Synthetic Methods

International Edition: DOI: 10.1002/anie.201608139
German Edition: DOI: 10.1002/ange.201608139

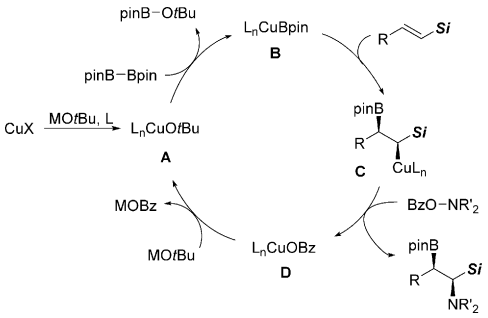
Synthesis of β-Boryl-α-Aminosilanes by Copper-Catalyzed Aminoboration of Vinylsilanes

Kodai Kato, Koji Hirano, and Masahiro Miura**

Abstract: *A copper-catalyzed regioselective and stereospecific aminoboration of vinylsilanes with bis(pinacolato)diboron (pinB-Bpin) and hydroxylamines has been developed. In the presence of a CuCl/MeO-dppbz catalyst, the boryl group and amino group are incorporated at the β position and α position, respectively, and the corresponding β-boryl-α-aminosilanes are obtained with good diastereoselectivity. The boryl group is a good latent functional group, and subsequent manipulations provide a variety of β-functionalized α-aminosilanes of great potential in medicinal chemistry. Additionally, preliminary application to asymmetric catalysis is also described.*

Organosilicon compounds are one of the indispensable synthetic reagents and intermediates in modern organic synthesis.[1] Additionally, the Si atom itself is a key element in many functional materials and bioactive molecules. Particularly, α-aminosilanes are known to show unique biological activity and are often incorporated in peptidomimetics, as exemplified by angiotensin-converting enzyme (ACE) inhibitor and serine protease human neutrophil elastase (HNE) inhibitor.[2] The most studied strategy for the preparation of the α-aminosilane relies on the nucleophilic silyl addition reaction: the highly diastereoselective addition of silyllithium to sulfinyl aldimines;[2c,d,3] the copper-catalyzed enantioselective addition of the silylborane to sulfonyl aldimines.[4] On the other hand, Buchwald[5] recently reported a copper-catalyzed enantioselective hydroamination of vinylsilanes with hydroxylamines as electrophilic amination reagents.[6] This approach is based on the nitrogen addition across alkenes and a good alternative to the above silyl addition protocols. Despite the above certain advances, there still remains a large demand for further development of catalysis directed toward versatile and highly functionalized α-aminosilanes.[7] Herein, we report a copper-catalyzed regioselective and stereospecific aminoboration of vinylsilanes with bis(pinacolato)diboron (pinB-Bpin) and hydroxylamines: the boryl group and amino group are simultaneously incorporated at the β position and α position, respectively, and the corresponding β-boryl-α-aminosilanes are obtained with good diastereoselectivity. The products can be useful synthetic platforms for highly functionalized α-aminosilanes via pinB-based post functionalization. Moreover, preliminary enantioselective copper catalysis with a chiral bisphosphine ligand is also developed.

On the basis of our recent studies on the copper-catalyzed aminoboration of alkenes,[8] we envisioned the working scenario for the catalytic aminoboration of the vinylsilane (Scheme 1). Initial salt metathesis of copper salts with the alkoxide base and coordination of the ancillary ligand generates the starting $L_nCuO\mathit{t}Bu$ **A**. Subsequent σ-bond metathesis with pinB-Bpin[9] is followed by *syn*-insertion[10] of the vinylsilane to the Cu–B bond of the borylcopper species **B** to generate the β-boryl-α-silylalkylcopper intermediate **C**. The stereoretentive[6c,8a] C–N bond formation then occurs with the *O*-benzoylhydroxylamine[11] to produce the desired *syn*-β-boryl-α-aminosilanes along with L_nCuOBz **D**. The catalytic cycle is closed by the final ligand exchange with the metal alkoxide. In the migratory insertion step (**B** to **C**), the regioselectivity issue is encountered, but hyperconjugation between the Cu–C σ orbital and proximal Si–C σ* orbital can lead to the desired regioisomer **C** preferably.[12]



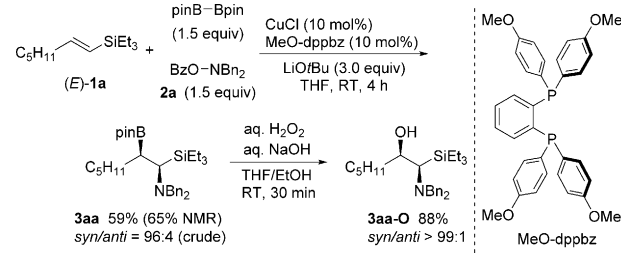
Scheme 1. Working hypothesis of copper-catalyzed aminoboration of vinylsilanes with bis(pinacolato)diboron (pinB-Bpin) and *O*-benzoylhydroxylamine. Bz = benzoyl.

On the basis of the above hypothesis, we began optimization studies with (*E*)-heptenylsilane (*E*)-**1a** and *O*-benzoyl-*N*,*N*-dibenzylhydroxylamine (**2a**) as model substrates. After extensive screening of various reaction parameters, we were pleased to find that the aminoboration occurred in the presence of a CuCl/MeO-dppbz catalyst and a Li*O*t*Bu* base in THF at room temperature, and the desired β-boryl-α-aminosilane **3aa** was obtained in 59% isolated yield (65% NMR yield) with high diastereoselectivity (*syn*/*anti* = 96:4).[13] Expectedly, the regioselectivity could be completely controlled. Additionally, upon treatment with basic aq. H_2O_2, **3aa** was readily oxidized into the corresponding β-hydroxyl-α-

[*] K. Kato, Prof. Dr. K. Hirano, Prof. Dr. M. Miura
Department of Applied Chemistry, Graduate School of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
E-mail: k_hirano@chem.eng.osaka-u.ac.jp
miura@chem.eng.osaka-u.ac.jp

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201608139.

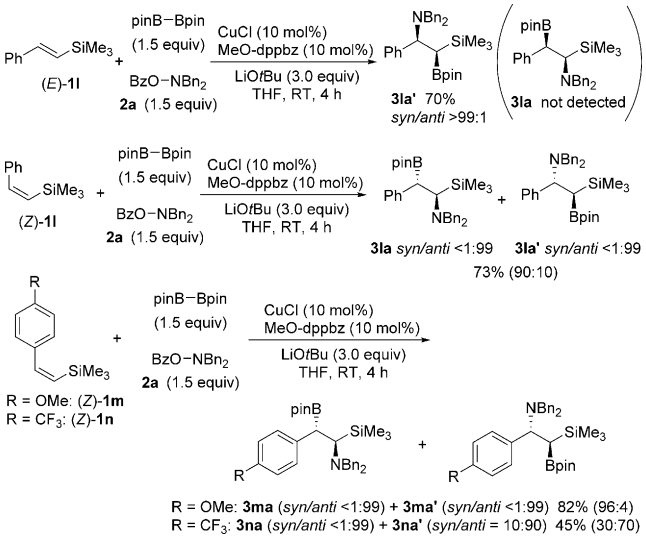
 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 2. Optimal conditions for copper-catalyzed aminoboration of vinylsilane (*E*)-**1a** and subsequent H_2O_2-promoted oxidation. Bn = benzyl.

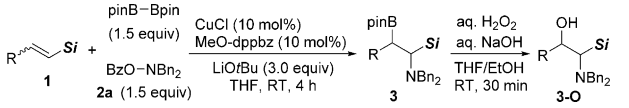
aminosilane **3aa-O** in 88% yield as the single *syn* isomer (Scheme 2).

Under conditions in Scheme 2, we performed the catalytic aminoboration of various vinylsilane **1** with pinB-Bpin and the hydroxylamine **2a** (Table 1). In addition to (*E*)-**1a** (entry 1), the substrates that bear the benzyl substitution and alkyl chloride moiety also underwent the reaction to form the β-boryl-α-aminosilanes **3ba** and **3ca** in 72 and 60% yields, respectively, with high *syn* selectivity (*syn*/*anti* > 99:1; entries 2 and 3).[14] The catalysis was compatible with the oxygen-based functionalities such as silyl ether and pivaloyl ester (entries 4 and 5). The terminal vinyl silane **1f** was employed for this transformation, and in this case the reaction could also be carried out on 5-fold larger scale with a comparable yield, thus indicating the good reproducibility and reliability of this process (entry 6). However, more sterically demanding cyclohexyl-substituted **1g** and (*Z*)-**1a** gave lower yields and in the latter case moderate *syn*/*anti* selectivity (entries 7 and 8). The substitution effects on Si were next examined. The introduction of the Ph group generally increased the reaction efficiency: dimethylphenylvinylsilane **1h** and methyldiphenylvinylsilane **1i** were converted into the corresponding β-hydroxyl-α-aminosilanes **3ha-O** and **3ia-O** with excellent yields, following the H_2O_2-mediated oxidation (entries 9 and 10). A similar positive Ph effect was observed



Scheme 3. Catalytic aminoboration of styrylsilanes.

Table 1: Copper-catalyzed aminoboration of various alkyl-substituted vinylsilanes **1** with bis(pinacolato)diboron and *O*-benzoyl-*N*,*N*-dibenzylhydroxylamine (**2a**).[a]



Entry	**1**	**3** or **3-O**, Yield [%],[b] *syn*/*anti*[c]
1	C_5H_{11}–SiEt$_3$ (*E*)-**1a**	**3aa**, 59, 96:4
2	Ph–SiEt$_3$ **1b**	**3ba**, 72, >99:1
3	Cl–(CH$_2$)$_4$–SiEt$_3$ **1c**	**3ca**, 60, >99:1
4	TBSO–(CH$_2$)$_3$–SiEt$_3$ **1d**	**3da**, 61, >99:1
5	PivO–(CH$_2$)$_3$–SiEt$_3$ **1e**	**3ea**, 72, >99:1
6	SiEt$_3$ **1f**	**3fa**, 80 (73),[d] –
7	SiEt$_3$ **1g**	**3ga**, (20), >99:1
8	C_5H_{11}, SiEt$_3$ (*Z*)-**1a**	**3aa**, (21), 32:68
9	SiMe$_2$Ph **1h**	**3ha-O**, 96, –
10	SiMePh$_2$ **1i**	**3ia-O**, 91, –
11	C_5H_{11}–SiMePh$_2$ **1j**	**3ja-O**, 78, >99:1
12	SiMePh$_2$ **1k**	**3ka-O**, 70, >99:1

[a] Cu-catalyzed conditions: CuCl (0.025 mmol), MeO-dppbz (0.025 mmol), **1** (0.25 mmol), pinB-Bpin (0.38 mmol), **2a** (0.38 mmol), LiO*t*Bu (0.75 mmol), THF (3.0 mL), RT, 4 h, N_2. Oxidation conditions: aq. H_2O_2 (30%, 0.50 mL), aq. NaOH (3.0 M, 0.50 mL), THF (1.0 mL)/EtOH (0.50 mL), RT, 30 min, open flask. [b] Isolated yields are given. ^{1}H NMR yields are in parentheses. [c] Determined by ^{1}H NMR of the crude mixture. [d] 1.3 mmol scale. TBS = *tert*-butyldimethylsilyl, Piv = *tert*-butylcarbonyl.

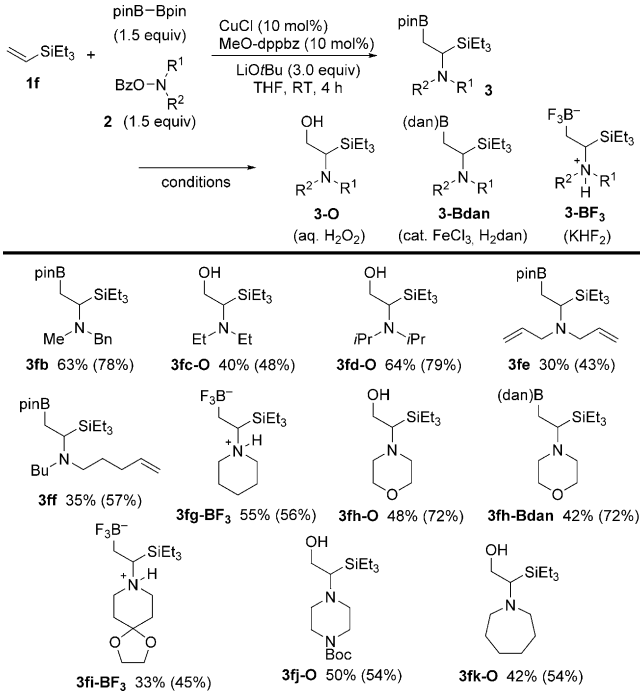
for the internal vinylsilane: **1j** and **1k** showed higher reactivity than triethylsilyl-substituted (*E*)-**1a** and **1g**, respectively (entry 11 vs. entry 1 and entry 12 vs. entry 7).[15] In several cases where the product yields were moderate, the starting vinylsilanes were recovered intact. The mass balance was generally good, and we could not observe any problematic side reactions.

On the other hand, (*E*)-styrylsilane (*E*)-**1l** afforded the opposite regioisomer β-aminosilane **3la′** exclusively (Scheme 3). The structure including the relative stereochemistry was confirmed by X-ray analysis.[16] Such a trend was also

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

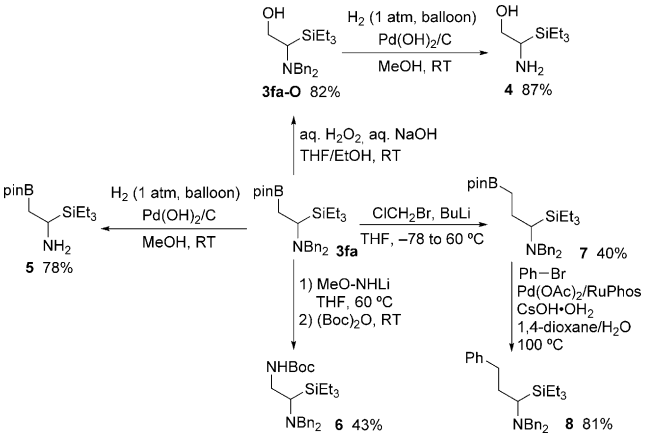
observed in the related copper-catalyzed hydroboration of vinylsilanes,[12d] and it can be explained by the effective Ph–vinyl conjugation[17] over the hyperconjugation proposed in Scheme 1. However, to our delight, the corresponding (*Z*)-**1l** preferably formed the desired α-aminosilanes **3la** with high diastereoselectivity (*syn*/*anti* < 1:99), probably because the 1,3-allylic strain of the (*Z*)-**1l** perturbed the above Ph–vinyl conjugation. Its regio- and diastereoselectivity were also determined by the crystallographic analysis.[16] An electron-donating MeO-substituted (*Z*)-**1m** also gave the *anti*-**3ma** selectively while the highly electron-withdrawing nature of CF_3 in (*Z*)-**1n** again increased the conjugation of the styrene part, leading to the regioisomer **3na′** as the major product.

Several *N*,*N*-dialkylhydroxylamine derivatives **2** participated in the reaction with **1f**. Representative products are illustrated in Scheme 4. Acyclic *N*-benzyl-*N*-methyl, *N*,*N*-diethyl, *N*,*N*-diisopropyl, and *N*,*N*-diallylamines provided the desired β-boryl-α-aminosilanes **3fb**–**3fe** in moderate to good yields. The aminoborated products **3fc** and **3fd** were relatively unstable and thus purified as the β-hydroxyl-α-aminosilanes **3fc-O** and **3fd-O** after the oxidation. The *N*-pentenylamine furnished the usual product **3ff**, thus suggesting an aminyl radical pathway is unlikely.[18] Although the Cu-based system accommodated cyclic amines such as piperidine, morpholine, acetal-protected piperidone, *N*-Boc piperazine, and azepane (**3fg**–**3fk**), all products were sensitive to silica gel in the column chromatography. However, we could pleasingly isolate them as the corresponding alcohol (**3fh-O**, **3fj-O**, and **3fk-O**) or more stable boryl derivatives such as B(dan) (dan = 1,8-diaminonaphthyl; **3fh-Bdan**)[19] and BF_3^- (**3fg-BF_3** and **3fi-BF_3**).[8a,20] Particularly in the last cases, the chromatographic purification was not necessary, and simple filtration furnished analytically pure internal ammonium borate salts **3fg-BF_3** and **3fi-BF_3**.



Scheme 4. Catalytic aminoboration with various hydroxylamines **2**. Isolated yields are given. ^{1}H NMR yield in the pinB form is in parentheses. See the Supporting Information for detailed conditions of the derivatization of the Bpin moiety. Boc = *tert*-butoxycarbonyl.

The obtained β-boryl-α-aminosilane **3fa** was readily transformed into functionalized α-aminosilanes (Scheme 5).



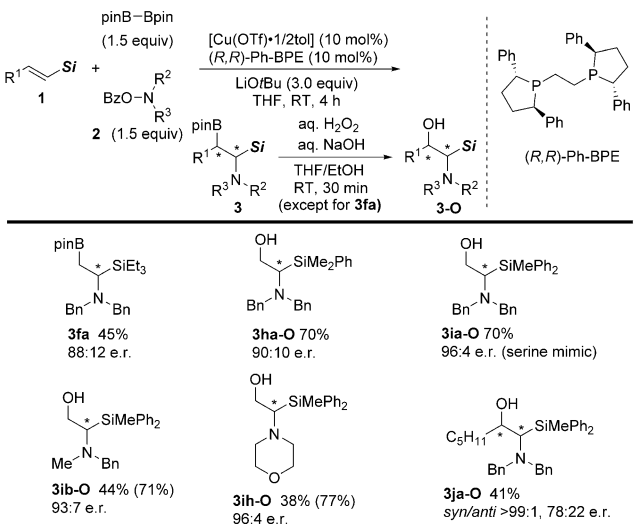
Scheme 5. Derivatization of β-boryl-α-aminosilane **3fa**. RuPhos = dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl.

The oxygenation (**3fa**→**3fa-O**) was followed by hydrogenolysis to deliver the 1,2-aminoalcohol **4** with free NH_2 and OH groups. The hydrogenolysis was also directly applicable to the parent **3fa**, and the pinB-retained primary amine **5** was obtained in 78% yield. The MeO-NHLi-promoted amination[6f] of the pinB moiety gave the corresponding diamine **6** with the orthogonal protecting groups on nitrogens. Moreover, the homologation/Suzuki–Miyaura coupling sequence was possible, and the arylated α-aminosilane **8** was formed in an acceptable overall yield.[21] These successful manipulations demonstrate the high synthetic utility of the aminoborated product **3** as a platform for the synthesis of a variety of α-aminosilanes.

Finally, we applied this protocol to a catalytic asymmetric reaction by using an optically active bisphosphine ligand. Preliminary ligand screening identified (*R*,*R*)-Ph-BPE to be a good candidate (Scheme 6). Namely, treatment of **1f** with pinB-Bpin and **2a** in the presence of a [Cu(OTf)·1/2tol]/(*R*,*R*)-Ph-BPE catalyst at room temperature afforded chiral **3fa** with 88:12 e.r.[22] Increasing the size of the silyl substituent from $SiEt_3$ to $SiMe_2Ph$ and $SiMePh_2$ improved the enantiomeric ratio to 90:10 and 96:4 e.r. (**3ha-O** and **3ia-O**). Notably, **3ia-O** is a silane analogue of an optically active α-aminoacid, serine.[2] Hydroxylamines other than **2a** could also be employed, and chiral α-aminosilanes **3ib-O** and **3ih-O** were obtained with 93:7 and 96:4 e.r., respectively. On the other hand, the heptenylsilane **1j** gave a moderate enantiomeric ratio of 78:22 (**3ja-O**). Thus the current limitation of the enantioselective catalyst is that internal vinylsilanes cannot be applied.

In conclusion, we have developed a copper-catalyzed regioselective and stereospecific aminoboration of vinylsi-

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 6. Catalytic enantioselective aminoboration of vinylsilanes. ^{1}H NMR yield in the pinB form is in parentheses.

lanes, leading to β-boryl-α-aminosilanes in good yields. By using the boron functionality at the β position, the products can be useful synthetic intermediates for various α-aminosilanes of potent interest in synthetic as well as medicinal chemistry. Moreover, asymmetric catalysis with a chiral bisphosphine ligand delivers silane analogues of optically active α-aminoacids in good to high enantiomeric ratios. Further manipulations of products, improvement of asymmetric catalysis, and development of related electrophilic amination reactions are ongoing in our laboratory.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Nos. JP 15K13696 (Grant-in-Aid for Exploratory Research) and JP 15H05485 (Grant-in-Aid for Young Scientists (A)) to K.H. and JP 24225002 (Grant-in-Aid for Scientific Research (S)) to M.M. We thank Wataru Miura for his assistance in X-ray analysis.

Keywords: α-aminosilanes · boron · copper · electrophilic amination · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 14400–14404
Angew. Chem. **2016**, *128*, 14612–14616

[1] a) T. Hiyama, T. Kusamoto in *Comprehensive Organic Synthesis*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, Chap. 3.12; b) *The Chemistry of Organosilicon Compounds* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**.

[2] a) J. Kim, S. M. Sieburth, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2853; b) J. Kim, G. Hewitt, P. Carroll, S. M. Sieburth, *J. Org. Chem.* **2005**, *70*, 5781; c) L. Nielsen, K. B. Lindsay, J. Faber, N. C. Nielsen, T. Skrydstrup, *J. Org. Chem.* **2007**, *72*, 10035; d) L. Nielsen, T. Skrydstrup, *J. Am. Chem. Soc.* **2008**, *130*, 13145; e) N. A. Meanwell, *J. Med. Chem.* **2011**, *54*, 2529; f) A. K. Franz, S. O. Wilson, *J. Med. Chem.* **2012**, *55*, 388.

[3] a) D. M. Ballweg, R. C. Miller, D. J. Gray, K. A. Scheidt, *Org. Lett.* **2005**, *7*, 1403; b) D. Hernández, K. B. Lindsay, L. Nielsen, T. Mittag, K. Bjerglund, S. Friis, R. Mose, T. Skrydstrup, *J. Org. Chem.* **2010**, *75*, 3283; c) D. Hernández, L. Nielsen, K. B. Lindsay, M. A. Lopez-Garcia, K. Bjerglund, T. Skrydstrup, *Org. Lett.* **2010**, *12*, 3528; d) D. Hernández, R. Mose, T. Skrydstrup, *Org. Lett.* **2010**, *12*, 732; e) Y. Bao, S. Singh, H. Q. Duong, C. Cao, S. M. Sieburth, *Org. Lett.* **2011**, *13*, 1787.

[4] a) A. Hensel, K. Nagura, L. B. Delvos, M. Oestreich, *Angew. Chem. Int. Ed.* **2014**, *53*, 4964; *Angew. Chem.* **2014**, *126*, 5064; b) T. Mita, M. Sugawara, K. Saito, Y. Sato, *Org. Lett.* **2014**, *16*, 3028; c) C. Zhao, C. Jiang, J. Wang, C. Wu, Q.-W. Zhang, W. He, *Asian J. Org. Chem.* **2014**, *3*, 851.

[5] a) N. Niljianskul, S. Zhu, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2015**, *54*, 1638; *Angew. Chem.* **2015**, *127*, 1658; also see: b) S. Zhu, N. Niljianskul, S. L. Buchwald, *J. Am. Chem. Soc.* **2013**, *135*, 15746; c) S. Zhu, S. L. Buchwald, *J. Am. Chem. Soc.* **2014**, *136*, 15913; d) S.-L. Shi, S. L. Buchwald, *Nat. Chem.* **2015**, *7*, 38; e) Y. Yang, S.-L. Shi, D. Niu, P. Liu, S. L. Buchwald, *Science* **2015**, *349*, 62.

[6] For selected examples of electrophilic amination reactions with the hydroxylamine, see: a) K. Narasaka, M. Kitamura, *Eur. J. Org. Chem.* **2005**, 4505; b) A. M. Berman, J. S. Johnson, *J. Am. Chem. Soc.* **2004**, *126*, 5680; c) M. J. Campbell, J. S. Johnson, *Org. Lett.* **2007**, *9*, 1521; d) S. Liu, L. S. Liebeskind, *J. Am. Chem. Soc.* **2008**, *130*, 6918; e) R. P. Rucker, A. M. Whittaker, H. Dang, G. Lalic, *J. Am. Chem. Soc.* **2012**, *134*, 6571; f) S. N. Mlynarski, A. S. Karns, J. P. Morken, *J. Am. Chem. Soc.* **2012**, *134*, 16449; g) C. Zhu, G. Li, D. H. Ess, J. R. Falck, L. Kürti, *J. Am. Chem. Soc.* **2012**, *134*, 18253; h) Z. Dong, G. Dong, *J. Am. Chem. Soc.* **2013**, *135*, 18350; i) S. L. McDonald, Q. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1867; *Angew. Chem.* **2014**, *126*, 1898; j) M. Shang, S.-H. Zeng, S.-Z. Sun, H.-X. Dai, J.-Q. Yu, *Org. Lett.* **2013**, *15*, 5286; k) P. Patel, S. Chang, *Org. Lett.* **2014**, *16*, 3328; l) J. He, T, Shigenari, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2015**, *54*, 6545; *Angew. Chem.* **2015**, *127*, 6645.

[7] For additional approaches to the α-aminosilane, see: a) C. Barberis, N. Voyer, *Tetrahedron Lett.* **1998**, *39*, 6807; b) S. M. Sieburth, H. K. O'Hare, J. Xu, Y. Chen, G. Liu, *Org. Lett.* **2003**, *5*, 1859; c) S. M. Sieburth, G. Liu, *Org. Lett.* **2003**, *5*, 4677.

[8] a) N. Matsuda, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2013**, *135*, 4934; b) R. Sakae, N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2014**, *16*, 1228; c) R. Sakae, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2015**, *54*, 613; *Angew. Chem.* **2015**, *127*, 623; d) R. Sakae, K. Hirano, M. Miura, *J. Am. Chem. Soc.* **2015**, *137*, 6460; also see: e) T. Kawano, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2010**, *132*, 6900; f) N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 3642; *Angew. Chem.* **2012**, *124*, 3702; g) N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 11827; *Angew. Chem.* **2012**, *124*, 11997; h) Y. Miki, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2013**, *52*, 10830; *Angew. Chem.* **2013**, *125*, 11030; i) D. Nishikawa, K. Hirano, M. Miura, *J. Am. Chem. Soc.* **2015**, *137*, 15620.

[9] D. S. Laitar, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* **2005**, *127*, 17196.

[10] D. S. Laitar, E. Y. Tsui, J. P. Sadighi, *Organometallics* **2006**, *25*, 2405.

[11] Recent computational studies suggest the S_N2-type oxidative addition/reductive elimination sequence in the C–N forming step; S. Tobisch, *Chem. Eur. J.* **2016**, *22*, 8290.

[12] a) H. Ito, Y. Kosaka, K. Nonoyama, Y. Sasaki, M. Sawamura, *Angew. Chem. Int. Ed.* **2008**, *47*, 7424; *Angew. Chem.* **2008**, *120*, 7534; b) H. Ito, T. Toyoda, M. Sawamura, *J. Am. Chem. Soc.* **2010**, *132*, 5990; c) K. Kubota, E. Yamamoto, H. Ito, *Adv. Synth. Catal.* **2013**, *355*, 3527; d) F. Meng, H. Jang, A. H. Hoveyda, *Chem. Eur. J.* **2013**, *19*, 3204; e) H. Yoshida, I. Kageyuki, K. Takaki, *Org. Lett.* **2013**, *15*, 952.

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[13] The *syn* stereochemistry can be eroded in the C–N forming step. For relevant observations of alkylcopper species, see: a) C. Zhong, S. Kunii, Y. Kosaka, M. Sawamura, H. Ito, *J. Am. Chem. Soc.* **2010**, *132*, 11440; b) K. M. Logan, K. B. Smith, M. K. Brown, *Angew. Chem. Int. Ed.* **2015**, *54*, 5228; *Angew. Chem.* **2015**, *127*, 5317; c) K. Semba, K. Ariyama, H. Zheng, R. Kameyama, S. Sakaki, Y. Nakao, *Angew. Chem. Int. Ed.* **2016**, *55*, 6275; *Angew. Chem.* **2016**, *128*, 6383. Additionally, the *syn*/*anti* diastereoselectivity was somewhat dependent on the external ligand. See the Supporting Information for more detailed optimization studies.

[14] The *syn* stereochemistry of **3ba** was determined by X-ray analysis after the derivatization into the corresponding ester (see the Supporting Information for details). The relative stereochemistry of other products from alkyl-substituted vinylsilanes was tentatively assigned by analogy.

[15] The β-boryl-α-aminosilanes bearing the Ph group on Si were somewhat unstable for the silica gel column chromatography and thus isolated after the oxidation.

[16] See the Supporting Information for details.

[17] a) L. Dang, H. Zhao, Z. Lin, T. B. Marder, *Organometallics* **2007**, *26*, 2824; b) L. Deng, Z. Lin, T. B. Marder, *Organometallics* **2008**, *27*, 4443.

[18] a) M. Noack, R. Göttlich, *Chem. Commun.* **2002**, 536; also see: b) T. Tsuritani, H. Shinokubo, K. Oshima, *Org. Lett.* **2001**, *3*, 2709; c) B. N. Hemric, K. Shen, Q. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 5813.

[19] a) H. Noguchi, K. Hojo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 758; b) J. L. Wood, L. D. Marciasini, M. Vaultier, M. Pucheault, *Synlett* **2014**, *25*, 551.

[20] J. Raushel, D. L. Sandrock, K. V. Josyula, D. Pakyz, G. A. Molander, *J. Org. Chem.* **2011**, *76*, 2762.

[21] Unfortunately, the β-aminoborane **3fa** could not be directly applied to the Suzuki–Miyaura coupling under the present conditions. This is probably because the intermolecular tight chelation of N to B in **3fa** interferes with the effective transmetalation between B and Pd.

[22] See the Supporting Information for optimization studies on asymmetric catalysis.

Received: August 19, 2016
Published online: October 18, 2016

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim