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Csp–Csp^3 Bond Formation via Iron(III)-Promoted Hydroalkynylation of Unactivated Alkenes

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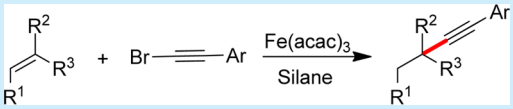
Supporting Information

ABSTRACT: An iron(III)-promoted hydroalkynylation of unactivated alkenes toward Csp–Csp^3 bond formation has been developed. Various alkenes, including mono-, di-, and trisubstituted alkenes, could all smoothly convert to structural diversified alkynes in this chemoselective protocol. Additionally, the scalability was unraveled and the further divergent transformations of products were conducted to demonstrate the synthetic utility.

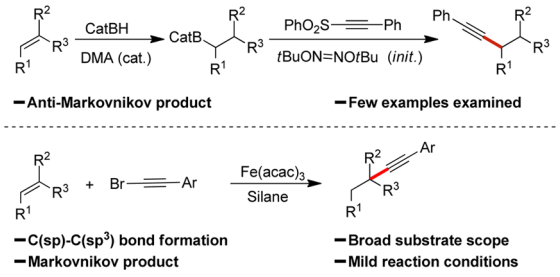


Alkynes are fundamental synthons in organic synthesis and important structural units of bioactive molecules.[1] Therefore, numerous efforts have been devoted to the investigation of alkyne synthesis. For example, the Sonogashira reaction has gained great success in the construction of Csp–Csp^2 bonds.[2] However, the coupling of nonactivated alkyl halides has proven challenging because of competing oxidative addition/β-hydride elimination. Thus, many explorations have been conducted to solve this issue. Fu and co-workers have made great progress in this area and reported a seminal work on the Sonogashira coupling of primary alkyl halides for the construction of a Csp–Csp^3 bond.[3] Afterward, Glorius and Hu independently expanded this scope.[4] Other coupling reactions toward Csp–Csp^3 bond formation, such as photoredox catalysis, oxidative coupling, and those using organometallic reagents, have also been extensively explored recently.[5] Meanwhile, Wang invented a Cu-catalyzed cross-coupling of *N*-tosylhydrazones and trisalkylsilylethynes for forging a Csp–Csp^3 bond.[6] Interestingly, Li reported a metal-free coupling between an alkyne and alkyl iodide with light in water.[7] On the other hand, the decarboxylative alkynylation of carboxylic acids has also been explored.[8]

Recently, the transition-metal-mediated hydrofunctionalization of alkenes has grown as a powerful approach for C–C and C–X (N, O, F, S, Cl) bond formation in the construction of diverse molecules.[9,10] A seminal work of Fe-catalyzed hydroamination of unactivated alkenes with butyl nitrite was reported by Mukaiyama.[11] Afterward, Carreira and co-workers contributed great work in alkene hydroamination, -cyanation, and -chlorination.[12] Recently, Boger investigated the scope of Fe-catalyzed alkene hydrofluorination.[13] Meanwhile, Shenvi established the alkene hydroarylation with a combination of Co/Ni catalysts.[14] More recently, Baran has invented Fe-mediated alkene conjugate addition, hydroamination, and hydromethylation reactions.[15] Notably, radical hydrofunctionalization has been recently applied in the total synthesis of natural products.[16] With respect to hydroalkynylation protocols, Suginome established the hydroalkynylation of methylenecyclopropanes and styrenes, while Kwong and Li reported the asymmetric hydroalkynylation of norbornadienes and enamides.[17] Despite advance in this field, the development of general hydroalkynylation of alkenes toward Csp–Csp^3 bond formation remains challenging.

The hydroalkynylation of alkenes for Csp–Csp^3 bond formation represents an important and promising transformation, since alkenes are readily available and structurally divergent. A two-step process of alkene hydroalkynylation was previously reported by Renaud and co-workers (Scheme 1).[18] In that protocol, the alkenes underwent hydroboration with catecholborane to give β-alkylcatecholboranes, which underwent sequential radical addition to phenylethynylsulfone to furnish alkynes. The process thus delivered anti-Markovnikov products, but few examples were examined. As part of our interest in functionalization of unactivated alkenes,[19] we hypothesized that the hydroalkynylation of alkenes might be possible. Herein, we would like to report an iron(III)-promoted hydroalkynylation of unactivated alkenes for rapid construction of a Csp–Csp^3 bond.

Scheme 1. Csp–Csp^3 Bond Formation via Hydroalkynylation of Unactivated Alkenes



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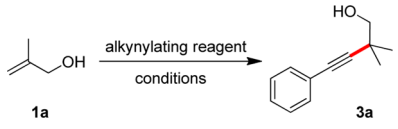
We commenced our study by investigating the 2-methylallyl alcohol **1a**. Initially we carried out the reaction using 20 mol % $Fe(acac)_3$ as the catalyst, $PhSiH_3$ as the reductant, and $NaHCO_3$ as the base in ethanol at 60 °C. Various alkynylating reagents were screened, and all the reagents **2** including **2a** and **2b** were reported as alkynylating reagents and tested in this reaction. The utilization of **2a** showed no alkynylating reaction and the alkenes were reduced to alkanes, while **2b** was slightly unstable to decompose (Table 1, entries 1 and 2).[20] The more electrophilic phenylethynyl phenyliodoniumtriflate (**2c**) was also found to be ineffective (entry 3).[21] Gratifyingly, the employment of phenylethynyl bromide (**2d**) led to formation of the expected alkynylation product **3a** in 26% yield (entry 4),[22] and the phenylethynyl benziodoxolone (**2e**) proved ineffective (entry 5).[23] When the amount of $Fe(acac)_3$ was increased to 50 mol %, the yields were significantly improved to 76% (entry 6). The next optimization was carried out using different catalysts, solvents, and reaction temperatures (entries 7−11). The results showed that the combination of $Fe(acac)_3/PhSiH_3$/EtOH was optimal. The removal of $NaHCO_3$ would lead to a lower yield thus demonstrating the essential role of $NaHCO_3$ as the base (entry 12). We also used a 1:1 molar ratio of alkenes, but this resulted in a slightly low yield (entry 13). The use of 3 equiv of **1a** could facilitate the reaction, and excess **1a** could be recovered.

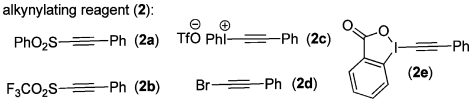
Table 1. Reaction Optimization[a]



1a **3a**

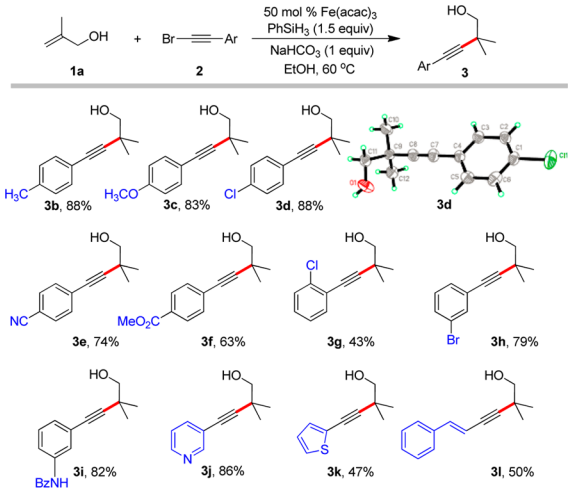
entry	metal salt	alkynylating reagent	solvent	t (°C)	yield (%)[b]
1[c]	$Fe(acac)_3$	**2a**	EtOH	60	–
2[c]	$Fe(acac)_3$	**2b**	EtOH	60	–
3[c]	$Fe(acac)_3$	**2c**	EtOH	60	–
4[c]	$Fe(acac)_3$	**2d**	EtOH	60	26
5[c]	$Fe(acac)_3$	**2e**	EtOH	60	–
6[d]	$Fe(acac)_3$	**2d**	EtOH	60	76
7[d]	$Mn(acac)_3$	**2d**	EtOH	60	44
8[d]	$Co(acac)_2$	**2d**	EtOH	60	<5
9[d]	$Ni(acac)_2$	**2d**	EtOH	60	–
10[d]	$Fe(acac)_3$	**2d**	THF	60	25
11[d]	$Fe(acac)_3$	**2d**	EtOH	25	–
12[d,e]	$Fe(acac)_3$	**2d**	EtOH	60	41
13[f]	$Fe(acac)_3$	**2d**	EtOH	60	42

[a]Reaction conditions: **1a** (0.6 mmol), **2** (0.2 mmol), $PhSiH_3$ (0.3 mmol), $NaHCO_3$ (0.2 mmol), solvent (2 mL), 2 h. [b]Yields refer to isolated products. [c]Metal amount (20 mol %). [d]Metal amount (50 mol %). [e]Removal of $NaHCO_3$. [f]**1a** (0.2 mmol) was used.



With the optimized reaction conditions in hand, we explored the substrate scope of alkynyl bromides (Scheme 2). The alkynyl bromides were easily prepared by bromination of alkynes with *N*-bromo succinimide (NBS), and various alkynyl bromides were employed as an alkynylating reagent. For example, the 4-substituted phenylethynyl bromides, regardless of the electron-donating or -withdrawing substitution, could engage in this process to deliver the corresponding homopropargyl alcohols in good to excellent yields (**3b**−**3f**), with a valuable functional group

Scheme 2. Scope of Alkynyl Bromides[a]



[a]Reaction conditions: $Fe(acac)_3$ (50 mol %), **1** (0.6 mmol), **2** (0.2 mmol), $PhSiH_3$ (0.3 mmol), $NaHCO_3$ (0.2 mmol), EtOH (2 mL), 60 °C, 2 h; yields refer to isolated products.

such as methyl, methoxy, chloro, cyano, and ester. In addition, the structure of **3d** was confirmed by X-ray analysis.[24] Moreover, the 2- and 3-substituted phenylethynyl bromides were both compatible in this transformation to deliver the alkynes in moderate to good yields (**3g**−**3i**). Notably, the heterocyclic alkynyl bromides, such as 3-pyridine and 2-thiophene, were also well applicable in this process (**3j**−**3k**). Interestingly, the styrenylethynyl bromide could proceed smoothly to give the enyne product in moderate yield (**3l**). When the alkyl alkynyl bromides were utilized, no hydroalkynylation product was observed, probably because of no stabilization of the resultant radical by aromatic rings.

We next examined the scope of unactivated alkenes (Scheme 3). A series of alkenes, including mono-, di-, and trisubstituted alkenes, were subject to this process. The terminal monosubstituted alkenes, such as allyl alcohol, hex-5-en-1-ol, allyl cyanide, allyl carboxamide, benzyl pent-4-enoate, and 1-allyl-4-methoxybenzene, could engage in this process to afford the products in moderate to good yields (**4a**−**4f**). The internal disubstituted alkenes, including (*Z*)-but-2-ene-1,4-diol and cyclic *N*-Boc-2,5-dihydro-1*H*-pyrrole, were well amenable to this protocol to furnish the products in moderate yields (**4g** and **4h**). With respect to terminal disubstituted alkenes, such as ketone-tethered alkene **1j** and piperidine functionalized alkene **1k**, these alkenes could undergo this transformation smoothly to give the diversified alkyne products in good yields (**4i** and **4j**). Those trisubstituted alkenes, such as cyclohexene tethered alcohol **1l** and amine **1m**, could proceed well to furnish the alkynes in good yields (**4k** and **4l**). Furthermore, the synthetic utility of this protocol was demonstrated by hydroalkynylation of natural product derivatives. For example, the (*S*)-(−)-*β*-citronellol and (±)-isopulegol could be easily transferred to the alkyne derivatives in moderate yields.[25] More interestingly, when quinine was used, the alkyne derivative **4o** could be furnished in 52% yield with a 3:1 *dr* ratio. And the 3-methyl estrone ether only delivered a single diastereomer, **4p**, in 57% yield, which was confirmed by X-ray analysis.[26] Therefore, this transformation enables the synthesis of diverse alkynes with high functional group compatibility from simple alkenes.

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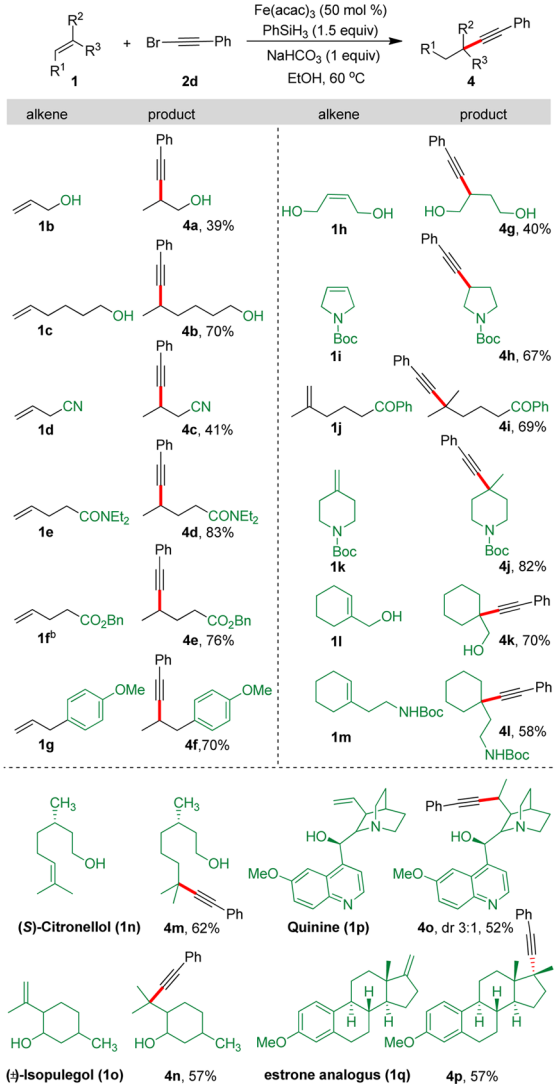
Scheme 3. Scope of Alkenes[a]



[a]Reaction conditions: $Fe(acac)_3$ (50 mol %), **1** (0.6 mmol), **2** (0.2 mmol), $PhSiH_3$ (0.3 mmol), $NaHCO_3$ (0.2 mmol), EtOH (2 mL), 60 °C, 2 h, yields refer to isolated products. [b]THF (2 mL) with EtOH (0.4 mmol) was used as solvent.

Furthermore, a scale-up reaction was conducted to unravel the synthetic potential. A 5 mmol scale reaction was carried out for allyl alcohol **1b** and phenylethynyl bromide **2d**, and the homopropargyl alcohol product **4a** was isolated in 42% yield (Figure 1). Further elaboration of **4a** was also conducted. For example, **4a** could be transferred to ketone **5** in the presence of $PdCl_2$, and the hydroxyl group was found to be converted to chlorine. Alternatively, **4a** could convert to but-3-ynoic acid **6** upon oxidation. Meanwhile, when **4a** was subject to the Rh(III)-catalyzed C−H activation/cyclization with *N*-pivaloylhydroxamic acid and oxime ester, the heterocycles **7** and **8** could be accessed rapidly.[27]

To gain insight into the reaction mechanism, control experiments were carried out (Figure 2). The vinylcyclopropane **1r** was prepared and subjected to the standard hydroalkynylation process, and the ring opening alkynylation product **9** was isolated, indicating a cyclopropane opening radical pathway.

Based on these results and literature,[9d−f,22] a plausible reaction mechanism is proposed in Figure 3. Initially, the Fe(III) is converted to Fe hydride species **A** upon treatment of phenylsilane and ethanol. Then **A** undergoes hydrogen atom transfer (HAT) to alkene **1** to form alkyl radical **B** and Fe(II) species **C** through radical cage pairing of **B** and **C**,[9d] which is trapped by alkynyl bromide **2** to generate the *β*-bromo radical **D**. The sequential elimination of **D** would furnish the alkynylated product (**3** or **4**) and a bromo radical, which would reoxidize **C** to Fe(III) to enable the catalytic cycle. We assumed that the bromo radical would partially deactivate the Fe(III) catalyst; thus, use of 50 mol % Fe-catalyst could facilitate the reaction and the addition of $NaHCO_3$ as the base is essential to remove HBr. Dependent on the alkynylating reagent utilized (**2a**−**2c**, **2e**), either decomposition or low reactivity was observed, thus disabling the hydroalkynylation.

In summary, a facile hydroalkynylation of unactivated alkynes toward Csp−Csp^3 bond formation has been developed. The alkene materials are readily available, the Fe catalyst is inexpensive, and the method can be scaled up. This protocol thus represents a simple and distinct method for alkynes synthesis, which would demonstrate valuable synthetic utility in natural products and bioactive molecules modification.

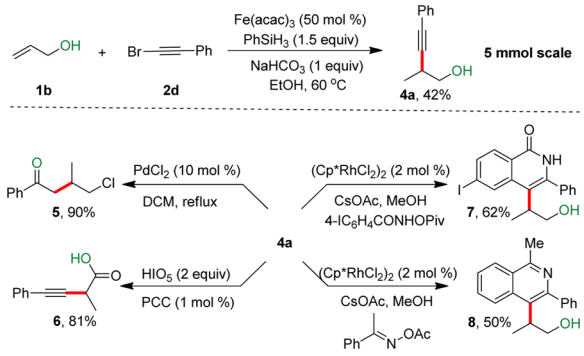


Figure 1. Scale-up reaction and synthetic application.

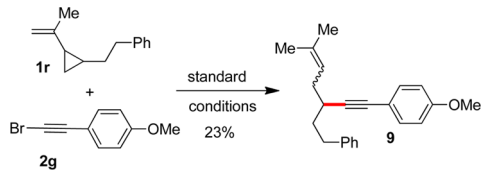


Figure 2. Reaction mechanism study.

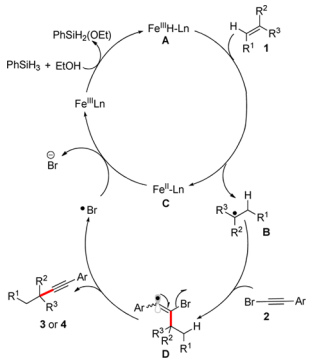


Figure 3. Proposed reaction mechanism.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00499.

Full experimental procedures, characterization data, and NMR spectra data (PDF)
Crystallographic data for **3d** (CIF)
Crystallographic data for **4p** (CIF)

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Notes

The authors declare no competing financial interest.

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