

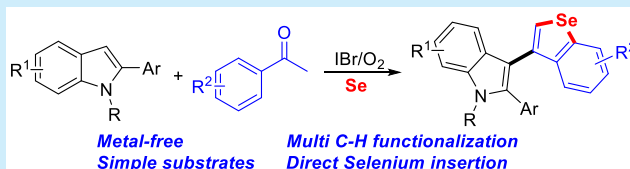
A Three-Component Strategy for Benzoselenophene Synthesis under Metal-Free Conditions Using Selenium Powder

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S Supporting Information

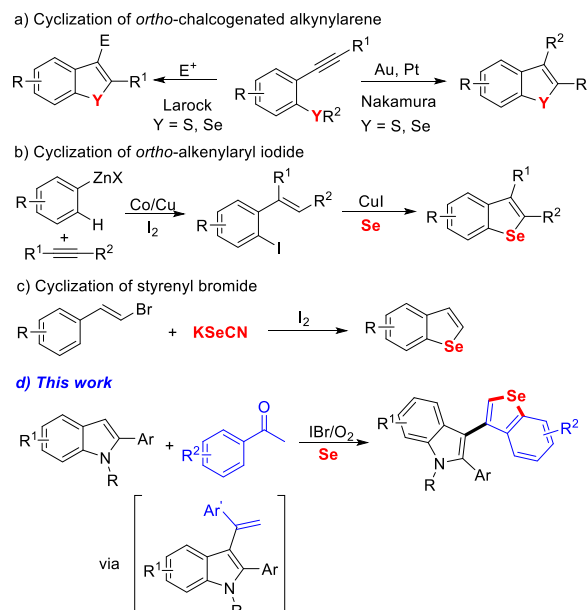
ABSTRACT: An efficient three-component benzoselenophenes formation has been developed from substituted indoles, acetophenones, and selenium powder under metal-free conditions. 2-Aryl indoles played an important role to promote benzoselenophene formation from acetophenone derivatives and selenium powder. One C–C and two C–Se bonds were selectively formed to provide 40 new benzoselenophenes in good yields.



Organoselenium compounds are of considerable interest, because of their potential biological activities, such as antiviral, antihypertensive, antioxidant, and antitumor properties.¹ In particular, aromatic benzoselenophene derivatives are attracting much attention as promising electronic materials for organic light-emitting diodes (OLED), organic conductors, and field-effect transistors.² Two general protocols for constructing C–Se bonds include (1) transition-metal-catalyzed cross-coupling reaction using active organoselenium compounds as substrates,³ and (2) elemental selenium as the selenium source. In recent years, the direct selenation of C–H bond with various reactive selenium reagents and even selenium powder has emerged as a very powerful and more direct approach for C–Se bond construction.⁴

Substituted benzoselenophenes can be constructed by annulation of either ring or by functionalization of the benzoselenophene core.⁵ In the early days, the benzoselenophene ring construction is mainly dependent on ethylbenzene via gaseous reaction from phenoselenide and acetylene at high temperature (400–600 °C).⁶ Cyclization of alkynyl arenes bearing an *ortho*-selenium functional group provides an general approach (Scheme 1a).⁷ Besides Larock's electrophilic cyclization^{7a,b} and Nakamura's transition-metal (Au or Pt)-catalyzed cyclization,⁸ a few other methods—particularly the reaction of *o*-haloethynylbenzenes and selenating reagents—are also available.⁹ Although phenylacetylenes can also be used as the raw materials, multiple steps are required and sensitive lithium or zinc reagent is usually involved (Scheme 1b).¹⁰ Recently, Ranu and co-workers found that substituted benzoselenophenes can be achieved using styrenyl bromides and potassium selenocyanate (KSeCN) as the reagents (Scheme 1c).¹¹ Besides these great progresses, versatile methods for benzoselenophene formation from readily available substrates under simple conditions are still highly desirable. Acetophenones are readily available, inexpensive, and easy to handle. Therefore, direct insertion of elemental selenium into acetophenones can provide an ideal approach for

Scheme 1. Selected Synthetic Approaches to Benzoselenophene Derivatives



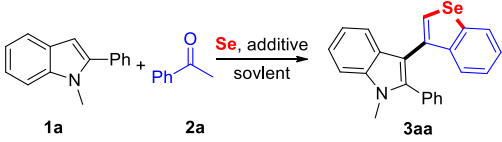
the construction of these heterocycles. However, as far as we know, there are no examples on direct insertion of selenium into acetophenones under mild conditions. In our previous indole-to-carbazole work based on indoles and ketones, we found that 3-vinylindole was in-situ-generated through dehydrative condensation, which could be used as the C4 source for heterocycle formation.¹² We also realized thieno-[2,3-*b*]indole formation through insertion of a S atom into the C2 position of indole and the vinyl group under metal-free

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conditions (Scheme 1a).¹³ We envisioned that it might be possible to insert a Se atom to 3-vinylindole to form benzoselenophene ring via [4 + 1] cycloaddition when the C2 position in indole is occupied, which can enable cyclization reaction occurring at the benzene ring (Scheme 1b). If this strategy can be realized, it will provide a convenient way for the construction of the benzoselenophene ring via in situ activation of acetophenones in the aid of indoles. Furthermore, the target products contain two important structures: indole and benzoselenophene, which will provide many new opportunities for further exploration on their properties. As our continuing efforts on indole functionalization under simple conditions,¹⁴ herein, we describe a three-component strategy for benzoselenophene formation from selenium powder and acetophenones under metal-free conditions (Scheme 1d).

We studied the three-component cycloaddition of 1-methyl-2-phenyl-1*H*-indole (**1a**) with acetophenone (**2a**) and selenium powder (Table 1). Several iodine-containing

Table 1. Screening the Reaction Conditions^a



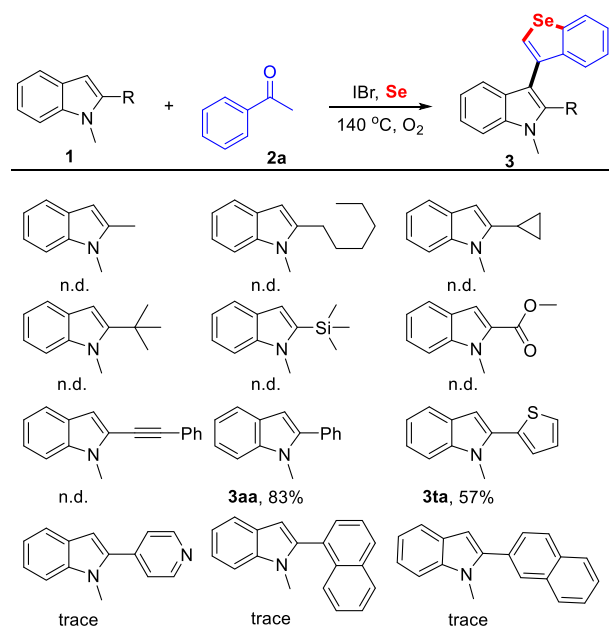
entry	oxidant	solvent	yield ^b (%)
1	HI	NMP	11
2	I ₂	NMP	20
3	ICl ₃	NMP	41
4	ICl	NMP	59
5	IBr	NMP	81
6	NIS	NMP	trace
7	NH ₄ I	NMP	n.d. ^c
8	IBr	PhCl	n.d. ^c
9	IBr	DMSO	n.d. ^c
10	IBr	DMF ^d	n.d. ^c
11	IBr	DEF ^e	26
12 ^f	IBr	NMP	89
13 ^g	IBr	NMP	66
14 ^h	IBr	NMP	76
15		NMP	n.d. ^c

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Se (0.3 mmol), additive (0.24 mmol), solvent (0.5 mL), 140 °C, 8 h, under an air atmosphere. ^bGC yield based on **2a**. ^cn.d. = not detected. ^dDMF = *N,N*-dimethylformamide. ^eDEF = *N,N*-diethylformamide. ^fUnder O₂. ^gIBr (50 mol %). ^h130 °C.

reagents, including HI, I₂, ICl₃, ICl, and IBr were investigated (Table 1, entries 1–5). IBr was preferable additive for this reaction, giving the desired product **3aa** in 81% yield (Table 1, entry 5). A sharp decline in yield was observed when NIS or NH₄I was used as the additive (Table 1, entries 6 and 7). Among the solvents examined, NMP resulted in the best reactivity (Table 1, entries 8–11). The yield could be slightly enhanced by performing the reaction under O₂ atmosphere (Table 1, entry 12). Decreasing the amount of IBr or the reaction temperature both led to lower yields of product (Table 1, entries 13 and 14). A control experiment was performed, indicating that the reaction did not proceed in the absence of IBr (Table 1, entry 15).

We also screened a range of 1-methyl-2-substituted-1*H*-indole under the optimized reaction conditions (Scheme 2).

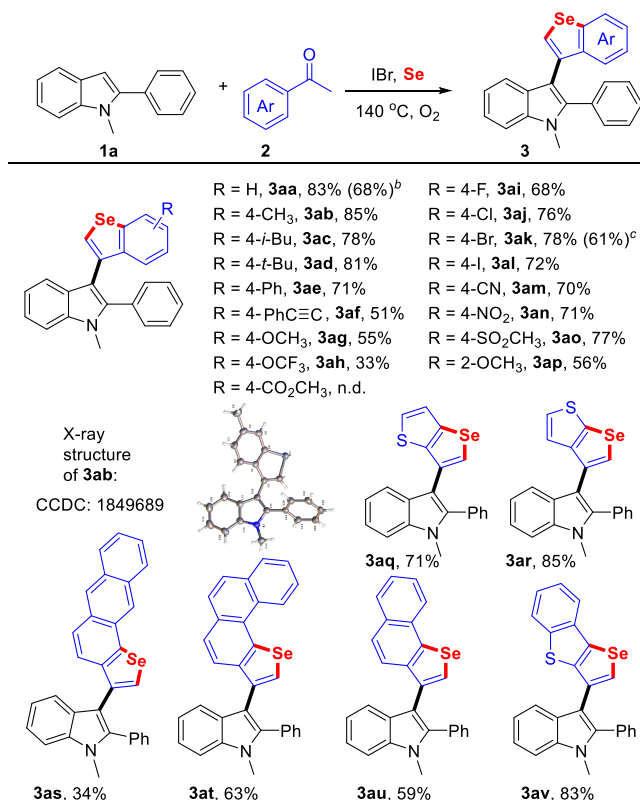
Scheme 2. Screening Different 1-Methyl-2-Substituted-1*H*-Indoles^a



^aReaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), Se (0.3 mmol), IBr (0.24 mmol), NMP (0.5 mL), 140 °C, 8 h, under O₂. Yields of isolated products.

The reaction could not proceed when the indole C-2 position was substituted by alkyl, silyl, ester, and alkynyl groups. 1-Methyl-2-phenyl-1*H*-indole could provide benzoselenophene **3aa** in good yield. The 1-methyl-2-(thiophen-2-yl)-1*H*-indole gave medium transformation, generating **3at** in 57% yield. Only a trace amount of product was observed via gas chromatography–mass spectrometry (GC-MS) when the large sterically hindered aromatic fused ring is substituted at the indole C-2 position.

With this three-component cycloaddition procedure in hand, we investigated the substrate scope of this selenium insertion process (Scheme 3). The isolated yield of model reaction product **3aa** was 83%. Acetophenones bearing methyl, butyl, and phenyl on the *para* position of the benzene ring reacted smoothly to give the similar yields (**3ab–3ae**). The structure of **3ab** was confirmed by X-ray crystallography. Note that the phenylethynyl was well-tolerated under standard conditions, giving the product **3af** in 51% yield. Trimethoxy (**2g**) and trifluoromethoxy (**2h**) were well-tolerated, affording the target products **3ag–3ah** in moderate yields. The results showed that substrates with a halo group on the phenyl ring are suitable for this transformation (**3ai–3al**). Substrates bearing strongly electron-withdrawing groups (–CN, –NO₂, and –SO₂CH₃) were also compatible with the reaction conditions, providing the corresponding products in good yields (**3am–3ao**), whereas the ester group is not compatible. As for *m*-substituted acetophenones, a mixture of two isomers (near 1:1 ratio) was obtained and difficult to be separated. The steric effect of the substituent has great influence on the yield. For example, 1-(2-methoxyphenyl)ethanone gave a moderate yield of the benzoselenophene **3ap**. The products (**3as–3au**) were given in modest yields when bulky aromatic ketones such as 1-(anthracen-2-yl)ethanone (**2s**), 1-(phenanthren-3-yl)ethanone (**2t**), and 1-(naphthalen-2-yl)ethanone (**2u**) were used. Notably, heteroaromatic ketone **2q–2r** and **2v** also reacted

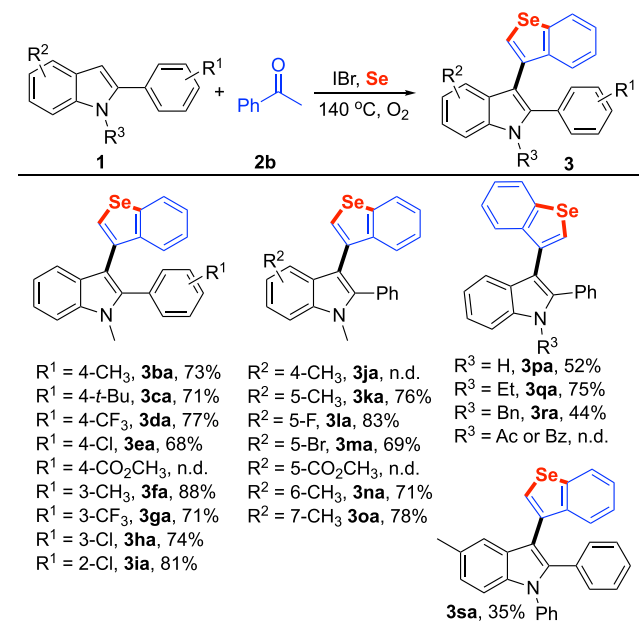
Scheme 3. Substrate Scope, with Respect to the Ketones^a

^aConditions: **1a** (0.3 mmol), **2** (0.2 mmol), Se (0.3 mmol), IBBr (0.24 mmol), NMP (0.5 mL), 140 °C, 8 h, under O₂. Yields of isolated products. ^b6 mmol scale. ^c5 mmol scale.

efficiently to afford corresponding **3aq–3ar** and **3av** in good yields. Propiophenone and aliphatic ketones were not suitable substrates for this transformation.

Next, several substituted indoles were evaluated to react with acetophenone (Scheme 4). 2-Phenyl-substituted indoles bearing methyl, butyl, trifluoromethyl, and chloro at the benzene rings were reacted smoothly to give the corresponding products **3ba–3ia** in moderate to good yields. Generally, indoles with a methyl group at the C-5, C-6, and C-7 positions underwent the cycloaddition smoothly to afford products **3ka**, **3na**, and **3oa** in 76%, 71%, and 78% yields, respectively. However, the methyl group (**1j**) at the C-4 position almost prevented the transformation, revealing a steric hindrance effect, and the ester group is also not compatible. Indole containing a fluoro group gave product **3la** in 83% yield, whereas the bromo substrate was to afford product **3ma** in lower yield (69%). In comparison with *N*-methylindole, the unprotected NH-indole (**1p**) also underwent the reaction giving product **3pa** in 52% yield. *N*-ethylindoles gave the target product in 75% yield (**3qa**). 1-Benzyl-2-phenyl-1H-indole (**1r**) and 5-methyl-1,2-diphenyl-1H-indole (**1s**) gave product yields of 44% and 35%, respectively. However, *N*-acetyl-2-phenylindole and *N*-benzoyl-2-phenylindole are not suitable for this reaction.

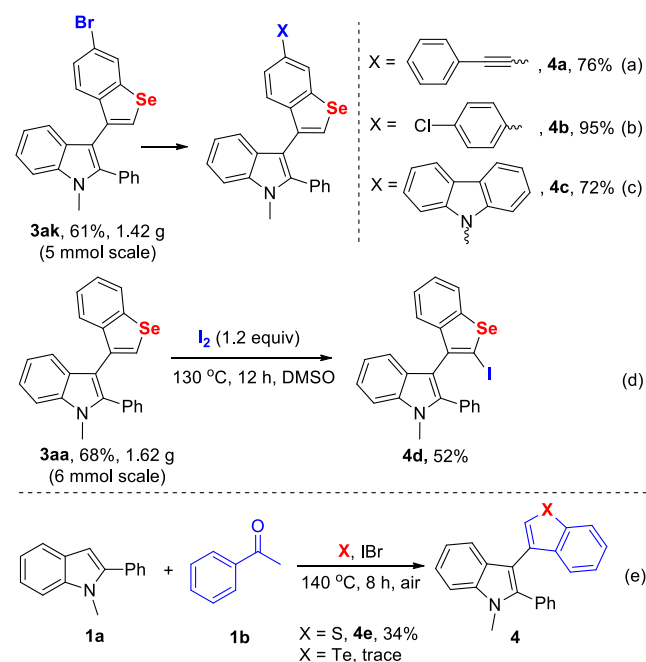
The benzoselenophene product **3ak** was obtained in 61% yield in a gram-scale reaction. Further synthetic modification of the bromo group of product **3ak** was investigated. Sonogashira coupling of **3ak** with phenylacetylene afforded the adduct **4a** in 76% yield. Moreover, Pd-catalyzed Suzuki–Miyaura cross-coupling and Buchwald–Hartwig amination of **3ak** could also

Scheme 4. Substrate Scope, with Respect to the Indoles^a

^aConditions: **1** (0.3 mmol), **2b** (0.2 mmol), Se (0.3 mmol), IBBr (0.24 mmol), NMP (0.5 mL), 140 °C, 8 h, under O₂. Yields of isolated products.

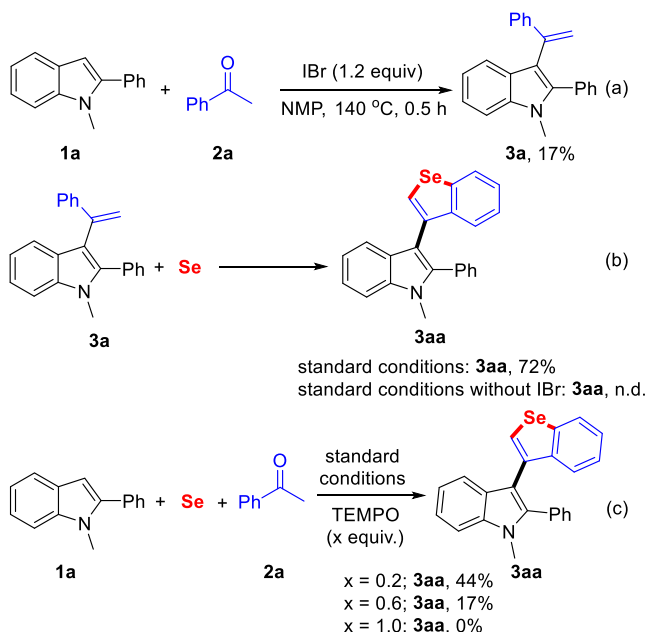
be smoothly introduced into products **4b** and **4c** in 95% and 72% yields, respectively.¹⁵ When **3aa** was treated with I₂ in dimethylsulfoxide (DMSO) under an air atmosphere, the iodization product **4d** was obtained in 52% yield. Subsequently, we investigated the same reaction using elemental sulfur powder and tellurium powder instead of selenium. Elemental sulfur gave the sulfuration product **4e** in only 34% yield, whereas tellurium powder did not produce the corresponding product (see Scheme 5).

Scheme 5. Application of the Present Work



Several control experiments were performed to elucidate the reaction mechanism (Scheme 6). In the absence of selenium

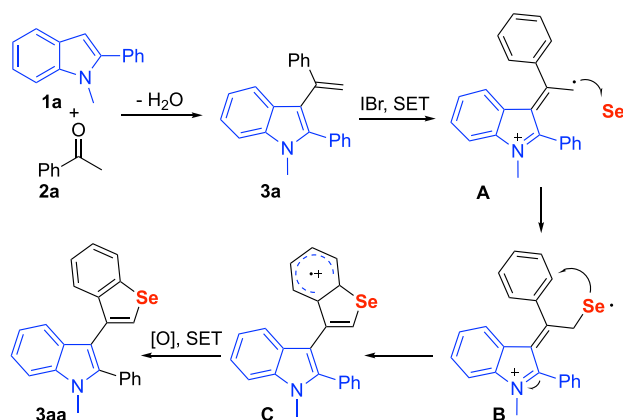
Scheme 6. Control Experiments under Various Conditions



powder, 1-methyl-2-phenyl-1H-indole (**1a**) reacts with acetophenone (**2a**) to form an intermediate **3a** in 17% yield after 0.5 h (Scheme 6a). The target benzoselenophene **3aa** was obtained in 72% yield, using the newly formed **3a** as a substrate under standard conditions, whereas no reaction was occurred in the absence of IBr (Scheme 6b). The reaction was completely suppressed when 1 equiv of 2,2,4,4-tetramethyl-1-piperidinyloxy (TEMPO) was added (Scheme 6c), suggesting that a radical pathway was probably involved in [4 + 1] cycloaddition with selenium powder.

The control experimental results indicated that **3a** is the key intermediate. Based on the above experimental observations and related references,^{4b,c,16} we proposed a plausible mechanism in Scheme 7. Dehydrative condensation from 2-phenyl-1H-indole (**1a**) and acetophenone (**2a**) generates intermediate **3a**. The process of dual C–H oxidative selenylation probably proceeded through a free radical. First, vinyl radical intermediate **A** was generated from 3-vinylindole

Scheme 7. Possible Reaction Mechanism



3a via single electron transfer. Then, intermediate **A** reacts with elemental selenium to give a selenium free radical **B**, which proceeds through intramolecular selenium cyclization to give intermediate **C**. The final desired product **3aa** is formed through the oxidation of **C**.

In summary, we have developed a versatile strategy for the synthesis of benzoselenophenes. The key 3-vinyl-indole intermediate was generated in situ through dehydrative condensation of aryl ketones and indoles under metal-free conditions. This simple method provides an efficient route for the preparation of a variety of new bis-heteroaryls containing both indole and benzoselenophene motifs from readily available starting materials.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00739.

Experimental procedures, characterization data, and ¹H NMR and ¹³C NMR spectra for all new products (PDF)

Accession Codes

CCDC 1849689 contains 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 emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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