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Short Communication

Metal- and additive-free cascade trifluoroethylation/cyclization of organic isoselenocyanates by phenyl(2,2,2-trifluoroethyl)iodonium triflate

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ABSTRACT

A novel and convenient cascade trifluoroethylation/cyclization of organic isoselenocyanates by phenyl(2,2,2-trifluoroethyl)iodonium triflate is reported. A series of 2-isoselenocyanobiaryls and aryl alkyl isoselenocyanates reacted with phenyl(2,2,2-trifluoroethyl)iodonium triflate in CH_2Cl_2 at 40 °C under metal- and additive-free conditions for 3 h to provide the corresponding trifluoroethylselenolated phenanthridines and 3,4-dihydroisoquinoline derivatives in good to excellent yields. The reaction represents the first general approach to access trifluoroethylselenolated phenanthridines and 3,4-dihydroisoquinolines from organic isoselenocyanates.

1. Introduction

Organofluorine compounds have played a significant role in chemistry, biology and material sciences [1]. Because of the unique features such as small atomic radius, high electronegativity, low polarizability, strong inductive effect, and good lipophilicity, the incorporation of fluorine and fluorine-containing groups into organic molecules can dramatically change their physical, chemical and biological properties, *e.g.* replacement of a C—H or C—O bond with a C—F bond in medicinally active compounds introduces desirable pharmacological properties like higher metabolic stability, increased binding to target molecules, and enhanced membrane permeability [2]. Among the commonly used fluorine-containing groups, CF_3CH_2 functionality has attracted great interest in the development of new pharmaceuticals, agrochemicals and functional materials [1–3]. A growing number of trifluoroethyl-containing compounds with potent biological activities have emerged in drug discovery in the past few decades [4]. Thus, developing effective and practical methods for the synthesis of trifluoroethylated compounds as many as possible is highly desirable. The direct 2,2,2-trifluoroethylation of organic scaffolds, such as arylboronic acids or esters, aryl iodides, arenes, alkynes, and alkenes, by using CF_3CH_2I, CF_3CH_2OTf, CF_3CH_2OTs, CF_3CHN_2, $CF_3CH_2NH_2$, CF_3CHCl_2, $(CF_3CH_2SO_2)_2Zn$, $CF_3CH_2SO_2Cl$, CF_3CO_2H, and aryl(2,2,2-trifluoroethyl)iodonium salts ($[ArICH_2CF_3]X$) as CF_3CH_2 transfer reagents has been successfully accomplished under transition-metal-catalyzed or -free conditions [5]. In these cases, aryl(2,2,2-trifluoroethyl)iodonium salts ($[ArICH_2CF_3]X$, X = OTf, NTf_2), first synthesized by Umemoto in 1985, have shown much powerful electrophilic trifluoroethylation reactivity toward a variety of nucleophiles [6,7]. The Pd-catalyzed reactions of aryl (2,2,2-trifluoroethyl)iodonium triflates with arylboronic acids, anilides, aromatic amides, indoles, and benzo[*h*]quinolines have represented the state-of-the-art transition-metal-catalyzed trifluoroethylations using [Ar-ICH_2CF_3][OTf] [6]. Notably, the catalyst-free reactions of $[ArICH_2CF_3]X$ with amines, peptides, alcohols, phenols, thiols, sulfides, carbohydrates, thioglycosides, fatty acids, phosphines, electron-rich arenes, and isothiocyanates have built a large number of useful trifluoroethylated molecules [7].

Phenanthridines and isoquinolines are privileged heteroaromatic skeletons found in natural products, pharmaceuticals, and functional materials, showing antitumor, antiviral, antibacterial activities, and/or optoelectronic properties [8]. A variety of 6-fluoroalkylated phenanthridines have been constructed by insertion of the *in situ* formed fluoroalkyl radicals into the isocyano groups of 2-isocyanobiaryls, which then undergo intramolecular cyclization to generate the final products [9]. 2-Isothiocyanobiaryls have also been employed as building blocks for the synthesis of phenanthridine derivatives by functionalization of the NCS moieties [7b,10]. Nonetheless, production of phenanthridine derivatives from 2-isoselenocyanobiaryls via reactions at the isoselenocyano (NCSe) groups has not been studied [11]. Furthermore, preparation of isoquinoline derivatives by intramolecular cyclization of aryl alkyl isothiocyanates in the presence of copper catalysts or acids has been explored [12], but the analogous transformations of aryl alkyl isoselenocyanates have never been known [11].

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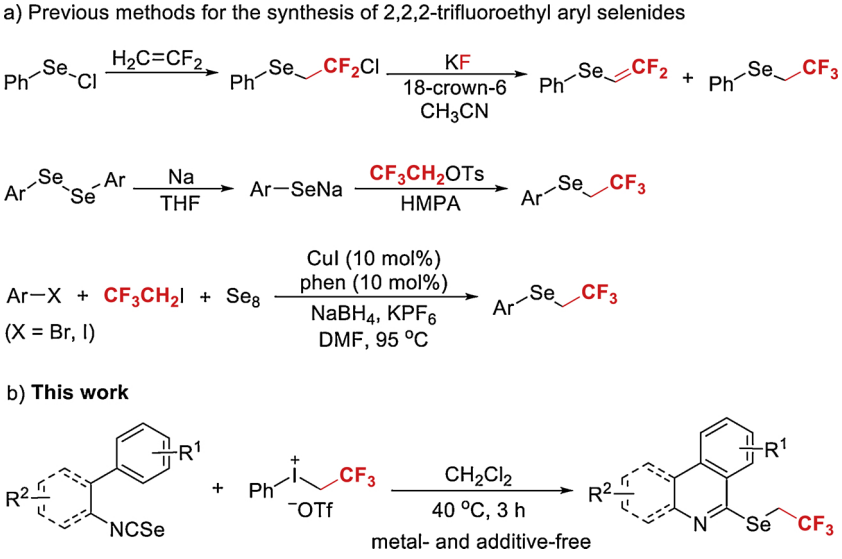
Despite that aryl(2,2,2-trifluoroethyl)iodonium salts are powerful electrophilic trifluoroethylation reagents toward a variety of nucleophiles, activation of isothiocyano groups by these salts without catalysts or additives was a really challenging task because the NCS groups in 2-isothiocyanobiaryls have much poor nucleophilicity [7b]. Since S and Se are elements of the same main group and the latter has better nucleophilicity, we wondered whether [ArICH$_2$CF$_3$][OTf] would initiate a metal- and acid-free cascade 2,2,2-trifluoroethylation/cyclization of organic isoselenocyanates.

Moreover, 2,2,2-trifluoroethyl selenoethers have been rarely explored, probably owing to the lack of relevant selenium substances or reagents [13]. Construction of 2,2,2-trifluoroethyl selenoethers is of significant importance in view of the biological potentials of organoselenium molecules. Previous methods for the synthesis of 2,2,2-trifluoroethyl aryl selenides included the elimination-addition of 2-chloro-2,2-difluoroethyl phenyl selenide with KF in the presence of a catalytic amount of 18-crown-6, the trifluoroethylation of aryl selenolate anions with 2,2,2-trifluoroethyl tosylate, which was generated *in situ* from reduction of diaryl diselenide by sodium, and the one-pot reaction of aryl halides with elemental selenium, 1,1,1-trifluoro-2-iodoethane and NaBH$_4$ using CuI/phen as a catalyst (Scheme 1) [13]. In this article, we found that reactions of 2-isoselenocyanobiaryls and aryl alkyl isoselenocyanates with phenyl(2,2,2-trifluoroethyl)iodonium triflate without any catalyst or additive provided trifluoroethylselenolated phenanthridines and 3,4-dihydroisoquinoline derivatives in good to excellent yields.

2. Results and discussion

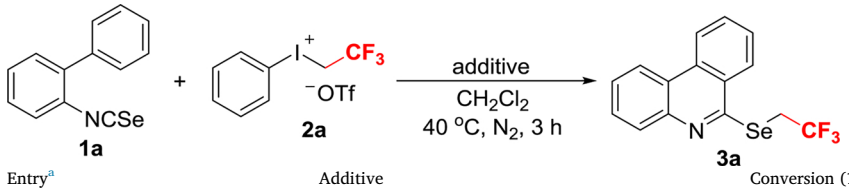
At the beginning, by following our previous procedure for the synthesis of trifluoroethylthiol phenanthridines from 2-isothiocyanobiaryls [7b], the reaction of 2-isoselenocyanato-1,1′-biphenyl (**1a**) with phenyl(2,2,2-trifluoroethyl)iodonium triflate (**2a**) was carried out in CH_2Cl_2 in the presence of TfOH (3 equiv) at 40 °C for 6 h, which, however, afforded 6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3a**) in a low yield (36%) (entry 1, Table 1). The result indicated that the optimal reaction conditions for trifluoroethylation/cyclization of 2-isothiocyanobiaryls with **2a** were not very applicable for that of 2-isoselenocyanobiaryls. Addition of bases such as KF, K_3PO_4, CH_3COOK, Et_3N and Cs_2CO_3 to the reaction mixture of **1a** and **2a** under the similar conditions led to **3a** in 37–59% yields (entries 2–6, Table 1). When the reaction of **1a** and **2a** was conducted with 4 Å molecular sieves in CH_2Cl_2 at 40 °C for 3 h, only 2% of **3a** was formed (entry 7, Table 1). Despite the relatively low yields of **3a**, most of the starting material (**1a**) was converted in the above reactions (entries 1–7, Table 1). Unexpectedly, when the same reaction of **1a** and **2a** was run without any additive at 40 °C for 3 h, **3a** was formed in 62% yield (entry 8, Table 1). All these results suggested that use of additives depressed trifluoroethylation/cyclization, which might be attributed to the decomposition of isoselenocyanate (**1a**) or both of isoselenocyanate (**1a**) and (2,2,2-trifluoroethyl)iodonium triflate (**2a**) by the additives at different levels. In addition, CH_2Cl_2 was found to be the best solvent for the reaction among all tested solvents, including $ClCH_2CH_2Cl$, CH_3CN, toluene and 1,4-dioxane (see the supporting information (SI)). Prolonging the reaction time from 3 h to 6 h did not significantly change the yield of **3a** (entry 9, Table 1). Increasing the molar equivalents of **2a** from 2.0 equiv to 3.0 equiv could slightly improve the yield of **3a** (67%, entry 10, Table 1). When **2a** was replaced by mesityl (2,2,2-trifluoroethyl)iodonium triflate [MesICH$_2$CF$_3$][OTf] (**2b**), a comparable yield of **3a** (65%) was obtained, implying that **2b** was also an effective reagent in this reaction (entry 11, Table 1).

With the optimized reaction conditions (entry 10, Table 1) in hand, the substrate scope of the metal- and additive-free trifluoroethylation/cyclization reaction was examined (Table 2). To our delight, the standard conditions enabled smooth cascade trifluoroethylation/cyclization of various electron-rich 2-isoselenocyanobiaryls. The electron-donating R^1 groups (*e.g.*, methyl (**1b**), methoxy (**1c**), *tert*-butyl (**1d**), benzyloxy (**1e**)) on the aryl rings of 2-isoselenocyanobiaryls benefited the reaction, affording **3b**-**e** in higher yields (58–68%) than that of **3a**. When 2-isoselenocyanato-4′-phenoxy-1,1′-biphenyl (**1f**) reacted with **2a** at 40 °C for 3 h, the expected 8-phenoxy-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3f**) was obtained in 39% yield. The lower yield of **3f** might be caused by the presence of a weak electron-withdrawing phenyl group in **1f**. Moreover, the similar reactions of 2-isoselenocyanobiaryls bearing electron-withdrawing R^1 groups such as chloro (**1g**) and cyano (**1h**) groups gave no desired products, even though the starting materials were completely consumed. All these results suggested that the electronic nature of R^1 group had a very big influence on the reaction. Furthermore, reactions of 2-isoselenocyanato-3′,5′-dimethyl-1,1′-biphenyl (**1i**), 2-isoselenocyanato-3′,5′-dimethoxy-1,1′-biphenyl (**1j**), and 2-isoselenocyanato-4′-methoxy-3′-methyl-1,1′-biphenyl (**1k**) with **2a** under the standard conditions furnished **3i** in 89% yield, **3j** in 95% yield, and **3k** in 71% yield. It seemed that the more electron-donating R^1 groups attached on the aryl rings of 2-isoselenocyanobiaryls provided the higher yields of the desired products. The position of substituents on the aryl rings of 2-isoselenocyanobiaryls also considerably



Scheme 1. The known methods for the synthesis of 2,2,2-trifluoroethyl aryl selenides.

Table 1
Screening of the optimal reaction conditions for trifluoroethylation/cyclization of **1a** by **2a**.



Entry[a]	Additive	Conversion (**1a**, %)[b]	Yield (**3a**, %)[b]
1[c,d]	TfOH (3.0 equiv)	> 99	36
2	KF (1.0 equiv)	97	59
3	K_3PO_4 (1.0 equiv)	87	37
4	CH_3COOK (1.0 equiv)	> 99	49
5	Et_3N (1.0 equiv)	68	38
6	Cs_2CO_3 (1.0 equiv)	98	43
7	4Å MS (50 mg)	87	2
8	none	> 99	62
9[d]	none	> 99	63
10[e]	**none**	> **99**	**67 (51**[f]**)**
11[e,g]	none	> 99	65

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), additive (x equiv), CH_2Cl_2 (2 mL), N_2, 40 °C, 3 h.
[b] The conversion of **1a** and the yields of **3a** were determined by HPLC (λ = 244 nm, water/methanol = 10 : 90 (v / v)) using pure 2-isoselenocyanato-1,1′-biphenyl (**1a**, t_R = 7.698 min) and 6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3a**, t_R = 10.157 min) as external standards, respectively.
[c] Under ambient atmosphere.
[d] 6 h.
[e] **1a** (0.2 mmol) and **2a** (0.6 mmol).
[f] Isolated yield.
[g] $[PhICH_2CF_3][OTf]$ (**2a**) was replaced by $[MesICH_2CF_3][OTf]$ (**2b**).

affected the conversion. Reactions of 2-isoselenocyanato-4′-methyl-1,1′-biphenyl (**1b**) and 2-isoselenocyanato-2′-methyl-1,1′-biphenyl (**1m**) with **2a** at 40 °C for 3 h formed **3b** (68%) and **3m** (56%) as the single products, while the same reaction of 2-isoselenocyanato-3′-methyl-1,1′-biphenyl (**1l**) with **2a** afforded a mixture of 7-methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3l**) and 9-methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3 l'**) in 77% total yield. The molar ratio of **3l** / **3l'** = 1 : 6.7 was determined by NMR analysis of the isolated product. In a similar manner, treatment of 1-(2-isoselenocyanatophenyl)naphthalene (**1n**) with **2a** furnished **3n** in 57% yield. Heteroaromatic systems were also suitable substrates for the reaction. 5-(2-Isoselenocyanatophenyl)benzo[d][1,3]dioxole (**1o**), 2-(2-isoselenocyanatophenyl)thiophene (**1p**), 3-(2-isoselenocyanatophenyl) thiophene (**1q**), 1-(2-isoselenocyanatophenyl)thianthrene (**1r**), and 4-(2-isoselenocyanatophenyl)dibenzo[*b*,d]furan (**1s**) reacted with **2a** under the standard conditions to give the corresponding trifluoroethyl cyclization products (**3o-s**) in up to 97% yield. The frustrated formation of 6-((2,2,2-trifluoroethyl)selanyl)benzo[5,6][1,4]dithiino[2,3-k]phenanthridine (**3r**) from **1r** was likely ascribed to the competitive reaction of **2a** at the sulfur centers of **1r** because these cites also have considerable nucleophilicity towards **2a** [14]. Again, the electronic properties of R^2 groups on the aryl rings of 2-isoselenocyanobiaryls have an impact on the reaction. Treatment of 2-isoselenocyanato-4-methyl-1,1′-biphenyl (**1t**) and 5-chloro-2-isoselenocyanato-1,1′-biphenyl (**1u**) with **2a** at 40 °C for 3 h afforded **3t** in 52% yield (*vs* 68% of **3b**) and **3 u** in 44% yield (*vs* 0% of **3g**), respectively. The substituent effects of R^2 groups appeared to be smaller than that of R^1 groups for the trifluoroethylation/cyclization reaction as the substrate (**1u**) containing a weak electron-withdrawing R^2 = Cl group on the aryl ring could give a moderate yield (**3u**). However, this reaction was not amenable for 2-isoselenocyanobiaryl bearing a strong electron-withdrawing R^2 group like NO_2 (**1v**) on the aryl ring, which afforded no desired product (**3v**).

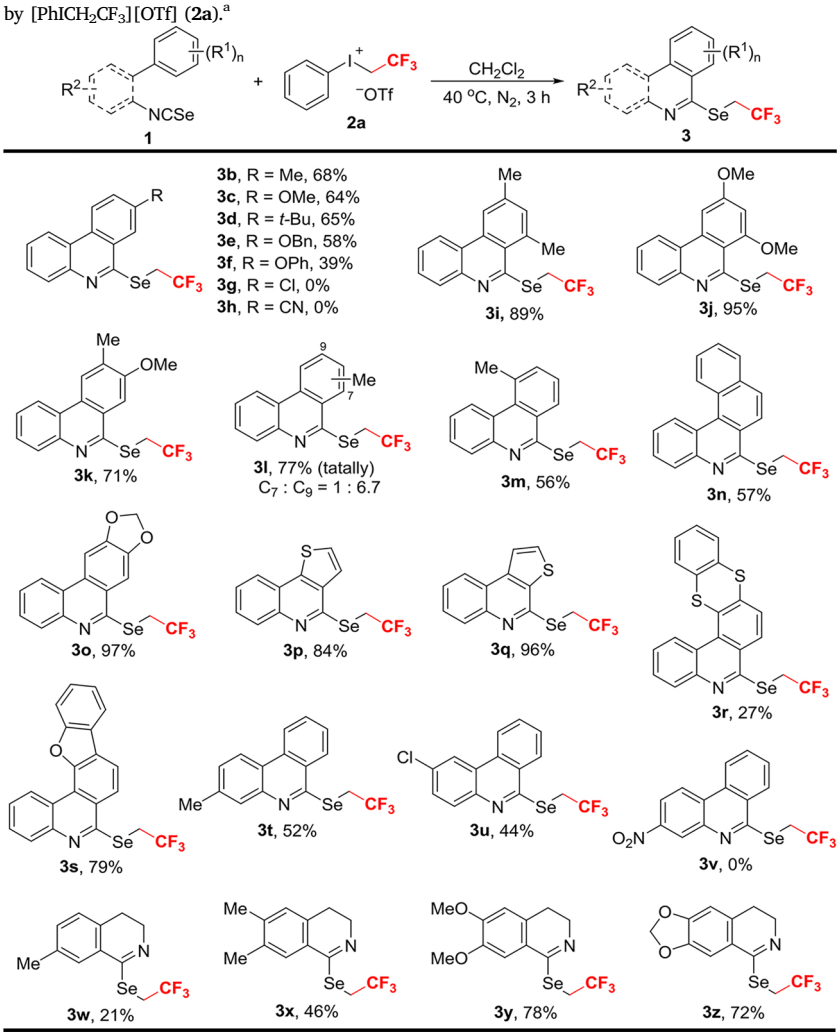
In addition, the metal- and additive-free cascade trifluoroethylation/cyclization reaction was applicable to electron-rich aryl alkyl isoselenocyanates (Table 2). Reaction of 1-(2-isoselenocyanatoethyl)-4-methylbenzene (**1w**) with **2a** under the standard conditions provided **3w** in 21% yield. Analogously, treatment of 4-(2-isoselenocyanatoethyl)-1,2-dimethylbenzene (**1x**), 4-(2-isoselenocyanatoethyl)-1,2-dimethoxybenzene (**1y**), and 5-(2-isoselenocyanatoethyl)benzo[d][1,3]dioxole (**1z**) with **2a** formed **3x-z** in 46–78% yields. The reactions occurred at both the electron-rich and least sterically hindered aromatic carbon sites to produce the trifluoroethylselenolated 3,4-dihydroisoquinolines with specific regioselectivity. When (2-isoselenocyanatoethyl)benzene (**1aa**) was mixed with **2a** in the same reaction, only trace amounts of the trifluoroethylselenolated product was formed, which was determined by both TLC and ^{19}F NMR analyses of the reaction mixture. These observations implied that the strong electron-donating groups on the aromatic rings of aryl alkyl isoselenocyanates favorably improved the reaction and that the transformation was very sensitive to the inherent electronic nature of the substituents. It should be noted that all trifluoroethylselenol 3,4-dihydroisoquinoline derivatives in Table 2 were unstable and tended to decompose when they were chromatographed on silica gel. To obtain good yields of the products, their separation should be performed by column chromatography on aluminum oxide as fast as possible.

On the basis of the above results and previous report [7b], a plausible reaction mechanism for the metal- and additive-free cascade trifluoroethylation/cyclization was suggested (Scheme 2). First, phenyl (2,2,2-trifluoroethyl)iodonium triflate (**2a**) is attacked at the iodonium center by the nucleophilic lone-pair electrons of selenium in isoselenocyanates (**1**) to form a cation intermediate (**4** or **5**) (path **a**). Then, intermediate **4** or **5** undergoes intramolecular Friedel-Crafts-type cyclization to afford **6**. Reductive elimination of trifluoroethyl group and selenium moiety from **6** at the iodine center followed by deprotonation provides the final product (**3**). Besides, the straightforward nucleophilic attack of **2a** at the α-carbon site of CH_2CF_3 group by the lone-pair electrons of Se atom of isoselenocyanates (**1**) is also possible, which produces complex **7** or **8** as a key cation intermediate (path **b**). Subsequently, intramolecular Friedel-Crafts-type cyclization of **7** or **8** generates **9**, which is deprotonated under the reaction conditions to eventually supply the desired product (**3**).

3. Conclusion

In summary, we have developed a convenient and efficient method for

Table 2
Transition-metal- and additive-free cascade trifluoroethylation/cyclization of 2-isoselenocyanobiaryls (**1**) by $[PhICH_2CF_3][OTf]$ (**2a**).[a]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), CH_2Cl_2 (2 mL), 40 °C, N_2, 3 h. Isolated yields.

the one-pot synthesis of trifluoroethylselenolated phenanthridines and 3,4-dihydroisoquinolines under metal- and additive-free conditions. The cascade trifluoroethylation/cyclization of 2-isoselenocyanobiaryls and aryl alkyl isoselenocyanates (**1**) by phenyl(2,2,2-trifluoroethyl)iodonium triflate (**2a**) in CH_2Cl_2 at 40 °C for 3 h afforded a variety of trifluoroethylselenol phenanthridines and 3,4-dihydroisoquinoline derivatives (**3**) in good to excellent yields. The electronic nature of substituents on the aryl rings of **1** greatly affected the reaction. The electron-donating substituents could significantly promote the yields of the products under standard conditions. This protocol is the first report to access trifluoroethylselenolated phenanthridine and isoquinoline derivatives from isoselenocyanates without using any transition metal or additive. Further application of aryl(2,2,2-trifluoroethyl)iodonium salts as promising trifluoroethylation reagents in new fluoroalkylation reactions is currently underway in our laboratory.

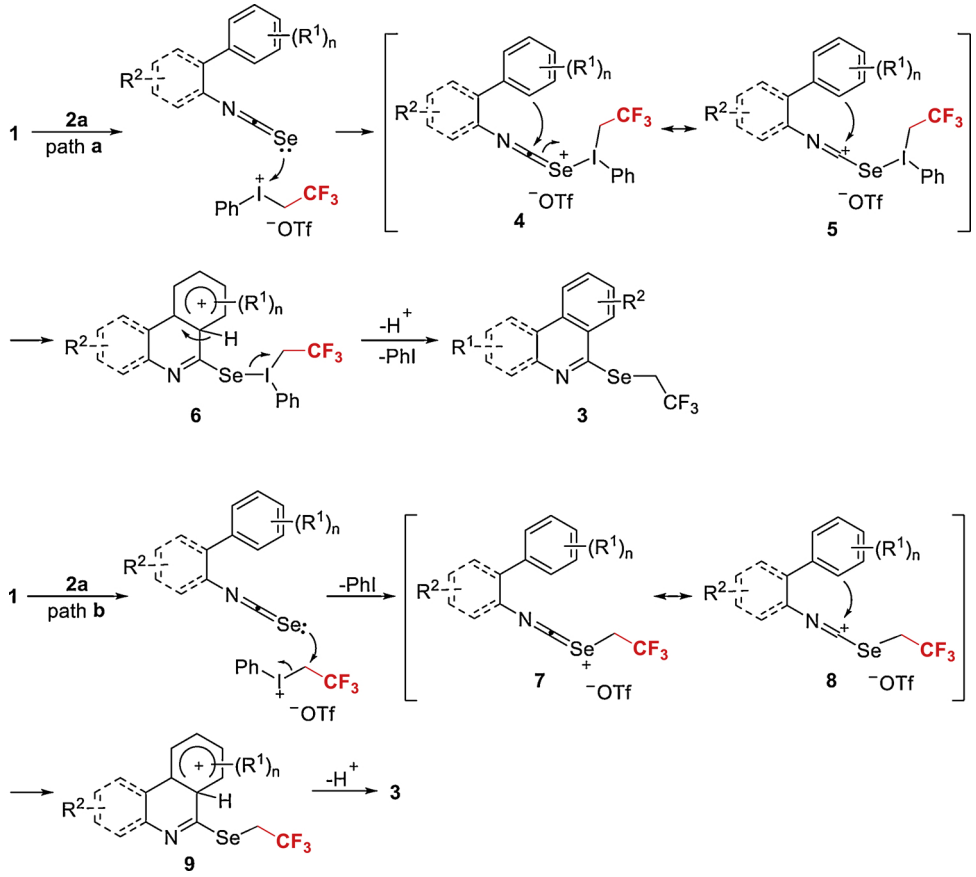
4. Experimental section

4.1. General considerations

All reactions were carried out under a nitrogen atmosphere unless otherwise specified. The NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^1H), 471 (for ^{19}F), and 126 or 100 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm for ^1H NMR) and $PhCF_3$ (63.5 ppm for ^{19}F NMR) as an internal or external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the HPLC yields of the product were determined by using the corresponding pure compound as the external standard. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI or EI instrument. Trifluoroethylation reagents **2a** and **2b** were synthesized according to the literature [15]. Substrates **1a-v** and **1 w-1z** were synthesized according to the literatures [16–18]. Solvents were dried before use according to the literature [19]. Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

4.2. General procedures for the reaction of isosocyanates with $[ArICH_2CF_3][OTf]$

Procedure A: Under a nitrogen atmosphere, a sealed tube was charged with isosocyanate (**1a-1v**, 0.2 mmol), $[PhICH_2CF_3][OTf]$ (261.6 mg, 0.6 mmol) and CH_2Cl_2 (2 mL) with stirring. The mixture was reacted at 40 °C for 3 h, cooled to room temperature, quenched with saturated aqueous $NaHCO_3$ solution, and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over anhydrous



Scheme 2. A proposed reaction mechanism for the metal- and additive-free cascade trifluoroethylation/cyclization of isoselenocyanates.

Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoroethylselenolated product (**3a-3v**).

Procedure B: Under a nitrogen atmosphere, a sealed tube was charged with isosocyanate (**1w-1z**, 0.2 mmol), $[PhICH_2CF_3][OTf]$ (261.6 mg, 0.6 mmol) and CH_2Cl_2 (2 mL) with stirring. The mixture was reacted at 40 °C for 3 h, cooled to room temperature, quenched with saturated aqueous $NaHCO_3$ solution, and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography (within 5 min) on aluminum oxide (basic) using a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoroethylselenolated product (**3w-3z**).

*4.2.1. 6-((2,2,2-Trifluoroethyl)selanyl)phenanthridine (**3a**)*

White solid, 29.7 mg, 51% yield, a mixture of petroleum ether and ethyl acetate (50:1 (v/v)) as eluents for column chromatography. M.p.: 101–103 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 8.3 Hz, 1 H), 8.49 (d, J = 8.1 Hz, 1 H), 8.10 (d, J = 8.2 Hz, 1 H), 8.07 (d, J = 8.1 Hz, 1 H), 7.86 (t, J = 7.5 Hz, 1 H), 7.73-7.68 (m, 2 H), 7.62 (t, J = 7.8 Hz, 1 H), 4.32 (q, J = 10.8 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 144.1, 132.4, 131.2, 129.0, 129.0, 127.8, 126.6, 126.6, 126.2 (q, J = 274.3 Hz), 126.1, 123.3, 122.6, 122.3, 25.4 (q, J = 33.4 Hz). IR (KBr): 3076, 3010, 2942, 2852, 1610, 1566, 1523, 1483, 1456, 1410, 1341, 1291, 1275, 1239, 1227, 1194, 1156, 1133, 1120, 1051, 946, 862, 843, 831, 755, 718, 632, 619 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{15}H_{11}F_3N^{74}Se$ ($[M+H]^+$): 336.0063; found: 336.0060.

*4.2.2. 8-Methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3b**)*

White solid, 48.4 mg, 68% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 136–138 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43-8.40 (m, 2 H), 8.04 (d, J = 8.1 Hz, 1 H), 7.83 (s, 1 H), 7.67 (tm, J = 7.5 Hz, 1 H), 7.63 (d, J = 8.4 Hz, 1 H), 7.59 (tm, J = 7.6 Hz, 1 H), 4.32 (q, J = 10.8 Hz, 2 H), 2.58 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.6 (t, J = 10.6 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 143.8, 138.0, 132.9, 130.1, 128.9, 128.5, 126.7, 126.5, 126.2 (q, J = 273.8 Hz), 125.5, 123.4, 122.4, 122.1, 25.3 (q, J = 33.2 Hz), 21.7. IR (KBr): 3073, 3006, 2940, 1623, 1611, 1567, 1532, 1480, 1461, 1409, 1383, 1367, 1345, 1294, 1266, 1238, 1212, 1175, 1158, 1114, 1061, 969, 949, 878, 859, 835, 817, 779, 755, 722, 709, 686, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{16}H_{13}F_3NSe$ ($[M+H]^+$): 356.0160; found: 356.0154.

*4.2.3. 8-Methoxy-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3c**)*

Light yellow solid, 41.4 mg, 64% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 116–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, J = 9.0 Hz, 1 H), 8.39 (d, J = 8.0 Hz, 1 H), 8.04 (d, J = 8.0 Hz, 1 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.45 (d, J = 9.0 Hz, 1 H), 7.36 (s, 1 H), 4.32 (q, J = 10.7 Hz, 2 H), 3.99 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 152.7, 143.2, 128.9, 128.0, 127.9, 126.6, 126.5, 126.2 (q, J = 274.7 Hz), 124.3, 123.5, 121.8, 121.8, 106.1, 55.6, 25.6 (q, J = 33.4 Hz). IR (KBr): 3060, 3020, 2999, 2968, 2935, 2848, 1674, 1620, 1568, 1529, 1484, 1462, 1446, 1421, 1403, 1361, 1294, 1275, 1243, 1216, 1189, 1173, 1151, 1115, 1063, 1040, 975, 946, 938, 886, 827, 759, 752, 726, 716, 655, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{16}H_{13}F_3NOSe$ ($[M+H]^+$): 372.0109; found: 372.0114.

*4.2.4. 8-(Tert-butyl)-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (**3d**)*

Gray solid, 51.2 mg, 65% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.:

111–113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, J = 8.7 Hz, 1 H), 8.47 (d, J = 8.1 Hz, 1 H), 8.06 (dd, J = 8.2, 0.9 Hz, 1 H), 8.04 (d, J = 1.8 Hz, 1 H), 7.94 (dd, J = 8.7, 1.9 Hz, 1 H), 7.68 (tm, J = 7.6 Hz, 1 H), 7.61 (tm, J = 7.6 Hz,), 4.34 (q, J = 10.8 Hz, 2 H), 1.49 (s, 9 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.6 (t, J = 10.9 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 151.2, 143.9, 130.2, 129.7, 128.9, 128.6, 126.6, 126.5, 126.2 (q, J = 274.1 Hz), 123.4, 122.5, 122.2, 121.6, 35.2, 31.3, 25.3 (q, J = 33.3 Hz). IR (KBr): 3063, 2999, 2961,2903, 2868, 1609, 1576, 1557, 1533, 1481, 1462, 1405, 1365, 1349, 1290, 1262, 1217, 1185, 1160, 1114, 1059, 967, 875, 867, 834, 783, 763, 724, 706, 670, 657, 631 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{19}H_{19}F_3NSe$ ([M + H]$^+$): 398.0629; found: 398.0624.

4.2.5. 8-(Benzyloxy)-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3e)

White solid, 52.0 mg, 58% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 143–145 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 9.0 Hz, 1 H), 8.43 (d, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.1 Hz, 1 H), 7.66 (tm, J = 7.5 Hz, 1 H), 7.61 (tm, J = 7.50 Hz, 1 H), 7.57-7.50 (m, 4 H), 7.45 (t, J = 7.5 Hz, 2 H), 7.38 (t, J = 7.4 Hz, 1 H), 5.26 (s, 2 H), 4.31 (q, J = 10.8 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 152.8, 143.4, 136.2, 128.9, 128.8, 128.4, 128.0, 127.9, 127.8, 126.7, 126.6, 126.1 (q, J = 274.8 Hz), 124.4, 123.5, 122.2, 121.8, 107.8, 70.6, 25.6 (q, J = 33.3 Hz). IR (KBr): 3068, 3040, 3012, 2945, 2909, 2872, 1615, 1568, 1531, 1486, 1462, 1414, 1387, 1359, 1299, 1275, 1245, 1222, 1208, 1179, 1128, 1055, 1034, 1017, 995, 947, 918, 899, 864, 836, 824, 755, 717, 707, 693, 634, 621 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{22}H_{17}F_3NOSe$ ([M + H]$^+$): 448.0422; found: 448.0429.

4.2.6. 8-Phenoxy-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3f)

Gray solid, 34.1 mg, 39% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 9.0 Hz, 1 H), 8.43 (d, J = 8.0 Hz, 1 H), 8.06 (dd, J = 8.1, 0.9 Hz, 1 H), 7.68 (tm, J = 7.6 Hz, 1 H), 7.63-7.60 (m, 2 H), 7.56 (dd, J = 9.0, 2.4 Hz, 1 H), 7.44 (tm, J = 8.0 Hz, 2 H), 7.23 (t, J = 7.5 Hz, 1 H), 7.14 (d, J = 7.7 Hz, 2 H), 4.27 (q, J = 10.8 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 156.3, 153.0, 143.6, 130.2, 129.0, 128.5, 128.0, 127.9, 126.8, 126.1 (q, J = 274.5 Hz), 124.7, 124.4, 123.4, 123.2, 122.0, 119.5, 113.2, 25.5 (q, J = 33.5 Hz). IR (KBr): 3064, 3011, 2938, 1617, 1598, 1587, 1567, 1529, 1480, 1459, 1409, 1352, 1298, 1243, 1220, 1170, 1155, 1115, 1074, 1056, 1023, 989, 907, 856, 830, 812, 758, 720, 711, 701, 688, 656, 634 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{21}H_{15}F_3NOSe$ ([M + H]$^+$): 434.0265; found: 434.0256.

4.2.7. 7,9-Dimethyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3i)

White solid, 65.9 mg, 89% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 113–115 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.1 Hz, 1 H), 8.18 (s, 1 H), 7.95 (dd, J = 8.1, 0.8 Hz, 1 H), 7.64 (tm, J = 7.5 Hz, 1 H), 7.54 (tm, J = 7.7 Hz, 1 H), 7.22 (s, 1 H), 4.29 (q, J = 11.0 Hz, 2 H), 3.03 (s, 3 H), 2.51 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.9 (t, J = 11.0 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 143.0, 140.4, 136.1, 134.5, 133.3, 128.7, 128.4, 126.4 (q, J = 274.4 Hz), 126.2, 125.2, 123.2, 122.4, 120.7, 27.3 (q, J = 32.3 Hz), 24.4, 21.7. IR (KBr): 3068, 3008, 2967, 2945, 1615, 1564, 1507, 1482, 1460, 1450, 1398, 1373, 1349, 1331, 1286, 1272, 1255, 1207, 1173, 1111, 1095, 1056, 1030, 973, 941, 931, 887, 859, 852, 834, 787, 757, 730, 706, 632, 621 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{17}H_{15}F_3NSe$ ([M + H]$^+$): 370.0316; found: 370.0308.

4.2.8. 7,9-Dimethoxy-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3 j)

White solid, 76.3 mg, 95% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 182–184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.1 Hz, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.64 (t, J = 7.5 Hz, 1 H), 7.50 (t, J = 7.7 Hz, 1 H), 7.36 (s, 1 H), 6.55 (s, 1 H), 4.18 (q, J = 11.3 Hz, 2 H), 4.00 (s, 3 H), 3.95 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5 (t, J = 11.4 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 158.5, 150.8, 144.1, 136.4, 129.1, 128.7, 127.0 (q, J = 274.2 Hz), 125.7, 122.5, 122.2, 113.3, 98.7, 95.6, 55.5, 55.4, 25.1 (q, J = 31.5 Hz). IR (KBr): 3105, 3093, 3012, 2993, 2937, 2856, 2835, 1617, 1582, 1565, 1516, 1488, 1459, 1440, 1412, 1363, 1341, 1271, 1212, 1166, 1136, 1113, 1054, 1034, 1025, 945, 884, 862, 833, 820, 780, 760, 722, 654, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{17}H_{15}F_3NO_2Se$ ([M + H]$^+$): 402.0215; found: 402.0216.

4.2.9. 8-Methoxy-9-methyl-6-((2,2,2-trifluoroethyl)selanyl) phenanthridine (3k)

White solid, 54.2 mg, 71% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 144–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1 H), 8.30 (s, 1 H), 8.04 (d, J = 8.1 Hz, 1 H), 7.65 (tm, J = 7.5 Hz, 1 H), 7.59 (tm, J = 7.5 Hz, 1 H), 7.25 (s, 1 H), 4.34 (q, J = 10.8 Hz, 2 H), 4.03 (s, 3 H), 2.49 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.6 (t, J = 10.7 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 152.3, 143.4, 133.3, 128.8, 127.7, 126.4, 126.3, 126.3, 126.2 (q, J = 274.5 Hz), 124.1, 123.3, 121.8, 103.8, 55.6, 25.5 (q, J = 33.4 Hz), 17.3. IR (KBr): 3066, 2999, 2962, 2938, 2835, 1623, 1569, 1517, 1494, 1464, 1447, 1406, 1365, 1296, 1266, 1243, 1211, 1191, 1153, 1115, 1061, 1045, 978, 946, 919, 874, 827, 790, 753, 716, 631 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{17}H_{15}F_3NOSe$ ([M + H]$^+$): 386.0265; found: 386.0270.

4.2.10. 7-Methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3l)

White solid, petroleum ether as eluent for preparative TLC plate. M.p.: 99–101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 8.3 Hz, 1 H), 8.48 (d, J = 8.3 Hz, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 7.70-7.66 (m, 2 H), 7.59 (t, J = 7.8 Hz, 1 H), 7.49 (d, J = 7.2 Hz, 1 H), 4.29 (q, J = 11.0 Hz, 2 H), 3.14 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.1 (t, J = 11.0 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 142.9, 136.5, 134.4, 131.7, 130.3, 128.9, 128.5, 127.3, 126.5, 126.3 (q, J = 274.3 Hz), 123.3, 122.5, 121.1, 27.4 (q, J = 32.2 Hz), 24.6. IR (KBr): 3059, 3015, 2958, 2917, 2849, 1601, 1581, 1567, 1520, 1475, 1458, 1446, 1396, 1376, 1286, 1265, 1218, 1186, 1112, 1050, 1034, 936, 832, 804, 755, 730, 704, 633 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{16}H_{12}F_3NNaSe$ ([M + Na]$^+$): 377.9979; found: 377.9981.

4.2.11. 9-Methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3l')

White solid, petroleum ether as eluent for preparative TLC plate. M.p.: 102–104 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 8.1 Hz, 1 H), 8.34 (s, 1 H), 8.04 (d, J = 8.1 Hz, 1 H), 7.97 (d, J = 8.3 Hz, 1 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.49 (d, J = 8.3 Hz, 1 H), 4.30 (q, J = 10.8 Hz, 2 H), 2.63 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 144.3, 141.9, 132.5, 129.5, 129.0, 128.9, 126.4, 126.3 (q, J = 274.4 Hz), 126.0, 124.8, 123.3, 122.3, 122.3, 25.3 (q, J = 33.2 Hz), 22.3. IR (KBr): 3060, 3040, 2991, 2927, 2849, 1621, 1571, 1518, 1495, 1461, 1417, 1374, 1348, 1338, 1287, 1270, 1213, 1155, 1108, 1058, 946, 873, 845, 831, 801, 753, 722, 717, 708, 691, 633, 622, 616 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{16}H_{13}F_3NSe$ ([M + H]$^+$): 356.0160; found: 356.0155.

4.2.12. 10-Methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3m)

White solid, 39.9 mg, 56% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 125–127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 8.4 Hz, 1 H), 8.11 (dd, J = 8.1, 1.3 Hz, 1 H), 8.02 (d, J = 8.0 Hz, 1 H), 7.72-7.68 (m, 2 H), 7.62-7.57 (m, 2 H), 4.31 (q, J = 10.8 Hz, 2 H), 3.09 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.6 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 144.9, 135.9, 135.4, 131.8, 129.3, 128.2, 127.9, 127.1, 126.7, 126.3 (q, J = 274.4 Hz), 125.8, 124.8, 124.7, 26.7, 25.8 (q, J

= 33.2 Hz). IR (KBr): 3064, 3018, 2969, 2949, 2880, 1573, 1526, 1477, 1457, 1442, 1404, 1381, 1344, 1290, 1262, 1213, 1178, 1131, 1108, 1062, 997, 866, 822, 804, 761, 719, 631 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{16}H_{13}F_3NSe$ ($[M+H]^+$): 356.0160; found: 356.0162.

4.2.13. 6-((2,2,2-Trifluoroethyl)selanyl)benzo[k]phenanthridine (3n)

Yellow oil, 44.4 mg, 57% yield, a mixture of petroleum ether and ethyl acetate (50:1 (v/v)) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.3 Hz, 1 H), 7.86 (d, J = 8.1 Hz, 1 H), 7.79 (d, J = 7.4 Hz, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 1 H), 7.43-7.37 (m, 2 H), 7.28 (tm, J = 7.2 Hz, 1 H), 7.20 (d, J = 7.7 Hz, 1 H), 3.93 (q, J = 10.9 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.3 (t, J = 10.9 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 144.7, 136.7, 135.8, 133.8, 132.9, 132.7, 132.3, 131.6, 128.7, 128.4, 127.6, 127.6, 127.4, 127.3, 127.1, 126.2 (q, J = 274.9 Hz), 125.4, 29.4 (q, J = 32.2 Hz). IR (KBr): 3056, 2995, 2927, 2852, 1632, 1607, 1587, 1502, 1485, 1458, 1439, 1423, 1367, 1287, 1265, 1240, 1219, 1165, 1112, 1073, 945, 872, 838, 818, 789, 770, 734, 705, 665, 632 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{19}H_{13}F_3NSe$ ($[M+H]^+$): 392.0160; found: 392.0178.

4.2.14. 6-((2,2,2-Trifluoroethyl)selanyl)-[1,3]dioxolo[4,5-j]phenanthridine (3o)

White solid, 74.6 mg, 97% yield, a mixture of petroleum ether and ethyl acetate (30:1 (v/v)) as eluents for column chromatography. M.p.: 157–159 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 8.2 Hz, 1 H), 8.02 (d, J = 8.2 Hz, 1 H), 7.85 (s, 1 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.57 (t, J = 7.9 Hz, 1 H), 7.41 (s, 1 H), 6.16 (s, 2 H), 4.29 (q, J = 10.8 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.9 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 151.5, 148.4, 143.7, 130.0, 128.9, 128.3, 126.2, 126.1 (q, J = 274.2 Hz), 123.6, 123.0, 122.0, 103.6, 102.2, 100.5, 25.7 (q, J = 33.3 Hz). IR (KBr): 3072, 3044, 2995, 2954, 2924, 2823, 2782, 1634, 1611, 1572, 1522, 1500, 1481, 1463, 1445, 1417, 1378, 1294, 1264, 1250, 1236, 1206, 1184, 1108, 1056, 1040, 980, 945, 857, 835, 783, 762, 721, 705, 633, 612 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{16}H_{11}F_3NO_2Se$ ($[M+H]^+$): 385.9902; found: 385.9898.

4.2.15. 4-((2,2,2-Trifluoroethyl)selanyl)thieno[3,2-c]quinolone (3p)

White solid, 58.4 mg, 84% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 79–81 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.3 Hz, 1 H), 8.05 (d, J = 7.9 Hz, 1 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.60-7.56 (m, 2 H), 7.53 (d, J = 5.4 Hz, 1 H), 4.32 (q, J = 10.7 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.9 (t, J = 10.9 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 144.4, 144.0, 133.1, 129.0, 128.7, 126.5, 126.5, 126.1 (q, J = 274.3 Hz), 123.3, 123.2, 122.8, 24.9 (q, J = 33.7 Hz). IR (KBr): 3108, 3005, 2963, 2940, 1609, 1550, 1540, 1504, 1468, 1446, 1402, 1389, 1338, 1293, 1264, 1214, 1151, 1138, 1112, 1063, 974, 947, 861, 833, 802, 781, 754, 733, 727, 707, 680, 631 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{13}H_9F_3NSSe$ ($[M+H]^+$): 347.9568; found: 347.9579.

4.2.16. 4-((2,2,2-Trifluoroethyl)selanyl)thieno[2,3-c]quinolone (3q)

White solid, 66.6 mg, 96% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 103–105 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.1, 0.9 Hz, 1 H), 8.14 (d, J = 8.3 Hz, 1 H), 7.96 (d, J = 5.3 Hz, 1 H), 7.81 (d, J = 5.3 Hz, 1 H), 7.69 (tm, J = 7.8 Hz, 1 H), 7.60 (tm, J = 7.6 Hz, 1 H), 4.32 (q, J = 10.7 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.0 (t, J = 10.5 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 144.9, 141.5, 134.0, 131.0, 128.8, 128.4, 126.3, 126.0 (q, J = 274.6 Hz), 123.5, 123.4, 122.1, 25.4 (q, J = 33.8 Hz). IR (KBr): 3116, 3059, 3003, 2940, 1612, 1562, 1543, 1494, 1456, 1432, 1412, 1384, 1331, 1296, 1276, 1244, 1219, 1189, 1158, 1134, 1111, 1092, 1069, 1051, 959, 899, 845, 834, 788, 759, 727, 709, 669, 640, 633 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{13}H_9F_3NSSe$ ($[M+H]^+$): 347.9568; found: 347.9567.

4.2.17. 6-((2,2,2-Trifluoroethyl)selanyl)benzo[5,6][1,4]dithiino[2,3-k]phenanthridine (3r)

White solid, 25.9 mg, 27% yield, a mixture of petroleum ether and ethyl acetate (60:1 (v/v)) as eluents for column chromatography. M.p.: 182–184 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, J = 8.2 Hz, 1 H), 8.09 (dd, J = 8.0, 0.8 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.78 (t, J = 7.5 Hz, 1 H), 7.72 (tm, J = 7.7 Hz, 1 H), 7.63 (d, J = 7.3 Hz, 1 H), 7.58 (d, J = 7.5 Hz, 1 H), 7.34 (td, J = 7.4, 0.8 Hz, 1 H), 7.28 (td, J = 7.7, 0.8 Hz, 1 H), 4.27 (q, J = 10.7 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 145.2, 140.7, 135.9, 135.7, 134.9, 132.3, 129.4, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 127.1, 126.1 (q, J = 274.2 Hz), 125.8, 125.2, 122.8, 26.1 (q, J = 33.7). IR (KBr): 3050, 3016, 2958, 2937, 2848, 1574, 1467, 1449, 1418, 1367, 1328, 1302, 1290, 1278, 1267, 1241, 1212, 1151, 1120, 1109, 1049, 983, 811, 754, 744, 729, 707, 669, 636 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{21}H_{13}F_3NS_2Se$ ($[M+H]^+$): 479.9601; found: 479.9603.

4.2.18. 6-((2,2,2-Trifluoroethyl)selanyl)benzofuro[3,2-k]phenanthridine (3s)

White solid, 74.6 mg, 97% yield, a mixture of petroleum ether and ethyl acetate (30:1 (v/v)) as eluents for column chromatography. M.p.: 190–192 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 9.52 (m, 1 H), 8.21 (d, J = 8.4 Hz, 1 H), 8.13 (m, 1 H), 8.09 (d, J = 7.6 Hz, 1 H), 8.06 (d, J = 8.4 Hz, 1 H), 7.82 (d, J = 8.3 Hz, 1 H), 7.81-7.75 (m, 2 H), 7.61 (tm, J = 7.8 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 4.35 (q, J = 10.8 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.6 (t, J = 10.6 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 153.4, 152.1, 144.3, 129.2, 128.7, 128.2, 127.4, 127.0, 126.2 (q, J = 274.5 Hz), 126.0, 125.9, 123.6, 123.2, 121.6, 121.1, 121.0, 120.1, 120.0, 112.2, 25.8 (q, J = 33.3 Hz). IR (KBr): 3047, 3009, 2943, 2850, 1629, 1605, 1578, 1567, 1526, 1490, 1470, 1457, 1417, 1399, 1363, 1336, 1290, 1261, 1215, 1197, 1180, 1150, 1116, 1062, 1015, 862, 837, 824, 804, 769, 754, 747, 730, 704, 688, 667, 650, 631 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{21}H_{13}F_3NOSe$ ($[M+H]^+$): 432.0109; found: 432.0095.

4.2.19. 3-Methyl-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3t)

Light yellow solid, 36.7 mg, 52% yield, a mixture of petroleum ether and ethyl acetate (30:1 (v/v)) as eluents for column chromatography. M.p.: 104–105 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 8.2 Hz, 1 H), 8.36 (d, J = 8.3 Hz, 1 H), 8.07 (d, J = 8.1 Hz, 1 H), 7.86 (s, 1 H), 7.82 (t, J = 7.3 Hz, 1 H), 7.65 (t, J = 7.4 Hz, 1 H), 7.44 (d, J = 8.3 Hz, 1 H), 4.31 (q, J = 10.8 Hz, 2 H), 2.59 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.6 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 144.2, 139.3, 132.5, 131.1, 128.6, 128.2, 127.3, 126.3, 126.2 (q, J = 274.8 Hz), 126.0, 122.4, 122.0, 121.0, 25.3 (q, J = 33.3 Hz), 21.5. IR (KBr): 3072, 3056, 3003, 2937, 2848, 1621, 1575, 1526, 1479, 1411, 1294, 1282, 1256, 1211, 1151, 1116, 1057, 954, 930, 885, 856, 832, 808, 776, 755, 721, 708, 685, 632, 603 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{16}H_{13}F_3NSe$ ($[M+H]^+$): 356.0160; found: 356.0169.

4.2.20. 2-Chloro-6-((2,2,2-trifluoroethyl)selanyl)phenanthridine (3u)

White solid, 33.2 mg, 44% yield, a mixture of petroleum ether and ethyl acetate (60:1 (v/v)) as eluents for column chromatography. M.p.: 117–119 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 8.3 Hz, 1 H), 8.39 (d, J = 2.1 Hz, 1 H), 8.07 (d, J = 8.1 Hz, 1 H), 7.96 (d, J = 8.7 Hz, 1 H), 7.85 (t, J = 8.0 Hz, 1 H), 7.71 (t, J = 7.7 Hz, 1 H), 7.62 (dd, J = 8.7, 2.2 Hz, 1 H), 4.27 (q, J = 10.8 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.6 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 142.4, 132.3, 131.5, 131.2, 130.3, 129.4, 128.4, 126.6, 126.1, 126.1 (q, J = 274.6 Hz), 124.3, 122.6, 121.9, 25.4 (q, J = 33.4 Hz). IR (KBr): 3068, 3016, 2952, 2844, 1603, 1574, 1562, 1518, 1483, 1424, 1400, 1332, 1293, 1257, 1217, 1197, 1163, 1116, 1085, 1065, 1041, 952, 942, 870, 862, 853, 828, 758, 734, 719, 707, 632, 621 cm^{-1}. HRMS-ESI (*m/z*) calcd. for $C_{15}H_{10}ClF_3NSe$ ($[M+H]^+$): 375.9614; found: 375.9627.

4.2.21. 7-Methyl-1-((2,2,2-trifluoroethyl)selanyl)-3,4-dihydroisoquinoline (3w)

Light yellow solid, 13.1 mg, 21% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 84–86 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 1 H), 7.21 (d, J = 7.6 Hz, 1 H), 7.10 (d, J = 7.6 Hz, 1 H), 3.84 (q, J = 10.8 Hz, 2 H), 3.79 (t, J = 7.4 Hz, 2 H), 2.72 (t, J = 7.4 Hz, 2 H), 2.38 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.8 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 137.0, 133.8, 132.1, 129.7, 127.4, 126.1 (q, J = 274.0 Hz), 125.8, 49.6, 26.0, 24.5 (q, J = 33.0 Hz), 21.2. IR (KBr): 3002, 2937, 2863, 1604, 1494, 1461, 1402, 1347, 1330, 1291, 1266, 1254, 1226, 1214, 1161, 1114, 1066, 1019, 981, 935, 879, 871, 838, 815, 718, 706, 689, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{12}H_{12}F_3NNaSe$ ($[M + Na]^+$): 329.0021; found: 329.0019.

4.2.22. 6,7-Dimethyl-1-((2,2,2-trifluoroethyl)selanyl)-3,4-dihydroisoquinoline (3x)

White solid, 29.4 mg, 46% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 85–87 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (s, 1 H), 7.00 (s, 1 H), 3.85 (q, J = 10.9 Hz, 2 H), 3.79 (t, J = 7.3 Hz, 2 H), 2.71 (t, J = 7.3 Hz, 2 H), 2.30 (s, 3 H), 2.30 (s, 3 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.9 Hz, 3 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 140.7, 135.5, 134.2, 128.9, 127.8, 126.4, 126.2 (q, J = 274.4 Hz), 49.7, 25.9, 24.4 (q, J = 33.2 Hz), 20.0, 19.6. IR (KBr): 3193, 3060, 3007, 2972, 2923, 2860, 1663, 1609, 1560, 1496, 1480, 1458, 1423, 1400, 1338, 1327, 1310, 1291, 1268, 1215, 1109, 1067, 1021, 945, 921, 873, 832, 718, 706, 632, 600 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{15}F_3NSe$ ($[M+H]^+$): 322.0316; found: 322.0320.

4.2.23. 6,7-Dimethoxy-1-((2,2,2-trifluoroethyl)selanyl)-3,4-dihydroisoquinoline (3y)

White solid, 54.6 mg, 78% yield, a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 110–112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 1 H), 6.69 (s, 1 H), 3.91 (s, 3 H), 3.91 (s, 3 H), 3.84 (q, J = 10.9 Hz, 2 H), 3.76 (t, J = 7.5 Hz, 2 H), 2.68 (t, J = 7.5 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 10.9 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 151.6, 147.9, 130.5, 126.1 (q, J = 274.5 Hz), 122.6, 110.3 108.6, 56.2, 56.1, 49.4, 26.0, 24.6 (q, J = 33.2 Hz). IR (KBr): 3192, 2996, 2966, 2942, 2921, 2860, 2836, 1657, 1605, 1570, 1513, 1471, 1438, 1410, 1348, 1283, 1270, 1256, 1226, 1214, 1198, 1124, 1054, 930, 858, 836, 801, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{15}F_3NO_2Se$ ($[M+H]^+$): 354.0215; found: 354.0227.

4.2.24. 5-((2,2,2-Trifluoroethyl)selanyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinoline (3z)

White solid, 48.2 mg, 72% yield, a mixture of petroleum ether and ethyl acetate (10:1 (v/v)) as eluents for column chromatography. M.p.: 126–128 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1 H), 6.67 (s, 1 H), 5.99 (s, 2 H), 3.82 (q, J = 10.9 Hz, 2 H), 3.73 (t, J = 7.5 Hz, 2 H), 2.66 (t, J = 7.6 Hz, 2 H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.7 (t, J = 11.0 Hz, 3 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 149.8, 146.7, 132.4, 126.1 (q, J = 274.6 Hz), 123.9, 107.9, 105.9, 101.6, 49.2, 26.7, 24.7 (q, J = 33.2 Hz). IR (KBr): 3026, 2945, 2906, 2860, 1622, 1592, 1505, 1482, 1403, 1365, 1339, 1324, 1294, 1270, 1241, 1213, 1173, 1158, 1108, 1078, 1063, 1039, 952, 937, 856, 838, 734, 709, 632, 609 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{12}H_{11}F_3NO_2Se$ ($[M+H]^+$): 337.9902; found: 337.9893.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfluchem.2019.109360.

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