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Copper-catalyzed remote double functionalization of allenynes†

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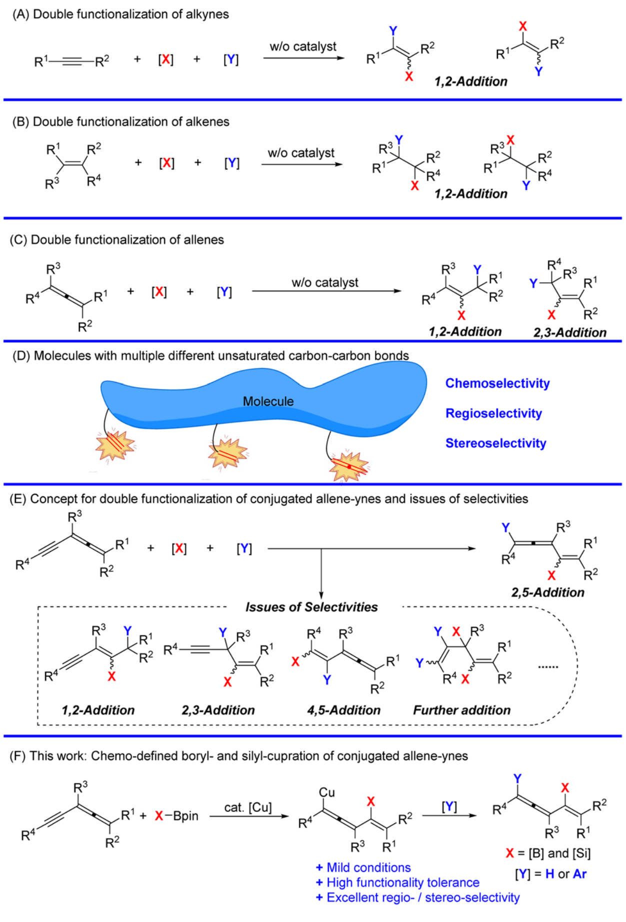
Addition reactions of molecules with conjugated or non-conjugated multiple unsaturated C–C bonds are very attractive yet challenging due to the versatile issues of chemo-, regio-, and stereo-selectivities. Especially for the readily available conjugated allenyne compounds, the reactivities have not been explored. The first example of copper-catalyzed 2,5-hydrofunctionalization and 2,5-difunctionalization of allenynes, which provides a facile access to versatile conjugated vinylic allenes with a C–B or C–Si bond, has been developed. This mild protocol has a broad substrate scope tolerating many synthetically useful functional groups. Due to the highly functionalized nature of the products, they have been demonstrated as platform molecules for the efficient syntheses of monocyclic products including poly-substituted benzenes, bicyclic compounds, and highly functionalized allene molecules.

Unsaturated hydrocarbons are a class of very important compounds due to their ubiquity in organic synthesis, natural products, materials, and pharmaceuticals.[1–4] Of particular interest, studies on versatile reactivities of C–C multiple bonds have been drawing more and more attention from organic, medicinal, and materials chemists.[5–7] The reactions of the C–C double bond and C–C triple bond, including hydro-functionalization and difunctionalization reactions, have been extensively developed with attractive regio- and stereo-selectivity (Schemes 1A and B).[8–42] Recently, the addition reactions of allenes, which deliver stereodefined olefins with decent regio-selectivities, have also been established (Scheme 1C).[43–60] Such reactions of molecules with multiple unsaturated C–C bonds are very attractive yet challenging due to the versatile issues of chemo-, regio-, and stereo-selectivities (Scheme 1D).[61–63] Although conjugated enynes and dienes have been studied,[64–66] the reaction of allenynes merging an alkyne unit and an allene unit in a conjugated manner has not been studied.[67–69] It would be challenging to control the related selectivities forming different 1,2-, 2,3-, 2,5-, 4,5-addition products with different unsaturated C–C bonds (Scheme 1E). Herein, we wish to disclose our recent observation on copper-catalyzed highly regioselective 2,5-boryl- and silyl-cupration of readily available conjugated allene-ynes for efficient synthesis of conjugated vinylic allenes with a versatile C–B or C–Si bond (Scheme 1F).

We initiated the study with the reaction of allenyne **1a**[70–89] and $B_2(pin)_2$ **2a** in the presence of MeOH with NaO^{t}Bu as the



Scheme 1 Double functionalization of alkynes, alkenes, allenes, and conjugated allene-ynes.

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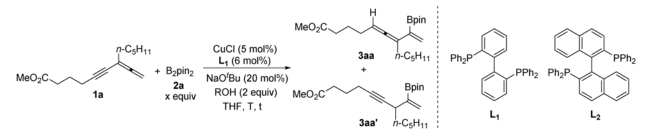
base and CuCl (5 mol%) and Biphep (**L$_1$**) (6 mol%) as the catalyst at 30 °C in THF for 16 h. To our delight, the 2,5-addition product, 1,3,4-trienyl boronate **3aa**, was formed in 33% yield with 3% yield of the 2,3-addition product, 1,4-enyne **3aa′** (entry 1, Table 1). Upon adjusting the ratio of **1a**/**2a** to 1/1, a much higher yield of the desired product **3aa** was achieved (entries 2–5, Table 1). When the reaction was conducted at 15 °C, the yield of **3aa** was improved to 85% with 5% yield of **3aa′** (entry 6, Table 1). Interestingly, when MeOH was replaced with ^{t}BuOH, the generation of **3aa′** was completely suppressed with 43% yield of 2,5-double functionalization product **3aa** (entry 9, Table 1). Further screening of the ligand and [Cu] with ^{t}BuOH led to the observation that the combination of Binap (**L$_2$**) and Cu(CH$_3$CN)$_4$PF$_6$ was better than that with Biphep and CuCl as the catalyst with the yield of 86% with 4% recovery of **1a** (entries 10–11, Table 1). Upon adjusting the ratio of **1a**/**2a** to 1/1.05, the reaction delivered the best results affording **3aa** in 87% yield with no recovery of **1a** and no formation of **3aa′** (entry 12, Table 1).

With the optimized reaction conditions in hand (entry 12, Table 1), we next investigated the reactivity of various allenynes (Table 2). A series of allenynes bearing different R^1 substituents incorporating functional groups, such as ester (**3aa**), highly strained cyclopropyl (**3ca**), benzyl (**3da**), halide (**3ea**), and nitrile (**3ga**) were all tolerated with the yields of 77–97%. In addition, the substrate with the OH group being protected as TBS ether also could undergo the reaction smoothly with the yield of 80% (**3fa**). Even the glucose-derived allenyne also afforded the boryl-substituted 1,3,4-triene **3ha** with the yield of 65%. R^1 may also be aryl groups; a variety of different substituents on the aryl units including electron-donating (**3ja** and **3ka**) and electron-withdrawing groups as well as biologically or synthetically useful groups such as F, Cl, Br, CF$_3$, CN, and COOMe at the *para*-, *ortho*-, or *meta*-position (**3la**–**3sa**) were accommodated to afford the 1,3,4-trien-2-yl boronates in moderate to good yields (64–87%). *p*-NO$_2$ on the benzene ring also survived with 48% yield of **3ta**. Different R^2 groups bearing halide (**3ua**, 76%) and benzyl (**3va**, 53%) were tolerated.

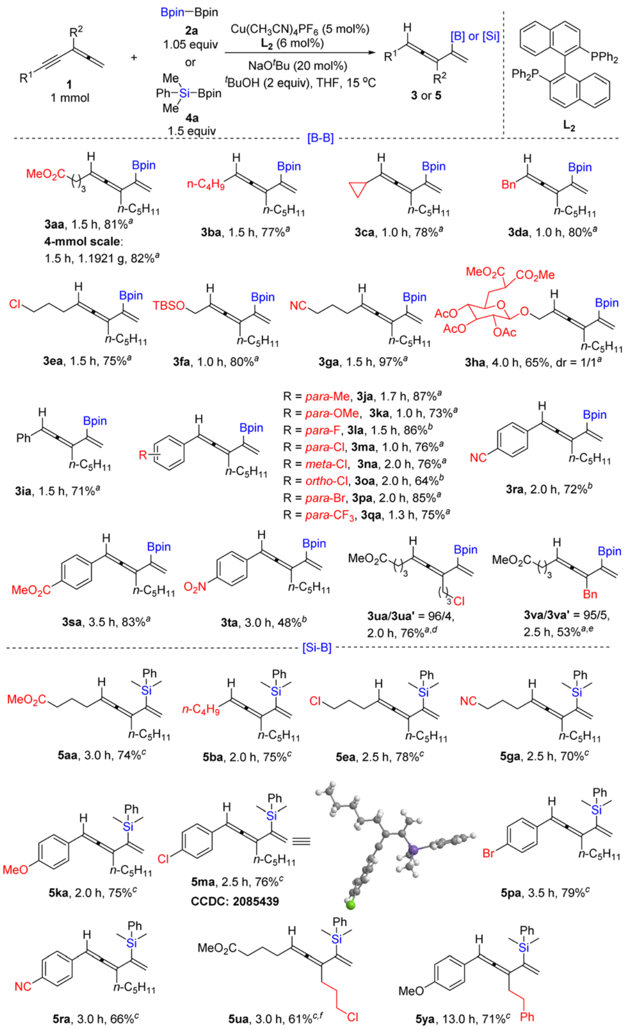
Table 1 Optimization of the conditions^a



Entry	ROH	*X*	*T* (°C)	*t* (h)	**1a** (%)^b	**3aa**/**3aa′** (%)^b
1	MeOH	2.0	30	16	0	33/3
2	MeOH	1.5	30	16	0	51/6
3	MeOH	1.2	30	15.5	0	62/7
4	MeOH	1.1	30	15.5	0	73/6
5	MeOH	1.0	30	15.5	0	80/6
6	MeOH	1.0	15	5.5	5	85/5
7	MeOH	1.0	40	5.5	4	80/4
8	MeOH	1.0	50	5	4	71/3
9	^{t}BuOH	1.0	15	16	35	43/0
10^c	^{t}BuOH	1.0	15	13	10	83/0
11^{c,d}	^{t}BuOH	1.0	15	1	4	86/0
12^{c,d}	^{t}BuOH	1.05	15	1	0	87/0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (*X* equiv.), CuCl (5 mol%), Biphep (**L$_1$**) (6 mol%), NaO^{t}Bu (20 mol%), and ROH (2 equiv.) in THF (1 mL). [b] Determined by ^{1}H NMR analysis of the crude product using mesitylene as the internal standard. [c] Binap (**L$_2$**) was applied instead of Biphep (**L$_1$**). [d] Cu(CH$_3$CN)$_4$PF$_6$ was applied instead of CuCl.

Table 2 Scope of 2,5-hydrofunctionalization



[a] Reaction conditions: **1**, **2a** (1.05 equiv.), ^{t}BuOH (2.0 equiv.), Cu(CH$_3$CN)$_4$PF$_6$ (5 mol%), Binap (**L$_2$**) (6 mol%), and NaO^{t}Bu in THF (5 mL) at 15 °C on a 1.0 mmol scale. [b] 1.1 equiv. **2a** was used. [c] Reaction conditions: **1** (1 equiv.), **4a** (1.5 equiv.), ^{t}BuOH (2.0 equiv.), Cu(CH$_3$CN)$_4$PF$_6$ (5 mol%), Binap (6 mol%) and NaO^{t}Bu in THF (5 mL) at 15 °C on a 1.0 mmol scale. [d] **3ua′** is 2-(3-(3-chloropropyl)-9-methoxy-9-oxonon-1-en-4-yn-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. [e] **3va′** is 2-(3-benzyl-9-methoxy-9-oxonon-1-en-4-yn-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. [f] On a 0.5 mmol scale.

Furthermore, B$_2$(pin)$_2$ **2a** may be replaced with Me$_2$PhSiBpin **4a**. The corresponding 1,3,4-trien-2-yl silanes bearing different R^1 functional groups, such as ester (**5aa**), halide (**5ea**), and nitrile (**5ga**), were obtained in yields of 70–78%. In addition, synthetically versatile *p*-OMe (**5ka**), -Cl (**5ma**), -Br (**5pa**), and -CN (**5ra**) on the benzene ring also survived with the yields of 66–

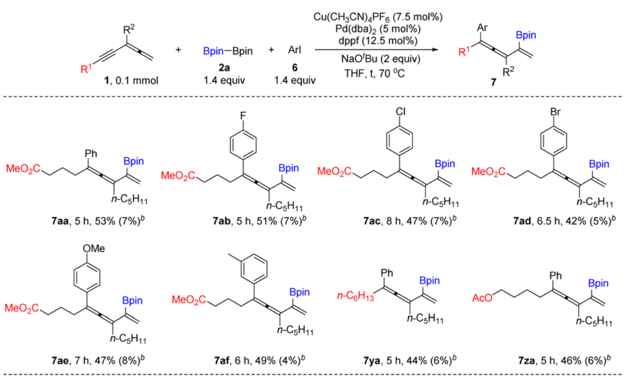
79%. As for different substitutions at the R^2 position, **1u** (R^2 = ClC$_3$H$_6$–) and **1y** (R^2 = PhC$_2$H$_4$–) were tested to afford the corresponding silane products **5ua** in 61% yield and **5ya** in 71% yield, respectively.

In addition, trisubstituted allenyne (**1w**) and tetrasubstituted allenyne (**1x**) are also suitable for affording the corresponding *Z*- and *E*-isomers of 1,3,4-trienyl boronates **3wa** in 68% yield and **3xa** in 68% yield. Furthermore, the reaction of **1w** also works with Me$_2$PhSiBpin **4a** affording 1,3,4-trien-2-yl silanes *E*-**5wa** in 75% yield (Scheme 2). When we tried iodobenzene as the electrophile under standard conditions, the target arylborylation product **7aa** was not produced. Interestingly, **7aa** was formed when an extra catalytic amount of Pd(dba)$_2$ was introduced (Table 3). Further screening of the temperature and ligand led to the formation of **7aa** in 53% yield. Aryl iodides with different electron-donating or -withdrawing groups afforded **7ab**, **7ac**, **7ad**, **7ae**, and **7af** in 42–51% yields. Allenynes with different alkyl substituents (R^2 = *n*-C$_6$H$_{13}$–, AcOC$_4$H$_8$–) also afforded the desired products **7ya** and **7za** (Table 3). 2,5-Hydrofunctionalization byproducts **3** were observed in all the cases, indicating that the Cu-catalyzed borylation reaction occurred before the Pd cross-coupling reaction with ArI.

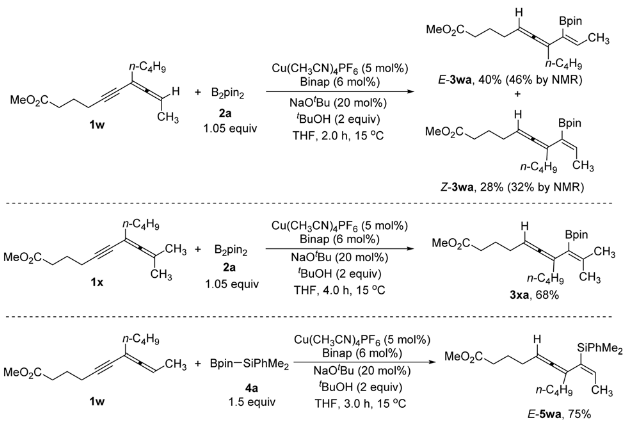
To gain insight into the mechanism, a deuterium-labelling experiment was conducted. When the reaction was performed with a stoichiometric amount of ^{t}BuOD, 70% of [D]-**3aa** with 75% deuterium incorporation at the allenic position was observed (Scheme 3A). When the R^1 group in **1z′** is a highly sterically hindered TMS group, the reaction failed to afford the 1,3,4-trienes. Instead, 1,4-enyne [D]-**3za′** with 66% deuterium incorporation was formed, indicating that the steric hindrance of TMS plays a critical role in determining the regioselectivity (Scheme 3B). On the basis of these experimental data, we proposed a possible mechanism (Scheme 3C). Initially, the copper–boryl complex **I** is generated *in situ via* the reaction of B$_2$(pin)$_2$ with the Cu precursor. Then, the C=C bond in the allene next to the C–C triple bond highly regioselectively inserted into the copper–boryl bond in **I** with the boron connected to the middle carbon atom to afford the propargylic copper species **II**, which would rapidly isomerize to allenyl copper species **III** and subsequently get trapped with ^{t}BuOD to produce the final product [D]-**3**, regenerating LCuO^{t}Bu to complete this catalytic cycle. Meanwhile, protonation of another isomeric form **II** at the γ position would also afford product [D]-**3**. When the R group is the sterically bulky TMS group, **II** would directly undergo protonolysis to form 1,4-enyne [D]-**3za′**. In the first step, the allene was inserted into the copper–boryl bond in intermediate **I** since the allene unit is more reactive than the alkyne unit. The regioselectivity for the protonolysis depended on the steric hindrance of the R^1 group in copper species **II** or **III**.

In order to showcase the synthetic utility of the products, further transformations of the 1,3,4-trien-2-yl boronates/silanes were demonstrated (Scheme 4): The one-pot sequential 2,5-

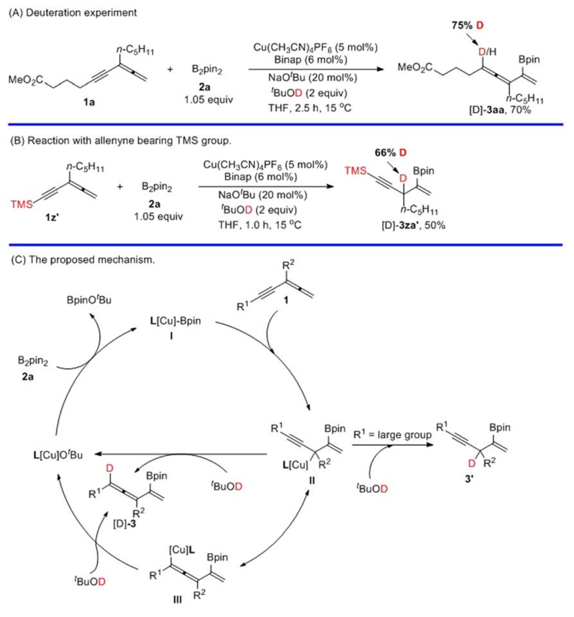
Table 3 Scope of 2,5-arylboration[a]



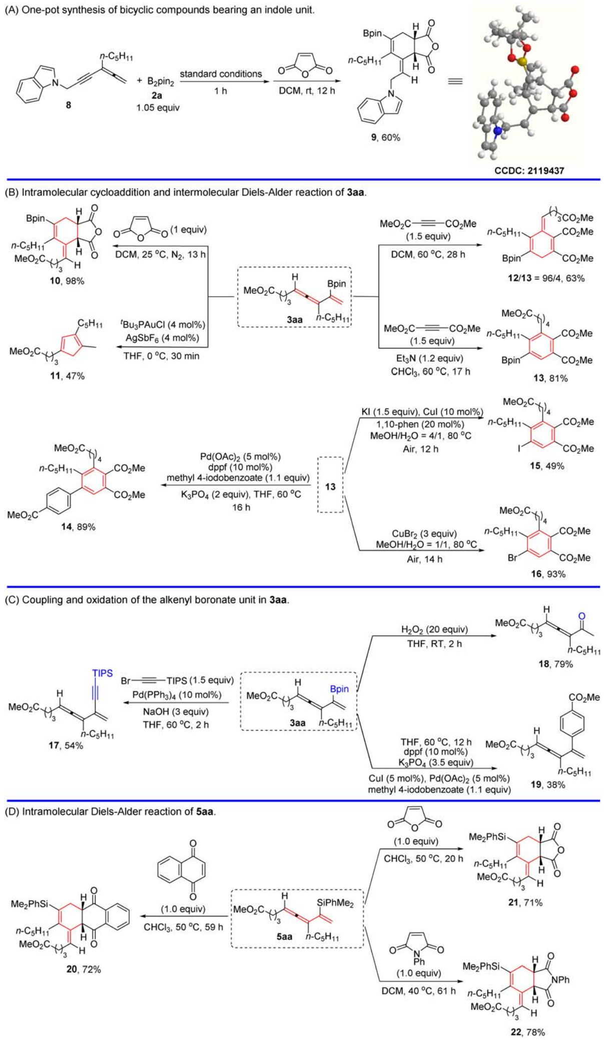
[a] Reaction conditions: **1** (0.1 mmol), **2a** (1.4 equiv.), **6** (1.4 equiv.), Cu(CH$_3$CN)$_4$PF$_6$ (7.5 mol%), Pd(dba)$_2$ (5 mol%), dppf (12.5 mol%), and NaO^{t}Bu (2 equiv.) in THF (1 mL) at 70 °C on a 0.1 mmol scale. [b] ^{1}H NMR yield of 2,5-hydroboration by-products **3aa**, **3ya**, and **3za** in parentheses.



Scheme 2 Scope of trisubstituted and tetrasubstituted allenynes



Scheme 3 Deuteration experiment and the proposed mechanism.



Scheme 4 Synthetic applications.

borylcurpration of allenyne **8** and a Diels–Alder reaction with maleic anhydride afforded stereodefined bicyclic lactonyl borate **9** (Scheme 4A).[90] Similarly, allenene **3aa** could also be readily converted to corresponding bicyclic lactone product **10**, 1,4-cyclohexadiene with a stereodefined exo-cyclic C═C double bond **12**, and penta-substituted benzene **13** *via* a Diels–Alder reaction with dimethyl but-2-ynedioate under different conditions. Such differently polysubstituted benzenes are difficult to prepare yet very useful.[91] In order to show the reactivity of the C–B bond, the Diels–Alder product **13** was employed for further transformation. Firstly, **13** was successfully coupled with methyl 4-iodobenzoate to afford **14** in 89% yield.[92] Secondly, the iodination of **13** with KI afforded the iodination product **15** in 49% yield catalyzed by copper iodide under air.[93] Thirdly, bromination of the C–B bond in **13** has been realized to afford **16** in an excellent yield by its treatment with copper bromide.[93] The intramolecular cycloisomerization of **3aa** also proceeded smoothly to give the corresponding cyclopentadienyl boronate **11** (Scheme 4B).[94] Moreover, **3aa** could be readily converted into 2-alkynyl-1,3,4-triene **17** *via* alkynylation with alkynyl bromide[79] and allenyl ketone **18** *via* oxidation with H_2O_2.[95] In addition, the C–B bond in **3aa** was successfully coupled with methyl 4-iodobenzoate to afford **19** in 38% yield even in the presence of a highly reactive allene unit (Scheme 4C). Meanwhile, other dienophiles, such as 1,4-naphthoquinone, maleic anhydride, and *N*-phenylmaleimide, could all undergo the Diels–Alder reaction with silane **5aa** to produce the corresponding products **20**, **21**, and **22** in decent yields (Scheme 4D).[90]

Conclusions

In summary, we have developed the first example of copper-catalyzed 2,5-boryl- or silyl-cupration of allenynes, providing an efficient protocol for substituted 1,3,4-trien-2-yl boronates or silanes with excellent regioselectivity. This method has advantages of a readily available catalyst and starting materials, high catalytic activity, mild conditions, a broad substrate scope tolerating many synthetically useful functional groups, and synthetically useful functionalities. The synthetic utility of this protocol has been demonstrated *via* the versatile transformations of the resulting products to furnish valuable functionalized molecules. Further studies are being actively pursued in our laboratory.

Data availability

The data supporting this article have been uploaded as the ESI.†

Author contributions

S. M. and J. Z. conceived and designed the experiments. Y. S., J. Z. performed the experiments. Y. S., C. F., J. Z., and S. M. wrote the manuscript. S. M. and J. Z. directed the research.

Conflicts of interest

There are no conflicts to declare.

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