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Copper(I)-Catalyzed Highly Regio- and Stereoselective Boron Addition–Protonolysis of Alkynamides to give Alkenamides

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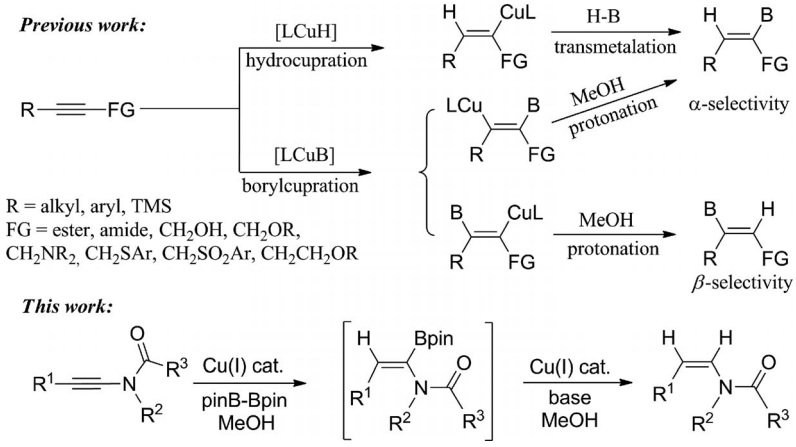
Copper-catalyzed and highly chemoselective reduction of *N*-alkynylamides by a boron addition–protonolysis protocol is presented. The reaction proceeds with the addition of borylcopper complex to *N*-alkynylamides with high regioselectivity and stereoselectivity, followed by regiocontrolled transmetallation of the α-site of the alkenylboronate with MeOCuL to afford *N*-alkenylamides in good yields. Deuterium labeling experiments indicated that both of the alkenyl hydrogen atoms originate from the additive methanol.

Introduction

Organoboron compounds are versatile building blocks in organic chemistry.[1] Among them, vinylboronates are of great significance for their utility as partners in Suzuki–Miyaura reaction[2] and because of their ability to undergo Rh-catalyzed[3] and metal-free[4] conjugate additions. Although several methods for the synthesis of vinylboronates have been developed,[5] hydroboration[6] of alkynes[7] is still a straightforward choice for the purpose, resulting in vinylboronates through *syn*-additions of the boron reagents with regio- and stereoselectivity.[8]

Renewed interest in the area has been spurred on by Cu^I-catalyzed hydroboration of functionalized internal alkynes by using bis(pinacolato)diboron (B_2pin_2) or pinacolborane (HBpin). Recently, Yun,[9] Lipshutz,[10] Hoveyda,[11] Tsuji,[12] Carretero,[13] and, more recently, McQuade[14] have developed related catalytic hydroboration of α,β-unsaturated alkynoates, alkynamides, and propargyl alcohol, amine and derivatives, affording the corresponding alkenyl boronates with α/β-site regioselectivity by matching the substrate, borylating reagent and catalyst (Scheme 1). However, to the best of our knowledge, the Cu-catalyzed borylation of *N*-(1-alkynyl)amides with borylating reagents,



Scheme 1. Cu^I-catalyzed semireduction of alkynamides by the boron addition–protonolysis protocol.

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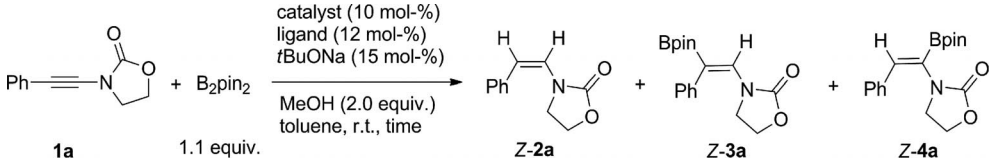
B_2pin_2 and HBpin, has not been explored.[15] Herein, we report the highly stereoselective Cu^I-catalyzed reduction of *N*-(1-alkynyl)amides in the presence of alcohol additive by a boron addition–protonolysis protocol.

Results and Discussion

In initial experiments, the reaction of 3-(2-phenylethynyl)oxazolidin-2-one (**1a**) with bis(pinacolato)diboron catalyzed by CuCl/*t*BuONa in the presence of phosphane ligands was carried out (Table 1). Surprisingly, apart from the β-site regioselective alkenyl boronate [(*Z*)-**3a**],[16] the reaction mainly afforded alkenylamide 3-[(*Z*)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-**2a**] in 71% NMR yield at room temperature employing $P(OEt)_3$ as the ligand (entry 1), that is, the carbon–carbon triple bond in substrate **1a** was stereoselectively reduced to the carbon–carbon double bond, which has seldom been observed in borylation of alkynes.[8c] However, the reactivity and chemoselectivity of the Cu-catalyzed reduction reaction was not satisfactory when choosing Xphos and $P(nBu)_3$ as the ligands (entries 2 and 3). To our delight, the isolated yield of alkenylamide (*Z*)-**2a** was improved to 90% with PPh_3 as ligand, while achieving high chemoselectivity (entry 4). Although cuprous bromide (CuBr) also promoted the reduction, a prolonged reaction time was required (entry 5). The catalytic system with CuI/*t*BuONa did not lead to the expected product, instead, yielding the α/β-borylated alkenylamide mixture with a (*Z*)-**3a**/(*Z*)-**4a** ratio of 80:20 (entry 6). In fact, the chemoselectivity was not further improved by conducting the reaction at 0 °C or by adjusting the amount of MeOH (entries 7–9). It was interesting that the reduction also proceeded smoothly when water was used as the additive instead of MeOH, despite the poor reactivity (entry 10). No reaction took place without a catalyst (entry 11).

It is clear that *N*-alkenylamides play a great part in organic synthesis.[17] Considering alkynamides are easily available from catalytic amidation of alkynyl bromides,[18] an appropriate synthetic tactic to obtain *Z*-enamides through catalytic reduction[18b] of ynamides is urgently needed, although a variety of methods for enamide synthesis have been developed.[19] Therefore, with the optimized conditions in hand (Table 1, entry 4), we investigated the scope and limitations of the Cu-catalyzed reduction (Table 2). Notably, both *N*-alkynylated oxazolidinones and pyrrolidin-2-ones underwent stereoselective reduction in good yields (entries 1–18). For *N*-arylalkynyl-substituted oxazolidinones, the functional groups on the arene, either electron-donating or electron-withdrawing, had no clear effect on the reactions, and good yields were obtained (entries 2–5). It is noteworthy that the trimethylsilyl-substituted ynamide **1f** was tolerant of the reduction conditions (entry 6), and oxazolidinones bearing different substituents, including phenyl and benzyl groups, also participated in the reaction, with the desired *N*-alkenylamides being isolated in 68–88% yield (entries 7–16). As mentioned above, *N*-alkynyl-3-acetylindoles could also be transformed into the corresponding alkenylamines in good yields (entries 19 and 20). The stereochemistry of the Cu-catalyzed reduction was further confirmed by an X-ray diffraction study of (*Z*)-**2m** (Figure 1).[20] Additionally, it was observed that when the alkyl alkynyl-substituted oxazolidinones were subjected to the reduction protocol, the reaction did not afford the expected alkenylamides but, instead, gave a mixture of α/β alkenylamide boronates. The reaction of vinyl alkynyl-substituted substrate 3-[(3*E*)-4-phenyl-3-buten-1-yn-1-yl]oxazolidin-2-one (**1u**) with B_2pin_2 gave an unidentified mixture, probably owing to its multiple reactive sites. Thus, the existence of an aryl group on the alkynes in the starting material is necessary.

Table 1. Screening reaction conditions of Cu^I-catalyzed reduction of 3-(2-phenylethynyl)oxazolidin-2-one (**1a**).[a]

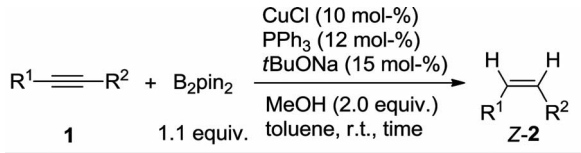


1a *Z*-**2a** *Z*-**3a** *Z*-**4a**

Entry	Cat.	Ligand	*t* [h]	NMR yield of (*Z*)-**2a** [%][b]	Ratio of (*Z*)-**2a**/(*Z*)-**3a**/(*Z*)-**4a**[c]
1	CuCl	$P(OEt)_3$	1.6	71	79:21:0
2	CuCl	Xphos	1.0	33	53:47:0
3	CuCl	$P(nBu)_3$	15	82	91:9:0
4	CuCl	PPh_3	2.5	91 (90)[d]	95:5:0
5	CuBr	PPh_3	23	81	89:11:0
6[e]	CuI	PPh_3	22	0	0:80:20
7[f]	CuCl	PPh_3	13	55	58.5:8.5:33
8[g]	CuCl	PPh_3	3.0	23	30:0:70
9[h]	CuCl	PPh_3	1.5	80	92:8:0
10[i]	CuCl	PPh_3	36	71	91:9:0
11[j]	–	PPh_3	46	0	0:0:0

[a] Reaction conditions: **1a** (0.3 mmol), B_2pin_2 (0.33 mmol), catalyst (0.03 mmol), ligand (0.036 mmol), base (0.045 mmol), methanol (0.6 mmol), toluene (1 mL), N_2, room temp. [b] NMR yield based on **1a** with mesitylene as the internal standard. [c] Determined by ^1H NMR analysis of the crude product. [d] Isolated yield. [e] Compound **1a** (56.5%) was recovered. [f] The reaction was conducted at 0 °C. [g] MeOH (1.0 equiv.) was used. [h] MeOH (4.0 equiv.) was used. [i] H_2O (2 equiv.) was used as the additive. [j] Compound **1a** (89%) was recovered.

Table 2. Scope of the copper-catalyzed semireduction of alkynamides **1** with B_2pin_2 through the boron addition–protonolysis protocol.[a]



Entry	R^1	R^2	t [h]	Isolated yield of Z-**2** [%]
1	Ph (**1a**)		2.5	90 (Z-**2a**)
2	*p*-MePh (**1b**)		3.0	78 (Z-**2b**)
3	*p*-MeOPh (**1c**)		3.5	77 (Z-**2c**)
4	*p*-AcPh (**1d**)		3.0	72 (Z-**2d**)
5	*p*-NO_2Ph (**1e**)		3.0	74 (Z-**2e**)
6	TMS (**1f**)		36	62 (Z-**2f**)
7	Ph (**1g**)		31	79 (Z-**2g**)
8	*p*-MePh (**1h**)		21	81 (Z-**2h**)
9	*p*-MeOPh (**1i**)		24	68 (Z-**2i**)
10	*p*-AcPh (**1j**)		24	80 (Z-**2j**)
11	*p*-NO_2Ph (**1k**)		4.0	76 (Z-**2k**)
12	Ph (**1l**)		6.0	88 (Z-**2l**)
13	*p*-MePh (**1m**)		6.0	83 (Z-**2m**)
14	*p*-MeOPh (**1n**)		9.0	85 (Z-**2n**)
15	*p*-AcPh (**1o**)		5.0	78 (Z-**2o**)
16	*p*-NO_2Ph (**1p**)		3.0	83 (Z-**2p**)
17	*p*-MePh (**1q**)		6.0	80 (Z-**2q**)
18	*p*-MeOPh (**1r**)		10	83 (Z-**2r**)
19	Ph (**1s**)		27	74 (Z-**2s**)
20	*p*-MePh (**1t**)		24	80 (Z-**2t**)

[a] Reaction conditions: **1** (0.3 mmol), B_2pin_2 (0.33 mmol), CuCl (0.03 mmol), PPh_3 (0.036 mmol), *t*BuONa (0.045 mmol), methanol (0.6 mmol), toluene (1 mL), N_2, room temp.

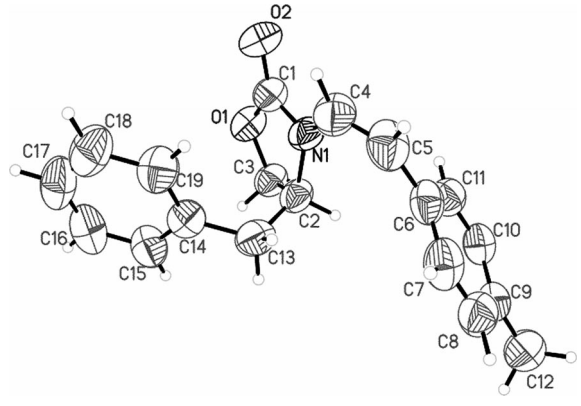
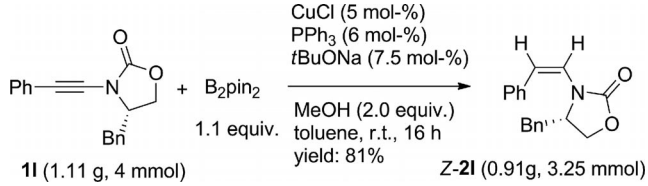


Figure 1. ORTEP drawing of the X-ray structure of (Z)-**2m** with 30% thermal ellipsoids.

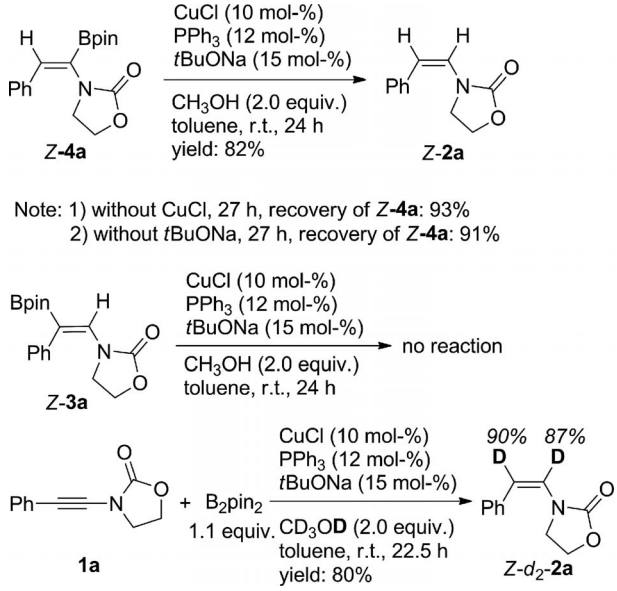
Although the Cu-catalyzed reduction reaction was routinely conducted on a 0.3 mmol scale, we confirmed that the process is amenable to 10-fold scale-up without loss of chemical efficiency; this was demonstrated in the case of product (Z)-**2l** (3.25 mmol, 81%). In addition, we found that the Cu^I catalyst loading could be reduced to 5 mol-% with comparable efficiency (Scheme 2).



Scheme 2. Scale-up experiment.

Initial investigation of reaction conditions showed that the reaction of ynamide **1a** with B_2pin_2 produced not only the regiocontrolled β-alkenylboronate (Z)-**3a** but also the α-regioisomer (Z)-**4a** in 33% NMR yield at lower temperature (Table 1, entry 7), which led us to suspect that ether of them was probably the essential intermediate leading to the final product (Z)-**2a**. Additionally, we observed that the reaction of ynamide **1a** with B_2pin_2 afforded reduced alkenylamide (Z)-**2a** in 23% NMR yield with a (Z)-**2a**/(Z)-**4a** ratio of 30:70 when MeOH (1.0 equiv.) was added (Table 1, entry 8).

To gain insight into the mechanism of the reaction, we carried out the reaction of (Z)-**4a** with MeOH under the standard conditions, which, as expected, afforded the reduced product (Z)-**2a** in 82% isolated yield. In fact, the reaction does not work at all in the absence of either CuCl or *t*BuONa. Control experiments also showed that, under the same standard conditions, (Z)-**3a** is not transformed into the reduced product (Z)-**2a**. Furthermore, a deuterium labeling experiment with **1a** in the presence of CD_3OD indicated that the resulting deuterated product (Z)-d_2-**2a**, bearing D at the original alkenyl copper and boronate positions, was obtained in 80% yield with deuterium content of 90 and 87%, respectively (Scheme 3). To gain further understanding, the Cu-catalyzed reaction of ynamide (Z)-**1n** and B_2pin_2 in toulene-d_8 was conducted and monitored by ^{11}B



Scheme 3. Deuterium labeling experiments with **1a** in the presence of CD_3OD.

NMR spectroscopic analysis at 0.5, 3.5, 8.0, 16, and 24 h (Figure 2).[21] The ^{11}B NMR spectroscopic investigation of the reaction mixture indicated that the enamide boronate intermediate (*Z*)-**4n** indeed displayed the chemical shift at δ = 31.2 ppm at the initial stage of the reaction. As the reaction proceeded, the signal for the species (*Z*)-**4n** in the ^{11}B NMR spectrum became gradually weaker until it eventually disappeared.

On the basis of the above observations, a plausible mechanism for the boron addition-protonlysis process promoted by MeOH is proposed in Scheme 4. A ligated copper-boryl complex, generated from *t*BuOCuL and B_2pin_2 in the presence of base,[22] adds to *N*-alkynylamide **1** in a *syn*-fashion with the boronate moiety adding at the α-carbon to the amide group, which provides the first (α-boryl)(alkenyl)-copper intermediate **A** with high regioselectivity, probably

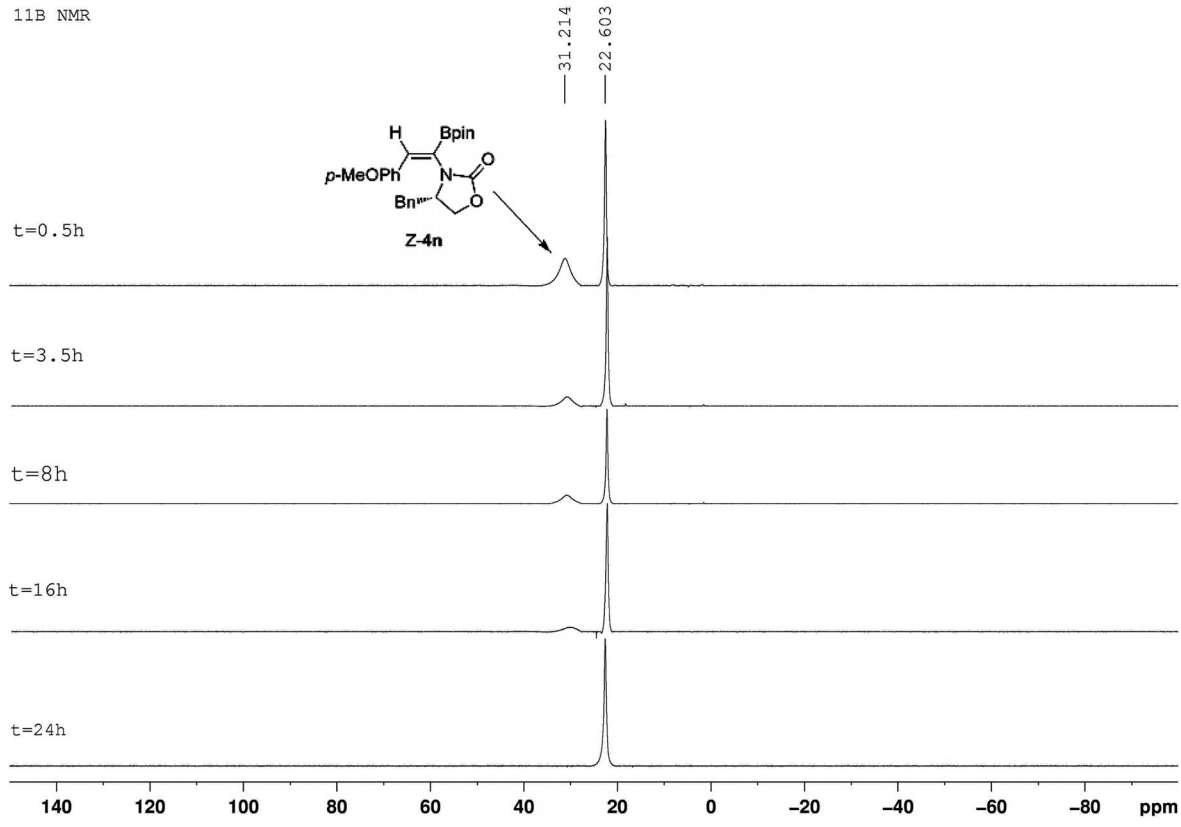
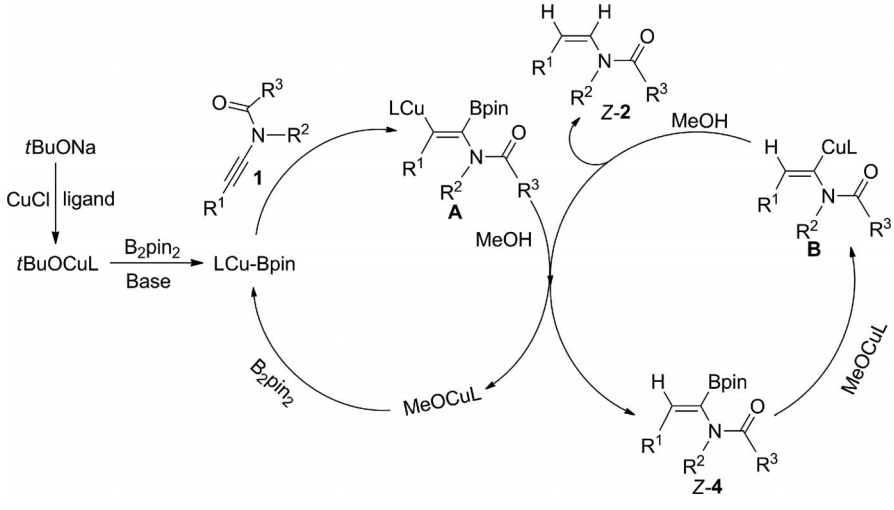


Figure 2. Monitoring Cu^I-catalyzed reduction of ynamide **1n** by ^{11}B NMR spectroscopic analysis at room temp.; chemical shifts determined by using $BF_3{\cdot}OEt_2$ as the external reference.



Scheme 4. Proposed catalytic cycle of Cu^I-catalyzed reduction of alkynamides.

owing to the strong electron-donating effect of the nitrogen atom.[23] Protonolysis of the carbon–copper bond provides the regiocontrolled α-alkenylboronate. Subsequent transmetallation reaction between (*Z*)-**4** and MeOCuL would yield the second alkenyl copper intermediate **B**.[22b,24] Finally, protonation of **B** with MeOH would afford the reduced product (*Z*)-**2** and regenerate the active species MeOCuL (Scheme 4).

Conclusions

We have developed an efficient catalytic reduction of *N*-alkynylamides by application of a boron addition-protonlysis protocol, which affords *N*-alkenylamides in good yields with high stereo- and chemoselectivity. Deuterium labeling experiments indicate that both of the alkenyl hydrogen atoms originate from the additive methanol. Further studies on the factors that control the regioselectivity of the boryl–copper complex addition to *N*-alkynylamides and application of the present catalytic system to other functionalized alkynes are underway in our laboratory.

Experimental Section

General Methods: All the reactions were carried out in anhydrous solvents and under inert atmosphere. Melting points were recorded in open-ended capillary tubes. NMR chemical shifts are reported relative to tetramethylsilane for ^{1}H and ^{13}C nuclei, and $BF_3{\cdot}OEt_2$ for ^{11}B as the external reference. ^{1}H NMR spectroscopic 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 determined at an ionizing voltage of 70 eV. HRMS were performed with 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 by using silica gel. Characterization data for those compounds not described in the literature is provided.

Copper(I) chloride, sodium *tert*-butoxide, B_2pin_2, triphenylphosphane, phenylacetylene, *p*-methylphenylacetylene, *p*-methoxylphenylacetylene, *p*-acetylphenylacetylene, *p*-nitrophenylacetylene, 1-phenylhexyne, trimethylsilylacetylene, oxazolidin-2-one, (*S*)-4-phenyloxazolidin-2-one, (*S*)-4-benzyloxazolidin-2-one, pyrrolidin-2-one, and 3-acetylindole were purchased from commercial sources and used as received.

Alkynyl bromides,[25] 2-bromotrimethylsilylethyne,[26] old compounds **1a**–**c**, **1f**–**i**, **1l**, **1n**, **1r**–**s** and new compounds **1d**–**e**, **1j**–**k**, **1m**, **1o**–**q** and **1t** were prepared according to the reported procedure.[18] Unless otherwise noted, commercially available reagents were used without purification. Toluene was freshly distilled from sodium/benzophenone ketyl.

Synthesis of Starting Materials

Synthesis of Ynamides; Typical Procedure I

3-[2-(4-Acetylphenyl)ethynyl]oxazolidin-2-one (1d): To a mixture of oxazolidin-2-one (173.3 mg, 2 mmol), K_2CO_3 (541.6 mg, 4 mmol), $CuSO_45H_2O$ (50.4 mg, 0.2 mmol), and 1,10-phenanthroline (71.6 mg, 0.4 mmol) in a reaction vial was added a solution of 1-[4-(2-bromoethynyl)phenyl]ethanone (445.8 mg, 2 mmol) in toluene (3.0 mL). The reaction mixture was capped and heated in an oil bath at 90 °C for 24 h and the reaction was monitored by TLC analysis. Upon completion, the reaction mixture was cooled to room temp., diluted with EtOAc, filtered through Celite, and the filtrate was concentrated in vacuo. The crude products were purified by flash chromatography on a silica gel column [petroleum ether (PE)/ethyl acetate (EtOAc)] to afford **1d** (185 mg, 40%) as a white solid, m.p. 156–157 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.87 (m, 2 H), 7.58–7.47 (m, 2 H), 4.53 (dd, *J* = 8.7, 7.2 Hz, 2 H), 4.05 (dd, *J* = 8.7, 7.2 Hz, 2 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 155.6, 136.0, 131.3, 128.2, 127.3, 82.2, 71.1, 63.1, 46.9, 26.6 ppm. MS (ESI): *m*/*z* (%) = 252 (37.83) [M^+ + Na], 481 (100) [$2M^+$ + Na]. IR (KBr): $\tilde{\nu}$ = 2966, 2912, 2265, 1758, 1681, 1470, 1427, 1403, 1269, 1220, 1163, 1023 cm^{-1}. $C_{13}H_{11}NO_3$ (229.23): calcd. C 68.11, H 4.84, N 6.11; found C 68.13, H 5.19, N 5.71.

3-[2-(4-Nitrophenyl)ethynyl]oxazolidin-2-one (1e): Prepared according to Typical Procedure I. The reaction of $CuSO_4{\cdot}5H_2O$ (50.1 mg, 0.2 mmol), 1,10-phenanthroline (71.6 mg, 0.4 mmol), K_2CO_3 (553.0 mg, 4.0 mmol), oxazolidin-2-one (174.8 mg, 2.0 mmol), and 1-(2-bromoethynyl)-4-nitrobenzene (484.2 mg, 2.2 mmol) in toluene (2.0 mL) at 80 °C for 17 h, afforded **1e** (278.0 mg, 60%) as a yellow solid, m.p. 153–154 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22–8.14 (m, 2 H), 7.59–7.51 (m, 2 H), 4.55 (t, *J* = 7.9 Hz, 2 H), 4.07 (t, *J* = 7.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 146.6, 131.4, 129.5, 123.6, 84.3, 70.5, 63.3, 46.8 ppm. MS (ESI): *m*/*z* (%) = 232 (100) [M^+], 487 (29.20) [$2M^+$ + Na]. IR (KBr): $\tilde{\nu}$ = 3107, 2972, 2914, 2255, 1765, 1510, 1416, 1341, 1198, 1165, 1106, 852 cm^{-1}. $C_{11}H_8N_2O_4$ (232.20): calcd. C 56.90, H 3.47, N 12.06; found C 56.74, H 3.42, N 12.14.

(*S*)-4-Phenyl-3-[2-(4-acetylphenyl)ethynyl]oxazolidin-2-one (1j): Prepared according to Typical Procedure I. The reaction of $CuSO_4{\cdot}5H_2O$ (49.2 mg, 0.2 mmol), 1,10-phenanthroline (71.6 mg, 0.4 mmol), K_2CO_3 (558.3 mg, 4 mmol), (*S*)-4-phenyloxazolidin-2-one (322.7 mg, 2 mmol), and 1-[4-(2-bromoethynyl)phenyl]ethanone (448.0 mg, 2 mmol) in toluene (3.0 mL) at 90 °C for 24 h, afforded **1j** (310.4 mg, 51%) as a white solid, m.p. 126–127 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = +202.3 (*c* = 1.03, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 2 H), 7.52–7.38 (m, 5 H), 7.37–7.27 (m, 2 H), 5.18 (dd, *J* = 8.8, 7.3 Hz, 1 H), 4.82 (t, *J* = 8.8 Hz, 1 H), 4.05 (dd, *J* = 8.8, 7.3 Hz, 1 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 155.2, 135.8, 135.7, 131.0, 129.7, 129.4, 128.1, 127.2, 126.9, 81.4, 70.8, 62.1, 26.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 305 (100) [M^+], 306 (19.88) [M^+ + 1]. IR (KBr): $\tilde{\nu}$ = 2926, 2253, 1772, 1685, 1600, 1404, 1360, 1261, 1190, 1129, 1087 cm^{-1}. $C_{19}H_{15}NO_3$ (305.33): calcd. C 74.74, H 4.95, N 4.59; found C 74.62, H 5.03, N 4.24.

(*S*)-3-[2-(4-Nitrophenyl)ethynyl]-4-phenyloxazolidin-2-one (1k): Prepared according to Typical Procedure I. The reaction of $CuSO_4{\cdot}5H_2O$ (49.6 mg, 0.2 mmol), 1,10-phenanthroline (72.1 mg, 0.4 mmol), K_2CO_3 (552.9 mg, 4.0 mmol), (*S*)-4-phenyloxazolidin-2-one (327.0 mg, 2.0 mmol), and 1-(2-bromoethynyl)-4-nitrobenzene (483.7 mg, 2.2 mmol) in toluene (2.0 mL) at 80 °C for 18 h, afforded **1k** (179.7 mg, 29%) as a yellow solid, m.p. 162–163 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = +205.8 (*c* = 1.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.05 (m, 2 H), 7.53–7.39 (m, 5 H), 7.38–7.30 (m, 2 H), 5.20 (dd, *J* = 8.7, 7.4 Hz, 1 H), 4.84 (t, *J* = 8.8 Hz, 1 H), 4.13 (dd, *J* = 8.7, 7.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 146.6, 135.5, 131.3, 129.8, 129.5, 129.4, 126.9, 123.5, 83.4, 72.2, 70.9, 62.1 ppm. MS (ESI): *m*/*z* (%) = 331 (100) [M^+ + Na]. IR (KBr): $\tilde{\nu}$ = 3009, 2247, 1767, 1594,

1516, 1415, 1342, 1191, 1107, 1032, 970, 854 cm^{-1}. $C_{17}H_{12}N_2O_4$ (308.29): calcd. C 66.23, H 3.92, N 9.09; found C 66.07, H 3.73, N 8.74.

(*S*)-4-Benzyl-3-[2-(4-methylphenyl)ethynyl]oxazolidin-2-one (1m): Prepared according to Typical Procedure I. The reaction of $CuSO_4·5H_2O$ (51.0 mg, 0.2 mmol), 1,10-phenanthroline (70.8 mg, 0.4 mmol), K_2CO_3 (553.8 mg, 4 mmol), (*S*)-4-benzyloxazolidin-2-one (351.5 mg, 2 mmol) and 1-(2-bromoethynyl)-4-methylbenzene (385.3 mg, 2 mmol) in toluene (3.0 mL) at 90 °C for 24 h, afforded **1m** (468.1 mg, 81%) as a white solid, m.p. 88–89 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = +225.8 (*c* = 1.01, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 4 H), 7.32–7.27 (m, 1 H), 7.27–7.22 (m, 2 H), 7.16–7.11 (m, 2 H), 4.45–4.31 (m, 2 H), 4.22–4.12 (m, 1 H), 3.35–3.25 (m, 1 H), 3.07–2.96 (m, 1 H), 2.36 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 138.5, 134.2, 131.7, 129.4, 129.1, 129.0, 127.5, 119.0, 73.3, 67.4, 58.5, 38.0, 21.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 291 (93.71) [M^+], 292 (19.15) [M^+ + 1], 156 (100). IR (KBr): $\tilde{\nu}$ = 3060, 2917, 2256, 1755, 1485, 1418, 1216, 1195, 1149, 1093, 1005 cm^{-1}. $C_{19}H_{17}NO_2$ (291.35): calcd. C 78.33, H 5.88, N 4.81; found C 77.96, H 6.08, N 4.54.

(*S*)-4-Benzyl-3-[2-(4-acetylphenyl)ethynyl]oxazolidin-2-one (1o): Prepared according to Typical Procedure I. The reaction of $CuSO_4·5H_2O$ (51.9 mg, 0.2 mmol), 1,10-phenanthroline (73.8 mg, 0.4 mmol), K_2CO_3 (553.8 mg, 4 mmol), (*S*)-4-benzyloxazolidin-2-one (351.5 mg, 2 mmol), and 1-[4-(2-bromoethynyl)phenyl]ethanone (440.3 mg, 2 mmol) in toluene (3.0 mL) at 90 °C for 24 h, afforded **1o** (394.8 mg, 62%) as a white solid, m.p. 124–125 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = +198.2 (*c* = 1.02, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.87 (m, 2 H), 7.57–7.47 (m, 2 H), 7.40–7.34 (m, 2 H), 7.34–7.28 (m, 1 H), 7.28–7.23 (m, 2 H), 4.46–4.36 (m, 2 H), 4.25–4.16 (m, 1 H), 3.34–3.26 (m, 1 H), 3.08–2.99 (m, 1 H), 2.61 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 155.2, 136.0, 134.0, 131.2, 129.4, 129.1, 128.2, 127.7, 127.3, 81.3, 73.1, 67.6, 58.4, 38.3, 26.6 ppm. MS (ESI): *m*/*z* (%) = 320 (20.42) [M^+ + 1], 342 (21.69) [M^+ + Na], 661 (100) [$2M^+$ + Na]. IR (KBr): $\tilde{\nu}$ = 3000, 2917, 2251, 1755, 1678, 1599, 1420, 1359, 1262, 1209, 1186, 1147, 1095, 1066, 994 cm^{-1}. $C_{20}H_{17}NO_3$ (319.36): calcd. C 75.22, H 5.37, N 4.39; found C 75.52, H 5.30, N 4.39.

(*S*)-4-Benzyl-3-[2-(4-nitrophenyl)ethynyl]oxazolidin-2-one (1p): Prepared according to Typical Procedure I. The reaction of $CuSO_4·5H_2O$ (50.4 mg, 0.2 mmol), 1,10-phenanthroline (71.5 mg, 0.4 mmol), K_2CO_3 (551.5 mg, 4.0 mmol), (*S*)-4-benzyloxazolidin-2-one (354.3 mg, 2.0 mmol), and 1-(2-bromoethynyl)-4-nitrobenzene (484.5 mg, 2.2 mmol) in toluene (2.0 mL) at 80 °C for 18 h, afforded **1p** (305.2 mg, 47%) as a yellow solid, m.p. 145–146 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = +192.3 (*c* = 1.03, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.15 (m, 2 H), 7.54–7.48 (m, 2 H), 7.40–7.34 (m, 2 H), 7.34–7.29 (m, 1 H), 7.29–7.23 (m, 2 H), 4.50–4.39 (m, 2 H), 4.28–4.17 (m, 1 H), 3.34–3.24 (m, 1 H), 3.12–2.99 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 146.6, 133.9, 131.4, 129.4, 129.3, 129.1, 127.7, 123.6, 83.5, 72.6, 67.8, 58.4, 38.4 ppm. MS (ESI): *m*/*z* (%) = 345 (100) [M^+ + Na]. IR (KBr): $\tilde{\nu}$ = 3027, 2990, 2925, 2250, 1773, 1594, 1510, 1416, 1340, 1200, 1103, 1002, 855 cm^{-1}. $C_{18}H_{14}N_2O_4$ (322.32): calcd. C 67.07, H 4.38, N 8.69; found C 66.90, H 4.16, N 8.76.

1-[1-(2-(4-Methylphenyl)ethynyl)-1*H*-indol-3-yl]ethanone (1t): Prepared according to Typical Procedure I. The reaction of $CuSO_4·5H_2O$ (50.3 mg, 0.2 mmol), 1,10-phenanthroline (72.8 mg, 0.4 mmol), K_2CO_3 (551.2 mg, 4.0 mmol), 3-acetylindole (318.1 mg, 2.0 mmol), and 1-(2-bromoethynyl)-4-methylbenzene (430.5 mg, 2.2 mmol) in toluene (2.0 mL) at 80 °C for 27 h, afforded **1t** (270.0 mg, 50%) as a yellow solid, m.p. 132–133 °C (*n*-hexane/EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.44–8.32 (m, 1 H), 7.96 (s, 1 H), 7.67–7.58 (m, 1 H), 7.54–7.44 (m, 2 H), 7.44–7.33 (m, 2 H), 7.24–7.15 (m, 2 H), 2.55 (s, 3 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 139.1, 138.5, 135.2, 131.6, 129.3, 125.0, 124.9, 124.2, 122.9, 119.7, 118.3, 111.3, 27.7, 21.5 ppm. MS (ESI): *m*/*z* (%) = 274 (69.27) [M^+ + 1], 296 (100) [M^+ + Na]. IR (KBr): $\tilde{\nu}$ = 3120, 2003, 2913, 2852, 2256, 1659, 1610, 1536, 1458, 1378, 1299, 1188, 1143, 1005, 936 cm^{-1}. $C_{19}H_{15}NO$ (273.33): calcd. C 83.49, H 5.53, N 5.12; found C 83.39, H 5.47, N 5.01.

1-[2-(4-Methylphenyl)ethynyl]pyrrolidin-2-one (1q): 1-(2-Bromoethynyl)-4-methylbenzene (650.0 mg, 3.3 mmol) and *N*,*N*′-dimethylethane-1,2-diamine (DMEDA) (65 µL, 0.6 mmol) were added to a stirred solution of pyrrolidin-2-one (260.0 mg, 3.0 mmol), K_2CO_3 (830.0 mg, 6.0 mmol), anhydrous $FeCl_3$ (49.8 mg, 0.3 mmol), and toluene (3 mL) under N_2 and the resulting mixture was stirred at 80 °C for 4 h. The suspension was filtered and the residue was washed with diethyl ether (3 × 15 mL). The crude products were purified by flash chromatography on a silica gel column (PE/EtOAc) to afford **1q** (200.0 mg, 28%) as a white solid, m.p. 120–121 °C (*n*-hexane/Et_2O). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 1 H), 7.12–7.08 (m, 1 H), 3.77 (t, *J* = 7.1 Hz, 2 H), 2.48 (t, *J* = 8.1 Hz, 2 H), 2.34 (s, 3 H), 2.21–2.11 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 138.0, 131.5, 128.9, 119.4, 79.6, 72.6, 50.1, 29.7, 21.4, 18.8 ppm. MS (ESI): *m*/*z* (%) = 222 (90.70) [M^+ + Na], 421 (100) [$2M^+$ + Na]. IR (KBr): $\tilde{\nu}$ = 2998, 2958, 2892, 2244, 1718, 1403, 1231, 1148, 814 cm^{-1}. $C_{13}H_{13}NO$ (199.25): calcd. C 78.36, H 6.58, N 7.03; found C 78.34, H 6.80, N 6.95.

Cu^I-Catalyzed Reduction of Alkynamides with Bis(pinacolato)diboron; Typical Procedure II

3-[(*Z*)-2-Phenylethenyl]oxazolidin-2-one [(*Z*)-2a]: An oven-dried Schlenk tube was charged with CuCl (3.1 mg, 0.03 mmol), *t*BuONa (4.4 mg, 0.045 mmol), B_2pin_2 (83.9 mg, 0.33 mmol), PPh_3 (9.4 mg, 0.036 mmol), and **1a** (56.1 mg, 0.3 mmol) and the apparatus was purged and backfilled with nitrogen (three times). To this mixture were added toluene (1.0 mL) and MeOH (24 µL, 0.6 mmol), and the resulting solution was stirred at room temp. until no starting material was detected by TLC analysis. The reaction was quenched by the addition of satd. aq. NH_4Cl (5.0 mL) and extracted with Et_2O (3 × 20 mL) and the combined organic extracts were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (PE/EtOAc, 5:1) afforded (*Z*)-**2a** (51.0 mg, 90%) as a colorless liquid.[27] ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.19 (m, 5 H), 6.66 (d, *J* = 9.8 Hz, 1 H), 6.00 (d, *J* = 9.8 Hz, 1 H), 4.27 (t, *J* = 8.0 Hz, 2 H), 3.37 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 135.5, 129.2, 127.9, 127.0, 124.1, 112.7, 62.6, 44.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 189 (89.86) [M^+], 190 (11.52) [M^+ + 1], 130 (100). IR (KBr): $\tilde{\nu}$ = 2987, 2910, 1759, 1651, 1483, 1411, 1240, 1074 cm^{-1}.

3-[(*Z*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-3a] and 3-[(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-4a]: An oven-dried Schlenk tube was charged with CuI (6.0 mg, 0.03 mmol), *t*BuONa (4.3 mg, 0.045 mmol), B_2pin_2 (83.3 mg, 0.33 mmol), PPh_3 (9.6 mg, 0.036 mmol), and **1a** (56.2 mg, 0.3 mmol) and the apparatus was purged and backfilled with nitrogen (three times). To this mixture were added toluene (1.0 mL) and MeOH (24 µL, 0.6 mmol), and the resulting solution was stirred for 22 h at room temp. The reaction was quenched by the addition of satd. aq. NH_4Cl (5.0 mL) and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Filtration, evaporation, and

chromatography on silica gel (PE/EtOAc, 10:1→3:1) afforded (*Z*)-**3a** (24.4 mg, 26%), **1a** (29.7 mg, recovery: 53%), and (*Z*)-**4a** (7.0 mg, 7%), respectively.

Compound (*Z*)-3a: White solid; m.p. 179–180 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 1 H), 7.32–7.25 (m, 2 H), 7.25–7.19 (m, 1 H), 7.16–7.11 (m, 2 H), 4.15 (t, J = 8.0 Hz, 2 H), 3.13 (t, J = 8.0 Hz, 2 H), 1.25 (s, 12 H) ppm; The carbon directly attached to the boron atom was not detected by ^{13}C NMR technique due to quadrupolar relaxation. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 138.1, 134.7, 129.8, 127.6, 126.4, 83.6, 62.6, 44.6, 24.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 315 (8.44) [M$^+$], 316 (3.63) [M$^+$ + 1], 256 (100). IR (KBr): $\tilde{\nu}$ = 2972, 2928, 1758, 1628, 1481, 1373, 1329, 1298, 1226, 1144, 1044, 978, 860 cm^{-1}. $C_{17}H_{22}BNO_4$ (315.18): calcd. C 64.78, H 7.04, N 4.44; found C 64.72, H 7.43, N 4.34.

Compound (*Z*)-4a: White solid; m.p. 120–121 °C (*n*-hexane/EtOAc). ^{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) ppm; The carbon directly attached to the boron atom was not detected by ^{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 ppm. MS (EI, 70 eV): *m*/*z* (%) = 315 (30.01) [M$^+$], 316(4.53) [M$^+$ + 1], 257 (100). IR (KBr): $\tilde{\nu}$ = 2984, 2923, 1744, 1628, 1486, 1421, 1328, 1267, 1222, 1144, 1083, 1033, 991 cm^{-1}. $C_{17}H_{22}BNO_4$ (315.18): calcd. C 64.78, H 7.04, N 4.44; found C 64.83, H 6.81, N 4.29.

3-[(*Z*)-2-(4-Methylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2b]: Prepared according to Typical Procedure II. The reaction of CuCl (3.2 mg, 0.03 mmol), PPh_3 (9.3 mg, 0.036 mmol), *t*BuONa (4.3 mg, 0.045 mmol), **1b** (60.5 mg, 0.3 mmol), B_2pin_2 (83.9 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 3 h, afforded (*Z*)-**2b** (49.0 mg, 78%) as a white solid, m.p. 88–89 °C (*n*-hexane/Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.08 (m, 4 H), 6.62 (d, J = 9.7 Hz, 1 H), 5.96 (d, J = 9.7 Hz, 1 H), 4.27 (t, J = 8.0 Hz, 2 H), 3.39 (t, J = 8.0 Hz, 2 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 136.9, 132.4, 129.1, 128.6, 123.8, 113.0, 62.6, 44.9, 21.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 203 (67.23) [M$^+$], 204 (9.67) [M$^+$ + 1], 144 (100). IR (KBr): $\tilde{\nu}$ = 2990, 2914, 1747, 1646, 1475, 1423, 1252 cm^{-1}. $C_{12}H_{13}NO_2$ (203.24): calcd. C 70.92, H 6.45, N 6.89; found C 70.55, H 6.63, N 6.59.

3-[(*Z*)-2-(4-Methoxylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2c]: Prepared according to Typical Procedure II. The reaction of CuCl (3.1 mg, 0.03 mmol), PPh_3 (10.0 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1c** (64.5 mg, 0.3 mmol), B_2pin_2 (83.6 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 3.5 h, afforded (*Z*)-**2c** (50.1 mg, 77%) as a white solid, m.p. 90–91 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.11 (m, 2 H), 6.90–6.82 (m, 2 H), 6.59 (d, J = 9.6 Hz, 1 H), 5.95 (d, J = 9.6 Hz, 1 H), 4.28 (t, J = 8.0 Hz, 2 H), 3.82 (s, 3 H), 3.40 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 157.3, 130.3, 127.6, 123.5, 113.3, 113.1, 62.6, 55.2, 44.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 219 (100) [M$^+$], 220 (15.15) [M$^+$ + 1]. IR (KBr): $\tilde{\nu}$ = 2968, 2914, 1746, 1652, 1606, 1510, 1422, 1329, 1296, 1249, 1177, 1081, 1040, 882 cm^{-1}. $C_{12}H_{13}NO_3$ (219.24): calcd. C 65.74, H 5.98, N 6.39; found C 65.78, H 5.80, N 6.22.

3-[(*Z*)-2-(4-Acetylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2d]: Prepared according to Typical Procedure II. The reaction of CuCl (3.0 mg, 0.03 mmol), PPh_3 (9.7 mg, 0.036 mmol), *t*BuONa (4.5 mg, 0.045 mmol), **1d** (69.2 mg, 0.3 mmol), B_2pin_2 (84.8 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 3.0 h, afforded (*Z*)-**2d** (50.6 mg, 72%) as a white solid, m.p. 89–90 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.90 (m, 2 H), 7.35–7.29 (m, 2 H), 6.76 (d, J = 9.8 Hz, 1 H), 5.99 (d, J = 9.8 Hz, 1 H), 4.31 (t, J = 8.0 Hz, 2 H), 3.38 (t, J = 8.0 Hz, 2 H), 2.61 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 157.0, 140.6, 135.6, 129.4, 127.9, 125.6, 111.3, 62.6, 45.0, 26.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 231 (26.87) [M$^+$], 232 (14.96) [M$^+$ + 1], 28 (100). IR (KBr): $\tilde{\nu}$ = 2974, 2915, 1772, 1653, 1404, 1338, 1233, 1073, 1043, 839, 758 cm^{-1}. $C_{13}H_{13}NO_3$ (231.25): calcd. C 67.52, H 5.67, N 6.06; found C 67.31, H 5.67, N 5.82.

3-[(*Z*)-2-(4-Nitrophenyl)ethenyl]oxazolidin-2-one [(*Z*)-2e]: Prepared according to Typical Procedure II. The reaction of CuCl (3.2 mg, 0.03 mmol), PPh_3 (9.8 mg, 0.036 mmol), *t*BuONa (4.4 mg, 0.045 mmol), **1e** (70.0 mg, 0.3 mmol), B_2pin_2 (83.4 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 4 h, afforded (*Z*)-**2e** (52.5 mg, 74%) as a yellow solid.[27c,28] M.p. 158–159 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.16 (m, 2 H), 7.43–7.34 (m, 2 H), 6.83 (d, J = 9.8 Hz, 1 H), 5.99 (d, J = 9.8 Hz, 1 H), 4.35 (t, J = 8.0 Hz, 2 H), 3.39 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 146.5, 142.6, 129.9, 126.8, 123.2, 110.0, 62.7, 45.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 234 (92.45) [M$^+$], 129 (100). IR (KBr): $\tilde{\nu}$ = 3110, 3070, 2983, 2919, 1745, 1647, 1591, 1511, 1420, 1337, 1254, 1218, 1105, 1081, 1037, 944, 891 cm^{-1}.

3-[(*Z*)-2-Trimethylsilyethenyl]oxazolidin-2-one [(*Z*)-2f]: Prepared according to Typical Procedure II. The reaction of CuCl (2.9 mg, 0.029 mmol), PPh_3 (9.2 mg, 0.035 mmol), *t*BuONa (4.2 mg, 0.044 mmol), **1f** (53.2 mg, 0.29 mmol), B_2pin_2 (81.5 mg, 0.32 mmol), and MeOH (23.3 μL, 0.58 mmol) in toluene (1.0 mL) at room temp. for 36 h, afforded (*Z*)-**2f** (33.4 mg, 62%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, J = 13.1 Hz, 1 H), 4.75 (d, J = 13.1 Hz, 1 H), 4.43 (t, J = 8.0 Hz, 2 H), 3.88 (t, J = 8.0 Hz, 2 H), 0.19 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 135.9, 107.6, 62.0, 44.4, 1.7 ppm. MS (ESI): *m*/*z* (%) = 208 (100) [M$^+$ + Na], 393 (31.84) [2M$^+$ + Na]. IR (neat): $\tilde{\nu}$ = 1742, 1615, 1410, 1385, 1239, 837 cm^{-1}. HRMS: calcd. for $C_8H_{16}NO_2Si$ [M + H]$^+$ 186.0945; found 186.0943.

(*S*)-4-Phenyl-3-[(*Z*)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-2g]: Prepared according to Typical Procedure II. The reaction of CuCl (3.3 mg, 0.03 mmol), PPh_3 (9.5 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1g** (79.4 mg, 0.3 mmol), B_2pin_2 (84.4 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 31 h, afforded (*Z*)-**2g** (58.3 mg, 79%) as a white solid, m.p. 102–103 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –159.8 (c = 1.01, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.21 (m, 4 H), 7.21–6.14 (m, 2 H), 7.05–6.73 (m, 2 H), 6.66–6.59 (m, 2 H), 6.49 (d, J = 9.6 Hz, 1 H), 5.88 (d, J = 9.6 Hz, 1 H), 4.90 (dd, J = 8.7, 4.1 Hz, 1 H), 4.62 (t, J = 8.7 Hz, 1 H), 4.12 (dd, J = 8.7, 4.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 138.1, 135.6, 129.0, 128.6, 128.4, 127.9, 127.1, 126.0, 122.1, 116.2, 70.2, 58.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 265 (82.46) [M$^+$], 266 (13.54) [M$^+$ + 1], 28 (100). IR (KBr): $\tilde{\nu}$ = 3058, 3030, 2971, 1772, 1652, 1448, 1403, 1341, 1240, 1072 cm^{-1}. $C_{17}H_{15}NO_2$ (265.31): calcd. C 76.96, H 5.70, N 5.28; found C 76.62, H 5.67, N 5.14.

(*S*)-4-Phenyl-3-[(*Z*)-2-(4-methylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2h]: Prepared according to Typical Procedure II. The reaction of CuCl (3.4 mg, 0.03 mmol), PPh_3 (9.2 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1h** (82.8 mg, 0.3 mmol), B_2pin_2 (84.4 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 21 h, afforded (*Z*)-**2h** (67.4 mg, 81%) as a white solid, m.p. 95–97 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –165.8 (c = 1.02,

CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.15 (m, 3 H), 7.14–7.08 (m, 2 H), 6.97–6.91 (m, 2 H), 6.70–6.64 (m, 2 H), 6.41 (d, J = 9.5 Hz, 1 H), 5.87 (d, J = 9.5 Hz, 1 H), 4.90 (dd, J = 8.7, 4.0 Hz, 1 H), 4.61 (t, J = 8.7 Hz, 1 H), 4.14 (dd, J = 8.7, 4.0 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 138.2, 137.0, 132.6, 128.9, 128.6, 128.5, 126.2, 121.7, 117.0, 70.2, 58.7, 21.2 ppm. MS (EI, 70 eV): m/z (%) = 279 (98.20) [M^+], 280 (24.77) [M^+ + 1], 144 (100). IR (KBr): $\tilde{\nu}$ = 3043, 2990, 2923, 1763, 1678, 1600, 1478, 1424, 1355, 1270, 1238, 1077, 1043, 956, 886 cm^{-1}. $C_{18}H_{17}NO_2$ (279.34): calcd. C 77.40, H 6.13, N 5.01; found C 77.32, H 5.91, N 4.76.

(*S*)-4-Phenyl-3-[(*Z*)-2-(4-methoxylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2i]: Prepared according to Typical Procedure II. The reaction of CuCl (3.1 mg, 0.03 mmol), PPh_3 (9.3 mg, 0.036 mmol), *t*BuONa (4.5 mg, 0.045 mmol), **1i** (87.7 mg, 0.3 mmol), B_2pin_2 (83.6 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 24 h, afforded (*Z*)-**2i** (58.2 mg, 68%) as a white solid, m.p. 86–87 °C (*n*-hexane/Et_2O). $[\alpha]_D^{20}$ = –164.3 (*c* = 1.02, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.17 (m, 3 H), 7.00–6.96 (m, 2 H), 6.86–6.81 (m, 2 H), 6.72–6.68 (m, 2 H), 6.36 (d, J = 9.4 Hz, 1 H), 5.85 (d, J = 9.4 Hz, 1 H), 4.91 (dd, J = 8.6, 4.1 Hz, 1 H), 4.62 (t, J = 6.8 Hz, 1 H), 4.14 (dd, J = 8.6, 4.1 Hz, 1 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 157.1, 138.2, 130.2, 128.7, 128.5, 127.9, 126.1, 121.2, 117.0, 113.4, 58.8, 55.3 ppm. MS (EI, 70 eV): m/z (%) = 295 (100) [M^+], 296 (27.94) [M^+ + 1]. IR (neat): $\tilde{\nu}$ = 2946, 2910, 2834, 1748, 1649, 1605, 1511, 1394, 1321, 1246, 1206, 1073, 1034, 1021, 843 cm^{-1}. $C_{18}H_{17}NO_3$ (295.34): calcd. C 73.20, H 5.80, N 4.74; found C 72.90, H 5.71, N 4.42.

(*S*)-4-Phenyl-3-[(*Z*)-2-(4-acetylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2j]: Prepared according to Typical Procedure II. The reaction of CuCl (3.3 mg, 0.03 mmol), PPh_3 (9.6 mg, 0.036 mmol), *t*BuONa (4.7 mg, 0.045 mmol), **1j** (91.6 mg, 0.3 mmol), B_2pin_2 (84.0 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 24 h, afforded (*Z*)-**2j** (73.4 mg, 80%) as a white solid, m.p. 138–139 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –163.2 (*c* = 1.01, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.85 (m, 2 H), 7.28–7.21 (m, 1 H), 7.21–7.14 (m, 2 H), 7.12–7.06 (m, 2 H), 6.65–6.55 (m, 3 H), 5.89 (d, J = 9.7 Hz, 1 H), 4.90 (dd, J = 8.7, 4.4 Hz, 1 H), 4.64 (t, J = 8.7 Hz, 1 H), 4.13 (dd, J = 8.7, 4.4 Hz, 1 H), 2.64 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 156.8, 140.8, 137.5, 135.5, 129.2, 128.8, 128.6, 127.9, 125.9, 123.7, 114.7, 70.3, 58.9, 26.6 ppm. MS (EI, 70 eV): m/z (%) = 307 (10.01) [M^+], 308 (15.61) [M^+ + 1], 40 (100). IR (KBr): $\tilde{\nu}$ = 3119, 3030, 2994, 1747, 1679, 1601, 1360, 1267, 1173, 1090, 1036 cm^{-1}. $C_{19}H_{17}NO_3$ (307.35): calcd. C 74.25, H 5.58, N 4.56; found C 74.08, H 5.71, N 4.31.

(*S*)-3-[(*Z*)-2-(4-Nitrophenyl)ethenyl]-4-phenyloxazolidin-2-one [(*Z*)-2k]: Prepared according to Typical Procedure II. The reaction of CuCl (3.2 mg, 0.03 mmol), PPh_3 (9.5 mg, 0.036 mmol), *t*BuONa (4.6 mg, 0.045 mmol), **1k** (93.0 mg, 0.3 mmol), B_2pin_2 (83.3 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 3 h, afforded (*Z*)-**2k** (70.7 mg, 76%) as a yellow solid, m.p. 151–152 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –166.5 (*c* = 1.02, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.07 (m, 2 H), 7.28–7.22 (m, 1 H), 7.22–7.15 (m, 2 H), 7.15–7.07 (m, 2 H), 6.68 (d, J = 9.8 Hz, 1 H), 6.65–6.60 (m, 2 H), 5.87 (d, J = 9.8 Hz, 1 H), 4.88 (dd, J = 8.7, 4.8 Hz, 1 H), 4.69 (t, J = 8.8 Hz, 1 H), 4.13 (dd, J = 8.7, 4.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 146.4, 142.7, 137.0, 129.6, 129.0, 128.8, 125.7, 124.7, 123.0, 113.0, 70.4, 59.2 ppm. MS (EI, 70 eV): m/z (%) = 310 (100) [M^+]. IR (KBr): $\tilde{\nu}$ = 3104, 3034, 2968, 2910, 1770, 1651, 1594, 1512, 1428, 1401, 1341, 1237, 1213, 1106, 1075, 861 cm^{-1}. $C_{17}H_{14}N_2O_4$ (310.31): calcd. C 65.80, H 4.55, N 9.03; found C 65.75, H 4.33, N 8.78.

(*S*)-4-Benzyl-3-[(*Z*)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-2l]: Prepared according to Typical Procedure II. The reaction of CuCl (3.0 mg, 0.03 mmol), PPh_3 (9.9 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1l** (83.0 mg, 0.3 mmol), B_2pin_2 (84.5 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 6 h, afforded (*Z*)-**2l** (73.5 mg, 88%) as a white solid, m.p. 108–109 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –177.5 (*c* = 1.01, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.36 (m, 3 H), 7.36–7.30 (m, 2 H), 7.17–7.09 (m, 3 H), 6.64 (d, J = 9.8 Hz, 1 H), 6.48–6.40 (m, 2 H), 6.11 (d, J = 9.8 Hz, 1 H), 4.20–4.00 (m, 3 H), 2.86–2.76 (m, 1 H), 2.25 (dd, J = 13.2, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 135.8, 135.2, 129.3, 129.0, 128.6, 128.4, 127.4, 126.9, 122.3, 114.2, 66.0, 55.5, 36.6 ppm. MS (EI, 70 eV): m/z (%) = 279 (44.64) [M^+], 280 (8.92) [M^+ + 1], 144 (100). IR (KBr): $\tilde{\nu}$ = 3060, 2985, 2928, 1760, 1649, 1485, 1447, 1409, 1233, 1084, 1013 cm^{-1}. $C_{18}H_{17}NO_2$ (279.34): calcd. C 77.40, H 6.13, N 5.01; found C 77.15, H 6.43, N 4.85.

(*S*)-4-Benzyl-3-[(*Z*)-2-(4-methylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2m]: Prepared according to Typical Procedure II. The reaction of CuCl (3.4 mg, 0.03 mmol), PPh_3 (9.5 mg, 0.036 mmol), *t*BuONa (4.4 mg, 0.045 mmol), **1m** (87.3 mg, 0.3 mmol), B_2pin_2 (84.7 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 6 h, afforded (*Z*)-**2m** (72.9 mg, 83%) as a white solid, m.p. 111–112 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –179.2 (*c* = 1.02, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.19 (m, 4 H), 7.17–7.10 (m, 3 H), 6.59 (d, J = 9.7 Hz, 1 H), 6.49–6.43 (m, 2 H), 6.08 (d, J = 9.7 Hz, 1 H), 4.19–4.01 (m, 3 H), 2.80 (dd, J = 13.1, 3.0 Hz, 1 H), 2.43 (s, 3 H), 2.25 (dd, J = 13.2, 10.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 137.3, 135.4, 132.8, 129.2, 129.1, 129.0, 128.6, 126.9, 121.9, 114.4, 66.0, 55.5, 36.6, 21.2 ppm. MS (EI, 70 eV): m/z (%) = 293 (41.94) [M^+], 294 (9.88) [M^+ + 1], 158 (100). IR (KBr): $\tilde{\nu}$ = 3025, 2973, 2922, 1743, 1652, 1474, 1449, 1409, 1235, 1191, 1078, 997, 859 cm^{-1}. $C_{19}H_{19}NO_2$ (293.36): calcd. C 77.79, H 6.53, N 4.77; found C 77.59, H 6.70, N 4.68.

(*S*)-4-Benzyl-3-[(*Z*)-2-(4-methoxylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2n]: Prepared according to Typical Procedure II. The reaction of CuCl (3.4 mg, 0.03 mmol), PPh_3 (9.1 mg, 0.036 mmol), *t*BuONa (4.3 mg, 0.045 mmol), **1n** (93.8 mg, 0.3 mmol), B_2pin_2 (84.3 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 9 h, afforded (*Z*)-**2n** (79.7 mg, 85%) as a white solid, m.p. 98–99 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –178.3 (*c* = 1.00, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.23 (m, 2 H), 7.21–7.13 (m, 3 H), 7.00–6.92 (m, 2 H), 6.57–6.49 (m, 3 H), 6.07 (d, J = 9.6 Hz, 1 H), 4.19–4.01 (m, 3 H), 3.87 (s, 3 H), 2.88–2.78 (m, 1 H), 2.29 (dd, J = 13.3, 9.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 156.7, 135.4, 130.4, 129.1, 128.7, 127.9, 126.9, 121.5, 114.7, 113.8, 66.0, 55.6, 55.4, 36.7 ppm. MS (EI, 70 eV): m/z (%) = 309 (58.20) [M^+], 310 (13.67) [M^+ + 1], 174 (100). IR (KBr): $\tilde{\nu}$ = 3004, 2974, 2911, 1756, 1657, 1508, 1419, 1399, 1252, 1230, 1178, 1076, 1021 cm^{-1}. $C_{19}H_{19}NO_3$ (309.36): calcd. C 73.77, H 6.19, N 4.53; found C 73.93, H 6.10, N 4.39.

(*S*)-4-Benzyl-3-[(*Z*)-2-(4-acetylphenyl)ethenyl]oxazolidin-2-one [(*Z*)-2o]: Prepared according to Typical Procedure II. The reaction of CuCl (3.6 mg, 0.03 mmol), PPh_3 (9.5 mg, 0.036 mmol), *t*BuONa (4.5 mg, 0.045 mmol), **1o** (94.3 mg, 0.3 mmol), B_2pin_2 (83.9 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 5 h, afforded (*Z*)-**2o** (73.8 mg, 78%) as a white solid, m.p. 88–89 °C (*n*-hexane/EtOAc). $[\alpha]_D^{20}$ = –173.2 (*c* = 1.02, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06–7.96 (m, 2 H),

7.47–7.39 (m, 2 H), 7.19–7.08 (m, 3 H), 6.73 (d, J = 9.7 Hz, 1 H), 6.50–6.42 (m, 2 H), 6.12 (d, J = 9.7 Hz, 1 H), 4.19–4.04 (m, 3 H), 2.80–2.70 (m, 1 H), 2.66 (s, 3 H), 2.36–2.24 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 156.4, 140.8, 135.9, 134.8, 129.4, 128.9, 128.8, 128.4, 127.1, 124.0, 113.2, 66.0, 55.6, 36.5, 26.4 ppm. MS (EI, 70 eV): m/z (%) = 321 (39.83) [M^+], 43 (100). IR (KBr): $\tilde{\nu}$ = 3059, 2981, 2916, 1763, 1679, 1651, 1602, 1421, 1398, 1264, 1229, 1203, 1080, 1014, 967, 861 cm^{-1}. $C_{20}H_{19}NO_3$ (321.38): calcd. C 74.75, H 5.96, N 4.36; found C 74.70, H 6.22, N 4.13.

(*S*)-4-Benzyl-3-[(*Z*)-2-(4-nitrophenyl)ethenyl]oxazolidin-2-one [(*Z*)-2p]: Prepared according to Typical Procedure II. The reaction of CuCl (3.2 mg, 0.03 mmol), PPh_3 (9.9 mg, 0.036 mmol), *t*BuONa (4.3 mg, 0.045 mmol), **1p** (97.1 mg, 0.3 mmol), B_2pin_2 (83.7 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 3 h, afforded (*Z*)-**2p** (81.1 mg, 83%) as a yellow liquid. $[\alpha]_D^{20}$ = –182.0 (c = 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33–8.25 (m, 2 H), 7.54–7.45 (m, 2 H), 7.21–7.11 (m, 3 H), 6.77 (d, J = 9.7 Hz, 1 H), 6.59–6.51 (m, 2 H), 6.13 (d, J = 9.7 Hz, 1 H), 4.25–4.16 (m, 1 H), 4.16–4.03 (m, 2 H), 2.75 (dd, J = 13.6, 3.3 Hz, 1 H), 2.37 (dd, J = 13.6, 3.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 146.6, 142.6, 134.5, 129.8, 128.9, 128.8, 127.3, 125.3, 123.4, 112.4, 66.1, 55.8, 36.5 ppm. MS (EI, 70 eV): m/z (%) = 324 (36.55) [M^+], 325 (8.23) [M^+ + 1], 233 (100). IR (KBr): $\tilde{\nu}$ = 3073, 2985, 2924, 1761, 1649, 1592, 1513, 1399, 1340, 1219, 1103, 1078, 1007, 862 cm^{-1}. HRMS: calcd. for $C_{18}H_{16}N_2O_4Na$ [M + Na]$^+$ 347.1002; found 347.1005.

1-[(*Z*)-2-(4-Methylphenyl)ethenyl]pyrrolidin-2-one [(*Z*)-2q]: Prepared according to Typical Procedure II. The reaction of CuCl (3.1 mg, 0.03 mmol), PPh_3 (9.5 mg, 0.036 mmol), *t*BuONa (4.5 mg, 0.045 mmol), **1q** (59.4 mg, 0.3 mmol), B_2pin_2 (84.0 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 6 h, afforded (*Z*)-**2q** (53.1 mg, 80%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.05 (m, 4 H), 6.74 (d, J = 9.8 Hz, 1 H), 5.97 (d, J = 9.8 Hz, 1 H), 3.22 (t, J = 7.1 Hz, 2 H), 2.43–2.39 (m, 2 H), 2.33 (s, 3 H), 1.98–1.89 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 136.6, 133.1, 129.0, 128.4, 123.4, 114.1, 48.0, 30.3, 21.1, 18.8 ppm. MS (EI, 70 eV): m/z (%) = 201 (100) [M^+], 202 (13.75) [M^+ + 1]. IR (KBr): $\tilde{\nu}$ = 2979, 2917, 2893, 1705, 1647, 1511, 1460, 1412, 1378, 1336, 1263, 1147, 1020, 813 cm^{-1}. HRMS: calcd. for $C_{13}H_{15}NONa$ [M + Na]$^+$ 224.1046; found 224.1038.

1-[(*Z*)-2-(4-Methoxylphenyl)ethenyl]pyrrolidin-2-one [(*Z*)-2r]: Prepared according to Typical Procedure II. The reaction of CuCl (3.5 mg, 0.03 mmol), PPh_3 (9.6 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1r** (64.7 mg, 0.3 mmol), B_2pin_2 (83.8 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 10 h, afforded (*Z*)-**2r** (54.2 mg, 83%) as a colorless liquid.[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.09 (m, 2 H), 6.89–6.81 (m, 2 H), 6.70 (d, J = 9.8 Hz, 1 H), 5.96 (d, J = 9.8 Hz, 1 H), 3.82 (s, 3 H), 3.23 (t, J = 7.0 Hz, 2 H), 2.41 (t, J = 8.0 Hz, 2 H), 2.00–1.92 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.6, 158.5, 130.2, 128.4, 123.2, 114.2, 113.2, 55.2, 48.0, 30.4, 18.8 ppm. MS (EI, 70 eV): m/z (%) = 217 (100) [M^+], 218 (18.84) [M^+ + 1]. IR (KBr): $\tilde{\nu}$ = 2962, 2896, 1703, 1649, 1606, 1510, 1460, 1409, 1251, 1176, 1031, 842 cm^{-1}.

1-[(*Z*)-2-Phenylethenyl-1*H*-indol-3-yl]ethanone [(*Z*)-2s]: Prepared according to Typical Procedure II. The reaction of CuCl (3.4 mg, 0.03 mmol), PPh_3 (9.8 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1s** (78.3 mg, 0.3 mmol), B_2pin_2 (83.6 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 27 h, afforded (*Z*)-**2s** (57.2 mg, 74%) as a white solid, m.p. 92–93 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.35 (m, 1 H), 7.60 (s, 1 H), 7.40–7.26 (m, 3 H), 7.26–7.20 (m, 3 H), 7.14–7.07 (m, 2 H), 6.92 (d, J = 9.1 Hz, 1 H), 6.53 (d, J = 9.1 Hz, 1 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 136.5, 133.8, 133.6, 128.5, 128.3, 125.9, 124.3, 124.0, 123.3, 122.6, 122.3, 118.6, 110.4, 27.4 ppm. MS (EI, 70 eV): m/z (%) = 261 (59.09) [M^+], 245 (100). IR (KBr): $\tilde{\nu}$ = 3115, 3048, 3019, 2983, 1769, 1644, 1526, 1452, 1387, 1311, 1207, 1078, 1005, 927 cm^{-1}. $C_{18}H_{15}NO$ (261.32): calcd. C 82.73, H 5.79, N 5.36; found C 82.86, H 5.58, N 4.95.

1-[(*Z*)-2-(4-Methylphenyl)ethenyl-1*H*-indol-3-yl]ethanone [(*Z*)-2t]: Prepared according to Typical Procedure II. The reaction of CuCl (3.2 mg, 0.03 mmol), PPh_3 (9.6 mg, 0.036 mmol), *t*BuONa (4.3 mg, 0.045 mmol), **1t** (81.4 mg, 0.3 mmol), B_2pin_2 (83.8 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 24 h, afforded (*Z*)-**2t** (65.6 mg, 80%) as a white solid, m.p. 125–126 °C (*n*-hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44–8.36 (m, 1 H), 7.65 (s, 1 H), 7.41–7.24 (m, 3 H), 7.08–6.95 (m, 4 H), 6.86 (d, J = 9.0 Hz, 1 H), 6.51 (d, J = 9.0 Hz, 1 H), 2.37 (s, 3 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 138.5, 136.5, 134.0, 130.6, 129.4, 128.5, 125.9, 124.9, 123.9, 123.2, 122.6, 121.6, 118.6, 110.4, 27.5, 21.3 ppm. MS (EI, 70 eV): m/z (%) = 275 (84.64) [M^+], 276 (15.53) [M^+ + 1], 260 (100). IR (KBr): $\tilde{\nu}$ = 3026, 2987, 2913, 1763, 1646, 1528, 1459, 1371, 1312, 1240, 1207, 1173, 1010, 937, 822 cm^{-1}. $C_{19}H_{17}NO$ (275.35): calcd. C 82.88, H 6.22, N 5.09; found C 82.45, H 6.02, N 4.97.

Large-Scale Reaction

Synthesis of (*S*)-4-Benzyl-3-[(*Z*)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-2l]: An oven-dried Schlenk tube was charged with CuCl (20.0 mg, 0.2 mmol), *t*BuONa (28.9 mg, 0.3 mmol), B_2pin_2 (1.1176 g, 4.4 mmol), PPh_3 (63.1 mg, 0.24 mmol), and **1l** (1.1082 g, 4.0 mmol) and the apparatus was purged and backfilled with nitrogen (three times). To this mixture were added toluene (13.0 mL) and MeOH (324.1 μL, 8.0 mmol), and the resulting solution was stirred at room temp. until no starting material was detected by TLC analysis. The reaction was then quenched by the addition of satd. aq. NH_4Cl (5.0 mL) and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Filtration, evaporation, and chromatography on silica gel (PE/EtOAc, 10:1) afforded (*Z*)-**2l** (908.2 mg, 81%) as a white solid.

Reaction Mechanism Studies

The Reaction of 3-[(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylethenyl]oxazolidin-2-one [(*Z*)-4a] with Methanol under Standard Conditions: The reaction of CuCl (3.2 mg, 0.03 mmol), PPh_3 (9.3 mg, 0.036 mmol), *t*BuONa (4.2 mg, 0.045 mmol), **1** (94.1 mg, 0.3 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 24 h, afforded (*Z*)-**2a** (46.1 mg, 82%) as a light-yellow liquid.

Deuterium Labeling Experiments with 1a; Synthesis of 3-[(*Z*)-2-Phenylethenyl-*1,2-d*$_2$]oxazolidin-2-one [(*Z*)-*d*$_2$-2a]: Starting material **1a** was dried in vacuo over P_2O_5 for one day. Toluene was freshly distilled from sodium/benzophenone under N_2. After distillation, the generated anhydrous toluene was stored in a bottle with 4 Å molecular sieves and placed in the glove box under nitrogen atmosphere. CD_3OD (99.8 atom-% D) was purchased from Sigma–Aldrich. All the operations were carried out in a glove box under nitrogen atmosphere. An oven-dried Schlenk tube was charged with CuCl (3.2 mg, 0.03 mmol), *t*BuONa (4.5 mg, 0.045 mmol), B_2pin_2 (83.9 mg, 0.33 mmol), PPh_3 (9.5 mg, 0.036 mmol), and **1a** (56.5 mg, 0.3 mmol). To this mixture were added toluene (1.0 mL) and CD_3OD (24 μL, 0.6 mmol), and the resulting solution was stirred

at room temp. for 22.5 h. The reaction mixture was then directly purified with flash chromatography on silica gel (PE/EtOAc, 5:1) to afford (*Z*)-d_2-**2a** (46.2 mg, 80%; deuteration degree: D_a 90%, D_b 87%) as a light-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 2 H), 7.27–7.25 (m, 1 H), 7.25–7.20 (m, 2 H), 4.27 (t, J = 8.0 Hz, 2 H), 3.37 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 135.4, 129.3, 127.9, 127.1, 123.8 (t, J = 26.9 Hz), 112.2 (t, J = 25.0 Hz), 62.6, 44.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 191 (90.38) [M$^+$], 192 (10.13) [M$^+$ + 1], 132 (100). IR (KBr): $\tilde{\nu}$ = 2924, 2856, 1761, 1633, 1482, 1403, 1315, 1214, 1101, 1045 cm^{-1}. HRMS: calcd. for $C_{11}H_{10}D_2NO_2$ [M + H]$^+$ 192.0988; found 192.0989.

(*S*)-4-Benzyl-3-[(*Z*)-2-(4-methoxylphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]oxazolidin-2-one [(*Z*)-4n]: The reaction of CuCl (3.0 mg, 0.03 mmol), PPh_3 (9.5 mg, 0.036 mmol), *t*BuONa (4.4 mg, 0.045 mmol), **1n** (92.5 mg, 0.3 mmol), B_2pin_2 (83.9 mg, 0.33 mmol), and MeOH (24 μL, 0.6 mmol) in toluene (1.0 mL) at room temp. for 3 h, afforded (*Z*)-**2n** (12.1 mg, 13%) and (*Z*)-**4n** (80.0 mg, 61.5%). Compound (*Z*)-**4n**: Viscous liquid. ^{1}H NMR (400 MHz, toluene-d_8): δ = 7.25 (m, 2 H), 7.06 (m, 1 H), 6.94 (m, 3 H), 6.66 (m, 2 H), 6.58 (m, 2 H), 4.04 (m, 1 H), 3.71 (m, 2 H), 3.33 (s, 3 H), 2.92 (dd, J = 13.3, 4.0 Hz, 1 H), 2.44 (dd, J = 13.3, 10.3 Hz, 1 H), 1.27 (s, 6 H), 1.23 (s, 6 H) ppm. ^{13}C NMR (100 MHz, toluene-d_8): δ = 160.2, 157.1, 137.5, 137.0, 136.6, 131.2, 129.3, 128.7, 126.8, 114.1, 84.3, 67.3, 56.9, 54.7, 38.9, 25.1, 24.6 ppm. ^{11}B NMR (128 MHz, toluene-d_8): δ = 31.2 ppm. IR (KBr): $\tilde{\nu}$ = 2980, 2928, 1756, 1605, 1509, 1403, 1252, 1142, 1031, 978 cm^{-1}. HRMS: calcd. for $C_{25}H_{31}BNO_5$[M + H]$^+$ 436.2290; found 436.2279.

Monitoring CuCl-Catalyzed Reduction of Ynamide 1n with ^{11}B NMR at Room Temperature: An oven-dried Schlenk tube was charged with CuCl (2.1 mg, 0.02 mmol), *t*BuONa (3.0 mg, 0.03 mmol), B_2pin_2 (56.0 mg, 0.22 mmol), PPh_3 (6.3 mg, 0.024 mmol), and **1n** (61.4 mg, 0.2 mmol) and the Schlenk tube was purged and backfilled with nitrogen (three times). To this mixture were added toluene-d_8 (0.7 mL) and MeOH (16 μL, 0.4 mmol), and the resulting solution was immediately transferred to an NMR tube by using a syringe under N_2 and the reaction was further monitored by ^{11}B NMR spectroscopic analysis at 0.5, 3.5, 8.0, 16, and 24 h.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H NMR, ^{13}C NMR spectra of all compounds and X-ray structure of (*Z*)-**3a**.

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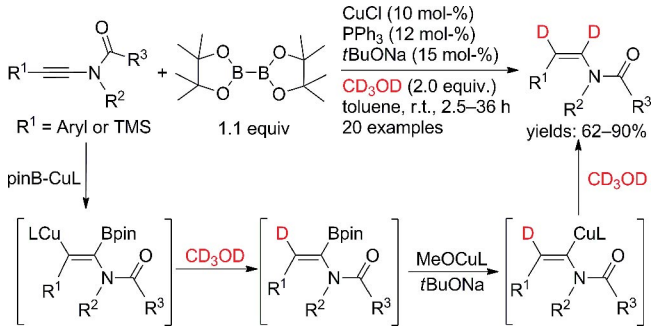
Chemoselective Reduction



The copper-catalyzed semireduction of *N*-alkynylamides by a boron addition–protonlysis protocol afforded *N*-alkenylamides in good yields with high stereo- and chemoselectivity. Deuterium labeling experiments indicated that both of the alkenyl hydrogen atoms of the *N*-alkenylamides originate from the additive methanol.

Keywords: Alkynes / Reduction / Boron / Copper / Regioselectivity

