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Diorganyl Diselenides and Iron(III) Chloride Drive the Regio- and Stereoselectivity in the Selenation of Ynamides

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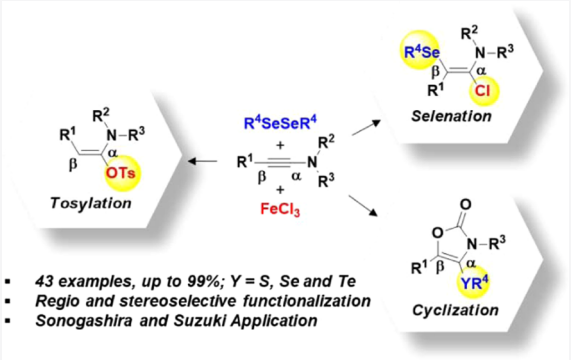
ABSTRACT: We report here our results on the application of ynamides as substrates in the reactions with diorganyl dichalcogenides and iron(III) chloride to give selectively three different types of compounds: *E*-α-chloro-β-(organoselenyl)enamides, 4-(organochalcogenyl)oxazolones, and vinyl tosylates. The results reveal that the selectivity in the formation of products was obtained by controlling the functional groups directly bonded to the nitrogen atom of the ynamides. Thus, α-chloro-β-(organoselenyl) enamide derivatives were exclusively obtained when the Ts*N*- and Ms*N*-ynamides were treated with a mixture of diorganyl diselenides (1.0 equiv) and $FeCl_3$ (3.0 equiv) in dichloroethane (DCE, 3 mL), at room temperature. The 4-(organochalcogenyl)oxazolones were selectively obtained with ynamides having an ester group, directly bonded to the nitrogen atom, upon treatment with a solution of $FeCl_3$ (1.5 equiv) and diorganyl dichalcogenides (1.0 equiv) in dichloromethane (3 mL) at room temperature. Finally, vinyl tosylates were obtained from ynamides having an ester group, directly bonded to the nitrogen atom, by reaction with *p*-toluenesulfonic acid. We also studied the application of the prepared compounds as substrates for Suzuki and Sonogashira cross-coupling reactions.



INTRODUCTION

Since 1958, when first identified,[1] the interest in ynamide chemistry has increased constantly.[2] However, in the last 20 years, works covering this class of compounds have intensified.[3] This is because of their special chemical behavior, which is influenced by the presence of the nitrogen atom directly bonded to the alkyne, conferring high regioselectivity in the reactions and making them extremely versatile substrates.[4] Although many different synthetic approaches have been developed regarding the synthesis of ynamides,[5] most of the practical syntheses reported to date involve the copper-catalyzed amidative cross-coupling of terminal or functionalized alkynes,[6] amidation of alkynyl iodonium salts,[7] and elimination reactions of dihalo or trihalo enamides.[8] Despite the extensive use of ynamides as a substrate in many different reactions, addition and cycloaddition reactions into the carbon−carbon triple bond are the most prominent.[9] The ynamides have a polarization of the lone-pair electron of nitrogen, making the α- and β-carbons of the triple bond electrophilic and nucleophilic, respectively. As a result, several options are available in the literature describing the regioselective addition of the electrophiles and nucleophiles onto the carbon−carbon triple bond of the ynamides, leading to functionalized enamides.[10] Most of these reduction reactions lead to the functionalization of α-[11] or β-carbons[12] (Scheme 1, paths a and b), whereas the reductions that lead to the functionalization of both α- and β-carbons are less explored[13] (Scheme 1, path b). Here, we report a selective approach to *E*-α-chloro-β-(organoselenyl)enamides, 4-(organochalcogenyl)oxazolones, and vinyl tosylates using ynamides as substrates in the reactions with diorganyl dichalcogenides and iron(III) chloride (Scheme 1). The improvement of our methodology, besides the selectivity, is the use of an organoselenium species to promote the activation of alkyne and to introduce the functionalities in both α- and β-carbons of the enamides. The enamide skeleton is frequently found in numerous natural products, especially in peptides.[14] Many enamide derivatives show a wide range of biological activities, such as sedative,[15] antiplasmodial,[16] antibacterial,[17] and anticancer,[18] among others.[19] Consequently, the development of useful and efficient methods for their preparation has attracted much attention. In addition, the incorporation of an organoselenium group in the structure of molecules has been receiving widespread interest because of its ability to construct new chemical bonds in a highly selective way,[20] as well as its wide range of biological properties.[21]

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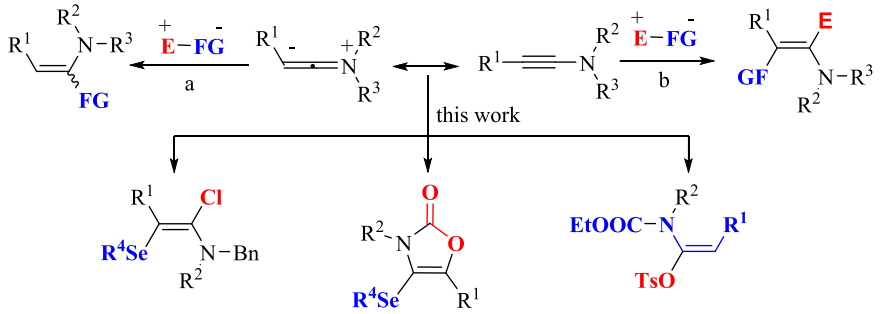
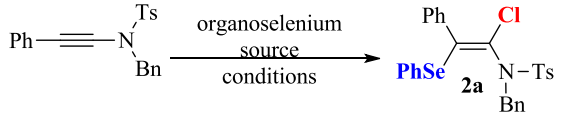
Scheme 1. General Scheme



RESULTS AND DISCUSSION

We started this work keeping in mind that an electrophilic selenium reagent would be able to activate the carbon−carbon triple bond of the ynamide for a further attack of the nucleophile. For this reason, we selected the ynamide **1a** and benzeneselenenyl bromide to optimize the general conditions. To this end, we added benzeneselenenyl bromide (1.0 equiv) to a solution of ynamide **1a** (0.25 mmol) in dichloroethane (3 mL), at room temperature, under a nitrogen atmosphere. Table 1 shows that after 15 min *α*-chloro-*β*-(phenylselenyl) enamide **2a** was obtained in 87% yield; however, the double-bond selectivity was lost, resulting in a 1:1 mixture of *E*/*Z* isomers (Table 1, entry 1). The use of benzeneselenenyl chloride instead of benzeneselenenyl bromide led to an increase in the yield of **2a**, but with no selectivity (Table 1, entry 2). The ability of iron salts to coordinate with the carbon−carbon bond and the nitrogen atom could activate the alkyne bonds and direct the nucleophile attack, influencing the selectivity of the reaction.[22] In addition, the combined use of iron salts with diorganyl diselenides has been used efficiently for the incorporation of an organoselenium moiety in different substrates.[23] Thus, we envisioned that the use of iron salts and diorganyl diselenide could positively influence the selectivity of the reduction of ynamide **1a**, leading to the formation of a single isomer. When ynamide **1a** was added to a solution of iron(III) chloride (1 equiv) and diphenyl diselenide (1 equiv) at room temperature, we found a small increase in the selectivity in favor of the *E*-isomer (2:1, *E*/*Z*) (Table 1, entry 3). The effects of increasing the reaction time and the loading of diphenyl diselenide were also investigated; with 2 h and 1.5 equiv of diphenyl diselenide, the product **2a** was obtained in high yields but still as an isomeric mixture (Table 1, entries 4 and 5). A significant improvement in selectivity was observed by increasing the loading of iron(III) chloride to 2.0 equiv. Under these conditions, although the product **2a** was formed in low yield, only the isomer *E* was obtained (Table 1, entry 6). In this reaction, we observed, by gas chromatography-mass spectrometry (GC-MS) analyses, the formation of enamide without the protecting group (Ts) as well as the terminal acetylene, formed from the cleavage of the Csp−N(Ts)Bn bond. Further increasing the amount of iron(III) chloride to 2.5 and 3.0 equiv led to a significant increase in the yield of product **2a** as the sole *E*-isomer (Table 1, entries 7 and 8). These results suggest that iron(III) chloride is competing for the formation of the selenium electrophilic species (PhSeCl) and for coordinating with the carbon−carbon triple bond and the nitrogen atom (see Scheme 3 for the mechanism discussion). To confirm that the reaction temperature did not influence a possible *E*/*Z* isomerization, we conducted the reaction at 0 °C; however, no effect was observed (Table 1, entry 9). To make the reaction more efficient, we also studied the effects of different solvents. In general, none of the solvents tested showed superior results obtained with dichloroethane, although dichloromethane gave **2a** in a similar yield (Table 1,

Table 1. Effects of Different Reaction Parameters for the Preparation of *E*-*α*-Chloro-*β*-(phenylselenyl) Enamide 2a[a]



entry	$FeCl_3$ (equiv)	organoselenium source (equiv)	solvent	yield
1		PhSeBr (1)	DCE	87% (E + Z)[b]
2		PhSeCl (1)	DCE	96% (E + Z)[b]
3	1	$(PhSe)_2$ (1)	DCE	81% (E + Z)[c]
4	1	$(PhSe)_2$ (1)	DCE	70% (E + Z)[d]
5	1	$(PhSe)_2$ (1.5)	DCE	78% (E + Z)
6	2	$(PhSe)_2$ (1)	DCE	34%[e]
7	2.5	$(PhSe)_2$ (1)	DCE	49%[e]
8	3	$(PhSe)_2$ (1)	DCE	57%[e]
9	3	$(PhSe)_2$ (1)	DCE	40%[e,f]
10	3	$(PhSe)_2$ (1)	CH_2Cl_2	51%[e]
11	3	$(PhSe)_2$ (1)	CH_3NO_2	
12	3	$(PhSe)_2$ (1)	dioxane	40%[e]
13	3	$(PhSe)_2$ (1)	toluene	
14	3	$(PhSe)_2$ (1)	CH_3CN	18%[e]
15	3	$(PhSe)_2$ (1)	CH_3OH	27%[e]
16	3	$(PhSe)_2$ (1)	DMF	40%[e]
17	3	$(PhSe)_2$ (1.5)	DCE	60%[e]
18	3	$(PhSe)_2$ (1)	DCE	47%[e,g]
19	[h]	$(PhSe)_2$ (1)	DCE	[i]

[a]The reaction was performed by the addition of the electrophilic organoselenium species (1.0 equiv), at room temperature, to a solution of ynamide **1a** in dichloroethane (3 mL). The reaction was stirred for 15 min at room temperature. [b]The mixture of 1:1 (*E*/*Z*) was obtained. [c]The reaction was performed by the addition of ynamide **1a** (0.25 mmol), at room temperature, under a nitrogen atmosphere, to a solution of $FeCl_3$ and diphenyl diselenide in dichloroethane (3 mL), which was prepared 10 min before. The reaction was stirred for 0.5 h at room temperature. Under these conditions, a mixture of 2:1 (*E*/*Z*) was obtained. [d]The reaction was stirred at room temperature for 2 h. [e]Only the *E*-isomer was obtained. [f]The reaction was carried out at 0 °C. [g]The reaction was carried out under an air atmosphere in an open tube. [h]$Fe(ClO_4)_3 \cdot xH_2O$ (1 equiv) and Et_4NCl (3 equiv) were used. [i]The ynamide **1a** was consumed, leading to the formation of a complex mixture of products.

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Scheme 2. Reactivity of Different *N*-Protecting Groups on Ynamides

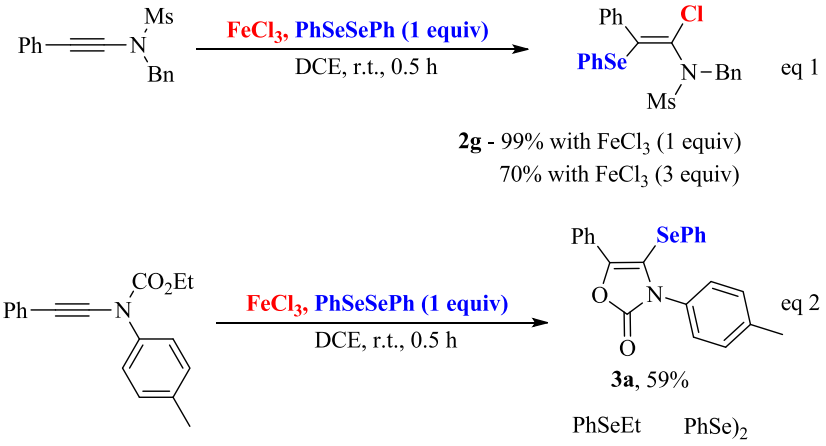
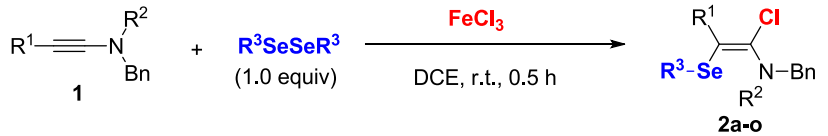
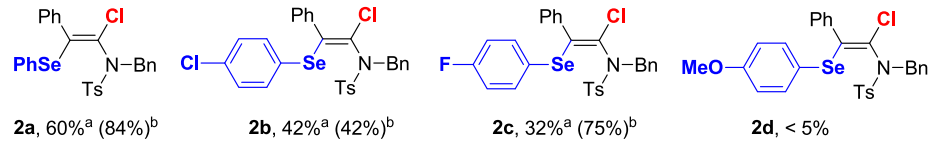
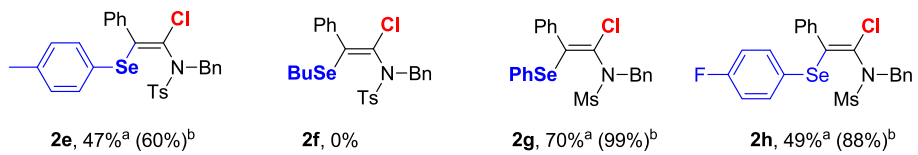
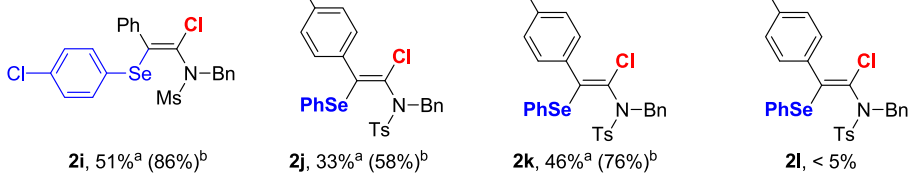


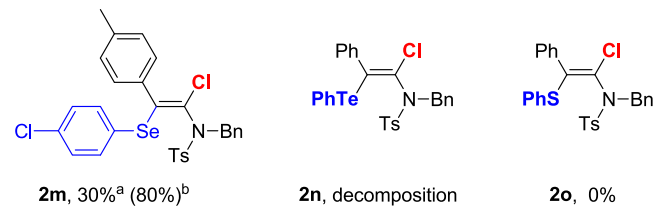
Table 2. Synthesis of α-Chloro-β-(organoselenyl) Enamides 2[a]











[a]The ynamides **1** (0.25 mmol) were added to a mixture of diorganyl diselenides (1.0 equiv) and $FeCl_3$ (3.0 equiv) in dichloroethane (3 mL), at room temperature, under a nitrogen atmosphere for 0.5 h. [b]The reaction was carried out using $FeCl_3$ (1 equiv).

entries 10−16). We also observed that increasing the quantity of diphenyl diselenide to 1.5 equiv did not improve the yield of the product **2a** (Table 1, entry 17). The use of an open tube instead of an inert nitrogen atmosphere also did not influence the reaction, affording *E*-α-chloro-β-(phenylselenyl) enamide **2a** in 47% yield (Table 1, entry 18). To prove the crucial role of iron(III) chloride, we conducted this reaction with iron(III) perchlorate in the presence of tetraethylammonium chloride as the source of chloride ions. In this experiment, the ynamide **1a** was consumed; however, a complex mixture of unidentified products was obtained (Table 1, entry 19). To determine the influence of *N*-substitution in the selenium electrophilic reduction reaction of the ynamide **1**, we tested the mesyl and ethyl ester groups directly bonded to the nitrogen atom in

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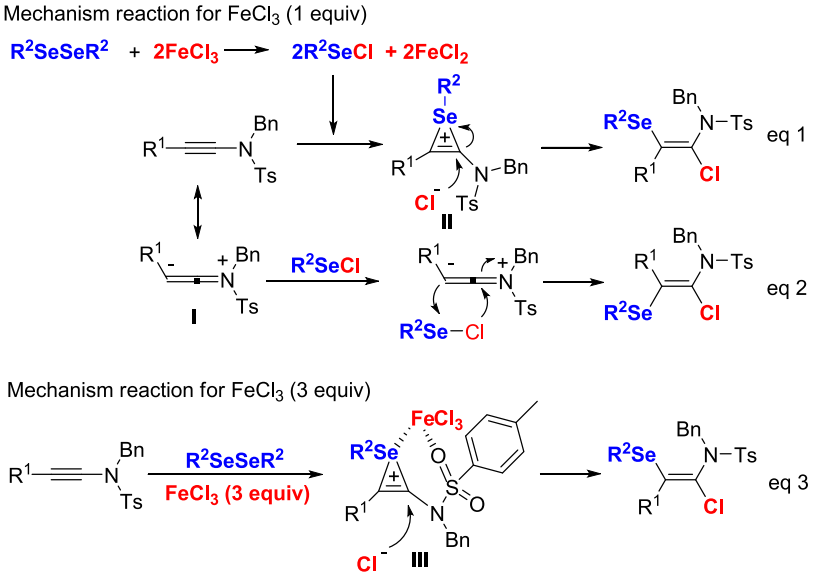
Scheme 3. Proposed Reaction Mechanism



addition to the tosyl group. Ynamide protected with the mesyl group was found to be very efficient, giving the enamide **2g** in high yield (Scheme 2, eq 1). In contrast, the alkynyl carbamate derivative did not afford the corresponding enamide (Scheme 2, eq 2). These reactions were monitored by GC-MS, which indicated that a mixture of products composed of 4-(phenylselanyl)oxazolone **3a** in 59% yield was obtained, together with diphenyl diselenide and ethyl(phenyl)selenide. After these studies, we concluded that *N*-tosyl and *N*-mesyl-ynamides could be used efficiently as substrates in the reduction reactions promoted by the electrophilic selenium species. In addition, our results also indicate that the addition of ynamides **1a** (0.25 mmol) to a mixture of diphenyl diselenide (1.0 equiv) and $FeCl_3$ (3.0 equiv) in dichloroethane (3 mL), at room temperature, under a nitrogen atmosphere, is the best condition to obtain the *E*-*α*-chloro-*β*-(phenylselenyl) enamide **2a** in higher yield (Table 1, entry 8). With this condition, although it provided the product in lower yield than with the authentic PhSeBr and PhSeCl (Table 1, entries 1 and 2), only the *E*-isomer was obtained as the product. This result evidences the crucial role of iron(III) chloride in the selectivity of this process. Because these structures presented tetrasubstituted carbon−carbon double bonds, assigning the region and stereochemistry using NMR experiments is not a simple task. Therefore, the compounds were identified using NMR and GC-MS experiments, while the structural confirmation was made using X-ray diffraction for compounds (*E*)-*N*-benzyl-*N*-(1-chloro-2-phenyl-2-(phenylselanyl)vinyl)-4-methylbenzenesulfonamide **2a** (CCDC 2034677), (*E*)-*N*-benzyl-*N*-(1-chloro-2-((4-chlorophenyl)selanyl)-2-(*p*-tolyl)vinyl)-4-methylbenzenesulfonamide **2m** (CCDC 2034678), phenyl-4-(phenylselanyl)-3-(*p*-tolyl)oxazol-2(3H)-one **3a** (CCDC 2034679), (*E*)-1-((ethoxycarbonyl)(*p*-tolyl)amino)-2-phenylvinyl 4-methylbenzenesulfonate **4a** (CCDC 2034680), and *N*-benzyl-2-phenyl-*N*-tosylacetamide **5a** (CCDC 2034682). See the complete information in the Supporting Information.

To investigate the generality of this methodology, we next studied the reactions using ynamides **1** with different substituents and a variety of diorganyl diselenides under optimized reaction conditions. The results are summarized in Table 2. These conditions were efficient for *N*-tosyl-ynamides with diaryl diselenides having electron-withdrawing and electron-donating substituents. Because this reaction involves cleavage of the selenium−selenium bond, we expected that electron-withdrawing groups in the aromatic ring of the diaryl diselenide would present a superior result than the electron-donor groups. This expectation is justified because electron-withdrawing groups should weaken the selenium−selenium bond, facilitating its cleavage. The results obtained did not follow this rule. The results show that there is no relationship between the yields and the electronic effects of substituents on the aromatic ring. For example, when the F atom, an electron-withdrawing group, is present in the aromatic ring, the reaction led to enamide **2c** in 32% yield. On the other hand, the presence of a strong electron-donating group in the aromatic ring, such as MeO, led to a trace amount of enamide **2d** (Table 2, compare **2c** and **2d**). Thus, an extensive discussion on the yields obtained related to the electronic or steric effects of substrates would make it speculative. However, a result that needs to be highlighted is the difference in the yields obtained for 1 equiv (yields in parentheses) and 3 equiv of iron(III) chloride. All reactions with 3.0 equiv of iron(III) chloride showed decomposition fragments of the starting material in the GC-MS analysis. Thus, we believe that, on the one hand, iron salt plays an important role in selectivity, but on the other hand, it causes the decomposition of the starting material. Finally, we also tested the reactions using dialkyl diselenide, such as dibutyl diselenide, and with other dichalcogenides, such as ditellurides and disulfides; however, in none of these cases we get the expected products. With dibutyl diselenide and diphenyl disulfide, there was no product formation. Probably, because the sulfur−sulfur bond of disulfides is stronger than the selenium−selenium bond of diselenides, the iron incorporation into disulfides should be hampered, influencing the reaction performance. With diphenyl ditelluride, the product **2n** was obtained; however, it decomposed during the purification process.

Based on the above experimental results and the knowledge that iron salts react with diorganyl diselenides promoting the selenium−selenium bond heterolytic cleavage,[23c,24] we propose that the formation of *E* and *Z*-*α*-chloro-*β*-(phenylselenyl) enamides **2** most likely proceeds via a selenium electrophilic

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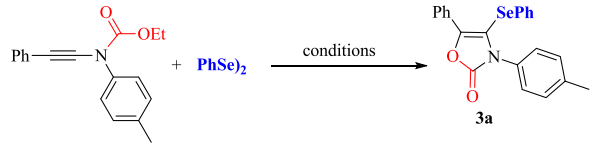
addition on the carbon−carbon triple bond, as outlined in Scheme 3. We believe that the key to the formation of the *E* and *Z* isomer mixture is the ability that ynamide has in the formation of the transient keteniminium ion **I**[25] (Scheme 3). The reaction of the electrophilic selenium species with the ynamide follows the well-known formation of the seleniranium ion **II**[26] with a subsequent antiattack of the nucleophilic portion, leading to the *E*-*α*-chloro-*β*-(phenylselenyl) enamides (Scheme 3, eq 1). However, the formation of *Z*-*α*-chloro-*β*-(phenylselenyl) enamides follows a syn addition of the electrophilic selenium species to the keteniminium ion **I** (Scheme 3, eq 2). The high selectivity obtained with iron(III) chloride (3 equiv) is the result of the contribution of the iron salt in the formation of the electrophilic species of selenium (R_2SeCl) and its complexation with selenium and oxygen atoms in intermediate **III**, blocking the nucleophile (Cl^-) approach from this side (Scheme 3, eq 3).

At this point in our studies, even knowing that alkynyl carbamates were cyclized to oxazolones using transition-metal catalysts,[27] we are pleased with the result obtained in Scheme 2, eq 2, because the synthesis of oxazolones with concomitant functionalization of the 4-position is rare.[28] Oxazolones are structural subunits found in several numbers of synthetic structures with various biological activities.[29] They are also valuable structures in organic synthesis due to the diversity of reactions that can participate. For this reason, we decided to study and expand the cyclization of alkynyl carbamate using iron(III) chloride and diorganyl diselenides to improve the yield of 4-(phenylselanyl)oxazolone **3a**. The results are shown in Table 3. When the reaction conditions described in Scheme 2, eq 2, were repeated using iron(III) chloride (1.5 equiv), the yield of **3a** increased to 68%; however, other changes in the amounts of iron salt were not satisfactory (Table 3, entries 1−7). A comparison with the efficiency of other solvents in promoting the cyclization showed that dichloromethane was more efficient, whereas nitromethane, acetonitrile, ethanol, and toluene did not improve the yields (Table 3, entries 8−11). When the amount of diphenyl diselenide was increased to 1.3 equiv, a 58% yield of **3a** was obtained, while reducing the amount to 0.75 equiv dropped the yield to 47%, even carrying out the reaction in an open atmosphere, which provides the oxidation of selenol to diselenide (Table 3, entries 12−14). We also found that the reaction at room temperature was more efficient than that of refluxing dichloromethane (Table 3, entry 15). The influence of other transition-metal salts was also investigated. No products were observed with iron(III) chloride hexahydrate and iron(II) chloride tetrahydrate, whereas cupric chloride gave a trace amount of product (Table 3, entries 16−18). We also examined the reaction using Lewis and Brønsted acids under the above conditions. However, both boron trifluoride diethyl etherate and *p*-toluenesulfonic acid failed to give the products (Table 3, entries 19−20). However, when we conducted the reaction with *p*-toluenesulfonic acid, vinyl tosylate **4a** was obtained in 82% yield.

Based on the high yield obtained in the experiment shown in Table 3, entry 5, these reaction conditions were applied to the cyclization to a variety of alkynyl carbamates, with different diorganyl diselenides, to explore the versatility of the method. The results are summarized in Table 4. First, we studied the influence of diorganyl dichalcogenides; for that, we kept the structure of alkynyl carbamate invariable. We observed that unsubstituted diphenyl diselenide and dibutyl diselenide

Table 3. Effects of Different Reaction Parameters for the Preparation of 4-(Phenylselanyl)oxazolone 3a[a]



entry	promoter (equiv)	solvent	reaction time (h)	yield (%)
1	$FeCl_3$ (1)	DCE	1	59
2	$FeCl_3$ (1.5)	DCE	0.5	68
3	$FeCl_3$ (1)	CH_2Cl_2	24	63
4	$FeCl_3$ (1.3)	CH_2Cl_2	16	66
5	$FeCl_3$ (1.5)	CH_2Cl_2	1	74
6	$FeCl_3$ (1.7)	CH_2Cl_2	1	34
7	$FeCl_3$ (0.3)	CH_2Cl_2	24	29
8	$FeCl_3$ (1.5)	CH_3NO_2	1	48
9	$FeCl_3$ (1.5)	CH_3CN	24	34
10	$FeCl_3$ (1.5)	EtOH	2	
11	$FeCl_3$ (1.5)	toluene	24	53
12	$FeCl_3$ (1.5)	CH_2Cl_2	2.5	58[b]
13	$FeCl_3$ (1.5)	CH_2Cl_2	2.5	47[c]
14	$FeCl_3$ (1.5)	CH_2Cl_2	1	18[d]
15	$FeCl_3$ (1.5)	CH_2Cl_2	1	64[e]
16	$FeCl_3{\cdot}6H_2O$ (1.5)	CH_2Cl_2	6	
17	$FeCl_2{\cdot}4H_2O$ (1.5)	CH_2Cl_2	24	
18	$CuCl_2$ (1.5)	CH_2Cl_2	6	<5
19	$BF_3{\cdot}OEt_2$ (1.5)	CH_2Cl_2	16	<5
20	$TsOH{\cdot}H_2O$ (1.5)	CH_2Cl_2	1	[f]

[a]The reaction was performed by the addition of ynamide (0.25 mmol), at room temperature, under a nitrogen atmosphere, to a solution of $FeCl_3$ and diphenyl diselenide in the solvent (3 mL), which was prepared 10 min before. The reaction was stirred at room temperature for the time indicated in Table 3. [b]Reaction was carried out with PhSeSePh (1.3 equiv). [c]Reaction was carried out with PhSeSePh (0.75 equiv). [d]The reaction was carried out under an air atmosphere in an open flask. [e]The reaction was carried out at 40 °C. [f]The product **4a** was obtained in 82% yield.

showed better results than diaryl diselenides with electron-donating and electron-withdrawing groups (Tables 4, **3a−h**). To study the influence of different aromatic systems directly bonded to the nitrogen atom, we selected diphenyl and dibutyl diselenides. The results showed that regardless of the aromatic system bonded to the nitrogen atom, the yields were similar, indicating that the electronic effects of these groups did not influence the yield of the products (Table 4, **3i−n**). For the substitutes directly bonded to the alkyne, we observed that aromatic groups provided the products in moderate yields, whereas alkyl groups led to the products in low yields (Table 4, **3o−t**). In these cases, it seems that the presence of the *π* bonds from the aromatic ring, increasing the electron density in the carbon−carbon triple bond, favored the seleniranium ion formation and, consequently, the yields (see the mechanism discussion, Scheme 4). We completed the alkynyl carbamate cyclization studies by applying the optimized reaction to other diorganyl dichalcogenides. Under these conditions, both diorganyl ditellurides and diorganyl disulfides with iron(III) chloride led to the formation of 4-(organochalcogenyl) oxazolone, in yields ranging from 20 to 77% (Table 4, **3u−x**).

To achieve more understanding of the reaction mechanism in the formation of oxazole derivatives **3**, we carried out a reaction under the condition described in entry 5, Table 3, and

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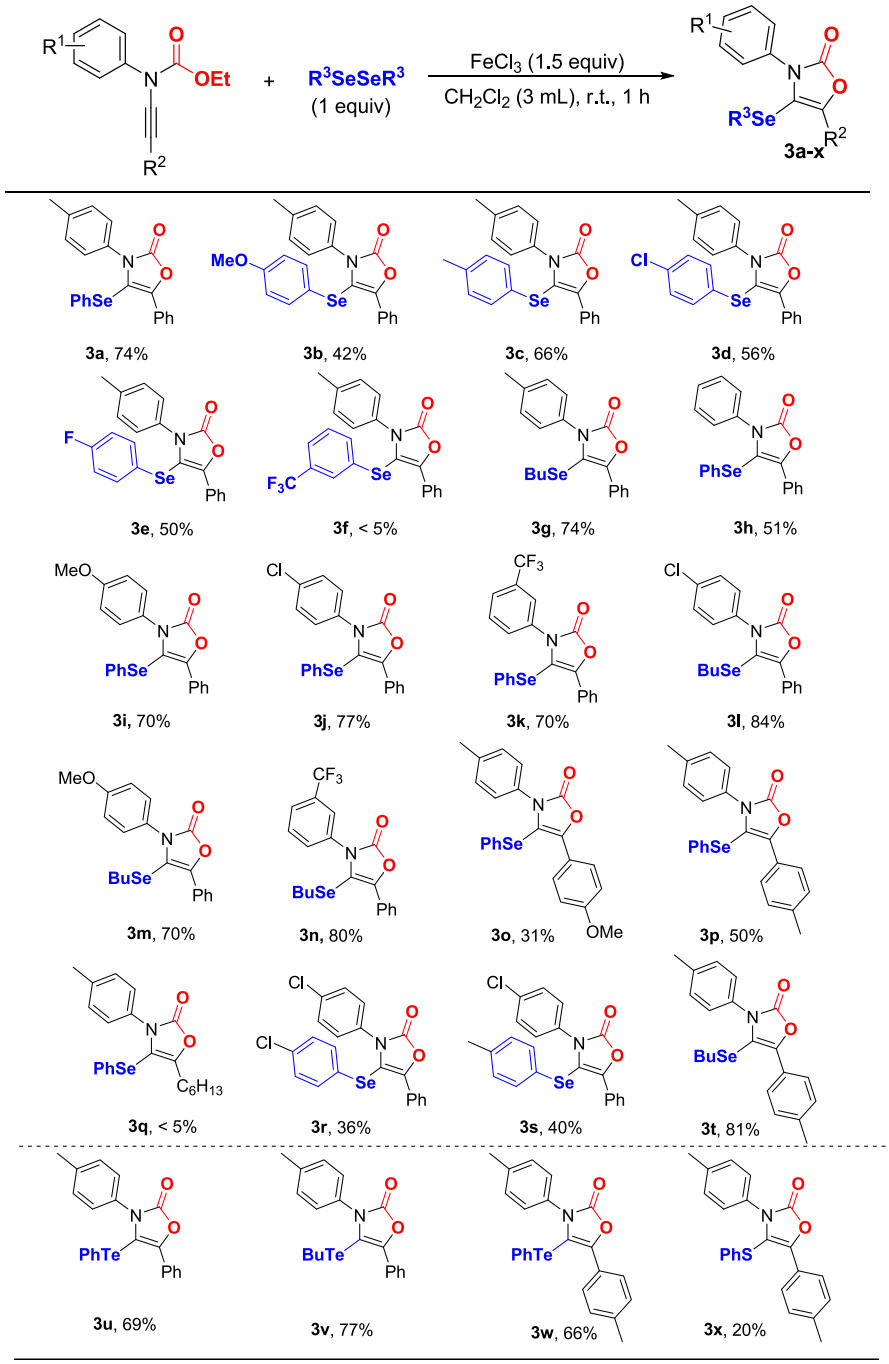
Table 4. Synthesis of 4-(Organoselenyl)oxazolone 3[a]



[a]The reaction was performed by the addition of alkynyl carbamates (0.25 mmol), at room temperature, under a nitrogen atmosphere, to a solution of $FeCl_3$ (1.5 equiv) and diorganyl diselenide (1 equiv) in dichloromethane (3 mL), which was prepared 10 min before. The reaction was stirred at room temperature for 1 h.

it was analyzed without purification via GC-MS. In this analysis, in addition to product **3a**, we found a significant sign showing the presence of PhSeEt. This result is very important because it indicates that a nucleophilic species of selenium removed the ethyl group from the ester. Thus, with this finding and the understanding that iron(III) chloride and diorganyl dichalcogenides can form a complex, which is polarized in a negative and a positive portion, becoming able to activate triple bonds for a nucleophilic attack,[24a] we proposed a plausible mechanism to support the formation of 4-(organoselenyl)-oxazolones **3**, as illustrated in Scheme 4. The iron-selenolate species coordinates to alkynes to generate the intermediate **I**, the antinucleophilic attack of the oxygen atom on the activated carbon−carbon triple bond produces the oxazolone **II**, and the removal of the ethyl group bonded to the oxygen atom via S_N2 displacement by the selenolate ion present in the reaction mixture affords the 4-(organoselenyl)oxazolones **3** (Scheme 4, path a). Although we have no evidence, considering that under some conditions the mixture of iron(III) chloride and diorganyl diselenides can also form an electrophilic species of

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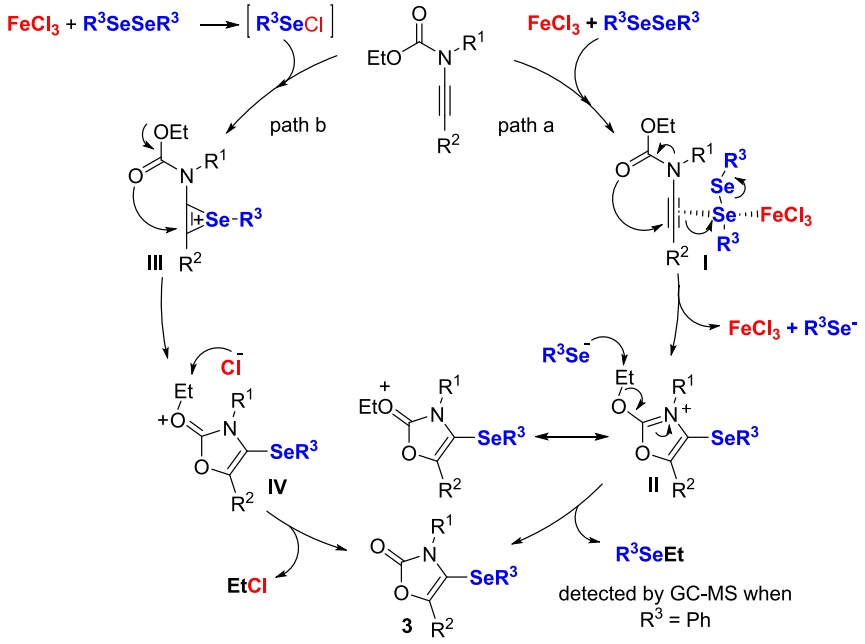
Scheme 4. Proposed Reaction Mechanism for the Formation of 4-(Organoselenyl)oxazolones 3

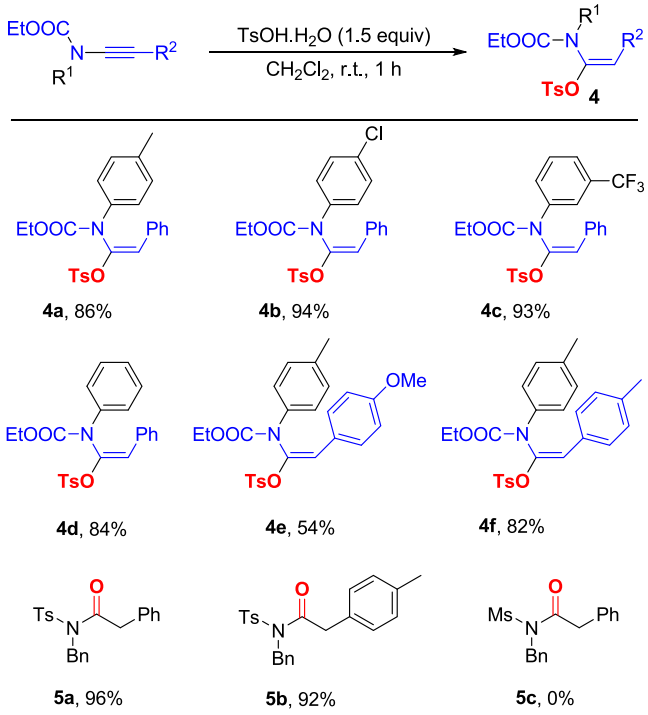


selenium, the hypothesis of this reaction, following a classical electrophilic cyclization of alkynes, cannot be ruled out. This proposal is represented in Scheme 4, path b. We also do not discard the mechanism involving the transfer of the seleneranium cationic intermediate from one alkene to another;[30] however, it is unlikely because of the coordination of alkyne with iron.

As shown in Table 3 (entry 20), when we reacted the alkynyl carbamate with *p*-toluenesulfonic acid, the vinyl tosylate **4a** was obtained in 82% yield. Vinyl tosylates are widely used in organic synthesis, especially as substrates for transition-metal-catalyzed cross-coupling reactions. However, there are few reports in the literature describing the direct sulfonylation of ynamides using only *p*-toluenesulfonic acid in the complete absence of other additives.[31] To explore the general effectiveness of these reaction conditions, several ynamides were subjected to react with *p*-toluenesulfonic acid, and the results are summarized in Table 5. The yields obtained were considered satisfactory with alkynyl carbamates with different substituents directly bonded to the alkynes and nitrogen atoms (Table 5, **4a**–**f**); however, when we used Ts*N*- and Ms*N*-protected ynamides as substrates, the expected products were not obtained. In these cases, the Ts*N*-protected ynamides gave the corresponding *N*-tosylacetamide, while Ms*N*-protected ynamides did not react (Table 5, **5a**–**c**).

To finish this work, we studied the synthetic utility of the prepared compounds. These compounds presented a functionalized double bond having an organochalcogen or a tosyl group in the structures. These substituents make them potential substrates for transition-metal-catalyzed cross-coupling reactions. This led us to explore the possibility of using 4-(butyltelluro)oxazolone **3v** and vinyl tosylate **4c** as substrates in palladium cross-coupling reactions. Under Suzuki conditions,[32] **3v** and **4c** reacted with boronic acids, affording the corresponding cross-coupled products **6** and **7** in moderate to good yields (Scheme 5, eqs 1 and 2). We then examined the possibility of using vinyl tosylate **4d** as a substrate in the Sonogashira cross-coupling reaction.[33] Under these conditions,

Table 5. Synthesis of *E*-Vinyl Tosylate 4[a]



[a]The reaction was performed by the addition of *p*-TsOH (1.5 equiv), at room temperature, under a nitrogen atmosphere, to a solution of ynamides (0.25 mmol) in CH_2Cl_2 (3 mL). The reaction was stirred at room temperature for 1 h.

vinyl tosylate **4d** underwent cross-coupling upon exposure to phenylacetylene, affording enyne **8a** in 92% yields as a mixture of *E*/*Z* isomers (7:3) (Scheme 5, eq 3). Moreover, we studied the reactivity of the Csp2–Se bond of *α*-chloro-*β*-(phenylselenyl) enamide **2a** in a reaction with organocuprate[34] to promote the replacement of the organoselenium group;

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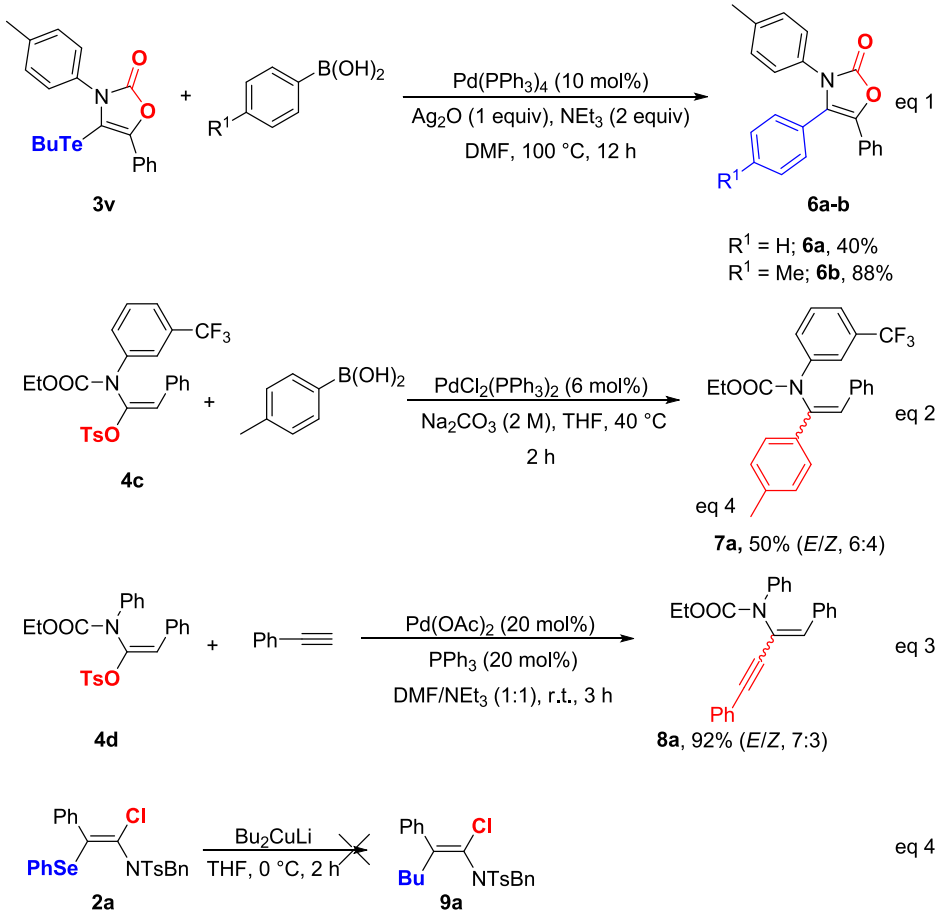
Scheme 5. Studies of the Synthetic Utility of 4-(Butyltelluro)oxazolone and Vinyl Tosylates



however, the vinyl chloride desired, **9a**, was not formed, and the starting material was recovered (Scheme 5, eq 4).

CONCLUSIONS

In summary, in this work, we expanded the application of ynamides as substrates in the reactions with diorganyl dichalcogenides and iron(III) chloride. The protocol provides facile access to three classes of different compounds, among them *E*-α-chloro-β-(organoselenyl)enamides, 4-(organochalcogenyl)oxazolones, and vinyl tosylates, which were selectively prepared in good yields from the same starting materials. A detailed study on the optimization of the reaction conditions in the product distribution indicated that the selectivity was governed by the functional group directly bonded to the nitrogen atom of the ynamide. Thus, α-chloro-β-(organoselenyl)enamide derivatives were obtained exclusively when the Ts*N*- and Ms*N*-ynamides were treated with a mixture of diorganyl diselenides (1.0 equiv) and $FeCl_3$ (3.0 equiv) in dichloroethane (3 mL), at room temperature. The 4-(organochalcogenyl)oxazolones were obtained selectively with ynamides having an ester group directly bonded to the nitrogen atom upon treatment with a solution of $FeCl_3$ (1.5 equiv) and diorganyl dichalcogenides (1.0 equiv) in dichloromethane (3 mL) at room temperature. Finally, vinyl tosylates were obtained from ynamides having an ester group directly bonded to the nitrogen atom by reaction with *p*-toluenesulfonic acid. We also demonstrated the potential application of the compounds prepared as substrates for transition-metal-catalyzed cross-coupling reactions. All compounds prepared were identified using NMR experiments; however, the absolute stereochemistry of the double bond of the α-chloro-β-(organoselenyl)enamides and the formation of 4-(organochalcogenyl) oxazolones via the 5-*endo*-dig-mode were confirmed via X-ray diffraction (see the Supporting Information).

EXPERIMENTAL SECTION

Materials and Methods. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on an NMR spectrometer at 400 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (*J*) in hertz, and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a 400 NMR spectrometer at 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), quart (quartet), quint (quintet), sex (sextet), dd (double doublet), and m (multiplet). The ^{77}Se NMR experiment was carried out using a capillary tube with diphenyl diselenide as the internal reference. High-resolution mass spectra were recorded on a mass spectrometer using electrospray ionization (ESI). Column chromatography was performed using silica gel (230−400 mesh). Thin-layer chromatography (TLC) was performed using Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light or stained with iodine vapor or acidic vanillin. Most reactions were monitored by TLC for disappearance of the starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from

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sodium with a benzophenone ketyl indicator. All other solvents were ACS or high performance liquid chromatography (HPLC) grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven-dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. The $FeCl_3$ was used in 99.99% purity purchased from commercial suppliers.

General Procedure for the Synthesis of α-Chloro-β-(organoselenyl) Enamides ***2a–o.*** In a Schlenk tube, under nitrogen, containing (3 mL) were added $FeCl_3$ (0.75 mmol; 3 equiv) and diorganyl dichalcogenides (0.25 mmol; 1 equiv). The resulting solution was stirred at room temperature for 15 min. After this time, appropriate substrate **1** (0.25 mmol) was added and the reaction was stirred at room temperature for 30 min. The mixture was concentrated in a vacuum, and the residue was purified by column chromatography over silica gel using a solution of hexane/ethyl acetate as the eluent to provide the products **2**.

*(E)-N-Benzyl-N-(1-chloro-2-phenyl-2-(phenylselanyl)vinyl)-4-methylbenzenesulfonamide (**2a**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.083 g (60%) and 0.621 g (56%) using ynamide (2 mmol); mp 110–112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.91 (d, *J* = 8.3 Hz, 2H), 7.61–7.55 (m, 2H), 7.41–7.39 (m, 3H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.02–6.98 (m, 4H), 6.90–6.74 (m, 6H), 4.96 (d, *J* = 12.7 Hz, 1H), 4.09 (d, *J* = 12.7 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (CDCl3, 100 MHz): δ (ppm) 144.4, 142.2, 137.1, 136.4, 135.5, 135.2, 133.7, 130.5, 129.7, 129.2, 128.7, 128.4, 128.3, 128.1, 127.7, 127.5, 127.3, 120.8, 52.2, 21.6. High-resolution mass spectrometry (HRMS) calcd. for $C_{28}H_{25}ClNO_2SSe$ (ESI-TOF, [M + H]$^+$): 554.0460. Found: 554.0463.

*(E)-N-Benzyl-N-(1-chloro-2-((4-chlorophenyl)selanyl)-2-phenylvinyl)-4-methylbenzenesulfonamide (**2b**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.061 g (42%); mp 96–98 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.89 (d, *J* = 8.4 Hz, 2H), 7.58–7.56 (m, 2H), 7.41–7.39 (m, 3H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.06–7.01 (m, 3H), 6.85–6.82 (m, 4H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.96 (d, *J* = 12.8 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.5, 141.6, 136.8, 136.5, 134.8, 134.0, 133.5, 130.4, 129.7, 129.1, 128.6, 128.4, 128.3, 128.2, 127.8, 127.5, 127.1, 121.4, 52.0, 21.6. HRMS calcd for $C_{28}H_{24}Cl_2NO_2SSe$ (ESI-TOF, [M + H]$^+$): 588.0070. Found: 588.0081.

*(E)-N-Benzyl-N-(1-chloro-2-((4-fluorophenyl)selanyl)-2-phenylvinyl)-4-methylbenzenesulfonamide (**2c**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow oil. Yield: 0.045 g (32%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90 (d, *J* = 8.4 Hz, 2H), 7.59–7.56 (m, 2H), 7.41–7.40 (m, 3H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.03–7.01 (m, 3H), 6.79–6.69 (m, 4H), 6.56 (t, *J* = 8.8 Hz, 2H), 4.95 (d, *J* = 12.9 Hz, 1H), 4.09 (d, *J* = 12.9 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.6 (d, CF, $^1J_{C-F}$ = 248.1 Hz), 144.5, 142.1, 137.7 (d, CF, $^3J_{C-F}$ = 8.1 Hz), 137.0, 135.1, 133.8, 130.5, 130.2, 129.7, 129.6, 129.5, 129.0, 128.7, 128.4, 128.3, 127.7, 127.5, 126.8, 123.6 (d, CF, $^4J_{C-F}$ = 3.6 Hz), 120.9, 115.3 (d, CF, $^2J_{C-F}$ = 21.4 Hz), 52.1, 21.6. HRMS calcd for $C_{28}H_{24}ClFNO_2SSe$ (ESI-TOF, [M + H]$^+$): 572.0366. Found: 572.0379.

*(E)-N-Benzyl-N-(1-chloro-2-phenyl-2-(p-tolylselanyl)vinyl)-4-methylbenzenesulfonamide (**2e**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.066 g (47%); mp 107–109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.91 (d, *J* = 8.3 Hz, 2H), 7.63–7.54 (m, 2H), 7.40–7.31 (m, 4H), 7.23–7.12 (m, 2H), 7.04–6.93 (m, 3H), 6.83–6.76 (m, 2H), 6.72–6.63 (m, 3H), 4.94 (d, *J* = 12.8 Hz, 1H), 4.10 (d, *J* = 12.8 Hz, 1H), 2.43 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.4, 142.4, 137.7, 137.2, 136.4, 135.5, 135.1, 133.7, 130.4, 129.6, 129.1, 128.9, 128.7, 128.3, 128.3, 127.4, 127.3, 125.1, 120.5, 52.1, 21.6, 21.0. HRMS calcd for $C_{29}H_{27}ClNO_2SSe$ (ESI-TOF, [M + H]$^+$): 568.0616. Found: 568.0596.

*(E)-N-Benzyl-N-(1-chloro-2-phenyl-2-(phenylselanyl)vinyl)-methanesulfonamide (**2g**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.083 g (70%); mp 74–76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.66–7.63 (m, 2H), 7.44–7.43 (m, 3H), 7.01–6.97 (m, 4H), 6.88–6.81 (m, 4H), 6.75–6.73 (m, 2H), 4.97 (d, *J* = 12.8 Hz, 1H), 4.41 (d, *J* = 12.8 Hz, 1H), 3.12 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 142.7, 136.6, 136.3, 135.4, 133.4, 130.5, 129.0, 128.6, 128.4, 128.1, 127.7, 127.6, 127.3, 119.7, 52.3, 39.1. HRMS calcd for $C_{22}H_{21}ClNO_2SSe$ (ESI-TOF, [M + H]$^+$): 478.0147. Found: 478.0132.

*(E)-N-Benzyl-N-(1-chloro-2-((4-fluorophenyl)selanyl)-2-phenylvinyl)methanesulfonamide (**2h**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.060 g (49%); mp 112–114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.66–7.63 (m, 2H), 7.46–7.44 (m, 3H), 7.09–7.03 (m, 3H), 6.80–6.77 (m, 2H), 6.68–6.65 (m, 2H), 6.60–6.53 (m, 2H), 4.98 (d, *J* = 12.8 Hz, 1H), 4.39 (d, *J* = 12.8 Hz, 1H), 3.13 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.6 (d, CF, $^1J_{C-F}$ = 248.2 Hz), 142.7, 137.7 (d, CF, $^3J_{C-F}$ = 8.1 Hz), 136.6, 133.5, 130.6, 128.9, 128.6, 128.4, 127.8, 127.5, 126.9, 123.2 (d, CF, $^4J_{C-F}$ = 3.5 Hz), 119.8, 115.3 (d, CF, $^2J_{C-F}$ = 21.3 Hz), 52.3, 39.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 528.8. HRMS calcd for $C_{22}H_{20}ClFNO_2SSe$ (ESI-TOF, [M + H]$^+$): 496.0053. Found: 496.0065.

*(E)-N-Benzyl-N-(1-chloro-2-((4-chlorophenyl)selanyl)-2-phenylvinyl)methanesulfonamide (**2i**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.065 g (51%); mp 89–91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.64–7.61 (m, 2H), 7.44–7.42 (m, 3H), 7.05–7.04 (m, 3H), 6.83 (d, *J* = 8.6 Hz, 4H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.97 (d, *J* = 12.8 Hz, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 3.12 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 142.2, 137.4, 136.6, 134.2, 133.4, 130.5, 130.0, 129.0, 128.6, 128.5, 128.3, 127.9, 127.5, 127.0, 126.8, 120.4, 52.3, 39.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 531.1. HRMS calcd for $C_{22}H_{20}Cl_2NO_2SSe$ (ESI-TOF, [M + H]$^+$): 511.9757. Found: 511.9766.

*(E)-N-Benzyl-N-(1-chloro-2-(phenylselanyl)-2-(p-tolyl)vinyl)-4-methylbenzenesulfonamide (**2j**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow oil. Yield: 0.048 g (33%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90 (d, *J* = 8.3 Hz, 2H), 7.59–7.54 (m, 2H), 7.41–7.31 (m, 5H), 7.03–6.97 (m, 1H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.84–6.71 (m, 6H), 4.94 (d, *J* = 12.8 Hz, 1H), 4.10 (d, *J* = 12.8 Hz, 1H), 2.44 (s, 3H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.4, 142.2, 137.4, 135.2, 135.1, 134.1, 133.7, 130.4, 129.6, 129.1, 128.7, 128.3, 128.1, 128.0, 127.5, 120.8, 52.1, 21.6, 21.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 530.9. HRMS calcd for $C_{29}H_{27}ClNO_2SSe$ (ESI-TOF, [M + H]$^+$): 568.0616. Found: 568.0625.

*(E)-N-Benzyl-N-(1-chloro-2-(4-chlorophenyl)-2-(phenylselanyl)-vinyl)-4-methylbenzenesulfonamide (**2k**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow oil. Yield: 0.067 g (46%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90 (d, *J* = 8.4 Hz, 2H), 7.56–7.54 (m, 2H), 7.40–7.33 (m, 5H), 7.05–6.89 (m, 5H), 6.77–6.74 (m, 4H), 4.94 (d, *J* = 12.8 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.5, 140.9, 135.7, 135.4, 135.0, 133.6, 133.4, 130.5, 130.4, 129.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.6, 121.6, 52.1, 21.6. HRMS calcd for $C_{28}H_{24}Cl_2NO_2SSe$ (ESI-TOF, [M + H]$^+$): 588.0070. Found: 588.0081.

*(E)-N-Benzyl-N-(1-chloro-2-((4-chlorophenyl)selanyl)-2-(p-tolyl)-vinyl)-4-methylbenzenesulfonamide (**2m**).* The product was isolated by column chromatography (hexane/ethyl acetate 97:3) as a yellow solid. Yield: 0.045 g (30%); mp 126–128 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.89 (d, *J* = 8.5 Hz, 2H), 7.56–7.54 (m, 2H), 7.39–7.19 (m, 6H), 6.86–6.84 (m, 3H), 6.75 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 8.2 Hz, 2H), 4.94 (d, *J* = 12.8 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 2.44 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ

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(ppm) 144.5, 141.6, 137.7, 137.3, 136.3, 135.0, 133.9, 133.8, 133.6, 130.4, 130.1, 129.7, 129.4, 129.1, 128.6, 128.4, 128.3, 128.2, 127.6, 127.5, 121.5, 52.1, 21.6, 21.1. HRMS calcd for $C_{29}H_{26}Cl_2NO_2SSe$ (ESI-TOF, $[M + H]^+$): 602.0227. Found: 602.0235.

*General Procedure for the Preparation of 4-(Phenylselanyl)-oxazolone **3a–x**.* In a Schlenk tube, under nitrogen, containing CH_2Cl_2 (3 mL) were added $FeCl_3$ (0.375 mmol; 1.5 equiv) and diorganyl dichalcogenides (0.25 mmol; 1 equiv). The resulting solution was stirred at room temperature for 15 min. After this time, appropriate substrate **1** (0.25 mmol) was added and the reaction was stirred at room temperature for 1 h. The mixture was concentrated in a vacuum, and the residue was purified by column chromatography over silica gel using a solution of hexane/ethyl acetate as the eluent to provide the products **3**.

*5-Phenyl-4-(phenylselanyl)-3-(p-tolyl)oxazol-2(3H)-one (**3a**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.075 g (74%); mp 119–121 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.03–8.01 (m, 2H), 7.42–7.34 (m, 3H), 7.19–7.11 (m, 7H), 6.99 (d, J = 8.4 Hz, 2H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.6, 143.8, 138.7, 130.9, 130.3, 129.5, 129.5, 129.2, 129.0, 128.5, 127.8, 127.6, 127.2, 125.9, 109.6, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 408 ([M + 1], 6), 407 (28), 194 (18), 165 (18), 105 (100), 77 (29). HRMS calcd for $C_{22}H_{18}NO_2Se$ (ESI-TOF, $[M + H]^+$): 408.0503. Found: 408.0512.

*4-((4-Methoxyphenyl)selanyl)-5-phenyl-3-(p-tolyl)oxazol-2(3H)-one (**3b**).* The product was isolated by column chromatography (hexane/ethyl acetate 93:7) as a yellow solid. Yield: 0.045 g (42%); mp 131–133 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.06–8.04 (m, 2H), 7.45–7.34 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 3H), 6.67 (d, J = 9.0 Hz, 2H), 3.73 (s, 3H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.8, 153.6, 143.0, 138.7, 133.4, 131.0, 129.5, 128.9, 128.5, 128.0, 127.4, 126.0, 118.8, 115.1, 110.7, 55.2, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 438 ([M + 2], 4), 437 (15), 357 (15), 224 (29), 105 (100), 77 (35). HRMS calcd for $C_{23}H_{20}NO_3Se$ (ESI-TOF, $[M + H]^+$): 438.0608. Found: 438.0607.

*5-Phenyl-3-(p-tolyl)-4-(p-tolylselanyl)oxazol-2(3H)-one (**3c**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.069 g (66%); mp 157–159 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.05–8.02 (m, 2H), 7.43–7.35 (m, 3H), 7.14 (d, J = 7.8 Hz, 2H), 7.03–6.95 (m, 6H), 2.36 (s, 3H), 2.27 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.6, 143.6, 138.7, 137.8, 131.0, 130.7, 130.3, 129.5, 129.0, 128.5, 127.9, 127.3, 126.0, 125.4, 110.0, 21.1, 21.0. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 261.9. MS (EI, 70 eV; m/z (relative intensity)): 422 ([M + 1], 5), 421 (22), 208 (23), 179 (11), 105 (100), 77 (25). HRMS calcd for $C_{23}H_{20}NO_2Se$ (ESI-TOF, $[M + H]^+$): 422.0659. Found: 422.0668.

*4-((4-Chlorophenyl)selanyl)-5-phenyl-3-(p-tolyl)oxazol-2(3H)-one (**3d**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.062 g (56%); mp 179–181 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.01–7.99 (m, 2H), 7.43–7.37 (m, 3H), 7.17–7.13 (m, 4H), 7.06–6.99 (m, 4H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.5, 144.0, 139.0, 134.1, 131.8, 130.8, 129.7, 129.3, 128.6, 127.9, 127.8, 127.2, 127.1, 126.0, 109.3, 21.2. MS (EI, 70 eV; m/z (relative intensity)): 443 ([M + 2], 12), 441 (27), 438 (13), 228 (12), 105 (100), 77 (29). HRMS calcd for $C_{22}H_{17}ClNO_2Se$ (ESI-TOF, $[M + H]^+$): 442.0113. Found: 442.0119.

*4-((4-Fluorophenyl)selanyl)-5-phenyl-3-(p-tolyl)oxazol-2(3H)-one (**3e**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.053 g (50%); mp 162–164 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.03–8.01 (m, 2H), 7.45–7.37 (m, 3H), 7.16 (dd, J = 8.6, 0.7 Hz, 2H), 7.10–7.05 (m, 2H), 7.00 (d, J = 8.3 Hz, 2H), 6.85 (t, J = 8.7 Hz, 2H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.6 (d, CF, $^1J_{C-F}$ = 248.7 Hz), 153.5, 143.5, 138.9, 133.2 (d, CF, $^3J_{C-F}$ = 8.0 Hz), 130.9, 129.6, 129.1, 128.6, 127.9, 127.2, 126.0, 123.3 (d, CF, $^4J_{C-F}$ = 3.4 Hz), 116.6 (d, CF, $^2J_{C-F}$ = 21.9 Hz), 109.9, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 426 ([M + 2], 4), 425 (17), 207 (20), 105 (100), 89 (17), 77 (28). HRMS calcd for $C_{22}H_{17}FNO_2Se$ (ESI-TOF, $[M + H]^+$): 426.0409. Found: 426.0410.

*4-(Butylselanyl)-5-phenyl-3-(p-tolyl)oxazol-2(3H)-one (**3g**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.072 g (74%); mp 69–71 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.04–7.99 (m, 2H), 7.44–7.38 (m, 2H), 7.36–7.27 (m, 5H), 2.47–2.38 (m, 5H), 1.39 (quint, J = 7.3 Hz, 2H), 1.16 (sext, J = 7.3 Hz, 2H), 0.72 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.9, 142.8, 138.9, 131.4, 129.8, 128.7, 128.5, 127.8, 127.7, 126.0, 109.1, 31.6, 29.4, 22.5, 21.3, 13.3. MS (EI, 70 eV; m/z (relative intensity)): 389 ([M + 2], 5), 387 (25), 331 (11), 251 (11), 207 (23), 105 (100). HRMS calcd for $C_{20}H_{22}NO_2Se$ (ESI-TOF, $[M + H]^+$): 388.0816. Found: 388.0817.

*3,5-Diphenyl-4-(phenylselanyl)oxazol-2(3H)-one (**3h**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.050 g (51%); mp 145–147 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.05–8.02 (m, 2H), 7.44–7.32 (m, 6H), 7.20–7.12 (m, 7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.5, 143.9, 133.5, 130.6, 129.5, 129.1, 129.0, 128.9, 128.6, 128.5, 128.1, 127.8, 127.2, 126.0, 109.5. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 271.3. MS (EI, 70 eV; m/z (relative intensity)): 394 ([M + 1], 6), 393 (25), 313 (08), 180 (17), 105 (100), 77 (32). HRMS calcd for $C_{21}H_{16}NO_2Se$ (ESI-TOF, $[M + H]^+$): 394.0346. Found: 394.0326.

*3-(4-Methoxyphenyl)-5-phenyl-4-(phenylselanyl)oxazol-2(3H)-one (**3i**).* The product was isolated by column chromatography (hexane/ethyl acetate 93:7) as a yellow solid. Yield: 0.074 g (70%); mp 126–128 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.04–8.01 (m, 2H), 7.43–7.35 (m, 3H), 7.19–7.14 (m, 5H), 7.00 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.6, 153.7, 143.6, 130.4, 129.5, 129.3, 129.1, 129.0, 128.5, 127.7, 127.2, 126.1, 125.9, 114.1, 109.9, 55.4. MS (EI, 70 eV; m/z (relative intensity)): 424 ([M + 1], 5), 423 (20), 207 (24), 165 (17), 105 (100), 77 (36). HRMS calcd for $C_{22}H_{18}NO_3Se$ (ESI-TOF, $[M + H]^+$): 424.0452. Found: 424.0445.

*3-(4-Chlorophenyl)-5-phenyl-4-(phenylselanyl)oxazol-2(3H)-one (**3j**).* The product was isolated by column chromatography (hexane/ethyl acetate 94:6) as a white solid. Yield: 0.082 g (77%); mp 161–163 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.04–7.99 (m, 2H), 7.40 (dt, J = 13.8, 7.1 Hz, 3H), 7.28 (d, J = 8.8 Hz, 2H), 7.24–7.10 (m, 5H), 7.05 (d, J = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.2, 144.1, 134.6, 132.0, 130.5, 129.6, 129.3, 129.0, 128.7, 128.6, 127.9, 127.0, 126.0, 109.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 271.0. MS (EI, 70 eV; m/z (relative intensity)): 429 ([M + 2], 7), 427 (16), 207 (38), 165 (18), 105 (100), 77 (38). HRMS calcd for $C_{21}H_{15}ClNO_2Se$ (ESI-TOF, $[M + H]^+$): 427.9957. Found: 427.9965.

*5-Phenyl-4-(phenylselanyl)-3-(3-(trifluoromethyl)phenyl)oxazol-2(3H)-one (**3k**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.081 g (70%); mp 117–119 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.04–8.02 (m, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.46–7.36 (m, 6H), 7.21–7.08 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.1, 144.3, 134.1, 131.4 (q, CF, $^2J_{C-F}$ = 33.2 Hz), 131.3, 130.7, 129.6, 129.5, 129.4, 128.6, 128.3, 128.1, 126.9, 126.1, 125.3 (q, CF, $^3J_{C-F}$ = 3.6 Hz), 125.10 (q, CF, $^3J_{C-F}$ = 3.9 Hz), 123.27 (q, CF, $^1J_{C-F}$ = 272.8 Hz), 109.0. MS (EI, 70 eV; m/z (relative intensity)): 462 ([M + 1], 6), 461 (25), 248 (20), 165 (17), 105 (100), 77 (33). HRMS calcd for $C_{22}H_{15}F_3NO_2Se$ (ESI-TOF, $[M + H]^+$): 462.0220. Found: 462.0218.

*4-(Butylselanyl)-3-(4-chlorophenyl)-5-phenyloxazol-2(3H)-one (**3l**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.085 g (84%); mp 98–100 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.01–7.99 (m, 2H), 7.49–7.32 (m, 7H), 2.43 (t, J = 7.3 Hz, 2H), 1.39 (quint, J = 7.3 Hz, 2H), 1.17 (sext, J = 7.3 Hz, 2H), 0.73 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.3, 143.2, 134.5, 132.4, 129.3, 129.1, 128.8, 128.4, 127.4, 126.0, 108.4, 31.4, 29.5, 22.3, 13.2. MS (EI, 70 eV; m/z (relative intensity)): 409 ([M + 2], 8), 407 (20), 351

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(13), 271 (10), 105 (100), 77 (33). HRMS calcd for $C_{19}H_{19}ClNO_2Se$ (ESI-TOF, $[M + H]^+$): 408.0270. Found: 408.0271.

*4-(Butylselanyl)-3-(4-methoxyphenyl)-5-phenyloxazol-2(3H)-one (**3m**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as an orange solid. Yield: 0.070 g (70%); mp 102−104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.02−8.00 (m, 2H), 7.43−7.39 (m, 2H), 7.35−7.29 (m, 3H), 7.00 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H), 2.43 (t, J = 7.3 Hz, 2H), 1.41 (quint, J = 7.3 Hz, 2H), 1.18 (sext, J = 7.3 Hz, 2H), 0.74 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.7, 153.9, 142.6, 129.2, 128.6, 128.4, 127.7, 126.6, 125.9, 114.4, 109.3, 55.5, 31.5, 29.2, 22.4, 13.2. MS (EI, 70 eV; m/z (relative intensity)): 463 ([M + 1], 3), 403 (16), 207 (37), 133 (11), 105 (100), 77 (31). HRMS calcd for $C_{20}H_{22}NO_3Se$ (ESI-TOF, $[M + H]^+$): 404.0765. Found: 404.0769.

*4-(Butylselanyl)-5-phenyl-3-(3-(trifluoromethyl)phenyl)oxazol-2(3H)-one (**3n**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.088 g (80%); mp 95−97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.02−8.00 (m, 2H), 7.74−7.61 (m, 4H), 7.45−7.35 (m, 3H), 2.43 (t, J = 7.3 Hz, 2H), 1.38 (quint, J = 7.3 Hz, 2H), 1.15 (sext, 7.3 Hz, 2H), 0.71 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.3, 143.6, 134.5, 131.71 (q, CF, $^2J_{C-F}$ = 33.2 Hz), 131.2, 129.7, 129.0, 128.5, 127.2, 126.1, 125.33 (q, CF, $^3J_{C-F}$ = 3.8 Hz), 125.0 (q, CF, $^3J_{C-F}$ = 3.9 Hz), 123.51 (q, CF, $^1J_{C-F}$ = 273.2 Hz), 108.2, 31.4, 29.7, 22.3, 13.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as the external reference) δ (ppm) 150.6. MS (EI, 70 eV; m/z (relative intensity)): 442 ([M + 1], 5), 441 (22), 385 (16), 261 (17), 105 (100), 77 (32). HRMS calcd for $C_{20}H_{19}F_3NO_2Se$ (ESI-TOF, $[M + H]^+$): 442.0533. Found: 442.0517.

*5-(4-Methoxyphenyl)-4-(phenylselanyl)-3-(p-tolyl)oxazol-2(3H)-one (**3o**).* The product was isolated by column chromatography (hexane/ethyl acetate 92:8) as a yellow solid. Yield: 0.034 g (31%); mp 155−157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.96 (d, J = 8.9 Hz, 2H), 7.20−7.12 (m, 7H), 7.00 (d, J = 8.3 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 160.2, 153.7, 144.3, 138.7, 130.9, 130.0, 129.5, 129.5, 127.7, 127.5, 119.8, 114.0, 107.6, 55.3, 55.3, 21.2, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 438 ([M + 1], 4), 437 (15), 357 (10), 194 (18), 135 (100), 77 (16). HRMS calcd for $C_{23}H_{20}NO_3Se$ (ESI-TOF, $[M + H]^+$): 438.0608. Found: 438.0609.

*4-(Phenylselanyl)-3,5-di-p-tolyloxazol-2(3H)-one (**3p**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.053 g (50%); mp 157−159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.92 (d, J = 8.3 Hz, 2H), 7.25−7.10 (m, 9H), 6.99 (d, J = 8.3 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.7, 144.2, 139.3, 138.7, 130.8, 130.1, 129.5, 129.4, 129.3, 129.2, 127.7, 127.5, 125.8, 124.3, 108.7, 21.3, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 422 ([M + 1], 5), 421 (21), 341 (09), 194 (16), 119 (100), 91 (30). HRMS calcd for $C_{23}H_{20}NO_2Se$ (ESI-TOF, $[M + H]^+$): 422.0659. Found: 422.0642.

*3-(4-Chlorophenyl)-4-((4-chlorophenyl)selanyl)-5-phenyloxazol-2(3H)-one (**3r**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.041 g (36%); mp 122−124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.01−7.96 (m, 2H), 7.46−7.36 (m, 3H), 7.35−7.28 (m, 2H), 7.17−7.12 (m, 2H), 7.10−7.02 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.1, 134.8, 134.4, 132.0, 131.9, 129.8, 129.5, 129.3, 129.2, 129.2, 128.7, 128.4, 126.8, 126.1, 108.7. MS (EI, 70 eV; m/z (relative intensity)): 463 ([M + 2], 8), 461 (11), 248 (09), 207 (20), 105 (100), 77 (36). HRMS calcd for $C_{21}H_{14}Cl_2NO_2Se$ (ESI-TOF, $[M + H]^+$): 461.9567. Found: 461.9563.

*3-(4-Chlorophenyl)-5-phenyl-4-(p-tolylselanyl)oxazol-2(3H)-one (**3s**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.044 g (40%); mp 136−138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.04−8.01 (m, 2H), 7.45−7.37 (m, 3H), 7.30 (d, J = 8.8 Hz, 2H), 7.08−7.06 (m, 2H), 6.99−6.98 (m, 4H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.3, 143.9, 138.2, 134.6, 132.1, 130.8, 130.4, 129.6, 129.3, 129.2, 129.1, 128.6, 128.4, 127.1, 126.1, 125.0, 109.5, 21.0. MS (EI, 70 eV; m/z (relative intensity)): 443 ([M + 2], 6), 441 (13), 207 (57), 133 (15), 105 (100), 77 (36). HRMS calcd for $C_{22}H_{17}ClNO_2Se$ (ESI-TOF, $[M + H]^+$): 442.0113. Found: 442.0111.

*4-(Butylselanyl)-3,5-di-p-tolyloxazol-2(3H)-one (**3t**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.081 g (81%); mp 81−83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90 (d, J = 8.3 Hz, 2H), 7.28 (s, 4H), 7.22 (d, J = 7.6 Hz, 2H), 2.42−2.38 (m, 8H), 1.39 (quint, J = 7.3 Hz, 2H), 1.16 (sext, J = 7.3 Hz, 2H), 0.72 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.8, 142.9, 138.7, 138.6, 131.2, 129.7, 129.0, 127.6, 125.8, 124.7, 108.0, 31.4, 29.2, 22.3, 21.2, 21.1, 13.1. MS (EI, 70 eV; m/z (relative intensity)): 402 ([M + 1], 6), 401 (24), 344 (09), 265 (10), 119 (100), 91 (25). HRMS calcd for $C_{21}H_{24}NO_2Se$ (ESI-TOF, $[M + H]^+$): 402.0972. Found: 402.0978.

*5-Phenyl-4-(phenyltellanyl)-3-(p-tolyl)oxazol-2(3H)-one (**3u**).* The product was isolated by column chromatography (hexane/ethyl acetate 94:6) as a yellow solid. Yield: 0.079 g (69%); mp 121−123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.97−7.95 (m, 2H), 7.43−7.31 (m, 5H), 7.25−7.21 (m, 1H), 7.15−7.10 (m, 4H), 6.99 (d, J = 8.3 Hz, 2H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.4, 146.1, 138.7, 136.2, 132.3, 129.6, 129.5, 129.1, 128.3, 128.0, 127.7, 126.6, 114.1, 93.8, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 457 (10), 327 (14), 207 (30), 105 (100), 89 (30), 77 (41). HRMS calcd for $C_{22}H_{18}NO_2Te$ (ESI-TOF, $[M + H]^+$): 458.0400. Found: 458.0373.

*4-(Butyltellanyl)-5-phenyl-3-(p-tolyl)oxazol-2(3H)-one (**3v**).* The product was isolated by column chromatography (hexane/ethyl acetate 94:6) as a yellow solid. Yield: 0.084 g (77%); mp 93−95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.95 (d, J = 7.1 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.35−7.24 (m, 5H), 2.45 (t, J = 7.3 Hz, 2H), 2.41 (s, 3H), 1.47 (quint, J = 7.3 Hz, 2H), 1.15 (sext, J = 7.3 Hz, 2H), 0.75 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.4, 145.1, 138.8, 132.6, 129.8, 128.7, 128.2, 128.0, 127.9, 126.5, 89.6, 32.8, 24.5, 21.2, 13.1, 11.2. MS (EI, 70 eV; m/z (relative intensity)): 437 (12), 281 (14), 207 (87),165 (11), 105 (100), 89 (28). HRMS calcd for $C_{20}H_{22}NO_2Te$ (ESI-TOF, $[M + H]^+$): 438.0713. Found: 438.0718.

*4-(Phenyltellanyl)-3,5-di-p-tolyloxazol-2(3H)-one (**3w**).* The product was isolated by column chromatography (hexane/ethyl acetate 94:6) as a yellow solid. Yield: 0.078 g (66%); mp 155−157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.85 (d, J = 8.3 Hz, 2H), 7.33 (dd, J = 8.1, 1.3 Hz, 2H), 7.24−7.21 (m, 3H), 7.14−7.10 (m, 4H), 6.99 (d, J = 8.3 Hz, 2H), 2.38 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.4, 146.51, 139.3, 138.7, 136.0, 132.3, 129.6, 129.5, 129.0, 128.2, 128.0, 126.6, 124.9, 114.3, 93.0, 21.3, 21.2. MS (EI, 70 eV; m/z (relative intensity)): 472 ([M + 1], 4), 471 (15), 341 (22), 119 (100), 91 (34), 77 (16). HRMS calcd for $C_{23}H_{20}NO_2Te$ (ESI-TOF, $[M + H]^+$): 472.0556. Found: 472.0536.

*4-(Phenylthio)-3,5-di-p-tolyloxazol-2(3H)-one (**3x**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.019 g (20%); mp 144−146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.93 (d, J = 8.3 Hz, 2H), 7.33−7.19 (m, 6H), 7.12−6.95 (m, 5H), 2.38 (s, 3H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.2, 144.63, 139.5, 138.7, 133.2, 130.0, 129.6, 129.4, 129.3, 128.6, 127.6, 127.1, 125.6, 124.0, 113.0, 21.4, 21.2. MS (EI, 70 eV; m/z (relative intensity)): 374 ([M + 1], 11), 373 (42), 226 (08), 135 (13), 119 (100), 91 (25). HRMS calcd for $C_{23}H_{20}NO_2S$ (ESI-TOF, $[M + H]^+$): 374.1215. Found: 374.1202.

*General Procedure for the Preparation of E-Vinyl Tosylate **4**.* In a Schlenk tube, under nitrogen, containing CH_2Cl_2 (3 mL) the appropriate substrate **1** (0.25 mmol) was added $TsOH{\cdot}H_2O$ (0.375 mmol; 1.5 equiv). The resulting solution was stirred at room temperature for 1 h. After this time, appropriate substrate **1** (0.25 mmol) was added and the reaction was stirred at room temperature for 1 h. The mixture was concentrated in a vacuum, and the residue was purified by column chromatography over silica gel using a solution of hexane/ethyl acetate as the eluent to provide the products **4** or **5**.

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*(E)-1-((Ethoxycarbonyl)(p-tolyl)amino)-2-phenylvinyl 4-methylbenzenesulfonate (**4a**).* The product was isolated by column chromatography (hexane/ethyl acetate 92:8) as a white solid. Yield: 0.097 g (86%) and 0.762 g (84%) using ynamide (2 mmol); mp 102−104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.71 (d, J = 8.4 Hz, 2H), 7.33−7.20 (m, 7H), 7.08 (s, 4H), 6.24 (s, 1H), 3.96 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 2.32 (s, 3H), 0.95 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.7, 145.1, 139.1, 136.5, 135.3, 132.8, 132.4, 129.5, 129.4, 128.7, 128.5, 128.4, 127.4, 125.0, 118.9, 62.5, 21.6, 20.9, 13.9. HRMS calcd for $C_{25}H_{26}NO_5S$ (ESI-TOF, [M + H]$^+$): 452.1532. Found: 452.1536.

*(E)-1-((4-Chlorophenyl)(ethoxycarbonyl)amino)-2-phenylvinyl 4-methylbenzenesulfonate (**4b**).* The product was isolated by column chromatography (hexane/ethyl acetate 92:8) as a white solid. Yield: 0.110 g (94%); mp 105−107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.69 (d, J = 8.3 Hz, 2H), 7.32−7.17 (m, 9H), 7.13 (d, J = 8.9 Hz, 2H), 6.32 (s, 1H), 3.99 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.5, 145.4, 138.5, 136.4, 132.6, 132.1, 132.1, 129.5, 128.9, 128.8, 128.6, 128.4, 127.4, 126.3, 119.4, 62.9, 21.6, 13.9. HRMS calcd for $C_{24}H_{23}ClNO_5S$ (ESI-TOF, [M + H]$^+$): 472.0985. Found: 472.0960.

*(E)-1-((Ethoxycarbonyl)(3-(trifluoromethyl)phenyl)amino)-2-phenylvinyl 4-methylbenzenesulfonate (**4c**).* The product was isolated by column chromatography (hexane/ethyl acetate 92:8) as a white solid. Yield: 0.117 g (93%); mp 87−89 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.69 (d, J = 8.4 Hz, 2H), 7.44−7.35 (m, 4H), 7.28−7.24 (m, 7H), 6.39 (s, 1H), 3.99 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.3, 145.6, 138.5, 138.2, 132.8, 132.0, 131.23 (q, CF, $^2J_{C-F}$ = 32.4 Hz), 129.6, 129.4, 128.9, 128.8, 128.3, 127.6, 127.4, 123.41 (q, CF, $^1J_{C-F}$ = 272.7 Hz), 123.11 (q, CF, $^3J_{C-F}$ = 3.8 Hz), 121.9 (q, CF, $^3J_{C-F}$ = 4.0 Hz), 120.2, 63.1, 21.5, 13.8. HRMS calcd for $C_{25}H_{23}F_3NO_5S$ (ESI-TOF, [M + H]$^+$): 506.1249. Found: 506.1255.

*(E)-1-((Ethoxycarbonyl)(phenyl)amino)-2-phenylvinyl 4-methylbenzenesulfonate (**4d**).* The product was isolated by column chromatography (hexane/ethyl acetate 92:8) as a white solid. Yield: 0.091 g (84%); mp 95−97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.70 (d, J = 8.3 Hz, 2H), 7.29−7.19 (m, 12H), 6.28 (s, 1H), 3.97 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 0.95 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.6, 145.2, 138.9, 137.9, 132.8, 132.3, 129.5, 128.8, 128.7, 128.5, 128.5, 127.4, 126.6, 125.1, 119.2, 62.7, 21.6, 13.9. HRMS calcd for $C_{24}H_{24}NO_5S$ (ESI-TOF, [M + H]$^+$): 438.1375. Found: 438.1362.

*(E)-1-((Ethoxycarbonyl)(p-tolyl)amino)-2-(4-methoxyphenyl)-vinyl 4-methylbenzenesulfonate (**4e**).* The product was isolated by column chromatography (hexane/ethyl acetate 90:10) as a white solid. Yield: 0.065 g (54%); 74−76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.71 (d, J = 8.1 Hz, 2H), 7.27−7.23 (m, 4H), 7.07 (s, 4H), 6.81 (d, J = 8.9 Hz, 2H), 6.19 (s, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H), 0.99 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.7, 152.8, 145.1, 137.6, 136.5, 135.2, 132.7, 129.4, 129.3, 128.9, 128.5, 124.9, 124.6, 118.9, 114.1, 62.6, 55.2, 21.6, 20.9, 14.0. HRMS calcd for $C_{26}H_{28}NO_6S$ (ESI-TOF, [M + H]$^+$): 482.1637. Found: 482.1631.

*(E)-1-((Ethoxycarbonyl)(p-tolyl)amino)-2-(p-tolyl)vinyl 4-methylbenzenesulfonate (**4f**).* The product was isolated by column chromatography (hexane/ethyl acetate 92:8) as a red solid. Yield: 0.095 g (82%); mp 104−106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.71 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.11−7.05 (m, 6H), 6.20 (s, 1H), 3.99 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 0.97 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.8, 145.1, 138.5, 138.3, 136.5, 135.2, 132.6, 129.5, 129.4, 129.3, 129.2, 128.5, 127.4, 125.0, 119.1, 62.5, 21.6, 21.2, 20.9, 14.0. HRMS calcd for $C_{26}H_{27}NNaO_5S$ (ESI-TOF, [M + Na]$^+$): 488.1508. Found: 488.1502.

*N-Benzyl-2-phenyl-N-tosylacetamide (**5a**).* The product was isolated by column chromatography (hexane/ethyl acetate 90:10) as a white solid. Yield: 0.091 g (96%); mp 124−126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.63 (d, J = 8.4 Hz, 2H), 7.33−7.20 (m, 10H), 6.99−6.97 (m, 2H), 5.06 (s, 2H), 3.86 (s, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 171.1, 144.8, 136.6, 136.5, 133.2, 129.6, 129.2, 128.6, 128.4, 127.8, 127.7, 127.6, 127.1, 49.6, 42.8, 21.5. HRMS calcd for $C_{22}H_{22}NO_3S$ (ESI-TOF, [M + H]$^+$): 380.1320. Found: 380.1319.

*N-Benzyl-2-(p-tolyl)-N-tosylacetamide (**5b**).* The product was isolated by column chromatography (hexane/ethyl acetate 90:10) as a white solid. Yield: 0.090 g (92%); mp 110−112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.64 (d, J = 8.4 Hz, 2H), 7.33−7.22 (m, 7H), 7.03 (d, J = 7.5 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 5.06 (s, 2H), 3.81 (s, 2H), 2.40 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 171.4, 144.77, 136.7, 136.6, 136.5, 130.1, 129.6, 129.2, 129.0, 128.6, 127.9, 127.6, 49.6, 42.4, 21.5, 21.0. HRMS calcd for $C_{23}H_{24}NO_3S$ (ESI-TOF, [M + H]$^+$): 394.1477. Found: 394.1502.

*General Procedure for the Suzuki Cross-Coupling Reaction of 4-(Butyltelluro)oxazolone **3v** with Boronic Acid.* Triethylamine (0.30 mmol; 2 equiv) was added to a suspension of 4-(butyltelluro)-oxazolone **3v** (0.15 mmol), boronic acid (0.30 mmol; 2 equiv), [$Pd(PPh_3)_4$] (10 mol %), and silver(I) oxide (0.15 mmol; 1 equiv) in dimethylformamide (DMF; 2 mL) under a nitrogen atmosphere. The reaction was then heated in an oil bath for 12 h at 100 °C. After that, the reaction was cooled to room temperature, diluted with ethyl acetate (3 mL), and then washed with a saturated solution of NH_4Cl (10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under a vacuum. The residue was purified by flash chromatography using a solution of hexane/ethyl acetate as the eluent.

*4,5-Diphenyl-3-(p-tolyl)oxazol-2(3H)-one (**6a**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow solid. Yield: 0.020 g (40%); mp 229−231 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38−7.29 (m, 5H), 7.26−7.21 (m, 5H), 7.09 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.8, 137.9, 134.9, 130.9, 130.3, 129.7, 129.4, 129.0, 128.5, 128.0, 127.6, 127.1, 126.7, 124.9, 123.6, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 328 ([M + 1], 14), 327 (64), 194 (100), 165 (37), 91 (33), 65 (19). HRMS calcd for $C_{22}H_{18}NO_2$ (ESI-TOF, [M + H]$^+$): 328.1338. Found: 328.1322.

*5-Phenyl-3,4-di-p-tolyloxazol-2(3H)-one (**6b**).* The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.045 g (88%); mp 154−156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38 (dd, J = 7.9, 1.8 Hz, 2H), 7.26−7.22 (m, 3H), 7.13−7.08 (m, 6H), 7.02 (d, J = 8.4 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.8, 139.5, 137.8, 134.7, 130.9, 130.0, 129.7, 129.6, 128.4, 127.8, 127.8, 126.7, 124.8, 124.0, 123.8, 21.4, 21.1. MS (EI, 70 eV; m/z (relative intensity)): 342 ([M + 1], 13), 341 (54), 208 (100), 165 (21), 91 (34), 65 (20). HRMS calcd for $C_{23}H_{20}NO_2$ (ESI-TOF, [M + H]$^+$): 342.1494. Found: 342.1497.

*General Procedure for the Suzuki Cross-Coupling Reaction of Vinyl Tosylate **4c** with Boronic Acid.* To a solution of vinyl tosylate **4c** (0.25 mmol) in THF (2 mL) under a nitrogen atmosphere were added *p*-tolylboronic acid (0.375 mmol; 1.5 equiv), $PdCl_2(PPh_3)_2$ (6 mol %), and 2 M Na_2CO_3 (0.5 mL, 0.96 mmol). The resulting solution was then heated in an oil bath for 2 h at 40 °C (monitored by TLC). After that, the reaction was cooled to room temperature, diluted with ethyl acetate (3 mL), and then washed with a saturated solution of NH_4Cl (10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under a vacuum. The residue was purified by flash chromatography using a solution of hexane/ethyl acetate as the eluent.

(E/Z)-Ethyl (2-Phenyl-1-(p-tolyl)vinyl)(3-(trifluoromethyl)phenyl)-carbamate (7a, Mixture E/Z (6:4)). The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a yellow oil. Yield: 0.053 g (50%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.76−7.69 (m, 2H), 7.61−7.51 (m, 2H), 7.43−7.32 (m, 5H), 7.29−7.11 (m, 11H), 7.04−6.99 (m, 1H), 6.95 (s, 1H), 6.60 (s, 1H), 4.16 (q, J = 7.1 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 2H), 1.10 (t, J = 7.1 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.8, 154.4, 142.9, 141.3, 139.9, 138.5, 138.4, 137.8, 135.7, 135.2, 135.1, 133.3, 131.1, 130.8, 129.5, 129.3, 129.2,

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129.1, 129.0, 128.9, 128.6, 128.3, 128.2, 128.0, 128.0, 127.3, 126.6, 126.1, 125.7, 125.2, 122.5, 122.4, 122.05 (q, J = 3.6 Hz), 121.82 (q, J = 3.7 Hz), 121.09 (q, J = 3.7 Hz), 120.33 (q, J = 3.7 Hz), 62.4, 62.3, 21.2, 21.1, 14.1, 13.9. MS (EI, 70 eV; m/z (relative intensity)): 426 ([M + 1], 15), 425 (57), 235 (10), 181 (23), 135 (35), 118 (100). HRMS calcd for $C_{25}H_{23}F_3NO_2$ (ESI-TOF, $[M + H]^+$): 426.1681. Found: 426.1716.

General Procedure for the Sonogashira Cross-Coupling Reaction of Vinyl Tosylate ***4d*** *with Phenylacetylene.* Triethylamine (1.5 mL) was added under a nitrogen atmosphere to a suspension of vinyl tosylate **4d** (0.15 mmol), $Pd(OAc)_2$ (20 mol %), PPh_3 (20 mol %), and phenylacetylene (0.225 mmol; 1.5 equiv) in DMF (1.5 mL). The resulting solution was stirred at room temperature for 3 h (monitored by TLC). After that, the reaction was diluted with ethyl acetate (3 mL) and then washed with a saturated solution of NH_4Cl (10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under a vacuum. The residue was purified by flash chromatography using a solution of hexane/ethyl acetate as the eluent.

(E/Z)-Ethyl (1,4-Diphenylbut-1-en-3-yn-2-yl)(phenyl)carbamate (8a, Mixture E/Z (7:3)). The product was isolated by column chromatography (hexane/ethyl acetate 95:5) as a white solid. Yield: 0.051 g (92%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.87 (d, J = 7.1 Hz, 1H), 7.51−7.44 (m, 5H), 7.43−7.21 (m, 16H), 7.21−7.15 (m, 1H), 6.91 (s, 1H), 6.85 (s, 1H), 4.28 (q, J = 7.1 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.6, 153.8, 141.8, 140.0, 136.1, 134.7, 134.4, 134.3, 131.5, 131.4, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 128.3, 128.2, 126.1, 126.0, 125.7, 124.6, 122.5, 122.4, 121.3, 121.2, 94.8, 89.0, 88.3, 86.8, 62.2, 62.1, 14.5, 14.2. MS (EI, 70 eV; m/z (relative intensity)): 368 ([M + 1], 5), 367 (27), 338 (52), 294 (100), 216 (29), 191 (57). HRMS calcd for $C_{25}H_{22}NO_2$ (ESI-TOF, $[M + H]^+$): 368.1651. Found: 368.1626.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02480.

^1H and ^{13}C NMR spectra for all new compounds and X-ray results and crystal data for compounds **2a**, **2m**, **3a**, **4a**, and **5a** (CCDC 2034677, 2034678, 2034679, 2034680, and 2034682, respectively) (PDF)

Accession Codes

CCDC 2034677−2034680 and 2034682 contain 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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