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Solvent-Controlled Pd(II)-Catalyzed Aerobic Chemoselective Intermolecular 1,2-Aminooxygenation and 1,2-Oxyamination of Conjugated Dienes for the Synthesis of Functionalized 1,4-Benzoxazines

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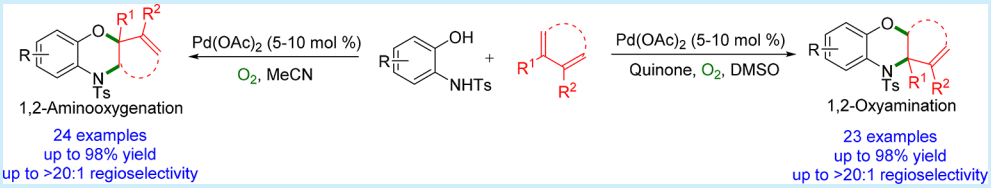
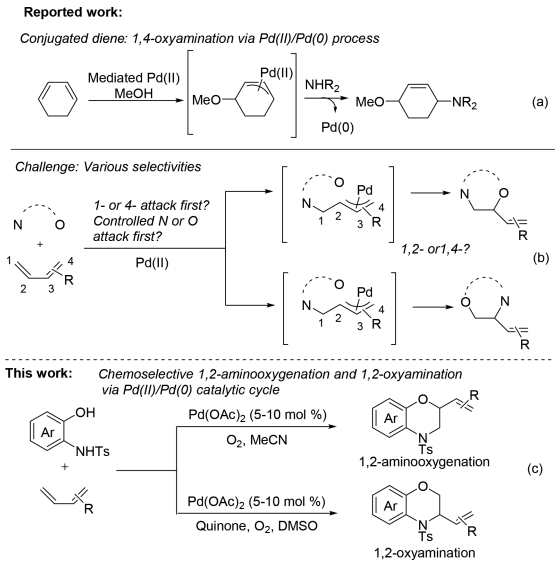
Supporting Information



ABSTRACT: Pd(II)-catalyzed intermolecular 1,2-aminooxygenation and 1,2-oxyamination of conjugated dienes have been developed. The chemoselective preparation of a variety of 2-functionalized and 3-functionalized 1,4-benzoxazine derivatives was accomplished via the adjustment of a coordinating solvent. Oxygen was successfully used in this oxidative difunctionalization of alkenes. Good yields and selectivities were obtained for most products. A product bearing a spiro structure was also obtained from a 2,3-disubstituted-1,3-diene.

Difunctionalization of alkenes is one of the most basic and efficient transformations in organic synthesis.[1−4] Among these transformations, vicinal aminooxygenation and oxyamination of alkenes are very important processes[2−4] because of their broad use for the synthesis of catalysts and ligands, biologically active molecules, and natural products.[5] Over the past few decades, a number of metal-catalyzed and metal-free methods have been designed.[2−4] Palladium, one of the most commonly used metals, has also been applied to the vicinal aminooxygenation and oxyamination of alkenes.[4] In particular, several palladium-catalyzed transformations have been developed for isolated alkenes, mainly using a Pd(II)/Pd(IV) catalytic cycle in the presence of a strong oxidant such as iodobenzene diacetate or hydrogen peroxide.[4e−l] However, in studies concerning the difunctionalization of conjugated dienes,[6] aminooxygenation or oxyamination strategies are limited because of the mechanistic differences with reactions involving isolated alkenes. Even so, the issue is worthy of research since the double bonds preserved in the difunctionalization products can be further functionalized. Bäckvall previously reported a Pd(II)-mediated 1,4-oxyamination via a Pd(II)/Pd(0) process. The reaction proceeds via the initial formation of a π-allylpalladium intermediate; a nitrogen source is then added to achieve the 1,4-oxyamination (Scheme 1a).[4d] Despite these successful examples, there are currently no reports concerning Pd(II)-catalyzed oxidative vicinal aminooxygenation or oxyamination of conjugated alkenes.[7] In addition, for the majority of palladium-catalyzed reactions, selective control remains challenging (Scheme 1b).[8] Furthermore, it is uncommon to use molecular oxygen as a terminal

Scheme 1. Aminooxygenation and Oxyamination of Conjugated Dienes Involving Palladium



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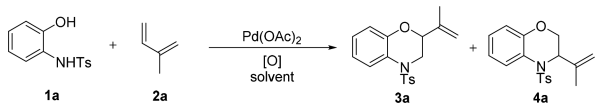
oxidant in Pd(II)-catalyzed oxidative difunctionalization reactions.[9] During our research on the palladium-catalyzed functionalization of alkenes,[10] we developed a Pd(II)-catalyzed chemoselective intermolecular 1,2-aminooxygenation and 1,2-oxyamination of conjugated dienes, mainly via the adjustment of a coordinating solvent (Scheme 1c). Molecular oxygen was successfully used in the reaction as a terminal oxidant. A variety of interesting functionalized 1,4-benzoxazine derivatives, a structural motif found in numerous biologically active molecules, were successfully prepared selectively.[5c−f]

Our study began with the reaction of *N*-tosyl protected 2-aminophenol **1a** with isoprene **2a**, using 1,4-benzoquinone (BQ) as the oxidant and 10 mol % $Pd(OAc)_2$ as the catalyst. The reaction was carried out in a series of solvents under a nitrogen atmosphere at 70 °C for 24 h (Table 1, entries 1−6).

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a 4a

entry	solvent	oxidant	yield (%)[b]	3a/4a[c]
1	DCE	BQ	trace	>20/1
2	toluene	BQ	trace	>20/1
3	DME	BQ	nd	−
4	1,4-dioxane	BQ	trace	>20/1
5	MeCN	BQ	33	5/1
6	DMSO	BQ	27	<1/20
7	MeCN	O_2 (1 atm)	23	9/1
8[d]	MeCN	Cu(II) + O_2 (1 atm)	nd	−
9	**MeCN**	**O_2 (sealed tube)**	**92**	**9/1**
10	MeCN	O_2 (10 atm)	94	8/1
11[e]	MeCN	O_2 (sealed tube)	57	9/1
12	MeCN	air (sealed tube)	22	9/1
13	DMSO	O_2 (sealed tube)	7	<1/20
14	DMSO	O_2 (10 atm)	7	<1/20
15	DMSO	duroquinone	38	<1/20
16	DMSO	*p*-chloranil	trace	<1/20
17[f]	DMSO	BQ_1	54	<1/20
18[g]	DMSO	BQ_2	53	<1/20
19	DMSO	BQ_1 + O_2 (1 atm)	66	<1/20
20	DMSO	BQ_1 + O_2 (10 atm)	79	<1/20
21	**DMSO**	**BQ_1 + O_2 (sealed tube)**	**78**	**<1/20**

[a]The reaction was carried out with **1a** (0.1 mmol, 1 equiv), **2a** (1 mmol, 10 equiv), and oxidant (0.2 mmol, 2 equiv) in the solvent (1 mL) in the presence of $Pd(OAc)_2$ (10 mol %) at 70 °C for 24 h, unless otherwise noted. [b]Isolated yields of the two chemoselective products. [c]Determined by ^{1}H NMR analysis. [d]20 mol % $Cu(OAc)_2$ was used. [e]5 mol % $Pd(OAc)_2$ was used. [f]BQ_1 = 2,5-dimethyl-BQ. [g]BQ_2 = 2,6-dimethyl-BQ.

We observed that palladium black precipitated quickly in noncoordinating solvents (DCE and toluene) and polar solvents (DME and 1,4-dioxane) (entries 1−4). To our delight, in the coordinating solvent MeCN, the oxidative cyclization proceeded smoothly to give the desired 2-functionalized product **3a** with moderate selectivity (entry 5). Intriguingly, the 3-functionalized product **4a** was obtained with high selectivity with the coordinating solvent DMSO (entry 6). These results indicate that the coordination between palladium and the coordinating solvent MeCN or DMSO could facilitate the reactions. We therefore optimized the reaction conditions using the solvents MeCN (entries 7−12) and DMSO (entries 13−21) to achieve the chemoselective 1,2-aminooxygenation and 1,2-oxyamination, respectively. When the oxidant was changed to O_2 (1 atm) in MeCN, the reaction proceeded with a lower yield and a higher selectivity (entry 7). Catalytic amounts of $Cu(OAc)_2$ (20 mol %) had a negative effect on the reaction (entry 8). Considering the solubility of isoprene (**2a**) in the reaction system, we carried out the reactions in a sealed tube. Fortunately, the reaction provided the desired product in 92% yield with 9/1 selectivity (entry 9). This may be due to the increase of **2a** in the reaction system in a sealed tube. A slightly higher yield of 94% was obtained in a pressure vessel with 10 atm O_2 (entry 10). Reducing the amount of $Pd(OAc)_2$ led to a corresponding reduction in yield (entry 11). Performing the reaction in a sealed tube with air led to an obvious decrease in the yield, indicating the importance of the concentration of oxygen in the reaction mixture (entry 12). We also carried out the reaction with the noncoordinating solvents DCE and toluene in a sealed tube of O_2 or a pressure vessel with O_2 (10 atm) (see the Supporting Information). However, only a trace amount of product was obtained in all cases, indicating the importance of the coordinating solvents (MeCN and DMSO) for this reaction. Using the promising reaction conditions identified with MeCN, we first attempted the reaction in DMSO using O_2 at 1 atm (entry 13) or a high pressure (10 atm) (entry 14), but both results were unsatisfactory. We therefore continued to optimize the reaction conditions using BQ as the oxidant. In consideration of the Diels−Alder reaction between **2a** and BQ resulting in the consumption of isoprene, a series of BQ reagents with different substituents were used for the reaction (entries 15−18). With the exception of *p*-chloranil (entry 16), other types of benzoquinones all led to improved yields (entries 15, 17, and 18) compared with BQ (entry 6). We next utilized 2,5-dimethyl-BQ and oxygen as oxidants to further improve the yield (entries 19−21). The yield of product **4a** increased to 78% using 2,5-dimethyl-BQ and oxygen (sealed tube) as oxidants (entry 21).

With the above optimized reaction conditions (method **A**: Table 1, entry 9; method **B**: Table 1, entry 21) in hand, a variety of *N*-toluenesulfonyl-protected 2-aminophenols **1** were studied to explore the substrate scope and selectivity (Table 2). We first surveyed the reaction in MeCN using method **A**. For 5-substituted 2-aminophenol substrates with either electron-donating or electron-withdrawing substituent groups, the reaction proceeded well, giving the corresponding products in good yields and selectivities (**3b−h**). Similar reactivity was observed for 4-substituted 2-aminophenol substrates (**3i−o**). A substrate possessing a 4,5-dimethyl group provided its corresponding product in good yield and selectivity (**3p**). A 4,5-dichloro-substituted substrate (**3q**) provided poor reactivity. For a 3-substituted 2-aminophenol substrate, low reactivity and inverse selectivity were observed (**3r**), which might be attributed to the effect of the steric bulk. For a naphthalene substrate, the reaction provided a high yield and good selectivity when method **A** was used (**3s**).

The reaction was also investigated in DMSO using method **B**, as shown in Table 3. For 5-substituted 2-aminophenol substrates with either electron-donating or electron-withdrawing substituent groups, chemoselective control could be achieved using method **B**. The corresponding products were obtained in good yields and selectivities (**4b−h**). For 4-substituted 2-aminophenol substrates, chemoselective control was also generally achieved in good yields and selectivities (**4i−o**). A substrate bearing a 4,5-dimethyl group also gave a

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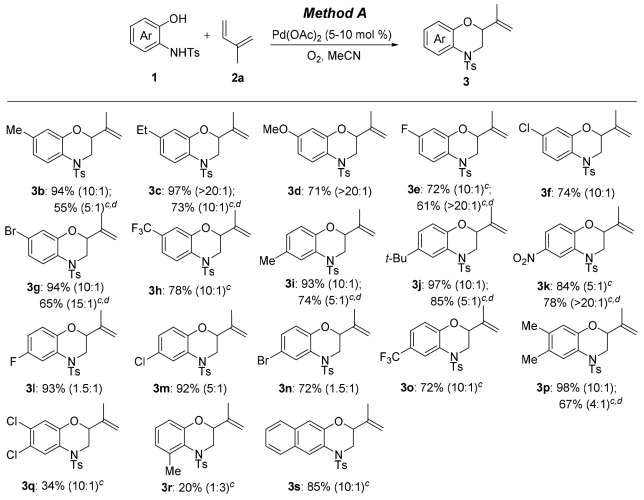
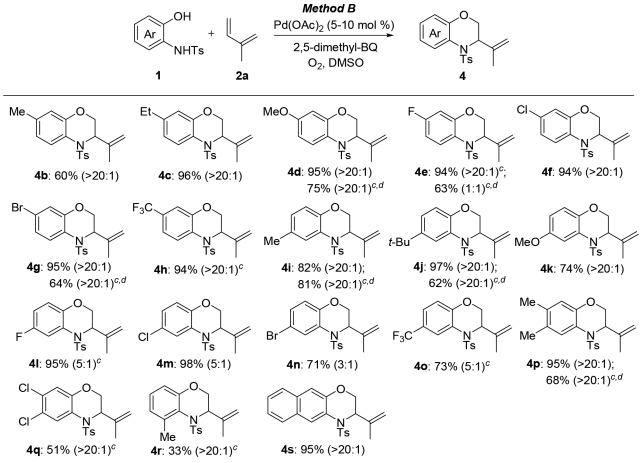
Table 2. Scope of 2-Aminophenols in MeCN[a,b]



[a]The reactions were carried out with **1** (0.1 mmol, 1 equiv) and **2a** (1 mmol, 10 equiv) in the presence of $Pd(OAc)_2$ (10 mol %) in MeCN (1 mL) at 70 °C for 24 h under oxygen in a sealed tube. [b]Isolated yields of the two chemoselective products are shown. The ratios were determined by ^1H NMR analysis. [c]The reaction was performed with O_2 (10 atm). [d]5 mol % $Pd(OAc)_2$ was used.

Table 3. Scope of 2-Aminophenols in DMSO[a,b]

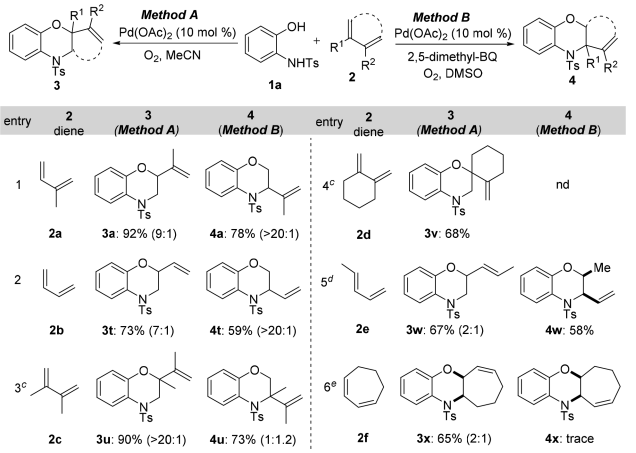


[a]The reaction was carried out with **1** (0.1 mmol, 1 equiv), **2a** (1 mmol, 10 equiv), and 2,5-dimethyl-BQ (2 equiv) in the presence of $Pd(OAc)_2$ (10 mol %) in DMSO (1 mL) at 70 °C for 24 h under oxygen in a sealed tube. [b]Isolated yields of the two chemoselective products are shown. The ratios were determined by ^1H NMR analysis. [c]The reaction was performed with O_2 (10 atm). [d]5 mol % $Pd(OAc)_2$ was used.

promising result (**4p**). However, a 4,5-dichloro-substituted substrate gave its corresponding product in only moderate yield (**4q**). The effect of the steric bulk was also significant, as evidenced by the use of a 3-substituted 2-aminophenol substrate. The desired product was obtained in low yield but with good selectivity using method **B** (**4r**). High yield and good selectivity were observed for a naphthalene substrate (**4s**).

We next turned our attention to investigating the scope of conjugated dienes (Table 4). We found that for linear dienes, in addition to isoprene (**2a**) (entry 1), 1,3-butadiene (**2b**) also underwent conversion in good yield with moderate selectivity using method **A** (entry 2, **3t**). The inversion of chemoselectivity was also achieved using method **B** in moderate yield

Table 4. Scope of Conjugated Dienes[a,b]

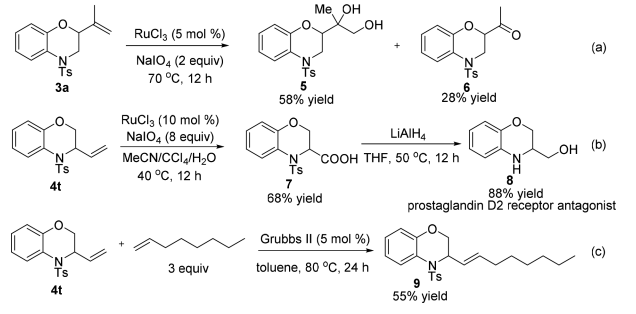


[a]The reactions were carried out with **1a** (0.1 mmol, 1 equiv) and **2** (1 mmol, 10 equiv) in the solvent (1 mL) in the presence of $Pd(OAc)_2$ (10 mol %) at 70 °C for 24 h. Method **A**: the reaction was carried out in MeCN under oxygen in a sealed tube. Method **B**: the reaction was carried out in DMSO with 2,5-dimethyl-BQ (2 equiv) under oxygen in a sealed tube. [b]Isolated yields of the two chemoselective products are shown. The ratios were determined by ^1H NMR analysis. [c]Conjugated dienes **2c** and **2d** (3 equiv). [d]Conjugated diene **2e** (5 equiv). [e]Conjugated diene **2f** (5 equiv) and O_2 (20 atm).

with high selectivity (entry 2, **4t**). For 2,3-dimethylbuta-1,3-diene (**2c**), the corresponding 2-functionalized product was obtained in high yield and selectivity using method **A** (entry 3, **3u**). Two isomers were obtained in 73% total yield with an approximately 1:1 ratio using method **B** (entry 3, **4u**). Interestingly, for 2,3-disubstituted-buta-1,3-diene **2d**, the spiro product **3v** (entry 4) was obtained in 68% yield using method **A**. For (*E*)-penta-1,3-diene (**2e**), the diene underwent conversion in 67% yield with 2:1 selectivity using method **A** (entry 5, **3w**). Interestingly, internal difunctionalization of the diene occurred using method **B**, giving the corresponding product in 58% yield (entry 5, **4w**). For the ring compound 1,3-cycloheptadiene (**2f**), the reaction proceeded well in 65% yield with 2:1 selectivity using method **A** (entry 6, **3x**).

The 2-functionalized and 3-functionalized products were able to partake in several transformations using different reaction conditions. Compound **5** was obtained through dihydroxylation of alkene **3a** in 58% yield, along with a small amount of ketone product (Scheme 2a). Additionally, the catalytic product **4t** could be oxidized to its corresponding acid **7** in 68% yield, which could then be reduced to afford a prostaglandin D_2 receptor antagonist[5f] in 88% yield (Scheme 2b). In addition, **4t**

Scheme 2. Further Derivation of 2-Functionalized and 3-Functionalized 1,4-Benzoxazine Derivatives



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also underwent olefin metathesis using Grubbs II catalyst to give the desired product in moderate yield (Scheme 2c), which is a good complement for those conjugated dienes obtained with difficulty.

In summary, we have developed a Pd(II)-catalyzed aerobic intermolecular chemoselective 1,2-aminooxygenation and 1,2-oxyamination of conjugated dienes for the preparation of a variety of 2-functionalized and 3-functionalized 1,4-benzoxazine derivatives in different systems. The oxidative difunctionalization of conjugated dienes was achieved using oxygen as oxidant. For most of the products, good yields and selectivities were obtained.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00352.

Experimental procedures and spectral data for all new compounds (PDF)

Accession Codes

CCDC 1449522−1449524, 1449527, and 1450754 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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