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# Metal-Free Three-Component Selenopheno[2,3-*b*]indole Formation through Double C–H Selenylation with Selenium Powder

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**Abstract.** A facile metal-free entry to novel selenopheno[2,3-*b*]indole motif is described. The three-component assembly of indoles, aromatic ketones, and selenium powder is enabled by the IBr-promoted highly selective double C–H selenylation/annulation. This protocol provides a novel access to a diverse variety of selenopheno[2,3-*b*]indoles with good efficacy and broad functional group compatibility.

**Keywords:** metal-free; selenopheno[2,3-*b*]indole; C–H selenylation; selenium powder

Organoselenium compounds are of great importance in chemistry constituting core structures of a number of drugs, naturally occurring products, and functional materials, among others,[1] as well as versatile building blocks in synthetic chemistry.[2] Accordingly, studies on the construction of C–Se bond has drawn considerable interest in synthetic chemistry.[3] With respect to selenium sources,[4] active organoselenium reagents such as selenol,[5] $ArSeSnR_3$[6] and diselenides[7] were frequently used as selenylation reagents in transition-metal-catalyzed cross coupling reactions. For example, Gu et al. reported a palladium-catalyzed selenation using selenoates as the selenium source *via* C(O)–Se bond cleavage process.[8] Recently, direct C–H selenylation with diselenides or selenium chlorides has emerged as an alternative approach for C–Se bond construction, in which the use of stoichiometric amount metal salts as the oxidant was required in most cases.[9] However, those selenylation reagents generally bear properties of unpleasant odors and air-/moisture-instability and thereby might prevent their practical applications.

A user-friendly strategy is the direct use of elemental selenium as the selenylation reagent as it is cheap and readily available and more importantly its properties of ambient stability make it easy-handling on bench. While the affinity of selenium may attenuate the catalytic activity of some metal catalysts, during the past several years, great progress has been made on the development of a copper-catalytic system for C–Se bond formation with selenium powder.[10] Therein, prefunctionalized substrates such as aryl halides were generally utilized as coupling partners. Notably, copper catalysts also proved to be effective to promote direct C–H oxidative selenylation.[11] For example, Ji and Wang disclosed selenium insertion reactions between isocyanides and amines.[12] Wu and co-workers developed direct C–H selenylation of alkynes and heteroarenes with selenium powder.[13]

Indole-involved synthesis is pharmacologically[14] and strategically important.[15] During the past several years, few reports on indole selenylation have been uncovered with different selenating reagents with or without the assistance of transition-metal catalysts.[16] In 2016, Wu et al. described copper-catalyzed C–Se bond formation between indoles and aryl iodides using selenium powder as the selenating reagent (Scheme 1, a).[17] Wang and Ji reported a four-component oxidative selenium insertion using TEMPO as the catalyst (Scheme 1, b).[18] Given the usual selectivity mode of selenylation at the C-3 position to give 3-selenyl-indoles, the C-2 position of indoles is quite less reactive. Silveira reported the first C-2 selenylation of indoles using selenium dichlorides as the selenylating reagent.[19] Within our continuing program on indole functionalization,[20]

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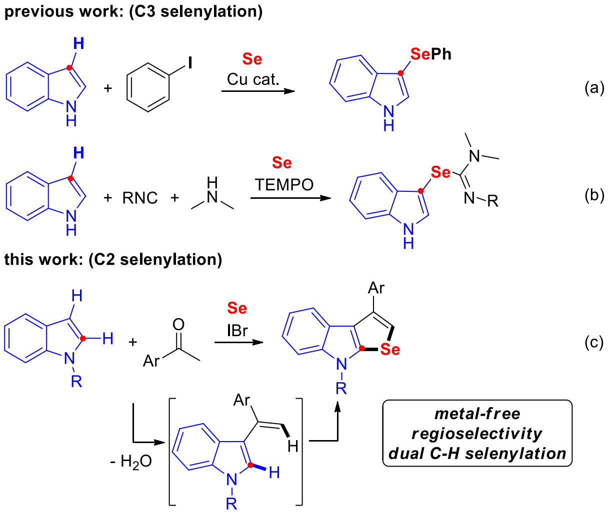
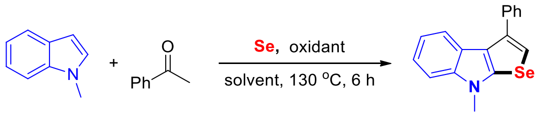
herein, we describe a general three-component selection reaction for the synthesis of selenopheno[2,3-*b*]indoles with elemental selenium under simple metal-free conditions. To complement our previous selective benzoselenophene formation,[20e] this protocol features high levels of regioselectivity towards C-2 selenylation of indoles through a tandem indole alkenylation/dual C–H oxidative selenylation (Scheme 1, c).



**Scheme 1.** Indole C–H selenylation with selenium powder.

On the basis of our previous indole-template synthesis of carbazoles and thieno[2,3-*b*]indoles,[20e,f] we reasonably proposed a selenopheno[2,3-*b*]indole formation through a similar cascade annulation. Hence, 1-methylindole (**1a**), acetophenone (**2a**) and selenium powder were initially handled as model reactants with iodine reagents (Table 1). To our delight, the desired selenylation/annulation product **3aa** was obtained in 21% yield when the reaction was treated with elemental iodine (1.0 equiv) in *N*-methyl pyrrolidone (NMP) at 130 °C for 6 h (entry 1). Among other iodide-containing oxidants including NIS, ICl, IBr and $ICl_3$ (entries 2-5), IBr was proved to be the most effective oxidant to afford the desired product in an excellent yield (entry 4). Investigations on reaction media revealed that NMP showed the best performance, while other organic solvents such as toluene, chlorobenzene, DMF, DMAc, DEF, and DMSO decreased the yield (entries 6-11). Increasing the amounts of IBr or decreasing the reaction temperature led to a lower yield of product (entries 12-13). The yield slightly declined when the reaction was performed under Ar atmosphere (entry 14). Finally, selenylation/annulation product was not observed in the absence of external oxidant (entry 15). Notably, with indole **1a** we did not observe the formation of benzo[b]selenophene, which was generated as the major product when 2-arylindoles were used.[20e] This result may indicate nucleophilic or radical C2 selenylation of indoles.

**Table 1.** Optimization of reaction conditions.[a]



1a 2a 3aa

| Entry | Oxidant | Solvent | Yield (%)[b] |
|---|---|---|---|
| 1 | $I_2$ | NMP | 21 |
| 2 | NIS | NMP | 35 |
| 3 | ICl | NMP | 47 |
| 4 | IBr | NMP | 66 |
| 5 | $ICl_3$ | NMP | 38 |
| 6 | IBr | toluene | n.d. |
| 7 | IBr | PhCl | n.d. |
| 8 | IBr | DMF | 19 |
| 9 | IBr | DMAc | 28 |
| 10 | IBr | DEF | 36 |
| 11 | IBr | DMSO | Trace |
| 12[c] | IBr | NMP | 65 |
| 13[d] | IBr | NMP | 59 |
| 14[e] | IBr | NMP | 61 |
| 15 | | NMP | n.d. |

[a] Conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Se (0.3 mmol), oxidant (0.12 mmol), solvent (0.6 mL), 130 °C, 6 h, under air atmosphere. DMF = *N,N*-dimethylformamide, DMAc = *N,N*-dimethylacetamid. DEF = *N,N*-diethylformamide.

[b] GC yield based on **2a**.

[c] IBr (0.2 mmol).

[d] 120 °C.

[e] Under Ar.

With the optimized reaction conditions in hand, the substrate scope of the tandem indole C-3 alkenylation/dual C–H oxidative selenylation was probed. First, a broad range of substituted acetophenones were subjected to the IBr-based system (Table 2). Among them, a series of *para*-substituted acetophenones bearing electron-donating groups (methyl, methoxyl) were smoothly converted into the corresponding products in moderate yields (**3ab**, **3ae**). Acetophenones bearing halo functionalities (F, Cl, Br, and I) were compatible to give the corresponding products in good yields (**3ag-3aj**, **3ap-3ar**). The structure of **3aj** was confirmed by X-ray crystallography. Strong electron-withdrawing substituents such as $CO_2CH_3$, CN, $NO_2$ and $SO_2CH_3$ were also compatible with the reaction conditions

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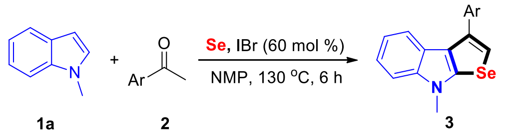
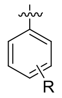
(**3ad**, **3ak-3am** and **3at**). When substituents were presented at the *ortho* position, lower yields were observed (**3au-3aw**). Acetophenones **2x** and **2y** bearing two substituents reacted well to yield the desired products **3ax** and **3ay**, respectively. The products (**3az-3aa'**, **3ae'**) were given in modest yields when bulky aromatic ketones such as 1-(naphthalen-1-yl)ethanone (**2z**), 1-(naphthalen-2-yl)ethanone (**2a'**), and 1-(phenanthren-3-yl)ethanone (**2e'**) were used. Notably, heteroaromatic ketones (**2b'-2d'**) also reacted efficiently to afford the corresponding products (**3ab'-3ad'**) in good yield. Unfortunately, aliphatic ketones such as 1-cyclohexylethanone and 3-methylbutan-2-one were not suitable substrates for this cascade transformation. We also tried non-methyl ketones such as propiophenone and 1,2-diphenylethan-1-one. Unfortunately, we did not observe the target products. Hence, non-methyl ketones featured no reactivity in the present system. 2-Bromo-1-phenylethan-1-one instead of acetophenone was also productive toward **3aa**, albeit in a low yield (34%). The robust nature of this metal-free system was reflected by the effective gram-scale preparation (**3aa**, **3ai**).

**Table 2.** Substrate scope with respect to ketones.[a]

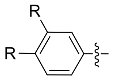


Ar =

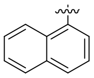


R = H, **3aa**, 70%, 63%[b], 34%[c]
R = 4-CH$_3$, **3ab**, 68%
R = 4-Ph, **3ac**, 60%
R = 4-CO$_2$CH$_3$, **3ad**, 63%
R = 4-OCH$_3$, **3ae**, 54%
R = 4-OCF$_3$, **3af**, 47%
R = 4-F, **3ag**, 70%
R = 4-Cl, **3ah**, 73%
R = 4-Br, **3ai**, 67%, 58%[b]
R = 4-I, **3aj**, 66%
R = 4-CN, **3ak**, 65%

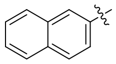
R = 4-NO$_2$, **3al**, 44%
R = 4-SO$_2$CH$_3$, **3am**, 57%
R = 3-CH$_3$, **3an**, 63%
R = 3-OCH$_3$, **3ao**, 59%
R = 3-F, **3ap**, 78%
R = 3-Cl, **3aq**, 75%
R = 3-Br, **3ar**, 71%
R = 3-CF$_3$, **3as**, 66%
R = 3-NO$_2$, **3at**, 62%
R = 2-OCH$_3$, **3au**, 63%
R = 2-F, **3av**, 59%
R = 2-Cl, **3aw**, 43%



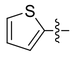
R = OCH$_3$, **3ax**, 54%
R = Cl, **3ay**, 72%



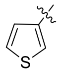
**3az**, 40%



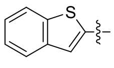
**3aa'**, 54%



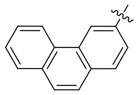
**3ab'**, 52%



**3ac'**, 65%



**3ad'**, 63%



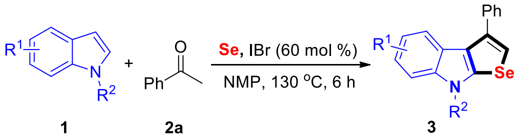
**3ae'**, 50%

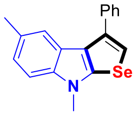
X-ray structure of **3aj**: CCDC: 1828980

[a] Conditions: **1a** (0.3 mmol), **2** (0.2 mmol), Se (0.3 mmol), IBr (0.12 mmol), NMP (0.6 mL), 130 ºC, 6 h, under air atmosphere, isolated yield based on **2**. [b] Yield of 6 mmol scale reaction. [c] 2-Bromo-1-phenylethan-1-one instead of acetophenone.

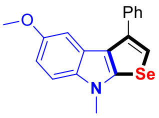
Thereafter, the substrate scope with respect to functionalized indoles was explored (Table 3). Unexpectedly, a methyl group at the C-4 position of indole component almost prevented the transformation, in which only a trace amount of product was observed by GC-MS. Moderate yields were obtained when substituents such as methyl and methoxy were presented at the indole C-5 position (**3ba** and **3ca**). Halogen functionalities such as chloro and bromo were well tolerated, giving the halo-substituted products in moderate yields (**3da** and **3fa**). While free NH-indole (**1h**) afforded the corresponding **3ha** in modest yield, other *N*-alkylindoles were also suitable to couple with ketone and selenium powder to give the target selenopheno[2,3-*b*]indoles in good yields (**3ia-3ja**).

**Table 3.** Substrate scope with respect to indoles.[a]

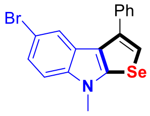




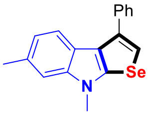
**3ba**, 63%



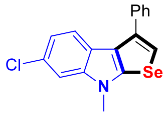
**3ca**, 58%



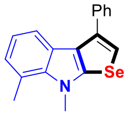
**3da**, 55%



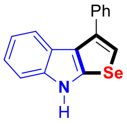
**3ea**, 62%



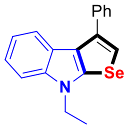
**3fa**, 53%



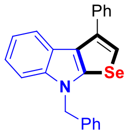
**3ga**, 58%



**3ha**, 48%



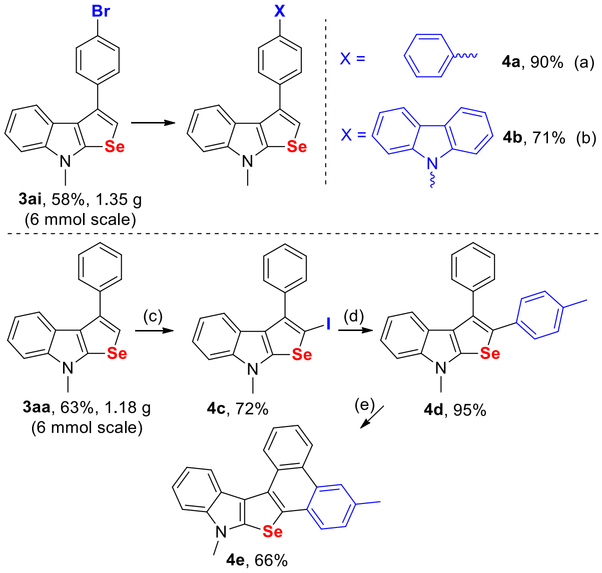
**3ia**, 60%



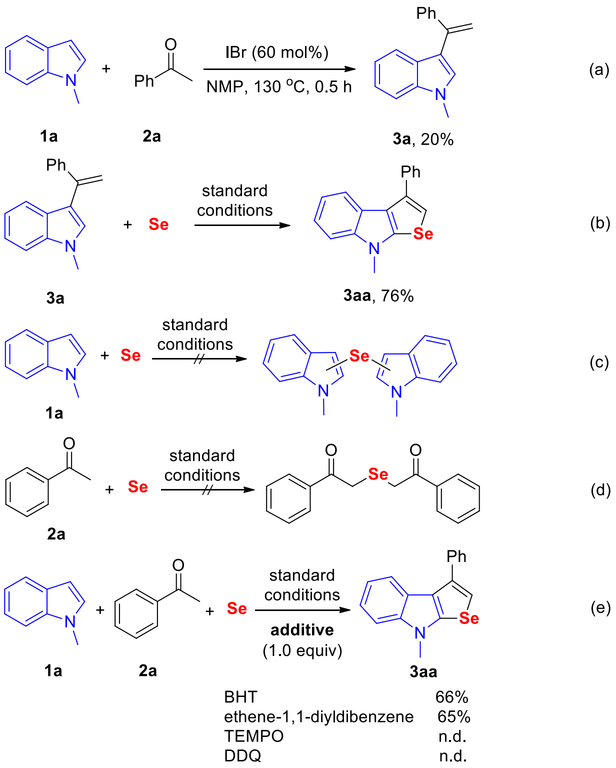
**3ja**, 55%

[a] Conditions: **1** (0.3 mmol), **2a** (0.2 mmol), Se (0.3 mmol), IBr (0.12 mmol), NMP (0.6 mL), 130 ºC, 6 h, under air atmosphere, isolated yield based on **2a**.

The selenophenoindoles product **3ai** was obtained in 58% yield in a gram-scale reaction (Scheme 2). Further synthetic modification of the bromo group of product **3ai** was investigated. Pd-catalyzed Suzuki−Miyaura cross coupling (Scheme 2, a) and Buchwald−Hartwig amination (Scheme 2, b) of **3ai** proceeded smoothly to afford products **4a** and **4b** in 90% and 71% yields, respectively.[21] When **3aa** was treated with I$_2$ in DMF under argon atmosphere, the iodization product **4c** was obtained in 72% yield (Scheme 2, c).[22] The Suzuki–Miyaura cross-coupling reaction of **4c** with *p*-tolylboronic acid proceeded well to give **4d** in 95% yield (Scheme 2, d). Finally, the **4d** was transformed to the 6,10-dimethyl-10*H* phenanthro[9',10':4,5]selenopheno[2,3-*b*]indole **4e** through dehydrogenative annulations with FeCl$_3$.[23] (Scheme 2, e).



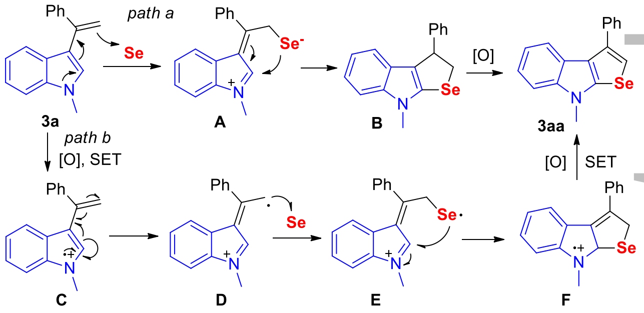
**Scheme 2.** Application of the present work. (a) **3ai** (0.2 mmol), phenylboronic acid (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), $Na_2CO_3$ (8.0 equiv), toluene-$H_2O$-EtOH (0.7, 0.7, 0.2 mL, respectively), 100 °C, 12 h, Ar; (b) **3ai** (0.2 mmol), carbazole (1.5 equiv), $Pd(OAc)_2$ (10 mol%), $K_2CO_3$ (3.0 equiv), $P(t\text{-}Bu)_3{\cdot}HBF_4$ (20 mol%), *o*-xylene (0.8 mL), 130 °C, 16 h, Ar; (c) **3aa** (0.2 mmol), $I_2$ (1.5 equiv.), KOH (3 equiv ), DMF (0.6 mL), 40 °C, 6 h, Ar; (d) **4c** (0.2 mmol), *p*-tolylboronic acid (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), $Na_2CO_3$ (8.0 equiv), toluene-$H_2O$-EtOH (0.7, 0.7, 0.2 mL, respectively), 100 °C, 12 h, Ar; (e) **4d** (0.1 mmol), $FeCl_3$ (6 equiv.), $CH_2Cl_2$ (0.8 mL), 45 °C, 12 h, Ar.



**Scheme 3.** Control experiments.

Based on our previous indole-template synthesis,[20b,c] we suspected the coupling of indole and ketone would be the initial step. Hence, we treated indole **1a** and ketone **2a** in the absence of selenium powder, which afforded 3-vinylindole **3a** within 0.5 h (Scheme 3, a). As expected, **3a** could smoothly convert into **3aa** with high efficacy by the treatment of elemental selenium under the standard reaction conditions (Scheme 3, b). Furthermore, we did not observe any product with C–Se bond formation in the absence of ketone or indole component (Scheme 3, c and d), in which indole and ketone were mainly recovered, respectively. This result also indicated that higher reactive 3-vinylindole **3a** was initially generated and then coupled with selenium. Finally, while the addition of scavenger BHT (butylated hydroxytoluene) or ethene-1,1-diyldibenzene did not affect the efficiency of the desired transformation, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and DDQ (2,3-dicyano-5,6-dichlorobenzoquinone) as the additive completely prevented the reaction (Scheme 3, e).

The experimental results above indicated 3-vinylindole **3a** to be the key intermediate for the three-component selenylation/annulation. On the basis of this and previous reports,[24] a possible reaction mechanism was proposed (Scheme 4). Starting from the 3-vinylindole **3a**, the process of dual C–H oxidative selenylation probably proceeded through two different pathways: path a) nucleophilic attack-involved cascade annulation and dehydrogenative aromatization;[10h,11a] and path b) SET (single electron transfer)-initiated radical annulation.[11b,12b]



**Scheme 4.** Possible reaction mechanism.

In summary, we have developed a three-component selenylation/annulation to give facile access to novel selenopheno[2,3-*b*]indole motif through a dual C–H oxidative selenylation under metal-free conditions. In this protocol, simple and readily available indoles, aromatic ketones, and selenium powder were used as the starting materials and a variety of functional groups attached to indoles and aromatic ketones were well tolerated. The C–Se bond formation unexpectedly occurred at the C-2 position of indole moiety with high levels of selectivity, which may inspire other cases of selenium powder-involved design for regioselective C–H selenylation.

# Experimental Section

### General procedure for the Synthesis of 3aa

IBr (25.0 mg, 0.12 mmol) and selenium powder (24.0 mg, 0.3 mmol) were added to an oven-dried reaction vessel (20 mL). The reaction vessel was sealed, 1-methyl-1*H*-indole (**1a**, 37.0 μL, 0.3 mmol), acetophenone (**2a**, 24.0 μL, 0.2 mmol) and *N*-methyl pyrrolidone (0.6 mL) were added by syringe. The reaction vessel was stirred at 130 ºC for 6 h under air atmosphere. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3aa** as colourless oily liquid (43.4 mg, 70 % yield). $R_f$ = 0.65 (100:1 petroleum ether/EtOAc). $^1$H NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.75-7.68 (m, 3H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.43-7.37 (m, 1H), 7.36-7.32 (m, 1H), 7.27-7.20 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H); $^{13}$C NMR (100 MHz, ppm) $\delta$ 144.9, 142.2, 138.5, 137.9, 128.5, 128.3, 127.5, 123.3, 122.1, 121.5, 119.2, 119.0, 116.1, 108.8, 33.2; HRMS (ESI) m/z calcd. for $C_{17}H_{14}NSe^+$ $(M+H)^+$ 312.0286, found 312.0283.

CCDC-1828980 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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# Metal-Free Three-Component Selenopheno[2,3-*b*]indole Formation through Double C–H Selenylation with Selenium Powder

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