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PIDA-Promoted Selective C_5 C–H Selenylations of Indolines *via* Weak Interactions

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Abstract: An efficient PIDA (phenyliodine(III) diacetate)-promoted positional selective C–H selenylations of indolines with diaryl diselenides has been developed. This transformation conducted under mild reaction conditions with a broad functional group tolerance, thus providing an efficient protocol to selenylated indolines. Preliminary mechanistic studies indicated a SET pathway was likely involved in this selenylation reaction.

Keywords: PIDA; Selenylations; Indoline; C–H functionalization; Radical reactions.

Introduction

The indole and indoline motifs have become privileged structures as they widely exist in numerous biologically active natural products, pharmaceuticals, agrochemicals and pigments.[1] Thus, the modifications of indoles and indolines for the diversification of the scaffolds have received increasing attentions over the last few years.[2] Recent advances in the transition-metal catalysed direct C–H functionalization provided a powerful strategy for the modification of indole and indoline structures.[3] Nevertheless, the derivation of indoles and indolines were generally limited to the C_1-C_4 and C_7 positions governed by the effect of directing groups or the inherent nucleophilic reactivity,[4] while the site-selective C–H functionalization on the remote less activated C_5 position has remained a great challenge.

In recent years, direct C–H functionalization *via* a radical pathway, which often complementary to traditional methods, has been achieved in significant advance and emerged as a sustainable approach for the synthesis of complicated molecules.[5] In particularly, the hypervalent iodine (III) reagents promoted radical C–H functionalization[6] which was first reported by Kita's group in early 1990s,[7] were widely explored in replacing of highly toxic heavy-metal oxidants in classical organic synthesis due to its low toxicity, mild reactivity, high oxidation ability and easy handling. (Scheme **1a**). For these oxidative coupling reactions of activation of aromatic rings with nucleophiles (NuH) and functionalized nucleophiles (Nu–FG) might be proceeded through single-electron-transfer (SET) pathway. Hence, in the past decades, a variety of nucleophiles (Nu-H or FG-Nu) such as $TMSN_3$, TMSOAc, PhSH and *β*-dicarbonyl compounds were employed as suitable coupling partners in the directly convert the C–H bonds for organic transformations to meet the strong demand of green chemistry.[8]

The C–Se bond was an important linkage in the biologically active compounds due to organic selenides display promising properties as antitumor, antibacterial, antioxidant, anti-inflammatory agents. [9] With the consideration the importance of indolines and chalcogenides, it is of great interest to combine the two into a single entity. Previous reports on the transition-metal catalysed regio-selective C–H chalcogenations of indoles and indolines with various chalcogen reagents have been disclosed by Kame, Glorious, Jain, Samanta, Wang and Ackermann groups.[10] However, some of examples suffer from limitations to some extent such as the use directing groups to govern its *ortho*-selectivity, stoichiometric amount of metal oxidant/catalyst, expensive transition metal catalysts, long reaction times with harsh reaction conditions and oxygen-free techniques.

More recently, transition-metal catalysed remote C_5 C–H functionalization of quinoline through oxidative radical pathway have been widely explored. [11] Transition metal catalyst coordinated with the bidentate directing groups to form a cation-radical

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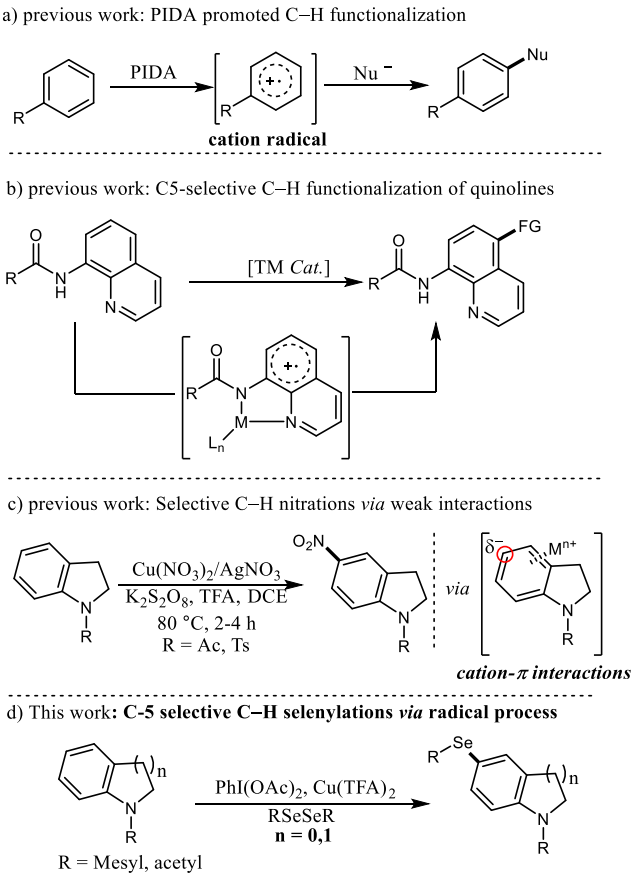
intermediate which enable coupling reactions with various free radicals, thus overcame the geometrically inaccessible cyclometallations to achieve the distal C–H functionalization. In this regard, C–C and C–heteroatom bonds formations on the C_5 position of 8-aminoquinolinamide derivatives have been widely developed to access diverse functionalized quinoline scaffolds. (Scheme **1b**). Furthermore, Mal and co-workers reported an unprecedented C–H mononitration of indolines at the C_5 position under mild condition *via* multiple weak interactions and factors. (Scheme **1c**). [12] To the best of our knowledge, the C–H selenylations occured at C_5 position of indolines or indoles have been rare reported so far.[13] Therefore, developing a general, mild and regioselective protocol for the preparation of 5-selenylated indoles and indolines is highly desirable.



Scheme 1. Regio-selective C–H functionalization

Inspired by these reports and our interest on the research of diaryl selenides synthesis [14], we herein report the first example of PIDA-promoted direct selective C_5-selenylations of indolines with readily available diselenides *via* radical process to access diversely selenylated indoline derivatives. (Scheme **1d**)

Results and Discussion

We commenced our investigations with probing reaction conditions for the C–H selenylations of indoline **1a** with diphenyl diselenide **2a** as selenium reagent. With $Cu(TFA)_2$ as the additive various oxidants were tested at 80 °C in THF, $PhI(OAc)_2$ proved to be optimal and furnished the selective C_5 selenylated product **3aa** in 85% yield, while the other oxidant such as silver salts, $Cu(OAc)_2$, *m*-CPBA, $K_2S_2O_8$ and TBHP resulted in lower isolated yields or simply no reaction. (Table 1, entries 1-10) Further optimization with a set of representative solvent, CH_3CN, 1,4-dioxane, MeOH, toluene, DMF and DMSO gave unsatisfied results. (entries 12–17) Screening of the additives indicated that $Cu(OTf)_2$ and AgOTf exhibited similar efficiency, affording product **3aa** in 85% and 82% yield respectively, (entries 18 and 22) whereas other additives, including AgTFA, $Zn(OTf)_2$ and CF_3CO_2H only gave inferior results (entries 19−21). Decreasing or increasing the reaction temperature led to a lower yield (entries 23 and 24). Control experiments revealed that less than 10% selenylated product was observed in the absence of the $Cu(TFA)_2$ or $PhI(OAc)_2$, demonstrating the indispensable of the oxidant and additive (Table 1, entries 11 and 25). Thus, the optimized reactions conditions were ultimately identified as $Cu(TFA)_2$ as additive, along with $PhI(OAc)_2$ as the oxidant in THF at 80 C under Ar.

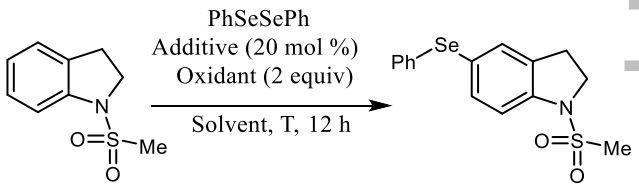


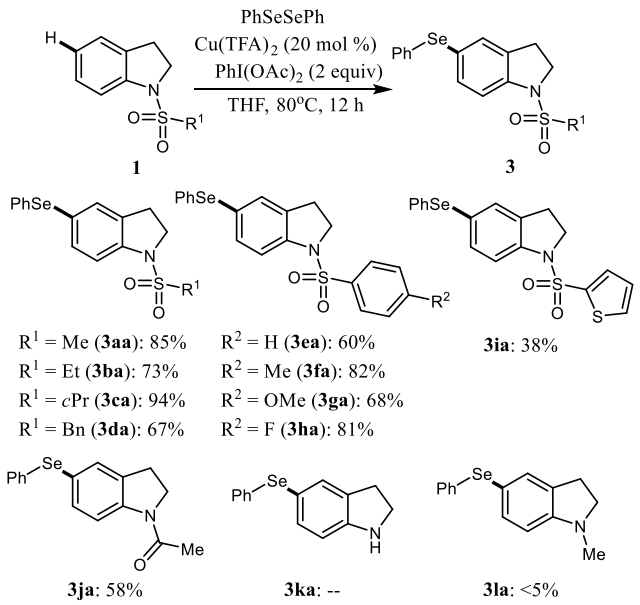
Table 1. Optimization of C–H selenylations[a]

Entry	Additive	Oxidant	Solvent	%Yields[b]
1	$Cu(TFA)_2$	Ag_2O	THF	8
2	$Cu(TFA)_2$	Ag_2CO_3	THF	5
3	$Cu(TFA)_2$	AgTFA	THF	28
4	$Cu(TFA)_2$	AgOAc	THF	--
5	$Cu(TFA)_2$	$AgNO_3$	THF	--
6	$Cu(TFA)_2$	$Cu(OAc)_2$	THF	--
7	$Cu(TFA)_2$	*m*-CPBA	THF	trace
8	$Cu(TFA)_2$	$K_2S_2O_8$	THF	--
9	$Cu(TFA)_2$	TBHP	THF	13
10	**$Cu(TFA)_2$**	**$PhI(OAc)_2$**	**THF**	**85**
11	$Cu(TFA)_2$	--	THF	--
12	$Cu(TFA)_2$	$PhI(OAc)_2$	DMF	72
13	$Cu(TFA)_2$	$PhI(OAc)_2$	DMSO	56
14	$Cu(TFA)_2$	$PhI(OAc)_2$	CH_3CN	--
15	$Cu(TFA)_2$	$PhI(OAc)_2$	MeOH	37
16	$Cu(TFA)_2$	$PhI(OAc)_2$	dioxane	32
17	$Cu(TFA)_2$	$PhI(OAc)_2$	toluene	76

18	**$Cu(OTf)_2$**	**$PhI(OAc)_2$**	**THF**	**85**
19	AgTFA	$PhI(OAc)_2$	THF	42
20	CF_3CO_2H	$PhI(OAc)_2$	THF	49
21	$Zn(OTf)_2$	$PhI(OAc)_2$	THF	67
22	AgOTf	$PhI(OAc)_2$	THF	82
23	$Cu(TFA)_2$	$PhI(OAc)_2$	THF	69[c]
24	$Cu(TFA)_2$	$PhI(OAc)_2$	THF	70[d]
25	--	$PhI(OAc)_2$	THF	<10

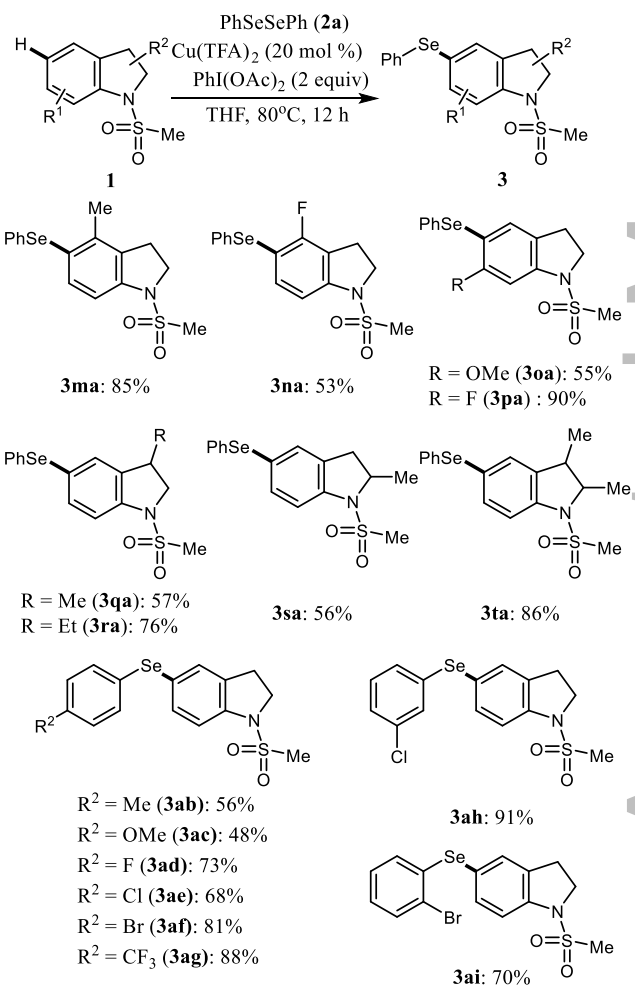
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (2.0 equiv, 0.5 mmol), Additive (20 mol%), solvent (2 mL), 12h, under Ar. [b] Isolated Yields. [c] 60 C. [d] 100 C

With the optimized conditions in hand, we next evaluated the effects of the *N*-substitutes of indolines **1**. (Scheme 2) Variety of alkyl substituted sulfonamide reacted with diphenyl diselenide smoothly, whereas the cyclopropyl substituted substrates gave the best yields of all. (**3aa**-**3da**). Gratifyingly, the more congested aryl substituted sulfonamide also proceeded efficiently to provide the desired products in good yields with excellent regioselectivity. Electron diversity groups presented on the aryl rings did not significantly affect the result. (**3ea**-**3ha**) Furthermore, heterocyclic sulfonamide such as **1i** was compatible, albeit resulted in lower yield. Additionally, the *N*-acetyl indoline was also viable, and affording the corresponding product in 58% yield. (**3ja**) Control experiments that were conducted with NH-free indolines or *N*-methyl indolines failed to give the desired product, thus highlighting the key importance of carbonyl or sulfone moieties.



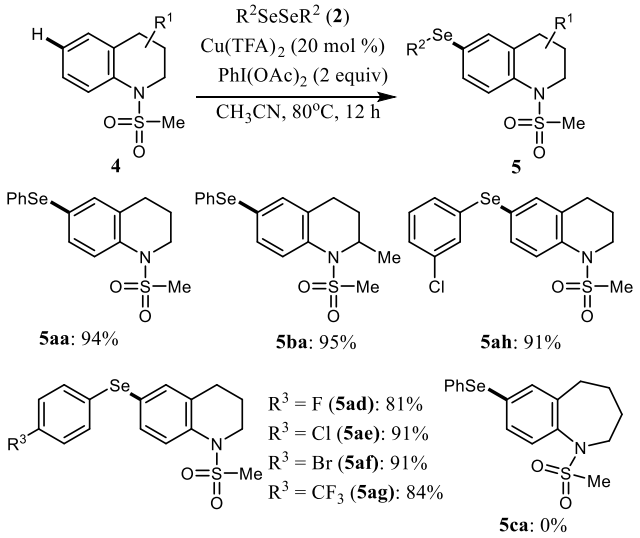
Scheme 2. Effect exerted on the *N*-substitutent.

Subsequently, the versatility of the established method was further probed with differently substutitued indolines **1** and diaryl diselenides **2**. (Scheme 3) The indolines bearing electron-donating or electron-withdraw directing groups on the C_2, C_3, C_4, C_6 positions participated well in this transformation and afforded the selective C_5 selenylated product up to 90% yields. Indoline with fluro at C_4 and methoxyl at C_6 positions exhibited decreased reactivity, and delivered the selenylated product in 53% and 55% respectively. (**3na** and **3oa**) Next, the substrate scope was further expanded to variety of substituted diaryl diselenides. As shown in scheme 3, electron-withdraw groups presented on the phenyl ring at the *para*, *ortho* and *meta* positions of the diaryl diselenides worked efficiently and gave the desired products in good yields under the standard conditions. (**3ad**-**3ag**, 68%–88% yields) The structure of compound **3ai** (CCDC 1912789) was further confirmed through crystal X-ray diffraction analysis. In contrast, the diaryl disulfides bearing electron-donating groups such as methyl and methoxyl only resulted in unsatisfied yields. (**3ab** and **3ac**) It was noteworthy that the methoxyl, fluro, chloro and bromo groups, were well tolerated under these reaction conditions which provided a possibility handle for further useful transformation.



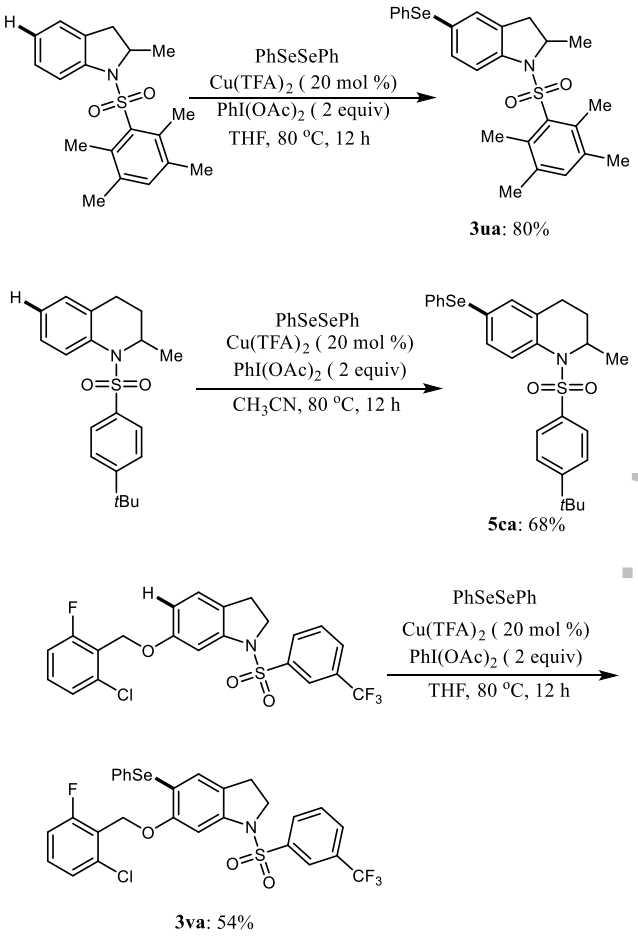
Scheme 3. Scope of the C–H selenylations of substituted indolines and diaryl diselenides

As expected, this optimized system was also found to be applicable to the C–H selenylations of tetrahydroquinolines derivatives **4** with different substituted diaryl diselenides **2**. Thus, tetrahydroquinoline sulfamide **4** smoothly reacted with different readily synthesized diaryl diselenides and afforded the corresponding products with more than 80% yields. (**5ad**-**5ah**) The structure of compound **5ae** (CCDC 1912788) was further confirmed through crystal X-ray diffraction analysis. However, seven-membered tetrahydro-1*H*-benzoazepine substrate was not compatible in this reaction and resulted no desired products probably due to its congested effect.



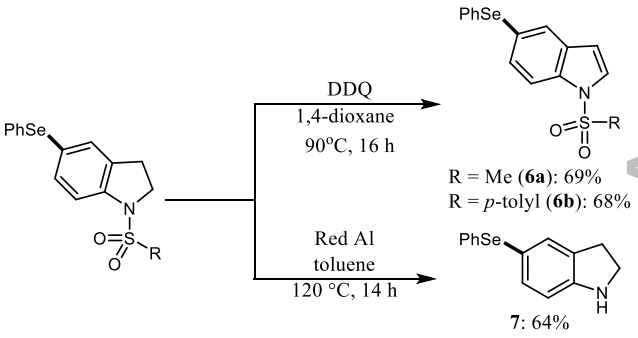
Scheme 4. Scope of C–H selenylations of tetrahydroquinolines

Subsequently, the synthetic utility of this selenylation established as a tool for late-stage modification of bioactive compounds was explored. For example, the compounds **1u** and **1v** that displayed a promising antiparasitic propertites, were also compatible in this selenylations and give the corresponding products in 80% and 68% respectively.[15] Meanwhile, the compound **4c**, a retinoic acid receptor-related orphan receptor γ (RORγ) agonist which is a key regulator of inflammatory gene programs involved in T helper 17 (TH17) cell proliferation that could regulate immune response for cancer immunotherapy, [16] participated in this selenylation reaction smoothly and provided the desired product in 54% yield.



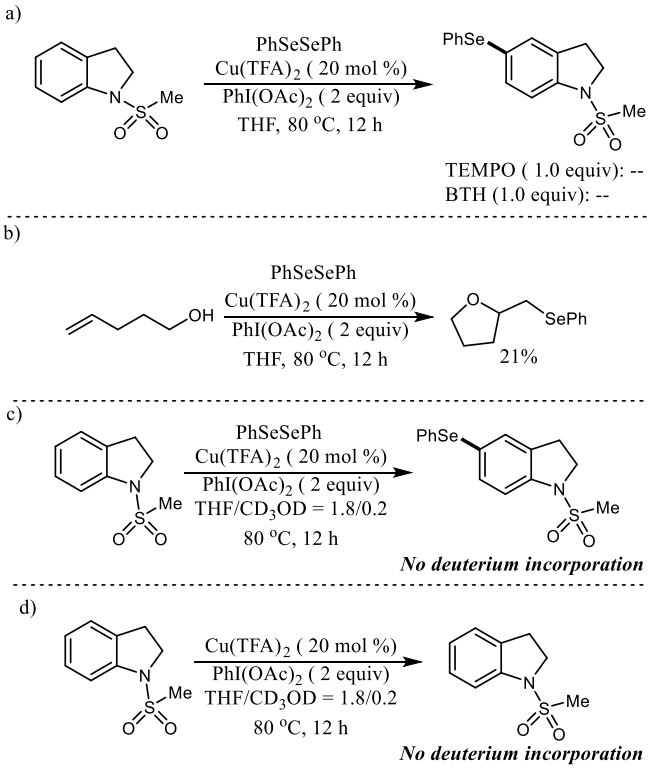
Scheme 5. Late-stage C–H selenylations

After the investigation of the substrate scope and synthetic utility, we went on to carry out further elaborations of the products, as depicted in scheme 6. The indolines could be easily converted into indoles in good yields in the presence of DDQ in 1,4-dioxane under mild conditions. Moreover, the directing group could be successfully removed by treatment with red-Al in toluene at 120 °C for 14 h, and affording the 5-selenylated NH-free indoline in 64% yield.



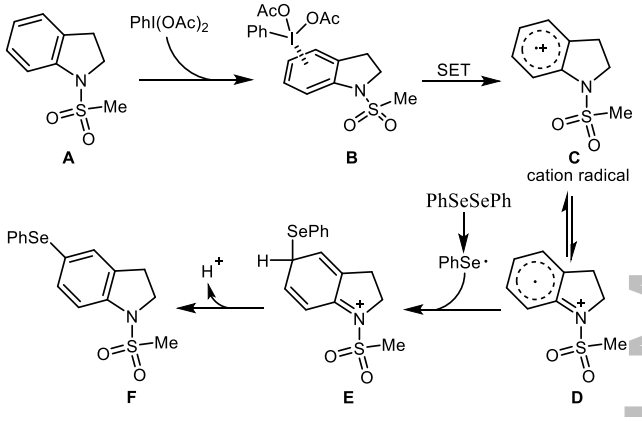
Scheme 6. Traceless removal of directing groups

To explore the reaction mechanism, a series of control experiments were carried out (Scheme 7). Two radical capture experiments conducted with stoichchiometric TEMPO and BHT as radical scavenger. These reactions were entirely suppressed and resulted no desired product, which suggested that a SET (single electron transfer) pathway might be involved in this transformation. (Scheme 7a) Furthermore, the subsequent radical clock experiment of pent-4-en-1-ol with diphenyl diselenide (**2a**) under the standard condition afforded 2-(phenylselanylmethyl) tetrahydrofuran in 21% yield which further supported the involvement of radical species in the reaction process. (Scheme 7b). [17] Finally, the selenylation reaction conducted with CD_3OD as cosolvent revealed no deuterium scrambling in the recovered starting material or the product (Scheme 7c and 7d), thus indicated the C−H bond cleavage is irreversible.



Scheme 7. Investigation of the mechanism

Although the detailed mechanism was still unclear at this stage and required further comprehensive investigation, a plausible mechanism involved cation radical pathway was proposed based on the preceding control experimental results and previous reports.[6], [8],[18] Firstly, the interaction between the $PhI(OAc)_2$ reagent and indolines facilitated the generation of intermediate **B**, followed by a SET oxidation process to give the cation radical species **C**. **C** could be transformed to intermediate **D** *via* extensively delocalization.[19] Meanwhile, the phenylthiol radical (PhS·) generated through a homolytic cleavage under thermal conditions attacked the C_5 position of **D** *via* the coupling reaction to give intermediate **E**. Finally, a deprotonation process occurred at the thus formed intermediated **E** to deliver the desired product **F**. The addition of $Cu(TFA)_2$ or the other metal additives could promote the reaction significantly probably due to the metal salts not only accelerated the formation of the cation radical[12], [20] but also coordinated to the radical pair *via* a cation–π interactions according to the soft acid–soft base nature,[21] thus enhanced the efficiency of the degradation to the free radical species of the reaction.[8b] Furthermore, the *N*-centers of the indolines protected with mesyl or acetyl groups were essential for this transformation, whereas the 1-Methyl indoline and 1-H indoline failed to give the desired product, probably due to the n-p* S=O or C=O non-covalent interaction the lone-pair of nitrogen could be avoided to react with highly oxidizing PIDA. [12], [22]



Scheme 8. Proposed mechanism

Conclusion

In summary, we have realized a novel and facile direct PIDA-promoted positional selective C−H selenylation of indolines and tetrahydroquinolines with diaryl diselanes though radical pathway under mild reaction conditions. This reaction tolerated a broad range of functional groups presented either on the indolines, tetrahydroquinolines or diaryl diselenids to access diversely selenylated indoline and tetrahydroquinoline derivatives. Furthermore, this method was also applicable for the modification of complex bioactive indoline compounds. The intense research on the detailed mechanistic study and development of this new selenylated reactions for the modification of indolines for drug discovery are currently being pursued in our laboratory, and will be reported in due course.

Experimental Section

A suspension of substituted indoline (**1a**) or tetrahydroquinoline (0.25 mmol), 1,2-diphenyldiselane (2a) (156 mg, 0.50 mmol), $Cu(TFA)_2$ (15.9 mg, 20 mol %), $PhI(OAc)_2$ (90.5 mg, 0.50 mmol) in THF (2.0 mL) was stirred under argon at 80 C for 12 h. At ambient temperature, the reaction mixture was quench with H_2O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether /EtOAc: 30/1→3/1) to yield **3aa** or **5aa** product.

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FULL PAPER

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