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Trialkylborane-Mediated Propargylation of Aldehydes Using γ-Stannylated Propargyl Acetates

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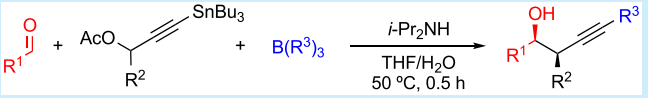
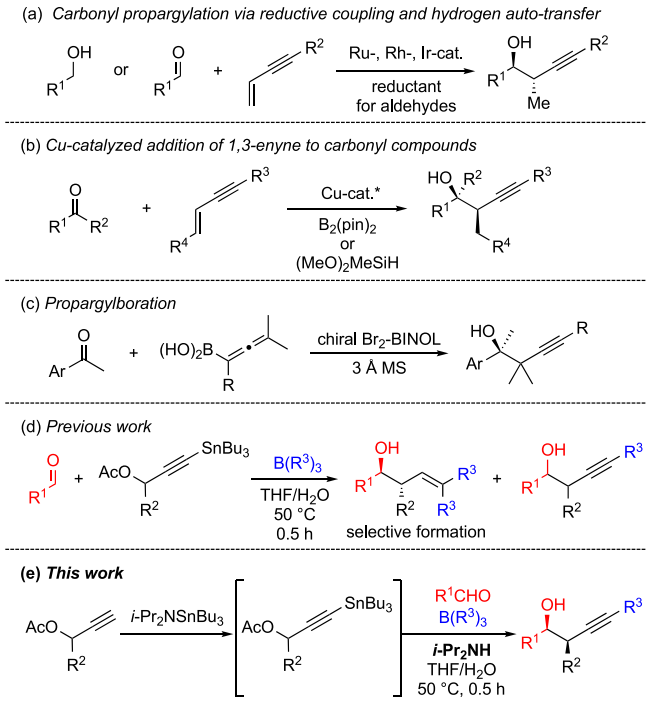
Supporting Information

ABSTRACT: A transition-metal-free three-component process that combines aldehydes, 3-(tributylstannyl)propargyl acetates formed in situ from readily available propargyl acetates, and trialkylboranes provides access to a range of 1,2,4-trisubstituted homopropargylic alcohols. The addition of diisopropylamine plays a crucial role in the selective formation of homopropargylic alcohols. Importantly, this methodology can be extended to a single-flask reaction sequence starting from propargyl acetates.



Homopropargylic alcohols are common structural motifs in natural products and valuable building blocks in organic synthesis.[1,2] Transition-metal-catalyzed carbonyl propargylation is emerging as an elegant approach for the highly diastereo- and enantioselective construction of homopropargylic alcohols. Enyne−aldehyde reductive coupling (Scheme 1a)[3] and copper-catalyzed stereoselective nucleophilic addition of a propargylic group to carbonyl compounds (Scheme 1b)[4] constitute the most straightforward catalytic route for the production of 1,2,4-substituted homopropargylic alcohols. Very recently, gold(I)-catalyzed propargylation of carbonyl compounds has also been reported.[5]

Scheme 1. Synthesis of 1,2,4-Substituted Homopropargylic Alcohols



In this context, addition reactions of propargyl metal or metalloid to aldehydes have been widely used as general synthetic methods; however, they have limited scope because of their ambident nucleophiles such as propargyl/allenyl organometallic reagents.[1d,6] So far, relatively few reports on transition-metal-free carbonyl propargylation for the synthesis of 1,2,4-substituted homopropargylic alcohols have appeared.[7,8] Recently, the limited scope of these methods was further expanded by Szabó and colleagues, who reported the copper-catalyzed preparation of tri- and tetrasubstituted allenylboronic acids and their improved application in the synthesis of sterically encumbered homopropargylic alcohols upon the formation of corresponding boroxines (Scheme 1c).[7] Nevertheless, the discovery of a conceptually distinct synthetic strategy for carbonyl propargylation without using transition-metal catalysis remains as an elusive research field.

Recently, we developed a free-radical-mediated multicomponent coupling reactions of aldehydes, γ-stannylated propargyl acetates, and trialkylboranes initiated by a trialkylborane/O_2 system, which provides rapid access to *anti*-δ,δ-disubstituted homoallylic alcohols with good to high diastereoselectivities (Scheme 1d).[9] Interestingly, a considerable amount of the corresponding homopropargylic alcohol was produced when the reaction was conducted with aromatic aldehydes containing a dimethylamino group (i.e., 4-dimethylaminobenzaldehyde) under otherwise identical conditions.[10] This observation led us to reason that the selective propargylation of aldehydes might be feasible in the presence of an amine. Furthermore, if the allenylmetal species could be

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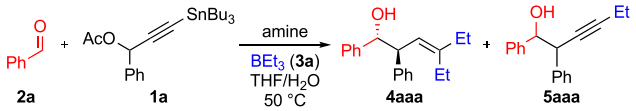
selectively produced, γ-stannylated propargyl acetates would be considered as a useful reagent for both allylation and propargylation of carbonyl compounds. Compared with conventional alkynylstannanes,[11,12] until now, the reactivities of alkynylstannanes possessing a leaving group at the propargylic position have received only limited attention and application in organic synthesis.[9] However, the practical and functional group-tolerant synthesis of γ-stannylated propargyl acetates has been well-established.[13] Herein, we report the development of a transition-metal-free three-component process that can combine aldehydes, 3-(tributylstannyl)-propargyl acetates formed in situ from readily available propargyl acetates, and trialkylboranes to afford a range of 1,2,4-trisubstituted homopropargylic alcohols (Scheme 1e). This method features mild reaction conditions, an operationally simple procedure, and good functional group tolerance. Noteworthy is that the addition of diisopropylamine plays a vital role in introducing selective carbonyl propargylation.

We hypothesized that the addition of amine could alter the reaction pathway dramatically by forming a Lewis acid−base complex with a trialkylborane and thereby suppressing down the formation of a free-radical species from the Lewis acid. Based on this hypothesis, our initial investigation focused on the three-component reaction of **1a**, **2a**, and **3a** in the presence of a variety of amines in THF/H_2O solvent system (Table 1).

Table 1. Optimization of Reaction Conditions[a]



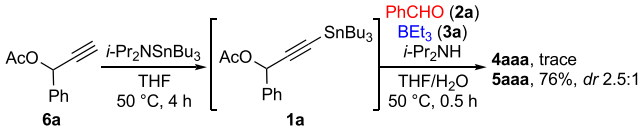
entry	amine	4aaa (%)	5aaa (%)	dr[b]
1	no amine	79	3	
2	1-phenylethylamine	47	10	2.6:1
3	diisopropylamine	3	78	2.5:1
4	TMP[c]	trace	35	2.6:1
5	triethylamine	38	45	2.7:1
6	pyridine	0	0	

[a]Reaction of **1a** (0.5 mmol) with **2a** (1.2 mmol), **3a** (1 M in hexane, 0.6 mmol), and amine (1.2 mmol) was carried out in THF/H_2O (2.5 mL, 4/1) at 50 °C under Ar. [b]The *syn* isomer is the major product. [c]TMP = 2,2,6,6-tetramethylpiperidine.

The optimization of amines was proven to be crucial for selectively obtaining homopropargylic alcohol **5aaa**. The use of a primary amine, namely, 1-phenethylamine, was less effective in governing selectivity and afforded **5aaa** in 10% yield (entry 2), whereas diisopropylamine exhibited the excellent selectivity toward the homopropargylic alcohol affording **5aaa** in 78% yield alongside 3% of **4aaa** (entry 3). The amount of diisopropylamine was also found to play an important role in the selective formation of **5aaa**.[14] Sterically bulky amines such as 2,2,6,6-tetramethylpiperidine (TMP) and triethylamine gave the desired product in moderate yield, presumably due to the steric hindrance of the amines (entries 4 and 5). No reaction resulted from the use of pyridine (entry 6). The reaction was markedly accelerated at 50 °C and was complete within 0.5 h whereas no reaction was observed at room temperature.

We also found that this methodology can be extended to a single-flask reaction sequence starting from propargyl acetate **6a** (Scheme 2). For example, the reaction of **6a** with *i*-Pr_2NSnBu_3 generated from LDA and Bu_3SnCl produced a

Scheme 2. Single-Flask Reaction Sequence[a]



[a]Key: **6a** (0.5 mmol), *i*-Pr_2NSnBu_3 (0.6 mmol), **2a** (1.2 mmol), **3a** (1 M in hexane, 0.6 mmol), and *i*-Pr_2NH (0.6 mmol) were used.

mixture of **1a** and diisopropylamine in situ,[13c] without further purification, which was subsequently treated with **2a** and **3a** to afford the **5aaa** in 76% isolated yield.

With optimal conditions using a single-flask reaction sequence in hand, the scope of the propargylation reaction was evaluated using various aldehydes (Scheme 3). In the case of aromatic aldehydes, the reaction conditions tolerated both electron-donating and electron-withdrawing substituents at either the *para*- or *meta*-positions of the aryl moiety without any erosion in the yield of the products (**5aba**−**afa**). Without any prior protection of the free hydroxyl group, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde furnished **5aga** and **5aha** in 50% and 58% yields, respectively. Further optimization of the reaction conditions revealed that the use of 3.6 equiv of diisopropylamine improved the yield of **5aga** and **5aha**. Interestingly, we found that the presence of *ortho*-substituents, such as *o*-hydroxyl, *o*-methoxy, and *o*-bromo on aromatic aldehydes, increased the diastereoselectivity of the homopropargylic alcohols **5aha**−**aka** as is known for carbonyl propargylation using allenylsilanes.[15] Similarly, the use of methyl 2-formylbenzoate gave isobenzofuranone derivative **5ala** with high diastereoselectivity, which is difficult to obtain through other synthetic methods.[16] The stereochemistry of **5aia** was carefully confirmed to be *syn* configuration by its derivatization to a known compound.[14] Importantly, this procedure is applicable in a gram-scale reaction to afford **5aia** in comparable yield. In contrast, **5ama** was obtained with poor diastereoselectivity when *o*-tolualdehyde was employed. Aryl groups on aldehydes can be replaced by a furyl group to yield **5ana**. Furthermore, both an α,β-unsaturated aldehyde (i.e., cinnamaldehyde) and a substantially less reactive aliphatic aldehyde (i.e., isobutyraldehyde) also participated in the three-component reaction affording the corresponding homopropargylic alcohols **5aoa** and **5apa**, respectively, both of which were given in 69% yield. In most cases, both diastereomers could be readily separated in analytically pure form by column chromatography.[14]

Next, we examined the scope of γ-stannylated propargyl acetates in this propargylation reaction. Substrates bearing both electron-withdrawing and electron-donating groups can be utilized to give **5baa**−**gaa**. Substrates bearing a heteroaryl substituent, such as 2-furyl and 2-thienyl groups, also underwent the reaction to give **5haa** and **5iaa**, respectively. Poor results in terms of the isolated yield were obtained in the reaction with substrates equipped with an alkyl substituent; i.e., homopropargylic alcohols **5jaa** and **5kaa** were obtained in 17% and 23% yields, respectively. In this context, the reaction with 3-(tributylstannyl)propargyl acetate gave only the corresponding homoallylic alcohol, 1-phenyl-4-ethyl-3-hexen-1-ol, in 18% yield. The use of 2-methoxybenzaldehyde instead of benzaldehyde increased the diastereoselectivity of the homopropargylic alcohols. Thereafter, we explored the generality of trialkylborane (Scheme 4). A commercially available tri-*n*-

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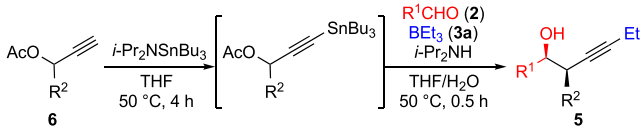
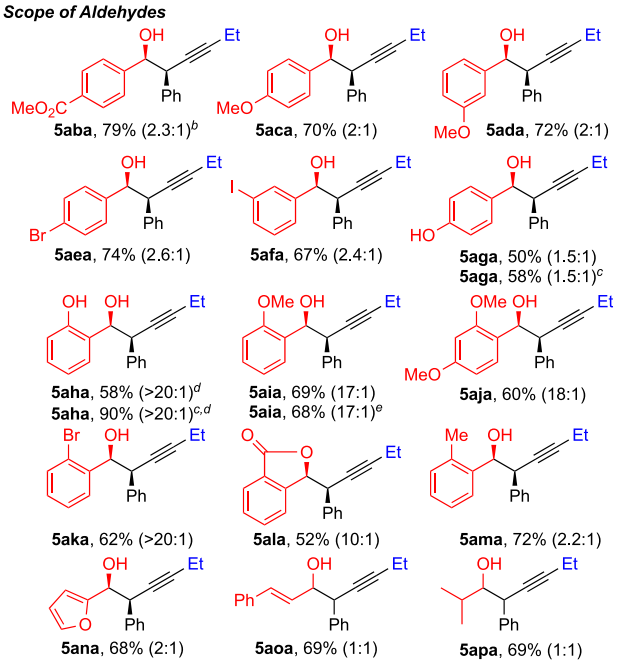
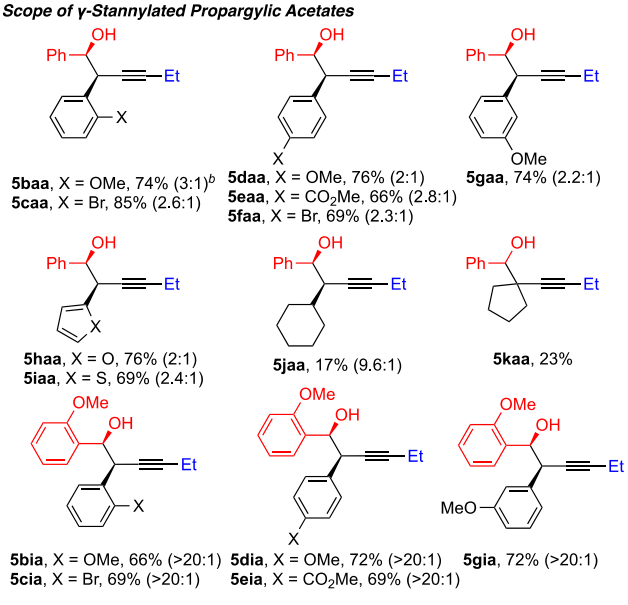
Scheme 3. Scope of the Et_3B-Mediated Three-Component Process[a]



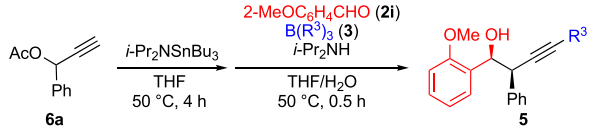


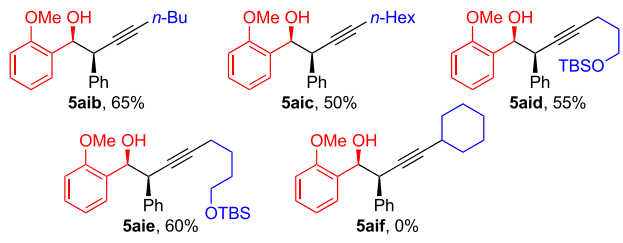


[a]**6** (1 equiv), *i*-Pr_2NSnBu_3 (1.2 equiv), **2** (2.4 equiv), **3a** (1 M in hexane, 1.2 equiv), and *i*-Pr_2NH (1.2 equiv) were used. [b]The bracket represents the ratios of *syn*/*anti* determined by ^{1}H NMR analysis of the crude reaction mixture, and the *syn* isomer is the major product. [c]*i*-Pr_2NH (3.6 equiv) was added. [d]NMR yield (1,3,5-trimethoxybenzene was used as an internal standard). [e]Isolated yield on 6 mmol scale reaction.

butylborane also underwent a three-component reaction to afford **5aib** in 65% yield. Additionally, unpurified trialkylboranes prepared from 1-hexene, TBS-protected allyl alcohol, and

Scheme 4. Scope with Respect to Triorganoboranes[a]





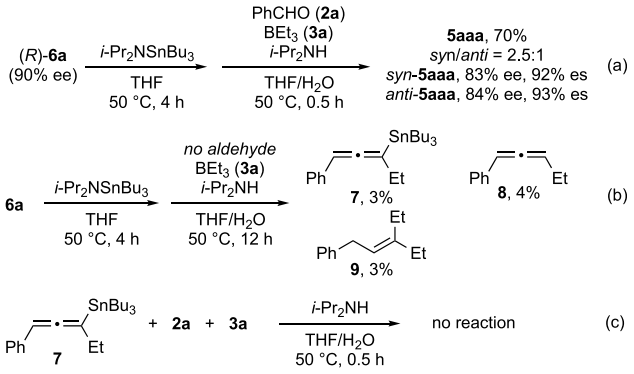
[a]Reaction conditions identical to those in Scheme 2. The ratio of *syn*/*anti* was determined by ^{1}H NMR analysis of the crude reaction mixture (*syn*/*anti* = >20:1). TBS = *tert*-butyldimethylsilyl.

TBS-protected homoallyl alcohol with $BH_3{\cdot}SMe_2$ gave **5aic**–**aie**, respectively, in moderate to good yields. Conversely, this present reaction did not proceed with either Ph_3B or tri-*sec*-alkylboranes such as tricyclohexylborane and tri-*sec*-butylborane.

A series of control experiments were conducted to clarify the mechanism of this propargylation reaction.

The reaction of (*R*)-**6a** (90% ee) with **2a** and **3a** afforded both *syn*- and *anti*-**5aaa** with a high degree of chirality transfer (Scheme 5a). Importantly, the absolute stereochemistry of *syn*-

Scheme 5. Mechanistic Studies



5aaa was determined to be (1*S*,2*S*) by transformation into a known compound.[14] Omitting an aldehyde from the reaction components gave a mixture of **7**, **8**, and **9**, albeit with poor combined yield (Scheme 5b). No desired product resulted when the reaction was conducted using the allenylstannane **7** which, therefore, could be ruled out as an intermediate (Scheme 5c).

Although it is premature to speculate on the reaction mechanism based on the above results, we have proposed a tentative reaction mechanism as exemplified with (*R*)-**1a**, **2a**, and **3a** in Scheme 6. The propargylation reaction would begin with the complexation of (*R*)-**1a** with triethylborane (**3a**) to generate a zwitterionic intermediate **A** in which the vinyl carbocation could be efficiently stabilized by hyperconjugation with the β-stannyl substituent[17] as well as the C–B bond of the resulting negatively charged tetravalent boryl group. Moreover, conventional neighboring group participation of both the

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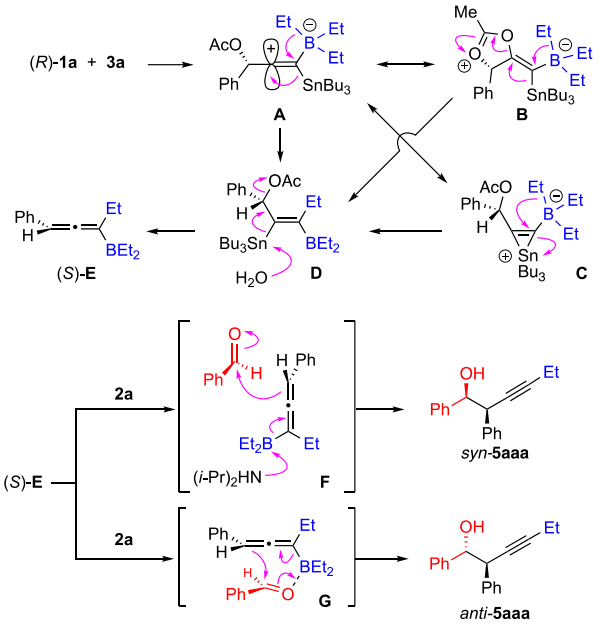
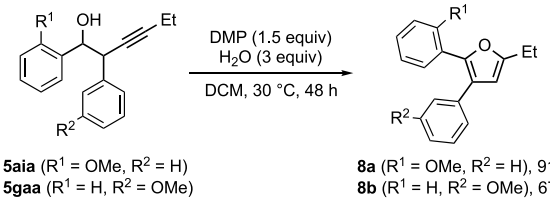
Scheme 6. Plausible Reaction Mechanism for Trialkylborane-Mediated Carbonyl Propargylation



acetoxy and tributylstannyl groups with the empty p orbital of the vinylic carbocation could further stabilize **A** through either oxonium **B** and the bridged stannylium **C**, respectively.[13b,18] The subsequent triethylvinylborate ate complex induced stannyl group rearrangement would occur spontaneously to afford the vinylstannane intermediate **D** with an acetoxy group at the vicinal position, which could then produce the optically active allenylborane (*S*)-**E** through the bimolecular *anti*-specific elimination.[19] Finally, the propargylation of benzaldehyde (**2a**) with allenylborane (*S*)-**E** affords both *syn*-**5aaa** and *anti*-**5aaa**, presumably via an open transition state **F** with the assistance of the amine[20] and a closed transition state **G**, respectively. The stereochemical outcome of (1*S*,2*S*)-**5aaa** reflects that the axially chiral (*S*)-**E** can be available from the centrally chiral (*S*)-**D** with a high level of chirality transfer during the reaction progress.[19,21]

Given the importance of furans in organic synthesis, medicinal chemistry, and material science,[22] we exploited a further synthetic utility of 1,2,4-trisubstituted homopropargylic alcohols for the preparation of 2,3,5-trisubstituted furans. Interestingly, Dess−Martin periodinane (DMP) oxidation of **5aia** and **5gaa** in the presence of 3 equiv of H_2O allowed a facile preparation of furans **8a** and **8b**, respectively (Scheme 7). Of note is that this is the first example demonstrating that DMP can promote a cascade process of oxidation/cyclization even though H_2O is known to accelerate the rate of DMP oxidation of alcohols.[23]

Scheme 7. Furan Synthesis from Products 5



5aia (R^1 = OMe, R^2 = H)
5gaa (R^1 = H, R^2 = OMe)

8a (R^1 = OMe, R^2 = H), 91%
8b (R^1 = H, R^2 = OMe), 67%

In summary, we have developed a trialkylborane-mediated three-component reaction of aldehydes, γ-stannylated propargyl acetates, and trialkylboranes, which provides access to a wide range of homopropargylic alcohols under mild reaction conditions. In addition, this methodology can be extended to a single-flask reaction sequence from readily available propargyl acetates. The addition of diisopropylamine plays a crucial role in the selective formation of homopropargylic alcohols. One of the most attractive aspects of the chemistry described herein is mild reaction conditions compatible with a wide range of functional groups. Further mechanistic studies of both the present carbonyl propargylation and furan synthesis are underway in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b03710.

All experimental procedures, analytical data, and copies of ^{1}H and ^{13}C NMR spectra of all newly synthesized products (PDF)

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Notes

The authors declare no competing financial interest.

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