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Article

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Cyclization of Thiopropargyl Benzimidazoles by Combining Iron(III) Chloride and Diorganyl Diselenides

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Abstract

A practical synthetic approach to the synthesis of 3-(organoselenyl)-imidazothiazines was developed. The methodology involved the regioselective 6-*endo*-dig cyclization of thiopropargyl benzimidazoles promoted by diorganyl diselenides and iron(III) chloride. The investigation to determine the best reaction conditions indicated the use of thiopropargyl benzimidazoles (0.25 mmol) with diorganyl diselenides (1.0 equiv) and iron(III) chloride (2.0 equiv) in dichloromethane at 40 ^{0}C for 30 min to be optimal. Under these conditions, the scope of the substrates was evaluated varying the structures of thiopropargyl benzimidazoles and diorganyl diselenides giving twenty-eight 3-(organoselenyl)-imidazothiazines in moderate to good yields. The reaction conditions were also applicable to diorganyl ditellurides; however, they did not work for diorganyl

disulfides. The mechanism studies were carried out indicating that the cyclization proceeds via a cooperative action of diorganyl diselenides and iron(III) chloride, but a direct electrophilic cyclization, promoted by the in situ formed electrophilic organoselenium species, cannot be ruled out.

Keywords: iron, cyclization, heterocycles, selenides, cyclization

Introduction

The metal-catalyzed cyclization reaction is a powerful method for the preparation of carbo- and heterocycle compounds that are biologically active or are used as potent building blocks in organic synthesis.[1] Many excellent reviews are available dealing with cyclization by using different metals, such as cobalt,[2] gold,[3] copper,[4] iron,[5] mercury,[6] palladium,[7] ruthenium,[8] rhodium,[9] silver,[10] platinum,[11] and others. In recent years, the necessity in the development of most user-friendly systems in the synthesis of heterocycles using environmentally, cost effective, green, and mild methodologies has grown significantly.[12] Therefore, to attend these requirements, iron salts have appeared as a versatile alternative, due to their low price and toxicity.[13] Thus, catalytic amounts of iron salts have been widely used in many transformations of organic synthesis, including the carbon-heteroatom bond formation.[14] Recently, the cooperative action between iron(III) chloride and diorganyl dichalcogenides was found to be an useful system to promote the cyclization of unsaturated substrates.[15] We have also developed significant improvements in the use of this combination as cyclizing agents for the preparation of chalcogen-heterocycles.[16] In the following article, we described the cyclization of thiopropargyl benzimidazoles **1** to 3-(organochalcogenyl)-imidazothiazines **2**

promoted by iron(III) chloride and diorganyl dichalcogenides (Figure 1). Up to now, only few examples for the cyclization of thiopropargyl benzimidazoles have been reported in the literature leading to imidazo-thiazoles via a 5-*endo*-dig mode.[17] Because few reports on the cyclization of thiopropargyl benzimidazoles via a 6-*endo*-dig mode are found in the literature, the preparation of imidazothiazines is rare.[18] The regiochemistry of this reaction is influenced by the reaction conditions, especially by the temperature control, thus the product formation depends on the thermodynamic versus kinetic reaction control.[17a] In addition, the cyclization with the concomitant functionalization of the heterocycles is not reported (Figure 1). The substituted imidazo-thiazoles have received much attention in different areas because they are present in a large number of molecules with pronounced biological activity.[19] In addition, many heterocycles having a thiazole group in the molecule present structural and electronic properties.[20] The main improvement of our methodology is the use of diorganyl diselenides to both to promote the cyclization and to functionalize the new heterocycles. It provides a useful and valuable method for further functionalization by using the peculiar reactivity of the Csp^2-selenium bond. The organochalcogen compounds have attracted much interest in the last decades because of their wide application in the chemistry and biochemistry.[21] They have become important in biochemistry since their application to prevent liver necrosis in rats fed a selenium-deficient Torula yeast,[22] their application as a nutritionally important trace element[23] and because they are present as selenocysteine in the active center of hepatic rat glutathione peroxidase.[24] Organochalcogens have been used much more often in the chemistry mainly because they promote a variety of stereoselective

synthetic transformations including, α-deprotonation, transition-metal-catalyzed cross-coupling, cyclization transmetallation, nucleophilic vinylic substitutions, oxidation, and reduction.[25]

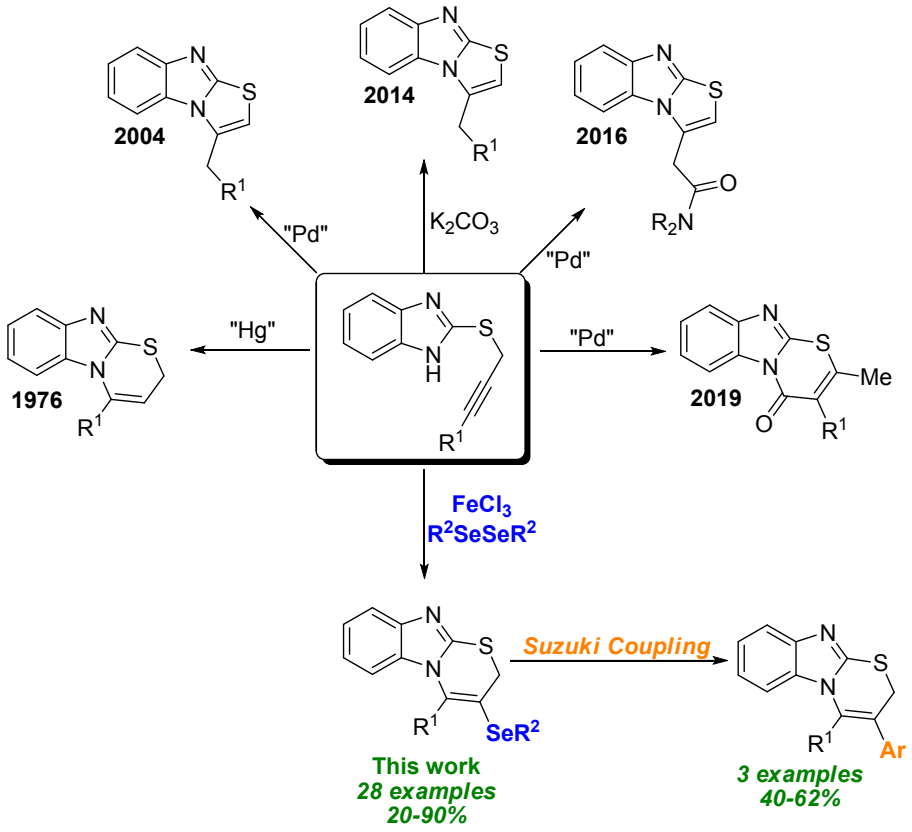
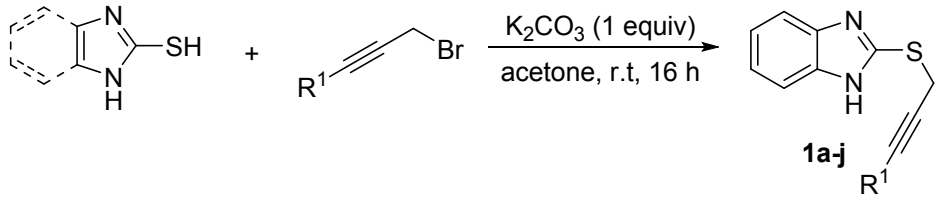


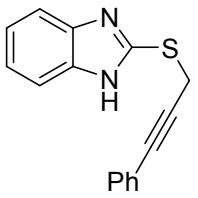
Figure 1. The cyclization reaction of thiopropargyl benzimidazoles reported.

Results and Discussion

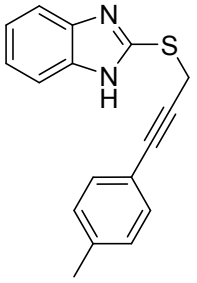
In order to determine the best reaction conditions for the cyclization reactions, we first prepared a series of thiopropargyl benzimidazoles **1** in a one-step procedure from 1*H*-benzo[*d*]imidazole-2-thiol and propargyl bromide derivatives (Table 1). The reaction consisted of mixing the reactants in acetone allowing to react at room temperature for 16 h.[18] Although, a number of thiopropargyl benzimidazoles **1** were prepared in moderate to good yields, the reactions to install substituents at the propargyl position failed.

Table 1. Synthesis of thiopropargyl benzimidazoles **1a**-**l**.

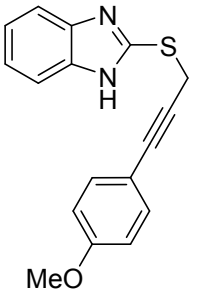




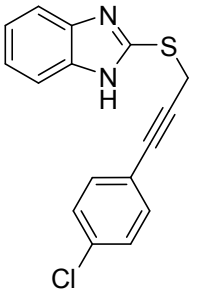
1a - 87%



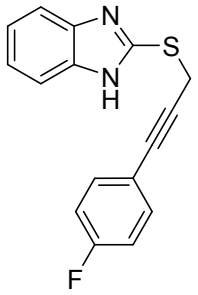
1b - 70%



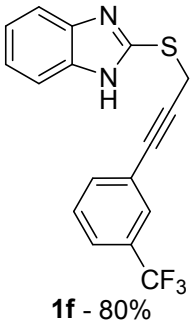
1c - 56%



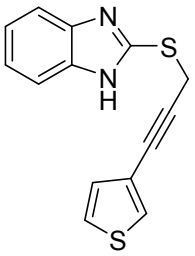
1d - 38%



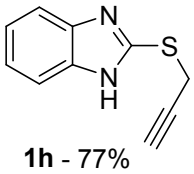
1e - 70%



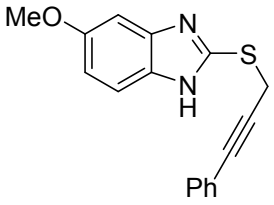
1f - 80%



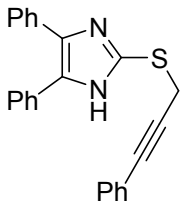
1g - 80%



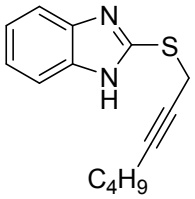
1h - 77%



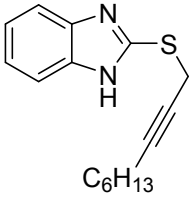
1i - 28%



1j - 61%



1k - 52%



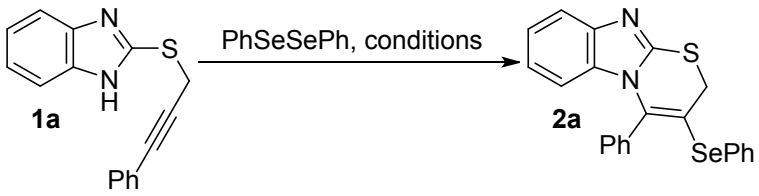
1l - 71%

We started the optimization studies adding diphenyl diselenide (1.0 equiv) to a solution of iron(III) chloride in dichloromethane (3 mL), under nitrogen atmosphere at room temperature. After 15 min, imidazole **1a** (0.25 mmol) was added. The resulting mixture was stirred for 30 min under room temperature. This condition gave only trace amounts of imidazothiazines **2a**, whereas the starting material was recovered (Table 2, entry 1). We then carried out the

reaction with 2 and 3 equiv of iron(III) chloride, which afforded **2a** in 53 and 20% yields, respectively (Table 2, entries 2 and 3). We credit the reduction in the yield by using 3 equiv of iron(III) chloride to the decrease in the reactivity of diphenyl diselenide by complexation with iron excess.[15a] We also observed that the reaction did not take place under a catalytic amount of iron(III) chloride. This result in association with the fact that the best yields were reached with 2 equiv suggests that iron(III) chloride should be required not only to activate the triple bond to promote the cyclization, but also to prepare a selenium electrophilic species (See the mechanism discussion and Scheme 3). In the course of further optimization reactions, we observed that increasing the temperature to 40 ^{0}C led to increase of the yield, whereas the variation of iron(III) chloride under this temperature was not beneficial (Table 2, entries 4-6). However, an even greater increase in the reaction temperature at 70 ^{0}C did not improve the reaction efficacy (Table 2, entry 7). Additional screening revealed that the yield of **2a** was not influenced by increasing the amount of diphenyl diselenide to 1.5 equiv, although the reduction to 0.75 equiv led to obtain **2a** in a poor yield (Table 2, entries 8 and 9). Next, our experimental protocol turned to the effect of solvents. Among the solvents tested, dichloromethane was the most suitable for this reaction, whereas the other solvents, such as dichloroethane, acetonitrile, ethanol, nitromethane, 1,4-dioxane, and toluene were inferior (Table 2, entries 10-15). We subsequently examined the effect of other iron salts on the cyclization of imidazole **1a**. All iron salts, with different ligand partner types in the iron complex, were completely inactive to promote the cyclization. In these cases, the starting material was recovered (Table 2, entries 16-20). The cyclization of imidazole **1a** using diphenyl diselenide with

other Lewis or Brønsted acids instead of iron salt, such as $BF_3{\cdot}OEt_2$ and PTSA did not give the imidazothiazines **2a** (Table 2, entries 21 and 22). Because the cyclization using iodine and bromine giving the five membered product via a 5-*exo*-dig mode is already described in the literature,[26] we did not use these cyclizing agents. Finally, neither running the reaction in more concentrated nor more diluted solutions gave better yields than those obtained with 3 mL of solvent (Table 2, entries 23 and 24). To determine the reaction time, we took samples of the reaction mixture every 10 min over 2 h and analyzed by TLC and CGMS, which showed that 30 min was the reaction time necessary to the complete consume of the starting material. Based on the optimization studies, we found that the best condition consisted of the addition of diphenyl diselenide (0.25 mmol) to a solution of iron(III) chloride (2 equiv) in dichloromethane (3 mL), under nitrogen atmosphere at room temperature. After 15 min, thiopropargyl benzimidazole **1a** (0.25 mmol) was added. The resulting mixture was stirred for 30 min under room temperature.

Table 2. Effect of different reaction parameters for the preparation of 3-(phenylselenyl)-imidazothiazines **2a**.[a]



1a **2a**

entry	promoter (equiv)	solvent	temperature (°C)	time (h)	yield (%)
1	$FeCl_3$ (1)	CH_2Cl_2	r.t.	24	>5[b]
2	$FeCl_3$ (2)	CH_2Cl_2	r.t.	0.5	53
3	$FeCl_3$ (3)	CH_2Cl_2	r.t.	0.5	20

4	$FeCl_3$ (2)	CH_2Cl_2	40	0.5	64
5	$FeCl_3$ (2.5)	CH_2Cl_2	40	0.5	46
6	$FeCl_3$ (1.5)	CH_2Cl_2	40	0.5	54
7	$FeCl_3$ (2)	DCE	70	0.5	40
8	$FeCl_3$ (2)	CH_2Cl_2	40	0.5	65[c]
9	$FeCl_3$ (2)	CH_2Cl_2	40	0.5	53[d]
10	$FeCl_3$ (2)	DCE	40	0.5	52
11	$FeCl_3$ (2)	CH_3CN	40	24	33[b]
12	$FeCl_3$ (2)	EtOH	40	24	>5[b]
13	$FeCl_3$ (2)	CH_3NO_2	40	0.5	30
14	$FeCl_3$ (2)	dioxane	40	24	-[e]
15	$FeCl_3$ (2)	toluene	40	24	<5[b]
16	$FeCl_3 \cdot 6H_2O$ (2)	CH_2Cl_2	40	24	-[e]
17	$Fe(acac)_3$ (2)	CH_2Cl_2	40	24	-[e]
18	$FeCl_2 \cdot 4H_2O$ (2)	CH_2Cl_2	40	24	-[e]
19	Fe^0 (2)	CH_2Cl_2	40	24	-[e]
20	Ferrocene (2)	CH_2Cl_2	40	24	-[e]
21	PTSA (2)	CH_2Cl_2	40	24	-[e]
22	$BF_3 \cdot OEt_2$ (2)	CH_2Cl_2	40	24	-[e]
23	$FeCl_3$ (2)	CH_2Cl_2	40	0.5	44[f]
24	$FeCl_3$ (2)	CH_2Cl_2	40	0.5	21[g]

[a] The reaction was performed by the addition of diphenyl diselenide (1.0 equiv) to a solution of promoter in solvent (3 mL), under nitrogen atmosphere at room temperature. After 15 min, imidazole **1a** (0.25 mmol) was added. The resulting mixture was stirred under temperature and time indicated in the table 1.

[b] Traces of the product were isolated and the starting material was recovered.

[c] Reaction was carried out with PhSeSePh (1.5 equiv).

[d] Reaction was carried out with PhSeSePh (0.75 equiv).

[e] The starting material was recovered.

[f] 1.5 mL of CH_2Cl_2 was used.

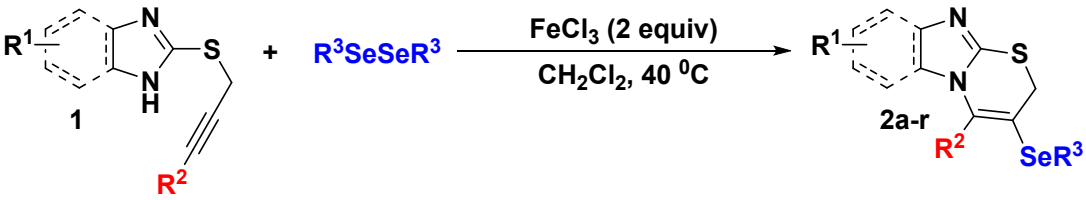
[g] 8 mL de CH_2Cl_2 was used.

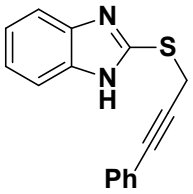
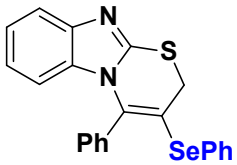
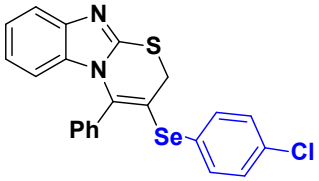
To determine the range of the optimized reaction conditions, further experiments were carried out using other thiopropargyl benzimidazoles **1** as well as other diorganyl dichalcogenides. The results are summarized in Tables 3 and 4. A wide range of thiopropargyl benzimidazoles bearing electron-donating or electron-withdrawing groups on either aromatic ring of the imidazole or directly bonded to the alkyne were compatible with these conditions. We also studied the effect of different diorganyl dichalcogenides on the outcome of the cyclization process. It was noted that the yields of the reaction with diaryl diselenides did not follow an expected reactivity order. According to our proposed mechanism (see the mechanism discussion and Scheme 3), we estimated that the electron-deficient aromatic ring would become the selenium atom more electropositive, which could increase the reactivity of diaryl diselenides toward interaction with the carbon-carbon triple bond. However, the results obtained did not indicate any relationship between the yields and electronic effects of substituents on the diorganyl diselenides. Under the optimized reaction conditions, a neutral diphenyl diselenide and an electron-deficient aryl diselenide having chlorine atom gave 3-(organochalcogenyl)-imidazothiazines **2a** and **2b** in good yields; however, diselenides having the aromatic ring substituted with fluoro and trifluoromethyl gave only moderate yields (Table 3, **2a**-**2d**). In addition to give the product in moderate yield, the

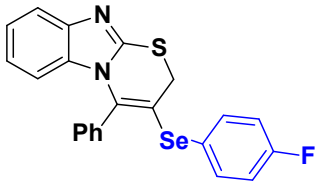
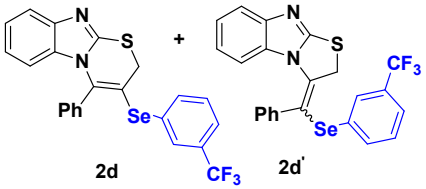
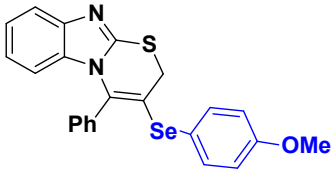
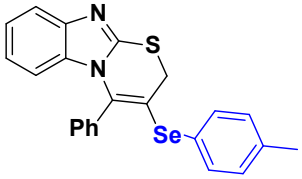
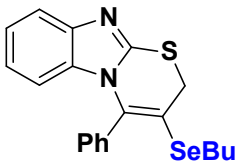
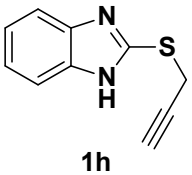
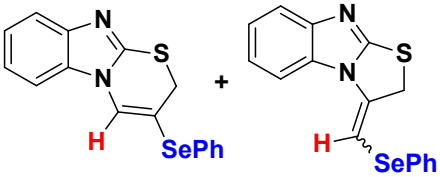
reaction with trifluoromethylphenyl diselenide suffered from lower selectivity affording an inseparable mixture of six and five membered ring products. In the case of diorganyl diselenides having electron-donating groups, the reaction using 4-methoxyphenyl diselenide failed to cyclize the thiopropargyl benzimidazole **1a**, whereas 4-methylphenyl diselenide gave the corresponding imidazothiazine **2f** in 76% yield (Table 3, **2e** and **2f**). We assume that the contrasting result obtained for 4-methoxyphenyl diselenide is because the oxophilic character of iron(III) chloride led to the decomposition of diselenide rather than promoting the formation of the species responsible for the cyclization. The optimized conditions were also efficient to dialkyl diselenide, which gave the corresponding imidazothiazine **2g** in moderate yields (Table 3, **2g**). Next, to determine the influence of substituents at the carbon-carbon triple bond of the alkyne, we kept the diphenyl diselenide invariable. Thus, the cyclization of thiopropargyl benzimidazole **1h**, which has a terminal alkyne, gave 40% yield of a 6:4 mixture of six and five membered, probably because of the absence of substituents on the triple bond enables the cyclization to occur on both C-1 and C-2 of the alkyne (Table 3, entry **2h**). In the examples, which have an alkyl chain directly bonded to the triple bond, the absence of pi (π) bonds next to the alkyne could become the carbon-carbon triple bond less reactive towards nucleophilic attack. However, under the optimized conditions both benzimidazoles **1K** and **1l** gave the products in good yields, indicating that the presence of alkyl groups at the alkyne did not influence the yields (Table 3, **2i** and **2j**). In all cases examined, with alkynes having aryl groups bearing electron-donating or electron-withdrawing substituents, the cyclized products were obtained in similar moderate yields, indicating that the cyclization was not

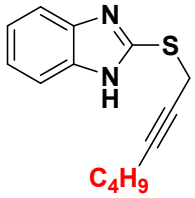
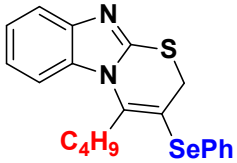
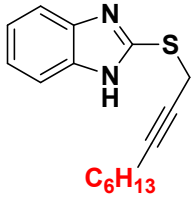
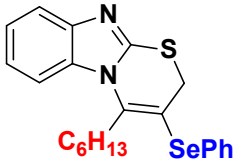
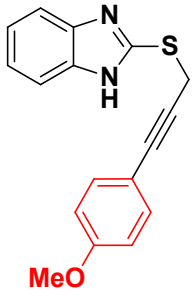
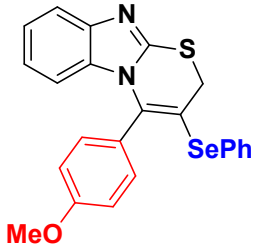
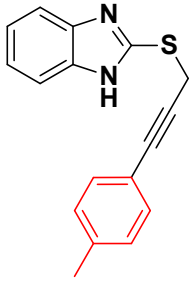
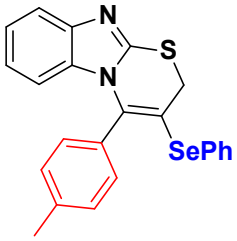
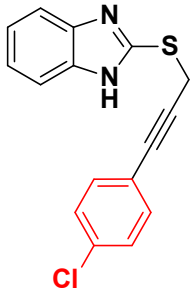
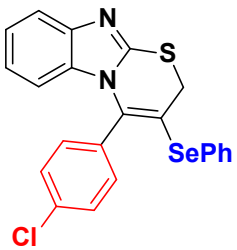
significantly influenced by the electronic effects of the aromatic rings (Table 3, **2k**-**2p**). When additional reactions were carried out with thiopropargyl benzimidazole having a methoxy group at the aromatic ring, the expected imidazothiazine **2q** was not formed (Table 3, **2q**). However, extended the reaction conditions to 4,5-diphenyl-imidazole derivative, the imidazothiazine **2r** was formed in 40% yield (Table 3, **2r**). We found an additional limitation in this methodology when the reaction of thiopropargyl benzimidazole **1a** was reacted under optimized reaction conditions in a larger scale (2 mmol). In this case, the product **2a** was obtained in 20% yield.

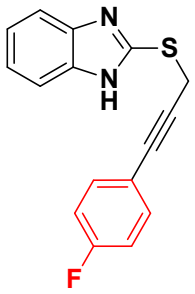
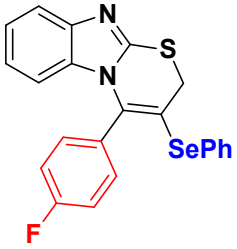
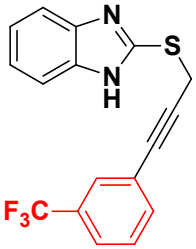
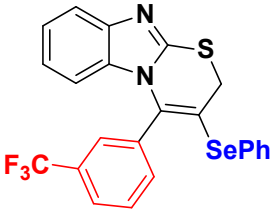
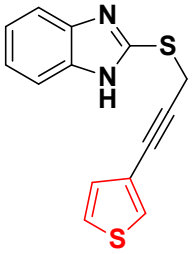
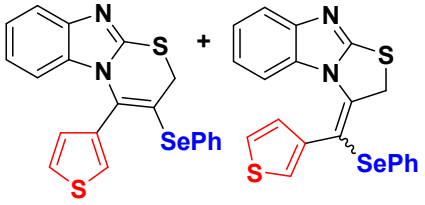
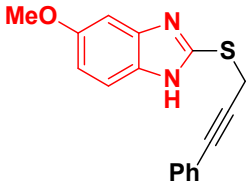
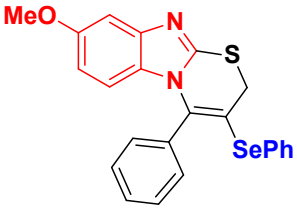
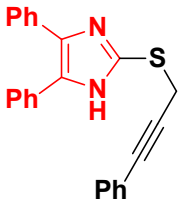
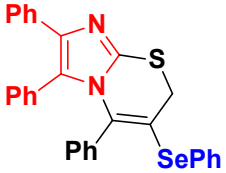
Table 3. Preparation of 3-(organochalcogenyl)-imidazothiazines **2a**-**r**.[a]



entry	substrate	$(R^3Se)_2$	product/yield/time
1	 **1a**	$(PhSe)_2$	 **2a**, 64% (0.5 h)
2	**1a**	$(p\text{-Cl-}C_6H_4Se)_2$	 **2b**, 75% (0.5 h)

3	**1a**	$(p\text{-F-}C_6H_4Se)_2$		**2c**, 46% (0.5 h)
4	**1a**	$(m\text{-}CF_3\text{-}C_6H_4Se)_2$		**2d** + **2d'**, 50% (73/27); (0.5 h)
5	**1a**	$(p\text{-MeO-}C_6H_4Se)_2$		**2e**, 0% (24 h)
6	**1a**	$(p\text{-Me-}C_6H_4Se)_2$		**2f**, 76% (0.5 h)
7	**1a**	$(BuSe)_2$		**2g**, 38% (1 h)
8	 **1h**	$(PhSe)_2$	 **2h** **2h'**	**2h** + **2h'**, 40% (60/40); (0.5 h)

9	 **1k**	$(PhSe)_2$	 **2i**, 68% (0.5 h)
10	 **1l**	$(PhSe)_2$	 **2j**, 74% (0.5 h)
11	 **1c**	$(PhSe)_2$	 **2k**, 30% (0.5 h)
12	 **1b**	$(PhSe)_2$	 **2l**, 46% (0.5 h)
13	 **1d**	$(PhSe)_2$	 **2m**, 42% (0.5 h)

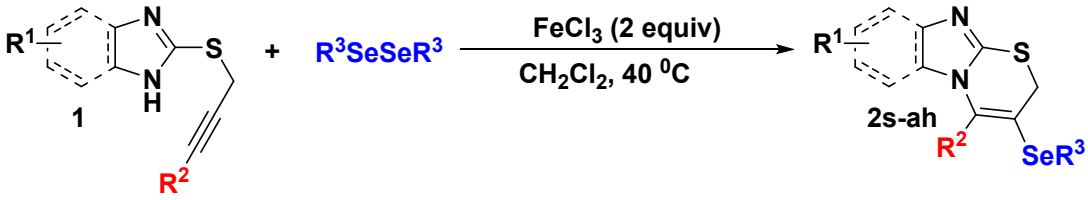
14	 **1e**	$(PhSe)_2$	 **2n**, 46% (0.5 h)
15	 **1f**	$(PhSe)_2$	 **2o**, 72% (0.5 h)
16	 **1g**	$(PhSe)_2$	 **2p** **2p'** **2p + 2p'**, 28% (84/16); (0.5 h)
17	 **1i**	$(PhSe)_2$	 **2q**, 0% (0.5 h)
18	 **1j**	$(PhSe)_2$	 **2r**, 40% (0.5 h)

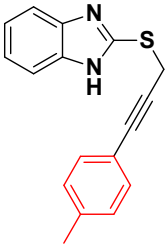
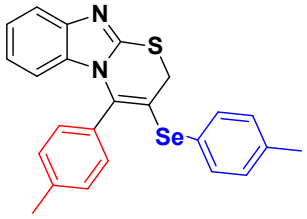
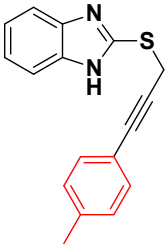
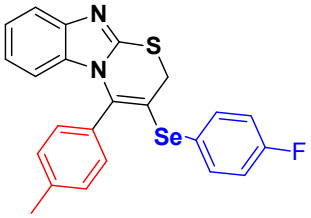
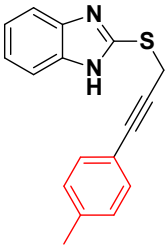
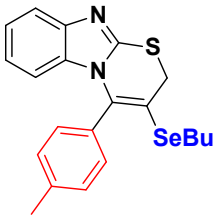
[a] The reaction was performed by the addition of diorganyl diselenides (1.0 equiv) to a $FeCl_3$ (2.0 equiv) solution in dichloromethane (3 mL), under air atmosphere, at room temperature. After 15 min, at this temperature, thiopropargyl benzimidazoles **1** (0.25 mmol) were added. The resulting mixture was stirred at room temperature for the time indicated in Table 3.

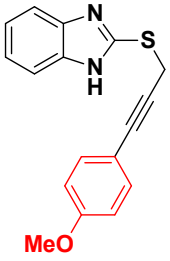
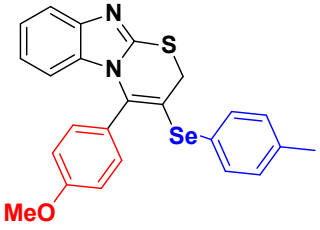
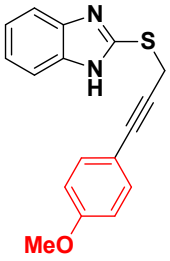
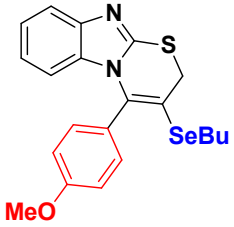
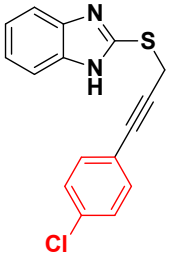
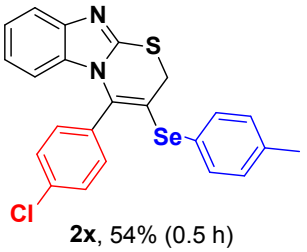
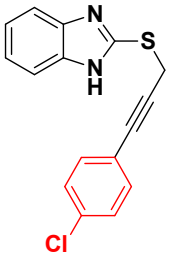
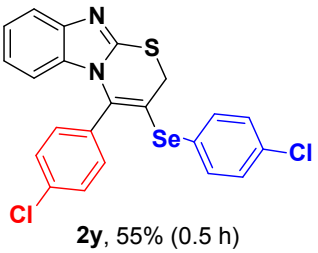
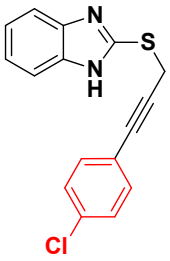
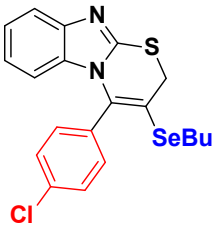
Furthermore, the optimal reaction conditions were then applied to other combination of thiopropargyl benzimidazoles **1** with diorganyl diselenides in which the cyclization proceeded in good yields, short reaction time and with complete selectivity in favor of six membered imidazothiazines (Table 4, **2s**-**2ah**). Concerning the use of other dichalcogenides, such as diorganyl ditellurides and diorganyl disulfides, we found additional limitations in the cyclization reactions. For example, the reaction with diphenyl ditelluride gave the product **2af** in poor yields and selectivity, whereas dibutyl ditelluride gave the product; however, it decomposed in the purification process (Table 4, **2ag**). Probably the alkyl group directly bonded to the tellurium atom could undergo a *beta*-telluroxide elimination, during the purification, promoting the decomposition. Besides, the reaction with diphenyl disulfide did not give any amount of desired product (Table 4, **2ah**). Probably, because the strength of the sulfur-sulfur bond hampers its cleavage by iron(III) chloride inhibiting the formation of desired products. The structural assignment of 3-(organochalcogenyl)-imidazothiazines **2** was based on NMR analysis and confirmed by the X-ray diffraction of three structures, which confirmed the cyclization as a 6-*endo*-dig process (Supporting Information, Figures S1-3,

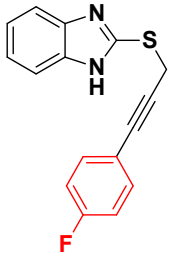
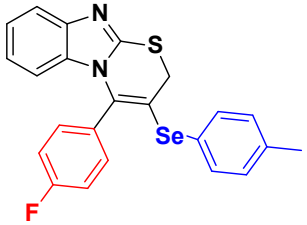
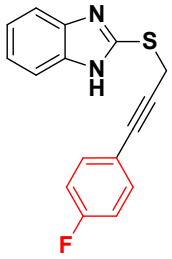
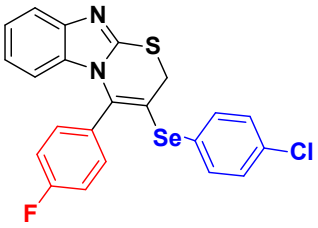
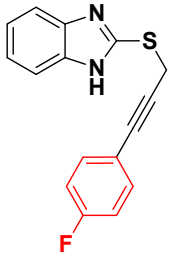
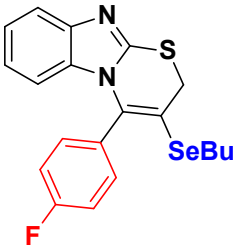
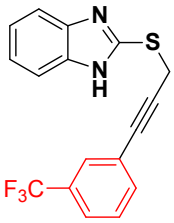
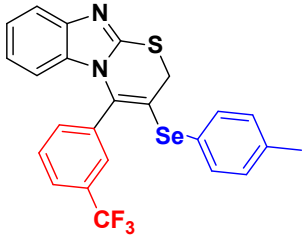
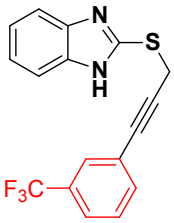
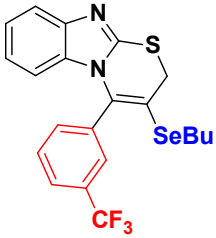
CCDC 1944844 for compound **2a**, 1944845 for compound **2m** and 1944843 for compound **2l**).

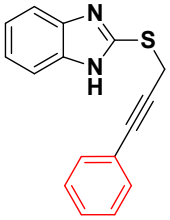
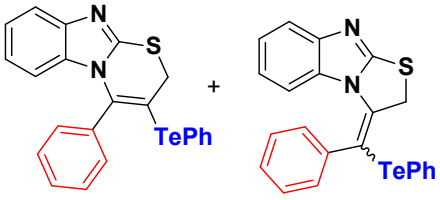
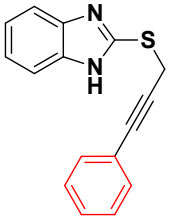
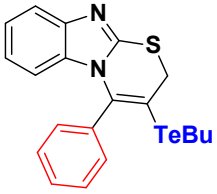
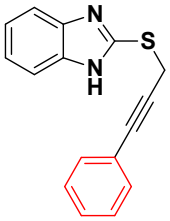
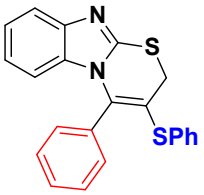
Table 4. Preparation of 3-(organochalcogenyl)-imidazothiazines **2s-ah**.[a]



Entry	Substrate	$(R^3Se)_2$	Product/Yield/Time
1	 **1b**	$(p\text{-Me-C}_6H_4Se)_2$	 **2s**, 44% (0.5 h)
2	 **1b**	$(p\text{-F-C}_6H_4Se)_2$	 **2t**, 40% (0.5 h)
3	 **1b**	$(BuSe)_2$	 **2u**, 55% (1 h)

4	 **1c**	$(p\text{-Me-C}_6\text{H}_4\text{Se})_2$	 **2v**, 20% (0.5 h)
5	 **1c**	$(\text{BuSe})_2$	 **2w**, 50% (1 h)
6	 **1d**	$(p\text{-Me-C}_6\text{H}_4\text{Se})_2$	 **2x**, 54% (0.5 h)
7	 **1d**	$(p\text{-Cl-C}_6\text{H}_4\text{Se})_2$	 **2y**, 55% (0.5 h)
8	 **1d**	$(\text{BuSe})_2$	 **2z**, 46% (1 h)

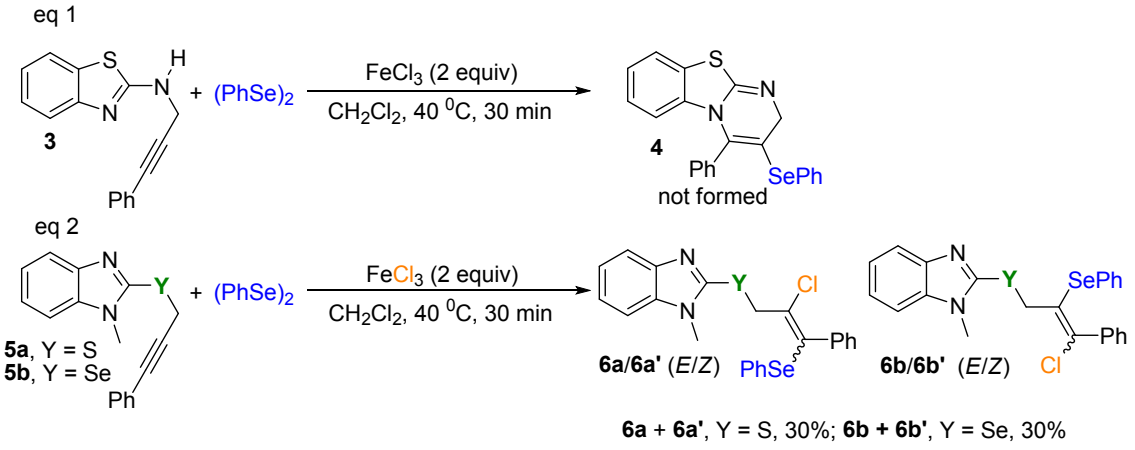
9	 **1e**	$(p\text{-Me-C}_6\text{H}_4\text{Se})_2$	 **2aa**, 90% (0.5 h)
10	 **1e**	$(p\text{-Cl-C}_6\text{H}_4\text{Se})_2$	 **2ab**, 28% (0.5 h)
11	 **1e**	$(\text{BuSe})_2$	 **2ac**, 65% (1 h)
12	 **1f**	$(p\text{-Me-C}_6\text{H}_4\text{Se})_2$	 **2ad**, 70% (0.5 h)
13	 **1f**	$(\text{BuSe})_2$	 **2ae**, 53% (1 h)

14	 **1a**	$(PhTe)_2$	 **2af** + **2af'** **2af + 2af'**, 28% (87/13); (1 h)
15	 **1a**	$(BuTe)_2$	 **2ag**, 0% (24 h)
16	 **1a**	$(PhS)_2$	 **2ah**, 0% (24 h)

[a] The reaction was performed by the addition of diorganyl dichalcogenides (1.0 equiv) to a $FeCl_3$ (2.0 equiv) solution in dichloromethane (3 mL), under air atmosphere, at room temperature. After 15 min, at this temperature, thiopropargyl benzimidazoles **1** (0.25 mmol) were added. The resulting mixture was stirred at room temperature for the time indicated in Table 4.

We next, applied the optimized conditions to the cyclization of other functionalized benzothiazoles and imidazoles, shown in scheme 1. For the cyclization of 2-*N*-propargyl benzothiazole **3** the expected cyclized thiazo pyrimidine **4** was not obtained. In this case, a complete decomposition of the starting material was observed (Scheme 1, eq 1). The reaction of *N*-methyl benzoimidazole derivatives **5** with iron(III) chloride and diphenyl diselenide was

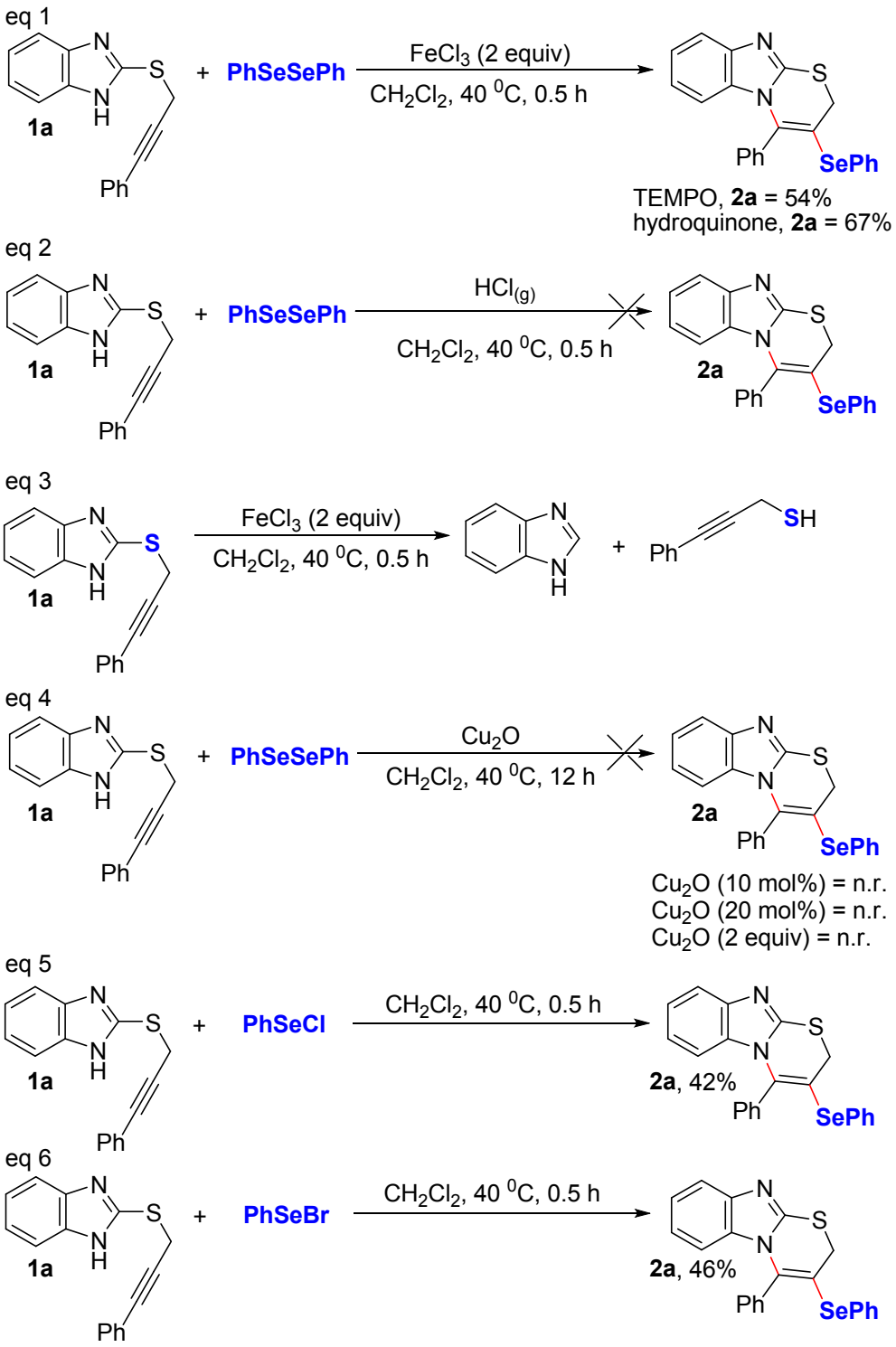
also investigated. Both thio and selenopropargyl-*N*-methyl benzoimidazoles failed in the formation of cyclized products. The major products in these reactions were the chlorovinyl chalcogenides **6a** and **6b**, which were probably formed via an electrophilic addition of phenylselenyl chloride to the carbon-carbon triple bond.



Scheme 1. Cyclization of 2-*N*-propargyl benzothiazole **3** and *N*-methyl benzoimidazole **5** derivatives.

Furthermore, a series of control experiments were performed to assist in the proposed mechanism for this cyclization reaction. These results are shown in scheme 2. Considering that iron complexes have been used to promote reactions via a radical pathway,[27] we conducted the cyclization of thiopropargyl benzimidazole **1a**, under optimized reaction conditions, in the presence of TEMPO and hydroquinone as free radical scavengers. Because the reaction yields were not altered in both cases, we assume that a radical mechanism, which could involve the PhSe radical species, is improbable (Scheme 2, eq 1). Next, to exclude that the HCl, released from $FeCl_3$, could act as the catalyst to promote the cleavage of diphenyl diselenide and the cyclization, the

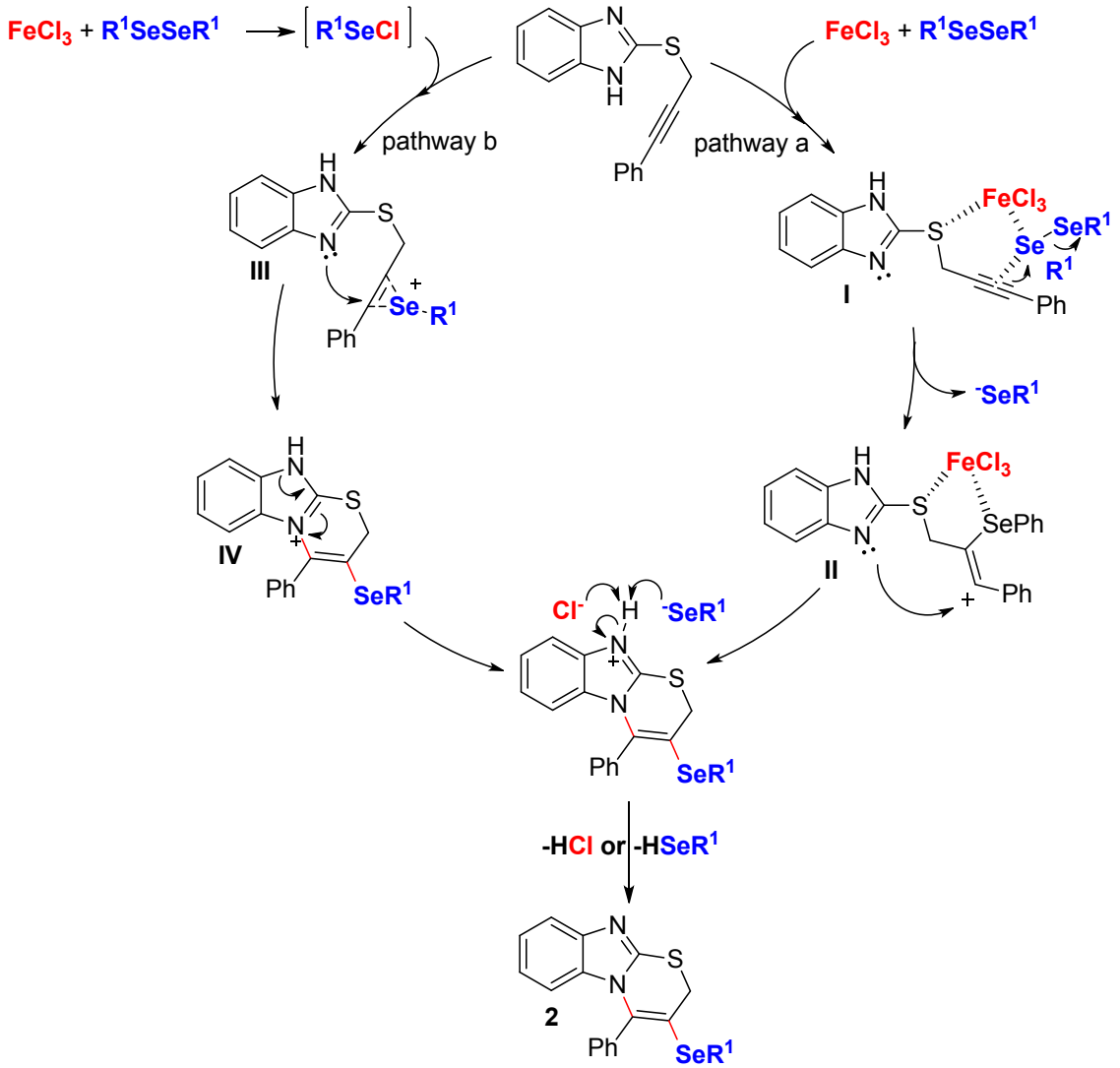
thiopropargyl benzimidazole **1a** was reacted with a mixture of diphenyl diselenide and $HCl_{(g)}$. Under these conditions, **2a** was not formed and the thiopropargyl benzimidazole and diphenyl diselenide were recovered (Scheme 2, eq 2). Subsequently, the reaction of thiopropargyl benzimidazole **1a** with iron(III) chloride under optimized reaction conditions, in the absence of diphenyl diselenide led to a complete decomposition of **1a** in benzoimidazole and propargyl mercaptan (Scheme 2, eq 3). These last two experiments indicated that the cooperative action between diphenyl diselenide and iron(III) chloride are essential to promote the cyclization. We described that a mixture of copper catalyst and diorganyl diselenide is highly active in promoting the cyclization of unsaturated substrates.[28] Thus, to eliminate the possibility that trace amounts of copper, present as impurity in the iron(III) chloride,[29] could act as the catalyst in the present cyclization, we performed three experiments using diselenides and copper as the catalyst. Compound **2a**, however, was not obtained in any of these reactions (Scheme 2, eq 4). Finally, to verify whether a selenium electrophilic species, generated in situ from the reaction of diorganyl diselenide with iron(III) chloride, could act as a promoter of the cyclization, we carried out two experiments using phenylselenyl chloride and phenylselenyl bromide. These reactions led to the formation of **2a** in 42 and 46% yields, respectively (Scheme 2, eq 5).



Scheme 2. Control experiments to support the proposed mechanisms.

On the basis of the above results, we can anticipate that a mixture of iron(III) chloride and diorganyl diselenides must be the main promoter of this cyclization; however, a direct action of organoselenyl chloride as the cyclizing agent can not

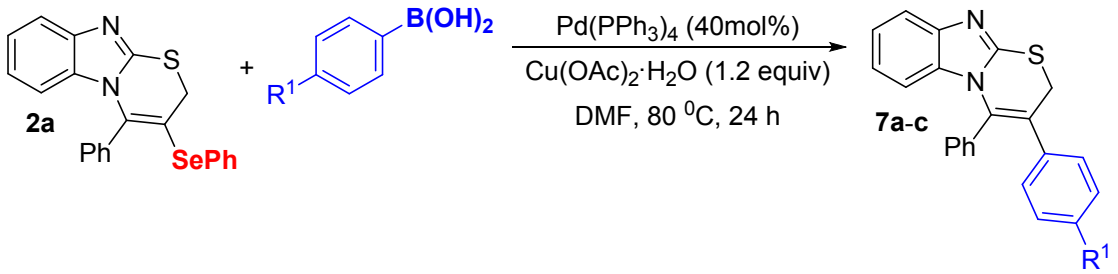
be discarded. For these reasons, two mechanisms can be proposed for the cyclization of thiopropargyl benzimidazoles **1** with diorganyl diselenides and iron(III) chloride (Scheme 3). In the pathway a, it is shown the mechanism involving a cooperative action of diorganyl diselenides and iron(III) chloride to promote the cyclization of thiopropargyl benzimidazoles **1**. It could include (i) the interaction of iron(III) chloride with one selenium atom from diorganyl diselenide activating the molecule towards a nucleophilic attack; (ii) the alkyne coordination to the electropositive selenium atom to form the intermediary **I**; (iii) nucleophilic *anti*-attack of the nitrogen atom on the activated triple bond leads to the intermediate **II**; (iv) removal of the hydrogen by breaking the N-H, promoted by the selenolate anion, restores the aromatic system and releases the 3-(organochalcogenyl)-imidazothiazines **2** (Scheme 3, pathway a). We suppose that the interaction of iron(III) chloride with sulfur and selenium atom in the intermediaries **I** and **II** directs the attack on the C-1 of the triple bond leading to products in a regioselective 6-*endo*-dig mode. In the pathway b, it is described the mechanism via an electrophilic cyclization, which involves: (i) the initial formation of selenium electrophilic species (RSeCl) by the reaction of diorganyl diselenides with iron(III) chloride; (ii) the alkyne coordination to the RSeCl leads to the seleniranium intermediate **III**; (iii) the subsequent nitrogen nucleophilic intramolecular *anti*-attack at the activated triple bond affords the intermediary **IV** and chloride ion; (iv) the removal of a hydrogen bonded to nitrogen by chloride ion gives the cyclized product **2** (Scheme 3, pathway b).



Scheme 3. Proposed mechanism for the cyclization of thiopropargyl benzimidazoles.

The high reactivity of the Csp^2-selenium bond becomes the 3-(organochalcogenyl)-imidazothiazines extremely versatile substrates to introduce different functional groups at the 3-position of thiazine ring, especially via the formation of new carbon-carbon bonds.[30] In order to prove the potential of 3-(organochalcogenyl)-imidazothiazine derivatives as substrates for increasing their molecular complexity, we tested the reactivity of these compounds toward the palladium-catalyzed Suzuki cross-coupling reactions.

Thus, the reaction of 3-(phenylselenyl)-imidazothiazines **2a** with boronic acids catalyzed by $Pd(PPh_3)_4$ in the presence of $Cu(AcO)_2 \cdot H_2O$, in DMF at 80 ^{0}C gave the 3-aryl substituted imidazothiazines **7a**-**c** in moderate yields (Scheme 4).



7a, R^1 = H, 60%; **7b**, R^1 = Me, 50%; **7c**, R^1 = OMe, 42%

Scheme 4. Reactivity of **2a** towards palladium-catalyzed Suzuki cross-coupling reactions.

Conclusion

In conclusion, we developed an iron(III) chloride/diorganyl diselenide-promoted cyclization of thiopropargyl benzimidazoles leading to 3-(organoselenyl)-imidazothiazines in moderate to good yields. The mechanism studies indicated that the cyclization took place via a regioselective 6-*endo*-dig mode through a cooperative action of diorganyl diselenides and iron(III) chloride; however, a direct electrophilic cyclization promoted by the in situ formed electrophilic organoselenium species cannot be ruled out. The main advantage of our methodology is that different from other cyclizations of thiopropargyl benzimidazoles current reported, our protocol allowed the preparation of the 6-membered heterocycles with the concomitant insertion of a new functionality, which becomes the heterocycles useful intermediates in many processes, including the transition-metal-catalyzed carbon-carbon bond formation. Another advantage is that the cyclization reaction generated the product with an

organoselenium moiety in the structure, which is important in terms of new applications in synthesis and medicinal chemistry.

Experimental Section

Materials and Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a 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 capillary tube with diphenyl diselenide as 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 starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All

other solvents were ACS or 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 FeCl3 was used in 99.99% purity purchased from commercial suppliers.

General procedure for the preparation of thiopropargyl benzimidazoles 1a-l, 5a and 5b[18]: Propargyl bromide (7.2 mmol; 1.2 equiv) and K_2CO_3 (0.828 g; 6 mmol; 1 equiv) were added to a solution of the 1*H*-imidazole-2-thione (6 mmol) in anhydrous acetone (40 mL) under nitrogen. The mixture was stirred at room temperature for 16 h. After evaporation of the solvent, water (30 mL) and AcOEt (30 mL) were sequentially added. The phases were separated and the organic layers were washed with brine and dried over Mg_2SO_4. After filtration and evaporation of the solvent, thiopropargyl benzimidazoles was purified by column chromatography on silica gel by using a solution of hexane/AcOEt.

2-((3-Phenylprop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1a)[17b]: The product was isolated by column chromatography (hexane:ethyl acetate 90:10) as an orange solid. Yield: 1.378 g (87%); mp 179-181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.59-7.54 (m, 2H), 7.34-7.19 (m, 8H), 4.28 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 148.5, 138.9, 131.7, 128.5, 128.2, 122.7, 122.3, 114.4, 84.4, 84.0, 22.7. MS (EI, 70 eV; *m/z* (relative intensity)): 265 ([M+1], 19), 264 (100), 207 (27), 187 (11), 115 (31), 103 (19). HRMS calcd for $C_{16}H_{13}N_2S$ (ESI-TOF, $[M + H]^+$): 265.0799. Found: 265.0812.

2-((3-(*p*-Tolyl)prop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1b): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a red solid. Yield: 1.234 g (70%); mp 152-154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55-7.52 (m, 2H), 7.24-7.18 (m, 4H), 7.03 (d, *J* = 7.7 Hz, 2H), 4.24 (s, 2H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 148.7, 138.6, 131.7, 129.0, 122.6, 119.4, 84.6, 83.5, 22.8, 21.4. MS (EI, 70 eV; *m/z* (relative intensity)): 279 ([M+1], 20), 278 (100), 207 (20), 128 (15), 115 (23), 91 (14). HRMS calcd for $C_{17}H_{15}N_2S$ (ESI-TOF, $[M + H]^+$): 279.0956. Found: 279.0948.

2-((3-(4-Methoxyphenyl)prop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1c): The product was isolated by column chromatography (hexane:ethyl acetate 90:10) as a red solid. Yield: 0.987 g (56%); mp 139-141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54-7.52 (m, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.20-7.18 (m, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 4.24 (s, 2H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 159.9, 148.7, 133.2, 122.6, 114.7, 114.0, 84.5, 82.8, 55.3, 22.9. MS (EI, 70 eV; *m/z* (relative intensity)): 295 ([M+1], 19), 294 (100), 207 (23), 192 (10), 103 (20), 77 (13). HRMS calcd for $C_{17}H_{15}N_2OS$ (ESI-TOF, $[M + H]^+$): 295.0905. Found: 295.0905.

2-((3-(4-Chlorophenyl)prop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1d): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a red solid. Yield: 0.679 g (38%); mp 169-171 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.50-7.48 (m, 2H), 7.41-7.35 (m, 4H), 7.16-7.14 (m, 2H), 4.43 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6. 100 MHz): δ (ppm) 148.8, 133.9, 133.6, 129.3, 122.1, 121.4, 87.7, 81.9, 21.3. MS (EI, 70 eV; *m/z* (relative intensity)): 300

([M+2], 33), 298 (100), 261 (16), 207 (52), 115 (39), 102 (42). HRMS calcd for $C_{16}H_{12}ClN_2S$ (ESI-TOF, $[M + H]^+$): 299.0410. Found: 299.0415.

2-((3-(4-Fluorophenyl)prop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1e): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a red solid. Yield: 1.184 g (70%); mp 185-187 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.51-7.49 (m, 2H), 7.42-7.39 (m, 2H), 7.18-7.13 (m, 4H), 4.42 (s, 2H). $^{13}C\{^1H\}$ NMR (DMSO-d_6. 100 MHz): δ (ppm) 162.3 (d, *J* = 247.4 Hz), 148.7, 134.0 (d, *J* = 8.7 Hz), 121.9, 118.87 (d, *J* = 3.6 Hz), 116.1 (d, *J* = 22.2 Hz), 85.9, 82.1, 21.3. MS (EI, 70 eV; *m/z* (relative intensity)): 283 ([M+1], 10), 282 (100), 207 (94), 133 (64), 102 (09), 75 (07). HRMS calcd for $C_{16}H_{12}FN_2S$ (ESI-TOF, $[M + H]^+$): 283.0705. Found: 283.0705.

2-((3-(3-(Trifluoromethyl)phenyl)prop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1f): The product was isolated by column chromatography (hexane:ethyl acetate 90:10) as an orange solid. Yield: 1.59 g (80%); mp 137-139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 10.53 (s, 1H), 7.61-7.53 (m, 2H), 7.53-7.44 (m, 2H), 7.40-7.35 (m, 1H), 7.33-7.26 (m, 1H), 7.24-7.16 (m, 2H), 4.29 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 148.4, 139.3, 130.8 (q, *J* = 32.3 Hz), 128.7, 128.4 (q, *J* = 3.9 Hz), 124.9 (q, *J* = 3.3 Hz), 123.7 (q, *J* = 273.0 Hz), 122.2, 114.4, 85.8, 82.7, 25.5. MS (EI, 70 eV; *m/z* (relative intensity)): 333 ([M+1], 21), 332 (100), 331 (23), 187 (23), 134 (17), 102 (21). HRMS calcd for $C_{17}H_{12}F_3N_2S$ (ESI-TOF, $[M + H]^+$): 333.0673. Found: 333.0680.

2-((3-(Thiophen-3-yl)prop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1g): The product was isolated by column chromatography (hexane:ethyl acetate 90:10) as an orange solid. Yield: 1.296 g (80%); mp 169-171 °C. ^{1}H NMR ($CDCl_3$, 400

MHz): δ (ppm) 7.54-7.52 (m, 2H), 7.35-7.34 (m, 1H), 7.20-7.19 (m, 3H), 7.01 (d, *J* = 4.5 Hz, 1H), 4.24 (s, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 148.4, 131.8, 129.9, 129.2, 128.3, 125.3, 122.7, 121.6, 83.9, 79.7, 22.8. MS (EI, 70 eV; *m/z* (relative intensity)): 271 ([M+1], 16), 270 (100), 237 (34), 207 (24), 134 (32), 90 (30). HRMS calcd for $C_{14}H_{11}N_2S_2$ (ESI-TOF, $[M + H]^+$): 271.0364. Found: 271.0364.

2-(Prop-2-yn-1-ylthio)-1H-benzo[d]imidazole (1h)[18a]: The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a white solid. Yield: 0.868 g (77%); mp 169-171 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 12.63 (s, 1H), 7.48 (s, 2H), 7.16-7.12 (m, 2H), 4.16 (d, *J* = 2.6 Hz, 2H), 3.18 (t, *J* = 2.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6. 100 MHz): δ (ppm) 148.8, 122.1, 118.3, 112.0, 110.8, 80.5, 74.5, 20.31. MS (EI, 70 eV; *m/z* (relative intensity)): 189 ([M+1], 14), 188 (100), 187 (53), 155 (12), 129 (14), 102 (15). HRMS calcd for $C_{10}H_9N_2S$ (ESI-TOF, $[M + H]^+$): 189.0486. Found: 189.0479.

5-Methoxy-2-((3-phenylprop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (1i): The product was isolated by column chromatography (hexane:ethyl acetate 90:10) as a red solid. Yield: 0.493 g (28%); mp 145-147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45 (d, *J* = 8.8 Hz, 1H), 7.30-7.21 (m, 5H), 7.04 (s, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.22 (s, 2H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 156.5, 147.4, 131.7, 128.4, 128.2, 122.5, 112.1, 84.4, 84.3, 55.8, 23.0. MS (EI, 70 eV; *m/z* (relative intensity)): 295 ([M+1], 17), 294 (100), 279 (38), 251 (47), 207 (34), 115 (44). HRMS calcd for $C_{17}H_{15}N_2OS$ (ESI-TOF, $[M + H]^+$): 295.0905. Found: 295.0905.

4,5-Diphenyl-2-((3-phenylprop-2-yn-1-yl)thio)-1H-imidazole (1j): The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a red solid. Yield: 1.335 g (61%); mp 142-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45-7.43 (m, 4H), 7.34-7.31 (m, 2H), 7.27-7.23 (m, 9H), 3.92 (s, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 138.2, 131.7, 128.5, 128.4, 128.3, 127.7, 127.5, 122.5, 85.2, 84.8, 24.7. MS (EI, 70 eV; *m/z* (relative intensity)): 367 ([M+1], 11), 366 (89), 207 (64), 193 (83), 115 (100), 103 (58). HRMS calcd for $C_{24}H_{19}N_2S$ (ESI-TOF, $[M + H]^+$): 367.1269. Found: 367.1273.

2-(hept-2-yn-1-ylthio)-1H-benzo[d]imidazole (1k): The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a white solid. Yield: 0.726 g (52%); mp 125-127 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.58-7.56 (m, 2H), 7.22-7.19 (m, 2H), 4.04 (t, J = 2.4 Hz, 2H), 2.13-2.08 (m, 2H), 1.40-1.26 (m, 4H), 0.81 (t, J = 7.3 Hz, 3H). 13C{1H} NMR (CDCl3. 100 MHz): δ (ppm) 149.3, 139.3, 122.4, 114.3, 85.3, 74.6, 30.5, 22.2, 21.8, 18.4, 13.4. MS (EI, 70 eV; m/z (relative intensity)): 245 ([M+1], 17), 244 (95), 202 (100), 187 (48), 169 (28), 144 (41). HRMS calcd for $C_{14}H_{17}N_2S$ (ESI-TOF, [M + H]+): 245.1107. Found: 245.1097.

2-(non-2-yn-1-ylthio)-1H-benzo[d]imidazole (1l): The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a white solid. Yield: 1.158 g (71%); mp 107-109 °C. 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.57-7.55 (m, 2H), 7.23-7.19 (m, 2H), 4.04 (t, *J* = 2.4 Hz, 2H), 2.13-2.08 (m, 2H), 1.44-1.37 (m, 2H), 1.31-1.18 (m, 6H), 0.84 (t, *J* = 6.9 Hz, 3H). 13C{1H} NMR (CDCl3. 100 MHz): δ (ppm) 149.3, 139.3, 122.4, 114.3, 85.3, 74.6, 31.2, 28.4, 22.4, 22.2, 18.8, 13.9. MS (EI, 70 eV; m/z (relative intensity)): 273 ([M+1], 14), 272

(81), 202 (100), 187 (43), 150 (26), 144 (44). HRMS calcd for $C_{16}H_{21}N_2S$ (ESI-TOF, [M + H]+): 273.1420. Found: 273.1413.

1-Methyl-2-((3-phenylprop-2-yn-1-yl)thio)-1H-benzo[d]imidazole (5a): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a red solid. Yield: 0.834 g (50%); mp 74-76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.77-7.65 (m, 1H), 7.40-7.31 (m, 2H), 7.31-7.16 (m, 6H), 4.37 (s, 2H), 3.66 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.2, 143.0, 136.6, 131.7, 128.3, 128.1, 122.5, 122.2, 122.0, 118.4, 108.7, 84.0, 83.9, 30.1, 22.7. HRMS calcd for $C_{17}H_{15}N_2S$ (ESI-TOF, $[M + H]^+$): 279.0956. Found: 279.0950.

1-Methyl-2-((3-phenylprop-2-yn-1-yl)selanyl)-1H-benzo[d]imidazole (5b): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a red solid. Yield: 0.938 g (48%); mp 69-71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.78-7.72 (m, 1H), 7.33-7.20 (m, 8H), 4.27 (s, 2H), 3.76 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 145.2, 143.5, 136.6, 131.7, 128.3, 128.2, 122.7, 122.2, 118.6, 109.0, 84.9, 84.7, 31.3, 15.0. HRMS calcd for $C_{17}H_{15}N_2Se$ (ESI-TOF, $[M + H]^+$): 327.0400. Found: 327.0412.

General procedure for the preparation of 3-(organochalcogenyl)-imidazothiazines 2a-ad: Diorganoyl dichalcogenides (0.25 mmol; 1 equiv) was added to a solution of CH_2Cl_2 (3 mL) and $FeCl_3$ (0.50 mmol; 2 equiv) under a nitrogen atmosphere. The resulting solution was stirred for 15 min at room temperature. After this time, the appropriate substrate **1** (0.25 mmol) was added and the resulting solution was heated in oil bath at 40 °C for the time indicated in Table 1 and Table 2. The mixture was filtered through silica gel with ethyl

acetate and concentrated under vacuum. The residue was purified by flash chromatography using a solution of hexane:ethyl acetate as eluent.

4-Phenyl-3-(phenylselanyl)-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine (2a): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a white solid. Yield: 0.067 g (64%); mp 160-162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62 (d, *J* = 8.5 Hz, 1H), 7.56-7.44 (m, 5H), 7.33-7.30 (m, 5H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 5.86 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.0, 142.9, 138.5, 134.2, 133.1, 133.0, 130.1, 129.9, 129.6, 129.3, 128.6, 128.0, 122.9, 122.4, 118.9, 112.2, 110.8, 31.98. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 413.4. MS (EI, 70 eV; *m/z* (relative intensity)): 422 ([M+2], 9), 420 (36), 263 (100), 237 (39), 180 (22), 134 (28). HRMS calcd for $C_{22}H_{17}N_2SSe$ (ESI-TOF, $[M + H]^+$):421.0278. Found: 421.0270.

3-((4-Chlorophenyl)selanyl)-4-phenyl-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2b): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.085 g (75%); mp 184-186 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62 (d, *J* = 8.0 Hz, 1H), 7.54-7.42 (m, 5H), 7.32-7.23 (m, 4H), 7.16-7.05 (m, 1H), 6.84-6.80 (m, 1H), 5.84 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 149.9, 142.8, 139.2, 134.3, 134.1, 134.1, 133.0, 130.1, 130.0, 129.8, 128.6, 127.5, 123.0, 122.5, 118.9, 112.1, 110.1, 32.0. MS (EI, 70 eV; *m/z* (relative intensity)): 477 ([M+1], 5), 263 (48), 237 (19), 207 (100), 134 (31), 77 (23). HRMS calcd for $C_{22}H_{16}ClN_2SSe$ (ESI-TOF, $[M + H]^+$): 454.9888. Found: 454.9879.

3-((4-Fluorophenyl)selanyl)-4-phenyl-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2c): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.049 g (46%); mp 166-168 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 8.0 Hz, 1H), 7.54-7.43 (m, 5H), 7.32-7.29 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.81 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.85 (dt, *J* = 8.3, 1.0 Hz, 1H), 3.75 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) δ 162.83 (d, *J* = 249.3 Hz), 149.8, 142.8, 138.3, 135.5 (d, *J* = 8.1 Hz), 134.1, 133.0, 130.1, 130.0, 128.7, 123.6 (d, *J* = 3.7 Hz), 122.9, 122.4, 118.9, 116.8 (d, *J* = 21.9 Hz), 112.1, 110.9, 31.7. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 405.4. MS (EI, 70 eV; *m/z* (relative intensity)): 440 ([M+2], 7), 438 (32), 281 (31), 263 (100), 237 (42), 207 (96). HRMS calcd for $C_{22}H_{16}FN_2SSe$ (ESI-TOF, $[M + H]^+$): 439.0183. Found: 439.0174.

4-Phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine (2d) and 3-(phenyl((3-(trifluoromethyl)phenyl)selanyl)methylene)-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazole (mixture E/Z; 2d'): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow oil. Yield: 0.061 g (50%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.76-7.03 (m, 29H), 4.91 (s, 1H), 4.52 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 148.7, 148.6, 138.6, 136.8, 131.7, 130.3, 130.2, 130.1, 129.9, 129.5, 129.2, 129.1, 128.8, 128.7, 128.2, 128.1, 127.8, 125.8, 125.4, 125.2, 124.8, 124.7, 124.0, 122.7, 122.6, 118.9, 112.3, 39.2, 32.5, 32.0, 29.6, 29.6. MS (EI, 70 eV; *m/z* (relative intensity)): 488 ([M+1], 39), 263 (100), 237 (44), 134 (14), 90 (05).

4-Phenyl-3-(p-tolylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2f): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.082 g (76%); mp 179-181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (dq, *J* = 8.0, 1.2, 1.0 Hz, 1H), 7.54-7.44 (m, 5H), 7.34-7.31 (m, 2H), 7.13-7.06 (m, 3H), 6.81 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.86 (dt, *J* = 8.3, 1.0 Hz, 1H), 3.74 (s, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.0, 142.9, 138.4, 137.5, 134.2, 133.7, 133.0, 130.4, 130.1, 129.9, 128.6, 125.1, 122.8, 122.3, 118.9, 112.1, 111.5, 31.5, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 436 ([M+2], 10), 434 (41), 263 (100), 237 (38), 194 (22), 134 (26). HRMS calcd for $C_{23}H_{19}N_2SSe$ (ESI-TOF, $[M + H]^+$): 435.0434. Found: 435.0437.

3-(Butylselanyl)-4-phenyl-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2g): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.038 g (38%); 104-106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 8.0 Hz, 1H), 7.60-7.41 (m, 3H), 7.27-7.24 (m, 2H), 7.11 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 6.79 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.82 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 1.65 (quint, *J* = 7.4 Hz, 2H), 1.32 (sext, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.1, 142.8, 139.0, 134.5, 133.0, 130.4, 129.6, 128.4, 122.8, 122.3, 118.8, 112.2, 108.6, 32.4, 32.1, 26.8, 22.7, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 402 ([M+2], 8), 400 (31), 263 (100), 237 (19), 231 (38), 133 (18). HRMS calcd for $C_{20}H_{21}N_2SSe$ (ESI-TOF, $[M + H]^+$): 401.0591. Found: 401.0593.

3-(Phenylselanyl)-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine (2h) and 3-((phenylselanyl)methylene)-2,3-dihydrobenzo[4,5]imidazo[2,1-b]thiazole (mixture E/Z; 2h'): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow oil. Yield: 0.034 g (40%); 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.67-7.63 (m, 2H), 7.58-7.56 (m, 3H), 7.48-7.46 (m, 2H), 7.34-7.22 (m, 10H), 6.71 (t, *J* = 2.3 Hz, 1H), 4.61 (d, *J* = 2.3 Hz, 1H), 3.80 (d, *J* = 1.1 Hz, 2H). 13C{1H} NMR (CDCl3. 100 MHz): δ (ppm) 159.1, 149.6, 146.6, 143.0, 138.3, 133.6, 132.5, 132.0, 130.6, 129.7, 129.6, 129.4, 128.6, 128.2, 127.9, 127.2, 126.9, 123.7, 123.6, 123.0, 122.6, 122.5, 119.2, 119.1, 110.2, 107.9, 107.3, 95.0, 38.7, 31.2. MS (EI, 70 eV; *m/z* (relative intensity)): 346 ([M+2], 14), 344 (61), 263 (24), 187 (100), 129 (39), 102 (22).

4-Butyl-3-(phenylselanyl)-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine (2i): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a colorless oil. Yield: 0.068 g (68%). 1H NMR (CDCl3, 400 MHz): δ (ppm) 7.68-7.66 (m, 1H), 7.58-7.55 (m, 2H), 7.52-7.49 (m, 2H), 7.35-7.21 (m, 4H), 3.63 (s, 2H), 3.26 (t, *J* = 7.2 Hz, 2H), 1.51-1.42 (m, 2H), 1.42-1.32 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). 13C{1H} NMR (CDCl3. 100 MHz): δ (ppm) 151.5, 143.3, 141.6, 132.9, 132.1, 131.4, 129.7, 127.7, 123.1, 122.9, 119.4, 111.8, 109.7, 32.4, 31.9, 30.4, 21.9, 13.7. MS (EI, 70 eV; m/z (relative intensity)): 402 ([M+2], 14), 400 (58), 243 (80), 201 (100), 161 (30), 134 (22). HRMS calcd for $C_{20}H_{21}N_2SSe$ (ESI-TOF, [M + H]+): 401.0585. Found: 401.0565.

4-Hexyl-3-(phenylselanyl)-2H-benzo[4,5]imidazo[2,1-b][1,3]thiazine (2j): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a colorless oil. Yield: 0.079 g (74%). 1H NMR (CDCl3, 400 MHz): δ

(ppm) 7.68-7.66 (m, 1H), 7.58-7.55 (m, 1H), 7.51-7.48 (m, 2H), 7.34-7.21 (m, 5H), 3.63 (s, 2H), 3.25 (t, *J* = 7.5 Hz, 3H), 1.50-1.44 (m, 2H), 1.36-1.33 (m, 2H), 1.25-1.21 (m, 4H), 0.84 (m, 3H). 13C{1H} NMR (CDCl3. 100 MHz): δ (ppm) 151.4, 143.2, 141.6, 132.7, 131.9, 131.4, 129.6, 127.6, 123.1, 122.8, 119.3, 111.7, 109.6, 32.3, 32.1, 31.2, 28.4, 28.2, 22.4, 13.9. MS (EI, 70 eV; m/z (relative intensity)): 430 ([M+2], 13), 428 (57), 271 (87), 201 (100), 161 (20), 151 (27). HRMS calcd for $C_{22}H_{25}N_2SSe$ (ESI-TOF, [M + H]+): 429.0876. Found: 429.0876.

4-(4-Methoxyphenyl)-3-(phenylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2k): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.033 g (30%); mp 122-124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.63-7.60 (m, 1H), 7.56-7.54 (m, 2H), 7.30-7.27 (m, 3H), 7.25-7.22 (m, 2H), 7.13 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 6.98-6.96 (m, 2H), 6.86 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.95 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 160.7, 150.1, 142.8, 138.3, 133.1, 133.0, 131.5, 129.6, 129.4, 128.0, 126.5, 122.9, 122.4, 118.8, 114.0, 112.4, 110.2, 55.3, 31.9. MS (EI, 70 eV; *m/z* (relative intensity)): 450 (09), 293 (87), 224 (31), 207 (100), 133 (30), 77 (33). HRMS calcd for $C_{23}H_{19}N_2OSSe$ (ESI-TOF, $[M + H]^+$): 451.0383. Found: 451.0383.

3-(Phenylselanyl)-4-(p-tolyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2l): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.050 g (46%); mp 159-161 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.65 (d, *J* = 7.9 Hz, 1H), 7.56-7.54 (m, 2H), 7.31-7.25 (m, 5H), 7.20-7.13 (m, 3H), 6.86 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.94 (d, *J* = 8.3 Hz,

1H), 3.78 (s, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.0, 141.2, 140.3, 138.0, 133.2, 132.7, 131.0, 130.0, 129.6, 129.4, 129.0, 128.1, 123.3, 122.7, 118.3, 112.5, 111.2, 31.7, 21.5. MS (EI, 70 eV; *m/z* (relative intensity)): 435 ([M+1], 9), 434 (35), 277 (100), 262 (26), 251 (32), 134 (18). HRMS calcd for $C_{23}H_{19}N_2SSe$ (ESI-TOF, $[M + H]^+$): 435.0434. Found: 435.0431.

4-(4-Chlorophenyl)-3-(phenylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2m): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.048 g (42%); mp 141-143 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.63 (d, *J* = 8.1 Hz, 1H), 7.54-7.51 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.31-7.24 (m, 5H), 7.15 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 6.89 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.96 (d, *J* = 8.3 Hz, 1H), 3.78 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.1, 142.1, 137.0, 136.1, 133.2, 132.4, 131.5, 129.7, 129.0, 128.8, 128.3, 123.3, 122.8, 118.8, 112.1, 112.0, 32.0. MS (EI, 70 eV; *m/z* (relative intensity)): 456 ([M+2], 17), 454 (35), 297 (65), 262 (100), 236 (40), 133 (31). HRMS calcd for $C_{22}H_{16}ClN_2SSe$ (ESI-TOF, $[M + H]^+$): 454.9888. Found: 454.9890.

4-(4-Fluorophenyl)-3-(phenylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2n): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.050 g (46%); mp 168-170 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62 (d, *J* = 8.2 Hz, 1H), 7.58-7.49 (m, 2H), 7.30-7.25 (m, 5H), 7.16-7.12 (m, 3H), 6.86 (t, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 163.4 (d, *J* = 251.0 Hz), 150.1, 142.9, 137.5, 133.0, 132.9, 132.1 (d, *J* = 8.5 Hz), 130.2 (d, *J* = 3.5 Hz), 129.6, 129.0, 128.1, 123.0, 122.5, 119.0, 115.8 (d, *J* = 22.0 Hz), 112.0,

111.2, 32.02. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -109.5. MS (EI, 70 eV; *m/z* (relative intensity)): 439 ([M+1], 6), 438 (26), 281 (100), 255 (33), 207 (68), 134 (25). HRMS calcd for $C_{22}H_{16}FN_2SSe$ (ESI-TOF, $[M + H]^+$): 439.0183. Found: 439.0181.

3-(Phenylselanyl)-4-(3-(trifluoromethyl)phenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2o): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a white solid. Yield: 0.087 g (72%); mp 141-143 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.75 (d, *J* = 7.8 Hz, 1H), 7.66-7.45 (m, 6H), 7.30-7.29 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 5.80 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.1, 143.0, 137.0, 134.9, 133.4, 133.2, 132.7, 131.1 (q, *J* = 32.8 Hz), 129.7, 129.2, 128.7, 128.3, 127.2 (q, *J* = 3.9 Hz), 126.5 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 274.6 Hz), 123.1, 122.6, 119.2, 112.4, 111.7, 32.3. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 415.2. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -62.7. MS (EI, 70 eV; *m/z* (relative intensity)): 490 ([M+2], 9), 488 (39), 331 (100), 305 (31), 207 (29), 134 (37). HRMS calcd for $C_{23}H_{16}F_3N_2SSe$ (ESI-TOF, $[M + H]^+$): 489.0152. Found: 489.0156.

2,3,5-Triphenyl-6-(phenylselanyl)-7H-imidazo[2,1-*b*][1,3]thiazine (2r): The product was isolated by column chromatography (hexane:ethyl acetate 80:20) as a yellow solid. Yield: 0.052 g (40%); 174-175 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.52-7.50 (m, 2H), 7.42-7.40 (m, 2H), 7.28-7.25 (m, 3H), 7.16-7.10 (m, 3H), 7.04-6.94 (m, 6H), 6.87-6.82 (m, 4H), 3.73 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 144.3, 138.1, 137.7, 135.3, 133.7, 133.6, 131.1, 130.5,

129.6, 129.5, 128.8, 127.9, 127.9, 127.5, 127.4, 126.8, 126.7, 115.1, 32.5. HRMS calcd for $C_{30}H_{23}N_2SSe$ (ESI-TOF, $[M + H]^+$): 523.0747. Found: 523.0747.

4-(*p*-Tolyl)-3-(p-tolylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2s): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.049 g (44%); mp 133-135 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.28-7.25 (m, 2H), 7.21-7.19 (m, 2H), 7.14-7.05 (m, 3H), 6.84 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.92 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 2H), 2.45 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.0, 142.7, 140.0, 138.4, 137.5, 133.7, 133.0, 132.3, 131.3, 130.4, 130.0, 129.3, 125.2, 122.8, 122.3, 118.7, 112.3, 111.2, 31.5, 21.6, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 450 ([M+2], 5), 448 (25), 281 (31), 287 (81), 207 (100), 91 (34). HRMS calcd for $C_{24}H_{21}N_2SSe$ (ESI-TOF, $[M + H]^+$): 449.0591. Found: 449.0589.

3-((4-Fluorophenyl)selanyl)-4-(*p*-tolyl)-2*H*-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2t): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.045 g (40%); mp 139-141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 8.0 Hz, 1H), 7.56-7.49 (m, 2H), 7.31-7.08 (m, 5H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.84 (ddd, *J* = 8.5, 7.3, 1.2 Hz, 1H), 5.91 (d, *J* = 7.4 Hz, 1H), 3.74 (s, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 162.3 (d, *J* = 249.3 Hz), 149.9, 142.8, 140.2, 138.4, 135.5 (d, *J* = 8.1 Hz), 133.0, 131.2, 130.0, 129.4, 123.8 (d, *J* = 3.7 Hz), 122.9, 122.4, 118.8, 116.8 (d, *J* = 21.9 Hz), 112.3, 110.6, 31.7, 21.5. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -112.6. MS (EI, 70 eV; *m/z* (relative intensity)): 453 ([M+1], 08),

452 (31), 277 (100), 251 (36), 207 (23), 134 (22). HRMS calcd for $C_{23}H_{18}FN_2SSe$ (ESI-TOF, $[M + H]^+$): 453.0340. Found: 453.0344.

3-(Butylselanyl)-4-(p-tolyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2u): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.057 g (55%); mp 91-93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.60 (d, *J* = 8.1 Hz, 1H), 7.28-7.20 (m, 2H), 7.16-7.07 (m, 3H), 6.81 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.88 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 1.65 (quint, *J* = 7.4 Hz, 2H), 1.32 (sext, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.0, 142.6, 139.7, 139.0, 132.9, 131.5, 130.2, 129.1, 122.7, 122.2, 118.7, 112.3, 108.2, 32.4, 32.0, 26.7, 22.7, 21.5, 13.4. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 289.99. MS (EI, 70 eV; *m/z* (relative intensity)): 415 ([M+1], 05), 414 (22), 277 (100), 251 (14), 245 (34), 134 (15). HRMS calcd for $C_{21}H_{23}N_2SSe$ (ESI-TOF, $[M + H]^+$): 415.0747. Found: 415.0747.

4-(4-Methoxyphenyl)-3-(p-tolylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2v): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.023 g (20%); mp 164-166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 8.0 Hz, 1H), 7.49-7.44 (m, 3H), 7.25-7.23 (m, 2H), 7.13-7.01 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.85 (t, *J* = 7.7 Hz, 1H), 5.95 (d, *J* = 8.1 Hz, 1H), 3.88 (s, 3H), 3.72 (s, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) δ 160.6, 142.7, 138.4, 137.2, 133.7, 133.0, 132.3, 131.5, 130.4, 129.9, 126.4, 125.2, 122.8, 122.3, 118.7, 113.9, 112.3, 111.0, 55.3, 31.5, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 464 (07),

293 (34), 281 (31), 224 (13), 207 (100), 191 (19). HRMS calcd for $C_{24}H_{21}N_2OSSe$ (ESI-TOF, $[M + H]^+$): 465.0540. Found: 465.0540.

3-(Butylselanyl)-4-(4-methoxyphenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2w): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.054 g (50%); mp 77-79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.11 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.83 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 5.92 (d, *J* = 8.2 Hz, 1H), 3.90 (s, 2H), 3.87 (s, 3H), 2.69 (t, *J* = 7.4 Hz, 2H), 1.65 (quint, *J* = 7.4 Hz, 2H), 1.33 (sext, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 160.4, 150.1, 142.7, 138.7, 133.0, 131.7, 126.7, 122.7, 122.2, 118.7, 113.7, 112.4, 108.1, 55.3, 32.4, 32.0, 26.8, 22.7, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 431 ([M+1], 06), 430 (22), 293 (100), 261 (24), 249 (07), 224 (14). HRMS calcd for $C_{21}H_{23}N_2OSSe$ (ESI-TOF, $[M + H]^+$): 431.0696. Found: 431.0691.

4-(4-Chlorophenyl)-3-(p-tolylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2x): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.063 g (54%); mp 137-139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62 (d, *J* = 8.0 Hz, 1H), 7.46-7.42 (m, 4H), 7.32-7.26 (m, 2H), 7.16-7.12 (m, 3H), 6.88 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.96 (dt, *J* = 8.3, 1.0 Hz, 1H), 3.73 (s, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.1, 142.8, 138.6, 136.3, 135.9, 133.7, 132.7, 132.5, 131.4, 130.4, 128.9, 124.8, 122.9, 122.4, 119.0, 112.3, 111.9, 31.7, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 470 ([M+2], 12), 468 (25), 297 (33), 281

(36), 262 (49), 207 (100). HRMS calcd for $C_{23}H_{18}ClN_2SSe$ (ESI-TOF, $[M + H]^+$): 469.0044. Found: 469.0050.

4-(4-Chlorophenyl)-3-((4-chlorophenyl)selanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2y): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.067 g (55%); mp 147-149 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.63 (d, *J* = 7.8 Hz, 1H), 7.50-7.39 (m, 3H), 7.31-7.10 (m, 6H), 6.88 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H), 5.94 (d, *J* = 8.3 Hz, 1H), 3.77 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 149.9, 142.8, 138.0, 136.1, 134.5, 134.2, 132.3, 131.4, 129.8, 129.0, 127.2, 123.2, 122.7, 119.1, 112.0, 110.9, 32.1. MS (EI, 70 eV; *m/z* (relative intensity)): 489 ([M+1], 04), 488 (06), 297 (14), 281 (30), 262 (23), 207 (100), 133 (14). HRMS calcd for $C_{22}H_{15}Cl_2N_2SSe$ (ESI-TOF, $[M + H]^+$): 488.9498. Found: 488.9496.

3-(Butylselanyl)-4-(4-chlorophenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2z): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.050 g (46%); mp 109-111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.13 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 6.86 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.92 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.64 (quint, *J* = 7.4 Hz, 2H), 1.33 (sext, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 142.7, 137.8, 135.6, 132.8, 132.7, 131.7, 128.7, 123.0, 122.5, 119.0, 112.0, 109.5, 32.4, 32.1, 29.6, 26.9, 22.6, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 436 ([M+1], 22), 435 (11), 297 (100), 262 (76), 236 (28), 134 (25). HRMS calcd for $C_{20}H_{20}ClN_2SSe$ (ESI-TOF, $[M + H]^+$): 435.0201. Found: 435.0211.

4-(4-Fluorophenyl)-3-(p-tolylselanyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2aa): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.101 g (90%); mp 179-181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 3H), 7.32-7.28 (m, 3H), 7.16-7.10 (m, 3H), 6.84 (t, *J* = 8.1 Hz, 1H), 5.91 (d, J = 8.3 Hz, 1H), 3.73 (s, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 163.4 (d, *J* = 250.9 Hz), 150.1, 142.9, 138.6, 136.5, 133.7, 132.9, 132.1 (d, *J* = 8.4 Hz), 130.46, 130.3 (d, *J* = 3.6 Hz), 125.0, 122.9, 122.4, 119.0, 115.8 (d, *J* = 22.0 Hz), 112.0, 31.7, 21.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 404.4. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -109.6. MS (EI, 70 eV; *m/z* (relative intensity)): 453 ([M+1], 5), 452 (20), 281 (99), 255 (28), 207 (100), 133 (27). HRMS calcd for $C_{23}H_{18}FN_2SSe$ (ESI-TOF, $[M + H]^+$): 453.0340. Found: 453.0344.

3-((4-Chlorophenyl)selanyl)-4-(4-fluorophenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2ab): The product was isolated by column chromatography (hexane:ethyl acetate 94:6) as a yellow solid. Yield: 0.033 g (28%); mp 189-191 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.63 (d, *J* = 8.0 Hz, 1H), 7.46-7.44 (m, 2H), 7.30-7.21 (m, 4H), 7.18-7.08 (m, 3H), 6.87 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.89 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 163.4 (d, *J* = 251.7 Hz), 149.9, 142.8, 138.1, 135.3, 134.4, 134.1, 132.8, 132.1 (d, *J* = 8.5 Hz), 130.0 (d, *J* = 3.3 Hz), 129.8, 127.2, 123.1, 122.6, 122.5, 119.0, 115.9 (d, *J* = 22.0 Hz), 112.0, 110.6, 32.03. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 410.5. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -109.2. MS (EI, 70 eV; *m/z* (relative intensity)): 474 ([M+2],

4), 472 (10), 281 (75), 255 (17), 207 (100), 133 (19). HRMS calcd for $C_{22}H_{15}ClFN_2SSe$ (ESI-TOF, $[M + H]^+$): 472.9794. Found: 472.9788.

3-(Butylselanyl)-4-(4-fluorophenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2ac): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.068 g (65%); mp 132-134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.61 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.26-7.22 (m, 2H), 7.14-7.10 (m, 3H), 6.84 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.88 (dt, *J* = 8.3, 1.0 Hz, 1H), 3.91 (s, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 1.65 (quint, *J* = 7.3 Hz, 2H), 1.32 (sext, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 163.1 (d, *J* = 250.8 Hz), 150.1, 142.8, 137.9, 132.8, 132.3 (d, *J* = 8.2 Hz), 130.5 (d, *J* = 3.6 Hz), 122.9, 122.3, 118.9, 115.5 (d, *J* = 22.0 Hz), 112.0, 109.1, 32.3, 32.0, 26.9, 22.6, 13.4. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -110.0. MS (EI, 70 eV; *m/z* (relative intensity)): 420 ([M+2], 7), 418 (31), 281 (100), 255 (20), 249 (33), 134 (16). HRMS calcd for $C_{20}H_{20}FN_2SSe$ (ESI-TOF, $[M + H]^+$): 419.0496. Found: 419.0489.

3-(*p*-Tolylselanyl)-4-(3-(trifluoromethyl)phenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2ad): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a white solid. Yield: 0.088 g (70%); mp 165-167 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.77 (d, *J* = 7.8 Hz, 1H), 7.64-7.56 (m, 3H), 7.50-7.45 (m, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.16-7.12 (m, 3H), 6.84 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.82 (d, *J* = 8.3 Hz, 1H), 3.77 (s, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.2, 142.9, 138.8, 135.9, 134.9, 133.9, 133.4, 132.6, 131.1 (q, *J* = 32.8 Hz), 130.5, 129.2, 127.1 (q, *J* = 3.8 Hz), 126.5 (q, *J* = 3.7 Hz), 124.6, 123.5 (q, *J* = 273.6 Hz), 123.1, 122.5, 119.1, 113.3,

111.7, 31.8, 21.4. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -62.7. MS (EI, 70 eV; *m/z* (relative intensity)): 504 ([M+2], 12), 502 (45), 331 (100), 305 (31), 262 (25), 134 (29). HRMS calcd for $C_{24}H_{18}F_3N_2SSe$ (ESI-TOF, $[M + H]^+$): 503.0308. Found: 503.0310.

3-(Butylselanyl)-4-(3-(trifluoromethyl)phenyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (2ae): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow solid. Yield: 0.062 g (53%); mp 97-99 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.75 (d, *J* = 7.8 Hz, 1H), 7.63-7.59 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.13 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 6.82 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.79 (dt, *J* = 8.3, 0.9 Hz, 1H), 3.94 (s, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 1.64 (quint, *J* = 7.3 Hz, 2H), 1.32 (sext, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.1, 142.8, 137.6, 135.2, 133.5, 132.6, 130.9 (q, *J* = 32.8 Hz), 128.9, 127.44 (q, *J* = 3.7 Hz), 126.2 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 273.0 Hz), 123.1, 122.5, 119.1, 111.7, 110.3, 32.3, 32.2, 27.0, 22.6, 13.3. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as internal reference) δ (ppm) 293.9. ^{19}F NMR (564.9 MHz, in $CDCl_3$) δ (ppm) -62.7. MS (EI, 70 eV; *m/z* (relative intensity)): 469 ([M+1], 8), 468 (31), 331 (100), 299 (36), 287 (15), 134 (19). HRMS calcd for $C_{21}H_{20}F_3N_2SSe$ (ESI-TOF, $[M + H]^+$): 469.0465. Found: 469.0468.

2-((2-Chloro-3-phenyl-3-(phenylselanyl)allyl)thio)-1-methyl-1H-benzo[d]imidazole (E/Z; 6a) or 2-((3-chloro-3-phenyl-2-(phenylselanyl)allyl)thio)-1-methyl-1H-benzo[d]imidazole (E/Z; 6a'): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow oil. Yield: 0.035 g (30%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.67-

7.59 (m, 3H), 7.45-7.35 (m, 10H), 7.25-6.98 (m, 19H), 4.66 (s, 1H), 4.49 (s, 2H), 3.73 (s, 5H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 134.7, 134.5, 134.0, 131.4, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 128.0, 127.6, 127.5, 125.6, 122.2, 122.1, 122.0, 121.9, 121.8, 118.5, 118.4, 108.6, 38.6, 30.3, 30.2, 29.6.

Mixture of 2-((2-chloro-3-phenyl-3-(phenylselanyl)allyl)selanyl)-1-methyl-1H-benzo[d]imidazole (E/Z; 6b) or 2-((3-chloro-3-phenyl-2-(phenylselanyl)allyl)selanyl)-1-methyl-1H-benzo[d]imidazole (E/Z; 6b'): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a yellow oil. Yield: 0.039 g (30%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.67-7.65 (m, 1H), 7.4-7.29 (m, 7H), 7.29-7.12 (m, 8H), 4.44 (s, 2H), 3.76 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$. 100 MHz): δ (ppm) 145.6, 138.9, 136.7, 136.6, 136.4, 136.3, 135.7, 134.7, 134.5, 134.2, 133.7, 132.5, 131.7, 131.5, 129.8, 129.2, 129.1, 129.0, 128.6, 128.2, 128.1, 127.2, 122.4, 121.9, 121.5, 118.9, 109.1, 108.9, 107.6, 55.5, 38.5, 33.7, 31.4, 29.6.

General procedure for Suzuki cross-coupling reaction of 3-(phenylselenyl)-imidazothiazines 2a with boronic acids:

To mixture of 3-(phenylselenyl)-imidazothiazines **2a** (0.105 g; 0.25 mmol), $Pd(PPh_3)_4$ (0.115 g; 0.4 equiv) and boronic acid (0.75 mmol; 3 equiv) in DMF (3 mL) was added at room temperature $Cu(OAc)_2.H_2O$ (0.060 g; 0.30 mmol; 1.2 equiv). The reaction was then heated in oil bath for 24 h at 80 °C. After that, the reaction was cooled to room temperature, diluted with ethyl acetate (3 mL) and then washed with saturated solution of NH_4Cl (10 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue

was purified by flash chromatography using a solution of hexane:ethyl acetate as eluent.

3,4-Diphenyl-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (7a): The product was isolated by column chromatography (hexane:ethyl acetate 95:5) as a red solid. Yield: 0.030 g (60%); mp 218-220 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.69 (d, *J* = 8.1 Hz, 1H), 7.35-7.31 (m, 1H), 7.28-7.13 (m, 6H), 7.11-7.05 (m, 4H), 6.83 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H), 5.88 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 150.5, 141.7, 138.3, 135.1, 133.0, 130.8, 129.2, 128.5, 128.3, 127.3, 123.1, 122.4, 120.9, 118.5, 112.9, 31.7. MS (EI, 70 eV; *m/z* (relative intensity)): 341 ([M+1], 27), 340 (100), 307 (48), 262 (26), 236 (50), 134 (28). HRMS calcd for $C_{22}H_{17}N_2S$ (ESI-TOF, $[M + H]^+$): 341.1112. Found: 341.1119.

4-Phenyl-3-(p-tolyl)-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (7b): The product was isolated by column chromatography (hexane:ethyl acetate 92:8) as a red solid. Yield: 0.026 g (50%); mp 162-164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.66 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.36-7.20 (m, 3H), 7.16-7.04 (m, 3H), 7.01-6.93 (m, 4H), 6.80 (ddd, *J* = 8.4, 7.3, 1.1 Hz, 1H), 5.86 (d, *J* = 8.3 Hz, 1H), 3.93 (s, 2H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 154.5, 142.4, 137.1, 135.4, 134.8, 133.3, 130.8, 129.6, 129.1, 129.0, 128.5, 122.9, 122.1, 120.8, 118.7, 112.8, 31.9, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 355 ([M+1], 26), 354 (100), 321 (37), 236 (53). 134 (38), 90 (24). HRMS calcd for $C_{23}H_{19}N_2S$ (ESI-TOF, $[M + H]^+$): 355.1269. Found: 355.1266.

3-(4-Methoxyphenyl)-4-phenyl-2H-benzo[4,5]imidazo[2,1-*b*][1,3]thiazine (7c): The product was isolated by column chromatography (hexane:ethyl

acetate 92:8) as a red solid. Yield: 0.023 g (42%); mp 147-149 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.64 (ddd, *J* = 8.1, 1.2, 0.7 Hz, 1H), 7.33-7.30 (m, 1H), 7.28-7.22 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 7.09-7.06 (m, 2H), 7.02-6.98 (m, 2H), 6.80 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 6.74-6.70 (m, 2H), 5.85 (dt, *J* = 8.2, 0.9 Hz, 1H), 3.92 (s, 2H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$. 100 MHz): δ (ppm) 158.6, 143.0, 134.6, 133.5, 133.1, 130.8, 130.4, 128.9, 128.5, 122.6, 121.9, 120.2, 118.9, 113.7, 112.7, 55.2, 32.0. MS (EI, 70 eV; *m/z* (relative intensity)): 371 ([M+1], 27), 370 (100), 355 (13), 293 (23), 237 (61), 134 (31). HRMS calcd for $C_{23}H_{19}N_2OS$ (ESI-TOF, $[M + H]^+$): 371.1218. Found: 371.1226.

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Notes

The authors declare no competing financial interest.

Supporting Information

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^{1}H and ^{13}C NMR spectra for all new compounds and X-ray results and crystal data for compounds **2a 2j** and **2k** (1944844, 1944845 and 1944843).

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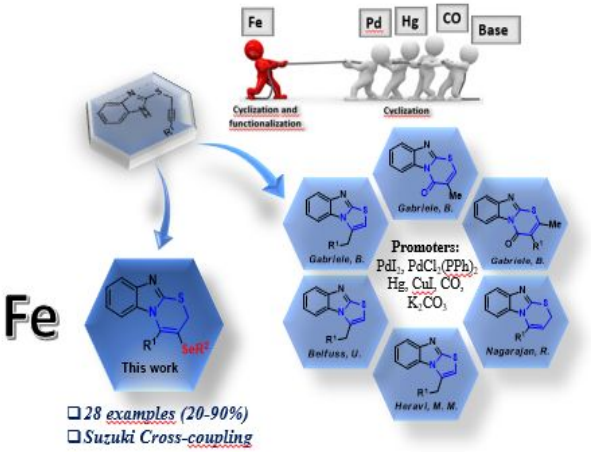
Graphical Table of Contents


Fe
Pd
Hg
CO
Base
Cyclization and functionalization
Cyclization
Promoters:
PdI2, PdCl2(PPh3)2
Hg, CuI, CO,
K2CO3
Gabriele, B.
Gabriele, B.
Gabriele, B.
Belfuss, U.
Nagarajan, R.
Heravi, M. M.
Fe
This work
28 examples (20-90%)
Suzuki Cross-coupling