric induction of the product reached 41% with 36% conversion.

The induction and catalytic activity of the system was greatly increased when Ti(OⁱPr)₄ was added to BIMBOL in a ratio 1:1. The forming catalyst was highly active even at a ratio of substrate/catalyst 1000/1. The ee of the final product varied, depending on the conditions, but reached 90% in some cases. We are going also to test polyols **5-7** hopefully to get better results.