ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

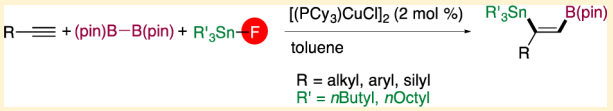
Copper-Catalyzed Borylstannylation of Alkynes with Tin Fluorides

Hiroto Yoshida,* Miki Kimura, Itaru Osaka, and Ken Takaki

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Supporting Information

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.

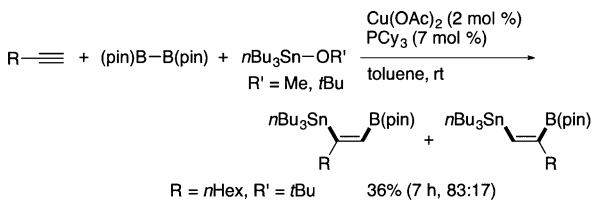


INTRODUCTION

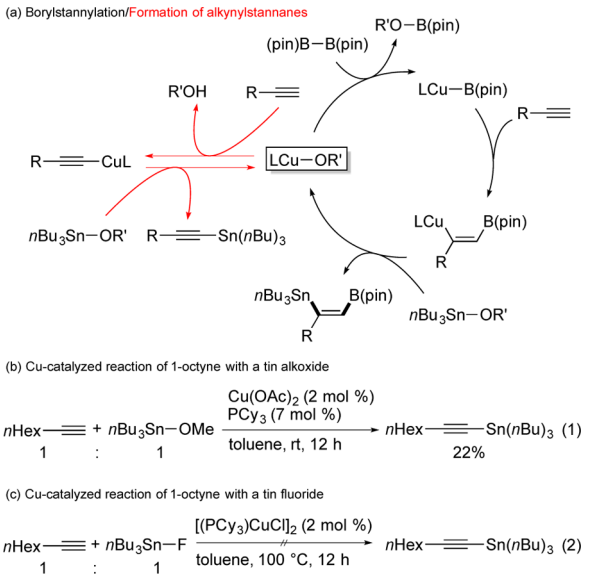
Borylstannylation[1] of unsaturated carbon–carbon bonds, which leads to synchronous carbon–boron and carbon–tin bond formation at vicinal positions, is of high synthetic value, because multifunctionalized organometallic compounds thus generated have bench-stable/easy-to-handle properties and can serve 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, which provides regio- and stereodefined *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 byproducts.

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 an 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 1. Cu-Catalyzed Borylstannylation with Tin Alkoxides



Scheme 2. Cu-Catalyzed Formation of Alkynylstannanes



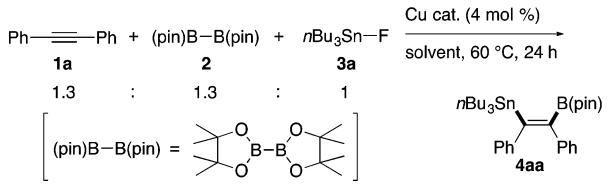
RESULTS AND DISCUSSION

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).

Received: January 24, 2017

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX–XXX

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	$PtBu_3$/CuCl	THF	38
4	$PnBu_3$/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

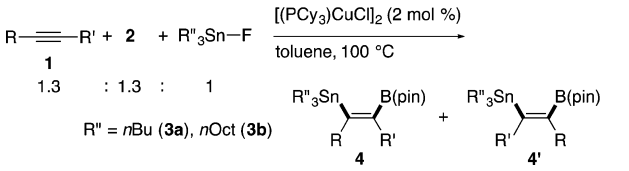
[a]Reaction conditions unless specified otherwise: ligand/Cu = 1, **1a** (0.39 mmol), **2** (0.39 mmol), **3a** (0.30 mmol), solvent (1 mL), 60 °C, 24 h. [b]Isolated yield. [c]1 mol %. [d]100 °C. [e]nBu_3SnCl was used instead of nBu_3SnF.

The use of PPh_3 or $PtBu_3$ as a ligand also gave a comparable yield of **4aa** (entries 2 and 3), whereas the reaction with $PnBu_3$ 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 internal alkynes such as 1-phenyl-1-propyne (**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–g**) (entries 6–8), and functionalized aliphatic alkynes (**1h,i**) were efficiently converted to the products (**4ha,ia**) (entries 9 and 10). Furthermore, trioctyltin fluoride (**3b**)[12,13] could participate in the reaction, where **1d,e** were transformed with efficacy similar to that with **3a** (entries 11 and 12). In addition to **1h,i**, aliphatic terminal alkynes having a C–Cl bond (**1j**) or silyl ether (**1k**) also afforded the borylstannylation products (**4hb–kb**) with these functional groups intact, although the regioselectivities dropped to some extent in comparison to that with **1d** (entries 13–16).[14] The reaction was applicable to trimethylsilylacetylene (**1l**) to give solely **4lb** (entry 17), and almost equal amounts 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

Table 2. Substrate Scope[a]

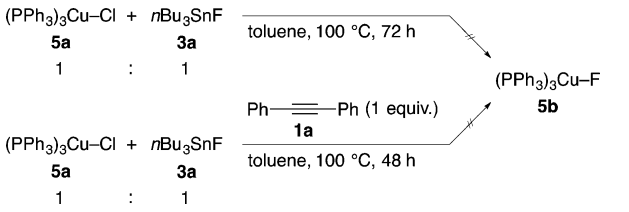


entry	R	R′	3	time (h)	yield (%)[b]	4:4′
1	Ph	Me (**1b**)	**3a**	32	74	>99:1
2	*n*Pent	Me (**1c**)	**3a**	48	44	97:3
3	*n*Hex	H (**1d**)	**3a**	24	78	93:7
4[c]	*n*Hex	H (**1d**)	**3a**	13	68	80:20
5[c,d]	*n*Hex	H (**1d**)	**3a**	24	27	68:32
6	Ph	H (**1e**)	**3a**	27	62	>99:1
7	4-BrC_6H_4	H (**1f**)	**3a**	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 unless specified otherwise: **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]nBu_3SnOMe was used instead of nBu_3SnF.

absence of **1a**, as described in Scheme 3. In each case, no halogen exchange reaction took place at all, showing that such a process is not operative in the induction period.

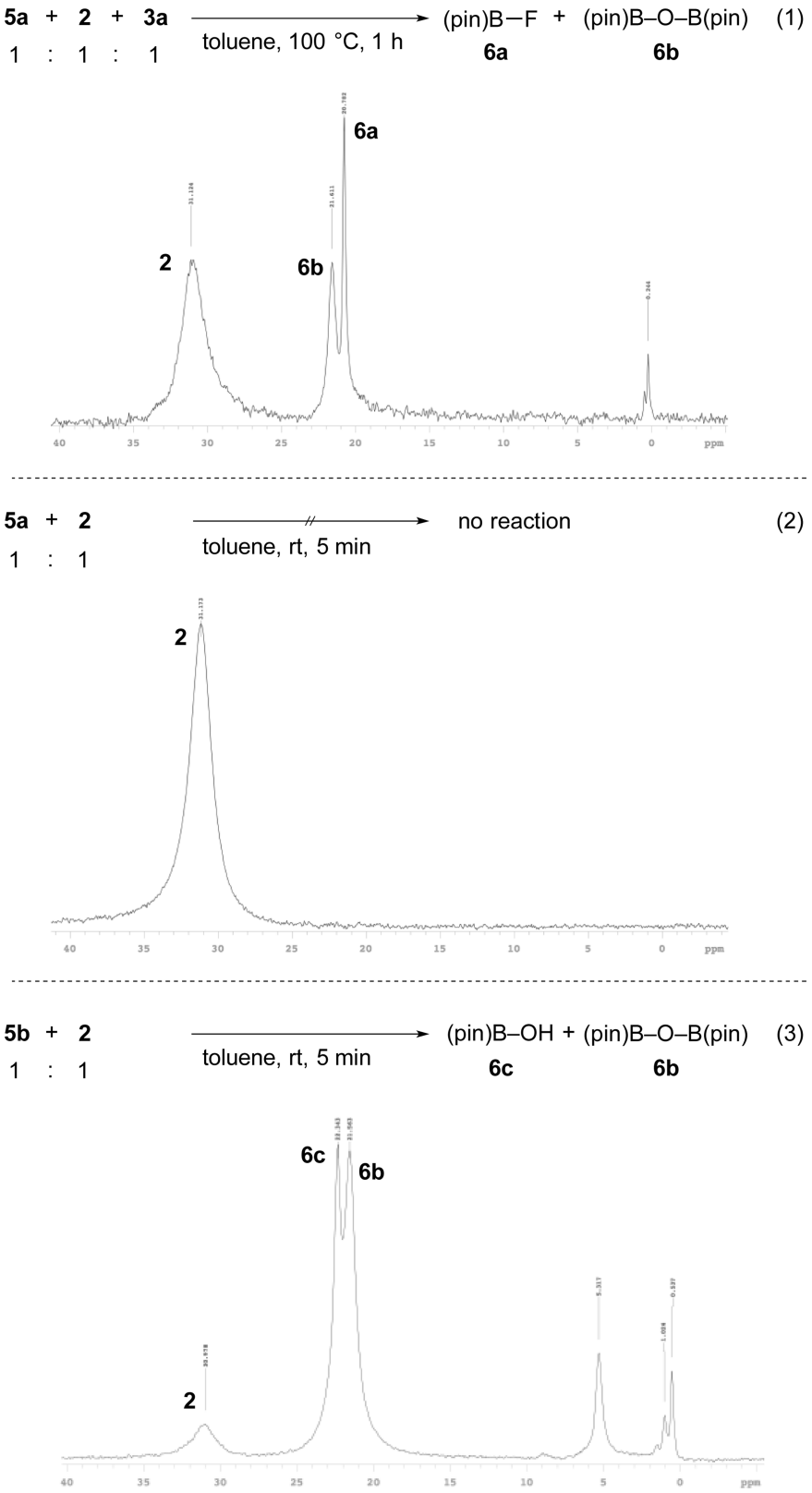
Scheme 3. Reaction of $(PPh_3)_3CuCl$ with a Tin Fluoride



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 the 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 the stoichiometric reaction of **2** with $(PPh_3)_3CuF$ (**5b**) (Scheme 4, eq 3).

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX–XXX

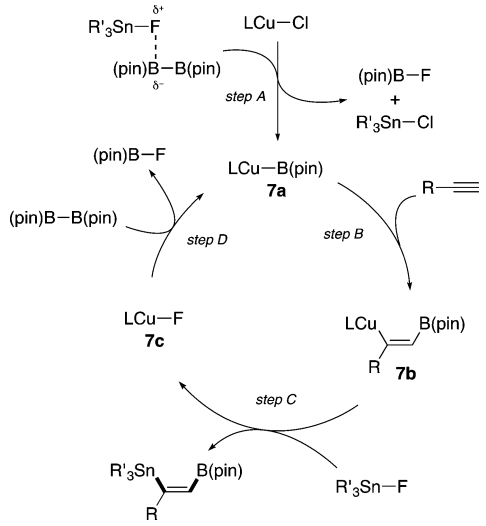
Scheme 4. ^{11}B NMR Experiments



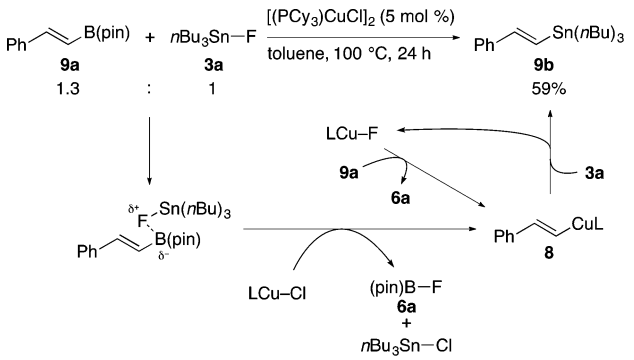
Although no signal of a borylcopper species was again observable in ^{11}B NMR, **6b** and (pin)B−OH (**6c**)[19] arising from hydrolysis[22] of **6a** were found to form with rapid consumption of **2**, demonstrating the facility of step D experimentally. In addition, the validity of step C was confirmed by the ready capture of the catalytically generated alkenylcopper species **8** (from (*E*)-borylstyrene **9a**)[23,24] with **3a**, which provided (*E*)-stannylstyrene **9b** (Scheme 6). A catalytic cycle similar to that of the borylstannylation may also be operative in this boron−tin exchange.

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX−XXX

Scheme 5. Plausible Catalytic Cycle



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 a 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 the 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 standard Schlenk techniques under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz; ^{119}Sn, 186 MHz) spectrometer using residual chloroform (^{1}H, 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. ^{1}H 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 a GL Science PU 614 instrument equipped with Shodex GPC H-2001L and -2002L columns (toluene as eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene and THF were distilled from sodium/benzophenone ketyl. DMF was 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: 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 column chromatography (10% w/w anhydrous K_2CO_3–silica gel; ethyl acetate as eluent), and the product was isolated by silica gel column chromatography (hexane/ethyl acetate as eluent) or gel permeation chromatography (toluene as 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] ^{1}H 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.

*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] ^{1}H 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.

*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] ^{1}H 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] ^{1}H 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**).* ^{1}H 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 $C_{22}H_{35}O_2BrBSn$, $[M - C_4H_9]^+$, 541.0930; found, m/z 541.0925. Anal. Calcd for $C_{26}H_{44}O_2BBrSn$: C, 52.22; H, 7.42. Found: C, 52.51; H, 7.41.

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX–XXX

*(Z)-Tributyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(m-tolyl)vinyl)stannane (**4ga**).* ^{1}H 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 $C_{27}H_{47}O_2BNaSn$, $[M + Na]^+$, 557.2583; found, m/z 557.2582. Anal. Calcd for $C_{27}H_{47}O_2BSn$: C, 60.82; H, 8.89. Found: C, 60.59; H, 8.96.

*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**).* ^{1}H 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 $C_{24}H_{46}O_2NBNaSn$, $[M + Na]^+$, 534.2536; found, m/z 534.2538. Elemental analysis results were outside the tolerance range.

*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**).* ^{1}H 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 $C_{32}H_{52}O_4NBNaSn$, $[M + Na]^+$, 668.2904; found, m/z 668.2911. Anal. Calcd for $C_{32}H_{52}O_4BNSn$: C, 59.66; H, 8.14. Found: C, 59.80; H, 8.25.

*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**).* ^{1}H 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**).* ^{1}H 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.

*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.

*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.

*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.

*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 $C_{40}H_{83}O_3BSiSn$: 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

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX−XXX

(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 $C_{35}H_{73}O_2BSiSn$: C, 61.50; H, 10.76. Found: C, 61.23; H, 11.08.

*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**).* ^1H 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 at DOI: 10.1021/acs.organomet.7b00058.

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for H.Y.: yhiroto@hiroshima-u.ac.jp.

ORCID

Hiroto Yoshida: 0000-0001-6890-4397

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This paper is dedicated to Prof. Tamejiro Hiyama on the occasion of his 70th birthday. This work was financially supported by JSPS KAKENHI Grant Number JP16H01031 in Precisely Designed Catalysts with Customized Scaffolding.

■ REFERENCES

(1) (a) Onozawa, S.-y.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450−5452. (b) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Tetrahedron Lett.* **1998**, *39*, 9043−9046. (c) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1999**, 1863−1864. (d) Weber, L.; Wartig, H. B.; Stammler, H. G.; Stammler, A.; Neumann, B. *Organometallics* **2000**, *19*, 2891−2895. (e) Singidi, R. R.; Ra-janBabu, T. V. *Org. Lett.* **2010**, *12*, 2622−2625. (f) Takemoto, Y.; Yoshida, H.; Takaki, K. *Chem. - Eur. J.* **2012**, *18*, 14841−14844. (g) Takemoto, Y.; Yoshida, H.; Takaki, K. *Synthesis* **2014**, *46*, 3024−3032. (h) Yoshida, H.; Takemoto, Y.; Takaki, K. *Chem. Commun.* **2015**, *51*, 6297−6300. (i) Jia, T.; Cao, P.; Wang, D.; Lou, Y.; Liao, J. *Chem. - Eur. J.* **2015**, *21*, 4918−4922.

(2) *Metal-Catalyzed Cross-Coupling Reactions and More*; de Meijere, A., Brase, S., Oestreich, M., Eds.; Wiley-VCH: Weinheim, Germany, 2014.

(3) For a review on carbon−heteroatom bond formation using organoboranes, see: (a) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400−5449. For examples on carbon−heteroatom bond formation using organostannanes, see: (b) Lam, P. Y. S.; Vincent, G.; Bonne, V.; Clark, C. G. *Tetrahedron Lett.* **2002**, *43*, 3091−3094. (c) Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 1662−1663.

(4) For a review on organic synthesis with organoboranes, see: *Boronic Acids*; Hall, D. G., Ed.: Wiley-VCH: Weinheim, Germany, 2011.

(5) For a review on organic synthesis with organostannanes, see: Orita, A.; Otera, J. Tin in Organic Synthesis. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 621−720.

(6) (a) Howell, A.; Robertson, J. F. R.; Quaresma Albano, J.; Aschermannova, A.; Mauriac, L.; Kleeberg, U. R.; Vergote, I.; Erikstein, B.; Webster, A.; Morris, C. *J. Clin. Oncol.* **2002**, *20*, 3396−3403. (b) Jordan, V. C. *J. Med. Chem.* **2003**, *46*, 1081−1111. (c) Kusama, M.; Miyauchi, K.; Aoyama, H.; Sano, M.; Kimura, M.; Mitsuyama, S.; Komaki, K.; Doihara, H. *Breast Cancer Res. Treat.* **2004**, *88*, 1−8.

(7) For reviews on copper-catalyzed borylations, see: (a) Yun, J. *Asian J. Org. Chem.* **2013**, *2*, 1016−1025. (b) Fujihara, T.; Semba, K.; Terao, J.; Tsuji, Y. *Catal. Sci. Technol.* **2014**, *4*, 1699−1709. (c) Semba, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Tetrahedron* **2015**, *71*, 2183−2197. (d) Yoshida, H. *ACS Catal.* **2016**, *6*, 1799−1811.

(8) For our reports on copper-catalyzed metalation reactions for synthesizing main-group organometallics containing boron, tin, or silicon, see: (a) Yoshida, H.; Kawashima, S.; Takemoto, Y.; Okada, K.; Ohshita, J.; Takaki, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 235−238. (b) Yoshida, H.; Kageyuki, I.; Takaki, K. *Org. Lett.* **2013**, *15*, 952−955. (c) Yoshida, H.; Shinke, A.; Takaki, K. *Chem. Commun.* **2013**, *49*, 11671−11673. (d) Kageyuki, I.; Yoshida, H.; Takaki, K. *Synthesis* **2014**, *46*, 1924−1932. (e) Yoshida, H.; Takemoto, Y.; Takaki, K. *Chem. Commun.* **2014**, *50*, 8299−8302. (f) Yoshida, H.; Takemoto, Y.; Takaki, K. *Asian J. Org. Chem.* **2014**, *3*, 1204−1209. (g) Yoshida, H.; Hayashi, Y.; Ito, Y.; Takaki, K. *Chem. Commun.* **2015**, *51*, 9440−9442. (h) Yoshida, H.; Shinke, A.; Kawano, Y.; Takaki, K. *Chem. Commun.* **2015**, *51*, 10616−10619. (i) Yoshida, H. *Chem. Rec.* **2016**, *16*, 419−434.

(9) For details on the distannane formation, see ref 1f.

(10) In the Zn-catalyzed synthesis of alkynylstannanes from terminal alkynes and a tin alkoxide, cuprous bromide was reported to also show moderate catalytic activity. See: Kiyokawa, K.; Tachikake, N.; Yasuda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10393−10396.

(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.

(12) Dandge, D. K.; Taylor, C.; Heller, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1053−1063.

(13) Tri-*n*-octyltin compounds exhibit almost no toxicity, in contrast to the moderately toxic nature of tri-*n*-butyltin compounds (LD_{50} (oral/rat): nBu$_3$SnCl (129 mg/kg) ≫ nOct$_3$SnCl (4000 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 effects on the regioselectivity and yield of the borylstannylation of **1h**, see the Supporting Information.

(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 a 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,b** (4 mol %) also promoted the borylstannylation of **1d** with **3a** under similar conditions depicted in Table 2 to afford

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX−XXX

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 the Supporting Information for details.

(19) The observed signals in ^{11}B NMR were assigned by comparison 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) Laitar, 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) Kleeberg, 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 an 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 $BF_3{\cdot}OEt_2$, 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 the Supporting Information.

(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.

(25) Bowmaker, G. A.; Boyd, S. E.; Hanna, J. V.; Hart, R. D.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2722−2730.

DOI: 10.1021/acs.organomet.7b00058
Organometallics XXXX, XXX, XXX−XXX