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Asymmetric Rh(I)-Catalyzed Addition of MIDA Boronates to *N*-*tert*-Butanesulfinyl Aldimines: Development and Comparison to Trifluoroborates

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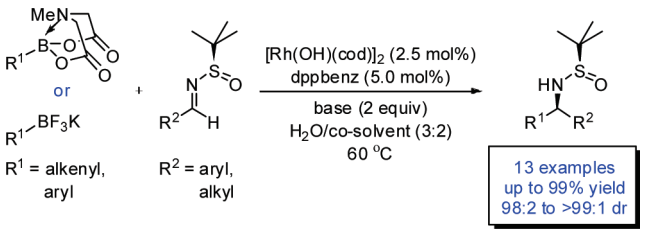

The Rh(I)-catalyzed addition of alkenyl and aryl MIDA boronates to *N*-*tert*-butanesulfinyl aromatic and aliphatic imines proceeds in good yields (up to 99%) and with very high selectivity (98:2 to > 99:1). In comparison to trifluoroborates, higher yields and selectivities are observed for the addition to *N*-*tert*-butanesulfinyl aromatic imines. This new method expands upon the versatility of the Rh(I)-catalyzed addition of boron reagents to imines, thereby further enabling the synthesis of chiral α-branched amines.

The development of efficient and practical methods for the asymmetric synthesis of chiral, α-branched amines is of great importance due to the ubiquitous nature of this motif in pharmaceutical agents and natural products.[1] The Rh(I)-catalyzed addition of boron reagents to activated imines has emerged as a general, functional-group tolerant method for the asymmetric synthesis of α-branched amines.[2−4] However, the efficiency of these additions is often limited due to competitive decomposition of the boron reagents. The same conditions, namely heat, water, and transition-metal catalysts, that promote the addition of boron reagents also accelerate their decomposition via pathways such as protodeboronation, oxidation, and/or polymerization.[5] Therefore, overcoming these undesired processes has posed a particular challenge.[6]

While boronic acids are highly versatile coupling reagents,[7] their limited stability and incompatibility with many synthetic reagents have resulted in the development of several important surrogates. Potassium trifluoroborates,[8] and even more recently *N*-methyliminodiacetic acid (MIDA) boronates,[9] have emerged as particularly attractive alternative organoboron coupling partners.[10,11] These boron reagents exhibit exceptional benchtop stability, are easy to synthesize and isolate, and are compatible with many synthetic reagents. Furthermore, MIDA boronates are stable to silica gel chromatography, allowing for expanded utility in the synthesis of complex organoboron building blocks.[12]

MIDA boronates are inert to many of the common pathways of decomposition; however, they are also unreactive toward transmetalation.[13] Burke and co-workers have elegantly demonstrated that cross-coupling of unstable boronic

(1) Breuer, M.; Ditrich, K.; Habicher, T.; Hauer, B.; Kesseler, M.; Sturmer, R.; Zelinski, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 788.

(2) The first report of a Rh(I)-catalyzed addition of arylboronic acids to imines: Ueda, M.; Saito, A.; Miyaura, N. *Synlett* **2000**, *11*, 1637.

(3) Asymmetric Rh(I)-catalyzed arylboron additions to imines: (a) Kuriyama, M.; Soeta, T.; Hao, X.; Chen, Q.; Tomioka, K. *J. Am. Chem. Soc.* **2004**, *126*, 8128. (b) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 13584. (c) Weix, D. J.; Shi, Y.; Ellman, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 1092. (d) Bolshan, Y.; Batey, R. A. *Org. Lett.* **2005**, *7*, 1481. (e) Jagt, R. B. C.; Toullec, P. Y.; Geerdink, D.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2789. (f) Duan, H.-F.; Jia, Y.-X.; Wang, L.-X.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 2567. (g) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336. (h) Nakagawa, H.; Rech, J. C.; Sindelar, R. W.; Ellman, J. A. *Org. Lett.* **2007**, *9*, 5155. (i) Trincado, M.; Ellman, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5623.

(4) Asymmetric Rh(I)-catalyzed alkenylboron additions to imines: Brak, K.; Ellman, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 3850.

(5) Protodeboronation of boronic acids occurs under protic conditions and has been shown to proceed via general acid catalysis: (a) Kuivila, H. G.; Nahabedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2159. Protonation of Ar-Rh(I) species occurs under acidic conditions: (b) Keim, W. J. *J. Organomet. Chem.* **1968**, *14*, 179. (c) Boyd, S. E.; Field, L. D.; Hambley, T. W.; Partridge, M. G. *Organometallics* **1993**, *12*, 1720. Lower molecular weight alkenylboronic acids, such as vinyl and propenylboronic acids, readily polymerize: (d) Matteson, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 4228.

(6) Improved yields have been achieved by the following: (I) Using a large excess of boronic acid: (a) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579. (II) Slow addition of the boronic acid: (b) Reference 3c.

(7) Hall, D. G. *Boronic Acids*; Wiley-VCH: Weinheim, Germany, 2005.

(8) For recent reviews on trifluoroborates, see: Molander, G. A.; Ellis, N. M. *Acc. Chem. Res.* **2007**, *40*, 275. Stefani, H. A.; Cella, R.; Vieira, A. S. *Tetrahedron* **2007**, *63*, 3623. Darses, S.; Genet, J.-P. *Chem. Rev.* **2008**, *108*, 288. Molander, G. A.; Canturk, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9240.

(9) For a review on MIDA boronates, see: Gillis, E. P.; Burke, M. D. *Aldrichim. Acta* **2009**, *42*, 17.

(10) For reviews that compare trifluoroborates, MIDA boronates, and 1,8-diaminonaphthalene boronates, see: (a) Tobisu, M.; Chatani, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 3565. (b) Molander, G. A.; Canturk, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9240.

(11) For select examples of other alternative organoboron coupling partners see the following: (I) Sterically bulky boronic esters: (a) Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Synlett* **2005**, *3*, 529. (b) Yang, D. X.; Colletti, S. L.; Wu, K.; Song, M.; Li, G. Y.; Shen, H. C. *Org. Lett.* **2009**, *11*, 381. (c) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1998**, *39*, 8479. (II) Boroximes: (d) Kerins, F.; O'Shea, D. F. *J. Org. Chem.* **2002**, *67*, 4968. (e) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976. (f) Kuriyama, M.; Soeta, T.; Hao, X.; Chen, Q.; Tomioka, K. *J. Am. Chem. Soc.* **2004**, *126*, 8128. (III) Tetraarylborates: (g) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc.* **2007**, *129*, 758. (IV) Trialkoxyborate salts: (h) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957. (i) Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 928. (V) Trihydroxyborate salts: (j) Cammidge, A. N.; Goddard, V. H. M.; Gopee, H.; Harrison, N. L.; Hughes, D. L.; Schubert, C. J.; Sutton, B. M.; Watts, G. L.; Whitehead, A. J. *Org. Lett.* **2006**, *8*, 4071. (VI) Diethanolamine adducts: (k) Gravel, M.; Thompson, K. A.; Zak, M.; Berube, C.; Hall, D. G. *J. Org. Chem.* **2002**, *67*, 3. (l) Bonin, H.; Delbrayelle, D.; Demonchaux, P.; Gras, E. *Chem. Comm.* **2010**. DOI: 10.1039/b926547n. (VII) 1,8-diaminonaphthalene adduct: (m) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc.* **2007**, *129*, 758.

(12) Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2008**, *130*, 14084.

(13) Gillis, E. P.; Burke, M. B. *J. Am. Chem. Soc.* **2007**, *129*, 6716.

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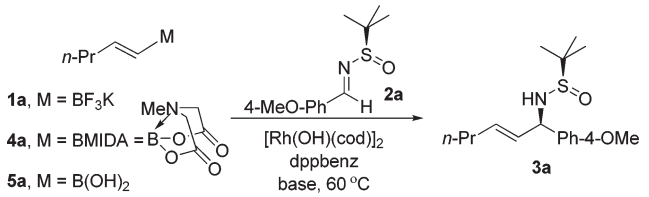
TABLE 1. Optimization of Reaction Conditions

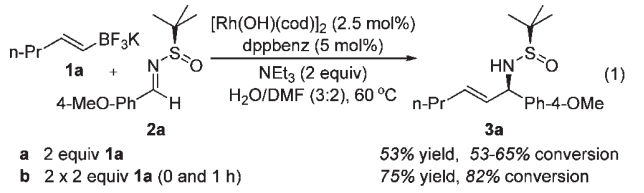


entry	M	base	solvent system	yield (%)[a,b]
1	BF_3K	NEt_3	H_2O/DMF (3:2)	53
2	BMIDA	NEt_3	H_2O/DMF (3:2)	17
3	BMIDA	K_3PO_4	H_2O/DMF (3:2)	61
4	BMIDA	K_3PO_4	H_2O/dioxane (3:2)	86
5	BMIDA	K_3PO_4	H_2O/dioxane (1:5)	60
6	$B(OH)_2$	K_3PO_4	H_2O/dioxane (3:2)	21

[a]Reaction conditions: 1 equiv of **2a**, 2 equiv of **1a** or **4a** or **5a**, 2.5 mol % of $[Rh(OH)(cod)]_2$, 5.0 mol % of 1,2-bis(diphenylphosphino)benzene (dppbenz), 2 equiv of NEt_3 or K_3PO_4, 0.125 M in 2:3 H_2O/cosolvent, 60 °C, 20 h. [b]Yields were determined by ^1H NMR relative to an external standard.

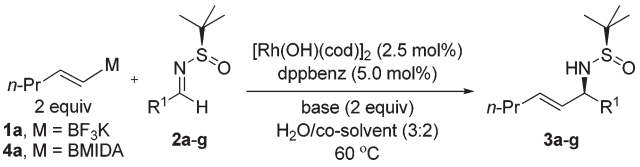
acids, via the in situ, rate-controlled hydrolysis of MIDA boronates, is a general solution for the Suzuki−Miyaura reaction.[14] The slow release of boronic acids from MIDA boronates maintains minimal amounts of free boronic acid throughout the reaction, which results in improved efficiency. Taking advantage of the hydrolytic stability of *N*-*tert*-butanesulfinyl aromatic imines, we disclose herein the first application of MIDA boronates in the Rh(I)-catalyzed addition to imines.

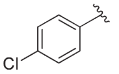
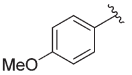
We previously reported the Rh(I)-catalyzed addition of alkenyltrifluoroborates to both aromatic and aliphatic *N*-*tert*-butanesulfinyl imines.[4] Even though trifluoroborates were found to be significantly more effective than the corresponding boronic acids, limitations still arose due to competitive decomposition of the boron reagent. For example, the addition of pentenyltrifluoroborate **1a** to electron-rich *N*-sulfinyl imine **2a** proceeded only in moderate yield (eq 1). After careful evaluation of the reaction conditions, it was found that the alkenylation reaction ceases after 1 h even though a significant quantity of the hydrolytically stable *N*-*tert*-butanesulfinyl imine was still present. Interestingly, the addition of another 2 equiv of the trifluoroborate after 1 h resulted in higher yields. This suggested that over a period of 1 h, the Rh(I)-catalyst remained active while significant consumption of the trifluoroborate had occurred through a combination of addition and decomposition.



While sequential addition of more trifluoroborate resulted in improved yields, we sought to develop a more efficient and practical process. We envisioned that higher yields could potentially be achieved via the slow release of boronic acids from MIDA boronates (Table 1). The optimal conditions for the Rh(I)-catalyzed addition of trifluoroborates, which utilize triethylamine as the base, were not effective for MIDA boronates (entry 2). It is known that K_3PO_4 in 1:5 H_2O/dioxane promotes the continuous release of boronic acids over approximately 3 h.[14] Fortunately, K_3PO_4 was previously established to be a compatible base for the Rh(I)-catalyzed addition of trifluoroborates[4] and proved to be competent for MIDA boronates as well (entry 3). While dioxane is a poor cosolvent for the trifluoroborate-mediated transformation, it resulted in higher yields for the MIDA boronate (entry 4). Similarly to the trifluoroborates, it was important to maintain the heterogeneous reaction conditions by having a solvent system composed of a minimum of 60% water (entry 5).[15] We also confirmed that the slow release of boronic acids is much more effective than simply using 2 equiv of boronic acid in the Rh-catalyzed alkenylation reaction (entry 6).

TABLE 2. Scope in *N*-Sulfinyl Imine with Alkenyl Boron Reagents



entry	imine **2**		**3**	M =	BF_3K[a]	BMIDA[b]	dr[c]
					isolated yield (%)		
1		**2b**	**3b**		82	98	99:1
2[d]					82	92	99:1
3[e]					75	96	99:1
4		**2c**	**3c**		83	99	>99:1
5		**2d**	**3d**		94	98	99:1
6		**2a**	**3a**		52	85	99:1
7		**2e**	**3e**		37	71	98:2
8		**2f**	**3f**		78	79	99:1
9		**2g**	**3g**		45	21	98:2

[a]Reactions were performed with 2 equiv of NEt_3 in 0.125 M H_2O/DMF (3:2). [b]Reactions were performed with 2 equiv of K_3PO_4 in 0.125 M H_2O/dioxane (3:2). [c]The diastereoselectivity was the same for M = BF_3K and BMIDA and was determined by HPLC on unpurified samples with comparison to authentic diastereomers.[17] [d]Reactions were set up in a fumehood using Schlenk technique. [e]Reactions were performed with 1.2 equiv of boron reagent.

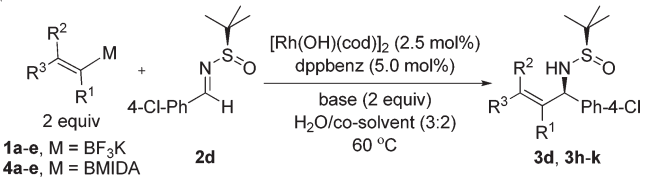
(14) Knapp, D. M.; Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 6961.

(15) Under the optimal reaction conditions (0.125 M in D_2O/dioxane-d_8 (3:2), 2 equiv of K_3PO_4, 60 °C), MIDA boronate **4a** was observed by ^1H NMR to slowly hydrolyze over 3 h.

(16) An isolated example of ligand-free Rh(I)-catalyzed addition of phenyltrifluoroborate to *N*-*tert*-butanesulfinyl 4-trifluoromethylbenzaldimine in 61% yield and 96:4 dr has been reported, see ref 3d.

(17) Authentic diastereomer mixtures were prepared according to the following: Brak, K.; Barrett, K. T.; Ellman, J. A. *J. Org. Chem.* **2009**, *74*, 3606.

TABLE 3. Scope in Alkenyl Organoboron Reagent



entry	organoboron reagent **1/4**	**3**	M = BF_3K[a] isolated yield (%)	BMIDA[b] isolated yield (%)	dr[c]
1	**1/4a**	**3d**	94	98	99:1
2	**1/4b**	**3h**	70	93	98:2
3	**1/4c**	**3i**	75	85	99:1
4	**1/4d**	**3j**	66	91	99:1
5	**1/4e**	**3k**	22	14	99:1

[a]Reactions were performed with 2 equiv of NEt_3 in 0.125 M H_2O/DMF (3:2). [b]Reactions were performed with 2 equiv of K_3PO_4 in 0.125 M H_2O/dioxane (3:2). [c]Diastereoselectivity was the same for M = BF_3K and BMIDA and was determined by HPLC on unpurified samples with comparison to authentic diastereomers.[17]

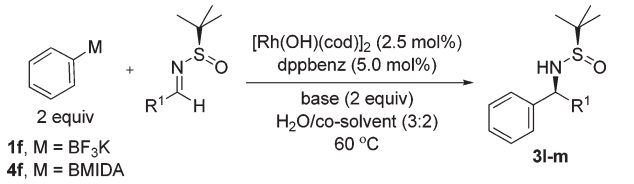
Encouraged by these results, we next evaluated the MIDA boronate slow-release method with a variety of *N*-*tert*-butanesulfinyl imines (Table 2). For the Rh(I)-catalyzed alkenylation of *N*-*tert*-butanesulfinyl aromatic aldimines, MIDA boronates performed better than the trifluoroborates (entries 1−7). The Rh(I)-catalyzed addition of pentenyl MIDA boronate to electron neutral (entries 1 and 4) and deficient (entry 5) *N*-sulfinyl imines provided the corresponding allylic amines in nearly quantitative yield and with excellent diastereoselectivities. Notably, the most dramatic improvements in yield were achieved for the addition to electron-rich imines (entries 6 and 7).

For *N*-sulfinyl imines **2** that are aliphatic, imine hydrolysis is the major side reaction competing with the alkenylation reaction. Consequently, this substrate class does not benefit from the slow release of boronic acids from MIDA boronates. For nonhindered aliphatic imines, MIDA boronates resulted in the same yield as trifluoroborates (entry 8). However, for sterically hindered aliphatic imines, the addition of the MIDA boronate resulted in a lower yield (entry 9).

It is important to note that the $[Rh(OH)(cod)]_2$ precatalyst and dppbenz ligand are air stable, and therefore the alkenylation reactions can be set up by using standard Schlenk techniques without requiring the use of an inert atmosphere box (entry 2, Table 2). Moreover, the equivalents of MIDA boronate reagent **4a** could be reduced without appreciably affecting the reaction yield (entry 3).

The scope of the organoboron coupling partner was next evaluated with *N*-sulfinyl 4-chlorobenzaldimine **2d** under the standard set of conditions (Table 3). The Rh(I)-catalyzed alkenylation was not especially sensitive to substitution on the alkene, with the addition of di- (entry 1), tri- (entry 2), and tetrasubstituted (entry 3) alkenyltrifluoroborates all proceeding in good yields and with high selectivities. While

TABLE 4. Additions of Aryl Boron Reagents to *N*-Sulfinyl Imines



entry	imine **2**	**3**	M	yield (%)[a]	dr[b]
1	**2d**	**3l**	BF_3K[c]	84	96:4
2			BMIDA[d]	97	98:2
3	**2a**	**3m**	BF_3K[c]	50	94:6
4			BMIDA[d]	89	98:2

[a]Isolated yield after chromatography. [b]Diastereoselectivity was determined by HPLC on unpurified samples with comparison to authentic diastereomers.[17] [c]Reactions were performed with 2 equiv of NEt_3 in 0.125 M H_2O/DMF (3:2). [d]Reactions were performed with 2 equiv of K_3PO_4 in 0.125 M H_2O/dioxane (3:2).

increased alkene substitution resulted in moderate decreases in yield for the trifluoroborates, the MIDA boronates maintained excellent yields (entries 2 and 3).

We were also interested in examining how the electronics of the boron coupling partner affect the efficiency of the reaction. The alkenylation was found to be strongly influenced by electronics with the additions of electron-deficient trifluoroborates proceeding in lower yield (entries 4 and 5). Although cinnamyl MIDA boronate **4d** added in significantly higher yield than the corresponding trifluoroborate (entry 4), the addition of the highly electron-deficient trifluoromethyl-substituted MIDA boronate **4e** proceeded in low yield (entry 5).[18] Electron-poor boron reagents are known to be less nucleophilic and undergo transmetalation at a slower rate in addition to being prone to homocoupling.[19]

The conditions developed for the alkenylation also were applicable to the arylation of *N*-*tert*-butanesulfinyl imines. The Rh(I)-catalyzed addition of aryl boron reagents to both electron deficient and rich *N*-sulfinyl aromatic imines **2d** and **2a**,[20] respectively, proceeded with high selectivity and yields for the MIDA boronates (Table 4).[16] Whereas the diastereoselectivity was found to be identical for MIDA boronates and trifluoroborates in the alkenylation reaction, a noticeable difference was observed in the arylation reaction with the MIDA boronate additions proceeding with higher selectivity.

In conclusion, the slow release of boronic acids from MIDA boronates minimizes the decomposition of the boron reagents and enables their Rh-catalyzed addition to *N*-*tert*-butanesulfinyl imines in very high yields and selectivities. This practical and general method enables the asymmetric synthesis of α-branched amines from stable and easily

(18) The addition of vinyltrifluoroborate (13%) and vinyl MIDA boronate (11%) to imine **2d** proceeds in low yields. The vinyl boron reagents most likely failed to couple efficiently due to their electron-deficient as well as unstable nature.

(19) (a) Wong, M. S.; Zhang, X. L. *Tetrahedron Lett.* **2001**, *42*, 4087. (b) Kuivila, H. G.; Reuwer, J. F.; Mangravite, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2666.

(20) The addition of phenylboronic acid to imine **2a** was reported to proceed in 45% yield and 91:9 dr with $[Rh(cod)(CH_3CN)_2]BF_4$ as the catalyst without any phosphine ligand, 1:2 dioxane/water as solvent, and Et_3N (2 equiv) as an additive, see ref 3d.

accessible *N*-sulfinyl imine and MIDA boronate starting materials.[21]

Experimental Section

General Procedure for the Addition of MIDA Boronates to *N*-*tert*-Butanesulfinyl Imines. Inert atmosphere box procedure: Reactions were set up in an inert atmosphere box. Hydroxy-(1,5-cyclooctadiene)rhodium(I) dimer (2.9 mg, 0.0063 mmol, 0.025 equiv) was dissolved in dioxane (0.4 mL, 0.62 M), and the resulting mixture was added to a vial containing 1,2-bis-(diphenylphosphino)benzene (5.6 mg, 0.013 mmol, 0.050 equiv). The mixture of catalyst and ligand was then added to a vial containing a stir-vane and the appropriate MIDA boronate (0.300−0.500 mmol, 1.2−2.0 equiv). To the mixture of catalyst, ligand, and MIDA boronate was added the appropriate sulfinyl imine (0.250 mmol, 1.0 equiv) dissolved in dioxane (0.4 mL, 0.62 M), followed by water (1.2 mL, 0.21 M) and K_3PO_4 (106 mg, 0.500 mmol, 2.0 equiv). The reaction vial was capped, removed from the inert atmosphere box, and placed in a heating block on the benchtop with stirring. The reaction mixture was heated to 60 °C and stirred for 20 h. Upon heating and stirring, the reaction mixture becomes biphasic with globules of starting imine/product in the reaction medium. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL). The organic layer was washed with brine (10 mL), and the aqueous layer was back-extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The products were isolated by silica gel chromatography with use of EtOAc/hexanes mixtures and were visualized with PMA stain. **Schlenk-line procedure:** Reactions were set up in a fumehood with Schlenk techniques. The appropriate sulfinyl imine (0.250 mmol, 1.0 equiv) was added to a 5 mL single-necked pear-shaped flask fitted with a rubber septum, which was subjected to three cycles of evacuation and refilling with nitrogen gas via an inlet needle. Water (1.2 mL) and K_3PO_4 (106 mg, 0.500 mmol, 2.0 equiv) were added to a separate 5 mL single-necked round-bottomed flask fitted with a rubber septum, which was subjected to three cycles of evacuation and refilling with nitrogen gas via an inlet needle. A 5 mL Schlenk tube equipped with a vacuum adaptor, septum, and stir bar was charged with hydroxy(1,5-cyclooctadiene)rhodium(I) dimer (2.9 mg, 0.0063 mmol, 0.025 equiv) and 1,2-bis(diphenylphosphino)benzene (5.6 mg, 0.013 mmol, 0.050 equiv). After evacuating and refilling the flask with N_2 gas (3×), freshly distilled dioxane (0.3 mL) was added by gas-tight syringe. The catalyst and ligand were stirred under N_2 atmosphere for 2 min, and then the septum was removed and the MIDA boronate (0.500 mmol, 2.0 equiv) was added while maintaining a strong N_2 gas flow. The mixture of catalyst, ligand, and MIDA boronate was stirred under a N_2 atmosphere until the solution was homogeneous. Then the sulfinyl imine dissolved in dioxane (0.5 mL) followed by the aqueous K_3PO_4 solution were added by cannula. The Schlenk tube was capped, and the reaction mixture was heated in a 60 °C oil bath with stirring for 20 h whereupon the reaction mixture becomes biphasic with globules of starting imine/product in the reaction medium. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL). The organic layer was washed with brine (10 mL), and the aqueous layer was back-extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The products were isolated by silica gel chromatography with use of EtOAc/hexanes mixtures and were visualized with PMA stain.

(R_S)-*N*-((*R*,*E*)-1-(4-Methoxyphenyl)hex-2-enyl)-2-methylpropanesulfinamide (3a). MIDA boronate addition: The general procedure was followed with use of sulfinyl imine **2a** (59.8 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12−100% EtOAc/hexanes) afforded 65.6 mg (85% yield, 99:1 dr) of **3a** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 17.8 min, t_{major} = 23.0 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[4] **Trifluoroborate addition:** The preparation of sulfinamide **3a** by the Rh(I)-catalyzed addition of trifluoroborate **1a** was previously reported.[4]

(R_S)-*N*-((*R*,*E*)-1-(Phenyl)hex-2-enyl)-2-methylpropanesulfinamide (3b). MIDA boronate addition (glovebox procedure): The general inert atmosphere box procedure was followed with use of sulfinyl imine **2b** (52.3 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12−100% EtOAc/hexanes) afforded 68.4 mg (98% yield, 99:1 dr) of **3b** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 210 nm): t_{minor} = 10.6 min, t_{major} = 12.5 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[4] **MIDA boronate addition (Schlenk procedure):** The general Schlenk-line procedure was followed with use of sulfinyl imine **2b** (52.3 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12−100% EtOAc/hexanes) afforded 64.2 mg (92% yield, 99:1 dr) of **3b** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 210 nm): t_{minor} = 10.4 min, t_{major} = 12.2 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1] **Trifluoroborate addition:** The preparation of sulfinamide **3b** by the Rh(I)-catalyzed addition of trifluoroborate **1a** was previously reported.[4]

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Supporting Information Available: General experimental methods and materials, synthesis and characterization of MIDA boronates **4**, specific reaction conditions, and copies of ^{1}H NMR and HPLC traces of sulfinamides **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

(21) For the addition of an alkenyl MIDA boronate and the corresponding trifluoroborate to more complex *N*-*tert*-butanesulfinyl imines in the context of a natural product synthesis, see: Brak, K.; Ellman, J. A. *Org. Lett*. DOI: 10.1021/ol100470g. Published Online: March 31, 2010.