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Substrate-Controlled $Cu(OAc)_2$-Catalyzed Stereoselective Semi-Reduction of Alkynes with MeOH as the Hydrogen Source

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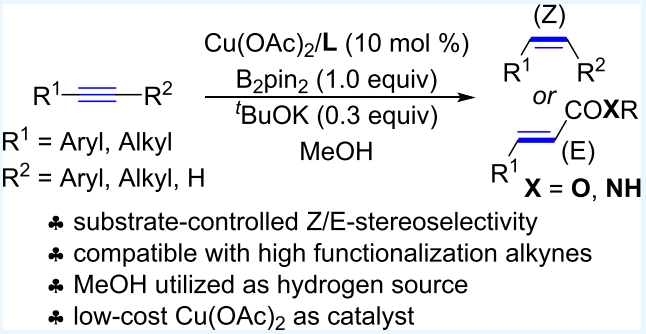
ABSTRACT: A substrate-controlled stereoselective semi-reduction of alkynes with MeOH as the hydrogen source has been developed, and readily available $Cu(OAc)_2$ (copper acetate) is utilized as an optimal catalyst. The detailed investigation of the mechanism revealed distinct catalytic processes for the (*Z*)- and (*E*)-alkenes, respectively. As a result, a diversity of alkynes (including terminal, internal alkynes etc.) were compatible under the mild reaction conditions. Furthermore, the high proportion of deuterium in *Z*-alkenes (up to 96%) was obtained using d_4-methanol as a solvent.

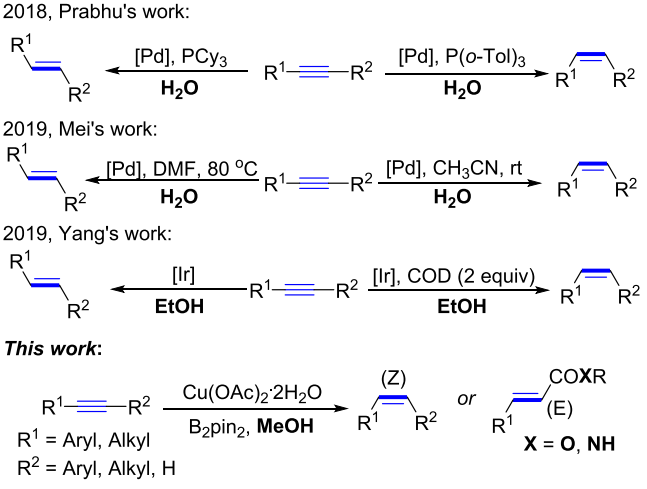


INTRODUCTION

Alkenes as chemical feedstock have a wide range of applications in the field of materials science, medicinal chemistry, and pesticides.[1] Ways to access the double bond include Wittig olefination, Julia olefination, Peterson olefination, cross-coupling, and olefin metathesis reaction.[2] Beyond this, the semi-reduction of alkynes to alkenes is undoubtedly an attractive means.[3] However, as one of the most primary procedures to produce alkenes, the semi-reduction of alkynes remains challenging. First, molecular hydrogen acts as the main hydrogen source in many transition-metal-based catalytic systems (such as Pd, Rh, Ir, Ru, Ni, Cu, etc.), but this source is flammable resulting in inconvenience and is potentially dangerous in large-scale industrial production. Secondly, absolute chemo- and stereoselectivity was hard to obtain under an H_2 atmosphere for other unsaturated functional groups (alkene, nitrile, nitro, etc.). Hence, efforts for exploiting new and more efficient tactics are highly desirable.

Obviously, a catalytic transfer hydrogenation (CTH) strategy is preferable in the reduction of unsaturated hydrocarbons.[4] Among the hydride donors, water and alcohols were safer and more eco-friendly than NH_3BH_3,[5] BpinH,[6] HCOOH,[7] and polymethylhydrosiloxane (PHMS).[8] For instance (Scheme 1), in 2018, Prabhu disclosed homogeneous palladium-catalyzed stereodivergent semi-reduction of alkynes to alkenes with water by employing ligand PCy_3 and P(*o*-Tol)$_3$.[9] The next year, the Mei group also developed a palladium-catalyzed stereoselective semi-reduction of alkynes by regulation of the solvent.[10] Yang and co-workers reported ligand-controlled iridium-catalyzed stereoselective semi-reduction of alkynes using ethanol as the hydrogen donor.[11] These are all distinguished methods for the stereoselective semi-reduction of alkynes. To the best of our knowledge, non-noble metal-catalyzed methods for stereodivergent semi-reduction of alkynes using a CTH strategy are still insufficient, although a few copper-catalyzed semi-reduction of alkynes are known with equivalent amounts of base and limited substrate scope.[12] With

Scheme 1. Stereodivergent Catalytic Transfer Hydrogenation (CTH) of Alkynes



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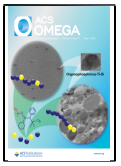


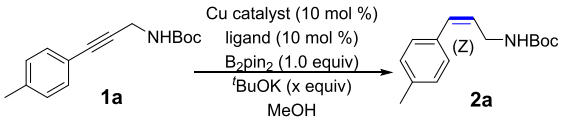
our interest in the catalytic systems of transition-metal and diboron compounds,[13] we herein developed the $Cu(OAc)_2$-catalyzed semi-reduction of alkynes under the aegis of B_2pin_2, and the absolute stereoselectivity of the products depended on the nature of substrates.

RESULTS AND DISCUSSION

We initiated the investigation using **1a** as a template substrate, and semi-reduction product (*Z*)-**2a** was first detected with 68% yield in the presence of 10 mol % of $Cu(OAc)_2$, 1.0 equiv of B_2pin_2 and 1.0 equiv of ^{t}BuOK in MeOH at 60 °C (Table 1, entry 1). Fortunately, the over-reduction product and (*E*)-**2a** were not detected in the mixture. Next, the screening of the copper catalysts revealed that Cu(II) species gave promising results while the reaction did not work with Cu powder. When $Pd(OAc)_2$ was used as the catalyst, substrate **1a** was recovered in quantitative yield.[8] $Cu(OAc)_2{\cdot}2H_2O$ was selected as the candidate for slightly increasing the yield (Table 1, entries 2−8). We investigated the effect of various nitrogen-containing ligands on the influence of this transformation. When strong coordinate ligand 2,2′-bpy, 1,10-phen, and tpy were utilized, the yield of (*Z*)-**2a** decreased significantly and the reaction was almost inhibited (Table 1, entries 9−11). To our delight, when 4,4′-bpy was used as the partner of the transition-metal catalyst, the yield of (*Z*)-**2a** was up to 92% (Table 1, entry 12). The weaker coordination ability of 4,4′-bpy played the role of a monodentate ligand, rather than bidentate ligands for $Cu(OAc)_2$.[14] The function of the base is activation of the diborane compound, we attempted to lower the equivalents of ^{t}BuOK. A comparison with the above conditions showed that 0.3 equivalent of ^{t}BuOK exhibited a tiny decrease of (*Z*)-**2a** (Table 1, entries 13−14). Next, we screened ethanol or water as the solvent, the results of the reactions were not satisfactory (Table 1, entries 15−16). In summary, the optimized reaction conditions were identified as 10 mol % $Cu(OAc)_2{\cdot}2H_2O$, 10 mol % 4,4′-bpy, 0.3 equiv of ^{t}BuOK, and 1.0 equiv of B_2pin_2 in methanol at 60 °C.

With the optimal reaction conditions established above, we investigated a variety of substituted N-protected arylpropargyl amine derivatives (Table 2). The substrates with substitutions in *para* and *meta*-positions including electron-donating and electron-withdrawing groups were well transformed and afforded the corresponding semi-reduction products in good to excellent yields (**2a−c**). It is worth noting that *ortho*-substitution of the benzene ring had little impact on the yield of (*Z*)-alkene (**2d**). In addition, the alkynes installed with a

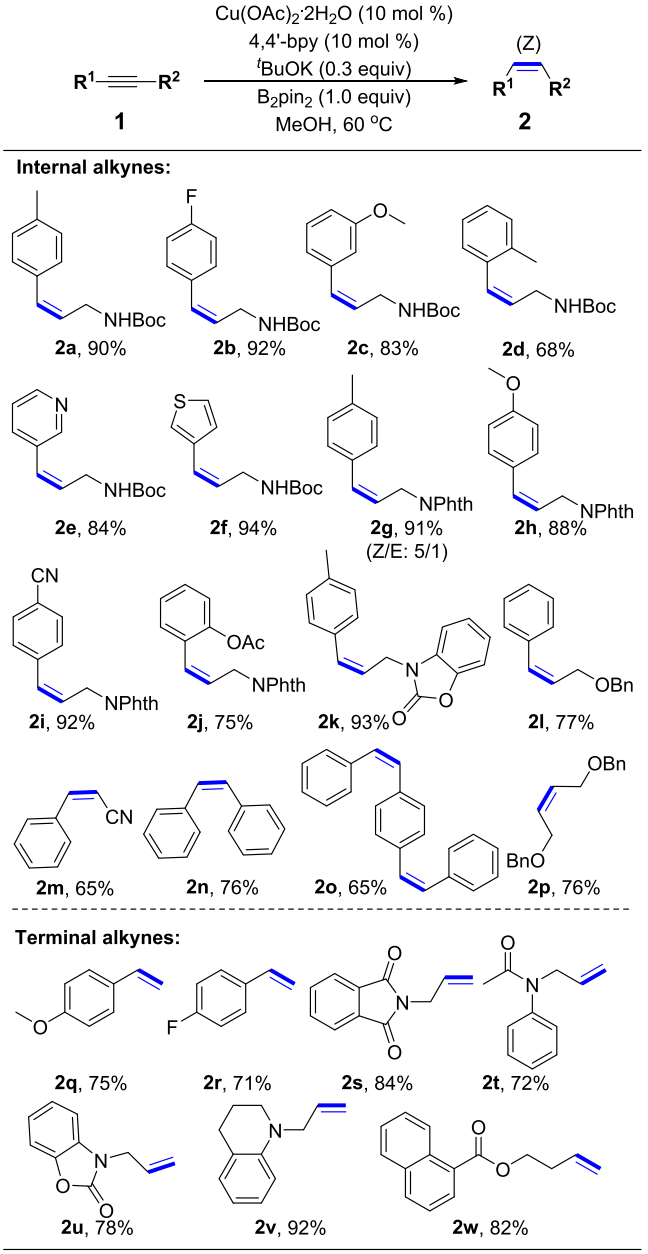
Table 1. Optimization of the Reaction Conditions[a]



entry	Cu catalyst	ligand	*x*	yield (%)[b]
1	$Cu(OAc)_2$	none	1.0	68
2	$Cu(OAc)_2{\cdot}2H_2O$	none	1.0	69
3	$Cu(OTf)_2$	none	1.0	55
4	CuCl	none	1.0	10
5	CuTc	none	1.0	16
6	Cu powder	none	1.0	<5
7	$Cu(CH_3CN)_4BF_4$	none	1.0	10
8	$Pd(OAc)_2$	none	1.0	<5
9	$Cu(OAc)_2{\cdot}2H_2O$	2,2′-bpy	1.0	18
10	$Cu(OAc)_2{\cdot}2H_2O$	1,10-phen	1.0	<5
11	$Cu(OAc)_2{\cdot}2H_2O$	tpy	1.0	<5
12	$Cu(OAc)_2{\cdot}2H_2O$	4,4′-bpy	1.0	92
13	$Cu(OAc)_2{\cdot}2H_2O$	4,4′-bpy	0.1	45
14	$Cu(OAc)_2{\cdot}2H_2O$	4,4′-bpy	0.3	90
15[c]	$Cu(OAc)_2{\cdot}2H_2O$	4,4′-bpy	0.3	23
16[d]	$Cu(OAc)_2{\cdot}2H_2O$	4,4′-bpy	0.3	0

[a]Conditions: substrate **1a** (0.3 mmol), Cu catalyst (10 mol %), ligand (10 mol %), B_2pin_2 (1.0 equiv), MeOH (2.0 mL) under a N_2 atmosphere at 60 °C for 18 h. [b]Yields determined by ^{1}H NMR with CH_2Br_2 as internal standard. [c]EtOH instead of MeOH. [d]H_2O instead of MeOH.

Table 2. Synthesis of (*Z*)-Alkenes[a]



[a]Conditions: substrate **1** (0.3 mmol), $Cu(OAc)_2{\cdot}2H_2O$ (10 mol %), 4,4′-bpy (10 mol %), B_2pin_2 (1.0 equiv), MeOH (2.0 mL) under a N_2 atmosphere at 60 °C for 18 h; Isolated yields; Unless otherwise noted, products *Z*/*E* > 20:1.

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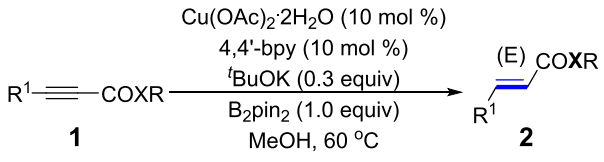
heteroaromatic ring such as pyridyl and thienyl were also compatible under the reaction conditions and delivered the target products (**2e**, **2f**) in good yields. Next, when the Boc protecting group of the nitrogen atom was replaced with phthalate or benzoxazolinone, that could convert into the desired products in satisfactory yields (**2g**–**k**). Especially, the nitrile and benzyl ether (BnO) functional group could be stable under the reductive conditions (**2i**, **2l**). It was noteworthy that **2m** was obtained with electron deficient 3-phenylpropiolonitrile as the substrate. Diaryl alkyne and diaryl diyne were also suitable substrates under the current conditions (**2n**, **2o**). Furthermore, internal alkyl alkyne also produced (*Z*)-alkene in moderate yield with excellent stereoselectivity (**2p**). Meanwhile, we examined terminal alkynes, including phenylacetylene derivatives (**2q**, **2r**), propargyl amine derivatives (**2s**–**v**), and long-chain terminal alkyne (**2w**), that could be smoothly converted to the corresponding terminal alkenes.

On the other hand, internal alkynes with a carboxylate or an amide group (Table 3), provided the (*E*)-geometric products (**2x**–**z**) rather than (*Z*)-isomers.

Table 3. Synthesis of (*E*)-Alkenes[a]



[a]Conditions: substrate **1** (0.3 mmol), $Cu(OAc)_2{\cdot}2H_2O$ (10 mol %), 4,4′-bpy (10 mol %), B_2pin_2 (1.0 equiv), MeOH (2.0 mL) under a N_2 atmosphere at 60 °C for 18 h; Isolated yields. Unless otherwise noted, products E/Z > 20:1.

Additionally, when d_4-methanol was used as the solvent in the transformation (Figure 1), highly deuterated (up to 96%)

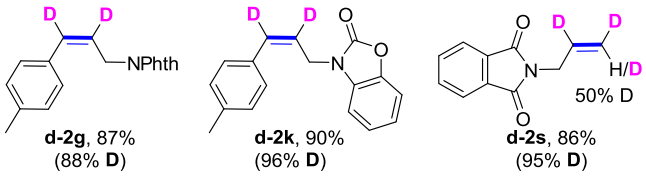
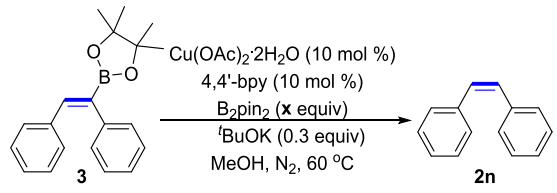


Figure 1. Synthesis of deuterated (*Z*)-alkenes. Conditions: substrate **1** (0.3 mmol), anhydrous $Cu(OAc)_2$ (10 mol %), 4,4′-bpy (10 mol %), B_2pin_2 (1.0 equiv), CD_3OD (2.0 mL) under a N_2 atmosphere at 60 °C for 18 h; Isolated yields. Unless otherwise noted, products Z/E > 20:1. The deuterium content was determined by ^1H NMR.

alkenes were obtained (**d-2g**, **d-2k**). As we observed by ^1H NMR of **d-2s**, the *cis*-terminal hydrogen was deuterated with 50% incorporation. Naturally, we postulated that the hydrogen atom of the terminal alkynes underwent hydrogen–deuterium exchange before the semi-reduction reaction, which was verified by the control experiments (see the Supporting Information (SI) for details).

To gain a deep understanding of this process, more control experiments were conducted (Scheme 2). We synthesized the

Scheme 2. Effect of Various Equivalents of B_2pin_2 for the Transformation of Possible Intermediates

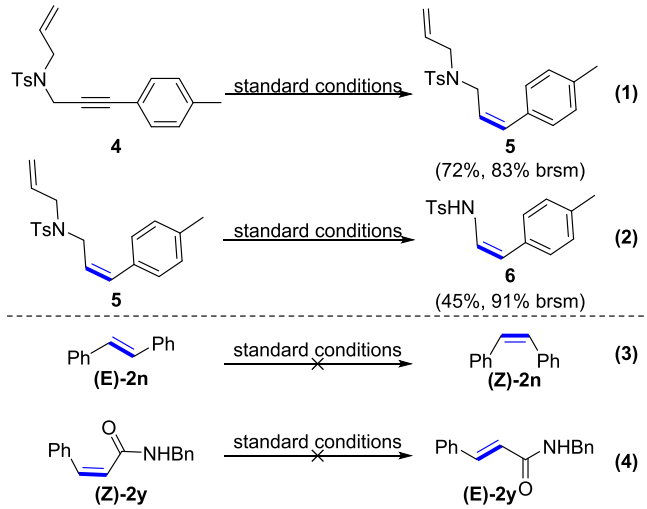


x	0	0.2	0.7	1.0	1.2
Yield (%)	43	81	76	<5	0

possible reaction intermediate vinyl boronate **3** that was employed under the standard conditions with various equivalents of B_2pin_2. One surprising result was that if the amount of B_2pin_2 used is **1** or more equivalents, the yield of **2n** was <5%. However, the use of less than one equivalent gave a high yield of **2n** (Scheme 2). This may be attributed to the transmetalation process of the vinyl copper intermediate with B_2pin_2 (see the Supporting Information (SI) for details).[15]

Next, in a control experiment (Scheme 3), compound **4** containing both an alkyne bond group and an allyl group could

Scheme 3. Control Experiments



be converted into (*Z*)-**5** with retention of the allyl group under the standard conditions (Scheme 3, 1). However, compound **5** would undergo deallylation under the standard conditions, which suggests the existence of a Cu-hydride species in the process (Scheme 3, 2).[16] Next, to ascertain if β-hydride elimination of a Cu(II)-alkyl intermediate may be involved in the process, isomerization experiments were performed, which were all negative (Scheme 3, 3–4).[3b]

Based on the results of control experiments as well as the literature precedents,[17] we speculate the proposed mechanism, as shown in Scheme 4. Initially, the copper–boryl complex (Bpin-CuL) was generated from 4,4′-bpy (L), B_2pin_2, and $Cu(OAc)_2$ with the aid of ^{t}BuOK. Then Bpin-CuL was added to the carbon–carbon triple bond of **1**, which produced the vinyl copper intermediate (path 1).[18] Finally, the protonolysis

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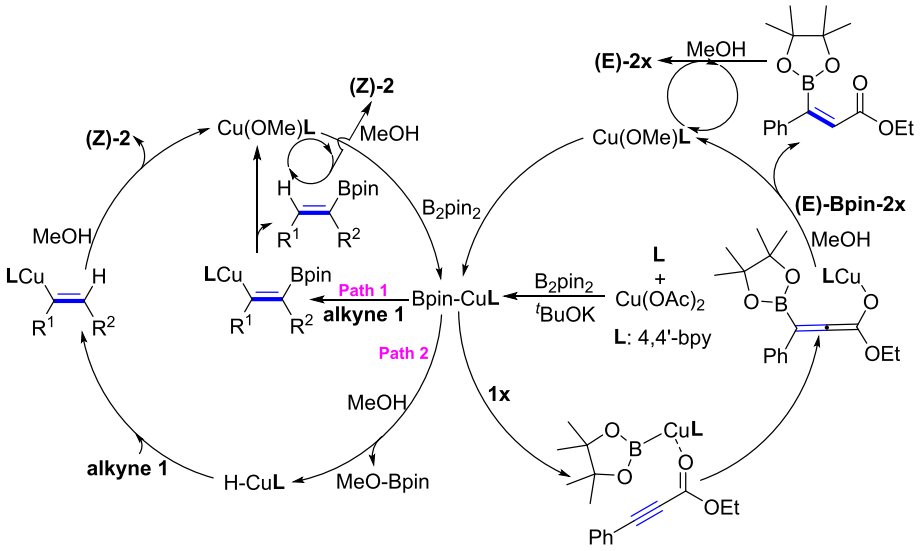
Scheme 4. Proposed Mechanism



of the vinyl C−Cu bond provided vinyl boronates, which could be transformed into the target product (*Z*)-**2** under the Cu-catalyzed protodeboronation and protonation. In path 2, the intermediate Bpin-CuL might facilitate the hydrogen atom transfer from MeOH to copper, affording a copper hydride species. Then, [CuH] was added to the alkyne to deliver the vinyl copper intermediate, and (*Z*)-**2** was formed from the protonolysis of the vinyl C−Cu bond.

On the other hand, Bpin-CuL could coordinate with one of the oxygen atoms of **1x**, and then the conjugate addition of Bpin to the alkynoate would produce the allenolate intermediate. The Cu−O cleavage associated with enol-isomerism affords acrylate (*E*)-Bpin-**2x** and Cu(OMe)L. Finally, (*E*)-**2x** was formed by C−B bond cleavage of (*E*)-Bpin-**2x** as described in path 1. The Cu(OMe)L returned to the catalytic cycle and was transformed into the active species Bpin-CuL.[19]

CONCLUSIONS

In conclusion, we discussed the interesting substrate-controlled copper-catalyzed stereoselective semi-reduction reactions of alkynes. Importantly, the high functionalized alkynes were compatible and the solvent also played the role of a hydrogen source in the process with the aid of B_2pin_2. On the basis of the comprehensive mechanism investigated, two rational catalytic cycles were proposed for different kinds of alkyne substrates. Efforts toward the reduction of other unsaturated bonds with the CTH strategy are currently underway in our lab.

EXPERIMENTAL SECTION

General Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. The HRMS data were obtained on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

Representative Procedure for the Synthesis of Internal Alkynes ***1****.* In a 25 mL round-bottom flask, aryl iodide (1 mmol), terminal alkyne (1.05 mmol), K_2CO_3 (2.0 mmol), $Pd(PPh_3)_4$ (0.1 mmol), and dimethylformamide (DMF) (10 mL) were successively added. The mixture was stirred at 60 °C for 24 h under a N_2 atmosphere. Then the reaction was diluted with EtOAc (100 mL) and washed with aqueous NH_4Cl (2 × 30 mL). The ethyl acetate layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluted with petroleum ether/ethyl acetate = 5/1−3/1) on silica gel to afford internal alkyne product **1**. The characterization data of **1a**,[20] **1b**,[21] **1d**,[20] **1e**,[22] **1h**,[23] **1i**,[24] and **1l**[25] were consistent with the reported literature.

Representative Procedure for Synthesis of Alkenes ***2****.* To a 20 mL sealed tube with a magnetic stirrer bar, $Cu(OAc)_2 \cdot 2H_2O$ (0.03 mmol), 4,4′-bpy (0.03 mmol), B_2pin_2 (0.30 mmol), ^{t}BuOK (0.09 mmol), alkyne **1** (0.30 mmol), and MeOH (2 mL) were successively added and vigorously stirred together at 60 °C under a N_2 atmosphere. After the reaction completed, the mixture was cooled to room temperature. The reaction was quenched with saturated aq NH_4Cl and extracted with EtOAc (3 × 15 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluted with petroleum ether/ethyl acetate) on silica gel to afford product **2**.

*Synthesis of (Z)-N-Allyl-4-methyl-N-(3-(p-tolyl)allyl)-benzenesulfonamide (****5****).* To a 20 mL sealed tube with a magnetic stirrer bar, $Cu(OAc)_2 \cdot 2H_2O$ (0.03 mmol), 4,4′-bpy (0.03 mmol), B_2pin_2 (0.30 mmol), ^{t}BuOK (0.09 mmol), **4** (0.30 mmol), and MeOH (2 mL) were successively added and vigorously stirred together at 60 °C under a N_2 atmosphere for 18 h. After the reaction completed, the mixture was cooled to room temperature. The reaction was quenched with saturated aq NH_4Cl and extracted with EtOAc (3 × 15 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed

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under vacuum. The crude product was purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 5:1) on silica gel to afford product **5** (74 mg, 72%) as a light yellow oil. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.53 (d, *J* = 11.7 Hz, 1H), 5.58 (ddt, *J* = 16.7, 10.0, 6.4 Hz, 1H), 5.47 (dt, *J* = 11.2, 6.4 Hz, 1H), 5.04−4.86 (m, 2H), 4.12 (dd, *J* = 6.5, 1.8 Hz, 2H), 3.77 (d, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 143.20, 137.34, 137.03, 133.30, 132.46, 132.32, 129.67, 128.95, 128.65, 127.23, 126.40, 118.99, 49.82, 44.65, 21.53, 21.19. High-resolution mass spectrometry-electrospray ionization (HRMS-ESI) (*m*/*z*): calcd for $C_{20}H_{23}NO_2SNa$, $[M + Na]^+$: 364.1347, found, 364.1354.

*Synthesis of (Z)-4-Methyl-N-(3-(p-tolyl)allyl)-benzenesulfonamide (**6**).*[26] To a 20 mL sealed tube with a magnetic stirrer bar, $Cu(OAc)_2{\cdot}2H_2O$ (0.02 mmol), 4,4′-bpy (0.02 mmol), B_2pin_2 (0.21 mmol), ^{t}BuOK (0.06 mmol), **5** (0.21 mmol), and MeOH (1.5 mL) were successively added and vigorously stirred together at 60 °C under a N_2 atmosphere for 18 h. After the reaction completed, the mixture was cooled to room temperature. The reaction was quenched with saturated aq NH_4Cl and extracted with EtOAc (3 × 15 mL). The combined ethyl acetate layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) on silica gel to afford product **6** (29 mg, 45%) as a light yellow oil. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.78−7.73 (m, 2H), 7.36−7.26 (m, 3H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.50 (d, *J* = 11.5 Hz, 1H), 5.52 (dt, *J* = 10.9, 6.7 Hz, 1H), 4.73−4.53 (m, 1H), 3.87 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 143.48, 137.32, 136.87, 132.94, 132.59, 129.73, 129.05, 128.53, 127.20, 125.67, 41.39, 21.55, 21.20.

Analytical Characterization Data of Substrates and Products. *tert-Butyl (3-(3-Methoxyphenyl)prop-2-yn-1-yl)-carbamate (**1c**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 2:1) as a brown oil (196 mg, 74%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.21 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 1.9 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.6 Hz, 1H), 4.87 (s, 1H), 4.16 (d, *J* = 5.3 Hz, 2H), 3.80 (s, 3H), 1.48 (s, 10H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.25, 155.32, 129.34, 124.20, 123.69, 116.54, 114.93, 85.23, 83.00, 80.00, 55.24, 31.20, 28.37. HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{19}NO_3Na$, $[M + Na]^+$: 284.1263, found, 284.1260.

*tert-Butyl (3-(Thiophen-3-yl)prop-2-yn-1-yl)carbamate (**1f**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 4:1) as a brown solid (193 mg, 80%), mp = 94−96 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.43 (d, *J* = 3.1 Hz, 1H), 7.32−7.22 (m, 1H), 7.09 (d, *J* = 4.8 Hz, 1H), 4.85 (s, 1H), 4.26−4.01 (m, 2H), 1.47 (d, *J* = 2.8 Hz, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 155.31, 129.85, 128.89, 125.28, 121.72, 85.03, 79.98, 78.26, 77.26, 31.19, 28.38. HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{15}NO_2SNa$, $[M + Na]^+$: 260.0721, found, 260.0722.

*2-(3-(p-Tolyl)prop-2-yn-1-yl)isoindoline-1,3-dione (**1g**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a yellow solid (262 mg, 94%), mp = 165−167 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.91 (dq, *J* = 5.5, 2.8 Hz, 2H), 7.77 (dt, *J* = 6.1, 3.1 Hz, 2H), 7.32 (dd, *J* = 8.1, 2.0 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 4.69 (d, *J* = 2.1 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.19, 138.63, 134.14, 132.12, 131.82, 128.95, 123.54, 119.22, 83.10, 81.90, 27.93, 21.47. HRMS-ESI (*m*/*z*): calcd for $C_{18}H_{14}NO_2$, $[M + H]^+$: 276.1025, found, 276.1031.

*2-(3-(1,3-Dioxoisoindolin-2-yl)prop-1-yn-1-yl)phenyl Acetate (**1j**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a light brown solid (180 mg, 56%), mp = 136−138 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.35 (td, *J* = 7.8, 1.7 Hz, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.70 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 169.09, 167.02, 152.03, 134.23, 133.39, 132.06, 129.85, 125.81, 123.55, 122.26, 116.43, 87.50, 77.95, 27.83, 20.77. HRMS-ESI (*m*/*z*): calcd for $C_{19}H_{14}NO_4$, $[M + H]^+$: 320.0923, found, 320.0925.

*3-(3-(p-Tolyl)prop-2-yn-1-yl)benzo[d]oxazol-2(3H)-one (**1k**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 2:1) as a light brown solid (243 mg, 91%), mp = 77−79 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.30−7.27 (m, 1H), 7.27−7.21 (m, 2H), 7.21−7.15 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.87 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 153.81, 142.67, 139.14, 131.72, 130.30, 129.12, 123.99, 122.80, 118.71, 110.09, 109.32, 85.66, 80.07, 32.79, 21.51. HRMS-ESI (*m*/*z*): calcd for $C_{17}H_{14}NO_2$, $[M + H]^+$: 264.1025, found, 264.1028.

*tert-Butyl (Z)-(3-(p-Tolyl)allyl)carbamate (**2a**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 4:1) as a white solid (66 mg, 90%), mp = 65−66 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.22−7.07 (m, 4H), 6.52 (dt, *J* = 11.5, 1.9 Hz, 1H), 5.64 (dt, *J* = 11.6, 6.6 Hz, 1H), 4.70 (s, 1H), 4.05 (d, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 155.84, 136.97, 133.56, 130.98, 129.00, 128.71, 128.15, 79.41, 39.06, 28.42, 21.19. HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{21}NO_2$, $[M + Na]^+$: 270.1470, found, 270.1475.

*tert-Butyl (Z)-(3-(4-Fluorophenyl)allyl)carbamate (**2b**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 4:1) as a white solid (70 mg, 92%), mp = 82−84 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.20 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 11.6 Hz, 1H), 5.67 (dt, *J* = 12.4, 6.5 Hz, 1H), 4.66 (s, 1H), 4.02 (s, 2H), 1.46 (d, *J* = 1.2 Hz, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 161.86 (d, *J* = 246.9 Hz), 155.77, 132.45 (d, *J* = 3.3 Hz), 130.37 (d, *J* = 8.0 Hz), 129.96, 128.82, 115.23 (d, *J* = 21.4 Hz), 79.55, 38.91, 28.39. HRMS-ESI (*m*/*z*): calcd for $C_{14}H_{19}NO_2F$, $[M + H]^+$: 252.1400, found, 252.1399.

*tert-Butyl (Z)-(3-(3-Methoxyphenyl)allyl)carbamate (**2c**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 2:1) as a light yellow oil (65 mg, 83%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.34−7.26 (m, 1H), 6.87−6.71 (m, 3H), 6.53 (d, *J* = 11.6 Hz, 1H), 5.69 (dt, *J* = 11.1, 6.6 Hz, 1H), 4.68 (s, 1H), 4.05 (d, *J* = 6.6 Hz, 2H), 3.82 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.48, 155.79, 137.78, 131.00, 129.28, 129.20, 121.25, 114.28, 112.79, 77.25, 55.21, 39.02, 28.40. HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{21}NO_3Na$, $[M + Na]^+$: 286.1419, found, 286.1428.

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*tert-Butyl (Z)-(3-(o-Tolyl)allyl)carbamate (**2d**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 5:1) as a light yellow oil (50 mg, 68%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30−7.15 (m, 4H), 7.11 (d, *J* = 6.3 Hz, 1H), 6.61 (d, *J* = 11.4 Hz, 1H), 5.76 (dt, *J* = 11.2, 6.7 Hz, 1H), 4.56 (s, 1H), 3.88 (d, *J* = 6.7 Hz, 2H), 2.28 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 155.77, 136.22, 135.46, 130.44, 129.92, 128.94, 128.64, 127.45, 125.52, 38.77, 28.41, 19.86. HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{21}NO_2Na$, $[M + Na]^+$: 270.1470, found, 270.1478.

*tert-Butyl (Z)-(3-(Pyridin-3-yl)allyl)carbamate (**2e**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 2:1) as a light yellow oil (66 mg, 84%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.50 (d, *J* = 2.5 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.32−7.28 (m, 1H), 6.51 (d, *J* = 11.8 Hz, 1H), 5.83 (dt, *J* = 11.2, 6.6 Hz, 1H), 4.73 (s, 1H), 4.01 (d, *J* = 6.6 Hz, 2H), 1.46 (d, *J* = 1.1 Hz, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 155.73, 149.78, 148.19, 135.73, 132.11, 131.55, 127.36, 123.18, 79.67, 38.93, 28.38. HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{18}N_2O_2Na$, $[M + Na]^+$: 257.1266, found, 257.1267.

*tert-Butyl (Z)-(3-(Thiophen-3-yl)allyl)carbamate (**2f**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 4:1) as a brown oil (67 mg, 94%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.34−7.28 (m, 1H), 7.22−7.11 (m, 1H), 7.07 (d, *J* = 5.0 Hz, 1H), 6.48 (d, *J* = 11.4 Hz, 1H), 5.62 (dt, *J* = 11.2, 6.5 Hz, 1H), 4.70 (s, 1H), 4.07 (d, *J* = 6.5 Hz, 2H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 155.84, 137.59, 128.39, 127.95, 125.46, 125.00, 123.71, 79.50, 77.25, 28.42. HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{17}NO_2NaS$, $[M + Na]^+$: 262.0878, found, 262.0883.

*(Z)-2-(3-(p-Tolyl)allyl)isoindoline-1,3-dione (**2g**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a white solid (75 mg, 91%), mp = 86−88 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.91−7.81 (m, 2H), 7.73 (dd, *J* = 5.6, 3.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.60 (d, *J* = 11.6 Hz, 1H), 5.63 (dt, *J* = 12.1, 6.4 Hz, 1H), 4.62 (dd, *J* = 6.5, 1.9 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 168.01, 137.09, 133.94, 132.17, 131.88, 129.10, 128.74, 126.44, 125.17, 123.26, 36.59, 21.24. HRMS-ESI (*m*/*z*): calcd for $C_{18}H_{16}NO_2$, $[M + H]^+$: 278.1181; found, 278.1181.

*(Z)-2-(3-(4-Methoxyphenyl)allyl)isoindoline-1,3-dione (**2h**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 2:1) as a white solid (77 mg, 88%), mp = 109−111 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.00−6.86 (m, 2H), 6.64−6.50 (m, 1H), 5.59 (dt, *J* = 11.3, 6.4 Hz, 1H), 4.61 (dd, *J* = 6.4, 1.9 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 168.05, 158.81, 133.95, 132.17, 131.46, 130.12, 128.86, 124.32, 123.26, 113.84, 55.28, 36.60. HRMS-ESI (*m*/*z*): calcd for $C_{18}H_{16}NO_3$, $[M + H]^+$: 294.1130, found, 294.1139.

*(Z)-4-(3-(1,3-Dioxoisoindolin-2-yl)prop-1-en-1-yl)-benzonitrile (**2i**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 2:1) as a white solid (79 mg, 92%), mp = 145−147 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.82 (dq, *J* = 6.7, 4.1, 3.3 Hz, 2H), 7.72 (dt, *J* = 5.2, 2.2 Hz, 2H), 7.65 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 6.61 (dd, *J* = 11.8, 2.0 Hz, 1H), 5.80 (dt, *J* = 11.3, 6.6 Hz, 1H), 4.51 (dd, *J* = 6.7, 2.0 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.86, 140.83, 134.17, 132.23, 131.98, 130.47, 129.42, 128.58, 123.36, 118.79, 110.94, 36.19. HRMS-ESI (*m*/*z*): calcd for $C_{18}H_{13}N_2O_2$, $[M + H]^+$: 289.0977, found, 289.0984.

*(Z)-2-(3-(1,3-Dioxoisoindolin-2-yl)prop-1-en-1-yl)phenyl Acetate (**2j**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a white solid (72 mg, 75%), mp = 98−100 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.90−7.82 (m, 2H), 7.73 (qt, *J* = 4.8, 2.4 Hz, 2H), 7.57 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.39−7.29 (m, 2H), 7.11 (dt, *J* = 7.7, 1.1 Hz, 1H), 6.51 (d, *J* = 11.3 Hz, 1H), 5.78 (dt, *J* = 11.2, 6.5 Hz, 1H), 4.44 (dt, *J* = 6.6, 1.3 Hz, 2H), 2.32 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 169.10, 167.93, 148.46, 133.97, 132.14, 130.26, 129.15, 128.81, 127.77, 126.96, 126.08, 123.26, 122.32, 36.39, 20.93. HRMS-ESI (*m*/*z*): calcd for $C_{19}H_{16}NO_4$, $[M + H]^+$: 322.1079, found, 322.1089.

*(Z)-3-(3-(p-Tolyl)allyl)benzo[d]oxazol-2(3H)-one (**2k**).* Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a white solid (74 mg, 93%), mp = 91−93 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32−7.16 (m, 5H), 7.10 (dq, *J* = 5.8, 3.4 Hz, 2H), 6.84−6.67 (m, 2H), 5.68 (dt, *J* = 12.1, 6.4 Hz, 1H), 4.77 (dd, *J* = 6.4, 1.8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 154.32, 142.66, 137.71, 133.48, 132.90, 130.77, 129.31, 128.76, 124.17, 123.75, 122.45, 109.93, 108.87, 40.49, 21.27. HRMS-ESI (*m*/*z*): calcd for $C_{17}H_{16}NO_2$, $[M + H]^+$: 266.1181, found, 266.1189.

*(Z)-(3-(Benzyloxy)prop-1-en-1-yl)benzene (**2l**).*[27] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 6:1) as a light yellow oil (52 mg, 77%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.46−7.26 (m, 10H), 6.68 (d, *J* = 11.9 Hz, 1H), 5.97 (dt, *J* = 12.2, 6.4 Hz, 1H), 4.58 (d, *J* = 3.2 Hz, 2H), 4.36 (dd, *J* = 6.3, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 138.19, 136.67, 131.82, 128.97, 128.81, 128.42, 128.25, 127.91, 127.82, 127.20, 72.52, 66.97.

*(Z)-3-Phenylacrylonitrile (**2m**).*[10] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 8:1) as a light yellow oil (25 mg, 65%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88−7.74 (m, 2H), 7.45 (p, *J* = 4.0, 3.4 Hz, 3H), 7.13 (d, *J* = 12.1 Hz, 1H), 5.45 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 148.73, 133.58, 130.99, 129.02, 128.94, 117.36, 95.08.

*(Z)-1,2-Diphenylethene (**2n**).*[10] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 20:1) as a light yellow oil (41 mg, 76%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 (dtt, *J* = 16.4, 6.7, 2.9 Hz, 10H), 6.75−6.64 (m, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 137.30, 130.32, 128.94, 128.28, 127.16.

*1,4-Di((Z)-styryl)benzene (**2o**).*[28] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 20:1) as a white solid (55 mg, 65%), mp = 85−87°C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.27 (dtd, *J* = 18.2, 8.0, 3.8 Hz, 10H), 7.15 (t, *J* = 1.7 Hz, 4H), 6.66−6.52 (m, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 137.32, 136.05, 130.30, 129.96, 128.86, 128.76, 128.21, 127.14.

*(Z)-1,4-Bis(benzyloxy)but-2-ene (**2p**).*[29] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 8:1) as a light yellow oil (61 mg, 76%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.35−7.26 (m, 10H), 5.83−5.71 (m, 2H), 4.50−4.43 (m, 4H), 4.05 (t, *J* = 3.5 Hz, 4H).

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^{13}C NMR (101 MHz, chloroform-*d*) δ 138.19, 129.59, 128.49, 127.87, 127.76, 72.31, 65.82.

1-Methoxy-4-vinylbenzene (**2q**).[30] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 20:1) as a light yellow oil (30 mg, 75%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.48−7.35 (m, 2H), 7.01−6.81 (m, 2H), 6.79−6.65 (m, 1H), 5.66 (dq, *J* = 17.4, 1.1 Hz, 1H), 5.17 (dt, *J* = 10.8, 1.3 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.38, 136.24, 130.45, 127.40, 113.92, 111.59, 55.30.

1-Fluoro-4-vinylbenzene (**2r**).[31] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 50:1) as a light yellow oil (26 mg, 71%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.51−7.36 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 162.49 (d, *J* = 246.8 Hz), 135.71, 133.76 (d, *J* = 3.4 Hz), 127.76 (d, *J* = 8.1 Hz), 115.42 (d, *J* = 21.6 Hz), 113.52 (d, *J* = 2.3 Hz).

2-Allylisoindoline-1,3-dione (**2s**).[32] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 8:1) as a white solid (47 mg, 84%), mp = 66−68 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.87 (dq, *J* = 6.0, 2.9 Hz, 2H), 7.73 (dt, *J* = 5.5, 2.7 Hz, 2H), 6.00−5.82 (m, 1H), 5.35−5.15 (m, 2H), 4.31 (dq, *J* = 5.7, 1.6 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.92, 133.98, 132.10, 131.53, 123.31, 117.73, 40.05.

N-Allyl-N-phenylacetamide (**2t**).[33] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 8:1) as a white solid (37.8 mg, 72%), mp = 43−45 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.41 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.38−7.32 (m, 1H), 7.17 (dd, *J* = 7.5, 1.7 Hz, 2H), 5.88 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.18−5.02 (m, 2H), 4.31 (dt, *J* = 6.2, 1.3 Hz, 2H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 170.15, 143.00, 133.14, 129.57, 128.10, 127.87, 117.80, 52.03, 22.72.

3-Allylbenzo[d]oxazol-2(3H)-one (**2u**).[34] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 8:1) as a white solid (41 mg, 78%), mp = 39−40 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.27−7.05 (m, 3H), 6.98 (d, *J* = 7.4 Hz, 1H), 5.91 (ddd, *J* = 21.4, 10.5, 5.3 Hz, 1H), 5.37−5.23 (m, 2H), 4.46 (dd, *J* = 5.4, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 154.35, 142.64, 130.93, 130.53, 123.80, 122.49, 118.75, 110.00, 108.90, 44.62.

1-Allyl-1,2,3,4-tetrahydroquinoline (**2v**).[35] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 6:1) as a brown oil (47 mg, 92%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.08 (t, *J* = 7.7 Hz, 1H), 7.00 (dd, *J* = 7.0, 1.6 Hz, 1H), 6.68−6.54 (m, 2H), 5.90 (dddd, *J* = 18.2, 10.1, 5.1, 1.1 Hz, 1H), 5.36−5.12 (m, 2H), 3.92 (dq, *J* = 4.7, 1.5 Hz, 2H), 3.34−3.30 (m, 2H), 2.82 (t, *J* = 6.3 Hz, 2H), 2.02 (dd, *J* = 6.6, 5.2 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 145.35, 133.58, 129.01, 127.08, 122.42, 115.91, 115.77, 111.03, 53.87, 49.19, 28.19, 22.35.

But-3-en-1-yl 1-Naphthoate (**2w**).[36] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 10:1) as a light yellow oil (56 mg, 82%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.98 (dd, *J* = 8.9, 3.6 Hz, 1H), 8.23 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.95−7.88 (m, 1H), 7.65 (tt, *J* = 8.3, 1.5 Hz, 1H), 7.54 (dt, *J* = 15.7, 7.4 Hz, 2H), 5.97 (ddtd, *J* = 17.0, 10.3, 6.7, 1.2 Hz, 1H), 5.35−5.14 (m, 2H), 4.52 (td, *J* = 6.6, 1.3 Hz, 2H), 2.63 (qd, *J* = 6.7, 1.3 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.56, 134.23, 133.86, 133.33, 131.38, 130.19, 128.56, 127.72, 127.33, 126.21, 125.89, 124.52, 117.47, 64.14, 33.30.

Ethyl Cinnamate (**2x**).[37] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 10:1) as a light yellow oil (47 mg, 90%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.54 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.40 (q, *J* = 3.0 Hz, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.36 (dd, *J* = 7.6, 6.7 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 166.97, 144.57, 134.48, 130.20, 128.87, 128.04, 118.30, 60.49, 14.33.

Benzyl Cinnamate (**2y**).[38] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 12:1) as a light yellow oil (55 mg, 78%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.75 (dd, *J* = 16.1, 3.4 Hz, 1H), 7.53 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.40 (ddt, *J* = 13.8, 10.5, 5.2 Hz, 8H), 6.51 (dd, *J* = 16.1, 2.9 Hz, 1H), 5.33−5.21 (m, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 166.81, 145.21, 136.10, 134.38, 130.38, 128.92, 128.63, 128.31, 128.29, 128.14, 117.91, 66.39.

N-Benzylcinnamamide (**2z**).[39] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 5:1) as a white solid (60 mg, 85%), mp = 108−110 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.69 (d, *J* = 15.6 Hz, 1H), 7.51 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.45−7.28 (m, 8H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.10 (s, 1H), 4.59 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 165.79, 141.41, 138.20, 134.79, 129.72, 128.82, 128.76, 127.93, 127.81, 127.59, 120.45, 43.88.

(Z)-2-(3-(p-Tolyl)allyl-2,3-d$_2$)isoindoline-1,3-dione (**d-2g**). Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a white solid (72 mg, 87%), mp = 85−87 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.62 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 168.02, 137.10, 133.94, 133.30, 132.17, 129.11, 128.74, 123.26, 36.50, 21.24. HRMS-ESI (*m*/*z*): calcd for $C_{18}H_{13}D_2NO_2$, [M + H]$^+$: 280.1307, found, 280.1306.

(Z)-3-(3-(p-Tolyl)allyl-2,3-d$_2$)benzo[d]oxazol-2(3H)-one (**d-2k**). Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 3:1) as a white solid (72 mg, 90%), mp = 90−92 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30−7.22 (m, 4H), 7.20 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.10 (dd, *J* = 5.8, 3.3 Hz, 2H), 6.73 (dd, *J* = 5.8, 3.3 Hz, 1H), 4.77 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 154.31, 142.65, 137.70, 132.83, 130.77, 129.31, 128.77, 123.76, 122.45, 109.92, 108.87, 77.44, 77.12, 76.80, 40.41, 21.28. HRMS-ESI (*m*/*z*): calcd for $C_{17}H_{13}D_2NO_2$, [M + H]$^+$: 268.1307, found, 268.1309.

(E)-2-(Allyl-2,3-d$_2$)isoindoline-1,3-dione (**d-2s**). Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 4:1) as a white solid (49 mg, 86%), mp = 62−64 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.87 (dd, *J* = 5.0, 2.5 Hz, 2H), 7.73 (dd, *J* = 5.5, 2.9 Hz, 2H), 5.24 (s, 0.5H), 4.30 (s, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.93, 133.98, 132.10, 123.31, 39.93. HRMS-ESI (*m*/*z*): calcd for $C_{11}H_{16}D_3NO_2$, [M + H]$^+$: 191.0900, found, 191.0901.

(Z)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**).[40] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 8:1) as a white solid, (235 mg, 88%), mp = 89−91 °C. ^{1}H NMR (400

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MHz, chloroform-*d*) δ 7.40 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.26−7.22 (m, 1H), 7.20 (dt, J = 8.1, 1.7 Hz, 2H), 7.17−7.12 (m, 3H), 7.12−7.04 (m, 2H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 143.17, 140.43, 136.98, 129.96, 128.85, 128.24, 127.85, 127.58, 126.26, 83.79, 77.23, 24.80.

*(Z)-N-Benzyl-3-phenylacrylamide ((Z)-**2y**).*[41] Purified by flash column chromatography (eluted with petroleum ether/ethyl acetate (v/v) = 5:1) as a white solid, (134 mg, 82%), mp = 110−112 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.46−7.39 (m, 2H), 7.33−7.26 (m, 6H), 7.17 (dd, J = 7.5, 2.1 Hz, 2H), 6.80 (d, J = 12.5 Hz, 1H), 6.04 (d, J = 12.5 Hz, 1H), 5.87 (s, 1H), 4.43 (d, J = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 166.93, 137.59, 136.51, 134.91, 128.91, 128.64, 128.57, 128.45, 127.99, 127.51, 124.72, 43.60.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01083.

Details of hydrogen-deuterium exchange and control experiments and ^{1}H and ^{13}C NMR spectra of all products (PDF)

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Notes

The authors declare no competing financial interest.

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