Synthesis of Benzoisoselenazolone Derivatives by Nickel-Catalyzed Dehydrogenative Direct Selenation of C(sp^2)–H Bonds with Elemental Selenium in Air

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Supporting Information Placeholder

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ABSTRACT: Nickel-catalyzed direct selenation of benzamides bearing an 8-quinolyl auxiliary with elemental selenium provides benzoisoselenazolones in good yield via carbon–selenium and nitrogen–selenium bond formation under aerobic conditions. In addition to aryl C–H bonds, the method can also be applied to alkenyl C–H bonds, constructing an isoselenazolone skeleton. Simple mechanistic analysis shows that the reaction proceeds through a rate-determining C–H bond cleavage. The obtained benzoisoselenazolones are transformed into various organoselenium compounds and utilized as the catalyst for bromolactonization of alkenoic acids.

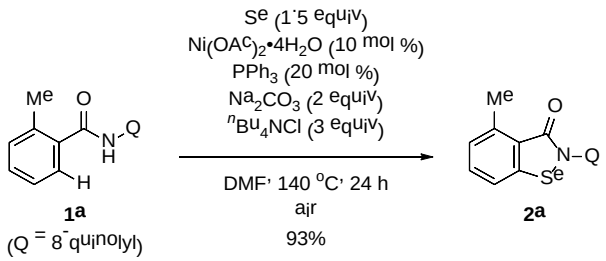
Benzoisoselenazolones consisting of 5-membered heterocycles having a nitrogen–selenium bond are attracting increasing interest as biologically active molecules. The representative compound ebselen and its derivatives have occupied a central position in organoselenium chemistry for some time. Ebselen is well known to exhibit an important antioxidant activity, mimicking glutathione peroxidase,[1] as well as having other medically promising qualities.[2] In addition, it was found to be a safe treatment for bipolar disorder, superior by far to the conventional drug, lithium.[3] Moreover, ebselen and its analogues have been used as catalysts for the oxidation of organic compounds.[4] Despite these fascinating properties, since their derivatization has not been well investigated, the construction of benzoisoselenazolone scaffolds is still challenging. Indeed, these compounds have been synthesized by either *ortho*-lithiation of benzamides and subsequent annulation with selenium electrophiles,[5] annulation of *o*-chloroselanylbenzoyl chloride with primary amines,[6] or radical cyclization of diselenides or their analogues.[7,8] These multi-step synthetic methods often gave low overall yields, and the frequently harsh reaction conditions were incompatible with many functional groups. Recently, Kumar reported the copper-catalyzed annulation of *o*-halobenzamides with elemental selenium.[9] Although that reaction can be conducted under mild conditions, expanding the substrate scope to some extent, the preparation of the starting aryl halides requires several tedious synthetic steps. Thus, there has been no convenient general method for constructing the benzoisoselenazolene skeleton.

In contrast, oxidative C–H functionalization has provided an efficient synthetic method for various heterocycles.[10] Therefore, the synthesis of benzoisoselenazolones by oxidative direct selenation would be desirable since simple benzamides can be used as the starting compounds. One of the key steps in this transformation was reported by Chatani and coworkers.[11] They found that the combination of nickel and an *N*,*N*'-bidentate chelating group in the substrate can yield the direct functionalization of benzamides. In addition, Hillhouse reported the insertion of elemental selenium in nickelacycles, giving selenium-containing heterocycles.[12] If these two fundamental reactions were aided by the use of a nickel catalyst, a powerful synthetic method for benzoisoselenazolones could be established. Although the chelate-assisted catalytic direct thiolation and selenation of aryl C–H bonds with disulfides and diselenides have been well developed,[13–16] the reaction with elemental selenium as an electrophilic reagent has yet to be reported. Herein, we report the nickel-catalyzed oxidative direct selenation of benzamides with elemental selenium. In addition, a reaction pathway including the unprecedented single-electron oxidation of a nickelacycle(II) intermediate in air is proposed.

With the hypothetical mechanism described above in mind, we first examined the reaction of benzamide **1a** with elemental selenium in the presence of the nickel catalyst. After extensive screening of various reaction parameters, we were pleased to find that direct selenation proceeded in the presence of $Ni(OAc)_2 \cdot 4H_2O$/PPh_3 as a catalyst, sodium carbonate, and $^nBu_4NCl$ in DMF at 140 °C in atmospheric air to yield the desired benzoisoselenazolone **2a** in 93% yield (Scheme 1). Under an argon atmosphere, the reaction provided **2a** in quantitative yields. The addition of $^nBu_4NCl$ improved the yield significantly, probably because the ammonium halide additive might help elemental selenium to dissolve in organic sol-

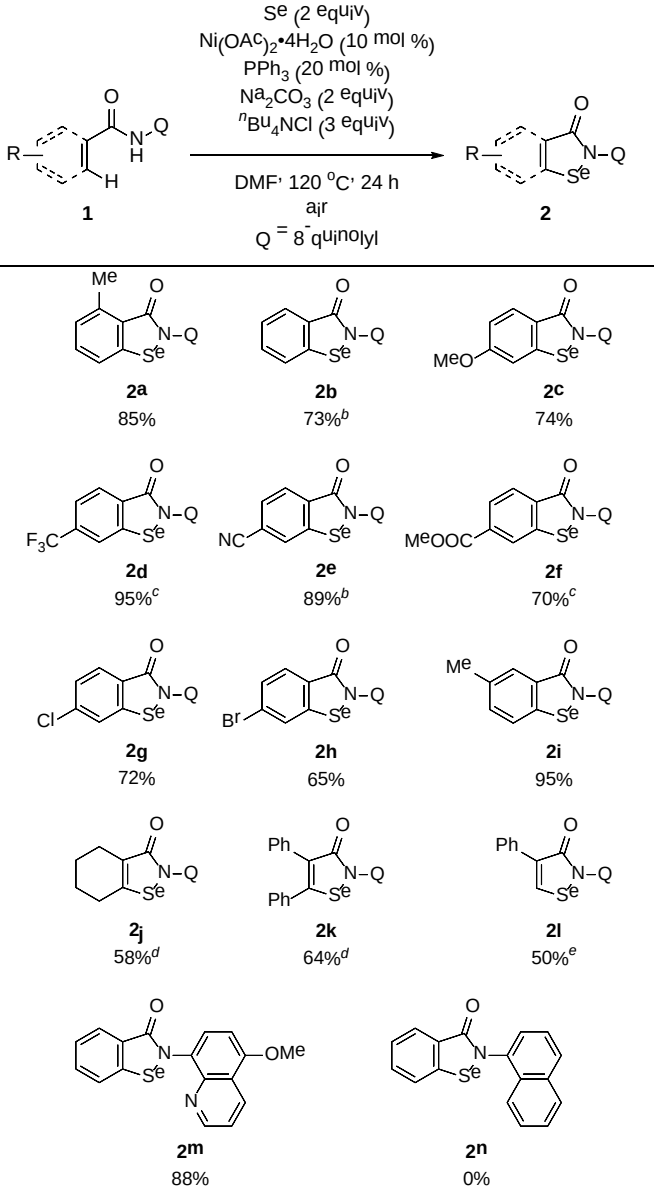
vents.[17] Using DMF as the solvent was crucial for the efficiency of the reaction. Other solvents gave poor results. The reaction had to be performed at high temperature, as lower temperatures produced lower yields. A detailed summary of the optimization process is in the Supporting Information.

SCHEME 1. Optimal Conditions for Nickel-Catalyzed Direct Selenation of Benzamide 1a with Elemental Selenium



Continuous optimization proved that the reaction of **1a** was complete even at 120 °C when 2 equiv of elemental selenium was employed. With the optimized conditions in hand, we sought to demonstrate the generality of the direct selenation with elemental selenium. As shown in Scheme 2, nonsubstituted benzamide **1b** also underwent the desired reaction to yield benzoisoselenazolone **2b** in 73% yield. A gram-scale direct selenation of **1b** on a 8 mmol scale was also achieved to provide 1.32 g of **2b** albeit in a slightly lower yield of 51%. A wide variety of functional groups were compatible under mild oxidative conditions, including an electron-donating methoxy group (**2c**) as well as electron-deficient trifluoromethyl (**2d**), cyano (**2e**), and methoxycarbonyl (**2f**) groups. Moreover, benzamides bearing chloro and bromo groups were also compatible with our protocol, permitting further transformations of benzoisoselenazolones **2g** and **2h** using cross-coupling techniques. Furthermore, a methyl substituent in the *meta* position of benzamide directed aromatic C–H bond cleavage to a less hindered *ortho* C–H bond (**2i**) with perfect selectivity. The structure of **2i** was unambiguously confirmed by X-ray diffraction analysis.[18] In addition to benzamides, acrylamides were also readily accommodated under these reaction conditions. The reactions of acrylamides **1j** and **1k** having either aliphatic or aromatic substituents also gave the corresponding isoselenazolones **2j** and **2k**. Additionally, acrylamide **1l** not substituted at the β-position could also be used in the present direct selenation (**2l**). With respect to a directing group on a nitrogen atom of benzamide, a 5-methoxy-substituted quinolyl group worked well to provide **2m** in 88% yield, while product **2n** was not obtained from **1n** having a 1-naphthyl group. *N*,*N*'-Bidentate auxiliaries were found to be essential for this direct selenation. In contrast, the corresponding thiolation and telluration with elemental sulfur and tellurium have not been successful to date, indicating that further modification of reaction conditions must be needed.

SCHEME 2. Nickel-Catalyzed Direct Selenation of Benzamides and Acrylamides 1 with Elemental Selenium[a]

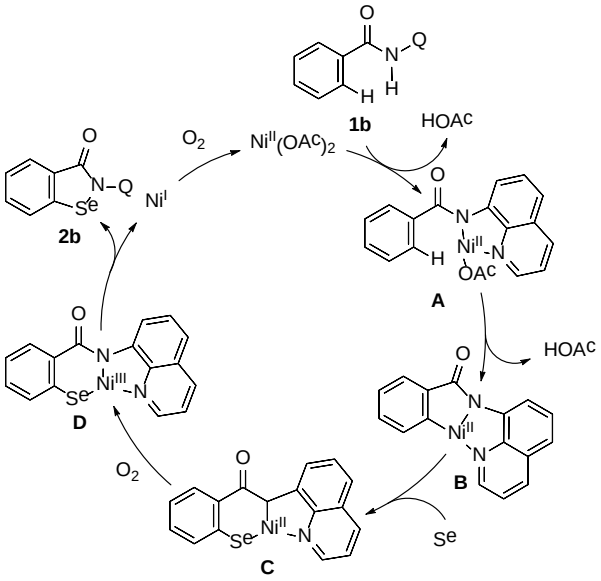


[a] **1**, elemental selenium (2 equiv), $Ni(OAc)_2•4H_2O$ (10 mol %), PPh_3 (20 mol %), Na_2CO_3 (2 equiv), and $^nBu_4NCl$ (3 equiv) in DMF (0.4 M) at 120 °C for 24 h. [b] 12 h. [c] 8 h. [d] 140 °C, 12 h. [e] 140 °C, 3 h.

Although we postulated that the reaction involves a chelate-assisted C–H bond cleavage and the direct incorporation of selenium, other alternative pathways cannot be ruled out, which might include a direct chlorination[19] of benzamide **1** with ammonium chloride and the subsequent oxidative annulation of *o*-chlorobenzamide with elemental selenium.[9] In order to confirm which pathway is operative, the identical reaction of **1b** was conducted without elemental selenium.[20] This did not produce the chlorinated product, while **1b** was recovered quantitatively, thus completely ruling out the direct chlorination pathway. It is worth mentioning that no alkylated product was observed, although ammonium halides are used as alkylating reagents under similar reaction conditions.[21] To gain more insight into the reaction mechanism, we next performed deuterium labeling experiments.[20] Intramolecular competitive reaction using deuterated benzamide provided a significant primary kinetic isotope effect (KIE) of 2.5. Similar KIEs were

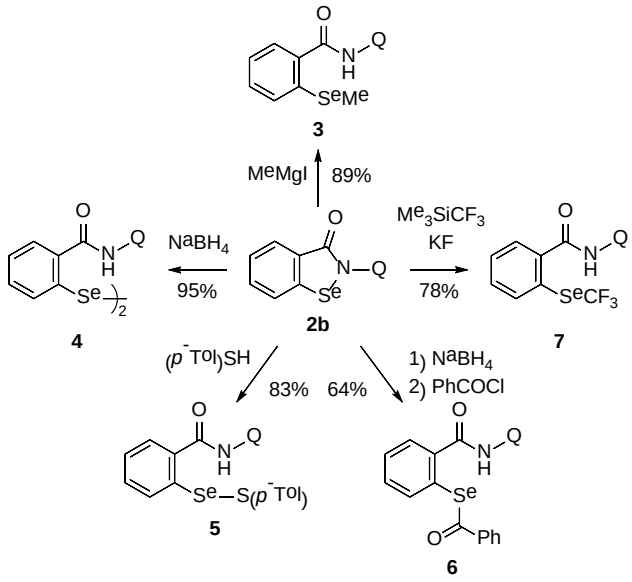
obtained in parallel experiments (2.4) and intermolecular competition (3.3). These observations strongly suggest that C–H bond cleavage is the rate-determining step of the reaction.[22]

SCHEME 3. A Plausible Reaction Mechanism



Synthetically versatile benzoisoselenazolones prepared by our method could be readily converted to a variety of useful organoselenium compounds (Scheme 4). For example, the reaction of **2b** with methylmagnesium iodide provided the ring-opening product **3** in 89% yield. In addition, reduction of **2b** with sodium borohydride, followed by aerobic treatment, yielded the corresponding diselenide **4** in 95% yield. Moreover, **2b** reacted with *p*-toluenethiol to construct the selenium–sulfur bond in **5**. Furthermore, the reactions of **2b** with benzoyl chloride and trifluoromethylsilane respectively furnished aryl selenide derivatives **6** and **7** in good yield. The prepared benzoisoselenazolone **2b** was also found to act as an efficient catalyst for bromolactonization of pentenoic acid with bromine.[25] Although the reaction gave the *5-exo-trig* cyclized product in 35% yield without any catalyst, the addition of even 1 mol % of **2b** greatly accelerated bromolactonization, for an 85% yield of the product.[21]

SCHEME 4. Transformation of Benzoisoselenazolone 2b



In summary, we have developed chelate-assisted direct selenation of aryl and alkenyl C–H bonds with elemental selenium catalyzed by nickel, which provides a new synthetic route to isoselenazolone derivatives. The present reaction was employed under mild oxidative conditions to expand substrate scope, and shows excellent functional group compatibility. Although the detailed mechanism remains to be investigated, we tentatively propose that the reaction proceeds through the unprecedented single electron oxidation of the stable nickelacycle(II) species in air. The synthetic utility of benzoisoselenazolones was unambiguously demonstrated by the further transformations giving rise to valuable organoselenium compounds and the catalytic bromolactonization of alkenoic acids.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

More detailed results of nickel-catalyzed reactions, and the ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interests.

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supposed that TEMPO might also act as the single electron oxidant for the stable nickelacycle(II) species.

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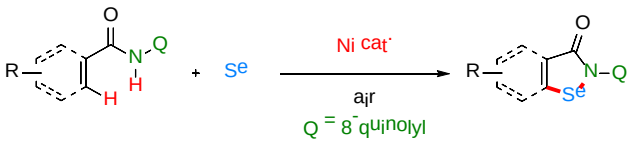
O
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Q = 8-quinolyl
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