Based-Catalyzed Stereoselective Thiosulfonylation of Ynones

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Abstract:

The first catalytic vicinal thiosulfonylation of ynones has been developed. Under the catalysis of 1-10 mol% Cs_2CO_3, various thiosulfonates underwent Michael addition/nucleophilic substitution tandem reaction with different ynones to form C-SO_2 and C-S bonds simultaneously and produce multifunctional vinyl sulfones in high yields and excellent *E*-selectivity.

Introduction

Organosulfur compounds are widely used in medicinal and biochemistry, organic synthesis and material science.[1] Thus, the development of efficient method for the construction of C-S bond and the installation of sulfur-containing functional groups into organic molecules are topics of continuous interest. Among different sulfur-containing compounds, vinyl sulfones often serve as the critical structural motifs in numerous pharmaceuticals and biologically active compounds.[2] Given the great significance, considerable efforts have been exerted to develop efficient methods for the synthesis of these important frameworks.[3] Except for the

classic Knoevenagel condensation reaction,[4] Horner-Wadsworth-Emmons olefination[5] and vinyl sulfides oxidation reactions,[6] atom transfer radical addition (ATRA)[7] has emerged as a powerful strategy for the synthesis of vinylsulfone derivatives. A number of difunctionalization of alkynes, including halosulfonylation,[8] selenosulfonylation,[9] aminosulfonylation,[10] disulfonylation,[11] thiocyanatosulfonylation,[12] carbosulfonylation[13] and carboxysulfonylation,[14] have been developed through ATRA reactions. In sharp contrast, thiosulfonylation of alkynes has only rarely investigated, which allows concomitant formation of C-SO_2 and C-S bond in one step. Recently, Xu and coworkers[15] reported an elegant dual gold/photoredox-cocatalyzed ATRA to alkynes, which provides a novel protocel for the synthesis of thio-functionalized vinylsulfones. Interestingly, using Eosin Y as photocatalyst, Jia and coworkers[16] realized a similar thiosulfonylation of alkynes under metal-free conditions, but with reversed regioselectivity. Very recently, Reddy and coworkers[17] reported that the same products can also be obtained through a new radical-involved vicinal thiosulfonylation of 1,1-dibromo-1-alkynes. However, these aforementioned radical reactions are not suitable for thiosulfonylation of ynones due to the dramatically reduced stability of α-ketone alkenyl radical intermediate as compared to alkenyl radical.

α-ketone alkenyl radical alkenyl radical

Scheme 1 α-ketone alkenyl radical and alkenyl radical

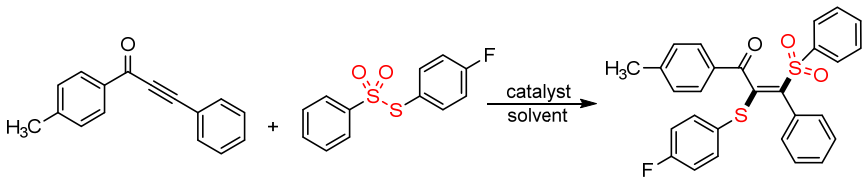
To the best of our knowledge, there is no method for vicinal thiosulfonylation of ynones has been disclosed to date. Therefore, the development of novel and mechanically different method for vicinal thiosulfonylation of ynones is highly desirable. As part of our continuous research on C-S bond formation reactions,[18] we envisaged that a base can catalyze the Michael-addition/nucleophilic substitution tandem reaction of ynones and thiosulfonates to produce multifunctional vinylsulfones through a novel non-radical process. Herein, we would like to report this result.

Results and discussion

At outset, we commenced our study with ynone **1a** and thiosulfonate **2a** as the model substrates. To our delight, in the presence of 10 mol% DBU, the vicinal thiosulfonylation reaction proceeded smoothly in THF at room temperature to produce the desired product **3a** in 87% yield (Table 1, entry 1). Encouraged by this success, several other common bases were then examined. TBD and DBN catalyzed the difunctionalization in high yield (Table 1, entries 2 and 3). Triethylamine, the Hunig's base, DABCO and Ph_3P cannot catalyze the reaction (Table 1, entries 4-7). ^tBuOK catalyzed the reaction in modest yield (Table 1, entry 8). Inorganic bases, such as NaOH, Na_2CO_3 and K_2CO_3 are inefficient for the reaction (Table 1, entries 9-11). Interestingly, Cs_2CO_3 catalyzed the reaction in high yield (Table 1,

entry 12). A brief evaluation of the reaction media indicated that acetonitrile was the best choice with respect to the yield (Table 1, entries 13-17) Reducing the amount of 1a to 1.2 equivalents led to slightly decreased reaction yield (Table 1, entry 18). Interestingly, reducing the catalyst loading to 5 mol%, excellent yield and stereoselectivity were maintained (Table 1, entry 19). However, further reducing the catalyst loading to 1 mol% resulted in decreased reaction yield (Table 1, entry 20). Finally, the control experiment showed that in the absence of a base, no desired product was formed (Table 1, entry 21).

Table 1 Optimization of reaction conditions [a]



1a 2a 3a

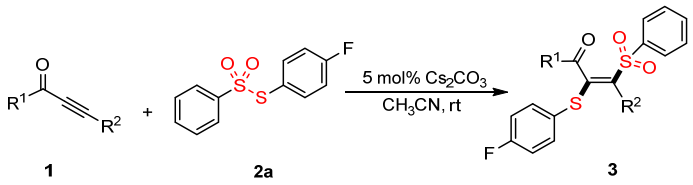
Entry	base	solvent	Time/h	E/Z[c]	Yield(%)[b]
1	DBU	THF	7	>25:1	87
2	TBD	THF	7	>25:1	97
3	DBN	THF	7	>25:1	76
4	Et_3N	THF	7	>25:1	nr
5	DIPEA	THF	7	>25:1	nr
6	DABCO	THF	7	>25:1	nr
7	PPh_3	THF	7	>25:1	nr
8	^tBuOK	THF	7	>25:1	34
9	NaOH	THF	7	>25:1	nr
10	Na_2CO_3	THF	7	>25:1	nr
11	K_2CO_3	THF	7	>25:1	nr
12	Cs_2CO_3	THF	7	>25:1	93
13	Cs_2CO_3	DCM	7	>25:1	22
14	Cs_2CO_3	DCE	7	>25:1	42
15	Cs_2CO_3	MeOH	7	>25:1	5

16	Cs_2CO_3	CH_3CN	7	>25:1	98
17	Cs_2CO_3	toluene	7	>25:1	6
18[d]	Cs_2CO_3	CH_3CN	7	>25:1	95
19[e]	Cs_2CO_3	CH_3CN	7	>25:1	98
20[f]	Cs_2CO_3	CH_3CN	8	>25:1	85
21	/	THF	24	/	nr

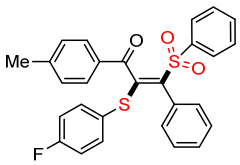
[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.4 mmol), base (10 mol%), CH_3CN（4.0 mL), 8 h, rt; [b] Isolated yield; [c] Ratio of *E/Z* isomers was determined by ^1H NMR analysis of the crude products; [d] **1a** (0.48 mmol), **2a** (0.4 mmol); [e] Cs_2CO_3 (5 mol%); [f] Cs_2CO_3 (1 mol%).

With the optimal reaction conditions in hand, we first examined the substrate scope of ynones, with the results summarized in Table 2. A variety of ynones with substituents on the aromatic rings underwent the thiosulfonylation efficiently to give the desired vinyl sulfones in high yield and excellent regio- and stereoselectivity (**3a-3q**). In addition, different positions and electronic properties have no apparent impact on the reaction yield and selectivity (**3r-3x**). The bulky naphthyl derived ynones **1y** and **1z** participated in the reaction to afford the corresponding products **3y** and **3z** in 98% and 88% yields, respectively. Heteroaryl substituted ynones were proven to be very good reactants for the reaction, furnishing the corresponding produces in excellent yield (**3aa-3ac**). Gratifyingly, different alkyl-substituted ynones also performed very well, giving the desired products in high yield and excellent *E*-selectivity (**3ad-3ai**).

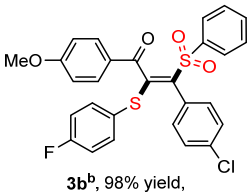
Table 2. Substrate scope of ynones [a]



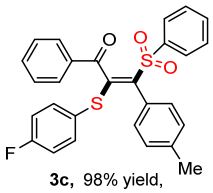
1 **2a** **3**



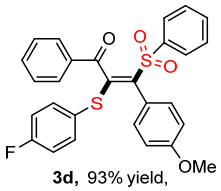
3a, 98% yield, E/Z > 25:1



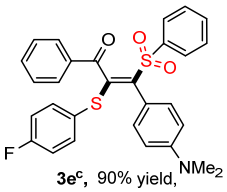
3b[b], 98% yield, E/Z > 25:1



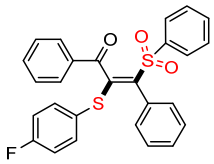
3c, 98% yield, E/Z > 25:1



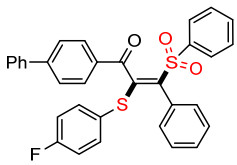
3d, 93% yield, E/Z > 25:1



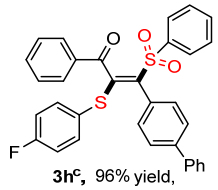
3e[c], 90% yield, E/Z > 25:1



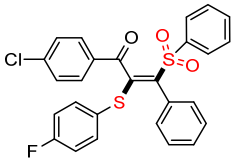
3f, 97% yield, E/Z > 25:1



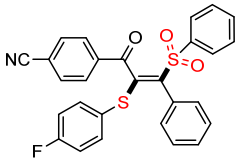
3g[c], 94% yield, E/Z > 25:1



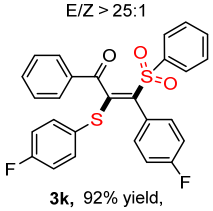
3h[c], 96% yield, E/Z > 25:1



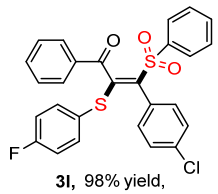
3i, 98% yield, E/Z > 25:1



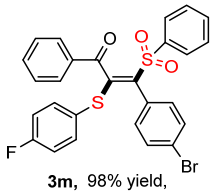
3j, 98% yield, E/Z > 25:1



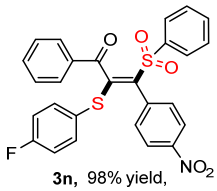
3k, 92% yield, E/Z > 25:1



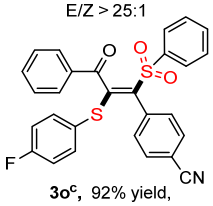
3l, 98% yield, E/Z > 25:1



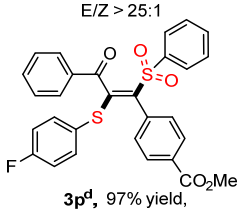
3m, 98% yield, E/Z > 25:1



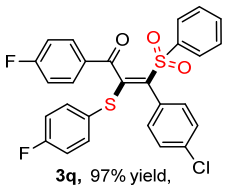
3n, 98% yield, E/Z > 25:1



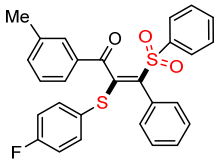
3o[c], 92% yield, E/Z > 25:1



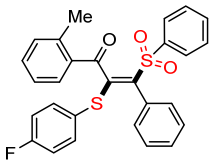
3p[d], 97% yield, E/Z > 25:1



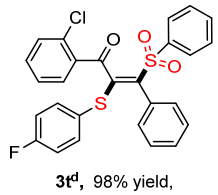
3q, 97% yield, E/Z > 25:1



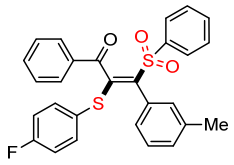
3r[d], 94% yield, E/Z > 25:1



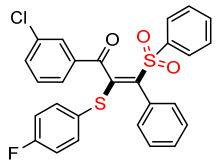
3s[d], 98% yield, E/Z > 25:1



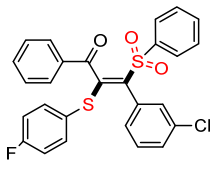
3t[d], 98% yield, E/Z > 25:1



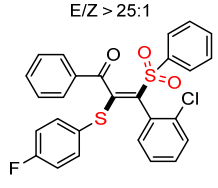
3u[d], 97% yield, E/Z > 25:1



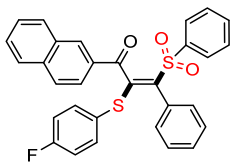
3v, 97% yield, E/Z > 25:1



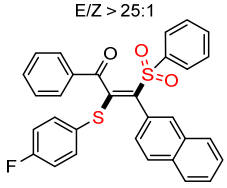
3w, 89% yield, E/Z > 25:1



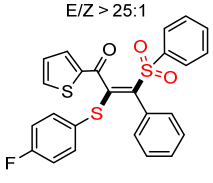
3x, 98% yield, E/Z > 25:1



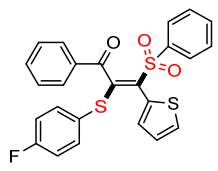
3y, 98% yield, E/Z > 25:1



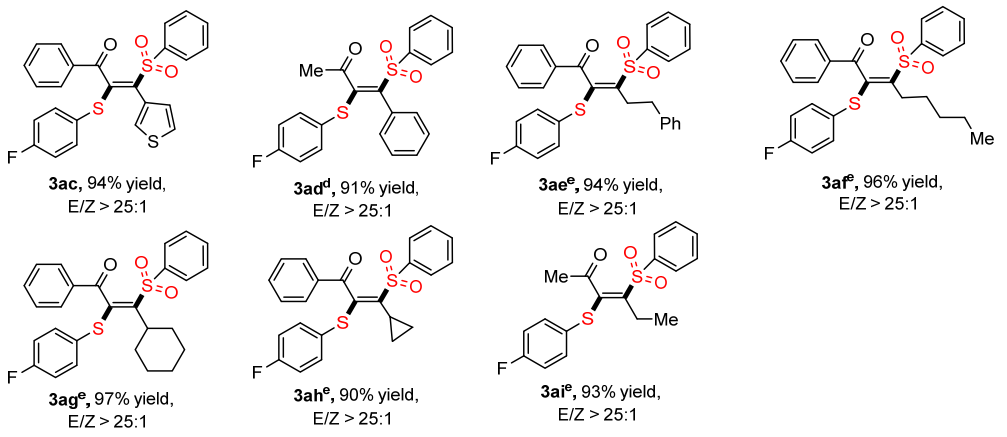
3z[d], 88% yield, E/Z > 25:1



3aa, 97% yield, E/Z > 25:1



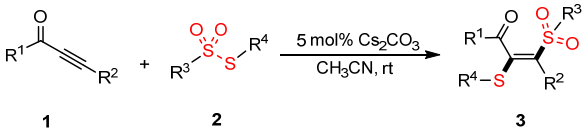
3ab, 95% yield, E/Z > 25:1



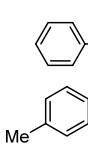
[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.4 mmol), Cs_2CO_3 (5 mol%), CH_3CN (4.0 mL), 8 h, rt; isolated yield, ratio of *E/Z* isomers was determined by ^1H NMR analysis of the crude products; [b] Cs_2CO_3 (1 mol%); [c] Cs_2CO_3 (2 mol%); [d] Cs_2CO_3 (10 mol%); [e] Cs_2CO_3 (20 mol%).

We next investigated the substrate scope of thiosulfonates in this transformation. Both symmetrical and unsymmetrical thiosulfonates smoothly underwent the reaction, affording the corresponding thio-functionalized vinylsulfones in high yields and excellent regioselectivity (Table 3). Substrates bearing electron-donating, -withdrawing and neutral-substituents coupled with ynones to produce the desired products in excellent yields (**3aj-3ap**). Different positions of the substituents have no obvious influence on the reaction yield and selectivity (**3aq-3as**). The bulky naphthyl-derived thiosulfonate **2l** reacted efficiently with ynone 1x to furnish **3at** in high yield. Heteroaryl-derived thiosulfonate **2m** underwent the reaction to provide **3au** in 95% yield. Notably, alkyl thiosulfonates performed smoothly to afford the corresponding products in high yields (**3av-3ax**). The configuration of **3ap** was unambiguously determined by X-ray crystallography analysis.[19]

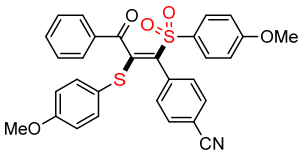
Table 3. Substrate scope of thiosulfonates [a]



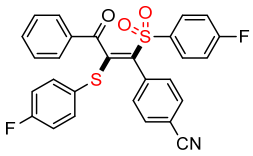
1 2 3



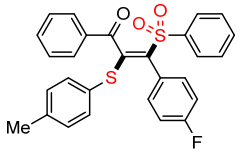
3aj, 98% yield
E/Z > 25:1



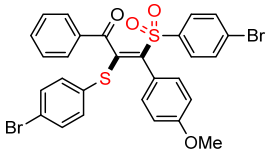
3ak[b], 92% yield
E/Z > 25:1



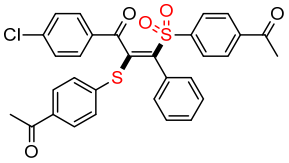
3al[c], 97% yield
E/Z > 25:1



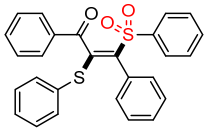
3am, 98% yield
E/Z > 25:1



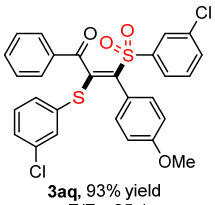
3an, 94% yield
E/Z > 25:1



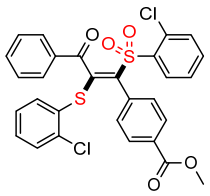
3ao, 97% yield
E/Z > 25:1



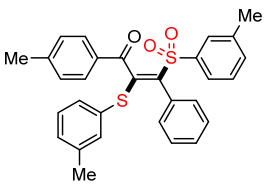
3ap, 98% yield
E/Z > 25:1



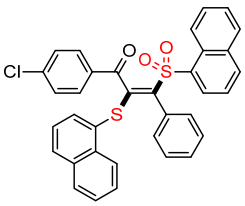
3aq, 93% yield
E/Z > 25:1



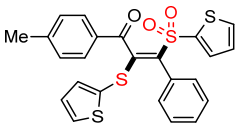
3ar[c], 95% yield
E/Z > 25:1



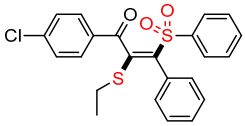
3as[c], 93% yield
E/Z > 25:1



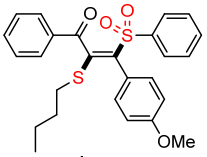
3at, 98% yield
E/Z > 25:1



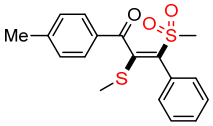
3au, 95% yield
E/Z > 25:1



3av[d], 97% yield
E/Z > 25:1



3aw[d], 95% yield
E/Z > 25:1

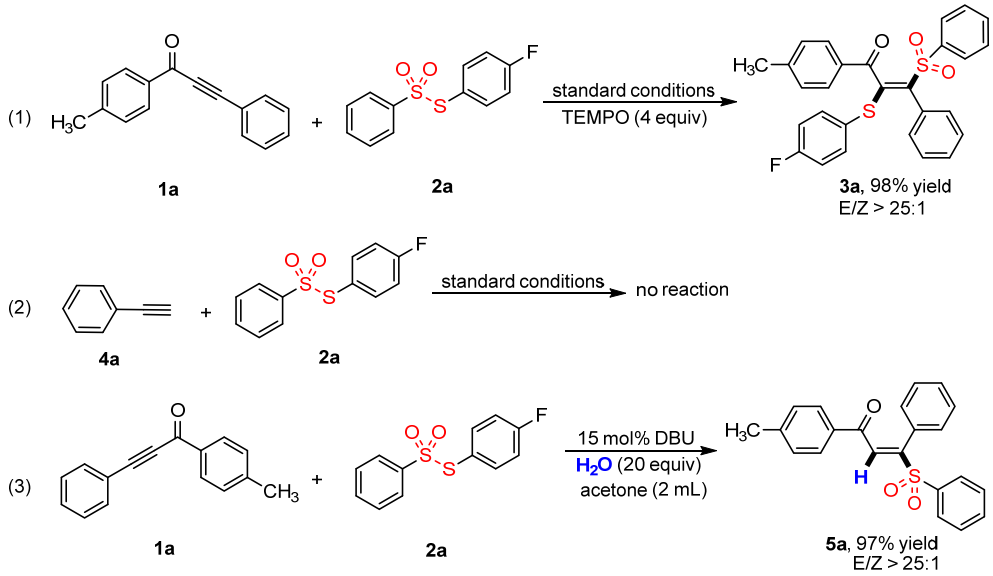


3ax[e], 89% yield
E/Z > 25:1

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.4 mmol), Cs_2CO_3 (5 mol%), CH_3CN（4.0 mL), 8 h, rt, isolated yield; [b] Cs_2CO_3 (1 mol%); [c] Cs_2CO_3 (2 mol%); [d] Cs_2CO_3 (10 mol%); [e] Cs_2CO_3 (20 mol%).

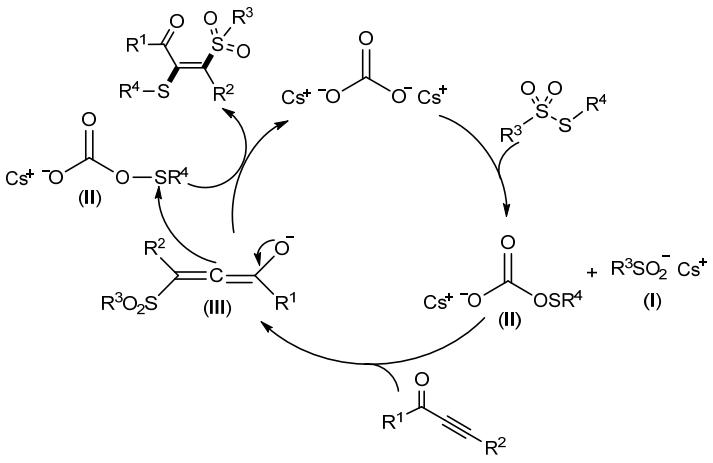
To gain insight into the reaction mechanism, several control experiments were performed (Scheme 2). The addition of a radical scavenger TEMPO to the reaction has no influence on the formation of the product (eq. 1). Phenylacetylene is a very good reactant in photoredox-catalyzed thiosulfonylation reaction. But under our standard conditions, phenylacetylene cannot react with ynone to give the vicinal

thiosulfonylation product (eq. 2). Under that catalysis of DBU, thiosulfonate underwent multicomponent reaction with ynone and H_2O to give vinylsulfone **5a** in 97% yield (eq. 3). When D_2O was used instead of H_2O, deuterated product **5b** was achieved in 85% yield with 99% D-incorporation. These results indicate that the reaction do not proceed through a radical process.



Scheme 2 Control experiments

Based on the results presented above, a plausible mechanism was proposed in Scheme 3. Base attacks thiosulfonate to generate sulfonyl anion **I** and species **II**. Sulfonyl anion **I** undergoes Michael addition with ynone to give allenoate **III**, which subsequently attacks the sulfur atom of species **II** to produce the final product with release of catalyst. In order to minimize the steric repulsion, the adjacent sulfonyl group and the thio group prefer to adopt a *trans*-conformation, which leads to the formation of *E*-isomer as the major product.



Scheme 3 Proposed mechanism

Conclusions

In summary, a base-catalyzed difunctionalization of ynones has been described. The metal-free conditions, broad substrate scope, high atom-economy, excellent reaction yield and stereoselectivity provide a novel method for the synthesis of multifunctionalized vinylsulfones. Further studies on a broader substrate scope and the applications of this method are ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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