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$Zn(OTf)_2$-catalyzed intra- and intermolecular selenofunctionalization of alkenes under mild conditions†

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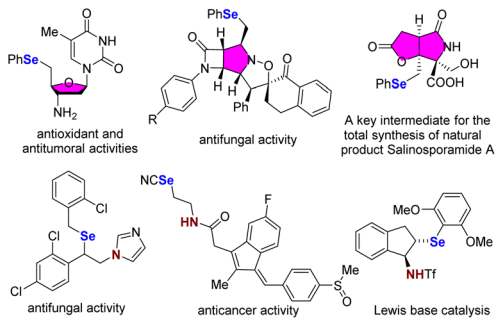
$Zn(OTf)_2$-catalyzed intra- and intermolecular selenofunctionalization of alkenes was achieved with electrophilic *N*-phenylselenophthalimide. This method provides straightforward and efficient access to various seleno-substituted heterocycles and vicinal Se heteroatom-disubstituted molecules under mild conditions. This reaction is compatible with various substrates/functional groups, and preliminary studies on the reaction mechanistic were also conducted.

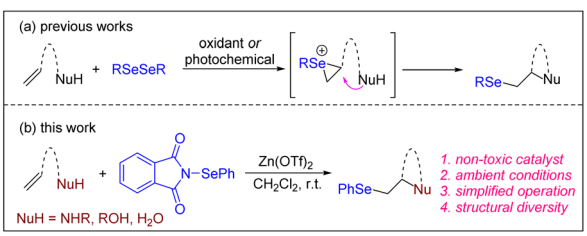
Introduction

Selenium (Se), a biological trace element, is essential for animal and human health. A deficiency or excess intake of Se can result in severe symptoms and is associated with various diseases.[1] Furthermore, organoselenium compounds have emerged as valuable building blocks in organic synthesis and are employed as radicals, electrophiles and nucleophiles to construct a wide range of chemical bonds.[2] Specifically, seleno-substituted heterocycles and vicinally functionalized selenides are highly notable due to their significance as chemical reagents, building blocks, and biologically active molecules (Scheme 1).[3] Hence, numerous attempts have been made to develop a synthetic route for accessing these compounds.



Scheme 1 Vital seleno-substituted heterocycles and vicinally functionalized selenides.

Among them, the intra- and intermolecular selenofunctionalization of olefins is considered one of the most straightforward methods because a selenium moiety can be simultaneously introduced with other synthetically valuable functionalities across a C=C bond, generating seleno-substituted heterocycles and vicinal Se, heteroatom-disubstituted molecules, in an atom-economical manner.[4] Typically, this process occurs *via* the formation of a seleniranium intermediate using electrophilic selenium reagents,[5] followed by the nucleophilic attack of suitable reagents. However, these organoselenium reagents are often undesirable and inconvenient to use. Their main drawbacks arise from their moisture-sensitive nature, the release of malodorous and highly toxic vapors, and the formation of various reactive by-products, during certain reactions (*e.g.*, HCl from PhSeCl). Seleno-functionalization can also be achieved through utilizing readily available and bench-stable diselenides as selenium reagents. Various oxidants,[6] photochemical,[7] and electrochemical approaches[8] have been used to produce selenium electrophilic species from the corresponding diselenides in these cases. Recently, we reported that hypervalent iodine,[9] N–F reagents,[10] and photochemical processes[11] can activate diselenides to produce highly reactive selenium species, which can induce intra- and intermolecular selenofunctionalization to produce functionalized Se-containing molecules (Scheme 2a).



Scheme 2 Previous work and current work.

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N-Phenylselenophthalimide (*N*-PSP), which was originally reported by K. C. Nicolaou and coworkers,[12] is a convenient source of electrophilic selenium for intra- and intermolecular selenofunctionalization because this compound is an odorless and colorless crystalline solid that can be readily obtained from potassium phthalimide and phenylselenenyl chloride. Additionally, the poor nucleophilicity of the phthalimide counteranion can eliminate chemoselectivity issues caused by competition between the desired nucleophiles and the phthalimide. Thus, various Lewis and Brønsted acids, such as $TiCl_4$,[13] $FeCl_3$,[14] BF_3,[15] $Ca(NTf_2)_2$,[16] phosphoric acid,[17] TMSOTf[18] and *p*-TsOH,[19] and base[20] have been used to promote selenofunctionalization reactions with *N*-PSP. Despite these advances, a general and modular method for the preparation of various vicinally functionalized selenides is still lacking. Furthermore, to the best of our knowledge, intramolecular selenoamination of *N*-alkenyl sulfonamides with *N*-PSP leading to selenomethylpyrrolidine has not been accomplished. Therefore, an efficient strategy to achieve the selenofunctionalization of alkenes is highly desirable and intensively sought after.

Zinc is an essential trace element for humans. Deficiencies in zinc may cause many diseases in adults and can lead to growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea in children.[21] Zinc is also a notably attractive element in synthetic chemistry due to its abundance, low cost, lack of toxicity, and environmentally benign properties.[22] Additionally, zinc displays Lewis acid interactions with a variety of functional groups. In previous studies, we revealed that zinc salts interact with C=C double bonds, ketones, and imines.[23] To demonstrate the powerful flexibility of zinc catalyst in the construction of a C–Se bond, herein, we wish to report a $Zn(OTf)_2$-catalyzed intra- and intermolecular selenofunctionalization of alkenes with electrophilic *N*-PSP as a continuation of our interest in the selenofunctionalization of different alkenes (Scheme 2b).[9–11,24]

Results and discussion

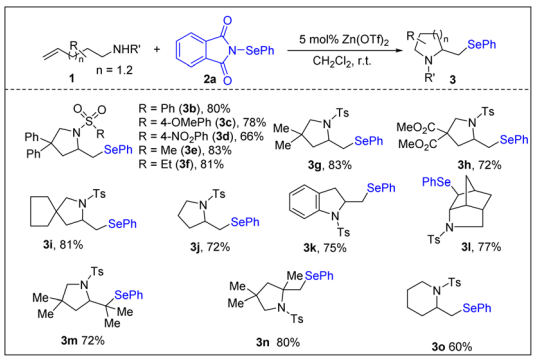
Initially, we investigated the reactions between **1a** and *N*-PSP **2a** with various catalysts in CH_2Cl_2 at room temperature (Table 1). During the initial screening of diverse zinc catalysts, including $ZnCl_2$, $ZnBr_2$, ZnI_2, and $Zn(OTf)_2$, we found that $Zn(OTf)_2$ was optimal for this reaction and afforded the corresponding phenylselenomethylpyrrolidine **3a** in 85% yield (entries 1–4). We rationalized this outcome with sufficient Lewis acidity of $Zn(OTf)_2$. Other metals, such as AgOTf, $MnBr_2$, CuCl and $InBr_3$, did not improve the yields (entries 5–8). Subsequent solvent screening experiments indicated that CH_2Cl_2 was the best solvent in terms of the reaction yield obtained (entries 9–13). Control experiments verified that the zinc catalyst was essential for the reaction, as the yield significantly decreased in its absence (entry 14).

Having established the optimized reaction conditions, we evaluated the scope of the alkene aminoselenation reaction. As indicated in Scheme 3, both *N*-aryl and *N*-alkyl sulfonamides underwent smooth 5-*exo* cyclization to furnish the corresponding selenomethylpyrrolidines (**3b–3f**). Remarkably, we

Table 1 Optimization of the reaction conditions[a]a

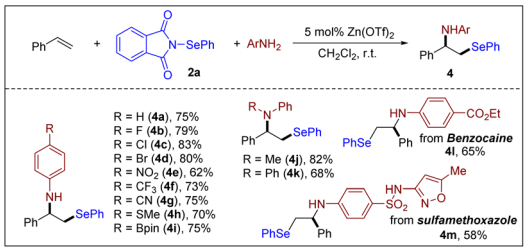
Entry	Cat.	Solvent	Isolated yield (%)
1	$ZnCl_2$	CH_2Cl_2	45
2	$ZnBr_2$	CH_2Cl_2	50
3	ZnI_2	CH_2Cl_2	51
4	$Zn(OTf)_2$	CH_2Cl_2	85
5	AgOTf	CH_2Cl_2	67
6	$MnBr_2$	CH_2Cl_2	33
7	CuCl	CH_2Cl_2	45
8	$InBr_3$	CH_2Cl_2	39
9	$Zn(OTf)_2$	MeOH	12
10	$Zn(OTf)_2$	Acetone	47
11	$Zn(OTf)_2$	THF	55
12	$Zn(OTf)_2$	CH_3CN	17
13	$Zn(OTf)_2$	Hexane	20
14	—	CH_2Cl_2	15

[a] Reaction conditions: **1a** (0.20 mmol, 1.00 equiv.), **2a** (0.20 mmol, 1.00 equiv.), cat. (0.010 mmol, 0.05 equiv.), solvent (2 mL), r.t., 5 h.

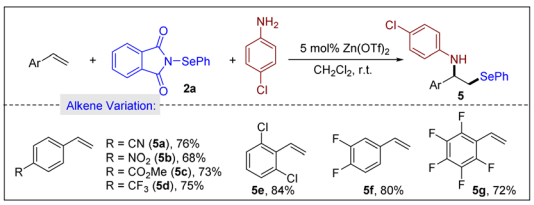


Scheme 3 Scope of olefinic sulfonamides. Reaction conditions: **1** (0.20 mmol), **2a** (0.20 mmol), $Zn(OTf)_2$ (0.010 mmol) and CH_2Cl_2 (2 mL), air, r.t., 5 h.

observed that the Thorpe–Ingold effect was not necessary for reactivity, as substrates bearing different *gem*-disubstituents or without substituents in the backbone exhibited similar reactivity (**3g–3i** *vs.* **3j**). *N*-Tosyl *o*-allyl aniline (**1k**) was an effective substrate, generating indoline **3k**. We were pleased to find that a more geometrically challenging 5-*endo* cyclization could be achieved with unsaturated amine **1l**, which afforded bridged ring skeleton **3l** with high diastereoselectivity. Di- and trisubstituted alkenes were efficiently converted into their corresponding pyrrolidines with good yields (**3m–3n**). Furthermore, 1-sulfonamido-5-hexene substrate was tolerated, although a lower yield was obtained (**3o**), possibly due to unfavorable entropy of the current cyclization.[25] Differing from the PhSeX-mediated cyclization of unsaturated amines that produces a mixture of (phenylselanyl)pyrrolidines and halopyrrolidines,[26] the current reaction was found to exclusively afford selenoaminated products.



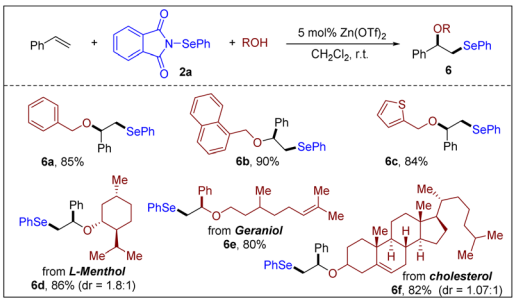
Scheme 4 Scope of amines. Reaction conditions: styrene (0.20 mmol), **2a** (0.20 mmol), amine (0.20 mmol), $Zn(OTf)_2$ (0.010 mmol) and CH_2Cl_2 (2 mL), air, r.t., 5 h.



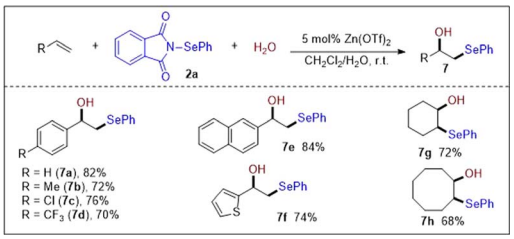
Scheme 5 Scope of styrenes. Reaction conditions: alkene (0.20 mmol), **2a** (0.20 mmol), 4-chloroaniline (0.20 mmol), $Zn(OTf)_2$ (0.010 mmol) and CH_2Cl_2 (2 mL), air, r.t., 5 h.

Although intermolecular alkene selenoamination is valuable for the synthesis of β-amino selenides, few methods possess a broad scope and wide applicability. This is largely due to the inherent challenges of chemoselectivity and regioselectivity issues as well as amine oxidation. Despite these challenges, significant progress has been made (often within restricted substrate classes),[7a,8b,27] in the areas of three-component alkene selenoamination. During the preparation of this manuscript, Wang, Yi and Hong *et al.* reported a $Ca(NTf_2)_2$-catalyzed intermolecular selenoamination of alkenes with *N*-PSP.[16] Encouraged by the above results, we hoped to expand the general utility of this catalyst system to include intermolecular examples and access biologically relevant amines. We chose challenging anilines as nucleophiles as they are susceptible to oxidation at nitrogen under previously reported oxidation selenofunctionalization conditions, thus limiting their application in this process. Fortunately, a broad range of anilines were found to be effective nucleophiles under the title conditions (Scheme 4). Remarkably, a diverse array of functional groups, such as halides, nitro, nitrile, thioether and pinacol borate, were well tolerated (**4a–4i**), providing an opportunity for further modifications to access biologically active selenium-containing compounds. This method is not limited to primary amines, as secondary anilines can also be aminated effectively (**4j–4k**). Additionally, the approved drugs benzocaine and sulfamethoxazole afforded products **4l** and **4m**, respectively.

Next, we examined a variety of challenging substrates, namely, electronically deactivated styrenes, under our optimized reaction conditions. As illustrated in Scheme 5, a variety of electron-deficient styrenes substituted with single CN, NO_2, CO_2Me and CF_3 groups reacted efficiently (**5a–5d**). Impressively, styrenes bearing up to two halides or up to five fluorine atoms on the aromatic ring were well tolerated (**5e–5g**).



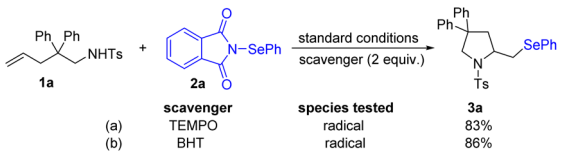
Scheme 6 Scope of alcohols. Reaction conditions: styrene (0.20 mmol), **2a** (0.50 mmol), alcohol (0.20 mmol), $Zn(OTf)_2$ (0.010 mmol) and CH_2Cl_2 (2 mL), air, r.t., 5 h.



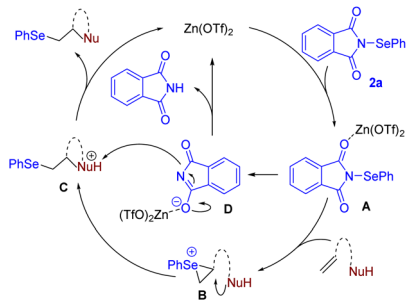
Scheme 7 Synthesis of β-hydroxy selenides. Reaction conditions: alkene (0.20 mmol), **2a** (0.20 mmol), $Zn(OTf)_2$ (0.010 mmol) and CH_2Cl_2 : H_2O (50 : 1, 2 mL), air, r.t., 5 h.

Encouraged by these results, we further explored the versatility of our method by investigating different alcohols as nucleophiles because the resulting β-alkoxyl selenides are valuable for synthetic chemists. Through the adjacent alkoxyl group, these molecules can be attached to solid-phase carriers for the development of recyclable heterogeneous catalysts.[28] Moreover, the neighboring oxygen and selenium groups can effectively coordinate with transition metals, leading to the creation of novel metal complexes with potentially distinctive catalytic activity.[29] As shown in Scheme 6, a variety of benzyl alcohols proved to be effective nucleophiles under the optimized conditions (**6a–6c**). Furthermore, natural alcohols that are more structurally complicated, such as L-(−)-menthol, geraniol and cholesterol, also afforded the desired β-alkoxy selenides in good yields (**6d–6f**). This result highlights the powerful ability of this catalytic system to create novel and potentially bioactive organoselenium compounds from complex natural products.

In the investigation of different nucleophiles, a trace amount of β-hydroxy selenide (*ca.* 5%) was detected as a byproduct. This product was formed by nucleophilic attack of adventitious water at the episelenonium ion intermediate. Given the importance of β-hydroxy selenides as valuable intermediates in the synthesis of allylic alcohols, olefins, vinyl, and heterocyclic compounds,[30] we modified the solvent system to include a combination of CH_2Cl_2 and water. This adjustment was made to facilitate the straightforward synthesis of β-hydroxy selenides. As shown in Scheme 7, hydroxyselenenylation of styrene and aliphatic alkenes in a mixture of CH_2Cl_2 and H_2O proceeded smoothly,



Scheme 8 Control experiments.



Scheme 9 Proposed plausible mechanistic pathway.

resulting in β-hydroxy selenides in good yields with exclusive Markovnikov selectivity.

To further determine the mechanism of this reaction, 2.0 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were introduced as radical trapping agents, and the reaction proceeded smoothly under the title conditions (Scheme 8), which clearly suggested that the reaction did not involve a free radical pathway.

Based on the above investigations and reported literature,[13,14,16] a plausible reaction mechanism was proposed, as shown in Scheme 9. Initially, $Zn(OTf)_2$ activates *N*-PSP **2a** by chelating to the amide carbonyl group to form intermediate **A**, which undergoes electrophilic attack on the C=C bond and results in the formation of episelenonium ion **B**. Subsequently, the ring-opening of **B** by nucleophilic attack generates cation **C**. Finally, deprotonation of intermediate **C** by species **D** affords the desired selenation products with the release of $Zn(OTf)_2$.

Conclusions

In conclusion, we have reported a $Zn(OTf)_2$-catalyzed selenofunctionalization of alkenes with *N*-phenylselenophthalimide for the assembly of vicinally functionalized selenoderivatives. Compared with previous approaches, the current method features ambient conditions and application of environmentally benign zinc catalysis. Moreover, this protocol achieves excellent substrate/functional group tolerance, and is suitable for the late-stage functionalization of complex molecules of biological importance. Future efforts will be directed toward the development of asymmetric variants of this reaction with chiral ligands.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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