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Controllable Activation of β-Alkyl Nitroalkenes: Regioselective Synthesis of Allyl and Vinyl Sulfones

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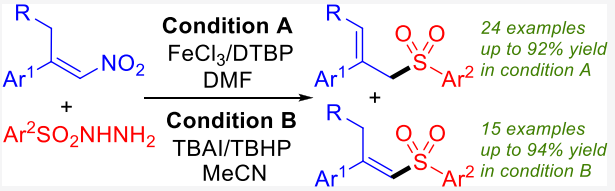
ABSTRACT: The regiospecific radical reactions of β-alkyl nitroalkenes with sulfonyl hydrazides depended to a great extent on the choice of a solvent and catalyst. In the presence of dimethylformamide (DMF), β-alkyl nitroalkenes more likely converted into electron-rich allyl nitro compounds, which reacted with sulfonyl hydrazides to afford allyl sulfones with high regioselectivity. While in acetonitrile (CH_3CN), vinyl sulfones were obtained directly *via* sulfonation of electron-deficient β-alkyl nitroalkenes. The mechanism investigation revealed that the regioselectivity was controlled by the equilibrium of β-alkyl nitroalkenes and allyl nitro compounds.

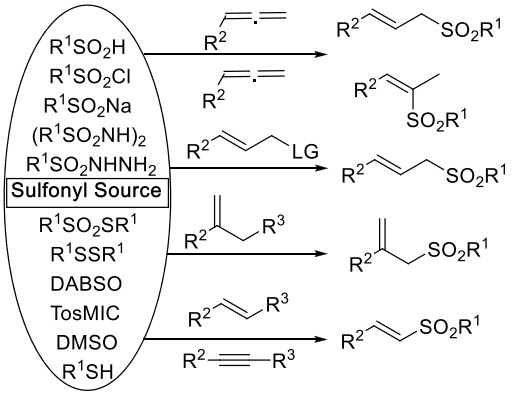


INTRODUCTION

The main challenge in free-radical reactions is the methods for activating specific reaction sites for organic substrates or control different reactive sites in a molecule.[1] The strategies for high selectivity are mainly reflected in the selection of a catalyst,[2] oxidant,[3] ligand,[4] solvent,[5] or acid/base.[6] Regioselective synthesis of different isomeric products from the same reactants is of great significance for method development. Allyl and vinyl sulfones are regioisomers; they are both important structural motifs, which widely exist in bioactive compounds.[7] Furthermore, they play important roles in the field of synthetic organic chemistry due to the general molecular framework of various organic transformations.[8] Thus, increasing attentions have been devoted to the preparation of allyl sulfones and vinyl sulfones (Scheme 1).[9] The directly method of preparing allyl sulfones is to oxidize the corresponding sulfides with stoichiometric strong oxidants.[10] Another approach is Pd or Ir-catalyzed allyl substitution (Tsuji−Trost reaction).[11] In general, these reactions require precise condition control, prefunctionalization of allyl compounds or expensive catalysts.[12] For the synthesis of vinyl sulfones, some methods have also been established, such as sulfide oxidation,[13] β-elimination seleno(halogenated) sulfones,[14] and direct cross coupling of sulfonyl derivatives with olefins[15] or alkynes.[16] In spite of these achievements, achieving regiospecific control in the synthesis of allyl sulfones and vinyl sulfones is challenging and rewarding.

Previously, we have developed a metal-free direct allyl sulfonation of β-alkyl nitroalkenes with sodium sulfites as a sulfonyl precursor, it was found that sodium sulfites or DMF/DMSO solvents could be served as a Lewis base[17] to promote the isomerization of β-alkyl nitroalkenes to allyl nitro compounds, and the sulfonyl radical tended to react with the electron-rich allyl nitro equilibrium isomers; in this case, vinyl sulfones could not be formed (Scheme 2A).[18] In continuation of the development of new reactivities of β-alkyl nitroalkenes, herein, we disclose an oxidative radical reaction of β-alkyl nitroalkenes and sulfonyl hydrazides. By tuning the sulfonyl radical source and choice of different solvents and catalysts, the reactions could form allyl sulfones and vinyl sulfones *via* a new equilibrium-control strategy of β-alkyl nitroalkenes and allyl nitro compounds (Scheme 2B).

Scheme 1. Synthesis of Allyl and Vinyl Sulfones



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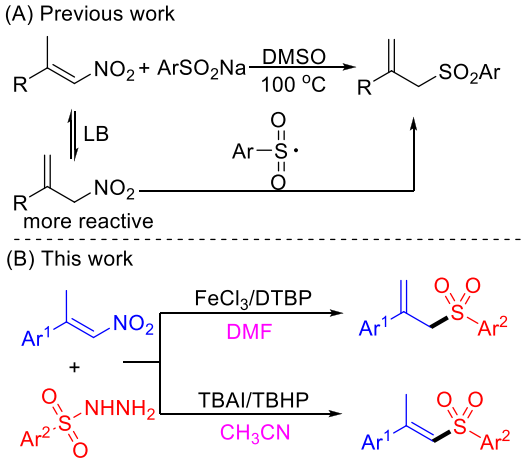
Scheme 2. Activation of β-Alkyl Nitroalkenes

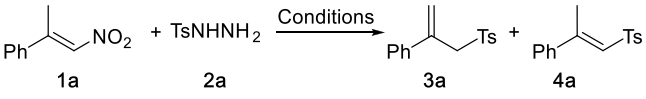


RESULTS AND DISCUSSION

We initiated our research on the model reaction of (*E*)-(1-nitroprop-1-en-2-yl)benzene (**1a**) with 4-methylbenzenesulfonohydrazide (**2a**) under different reaction conditions (Table 1). When the reaction ran in DMSO at 100 °C, the allyl sulfone **3a** was obtained as only product in 45% yield (entry 1). If the reaction performed using an I_2/TBHP catalytic system, **3a** was obtained in 61% yield; however, the vinyl sulfone **4a** was also formed (entry 2). In addition, the TBAI/TBHP reaction system gave a similar result (entry 3). Then, other catalysts were tested (for detailed results see the Supporting Information). It was found that $FeCl_3$ was the most effective catalyst to obtain **3a** (entries 4−6). Gratefully, a higher yield was obtained when DMF was used as a solvent (entry 7). Different types of oxidants including DTBP, H_2O_2, and $K_2S_2O_8$ were also screened (entries 8−10), and it turned out that DTBP exhibited the best result, the yield of **3a** was up to 92%, and **4a** was totally inhibited (entry 8). Moreover, reducing the temperature is unfavorable to the reaction (entry 11).

Exceptionally, under the I_2/TBHP system, when DMF was replaced by CH_3CN, **4a** was obtained as the major product (entry 12). Then, other conditions were also tested, the results showed that, no matter what catalytic system was chosen ($FeCl_3$/DTBP, $FeCl_3$/TBHP, TBAI/TBHP, entries 13−15), **4a** was the major product as long as CH_3CN served as the solvent (for more solvent studies see the Supporting Information); under the TBAI/TBHP system, the formation of **3a** was inhibited totally, and **4a** was obtained with 94% yield. Replacing different oxidants, such as $K_2S_2O_8$ and H_2O_2, resulted in a slight decrease in the yield of **4a** (entries 16−17). It was noteworthy that the addition of DMF or other base was in favor of the formation of **3a** and reduced the yield of **4a** (entries 18−20), which implied that DMF or other bases were probably served as a Lewis base to promote the formation of allyl sulfones.[17,18]

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a 4a

entry	catalyst	oxidant	additive	solvent	3a/4a/conv. (%)[b]
1				DMSO[c]	45/0/100
2	I_2	TBHP[e]		DMSO[c]	61/5/100
3	TBAI[f]	TBHP		DMSO[c]	65/7/100
4	$FeCl_2$	TBHP		DMSO[c]	54/6/100
5	$Fe(NO_3)_3$	TBHP		DMSO[c]	63/12/100
6	$FeCl_3$	TBHP		DMSO[c]	68/9/100
7	$FeCl_3$	TBHP		DMF[c]	87/3/100
8	$FeCl_3$	DTBP[g]		DMF[c]	92/0/100
9	$FeCl_3$	$K_2S_2O_8$		DMF[c]	61/5/100
10	$FeCl_3$	H_2O_2		DMF[c]	19/9/100
11	$FeCl_3$	DTBP		DMF[d]	47/0/80
12	I_2	TBHP		CH_3CN[d]	9/72/100
13	$FeCl_3$	TBHP		CH_3CN[d]	13/80/100
14	$FeCl_3$	DTBP		CH_3CN[c]	12/75/100
15	TBAI	TBHP		CH_3CN[d]	0/94/100
16	TBAI	$K_2S_2O_8$		CH_3CN[d]	8/81/100
17	TBAI	H_2O_2		CH_3CN[d]	10/78/100
18	TBAI	TBHP	DMF	CH_3CN[d]	54/27/100
19	TBAI	TBHP	NaOAc	CH_3CN[d]	62/30/100
20	TBAI	TBHP	Et_3N	CH_3CN[d]	0/84/100

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), catalyst (0.1 mmol), oxidant (1 mmol), additive (2 mmol), open air. [b]Isolated yield. [c]Reacted in 100 °C (oil bath), 2 h. [d]Reacted in 80 °C (oil bath), 2 h. [e]TBHP: 2-hydroperoxy-2-methylpropane. [f]TBAI: tetrabutylammonium iodide. [g]DTBP: 2-(*tert*-butylperoxy)-2-methylpropane.

With the optimal condition in hand, we start to investigate the scope of the reactions. For the synthesis of allyl sulfones, the results are summarized in Table 2. The reactions of β-alkyl nitroalkenes containing electron-donating or electron-withdrawing groups with sulfonyl hydrazides proceeded efficiently and provided the corresponding products in moderate-to-good yields. Meanwhile, it was found that yields of sulfonyl hydrazides with electron-donating groups (R = CH_3, OMe) were higher than that with electron-withdrawing groups (R = F, Cl, Br, NO_2), but reactions of *p*-nitrobenzenesulfonyl hydrazides with β-alkyl nitroalkenes resulted in lower yields.

The scope of vinyl sulfones was also investigated (Table 3). Different β-alkyl nitroalkenes and sulfonyl hydrazides were also suitable substrates, which all afforded *E*-products with good-to-excellent yields, and β-ethyl nitroalkene also provided good yields (**4m** and **4o**). The same substituent effect was also observed, it showed that the sulfonyl hydrazides with electron-donating groups gave higher yields, and the substituent effects were not obvious for β-alkyl nitroalkenes.

To gain insights into the reaction mechanism, **1a** and **2a** reacted in the presence of 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 3 equiv). However, **3a** or **4a** was not detected, which implied that the reaction could involve a radical process. During the formation of **3a** (under condition A), we detected the isomeric **1a′** intermediate; further investigation showed that **3a** was obtained with 94% isolated yield in only 1.5 h under condition A for the reaction of **1a′** and **2a**, which revealed that allyl sulfones could be formed from isomeric allyl nitro compounds (Scheme 3A).

To explore the isomerization of β-alkyl nitroalkenes, following experiments were carried out (Scheme 3B). The results showed that **1a** did not convert to **1a′** at DMF in 30 °C or at CH_3CN in 80 °C with **2a**. However, **1a** gradually converted to **1a′** at DMF in 100 °C and remained an equilibrium at 50% conversion, which demonstrated that DMF could be served as a Lewis base[17] to effectively promote the isomerization of **1a** at 100 °C; a proposed mechanism is

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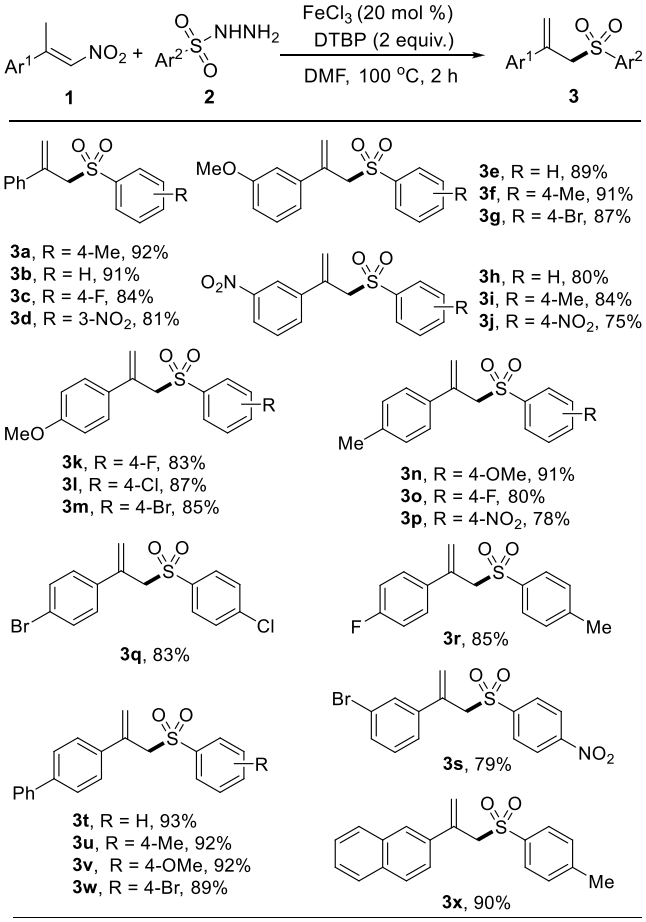
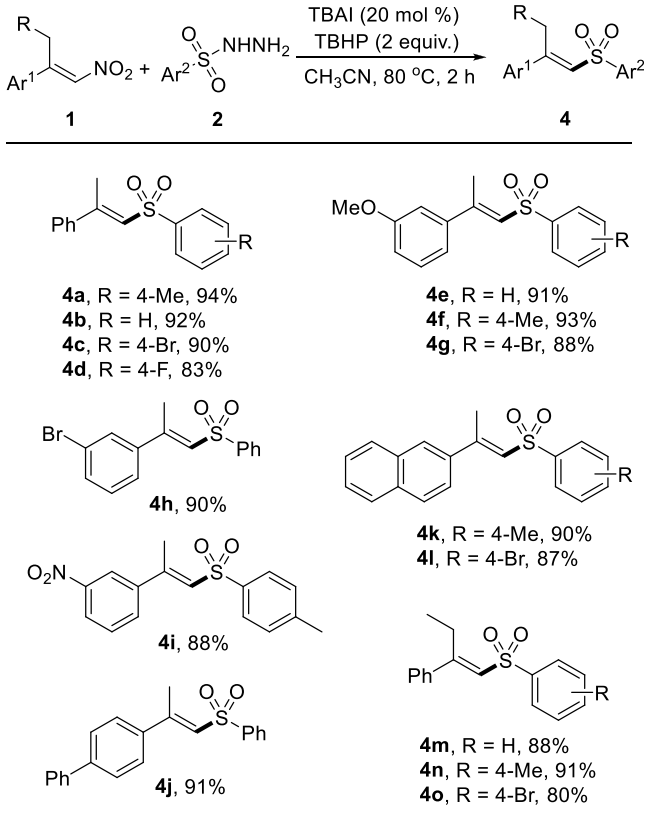
J. Org. Chem. 2021, 86, 4018−4026

Table 2. Scope of Allyl Sulfones[a]



[a]General conditions: *β*-alkyl nitroalkenes (0.5 mmol), sulfonyl hydrazides (1 mmol), $FeCl_3$ (0.1 mmol), and DTBP (1 mmol) in 3 mL of DMF, in 100 °C (oil bath) for 2 h; isolated yield based on *β*-alkyl nitroalkenes.

Table 3. Scope of Vinyl Sulfones[a]



[a]General conditions: *β*-alkyl nitroalkenes (0.5 mmol), sulfonyl hydrazides (1 mmol), TBAI (0.1 mmol), and TBHP (1 mmol) in 3 mL of CH_3CN, in 80 °C (oil bath) for 2 h; isolated yield based on *β*-alkyl nitroalkenes.

outlined in Scheme 3C. Meanwhile, **1a′** could not be obtained from **1a** under the condition of $FeCl_3$/DTBP and CH_3CN as solvents at 80 °C. It is noteworthy that **1a** could be converted to **1a′** in a small amount under the TBAI/TBHP condition with CH_3CN as the solvent in 80 °C.

To disclose the reaction process of **1a** and **2a** under the condition A or B, the content of each component was monitored (Scheme 3D). Under the condition A, **1a** was consumed rapidly; with the formation of **3a**, **1a′** was formed instantly. Overall, the **1a** and **1a′** should be all converted to product **3a**. Under the condition B, the conversion of **1a** to **1a′** is not likely to be the dominant one, so **2a** reacted with **1a** directly to obtain **4a**. Notably, the precursor *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate **2a′** of the sulfonylhydrazine radical could be obtained under $FeCl_3$/DTBP to participate in the reaction. Under condition B, the reaction of **1a′** and **2a′** still gave **3a**, which revealed the reaction selectivity was not controlled by the sulfonyl radical source (Scheme 3E).

In addition, the conversion between **3a** and **4a** was systematically attempted (Scheme 4). It found that **4a** did not converted to **3a** under the condition A, and **3a** could yield **4a** in only 12% yield under the condition B, which demonstrated that **4a** is not likely formed from the isomerization of **3a**.

Based on these results, a possible mechanism is proposed in Scheme 5. In the TBAI/TBHP or $FeCl_3$/DTBP reaction system, sulfonyl hydrazine converted to a sulfonyl radical. Under the condition A, **1a** was isomerized to an allyl nitro compound (**1a′**), which reacted with sulfonyl radical easily to afford allyl sulfone (**3a**). Under the condition B, the sulfonyl radical preferentially reacted with **1a** directly to obtain alkenyl sulfone (**4a**). The key for the selectivity is not the formation of the sulfonyl radical but the equilibrium of *β*-alkyl nitroalkene and allyl nitro compound.

CONCLUSIONS

In conclusion, we have developed an oxidative radical reaction of *β*-alkyl nitroalkenes and sulfonyl hydrazides. The reaction proceeded under mild conditions and showed a wide substrate scope. By tuning the solvent and catalytic system, the vinyl and allyl sulfones could be selective obtained in good-to-excellent yields. This work sheds some lights on the study of the diverse reactivity of *β*-alkyl nitroalkenes.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all chemicals used in the experiments were obtained from commercial sources and used directly without further treatment. TLC was performed with the detection of compounds with UV light. Flash column chromatography purification of the products was accomplished on silica gel (200−300 mesh). Petroleum ether (PE) (60−90 °C) and ethyl acetate (EA) were used as eluents for silica gel chromatography. Melting points for

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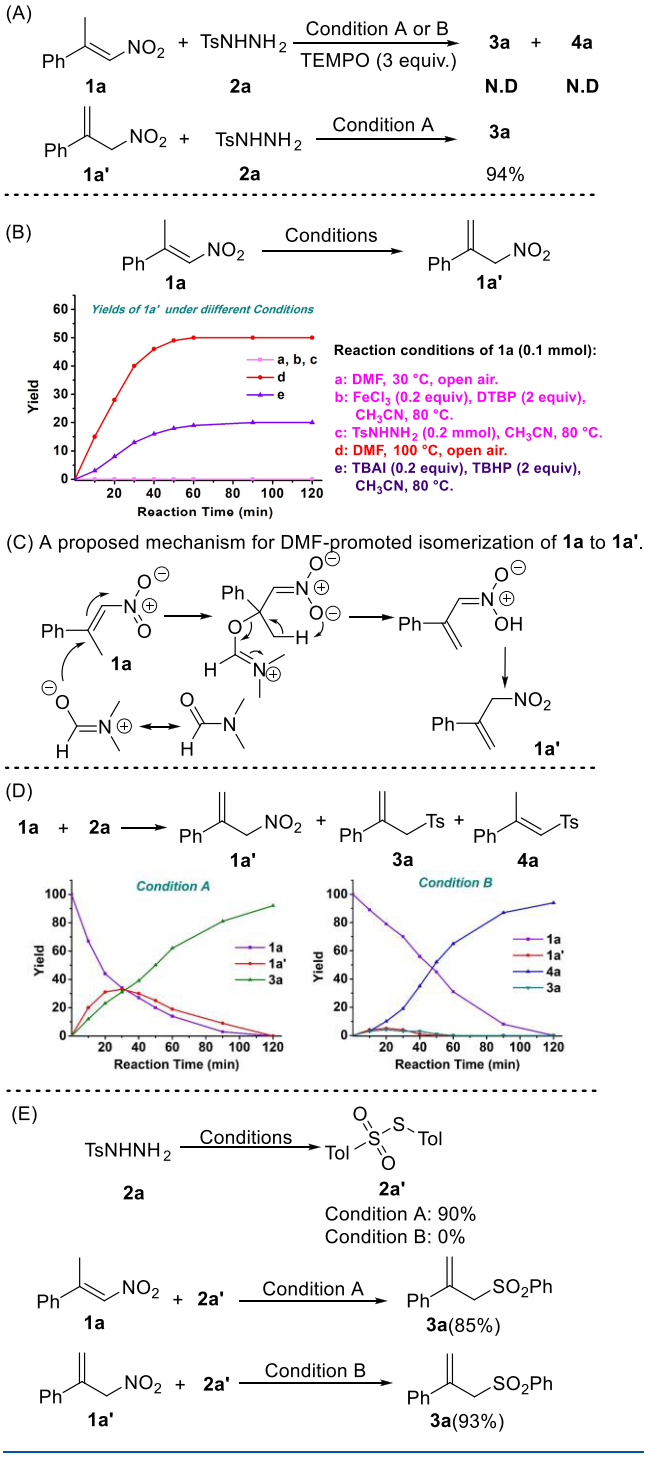
J. Org. Chem. 2021, 86, 4018−4026

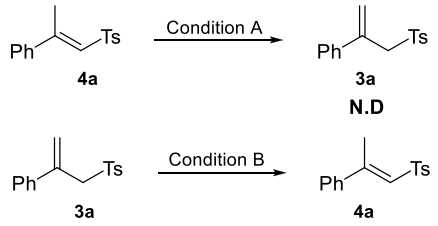
Scheme 3. Control Experiments



all solid products were measured on an X − 4A melting point apparatus without correction. ^{1}H and ^{13}C NMR spectra were recorded at 22 °C on Bruker AV 400 MHz spectrometers with tetramethylsilane (TMS) as an internal standard. ^{1}H and ^{13}C chemical shifts in NMR spectra were referenced relative to signals of $CDCl_3$ (δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). High-resolution mass spectra (HRMS) were acquired on Waters Acquity UPLC Class I/Xevo G2Q−TOF.

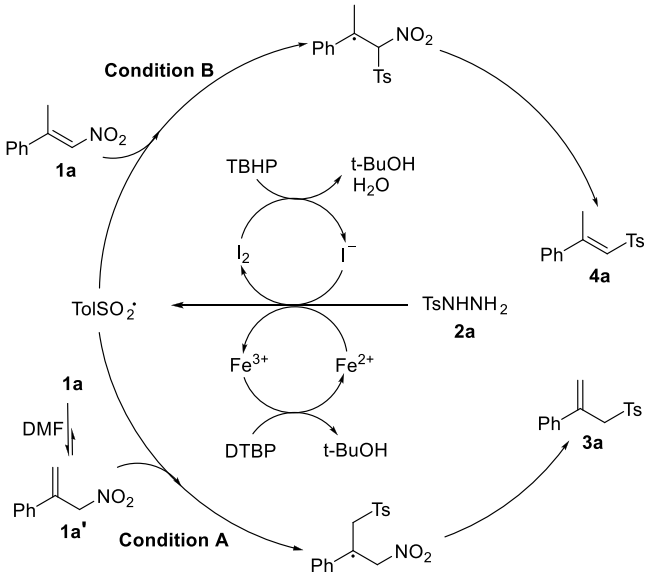
General Procedure for the Synthesis of Allyl Sulfones. A mixture of (*E*)-(1-nitroprop-1-en-2-yl)benzene (**1a**) (0.5 mmol), 4-methylbenzenesulfonohydrazide (**2a**) (1 mmol), $FeCl_3$ (0.1 mmol), and DTBP (1 mmol) in 3 mL of DMF was stirred under an air atmosphere in a 10 mL tube at 100 °C (oil bath). After the reaction finished (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel by eluting with petroleum ether/ethyl acetate to provide the product.

Scheme 4. Interconversion of 3a and 4a



1.5 h, **3a**/**4a**/conv.(67/7/33).
2.0 h, **3a**/**4a**/conv.(58/12/42).
5.0 h, **3a**/**4a**/conv.(58/12/42).

Scheme 5. Plausible Mechanism



finished (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel by eluting with petroleum ether/ethyl acetate to provide the product.

General Procedures for the Synthesis of 3a in the Gram Scale. A mixture of (*E*)-(1-nitroprop-1-en-2-yl)benzene (**1a**) (5 mmol), 4-methylbenzenesulfonohydrazide (**2a**) (10 mmol), $FeCl_3$ (1 mmol), and DTBP (10 mmol) in 12 mL of DMF was stirred under an air atmosphere in a 25 mL tube at 100 °C (oil bath). After the reaction finished (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel by eluting with petroleum ether/ethyl acetate to provide the product **3a** (1.12 g, 82%).

General Procedure for the Synthesis of Vinyl Sulfones. A mixture of (*E*)-(1-nitroprop-1-en-2-yl)benzene (**1a**) (0.5 mmol), 4-methylbenzenesulfonohydrazide (**2a**) (1 mmol), TBAI (0.1 mmol), and TBHP (1 mmol) in 3 mL of CH_3CN was stirred under an air atmosphere in a 10 mL tube at 80 °C (oil bath). After the reaction finished (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel by eluting with petroleum ether/ethyl acetate to provide the product.

General Procedures for the Synthesis of 4a in the Gram Scale. A mixture of (*E*)-(1-nitroprop-1-en-2-yl)benzene (**1a**) (5 mmol), 4-methylbenzenesulfonohydrazide (**2a**) (10 mmol), TBAI (1

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J. Org. Chem. 2021, 86, 4018−4026

mmol), and TBHP (10 mmol) in 12 mL of CH_3CN was stirred under an air atmosphere in a 25 mL tube at 80 °C (oil bath). After the reaction finished (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel by eluting with petroleum ether/ethyl acetate to provide the product **4a** (1.13 g, 83%).

Characterization Data. *S-(p-Tolyl) 4-Methylbenzenesulfonothioate (**2a'**).*[19] White solid (125.1 mg, 90%); mp 76−78 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.21); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 8.3 Hz, 2H), 7.25−7.19 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 144.6, 142.0, 140.3, 136.4, 130.1, 129.3, 127.5, 124.5, 21.6, 21.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_2S_2Na$ 301.0327; found 301.0315.

*1-Methyl-4-((2-phenylallyl)sulfonyl)benzene (**3a**).*[9c] White solid (125.1 mg, 92%); mp 97−98 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.64 (d, J = 5.32 Hz, 2H), 7.28−7.17 (m, 7H), 5.56 (s, 1H), 5.19 (s, 1H), 4.23 (s, 2H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 144.5, 138.7, 136.4, 135.3, 129.4, 128.5, 128.2, 127.8, 126.1, 121.6, 62.0, 21.4.

*((2-Phenylallyl)sulfonyl)benzene (**3b**).*[9c] White solid (117.4 mg, 91%); mp 45−47 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.11); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.77 (d, J = 5.20 Hz, 2H), 7.52 (t, J = 4.92 Hz, 1H), 7.40 (t, J = 5.12 Hz, 2H), 7.27−7.20 (m, 5H), 5.57 (s, 1H), 5.20 (s, 1H), 4.26 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 138.6, 138.3, 136.3, 133.5, 128.8, 128.5, 128.3, 127.9, 126.1, 121.7, 61.9.

*1-Fluoro-4-((2-phenylallyl)sulfonyl)benzene (**3c**).*[18] White solid (115.9 mg, 84%); mp 84−86 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.12); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76 (dd, J = 5.68, 3.44 Hz, 2H), 7.23 (m, 5H), 7.07 (t, J = 5.64 Hz, 2H), 5.60 (s, 1H), 5.24 (s, 1H), 4.28 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 165.7 (d, J = 256.3 Hz), 138.5, 136.5, 134.3 (d, J = 2.9 Hz), 131.5 (d, J = 9.6 Hz), 128.4, 128.1, 126.1, 122.0, 116.1 (d, J = 22.7 Hz), 62.2.

*1-Nitro-3-((2-phenylallyl)sulfonyl)benzene (**3d**).* White solid (122.7 mg, 81%); mp 110−111 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.14); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.48 (s, 1H), 8.31 (d, J = 8.16 Hz, 1H), 8.05 (d, J = 7.72 Hz, 1H), 7.59 (t, J = 7.96 Hz, 1H), 7.16 (s, 5H), 5.63 (s, 1H), 5.35 (s, 1H), 4.37 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) 147.8, 140.3, 137.9, 136.0, 134.0, 128.5, 128.3, 128.0, 126.1, 124.2, 122.8, 62.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{13}NO_4SNa$ 326.0457; found 326.0443.

*1-Methoxy-3-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (**3e**).* White solid (128.2 mg, 89%); mp 78−80 °C; purification by silica gel chromatography (eluent: PE/EA = 12:1, R_f = 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81−7.73 (m, 2H), 7.50 (t, J = 7.32 Hz, 1H), 7.40 (t, J = 7.96 Hz, 2H), 7.12 (t, J = 7.96 Hz, 1H), 6.83 (dt, J = 7.76, 0.68 Hz, 1H), 6.80−6.69 (m, 2H), 5.57 (s, 1H), 5.20 (s, 1H), 4.25 (s, 2H), 3.72 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.2, 140.0, 138.1, 136.1, 133.5, 129.2, 128.7, 128.4, 121.8, 118.5, 113.2, 111.9, 61.8, 55.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{16}O_3SNa$ 311.0712; found 311.0698.

*1-Methoxy-3-(3-tosylprop-1-en-2-yl)benzene (**3f**).*[9g] White solid (137.5 mg, 91%); mp 89−90 °C; purification by silica gel chromatography (eluent: PE/EA = 12:1, R_f = 0.11); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, J = 8.24 Hz, 2H), 7.24−7.10 (m, 3H), 6.89−6.80 (m, 1H), 6.80−6.70 (m, 2H), 5.57 (s, 1H), 5.21 (s, 1H), 4.23 (s, 2H), 3.75 (s, 3H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.3, 144.5, 140.2, 136.4, 135.2, 129.4, 129.2, 128.5, 121.8, 118.6, 113.2, 112.0, 62.1, 55.1, 21.4.

*1-(3-((4-Bromophenyl)sulfonyl)prop-1-en-2-yl)-3-methoxybenzene (**3g**).* White solid (159.2 mg, 87%); mp 138−140 °C; purification by silica gel chromatography (eluent: PE/EA = 12:1, R_f = 0.12); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59 (d, J = 8.56 Hz, 2H), 7.52 (d, J = 8.60 Hz, 2H), 7.15 (t, J = 7.96 Hz, 1H), 6.78 (dd, J = 7.88, 2.08 Hz, 2H), 6.68 (m, 1H), 5.60 (s, 1H), 5.26 (s, 1H), 4.25 (s, 2H), 3.76 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.5, 139.9, 137.3, 136.3, 132.1, 130.2, 129.5, 129.1, 122.4, 118.7, 113.1, 112.5, 62.3, 55.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}BrO_3SNa$ 388.9817; found 388.9806.

*1-Nitro-3-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (**3h**).* White solid (121.2 mg, 80%); mp 105−106 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.13−8.02 (m, 2H), 7.79 (d, J = 7.60 Hz, 2H), 7.68 (d, J = 7.64 Hz, 1H), 7.57 (t, J = 7.40 Hz, 1H), 7.46 (t, J = 7.60 Hz, 3H), 5.72 (s, 1H), 5.38 (s, 1H), 4.29 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 148.1, 140.4, 138.0, 134.6, 133.9, 132.2, 129.5, 129.1, 128.5, 124.5, 122.8, 121.1, 61.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}NO_4SH$ 304.0638; found 304.0638.

*1-Nitro-3-(3-tosylprop-1-en-2-yl)benzene (**3i**).* White solid (133.2 mg, 84%); mp 143−145 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.11); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09−7.94 (m, 2H), 7.66 (dd, J = 0.72, 6.68 Hz, 3H), 7.44 (t, J = 8.04 Hz, 1H), 7.21 (d, J = 7.96 Hz, 2H), 5.69 (s, 1H), 5.35 (s, 1H), 4.27 (s, 2H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 148.0, 145.0, 140.4, 134.9, 134.7, 132.3, 129.6, 129.4, 128.4, 124.3, 122.5, 121.0, 61.7, 21.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NO_4SNa$ 340.0614; found 340.0601.

*1-Nitro-3-(3-((4-nitrophenyl)sulfonyl)prop-1-en-2-yl)benzene (**3j**).* White solid (130.5 mg, 75%); mp 115−117 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.12); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.35 (d, J = 7.84 Hz, 2H), 8.15 (d, J = 8.92 Hz, 2H), 8.04 (d, J = 7.68 Hz, 2H), 7.72 (d, J = 7.96 Hz, 1H), 7.52 (t, J = 7.96 Hz, 1H), 5.79 (s, 1H), 5.38 (s, 1H), 4.36 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 150.9, 143.6, 139.9, 134.0, 132.2, 130.1, 129.8, 125.2, 124.3, 123.2, 121.1, 61.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{12}N_2O_6SNa$ 371.0308; found 371.0295.

*1-Fluoro-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3k**).*[18] White solid (127.0 mg, 83%); mp 131−132 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.11); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81−7.72 (m, 2H), 7.18 (dt, J = 2.08, 4.64 Hz, 2H), 7.13−7.04 (m, 2H), 6.77 (dt, J = 2.12, 4.64 Hz, 2H), 5.61 (s, 1H), 5.32 (s, 1H), 4.22 (s, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 165.7 (d, J = 256.2 Hz), 159.6, 135.9, 134.5, 131.5 (d, J = 9.6 Hz), 130.9, 127.4, 120.1, 116.0 (d, J = 22.7 Hz), 113.8, 62.4, 55.3.

*1-Chloro-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3l**).*[18] White solid (140.1 mg, 87%); mp 120−121 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.14); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, J = 8.56 Hz, 2H), 7.37 (d, J = 8.52 Hz, 2H), 7.16 (dt, J = 1.92, 4.84 Hz, 2H), 6.76 (dt, J = 1.92, 4.88 Hz, 2H), 5.50 (s, 1H), 5.11 (s, 1H), 4.24 (s, 2H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.6, 140.2, 136.9, 135.8, 130.8, 130.1, 129.0, 127.4, 120.2, 113.8, 62.4, 55.3.

*1-Bromo-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3m**).*[18] Yellow oil (155.6 mg, 85%); purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.11); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.71 (d, J = 8.88 Hz, 2H), 7.30−7.26 (m, 2H), 7.00−6.89 (m, 4H), 5.55 (s, 1H), 5.20 (s, 1H), 4.24 (s, 2H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 163.8, 137.7, 135.9, 131.5, 130.8, 129.7, 127.9, 122.2, 122.1, 114.1, 62.3, 55.7.

*1-Methoxy-4-((2-(p-tolyl)allyl)sulfonyl)benzene (**3n**).* White solid (137.5 mg, 91%); mp 93−94 °C; purification by silica gel chromatography (eluent: PE/EA = 12:1, R_f = 0.10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm), δ 7.68 (d, J = 8.72 Hz, 2H), 7.17 (d, J = 8.00 Hz, 2H), 7.05 (d, J = 7.88 Hz, 2H), 6.87 (d, J = 8.72 Hz, 2H), 5.54 (s, 1H), 5.12 (s, 1H), 4.23 (s, 2H), 3.83 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 163.5, 137.7, 136.5, 135.8, 130.7, 129.8, 129.0, 126.0, 120.7, 113.9, 62.2, 55.5, 21.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}O_3SNa$ 325.0869; found 325.0855.

*1-Fluoro-4-((2-(p-tolyl)allyl)sulfonyl)benzene (**3o**).*[18] White solid (116.1 mg, 80%); mp 83−84 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80−7.73 (m, 2H), 7.15−7.01 (m, 6H), 5.56

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J. Org. Chem. 2021, 86, 4018−4026

(s, 1H), 5.16 (s, 1H), 4.26 (s, 2H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 165.72 (d, J = 256.2 Hz), 138.1, 136.3, 135.6, 134.4 (d, J = 3.2 Hz), 131.52 (d, J = 9.6 Hz), 129.1, 126.0, 121.0, 116.0 (d, J = 22.7 Hz), 62.3, 21.0.

1-Methyl-4-(3-((4-nitrophenyl)sulfonyl)prop-1-en-2-yl)benzene ***(3p)***. White solid (123.7 mg, 78%); mp 113−114 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.12); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (dt, J = 1.96, 8.88 Hz, 2H), 7.90 (dt, J = 2.24, 8.92 Hz, 2H), 7.13−6.94 (m, 4H), 5.58 (s, 1H), 5.22 (s, 1H), 4.33 (s, 2H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 150.5, 143.8, 138.5, 135.8, 135.0, 130.2, 129.2, 126.0, 123.8, 121.8, 62.3, 21.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NO_4SNa$ 340.0614; found 340.0601.

1-Bromo-4-(3-((4-chlorophenyl)sulfonyl)prop-1-en-2-yl)benzene ***(3q)***.[18] Yellow oil (153.5 mg, 83%); purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.15); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, J = 5.72 Hz, 2H), 7.41 (dd, J = 5.76, 6.96 Hz, 4H), 7.14 (d, J = 5.68 Hz, 2H), 5.60 (s, 1H), 5.22 (s, 1H), 4.23 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.7, 137.4, 136.6, 135.4, 131.6, 130.1, 129.3, 127.8, 122.6, 122.4, 62.1.

1-Fluoro-4-(3-tosylprop-1-en-2-yl)benzene (3r).[9g] White solid (123.3 mg, 85%); mp 108−110 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.11); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, J = 8.24 Hz, 2H), 7.31−7.24 (m, 4H), 6.93 (t, J = 6.56 Hz, 2H), 5.53 (s, 1H), 5.17 (s, 1H), 4.21 (s, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 162.5 (d, J = 247.8 Hz), 144.8, 135.7, 135.4, 135.0 (d, J = 3.3 Hz), 129.6, 128.6, 128.1 (d, J = 8.2 Hz), 121.7, 115.2 (d, J = 21.6 Hz), 62.3, 21.5.

1-Bromo-3-(3-((4-nitrophenyl)sulfonyl)prop-1-en-2-yl)benzene ***(3s)***. Yellow oil (150.5 mg, 79%); purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.14); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.25 (dt, J = 2.20, 8.84 Hz, 2H), 7.92 (dt, J = 2.24, 8.84 Hz, 2H), 7.34 (dt, J = 1.20, 7.84 Hz, 1H), 7.21−7.14 (m, 2H), 7.15−7.07 (m, 1H), 5.64 (s, 1H), 5.36 (s, 1H), 4.31 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 150.7, 143.7, 140.1, 134.8, 131.3, 130.1, 130.1, 129.3, 124.9, 124.0, 123.9, 122.7, 62.1. HRMS (ESI-TOF) m/z: $[M + K]^+$ calcd for $C_{15}H_{12}BrNO_4SK$ 419.9302; found 419.9285.

4-(3-(Phenylsulfonyl)prop-1-en-2-yl)-1,1′-biphenyl ***(3t)***. Yellow solid (155.4 mg, 93%); mp 106−108 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.12); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87−7.76 (m, 2H), 7.59−7.52 (m, 3H), 7.50−7.41 (m, 6H), 7.50−7.41 (m, 3H), 5.66 (s, 1H), 5.24 (s, 1H), 4.32 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 140.8, 140.3, 138.3, 137.5, 136.0, 133.6, 128.9, 128.8, 128.6, 127.5, 127.0, 126.9, 126.6, 121.7, 62.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{18}O_2SNa$ 357.0920; found 357.0904.

4-(3-Tosylprop-1-en-2-yl)-1,1′-biphenyl ***(3u)***.[9c] White solid (160.2 mg, 92%); mp 112−114 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.15); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, J = 8.24 Hz, 2H), 7.62−7.53 (m, 2H), 7.52−7.41 (m, 4H), 7.40−7.32 (m, 3H), 7.22 (d, J = 7.96 Hz, 2H), 5.66 (s, 1H), 5.23 (s, 1H), 4.30 (s, 2H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 144.6, 140.7, 140.3, 137.5, 136.0, 135.3, 129.4, 128.7, 128.6, 127.4, 126.9, 126.9, 126.6, 121.6, 62.0, 21.5.

4-(3-((4-Methoxyphenyl)sulfonyl)prop-1-en-2-yl)-1,1′-biphenyl ***(3v)***. Yellow solid (167.5 mg, 92%); mp 118−120 °C; purification by silica gel chromatography (eluent: PE/EA = 12:1, R_f = 0.13); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79−7.63 (m, 2H), 7.56 (d, J = 3.68 Hz, 2H), 7.50−7.40 (m, 4H), 7.39−7.30 (m, 3H), 6.91−6.81 (m, 2H), 5.65 (s, 1H), 5.24 (s, 1H), 4.29 (s, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 163.6, 140.7, 140.3, 137.5, 136.3, 130.8, 129.8, 128.8, 127.5, 127.0, 126.9, 126.6, 121.6114.0, 62.3, 55.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}O_3SH$ 365.1206; found 365.1191.

4-(3-((4-Bromophenyl)sulfonyl)prop-1-en-2-yl)-1,1′-biphenyl ***(3w)***. Yellow oil (183.4 mg, 89%); purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.16); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.66−7.51 (m, 6H), 7.50−7.41 (m, 4H), 7.40−7.27 (m, 3H), 5.67 (s, 1H), 5.27 (s, 1H), 4.32 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 141.0, 140.2, 137.2, 137.1, 135.9, 132.1, 130.2, 129.0, 128.8, 127.5, 127.1, 127.0, 126.6, 122.0, 62.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{17}BrO_2SNa$ 435.0025; found 435.0008.

2-(3-Tosylprop-1-en-2-yl)naphthalene ***(3x)***.[9c] White solid (145.0 mg, 90%); mp 114−116 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.12); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80−7.74 (m, 1H), 7.73−7.67 (m, 2H), 7.64 (d, J = 8.20 Hz, 2H), 7.57 (d, J = 0.84 Hz, 1H), 7.50−7.37 (m, 3H), 7.09 (d, J = 8.04 Hz, 2H), 5.73 (s, 1H), 5.34 (s, 1H), 4.37 (s, 2H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 144.6, 136.5, 135.8, 135.3, 132.9, 132.7, 129.4, 128.6, 128.1, 127.9, 127.4, 126.2, 126.2, 125.4, 124.0, 122.0, 62.2, 21.3.

(E)-1-Methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene ***(4a)***.[9b] White solid (127.9 mg, 94%); mp 90−91 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.12); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, J = 8.32 Hz, 2H), 7.47−7.30 (m, 7H), 6.59 (d, J = 1.24 Hz, 1H), 2.52 (d, J = 1.20 Hz, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 152.9, 144.1, 140.2, 139.3, 129.8, 129.8, 128.7, 127.8, 127.3, 126.3, 21.6, 17.2.

(E)-((2-Phenylprop-1-en-1-yl)sulfonyl)benzene ***(4b)***.[9i] Colorless oil (118.7 mg, 92%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.11); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (dt, J = 1.96, 7.24 Hz, 2H), 7.65−7.59 (m, 1H), 7.58−7.51 (m, 2H), 7.45−7.32 (m, 5H), 6.61 (d, J = 1.20 Hz, 1H), 2.53 (d, J = 1.12 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 153.4, 142.1, 140.0, 133.1, 129.8, 129.2, 128.6, 127.3, 127.1, 126.2, 17.1.

(E)-1-Bromo-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene ***(4c)***. Yellow oil (151.2 mg, 90%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.13); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (dt, J = 1.92, 8.60 Hz, 2H), 7.69 (dt, J = 1.84, 8.60 Hz, 2H), 7.46−7.33 (m, 5H), 6.57 (d, J = 1.16 Hz, 1H), 2.52 (d, J = 1.16 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 154.2, 141.2, 139.9, 132.5, 130.0, 128.8, 128.8, 128.4, 127.0, 126.3, 17.3. HRMS (ESI-TOF) m/z: $[M + K]^+$ calcd for $C_{15}H_{13}BrO_2SK$ 374.9451; found 374.9442.

(E)-1-Fluoro-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene ***(4d)***.[9b] Colorless oil (114.6 mg, 83%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.14); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03−7.93 (m, 2H), 7.43−7.32 (m, 5H), 7.27−7.19 (m, 2H), 6.58 (d, J = 1.20 Hz, 1H), 2.53 (d, J = 1.16 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 165.5 (d, J = 254.1 Hz), 153.8, 140.1, 138.3, 130.1, 130.0 (d, J = 1.6 Hz), 128.8, 127.3, 126.3, 116.5 (d, J = 22.5 Hz), 17.2.

(E)-1-Methoxy-3-(1-(phenylsulfonyl)prop-1-en-2-yl)benzene ***(4e)***.[9i] White solid (131.1 mg, 91%); mp 64−66 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.11); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01−7.93 (m, 2H), 7.65−7.51 (m, 3H), 7.30−7.24 (m, 1H), 7.00−6.87 (m, 3H), 6.60 (d, J = 1.20 Hz, 1H), 3.80 (s, 3H), 2.51 (d, J = 1.20 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 153.4, 142.2, 141.6, 133.3, 129.8, 129.3, 127.6, 127.3, 118.7, 115.2, 112.2, 55.4, 17.3.

(E)-1-Methoxy-3-(1-tosylprop-1-en-2-yl)benzene ***(4f)***.[20] White solid (140.5 mg, 93%); mp 70−72 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.15); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, J = 8.28 Hz, 2H), 7.34 (d, J = 8.12 Hz, 2H), 7.26 (t, J = 7.52 Hz, 1H), 7.02−6.84 (m, 3H), 6.59 (d, J = 0.96 Hz, 1H), 3.80 (s, 3H), 2.50 (d, J = 0.88 Hz, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.7, 152.9, 144.2, 141.7, 139.3, 129.9, 129.8, 128.0, 127.3, 118.7, 115.1, 112.2, 55.4, 21.6, 17.3.

(E)-1-(1-((4-Bromophenyl)sulfonyl)prop-1-en-2-yl)-3-methoxybenzene ***(4g)***. Yellow oil (161.1 mg, 88%); purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.18); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (dt, J = 2.24, 8.64 Hz, 2H), 7.69 (dt, J = 1.72, 8.64 Hz, 2H), 7.29 (d, J = 7.96 Hz, 1H), 7.00−6.86 (m, 3H), 6.57 (d, J = 1.20 Hz, 1H), 3.81 (s, 3H), 2.50 (d, J = 1.16 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 154.1, 141.5, 141.2, 132.6, 132.5, 129.9, 128.8, 127.1, 118.7, 115.3, 112.2, 55.4, 17.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}BrO_3SNa$ 388.9817; found 388.9805.

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J. Org. Chem. 2021, 86, 4018−4026

(E)-1-Bromo-3-(1-(phenylsulfonyl)prop-1-en-2-yl)benzene ***(4h)***.[7a] White solid (151.2 mg, 90%); mp 82−84 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00−7.92 (m, 2H), 7.64−7.60 (m, 1H), 7.60−7.54 (m, 2H), 7.53−7.46 (m, 2H), 7.31 (dt, J = 1.40, 7.76 Hz, 1H), 7.25−7.20 (m, 1H), 6.58 (q, J = 1.28 Hz, 1H), 2.51 (d, J = 1.24 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 151.8, 142.3, 141.9, 133.5, 132.8, 130.3, 129.4, 129.3, 128.6, 127.3, 125.0, 122.9, 17.2.

(E)-1-Nitro-3-(1-tosylprop-1-en-2-yl)benzene ***(4i)***.[9i] Yellow oil (139.5 mg, 88%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.12); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22−8.21 (m, 2H), 7.86 (d, J = 8.28 Hz, 2H), 7.71 (d, J = 7.88 Hz, 1H), 7.58−7.56 (m, 1H), 7.37 (d, J = 8.04 Hz, 2H), 6.65 (d, J = 0.76 Hz, 1H), 2.58 (d, J = 1.12 Hz, 3H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 149.9, 148.4, 144.8, 142.0, 138.6, 132.2, 130.3, 130.1, 129.9, 127.5, 124.3, 121.3, 21.6, 17.2.

(E)-4-(1-(Phenylsulfonyl)prop-1-en-2-yl)-1,1′-biphenyl ***(4j)***. Yellow oil (152.0 mg, 91%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01−7.99 (m, 2H), 7.62−7.59 (m, 7H), 7.57−7.47 (m, 4H), 7.37 (t, J = 7.16 Hz, 1H), 6.69 (d, J = 1.08 Hz, 1H), 2.58 (d, J = 0.96 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 153.0, 142.9, 142.3, 139.9, 138.8, 133.3, 129.3, 129.0, 127.9, 127.4, 127.3, 127.2, 127.1, 126.8, 17.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}O_2SNa$ 335.1100; found 335.1101.

(E)-2-(1-Tosylprop-1-en-2-yl)naphthalene ***(4k)***. White solid (144.9 mg, 90%); mp 124−126 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.14); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93−7.89 (m, 3H), 7.85−7.82 (m, 3H), 7.54−7.51 (m, 3H), 7.40−7.38 (m, 2H), 6.77 (s, 1H), 2.66 (s, 3H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 152.8, 144.2, 139.4, 137.4, 133.8, 133.0, 129.9, 128.6, 128.5, 128.1, 127.6, 127.4, 127.2, 126.8, 126.3, 123.5, 21.6, 17.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}O_2SNa$ 345.0920; found 345.0905.

(E)-2-(1-((4-Bromophenyl)sulfonyl)prop-1-en-2-yl)naphthalene ***(4l)***. Yellow oil (167.9 mg, 87%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.15); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91−7.79 (m, 6H), 7.77−7.67 (m, 2H), 7.53−7.46 (m, 3H), 6.72 (d, J = 1.16 Hz, 1H), 2.63 (d, J = 1.16 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 154.0, 141.3, 137.1, 133.9, 132.9, 132.6, 132.3, 130.1, 128.9, 128.6, 127.7, 127.4, 127.3, 126.9, 126.4, 123.4, 17.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{15}BrO_2SNa$ 408.9868; found 408.9883.

(E)-((2-Phenylbut-1-en-1-yl)sulfonyl)benzene ***(4m)***.[18] Yellow oil (119.7 mg, 88%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.16); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00−7.95 (m, 2H), 7.65−7.58 (m, 1H), 7.58−7.52 (m, 2H), 7.40−7.33 (m, 5H), 6.48 (s, 1H), 3.07 (q, J = 7.48 Hz, 2H), 0.97 (t, J = 7.44 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 142.4, 138.8, 133.2, 129.8, 129.3, 128.8, 127.2, 127.2, 126.8, 23.7, 13.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{16}O_2SNa$ 295.0763; found 295.0750.

(E)-1-Methyl-4-((2-phenylbut-1-en-1-yl)sulfonyl)benzene ***(4n)***.[15a] Yellow oil (130.2 mg, 91%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.11); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (dd, J = 8.08, 8.24 Hz, 2H), 7.39−7.33 (m, 7H), 6.46 (s, 1H), 3.06 (q, J = 7.48 Hz, 2H), 2.43 (s, 3H), 0.97 (t, J = 7.48 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 159.2, 144.1, 139.5, 139.0, 129.9, 129.6, 128.8127.5, 127.3, 126.8, 23.7, 21.6, 13.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}O_2SH$ 287.1100; found 287.1091.

(E)-1-Bromo-4-((2-phenylbut-1-en-1-yl)sulfonyl)benzene ***(4o)***. Yellow oil (140.0 mg, 80%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (dt, J = 2.36, 8.68 Hz, 2H), 7.69 (dt, J = 2.32, 8.68 Hz, 2H), 7.40−7.35 (m, 5H), 6.44 (s, 1H), 3.05 (q, J = 7.48 Hz, 2H), 0.99 (t, J = 7.48 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 160.5, 141.4, 138.7, 132.6, 129.9, 128.8, 128.8, 128.4, 126.8, 126.6, 23.8, 13.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}BrO_2SNa$ 372.9868; found 372.9868.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02869.

NMR spectra data of the compounds, other optimization of reaction conditions, and the copy of HRMS data (PDF)

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Notes

The authors declare no competing financial interest.

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