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Relation	

Copper-Catalyzed Borylstannylation of Alkynes with Tin Fluorides

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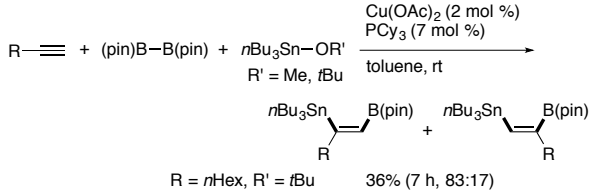
Supporting Information Placeholder

ABSTRACT: Tin fluorides were found to be suitable electrophiles for the copper-catalyzed borylstannylation of terminal alkynes with bis(pinacolato)diboron to afford *cis*-*vic*-boryl(stannyl)alkenes straightforwardly. A fluorine atom proved to play a pivotal role in generating a key catalytic intermediate, a borylcopper species, both in the induction period and in the σ-bond metathesis step.

INTRODUCTION

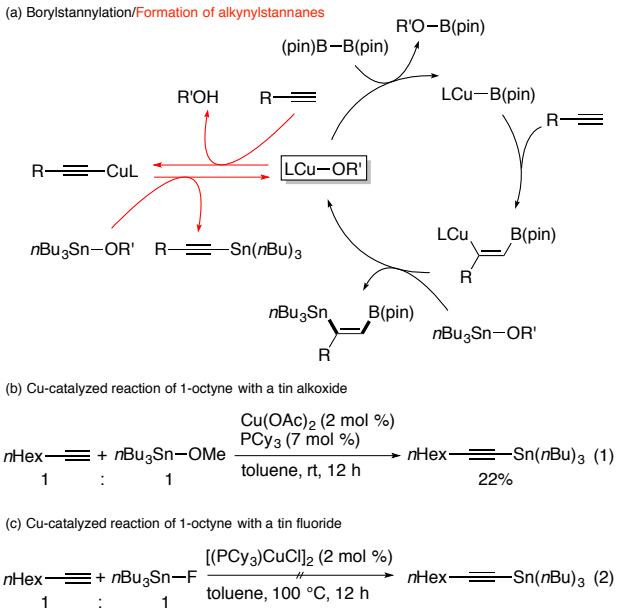
Borylstannylation[1] of unsaturated carbon–carbon bonds, which leads to synchronous carbon–boron and carbon–tin bond formation at *vicinal* positions, is of high synthetic value, because multifunctionalized organometallic compounds thus generated have bench stable/easy-to-handle properties, and can serve as convenient and potent intermediates for constructing complex molecular skeletons by site-selective carbon–carbon (*e.g.* Suzuki–Miyaura and Migita–Kosugi–Stille coupling)[2] and/or carbon–heteroatom[3] bond-forming processes at their C–B[4] and C–Sn[5] moieties. In particular, much attention has thus far been focused on the reaction of alkynes, that provides regio- and stereo-defined *vic*-boryl(stannyl)alkenes, owing to the potential utility for accessing diverse multisubstituted alkenes of biological and pharmacological significance.[6] Within this context, we have already developed the copper-catalyzed three-component borylstannylation of alkynes[1f] using bis(pinacolato)diboron [(pin)B–B(pin)] and tin alkoxides, where a copper alkoxide acts as a key catalytic species.[7,8] Although a variety of *vic*-boryl(stannyl)alkenes are efficiently accessible by this reaction, terminal alkynes, especially aliphatic ones, turned out to give the respective products only in moderate yield (Scheme 1), which is ascribed to the formation of alkynylstannanes and a distannane[9] as by-products.

Scheme 1. Cu-Catalyzed Borylstannylation with Tin Alkoxides



The former should come from a reaction of an intermediary generated alkynylcopper species with a tin alkoxide (Scheme 2, red arrow), which has been demonstrated by the independent reaction (Scheme 2, eq 1).[10] The catalytic involvement of a copper alkoxide of relatively high basicity should rationalize the facile generation of an alkynylcopper species,[11] and thus we envisaged that the use of another tin electrophile with a less basic leaving group (X), which inevitably diminishes the basicity of a Cu–X intermediate, should retard the alkynylcopper formation to result in the successful borylstannylation of terminal alkynes. We report herein that a tin fluoride serves as an effective tin electrophile for this purpose (Scheme 2, eq 2), and that the reaction becomes more practical due to the extremely bench-stable property of a tin fluoride as opposed to a moisture-sensitive tin alkoxide.

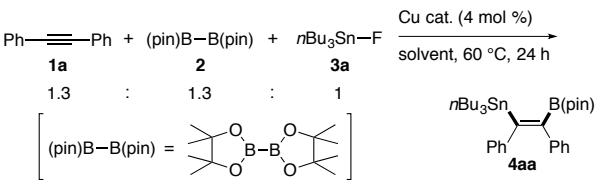
Scheme 2. Cu-Catalyzed Formation of Alkynylstannanes



RESULTS AND DISCUSSION

At the outset, we conducted the reaction of diphenylacetylene (**1a**) with (pin)B–B(pin) (**2**) using tributyltin fluoride (**3a**) as a tin electrophile in THF in the presence of PCy_3–CuCl catalyst to observe the stereoselective formation of a *syn*-borylstannylated product (**4aa**) in 50% yield (entry 1, Table 1). The use of PPh_3 or P*t*Bu_3 as a ligand also gave a comparable yield of **4aa** (entries 2 and 3), whereas the reaction with P*n*Bu_3

Table 1. Optimization of Reaction Conditions[a]



entry	Cu cat.	solvent	yield (%)[b]
1	PCy_3/CuCl	THF	50
2	$[(PPh_3)CuCl]_4$[c]	THF	45
3	P*t*Bu_3/CuCl	THF	38
4	P*n*Bu_3/CuCl	THF	0
5	IMesCuCl	THF	trace
6	IPrCuCl	THF	trace
7	PCy_3/CuCl	toluene	61
8[d]	PCy_3/CuCl	toluene	74
9	PCy_3/CuCl	DMF	41
10[d,e]	PCy_3/CuCl	toluene	0

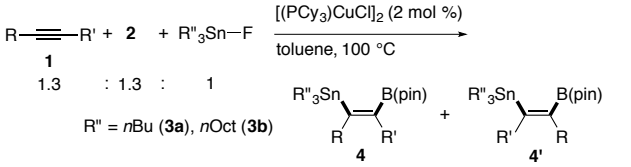
[a]Reaction conditions: ligand/Cu = 1, **1a** (0.39 mmol), **2** (0.39 mmol), **3a** (0.30 mmol), solvent (1 mL), 60 °C, 24 h. [b]Isolated yield. [c]1 mol %. [d]100 °C. [e]*n*Bu_3SnCl was used instead of *n*Bu_3SnF.

or an *N*-heterocyclic carbene (IMes or IPr) was found to be unsuccessful (entries 4–6). The reaction turned out to proceed best in toluene (entries 7 and 8, 61% at 60 °C; 74% at 100 °C), and a polar solvent such as DMF was unfit (entry 9). It should be noted that **4aa** did not form at all with tributyltin chloride (entry 10), demonstrating the crucial role of a fluorine atom in the catalytic process (*vide infra*).

In addition to such internal alkynes as 1-phenyl-1-proyne (**1b**) and 2-octyne (**1c**), which provided regioselectively the respective products (**4ba** and **4ca**) bearing a B(pin) moiety *geminal* to a methyl group (entries 1 and 2, Table 2), an aliphatic terminal alkyne, 1-octyne (**1d**) proved to be facilely convertible into **4da** in 78% yield with the preferential installation of B(pin) into a terminal carbon (93:7, entry 3). With tributyltin fluoride, cuprous chloride alone similarly promoted the reaction, albeit at the cost of its yield and regioselectivity (68%, 80:20), while the reaction with tributyltin methoxide again resulted in low yield (27%, 68:32) (entries 4 and 5). Perfect regioselectivity was observed with arylacetylenes (**1e**–**1g**) (entries 6–8), and functionalized aliphatic alkynes (**1h** and **1i**) were efficiently converted to the products (**4ha** and **4ia**) (entries 9 and 10). Furthermore, trioctyltin fluoride (**3b**)[12,13] could participate in the reaction, where **1d** and **1e** were transformed with similar efficacy to that with **3a** (entries 11 and 12). In addition to **1h** and **1i**, aliphatic terminal alkynes having a C–Cl bond (**1j**) or silyl ether (**1k**) also afforded the borylstannylation products (**4hb**–**4kb**) with these functional groups intact, although the regioselectivities dropped to some extent as compared to that with **1d** (entries 13–16).[14] The reaction was applicable to trimethylsilylacetylene (**1l**) to give **4lb** solely (entry 17), and an almost equal amount of regioisomers (**4mb** and **4'mb**) were produced with a propargyl ether (**1m**) (entry 18).

Assuming that facile conversion of a Cu–Cl complex into a Cu–F complex, which should undergo σ-bond metathesis with **2** in some borylations,[15,16] may occur in the borylstannylation, $(PPh_3)_3CuCl$ (**5a**)[17] was treated with **3a** in the presence or absence of **1a** as described in Scheme 3. In each case, no

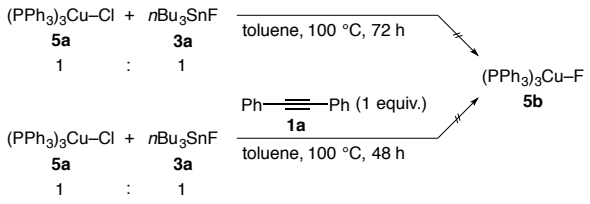
Table 2. Substrate Scope[a]



entry	R	R'	**3**	time (h)	yield (%)[b]	**4**:**4'**
1	Ph	Me (**1b**)	**3a**	32	74	>99:1
2	*n*Pent	Me (**1c**)	**3a**	48	44	97:3
3	*n*Hex	H (**1d**)	**3a**	24	78	93:7
4[c]	*n*Hex	H (**1d**)	**3a**	13	68	80:20
5[c,d]	*n*Hex	H (**1d**)	**3a**	24	27	68:32
6	Ph	H (**1e**)	**3a**	27	62	>99:1
7	4-BrC_6H_4	H (**1f**)	**3a**	37	43	>99:1
8	3-MeC_6H_4	H (**1g**)	**3a**	37	48	>99:1
9	$NC(CH_2)_3$	H (**1h**)	**3a**	37	61	84:16
10	$Phth(CH_2)_4$	H (**1i**)	**3a**	37	68	88:12
11	*n*Hex	H (**1d**)	**3b**	5	70	88:12
12	Ph	H (**1e**)	**3b**	32	68	>99:1
13	$NC(CH_2)_3$	H (**1h**)	**3b**	34	70	71:29
14	$Phth(CH_2)_4$	H (**1i**)	**3b**	31	64	72:28
15	$Cl(CH_2)_3$	H (**1j**)	**3b**	16	59	79:21
16	$TBSO(CH_2)_2$	H (**1k**)	**3b**	48	58	71:29
17	TMS	H (**1l**)	**3b**	48	30	>99:1
18	$BnOCH_2$	H (**1m**)	**3b**	22	56	44:56

[a]Reaction conditions: **1** (0.39 mmol), **2** (0.39 mmol), **3** (0.30 mmol), toluene (1 mL), 100 °C. [b]Isolated yield. [c]CuCl (4 mol %) was used instead of $[(PCy_3)CuCl]_2$. [d]*n*Bu_3SnOMe was used instead of *n*Bu_3SnF.

Scheme 3. Reaction of $(PPh_3)_3CuCl$ with a Tin Fluoride

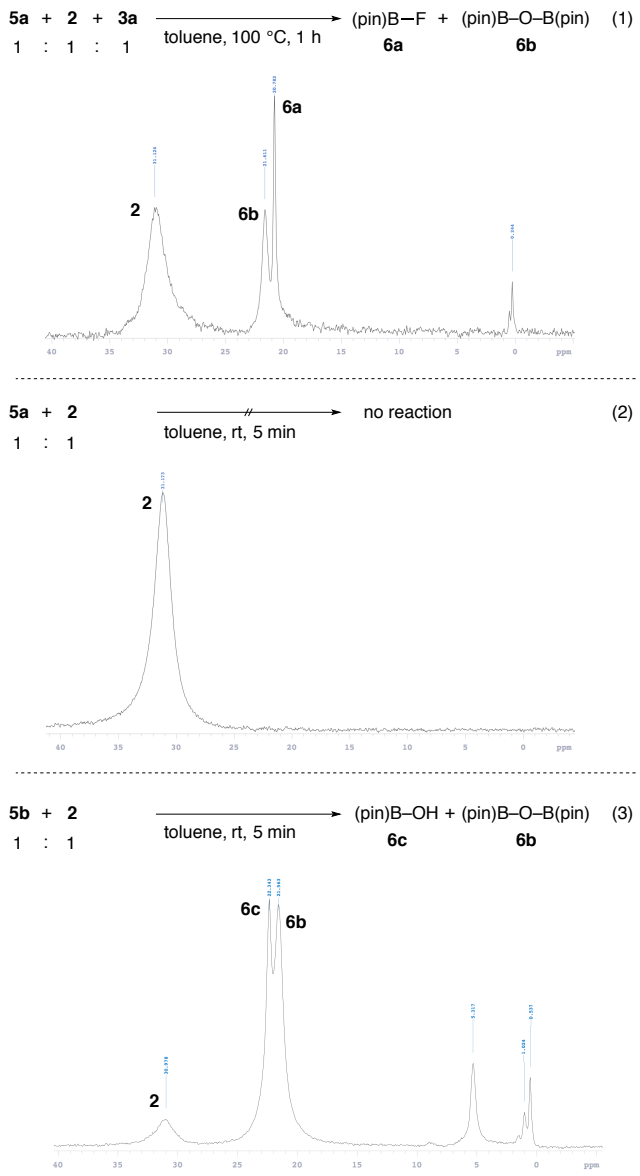


halogen exchange reaction took place at all, showing that such process is not operative in the induction period.

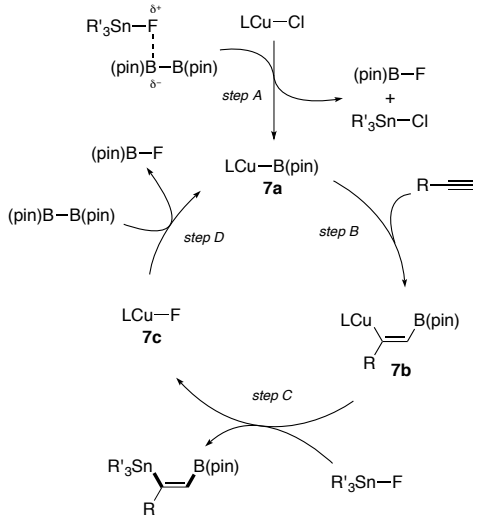
On the other hand, the reaction of **5a** with **2** and **3a** was found to readily produce (pin)B–F (**6a**)[18] and its hydrolyzed product [(pin)B–O–B(pin)] (**6b**) (Scheme 4, eq 1),[19] which indicates that **5a** may be converted into a borylcopper species $[(PPh_3)_3Cu–B(pin)]$, although we could not confirm the formation by ^{11}B NMR probably owing to its instability under the reaction conditions.[20] In addition to these results, the fact that nothing happened by simply mixing **5a** and **2** (Scheme 4, eq 2) leads to the conclusion that tin fluoride-assisted generation of a borylcopper species (**7a**, Scheme 5, *step A*)[21] may trigger the borylstannylation. Then the resulting borylcopper accepts insertion of an alkyne to form an alkenylcopper species (**7b**,

step B), which is captured by a tin fluoride to afford the product and a cuprous fluoride complex (**7c**, *step C*). Regeneration of **7a** by σ-bond metathesis between **2** and **7c** (*step D*) has been examined by stoichiometric reaction of **2** with $(PPh_3)_3CuF$ (**5b**) (Scheme 4, eq 3). Although no signal of a borylcopper species was again observable in ^{11}B NMR, **6b** and (pin)B–OH (**6c**)[19] arising from hydrolysis[22] of **6a** was found to

Scheme 4. ^{11}B NMR Experiments

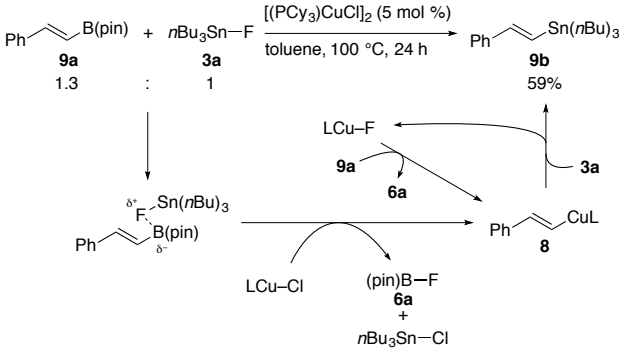


Scheme 5. A Plausible Catalytic Cycle



form with rapid consumption of **2**, demonstrating the facility of *step D* experimentally. In addition, the validity of *step C* was confirmed by ready capture of a catalytically generated alkenylcopper species (**8**) (from (*E*)-borylstyrene **9a**)[23,24] with **3a**, that provided (*E*)-stannylstyrene **9b** (Scheme 6). A similar catalytic cycle to that of the borylstannylation may also be operative in this boron–tin exchange.

Scheme 6. Capture of an Alkenylcopper Species with a Tin Fluoride



CONCLUDING REMARKS

In conclusion, we have disclosed that tin fluorides act as effective electrophiles for capturing catalytically generated alkenylcopper species, enabling the facile borylstannylation of alkynes. The mechanistic studies revealed that a fluorine atom played the pivotal role both in the induction period and in the σ-bond metathesis step. Further studies on copper-catalyzed three-component couplings using fluorine-containing electrophiles as well as on synthetic application of tin fluorides to catalytic stannylations are in progress.

EXPERIMENTAL SECTION

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^1H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz; ^{119}Sn, 186 MHz) spectrometer using residual chloroform (^1H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) or tetramethyltin (^{119}Sn, δ = 0.00) as an external standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d =

doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merk Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene and THF were distilled from sodium/benzophenone ketyl. DMF were distilled from CaH_2.

Materials. Trioctyltin fluoride (**3b**),[12] 2-fluoro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**),[19a] 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**6b**),[19b] 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-ol (**6c**)[19c] and $[(PCy_3)CuCl]_2$[25] were prepared according to reported procedures.

Cu-Catalyzed Borylstannylation of Alkynes: A General Procedure. A Schlenk tube equipped with a magnetic stirring bar was charged with $[(PCy_3)CuCl]_2$ (6.0 μmol). To the residue were added an alkyne (0.39 mmol), bis(pinacolato)diboron (0.39 mmol), a tin fluoride (0.30 mmol) and toluene (1.0 mL), and the resulting mixture was stirred at 100 °C for the period as specified in Table 2. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The residual tin fluoride was removed by passing through column chromatography (10% w/w anhydrous K_2CO_3–silica gel; ethyl acetate as an eluent), and the product was isolated by silica gel-column chromatography (hexane/ethyl acetate as an eluent) or gel permeation chromatography (toluene as an eluent). In ^{13}C NMR spectra, boron-bound carbons were not detected because of quadrupolar relaxation.

Characterization of Borylstannylation Products.

(E)-Tributyl(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)stannane (**4ba**).[1f] ^1H NMR ($CDCl_3$) δ 0.70-0.78 (m, 6H), 0.83 (t, J = 7.3 Hz, 9H), 1.16-1.25 (m, 6H), 1.30 (s, 12H), 1.32-1.39 (m, 6H), 1.64 (s, $J_{H–Sn}$ = 9.9 Hz, 3H), 6.75-6.79 (m, 2H), 7.07 (t, J = 7.3 Hz, 1H), 7.26 (t, J = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.48 ($J_{C–Sn}$ = 334.6 Hz), 13.70, 18.85 ($J_{C–Sn}$ = 51.4 Hz), 24.82, 27.54 ($J_{C–Sn}$ = 59.8 Hz), 29.14 ($J_{C–Sn}$ = 19.7 Hz), 83.52, 124.33, 125.68 ($J_{C–Sn}$ = 15.1 Hz), 127.88, 147.84 ($J_{C–Sn}$ = 35.5 Hz), 166.95. ^{119}Sn NMR ($CDCl_3$) δ -57.08.

A mixture of *(E)-tributyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-3-yl)stannane* (**4ca**) and *(E)-tributyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-2-yl)stannane* (**4'ca**).[1f] ^1H NMR ($CDCl_3$) δ 0.79-0.94 (m, 18H), 1.17-1.36 (m, 24H), 1.39-1.53 (m, 6H), 1.80 (s, $J_{H–Sn}$ = 10.7 Hz, 3H), 2.33 (t, J= 7.7 Hz, $J_{H–Sn}$ = 59.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.07 ($J_{C–Sn}$ = 327.9 Hz), 13.77, 14.11, 15.96 ($J_{C–Sn}$ = 62.0 Hz), 22.67, 24.76, 27.70 ($J_{C–Sn}$ = 60.3 Hz), 28.45, 29.40 ($J_{C–Sn}$ = 18.6 Hz), 32.10, 35.78 ($J_{C–Sn}$ = 47.6 Hz), 83.23, 166.77. ^{119}Sn NMR ($CDCl_3$) δ -55.40.

A mixture of *(Z)-tributyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-2-yl)stannane* (**4da**) and *(E)-tributyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)stannane* (**4'da**).[1f] ^1H NMR ($CDCl_3$) δ 0.82-1.01 (m, major/minor, 18H), 1.21-1.35 (m, major/minor, 24H), 1.36-1.57 (m, major/minor, 8H), 2.22 (t, J = 7.4 Hz, minor, 2H), 2.31 (t, J = 6.6 Hz, major, 2H), 6.09 (s, $J_{H–Sn}$ = 152.9 Hz, major, 1H), 6.69 (s, $J_{H–Sn}$ = 81.9 Hz, minor, 1H). ^{13}C NMR ($CDCl_3$) δ 11.44 ($J_{C–Sn}$ = 329.5 Hz), 13.73, 14.08, 22.62, 22.67, 24.74, 27.46, 27.59 ($J_{C–Sn}$ = 59.1 Hz), 28.80, 29.00, 29.26, 29.33, 29.40, 29.76, 31.82, 40.53, 45.42 ($J_{C–Sn}$ = 45.6 Hz), 82.99, 83.25, 149.58, 177.63. ^{119}Sn NMR ($CDCl_3$) δ -55.89 (major), -68.34 (minor).

(Z)-Tributyl(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)stannane (**4ea**).[1f] ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 7.2 Hz, 9H), 0.89-0.95 (m, 6H), 1.20-1.27 (m, 6H), 1.31 (s, 12H), 1.37-1.47 (m, 6H), 6.27 (s, $J_{H–Sn}$ = 137.2 Hz, 1H), 6.98-7.02 (m, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.26 (t, J = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.31 ($J_{C–Sn}$ = 335.7 Hz), 13.70, 24.80, 27.44 ($J_{C–Sn}$ = 59.3 Hz), 29.09 ($J_{C–Sn}$ = 19.1 Hz), 83.34, 125.79, 125.85 ($J_{C–Sn}$ = 13.7 Hz), 127.79, 150.11, 175.77. ^{119}Sn NMR ($CDCl_3$) δ -51.68.

(Z)-(1-(4-Bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)tributylstannane (**4fa**). ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 9H), 0.89-1.00 (m, 6H), 1.18-1.27 (m, 6H), 1.30 (s, 12H), 1.33-1.49 (m, 6H), 6.24 (s, J_{H-Sn}= 132.5 Hz, 1H), 6.84-6.91 (m, 2H), 7.36-7.41 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 12.30 (J_{C-Sn} = 335.6 Hz), 13.70, 24.80, 27.42 (J_{C-Sn} = 51.5 Hz), 29.08 (J_{C-Sn} = 20.1 Hz), 83.46, 127.48, 127.53, 127.58, 130.86, 149.11, 174.38. ^{119}Sn NMR ($CDCl_3$) δ -50.98. HRMS Calcd for $C_{32}H_{55}O_2BrBSn$: $[M-C_4H_9]^+$, 541.0930; Found: *m/z* 541.0925. Anal Calcd for $C_{28}H_{46}O_2BBrSn$: C, 52.22; H, 7.42. Found: C, 52.51; H, 7.41.

(Z)-Tributyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(m-tolyl)vinyl)stannane (**4ga**). ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 7.2 Hz, 9H), 0.88-1.00 (m, 6H), 1.19-1.27 (m, 6H), 1.30 (s, 12H), 1.33-1.53 (m, 6H), 2.32 (s, 3H), 6.27 (s, J_{H-Sn}= 138.3 Hz, 1H), 6.78-6.84 (m, 2H), 6.97 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 12.34 (J_{C-Sn} = 331.3 Hz), 13.71, 21.44, 24.80, 27.46 (J_{C-Sn} = 60.2 Hz), 29.11 (J_{C-Sn} = 19.9 Hz), 83.32, 122.97, 126.54, 126.67, 127.69, 137.22, 150.01, 175.89. ^{119}Sn NMR ($CDCl_3$) δ -52.19. HRMS Calcd for $C_{27}H_{45}O_2BNaSn$: $[M+Na]^+$, 557.2583; Found: *m/z* 557.2582. Anal Calcd for $C_{27}H_{45}O_2BSn$: C, 60.82; H, 8.89. Found: C, 60.59; H, 8.96.

A mixture of *(Z)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(tributylstannyl)hex-5-enenitrile* (**4ha**) and *(E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(tributylstannyl)hex-5-enenitrile* (**4'ha**). ^1H NMR ($CDCl_3$) δ 0.85-1.00 (m, major/minor, 15H), 1.21-1.35 (m, major/minor, 18H), 1.42-1.51 (m, major/minor, 6H), 1.68-1.75 (m, major, 2H), 1.76-1.83 (m, minor, 2H), 2.27 (t, J = 7.4 Hz, minor, 2H), 2.29 (t, J = 7.4 Hz, major, 2H), 2.35 (t, J = 7.3 Hz, minor, 2H), 2.45 (t, J = 7.1 Hz, major, 2H), 6.16 (s, J_{H-Sn}= 144.7 Hz, major, 1H), 6.79 (s, J_{H-Sn}= 74.4 Hz, minor, 1H). ^{13}C NMR ($CDCl_3$) δ 11.43 (J_{C-Sn} = 328.9 Hz, major), 11.48 (minor), 13.71, 13.75, 16.31, 24.56, 24.73, 27.39, 27.46, 27.52 (J_{C-Sn} = 58.7 Hz), 29.26, 30.61, 39.50, 43.45 (J_{C-Sn} = 46.4 Hz), 83.28 (major), 83.58 (minor), 119.57, 120.05, 153.29, 174.10. ^{119}Sn NMR ($CDCl_3$) δ -53.74 (major), -67.09 (minor). HRMS Calcd for $C_{28}H_{54}O_2NBNaSn$: $[M+Na]^+$, 534.2536; Found: m/z 534.2538. Elemental analysis results were outside the tolerance range.

A mixture of *(Z)-2-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(tributylstannyl)hex-5-en-1-yl)isoindoline-1,3-dione* (**4ia**) *and (E)-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(tributylstannyl)hex-5-en-1-yl)isoindoline-1,3-dione* (**4'ia**). ^1H NMR ($CDCl_3$) δ 0.81-0.96 (m, major/minor, 15H), 1.20-1.30 (m, major/minor, 18H), 1.34-1.50 (m, major/minor, 8H), 1.61-1.71 (m, major/minor, 2H), 2.25 (t, J = 7.2 Hz, minor, 2H), 2.34 (t, J = 7.6 Hz, J_{H-Sn} = 44.8 Hz, major, 2H), 3.67 (t, J = 7.2 Hz, major/minor, 2H), 6.08 (s, J_{H-Sn} = 149.8 Hz, major, 1H), 6.71 (s, J_{H-Sn} = 80.1 Hz, minor, 1H), 7.67-7.73 (m, major/minor, 2H), 7.80-7.85 (m, major/minor, 2H). ^{13}C NMR ($CDCl_3$) δ 11.38 (J_{C-Sn} = 329.1 Hz, major), 11.45 (minor), 13.72, 24.74, 26.45, 27.42, 27.52 (J_{C-Sn} = 59.5 Hz), 28.25, 29.24 (J_{C-Sn} = 19.0 Hz), 37.91 (J_{C-Sn} = 33.8 Hz), 44.68 (J_{C-Sn} = 47.2 Hz), 83.05, 83.32, 123.04, 123.10, 132.14, 133.75, 168.32, 176.52. ^{119}Sn NMR ($CDCl_3$) δ -55.43 (major), -68.18 (minor). HRMS Calcd for $C_{32}H_{53}O_4NBNaSn$: $[M+Na]^+$, 668.2904; Found: *m/z* 668.2911. Anal Calcd for $C_{32}H_{53}O_4BNSn$: C, 59.66; H, 8.14. Found: C, 59.80; H, 8.25.

A mixture of *(Z)-trioctyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-2-yl)stannane* (**4db**) and *(E)-trioctyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)stannane* (**4'db**). ^1H NMR ($CDCl_3$) δ 0.82-0.94 (m, major/minor, 18H), 1.18-1.34 (m, major/minor, 50H), 1.45-1.55 (m, major/minor, 6H), 2.22 (t, J = 7.1 Hz, minor, 2H), 2.31 (t, J = 7.1 Hz, $J_{H–Sn}$ = 44.9 Hz, major, 2H), 6.09 (s, $J_{H–Sn}$ = 151.6 Hz, major, 1H), 6.70 (s, $J_{H–Sn}$ = 81.8 Hz, minor, 1H). ^{13}C NMR ($CDCl_3$) δ 11.83 ($J_{C–Sn}$ = 328.3 Hz), 14.12, 22.65, 22.71, 24.75, 26.99, 27.08, 27.17, 28.88, 29.07, 29.31, 29.37, 29.45, 29.78, 31.86, 31.98, 34.53, 34.67 ($J_{C–Sn}$ = 55.3 Hz), 40.50, 45.44, 82.99 (major), 83.25 (minor), 149.73, 177.79. ^{119}Sn NMR ($CDCl_3$) δ -56.12 (major), -68.57 (minor). HRMS Calcd for $C_{30}H_{60}O_2BSn$: $[M-C_8H_{17}]^+$, 583.3703; Found: m/z 583.3702. Anal Calcd for $C_{38}H_{77}O_2BSn$: C, 65.62; H, 11.16. Found: C, 65.41; H, 11.38.

(Z)-Trioctyl(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)stannane (**4eb**). ^1H NMR ($CDCl_3$) δ 0.85-0.94 (m, 15H), 1.18-1.32 (m, 42H), 1.39-1.47 (m, 6H), 6.26 (s, $J_{H–Sn}$ = 136.2 Hz, 1H), 7.00 (d, J = 8.3 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 6.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.72 ($J_{C–Sn}$ = 334.4 Hz), 14.13, 22.69, 24.81, 26.87 ($J_{C–Sn}$ = 19.7 Hz), 29.26, 29.33, 31.94, 34.54 ($J_{C–Sn}$ =55.6

Hz), 83.33, 125.80, 125.88, 127.78, 150.10, 175.93. ^{119}Sn NMR ($CDCl_3$) δ -52.06. HRMS Calcd for $C_{30}H_{52}O_2BSn$: $[M-C_8H_{17}]^+$, 575.3077; Found: *m/z* 575.3078. Elemental analysis results were outside the tolerance range.

A mixture of *(Z)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trioctylstannyl)hex-5-enenitrile* (**4hb**) and *(E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trioctylstannyl)hex-5-enenitrile* (**4'hb**). ^{1}H NMR ($CDCl_3$) δ 0.84-0.98 (m, major/minor, 15H), δ 1.19-1.34 (m, major/minor, 42H), 1.41-1.54 (m, major/minor, 6H), 1.66-1.75 (m, major, 2H), 1.76-1.84 (m, minor, 2H), 2.26 (t, *J* = 7.5 Hz, minor, 2H), 2.28 (t, *J* = 7.2 Hz, major, 2H), 2.35 (t, *J* = 7.0 Hz, minor, 2H), 2.45 (t, *J* = 7.1 Hz, J_{H-Sn} = 41.6 Hz, major, 2H), 6.12 (s, J_{H-Sn} = 144.2 Hz, major, 1H), 6.79 (s, J_{H-Sn} = 75.7 Hz, minor, 1H). ^{13}C NMR ($CDCl_3$) δ 11.81 (J_{C-Sn} = 330.3 Hz, major), 11.85 (minor), 14.11, 16.32, 22.67, 24.58, 24.74, 26.95, 27.02 (J_{C-Sn} = 19.2 Hz), 29.23, 29.27, 29.32, 31.92, 34.48, 34.60 (J_{C-Sn} =56.1 Hz), 39.50, 43.46, 83.27 (major), 83.58 (minor), 119.55, 153.42, 174.23. ^{119}Sn NMR ($CDCl_3$) δ -54.11 (major), -67.38 (minor). HRMS Calcd for $C_{36}H_{70}O_2NBNaSn$: $[M+Na]^+$, 702.4420; Found: m/z 702.4419. Elemental analysis results were outside the tolerance range.

A mixture of *(Z)-2-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trioctylstannyl)hex-5-en-1-yl)isoindoline-1,3-dione* (**4ib**) and *(E)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trioctylstannyl)pent-4-en-1-yl)isoindoline-1,3-dione* (**4'ib**). ^{1}H NMR ($CDCl_3$) δ 0.83-0.95 (m, major/minor, 15H), 1.17-1.31 (m, major/minor, 40H), 1.35-1.53 (m, major/minor, 10H), 1.63-1.70 (m, major/minor, 2H), 2.25 (t, *J* = 7.5 Hz, minor, 2H), 2.34 (t, *J* = 7.5 Hz, J_{H-Sn} = 42.0 Hz, major, 2H), 3.67 (t, *J* = 7.2 Hz, major/minor, 2H), 6.01 (s, J_{H-Sn} = 150.7 Hz, major, 1H), 6.72 (s, J_{H-Sn} = 78.4 Hz, minor, 1H), 7.68-7.72 (m, major/minor, 2H), 7.81-7.85 (m, major/minor, 2H). ^{13}C NMR ($CDCl_3$) δ 11.73 (J_{C-Sn} = 329.6 Hz, major), 14.09 (J_{C-Sn} = 219.7 Hz major), 14.19, 22.59, 22.65, 24.62, 24.68 (J_{C-Sn} = 222.2 Hz), 24.74 (J_{C-Sn} = 22.2 Hz), 24.81, 26.39, 26.91, 26.98, 27.05, 28.22, 29.21, 29.31, 31.91, 34.36, 34.58 (J_{C-Sn} = 56.0 Hz), 34.81, 37.85, 38.33, 44.53, 44.60, 44.65, 83.00 (major), 83.28 (minor), 122.96, 123.14, 132.13, 132.19, 133.66, 133.67, 133.75, 168.23, 176.59. ^{119}Sn NMR ($CDCl_3$) δ -55.79 (major), -63.54 (minor). HRMS Calcd for $C_{44}H_{76}O_4NBNaSn$: $[M+Na]^+$, 836.4787; Found: m/z 836.4788. Elemental analysis results were outside the tolerance range.

A mixture of *(Z)-(5-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)trioctylstannane* (**4jb**) and *(E)-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)trioctylstannane* (**4'jb**). ^{1}H NMR ($CDCl_3$) δ 0.84-1.01 (m, major/minor, 15H), 1.18-1.35 (m, major/minor, 42H), 1.41-1.57 (m, major/minor, 6H), 1.78-1.86 (m, major, 2H), 1.86-1.94 (m, minor, 2H), 2.35 (t, *J* = 7.4 Hz, minor, 2H), 2.46 (t, *J* = 7.5 Hz, J_{H-Sn} = 41.6 Hz, major, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 6.14 (s, J_{H-Sn} = 146.6 Hz, major, 1H), 6.78 (s, J_{H-Sn} = 76.9 Hz, minor, 1H). ^{13}C NMR ($CDCl_3$) δ 11.43 (J_{C-Sn} = 329.3 Hz), 13.73, 24.70 (J_{C-Sn} = 21.7 Hz), 24.79 (J_{C-Sn} = 22.5 Hz), 27.47, 27.55 (J_{C-Sn} = 59.5 Hz), 27.63, 29.17, 29.28, 29.39, 31.71, 31.89, 32.07, 41.94 (J_{C-Sn} = 46.1 Hz), 44.36 (J_{C-Sn} = 154.0 Hz), 44.67, 83.18 (major), 83.48 (minor), 175.16 (J_{C-Sn} = 357.5 Hz, major). ^{119}Sn NMR ($CDCl_3$) δ -54.66 (major), -67.38 (minor). HRMS Calcd for $C_{27}H_{53}O_2BClSn$: $[M-C_8H_{17}]^+$, 575.2849; Found: m/z 575.2839. Anal Calcd for $C_{35}H_{70}O_2BClSn$: C, 61.11; H, 10.26. Found: C, 60.92, H, 10.51.

A mixture of *(Z)-tert-butyldimethyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trioctylstannyl)but-3-en-1-yl)oxy)silane* (**4kb**) and *(E)-tert-butyldimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trioctylstannyl)but-3-en-1-yl)oxy)silane* (**4'kb**). ^{1}H NMR ($CDCl_3$) δ 0.04 (s, major/minor, 6H), 0.84-1.96 (m, major/minor, 24H), 1.20-1.31 (m, major/minor, 42H), 1.45-1.53 (m, major/minor, 6H), 2.46 (t, *J* = 7.0 Hz, minor, 2H), 2.56 (t, *J* = 7.6 Hz, J_{H-Sn} = 44.0 Hz, major, 2H), 3.56 (t, *J* = 7.3 Hz, major, 2H), 3.62 (t, *J* = 7.3 Hz, minor, 2H), 6.16 (s, J_{H-Sn} = 148.9 Hz, major, 1H), 6.81 (s, J_{H-Sn} = 14.6 Hz, minor, 1H). ^{13}C NMR ($CDCl_3$) δ -5.20 (major), -5.15 (minor), 11.80 (J_{C-Sn} = 332.0 Hz), 14.13, 18.38, 22.70, 24.73, 24.79, 26.01, 26.05, 26.96, 27.03 (J_{C-Sn} = 19.3 Hz), 29.28, 29.36, 31.96, 34.53, 34.64 (J_{C-Sn} = 56.0 Hz), 44.24, 47.91 (J_{C-Sn} = 42.6 Hz), 63.00, 63.60, 83.11 (major), 83.36 (minor), 153.91, 172.75. ^{119}Sn NMR ($CDCl_3$) δ -54.61 (major), -69.55 (minor). HRMS Calcd for $C_{40}H_{83}O_3BNaSiSn$: $[M+Na]^+$, 793.5124; Found: m/z 793.5128. Anal Calcd for $C_{46}H_{92}O_3BSiSn$: C, 62.42; H, 10.87. Found: C, 62.18; H, 11.09.

(Z)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trioctylstannyl)vinyl)silane (**4lb**). ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9H), 0.86-0.97 (m, 15H), 1.22-1.31 (m, 42H), 1.41-1.52 (m, 6H), 7.11 (s, J_{H-Sn} = 201.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ -0.79, 12.65 (J_{C-Sn} = 320.5 Hz), 14.13, 22.70, 24.80, 27.12 (J_{C-Sn} = 18.7 Hz), 29.29, 29.36, 31.97, 34.69 (J_{C-Sn} = 58.1 Hz), 83.41, 182.23. ^{119}Sn NMR ($CDCl_3$) δ -56.62. HRMS Calcd for $C_{27}H_{56}O_2BSiSn$: $[M-C_8H_{17}]^+$, 571.3165; Found: *m/z* 571.3158. Anal Calcd for $C_{35}H_{71}O_2BSiSn$: C, 61.50; H, 10.76. Found: C, 61.23; H, 11.08.

A mixture of *(Z)-(3-(benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)trioctylstannane* (**4mb**) and *(E)-(3-(benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)trioctylstannane* (**4'mb**). ^{1}H NMR ($CDCl_3$) δ 0.83-0.99 (m, major/minor, 15H), 1.19-1.36 (m, major/minor, 42H), 1.43-1.57 (m, major/minor, 6H), 4.16-4.19 (m, major, 2H), 4.20-4.23 (m, minor, 2H), 4.49 (s, minor, 2H), 4.52 (s, major, 2H), 6.49 (s, J_{H-Sn} = 140.9 Hz, minor, 1H) 7.18 (s, J_{H-Sn} = 77.3 Hz, major, 1H), 7.23-7.39 (m, major/minor, 5H). ^{13}C NMR ($CDCl_3$) δ 11.61 (J_{C-Sn} = 334.4 Hz, minor), 11.79 (J_{C-Sn} = 340.9 Hz, major), 14.12, 22.68, 24.74, 24.76, 26.98 (J_{C-Sn} = 19.5 Hz), 29.27, 29.29, 29.34, 31.95, 34.54 (J_{C-Sn} = 53.8 Hz, major), 34.59 (J_{C-Sn} = 56.7 Hz, minor) 71.80, 72.04, 75.12, 79.42, 83.20, 83.46, 127.22, 127.27, 127.45, 127.55, 128.16, 138.54, 138.94, 151.56, 171.21. ^{119}Sn NMR ($CDCl_3$) δ -57.60 (minor), -64.92 (major). HRMS Calcd for $C_{40}H_{73}O_3BNaSn$: $[M+Na]^+$, 755.4572; Found: m/z 755.4576. Elemental analysis results were outside the tolerance range.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Ligand effect on the borylstannylation of **1h**, ^{19}F NMR experiments and ^{1}H and ^{13}C NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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(11) For generation of alkynylcopper species from copper alkoxides and terminal alkynes, see: (a) Osakada, K.; Takizawa, T.; Yamamoto, T. *Organometallics* **1995**, *14*, 3531–3538. (b) Whittaker, A. M.; Lalic, G. *Org. Lett.* **2013**, *15*, 1112–1115. (c) Cox, N.; Dang, H.; Whittaker, A. M.; Lalic, G. *Tetrahedron* **2014**, *70*, 4219–4231. (d) Jin, L.; Romero, E. A.; Melaimi, M.; Bertrand, G. *J. Am. Chem. Soc.* **2015**, *137*, 15696–15698.

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(13) Tri-*n*-octyltin compounds exhibit almost no toxicity, being in contrast to the moderately toxic nature of tri-*n*-butyltin compounds (LD_{50} (oral/rat): $n$$Bu_3$SnCl (129 mg/kg) >> $n$$Oct_3$SnCl (4,000 mg/kg); *cf.* caffeine (192 mg/kg)). See: (a) Seinen, W.; Vos, J. G.; Van Spanje, I.; Snoek, M.; Brands, R.; Hooykaas, H. *Toxicol. Appl. Pharmacol.* **1977**, *42*, 197–212. (b) Snoeij, N. J.; Van Iersel, A. A. J.; Penninks, A. H.; Seinen, W. *Toxicol. Appl. Pharmacol.* **1985**, *81*, 274–286. (c) Cooney, J. J.; Wuertz, S. *J. Ind. Microbiol.* **1989**, *4*, 375–402.

(14) For ligand effect on the regioselectivity and yield of the borylstannylation of **1h**, see SI.

(15) (a) Welle, A.; Cirriez, V.; Riant, O. *Tetrahedron* **2012**, *68*, 3435–3443. (b) Luo, Y.; Roy, I. D.; Madec, A. G. E.; Lam, H. W. *Angew. Chem. Int. Ed.* **2014**, *53*, 4186–4190.

(16) For theoretical study on facile σ-bond metathesis between a Pd–F complex with a diboron, see: Sumimoto, M.; Iwane, N.; Takahama, T.; Sakaki, S. *J. Am. Chem. Soc.* **2004**, *126*, 10457–10471.

(17) Complexes **5a** and **5b** (4 mol %) also promoted the borylstannylation of **1d** with **3a** under similar conditions depicted in Table 2 to afford **4da** and **4'da**: 86% (**4da**:**4'da** = 74:26) with **5a**, 76% (**4da**:**4'da** = 74:26) with **5b**.

(18) The formation of **6a** was also confirmed by ^{19}F NMR. See SI for details.

(19) The observed signals in ^{11}B NMR were assigned by comparing with prepared compounds. For **6a** (20.8 ppm), see: (a) Cresswell, A. J.; Davies, S. G.; Figuccia, A. L. A.; Fletcher, A. M.; Heijnen, D.; Lee, J. A.; Morris, M. J.; Kennett, A. M. R.; Roberts, P. M.; Thomson, J. E. *Tetrahedron Lett.* **2015**, *56*, 3373–3377. For **6b** (21.6 ppm), see: (b) Ojha, D. P.; Gadde, K.; Prabhu, K. R. *Org. Lett.* **2016**, *18*, 5062–5065. For **6c** (22.4 ppm), see: (c) Fandrick, D. R.; Reeves, J. T.; Bakonyi, J. M.; Nyalapatla, P. R.; Tan, Z.; Niemeier, O.; Akalay, D.; Fandrick, K. R.; Wohlleben, W.; Ollenberger, S.; Song, J. J.; Sun, X.; Qu, B.; Haddad, N.; Sanyal, S.; Shen, S.; Ma, S.; Byrne, D.; Chitroda, A.; Fuchs, V.; Narayanan, B. A.; Grinberg, N.; Lee, H.; Yee, N.; Brenner, M.; Senanayake, C. H. *J. Org. Chem.* **2013**, *78*, 3592–3615.

(20) (a) Litar. D. S.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197. (b) Segawa, Y.; Yamashita, M.; Nozaki, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 6710–6713. (c) Kleeverg, C.; Dang, L.; Lin, Z.; Marder, T. B. *Angew. Chem. Int. Ed.* **2009**, *48*, 5350–5354. (d) Semba, K.; Shinomiya, M.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. –Eur. J.* **2013**, *19,* 7125–7132.

(21) We could not observe apparent interaction between **2** and **3a** in ^{11}B NMR, however, coordination of a fluoride ion to a boron center of **2** has already been reported. See: (a) Pietsch, S.; Neeve, E. C.; Apperley, D. C.; Bertermann, R.; Mo, F.; Qiu, D.; Cheung, M. S.; Dang, L.; Wang, J.; Radius, U.; Lin, Z.; Kleeberg, C.; Marder, T. B. *Chem. –Eur. J.* **2015**, *21*, 7082–7098. For interaction between a trialkyltin fluoride and BF_3•OEt_2, see: (b) Lorberth, J. *J. Organomet. Chem.* **1969**, *17*, 151–154.

(22) Commercial **5b** has been found to partially exist as an ethanol complex and a hydrate, which results in the complete conversion of **6a** into **6b** and **6c**. For the ^{1}H NMR spectrum of **5b**, see SI.

(23) For smooth generation of an arylcopper species by transmetalation between an arylboronate and a Cu(I) complex, see: (a) Whittaker, A. M.; Rucker, R. P.; Lalic, G. *Org. Lett.* **2010**, *12*. 3216–3218. (b) Shintani, R.; Takatsu, K.; Hayashi, T. *Chem. Commun.* **2010**, *46*, 6822–6824.

(24) We have also demonstrated that a catalytically generated alkenylcopper species can be captured with a tin alkoxide. See: ref. 1f.

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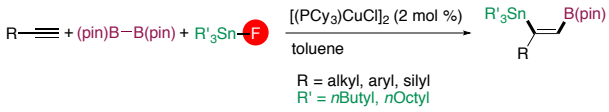
R
+ (pin)B—B(pin) + R'3Sn
F
[(PCy3)CuCl]2 (2 mol %)
toluene
R = alkyl, aryl, silyl
R' = nButyl, nOctyl
R'3Sn
B(pin)
R