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Allylic C−S Bond Construction through Metal-Free Direct Nitroalkene Sulfonation

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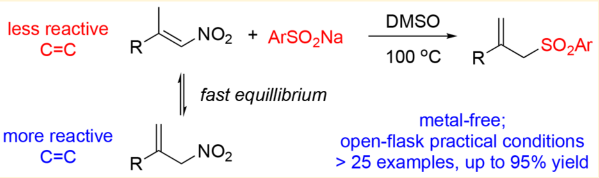
Supporting Information

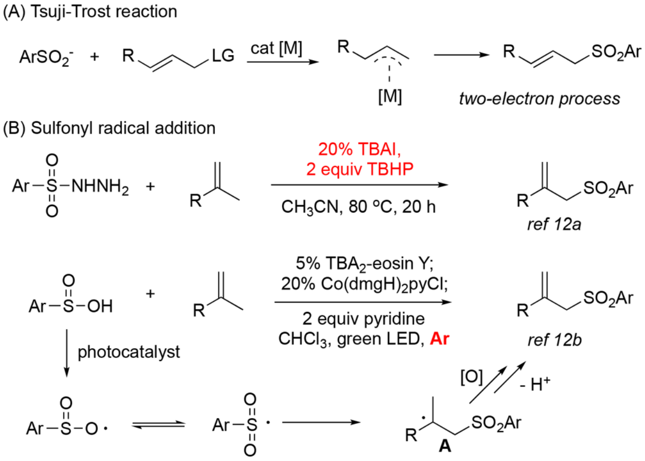
ABSTRACT: A metal-free, open-flask protocol was developed for the preparation of allylic sulfones through direct condensation of sodium arylsulfinates and *β*,*β*-disubstituted nitroalkenes. The key step of this process was the Lewis base-promoted equilibrium between nitroalkenes and allylic nitro compounds. Through this process, the readily available conjugated nitroalkenes can be easily converted into allylic nitro compounds, which contain more reactive C═C bonds toward the sulfonyl radical addition. As a result, allylic sulfones were prepared in excellent yields with a broad substrate scope under mild conditions.



INTRODUCTION

One of the general goals of synthetic methodology research is to develop new approaches for an important chemical bond construction with a high chemical efficiency and practical operation protocols.[1] Due to the significant role of sulfur-containing compounds in chemical,[2] biological,[3] and medicinal research,[4] more and more attention has been paid to the development of efficient new approaches to construct C−S bonds in recent years.[5] Allyl sulfones are interesting and versatile sulfur-containing building blocks in organic synthesis.[6] With the electron-withdrawing RSO_2 moiety, allyl sulfones can serve as synthons for many useful transformations.[7] The general synthetic strategy of allyl sulfone synthesis can be divided into two major approaches: (A) two-electron nucleophilic addition and (B) sulfonyl radical addition.

Scheme 1. General Synthetic Strategy for Allyl Sulfones



As shown in Scheme 1A, one popular method for the synthesis of allyl sulfones is the Tsuji−Trost reaction, especially under Pd- or Ir-catalyzed nucleophilic addition to metal *π*-allyl intermediates.[8,9] Although these occur with an overall good reaction scope, this transformation usually requires an exquisite condition control in order to avoid catalyst deactivation caused by sulfur coordination.[10] In recent years, sulfonyl radical-mediated reactions have gained more and more attention due to its good reactivity toward C−C multiple bonds and ability to avoid undesired side reactions.[11] In fact, this strategy has been applied to allyl sulfone synthesis.[12] Two representative examples are shown in Scheme 1B.

In 2012, Li and co-workers reported the application of sulfonyl hydrazine as a radical precursor and TBHP (*tert*-butyl hydroperoxide) (2 equiv) as an oxidant.[12a] Under TBAI (tetrabutylammonium iodide) catalytic conditions, allyl sulfones were formed in modest to good yields. Another important recent development was the direct condensation of sulfinic acids and alkenes with the combination of a photocatalyst and metal catalysts reported by Lei and co-workers.[12b] TBA_2-eosin Y was applied as an effective photocatalyst to initiate the formation of sulfonyl radicals. A sequential radical addition and $Co(dmgH)_2pyCl$-catalyzed dehydrogenation produced the desired allyl sulfones without additional external oxidants. This seminal work revealed one important reaction perspective, which was that sulfonyl radicals can be formed directly from sulfinic acids under the proper conditions with a high efficiency. The major drawback of this process was the requirement of strict degassing and argon protection, which made the process less practical. Herein, we report a direct condensation of sodium arylsulfinates and nitroalkenes for the synthesis of allyl sulfones. Notably, this

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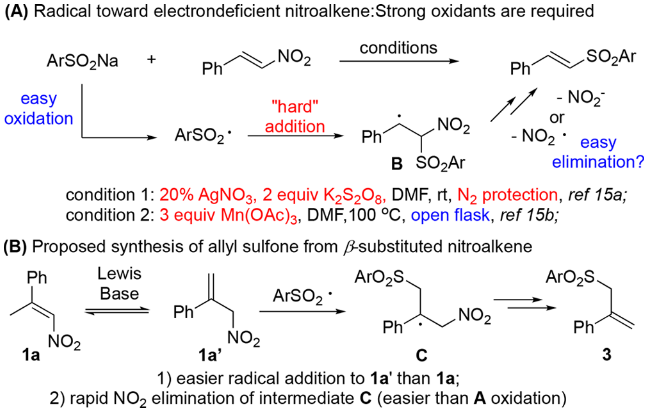
reaction not only provided allyl sulfones in moderate to high yields but also was performed in open-flask, metal-free conditions, highlighting the efficiency and practicality of this strategy.

Our interest in developing new methods for the preparation of allyl sulfones was initiated from the Lewis base-catalyzed nitroalkene activation previously conducted in our group.[13] In those studies, the designated β-elimination was employed to promote the challenging intermolecular cascade condensation from a competing reaction equilibrium. While nitroalkenes are good Lewis base receptors (two-electron receptor),[14] we were wondering whether these highly electron-deficient C═C double bonds (compared with regular alkene) would react with radicals. Notably, sulfonyl radical is also electron deficient. Thus, it is expected that harsh conditions or strong oxidants are required to promote this transformation. Two examples are shown in Scheme 2A.[15] According to literature, sulfonylation of nitroalkenes can be achieved in the presence of strong oxidants. For example, with a silver catalyst (20%) and using $K_2S_2O_8$ (2 equiv) as an oxidant, the desired vinyl sulfones can be prepared.[15a] However, N_2 protection was required to avoid the formation of oxidative side products. Recently, we reported the application of $Mn(OAc)_3$ as the oxidant to achieve the same transformation.[15b] In this case, inert atmosphere was not necessary, which made the process more practical. Based on the proposed reaction mechanism, both examples produced radical intermediate **B**. It is reasonable to assume that the most challenging step in both reactions is the sulfonyl radical addition toward electron deficient nitroalkenes. Although the elimination step remains unclear (through either a NO_2 anion or NO_2 radical), the oxidation of radical **B** is not likely involved in forming the carbocation, as occurring in the direct alkene sulfonylation examples shown in Scheme 1B. On the basis of this analysis, we postulated the reaction of β,β-disubstituted nitroalkene **1a** with sodium arylsulfinates as a plausible new reaction path toward the synthesis of allyl sulfone **3** as shown in Scheme 2B.

Scheme 2. Sulfonyl Radical Addition to Nitroalkene

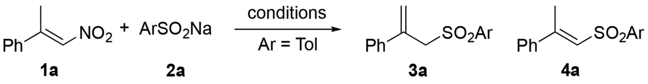


It is clear that the sulfonyl radical addition will be feasible on allylic compound **1a′** with a more electron-rich C═C double bond, giving the radical intermediate **C**. Elimination of NO_2 (similar to intermediate **B**) will afford the desired allyl sulfone **3**. Compared with the dehydrogenation approach,[12b] this new route successfully avoids the oxidation of radical to carbocation, which permits a higher overall efficiency with potentially milder conditions (no need for second oxidants or a dehydrogenation catalyst). Moreover, although the allylic compound **1a′** is not easy to prepare (compared with nitroalkene **1a**), we have demonstrated the fast equilibrium between these two compounds with the presence of a Lewis base catalyst.[16] Since sulfinate salt can serve as a mild base, it will be expected that the same equilibrium should be established under the reaction conditions.

RESULTS AND DISCUSSION

To testify our hypothesis, reactions between nitroalkene **1a** and sodium p-toluenesulfinate **2a** were performed under various conditions (Table 1).

Table 1. Reaction Conditions Screening[a]



entry	reaction conditions	convn **1a** (%)	**3a** yield (%)[b]	**4a** yield (%)[b]
1	3 equiv of $Mn(OAc)_3$, DMF, 100 °C, 4 h	58	10	27
2	10% TBAI, 2 equiv of TBHP, CH_3CN, 80 °C, 4 h	95	trace	0
3	20% $AgNO_3$, 2 equiv of $K_2S_2O_8$, DMF, rt, Ar, 4 h	40	10	0
4	20% $AgNO_3$, DMSO, 100 °C, 4 h	100	75	6
5	DMSO, 100 °C, 4 h	100	88	trace
6	DMSO, 80 °C, 4 h	75	50	trace
7	DMSO, 100 °C, 4 h, Ar, (degassed)	50	35	trace
8	100% I_2, DMSO, 80 °C, 4 h	44	12	0
9	10% I_2, 2 equiv of TBHP, DMSO, 80 °C, 2 h	100	90	0
10	other conditions (in the Supporting Information)			

[a] Reaction conditions: **1a** (0.3 mmol, 1 equiv), **2a** (1.5 equiv), catalyst (mol %), oxidant (equiv) in DMSO (3.0 mL), open air. [b] Isolated yield. DMF = dimethylformamide. DMSO = dimethyl sulfoxide.

Very low yields of the desired products were observed with a poor chemoselectivity (entries 1−3) when we used the previously reported conditions. These results clearly revealed the different reactivity between regular nitroalkene and β,β-alkyl-nitroalkene under these radical addition conditions. Our breakthrough was from two unexpected control experiments: (1) using a catalytic amount (20%) of $AgNO_3$ resulted in the formation of allyl sulfone **3a** in 75% and vinyl sulfone **4a** in 6%, and (2) simply treating reaction mixtures with DMSO at 100 °C (without any catalyst) gave the desired allyl sulfone **3a** in 88% yield (entry 5). Notably, an excellent regioselectivity was obtained with a trace amount of vinyl sulfone **4a** formed under this simple condition. Conducting the reaction under oxygen-free conditions (entry 7) gave a lower yield, which suggested the important role of oxygen in the formation of the sulfinic radical under this catalyst-free condition. Reducing the reaction temperature to 80 °C gave a significantly lower yield, likely due to the competing sulfinate oxidation side reaction. To enhance the formation of the sulfinic radical process, 10% I_2 along with TBHP as the oxidant was tested. As expected, **3a** was formed in an excellent yield (90% isolated yield) even at a lower temperature (entry 9).[17] Compared with the catalyst-free conditions, the I_2/TBHP conditions gave a much cleaner reaction with **3a** as the only product observed in crude NMR. It is important to note that the application of 1 equiv of I_2 will quench the reaction significantly (entry 8). Monitoring the reaction confirmed that no formation of allylic nitro compound **1a**′ of 1 equiv of I_2 was used because I_2 will react with arylsulfinate salt and cause almost no formation of **1a**′ for the sulfonyl radial addition. With the two optimal conditions revealed, we evaluated the reaction scope. The results are summarized in Figure 1.

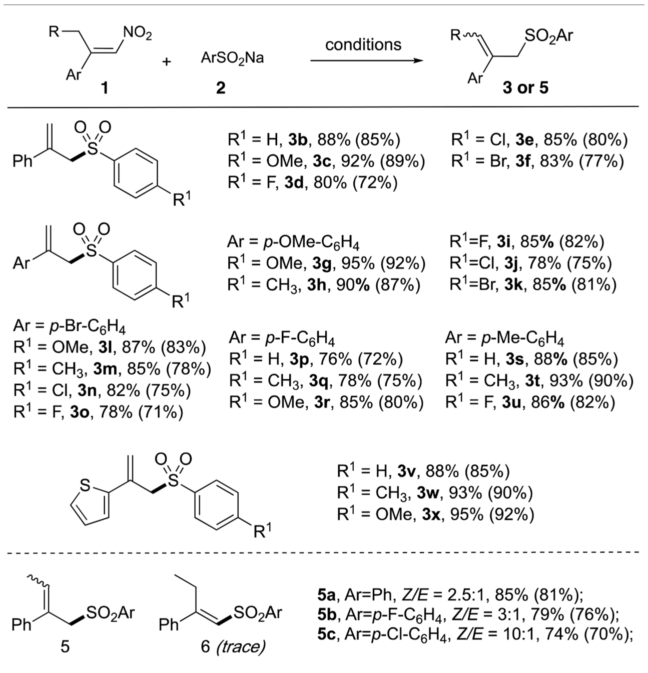


Figure 1. Substrate scope. Reaction conditions: nitroolefins (0.3 mmol), sodium sulfinates (0.45 mmol), I_2 (0.03 mmol), TBHP (0.6 mmol), DMSO (3 mL), 80 °C, 2 h, open air. Reaction conditions in parentheses: nitroolefins (0.3 mmol), sodium sulfinates (0.45 mmol), DMSO (3 mL), 100 °C, 4 h, open air. The isolated yields are shown.

In summary, all substrates tested gave good yields under both conditions, while the TBHP/I_2 system provided a slightly better yield and faster reaction rate. An array of sodium arylsulfinates with both electron-donating and electron-withdrawing groups on the phenyl ring have been tested, and satisfactory yields were obtained. Investigations on different nitroolefins showed that the nitroolefins with an electron-donating group (Ar = *p*-OMe-C_6H_4, **3g**−**k**; *p*-Me-C_6H_4, **3s**−**u**) gave higher yields than those with an electron-withdrawing group (Ar = *p*-F-C_6H_4, **3p**−**r**). Notably, heterocyclic-containing nitroolefins also give the corresponding products in good yields (**3v**−**x**). Furthermore, *α*-ethyl nitroolefins were also tested for this reaction (**5a**−**b**). According to the structure of the substrate and the mechanism that we proposed above, compound **6** was expected. However, under standard reaction conditions, compound **5** was obtained in all cases, which involved sequential sulfonyl radical additions.[18] The isolated yield of (2-phenylbut-2-enylsulfonyl)benzene **5a** (*Z* isomer and *E* isomer) was up to 85%, and the *Z*/*E* ratio was up to 10:1 for sodium 4-chlorobenzenesulfinate. Although the *Z*/*E* ratio was not very high for some cases, the high regioselectivity and good yield made this transformation a good option for the synthesis of the similar multisubstituted allyl sulfones.

To further explore the substrate scope of the reaction, (nitromethylene)cyclohexane was reacted with sodium sulfinates (Figure 2A). However, no sulfonation products were observed under either thermal or oxidation conditions. Instead,

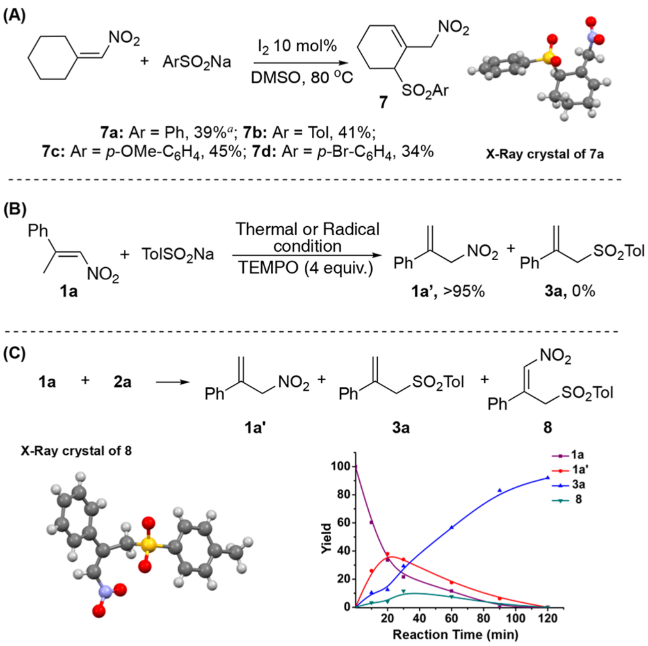


Figure 2. Aliphatic substrates and reaction profile. Reaction conditions: nitroolefins (0.3 mmol), sodium sulfinates (0.45 mmol), I_2 (0.03 mmol), TBHP (0.6 mmol), DMSO, 80 °C, open air.

we found the reaction worked well with I_2 (0.1 equiv) at 80 °C for 8 h and products **7a**−**7d** were obtained. Product **7a** was selected as the representative compound and characterized by X-ray crystallography, as shown in Figure 2A.

A radical trapping experiment was performed to support the radical mechanism (Figure 2B). The reaction with a stoichiometric amount of radical inhibitor (TEMPO) was performed under two optimal conditions (either DMSO at 100 °C or 10% I_2/TBHP at 80 °C). Notably, only the conversion of **1a** to **1a**′ was observed, while desired product **3a** was not detected. This result implied the further step involved a free radical process. Furthermore, the time-dependent reaction profile of **1a** with sodium *p*-tolylsulfinate was obtained using ^1H NMR (Figure 2C). The Lewis base-promoted equilibrium between **1a** and **1a**′ occurred within 20 min. The product **3a** was formed accompanied by a small amount of **8** (confirmed by X-ray crystallography). Intermediate **8** could also slowly convert into desired product **3a** based on our experimental observations. Addition of 100% I_2 inhibited the formation of allylic compound **1a**′. (See the Supporting Information.) Overall, these observations verified the mechanism we proposed.

CONCLUSION

In conclusion, we report here a metal-free direct nitroalkene sulfonylation reaction between sodium arylsulfinates and *β*,*β*-disubstituted nitroalkenes. This method can give allyl sulfones with a high efficiency. By tuning the substituents on both reactants, the allyl sulfones can be obtained in a high selectivity and yield. Further mechanistic studies and the synthetic application of this transformation are the focus of ongoing investigations.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification; ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AscendTM 600 or Bruker AV400 spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (TMS) (0.00 ppm) or $CDCl_3$ (7.26 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C. Flash column chromatography was performed on 200−300 mesh silica gel.

Mass analysis was performed on a Waters Xevo G2 QTOFMS mass spectrometer. A high-resolution TOFMS with an ESI source was used to detect the analytes of interest in positive mode or negative mode. Melting points were measured on a melting point tester RY-1G apparatus and were uncorrected.

General Procedure to Synthesize Nitroalkenes.[19−21] *Synthesis of (E)-β-Aryl-β-methyl Nitroalkenes. (E)-(1-Nitroprop-1-en-2-yl)benzene (**1a**):*[21a] yellow oil (6.8 g, 50% yield); eluent = petroleum ether; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.44 (s, 5H), 7.29 (d, *J* = 1.0 Hz, 1H), 2.63 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 149.8, 138.1, 136.2, 130.3, 128.9, 126.7, 18.4.

*(E)-1-Methoxy-4-(1-nitroprop-1-en-2-yl)benzene (**1b**):*[21a] yellow oil (6.2 g, 48% yield); eluent = petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 1.2 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.63 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.6, 149.7, 135.1, 130.1, 128.4, 114.4, 55.4, 18.3.

*(E)-1-Bromo-4-(1-nitroprop-1-en-2-yl)benzene (**1c**):*[21a] yellow oil (5.5 g, 45% yield); eluent = petroleum ether; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.60−7.56 (m, 2H), 7.34−7.31 (m, 2H), 7.28 (d, *J* = 1.5 Hz, 1H), 2.62 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 148.6, 137.2, 136.4, 132.3, 128.4, 124.9, 18.4.

*(E)-1-Fluoro-4-(1-nitroprop-1-en-2-yl)benzene (**1d**):*[21a] yellow oil (5.7 g, 43% yield); eluent = petroleum ether; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.48−7.43 (m, 2H), 7.28 (d, *J* = 1.5 Hz, 1H), 7.13 (t, *J* = 8.5 Hz, 2H), 2.63 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 164.0 (d, *J* = 251.7 Hz), 148.7, 136.2, 134.3, 128.8 (d, *J* = 8.5 Hz), 116.2 (d, *J* = 21.9 Hz), 18.6.

*(E)-1-Methyl-4-(1-nitroprop-1-en-2-yl)benzene (**1e**):*[21b] yellow oil (7.2 g, 55% yield); eluent = petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.63 (d, *J* = 1.2 Hz, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.9, 140.8, 135.7, 135.2, 129.7, 126.7, 21.2, 18.3.

*(E)-2-(1-Nitroprop-1-en-2-yl)thiophene (**1f**):*[21c] yellow oil (7.8 g, 58% yield); eluent = petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.57 (s, 1H), 7.49−7.46 (m, 2H), 7.13 (t, *J* = 4.4 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.9, 140.5, 133.7, 129.6, 129.2, 128.6, 17.9.

*(E)-(1-Nitrobut-1-en-2-yl)benzene (**1g**):*[21b] yellow oil (6.9 g, 52% yield); eluent = petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.43 (m, 5H), 7.22 (s, 1H), 3.12 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 137.0, 135.7, 130.2, 129.0, 127.1, 24.7, 12.7.

*(3-Nitroprop-1-en-2-yl)benzene (**1a′**):*[21d] yellow oil (8 g, 80% yield); eluent = petroleum ether; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.45−7.43 (m, 2H), 7.40−7.33 (m, 3H), 5.83 (s, 1H), 5.54 (s, 1H), 5.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 137.9, 136.0, 128.8, 128.8, 125.8, 121.8, 79.6.

*Synthesis of (Nitromethylene)cyclohexane. (Nitromethylene)-cyclohexane (**1h**) and 1-(Nitromethyl)cyclohex-1-ene (**1h′**):*[20b,21e] yellow oil (6.5 g, 45% yield); eluent = petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) **1h** δ 6.89 (s, 1H), 2.86−2.81 (m, 2H), 2.22−2.17 (m, 2H), 1.73−1.58 (m, 6H); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) **1h′** δ 5.92 (s, 1H) 4.78 (s, 2H), 2.13−2.03 (m, 4H), 1.73−1.58 (m, 4H).

Procedures for the Synthesis of Allyl Sulfones. To the solution of nitroolefins **1a**−**1g** (0.3 mmol) and sodium sulfinates **2** (0.45 mmol) in DMSO (3 mL) were added I_2 (10% mmol) and TBHP (0.6 mmol). The mixture was stirred at 80 °C for 2 h. After the completion of the reaction, the mixture was poured into water, extracted by ethyl acetate, washed with NaCl (aq), and dried with anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure to obtain the crude product. Further purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) gave the allyl sulfones.

The solution of nitroolefins **1a**−**1g** (0.3 mmol) and sodium sulfinates **2** (0.45 mmol) in DMSO (3 mL) was stirred at 100 °C for 4 h. After the completion of the reaction, the mixture was poured into water, extracted by ethyl acetate, washed with NaCl (aq), and dried with anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure to obtain the crude product. Further purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) gave the allyl sulfones.

*1-Methyl-4-((2-phenylallyl)sulfonyl)benzene (**3a**):*[12a] white solid (71.9 mg, 88% yield; 73.5 mg, 90% yield); mp 97−98 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.64 (d, *J* = 7.8 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 NMR (150 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**):*[12a] white solid (65.9 mg, 85% yield; 68.2 mg, 88% yield); mp 45−47 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.27−7.20 (m, 5H), 5.57 (s, 1H), 5.20 (s, 1H), 4.26 (s, 2H); ^{13}C NMR (150 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-Methoxy-4-((2-phenylallyl)sulfonyl)benzene (**3c**):*[12b] yellow oil (77.0 mg, 89% yield; 79.6 mg, 92% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 9.0 Hz, 2H), 7.26−7.20 (m, 5H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.57 (s, 1H), 5.19 (s, 1H), 4.23 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 163.6, 138.8, 136.7, 130.7, 129.8, 128.3, 127.9, 126.1, 121.6, 114.0, 62.2, 55.6.

*1-Fluoro-4-((2-phenylallyl)sulfonyl)benzene (**3d**):* white solid (59.7 mg, 72% yield; 68.2 mg, 66.3% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.76 (dd, *J* = 8.4, 4.8 Hz, 2H), 7.23 (s, 5H), 7.07 (t, *J* = 8.4 Hz, 2H), 5.60 (s, 1H), 5.24 (s, 1H), 4.28 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 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; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{13}FO_2SNa$ 299.0512, found 299.0515.

*1-Chloro-4-((2-phenylallyl)sulfonyl)benzene (**3e**):*[21f] white solid (70.2 mg, 80% yield; 74.7 mg, 85% yield); mp 117−118 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.27−7.19 (m, 5H), 5.59 (s, 1H), 5.23 (s, 1H), 4.27 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 140.3, 138.4, 136.7, 136.4, 130.1, 129.1, 128.4, 128.1, 126.1, 122.0, 62.2.

*1-Bromo-4-((2-phenylallyl)sulfonyl)benzene (**3f**):*[12a] white solid (77.9 mg, 77% yield; 84.0 mg, 83% yield); mp 127−128 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.21 (s, 5H), 5.58 (s, 1H), 5.22 (s, 1H), 4.26 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 138.3, 137.1, 136.2, 132.0, 130.0, 128.8, 128.3, 128.0, 126.0, 122.0, 62.0.

*1-Methoxy-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3g**):* yellow oil (87.9 mg, 92% yield; 90.7 mg, 95% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.71−7.66 (m, 2H), 7.25−7.19 (m, 2H), 6.91−6.84 (m, 2H), 6.80−6.74 (m, 2H), 5.49 (s, 1H), 5.07 (s, 1H), 4.21 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.6, 159.5, 136.2, 131.3, 130.8, 130.1, 127.4, 119.8, 114.0, 113.7, 62.5, 55.6, 55.2; HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{17}H_{19}O_4S$ 319.0999, found 319.1006.

*1-Methoxy-4-(3-tosylprop-1-en-2-yl)benzene (**3h**):*[12a] white solid (78.9 mg, 87% yield; 81.6 mg, 90% yield); mp 62−63 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 6.0 Hz, 4H), 6.79−6.73 (m, 2H), 5.48 (s, 1H), 5.06 (s, 1H), 4.21 (s, 2H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.4, 144.4, 135.9, 135.5, 131.2, 129.4, 128.6, 127.4, 119.8, 113.6, 62.2, 55.2, 21.4.

1-Fluoro-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3i**): white solid (75.4 mg, 82% yield; 78.1 mg, 85% yield); mp 131−132 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80−7.74 (m, 2H), 7.21−7.16 (m, 2H), 7.12−7.05 (m, 2H), 6.80−6.74 (m, 2H), 5.50 (s, 1H), 5.10 (s, 1H), 4.25 (s, 2H), 3.78 (s, 3H); ^{13}C 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; HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{16}FO_3S$: 307.0799, found 307.0800.

1-Chloro-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3j**): white solid (72.6 mg, 75% yield; 75.5 mg, 78% yield); mp 120−121 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.40−7.34 (m, 2H), 7.19−7.13 (m, 2H), 6.79−6.73 (m, 2H), 5.50 (s, 1H), 5.11 (s, 1H), 4.24 (s, 2H), 3.78 (s, 3H); ^{13}C 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; HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{16}ClO_3S$ 323.0503, found 323.0501.

1-Bromo-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (**3k**): white solid (89.2 mg, 81% yield; 93.7 mg, 85% yield); mp 114−115 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 5.51 (s, 1H), 5.12 (s, 1H), 4.24 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.7, 137.4, 135.8, 132.1, 130.8, 130.2, 128.9, 127.4, 120.3, 113.8, 62.5, 55.3; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{15}BrO_3SNa$ 388.9817, found 388.9830.

1-Bromo-4-(3-((4-methoxyphenyl)sulfonyl)prop-1-en-2-yl)-benzene (**3l**): yellow oil (91.4 mg, 83% yield; 95.9 mg, 87% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.71 (d, *J* = 8.8 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 NMR (150 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; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{15}BrO_3SNa$ 388.9817, found 388.9827.

1-Bromo-4-(3-tosylprop-1-en-2-yl)benzene (**3m**):[12a] white solid (82.2 mg, 78% yield; 68.2 mg, 89.6% yield); mp 130−132 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.57 (s, 1H), 5.22 (s, 1H), 4.20 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 144.9, 137.7, 135.7, 135.3, 131.4, 129.6, 128.6, 127.9, 122.3, 122.1, 62.0, 21.6.

1-Bromo-4-(3-((4-chlorophenyl)sulfonyl)prop-1-en-2-yl)benzene (**3n**): yellow oil (83.6 mg, 75% yield; 91.4 mg, 82% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 19.2, 8.4 Hz, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.60 (s, 1H), 5.22 (s, 1H), 4.23 (s, 2H); ^{13}C NMR (150 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; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{12}BrClO_2SNa$ 392.9302, found 392.9305.

1-Bromo-4-(3-((4-fluorophenyl)sulfonyl)prop-1-en-2-yl)benzene (**3o**): yellow oil (75.7 mg, 71% yield; 83.1 mg, 78% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.78 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.16−7.11 (m, 8.4 Hz, 4H), 5.60 (s, 1H), 5.22 (s, 1H), 4.23 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 165.8 (d, *J* = 256.9 Hz), 137.5, 135.5, 134.2, 131.6, 131.5 (d, *J* = 9.6 Hz), 127.8, 122.5, 122.4, 116.3 (d, *J* = 22.7 Hz), 62.1; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{12}BrFO_2SNa$ 378.9597, found 378.9590.

1-Fluoro-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (**3p**):[21g] white solid (59.7 mg, 72% yield; 63.0 mg, 76% yield); mp 87−88 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.27−7.23 (m, 2H), 6.93 (t, *J* = 8.8 Hz, 2H), 5.54 (s, 1H), 5.19 (s, 1H), 4.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 162.5 (d, *J* = 248.0 Hz), 138.4, 135.5, 134.9 (d, *J* = 3.4 Hz), 133.7, 128.9, 128.6, 128.0 (d, *J* = 8.2 Hz), 121.9, 115.3 (d, *J* = 21.6 Hz), 62.2.

1-Fluoro-4-(3-tosylprop-1-en-2-yl)benzene (**3q**):[12a] white solid (65.3 mg, 75% yield; 67.9 mg, 78% yield); mp 108−110 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.31−7.24 (m, 4H), 6.96 (t, *J* = 8.8 Hz, 2H), 5.55 (s, 1H), 5.20 (s, 1H), 4.24 (s, 2H), 2.43 (s, 3H); ^{13}C 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-Fluoro-4-(3-((4-methoxyphenyl)sulfonyl)prop-1-en-2-yl)-benzene (**3r**): white solid (73.5 mg, 80% yield; 78.1 mg, 85% yield); eluent = EtOAc/petroleum ether (v/v = 1:10); mp 69−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.28 (dd, *J* = 8.8, 5.2 Hz, 2H), 6.99−6.90 (m, 4H), 5.55 (s, 1H), 5.20 (s, 1H), 4.24 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.7 (d, *J* = 3.6 Hz), 161.2, 135.8, 135.0 (d, *J* = 3.3 Hz), 130.7, 129.9, 128.0 (d, *J* = 8.1 Hz), 121.6, 115.2 (d, *J* = 21.6 Hz), 114.1, 62.5, 55.6; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{15}FO_3SNa$ 329.0618, found 329.0633.

1-Methyl-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (**3s**): white solid (69.4 mg, 85% yield; 71.9 mg, 88% yield); eluent = EtOAc/petroleum ether (v/v = 1:15); mp 68−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 1H), 5.14 (s, 1H), 4.26 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.4, 137.9, 136.2, 135.8, 133.5, 129.0, 128.8, 128.6, 126.0, 120.9, 62.1, 21.0; HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{17}O_2S$ 273.0949, found 273.0954.

1-Methyl-4-((2-(p-tolyl)allyl)sulfonyl)benzene (**3t**):[12a] white solid (77.3 mg, 90% yield; 79.9 mg, 93% yield); mp 81−83 °C; eluent = EtOAc/petroleum ether (v/v = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 16.0, 8.0 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.54 (s, 1H), 5.12 (s, 1H), 4.23 (s, 2H), 2.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 137.7, 136.3, 135.8, 135.4, 129.4, 128.9, 128.5, 126.0, 120.7, 62.1, 21.5, 21.0.

1-Fluoro-4-((2-(p-tolyl)allyl)sulfonyl)benzene (**3u**): white solid (71.4 mg, 82% yield; 74.9 mg, 86% yield); mp 83−84 °C; eluent = EtOAc/petroleum ether (v/v = 1:15); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.10−7.04 (m, 4H), 5.56 (s, 1H), 5.16 (s, 1H), 4.26 (s, 2H), 2.31 (s, 3H); ^{13}C 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; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{15}FO_2SNa$ 313.0669, found 313.0670.

2-(3-(Phenylsulfonyl)prop-1-en-2-yl)thiophene (**3v**): white solid (67.4 mg, 85% yield; 69.8 mg, 88% yield); mp 71−73 °C; eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 5.2 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.88−6.84 (m, 1H), 5.63 (s, 1H), 5.03 (s, 1H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.8, 142.7, 130.9, 130.4, 129.7, 127.5, 125.2, 119.4, 114.1, 62.6, 55.6; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{12}O_2S_2Na$ 287.0171, found 287.0175.

2-(3-Tosylprop-1-en-2-yl)thiophene (**3w**):[12a] white solid (75.2 mg, 90% yield; 77.7 mg, 93% yield); mp 83−84 °C; eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 5.2 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.85 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.60 (s, 1H), 4.99 (s, 1H), 4.17 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.7, 142.6, 135.2, 130.2, 129.5, 128.7, 127.5, 125.3, 125.2, 119.5, 62.4, 21.6.

2-(3-((4-Methoxyphenyl)sulfonyl)prop-1-en-2-yl)thiophene (**3x**): white solid (75.6 mg, 92% yield; 78.0 mg, 95% yield); mp 79−80 °C; eluent = EtOAc/petroleum ether (v/v = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 5.2 Hz, 1H), 6.89 (m, 4H), 5.62 (s, 1H), 5.01 (s, 1H), 4.19 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.8, 142.7, 131.0, 130.4, 129.7, 127.6, 125.3, 125.3, 119.5, 114.1, 62.6, 55.7; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{14}O_3S_2$ 317.0277, found 317.0284.

((2-Phenylbut-2-en-1-yl)sulfonyl)benzene (**5a**): colorless oil (66.2 mg, 81% yield; 69.5 mg, 85% yield); eluent = EtOAc/petroleum ether

(v/v = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) *Z* isomer δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.46−7.34 (m, 4H), 7.27−7.03 (m, 4H), 6.09 (q, *J* = 7.2 Hz, 1H), 4.37 (s, 2H), 1.66 (d, *J* = 7.2 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) *E* isomer δ 7.75 (d, *J* = 7.6 Hz, 2H), δ 7.58−7.48 (m, 4H), 7.27−7.03 (m, 4H), 5.78 (q, *J* = 7.2 Hz, 1H), 4.13 (s, 2H), 1.63 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.9, 138.9, 137.9, 133.4, 133.3, 133.0, 132.9, 128.9, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 127.1, 127.1, 126.2, 64.9, 57.3, 15.3, 14.9; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{16}O_2SNa$ 295.0763, found 295.0758.

*1-Fluoro-4-((2-phenylbut-2-en-1-yl)sulfonyl)benzene (**5b**):* colorless oil (66.2 mg, 76% yield; 68.8 mg, 79% yield); eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) *Z* isomer δ 7.74−7.70 (m, 2H), 7.25−6.99 (m, 7H), 6.11 (q, *J* = 7.2 Hz, 1H), 4.38 (s, 2H), 1.74 (d, *J* = 7.2 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) *E* isomer δ 7.74−7.70 (m, 2H), 7.25−6.99 (m, 7H), 5.82 (q, *J* = 7.2 Hz, 1H), 4.14 (s, 2H), 1.66 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 256.2 Hz), 140.7, 135.0, 133.2, 133.0, 131.4 (d, *J* = 9.6 Hz), 131.2 (d, *J* = 9.6 Hz), 128.9, 128.8, 128.6, 128.3, 128.2, 127.3, 127.2, 126.2, 65.3, 57.5, 15.4, 15.1; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{15}FO_2SNa$ 313.0669, found 313.0680.

*1-Chloro-4-((2-phenylbut-2-en-1-yl)sulfonyl)benzene (**5c**):* colorless oil (64.4 mg, 70% yield; 68.1 mg, 74% yield); eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) *Z* isomer δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.19 (dd, *J* = 4.8, 1.6 Hz, 3H), 7.10 (dd, *J* = 6.8, 2.8 Hz, 2H), 6.11 (q, *J* = 6.8 Hz, 1H), 4.38 (s, 2H), 1.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.2, 137.3, 133.3, 133.1, 129.9, 129.8, 129.0, 128.7, 128.6, 128.3, 128.1, 127.1, 126.2, 65.2, 57.4, 15.4, 15.1; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{15}ClO_2SNa$ 329.0373, found 329.0382.

Procedure for the Synthesis of Aliphatic Nitrocompounds. To the solution of (nitromethylene)cyclohexane **1h** (0.3 mmol) and sodium sulfinates **2** (0.45 mmol) in DMSO (3 mL) was added I_2 (10% mmol), and the mixture was stirred at 80 °C for 8 h. After the completion of the reaction, the mixture was poured into water, extracted by ethyl acetate, washed with NaCl (aq), and dried with anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure to obtain the crude product. Further purification by column chromatography on silica gel gave the allyl sulfones.

*((2-(Nitromethyl)cyclohex-2-en-1-yl)sulfonyl)benzene (**7a**):* white solid (32.9 mg, 39% yield); mp 77−79 °C; eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93−7.91 (m, 2H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 6.48 (t, *J* = 3.5 Hz, 1H), 5.75 (d, *J* = 14.0 Hz, 1H), 4.97 (d, *J* = 14.0 Hz, 1H), 4.12−4.07 (m, 1H), 2.34−2.26 (m, 1H), 2.22−2.13 (m, 1H), 2.07−1.91 (m, 2H), 1.63−1.73 (m, 1H), 1.61−1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.0, 134.0, 129.4, 128.7, 120.5, 80.5, 60.7, 25.0, 23.5, 15.7; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{15}NO_4SNa$ 304.0614, found 304.0603.

*1-Methyl-4-((2-(nitromethyl)cyclohex-2-en-1-yl)sulfonyl)benzene (**7b**):* white solid (36.3 mg, 41% yield); mp 87−89 °C; eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80−7.77 (m, 2H), 7.40−7.37 (m, 2H), 6.46 (t, *J* = 3.5 Hz, 1H), 5.74 (d, *J* = 14.0 Hz, 1H), 4.96 (d, *J* = 14.0 Hz, 1H), 4.08−4.05 (m, 1H), 2.47 (s, 3H), 2.33−2.12 (m, 2H), 2.06−1.91 (m, 2H), 1.73−1.64 (m, 1H), 1.57−1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.4, 135.0, 123.0, 128.7, 120.7, 80.5, 60.7, 25.0, 23.5, 21.7, 15.8; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{17}NO_4SNa$ 318.0770, found 318.0762.

*1-Methoxy-4-((2-(nitromethyl)cyclohex-2-en-1-yl)sulfonyl)benzene (**7c**):* colorless oil (42.0 mg, 45% yield); eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.45 (s, 1H), 5.73 (d, *J* = 13.8 Hz, 1H), 4.95 (d, *J* = 14.4 Hz, 1H), 4.03 (d, *J* = 3.0 Hz, 1H), 3.89 (s, 3H), 2.27 (d, *J* = 19.2 Hz, 1H), 2.20−2.12 (m, 1H), 1.95 (d, *J* = 15.0 Hz, 2H), 1.71−1.65 (m, 1H), 1.59−1.51 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 143.3, 130.8, 129.3, 120.8, 114.5, 80.5, 60.9, 55.7, 25.0, 23.5 15.8; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{17}NO_5SNa$ 334.0720, found 334.0718.

*1-Bromo-4-((2-(nitromethyl)cyclohex-2-en-1-yl)sulfonyl)benzene (**7d**):* colorless oil (36.7 mg, 34% yield); eluent = EtOAc/petroleum ether (v/v = 1:20); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 21.0, 8.4 Hz, 4H), 6.50 (s, 1H), 5.75 (d, *J* = 13.8 Hz, 1H), 4.98 (d, *J* = 13.8 Hz, 1H), 4.09 (s, 1H), 2.31 (d, *J* = 19.2 Hz, 1H), 2.23−2.15 (m, 1H), 1.98−2.02 (m, 1H), 1.90 (dd, *J* = 15.0, 2.4 Hz, 1H), 1.68−1.74 (m, 1H), 1.60 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 136.9, 132.79, 130.29, 129.59, 120.2, 80.5, 60.7, 24.9, 23.5, 15.7; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{14}BrNO_4SNa$ 383.9699, found 383.9693.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b02595.

Other reaction conditions screening, reaction profile, deuterium-labeling experiments, scanned copies of ^{1}H and ^{13}C NMR spectra of the synthesized compounds, and X-ray diffraction analysis of compounds **7a** and **8** (PDF)

Crystallographic data for compound **7a** (CCDC 1565191) (CIF)

Crystallographic data for compound **8** (CCDC 1565190) (CIF)

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Notes

The authors declare no competing financial interest.

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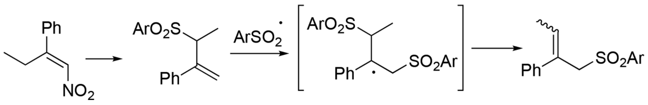
(17) A 10 mmol scale of the reaction between **1a** and **2a** was operated under either thermal or radical conditions. Both conditions gave a similar isolated yield of **3a** (80% in thermal conditions and 83% in oxidative conditions), which indicated this protocol is practical.

(18) Proposed mechanism involved in a sequential sulfonyl radical addition:



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■ NOTE ADDED AFTER ASAP PUBLICATION

The enantioselectivity was removed from the names of compound **7a−d** on February 16, 2018.

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