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Palladium-catalyzed regioselective hydrosulfonylation of allenes with sulfinic acids†

 Luan-Ying Li,^{‡a} Bo-Rong Leng,^{‡ab} Jia-Zhuo Li,^a Qing-Quan Liu,^a Jianguang Yu,^{*a} Ping Wei,^a De-Cai Wang^{*a} and Yi-Long Zhu^{id} ^{*a}

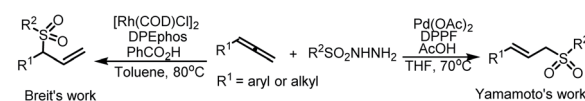
An atom-economic method of preparing allylic sulfones *via* hydrosulfonylation of allenes with sulfinic acids under Pd(0)-catalysis was reported. This process has a high degree of regio- and stereoselectivity, and provides the target product with a moderate to excellent yield. A wide range of nitrogen- or oxygen-containing linear *E*-allylic sulfones have been synthesized. With the support of experimental research, a possible mechanism was proposed.

Introduction

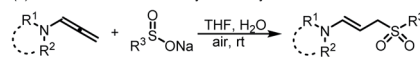
Since the allyl moiety has the potential for further functionalization and construction of new stereogenic centers through asymmetric synthesis, there is an urgent need to develop various atom-economic methods to convert simple and easily available raw materials into allylic derivatives.¹ Allylic sulfones, as an important structural motif of allyl derivatives, are widely used in organic synthesis and the development of pharmaceutical active molecules.² Understandably, many efforts have been made toward synthetic methodologies for allylic sulfones. Transition metal-catalyzed allylic substitution reactions represent one of the most fundamental and versatile methods widely used in modern organic chemistry to construct allylic sulfones.³ However, most of these methods require the preinstallation of a leaving group or the use of a stoichiometric amount of oxidant⁴ or base.⁵ Thus, how to realize the efficient construction of allylic sulfone compounds without the installation of leaving groups under mild conditions has become a challenging problem. In the past decades, allenes have progressively risen from an unenviable status of being a structural curiosity to becoming powerful and versatile synthetic building blocks in organic synthesis.⁶ For example, Yamamoto *et al.* reported an atom-economic example of palladium-catalyzed hydro-sulfonylation of allenes employing sulfonyl hydrazides, providing the corresponding linear allylic sulfones (Scheme 1a).⁷ Subsequently, Breit's research group reported on the strategy of synthesizing branched allylic sulfone with allenes under the

catalysis of Rh (Scheme 1a).⁸ However, in the previous studies, allylic sulfones was mainly produced in one step through addition of sulfonyl hydrazides to allenes in high temperature and have the by-products of hydrogen and nitrogen generation. Comparing to these strategies, Monnier and co-workers⁹ established a transition-metal-free approach to prepare allylic sulfones through the addition of aryl or alkyl sodium sulfinates to allenamides (Scheme 1b). Unfortunately, when arylsulfinic acid was used instead of the corresponding sodium salt, no product was formed.

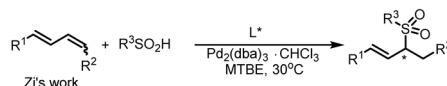
As one of the electron-rich allenes, allenamide has recently become a versatile starting material and application in a variety of interesting transformations through sequential reactions, providing a new and effective method for the preparation of synthetic or biologically important nitrogen-containing compounds.¹⁰ In particular, the intermolecular addition

 (a) Pd or Rh catalyzed hydrosulfonylation of allene with R²SO₂NHNH₂


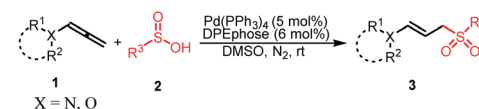
(b) Brønsted acid-mediated hydrosulfonylation of allenamides



(c) Pd catalyzed hydrosulfonylation of 1,3-dienes with sulfinic acid



(d) This work: Pd catalyzed hydrosulfonylation of allenes with sulfinic acid



Scheme 1 Profiles of hydrosulfonylation of allenes or allenamides.

^aSchool of Pharmaceutical Sciences, Nanjing Tech University, Nanjing 211816, P. R. China. E-mail: zhuyilong_88@njtech.edu.cn; dcwang@njtech.edu.cn; yljg@njtech.edu.cn

^bCollege of Life and Health, Nanjing Polytechnic Institute, Nanjing 210048, P. R. China

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‡ These authors contributed equally.



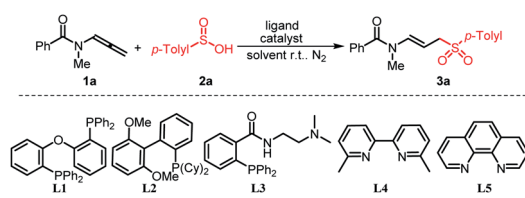
reaction of allenes and nucleophiles catalyzed by transition metals has been widely used in recent years and become one of the effective methods for constructing multifunctional nitrogen-containing allylic derivatives.¹¹ Despite these significant advances, the transition metal catalyzed assemble allylic sulfones from readily attained sulfinic acids are still highly demanded. Recently, Zi *et al.* reported the hydrosulfonylation of 1,3-dienes with sulfinic acids under the catalysis of palladium, which provides an economical way to obtain 1,3-disubstituted chiral allylic sulfones (Scheme 1c).¹² Enlightened by these excellent works, we envisage that a simple palladium-based catalytic system for hydrosulfonylation of allenamides and sulfinic acids can be established. Herein, we describe the Pd-catalyzed nucleophilic addition of sulfinic acids to allenes (Scheme 1d). A wide range of nitrogen- or oxygen-containing linear *E*-allylic sulfones can be selectively obtained through the π -allylic palladium process assisted by the ligand.

Results and discussion

Our initial investigation commenced with the reaction of *N*-methyl-*N*-(propa-1,2-dien-1-yl)benzamide (**1a**) and *p*-methylbenzenesulfinic acid (**2a**) in a 1.0 : 1.5 molar ratio by employing Pd(OAc)₂ (5 mol%) as the catalyst and L1 (DPEphos, 6 mol%) as the ligand. The reaction was performed in anhydrous dimethyl sulfoxide (DMSO) at room temperature under N₂ conditions, delivering the expected hydrosulfonylation product **3a** in 60% yield (Table 1, entry 1). Subsequently, an alternative Pd-catalyst including Pd₂(dba)₃, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, Pd(dba)₂ and Pd/C was examined respectively (entries 2–6). Among them, it was found that Pd(PPh₃)₄ showed the best performance in promoting the conversion of **1a** into **3a**. Other metal catalysts, such as Cu(OTf)₂ and Ni(PPh₃)₂Cl₂ showed no catalytic activities (entries 7 and 8). The replacement of L1 to frequently used mono-, bi- and tri-dentate ligands (L2–L5), which are often used in palladium catalysis, by combining with Pd(PPh₃)₄ did not further increase the reaction yield (entry 4 *vs.* entries 9–12). Then, we investigated the solvent effect by using different solvents such as THF, DMF, 1,4-dioxane, and toluene, but all these attempted solvents did not show any improvement in reaction yield (entry 4 *vs.* entries 13–16). Using 1.2 or 1.3 eq. *p*-methylbenzenesulfinic acid had no effect on the yield, but when it was reduced to 1.1 eq., the yield decreases (entry 17 *vs.* entries 18 and 19). Probably suitable acidic conditions can promote the reaction. No addition of Pd(PPh₃)₄ or L1 results in trace formation of the desired product **3a** (entries 20 and 21).

With the optimized conditions established, we first explored the scope and limitations of the method for the hydrosulfonylation of various readily available allenamides **1a–1z** with *p*-methylbenzenesulfinic acid **2a** (Scheme 2). Different substituents on the aryl ring of benzoyl were well tolerated, including F, Cl, Br, CF₃, Me, MeO, *t*-Bu, and afforded a set of nitrogen-containing linear allyl aryl sulfones **3a–3l** in 82–96% yields. Among them, the electron has little effect on the reaction. Both electron-rich and electron-poor substituents were all successfully engaged in the reaction with a high efficiency. Of these groups, the *o*-chlorophenyl (**1i**) and *o*-fluorophenyl (**1j**)

Table 1 Screening of reaction conditions^a

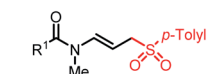
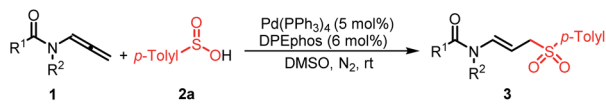


Entry	Catalyst	Ligand	Solvent	Yield ^b (%)
1	Pd(OAc) ₂	L1	DMSO	60%
2	Pd ₂ (dba) ₃	L1	DMSO	91%
3	Pd(PPh ₃) ₂ Cl ₂	L1	DMSO	88%
4	Pd(PPh ₃) ₄	L1	DMSO	96%
5	Pd(dba) ₂	L1	DMSO	88%
6	Pd/C	L1	DMSO	30%
7	Cu(OTf) ₂	L1	DMSO	Trace
8	Ni(PPh ₃) ₂ Cl ₂	L1	DMSO	Trace
9	Pd(PPh ₃) ₄	L2	DMSO	34%
10	Pd(PPh ₃) ₄	L3	DMSO	36%
11	Pd(PPh ₃) ₄	L4	DMSO	30%
12	Pd(PPh ₃) ₄	L5	DMSO	Trace
13	Pd(PPh ₃) ₄	L1	DMF	73%
14	Pd(PPh ₃) ₄	L1	Dioxane	56%
15	Pd(PPh ₃) ₄	L1	THF	90%
16	Pd(PPh ₃) ₄	L1	Toluene	15%
17 ^c	Pd(PPh ₃) ₄	L1	DMSO	86%
18 ^d	Pd(PPh ₃) ₄	L1	DMSO	96%
19 ^e	Pd(PPh ₃) ₄	L1	DMSO	96%
20	Pd(PPh ₃) ₄	None	DMSO	Trace
21	None	L1	DMSO	Trace

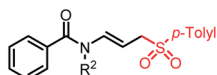
^a Reaction condition: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (5 mol%), ligand (6 mol%), solvent (2.0 mL), nitrogen condition, at room temperature for 6 hours. ^b Isolated yield based on **1a**. ^c **1a** : **2a** = 1 : 1.1. ^d **1a** : **2a** = 1 : 1.2. ^e **1a** : **2a** = 1 : 1.3.

counterparts with strong steric congestion exhibited a good tolerance, but partial *Z*-configuration products were formed (**3i** and **3j**). We conjectured that this may be due to the steric hindrance between the vicinal substituents of the aryl ring and the ligands. Thus, other positions of the substituents on the aryl had no effect on the stereoselectivity and complete *E*-selectivity was observed. Notably, 2-thienyl substituted counterpart **1m** also showed high reactivity, furnishing 95% yield and *E*-selectivity for product **3m**. Various substituents on the nitrogen atom, such as Ph, Bn, Et, *n*-pentyl and *t*-Bu groups, were well-tolerated, and the desired products **3n–3q** were afforded in 81–92% yields with *E*-selectivity. The absolute configuration of the compound was confirmed by examination of the X-ray crystal of **3a**. In view of the influence of the substituents on the aromatic ring of the benzoyl group on the stereoselectivity of the product, we then investigated the electronic effects of the substituents on the *N*-aromatic ring. All the substituents can participate in the reaction well, and the *ortho*-substituents did not exhibit an effect on the stereoselectivity of the reaction, and all the products were obtained in the *E* configuration. Additionally, allenamides bearing cyclic carbamates **1z** also showed high reactivity, furnishing 61% yield for

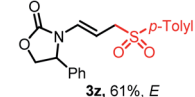




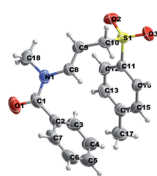
- 3a, R¹ = Ph (96%, *E*)
 3b, R¹ = 4-FC₆H₄ (93%, *E*)
 3c, R¹ = 4-ClC₆H₄ (93%, *E*)
 3d, R¹ = 4-BrC₆H₄ (94%, *E*)
 3e, R¹ = 4-CF₃C₆H₄ (82%, *E*)
 3f, R¹ = 4-MeC₆H₄ (91%, *E*)
 3g, R¹ = 4-MeOC₆H₄ (93%, *E*)
 3h, R¹ = 4-^tBuC₆H₄ (93%, *E*)
 3i, R¹ = 2-ClC₆H₄ (94%, *Z,E* = 1:2)
 3j, R¹ = 2-FC₆H₄ (91%, *Z,E* = 1:2)
 3k, R¹ = 3-ClC₆H₄ (93%, *E*)
 3l, R¹ = 3-FC₆H₄ (93%, *E*)
 3m, R¹ = 2-Thienyl (94%, *E*)



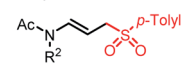
- 3n, R² = Ph (81%, *E*)
 3o, R² = Bn (92%, *E*)
 3p, R² = Et (90%, *E*)
 3q, R² = *n*-Pentyl (89%, *E*)
 3r, R² = *t*-Bu (80%, *E*)



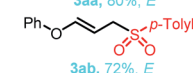
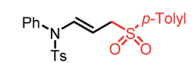
3z, 61%, *E*



X-ray structure of 3a



- 3aa, 80%, *E*
 3ab, 72%, *E*
 3ac, 0%



Scheme 2 Substrate scope for the synthesis of products **3**. ^aReaction conditions: **1a** (0.20 mmol), **2** (0.24 mmol), Pd(PPh₃)₄ (5 mol%) and DPEphos (6 mol%) in dry DMSO (2.0 mL) at room temperature for 6 h. ^bAll yields refer to the isolated yields. ^cThe stereoselectivity was determined by ¹H NMR.

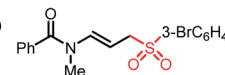
product **3z** with *E*-selectivity. Replacing the aryl group with *p*-toluenesulfonyl also provides the desired product smoothly (**3aa**). In addition, *O*-substituted allene also performed well under this catalytic protocol (**3ab**). When replaced with electron withdrawing substituents, the desired product **3ac** was not produced.

A series of arylsulfonic acid **2** reacted with *N*-methyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** to give the corresponding (*E*)-linear sulfone-containing allyl amides (Scheme 3, **4a–4h**). The arylsulfonic acid containing large hindered substituents on the aromatic ring could also participate in the reaction smoothly, and didn't exhibit inhibition of stereoselectivity (**4g** and **4h**). Under reaction conditions B, the alkyl and benzyl substituted allyl sulfone products can also be formed well with excellent yield and stereoselectivity (**4i** and **4j**).

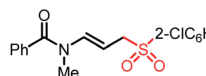
To gain mechanistic insight into the hydrosulfonation of allenes, deuterium-labeling experiments were conducted. When the reaction of **1m** was detected in the presence of 2 eq. D₂O, *d*-**3m** was not observed, which confirmed that water is not a source of hydrogen (Scheme 4a). The same result was obtained using *d*₆-DMSO as the solvent (Scheme 4b). These observations indicate that the hydrogen on allylic sulfones may come from the only other hydrogen source, sulfonic acids. In addition, the reaction cannot proceed without the catalyst under standard conditions, indicating that the catalyst and ligand was



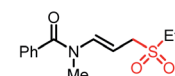
- 4a, R¹ = H (94%, *E*)
 4b, R¹ = OMe (93%, *E*)
 4c, R¹ = ^tBu (54%, *E*)
 4d, R¹ = Cl (59%, *E*)
 4e, R¹ = Br (80%, *E*)
 4f, R¹ = NO₂ (87%, *E*)



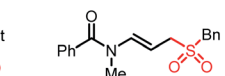
4g, 64%, *E*



4h, 89%, *E*



4i^b, 94%, *E*

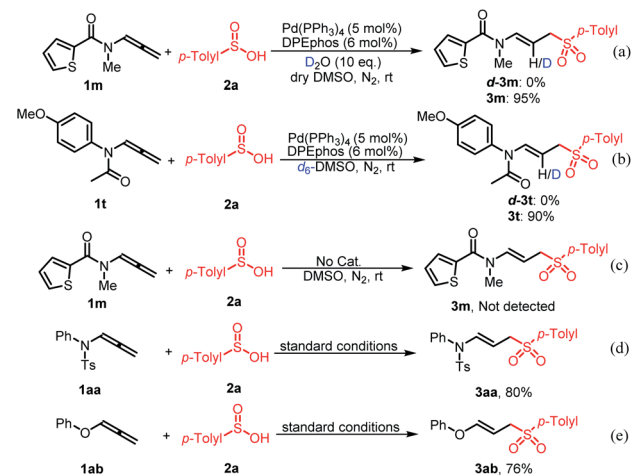


4j^b, 90%, *E*

Scheme 3 Substrate scope for the synthesis of products **4**. ^aReaction condition A: **1a** (0.20 mmol), **2** (arylsulfonic acid, 0.24 mmol), Pd(PPh₃)₄ (5 mol%) and DPEphos (6 mol%) in dry DMSO (2.0 mL) at room temperature for 6 h. ^bReaction condition B: **1a** (0.20 mmol), **2** (sodium alkyl sulfinate, 0.24 mmol), PhCOOH (0.24 mmol), Pd(PPh₃)₄ (5 mol%) and DPEphos (6 mol%) in dry DMSO (2.0 mL) at room temperature for 6 h. ^cAll yields refer to the isolated yields. ^dThe stereoselectivity was determined by ¹H NMR.

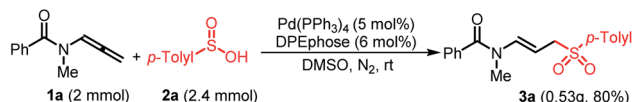
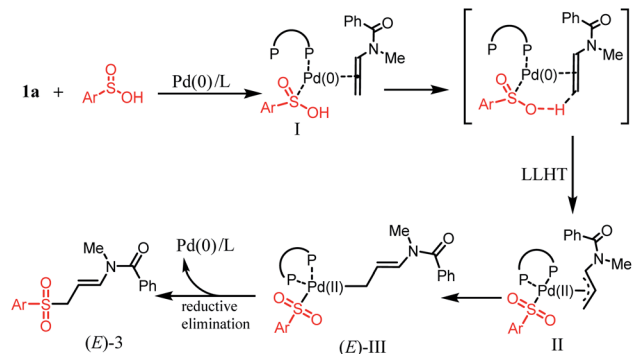
indispensable in the reaction process (Scheme 4c). In order to confirm the role of the carbonyl-directing group and *N*-substituent, the preformed *p*-toluenesulfonyl substituted allenamide **1aa** or *O*-substituted allene was reacted with **2a** under standard conditions respectively (Schemes 4d and e). These two transformations also worked well, indicating that the carbonyl group or *N*-substituent is not indispensable. To expand the potential application of this method, an amplification reaction was conducted under the standard conditions. We were delighted to find that product **3a** was isolated in 80% yield on a 2.0 mmol scale (Scheme 5).

Based on the above results and related literature precedents,^{12–14} a reasonable reaction mechanism of the palladium-catalyzed regioselective hydrosulfonation is proposed in Scheme 6. We suggest that Pd(0) is firstly coordinated with DPEphos, arylsulfonic acid **2** and allene **1** to form Intermediate **I**.



Scheme 4 Control experiments.



Scheme 5 An amplification reaction of **1a** with **2a**.Scheme 6 Proposed mechanisms for forming products **3a**.

Then Intermediate **I** convert to π palladium-allyl species **II** by ligand-to ligand hydrogen transfer (LLHT)^{12,13} from sulfonic acid to allene. Intermediate **II** is then transformed to more thermally stable intermediate (*E*)-**III**. Subsequent reductive elimination from intermediate (*E*)-**III** affords *E*-**3a** selectively and regenerates Pd(0).

Conclusions

To conclude, we reported an unprecedented palladium-catalyzed hydrosulfonylation of allene by directly adding sulfonic acid to allenyl derivatives. The derivative selectively provides a series of N- or O-substituent linear *E*-allylic sulfones with medium to excellent yield in 100% atom utilization. With the support of experimental research, we also proposed a reaction mechanism that the hydrogen atom might be transferred directly from the sulfonic acid to allene *via* a ligand-to ligand hydrogen transfer process. We are currently focusing on further expanding our understanding of this reaction mechanism and developing more LLHT-assisted functionalization of allenes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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