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Reciprocal-Activation Strategy for Allylic Sulfination with Unactivated Allylic Alcohols

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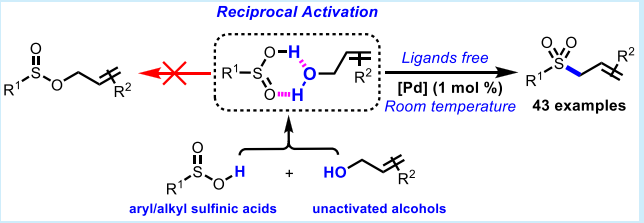
ABSTRACT: A reciprocal-activation strategy for allylic sulfination with unactivated allylic alcohols was developed. In this reaction, the hydrogen bond interaction between allylic alcohols and sulfinic acids allowed for reciprocal activation, which enabled a dehydrative cross-coupling process to occur under mild reaction conditions. This reaction worked in an environmentally friendly manner, yielding water as the only byproduct. A variety of allylic sulfones could be obtained in good to excellent yields with wide functional group tolerance. In gram scale reactions, allylic sulfones could be conveniently isolated in high yield by filtration.



Allylic sulfones are important moieties in both organic synthesis[1] and pharmaceutical development because they are featured widely in many biologically and pharmaceutically active molecules[2] (such as anticancer agents,[2a] cysteine protease inhibitors,[2b] antibacterial agents,[2c] etc.[2d−j]). Therefore, great attention has been devoted to accessing this framework. Common methods reported in the literature usually employed the classical transition metal-catalyzed allylic substitution reactions.[3] Unfortunately, only functionalized allylic compounds (allylic halides or their equivalents) and active sulfonyl precursors could be incorporated into the desired transformations.[3] Moreover, the hazardous stoichiometric byproducts of these reactions are incongruous with the principles of atom economy and are of environmental concerns. Despite some impressive advancements in the preparation of allylic sulfones, such as transition metal-catalyzed hydrosulfination,[4] SO_2 insertion protocols,[5] etc.,[6,7] tedious preparation of the starting materials and the low atom efficiency for the overall transformation limit the wide application of these methods. To date, allylic alkylation of sulfonyl precursors was the state of art to access allylic sulfones. Therefore, an alternative catalytic reaction that utilizes inexpensive, innocuous, and readily available starting materials to yield allylic sulfones under mild reaction conditions is extremely attractive and essential.

Alcohols are abundant and easily available, and they are thus a synthetically reliable feedstock.[8] Incorporating allylic alcohols into cross-coupling reactions with sulfonyl precursors should be an ideal and practical strategy for the preparation of allylic sulfones. A high temperature and/or a stoichiometric amount of an acidic additive was required to overcome the high activation barrier of C−OH scission. Unfortunately, only aromatic sulfonyl sources were compatible with such conditions. For instance, the groups of Chandrasekhar, Tian, and Sreedhar have pioneered investigations on the choice of reaction additives, such as Et_3B (2.0 equiv),[9] $B(OH)_3$ (4.0 equiv),[10] and TMSCl (1.2 equiv),[11] showing the reaction was highly dependent on additive selection (Figure 1a). For activated allylic alcohols [equipped with electron-withdrawing groups or (multi)-aryl substituents and aryl-sulfinates], the Reddy group reported that arenesulfonyl cyanides can realize sulfonation in the presence of quantitative amines under metal-

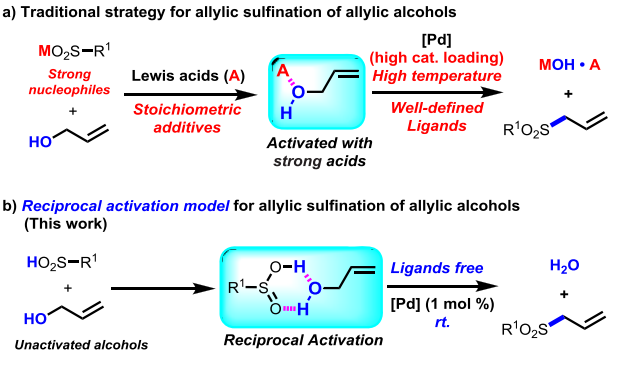


Figure 1. Strategies for direct allylic sulfination of unactivated allylic alcohols.

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free conditions.[12] In our continuing effort to develop catalysts consistent with green and sustainable chemistry,[13] our group has developed a water-promoted dehydrative cross-coupling strategy for preparing allylic sulfones from activated allylic alcohols.[14] Although remarkable progress has been made toward this objective, a cross-coupling reaction with unactivated allylic alcohols remains extremely challenging. Consequently, few procedures have been reported because of the much more robust C−OH bond. Herein, we report a reciprocal-activation strategy for allylic sulfination synthesis utilizing unactivated allylic alcohols and alkyl/aryl sulfonic acids (Figure 1b). In this strategy, the hydrogen bond interaction activates the alcohol toward oxidative addition, and the same interaction activates the sulfinic acid by preventing it from acting as an oxygen nucleophile and pushing it toward being a stronger sulfur nucleophile. The reciprocal activation enables the Pd/Ca-co-catalyzed dehydrative cross-coupling to proceed smoothly at room temperature with water as the only byproduct. Using our method, a wide variety of allylic sulfones can be obtained in good to excellent yields with wide functional group tolerance (Figure 2).

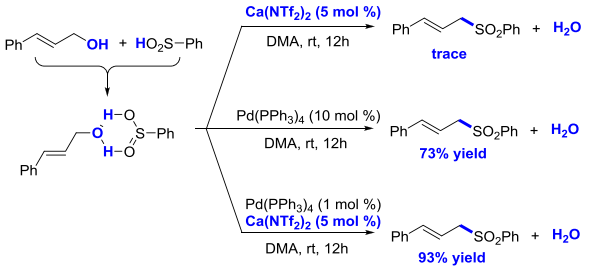
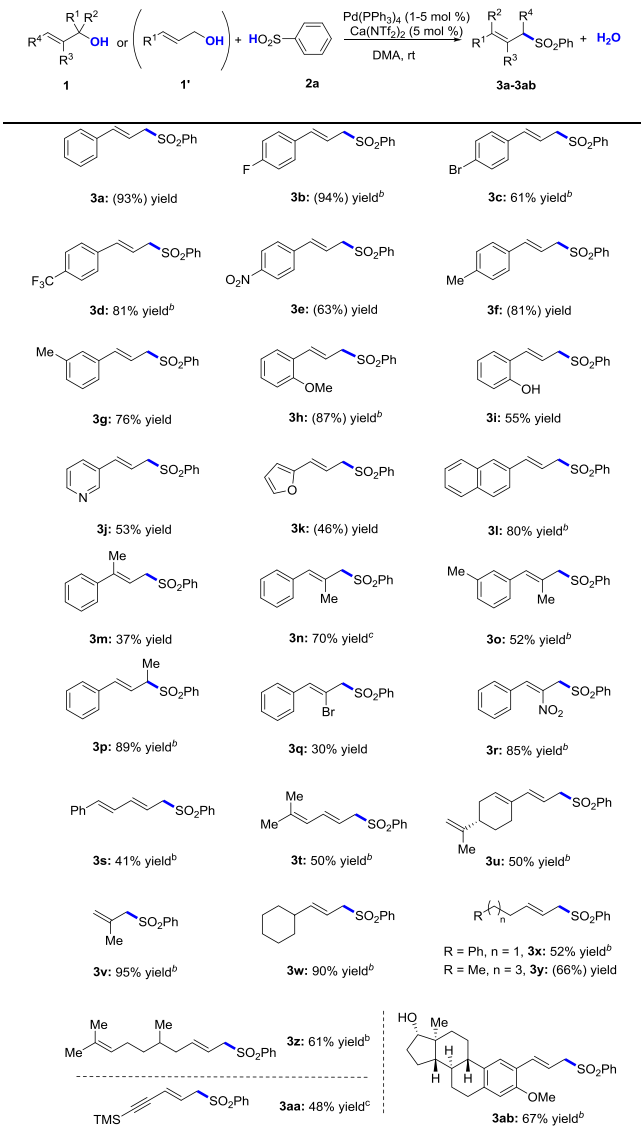


Figure 2. Reaction between unactivated allylic alcohols and sulfinic acids.

Initially, cinnamyl alcohol (**1a**) and benzenesulfinic acid (**2a**) were selected as the model substrates to attempt to access the desired (cinnamylsulfonyl)benzene (**3a**).[15] Because of the difficulty in cleaving the robust C−OH bond of **1a**, **3a** could not be detected even though a wide variety of solvents, such as EtOH/H_2O, DCM (dichloromethane), THF, etc., were screened (Table 1 of the Supporting Information, entries 1−8). Subsequently, $Ca(NTf_2)_2$ was then introduced to activate the C−OH bond[16] (Table 1 of the Supporting Information, entries 9−15). In the solvent DMA (*N*,*N*-dimethylacetamide), a trace amount of **3a** could be detected after 48 h at room temperature (Table 1 of the Supporting Information, entry 15). In all test cases, transition metals, such as Cu and Ni, were found to be ineffective at promoting this transformation (Table 1 of the Supporting Information, entries 16−19 and 21−24). To our delight, **3a** was obtained in 73% yield in the presence of $Pd(PPh_3)_4$ (10 mol %) (Table 1 of the Supporting Information, entry 20). Subsequent efforts demonstrated that the yield of **3a** (CCDC: 1949076) could be dramatically improved to 90% by a combination of palladium and calcium catalysts (Table 1 of the Supporting Information, entry 21). **3a** also can be isolated in 93% yield when the loads (Table 1 of the Supporting Information, entries 25−29) of $Pd(PPh_3)_4$ and $Ca(NTf_2)_2$ are decreased to 1 and 5 mol %, respectively (Table 1 of the Supporting Information, entry 27). **3a** can also be obtained in moderate yield with 0.5 mol % palladium (Table 1 of the Supporting Information, entries 28 and 29). However, other Lewis acids ($ZnCl_2$, $AlCl_3$, and $FeCl_3$) result in diminished yields (Table 1 of the Supporting Information, entries 30−32, respectively).

Subsequently, the generalizability of this reaction was evaluated using a wide variety of allylic alcohols. As shown in Scheme 1, allylic alcohols bearing a wide variety of

Scheme 1. Dehydrative Cross-Coupling Concerning Allylic Alcohols[a]



[a]Experimental conditions: **1** (0.3 mmol), **2a** (0.45 mmol), $Ca(NTf_2)_2$ (5.0 mol %), and $Pd(PPh_3)_4$ (1.0 mol %) in DMA (2.0 mL) under a N_2 atmosphere at room temperature (30 °C, oil bath). Isolated yield. Yields in parentheses were generated from **1′**. [b]$Pd(PPh_3)_4$ (3.0 mol %) and $Ca(NTf_2)_2$ (10.0 mol %) were used. [c]$Pd(PPh_3)_4$ (5.0 mol %) and $Ca(NTf_2)_2$ (10.0 mol %) were used

functional groups were found to be suitable substrates for this transformation, delivering the corresponding allylic sulfones in good to excellent yields. Both electron-withdrawing (**3b**−**3e**) and electron-donating (**3f**−**3h**) aryl-substituted allylic alcohols were amenable to this protocol. The positions of the substituents (at the *para* or *meta* positions) on the phenyl ring have limited effects on the overall transformation (**3f**−**3h**). Even *o*-hydroxyl groups on the phenyl were well

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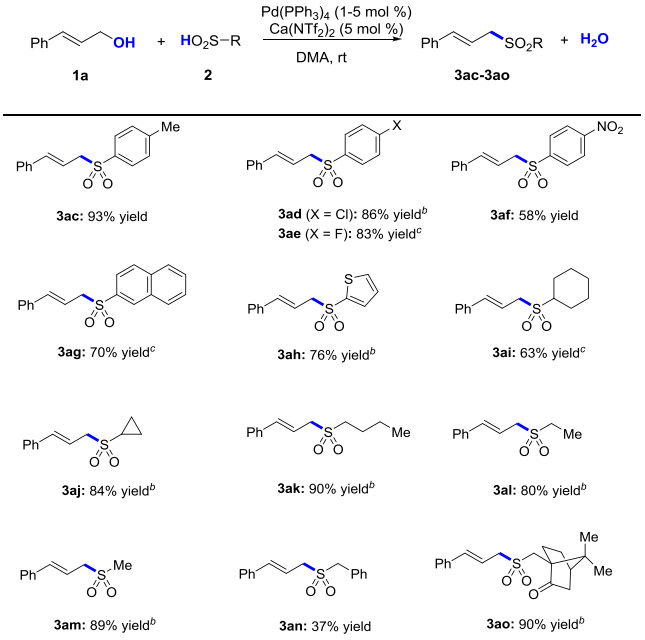
tolerated, albeit delivering the desired **3i** in an only moderate yield. In addition, allylic alcohols bearing heteroaryl substituents, such as pyri-dien-2-yl (**3j**) and furan-2-yl (**3k**), were also well tolerated. Fused aromatic allylic alcohols can be utilized in this reaction, generating **3l** in a high yield. In addition to monosubstituted allylic alcohols, multisubstituted versions with substituents at position 1, 2, or 3 of allylic alcohols were compatible with the reaction (**3m**−**3r**). In such a case, the configuration of the double (**3n**, **3o**, **3q**, and **3r**) was determined by NOE spectrum (**3m**) or X-ray analysis (**3n**, CCDC: 1949077). (*R*,*E*)-4-Phenylbut-3-en-2-ol was selected to investigate the enantioselectivity of this process. Unfortunately, only racemic **3p** was obtained, which may be ascribed to the epimerization of enantioenriched allylic alcohols in the presence of Lewis acids.[9] Remarkably, (*Z*)-2-nitro-3-phenylprop-2-en-1-ol and (*Z*)-2-bromo-3-phenylprop-2-en-1-ol both showed effective reactivity and yielded the functionalized allylic sulfones highly efficiently (**3q** and **3r**, respectively). These results have the potential to greatly enhance the utility of the product sulfones in further reactions.

Notably, this method also allows access to diverse 2,4-dien-1-yl sulfone skeletons (**3s**−**3u**) from vinyl-substituted allylic alcohols. This access will increase the opportunities for further structural modification. For allylic alcohols with adjacent C−H bonds, preparing alkyl-substituted allylic sulfone skeletons can be a challenge due to the competitive self-dehydration process that often yields the undesired 1,3-diene byproduct. In this investigation, both cyclic and straight chain alkyl-substituted allylic alcohols can be successfully incorporated into this transformation (**3u**−**3y**). A citronellal derivative also served as a productive reaction partner to afford **3z** in a 95% yield. Moreover, alcohols containing alkynyl groups were feasible under the reaction conditions, giving **3aa** in a moderate yield. Remarkably, a steroid moiety with another active hydroxyl group was also well tolerated (**3ab**) (Scheme 2). These results further highlight the utility of this method in pharmaceutical studies.

Then, we focused our attention on exploring functionalization of the sulfinic acids. In addition to benzenesulfinic acid **1a**, many different kinds of aromatic sulfinic acids possessing different electronic effects were suitable substrates for this transformation (**3ac**−**3af**). Both electron-withdrawing (**3ac**) and electron-donating groups (**3ad**−**3af**) on the phenyl group were tolerated. Moreover, thiophene-2-sulfinic acid and naphthalene-2-sulfinic acid can also react well and deliver the corresponding allylic sulfones in high yields (**3ag** and **3ah**). To date, it has been a challenge to incorporate aliphatic sulfinic acids into allylic sulfones due to their instability and lower reactivities. Remarkably, either cyclic (**3ai** and **3aj**) or acyclic (**3ah**−**3an**) alkyl sulfinic acids were compatible with our developed transformation. An even bulkier acid, camphorsulfinic acid, can be incorporated into the corresponding allylic sulfone (**3ao**) with an excellent yield.

The synthetic utility of this transformation was then preliminarily studied. It has been noted that 1-{4-[(trimethylsilyl)ethynyl]phenyl}prop-2-en-1-ol reacted well with benzenesulfinic acid, and the alkynyl group was well tolerated. This observation allowed for further functionalization by a Cu-catalyzed azide−alkyne cycloaddition. After the TMS moiety had been removed from **3ap**, the allylic sulfones (**4**) can be conveniently linked with an antivirus drug Zidovudine[17] via click reaction, delivering new compound **5** in 85% yield (Figure 3). Moreover, the reaction can be scaled

Scheme 2. Substrate Scope of Sulfinic Acids[a]



[a]Experimental conditions: **1** (0.3 mmol), **2a** (0.45 mmol), $Ca(NTf_2)_2$ (5.0 mol %), and $Pd(PPh_3)_4$ (1.0 mol %) in DMA (2.0 mL) under a N_2 atmosphere at room temperature (30 °C, oil bath). Isolated yield. [b]$Pd(PPh_3)_4$ (3.0 mol %) was used. [c]$Pd(PPh_3)_4$ (5.0 mol %) was used.

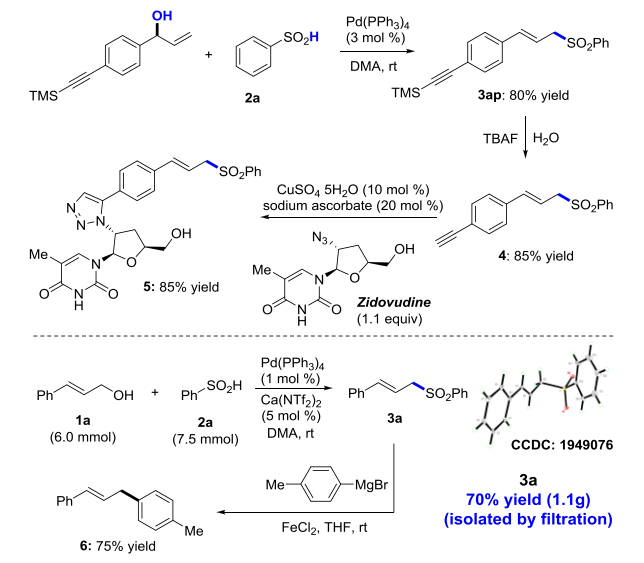


Figure 3. Utility of this protocol and synthetic transformation of allylic sulfones.

up to 6.0 mmol without significant erosion of the outcome, and product **3a** can be isolated without chromatography (in 70% yield, by filtration). Further functionalization of **3a** via nucleophilic allylic substitution[18] with PhMgBr was realized by using an Fe^{II} catalyst, affording **6** in good yield.

To gain more insight into the reaction mechanism, control experiments were then conducted under the identified reaction conditions. As is shown in Figure 4, no reaction occurred when benzenesulfinic acid (Figure 4a) was replaced by sodium benzenesulfinate (Figure 4b); even 2.0−4.0 equiv of HCl (aqueous, 37%) was introduced (Figure 4c). This result indicated that the benzenesulfinic acid was probably crucial for

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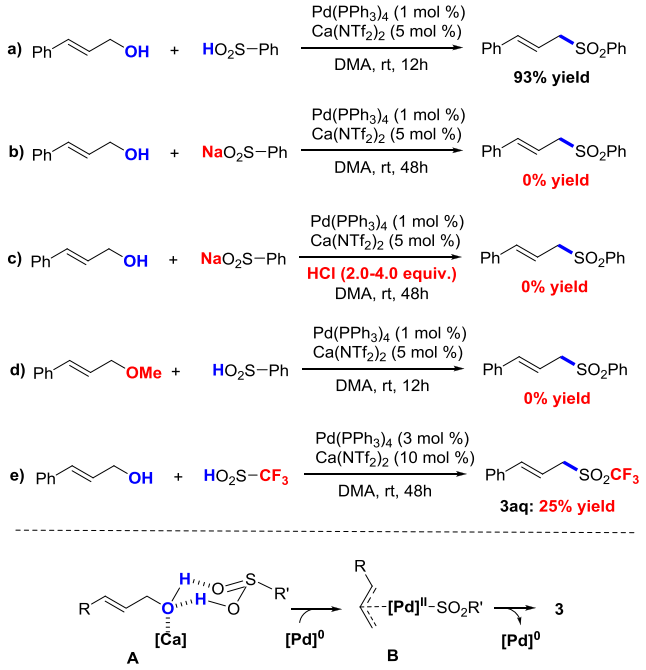

Figure 4. Control experiments and proposed mechanism.

C−OH bond activation. In addition, no desired product was obtained if the hydroxyl group of cinnamyl alcohol was methylated (Figure 4d). Furthermore, an increase in the acidity of the sulfinic acids (Figure 4e) resulted in diminished yields, which was also consistent with the outcome concerning **3ac**−**3af**. Thus, we came to the conclusion that C−OH bond activation was insufficient for the overall transformation, but a suitably nucleophilic sulfonyl anion was also required. Hydrogen bonding interaction of the sulfinic acid activates the alcohol toward oxidative addition, and the same interaction activates the sulfinic acid by preventing it from acting as an oxygen nucleophile and pushing it toward being a stronger sulfur nucleophile. Thus, in this model, the reciprocal activation was realized. The calcium salt was not indispensable for this process but might facilitate the generation of intermediate **A**, which was followed by the convenient palladium insertion that delivered the key intermediate **B**. Then the desired **3** was afforded with the regeneration of palladium.

In summary, we developed a reciprocal-activation strategy for allylic sulfination of unactivated allylic alcohols in an environmentally friendly manner. In this protocol, the hydrogen bond interactions between the sulfinic acids and allylic alcohols allow for the reciprocal activation, which enabled the dehydrative cross-coupling reaction to proceed smoothly at room temperature with water as the only byproduct. A variety of allylic sulfones can be isolated in good to excellent yields with wide-spectrum functional groups tolerated. Remarkably, the reaction can be performed on a gram scale where allylic sulfones can be isolated without chromatography.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01747.

Experimental procedures, screening reaction conditions, analytical data for all new compounds, and NMR spectra of products (PDF)

Accession Codes

CCDC 1949076−1949077 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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