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Simple Branched Sulfur−Olefins as Chiral Ligands for Rh-Catalyzed Asymmetric Arylation of Cyclic Ketimines: Highly Enantioselective Construction of Tetrasubstituted Carbon Stereocenters

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Supporting Information

ABSTRACT: New, simple, sulfinamide-based branched olefin ligands have been developed and successfully used in Rh-catalyzed asymmetric arylations of cyclic ketimines, providing efficient and highly enantioselective access to valuable benzosultams and benzosulfamidates containing a stereogenic quaternary carbon center. This is the first example of applying a sulfur−olefin ligand in catalytic asymmetric addition of imines.

Cyclic amines bearing sulfonamide functionality in the ring, such as sultams and sulfamidates, have emerged as an intriguing class of synthetic targets because they often exhibit a broad spectrum of biological activities[1] and are useful as chiral auxiliaries[2] and important synthetic reagents.[3] However, despite the development of many synthetic strategies,[4−6] catalytic asymmetric procedures for the generation of optically active sultams and sulfamidates are very limited.[5,6]

Transition-metal-catalyzed asymmetric reduction of cyclic *N*-sulfonyl ketimines is an efficient approach for the enantioselective synthesis of benzosultams or benzosulfamidates containing an α-stereogenic center in the amine moiety,[6] but it cannot be used for the construction of quaternary carbon stereocenters. Katsuki recently disclosed an Ir-catalyzed enantioselective intramolecular C−H amination approach,[7] but it also is not applicable to α-quaternary benzosultams. Catalytic asymmetric addition of organometallic reagents to cyclic *N*-sulfonyl ketimines is an attractive and direct route to this target class, but it is far less developed because of the significant difficulty of reaction stereochemical control.[8] Only very recently has Rh-catalyzed highly enantioselective addition of arylboroxines using chiral diene ligands been successfully realized,[9] giving α-triaryl-substituted benzosultams with excellent enantioselectivities; also, a related report described the construction of a quaternary benzosultam structure using potassium (*E*)-1-hexenyltrifluoroborate.[10] Therefore, new approaches for catalytic enantioselective addition are still in high demand.

We recently developed a new and promising class of chiral sulfur-based olefin ligands (SOLs)[11,12] and successfully employed them in a series of Rh-catalyzed asymmetric reactions.[13,14] A particularly fascinating finding is that simple chiral *N*-(sulfinyl)cinnamylamine ligands can promote highly enantioselective 1,2-additions of arylboronic acids to both α-keto esters and α-diketones to give tertiary α-hydroxy carbonyl compounds with excellent enantioselectivities (up to 99% ee) at ambient temperature.[13d] These results encouraged us to explore their application in the more challenging but much less studied enantioselective 1,2-addition to cyclic *N*-sulfonyl ketimines to construct functionalized sultams and sulfamidates bearing quaternary stereogenic centers. To date, the use of chiral SOLs in catalytic asymmetric additions of C═N bonds remains unprecedented. Herein we describe the first example of Rh/SOL-catalyzed highly enantioselective arylation of ketimines with arylboronic acids. With a structurally simple chiral sulfonamide-based branched olefin ligand, the reaction provides efficient access to a wide range of highly enantiomerically enriched α-quaternary cyclic amines, benzosultams, and benzosulfamidates.

In conjuction with our interest in optically active non-proteinogenic amino acids,[15] we initially wished to access 3-carboxy-substituted benzosultams containing a unique α-amino acid framework. Such molecules would be attractive to organic and medicinal chemists, but there are no reports of their asymmetric synthesis via enantioselective catalysis.[16] We started with the reaction between cyclic *N*-sulfonyl α-iminoester **1a** and *p*-anisylboronic acid (**2a**) using the previously developed SOLs **L1**−**L3** as chiral ligands (Table 1). We found that the reaction proceeds very well in the presence of 1.5 mol % $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) and 3.3 mol % **L1** in aqueous KF (1.5 M)/toluene at room temperature (rt), giving a 96% isolated yield of the expected 3-aryl-3-carboxybenzosultam **3a** with 50% ee (entry 1). A solvent screen showed that dioxane, MeOH, DME, and THF led to only trace amounts of product (entries 4−7). Though slightly higher ee (56%) was obtained in CH_2Cl_2, the yield decreased significantly (58%) (entry 8). Changing the inorganic base failed to improve the enantioselectivity (entries 9−12).

After showing that simple *N*-(sulfinyl)cinnamylamines can promote this arylation reaction, we systematically modified the chiral SOL framework in an attempt to improve the catalyst performance (Scheme 1). Like **L2**, *N*-sulfinyl homoallylic amine **L4** gave a low yield and enantioselectivity. It was also disappointing that *N*-(sulfinyl)cinnamylamine analogues **L5**−**L7** containing substituents with different steric and electronic natures were either less effective or almost inactive and gave no higher ee. In sharp contrast, the equally simple but branched olefin ligand **L8** exhibited both high catalytic activity and enantioselectivity, giving **3a** in 89% yield with a promising 70% ee. This led us to design and synthesize the new sulfonamide-based branched olefin ligands **L9**−**L15** with different R

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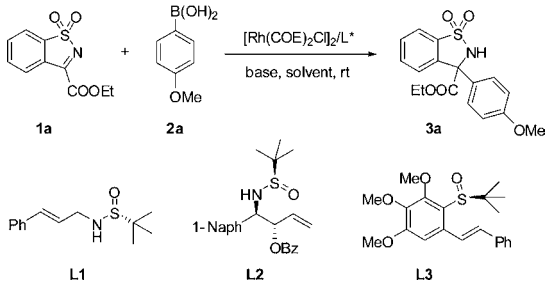
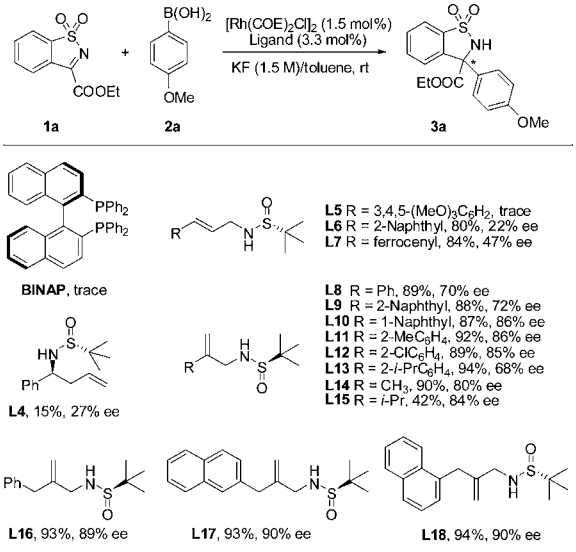
Table 1. Screen of Ligands, Solvents, and Bases[a]



entry	ligand	solvent	base[b]	yield (%)[c]	ee (%)[d]
1	**L1**	toluene	KF (1.5 M)	96	50
2	**L2**	toluene	KF (1.5 M)	11	33
3	**L3**	toluene	KF (1.5 M)	trace	–
4	**L1**	dioxane	KF (1.5 M)	trace	–
5	**L1**	CH_3OH	KF (1.5 M)	trace	–
6	**L1**	DME	KF (1.5 M)	trace	–
7	**L1**	THF	KF (1.5 M)	trace	–
8	**L1**	CH_2Cl_2	KF (1.5 M)	58	56
9	**L1**	toluene	K_3PO_4 (1.5 M)	19	36
10	**L1**	toluene	K_2CO_3 (1.5 M)	15	48
11	**L1**	toluene	KH_2F (1.0 M)	67	50
12	**L1**	toluene	KOH (0.1 M)[e]	73	49

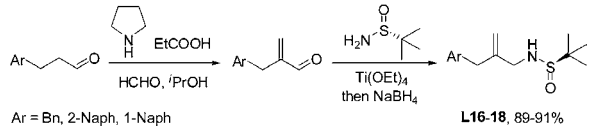
[a]Conditions: **1a** (0.25 mmol), **2a** (2.0 equiv), [Rh] (3 mol %), ligand (3.3 mol %), and base in 2.0 mL of solvent. [b]Unless noted, 1.0 equiv of base was used. [c]Isolated yields. [d]Determined by chiral HPLC. [e]0.1 equiv of KOH (0.1 M) was used.

Scheme 1. Further Ligand Screen



substituents for evaluation. Changing the phenyl group in **L8** to the more bulky 1-naphthyl group in **L10** increased the enantiocontrol (86% ee). **L11** and **L12** with ortho substitution (CH_3, Cl) on the phenyl ring gave similar results as **L10**, but **L13** with the larger *i*-Pr substituent afforded decreased ee, suggesting that having the appropriate steric demand of the R group is important for the stereocontrol. Surprisingly, when the aryl group was replaced with an alkyl group (CH_3, **L14**), the ee was maintained at 80%. **L15** with an *i*-Pr group directly attached to the double bond gave **3a** with higher enantioselectivity (84% ee), although the yield was much lower. These results showed that fine-tuning of the ligand rigidity and the steric demand of the R substituent is essential. Gratifyingly, an improved ee (89%) was observed when benzyl-substituted **L16** was used. The incorporation of a large naphthyl group was even more beneficial, as **L17** and **L18** gave the best enantioselectivity (90% ee) and yield (>90%). Remarkably, these optimal ligands can be easily prepared in high yields (Scheme 2).[17] It should be noted that

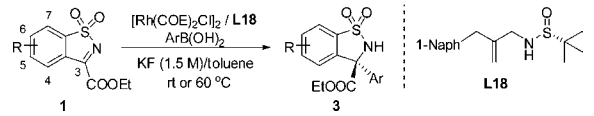
Scheme 2. Synthesis of Optimal Ligands L16–18



the widely used diphosphine ligand BINAP was ineffective in this arylation reaction, indicating the unique catalytic performance of the class of chiral SOLs.

With effective ligands in hand, we examined the substrate scope under the optimized conditions (Table 2).[18] A wide range

Table 2. Rh/L18-Catalyzed Asymmetric Arylation of 1[a]



entry	R	Ar	3	yield (%)[b]	ee (%)[c]
1	H	4-$MeOC_6H_4$	**3a**	94	90
2	H	4-MeC_6H_4	**3b**	94	90
3[d]	H	4-ClC_6H_4	**3c**	68	93
4[d]	H	Ph	**3d**	89	93
5	H	1-naphthyl	**3e**	90	99
6	H	2-naphthyl	**3f**	90	94
7[d]	H	3-$MeOC_6H_4$	**3g**	78	91
8[d]	H	3-MeC_6H_4	**3h**	84	92
9[d]	H	3-ClC_6H_4	**3i**	62	97
10[d]	H	2-$MeOC_6H_4$	**3j**	35	95
11	5-OMe	4-$MeOC_6H_4$	**3k**	96	90
12	5-OMe	2-naphthyl	**3l**	84	92
13	5-Me	1-naphthyl	**3m**	91	99
14[d]	5-Me	3-MeC_6H_4	**3n**	80	90
15[d]	5-Me	3-ClC_6H_4	**3o**	59	99
16	5-F	1-naphthyl	**3p**	86	99
17[d]	5-F	3-MeC_6H_4	**3q**	76	90
18	5-Cl	2-naphthyl	**3r**	81	94
19[d]	5-*t*-Bu	3-MeC_6H_4	**3s**	91	88
20	7-Cl	1-naphthyl	**3t**	85	97
21	6,7-$(CH)_4$	4-$MeOC_6H_4$	**3u**	94	85

[a]Conditions: **1** (0.25 mmol), $ArB(OH)_2$ (2.0 equiv), [Rh] (3 mol %), **L18** (3.3 mol %), and KF (1.5 M, 1.0 equiv) in 2.0 mL of toluene at rt for 3–5 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]The reaction was performed at 60 °C.

of arylboronic acids with varying electronic and steric demands were successfully reacted with cyclic *N*-sulfonyl α-iminoesters **1**, giving the corresponding addition products mostly in high yields with excellent enantioselectivities. In some cases with electron-deficient or sterically bulky arylboronic acids, the reaction was performed at 60 °C to improve the yield. Higher enantioselectivities were observed with less reactive arylboronic acids bearing an electron-withdrawing group on the benzene ring (entries 1 and 2 vs 3; 7 and 8 vs 9; and 14 vs 15). Notably, the reactions with more sterically hindered arylboronic acids such as

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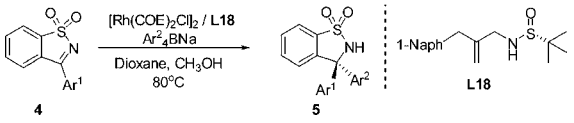
1-naphthylboronic acid gave the products with extremely high enantioselectivities (99% ee; entries 5, 13, and 16). The absolute configuration at the newly created stereocenter was determined to be *R* by X-ray crystallographic analysis of **3e**.[19]

After demonstrating the first catalytic enantioselective synthesis of 3-carboxysubstituted benzosultams **3**, we applied our catalytic system to the construction of benzosultams bearing an α-triaryl-substituted stereogenic center.[9] The reaction of various cyclic *N*-sulfonyl ketimines **4** with sodium tetraarylborates was successfully promoted by the Rh/**L18** complex (3 mol %) at 80 °C in dioxane/MeOH (Table 3). In all cases, excellent

Table 3. Rh/L18-Catalyzed Asymmetric Arylation of 4[a]



4 5

entry	Ar^1	Ar^2	5	yield (%)[b]	ee (%)[c]
1	Ph	4-$MeOC_6H_4$	**5a**	90	97 (98)
2	Ph	4-ClC_6H_4	**5b**	90	97 (94)
3	Ph	3-MeC_6H_4	**5c**	81	96 (97)
4	4-$MeOC_6H_4$	Ph	**5a′**	84	96
5	4-$MeOC_6H_4$	3-MeC_6H_4	**5d**	85	95
6	4-MeC_6H_4	4-$MeOC_6H_4$	**5e**	91	98
7	4-MeC_6H_4	4-ClC_6H_4	**5f**	74	96
8	4-ClC_6H_4	4-MeC_6H_4	**5f′**	85	97 (97)
9	4-ClC_6H_4	3-MeC_6H_4	**5g**	82	96
10	3-MeC_6H_4	Ph	**5c′**	83	97
11	3-MeC_6H_4	4-$MeOC_6H_4$	**5d′**	88	98
12	3-ClC_6H_4	3-MeC_6H_4	**5h**	72	96

[a]Conditions: **4** (0.25 mmol), $NaBAr^2{}_4$ (1.5 equiv), [Rh] (3 mol %), **L18** (3.3 mol %), and CH_3OH (3.0 equiv) in 1.0 mL of dioxane at 80 °C for 8–12 h. [b]Isolated yields. [c]Determined by chiral HPLC. Values in parentheses were reported in ref 9.

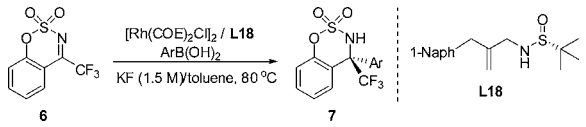
enantioselectivities (95–98% ee) comparable to those obtained using a Rh/chiral diene complex (5 mol %)[9] were observed. In the case of **5b**, a slightly better ee was obtained (97 vs 94%). In entries 1 and 4, 3 and 10, 5 and 11, and 7 and 8, both enantiomers of the product were obtained using the same catalyst simply by switching the corresponding aryl acceptor and donor.

We next investigated the asymmetric arylation of benzo-fused six-membered cyclic imine **6** to yield cyclic benzosulfamidates **7** bearing a CF_3 group on the quaternary carbon stereogenic center (Table 4). F-containing heterocyclic chiral amines are particularly interesting because of their wide range of biological activities.[20] The reaction proceeded smoothly with a sterically and electronically diverse range of arylboronic acids in the presence of $[Rh(COE)_2Cl]_2$ (1.5 mol %) and **L18** (3.3 mol %) in aqueous KF (1.5 M)/toluene at 80 °C, providing **7a–g** in good yields with extremely high enantioselectivities (98–99% ee).

Finally, we found that cyclic aldimines **8** were also viable substrates (Table 5). Under the same catalytic conditions, aldimines with either an electron-donating or electron-withdrawing group (R) on any aromatic carbon readily underwent the asymmetric arylation with arylboronic acids at rt, affording chiral cyclic sulfamidates **9** in extremely high yields and enantioselectivities (99% ee). To our knowledge, enantioselective aryl addition of cyclic imines **8** has not been reported to date; it represents the most efficient and convenient route to **9**.

On the basis of the reaction stereochemical outcome, an empirical transition state model[21,22] is proposed (Figure 1). We

Table 4. Rh/L18-Catalyzed Asymmetric Arylation of 6[a]

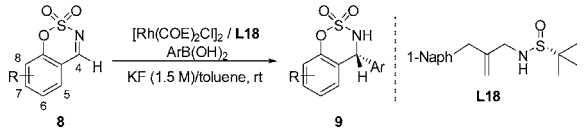


6 7

entry	Ar	7	time (h)	yield (%)[b]	ee (%)[c]
1	4-MeC_6H_4	**7a**	3	75	99
2	4-FC_6H_4	**7b**	3	81	99
3	4-ClC_6H_4	**7c**	3	78	98
4	3-$MeOC_6H_4$	**7d**	5	72	99
5	2-MeC_6H_4	**7e**	8	26	99
6	1-naphthyl	**7f**	5	75	99
7	2-naphthyl	**7g**	3	84	99

[a]Conditions: **6** (0.25 mmol), $ArB(OH)_2$ (2.0 equiv), [Rh] (3 mol %), **L18** (3.3 mol %), and KF (1.5 M, 1.0 equiv) in 2.0 mL of toluene at 80 °C. [b]Isolated yields. [c]Determined by chiral HPLC.

Table 5. Rh/L18-Catalyzed Asymmetric Arylation of 8[a]



8 9

entry	R	Ar	9	yield (%)[b]	ee (%)[c]
1	H	4-MeC_6H_4	**9a**	96	99
2	H	3-ClC_6H_4	**9b**	98	99
3	H	2-MeC_6H_4	**9c**	99	99
4	5,6-$(CH)_4$	Ph	**9d**	96	99
5	6-Me	4-MeC_6H_4	**9e**	99	99
6	6-Cl	3-ClC_6H_4	**9f**	98	99
7	7-OMe	Ph	**9g**	99	99
8	8-Me	4–Br-C_6H_4	**9h**	98	99

[a]Conditions: **8** (0.25 mmol), $ArB(OH)_2$ (2.0 equiv), [Rh] (3 mol %), **L18** (3.3 mol %), and KF (1.5 M, 1.0 equiv) in 1.0 mL of toluene at rt for 5–6 h. [b]Isolated yields. [c]Determined by chiral HPLC.

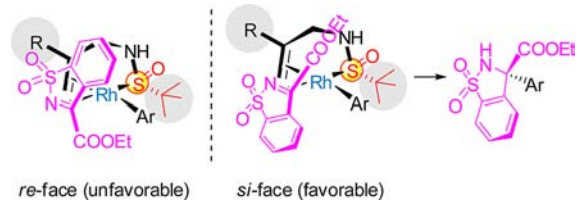


Figure 1. Proposed transition state model.

assume that the arylrhodium species has a preferred conformation with a specific geometry in which the aryl group is positioned trans to the olefin ligand and the *t*-Bu moiety is staggered. To minimize unfavorable steric interactions with the R group attached to the double bond, the sulfonyl moiety of the imine substrate coordinates to the Rh in such a way that the ring oriented away from R; thus, carborhodation takes place from the *si* face of the imine to give the *R* product.

In summary, we have discovered new simple sulfonamide-based branched olefin ligands for asymmetric catalysis. With these readily available ligands, highly efficient Rh-catalyzed asymmetric additions of arylboronic acids to cyclic *N*-sulfonyl ketimines have been successfully developed. The reaction provides the first access to valuable benzosultams and benzosulfamidates having a carboxylic or CF_3 function at the quaternary carbon in a highly enantioselective manner. More-

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over, this is also the first example of the use of a sulfur−olefin ligand for asymmetric addition of imines. This study further demonstrates the usefulness of this recently developed class of ligands[13,14] and sets the stage for further exploration of their use in other asymmetric transformations and the development of other kinds of unique olefin ligands.

■ ASSOCIATED CONTENT

Supporting Information

Experimental methods and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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