

Article

Aerial Oxygen-Driven Selenocyclization of *O*-Vinylanilides Mediated by Coupled $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_2/I^- Redox Cycles

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Abstract: In the past decade, selenocyclization has been extensively exploited for the preparation of a wide range of selenylated heterocycles with versatile activities. Previously, selenium electrophile-based and FeCl_3 -promoted methods were employed for the synthesis of selenylated benzoxazines. However, these methods are limited by starting material availability and low atomic economy, respectively. Inspired by the recent catalytic selenocyclization approaches based on distinctive pathways, we rationally constructed an efficient and greener double-redox catalytic system for the access to diverse selenylated benzoxazines. The coupling of I_2/I^- and $\text{Fe}^{3+}/\text{Fe}^{2+}$ catalytic redox cycles enables aerial O_2 to act as the driving force to promote the selenocyclization. Control and test redox experiments confirmed the roles of each component in the catalytic system, and a PhSeI -based pathway is proposed for the selenocyclization process.

Keywords: diselenide; *o*-vinylanilide; redox cycle; aerial oxygen; multivalent metal; benzoxazine



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1. Introduction

Selenium-containing organic compounds, also known as organoselenium compounds, are an important and unique category of organic molecules. As shown in Figure 1, organoselenium compounds (**1–8**) exhibit versatile biological and pharmacological activities [1–3], such as antioxidant [4–8], antimicrobial [9–11], antiproliferative [12–15], and antiinflammatory activities [16]. Selenium-based probes (**9–10**) [17] have also been developed for highly sensitive fluorimetric detection of reactive oxygen species (ROS), such as ClO^- [18] and $\text{O}_2^{\bullet-}$ [19], in living cells. In addition, the selenium-containing fused bicyclic heterocycle (**11**) and its analogs have been demonstrated as active organic field effect transistor materials [20]. In the realm of organic synthesis, organoselenium compounds also have a wide range of applications, such as ligands for organometallic catalysts (**12**) [21], synthetic intermediates [22–24], and even direct catalysts [25]. Therefore, a huge amount effort has been devoted to developing efficient synthetic methods for selenylated heterocycles over the past decade [26–28].

As an important heterocyclic scaffold, 3,1-benzoxazine is widely found in natural products and bioactive molecules [29–31]. Numerous types of substituted benzoxazines have been synthesized via either cation- or radical-initiated tandem cyclizations [32–35]. Among them, selenylated benzoxazines have been successfully synthesized from the selenocyclization of selenium electrophiles, such as PhSeCl , $\text{PhSe}^+\text{CF}_3\text{COO}^-$ [36], and *N*-(PhSe)succinimide with *o*-vinylanilides [37] (Figure 2a). However, this approach is limited by the availability of selenium electrophiles (RSeX) and difficult to apply to *R*-modified selenocyclizations. Fe^{3+} -promoted selenocyclization with readily available diorganyl diselenides could be a good alternative approach [38–41]. In our experiments (Figure 2b), excess FeCl_3 (2 equiv) was required to afford the desired products in 3–4 h due to the chelation of in situ-generated PhSe^- with Fe^{3+} . Since the generation of one PhSe^+ is accompanied by the formation of one PhSe^- and the consumption of one molecule of Fe^{3+} , the efficiency

of this method is low in terms of atomic economy. It is worth noting that Zhang and coworkers reported that the combination of a catalytic amount of FeCl_3 /benzoyl peroxide (BPO) and 2 equiv of I_2 with diselenides afforded the desired products via both cation- and radical-initiated pathways [42] (Figure 2c). According to the mechanism proposed by Zhang et al., BPO facilitated the generation of RSeI and $\text{RSe}^\bullet$, while FeCl_3 catalyzed the electrophilic cyclization of the neighboring aryl ring. More recently, Zhang et al. reported that $\text{I}^\bullet$ generated from the redox reaction of FeCl_3 and KI induced the $\text{RSe}^\bullet$ -initiated reaction pathway and the oxidation of the radical intermediates by Fe^{3+} , and aerial oxygen yielded the desired products in 24 h under refluxing conditions [43] (Figure 2d). Inspired by these previous research, we envisioned that only catalytic amount of I_2 is actually needed to convert diselenide to RSeI , an ideal selenium electrophile [23,44], if the resulting I^- could be recycled to I_2 by a second oxidant. Many high-valent metals are capable of oxidizing I^- , but their low-valent counterparts are prone to be oxidized by O_2 . Therefore, the insertion of a multivalent metal redox cycle into the I_2/I^- redox cycle and O_2 may construct a double-redox catalytic system for selenylated benzoxazines, featuring greener reaction conditions and high atomic economy. Herein, we report an efficient aerial O_2 -driven selenocyclization approach mediated by coupled $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_2/I^- redox cycles (Figure 2e). Mechanistic investigation confirmed the roles of each component in this novel double-redox catalytic system and revealed the reasons why Fe^{3+} exhibited the best catalytic reactivity.

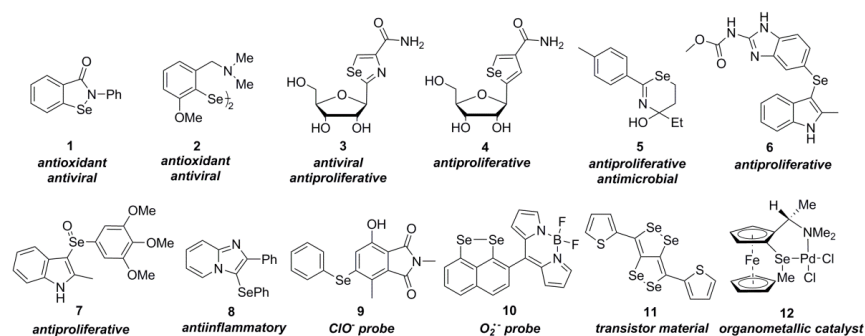
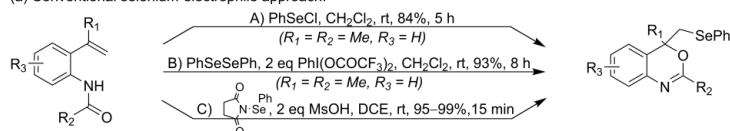


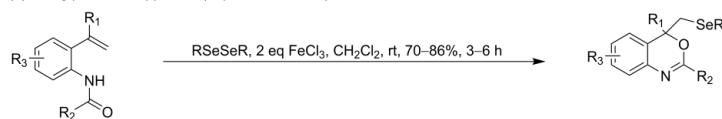
Figure 1. Representative organoselenium compounds.

Previous work:

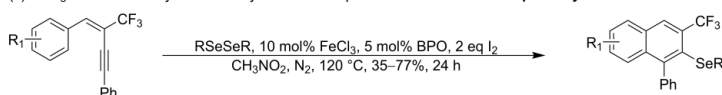
(a) Conventional selenium-electrophile approach:



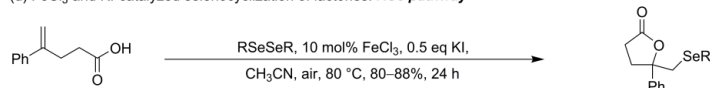
(b) FeCl_3 -promoted approach (unpublished result):



(c) FeCl_3 and BPO-catalyzed selenocyclization of naphthalenes: ***RSeI* and *RSe*[•] pathways**



(d) FeCl_3 and KI-catalyzed selenocyclization of lactones: ***RSe*[•] pathway**



This work:

(e) Aerial O_2 -driven double-redox catalytic selenocyclization of benzoxazines: ***RSeI* pathway**

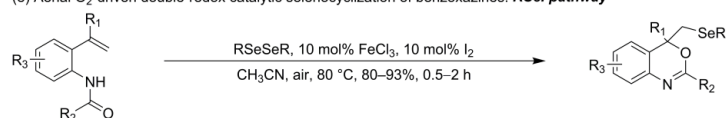


Figure 2. Previous and current selenocyclization methods.

2. Results and Discussion

In the preliminary experiments, the catalytic reactivities of a series of multivalent transition metal salts, including Cu(acac)₂, Co(acac)₃, VO(acac)₂, Ce(NH₄)₂(NO₃)₆, Ni(acac)₂, MoO₂(acac)₂, PMA, Fe(acac)₃, Fe(OTf)₃, and FeCl₃, were tested. The reaction of 1.0 equiv of *o*-vinylanilide **1a**, 0.6 equiv of diselenide **2a**, and 0.1 equiv of metal salt and I₂ in CH₃CN was refluxed under air atmosphere. The data summarized in Table 1 (Entry 1–10) indicate that all of these multivalent transition metals showed some catalytic effect. A major problem with these metal catalysts is that these reactions had difficulty in terms of completion. Among these metals, Fe³⁺ salts exhibited remarkably superior reactivity. In the presence of 10 mol% FeCl₃, the selenocyclization took only 30 min to afford the desired benzoxazine product **3a** with 93% yield. In addition, the experimental results (Table 1, Entry 11–14) showed that the FeCl₃-catalyzed reaction exhibited notable solvent effects. Acetonitrile was proved as the most suitable solvent. In addition, we further reduced the amount of FeCl₃ and I₂ and found that the reaction could not go to completion when the amount of either FeCl₃ or I₂ was lowered to 5%.

Table 1. Optimization of reaction conditions ¹.

Entry	M ⁿ⁺	Solvent	Reaction Time (h)	Isolated Yield (%)
1	Cu(acac) ₂	CH ₃ CN	8	55
2	Co(acac) ₃	CH ₃ CN	8	51
3	VO(acac) ₂	CH ₃ CN	12	45
4	Ce(NH ₄) ₂ (NO ₃) ₆	CH ₃ CN	2	52
5	Ni(acac) ₂	CH ₃ CN	8	22
6	MoO ₂ (acac) ₂	CH ₃ CN	8	27
7	PMA	CH ₃ CN	5	28
8	Fe(OTf) ₃	CH ₃ CN	9	92
9	Fe(acac) ₃	CH ₃ CN	1	94
10	FeCl ₃	CH ₃ CN	0.5	93
11	FeCl ₃	DCE	3	55
12	FeCl ₃	THF	4	73
13	FeCl ₃	DMSO	3	80
14	FeCl ₃	EtOH	6	81

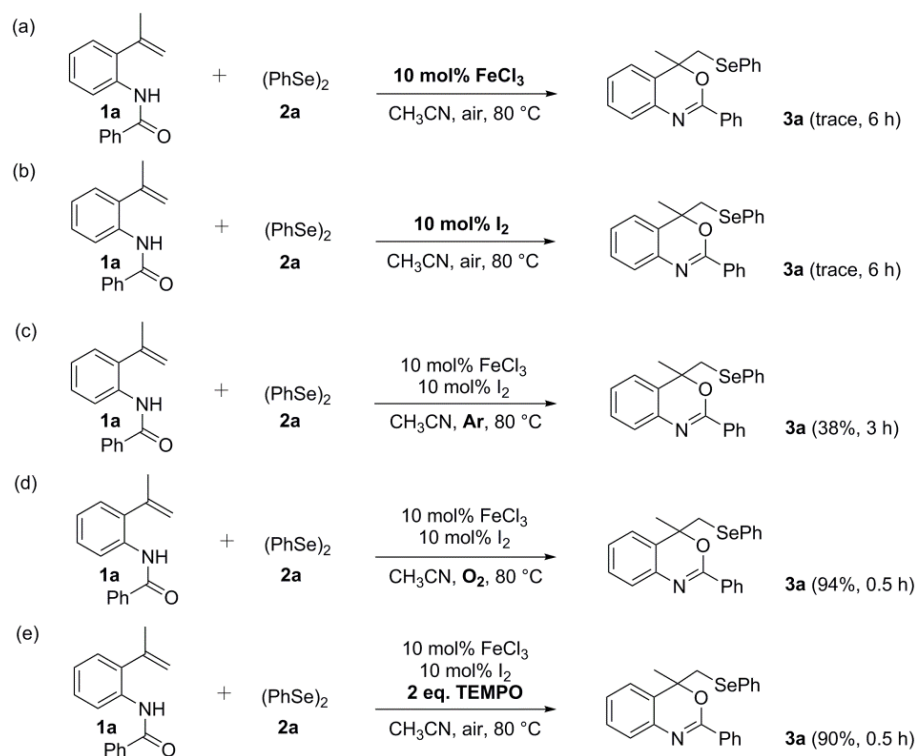
¹ Reaction conditions: **1a** (0.10 mmol), **2a** (0.06 mmol), FeCl₃ (0.01 mmol), I₂ (0.01 mmol), solvent (2.0 mL), 80 °C, air.

With the optimized reaction conditions, we further explored the scope of this double-redox catalytic system in the synthesis of selenylated benzoxazines. The data in Table 2 showed that the new method tolerated a variety of substituents on both *o*-vinylanilide and diorganyl diselenide substrates at different positions. Generally, both strong electron-withdrawing -NO₂ on the benzoyl moiety and more sterically hindered phenyl on the vinyl moiety resulted in lowered reaction rate. As shown in Table 2, selenylated benzoxazines **3a–3t** were obtained in 80–93% yields in 0.5–2 h.

To elucidate the proposed roles of each key component in the catalytic system, a series of control experiments were performed. As shown in Scheme 1a,b, the absence of either catalytic amount of FeCl₃ or I₂ resulted in the formation of only a trace amount of **3a**. When the reaction was conducted in argon atmosphere, it simply afforded **3a** in 38% yield (Scheme 1c). The above experimental results clearly indicate that FeCl₃, I₂, and aerial O₂ are essential to the catalytic system, but replacement of aerial O₂ with pure O₂ did not lead to improvement in the catalytic efficacy, suggesting that the proposed O₂ oxidation of Fe²⁺ was not the rate-limiting step (Scheme 1d). Finally, the ineffectiveness of TEMPO on the

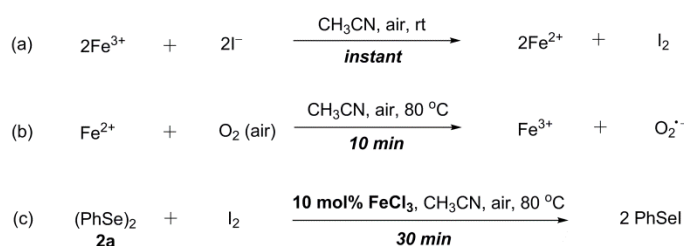
proceeding of this reaction implies that radical species ($RSe^{\bullet}$) should not be involved in reaction pathway [45,46] (Scheme 1e).

Table 2. Aerial O_2 -driven double-redox synthesis of selenylated benzoxazines (**3a–3t**).



Scheme 1. Control experiments.

To prove the existence and coupling of the proposed $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_2/I^- redox cycles, we further performed a series of control redox reactions without *o*-vinylanilide. As shown in Scheme 2a, a qualitative chromogenic assay (Figure S1a,b) showed that the treatment of Fe^{3+} with I^- at ambient temperature caused an abrupt formation of a large amount of Fe^{2+} and I_2 . In another experiment, the exposure of FeCl_2 in CH_3CN to air at 80°C for 10 min led to complete oxidation of Fe^{2+} to Fe^{3+} (Scheme 2b) as indicated by a chromogenic assay (Figure S1c). Surprisingly, we found that almost no Fe^{3+} could be detected after the aqueous solution of FeCl_2 was exposed to air for 30 min at 80°C . This result indicates that the efficacy of the aerial oxidation of Fe^{2+} is solvent dependent, which may possibly be one important reason why CH_3CN is most suitable for this reaction. Finally, we tested the reaction of I_2 with PhSeSePh (Scheme 2c). As shown in Figure S2a, the reaction proceeded very slowly at ambient temperature. As indicated by the decoloration of I_2 , refluxing at 80°C significantly promoted the formation of PhSeI . However, it still took 3 h for the reaction to reach equilibrium (Figure S2b). When a catalytic amount of Fe^{3+} (10 mol%) was added, the decoloration time was significantly shortened to 30 min (Figure S2c). This result could be explained by the specific chelation of Fe^{3+} with diselenide and induced polarization of Se-Se bonds, which have been reported in numerous previous reports [38–41,47]. The revealed dual roles of Fe^{3+} well explained its superior catalytic activity compared with other multivalent metals in this selenocyclization reaction.



Scheme 2. Separated control redox reactions without *o*-vinylanilide.

On the basis of the above control experiments and tested redox reactions, a plausible mechanism was proposed for the current catalytic selenocyclization system (Figure 3). At the beginning of the reaction, Fe^{3+} catalyzed the formation of PhSeI (2a), the reactive selenium electrophile, which quickly reacted with *o*-vinylanilide (1a) and formed the seleniranium intermediate (INT1). The intramolecular nucleophilic cyclization (INT2) followed by the deprotonation by the superoxide radical anion ($\text{O}_2^{\bullet-}$) afforded the desired benzoxazine (3a). Meanwhile, the released I^- was instantly oxidized back to I_2 by Fe^{3+} to provide a continuous resource of PhSeI . The consumed Fe^{3+} was also quickly recycled by the aerial oxidation of Fe^{2+} . Therefore, the selenocyclization was pushed forward by a green oxidant, aerial oxygen, and only catalytic amounts of FeCl_3 and I_2 were needed. Since $k_2 > k_1 > k_3$ in the redox cycles, the majority of ion metal existed as Fe^{3+} , and iodine existed as I_2 during the reaction process, which was verified by a chromogenic assay (Figure S3).

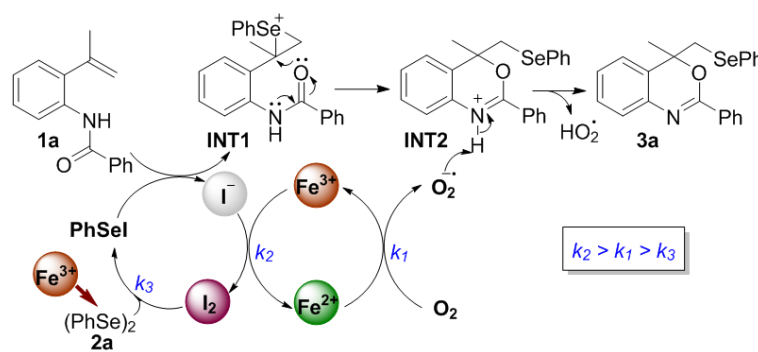


Figure 3. Proposed reaction mechanism.

3. Materials and Methods

3.1. General Methods

The solvents and chemical reagents used in the current research work were purchased from commercial suppliers. All of the reactions were monitored by TLC plates coated with 0.25 mm silica gel 60 F₂₅₄ and visualized by 254 nm UV. The silica gel used in column chromatography (particle size 32–63 µm) was purchased from Qingdao Haiyang Chemicals, China. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on an AV-400 instrument (Bruker BioSpin, Faellanden, Switzerland) with chemical shifts referenced to DMSO-*d*₆ or CDCl₃ and reported in parts per million. Infrared spectra were obtained with a Vertex-70 instrument (Bruker Optics, Billerica, MA, US). HRMS spectra were acquired with a micrOTOF-Q II instrument (Bruker Daltonics, Billerica, MA, US) and reported as *m/z*. Melting points were measured on an X-4 melting point apparatus and were uncorrected (Tech Instrument, Beijing, China). The characterization data of new *o*-vinylanilides [37,48–51] including **1e**, **1f**, **1g**, and **1h** and known selenylated benzoxazines [36,52] including **3a**, **3d**, **3q**, and **3r** are listed in the Supplementary Materials. The NMR spectra of new *o*-vinylanilides and benzoxazines are provided in the Supplementary Materials.

3.2. General Synthetic Procedure and the Characterization of Selenylated Benzoxazines (3a–3t)

To a mixture of *o*-vinylanilide (0.1 mmol) and diorganyl diselenide (0.06 mmol) in CH₃CN (2 mL), FeCl₃ (0.01 mmol) and I₂ (0.01 mmol) were added. The reaction was heated at 80 °C for 0.5–2 h and then concentrated *in vacuo*. Flash column chromatography on silica gel (PE/EA = 10:1) afforded the desired products **3a–3t** in pure form.

4-Methyl-2-(4-nitrophenyl)-4-((phenylselenanyl)methyl)-4*H*-benzo[*d*][1,3]oxazine (**3b**): a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.23 (s, 4H), 7.39–7.35 (m, 4H), 7.28–7.22 (m, 1H), 7.17–7.12 (m, 4H), 3.58 (d, *J* = 13.0 Hz, 1H), 3.38 (d, *J* = 13.0 Hz, 1H), 1.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 153.9, 149.2, 147.0, 138.4, 138.2, 132.8 (×2), 129.2, 129.0, 128.7 (×3), 127.6, 127.1 (×2), 125.8, 124.4, 123.9, 123.2 (×2), 119.1, 80.8, 59.5, 29.6; IR (KBr): *v*_{max} 3464, 3088, 3002, 2935, 1635, 1590, 1522, 1385, 1346, 1185, 1085, 939, 893, 810, 745 cm^{−1}; HRMS (ESI⁺): *m/z* calcd for C₂₂H₁₉N₂O₃Se [M + H]⁺ 439.0555; found 439.0552.

4-Methyl-4-((phenylselenanyl)methyl)-2-(thiophen-2-yl)-4*H*-benzo[*d*][1,3]oxazine (**3c**): a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.38 (d, *J* = 3.9 Hz, 1H), 7.31–7.30 (m, 2H), 7.21–7.18 (m, 2H), 7.06 (t, *J* = 4.8 Hz, 5H), 6.99 (t, *J* = 3.7 Hz, 1H), 3.49 (d, *J* = 10.2 Hz, 1H), 3.26 (d, *J* = 10.2 Hz, 1H), 1.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.9, 137.7, 135.8, 131.8 (×2), 129.4, 129.2, 129.0, 128.0, 127.9 (×3), 127.6, 126.6, 125.9, 125.3, 123.9, 122.1, 79.4, 38.6, 25.3; IR (KBr): *v*_{max} 3724, 2962, 1589, 1479, 1426, 1367, 1314, 1263, 1218, 1028, 804 cm^{−1}; HRMS (ESI⁺): *m/z* calcd for C₂₂H₁₈NOS₂Se [M + H]⁺ 400.0269; found 400.0266.

8-Methyl-6-phenyl-8-((phenylselenanyl)methyl)-8*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*][1,3]oxazine (**3e**): a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.48–7.38 (m, 5H), 7.15–7.14 (m, 3H), 6.82 (s, 1H), 6.61 (s, 1H), 5.95 (d, *J* = 12.8 Hz, 1H), 5.92 (d, *J* = 12.8 Hz, 1H), 3.48 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 1.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 155.0, 147.7, 146.1, 134.0, 132.8 (×2), 132.5, 131.1, 130.4, 128.9 (×3), 128.1 (×2), 127.8 (×2), 126.9, 121.7, 106.2, 103.5, 101.3, 79.9, 39.5, 26.4; IR (KBr): *v*_{max} 3722, 2963, 1624, 1593, 1482, 1401, 1317, 1262, 1162, 1091, 1019, 805, 765 cm^{−1}; HRMS (ESI⁺): *m/z* calcd for C₂₃H₂₀NO₃Se [M + H]⁺ 438.0603; found 438.0604.

6-(4-Chlorophenyl)-8-methyl-8-((phenylselenanyl)methyl)-8*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*][1,3]oxazine (**3f**): a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.38–7.35 (m, 4H), 7.16–7.13 (m, 3H), 6.79 (s, 1H), 6.59 (s, 1H), 5.95 (d, *J* = 1.2 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 1H), 3.46 (d, *J* = 12.9 Hz, 1H), 3.31 (d, *J* = 12.9 Hz, 1H), 1.83 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 154.0, 147.7, 146.2, 137.2, 133.8, 132.7 (×2), 131.0, 130.3, 129.1 (×2),

129.0 ($\times 3$), 128.4 ($\times 2$), 127.0, 121.6, 106.2, 103.4, 101.3, 80.1, 39.6, 26.5; IR (KBr): $\nu_{\max}$ 3721, 2891, 1574, 1478, 1441, 1368, 1312, 1263, 1192, 1036, 939, 863, 830, 736 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{ClNO}_3\text{Se}$ $[\text{M} + \text{H}]^+$ 474.8455; found 474.8457.

8-Methyl-8-((phenylselanyl)methyl)-6-(thiophen-2-yl)-8*H*-[1,3]dioxolo[4',5':4,5]benzo [1,2-*d*][1,3]oxazine (**3g**): a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 3.4$ Hz, 1H), 7.45 (d, $J = 4.8$ Hz, 1H), 7.40–7.37 (m, 2H), 7.16–7.15 (m, 3H), 7.06 (t, $J = 4.2$ Hz, 1H), 6.76 (s, 1H), 6.59 (s, 1H), 5.94 (s, 1H), 5.92 (s, 1H), 3.47 (d, $J = 12.8$ Hz, 1H), 3.32 (d, $J = 12.8$ Hz, 1H), 1.82 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.7, 147.7, 145.9, 136.9, 133.9, 132.7 ($\times 2$), 130.4, 129.9, 129.7, 128.9 ($\times 3$), 127.6, 126.9, 121.6, 105.9, 103.6, 101.2, 80.4, 39.3, 26.3; IR (KBr): $\nu_{\max}$ 3725, 2944, 1626, 1591, 1478, 1421, 1365, 1308, 1263, 1183, 1035, 852, 804, 734 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_3\text{SSe}$ $[\text{M} + \text{H}]^+$ 444.0167; found 444.0163.

6-(4-Methoxyphenyl)-8-methyl-8-((phenylselanyl)methyl)-8*H*-[1,3]dioxolo[4',5':4,5]benzo [1,2-*d*][1,3]oxazine (**3h**): a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, $J = 8.7$ Hz, 2H), 7.41–7.39 (m, 2H), 7.17–7.16 (m, 3H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.80 (s, 1H), 6.62 (s, 1H), 5.96 (s, 1H), 5.94 (s, 1H), 3.88 (s, 3H), 3.48 (d, $J = 12.7$ Hz, 1H), 3.34 (d, $J = 12.7$ Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 155.0, 147.7, 145.7, 134.3, 132.7 ($\times 2$), 129.6 ($\times 2$), 128.9 ($\times 3$), 126.9, 113.5 ($\times 2$), 105.9, 103.4, 101.2, 79.7, 55.3, 39.4, 26.2; IR (KBr): $\nu_{\max}$ 3715, 2963, 1601, 1505, 1478, 1367, 1310, 1258, 1172, 1088, 1032, 941, 763 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_4\text{Se}$ $[\text{M} + \text{H}]^+$ 468.0709; found 468.0712.

2,4-Diphenyl-4-((phenylselanyl)methyl)-4*H*-benzo[*d*][1,3]oxazine (**3i**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.17 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 7.0$ Hz, 1H), 7.45–7.37 (m, 8H), 7.32–7.26 (m, 3H), 7.22–7.14 (m, 5H), 3.95 (d, $J = 13.1$ Hz, 1H), 3.90 (d, $J = 13.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.2, 142.3, 139.4, 133.4 ($\times 3$), 132.3, 131.4 ($\times 2$), 130.4, 129.2, 129.0 ($\times 2$), 128.4 ($\times 2$), 128.2 ($\times 2$), 128.0 ($\times 2$), 127.5, 127.1, 126.4, 126.0, 125.5, 124.6, 83.5, 39.3; IR (KBr): $\nu_{\max}$ 3515, 3438, 1956, 1628, 1482, 1455, 1316, 1260, 1082, 1022, 801, 763 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{27}\text{H}_{22}\text{NOSe}$ $[\text{M} + \text{H}]^+$ 456.0861; found 456.0862.

4-Phenyl-4-((phenylselanyl)methyl)-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazine (**3j**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, $J = 8.2$ Hz, 2H), 7.52–7.48 (m, 1H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.34–7.26 (m, 4H), 7.19–7.18 (m, 2H), 7.09–7.05 (m, 1H), 7.02–6.97 (m, 1H), 3.60 (d, $J = 12.6$ Hz, 1H), 3.43 (d, $J = 12.6$ Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.1, 138.8, 135.8, 132.5, 132.3 ($\times 2$), 131.3, 130.7, 129.4, 129.1 ($\times 2$), 128.6 ($\times 3$), 128.1 ($\times 2$), 128.0 ($\times 2$), 127.7, 127.0, 126.6, 125.3, 123.0, 79.8, 38.2, 26.6; IR (KBr): $\nu_{\max}$ 3436, 1628, 1484, 1446, 1385, 1318, 1262, 1162, 1089, 1024, 758 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{28}\text{H}_{24}\text{NOSe}$ $[\text{M} + \text{H}]^+$ 470.1018; found 470.1015.

2-(4-Chlorophenyl)-4-phenyl-4-((phenylselanyl)methyl)-4*H*-benzo[*d*][1,3]oxazine (**3k**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, $J = 8.6$ Hz, 2H), 7.44–7.36 (m, 8H), 7.33–7.29 (m, 3H), 7.24–7.12 (m, 5H), 3.93 (d, $J = 13.2$ Hz, 1H), 3.89 (d, $J = 13.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.2, 142.1, 139.2, 137.6, 133.3 ($\times 2$), 130.8, 129.3 ($\times 2$), 129.0 ($\times 2$), 128.5 ($\times 3$), 128.4 ($\times 2$), 128.3 ($\times 2$), 127.4, 127.2, 126.6, 125.9, 125.6, 124.6, 83.7, 39.1; IR (KBr): $\nu_{\max}$ 3399, 1658, 1481, 1446, 1398, 1315, 1259, 1085, 1022, 939, 801, 736 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{27}\text{H}_{21}\text{ClNOSe}$ $[\text{M} + \text{H}]^+$ 490.0471; found 490.0472.

2-(4-Nitrophenyl)-4-phenyl-4-((phenylselanyl)methyl)-4*H*-benzo[*d*][1,3]oxazine (**3l**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.24 (s, 4H), 7.44–7.27 (m, 10H), 7.20–7.13 (m, 4H), 3.94 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.0, 149.4, 142.0, 138.8, 133.2 ($\times 2$), 130.6, 129.4, 129.0 ($\times 2$), 128.7 ($\times 2$), 128.5 ($\times 3$), 127.4, 127.2, 126.0, 125.9 ($\times 2$), 124.8, 123.9, 123.3 ($\times 2$), 84.3, 39.0; IR (KBr): $\nu_{\max}$ 3399, 2963, 1628, 1521, 1499, 1446, 1390, 1316, 1260, 1083, 1024, 801, 762 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}_3\text{Se}$ $[\text{M} + \text{H}]^+$ 501.0712; found 501.0709.

4-Phenyl-4-((phenylselanyl)methyl)-2-(thiophen-2-yl)-4*H*-benzo[*d*][1,3]oxazine (**3m**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, J = 3.6 Hz, 1H), 7.48–7.45 (m, 3H), 7.41–7.26 (m, 8H), 7.23–7.17 (m, 4H), 7.15–7.09 (m, 2H), 3.95 (d, J = 13.1 Hz, 1H), 3.86 (d, J = 13.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.9, 142.1, 139.5, 133.3 ($\times 2$), 130.9, 130.4, 130.2, 129.3, 129.0 ($\times 2$), 128.4 ($\times 3$), 128.3 ($\times 2$), 127.7, 127.3, 127.1, 126.2, 126.0, 125.3, 124.7, 83.9, 39.1; IR (KBr): ν_{max} 3401, 2963, 1628, 1521, 1465, 1400, 1261, 1088, 1025, 802, 755 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{25}\text{H}_{20}\text{NOSe}$ [$\text{M} + \text{H}$] $^+$ 462.0425; found 462.0415.

6-Bromo-2,4-diphenyl-4-((phenylselanyl)methyl)-4*H*-benzo[*d*][1,3]oxazine (**3n**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, J = 6.2 Hz, 2H), 7.43 (t, J = 6.0 Hz, 1H), 7.38–7.32 (m, 5H), 7.29 (d, J = 5.8 Hz, 2H), 7.25–7.20 (m, 3H), 7.15–7.07 (m, 5H), 3.81 (d, J = 10.6 Hz, 1H), 3.77 (d, J = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 140.5, 137.5, 132.6 ($\times 2$), 131.2, 130.8, 130.6 ($\times 2$), 129.4, 128.2, 128.0 ($\times 3$), 127.5 ($\times 2$), 127.4 ($\times 2$), 127.2 ($\times 2$), 127.0, 126.6, 126.3, 126.1, 124.9, 118.2, 82.3, 38.1; IR (KBr): ν_{max} 3758, 2921, 1617, 1573, 1471, 1385, 1315, 1257, 1176, 1156, 1079, 1024, 966, 827, 735 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{27}\text{H}_{21}\text{BrNOSe}$ [$\text{M} + \text{H}$] $^+$ 533.9966; found 533.9949.

6-Bromo-2-methyl-4-phenyl-4-((phenylselanyl)methyl)-4*H*-benzo[*d*][1,3]oxazine (**3o**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.36–7.35 (m, 2H), 7.30–7.23 (m, 6H), 7.15–7.14 (m, 3H), 6.94 (d, J = 6.2 Hz, 2H), 3.68 (d, J = 10.6 Hz, 1H), 3.63 (d, J = 10.6 Hz, 1H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.0, 141.0, 136.8, 132.4 ($\times 2$), 131.2, 129.4 ($\times 2$), 128.0 ($\times 2$), 127.6, 127.5 ($\times 2$), 127.3, 126.8, 126.4, 125.2, 124.9, 117.9, 82.0, 38.0, 20.6; IR (KBr): ν_{max} 3722, 2890, 1598, 1574, 1478, 1411, 1368, 1312, 1263, 1193, 1036, 936, 863, 831, 783 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{22}\text{H}_{19}\text{BrNOSe}$ [$\text{M} + \text{H}$] $^+$ 471.9810; found 471.9803.

4-(((2-Chlorophenyl)selanyl)methyl)-4-methyl-2-phenyl-4*H*-benzo[*d*][1,3]oxazine (**3p**): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, J = 7.7 Hz, 3H), 7.50–7.42 (m, 3H), 7.34–7.27 (m, 4H), 7.19 (s, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 3.60 (d, J = 12.6 Hz, 1H), 3.42 (d, J = 12.6 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.1, 147.0, 138.8, 132.4, 131.2, 129.4, 128.1 ($\times 2$), 128.0 ($\times 2$), 127.7, 126.6, 125.3, 124.4, 123.9, 123.0, 119.1, 79.8, 38.2, 26.6; IR (KBr): ν_{max} 3742, 2942, 2883, 1624, 1593, 1572, 1487, 1451, 1319, 1284, 1245, 1173, 1092, 1067, 1029, 935, 819, 760 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{22}\text{H}_{19}\text{ClNOSe}$ [$\text{M} + \text{H}$] $^+$ 428.0315; found 428.0307.

6-(4-Methoxyphenyl)-8-methyl-8-((methylselanyl)methyl)-8*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*][1,3]oxazine (**3s**): a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.82 (s, 1H), 6.69 (s, 1H), 5.98 (s, 2H), 3.97 (s, 3H), 3.05 (d, J = 13.0 Hz, 1H), 2.95 (d, J = 13.0 Hz, 1H), 1.84 (d, J = 8.7 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.2, 155.1, 147.6, 145.8, 134.4, 129.6 ($\times 2$), 121.9, 113.6 ($\times 2$), 105.9, 103.4, 101.2, 80.0, 55.3, 36.9, 31.4, 30.2, 26.0, 6.4; IR (KBr): ν_{max} 3741, 3410, 2960, 2899, 2836, 1614, 1505, 1479, 1311, 1256, 1172, 1086, 1034, 941, 838, 806 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_4\text{Se}$ [$\text{M} + \text{H}$] $^+$ 406.0552; found 406.0550.

4-(((4-Methoxyphenyl)selanyl)methyl)-4-methyl-2-phenyl-4*H*-benzo[*d*][1,3]oxazine (**3t**): a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, J = 7.2 Hz, 2H), 7.55–7.48 (m, 3H), 7.44 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 4.1 Hz, 2H), 7.28–7.23 (m, 1H), 7.19 (d, J = 7.4 Hz, 1H), 6.84 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.69 (d, J = 11.0 Hz, 1H), 3.50 (d, J = 11.0 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.2, 156.0, 138.8, 134.6, 132.3 ($\times 2$), 131.6, 129.5, 128.4 ($\times 2$), 128.2 ($\times 2$), 127.0, 126.8, 125.6, 123.0, 122.1, 115.0 ($\times 2$), 55.3, 26.6, 15.7; IR (KBr): ν_{max} 3727, 3046, 2996, 2941, 2907, 2837, 1932, 1849, 1794, 1618, 1592, 1272, 1489, 1448, 1369, 1318, 1029, 967, 838, 890, 835, 814, 751 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2\text{Se}$ [$\text{M} + \text{H}$] $^+$ 424.0810; found 424.0805.

4. Conclusions

In summary, a novel double-redox catalytic system was rationally constructed to provide efficient access to a variety of selenylated benzoxazines. The combination of only catalytic amounts of FeCl_3 and I_2 and the use of aerial oxygen as the end oxidant make this approach greener and more atomically efficient than conventional methods based on selenium electrophiles and FeCl_3 . This new method is widely applicable to a great diversity of *o*-vinylanilide and diorganyl diselenide substrates. Mechanistic investigation confirmed that the coupling of I_2/I^- and $\text{Fe}^{3+}/\text{Fe}^{2+}$ catalytic redox cycles enabled aerial O_2 to act as the driving force to promote the selenocyclization reaction, which proceeds via a PhSeI -based pathway.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/molecules27217386/s1>: characterization data of new *o*-vinylanilides and known selenylated benzoxazines, Figures S1–S3: The chromogenic assays of the control redox reactions without *o*-vinylanilide and Figures S4–S51: The NMR spectra of new *o*-vinylanilides and all products.

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