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

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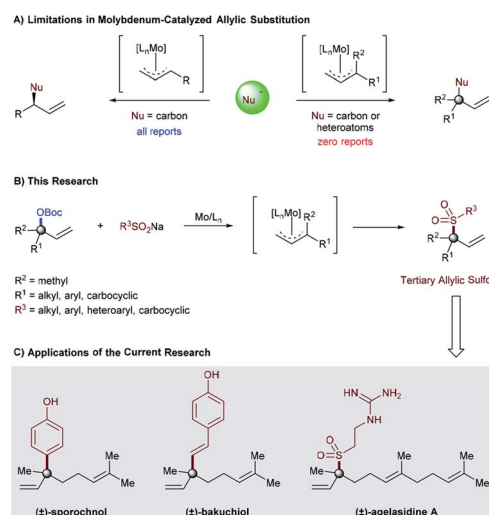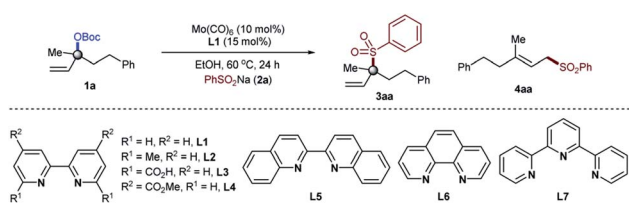
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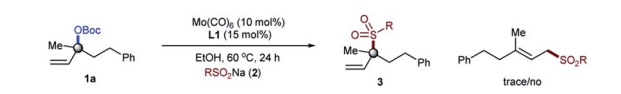
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Fig. 1 (A) Limitations in molybdenum-catalyzed allylic substitution, (B) our research, and (C) applications of the current research.

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	$(C_7H_8)_3Mo(CO)_3$ 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	^iPrOH 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), $PhSO_2Na$ 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]

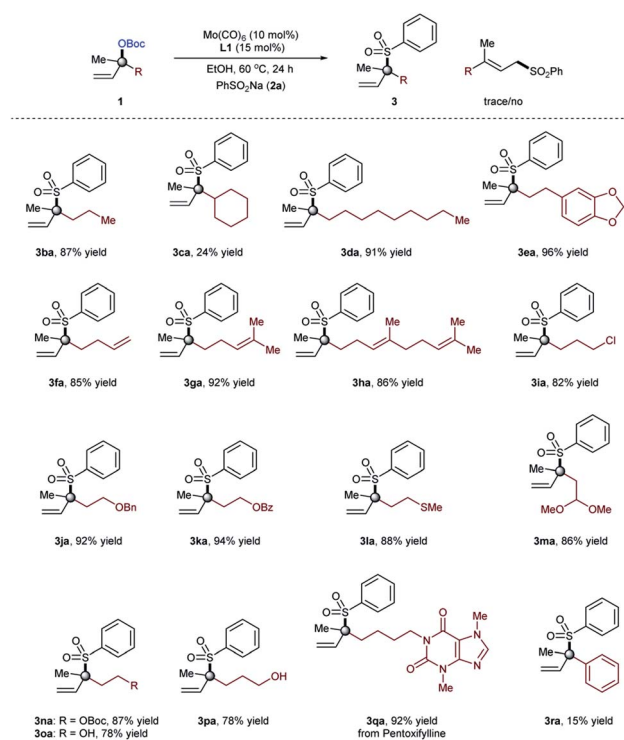| Entry	2	3[b]	Yield[c] (%)
1	2a (R = Ph)	3aa	92
2	2b (R = 4-MeC₆H₄)	3ab	93
3	2c (R = 4-MeOC₆H₄)	3ac	90
4	2d (R = 4-ClC₆H₄)	3ad	87
5	2e (R = 4-FC₆H₄)	3ae	85
6	2f (R = 4-NO₂C₆H₄)	3af	75
7	2g (R = 4-CNC₆H₄)	3ag	72
8	2h (R = 2-FC₆H₄)	3ah	88
9	2i (R = 2-ClC₆H₄)	3ai	87
10	2j (R = 2-OCF₃C₆H₄)	3aj	72
11	2k (R = 3-BrC₆H₄)	3ak	82
12	2l (R = 3-CNC₆H₄)	3al	78
13	2m (R = 2,4-MeOC₆H₃)	3am	94
14	2n (R = 3,5-CF₃C₆H₃)	3an	95
15	2o (R = 2-MeO, 5-BrC₆H₃)	3ao	84
16	2p (R = 3,4-ClC₆H₃)	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 = ^iPr)	3ax	82
25	2y (R = cyclopropyl)	3ay	78
26	2z (R = CH₃OCOCH₂CH₂)	3az	72

[a] Reaction conditions: $Mo(CO)_6$ (10 mol%), L1 (15 mol%), 1a (0.2 mmol), RSO_2Na 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

Table 3 Allylic carbonate substrate scope[a,b,c]

^{a} Reaction conditions: Mo(CO)$_6$ (10 mol%), **L1** (15 mol%), **1** (0.2 mmol), PhSO$_2$Na **2a** (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. ^{b} Regioselectivity was determined by ^{1}H-NMR of the crude reaction mixture. ^{c} Isolated yields of the products.

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 sulfinate salts react smoothly with **1a**, affording the corresponding α,α-disubstituted allylic products in high yields (**3aa–3ap**). Sodium sulfinates with bulky naphthyl (**3aq**), quinoline (**3ar**), 2,3-dihydrobenzofuran (**3as**), and heteroaryl (**3at**, **3au**) moieties were also tolerated under the current optimized conditions. Likewise, the targeted tertiary allylic sulfone formation could be extended to sulfinate salts with alkyl substituents. Both primary and secondary alkyl substituted sodium sulfinates worked well to provide α,α-disubstituted allylic sulfones in high yields (**3av–3ay**). Furthermore, a more functionalized sodium sulfinate **2z**, when used as 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 carbonates **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**), benzoyl (**1k**), thioether (**1l**), acetal (**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 (±)-agelasidine A.[18] 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 (±)-agelasidine A by following the literature procedure.[13f] We further demonstrate that the current methodology can be utilized to prepare other related compounds containing sulfone-bearing quaternary carbon centers.[19]

Due to their ambiphilic nature, allylic sulfones are synthetically important electrophiles and have recently been utilized in Suzuki cross-coupling[10a] as well as allylic substitution reactions.[11d] However, selective cross-coupling of tertiary allylic sulfones remains highly challenging in Suzuki–Miyaura cross-coupling reactions.[10] Indeed, we employed our tertiary allylic sulfone product **3ga** along with typical boronic acids as
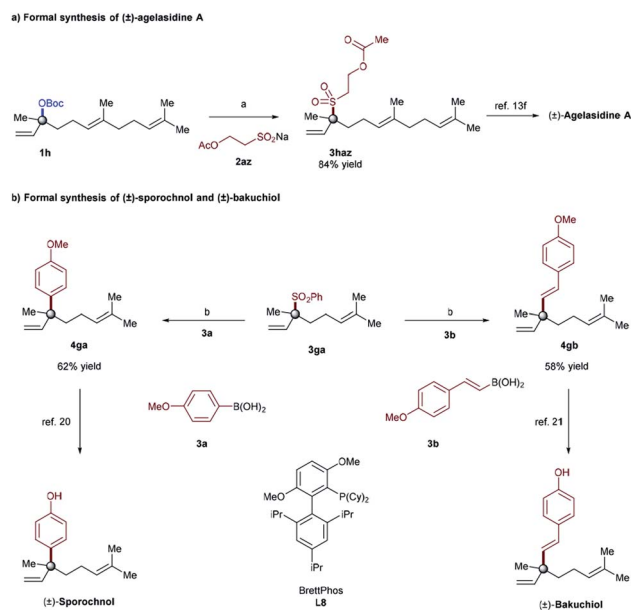
Fig. 2 Importance of current research towards the synthesis of age-lasidine A, sporochnol, and bakuchiol. Reaction conditions: (a) Mo(CO)$_6$ (10 mol%), L1 (15 mol%), 1h (0.2 mmol), 2az (0.3 mmol), EtOH (1.0 mL, 0.2 M), 60 °C, 24 hours. (b) Ni(cod)$_2$ (10 mol%) ligand L8 (12 mol%), 3ga (0.2 mmol), 3a or 3b (0.7 equiv.), NaOEt (2.2 equiv.), PhMe (0.2 M), 24 h, 80 °C.

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 [Mo^{0}L$_n$] species (Fig. 3). The [Mo(bpy)(CO)$_4$] complex[23] was prepared on a large scale by reacting Mo(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

[Mo(bpy)(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 [Mo(CO)$_6$]/L1 catalyst system was observed, thus providing evidence that a [Mo(bpy)(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 (Mo(CO)$_6$/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. 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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Fig. 3 Mechanistic experiments.

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