Regioselective molybdenum-catalyzed allylic substitution of tertiary allylic electrophiles: methodology development and applications†

Muhammad Salman,‡ Yaoyao Xu,‡ Shahid Khan, Junjie Zhang and Ajmal Khan*†

The first molybdenum-catalyzed allylic sulfonylation of tertiary allylic electrophiles is described. The method employs a readily accessible catalyst (Mo(CO)\(_6\)/2,2'-bipyridine, both are commercially available) and represents the first example of the use of a group 6 transition-metal catalyst for allylic sulfonylation of substituted tertiary allylic electrophiles to form carbon–sulfur bonds. This atom economic and operationally simple methodology is characterized by its relatively mild conditions, wide substrate scope, and excellent regioselectivity profile, thus unlocking a new platform to forge sulfone moieties, even in the context of late-stage functionalization and providing ample opportunities for further derivatization through traditional Suzuki cross-coupling reactions.

Introduction

The concept of the \(\pi\)-allyl metal-complex was first formulated by Tsuji in 1965 (ref. 1a) and, later, properly adopted by Trost in 1973.\(^{1b}\) Since then, this technology has enabled organic chemists to create a host of novel procedures for the synthesis of simple to complex molecules.\(^2\) Among these is the development and utilization of heteroatom nucleophile reagents, such as oxygen, nitrogen, and sulfur-based nucleophiles.\(^{2,3}\) Despite the massive development that has been made in this area, there still remain untapped opportunities in the potential application of these heteroatom nucleophile reagents in transition metal-catalyzed allylic substitution. For example, molybdenum-catalyzed allylic substitution reactions of heteroatom nucleophiles are unknown and largely limited only to carbon–carbon bond formation procedures (Fig. 1A, left).\(^4\) Furthermore, the substrate scope with respect to the allylic electrophile has also remained unchanged and restricted to the ones that provide products containing a tertiary center at the allylic position.\(^5\) Regardless of the longstanding interest in the formation of carbon–heteroatom bonds within the synthetic organic community, as well as the advancement of other transition-metal-catalyzed reactions to provide heteroatom bearing quaternary and/or tertiary allylic centers,\(^6\) molybdenum-catalyzed allylic substitution reactions that provide products containing such a stereocenter remain prominently absent from the literature and yet to be discovered (Fig. 1A, right).\(^7\)

Due to the high importance of allylic sulfones as pharmaceuticals\(^8\) and synthetic candidates,\(^9\) organic chemists have recently been designing catalytic C–S bond cleavage procedures as a new tool for carbon–carbon bond formation through Suzuki cross-coupling\(^10\) and/or allylic substitution reactions.\(^11\) Despite the considerable development realized in this area, allylic sulfone formation is still a challenging task and confined to the use of transition metal-catalyzed allylic sulfonylation procedures.\(^12,13\) However, using these...
For the synthesis of allylic sulfones containing tetrasubstituted carbon centers is limited and largely unexplored. Therefore, at the beginning of our study it was unclear whether a molybdenum-catalyzed allylic substitution could ever be implemented with a heteroatom (sodium sulfinate) nucleophile or even with α,α-disubstituted allylic precursors. If successful, such unexplored areas of allylic substitution chemistry might not only provide an opportunity to realize currently inaccessible chemical space (carbon-heteroatom bond formation) in molybdenum-catalyzed allylic substitution, but also provide a new synthetic approach for rapidly generating quaternary all-carbon centers through Suzuki cross-coupling of the sulfone functionality. As part of our ongoing program in developing molybdenum-catalyzed allylic substitution technology and our continued interest in the catalytic asymmetric synthesis of quaternary stereocenters, we were attracted to this unmet challenge and report herein the successful implementation of this idea (Fig. 1B). The salient features of this process are the atom-economic procedures, high regioselectivity, and excellent functional group tolerance for both sulfinate salt and tertiary allylic carbonates, even in the context of late-stage functionalization. Furthermore, the high reactivity of tertiary allylic sulfones as a new class of electrophiles to yield structurally diverse products containing quaternary all-carbon centers through Suzuki cross-coupling is a special characteristic feature of this catalytic system (Fig. 1C).

## Results and discussion

Our optimization began by evaluating the allylic substitution of tertiary allylic carbonate 1a, readily prepared from the corresponding alcohol on a large scale, with sodium benzenesulfinate 2a (Table 1). Interestingly, a disappointing amount of either 3aa or 4aa was detected under reaction conditions previously reported for other molybdenum-catalyzed allylic substitution reactions. After several experiments, we concluded that a combination of the inexpensive commercially available Mo(CO)₆ precursor and 2,2’-bipyridine as a ligand (L1) in EtOH at 60 °C afforded 3aa in 92% yield upon isolation with excellent branched to linear selectivity (3aa/4aa = 99 : 1).

**Table 1. Optimization of the reaction parameters**

| Entry | Deviation in conditions | 3aa/4aa | 3aa (%) |
|-------|-------------------------|---------|---------|
| 1     | None                    | 99 : 1  | 92      |
| 2     | L2 was used instead of L1| 99 : 1  | 87      |
| 3     | L3 was used instead of L1| 99 : 1  | 77      |
| 4     | L4 was used instead of L1| 99 : 1  | 52      |
| 5     | L5 was used instead of L1| 25 : 1  | 16      |
| 6     | L6 was used instead of   | —       | 0       |
| 7     | L7 was used instead of   | —       | >5      |
| 8     | [(C₅H₄)₂Mo(CO)₃] was    | 99 : 1  | 82      |
| 9     | THF was used as solvent  | —       | >5      |
| 10    | Toluene was used as      | —       | >5      |
| 11    | DCE was used as solvent  | 25 : 1  | 35      |
| 12    | PrOH was used as solvent | 99 : 1  | 77      |
| 13    | THF/EtOH (5:1) as solvent| 25 : 1  | 25      |
| 14    | DCE/EtOH (5:1) as solvent| 25 : 1  | 63      |
| 15    | Without Mo or L1        | —       | 0       |

* Reaction conditions: Mo-catalyst (10 mol%), ligand (15 mol%), 1a (0.2 mmol), PhSO₂Na 2a (0.3 mmol), solvent (1.0 mL, 0.2 M), 60 °C, 24 hours. * Determined by ¹H-NMR of the crude reaction mixture. * Isolated yields.

**Table 2. Sodium sulfinate substrate scope**

| Entry  | 2              | 3aa | Yield (%) |
|--------|----------------|-----|-----------|
| 1      | 2a (R = Ph)    | 3aa | 92        |
| 2      | 2b (R = 4-MeC₆H₄) | 3ab | 93        |
| 3      | 2c (R = 4- MeOC₆H₄) | 3ac | 90        |
| 4      | 2d (R = 4-ClC₆H₄) | 3ad | 87        |
| 5      | 2e (R = 4-FC₆H₄)  | 3ae | 85        |
| 6      | 2f (R = 4-N NO₂C₆H₄) | 3af | 75        |
| 7      | 2g (R = 4-CN C₆H₄) | 3ag | 72        |
| 8      | 2h (R = 2-FC₆H₄)  | 3ah | 88        |
| 9      | 2i (R = 2-CIC₆H₄) | 3ai | 87        |
| 10     | 2j (R = 2-OCF₃C₆H₄) | 3aj | 72        |
| 11     | 2k (R = 3-BrC₆H₄) | 3ak | 82        |
| 12     | 2l (R = 3-CNC₆H₄) | 3al | 78        |
| 13     | 2m (R = 2,4-MeOC₆H₄) | 3am | 94        |
| 14     | 2n (R = 3,5-C₂F₅C₆H₄) | 3an | 95        |
| 15     | 2o (R = 2-MeO, 5-BrC₆H₄) | 3ao | 84        |
| 16     | 2p (R = 3,4-CIC₆H₄) | 3ap | 87        |
| 17     | 2q (R = 2-naphthyl) | 3aq | 82        |
| 18     | 2r (R = 1quinoline) | 3ar | 78        |
| 19     | 2s (R = 2,3-dihydrobenzofuran) | 3as | 92        |
| 20     | 2t (R = 3-pyridine) | 3at | 82        |
| 21     | 2u (R = 2-thiophene) | 3au | 86        |
| 22     | 2v (R = Me)      | 3av | 72        |
| 23     | 2w (R = Et)      | 3aw | 78        |
| 24     | 2x (R = Pr)      | 3ax | 82        |
| 25     | 2y (R = cyclopropyl) | 3ay | 78        |
| 26     | 2z (R = CH₂OCOCH₂CH₃) | 3az | 72        |

* Reaction conditions: Mo(CO)₆ (10 mol%), L1 (15 mol%), 1a (0.2 mmol), PhSO₂Na 2a (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. * Determined by ¹H-NMR of the crude reaction mixture. * Isolated yields.
molybdenum precursor and/or solvent, however, had a negative influence on the reaction, consistently providing lower yields if any (entries 8–14). As anticipated, control experiments revealed that all of the reaction parameters were necessary for the reaction to occur (entry 15).

With reliable access to 3aa, we next turned our attention to examine the generality of our newly developed molybdenum-catalyzed regioselective sulfonylation of tertiary allylic electrophiles with sodium sulfinate by using the Mo/L1 catalyst system as shown in Table 2. In all cases analysed for sulfinate salts (2), excellent reactivity and selectivity was observed. Both the electron-withdrawing and electron-donating substituents on the aromatic ring of the sulfonylation partner, the branched product 3az was obtained in 72% of isolated yield. The reaction leading to tertiary allylic sulfone 3aa was easily scaled up to gram-scale without significant decrease in yield. Of particular note is that, almost in all cases, the reactions proceeded with excellent branched regioselectivity (>99 : 1).

We then focused on investigating the scope of the α,α-disubstituted allylic carbonates and the results obtained were compiled in Table 3. Tertiary allylic carbonate with simple propyl substituent (1b) reacted efficiently with sodium benzenesulfinate (2a) to deliver the branched allylic sulfone 3ba in high yield (87%). However, allylic carbonate with a cyclohexyl moiety afforded the desired branched product in comparatively low yield (24%, 3ca) due to the steric hindrance problem. However, tertiary allylic carbonate (1d) having a longer alkyl chain provided the desired product even at high yield (91%, 3da). When tertiary allylic carbones 1e, 1f, 1g and 1h with different groups on the alkyl chain were coupled with sulfinate salt 2a, high yields of the branched allylic products were obtained (85–96%, 3ea, 3fa, 3ga and 3ha). Notably, various common functional groups such as Cl (1i), benzyl (1j), benzyol (1k), thioether (1l), acetyl (1m), and carbonate (1n) on the alkyl chain of the tertiary allylic carbonates were tolerated, and the sulfonylation branched products (3ia–3na) were isolated in high yields (82–94%). In addition, the unprotected hydroxy group on the alkyl chain of the tertiary allylic carbonates 1o and 1p do not interfere with productive tertiary allylic sulfone formation (3oa and 3pa), thus providing opportunities for further derivatization. Notably, the reaction can be easily applied within the context of late-stage functionalization, supported by the formation of branched allylic sulfone 3qa, derived from pentoxifylline. As expected, the allylic sulfonylation of phenyl substituted allylic carbonate occurred exclusively at the less-hindered position. The present optimized conditions were unsatisfactory with such substrates and provided the desired branched product (3ra) with a low branched to linear ratio (b/l = 1 : 5); indicating some [steric] limitation of the current protocol. Besides methyl-substituted tertiary allylic substrates 1a–1r, other alkyl or aryl substituted substrates provide only starting materials when used under the optimized conditions, indicating some limitation of the present protocol.

In order to illustrate the synthetic utility of these elusive tertiary allylic sulfones, we focused on the reaction of α,α-disubstituted allylic carbonate (1h), and sodium sulfinate 2az, to achieve the formal synthesis of (+)-agelasidene A. The desired tertiary allylic sulfone 3haz was isolated in 84% yield under the standard conditions (Fig. 1A). This compound (3haz) can be readily converted to (+)-agelasidene A by following the literature procedure. We further demonstrate that the current methodology can be utilized to prepare other related compounds containing sulfone-bearing quaternary carbon centers.

Due to their ambiphilic nature, allylic sulfones are synthetically important electrophiles and have recently been utilized in Suzuki cross-coupling as well as allylic substitution reactions. However, selective cross-coupling of tertiary allylic sulfones remains highly challenging in Suzuki–Miyaura cross-coupling reactions. Indeed, we employed our tertiary allylic sulfone product 3ga along with typical boronic acids as
a coupling partner in order to achieve the formal synthesis of \((\pm\)-sporochin\), and \((\pm\)-bakuchiol, both of which are natural products possessing a quaternary all-carbon center. Our synthesis is illustrated in Fig. 1B. The key step involves a previously reported Suzuki–Miyaura cross-coupling reaction of tertiary allylic sulfone \(3ga\) to afford \(4ga\), and \(4gb\) efficiently with 62% and 58% of isolated yields respectively. Subsequent deprotection of phenol then could complete the formal synthesis of \((\pm\)-sporochin and \((\pm\)-bakuchiol (Fig. 1B). Starting from \(3ga\) in 2 steps our tertiary allylic sulfones can be used to prepare such natural products and other related compounds bearing all-carbon quaternary centers in a modular way.

To gain mechanistic insight and the initial understanding on how the reaction works, we decided to study the reactivity of \([\text{Mo}^\text{III}]_2\) species (Fig. 3). The \([\text{Mo}(bpy)(CO)_4]_2\) complex was prepared on a large scale by reacting \(\text{Mo}^{0L_1}\) and \(2,2\)-bipyridine. To the best of our knowledge, the first example of the use of sodium sulfinates as the heteroatom nucleophile reagent with tertiary allylic electrophiles to form \(C-S\) bonds. The process is characterized by its atom economic procedure, wide substrate scope, and excellent regioselectivity profile even in the context of late-stage functionalization, thus providing ample opportunities for further derivatization through traditional Suzuki cross-coupling reactions (as presented in Fig. 2b).

Investigations of enantioselective reactions, the mechanism and extension to other heteroatom nucleophiles are currently ongoing and will be reported in due course.

### Conclusions

In conclusion we have developed a method for the allylic sulfonylation of \(\alpha,\alpha\)-disubstituted allylic electrophiles, using inexpensive and commercially available catalyst components (\(\text{Mo}^{0L_1}/2,2\)-bipyridine). To the best of our knowledge, the presented methodology is the first example of the use of sodium sulfinates as the heteroatom nucleophile reagent with tertiary allylic electrophiles to employ the group 6 catalyst in allylic substitution of tertiary allylic electrophiles to form \(C-S\) bonds.

### Conflicts of interest

The authors declare no conflicts of interest.

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**Fig. 2** Importance of current research towards the synthesis of age-lasidine A, sporochin, and bakuchiol. Reaction conditions: (a) \(\text{Mo}^{15\text{L}}\) (1.0 mmol), L1 (15 mmol), 1h (0.2 mmol), 2az (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. (b) Ni(cod)_2 (10 mol%) ligand L8 (12 mol%), 3ga (0.2 mmol), 3a or 3b (0.7 equiv.), NaOEt (2.2 equiv.), PhMe (0.2 M), 24 h, 80 °C.

**Fig. 3** Mechanistic experiments.
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