Letter

# Copper-Catalyzed Disulfonation of Terminal Alkynes with Sodium Arylsulfinates

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Vinyl sulfide moiety has attracted extensive attention in the territories of biochemistry, medicinal chemistry, materials science, and organic chemistry.<sup>1</sup> Among them, 1,2-disulfony-lethenes are considerable organosulfone molecules<sup>2,3</sup> and emerge as versatile synthons in synthetic applications such as cycloaddition,<sup>4</sup> radical elimination,<sup>5</sup> and 1,2-rearrangement reaction.<sup>6</sup> To date, several classic methods including oxidation,<sup>7</sup> condensation,<sup>8</sup> and addition reactions<sup>9</sup> were well established for the production of the 1,2-disulfonylethenes. However, these approaches are always restricted to predecorated feedstocks, narrow substrate scopes, and/or multiple synthetic steps.

Alkynes with flexible reactivity are easily available building blocks and widely used in modern organic synthesis.<sup>10</sup> Direct 1,2-difunctionalization of alkynes, an ideal strategy for generating the functionalized olefins, has been substantially streamlined in last few decades.<sup>11</sup> Among these, radicalinvolved vicinal difunctionalization of alkynes by both carbon-<sup>12</sup> and heteroatom-centered radicals<sup>13</sup> appears as the efficient and modular means to deliver polysubstituted alkenes via excellent step- and atom-economy. During this process, the reactive vinyl radical intermediates are suggested to further couple with another partner to produce the target alkenes.<sup>14</sup> However, such vinyl radical species easily undergo hydrogenation by H atom abstraction,<sup>15</sup> which is a significant challenge in utilization of alkyne via radical 1,2-difunctionalization reaction. Therefore, achieving the alternative and direct efficient strategy to constitute 1,2-disulfonylethene skeleton is of significant interesting and appealing in the synthetic chemistry. Considerable attention has been fixed on the construction of adjacent C-S bonds by the addition of preactivated alkynes with sulfinyl precursors. For example, Kataoka et al. provided a reaction between alkynylselenonium salts and sodium benzenesulfinates for assembling 1,2-bis-(phenylsulfonyl)ethylenes (Scheme 1a).<sup>16</sup> Tang and coworkers developed the HCl-dependent disulfonylation of







alkynyl bromides with sodium arylsulfinates (Scheme 1b).<sup>17</sup> Recently, a Cu-catalyzed disulfonylation reaction after decarboxylation of alkynyl carboxylic acids was also discovered by Li's group by using excess amounts of oxidants (Scheme 1c).<sup>18</sup> Despite these advances, the composition of 1,2disulfonylethenes still suffered from some drawbacks such as preactivated aryl-substituted alkynes, excessive strong oxidants, or acidic conditions. Given our substantial interest in copper catalyzed organic reactions,<sup>19</sup> we herein report an initial copper-catalyzed 1,2-disulfonation of unactivated terminal

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alkynes with arylsulfinates with the help of bromodifluoroacetate to rapidly furnish diverse (E)-1,2-disulfonylethenes without any oxidant or acid (Scheme 1d).

We carried out our investigation with **1a** and **2a** as model reactants to optimize the best conditions for disulfonylation conversion. The desired product **3a** was not observed under metal-free conditions (Table1, entry 1). Excitingly, the yield of

Table 1. Oblimization of the Reaction Conditions	Tab	ble	1.	Optimization	of the	Reaction	<b>Conditions</b>
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	Ph <del>-==</del> + TsNa	Cat. (0.2 eq.) BrCF <sub>2</sub> CO <sub>2</sub> Et (2.0 eq.) Sol., 100 °C	Ph Ts
	1a 2a		3a
entry	[M]	sol	yield (%)
1		DMSO	0
2	CuI	DMSO	85
3	CuI	DMSO	0 <sup>b</sup>
4	CuI	DMSO	70 <sup>c</sup>
5	CuI	DMSO	61 <sup><i>d</i></sup>
6	$Ag_2CO_3$	DMSO	0
7	NiCl <sub>2</sub>	DMSO	0
8	$Cu(OAc)_2$	DMSO	75
9	CuCl <sub>2</sub>	DMSO	80
10	CuBr	DMSO	69
11	CuI	DMF	70
12	CuI	EG	0
13	CuI	toluene	0
14	CuI	CH <sub>3</sub> CN	0
15	CuI	DCE	0
16	CuI	DMSO	trace <sup>e</sup>
17	CuI	DMSO	56 <sup>f</sup>

<sup>*a*</sup>Conditions: **1a** (0.5 mmol), **2a** (2.0 mmol, 4.0 equiv), CuI (0.1 mmol, 0.1 equiv), BrCF<sub>2</sub>CO<sub>2</sub>Et (1.0 mmol, 2.0 equiv), in solvent (1 mL) at 100 °C in oil bath under air for 3 h; yields of isolated products. <sup>*b*</sup>Without BrCF<sub>2</sub>CO<sub>2</sub>Et (2.0 equiv). <sup>*c*</sup>80 °C. <sup>*d*</sup>At 120 °C. <sup>*e*</sup>With 2.0 equiv of NaI. <sup>*f*</sup>With 2.0 equiv of Et<sub>3</sub>N. EG = ethanediol.

product **3a** was remarkable increased to 85% when CuI (0.2 equiv) was employed into the reaction (Table1, entry 2). The next control experiments (Table1, entry 3) identified that BrCF<sub>2</sub>CO<sub>2</sub>Et was found to be the vital parameter for the reaction. The adverse impact on the yield of product **3a** was showed whether the reaction was took place at higher or lower temperature (Table 1, entries 4 and 5). The poor efficiency to construct disulfonylated product **3a** were obtained by using other metal catalysts (Table1, entries 6–10). Varying other solvents (Table1, entries 11–15) for the reaction led to the low conversion of **3a**, confirming DMSO as best the choice. Similarly, other additives and the decreased amount of BrCF<sub>2</sub>CO<sub>2</sub>Et were also studied, revealing that the standard reaction was hampered (Table1, entries 16–17, and Supporting Information).

Based on above optimal reaction conditions, we focused on the efficacy of this disulfonylation by reacting various alkynes with 2a to produce desired products 3 (Scheme 2). Initially, alkynes with *para*-substituted functional groups were injected into the standard reaction and proceeded well for products 3b-31 with good yields, regardless of their electronic properties and steric effect. For instance, the substrates with alkyl chains (1b-1f) and alkoxy substituents (1g-1h) were good substrates, delivering the expected product 3b-3h in 80-86% yields. The substrates 1i-1k bearing halogen atoms worked smoothly for the products 3i-3k, while leaving labile

## Scheme 2. Scope of Alkynes<sup>a</sup>

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<sup>*a*</sup>Conditions: 1 (0.5 mmol), 2a (2.0 mmol), CuI (0.1 mmol), BrCF<sub>2</sub>CO<sub>2</sub>Et (1.0 mmol), in DMSO (1 mL) at 100 °C under air for 3 h. Yields of isolated products.

functional groups intact for further coupling modification. Additionally, the absolute configuration was precisely confirmed by the crystal structure of product 3k (CCDC 1954576). The electron-deficient substrate 11 with an acetyl group also gave 1,2-disulfonylethene 31 under standard conditions. Subsequently, terminal alkynes containing metasubstitutions on the aryl ring (1m-1p) also underwent disulfonylation reactions in all cases (3m-3p) without a hitch, thus furnishing the satisfactory yield of products with different deactivating substituents. When the substrates anchored ortho-substituted groups (1q-1s), the yield of 3q-3s exhibited that the groups in the ortho position were well compatible in the reaction. Replacing the phenyl group with a condensed ring (1t-1u) or thienyl derivatives (1v-1x) proved good adaptability for the corresponding adducts 3t-3x in good yields. As the clearly more challenging substrates of nonaryl alkynes in radical difunctionalization,<sup>14</sup> encynes 1y-1z proved to be the good coupling partner with appreciable yield of the product. To the best of our knowledge, this protocol gives the first access to synthesis of the 1,2-diarylsulfonyl 1,3-diene. However, Alkyl substituted alkynea 1za-1zb were shut down in the reaction, presumably caused by the instability of the involved sulfone radical species.<sup>14</sup>

Moreover, sulfonates 2 with a variety of aryl groups were next performed to study the efficiency of the copper-catalyzed disulfonylation process, generating the target products under the standard reaction conditions (Scheme 3). For instance, the use of phenylsulfinates 2a-2c with electron-rich groups, sulfinate 2d with condensed rings, as well as sulfinate 2e with sulfur heterocycle were favorably competent for the construction of privileged vinyl sulfones 4a-4e in 70–82%

## Scheme 3. Reaction Scope of Sodium Sulfonates<sup>a</sup>



<sup>*a*</sup>Conditions: 1a (0.5 mmol), 2 (2.0 mmol), CuI (0.1 mmol), BrCF<sub>2</sub>CO<sub>2</sub>Et (1.0 mmol), in DMSO (1 mL) at 100  $^{\circ}$ C under air for 3 h. Yields of isolated products.

yield. Unfortunately, ethyl-substituted sulfonate 2f did not share this disulfonylation conversion.

Furthermore, to extend the scalability and practicality of this method, we conducted the large-scale reaction with this bromodifluoroacetate-induced disulfonation of alkyne (Scheme 4). The corresponding product **3a** was delivered in

#### Scheme 4. Large-Scale Reaction

Ph-=== +	TsNa	Cul (0.2 eq.) BrCF <sub>2</sub> CO <sub>2</sub> Et (2.0 eq.) DMSO, 100 °C	Ph Ts
1a	Za		3a
1 mmol, 0.1	0 g		83%
5 mmol, 0.5	i1 g		78%

good yield, which demonstrated the preferably potential value of the convenient fabrication pathway to access 1,2disulfonylethenes in the industry.

To probe the insights on the mechanism of disulfonylation reaction, the contrast experiments were designed and implemented as shown in Scheme 5. When 2,2,6,6tetramethyl-1-piperidinyloxy (TEMPO) as radical scavenger was subjected into the reaction, the desired conversion was shut down (Scheme 5a). This meant that the reaction was probably involved in the radical species.<sup>20</sup> Replacing 2a with TsH caused the sharp suppression of the standard disulfonylated reaction (Scheme 5b). This indicated that TsH was not the supposed intermediate in the reaction (Scheme 5b). The assumed acetylene copper intermediate 1a-Cu yielded the vinylsulfone 5 instead of 3a (Scheme 5c), implying the absence of simple 1a-Cu compound in the reaction. When 5 as partner was further treated with 2a in standard reaction, no desired product 3a was observed (Scheme 5d), confirming the missing formation of intermediate 5 in the reaction. The subjection of 1a-D in place of 1a produced the mixture of 3a/3a-D. When 2.0 equiv of H<sub>2</sub>O was added in the reaction, only product 3a was obtained (Scheme 5e). Those results suggested the cleavage of C(sp)-H bond during the standard reaction. Copper catalyst could accelerate the target transformation from intermediate 6 to product 3a, which probably signified the presence of **6** in the formation of **3a** (Scheme 5f).

## Scheme 5. Mechanistic Investigations



In light of the above preliminary results and previous literature,  $^{17-20}$  a plausible mechanism via radical pathway for this transformation was proposed and described in Scheme 6.

Scheme 6. Possible Mechanism for the Reaction



These results (Scheme 5c,e) implied that the activation of 1a might occurred in the help of some copper complex via cleavage of the C(sp)–H bond. In addition, some literature<sup>21</sup> reported the complex between copper and BrCF<sub>2</sub>CO<sub>2</sub>Et during the reaction. Therefore, we proposed that a Cu(III) species  $A^{21}$  was first afforded by an oxidative addition of copper catalyst into the C–halogen bond of BrCF<sub>2</sub>CO<sub>2</sub>Et. Intermediate A subsequently reacted with A and led to the Cu(III) complex B, which could coordinate with 2a for the formation of C. The in situ generation of Ts radical from complex C and a consecutive radical addition quickly occurred to give vinyl radical D.<sup>22</sup> An elimination<sup>23</sup> of D produced 6 and regenerated Cu(I) for the next catalytic cycle. Finally, product 3a was

obtained through nucleophilic addition between 6 and 2a with the assistance of copper species.

In summary, we have successfully achieved a novel and efficient copper-catalyzed disulfonylation protocol to straightforwardly synthesize a wide range of (E)-1,2-disulfonylethenes from readily available terminal alkynes in good yields. Compared to the existing preactivated synthetic strategy, this is an attractive alternative for preparing 1,2-disulfonylethene motifs in synthetic chemistry. A possible radical mechanism was also proposed on the base of preliminary control studies. Further exploitations of the difluorobromoacetate-triggered catalytic system in organic synthesis are currently underway in our laboratory.

# ASSOCIATED CONTENT

## **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00575.

Typical experimental procedure and characterization for all products (PDF)

#### Accession Codes

CCDC 1954576 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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