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

Muhammad Salman,‡ Yaoyao Xu,‡ Shahid Khan, Junjie Zhang and Ajmal Khan^{ID}*

The first molybdenum-catalyzed allylic sulfonylation of tertiary allylic electrophiles is described. The method employs a readily accessible catalyst ($\text{Mo}(\text{CO})_6/2,2'$ -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 π -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 pharmaceuticals⁸ 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-coupling¹⁰ 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

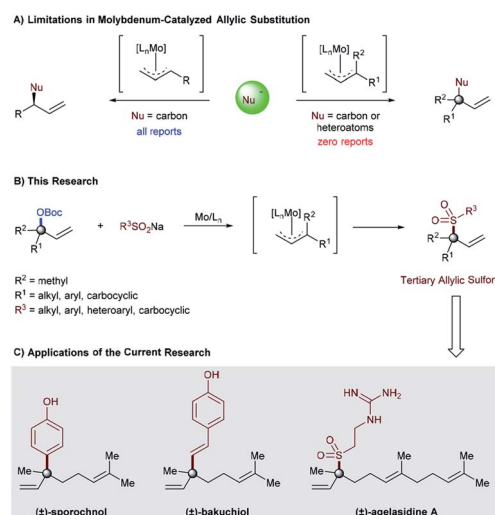


Fig. 1 (A) Limitations in molybdenum-catalyzed allylic substitution, (B) our research, and (C) applications of the current research.

Department of Applied Chemistry, School of Science, Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, Xi'an Jiao Tong University, Xi'an 710049, P. R. China. E-mail: ajmalkhan@xjtu.edu.cn

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‡ These authors contributed equally.

Table 1 Optimization of the reaction parameters^a

Entry	Deviation in conditions	3aa/4aa ^b	3aa ^c (%)
1	None	99 : 1	92
2	L2 was used instead of L1	99 : 1	87
3	L3 was used instead of L1	99 : 1	35
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 L1	—	0
7	L7 was used instead of L1	—	>5
8	(C ₇ H ₈) ₃ Mo(CO) ₃ was used	99 : 1	82
9	THF was used as solvent	—	>5
10	Toluene was used as solvent	—	>5
11	DCE was used as solvent	25 : 1	35
12	ⁱ 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

^a 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.

^b Determined by ¹H-NMR of the crude reaction mixture. ^c Isolated yields.

procedures for the synthesis of allylic sulfones containing tetrasubstituted carbon centers is limited and largely unexplored.¹⁴ 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,^{14a,15} 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).^{10a}

Table 2 Sodium sulfinate substrate scope^{a,b,c}

Entry	2	3 ^b	Yield ^c (%)
1	2a (R = Ph)	3aa	92
2	2b (R = 4-MeC ₆ H ₄)	3ab	93
3	2c (R = 4-MeOC ₆ H ₄)	3ac	90
4	2d (R = 4-ClC ₆ H ₄)	3ad	87
5	2e (R = 4-FC ₆ H ₄)	3ae	85
6	2f (R = 4-NO ₂ C ₆ H ₄)	3af	75
7	2g (R = 4-CNC ₆ H ₄)	3ag	72
8	2h (R = 2-FC ₆ H ₄)	3ah	88
9	2i (R = 2-ClC ₆ H ₄)	3ai	87
10	2j (R = 2-OCF ₃ C ₆ H ₄)	3aj	72
11	2k (R = 3-BrC ₆ H ₄)	3ak	82
12	2l (R = 3-CNC ₆ H ₄)	3al	78
13	2m (R = 2,4-MeOC ₆ H ₃)	3am	94
14	2n (R = 3,5-CF ₃ C ₆ H ₃)	3an	95
15	2o (R = 2-MeO, 5-BrC ₆ H ₃)	3ao	84
16	2p (R = 3,4-ClC ₆ H ₃)	3ap	87
17	2q (R = 2-naphthyl)	3aq	82
18	2r (R = 1-quinoline)	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 = ⁱ Pr)	3ax	82
25	2y (R = cyclopropyl)	3ay	78
26	2z (R = CH ₃ OCOCH ₂ CH ₂)	3az	72

^a Reaction conditions: Mo(CO)₆ (10 mol%), **L1** (15 mol%), **1a** (0.2 mmol), RSO₂Na **2** (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours.

^b Determined by ¹H-NMR of the crude reaction mixture. ^c Isolated yields.

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.⁴ After several experiments,¹⁶ we concluded that a combination of the inexpensive commercially available Mo(CO)₆ precursor and 2,2'-bipyridine as a ligand (**L1**)¹⁷ in EtOH at 60 °C afforded **3aa** in 92% yield upon isolation with excellent branched to linear selectivity (**3aa/4aa** = >99 : 1). Amongst all of the ligands utilized, 2,2'-bipyridine motifs were crucial for achieving the targeted transformation. While excellent reactivity towards **3aa** was found with 2,2'-bipyridines and 6,6'-dimethyl-2,2'-bipyridine, better yields were obtained for the first one (entries 1–7). Interestingly, the bench-stable terpyridine **L7** failed to provide product **3aa**. These results indicate that the coordination geometry of the ligand dictates the reactivity, with 2,2'-bipyridine ligands being particularly suited for the high yield and selectivity of **3aa**. Subtle changes in the





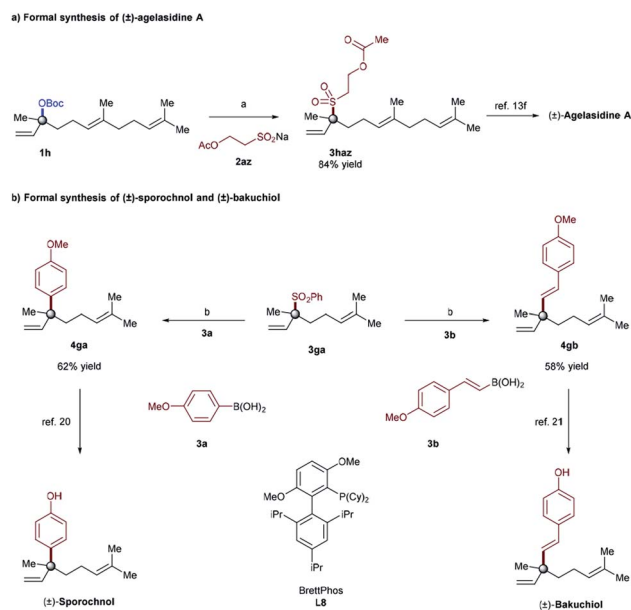


Fig. 2 Importance of current research towards the synthesis of agelasidine A, sporochnol, and bakuchiol. Reaction conditions: (a) $\text{Mo}(\text{CO})_6$ (10 mol%), **L1** (15 mol%), **1h** (0.2 mmol), **2az** (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. (b) $\text{Ni}(\text{cod})_2$ (10 mol%) 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.

a coupling partner in order to achieve the formal synthesis of (±)-sporochnol,²⁰ and (±)-bakuchiol,²¹ 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 (±)-sporochnol and (±)-bakuchiol (Fig. 1B).^{20,21} 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.²²

To gain mechanistic insight and the initial understanding on how the reaction works, we decided to study the reactivity of $[\text{Mo}^0\text{L}_n]$ species (Fig. 3). The $[\text{Mo}(\text{bpy})(\text{CO})_4]$ complex²³ was prepared on a large scale by reacting $\text{Mo}(\text{CO})_6$ and 2,2'-bipyridine (**L1**) in THF at 60 °C.¹⁶ As shown in Fig. 3, the structure was confirmed and further analyzed.²⁴ Interestingly, the

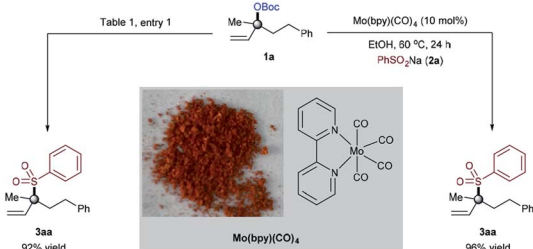


Fig. 3 Mechanistic experiments.

$[\text{Mo}(\text{bpy})(\text{CO})_4]$ complex was found to be catalytically more efficient when used under the standard conditions, supported by the formation of branched allylic sulfone product **3aa** in 96% yield. A small decline in yield of **3aa** in the $[\text{Mo}(\text{CO})_6]/\text{L1}$ catalyst system was observed, thus providing evidence that a $[\text{Mo}(\text{bpy})(\text{CO})_4]$ complex is likely to be the active precatalyst species in this allylic sulfonylation reaction.²⁵

Conclusions

In conclusion we have developed a method for the allylic sulfonylation of α,α -disubstituted allylic electrophiles, using inexpensive and commercially available catalyst components ($\text{Mo}(\text{CO})_6/2,2'$ -bipyridine). To the best of our knowledge, the presented methodology is the first example of the use of sodium sulfonates 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. 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.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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