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Copper-Catalyzed Asymmetric Hydroboration of 1,1-Disubstituted Alkenes

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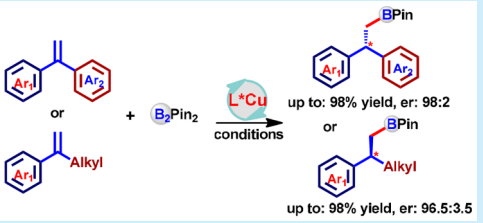
Supporting Information

ABSTRACT: A mild and efficient approach for highly regio- and enantioselective copper-catalyzed hydroboration of 1,1-diaryl substituted alkenes with bis(pinacolato)diboron (B_2Pin_2) was developed for the first time, providing facile access to a series of valuable β,β-diaryl substituted boronic esters with high enantiomeric purity. Moreover, this approach could also be suitable for hydroboration of α-alkyl styrenes for the synthesis of enantioenriched β,β-arylalkyl substituted boronic esters. Gram-scale reaction, stereospecific derivatizations, and the application of important antimuscarinic drug (*R*)-tolterodine for concise enantioselective synthesis further highlighted the attractiveness of this new approach.



As ubiquitous substructures, *gem*-diaryl- and arylalkyl substituted chiral tertiary carbon motifs are found in a broad range of biologically active compounds and pharmaceuticals,[1] such as podophyllotoxin,[1c] (*R*)-tolterodine,[1d] H_1-antihistamine,[1e] (+)-sertraline,[1f] ramelteon,[1g] and (*R*)-naproxen[1h] (Figure 1). Therefore, the development of approaches for

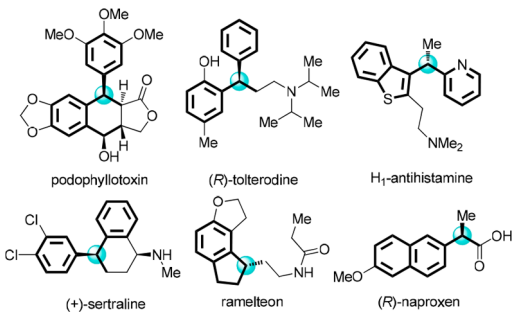


Figure 1. Representative bioactive molecules containing chiral tertiary carbon motifs.

efficient enantioselective installation of these subunits has attracted considerable attention, and a variety of strategies, such as the asymmetric conjugate additions of organometallic reagents[2] and the cross-coupling benzylic electrophiles with nucleophiles,[3] has been successfully exploited. 1,1-Disubstituted unactivated alkene is the readily available feedstock, and thus, the corresponding asymmetric transformation represents one of most ideal strategies to access such valuable chiral substructures.

Enantioselective alkene hydroboration has attracted special attention and emerged as a powerful protocol for enabling access to the versatile optically pure organoboron compounds, which are amenable to a wide variety of stereospecific transformations.[4] Undoubtedly, compared with the early reports on employing stoichiometric amounts of expensive and difficult-to-access chiral organoboranes,[5] transition-metal-catalyzed asymmetric hydroboration of alkenes with inexpensive and readily available organoboronic reagents has provoked more significant attention, and numerous transformations have been well disclosed in recent years.[6] For example, recently, amide-directed highly enantioselective hydroboration of 1,1-dialkyl alkenes has been developed with chiral Rh catalyst by Takacs and co-workers.[7] In addition, on the basis of the seminal works on Rh-catalyzed asymmetric hydroboration of unactivated α-alkylstyrenes, reported by the groups of Burgess,[8] Suzuki,[9] Hayashi and Ito[10] and, more recently, Mazet,[11] Diéguez,[12] and Tang[13] have well disclosed highly enantioselective hydroboration of α-alkyl- or amino-substituted styrenes with noble chiral Ir or Rh catalysts. To avoid using the traditional precious-metal catalysts, the groups of Huang[14] and Lu[15] have realized the Co- or Fe-catalyzed asymmetric hydroboration of α-alkyl substituted styrenes. Additionally, the asymmetric hydrofunctionalization reactions of unsaturated hydrocarbons through the use of low cost and high earth abundance copper catalysts have received significant attention in recent years, and various C−X (X: C, N, Si, B, etc.) bonds have been successfully forged in an enantioselective manner.[16] In this content, Yun and Hoveyda have independently reported Cu-catalyzed highly site- and enantioselective hydroboration of styrenes or 1,1-arylalkyl substituted alkenes (Scheme 1A).[17] Despite these advances, to our knowledge, the asymmetric hydroboration version of unactivated 1,1-diaryl substituted alkenes, is still an ultimate challenge, owing to the hurdle in discriminating the two enantiotopic faces of such prochiral substrates. Indeed, so far, no effective catalytic system has been exploited for asymmetric hydroboration of such substrate type

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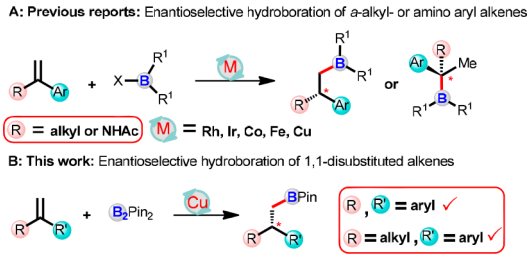
Scheme 1. Asymmetric Hydroboration of 1,1-Disubstituted Alkenes

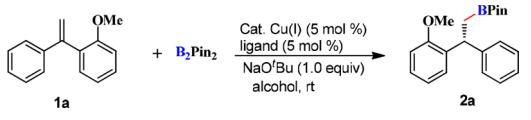


and only two examples have been hitherto reported by Huang and co-workers, but showed low enantioselectivities (8% and 54% ee).[14] In actual fact, the catalytic asymmetric versions of 1,1-disubstituted unactivated alkenes with high enantioselectivities (>90% ee) have only been nicely achieved in asymmetric hydrogenation,[18] along with some sporadic reports on asymmetric dihydroxylation[19] and hydrosilylation.[20] Herein, we reported the first highly enantioselective hydroboration of 1,1-diaryl substituted unactivated alkenes with chiral Cu catalyst, furnishing the synthetic valuable boronic esters bearing chiral *β,β*-diaryl substituted tertiary carbon motifs. Furthermore, this method can also be applied to the asymmetric hydroboration of 1,1-arylalkyl substituted alkenes with high enantiomeric purity (Scheme 1B).

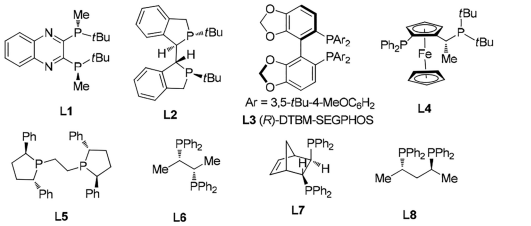
We initiated our investigation using *α*-(*o*-methoxylphenyl)-styrene **1a** and B_2Pin_2 as model reactants (Table 1). Pleasing, when the reaction was conducted at room temperature in the presence of CuCl (5 mol %), NaO^{t}Bu (1.0 equiv), MeOH (2.0 equiv), and (*R,R*)-QuinoxP* **L1** (5 mol %) in THF, affording the desired chiral *anti*-Markovnikov hydroboration product **2a** in high yield with moderate level of enantioselectivity (Table 1, entry 1). This promising result prompted us to further evaluate the effectiveness of other chiral ligands, such as **L2**−**L8** (Table 1, entries 2−8). To our delight, good yield and high enantioselectivity was obtained by employing (*S,S*)-BDPP **L8** as the chiral ligand (Table 1, entry 8). Then, we next proceeded to evaluate the reactivities of various copper catalysts and the nature of the proton source. The experimental results revealed that, through the combination of CuCl and NaBArF with MeOH as the proton supplier, the hydroboration product **2a** could be furnished in excellent yield and enantioselectivity (Table 1, entries 8−14). Note that the hydroboration reactions occurred specifically in an *anti*-Markovnikov fashion. The further screening of the base, temperature, and solvent were also performed (see the Supporting Information for details).

With the optimal reaction conditions in hand, we then evaluated the reactions of various 1,1-disubstituted alkenes (Scheme 2). 1,1-Diaryl alkenes bearing either weak or strong electro-donating groups at *ortho* positions of the aromatic rings, such as **1a**−**1g**, worked well under the optimal conditions and provided desired hydroboration products **2a**−**2g** in moderate to excellent yields with high enantiomeric ratios. Previous Co-catalyzed asymmetric hydroboration of substrate **1b** provided chiral boronic ester **2b** in low yield and moderate enantioselectivity (19% yield and 54% ee).[14] This copper catalytic system showed high effectiveness for **1b**, furnishing boronic ester **2b** in both excellent yield and enantioselectivity (86% yield and er = 98:2). We next examined whether this developed approach would efficiently differentiate two different vinyl units in one molecule, such as **1h**. To our delight, this transformation proceeded with excellent chemoselectivity and furnished chiral

Table 1. Optimization of Reaction Conditions[a,b]



entry	cat.	ligand	alcohol	yield (%)	er (%)[c]
1	CuCl	**L1**	MeOH	82	77.5:22.5
2	CuCl	**L2**	MeOH	85	83:17
3	CuCl	**L3**	MeOH	0	--
4	CuCl	**L4**	MeOH	0	--
5	CuCl	**L5**	MeOH	60	70:30
6	CuCl	**L6**	MeOH	69	35:65
7	CuCl	**L7**	MeOH	27	78.5:21.5
8	CuCl	**L8**	MeOH	85	92:8
9	CuOAc	**L8**	MeOH	78	91:9
10	$Cu(OAc)_2$	**L8**	MeOH	80	91:9
11[d]	CuX	**L8**	MeOH	75	92.5:7.5
12[e]	CuCl	**L8**	MeOH	88	92:8
13[e]	CuCl	**L8**	^{t}BuOH	63	74.5:25.5
14[e]	CuCl	**L8**	^{i}PrOH	84	79:21



[a]Reaction conditions: **1a** (0.15 mmol), B_2pin_2 (1.2 equiv), catalyst (5 mol %), ligand (5 mol %), NaO^{t}Bu (1.0 equiv), and alcohol (2.0 equiv) in 2 mL of THF at room temperate. [b]Isolated yields. [c]Enantioselectivity of the purified product was determined by chiral HPLC. er: enantiomeric ratio. [d]CuX: $Cu(CH_3CN)_4PF_6$. [e]NaBArF (5 mol %) was added to the reaction. NaBArF: sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate.

β,β-diaryl boronic ester **2h** in good yield and excellent enantioselectivity. 1-(1-Naphthyl)styrene **1i** and **1j** bearing strong electro-withdrawing group (CF_3) at the *ortho* position of aromatic ring were also the good substrates for these transformations, providing desired boronic ester **2i** and **2j** in good yields with high enantioselectivities. Furthermore, heterocycles, such as thiophene and indole, which are frequently found in many bioactive molecules, were also accommodated and converted into the products **2k** and **2l** with excellent enantiocontrol, although low yield was observed for **1l** under this transformation conditions. Additionally, alkenes **1m**−**1p** bearing multi-substitutents at one or two aromatic rings could also be efficiently converted into corresponding boronic esters **2m**−**2p** in good yields with high level of enantioselectivities. By increasing the steric congestion in the vicinity of the alkenyl units by installation of the *tert*-butyldimethylsilyl (TBS) group, which is widely used as protecting group in the synthesis of complex molecules, to our delight, the transformation proceeded smoothly to give the target product in both excellent yield and enantioselectivity. Moreover, the preliminary experimental results showed that the cyclic internal olefin **1r** and **1s** could be successfully transformed into the corresponding structurally important cyclic secondary boronic esters **2r** and **2s** in good yields and enantiocontrols. 1,1-Diaryl alkene **1t** and **1u** without *ortho*-site substituent were also examined under the present

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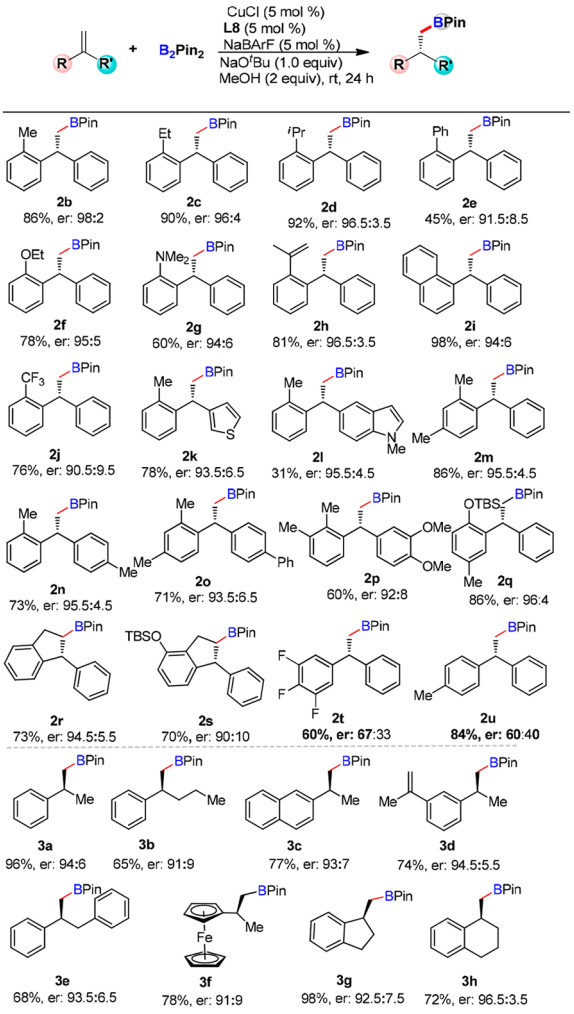
Scheme 2. Copper-Catalyzed Asymmetric Hydroboration of 1,1-Disubstituted Alkenes[a,b]



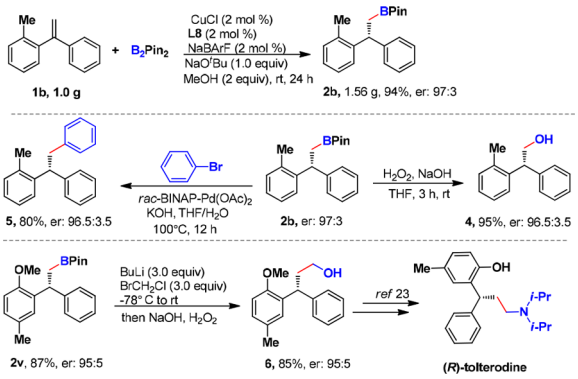
[a]Reaction conditions: **1** (0.15 mmol), B_2pin_2 (1.2 equiv), catalyst (5 mol %), ligand (5 mol %), NaO^{t}Bu (1.0 equiv), NaBArF (5 mol %), and MeOH (2.0 equiv) in 2 mL of THF at room temperate. [b]Isolated yields.

catalytic conditions, and the desired products could be obtained in good yields, while the enantioselectivities dropped significantly. The above results suggest that the *ortho* position substituent of the 1,1-diaryl alkene plays a key role for effective discriminating the two enantiotopic faces and is essential for inducing the high enantioselectivity.[21]

To further highlight this method, 1,1-disubstituted arylalkyl alkenes were examined under the optimal conditions. To our delight, aryl ethenes bearing different alkyl chain-length at the α-position were valid substrates and gave the corresponding hydroboration products **3a**, **3b**, and **3c** in moderate to excellent yields with high enantioselectivities. In addition, substrate bearing two symmetrical alkenyl units was also examined; as a result, the asymmetric transformation gave monohydroboration product **3d** exclusively in good yield with excellent enantiocontrol, without observation of over hydroboration reaction under this conditions. Benzyl substituted styrene and ferrocenyl olefin can also undergo the transformations to yield the corresponding chiral boronic esters in good level of enantiocontrol. Additionally, the hydroboration of exocyclic 1,1-disubstituted arylalkyl olefins showed good reactivities and provided chiral boronic esters **3g** and **3h** in good to nearly quantitative yields with impressive enantioselectivities. The absolute configurations of hydroboration products **2b** and **3c** was determined by means of the comparison of HPLC data with reported data.[14,22]

To illustrate the potential and versatile synthetic utility of the present approach, Gram-scale synthesis and stereospecific transformations of enantioenriched boronic esters to construct an array of chiral hydrocarbon building blocks were conducted (Scheme 3). The chiral boronic ester **2b** and target molecules **4** and **5** were obtained in excellent yields without erosion of enantiomeric excess. To further highlight the applicability of this newly developed method, we completed the enantioselective synthesis of an intermediate that had previously been converted to the important antimuscarinic drug (*R*)-tolterodine, a therapeutic used for the treatment of urinary incontinence. Briefly, a three-step sequence involving asymmetric hydroboration, boronate homologation/oxidation providing the clinically used therapeutic precursor **6** in good yield with excellent enantiocontrol, followed by an amination process could furnish (*R*)-tolterodine (Scheme 3).[23]

Scheme 3. Gram-Scale Synthesis and Applications of Chiral Boronic Ester



In summary, we have successfully developed a unified, mild, and efficient approach for copper-catalyzed asymmetric hydroboration of 1,1-disubstituted alkenes with readily available B_2Pin_2. This copper catalysis system exhibited high efficiency for 1,1-diaryl- and arylalkyl olefins, thus allowing access to a range of valuable chiral β,β-diaryl substituted boronic esters in good yields and high level of regio- and enantioselectivities for the first time. The optical active boronic esters were not only envisioned as versatile building blocks for further stereospecific derivatizations but also suitable for Gram-scale synthesis, as well as application for enantioselective synthesis of an important urological drug (*R*)-tolterodine. Additional studies of asymmetric transformations for other types of alkenes are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01135.

Experiment procedure and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For selected recent reviews, see: (a) Ameen, D.; Snape, T. J. *MedChemComm* **2013**, *4*, 893. (b) Soussi, M. A.; Provot, O.; Bernadat, G.; Bignon, J.; Desravines, D.; Dubois, J.; Brion, J.-D.; Messaoudi, S.; Alami, M. *ChemMedChem* **2015**, *10*, 1392. For represented examples, see: (c) Xu, H.; Tian, X. *Curr. Med. Res. Opin.* **2009**, *16*, 327. (d) Wefer, J.; Truss, M. C.; Jonas, U. *World J. Urol.* **2001**, *19*, 312. (e) Moree, W. J.; Li, B.-F.; Jovic, F.; Coon, T.; Yu, J.; Gross, R. S.; Tucci, F.; Marinkovic, D.; Zamani-Kord, S.; Malany, S.; Bradbury, M. J.; Hernandez, L. M.; O'Brien, Z.; Wen, J.; Wang, H.; Hoare, S. R. J.; Petroski, R. E.; Sacaan, A.; Madan, A.; Crowe, P. D.; Beaton, G. *J. Med. Chem.* **2009**, *52*, 5307. (f) McRae, A. L.; Brady, K. T. *Expert Opin. Pharmacother.* **2001**, *2*, 883. (g) Zlotos, D. P.; Jockers, R.; Cecon, E.; Rivara, S.; Witt-Enderby, P. A. *J. Med. Chem.* **2014**, *57*, 3161. (h) Adeniji, A.; Uddin, Md. J.; Zang, T.; Tamae, D.; Wangtrakuldee, P.; Marnett, L. J.; Penning, T. M. *J. Med. Chem.* **2016**, *59*, 7431.

(2) For representative reviews, see: (a) *Conjugate Addition Reactions in Organic Synthesis*; Perlmutter, P., Ed.; Tetrahedron Organic Chemistry Series 9; Pergamon: Oxford, 1992. (b) *Catalytic Asymmetric Conjugate Reactions*; Cordova, A., Ed.; Wiley-VCH: Weinheim, 2010.

(3) For recent reviews and selective examples towards stereospecific formation of chiral diarylalkanes, see: (a) Swift, E. C.; Jarvo, E. R. *Tetrahedron* **2013**, *69*, 5799−5817. (b) Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *Chem. Rev.* **2015**, *115*, 9587. (c) Imao, D.; Glasspoole, B. W.; Laberge, V. S.; Crudden, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 5024. (d) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 280. (e) Zhou, Q.; Cobb, K. M.; Tan, T.; Watson, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 12057. (f) Zhou, Q.; Srinivas, H. D.; Zhang, S.; Watson, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 11989. (g) Konev, M. O.; Hanna, L. E.; Jarvo, E. R. *Angew. Chem., Int. Ed.* **2016**, *55*, 6730. For selective stereoconvergent reactions with racemic electrophiles, see: (h) Binder, J. T.; Cordier, C. J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 17003. (i) Do, H.-Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 16288. For enantioselective cross-coupling with in situ formation of benzyl nucleophiles, see: (j) Friis, S. D.; Pirnot, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **2016**, *138*, 8372.

(4) (a) Mikhailov, B. M.; Bubnov, Y. N. *Organoboron Compounds in Organic Synthesis*; Harwood Academic: Amsterdam, 1983. (b) Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*; Wiley-VCH: Weinheim, 2011. (c) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417.

(5) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 3222. (b) Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964**, *86*, 397. (c) Masamune, S.; Kim, B. M.; Petersen, J. S.; Sato, T.; Veenstra, S. J.; Imai, T. *J. Am. Chem. Soc.* **1985**, *107*, 4549. (d) Brown, H. C.; Singaram, B. *Acc. Chem. Res.* **1988**, *21*, 287. (e) Gonzalez, A. Z.; Román, J. G.; Gonzalez, E.; Martinez, J.; Medina, J. R.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 9218.

(6) For reviews, see: (a) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179. (b) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, *2003*, 4695. (c) Carroll, A. M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal.* **2005**, *347*, 609. (d) Thomas, S. P.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 1896.

(7) (a) Smith, S. M.; Takacs, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 1740. (b) Smith, S. M.; Hoang, G. L.; Pal, R.; Khaled, M. O. B.; Pelter, L. S. W.; Zeng, X. C.; Takacs, J. M. *Chem. Commun.* **2012**, *48*, 12180. (c) Shoba, V. M.; Thacker, N. C.; Bochat, A. J.; Takacs, J. M. *Angew. Chem., Int. Ed.* **2016**, *55*, 1465.

(8) (a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. (b) Burgess, K.; van der Donk, W. A.; Ohlmeyer, M. J. *Tetrahedron: Asymmetry* **1991**, *2*, 613.

(9) Sato, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231.

(10) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 601.

(11) Mazet, C.; Gérard, D. *Chem. Commun.* **2011**, *47*, 298.

(12) Magre, M.; Biosca, M.; Pàmies, O.; Diéguez, M. *ChemCatChem* **2015**, *7*, 114.

(13) Hu, N.; Zhao, G.; Zhang, Y.; Liu, X.; Li, G.; Tang, W. *J. Am. Chem. Soc.* **2015**, *137*, 6746.

(14) Zhang, L.; Zuo, Z.; Wan, X.; Huang, Z. *J. Am. Chem. Soc.* **2014**, *136*, 15501.

(15) (a) Chen, J.-H.; Xi, T.; Ren, X.; Guo, J.; Cheng, B.; Lu, Z. *Org. Chem. Front.* **2014**, *1*, 1306. (b) Chen, J.; Xi, T.; Lu, Z. *Org. Lett.* **2014**, *16*, 6452. (c) Zhang, H.; Lu, Z. *ACS Catal.* **2016**, *6*, 6596.

(16) For selective reviews on Cu-catalyzed asymmetric hydrofunctionalization of unsaturated alkanes, see: (a) Deutsch, C.; Krause, N.; Lipshutz, B. H. *Chem. Rev.* **2008**, *108*, 2916. (b) Fujihara, T.; Semba, K.; Terao, J.; Tsuji, Y. *Catal. Sci. Technol.* **2014**, *4*, 1699. (c) Jordan, A. J.; Lalic, G.; Sadighi, J. P. *Chem. Rev.* **2016**, *116*, 8318. (d) Nguyen, K. D.; Park, B. Y.; Luong, T.; Sato, H.; Garza, V. J.; Krische, M. J. *Science* **2016**, *354*, aah5133.

(17) (a) Noh, D.; Chea, H.; Ju, J.; Yun, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6062. (b) Corberán, R.; Mszar, N. W.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 7079.

(18) For reviews towards asymmetric hydrogenation of 1,1-disubstituted alkenes, see: (a) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272. (b) Källström, K.; Munslow, I.; Andersson, P. G. *Chem. - Eur. J.* **2006**, *12*, 3194. (c) Roseblade, S. J.; Pfaltz, A. *Acc. Chem. Res.* **2007**, *40*, 1402. (d) Church, T. L.; Andersson, P. G. *Coord. Chem. Rev.* **2008**, *252*, 513−531. (e) Zhu, Y.; Burgess, K. *Acc. Chem. Res.* **2012**, *45*, 1623. (f) Xie, J.; Zhou, Q. *Huaxue Xuebao* **2012**, *70*, 1427. (g) Chirik, P. J. *Acc. Chem. Res.* **2015**, *48*, 1687. (h) Margarita, C.; Andersson, P. G. *J. Am. Chem. Soc.* **2017**, *139*, 1346. For recent selected examples, see: (i) Bell, S.; Wüstenberg, B.; Kaiser, S.; Menges, F.; Netscher, T.; Pfaltz, A. *Science* **2006**, *311*, 642. (j) Diéguez, M.; Mazuela, J.; Pàmies, O.; Verendel, J. J.; Andersson, P. G. *J. Am. Chem. Soc.* **2008**, *130*, 7208. (k) Bess, N.; Sigman, M. S. *Org. Lett.* **2013**, *15*, 646. (l) Zhu, S.-F.; Yu, Y.-B.; Zhou, Q.-L.; Song, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 1556. (m) Besset, T.; Gramage-Doria, R.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 8795. (n) Chen, J.; Chen, C.; Ji, C.; Lu, Z. *Org. Lett.* **2016**, *18*, 1594. (o) Friedfeld, M. R.; Shevlin, M.; Margulieux, G. W.; Campeau, L.-C.; Chirik, P. J. *J. Am. Chem. Soc.* **2016**, *138*, 3314.

(19) (a) Becker, H.; King, S. B.; Taniguchi, M.; Vanhessche, K. P. M.; Sharpless, K. B. *J. Org. Chem.* **1995**, *60*, 3940. (b) Wang, X.; Zak, M.; Maddess, M.; O'Shea, P.; Tillyer, R.; Grabowski, E. J. J.; Reider, P. J. *Tetrahedron Lett.* **2000**, *41*, 4865.

(20) (a) Chen, J.; Cheng, B.; Cao, M.; Lu, Z. *Angew. Chem., Int. Ed.* **2015**, *54*, 4661. For a recent review of base-metal-catalyzed alkene hydrosilyation, see: (b) Du, X.; Huang, Z. *ACS Catal.* **2017**, *7*, 1227.

(21) The detailed interaction between 1,1-diaryl alkene and (*S*,*S*)-BDPP-ligated copper catalyst is not clear at the present stage and need to further elaborate.

(22) Jia, T.; Cao, P.; Wang, B.; Lou, Y.; Yin, X.; Wang, M.; Liao, J. *J. Am. Chem. Soc.* **2015**, *137*, 13760.

(23) (a) Jonsson, N. A.; Sparf, B. A.; Mikiver, L.; Moses, P.; Nilvebrant, L.; Glas, G. U.S. Patent 5,382,600 A1, 1995. (b) Sun, C.; Potter, B.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 6534. (c) Guduguntla, S.; Hornillos, V.; Tessier, R.; Fañanás-Mastral, M.; Feringa, B. F. *Org. Lett.* **2016**, *18*, 252.

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