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Fe-Promoted Chlorobenzylation of Terminal Alkynes through Benzylic C(sp^3)−H Bond Functionalization

Jiang-Ling Shi,[†] Ji-Cheng Zhang,[‡] Bi-Qin Wang,[*,†] Ping Hu,[†] Ke-Qing Zhao,[†] and Zhang-Jie Shi[*,‡,§]

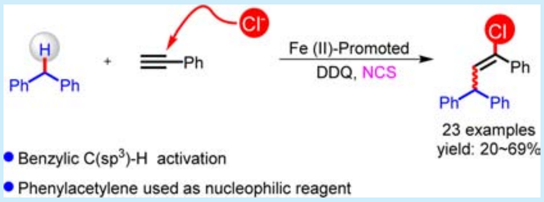
[†]College of Chemistry and Material Chemistry, Sichuan Normal University, Sichuan 610066, China

[‡]Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

[§]State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

ABSTRACT: A chlorobenzylation of terminal alkynes through Fe(II)-promoted benzylic C(sp^3)−H bond functionalization in the presence of NCS as a chloride source was developed. Compared with previous methods to prepare polysubstituted alkenyl halides, the presented procedure provides an efficient alternative with high atom and step economy under mild conditions. The transformation was established to proceed through a single-electron transfer (SET) process with benzyl cations as key intermediates.

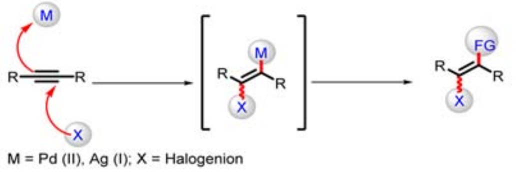


Alkenyl halides are versatile substrates in organic transformations as fundamental starting materials.[1] They are often costly and less available due to their rare availability from nature. Chemists have developed many efficient methods to synthesize vinyl halides, for example, the reaction between corresponding carbonyl compounds and halogenated reagents,[2] Wittig reactions,[3] Julia olefination reactions,[4] and others.[5−7] Transition-metal-catalyzed difunctionalization of alkynes provides another efficient and versatile method for the synthesis of polysubstituted alkenes (Scheme 1A).[8] The halocarbonylation of alkynes in the presence of a stoichiometric strong base or Lewis acids has also been established as an efficient method to synthesize alkenyl chlorides.[9−13]

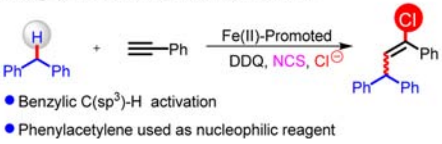
Recently, much attention has been paid to direct C−H functionalization, and remarkable progress has been made in the past two decades.[14] Among many transformations based on direct C−H functionalization, alkynes have been found as unique partners for hydroarylations[15] as well as various annulations.[16] Other than annulations, intermolecular difunctionalization of alkynes initiated from C−H functionalization was comparatively rarely reported. Because of the importance of alkenyl halides, we set out to explore new chemistry by combining the bifunctionalization of alkynes and direct C−H fucntionaliztion to produce the multisubstituted alkenyl halides starting from easily available and inexpensive chemicals. Herein we demonstrate an Fe(II)-promoted chlorobenzylation of phenylacetylene through benzyl C(sp^3)−H functionalization in the presence of NCS as a chloride source (Scheme 1B). This chemistry showed high regioselectivity and excellent *Z*/*E* selectivity in most cases.[12,13]

Scheme 1. Carbochlorination of Arylacetylene

(A) Traditional process-Synthesis of alkenyl halides via transition-metal-catalyzed difunctionalization of alkynes



(B) **This work**-Chlorobenzylation of terminal alkynes through benzylic C(sp^3)-H bond functionalization



Benzylic C−H bonds have been found to be relatively active, and various different transformations have been developed from aryl/diarylmethanes in recent decades. Many pioneering groups, for example those of Li,[17] Li,[18] Chatani, and others[19] have made significant contributions in this field. Our group also developed the oxidative coupling of benzyl C−H bonds with arenes and vinyl acetates via Fe catalysis.[20,21] Subsequently, the Jiao group reported a beautiful example to demonstrate the Fe(II)-catalyzed amidation reaction via C−H and C−C bond cleavage of diphenylmethane in the presence of azides.[22] According to our experience and previous reports,[9−13,20,21] we chose the relatively active diphenylmethane **1a** as an objective to investigate the difunctionalization of alkynes.

We first tested the reaction between phenylacetylene **1b** (0.2 mmol) and diphenylmethane **1a** with a stoichiometric amount of $CuCl_2$ and 1,2-dichloro-4,5-dicyanobenzoquinone (DDQ,

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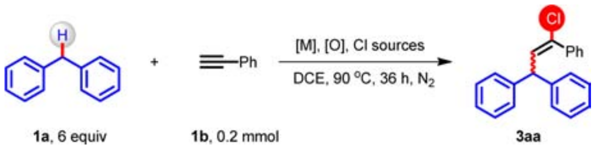
0.4 mmol) as an oxidant in 1,2-dichloroethane (DCE) as solvent. We observed the desired chlorobenzylation product **3aa** albeit in a very low yield (entry 1, Table 1). Other chloride salts also showed the reactivity to some extent, while $FeCl_2$ showed better performance (cf: entry 5 to entries 1−4). Different chlorides as the chloride source were screened in the presence of DDQ as an oxidant and 1.0 equiv of $FeCl_2$. We found that NCS promoted this reaction to 52% isolated yield (entries 6−10). It was noticed that the reaction was significantly improved by 1.2 equiv of DDQ and **3aa** was obtained in 61% isolated yield (entries 10−12). Other Fe salts, such as $FeCl_3$, Fe(acac)$_2$, $FeSO_4$, and Fe(OAc)$_2$, completely failed (entries 13−16). Since NCS also exhibited an oxidative ability, we tested the reaction in the absence of DDQ as an oxidant. No desired product was observed at all (entry 17). Other than DDQ, different oxidants, such as ^{t}BuOO^{t}Bu, $K_2S_2O_8$, BQ, and PhI(OAc)$_2$, were examined. Most of them were not suitable (entries 18−21), while ^{t}BuOO^{t}Bu showed a lower reactivity (entry 18). Different solvents were screened, including CH_2Cl_2, $CHCl_3$, DMF, toluene, and so on, and DCE performed the best. Control experiments showed that no reaction occurred in the absence of $FeCl_2$ (entry 22). Unfortunately, NBS and NIS were not workable to produce the corresponding Br/I substituted products.

Table 1. Optimization of Reaction Conditions[a]

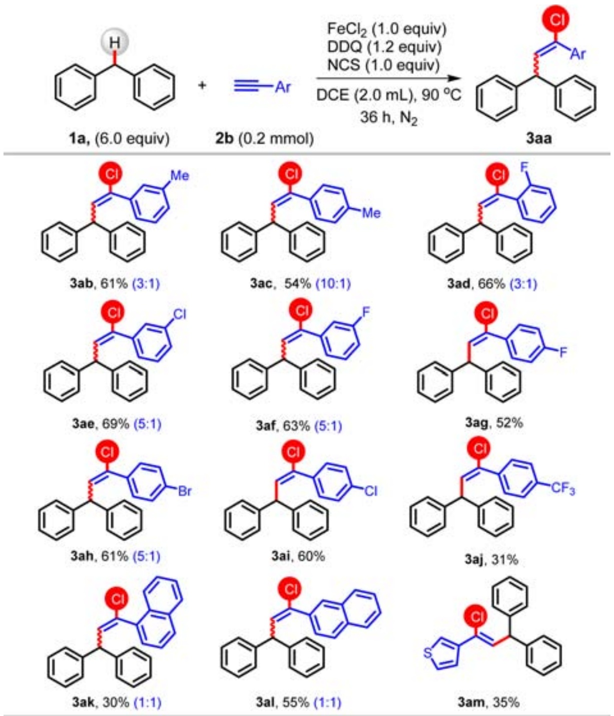


entry	[M] (*x* equiv)	[O] (*x* equiv)	[Cl] (1.0 equiv)	yield (%)[b]
1	$CuCl_2$ (1.0)	DDQ (2.0)	−	5
2	$InCl_3$ (1.0)	DDQ (2.0)	−	7
3	LiCl (2.0)	DDQ (2.0)	−	trace
4	$FeCl_2$ (1.0)	DDQ (2.0)	−	20
5	$FeCl_2$ (0.2)	DDQ (2.0)	−	trace
6	$FeCl_2$ (1.0)	DDQ (2.0)	NH_4Cl	28
7	$FeCl_2$ (1.0)	DDQ (2.0)	LiCl	23
8	$FeCl_2$ (1.0)	DDQ (2.0)	KCl	trace
9	$FeCl_2$ (1.0)	DDQ (2.0)	TMAC[b]	25
10	$FeCl_2$ (1.0)	DDQ (2.0)	NCS[c]	52
11	$FeCl_2$ (1.0)	DDQ (1.2)	NCS	61[c]
12	$FeCl_2$ (1.0)	DDQ (3.0)	NCS	43
13	$FeCl_3$ (1.0)	DDQ (2.0)	NCS	32
14	Fe(acac)$_2$ (1.0)	DDQ (2.0)	NCS	−[d]
15	$FeSO_4$ (1.0)	DDQ (2.0)	NCS	−[d]
16	Fe(OAc)$_2$ (1.0)	DDQ (2.0)	NCS	−[d]
17	$FeCl_2$ (1.0)	−	NCS	−[d]
18	$FeCl_2$ (1.0)	^{t}BuOO^{t}Bu (2.0)	NCS	19
19	$FeCl_2$ (1.0)	$K_2S_2O_8$ (2.0)	NCS	−[d]
20	$FeCl_2$ (1.0)	BQ (2.0)	NCS	−[d]
21	$FeCl_2$ (1.0)	PhI(OAc)$_2$ (2.0)	NCS	−[d]
22	−	DDQ (1.2)	NCS	−[d]

[a]The reaction was carried out with **1a** (1.2 mmol) and **1b** (0.2 mmol) in the presence of $FeCl_2$ (0.2 mmol), DDQ (2.4 mmol), NCS (0.2 mmol), and DCE (2.0 mL) at 90 °C for 36 h under N_2. TMAC: tetramethylammonium chloride, NCS: *N*-chlorosuccinimide. [b]GC yields with *n*-decane as an internal standard. [c]Isolated yield. [d]No desired products.

With the optimized reaction conditions in hand, we first investigated the scope of different substituted phenylacetylenes with **1a** as a partner. The results are summarized in Scheme 2.

Scheme 2. Scope of Different Substituted of Arylacetylenes

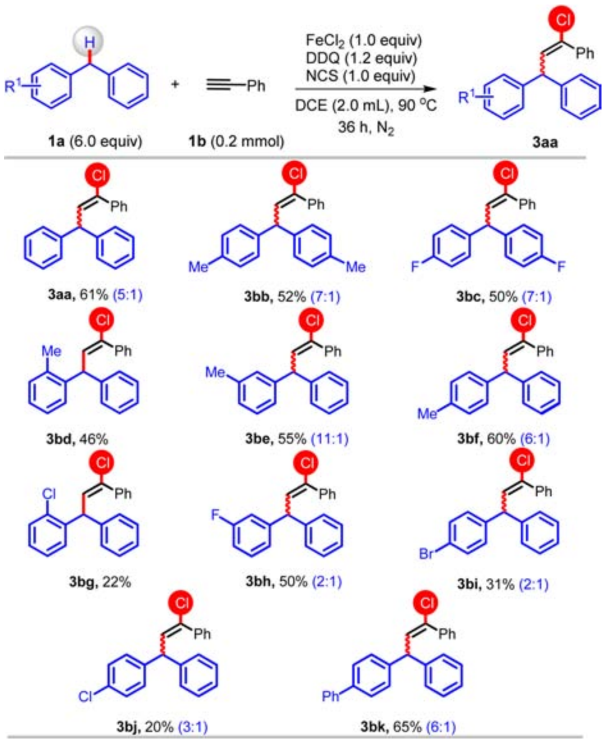


[a]The reaction was carried out with **1a** (1.2 mmol) and **2b** (0.2 mmol) in the presence of $FeCl_2$ (0.2 mmol), DDQ (2.4 mmol), NCS (0.2 mmol), and DCE (2.0 mL) at 90 °C for 36 h under N_2. The *E*/*Z* ratios were determined by ^{1}H NMR (400 MHz) and shown in parentheses.

Electron-withdrawing groups and slightly electron-donating groups on the phenyl ring were tolerated (**3ab**−**3aj**). Strong electron-donating groups were not compatible, which might indicate a Friedel−Crafts-type process or oxidation. Steric effects affected the efficiency: ortho substituted arylacetylenes slightly lowered the yield (**3ak**, **3al**). It is worth noting that C−X groups (X = Cl, Br) were tolerated, providing the possibility for further functionalization (**3ae**, **3ah**, **3ai**).[23] In addition, F and CF_3 groups were compatible under the standard conditions, which show some promise for pharmaceuticals and material chemistry (**3ad**, **3af**, **3ag**, **3aj**).[24] In addition, a thiophene substituted alkyne was also suitable for this transformation, albeit the product was generated in a lower yield (**3am**). Unfortunately, internal alkynes were not suitable. It was interesting that only *E*-selective products were dominantly observed in most of the cases. When the para-position of the phenyl ring was substituted, the *Z*/*E* ratio of the products is highly enhanced. Halo- substituents at the para-position on the phenyl ring only gave *E* isomers (**3ag**, **3ai**, **3aj**).

Subsequently, the scope of substituted diarylmethanes **1a** was explored (Scheme 3). Both electron-rich and weakly electron-deficient symmetrical diphenylmethane derivatives reacted smoothly to produce the desired products in good yields with complete regioselectivity (Markovnikov product) and high *E* selectivity (**3aa**−**3bc**). For example, bi(*p*-toluyl) and bi(*p*-florophenyl) methanes gave the desired products in moderate to good yields (**3bb** and **3bc**). Electronic effects seemingly

Scheme 3. Scope of Different Diarylmethanes

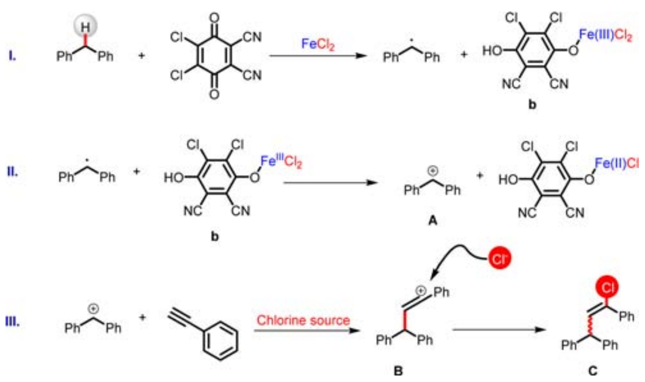


[a]The reaction was carried out with **1a** (1.2 mmol) and **1b** (0.2 mmol) in the presence of $FeCl_2$ (0.2 mmol), DDQ (2.4 mmol), NCS (0.2 mmol), and DCE (2.0 mL) at 90 °C for 36 h under N_2. The *E*/*Z* ratios determined by ^1H NMR (400 MHz) and shown in parentheses.

played an important role, and strong electron-donating groups, such as methoxyl and amino groups, on the phenyl ring were tolerated. It is understandable that the electron-rich ring bearing such electron-donating groups might be oxidized under these oxidizing conditions. However, electron-deficient substrates, especially those containing different halo- groups, survived well to give the desired products, which can be further transformed into different functional groups (**3bg**, **3bi**, **3bj**). This reaction is also slightly sensitive to steric effects, and an ortho substituted substrate gave a lower yield (**3bd**).

Based on previous reports and our observations, we assumed that the reaction was initiated by the Fe(II)-assisted single electron transfer (SET) oxidation to form the benzyl radical (Scheme 4I). The benzyl radical can be further oxidized to the benzyl cation **A** with generated Fe(III) species, while the Fe(II) species was regenerated (II). **A** subsequently underwent electrophilic attack with phenylacetylene to form vinyl cation **B**, which was captured by chloride to produce the corresponding product **C** (III). The steric and stereoelectronic effects made the *E*-isomers the dominant products. This hypothesis is consistent with the electronic effects on both substrates in this transformation.

Scheme 4. Proposed Mechanism



In summary, we have described a novel method to carry out chlorobenzylation of phenylacetylene via Fe(II)-promoted benzylic C−H activation under mild conditions. Functionalized alkenyl chlorides were obtained in high regioselectivity, and they can be applied as building blocks for further transformation in organic synthesis. To the best of our knowledge, this is the first example that shows chlorobenzylation of phenylacetylene initiated from a $C(sp^3)$−H bond functionalization. Compared to the reported methods, the desirable chemistry exhibited both atom and step economy. Considering the great potential of C−H functionalization and vast applicability of iron chemistry, we envisioned that this powerful combination may generate some synthetic possibilities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02472.

Experimental procedures and spectral data for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zshi@pku.edu.cn.
*E-mail: wangbiqin1964@126.com.

Notes

The authors declare no competing financial interest.

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