RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2022, **12**, 8443

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 *[a]

Received 14th December 2021
Accepted 9th March 2022

DOI: 10.1039/d1ra09036d

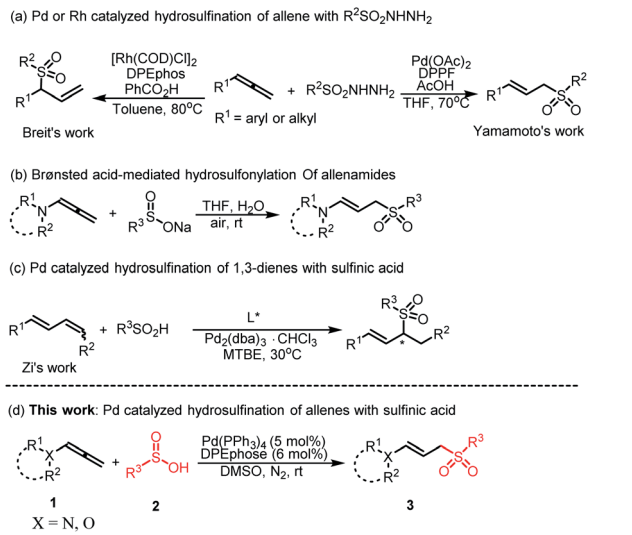
rsc.li/rsc-advances

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 oxidant[4] 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 hydrosulfination 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-workers[9] 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



Scheme 1 Profiles of hydrosulfination of allenes or allenamides.

[a]*School of Pharmaceutical Sciences, Nanjing Tech University, Nanjing 211816, P. R. China. E-mail: zhuyilong_88@njtech.edu.cn; dcwang@njtech.edu.cn; yjg@njtech.edu.cn*

[b]*College of Life and Health, Nanjing Polytechnic Institute, Nanjing 210048, P. R. China*

† Electronic supplementary information (ESI) available. CCDC 2122809 (**3a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra09036d

‡ These authors contributed equally.

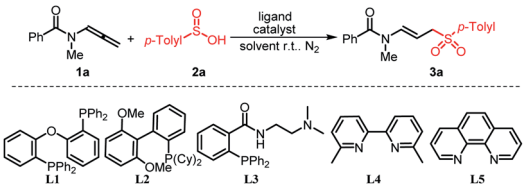
reaction of allenes and nucleophiles catalyzed by transition metals has been widely used in recent years and become one of the effective methods for constructing multifunctional nitrogen-containing allylic derivatives.[11] Despite these significant advances, the transition metal catalyzed assemble allylic 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 N_2 conditions, delivering the expected hydrosulfonylation product **3a** in 60% yield (Table 1, entry 1). Subsequently, an alternative Pd-catalyst including $Pd_2(dba)_3$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $Pd(dba)_2$ and Pd/C was examined respectively (entries 2–6). Among them, it was found that $Pd(PPh_3)_4$ showed the best performance in promoting the conversion of **1a** into **3a**. Other metal catalysts, such as $Cu(OTf)_2$ and $Ni(PPh_3)_2Cl_2$ 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 $Pd(PPh_3)_4$ 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 $Pd(PPh_3)_4$ 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, CF_3, 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**)

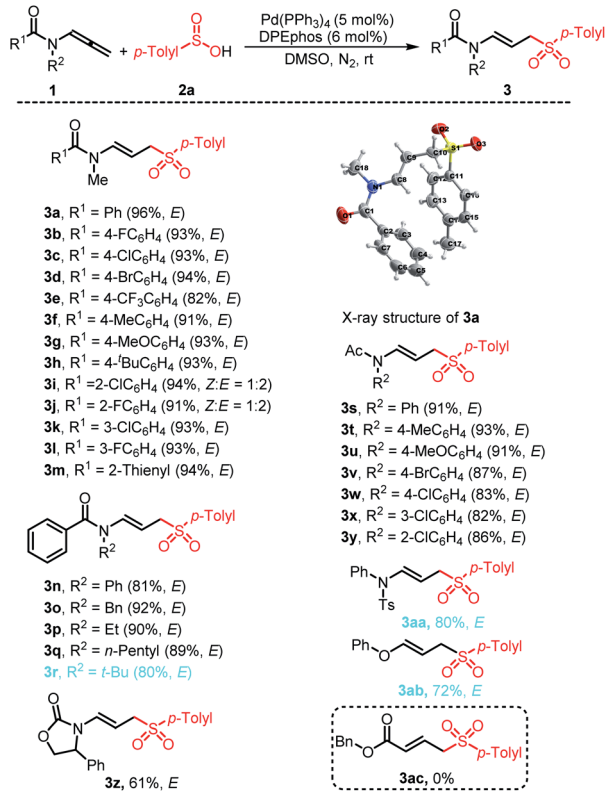
Table 1 Screening of reaction conditions[a]



Entry	Catalyst	Ligand	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	L1	DMSO	60%
2	$Pd_2(dba)_3$	L1	DMSO	91%
3	$Pd(PPh_3)_2Cl_2$	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	$Ni(PPh_3)_2Cl_2$	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]c	$Pd(PPh_3)_4$	L1	DMSO	86%
18[d]d	$Pd(PPh_3)_4$	L1	DMSO	96%
19[e]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 aroyl 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

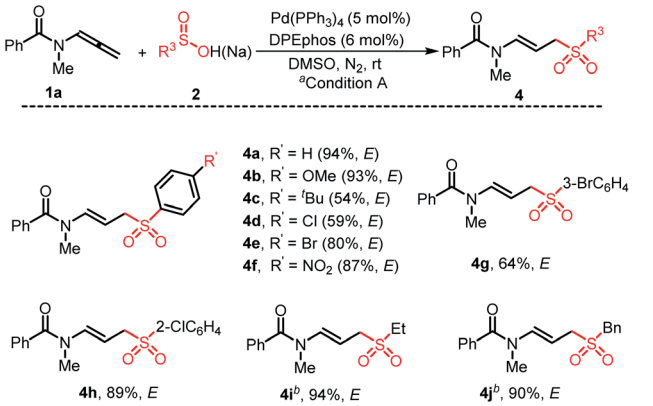


Scheme 2 Substrate scope for the synthesis of products **3**. [a]Reaction conditions: **1a** (0.20 mmol), **2** (0.24 mmol), $Pd(PPh_3)_4$ (5 mol%) and DPEphos (6 mol%) in dry DMSO (2.0 mL) at room temperature for 6 h. [b]All yields refer to the isolated yields. [c]The stereoselectivity was determined by ^1H NMR.

product **3z** with *E*-selectivity. Replacing the aroyl 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 arylsulfinic 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 arylsulfinic 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**).

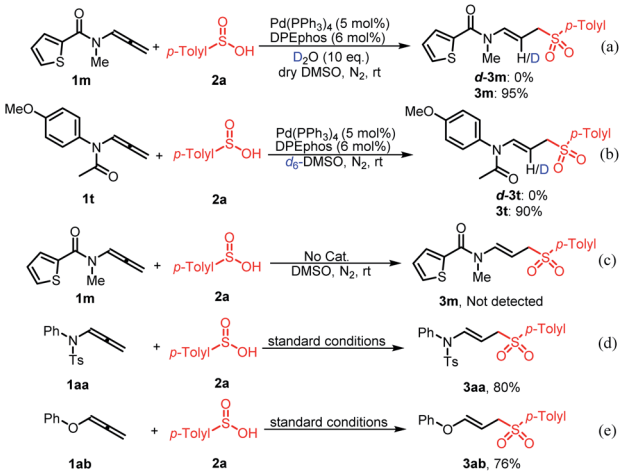
To gain mechanistic insight into the hydrosulfination of allenes, deuterium-labeling experiments were conducted. When the reaction of **1m** was detected in the presence of 2 eq. D_2O, *d*-**3m** was not observed, which confirmed that water is not a source of hydrogen (Scheme 4a). The same result was 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, sulfinic acids. In addition, the reaction cannot proceed without the catalyst under standard conditions, indicating that the catalyst and ligand was



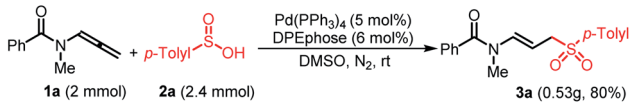
Scheme 3 Substrate scope for the synthesis of products **4**. [a]Reaction condition A: **1a** (0.20 mmol), **2** (arylsulfinic acid, 0.24 mmol), $Pd(PPh_3)_4$ (5 mol%) and DPEphos (6 mol%) in dry DMSO (2.0 mL) at room temperature for 6 h. [b]Reaction condition B: **1a** (0.20 mmol), **2** (sodium alkyl sulfinate, 0.24 mmol), PhCOOH (0.24 mmol), $Pd(PPh_3)_4$ (5 mol%) and DPEphos (6 mol%) in dry DMSO (2.0 mL) at room temperature for 6 h. [c]All yields refer to the isolated yields. [d]The 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-substituent 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).

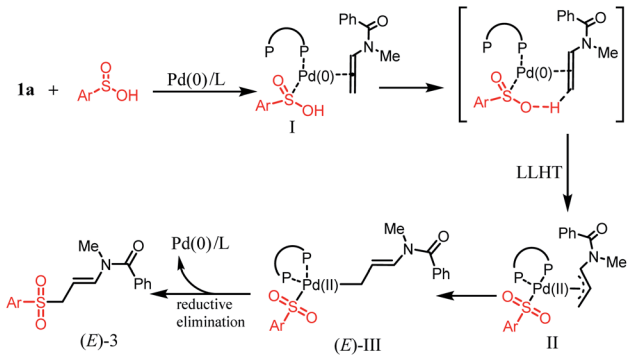
Based on the above results and related literature precedents,[12–14] a reasonable reaction mechanism of the palladium-catalyzed regioselective hydrosulfonylation is proposed in Scheme 6. We suggest that Pd(0) is firstly coordinated with DPEphos, arylsulfinic acid **2** and allene **1** to form Intermediate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

We are grateful for financial support from the NSFC (No. 21801130) and the NSF of Jiangsu Province (BK20180689).

Notes and references

1 (*a*) N. A. Butt and W. Zhang, Transition metal-catalyzed allylic substitution reactions with unactivated allylic substrates, *Chem. Soc. Rev.*, 2015, **44**, 7929–7967; (*b*) Q. Cheng, H. F. Tu, C. Zheng, J. P. Qu, G. Helmchen and S. L. You, Iridium-Catalyzed Asymmetric Allylic Substitution Reactions, *Chem. Rev.*, 2019, **119**, 1855–1969; (*c*) J. Feng, M. Holmes and M. J. Krische, Acyclic Quaternary Carbon Stereocenters via Enantioselective Transition Metal Catalysis, *Chem. Rev.*, 2017, **117**, 12564–12580; (*d*) D. Kumar, S. R. Vemula, N. Balasubramanian and G. R. Cook, Indium-Mediated Stereoselective Allylation, *Acc. Chem. Res.*, 2016, **49**, 2169–2178; (*e*) J. Qu and G. Helmchen, Applications of Iridium-Catalyzed Asymmetric Allylic Substitution Reactions in Target-Oriented Synthesis, *Acc. Chem. Res.*, 2017, **50**, 2539–2555; (*f*) R. Jiang, L. Ding, C. Zheng and S.-L. You, Iridium-catalyzed Z-retentive asymmetric allylic substitution reactions, *Science*, 2021, **371**, 380–386; (*g*) C. Zheng and S. L. You, Exploring the Chemistry of Spiroindolenines by Mechanistically-Driven Reaction Development: Asymmetric Pictet-Spengler-type Reactions and Beyond, *Acc. Chem. Res.*, 2020, **53**, 974–987; (*h*) C. X. Zhuo, C. Zheng and S. L. You, Transition-metal-catalyzed asymmetric allylic dearomatization reactions, *Acc. Chem. Res.*, 2014, **47**, 2558–2573.

2 (*a*) D. Rotulo-Sims and J. Prunet, Tandem Conjugate Addition-Elimination for the Diastereoselective Synthesis of 4E-Alkenyl syn-1,3-Diols, *Org. Lett.*, 2007, **9**, 4147–4150; (*b*) P. Chen, Y. Wu, S. Zhu, H. Jiang and Z. Ma, Ir-Catalyzed reactions in natural product synthesis, *Org. Chem. Front.*, 2018, **5**, 132–150; (*c*) D. Díez, P. Garcia, I. S. Marcos, N. M. Garrido, P. Basabe, H. B. Broughton and J. G. Urones, Stereocontrolled Synthesis of Cyclopropanol Amino Acids from Allylic Sulfones: Conformationally Restricted Building Blocks, *Org. Lett.*, 2003, **5**, 3687–3690; (*d*) V. Gembus, S. Postikova, V. Levacher and J. F. Briere, Highly regio- and diastereoselective anionic [3 + 2] cycloaddition under phase transfer catalytic conditions, *J. Org. Chem.*, 2011, **76**, 4194–4199; (*e*) Z. S. Liu, W. K. Li, T. R. Kang, L. He and Q. Z. Liu, Palladium-catalyzed asymmetric cycloadditions of vinylcyclopropanes and in situ formed unsaturated imines: construction of structurally and optically enriched spiroindolenines, *Org. Lett.*, 2015, **17**, 150–153; (*f*) P. Vogel, M. Turks, L. Bouchez, D. Markovic, A. Varela-Álvarez and J. Á. Sordo, New Organic Chemistry of Sulfur Dioxide, *Acc. Chem. Res.*, 2007, **40**, 931–942; (*g*) B. M. Trost and C. A. Kalnmals, Annulative Allylic Alkylation Reactions between Dual Electrophiles and Dual Nucleophiles: Applications in Complex Molecule Synthesis, *Chem.–Eur. J.*, 2020, **26**, 1906–1921; (*h*) G. C. Tsui and M. Lautens, Linear-selective rhodium(I)-catalyzed addition of arylboronic acids to allyl sulfones, *Angew. Chem., Int. Ed.*, 2010, **49**, 8938–8941.

3 (*a*) B. M. Trost, M. G. Organ and G. A. O'Doherty, Asymmetric Synthesis of Allylic Sulfones. Useful Asymmetric Building Blocks, *J. Am. Chem. Soc.*, 1995, **117**, 9662–9670; (*b*) M. Ueda and J. F. Hartwig, Iridium-Catalyzed, Regio- and Enantioselective Allylic Substitution with Aromatic and Aliphatic Sulfinates, *Org. Lett.*, 2010, **12**, 92–94; (*c*) A. B. Pritzius and B. Breit, Asymmetric rhodium-catalyzed

addition of thiols to allenes: synthesis of branched allylic thioethers and sulfones, *Angew. Chem., Int. Ed.*, 2015, **54**, 3121–3125; (*d*) A. B. Pritzius and B. Breit, Z-Selective Hydrothiolation of Racemic 1,3-Disubstituted Allenes: An Atom-Economic Rhodium-Catalyzed Dynamic Kinetic Resolution, *Angew. Chem., Int. Ed.*, 2015, **54**, 15818–15822; (*e*) S. Zheng, N. Gao, W. Liu, D. Liu, X. Zhao and T. Cohen, Regio- and Enantioselective Iridium-Catalyzed Allylation of Thiophenol: Synthesis of Enantiopure Allyl Phenyl Sulfides, *Org. Lett.*, 2010, **12**, 4454–4457; (*f*) T. T. Wang, F. X. Wang, F. L. Yang and S. K. Tian, Palladium-catalyzed aerobic oxidative coupling of enantioenriched primary allylic amines with sulfonyl hydrazides leading to optically active allylic sulfones, *Chem. Commun.*, 2014, **50**, 3802–3805; (*g*) X. S. Wu, Y. Chen, M. B. Li, M. G. Zhou and S. K. Tian, Direct substitution of primary allylic amines with sulfinate salts, *J. Am. Chem. Soc.*, 2012, **134**, 14694–14697; (*h*) P. X. Zhou, Y. Y. Ye, L. B. Zhao, J. Y. Hou, X. Kang, D. Q. Chen, Q. Tang, J. Y. Zhang, Q. X. Huang, L. Zheng, J. W. Ma, P. F. Xu and Y. M. Liang, Using N-tosylhydrazone as a double nucleophile in the palladium-catalyzed cross-coupling reaction to synthesize allylic sulfones, *Chem.–Eur. J.*, 2014, **20**, 16093–16096.

4 (*a*) X. Li, X. Xu and Y. Tang, Tetrabutylammonium iodide catalyzed allylic sulfonylation of Baylis-Hillman acetates with sulfonylhydrazides in water, *Org. Biomol. Chem.*, 2013, **11**, 1739–1742; (*b*) Y. Wang, G. Xiong, C. Zhang and Y. Chen, Controllable Activation of beta-Alkyl Nitroalkenes: Regioselective Synthesis of Allyl and Vinyl Sulfones, *J. Org. Chem.*, 2021, **86**, 4018–4026.

5 (*a*) H. J. Gais, T. Jagusch, N. Spalthoff, F. Gerhards, M. Frank and G. Raabe, Highly selective palladium catalyzed kinetic resolution and enantioselective substitution of racemic allylic carbonates with sulfur nucleophiles: asymmetric synthesis of allylic sulfides, allylic sulfones, and allylic alcohols, *Chem.–Eur. J.*, 2003, **9**, 4202–4221; (*b*) W. B. Liu, S. C. Zheng, H. He, X. M. Zhao, L. X. Dai and S. L. You, Iridium-catalyzed regio- and enantioselective allylic alkylation of fluorobis(phenylsulfonyl)methane, *Chem. Commun.*, 2009, **43**, 6604–6606; (*c*) K. Spielmann, M. Xiang, L. A. Schwartz and M. J. Krische, Direct Conversion of Primary Alcohols to 1,2-Amino Alcohols: Enantioselective Iridium-Catalyzed Carbonyl Reductive Coupling of Phthalimido-Allene via Hydrogen Auto-Transfer, *J. Am. Chem. Soc.*, 2019, **141**, 14136–14141; (*d*) S. Zheng, W. Huang, N. Gao, R. Cui, M. Zhang and X. Zhao, One pot iridium-catalyzed asymmetrical double allylations of sodium sulfide: a fast and economic way to construct chiral C2-symmetric bis(1-substituted-allyl)sulfane, *Chem. Commun.*, 2011, **47**, 6969–6971.

6 (*a*) M. Bandini, Gold-catalyzed decorations of arenes and heteroarenes with C–C multiple bonds, *Chem. Soc. Rev.*, 2011, **40**, 1358–1367; (*b*) M. Holmes, L. A. Schwartz and M. J. Krische, Intermolecular Metal-Catalyzed Reductive Coupling of Dienes, Allenes, and Enynes with Carbonyl Compounds and Imines, *Chem. Rev.*, 2018, **118**, 6026–6052; (*c*) X. Huang and S. Ma, Allenation of Terminal Alkynes with Aldehydes and Ketones, *Acc. Chem. Res.*, 2019, **52**, 1301–1312; (*d*) G. Li, X. Huo, X. Jiang and W. Zhang, Asymmetric synthesis of allylic compounds via hydrofunctionalisation and difunctionalisation of dienes, allenes, and alkynes, *Chem. Soc. Rev.*, 2020, **49**, 2060–2118; (*e*) J. L. Mascarenas, I. Varela and F. Lopez, Allenes and Derivatives in Gold(I)- and Platinum(II)-Catalyzed Formal Cycloadditions, *Acc. Chem. Res.*, 2019, **52**, 465–479; (*f*) Z. Wang, X. Xu and O. Kwon, Phosphine catalysis of allenes with electrophiles, *Chem. Soc. Rev.*, 2014, **43**, 2927–2940; (*g*) W. Yang and A. S. Hashmi, Mechanistic insights into the gold chemistry of allenes, *Chem. Soc. Rev.*, 2014, **43**, 2941–2955; (*h*) Y.-M. Wang, A. D. Lackner and F. D. Toste, Development of Catalysts and Ligands for Enantioselective Gold Catalysis, *Acc. Chem. Res.*, 2014, **47**, 889–901; (*i*) J. Ye and S. Ma, Palladium-Catalyzed Cyclization Reactions of Allenes in the Presence of Unsaturated Carbon–Carbon Bonds, *Acc. Chem. Res.*, 2014, **47**, 989–1000.

7 S. Kamijo, M. Al-Masum and Y. Yamamoto, Palladium Catalyzed Hydrosulfination of Allenes with Tosyihydrazine Leading to Allylsulfones, *Tetrahedron Lett.*, 1998, **39**, 691–694.

8 V. Khakyzadeh, Y. H. Wang and B. Breit, Rhodium-catalyzed addition of sulfonyl hydrazides to allenes: regioselective synthesis of branched allylic sulfones, *Chem. Commun.*, 2017, **53**, 4966–4968.

9 L. Pages, S. Lemouzy, M. Taillefer and F. Monnier, *J. Org. Chem.*, 2021, **86**, 15695–15701.

10 (*a*) R. Blieck, M. Taillefer and F. Monnier, Metal-Catalyzed Intermolecular Hydrofunctionalization of Allenes: Easy Access to Allylic Structures via the Selective Formation of C–N, C–C, and C–O Bonds, *Chem. Rev.*, 2020, **120**, 13545–13598; (*b*) X. Li, Y. Liu, N. Ding, X. Tan and Z. Zhao, Recent progress in transition-metal-free functionalization of allenamides, *RSC Adv.*, 2020, **10**, 36818–36827; (*c*) L.-L. Wei, H. Xiong and R. P. Hsung, The Emergence of Allenamides in Organic Synthesis,, *Acc. Chem. Res.*, 2003, **36**, 773–782; (*d*) T. Lu, Z. Lu, Z. X. Ma, Y. Zhang and R. P. Hsung, Allenamides: a powerful and versatile building block in organic synthesis, *Chem. Rev.*, 2013, **113**, 4862–4904.

11 (*a*) R. Blieck, R. Abed Ali Abdine, M. Taillefer and F. Monnier, Regio- and Stereoselective Copper-Catalyzed Allylation of 1,3-Dicarbonyl Compounds with Terminal Allenes, *Org. Lett.*, 2018, **20**, 2232–2235; (*b*) R. Blieck, M. Taillefer and F. Monnier, Copper-Catalyzed Hydrocarboxylation of N-Allenyl Derivatives, *J. Org. Chem.*, 2019, **84**, 11247–11252; (*c*) E. Skucas, J. R. Zbieg and M. J. Krische, anti-Aminoallylation of Aldehydes via Ruthenium-Catalyzed Transfer Hydrogenative Coupling of Sulfonamido Allenes: 1,2-Aminoalcohols, *J. Am. Chem. Soc.*, 2009, **131**, 5054–5055; (*d*) M. C. Kimber and A. Facile, Mild Synthesis of Enamides using a Gold-Catalyzed Nucleophilic Addition to Allenamides, *Org. Lett.*, 2010, **12**, 1128–1131; (*e*) Y. Liu, A. Cerveri, A. De Nisi, M. Monari, O. Nieto Faza, C. S. Lopez and M. Bandini, Nickel catalyzed regio- and

stereoselective arylation and methylation of allenamides via coupling reactions. An experimental and computational study, *Org. Chem. Front.*, 2018, **5**, 3231–3239; (*f*) T. R. Pradhan, H. W. Kim and J. K. Park, Regiodivergent Synthesis of 1,3- and 1,4-Enynes through Kinetically Favored Hydropalladation and Ligand-Enforced Carbopalladation, *Angew. Chem., Int. Ed.*, 2018, **57**, 9930–9935; (*g*) Y. Wang, P. Zhang, D. Qian and J. Zhang, Highly Regio-, Diastereo-, and Enantioselective Gold(I)-Catalyzed Intermolecular Annulations with N-Allenamides at the Proximal C=C Bond, *Angew. Chem., Int. Ed.*, 2015, **54**, 14849–14852.

12 Q. Zhang, D. Dong and W. Zi, Palladium-Catalyzed Regio- and Enantioselective Hydrosulfonylation of 1,3-Dienes with Sulfinic Acids: Scope, Mechanism, and Origin of Selectivity, *J. Am. Chem. Soc.*, 2020, **142**, 15860–15869.

13 For LLHT in metal catalysis: (*a*) J. S. Bair, Y. Schramm, A. G. Sergeev, E. Clot, O. Eisenstein and J. F. Hartwig, *J. Am. Chem. Soc.*, 2014, **136**, 13098–13101; (*b*) L. J. Xiao, X. N. Fu, M. J. Zhou, J. H. Xie, L. X. Wang, X. F. Xu and Q. L. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 2957–2960; (*c*) J. Guihaumé, S. Halbert, O. Eisenstein and R. N. Perutz, *Organometallics*, 2011, **31**, 1300–1314; (*d*) S. Tang, O. Eisenstein, Y. Nakao and S. Sakaki, *Organometallics*, 2017, **36**, 2761–2771.

14 (*a*) R. A. A. Abdine, L. Pagès, M. Taillefer and F. Monnier, Hydroarylation of N-Allenyl Derivatives Catalyzed by Copper, *Eur. J. Org. Chem.*, 2020, **48**, 7466–7469; (*b*) U. Gellrich, A. Meissner, A. Steffani, M. Kahny, H. J. Drexler, D. Heller, D. A. Plattner and B. Breit, Mechanistic investigations of the rhodium catalyzed propargylic CH activation, *J. Am. Chem. Soc.*, 2014, **136**, 1097–1104; (*c*) Y. Liu, N. Ding, X. Tan, X. Li and Z. Zhao, Iron(ii)-chloride-catalyzed regioselective azidation of allenamides with $TMSN_3$, *Chem. Commun.*, 2020, **56**, 7507–7510; (*d*) L. A. Perego, R. Blieck, A. Groué, F. Monnier, M. Taillefer, I. Ciofini and L. Grimaud, Copper-Catalyzed Hydroamination of Allenes: from Mechanistic Understanding to Methodology Development, *ACS Catal.*, 2017, **7**, 4253–4264; (*e*) K. Xu, V. Khakyzadeh, T. Bury and B. Breit, Direct transformation of terminal alkynes to branched allylic sulfones, *J. Am. Chem. Soc.*, 2014, **136**, 16124–16127.