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A New Type of Chiral Cyclic sulfinamide-Olefin Ligands for Rhodium-Catalyzed Asymmetric Addition**

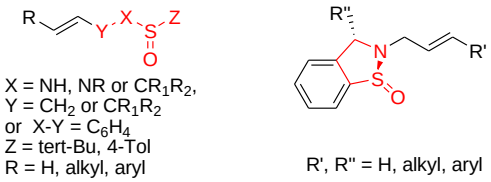
Quan Wen, Li Zhang, and Jing Xiong, Qingle Zeng*

Abstract: A new type of chiral cyclic sulfinamide-olefin ligands N-allylic 2,3-dihydro-1,2-benzoisothiazole 1-oxides with 2,3-dihydro-1,2-benzoisothiazole 1-oxide as unique chiral skeleton is developed for highly enantioselective rhodium-catalyzed asymmetric 1,4-additions of α,β-unsaturated cyclic carbonyl compounds and 1,2-addition of benzil. Both enantiomers with 99%ee of chiral cyclic sulfinamide-olefin ligands could be easily prepared from inexpensive and commercially available starting materials and directly used in asymmetric catalysis, and thus both enantiomers of the addition products could be obtained in high yields (up to 98%) and excellent enantioselectivities (up to 98%ee).

Chiral compounds exhibit more and more extensive applications in pharmaceuticals, agricultural chemicals and materials. Transition metal-catalyzed asymmetric syntheses with chiral ligands are one of the most efficient approaches to prepare chiral compounds.[1] Chiral ligands with appropriate chiral skeletons are the key factor to achieve high enantioselectivity for asymmetric reactions. Therefore, in addition to the extensively investigated phosphorus-based chiral ligands,[2] to explore novel chiral ligands with other kinds of coordination atoms and/or functional groups is of great interest in organic and organometallic chemistry.[3]

Among them, chiral ligands, such as chiral sulfoxides,[4] chiral sulfoxide-phosphines,[5] chiral dienes,[6] P/N-olefins[7] are becoming the focus of asymmetric catalysis.

Most recently, a series of chiral sulfinamide/sulfoxide-based olefin ligands are developed in Knochel,[8] Xu,[9] Du,[10] Liao,[11] Wan,[12] and Chen[13] groups. All of the reported ligands hold an open chain sulfinyl group (Figure 1). Therefore it occurred to us that whether the activity and enantioselectivity of catalytic reaction would be maintained or improved if rigid chiral cyclic sulfinamides was introduced into the ligands (Figure 1).

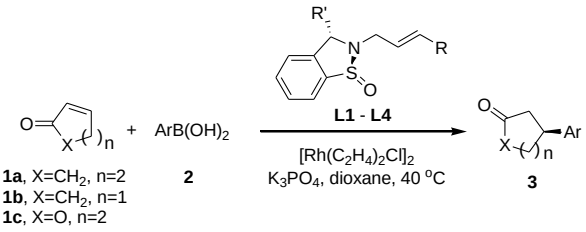


sulfinamide/sulfoxide-based olefin cyclic sulfinamide-olefin

Figure 1. The general formula of chiral sulfinamide/sulfoxide-based olefin ligands and our designed chiral cyclic sulfinamide-olefin ligands.

During our research in chiral sulfur chemistry,[14] we noticed unsubstituted chiral cyclic sulfinamide, namely, 2,3-dihydro-1,2-benzoisothiazole 1-oxide, was firstly reported by Fensterbank group,[15] which is readily synthesized with 94%ee via intramolecular radical cyclization. Although only 94%ee enantiomeric purity of 2,3-dihydro-1,2-benzoisothiazole 1-oxide is not high enough to be used as chiral ligand source, we thought that a modified procedure or an additional recrystallization may improve its enantiomer purity. Later Rodríguez-Fernández's group further developed the synthetic method of 3-substiuted chiral cyclic sulfinamides with 98%de,[16] which offers more chances to modify the chiral structural motif.

To the best of our knowledge, chiral cyclic sulfinamide 2,3-dihydro-1,2-benzoisothiazole 1-oxide are not used as chiral ligand skeleton in catalytic asymmetric transformation. Herein we describe our discovery of chiral N-allylic 2,3-dihydro-1,2-benzoisothiazole 1-oxides, especially N-cinnamyl 2,3-dihydro-1,2-benzoisothiazole 1-oxide, as efficient chiral ligands used in highly enantioselective rhodium-catalyzed asymmetric 1,4-addition reaction of arylboronic acids to α,β-unsaturated carbonyl compounds (Scheme 1).



Scheme 1. Rhodium-catalyzed asymmetric 1,4-addition with chiral N-allylic 2,3-dihydro-1,2-benzoisothiazole 1-oxides

We started our research by preparing the unsubstituted chiral cyclic sulfinamide (S)-2,3-dihydro-1,2-benzoisothiazole 1-oxide (Fig. 2). Fortunately, modification on the base of Fensterbank's procedure[15] by using toluene in place of benzene, increasing reaction temperature to 110 °C, and prolonging injection time of a toluene solution of AIBN and Bn_3SnH, afforded the cyclic sulfinamide (S)-2,3-dihydro-1,2-benzoisothiazole 1-oxide with extremely high ee value up to 99%ee, which was directly used in synthesis of chiral ligands. And then chiral 3-ethyl and 3-phenyl 2,3-dihydro-1,2-benzoisothiazole 1-oxides were prepared

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according to Rodríguez-Fernández's procedure,[16] which are reported to have >98%dr diastereomer purity.

Once chiral cyclic sulfinamides were prepared, chiral cyclic sulfinamide-olefin ligands were readily synthesized via simple S_N2 nucleophilic substitution of allylic halides and chiral cyclic sulfinamide in the presence of the base sodium hydride. Luckily, chirality of N-cinnamyl-2,3-dihydro-1,2-benzoisothiazole 1-oxide (**L1**) was well kept and no any racemization occurred during the basic reaction conditions, and thus chiral ligand **L1** had 99%ee.

The absolute configurations were established by single-crystal X-ray diffraction analysis of (S)-N-cinnamyl 2,3-dihydro-1,2-benzoisothiazole 1-oxide (**L1**) (Figure 2), whose crystal structure data has been deposited at the Cambridge Crystallographic Data Centre with a CCDC deposition number of CCDC 1501739. The single crystal X-ray diffraction analysis confirmed that the chiral configuration was completely inverted at the sulfur atom during the intramolecular homolytic substitution, which is conformed to Fensterbank's[15] and Rodríguez-Fernández's results.[16] From the crystal diagram, we can imagine that the two aromatic rings will be like two chiral fences to produce an excellent chiral surrounding when it coordinates with rhodium or other appropriate center metal to form a complex. Unfortunately, attempts to obtain single crystals of the rhodium complex of **L1** failed.

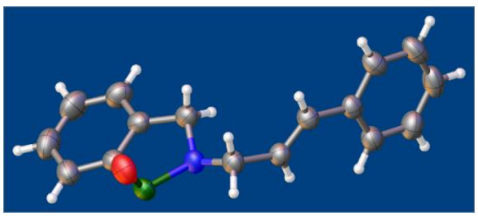


Figure 2. X-ray crystal structures of (S)-N-cinnamyl 2,3-dihydro-1,2-benzoisothiazole 1-oxide **(L1**)

With chiral cyclic sulfinamide-olefin ligands in hand, we chose the Rh-catalyzed 1,4-addition of phenylboronic acid to cyclohexenone as the model reaction to evaluate their catalytic performance (Table 1). To our delight, the products were obtained in good yield (82%) and pretty good enantioselectivity (90%ee) in the presence of 1 mol% $[Rh(C_2H_4)_2Cl]_2$ and 2 mol% chiral ligand (S)-**L1** (Entry 1).

When allyl group took place of cinnamyl group on the chiral sulfinamide ligand, the yield is similar to the former, but the ee value of the product was decreased to 82%ee (Entry 2). It seems that a phenyl moiety at the end of allyl group acts as a chiral shield and favors the chiral induction.

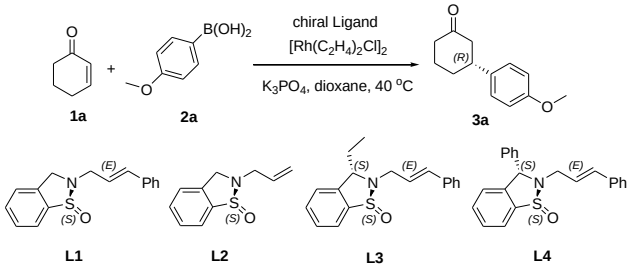
However, chiral sulfinamide ligands with 3-substituted groups, both with ethyl (**L3**) and with phenyl (**L4**), did not benefit chiral induction as well as the reaction rate for this reaction (Entries 3 and 4). It seems that a 3-substituted group hinders the coordination efficiency of rhodium and the sulfinamide-olefin ligand.

All of the four chiral sulfinamide ligands afforded R form addition product 3-phenycyclohexanone (Entries 1 to 4), which proves that the stereochemistry of catalytic reaction is governed by S-chirality.

Increase the amount of catalyst $[Rh(C_2H_4)_2Cl]_2$ and chiral ligand **L1** resulted in the rise of yields and enantioselectivities (Entries 5 to 8), and at last 96%ee and 98% yield were obtained in the presence of 2.5 (mol)% $[Rh(C_2H_4)_2Cl]_2$ and 5 (mol)% chiral ligand **L1** (Entry 8). Further increase of rhodium catalyst and **L1** did not give better results.

Encouraged by the preliminary results, we hope to further improve the enantioselectivity and yield of reaction through optimizing the base and solvent. However, further screening of base kinds and solvent types did not improve the results (see the supporting information).

Table 1. Screening of chiral cyclic sulfinamide-olefin ligand in rhodium-catalyzed 1,4-addition of 4-methoxyphenylboronic acid to cyclohexenone.



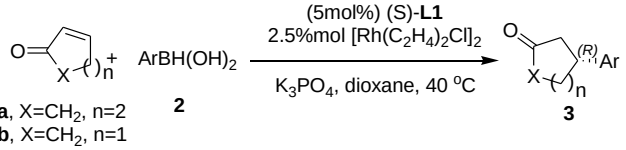
Entry	Rh (%)	Ligand	Ligand (%)	Yield (%)[b]	ee (%)[c]
1[d]	2	(S)-**L1**	2	82	90
2	2	(S)-**L2**	2	80	82
3[e]	2	(1S,3S)-**L3**	2	72	70
4[e]	2	(1S,3S)-**L4**	2	79	65
5	2	(S)-**L1**	3	82	92
6	4	(S)-**L1**	4	89	93
7	5	(S)-**L1**	4	95	94
8	5	(S)-**L1**	5	98	96

[a] Reaction conditions: Cyclohexenone (0.5 mmol), arylboronic acid (1 mmol), $[Rh(C_2H_4)_2Cl]_2$, chiral sulfinamide ligand, K_3PO_4 (0.25 mmol), dioxane (5 mL), water (1 mL), argon, 40 °C, 4 h. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase. All products are R form. [d] With 99%ee (S)-**L1** as chiral ligand. [e] **L3** and **L4** with 98%de according to the literature.[16]

With the optimized conditions in hand, reaction of α,β-unsaturated cyclic carbonyl compounds **1a**-**1c** and various arylboronic acids **2** were evaluated (Table 2).

Several points are noteworthy: Firstly, all of the reactions for which **L1** were used as ligands furnished high yields (80%~98%) and excellent enantioselectivities (86%ee~98%ee) (Entries 1 to 21). All confirmed configuration of the products with (S)-L1 as ligand were R form, while (R)-L1 afforded S form 3-tolylhexanone. As means extremely strong chiral induction ability with **L1**.

Table 2. Evaluation of reaction of α,β-unsaturated cyclic carbonyl compounds **1a**-**1c** and arylboronic acids **2**.[a]



1a, X=CH_2, n=2
1b, X=CH_2, n=1
1c, X=O, n=2

2

3

Entry	1	Ar	3	Yield (%)[b]	ee (%)[c]	Config.[d]
1	**1a**	4-$MeOC_6H_5$	**3a**	98	96	R[8]
2	**1a**	C_6H_5	**3b**	90	97	R[9d]
3	**1a**	4-MeC_6H_5	**3c**	97	98	R[17]
4	**1a**	4-MeC_6H_5	**3c**	97	97	S[e],[17]
5	**1a**	3-MeC_6H_5	**3d**	96	95	R[10a]
6	**1a**	2-MeC_6H_5	**3e**	97	98	NC[9c]
7	**1a**	4-t-BuC_6H_5	**3f**	98	98	R[18]
8	**1a**	4-ClC_6H_5	**3g**	95	94	R[19]
9	**1a**	3-ClC_6H_5	**3h**	97	93	R[10a]
10	**1a**	2-ClC_6H_5	**3i**	94	91	R[10a]
11	**1a**	4-FC_6H_5	**3j**	95	95	NC[9c]
12	**1a**	4-BrC_6H_5	**3k**	96	95	NC[20]
13	**1a**	2-naphthyl	**3l**	86	94	R[21]
14	**1a**	4-$C_2H_3C_6H_5$	**3m**	80	93	NC[22]
15	**1b**	C_6H_5	**3n**	97	89	R[18]
16	**1b**	4-MeC_6H_5	**3o**	92	91	NC[9c]
17	**1b**	2-MeC_6H_5	**3p**	94	86	NC[23]
18	**1b**	4-t-BuC_6H_5	**3q**	83	88	NC[13]
19	**1b**	4-$MeOC_6H_5$	**3r**	96	92	R[24]
20	**1c**	4-MeC_6H_5	**3s**	96	96	R[25]
21	**1c**	4-$MeOC_6H_5$	**3t**	97	94	NC[26]

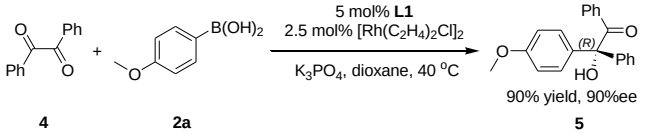
[a] Reaction conditions: Cyclohexenone (0.5 mmol), arylboronic acid (1 mmol), $[Rh(C_2H_4)_2Cl]_2$ (0.0125 mmol), 99%ee (S)-**L1** (0.025 mmol), K_3PO_4 (0.25 mmol), dioxane (5 mL), water (1 mL), argon, 40 °C, 3 h, unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase. [d] The absolute configurations of **3a**-**3t** were determined by comparison of their chiral HPLC elution order with those reported (see the supporting information). NC means no comparison of the configuration with the literature data. [e] Ligand (R)-**L1** (0.025 mmol) was used.

Secondly, both enantiomers of a chiral compound are often required in organic synthesis, fine chemicals, medicinal and pharmaceutical industries. To our gratification, both enantiomers of the product 3-(4-tolyl)cyclohexanones could be obtained in high yields and with 98%ee (R form) and 97%ee (S form), respectively, when the sulfinamide ligands (S)- and (R)-**L1** were applied (Entries 3 and 4).

Thirdly, para- and ortho-methyl- and para-tert-butyl-phenylboronic acid afforded the highest enantioselectivities of 98%ee among the tested arylboronic acids (Entries 3, 6 and 7). It should be emphasized that 98%ee of the products are produced not by 100%ee but by only 99%ee chiral ligand (S)-**L1**.

Fourthly, halo, vinyl and alkoxyl groups are compatible in the addition. These addition product is easily further derived into various valuable compounds.

Fifthly, cyclic lactone 5,6-dihydropyran-2-one afforded nearly the same high yields and enantioselectivities as cyclohexenone (Entries 20-21). However, cyclopentenone is a homologen of cyclohexenone, but for the same kinds of arylboronic acids, cyclopentenone generally afforded lower ee values (Entries 15 to 19). The reason probably is that four hydrogen atoms of two methylene groups out of the plane of cyclopentenone hamper efficiency of rhodium's vertical coordination with cyclopentenone. Although Xu[27] and Kiar[28] have reported efficient rhodium-catalyzed 1,2-additions of arylboronic acids to benzil, to our delight, this new type of chiral ligand also performed well in rhodium-catalzyed 1,2-addition reaction of benzil and phenylboronic acid, and (R)-form product with 90% yield and 90%ee was obtained (Scheme 3).



4 **2a** **5**

Scheme 2. Rh-catalyzed 1,2-addition reaction of benzil and phenylboronic acid with (S)-**L1** as ligand.

In summary, we have developed a new type of chiral cyclic sulfinamide-olefin ligands from commercially available, inexpensive starting materials. Wide structural diversity of chiral ligands can be achieved by changing the synthetic routes. For rhodium-catalyzed asymmetric addition reactions, both enantiomers could be furnished in high yields with excellent enantioselectivity by employment of (S)- and (R)-**L1**, respectively. Chiral cyclic sulfinamide-olefin ligand with only 99%ee afforded 1,4-addition products with up to 98%ee. The salient features of these new chiral ligands, including their rigid cyclic structure, air stability, the practical preparation from readily available starting materials, easy modification, and good results in enantioselective transformations, render these ligands very attractive. Further studies, such as investigation of the performance of these ligands in other metal-catalyzed asymmetric reactions, are currently underway in our laboratory.

Experimental Section

Typical procedure for the synthesis of chiral cyclic sulfinamide (S)-2,3-dihydro-1,2-benzoisothiazole 1-oxide: To an oven-dried 25 mL test tube with ground joint equipped with a stir bar were added (R)-N-(2-iodobenzyl)-2-methylpropane-2-sulfinamide (1 mmol, 337 mg), AIBN (0.38 mmol, 64 mg), and degassed toluene (2 mL). The test tube was sealed and evacuated and refilled with argon for three cycles. And it was put into an oil bath preheated at 110 °C. A solution of AIBN (1.09 mmol, 179 mg), Bn_3SnH (0.9 mmol, 264 mg) and degassed toluene (5 mL) was injected into the test tube via syringe with two hours. After injection the test tube kept stirring at 110 °C for another four hours. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried with anhydrous $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluted using gradient mixtures of petroleum ether and ethyl acetate (0-100% ethyl acetate)) on silica gel to afford (S)-2,3-dihydro-1,2-benzoisothiazole 1-oxide as a white solid (0.994 g, 65%, 99%ee). Mp: 125-126 °C for 99%ee (lit.[15b]: mp. 120 °C for 94%ee). $[\alpha]_D^{21.5}$ = −123.39° (c = 0.124, CH_2Cl_2) (lit. [15b] $[\alpha]_D^{20}$ = −98.9° (c = 1, EtOH)).

Typical procedure for the synthesis of (S)-cinnamyl-2,3-dihydro-1,2-benzoisothiazole 1-oxide (**L1**): To an oven-dried 25 mL test tube with ground joint equipped with a stir bar were added (S)-2,3-dihydro-1,2-benzoisothiazole 1-oxide (1 mmol, 153.0 mg), 60% NaH (2 mmol, 40 mg), THF (2 mL). The test tube was sealed and evacuated and refiled with argon for three cycles. The test tube was put into an ice water bath and stirred for a half hour. A solution of cinnamyl bromide (1.01 mmol, 0.199

g) and THF (3 mL) was injected into the test tube via a syringe. And the test tube was sealed and evacuated and refiled with argon for three cycles. The test tube was put into an ice water bath and stirred for five hours. The reaction mixture was quenched with water (15 mL) and extracted with ethyl acetate (15 mL) for three times. The combined organic layer was dried with anhydrous $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography (eluent: gradient mixtures of petroleum ether and ethyl acetate (0-100% ethyl acetate)) on silica gel to afford (S)-cinnamyl-2,3-dihydro-1,2-benzoisothiazole 1-oxide (L1) as a white solid (245 mg, 91% yield, 99%ee). $[\alpha]_D^{20.7}$ +52.27 (c 0.2, CH_2Cl_2), mp. 114-116 ^oC.

Typical procedure for the synthesis of optically active 3-(4-methoxyphenyl)cyclohexan-1-one (**3a**): To an oven-dried 25 mL test tube with ground joint equipped with a stir bar were added 4-methoxyphenylboronic acid (1 mmol, 0.152 g), (S)-N-cinnamyl 2,3-dihydro-1,2-benzoisothiazole 1-oxide (0.025 mmol, 0.0067 g), $[Rh(C_2H_4)_2Cl]_2$ (0.0125 mmol, 0.0048 g), 1,4-dioxane (2 mL). The test tube was sealed with a sleeve rubber stopper and evacuated and refilled with argon for three cycles. It was put into an oil bath preheated at 40 ^oC for 0.5 hour. And then a solution of cyclohexenone (0.5 mmol, 0.048 g), K_3PO_4 (0.25 mmol, 0.053 g), 1,4-dioxane (3 mL) and water (1 mL) was transferred to the test tube by a syringe. The test tube was further evacuated and refilled with argon for three cycles. And it was put into the oil bath preheated at 40 ^oC for 3 hour. The reaction mixture was added water (15 mL) and extracted with ethyl acetate (15 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtrated. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **3a** (100 mg, 98% yield, 96%ee).

Keywords: asymmetric catalysis • enantioselectivity • cyclic sulfinamide-olefin • addition reaction • rhodium

[1] a) B. M. Trost, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5348-5355; b) *Comprehensive Asymmetric Catalysis* I–III, ed. E. N. Jacobsen, A. Pfaltz, H. Yamamoto, Springer-Verlag, New York, **1999**.

[2] a) *Phosphorus Ligands in Asymmetric Catalysis* 1-3, ed. A. Börner, Wiley-VCH, Weinheim, **2008**; b) *Privileged Chiral Ligands and Catalysts*, ed. Q.-L. Zhou, Wiley-VCH, Weinheim, **2011**.

[3] a) R. Shintani, T. Hayashi, *Aldrichimica Acta* **2009**, *42*, 31-38; b) C. Defieber, H. Grützmacher, E. M. Carreira, *Angew. Chem., Int. Ed.* **2008**, *47*, 4482-4502; c) J. B. Johnson, T. Rovis, *Angew. Chem., Int. Ed.* **2008**, 47, 840-871.

[4] a) F. Ferreira, C. Botuha, F. Chemla, A. Pérez-Luna, *Chem. Soc. Rev.* **2009**, *38*, 1162-1186; c) M. T. Robak, M. A. Herbage, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 3600-3740; d) Mariz, R.; Luan, X. J.; Gatti, M.; Linden, A.; Dorta, R. *J. Am. Chem. Soc*. **2008**, *130*, 2172-2173; f) Chen, J.; Chen, J. M.; Lang, F.; Zhang, X. Y.; Cun, L. F.; Zhu, J.; Deng, J. G.; Liao, J. *J. Am. Chem. Soc*. **2010**, *132*, 4552-4553.

[5] a) Owens, T. D.; Hollander, F. J.; Oliver, A. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 1539-1540; b) Lang, F.; Chen, G. H.; Li, L. C.; Xing, J. W.; Han, F. Z.; Cun, L. F.; Liao, J. *Chem. Eur. J.* **2011**, 5242-5245.

[6] a) C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, *J. Am. Chem. Soc.* **2004**, *126*, 1628-1629; b) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13584-13585; c) Z.-Q. Wang, C.-G. Feng, M.-H. Xu, G.-Q. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 5336-5337; d) X. Hu, M. Zhang, Z. Cao, H. Du, *Org. Lett.* **2009**, *11*, 4744-4747.

[7] a) P. Maire, S. Deblon, F. Breher, J. Geier, C. Böhler, H. Rüegger, H. Schönberg, H. Grützmacher, *Chem. Eur. J.* **2004**, *10*, 4198-4205; b) R. Shintani, W.-L. Duan, T. Nagano, A. Okada, T. Hayashi, *Angew. Chem., Int. Ed.*, **2005**, *44*, 4611-4614; c) P. Kasák, V. B. Arion, M. Widhalm, *Tetrahedron: Asymm.* **2006**, *17*, 3084-3090; d) B. T. Hahn, F. Tewes, R. Frölich, F. Glorius, *Angew. Chem., Int. Ed.* **2010**, *49*, 1143-1146.

[8] T. Thaler, L.-N. Guo, A. K. Steib, M. Raducan, K. Karaghiosoff, P. Mayer, P. Knochel, *Org. Lett.* **2011**, *13*, 3182-3185.

[9] a) Y. Li, M.-H. Xu. *Chem. Commun.,* **2014**, *50*, 3771-3782; b) W. Y. Qi, T. S. Zhu, M. H. Xu, *Org. Lett*. **2011**, *13*, 3410-3413; c) S. S. Jin, H. Wang, M. H. Xu, *Chem. Commun*. **2011**, *47*, 7230-7232; d) S. S. Jin, H. Wang, T. S. Zhu, M. H. Xu, *Org. Biomol. Chem*. **2012**, *10*, 1764-1768; e) T. S. Zhu, S. S. Jin, M. H. Xu, *Angew. Chem*., *Int. Ed*. **2012**, *51*, 780-783; f) H. Wang, T. Jiang, M. H. Xu, *J. Am. Chem. Soc*. **2013**, *135*, 971-974.

[10] a) X. Feng, Y. Wang, B. Wei, J. Yang, H. Du, *Org. Lett.* **2011**, *13*, 3300-3303; b) X. Q. Feng, Y. Z. Nie, J. Yang, H. F. Du, *Org. Lett*. **2012**, *14*, 624-627; c) Y. Z. Wang, X. Q. Feng, H. F. Du, *Org. Lett*. **2011**, *13*, 4954-4957; d) Z. Q. Liu, X. Q. Feng, H. F. Du, *Org. Lett*. **2012**, *14*, 3154-3157.

[11] a) G. Chen, J. Gui, L. Li, J. Liao, *Angew. Chem., Int. Ed.*, **2011**, *50*, 7681-7685; b) L. Du, P. Cao, J. W. Xing, Y. Z. Lou, L. Y. Jiang, L. C. Li, J. Liao, *Angew. Chem*., *Int. Ed*. **2013**, 52, 4207-4211.

[12] F. Xue, X. Li, B. Wan, J. Org. Chem., 2011, 76, 7256-7262.

[13] Q. Chen, C. Chen, F. Guo, W. Xia, *Chem. Commun.,* 2013, **49**, 6433-6435.

[14] a) X. Sun, X. Tu, C. Dai, X. Zhang, B. Zhang, Q. Zeng, *J. Org. Chem.* **2012**, *77*, 4454–4459; b) Q. Zeng, W. Weng, X. Xue, *Inorg. Chim. Comm.* 2012, **388**, 11-16; c) Q. Zeng, H. Wang, T. Wang, Y Cai, W. Weng, Y Zhao, *Adv. Synth. Catal.* **2005**, *347*, 1933-1936; d) Q. Zeng**,** H. Wang, W. Weng, W. Lin, Y. Gao, X. Huang, Y. Zhao, *New J. Chem.* **2005**, *29,* 1125-1127; e) Q.-L. Zeng, H.-Y. Tang, S. Zhang, J.-C. Liu, *Chin. J. Chem.* **2008**, 26, 1435-1439.

[15] a) J. Coulomb, V. Certal, L. Fensterbank, E. Lacôte, M. Malacria. *Angew. Chem. Int. Ed.* **2006**, *45*, 633-637; b) J. Coulomb, V. Certal, M.-H. Larraufie, C. Ollivier, J.-P. Corbet, G. Mignani, L. Fensterbank, E. Lacôte, M. Malacria. *Chem. Eur. J.* **2009**, *15*, 10225-10232.

[16] J. A. Fernández-Salas, M. M. Rodríguez-Fernández, M. C. Maestro, J. L. García-Ruano. *Chem. Commun,* **2014**, *50*, 6046-6048.

[17] Y.-S. Zhao, J.-K. Liu, Z.-T. He, J.-C. Tao, P. Tian, G.-Q. Lin. *Org. Biomol. Chem.* **2016**, *14*, 3686-3689.

[18] T. Yasukawa, H. Miyamura, S. Kobayashi. *J. Am. Chem. Soc.* **2012**, *134*, 16963-16966.

[19] J. Dong, Y. Liu, Y. Cui. *Chem. Commun.* **2014**, *50*, 14949-14952.

[20] C.-G. Feng, Z.-Q. Wang. *Org. Lett.* **2008**, *10*, 4101-4104.

[21] A. Lee, H. Kim, *J. Org. Chem.* **2016**, *81*, 3520-3527.

[22] Q. Naeemi, M. Dindaroğlu, D. P. Kranz, J. Velder, H.-G. Schmalz. *Eur. J. Org. Chem.* **2012**, *6*, 1179-1185.

[23] Y. Otomaru, K. Okamoto, *J. Org. Chem.* **2005**, *70*, 2503-2508.

[24] H. Yang, M. Xu. *Chin. J. Chem.* **2013**, *31*, 119-122.

[25] C.-C. Liu, D. Janmanchi, C.-C. Chen, H.-L. Wu. *Eur. J. Org. Chem.* **2012**, *2012*, 2503-2507.

[26] T. Gendrineau, O. Chuzel, H. Eijsberg, J.-P. Genet, S. Darses. *Angew. Chem. Int. Ed.* **2008**, 47, 7669 -7672.

[27] T.-S. Zhu, S.-S. Jin, M.-H. Xu, *Angew. Chem. Int. Ed.* **2012**, *51*, 780-783.

[28] N. Khiar, V. Valdivia, Á. Salvador, A. Chelouan, A. Alcudia, I. Fernández, *Adv. Synth. Catal.* **2013**, *355*, 1303-1307.

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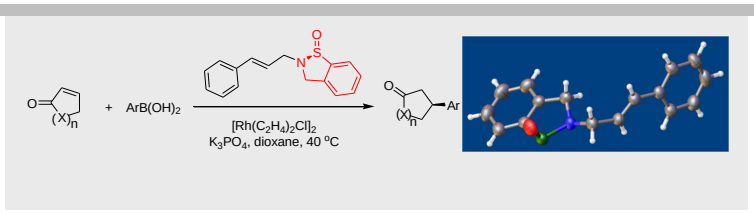

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A New Type of Chiral Cyclic sulfinamide-Olefin Ligands for Rhodium-Catalyzed Asymmetric Addition

Rigid cyclic sulfinamide 2,3-dihydro-1,2-benzoisothiazole 1-oxide acts as chiral skeleton of a new type of chiral cyclic sulfinamide-olefin ligands, which demonstrate excellent enantioselective catalytic performance in rhodium-catalyzed asymmetric 1,4-additions of α,β-unsaturated cyclic carbonyl compounds and 1,2-addition of benzil. Both enantiomers of chiral ligands are easily prepared and directly used in catalysis, and thus both high ee enantiomers of the products are obtained.