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Copper-Catalyzed Geminal Difunctionalization of Terminal Alkynes by Splitting Sulfonyl Hydrazones into Two Parts

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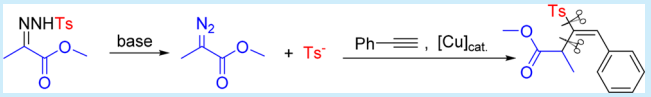
Supporting Information

ABSTRACT: A copper(I)-catalyzed geminal difunctionalization of terminal alkynes was developed via a carbene migratory insertion and an addition of a sulfonyl anion to the triple bond at the same time under mild reaction conditions, providing a variety of vinyl sulfones with good yields and excellent stereoselectivities.

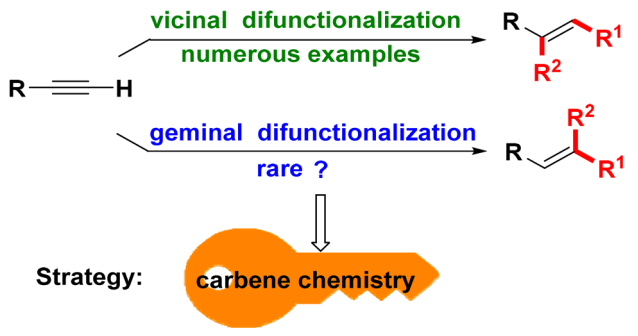


Difunctionalization of terminal alkynes has long served as a powerful strategy to access multisubstituted olefins.[1] In most of the previous strategies, the difunctionalization of terminal alkynes was achieved by electrophilic additions or radical additions. As a common reaction mode for the addition to C−C multiple bonds, these methods almost exclusively result in 1,2-difunctionalization (vicinal) regardless of the difference in the synthetic routes.[2] In contrast, the reports on the geminal difunctionalization of terminal alkyne are scarce. Recently, a remarkable breakthrough of the 1,1-diboration of alkynes was achieved by Sawamura's group and Chirik's group.[3] However, a general one-step approach or strategy for 1,1-difunctionalization (geminal) of terminal alkynes is still highly demanded (Scheme 1). In this context, we envisioned that a strategy involving carbene chemistry might be a solution for this long-standing problem.

As one of the functionalized products of terminal alkynes, vinyl sulfones display special physiological properties and biological activities,[4] such as the inhibitors of SrtA, inhibitors of cysteine protease, and a potential treatment for Chagas' disease. At the same time they are frequently employed as building blocks in organic synthesis due to their versatility in structural transformation.[5] In recent years, typical methods of direct sulfonyl radical additions have been extensively investigated, in which the anti-Markovnikov products were obtained exclusively owing to the Kharasch effect.[6] In order to synthesize α-substituted vinyl sulfones under the transition-metal-free and visible light conditions, a novel radical Markovnikov addition was proposed by Lei's group.[7] Recently, a one-step procedure was developed in the presence of DABCO·2SO_2 (DABSO) via an insertion of sulfur dioxide.[8] Another one-step strategy by ultilizing benzenesulfonyl chloride as the sulfonyl radical source was developed by Nevado and co-workers to prepare β,β-disubstituted vinyl sulfones.[9] Besides, nonradical processes were also employed for the synthesis of vinyl sulfones by using sulfonyl hydrazides,[10] sodium sulfinates,[11] and sulfinic acids[12] as the sulfonyl anion sources. However, these reported methods suffer from harsh conditions or toxic reagents. Low atomic economical efficiency also limited their synthetic utility since only the sulfonyl anion was used in the previous methods.

Sulfonyl hydrazones as a safe precursor for diazo compounds[13] have been extensively explored to access various skeletons by inter- or intramolecular carbene insertions.[14−17] However, in the generation of diazos, sulfonyl anions as a byproduct are commonly discarded,[18] which significantly restricts the atom economy of the transformations (Scheme 2). Herein, we proposed that sulfonyl hydrazones could be split into two fragments, a carbene and a sulfonyl equivalent. Indeed, a copper(I)-catalyzed geminal difunctionalization of terminal alkynes was achieved with this difunctional reagent. In this efficient protocol, an allene species, which was generated by the carbene insertion of alkyne, was identified as the key intermediate to access trisubstituted vinyl sulfones (Scheme 2). In comparison with the previous synthetic routes of vinyl sulfones, this method is not only a multifunctional reaction

Scheme 1. Vicinal or Geminal Difunctionalization of Terminal Alkynes



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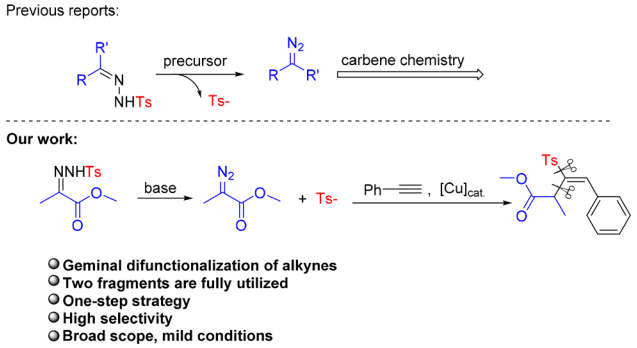
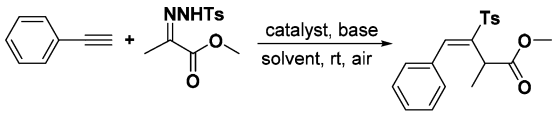
Scheme 2. Sulfonyl Hydrazones As a Precursor of Carbene in Transformations



(including sulfonyl radicals, sulfur dioxide reagent, or sulfonyl anions) but also a highly efficient reaction (excellent functional-group tolerance, mild conditions, and high stereoselectivity).

To find the optimal reaction conditions, phenylacetylene **1a** and *N*-tosylhydrazone **2a** were initially selected as the model substrates (Table 1). The expected product **3aa** could be obtained in 11% isolated yield under catalysis of CuCl in the presence of Et_3N (entry 1, Table 1). Various copper salts were studied in this reaction, and CuI was found to be the best catalyst with a yield of 89% of the desired product **3aa** (entries 2−5, Table 1). The screening of solvents indicated that DCM was the ideal solvent (entries 6−9, Table 1). The effect of bases was then examined, and Et_3N was found to give the optimal result (entries 10−12, Table 1). Temperature screening showed that the reaction temperature had a great impact on this reaction. For instance, when the reaction was carried out at 0 °C, only a low reaction yield was obtained (entry 13, Table 1). The higher temperature did not improve the yield either (entries 13−14, Table 1).

Table 1. Optimization of the Reaction Conditions[a]

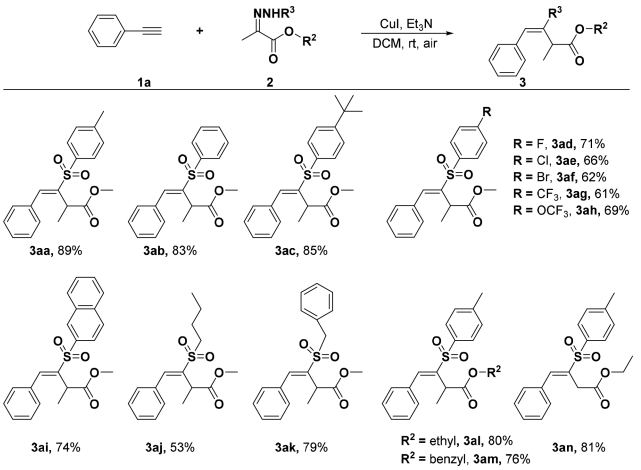


entry	catalyst	solvent	base	yield (%)[b]
1	CuCl	DCM	Et_3N	11
2	CuBr	DCM	Et_3N	17
3	CuI	DCM	Et_3N	89
4	$Cu(MeCN)_4PF_6$	DCM	Et_3N	n.d.
5	$Cu(MeCN)_4BF_4$	DCM	Et_3N	n.d.
6	CuI	MeCN	Et_3N	n.d.
7	CuI	toluene	Et_3N	n.d.
8	CuI	DMF	Et_3N	n.d.
9	CuI	$CHCl_3$	Et_3N	78
10	CuI	DCM	K_2CO_3	n.d.
11	CuI	DCM	LiO^tBu	n.d.
12	CuI	DCM	DBU	n.d.
13[c]	CuI	DCM	Et_3N	75
14[d]	CuI	DCM	Et_3N	82

[a]The reaction was carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (10 mol %), and base (0.6 mmol) in solvent (1 mL) at room temperature for 11 h. [b]The yields refer to the isolated products. [c]0 °C. [d]50 °C.

With the optimal reaction conditions in hand (entry 3, Scheme 3), we then explored the scope of the substrates. As shown in Scheme 3, *N*-tosylhydrazones, bearing various functional groups at the para-position of the phenyl ring, reacted smoothly with phenylacetylene **1a** to afford the desired products. Both electron-donating (**3aa**, **3ac**, Scheme 3) and electron-withdrawing (**3ag**, **3ah**, Scheme 3) groups on the phenyl ring could be tolerated under this condition. Nevertheless, the electron-withdrawing groups had a negative influence on this reaction (**3ad**−**3ah**, Scheme 3) while electron-donating groups favored this reaction slightly more (**3aa**, **3ac**, Scheme 3). On the other hand, when naphthylsulfonyl hydrazone was employed as the substrate, the corresponding product can be obtained efficiently (**3ai**, Scheme 3). Pleasingly, butylsulfonyl hydrazone can also be the reaction substrate to give the desired product with a moderate yield (**3aj**, Scheme 3). Moreover, *N*-(4-sulfo-benzyl)-hydrazone can be employed as the substrate and the reaction was carried out smoothly to yield the product in 79% yield (**3ak**, Scheme 3). The R^2 on the ester of the substrate **2** can also be varied. When the substrate **2l** and **2n** were employed in this reaction, the desired products **3al** and **3am** can be obtained with yields of 80% and 76%, respectively. The substituent on the carbon of the double bond of hydrazone can be changed to give the desired product with good yield (**3an**, Scheme 3).

Scheme 3. Reaction Scope of Sulfonyl Hydrazones[a,b]



[a]The reaction was carried out with **1a** (0.2 mmol), **2** (0.4 mmol), CuI (10 mol %), and Et_3N (0.6 mmol) in DCM (1 mL) at room temperature. [b]Isolated yield.

Next, we turned our attention to assess the scope of the alkynes. A series of terminal alkynes (**1b**−**1l**, Scheme 4) were employed to react with *N*-tosylhydrazone **2a** under the optimized reaction conditions. The electronic effect of substituents on the aryl ring of the alkynes was examined first. Aromatic alkynes bearing either electron-donating groups (**3ba**−**3da**, **3ha**, Scheme 4) or electron-withdrawing groups (**3ea**−**3ga**, **3ia**, Scheme 4) on the aryl ring could afford the corresponding products in good yields. Furthermore, the phenylacetylene with an ortho- or a meta-substituent on the phenyl ring could be efficiently converted to the corresponding products with good yields (**3ja**, **3ka**, Scheme 4). All aromatic alkynes underwent the reaction to give the desired products in good yields. Moreover, the high selectivity could be maintained regardless of the properties and the positions of the

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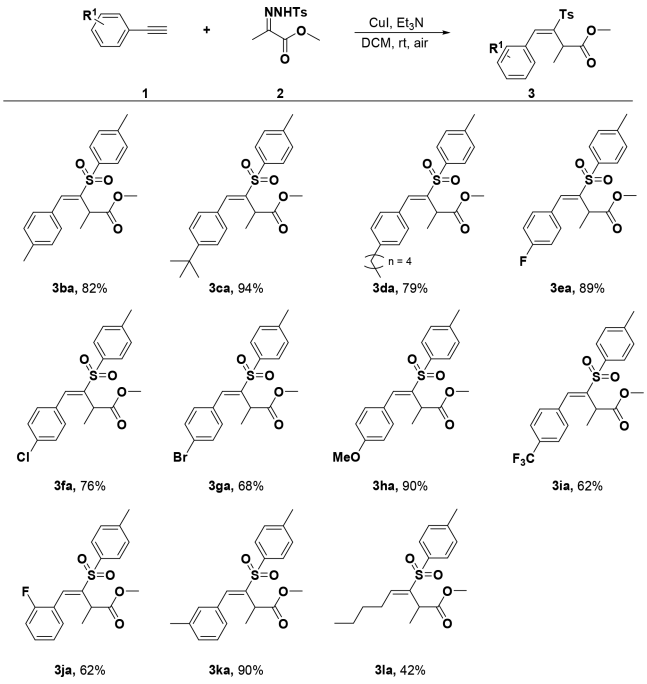
Scheme 4. Reaction Scope of Terminal Alkynes[ab]



[a]The reaction was carried out with **1** (0.2 mmol), **2** (0.4 mmol), CuI (10 mol %), and Et_3N (0.6 mmol) in DCM (1 mL) at room temperature. [b]Isolated yield.

substituents. To our delight, an aliphatic alkyne could also be employed as the substrate to afford the desired product with moderate yield (**3la**, Scheme 4). More importantly, the absolute configuration of the product **3ac** was confirmed by X-ray crystal diffraction (Figure 1, CCDC 1852379).

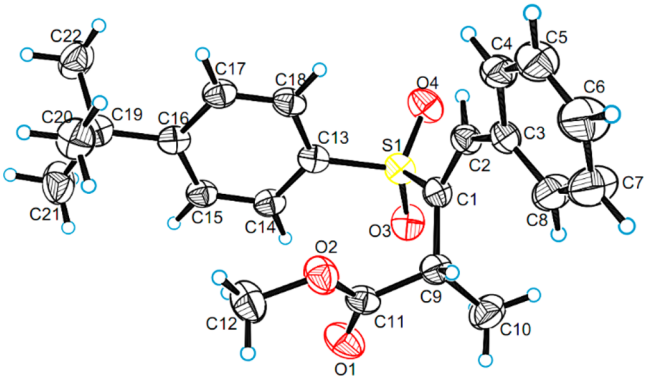
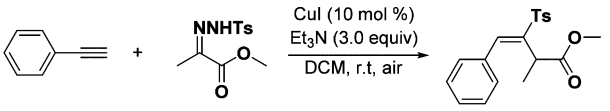


Figure 1. X-ray structure of product **3ac**.

This developed methodology features high efficiency, simple manipulation, and a broad scope. Encouraged by these features, we then scaled-up the reaction to examine the synthetic utility. When 5.0 mmol of phenylacetylene **1a** were reacted with 10.0 mmol of *N*-tosylhydrazone **2a**, the corresponding product **3aa** can be obtained with a satisfactory yield of 81%, demonstrating great potential in pharmaceutical synthesis (Scheme 5).

Several control experiments were conducted to unravel the reaction mechanism. First, when the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or *tert*-butylhydroxytoluene (BHT) was added to the reaction under the

Scheme 5. Scale-up Reaction[a,b]

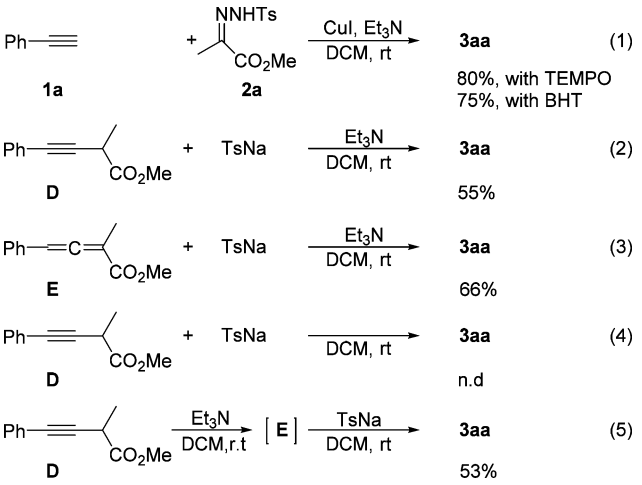


1a	2a	3aa
0.51 g, 5.0 mmol	2.70 g, 10.0mmol	1.39 g, 81%

[a]The scale-up reaction was carried out with **1a** (5.0 mmol), **2a** (10.0 mmol), CuI (10 mol %), and Et_3N (15.0 mmol) in DCM (20 mL) at room temperature. [b]Isolated yield

conditions, **3aa** was obtained smoothly although the yield was decreased slightly [Scheme 6, eq 1]. These results

Scheme 6. Control Experiments[a,b]



[a]TsNa = sodium *p*-toluenesulfinate. [b]Isolated yield

excluded the possibility of a radical process. Furthermore, when compounds **D** and **E** were prepared and reacted with sodium *p*-toluenesulfinate in the presence of Et_3N, **3aa** was generated in moderate yields [Scheme 6, eqs 2 and 3]. However, no product could be obtained when **D** reacted with *p*-toluenesulfinate in the absence of Et_3N [Scheme 6, eq 4]. In order to figure out which might be the intermediate in this reaction, **D** was employed to react with Et_3N, followed by addition of sodium *p*-toluenesulfinate after 2 h. It was found that **3aa** could be obtained in 49% yield [Scheme 6, eq 5]. These results implied that **E** should be quickly formed from **D** in the presence of Et_3N. With increasing time, **E** was consumed gradually and the product formed; that is, **E** should be the real intermediate for this transformation.

Inspired by these results and previous reports,[13,14,19,20] a plausible mechanism was postulated to account for the current copper(I)-catalyzed coupling (Scheme 7). Diazo **2a′** is generated from *N*-tosylhydrazone **2a** in the presence of Et_3N, and reacts with copper acetylide **A** which is formed from phenylacetylene **1a**, leading to the construction of coppercarbenoid **B**. Migratory insertion of alkynyl group to the carbenic carbon atom gives the intermediate **C**, and the formation of **D** is accompanied by the protonation at the carbon atom attached the copper center; then, the released copper can sustain the next catalytic cycle. Finally, **E** can be formed rapidly under the promotion of Et_3N to then react with the sulfonyl anion generated in situ from **2a**. It is noteworthy

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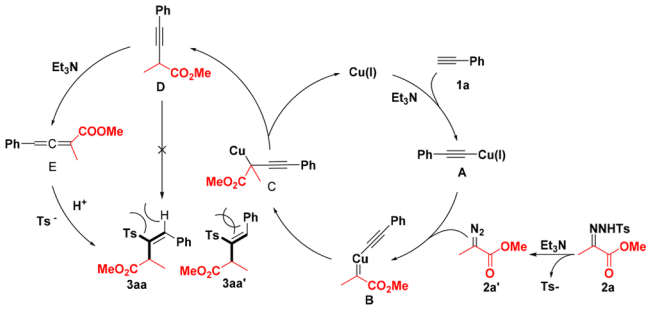
Scheme 7. Mechanistic Proposal



that when the allene intermediate **E** reacts with sulfonyls, the final product can be obtained with excellent stereoselectivity because of the influence of steric hindrance. We noted that **2n**, which had no methyl group adjacent to the hydrozone functional group, can also be employed in this reaction. This implied that the steric hindrance between the phenyl group of the alkyne and the sulfonyl group led to the stereoselectivity of the product rather than that between the phenyl group and the methyl group of the hydrozone. No ligands or additives are required in this process.

In conclusion, we developed a novel one-step method for the synthesis of α, β-disubstituted vinyl sulfones through the cross-coupling of *N*-tosylhydrazones and terminal alkynes. This reaction represents an unprecedented example for the geminal difunctionalization of terminal alkynes in a stereoselective manner. The method exhibits broad functional-group tolerance and can be extended to a larger scale. Moreover, the use of stable facile materials under mild conditions without any additional ligands presents great potential in industrial application. The proposed mechanism involved intermolecular copper carbene migratory insertion of terminal alkynes and sulfonyl anion addition. Research including further mechanistic details and synthetic applications is underway in our laboratory

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02268.

Experimental procedures, characterization data, copies of ^{1}H NMR, ^{13}C NMR of new compounds, and crystallographic data for compound **3ac** (PDF)

Accession Codes

CCDC 1852379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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