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Palladium(II)-catalyzed switchable mono-/diselenylation of arenes controlled by solvent effects

Weiwei Jin, Poonnapa Zheng, Ga-Lai Law, Wing-Tak Wong*

State Key Laboratory of Chirosciences, Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hum, Kowloon, Hong Kong

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This paper is dedicated to the memory of Prof. The Lord Lewis of Newnham, FRS.

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ABSTRACT

Organic selenides were efficient regioselective synthesized by palladium-catalyzed switchable mono- and diselenylation of arenes sp^2 C–H bonds through simply tuning the DMSO to water ratio. The present protocol was also successfully extended to the monoselenylation of 2-phenoxypyridines, which bore a removable directing group, in modest yields.

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1. Introduction

As a kind of useful building blocks, organic selenides have been widely used in the areas of natural products, pharmaceutical chemistry and functionalized materials [1]. Recently, transition-metal-catalyzed C–H functionalization has emerged as one of the most powerful methods for the cleavage of inert carbon–hydrogen bonds and simultaneous construction of new carbon–carbon and carbon–heteroatom bonds [2]. The direct catalytic selenylation of sp^2 and sp^3 C–H bonds via palladium, rhodium and nickel catalysts to the formation of C–Se bonds has also been reported very recently [3–7,9]. For example, Nishihara and co-workers demonstrated the first Palladium-catalyzed direct activation and selenylation of aromatic sp^2 C–H bonds with diselenides or selenols [3a]. Glorius et al. realized the first heterogeneous selenylation of heteroarenes C–H bond by using Pd/Al_2O_3 as the catalyst [4]. Rhodium [5] and nickel [6] catalysts are also effective in the direct selenylation of aryl sp^2 C–H bonds. At present, the activation of unreactivated sp^3 C–H bonds has only been achieved by employing nickel salts in relative poor efficiency [7]. As part of our continuing work on the transition-metal-catalyzed direct sp^2 C–H functionalization [8], we successfully developed the palladium(II)-catalyzed direct C–H selenylation of arenes and heteroarenes with *N*-(Phenylseleno)phthalimide (N-PSP) in boiling water without any additives (Scheme 1a) [9].

Although tremendous progress has been made in this area, the control of the selectivity for starting materials bearing two identical *ortho* C–H bonds between mono- and diselenylation products is still a big challenge [10]. Herein, we report our further studies on palladium-catalyzed switchable mono- and diselenylation of arenes sp^2 C–H bonds tuned by solvent effects (Scheme 1b) [11].

2. Results and discussion

Initially, we carried out the reaction of 2-phenylpyridine **1a** with N-PSP **2a** as the model reaction in a variety of organic solvents (Table 1). The desired products **3a** and **4a** can be formed in poor to excellent conversions and selectivities under various tested organic solvents. When DMF or DMSO was used as the reaction medium, selectivity reversal was clearly observed (Table 1, entries 11–12). DMSO seemed to be a suitable candidate for further examinations to the formation of disubstituted product **4a**.

According to the already achieved moderate to good monoselectivity using pure water in our previous studies [9], the model

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* Corresponding author.
E-mail address: wing-tak.wong@polyu.edu.hk (W.-T. Wong).

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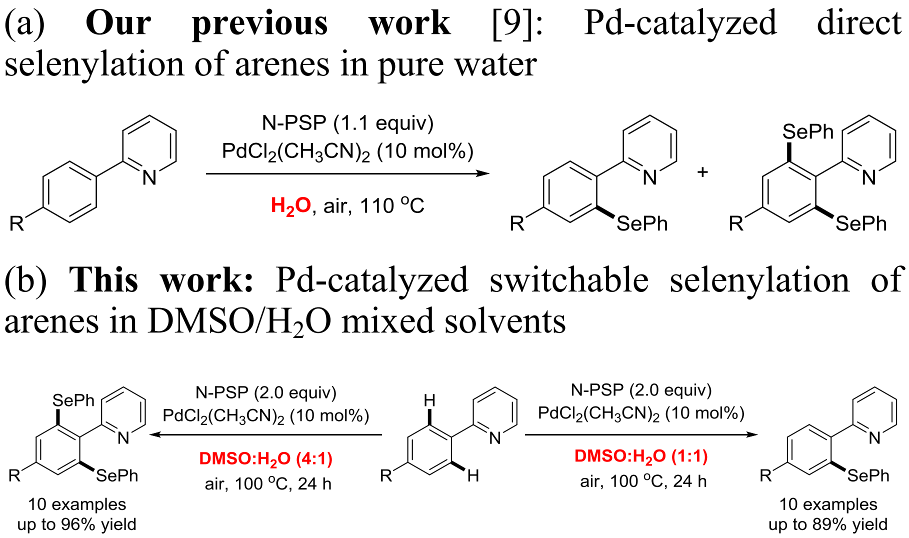


Scheme 1. Palladium-catalyzed switchable mono- and diselenylation of aromatic sp^2 C–H bonds.

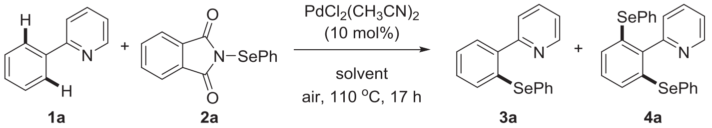
reaction was conducted in variational ratio of DMSO/H_2O mixed solvents in order to evaluate the influence of solvent effects on selectivities (Table 2). The experimental results showed that DMSO/H_2O (4:1) favored the diselenylation product **4a** as the major product (entry 3), while DMSO/H_2O (1:1) tended to mainly produce the monoselenylation product **3a** (entry 6).

After a systemic screening of diversified reaction parameters involving four other selenylation reagents **2b-d**, the best reaction conditions for controllable mono- and diselenylation of aryl sp^2 C–H bonds were optimized as shown in entries 7 and 13 respectively in Table 3. However, Nickel (II), Ruthenium (II) and Rhodium (III) catalysts, which are widely used in transition-metal-catalyzed C–H activation reaction, were useless in this reaction (entries 20–22).

With the optimized conditions in hand, the scope with respect to this methodology was then investigated (Table 4). In order to explore the generality of this method, only substrates with a *para* substituent attached at the phenyl ring of 2-arylpyridines **1** which bore two identical *ortho* C–H bonds were chosen as starting materials. In both the mono- and diselenylation, both electron-donating and -withdrawing groups were tolerated in the reaction smoothly to generate the corresponding products **3** and **4** in good to excellent yields. The selenylation reaction was compatible with methyl, *tert*-butyl, methoxy, fluoro, chloro, bromo, trifluoromethyl, trifluoromethoxy and formyl groups; this showed the universality of this protocol. The presence of F, Cl, Br and formyl in the target products highlights the significance of this method due to their potential subsequent synthetic transformation into some useful complicated molecules. The electronic effect has no vital influence on this reaction.

In the loading of 20 mol% $PdCl_2(CH_3CN)_2$ as the catalyst, the starting material 2-phenoxypyridines **5a-c** containing a removable directing group could also take part in this reaction to yield the monoselenylation products **6a-c** in modest yields (Scheme 2). The directing group of products **6a-c** can be easily removed by a known procedure to give the *o*-selenylation phenols [12].

Table 1
The conversions of 1a and selectivities of 3a/4a in various organic solvents.[a]



Entry	Solvent	Conv. of 1a (%)[b]	3a: 4a[b]
1	Toluene	86	84:16
2	CH_3CN	80	70:30
3	MeOH	86	88:12
4	EtOH	43	94:6
5	*i*-PrOH	19	90:10
6	*t*-BuOH	12	90:10
7	*t*-AmylOH	73	97:3
8	CF_3CH_2OH	32	96:4
9	Dioxane	87	86:14
10	THF	71	98:2
11	DMF	88	44:56
12	DMSO	97	24:76

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.11 mmol), $PdCl_2(CH_3CN)_2$ (10 mol%), solvent (1.0 mL), in air, 110 °C, 17 h.
[b] Determined by GC analysis using mesitylene as the internal standard.

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