Synthetic Methods

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Copper-Catalyzed Intermolecular Aminocyanation and Diamination of Alkenes**

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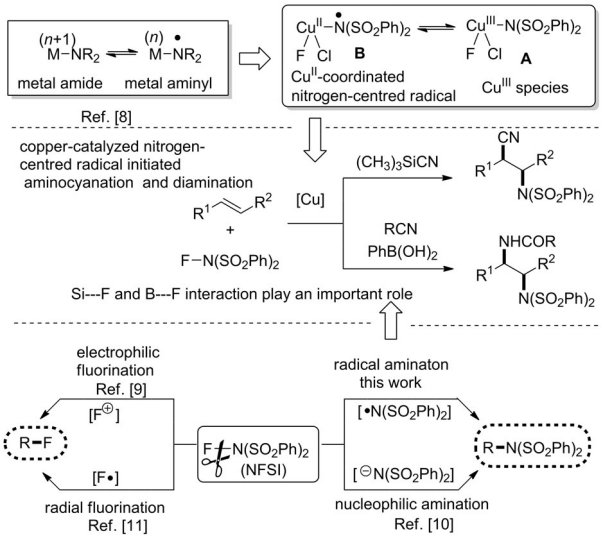
The alkene functional group is ubiquitous, and alkene difunctionalization, the addition of two functional groups across a double bond, exemplifies a class of reactions with significant synthetic potential.[1] In this context, metal-catalyzed aminative difunctionalization of alkenes, such as diamination, aminooxygenation, aminofluorination, aminochlorination, aminobromination, and carboamination have been successfully used to provide important strategies for the syntheses of very useful molecules with vicinal amino-heteroatom or amino-carbon substitution.[1] However, the dominant pathways for aminative difunctionalization of alkenes focus on alkenes bearing a tethered nitrogen nucleophile to perform a necessary intramolecular amination step. Therefore, a general methodology towards effective intermolecular aminative difunctionalization of alkenes is highly desirable. A well-known intermolecular difunctionalization of alkenes, the Meerwein arylation reaction, initiated by aryl radical is a good example as the key step.[2] We reasoned that facile generation of a nitrogen-centred radical could be key for a general pathway towards intermolecular aminative difunctionalization of alkenes.

Nitrogen-centred radicals play an important role in many chemical and biological processes.[3] However, the synthetic potential for nitrogen-centred radicals has remained largely unexplored, especially when compared with carbon radicals. The core challenge can be attributed to the deficiency of a convenient route for the generation of relatively stable nitrogen-centred radical species.[4–7] Recently, Grützmacher and co-workers succeeded in the isolation of a stable metal-coordinated aminyl radical complexes and highlighted the potential role of their application as a hydrogen-atom abstractor.[8] It was recognized that an equilibrium existed between an M(n+1) amide and M(n) aminyl through a redox procedure (Scheme 1).[8a,b] Therefore, we tried to obtain the metal-coordinated nitrogen-centred radical generated from a M–N bond with higher metal oxidation state. For example, the formation of the copper(II)-coordinated nitrogen-centred radical species **B** from the copper(III) complex **A** (Scheme 1). *N*-Fluorobenzenesulfonimide (NFSI) has been widely used as both an electrophilic fluorination reagent[9] and nucleophilic aminating reagent (Scheme 1).[10] Very recently, NFSI was also successfully utilized as a fluorine-transfer reagent to alkyl radicals by homolytic cleavage of an N–F bond.[11] Therefore, NFSI was chosen as a potential radical nitrogen source, which has not been previously reported, for this work.



Scheme 1. Aminative difunctionalization of alkenes with NFSI.

β-Amino acids have gained considerable attention because of their antibiotic, antifungal, cytotoxic, and other important pharmacological properties.[12] Direct aminocyanation of alkenes might provide the most straightforward procedure for the synthesis of β-amino acids from simple alkenes. Although Ni-, Pd-, Ga-, and Pt-catalyzed cyanodifunctionalization reactions,[13] such as silylcyanation, germylcyanation, stannylcyanation, borylcyanation, carbocyanation, thiocyanation, bromocyanation, and oxycyanation, have gained increasing attention in the past decade, to our knowledge, aminocyanation reactions directly from alkenes have never been reported. In the present work, we report the first copper-catalyzed aminocyanation (Scheme 1) of alkenes with NFSI and trimethylsilyl cyanide (TMSCN) with high regioselectivity by the facile construction of a C–N bond through the addition of a nitrogen-centred radical to alkenes. In addition, novel copper-catalyzed diaminations (Scheme 1) of styrenes with NFSI and various nitriles were also developed. The Si–F and B–F interactions play an important role in

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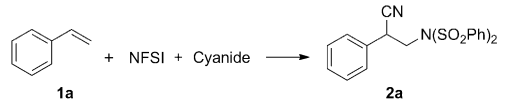
the efficient aminocyanation and diamination reactions, respectively.

As part of our continuing interest in employing efficient the nitrogen sources for the construction of a C–N bond directly from a C–H bond,[10b,14] we attempted the copper-catalyzed aminocyanation reaction of alkenes with NFSI and cyanides. In the presence of 10 mol% CuBr, the reaction of styrene (**1a**, 0.5 mmol), NFSI (1.4 equiv), and TMSCN (1.4 equiv) in 2 mL of 1,2-dichloroethane (DCE) at 70°C was performed for 1 hour under air, and trace amounts of desired aminocyanation product **2a** were obtained (Table 1, entry 2). The yield of **2a** was increased to 60% and 52% by employing 10% pyridine and bathocuproine, respectively, as ligands (Table 1, entries 3 and 4). We identified 1,10-phenanthroline as the best ligand, which gave **2a** in 85% yield (Table 1, entry 5). With CuCl, CuI, CuOAc, CuCN, and $Cu(OAc)_2$ as catalysts, **2a** was provided in 70, 82, 53, 67, and 40% yields, respectively (Table 1, entries 6–10). $CuBr_2$ and $Cu(OTf)_2$ were not effective (Table 1, entries 11 and 12), and cyanides such as $Zn(CN)_2$, CuCN, and K_3FeCN_6 were not as effective as TMSCN (Table 1, entries 13–16). Acetonitrile and nitromethane were also good solvents for this transformation (Table 1, entries 17 and 18). Finally, the best result (90% yield) was obtained when this reaction was performed in a sealed tube with dichloromethane (CH_2Cl_2) as the solvent (Table 1, entry 20). Notably, the transformation from **1a** into **2a** represents the first direct aminocyanation from alkenes. Recently, with palladium as a catalyst, Liu and co-workers[15] developed an aminofluorination of styrenes with NFSI. Interestingly, under our reaction conditions, the regioselectivity of the aminocyanation reaction of NFSI with styrene is different from that of the aminofluorination with regard to the position of the construction of the C–N bond.

With the optimized reaction conditions in hand (Table 1, entry 20), the scope of the aminocyanation was examined and the results are summarized in Table 2. The reaction of NFSI, TMSCN, and variety of styrene derivatives afforded the desired aminocyanation products **2** in 20–90% yields. In these reactions, halo-substituted styrenes were tolerated in the aminocyanation reaction, and could be very useful for further transformations (**2b–f**). Some other alkenes, such as ethoxyethene (**1o**) and 2-(vinyloxy)propane (**1p**) underwent this aminocyanation reaction to provide the aminocyanation

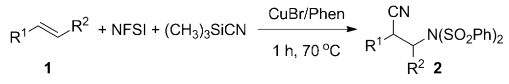
Table 1: Optimization of the aminocyanation.[a]

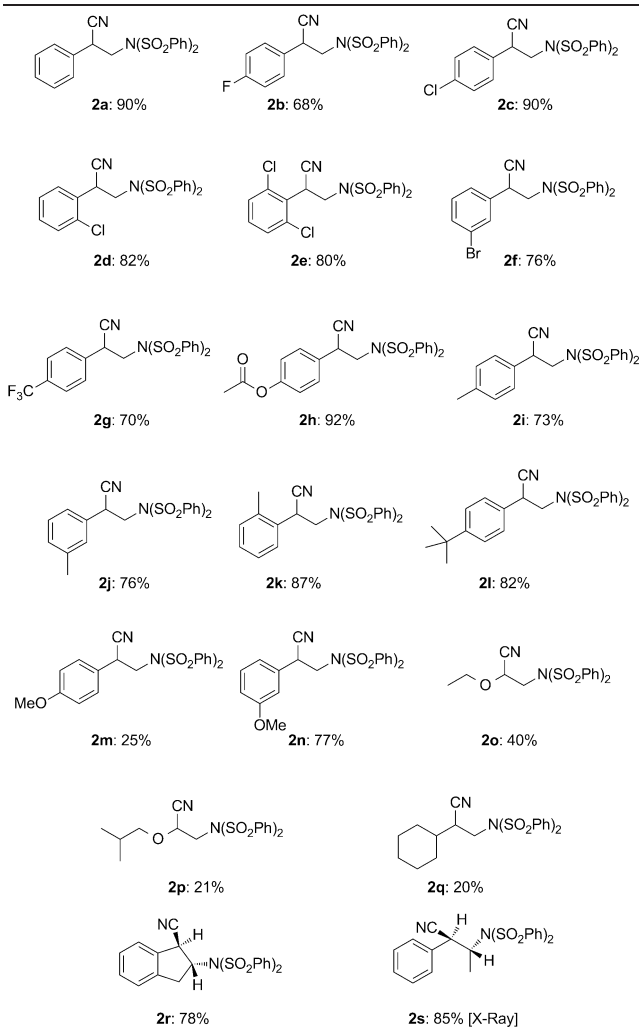


Entry	Metal	Cyanide	Ligand	Solvent	Yield [%][b]
1	None	TMSCN	none	DCE	0
2	CuBr	TMSCN	none	DCE	trace
3	CuBr	TMSCN	Pyridine	DCE	60
4	CuBr	TMSCN	BC	DCE	52
5	CuBr	TMSCN	Phen	DCE	85
6	CuCl	TMSCN	Phen	DCE	70
7	CuI	TMSCN	Phen	DCE	82
8	CuCN	TMSCN	Phen	DCE	67
9	CuOAc	TMSCN	Phen	DCE	53
10	$Cu(OAc)_2$	TMSCN	Phen	DCE	40
11	$CuBr_2$	TMSCN	Phen	DCE	trace
12	$Cu(OTf)_2$	TMSCN	Phen	DCE	0
13	CuBr	$Zn(CN)_2$	Phen	DCE	0
14	CuBr	$Zn(CN)_2$	Phen	MeCN	32
15	CuBr	CuCN	Phen	MeCN	23
16	CuBr	K_3FeCN_6	Phen	MeCN	0
17	CuBr	TMSCN	Phen	MeCN	72
18	CuBr	TMSCN	Phen	CH_3NO_2	73
19[c]	CuBr	TMSCN	Phen	DCE	60
20	CuBr	TMSCN	Phen	CH_2Cl_2	90

[a] Reactions were carried out with **1a** (0.5 mmol), NFSI (1.4 equiv), cyanide (1.4 equiv), metal (0.1 equiv) and ligand (0.1 equiv) in 2 mL solvent under air atmosphere at 70°C for 1 h, unless noted otherwise. [b] Yield of the isolated product. [c] The reaction was performed for 1.5 h and 0.05 equiv of CuBr and 0.05 equiv of Phen were used. BC = bathocuproine, Phen = 1,10-phenanthroline, Tf = trifluoromethanesulfonyl.

Table 2: The scope of the aminocyanation.[a,b]





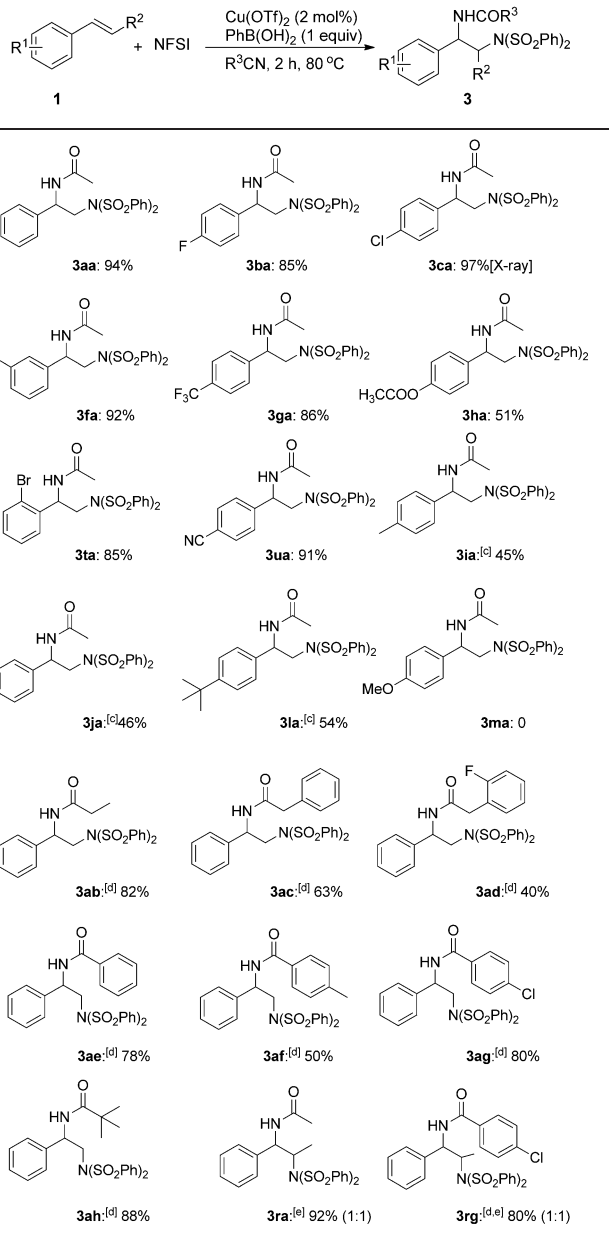
[a] Reactions were carried out with **1** (0.5 mmol), NFSI (1.4 equiv), TMSCN (1.4 equiv), CuBr (0.1 equiv), 1,10-phenanthroline (0.1 equiv), and 2 mL CH_2Cl_2 in sealed tube at 70°C for 1 h, unless otherwise noted. [b] Yield of the isolated product.

products **2o** (40% yield) and **2p** (21% yield), respectively. The non-activated aliphatic alkenes, such as vinylcyclohexane (**1q**), also provided the desired aminocyanation product **2q** in 20% yield. Notably, the aminocyanation reaction of 1*H*-indene (**1r**) provided the *trans*-aminocyanation product **2r** in 78% yield. More interestingly, starting from either of the internal alkenes (*E*)-prop-1-enylbenzene (**1s**) or (*Z*)-prop-1-enylbenzene (**1s′**), only the *trans*-aminocyanation product **2s** was obtained (85% yield). Since the yield of **2a** fell dramatically by employing cyanides, such as $Zn(CN)_2$, CuCN, and K_3FeCN_6 (Table 1, entries 13–16), and given the high affinity of silicon for fluoride anion, the interaction between TMSCN with fluoride[16] might play an important role in the efficient aminocyanation reactions.

Considering the facile formation of a Si–F bond, we attempted to broaden this aminocyanation methodology of alkenes to their carboamination reactions with NFSI and $PhB(OH)_2$ (utilizing B–F bond formation). Surprisingly, in the presence of 10 mol% $Cu(OTf)_2$, the reaction of styrene (**1a**, 0.5 mmol), NFSI (2 equiv), $PhB(OH)_2$ (1 equiv), and acetonitrile (2 mL) was carried out at 80°C for 2 hours under air to give a quantitative conversion of **1a** into the diamination product **3aa** (Table 3). During this process, both NFSI and acetonitrile were efficiently utilized as nitrogen sources. Recently, interesting research demonstrated that nitriles can also be reacted as a nucleophile through hydrolysis in a highly electrophilic gold(III)-mediated process (formed by oxidation of Au^I with the F^+ oxidant Selectfluor).[17] To our knowledge, this is the first example of generating amide groups by combining nitriles and phenylboronic acid. 1,2-Diamines exist in many biologically active compounds and chiral catalysts. In fact, most of the copper-mediated and copper-catalyzed diaminations are limited to alkenes bearing tethered nitrogen nucleophiles.[18] Shi and co-workers realized the copper-catalyzed diamination of alkenes by employing three-membered ring nitrogen sources, in which an intramolecular amination step was also involved.[19] Therefore, the transformation from **1a** into **3aa** represents the first copper-catalyzed intermolecular (no intramolecular amination involved for both amination steps) diamination of styrene. We next investigated this efficient intermolecular diamination reaction in detail. $B(OH)_3$ was not as efficient as $PhB(OH)_2$ as **3aa** was provided in 60% yield. $Cu(OAc)_2$, CuCl, and CuBr were also effective in providing **3aa** in 93, 76, and 85% yields, respectively. Furthermore, the $Cu(OTf)_2$ loading could be reduced to 2 mol% without a significant reduction in the yield (94%).

The scope of the copper-catalyzed diamination reaction was next explored. As described in Table 3, the substrates **1**, containing either electron-withdrawing or electron-donating groups on the benzene ring, reacted with NFSI in CH_3CN smoothly to afford the desired diamination products **3** in moderate to excellent yields. Reactions of styrenes bearing electron-withdrawing groups gave higher yields than those containing electron-donating groups. No desired diamination product was obtained when starting from 4-methoxystyrene (**1m**); instead, a mixture of unidentified compounds was obtained (even the reaction was performed at 0°C). In contrast, for the diamination of styrenes reported by Shi and co-workers,[19a] the higher reactivities were displayed with electron-rich alkenes as compared to electron-poor alkenes. The copper-catalyzed diamination reactions were also effective with respect to a range of nitriles, such as propiononitrile, benzylnitrile derivatives, benzonitrile derivatives, and even pivalonitrile, which provided the diamination products **3ab**–**ah** in moderate to high yields. However, when starting from the enol ethers **1o** and **1p** and the non-activated aliphatic alkene **1q**, no desired diamination products were obtained and only the starting materials were recovered. When using the internal alkene (*E*)-prop-1-enylbenzene (**1r**), the diami-

Table 3: The scope of the diamination of styrenes.[a,b]

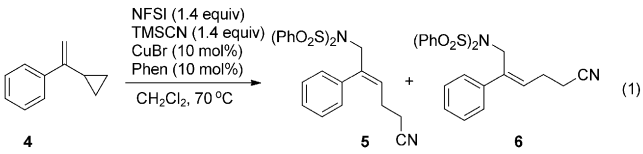


[a] Reactions were carried out with **1** (0.5 mmol), NFSI (2.0 equiv), $PhB(OH)_2$ (1.0 equiv), and $Cu(OTf)_2$ (0.02 equiv) at 80°C for 2 h, unless otherwise noted. [b] Yield of the isolated product. [c] Performed at 50°C. [d] 5 equiv nitriles were used in 2 mL DCE. [e] The ratio of two diastereoisomers.

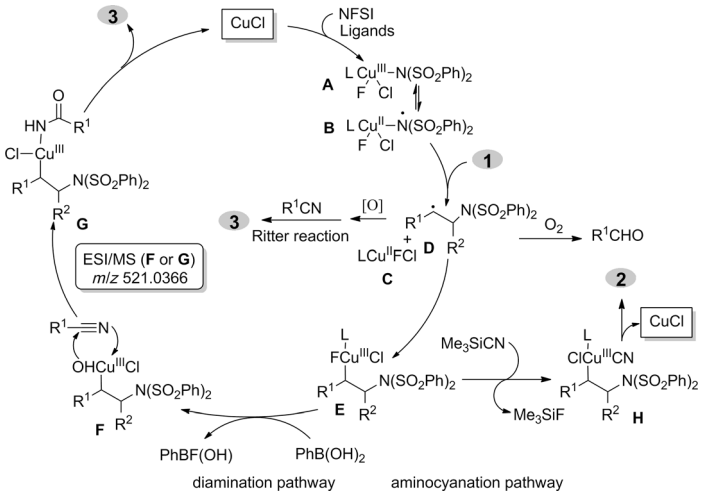
nation products **3ra** (92%) and **3rg** (80%) were obtained with the same *trans*/*cis* ratio. Recently, Muñiz and co-workers realized a remarkable and general palladium(II/IV)-catalyzed diamination reaction for internal alkenes with different nitrogen sources, and it was not suitable for terminal styrene substrates and the *E* isomer of styrenes such as **1r**.[20] Therefore, the copper-catalyzed intermolecular diamination reactions provide a useful complementary method with regard to palladium catalyst.

Although the mechanistic details of aminocyanation and diamination are not very clear at the moment, we presently favor the catalytic cycle involving Cu^{I}, Cu^{II}, and Cu^{III} species (Scheme 2). Initially, the oxidation of CuCl with NFSI[21] provides the Cu^{III} complex **A**,[14c] which could generate the copper(II)-stabilized benzenesulfonimide radical **B** through an equilibrium.[8a,19a] Subsequently, the addition of alkenes to **B** affords the Cu^{II} species **C** and the carbon radical intermediate **D**. The combination of **D** with **C** gives the Cu^{III} species **E** having a C–Cu bond. The interaction between B and F[22] of the intermediate **E** and $PhB(OH)_2$ leads to the organocopper (III) hydroxy species **F**,[23] which could deliver the OH moiety to nitriles for the formation the Cu^{III} species **G**.[24] The following reductive elimination of **G** affords the final product **3aa**. Given the observed 1:1 mixture of diastereomers **3ra** and **3rg**, the benzylic radical intermediate **D** could be oxidized to a benzylic carbon cation, thus involving a pathway with a Ritter-type nucleophilic attack,[25] which cannot be excluded (Scheme 2). For the mechanism of the aminocyanation reaction of styrene, **E** would react with TMSCN to provide the Cu^{III} species **H** (containing both a Cu–CN and Cu–C bond), which undergoes the final reductive elimination to give the aminocyanation product **2a**.

Further evidence for the possible mechanism was provided by some additional experiments. In the presence of 1 equivvalent of 2,6-di-*tert*-butyl-4-methylphenol (BHT), under the standard reaction conditions (Table 3), the yield of **3aa** fell to 28%. Moreover, when 1 equivalent of 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) was added, the yield of **3aa** fell to 50%. These experimental results suggested a possible radial mechanism. In addition, the aminocyanation of **1c** under reaction conditions identical to those described in entry 5 of Table 1, except under an O_2 atmosphere was investigated. The desired aminocyanation product **2c** was only obtained in 12% yield, along with 21% yield of 4-chlorobenzaldehyde and some unidentified complexes. 4-Chlorobenzaldehyde might be generated by the oxidation of the carbon radical intermediate **D** in the presence of oxygen.[26] Moreover, starting from substrate **4** with a typical radical clock cyclopropane moiety, the ring-opened aminocyanation products **5** and **6** were obtained in 10% and 5% yield, respectively [Eq. (1)]. This result supported the generation of the benzylic radical intermediate **D**. In addition, ESI/MS experiments were performed to gain evidence for the possible intermediates in the proposed mechanism. A mixture of styrene (0.25 mmol), NFSI (2.0 equiv), $PhB(OH)_2$ (1.0 equiv), and CuCl (1.0 equiv) in CH_3CN (1.0 mL) was reacted at room temperature for 10 minutes and 50 μL of the mixture was used for the ESI analysis in CH_3CN. The ESI/MS analyses showed a peak at *m*/*z* 521.0366, which was identified as an organocopper (III) species (possible structure was identified as either the cationic intermediate **F** or **G**; see the Supporting Information). Although the mechanism proceeding through the reductive elimination of a copper(III) allyl intermediate, formed from copper(II) ions trapping an allyl radical, was proposed in the allylation reaction,[2,27] the possible evidence for the existence of copper(III) benzylic intermediate has been provided for the first time.



In summary, a new facile copper-mediated methodology for the generation of a nitrogen-centred radical from NFSI has been developed. Thus, the first copper-catalyzed aminocyanation reaction of alkenes with NFSI and TMSCN has been realized. This protocol was successfully applied to the copper-catalyzed intermolecular diamination of styrenes by employing commercially available nitriles and NFSI as nitrogen sources. The interaction between trimethylsilyl cyanide, and fluoride and phenylboronic acid and fluoride might play an important role for the efficient aminocyanation reaction and diamination, respectively. The high regioselectivity, along with low loading of the copper catalyst, mild reaction conditions, and compatibility with a wide variety of functional groups make these aminative difunctionalization reactions very attractive. To gain widespread use, the alkene scope in this type of reaction still needs to be extended. In addition, studies for the utilization of the novel radical amination reaction to form various C–N bonds, as well as the application of this methodology for a broad range of difunctionalization reactions of alkenes are ongoing in our laboratory.



Scheme 2. The proposed mechanism.

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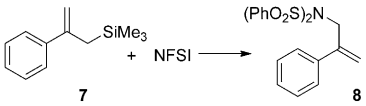

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