

# Anti-Selective Vicinal Silaboration and Diboration of Alkynoates through Phosphine Organocatalysis

Kazunori Nagao, Hirohisa Ohmiya,\* and Masaya Sawamura\*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

**(5)** Supporting Information

**ABSTRACT:** Trialkylphosphine organocatalysts have enabled *anti*selective vicinal silaboration and diboration of the C–C triple bond in alkynoates to produce  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha$ , $\beta$ -diboryl acrylates, respectively. The *anti* stereoselectivity was complete and robust. A variety of functional groups were tolerated in the alkynoates. The two vicinally installed heteroatom substituents of the  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha$ , $\beta$ -diboryl acrylates could be



differentiated and transformed in a stepwise manner, allowing the synthesis of a diverse array of unsymmetrical tetrasubstituted alkenes.

A lkenylborons and alkenylsilanes are useful synthetic intermediates in organic synthesis because of their chemical stability and their applicability toward various transformations.<sup>1</sup> 1-Boryl-2-silyl-, 1,2-diboryl-, and 1,2-disilylalkenes are thus likely to represent platforms for the synthesis of various tetrasubstituted alkenes that are found in many important pharmaceuticals and bioactive natural compounds (Figure 1).<sup>2</sup> Addition of





interelement compounds such as silylborons (Si–B), diborons (B–B), or disilanes (Si–Si) across C–C triple bonds is the most straightforward and attractive method for formation of densely functionalized alkenes.<sup>3</sup> Most of the reported alkyne silaborations, diborations, and disilylations occurred in *syn* addition mode.<sup>4–8</sup> *anti*-Selective additions were also reported, but they were rare. For example, Suginome et al. reported the Pd-catalyzed *anti*-selective silaboration of terminal alkynes with silylboronates, but the stereoselectivity was not complete.<sup>9a</sup> Recently, Uchiyama, Hirano, and co-workers reported the completely *anti*-selective diboration of the C–C triple bond in propargylic alkoxide anions.<sup>9b</sup>

We previously developed a nucleophilic phosphine catalysis that promoted *anti*-selective carboboration of alkynoates with alkyl-, alkenyl-, or arylboranes to form  $\beta$ -boryl acrylate derivatives.<sup>10</sup> Herein, we report that similar protocols were applicable to the silaboration and diboration of alkynoates, providing a versatile and efficient approach to densely functionalized alkenes such as  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha$ , $\beta$ -diboryl acrylates.<sup>11</sup> The *anti*-stereoselectivity was exclusive and robust irrespective of substrate structures. The regioselectivity of the silaboration across the polar C–C triple bond exhibited inverse electronic demand, with the intrinsically electrophilic B-atom being delivered to the positively charged  $\beta$ -carbon atom of the  $\alpha,\beta$ -unsaturated ester (alkynoate). A variety of functional groups were tolerated in the alkynoates. Importantly, the two vicinally installed heteroatom substituents of the  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha,\beta$ -diboryl acrylates could be differentiated and transformed in a stepwise manner, allowing the use of these densely functionalized alkenes as a platform for the synthesis of a diverse array of unsymmetrical tetrasubstituted alkenes. The potential of this strategy was demonstrated by molecular transformations toward the synthesis of tamoxifen-type compounds.

It should be noted that bis(pinacolato)diboron and a silylboron reagent PhMe<sub>2</sub>SiB(pin) have been used as reagents for protoboration or protosilylation of electron-deficient alkenes under metal-free Lewis base catalyzed conditions.<sup>12</sup> More recently, the chemistry of the Lewis base catalyzed transformation of the interelement compounds has been extended to diboration and silaboration of the C–C double bonds in styrenes and allylic alcohols.<sup>13</sup> Importantly, however, the vicinal difunctionalization of alkynes under transition-metal-free conditions is still limited to the Uchiyama's diboration of the propargylic alkoxide anions discussed above.<sup>9b</sup>

Specifically, the reaction of ethyl 3-phenylpropiolate (2a) (1.1 g, 6 mmol) with PhMe<sub>2</sub>SiB(pin) (1a) (1.57 g, 6 mmol) in the presence of PBu<sub>3</sub> (10 mol %) without a solvent at 80 °C over 8 h gave  $\beta$ -boryl- $\alpha$ -silyl acrylate 3aa in isomerically pure form in 84% isolated yield (based on 2a; 99% NMR yield; complete conversion of 2a) (eq 1).<sup>14</sup> The Si–B bond addition was completely regioselective and *anti*-stereoselective. The <sup>11</sup>B NMR spectrum of 3aa indicated that the carbonyl oxygen was coordinated with the boron atom. The PBu<sub>3</sub> loading could be reduced to 5 mol % without affecting the yield of 3aa (84%).

The scope of the phosphine-catalyzed silaboration is shown in Table 1. The reaction of (*i*-PrO)Me<sub>2</sub>SiB(pin) (1b) with 2a

Received: January 30, 2015



Table 1. Phosphine-Catalyzed Silaboration<sup>a</sup>



<sup>*a*</sup>Conditions of silaboration reaction: **2**, 0.3 mmol; **1**, 0.3 mmol; PBu<sub>3</sub>, 10 mol %; 80 °C, 8 h. <sup>*b*</sup>Yield of the isolated product (silica gel chromatography). <sup>*c*1</sup>H NMR yield. <sup>*d*</sup>**2i** (0.45 mmol) was used.

occurred cleanly without touching the potentially sensitive Si–O bond to give  $\beta$ -boryl- $\alpha$ -alkoxysilyl acrylate **3ba** in excellent yield (Table 1, entry 1). Substituted phenylpropiolates (**2b**-**f**) with a methoxy, fluoro, ketone, ester, or 2-(dimethylamino)ethoxy group at the *meta-* or *para*-position of the aromatic  $\beta$ -substituent and 2-thienyl-substituted alkynoate (**2g**) reacted with

PhMe<sub>2</sub>SiB(pin) (1a) in high yields (entries 2–7). Alkylsubstituted alkynoates 2h-l also underwent efficient silaboration (entries 8–12).<sup>15</sup>

The diboration was possible by using a symmetrical diboron compound bis(pinacolato)diboron (4a) as a reagent, allowing the selective preparation of *trans-\alpha,\beta*-diboryl acrylate derivatives (Table 2). For instance, the phosphine-catalyzed diboration of 2a

Table 2. Phosphine-Catalyzed Diboration<sup>a</sup>



<sup>*a*</sup>Conditions of diboration reaction: **2**, 0.3 mmol; **4a**, 0.3 mmol; PBu<sub>3</sub>, 10 mol %; THF (0.05 mL, entries 2–5 and 7) or neat (entries 8 and 9), 80 °C, 8 h. <sup>*b*1</sup>H NMR yield. Yield of the isolated product is in parentheses (silica gel chromatography; entries 1–5 and 7–9, recrystallization; entry 6). <sup>*c*</sup>The isolated yield was significantly lower than the <sup>1</sup>H NMR yield due to material loss during silica gel chromatography or recrystallization. <sup>*d*</sup>Reaction at 6 mmol scale.

with **4a** occurred with complete *anti*-stereoselectivity to afford the corresponding  $\alpha,\beta$ -diboryl acrylate **5aa** (entry 1). Neither Batom in **5aa** had an interaction with the carbonyl oxygen as indicated by <sup>11</sup>B NMR spectroscopy. The use of bis(neopentylglycolato)diboron or bis(catecholato)diboron instead of **4a** resulted in no reaction (data not shown).

Functional groups such as methoxy, fluoro, ketone, ester, and 2-(dimethylamino)ethoxy moieties were tolerated at the *meta*- or *para*-position of the  $\beta$ -substituent in the alkynoates (Table 2,

entries 2–6). The thiophene-substituted propiolate 2g was a suitable substrate (entry 7). The reaction of alkyl-substituted propiolates such as 2-butynoate 2h and 2-pentynoate 2i gave alkyl-substituted alkenylboranes 5ah and 5ai, respectively, in good yields (entries 8 and 9).<sup>15</sup>

A possible catalytic cycle for the silaboration and diboration is illustrated in Figure 2. As proposed for the carboboration of



Figure 2. A possible catalytic cycle.

alkynoates with organoboranes,<sup>10</sup> the phosphine catalysis should be initiated by the conjugate addition of PBu<sub>3</sub> to the alkynoate **2** with the assistance of Lewis acidic activation of the carbonyl group to form a zwitterionic allenolate intermediate (**A**).<sup>16</sup> The B-atom of the silylboronate (**1**) or diboron (**4**) should be a Lewis acid center in the present case. The terminal silyl or boryl groups migrate to the *sp*-hybridized central carbon of the allene moiety to form ylide intermediates (**B1**/**B2**).<sup>17</sup> Next, the ylide carbon of **B2** attacks the B-atom bound to the enolate oxygen to form cyclic borate **C**. Finally, elimination of Bu<sub>3</sub>P associated with B–O cleavage affords **3** or **5**.

The two vicinally installed heteroatom substituents of the  $\beta$ boryl- $\alpha$ -silyl acrylates and  $\alpha$ , $\beta$ -diboryl acrylates could be differentiated and transformed in a stepwise manner (eqs 2–



4). For example,  $\beta$ -boryl- $\alpha$ -silyl acrylate **3aa** underwent Suzuki– Miyaura coupling with 1-bromo-4-fluorobenzene at the boron site [Pd(OAc)<sub>2</sub>-DtBPF (1,1'-bis(di-*tert*-butylphosphino)ferrocene) catalyst/K<sub>3</sub>PO<sub>4</sub>] to afford the corresponding trisubstituted alkenylsilane **6aa** with excellent yield and complete *E* selectivity; the C–Si bond remained untouched (eq 2). The obtained **6aa** could be derivatized to the trisubstituted alkenyl bromide **7aa** without E/Z isomerization.<sup>18</sup>

We were delighted to find that the two boron sites in **5aa** could be efficiently differentiated for a stepwise twofold cross-coupling. Thus, the cross-coupling between the  $\alpha$ , $\beta$ -diboryl acrylate **5aa**  and 4-bromoanisole under the influence of a Pd(OAc)<sub>2</sub>-DtBPF catalyst and *i*-Pr<sub>2</sub>NEt base occurred selectively at the  $\alpha$ -boron site to give alkenylboronate 8aa (83%, E/Z > 99:1), and no diarylation occurred (eq 3).<sup>19</sup> The second arylation with 4bromotoluene (Z/E > 99:1) was possible by subjecting 8aa to the coupling conditions using the  $Pd(OAc)_2/DtBPF/K_3PO_4$ system: isomerically pure tetrasubstituted alkene 9aa was obtained in good yield (eq 3). The site selectivity in the first cross-coupling favoring  $C(\alpha)$ -B bond transformation is likely due to the electron-withdrawing resonance effect of the ester group rendering  $C(\beta)$  less nucleophilic. Additionally, the  $\alpha,\beta$ diborvl acrylate 5aa underwent site-selective Rh-catalvzed conjugate addition to tert-butyl acrylate followed by Pd-catalyzed cross-coupling with 4-bromoanisole to produce tetrasubstituted alkene 11aa (eq 4). Overall, these transformations (eqs 2-4) demonstrated the usefulness of the  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha,\beta$ -diboryl acrylates as precursors to a diverse array of unsymmetrical tetrasubstituted alkenes.

We then used this strategy for molecular transformations toward the synthesis of (Z)-tamoxifen, an antiestrogenic anticancer drug, and its analogues (Scheme 1).<sup>20</sup> The Pd-



catalyzed  $\alpha$ -selective cross-coupling of the  $\alpha,\beta$ -diboryl acrylate **Saf** with an aryl bromide (Ar<sup>1</sup>-Br) followed by a second coupling with the same or different (hetero)aryl bromide (Ar<sup>2</sup>-Br) afforded the diarylated products **9af-a**-d in isomerically pure forms. The reduction of the ester group in **9af-a** (Ar<sup>1</sup> = Ar<sup>2</sup> = Ph) with DIBAL-H produced the alcohol **12af-a**. The synthesis of (*Z*)-tamoxifen from **12af-a** was reported previously.<sup>20c,i,l</sup> Thus, a formal total synthesis of (*Z*)-tamoxifen was achieved.

In summary, we have developed phosphine-catalyzed antiselective silaboration and diboration of the C-C triple bond in alkynoates to produce  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha$ , $\beta$ -diboryl acrylates, respectively. The anti-stereoselectivity was exclusive and robust irrespective of substrate structures. The silaboration across the polar C-C triple bond occurred with inverse electronic demand with regard to the regioselectivity, with the intrinsically electrophilic B-atom being delivered to the positively charged  $\beta$ -C atom. A variety of functional groups were tolerated in the alkynoates. Importantly, the two vicinally installed heteroatom substituents of the  $\beta$ -boryl- $\alpha$ -silyl acrylates and  $\alpha_{\beta}$ -diboryl acrylates could be differentiated and transformed in a stepwise manner, allowing the use of these densely functionalized alkenes as a platform for the synthesis of a diverse array of unsymmetrical tetrasubstituted alkenes. The power of this strategy was demonstrated by molecular transformations toward the synthesis of tamoxifen-type compounds.

#### **Organic Letters**

ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

# AUTHOR INFORMATION

## **Corresponding Authors**

\*E-mail: ohmiya@sci.hokudai.ac.jp. \*E-mail: sawamura@sci.hokudai.ac.jp.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Young Scientists (A) and Challenging Exploratory Research, JSPS to H.O. and by CREST, JST to M.S. K.N. thanks JSPS for scholarship support.

## REFERENCES

(1) (a) Boronic Acids; Hall, D. G., Ed.; Wiley-VCH: Weinheim, Germany, 2005. (b) Brook, M. A. Silicon in Organic, Organometallic and Polymer Chemistry; Wiley: New York, 2000.

(2) For a review on the synthesis of multisubstituted alkenes, see: Flynn, A. B.; Ogilvie, W. W. *Chem. Rev.* **2007**, *107*, 4698.

(3) For reviews, see: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, 99, 3435. (b) Han, L. B.; Tanaka, M. *Chem. Commun.* **1999**, 395. (c) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, 100, 3221. (d) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, 106, 2320. (e) Ito, Y. *J. Organomet. Chem.* **1999**, 576, 300.

(4) For reviews on silaboration of unsaturated compounds, see:
(a) Ohmura, T.; Suginome, M. Bull. Chem. Soc. Jpn. 2009, 82, 29.
(b) Oestreich, M.; Hartmann, E.; Mewald, M. Chem. Rev. 2013, 113, 402.

(5) For selected papers on transition-metal-catalyzed syn-selective silaboration with silylborons of alkynes, see: (a) Suginome, M.; Nakamura, H.; Ito, Y. Chem. Commun. 1996, 2777. (b) Suginome, M.; Matsuda, T.; Ito, Y. Organometallics 1998, 17, 5233. (c) Suginome, M.; Matsuda, T.; Nakamura, H.; Ito, Y. Tetrahedron 1999, 55, 8787. (d) Suginome, M.; Noguchi, H.; Hasui, T.; Murakami, M. Bull. Chem. Soc. Jpn. 2005, 78, 323. (e) Ohmura, T.; Oshima, K.; Suginome, M. Organometallics 2013, 32, 2870. (f) Ohmura, T.; Oshima, K.; Taniguchi, H.; Suginome, M. J. Am. Chem. Soc. 2010, 132, 12194. (g) Da Silva, J. C. A.; Birot, M.; Pillot, J.-P.; Pétraud, M. J. Organomet. Chem. 2002, 646, 179. (h) Jiao, J.; Nakajima, K.; Nishihara, Y. Org. Lett. 2013, 15, 3294. (i) Saito, N.; Saito, K.; Sato, H.; Sato, Y. Adv. Synth. Catal. 2013, 355, 853. (j) Zhou, H.; Moberg, C. J. Am. Chem. Soc. 2012, 134, 15992. (k) Gryparis, C.; Stratakis, M. Org. Lett. 2014, 16, 1430.

(6) For reviews on diboration of unsaturated compounds, see: (a) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63. (b) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. Chem. Rev. **1998**, *98*, 2685. (c) Takaya, J.; Iwasawa, N. ACS Catal. **2012**, *2*, 1993.

(7) For selected papers on transition-metal-catalyzed syn-selective diboration with diborons of alkynes, see: (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. J. Am. Chem. Soc. **1993**, *115*, 11018. (b) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. Organometallics **1996**, *15*, 713. (c) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. Organometallics **1996**, *15*, 5137. (d) Thomas, R. L.; Souza, F. E. S.; Marder, T. B. J. Chem. Soc., Dalton Trans. **2001**, 1650. (e) Hyodo, K.; Suetsugu, M.; Nishihara, Y. Org. Lett. **2014**, *16*, 440. (f) Iwadate, N.; Suginome, M. J. Am. Chem. Soc. **2010**, *132*, 2548. (g) Lillo, V.; Fructos, M. R.; Ramírez, J.; Braga, A. A. C.; Maseras, F.; Díaz-Requejo, M. M.; Pérez, P. J.; Fernández, E. Chem.—Eur. J. **2007**, *13*, 2614. (h) Yoshida, H.; Kawashima, S.; Takemoto, Y.; Okada, K.; Ohshita, J.; Takaki, K. Angew. Chem., Int. Ed.

**2012**, *51*, 235. (i) Chen, Q.; Zhao, J.; Ishikawa, Y.; Asao, N.; Yamamoto, Y.; Jin, T. Org. Lett. **2013**, *15*, 5766. (j) Iverson, C. N.; Smith, M. R., III. Organometallics **1996**, *15*, 5155. (k) Adams, C. J.; Baber, R. A.; Batsanov, A. S.; Bramham, G.; Charmant, J. P. H.; Haddow, M. F.; Howard, J. A. K.; Lam, W. H.; Lin, Z.; Marder, T. B.; Norman, N. C.; Orpen, A. G. Dalton Trans. **2006**, 1370.

(8) For a review on disilylation of unsaturated compounds, see: Suginome, M.; Ito, Y. J. Organomet. Chem. 2003, 685, 218.

(9) (a) Ohmura, T.; Oshima, K.; Suginome, M. Chem. Commun. 2008, 1416. (b) Nagashima, Y.; Hirano, K.; Takita, R.; Uchiyama, M. J. Am. Chem. Soc. 2014, 136, 8532.

(10) Nagao, K.; Ohmiya, H.; Sawamura, M. J. Am. Chem. Soc. 2014, 136, 10605.

(11) For recent papers on Cu-catalyzed  $\beta$ -silylation of alkynoates with the silylboron reagent, see: (a) Xu, Y.-H.; Wu, L.-H.; Wang, J.; Loh, T.-P. *Chem. Commun.* **2014**, *50*, 7195. (b) Calderone, J. A.; Santos, W. L. *Angew. Chem., Int. Ed.* **2014**, *53*, 4154. (c) Linstadt, R. T. H.; Peterson, C. A.; Lippincott, D. J.; Jette, C. I.; Lipshutz, B. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 4159. (d) Vercruysse, S.; Cornelissen, L.; Nahra, F.; Collard, L.; Riant, O. *Chem.—Eur. J.* **2014**, *20*, 1834.

(12) (a) O'Brien, J. M.; Hoveyda, A. H. J. Am. Chem. Soc. 2011, 133, 7712. (b) Lee, K.-S.; Zhugralin, A. R.; Hoveyda, A. H. J. Am. Chem. Soc. 2009, 131, 7253. (c) Wu, H.; Radomkit, S.; O'Brien, J. M.; Hoveyda, A. H. J. Am. Chem. Soc. 2012, 134, 8277. (d) Bonet, A.; Gulyás, H.; Fernández, E. Angew. Chem., Int. Ed. 2010, 49, 5130. (e) Pubill-Ulldemolins, C.; Bonet, A.; Bo, C.; Gulyás, H.; Fernández, E. Chem.— Eur. J. 2012, 18, 1121. (f) Pubill-Ulldemolins, C.; Bonet, A.; Gulyás, H.; Bo, C.; Fernández, E. Org. Biomol. Chem. 2012, 10, 9677. (g) Bonet, A.; Pubill-Ulldemolins, C.; Bo, C.; Gulyás, H.; Fernández, E. Angew. Chem., Int. Ed. 2011, 50, 7158. (h) Bonet, A.; Sole, C.; Gulyás, H.; Fernández, E. Org. Biomol. Chem. 2012, 10, 6621.

(13) (a) Ito, H.; Horita, Y.; Yamamoto, E. Chem. Commun. 2012, 48, 8006. (b) Blaisdell, T. P.; Caya, T. C.; Zhang, L.; Sanz-Marco, A.; Morken, J. P. J. Am. Chem. Soc. 2014, 136, 9264–9267.

(14) Catalyst screening revealed that phosphines were useful,  $PBu_3$  being the most effective. See Supporting Information for catalyst effects. (15) For Table 1, entries 8–12 and Table 2, entries 8 and 9, unreacted alkynoate was detected in the crude materials.

(16) For reviews on nucleophilic catalysis by phosphines, see:
(a) Methot, J. L.; Roush, W. R. Adv. Synth. Catal. 2004, 346, 1035.
(b) Ye, L.-W.; Zhou, J.; Tang, Y. Chem. Soc. Rev. 2008, 37, 1140. (c) Lu, X.; Zhang, C.; Xu, Z. Acc. Chem. Res. 2001, 34, 535. For a review on Lewis base catalysis in organic synthesis, see: (d) Denmark, S. E.; Beutner, G. L. Angew. Chem., Int. Ed. 2008, 47, 1560.

(17) Hata, T.; Kitagawa, H.; Masai, H.; Kurahashi, T.; Shimizu, M.; Hiyama, T. Angew. Chem., Int. Ed. **2001**, 40, 790.

(18) Miller, R. B.; McGarvey, G. J. Org. Chem. 1978, 43, 4424.

(19) Lipshutz, B. H.; Bošković, Z. V.; Aue, D. H. Angew. Chem., Int. Ed. 2008, 47, 10183.

(20) For syntheses of tamoxifen, see: (a) Millar, R. B.; Al-Hassan, M. I. J. Org. Chem. 1985, 50, 2121. (b) Potter, G. A.; McCague, R. J. Org. Chem. 1990, 55, 6184. (c) Brown, S. D.; Armstrong, R. W. J. Org. Chem. 1997, 62, 7076. (d) Stüdemann, T.; Knochel, P. Angew. Chem., Int. Ed. 1997, 36, 93. (e) Tessier, P. E.; Penwell, A. J.; Souza, F. E. S.; Fallis, A. G. Org. Lett. 2003, 5, 2989. (f) Itami, K.; Kamei, T.; Yoshida, J.-i. J. Am. Chem. Soc. 2003, 125, 14670. (g) Shimizu, M.; Nakamaki, C.; Shimono, K.; Schelper, M.; Kurahashi, T.; Hiyama, T. J. Am. Chem. Soc. 2005, 127, 12506. (h) Zhou, C.; Larock, R. C. J. Org. Chem. 2005, 70, 3765. (i) Shimizu, K.; Takimoto, M.; Mori, M.; Sato, Y. Synlett 2006, 3182. (j) Nishihara, Y.; Miyasaka, M.; Okamoto, M.; Takahashi, H.; Inoue, E.; Tanemura, K.; Takagi, K. J. Am. Chem. Soc. 2007, 129, 12634. (k) Ishida, N.; Shimamoto, Y.; Murakami, M. Org. Lett. 2009, 11, 5434. (l) He, Z.; Kirchberg, S.; Fröhlich, R.; Studer, A. Angew. Chem., Int. Ed. 2012, 51, 3699.