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Application of chiral *N-tert*-butylsulfinyl vinyl aziridines in Rh(I) catalyzed 1,4-addition of aryl boronic acids to cyclic enones†‡

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Chiral *N-tert*-butylsulfinyl vinyl aziridine ligands prepared from a readily available (*R*)-*tert*-butanesulfinamide have been applied in the rhodium-catalyzed asymmetric 1,4-addition of aryl boronic acids to cyclic enones, which gives high yields and excellent enantioselectivities.

Chiral molecules were broadly applied in the field of pharmaceuticals, agricultural chemicals, fine chemicals and materials. Asymmetric synthesis of chiral compounds catalyzed by transition-metals in the presence of chiral ligands has been proven to be one of the most efficient approaches.[1] The design and synthesis of novel chiral ligands have therefore been topics of great interest in organic and organometallic chemistry. Among them, the development of phosphorus-based chiral ligands has been most extensively investigated.[2] Despite these advances, the introduction of coordination atoms and/or functional groups other than phosphorus would greatly enrich the chiral ligand libraries, and sometimes lead to higher enantioselectivity. Among the recently developed ligands, chiral dienes, and alkene, P- and/or N-hybrid ligands have shown novel coordination ability and higher catalytic performance in asymmetric catalysis, and attracted considerable attention from several research groups.[3–6]

Besides these, chiral sulfoxide is also one of the most important ligands and has been broadly used in asymmetric synthesis.[7] Thanks for the pioneering work of Dorta's group who have achieved a significant breakthrough by fixing the sulfoxide to the privileged atropisomeric 1,1′-binaphthyl backbone,[8] the subsequent research by groups of Liao, Xu and Du independently led to the development of chiral *tert*-butyl sulfoxide- and/or sulfinamide–olefin hybrid ligands and satisfactory results were attained (Fig. 1).[9–11] It occurs to us that whether the activity and enantioselectivity of catalytic reaction would be maintained or improved if a rigid three-membered ring with *N-tert*-butylsulfinyl vinyl aziridines was introduced into the ligands (Fig. 1). To our acknowledgement, efficient approaches for preparing chiral *N-tert*-butylsulfinyl vinyl aziridines from sulfinimines have been established for several years,[12–14] however, their utility as chiral ligands in catalytic asymmetric transformations has not been reported. Herein we describe our discovery of *N-tert*-butylsulfinyl vinyl aziridines as efficient hybrid ligands for highly enantioselective rhodium-catalyzed asymmetric 1,4-addition reactions.

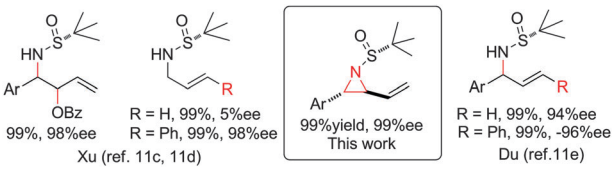

Fig. 1 Work proposal of chiral S, olefin-ligands for Rh(I) catalyzed asymmetric arylation.

We started our research by preparing a variety of *N-tert*-butylsulfinyl vinyl aziridines according to the procedure established by Stockman *et al.* (Fig. 2).[13,15] Fortunately, both *cis*- and *trans*-diastereomers could be separated by silica gel chromatography.[16]

With chiral *N-tert*-butylsulfinyl vinyl aziridines in hand, we chose the Rh-catalyzed 1,4-addition of phenylboronic acid to cyclohexenone as the model reaction to evaluate their catalytic performance.[17] To our gratification, the products were obtained in high yield (95%) and excellent enantioselectivity (96%) in the presence of 3 mol% Rh–*cis*-**1a** complex (Table 1, entry 1). Under the same conditions, a similar result was obtained when *cis*-**1a** was replaced by *trans*-**1a** (95% yield and 97% ee) (Table 1, entry 2). It should be noted that both ligands

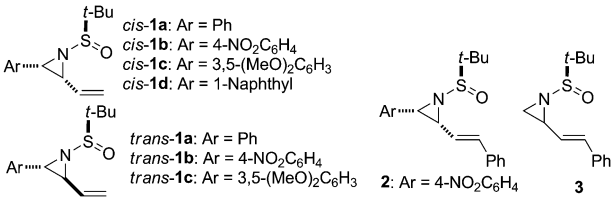

Fig. 2 *N-tert*-Butylsulfinyl vinyl aziridines applied in Rh(I) catalyzed 1,4-addition of arylboronic acids to enones.

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† This paper is dedicated to Professor Kiyoshi Tomioka on the occasion of his 65th birthday.

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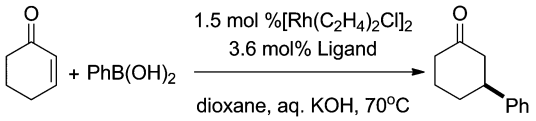
Table 1 Survey of the *N-tert*-butylsulfinyl vinyl aziridine ligands for Rh catalyzed asymmetric addition of phenylboronic acids to cyclohexenones



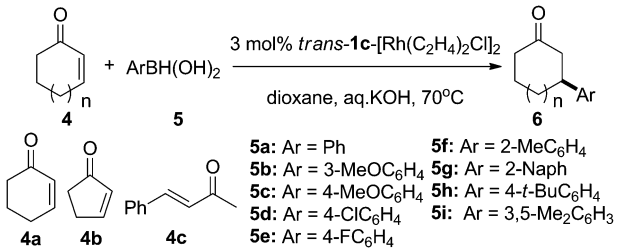
Entry	Ligand	Time (h)	Yield[a] (%)	ee[b] (%)
1	*cis*-**1a**	10	95	96
2	*trans*-**1a**	10	95	97
3	*cis*-**1b**	12	80	94
4	*trans*-**1b**	12	95	96
5	*cis*-**1c**	8	70	98
6	*trans*-**1c**	8	99	99
7	*cis*-**1d**	8	99	96
8	**2**	10	85	93
9[c]	**3**	12	—	—

[a] Isolated yield. [b] Determined by chiral HPLC with hexane–2-propanol. [c] Trace of the target product.

gave the same configuration products, indicating that the stereochemistry of catalytic reaction was determined by the inherent *S*-chirality of *N-tert*-butylsulfinyl vinyl aziridine ligands, and the independent new chiral carbon center and relative configuration.[11c,e] Encouraged by the preliminary results, we hope to further improve the enantioselectivity of reaction through modifying and optimizing the structure of ligands. Chiral ligands **1b–3** were thus prepared and their catalytic efficiencies were examined under the same reaction conditions. As shown in Table 1, except for ligand **3**, all of the chiral ligands led to the desired product in good yield and excellent enantioselectivity in 93–99% ee (entries 1–9). The electronic effect of aryl groups in chiral *N-tert*-butylsulfinyl vinyl aziridines has no distinct influence on catalytic activity and enantioselectivity (entries 1 and 3 *vs.* 5; 2 and 4 *vs.* 6), whereas the *cis*-isomer showed a little lower catalytic activity in spite of maintaining the same high enantioselectivity (entry 3 *vs.* 4 and 5 *vs.* 6). Notably, *trans*-**1c** shows the best catalytic activity and enantioselectivity (entry 6). Ligand **2** possessing phenylvinyl that is an internal olefin led to the product with the same absolute *S*-configuration as *cis*-**1b** (entry 3 *vs.* 8), which was different from the phenomenon that the substituted model of olefins could reverse the absolute configuration of the product observed by Liao *et al.*[10a] and Du *et al.*[11e] This result further proves that the stereochemistry of catalytic reaction is governed by *S*-chirality.[11c,e] Unfortunately, examination of ligand **3** led to a trace of the target product and ambiguous mixture (entry 9). However, such a result suggested the importance of aryl groups in the *N-tert*-butylsulfinyl vinyl aziridine ligands for maintaining a high catalytic performance despite that it is still unclear why aryl groups in the *N-tert*-butylsulfinyl vinyl aziridine ligands are critical to the reactivity and selectivity.

Having identified optimal reaction conditions (Table 1, entry 6), we next evaluated the substrate scope of this rhodium-catalyzed asymmetric 1,4-addition. As shown in Table 2, the nature of the substituent on the phenyl ring of arylboronic acid had very little effect on the stereoselectivity of the reaction. Aryl groups having electron-donating and -withdrawing substituted groups, for example, 3-methoxyphenyl, 4-methoxyphenyl, 4-chlorophenyl, and 4-fluorophenyl groups were successfully introduced into **4a**, giving the corresponding **6** with high ee (85–98%) in high yields (70–99%) (Table 2, entries 2–5). 2-Methylphenyl, 2-naphthyl,

Table 2 Rh/*trans*-**1c**-catalyzed asymmetric addition of arylboronic acids **5** to enones **4**



Entry	Enones	$ArB(OH)_2$	Time (h)	**6**	Yield[a] (%)	ee[b] (%)
1	**4a**	**5a**	10	**6aa**	99	99
2	**4a**	**5b**	8	**6ab**	99	96
3	**4a**	**5c**	8	**6ac**	85	85
4	**4a**	**5d**	8	**6ad**	77	98
5	**4a**	**5e**	8	**6ae**	70	98
6	**4a**	**5f**	8	**6af**	95	87
7	**4a**	**5g**	8	**6ag**	99	96
8	**4a**	**5h**	10	**6ah**	99	93
9	**4b**	**5a**	8	**6ba**	85	51
10	**4b**	**5c**	12	**6bc**	55	85
11	**4b**	**5d**	10	**6bd**	88	30
12	**4b**	**5h**	8	**6bh**	99	64
13	**4b**	**5i**	8	**6bi**	99	41
14	**4c**	**5c**	12	**6cc**	30	67

[a] Isolated yield. [b] Determined by chiral HPLC with hexane–2-propanol.

and 4-*tert*-butylphenyl groups were also introduced into **4a**, affording the corresponding **6** in excellent yield (95–99%) with high ee (87–96%) (Table 2, entries 6–8). Cyclopentenone **4b** was also a good substrate for this transformation to give the corresponding **6** in high yield (55–99%) with moderate to high ee (entries 9–13). Furthermore, when linear enone (*E*)-4-phenylbut-3-en-2-one **4c** was reacted with 4-methoxyphenyl boronic acid, moderate yield and good enantioselectivity were observed (entry 14).

The absolute configuration of **6aa** obtained in this reaction was determined to be *S* by comparison of its optical rotation value with that in the literature.[18] On the basis of this outcome, an empirical stereochemical model can be rationalized as shown in Fig. 3.[10b,d,11a,d] Thus, the arylrhodium species has a *trans*-relationship between the aryl group and the olefin of *trans*-**1c**. To avoid the steric repulsion between *tert*-butyl of the ligand and methylene at 5- and/or 6-position in cyclohexenone **4a**, it preferentially approaches the vacant position of rhodium with its *si*-face to give (*S*)-**6aa** with high selectivity. Moreover, bidentate coordination of ligand **1** to rhodium requires the *cis* relationship between olefin and sulfur, which causes severe steric repulsion in *cis*-**1** due to the all-*cis* relationship between olefin, aryl and sulfinyl groups. This might be the reason for less efficiency of *cis*-**1** than *trans*-**1** (Table 1).

In conclusion, we have demonstrated that chiral *N-tert*-butylsulfinyl vinyl aziridines with a rigid three-membered ring backbone can be

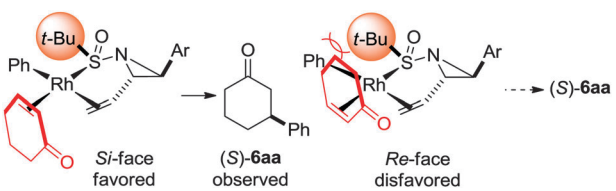


Fig. 3 Proposed stereochemical model.

used as efficient chiral sulfur–olefin hybrid ligands for highly enantioselective rhodium-catalyzed asymmetric 1,4-addition reactions. This work presents the first example of application of *N*-*tert*-butylsulfinyl vinyl aziridines as chiral ligands in transition metal catalysis. The key point to the success was that aryl, alkenyl, and *tert*-butyl sulfoxide were correctly installed on the vertex of the rigid aziridine ring, which favored the coordination of Rh with olefin and S, and thus accomplished a highly catalytic activity and stereocontrol performance. Further modification of more effective chiral sulfur–olefin hybrid ligands with ring backbones and their applications in other asymmetric reactions are currently underway in our laboratory.

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