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Phosphoric Acid-Mediated Synthesis of Vinyl Sulfones through Decarboxylative Coupling Reactions of Sodium Sulfinates with Phenylpropiolic Acids

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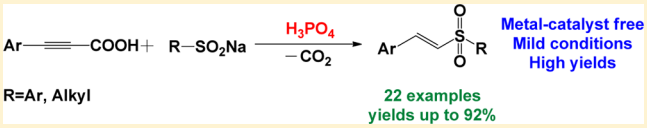
Supporting Information

ABSTRACT: A novel phosphoric acid -mediated synthesis of vinyl sulfones through decarboxylative coupling reactions of sodium sulfinates with phenylpropiolic acids is described. This transformation is efficient and environmentally friendly.



INTRODUCTION

Vinyl sulfones are important structural units that have received considerable attention in synthetic chemistry, mainly because they constitute a significant component in biologically active compounds[1] and also serve as useful chemical intermediates for synthesis.[2] Conventional methods for the synthesis of vinyl sulfones involve the oxidation of the corresponding sulfides,[3] β-elimination of selenosulfones and halosulfones,[4] and addition of $PhSO_2X$ (X = I, Cl, etc.) to alkynes/alkenes.[5] In contrast to known strategies that often require a stoichiometric amount of metallic reagents and harsh reaction conditions,[3−5] transition metal-catalyzed cross coupling reactions adopt the advantages of mild conditions, low catalyst loading and good availability of starting materials, and thus, they have been extensively explored in recent years. In 1983, Kamigata's group reported the reactions of arenesulfonyl chlorides with olefins catalyzed by a ruthenium(II) complex.[6] A high level of conversion of vinyl sulfones was achieved, while the use of the noble catalyst made the method less economic. Thereafter, much cheaper and greener catalysts such as copper complexes were developed by the research groups of Nair, Taniguchi, Jiang, etc.[7] For example, the Taniguchi group revealed an aerobic copper-catalyzed synthesis of (*E*)-alkenyl sulfones via the addition of sodium sulfinates to alkynes, including internal alkynes that have been scarcely exploited.[7e] Recently, Guo's group explored a copper-catalyzed aerobic decarboxylative sulfonylation reaction in which cinnamic acids and sodium sulfinates were chosen as the starting materials. Further studies of preparing vinyl sulfone derivatives were focused on more environmentally benign, operationally simple, and efficient cross coupling strategies.[7−9] Such work was conducted by Chutima and Nair's group by using alkenes and sodium sulfinates in the presence of a stoichiometric amount of oxidant and iodine compounds.[7] In 2012, Yadava's group also reported a green method for synthesizing vinyl sulfones from terminal epoxides and sodium sulfinates. However, two regioisomers (both linear and branched vinyl sulfones) were obtained in most cases.[8] Very recently, significant progress on the green synthesis of vinyl sulfones was made by Jiang and co-workers, who revealed a transition metal-free approach via tandem cross decarboxylative reactions between sodium sulfinates and cinnamic acids.[9c] In the past decades, decarboxylative coupling reactions have been a prominent research topic because they provided straightforward and efficient pathways to the formation of carbon−carbon and carbon−heteroatom bonds under relatively mild conditions.[10] In this regard, the application of the decarboxylative coupling method to the synthesis of vinyl sulfones has been studied little in recent years. Except for the results of Guo and Jiang mentioned above,[9] another work accomplished by the latter group introduced a new protocol for preparing such compounds, i.e., a palladium-catalyzed decarboxylative coupling reaction between propiolic acids and sodium sulfinates.[9d] Inspired by these works and our recent success with transition metal-free synthesis,[11] we were dedicated to exploring a greener and more sustainable approach to the decarboxylative coupling based upon the same substrates without the use of noble palladium catalysts. Herein, we report our results on a green, effective phosphorus acid-mediated synthesis of vinyl sulfones under catalyst-free conditions (Scheme 1).

RESULTS AND DISCUSSION

We initiated the study by reacting phenylpropiolic acid (**1a**) with sodium benzenesulfinate (**2a**) in the presence of a catalytic amount of CuI (20 mol %) in DMSO at 80 °C for 12 h. However, no desired product was detected from the reaction

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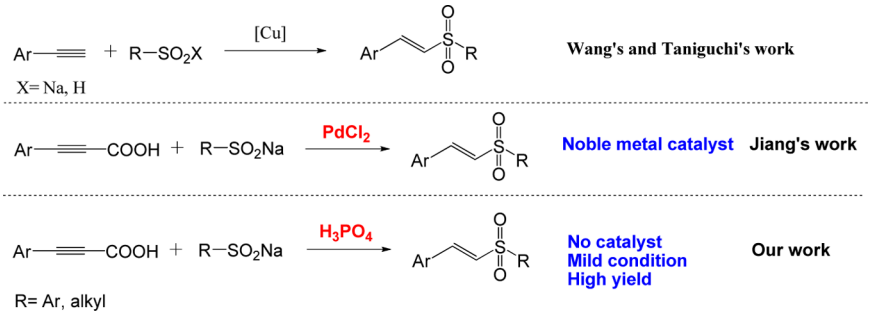
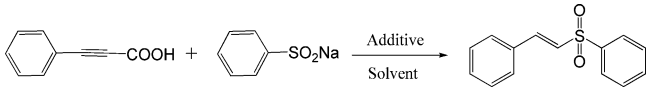
Scheme 1. Comparison of Our Work with Previous Work on the Synthesis of Vinyl Sulfones



mixture. Next, various additives such as bases and acids were tested. Although the addition of sodium carbonate as a base did not promote the reaction, much to our excitement, 23% of **3a** as a desired decarboxylative product was obtained with an exclusively *E* isomer when acetic acid was added to the reaction system. Interestingly, the yield can be further increased to 30% after the catalyst has been removed. Encouraged by this result, we examined some different protic acids. Apparently, strong protic acids, including sulfuric acid and TFA (trifluoroacetic acid), disfavored the reaction, as do very weak acid like ethanol (entries 5–7 of Table 1). However, moderate yields were achieved when several organic acids such as pivalic acid, malonic acid, and terephthalic acid were used (entries 8–10). It was pleasing to find that 73% of **3a** was isolated when phosphorus acid was employed in the reaction, and the result was remarkably improved by increasing the amount of sodium benzenesulfinate (3.0 equiv), from which a high yield (92%) for **3a** was reached (entry 13). The solvent effect was subsequently evaluated, yet much inferior results were observed when solvents other than DMSO were used (entries 14–16). It is worth mentioning that the high yield did not decrease obviously even if the reaction was conducted under an argon atmosphere (entry 17).

Table 1. Condition Optimization of Decarboxylative Coupling between Phenylpropiolic Acid and Sodium Benzenesulfinate[a]



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

entry	catalyst	additive	solvent	yield (%)[b]
1	CuI	–	DMSO	nd
2	CuI	Na_2CO_3	DMSO	nd
3	CuI	HOAc	DMSO	23
4	–	HOAc	DMSO	30
5	–	ethanol	DMSO	nd
6	–	H_2SO_4	DMSO	nd
7	–	TFA	DMSO	nd
8	–	pivalic acid	DMSO	34
9	–	malonic acid	DMSO	56
10	–	terephthalic acid	DMSO	68
11	–	pyruvic acid	DMSO	73
12	–	phosphorus acid	DMSO	75
13[c]	–	phosphorus acid	DMSO	92
14	–	phosphorus acid	CH_3CN	82
15	–	phosphorus acid	1,4-dioxane	23
16	–	phosphorus acid	DCE	35
17[c,d]	–	phosphorus acid	DMSO	91

[a]Reaction conditions: phenylpropiolic acid **1a** (0.3 mmol), sodium benzenesulfinate **2a** (2 equiv, 0.6 mmol), catalyst (20 mol %), additive (0.6 mmol), solvent (2 mL), 80 °C, 12 h, air. [b]nd, not detected. [c]Sodium benzenesulfinate **2a** (3 equiv, 0.9 mmol). [d]Argon atmosphere.

With the optimized reaction conditions described above in hand, we next explored the substrate scope that is applicable for the current reaction. Therefore, a series of substituted aromatic propiolic acids were introduced to react with sodium benzenesulfinate. Alkyl-substituted phenylpropiolic acids tended to afford the corresponding products in high yields (**3a**, **3b**, and **3d**), while a much lower yield of **3c** was gained when the substrate was phenylpropiolic acid bearing an electron-withdrawing group on the phenyl ring (Table 2). All reactions proceeded smoothly when *para*-halogen-substituted substrates were utilized to react with sodium benzenesulfinate, affording **3e**, **3f**, and **3g** in 88, 84, and 80% yields, respectively. Because of the steric hindrance effect of *ortho*-position substitution, only 23% of **3i** was formed, which is in contrast with the case for **3h**, where the chloro group is located on the *meta* position of the phenyl ring. This effect was then confirmed when comparing the results for products **3l** and **3m**. It was found that only a trace amount of **3l** was detected for the reaction involving naphth-1-ylpropiolic acid, whereas naphth-2-ylpropiolic acid proved to be an excellent substrate, providing **3m** in 90% yield. To our delight, substrates such as **2n** and **2o** bearing active functional groups (ketone or aldehyde) were also compatible with the reaction conditions and the corresponding products **3n** and **3o** were both isolated in good yields.

To further extend the applications of the reaction presented here, the substrate scope of sodium sulfinates was investigated under standard conditions. All reactions that were performed here afforded the desired vinyl sulfone products in moderate to good yields; sodium benzenesulfinates having very strong electron-withdrawing substituents were less effective substrates, and the yields for **3t** and **3u** were somewhat lower. Generally, halogen substitution favored high conversions giving the expected products in good yields. It was interesting to note that aliphatic sodium sulfinates, including sodium methanesulfinate and sodium ethanesulfinate, were also suitable substrates for this transformation, generating the corresponding products **3w** and **3x** in excellent yields.

To gain insights into the mechanistic aspect of the reaction, phenylacetylene was employed to react with sodium benzenesulfinate under standard conditions. However, an unexpected product **4** was isolated in 25% yield, instead of the vinyl sulfone **3a**, which indicated the reaction between **1** and **2** did not involve a process in which phenylpropiolic acid was first converted to phenylacetylene before reacting with

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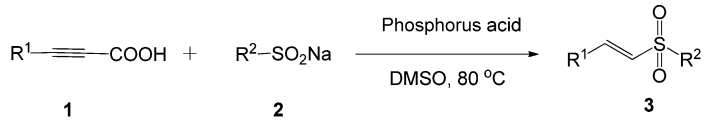
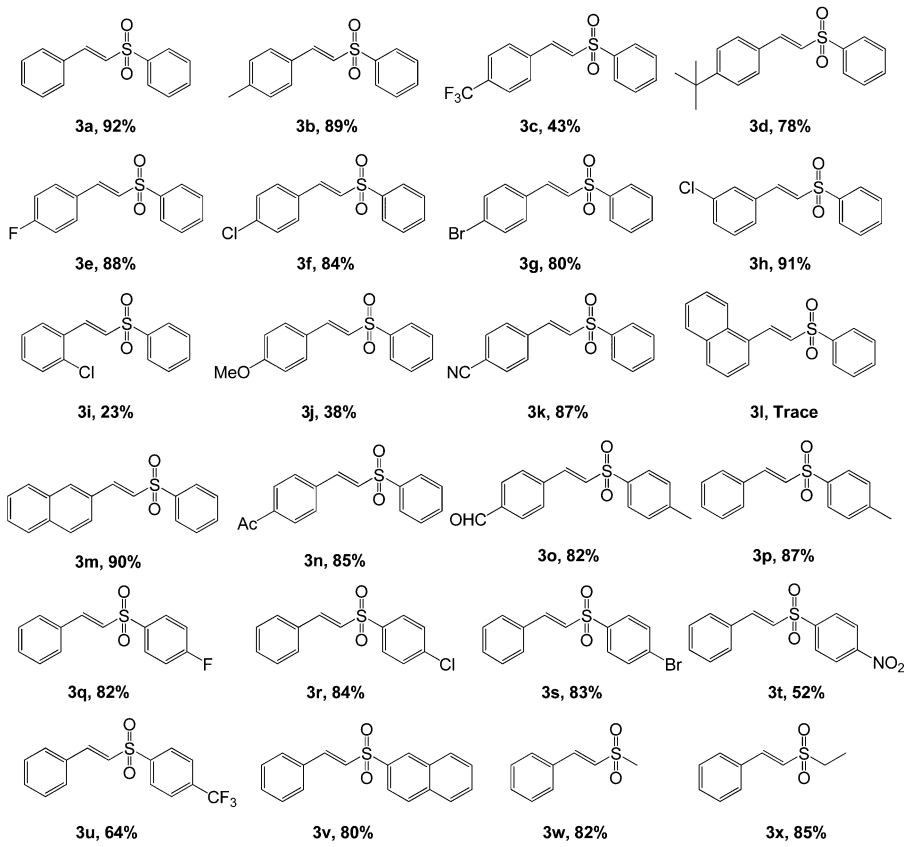
Table 2. Substrate Scope for the Synthesis of Various Vinyl Sulfones[a]





[a]Reaction conditions: aromatic propiolic acid **1** (0.3 mmol), sodium sulfinate (3 equiv, 0.9 mmol), phosphorus acid (0.6 mmol), DMSO (2 mL), 80 °C, 12 h, air.

sodium sulfinate. On the other hand, the reaction of **1a** with **2a** was dramatically inhibited while a radical scavenger, 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 4.0 equiv), was added to the reaction mixture under standard conditions (Scheme 2, eq 2). This suggests that a radical process was likely to be involved in the reaction. In addition, sodium phenylpropioate reacted smoothly with sodium sulfinate under the standard conditions, although the yield was a little lower (eq 3). Interestingly, another moderately strong acid, benzenesulfinic acid, was chosen to replace phosphorus acid for the same reaction, and a comparable yield was obtained. However, the reaction did not proceed in the absence of sodium sulfinate **2a** (eqs 4 and 5). Furthermore, the reaction mediated by benzene sulfinic acid was also conducted by adding 2.0 equiv of D_2O, and a deuterated product **3a′** was observed in approximately 10% yield, except for the major product **3a** (eq 6). According to these findings, we assume that sodium sulfinate should act as both a base for the deacrboxylation of phenylpropiolic acid and the sulfonylating reagent, and phosphorus acid could perform as a protonating reagent during the reaction.

On the basis of the results described above and previous literature reports,[12] a plausible mechanism was proposed in Scheme 3. An oxygen-centered radical **A** was initially generated through the oxidation of sodium sulfinate **2** by DMSO upon heating, which could be resonance-stabilized with a sulfonyl radical **B**.[13] Next, intermediate **D** was formed through the *trans* addition of **B** to the triple bond of **C** resulting from the deprotonation of phenylpropiolic acid in the presence of basic sodium sulfinate. An anionic **E** was readily produced after the removal of one molecule of carbon dioxide from **D** followed by the abstraction of a hydrogen radical from phosphoric acid.[12] **E** was eventually converted to the desired product **3** with the assistance of phosphoric acid.[9c,12e]

CONCLUSIONS

In summary, we have developed a green and efficient phosphoric acid-mediated synthesis of vinyl sulfones through decarboxylative coupling reactions of sodium sulfinates with phenylpropiolic acids. A broad range of substrates, including both substituted propiolic acids and sodium sulfinates, were tolerated with our protocol under optimal conditions, and a variety of vinyl sulfone products were obtained in moderate to excellent yields. The synthetic method presented here features many advantages such as simple operation, catalyst-free and green reaction conditions, a broad substrate scope, and good yields, which is promising for practical applications in relevant industrial and manufacturing processes in the future.

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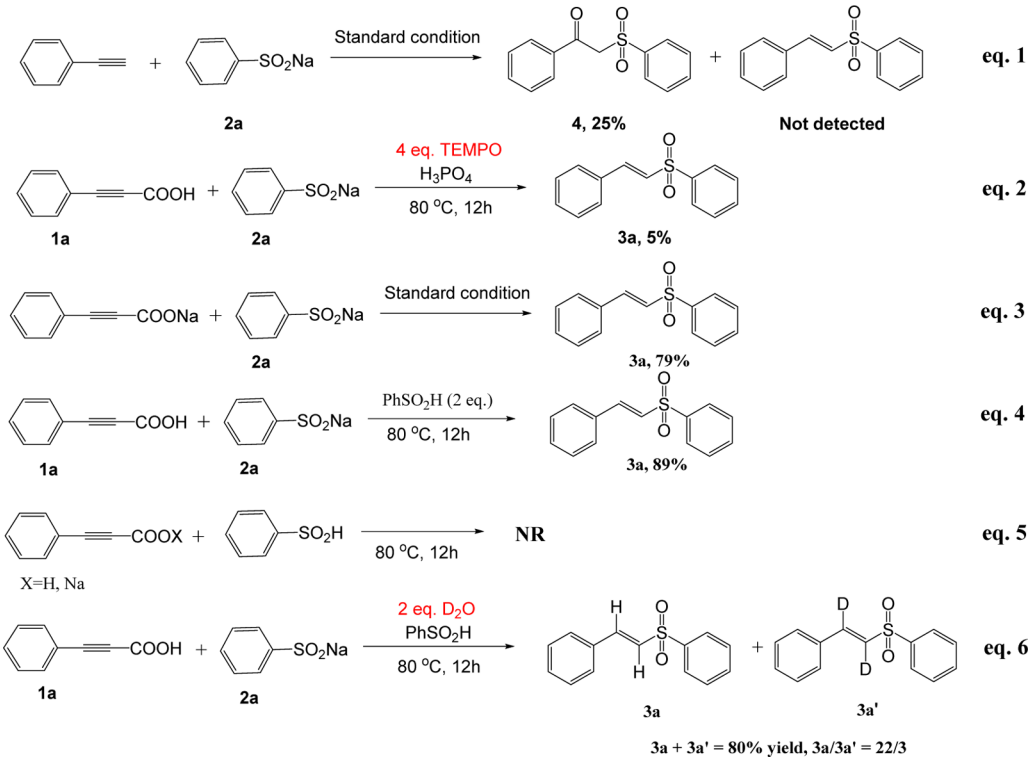
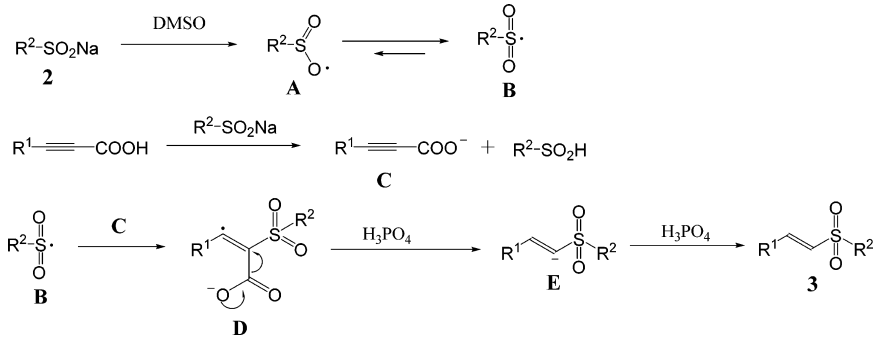
Scheme 2. Relevant Experiments for the Mechanistic Studies



Scheme 3. A Plausible Mechanism for the Formation of Product 3



EXPERIMENTAL SECTION

General Information. All reactions were conducted under an air atmosphere. Various phenylpropiolic acids and various sodium sulfinates were commercially available. The cuprous iodide (99%) was purchased from known corporations. Flash column chromatography was performed using silica gel (100−200 mesh). Analytical thin-layer chromatography was performed using glass plates precoated with 200−300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on a 400 MHz NMR or 300 MHz NMR spectrometer with TMS as an internal reference. Products were characterized by comparison of ^1H NMR, ^{13}C NMR, MS, and TOF-MS data in the literature.

General Procedure for the Reaction between Phenylpropiolic Acids and Sodium Benzenesulfinate. To a Schlenk tube equipped with a magnetic stir bar were added phenylpropiolic acid (0.3 mmol, 43.8 mg), sodium benzenesulfinate (3 equiv, 0.9 mmol, 147.7 mg), phosphoric acid (85 wt % in water, 0.6 mmol, 69.2 mg), and DMSO (2.0 mL). The resulting reaction mixture was stirred at 80 °C for 12 h. At the end of the reaction, the reaction mixture was cooled to room temperature amd water (10 mL) was added. The mixture was then diluted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate/petroleum ether mixtures to afford the desired product in high purity.

*(E)-[2-(Phenylsulfonyl)vinyl]benzene (**3a**).*[9c] White solid: mp 67−69 °C; yield 92% (67.4 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.94 (m, 2H), 7.69 (d, J = 15.6 Hz, 1H), 7.64−7.59 (m, 1H), 7.58−7.52 (m, 2H), 7.50−7.46 (m, 2H), 7.42−7.37 (m, 3H), 6.87 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 140.2, 132.9, 131.9, 130.8, 128.9, 128.6, 128.1, 127.2, 126.8; MS calcd for $C_{14}H_{12}O_2S$ m/z 244.1, found m/z 245.1 $(M + H)^+$.

*(E)-1-Methyl-4-[2-(phenylsulfonyl)vinyl]benzene (**3b**).*[9c] White solid: mp 130−132 °C; yield 89% (69.0 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.92 (m, 2H), 7.65 (d, J = 15.6 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 15.2 Hz, 1H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.6, 141.9, 140.9, 133.3, 129.8, 129.6, 129.3, 128.6, 127.6, 126.0, 21.5; MS calcd for $C_{15}H_{14}O_2S$ m/z 258.1, found m/z 259.1 $(M + H)^+$.

*(E)-1-[2-(Phenylsulfonyl)vinyl]-4-(trifluoromethyl)benzene (**3c**).*[9c] White solid: mp 133−135 °C; yield 43% (40.3 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.94 (m, 2H), 7.81 (d, J = 15.6 Hz, 1H), 7.68−7.63 (m, 3H), 7.62−7.55 (m, 4H), 6.97 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$

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NMR (100 MHz, $CDCl_3$) δ 140.4, 140.1, 135.7, 133.7, 132.6 (q, J = 32.7 Hz), 130.0, 129.5, 128.8, 127.8, 126.0 (q, J = 3.7 Hz), 123.6 (d, J = 270.8 Hz); MS calcd for $C_{15}H_{11}F_3O_2S$ m/z 312.0, found m/z 313.0 $(M + H)^+$.

(E)-1-tert-Butyl-4-[2-(phenylsulfonyl)vinyl]benzene (**3d**).[7c] White solid: mp 116−118 °C; yield 78% (70.3 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.93 (m, 2H), 7.68 (d, J = 15.6 Hz, 1H), 7.63−7.58 (m, 1H), 7.56−7.51 (t, J = 8.0 Hz, 2H), 7.45−7.39 (m, 4H), 6.83 (d, J = 15.2 Hz, 1H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.0, 142.5, 140.9, 133.3, 129.6, 129.3, 128.5, 127.6, 126.2, 126.1, 35.0, 31.1; MS calcd for $C_{18}H_{20}O_2S$ m/z 300.1, found m/z 301.1 $(M + H)^+$.

(E)-1-Fluoro-4-[2-(phenylsulfonyl)vinyl]benzene (**3e**).[9c] White solid: mp 108−110 °C; yield 88% (69.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.68−7.60 (m, 2H), 7.58−7.52 (m, 2H), 7.51−7.46 (m, 2H), 7.11−7.04 (m, 2H), 6.82 (dd, J = 15.2, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.3 (d, J = 251.5 Hz), 141.2, 140.6, 133.5, 130.6 (d, J = 8.7 Hz), 129.4, 128.6 (d, J = 3.4 Hz), 127.6, 127.0 (d, J = 2.3 Hz), 116.3 (d, J = 22.0 Hz); MS calcd for $C_{14}H_{11}FO_2S$ m/z 262.0, found m/z 285.0 $(M + Na)^+$.

(E)-1-Chloro-4-[2-(phenylsulfonyl)vinyl]benzene (**3f**).[9c] White solid: mp 128−130 °C; yield 84% (70.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.93 (m, 2H), 7.66−7.61 (m, 2H), 7.58−7.53 (m, 2H), 7.44−7.40 (m, 2H), 7.38−7.33 (m, 2H), 6.87 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 140.4, 137.2, 133.6, 130.8, 129.8, 129.4, 129.4, 127.9, 127.7; MS calcd for $C_{14}H_{11}ClO_2S$ m/z 278.0, found m/z 279.0 $(M + H)^+$.

(E)-1-Bromo-4-[2-(phenylsulfonyl)vinyl]benzene (**3g**).[9c] White solid: mp 152−154 °C; yield 80% (77.6 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.92 (m, 2H), 7.66−7.63 (m, 1H), 7.62−7.59 (m, 1H), 7.58−7.53 (m, 2H), 7.53−7.49 (m, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 15.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.1, 140.4, 133.6, 132.4, 131.3, 130.0, 129.4, 128.0, 127.7, 125.6; MS calcd for $C_{14}H_{11}BrO_2S$ m/z 322.0, found m/z 323.0 $(M + H)^+$.

(E)-1-Chloro-3-[2-(phenylsulfonyl)vinyl]benzene (**3h**).[7f] White solid: mp 98−100 °C; yield 91% (76.1 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84−7.78 (m, 2H), 7.72−7.65 (m, 3H), 7.51−7.46 (m, 2H), 7.44−7.36 (m, 3H), 6.84 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.6, 139.3, 132.2, 131.7, 131.0, 128.7, 128.7, 128.2, 126.3; MS calcd for $C_{14}H_{11}ClO_2S$ m/z 278.0, found m/z 279.0 $(M + H)^+$.

(E)-1-Chloro-2-[2-(phenylsulfonyl)vinyl]benzene (**3i**).[9c] White solid: mp 102−104 °C; yield 23% (19.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 15.2 Hz, 1H), 8.00−7.95 (m, 2H), 7.67−7.61 (m, 1H), 7.60−7.54 (m, 2H), 7.51 (dd, J = 7.6, 1.6 Hz, 1H), 7.43 (dd, J = 8.0, 1.2 Hz, 1H), 7.34 (td, J = 7.6, 1.6 Hz, 1H), 7.29−7.24 (m, 1H), 6.90 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.8, 137.9, 134.9, 133.1, 131.4, 130.2, 129.9, 129.6, 128.9, 127.8, 127.4, 126.7; MS calcd for $C_{14}H_{11}ClO_2S$ m/z 278.0, found m/z 279.0 $(M + H)^+$.

(E)-1-Methoxy-4-[2-(phenylsulfonyl)vinyl]benzene (**3j**).[9c] White solid: mp 108−110 °C; yield 38% (31.3 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.92 (m, 2H), 7.66−7.58 (m, 2H), 7.56−7.51 (m, 2H), 7.46−7.41 (m, 2H), 6.92−6.88 (m, 2H), 6.71 (d, J = 15.2 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 142.3, 141.1, 133.2, 130.4, 129.3, 127.5, 125.0, 124.4, 114.5, 55.5; MS calcd for $C_{15}H_{14}O_3S$ m/z 274.1, found m/z 275.1 $(M + H)^+$.

(E)-4-[2-(Phenylsulfonyl)vinyl]benzonitrile (**3k**).[7f] White solid: mp 113−115 °C; yield 87% (70.3 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.94 (m, 2H), 7.71−7.64 (m, 4H), 7.62−7.55 (m, 4H), 6.71 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.8, 136.6, 133.9, 132.8, 131.0, 129.6, 129.0, 127.9, 118.1, 114.3; MS calcd for $C_{15}H_{11}NO_2S$ m/z 269.0, found m/z 270.1 $(M + H)^+$.

(E)-2-[2-(Phenylsulfonyl)vinyl]naphthalene (**3m**).[9c] White solid: mp 102−104 °C; yield 90% (79.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02−7.97 (m, 2H), 7.90 (s, 1H), 7.87−7.78 (m, 4H), 7.61 (tt, J = 7.2, 2.8 Hz, 1H), 7.58−7.48 (m, 5H), 6.98 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.5, 140.7, 134.4, 133.4, 133.0, 130.9, 129.7, 129.3, 128.9, 128.7, 127.8, 127.6, 127.2, 127.0, 123.4; MS calcd for $C_{18}H_{14}O_2S$ m/z 294.1, found m/z 295.1 $(M + H)^+$.

(E)-1-{4-[2-(Phenylsulfonyl)vinyl]phenyl}ethanone (**3n**).[14] White solid: mp 148−150 °C; yield 85% (73.1 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.93 (m, 4H), 7.69 (d, J = 15.5 Hz, 1H), 7.65−7.60 (m, 1H), 7.59−7.53 (m, 4H), 6.96 (d, J = 15.5 Hz, 1H), 2.61−2.58 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.1, 140.8, 140.2, 138.7, 136.6, 133.7, 129.8, 129.5, 128.9, 128.7, 127.8, 26.7; MS calcd for $C_{16}H_{14}O_3S$ m/z 286.1, found m/z 287.1 $(M + H)^+$.

(E)-4-[2-(Phenylsulfonyl)vinyl]benzaldehyde (**3o**).[15] White solid: mp 162−164 °C; yield 82% (67.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.98−7.93 (m, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 15.5 Hz, 1H), 7.66−7.61 (m, 3H), 7.59−7.53 (m, 2H), 7.00 (d, J = 15.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.8, 140.1, 139.6, 137.4, 137.2, 133.3, 130.0, 129.7, 129.0, 128.6, 127.4; MS calcd for $C_{15}H_{12}O_3S$ m/z 272.1, found m/z 273.1 $(M + H)^+$.

(E)-1-Methyl-4-(styrylsulfonyl)benzene (**3p**).[7f] White solid: mp 118−120 °C; yield 87% (67.4 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 15.2 Hz, 1H), 7.49−7.44 (m, 2H), 7.41−7.36 (m, 3H), 7.33 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 15.6 Hz, 1H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 142.0, 137.7, 132.4, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6, 21.6; MS calcd for $C_{15}H_{14}O_2S$ m/z 258.1, found m/z 259.1 $(M + H)^+$.

(E)-1-Fluoro-4-(styrylsulfonyl)benzene (**3q**).[11b] White solid: mp 80−82 °C; yield 82% (64.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00−7.93 (m, 2H), 7.68 (d, J = 15.6 Hz, 1H), 7.52−7.46 (m, 2H), 7.43−7.37 (m, 3H), 7.25−7.18 (m, 2H), 6.86 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4 (d, J = 254.5 Hz), 142.5, 136.6 (d, J = 3.1 Hz), 132.0, 131.2, 130.4 (d, J = 9.6 Hz), 129.0, 128.5, 126.9, 116.5 (d, J = 22.5 Hz); MS calcd for $C_{14}H_{11}FO_2S$ m/z 262.0, found m/z 263.0 $(M + H)^+$.

(E)-1-Chloro-4-(styrylsulfonyl)benzene (**3r**).[7f] White solid: mp 86−88 °C; yield 84% (70.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.86 (m, 2H), 7.69 (d, J = 15.2 Hz, 1H), 7.53−7.46 (m, 4H), 7.44−7.36 (m, 3H), 6.85 (d, J = 15.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.6, 139.6, 138.8, 131.7, 130.9, 129.2, 128.7, 128.7, 128.2, 126.4; MS calcd for $C_{14}H_{11}ClO_2S$ m/z 278.0, found m/z 279.0 $(M + H)^+$.

(E)-1-Bromo-4-(styrylsulfonyl)benzene (**3s**).[7f] White solid: mp 98−100 °C; yield 83% (80.5 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83−7.78 (m, 2H), 7.72−7.66 (m, 3H), 7.50−7.46 (m, 2H), 7.44−7.36 (m, 3H), 6.65 (d, J = 15.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.1, 139.8, 132.7, 132.2, 131.5, 129.2, 129.2, 128.7, 126.8; MS calcd for $C_{14}H_{11}BrO_2S$ m/z 322.0, found m/z 223.0 $(M + H)^+$.

(E)-1-Nitro-4-(styrylsulfonyl)benzene (**3t**).[9c] White solid: mp 156−158 °C; yield 52% (45.1 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.41−8.37 (tt, J = 8.8, 2.4 Hz, 2H), 8.15 (tt, J = 9.2, 2.0 Hz, 2H), 7.77 (d, J = 15.2 Hz, 1H), 7.54−7.49 (m, 2H), 7.48−7.39 (m, 3H), 6.87 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.5, 146.6, 145.0, 131.9, 131.8, 129.3, 129.0, 128.9, 125.7, 124.6; MS calcd for $C_{14}H_{11}NO_4S$ m/z 289.0, found m/z 312.0 $(M + Na)^+$.

(E)-1-(Styrylsulfonyl)-4-(trifluoromethyl)benzene (**3u**).[7f] White solid: mp 125−127 °C; yield 64% (60.0 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 15.2 Hz, 1H), 7.52−7.48 (m, 2H), 7.46−7.38 (m, 3H), 6.85 (d, J = 15.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.2, 143.9, 134.8 (q, J = 33.0 Hz), 131.9, 131.5, 129.1, 128.6, 128.1, 126.4 (q, J = 3.7 Hz), 126.1, 123.0 (d, J = 271.4 Hz); MS calcd for $C_{15}H_{11}F_3O_2S$ m/z 312.0, found m/z 313.0 $(M + H)^+$.

(E)-2-(Styrylsulfonyl)naphthalene (**3v**).[11b] White solid: mp 138−140 °C; yield 80% (70.6 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 1.2 Hz, 1H), 8.02−7.97 (m, 2H), 7.94−7.87 (m, 2H), 7.75 (d, J = 15.2 Hz, 1H), 7.70−7.60 (m, 2H), 7.52−7.47 (m, 2H), 7.43−7.36 (m, 3H), 6.93 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.4, 137.3, 135.0, 132.2, 132.1, 131.1, 129.5, 129.2, 129.1, 129.1, 128.9, 128.4, 127.8, 127.5, 127.1, 122.4; MS calcd for $C_{18}H_{14}O_2S$ m/z 294.1, found m/z 295.1 $(M + H)^+$.

(E)-[2-(Methylsulfonyl)vinyl]benzene (**3w**).[9c] White solid: mp 75−77 °C; yield 82% (44.8 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 15.6 Hz, 1H), 7.54−7.50 (m, 2H), 7.46−7.39 (m, 3H), 6.94 (d, J = 15.6 Hz, 1H), 3.04 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ

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J. Org. Chem. 2015, 80, 7652−7657

143.5, 131.6, 130.9, 128.7, 128.1, 125.7, 42.8; MS calcd for $C_9H_{10}O_2S$ m/z 182.0, found m/z 183.0 $(M + H)^+$.

*(E)-[2-(Ethylsulfonyl)vinyl]benzene (**3x**).*[9c] White solid: mp 66−68 °C; yield 85% (50.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 15.2 Hz, 1H), 7.55−7.51 (m, 2H), 7.47−7.41 (m, 3H), 6.82 (d, J = 15.2 Hz, 1H), 3.09 (q, J = 7.6 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.7, 131.8, 130.9, 128.7, 128.1, 123.5, 49.0, 6.8; MS calcd for $C_{10}H_{12}O_2S$ m/z 196.1, found m/z 219.0 $(M + Na)^+$.

*1-Phenyl-2-(phenylsulfonyl)ethanone (**4**).*[13d] White solid: mp 90−92 °C; yield 25% (19.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.87 (m, 4H), 7.69−7.59 (m, 2H), 7.58−7.52 (t, J = 8.0 Hz, 2H), 7.51−7.45 (t, J = 7.6 Hz, 2H), 4.74 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.5, 138.2, 135.2, 133.9, 133.8, 128.8, 128.7, 128.4, 128.1, 63.0; MS calcd for $C_{14}H_{12}O_3S$ m/z 260.1, found m/z 261.1 $(M + H)^+$.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01212.

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Notes

The authors declare no competing financial interest.

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