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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Synthesis of Chiral α-Amino Tertiary Boronic Esters by Enantioselective Hydroboration of α-Arylenamides

Naifu Hu,† Guoqing Zhao,† Yuanyuan Zhang, Xiangqian Liu, Guangyu Li, and Wenjun Tang*

State Key Laboratory of Bio-Organic and Natural Products Chemistry and Collaborative Innovation Center of Chemistry for life Sciences, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200032, China

Supporting Information

ABSTRACT: The rhodium-catalyzed asymmetric hydroboration of α-arylenamides with BI-DIME as the chiral ligand and $(Bpin)_2$ as the reagent yields for the first time a series of α-amino tertiary boronic esters in good yields and excellent enantioselectivities (up to 99% ee).

Chiral α-amino boronic acid derivatives have emerged as important pharmacores in medicinal chemistry,[1] most notably served as key constituents of proteasome inhibitors bortezomib and delanzomib[2] as well as dipeptidyl peptidase-4 (DPP-4) inhibitor dutogliptin.[3] In addition, they have increasingly become important chiral building blocks in synthetic organic chemistry.[4] Synthesis of chiral α-amino boronic esters has thus gained significant interests. Work by Matteson,[5] Ellman,[6] Časar,[7] Morken,[8] Fernández,[9] Tian and Lin,[10] and Yudin[11] has provided a number of efficient methods for the synthesis of chiral α-amino secondary boronic esters by either use of chiral auxiliaries[5,6] or asymmetric catalytic transformations.[7−9] In contrast, few efficient synthetic methods are available for chiral α-amino tertiary boronic esters. Using a chiral auxiliary, Ellman[6b] reported good diastereoselectivities in copper-catalyzed borylation of *N*-*tert*-butanesufinyl ketimines. However, efficient asymmetric catalytic synthesis of chiral α-amino tertiary boronic esters is yet to be reported to our knowledge. Herein we report the first enantioselective synthesis of chiral α-amino tertiary boronic esters by rhodium-catalyzed hydroboration of α-arylenamides (Figure 1).

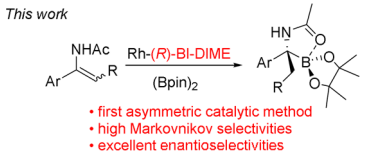


Figure 1. An asymmetric synthetic method for chiral α-amino tertiary boronic esters.

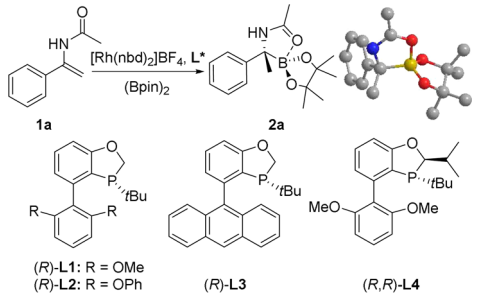
Transition-metal-catalyzed asymmetric hydroboration[12] has become a powerful method for the synthesis of chiral organoboronic esters complementary to the noncatalytic process with chiral hydroboration reagents.[13] In particular, transition-metal-catalyzed asymmetric hydroboration of styrenes have led to chiral secondary boronic esters in high Markovnikov selectivities and enantioselectivities.[14] In a more complex context, asymmetric hydroboration of α-substituted vinylarenes would result in tertiary boronic esters as the Markovnikov products or primary boronic esters as the *anti*-Markovnikov products. While excellent regioselectivities and enantioselectivities have been recently achieved for the synthesis of chiral primary boronic esters with chiral Ir, Cu, Co catalysts,[15] efficient synthesis of chiral tertiary boronic esters by asymmetric hydroboration remains an unsolved problem.[16] Taken into consideration of the challenging regioselectivity issue in forming tertiary boronic esters and enlightened by Evans, Gevorgyan, and Takacs' beautiful work on carbonyl-directed asymmetric hydroboration,[17] we reasoned that hydroboration of α-arylenamides, the α-substituted vinylarene substrates equipped with carbonyl directing groups, could form preferentially the α-amino tertiary boronic esters. With an efficient chiral phosphorus ligand, enantioselective synthesis of chiral α-amino tertiary boronic esters could be realized for the first time by asymmetric hydroboration.

We studied the asymmetric hydroboration of *N*-(1-phenylvinyl)acetamide (**1a**) with $(Bpin)_2$ as the reagent (Table 1). With $[Rh(nbd)_2]BF_4$ (2 mol %) as the catalyst precursor and (*R*)-**L1** ((*R*)-BI-DIME, 2 mol %)[19] as the chiral ligand, the reactions were performed under nitrogen at 60 °C for 12 h. When dioxane was employed as the solvent (entry 1), the desired hydroboration product **2a** (7%) was formed in 93% ee along with diboration product **3a** (7%), *anti*-Markovnikov regio-isomer **4a** (45%), and reduction side-product **5a** (35%). In order to improve the chemoselectivity of the reaction and the yield of **2a**, various solvents were then studied (entries 1−5). Whereas a polar solvent such as THF or dichloroethane provided a similarly low yield, an improved yield (~50%) was observed when a nonpolor solvent such as toluene or hexafluorobenzene was employed. Apparently, the formation of regio-isomer **4a** and reduction side-product **5a** was much inhibited in a nonpolar solvent. An excellent enantioselectivity (99%) was achieved when hexafluorobenzene was employed, and it was thus chosen as the solvent for further study (entry 5). Use of a neutral rhodium precursor $[Rh(cod)Cl]_2$ provided a diminished yield and ee (entry 6). To further improve the yield, various nucleophilic additives were investigated (entries 7−10). Although triethylamine and cesium fluoride led to lower yields, NaO*t*Bu provided an improved yield (56%) albeit with a diminished ee. The best isolated yield (65%) was achieved when a nucleophilic base DABCO was employed (entry 10). Apparently, the formation of the reduction product **5a** was

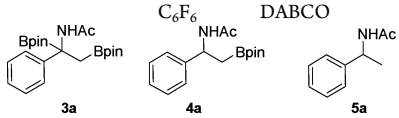
Received: April 11, 2015
Published: May 4, 2015

DOI: 10.1021/jacs.5b03760
J. Am. Chem. Soc. 2015, 137, 6746−6749

Table 1. Asymmetric hydroboration of *N*-(1-phenylvinyl)acetamide[a]



entries	ligand	solvent	additive	yield (%)	ee (%)
1	**L1**	dioxane	–	7	93
2	**L1**	THF	–	11	97
3	**L1**	DCE	–	5	90
4	**L1**	toluene	–	51	68
5	**L1**	C_6F_6	–	50	99
6[b]	**L1**	C_6F_6	–	19	61
7	**L1**	C_6F_6	TEA	35	99
8	**L1**	C_6F_6	CsF	37	99
9	**L1**	C_6F_6	NaO*t*Bu	56	85
10	**L1**	C_6F_6	DABCO	69(65)[f]	99
11[c]	**L1**	C_6F_6	DABCO	58	99
12[d]	**L1**	C_6F_6	DABCO	55	53
13	**L2**	C_6F_6	DABCO	11	99
14	**L3**	C_6F_6	DABCO	<5	–
15	**L4**	C_6F_6	DABCO	<5	–
16	(*S*)-BINAP	C_6F_6	DABCO	<5	–
17	(*S*,*S*)-Me-Duphos	C_6F_6	DABCO	<5	–
18	dppb	C_6F_6	DABCO	<5	–
19	SPhos	C_6F_6	DABCO	<5	–
20[e]	**L1**	C_6F_6	DABCO	62[f]	92



[a]Unless otherwise specified, all reactions were performed under nitrogen at 60 °C for 12 h with **1a** (0.3 mmol), $(Bpin)_2$ (0.45 mmol), and $[Rh(nbd)_2]BF_4$ (0.006 mmol, 2 mol %), and ligand (0.006 mmol, 2 mol %), additive (0.06 mmol, 20 mol %), HPLC assay yields, enantiomeric excesses were determined by chiral HPLC on a chiralcel OD-H column. The absolute configuration of **2a** was determined by X-ray crystallography.[18] The major side products are diborylated product **3a**, regio-isomer **4a**, and reduction product **5a**. See Supporting Information for yield distributions. [b]$[Rh(cod)Cl]_2$ was employed as the metal precursor. [c]T = 80 °C. [d]Pinacolborane was employed as the reagent. [e]Scale-up experiment with **1a** (1 g, 6.2 mmol), [Rh((*R*)-**L1**)(nbd)]BF_4 (2 mol %) was employed as the catalyst. [f]Isolated yields.

further inhibited in the presence of DABCO. Reaction at an elevated temperature (80 °C) did not further improve the yield (entry 11). A significant low ee was observed when pinacolborane instead of $(Bpin)_2$ was employed as the reagent (entry 12). Various other chiral phosphorus ligands were also investigated. A P-chiral monophosphorus ligand with phenoxy moieties (entry 13) did not provide a better yield. AntPhos (**L3**) with a 9-anthracenyl moiety proved to be ineffective (entry 14). Nearly no formation of **2a** was observed when a chiral ligand **L4** with an isopropyl substituent on the upper aryl ring was employed (entry 15). The fact that ligands BINAP, Me-DuPhos, dppb, and SPhos provided little or no formation of **2a** (entries 16−19) strongly demonstrated the uniqueness of BI-DIME in promoting the high activity, Markovnikov selectivity, and enantioselectivity of this reaction. Compound **2a** was isolated as a colorless crystalline solid, whose absolute configuration was unambiguously confirmed by X-ray crystallography.[18] The coordination between the boron atom and the carbonyl group of the acetyl moiety makes such alkyl boronic ester highly stable at room temperature.

Because of the possible tautomerism[20] between **1a** and its *N*-acyl imine isomer **1a′**, product **2a** could be possibly formed by two different pathways: hydroboration of olefin and diboration of *N*-acyl imine **1a′**. To shed light on its mechanism, we conducted the following experiments (Figure 2). First, the reaction of *N*-benzylidenebenzamide (**6**) as the substrate under similar reaction conditions was sluggish, and the borylated product **7** was isolated in only 20% yield and 13% ee. Second, treatment of *N*-tosylimine **8** did not form the borylated product **9**, only reduction product **10**.[21b] These results indicated that the diboration[22] of *N*-acyl imine **1a′** to form **2a** was slow and unlikely to be the major pathway. Next, we investigated the role of the N−H in **1a** for the reactivity. *N*-benzyl-*N*-(1-phenylvinyl)-acetamide (**11**) was found inactive under similar reaction conditions, indicating that the olefin diboration process was also slow and the N−H of **1a** was important for the reactivity of hydroboration. When the deuterated enamide **12** was employed, both products **13** and **14** were found to have deuterium incorporation, further demonstrating the role of N−H for the reaction. Finally, in the case of the deuterated enamide **15** as the substrate, the deuterium at vinyl group in **15** was fully transformed into the methyl substituent of **16**, indicating the high fidelity of olefin insertion−reductive elimination process during the hydroboration, with no involvement of β-H elimination.[14d,21]

The cationic rhodium complex [Rh((*R*)-**L1**)(nbd)]BF_4 was successfully prepared, and its square planar structure was revealed by X-ray crystallography.[18] Importantly, this complex was well applicable as the catalyst for the hydroboration reaction

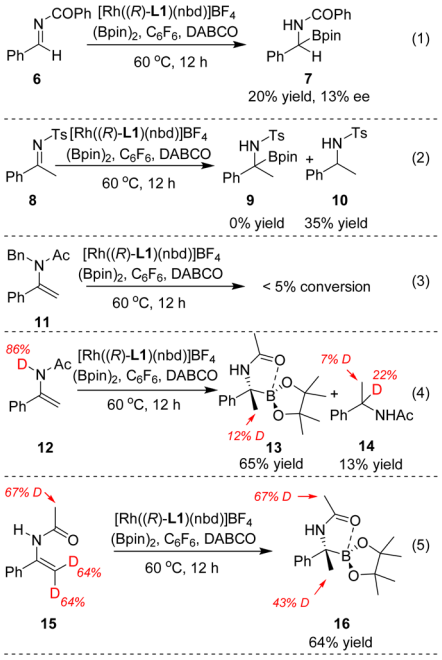


Figure 2. Mechanistic studies of asymmetric hydroboration.

DOI: 10.1021/jacs.5b03760
J. Am. Chem. Soc. 2015, 137, 6746−6749

at 1 g scale to provide **2a** in 62% isolated yield and 92% ee (Table 1, entry 20), demonstrating the practicality of this transformation. Further study with a scalemic composition of BI-DIME ligand revealed a linear relationship between the ee values of the ligand and of product **2a**, strongly indicating the hydroboration affected by a single BI-DIME-coordinated rhodium catalyst. A simplified catalytic cycle is proposed in Figure 3. Oxidative addition of $(BPin)_2$ to the Rh(I)-(*R*)-BI-

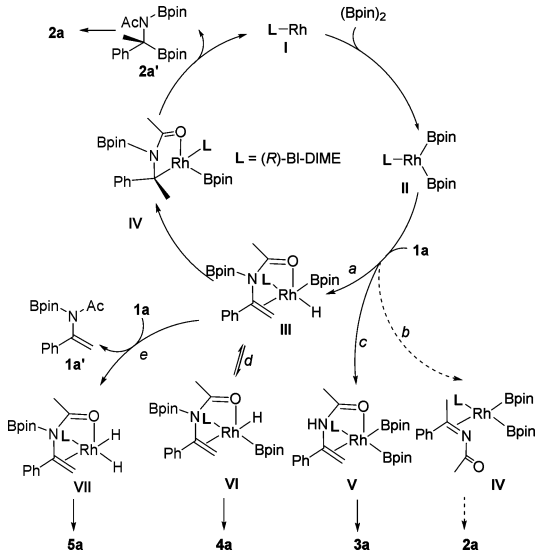


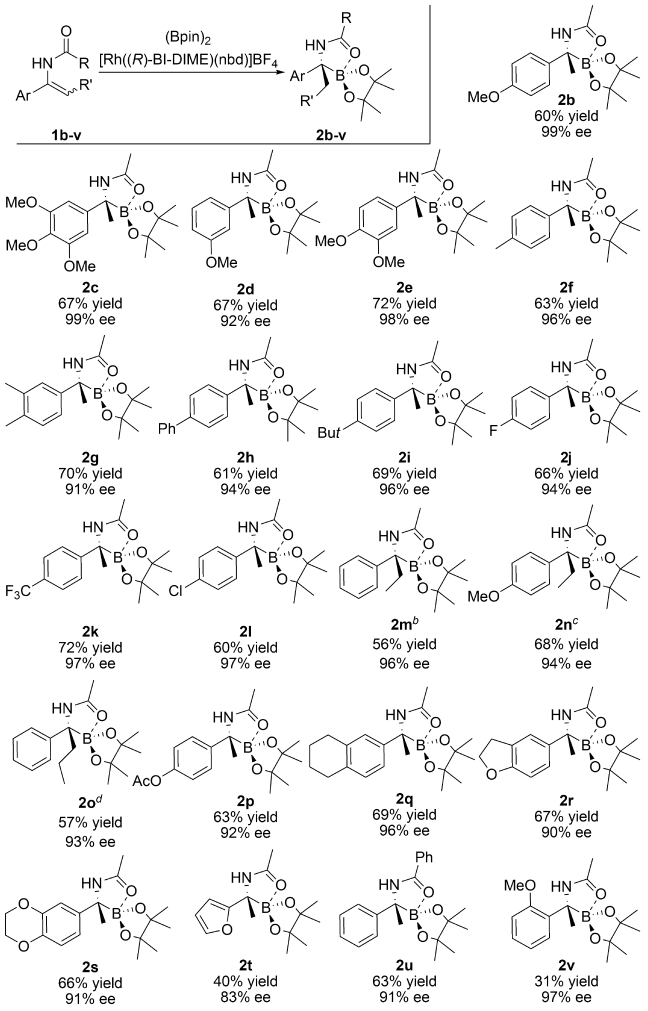
Figure 3. A proposed catalytic cycle.

DIME species **I** leads to the formation of the bis(boryl) Rh(III) species **II**, which subsequently reacts with the N−H of **2a** to provide the boryl Rh(III) hydride **III**. Olefin insertion to the Rh hydride bond followed by reductive elimination provides product **2a**′ and regenerates the Rh(I)-(*R*)-BI-DIME species **I**. Concomitantly, diboration product **3a**, regio-isomer **4a**, and reduction product **5a** can also be formed respectively through *c*, *d*, *e* pathways[21] as minor products. The diboration[22] of *N*-acyl imine through pathway *b* is unlikely to occur during the course.

We then looked into the substrate scope of this hydroboration. As can be seen in Table 2, a series of α-amino tertiary boronic esters were prepared for the first time in good yields and excellent ees. The yields and enantioselectivities were insensitive to the electronic properties and substitution patterns on the aryl groups. Substrates with electron-donating (**2b**−**e**), -neutral (**2f**−**i**), and -withdrawing (**2j**−**l**) substituents all provided good yields (60−72%) and excellent enantioselectivities (91−99% ee). Functional groups such as halogen, ether, and ester were well tolerated. Various α-alkyl α-amino tertiary boronic esters (**2m**−**o**) were successfully formed in excellent ees from 2-substituted arylenamides. An *E*/*Z* mixture of **1n** was also applicable. An α-amino tertiary boronic ester **2t** with an α-(2-furanyl) substituent was also successfully prepared, albeit with a slightly low ee. Besides *N*-acetyl enamides, an *N*-benzoyl α-arylenamide **1u** was equally suitable for the asymmetric hydroboration to provide compound **2u** in 91% ee. An *ortho*-methoxy-substituted arylenamide **1v** was also applicable to form **2v** in excellent enantioselectivity, albeit with a low yield (31%).

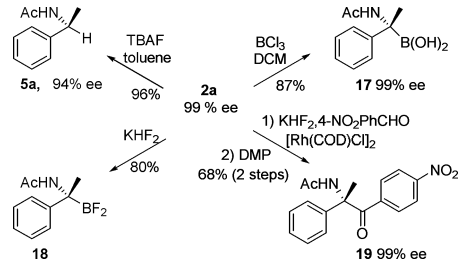
The chiral α-amino tertiary boronic esters can be employed for the synthesis of various chiral products by simple transformations (Scheme 1).[23] For example, chiral amino boronate **2a** was transformed to the corresponding boronic acid **17** in 87% yield

Table 2. Asymmetric Hydroboration of α-Arylenamides[a]



[a]Conditions unless otherwise specified: α-arylenamide (0.3 mmol), $(BPin)_2$ (0.45 mmol), [Rh((*R*)-**L1**)(nbd)]BF_4 (0.006 mmol, 2 mol %), DABCO (0.06 mmol), C_6F_6 (1 mL), 60 °C, 12 h, isolated yields, enantiomeric excesses were determined by chiral HPLC on a chiralcel OD-H or AD-H column, and absolute configurations were assigned by analogy. [b](*Z*)-**1m** was employed. [c](*E*/*Z*)-**1n** (*E*/*Z* = 3/5) was employed. [d](*Z*)-**1o** was employed.

Scheme 1. Transformations of 2a As Chiral Building Block



under conditions of BCl_3. Deboronation of **2a** provided the corresponding chiral amine **5a** by treatment of TBAF.[24] Reaction of **2a** with KHF_2 provided the corresponding difluoroborane **18**.[25] Treatment[26,16g] of **2a** with KHF_2, 4-nitrobenzoaldehyde in the presence of a rhodium catalyst followed by DMP oxidation provided α-acetylamino ketone **19** in 68% overall yield and 99% ee.

DOI: 10.1021/jacs.5b03760
J. Am. Chem. Soc. 2015, 137, 6746−6749

In summary, we have successfully developed a novel and efficient rhodium-catalyzed asymmetric hydroboration of α-arylenamides with $(Bpin)_2$ as the reagent that has allowed for the first time the synthesis of a series of chiral α-amino tertiary boronic esters in good yields and excellent enantioselectivities. The P-chiral monophosphorus ligand BI-DIME is responsible for its remarkable Markovnikov selectivity and enantioselectivity to form chiral tertiary boronic esters by hydroboration. Preliminary study supports the transformation proceeds through hydroboration over diboration of acyl imine pathway. The stable α-amino tertiary boronic esters can be envisioned as not only important building blocks for peptidomimetics but also versatile chiral intermediates in synthetic organic chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details and characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03760.

■ AUTHOR INFORMATION

Corresponding Author

*tangwenjun@sioc.ac.cn

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by NSFC-21432007, 21272254, STCSM- 13PJ1410900, and the "Thousand Plan" Youth program.

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DOI: 10.1021/jacs.5b03760
J. Am. Chem. Soc. 2015, 137, 6746−6749