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Quaternary and Tertiary Carbon Centers Synthesized via Gallium-Catalyzed Direct Substitution of Unfunctionalized Propargylic Alcohols with Boronic Acids

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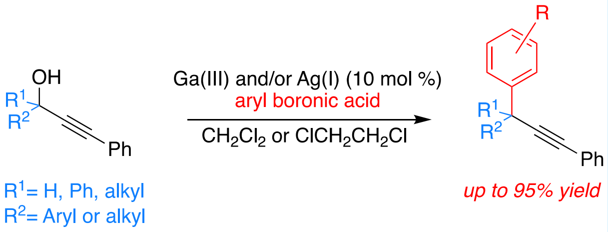
ABSTRACT: (IPr)$GaCl_3$/$AgSbF_6$, $AgSbF_6$, and $GaCl_3$ catalyzed substitution of the hydroxyl of secondary and tertiary propargylic alcohols with organoboronic acids via C−C bond formation, and $GaCl_3$ effectively synthesized all-carbon quaternary propargylic centers. These catalysts performed the substitution at carbons bearing alkyl substituents, which has been problematic for other systems. Highly hindered carbon stereocenters were thus produced, including quaternary centers bearing doubly ortho-substituted aryl rings, that are difficult to access with traditional methods.



Alkynes are very versatile functional groups for organic synthesis. They are precursors for allenes, substrates for C−C bond formations, cycloaddition participants, and much more.[1−10] To access more complex alkynyl building blocks,[11−13] propargylic substitution reactions allow functional diversification adjacent to the alkyne originating from readily accessed propargylic alcohols. Most of these reactions result in tertiary carbon formation.[14−16] There are only limited examples of quaternary carbon center formation and even fewer where that carbon is chiral.[17−19] Quaternary carbon centers appear in biologically active natural products[20,21] and are desired to control three-dimensionality in small-molecule pharmaceuticals.[22,23] However, they are still exceptionally difficult to access, especially in a catalytic manner, due to the high steric congestion at that carbon.[24] One of the earliest propargylic substitution reactions was the Nicholas reaction.[25] While still used synthetically, this strategy has major drawbacks: stoichiometric amounts of the Co reagent, strong acid, and stoichiometric amounts of oxidant to remove the Co in a multireaction sequence. Ideally, propargylic substitution would be accomplished in a single step catalytically. Cu, Ru, and Rh catalysts have been examined for propargylic nucleophilic substitution where hydroxyl or acetates are used as leaving groups (Figure 1a).[26−29] One common restriction of these metal catalysts is that they go through an allenylidene mechanistic intermediate (see **2**) and consequently only accept terminal alkyne substrates. Additionally, there are few examples that produce quaternary centers, and these metals have little tolerance of aliphatic substituents, which limits synthetic utility. Here, we report the use of Ga or Ag catalysis for the direct substitution of the hydroxyl of propargylic alcohol with boronic acids to synthesize propargylic tertiary and quaternary carbon centers, including those with internal alkynes and with aliphatic substituents, which are inaccessible to most metal-catalyzed propargylic substitution reactions (Figure 1d).

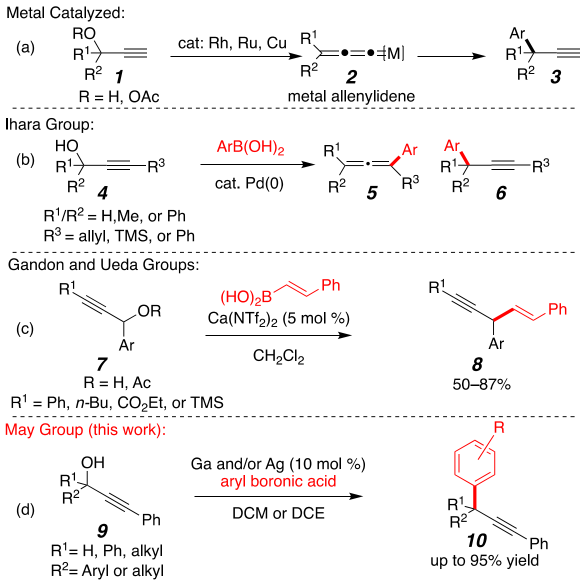


Figure 1. Propargylic substitution examples.

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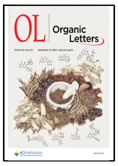

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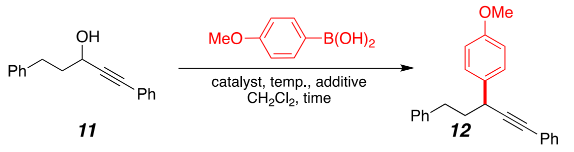
Propargylic nucleophilic substitutions using boronic acids are still underexplored, though boronic acids are highly effective at controlling regioselectivity and increasing the nucleophilicity of pi systems; they thus afford greater regiocontrol and reactivity than Friedel−Crafts approaches. Ihara developed a Pd(PPh$_3$)$_4$-catalyzed propargylic substitution to install a propargylic aryl group (Figure 1b).[30] However, allene formation (see **5**) outcompeted substitution if both R^1 or R^2 $\neq$ H or if an R group were large. Gandon and Ueda showed the addition of styrenyl and aryl boronic acids to diaryl secondary propargylic alcohols using Ca^{2+} or no catalyst, respectively.[6,7] Neither allowed for propargylic quaternary carbon formation, though. Additionally, propargylic substitutions have not been shown to be generally compatible with aliphatic propargylic alcohols. These issues were addressed while maintaining the benefits of using boronic acid nucleophiles and an unmodified hydroxyl leaving group.

To increase compatibility with aliphatic propargylic alcohols, Brønsted acids that could generate a stable propargylic cation or activate the hydroxyl as a leaving group were analyzed,[31] but they caused hydroxyl elimination instead of nucleophilic substitution (Table 1, entry 1). The use of common Lewis acids had a similar outcome (entry 2). However, when equimolar amounts of IPrGaCl$_3$ and AgSbF$_6$ were employed (10 mol % each),[32] the reaction proceeded in just 2 h with 90% yield (entry 3). In entry 4, an aryl trifluoroborate salt was used, but conversion to the product was very low (<5%), which is consistent with our prior observations with Ga catalysis.[28] AgSbF$_6$ was initially added to generate an active cationic Ga catalyst, which could also be achieved using NaBArF$_{24}$, though in a lower yield (entry 5).[33] However, when AgSbF$_6$ was used alone, it still produced the product in a similar yield, though the reaction had to be heated to 40 °C and given an extended reaction time of 12 h (entry 6). The higher reactivity of the mixed system indicated that the Lewis acidity of the cationic IPrGaCl$_2^+$ complex accelerated substitution. GaCl$_3$ was also examined here, but product yield maximized at only 72% (entry 7). Additional control experiments were then conducted to understand the catalyst roles. HCl was examined in place of Ga chlorides to see if reactivity was from adventitious acid formed in situ; however, no nucleophilic substitution was observed. 4-Methoxyphenylboronic acid was also replaced with anisole to see if nucleophilic substitution would occur via a Friedel−Crafts pathway. Again, no nucleophilic substitution was observed. These experiments further support that both the catalyst and the boronic acid play a significant role in the successful nucleophilic substitution.

Table 1. Reaction Condition Evaluation

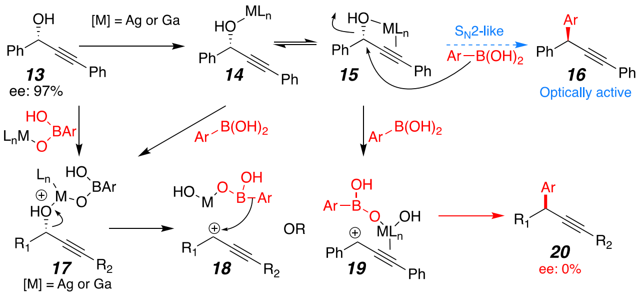


entry	catalyst (mol %)	temp (°C)	additive	time (h)	yield[a] (%)
1	Brønsted acids[b] (10−50%)	23	none	24−48	<5[c]
2	Lewis acids[d]	−78 to 40	none	24−48	<5[c]
3	IPrGaCl$_3$ (10%)	0 to 23	AgSbF$_6$ (10%)	2	90
4[e]	IPrGaCl$_3$ (10%)	0 to 23	AgSbF$_6$ (10%)	24	<5
5	IPrGaCl$_3$ (10%)	0 to 23	NaBArF$_{24}$ (12%)	18	40
6	AgSbF$_6$ (10%)	40	none	12	91
7	GaCl$_3$ (50%)	0	none	5	72

[a]NMR yield, [b]Acids = (*n*-Bu)$_4$NHSO$_4$, *p*-TSA, TFA, [c]Alkene from hydroxyl elimination was primarily observed. [d]See Supporting Information Table SI-2 for a complete list. [e]Aryl trifluoroborate was used instead of aryl boronic acid. Starting alcohol was recovered.

Mechanistic routes for the cationic Ga- or Ag-catalyzed propargylic substitution reaction were postulated (Scheme 1).

Scheme 1. Proposed Mechanistic Pathways



It was thought that the metal could coordinate with the hydroxyl of **13** (see **14**) or both the alkyne and the hydroxyl to form pi-coordinated **15**, which corresponds to the need for a soft Lewis acid.[33,34] Since trifluoroborate salts did not serve as good nucleophiles in this reaction, the hydroxyl group of the boronic acid might be playing a role in the reaction mechanism. Recruitment of the boronic acid by the metal could then produce adduct **17**. From **14**, **15**, or **17**, two pathways are plausible. The first is an S$_N$2 type attack of the nucleophile (shown for **15**), which would result in an inversion of stereochemistry if starting with an optically active alcohol **13**. The second possible pathway is S$_N$1-like, which would pass through carbocation **18** or **19** and would form a racemic product as a result. To differentiate these hypotheses, we synthesized enantioenriched propargylic alcohol **13** (97% ee) and found the substitution product to be racemic, suggesting that the mechanistic pathway goes through an S$_N$1-like reaction (e.g., **18** or **19**).

Since (IPr)GaCl$_3$, AgSbF$_6$, and GaCl$_3$ catalysts do not proceed through allenylidene intermediates, internal alkynyl substrates could be used. Two catalytic conditions, (IPr)-GaCl$_3$/AgSbF$_6$ (method A) and AgSbF$_6$ alone (method B), were examined with a variety of secondary propargylic alcohols. Both conditions were generally compatible with alkyl substituted substrates (**21**−**25**, Figure 2), which is a significant advance for catalytic propargylic substitution. An electron-poor aromatic on the alkyne gave a low yield with method A but performed much better with method B at a higher temperature (see **25**). When the alkynyl aryl was electron rich, the corresponding product **26** was not formed, elimination of the hydroxyl was observed, and the modification used for **25** did not help for **26** or forming the *n*-butyl alkyne product **27** (R = *n*-Bu). Likewise, a substrate bearing a terminal alkyne did not afford any product (see **27**, R = H), which indicates that conjugative stabilization of intermediate cationic charge is important for the reaction. To further illustrate this, **28** and **29**, which would generate cationic intermediates with

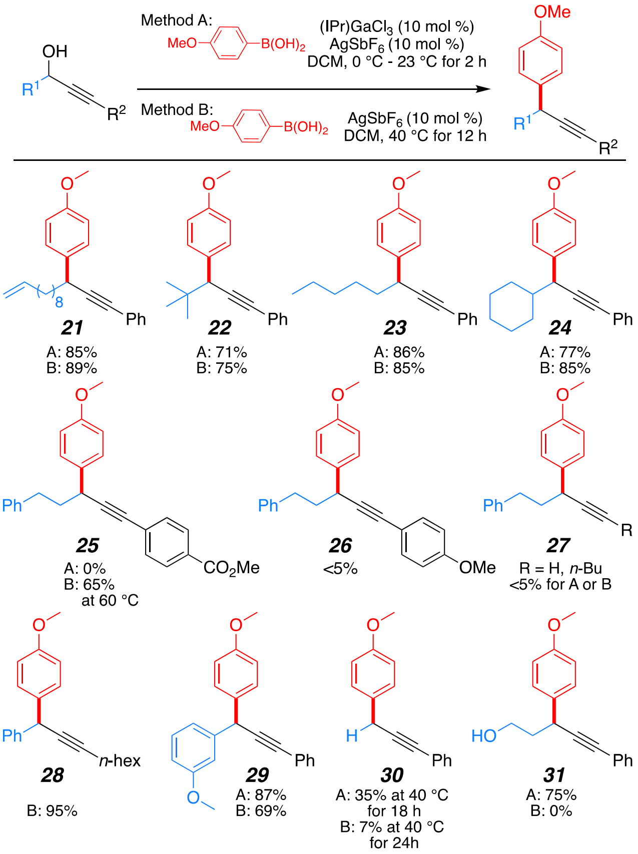


Figure 2. Electrophile substituent scope (reacted until alcohol was consumed; mass balance in each case was hydroxyl elimination; see the Supporting Information for details).

additional benzylic stabilization, produced product with excellent yields, even with *n*-hexyl alkynyl substitution (**28**). The use of a primary propargylic alcohol resulted in a low yield (see **30**), but successful substitution for such a substrate has been rare.[30] Formation of **30** suggests that a more S_N2-like mechanism could also be operative and that some mechanistic flexibility between substrates is possible, since the intermediacy of a discrete primary cation (**18**, R^1 = H) is less likely.[28] The use of 10 mol % of (IPr)$GaCl_3$ and $AgSbF_6$ with a boronic acid at 0−23 °C reacted chemoselectively with a tertiary propargylic hydroxyl over an aliphatic hydroxyl (see **31**).

We then examined variations in the aryl nucleophile. Electron rich aryl boronic acids provided good yields when utilizing the (IPr)$GaCl_3$/$AgSbF_6$ system (see **32−36**, Figure 3). A heterocyclic boronic acid tended to give higher yields by using only $AgSbF_6$ at 40 °C (see **34**). For the electron poor and weakly nucleophilic 2-nitrophenyl and 3-nitrophenyl boronic acids, we found neither method worked well, since substitution was outcompeted by hydroxyl elimination. Consequently, we employed a third method with $GaCl_3$ (see also Table 1, entry 7) to improve the reaction to synthesize the substitution product **37**. Nevertheless, **38** and **39** showed inconsistent reactivity.[35]

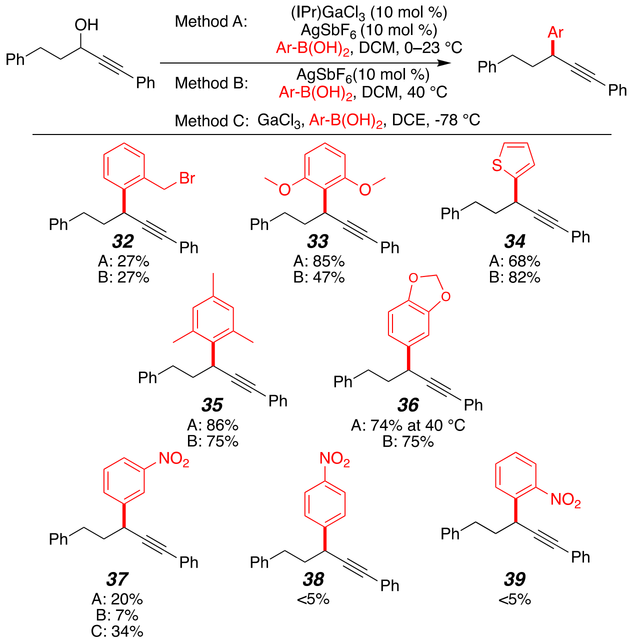
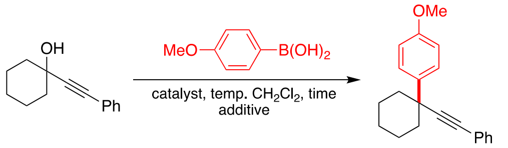


Figure 3. Nucleophile scope (reacted until alcohol wasconsumed; mass balance in each case was hydroxyl elimination; see the Supporting Information for details).

Table 2. Optimization of Quaternary Carbon Formation



entry	catalyst (mol %)	temp (°C)	additive	time (h)	yield[a] (%)
1	Lewis acids	−78 to 40	none	24−48	<5%[b]
2	Brønsted acids (10−50%)	23	none	24−8	<5%[b]
3	IPrGaBr$_3$ (10%)	0 to 23	AgSbF$_6$ (10%)	8	14
4	IPrGaCl$_3$ (10%)	0 to 23	NaBArF$_{24}$ (10%)	16	51
5	GaCl$_3$ (30%)	−78	none	2	66
6[c]	GaCl$_3$ (30%)	−78	none	2	71

[a] NMR yield. [b] Alkene from hydroxyl elimination was exclusively observed. [c] DCE was used instead of CH_2Cl_2.

The ability to construct all carbon quaternary centers adjacent to an alkyne has been very limited to this point.[17−19] The difficulty of the problem was confirmed when methods A and B did not perform well in that context. The yield using a cationic Ga catalyst was only 14−51% (Table 2, entries 3 and 4), and the mass balance was mainly the hydroxyl elimination product. Many other additives and catalysts were examined to improve the yield, including a wide array of Lewis acids, Brønsted acids, and Ag salts, but they resulted in no reaction or elimination (entries 1 and 2). Though (IPr)$GaCl_3$ has the advantages of being bench stable (not moisture or oxygen sensitive), its inactivity prompted deeper examination of its synthetic precursor, $GaCl_3$. Although $GaCl_3$ is hygroscopic and quickly generates hydrochloric acid upon exposure to atmospheric moisture, it proved to be highly reactive and capable of quaternary carbon formation when used with standard Schlenk techniques (entry 5). After completing a solvent screen, 1,2-dichloroethane (DCE) proved to be a better solvent than dichloromethane (entry 6).[33]

With improved reaction conditions in hand, we explored the tolerance of a variety of aryl boronic acids (Figure 4). Electron rich boronic acid nucleophiles reacted well to form quaternary

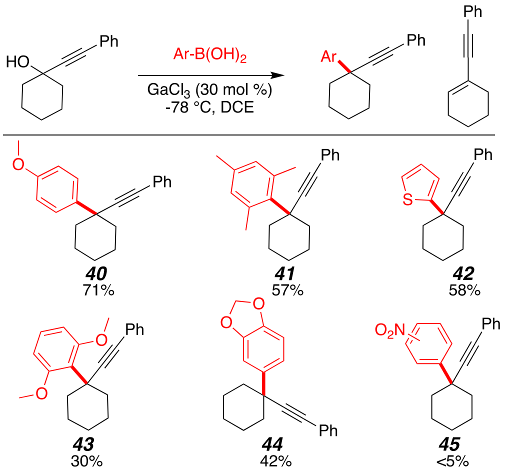


Figure 4. Nucleophile scope for quaternary carbon (reacted until alcohol was consumed; yields are averaged from two trials; mass balance in each case was hydroxyl elimination; see the Supporting Information for details).

carbon centers (see **40**−**44**). Remarkably, quite sterically crowded carbon centers could be formed, such as those with double ortho-substitution on the aryl ring as in **41** and **43**. Very few such examples exist in the literature.[17,18] Heteroaryl nucleophiles also resulted in nucleophilic addition. Unfortunately, electron poor nucleophiles, such as nitro phenylboronic acids (see **45**), only resulted in hydroxyl elimination due to slow nucleophilic substitution.

When varying the propargylic substituents for quaternary carbon centers, three different product types were possible from each substrate: one with a propargylic quaternary carbon center, one from hydroxyl elimination, or an allene product formed from the nucleophile attacking the alkyne with π-bond migration. For acyclic examples with alkyl substitution, hydroxyl elimination or quaternary center formation were primarily observed, with the latter usually dominating (**46**−**49**, Figure 5). When the starting material had propargyl phenyl rings instead of alkyl groups, hydroxyl elimination could not occur, so there was more formation of the quaternary carbon or allene products (**50**). Unfortunately, these complicated mixtures were often inseparable by column chromatography, so attempts at purification and characterization were futile. No clear correlation to either steric encumbrance or substituent electronics explained the ratio of products. However, disrupting benzylic planarity for cation stabilization through ortho substitution allowed for chemoselectivity and quaternary carbon synthesis (**51**).

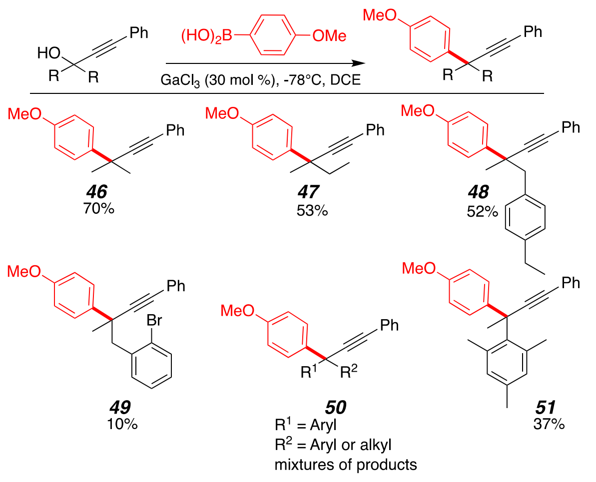


Figure 5. Substrate scope (reacted until alcohol was consumed; yields are averaged from two trials; mass balance in each case was hydroxyl elimination; see the Supporting Information for details).

In conclusion, we have developed three novel methods with Ag and Ga catalyst systems to accomplish the propargylic substitution of propargylic alcohols that bear alkyl substituents using commercially available aryl and heteroaromatic boronic acid nucleophiles. IPrGaCl$_3$/AgSbF$_6$, AgSbF$_6$, and GaCl$_3$ have been used successfully for secondary and tertiary propargylic alcohol substrates, while GaCl$_3$ proved to be the best catalyst to synthesize propargylic quaternary carbons. These catalysts promote the formation of a variety of tertiary and quaternary chiral centers, which are historically difficult to access through traditional chemical routes. This propargylic substitution forms a greater variety of quaternary carbon centers than what was previously possible and even allows access to doubly ortho-substituted aryl quaternary centers. The use of the NHC-coordinated Ga catalyst also provides an entry into future enantioselective catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c02612.

Complete experimental details, catalyst trials, reaction optimization, and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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(35) Yields varied between 0% and 34%. These conditions were also examined with the other low-yielding substrates in Figures 2 and 3 but performed poorly.