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Iron-Catalyzed Cyclization of Alkynols with Diorganyl Diselenides: Synthesis of 2,5-Dihydrofuran, 3,6-Dihydro-2*H*-pyran, and 2,5-Dihydro-1*H*-pyrrole Organoselanyl Derivatives

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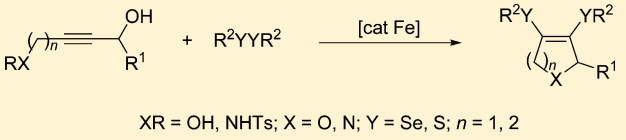
Supporting Information

ABSTRACT: An iron-catalyzed system, using diorganyl diselenides as an organoselenium source, was used for the cyclization of 1,4-butyne-diols in the preparation of 3,4-bis(organoselanyl)-2,5-dihydrofurans. The optimized reaction conditions are compatible with many functional groups in 1,4-butyne-diols and diorganyl diselenides. In addition, this catalyst system was also efficient with diorganyl disulfides, but it did not work for diorganyl ditellurides. The same reaction conditions were also extended to pentyne-1,5-diol for the preparation of 4,5-bis(organoselanyl)-3,6-dihydro-2*H*-pyrans and to 4-amino-butynol for the preparation of 2,5-dihydro-1*H*-pyrrole derivatives. The synthetic utility of these heterocycles was studied using 5-bis(organoselanyl)-3,6-dihydro-2*H*-pyrans as substrate in a Kumada-type cross-coupling reaction.



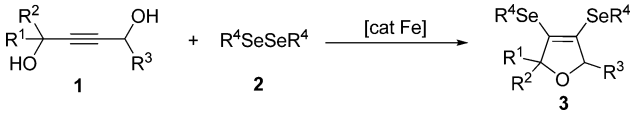
XR = OH, NHTs; X = O, N; Y = Se, S; *n* = 1, 2

INTRODUCTION

Organoselenium compounds have received much attention in the research area because they are useful and versatile intermediates in organic synthesis[1] and have a wide spectrum of biological properties.[2] As a result, a number of methodologies for the preparation of organoselenium compounds based on nucleophilic,[3] electrophilic,[4] or radical selenium reagents[5] have been developed over the last few decades. Thus, a large variety of organoselenium compounds, such as aryl and vinyl selenides, diorganyl diselenides, and selenium heterocycles, have been prepared.[6] The main advantage of introducing a selenium moiety into organic substrates is its efficiency in further transformations via a regio- and stereocontrolled fashion, making it very useful for the formation of new carbon−carbon,[7] carbon−lithium,[8] carbon−halogen,[9] and carbon−hydrogen bonds.[10] In addition to the progress in organic synthesis, organochalcogens exhibit different pharmacological activity profiles.[11] For example, reports have shown that organochalcogen derivatives have the potential to be used as anticancer,[12] antiinflammatory,[13] antibacterial, and antifungal agents.[14] In recent years, cyclization processes of unsaturated substrates into heterocycles using transition metals and diorganyl dichalcogenides have been intensively studied.[15] Generally, these transformations provide access to electrophilic organoselenium species generated from diorganyl diselenides and metal sources. New approaches in the cyclization reactions using cooperative action between iron(III) chloride and diorganyl dichalcogenides have recently been developed.[16] The use of iron salts in organic synthesis has emerged as a powerful methodology to promote several transformations: (i) cross coupling reaction of Grignard reagents with organic electrophiles;[17] (ii) carbon−heteroatom (C−N, C−O, C−S, and C−Se) bond formation;[18] (iii) heteroatom−heteroatom and carbon−carbon bond formation;[19] and (iv) for the synthesis of heterocycle compounds.[20]

Compared to other transition metals, iron chemistry has been reported to have many advantages, such as relative stability, abundance, low toxicity, economic and ecological advantages, and excellent tolerance toward various functional groups.[21] In this article, we propose a protocol for the preparation of 3,4-bis(organoselanyl)-2,5-dihydrofurans **3** from 1,4-butyne-diols **1** and diorganyl diselenides **2** using iron salt as the catalyst (Scheme 1).

Scheme 1



Furan derivatives are a structural motif of particular interest because they are present in a large number of natural products, many of which have biological activity. Among the methods used for their preparation, transition metal-catalyzed cyclization and electrophilic cyclization of acyclic precursors are the most promising.[22] Our methodology combines the ability of both iron(III) chloride and diorganyl dichalcogenides to transform the acyclic substrates to different heterocycles and to incorporate a new functionality in the final structure, making the heterocycles suitable for further transformations.

RESULTS AND DISCUSSION

First, we wished to explore what conditions would be able to promote the cyclization of 1,4-butyne-diols **1**.[23] In a model reaction, the cyclization of 1,4-butyne-diol **1a** was examined with

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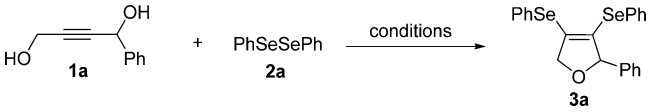
diphenyl diselenide in the presence of a catalytic amount of $FeCl_3$. The reaction was performed by the addition of diphenyl diselenide (1.1 equiv) to a solution of $FeCl_3$ (20 mol %) in CH_2Cl_2 (2.5 mL) at room temperature under argon atmosphere. After 15 min, 1,4-butyne-diol **1a** (0.25 mmol) was added, and the reaction mixture was kept at room temperature for 1 h. The results of evaluating suitable solvents showed that good yields of **3a** were obtained when the reaction was carried out in the presence of dichloromethane and 1,2-dichloroethane (Table 1, entries 1−10). The effect of different iron catalysts on the cyclization of 1,4-butyne-diol **1a** was also examined. The results in Table 1 show that with elemental iron, $Fe(acac)_3$, Fe_2O_3, and $Fe_2(SO_4)_3{\cdot}xH_2O$ the reaction did not proceed, and the starting material was recovered (Table 1, entries 11−14). The catalyst

Table 1. Effect of Different Reaction Parameters on the Preparation of 3,4-Bis(phenylselanyl)-2,5-dihydrofuran 3a[a]



entry	catalyst	solvent	yields (%)
1	$FeCl_3$	CH_2Cl_2	75
2	$FeCl_3$	DCE	76
3	$FeCl_3$	$CHCl_3$	65
4	$FeCl_3$	CH_3CN	55
5	$FeCl_3$	toluene	30
6	$FeCl_3$	DMF	*b*
7	$FeCl_3$	DMSO	*b*
8	$FeCl_3$	EtOH	*b*
9	$FeCl_3$	1,4-dioxane	*b*
10	$FeCl_3$	THF	*b*
11	Fe^0	CH_2Cl_2	*b*
12	$Fe(acac)_3$	CH_2Cl_2	*b*
13	Fe_2O_3	CH_2Cl_2	*b*
14	$Fe_2(SO_4)_3{\cdot}xH_2O$	CH_2Cl_2	*b*
15	$FeCl_3{\cdot}4H_2O$	CH_2Cl_2	69
16	$FeCl_3{\cdot}6H_2O$	CH_2Cl_2	75
17	$PdCl_2$	CH_2Cl_2	*b*
18	$CuBr_2$	CH_2Cl_2	*b*
19	$HCl_{(aq)}$	CH_2Cl_2	trace
20	$HCl_{(g)}$	CH_2Cl_2	trace
21[c]	$FeCl_3{\cdot}6H_2O$	DCE	90
22[c,d]	$FeCl_3{\cdot}6H_2O$	DCE	85
23[c,e]	$FeCl_3{\cdot}6H_2O$	DCE	40
24[c,f]	$FeCl_3{\cdot}6H_2O$	DCE	76

[a]The reaction was performed by the addition of diphenyl diselenide (1.1 equiv) to a solution of iron salt (20 mol %) in solvent (2.5 mL) at room temperature under argon atmosphere. After 15 min at this temperature, 1,4-butyne-diol **1a** (0.25 mmol) was added. The resulting mixture was stirred for 1 h at room temperature. [b]Product **3a** was not formed. [c]Reaction was carried out under air atmosphere. [d]Reaction was carried out with diphenyl diselenide (1.5 equiv). [e]Reaction was carried out with diphenyl diselenide (0.5 equiv). [f]Catalyst was 10 mol % $FeCl_3{\cdot}6H_2O$.

screening also revealed that ferrous chloride tetrahydrate and ferric chloride hexahydrate catalyzed the cyclization of **1a** as efficiently as anhydrous iron(III) chloride (Table 1, entries 15 and 16, respectively). Among the other metal sources, neither copper salt nor palladium salt was active to catalyze the cyclization (Table 1, entries 17 and 18, respectively). To determine if HCl could be liberated from $FeCl_3$ acting as a catalyst, the reaction was conducted in the presence of hydrochloric acid(aq) and HCl(g), but only a trace amount of **3a** was obtained (Table 1, entries 19 and 20, respectively). We believed that the formation of diphenyl diselenide, via a phenylselenol oxi-reducing property, would be hampered under an inert atmosphere. To confirm this hypothesis, we carried out the reaction under air atmosphere (Table 1, entry 21). The use of this reaction condition was highly effective to improve the yield of desired product **3a**. This implicates that selenolate anion ($PhSe^-$) is generated in the reaction medium and, in the presence of oxygen, returns to the catalytic cycle. Through control experiments, we found that increasing the amount of diphenyl diselenides to 1.5 equiv proved unnecessary (Table 1, entry 22). However, reducing the amount of dipenyl diselenide to 0.5 equiv resulted in a considerable decrease in the yield (Table 1, entry 23). These results indicate that the two portions of diphenyl diselenide (PhSe) were incorporated in the final product. With this result, we also concluded that a minimum of 1.0 equiv of diphenyl diselenide is necessary to give the product in high yield. Furthermore, we also investigated the effect of different amounts of iron salt. The results showed that the use of 10 mol % of catalyst was less effective (Table 1, entry 24). To obtain more details about the reaction mechanism, we conducted some control experiments, and some factors that could govern the mechanism aspects of this cyclization reaction are summarized as follows: (1) When we ran the reaction of 1,4-butyne-diol **1a** with PhSeCl[24] in DCE at room temperature, product **3a** was not obtained. This finding strongly suggests that the in situ formation of PhSeCl, which is the cyclization promoter, is improbable. (2) When the standard reaction described in Table 1, entry 21, was carried out in the presence of a radical inhibitor (hydroquinone), product **3a** was obtained in 85% yield. This result indicates that this cyclization might not follow a radical process in which diphenyl diselenide is the radical source. (3) When the optimized reaction conditions were carried out in the absence of iron salt or diphenyl diselenide, any amount of product **3a** was formed. These experiments indicate that iron salt or selenium species alone are not sufficient to promote the cyclization of 1,4-butyne-diol **1a** and that a cooperative action between diphenyl diselenide and iron salt is essential to provide a good yield of the cyclized product. Our data led us to suggest that the cyclization of 1,4-butyne-diol **1a** to the corresponding dihydrofuran **3a** occurs through coordination of the iron and diselenide species with the oxygen atom, leading to the formation of cation **I**, which is in resonance with allene **II**. The nucleophilic attack of the selenolate anion at the carbon center of allene **II** affords allenic selenide **III**. The allene coordination to [Fe(SePh)]-Ln provides the seleniranium ion **IV**. The nucleophilic oxygen antiattack at the activated double bond gives dihydrofuran **3a** (Scheme 2).

The standard condition was further applied to a variety of 1,4-butyne-diols **1** and diorganyl diselenides to test the tolerance of functional groups as well as their effects on conversion. These results are shown in Table 2. We first studied the influence of the aryl diselenide substituents in the reactivity of the cyclization of **1a**. We found that aryl diselenides containing neutral, electron-donating, and electron-withdrawing groups **2a−e** worked well with 1,4-butyne-diol **1a**, giving the corresponding 3,4-bis-(arylselanyl)-2,5-dihydrofurans **3a−e** in good yields, although the presence of a sterically hindered mesityl group gave product **3e** in moderate yield (Table 2, entries 1−5). The cyclization of 1,4-butyne-diol **1a** with dialkyl diselenides, such as dibutyl diselenide, gave the corresponding dihydrofuran **3f** in 62% overall yield

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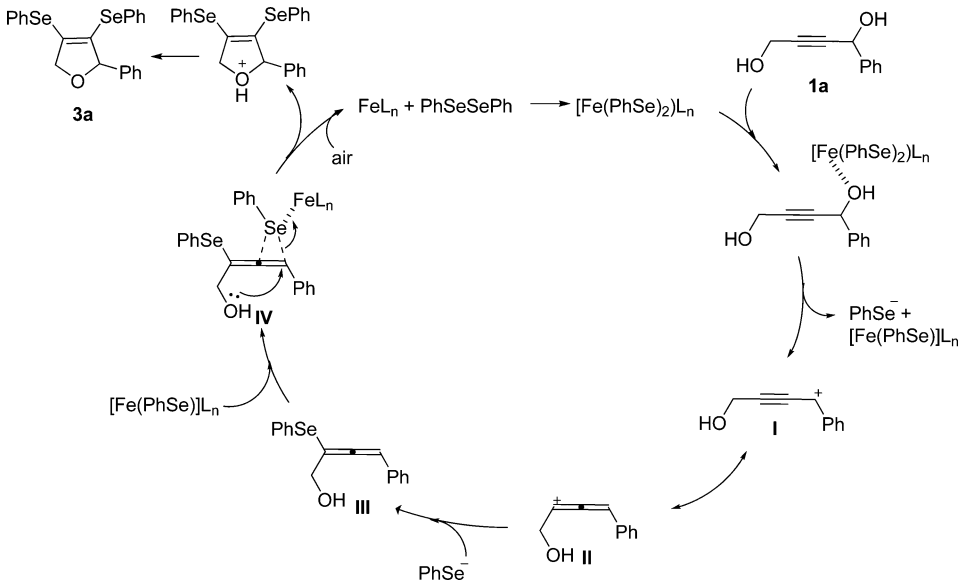
Scheme 2



(Table 2, entry 6). In addition, the reaction conditions also allowed scale-up to afford a large amount of 3,4-bis(phenylselanyl)-2,5-dihydrofuran **3a**. Indeed, when the cyclization reaction of 1,4-butyne-diol **1a** was carried out with a 5 mmol scale, 2,5-dihydrofuran **3a** was obtained in 80% yield (1.82 g). This result is very similar to that of performing the experiment on a 0.25 mmol scale (Table 2, entry 1). Next, a series of 1,4-butyne-diols containing different substituents were investigated. 1,4-Butyne-diols **1b−e** bearing methyl, chloro, and methoxyl groups at the aromatic ring underwent the cyclization with diselenides to produce the corresponding dihydrofurans in 75−95% yields (Table 2, entries 7−14). The lower reactivity of the 1,4-butyne-diol **1d** would be attributed to the steric hindrance for the chlorine atom at the *ortho* position of the aryl group (Table 2, entry 13). Treatment of 1,4-butyne-diol **1e** with bis-*p*-tolyl diselenide gave dihydrofuran **3n** in high yield; however, the reaction with bis-*p*-fluorophenyl diselenide gave **3o** in only 36% yield (Table 2, entries 14 and 15, respectively). The reaction conditions were also compatible with a sterically hindered naphthyl group, which resulted in the formation of dihydrofurans **3p−r** in good yields (Table 2, entries 16−18, respectively). Changing hydrogen at the second propargyl position for the methyl or cyclohexyl substituent did not affect the cyclization, and dihydrofurans **3s−y** were obtained in high yields (Table 2, entries 19−24). Although the absence of an aryl group at any propargyl position led to low reactivity of 1,4-butyne-diol **1j**, giving the cyclized product in 15% yield (Table 2, entry 25). Further, the cyclization reaction was investigated with diorganyl disulfides under the same reaction conditions. Thus, when 1,4-butyne-diols **1a−c** were treated with diphenyl disulfide under identical reaction condition used for diselenides, corresponding dihydrofurans **3z−3ab** were isolated in moderated yields (Table 2, entries 26−28, respectively). However, no reactivity was observed when 1,4-butyne-diols were reacted with dialkyl disulfides. Next, the same reaction conditions were employed for diorganyl ditellurides, but both dialkyl and diaryl ditellurides failed to provide the desired cyclized products. Dihydrofurans **3** were identified by their NMR data, and the structures were confirmed by single crystal X-ray diffraction (Figure S1, Supporting Information; CCDC 1058759).

In addition to the preparation of dihydrofurans **3** described in Table 2, the cyclization reaction was attempted with pentyne-1,5-diol **4a** with the aim of preparing 4,5-bis(organoselanyl)-3,6-dihydro-2*H*-pyrans **5** (Table 3). Thus, the reaction conditions described in Table 1 (entry 21) were applied to pentyne-1,5-diol **4a** with diorganyl diselenides. Good yields were obtained for diphenyl diselenide and bis-*p*-tolyl diselenide (Table 3, entries 1 and 2). On the contrary, the substituent electron-withdrawing in the *para* position of diaryl diselenide gave dihydro-2*H*-pyran **5c** in a moderate 48% yield (Table 3, entry 3). When dibutyl diselenide was allowed to react with pentyne-1,5-diol **4a** under the standard reaction conditions, dihydro-2*H*-pyran **5c** was obtained in 61% yield (Table 3, entry 4). Diorganyl disulfide, like diphenyl disulfide, failed to give the desired cyclized product (Table 3, entry 5).

Dihydropyrroles consist of an important heterocyclic class due to the wide application in the biological field. Some dihydropyrroles have been described to display anticancer,[25] anti-inflammatory,[26] and antifungal activities.[27] In addition, they are the key intermediates in organic synthesis, including in the preparation of natural products.[28] Accordingly, the development of synthetic approaches for synthesis of dihydropyrroles has been continuously required. To test the utility of our synthetic methodology, we next focused our attention on the cyclization of 4-amino-butynol **6a** under the reaction conditions described in Table 1 (entry 21) in the preparation of 2,5-dihydro-1*H*-pyrrole derivatives **7** (Table 4). Thus, the reaction of 4-amino-butynol **6a** with electron neutral or electron rich aryl diselenides provided high yields of the desired cyclized products **7a** and **7b** (Table 4, entries 1 and 2, respectively). Under these conditions, electron-deficient aryl diselenide was less effective but also gave 2,5-dihydro-1*H*-pyrrole **7c** in acceptable yield (Table 4, entry 3). From the reactions between amino-butynol **6a** with dibutyl diselenide, the corresponding 2,5-dihydro-1*H*-pyrrole **7d** was also produced in moderate yield (Table 4, entry 4). This moderated yield can be explained by the low stability of alkyl selenides, which undergo β-selenoxide elimination[29] during the purification or workup process, giving the final product without the selenium group incorporated in the structure. In the case of diphenyl disulfide, 2,5-dihydro-1*H*-pyrrole **7e** was obtained in low yield

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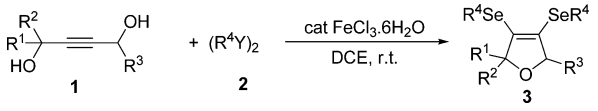
Table 2. Synthesis of 3,4-Bis(organoselanyl)-2,5-dihydrofurans 3[a]



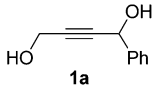
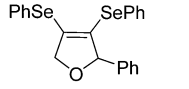
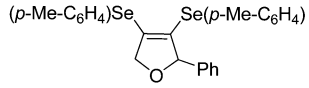
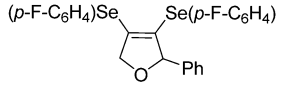
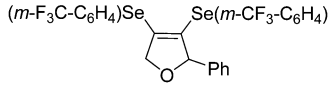
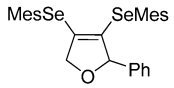
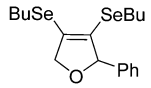
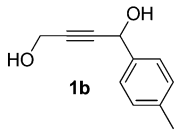
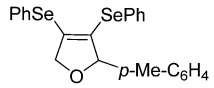
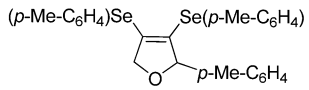
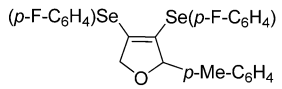
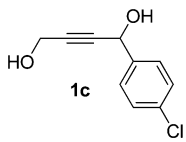
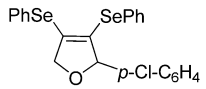
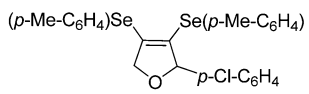
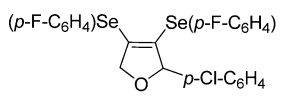
entry	1,4-butyne-diols 1	$(R^4Y)_2$	3,4-bis(organoselanyl)-2,5-dihydrofuran 3	yield (%) (time)
1	 **1a**	$(PhSe)_2$ **2a**	 **3a**	90 (80)[b] (1h)
2	**1a**	$(p\text{-Me-}C_6H_4Se)_2$ **2b**	 **3b**	82 (2h)
3	**1a**	$(p\text{-F-}C_6H_4Se)_2$ **2c**	 **3c**	81 (1h)
4	**1a**	$(m\text{-}CF_3\text{-}C_6H_4Se)_2$ **2d**	 **3d**	68 (1.5h)
5	**1a**	$(MesSe)_2$ **2e**	 **3e**	52 (1h)
6	**1a**	$(BuSe)_2$ **2f**	 **3f**	62 (1h)
7	 **1b**	$(PhSe)_2$ **2a**	 **3g**	92 (1h)
8	**1b**	$(p\text{-Me-}C_6H_4Se)_2$ **2b**	 **3h**	95 (1h)
9	**1b**	$(p\text{-F-}C_6H_4Se)_2$ **2c**	 **3i**	75 (0.5h)
10	 **1c**	$(PhSe)_2$ **2a**	 **3j**	76 (1.5h)
11	**1c**	$(p\text{-Me-}C_6H_4Se)_2$ **2b**	 **3k**	87 (1.5h)
12	**1c**	$(p\text{-F-}C_6H_4Se)_2$ **2c**	 **3l**	84 (1h)

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Table 2. continued

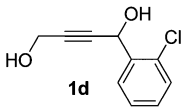
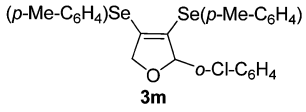
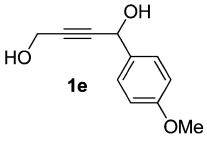
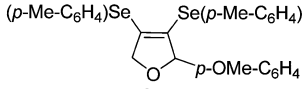
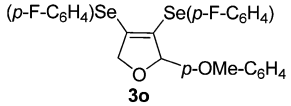
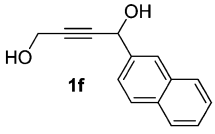
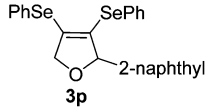
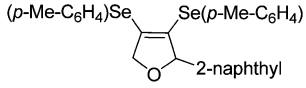
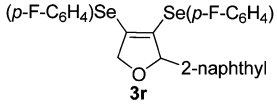
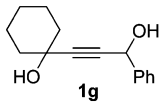
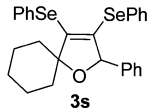
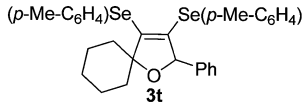
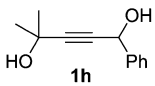
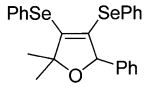
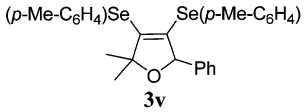
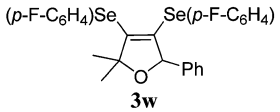
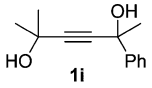
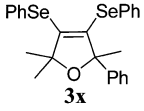
entry	1,4-butyne-diols 1	$(R^4Y)_2$	3,4-bis(organoselanyl)-2,5-dihydrofuran 3	yield (%) (time)
13	 **1d**	$(p\text{-Me-C}_6H_4Se)_2$ **2b**	 **3m**	50 (24h)
14	 **1e**	$(p\text{-Me-C}_6H_4Se)_2$ **2b**	 **3n**	88 (1h)
15	**1e**	$(p\text{-F-C}_6H_4Se)_2$ **2c**	 **3o**	36 (1.5h)
16	 **1f**	$(PhSe)_2$ **2a**	 **3p**	94 (2h)
17	**1f**	$(p\text{-Me-C}_6H_4Se)_2$ **2b**	 **3q**	86 (2h)
18	**1f**	$(p\text{-F-C}_6H_4Se)_2$ **2c**	 **3r**	72 (2h)
19	 **1g**	$(PhSe)_2$ **2a**	 **3s**	91 (4h)
20	**1g**	$(p\text{-Me-C}_6H_4Se)_2$ **2b**	 **3t**	75 (1h)
21	 **1h**	$(PhSe)_2$ **2a**	 **3u**	97 (18h)
22	**1h**	$(p\text{-Me-C}_6H_4Se)_2$ **2b**	 **3v**	65 (5h)
23	**1h**	$(p\text{-F-C}_6H_4Se)_2$ **2c**	 **3w**	75 (5.5h)
24	 **1i**	$(PhSe)_2$ **2a**	 **3x**	70 (3h)

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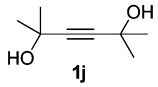
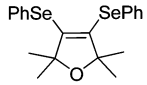
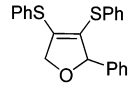
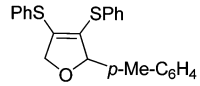
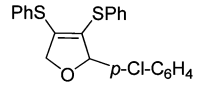
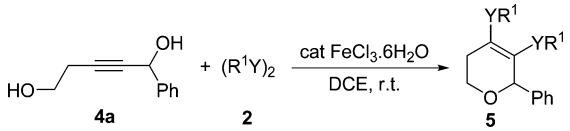
Table 2. continued

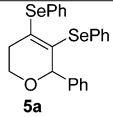
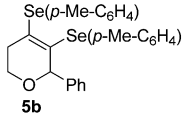
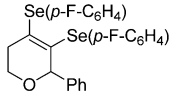
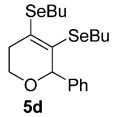
entry	1,4-butyne-diols 1	$(R^4Y)_2$	3,4-bis(organoselanyl)-2,5-dihydrofuran 3	yield (%) (time)
25	 1j	$(PhSe)_2$ 2a	 3y	15 (24h)
26	1a	$(PhS)_2$ 2g	 3z	65 (24h)
27	1b	$(PhS)_2$ 2g	 3aa	64 (18h)
28	1c	$(PhS)_2$ 2g	 3ab	55 (20h)

[a]The reaction was performed by the addition of diorganyl diselenides or diorganyl disulfides (1.1 equiv) to a $FeCl_3{\cdot}6H_2O$ (20 mol %) solution in DCE (2.5 mL) under air atmosphere at room temperature. After 15 min at this temperature, 1,4-butyne-diol **1** (0.25 mmol) was added. The resulting mixture was stirred at room temperature for the times indicated in Table 2. [b]Yield for reaction carried out on a 5 mmol scale.

Table 3. Synthesis of 3,6-Dihydro-2*H*-pyrans 5[a]



4a 2 5

entry	$(R^1Y)_2$	dihydro-2*H*-pyran 5	yield (%) (time)
1	$(PhSe)_2$ 2a	 5a	74 (18h)
2	$(p\text{-Me-}C_6H_4Se)_2$ 2b	 5b	74 (15h)
3	$(p\text{-F-}C_6H_4Se)_2$ 2d	 5c	48 (12h)
4	$(BuSe)_2$ 2g	 5d	61 (3h)
5	$(PhS)_2$ 2h		–[b]

[a]The reaction was performed by the addition of diorganyl diselenides (1.1 equiv) to a $FeCl_3{\cdot}6H_2O$ (20 mol %) solution in DCE (2.5 mL) under air atmosphere at room temperature. After 15 min at this temperature, pentyne-1,5-diol **4a** (0.25 mmol) was added. The resulting mixture was stirred at room temperature for the time indicated. [b]Product not detected

even though the reaction parameters, such as temperature, time, and stoichiometric ratio of the reagent, have been restudied. Because the strength of the sulfur−sulfur bond of disulfides is stronger than the selenium−selenium bond of diselenides, the iron incorporation into disulfides should be hampered and thus influence the reaction yields.

Finally, we turned our attention toward the development of a synthetic application for these heterocycles. Considering that organoselenium substrates that contain a Csp^2−Se bond are potential starting materials for regio- and stereoselective transition metal-catalyzed cross-coupling reactions, we decided to further explore the use of these compounds in the Kumada reaction. Thus, the palladium-catalyzed cross-coupling of 3,6-dihydro-2*H*-pyran derivative **5d** with Grignard reagent proceeded smoothly in THF by using a catalytic amount of $Pd(PPh_3)_4$ to give Kumada product **8** in 57% yield (Scheme 3).

CONCLUSIONS

Iron salt catalyzed the cyclization reaction of 4-butyne-diols for the preparation of 3,4-bis(organoselanyl)-2,5-dihydrofurans through an intramolecular sequence of carbon−oxygen/carbon−selenium bond formation. The experimental mechanistic studies suggest that the use of 1.1 equiv of diselenides (RSeSeR) implies that one portion may act as a nucleophilic species (RSe^-) while another acts as an electrophilic species (RSe^+), demonstrating that the two portions of diorganyl diselenides are incorporated in the final product, which is useful and valuable in terms of atom economy. When the same reaction conditions were applied to pentyne-1,5-diol and 4-amino-butynol, the cyclized 4,5-bis(organoselanyl)-3,6-dihydro-2*H*-pyran and 3,4-bis(organoselanyl)-2,5-dihydro-1*H*-pyrrole derivatives, respectively, were obtained. These results are significant because, using the same reaction conditions, we obtained three classes of heterocycles. The reaction conditions are compatible with many functional groups in the substrates and with diaryl, dialkyl diselenides and diaryl disulfides, although dialkyl diselenides and diaryl disulfides gave the products in moderate yields. The moderate yields obtained for dialkyl diselenides can be explained by the low stability of alkyl selenides,

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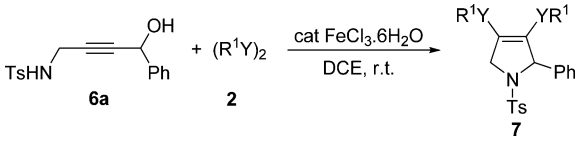
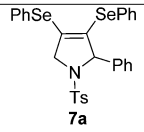
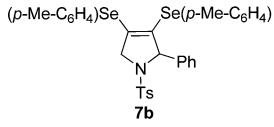
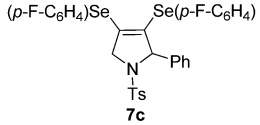
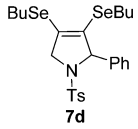
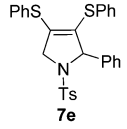
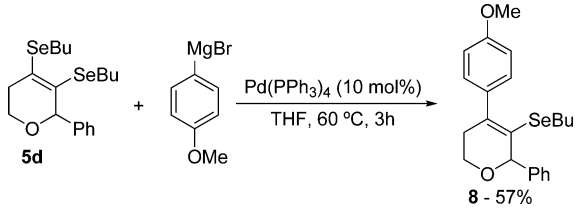
Table 4. Synthesis of 2,5-Dihydro-1*H*-pyrrole 7[a]



entry	$(R^1Y)_2$	2,5-dihydro-1*H*-pyrroles 7	yield (%) (time)
1	$(PhSe)_2$ **2a**	 **7a**	85 (10h)
2	$(p\text{-Me-}C_6H_4Se)_2$ **2b**	 **7b**	82 (15h)
3	$(p\text{-F-}C_6H_4Se)_2$ **2d**	 **7c**	60 (15h)
4	$(BuSe)_2$ **2g**	 **7d**	46 (18h)
5	$(PhS)_2$ **2h**	 **7e**	35 (24h)

[a]The reaction was performed by the addition of diorganyl diselenides or diphenyl disulfide (1.1 equiv) to a $FeCl_3{\cdot}6H_2O$ (20 mol %) solution in DCE (2.5 mL) under air atmosphere at room temperature. After 15 min at this temperature, 4-amino-butynol **6a** (0.25 mmol) was added. The resulting mixture was stirred at room temperature for the times indicated.

Scheme 3



which undergo β-selenoxide elimination during the purification or workup process, giving the final product without the selenium group incorporated in the structure. In the case of disulfides, because the strength of the sulfur−sulfur bond of disulfides is stronger than the selenium−selenium bond of diselenides, we suggest that iron incorporation into disulfides should be hampered, thereby decreasing the yields.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of 3a−ac, 5a−d, and 7a−e. In a Schlenk tube under air atmosphere containing DCE (2.5 mL) was added $FeCl_3{\cdot}6H_2O$ (0.013 g, 0.05 mmol) and diorganyl dichalcogenides (0.275 mmol). The resulting solution was stirred at room temperature for 15 min. After this time, appropriate substrate **1**, **4**, or **6** (0.25 mmol) was added, and the reaction was stirred at room temperature for the times indicated in Tables 2−4. The mixture was dissolved in ethyl acetate, washed with a saturated solution of NH_4Cl, dried with $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography over silica gel (hexane/ethyl acetate 99:1) to provide the respective product 2-phenyl-3,4-bis(phenylselanyl)-2,5-dihydrofuran (**3a**), obtained as a yellow solid. Yield: 0.103 g (90%); mp 46.5−49.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59−7.56 (m, 2H), 7.31−7.08 (m, 13H), 5.59 (dd, J = 5.3 Hz, J = 3.0 Hz, 1H), 4.69 (dd, J = 12.8 Hz, J = 5.3 Hz, 1H), 4.60 (dd, J = 12.8 Hz, J = 3.0 Hz, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 140.0, 134.5, 134.4, 133.1, 130.0, 129.1, 128.8, 128.3, 128.0, 127.9, 127.7, 127.4, 127.0, 126.3, 91.8, 78.9. EIMS (70 eV, m/z (relative intensity)): 458 (8), 301 (6), 207 (9), 191 (14), 144 (100), 115 (72), 77 (31), 51 (12). HRMS: calcd for $C_{22}H_{19}OSe_2$ (ESI-TOF, M + H$^+$), 458.9766; found, 458.9769.

*2-Phenyl-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3b**).* Obtained as a yellow solid. Yield: 0.094 g (78%); mp 83.0−85.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58−7.47 (m, 2H), 7.25−7.20 (m, 5H), 7.12−7.08 (m, 4H), 7.02−6.96 (m, 2H), 5.55 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 4.67 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.55 (dd, J = 12.7 Hz, J = 3.0 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 140.3, 138.6, 137.6, 135.0, 134.3, 133.6, 130.0, 129.8, 129.4, 128.1, 128.0, 127.2, 124.0, 122.6, 92.0, 79.1, 21.1, 21.0. EIMS (70 eV, m/z (relative intensity)): 484 (11), 382 (7), 234 (5), 144 (100), 129 (29), 115 (27), 91 (33), 77 (22). HRMS: calcd for $C_{24}H_{23}OSe_2$ (ESI-TOF, M + H$^+$), 487.0079; found, 487.0083.

*3,4-Bis((4-fluorophenyl)selanyl)-2-phenyl-2,5-dihydrofuran (**3c**).* Obtained as a yellow solid. Yield: 0.100 g (81%); mp 65.0−67.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65−7.58 (m, 2H), 7.29−7.23 (m, 5H), 7.09−6.82 (m, 6H), 5.53 (dd, J = 5.3 Hz, J = 3.2 Hz, 1H), 4.65 (dd, J = 12.7 Hz, J = 5.3 Hz, 1H), 4.55 (dd, J = 12.7 Hz, J = 3.2 Hz, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 116.2 (d, J = 248.4 Hz), 162.9 (d, J = 248.4 Hz), 139.9, 137.1 (d, J = 8.1 Hz), 136.0 (d, J = 8.1 Hz), 134.0, 129.8, 128.3, 128.2, 127.2, 122.0 (d, J = 3.1 Hz), 120.8 (d, J = 3.1 Hz), 116.6 (d, J = 21.8 Hz), 116.2 (d, J = 21.8 Hz), 92.2, 79.0. EIMS (70 eV, m/z (relative intensity)): 492 (9), 319 (5), 209 (7), 174 (7), 144 (100), 133 (43), 115 (22), 77 (12). HRMS: calcd for $C_{22}H_{17}F_2OSe_2$ (ESI-TOF, M + H$^+$), 494.9577; found, 494.9582.

*2-Phenyl-3,4-bis((3-(trifluoromethyl)phenyl)selanyl)-2,5-dihydrofuran (**3d**).* Obtained as a yellow oil. Yield: 0.101 g (68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (s, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.51−7.41 (m, 4H), 7.29−7.19 (m, 4H), 7.09−7.04 (m, 2H), 5.60 (dd, J = 5.4 Hz, J = 3.4 Hz, 1H), 4.73 (dd, J = 12.9 Hz, J = 5.4 Hz, 1H), 4.63 (dd, J = 12.9 Hz, J = 3.4 Hz, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 139.4, 137.4, 136.8, 134.1, 132.1, 131.9 (quart, J = 32.7 Hz), 131.4 (quart, J = 32.7 Hz), 130.8 (quart, J = 3.7 Hz), 130.2 (quart, J = 3.7 Hz), 129.8, 129.3, 128.5, 128.4, 127.7, 127.1, 125.4 (quart, J = 3.7 Hz), 124.6 (quart, J = 3.7 Hz), 123.6 (quart, J = 272.8 Hz), 92.2, 79.1. EIMS (70 eV, m/z (relative intensity)): 594 (13), 369 (16), 262 (10), 183 (27), 144 (100), 115 (23), 105 (14), 77 (8). HRMS: calcd for $C_{24}H_{17}F_6OSe_2$ (ESI-TOF, M + H$^+$), 594.9514; found, 594.9520.

*3,4-Bis(mesitylselanyl)-2-phenyl-2,5-dihydrofuran (**3e**).* Obtained as a yellow solid. Yield: 0.069 g (52%); mp 151.9−153.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25−7.18 (m, 3H), 6.94−6.82 (m, 6H), 5.17 (dd, J = 5.0 Hz, J = 2.8 Hz, 1H), 4.42 (dd, J = 12.1 Hz, J = 5.0 Hz, 1H), 4.26 (dd, J = 12.1 Hz, J = 2.8 Hz, 1H), 2.54 (s, 6H), 2.27−2.26 (m, 6H), 2.16 (s, 6H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 143.2, 143.1, 140.2, 139.0, 138.5, 128.7, 128.4, 128.2, 128.1, 127.8, 127.4, 124.5, 124.5, 92.2, 79.0, 24.5, 23.9, 20.9, 20.8. EIMS (70 eV, m/z (relative intensity)): 542 (15), 341 (10), 281 (14), 199 (23), 144 (35), 119 (100), 91 (28), 77 (20). HRMS: calcd for $C_{28}H_{31}OSe_2$ (ESI-TOF, M + H$^+$), 543.0705; found, 543.0709.

*3,4-Bis(butylselanyl)-2-phenyl-2,5-dihydrofuran (**3f**).* Obtained as a yellow oil. Yield: 0.064 g (62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37−7.28 (m, 5H), 5.66 (dd, J = 5.3 Hz, J = 3.3 Hz, 1H), 4.94 (dd, J = 12.2 Hz, J = 5.3 Hz, 1H), 4.83 (dd, J = 12.2 Hz, J = 3.3 Hz, 1H),

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2.84−2.79 (m, 2H), 2.45−2.32 (m, 2H), 1.71 (quint, J = 7.5 Hz, 2H), 1.50−1.40 (m, 4H), 1.25 (sex, J = 7.2 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H), 0.81 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 140.6, 132.5, 128.4, 128.3, 127.7, 127.3, 92.5, 78.6, 33.1, 32.6, 25.5, 24.2, 22.8, 22.6, 13.5, 13.4. EIMS (70 eV, m/z (relative intensity)): 416 (8), 281 (8), 195 (4), 144 (100), 115 (46), 93 (3), 77 (12), 57 (17). HRMS: calcd for $C_{18}H_{27}OSe_2$ (ESI-TOF, M + H^+), 419.0392; found, 419.0399.

*3,4-Bis(phenylselanyl)-2-(p-tolyl)-2,5-dihydrofuran (**3g**).* Obtained as a white solid. Yield: 0.108 g (92%); mp 74.5−77.0 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63−7.60 (m, 2H), 7.35−7.15 (m, 8H), 7.06 (d, J = 8.1, 2H), 6.99 (d, J = 8.1, 2H), 5.55 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 4.68 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.56 (dd, J = 12.7 Hz, J = 3.0 Hz, 1H), 2.30 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 137.8, 137.1, 134.7, 134.4, 133.3, 130.3, 129.2, 128.9, 128.9, 128.4, 127.9, 127.5, 127.1, 126.5, 91.8, 78.9, 21.2. EIMS (70 eV, m/z (relative intensity)): 472 (7), 205 (8), 158 (100), 129 (28), 115 (64), 77 (39), 65 (9), 51 (25). HRMS: calcd for $C_{23}H_{21}OSe_2$ (ESI-TOF, M + H^+), 472.9922; found, 472.9929.

*2-(p-Tolyl)-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3h**).* Obtained as an orange solid. Yield: 0.118 g (95%); mp 104.5−105.9 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 7.01−6.97 (m, 4H), 5.25 (dd, J = 5.4 Hz, J = 3.0 Hz, 1H), 4.66 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.54 (dd, J = 12.7 Hz, J = 3.0 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 6H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 138.6, 137.8, 137.6, 137.3, 135.0, 134.4, 133.6, 130.0, 129.8, 129.7, 128.9, 127.1, 124.1, 122.7, 91.9, 78.9, 21.2, 21.1, 21.0. EIMS (70 eV, m/z (relative intensity)): 500 (7), 328 (5), 219 (8), 171 (14), 158 (100), 119 (31), 91 (94), 65 (25). HRMS: calcd for $C_{25}H_{25}OSe_2$ (ESI-TOF, M + H^+), 501.0235; found, 501.0240.

*3,4-Bis((4-fluorophenyl)selanyl)-2-(p-tolyl)-2,5-dihydrofuran (**3i**).* Obtained as a brown solid. Yield: 0.095 g (75%); mp 52.8−55.1 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.62−7.57 (m, 2H), 7.29−7.24 (m, 2H), 7.05−6.94 (m, 6H), 6.89−6.82 (m, 2H), 5.48 (dd, J = 5.4 Hz, J = 3.1 Hz, 1H), 4.63 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.52 (dd, J = 12.7 Hz, J = 3.1 Hz, 1H), 2.30 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 163.1 (d, J = 249.5 Hz), 162.6 (d, J = 249.5 Hz), 138.1, 137.0 (d, J = 8.1 Hz), 136.9, 136.0 (d, J = 8.1 Hz), 133.8, 130.1, 129.0, 127.2, 122.1 (d, J = 3.3 Hz), 120.9 (d, J = 3.3 Hz), 116.6 (d, J = 21.8 Hz), 116.1 (d, J = 21.8 Hz), 92.0, 78.8, 21.1. EIMS (70 eV, m/z (relative intensity)): 508 (10), 333 (10), 212 (8), 158 (100), 133 (42), 119 (20), 91 (11), 77 (2), 65 (2). HRMS: calcd for $C_{23}H_{19}F_2OSe_2$ (ESI-TOF, M + H^+), 508.9734; found, 508.9737.

*2-(4-Chlorophenyl)-3,4-bis(phenylselanyl)-2,5-dihydrofuran (**3j**).* Obtained as a yellow solid. Yield: 0.093 g (76%); mp 70.4−71.8 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.65−7.61 (m, 2H), 7.37−7.29 (m, 5H), 7.27−7.15 (m, 5H), 7.02−6.98 (m, 2H), 5.54 (dd, J = 5.4 Hz, J = 3.2 Hz, 1H), 4.68 (dd, J = 12.8 Hz, J = 5.4 Hz, 1H), 4.58 (dd, J = 12.8 Hz, J = 3.2 Hz, 1H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 138.8, 135.1, 134.9, 134.0, 133.5, 129.5, 129.4, 129.1, 128.7, 128.6, 128.4, 127.7, 127.6, 126.3, 91.3, 79.2. EIMS (70 eV, m/z (relative intensity)): 492 (12), 335 (9), 225 (8), 178 (100), 157 (21), 139 (29), 115 (96), 77 (33). HRMS: calcd for $C_{22}H_{18}ClOSe_2$ (ESI-TOF, M + H^+), 492.9376; found, 492.9379.

*2-(4-Chlorophenyl)-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3k**).* Obtained as a light yellow solid. Yield: 0.113 g (87%); mp 131.9−133.2 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 7.8 Hz, 2H), 7.21−7.14 (m, 4H), 7.10 (d, J = 7.8 Hz, 2H), 7.00−6.97 (m, 4H), 5.10 (dd, J = 5.1 Hz, J = 3.1 Hz, 1H), 4.63 (dd, J = 12.8 Hz, J = 5.1 Hz, 1H), 4.53 (dd, J = 12.8 Hz, J = 3.1 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 138.9, 138.8, 137.8, 135.1, 135.0, 133.8, 133.7, 130.1, 129.8, 128.7, 128.5, 128.2, 123.8, 122.5, 91.4, 79.1, 21.1, 21.0. EIMS (70 eV, m/z (relative intensity)): 520 (15), 207 (18), 178 (79), 149 (28), 129 (53), 91 (100), 77 (7), 65 (24). HRMS: calcd for $C_{24}H_{22}ClOSe_2$ (ESI-TOF, M + H^+), 520.9689; found, 520.9693.

*2-(4-Chlorophenyl)-3,4-bis((4-fluorophenyl)selanyl)-2,5-dihydrofuran (**3l**).* Obtained as a yellow solid. Yield: 0.111 g (84%); mp 38.9−41.7 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63−7.60 (m, 2H), 7.27−7.19 (m, 4H), 7.06−6.98 (m, 4H), 6.91−6.86 (m, 2H), 5.50 (dd, J = 5.4 Hz, J = 3.2 Hz, 1H), 4.62 (dd, J = 12.8 Hz, J = 5.4 Hz, 1H), 4.53 (dd, J = 12.8 Hz, J = 3.2 Hz, 1H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 163.3 (d, J = 249.9 Hz), 162.7 (d, J = 248.7 Hz), 138.5, 137.3 (d, J = 8.2 Hz), 136.0 (d, J = 8.1 Hz), 134.7, 134.1, 129.0, 128.6, 128.4, 121.9 (d, J = 3.5 Hz), 120.6 (d, J = 3.6 Hz), 116.7 (d, J = 21.8 Hz), 116.3 (d, J = 21.5 Hz), 91.4, 79.0. EIMS (70 eV, m/z (relative intensity)): 528 (16), 353 (11), 213 (9), 178 (100), 139 (23), 133 (61), 115 (13), 83 (6). HRMS: calcd for $C_{22}H_{16}ClF_2OSe_2$ (ESI-TOF, M + H^+), 528.9188; found, 528.9190.

*2-(2-Chlorophenyl)-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3m**).* Obtained as a yellow oil. Yield: 0.061 g (50%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54−7.51 (m, 2H), 7.24−7.11 (m, 8H), 6.97−6.94 (m, 2H), 6.07 (dd, J = 5.4 Hz, J = 3.2 Hz, 1H), 4.62 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.54 (dd, J = 12.7 Hz, J = 3.2 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 138.8, 137.9, 137.1, 135.1, 134.9, 134.1, 134.0, 130.1, 129.8, 129.6, 129.4, 129.3, 128.3, 126.8, 123.6, 122.6, 88.4, 79.1, 21.2, 21.1. EIMS (70 eV, m/z (relative intensity)): 520 (14), 313 (17), 281 (20), 207 (100), 178 (97), 149 (22), 115 (25), 91 (60). HRMS: calcd for $C_{24}H_{22}ClOSe_2$ (ESI-TOF, M + H^+), 520.9689; found, 520.9692.

*2-(4-Methoxyphenyl)-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3n**).* Obtained as a dark yellow solid. Yield: 0.113 g (88%); mp 86.6−88.9 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 8.1 Hz, 2H), 7.25−7.20 (m, 2H), 7.11 (d, J = 7.8 Hz, 2H), 7.02−6.97 (m, 4H), 6.77 (dd, J = 6.6 Hz, J = 2.0 Hz, 2H), 5.51 (dd, J = 5.3 Hz, J = 3.1 Hz, 1H), 4.63 (dd, J = 12.7 Hz, J = 5.3 Hz, 1H), 4.54 (dd, J = 12.7 Hz, J = 3.1 Hz, 1H), 3.75 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 159.6, 138.6, 137.6, 135.0, 133.9, 133.8, 132.5, 130.1, 130.0, 129.7, 128.5, 124.1, 122.8, 113.6, 91.7, 78.8, 55.2, 21.1, 21.0. EIMS (70 eV, m/z (relative intensity)): 516 (11), 345 (16), 174 (100), 159 (10), 135 (30), 115 (7), 91 (17), 77 (6). HRMS: calcd for $C_{25}H_{25}O_2Se_2$ (ESI-TOF, M + H^+), 517.0185; found, 517.0187.

*3,4-Bis((4-fluorophenyl)selanyl)-2-(4-methoxyphenyl)-2,5-dihydrofuran (**3o**).* Obtained as a yellow oil. Yield: 0.047 g (36%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63−7.58 (m, 2H), 7.30−7.25 (m, 2H), 7.05−6.96 (m, 4H), 6.87 (t, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 5.49 (dd, J = 5.3 Hz, J = 3.2 Hz, 1H), 4.61 (dd, J = 12.7 Hz, J = 5.3 Hz, 1H), 4.50 (dd, J = 12.7 Hz, J = 3.2 Hz, 1H), 3.77 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 163.1 (d, J = 248.5 Hz), 162.7 (d, J = 248.5 Hz), 159.7, 137.0 (d, J = 8.0 Hz), 136.1 (d, J = 8.0 Hz), 133.4, 132.0, 130.0, 128.6, 122.0 (d, J = 3.5 Hz), 120.9 (d, J = 3.5 Hz), 116.6, (d, J = 21.8 Hz), 116.1 (d, J = 21.8 Hz), 113.7, 91.8, 78.7, 55.2. EIMS (70 eV, m/z (relative intensity)): 524 (9), 349 (19), 281 (8), 213 (21), 174 (100), 133 (96), 96 (9), 77 (10). HRMS: calcd for $C_{23}H_{19}F_2O_2Se_2$ (ESI-TOF, M + H^+), 524.9683; found, 524.9688.

*2-(Naphthalen-2-yl)-3,4-bis(phenylselanyl)-2,5-dihydrofuran (**3p**).* Obtained as a yellow solid. Yield: 0.118 g (94%); mp 90.9−92.1 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78−7.63 (m, 5H), 7.44−7.40 (m, 3H), 7.35−7.25 (m, 6H), 7.19−7.15 (m, 1H), 7.11−7.07 (m, 2H), 5.75 (dd, J = 5.4 Hz, J = 3.1 Hz, 1H), 4.78 (dd, J = 12.8 Hz, J = 5.4 Hz, 1H), 4.65 (dd, J = 12.8 Hz, J = 3.1 Hz, 1H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 137.4, 134.7, 134.2, 133.5, 133.3, 133.0, 130.2, 129.3, 128.9, 128.5, 128.2, 128.0, 127.7, 127.6, 127.5, 126.6, 126.4, 125.9, 125.8, 124.6, 92.2, 79.3. EIMS (70 eV, m/z (relative intensity)): 508 (9), 351 (12), 281 (17), 207 (88), 194 (100), 165 (56), 115 (75), 77 (14). HRMS: calcd for $C_{26}H_{21}OSe_2$ (ESI-TOF, M + H^+), 508.9922; found, 508.9928.

*2-(Naphthalen-2-yl)-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3q**).* Obtained as a white solid. Yield: 0.114 g (86%); mp 125.6−127.0 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78−7.66 (m, 3H), 7.53 (d, J = 8.0 Hz, 2H), 7.44−7.39 (m, 3H), 7.24 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.20−7.11 (m, 4H), 6.86 (d, J = 8.0 Hz, 2H), 5.52 (dd, J = 5.4 Hz, J = 3.1 Hz, 1H), 4.75 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.61 (dd, J = 12.7 Hz, J = 3.1 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 138.7, 137.7, 137.6, 135.0, 133.9, 133.3, 133.0, 130.1, 129.7, 129.6, 128.1, 128.0, 127.6, 126.7, 125.9, 125.8, 124.7, 123.7, 122.7, 92.3, 79.3, 21.2, 21.0. EIMS (70 eV, m/z (relative intensity)): 536 (9), 365 (8), 194 (100), 165 (56), 129 (51), 115 (13), 91 (44), 77 (5). HRMS: calcd for $C_{28}H_{25}OSe_2$ (ESI-TOF, M + H^+), 537.0235; found, 537.0239.

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*3,4-Bis((4-fluorophenyl)selanyl)-2-(naphthalen-2-yl)-2,5-dihydrofuran (**3r**).* Obtained as a yellow solid. Yield: 0.098 g (72%); mp 99.8−102.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79−7.62 (m, 5H), 7.47−7.41 (m, 3H), 7.22−7.18 (m, 3H), 7.03 (t, J = 8.6 Hz, 2H), 6.73 (t, J = 8.7 Hz, 2H), 5.69 (dd, J = 5.4 Hz, J = 3.2 Hz, 1H), 4.72 (dd, J = 12.7 Hz, J = 5.4 Hz, 1H), 4.60 (dd, J = 12.7 Hz, J = 3.2 Hz, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 163.2 (d, J = 248.4 Hz), 162.7 (d, J = 248.4 Hz), 137.2, 137.1 (d, J = 8.1 Hz), 136.2 (d, J = 8.1 Hz), 133.8, 133.4, 133.0, 129.9, 128.3, 128.0, 127.6, 126.7, 126.1, 126.0, 124.6, 121.8 (d, J = 3.5 Hz), 120.9 (d, J = 3.5 Hz), 116.6 (d, J = 21.6 Hz), 116.0 (d, J = 21.6 Hz), 92.4, 79.2. EIMS (70 eV, m/z (relative intensity)): 544 (9), 369 (11), 281 (18), 194 (100), 165 (59), 133 (96), 115 (12), 96 (20). HRMS: calcd for $C_{26}H_{19}F_2OSe_2$ (ESI-TOF, M + H$^+$), 544.9734; found, 544.9738.

*2-Phenyl-3,4-bis(phenylselanyl)-1-oxaspiro[4.5]dec-3-ene (**3s**).* Obtained as a yellow oil. Yield: 0.119 g (91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57−7.52 (m, 2H), 7.29−7.13 (m, 9H), 7.10−7.04 (m, 2H), 6.98−6.93 (m, 2H), 5.53 (s, 1H), 1.87−1.77 (m, 1H), 1.70−1.47 (m, 8H), 1.17−1.0 (m, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 141.3, 140.3, 136.8, 134.9, 131.7, 130.3, 129.1, 128.8, 128.0, 127.9, 127.8, 127.7, 127.1, 126.7, 92.9, 88.2, 36.9, 35.5, 24.9, 22.3, 21.9. EIMS (70 eV, m/z (relative intensity)): 526 (29), 369 (36), 289 (19), 212 (100), 191 (62), 115 (37), 91 (24), 77 (32). HRMS: calcd for $C_{27}H_{27}OSe_2$ (ESI-TOF, M + H$^+$), 527.0392; found, 527.0397.

*2-Phenyl-3,4-bis(p-tolylselanyl)-1-oxaspiro[4.5]dec-3-ene (**3t**).* Obtained as a light yellow solid. Yield: 0.104 g (75%); mp 115.4−117.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 8.0 Hz, 2H), 7.22−7.14 (m, 3H), 7.06 (dd, J = 12.1 Hz, J = 8.0 Hz, 4H), 6.96−6.94 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 5.49 (s, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 1.86−1.77 (m, 1H), 1.68−1.50 (m, 8H), 1.13−1.03 (m, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 141.2, 140.4, 138.0, 137.0, 136.3, 135.2, 131.9, 130.0, 129.5, 128.0, 127.9, 127.8, 126.5, 122.8, 93.0, 88.1, 36.9, 35.5, 24.9, 22.3, 21.9, 21.1, 21.0. EIMS (70 eV, m/z (relative intensity)): 554 (3), 340 (5), 281 (20), 207 (100), 165 (7), 133 (16), 115 (10), 91 (16). HRMS: calcd for $C_{29}H_{31}OSe_2$ (ESI-TOF, M + H$^+$), 555.0705; found, 555.0710.

*2,2-Dimethyl-5-phenyl-3,4-bis(phenylselanyl)-2,5-dihydrofuran (**3u**).* Obtained as a light yellow solid. Yield: 0.118 g (97%); mp 63.9−65.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64−7.58 (m, 2H), 7.31−7.25 (m, 3H), 7.21−7.14 (m, 6H), 7.10−7.06 (m, 2H), 6.97−6.93 (m, 2H), 5.51 (s, 1H), 1.40 (s, 3H), 1.35 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 140.0, 139.7, 136.3, 135.1, 132.4, 129.6, 129.2, 128.8, 128.1, 128.0 (2C), 127.9, 127.4, 126.3, 92.1, 88.2, 28.8, 27.7. EIMS (70 eV, m/z (relative intensity)): 486 (9), 329 (12), 207 (24), 172 (100), 128 (49), 105 (37), 77 (42), 51 (10). HRMS: calcd for $C_{24}H_{23}OSe_2$ (ESI-TOF, M + H$^+$), 487.0079; found, 487.0088.

*2,2-Dimethyl-5-phenyl-3,4-bis(p-tolylselanyl)-2,5-dihydrofuran (**3v**).* Obtained as an orange solid. Yield: 0.083 g (65%); mp 67.8−69.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 8.1 Hz, 2H), 7.22−7.15 (m, 3H), 7.11−7.05 (m, 4H), 6.97−6.94 (m, 2H), 6.88 (d, J = 8.1 Hz, 2H), 5.46 (s, 1H), 2.33 (s, 3H), 2.28 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 139.9, 139.6, 138.1, 137.5, 136.2, 135.3, 132.8, 130.0, 129.5, 128.0, 127.9 (2C), 125.8, 122.6, 92.1, 88.2, 28.8, 27.8, 21.1 (2C). EIMS (70 eV, m/z (relative intensity)): 514 (11), 499 (10), 328 (48), 248 (47), 172 (100), 128 (25), 91 (38), 77 (13). HRMS: calcd for $C_{26}H_{27}OSe_2$ (ESI-TOF, M + H$^+$), 515.0392; found, 515.0401.

*3,4-Bis((4-fluorophenyl)selanyl)-2,2-dimethyl-5-phenyl-2,5-dihydrofuran (**3w**).* Obtained as a yellow oil. Yield: 0.098 g (75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63−7.59 (m, 2H), 7.23−7.16 (m, 3H), 7.10 (dd, J = 8.6 Hz, J = 5.4 Hz, 2H), 7.02 (t, J = 8.6 Hz, 2H), 6.96−6.92 (m, 2H), 6.75 (t, J = 8.6 Hz, 2H), 5.43 (s, 1H), 1.38 (s, 3H), 1.32 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 162.9 (d, J = 249.3 Hz), 162.7 (d, J = 249.3 Hz), 139.6, 139.5, 137.5 (d, J = 8.1 Hz), 136.2, 135.0 (d, J = 8.1 Hz), 128.2, 128.1, 127.9, 124.0 (d, J = 3.7 Hz), 120.6 (d, J = 3.7 Hz), 116.5 (d, J = 22.0 Hz), 115.9 (d, J = 22.0 Hz), 92.0, 88.3, 28.8, 27.7. EIMS (70 eV, m/z (relative intensity)): 522 (15), 332 (83), 252 (50), 209 (31), 186 (13), 172 (100), 115 (23), 77 (21). HRMS: calcd for $C_{24}H_{21}F_2OSe_2$ (ESI-TOF, M + H$^+$), 522.9890; found, 522.9899.

*2,2,5-Trimethyl-5-phenyl-3,4-bis(phenylselanyl)-2,5-dihydrofuran (**3x**).* Obtained as a yellow oil. Yield: 0.087 g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49−7.42 (m, 4H), 7.27−7.05 (m, 11H), 1.75 (s, 3H), 1.41 (s, 3H), 1.35 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 144.1, 142.0 140.8, 133.5, 132.7, 129.2, 129.1, 128.9, 128.8, 127.9, 127.7, 127.2, 127.1, 126.2, 91.5, 90.6, 29.8, 28.6, 27.8. EIMS (70 eV, m/z (relative intensity)): 500 (11), 481 (29), 328 (93), 248 (55), 186 (66), 143 (79), 128 (100), 77 (64). HRMS: calcd for $C_{25}H_{25}OSe_2$ (ESI-TOF, M + H$^+$), 501.0235; found, 501.0241.

*2,2,5,5-Tetramethyl-3,4-bis(phenylselanyl)-2,5-dihydrofuran (**3y**).* Obtained as a dark yellow oil. Yield: 0.012 g (15%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49−7.46 (m, 3H), 7.26−7.20 (m, 7H), 1.28 (s, 12H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 141.9, 133.0, 129.5, 129.1, 127.5, 89.4, 29.4. EIMS (70 eV, m/z (relative intensity)): 421 (15), 281 (29), 207 (100), 191 (59), 157 (22), 105 (62), 91 (23), 77 (31). HRMS: calcd for $C_{20}H_{23}OSe_2$ (ESI-TOF, M + H$^+$), 439.0079; found, 439.0085.

*2-Phenyl-3,4-bis(phenylthio)-2,5-dihydrofuran (**3z**).* Obtained as an orange oil. Yield: 0.058 g (65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53−7.48 (m, 2H), 7.37−7.31 (m, 3H), 7.27−7.20 (m, 8H), 7.12−7.07 (m, 2H) 5.63 (dd, J = 5.2 Hz, J = 2.8 Hz, 1H), 4.74 (dd, J = 12.7 Hz, J = 5.2 Hz, 1H), 4.63 (dd, J = 12.7 Hz, J = 2.8 Hz, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 140.0, 136.0, 132.6, 132.2, 131.4, 131.1, 129.2, 128.8, 128.3, 128.2, 127.2, 127.1, 90.2, 77.2. EIMS (70 eV, m/z (relative intensity)): 362 (39), 253 (54), 207 (51), 147 (85), 144 (100), 115 (80), 77 (53), 51 (16). HRMS: calcd for $C_{22}H_{19}OS_2$ (ESI-TOF, M + H$^+$), 363.0877; found, 363.0885.

*3,4-Bis(phenylthio)-2-(p-tolyl)-2,5-dihydrofuran (**3aa**).* Obtained as an orange oil. Yield: 0.060 g (64%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.47 (m, 2H), 7.37−7.31 (m, 3H), 7.25−7.20 (m, 5H), 7.09 (d, J = 7.9 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 5.61 (dd, J = 5.1 Hz, J = 2.7 Hz, 1H), 4.73 (dd, J = 12.7 Hz, J = 5.2 Hz, 1H), 4.62 (dd, J = 12.7 Hz, J = 2.8 Hz, 1H), 2.31 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 138.0, 137.0, 135.9, 132.6, 132.3, 131.6, 131.1, 131.0, 129.2, 129.0, 128.9, 128.3, 127.2, 127.0, 90.0, 77.1, 21.2. EIMS (70 eV, m/z (relative intensity)): 376 (78), 267 (67), 207 (37), 158 (100), 129 (38), 115 (18), 91 (29), 77 (64). HRMS: calcd for $C_{23}H_{21}OS_2$ (ESI-TOF, M + H$^+$), 337.1033; found, 337.1039.

*2-(4-Chlorophenyl)-3,4-bis(phenylthio)-2,5-dihydrofuran (**3ab**).* Obtained as an orange solid. Yield: 0.050 g (55%); mp 60.5−62.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.49 (m, 2H), 7.37−7.32 (m, 3H), 7.25−7.21 (m, 7H), 7.01 (d, J = 8.5 Hz, 2H), 5.59 (dd, J = 5.1 Hz, J = 3.0 Hz, 1H), 4.71 (dd, J = 12.8 Hz, J = 5.1 Hz, 1H), 4.62 (dd, J = 12.8 Hz, J = 3.0 Hz, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 138.6, 136.7, 134.1, 132.8, 132.1, 131.2, 130.9, 130.6, 129.3, 129.0, 128.8, 128.6, 128.5, 127.4, 89.5, 77.2. EIMS (70 eV, m/z (relative intensity)): 396 (55), 287 (54), 221 (22), 147 (90), 115 (34), 103 (100), 77 (38), 65 (16). HRMS: calcd for $C_{22}H_{18}ClOS_2$ (ESI-TOF, M + H$^+$), 397.0487; found, 397.0493.

*6-Phenyl-4,5-bis(phenylselanyl)-3,6-dihydro-2H-pyran (**5a**).* Obtained as a light yellow solid. Yield: 0.088 g (74%); mp 109.4−110.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67−7.63 (m, 2H), 7.38−7.17 (m, 13H), 5.11−5.10 (m, 1H), 3.83−3.77 (m, 1H), 3.68−3.62 (m, 1H), 2.33−2.30 (m, 2H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 139.5, 139.3, 136.4, 132.2, 130.0, 129.2, 129.1, 129.0, 128.6, 128.3, 128.2, 128.1, 127.7, 127.1, 81.4, 61.6, 33.7. EIMS (70 eV, m/z (relative intensity)): 472 (8), 315 (22), 235 (48), 128 (100), 115 (19), 91 (11), 77 (38), 51 (11). HRMS: calcd for $C_{23}H_{21}OSe_2$ (ESI-TOF, M + H$^+$), 472.9922; found, 472.9925.

*6-Phenyl-4,5-bis(p-tolylselanyl)-3,6-dihydro-2H-pyran (**5b**).* Obtained as a white solid. Yield: 0.092 g (74%); mp 110.9−113.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 7.5 Hz, 2H), 7.29−7.20 (m, 7H), 7.15−7.12 (m, 2H), 7.02−6.99 (m, 2H), 5.08−5.07 (m, 1H), 3.80−3.73 (m, 1H), 3.66−3.59 (m, 1H), 2.35 (s, 3H), 2.30−2.26 (m, 5H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 139.4, 139.1, 128.7, 137.1, 136.5, 132.6, 130.0, 129.9, 129.1, 128.0, 127.3, 126.2, 124.6, 81.2, 61.5, 33.5, 21.2, 21.1. EIMS (70 eV, m/z (relative intensity)): 500 (7), 329 (12), 281 (33), 207 (100), 128 (38), 105 (33), 91 (46), 77 (18). HRMS: calcd for $C_{25}H_{25}OSe_2$ (ESI-TOF, M + H$^+$), 501.0235; found, 501.0241.

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*4,5-Bis((4-fluorophenyl)selanyl)-6-phenyl-3,6-dihydro-2H-pyran (**5c**).* Obtained as a yellow solid. Yield: 0.060 g (48%); mp 99.7−101.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65−7.61 (m, 2H), 7.32−7.19 (m, 7H), 7.04 (t, J = 8.6 Hz, 2H), 6.88 (t, J = 8.6 Hz, 2H), 5.07−5.03 (m, 1H), 3.83−3.77 (m, 1H), 3.67−3.61 (m, 1H), 2.27−2.24 (m, 2H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 163.3 (d, J = 249.6 Hz), 162.5 (d, J = 249.6 Hz), 138.9, 138.5 (d, J = 8.0 Hz), 134.9 (d, J = 8.0 Hz), 129.0, 128.3, 128.1 (2C), 124.1 (d, J = 3.3 Hz), 122.8 (d, J = 3.3 Hz), 116.5 (d, J = 21.4 Hz), 116.2 (d, J = 21.4 Hz), 81.3, 61.6, 33.6. EIMS (70 eV, m/z (relative intensity)): 506 (13), 333 (34), 253 (90), 175 (23), 146 (100), 128 (61), 105 (48), 77 (36). HRMS: calcd for $C_{23}H_{19}F_2OSe_2$ (ESI-TOF, M + H$^+$), 508.9734; found, 508.9739.

*4,5-Bis(butylselanyl)-6-phenyl-3,6-dihydro-2H-pyran (**5d**).* Obtained as a dark yellow oil. Yield: 0.065 g (61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.27 (m, 5H), 5.17−5.16 (m, 1H), 3.97−3.92 (m, 1H), 3.78−3.72 (m, 1H), 2.83−2.39 (m, 6H), 1.71 (quint, J = 7.5 Hz, 2H), 1.55−1.42 (m, 4H), 1.28 (sex, J = 7.3 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H), 0.84 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 139.7, 136.0, 129.0, 128.2, 128.1, 126.4, 82.3, 61.9, 32.8, 32.6, 32.2, 27.1, 24.3, 23.1, 22.8, 13.6, 13.5. EIMS (70 eV, m/z (relative intensity)): 432 (35), 295 (100), 239 (34), 207 (32), 158 (48), 128 (93), 105 (54), 77 (28). HRMS: calcd for $C_{19}H_{29}OSe_2$ (ESI-TOF, M + H$^+$), 433.0548; found, 433.0553.

*2-Phenyl-3,4-bis(phenylselanyl)-1-tosyl-2,5-dihydro-1H-pyrrole (**7a**).* Obtained as a white solid. Yield: 0.129 g (85%); mp 121.1−123.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50−7.47 (m, 2H), 7.38−7.09 (m, 15H), 7.00−6.96 (m, 2H), 5.33 (dd, J = 4.8 Hz, J = 1.5 Hz, 1H), 4.25 (dd, J = 14.9 Hz, J = 1.5 Hz, 1H), 4.17 (dd, J = 14.9 Hz, J = 4.8 Hz, 1H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 143.1, 139.2, 135.6, 134.8, 133.9, 132.3, 132.2, 129.5, 129.4 (2C), 129.1, 128.7, 128.2, 128.0, 127.8, 127.5, 127.2, 126.6, 74.4, 59.6, 21.4. EIMS (70 eV, m/z (relative intensity)): 611 (10), 453 (8), 297 (48), 219 (30), 142 (86), 115 (100), 91 (67), 77 (17). HRMS: calcd for $C_{29}H_{26}NO_2SSe_2$ (ESI-TOF, M + H$^+$), 612.0014; found, 612.0020.

*2-Phenyl-3,4-bis(p-tolylselanyl)-1-tosyl-2,5-dihydro-1H-pyrrole (**7b**).* Obtained as a white solid. Yield: 0.130 g (82%); mp 94.4−96.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.24−7.10 (m, 7H), 7.05−6.97 (m, 6H), 5.27−5.26 (m, 1H), 4.22−4.10 (m, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 143.1, 139.2, 139.0, 138.1, 135.2, 135.0, 134.1, 132.1, 131.2, 130.3, 129.9, 129.4, 128.2, 128.0, 127.8, 127.2, 123.5, 122.6, 74.3, 59.5, 21.5, 21.2, 21.1. EIMS (70 eV, m/z (relative intensity)): 639 (11), 483 (4), 312 (44), 233 (36), 142 (91), 91 (100), 77 (8), 65 (18). HRMS: calcd for $C_{31}H_{30}NO_2SSe_2$ (ESI-TOF, M + H$^+$), 640.0327; found, 640.0330.

*3,4-Bis((4-fluorophenyl)selanyl)-2-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (**7c**).* Obtained as a yellow solid. Yield: 0.097 g (60%); mp 120.5−122.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.47 (m, 2H), 7.28−7.10 (m, 9H), 7.03 (t, J = 8.7 Hz, 2H), 6.97−6.94 (m, 2H), 6.87 (t, J = 8.7 Hz, 2H), 5.26 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 4.19 (dd, J = 14.8 Hz, J = 1.6 Hz, 1H), 4.12 (dd, J = 14.8 Hz, J = 4.8 Hz, 1H), 2.40 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 163.3 (d, J = 250.2 Hz), 162.9 (d, J = 250.2 Hz), 143.3, 138.7, 137.1 (d, J = 8.1 Hz), 136.4 (d, J = 8.1 Hz), 135.3, 131.9, 131.7, 129.4, 128.3, 128.2, 127.8, 127.1, 121.6 (d, J = 3.3 Hz), 120.9 (d, J = 3.3 Hz), 116.8 (d, J = 21.7 Hz), 116.3 (d, J = 21.7 Hz), 74.3, 59.4, 21.4. EIMS (70 eV, m/z (relative intensity)): 645 (8), 491 (9), 316 (58), 297 (40), 207 (71), 142 (100), 115 (53), 91 (90). HRMS: calcd for $C_{29}H_{24}F_2NO_2SSe_2$ (ESI-TOF, M + H$^+$), 647.9826; found, 647.9831.

*4-(Butylselanyl)-3-(pentylselanyl)-2-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (**7d**).* Obtained as a light yellow solid. Yield: 0.065 g (46%); mp 56.2−58.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, J = 8.3 Hz, 2H), 7.27−7.14 (m, 7H), 5.45 (dd, J = 4.5 Hz, J = 1.7 Hz, 1H), 4.50 (dd, J = 14.0 Hz, J = 1.7 Hz, 1H), 4.36 (dd, J = 14.0 Hz, J = 5.0 Hz, 1H), 2.82−2.71 (m, 2H), 2.44−2.27 (m, 5H), 1.62 (quint, J = 7.5 Hz, 2H), 1.47−1.17 (m, 6H), 0.92 (t, J = 7.3 Hz, 3H), 0.79 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 143.2, 139.4, 135.6, 131.0, 129.4, 129.0, 128.3, 128.1, 127.9, 127.1, 74.7, 59.0, 32.8, 32.4, 25.8, 24.8, 22.7, 22.6, 21.4, 13.5, 13.3. EIMS (70 eV, m/z (relative intensity)): 571 (20), 413 (11), 297 (49), 222 (21), 142 (100), 115 (37), 91 (69), 77 (4). HRMS: calcd for $C_{25}H_{34}NO_2SSe_2$ (ESI-TOF, M + H$^+$), 572.0630; found, 572.0647.

*2-Phenyl-3,4-bis(phenylthio)-1-tosyl-2,5-dihydro-1H-pyrrole (**7e**).* Obtained as an orange solid. Yield: 0.045 g (35%); mp 105.1−107.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39−7.17 (m, 15H), 7.03−6.95 (m, 4H), 5.34 (dd, J = 4.7 Hz, J = 1.4 Hz, 1H), 4.28 (dd, J = 15.0 Hz, J = 1.4 Hz, 1H), 4.18 (dd, J = 15.0 Hz, J = 4.7 Hz, 1H), 2.44 (s, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 143.4, 139.0, 135.3, 133.8, 133.3, 132.7, 131.8, 131.5, 130.9, 126.5, 129.4, 129.0, 128.6, 128.3, 128.2, 127.8, 127.7, 127.3, 72.2, 57.5, 21.5. EIMS (70 eV, m/z (relative intensity)): 512 (32), 359 (35), 250 (100), 207 (66), 147 (78), 115 (24), 91 (74), 77 (16). HRMS: calcd for $C_{29}H_{26}NO_2S_3$ (ESI-TOF, M + H$^+$), 516.1125; found, 516.1130.

Procedure for Kumada Cross-Coupling Reaction of Dihydro-2*H*-pyran with Organo Magnesium Reagents. To mixture of 3,6-dihydro-2*H*-pyran **5d** (0.25 mmol) and $Pd(PPh_3)_4$ (0.1 equiv) in THF (2 mL) was added the (4-methoxyphenyl)magnesium bromide (4 equiv). The mixture was heated in an oil bath for 3 h at 60 °C. After which the reaction was cooled to ambient temperature, diluted with ethyl acetate (3 mL), and washed with saturated solution of NH_4Cl (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane to yield 5-(butylselanyl)-4-(4-methoxyphenyl)-6-phenyl-3.6-dihydro-2*H*-pyran (**8**), obtained as a yellow oil. Yield: 0.057 g (57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49−7.46 (m, 2H), 7.41−7.30 (m, 5H), 6.91−6.88 (m, 2H), 5.24−5.23 (m, 1H), 4.03−3.96 (m, 1H), 3.87−3.80 (m, 4H), 2.69−2.55 (m, 2H), 2.17−2.02 (m, 2H), 1.33 (quint, J = 7.3 Hz, 2H), 1.19−1.07 (m, 2H), 0.74 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 158.7, 140.1, 139.8, 134.5, 129.3, 129.1, 128.2, 125.4, 113.4, 80.8, 61.9, 55.1, 33.6, 31.7, 26.0, 22.6, 13.4. EIMS (70 eV, m/z (relative intensity)): 402 (7), 265 (89), 207 (100), 133 (33), 115 (26), 105 (55), 96 (25), 77 (25). HRMS: calcd for $C_{22}H_{27}O_2Se$ (ESI-TOF, M + H$^+$), 403.1176; found, 403.1181.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and CIF files giving spectroscopic data for all new compounds and X-ray results (CCDC 1058759). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01448.

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Notes

The authors declare no competing financial interest.

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