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Copper Promoted Regio- and Stereo-selective Aminochlorination of Alkynes and Alkenes with NFSI

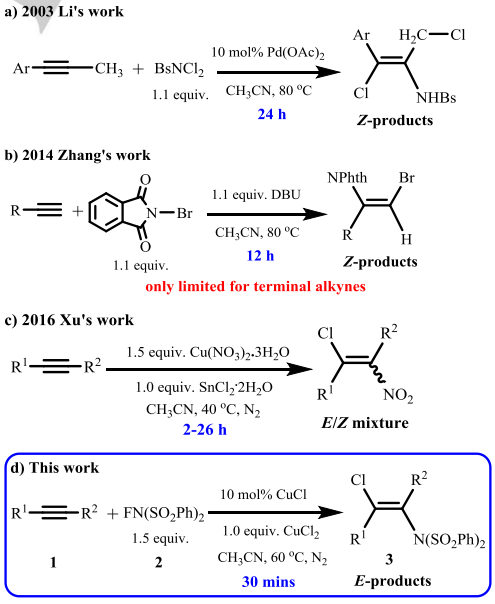
Weilin Wang,[a] Lingyan Liu*[a] , Weixing Chang,[a] Jing Li*[a,b]

Dedication ((optional))

Abstract: A simple and rapid copper promoted aminochlorination of unactivated alkynes and alkenes with NFSI was developed. Two series of chloroenamines and chloroamines were obtained in good to high yields, respectively. And the chlorinated enamines could be obtained in a single *E*-configuration. This reaction involved a radical process, and the $CuCl_2$ acting as *Cl* source, the NFSI as *N* source.

The bifunctionalization of carbon-carbon unsaturated bonds has attracted increasing attention in the field of mordern organic methodology due to its high efficiency and atom economy. Among them, the vicinal aminohalogenation reactions of alkenes has also been well developed in the past decades.[1] And the corresponding haloamines can be further transformed to the other complex compounds. As a comparison, the amino-halogenation of common alkynes are rarely reported.[2] For example, Li's research group developed a Pd-catalyzed mutiple-site functionalization of alkynes using *N*,*N*-dichlorobenzene-sulfonamide as both *N* and *Cl* sources in 2003 (Scheme 1a).[2a] In the following decade, there are scarce literatures about the aminohalogenation of alkynes. Until 2014, Zhang's group employed *N*-bromophthalimide (NBP) to react with common alkynes in the presence of Lewis base 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and gave the *Z*-bromoenamines products. Notably, this reaction was limited to the terminal alkynes (Scheme 1b).[2b] The chloronitration of alkynes was then developed using the combination of $Cu(NO_3)_2{\cdot}3H_2O$ and $SnCl_2{\cdot}2H_2O$ in 2016, and a *Z*/*E*-mixture of α-chloro-β-nitroolefins was obtained (Scheme 1c).[2c] As we all know, the haloenamines are significant intermediates of bioactive natural products and medicines, as well as versatile building blocks in organic synthesis due to their multi-functional groups, such as halogen, amino and carbon-carbon double bond. Therefore, it remains great desirable to develop novel methodologies for the aminohalogenation of unactivated alkynes, thus for the construction of haloenamines.

On the other hand, *N*-fluorobenzenesulfonimide (NFSI), commercially available and bench stable, is traditionally utilized as an electrophilic fluorination reagent or as an oxidant in transition metal catalyzed reactions.[3] In recent years, the NFSI has been exploited as *N* source in the bifunctionalization reactions of alkenes or alkynes. Most of these reactions employed Cu salts as catalysts with the combination of NFSI and ligands. Zhang's research group has made great achievements in this field.[4] And there were two typical examples of alkynes (simple terminal alkynes[4a] and functionalized alkynes-propargylic alcohols[4b]) using NFSI as *N* source to generate the α-amino-α-aryl ketones and α-amino-β-aryl unsaturated carbonyl compounds, respectively. Although the aminohalogenation of alkenes has been maturely developed, it remains elusive and great challenge for the bifunctionalization of alkynes. Considering that and based on the Zhang's work, we attempted to employ the combination system of Cu salts and NFSI to transform the unactivated alkynes. As a result, a simple and rapid methodology was developed for the construction of *E*-chloroenamines through the aminochlorination reaction of alkynes (Scheme 1d). And this reaction was carried out without any ligands.



Scheme 1. The 1,2-bifunctionalization reactions of alkynes

In our initial study, the phenylacetylene **1a** was selected to react with NFSI **2** in the presence of CuCl at 50 °C in CH_3CN with the expectation of generating the fluoroenamine. However, the trace of chloroenamine **3a** was obtained with the great amount of substrates decomposed (Table 1, entry 1). In view of chloroenamine obtained, we attempted to introduce additional *Cl* source, such as NaCl, $ZnCl_2$, $AlCl_3$ and $FeCl_3$, the reaction was still sluggish (entries 2-5). In the presence of chlorosuccinimide

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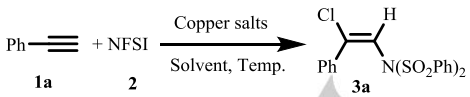
(NCS), the reaction of phenylacetylene and NFSI was complicated (entry 6). Directly using 1.0 equiv. CuCl, the chloroenamine **3a** could be produced in 33% yield (entry 7). Intrigued by this and based on the previous literatures about the system of CuXn/NFSI, both Cu(I) and Cu(II) as well as Cu(III) intermediates are generally involved, the $CuCl_2$ was then employed to act as a *Cl* source. Consequently, the yield of chloroenamine **3a** could be improved to the moderate level yield of 56% (entry 8). Increasing the reaction temperature from 50 to 60 °C and the amount of NFSI, the yield of target prodcut were gradually improved to 65% and 74% (entries 9-10). But increasing the amount of $CuCl_2$ to 1.5 equiv., the reaction gave decreased yield of chloroenamine **3a** in 47% on the contrary (entry 11). It may be due to the decomposition of NFSI by the excess $CuCl_2$. Diluting the reaction concentration with 2 mL CH_3CN or decreasing the reaction temperature to r.t., or finely tuning the amount of CuCl as well as changing $CuCl_2$ to $CuCl_2{\cdot}2H_2O$, no obvious improved results were obtained (entries 12-17). Using the other solvents, such as PhMe, DCE, DMF and MeOH, no products were obtained with the substrate **1a** nearly remaining untouched in all above cases in the presence of CuCl (0.1 equiv.) / $CuCl_2$ (1.0 equiv.) and NFSI (1.5 equiv.). In PhCN, low yield of chloroenamine **3a** was generated. Empolying a single $CuBr_2$, the reaction was fast and complicated at room temperature in 10 mins, and no expected bromoenamine was produced even at 0 °C for 30 mins (entries 18-19). Continuing to decrease the reaction temperature to -30 °C, the reaction gave only 7% yield of bromoenamine (entry 20). Summarily, the optimal reaction conditions were as follows: alkynes (0.2 mmol), NFSI (1.5 equiv.), CuCl (0.1 equiv.) and $CuCl_2$ (1.0 equiv.) at 60 °C in CH_3CN (1 mL) for 25-30 mins. It should be noted that the chloroenamines were obtained in a single *E*-configuration in all cases.

Table 1. The screening of experimental parameters in the aminochlorination of phenylacetylene **1a**[a]

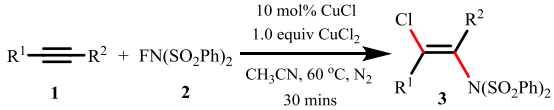


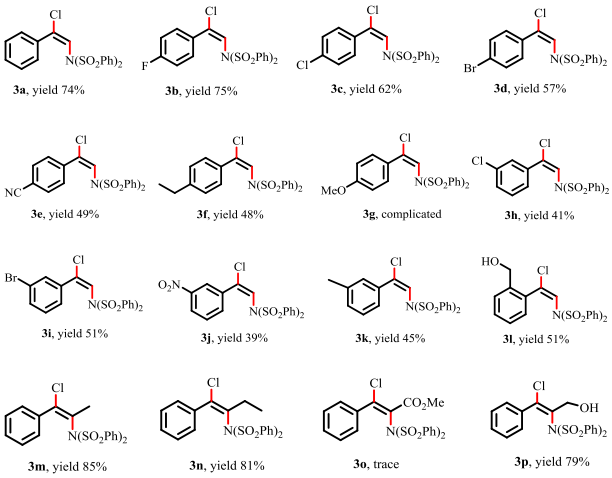
entry	Catal (equiv.)	Cl source (equiv.)	Yield (%)[b]
1[c]	CuCl (0.1)	--	5
2[c]	CuCl (0.1)	NaCl (1.0)	< 5
3[c]	CuCl (0.1)	$ZnCl_2$ (1.0)	< 5
4[c]	CuCl (0.1)	$AlCl_3$ (1.0)	< 5
5[c]	CuCl (0.1)	$FeCl_3$ (1.0)	< 5
6[c]	CuCl (0.1)	NCS (1.0)	Complicated
7[c]	CuCl (1.0)	--	33
8[c]	CuCl (0.1)	$CuCl_2$ (1.0)	56
9	CuCl (0.1)	$CuCl_2$ (1.0)	65
10	**CuCl (0.1)**	**$CuCl_2$ (1.0)**	**74**
11	CuCl (0.1)	$CuCl_2$ (1.5)	47
12[d]	CuCl (0.1)	$CuCl_2$ (1.0)	42
13	--	$CuCl_2$ (1.0)	48
14	CuCl (0.2)	$CuCl_2$ (1.0)	54
15	CuCl (0.05)	$CuCl_2$ (1.0)	49
16	CuCl (0.1)	$CuCl_2{\cdot}2H_2O$ (1.0)	51
17[e]	CuCl (0.1)	$CuCl_2$ (1.0)	51
18[f]	--	$CuBr_2$ (1.0)	Complicated
19[g]	--	$CuBr_2$ (1.0)	Complicated
20[h]	--	$CuBr_2$ (1.0)	7

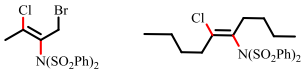
Note: entries 1-9 NFSI (69 mg, 1.1 equiv.); entries 10-20 NFSI (94.6 mg, 1.5 equiv.). [a] The procedure: To the Schlenk tube was added the phenylacetylene **1a** (0.2 mmol), a certain amount of catalyst, *Cl* source and NFSI in CH_3CN (1.0 mL) at 60 °C under N_2 for 25 mins. [b] Isolated yield. [c] The reaction temperature was 50 °C. [d] The solvent is 2 mL. [e] The reaction time was 6 h at r.t.. [f] The reaction time was 10 mins at r.t.. [g] The reaction time was 30 mins at 0 °C. [h] The reaction time was 30 mins at -30 °C and the yield was determined by the ^1H NMR of crude product through using 1,4-dioxane as an internal standard sample.

The scope and limitation of this conversion was then investigated with the optimized reaction conditions (Table 2). Remarkably, all alkynes, whether terminal alkynes or internal alkynes, whether alkyl alkynes or aryl alkynes, were competent in this aminochlorination reaction and produced the corresponding chloroenamines derivatives in good yields. For instance, the phenylacetylene derivatives bearing with electron-withdrawing substituents generally gave better yields than that with electron-donating groups (**3b-3e**, **3h** and **3i** vs **3f-3g**, **3k**). For the *p*-methoxyphenylacetylene, the reaction was complicated (**3g**). The reason remained unclear at present. Interestingly, the *o*-hydroxyethylphenylacetylene was also tolerant to deliver the corresponding chloroenamine **3l** in moderate yield of 51%. Furthermore, the internal alkylphenylacetylenes (methyl, ethyl and hydroxymethyl) rendered the best yields of 85% (**3m**), 81% (**3n**) and 79% (**3p**), respectively. Nevertheless, the methyl 3-phenyl propiolate was unsuitable for this methodology (**3o**). In the case of the dec-5-yne, this reaction could smoothly proceed and afford the chloroenamine **3r** in 36% yield. But for the 1-bromobut-2-yne, no target compound (**3q**) was obtained with the complicated reaction system. The absolute structure of product **3b** was unambiguously determined by the single crystal X-ray diffraction (Figure 1).[5]

Table 2. The scope of alkynes[a]







3q, complicated **3r**, yield 36%

[a] Standard conditions: **1a**-**1r** (0.2 mmol), 10 mol% CuCl, $CuCl_2$ (1.0 equiv., 0.2 mmol) and NFSI (1.5 equiv, 0.3 mmol) in CH_3CN (1.0 mL) under argon. [b] Isolated yields. [c] All of the products are E-configuration.

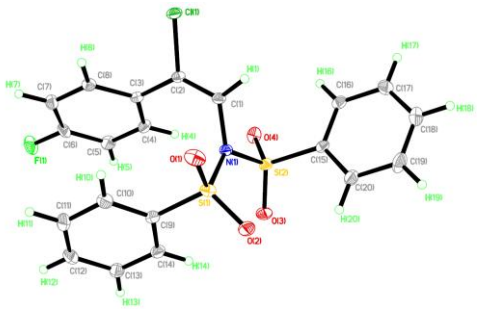
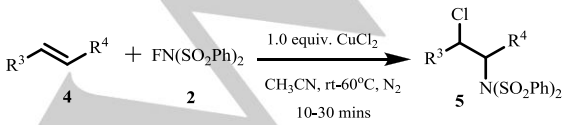


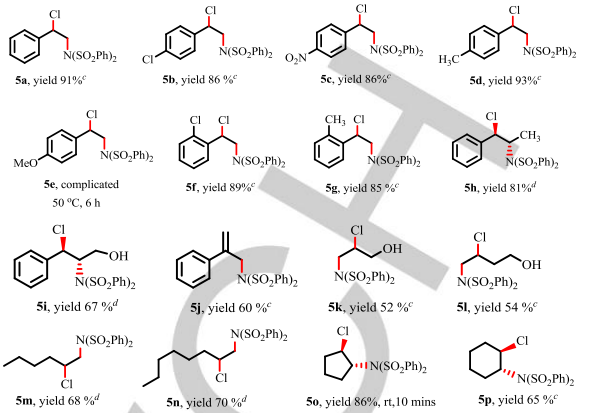
Figure 1. The ORTEP drawing of **3b**

Then this methodology was also applied into the alkenes. Due to the reactivity differences between the alkene and alkynes, some screenings of reaction conditions were also made as shown in Table S1. It was found that only using a single $CuCl_2$, the reaction of styrene **4a** and NFSI (1.1 equiv.) could afford the chloroamine **5a** with high up to 91% yield at 50 °C for 25 mins. Therefore, other styrene derivatives or alkenes were further explored (Table 3). Similarly, all alkenes were good candidates for this methodology, providing the vicinal chloroamines compounds in good to high yields. In detail, styrenes with various substituents, such as Cl, NO_2 and CH_3 whether at the *ortho*- and *para*-position of the aromatic ring, could easily undergo this transformation (**5b**-**5d**, **5f**-**5g**). The *p*-methoxystyrene, similar with the *p*-methoxyphenylacetylene, was sluggish in this reaction (**5e**). The β-substituted styrenes, **4h** and **4i**, also delivered the corresponding chloroamines in good yields (**5h**, 81%; **5i**, 67%). However, in the case of the α-methylstyrene, the reaction gave *N*-(2-phenylallyl)-*N*-(phenylsulfonyl)-benzene sulfonamide **5j** as a major product via a single electron transfer and elimination of proton process from the α-methylbenzyl radical **E** intermediate rather than capture by Cl anion from $CuCl_2$. For the terminal olefins (**4k**-**4n**) or cycloalkenes (**4o**-**4p**), the aminochlorination reactions could also smoothly proceed and afford the target compounds in good yields (**5k**-**5p**). Notably, the stereostructures of **5h** and **5i**, **5o** and **5p** were all *anti*-configurations based on the NMR data.[6]

Table 3. The scope of alkenes[a]

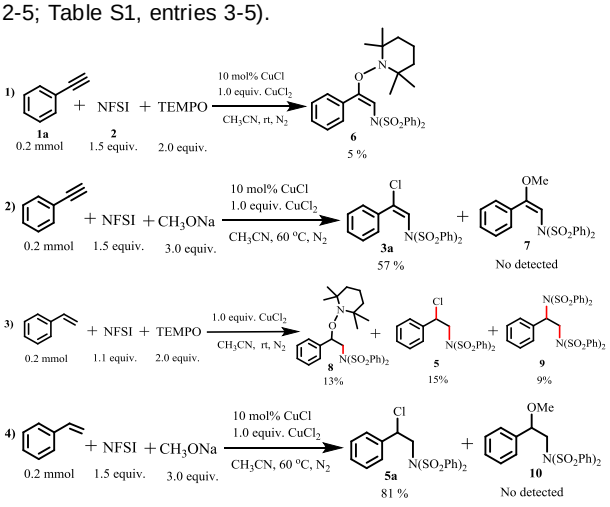


4 + 2 → 5



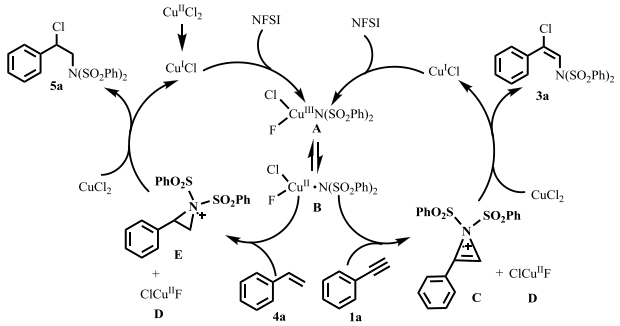
[a] Standard conditions: **4a**-**4p** (0.2 mmol), $CuCl_2$ (27 mg, 0.2 mmol, 1.0 equiv.) and NFSI (69 mg, 0.22 mmol, 1.1 equiv.) in CH_3CN (1.0 mL) under N_2. [b] Isolated yields. [c] 50 °C, 25 mins. [d] 60 °C, 30 mins.

To probe the reaction mechanism, several controlled experiments were performed (Scheme 2). The TEMPO was first added into the reaction of phenylacetylene or styrene and NFSI at r.t., the small amount of compounds **6** and **8** trapped by TEMPO were isolated with the great amount of starting materials decomposition. It demonstrated that the reaction involved the 1-phenyl-2-(N-(phenylsulfonyl) phenylsulfonamido)ethenyl radical or 1-phenyl-2-(N-(phenyl sulfonyl)-phenylsulfonamido)ethyl radical, respectviely (Scheme 2, eq.1 and 3). And the aminomethoxylation products **7** and **10** were not observed with the addition of MeONa, as indicated that the 1-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)ethen-1-ylium or 1-phenyl-2-(N-(phenylsulfonyl)phenyl-sulfonamido)ethan-1-ylium were not involved (Scheme 2, eq.2 and eq.4). Moreover, it could also explain that the addition of other Cl anion sources has no effect on the reactions of alkynes or alkenes and NFSI in the presence of $CuCl_2$ (Table 1, entries 2-5; Table S1, entries 3-5).



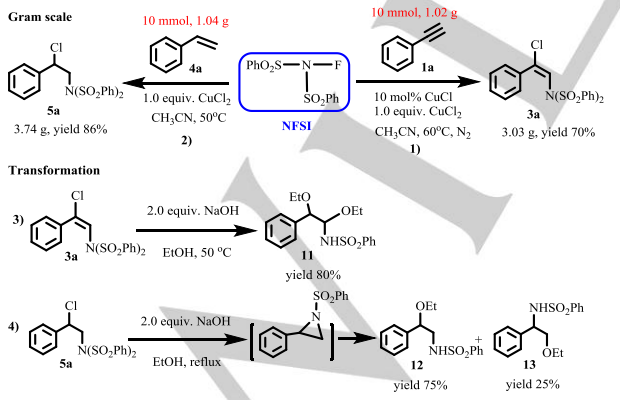
Scheme 2. The controlled experiments

Based on the above results and combination with previous literatures,[4,7] a plausible mechanism was then proposed as shown in Scheme 3. For the alkynes and alkenes, the same high active species **B** was genarated from the NFSI and CuCl. This N radical attacked the phenylacetylene and styrene to give the azirinium **C** and azidinium **E**, which further trapped Cl anion from the $CuCl_2$ which was accompanied with a single electron transfer to produce the target compounds **3a** and **5a** with the release of CuCl, respectively.



Scheme 3. The possible aminochlorination reaction mechanism of alkynes and alkenes.

The gram scale and transformation of the aminochlorination of alkynes and alkenes were further investigated (Scheme 4). It was observed that the corresponding chloroenamine **3a** and chloroamine **5a** could be produced in 70% and 86% yields in the 10 mmol scale of starting materials, respectively (Scheme 4, eq. 1 and eq.2). Treating the chloroenamine **3a** with the NaOH in EtOH at 50 °C, the N-(1,2-diethoxy-2-phenylethyl) benzenesulfonamide **11** was obtained, whereas for the chloroamine **5a**, the N-(2-ethoxy-2-phenylethyl) benzene sulfonamide **12** was generated as a major product under the similar reaction conditions accompanied by the small amount of **13** (eq.3 and eq.4).



Scheme 4. The gram scale of the aminochlorination of alkynes or alkenes and transformations of chloroenamine **3a** and chloroamine **5a**.

In summary, we have established a simple and rapid methodology for the aminochlorination of unactivated alkynes and alkenes, and thus for the construction of functionalized chloroenamines and chloroamines in good to high yields, respectively. The reaction displays some advantages, such as the mild reaction conditions, simple and rapid, no ligand and wide broad substrates application. The azirinium and azidinium intermediates were involved in the aminochlorination reactions of alkynes and alkenes. Our ongoing studies focus on more diverse transformations of chloroenamines and chloroamines as well as functionalized alkynes and alkenes.

Experimental Section

To a Schlenk tube was added NFSI (95 mg, 0.3 mmol, 1.5 equiv.), CuCl (2 mg, 0.02 mmol, 0.1 equiv.) and $CuCl_2$ (27 mg, 0.2 mmol, 1.0 equiv.) under N_2 atmosphere. Then alkynes **1** (0.2 mmol, 1.0 equiv.) and CH_3CN (1.0 mL) were sequentially added into a Schlenk tube. The reaction mixture was stirred at 60 °C for about 0.5 h until complete disappearance of **1** (monitored by TLC). The mixture was passed through a short kieselguhr column by using CH_2Cl_2 as elution and concentrated in vacuo, purified by flash chromatography on silica gel (gradient elution of EtOAc /petroleum ether, PE : EA = 10 : 1).

Acknowledgements

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Keywords: aminochlorination • alkynes • alkenes• NFSI • chloroenamine

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[5] Crystal data for the compound **3b**: $C_{20}H_{15}Cl_1F_1N_1O_4S_2$, MW) 451.90, Triclinic, P1, Final R indices [I> 2σ(I)], R1) 0.0395, wR2) 0.0773, R indices (all data) R1) 0.0509, wR2) 0.0837, a = 8.5698(17) Å, b = 8.9797(18) Å, c = 15.186(3) Å, V) 985.9 (3) A^3, T) 113 K, Z) 2. Reflections collected / unique: 11682 / 8311 [R(int) = 0.0224], number of observations [>2σ(I)] 8311, parameters) 523, Goodness-of-fit on F^2) 0.987. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC 1818546.

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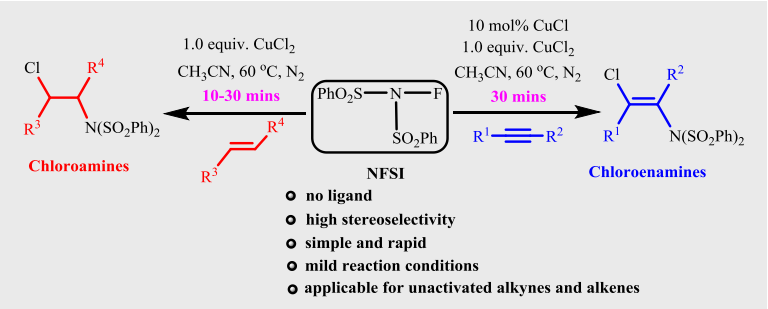

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Copper Promoted Regio- and Stereo-selective aminochlorination of alkynes and alkenes with NFSI

A novel aminochlorination reaction of alkynes and alkenes was developed using $CuCl_2$/NFSI. And high yields, high stereoselectivities of chloroenamines and choroamines were obtained.