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Catalytic asymmetric synthesis using rotaxanes

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

Introduction

Rotaxanes (from Latin rota 'wheel' and axis 'hub') are a branch of mechanically contiguous molecular machines which have been formed from a macrocycle wrapped around a linear axle [1]. The first reports of synthetic rotaxanes were introduced in the 1960s. The 2016 Nobel Prize in chemistry was awarded to Jean-Pierre Sauvage, Fraser Stoddart and Ben Feringa for their research on the designing and synthesis of rotaxanes [2]. Incidentally, rotaxanes are also known as chiral systems, especially if the two sides of the macrocycle ring are different. Overally, the synthetic methods of rotaxanes are covering capping, snapping, clipping, slipping and active metal templating (**Fig. 1**).

The capping way is the method in which the "linear axle" is kept in the "macrocycle" by non-covalent interactions. Then, it is converted into rotaxane by the reaction of the end of the linear axle guest with large groups and prevents dissociation [3]. The snapping method is similar to the capping method, except that the snapping method involves the pre-assembly of semi-rotaxane and covalent bonding with a stopper. In the slipping method, the macrocycle and the dumbbell-shaped part are made completely and separately from each other [4]. In the clipping method, the partial macrocycle is attached to a complete dumbbell-shaped molecule and the partial macrocycle then undergoes a ring closing reaction around the dumbbell-shaped molecule [5]. Finally, the active metal template method is another synthetic route for the preparation of rotaxanes in which a substrate was applied as a template by critical role in enhancing the strong covalent bond formation [6]. In recent years, rotaxanes have been widely used in various fields. In addition to fantastic and unique chemical properties of rotaxane-based systems, these materials were used as substrates as well as catalysts [7].

These materials as an emerging type of chemical backbones have been considered in many scientific and interdisciplinary studies such as biological active compounds [8,9], chemical sensors [10],

electrochemical compounds [11], molecular electronics [12], host-guest chemistry [13], drug delivery [14] and catalytic systems [15] and have developing trend. Rotaxanes have received increased consideration as scaffolds for the expansion of new catalysts and there are immense reports of their catalytic applications in organic synthesis. These catalytic systems have a key role in the impressive and efficient conversion of readily available chemical scaffolds into beneficial functional molecules [16].

For instance, asymmetric catalysis [17], coupling reactions [18], hydrogenation reactions [19], oxidation reactions [20], cyclopropanation [21], electrocatalytic H_2O_2 evolution [22] and photocatalytic applications [23] are only few examples of the catalytic applications of rotaxanes. In this disquisition, we have reviewed the recent developments in the catalytic applications of interlocked rotaxanes which are superior to their non-interlocked counterparts in terms of reaction rates and stereoselectivities.

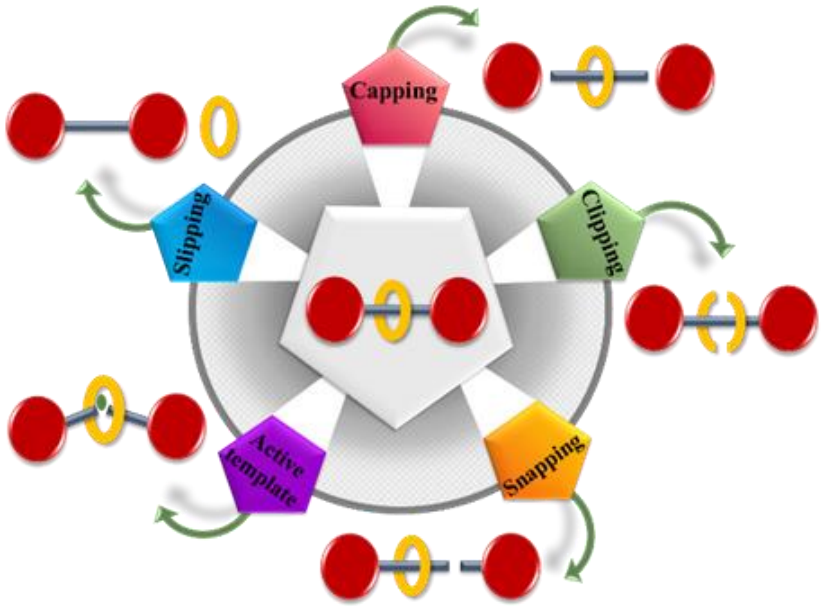
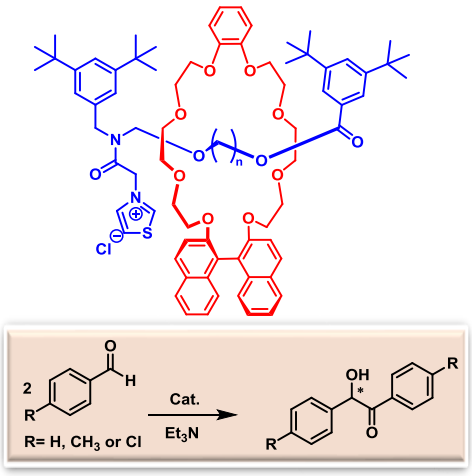


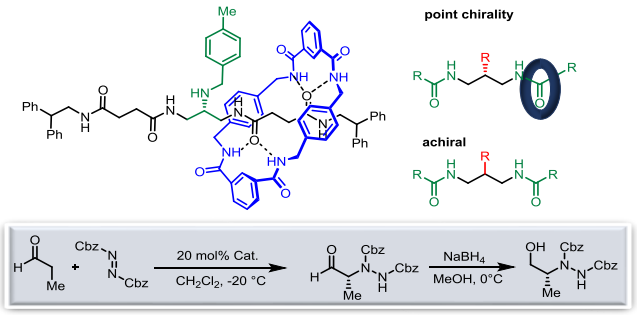
Fig. 1. Rotaxane synthetic methods.

Abstracts

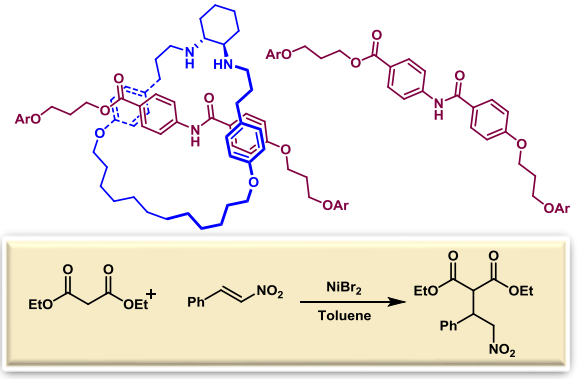
(A) The first example of chiral rotaxane-based catalysts was reported by Takata and his group in 2004. This rotaxane has a thiazolium part and a binaphthyl chiral part in its structure. This chiral moiety performed the condensation of benzoin with high enantioselectivity. It goes without saying that the role of thiazolium unit is undeniable. The asymmetric condensation of benzoin catalyzed by chiral rotaxanes in the presence of triethylamine can be achieved in high yields (up to 90%). Rotaxane catalyst showed better enantioselectivity than its non-interlocked thread peer [24].



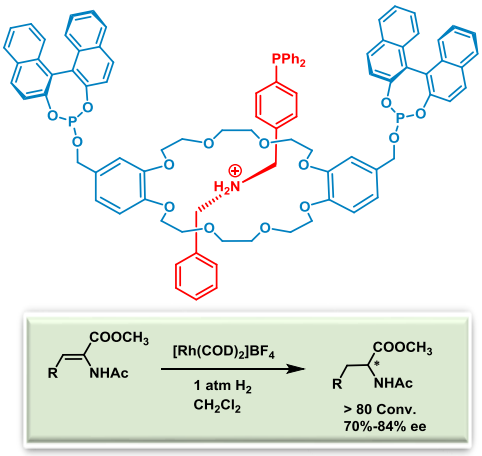
(B) In 2016, Leigh and co-workers have been used the point mechanical chirality in rotaxanes, which applied it in asymmetric catalysis. In this example, 4-tolyamine moiety prevents the movement of the macrocycle between the two succinamide localities (prochiral center), which leads to the loss of symmetry and the creation of point chirality. The mentioned catalyst was applied in enantioselective enamine and Michael addition reactions [25].



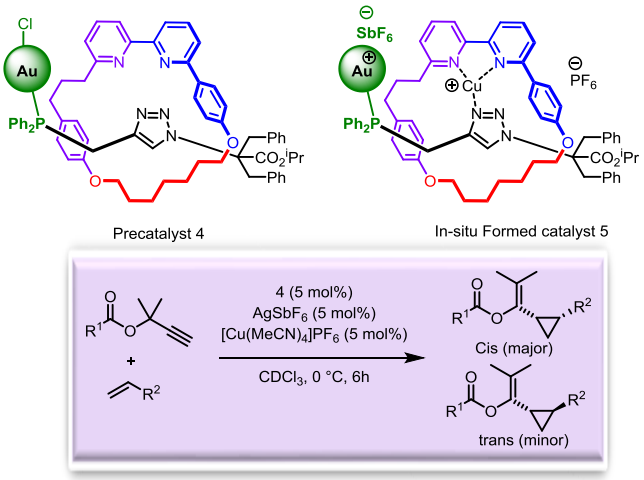
(C) In 2015, Leigh and co-workers synthesized a model of active metal rotaxane containing a C_2-symmetric trans-cyclohexanediamine macrocycle which was used for enantioselective nickel catalysis. The enantioselective rotaxane revealed better selectivity compared to the similar acyclic ligand. Moreover, the reaction time was significantly slower than previous related reports [26].



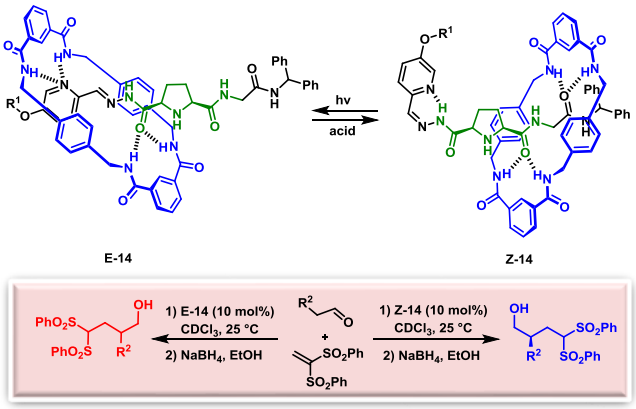
(D) Li et al. reported a pseudotaxane complex with chiral phosphorus ligands in 2008. This ligand was prepared *via* complexation of dibenzylammonium salt and dibenzo macrocycle-24-crown-8 for Rh-catalyzed asymmetric hydrogenation. The phosphite ligand has moderate to high enantioselectivity in most cases under optimal reaction conditions. The catalyst containing a double supramolecular ligand has excellent catalytic activity for all substrates and higher enantioselectivity than a single ligand [27].



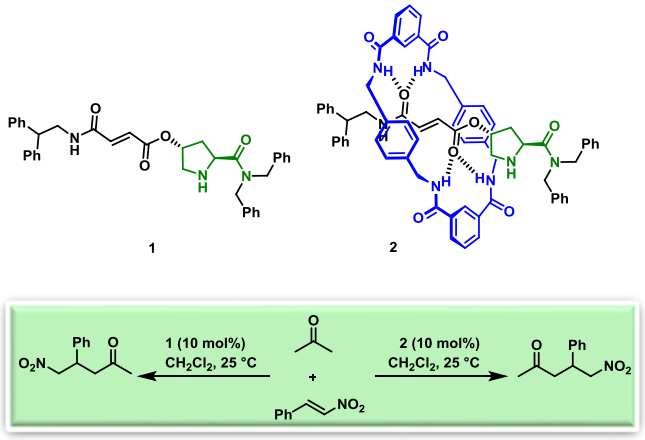
(E) Goldup's research group have been used mechanical planar chirality, which enables the mechanical bonding of only one element of the system. This rotaxane system was constructed in three separate parts. Complex 5 was tested as a catalyst in the asymmetric Ohe-Uemura cyclopropanation with gold (I). The interlocking components allowed the reaction to proceed diastereoselectively and enantioselectively, giving enantioenriched cis cyclopropanes. This work confirms that interlocked molecules which have mechanical linkage can be successfully used as catalysts in asymmetric catalysis [28].



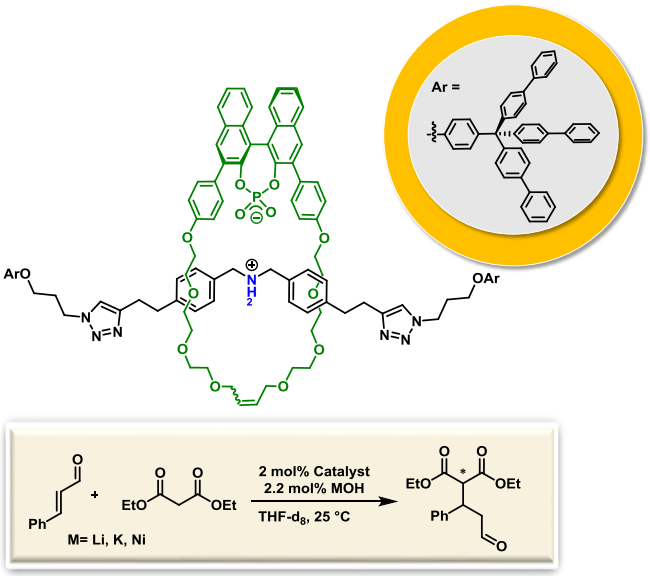
(F) In 2019, Marcel and co-workers designed a rotaxane-based catalyst with a polyamide macrocycle entwined firstly on the pyridyl-acylhydrazone (E-14). Light irradiation can lead to a change in the position of the macrocycle. This reversible change creates two active catalytic states. This attractive functionality was used to develop an enamine-mediated conjugate addition of aldehydes to vinyldisulfone. Each isomer of the catalyst controls the enantioselectivity in opposite directions and depending on the position of the macrocycle along the strand, gives rise to both possible enantioenriched adducts. This new strategy effectively changes the environment around the catalyst site, sensing changes the enantioselectivity [29].



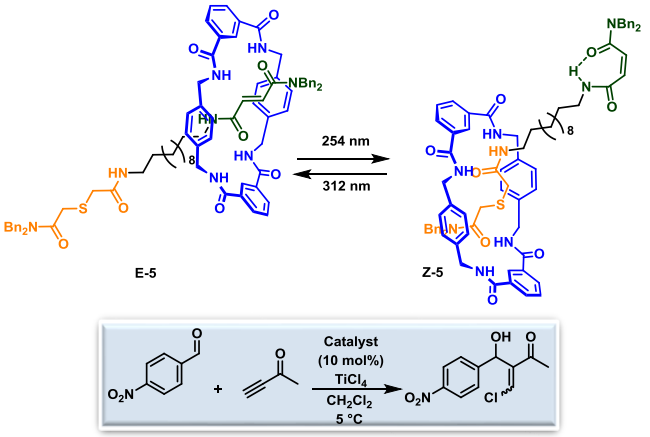
(G) In 2019, the catalytic addition of enantiocyclic ketones to *β*-nitrostyrene by using chiral proline amide-containing molecule 1 and its corresponding polyamide-based rotaxane 2 were reported by Martinez-Cuezva. They have realized that the interaction between acetone and nitrostyrene catalyzed by molecule 1 produced the Michael adduct (S), while the same reaction with rotaxane 2 produced the (R) adduct with a similar degree of selectivity. Interestingly, both molecule 1 and rotaxane exhibit similar reaction rates and do not observe catalyst deactivation due to the presence of bulky macrocycles [30].



(H) In 2019, Noel and co-workers designed a unique and applicable rotaxane which consisted of an amine-based section and a chiral 1,1'-binaphthyl-phosphoric acid macrocycle. This catalytic methodology exhibits extraordinary reactivity and selectivity in comparison with related counterparts. Due to the addition of diethyl malonate to cinnamaldehyde, a chiral Michael-based compound was achieved. The cooperativity of two functional groups in asymmetric catalysis is enhanced by mechanical coupling, thereby leading to increased reaction rates and stereoselectivity [31].



(I) Brenna and co-workers have designed a photoswitchable rotaxane system. This system contains an amide-based macrocycle which can switch between the fumaramide and amide positions of thiodiglycol yarn. In the (E) isomer, the macrocycle prefers to bind to the fumaramide position and occupy it, so that the sulfide can act as a nucleophile. As a result, 60% diastereoselectivity (de) is produced for the catalytic reaction. The (Z) isomer, is obtained reversibly upon light irradiation. In the comparative study, the titanium-mediated Baylis-Hillman reaction between aldehydes and alkynes in the absence of described catalyst, yields the target product without diastereoselectivity [32].



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