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# Tungsten-Catalyzed Allylic Substitution with a Heteroatom Nucleophile: Reaction Development and Synthetic Applications

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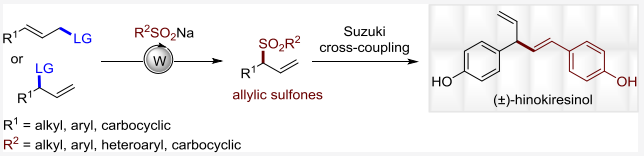
**ABSTRACT:** A tungsten-catalyzed allylic allylation of sodium sulfinate as the heteroatom nucleophile was developed. The reaction utilizes inexpensive and readily available $(CH_3CN)_3W(CO)_3$ as a precatalyst and proceeds at 60 °C temperature in the presence of 2,2′-bipyridine and its derivatives as ligand. The synthetic utility of allylic sulfones as electrophile was further demonstrated through Suzuki−Miyaura cross-coupling as showcased by the formal synthesis of (±)-hinokiresinol.




## INTRODUCTION

Transition-metal-catalyzed allylic substitution reactions have enjoyed widespread applications in organic synthesis over the past 50 years. While palladium catalysis has always been a choice in the vast majority of these reactions,[1] other metal catalysis has found application in selected cases. Catalysts derived from other transition metals[2] were relatively less studied, but showed high regioselectivity, with iridium catalysis being the most effective.[3] The Trost group[4,5] in 1983 discovered that (group 6 metals) molybdenum (Mo) and tungsten (W) provided regiochemistry, which was complementary to palladium catalysis, with Mo and W affording a branched product compared to that derived from Pd catalysis. Further significant contributions to this area have been reported by the groups of Moberg,[6] Hughes,[7] Pfaltz,[8] and others,[9] realizing transformations with only carbon-based nucleophiles. In addition, very recently, we have disclosed the first general example of Mo-catalyzed allylic substitution to form a tetrasubstituted C−S bond, demonstrating the prospects of group 6 metal catalysis in the context of carbon−heteroatom bond formation chemistry.[10] On the other hand, since its discovery, studies into the corresponding catalysis with tungsten (W) have remained underdeveloped for decades. In contrast to the potential advantages of W catalysis, which include inherent similarity to the versatile Mo (and Pd) catalysts, literature reports on W-catalyzed allylic substitution revealed only a few examples with carbon nucleophiles (Figure 1A, left),[11] with the allylic substitution of heteroatom nucleophiles remaining unknown (Figure 1A, right).[12] Therefore, given the utility of the branched, α-substituted vinylated heteroatom compounds and the difficulty of accessing them by conventional methods, development of such reactions would be highly important.

Considering these circumstances, our interest in group 6 metal catalysis[10,13] arose from a need to find a novel W-catalyzed allylic substitution reaction to form carbon−heteroatom bond with characteristic synthetic utility. This study will provide a direct approach to the regioselective formation of branched allylic sulfones since they serve as building blocks in various organic transformation and pharmaceutical industry (Figure 1B).[14,15] Herein, we report our investigation from this study. The salient features of this methodology are the cost-efficient and simple procedures, high regioselectivity, and excellent functional-group tolerance for both allylic electrophiles and sodium sulfinate. Furthermore, the high reactivity of allylic sulfones as a new class of electrophile[16] to form biologically important compounds through cross-coupling reactions is the special characteristic of this catalytic system.

## RESULTS AND DISCUSSION

To develop a catalytic reaction, we used allyl acetate (**1a**) and **2a** as the test reaction in tetrahydrofuran (THF) at 60 °C. We found that $W(CO)_6$ failed to catalyze the reaction (Table 1, entry 1). Similarly, $(CH_3CN)_3W(CO)_3$ led to a slow reaction (entry 2). Based on literature reports and our recent work,[10] the use of a stronger σ-donor-type ligand such as bipyridine[17] is to facilitate opening a coordination site on the tungsten, which leads to a significant improvement (entry 3). A more general reaction resulted when allylic carbonate (**1b**), a slightly better leaving group, was replaced for **1a** (entry 4). To further investigate the role of leaving group on allylic electropile, substrate **1c** was able to provide the desired branched product in a comparatively high yield (entry 5). By changing the reaction medium from THF to EtOH, the reaction efficiency was remarkably improved and the expected branched product

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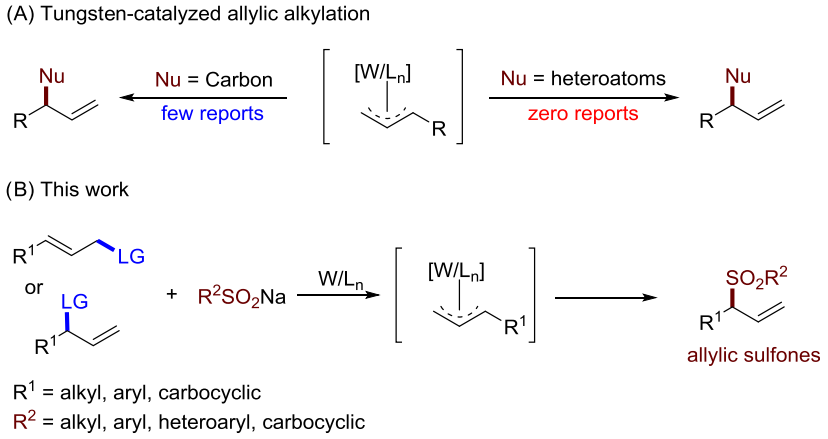
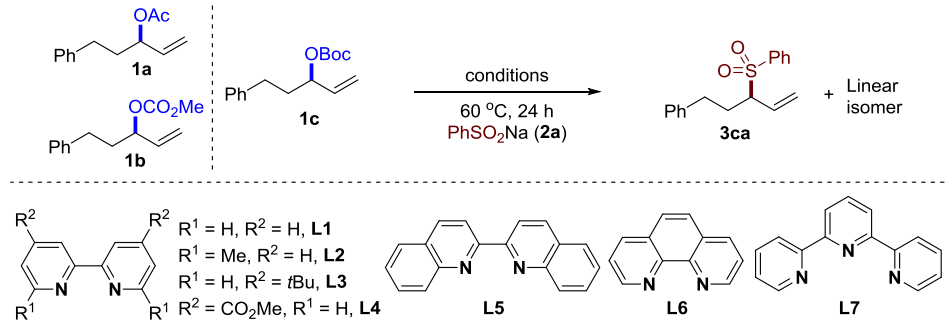



**Figure 1.** Limitations in W-catalyzed allylic alkylation (A), current work (B).

**Table 1. Optimization of the Reaction Parameters**[a]




| entry | conditions | b/l[b] | yield (%)[c] |
|---|---|---|---|
| 1 | **1a**, $W(CO)_6$/THF | | |
| 2 | **1a**, $(CH_3CN)_3W(CO)_3$/THF | | <5[d] |
| 3 | **1a**, $(CH_3CN)_3W(CO)_3$/**L1**/THF | 10:1 | 15 |
| 4 | **1b**, $(CH_3CN)_3W(CO)_3$/**L1**/THF | 10:1 | 22 |
| 5 | **1c**, $(CH_3CN)_3W(CO)_3$/**L1**/THF | 10:1 | 32 |
| 6 | **1c**, $(CH_3CN)_3W(CO)_3$/**L1**/EtOH | >20:1 | 91 |
| 7 | **1c**, $(CH_3CN)_3W(CO)_3$/**L1**/$^i$PrOH | >19:1 | 45 |
| 8 | **1c**, $(CH_3CN)_3W(CO)_3$/**L1**/toluene | | <10[d] |
| 9 | **1c**, $(CH_3CN)_3W(CO)_3$/**L1**/$CH_2Cl_2$ | | <10[d] |
| 10 | **1c**, $(CH_3CN)_3W(CO)_3$/**L2**/EtOH | >20:1 | 87 |
| 11 | **1c**, $(CH_3CN)_3W(CO)_3$/**L3**/EtOH | >20:1 | 95 |
| 12 | **1c**, $(CH_3CN)_3W(CO)_3$/**L4**/EtOH | >20:1 | 65 |
| 13 | **1c**, $(CH_3CN)_3W(CO)_3$/**L5**/EtOH | 15:1 | 20 |
| 14 | **1c**, $(CH_3CN)_3W(CO)_3$/**L6**/EtOH | | <10[d] |
| 15 | **1c**, $(CH_3CN)_3W(CO)_3$/**L7**/EtOH | | <10[d] |
| 16[d] | **1c**, $(CH_3CN)_3W(CO)_3$/**L1**/EtOH | >20:1 | 36 |
| 17 | **1c**, without W or ligand | | |

[a]Reaction conditions: W catalyst (10 mol %), ligand (15 mol %), **1a**–**c** (0.2 mmol), $PhSO_2Na$ **2a** (0.30 mmol), solvent (1.0 mL, 0.2 M), 60 °C, 24 h. [b]Branched-to-linear ratio was determined by $^1H$ NMR of crude reaction mixture. [c]Isolated yields. [d]The reaction was performed at room temperature (25 °C).

**3ca** was obtained in 91% isolated yield with excellent branched regioselectiviy (entry 6). Subtle changes on the solvent, however, had a negative effect on the reaction to occur, consistently providing lower yields if any (entries 7–9). A further evaluation of ligands revealed that 6,6′-dimethyl-2,2′-bipyridine (**L2**) decreases the efficiency, while 4,4′-di-tert-butyl-2,2′-bipyridine (**L3**) demonstrated superior performance to all of the ligands utilized (entries 10–15). The reaction was also performed at room temperature, providing excellent regioselectivity albeit with a reasonable decrease in performance (entry 16). As expected, control experiments supported that all of the catalyst components (W and ligand) were necessary for the reaction to proceed (entry 17).

The substrate scope of the W-catalyzed allylic sulfonylation with respect to allylic electrophile is summarized in Table 2. Branched allyl carbonates with alkyl substituents (entries, 1–6) afforded branched products in excellent yield and regioselectivity, irrespective of the size of the alkyl group (**1c**–**h**). Allylic electrophiles with unsubstituted or substituted group on the phenyl ring were successfully employed in the


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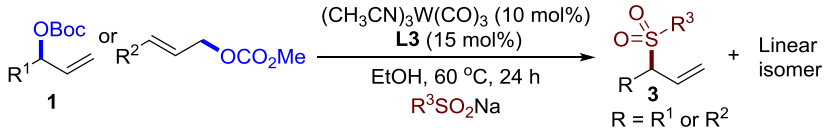
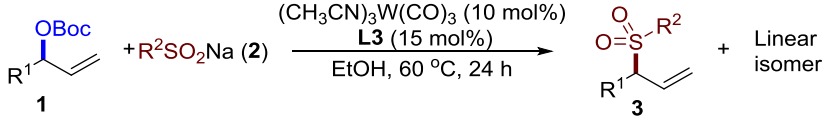
**Table 2. Reaction Scope with Respect to Allylic Electrophiles**[a]




| entry | 1 | $R^3$ | b/l[b] | yield (%)[c] |
|---|---|---|---|---|
| 1 | $R^1$ = $CH_2CH_2Ph$ (**1c**) | Ph | >20:1 | 95 (**3ca**) |
| 2 | $R^1$ = $CH_3CH_2CH_2$ (**1d**) | Ph | >20:1 | 87 (**3da**) |
| 3 | $R^1$ = Cy (**1e**) | Ph | 9:1 | 56 (**3ea**) |
| 4 | $R^1$ = $CH_2(CH_2)_7CH_3$ (**1f**) | Ph | >20:1 | 89 (**3fa**) |
| 5 | $R^1$ = $CH_2CH_2CHCH_2$ (**1g**) | Ph | >20:1 | 91 (**3ga**) |
| 6 | $R^1$ = $Cl(CH_2)_2CH_2$ (**1h**) | Ph | >20:1 | 82 (**3ha**) |
| 7 | $R^1$ = Ph (**1i**) | Ph | >19:1 | 84 (**3ia**) |
| 8 | $R^1$ = 4-$ClC_6H_4$ (**1j**) | Ph | >19:1 | 82 (**3ja**) |
| 9 | $R^1$ = 4-$MeOC_6H_4$ (**1k**) | Ph | >19:1 | 92 (**3ka**) |
| 10 | $R^2$ = Me (**1l**) | Ph | >19:1 | 76 (**3la**) |
| 11 | $R^2$ = Ph (**1m**) | Ph | >19:1 | 81 (**3ia**) |
| 12 | $R^2$ = 4-$MeOC_6H_4$ (**1n**) | Ph | >19:1 | 85 (**3ka**) |
| 13 | $R^2$ = $PhCH_2CH_2$ (**1o**) | *p*-tol | >19:1 | 89 (**3ob**) |
| 14 | $R^2$ = Cy (**1p**) | *p*-tol | 10:1 | 72 (**3pb**) |

[a]Reaction conditions: W catalyst (10 mol %), ligand **L3** (15 mol %), **1** (0.2 mmol), $R^3SO_2Na$ (**2a** or **2b**) (0.30 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 h. [b]Branched-to-linear ratio was determined by $^1H$ NMR of crude reaction mixture. [c]Isolated yields.

**Table 3. Reaction Scope with Respect to Sulfinate Nucleophile**[a]




| entry | 1 | 2 | 3 | b/l[b] | yield (%)[c] |
|---|---|---|---|---|---|
| 1 | **1c** | **2b** ($R^2$ = 4-$MeC_6H_4$) | **3ob** | >20:1 | 94 |
| 2 | **1c** | **2c** ($R^2$ = 4-$MeOC_6H_4$) | **3cc** | >20:1 | 92 |
| 3 | **1c** | **2d** ($R^2$ = 4-$ClC_6H_4$) | **3cd** | >19:1 | 89 |
| 4 | **1c** | **2e** ($R^2$ = 4-$FC_6H_4$) | **3ce** | >19:1 | 85 |
| 5 | **1c** | **2f** ($R^2$ = 2,4-$MeOC_6H_3$) | **3cf** | >20:1 | 90 |
| 6 | **1c** | **2g** ($R^2$ = 2-MeO, 5-$BrC_6H_3$) | **3cg** | >20:1 | 86 |
| 7 | **1c** | **2h** ($R^2$ = 2-naphthyl) | **3ch** | >19:1 | 94 |
| 8 | **1c** | **2i** ($R^2$ = 2,3-dihydrobenzofuryl) | **3ci** | >19:1 | 92 |
| 9 | **1c** | **2j** ($R^2$ = 2-thienyl) | **3cj** | >19:1 | 85 |
| 10 | **1c** | **2k** ($R^2$ = Me) | **3ck** | >20:1 | 78 |
| 11 | **1c** | **2l** ($R^2$ = Et) | **3cl** | >20:1 | 82 |
| 12 | **1c** | **2m** ($R^2$ = cyclopropyl) | **3cm** | >20:1 | 76 |
| 13 | **1i** | **2b** ($R^2$ = 4-$MeC_6H_4$) | **3ib** | >19:1 | 87 |
| 14 | **1i** | **2c** ($R^2$ = 4-$MeOC_6H_4$) | **3ic** | >19:1 | 90 |
| 15 | **1i** | **2d** ($R^2$ = 4-$ClC_6H_4$) | **3id** | >19:1 | 86 |
| 16 | **1i** | **2e** ($R^2$ = 4-$FC_6H_4$) | **3ie** | >19:1 | 78 |
| 17 | **1i** | **2n** ($R^2$ = 4-$CNC_6H_4$) | **3in** | >19:1 | 80 |
| 18 | **1i** | **2o** ($R^2$ = 4-$NO_2C_6H_4$) | **3io** | >19:1 | 81 |
| 19 | **1i** | **2p** ($R^2$ = 3-$BrC_6H_4$) | **3ip** | >19:1 | 86 |

[a]Reaction conditions: W catalyst (10 mol %), ligand **L3** (15 mol %), **1** (0.2 mmol), $R^2SO_2Na$ **2** (0.30 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 h. [b]Branched-to-linear ratio was determined by $^1H$ NMR of crude reaction mixture. [c]Isolated yields.

desired C−S bond formation (entries 7−9). Linear allyl carbonates with methyl (**1l**) or phenyl (**1m**) groups exclusively afforded the branched product (entries 10 and 11), suggesting a negligible decrease in yield. Allyl carbonate containing a 4-methoxyphenyl (**1n**), $PhCH_2CH_2$ (**1o**), or cyclohexyl (**1p**) group produced the products in a high yield while maintaining the excellent regioselectivity (entries 12−14).

The substrate scope with respect to sulfinate nucleophile is summarized in Table 3. Sulfinate salt with both electron-withdrawing and electron-donating substituents on the aromatic ring underwent sulfonylation in high yield and absolute regioselectivity (entries 1−6). The sulfinate salt with bulky naphthyl (**2h**), 2,3-dihydrobenzofuryl (**2i**), and 2-thienyl (**2j**) as nucleophile also afforded satisfactory results (entries 7−9). Alkyl-substituted sodium sulfinates also returned the desired branched product in high yields (entries 10−12). Various sulfinate salts with different electronic nature were coupled with phenyl allylic carbonate (**1i**) in good yield with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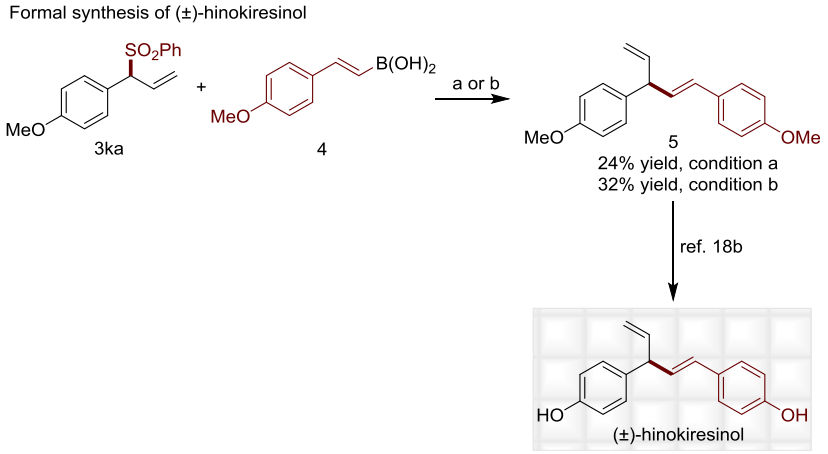
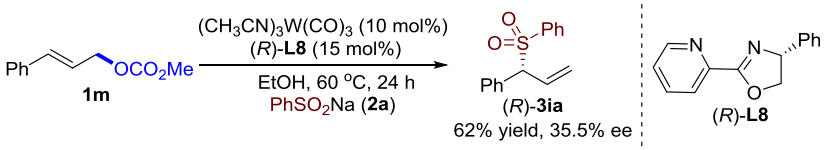



**Figure 2.** Formal synthesis of (±)-hinokiresinol. Reaction conditions: (a) $Ni(cod)_2$ (10 mol %) BrettPhos (12 mol %), **3ka** (0.2 mmol), **4** (0.2 mmol), NaOEt (2.2 equiv), PhMe (0.2 M), 24 h, 80 °C. (b) **3ka** (0.2 mmol), **4** (0.4 mmol), $[\{PdCl(allyl)\}_2]$ (5 mol %), SIPr·HCl (10 mol %), NaOH (3 equiv), dioxane/$H_2O$ = 5:3, 120 °C, 15 h.

**Scheme 1. Attempted Asymmetric W-Catalyzed Allylic Sulfonylation**




excellent regioselectivity (entries 13−19). Of particular note, in almost all cases, the reactions proceeded with excellent branched regioselectivity (>19:1).

Due to their ambiphilic nature, (allylic) sulfones have attracted special attention in allylic substitution and in Suzuki cross-coupling reactions.[16] Therefore, we decided to utilize allyl sulfone **3ka** in Suzuki−Miyaura cross-coupling to achieve formal synthesis of the (±)-hinokiresinol natural product.[18] For this purpose, synthesis of **3ka** was performed on a large scale (5.0 mmol) under standard conditions and isolated in 89% yield (1.3 g) without any loss in regioselectivity, which proved the practical use of the current protocol.[19] As illustrated in Figure 2, exposure of allylic sulfone **3ka** to boronic acid **4** (1.1 equiv) under previously reported conditions[16] produces compound **5**, which could be converted to (±)-hinokiresinol through the known procedures reported by Carreira and co-workers.[18b] Furthermore, we invision that this approach could find significant utility in the target-directed synthesis of other related compounds containing *gem*-diarylalkyl group,[20] which would have proven challenging to prepare via more conventional approaches.

To investigate the potential application of this newly developed methodology in asymmetric synthesis of allylic sulfone, a preliminary study on chiral ligand screening was probed. One result with the chiral ligand (*R*)-**L8**, the branched allylic sulfone (*R*)-**3ia** was obtained with 62% of isolated yield, excellent branched regioselectivity (>19:1), and a promising 35.5% enantiomeric excess (ee), as shown in Scheme 1.[19]

## CONCLUSIONS

In summary, a relatively mild (tungsten) W-catalyzed sulfonylation of both linear and $\alpha$-branched allylic electrophiles has been developed. By modifying the sodium sulfinate, a variety of allylic sulfones can be obtained using a simple and inexpensive catalyst system. This operationally simple reaction proceeds at a mild temperature, affording the allyl sulfones with excellent regioselectivity, good to excellent yields, and good functional-group tolerance, thus providing ample opportunities for further derivatization. Through the desulfinative cross-coupling of allylic sulfone **3ka**, we were able to achieve the formal synthesis of (±)-hinokiresinol (as presented in Figure 2). Investigations of enantioselective reactions and extension of current catalyst system to other nucleophiles are currently ongoing in our lab and will be reported in due course.

## EXPERIMENTAL SECTION

Preparative column chromatography was performed according to the Still method. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Xi'an Jiao Tong University using a QTOF microspectrometer. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded with a Varian Mercury Plus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta ($\delta$) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta ($\delta$) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. $^{13}$C NMR spectra were routinely run with broad-band decoupling. High-performance liquid chromatography (HPLC) was performed with FuLi Instruments spectrometers using a chiralcel OD-H column. Optical rotations were measured on an SGW-1 polarimeter. $W(CO)_6$, $(CH_3CN)_3W(CO)_3$, and bipyridine compounds were purchased from Energy Chemicals and Aladin/Sigma-Aldrich companies and used as received. Allylic carbonates were synthesized according to the previously reported procedure.[21] Sodium sulfinates were prepared according to a method reported in the literature.[22] All other chemicals were used as received from commercial resources.

**Synthesis and Characterization of Allylic Carbonates.** Allylic carbonates **1** were synthesized according to the previously reported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procedures.[21] All characterization data are in accordance with the literature. New substrates have been fully characterized.

*tert-Butyl Dodec-1-en-3-yl Carbonate (**1f**).* Obtained as a colorless oil (85% yield, 1.3 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.77 (ddd, $J$ = 17.2, 10.4, 7.2 Hz, 1H), 5.25 (d, $J$ = 17.2 Hz, 1H), 5.21 (d, $J$ = 10.4 Hz, 1H), 4.78 (t, $J$ = 7.2 Hz, 1H), 1.77−1.73 (m, 2H), 1.42 (s, 9H), 1.24−1.10 (m, 14H), 0.85 (t, $J$ = 6.4 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 151.9, 137.1, 115.4, 83.6, 79.0, 36.0, 31.9, 29.8, 29.5, 29.3, 27.8, 25.2, 22.6, 14.0. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{17}H_{32}O_3Na$ 307.2249; found 307.2241.

*tert-Butyl (6-Chlorohex-1-en-3-yl) Carbonate (**1h**).* Obtained as a colorless oil (80% yield, 1.4 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.99−5.92 (m, 1H), 5.17−5.11 (m, 2H), 4.69 (t, $J$ = 7.2 Hz, 1H), 3.52−3.47 (m, 2H), 1.93−1.75 (m, 4H), 1.42 (s, 9); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 151.7, 136.7, 115.8, 82.8, 79.7, 44.9, 30.7, 27.7, 27.0. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{11}H_{19}ClO_3Na$: 257.0920; found 257.0914.

*tert-Butyl (1-(4-Chlorophenyl)allyl) Carbonate (**1j**).* Obtained as colorless oil (70% yield, 1.1 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.38−7.31 (m, 4H), 6.06−5.97 (m, 2H), 5.36−5.26 (m, 2H), 1.49 (s, 9); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 152.6, 137.2, 135.7, 134.0, 128.7, 128.4, 117.6, 82.6, 78.4, 27.7. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{14}H_{17}ClO_3Na$ 291.0764; found 291.0758.

*tert-Butyl (1-(4-Methoxyphenyl)allyl) Carbonate (**1k**).* Obtained as a colorless oil (72% yield, 1.2 g); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.33 (d, $J$ = 8.4 Hz, 2H), 7.12 (d, $J$ = 8.4 Hz, 2H), 5.99−5.91 (m, 1H), 5.28 (d, $J$ = 17.2 Hz, 1H), 5.14 (d, $J$ = 10.0 Hz, 1H), 5.10 (t, $J$ = 7.2 Hz, 1H), 3.79 (s, 3H), 1.54 (s, 9); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 156.6, 150.2, 140.1, 139.9, 127.3, 121.1, 115.0, 83.4, 74.4, 55.3, 27.5. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{15}H_{20}O_4Na$ 287.1259; found 287.1251.

**General Procedure for W-Catalyzed Allylic Sulfonylation of α-Substituted Allylic Carbonate 1 with Sodium Sulfinate 2.** To an oven-dried screw-cap reaction tube equipped with a magnetic stir bar, $(CH_3CN)_3W(CO)_3$ (10 mol %), bipyridine ligand (**L3**) (15 mol %), allylic carbonate **1** (0.2 mmol), and sodium sulfinate **2** (0.3 mmol) were added. The reaction tube was sealed with a rubber septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 1 mL) was added via a syringe. The resulting mixture was stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature, and the residue was purified by flash column chromatography on silica gel to afford the pure allylic sulfone **3**.

*((5-Phenylpent-1-en-3-yl)sulfonyl)benzene (**3ca**).* Prepared from **1c** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 95% yield (54.42 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81−7.79 (m, 2H), 7.64−7.60 (m, 1H), 7.53−7.50 (m, 2H), 7.29−7.25 (m, 2H), 7.22−7.18 (m, 1H), 7.13−7.10 (m, 2H), 5.67 (dt, $J$ = 9.6, 17.2 Hz, 1H), 5.37 (d, $J$ = 10.0 Hz, 1H), 5.07 (d, $J$ = 17.2 Hz, 1H), 3.49 (t, $J$ = 7.2 Hz, 1H), 2.82−2.75 (m, 1H), 2.57−2.40 (m, 2H), 2.02−1.93 (m, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 135.1, 133.6, 130.8, 129.8, 129.4, 128.5, 128.4, 126.6, 124.2, 69.3, 32.5, 28.6. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{17}H_{18}O_2SNa$ 309.0925; found 309.0917.

*(Hex-1-en-3-ylsulfonyl)benzene (**3da**).* Prepared from **1d** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 87% yield (39.0 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.74−7.71 (m, 2H), 7.57−7.53 (m, 1H), 7.46−7.42 (m, 2H), 5.60 (dt, $J$ = 9.6, 17.2 Hz, 1H), 5.30 (d, $J$ = 10.0 Hz, 1H), 5.00 (d, $J$ = 17.2 Hz, 1H), 3.42 (t, $J$ = 7.2 Hz, 1H), 1.95−1.86 (m, 2H), 1.51−1.26 (m, 2H), 0.91 (t, $J$ = 7.4 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 136.9, 135.4, 133.5, 130.8, 128.3, 120.3, 69.6, 35.3, 16.6, 14.1. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{12}H_{16}O_2SNa$ 247.0769; found 247.0761.

*((1-Cyclohexylallyl)sulfonyl)benzene (**3ea**).* Prepared from **1e** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 56% yield (29.6 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.72−7.69 (m, 2H), 7.58−7.49 (m, 3H), 5.62 (dt, $J$ = 9.6, 17.2 Hz, 1H), 5.11 (d, $J$ = 10.0 Hz, 1H), 4.76 (d, $J$ = 17.2 Hz, 1H), 3.46 (t, $J$ = 7.2 Hz, 1H), 2.23−2.09 (m, 2H), 1.82−1.58 (m, 4H), 1.30−0.95 (m, 5H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 143.3, 136.7, 133.2, 130.5, 128.1, 119.2, 74.6, 43.1, 30.8, 30.6, 26.9, 26.6, 26.3. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{15}H_{20}O_2SNa$ 287.1082; found 287.1076.

*(Dodec-1-en-3-ylsulfonyl)benzene (**3fa**).* Prepared from **1f** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 89% yield (54.9 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.82−7.80 (m, 2H), 7.63−7.61 (m, 1H), 7.52−7.49 (m, 2H), 5.60 (dt, $J$ = 9.6, 17.2 Hz, 1H), 5.34 (d, $J$ = 10.0 Hz, 1H), 4.90 (d, $J$ = 17.2 Hz, 1H), 3.47 (t, $J$ = 7.2 Hz, 1H), 1.95−1.86 (m, 2H), 1.30−1.23 (m, 14H), 0.88 (t, $J$ = 6.4 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 135.4, 134.8, 133.5, 130.8, 128.3, 120.4, 69.5, 33.8, 31.9, 29.9, 29.5, 29.4, 29.3, 23.7, 22.7, 14.1. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{18}H_{28}O_2SNa$ 331.1708; found 331.1702.

*(Hepta-1,6-dien-3-ylsulfonyl)benzene (**3ga**).* Prepared from **1g** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 91% yield (43.0 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83−7.81 (m, 2H), 7.64−7.61 (m, 1H), 7.53−7.50 (m, 2H), 5.81−5.75 (m, 1H), 5.65−5.59 (m, 1H), 5.37 (d, $J$ = 6.8 Hz, 1H), 5.34 (d, $J$ = 10.0 Hz, 1H), 4.98 (d, $J$ = 6.8 Hz, 1H), 5.92 (d, $J$ = 17.0 Hz, 1H), 3.53 (t, $J$ = 7.2 Hz, 1H), 2.08−1.96 (m, 4H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 135.6, 135.3, 135.1, 133.6, 130.8, 128.4, 120.7, 115.3, 69.2, 31.1, 29.4. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{13}H_{16}O_2SNa$ 259.0769; found 259.0764.

*((6-Chlorohex-1-en-3-yl)sulfonyl)benzene (**3ha**).* Prepared from **1h** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 82% yield (42.4 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83−7.81 (m, 2H), 7.65−7.62 (m, 1H), 7.54−7.51 (m, 2H), 5.65 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.37 (d, $J$ = 10.0 Hz, 1H), 5.07 (d, $J$ = 17.2 Hz, 1H), 4.47−4.42 (m, 1H), 3.53 (t, $J$ = 4.4 Hz, 2H), 2.15−2.02 (m, 2H), 1.83−1.69 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 137.0, 134.3, 133.7, 130.8, 128.4, 120.9, 68.7, 43.4, 31.9, 30.4. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{12}H_{15}ClO_2SNa$ 281.0379; found 281.0371.

*((1-Phenylallyl)sulfonyl)benzene (**3ia**).*[21f] Prepared from **1i** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 84% yield (43.4 mg); NMR spectra of the obtained product were consistent with the reported one.[1f] $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.64−7.62 (m, 2H), 7.59−7.55 (m, 1H), 7.44−7.40 (m, 2H), 7.32−7.22 (m, 5H), 6.32 (dt, $J$ = 9.6, 17.2 Hz, 1H), 5.46 (d, $J$ = 10.0 Hz, 1H), 5.31 (d, $J$ = 17.2 Hz, 1H), 4.69 (d, $J$ = 8.8 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 137.4, 133.8, 132.1, 129.7, 129.3, 129.2, 128.8, 128.6, 123.5, 75.6. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{15}H_{14}O_2SNa$ 281.0612; found 281.0604.

*1-Chloro-4-(1-(phenylsulfonyl)allyl)benzene (**3ja**).* Prepared from **1j** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 82% yield (48.0 mg); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66−7.60 (m, 2H), 7.58−7.55 (m, 1H), 7.42−7.40 (m, 2H), 7.34−7.24 (m, 4H), 6.31 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.50 (d, $J$ = 10.0 Hz, 1H), 5.36 (d, $J$ = 17.2 Hz, 1H), 4.69 (d, $J$ = 8.4 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 139.1, 135.7, 131.7, 130.7, 129.7, 129.1, 129.0, 128.8, 128.7, 124.1, 75.8. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for $C_{15}H_{13}ClO_2SNa$ 315.0222; found 315.0214.

*1-Methoxy-4-(1-(phenylsulfonyl)allyl)benzene (**3ka**).*[21f] Prepared from **1k** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 92% yield (53.1 mg); NMR spectra of the obtained product were consistent with the reported one.[1f] $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.64−7.59 (m, 2H), 7.57−7.55 (m, 1H), 7.44−7.42 (m, 2H), 7.15 (d, $J$ = 9.0 Hz,


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2H), 6.82 (d, $J$ = 9.0 Hz, 2H), 6.27 (dt, $J$ = 17.0, 9.0 Hz, 1H), 5.43 (d, $J$ = 9.6 Hz, 1H), 5.27 (d, $J$ = 17.0 Hz, 1H), 4.64 (d, $J$ = 9.0 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 160.2, 133.7, 131.1, 129.7, 129.3, 129.2, 128.8, 128.6, 123.5, 114.2, 75.1, 55.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{16}H_{16}O_3SNa$ 311.0718; found 311.0712.

*(But-3-en-2-ylsulfonyl)benzene (**3la**).* Prepared from **1l** and **2a** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 76% yield (29.8 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.87−7.79 (m, 2H), 7.67−7.61 (m, 1H), 7.56−7.50 (m, 2H), 5.81 (ddd, $J$ = 17.5, 10.4, 7.6 Hz, 1H), 5.26 (d, $J$ = 10.4 Hz, 1H), 5.10 (d, $J$ = 17.2 Hz, 1H), 3.75−3.69 (m, 1H), 1.45 (d, $J$ = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 136.4, 133.5, 130.2, 128.8, 128.4, 121.5, 63.7, 12.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{10}H_{12}O_2SNa$ 219.0456; found 219.0448.

*1-Methyl-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3ob**).*[21f] Prepared from **1o** and **2b** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 89% yield (53.5 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.68−7.66 (m, 2H), 7.34−7.18 (m, 5H), 7.13−7.08 (m, 2H), 5.66 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.37 (d, $J$ = 10.0 Hz, 1H), 5.08 (d, $J$ = 17.2 Hz, 1H), 3.50−3.44 (m, 1H), 2.81−2.74 (m, 1H), 2.68−2.47 (m, 2H), 2.43 (s, 3H), 2.00−1.90 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 140.0, 134.3, 130.2, 129.4, 129.2, 128.5, 128.4, 126.3, 124.0, 69.0, 32.3, 28.4, 21.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{18}H_{20}O_2SNa$ 323.1082; found 323.1076.

*1-((1-Cyclohexylallyl)sulfonyl)-4-methylbenzene (**3pb**).*[21f] Prepared from **1p** and **2b** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 72% yield (40.1 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.59−7.56 (m, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 5.75 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.12 (d, $J$ = 10.0 Hz, 1H), 5.72 (d, $J$ = 17.2 Hz, 1H), 3.18−3.15 (m, 1H), 2.34 (s, 3H), 2.24−2.02 (m, 2H), 1.90−1.65 (m, 4H), 1.37−1.32 (m, 2), 1.20−1.02 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 143.3, 135.8, 129.0, 128.8, 128.4, 123.7, 75.7, 36.7, 32.1, 28.8, 26.5, 26.1, 26.0, 21.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{15}H_{20}O_2SNa$ 287.1082; found 287.1074.

*1-Methoxy-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3cc**).* Prepared from **1c** and **2c** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 92% yield (58.2 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.73−7.70 (m, 2H), 7.29−7.24 (m, 2H), 7.22−7.18 (m, 1H), 7.13−7.11 (m, 2H), 6.98−6.95 (m, 2H), 5.67 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.37 (d, $J$ = 10.0 Hz, 1H), 5.09 (d, $J$ = 17.2 Hz, 1H), 3.88 (s, 3H), 3.49−3.43 (m, 1H), 2.81−2.74 (m, 1H), 2.57−2.39 (m, 2H), 2.02−1.90 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 163.6, 140.1, 131.4, 130.4, 128.8, 128.5, 128.4, 126.3, 123.9, 114.0, 69.2, 55.6, 32.3, 28.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{18}H_{20}O_3SNa$ 339.1031; found 339.1024.

*1-Chloro-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3cd**).* Prepared from **1c** and **2d** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 89% yield (57.1 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.74−7.70 (m, 2H), 7.52−7.47 (m, 2H), 7.25−7.19 (m, 3H), 7.05−6.98 (m, 2H), 5.67 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.39 (d, $J$ = 10.0 Hz, 1H), 5.08 (d, $J$ = 17.0 Hz, 1H), 3.50−3.44 (m, 1H), 2.83−2.76 (m, 1H), 2.58−2.44 (m, 2H), 2.02−1.93 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.4, 138.9, 135.7, 130.6, 129.6, 129.5, 128.5, 128.4, 126.3, 124.5, 69.0, 34.6, 28.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{17}H_{17}ClO_2SNa$ 343.0535; found 343.0527.

*1-Fluoro-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3ce**).* Prepared from **1c** and **2e** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 85% yield (51.7 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.82−7.79 (m, 2H), 7.30−7.09 (m, 7H), 5.67 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.38 (d, $J$ = 10.0 Hz, 1H), 5.07 (d, $J$ = 17.0 Hz, 1H), 3.50−3.44 (m, 1H), 2.83−2.76 (m, 1H), 2.58−2.41 (m, 2H), 2.02−1.93 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 167.0, 166.7, 164.5, 164.2, 139.9, 132.1, 132.0, 130.9, 130.8, 130.0, 128.6, 128.5, 128.4, 126.4, 124.4, 116.6, 116.3, 116.2, 116.0, 69.1, 32.2, 28.3. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{17}H_{17}FO_2SNa$ 327.0831; found 327.0824.

*2,4-Dimethoxy-1-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (**3cf**).* Prepared from **1c** and **2f** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a white solid in 90% yield (62.4 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (dd, $J$ = 2.2, 8.8 Hz, 1H), 7.29−7.18 (m, 4H), 7.12−7.10 (m, 2H), 6.94 (d, $J$ = 8.4 Hz, 1H), 5.69 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.39 (d, $J$ = 10.0 Hz, 1H), 5.12 (d, $J$ = 17.0 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.50−3.44 (m, 1H), 2.81−2.75 (m, 1H), 2.57−2.49 (m, 1H), 2.45−2.36 (m, 1H), 2.02−1.92 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 153.2, 148.8, 140.0, 130.2, 128.9, 128.5, 128.4, 126.3, 123.9, 123.3, 111.3, 110.3, 69.1, 56.2, 56.1, 32.3, 28.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{19}H_{22}O_4SNa$ 369.1136; found 369.1128.

*4-Bromo-1-methoxy-2-((5-phenylpent-1-en-3-yl)sulfonyl)-benzene (**3cg**).* Prepared from **1c** and **2g** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a white solid in 86% yield (68.0 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$ = 1.2 Hz, 1H), 7.63 (dd, $J$ = 1.2, 8.8 Hz, 1H), 7.33−7.12 (m, 5H), 6.82 (d, $J$ = 8.8 Hz, 1H), 5.72 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.35 (d, $J$ = 10.0 Hz, 1H), 5.14 (d, $J$ = 17.0 Hz, 1H), 4.05−3.99 (m, 1H), 3.73 (s, 3H), 2.88−2.81 (m, 1H), 2.60−2.50 (m, 1H), 2.36−2.28 (m, 1H), 2.15−2.05 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 156.1, 140.1, 137.9, 136.9, 133.4, 128.5, 128.4, 126.2, 123.7, 121.0, 113.7, 112.8, 66.3, 56.2, 32.0, 27.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{18}H_{19}BrO_3SNa$ 417.0136; found 417.0128.

*2-((5-Phenylpent-1-en-3-yl)sulfonyl)naphthalene (**3ch**).* Prepared from **1c** and **2h** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a white solid in 94% yield (63.3 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.38 (s, 1H), 8.01−7.93 (m, 2H), 7.81−7.77 (m, 1H), 7.68−7.62 (m, 2H), 7.27−7.16 (m, 3H), 7.12−7.05 (m, 3H), 5.72 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.36 (d, $J$ = 10.0 Hz, 1H), 5.07 (d, $J$ = 17.0 Hz, 1H), 3.61−3.56 (m, 1H), 2.83−2.75 (m, 1H), 2.58−2.45 (m, 2H), 2.08−1.98 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.6, 135.0, 132.2, 131.0, 129.7, 129.5, 129.3, 129.1, 128.5, 128.4, 127.9, 127.6, 127.5, 126.3, 126.2, 123.0, 69.0, 34.7, 28.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{21}H_{20}O_2SNa$ 359.1082; found 359.1076.

*6-((5-Phenylpent-1-en-3-yl)sulfonyl)-2,3-dihydrobenzofuran (**3ci**).* Prepared from **1c** and **2i** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a white solid in 92% yield (60.4 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.70−7.56 (m, 2H), 7.30−7.26 (m, 2H), 7.22−7.18 (m, 1H), 7.14−7.10 (m, 2H), 6.83 (d, $J$ = 8.4 Hz, 1H), 5.68 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.39 (d, $J$ = 10.0 Hz, 1H), 5.12 (d, $J$ = 17.0 Hz, 1H), 4.69 (t, $J$ = 8.8 Hz, 2H), 3.49−3.43 (m, 1H), 3.26 (t, $J$ = 8.8 Hz, 2H), 2.82−2.74 (m, 1H), 2.56−2.39 (m, 2H), 1.99−1.90 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 164.6, 140.1, 130.9, 130.4, 128.7, 128.5, 128.4, 128.1, 126.2, 123.9, 109.3, 72.3, 69.2, 32.3, 28.9, 28.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{19}H_{20}O_3SNa$ 351.1031; found 351.1023.

*2-((5-Phenylpent-1-en-3-yl)sulfonyl)thiophene (**3cj**).* Prepared from **1c** and **2j** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 85% yield (49.7 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 (dd, $J$ = 1.2, 5.2 Hz, 1H), 7.60 (dd, $J$ = 1.2, 5.2 Hz, 1H), 7.30−7.27 (m, 2H), 7.23−7.19 (m, 1H), 7.15−7.12 (m, 3H), 5.73 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.44 (d, $J$ = 10.0 Hz, 1H), 5.19 (d, $J$ = 17.0 Hz, 1H), 3.00−3.54 (m, 1H), 2.83−2.77 (m, 1H), 2.60−2.45 (m, 2H), 2.05−1.96 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.9, 138.0, 135.2, 134.2,


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129.9, 128.6, 128.4, 127.6, 126.4, 124.4, 70.1, 32.3, 28.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{15}H_{16}O_2S_2Na$ 315.0489; found 315.0481.

*(3-(Methylsulfonyl)pent-4-en-1-yl)benzene (**3ck**).* Prepared from **1c** and **2k** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 78% yield (35.0 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.34−7.17 (m, 5H), 5.87 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.58 (d, $J$ = 10.0 Hz, 1H), 5.44 (d, $J$ = 17.2 Hz, 1H), 3.46−3.40 (m, 1H), 2.89−2.83 (m, 1H), 2.82 (s, 3H), 2.63−2.44 (m, 2H), 2.08−1.99 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.8, 131.3, 128.6, 128.5, 126.4, 124.1, 67.7, 38.1, 32.0, 27.0. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{12}H_{16}O_2SNa$ 247.0769; found 247.0763.

*(3-(Ethylsulfonyl)pent-4-en-1-yl)benzene (**3cl**).* Prepared from **1c** and **2l** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a colorless oil in 82% yield (39.1 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.34−7.17 (m, 5H), 5.85 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.54 (d, $J$ = 10.0 Hz, 1H), 5.40 (d, $J$ = 17.0 Hz, 1H), 3.49−3.43 (m, 1H), 2.97 (dd, $J$ = 11.6, 19.2 Hz, 2H), 2.88−2.81 (m, 1H), 2.62−2.43 (m, 2H), 2.10−2.01 (m, 1H), 1.33 (t, $J$ = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.9, 131.4, 128.6, 128.4, 126.4, 121.1, 65.5, 44.5, 32.1, 26.8, 6.0. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{13}H_{18}O_2SNa$ 261.0925; found 261.0916.

*(3-(Cyclopropylsulfonyl)pent-4-en-1-yl)benzene (**3cm**).* Prepared from **1c** and **2m** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 20:1) on silica gel to obtain the title compound as a white colorless oil in 76% yield (38.1 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.33−7.17 (m, 5H), 5.87 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.54 (d, $J$ = 10.0 Hz, 1H), 5.44 (d, $J$ = 17.0 Hz, 1H), 3.51−3.45 (m, 1H), 2.87−2.80 (m, 1H), 2.62−2.55 (m, 1H), 2.52−2.43 (m, 1H), 2.40−2.34 (m, 1H), 2.12−2.02 (m, 1H), 1.31−1.22 (m, 2H), 1.03−0.94 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.1, 131.0, 128.5, 128.4, 126.3, 123.7, 67.2, 32.1, 27.6, 27.4, 4.8, 4.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{14}H_{18}O_2SNa$ 273.0925; found 273.0916.

*1-Methyl-4-((1-phenylallyl)sulfonyl)benzene (**3ib**).*[21f] Prepared from **1i** and **2b** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 87% yield (47.4 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.50 (d, $J$ = 8.4 Hz, 2H), 7.32−7.23 (m, 7H), 6.30 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.45 (d, $J$ = 10.0 Hz, 1H), 5.30 (d, $J$ = 17.2 Hz, 1H), 4.67 (d, $J$ = 9.2 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 134.2, 132.1, 129.7, 129.3, 129.2, 128.8, 128.6, 123.5, 75.6, 21.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{16}H_{16}O_2SNa$ 295.0769; found 295.0762.

*1-Methoxy-4-((1-phenylallyl)sulfonyl)benzene (**3ic**).* Prepared from **1i** and **2c** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 90% yield (51.9 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, $J$ = 8.8 Hz, 2H), 7.33−7.22 (m, 5H), 6.87 (d, $J$ = 8.8 Hz, 2H), 6.31 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.45 (d, $J$ = 10.0 Hz, 1H), 5.31 (d, $J$ = 17.2 Hz, 1H), 4.66 (d, $J$ = 9.2 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 163.6, 132.4, 131.4, 129.7, 129.4, 128.7, 128.5, 123.4, 113.8, 75.8, 55.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{16}H_{16}O_3SNa$ 311.0718; found 311.0718.

*1-Chloro-4-((1-phenylallyl)sulfonyl)benzene (**3id**).* Prepared from **1i** and **2d** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 86% yield (50.4 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.56 (d, $J$ = 8.0 Hz, 2H), 7.64−7.23 (m, 7H), 6.30 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.49 (d, $J$ = 10.0 Hz, 1H), 5.35 (d, $J$ = 17.2 Hz, 1H), 4.68 (d, $J$ = 9.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.4, 135.6, 131.7, 130.7, 129.7, 129.1, 128.9, 128.8, 128.7, 124.1, 75.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{15}H_{13}ClO_2SNa$ 315.0222; found 315.0214.

*1-Fluoro-4-((1-phenylallyl)sulfonyl)benzene (**3ie**).* Prepared from **1i** and **2e** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a yellow solid in 78% yield (43.1 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.64−7.61 (m, 2H), 7.33−7.23 (m, 5H), 7.12−7.07 (m, 2H), 6.31 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.49 (d, $J$ = 10.0 Hz, 1H), 5.35 (d, $J$ = 17.2 Hz, 1H), 4.68 (d, $J$ = 9.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 167.0, 164.5, 133.2, 133.1, 132.1, 132.0, 131.9, 129.6, 129.0, 128.9, 128.7, 124.0, 116.0, 115.8, 75.8. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{15}H_{13}FO_2SNa$ 299.0518; found 299.0512.

*4-((1-Phenylallyl)sulfonyl)benzonitrile (**3in**).* Prepared from **1i** and **2n** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 80% yield (56.3 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.75−7.70 (m, 4H), 7.36−7.29 (m, 3H), 7.25−7.22 (m, 2H), 6.30 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.53 (d, $J$ = 10.0 Hz, 1H), 5.42 (d, $J$ = 17.2 Hz, 1H), 4.71 (d, $J$ = 9.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 141.5, 132.3, 131.1, 129.9, 129.6, 129.3, 128.9, 128.2, 124.6, 117.3, 117.1, 75.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{16}H_{13}NO_2SNa$ 306.0565; found 306.0558.

*1-Nitro-4-((1-phenylallyl)sulfonyl)benzene (**3io**).* Prepared from **1i** and **2o** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a white solid in 81% yield (49.1 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.26 (d, $J$ = 8.8 Hz, 2H), 7.82 (d, $J$ = 8.8 Hz, 2H), 7.36−7.24 (m, 5H), 6.32 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.54 (d, $J$ = 10.0 Hz, 1H), 5.39 (d, $J$ = 17.2 Hz, 1H), 4.74 (d, $J$ = 9.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 150.7, 143.0, 130.7, 129.7, 129.4, 128.9, 128.1, 124.8, 123.7, 118.2, 75.8. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{15}H_{13}NO_4SNa$ 326.0463; found 326.0455.

*1-Bromo-3-((1-phenylallyl)sulfonyl)benzene (**3ip**).* Prepared from **1i** and **2p** by following the general procedure. Purification was performed with flash column chromatography (PE/EA = 10:1) on silica gel to obtain the title compound as a yellow oil in 86% yield (58.0 mg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (s, 1H), 7.69 (d, $J$ = 8.0 Hz, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.36-7.24 (m, 6H), 6.31 (dt, $J$ = 10.0, 17.2 Hz, 1H), 5.50 (d, $J$ = 10.0 Hz, 1H), 5.35 (d, $J$ = 17.2 Hz, 1H), 4.69 (d, $J$ = 9.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.9, 136.6, 132.1, 131.5, 130.0, 129.7, 129.1, 128.7, 128.6, 127.8, 124.2, 122.7, 75.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{15}H_{13}BrO_2SNa$ 358.9717; found 358.9709.

**Scale-up Experiment and Synthesis of (±)-Hinokiresinol.** *Scale-up Experiment.* To an oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar, $(CH_3CN)_3W(CO)_3$ (145.5 mg, 10 mol %), 4,4′-di-*tert*-butyl-2,2′-bipyridine ligand (**L3**) (201.3 mg, 15 mol %), allylic carbonate **1k** (1.32 g, 5.0 mmol), and sodium benzenesulfinate **2a** (1.23 g, 7.5 mmol) were added. The reaction flask was sealed with a rubber septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 25 mL) was added via a syringe. The resulting mixture was stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature and concentrated. The obtained crude mixture was purified by flash column chromatography on silica gel to afford the pure allylic sulfone **3ka** in 89% (1.3 g) isolated yield. The branched-to-linear ratio is 19:1.

**Synthesis of (±)-Hinokiresinol.** *Condition A.* Following the literature procedure[16a] by Crudden and co-workers, with some modifications: under nitrogen environment, to an oven-dried screw-cap reaction tube equipped with a magnetic stir bar, $Ni(cod)_2$ (10 mol %), BrettPhos (12 mol %), and NaOEt (2.2 equiv) were added. Then, allylic sulfone **3ka** (0.2 mmol), boronic acid **4** (1.0 equiv), and toluene (0.2 M) were also added. The reaction tube was capped, sealed, and stirred at 80 °C for 20 h. After completion, the reaction mixture was cooled to room temperature and then diluted with EtOAc and saturated aqueous $NH_4Cl$ (0.2 mL) was added. The reaction mixture was then filtered and washed with EtOAc. The obtained residue was concentrated and purified by flash column chromatography on silica gel to afford pure **5** as a colorless oil (15.6 mg, 24%).

*Condition B.* By following the literature procedure,[16b] to an oven-dried screw-cap reaction tube (10 mL) with a magnetic stir bar, $[PdCl(allyl)]_2$ (3.7 mg, 5 mol %), SIPr·HCl (8.5 mg, 10 mol %), dry


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dioxane (0.5 mL), and 1M $NaOH_{aq}$ (0.6 mL, 0.6 mmol) were added at room temperature under the nitrogen atmosphere. After stirring for 30 min, allylic sulfone **3ka** (57.67 mg, 0.2 mmol), boronic acid **4** (71.2 mg, 0.4 mmol), and dry dioxane (0.5 mL) were added. The reaction tube was sealed and was stirred at 120 °C for 15 h. The reaction mixture was cooled to room temperature and then diluted with EtOAc, and saturated aqueous $NH_4Cl$ (0.2 mL) was added. The mixture was filtered and washed with EtOAc. The obtained residue was concentrated and purified by flash column chromatography on silica gel to afford pure **5** as a colorless oil (18 mg, 32%). This compound can be converted to (±)-**hinokiresinol** by following the reported literature procedures.[18b] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.36−7.31 (m, 2H), 7.22−7.17 (m, 2H), 6.92−6.83 (m, 4H), 6.39 (d, $J$ = 16.0 Hz, 1H), 6.27 (dd, $J$ = 16.0, 6.8 Hz, 1H), 6.11 (ddd, $J$ = 17.1, 10.2, 6.8 Hz, 1H), 5.17 (dt, $J$ = 10.2, 1.6 Hz, 1H), 5.14 (dt, $J$ = 17.1, 1.6 Hz, 1H), 4.18 (t, $J$ = 6.8 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 158.7, 158.1, 140.5, 134.7, 130.1, 130.0, 129.8, 129.1, 127.4, 115.2, 113.8, 55.1, 51.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for $C_{13}H_{18}O_3SNa$ 277.0869; found 277.0871. The overall spectroscopic data are in complete agreement with assigned structures and fully consistent with the reported literature.[18b]

*W-Catalyzed Asymmetric Allylic Sulfonylation*. As described in Scheme 1 of the main text, allylic sulfonylation of **1m** with (*R*)-**L8** as a chiral ligand occurred in 35.5% ee. Further studies including evaluation of other reaction parameters and chiral ligands are currently in progress.

## EXPERIMENTAL PROCEDURE

To an oven-dried screw-cap reaction tube equipped with a magnetic stirrer, $(CH_3CN)_3W(CO)_3$ (7.8 mg, 10 mol %), (*R*)-**L8** as the chiral ligand (6.7 mg, 15 mol %), allylic carbonate **1m** (38.44 mg, 0.2 mmol), and sodium benzenesulfinate **2a** (49.25 mg, 0.3 mmol) were added. The reaction tube was sealed with a rubber septum, then evacuated and backfilled with nitrogen. Anhydrous ethanol (0.2 M, 1 mL) was added via a syringe. The resulting mixture was stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature, and the residue was purified by flash column chromatography on silica gel to afford the pure allylic sulfone (*R*)-**3ia** with 62% isolated yield. The branched-to-linear ratio was determined to be 10:1. Analytical data of the pure (*R*)-**3ia** product are similar to the corresponding racemate **3ia**. Enantiomeric excess of (*R*)-**3ia** was determined by HPLC analysis.[21f] HPLC conditions: Chiralcel OD-H column, 254 nm; flow rate: 1 mL/min; *i*-PrOH/hexanes: 1/9; $t_{minor}$: 10.87 min; $t_{major}$: 11.72 min; 35.5% ee. $[\alpha]_D^{25}$ = 19.5 ($c$ = 0.52, $CHCl_3$).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01632.

Spectral data of all prepared compounds with copies of $^1H$, $^{13}C$ NMR spectra and HPLC chromatograms (PDF)

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### Author Contributions

†Y.X. and M.S. contributed equally to this work.


### Notes

The authors declare no competing financial interest.

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