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Asymmetric Synthesis of (Triaryl)methylamines by Rhodium-Catalyzed Addition of Arylboroxines to Cyclic *N*-Sulfonyl Ketimines

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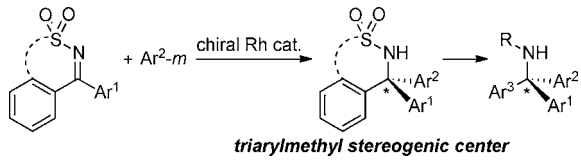
Supporting Information

ABSTRACT: Asymmetric addition of arylboroxines to cyclic *N*-sulfonyl ketimines proceeded in the presence of a rhodium catalyst coordinated with a chiral diene ligand to give high yields of benzosultams, where a triaryl-substituted stereogenic carbon center was created with high enantioselectivity (93−99% ee). The chiral benzosultams were transformed into the chiral (triaryl)methylamines by breaking the cyclic structure.

The transition-metal-catalyzed asymmetric addition of organometallic reagents to imines offers one of the most reliable methods available for the synthesis of enantioenriched α-chiral amines.[1] A variety of useful catalytic systems based on copper,[2] zirconium,[3] rhodium,[4] and palladium[5] complexes have been reported in the asymmetric alkylation and arylation of imines derived from aldehydes. In contrast, the asymmetric addition of organometallic reagents to ketimines, which provides chiral amines bearing an α-tetrasubstituted carbon stereocenter, remains significantly underdeveloped,[6] and there have been only a few reports to date.[7−10] Copper-catalyzed asymmetric addition of allylboronates have been reported by Kanai and Shibasaki.[7] The asymmetric addition of dialkylzinc has been reported by Charette (Cu),[8] and Snapper and Hoveyda (Zr).[9] In this context, we recently reported the rhodium-catalyzed asymmetric addition of arylboron reagents to *N*-sulfonyl ketimines derived from alkyl aryl ketones giving α-diaryl alkyl amines with high enantioselectivity.[11] In the rhodium-catalyzed arylation of imines, the enantioface of the C═N bond is differentiated by the steric interactions between a substituent on the chiral ligand and a sulfonyl moiety on the nitrogen atom of the imine.[4] Thus, the geometry (*E* or *Z*) of the imine greatly affects the enantioselectivity. It follows that the arylation of ketimines derived from diaryl ketones has inherent difficulty in controlling the enantioselectivity due to the lack of sufficient steric difference between the two aryl rings.[12] To the best of our knowledge, there have been no examples to date that report the catalytic asymmetric arylation of diaryl-substituted keimines.[13] We focused on the cyclic *N*-sulfonyl ketimines bearing the diaryl-substituted azomethine carbon toward the synthesis of benzosultams bearing a triaryl-substituted stereogenic carbon center, which can lead to chiral (triaryl)methylamines (Scheme 1).[14]

Enantiopure sultams are an important class of compounds in organic and medicinal chemistry, which have been used as chiral auxiliaries[15] and as key intermediates for the synthesis of biologically active compounds.[16] Enantioselective synthesis of benzosultams possessing an α-trisubstituted carbon center has been reported in the metal-catalyzed intramolecular C−H amination[17] and asymmetric reduction of cyclic *N*-sulfonyl ketimines.[15a,16b,18] As an example of constructing an α-tetrasubstituted carbon center of benzosultams, the chiral NHC-catalyzed enantioselective annulation of a cyclic *N*-sulfonyl ketimine with cinnamaldehyde has been reported by Bode et al.[19] Here we report the rhodium-catalyzed asymmetric addition of arylboroxines to cyclic *N*-sulfonyl ketimines to give high yields of benzosultams with high enantioselectivity.

Scheme 1. Asymmetric Arylation of Cyclic *N*-Sulfonyl Ketimines



We found that cyclic *N*-sulfonyl ketimine **1a**, which is readily derived from saccharin,[16b,20] is a good substrate for constructing a triaryl-substituted stereogenic carbon center enantioselectively in the rhodium-catalyzed addition of arylboroxines. Thus, treatment of **1a** with *p*-tolylboroxine (**2m**) (2 equiv of B) in the presence of a rhodium/bisphosphine catalyst $[RhCl((R)\text{-binap})]_2$[21] (5 mol % of Rh), K_3PO_4 (1 equiv), and *tert*-amyl alcohol (3 equiv) in 1,4-dioxane at 60 °C for 12 h gave benzosultam **3am** in 93% yield, whose enantiomeric purity was 39% (Table 1, entry 1). A higher enantioselectivity (71% ee) for **3am** was observed by use of (*R*)-segphos (entry 2), but the bulky ligand DTBM-segphos decreased both the catalytic activity and enantioselectivity (10% yield, 9% ee; entry 3). Chiral diene ligands[22] were effectively applied to the present arylation. Thus, the reaction by use of $[RhCl((S,S)\text{-Fc-tfb*})]_2$[23] (Fc = ferrocenyl), which is one of the most active catalysts displaying high enantioselectivity in the rhodium-catalyzed arylation, gave **3am** in 96% yield with 90% ee (entry 4). Chiral diene ligands **L1**−**L3**,[4c,l,24] which are readily prepared from a natural product in enantiopure form, also displayed high catalytic activity (entries 5−7), and the use of ligand **L3** bearing a bulky (2,6-diisopropyl)phenyl ester moiety gave **3am** in 99% yield with 98% ee (entry 7).[25] The absolute configuration of **3am** was assigned to be *R* by analogy

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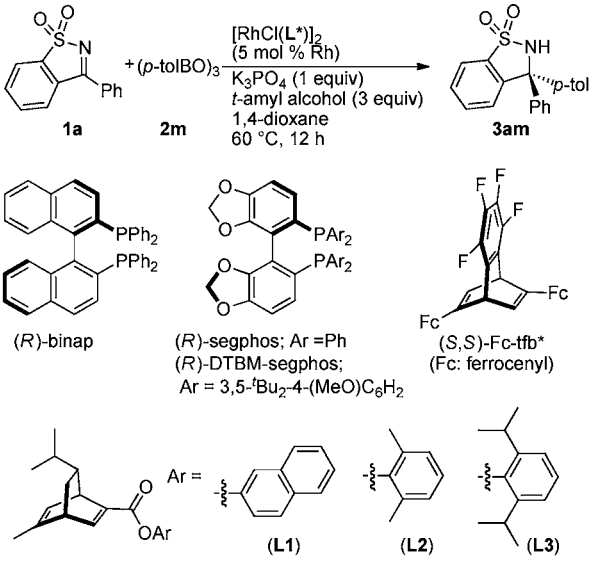
Table 1. Rhodium-Catalyzed Asymmetric Addition of *p*-Tolylboroxine (2m) to Ketimine 1a[a]



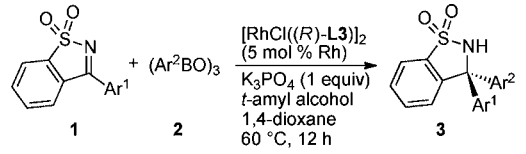
entry	ligand	yield (%)[b]	ee (%)[c]
1	(*R*)-binap	93	39
2	(*R*)-segphos	73	71
3	(*R*)-DTBM-segphos	10	9
4	(*S,S*)-Fc-tfb*	96	90
5	(*R*)-**L1**	94	78
6	(*R*)-**L2**	97	94
7	(*R*)-**L3**	99	98 (*R*)

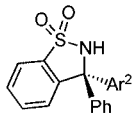
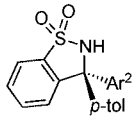
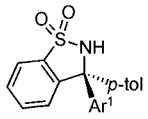
[a]Reaction conditions: ketimine **1a** (0.20 mmol), **2m** (0.13 mmol), [RhCl(**L***)]$_2$ (5 mol % of Rh), K_3PO_4 (0.20 mmol), *tert*-amyl alcohol (0.60 mmol), 1,4-dioxane (0.8 mL) at 60 °C for 12 h. [b]Isolated yields. [c]Determined by chiral HPLC analysis.

with (*R*)-**3au**, which was determined by X-ray crystallography (vide infra).

The present catalytic system can be applied to the asymmetric addition of several arylboroxines **2** to cyclic *N*-sulfonyl ketimines **1** with high enantioselectivity (Table 2). Aryl groups having a variety of substituents at the *ortho*, *meta*, and *para* position of phenyl were successfully introduced to the azomethine carbon of **1a** to give the corresponding benzosultams **3am**−**3aw** in high yields with over 94% ee (entries 1−11). The addition of phenylboroxine (**2x**) to ketimine **1b** substituted with a *p*-tolyl group, which is a reverse combination of the reaction of **1a** with **2m**, gave an opposite enantiomer ((*S*)-**3bx**) of **3am** in 94% yield with 97% ee (entry 12). A benzosultam **3bn** substituted with a *meta*- and a *para*-tolyl group was also synthesized with 97% ee (entry 13). The addition of *p*-tolylboroxine to ketimines **1c**−**1g** possessing several aromatic rings substituted with both an electron-donating (MeO) and -withdrawing groups (F, Cl, CF_3) proceeded to give the corresponding benzosultams **3cm**−**3gm** in high yields with high enantioselectivity (entries 14−18). Ketimines bearing heteroaromatic rings, 2-furyl (**1h**) and 2-thienyl (**1i**), are also good substrates to give the corresponding benzosultams **3hm** and **3im** with 99% and 93% ee, respectively (entries 19 and 20).

Table 2. Rhodium-Catalyzed Asymmetric Addition of Arylboroxines 2 to Ketimine 1[a]

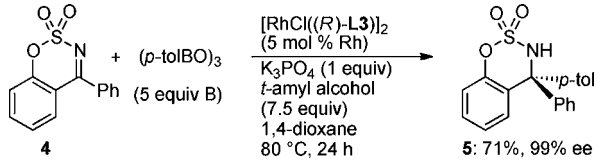


products	entry		Ar^1 or Ar^2	isolated yield (%)	ee (%)[b]
	1	**3am**	Ar^2 = 4-MeC_6H_4	99	98
	2	**3an**	Ar^2 = 3-MeC_6H_4	99	97
	3[c]	**3ao**	Ar^2 = 2-MeC_6H_4	76	99
	4	**3ap**	Ar^2 = 4-MeOC_6H_4	97	98
	5[d]	**3aq**	Ar^2 = 3-MeOC_6H_4	96	99
	6[d]	**3ar**	Ar^2 = 3,4-(CH_2OCH_2)C_6H_3	99	98
	7[e]	**3as**	Ar^2 = 3,4,5-(MeO)$_3C_6H_2$	98	95
	8[d]	**3at**	Ar^2 = 2-naphthyl	95	98
	9	**3au**	Ar^2 = 4-FC_6H_4	92	94
	10[d]	**3av**	Ar^2 = 4-ClC_6H_4	91	94
	11[d]	**3aw**	Ar^2 = 4-$CF_3C_6H_4$	70	94
	12	**3bx** (**3am**)	Ar^2 = Ph	94	97
	13	**3bn**	Ar^2 = 3-MeC_6H_4	97	97
	14[e]	**3cm**	Ar^1 = 4-MeOC_6H_4	92	98
	15	**3dm**	Ar^1 = 3-FC_6H_4	97	97
	16	**3em**	Ar^1 = 3-ClC_6H_4	98	98
	17	**3fm**	Ar^1 = 4-ClC_6H_4	98	97
	18	**3gm**	Ar^1 = 4-$CF_3C_6H_4$	94	98
	19	**3hm**	Ar^1 = 2-furyl	97	99
	20	**3im**	Ar^1 = 2-thienyl	99	93

[a]Reaction conditions: ketimine **1** (0.20 mmol), arylboroxine **2** (0.13 mmol), [RhCl((*R*)-**L3**)]$_2$ (5 mol % of Rh), K_3PO_4 (0.20 mmol), *tert*-amyl alcohol (0.60 mmol), 1,4-dioxane (0.8 mL) at 60 °C for 12 h. [b]Determined by chiral HPLC analysis. [c]At 80 °C for 24 h using 0.33 mmol of **2m** with *tert*-amyl alcohol (1.50 mmol). [d]For 24 h using 0.20 mmol of **2** with *tert*-amyl alcohol (0.90 mmol). [e]Performed using 0.20 mmol of **2** with *tert*-amyl alcohol (0.90 mmol).

The reaction of the cyclic ketimine **4** with *p*-tolylboroxine (**2m**) in the presence of the Rh/(*R*)-**L3** catalytic system also proceeded to give the sulfamidate **5** in 71% yield with 99% ee (Scheme 2).

Scheme 2. Asymmetric Arylation of Ketimine 4



The absolute configuration of the benzosultam **3au** was determined to be *R* by X-ray crystallographic analysis (Figure 1). The absolute configuration is in good agreement with the stereochemical model shown in Scheme 3. Thus, imine **1a** coordinates to a rhodium with its *re*-face avoiding the steric interaction between the sulfonyl moiety of **1a** and the ester group on the ligand, which is similar to the arylation of imines that we previously reported.[4c]

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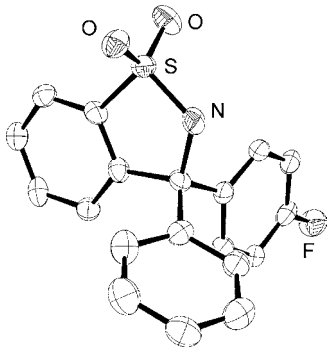
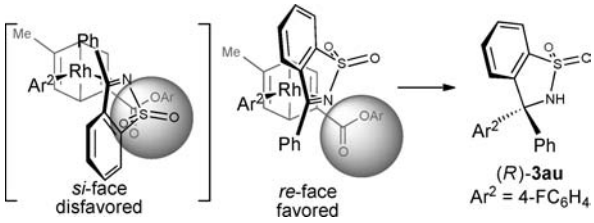


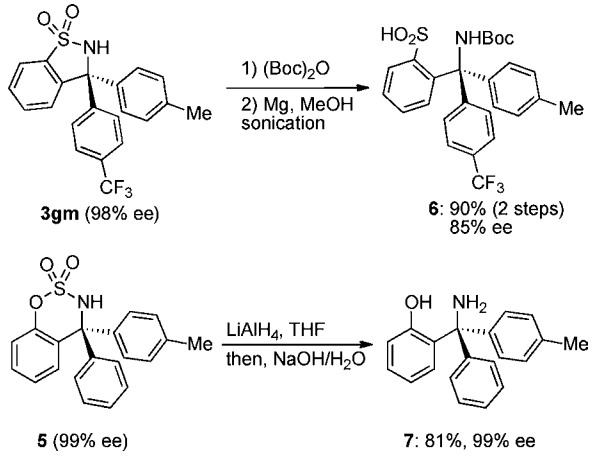
Figure 1. ORTEP illustration of **3au** with thermal ellipsoids drawn at 50% probability level (hydrogens are omitted for clarity).

Scheme 3. Stereochemical Model



The benzosultams obtained here with high enantioselectivity can be converted into chiral (triaryl)methylamines (Scheme 4).

Scheme 4. Transformations into (Triaryl)methylamines



Thus, introduction of a Boc group on the nitrogen atom of **3gm** (98% ee) followed by reductive cleavage of the S−N bond by magnesium in methanol[26] gave (triaryl)methylamine **6** in 90% yield in two steps, although partial racemization was observed (85% ee).[27] On the other hand, treatment of sulfamidate **5** (99% ee) with $LiAlH_4$[18d] gave the corresponding (triaryl)methylamine **7** in 81% yield without loss of the enantiomeric purity.

In summary, we have developed the asymmetric synthesis of benzosultams bearing an α-triaryl-substituted stereogenic center in the enantioselective addition of arylboroxines to cyclic *N*-sulfonyl ketimines catalyzed by a rhodium/chiral diene complex.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and compound characterization data (PDF and CIF). 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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