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Use of Copper(II)/Diamine Catalysts in the Desymmetrisation of meso-Diols and Asymmetric Henry Reactions: Comparison of (-)-Sparteine and (+)-Sparteine Surrogates

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(-)-Sparteine versus (+)-Sparteine Surrogates in Copper(II)-Diamine-Catalyzed Reactions

$$\begin{array}{c} R^1 \longrightarrow OH \\ R^2 \longrightarrow OH \end{array} \xrightarrow{\begin{array}{c} Cu(\text{diamine}) Cl_2 \ (5 \text{ mol}\%) \\ DIPEA \ (2 \text{ equiv}) \\ \hline \\ BzCl \ (1 \text{ equiv}) \\ CH_2Cl_2, \ 0 \ ^{\circ}C, \ 2 \ h \\ \hline \\ 3 \ (1S,2R) \end{array} \xrightarrow{\begin{array}{c} R^1 \longrightarrow OH \\ R^2 \longrightarrow OH \\ \hline \\ 3 \ (1S,2R) \end{array}} \xrightarrow{\begin{array}{c} H \longrightarrow OH \\ A \ (1R,2S) \end{array}} \begin{array}{c} H \longrightarrow OH \\ \hline \\ 1 \ (-)\text{-sparteine} \end{array}$$

68% yield

Application in the asymmetric Henry reaction, preparation of a chiral morpholine:

70% yield

$$\begin{array}{c} \text{Cu}(\text{diamine 2}) \text{ Cl}_2 \\ \text{(20 mol\%)} \\ \text{Et}_3 \text{N (3 mol\%)} \\ \text{MeNO}_2 \text{ (2 equiv)} \\ \text{MeOH, 0 °C, 12 h} \\ \hline \\ \textbf{t-BuOK, t-AmOH} \\ \textbf{r.t., 3 h} \\ \text{Ph} \\ \text{(S)} \\ \text{$$

35% yield

Significance: O'Brien and co-workers present an evaluation of copper(II)-diamine complexes comprising (-)-sparteine, (+)-sparteine surrogates, and Alexakis diamine in the desymmetrization of meso-diols and asymmetric Henry reaction. One of the nitro alcohol products was utilized in a concise synthesis of a chiral morpholine.

Comment: In order to compare the reactivity in asymmetric induction, the copper(II)-diamine catalysts, containing diamine 1 and 2, were investigated in the enantioselective monobenzoylation of meso-1,2-diols and in the asymmetric Henry reaction. In both reactions the products were obtained in good to high enantioselectivities with the opposite sense of induction depending on the used diamine. As expected, (+)-sparteine surrogate 2 generated the antipodal products of those obtained using (-)-sparteine.

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Category

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