Asymmetric Allylation

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Enantioselective Rhodium-Catalyzed Nucleophilic Allylation of Cyclic Imines with Allylboron Reagents**

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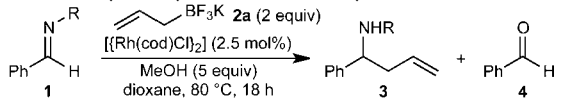
Enantioselective rhodium(I)-catalyzed additions of organoboron reagents to π electrophiles are a major class of reactions for the generation of enantioenriched chiral compounds.[1] Attractive features of these reactions include: (i) the availability of a wide range of chiral ligands that impart high enantioselectivities across several classes of electrophiles; (ii) relatively mild reaction conditions, and (iii) the availability, stability, functional group tolerance, and usually low toxicity of organoboron reagents. To date, this field has been dominated by the enantioselective addition of arylboron reagents,[1] although there have also been reports of additions of alkenylboron[2] and alkynylboron reagents.[3–5] Notably, the corresponding rhodium-catalyzed enantioselective additions of allylboron reagents have not been described,[6,7] despite the widespread importance of nucleophilic allylations in synthesis.[8,9] Herein, we describe the first enantioselective rhodium-catalyzed additions of allylboron reagents to π electrophiles in the form of asymmetric allylation reactions involving cyclic imines and potassium allyltrifluoroborates. Not only do aldimines undergo highly enantioselective allylations, ketimines are also effective substrates. Furthermore, highly stereoselective additions of substituted allyltrifluoroborates are described.

The importance of chiral homoallylic amines as building blocks for chemical synthesis has led to significant efforts to develop catalytic enantioselective nucleophilic allylations of imines and their derivatives.[8b,10,11] However, processes that employ allylboron reagents constitute a field that is still in its infancy,[8b,10,12,13] and we therefore selected this area in which to develop a new rhodium-catalyzed variant that could offer increased substrate scope and utility. Our experiments began with attempted allylation reactions involving various benzaldehyde-derived imines and potassium allyltrifluoroborate (2 equivalents)[14,15] in the presence of 2.5 mol% of [{Rh(cod)Cl}$_2$] and MeOH (5 equivalents) in dioxane at 80°C (Table 1). Unfortunately, satisfactory results were not obtained. With *N*-phenyl or *N*-diphenylphosphinoyl imines, only starting material was recovered (Table 1, entries 1 and 2), whereas trace quantities of the allylation product were observed using a dimethylsulfamyl imine (Table 1, entry 3).

Table 1: Rh-catalyzed allylation of benzaldehyde-derived imines.[a]



Entry	R	**1** [%][b]	**3** [%][b]	**4** [%][b]
1	Ph	>95	<5	<5
2	P(O)Ph$_2$	>95	<5	<5
3	SO_2NMe_2	85	5	10
4	Ts	60	25	15
5	Ns	42	28	30

[a] Reactions were conducted using 0.10 mmol of **1**. [b] Determined by ^{1}H NMR analysis of the unpurified reaction mixtures. cod = 1,5-cyclooctadiene, Ns = *p*-nitrobenzenesulfonyl, Ts = *p*-toluenesulfonyl.

With more reactive *N*-sulfonylimines, appreciable quantities of homoallylic sulfonamides were obtained, but significant quantities of starting imine remained, along with benzaldehyde resulting from imine hydrolysis (Table 1, entries 4 and 5).

In light of our recent discovery that cyclic imines are highly effective substrates for enantioselective rhodium-catalyzed alkenylations,[16] the allylation of benzoxathiazine-2,2-dioxide **5a** was investigated (Table 2). Under reaction conditions identical to those employed in Table 1, complete consumption of **5a** was observed after 3 h to give **6a** in 87% yield upon isolation (Table 2, entry 1). Next, the use of chiral ligands was examined. Whereas the use of (*R*)-binap (**L1**) was totally ineffective in promoting the reaction (Table 2, entry 2), the use of chiral diene **L2**[17,18] provided (*R*)-**6a** in 60% conversion with a promising 67% *ee* (Table 2, entry 3). However, using 2.5 mol% of the rhodium complex derived from chiral diene **L3**,[16,19] (*R*)-**6a** was obtained in greater than 95% conversion and 93% *ee* (Table 2, entry 4).[20] The results tabulated in Tables 1 and 2 clearly highlight the benefits of a cyclic imine structure in facilitating efficient allylation.[21] It should be noted that the use of potassium allyltrifluoroborate (**2a**) was essential for high enantioselectivity; repeating the reaction in Table 2, entry 4 using allylboronic acid pinacol ester in place of **2a**, with the addition of aqueous K_3PO_4 (0.5 equivalents), led to (*R*)-**6a** in greater than 95% conversion, but in only 28% *ee*. The reasons for this lower selectivity are not clear at the present time.

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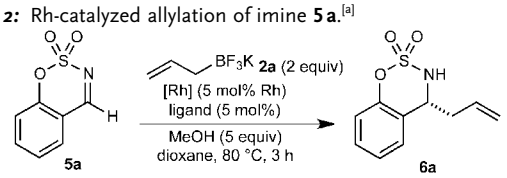
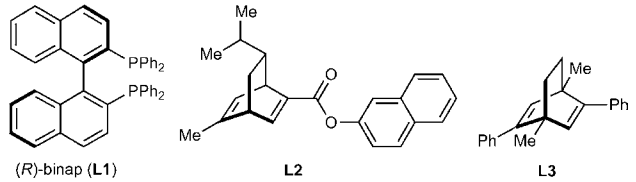
Table 2: Rh-catalyzed allylation of imine **5a**.[a]





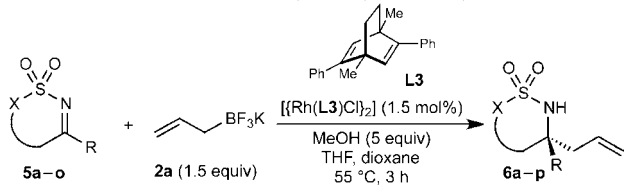
Entry	[Rh] (2.5 mol%)	Ligand (5 mol%)	Conv [%][b]	*ee* [%][c]
1	$[\{Rh(cod)Cl\}_2]$	none	>95[d]	–
2	$[\{Rh(C_2H_4)_2Cl\}_2]$	**L1**	<5	–
3	$[\{Rh(C_2H_4)_2Cl\}_2]$	**L2**	60	67
4	$[\{Rh(\mathbf{L3})Cl\}_2]$	none	>95	93

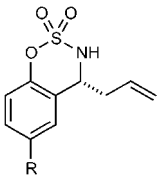
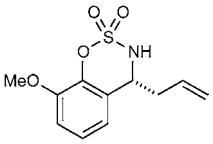
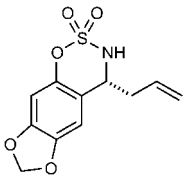
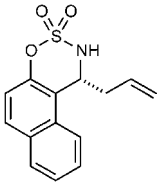
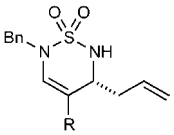
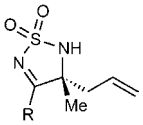
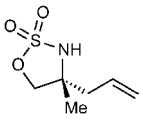
[a] Reactions were conducted using 0.10 mmol of **5a**. [b] Determined by ^{1}H NMR analysis of the unpurified reaction mixtures. [c] Determined by HPLC analysis on a chiral stationary phase. [d] *rac*-**6a** isolated in 87% yield.

With an effective ligand identified, the scope of this process was investigated under slightly modified reaction conditions (Table 3). Using 1.5 mol% of $[\{Rh(\mathbf{L3})Cl\}_2]$ and MeOH (5 equivalents) in a THF/dioxane mixture at 55°C, a wide range of cyclic imines underwent highly enantioselective allylations (90–99% *ee*) in generally good yields. Benzoxathiazine-2,2-dioxides containing various substituents (methyl, methoxy, halogen, cyano, or dioxole) were effective substrates (Table 3, entries 1–10), although in certain cases, the use of *i*PrOH (13 equivalents) in toluene/dioxane rather than MeOH in THF/dioxane was required to maintain high enantioselectivities (Table 3, entries 4–7). Other cyclic aldimines such as 1,2,6-thiadiazine-1,1-dioxides also underwent allylation (Table 3, entries 11–13), although the yields were lower in these cases. The process is not restricted to aldimines; cyclic ketimines such as 1,2,5-thiadiazolidine-1,1-dioxides (Table 3, entries 14 and 15) and a cyclic sulfamidate imine (Table 3, entry 16) are also viable substrates. These results (Table 3, entries 14–16) are notable because catalytic enantioselective allylations of ketimines are rare.[9g,12a,b]

The allylation of cyclic imines **5a** and **5o**[22] with more highly substituted potassium allyltrifluoroborates **2b—e** were also carried out (Table 4). In these reactions, clean allylic transposition took place to form a new carbon–carbon bond at the more substituted γ carbon atom of the allyltrifluoroborate. *E*-Crotyltrifluoroborate (**2b**) underwent highly enantioselective additions to **5a** and **5o** to afford *anti* products **7a** and **7e**, respectively, with high diastereoselectivities. Importantly, *Z*-crotyltrifluoroborate (**2c**) afforded the corresponding *syn* products **7b** and **7f** with high enantioselectivities, although the diastereomeric ratio in the case of **7b** was more modest (6:1 d.r.). Similar to **2b**, *E*-2-hexen-1-yltrifluoroborate (**2d**) afforded *anti* products with high levels of diastereo- and enantioselection (products **7c** and **7g**). Finally, prenyltrifluoroborate **2e** was also highly effective, reacting with aldimine **5a** to deliver reverse prenylation product **7d** from aldimine **5a** in 97% *ee*, and with ketimine **5o** to give **7h**, which contains two vicinal quaternary centers, in 95% *ee*.

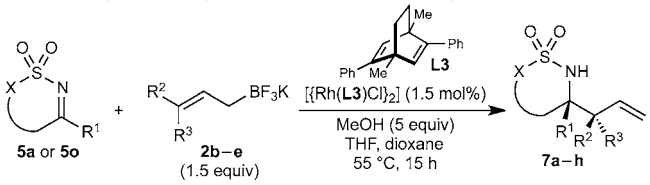
Table 3: Enantioselective Rh-catalyzed allylation of cyclic imines.

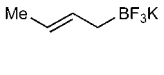
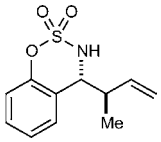
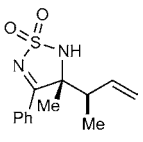
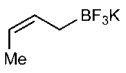
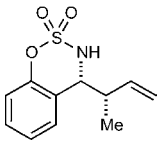
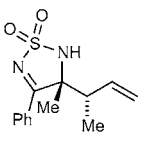
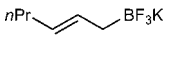
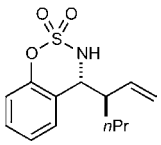
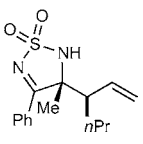
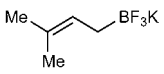
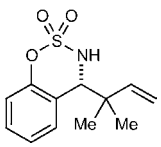
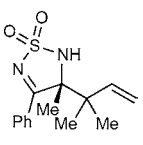


Entry	Product		Yield [%][a]	*ee* [%][b]
1		**6a** R = H	87	96
2		**6b** R = Me	93	97
3		**6c** R = OMe	92	91
4[c]		**6d** R = F	86	98
5[c]		**6e** R = Cl	96	96
6[c]		**6f** R = Br	79	94
7[c]		**6g** R = CN	97	98
8		**6h**	>95	95
9		**6i**	94	98
10		**6j**	95	93
11[d]		**6k** R = H	59	95
12[d]		**6l** R = Cl	65	94
13[d]		**6m** R = Br	45	90
14		**6n** R = Me	84	99[e]
15[f]		**6o** R = Ph	88	97
16[g]		**6p**	83	93[e]

[a] Yield of isolated product. [b] Determined by HPLC analysis on a chiral stationary phase. [c] Using *i*PrOH (13 equiv) in toluene/dioxane for a reaction time of 18 h. [d] Reaction time of 15 h. [e] Enantiomeric excess determined on the *N*-benzyl derivative. [f] Reaction time of 12 h. [g] Using dioxane in place of THF, at 80°C, for 15 h. Bn = benzyl.

Table 4: Allylation of cyclic imines with various allyltrifluoroborates.[a]

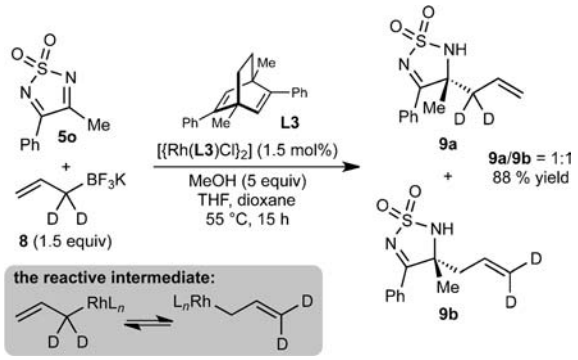


Allyltrifluoroborate	Product using **5a**	Product using **5o**
 **2b**	 **7a** 91% 15:1 d.r., 99% *ee*	 **7e** 68% >19:1 d.r., 97% *ee*
 **2c**	 **7b** 89%[b] 6:1 d.r., 99% *ee*	 **7f** 89% >19:1 d.r., 99% *ee*[c]
 **2d**	 **7c** 76%[b] 11:1 d.r., 99% *ee*	 **7g** 61%[b] 17:1 d.r., 99% *ee*
 **2e**	 **7d** 91% 97% *ee*	 **7h** 75% 95% *ee*

[a] Cited yields are of isolated pure major diastereomers (where relevant). Diastereomeric ratios were determined by ^{1}H NMR analysis of the unpurified reaction mixtures. Enantiomeric excess values were determined by HPLC analysis on a chiral stationary phase. [b] Yield of an isolated inseparable mixture of diastereomers. [c] Reaction time of 12 h.

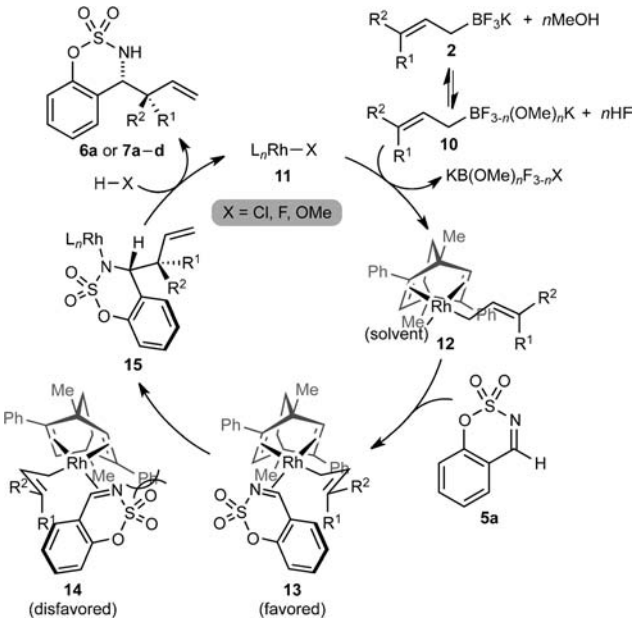
To gain some insight into the mechanism of these reactions, allylation of ketimine **5o** with dideuterated potassium allyltrifluoroborate **8** was conducted (Scheme 1).[23] This reaction resulted in a 1:1 mixture of products **9a** and **9b** in 88% yield, a result, which suggests that allylation proceeds via an allylrhodium(I) species that undergoes rapid interconversion between the two σ-allyl haptomers, thus scrambling the deuterium label.[24] Alternative mechanisms involving an allylboron species as the reactive intermediate would be expected to furnish **9b** only.[8]

Because *E*- and *Z*-crotyltrifluoroborates (**2b**) and (**2c**) provided *anti*- and *syn*-allylation products, respectively, with good to high diastereoselectivities (Table 2), it is likely that: (i) 6-membered cyclic transition states are operative, and (ii) the corresponding allylrhodium(I) intermediates have appreciable configurational stability during their lifetime in the reaction mixture despite the possibility of rapid interconversion between the two σ-allyl isomers, a process which could erode *E*/*Z* stereochemistry.[24,25]



Scheme 1. Deuterium-labeling experiment.

On the basis of these features, a possible catalytic cycle for these reactions, using imine **5a** for illustrative purposes, is shown in Scheme 2. Presumably, in the presence of MeOH, potassium allyltrifluoroborates can undergo reversible methanolysis to generate a mixed alkoxide/fluoride boron ate complex **10**,[26] which engages in transmetalation with the chiral diene-ligated rhodium complex **11** (where X = Cl, F, or OMe) to form the allylrhodium species **12**. Coordination of the imine **5a** then occurs in a way that minimizes unfavorable steric interactions between the imine activating group and a phenyl substituent of the ligand, as shown in **13**; such steric interactions would be present in the disfavored diastereomeric complex **14**. Allylation of the bound imine in **13** via a cyclic chairlike transition state would give **15**, which is then protonated through proton transfer from HX (X = Cl, F, or OMe) to release the product and regenerate **11**.



Scheme 2. Possible catalytic cycle.

In conclusion, a chiral diene-ligated rhodium complex has been shown to be highly effective in catalyzing the addition of potassium allyltrifluoroborates to cyclic aldimines and ketimines. To our knowledge, these reactions represent the first rhodium-catalyzed enantioselective nucleophilic allylations of π electrophiles with allylboron compounds, and proceed with generally good yields and high levels of diastereo- and enantioselection. Where relevant, the chiral allylrhodium(I) intermediates have appreciable *E*/*Z* configurational stability during the time scale of allylation, thus allowing access to different product diastereomers through the use of either *E*- or *Z*-allyltrifluoroborates. Further investigations of enantioselective rhodium-catalyzed nucleophilic allylations are underway, and the results of these studies will be reported in due course.

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Keywords: allyltrifluoroborates · asymmetric catalysis · enantioselectivity · imines · rhodium

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