Asymmetric Cyclopropanation

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Highly Diastereo- and Enantioselective Cyclopropanation of 1,2-Disubstituted Alkenes**

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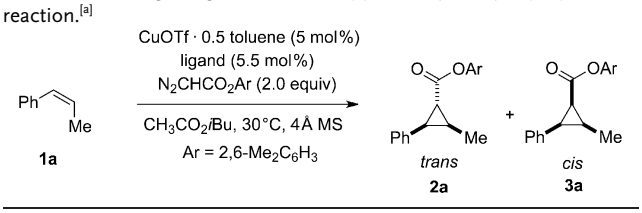
Since Nozaki et al. reported the first enantioselective synthesis of cyclopropanes, a reaction that involved copper-catalyzed transfer of a carbene moiety from diazo compounds to alkenes,[1] much effort has been devoted to the area of transition-metal-catalyzed asymmetric cyclopropanation reactions because it is a straightforward method for accessing optically active cyclopropanes.[2–7] However, there are only a few examples where 1,2-disubstituted alkenes have been transformed through a transition-metal-catalyzed asymmetric cyclopropanation reaction with high levels of diastereo- and enantioselectivity;[8] these reactions usually involve cyclic alkenes[8c] and trisubstituted alkenes.[8a,e] In 1991, Masamune et al. reported a double-asymmetric-induction approach in which *cis*-β-methyl styrene was transformed using a Cu^{I}/BOX-catalyzed cyclopropanation reaction involving L-menthol-derived diazoacetate to give product in 92% *ee* and 76% *de*.[8a] High enantioselectivity was achieved by Ito and Katsuki when they used chiral bipyridine ligands in the cyclopropanation of *trans*-β-methyl styrene, although the diastereoselectivity was low (*trans*/*cis* 40:60).[8b] Recently, Katsuki and co-workers reported the use of an aryliridium/salen catalyst, which led to remarkably high levels of enantio- and diastereoselectivity (favoring the *cis* product) in the cyclopropanation of terminal and cyclic alkenes. However, when *cis*-β-methyl styrene was used as a substrate, a relatively low yield of product (29%) was obtained and for *trans*-β-methyl-styrene only a trace amount of cyclopropanation product was obtained.[8c] The unsatisfactory results obtained in the cases of 1,2-disubstituted alkenes can be mainly ascribed to the high sensitivity of metallocarbenes to the steric hindrance and geometry of the alkene.[8] Therefore, a cyclopropanation catalyst that is efficient and applicable to the highly stereoselective cyclopropanation of both *cis*- and *trans*-1,2-disubstituted alkenes, especially simple *trans* alkenes, is still in high demand. Herein, we report that the use of bis(oxazoline) (BOX) ligands that contain C_2-symmetry-breaking pendant groups in the copper-catalyzed cyclopropanation of both *cis*- and *trans*-1,2-disubstituted alkenes can lead to high levels of diastereo- and enantioselectivity.

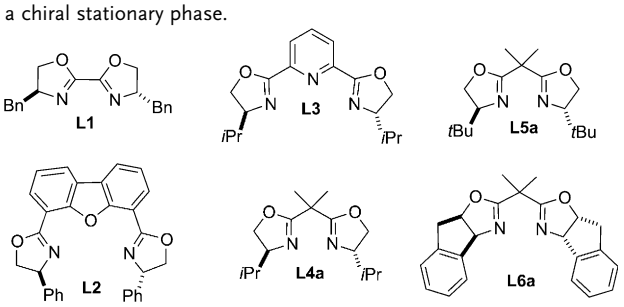
We commenced our study by screening copper salts in combination with several BOX ligands in the cyclopropanation reaction of *cis*-β-methyl styrene (Table 1). When using 2,6-dimethylphenyl diazoacetate as the carbene source,[9] all ligands tested exhibited the required activity, except Ph-DBFOX (**L2**; Table 1, entry 2); only low levels of enantioselectivity were obtained with **L1** and **L3** (Table 1, entries 1 and 3). Because *i*Pr-BOX (**L4a**) gave the most promising enantioselectivity (89% *ee*; Table 1, entry 4), we prepared and tested ligands **L5a** and **L6a**, which have different substituents on the C4 atom. Unfortunately, the levels of enantioselectivity that were obtained using these ligands were not an improvement on that obtained using **L4a** and were thus impractical (Table 1, entries 5 and 6).

Table 1: Screening of ligands for the copper-catalyzed cyclopropanation reaction.[a]



Entry	Ligand	Yield [%][b]	*Trans*/*cis*[c]	ee_{trans} [%][d]
1	**L1**	25	75/25	7
2	**L2**	0	–	–
3	**L3**	45	86/14	7
4	**L4a**	61	95/5	89
5	**L5a**	53	97/3	87
6	**L6a**	50	94/6	80

[a] **1a** (0.5 mmol), CH_3CO_2iBu (3.5 mL). [b] Yield of isolated product. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC using a chiral stationary phase.



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It is well known that the origin of enantioselectivity in these reactions lies in the interaction between the ester group of the carbene and the C4 substituent of the BOX ligand.[10] Recently, García, Salvatella, and co-workers reported that the copper atom of the carbene complex has a distorted trigonal arrangement of ligands and that the metal–carbon bond of the complex deviates from the symmetry axis of the catalyst ligand.[11] During their elegant studies on asymmetric catalysis, Gade and co-workers observed that the pendant groups of BOX–metal complexes bend toward and cover the metal center;[12] a similar orientation of pendant groups is evident in the X-ray structure of the **L6d**/$CuBr_2$ complex (Figure 1);[13]

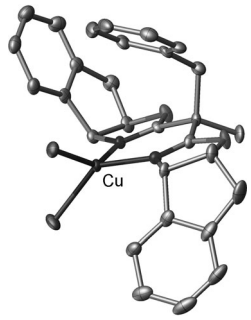


Figure 1. Crystal structure of **L6d**/$CuBr_2$. Thermal ellipsoids are shown at 30% probability and hydrogen atoms are omitted for clarity.[13]

such an orientation can tune both the steric interaction between the groups on the BOX and the carbene moieties and the level of deviation of the metal–carbene bond from the symmetry axis of the complex, thus influencing the stereoselectivity. Therefore, it should be possible to further improve the stereoselectivity by using a BOX ligand containing a suitable pendant group.[14]

With this concept in mind, a number of BOX ligands with different pendant groups were synthesized (Figure 2). The replacement of one the methyl groups of **L5a** with an aryl group, that is, *t*Bu-BOX **L5b**, led to a slight increase in enantioselectivity, although the yield of product was lower (Table 2, entry 1 versus Table 1, entry 5). The replacement of one of the methyl groups of **L6a** with an oxazoline group led to a 9% decrease in enantioselectivity (Table 1, entry 6 versus Table 2, entry 3). The use of ligand **L6d**, which contains

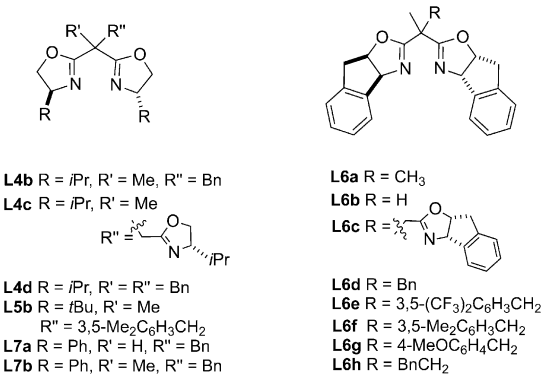
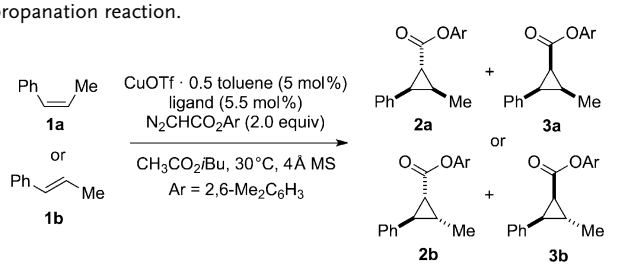


Figure 2. BOX ligands containing pendant groups.

Table 2: The effect of ligand on the Cu-catalyzed asymmetric cyclopropanation reaction.



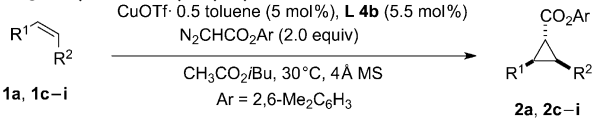
Entry[a]	Alkene	Ligand	Yield [%][b]	*Trans*/*cis*[c]	ee_{trans} [%][d]
1	**1a**	**L5b**	52	96/4	93
2	**1a**	**L6b**	75	82/18	47
3	**1a**	**L6c**	65	88/12	71
4	**1a**	**L6d**	81	94/6	89
5	**1a**	**L6e**	39	89/11	89
6	**1a**	**L6f**	74	93/7	89
7	**1a**	**L6g**	76	94/6	89
8	**1a**	**L6h**	78	94/6	84
9	**1a**	**L4b**	84	96/4	92
10	**1a**	**L4c**	43	92/8	84
11	**1a**	**L7b**	53	93/7	89
12	**1a**	**L4d**	43	95/5	83
13	**1b**	**L4b**	43	>99/1	89
14	**1b**	**L4c**	68	>99/1	85
15	**1b**	**L7a**	58	>99/1	60
16	**1b**	**L7b**	89	>99/1	96

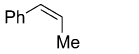
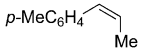
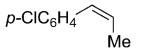
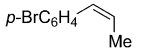
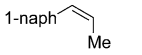
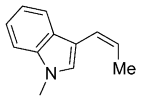
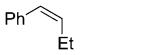
[a] **1a** or **1b** (0.5 mmol), CH_3CO_2iBu (3.5 mL). [b] Yield of isolated product. [c] Determined by ^1H NMR analysis. [d] Determined by HPLC using a chiral stationary phase.

a pendant benzyl group, led to higher enantioselectivity (89% *ee*; Table 2, entry 4), although further variation of the aryl group led to no improvement in the enantioselectivity (Table 2, entries 4–8). *i*Pr-BOX **L4b**, which contains a pendant benzyl group, was the best ligand for this reaction (Table 1, entry 4 versus Table 2, entry 9); the use of this ligand gave the desired cyclopropane **2a** in 84% yield and with 92% *ee*, together with high *trans* selectivity (*trans*/*cis* 96:4). Ligand **L4d**, which contains two identical pendant groups, gave lower selectivity (Table 2, entry 12). Further studies showed that these modified BOX ligands also worked extraordinarily well when applied to the cyclopropanation of *trans*-β-methyl styrene (Table 2, entries 13–16). For example, when **L4b** was employed, the desired cyclopropane **2b** was obtained in 43% yield with high diastereoselectivity (*trans*/*cis* greater than 99:1), the major diastereomer having an *ee* value of 89% (Table 2, entry 13). When ligand **L7b** was used, the *ee* value of the product was further increased to 96% and the diastereoselectivity remained very high (Table 2, entry 16).

With the optimum ligands for the cyclopropanation reaction of both *cis*- and *trans*-β-methyl styrenes in hand, we then explored the scope of the reaction. The cyclopropanation of a series of *cis*-β-methyl styrenes proceeded smoothly regardless of their electronic nature (Table 3, entries 1–4). The desired cyclopropanes were obtained in high yields (72–84%) with high levels of diastereoselectivity (*trans*/*cis* from 95:5 to 97:3) and enantioselectivity (92–94% *ee*). A dihydronaphthalene- and an indole-derived alkene were good substrates for this reaction (Table 3,

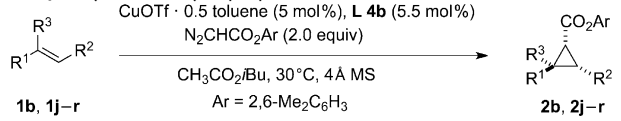
Table 3: Asymmetric cyclopropanation of *Z* alkenes.[a]

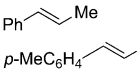
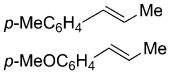
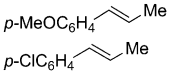
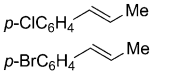
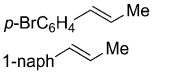
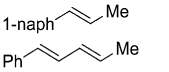
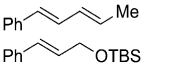
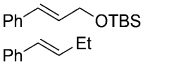
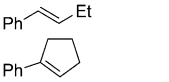


Entry	Alkene		Yield [%][b]	*Trans*/*cis*[c]	ee_{trans} [%][d]
1	**1a**:		84	96/4	92
2	**1c**:		78	96/4	93
3	**1d**:		72	95/5	94
4	**1e**:		72	95/5	93
5	**1f**:		60	97/3	89
6	**1g**:		95	97/3	89
7	**1h**:		60	97/3	86
8[e]	**1i**:		66	93/7	86

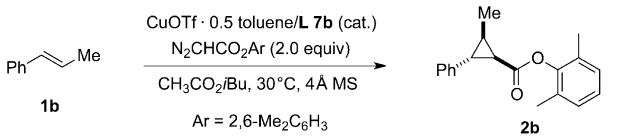
[a] Alkene (0.5 mmol), CH_3CO_2iBu (3.5 mL). [b] Yield of isolated product. [c] Determined by ^1H NMR analysis. [d] Determined by HPLC using a chiral stationary phase. [e] 4 equivalents of diazo acetate were used.

Table 4: Asymmetric cyclopropanation of *E* alkenes.[a]



Entry	Alkene		Yield [%][b]	*Trans*/*cis*[c]	ee_{trans} [%][d]
1	**1b**:		89	>99/1	96
2	**1j**:		99	>99/1	96
3	**1k**:		96	>99/1	94
4	**1l**:		96	>99/1	97
5[e]	**1m**:		73	>99/1	96
6	**1n**:		60	>99/1	96
7	**1o**:		97	93/7	96
8	**1p**:		64	>99/1	98
9	**1q**:		84	>99/1	97
10	**1r**:		82	>99/1	96

[a] Alkene (0.5 mmol), CH_3CO_2iBu (3.5 mL). [b] Yield of isolated product. [c] Determined by ^1H NMR analysis. [d] Determined by HPLC using a chiral stationary phase. [e] The absolute configuration was determined to be (1*R*,2*R*,3*R*) by X-ray crystallography.[14]



Scheme 1. Reactions with reduced catalyst loading.

entries 6 and 7). Although a relatively low yield was obtained in the reaction of the more sterically demanding *cis*-β-ethyl styrene, high diastereoselectivity (93:7) and enantioselectivity (86% *ee*) were observed (Table 3, entry 8).

The cyclopropanation reaction of 1,2-*trans*-disubstituted alkenes had broad substrate scope and high levels of stereoselectivity (Table 4). Using **L7b**/CuOTf as the catalyst, various *trans* β-methyl styrene derivatives bearing electron-donating and electron-withdrawing substituents on the phenyl ring, underwent cyclopropanation with perfect levels of diastereoselectivity (>99:1) and high levels of enantioselectivity (94–97% *ee*; Table 4, entries 1–5). 1-Naphthyl and 1-cinnamyl alkene were also suitable substrates and were transformed into the corresponding cyclopropanes with high levels of *trans* selectivity and enantioselectivity (Table 4, entries 6–7). Notably, under the optimized reaction conditions, more hindered *trans* alkenes, such as cinnamyl-alcohol derivative **1p** and β-ethyl styrene **1q**, can also be converted into the desired cyclopropanes with high levels of stereoselectivity (Table 4, entries 8 and 9), and a Sommelet–Hauser rearrangement product was not observed in the reaction of **1p**. Moreover, the reaction of trisubstituted alkene **1r** also proceeded well, affording fused bicyclic product **2r** in 82% yield with greater than 99:1 *trans*/*cis* and 96% *ee* (Table 4, entry 10).

Considering the high efficiency of the **L7b**/CuOTf catalyzed cyclopropanation of *trans* alkenes, a scaled-up reaction (50 mmol) was performed. In the event, high yields and high levels of enantioselectivity were obtained when 0.5 mol% of catalyst was used (Scheme 1). The cyclopropanation of *trans*-β-methyl styrene also proceeded well even with only 0.05 mol% catalyst loading, giving the desired propane **2b** in 44% yield with 98% *ee*. To our knowledge, 0.05 mol% is the lowest catalyst loading used in a copper-catalyzed cyclopropanation reaction.

In summary, an efficient BOX/Cu^I-catalyzed cyclopropanation reaction has been designed and developed. *Cis*- and *trans*-1,2-substituted alkenes can be converted into the corresponding trisubstituted cyclopropanes with high levels of diastereo- and enantioselectivity (>99:1 *trans*/*cis* and up to 98% *ee*). The effect of the pendant group of BOX ligands was investigated, thus leading to the discovery of the BOX ligand **L4b** and **L7b**, the copper complexes of which were the best catalysts. This reaction features high catalytic efficiency and excellent stereoselectivity, especially for *trans* alkenes, the generality and high diastereoselectivity of which are unprecedented. Further investigations of this catalytic reaction are underway.

Experimental Section

A typical procedure using the reaction that gives the product **2a** as an example: a mixture of CuOTf·0.5 $PhCH_3$ (0.025 mmol), **L4b** (0.0275 mmol), and activated 4 Å MS (300 mg) in CH_3CO_2iBu (1 mL) was stirred at 30°C for 1 h under N_2 atmosphere. **1a** (0.5 mmol) in CH_3CO_2iBu (0.5 mL) were added, followed by the diazo acetate (1.0 mmol) in CH_3CO_2iBu (0.5 mL) which was added

dropwise using a syringe pump over 8 h. After the reaction was complete, the mixture was filtered through a thin layer of silica gel, eluting with CH_2Cl_2, and the filtrate was concentrated. The residue was purified by column chromatography over silica gel using CH_2Cl_2/petroleum ether 6:1 as eluent to afford **2a** (118 mg, 84% yield).

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