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Cooperative action between Iron(III) chloride and diorganyl dichalcogenides for the cyclization of *N*-(*ortho*-Alkynyl)aryl-pyrroles

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ABSTRACT

We report the ability of iron(III) chloride and diorganyl dichalcogenides to promote de cyclization of *N*-(*ortho*-alkynyl)aryl-pyrroles leading to 5-(organochalcogenyl)pyrrolo[1,2-*a*]quinolines. The combination of diorganyl dichalcogenides and iron(III) chloride was crucial for the cyclization reaction to occur because neither the iron salt nor diorganyl diselenide alone were able to promote the cyclization. The effects of solvent, temperature, reaction time, and stoichiometry on the efficiency of cyclization reactions were investigated. The standard reaction conditions were compatible with many functional groups in the substrates, such as methyl, chlorine, and methoxy. In addition, under these conditions, not only diaryl, but also dialkyl dichalcogenides have been cyclized in moderate to good yields. The 5-(organochalcogenyl)pyrrolo[1,2-*a*]quinolines prepared underwent a Suzuki cross-coupling reaction with boronic acids under palladium catalyze to give the cross-coupled products in good yields.

1. Introduction

Alkynes represent an important class of functional groups which present in organic substrates give them a peculiar reactivity by under its behaves both as an electrophile and as a nucleophile [1]. Despite these, both metal-free and metal-catalyzed cyclization reactions of alkynes have emerged as one of the best choices for the preparation of carbocycles and heterocycles [2]. Among them, the electrophile-promoted nucleophilic cyclization has become an effective tool to promote the cyclization of alkynes [3]. The advantages of these methodologies is that an electrophilic source is generally used to activate the carbon-carbon triple bond of alkyne as well as to introduce new functionality in the structure of the final product. The halogens are the most used electrophilic agents [4], although the organoselenium compounds have emerged as a versatile and convenient alternative source [5]. The application of an electrophilic organoselenium species to active the alkynes has been a useful tool for the synthesis of carbocycles or heterocycles containing an organoselenim function [6]. However, in some cases in the cyclization reactions in which an electrophilic organoselenium species is the activator, only the reduction of the carbon-carbon triple bond is observed giving the addition product without cyclization taking place [7]. To prevent this drawback, the application of iron(III) chloride and diorganyl diselenides, as a tool to promote de cyclization of unsaturated substrates, has recently attracted much attention [8]. The preparation of organoselenium compounds has stimulated intensive research because of the exclusive reactivity of the carbon-selenium bond, which enables the chemioselective formation of new compounds [9], as well as because of their promising pharmacological applications as therapeutic agents in the treatment of several diseases [10]. The use of iron reagents is a rapidly growing area because of their high efficiency, relative stability, abundance, low toxicity, economic, and ecologic advantages [11]. The wide range of application of the intramolecular hydroarylation reaction [12] and the high ability that the mixture diorganyl diselenides and iron(III) chloride has in promoting the concomitant cyclization and functionalization of unsaturated substrates, avoiding the reduction product **3**, prompted us to propose the synthesis of 5-(organochalcogenyl)pyrrolo[1,2-*a*]quinolines **2** from *N*-(*ortho*-alkynyl)aryl-pyrroles (Scheme 1). Pyrrolo[1,2-*a*]quinolines are an important class of *N*-heterocycles because they present significant biological properties, such as antimicrobial, antibacterial, and antitumor, activities [13]. Furthermore, pyrrolo[1,2-*a*]quinolines also have been found to have optoelectronic properties [14].

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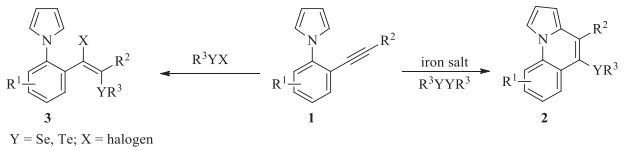


Scheme 1. General scheme.

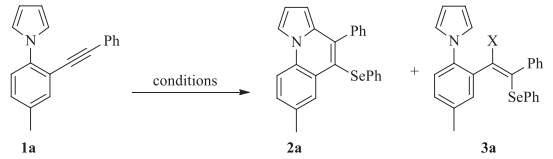
2. Results and discussion

The requisite *N*-(*ortho*-alkynyl)aryl-pyrrole precursors are readily synthesized from the corresponding 1-(2-iodophenyl)-1*H*-pyrroles [15] via Sonogashira cross-coupling with terminal alkynes [16]. After that, to study the optimization of the reaction conditions of the proposed procedure, the cyclization reaction of *N*-(*ortho*-alkynyl)aryl-pyrrole **1a** was tested by varying several reaction parameters. The results are shown in Table 1. Considering the nucleophilic nature of the triple bond, we planned that the use of phenylselanyl bromide (PhSeBr) would promote activation of the carbon-carbon triple bond followed by cyclization upon a nucleophilic attack of the pyrrole ring, to give the 5-(phenylselanyl)pyrrolo[1,2-*a*]quinoline **2a**. To this end, the addition of phenylselanyl bromide (1.5 equiv) to a solution of *N*-(*ortho*-alkynyl)aryl-pyrrole **1a** (0.2 mmol) in dichloroethane (3 mL), was carried out at room temperature under a nitrogen atmosphere for 24 h. These conditions led to the formation of **2a** in 20% yields in a mixture of reduced **3a** (Table 1, entry 1). Further studies revealed that the increase of PhSeBr amount to 2.0 equiv and the addition of base did not improve the yield of **2a** (Table 1, entries 2 and 3). As indicated in the introduction, the use of diorganyl diselenides and iron salts may overcome these unsatisfactory results. For this purpose, we promoted the addition of *N*-(*ortho*-alkynyl)aryl-pyrrole **1a** (0.20 mmol), at room temperature, under nitrogen atmosphere, to a solution of FeCl3·6H2O (2.0) and diphenyl diselenide (1.1 equiv) in dichloromethane (3 mL), which was prepared 15 min before. The reaction was stirred at room temperature for 24 h. However, there was no significant improvement in the reaction yield (Table 1, entry 4). Other iron salts were examined revealing that FeCl3 was the most effective giving the product **2a** in 81% yield (Table 1, entries 5–7). No significant effect on the reaction yield was observed by using diphenyl diselenide with other Lewis or Brønsted acids instead of iron(III) chloride (Table 1, entries 8–12). The employment of 1.5 and 1.0 equiv or catalytic amount of iron(III) chloride gave the product **2a** in lower yields, even under heating and long reaction time (Table 1, entries 13–16). The amount of diphenyl diselenide had a pronounced effect on the cyclization reaction in which the decrease to 0.85 or 0.6 equiv led to a significant reduction in the yield of 2a (Table 1, entries 17–19). Among the solvents screened for the reaction, dichloroethane, nitromethane, and acetonitrile gave the product 2a in inferior yields than dichloromethane, while dimethylformamide and tetrahydrofuran did not give the product (Table 1, entries 20–24). We used TLC for measuring the time for complete consumption of the starting material and we found that 0.5 h was the time required for the reaction to reach completion (Table 1, entries 25 and 26). We made other changes in the reaction parameters such as the addition of bases, heating, and concentration of the solution; however, none of these changes had any positive effects on the reaction yields (Table 1, entries 27–32). Once studied the variations of the reaction parameters, we concluded that the addition of *N*-(*ortho*-alkynyl) aryl-pyrrole 1a (0.2 mmol) to a mixture of diphenyl diselenide (1.1 equiv) and FeCl3 (2.0 equiv) in dichloromethane (3 mL), under an argon atmosphere, at room temperature, for 0.5 h, was the ideal condition to obtain the 5-(phenylselanyl)pyrrolo[1,2-*a*]quinoline 2a in high yield (Table 1, entry 24).

We then used the optimal reaction conditions (Table 1, entry 24) to explore the synthetic utility of this protocol for the variation of the *N*-(*ortho*-alkynyl)aryl-pyrroles and diorganyl dichalcogenides. The experimental results from these studies are shown in Table 2. *N*-(*ortho*-alkynyl)aryl-pyrrole having electron-neutral, electron-rich, and electron-poor aryl groups directly bonded to alkyne reacted very well under optimized reactions conditions, in a very short reaction time, to give the corresponding 5-(phenylselanyl) pyrrolo[1,2-*a*]quinolines in good yields (Table 2, **2a-f**). The reaction yield was reduced with an alkyl chain at the alkyne (Tables 2 and **2g**). This poor yield is probably because of the absence of pi (π) bonds next to the alkyne, which becomes the carbon-carbon triple bond less reactive towards iron activation and nucleophilic attack (see Scheme 2, mechanism proposal). We also studied the introduction of heteroatoms on the alkyne terminus. The reaction of silylacetylene with standard conditions gave a mixture of desired product 2 h and the hydrogenated derivative **2h'** (Table 2, **2h** and **2h′**). In this case, the formation of **2h′** may be attributed to the cleavage of the carbon-silicon bond on the starting material leading to the in situ formation of a terminal alkyne, which cyclizes to give the product **2h'**. When we introduced an iodine atom on the alkyne terminus, the product of the reduction of the carbon-carbon triple bond was formed with the entry of the SePh groups into carbons 1 and 2, respectively. We believe that this product was formed through the in situ formation of selenoacetylene, which is further reduced to 2i (Tables 2 and **2i**). Another limitation of our methodology was observed when we extended the optimized conditions to *N*-(*ortho*-alkynyl)aryl-pyrrole having a terminal alkyne. This substrate gave the product **2j** in 14% yield together with the starting material even though by texting other reaction conditions (Tables 2 and **2j**). Next, we evaluated the influence of groups directly bonded to the aromatic ring. In this study, we observed that the presence of a chlorine atom in the aromatic ring greatly reduced the reaction yield demonstrating the influence of the electronic effect in this process (Table 2, **2k** and **2l**). From the results obtained by using substituted diaryl diselenides, it is apparent that the electronic effect of these substitutes did not have a great influence, although diselenides having a methoxy group did not provide the product (Table 2, **2m-s**). However, the product **2n** was detected by GC-MS in the crude reaction, but it was not stable during the purification process. The reaction rate of mesityl diselenide is slower compared to that with diphenyl diselenide showing a strong steric influence of the substituents (Tables 2 and 2s). In further screening, it was found that similar yields were obtained by changing diaryl diselenides to dialkyl diselenides in which dibutyl diselenide lead to the formation of the expected products in good yields (Table 2, 2t and 2u). The optimized conditions were then extended to the disulfide and ditelluride derivatives. The reaction with diphenyl disulfide did not afford the quinoline 2v corresponding (Tables 2 and 2v). We suppose that the iron incorporation into disulfides was blocked because the sulfur-sulfur bond of disulfides is stronger than the selenium-selenium bond. The cyclization with diphenyl ditelluride resulted in the quinoline 2w in 84% yield, while with dibutyl ditellurides only a trace amount of 2x was obtained (Table 2, **2w** and **2x**). All the compounds were characterized by 1H and 13C NMR spectroscopy. Furthermore, the 6-*endo*-dig cyclization sequence was confirmed by X-ray analysis of the crystalline sample (Supporting Information, Figures F1 and F2, CCDC 2054305 and 2054306 for compounds **2b a**nd **2m**, respectively) [17].

Based on the above results and the previous report [18], a possible reaction mechanism is shown in Scheme 2. The reaction of FeCl3 and diorganyl diselenide would give the iron-seleno complex, in which the electrophilic portion of the selenium species coordinates to the carbon-carbon bond of alkyne to generate the

Table 1
Effects of different reaction parameters on the preparation of 5-(phenylselanyl)pyrrolo[1,2-*a*]quinoline **2a**.[a].



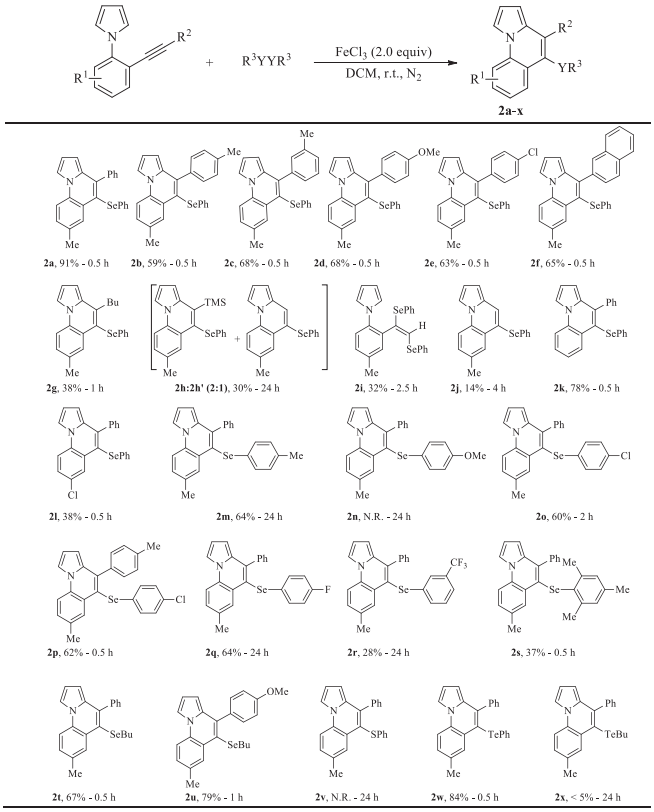
Entry	promoter (equiv)	$(PhSe)_2$ (equiv)	solvent	reaction time (h)	Yields (%)[b]
1	PhSeBr (1.5)	–	DCE	24	20[c]
2	PhSeBr (2.0)	–	DCE	24	29[c,d]
3	PhSeBr (2.0)	–	DCE	24	N.D.[c,e]
4	$FeCl_3·6H_2O$ (2.0)	1.1	DCM	24	33
5	Fe_2O_3 (2.0)	1.1	DCM	24	N.D.[e]
6	$FeSO_4·7H_2O$ (2.0)	1.1	DCM	24	N.D.[e]
7	$FeCl_3$ (2.0)	1.1	DCM	24	81
8	$BF_3·OEt_2$ (2.0)	1.1	DCM	24	19
9	$TsOH·H_2O$ (2.0)	1.1	DCM	24	N.D.[e]
10	$AgCl_2$ (2.0)	1.1	DCM	24	33
11	$AlCl_3$ (2.0)	1.1	DCM	24	N.D.[e]
12	$CuCl_2$	1.1	DCM	24	N.D.[e]
13	$FeCl_3$ (1.5)	1.1	DCM	24	64
14	$FeCl_3$ (1.0)	1.1	DCM	24	39
15	$FeCl_3$ (1.0)	1.1	DCM	24	46[f]
16	$FeCl_3$ (0.3)	1.1	DCM	24	N.D.[e]
17	$FeCl_3$ (2.0)	0.85	DCM	0.5	52
18	$FeCl_3$ (2.0)	0.6	DCM	24	57
19	$FeCl_3$ (2.0)	0.6	DCM	24	47[g]
20	$FeCl_3$ (2.0)	1.1	DCE	0.5	59
21	$FeCl_3$ (2.0)	1.1	$MeNO_2$	1	65
22	$FeCl_3$ (2.0)	1.1	MeCN	24	40
23	$FeCl_3$ (2.0)	1.1	DMF	24	N.D.[e]
24	$FeCl_3$ (2.0)	1.1	THF	24	N.D.[e]
25	$FeCl_3$ (2.0)	1.1	DCM	1	93
26	$FeCl_3$ (2.0)	1.1	DCM	0.5	91
27	$FeCl_3$ (2.0)	1.1	DCM	0.5	70[h]
28	$FeCl_3$ (2.0)	1.1	DCM	0.5	76[i]
29	$FeCl_3$ (2.0)	1.1	DCM	0.5	52[j]
30	$FeCl_3$ (2.0)	1.1	DCM	24	75[k]
31	$FeCl_3$ (2.0)	1.1	DCM	0.5	25[l]
32	$FeCl_3$ (2.0)	–	DCM	24	N.D.[e,m]

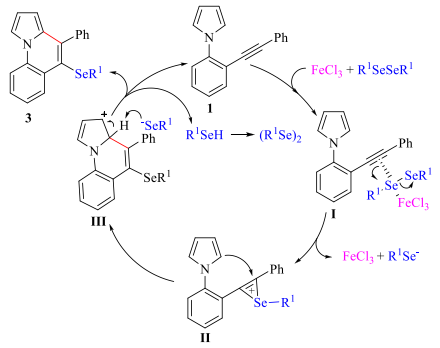
[a] The reaction was performed by the addition of *N*-(*ortho*-alkynyl)aryl-pyrrole 1a (0.20 mmol), at room temperature, under argon atmosphere, to a solution of promoter and diphenyl diselenide in solvent (3 mL), which was prepared 15 min before. The reaction was stirred at room temperature for the time indicated in Table 1.
[b] Isolated yield after column chromatography.
[c] **3a** (X = Br) was also detected, however in an inseparable mixture.
[d] $NaHCO_3$ (2 equiv) was used.
[e] N.D. = not detected.
[f] The reaction was heated at 40 °C.
[g] The reaction was carried out under air atmosphere in an open flask.
[h] K_2CO_3 (2 equiv) was used.
[i] K_3PO_4 (2 equiv) was used.
[j] The *N*-(*ortho*-alkynyl)aryl-pyrrole 1a was added at 0 °C.
[k] DCM (1 mL) was used.
[l] DCM (5 mL) was used.
[m] The reaction was carried out in the absence of diphenyl diselenide.

intermediate I. The carbon-carbon triple bond is activated by the iron-seleno complex forming the seleniranium ion II. The selective intramolecular 6-*endo*-dig cyclization promoted by anti nucleophilic attack of the pyrrole ring gives the intermediate III. The removal of the hydrogen by the selenolate anion, restores the aromatic system affording the cyclized product. Because the cyclization promoted by iron salts can also form radical species, the hypothesis of this reaction following a classical radical pathway cannot be ruled out.

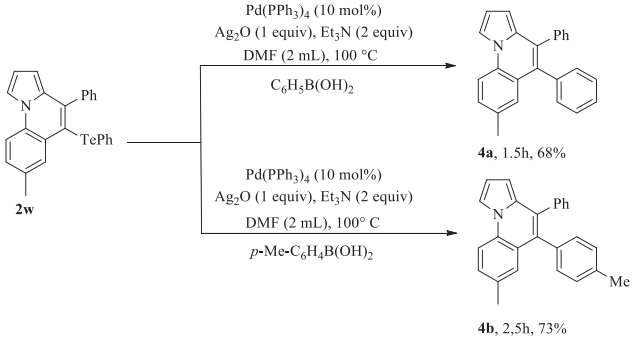
Organochalcogen compounds have received considerable attention in modern organic chemistry because of their chemo, regio, and stereoselective reactions. In this context, organic compounds that exhibit Csp2-Se or Csp2-Te bonds in the structure are useful substrates for the formation of new carbon-carbon bonds including carbon-alkynyl, carbon-vinyl, carbon-aryl, and carbon-heteroaryl bond formation [19]. Thus, the presence of an organochalcogenyl group at the 5-position of the quinolines making them potential substrates for further transformations. In this context, we evaluated the use of quinoline **2w** as the substrate in the reaction with boronic acids in a Suzuki cross-coupling reaction [20]. A brief optimization of this reaction condition revealed that the reaction of quinoline **2w** with phenylboronic acid and *p*-tolylboronic acid, using palladium(0) as the catalyst in DMF at 100 °C gave the cross-coupled products **4a** and **4b** in 68% and 73% yields, respectively

Table 2
Preparation of 5-(phenylselanyl)pyrrolo[1,2-*a*]quinoline 2.[a].





Scheme 2. Reaction mechanism for the formation of 5- (phenylselanyl) pyrrolo [1,2-a] quinoline.



Scheme 3. Application of quinoline 2w as the substrate in the Suzuki cross-coupling reactions.

(Scheme 3).

3. Conclusion

In summary, we demonstrated that the cooperative action between diorganyl dichalcogenides and iron(III) chloride was very efficient to promote de cyclization of *N*-(*ortho*-alkynyl)aryl-pyrroles leading to 5-(organochalcogenyl)pyrrolo[1,2-*a*]quinolines. The reaction parameters were studied and the standard condition works well with a wide range of substituents in both diorganyl dichalcogenides and *N*-(*ortho*-alkynyl)aryl-pyrroles, resulting in the formation of products in good yields, and proceed under relatively mild conditions. The resulting products proved to be versatile as precursors for the synthesis of more highly functionalized quinolines through palladium-catalyzed cross-coupling reactions with aryl boronic acid. The main advantages of this methodology are based on the incorporation of the useful organochalcogen functionalities in the structure and the high regioselectivity of the intramolecular 6-*endo*-dig over the 5-*exo*-dig mode.

4. Experimental section

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz or at 400 MHz spectrometer. Spectra were recorded in $CDCl_3$ solutions. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either at 50 MHz or at 100 MHz

spectrometer. Spectra were recorded in $CDCl_3$ solutions. Mass spectra were recorded on a spectrometer using EI at 70 eV. High resolution mass spectra were recorded on a LC-MS-IT-TOF. Column chromatography was performed using Silica Gel (230–400 mesh). Thin layer chromatography (TLC) was performed using Silica Gel GF_{254}, 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.

General procedure for the preparation of 5-(organochalcogenyl)pyrrolo[1,2-*a*]quinolines 2a-x: In a Schlenke flask, under argon atmosphere, at room temperature *N*-(*ortho*-alkynyl)aryl-pyrroles (0.25 mmol) was added to a solution of $FeCl_3$ (2.0 equiv) and diorganyl dichalcogenides (1.1 equiv) in DCM (3 mL), which was prepared 15 min before. The reaction was stirred at room temperature for the time indicated in Table 2. The mixture was diluted with ethyl acetate and washed with concentrated NH_4Cl solution. The organic phase was dried with MgSO4, the solvent was removed under reduced pressure. The residue was purified by column chromatography.

7-methyl-4-phenyl-5-(phenylselanyl)pyrrolo[1,2-a]quinolone **(2a)**. The product was isolated by column chromatography (hexane as eluent) as a brown solid. Yield: 0.075 g (91%); mp. 104–108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.20–8.14 (m, 1H), 7.91 (dd, J = 2.9, 1.5 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.40-7.34 (m, 3H), 7.34-7.27 (m, 3H), 7.16–7.08 (m, 2H), 7.09–7.03 (m, 3H), 6.72 (dd, J = 3.9, 2.8 Hz, 1H), 6.13 (dd, J = 3.9, 1.5 Hz, 1H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.8, 139.7, 134.0, 133.7, 131.9, 131.1, 130.7, 129.3, 129.3, 129.2, 128.9, 127.8, 127.8, 125.6, 124.8, 117.2, 114.2, 113.2, 112.9, 106.2, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 413 (50), 411 (25), 333 (100), 255 (17), 158 (12). HRMS calcd for $C_{25}H_{20}NSe$ (ESI-TOF, [M + H$^+$]), 414.0761, found 414.0772.

7-methyl-5-(phenylselanyl)-4-(p-tolyl)pyrrolo[1,2-a]quinolone **(2b)**. The product was isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.063 g (59%); mp. 149–154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.16–8.14 (m, 1H), 7.93–7.87 (m, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.25–7.16 (m, 4H), 7.16–7.10 (m, 2H), 7.10–7.03 (m, 3H), 6.71 (dd, J = 3.8, 2.9 Hz, 1H), 6.16 (dd, J = 3.9, 1.4 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.9137.5, 136.9, 134.1, 133.7, 132.1, 131.1, 130.8, 129.2, 129.2, 128.9, 128.6, 125.6, 124.9, 117.1, 114.0, 113.1, 112.9, 106.3, 21.34, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 427 (43), 347 (100), 331 (13), 268 (12), 254 (13), 207 (08), 165 (12), 158 (11). HRMS calcd for $C_{26}H_{22}NSe$ (ESI-TOF, [M + H$^+$]), 428.0917, found 428.0926.

7-methyl-5-(phenylselanyl)-4-(m-tolyl)pyrrolo[1,2-a]quinolone **(2c)**. The product was isolated by column chromatography (hexane as eluent) as a brown solid. Yield: 0.073 g (68%); mp. 108–112 °C. ^{1}H NMR (CDCl3, 400 MHz): δ (ppm) 8.18 (d, J = 1.5 Hz, 1H), 7.87 (dd, J = 2.9, 1.5 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.29–7.25 (m, 2H), 7.19–7.15 (m, 1H), 7.14–7.09 (m, 3H), 7.09–7.06 (m, 2H), 7.06–7.02 (m, 3H), 6.70 (dd, J = 3.9, 2.8 Hz, 1H), 6.14 (dd, J = 3.9, 1.5 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.9, 139.6, 137.3, 134.2, 133.6, 131.9, 131.0, 130.7, 130.0, 129.3, 129.2, 128.9, 128.5, 127.7, 126.3, 125.6, 124.9, 117.1, 114.0, 113.1, 112.8, 106.2, 21.4, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 427 (13), 347 (100), 331 (12), 268 (15), 165 (09), 127. HRMS calcd for $C_{26}H_{22}NSe$ (ESI-TOF, [M + H$^+$]), 428.0917, found 428.0902.

4-(4-methoxyphenyl)-7-methyl-5-(phenylselanyl)pyrrolo[1,2-a] quinoline **(2d)**. The product was isolated by column chromatography (hexane as eluent) as a brown solid. Yield: 0.075 g (68%); mp. 162–165 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.16 (s, 1H), 7.90 (dd, J = 2.8, 1.5 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.30 (dd, J = 8.5, 1.5 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 7.23 (d, J = 3.8 Hz, 1H), 7.14–7.10 (m, 2H), 7.10–7.04 (m, 3H), 6.90 (d, J = 8.7 Hz, 2H), 6.72 (dd, J = 3.8, 2.9 Hz, 1H), 6.18 (dd, J = 3.9, 1.4 Hz, 1H), 3.83 (s, 3H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.2, 140.5, 134.1, 133.7, 132.2, 132.1, 131.0, 130.7, 130.6, 129.2, 129.1, 129.0, 125.6, 124.9, 117.3, 114.0, 113.2, 113.1, 112.8, 106.2, 55.2, 21.1. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 294.3. HRMS calcd for $C_{26}H_{22}NOSe$ (ESI-TOF, [M + H$^+$]), 444.0867, found 444.0875.

4-(4-chlorophenyl)-7-methyl-5-(phenylselanyl)pyrrolo[1,2-a]quinolone **(2e)**. The product was isolated by column chromatography (hexane as eluent) as a green solid. Yield: 0.070 g (63%); mp. 133–136 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.18–8.16 (m, 1H), 7.91 (dd, J = 2.9, 1.5 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.36–7.30 (m, 3H), 7.25–7.20 (m, 2H), 7.12–7.03 (m, 5H), 6.73 (dd, J = 3.9, 2.8 Hz, 1H), 6.12 (dd, J = 3.9, 1.4 Hz, 1H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 139.4, 138.0, 133.9, 133.8, 133.7, 131.5, 131.0, 130.7, 130.6, 129.6, 129.1, 129.0, 128.1, 125.7, 124.7, 117.4, 114.1, 113.3, 113.0, 106.0, 21.23. MS (EI, 70 eV; *m/z* (relative intensity)): 447 (48), 367 (100), 331 (27), 254 (21), 158 (30). HRMS calcd for $C_{25}H_{19}ClNSe$ (ESI-TOF, [M + H$^+$]), 448.0371, found 448.0360.

7-methyl-4-(naphthalen-2-yl)-5-(phenylselanyl)pyrrolo[1,2-a] quinolone **(2f)**. The product was isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.075 g (65%); mp. 117–121 °C. ^{1}H NMR (CDCl3, 400 MHz): δ (ppm) 8.24–8.18 (m, 1H), 7.90 (dd, J = 2.9, 1.5 Hz, 1H), 7.87–7.83 (m, 2H), 7.82–7.77 (m, 1H), 7.78–7.72 (m, 1H), 7.74–7.70 (m, 1H), 7.49–7.41 (m, 3H), 7.31 (ddd, J = 8.4, 2.0, 0.5 Hz, 1H), 7.12–7.07 (m, 2H), 7.06–7.01 (m, 3H), 6.70 (dd, J = 3.9, 2.8 Hz, 1H), 6.14 (dd, J = 3.9, 1.5 Hz, 1H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.6, 137.2, 134.1, 133.8, 133.0, 132.0, 132.0, 131.1, 130.768, 129.4, 129.3, 128.9, 128.4, 128.2, 127.7, 127.6, 127.4, 126.1, 126.0, 125.7, 124.9, 117.5, 114.1, 113.2, 113.0, 106.3,21.2. HRMS calcd for $C_{29}H_{22}NSe$ (ESI-TOF, [M + H$^+$]), 464.0917, found 464.0908.

4-butyl-7-methyl-5-(phenylselanyl)pyrrolo[1,2-a]quinoline **(2g).** The product was isolated by column chromatography (hexane as eluent) as a black oil. Yield: 0.037 g (38%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 1H), 7.85 (dd, J = 2.8, 1.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.23 (dd, J = 8.6, 1.9 Hz, 1H), 7.20–7.15 (m, 2H), 7.12–7.05 (m, 3H), 6.79 (dd, J = 3.8, 2.9 Hz, 1H), 6.67 (dd, J = 3.9, 1.4 Hz, 1H), 3.22–3.16 (m, 2H), 2.35 (s, 3H), 1.64 (qt, J = 7.4 Hz, 2H), 1.44 (sext, J = 7.3 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 140.5, 133.6, 133.5, 131.1, 130.7, 130.2, 129.1, 128.7, 128.5, 125.6, 125.1, 116.6, 113.9, 112.9, 112.6, 103.6, 34.5, 32.4, 23.1, 21.2, 13.9. MS (EI, 70 eV; *m/z* (relative intensity)): 393 (78), 316 (74), 270 (63), 254 (17), 236 (100), 220 (18), 194 (73), 127 (15). HRMS calcd for $C_{23}H_{24}NSe$ (ESI-TOF, [M + H$^+$]), 394.1074, found 394.1050.

7-methyl-5-(phenylselanyl)pyrrolo[1,2-a]quinoline **(2j)**. The product was isolated by column chromatography (hexane as eluent) as a black oil. Yield: 0.014 g (14%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.96–7.90 (m, 1H), 7.85–7.79 (m, 1H), 7.78–7.72 (m, 2H), 7.39–7.35 (m, 2H), 7.30 (dd, J = 8.3, 1.8 Hz, 1H), 7.22–7.16 (m, 3H), 6.78–6.74 (m, 1H), 6.50 (d, J = 3.8 Hz, 1H), 2.40 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ 133.6, 132.1, 131.5, 131.2, 130.7, 130.7, 129.5, 129.2, 128.3, 126.6, 124.0, 117.9, 114.2, 112.9, 112.6, 103.7, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 337 (25), 257(100), 180 (19), 168 (24), 127 (14). HRMS calcd for $C_{19}H_{16}NSe$ (ESI-TOF, [M + H$^+$]), 338.0448, found 338.0445.

4-phenyl-5-(phenylselanyl)pyrrolo[1,2-a]quinoline **(2k).** The product was isolated by column chromatography (hexane as eluent) as a grey solid. Yield: 0.078 g (78%); mp. 103–104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.35 (dd, J = 8.2, 1.2 Hz, 1H), 7.93 (dd, J = 2.9, 1.5 Hz, 1H), 7.88 (dd, J = 8.3, 1.0 Hz, 1H), 7.47 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.39–7.36 (m, 3H), 7.35–7.31 (m, 2H), 7.25 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.13–7.09 (m, 2H), 7.07–7.03 (m, 3H), 6.73 (dd, J = 3.9, 2.9 Hz, 1H), 6.16 (dd, J = 3.9, 1.5 Hz, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$,

100 MHz): δ 140.8, 139.6, 133.9, 133.0, 132.0, 130.9, 129.3, 129.0, 129.0, 128.1, 127.9, 127.8, 125.6, 124.8, 124.2, 117.1, 114.1, 113.4, 113.2, 106.5. MS (EI, 70 eV; *m/z* (relative intensity)): 399 (42), 397 (22), 319 (100), 241 (34), 159(15). HRMS calcd for $C_{24}H_{18}NSe$ (ESI-TOF, $[M + H^+]$), 400.0604, found 400.0611.

7-chloro-4-phenyl-5-(phenylselanyl)pyrrolo[1,2-a]quinoline **(2l)**. The product was isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.041 g (38%); mp. 120–120 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.38 (d, *J* = 2.3 Hz, 1H), 7.86 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.44–7.35 (m, 4H), 7.31–7.27 (m, 2H), 7.12–7.02 (m, 5H), 6.73 (dd, *J* = 3.9, 2.9 Hz, 1H), 6.17 (dd, *J* = 3.9, 1.4 Hz, 1H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 141.9, 139.2, 133.2, 131.8, 131.5, 130.2, 129.7, 129.4, 129.2, 129.1, 128.1, 128.0, 127.9, 126.6, 126.0, 116.3, 115.6, 113.6, 113.6, 107.1. MS (EI, 70 eV; *m/z* (relative intensity)): 437 (03), 433 (51), 353 (100), 317 (27), 275 (15), 240 (21), 213 (08), 158 (20). HRMS calcd for $C_{24}H_{17}ClNSe$ (ESI-TOF, $[M + H^+]$), 434.0215, found 434.0203.

7-methyl-4-phenyl-5-(p-tolylselanyl)pyrrolo[1,2-a]quinolone **(2m)**. The product was isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.068 g (64%). mp. 144–146 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.19 (s, 1H), 7.86 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.39–7.24 (m, 6H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.69 (dd, *J* = 3.9, 2.8 Hz, 1H), 6.12 (dd, *J* = 3.8, 1.3 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 140.6, 139.9, 135.5, 133.6, 132.0, 131.1, 130.9, 130.1, 129.8, 129.5, 129.4, 129.3, 127.8, 127.7, 125.0, 117.6, 114.0, 113.1, 112.9, 106.1, 21.2, 20.9. MS (EI, 70 eV; *m/z* (relative intensity)): 427 (41), 347 (100), 331 (12), 255 (15), 165 (16). HRMS calcd for $C_{26}H_{22}NSe$ (ESI-TOF, $[M + H^+]$), 428.0917, found 428.0915.

*5-((4-chlo*rophenyl)selanyl)-7-methyl-4-phenylpyrrolo[1,2-*a*]quinoline **(2o)**. The product was isolated by column chromatography (hexane as eluent) as a yellow solid. Yield: 0.067 g (60%); mp. 141–143 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.12–8.10 (m, 1H), 7.89 (dd, *J* = 2.9, 1.5 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.40–7.35 (m, 3H), 7.32–7.26 (m, 3H), 7.02 (d, *J* = 0.6 Hz, 4H), 6.71 (dd, *J* = 3.9, 2.8 Hz, 1H), 6.14 (dd, *J* = 3.9, 1.5 Hz, 1H), 2.38 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 140.9, 139.6, 133.8, 132.2, 131.7, 131.6, 131.4, 131.1, 130.4, 129.5, 129.2, 129.0, 127.9, 127.9, 124.6, 116.7, 114.1, 113.3, 113.0, 106.4, 21.2. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ (ppm) 295.8.MS (EI, 70 eV; *m/z* (relative intensity)): 447 (51), 367 (100), 331 (24), 255 (28), 226 (06), 158 (27). HRMS calcd for $C_{25}H_{19}ClNSe$ (ESI-TOF, $[M + H^+]$), 448.0371, found 448.0363.

5-((4-chlorophenyl)selanyl)-7-methyl-4-(p-tolyl)pyrrolo[1,2-a]quinolone **(2p)**. The product was isolated by column chromatography (hexane as eluent) as a brown solid. Yield: 0.072 g (62%); mp. 162–166 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.10–8.07 (m, 1H), 7.90 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.19 (s, 4H), 7.03 (s, 4H), 6.72 (dd, *J* = 3.8, 2.9 Hz, 1H), 6.17 (dd, *J* = 3.9, 1.4 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 141.0, 137.6, 136.7, 133.8, 132.3, 131.9, 131.6, 131.1, 130.4, 130.3, 129.4, 129.1, 129.0, 128.6, 124.6, 116.6, 114.1, 113.3, 113.0, 106.5, 21.4, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 461 (56), 383 (37), 381 (100), 345 (18), 268(14), 165 (18). HRMS calcd for $C_{26}H_{21}ClNSe$ (ESI-TOF, $[M + H^+]$), 462.0528, found 462.0537.

5-((4-fluorophenyl)selanyl)-7-methyl-4-phenylpyrrolo[1,2-a]quinolone **(2q)**. The product was isolated by column chromatography (hexane as eluent) as a yellow oil. Yield: 0.069 g (64%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) δ 8.17 (s, 1H), 7.87 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.40–7.33 (m, 3H), 7.32–7.24 (m, 3H), 7.06 (dd, *J* = 8.2, 5.6 Hz, 2H), 6.76 (t, *J* = 8.7 Hz, 2H), 6.70 (t, *J* = 3.1 Hz, 1H), 6.12 (d, *J* = 3.7 Hz, 1H), 2.38 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): 161.6 (d, *J* = 245.6 Hz), 140.6, 139.6, 133.7, 131.8, 131.4 (d, *J* = 7.9 Hz), 131.1, 130.5, 129.4, 128.2, 128.3 (d, *J* = 3.4 Hz), 127.9, 127.8, 124.7, 117.6, 116.0 (d, *J* = 21.9 Hz), 114.1, 113.2, 113.0, 106.3, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 431(48), 351 (100), 335 (17), 321 (08), 255(20), 241(11), 167(13). HRMS calcd for $C_{25}H_{19}FNSe$ (ESI-TOF, $[M + H^+]$),432.0667, found 432.0648.

7-methyl-4-phenyl-5-((3-(trifluoromethyl)phenyl)selanyl)pyrrolo[1,2-a]quinolone **(2r)**. The product was isolated by column chromatography (hexane as eluent) as a brown oil solid. Yield: 0.034 g (28%); ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.12 (s, 1H), 7.94 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.44–7.31 (m, 6H), 7.31–7.24 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.74 (t, *J* = 3.2 Hz, 1H), 6.16 (d, *J* = 3.3 Hz, 1H), 2.40 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 141.0, 139.4, 135.1, 133.9, 132.5, 131.7, 131.1 (q, *J* = 32.3 Hz), 131.1, 130.2, 129.6, 129.2, 129.21, 128.0, 127.9, 126.0 (q, *J* = 4.0 Hz), 124.5, 123.7 (q, *J* = 272.7 Hz), 122.5 (q, *J* = 3.7 Hz), 116.4, 114.2, 113.4, 113.0, 106.5, 21.2. MS (EI, 70 eV; *m/z* (relative intensity)): 481 (46), 401 (100), 336 (17), 255 (30), 241 (16), 127 (11). HRMS calcd for $C_{26}H_{19}F_3NSe$ (ESI-TOF, $[M + H^+]$), 482.0635, found 482.0612.

5-(mesitylselanyl)-7-methyl-4-phenylpyrrolo[1,2-a]quinolone **(2s)**. The product was isolated by column chromatography (hexane as eluent) as a black oil. Yield: 0.042 g (37%); ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.98 (s, 1H), 7.81 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 3H), 7.23 (d, *J* = 9.1 Hz, 1H), 7.19 (d, *J* = 7.1 Hz, 2H), 6.65 (d, *J* = 10.8 Hz, 3H), 5.98–5.92 (m, 1H), 2.34 (s, 3H), 2.16 (s, 3H), 2.11 (s, 6H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 141.2, 139.3, 137.2, 137.0, 133.0, 132.4, 130.7, 130.2, 129.6, 129.2, 129.0, 128.6, 127.8, 127.5, 124.8, 119.6, 114.0, 112.5, 112.4, 104.3, 23.8, 21.1, 20.8. MS (EI, 70 eV; *m/z* (relative intensity)): 455 (23), 257 (100), 241 (09). HRMS calcd for $C_{28}H_{26}NSe$ (ESI-TOF, $[M + H^+]$), 456.1230, found 456.1223.

5-(butylselanyl)-7-methyl-4-phenylpyrrolo[1,2-a]quinoline **(2t)**. The product was isolated by column chromatography (hexane as eluent) as a brown oil. Yield: 0.066 g (67%); ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.36–8.34 (m, 1H), 7.83 (dd, *J* = 2.8, 1.5 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.47–7.41 (m, 3H), 7.41–7.37 (m, 2H), 7.33–7.29 (m, 1H), 6.66 (dd, *J* = 3.8, 2.8 Hz, 1H), 6.06 (dd, *J* = 3.8, 1.5 Hz, 1H), 2.54 (d, *J* = 7.3 Hz, 2H), 2.50 (s, 3H), 1.41 (qt, *J* = 7.3 Hz, 2H), 1.19 (sext, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 140.1, 139.7, 133.4, 132.0, 131.0, 130.7, 129.9, 129.0, 127.8, 127.6, 125.4, 118.0, 114.1, 112.7, 112.5, 105.2, 32.0, 29.1, 22.7, 21.3, 13.4. ^{77}Se NMR (77 MHz, in $CDCl_3$ with diphenyl diselenide as external reference) δ(ppm) 168.2. MS (EI, 70 eV; *m/z* (relative intensity)): 393(69), 390 (38), 335 (100), 332 (28), 320 (22), 257 (63), 254 (19) 241 (15). HRMS calcd for $C_{23}H_{24}NSe$ (ESI-TOF, $[M + H^+]$), 394.1074, found 394.1069.

5-(butylselanyl)-4-(4-methoxyphenyl)-7-methylpyrrolo[1,2-a]quinoline **(2u)**. The product was isolated by column chromatography (hexane as eluent) as a brown oil. Yield: 0.084 g (79%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.36–8.31 (m, 1H), 7.81 (dd, *J* = 2.8, 1.5 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.34–7.30 (m, 2H), 7.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.00–6.96 (m, 2H), 6.66 (dd, *J* = 3.8, 2.8 Hz, 1H), 6.10 (dd, *J* = 3.8, 1.5 Hz, 1H), 3.85 (s, 3H), 2.53 (d, *J* = 7.3 Hz, 2H), 2.49 (s, 3H), 1.39 (qt, *J* = 7.3 Hz, 2H), 1.19 (sext, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). ^{13}C {^1H}NMR ($CDCl_3$, 100 MHz): δ 159.0, 139.2, 133.3, 132.5, 132.1, 131.0, 130.8, 130.6, 128.9, 125.3, 118.1, 114.1, 113.2, 112.6, 112.5, 105.1, 55.1, 31.9, 29.0, 22.7, 21.2, 13.4. MS (EI, 70 eV; *m/z* (relative intensity)): 423 (74), 366 (100), 335 (10), 323 (24), 287 (52), 242 (36), 207 (10), 161 (07), 120 (07). HRMS calcd for $C_{24}H_{26}NOSe$ (ESI-TOF, $[M + H^+]$), 424.1180, found 424.1187.

7-methyl-4-phenyl-5-(phenyltellanyl)pyrrolo[1,2-a]quinolone **(2w)**. The product was isolated by column chromatography (hexane as eluent) as a green solid. Yield: 0.097 g (84%); mp. 98–102 °C. ^1H NMR ($CDCl_3$, 400 MHz): 8.18 (s, 1H), 7.88–7.85 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 6.5 Hz, 3H), 7.32 (d, *J* = 7.1 Hz, 2H), 7.27 (t, *J* = 6.4 Hz, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.3 Hz, 2H), 6.71–6.68 (m, 1H), 6.09–6.07 (m, 1H), 2.36 (s, 3H). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ 143.6, 143.1, 135.4, 135.1, 133.7, 131.5, 131.3, 130.4, 129.3, 129.2, 127.9, 127.8, 126.7, 126.0, 117.3, 114.1, 112.9, 112.8,

109.4, 106.1, 21.1. MS (EI, 70 eV; *m/z* (relative intensity)): 463(37), 384(15), 333(100), 255(44), 241(32), 158(10). HRMS calcd for $C_{25}H_{20}NTe$ (ESI-TOF, $[M + H^+]$), 464.0658, found 464.0655.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary data

Experimental procedures, characterization data, and copies of the ^1H NMR and ^{13}C NMR spectra for the products are available. Supplementary data associated with this article can be found in the online version.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132188.

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