

# New and Efficient Iron Halide Mediated Synthesis of Alkenyl Halides through Coupling of Alkynes and Alcohols

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**Keywords:** Alkenyl halides / Alkynes / Alcohols / Iron / Sustainable chemistry

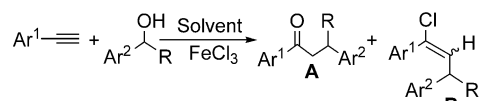
A novel, simple, and straightforward one-pot reaction of alkynes with various alcohols in the presence of iron salts (FeCl<sub>3</sub> and FeBr<sub>3</sub>) was described to yield the corresponding alkenyl halides with complete regioselectivity and high stereoselectivity. The reaction is high yielding and works under mild conditions. The iron salts act as Lewis acids and a

source of halides. The reaction tolerates a wide variety of functional groups. Noteworthy is that this method is cheap, efficient, and environmentally friendly.

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## Introduction

Very recently, we disclosed an iron salt catalyzed addition reaction between aryl alkynes and benzylic alcohols to synthesize aryl ketones.<sup>[1]</sup> We reported that the course of the reaction was highly solvent dependent; the product ketone (**A**) was only obtained exclusively in nitromethane solvent in the presence of FeCl<sub>3</sub> (15 mol-%), whereas in halogenated solvent, such as dichloromethane, the same reaction gave only a trace amount of the desired product along with an alkenyl halide (**B**) as a major product (Scheme 1). This observation encouraged us to study systematically the scope of this new reaction to develop an alternative method for the synthesis of alkenyl halides.



Scheme 1.

The synthesis of alkenyl and aromatic halides is of great academic and industrial importance, as they can be easily converted into other valuable compounds. Moreover, halides are common structural motifs in organic synthesis for C–C and C–N bond formation in transition-metal-catalyzed cross-coupling reactions, such as Suzuki–Miyaura, Stille, Sonogashira, and Buchwald–Hartwig reactions,<sup>[2]</sup> and the necessity of these compounds is also increased accordingly. Alkenyl halides, in particular, are versatile substrates in a variety of chemical transformations;<sup>[3]</sup> however,

the availability of alkenyl halides is low and they are often costly. Consequently, the preparation of such compounds is still challenging and of much interest to synthetic chemists. Traditionally, vinyl halides are prepared from the corresponding carbonyl compounds with halogenated reagents,<sup>[4]</sup> such as phosphorus halides or thionyl halides under prolonged heating in high-boiling solvents or by Wittig<sup>[5]</sup> and Julia<sup>[6]</sup> olefination reactions and other related reactions.<sup>[7]</sup> Alkynes are another class of compounds used for the synthesis of alkenyl halides, such as the addition of hydrogen halide and alkyl halides to alkynes in the presence of an excess amount of ZnCl<sub>2</sub>.<sup>[8]</sup> Very recently, Kabalka et al. reported a new strategy to synthesize alkenyl halides by direct reaction of alkynes and alcohols in the presence of a stoichiometric amount of a strong base such as *n*BuLi or boron trichloride.<sup>[9]</sup> Few of the above-said methods are very useful for the stereoselective synthesis of alkenyl halides, and most of these methods are associated with significant practical drawbacks including nonavailability of the substrates, drastic reaction conditions, long reaction times, use of toxic and expensive chemicals, multistep reactions, and production of large amounts of waste throughout the reaction sequences, which limit their massive applications for industrial purposes. Therefore, development of simple, straightforward, and environmentally friendly method for the synthesis of such halogenated derivative represents a highly desirable goal.

In this regard, the development of a new reaction by using iron<sup>[10]</sup> and alcohols<sup>[11]</sup> has earned much attention in organic synthesis, as iron is an abundant, economical, and environmentally friendly metal, and carbon–carbon bond-formation reactions with the use of alcohols is highly atom economical and consequently environmentally friendly. In this context, very recently we<sup>[1,12]</sup> and others<sup>[13]</sup> reported the direct catalytic activation of alcohols by using iron salts for various useful organic transformations.

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Herein, we present our new discovery for the synthesis of structurally varied alkenyl halides in one pot from alkynes and alcohols in the presence of iron salts under neutral conditions, and in this reaction, the iron salts act as Lewis acids and a source of halide.<sup>[14]</sup>

## Results and Discussion

For optimization of the reaction conditions, we initially tested the reaction between phenylacetylene (**1a**) and benzhydrol (**2a**) in the presence of varying amounts of anhydrous FeCl<sub>3</sub> in dichloromethane solvent (Table 1, Entries 1–7). The results showed that 40 mol-% FeCl<sub>3</sub> was the optimum amount (Table 1, Entry 5) and desired alkenyl halide **3a** was obtained in 68% in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Although the use of a larger amount of FeCl<sub>3</sub> reduced the reaction time, the yield of the product remain unchanged. The effect of other halogenated solvents, such as CCl<sub>4</sub>, 1,2-dichloroethane, and CHCl<sub>3</sub>, and non-halogenated solvents, such as benzene, acetone, and acetonitrile, were also tested. Although halogenated solvents worked efficiently for this transformation, dichloromethane was found to be the most effective. Apart from this study, it was also observed that no reaction took place in the presence of other metal halides such as FeCl<sub>2</sub> and NiCl<sub>2</sub>·6H<sub>2</sub>O (Table 1, Entries 15 and 16), whereas only 26% product was formed in case of InCl<sub>3</sub> (Table 1, Entry 17).

Table 1. Reaction of phenylacetylene (**1a**) and benzhydrol (**2a**) with different Lewis acids (in different amounts) and solvents.<sup>[a]</sup>

Entry	Lewis acid (mol-%)	Solvent	Time [h]	Yield <sup>[b]</sup> [%]	<i>E</i> : <i>Z</i> <sup>[c]</sup>
1	FeCl <sub>3</sub> (15)	CH <sub>2</sub> Cl <sub>2</sub>	3	24	91:9
2	FeCl <sub>3</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub>	3	32	90:10
3	FeCl <sub>3</sub> (30)	CH <sub>2</sub> Cl <sub>2</sub>	3	44	90:10
4	FeCl <sub>3</sub> (35)	CH <sub>2</sub> Cl <sub>2</sub>	2	56	91:9
5	FeCl <sub>3</sub> (40)	CH <sub>2</sub> Cl <sub>2</sub>	1.5	68	91:9
6	FeCl <sub>3</sub> (50)	CH <sub>2</sub> Cl <sub>2</sub>	1	68	89:11
7	FeCl <sub>3</sub> (60)	CH <sub>2</sub> Cl <sub>2</sub>	0.5	67	88:12
8	FeCl <sub>3</sub> (40)	CHCl <sub>3</sub>	9	52	90:10
9	FeCl <sub>3</sub> (40)	CCl <sub>4</sub>	9	44	91:9
10	FeCl <sub>3</sub> (40)	1,2 DCE	3	67	88:12
11	FeCl <sub>3</sub> (40)	CH <sub>3</sub> CN	5	0	—
12	FeCl <sub>3</sub> (40)	C <sub>6</sub> H <sub>6</sub>	5	0	—
13	FeCl <sub>3</sub> (40)	THF	5	N.R.	—
14	FeCl <sub>3</sub> (40)	(CH <sub>3</sub> ) <sub>2</sub> CO	5	N.R.	—
15	FeCl <sub>2</sub> (50)	CH <sub>2</sub> Cl <sub>2</sub>	5	0	—
16	NiCl <sub>2</sub> ·6H <sub>2</sub> O (50)	CH <sub>2</sub> Cl <sub>2</sub>	5	N.R.	—
17	InCl <sub>3</sub> (40)	CH <sub>2</sub> Cl <sub>2</sub>	7	26	89:11





















[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), solvent (3 mL), Lewis acid (amount as indicated in the table), r.t. [b] Pure, isolated yield after column chromatography. [c] Ratio calculated by <sup>1</sup>H NMR spectroscopic analysis of the products containing nonseparable *E/Z* mixtures.

The reaction procedure was very simple: a mixture of phenyl acetylene (1 mmol), benzhydrol (1 mmol), and FeCl<sub>3</sub> (0.4 mmol) was stirred at room temperature for 1.5 h. The progress of the reaction was followed by TLC. Usual workup and purification gave product **3a** as mixture of *E/Z* (91:9) isomers in 68% yield. The ratio was calculated by <sup>1</sup>H NMR spectroscopy and compared with the literature value.<sup>[8c,9c]</sup>

Having optimized the reaction conditions, the scope of this new reaction was investigated by using various benzylic alcohols with phenylacetylene. The results are summarized in Table 2. In general, the reaction proceeded smoothly at room temperature without removal of air and moisture. Both electron-rich and weakly electron-deficient benzylic alcohols reacted under the optimized reaction conditions to produce the desired products in good yield with complete regioselectivity (Markovnikov product) and with high *E* selectivity. The high regioselectivity may be explained by the formation of the more stable alkenyl carbocation intermediate during the addition of the benzylic carbocation onto the alkyne  $\pi$  bond (Scheme 2), and *E* selectivity can be explained from the preferred *trans* attack of the halide ions to the alkenyl carbocation. Alcohols that are sensitive towards acid-catalyzed dehydration can also tolerate the present reaction conditions (Table 2, Entries 3–8). In all cases, the *E* isomers predominated over the *Z* isomers of the substituted vinyl chloride derivatives. Notably, propargylic alcohol **2i** reacted smoothly with phenyl acetylene **1a** to produce the corresponding 1-chloro-1,4-enyne **3i** in high yield (63%) and with high selectivity in chloroform solvent (Table 2, Entry 9). 1-Halo-1,4-enynes are valuable synthetic intermediates because of their further synthetic manipulation. 1,4-Enynes are usually prepared by stoichiometric reaction of allyl halides with alkyne metal salts or by metal-catalyzed cross-coupling reactions of allyl halides with alkynes or alkynylborates.<sup>[9d,15]</sup> Similarly, the reaction of allylic alcohol **2j** with phenylacetylene gave 1-halo-1,4-diene **3j** in 46% yield (Table 2, Entry 10). Functionalized 1,4-pentadienes are very useful compounds in organic synthesis<sup>[16]</sup> and biological systems.<sup>[17]</sup> However, only few methods are available for the synthesis of 1,4-pentadienes, such as the cross-coupling of potassium vinyl trifluoroborates and allyl acetate in the presence of a palladium catalyst and related reactions.<sup>[18]</sup>

After having satisfactory results with various alcohols, we then applied this new protocol for various aromatic ring substituted alkynes (–Cl, –Br, –NHTs-*p*, –methyl). The results are summarized in Table 3. It was observed that the reaction was quite general with respect to the substituents of the terminal aromatic alkyne (Table 3, Entries 1–9). Aryl alkynes bearing weakly electron-withdrawing substituents, such as –Cl and –Br, reacted smoothly to furnish the desired products in high yield. However, aryl alkynes bearing strong electron-withdrawing groups, such as nitro, did not work. Furthermore, aromatic alkyne-bearing electron-donating substituents like –CH<sub>3</sub> reacted well and produced the desired product in satisfactory yield (Table 3, Entry 8). This reaction was also employed for aliphatic and internal alkynes, respectively (Table 3, Entries 10 and 11). Interest-

Table 2. Reaction of phenylacetylene (**1a**) with various alcohols (**2**) in the presence of FeCl<sub>3</sub>.<sup>[a]</sup>

Entry	Alcohol	Product	Time [h]	Yield [%] <sup>[b]</sup>	<i>E</i> : <i>Z</i> <sup>[c]</sup>
1			1.5	68	91:9
2			2	73	87:13
3			2	78	85:15
4			2.5	62	85:15
5			2	70	85:15
6			2	48	89:11
7			5	54	83:17
8			12	51 <sup>[d]</sup>	85:15
9			7	63 <sup>[d]</sup>	94:6
10			9	46 <sup>[d]</sup>	85:15

[a] Reaction conditions: **1a** (1 mmol), **2** (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), anhydrous FeCl<sub>3</sub> (0.4 mmol), r.t. for the set period of time. [b] Pure, isolated yield after column chromatography. [c] Ratio calculated by <sup>1</sup>H NMR spectroscopic analysis of the products containing nonseparable *E/Z* mixtures. [d] CHCl<sub>3</sub> was used in place of CH<sub>2</sub>Cl<sub>2</sub> to improve the product yield.

ingly, the formation of the desired products was observed in both cases. In the case of an internal alkyne, the reaction proceeded smoothly, producing the corresponding vinyl chloride in a moderate 45% yield (Table 3, Entry 11), whereas a lower yield of the desired product was obtained in the case of an aliphatic alkyne (Table 3, Entry 10).

To explore the generality of iron salts, we investigated this reaction with FeBr<sub>3</sub>; in principle, it should give the corresponding alkenyl bromides. However, it was observed that FeBr<sub>3</sub> also reacted efficiently under the same reaction conditions (Table 4, Entries 1–9) with various benzylic alcohols and alkynes and gave the corresponding alkenyl bromides in moderate to high yield and selectivity. Propargylic alcohol also reacted smoothly with phenylacetylene in the presence of FeBr<sub>3</sub> to produce the corresponding 1-bromo-1,4-enyne derivatives in moderate to good yield (Table 4, Entry 7 and 9) with exclusive formation of the *E* isomer. Likewise, 52% yield of the product was obtained in case of allylic alcohol in chloroform solvent (Table 4, Entry 8). The reaction of alkynes and alcohols in the presence of FeBr<sub>3</sub> is remarkable, as alkenyl bromide compounds are more popular in transition-metal-catalyzed cross-coupling reactions.

Except for a few limitations, such as the reaction did not proceed for nitro-substituted alkynes and alcohols and aliphatic alkynes gave lower yields of the desired product, the reaction is quite general with respect to alcohols and alkynes. In general, the reaction is quite efficient, high yielding, and simple, and it can be performed in the presence of air and moisture at room temperature. A wide range of functional groups, such as –OMe, –OBn, –NHTs-*p*, –Cl, –Br, and double and triple bonds remained unaffected under the reaction conditions.

On the basis of experimental observations, a possible mechanism of this reaction is proposed in Scheme 2, which is very similar to our previous mechanism for the synthesis of aryl ketones.<sup>[1]</sup> It was observed from our previous work and reported by others<sup>[1,13,19]</sup> that in the presence of a catalytic amount of FeCl<sub>3</sub>, benzylic alcohols were rapidly converted into dimeric ether **A** by eliminating water. Presumably, an incipient benzylic carbocation<sup>[20]</sup> is generated by the complexation of iron salts and ether, followed by nucleophilic attack of the alkyne moiety<sup>[21]</sup> onto the resulting benzylic carbocation to generate a more stable alkenyl cation **C** and an iron complex **B**. However, in contrast to our pre-

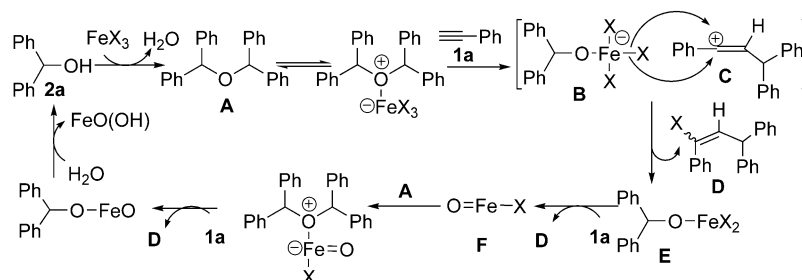


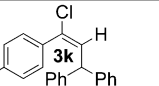

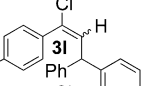

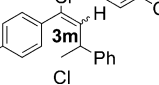

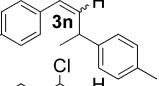

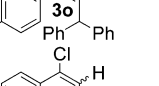
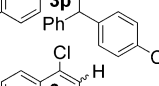
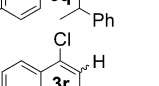

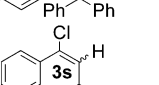

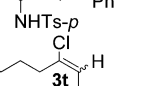

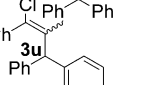

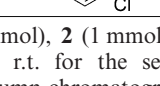
Scheme 2. Tentative mechanism for the FeX<sub>3</sub>-mediated synthesis of alkenyl halides.



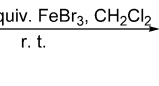

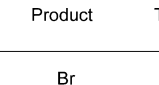

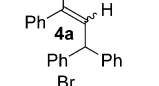

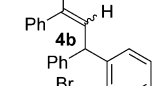

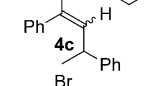

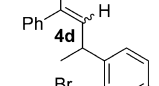

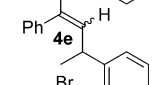

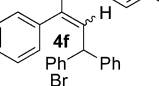

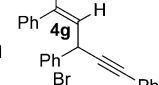
Table 3. Reaction of various alkynes **1** with various alcohols **2** in the presence of FeCl<sub>3</sub>.<sup>[a]</sup>

Entry	Alkyne	Alcohol	Product	Time [h]	Yield [%] <sup>[b]</sup>	<i>E:Z</i> <sup>[c]</sup>
1				5	55	100:0
2	<b>1b</b>			5	56	89:11
3	<b>1b</b>			2	65	87:13
4	<b>1b</b>			3	60	89:11
5		<b>2a</b>		3	52	87:13
6	<b>1c</b>	<b>2b</b>		5	66	88:12
7	<b>1c</b>	<b>2c</b>		5	64	82:18
8		<b>2a</b>		4	50	89:11
9		<b>2c</b>		5	71	88:12
10		<b>2a</b>		6	26 <sup>[d]</sup>	77:23
11		<b>2b</b>		3	45	71:29

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), anhydrous FeCl<sub>3</sub> (0.4 mmol), r.t. for the set period of time. [b] Pure, isolated yield after column chromatography. [c] Ratio calculated by <sup>1</sup>H NMR spectroscopic analysis of the products containing nonseparable *E/Z* mixtures. [d] 2 mmol alkyne **1f** was used.

vious mechanism, in this case the ion pairs (alkenyl cation **C** and iron complex **B**) are less stable in dichloromethane solvent (less polar) in comparison to nitromethane, and hence, in order to produce stability of the intermediates, the halide ion of the iron complex immediately reacts with alkenyl cation **C** to give the *E/Z* mixture of final product **D**. Moreover, a mixture of water and dichloromethane is a heterogeneous system, so the water molecules have less contact with the alkenyl cations. Hence, dichloromethane solvent gave exclusively alkenyl halides. Furthermore, the interaction of halogenated solvent with FeX<sub>3</sub> cannot be ruled out.<sup>[22]</sup> In this reaction, 40 mol-% of iron salts was sufficient to push the reaction forward, so the intermediate iron com-

Table 4. Reaction of various alkynes **1** with various alcohols **2** in the presence of FeBr<sub>3</sub>.<sup>[a]</sup>

Entry	Alkyne	Alcohol	Product	Time [h]	Yield [%] <sup>[b]</sup>	<i>E:Z</i> <sup>[c]</sup>
1				2	56	91:9
2	<b>1a</b>			3	62	87:13
3	<b>1a</b>			2	74	88:12
4	<b>1a</b>			4	81	86:14
5	<b>1a</b>			8	59 <sup>[d]</sup>	86:14
6		<b>2a</b>		16	75 <sup>[d]</sup>	73:27
7	<b>1a</b>			6	65 <sup>[d]</sup>	100:0
8	<b>1a</b>			8	52 <sup>[d]</sup>	84:16
9		<b>2i</b>		16	40 <sup>[d]</sup>	100:0

[a] Reaction conditions: **1a** (1 mmol), **2** (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), FeBr<sub>3</sub> (0.4 mmol), r.t. for the set period of time. [b] Pure, isolated yield after column chromatography. [c] Ratio calculated by <sup>1</sup>H NMR spectroscopic analysis of the products containing nonseparable *E/Z* mixtures. [d] CHCl<sub>3</sub> was used in place of CH<sub>2</sub>Cl<sub>2</sub> to improve the product yield.

plex **E** and iron oxyhalide **F** reacted successively with alkynes and ether for complete conversion of the reactants. After completion of the reaction, a solid precipitate was observed in the reaction mixture, which was probably due to the formation of iron oxyhydroxide. However, in the case of propargylic and allylic alcohols, formation of ether was not observed, and possibly the carbocation was generated directly from the alcohol without formation of ether.

## Conclusions

In summary, we have developed a novel sequential reaction of alkynes and alcohols (benzylic, allylic, and propargylic) in the presence of FeX<sub>3</sub> (X = Cl and Br) to synthesize



various substituted vinylic chlorides and bromides, which represents an excellent complement to the previously reported method by Kabalka et al. and others. In comparison to recently reported methods<sup>[14]</sup> our reaction conditions are more efficient and general, as propargylic and allylic alcohols also worked under our reaction conditions. Furthermore, other notable advantages of this method include operational simplicity (one-pot reaction, without removal of air or moisture), mild reaction conditions (room temperature), use of inexpensive and nontoxic iron salts, and direct use of alcohols (highly atom economic). Considering all these, this method is energy saving and environmentally friendly. In addition, as a result of the availability of all the starting materials, this reaction may prove very useful in organic synthesis. Further studies to explore the reaction mechanism and scope of this reaction are in progress in our laboratory.

## Experimental Section

**Representative Experimental Procedure for the Synthesis of (3-Chloroprop-2-ene-1,1,3-triyl)tribenzene (3a):** To a stirred solution of anhydrous ferric chloride (0.4 mmol) and benzhydrol (**2a**; 1 mmol) in dry dichloromethane (3 mL) was added phenylacetylene (**1a**; 1 mmol). The reaction mixture was stirred vigorously at room temperature, keeping the container tightly closed with a glass stopper. After completion of the reaction (by TLC), dichloromethane was evaporated under reduced pressure and the residue was purified by silica-gel (60–120 mesh) column chromatography (petroleum ether) to afford a mixture of *E* and *Z* isomers of desired product **3a** (*E*:*Z*, 91:9) as a white solid (0.68 mmol, 68%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.80 (d, *J* = 11.0 Hz, 1 H, **3a-E**, 3-H), 5.44 (d, *J* = 9.5 Hz, 1 H, **3a-Z**, 3-H), 6.47 (d, *J* = 11.0 Hz, 1 H, **3a-E**, 2-H), 6.63 (d, *J* = 9.5 Hz, 1 H, **3a-Z**, 2-H), 7.13–7.38 (m, 15 H, **3a-E**, arom-H; m, 15 H, **3a-Z**, arom-H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 50.7, 50.8, 126.7, 128.2, 128.3, 128.4, 128.7, 128.7, 128.9, 129.6, 131.4, 131.5, 136.9, 143.0, 143.4 ppm.<sup>[9c]</sup>

**Supporting Information** (see footnote on the first page of this article): Experimental details and spectroscopic data of all compounds.

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