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Studies on copper(I)-catalyzed highly regio- and stereo-selective hydroboration of alkynamides†

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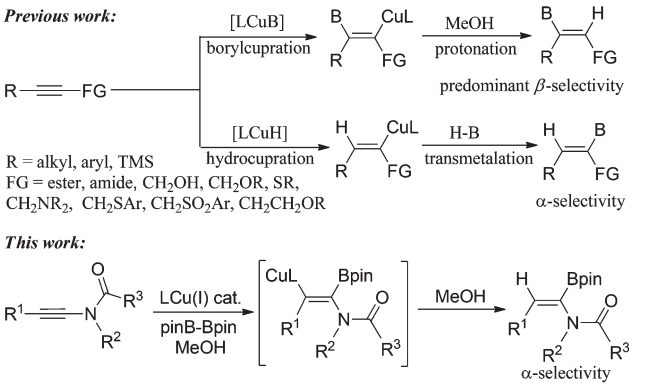
The copper(I)-catalyzed hydroboration of alkynamides with B_2pin_2 afforded the alkenamide boronates in 66% to nearly quantitative yields with high regio- and stereo-selectivity. It was interesting to note that the regio-selectivity of the reaction is opposite to that observed in the carbometallation reaction of alkynamides, and the resulting alkenyl boronates provided access to α,β-disubstituted (*Z*)-alkenamides through further elaboration.

1. Introduction

Vinylboronates are essential building blocks in organic synthesis.[1] Their utility as partners in Suzuki–Miyaura coupling reaction[2] and their ability[3] to undergo Rh-catalyzed[3] and metal-free[4] conjugate additions make them highly versatile intermediates in the construction of complex molecules. Although several approaches to alkenyl boronates[5] have been disclosed in the past few years, hydroboration[6] of alkynes[7] is still a direct and efficient method for obtaining vinylboronates with regio- and stereo-selectivity.[8]

Renewed interest in the field has been spurred on by Cu(I)-catalyzed hydroboration of functionalized internal alkynes utilizing two different catalytic species ([LCuB] and [LCuH]) generated from bis(pinacolato)diboron (B_2pin_2) and pinacolborane (HBpin), respectively (Scheme 1). Recently, Yun,[9] Carretero,[10] McQuade[11] and Zhu[12] have developed the stereoselective addition of boryl copper species [LCuB] to functionalized alkynes, affording the corresponding alkenyl boronates with β-site regioselectivity predominantly. In the meantime, Lipshutz[13] and Tsuji[14] have also described the copper hydride species [LCuH] catalyzed stereoselective hydroboration of unsymmetrical internal alkynes with high α-site regioselectivity. However, the Cu-catalyzed borylation of *N*-(1-alkynyl)-amides with borylating reagents, B_2pin_2 and HBpin, has not been explored.[15] In previous studies, we have demonstrated that aryl- and TMS-substituted alkynamides could be catalytically reduced to (*Z*)-alkenamides with high stereoselectivity by the boron addition-protonolysis protocol.[16] Herein, we report the copper(I)-catalyzed highly regio- and stereo-selective hydroboration of alkynamides and further elaboration of products.



Scheme 1 Cu(I)-catalyzed regio- and stereo-selective hydroboration of alkynamides.

2. Results and discussion

In the initial experiments, the CuCl/*t*-BuONa catalyzed hydroboration of 3-(2-phenylethynyl)oxazolidin-2-one (**1a**) with B_2pin_2 was investigated in anhydrous toluene at room temperature with monodentate phosphine ligands (Table 1, entries 1–6). The experimental results showed that the reactions with PPh_3, $P(Bu\text{-}n)_3$ and $P(OEt)_3$ gave no desired α-site regio-controlled alkenamide boronate (*Z*)-**2a**, but the mixture of the β-site regio-isomer (*Z*)-**3a** and semi-reduced alkenamide (*Z*)-**4a** (entries 1–3).[16] When SPhos or XPhos was selected as the ligand of the present system, the reaction only afforded (*Z*)-**2a** in very poor yields, and the corresponding regio- and chemo-

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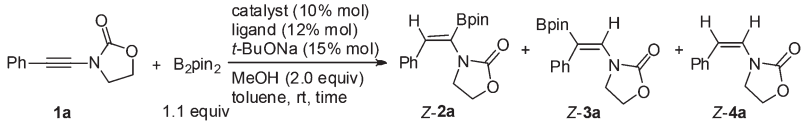
†Electronic supplementary information (ESI) available: Copies of ^1H NMR and ^{13}C NMR spectra of compounds **1k**, **1p**, (*Z*)-**2a**–(*Z*)-**2p**, (*Z*)-**5a** and (*Z*)-**5j**. CCDC 944761. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob00979g

Table 1 Screening reaction conditions of Cu(I)-catalyzed hydroboration of 3-(2-phenylethynyl)oxazolidin-2-one (**1a**) with B_2pin_2 [a]



Entry	Catalyst	Ligand	Time (h)	NMR yield of (*Z*)-**2a**[b]	Ratio of (*Z*)-**2a**/(*Z*)-**3a**/(*Z*)-**4a**[c]	Recovery of **1a**
1	CuCl	PPh_3	2.5	0%	0/5/95	0%
2	CuCl	$P(Bu\text{-}n)_3$	15	0%	0/9/91	3.5%
3	CuCl	$P(OEt)_3$	1.6	0%	0/21/79	0%
4	CuCl	SPhos	4.0	4%	5/13/82	5.5%
5	CuCl	XPhos	1.0	29%	36/41/23	0%
6	CuCl	LB-Phos·HBF_4	6.0	84%	94/2/4	0%
7	CuCl	Xantphos	4.5	84% (80%)[d]	95/5/0	0%
8	CuCl	DPEphos	16	64%	84/16/0	12%
9	CuBr	Xantphos	24	34%	89.5/10.5/0	58%
10	CuI	Xantphos	24	11%	78.5/21.5/0	76%
11	—	Xantphos	48	0%	0/0/0	92%

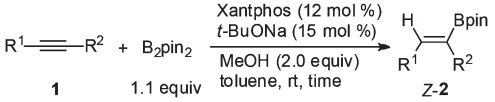
[a] Reaction conditions: **1a** (0.3 mmol), B_2pin_2 (0.33 mmol), catalyst (0.03 mmol), ligand (0.036 mmol), *t*-BuONa (0.045 mmol), methanol (0.6 mmol), toluene (1 mL), N_2, rt. [b] NMR yield based on **1a** using mesitylene as the internal standard. [c] The molar ratio of (*Z*)-**2a**/(*Z*)-**3a**/(*Z*)-**4a** was determined by ^1H NMR analysis of the crude product. [d] Isolated yield.

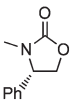
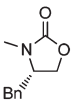
selectivity were not satisfactory (entries 4–5). Surprisingly, in the case of LB-Phos·HBF_4,[17] the yield of the Cu(I)-catalyzed hydroboration reaction could be dramatically increased to 84% with good reactivity and selectivity (entry 6). Further screenings indicated that bidentate phosphine ligands had a pronounced effect on the reaction. To our delight, the reactivity was greatly enhanced with the xantphos ligand while obtaining the excellent α-site regioselectivity (entry 7). In contrast, DPEphos was much less reactive and regioselective (entry 8). Other copper salt catalysts, such as CuBr and CuI, cannot exhibit good catalytic reactivity under otherwise identical conditions (entries 9–10). No reaction was observed without a catalyst (entry 11).

With the optimized conditions in hand (Table 1, entry 7), we next investigated the scope and limitations of the Cu-catalyzed hydyoboration. Notably, both *N*-arylalkynylated and *N*-alkylalkynylated oxazolidinones were suitable for the α-site regio-selective transformation (Table 2, entries 1–5). For *N*-arylalkynyl substituted oxazolidinones, the alkynamide with a strong electron-donating group on the arene exhibited higher reactivity and required shorter time for completion than that with a strong electron-withdrawing group (compare entry 2 with entry 3). However, the α-borylation of the sterically demanding *t*-butyl substituted substrate with B_2pin_2 cannot work well and gave the alkenamide boronate (*Z*)-**2e** in very poor yield (entry 5). And oxazolidinones bearing different substituents, including phenyl and benzyl groups, also participated in the reaction with the desired alkenylamide boronates being isolated in 75–82% yields (entries 6–9). Additionally, it was observed that the phenyl-substituted acyclic sulfonamide (**1j**) can be also compatible with the conditions but with relatively lower yield (entry 10).

The initial condition screening showed that the reactivity and regio-selectivity of the Cu-catalyzed hydroboration strongly depended upon the nature of ligands (Table 1, entries 1–8).

Table 2 Scope of the copper-catalyzed hydroboration of alkynamides (**1**) with B_2pin_2 [a]

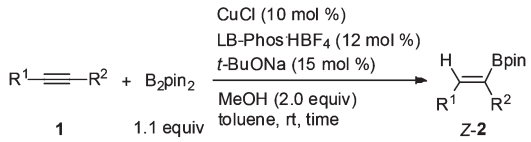


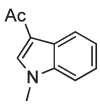
Entry	R^1	R^2	Time (h)	Isolated yield of (*Z*)-**2** (%)
1	Ph (**1a**)		6	80 (*Z*-**2a**)
2	*p*-MeOPh (**1b**)		6	85 (*Z*-**2b**)
3	*p*-NO_2Ph (**1c**)		12	66 (*Z*-**2c**)
4	*n*-Pent (**1d**)		12	76 (*Z*-**2d**)
5[b]	*t*-Bu (**1e**)		24	12 (*Z*-**2e**)
6	Ph (**1f**)		36	75 (*Z*-**2f**)
7	*n*-Pent (**1g**)		24	82 (*Z*-**2g**)
8	Ph (**1h**)		24	75 (*Z*-**2h**)
9	*n*-Pent (**1i**)		18	82 (*Z*-**2i**)
10[c]	Ph (**1j**)		24	38 (*Z*-**2j**)

[a] Reaction conditions: **1** (0.30 mmol), B_2pin_2 (0.33 mmol), CuCl (0.03 mmol), xantphos (0.036 mmol), *t*-BuONa (0.045 mmol), methanol (0.6 mmol), toluene (1 mL), N_2, rt. [b] **1e** (54%) was recovered. [c] **1j** (61%) was recovered.

Therefore we attempted to re-evaluate the steric and electronic properties of various phosphine ligands in order to find the appropriate one for the acyclic alkynamides. Gratifyingly, the acylic alkenyl sulfonamide boronates can be obtained in nearly quantitative yields with high regio- and stereoselectivity using LB-Phos·HBF_4 [17] as the ligand (Table 3, entries 1, 2

Table 3 The copper-catalyzed hydroboration of alkynamides (**1**) with B_2pin_2 using LB-Phos·HBF_4 as the ligand[a]



Entry	R^1	R^2	Time (h)	Isolated yield of (*Z*)-**2** (%)
1	Ph (**1j**)		12	100 (*Z*-**2j**)
2	*n*-Pent (**1k**)		18	76 (*Z*-**2k**)
3	H (**1l**)		6	74 (**2l**)
4[b]	Ph (**1m**)		72	90 (*Z*-**2m**)
5	H (**1n**)		12	85 (**2n**)
6	Ph (**1o**)		30	80 (*Z*-**2o**)
7	*n*-Pent (**1p**)		36	66 (*Z*-**2p**)
8	*t*-Bu (**1e**)		24	71 (*Z*-**2e**)

[a] Reaction conditions: **1** (0.30 mmol), B_2pin_2 (0.33 mmol), CuCl (0.03 mmol), LB-Phos·HBF_4 (0.036 mmol), *t*-BuONa (0.045 mmol), methanol (0.6 mmol), toluene (1 mL), N_2, rt. [b] CuCl (20 mol%) was used and **1m** (6%) was recovered.

and 4). As mentioned, *N*-alkynyl-3-acetylindoles would also be transformed into the corresponding alkenylboronates in moderate to good yields (entries 6–7). It is surprising that the yield of sterically bulky alkynamide (**1e**) can be significantly improved from 12% to 71% (Table 2, entry 5 *vs.* Table 3, entry 8). It is noteworthy that when the unsubstituted *N*-ethynylamides were subjected to the present reaction conditions, the single α-site regio-controlled alkenyl boronates were also afforded in good yields with high stereoselectivity (entries 3 and 5), which were vastly different from the β-site regio-controlled hydroboration of *N*-ethynylamides with borane in the literature.[15a,b] The stereochemistry of the Cu-catalyzed hydroboration was further confirmed by X-ray diffraction study of (*Z*)-**2j** (Fig. 1).[18]

Despite the Cu-catalyzed hydroboration was routinely conducted at 0.3 mmol scale, we confirmed that the process is amenable to 10-fold scale-up without compromising reactivity. In addition, we found that the Cu(I) catalyst loading can be reduced to 5% mol with comparable efficiency (Scheme 2).

The vinylboronates obtained in this study are useful organic intermediates for the stereoselective synthesis of α,β-disubstituted alkenamides (Scheme 3).[19] The Suzuki–Miyaura coupling was performed on ynamides (*Z*)-**2a** and (*Z*)-**2j** in THF by using 1.1 equiv. of *p*-bromoacetophenone to furnish the α,β-disubstituted (*Z*)-alkenamides (*Z*)-**5a** and (*Z*)-**5j** in 84% and 91% isolated yields, respectively.

In accordance with literature precedents,[20] the hydroboration of alkynamides promoted by MeOH occurred in the following stages: a ligated and nucleophilic boryl-copper species, generated from *t*-BuOCuL and B_2pin_2 in the presence of a base,[21] adds to the *N*-alkynylamide (**1**) in a *syn*-fashion with the boronate moiety adding at the α-carbon to the amide group, followed by protonolysis of the carbon–copper bond providing the α-site regio-controlled alkenylamide boronate. It is interesting to observe that *the regio-selectivity is just opposite to that observed in the carbometallation reaction of ynamides*.[22] In the latter case, the organometallic species adds to the *N*-alkynylamide in a *syn*-fashion with the metal atom adding at the α-carbon to the amide group because of the impressive metal-coordinating ability of ynamido carbonyl oxygen (Scheme 4). However, it is unclear what is responsible for the

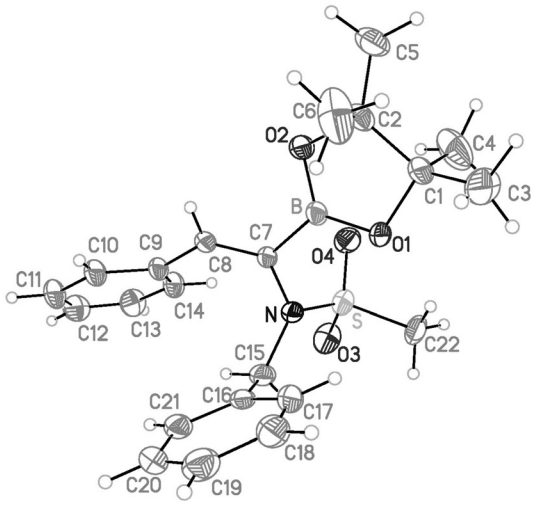
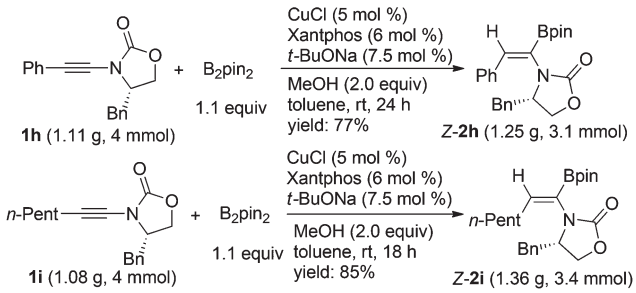
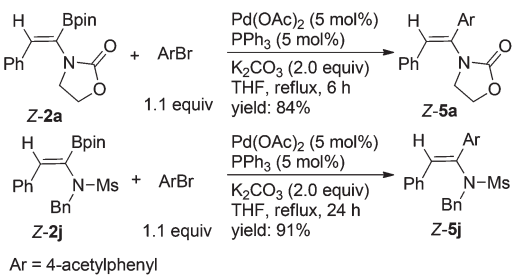


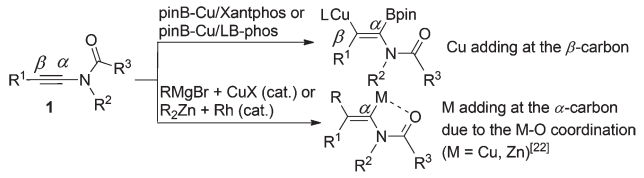
Fig. 1 ORTEP-drawing of the X-ray structure of (*Z*)-**2j** with 30% thermal ellipsoids.



Scheme 2 Scale-up experiments.



Scheme 3 Synthetic application of alkenylamide boronates: synthesis of α,β-disubstituted (*Z*)-alkenamides *via* Suzuki–Miyaura coupling.



Scheme 4 Regioselective addition comparison between the hydroboration and the carbometallation of alkynamides.

observed regioselectivity of borylcupration of alkynamide up to now.[23]

3. Conclusions

In summary, we have developed the copper-catalyzed highly regio- and stereo-selective hydroboration of alkynamides in the presence of methanol. The protocol provided an efficient and simple procedure to afford α-site regio-controlled alkenylamide boronates in good to excellent yields from readily available materials, thus allowing an easy access to α,β-disubstituted (*Z*)-alkenamides through further elaboration. Further studies on the factors controlling regioselectivity of the boryl-copper complex addition to *N*-alkynylamides are underway in our laboratory.

4. Experimental

4.1. General methods

All the reactions were carried out in anhydrous solvents and under inert atmosphere. Melting points were taken in open-end capillary tubes. Chemical shifts were reported relative to tetramethylsilane for ^{1}H and ^{13}C. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, br = broad, m = multiplet), coupling constants (Hz), integration. Mass spectra (MS) were obtained at an ionizing voltage of 70 eV. HRMS were performed on a time-of-flight mass spectrometer equipped with an ESI source. Reactions were monitored by thin-layer chromatography, carried out on 0.25 mm silica gel plates. Flash column chromatography was performed using silica gel. Characterization data for those compounds not described in the literature are provided.

Copper(I) chloride, sodium *tert*-butoxide, B_2pin_2, xantphos, 3,3-dimethylbutyne, heptyne, phenylacetylene, *p*-methoxylphenylacetylene, *p*-nitrophenylacetylene, trimethylsilylacetylene, oxazolidin-2-one, (*S*)-4-phenyl-oxazolidin-2-one, (*S*)-4-benzyloxazolidin-2-one, pyrrolidin-2-one and 3-acetylindole were purchased from commercial sources and used as received.

Alkynyl bromides,[24] 2-bromotrimethylsilylethyne,[25] old compounds **1a–j**, **1l–o** and new compounds **1k** and **1p** were prepared according to the reported procedure.[26] Unless otherwise noted, commercially available reagents were used without purification. Toluene was freshly distilled from sodium/benzophenone ketyl.

4.1.1. Synthesis of starting materials

Typical procedure for the synthesis of ynamides. To a mixture of *N*-nucleophiles (5 mmol), K_2CO_3 (10 mmol), $CuSO_4{\cdot}5H_2O$ (0.5 mmol), and 1,10-phenanthroline (1.0 mmol) in a reaction vial was added a solution of alkynyl bromides (5.5 mmol) in toluene (5.0 mL). The reaction mixture was capped and heated in an oil bath at 80 °C for the indicated time. Upon completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate and filtered through Celite, and the filtrate was concentrated under vacuum. The crude products were purified by flash chromatography on a silica gel column with petroleum ether (PE) and ethyl acetate (EA) as the eluent to afford the desired product.

(1) *N*-Benzyl-*N*-(hept-1-ynyl)methanesulfonamide (1k)

The reaction of $CuSO_4{\cdot}5H_2O$ (125.2 mg, 0.5 mmol), 1,10-phenanthroline (180.0 mg, 1.0 mmol), K_2CO_3 (1.3208 g, 10.0 mmol), *N*-benzylmethanesulfonamide (925.7 mg, 5.0 mmol) and 1-heptynyl bromide (957.2 mg, 5.5 mmol) in toluene (5.0 mL) at 80 °C for 12 h afforded **1k** (1.3253 g, yield: 95%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.32 (m, 5 H), 4.57 (s, 2 H), 2.86 (s, 3 H), 2.25 (t, J = 7.0 Hz, 2 H), 1.52–1.40 (m, 2 H), 1.36–1.21 (m, 4 H), 0.93–0.82 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 128.9, 128.6, 128.5, 72.9, 71.4, 55.6, 38.2, 30.9, 28.5, 22.1, 18.4, 14.0; MS (ESI) *m*/*z* (%) 280 (M^+ + 1, 45.5), 302 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 3032, 2957, 2932, 2861, 2045, 1683, 1535, 1455, 1357, 1163, 1078, 960. HRMS calcd for $C_{15}H_{22}NO_2S$ $(M + H)^+$: 280.1366. Found: 280.1384.

(2) 1-(1-(Hept-1-ynyl)-1*H*-indol-3-yl)ethanone (1p)

The reaction of $CuSO_4{\cdot}5H_2O$ (125.3 mg, 0.5 mmol), 1,10-phenanthroline (180.6 mg, 1.0 mmol), K_2CO_3 (1.3205 g, 10.0 mmol), 3-acetylindole (796.1 mg, 5.0 mmol) and 1-heptynyl bromide (957.1 mg, 5.5 mmol) in toluene (5.0 mL) at 80 °C for 27 h afforded **1p** (316.3 mg, yield: 25%) as a light red solid. Mp 70–71 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38–8.32 (m, 1 H), 7.81 (s, 1 H), 7.55–7.51 (m, 1 H), 7.41–7.30 (m, 2 H), 2.52 (s, 1 H), 2.48 (t, J = 7.1 Hz, 2 H), 1.73–1.63 (m, 2 H), 1.53–1.34 (m, 4 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 138.7, 135.5, 124.9, 124.6, 123.9, 122.7, 119.0, 111.1, 72.0, 70.6, 31.1, 28.4, 27.6, 22.2, 18.3, 14.0; MS (ESI) *m*/*z* (%) 254 (M^+ + 1, 100); IR ν (KBr, cm^{-1}) 3101, 3043, 2959, 2930, 2854, 2268, 1751, 1649, 1532, 1460, 1375, 1298, 1219, 1141, 1101, 1010. Anal. calcd for $C_{17}H_{19}NO$: C 80.60, H 7.56, N 5.53. Found: C 80.72, H 7.37, N 5.19.

4.1.2. Cu(I)-catalyzed hydroboration of alkynamides with B_2pin_2

Typical procedure. An oven-dried Schlenk tube was charged with CuCl (0.05 mmol), *t*-BuONa (0.075 mmol), B_2pin_2 (0.55 mmol), **L1** (xantphos) or **L2** (LB-Phos·HBF_4) (0.06 mmol), and alkynamides **1** (0.5 mmol) and the Schlenk tube was purged and backfilled with nitrogen (three times). To this mixture were added toluene (1.5 mL) and MeOH (40 μL, 0.6 mmol), and the resulting solution was stirred at room temperature until no starting material was detected by TLC monitoring. Then, the reaction was quenched by the addition of saturated aqueous NH_4Cl

(5.0 mL) and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine (5 mL) and dried over anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel column with petroleum ether (PE) and ethyl acetate (EA) as the eluent afforded the desired product (*Z*)-**2**.

(1) 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylethenyl]oxazolidin-2-one (*Z*-2a)

The reaction of CuCl (5.1 mg, 0.05 mmol), xantphos (34.6 mg, 0.06 mmol), *t*-BuONa (7.3 mg, 0.075 mmol), **1a** (93.6 mg, 0.5 mmol), B_2pin_2 (139.9 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 6.0 h afforded *Z*-**2a** (132.4 mg, yield: 80%) as a white solid. Mp 120–121 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 2 H), 7.37–7.31 (m, 2 H), 7.31–7.25 (m, 1 H), 6.85 (s, 1 H), 4.35 (t, J = 7.9 Hz, 2 H), 3.52 (t, J = 7.9 Hz, 2 H), 1.33 (s, 12 H). The carbon directly attached to the boron atom was not detected by the ^{13}C NMR technique due to quadrupolar relaxation. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 135.4, 135.2, 129.0, 128.4, 128.3, 84.4, 62.9, 45.1, 24.7; MS (ESI) *m*/*z* (%) 315 (M^+, 30.01), 316 (M^+ + 1, 4.53), 257 (100); IR ν (KBr, cm^{-1}) 2984, 2923, 1744, 1628, 1486, 1421, 1328, 1267, 1222, 1144, 1083, 1033, 991. Anal. calcd for $C_{17}H_{22}BNO_4$: C 64.78, H 7.04, N 4.44. Found: C 64.83, H 6.81, N 4.29.

(2) 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-methoxylphenyl)ethenyl]oxazolidin-2-one (*Z*-2b)

The reaction of CuCl (5.3 mg, 0.05 mmol), xantphos (34.2 mg, 0.06 mmol), *t*-BuONa (7.3 mg, 0.075 mmol), **1b** (108.6 mg, 0.5 mmol), B_2pin_2 (140.1 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2b** (146.6 mg, yield: 85%) as a yellow solid. Mp 161–162 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2 H), 6.91–6.87 (m, 2 H), 6.86 (s, 1 H), 4.38 (t, J = 7.9 Hz, 2 H), 3.82 (s, 3 H), 3.60 (t, J = 7.9 Hz, 2 H), 1.32 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 157.7, 137.5, 130.7, 127.6, 113.9, 84.3, 62.8, 55.2, 45.2, 24.7; MS (ESI) *m*/*z* (%) 346 (M^+ + 1, 100), 368 (M^+ + Na, 59.3); IR ν (KBr, cm^{-1}) 2983, 2915, 1752, 1605, 1511, 1415, 1339, 1253, 1174, 1143, 1076, 986. Anal. calcd for $C_{18}H_{24}BNO_5$: C 62.63, H 7.01, N 4.06. Found: C 62.66, H 6.88, N 3.81.

(3) 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-nitrophenyl)ethenyl]oxazolidin-2-one (*Z*-2c)

The reaction of CuCl (5.4 mg, 0.05 mmol), xantphos (34.6 mg, 0.06 mmol), *t*-BuONa (7.5 mg, 0.075 mmol), **1c** (116.1 mg, 0.5 mmol), B_2pin_2 (139.4 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2c** (113.4 mg, yield: 63%) as a yellow solid. Mp 191–193 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.17 (m, 2 H), 7.56–7.50 (m, 2 H), 6.83 (s, 1 H), 4.40 (t, J = 7.9 Hz, 2 H), 3.58 (t, J = 7.9 Hz, 2 H), 1.34 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 147.0, 142.1, 131.5, 129.6, 123.6, 84.8, 63.0, 45.4, 24.7; MS (ESI) *m*/*z* (%) 360 (M^+, 25.2), 383 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 2987, 2913, 1749, 1618, 1514, 1417, 1344, 1265, 1142, 1079, 1029, 993. Anal. calcd for $C_{17}H_{21}BN_2O_6$: C 56.69, H 5.88, N 7.78. Found: C 56.23, H 5.78, N 7.54.

(4) 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-heptenyl]oxazolidin-2-one (*Z*-2d)

The reaction of CuCl (5.4 mg, 0.05 mmol), xantphos (34.2 mg, 0.06 mmol), *t*-BuONa (7.3 mg, 0.075 mmol), **1d** (90.6 mg, 0.5 mmol), B_2pin_2 (140.0 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 12 h afforded *Z*-**2d** (117.4 mg, yield: 76%) as a white solid. Mp 78–79 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1 H), 4.40 (dd, J_1 = 8.9 Hz, J_2 = 7.0 Hz, 1 H), 4.06 (dd, J_1 = 8.9 Hz, J_2 = 7.0 Hz, 1 H), 2.20 (t, J = 7.5 Hz, 2 H), 1.42–1.20 (m, 20 H), 0.88 (t, J = 6.7 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 133.1, 83.2, 62.2, 45.0, 31.7, 31.3, 26.9, 24.7, 22.6, 14.0; MS (ESI) *m*/*z* (%) 310 (M^+ + 1, 48.7), 322 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 2929, 2866, 1748, 1628, 1489, 1376, 1283, 1219, 1144, 1084, 1040, 963. Anal. calcd for $C_{16}H_{28}BNO_4$: C 62.15, H 9.13, N 4.53. Found: C 62.06, H 8.89, N 4.30.

(5) 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethylbutenyl]-oxazolidin-2-one (*Z*-2e)

The reaction of CuCl (5.1 mg, 0.05 mmol), xantphos (27.1 mg, 0.06 mmol), *t*-BuONa (7.2 mg, 0.075 mmol), **1e** (84.7 mg, 0.5 mmol), B_2pin_2 (139.8 mg, 0.55 mmol), and MeOH (40.0 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2e** (23.6 mg, yield: 12%) as a white solid. Recovery of **1e** was 50%. Mp 153–154 °C (*n*-hexane–Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (s, 1 H), 4.36 (t, J = 7.9 Hz, 2 H), 4.43 (t, J = 7.9 Hz, 2 H), 1.26 (s, 12 H), 1.17(s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 157.8, 84.1, 62.1, 47.9, 34.9, 29.6, 24.8; MS (ESI) *m*/*z* (%) 318 (M^+ + Na, 100), 613 ($2M^+$ + Na, 53.33); IR ν (KBr, cm^{-1}) 2964, 1750, 1641, 1473, 1392, 1332, 1265, 1220, 1148, 1084, 1036, 973. Anal. calcd for $C_{15}H_{26}BNO_4$: C 61.03, H 8.88, N 4.75. Found: C 61.01, H 8.85, N 4.38.

(6) (*S*)-4-Phenyl-3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenyl-ethenyl]oxazolidin-2-one (*Z*-2f)

The reaction of CuCl (5.4 mg, 0.05 mmol), xantphos (35.0 mg, 0.06 mmol), *t*-BuONa (7.5 mg, 0.075 mmol), **1f** (131.4 mg, 0.5 mmol), B_2pin_2 (139.6 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 36 h afforded *Z*-**2f** (146.6 mg, yield: 75%) as a white solid. Mp 89–90 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.14 (m, 8 H), 7.02–6.95 (m, 2 H), 6.87 (s, 1 H), 4.95 (t, J = 8.5 Hz, 1 H), 4.60 (t, J = 8.7 Hz, 1 H), 4.17 (t, J = 8.4 Hz, 1 H), 1.27 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 138.5, 137.3, 135.6, 129.1, 128.5, 128.4, 128.3, 128.2, 127.6, 84.3, 70.7, 60.2, 24.8, 24.5; MS (ESI) *m*/*z* (%) 392 (M^+ + 1, 100), 414 (M^+ + Na, 21.0); IR ν (KBr, cm^{-1}) 3059, 2979, 2927, 1754, 1620, 1454, 1400, 1346, 1241, 1138, 1091, 1023, 973. Anal. calcd for $C_{23}H_{26}BNO_4$: C 70.60, H 6.70, N 3.58. Found: C 70.68, H 6.74, N 3.42.

(7) (*S*)-4-Phenyl-3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-hepten-yl]oxazolidin-2-one (*Z*-2g)

The reaction of CuCl (5.4 mg, 0.05 mmol), xantphos (34.5 mg, 0.06 mmol), *t*-BuONa (7.0 mg, 0.075 mmol), **1g** (128.6 mg, 0.5 mmol), B_2pin_2 (139.5 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2g** (157.6 mg, yield: 82%) as a white

solid. Mp 98–99 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.30 (m, 3 H), 7.23–6.92 (m, 2 H), 6.96 (s, 1 H), 5.27 (dd, J_1 = 8.5 Hz, J_2 = 3.8 Hz, 1 H), 4.65 (t, J = 8.5 Hz, 1 H), 4.12 (dd, J_1 = 8.4 Hz, J_2 = 3.8 Hz, 1 H), 2.00–1.86 (m, 2 H), 1.28–0.93 (m, 18 H), 0.84 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 139.1, 131.2, 129.3, 128.6, 125.4, 83.2, 70.3, 59.8, 31.9, 29.9, 27.7, 24.6, 22.6, 14.0; MS (ESI) *m*/*z* (%) 386 (M^+ + 1, 100), 408 (M^+ + Na, 39.1); IR ν (KBr, cm^{-1}) 2983, 2952, 2861, 1748, 1632, 1372, 1312, 1212, 1144, 1080, 1044. Anal. calcd for $C_{22}H_{32}BNO_4$: C 68.58, H 8.37, N 3.64. Found: C 68.44, H 8.10, N 3.51.

(8) (*S*)-4-Benzyl-3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenyl-ethenyl]oxazolidin-2-one (*Z*-2h)

The reaction of CuCl (5.0 mg, 0.05 mmol), xantphos (34.2 mg, 0.06 mmol), *t*-BuONa (7.4 mg, 0.075 mmol), **1h** (138.6 mg, 0.5 mmol), B_2pin_2 (140.0 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2h** (151.9 mg, yield: 75%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 2 H), 7.41–7.29 (m, 3 H), 7.23–7.14 (m, 3 H), 7.00 (s, 1 H), 6.86–6.74 (m, 2 H), 4.21–4.01 (m, 3 H), 2.91 (dd, J_1 = 13.6 Hz, J_2 = 3.4 Hz, 1 H), 2.49 (dd, J_1 = 13.4 Hz, J_2 = 9.3 Hz, 1 H), 1.34 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 137.1, 136.0, 135.4, 129.1, 128.9, 128.6, 128.5, 128.4, 126.8, 84.4, 67.7, 56.7, 38.4, 25.0, 24.5; MS (ESI) *m*/*z* (%) 405 (M^+, 46.56), 428 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 3060, 2979, 2930, 1755, 1627, 1490, 1408, 1231, 1142, 1081, 1030, 974. HRMS calcd for $C_{24}H_{29}BNO_4$ $(M + H)^+$: 406.2184. Found: 406.2196.

(9) (*S*)-4-Benzyl-3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-hepten-yl]oxazolidin-2-one (*Z*-2i)

The reaction of CuCl (5.3 mg, 0.05 mmol), xantphos (34.9 mg, 0.06 mmol), *t*-BuONa (7.5 mg, 0.075 mmol), **1i** (135.6 mg, 0.5 mmol), B_2pin_2 (140.1 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 18 h afforded *Z*-**2i** (163.6 mg, yield: 82%) as a white solid. Mp 86–87 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.24 (m, 3 H), 7.20–7.14 (m, 2 H), 6.96 (s, 1 H), 4.50–4.40 (m, 1 H), 4.22–4.13 (m, 2 H), 3.17 (dd, J_1 = 13.8 Hz, J_2 = 3.3 Hz, 1 H), 2.63 (dd, J_1 = 13.8 Hz, J_2 = 10.1 Hz, 1 H), 2.38–2.20 (m, 2 H), 1.54–1.40 (m, 2 H), 1.38–1.30 (m, 4 H), 1.27 (s, 12 H), 0.90 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 135.3, 131.8, 129.2, 129.0, 127.3, 83.4, 65.8, 56.8, 37.6, 31.8, 29.4, 28.0, 24.8, 24.7, 22.6, 14.0; MS (ESI) *m*/*z* (%) 400 (M^+ + 1, 48.7), 422 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 2958, 1751, 1621, 1379, 1337, 1266, 1218, 1144, 1086, 1002, 965. Anal. calcd for $C_{23}H_{34}BNO_4$: C 69.18, H 8.58, N 3.51. Found: C 69.14, H 8.34, N 3.34.

(10) (*Z*)-*N*-Benzyl-*N*-[2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]methanesulfonamide (*Z*-2j)

The reaction of CuCl (5.0 mg, 0.05 mmol), xantphos (34.6 mg, 0.06 mmol), *t*-BuONa (7.4 mg, 0.075 mmol), **1j** (142.4 mg, 0.5 mmol), B_2pin_2 (139.5 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2j** (78.4 mg, yield: 38%) as a white solid. Recovery of **1j** was 56%. Mp 122–123 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.56 (m, 2 H), 7.35–7.27 (m, 3 H), 7.21–7.15 (m, 5 H), 7.08 (s, 1 H), 4.46 (s, 2 H), 3.07 (s, 3 H), 1.29 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 136.0, 134.6, 129.8, 129.0, 128.9, 128.3, 128.1, 127.7, 84.3, 52.9, 39.9, 24.8; MS (ESI) *m*/*z* (%) 414 (M^+ + 1, 26.67), 436 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 3064, 3031, 2984, 2934, 1626, 1455, 1382, 1333, 1141, 1050, 957. Anal. calcd for $C_{22}H_{28}BNO_4S$: C 63.93, H 6.83, N 3.39. Found: C 63.74, H 6.80, N 3.26.

(11) (*Z*)-*N*-Benzyl-*N*-[2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]methanesulfonamide (*Z*-2j)

The reaction of CuCl (4.9 mg, 0.05 mmol), LB-Phos·HBF_4 (27.3 mg, 0.06 mmol), *t*-BuONa (7.5 mg, 0.075 mmol), **1j** (142.6 mg, 0.5 mmol), B_2pin_2 (140.1 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 12 h afforded *Z*-**2j** (206.4 mg, yield: 100%) as a white solid.

(12) (*Z*)-*N*-Benzyl-*N*-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptenyl]-methanesulfonamide (*Z*-2k)

The reaction of CuCl (5.4 mg, 0.05 mmol), LB-Phos·HBF_4 (27.2 mg, 0.06 mmol), *t*-BuONa (7.1 mg, 0.075 mmol), **1k** (139.5 mg, 0.5 mmol), B_2pin_2 (139.4 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 18 h afforded *Z*-**2k** (143.8 mg, yield: 71%) as a white solid. Mp 97–98 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5 H), 6.50 (t, J = 7.2 Hz, 1 H), 4.52 (s, 2 H), 2.98 (s, 3 H), 2.05 (q, J = 7.6 Hz, 2 H), 1.30 (s, 12 H), 1.20–1.10 (m, 2 H), 1.08–0.98 (m, 2 H), 0.96–0.86 (m, 2 H), 0.80 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 136.6, 129.3, 128.2, 127.6, 84.1, 53.3, 38.3, 31.6, 29.3, 27.8, 24.8, 22.4, 13.9; MS (ESI) *m*/*z* (%) 408 (M^+ + 1, 100), 430 (M^+ + Na, 45.2); IR ν (KBr, cm^{-1}) 2973, 2932, 2865, 1633, 1456, 1380, 1328, 1270, 1140, 1053, 981. Anal. calcd for $C_{21}H_{34}BNO_4S$: C 61.91, H 8.41, N 3.44. Found: C 61.93, H 8.19, N 3.16.

(13) *N*-Benzyl-*N*-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]methanesulfonamide (2l)

The reaction of CuCl (5.3 mg, 0.05 mmol), LB-Phos·HBF_4 (27.0 mg, 0.06 mmol), *t*-BuONa (7.6 mg, 0.075 mmol), **1l** (104.5 mg, 0.5 mmol), B_2pin_2 (140.2 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 6 h afforded **2l** (124.7 mg, yield: 74%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5 H), 5.04 (s, 1 H), 4.98 (s, 1 H), 4.78 (s, 2 H), 3.09 (s, 3 H), 1.31 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 128.5, 127.3, 127.0, 112.4, 84.4, 50.3, 39.8, 24.7; MS (ESI) *m*/*z* (%) 360 (M^+ + Na, 100); IR ν (neat, cm^{-1}) 3036, 2981, 2934, 1595, 1455, 1408, 1326, 1214, 1144, 1984, 1061, 959. HRMS calcd for $C_{16}H_{24}BNNaO_4S$ $(M + Na)^+$: 360.1411. Found: 360.1407.

(14) (*Z*)-*N*-Benzyl-*N*-[2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]-4-methylbenzenesulfonamide (*Z*-2m)

The reaction of CuCl (10.3 mg, 0.10 mmol), LB-Phos·HBF_4 (54.5 mg, 0.12 mmol), *t*-BuONa (14.6 mg, 0.15 mmol), **1m** (180.5 mg, 0.5 mmol), B_2pin_2 (140.2 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 72 h afforded *Z*-**2m** (220.1 mg, yield: 90%) as a white solid. Recovery of **1m** was 6%. Mp 138–139 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2 H), 7.51–7.44 (m, 2 H), 7.32–7.26 (m, 2 H), 7.25–7.18 (m, 3 H), 7.15–7.08 (m,

5 H), 7.07 (s, 1 H), 4.52 (s, 2 H), 2.43 (s, 3 H), 1.14 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 143.0, 136.7, 135.9, 134.8, 130.1, 129.3, 129.2, 128.9, 128.2, 127.9, 127.4, 83.8, 52.4, 24.6, 21.5; MS (ESI) *m*/*z* (%) 490 (M^+ + 1, 100), 512 (M^+ + Na, 62.2); IR ν (KBr, cm^{-1}) 3055, 3026, 3000, 2971, 1621, 1494, 1447, 1398, 1333, 1161, 1144, 1047, 981. Anal. calcd for $C_{28}H_{32}BNO_4S$: C 68.71, H 6.59, N 2.86. Found: C 68.81, H 6.52, N 2.63.

(15) *N*-Benzyl-*N*-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]-4-methylbenzenesulfonamide (2n)

The reaction of CuCl (5.2 mg, 0.05 mmol), LB-Phos·HBF_4 (27.2 mg, 0.06 mmol), *t*-BuONa (7.1 mg, 0.075 mmol), **1n** (142.5 mg, 0.5 mmol), B_2pin_2 (139.4 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 12 h afforded **2n** (175.5 mg, yield: 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2 H), 7.32–7.27 (m, 2 H), 7.26–7.18 (m, 5 H), 5.15 (s, 1 H), 5.02 (s, 1 H), 4.52 (s, 2 H), 2.42 (s, 3 H), 1.26 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 135.7, 135.6, 129.5, 128.3, 127.8, 127.4, 127.2, 116.5, 84.0, 49.8, 24.6, 21.5; MS (ESI) *m*/*z* (%) 414 (M^+ + 1, 44.6), 436 (M^+ + Na, 100), 452 (M^+ + K, 33.8); IR ν (neat, cm^{-1}) 3132, 2977, 2927, 1618, 1401, 1333, 1162, 1139, 1086, 815. HRMS calcd for $C_{22}H_{29}BNO_4S$ $(M + H)^+$: 414.1905. Found: 414.1900.

(16) 1-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylethenyl-1*H*-indol-3-yl]ethanone (*Z*-2o)

The reaction of CuCl (5.3 mg, 0.05 mmol), LB-Phos·HBF_4 (26.9 mg, 0.06 mmol), *t*-BuONa (7.5 mg, 0.075 mmol), **1o** (129.6 mg, 0.5 mmol), B_2pin_2 (140.2 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 30 h afforded *Z*-**2o** (154.8 mg, yield: 80%) as a white solid. Mp 137–138 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 4.8 Hz, 1 H), 7.63 (s, 1 H), 7.47 (s, 1 H), 7.32–7.22 (m, 1 H), 7.21–7.02 (m, 5 H), 6.85–6.73 (m, 2 H), 2.47 (s, 3 H), 1.31 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 142.9, 136.0, 134.7, 133.3, 129.5, 129.4, 128.6, 126.2, 123.1, 122.5, 122.3, 118.3, 111.5, 84.8, 27.6, 24.7; MS (ESI) *m*/*z* (%) 387 (M^+, 100); IR ν (KBr, cm^{-1}) 3114, 2979, 1651, 1523, 1459, 1379, 1351, 1208, 1139, 1093, 970. Anal. calcd for $C_{24}H_{26}BNO_3$: C 74.43, H 6.77, N 3.62. Found: C 74.09, H 6.66, N 3.24.

(17) 1-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-heptenyl-1*H*-indol-3-yl]ethanone (*Z*-2p)

The reaction of CuCl (5.4 mg, 0.05 mmol), LB-Phos·HBF_4 (27.3 mg, 0.06 mmol), *t*-BuONa (7.2 mg, 0.075 mmol), **1p** (124.8 mg, 0.5 mmol), B_2pin_2 (139.9 mg, 0.55 mmol), and MeOH (40 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 36 h afforded *Z*-**2p** (124.0 mg, yield: 66%) as a white solid. Mp 90–91 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.34 (m, 1 H), 7.87 (s, 1 H), 7.48–7.40 (m, 2 H), 7.36–7.28 (m, 2 H), 2.54 (s, 3 H), 2.35 (t, J = 7.7 Hz, 2 H), 1.58–1.48 (m, 2 H), 1.33 (s, 12 H), 1.32–1.22 (m, 4 H), 0.86 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 137.3, 133.9, 132.1, 125.7, 123.8, 123.2, 122.5, 118.6, 110.6, 83.9, 31.8, 29.1, 28.4, 27.5, 24.7, 22.4, 13.9; MS (ESI) *m*/*z* (%) 382 (M^+ + 1, 100); IR ν (KBr, cm^{-1}) 2969, 2931, 2868, 1660, 1532, 1460, 1372, 1322, 1213, 1128, 1008, 962. Anal. calcd for $C_{23}H_{32}BNO_3$: C 72.45, H 8.46, N 3.67. Found: C 72.64, H 8.24, N 3.34.

(18) 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethylbutenyl]oxazolidin-2-one (*Z*-2e)

The reaction of CuCl (5.1 mg, 0.05 mmol), LB-Phos·HBF_4 (27.1 mg, 0.06 mmol), *t*-BuONa (7.2 mg, 0.075 mmol), **1e** (84.7 mg, 0.5 mmol), B_2pin_2 (139.8 mg, 0.55 mmol), and MeOH (40.0 μL, 1.0 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded *Z*-**2e** (139.6 mg, yield: 71%) as a white solid.

4.1.3. Large scale reactions. (1) Synthesis of (*S*)-4-benzyl-3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylethenyl]oxazolidin-2-one (*Z*-2h)

An oven-dried Schlenk tube was charged with CuCl (20.6 mg, 0.2 mmol), *t*-BuONa (28.0 mg, 0.3 mmol), B_2pin_2 (1.1179 g, 4.4 mmol), xantphos (138.4 mg, 0.24 mmol), and **1h** (1.1082 g, 4.0 mmol) and the Schlenk tube was purged and backfilled with nitrogen (three times). To this mixture were added toluene (13.0 mL) and MeOH (0.32 mL, 8.0 mmol), and the resulting solution was stirred at room temperature until no starting material was detected by TLC monitoring. Then, the reaction was quenched by the addition of saturated aqueous NH_4Cl (5.0 mL) and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine (5.0 mL) and dried over anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether–ethyl acetate = 10/1) afforded *Z*-**2h** (1.2509 g, yield: 77%) as a white solid.

(2) (*S*)-4-Benzyl-3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptenyl]oxazolidin-2-one (*Z*-2i)

The reaction of CuCl (20.1 mg, 0.2 mmol), xantphos (138.6 mg, 0.24 mmol), *t*-BuONa (28.8 mg, 0.3 mmol), **1i** (1.0842 g, 4.0 mmol), B_2pin_2 (1.1175 g, 4.4 mmol), and MeOH (0.32 ml, 8.0 mmol) in toluene (13.0 mL) at room temperature for 18 h afforded *Z*-**2i** (1.3566 g, yield: 85%) as a white solid.

4.1.4. Synthetic application of alkenylamide boronates: synthesis of α,β-disubstituted (*Z*)-alkenamides *via* Suzuki–Miyaura coupling. (1) 3-[(*Z*)-1-(4-Acetylphenyl)-2-phenylethenyl]-oxazolidin-2-one (*Z*-5a)

The reaction of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol), PPh_3 (6.6 mg, 0.025 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) and *Z*-**2a** (157.7 mg, 0.5 mmol) in THF (1.5 mL) refluxed for 6 h to afford *Z*-**5a** (128.9 mg, yield: 84%) as a white solid. Mp 147–148 °C (*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.95 (m, 2 H), 7.59–7.53 (m, 2 H), 7.49–7.36 (m, 4 H), 7.36–7.28 (m, 1 H), 6.96 (s, 1 H), 4.48 (dd, J_1 = 8.8 Hz, J_2 = 7.4 Hz, 2 H), 3.69 (dd, J_1 = 8.7 Hz, J_2 = 7.4 Hz, 2 H), 2.62 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 156.3, 141.0, 137.0, 134.7, 133.7, 128.88, 128.85, 128.76, 128.6, 128.4, 125.9, 62.6, 45.2, 26.6; MS (ESI) *m*/*z* (%) 308 (M^+ + 1, 8.7), 330 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 3056, 2897, 1758, 1674, 1597, 1417, 1354, 1268, 1172, 1076, 1033, 958. Anal. calcd for $C_{19}H_{17}NO_3$: C 74.25, H 5.58, N 4.56. Found: C 74.19, H 5.38, N 4.21.

(2) (*Z*)-*N*-Benzyl-*N*-[2-phenyl-1-(4-acetylphenyl)ethenyl]methanesulfonamide (*Z*-5j)

The reaction of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (6.5 mg, 0.025 mmol), K_2CO_3 (138.1 mg, 1.0 mmol) and *Z*-**2j** (206.5 mg, 0.5 mmol) in THF (1.5 mL) reflux for 24 h afforded *Z*-**5j** (184.3 mg, yield: 91%) as a white solid. Mp 141–142 °C

(*n*-hexane–EA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.88 (m, 2 H), 7.45–7.40 (m, 2 H), 7.40–7.22 (m, 10 H), 6.84 (s, 1 H), 4.48 (s, 1 H), 2.60 (s, 3 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 143.1, 137.7, 136.9, 135.8, 135.1, 130.9, 130.0, 128.9, 128.8, 128.70, 128.65, 128.5, 127.7, 53.2, 42.8, 26.7; MS (ESI) *m*/*z* (%) 406 (M^+ + 1, 29.0), 428 (M^+ + Na, 100); IR ν (KBr, cm^{-1}) 3113, 3066, 3032, 2933, 1673, 1601, 1408, 1332, 1270, 1147, 1096, 1036, 976. Anal. calcd for $C_{19}H_{17}NO_3$: C 71.09, H 5.72, N 3.45. Found: C 71.02, H 5.52, N 3.18.

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Notes and references

1 (*a*) *Contemporary Boron Chemistry*, ed. M. G. Davidson, K. Wade, T. B. Marder and A. K. Hughes, Royal Society of Chemistry, Cambridge, 2000; (*b*) D. G. Hall, *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*, Wiley-VCH, Weinheim, 2005; (*c*) N. Miyaura, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 1535; (*d*) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890.

2 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.

3 T. Hayashi and K. Yamasaki, *Chem. Rev.*, 2003, **103**, 2829.

4 T. R. Wu and M. J. Chong, *J. Am. Chem. Soc.*, 2007, **129**, 4908.

5 Quenching reactive alkenyl metal species with $B(OR)_3$: (*a*) H. C. Brown and N. G. Bhat, *Tetrahedron Lett.*, 1988, **29**, 21; (*b*) T. E. Cole and R. Quintanilla, *Organometallics*, 1991, **10**, 3777; (*c*) K. Itami, T. Kamei and J.-i. Yoshida, *J. Am. Chem. Soc.*, 2003, **125**, 14670 Pd- or Pt-catalyzed halogen/boron exchange with $HB(OR)_2$: (*d*) M. Murata, T. Oyama, S. Watanabe and Y. Masuda, *Synthesis*, 2000, 778; (*e*) J. Takagi, K. Takahashi, T. Ishiyama and N. Miyaura, *J. Am. Chem. Soc.*, 2002, **124**, 8001 Olefin metathesis: (*f*) C. Morrill and R. H. Grubbs, *J. Org. Chem.*, 2003, **68**, 6031.

6 For the pioneering hydroboration with HBpin, see: (*a*) C. E. Tucker, J. Davidson and P. Knochel, *J. Org. Chem.*, 1992, **57**, 3482 For the NHC-Cu-catalyzed direct borylation of terminal alkynes, see: (*b*) Y. Lee, H. Jang and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2009, **131**, 18234; (*c*) H. Jang, A. R. Zhugralin, Y. Lee and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2011, **133**, 7859 For the nonclassical ruthenium hydride pincer complex catalyzed *anti*-Markovnikov addition of HBpin to terminal alkynes, see: (*d*) C. Gunanathan, M. Hölscher, F. Pan and W. Leitner, *J. Am. Chem. Soc.*, 2012, **134**, 14349.

7 For a copper-catalyzed formal carboboration of alkynes, see: (*a*) R. Alfaro, A. Parra, J. Alemán, J. L. G. Ruano and M. Tortosa, *J. Am. Chem. Soc.*, 2012, **134**, 15165; (*b*) H. Yoshida, I. Kageyuki and K. Takaki, *Org. Lett.*, 2013, **15**, 952 For an N-heterocyclic carbene copper-catalyzed boracarboxylation of alkynes with B_2pin_2 and CO_2, see: (*c*) L. Zhang, J. Cheng, B. Carry and Z. Hou, *J. Am. Chem. Soc.*, 2012, **134**, 14314 For a copper-catalyzed di- and triborylation of alkynes, see: (*d*) H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita and K. Takaki, *Angew. Chem., Int. Ed.*, 2012, **51**, 235; (*e*) H.-Y. Jung and J. Yun, *Org. Lett.*, 2012, **14**, 2606.

8 Pioneering B_2pin_2-borylation under stoichiometric Cu^I: (*a*) K. Takahashi, T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2001, **625**, 47 Cu-catalyzed $B_2(pin)_2$-borylation of alkynes that afforded the vinylboronates: (*b*) H. R. Kim, I. G. Jung, K. Yoo, K. Jang, E. S. Lee, J. Yun and S. U. Son, *Chem. Commun.*, 2010, **46**, 758; (*c*) H. R. Kim and J. Yun, *Chem. Commun.*, 2011, **47**, 2943; (*d*) Y. Sasaki, Y. Horita, C. Zhong, M. Sawamura and H. Ito, *Angew. Chem., Int. Ed.*, 2011, **50**, 2778; (*e*) A. Grirrane, A. Corma and H. Garcia, *Chem. – Eur. J.*, 2011, **17**, 2467; (*f*) W. Yuan and S. Ma, *Org. Biomol. Chem.*, 2012, **10**, 7266; (*g*) K. Wen, J. Chen, F. Gao, P. S. Bhadury, E. Fanb and Z. Sun, *Org. Biomol. Chem.*, 2013, **11**, 6350.

9 (*a*) J. E. Lee, J. Kwon and J. Yun, *Chem. Commun.*, 2008, 733; (*b*) H.-Y. Jung, X. Feng, H. Kim and J. Yun, *Tetrahedron*, 2012, **68**, 3444; (*c*) J. Yun, *Asian J. Org. Chem.*, 2013, **2**, 1016.

10 A. L. Moure, R. Gómez-Arrayás, D. J. Cárdenas, I. Alonso and J. C. Carretero, *J. Am. Chem. Soc.*, 2012, **134**, 7219.

11 J. K. Park, B. A. Ondrusek and D. T. McQuade, *Org. Lett.*, 2012, **14**, 4790.

12 G. Zhu, W. Kong, H. Feng and Z. Qian, *J. Org. Chem.*, 2014, **79**, 1786.

13 B. H. Lipshutz, Ž. V. Bošković and D. H. Aue, *Angew. Chem., Int. Ed.*, 2008, **47**, 10183.

14 K. Semba, T. Fujihara, J. Terao and Y. Tsuji, *Chem. – Eur. J.*, 2012, **18**, 4179.

15 For the direct hydroboration of *N*-ethynylamides with catecholborane afforded the labile (*E*)-β-alkenylamide boronates, see: (*a*) R. W. Hoffmann and D. Brückner, *New J. Chem.*, 2001, **25**, 369; (*b*) B. Witulski, N. Buschmann and U. Bergsträßer, *Tetrahedron*, 2000, **56**, 8473.

16 G. He, Q. Zhang, H. Huang, S. Chen, Q. Wang, D. Zhang, R. Zhang and H. Zhu, *Eur. J. Org. Chem.*, 2013, 6979.

17 (*a*) B. Lü, C. Fu and S. Ma, *Chem. – Eur. J.*, 2010, **16**, 6434; (*b*) B. Lü, C. Fu and S. Ma, *Tetrahedron Lett.*, 2010, **51**, 1284.

18 Crystal data for (*Z*)-**2j**: $C_{22}H_{28}BNO_4S$, M = 413.32, orthorhombic, space group *Pbca*, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0680, wR_2 = 0.1238, R indices (all data): R_1 = 0.1949, wR_2 = 0.1719, a = 30.245(6), b = 14.537(3), c = 10.379(2) Å, β = 90.00°, V = 4563.4(16) Å^3, T = 293(2) K, Z = 8, reflections collected/unique: 4154/4114 (R_{int} = 0.0922), number of observations [$I > 2\sigma(I)$]: 1686, parameters: 262. CCDC 944761

contains the supplementary crystallographic data for this paper.

19 For the stereoselective synthesis of substituted alkenamides, see: (*a*) M. Arndt, K. S. M. Salih, A. Fromm, L. J. Goossen, F. Menges and G. Niedner-Schatteburg, *J. Am. Chem. Soc.*, 2011, **133**, 7428, and references cited therein (*b*) L. J. Gooßen, K. S. M. Salih and M. Blanchot, *Angew. Chem., Int. Ed.*, 2008, **47**, 8492; (*c*) H. Tsujita, Y. Ura, S. Matsuki, K. Wada, T. Mitsudo and T. Kondo, *Angew. Chem., Int. Ed.*, 2007, **46**, 5160; (*d*) P. García-Reynaga, A. K. Carrillo and M. S. VanNieuwenhze, *Org. Lett.*, 2012, **14**, 1030; (*e*) N. Panda and R. Mothkuri, *J. Org. Chem.*, 2012, **77**, 9407; (*f*) N. Saito, T. Katayama and N. Sato, *Org. Lett.*, 2008, **10**, 3829; (*g*) J. R. Dehli, J. Legros and C. Bolm, *Chem. Commun.*, 2005, 973; (*h*) Y. Zhang, R. P. Hsung, X. Zhang, J. Huang, B. W. Slafer and A. Davis, *Org. Lett.*, 2005, **7**, 1047; (*i*) T. Ryoichi, H. Shuji, U. Hirokazu and S. Fumie, *Org. Lett.*, 2003, **5**, 67.

20 For the borylcupration of alkenes, see: D. S. Laitar, E. Y. Tsui and J. P. Sadighi, *Organometallics*, 2006, **25**, 2405.

21 (*a*) N. P. Mankad, D. S. Laitar and J. P. Sadighi, *Organometallics*, 2004, **23**, 3369; (*b*) T. Ohishi, M. Nishiura and Z. Hou, *Angew. Chem., Int. Ed.*, 2008, **47**, 5792.

22 For the catalytic carbometalation of alkynamides, see: (*a*) A. Basheer and I. Marek, *Beilstein J. Org. Chem.*, 2010, **6**, 77; (*b*) J. P. Das, H. Chechik and I. Marek, *Nat. Chem.*, 2009, **1**, 128; (*c*) H. Chechik-Lankin, S. Livshin and I. Marek, *Synlett*, 2005, 2098; (*d*) B. Gourdet and H. W. Lam, *J. Am. Chem. Soc.*, 2009, **131**, 3802; (*e*) B. Gourdet, M. E. Rudkin, C. A. Watts and H. W. Lam, *J. Org. Chem.*, 2009, **74**, 7849.

23 The observed regioselectivity presumably depended on the relatively strong electron-donating effect of the nitrogen atom on the amide group.

24 Z. Mu, L. Shu, H. Fuchs, M. Mayor and L. Chi, *J. Am. Chem. Soc.*, 2008, **130**, 10840.

25 M. A. Fox, A. M. Cameron, P. J. Low, M. A. J. Paterson, A. S. Batsanov, A. E. Goeta, D. W. H. Rankin, H. E. Robertson and J. T. Schirlin, *Dalton Trans.*, 2006, 3544.

26 (*a*) B. Yao, Z. Liang, T. Niu and Y. Zhang, *J. Org. Chem.*, 2009, **74**, 4630; (*b*) X. Zhang, Y. Zhang, J. Huang, R. P. Hsung, K. C. M. Kurtz, J. Oppenheimer, M. E. Petersen, I. K. Sagamanova, L. Shen and M. R. Tracey, *J. Org. Chem.*, 2006, **71**, 4170; (*c*) G. Evano, K. Jouvin and A. Coste, *Synthesis*, 2013, 17; (*d*) J. A. Mulder, K. C. M. Kurtz and R. P. Hsung, *Synlett*, 2003, 1379.