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# Palladium-Catalyzed/Mn(OAc)<sub>3</sub>-Mediated 1,2-Diazidation and 1,2-Acetoxy/Hydroxylation of *N*-Allyl Sulfonamides

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**Abstract.** Palladium-catalyzed conditions for diazidation or acetoxy/hydroxylation of *N*-allyl sulfonamides by using Pd(OAc)<sub>2</sub> as the catalyst combined with Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O have been developed. The 1,2-diazidation reaction of the carbon-carbon double bond occurs in mild conditions (*i.e.* NaN<sub>3</sub> as azide source in THF at room temperature) in the presence of NaN<sub>3</sub> as azide source, whereas the 1,2-acetoxy/hydroxylation requires an excess of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O. The well-known ability of this reagent to act through single-electron transfer (SET) makes plausible a radical mechanism involving high valent palladium complexes.

**Keywords:** Allylic compounds; Azides; Homogeneous catalysis; Manganese; Palladium; Radical reactions; Synthetic methods; Sulfonamides

The simultaneous installation of two functional groups on unsaturated bonds is a useful tool in organic synthesis to rapidly increase molecular complexity.<sup>[1]</sup> In particular, dual functionalization of alkenes has become a versatile tool for accessing compounds containing several combinations of vicinal functional groups through the concomitant formation of C–C and C–heteroatom bonds.<sup>[2]</sup> These transformations can be catalyzed by a wide variety of transition metals involving different reaction conditions.<sup>[3]</sup> Among them, oxidative Pd-catalyzed reactions occupy a pivotal role due to their versatility in introducing several combinations of functional groups by inter-, intra- and inter/intramolecular processes.<sup>[4]</sup> The ease of switch of this catalysis, typically between 0/II or II/IV oxidation states depending on the type of the chosen secondary oxidant, ensures general success in many applications for the preparation of fine chemicals, pharmaceutically active compounds, agrochemicals and advanced materials.<sup>[5]</sup>

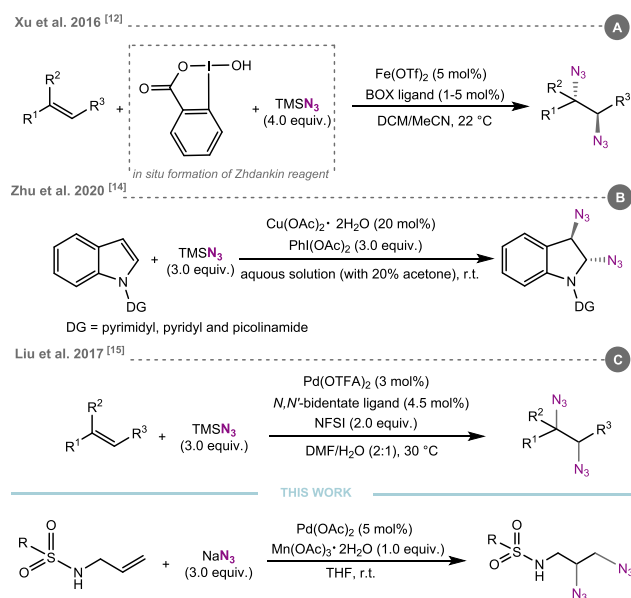
Due to the widespread interest in compounds with a high nitrogen content, reactions involving difunctionalization through the formation of two C–N bonds are attracting a great deal of interest in organic

synthesis.<sup>[6]</sup> To this purpose, we recently reported a new palladium-catalyzed procedure to convert aminoalkenes into azidomethyl substituted nitrogen-containing heterocycles.<sup>[7]</sup> The protocol required the use of H<sub>2</sub>O<sub>2</sub> as inexpensive oxidant, which is essential to generate a Pd(IV) species as the key-intermediate for the reaction.

Following our interest in difunctionalization of unsaturated C–C bonds,<sup>[8]</sup> we have now found a new method for the 1,2-diazidation of allyl sulfonamides.<sup>[9]</sup> 1,2-Diazide compounds are ideal precursors of vicinal primary diamines or bis-triazolyl derivatives, which have proven to be important motifs in biologically active compounds.<sup>[10]</sup> The literature reports different approaches to obtain 1,2-diazides from alkenes. As to the transition-metal catalyzed protocols, iron- and copper-based catalysts are the most used for the generation of an azido radical that in turn interacts with an appropriate alkene function enabling a cascade difunctionalization.<sup>[11]</sup>

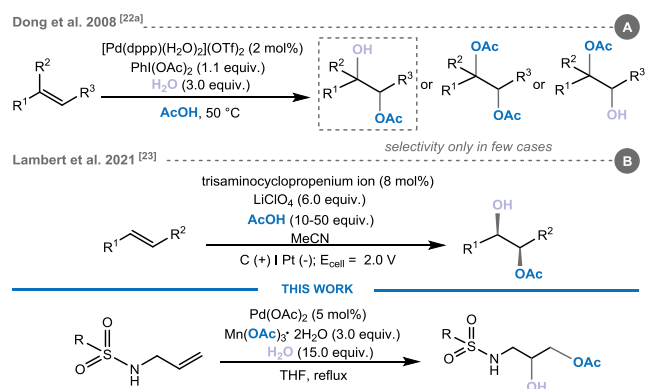
Scheme 1 illustrates a selection of the most relevant transition metal-catalyzed 1,2-alkene diazidations. The iron-catalyzed approach of Xu et al. involves the use of the expensive TMSN<sub>3</sub> (compared to NaN<sub>3</sub>) combined with benziodoxole to generate *in situ* the corresponding hazardous azidoiodinane ABX (Zhdankin reagent) (eq. A).<sup>[12,13]</sup> Analogously, the copper-catalyzed approach of Zhu et al. generates the transient azido radical by the reaction between PhI(OAc)<sub>2</sub> and TMSN<sub>3</sub> (eq. B).<sup>[14]</sup> The only Pd-catalyzed 1,2-diazidation, by Liu et al. involves alkenes devoid of a sulfonamide group, and the not-so-sustainable DMF as solvent (eq. C).<sup>[15]</sup>

Furthermore, some procedures involve electrochemical activation, often combined with a transition-metal catalyst,<sup>[16]</sup> with only one example concerning an *N*-allyl sulfonamide<sup>[16c]</sup> and no examples concerning a secondary *N*-allyl sulfonamide. Herein, we propose a diazidation method based on the use of palladium catalysis combined with Mn(OAc)<sub>3</sub> as oxidant.



**Scheme 1.** Selection of transition-metal catalyzed diazidation procedures vs our Pd-catalyzed/ $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ -mediated diazidation of *N*-allyl sulfonamides.

Furthermore, we also found that the same catalytic system is able to promote the regioselective 1,2-acetoxylation/hydroxylation of the C-C double bond. The regioselective synthesis of 1,2-diols monoesters is a key and often non-trivial task in organic synthesis. This goal is typically obtained by monoacylation of the parent 1,2-diol. However, this protocol often results in a mixture of starting diol, monoacylated, and diacylated product that can be alleviated only by employing a large excess of the starting diol. Some partial success has been obtained through direct monoacylation catalyzed by different agents such as silica gel supported sulfates,<sup>[17]</sup> ion-exchange resins,<sup>[18]</sup>  $\text{YbCl}_3$ ,<sup>[19]</sup> or by in situ acylation of the corresponding transient dibutylstannylene acetals,<sup>[20]</sup> or via acidic hydrolysis of the transient cyclic orthoesters.<sup>[21]</sup> Only a few oxidative examples of alkene 1,2-acetoxy/hydroxylation have been reported. Two of them are catalyzed by Pd(II), in the presence of  $\text{PhI}(\text{OAc})_2$  and water (Scheme 2, eq. A),<sup>[22]</sup> while the other is catalyzed by a trisaminocyclopropenium ion, under visible light irradiation and an electrochemical potential (Scheme 2, eq. B).<sup>[23]</sup>



**Scheme 2.** Reported acetoxy/hydroxylation reactions vs our Pd-catalyzed/ $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ -mediated approach.

In order to investigate new diazidation conditions, we have chosen the *N*-allyl *o*-nosylsulfonamide **1a** as model substrate. As shown by the preliminary experiments collected in Table 1,  $\text{H}_2\text{O}_2$  was initially used as the oxidant with a palladium(II) catalyst (see Supporting Information for the complete optimization Table). The 2,3-diazidation product **2a** was obtained working with  $\text{Pd}(\text{OAc})_2$  and  $\text{NaN}_3$  as azide source in THF either at room temperature or at reflux, although in low yield (entries 1-2). On the other hand, using  $\text{MeCN}$  as the solvent or  $\text{PdCl}_2(\text{MeCN})_2$  as the catalyst was unsuccessful (entries 3-4). The single-crystal X-ray structure analysis of compound **2a** gave unambiguous proof for the formation of the diazide product **2a**.<sup>[24]</sup> The use of benzoquinone or hypervalent iodine derivatives precluded the conversion of the substrate (entries 5-7), while copper(II) chloride led to the formation of **2a** in low yields (entries 8 and 9). A remarkable improvement in the formation of **2a** was obtained by employing  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  in the presence of  $\text{Pd}(\text{OAc})_2$  and  $\text{NaN}_3$  in THF as solvent (entries 10 and 11).<sup>[25]</sup> These conditions afforded the diazidation product in satisfactory yield working at room temperature as well as at reflux. Other combinations of palladium sources and solvents did not prove suitable for the conversion of sulfonamide **1a** (entries 12-14). Finally, a test using the same reaction conditions as in entry 10, but with the exclusion of  $\text{Pd}(\text{OAc})_2$  gave no reaction, thus confirming the need of the transition metal (entry 15).<sup>[26]</sup>

**Table 1.** Optimization of the diazidation conditions<sup>[a]</sup>

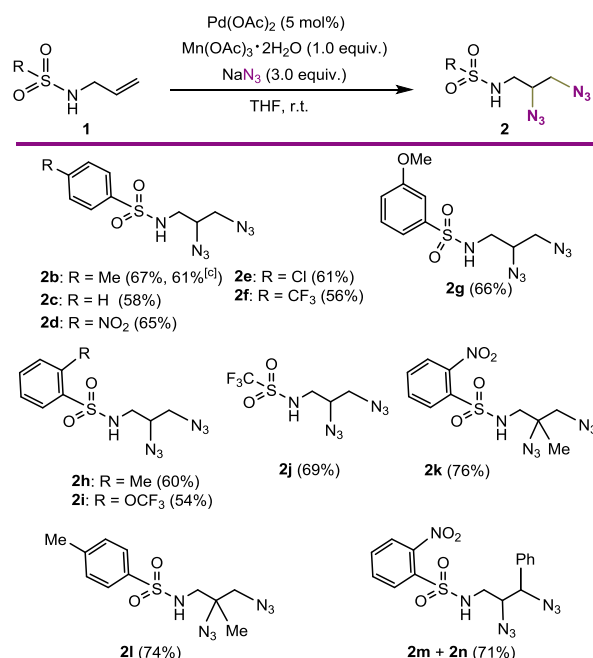
Entry	Pd-Catalysts	Oxidant	Solvent	Temperature	Time	Yield <sup>[b]</sup> (%)
1	$\text{Pd}(\text{OAc})_2$	$\text{H}_2\text{O}_2$	THF	rt	12 h	10
2	$\text{Pd}(\text{OAc})_2$	$\text{H}_2\text{O}_2$	THF	reflux	12 h	15
3	$\text{PdCl}_2(\text{MeCN})_2$	$\text{H}_2\text{O}_2$	MeCN	reflux	12 h	0
4	$\text{PdCl}_2(\text{MeCN})_2$	$\text{H}_2\text{O}_2$	THF	reflux	12 h	0
5	$\text{Pd}(\text{OAc})_2$	benzoquinone	THF	reflux	12 h	0
6	$\text{Pd}(\text{OAc})_2$	benzoquinone	MeCN	reflux	12 h	0
7	$\text{Pd}(\text{OAc})_2$	benzoquinone	THF	reflux	12 h	0
8	$\text{CuCl}_2$	$\text{H}_2\text{O}_2$	THF	reflux	12 h	5
9	$\text{CuCl}_2$	$\text{H}_2\text{O}_2$	MeCN	reflux	12 h	5
10	$\text{Pd}(\text{OAc})_2$	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$	THF	rt	12 h	45
11	$\text{Pd}(\text{OAc})_2$	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$	THF	reflux	12 h	55
12	$\text{Pd}(\text{OAc})_2$	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$	MeCN	reflux	12 h	0
13	$\text{Pd}(\text{OAc})_2$	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$	THF	reflux	12 h	0
14	$\text{Pd}(\text{OAc})_2$	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$	THF	reflux	12 h	0
15	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$	$\text{NaN}_3$	THF	reflux	12 h	0

1	Pd(OAc) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	THF	r.t.	48	24
2	Pd(OAc) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	THF	reflux	24	18
3	Pd(OAc) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	MeCN	reflux	24	-
4	PdCl <sub>2</sub> (MeCN) <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	THF	r.t.	24	trace
5	Pd(OAc) <sub>2</sub>	Benzoquinone	THF	r.t.	72	-
6	Pd(OAc) <sub>2</sub>	PIDA	THF	r.t.	72	-
7	Pd(OAc) <sub>2</sub>	PIFA	THF	r.t.	72	-
8	Pd(OAc) <sub>2</sub>	CuCl <sub>2</sub>	THF	r.t.	72	22
9	Pd(OAc) <sub>2</sub>	CuCl <sub>2</sub>	THF	reflux	48	19
<b>10</b>	<b>Pd(OAc)<sub>2</sub></b>	<b>Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O</b>	<b>THF</b>	<b>r.t.</b>	<b>48</b>	<b>61</b>
11	Pd(OAc) <sub>2</sub>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	THF	reflux	24	55
12	PdCl <sub>2</sub> (MeCN) <sub>2</sub>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	THF	r.t.	48	27
13	Pd(OAc) <sub>2</sub>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	MeCN	r.t.	48	trace
14	Pd(OAc) <sub>2</sub>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	DMF	r.t.	48	-
15	-	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	THF	reflux	24	-

<sup>[a]</sup> Reaction conditions: **1a** (1.0 mmol), Pd-catalyst (5 mol%), oxidant (1.0 mmol), THF (0.1 M). <sup>[b]</sup> Isolated yields.

We then passed to evaluate the scope of the reaction by testing different *N*-allyl sulfonamides under the optimized reaction conditions of entry 10, Table 1 [Pd(OAc)<sub>2</sub> (5 mol%), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (1.0 equiv.) and NaN<sub>3</sub> (3.0 equiv.) in THF at room temperature]. A range of arylsulfonamides bearing ortho, meta and para electron-donor or withdrawing substituents gave the 1-sulfonamido-2,3-diazidopropanes **2b-i** in satisfactory (54-67%) yields (Table 2). The reaction conditions were also compatible with the trifluoromethyl sulfonamide, which afforded the expected product **2j** in 69% yield.<sup>[27]</sup> Among the substrates bearing substituents on the allyl moiety, only methallyl and cinnamyl sulfonamides afforded the expected diazidation products. In the first case, compounds **2k,l** were achieved in good yields, while a mixture of inseparable diastereoisomers (**2m,n**) was obtained from cinnamyl *o*-nosylsulfonamide.<sup>[28]</sup>

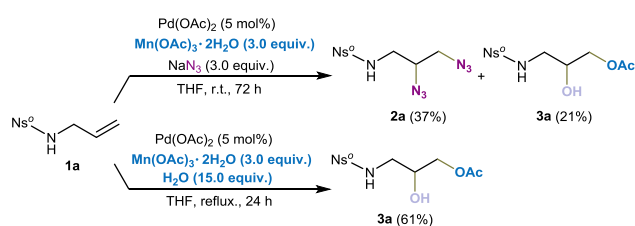
**Table 2.** Diazidation of *N*-allyl sulfonamides.<sup>[a,b]</sup>



<sup>[a]</sup> Reaction conditions: substrate (1.0 mmol), Pd(OAc)<sub>2</sub> (5 mol%), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (1.0 mmol), NaN<sub>3</sub> (3.0 mmol), THF (0.1M), r.t., 48h. <sup>[b]</sup> Isolated yields. <sup>[c]</sup> Scale-up: performing the reaction on 5.0 mmol of substrate **1b** at r.t., after for 72h **2b** was obtained with 61% yield.

During the optimization tests, we found that when substrate **1a** was treated with a larger amount of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (3.0 equivalents), product **3a**, arising from a regioselective 1,2-acetoxylation/hydroxylation process, was concurrently formed besides the diazidation product **2a** (Scheme 3). This new compound was selectively obtained carrying out the reaction overnight at reflux, without the azide source. Again, solvents other than THF inhibited the conversion, but the addition of 15.0 equivalents of water in the reaction medium increased the yield to 61%. Also in this case, the reaction carried out only with an excess of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O did not afford the expected product,

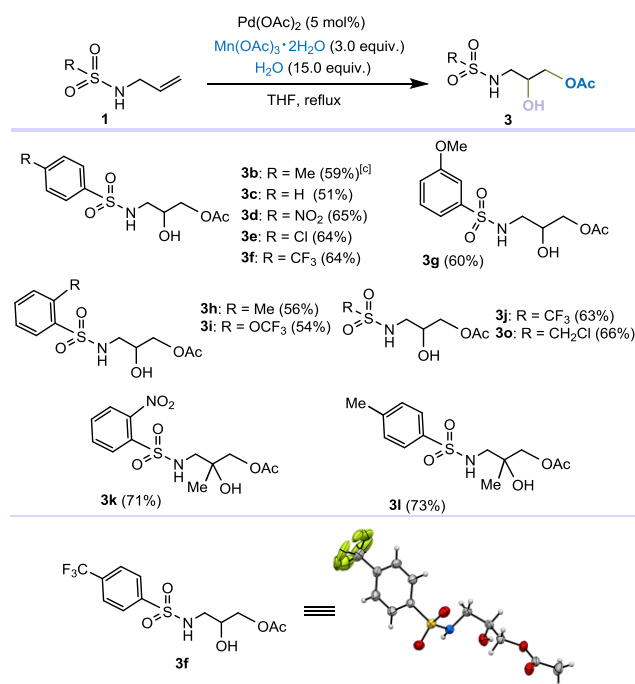
which confirmed the involvement Pd-catalyst in this transformation as well.



**Scheme 3.** Pd-catalyzed acetoxylation/hydroxylation of *N*-allyl *o*-nosyl-sulfonamide.

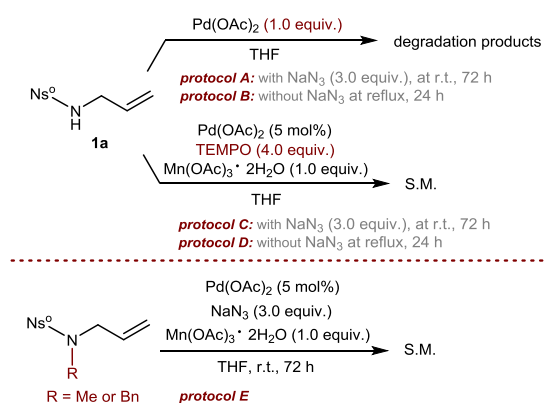
With the optimal acetoxy/hydroxylation conditions in hand, the scope was evaluated (Table 3). The *N*-allyl sulfonamides tested, generated the corresponding 1-sulfonamido-2-acetoxy-3-hydroxypropanes in satisfactory yields.<sup>[29]</sup> Various functional groups on the aromatic ring were also well-tolerated. For example, as seen for the diazidation procedure, the halomethyl substituted substrates **1j,o** afforded the expected products **3j,o** and the methallyl sulfonamides **1k,l** reacted satisfactorily under the standard conditions.<sup>[30]</sup>

**Table 3.** Acetoxy/hydroxylation of *N*-allyl sulfonamides.<sup>[a,b,c]</sup>



<sup>[a]</sup> Reaction conditions: substrate (1.0 mmol), Pd(OAc)<sub>2</sub> (5 mol%), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (3.0 mmol), H<sub>2</sub>O (15.0 mmol), THF (0.1M), reflux in oil bath for 24h. <sup>[b]</sup> Isolated yields. <sup>[c]</sup> Scale-up: performing the reaction on 5.0 mmol of substrate **1b** at reflux in oil bath, after for 72h **3b** was obtained with 53% yield.

In search of evidences to propose plausible mechanisms for these transformations, the following considerations were taken into account: a) although Mn(OAc)<sub>3</sub>-promoted alkene azidations are known,<sup>[31]</sup> our protocol provides the azidation only with the associated presence of catalytic Pd(OAc)<sub>2</sub>; b) Pd-catalyzed alkene azidations are known when carried out in the presence of strong terminal oxidants;<sup>[32]</sup> c) recent studies suggest that Mn(OAc)<sub>3</sub> can oxidize Pd(II) complexes to high valent complexes;<sup>[33]</sup> d) an *ad-hoc* experiment carried out in the presence of stoichiometric amounts of Pd(OAc)<sub>2</sub>, but in the absence of Mn(OAc)<sub>3</sub>, gave only degradation products (Scheme 4, protocol A, B); e) the experiments carried out in the presence of the radical scavenger TEMPO suggested the involvement of radical intermediates in the mechanism (Scheme 4, protocol C, D);<sup>[34]</sup> f) tertiary *N*-allyl sulfonamides proved to be unreactive in the standard reaction conditions (Scheme 4, protocol E).



**Scheme 4.** *Ad-hoc* experiments for mechanistic purpose.

Given these findings, it is plausible to think of a mechanism for diazidation procedure which involves a Pd(III)-intermediate that may engage nucleopalladation followed by reductive elimination or an outcome triggered by the azide radical (see Supporting Information). Concerning the acetoxy/hydroxylation process, plausibly the formation of an acetoxy radical is involved, although we cannot rule out the generation of a 1,3-dioxolenium cation (see Supporting Information).

In summary, the combination of palladium and Mn(OAc)<sub>3</sub> can catalyze the divergent 1,2-difunctionalization of *N*-allyl sulfonamides, switching at will from diazidation to acetoxy/hydroxylation processes depending on the presence or absence of NaN<sub>3</sub>. While the diazidation process emerges as a mild method (*i.e.* NaN<sub>3</sub> as azide source in THF at room temperature) alternative to those already known in the literature, the acetoxy/hydroxylation protocol is a method to regioselectively convert alkenes into vicinal hydroxy-acetoxy derivatives.

## Experimental Section

## General procedure for the diazidation reaction.

In a bottom flask, Pd(OAc)<sub>2</sub> (0.05 equiv., 0.05 mmol, 11.2 mg), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (1.0 equiv., 1.0 mmol, 268.1 mg), NaN<sub>3</sub> (3.0 equiv., 3.0 mmol, 195.0 mg), were poured in a solution of the appropriate allyl sulfonamide (1.0 equiv., 1.0 mmol) in THF (10 mL). The resulted solution was magnetically stirred at room temperature for 48 hours under air atmosphere. The solvent was evaporated under reduced pressure. The resulting residue was recovered with AcOEt (10 mL) and filtered on silica pad. The solvent was evaporated under reduced pressure. The residue was purified by FCC.

## General procedure for the acetoxy/hydroxylation reaction.

In a sealed tube, Pd(OAc)<sub>2</sub> (0.05 equiv., 0.05 mmol, 11.2 mg), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (3.0 equiv., 3.0 mmol, 804.3 mg) and H<sub>2</sub>O (15.0 equiv., 15.0 mmol), were poured in a solution of the appropriate allyl sulfonamide (1.0 equiv., 1.0 mmol) in THF (10 mL). The resulted solution was magnetically stirred at reflux in oil bath for 24 hours. The solvent was evaporated under reduced pressure. The resulting residue was filtered on silica pad. The solvent was evaporated under reduced pressure. The residue was purified by FCC.

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