Asymmetric Catalysis

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High Performance of a Palladium Phosphinooxazoline Catalyst in the Asymmetric Arylation of Cyclic *N*-Sulfonyl Ketimines**

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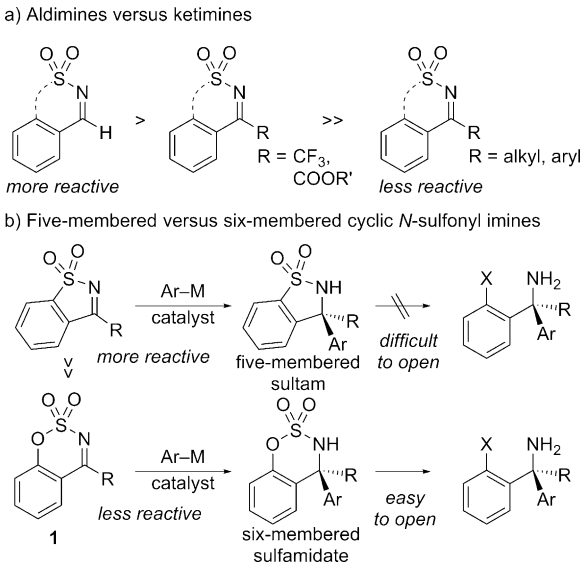
Abstract: *A cationic palladium complex with a chiral phosphine-oxazoline ligand (iPr-phox) showed high catalytic activity and enantioselectivity in the asymmetric addition of arylboronic acids to six-membered cyclic N-sulfonyl ketimines to give high yields of the corresponding chiral cyclic sulfamidates with 96–99.9% ee. The products have tetrasubstituted stereogenic centers with an amino group and a triaryl or alkyldiaryl group as substituents.*

The rhodium- or palladium-catalyzed asymmetric addition of arylboron reagents to imines is one of the most efficient methods of producing chiral disubstituted and trisubstituted methylamines.[1,2] Among the imines used for the asymmetric arylation, cyclic *N*-sulfonyl imines have recently attracted considerable attention owing to their advantages over others; they have generally higher reactivity towards the catalytic arylation and their cyclic structure makes the enantioface differentiation of imines easier and simpler because no *syn*–*anti* equilibration takes place.[3–6] A summary of the catalytic asymmetric arylation reactions of cyclic *N*-sulfonyl imines reported to date with rhodium (Hayashi,[3] Lam,[4] Xu[5]) and palladium (Zhang)[6] complexes as catalysts is illustrated in Scheme 1. The cyclic *N*-sulfonyl imines used as the arylation substrates are classified into aldimines and ketimines, of which the former are in general more reactive than the latter and some of the ketimines substituted with electron-withdrawing groups such as ester and CF_3 are as reactive as aldimines. The cyclic *N*-sulfonyl imines used so far are either five-membered ring imines leading to benzosultams or six-membered ring imines **1** leading to benzosulfamidates. Although the five-membered ring imines are highly reactive, giving the corresponding sultams upon arylation even for ketimines, the ring cleavage giving the corresponding chiral methylamines without loss of enantiomeric purity is not trivial.[3a] On the other hand, the six-membered imines **1** are less reactive toward the arylation, whereas the resulting sulfamidates are known to undergo ring opening without loss of enantiomeric purity.[3a,4a,5b,7] To date there have been very few reports on the catalytic asymmetric addition to six-membered ketimines **1** (R = alkyl, aryl) in high yields.[3–6]



Scheme 1. Reactivity and utility of cyclic *N*-sulfonyl imines.

During our studies on the catalytic asymmetric addition of organoboron reagents to carbon–carbon and carbon–heteroatom double bonds,[8,9] we found that a cationic palladium complex containing a chiral phosphine-oxazoline ligand showed high catalytic activity and high enantioselectivity in the asymmetric addition of arylboronic acids to cyclic *N*-sulfonyl ketimines **1** (R = alkyl, aryl), giving high yields of the corresponding chiral cyclic sulfonamides, which bear a tetrasubstituted stereogenic center.[10]

The results obtained for the addition of phenylboronic acid (**2m**) to *N*-sulfonyl aldimine **1a** (R = H) and ketimine **1b** (R = Me) in the presence of a cationic palladium complex coordinated with (*S*)-*i*Pr-phox[11] are summarized in Table 1. For comparison, this Table also contains the results of reactions in the presence of other palladium and rhodium complexes, which have been previously reported as effective catalysts for the asymmetric arylation of *N*-sulfonyl imines. The best result was obtained with the catalyst generated in situ from $PdCl_2$[(*S*)-*i*Pr-phox][12] and $AgBF_4$ in dichloroethane. Thus, aldimine **1a** was reacted with **2m** (2 equiv relative to **1a**) in the presence of 5 mol% of the cationic palladium catalyst in dichloroethane at 65–70 °C for 12 h to give a quantitative yield of the *R* isomer[5a] of the phenylation product **3am** with 99.6% *ee* (entry 1). The same conditions

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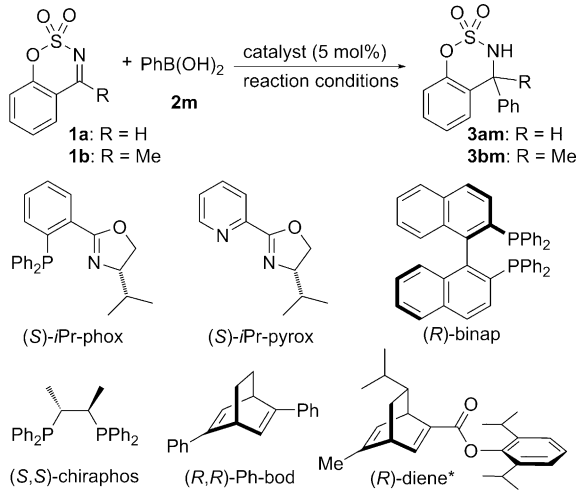
Table 1: Catalytic asymmetric addition of phenylboronic acid (**2m**) to cyclic *N*-sulfonyl aldimine **1a** and ketimine **1b**.[a]



	Catalyst [5 mol%] additives	Solvent T [°C], t [h]	**3am** Yield[b] (*ee*[c])	**3bm** Yield[b] (*ee*[c])
1	$PdCl_2$[(*S*)-*i*Pr-phox] $AgBF_4$	$ClCH_2CH_2Cl$ 65–70, 12	99% (99.6% *ee*, *R*)	**99%** (99.5% *ee*, *R*)
2	$PdCl_2$[(*S*)-*i*Pr-phox]	$ClCH_2CH_2Cl$ 65–70, 12	0% (–)	0% (–)
3	$PdCl_2$[(*S*)-*i*Pr-phox] AgOTf	$ClCH_2CH_2Cl$ 65–70, 12	10% (–)	0% (–)
4	$Pd(OCOCF_3)_2$ (*S*)-*i*Pr-phox	CF_3CH_2OH 80, 20	99% (92% *ee*, *R*)	58% (99.8% *ee*, *R*)
5	$PdCl_2$[(*S*,*S*)-chiraphos] $AgBF_4$	$ClCH_2CH_2Cl$ 65–70, 12	50% (84% *ee*, *S*)	0% (–)
6	$PdCl_2$[(*S*)-binap] $AgBF_4$	$ClCH_2CH_2Cl$ 65–70, 12	42% (94% *ee*, *S*)	0% (–)
7	$Pd(OCOCF_3)_2$ (*S*)-*i*Pr-pyrox	CF_3CH_2OH 80, 20	90% (68% *ee*, *R*)	7% (–)
8	$PdCl_2$[(*S*)-*i*Pr-pyrox] $AgBF_4$	CF_3CH_2OH 80, 20	99% (77% *ee*, *R*)	0% (–)
9	$PdCl_2$[(*S*)-*i*Pr-pyrox] $AgBF_4$	$ClCH_2CH_2Cl$ 65–70, 12	99% (80% *ee*, *R*)	0% (–)
10	$[RhCl((R,R)\text{-Ph-bod})]_2$ K_3PO_4, *t*-amyl alcohol	dioxane 60, 12	99% (98.0% *ee*, *R*)	76% (97.0% *ee*, *R*)
11	$[RhCl((R)\text{-diene}^*)]_2$ K_3PO_4, *t*-amyl alcohol	dioxane 60, 12	99% (99.6% *ee*, *R*)	30% (99.3% *ee*, *R*)
12	$[RhCl((S)\text{-binap})]_2$ K_3PO_4, *t*-amyl alcohol	dioxane 60, 12	26% (89% *ee*, *S*)	<3% (–)

[a] Reaction conditions: **1a** (0.10 mmol), **2m** (0.20 mmol), catalyst (5 mol%), additive, solvent (1.0 mL) at a given temperature for 12 h. [b] Yield of isolated **3am** or **3bm**. [c] Determined by HPLC analysis with a chiral stationary phase. The absolute configurations of **3am** and **3bm** were determined by comparison of their optical rotations with those reported.[5a,6]

were successfully applied to the reaction of ketimine **1b**, which gave the corresponding phenylation product (*R*)-**3bm**[6] in 99.5% *ee* and a quantitative yield (entry 1). The generation of the cationic palladium species is essential for the high catalytic activity. In the absence of $AgBF_4$, no phenylation was observed for either aldimine **1a** or ketimine **1b** (entry 2). Using AgOTf as the silver salt is not a good choice and resulted in a low yield (10%) of **3am** and no reaction to **3bm** (entry 3). A palladium complex generated from $Pd(OCOCF_3)_2$ and (*S*)-*i*Pr-phox efficiently catalyzed the phenylation of aldimine **1a** in CF_3CH_2OH at 80°C, but its catalytic activity was lower for ketimine **1b**, giving a modest yield (58%) of (*R*)-**3bm** although the enantioselectivity was high (99.8% *ee*) (entry 4). Cationic palladium bisphosphine complexes[13] generated by mixing $PdCl_2$[(*S*,*S*)-chiraphos] and $PdCl_2$[(*S*)-binap] with $AgBF_4$ were less catalytically active than that with the phosphine-oxazoline, (*S*)-*i*Pr-phox, as a ligand. They catalyzed the phenylation of aldimine **1a** to some extent, but did not convert ketimine **1b** (entries 5 and 6). Palladium complexes with the chiral oxazoline-pyridine ligand (*S*)-*i*Pr-pyrox and its derivatives, have been reported by Zhang and co-workers to be catalytically active for the addition to five-membered-ring ketimines.[6] In our hands, the palladium catalyst system described by Zhang and co-workers, $Pd(OCOCF_3)_2$ and (*S*)-*i*Pr-pyrox in CF_3CH_2OH, did not catalyze the phenylation of ketimine **1b** well,[14,15] whereas it was highly active in the phenylation of aldimine **1a** (entry 7). A cationic palladium complex generated by the addition of $AgBF_4$ to $PdCl_2$[(*S*)-*i*Pr-pyrox] also catalyzed the addition to aldimine **1a** very efficiently, but was not active for ketimine **1b** in either CF_3CH_2OH or dichloroethane (entries 8 and 9). Chiral diene/rhodium catalysts, which we previously reported to be the most active in the asymmetric arylation of ketimines including the five-membered-ring ketimines, catalyzed the phenylation of aldimine **1a** to give **3am** with high *ee* and a quantitative yield (entries 10 and 11). They also catalyzed the asymmetric phenylation of ketimine **1b** with high enantioselectivity, but the yields of **3bm** are not as high as those obtained with the present cationic palladium/(*S*)-*i*Pr-phox catalyst. The binap–rhodium catalyst was less active than the diene–rhodium as was reported previously[3a] (entry 12).

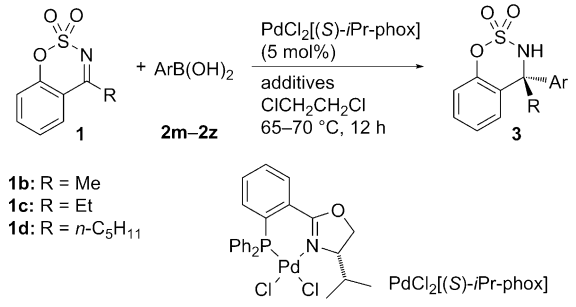
By monitoring the reaction progress of the palladium-catalyzed addition of boron reagents to ketimine **1b** to compare the Pd/phox catalyst with the Pd/pyrox catalyst (entry 1 versus 7), we found that the low yield with the Pd/pyrox catalyst is mainly due to the short lifetime of the catalyst system. Thus, the reaction with Pd/pyrox catalyst gave 7% yield of the product **3bm** within 10 min, but the yield did not increase after a reaction time of 10 min. In contrast, the Pd/phox catalyst was found to keep its high catalytic activity for at least one hour to give a high yield of **3bm.**

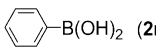
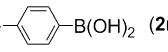
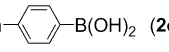
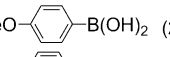
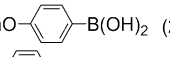
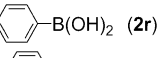
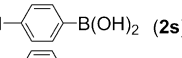
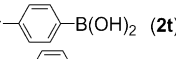
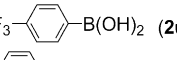
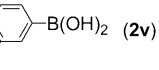
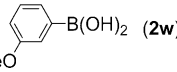
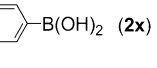
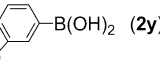
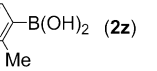
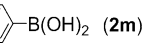
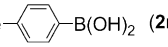
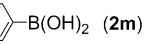
The cationic palladium catalyst generated from $PdCl_2$[(*S*)-*i*Pr-phox] and $AgBF_4$ was widely applicable in the asymmetric addition of arylboronic acids to the methyl-substituted ketimine **1b** (Table 2). The addition of phenylboronic acids with a substituent (methyl, phenyl, phenoxy, and halides) at the *para* position gave the corresponding arylation products in high enantioselectivities (>98% *ee*) and yields (entries 3, 5–8). For those arylboronic acids which are not reactive enough to give high yields of the arylation products under the standard conditions (conditions A), the use of $AgSbF_6$ and K_3PO_4 as additives (conditions B) increased the chemical yields and maintained the high enantioselectivity. The effects of the additives are summarized in entries 12–15 for the addition of 3-$MeOC_6H_4B(OH)_2$ (**2w**) to ketimine **1b**. The reaction under the reaction conditions A ($AgBF_4$) gave only a modest yield (56%) of the arylation product **3bw**, though

the enantioselectivity was high (99.5% *ee*). With $AgSbF_6$ (conditions C) the yield was increased to 90%, but the product was racemic. This is probably due to acid-contaminated $AgSbF_6$, which causes the racemization of the product via a benzylic cation intermediate. Addition of K_3PO_4 as a weak base together with $AgSbF_6$ inhibited the racemization and resulted in a high yield and *ee* of **3bw**. The combination of K_3PO_4 and $AgBF_4$ did not improve the yield of the product. Under the reaction conditions B, *meta*- and *ortho*-substituted phenylboronic acids gave the corresponding arylation products with high *ee* (entries 16–18). The high catalytic activity and high enantioselectivity were also observed in the addition of boronic acids to cyclic ketimines **1c** and **1d**, which are ethyl and pentyl imines, respectively (entries 19–21).

The asymmetric addition of boron reagents to cyclic ketimines with aryl groups on the imine carbon is more challenging, because these ketimines are less reactive than those with alkyl groups, and the arylation products (triarylmethylamines) are more likely to undergo racemization under the reaction conditions (Table 3). The reaction of

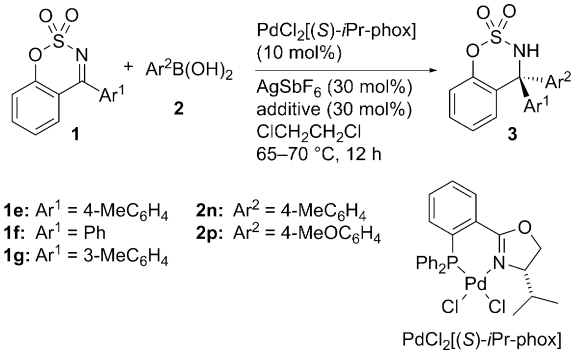
Table 2: Palladium-catalyzed asymmetric addition of arylboronic acids **2m–z** to cyclic *N*-sulfonyl ketimines **1b–d**.[a]

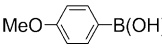
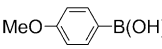
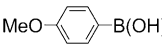
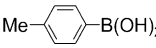


	1, conditions[b]	$ArB(OH)_2$ 2	3, yield [%][c]	*ee* [%][d]
1	**1b**, A	 (**2m**)	**3bm**, 99	99.5 (*R*)
2	**1b**, B		**3bm**, 99	99.6 (*R*)
3	**1b**, A	 (**2n**)	**3bn**, 99	98.1 (*R*)
4	**1b**, A	 (**2o**)	**3bo**, 99	98.8 (*R*)
5	**1b**, B	 (**2p**)	**3bp**, 99	99.9 (*R*)
6	**1b**, A	 (**2q**)	**3bq**, 99	98.6 (*R*)
7	**1b**, A	 (**2r**)	**3br**, 87	98.4 (*R*)
8	**1b**, A	 (**2s**)	**3bs**, 88	99.4 (*R*)
9	**1b**, A	 (**2t**)	**3bt**, 95	99.9 (*R*)
10	**1b**, B	 (**2u**)	**3bu**, 51	99.4 (*R*)
11	**1b**, A	 (**2v**)	**3bv**, 99	99.4 (*R*)
12	**1b**, A		**3bw**, 56	99.5 (*R*)
13	**1b**, B	 (**2w**)	**3bw**, 88	99.9 (*R*)
14	**1b**, C[e]		**3bw**, 90	0
15	**1b**, D[e]		**3bw**, 48	99.7 (*R*)
16	**1b**, B	 (**2x**)	**3bx**, 95	99.7 (*R*)
17	**1b**, B	 (**2y**)	**3by**, 98	99.9 (*R*)
18	**1b**, B	 (**2z**)	**3bz**, 51	99.9 (*R*)
19	**1c**, B	 (**2m**)	**3cm**, 99	99.5 (*R*)
20	**1c**, A	 (**2n**)	**3cn**, 99	99.5 (*R*)
21	**1d**, A	 (**2m**)	**3dm**, 99	99.4 (*R*)

[a] Reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), $PdCl_2$[(*S*)-*i*Pr-phox] (5 mol%), additive, dichloroethane (1.0 mL) at 65–70°C for 12 h. [b] Conditions A: $AgBF_4$ (15 mol%). Conditions B: $AgSbF_6$ (15 mol%) and K_3PO_4 (15 mol%). [c] Yield of the isolated product. [d] Determined by HPLC analysis with a chiral stationary phase. The absolute configurations are proposed to be *R* by similarity of the stereochemical pathway to that giving (*R*)-**3bm**. [e] Conditions C: $AgSbF_6$ (15 mol%). Conditions D: $AgBF_4$ (15 mol%) and K_3PO_4 (15 mol%).

Table 3: Palladium-catalyzed asymmetric addition of arylboronic acids **2** to cyclic *N*-sulfonyl aryl ketimines **1e–g**.[a]



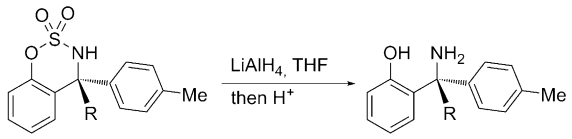
	1, additive	$Ar^2B(OH)_2$ 2	3, yield [%][b]	*ee* [%][c]
1	**1e**, –		**3ep**, 75	0
2	**1e**, K_3PO_4		**3ep**, 73	0
3	**1e**, K_2CO_3	 (**2p**)	**3ep**, 70	0
4	**1e**, NEt_3		**3ep**, 63	81
5	**1e**, proton sponge		**3ep**, 80	99.2
6	**1f**, proton sponge	 (**2p**)	**3fp**, 65	99.6
7	**1g**, proton sponge	 (**2p**)	**3gp**, 75	96
8	**1g**, proton sponge	 (**2n**)	**3gn**, 68	97

[a] Reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), $PdCl_2$[(*S*)-*i*Pr-phox] (10 mol%), $AgSbF_6$ (30 mol%), additive (30 mol%), dichloroethane (1.0 mL) at 65–70°C for 12 h. [b] Yield of isolated product. [c] Determined by HPLC analysis with a chiral stationary phase.

ketimine **1e** with 4-methoxyphenylboronic acid (**2p**) in the presence of $PdCl_2$[(*S*)-*i*Pr-phox] (10 mol%) and $AgSbF_6$ (30 mol%) proceeded well to give the corresponding arylation product **3ep** in 75% yield as a racemate (entry 1). The formation of racemic product was also observed in the presence of the inorganic base K_3PO_4 (30 mol%), which corresponds to conditions B in Table 2, or K_2CO_3 (entries 2 and 3).[16] Finally, it was found that the addition of proton sponge prevents the product from racemization under the reaction conditions (entry 5). In the presence of proton

sponge, several triarylmethylamine products were obtained with high enantioselectivity (entries 6–8).

Treatment of the asymmetric arylation products **3cn** and **3gn** with $LiAlH_4$ gave the corresponding 2-hydroxyphenylmethylamines **4cn** and **4gn**, respectively, without loss of their enantiomeric purity (Scheme 2).[7b]



R = Et: (*R*)-**3cn** (99.5% *ee*) — 81% yield: (*R*)-**4cn** (99.4% *ee*)
R = 3-MeC_6H_4: (*S*)-**3gn** (97% *ee*) — 75% yield: (*S*)-**4gn** (97% *ee*)

Scheme 2. Ring opening of the asymmetric arylation products **3**.

In summary, a cationic palladium complex with a chiral phosphine-oxazoline ligand (*i*Pr-phox) showed high catalytic activity and enantioselectivity in the asymmetric addition of arylboronic acids to six-membered cyclic *N*-sulfonyl ketimines to give the chiral cyclic sulfamidates in high yields and with 96–99.9% *ee*. The products bear a tetrasubstituted stereogenic center.

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