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Sidearm Modified Bisoxazoline Ligands and Their Applications†

Lijia Wang,[a] Jian Zhou,[b] and Yong Tang*[,a]

What is the most favorite and original chemistry developed in your research group?
Sidearm strategy for the design and modification of organometallic catalysts.

How do you get into this specific field? Could you please share some experiences with our readers?
Initailly, intrigued by the beauty of C_3-symmetry, we try to develop C_3-symmetric trisoxazolines. However, we met a big problem to access it. As the key point to control the catalyst behaviors is cooperative effects of ligand and metal, we envisioned that the installation of a coordination group as a sidearm around the electronic property- and micro environment-sensitive area of the active site might tune the selectivity and activity. Thus, a third oxazoline the sidearm is fixed at the bridge carbon of traditional bisoxazoline ligands and novel pseudo-C_3-symmetric trisoxazoline (TOX) is developed. Later on, different groups are introduced as the sidearms and various sidearmed bisoxazolines (SaBOX) are developed. Metal catalysts based on TOX and SaBOX prove highly efficient for more than 20 asymmetric transformations, such as Friedel-Crafts reaction, Kinugasa reaction, Nazarov reaction, Cannizzaro reaction and cyclopropanation. Importantly, compared with the parent BOX ligand, these catalysts exhibit higher efficiency, higher diastereo- and enantio-selectivity, together with better impurity-tolerance and stability in these transformations. This strategy has also been extended successfull to the ylide chemistry and the catalyst modification (design) of olefin polymerization. In fact, failure is the prelude to success.

What is the most important personality for scentific research?
Be diligent, active, and creative, with perseverance, flexible and stay true to your original intention.

How do you keep balance between research and family?
As for a scientist, understanding and support from my family will be my strongest backing. As I can't spend too much time staying with my family, what I can do is to care more about them at some important moment when they need me.

What's your hobbies?
Swimming, walking and reading.

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Research Interests:
Asymmetric catalysis, ylide chemistry, polymer chemistry especially on polyethylenes

ABSTRACT Developing novel and highly efficient chiral ligands is the eternal theme in chiral catalysis research, since none of ligands or catalysts is universal for all the reactions. We are aiming at searching for a facile and effective strategy in developing new chiral ligands that could be employed in a broad range of asymmetric reactions. By introducing additional (sidearm) groups to a classic chiral ligand, both the electron nature and steric environment of the catalyst could be adjusted, and thus the reactivity, selectivity and functional group tolerance of a catalyst could be modulated. Based on this strategy, a variety of sidearm modified bisoxazoline ligands have been designed and developed, including TOX, SaBOX, diSaBOX and Wing-BOX. The account presents a brief introduction on their discovery and representative applications.

KEYWORDS chiral ligands, enantioselective, bisoxazoline, asymmetric catalysis, sidearm

Contents

1. Introduction

Since the 20th century, in the technological revolution of the modern chemical industry, the development and application of new high-efficiency catalytic systems have played a vital role. For example, the evolution of cobalt and rhodium catalysts in hydroformylation of petrochemicals,[1] the development of Ziegler-Natta catalyst in olefin polymerization,[2] and the application of chiral rhodium and ruthenium complexes catalyzed asymmetric hydrogenation in the chiral pharmaceutical industry,[3] make great impacts on both the chemical industry and people's life. For complex catalysts, the key to catalyst development is the design of the

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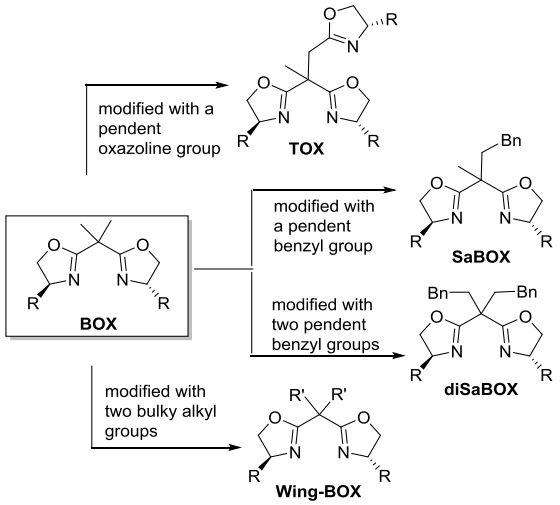
† Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

ligand. By adjusting the steric hindrance and electronic properties of the ligand, the catalytic behavior of the catalyst can be directly affected, thereby effecting the reactivity and selectivity of the reaction. Especially in asymmetric catalysis, the structure of chiral ligands usually plays a crucial role in the stereoselectivity of the reaction. After decades of vigorous development in the field of asymmetric catalysis, hundreds of excellent chiral ligands have been synthesized. Many privileged chiral ligands and catalysts have emerged, for instance, the BINAP, DuPhos, Josiphos, spiro ligands, BOX, PHOX, Salen complexes, BINOL, TADDOL, *N,N'*-dioxide ligands, cinchona alkaloids and proline.[4] Since none of ligands or catalysts is universal for all the reactions, developing novel chiral ligands is still an eternal theme in chiral catalysis research.

We conceived that by introducing an additional (sidearm) group to a classic chiral ligand, it can either coordinate to the metal center of the catalyst or serve as a sterically hindered group, which in turn will change the electron nature and steric environment around the active center, thus modulating the reactivity, selectivity and functional group tolerance of a catalyst. Therefore, the sidearm strategy could be employed as a simple but effective approach for the modulation of a given reaction.[5] Based on this concept, we choose chiral bisoxazoline (BOX) ligands as an object to modify, since chiral BOX ligands generally prepared from amino acid derivatives are of interest to chemists due to their highly enantioinductive ability, abundant availability of less expensive chiral material and the ease to prepare and modify.[6] During the past ten years, we have developed a series of new chiral BOX ligands assembled with various sidearm groups, including TOX, SaBOX, diSaBOX and so on (Scheme 1). These chiral ligands have been employed to a range of different asymmetric catalytic reactions, and have behaved better than the parent BOX ligands on both reaction efficiency and stereoselectivity. In this accounts, we briefly review our journey toward the design and synthesis of chiral sidearm modified BOX ligands, and their applications in a number of enantioselective reactions.

Scheme 1 Sidearm modification of bisoxazoline ligands



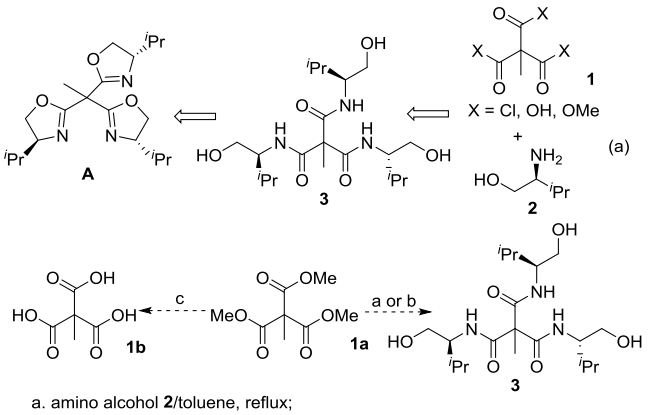
2. Sidearm Modified Bisoxazoline Ligands and Their Applications

2.1. TOX ligands

2.1.1. Initial studies on developing TOX ligands. Chiral BOX ligands are usually C_2 symmetric, and they could coordinate with various metal salts, such as copper, nickel, cobalt, iron. It is generally believed that introducing axial symmetry in ligands design is sometimes important, because the axial symmetry can reduce the number of possible transition states in an enantioselective reaction and therefore increase the catalytic efficiency. In a view of topology, C_3-symmetric ligands might lead to less transition state diastereomers than C_2-symmetric ligands in an octahedral catalytic environment.[7] Accordingly, we originally attempted to synthesize a C_3-symmetric chiral trisoxazoline ligand **A**.

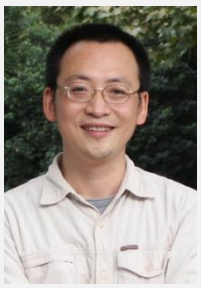
Initially, we planned a route for the synthesis of C_3-symmetric ligand **A**. As shown in Scheme 2, by route a, ligand **A** was designed to be prepared directly from the condensation of **3**, which might be furnished from the amidation of a tricarboxylic acid derivatives **1** and chiral amino alcohol **2**. A tricarboxylic ester **1a** was prepared according to the references. However, direct amidation of **1** with amino alcohol **2** could not work even at a harsh reaction condition, probably due to the disadvantage of the steric hindrance of the starting material. Thus, we tried to hydrolyze the triester **1a** to tricarboxylic acid **1b**, which could be further transformed to the corresponding acyl chloride. Unfortunately, no desired product was observed but the triester was decomposed to the decarboxylic by-product.

Scheme 2 Synthesis of the C_3-symmetric chiral trisoxazoline **A**



a. amino alcohol **2**/toluene, reflux;
b. amino alcohol **2**, solvent-free, 120 °C
c. LiOH, H_2O/THF

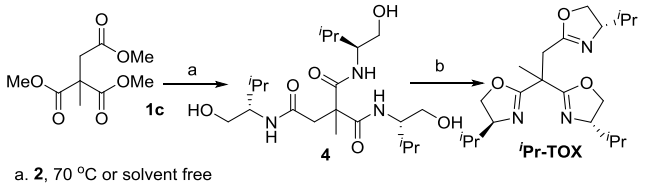
Lijia Wang received her BSc (2004) and PhD (2009) from Sichuan University under the supervision of Prof. Xiaoming Feng. She was a postdoctoral fellow with Prof. Keiji Maruoka at Kyoto University from 2009 to 2011. Then she joined Shanghai Institute of Organic Chemistry, where she was appointed as an associate professor in Prof. Yong Tang's group. Her research interest is in the area of developing new methodologies in asymmetric catalysis, and their applications in total synthesis of natural products.



Jian Zhou received his BSc (1997) from Sichuan Normal University. After spending two years in the personnel departments of Sichuan College of Education, he continued to study chemistry in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. He received his PhD degree in 2004 under the supervision of Prof. Yong Tang. He was a postdoctoral fellow with Prof. Shu Kobayashi at the University of Tokyo from 2004 to 2005. He worked with Prof. Benjamin List as a postdoctoral fellow in Max-Planck-Institut from 2005 to 2008. Then he joined East China Nomal University, where he was appointed as a professor. His research interest is in the area of asymmetric catalysis.

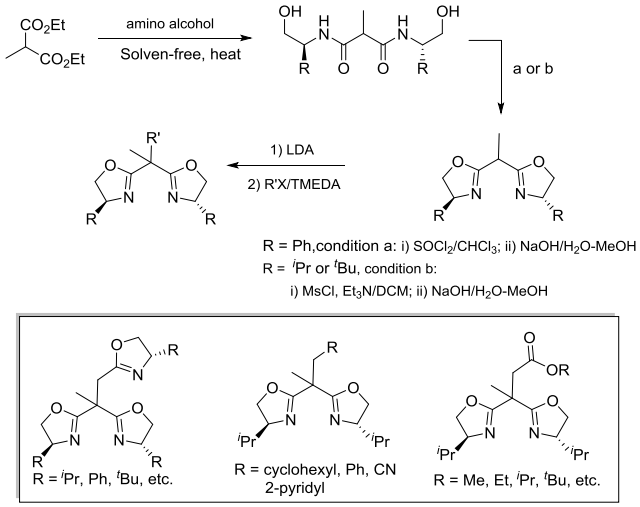
Considering the tricarboxylic ester **1a** is highly congested and the possible carbanion [$^-C(CH_3)(CO_2Me)_2$] is a better leaving group than the methoxy group, we think of extending a carbon atom to the tricarboxylic ester in order to solve the problem, which is envisioned to have a less effect on the space and electronic properties of the catalytic center. Thus, triester **1c** was used as the starting material for the synthesis of a pseudo-C_3-symmetric chiral trisoxazoline (**TOX**) (Scheme 3).

Scheme 3 Synthesis of the pseudo-C_3-symmetric chiral trisoxazoline



Later on, we improved the synthetic protocol by combining the parent bisoxazoline backbone with diverse functional groups (sidearm), such as oxazoline, aryl group, alkyl group, and so on (Scheme 4). This strategy provides rapid and practical construction of a bisoxazoline-based ligand library.[8]

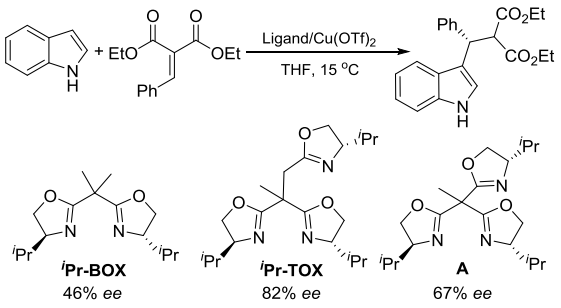
Scheme 4 Synthesis of a bisoxazoline-based ligand library



2.1.2. TOX ligands in asymmetric catalysis. Previous studies on the enantioselective Friedel-Crafts reaction of indoles with alkylidene manolates suggest that typical chiral BOX ligands, for example, ^{t}Bu-BOX and Ph-BOX, could only lead to moderate levels of *ee* values.[9] By employing **^{i}Pr-TOX** as ligand, we were delighted to find that the enantioselectivity was greatly enhanced (up to 93% *ee* was obtained).[10] The catalyst system is insensitive to air atmosphere and moisture. 75% yield with 90% *ee* could be obtained even in the presence of 50 equivalents of water as additives.[11] Notably, during our study on the **^{i}Pr-TOX** ligand, Gade and co-workers reported the synthesis of C_3-symmetric chiral trisoxazoline **A**.[12] In comparison with the **^{i}Pr-TOX** ligand, ligand **A** gave a lower *ee* value in the asymmetric Friedel-Crafts reaction with THF as solvent at 15 °C (Scheme 5).[8]

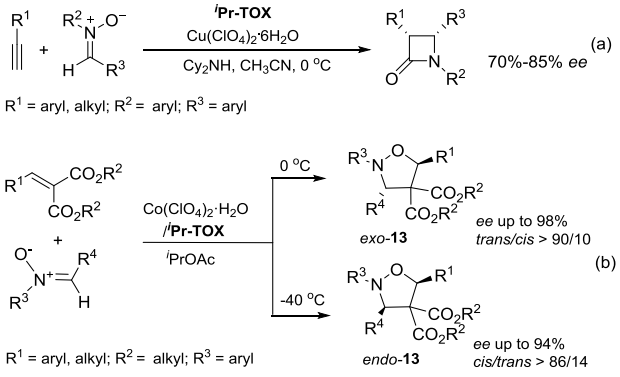
In 2003, we developed a chiral **^{i}Pr-TOX**/$Cu(ClO_4)_2{\cdot}6H_2O$ catalyzed Kinugasa reaction of terminal acetylenes with nitrones, affording *cis*-disubstituted β-lactams in good yield with up to 97/3 dr and 70%—85% *ee* (Scheme 6a).[13a] In this reaction, **^{i}Pr-TOX** once again showed obvious superiority to the corresponding

Scheme 5 Applications of **^{i}Pr-TOX** in Friedel-Crafts reaction



^{i}Pr-BOX ligand. It not only allowed the first use of water- and air-toleratent Cu(II) to develop Kinagusa reaction, but also showed much higher reactivity and enantioselectivity (19 h, 60% yield, 80% *ee vs*. 6 d, 33% yield, 36% *ee*).[13b] This is a vivid demonstration of sidearm approach to modulate the properties of a chiral ligand in modulating the reactivity and enantioselectivity of a catalytic enantioselective reaction. The chiral **^{i}Pr-TOX** ligand was also employed in a cobalt catalyzed highly enantioselective 1,3-dipolar cycloaddition of nitrones to alkylidene malonates (Scheme 6b).[14] When the reaction was carried out at 0 °C, the isoxazolidines were obtained with both high enantioselectivity and high exo selectivity. Meanwhile, when the temperature was lowered from 0 to –40 °C, the same cycloaddition afforded endo isomers as the major products with good to high enantioselectivity.

Scheme 6 Other applications of **^{i}Pr-TOX**



Subsequently, a library of chiral TOX ligands were developed, including various chiral skeletons, such as **^{i}Pr-TOX**, **In-TOX**, **^{t}Bu-TOX** and **cy-TOX** (Figure 1). These chiral ligands are successfully applied to a broad range of asymmetric catalytic reactions.

The **In-TOX** ligand was firstly reported by us in 2010, and then in 2012, the **In-TOX**/$Ni(ClO_4)_2$ complex was used as catalyst in the enantioselective ring-opening reactions and kinetic resolution of donor-acceptor (D-A) cyclopropanes with amines (Scheme 7a).[15] In this study, the ligand sidearm played an important role in achieving both the high yields and the excellent enantioselectivities. The single-crystal structure of a TOX/Ni complex was determined by X-ray diffraction, and an asymmetric induction model was proposed based on the catalyst structure. This method provides an effective access to the synthesis of chiral γ-substituted γ-amino acid derivatives. Recently, we developed an **In-TOX**/$Ni(ClO_4)_2$ catalyzed asymmetric annulation of 3-aminophenols with β,γ-unsaturated α-ketoesters, leading to a concise protocol for a variety of 7-aminated chromans in high yields with excellent diastereoselectivities and enantioselectivities under mild conditions (Scheme 7b).[16] The catalyst system was highly efficient that

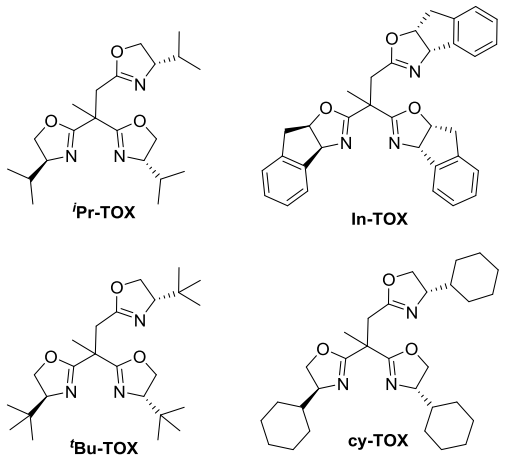
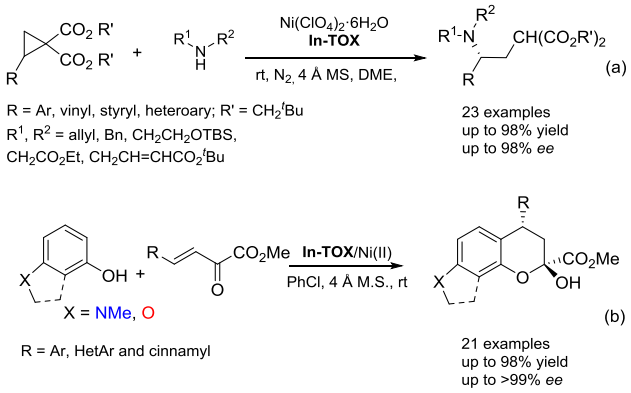


Figure 1 Typical chiral TOX ligands.

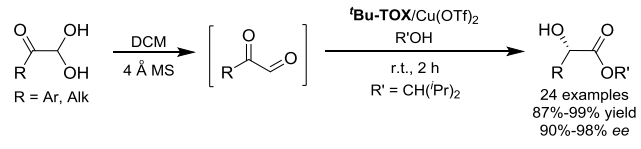
Scheme 7 Applications of **In-TOX**



the reaction could be readily enlarged to gram scale and applied to the synthesis of two potential anticancer agents 7-aminated 4-arylchromans.

Chiral **^{t}Bu-TOX** was structurally more congested than other TOX ligands. It was employed in a copper catalyzed enantioselective intramolecular Cannizzaro reaction of aryl and alkyl glyoxals with alcohols (Scheme 8).[17] Comparing with the classic ^{t}Bu-BOX ligand, the **^{t}Bu-TOX** ligand could promote the reaction much more efficiently in terms of both the reactivity and enantioselectivity.

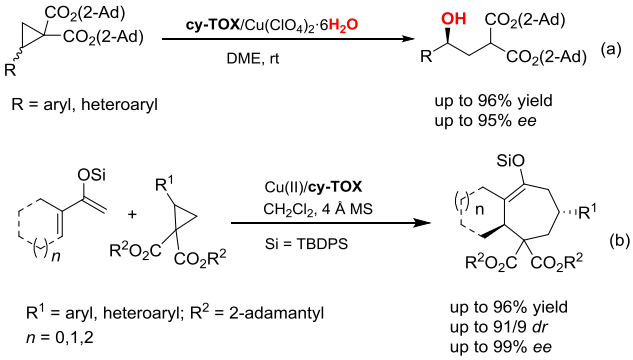
Scheme 8 Application of **^{t}Bu-TOX**



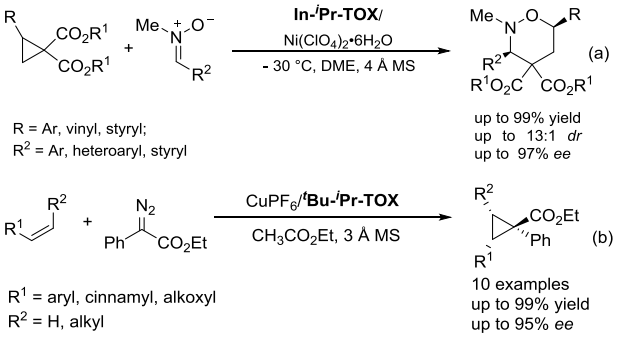
Recently, a new type of TOX ligand containing cyclohexyl groups at the chiral backbones, **cy-TOX**, has been designed and synthesized by our group. It has been successfully used in the asymmetric ring-opening reactions of D-A cyclopropanes with water as nucleophile (Scheme 9a),[18] as well as the [4+3] annulations of D-A cyclopropanes with dienes (Scheme 9b).[19]

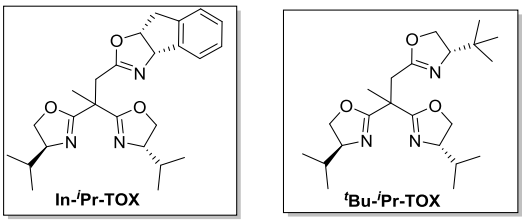
On the other hand, TOX ligands, which bear an oxazoline sidearm diverged from the parent BOX skeleton, could also be very efficient. For example, **In-^{i}Pr-TOX**/Ni(II) promoted a highly enantioselective and diastereoselective cycloaddition of D-A cyclopropanes with nitrones (Scheme 10a).[20] The same ligand coordinated with $Cu(OTf)_2$ was employed in an asymmetric catalytic intramolecular Friedel-Crafts alkylation reaction of indoles;[21] **^{t}Bu-^{i}Pr-TOX** was proved to be the best ligand in the enantioselective cyclopropanation of alkenes with aryldiazoacetates (Scheme 10b);[22] **^{t}Bu-In-TOX** was used in the enantioselective Kinugasa reaction.[23]

Scheme 9 Applications of **cy-TOX**



Scheme 10 Applications of other **TOX** ligands





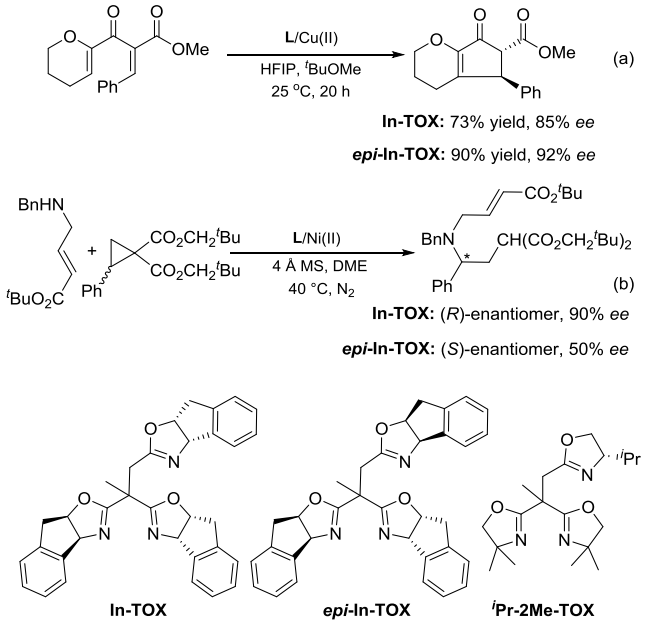
Furthermore, the stereogenic oxazoline sidearm in the TOX ligand played an important role in the enantioselective reactions. In an asymmetric Nazarov reaction, when **In-TOX** was used as the chiral ligand, 85% *ee* was obtained. When ***epi*-In-TOX** was employed, the *ee* value was increased to 92% (Scheme 11a).[24] Furthermore, in the ring-opening reaction of D-A cyclopropanes with amine, the enantiogenic structure of the sidearm group is crucial for the enantioselectivity, in which **In-TOX** is favorable for the (*R*)-product, while ***epi*-In-TOX** prefers to give the (*S*) one (Scheme 11b).[15] Inspired by these results, we conceived that it would be possible to develop a new type of trisoxazoline ligands, which are in the absence of chiral motif on the parent BOX skeleton and contain a chiral backbone on the sidearm. To our delight, the **^{i}Pr-2Me-TOX** ligand promoted the amine nucleophilic ring opening reaction of 1,1-cyclopropane diesters smoothly, affording a broad range of γ-amino acid derivatives in high yield with moderate to good enantioselectivity (Scheme 11c).[25]

2.2. SaBOX ligands

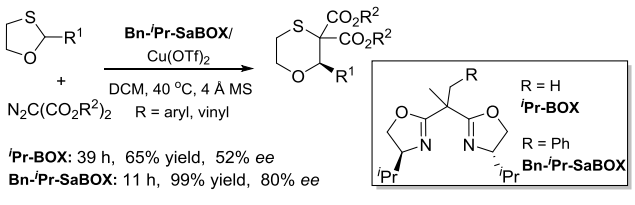
Chiral SaBOX ligand based on a parent ^{i}Pr-BOX motif was firstly applied to Friedels-Crafts reaction, and later, the asymmetric [1,2]-Stevens rearrangement of sulfur ylides *in-situ* generated

from the decomposition of diazomalonates with copper(I) (Scheme 12).[26] Obvious acceleration effect of the sidearm modified **Bn-^{i}Pr-SaBOX** ligand was found in this reaction. Compared with the ^{i}Pr-BOX ligand, **Bn-^{i}Pr-SaBOX** promoted the [1,2]-Stevens rearrangement reaction much faster and resulted in a much higher yield and a better enantioslectivity.

Scheme 11 The effects of the stereogenic oxazoline sidearm group on the control of the enantioselectivity



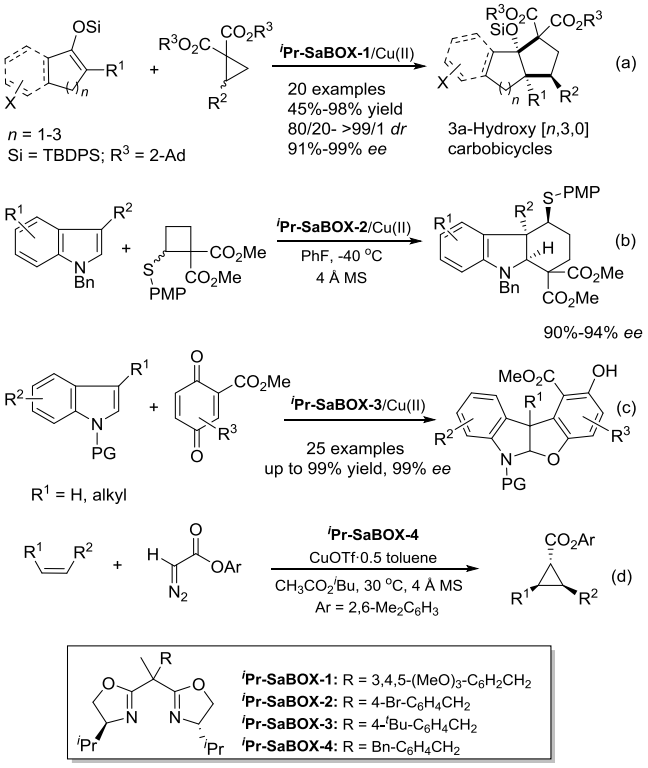
Scheme 12 Application of Bn-^{i}Pr-SaBOX



Other chiral ^{i}Pr-SaBOX ligands are developed and successfully applied to a diverse range of asymmetric reactions. For example, **^{i}Pr-SaBOX-1** was used in an enantioselective [3+2] annulation of cyclic enol silyl ethers with D-A cyclopropanes, leading to various 3a-hydroxy [*n*.3.0]carbobicycles in high yield with excellent enantioselectivity (Scheme 13a).[27] In a **^{i}Pr-SaBOX-2** promoted catalytic [4+2] annulation reaction of indole derivatives and D-A cyclobutanes, excellent enantioselectivity was obtained (Scheme 13b);[28] the **^{i}Pr-SaBOX-3** ligand showed its best advantage in the enantioselective [3+2] annulation of indoles with quinones (Scheme 13c);[29] when **^{i}Pr-SaBOX-4** was employed in a copper carbene involed enantioselective cyclopropanation of 1,2-disubstituted alkenes, the *trans*-cyclopropane was obtained with > 99 : 1 *dr* and 89% *ee* (Scheme 13d).[30]

In addition, chiral SaBOX ligands modified from other parent BOX motif, such as Ph-BOX, In-Box, diPh-BOX and cy-BOX, were designed and synthesized by the same protocol from different

Scheme 13 Application of **^{i}Pr-SaBOX 1—4** ligands



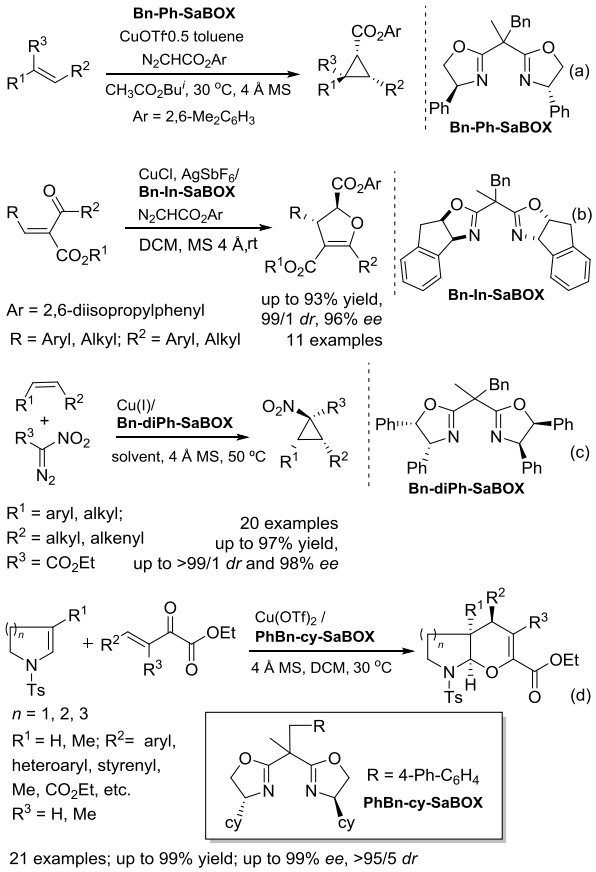
chiral amino acid derivatives. When ligand **Bn-Ph-SaBOX** was used, the copper catalyzed *cis*-cyclopropanations of internal olefins were realized with > 99 : 1 *dr* and 96% *ee* (Scheme 14a).[30] **Bn-In-SaBOX**/Cu(II) served as a highly efficient catalyst in the asymmetric [4+1] cycloadditions of α-benzylidene-β-ketoester with diazo compound (Scheme 14b).[31] In a **Bn-diPh-SaBOX**/copper catalyzed enantioselective cyclopropanation of 1,2-disubstituted olefins with α-nitrodiazo acetates, a number of nitrocyclopropans were obtained in up to 97% yields with up to > 99/1 *dr* and up to 98% *ee*, which provides an efficient access to the synthesis of optical active cyclopropane α-amino acids and unnatural α-amino acid derivatives (Scheme 14c).[32] Moreover, **PhBn-diPh-SaBOX** gives the best results in the copper(II)-catalyzed diastereo- and enantioselective synthesis of bicyclic *N*,*O*-acetals (Scheme 14d).[33]

2.3. diSaBOX ligands

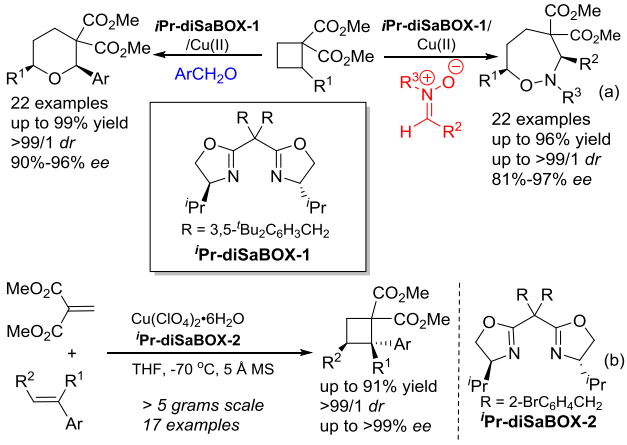
We have developed several effective chiral diSaBOX ligands bearing many different chiral BOX backbones, including ^{i}Pr-BOX, Ph-BOX, In-BOX and cy-BOX. In the diastereo- and enantioselective [4+*n*] annulations of D-A cyclobutanes with nitrones (*n*＝3) and aldehyde (*n*＝2), **^{i}Pr-diSaBOX-1** could give the best results among a variety of chiral BOX, TOX and SaBOX ligands (Scheme 15a).[34] **^{i}Pr-diSaBOX-2** proved to be highly efficient in an enantioselective construction of cyclobutanes, which provided a new and concise approach to the total synthesis of (+)-piperarborenine B (Scheme 15b).[35]

Meanwhlie, a cagelike chiral catalyst **Ph-diSaBOX**/Cu(I) promoted the enantioselective cyclopropanation of multisubstituted olefins with phenyliodonium ylide malonate in up to 99% yield with up to > 99% *ee* (Scheme 16a).[36] In a copper-catalyzed asymmetric cyclopentannulation of indoles with D-A cyclopropanes, the **In-diSaBOX** ligand could give the best results (Scheme 16b).[37a] Recently, **cy-diSaBOX** was successfully applied to the catalytic enantioselective construction of tetracyclic indolines containing four continuous stereocenters (Scheme 16c).[38]

Scheme 14 Applications of other **SaBOX** ligands



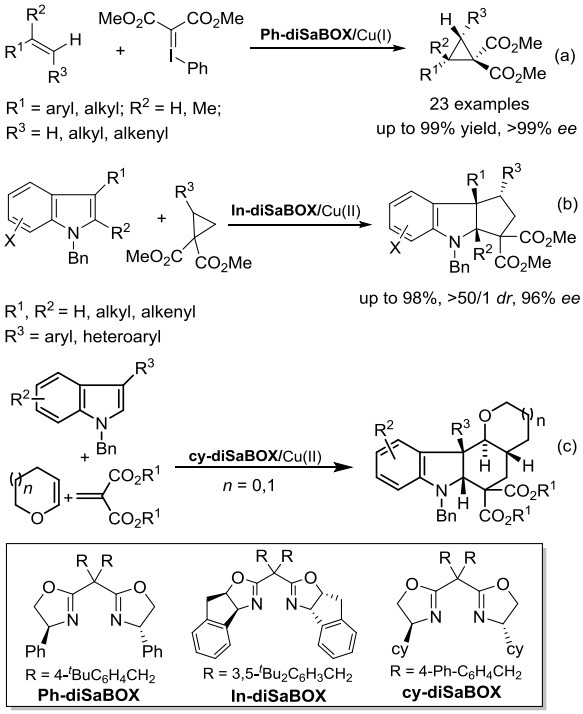
Scheme 15 Application of *i*Pr-diSaBOX 1-2 ligands



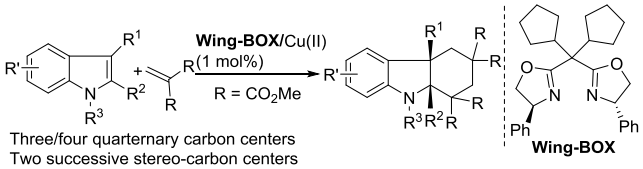
2.4. Wing-BOX ligands

According to pervious reports by Davies[39] and Denmark,[40] in a chiral BOX ligand catalyzed asymmetric reaction, the bridge angle of the two oxazolines sometimes could influence the enantioselectivity. Our recent studies found a Thorpe-Ingold effect that both the lengths of the coordination bond and the steric hindrance of the catalytic reactive center could be tuned by choosing different substituents on the bridge carbon of the BOX ligands. Thus, a new type of **Wing-BOX**/Cu(II) catalyst was designed, and applied to the asymmetric cyclization reaction of methylenemalonate with indoles. With this newly modified Wing-BOX ligand, a concise method for the enantioselective furnishing of hexahydrocarbazoles bearing three quaternary carbon centers was realized in up to 99% yield with > 99/1 dr and up to >99% *ee* (Scheme 17).[41] In a Thorpe-Ingold effect consideration, an enantioselective cyclopropanation of trisubstituted olefins was promoted by employing a diisoproply substituted **Wing-BOX** ligand.[42]

Scheme 16 Application of other **diSaBOX** ligands



Scheme 17 Application of **Wing-BOX** ligand



3. Conclusions and Outlook

By simply assembling versatile sidearm groups, a library of modified chiral bisoxazoline ligands have been designed and developed, including TOX, SaBOX, diSaBOX and Wing-BOX. These chiral ligands can coordinate with a variety of different metal salts, such as copper(I), copper(II), nickel(II) and cobalt(II), and have been successfully applied to a number of asymmetric catalytic reactions, including enantioselective Friedel-Crafts reaction, Kinugasa reaction, intramolecular Cannizzaro reaction, Nazarov reaction, [1,2]-Stevens rearrangement, hetero-Diels-Alder reaction, 1,3-dipolar cycloaddition, tandem cyclization reactions, enantioselective cyclopropanation and cyclobutanation, ring-opening/annulation reactions of D-A cyclopropane and cyclobutane. Some of the products are easily transformed to synthetically useful molecules and natural products. The sidearm groups play a critical role in promoting both the reactivity and the stereoselectivity of these reactions. They could serve as coordinating groups, sterically kinetic hindered groups or even directing groups in the enantioselective catalysis. The sidearm modifying strategy offers a facile and practical protocol to various chiral ligands, which provides exciting prospects in applying those ligands to a broad type

of reactions in future asymmetric catalysis.

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