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

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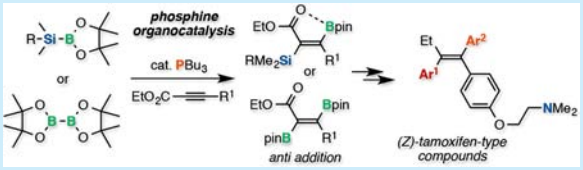
Supporting Information

**ABSTRACT:** Trialkylphosphine organocatalysts have enabled *anti*-selective vicinal silaboration and diboration of the C−C triple bond in alkynoates to produce *β*-boryl-*α*-silyl acrylates and *α,β*-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 *β*-boryl-*α*-silyl acrylates and *α,β*-diboryl acrylates could be differentiated and transformed in a stepwise manner, allowing the synthesis of a diverse array of unsymmetrical tetrasubstituted alkenes.




Alkenylborons and alkenylsilanes are useful synthetic intermediates in organic synthesis because of their chemical stability and their applicability toward various transformations.[1] 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).[2] Addition of

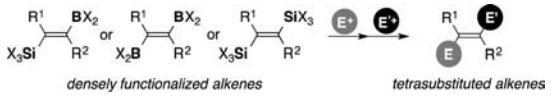



**Figure 1.** Synthesis of tetrasubstituted alkenes.

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.[3] Most of the reported alkyne silaborations, diborations, and disilylations occurred in *syn* addition mode.[4−8] *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.[9a] Recently, Uchiyama, Hirano, and co-workers reported the completely *anti*-selective diboration of the C−C triple bond in propargylic alkoxide anions.[9b]

We previously developed a nucleophilic phosphine catalysis that promoted *anti*-selective carboboration of alkynoates with alkyl-, alkenyl-, or arylboranes to form *β*-boryl acrylate derivatives.[10] 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 *β*-boryl-*α*-silyl acrylates and *α,β*-diboryl acrylates.[11] 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 *β*-carbon atom of the *α,β*-unsaturated ester (alkynoate). A variety of functional groups were tolerated in the alkynoates. Importantly, the two vicinally installed heteroatom substituents of the *β*-boryl-*α*-silyl acrylates and *α,β*-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 $PhMe_2SiB(pin)$ have been used as reagents for protoboration or protosilylation of electron-deficient alkenes under metal-free Lewis base catalyzed conditions.[12] 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.[13] 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.[9b]

Specifically, the reaction of ethyl 3-phenylpropiolate (**2a**) (1.1 g, 6 mmol) with $PhMe_2SiB(pin)$ (**1a**) (1.57 g, 6 mmol) in the presence of $PBu_3$ (10 mol %) without a solvent at 80 °C over 8 h gave *β*-boryl-*α*-silyl acrylate **3aa** in isomerically pure form in 84% isolated yield (based on **2a**; 99% NMR yield; complete conversion of **2a**) (eq 1).[14] The Si−B bond addition was completely regioselective and *anti*-stereoselective. The $^{11}B$ NMR spectrum of **3aa** indicated that the carbonyl oxygen was coordinated with the boron atom. The $PBu_3$ 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 $(i\text{-PrO})Me_2SiB(pin)$ (**1b**) with **2a**

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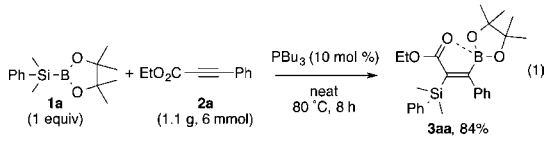
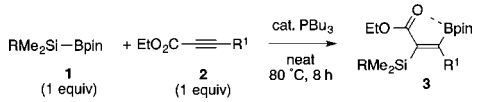



**Table 1. Phosphine-Catalyzed Silaboration**[a]



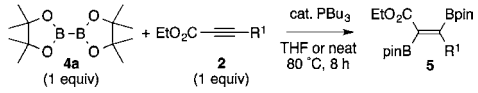

| entry | silylboron | alkynoate | product | yield (%)[b] |
|---|---|---|---|---|
| 1 | (PrO)Me$_2$Si–Bpin **1b** | **2a** | **3ba** | 96 |
| 2 | **1a** | **2b** | **3ab** | 99 |
| 3 | **1a** | **2c** | **3ac** | 92 |
| 4 | **1a** | **2d** | **3ad** | 77 |
| 5 | **1a** | **2e** | **3ae** | 76 |
| 6 | **1a** | **2f** | **3af** | 76[c] |
| 7 | **1a** | **2g** | **3ag** | 94 |
| 8 | **1a** | **2h** | **3ah** | 70 |
| 9[d] | **1a** | **2i** | **3ai** | 84 |
| 10 | **1a** | **2j** | **3aj** | 90 |
| 11 | **1a** | **2k** | **3ak** | 71 |
| 12 | **1a** | **2l** | **3al** | 75 |

[a]Conditions of silaboration reaction: **2**, 0.3 mmol; **1**, 0.3 mmol; $PBu_3$, 10 mol %; 80 °C, 8 h. [b]Yield of the isolated product (silica gel chromatography). [c]$^1$H NMR yield. [d]**2i** (0.45 mmol) was used.

occurred cleanly without touching the potentially sensitive Si–O bond to give *β*-boryl-*α*-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 *β*-substituent and 2-thienyl-substituted alkynoate (**2g**) reacted with PhMe$_2$SiB(pin) (**1a**) in high yields (entries 2–7). Alkyl-substituted alkynoates **2h–l** also underwent efficient silaboration (entries 8–12).[15]

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

**Table 2. Phosphine-Catalyzed Diboration**[a]




| entry | alkynoate | product | yield (%)[b,c] |
|---|---|---|---|
| 1[d] | **2a** | **5aa** | 97 (64) |
| 2 | **2b** | **5ab** | 99 (82) |
| 3 | **2c** | **5ac** | 99 (70) |
| 4 | **2d** | **5ad** | 71 (56) |
| 5 | **2e** | **5ae** | 83 (70) |
| 6[e] | **2f** | **5af** | 93 (78) |
| 7 | **2g** | **5ag** | 99 (68) |
| 8 | **2h** | **5ah** | 55 (55) |
| 9 | **2i** | **5ai** | 43 (37) |

[a]Conditions of diboration reaction: **2**, 0.3 mmol; **4a**, 0.3 mmol; $PBu_3$, 10 mol %; THF (0.05 mL, entries 2–5 and 7) or neat (entries 8 and 9), 80 °C, 8 h. [b]$^1$H NMR yield. Yield of the isolated product is in parentheses (silica gel chromatography; entries 1–5 and 7–9, recrystallization; entry 6). [c]The isolated yield was significantly lower than the $^1$H NMR yield due to material loss during silica gel chromatography or recrystallization. [d]Reaction at 6 mmol scale. [e]Reaction at 0.9 mmol scale.

with **4a** occurred with complete *anti*-stereoselectivity to afford the corresponding *α*,*β*-diboryl acrylate **5aa** (entry 1). Neither B-atom in **5aa** had an interaction with the carbonyl oxygen as indicated by $^{11}$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 *β*-substituent in the alkynoates (Table 2,



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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).[15]

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

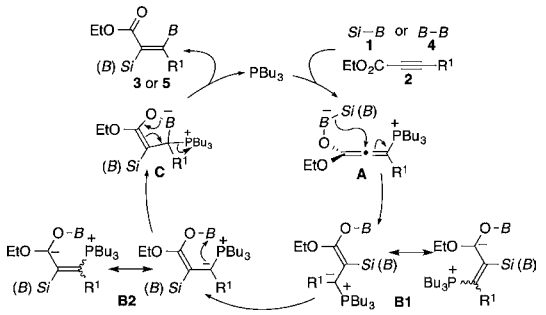
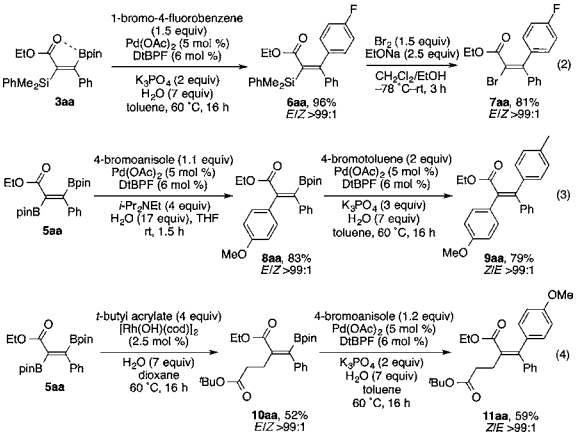


**Figure 2.** A possible catalytic cycle.

alkynoates with organoboranes,[10] the phosphine catalysis should be initiated by the conjugate addition of $PBu_3$ to the alkynoate **2** with the assistance of Lewis acidic activation of the carbonyl group to form a zwitterionic allenolate intermediate (**A**).[16] 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**).[17] Next, the ylide carbon of **B2** attacks the B-atom bound to the enolate oxygen to form cyclic borate **C**. Finally, elimination of $Bu_3P$ associated with B−O cleavage affords **3** or **5**.

The two vicinally installed heteroatom substituents of the *β*-boryl-*α*-silyl acrylates and *α*,*β*-diboryl acrylates could be differentiated and transformed in a stepwise manner (eqs 2−

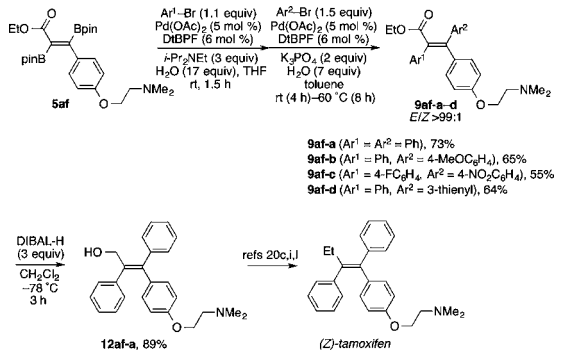


4). For example, *β*-boryl-*α*-silyl acrylate **3aa** underwent Suzuki−Miyaura coupling with 1-bromo-4-fluorobenzene at the boron site [$Pd(OAc)_2$−DtBPF (1,1′-bis(di-*tert*-butylphosphino)-ferrocene) catalyst/$K_3PO_4$] to afford the corresponding trisubstituted alkenylsilane **6aa** with excellent 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.[18]

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 *α*,*β*-diboryl acrylate **5aa** and 4-bromoanisole under the influence of a $Pd(OAc)_2$−DtBPF catalyst and *i*-$Pr_2NEt$ base occurred selectively at the *α*-boron site to give alkenylboronate **8aa** (83%, *E*/*Z* > 99:1), and no diarylation occurred (eq 3).[19] The second arylation with 4-bromotoluene (*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(*α*)−B bond transformation is likely due to the electron-withdrawing resonance effect of the ester group rendering C(*β*) less nucleophilic. Additionally, the *α*,*β*-diboryl acrylate **5aa** underwent site-selective Rh-catalyzed 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 *β*-boryl-*α*-silyl acrylates and *α*,*β*-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).[20] The Pd-

**Scheme 1. Synthesis of Tamoxifen-Type Compounds**



catalyzed *α*-selective cross-coupling of the *α*,*β*-diboryl acrylate **5af** with an aryl bromide ($Ar^1$−Br) followed by a second coupling with the same or different (hetero)aryl bromide ($Ar^2$−Br) afforded the diarylated products **9af-a**−**d** in isomerically pure forms. The reduction of the ester group in **9af-a** ($Ar^1 = Ar^2$ = Ph) with DIBAL-H produced the alcohol **12af-a**. The synthesis of (*Z*)-tamoxifen from **12af-a** was reported previously.[20c,i,l] Thus, a formal total synthesis of (*Z*)-tamoxifen was achieved.

In summary, we have developed phosphine-catalyzed *anti*-selective silaboration and diboration of the C−C triple bond in alkynoates to produce *β*-boryl-*α*-silyl acrylates and *α*,*β*-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 *β*-C atom. A variety of functional groups were tolerated in the alkynoates. Importantly, the two vicinally installed heteroatom substituents of the *β*-boryl-*α*-silyl acrylates and *α*,*β*-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.



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## ■ ASSOCIATED CONTENT

### 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


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### Notes

The authors declare no competing financial interest.

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## ■ 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.




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