Česká společnost chemická, pobočka Brno

Vás zve na přednášku, která se koná v místnosti 132, 1.NP, budova A11, Kamenice 5, Přírodovědecká fakulty Masarykovy univerzity, Brno

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Axially Chiral Bipyridine N,N'-Dioxides as Catalysts in Enantioselective Reactions

N,N'-dioxides with axially chiral bipyridine framework belong to the group of strong Lewis bases that can activate silane and used in several enantioselective reactions such as allylation, epoxide ring opening, conjugated addition, etc. giving rise to products with high asymmetric induction.

We have developed a simple and efficient method for preparation of new symmetrically and unasymmetrically substituted axially chiral bis(tetrahydroisoquinolyl) N,N-dioxides **1** and **2**, based on $CpCo(CO)_2$ catalyzed cyclotrimerization of 1,7,9,15-hexadecatetrayne with appropriate nitriles under microwave irradiation followed by oxidation (Scheme 1).^{1,2}.

The prepared chiral bis(tetrahydroisoquinolyl) N,N'-dioxides **1** and **2** were tested as catalysts in enantioselective allylation of variously substituted aromatic aldehydes, α,β —unsaturated aldehydes, and dienals with allyltrichlorosilane to provide chiral homoallyl alcohols (Scheme 2). Some of the prepared homoallyl alcohols were used as intermediates for syntheses of several natural compounds, e.g. (S)-goniothalamin. Both symmetrically and unsymmetrically substituted chiral bis(tetrahydroisoquinolyl) N,N'-dioxides exhibited high catalytic activity as well as high asymmetric induction (up to 99%). The course of the reaction and asymmetric induction strongly depends on the solvent used and could be related to different reaction mechanisms in each group of solvents. The prepared catalysts have also been preliminarily tested for epoxide ring opening with SiCl₄.

Scheme 1

$$\frac{R-CN}{CpCo(CO)_2} \xrightarrow{N} \frac{Oxid.}{N} \xrightarrow{N} O \longrightarrow{N} O \xrightarrow{N} O \longrightarrow{N} O \longrightarrow{N}$$

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