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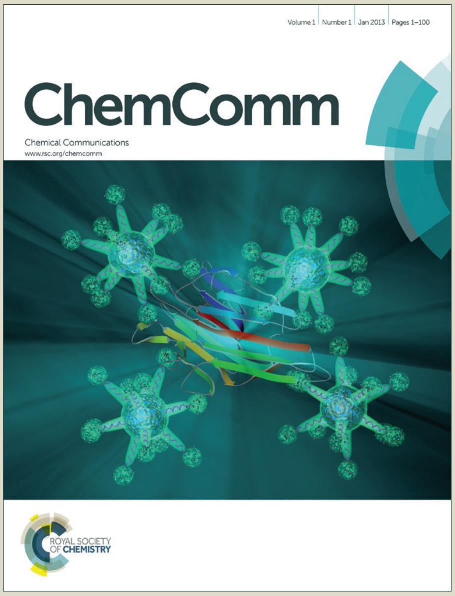

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Highly Selective Copper-Catalyzed Trifunctionalization of Alkynyl Carboxylic Acids: An Efficient Route to Bis-Deuterated β-Borylated α, β-Styrene

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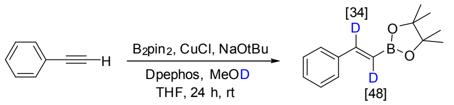
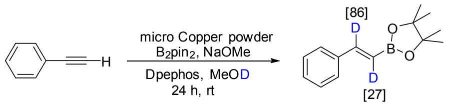
Abstract: A copper-catalyzed highly efficient protocol for the synthesis of bis-deuterated β-borylated α, β-styrene derivatives, which can be further transformed to practical isotopically labeled compounds, has been developed. Alkynyl carboxylic acids are employed as alkyne synthons yet demonstrate a sharp discrepancy in reactivity and selectivity from terminal alkynes. Meanwhile, this reaction offers a novel and efficient strategy to highly selective trifunctionalization of carbon-carbon triple bond at ambient temperature.

Efficient incorporation of deuterium is a valuable transformation for the preparation of isotopically labeled compounds that have wide applications in mechanistic investigations of organic transformations, spectroscopic analysis, or the monitoring of metabolism.[1] Alkenylboron compounds are especially versatile building blocks that are widely employed as vinyl anionic or cationic synthons in a myriad of coupling reactions,[2] as well as they can be readily transformed into various vinylic derivatives.[3] Owing to the versatile application of vinylic derivatives in organic synthesis, especially in the C-H functionalization of C=C bond,[4] alkenylboron compounds with deuteration at α, β positions would be increasingly attractive in organic synthesis for mechanistic study[5]. Over the past decade, great progress have been achieved on the transition-metal-catalyzed formations of alkenylboron compounds.[6] Among them, hydroborylation of C≡C bonds presents a convenient and important strategy for alkenylboron synthesis.[7] To the best of our knowledge, however, no straightforward and highly efficient approach to alkenylboron compounds with deuteration at α, β positions under ambient temperature has been reported yet. Existing methods for accessing the (*E*)-bis-deuterated β-borylated α, β-styrene suffer from low deuteration at α, β positions [Eqs. (**1**)-(**2**)].[7c], [8] It remains a big challenge to selectively synthesize bis-deuterated β-borylated α, β-styrene as one single isomer with high deuterium incorporation.

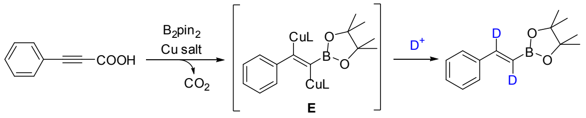


(1)



(2)

As part of our ongoing research on the development of highly efficient and versatile copper-catalyzed decarboxylative reactions,[9] decarboxylative coupling from alkynyl carboxylic acid also attracted our great interest. Inspired by the mechanistic investigations on both the copper-catalyzed decarboxylation from alkynyl carboxylic acid[10] and the copper-catalyzed hydroborylation reaction[11], we envisioned that a (*E*)-alkenyl-bis-copper reactive intermediate **E**, which has two reactive positions with two copper atoms on, could be generated *in situ* from alkynyl carboxylic acid with diboron reagent in the presence of copper salt under proper conditions. We anticipated that if electrophiles, such as D^+, were added, the two active copper atoms would react to afford the (*E*)-bis-deuterated β-borylated α, β-styrene with both high regio- and chemoselectivitives (Scheme 1).



(3)

Scheme 1. Putative mechanism

Herein, we reported a copper-catalyzed straightforward and highly efficient protocol for the synthesis of (*E*)-bis-deuterated β-borylated α, β-styrene derivatives from alkynyl acids with bis(pinacolato)diboron by employing readily available and cheap D_2O as a deuterium source under mild reaction conditions. In this protocol, alkynyl acids serve as alkyne synthons yet demonstrate superior reactivity and regio- and chemo-selectivities in comparison to phenylacetylenes [Eqs. (**4**)-(**5**)]. Comparative studies with phenylacetylenes and bis(pinacolato)diboron based on precedent methods [Eqs. (**1**)-(**2**)] further emphasize the significance, essential and superiority of alkynyl carboxylic acids in this protocol. Moreover, this protocol might provide a general strategy to highly selective trifunctionalization of C≡C bond at mild conditions, which

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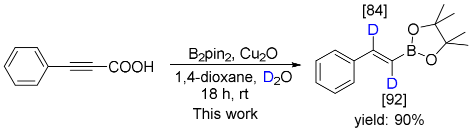
hopefully will attract more organic chemists working on this appealing field.



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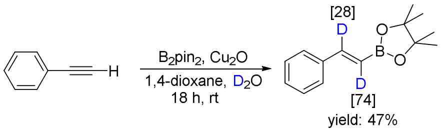


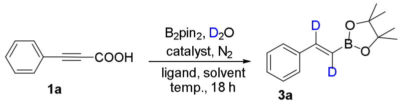
(5)

Our initial efforts towards the copper-catalyzed synthesis of (*E*)-bis-deuterated β-borylated α, β-styrene derivatives commenced with the treatment of phenylpropiolic acid **1a** (0.5 mmol) and bis(pinacolato)diboron **2** (1.2 equiv., 0.6 mmol) with copper salts (10 mol%) as catalysts, D_2O (6 equiv., 3 mmol) as deuterium source in the presence of bases and solvents (1 mL) at various temperature under 1 atm N_2 (SI, Table 1). According to the previous reports, most of transition-metal catalyzed additions of diboron to C≡C bonds were performed successfully with essential bases. Surprisingly, in our process of condition screening, (*E*)-bis-deuterated β-borylated α, β-styrene (**3a**) was obtained in 37% yield (Table 1, entry 2) in the absence of base. This result inspired us and then we attempted to conduct the reaction under base-free conditions (SI, Table 2). To our delight, when the reaction was conducted with Cu_2O (10 mol%) at 80 ^{o}C, (*E*)-bis-deuterated β-borylated α, β-styrene (**3a**) was obtained in a 76% yield (entry 3), which was similar to the optimal reaction conditions with base (entry 1). Further solvents screening demonstrated that 1, 4-dioxane was the best solvent (entries 3-8). Most remarkably, (*E*)-bis-deuterated β-borylated α, β-styrene (**3a**) was obtained in 96% GC yield (entry 10) at room temperature vs. 31% GC yield at 80 ^{o}C when PPh_3 was employed (10 mol%) as ligand, probably due to an enormous ligand effect on the reactivity of copper complex. Encouraged by this result, further ligand screenings suggested that Xantphos is the superior one over PCy_3, DPPE, Dpephos, 1,10-Phen, P(*n*-Bu)$_3$ and NHC in this transformation, yet PPh_3, DPPB might be alternatives for this reaction (entries 17–23**)**. Among copper catalysts, $Cu(OAc)_2$ also exhibited a good reactivity (85% GC yield) (entry 21), yet no reaction was detected in the presence of CuCl, CuI, and CuO (entries 12, 14, 15).

Eventually, the optimal reaction conditions emerged as phenylpropiolic acid (**1a**) (0.5 mmol), bis(pinacolato)diboron (**2**) (1.2 equiv., 0.6 mmol), Cu_2O (10 mol%), Xantphos (10 mol%), D_2O (6 equiv., 3 mmol), 1,4-dioxane (1 mL) at ambient temperature. Notably, (*E*)-β-vinylboronate was detected as the single product, and no other isomers such as α-vinylbonate and (*Z*)-β-vinylboronate which are either products or by-products in the previous reports were ever detected.

After establishing the optimized reaction conditions, a variety of alkynyl carboxylic acids were subjected to the optimized conditions to evaluate the scope of copper-catalyzed formation of bis-deuterated β-borylated α, β-styrene derivatives. As shown in Scheme 2, arylpropiolic acids with electron-rich groups on the aromatic ring (**3b–3g**) could be smoothly converted into the desired products in excellent yields. Arylpropiolic acids bearing electron-deficient substituents (**3h–3p, 3q–3r**) were less effective with the formation of the desired products in moderate to good yields, yet the deuterium incorporation was >95%. The position of the substitutes on the aromatic rings had great effect on yields (**3h–3j, 3k–3m, 3n–3p**), with *ortho*-substitution usually giving lower yields of desired products when compared to *meta*- and *para*-substitution, probably as a result of steric hindrance. It is noteworthy that halo-substituted aryl groups survived well in this transformation, leading to halo-substituted aromatic bis-deterated β-borylated α, β-styrene which could be used for further structural manipulations. In addition, 1-naphthyl, *para*-phenyl substituted phenylpropiolic acid (**3s–3t**) were also transformed well into corresponding desired products in excellent yields, and heteroaromatic propiolic acid, for instance 3-(thiophen-2-yl) propiolic acid (**3u**) was competent in this transformation as well and afforded the desired product in a moderate yield. Significantly, base sensitive functional groups, such as alchohol, ketone and ester groups were also compatible in this transformation and readily turned into corresponding bis-deuterated β-borylated α, β-styrene in this protocol (**3v–3x**). Finally, aliphatic alkynyl carboxylic acids (**3y–3z**) were also proven to be good candidates in this general protocol, further emphasizing the wide scope of this transformation.

Table1. Optimization of the reaction parameters.[a]



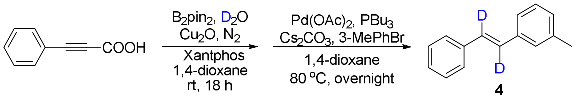
entry	catalyst [10 mol%]	ligand [10 mol%]	base [2.2 equiv.]	solvent	temp [^{o}C]	yield [%][b]
1	$Cu(TFA)_2.xH_2O$	_	Na_2CO_2	1,4-dioxane	80	75
2	$Cu(TFA)_2.xH_2O$	_	_	1,4-dioxane	80	37
3	Cu_2O	_	_	1,4-dioxane	80	76
4	Cu_2O	_	_	THF	80	49
5	Cu_2O	_	_	DMSO	80	19
6	Cu_2O	_	_	DMF	80	26
7	Cu_2O	_	_	toluene	80	25
8	Cu_2O	_	_	CH_3CN	80	32
9	Cu_2O	PPh_3	_	1,4-dioxane	80	31
10	Cu_2O	PPh_3	_	1,4-dioxane	rt	96
11	Cu_2O	Xantphos	_	1,4-dioxane	rt	99 (90)[c]
12	CuCl	Xantphos	_	1,4-dioxane	rt	0
13	$Cu(OAc)_2$	Xantphos	_	1,4-dioxane	rt	85
14	CuI	Xantphos	_	1,4-dioxane	rt	0
15	CuO	Xantphos	_	1,4-dioxane	rt	0
16	Cu_2O	_	_	1,4-dioxane	rt	0
17	Cu_2O	Dpephos	_	1,4-dioxane	rt	28
18	Cu_2O	PCy_3	_	1,4-dioxane	rt	87
19	Cu_2O	DPPE	_	1,4-dioxane	rt	88
20	Cu_2O	1,10-Phen	_	1,4-dioxane	rt	4
21	Cu_2O	DPPB	_	1,4-dioxane	rt	95
22	Cu_2O	P(*n*-Bu)$_3$	_	1,4-dioxane	rt	29
23	Cu_2O	NHC	_	1,4-dioxane	rt	trace

[a] Reaction conditions: phenylpropiolic acids (1a) (0.5 mmol), bis(pinacolato)diboron (1.2 equiv., 0.6 mmol), catalyst, ligand, base,solvent (1 mL) in a sealed tube under the corresponding atmosphere.

[b] GC yields.

[c] Isolated yields

To demonstrate the synthetic utility of the (*E*)-bis-deuterated β-borylated α, β-styrene derivatives obtained by the present method, Suzuki–Miyaura cross-coupling reaction[12] was first conducted with the *in situ* generated **3a**, and (*E*)-bis-deuterated diphenylethene **4** was obtained in 78% overall yield via the two-step one-pot sequence [(Eq. (**6**)].



4

one pot yield: 78%

(6)

Moreover, the usefulness of these novel bis-deuterated styrene derivatives was further emphasized by transformation of the boron substituent into various functional groups (Scheme 3). (*E*)-Bis-

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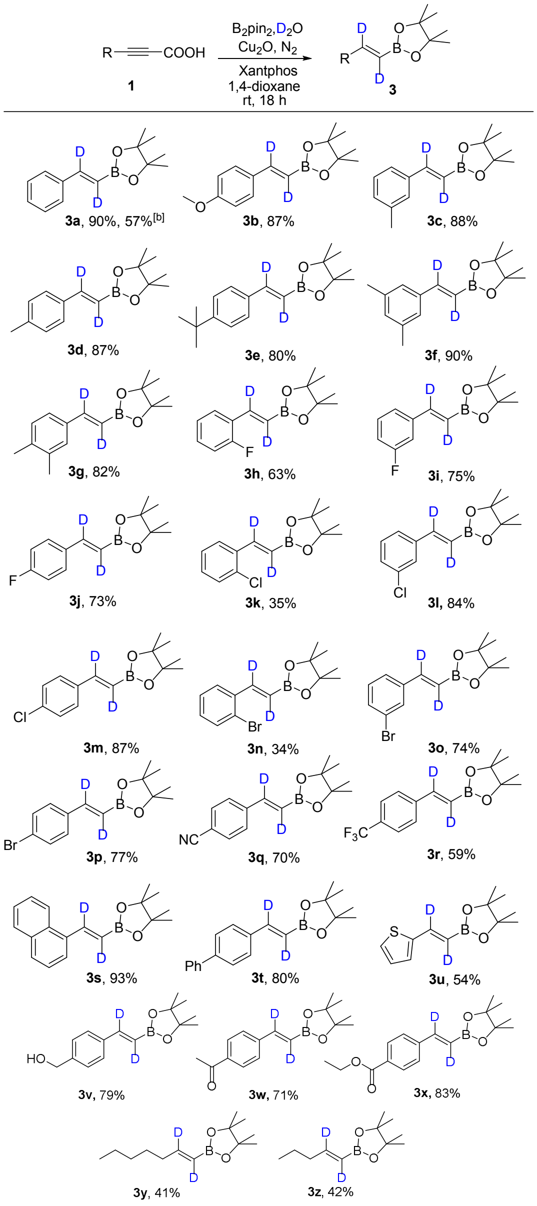
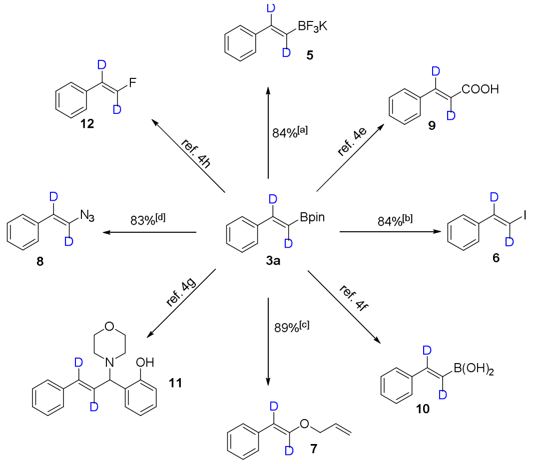


[a] Reaction conditions: alkynyl carboxylic acids (0.5 mmol), diboron reagents (1.2 equiv., 0.6 mmol), Cu_2O (10mol%), Xantphos (10 mol%), D_2O (6 equiv., 3 mmol), 1,4-dixoane (1 mL), rt, 18 h. The reactions were carried out in a 50 mL Schlenck Tube. Deuterium determined by ^{1}H NMR spectroscopic analysis. Isolated yield.

[b] gram-scale reaction conditions: phenylacetic acids 1 (5 mmol), bis(pinacolato)diboron 2 (1.2 equiv., 6 mmol), Cu_2O (10 mol%), Xantphos (10 mol%), D_2O (6 equiv., 30 mmol), 1,4-dixoane (1 mL), rt, 36 h.

Scheme 2. Copper-catalyzed formation of (E)-bis-deuterated β-borylated α, β-styrene derivatives from various alkynyl carboxylic acids.[a]

deuterated potassium alkenyltrifluoroborate **5** and vinyl iodide **6,** which have been designated as one of the most important coupling partners in transition-metal-catalyzed syntheses, were prepared from (*E*)-bis-deuterated β-borylated α, β-styrene over two steps in 84%[4a] and 84%[4b] yields respectively. Furthermore, (*E*)-(2-(allyloxy)vinyl-1,2-d_2)benzene **7**, one of valuable enol ethers which have been considered as synthetic intermediates in various organic reactions such as in the [2+2]-cycloaddition and Claisen rearrangement, was obtained in 89% yield from (*E*)-bis-deuterated β-borylated α, β-styrene with allyl achohol in the presence of cupric acetate.[4c] As vinyl azides are useful intermediates in the synthesis of various heterocyclic compounds and transition metal complexes, as well as important components in many functional materials like the photo-affinity labeling agents for proteins, (*E*)-(2-azidovinyl-1,2-d_2)benzene **8** were prepared from (*E*)-bis-deuterated β-borylated α, β-styrene with sodium azide in 83% yield.[4d] In addition, some other important molecules such as cinnamic-2,3-d_2 acid **9**, (*E*)-(2-phenylvinyl-1,2-d_2)boronic acid **10**, (*E*)-2-(1-morpholino-3-phenylallyl-2,3-d_2)phenol **11**, (*E*)-(2-fluorovinyl-1,2-d_2)benzene **12** could also be prepared under mild conditions according to the reported literature.[4e-4h]



[a] Reaction condition: **3a** (0.5 mmol), MeOH (1 mL), saturated aqueous KHF_2 (~4.5 M, 0.6 mL), rt, 2 h.

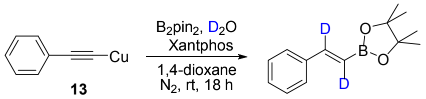
[b] Reaction condition: **3a** (0.5 mmol), NaN_3 (1.5 equiv, 0.75 mmol), $CuSO_4$ (0.6 equiv, 1.3 mmol), MeOH (3 mL), rt, 4h.

[c] Reaction condition: **3a** (0.5 mmol), allyl alcohol (3 mL), $Cu(OAc)_2$ (2 equiv., 1mmol), NEt_3 (4 equiv., 2 mmol), rt, overnight.

[d] Reaction condition: **3a** (0.5 mmol), NaOH (3 equiv., 1.5 mmol), H_2O (0.5 mL), I_2 (2 equiv., 1 mmol), THF (5 mL), rt, 2 h.

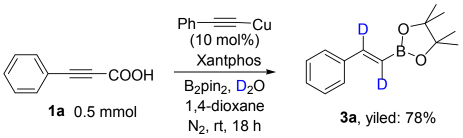
Scheme 3. Synthetic transformations from (E)-bis-deuterated β-borylated α, β-styrene 3a.

In order to investigate the reaction mechanism, (phenylethynyl)copper[13] **13** was employed under the standard condition. However, the starting material was remained and no desired product (*E*)-bis-deuterated β-borylated α, β-styrene **3a** was detected. Probably, the very low solubility of (phenylethynyl)copper in 1,4-dixoane leads to inactivity of this reaction. Thus, we employed catalytic amount of (phenylethynyl)copper as the catalyst under the standard conditions. To our delight, (*E*)-bis-deuterated β-borylated α,β-styrene was afforded in 78% yield [(Eq. (8)]. This result suggested that this transformation might proceed through a (phenylethynyl)copper intermediate, following by the formation of (*E*)-alkenyl-bis-copper reactive intermediate **E** in Scheme 1**.**



3a, with Cu_2O, 0%
without Cu_2O, 0%

(7)



1a 0.5 mmol

3a, yiled: 78%

(8)

To evaluate the influence of active hydrogen from the alkynyl acids on both yield and degree of deuterium incorporation, potassium 3-phenylpropiolate **14,** which was prepared according

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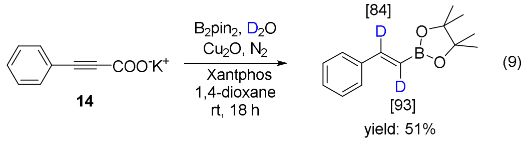
the reported literature[14], was utilized as the alkyne synthon under the standard condition. Significantly, little discrepancy was detected on the degree of deuterium incorporation of (*E*)-bis-deuterated β-borylated α, β-styrene **3a,** even though the yield declined to 51%, probably as a result of low solubility of carboxylate **14** [(Eq. (9)]. This result demonstrated that active hydrogen from the alkynyl acids almost has no influence on the degree of deuterium incorporation.



In addition, the reactions between phenylacetylene and bis(pinacolato)diboron were also performed according to the precedent literatures [Eqs. (1)-(2)] and under the present conditions [Eqs. (3)]. It is clearly demonstrated that alkynyl carboxylic acids play indispensible roles on the success of this transformation.

Conclusions

In conclusion, we have developed a copper-catalyzed highly efficient protocol for the synthesis of bis-deuterated β-borylated α, β-styrene derivatives from alkynyl acids with bis(pinacolato)diboron at ambient temperature. Readily available and cheap D_2O was employed as the deuterium source, and alkynyl acids play a pivotal role in this protocol. Owing to potential applications of bis-deuterated β-borylated α, β-styrene derivatives in organic chemistry, this protocol has potential in the development of preparation of isotopically labeled compounds. Moreover, this reaction offers an efficient strategy to highly selective trifunctionalization of carbon-carbon triple bond at ambient temperature, which may open a door for organic chemists to explore further trifunctionalization of carbon-carbon triple bonds.

Acknowledgement

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