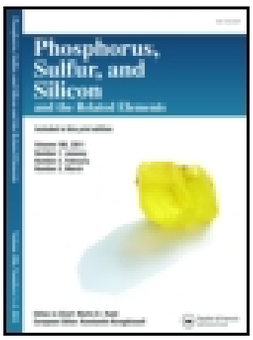


Taylor & Francis
Taylor & Francis Group

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

Metal-free synthesis of (*E*)-vinyl sulfones *via* denitrative coupling reactions of β-nitrostyrenes with sodium sulfinates

Guang-Feng Hong, Jin-Wei Yuan, Zhen-Hua Dong, Yong-Mei Xiao, Pu Mao & Ling-Bo Qu

To cite this article: Guang-Feng Hong, Jin-Wei Yuan, Zhen-Hua Dong, Yong-Mei Xiao, Pu Mao & Ling-Bo Qu (2018): Metal-free synthesis of (*E*)-vinyl sulfones *via* denitrative coupling reactions of β-nitrostyrenes with sodium sulfinates, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2018.1513518

To link to this article: https://doi.org/10.1080/10426507.2018.1513518

PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
https://doi.org/10.1080/10426507.2018.1513518

Metal-free synthesis of (*E*)-vinyl sulfones *via* denitrative coupling reactions of *β*-nitrostyrenes with sodium sulfinates

Guang-Feng Hong[a], Jin-Wei Yuan[b], Zhen-Hua Dong[b], Yong-Mei Xiao[b], Pu Mao[b], and Ling-Bo Qu[b,c]

[a]Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou, PR China; [b]School of Chemistry & Chemical Engineering, Henan University of Technology; Academician Workstation for Natural Medicinal Chemistry of Henan Province, Zhengzhou, PR China; [c]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, PR China

ABSTRACT

A practical metal-free procedure for the synthesis of (*E*)-vinyl sulfones has been developed through the coupling of *β*-nitrostyrenes with sodium sulfinates under microwave irradiation. This methodology provides a convenient and efficient approach to various (*E*)-vinyl sulfones from readily available starting materials with excellent regioselectivity. The present oxidative reaction involves an efficient denitrative radical cross-coupling of *β*-nitrostyrenes with sodium sulfinates *via* using AcOH as an additive.

ARTICLE HISTORY
Received 17 April 2018
Accepted 9 August 2018

KEYWORDS
β-nitrostyrene; sodium sulfinate; acid-promotion; radical reaction; sulfonylation

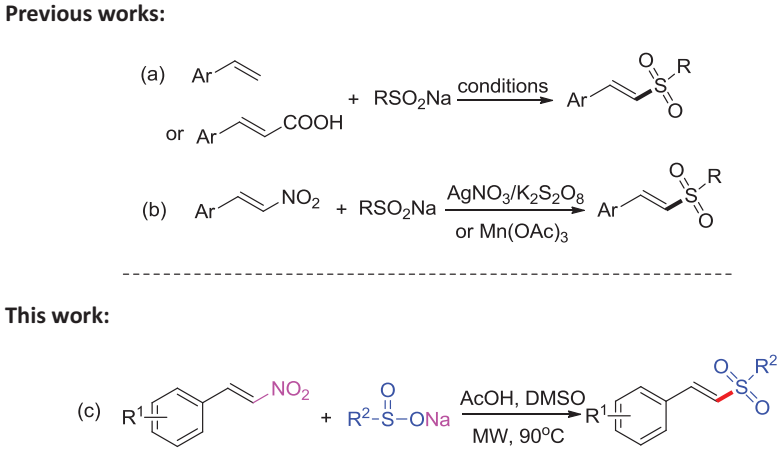
GRAPHICAL ABSTRACT

Introduction

Vinyl sulfones as an important class of sulfur-containing compounds play a significant role in organic synthesis and material sciences due to the chemical versatility of the sulfonyl moiety.[1–10] Vinyl sulfone containing molecules have been shown to exhibit important biological activities; for example, as cysteine protease inhibitors,[11–14] HIV-1 inhibitors,[15] and inhibitors of sortase, and protein tyrosine phosphatases.[16–19] Owing to the significance of these compounds, various approaches to produce vinyl sulfones have been developed. Traditionally, Knoevenagel condensation of aromatic aldehydes with sulfonylacetic acids,[20] *β*-elimination of selenosulfones or halosulfones,[21,22] Wittig reaction of α-sulfinylphosphonium ylides,[23] and the oxidation of the corresponding sulfides[24,25] are perhaps the most common methods. However, these methods suffer from inaccessible substrates, the multi-steps, strong bases and strong oxidants involved in these transformations, which limits their wide application. Recently, a series of alternative methods for vinyl sulfones synthesis have also been developed, such as the transition-metal-catalyzed cross-coupling of sulfinate salts with vinyl bromides, vinyl triflates, or vinylboronic acids;[26–29] the oxidation of preformed vinyl sulfides with stoichiometric oxidants,[24, 30] the coupling reactions of alkenes or cinnamic acids with sulfonyl halides, and sulfonyl hydrazides;[31–38] and the addition of sulfinic acids, sulfonyl hydrazides, or dimethyl sulfoxide to alkynes.[39–43] Nevertheless, most of these reactions might suffer from some limitations, such as the need of inaccessible starting materials, tedious procedures, harsh reaction conditions, low atom economy, and poor regioselectivity or toxic metal catalysis.

Sodium arenesulfinates are readily accessible synthetic intermediates that can be used as aryl sources by means of C-S bond cleavage. More significantly, they could also serve as sulfone or thioether sources.[44–47] Compared to other sulfenylation/sulfonation agents, sodium arenesulfinates are relative stable and moisture-insensitive.[48–51] They have been widely used as arylsulfonylation reagents for preparing organosulfonyl compounds.[52–55] Recently, the oxidative cross-coupling reaction of alkenes or cinnamic acids with sodium sulfinates has been developed (Scheme 1a).[56–67] Nitro-olefins are relatively stable, simply obtained by Henry reaction from aldehydes and nitromethane, which have been widely used to synthesized useful organic molecules. In some cases, *β*-nitrostyrenes have been used for denitrative

CONTACT Jin-Wei Yuan yuanjinweigs@126.com School of Chemistry & Chemical Engineering, Henan University of Technology; Academician Workstation for Natural Medicinal Chemistry of Henan Province, Zhengzhou 450001, PR China.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.
Supplemental data for this article can be accessed at https://doi.org/10.1080/10426507.2018.1513518.



Scheme 1. Synthesis of (*E*)-vinyl sulfones from sodium sulfinates and alkene derivatives.

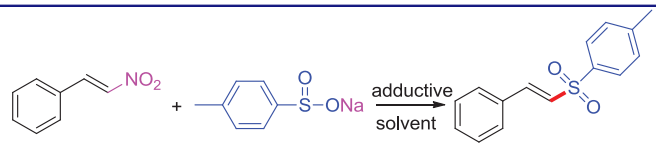
C-C bond formation by an addition/elimination reaction.[68–71] In 2016, Yadav's group reported a silver-catalyzed coupling reaction of nitro-olefins and sodium sulfinates in the presence of oxidant and under nitrogen atmosphere.[72] Subsequently, a Mn(III)-mediated coupling reaction of sodium sulfinates with nitro-olefins has also been developed by Chen's group (Scheme 1b).[73] Despite some great advantage of these reactions, there are still certain limitations including harsh reaction conditions and toxic metal catalysts. Therefore, it still remains an attractive task to develop more economic, efficient, and highly selective methods to access vinyl sulfones under metal-free conditions. The present protocol of AcOH-mediated direct oxidative coupling *β*-nitrostyrenes with sodium sulfinates under microwave irradiation provides a facile and efficient approach to various (*E*)-vinyl sulfones in moderate to good yields (Scheme 1c). The advantages of this approach are commercially available substrates, high regioselectivity, and avoidance to use any metal catalyst.

Results and discussion

Initially, (*E*)-*β*-nitrostyrene (**1a**) and sodium 4-methylbenzenesulfinate (**2a**) were selected as the model substrates to optimize the reaction conditions under microwave irradiation. As shown in Table 1, only a trace amount of desired product **3aa** was obtained when the model reaction was performed at 80 °C in DMSO for 20 min under microwave irradiation (Table 1, entry 1). Vinyl sulfones have been efficiently synthesized by treatment of alkenes with sodium arenesulfinates using potassium iodide and sodium periodate in the presence of a catalytic amounts of acetic acid by Das' group,[74] and Zhang's group has also developed a phosphoric acid-mediated synthesis of vinyl sulfones through decarboxylative coupling reactions of sodium sulfinates with phenylpropiolic acids.[34] These facts showed that the acid plays an important role for this cross-coupling reactions. We envisioned whether the acid could promote this transformation. When 2.0 equiv H_3PO_4 was added to the reaction system, much to our excitement 40% of **3aa** was obtained (Table 1, entry 2). The *E* or *Z* stereochemistry of **3aa** is easily established by the ^{1}H NMR analysis. The chemical shifts of the α- and *β*-protons are 7.65 ppm and 6.85 ppm, respectively. They have a coupling constant $J_{H\text{-}H} = 15.4$ Hz typical of trans positioned protons, which proves that configuration of **3aa** is an *E* stereoisomer. Encouraged by this result, we examined some different protic acids. However, moderate yields were achieved when several inorganic and organic acids such as H_2SO_4, HNO_3, TsOH, TFA, and $MeSO_3H$ were used (Table 1, entries 3–6, 8, 9). It was pleasing to find that 70% of **3aa** was isolated when AcOH was employed in the reaction (Table 1, entry 7). The suitable amount of AcOH was subsequently screened (Table 1, entries 7, 10–12). The results indicated that increasing or decreasing the amount of AcOH did not increase the yield. Then, the screening of a range of solvents demonstrated that the reaction performed in DMSO was significantly better than those conducted in H_2O, CH_3CN, 1,4-dioxane, CH_3OH, DCE, and THF (Table 1, entries 7, 13–18). The ratio of (*E*)-*β*-nitrostyrene with sodium 4-methylbenzenesulfinate was investigated, and the ratio of 1:1.5 proved to give the best result, providing 70% yield of **3aa** (Supporting information, Table S1, entries 1–4). Next, various reaction temperatures were also examined, and 90 °C was found to be the best choice (Table 1, entries 7, 19–21). Finally, the effect of reaction time was investigated, and good yields (80%) could be obtained in 40 min (Table 1, entries 7, 22–25). Therefore, the optimal reaction conditions are: 1.5 equiv of sodium sulfinate, and 2.0 equiv of AcOH in DMSO at 90 °C for 40 min under microwave irradiation as shown in Table 1, entry 24.

Under the optimized conditions in hand, the scope of the AcOH-mediated oxidative coupling of *β*-nitrostyrenes with various sodium arenesulfinates for the construction of (*E*)-vinyl sulfones was explored. The results are summarized in Table 2. In general, the reaction worked very well for a range of sodium arenesulfinates with various substituents at the phenyl ring, and the products were isolated in yields ranging from 38% to 85%. Sodium arenesulfinates with electron-donating substituents at the phenyl ring afforded the desired vinyl sulfones in 78% to 85% yield (**3aa**–**3ad**), whereas sodium arenesulfinates bearing electron-withdrawing substituents at the phenyl ring provided the desired vinyl sulfones in 38%–55% yield (**3ae**–**3ai**). Especially, the strong electron-withdrawing trifluoromethyl group (CF_3) at

Table 1. Optimization of reaction conditions.[a]



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

Entry	Additive (eq.)	Solvent	Temp (°C)	Time (mins)	Yield[b] (%)
1	–	DMSO	80	20	trace
2	H_3PO_4 (2.0)	DMSO	80	20	40
3	H_2SO_4 (2.0)	DMSO	80	20	48
4	HCl (2.0)	DMSO	80	20	<5
5	HNO_3 (2.0)	DMSO	80	20	40
6	TsOH (2.0)	DMSO	80	20	45
7	AcOH (2.0)	DMSO	80	20	70
8	TFA (2.0)	DMSO	80	20	35
9	$MeSO_3H$ (2.0)	DMSO	80	20	53
10	AcOH (0.5)	DMSO	80	20	10
11	AcOH (1.0)	DMSO	80	20	48
12	AcOH (3.0)	DMSO	80	20	50
13	AcOH (2.0)	H_2O	80	20	trace
14	AcOH (2.0)	CH_3CN	80	20	50
15	AcOH (2.0)	1,4-dioxane	80	20	45
16	AcOH (2.0)	CH_3OH	80	20	65
17	AcOH (2.0)	DCE	80	20	50
18	AcOH (2.0)	THF	80	20	60
19	AcOH (2.0)	DMSO	70	20	65
20	AcOH (2.0)	DMSO	90	20	75
21	AcOH (2.0)	DMSO	100	20	73
22	AcOH (2.0)	DMSO	90	10	30
23	AcOH (2.0)	DMSO	90	30	77
24	AcOH (2.0)	DMSO	90	40	80
25	AcOH (2.0)	DMSO	90	60	80

[a]Reaction conditions: (*E*)-(2-nitrovinyl)benzene **1a** (0.2 mmol, 29.8 mg), sodium 4-methylbenzenesulfinate **2a** (0.3 mmol, 53.4 mg), additive and solvent (2.0 mL) under microwave irradiation.
[b]Isolated yield.

the para-position of the phenyl ring had a noticeable effect, resulting in relatively lower yield (**3ah**). It was found that halogen substituents, such as F, Cl, and Br, were all well tolerated, which made this protocol more useful for further structural modification (**3ae–3ag**, **3ai**). To our delight, sodium 2-chlorobenzenesulfinate **2i** reacted smoothly with *β*-nitrostyrene, resulting in a moderate yield of the desired product **3ai** (55%), which showed that the steric effect played a weak role during this transformation. It is noteworthy that sodium alkanesulfinates, such as sodium methanesulfinate, sodium ethanesulfinate, and sodium cyclopropanesulfinate, could also be used in the reactions to give the corresponding products **3aj**, **3ak**, and **3al** in moderate yields. The scope of this oxidative coupling reaction was further expanded to a variety of substituted *β*-nitrostyrenes. Substituted *β*-nitrostyrenes with electron-donating substituents and with electron-withdrawing substituents were all tolerated under the standard reaction conditions (**3bb–3bd**). Unfortunately, when other substrates such as styrenes and cinnamic acid were employed for this coupling reaction, the desired products were not formed under the present conditions.

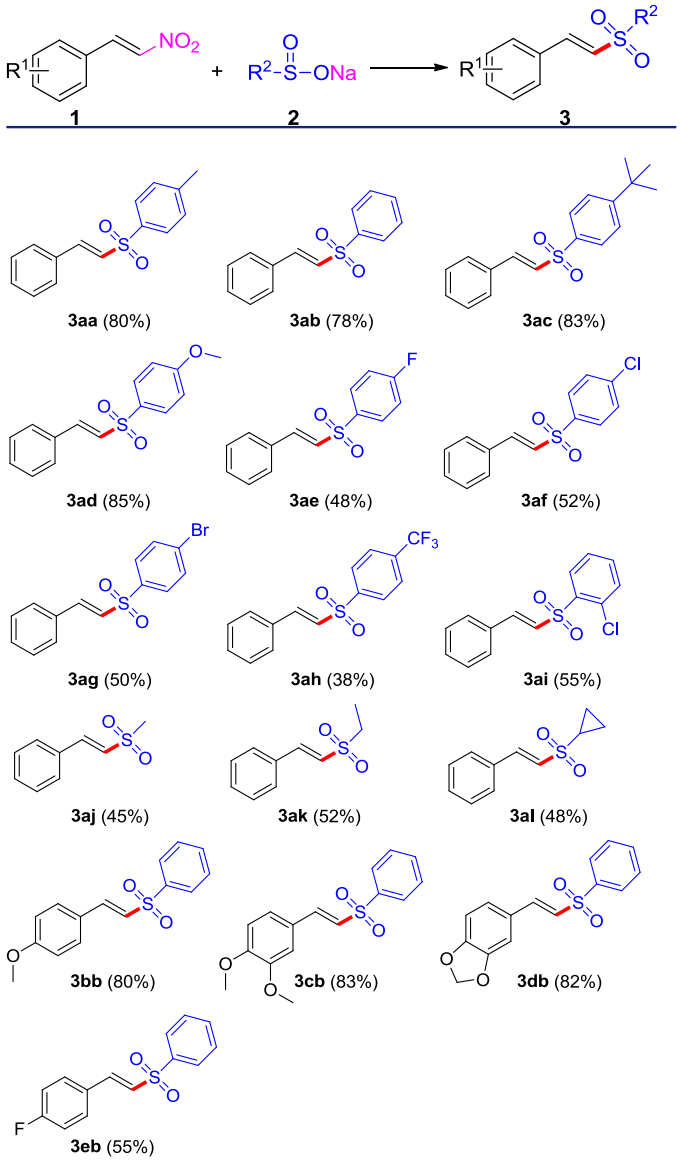
In order to gain some further insight into the reaction mechanism, several control experiments were carried out (Scheme 2). Initially, (*E*)-1-methyl-4-(styrylsulfonyl)benzene (**3aa**) was isolated in 80% yield when the reaction of *β*-nitrostyrene with sodium 4-methylbenzenesulfinate was conducted under the standard conditions. However, (*E*)-1-methyl-4-(styrylsulfonyl)benzene (**3aa**) was isolated in only 35% yield when 1.5 equiv. 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), a radical scavenger, was added into the reaction system. Only trace amounts of product (**3aa**) were dectected in the presence of TEMPO (2.5 equiv). These facts indicated that the reaction might occur via a radical mechanism.

Based on the above experimental results and previous reports,[34,73–75] a possible reaction pathway was proposed as shown in Scheme 3. Initially, the benzenesulfinate anion is oxidized by DMSO via a single electron transfer (SET) to induce the formation of a radical (i. e. a resonance hybrid **A** ↔ **B**).[76,77] Subsequently, this radical selectively adds to the *β*-position of (*E*)-*β*-nitrostyrene to form a carbon-centered radical **C**. The benzyl radical **C** adopts a more stable conformation **D**, and subsequently abstracts a hydrogen radical from AcOH to form the compound **E**. AcOH could also act as a protonating reagent during the reaction.[34] Finally, **E** is converted to the desired product **3ab** by elimination of HNO_2.

Conclusion

In summary, we have developed an efficient and practical method for the preparation of (*E*)-vinyl sulfones *via* AcOH-promoted oxidative cross-coupling reaction of *β*-nitrostyrenes with sodium sulfinates. This reaction is initiated by generation of a sulfonyl radical from the sodium sulfinate. A plausible reaction mechanism is proposed on the basis of control experiments.

Table 2. Synthesis of (*E*)-vinyl sulfones from *β*-nitrostyrenes with sodium sulfinates.[a,b]



[a]Reaction conditions: *β*-nitrostyrenes **1** (0.2 mmol), sodium sulfinate **2** (0.3 mmol), and AcOH (0.4 mmol, 24 mg) in 2.0 mL DMSO solvent, 90 °C for 40 min under microwave irradiation.
[b]Isolated yield.

Experimental

General information

All substrates purchased from *J* & *K* Scientific Ltd. were used without further purification. Column chromatography was performed using 300–400 mesh silica with the indicated solvent system according to standard techniques. A CEM Discover microwave reactor with an infrared pyrometer and a pressure control system was used. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts for ^{1}H NMR spectra are recorded in ppm from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from tetramethylsilane. MS were obtained on a Thermo Scientific LTQ Orbitrap XL instrument using the ESI technique. IR spectra, ν(cm^{-1}), were recorded on a Shimadazu IR-408 FTIR spectrophotometer using a thin film supported on KBr pellets. Melting points were measured on an XT4A microscopic apparatus uncorrected. The Supplemental Materials contains additional catalyst and product characterization results (Figures S 1–S 4).

General experimental procedure for the synthesis of (E)-vinyl sulfones (3)

β-Nitrostyrenes **1** (0.2 mmol), sodium sulfinate **2** (0.3 mmol), and AcOH (0.4 mmol, 24 mg) in DMSO (2 mL) were added to a 5.0 mL microwave reaction tube. The reactant mixture was heated at 90 °C for 40 min under microwave irradiation. After completion of the reaction, the solvent was distilled under vacuum. The residue was dissolved in EtOAc (10 mL), washed with 10% $NaHCO_3$ (10 mL ×2), then washed with saturated brine (10 mL ×2). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography to give the desired products **3**.

(E)-1-Methyl-4-(styrylsulfonyl)benzene (3aa)

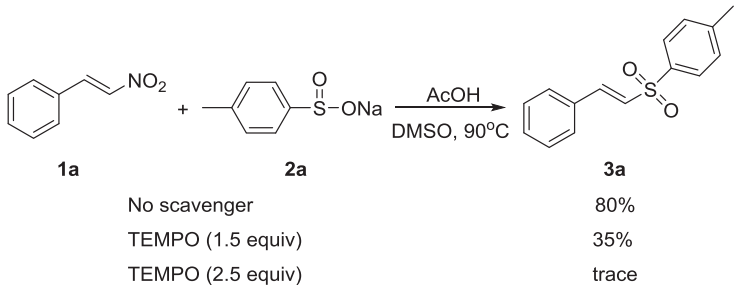
Light yellow solid, mp 95–96 °C [lit.[26] mp 98–99 °C]. IR: 2956, 2918, 2850, 1617, 1558, 1250, 1144. ^{1}H NMR *δ*: 7.82 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.65 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.48-7.46 (m, 2H), 7.39-7.33 (m, 5H), 6.85 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR *δ*: 144.4, 141.9 (CH), 137.7, 132.5, 131.1 (CH), 129.9 (CH), 129.0 (CH), 128.5 (CH), 127.7 (CH), 127.6 (CH), 21.6 (CH_3). MS *m/z*: 259.2 $[M+H]^+$ (calcd for $C_{15}H_{15}O_2S^+$ 259.1).

(E)-[2-(Benzenesulfonyl)vinyl]benzene (3ab)

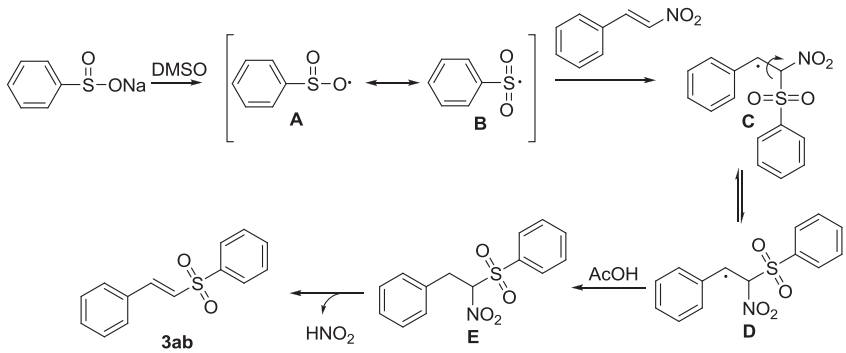
Colorless solid, mp 74–75 °C [lit.[78] mp 75–76 °C]. IR: 2956, 2920, 2850, 1558, 1446, 1308, 1147, 1086. ^{1}H NMR *δ*: 7.95 (d, $J_{H\text{-}H}$ = 7.2 Hz, 2H), 7.69 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.64-7.60 (m, 1H), 7.55 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.50-7.47 (m, 2H), 7.42-7.39 (m, 3H), 6.86 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR *δ*: 142.5 (CH), 140.7, 133.4 (CH), 132.3, 131.2 (CH), 129.4 (CH), 129.1 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH). MS *m/z*: 244.3 $[M+H]^+$ (calcd for $C_{14}H_{12}O_2S^+$ 244.1).

(E)-1-tert-Butyl-4-(styrylsulfonyl)benzene (3ac)[33]

Light yellow solid, mp 98–100 °C. IR: 2956, 2927, 2856, 1743, 1558, 1309, 1147. ^{1}H NMR *δ*: 7.86 (d, $J_{H\text{-}H}$ = 8.5 Hz, 2H), 7.66 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.55 (d, $J_{H\text{-}H}$ = 8.5 Hz, 2H), 7.48-7.46 (m, 2H), 7.39-7.35 (m, 3H), 6.68 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR *δ*: 157.4, 141.9 (CH), 137.7, 132.5, 131.1 (CH), 129.1 (CH), 128.5 (CH), 127.7 (CH), 127.6 (CH), 126.4 (CH), 35.3, 31.0 (CH_3). MS *m/z*: 301.0 $[M+H]^+$ (calcd for $C_{18}H_{21}O_2S^+$ 301.1).



Scheme 2. Control experiments.



Scheme 3. Proposed reaction mechanism.

(E)-1-Methoxy-4-(styrylsulfonyl)benzene (3ad)

Light yellow solid, mp 110–111 °C [lit.[72] mp 109–111 °C]. IR: 2956, 2918, 2850, 1596, 1558, 1506, 261, 1142, 1086. ^{1}H NMR δ: 7.87 (d, $J_{H\text{-}H}$ = 8.9 Hz, 2H), 7.64 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.48-7.46 (m, 2H), 7.39-7.38 (m, 3H), 7.01 (d, $J_{H\text{-}H}$ = 8.9 Hz, 2H), 6.85 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR δ: 163.6, 141.4 (CH), 132.5, 132.2, 131.1 (CH), 129.9 (CH), 129.1 (CH), 128.5 (CH), 127.9 (CH), 114.6 (CH), 55.7 (CH_3). MS *m/z*: 275.2 $[M+H]^+$ (calcd for $C_{15}H_{15}O_3S^+$ 275.1).

(E)-1-Fluoro-4-(styrylsulfonyl)benzene (3ae)

Colorless solid, mp 85–86 °C [lit.[79] mp 85–87 °C]. IR: 2956, 2924, 2850, 1591, 1558, 1495, 1319, 1290, 1144, 1086. ^{1}H NMR δ: 7.98-7.94 (m, 2H), 7.68 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.50-7.47 (m, 2H), 7.43-7.39 (m, 3H), 7.21 (d, $J_{H\text{-}H}$ = 8.6 Hz, 2H), 6.84 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR δ: 142.7 (CH), 132.2, 131.4 (CH), 130.5 (d, $J_{F\text{-}C}$ = 9.5 Hz, CH), 129.2 (CH), 128.6 (CH), 127.1 (CH), 116.6 (d, $J_{F\text{-}C}$ = 22.6 Hz, CH). ^{19}F NMR (376 MHz) δ: −103.9. MS *m/z*: 262.2 $[M+H]^+$ (calcd for $C_{14}H_{11}FO_2S^+$ 262.0).

(E)-1-Chloro-4-(styrylsulfonyl)benzene (3af)

Colorless solid, mp 82–83 °C [lit.[72] mp 78–80 °C]. IR: 3128, 3039, 1610, 1576, 1473, 1394, 1315, 1147, 1086. ^{1}H NMR δ: 7.88 (d, $J_{H\text{-}H}$ = 8.6 Hz, 2H), 7.68 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.48-7.45 (m, 4H), 7.38-7.33 (m, 3H), 6.92 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR δ: 143.1 (CH), 139.9, 139.3, 132.2, 131.4 (CH), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 126.9 (CH). MS *m/z*: 279.1 $[M+H]^+$ (calcd for $C_{14}H_{12}ClO_2S^+$ 279.0).

(E)-1-Bromo-4-(styrylsulfonyl)benzene (3ag)

Light yellow solid, mp 110–112 °C [lit.[72] mp 113–117 °C]. IR: 2956, 2918, 2850, 1558, 1315, 1142, 1082. ^{1}H NMR δ: 7.80 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 7.71-7.67 (m, 3H), 7.48 (d, $J_{H\text{-}H}$ = 7.4 Hz, 2H), 7.43-7.38 (m, 3H), 6.83 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR δ: 143.1 (CH), 139.8, 132.7 (CH), 132.2, 131.4 (CH), 129.2 (CH), 129.1 (CH), 128.6 (CH), 126.8 (CH). MS *m/z*: 322.1 $[M+H]^+$ (calcd for $C_{14}H_{11}BrO_2S^+$ 321.9).

(E)-1-(Styrylsulfonyl)-4-(trifluoromethyl)benzene (3ah)

Light yellow solid, mp 93–94 °C [lit.[72] mp 79–82 °C]. IR: 3047, 2960, 1734, 1558, 1321, 1144, 1061. ^{1}H NMR δ: 8.08 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.82 (d, $J_{H\text{-}H}$ = 8.3 Hz, 2H), 7.70 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.51-7.48 (m, 2H), 7.44-7.39 (m, 3H), 6.85 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR δ: 144.4, 144.0 (CH), 135.0 (d, $J_{F\text{-}C}$ = 32.9 Hz), 132.0, 131.6 (CH), 129.2 (CH), 128.7 (CH), 128.3 (CH), 126.4 (t, $J_{F\text{-}C}$ = 3.7 Hz, CH), 126.2 (CH), 124.5. ^{19}F NMR (376 MHz) δ: -63.2. MS *m/z*: 312.1 $[M+H]^+$ (calcd for $C_{15}H_{11}F_3O_2S^+$ 312.0).

(E)-1-Chloro-2-(styrylsulfonyl)benzene (3ai)

Pale Yellow solid, mp 200–201 °C [lit.[65] mp 75–76 °C]. IR: 1574, 1448, 1311, 1146, 1043. ^{1}H NMR δ: 8.22 (dd, $J_{H\text{-}H}$ = 7.9 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 1H), 7.77 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.56-7.38 (m, 8H), 7.08 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR δ: 145.3 (CH), 138.3, 134.5 (CH), 132.8, 132.3, 131.9 (CH), 131.4 (CH), 130.7 (CH), 129.1 (CH), 128.7 (CH), 127.4 (CH), 125.4 (CH). MS *m/z*: 278.1 $[M+H]^+$ (calcd for $C_{14}H_{11}ClO_2S^+$ 278.0).

(E)-[2-(Methanesulfonyl)vinyl]benzene (3aj)

Colorless solid, mp 78–79 °C [lit.[79] mp 79–81 °C]. IR: 3045, 2925, 1622, 1300, 1134. ^{1}H NMR δ: 7.62 (d, $J_{H\text{-}H}$ = 15.5 Hz, 1H), 7.52-7.50 (m, 2H), 7.44-7.40 (m, 3H), 6.95 (d, $J_{H\text{-}H}$ = 15.5 Hz, 1H), 3.04 (s, 3H). ^{13}C NMR δ: 143.9 (CH), 132.1, 131.4 (CH), 129.2 (CH), 128.6 (CH), 126.3 (CH), 43.2 (CH_3). MS *m/z*: 183.1 $[M+H]^+$ (calcd for $C_9H_{11}O_2S^+$ 183.0).

(E)-[2-(Ethanesulfonyl)vinyl]benzene (3ak)[72]

Pale yellow oil. IR: 3056, 2960, 1624, 1304, 1128. ^{1}H NMR δ: 7.61 (d, $J_{H\text{-}H}$ = 15.5 Hz, 1H), 7.52 (d, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.45-7.42 (m, 3H), 6.82 (d, $J_{H\text{-}H}$ = 15.5 Hz, 1H), 3.09 (q, $J_{H\text{-}H}$ = 7.4 Hz, 2H), 1.39 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H). ^{13}C NMR δ: 145.2 (CH), 132.3, 131.4 (CH), 129.2 (CH), 128.6 (CH), 124.0 (CH), 49.5 (CH_2), 7.3 (CH_3). MS *m/z*: 197.2 $[M+H]^+$ (calcd for $C_{10}H_{13}O_2S^+$ 197.1).

(E)-[2-(Cyclopropanesulfonyl)vinyl]benzene (3al)

Colorless solid, mp 89–90 °C [lit.[80] pale yellow oil]. IR: 3045, 1616, 1577, 1452, 1317, 1292, 1126, 1038. ^{1}H NMR δ: 7.56-7.50 (m, 3H), 7.45-7.38 (m, 3H), 6.93 (d, $J_{H\text{-}H}$ = 15.5 Hz, 1H), 2.49-2.43 (m, 1H), 1.30-1.26 (m, 2H), 1.08-1.03 (m, 2H). ^{13}C NMR δ: 143.1 (CH), 132.4, 131.2 (CH), 129.1 (CH), 128.5 (CH), 125.7 (CH), 31.4 (CH), 5.4 (CH_2). MS *m/z*: 209.3 $[M+H]^+$ (calcd for $C_{11}H_{13}O_2S^+$ 209.1).

(E)-1-Methoxy-4-[2-(benzenesulfonyl)vinyl]benzene (3bb)

Colorless solid, mp 200–201 °C [lit.[62] mp 100–101 °C]. IR: 3062, 2918, 2848, 1603, 1512, 1444, 1263, 1144, 1084. ^{1}H NMR δ: 7.94 (d, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.65-7.58 (m, 2H), 7.53 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.43 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.89 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.71 (d, $J_{H\text{-}H}$ = 15.3 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR δ: 162.1, 142.3 (CH), 141.1, 133.2 (CH), 130.4 (CH), 129.3 (CH), 127.5 (CH), 124.9, 124.4 (CH), 114.5 (CH), 55.5 (CH_3). MS *m/z*: 275.2 $[M+H]^+$ (calcd for $C_{15}H_{15}O_3S^+$ 275.1).

(E)-1,2-Dimethoxy-4-[2-(benzenesulfonyl)vinyl] benzene (3cb)

Colorless solid, mp 145–146 °C [lit.[67] mp 153–154 °C]. IR: 3047, 2935, 2844, 1610, 1510, 1464, 1271, 1142, 1024. ^{1}H NMR δ: 7.95 (d, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.64-7.59 (m, 2H), 7.56-7.52 (m, 2H), 7.09 (dd, $J_{H\text{-}H}$ = 8.3 Hz, $J_{H\text{-}H}$ = 1.9 Hz, 1H), 6.98 (d, $J_{H\text{-}H}$ = 1.9 Hz, 1H), 6.86 (d, $J_{H\text{-}H}$ = 8.3 Hz, 1H), 6.76 (d, $J_{H\text{-}H}$ = 15.3 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 151.8, 149.3, 142.6 (CH), 141.1, 133.2 (CH), 129.3 (CH), 127.5 (CH), 125.2, 124.6 (CH), 123.6 (CH), 111.0 (CH), 109.9 (CH), 56.0 (CH_3), 55.9 (CH_3). MS *m/z*: 304.0 $[M+H]^+$ (calcd for $C_{16}H_{16}O_4S^+$ 304.1).

(E)-5-[2-(Benzenesulfonyl)vinyl]benzo[d] [1, 3]dioxole (3db)

Colorless solid, mp 97–98 °C [lit.[33] mp 95–96 °C]. IR: 3058, 2937, 1605, 1460, 1282, 1078. ^{1}H NMR δ: 7.93 (d, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.62-7.51 (m, 4H), 6.99 (dd, $J_{H\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 1.6 Hz, 1H), 6.93 (d, $J_{H\text{-}H}$ = 1.5 Hz, 1H), 6.80 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H), 6.68 (d, $J_{H\text{-}H}$ = 15.3 Hz, 1H), 5.99 (s, 2H). ^{13}C NMR δ: 150.4, 148.5, 142.3 (CH), 140.9, 133.3 (CH), 129.3 (CH), 127.5 (CH), 126.6, 125.4 (CH), 124.9 (CH), 108.7 (CH), 106.8 (CH), 101.8 (CH_2). MS *m/z*: 289.3 $[M+H]^+$ (calcd for $C_{15}H_{13}O_4S^+$ 289.1).

(E)-1-Fluoro-4-[2-(benzenesulfonyl)vinyl]benzene (3eb)

Colorless solid, mp 91–92 °C [lit.[33] mp 92–93 °C]. IR: 3057, 2924, 1716, 1558, 1508, 1306, 1232, 1146, 1084. ^{1}H NMR δ: 7.95-7.93 (m, 2H), 7.67-7.61 (m, 2H), 7.55 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.50-7.46 (m, 2H), 7.08 (d, $J_{H\text{-}H}$ = 8.6 Hz, 2H), 6.80 (d, $J_{H\text{-}H}$ = 15.4 Hz, 1H). ^{13}C NMR δ: 164.3 (d, $J_{F\text{-}C}$ = 251.6 Hz), 141.2 (CH), 140.6, 133.5 (CH), 130.6 (d, $J_{F\text{-}C}$ = 8.7 Hz, CH), 129.4 (CH), 128.6 (d, $J_{F\text{-}C}$ = 3.5 Hz), 127.7 (CH), 127.0 (d, $J_{F\text{-}C}$ = 2.5 Hz, CH), 116.3 (d, $J_{F\text{-}C}$ = 21.9 Hz, CH). ^{19}F NMR (376 MHz) δ: -107.7. MS *m/z*: 263.3 $[M+H]^+$ (calcd for $C_{14}H_{12}FO_2S^+$ 263.1).

Acknowledgement

We gratefully acknowledge the Department of Henan Province Natural Science and Technology Foundation (No. 172102210225), Natural Science Foundation in Henan Province Department of Education (No. 17A150005, 17A150007), the Program for Innovative Research Team from Zhengzhou (No. 131PCXTD605), and Project of Youth Backbone Teachers of Henan University of Technology (No. 2016003).

Disclosure statement

No potential conflict of interests was reported by the authors.

References

[1] Aziz, J.; Messaoudi, S.; Alami, M.; Hamze, A. Sulfinate Derivatives: Dual and Versatile Partners in Organic Synthesis. *Org. Biomol. Chem.* **2014**, *12*, 9743–9759. https://doi.org/10.1039/C4OB01727G.

[2] Noshi, M. N.; El-Awa, A.; Torres, E.; Fuchs, P. L. Conversion of Cyclic Vinyl Sulfones to Transposed Vinyl Phosphonates. *J. Am. Chem. Soc.* **2007**, *129*, 11242–11247. https://doi.org/10.1021/ja072890p.

[3] Li, H.-M.; Song, J.; Liu, X.-F.; Deng, L.-J. Catalytic Enantioselective C-C Bond Forming Conjugate Additions with Vinyl Sulfones. *J. Am. Chem. Soc.* **2005**, *127*, 8948–8949. https://doi.org/10.1021/ja0511063.

[4] Fang, Y.; Luo, Z.; Xu, X. Recent Advances in the Synthesis of Vinyl Sulfones. *RSC Adv.* **2016**, *6*, 59661–59676. https://doi.org/10.1039/C6RA10731A.

[5] Zhu, Q.; Lu, Y. Enantioselective Conjugate Addition of Nitroalkanes to Vinyl Sulfone: An Organocatalytic Access to Chiral Amines. *Org. Lett.* **2009**, *11*, 1721–1724. https://doi.org/10.1021/ol9003349.

[6] Clive, D. L. J.; Li, Z.; Yu, M. Intramolecular Conjugate Displacement: A General Route to Hexahydroquinolizines,

Hexahydroindolizines, and Related [m,n,0]-Bicyclic Structures with Nitrogen at a Bridgehead. *J. Org. Chem.* **2007**, *72*, 5608–5617. https://doi.org/10.1021/jo070664s.

[7] Wardrop, D. J.; Fritz, J. Total Synthesis of (±)-Magnofargesin. *Org. Lett.* **2006**, *8*, 3659–3662. https://doi.org/10.1021/ol0609053.

[8] López-Pérez, A.; Robles-Machín, R.; Adrio, J.; Carretero, J. C. Oligopyrrole Synthesis by 1,3-Dipolar Cycloaddition of Azomethine Ylides with Bis-sulfonyl Ethylenes. *Angew. Chem. Int. Ed.* **2007**, *46*, 9261–9264. https://doi.org/10.1002/anie.200703258.

[9] Padwa, A.; Lipka, H.; Watterson, S. H.; Murphree, S. S. Phenylsulfonyl Ene-Allenes as Efficient Precursors to Bicyclic Synthesis via Intramolecular [2 + 2]-Cycloaddition Reactions. *J. Org. Chem.* **2003**, *68*, 6238–6250. https://doi.org/10.1021/jo0345796.

[10] Carr, R. V. C.; Paquette, L. A. An Ethylene and Terminal Olefin Equivalent in [4 + 2]π Cycloadditions. General Synthetic Application of Phenyl Vinyl Sulfone to the Construction of Functionalized Six-Membered Rings. *J. Am. Chem. Soc.* **1980**, *102*, 853–855. https://doi.org/10.1021/ja00522a075.

[11] Steert, K.; El-Sayed, I.; Van der Veken, P.; Krishtal, A.; Van Alsenoy, C.; Westrop, G. D.; Mottram, J. C.; Coombs, G. H.; Augustyns, K.; Haemers, A. Dipeptidyl α-Fluorovinyl Michael Acceptors: Synthesis and Activity against Cysteine Proteases. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6563–6566. https://doi.org/10.1016/j.bmcl.2007.09.075.

[12] Uttamchandani, M.; Liu, K.; Panicker, R. C.; Yao, S. Q. Activity-based Fingerprinting and Inhibitor Discovery of Cysteine Proteases in a Microarray. *Chem. Commun.* **2007**, *0*, 1518–1520. https://doi.org/10.1039/B702826A.

[13] Reddick, J. J.; Cheng, J.; Roush, W. R. Relative Rates of Michael Reactions of 2′-(Phenethyl)thiol with Vinyl Sulfones, Vinyl Sulfonate Esters, and Vinyl Sulfonamides Relevant to Vinyl Sulfonyl Cysteine Protease Inhibitors. *Org. Lett.* **2003**, *5*, 1967–1970. https://doi.org/10.1021/ol034555l.

[14] Palmer, J. T.; Rasnick, D.; Klaus, J. L.; Brömme, D. Vinyl Sulfones as Mechanism-Based Cysteine Protease Inhibitors. *J. Med. Chem.* **1995**, *38*, 3193–3196. https://doi.org/10.1021/jm00017a002.

[15] Meadows, D. C.; Sanchez, T.; Neamati, N.; North, T. W.; Gervay-Hague, J. Ring Substituent Effects on Biological Activity of Vinyl Sulfones as Inhibitors of HIV-I. *Bioorg. Med. Chem.* **2007**, *15*, 1127–1137. https://doi.org/10.1016/j.bmc.2006.10.017.

[16] Frankel, B. A.; Bentley, M.; Kruger, R. G.; McCafferty, D. G. Vinyl Sulfones: Inhibitors of SrtA, a Transpeptidase Required for Cell Wall Protein Anchoring and Virulence in *Staphylococcus Aureus*. *J. Am. Chem. Soc.* **2004**, *126*, 3404–3405. https://doi.org/10.1021/ja0390294.

[17] Kudryavtsev, K. V.; Bentley, M. L.; McCafferty, D. G. Probing of *cis*-5-Phenyl Proline Scaffold as a Platform for the Synthesis of Mechanism-Based Inhibitors of the Staphylococcus Aureus Sortase SrtA Isoform. *Bioorg. Med. Chem.* **2009**, *17*, 2886–2893. https://doi.org/10.1016/j.bmc.2009.02.008.

[18] Singh, A.; Rosenthal, P. J. Positive Role of the Mammalian TBPIP/HOP2 Protein in DMC1-Mediated Homologous Pairing. *J. Biol. Chem.* **2004**, *279*, 35263–35272. https://doi.org/10.1074/jbc.M402481200.

[19] Liu, S.; Zhou, B.; Yang, H.; He, Y.; Jiang, Z. X.; Kumar, S.; Wu, L.; Zhang, Z. Y. Aryl Vinyl Sulfonates and Sulfones as Active Site-Directed and Mechanism-Based Probes for Protein Tyrosine Phosphatases. *J. Am. Chem. Soc.* **2008**, *130*, 8251–8260. https://doi.org/10.1021/ja711125p.

[20] Chodroff, S.; Whitmore, W. F. The Preparation of Unsaturated Sulfones by Condensation Reactions. *J. Am. Chem. Soc.* **1950**, *72*, 1073–1076. https://doi.org/10.1021/ja01159a005.

[21] Gancarz, R. A.; Kice, J. L. Photodecomposition of Selenosulfonates and Their Facile Photoaddition to Alkenes. *Tetrahedron Lett.* **1980**, *21*, 4155–4158. https://doi.org/10.1016/S0040-4039(00)93676-1.

[22] Hopkin, P. B.; Fuchs, P. L. Chlorosulfenylation-Dehydrochlorination Reactions. New and Improved Methodology for the Synthesis of Unsaturated Aryl Sulfides and Aryl Sulfones. *J. Org. Chem.* **1978**, *43*, 1208–1217. https://doi.org/10.1021/jo00400a041.

[23] van Steenis, J. H.; van Es, J. J. G. S.; van der Gen, A. Stereoselective Synthesis of (E)-Vinyl Sulfoxides by the Horner-Wittig Reaction. *Eur. J. Org. Chem.* **2000**, *2000*, 2787–2793. https://doi.org/10.1002/1099-0690(200008)2000:15 < 2787:AID-EJOC2787 > 3.0.CO;2-Z.

[24] Xue, Q.; Mao, Z.; Shi, Y.; Mao, H.; Cheng, Y.; Zhu, C. Metal-Free, One-Pot Highly Selective Synthesis of (*E*)-Vinyl Sulfones and Sulfoxides via Addition-Oxidation of Thiols with Alkynes. *Tetrahedron Lett.* **2012**, *53*, 1851–1854. https://doi.org/10.1016/j.tetlet.2012.01.135.

[25] Lindén, A. A.; Krüger, L.; Bäckvall, J. Highly Selective Sulfoxidation of Allylic and Vinylic Sulfides by Hydrogen Peroxide Using a Flavin as Catalyst. *J. Org. Chem.* **2003**, *68*, 5890–5896. https://doi.org/10.1021/jo034273z.

[26] Reeves, D. C.; Rodriguez, S.; Lee, H.; Haddad, N.; Krishnamurthy, D.; Senanayake, C. H. Palladium-Catalyzed Coupling of Vinyl Tosylates with Arylsulfinate Salts. *Tetrahedron Lett.* **2009**, *50*, 2870–2873. https://doi.org/10.1016/j.tetlet.2009.03.174.

[27] Huang, F.; Batey, R. A. Cross-Coupling of Organoboronic Acids and Sulfinate Salts Using Catalytic Copper(II) Acetate and 1, 10-Phenanthroline: Synthesis of Aryl and Alkenylsulfones. *Tetrahedron* **2007**, *63*, 7667–7672. https://doi.org/10.1016/j.tet.2007.05.029.

[28] Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M.; Bernini, R. Unsymmetrical Diaryl Sulfones and Aryl Vinyl Sulfones through Palladium-Catalyzed Coupling of Aryl and Vinyl Halides or Triflates with Sulfinic Acid Salts. *J. Org. Chem.* **2004**, *69*, 5608–5614. https://doi.org/10.1021/jo0493469.

[29] Kabalka, G. W.; Guchhait, S. K. Convenient Synthesis of α,β-Unsaturated Sulfones via a Mizoroki-Heck Reaction of Arylboronic Acids with Phenyl Vinyl Sulfones. *Tetrahedron Lett.* **2004**, *45*, 4021–4022. https://doi.org/10.1016/j.tetlet.2004.03.179.

[30] Kirihara, M.; Yamamoto, J.; Noguchi, T.; Hirai, Y. Selective Synthesis of Sulfoxides and Sulfones by Tantalum(V) Catalyzed Oxidation of Sulfides with 30% Hydrogen Peroxide. *Tetrahedron Lett.* **2009**, *50*, 1180–1183. https://doi.org/10.1016/j.tetlet.2008.12.064.

[31] Wang, L.; Yue, H.; Yang, D.; Cui, H.; Zhu, M.; Wang, J.; Wei, W.; Wang, H. Metal-Free Oxidative Coupling of Aromatic Alkenes with Thiols Leading to (*E*)-Vinyl Sulfones. *J. Org. Chem.* **2017**, *82*, 6857–6864. https://doi.org/10.1021/acs.joc.7b00994.

[32] Cai, S.; Xu, Y.; Chen, D.; Li, L.; Chen, Q.; Huang, M.; Weng, W. Visible-Light-Enabled Decarboxylative Sulfonylation of Cinnamic Acids with Sulfonylhydrazides under Transition-Metal-Free Conditions. *Org. Lett.* **2016**, *18*, 2990–2993. https://doi.org/10.1021/acs.orglett.6b01353.

[33] Katrun, P.; Hlekhlai, S.; Meesin, J.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. $PhI(OAc)_2$ Mediated Decarboxylative Sulfonylation of β-Aryl-α,β-unsaturated Carboxylic Acids: A Synthesis of (*E*)-Vinyl Sulfones. *Org. Biomol. Chem.* **2015**, *13*, 4785–4794. https://doi.org/10.1039/C5OB00417A.

[34] Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. Phosphoric Acid-Mediated Synthesis of Vinyl Sulfones through Decarboxylative Coupling Reactions of Sodium Sulfinates with Phenylpropiolic Acids. *J. Org. Chem.* **2015**, *80*, 7652–7657. https://doi.org/10.1021/acs.joc.5b01212.

[35] Singh, R.; Allam, B. K.; Singh, N.; Kumari, K.; Singh, S. K.; Singh, K. N. A Direct Metal-Free Decarboxylative Sulfono Functionalization (DSF) of Cinnamic Acids to α,β-unsaturated Phenyl Sulfones. *Org. Lett.* **2015**, *17*, 2656–2659. https://doi.org/10.1021/acs.orglett.5b01037.

[36] Tang, S.; Wu, Y.; Liao, W.-Q.; Bai, R.-P.; Liu, C.; Lei, A.-W. Revealing the Metal-Like Behavior of Iodine: An Iodide-

Catalysed Radical Oxidative Alkenylation. *Chem. Commun.* **2014**, *50*, 4496–4499. https://doi.org/10.1039/C4CC00644E.

[37] Li, X.-W.; Xu, Y.-L.; Jiang, C.; Qi, C.-R.; Jiang, H.-F.; Wu, W. Copper-Catalyzed Aerobic Oxidative N-S Bond Functionalization for C-S Bond Formation: Regio- and Stereoselective Synthesis of Sulfones and Thioethers. *Chem. Eur. J.* **2014**, *20*, 7911–7915. https://doi.org/10.1002/chem.201402815.

[38] Rong, G.-W.; Mao, J.-C.; Yan, H.; Zheng, Y.; Zhang, G.-Q. Iron/Copper Co-Catalyzed Synthesis of Vinyl Sulfones from Sulfonyl Hydrazides and Alkyne Derivatives. *J. Org. Chem.* **2015**, *80*, 4697–4703. https://doi.org/10.1021/acs.joc.5b00558.

[39] Jiang, Y.-J.; Loh, T. P. Catalytic and Direct Methyl Sulfonylation of Alkenes and Alkynes Using a Methyl Sulfonyl Radical Generated from a DMSO, Dioxygen and Copper System. *Chem. Sci.* **2014**, *5*, 4939–4943. https://doi.org/10.1039/C4SC01901F.

[40] Xu, Y.-L.; Zhao, J.-W.; Tang, X.-D.; Wu, W.-Q.; Jiang, H.-F. Chemoselective Synthesis of Unsymmetrical Internal Alkynes or Vinyl Sulfones via Palladium-Catalyzed Cross-Coupling Reaction of Sodium Sulfinates with Alkynes. *Adv. Synth. Catal.* **2014**, *356*, 2029–2039. https://doi.org/10.1002/adsc.201300945.

[41] Xi, Y.; Dong, B.; McClain, E. J.; Wang, Q.; Gregg, T. L.; Akhmedov, N. G.; Petersen, J. L.; Shi, X. Gold-Catalyzed Intermolecular C-S Bond Formation: Efficient Synthesis of α-Substituted Vinyl Sulfones. *Angew. Chem. Int. Ed.* **2014**, *53*, 4657–4661. https://doi.org/10.1002/ange.201310142.

[42] Wei, W.; Li, J.; Yang, D.; Wen, J.; Jiao, Y.; You, J.; Wang, H. Copper-Catalyzed Highly Selective Direct Hydrosulfonylation of Alkynes with Arylsulfinic Acids Leading to Vinyl Sulfones. *Org. Biomol. Chem.* **2014**, *12*, 1861–1864. https://doi.org/10.1039/C3OB42522C.

[43] Zhao, Y.; Lai, Y.-L.; Du, K.-S.; Lin, D.-Z.; Huang, J.-M. Electrochemical Decarboxylative Sulfonylation of Cinnamic Acids with Aromatic Sulfonylhydrazides to Vinyl Sulfones. *J. Org. Chem.* **2017**, *82*, 9655–9661. https://doi.org/10.1021/acs.joc.7b01741.

[44] Lin, Y.; Lu, G.; Wang, G.; Yi, W. Odorless, Regioselective Synthesis of Diaryl Sulfides and α-Thioaryl Carbonyls from Sodium Arylsulfinates via a Metal-Free Radical Strategy in Water. *Adv. Synth. Catal.* **2016**, *358*, 4100–4105. https://doi.org/10.1002/adsc.201600846.

[45] Lin, Y.; Lu, G.; Wang, G.; Yi, W. Acid/Phosphide-Induced Radical Route to Alkyl and Alkenyl Sulfides and Phosphonothioates from Sodium Arylsulfinates in Water. *J. Org. Chem.* **2017**, *82*, 382–389. https://doi.org/10.1021/acs.joc.6b02459.

[46] Lin, Y.; Lu, G.; Cai, C.; Yi, W. Odorless, One-Pot Regio- and Stereoselective Iodothiolation of Alkynes with Sodium Arenesulfinates under Metal-Free Conditions in Water. *Org. Lett.* **2015**, *17*, 3310–3313. https://doi.org/10.1021/acs.orglett.5b01488.

[47] Xiao, F.; Chen, S.; Tian, J.; Huang, H.; Liu, Y.; Deng, G. Chemoselective Cross-Coupling Reaction of Sodium Sulfinates with Phenols under Aqueous Conditions. *Green Chem.* **2016**, *18*, 1538–1546. https://doi.org/10.1039/C5GC02292D.

[48] Wei, W.; Cui, H.; Yang, D.; Yue, H.; He, C.; Zhang, Y.; Wang, H. Visible-Light-Enabled Spirocyclization of Alkynes Leading to 3-Sulfonyl and 3-Sulfenyl Azaspiro[4,5]trienones. *Green Chem.* **2017**, *19*, 5608–5613. https://doi.org/10.1039/C7GC02330H.

[49] Wei, W.; Wen, J.; Yang, D.; Jing, H.; You, J.; Wang, H. Direct Difunctionalization of Alkynes with Sulfinic Acids and Molecular Iodine: A Simple and Convenient Approach to (*E*)-β-Iodovinyl Sulfones. *RSC Adv.* **2015**, *5*, 4416–4419. https://doi.org/10.1039/C4RA13998D.

[50] Wei, W.; Wen, J.; Yang, D.; Du, J.; You, J.; Wang, H. Catalyst-Free Direct Arylsulfonylation of N-Arylacrylamides with Sulfinic Acids: A Convenient and Efficient Route to Sulfonated Oxindoles. *Green Chem.* **2014**, *16*, 2988–2991. https://doi.org/10.1039/C4GC00231H.

[51] Wei, W.; Cui, H.; Yang, D.; Liu, X.; He, C.; Dai, S.; Wang, H. Metal-free Molecular Iodine-catalyzed Direct Sulfonylation of Pyrazolones with Sodium Sulfinates Leading to Sulfonated Pyrazoles at Room Temperature. *Org. Chem. Front.* **2017**, *4*, 26–30.

[52] Wu, X.-S.; Chen, Y.; Li, M.-B.; Zhou, M.-G.; Tian, S.-K. Direct Substitution of Primary Allylic Amines with Sulfinate Salts. *J. Am. Chem. Soc.* **2012**, *134*, 14694–14697. https://doi.org/10.1021/ja306407x.

[53] Maloney, K.; Kuethe, J.; Linn, K. A Practical, One-Pot Synthesis of Sulfonylated Pyridines. *Org. Lett.* **2011**, *13*, 102–105. https://doi.org/10.1021/ol102629c.

[54] Ueda, M.; Hartwig, J. F. Iridium-Catalyzed, Regio- and Enantioselective Allylic Substitution with Aromatic and Aliphatic Sulfinates. *Org. Lett.* **2010**, *12*, 92–94. https://doi.org/10.1021/ol9023248.

[55] Li, Y.; Cheng, K.; Lu, X.; Sun, J. A Facile and Efficient Approach to *N*-Protected β-Sulfinyl-Enamines *via* C-Sulfinylation of Enamides and Enecarbamates. *Adv. Synth. Catal.* **2010**, *352*, 1876–1880. https://doi.org/10.1002/adsc.201000084.

[56] Katrun, P.; Chiampanichayakul, S.; Korworapan, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Kuhakarn, C. $Ph(OAc)_2$/KI-Mediated Reaction of Aryl Sulfinates with Alkenes, Alkynes, and α,β-Unsaturated Carbonyl Compounds: Synthesis of Vinyl Sulfones and β-Iodovinyl Sulfones. *Eur. J. Org. Chem.* **2010**, *2010*, 5633–5641. https://doi.org/10.1002/ejoc.201000641.

[57] Zhang, N.; Yang, D.; Wei, W.; Yuan, L.; Cao, Y.; Wang, H. Metal-Free Iodine-Mediated Synthesis of Vinyl Sulfones at Room Temperature Using Water as Solvent. *RSC Adv.* **2015**, *5*, 37013–37017. https://doi.org/10.1039/C5RA02927A.

[58] Taniguchi, N. Stereoselective Synthesis of (*E*)-Alkene Sulfones from Alkenes or Alkynes via Copper-Catalyzed Oxidation of Sodium Sulfinates. *Synlett.* **2011**, *2011*, 1308–1312. https://doi.org/10.1055/s-0030-1260544.

[59] Nair, V.; Augustine, A.; Suja, T. D. CAN Mediated Reaction of Aryl Sulfinates with Alkenes and Alkynes: Synthesis of Vinyl Sulfones, β-Iodovinyl Sulfones and Acetylenic Sulfones. *Synthesis* **2002**, *2002*, 2259–2265. https://doi.org/10.1055/s-2002-34838.

[60] Meyer, A. U.; Jäger, S.; Hari, D. P.; König, B. Visible Light-Mediated Metal-Free Synthesis of Vinyl Sulfones from Aryl Sulfinates. *Adv. Synth. Catal.* **2015**, *357*, 2050–2054. https://doi.org/10.1002/adsc.201500142.

[61] Luo, Y.-C.; Pan, X.-J.; Yuan, G.-Q. An Efficient Electrochemical Synthesis of Vinyl Sulfones from Sodium Sulfinates and Olefins. *Tetrahedron* **2015**, *71*, 2119–2123. https://doi.org/10.1016/j.tet.2015.02.048.

[62] Qian, P.; Bi, M.; Su, J.; Zha, Z.; Wang, Z. Electrosynthesis of (*E*)-Alkene Sulfones Directly from Cinnamic Acids and Sodium Sulfinates via Decarboxylative Sulfono Functionalization. *J. Org. Chem.* **2016**, *81*, 4876–4882. https://doi.org/10.1021/acs.joc.6b00661.

[63] Guo, R.; Gui, Q.; Wang, D.; Tan, Z. Synthesis of Vinysulfones via Palladium-catalyzed Decarboxylative Coupling of Cinnamic Acids with Aromatic Sulfinic Acid Sodium Salts. *Catal. Lett.* **2014**, *144*, 1377–1383. https://doi.org/10.1007/s10562-014-1286-5.

[64] Gao, J.; Lai, J.; Yuan, G. Iodine-Mediated Synthesis of (*E*)-Alkene Sulfones from Sodium Sulfinates and Cinnamic Acids in Aqueous Medium. *RSC Adv.* **2015**, *5*, 66723–66726. https://doi.org/10.1039/C5RA10896A.

[65] Xu, Y.; Tang, X.; Hu, W.; Wu, W.; Jiang, H. Transition-Metal-Free Synthesis of Vinyl Sulfones via Tandem Cross-decarboxylative/Coupling Reactions of Sodium Sulfinates and Cinnamic Acids. *Green Chem.* **2014**, *16*, 3720–3723. https://doi.org/10.1039/C4GC00542B.

[66] Jiang, Q.; Xu, B.; Jia, J.; Zhao, A.; Zhao, Y.-R.; Li, Y.-Y.; He, N.-N.; Guo, C.-C. Copper-Catalyzed Aerobic Decarboxylative

Sulfonylation of Cinnamic Acids with Sodium Sulfinates: Stereospecific Synthesis of (*E*)-Alkene Sulfones. *J. Org. Chem.* **2014**, *79*, 7372–7379. https://doi.org/10.1021/jo5010845.

[67] Chen, J.; Mao, J.; Zheng, Y.; Liu, D.; Rong, G.; Yan, H.; Zhang, C.; Shi, D. Iodine-Promoted Decarboxylative C-S Cross-Coupling of Cinnamic Acids with Sodium Benzene Sulfinates. *Tetrahedron* **2015**, *71*, 5059–5063. https://doi.org/10.1016/j.tet.2015.05.115.

[68] Jang, Y.-J.; Yan, M.-C.; Lin, Y.-F.; Yao, C.-F. A Simple Radical Addition-Elimination Route to Geometrically Pure (*E*)-Alkene and Chromanone Derivatives via *β*-Nitrostyrenes. *J. Org. Chem.* **2004**, *69*, 3961–3963. https://doi.org/10.1021/jo049763l.

[69] Jang, Y.-J.; Liu, J.-Y.; Kuo, W.-Y.; Yao, C.-F. Improved One-Pot Synthesis of Styryl Tetrahydrofurans and Cyclohexanes by Radical Addition to *β*-Nitrostyrenes in the Presence of Benzoyl Peroxide. *Chem. Eur. J.* **2003**, *9*, 2123–2128. https://doi.org/10.1002/chem.200204571.

[70] Liu, J. T.; Jang, Y. J.; Shih, Y. K.; Hu, S. R.; Chu, C. M.; Yao, C. F. Novel Synthesis of Alkenes via Triethylborane-Induced Free-Radical Reactions of Alkyl Iodides and *β*-Nitrostyrenes. *J. Org. Chem.* **2001**, *66*, 6021–6028. https://doi.org/10.1021/jo010213m.

[71] Yao, C. F.; Chu, C. M.; Liu, J. T. Free-Radical Reactions of Trialkylboranes with *β*-Nitrostyrenes to Generate Alkenes. *J. Org. Chem.* **1998**, *63*, 719–722. https://doi.org/10.1021/jo9716901.

[72] Keshari, T.; Kapoorr, R.; Yadav, L. D. S. Silver-Catalyzed Denitrative Sulfonylation of *β*-Nitrostyrenes: A Convenient Approach to (*E*)-vinyl Sulfones. *Eur. J. Org. Chem.* **2016**, *2016*, 2695–2699. https://doi.org/10.1002/ejoc.201600237.

[73] Nie, G.; Deng, X.; Lei, X.; Hu, Q.; Chen, Y. Mn(III)-Mediated Regioselective Synthesis of (*E*)-Vinyl Sulfones from Sodium Sulfinates and Nitro-Olefins. *RSC Adv.* **2016**, *6*, 75277–75281. https://doi.org/10.1039/C6RA17842A.

[74] Das, B.; Lingaiah, M.; Damodar, K.; Bhunia, N. An Efficient Synthesis of Vinyl Sulfones from Alkenes and Aryl Sulfinates. *Synthesis* **2011**, *2011*, 2941–2944. https://doi.org/10.1055/s-0030-1260142.

[75] Nair, V.; Augustine, A.; George, T. G.; Nair, L. G. An Efficient One-Pot Synthesis of Vinyl Sulphones via CAN Mediated Reaction of Aryl Sulphinates and Alkenes. *Tetrahedron Lett.* **2001**, *42*, 6763–6765. https://doi.org/10.1016/S0040-4039(01)01377-6.

[76] Lu, Q.; Zhang, J.; Wei, F.; Qi, Y.; Wang, H.; Liu, Z.; Lei, A. Aerobic Oxysulfonylation of Alkenes Leading to Secondary and Tertiary *β*-Hydroxysulfones. *Angew. Chem. Int. Ed.* **2013**, *52*, 7156–7259. https://doi.org/10.1002/ange.201301634.

[77] Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. Dioxygen-Triggered Oxidative Radical Reaction: Direct Aerobic Difunctionalization of Terminal Alkynes toward *β*-keto Sulfones. *J. Am. Chem. Soc.* **2013**, *135*, 11481–11484. https://doi.org/10.1021/ja4052685.

[78] Liu, X.-T.; Ding, Z.-C.; Ju, L.-C.; Xu, S.-X.; Zhan, Z.-P. Copper(II)-Catalyzed Chemo- and Stereocontrolled Synthesis of (*E*)-Viinyl Sulfones and (*Z*)-*β*-Chlorovinyl Sulfones from Terminal Alkynes and Arylsulfonyl Hydrazides. *Synthesis* **2017**, *49*, 1575–1582. https://doi.org/10.1055/s-0036-1588918.

[79] Lin, Y.-M.; Lu, G.-P.; Wang, R.-K.; Yi, W.-B. Stereoselective Synthesis of Alkenyl Silanes, Sulfones, Phosphine Oxides, and Nitroolefins by Radical C-S Bond Cleavage of Arylalkenyl Sulfides. *Org. Lett.* **2017**, *19*, 1100–1103. https://doi.org/10.1021/acs.orglett.7b00126.

[80] Xu, Y.-L.; Zhao, J.-W.; Tang, X.-D.; Wu, W.-Q.; Jiang, H.-F. Chemoselective Synthesis of Unsymmetrical Internal Alkynes or Vinyl Sulfones via Palladium-catalyzed Cross-coupling Reaction of Sodium Sulfinates with Alkynes. *Adv. Synth. Cat.* **2014**, *356*, 2029–2039. https://doi.org/10.1002/adsc.201300945.