DOI: 10.1002/ejoc.201500766

Synthesis of 3-Organoseleno-Substituted Quinolines through Cyclization of 2-Aminophenylprop-1-yn-3-ols Promoted by Iron(III) Chloride with Diorganyl Diselenides

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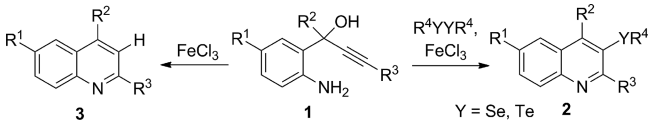
Keywords: Synthetic methods / Nitrogen heterocycles / Cyclization / Regioselectivity / Selenium / Iron

We have described the application of iron(III) chloride and diorganyl diselenides as cooperative partners in the cyclization of (2-aminoaryl)-2-ynols for the regioselective synthesis of 3-organoseleno quinolines. The optimized reaction conditions were applied to (2-aminoaryl)-2-ynols that contain a wide range of functional groups, including electron-rich and electron-poor substituents. The reaction showed regioselectivity for six-membered quinoline products, which were formed by a 6-*endo-dig* ring closure, instead of a 5-*exo-dig* process for the formation of indole products. In addition, we also found that (2-aminoaryl)-2-ynols and a catalytic amount of iron(III) chloride, in the absence of diorganyl diselenides, afforded the corresponding quinoline derivatives without the organoseleno moiety at the 3-position.

Introduction

In recent years, great progress has been made in the area of organochalcogen chemistry, a subject of intensive research in organic synthesis. Traditional methods to the introduce an organochalcogen group into an organic structure have involved the use of nucleophilic,[1] electrophilic,[2] and radical species.[3] The incorporation of an organochalcogen moiety into an organic structure can result in the formation of sp^3-, sp^2-, and sp-hybridized chemical bonds and thus provide useful building blocks for further transformations. Thus far many methods have been reported that use organochalcogen chemistry to form new carbon–carbon,[4] carbon-lithium,[5] carbon-halogen,[6] and carbon-hydrogen bonds.[7] Organochalcogen chemistry has also been proven useful in the synthesis of natural products.[8] Moreover, organochalcogens can exhibit pharmacological activity.[9] For example, reports have shown that organochalcogen derivatives have potential use as anticancer,[10] anti-inflammatory, antibacterial, and antifungal agents.[11]

Herein, we have developed a protocol for the synthesis of 3-organoseleno quinolines **2** by employing the regioselective cyclization of (2-aminoaryl)-2-ynols **1** promoted by the cooperative action between iron(III) chloride and diorganyl diselenides (Scheme 1). Recently, the transformation of unsaturated substrates into heterocycles by using iron salts and diorganyl dichalcogenides has received increasing interest.[12] The use of iron salts in organic synthesis has emerged as a powerful method to promote the following transformations: (i) cross-coupling reactions of Grignard reagents with organic electrophiles,[13] (ii) carbon-heteroatom (i.e., C–N, C–O, C–S) bond formation,[14] (iii) heteroatom-heteroatom and carbon-carbon bond formation,[15] and (iv) the synthesis of heterocyclic compounds.[16] It has been reported that iron has many advantages over other transition metals such as its relative stability, abundance, low toxicity, economic and ecological advantages, and excellent tolerance towards various functional groups.[17]



Scheme 1.

The quinoline structural motif is of particular interest, as it is found in a large number of natural products, many of which have biological activity.[18] Among the methods that have been used for their preparation, transition-metal-catalyzed cyclizations of acyclic precursors are one of the most promising.[19] Similarly, electrophile-promoted nucleophilic cyclizations have also been recognized as a key synthetic process for their preparation.[20] Although most methods described the use of transition-metal-catalyzed or electrophile-promoted cyclizations for the preparation of quinolines, the cooperative action between iron(III) chloride and diorganyl dichalcogenides has not yet been employed. The main advantage of this strategy includes the ability of both iron(III) chloride and diorganyl dichalcogenides to transform acyclic substrates into different hetero-

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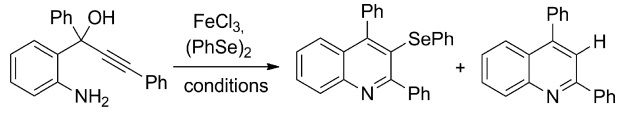
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201500766.

cycles and incorporate new functionality into the final structure, making heterocycles that are suitable for further transformations.

Results and Discussion

First, we explored the reaction conditions to promote the cyclization of (2-aminoaryl)-2-ynols **1**[21] by screening parameters such as the molar ratio of the reagents, the temperature, solvent, and iron source, that could affect the cyclization reaction (Table 1). Our study was initiated by treating diphenyl diselenide with an iron source in CH_2Cl_2 (3 mL) at room temperature for 15 min under argon. Then, *o*-(2-aminoaryl)-2-ynol **1a** was added, and the reaction was conducted at 40 °C for the time indicated in Table 1. The initial screening of the iron source showed that the best results were obtained by using iron(III) chloride, which gave 3-(phenylselenyl)quinoline (**2a**) in 68% yield along with quinoline **3a** in 13% yield (Table 1, Entry 5). Other iron salts gave only quinoline **3a** without the phenylselenyl group at the 3-position (Table 1, Entries 1–4). No significant change to the yield or selectivity was observed by lowering the temperature, but the reaction was slower (Table 1, Entry 6). The effect of changing the amounts of iron(III) chloride and diphenyl diselenide were then evaluated. The reaction was performed with 0.5, 0.75, and 1.5 equiv. of diphenyl diselenide, respectively, and the amount of iron(III) chloride was kept constant at 1.5 equiv. Next, we varied the amount of iron(III) chloride and kept the amount of diphenyl diselenide constant. As a result, we confirmed that an iron(III) chloride/diphenyl diselenide ratio of 1.0:1.5 afforded the best yields (Table 1, Entries 5 and 7–12).

Table 1. Effect of different reaction parameters on the preparation of 3-(phenylselenyl)quinoline (**2a**).[a]



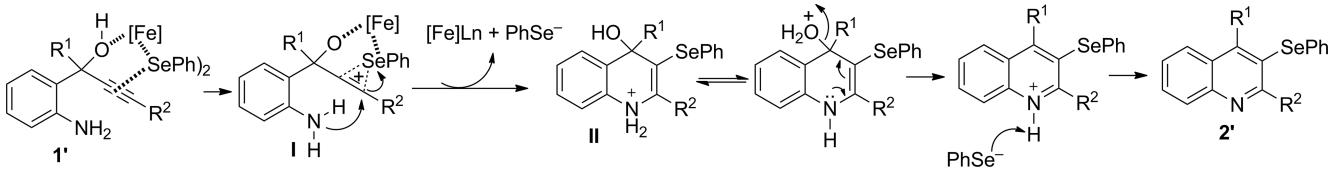
1a **2a** **3a**

Entry	Solvent	$(PhSe)_2$ [equiv.]	Iron salt [equiv.]	Time [h]	% Yield **2a**/**3a**[b]
1	CH_2Cl_2	1.0	Fe^0 (1.5)	24	–/12
2	CH_2Cl_2	1.0	$Fe(acac)_3$[c] (1.5)	24	–/10
3	CH_2Cl_2	1.0	$FeCl_2{\cdot}4H_2O$ (1.5)	24	–/49
4	CH_2Cl_2	1.0	$FeCl_3{\cdot}6H_2O$ (1.5)	24	–/56
5	CH_2Cl_2	1.0	$FeCl_3$ (1.5)	4	68:13
6[d]	CH_2Cl_2	1.0	$FeCl_3$ (1.5)	12	66:13
7	CH_2Cl_2	0.5	$FeCl_3$ (1.5)	4	53:5
8	CH_2Cl_2	0.75	$FeCl_3$ (1.5)	4	58:10
9	CH_2Cl_2	1.5	$FeCl_3$ (1.5)	4	50:16
10	CH_2Cl_2	1.0	$FeCl_3$ (1.0)	4	25:20
11	CH_2Cl_2	1.0	$FeCl_3$ (2.0)	4	64:14
12	CH_2Cl_2	1.0	$FeCl_3$ (3.0)	4	23:23
13[e]	CH_2Cl_2	1.0	$FeCl_3$ (1.5)	4	44:46
14	MeCN	1.0	$FeCl_3$ (1.5)	12	12:48
15	toluene	1.0	$FeCl_3$ (1.5)	12	10:40
16	DCE	1.0	$FeCl_3$ (1.5)	4	48:35
17	$CHCl_3$	1.0	$FeCl_3$ (1.5)	4	50:18
18	THF	1.0	$FeCl_3$ (1.5)	4	–/70
19	EtOH	1.0	$FeCl_3$ (1.5)	6	–/70
20	DMSO	1.0	$FeCl_3$ (1.5)	24	–/10
21	1,4-dioxane	1.0	$FeCl_3$ (1.5)	12	–/58

[a] The reaction was performed by the addition of diphenyl diselenide to a solution of the iron salt in solvent (3 mL) at room temperature under argon. After 15 min, (2-aminoaryl)-2-ynol **1a** (0.25 mmol) was added at this temperature, and the resulting mixture was heated at 40 °C for the time indicated above. [b] Yield of isolated products. [c] acac = acetylacetonate. [d] Reaction performed at room temperature. [e] Reaction carried out under air.

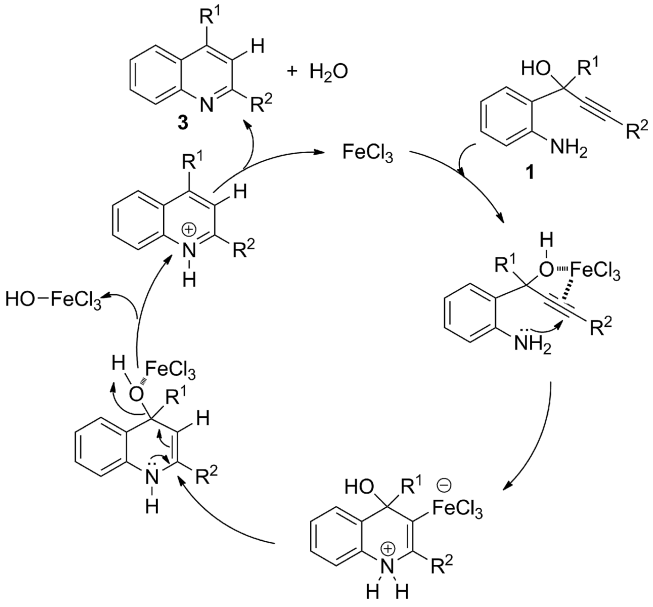
We suspected that the inert atmosphere would hamper the oxidation of the selenolate anion into diphenyl diselenide. To confirm this hypothesis, the reaction was carried out under aerobic conditions (Table 1, Entry 13). However, these reaction conditions did not improve the yield of the desired product **2a**, which implies that the cyclization reaction requires both selenolate moieties in the starting reagent to form the product in good yields. We assumed that the coordination of one portion of diphenyl diselenide with iron(III) chloride forms an intermediate, which promotes the cyclization and the incorporation of PhSe into the heterocycle. The other portion of selenolate anion ($PhSe^-$) acts as a base in the final step of the product formation (Scheme 2, mechanism proposal). An investigation of various solvents indicated that CH_2Cl_2 was the most efficient (Table 1, Entry 5). Other solvents such as MeCN, toluene, 1,2-dichloroethane (DCE), and $CHCl_3$ were less efficient (see Table 1, Entries 14–17), whereas tetrahydrofuran (THF), EtOH, dimethyl sulfoxide (DMSO), and 1,4-dioxane gave quinoline **3a** as the sole product (Table 1, Entries 18–21).

In additional studies, we carried out experiments to find parameters that could affect the cyclization reaction mechanism. For example, when we ran the cyclization under the optimized conditions (Table 1, Entry 5) in the presence of the PhSeCl, previously prepared by the reaction of diphenyl diselenide with thionyl chloride,[22] and the absence of iron(III) chloride and diphenyl diselenide, product **2a** was obtained in 66% yield. These results indicate that the combination of iron(III) chloride and diphenyl diselenide could



Scheme 2. Proposed mechanism for the synthesis of 3-organoseleno quinolines **2**.

lead to an in situ formation of PhSeCl, a selenium electrophilic source, which could promote the cyclization. However, when the reaction of (2-aminoaryl)-2-ynol **1a** was carried out under the optimized reaction conditions by adding PhSeCl instead of diphenyl diselenide, product **2a** was obtained only in 34% yield. In addition, the reaction of (2-aminoaryl)-2-ynol **1a** with iron(III) chloride in the absence of diphenyl diselenide and PhSeCl gave quinoline **3a**. When $FeCl_3$ and diphenyl diselenide were treated with quinoline **3a** as the substrate under the optimized reaction conditions, no amount of product **2a** was formed. This implies that a cyclization mediated by $FeCl_3$ followed by an attack on the C–Fe bond by diphenyl diselenide, which would act as an electrophile source, does not occur. Finally, to check if HCl could be liberated from $FeCl_3$ acting as a catalyst, the reaction was conducted in the presence of hydrochloric acid and HCl (g), but only a trace amount of **3a** was obtained. These experiments clearly indicate that when diphenyl diselenide is used as a reagent, the presence of an iron salt is necessary to promote the cyclization of (2-aminoaryl)-2-ynol **1a** and that the cooperative action between diphenyl diselenide and iron(III) chloride is essential to provide a good yield of the cyclized product. With this information, we believed that the cyclization of (2-aminoaryl)-2-ynols **1′** to give 3-phenylselenyl quinolines **2′** involves iron(III) coordination with the oxygen atom of **1′** and with one selenium atom of diphenyl diselenide, which activates the other selenium atom towards a nucleophilic attack by the alkyne to give seleniranium ion **I** (Scheme 2). A nucleophilic *anti* attack of the nitrogen atom on activated seleniranium ion **I** leads to dihydroquinoline **II** and a selenolate anion. Dehydration followed by deprotonation of the nitrogen atom by the selenolate anion gives 3-phenylselenyl quinoline **2′**. For the formation of quinoline **3**, we propose that the iron(III) chloride acts as a Lewis acid to activate the triple bond toward a nucleophilic attack by the nitrogen atom, giving quinoline **3** after dehydration (Scheme 3).

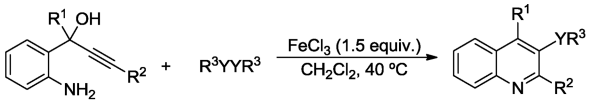


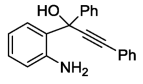
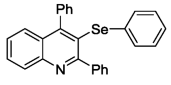
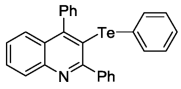
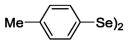
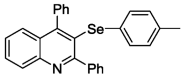
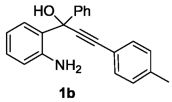
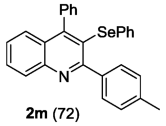
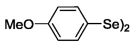
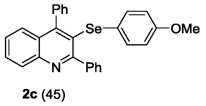
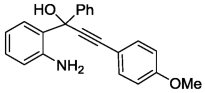
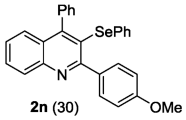
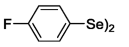
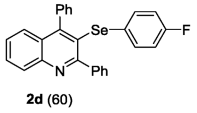
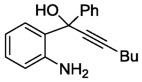
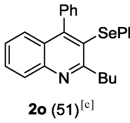
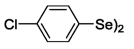
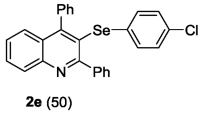
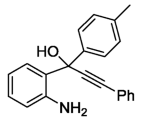
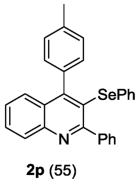
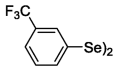
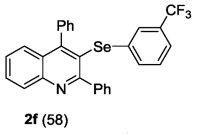
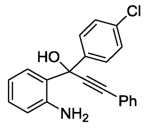
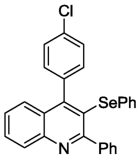
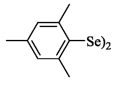
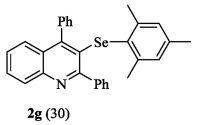
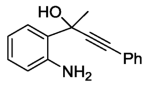
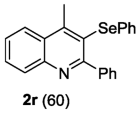
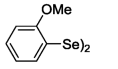
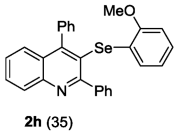
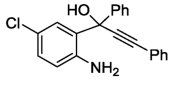
Scheme 3. Proposed mechanism for the synthesis of quinolines **3**.

The results in Table 1 indicate that the cyclization of (2-aminoaryl)-2-ynol **1a** gave the desired 3-(phenylselenyl)-quinoline **2a** in better yields when the reaction was carried out by adding diphenyl diselenide (1.0 equiv.) to a solution of iron(III) chloride (1.5 equiv.) in CH_2Cl_2 (3 mL) at room temperature under argon. After 15 min, (2-aminoaryl)-2-ynol **1a** (0.25 mmol) was added at this temperature, and the resulting mixture was heated at 40 °C for 4 h. These standard conditions were then applied to a variety of (2-aminoaryl)-2-ynols **1** and diorganyl diselenides to investigate the tolerance of the functional groups and their effects on the conversion (Table 2). We first investigated the influence of various diorganyl diselenides on the yield of the cyclization. The results indicate that the reaction is not sensitive to the electronic effects of the substituents on the aromatic ring of the diaryl diselenides, as neutral, electron-donating, and electron-withdrawing groups provided the 3-(arylselenyl)-quinolines in similar yields (Table 2, Entries 1–6). In contrast, the steric hindrance of the methyl and methoxy groups at the *ortho* position of the aromatic ring exerted significant negative effects and afforded 3-(arylselenyl)-quinolines **2g** and **2h** in low yields (Table 2, Entries 7 and 8). In addition, the optimized reaction conditions were applied to dibenzyl diselenide, but they failed to afford the desired 3-(benzylselenyl)quinolines **2i** (Table 2, Entry 9). This failure can be explained by the low stability of benzyl selenides, which can undergo β-selenoxide elimination[23] during the purification or workup process to give the final product without a selenium group incorporated into the structure. We also found that using a dialkyl diselenide in the reaction worked well under the standard reaction conditions and led to formation of the expected product in moderate yield (Table 2, Entry 10). The reaction with diphenyl disulfide did not give any of the desired product, whereas the use of diphenyl ditelluride gave the cyclized product in low yield (Table 2, Entries 11 and 12).

Next, to elaborate on the general reactivity of the present protocol, we added functional groups to different positions of the (2-aminoaryl)-2-ynols **1**. The experimental results show that the reactions of substrates with different substituted aryl groups directly bonded to the triple bond also worked well under the standard reaction conditions. However, the presence of a *p*-methoxy substituent on the aryl group gave the product in low yield (Table 2, Entries 13 and 14). (2-Aminoaryl)-2-ynol **1d**, which has an alkyl chain off the alkyne, was also employed in the cyclization reaction and afforded cyclized product **2o** in 51% yield (Table 2, Entry 15). Changing the phenyl group at the propargyl position to an aryl or methyl substituent did not affect the cyclization, and 3-(arylselenyl)quinolines **2p**–**2r** were obtained in moderated yields (Table 2, Entries 16–18). Finally, extending the optimized conditions to (2-aminoaryl)-2-ynols **1h** and **1i**, which have a Cl- and strongly electron-withdrawing NO_2-substituted aromatic ring, gave good yields of the expected cyclized products (Table 2, Entries 19 and 20).

Table 2. Synthesis of 3-organoseleno quinoline derivatives **2**.[a]



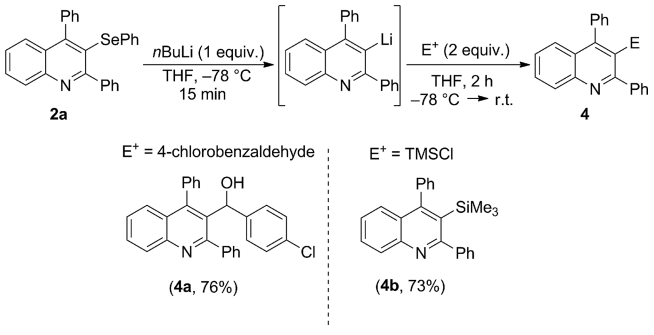
Entry	(2-Aminoaryl)-2-ynols	R^3YYR^3	Product, yield (%)[b]	Entry	(2-Aminoaryl)-2-ynols	R^3YYR^3	Product, yield (%)[b]
1	 **1a**		 **2a** (68)	12	**1a**		 **2l** (25)
2	**1a**		 **2b** (62)	13	 **1b**		 **2m** (72)
3	**1a**		 **2c** (45)	14	 **1c**		 **2n** (30)
4	**1a**		 **2d** (60)	15	 **1d**		 **2o** (51)[c]
5	**1a**		 **2e** (50)	16	 **1e**		 **2p** (55)
6	**1a**		 **2f** (58)	17	 **1f**		 **2q** (47)
7	**1a**		 **2g** (30)	18	 **1g**		 **2r** (60)
8	**1a**		 **2h** (35)	19	 **1h**		**2s** (72)
9	**1a**		**2i** (-)	20	**1i**		**2t** (78)
10	**1a**	$(n\text{-BuSe})_2$	**2j** (54)				
11	**1a**		**2k** (-)				

[a] The reaction was performed by adding diorganyl dichalcogenides (1.0 equiv.) to a solution of iron(III) chloride (1.5 equiv.) in CH_2Cl_2 (3 mL) at room temperature under argon. After 15 min, (2-aminoaryl)-2-ynols **1** (0.25 mmol) were added at this temperature, and the resulting mixture was heated at 40 °C for 4 h. [b] Yield of isolated products. [c] The reaction was heated at 40 °C for 24 h.

After the result obtained in Table 1, Entry 18, in which quinoline **3a** was generated in 70% yield, we focused on the cyclization of (2-aminoaryl)-2-ynols **1** by using iron(III) chloride in the absence of the organoseleno source. For this

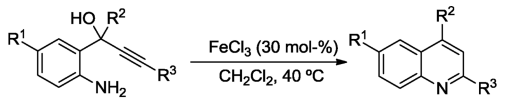
purpose, we systematically evaluated different parameters to determine the best reaction conditions by subjecting (2-aminoaryl)-2-ynols **1a** to the cyclization process (Supporting Information, Table S1) Thus, careful analysis of the reactions revealed that the best conditions for this cyclization involved (2-aminoaryl)-2-ynol **1a** (0.25 mmol) and a catalytic amount of iron(III) chloride (30 mol-%) in CH_2Cl_2 (3 mL) at 40 °C for 4 h. By using these conditions, we were able to prepare quinoline **3a** in 85% yield. To demonstrate the efficiency of this protocol, we explored its generality by extending the reaction to several (2-aminoaryl)-2-ynols **1** (Table 3). The corresponding quinolines **3** were produced in good to excellent yields under the optimized conditions (Table 3). With regard to the scope of the substrate, we first examined the aryl substituent directly bonded to the alkyne moiety. Neutral and electron-donating groups on the aryl unit such as *p*-methyl and *p*-methoxy afforded the corresponding quinoline products in good yields (Table 3, Entries 2 and 3). However, the yield decreased considerably when a straight chain alkyl group was bonded to the alkyne (Table 3, Entry 4). We then focused on the effect of other substituents at the propargyl position of the (2-aminoaryl)-2-ynols. The presence of a *p*-tolyl, *p*-chlorophenyl, or methyl group instead of a phenyl unit did not have a significant influence on the yield (Table 3, Entries 5–7). The effect of a substituent on the main aromatic ring of the (2-aminoaryl)-2-ynols was also investigated. In this case, chloro-substituted compound **1h** afforded quinoline **3h** in 74% yield, whereas nitro-substituted **1i** gave a poor 49% yield of quinoline **3i** (Table 3, Entries 8 and 9).

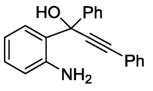
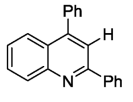
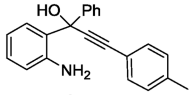
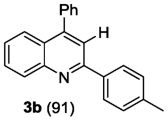
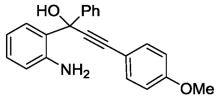
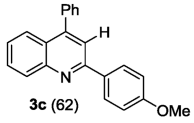
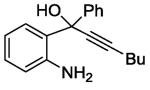
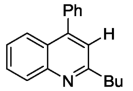
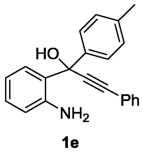
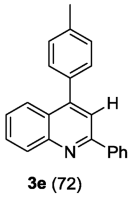
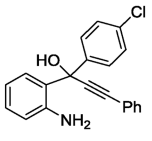
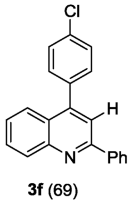
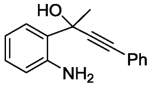
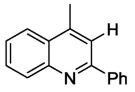
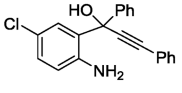
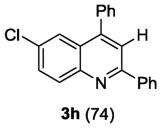
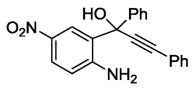
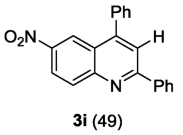
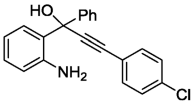
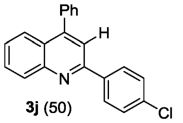
An interesting feature of 3-organoseleno-substituted quinolines is their ability to undergo chalcogen-lithium exchange reactions with lithium reagents.[24] To introduce different functional groups at the 3-position of the quinoline ring and improve the synthetic utility of our methodology, a 3-organoseleno quinoline was treated with *n*-butyllithium followed by the addition of an electrophile. As expected, the reaction of *n*-butyllithium (1.0 equiv.) with 3-organoseleno quinoline **1a** (1.0 equiv.) in THF (3 mL) at –78 °C gave the lithium intermediate,[25] which upon the addition of an aldehyde or TMSCl (TMS = trimethylsilyl) afforded the corresponding secondary alcohol **4a** and 3-(trimethylsilyl)quinoline (**4b**) in 76 and 73% yields, respectively (Scheme 4).



Scheme 4. Organoseleno-lithium exchange reaction of 3-organoseleno-substituted quinoline **2a**.

Table 3. Synthesis of quinoline derivatives **3**.[a]



Entry	(2-Aminoaryl)-2-ynols	Quinolines, yield (%)[b]
1	 **1a**	 **3a** (85)
2	 **1b**	 **3b** (91)
3	 **1c**	 **3c** (62)
4[c]	 **1d**	 **3d** (30)
5	 **1e**	 **3e** (72)
6	 **1f**	 **3f** (69)
7	 **1g**	 **3g** (60)
8	 **1h**	 **3h** (74)
9	 **1i**	 **3i** (49)
10	 **1j**	 **3j** (50)

[a] The reaction was performed by adding (2-aminoaryl)-2-ynols **1** (0.25 mmol) to a solution of iron(III) chloride (30 mol-%) in CH_2Cl_2 (3 mL) at room temperature under argon. After 15 min at this temperature, the resulting mixture was heated at 40 °C for 4 h. [b] Yield of isolated products. [c] A reaction time of 24 h was necessary.

Conclusions

In summary, we have shown that the cooperative action between iron(III) chloride and diorganyl diselenides can be efficiently used for the cyclization of (2-aminoaryl)-2-ynols for the regioselective synthesis of 3-organoseleno quinolines. The reaction showed high regioselectivity for six-membered quinoline products that were formed by a 6-*endo*-*dig* instead of 5-*exo*-*dig* ring closure. The experiments revealed that the selectivity favoring the former cyclization process is controlled by the iron intermediate. In addition, when the reaction of the (2-aminoaryl)-2-ynols were carried out with a catalytic amount of iron(III) chloride, in the absence of the diorganyl diselenides, the quinolone derivatives without the organoseleno group at the 3-position were exclusively obtained. This result is significant because similar reaction conditions were used to obtain two classes of quinolones. To introduce different functional groups at the 3-position of the quinoline ring and improve the synthetic utility of our methodology, the 3-organoseleno quinoline was treated with *n*-butyllithium followed by the addition of an aldehyde or TMSCl, which afforded the corresponding secondary alcohol and 3-(trimethylsilyl)quinoline, respectively.

Experimental Section

General Procedure for the Preparation of the 3-Organochalcogen Quinoline Derivatives: To a Schlenk tube that contained dichloromethane (3 mL) under argon were added iron(III) chloride (99.99% purity from commercial suppliers, 0.061 g, 1.5 equiv.) and diorganyl dichalcogenides (0.25 mmol, 1.0 equiv.), and the resulting mixture was stirred at room temperature for 15 min. After this time, a solution of 2-aminophenylprop-1-yn-3-ol **1a**–**1j** (0.25 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added. The mixture was stirred for the desired time at 40 °C and then diluted with dichloromethane (20 mL). The resulting mixture was washed with a saturated solution of $NaHCO_3$ (20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography (hexane/acetate, 97:3).

2,4-Diphenyl-3-(phenylselenyl)quinoline (2a): Yellow solid (0.074 g, 68% yield); m.p. 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.1 Hz, 1 H), 7.68–7.63 (m, 1 H), 7.52–7.50 (m, 2 H), 7.45–7.43 (m, 1 H), 7.37–7.34 (m, 4 H), 7.28–7.26 (m, 3 H), 7.21–7.29 (m, 2 H), 6.98–6.94 (m, 1 H), 6.86 (t, J = 7.7 Hz, 2 H), 6.74–6.73 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 154.4, 147.2, 142.0, 138.6, 132.9, 131.6, 129.8, 129.4, 129.3, 128.9, 128.4, 127.9, 127.8, 127.4, 127.1, 126.7, 126.6, 126.2, 125.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 437 (66), 359 (100), 280 (31), 252 (14), 176 (45), 77 (17). HRMS (ESI-TOF): calcd. for $C_{27}H_{19}NSe$ [M +H]$^+$ 438.0761; found 438.0766.

2,4-Diphenyl-3-(*p*-tolylselenyl)quinoline (2b): Yellow solid (0.070 g, 62% yield); m.p. 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.16 (m, 1 H), 7.70–7.66 (m, 1 H), 7.52–7.48 (m, 2 H), 7.46–7.44 (m, 1 H), 7.41–7.39 (m, 4 H), 7.32–7.29 (m, 3 H), 7.23–7.20 (m, 2 H), 6.76 (d, J = 7.9 Hz, 2 H), 6.68–6.65 (m, 2 H), 2.17 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 154.3, 147.2, 142.1, 138.7, 136.2, 132.0, 129.8, 129.5, 129.4, 129.3, 129.1, 129.0, 128.0, 127.8, 127.5, 127.2, 126.7, 126.6, 126.4, 20.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 451 (5), 374 (12), 207 (100), 73 (79). HRMS (ESI-TOF): calcd. for $C_{28}H_{21}NSe$ [M + H]$^+$ 452.0917; found 452.0920.

3-(*p*-Methoxyphenylselenyl)-2,4-diphenylquinoline (2c): Yellow solid (0.053 g, 45% yield); m.p. 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.4 Hz, 1 H), 7.71–7.66 (m, 1 H), 7.53–7.22 (m, 12 H), 6.75–6.42 (m, 4 H), 3.68 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 158.7, 153.8, 147.1, 142.2, 138.7, 134.2, 129.7, 129.6, 129.5, 129.1, 128.1, 127.9, 127.7, 127.6, 127.3, 126.6, 126.0, 122.8, 114.3, 55.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 467 (100), 360 (58), 278 (24), 176 (38), 151 (18). HRMS (ESI-TOF): calcd. for $C_{28}H_{21}NOSe$ [M + H]$^+$ 468.0867; found 468.0871.

3-(*p*-Fluorophenylselenyl)-2,4-diphenylquinoline (2d): Yellow solid (0.068 g, 60% yield); m.p. 127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.4 Hz, 1 H), 7.69 (td, J = 6.4 and 1.7 Hz, 1 H), 7.52–7.21 (m, 12 H), 6.70–6.57 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 161.8 (d, J = 246 Hz), 153.9, 147.2, 142.0, 138.6, 134.2 (d, J = 8.1 Hz), 129.9, 129.6, 129.5, 129.0, 128.1, 128.0, 127.7, 127.2, 127.1, 127.0, 126.9, 126.6, 125.5, 115.6 (d, J = 21.3 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 454 (31), 360 (100), 278 (32), 207 (78), 75 (18). HRMS (ESI-TOF): calcd. for $C_{27}H_{18}FNSe$ [M + H]$^+$ 456.0667; found 456.0671.

3-(*p*-Chlorophenylselenyl)-2,4-diphenylquinoline (2e): Yellow oil (0.059 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.4 Hz, 1 H), 7.73–7.70 (m, 1 H), 7.51–7.40 (m, 7 H), 7.32–7.31 (m, 3 H), 7.23–7.18 (m, 2 H), 6.88–6.84 (m, 2 H), 6.66–6.64 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 154.3, 147.3, 141.9, 138.5, 135.7, 133.2, 132.5, 131.0, 130.0, 129.6, 129.4, 129.0, 128.6, 128.1, 128.0, 127.6, 127.2, 126.9, 126.7, 124.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 471 (38), 392 (29), 281 (38), 207 (100), 176 (37), 73 (58). HRMS (ESI-TOF): calcd. for $C_{27}H_{18}ClNSe$ [M + H]$^+$ 472.0371; found 472.0377.

2,4-Diphenyl-3-(*m*-trifluoromethylphenylselenyl)quinoline (2f): Yellow solid (0.073 g, 58% yield); m.p. 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.4 Hz, 1 H), 7.73 (td, J = 6.4 and 1.7 Hz, 1 H), 7.50–7.42 (m, 7 H), 7.31–7.21 (m, 6 H), 7.05–7.01 (m, 1 H), 6.98–6.97 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 154.3, 147.5, 147.8, 138.5, 135.4, 130.8 (q, J = 32.3 Hz), 130.2, 129.7, 129.0, 128.8, 128.6 (q, J = 3.7 Hz), 128.2, 127.7, 127.2, 127.0, 126.7, 124.8, 123.5 (q, J = 272 Hz), 123.3 (q, J = 3.7 Hz), 121.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 505 (10), 360 (31), 281 (36), 207 (100), 133 (23). HRMS (ESI-TOF): calcd. for $C_{28}H_{18}F_3NSe$ [M + H]$^+$ 506.0635; found 506.0640.

2,4-Diphenyl-3-(2,4,6-trimethylphenylselenyl)quinoline (2g): Dark yellow solid (0.036 g, 30% yield); m.p. 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.4 Hz, 1 H), 7.65 (t, J = 7.9 Hz, 1 H), 7.52–7.51 (m, 2 H), 7.37–7.29 (m, 8 H), 7.06 (d, J = 7.9 Hz, 2 H), 6.48 (s, 2 H), 2.12 (s, 3 H), 1.77 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 151.1, 146.6, 142.4, 141.1, 138.4, 137.2, 130.5, 129.7, 129.1, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.5, 126.6, 126.5, 125.9, 23.5, 20.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 479 (9), 281 (18), 207 (100), 77 (9). HRMS (ESI-TOF): calcd. for $C_{30}H_{25}NSe$ [M + H]$^+$ 480.1230; found 480.1234.

3-(*o*-Methoxyphenylselenyl)-2,4-diphenylquinoline (2h): Yellow oil (0.041 g, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.9 Hz, 1 H), 7.73–7.69 (td, J = 8.4 and 2.0 Hz, 1 H), 7.55–7.52 (m, 2 H), 7.46–7.41 (m, 2 H), 7.40–7.36 (m, 3 H), 7.30–7.25 (m, 3 H), 7.22–7.20 (m, 2 H), 7.01–6.97 (m, 1 H), 6.62–6.55 (m, 2 H), 6.50 (d, J = 8.2 Hz, 1 H), 3.51 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 156.9, 155.0, 147.4, 142.0, 138.7, 131.6, 129.9, 129.6, 128.3, 128.9, 127.9, 127.8, 127.7, 127.4, 127.3, 127.2, 126.8, 126.7, 124.0, 122.8, 121.2, 110.3, 55.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 467 (3), 271 (35), 207 (100), 133 (23), 73 (8). HRMS: calcd. for $C_{28}H_{21}NOSe$ [M + H]$^+$ 468.0867; found 468.0872.

3-Butylselenyl-2,4-diphenylquinoline (2j): Yellow solid (0.056 g, 54% yield); m.p. 62–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.4 Hz, 1 H), 7.80–7.77 (m, 2 H), 7.70 (m, 1 H), 7.55–7.38 (m, 8 H), 7.36–7.34 (m, 2 H), 2.03 (t, J = 7.3 Hz, 2 H), 1.13 (quint, J = 7.3 Hz, 2 H), 1.00 (sext, J = 7.3 Hz, 2 H), 0.65 (q, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 153.9, 146.9, 142.3, 139.1, 129.8, 129.5, 129.4, 129.3, 128.2, 128.1, 127.9, 127.8, 127.0, 126.7, 126.4, 123.2, 31.8, 28.6, 22.5, 13.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 416 (7), 360 (100), 281 (41), 206 (68), 73 (29). HRMS (ESI-TOF): calcd. for $C_{25}H_{23}NSe$ [M + H]$^+$ 418.1074; found 418.1080.

2,4-Diphenyl-3-(phenyltelluryl)quinoline (2l): Yellow oil (0.030 g, 25% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.4 Hz, 1 H), 7.68 (td, J = 8.4 and 1.7 Hz, 1 H), 7.49–7.37 (m, 7 H), 7.30 (d, J = 2.0 Hz, 2 H), 7.29 (d, J = 1.7 Hz, 1 H), 7.20–7.18 (m, 2 H), 7.08–7.01 (m, 3 H), 6.87 (t, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 157.0, 147.5, 144.1, 141.6, 137.4, 129.9, 129.5, 128.9, 128.8, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 128.0, 126.8, 126.7, 117.5, 114.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 485 (18), 281 (50), 207 (100), 132 (23), 73 (63). HRMS (ESI-TOF): calcd. for $C_{27}H_{19}NTe$ [M + H]$^+$ 488.0658; found 488.0663.

4-Phenyl-3-(phenylselenyl)-2-(*p*-tolylphenyl)quinoline (2m): Yellow solid (0.081 g, 72% yield); m.p. 125–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.6 Hz, 1 H), 7.68 (td, J = 6.4 and 1.7 Hz, 1 H), 7.44–7.34 (m, 7 H), 7.19–7.16 (m, 2 H), 7.12 (d, J = 7.6 Hz, 2 H), 7.01–6.97 (m, 1 H), 6.89 (t, J = 7.5 Hz, 2 H), 6.76–6.74 (m, 2 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 154.5, 147.3, 139.2, 138.7, 133.2, 131.6, 129.9, 129.5, 129.4, 128.9, 128.7, 128.5, 128.2, 127.9, 127.8, 127.2, 126.7, 126.6, 126.2, 125.1, 21.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 451 (2), 374 (5), 207 (100), 73 (77). HRMS (ESI-TOF): calcd. for $C_{28}H_{21}NSe$ [M + H]$^+$ 452.0917; found 452.0920.

2-(*p*-Methoxyphenyl)-4-phenyl-3-(phenylselenyl)quinoline (2n): Yellow solid (0.035 g, 30% yield); m.p. 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.9 Hz, 1 H), 8.15 (dt, J = 8.9 and 2.2 Hz, 2 H), 7.85 (dd, J = 8.3 and 0.7 Hz, 1 H), 7.59–6.67 (m, 16 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 156.3, 148.9, 148.8, 138.5, 132.2, 129.9, 129.5, 129.4, 128.9, 128.5, 128.3, 126.0, 125.5, 125.4, 118.8, 114.2, 55.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 467 (100), 390 (95), 267 (33), 207 (30), 163 (35). HRMS (ESI-TOF): calcd. for $C_{28}H_{21}NOSe$ [M + H]$^+$ 468.0867; found 468.0870.

2-Butyl-4-phenyl-3-(phenylselenyl)quinoline (2o): Brown oil (0.053 g, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.4 Hz, 1 H), 7.71 (m, 1 H), 7.42–7.37 (m, 5 H), 7.16–7.01 (m, 7 H), 3.24 (t, J = 7.3 Hz, 2 H), 1.80 (quint, J = 7.3 Hz, 2 H), 1.42 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 155.0, 147.7, 139.0, 135.6, 129.9, 129.1, 129.0, 128.8, 127.8, 127.7, 127.0, 126.6, 126.0, 124.3, 39.4, 32.1, 22.8, 13.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 416 (4), 374 (54), 207 (100), 132 (20), 76 (49). HRMS (ESI-TOF): calcd. for $C_{25}H_{23}NSe$ [M + H]$^+$ 418.1074; found 418.1081.

2-Phenyl-3-(phenylselenyl)-4-*p*-tolylquinoline (2p): Yellow oil (0.062 g, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.4 Hz, 1 H), 7.69 (d, J = 7.5 Hz, 1 H), 7.50–7.39 (m, 4 H), 7.28–7.22 (m, 5 H), 7.12 (d, J = 7.9 Hz, 2 H), 7.01–6.97 (t, J = 7.3 Hz, 1 H), 6.90 (t, J = 7.3 Hz, 2 H), 6.74 (d, J = 7.9 Hz, 2 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 154.6, 147.3, 142.1, 139.4, 137.7, 135.8, 133.1, 132.0, 129.8, 129.5, 129.0, 128.8, 128.5, 127.8, 127.5, 127.4, 126.9, 126.7, 126.2, 125.2, 21.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 451 (4), 374 (10), 207 (100), 73 (78). HRMS (ESI-TOF): calcd. for $C_{28}H_{21}NSe$ [M + H]$^+$ 452.0917; found 452.0923.

4-(*p*-Chlorophenyl)-2-phenyl-3-(phenylselenyl)quinoline (2q): Yellow solid (0.055 g, 47% yield); m.p. 163–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.4 Hz, 1 H), 7.76–7.69 (m, 1 H), 7.53–7.50 (m, 2 H), 7.43–7.41 (m, 2 H), 7.36–7.31 (m, 5 H), 7.11 (dt, J = 8.4 and 2.0 Hz, 2 H), 7.03 (tt, J = 7.5 and 1.8 Hz, 1 H), 6.92 (t, J = 7.7 Hz, 2 H), 6.77–6.74 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 153.0, 147.3, 141.9, 136.9, 134.0, 133.0, 131.8, 130.9, 130.1, 129.7, 129.0, 128.5, 128.3, 128.1, 127.7, 127.1, 127.0, 126.5, 126.3, 125.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 471 (26), 394 (36), 281 (37), 207 (100), 176 (24), 73 (58). HRMS (ESI-TOF): calcd. for $C_{27}H_{18}ClNSe$ [M + H]$^+$ 472.0371; found 472.0379.

4-Methyl-2-phenyl-3-(phenylselenyl)quinoline (2r): Yellow solid (0.056 g, 60% yield); m.p. 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.1 Hz, 1 H), 8.03 (d, J = 7.9 Hz, 1 H), 7.76–7.70 (m, 1 H), 7.59–7.55 (m, 1 H), 7.48–7.45 (m, 2 H), 7.37–7.34 (m, 3 H), 7.08–7.06 (m, 3 H), 7.01–6.98 (m, 2 H), 2.93 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 150.6, 146.9, 142.6, 133.1, 130.2, 130.0, 129.8, 129.1, 128.9, 128.0, 127.6, 127.3, 126.7, 126.1, 124.9, 124.5, 20.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 374 (62), 340 (16), 281 (32), 206 (100), 132 (20), 73 (49). HRMS (ESI-TOF): calcd. for $C_{22}H_{17}NSe$ [M + H]$^+$ 376.0604; found 376.0609.

6-Chloro-2,4-diphenyl-3-(phenylselenyl)quinoline (2s): Yellow solid (0.073 g, 72% yield); m.p. 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.9 Hz, 1 H), 7.63 (dd, J = 8.9 and 2.3 Hz, 1 H), 7.50–7.48 (m, 2 H), 7.44–7.41 (m, 4 H), 7.31–7.28 (m, 3 H), 7.22–7.18 (m, 2 H), 7.01 (tt, J = 7.3 and 1.1 Hz, 1 H), 6.91–6.87 (m, 2 H), 6.74–6.71 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0, 153.5, 145.7, 141.8, 138.1, 132.8, 132.7, 132.1, 131.3, 130.8, 129.4, 129.0, 128.7, 128.4, 128.3, 128.1, 128.0, 127.7, 126.7, 126.6, 125.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 471 (94), 469 (50), 390 (25), 279 (33), 176 (35). HRMS (ESI-TOF): calcd. for $C_{27}H_{18}ClNSe$ [M + H]$^+$ 472.0371; found 472.0375.

6-Nitro-2,4-diphenyl-3-(phenylselenyl)quinoline (2t): Yellow solid (0.094 g, 78% yield); m.p. 197–199 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, J = 9.1 and 2.5 Hz, 1 H), 8.41 (dd, J = 2.5 and 0.6 Hz, 1 H), 8.26 (dd, J = 9.1 and 0.6 Hz, 1 H), 7.55–7.45 (m, 5 H), 7.36–7.32 (m, 3 H), 7.25–7.22 (m, 2 H), 7.03 (tt, J = 7.4 and 1.2 Hz, 1 H), 6.92–6.88 (m, 2 H), 6.74–6.71 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 155.7, 149.2, 145.8, 141.3, 137.2, 132.4, 132.0, 131.4, 129.4, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.8, 126.9, 126.3, 123.5, 123.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 482 (68), 405 (30), 357 (19), 207 (100), 77 (29). HRMS (ESI-TOF): calcd. for $C_{27}H_{18}N_2O_2Se$ [M + H]$^+$ 483.0612; found 483.0620.

General Procedure for the Preparation of the Quinoline Derivatives 3: To a Schlenk tube that contained CH_2Cl_2 (3 mL) under argon were added iron(III) chloride (99.99% purity from commercial suppliers, 0.012 g, 30 mol-%) and 2-aminophenylprop-1-yn-3-ol **1a**–**1j** (0.25 mmol), and the resulting mixture was stirred at room temperature for 4 h. After this period of time, the mixture was diluted with dichloromethane (20 mL), and the resulting mixture was washed with a saturated solution of $NaHCO_3$ (20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography (hexane/acetate, 99:1).

2,4-Diphenylquinoline (3a): Pale yellow solid (0.060 g, 85% yield); m.p. 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 8.1 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 2 H), 7.86 (d, J = 8.4 Hz, 1 H),

7.78 (s, 1 H), 7.68 (t, J = 8.1 Hz, 1 H), 7.50–7.39 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 149.0, 148.7, 139.5, 138.3, 130.0, 129.4, 129.4, 129.2, 128.7, 128.5, 128.3, 127.5, 126.2, 125.7, 125.5, 119.2 ppm. MS (EI, 70 eV): m/z (%) = 281 (75), 280 (100), 207 (13), 139 (16), 77 (5). HRMS (ESI-TOF): calcd. for $C_{21}H_{15}N$ $[M + H]^+$ 282.1283; found 282.1289.

4-Phenyl-2-(*p*-tolyl)quinoline (3b): Yellow solid (0.067 g, 91% yield); m.p. 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, J = 8.4 Hz, 1 H), 8.09 (d, J = 8.1 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.78 (s, 1 H), 7.69 (dd, J = 7.0 and 1.2 Hz, 1 H), 7.55–7.40 (m, 6 H), 7.31 (d, J = 8.1 Hz, 2 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 149.0, 148.8, 139.7, 138.5, 136.8, 130.0, 129.5, 129.4, 129.3, 128.5, 128.3, 127.4, 126.1, 125.7, 125.6, 119.1, 21.2 ppm. MS (EI, 70 eV): m/z (%) = 295 (74), 294 (100), 201 (16), 139 (10), 73 (2). HRMS (ESI-TOF): calcd. for $C_{22}H_{17}N$ $[M + H]^+$ 296.1439; found 296.1443.

2-(*p*-Methoxy)-4-phenylquinoline (3c): Yellow solid (0.048 g, 62% yield); m.p. 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.9 Hz, 1 H), 8.15 (dt, J = 8.9 and 2.2 Hz, 2 H), 7.85 (dd, J = 8.4 and 0.7 Hz, 1 H), 7.75 (s, 1 H), 7.68 (td, J = 8.4 and 1.6 Hz, 1 H), 7.55–7.48 (m, 5 H), 7.41 (td, J = 8.1 and 1.2 Hz, 1 H), 7.02 (dt, J = 8.9 and 2.1 Hz, 2 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 156.4, 149.0, 148.8, 138.5, 132.2, 129.9, 129.5, 129.4, 128.9, 128.5, 128.3, 125.9, 125.5, 125.4, 118.8, 114.2, 55.3 ppm. MS (EI, 70 eV): m/z (%) = 311 (14), 207 (100), 132 (4), 73 (94). HRMS (ESI-TOF): calcd. for $C_{22}H_{17}NO$ $[M + H]^+$ 312.1388; found 312.1392.

2-Butyl-4-phenylquinoline (3d): Brown oil (0.020 g, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, J = 8.4 and 0.7 Hz, 1 H), 7.86 (dd, J = 8.4 and 1.2 Hz, 1 H), 7.67 (td, J = 7.0 and 1.2 Hz, 1 H), 7.55–7.46 (m, 5 H), 7.42 (td, J = 7.0 and 1.2 Hz, 1 H), 7.24 (s, 1 H), 3.01 (t, J = 7.3 Hz, 2 H), 1.88–1.80 (m, 2 H), 1.47 (sext, J = 7.3 Hz, 2 H), 0.97 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 148.5, 148.4, 138.3, 129.5, 129.2, 129.1, 128.5, 128.2, 125.7, 125.6, 125.3, 121.6, 39.1, 32.2, 22.7, 13.9 ppm. MS (EI, 70 eV): m/z (%) = 261 (2), 219 (100), 178 (5), 108 (8), 73 (14). HRMS (ESI-TOF): calcd. for $C_{19}H_{19}N$ $[M + H]^+$ 262.1596; found 262.1599.

2-Phenyl-4-(*p*-tolyl)quinoline (3e): Yellow solid (0.053 g, 72% yield); m.p. 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.4 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 2 H), 7.90 (d, J = 8.4 Hz, 1 H), 7.77 (s, 1 H), 7.68 (t, J = 8.1 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.44–7.40 (m, 4 H), 7.31 (d, J = 7.6 Hz, 2 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 149.3, 148.9, 139.8, 138.3, 135.6, 130.2, 129.5, 129.4, 129.3, 128.9, 127.6, 126.3, 126.0, 125.8, 119.3, 21.3 ppm. MS (EI, 70 eV): m/z (%) = 295 (73), 201 (16), 145 (10), 73 (3). HRMS (ESI-TOF): calcd. for $C_{22}H_{17}N$ $[M + H]^+$ 296.1439; found 296.1444.

4-(*p*-Chlorophenyl)-2-phenylquinoline (3f): Yellow oil (0.054 g, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.4 Hz, 1 H), 8.16 (d, J = 7.3 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.75 (s, 1 H), 7.70 (td, J = 8.4 and 1.2 Hz, 1 H), 7.52–7.42 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 148.8, 147.8, 139.4, 136.8, 134.6, 130.8, 130.2, 129.6, 129.4, 128.8, 127.5, 126.5, 125.5, 125.2, 119.2 ppm. MS (EI, 70 eV): m/z (%) = 316 (6), 281 (23), 207 (100), 156 (50), 73 (39). HRMS (ESI-TOF): calcd. for $C_{21}H_{14}ClN$ $[M + H]^+$ 316.0893; found 316.0899.

4-Methyl-2-phenylquinoline (3g): Yellow oil (0.033 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.12 (m, 3 H), 7.97 (dd, J = 8.1 and 0.9 Hz, 1 H), 7.74–7.66 (m, 2 H), 7.56–7.44 (m 4 H), 2.74 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 148.0, 144.7, 139.8, 130.2, 129.3, 129.1, 128.7, 127.5, 127.2, 126.6, 126.0, 119.7, 18.9 ppm. MS (EI, 70 eV): m/z (%) = 219 (100), 218 (41), 204 (82), 176 (5), 108 (22). HRMS (ESI-TOF): calcd. for $C_{16}H_{13}N$ $[M + H]^+$ 220.1126; found 220.1130.

6-Chloro-2,4-diphenylquinoline (3h): Yellow solid (0.058 g, 74% yield); m.p. 127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.15 (m, 3 H), 7.85 (d, J = 2.3 Hz, 1 H), 7.82 (s, 1 H), 7.97 (dd, J = 8.9 and 2.3 Hz, 1 H), 7.58–7.44 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 148.4, 147.2, 139.2, 137.8, 132.2, 131.7, 130.4, 129.6, 129.4, 128.9, 128.8, 128.7, 127.5, 126.5, 124.5, 120.0 ppm. MS (EI, 70 eV): m/z (%) = 316 (42), 314 (82), 207 (100), 139 (30), 73 (31). HRMS (ESI-TOF): calcd. for $C_{21}H_{14}ClN$ $[M + H]^+$ 316.0893; found 316.0898.

6-Nitro-2,4-diphenylquinoline (3i): Yellow solid (0.040, 49% yield); m.p. 206–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (d, J = 2.5 Hz, 1 H), 8.48 (dd, J = 9.1 and 2.5 Hz, 1 H), 8.33 (d, J = 9.1 Hz, 1 H), 8.25–8.23 (m, 2 H), 7.97 (s, 1 H), 7.64–7.52 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 151.3, 151.0, 145.4, 138.5, 136.9, 131.8, 130.4, 129.5, 129.3, 129.1, 129.0, 127.8, 124.8, 123.0, 122.9, 120.7 ppm. MS (EI, 70 eV): m/z (%) = 326 (78), 279 (100), 202 (19), 176 (16), 139 (28). HRMS (ESI-TOF): calcd. for $C_{21}H_{14}N_2O_2$ $[M + H]^+$ 327.1134; found 327.1145.

2-(*p*-Chlorophenyl)-4-phenylquinoline (3j): Yellow solid (0.039 g, 50% yield); m.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (dd, J = 8.4 and 0.7 Hz, 1 H), 8.13 (dt, J = 8.7 and 2.0 Hz, 2 H), 7.88 (dd, J = 8.4 and 0.7 Hz, 1 H), 7.75 (s, 1 H), 7.71 (td, J = 6.8 and 1.5 Hz, 1 H), 7.54–7.43 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 149.3, 148.7, 139.5, 139.0, 138.2, 130.7, 129.6, 129.5, 129.0, 128.8, 128.6, 128.5, 126.5, 125.8, 125.6, 118.8 ppm. MS (EI, 70 eV): m/z (%) = 316 (45), 314 (100), 206 (20), 139 (33), 73 (11). HRMS (ESI-TOF): calcd. for $C_{21}H_{14}ClN$ $[M + H]^+$ 316.0893; found 316.0898.

General Procedure for the Preparation of Quinolines 4a and 4b: To a two-necked round-bottomed flask that contained a solution of **2a** (0.25 mmol) in THF (2 mL) at –78 °C under argon was added dropwise *n*BuLi (2.5 M solution in hexane, 0.25 mmol). The reaction mixture was stirred for 15 min, and the appropriate electrophile (0.50 mmol) in THF (2 mL) at –78 °C was then added slowly. The resulting mixture was stirred at room temperature for 2 h. After this time, the mixture was diluted in ethyl acetate (20 mL), and the resulting solution was then washed with a saturated aqueous solution of NH_4Cl (3 × 10 mL). The organic phases were separated, and the combined organic extracts were dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography (hexane/acetate, 9:1).

(4-Chlorophenyl)(2,4-diphenylquinolin-3-yl)methanol (4a): Pale yellow solid (0.080 g, 76% yield); m.p. 198–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.3 Hz, 1 H), 7.72 (td, J = 8.3 and 1.2 Hz, 1 H), 7.50–7.39 (m, 4 H), 7.35–7.27 (m, 7 H), 7.00 (d, J = 8.6 Hz, 2 H), 6.95 (d, J = 8.6 Hz, 1 H), 6.71 (d, J = 7.9 Hz, 2 H), 5.98 (d, J = 8.4 Hz, 1 H), 1.61 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 148.9, 146.7, 142.6, 140.9, 136.1, 132.3, 131.9, 129.9, 129.6, 129.5, 129.4, 128.9, 128.3, 128.2, 128.1, 128.0, 127.7, 126.7, 126.5, 126.3, 71.4 ppm. MS (EI, 70 eV): m/z (%) = 422 (47), 421 (100), 344 (65), 280 (34), 154 (25). HRMS (ESI-TOF): calcd. for $C_{28}H_{20}ClNO$ 422.1312; found 422.1315.

2,4-Diphenyl-3-(trimethylsilyl)quinoline (4b): Pale yellow solid (0.065 g, 73% yield); m.p. 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.4 Hz, 1 H), 7.70–7.56 (m, 4 H), 7.51–7.37 (m, 9 H), –0.36 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 157.6, 146.9, 145.1, 139.7, 131.1, 130.1, 129.8, 129.4,

129.3, 128.4, 128.2, 128.1, 128.0, 126.1, 126.0, 125.8, 2.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 353 (16), 338 (100), 308 (12), 161 (18), 73 (10). HRMS (ESI-TOF): calcd. for $C_{24}H_{23}NSi$ $[M + H]^+$ 354.1678; found 354.1682.

Acknowledgments

The authors are grateful to Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support. CNPq is also acknowledged for the fellowships to A. R. R., A. L. S., and G. Z.

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Received: June 10, 2015
Published Online: July 30, 2015

