Asymmetric Catalysis

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Enantioselective Rhodium-Catalyzed Addition of Potassium Alkenyltrifluoroborates to Cyclic Imines**

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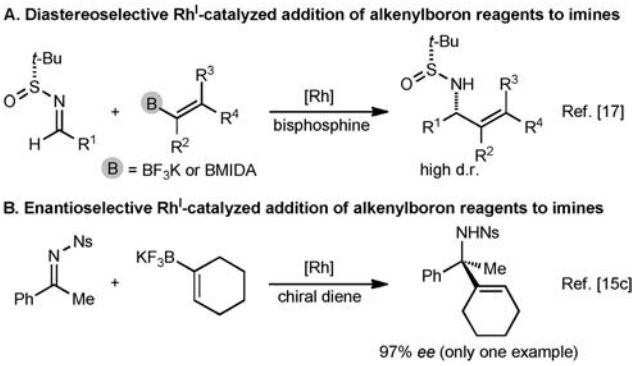
Chiral α-branched allylic amines are important building blocks for organic synthesis, and several catalytic asymmetric methods have been developed for their synthesis. For example, the enantioselective metal-catalyzed amination of allylic electrophiles[1–3] and the rearrangement of allylic imidates[4–6] have proven to be highly effective. An alternative approach to chiral allylic amines that can be advantageous from the viewpoint of convergency is the catalytic enantioselective union of an alkenyl nucleophile with an imine.[7–12] In view of the widespread success of enantioselective Rh^I-catalyzed additions of arylboron reagents to imines as a means to access chiral α-aryl-branched amines,[13–15] the development of the corresponding reactions of alkenylboron reagents to prepare chiral α-branched allylic amines should be an attractive goal. Surprisingly, however, only very limited precedent exists for this transformation.[16] Brak and Ellman have developed highly diastereoselective Rh^I-catalyzed additions of alkenylboron reagents to *N*-tert-butanesulfinyl aldimines (Scheme 1 A).[17] The only existing enantioselective variant is that of Shintani, Hayashi, and co-workers, who, as part of a study involving additions of potassium aryltrifluoroborates to *N*-sulfonyl ketimines, also described one example using an alkenyltrifluoroborate (Scheme 1 B).[15c] Also of relevance is a single example of an enantioselective Rh^I-catalyzed addition of an alkenylsilane to an *N*-sulfonyl aldimine.[18] Therefore, a general enantioselective Rh^I-catalyzed addition of alkenylboron reagents to imines remains undeveloped.

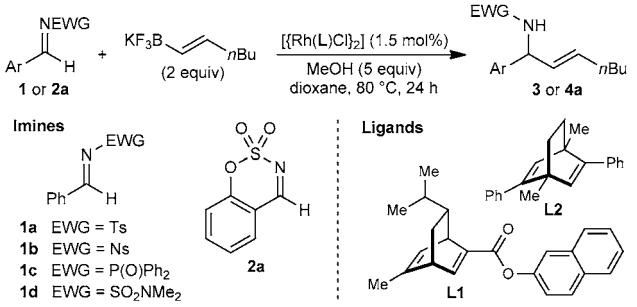
Herein, we demonstrate that cyclic imines are highly effective substrates for enantioselective Rh^I-catalyzed additions of potassium alkenyltrifluoroborates,[19,20] providing products in excellent enantioselectivities and generally good yields. The cyclic structure of these imines, in which the C=N bond is constrained in the *Z* geometry, appears to be important for the success of the reactions.



Scheme 1. Rh^I-catalyzed additions of alkenylborons to imines. MIDA = *N*-methyliminodiacetic acid.

This study began with the attempted alkenylation of acyclic imines **1a–d** with potassium (*E*)-1-hexenyltrifluoroborate (2 equiv) at 80 °C in dioxane for 24 h in the presence of MeOH (5 equiv) and 1.5 mol % of the dimeric rhodium complexes derived from chiral diene ligands[21,22] **L1**[15a] or **L2**[23] (Table 1). Given that imines **1a–d** are highly effective

Table 1: Attempted Rh-catalyzed alkenylation of various imines.



Entry	Imine	Ligand	Product	Yield [%][a]	*ee* [%][b]
1	**1a**	**L1**	**3a**	< 5	–
2		**L2**		< 5	–
3	**1b**	**L1**	**3b**	11	23
4		**L2**		80	7
5	**1c**	**L1**	**3c**	< 5[c]	–
6		**L2**		< 5[c]	–
7	**1d**	**L1**	**3d**	45	43
8		**L2**		55	55
9	**2a**	**L1**	**4a**	76	96
10		**L2**		> **95**	**98**

[a] Yield determined by NMR analysis using nitromethane as an internal standard. [b] Determined by HPLC analysis on a chiral stationary phase. [c] Significant decomposition of **1c** was observed.

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substrates for enantioselective Rh^I-catalyzed additions of arylboron reagents,[14] and chiral diene **L1** has provided excellent results in these types of reactions,[15a] we were surprised to find that imine alkenylation was far from straightforward.

Tosylimine **1a** and diphenylphosphinoylimine **1c** were not viable substrates, and no alkenylation was observed using **L1** (Table 1, entries 1 and 5). In these reactions, imine **1a** remained largely intact, but imine **1c** underwent significant decomposition. While appreciable alkenylation was observed using **L1** with both nosylimine **1b** and *N*,*N*-dimethylsulfamylimine **1d**, the enantiomeric excesses of the corresponding products were low (Table 1, entries 3 and 7). Similar results were obtained using **L2** as the ligand (Table 1, entries 2, 4, 6, and 8), with the exception that alkenylation was significant with nosylimine **1b** (entry 4).

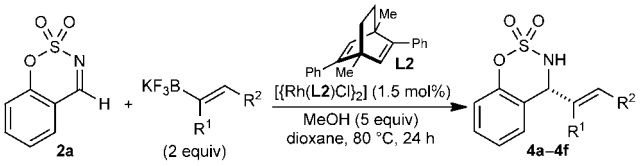
The results listed in Table 1, entries 1–8 clearly highlight the difficulties of these alkenylation reactions compared with the corresponding arylations.[13–15] The mostly poor conversions into the desired products may be explained by the fact that alkenylrhodium species are less stable than arylrhodium species, which renders protodeboronation or other decomposition pathways highly competitive with imine addition.[24] However, it is more difficult to rationalize the low enantioselectivities obtained when alkenylation was successful (Table 1, entries 3, 4, 7, and 8). One factor to consider in all catalytic asymmetric additions to imines is the possibility of *E*/*Z* isomerization of the imine during the reaction, which usually has a negative impact upon stereoselectivity.[7a] Although this issue does not appear to be problematic for Rh^I-catalyzed imine arylation,[13–15] we surmised that it could be important in imine alkenylation.

To test this theory, the alkenylation of benzoxathiazine-2,2-dioxide **2a**, a cyclic imine in which *E*/*Z* isomerization is precluded, was examined. Surprisingly, to our knowledge, benzoxathiazine-2,2-dioxides have been virtually unexplored as electrophiles in reactions with carbon nucleophiles.[25,26] We were therefore delighted to observe that under conditions identical to those employed for imines **1a–d**, imine **2a** provided the alkenylation product **4a** in high conversions and enantioselectivities (Table 1, entries 9 and 10), with ligand **L2** giving the best results (entry 10).[27]

Under the optimized conditions, imine **2a** smoothly reacted with various alkenyltrifluoroborates[28] containing alkyl (Table 2, entries 1, 3, and 4) or aryl (entry 5) substituents at the β-carbon to provide alkenylation products in good yields and high enantioselectivities (95–99% *ee*). In addition, vinylation was successful (Table 2, entry 2), and substitution at the α-carbon of the alkenyltrifluoroborate was tolerated (entry 6). Interestingly, conducting the experiments in Table 2, entries 2 and 3 with the corresponding alkenyl MIDA (*N*-methyliminodiacetic acid) in place of the alkenyltrifluoroborates under the conditions described by Brak and Ellman[17b] proceeded with less than 20% conversion into **4b** and **4c**, respectively.

Table 3 presents the alkenylation of more highly substituted benzoxathiazine-2,2-dioxides. Imines containing a range of arene substituents (including methyl, methoxy, chloro, bromo, and fluoro) at various positions were competent

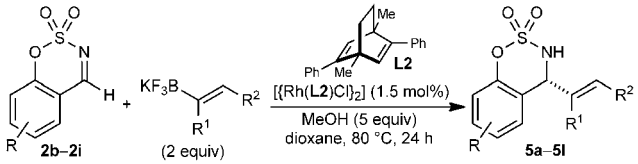
Table 2: Alkenylation of benzoxathiazine-2,2-dioxide **2a**.

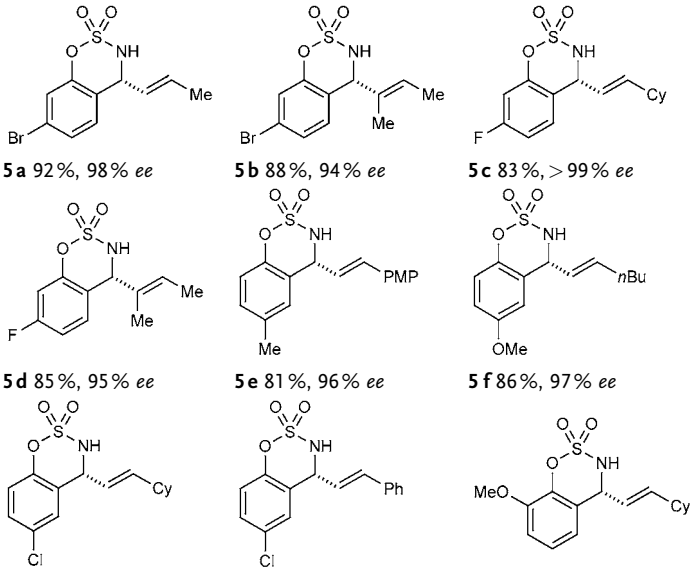


Entry	Trifluoroborate	Product	Yield [%][a]	*ee* [%][b]
1	KF_3B–*n*Bu	**4a**	90	98
2	KF_3B–	**4b**	75	98
3	KF_3B–Me	**4c**	79	97
4	KF_3B–Cy	**4d**	94	99
5	KF_3B–PMP	**4e**	88	95
6	KF_3B–Me, Me	**4f**	94	94

[a] Yield of isolated product. [b] Determined by HPLC analysis on a chiral stationary phase. PMP = *para*-methoxyphenyl, Cy = cyclohexyl.

Table 3: Alkenylation of various benzoxathiazine-2,2-dioxides.[a]

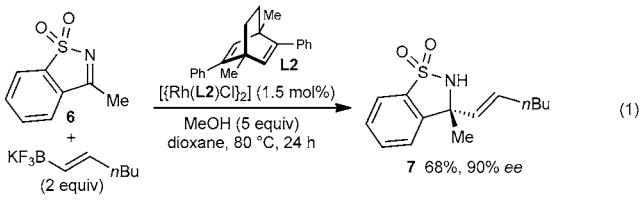




[a] Cited yields refer to isolated material. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase.

substrates, providing alkenylation products in ≥81% yield and ≥94% *ee* (products **5a–i**). However, the reaction of potassium vinyltrifluoroborate with a benzoxathiazine-2,2-dioxide containing the electron-donating dioxole group provided **5j** in only 50% yield, though in 97% *ee*. Presumably, the modest yield observed here is due to the greater propensity of potassium vinyltrifluoroborate to undergo protodeboronation or polymerization compared with its more sterically hindered counterparts, a problem that is compounded by the lower electrophilicity of this imine. As expected, a more highly substituted alkenyltrifluoroborate provided better results, with **5k** being formed in 93% yield and 94% *ee*. Finally, the benzoxathiazine-2,2-dioxide derived from 2-hydroxy-1-naphthaldehyde was also a suitable substrate, though owing to the steric hindrance associated with this imine, product **5l** was formed in a modest 55% yield.

Cyclic *N*-sulfonyl ketimine **6** was also a viable substrate, providing sultam **7** in 68% yield and 90% *ee* [Eq. (1)].[29] This result further confirms the beneficial effect of a cyclic imine structure, and demonstrates that the high efficiency of these reactions is not confined to benzoxathiazine-2,2-dioxides.



(1)

The sense of enantioinduction of these reactions[27] is consistent with the stereochemical model proposed for the 1,4-arylation of cyclic enones.[21a] Following this model, binding of the imine to the chiral diene-ligated alkenylrhodium species is suggested to occur in a manner that minimizes unfavorable nonbonding interactions between the imine activating group and one phenyl substituent of the ligand (Figure 1). Carborhodation from the *re* face of the imine then occurs to eventually provide the product.[30,31]

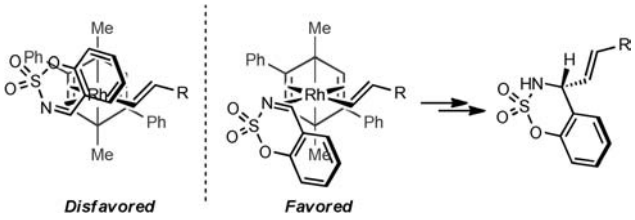
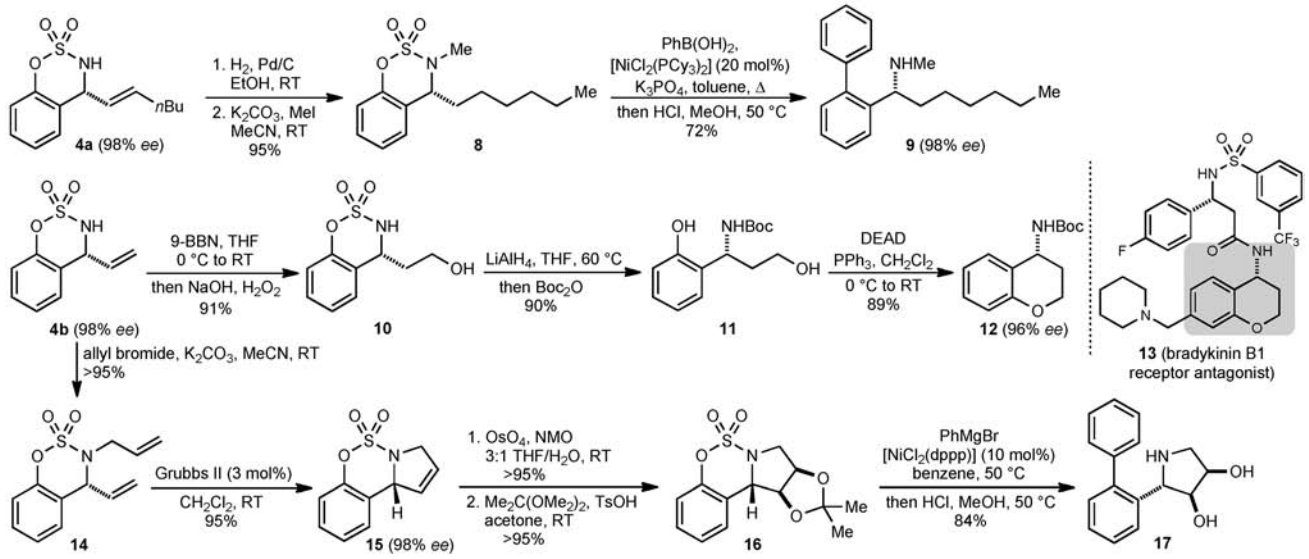


Figure 1. Possible stereochemical model for the formation of **4**.

Scheme 2 illustrates the utility of the alkenylation products. Aryl sulfamates have recently been shown to be highly effective in a range of nickel-catalyzed cross-coupling reactions.[32–34] For example, Wehn and Du Bois have described Kumada couplings of cyclic aryl sulfamates,[32b] and Garg and co-workers have developed Suzuki–Miyaura reactions of their acyclic counterparts.[33a,b] It was therefore of interest to ascertain whether nickel-catalyzed Suzuki–Miyaura reactions would be successful with cyclic aryl sulfamates derived from the alkenylation products of this study. To this end, **4a** was converted into cyclic sulfamate **8** by alkene hydrogenation followed by N-methylation. Gratifyingly, application of Garg's conditions[33a,b] for the Suzuki–Miyaura coupling of **8** with $PhB(OH)_2$ smoothly delivered the biaryl compound **9** in 72% yield after acid-mediated cleavage of the sulfamic acid intermediate.

Next, a hydroboration/oxidation sequence applied to **4b** gave alcohol **10** in 91% yield. Treatment of **8** with $LiAlH_4$ at reflux[35] followed by Boc_2O provided carbamate **11**, which was then converted into chroman-4-amine **12** by means of a Mitsunobu cyclization. Chroman-4-amines appear as core scaffolds in several drug candidates, for example in the human bradykinin B1 receptor antagonist **13**.[36]



Scheme 2. Further transformations of alkenylation products. 9-BBN = 9-borabicyclo[3.3.1]nonane, Boc = *tert*-butoxycarbonyl, DEAD = diethyl azodicarboxylate, NMO = *N*-methylmorpholine-*N*-oxide, dppp = 1,3-bis(diphenylphosphino)propane.

Finally, N-allylation of **4b** gave diene **14** which underwent efficient ring-closing metathesis using the second-generation Grubbs catalyst[37] to give dihydropyrrole **15**. Dihydroxylation of **15** from the least hindered face followed by acetonide protection of the resulting diol provided **16**, which was then transformed into the biaryl-containing dihydroxylated pyrrolidine **17** in 84% yield by nickel-catalyzed Kumada coupling with PhMgBr and acidic workup according to the method of Wehn and Du Bois.[32b] Dihydroxylated 2-aryl pyrrolidines similar to **17** are of interest as potential glycosidase inhibitors.[38]

In conclusion, the first enantioselective Rh-catalyzed additions of alkenylboron compounds to cyclic imines have been described. The cyclic structure of these imines, in which the C=N bond is constrained in the *Z* geometry, appears to be important, allowing alkenylation to proceed in generally good yields and high enantioselectivities ($\geq 94\%$ *ee*). Moreover, products containing aryl sulfamates may be exploited in subsequent reactions, including nickel-catalyzed cross-couplings, to generate further useful compounds.

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[1] For seminal references, see: a) B. M. Trost, D. L. Van Vranken, C. Bingel, *J. Am. Chem. Soc.* **1992**, *114*, 9327 – 9343; b) T. Ohmura, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 15164 – 15165.

[2] For reviews, see: a) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395 – 422; b) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921 – 2943; c) G. Helmchen, A. Dahnz, P. Dubon, M. Schelwies, R. Weihofen, *Chem. Commun.* **2007**, 675 – 691; d) Z. Lu, S. Ma, *Angew. Chem.* **2008**, *120*, 264 – 303; *Angew. Chem. Int. Ed.* **2008**, *47*, 258 – 297; e) J. F. Hartwig, L. M. Stanley, *Acc. Chem. Res.* **2010**, *43*, 1461 – 1475.

[3] For selected recent examples, see: a) L. M. Stanley, J. F. Hartwig, *Angew. Chem.* **2009**, *121*, 7981 – 7984; *Angew. Chem. Int. Ed.* **2009**, *48*, 7841 – 7844; b) M. J. Pouy, L. M. Stanley, J. F. Hartwig, *J. Am. Chem. Soc.* **2009**, *131*, 11312 – 11313; c) M. Gärtner, M. Jaekel, M. Achatz, C. Sonnenschein, O. Tverskoy, G. Helmchen, *Org. Lett.* **2011**, *13*, 2810 – 2813; d) K.-Y. Ye, H. He, W.-B. Liu, L.-X. Dai, G. Helmchen, S.-L. You, *J. Am. Chem. Soc.* **2011**, *133*, 19006 – 19014; e) M. Lafrance, M. Roggen, E. M. Carreira, *Angew. Chem.* **2012**, *124*, 3527 – 3530; *Angew. Chem. Int. Ed.* **2012**, *51*, 3470 – 3473.

[4] For a seminal reference: M. Calter, T. K. Hollis, L. E. Overman, J. Ziller, G. G. Zipp, *J. Org. Chem.* **1997**, *62*, 1449 – 1456.

[5] For a review, see: H. Nomura, C. J. Richards, *Chem. Asian J.* **2010**, *5*, 1726 – 1740.

[6] For selected recent examples, see: a) D. F. Fischer, A. Barakat, Z.-q. Xin, M. E. Weiss, R. Peters, *Chem. Eur. J.* **2009**, *15*, 8722 – 8741; b) R. Peters, Z.-q. Xin, F. Maier, *Chem. Asian J.* **2010**, *5*, 1770 – 1774.

[7] For recent reviews covering catalytic asymmetric additions of nonstabilized carbon nucleophiles to imines, see: a) S. Kobayashi, Y. Mori, J. S. Fossey, M. M. Salter, *Chem. Rev.* **2011**, *111*, 2626 – 2704; b) A. B. Charette in *Chiral Amine Synthesis: Methods, Developments and Applications* (Ed.: T. C. Nugent), Wiley-VCH, Weinheim, **2010**.

[8] Enantioselective metal-catalyzed reductive coupling of alkynes and imines: a) S. J. Patel, T. F. Jamison, *Angew. Chem.* **2004**, *116*, 4031 – 4034; *Angew. Chem. Int. Ed.* **2004**, *43*, 3941 – 3944; b) E. Skucas, J. R. Kong, M. J. Krische, *J. Am. Chem. Soc.* **2007**, *129*, 7242 – 7243; c) M.-Y. Ngai, A. Barchuk, M. J. Krische, *J. Am. Chem. Soc.* **2007**, *129*, 12644 – 12645; d) C.-Y. Zhou, S.-F. Zhu, L.-X. Wang, Q.-L. Zhou, *J. Am. Chem. Soc.* **2010**, *132*, 10955 – 10957.

[9] Catalytic enantioselective Petasis reactions: a) Y. Yamaoka, H. Miyabe, Y. Takemoto, *J. Am. Chem. Soc.* **2007**, *129*, 6686 – 6687; b) S. Lou, S. E. Schaus, *J. Am. Chem. Soc.* **2008**, *130*, 6922 – 6923; c) T. Inokuma, Y. Suzuki, T. Sakaeda, Y. Takemoto, *Chem. Asian J.* **2011**, *6*, 2902 – 2906; d) T. Kodama, P. N. Moquist, S. E. Schaus, *Org. Lett.* **2011**, *13*, 6316 – 6319.

[10] Enantioselective additions of alkenylmetal reagents to dihydroisoquinoline derivatives: a) S. Wang, C. T. Seto, *Org. Lett.* **2006**, *8*, 3979 – 3982; b) A. Saito, K. Iimura, M. Hayashi, Y. Hanzawa, *Tetrahedron Lett.* **2009**, *50*, 587 – 589.

[11] Enantioselective chiral Brønsted acid-catalyzed additions of α,β-unsaturated hydrazones to imines: T. Hashimoto, H. Kimura, K. Maruoka, *Angew. Chem.* **2010**, *122*, 6996 – 6999; *Angew. Chem. Int. Ed.* **2010**, *49*, 6844 – 6847.

[12] For selected examples of catalytic enantioselective aza-Morita–Baylis–Hillman reactions, see: a) M. Shi, Y. M. Xu, *Angew. Chem.* **2002**, *114*, 4689 – 4692; *Angew. Chem. Int. Ed.* **2002**, *41*, 4507 – 4510; b) K. Matsui, S. Takizawa, H. Sasai, *J. Am. Chem. Soc.* **2005**, *127*, 3680 – 3681; c) M. Shi, L. H. Chen, C. Q. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3790 – 3800; d) I. T. Raheem, E. N. Jacobsen, *Adv. Synth. Catal.* **2005**, *347*, 1701 – 1708; e) N. Abermil, G. Masson, J. Zhu, *J. Am. Chem. Soc.* **2008**, *130*, 12596 – 12597; f) T. Yukawa, B. Seelig, Y. J. Xu, H. Morimoto, S. Matsunaga, A. Berkessel, M. Shibasaki, *J. Am. Chem. Soc.* **2010**, *132*, 11988 – 11992.

[13] For seminal references, see: a) M. Kuriyama, T. Soeta, X. Y. Hao, O. Chen, K. Tomioka, *J. Am. Chem. Soc.* **2004**, *126*, 8128 – 8129; b) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13584 – 13585.

[14] For a review, see: C. S. Marques, A. J. Burke, *ChemCatChem* **2011**, *3*, 635 – 645.

[15] For selected recent examples, see: a) K. Okamoto, T. Hayashi, V. H. Rawal, *Chem. Commun.* **2009**, 4815 – 4817; b) R. Shintani, M. Takeda, T. Tsuji, T. Hayashi, *J. Am. Chem. Soc.* **2010**, *132*, 13168 – 13169; c) R. Shintani, M. Takeda, Y.-T. Soh, T. Ito, T. Hayashi, *Org. Lett.* **2011**, *13*, 2977 – 2979; d) R. Shintani, R. Narui, Y. Tsutsumi, S. Hayashi, T. Hayashi, *Chem. Commun.* **2011**, *47*, 6123 – 6125; e) X. Hao, Q. Chen, K.-i. Yamada, Y. Yamamoto, K. Tomioka, *Tetrahedron* **2011**, *67*, 6469 – 6473; f) Z. Cui, H.-J. Yu, R.-F. Yang, W.-Y. Gao, C.-G. Feng, G.-Q. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 12394 – 12397; g) T. Nishimura, A. Noishiki, G. Chit Tsui, T. Hayashi, *J. Am. Chem. Soc.* **2012**, *134*, 5056 – 5059.

[16] For early racemic work involving alkenyltin or alkenylzirconium reagents, see: a) S. Oi, M. Moro, H. Fukuhara, T. Kawanishi, Y. Inoue, *Tetrahedron Lett.* **1999**, *40*, 9259 – 9262; b) A. Kakuuchi, T. Taguchi, Y. Hanzawa, *Tetrahedron Lett.* **2003**, *44*, 923 – 926.

[17] a) K. Brak, J. A. Ellman, *J. Am. Chem. Soc.* **2009**, *131*, 3850 – 3851; b) K. Brak, J. A. Ellman, *J. Org. Chem.* **2010**, *75*, 3147 – 3150; c) K. Brak, J. A. Ellman, *Org. Lett.* **2010**, *12*, 2004 – 2007.

[18] Y. Nakao, M. Takeda, J. Chen, T. Hiyama, Y. Ichikawa, R. Shintani, T. Hayashi, *Chem. Lett.* **2008**, *37*, 290 – 291.

[19] For reviews on organotrifluoroborates, see: a) G. A. Molander, D. L. Sandrock, *Curr. Opin. Drug Discovery Dev.* **2009**, *12*, 811 – 823; b) S. Darses, J.-P. Genet, *Chem. Rev.* **2008**, *108*, 288 – 325.

[20] For related metal-catalyzed additions of potassium allyltrifluoroborates to imines, see: a) N. Solin, O. A. Wallner, K. J. Szabó, *Org. Lett.* **2005**, *7*, 689 – 691; b) J. Aydin, K. S. Kumar, M. J. Sayah, O. A. Wallner, K. Szabó, *J. Org. Chem.* **2007**, *72*, 4689 –

4697; c) T. R. Ramadhar, R. A. Batey, *Synthesis* **2011**, 1321 – 1346.
[21] For seminal references of chiral dienes in asymmetric catalysis, see: a) T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508 – 11509; b) C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, *J. Am. Chem. Soc.* **2004**, *126*, 1628 – 1629.
[22] For reviews of chiral diene ligands, see: a) C.-G. Feng, M.-H. Xu, G.-Q. Lin, *Synlett* **2011**, 1345 – 1356; b) R. Shintani, T. Hayashi, *Aldrichimica Acta* **2009**, *42*, 31 – 38; c) J. B. Johnson, T. Rovis, *Angew. Chem.* **2008**, *120*, 852 – 884; *Angew. Chem. Int. Ed.* **2008**, *47*, 840 – 871; d) C. Defieber, H. Grutzmacher, E. M. Carreira, *Angew. Chem.* **2008**, *120*, 4558 – 4579; *Angew. Chem. Int. Ed.* **2008**, *47*, 4482 – 4502.
[23] Y. Luo, A. J. Carnell, *Angew. Chem.* **2010**, *122*, 2810 – 2814; *Angew. Chem. Int. Ed.* **2010**, *49*, 2750 – 2754.
[24] For similar observations, see Ref. [17b] and G. Pattison, G. Piraux, H. W. Lam, *J. Am. Chem. Soc.* **2010**, *132*, 14373 – 14375.
[25] a) M. Tripathi, D. N. Dhar, *J. Heterocycl. Chem.* **1988**, *25*, 1191 – 1192; b) B.-H. Zhu, J.-C. Zheng, C.-B. Yu, X.-L. Sun, Y.-G. Zhou, Q. Shen, Y. Tang, *Org. Lett.* **2010**, *12*, 504 – 507.
[26] During the preparation of this manuscript the group of Hayashi and Nishimura reported the enantioselective rhodium-catalyzed arylation of cyclic *N*-sulfonyl ketimines. See: Ref. [15g].
[27] The absolute configurations of the products obtained herein were assigned by analogy with that of **4 f**, which was determined by X-ray crystallography. See the Supporting Information for details. CCDC 870995 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[28] While use of alkenylboronic acids or alkenyl pinacolboronic esters was successful in certain cases, potassium alkenyltrifluoroborates are the reagents of choice in these reactions. See the Supporting Information for full details.
[29] For another application of these cyclic *N*-sulfonyl ketimines in catalysis, see: M. Rommel, T. Fukuzumi, J. W. Bode, *J. Am. Chem. Soc.* **2008**, *130*, 17266 – 17267.
[30] Although this model successfully explains the stereochemical outcome, it is empirical in nature, and recent DFT calculations on the origin of enantioselectivity in Rh/chiral-diene-catalyzed 1,4-arylation of cyclohexenone suggest the situation may actually be more complex. See: a) E. A. B. Kantchev, *Chem. Commun.* **2011**, *47*, 10969 – 10971; b) S. Gosiewska, J. A. Raskatov, R. Shintani, T. Hayashi, J. M. Brown, *Chem. Eur. J.* **2012**, *18*, 80 – 84; c) Y. Luo, N. G. Berry, A. J. Carnell, *Chem. Commun.* **2012**, *48*, 3279 – 3281.
[31] For a proposed catalytic cycle for these reactions, see the Supporting Information.
[32] Kumada couplings: a) T. K. Macklin, V. Snieckus, *Org. Lett.* **2005**, *7*, 2519 – 2522; b) P. M. Wehn, J. Du Bois, *Org. Lett.* **2005**, *7*, 4685 – 4688.
[33] Suzuki–Miyaura couplings: a) K. W. Quasdorf, M. Riener, K. V. Petrova, N. K. Garg, *J. Am. Chem. Soc.* **2009**, *131*, 17748 – 17749; b) K. W. Quasdorf, A. Antoft-Finch, P. Liu, A. L. Silberstein, A. Komaromi, T. Blackburn, S. D. Ramgren, K. N. Houk, V. Snieckus, N. K. Garg, *J. Am. Chem. Soc.* **2011**, *133*, 6352 – 6363; c) M. Baghbanzadeh, C. Pilger, C. O. Kappe, *J. Org. Chem.* **2011**, *76*, 1507 – 1510.
[34] Aminations: S. D. Ramgren, A. L. Silberstein, Y. Yang, N. K. Garg, *Angew. Chem.* **2011**, *123*, 2219 – 2221; *Angew. Chem. Int. Ed.* **2011**, *50*, 2171 – 2173.
[35] Y.-Q. Wang, C.-B. Yu, D.-W. Wang, X.-B. Wang, Y.-G. Zhou, *Org. Lett.* **2008**, *10*, 2071 – 2074.
[36] K. Biswas, A. Li, J. J. Chen, D. C. D'Amico, C. Fotsch, N. Han, J. Human, Q. Liu, M. H. Norman, B. Riahi, C. Yuan, H. Suzuki, D. A. Mareska, J. Zhan, D. E. Clarke, A. Toro, R. D. Groneberg, L. E. Burgess, D. Lester-Zeiner, G. Biddlecome, B. H. Manning, L. Arik, H. Dong, M. Huang, A. Kamassah, R. Loeloff, H. Sun, F.-Y. Hsieh, G. Kumar, G. Y. Ng, R. W. Hungate, B. C. Askew, E. Johnson, *J. Med. Chem.* **2007**, *50*, 2200 – 2212.
[37] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953 – 956.
[38] T. M. Chapman, S. Courtney, P. Hay, B. G. Davis, *Chem. Eur. J.* **2003**, *9*, 3397 – 3414.

