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FULL PAPER

Metal-free Synthesis of Selenodihydronaphthalenes by Selenoxide-mediated Electrophilic Cyclization of Alkynes

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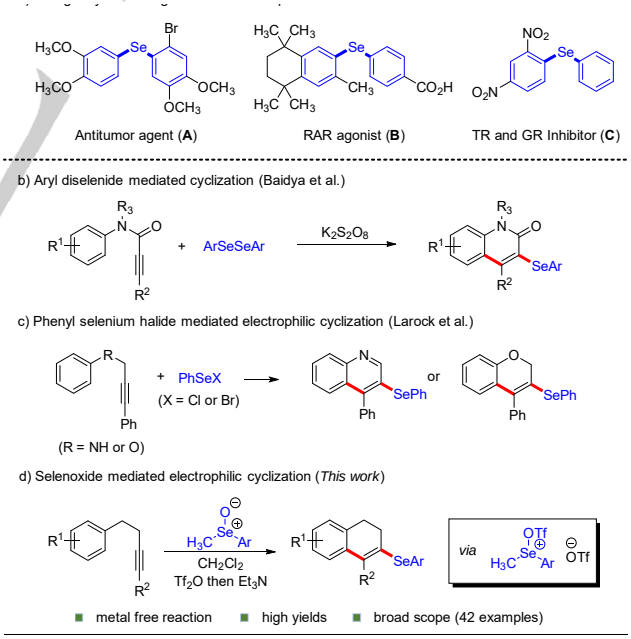
Abstract: A transition-metal-free, selenium mediated electrophilic cyclization reaction was realized through a one-pot procedure between simple alkynes and triflic anhydride-activated selenoxides to give selenium containing dihydronaphthalene products. This method gave good to very high yields for all products including selenium-substituted phenanthrene, dihydroquinoline, 2*H*-chromene, and coumarin, which can be further transformed to other functionalized compounds.

Introduction

Aryl bicyclic structure are ubiquitous in modern synthetic chemistry, which not only exist in many biologically and medicinally important compounds, but can be further converted to more useful compounds such as chiral ligands and catalysts.[1] In recent years, easily available methods towards the construction and derivatization of such cyclic scaffold are of particular interest and numerous strategies have been explored, including alkyne insertion cyclization,[2] free radical-induced intramolecular cyclization,[3] visible-light initiated cyclization,[4] Diels−Alder reaction,[5] Suzuki−Miyaura coupling[6] and others.[7] Recently, electrophile-mediated cyclization of internal alkynes has become one of the most effective method for synthesizing carbocycles and heterocycles,[1c] which provides cyclic structures with different substituents, such as halogen,[8] sulfur,[9] boron,[10] phosphorus[11] and so on.[12]

Organoselenium compounds are important structural motifs because of their biological activities and pharmacological properties.[13] For instance, the diaryl selenide **A** is used as an antitumor agent,[14] the carboxylic acid **B** is a retinoic acid receptor (RAR) agonist,[15] and the nitro compound **C** can serve as a thioredoxin reductase (TR) and glutathione reductase (GR) inhibitor (Scheme 1a).[16] With these unique features, the incorporation of selenium groups into arenes[17] and alkenes[18] has gained much attention in recent years. Besides, several selenium-involved alkyne reactions, especially the alkyne cyclization reactions, have also been realized.[9a-d, 19] Baidya's group designed an ortho-cyclization of *N*-aryl alkynamides with diaryl diselenides to provide 3-selenyl quinolin-2-ones (Scheme 1b).[4c] Larock's group achieved electrophilic cyclization of *N*-(2-alkynyl)aniline[8c] and (3-phenoxyprop-1-yn-1-yl)benzene[8d], respectively, with phenyl selenium halide as electrophilic reagent (Scheme 1c). However, electrophilic cyclization of non-heteroatom alkyne substrates using aromatic ring as nucleophile still remain unexplored.

Inspired by the wide range of reactions of anhydride-activated sulfoxide[20-21], we were interested in whether the similarly electrophilic triflic anhydride-activated selenoxide could be suitable for the synthesis of selenium-substituted dihydronaphthalenes (Scheme 1d). Herein, we describe the substrate scope of our investigation of such metal-free selenium-involved electrophilic cyclization, which provides selenium containing products with better derivatization reactivities than the corresponding sulfur counterparts.[21]



Scheme 1. Biologically active organoselenium compounds and selenium involved cyclization of alkynes.

Results and Discussion

For optimization of the reaction conditions, the 1,4-diphenyl-1-butyne **1a** and the phenyl methyl selenoxide **2a** were selected as the standard substrates (Table 1). Initially, the experiments were

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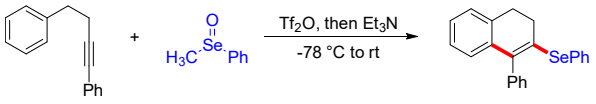
started under previous optimization conditions of the sulfoxide-attended cyclization reaction,[21] which conducted at -78 °C in methylene chloride with Tf_2O as activator and Et_3N as basic nucleophile to leave the methyl group. Gratifyingly, **2a** was effectively activated leading to the desired product 2-phenylselenyl-1-phenyl-3,4-dihydronaphthalene (**3aa**) in 92% isolated yield (entry 2). Subsequently, different time of electrophilic cyclization was examined to further improve existing yield and it was found that neither increasing nor decreasing the reaction time could not have a good effect on yield (entries 1 and 3, respectively). Next, we tried to reduce the loading of base, but slightly lower yield of 85% was afforded (entry 4), which in the same time 90% and 87% was yielded when we increase to 5 and 6 equiv., respectively (entries 5 and 6, respectively). Ultimately, changing solvent to 1,2-dichloromethane was not led to improve the conversion of **1a** into the target product (entry 7) and the condition of entry 2 was proved to be optimal.

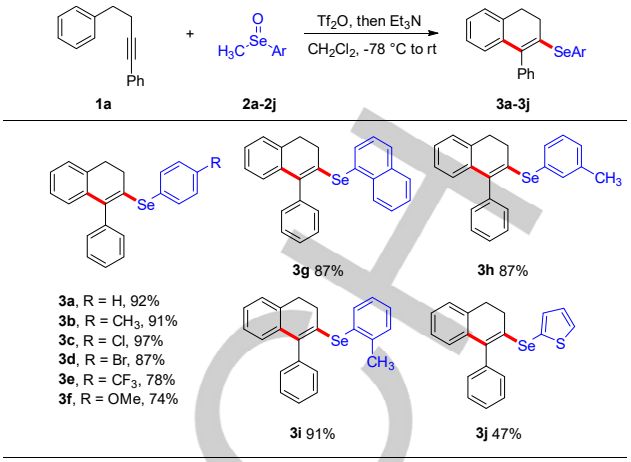
Table 1. Optimization of reaction conditions[a]



Entry	Solvent	Et_3N (equiv.)	Time (h)	Yield[b] (%)
1	CH_2Cl_2	4	1	85
2	CH_2Cl_2	4	2	92
3	CH_2Cl_2	4	12	84
4	CH_2Cl_2	3	2	85
5	CH_2Cl_2	5	2	90
6	CH_2Cl_2	6	2	87
7	CH_2ClCH_2Cl	4	2	85

[a] Reaction conditions: A solution of **1a** (0.4 mmol) and **2a** (0.48 mmol) in 2 mL of solvent was treated with Tf_2O (0.48 mmol) at -78 °C and then warmed up to room temperature, and Et_3N was added. [b] Yields are of the isolated product after column chromatography.

Encouraged by these outcomes, we started to investigate the substrate scope of this reaction by using various aryl methyl selenoxides with alkyne **1a** (Scheme 2). As the extension of the previous method, we synthesized a series of selenoxides with different substituents. In addition to example of phenyl, the aryl ring bearing methyl on the *para*, *ortho* and *meta* position can proceed smoothly to give the corresponding products **3b**, **3h** and **3i** with good results. We also examined electron-withdrawing groups, including halo and trifluoromethyl, and afforded the products **3c**-**3e** in good yields. The reaction of sulfoxides **2f** bearing electron-donating group could also work, although with a moderate yield. Furthermore, 1-naphthyl methyl selenoxide can also be used in this reaction, furnished the expected products **3g** in 87% yield. In order to expand the types of substrates, heteroaryl methyl selenoxide **2j** was then examined and furnished the expected products **3j** in 47% yield under the standard conditions.



Scheme 2. Substrate scope of aryl methyl selenium reagents. Reaction conditions: A solution of **1a** (0.4 mmol) and **2** (0.48 mmol) in 2 mL of solvent was treated with Tf_2O (0.48 mmol) at -78 °C for 0.5 h and stirred at room temperature for another 0.5 h. Then 1.6 mmol Et_3N was added and stirred for 2 h. Yields are of the isolated product after column chromatography.

Next, we continued to test the generality of alkynes by reacting them with the phenyl methyl selenoxide **2a** (Scheme 3). We first examined the aromatic rings of R^2 containing electron-donating or electron-withdrawing groups. To our delight, all these reactions proceeded smoothly, furnishing the corresponding cyclization products **4**-**16** in good to excellent yields. Notably, halogen (**5**-**7**), methoxy (**8**), and ester (**9**) at the para position were well tolerated in this reaction in 86−96% yields and some strong electron-withdrawing group like trifluoromethyl (**10**) and nitro (**29**) could also work, although with moderate yields. In addition, the substrates bearing *meta* and *ortho* functional groups could also provide the expected products **11**-**16** with good results. We also verified naphthyl and heteroaryl alkynes posed no problem to this reaction, and the coupling products **17**-**19** were obtained in good efficiency.

Apart from these substrates above, various 4-aryl-1-phenyl-1-butynes were examined in the reaction (Scheme 3). Different substituent at the *para* and *ortho* position were well tolerated with good yields, especially in the cases of halo (**21**, **22**, **27**) and cyano (**24**). Again, 1-naphthyl has no deleterious effect on the target reaction, leading to the corresponding product **28** in 84% yield. Because of the issue of regioselectivity during the cyclization, both meta-substituted products **25** and **25'** were obtained in 54% and 23% yields, respectively.

It is remarkable that this method can also be applied for the synthesis of phenyl(10-phenylphenanthren-9-yl)selane **30** by using 2-(phenylethynyl)-1,1′-biphenyl, albeit with moderate yield. Also, this methodology is not limited to the preparation of dihydronaphthalenes but includes heterocyclic system, such as oxygen and nitrogen heterocycle. 2*H*-Chromene derivative **31** and dihydroquinoline derivatives **32** can be prepared in 93% and 91%, respectively. Lactone and lactam substrates can also be used in this reaction, afforded the corresponding products **33** and **34** in 45% and 38% yields, respectively. In addition, bicyclization product **35** can also be performed in 73% yield.

To further demonstrate the synthetic utilities of the products, we performed a large-scale reaction of 1,4-diphenyl-1-butyne **1a**, giving products **3a** in 88% yield (Scheme 4). Compared to the

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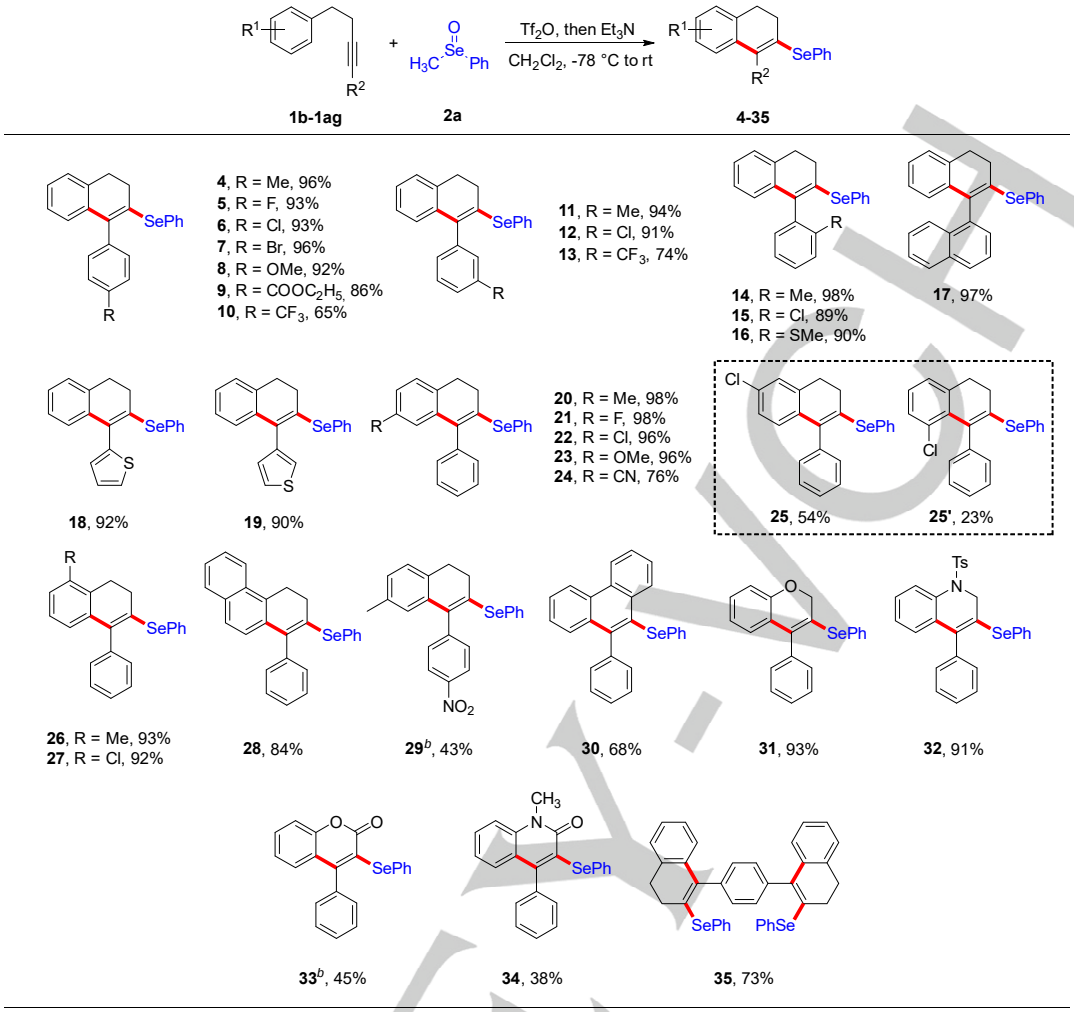
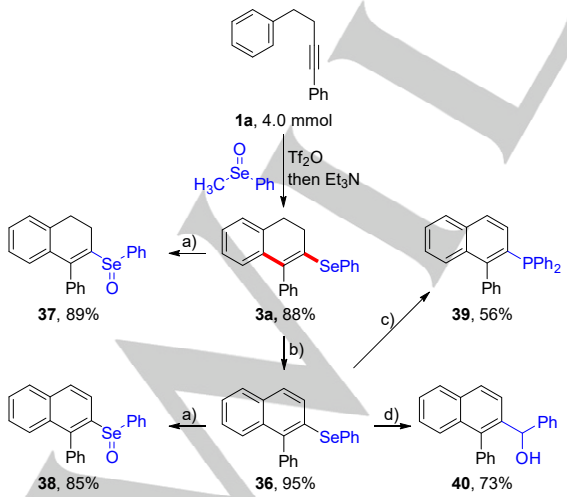
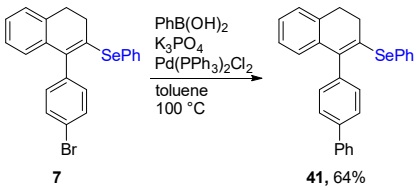


Scheme 3. Substrate scope of alkyne. Reaction conditions: Unless otherwise specified, reactions were performed on a 0.4 mmol scale of the alkynes using 0.48 mmol phenyl methyl selenoxide **2a** in 2 mL of CH_2Cl_2 which was treated with Tf_2O (0.48 mmol) at -78 °C for 0.5 h and stirred at room temperature for another 0.5 h. Then 1.6 mmol Et_3N was added and stirred for 2 h. Yields are of the isolated product after column chromatography. [b]Phenyl methyl selenoxide (0.96 mmol), Tf_2O (0.96 mmol) and Et_3N (3.2 mmol) were used.



Scheme 4. Gram scale synthesis and further transformations. Reaction conditions: a) *m*-CPBA (1.05 eq), CH_2Cl_2, r.t., 2 h; b) DDQ, CH_2Cl_2, r.t., 12 h; c) *n*-BuLi (1.0 eq), THF, -78 °C, 1 h, then PPh_2Cl, THF, r.t., 3 h; d) *n*-BuLi (1.0 eq), THF, -78 °C, 30 min; then PhCHO, THF, r.t., 1 h. Isolated yield.

example of sulfur[21], some further transformations were carried out. For instance, **3a** was easily transformed to aromatization product **36** under mild conditions[11] and same to the method of selenium oxidation,[4c] **3a** and **36** can be further oxidized to the corresponding selenoxide **37** and **38** in high yields. With the treatment of butyl lithium, phenyl selenyl of **36** can be lithiated and react with electrophiles to transfer to the corresponding product **39** and **40** in moderate yields.[1e, 19e] These results all reflect the scalability and application prospects of the method. Also, the Suzuki reaction of bromine substitution product **7** can be implemented,[8g] proving that the substrate can be further modified.



On the basis of the experimental results, we proposed the mechanism of the reaction outlined in Scheme 5. First, triflic anhydride-activated selenoxide reacted with the carbon-carbon

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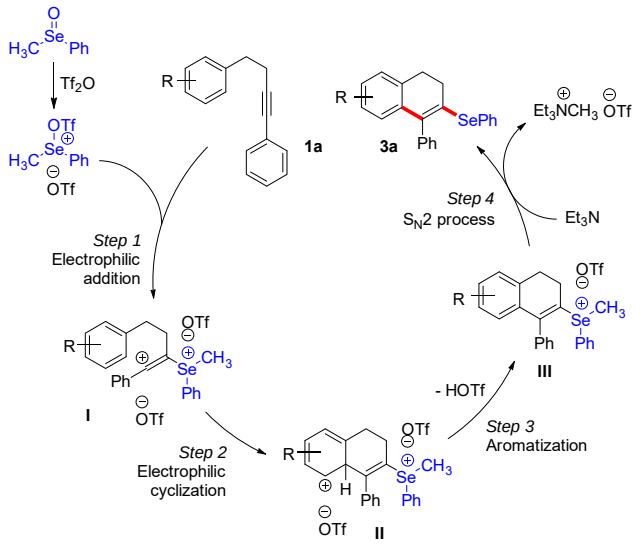
triple bond to generate vinyl cation intermediates **I** regioselectively due to the stabilization of phenyl group. Then vinyl cation **I** can be captured by the tethered aryl ring and then aromatized to selenium salts **III**. Finally, the desired products were afforded after demethylation with Et_3N as nucleophile by S_N2 process.



Scheme 5. Proposed mechanism.

Conclusion

In summary, we have developed a selenium-mediated electrophilic cyclization of internal alkynes in one pot, which complements current strategies for synthesizing binary rings. The metal free condition and functional-group tolerance allowed us to afford 2-phenylselenyl-3,4-dihydronaphthalene and other derivatives easily, including selenium-substituted phenanthrene, dihydroquinoline, 2*H*-chromene, and coumarin. The obtained products could be further converted into various valuable aryl-aryl compounds in simple steps. Further exploration of the current method for the asymmetric version is underway in our lab.

Experimental Section

General Information: Unless otherwise noted, all materials were purchased from commercial suppliers. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were refluxed over CaH_2. Tetrahydrofuran (THF) was refluxed with sodium/benzophenone. All solvents mentioned above were freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200 - 300 mesh) from Anhui Liangchen Silicon Material Co., Ltd., with petroleum ether (PE, bp 60 - 90 °C), dichloromethane (DCM), hexane, and ethyl acetate (EA) as eluents. Reactions were monitored by thin-layer chromatography (TLC) on G254 silica gel plates (0.2 mm) from Anhui Liangchen Silicon Material Co., Ltd. The plates were visualized under UV light, as well as other TLC stains (phosphomolybdic acid: 10% in ethanol; potassium permanganate: 1% in water; iodine: 10 g iodine absorbed on 30 g silica gel). ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker 400 MHz spectrometer, usually in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) were reported in parts per million (ppm). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), dt (double of triplet), td (triple of doublet), ddd (double of doublet of doublet) and m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and were uncorrected. Alkynes **1a**−**1ab** and **1ag** were synthesized by Sonogashira coupling and the characterization of **1a**[10], **1b**[10], **1c**[22], **1d**[10], **1e**[22], **1f**[10], **1g**[10], **1h**[22], **1k**[10], **1l**[10], **1m**[10], **1o**[10], **1r**[10], **1s**[21], **1t**[22], **1u**[10], **1v**[21], **1w**[10], **1y**[21], **1z**[23] and **1ab**[8b] can be found in published procedures. **1ac**,[24] **1ad**,[24] **1ae**[4b, 25] and **1af**[25] were prepared according to published procedures. All selenoxide were synthesized from diselenide derivatives[17c, 26] and diselenide derivatives were prepared by the known procedure[17b, 27].

Procedure for the Preparation of the Aryl Alkynes: Take the synthesis of **1a** as an example. To a solution of trimethyl(prop-1-yn-1-yl)silane (2.69 g, 24 mmol) in anhydrous THF (50 mL) in a 100 mL round-bottom flask was added *n*-BuLi (2.4 M in Hexane, 22 mmol, 9.2 mL) at -78 °C under a nitrogen atmosphere. Then the reaction was stirred for 2 hours at the same temperature followed by adding benzyl chloride (2.53 g, 20 mmol) in the 10 mL THF and moving to room temperature. After a further hour, the solution was quenched with 30 mL sat. NaCl (aq) and the aqueous layer was extracted with ethyl acetate. The extracts were combined with the above organic layer and the merged solution was dried over Na_2SO_4. After evaporation of the solvent, the crude residue was directly dissolved in THF (30 mL) and TBAF (6.7 g, 24 mmol) was then added the solution, which was stirred overnight. The reaction was neutralized with 12 mL HCl (2 N) and was extracted with ethyl acetate and the combined organic solution was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2, 50/1 (*v*/*v*)) to afford 1a' (70 %). After the preparation of **1a'**, to a new flame-dried flask were added $Pd(PPh_3)_2$ (167 mg, 0.15 mmol) and CuI (58 mg, 0.30 mmol), then THF (10 mL) was injected under a nitrogen atmosphere, which the suspension was stirred for five minutes. After adding iodobenzene (612 mg, 3.0 mmol) and Et_3N (3.75 mL, 27 mmol) and stirring another five minutes, 4-phenyl-1-butyne (430 mg, 3.3 mmol) was added and the system was stirred and refluxed for 12 h. After the reaction completed, the solution was cooled to room temperature, filtered and eluted with ethyl acetate. The organic phase was collected and concentrated under reduced pressure. The crude material was purified via column chromatography on silica gel (petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)) to yield **1a** (87 %).

1-Methyl-3-(4-phenylbut-1-yn-1-yl)benzene (1i): Yellow oil (yield 88%): R_f = 0.43 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 − 7.12 (m, 8H), 7.07 (d, *J* = 6.6 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.7, 137.9, 132.1, 128.6, 128.5, 128.5, 128.4, 128.1, 126.3, 123.6, 89.1, 81.4, 35.2, 21.7, 21.2; HRMS (ESI) calcd for $C_{17}H_{17}^+$ $[M + H]^+$ *m*/*z* 221.1325, found 221.1323.

1-Chloro-3-(4-phenylbut-1-yn-1-yl)benzene (1j): Colorless oil (yield 84%): R_f = 0.50 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.33 − 7.27 (m, 2H), 7.27 − 7.18 (m, 5H), 7.18 − 7.12 (m, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.4, 133.9, 131.4, 129.6, 129.3, 128.5, 128.4, 127.9, 126.3, 125.5, 90.9, 80.1, 35.0, 21.6; HRMS (ESI) calcd for $C_{16}H_{14}Cl^+$ $[M + H]^+$ *m*/*z* 241.0779, found 241.0782.

Methyl(2-(4-phenylbut-1-yn-1-yl)phenyl)sulfane (1n): Colorless oil (yield 41%): R_f = 0.23 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 − 7.30 (m, 1H), 7.30 − 7.26 (m, 4H), 7.26 − 7.17 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.03 (td, *J* = 7.5, 1.1 Hz, 1H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.1, 140.6, 132.3, 128.5, 128.4, 128.3, 128.1, 126.2, 124.1, 123.8, 121.8, 96.3, 78.7, 35.1, 21.9, 15.0; HRMS (ESI) calcd for $C_{17}H_{17}S^+$ $[M + H]^+$ *m*/*z* 253.1045, found 253.1040.

2-(4-Phenylbut-1-yn-1-yl)thiophene (1p): Brown oil (yield 91%): R_f = 0.32 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 − 7.27 (m, 2H), 7.27 − 7.18 (m, 3H), 7.14 (d, *J* = 5.2 Hz, 1H), 7.12 −

7.07 (m, 1H), 6.94 − 6.87 (m, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.5, 131.0, 128.5, 128.4, 126.7, 126.3, 126.0, 123.9, 93.5, 74.5, 34.9, 21.9; HRMS (ESI) calcd for $C_{14}H_{13}S^+$ $[M + H]^+$ *m*/*z* 213.0732, found 213.0733.

3-(4-Phenylbut-1-yn-1-yl)thiophene (1q): Dark-yellow oil (yield 89%): R_f = 0.30 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 − 7.21 (m, 5H), 7.21 − 7.17 (m, 1H), 7.03 (dd, *J* = 5.0, 1.0 Hz, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.6, 129.9, 128.5, 128.3, 127.6, 126.3, 125.0, 122.7, 89.0, 76.3, 35.1, 21.6; HRMS (ESI) calcd for $C_{14}H_{13}S^+$ $[M + H]^+$ *m*/*z* 213.0732, found 213.0741.

1-Methyl-2-(4-phenylbut-3-yn-1-yl)benzene (1x): Light-yellow oil (yield 84%): R_f = 0.25 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.27 − 7.17 (m, 4H), 7.13 (d, *J* = 4.7 Hz, 3H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.7, 135.9, 131.5, 130.2, 128.9, 128.1, 127.5, 126.4, 126.0, 123.8, 89.6, 81.1, 32.4, 20.3, 19.2; HRMS (ESI) calcd for $C_{17}H_{17}^+$ $[M + H]^+$ *m*/*z* 221.1325, found 221.1323.

1-Methyl-4-(4-(4-nitrophenyl)but-3-yn-1-yl)benzene (1aa): White solid (yield 64%): R_f = 0.37 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 80−81 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.19 − 7.08 (m, 4H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.6, 137.1, 136.0, 132.2, 130.9, 129.1, 128.3, 123.4, 95.8, 79.9, 34.3, 21.9, 21.0; HRMS (ESI) calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$ *m*/*z* 266.1176, found 266.1170.

1,4-Bis(4-phenylbut-1-yn-1-yl)benzene (1ag): To a flame-dried flask were added $Pd(PPh_3)_2$ (58 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) ,then THF (5 mL) was injected under a nitrogen atmosphere, which the suspension was stirred for five minutes. After adding iodobenzene (330 mg, 1.0 mmol) and Et_3N (1.3 mL, 9 mmol) and stirring another five minutes, the alkyne **1a'** (325 mg, 2.5 mmol) was added and the system was stirred and refluxed for 12 h. After the reaction completed, the solution was cooled to room temperature, filtered and eluted with ethyl acetate. The organic phase was collected and concentrated under reduced pressure. The crude material was purified via column chromatography on silica gel (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)) to yield 1af as a white solid (254 mg, 76%): R_f = 0.34 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 92−94 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.28 (m, 4H), 7.27 (d, *J* = 2.2 Hz, 6H), 7.26 − 7.20 (m, 4H), 2.91 (t, *J* = 7.5 Hz, 4H), 2.69 (t, *J* = 7.6 Hz, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.6, 131.3, 128.5, 128.4, 126.3, 123.1, 91.0, 81.1, 35.1, 21.7; HRMS (ESI) calcd for $C_{26}H_{23}^+$ $[M + H]^+$ *m*/*z* 335.1794, found 335.1791.

General Procedure for the Preparation of the Selenoxide Substrates: Take the synthesis of **2a** as an example. To a new flame-dried three neck flask was added diphenyl diselenide (3.88 g, 12.4 mmol) and then they were dissolved with ethanol (30 mL) under a nitrogen atmosphere. Sodium borohydride (26.4 mmol) dissolved in 20 mL ethanol was added dropwise and the reaction mixture stirred for 0.5 h at 25 °C, followed by addition of 2.0 mL (0.321 mol) iodomethane. After stirring overnight, the mixture was treated with 50 mL water and extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel (petroleum ether) and afforded methylphenyl selenide. Then methylphenyl selenide (168 mg, 1.0 mmol) was dissolved in 10 mL CH_2Cl_2. The reaction mixture was cooled to 0 °C, and *m*-CPBA (190 mg, 1.1 mmol) was added in one portion. The mixture was stirred at 0 °C for 30 minutes and at room temperature for additional 30 minutes. The organic phase was washed with a saturated aqueous solution of potassium carbonate (10 mL) and the aqueous phase was extracted with CH_2Cl_2. The organics were combined and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc then CH_2Cl_2/CH_3OH, 20:1 (*v*/*v*)) to provide **2a** (159 mg, 85%). The characterization of **2a** can be found in our previous work[17c].

1-Methyl-4-(methylseleninyl)benzene (2b): White solid (yield 71%): R_f = 0.49 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 98−101 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 2.63 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.7, 138.5, 130.4, 125.4, 37.3, 21.3; HRMS (ESI) calcd for $C_8H_{11}OSe^+$ $[M + H]^+$ *m*/*z* 202.9970, found 202.9981.

1-Chloro-4-(methylseleninyl)benzene (2c): White solid (yield 81%): R_f = 0.53 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 113−115 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 2.63 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.1, 137.7, 130.0, 126.9, 37.6; HRMS (ESI) calcd for $C_7H_8ClOSe^+$ $[M + H]^+$ *m*/*z* 222.9423, found 222.9427.

1-Bromo-4-(methylseleninyl)benzene (2d): White solid (yield 75%): R_f = 0.52 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 43−45 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 − 7.66 (m, 2H), 7.66 − 7.60 (m, 2H), 2.64 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.6, 132.8, 127.0, 125.9, 37.4; HRMS (ESI) calcd for $C_7H_8BrOSe^+$ $[M + H]^+$ *m*/*z* 266.8918, found 266.8922.

1-(Methylseleninyl)-4-(trifluoromethyl)benzene (2e): White solid (yield 43%): R_f = 0.43 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 77−78 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.2, 133.4 (q, *J* = 33.3 Hz), 126.5 (d, *J* = 3.0 Hz), 126.0, 123.4 (d, *J* = 273.7 Hz), 37.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.91; HRMS (ESI) calcd for $C_8H_8F_3OSe^+$ $[M + H]^+$ *m*/*z* 256.9687, found 256.9679.

1-(4-Methoxyphenyl)ethan-1-one (2f): White solid (yield 65%): R_f = 0.41 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 98−99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.7, 131.9, 126.9, 126.8, 114.9, 55.2, 37.0; HRMS (ESI) calcd for $C_8H_{11}O_2Se^+$ $[M + H]^+$ *m*/*z* 218.9919, found 218.9927.

1-(Methylseleninyl)naphthalene (2g): Wine red solid (yield 56%): R_f = 0.46 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 94−96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.03 − 7.95 (m, 2H), 7.87 − 7.80 (m, 1H), 7.70 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.65 − 7.56 (m, 2H), 2.71 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.6, 133.8, 131.3, 130.1, 129.2, 127.5, 126.7, 126.0, 123.9, 122.0, 36.5; HRMS (ESI) calcd for $C_{11}H_{11}OSe^+$ $[M + H]^+$ *m*/*z* 238.9970, found 238.9978.

1-Methyl-3-(methylseleninyl)benzene (2h): White solid (yield 73%): R_f = 0.48 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 100−102 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 2.62 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.6, 140.0, 132.0, 129.3, 125.5, 122.4, 37.2, 21.3; HRMS (ESI) calcd for $C_8H_{11}OSe^+$ $[M + H]^+$ *m*/*z* 202.9970, found 202.9982.

1-Methyl-2-(methylseleninyl)benzene (2i): White solid (yield 69%): R_f = 0.49 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 79−82 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.47 (t, *J* = 7.1 Hz, 1H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 2.59 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.7, 135.3, 131.0, 130.5, 127.6, 124.5, 35.7, 19.2; HRMS (ESI) calcd for $C_8H_{11}OSe^+$ $[M + H]^+$ *m*/*z* 202.9970, found 202.9981.

2-(Methylseleninyl)thiophene (2j): Light-yellow oil (yield 52%): R_f = 0.57 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.18 (dd, *J* = 5.0, 3.6 Hz, 1H), 2.85 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.8, 131.1, 130.2, 127.6, 38.1. HRMS (ESI) calcd for $C_5H_7OSSe^+$ $[M + H]^+$ *m*/*z* 194.9377, found 194.9387.

General Procedure for Electrophilic Cyclization of Alkynes: To a flame-dried Schlenk tube were added alkyne **1** (0.4 mmol) and sulfoxide **2** (0.48 mmol), and then they were dissolved with dichloromethane (2 mL)

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under a nitrogen atmosphere before being cooled to −78 °C (liquid N_2/ethyl acetate bath). Tf_2O (81 µL, 0.48 mmol) was added dropwise. After being stirred for 0.5 h, the mixture was warmed to room temperature and stirred for an additional 0.5 h, and then Et_3N (162 mg, 1.6 mmol) was added. After being stirred for 2 h, the solution was diluted with CH_2Cl_2, transferred to a round-bottom flask, and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel and afforded pure product.

Phenyl(1-phenyl-3,4-dihydronaphthalen-2-yl)selane (3a): Synthesized from **1a** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 25/1 (*v*/*v*)], to give the product as a white solid (133 mg, 92%): R_f = 0.43 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 87−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.48 (m, 2H), 7.48−7.41 (m, 2H), 7.41−7.35 (m, 1H), 7.32−7.21 (m, 5H), 7.14−7.08 (m, 2H), 7.04 (ddd, *J* = 8.8, 5.6, 3.4 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 2.91−2.77 (m, 2H), 2.58−2.46 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 139.4, 136.1, 134.9, 134.3, 132.1, 130.3, 130.0, 129.1, 128.4, 127.6, 127.5, 127.2, 126.8, 126.4, 125.8, 30.6, 29.7; HRMS (ESI) calcd for $C_{22}H_{19}Se^+$ [M + H]$^+$ *m*/*z* 363.0646, found 363.0641.

(1-Phenyl-3,4-dihydronaphthalen-2-yl)(p-tolyl)selane (3b): Synthesized from **1a** (0.4 mmol) and **2b** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 50/1 (*v*/*v*)], to give the product as a light-yellow solid (137 mg, 91%): R_f = 0.33 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 − 7.36 (m, 5H), 7.32 − 7.27 (m, 2H), 7.14 − 7.08 (m, 4H), 7.08 − 7.01 (m, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 2.83 (t, *J* = 7.9 Hz, 2H), 2.53 − 2.45 (m, 2H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 138.4, 137.8, 136.2, 134.9, 134.8, 132.7, 130.0, 129.9, 128.4, 127.5, 127.1, 126.6, 126.4, 126.2, 125.6, 30.2, 29.6, 21.2; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0785.

(4-Chlorophenyl)(1-phenyl-3,4-dihydronaphthalen-2-yl)selane (3c): Synthesized from **1a** (0.4 mmol) and **2c** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 40/1 (*v*/*v*)], to give the product as a yellow solid (154 mg, 97%): R_f = 0.41 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 74−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 4H), 7.42 − 7.37 (m, 1H), 7.27 (s, 1H), 7.24 (s, 3H), 7.14 (d, *J* = 4.1 Hz, 2H), 7.06 (dt, *J* = 8.4, 4.3 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.60 − 2.45 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.02, 139.95, 135.9, 135.5, 134.8, 133.9, 131.4, 129.9, 129.3, 128.6, 128.5, 127.6, 127.2, 127.0, 126.5, 125.9, 30.7, 29.7; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0261.

(4-Bromophenyl)(1-phenyl-3,4-dihydronaphthalen-2-yl)selane (3d): Synthesized from **1a** (0.4 mmol) and **2d** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a yellow solid (153 mg, 87%): R_f = 0.43 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 95−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 − 7.43 (m, 2H), 7.43 − 7.35 (m, 5H), 7.27 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 1.1 Hz, 1H), 7.16 − 7.11 (m, 2H), 7.10 − 7.02 (m, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 2.90 − 2.83 (m, 2H), 2.57 − 2.49 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.2, 139.9, 135.9, 135.7, 134.8, 132.2, 131.3, 129.8, 129.3, 128.5, 127.7, 127.2, 127.0, 126.5, 125.9, 122.0, 30.7, 29.7; HRMS (ESI) calcd for $C_{22}H_{18}BrSe^+$ [M + H]$^+$ *m*/*z* 440.9752, found 440.9757.

(1-Phenyl-3,4-dihydronaphthalen-2-yl)(4-(trifluoromethyl)-phenyl)-selane (3e): Synthesized from **1a** (0.4 mmol) and **2e** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 15/1 (*v*/*v*)], to give the product as a light-yellow solid (135 mg, 78%): R_f = 0.56 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 71−72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.49 − 7.37 (m, 3H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.26 − 7.23 (m, 1H), 7.17 (d, *J* = 4.1 Hz, 2H), 7.08 (dp, *J* = 7.6, 3.5 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 3.04 − 2.80 (m, 2H), 2.76 − 2.52 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.2, 139.9, 136.3 (d, *J* = 1.0 Hz), 135.7, 135.0, 132.99, 132.95, 130.0, 129.7, 129.2 (d, *J* = 32.3 Hz), 128.4, 127.7, 127.3 (d, *J* = 2.0 Hz), 126.5, 126.3, 125.8 (q, *J* = 4.0 Hz), 124.1 (d, *J* = 272.7 Hz), 31.4, 29.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.58; HRMS (ESI) calcd for $C_{23}H_{18}F_3Se^+$ [M + H]$^+$ *m*/*z* 431.0520, found 431.0521.

(4-Methoxyphenyl)(1-phenyl-3,4-dihydronaphthalen-2-yl)selane (3f): Synthesized from **1a** (0.4 mmol) and **2f** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)], to give the product as a light-yellow solid (116 mg, 74%): R_f = 0.56 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 92−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 − 7.42 (m, 4H), 7.38 (tdd, *J* = 7.4, 3.4, 1.6 Hz, 1H), 7.28 (ddd, *J* = 8.0, 3.7, 1.5 Hz, 2H), 7.12 − 7.05 (m, 2H), 7.03 (dtd, *J* = 7.7, 6.0, 5.1, 2.6 Hz, 1H), 6.86 − 6.77 (m, 2H), 6.63 (dd, *J* = 7.6, 3.9 Hz, 1H), 3.82 − 3.74 (m, 3H), 2.85 − 2.74 (m, 2H), 2.42 (ddd, *J* = 9.2, 7.7, 3.9 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.7, 140.0, 137.2, 137.0, 136.2, 134.6, 133.3, 129.9, 128.5, 127.5, 127.1, 126.4, 126.3, 125.3, 119.7, 114.7, 55.2, 29.8, 29.5; HRMS (ESI) calcd for $C_{23}H_{21}OSe^+$ [M + H]$^+$ *m*/*z* 393.0752, found 393.0754.

Naphthalen-1-yl(1-phenyl-3,4-dihydronaphthalen-2-yl)selane (3g): Synthesized from **1a** (0.4 mmol) and **2g** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (144 mg, 87%): R_f = 0.55 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 119−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.95 − 7.83 (m, 3H), 7.55 (ddd, *J* = 7.6, 5.9, 1.7 Hz, 4H), 7.50 − 7.38 (m, 4H), 7.17 − 7.04 (m, 3H), 6.72 (dd, *J* = 5.6, 2.7 Hz, 1H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.36 − 2.28 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 138.1, 136.2, 135.1, 134.9, 134.8, 134.0, 133.0, 129.8, 129.4, 128.9, 128.6, 128.5, 128.1, 127.7, 127.1, 126.8, 126.6, 126.4, 126.3, 125.7, 125.4, 29.9, 29.4; HRMS (ESI) calcd for $C_{26}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 413.0803, found 413.0796.

(1-Phenyl-3,4-dihydronaphthalen-2-yl)(m-tolyl)selane (3h): Synthesized from **1a** (0.4 mmol) and **2h** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a yellow solid (132 mg, 87%): R_f = 0.45 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 76−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 − 7.41 (m, 2H), 7.41 − 7.36 (m, 1H), 7.33 (q, *J* = 7.6, 7.0 Hz, 2H), 7.30 − 7.24 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.13 − 7.07 (m, 3H), 7.04 (tt, *J* = 5.2, 2.8 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.52 (td, *J* = 8.3, 7.6, 2.2 Hz, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 139.1, 138.8, 136.1, 135.0, 134.9, 132.2, 131.4, 129.9, 128.8, 128.4, 128.4, 127.5, 127.1, 126.7, 126.4, 125.7, 30.6, 29.7, 21.3; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0806.

(1-Phenyl-3,4-dihydronaphthalen-2-yl)(o-tolyl)selane (3i): Synthesized from **1a** (0.4 mmol) and **2i** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a yellow solid (138 mg, 91%): R_f = 0.39 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.52 − 7.45 (m, 2H), 7.45 − 7.39 (m, 1H), 7.34 − 7.29 (m, 2H), 7.25 − 7.22 (m, 2H), 7.16 − 7.10 (m, 3H), 7.07 (ddd, *J* = 8.9, 5.4, 3.6 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 2.89 − 2.83 (m, 2H), 2.49 − 2.43 (m, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 140.2, 139.3, 136.2, 135.4, 134.9, 132.0, 130.8, 130.1, 129.7, 128.4, 128.2, 127.5, 127.1, 126.7, 126.4, 126.4, 125.6, 30.3, 29.6, 22.8; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0797.

2-((1-Phenyl-3,4-dihydronaphthalen-2-yl)selanyl)thiophene (3j): Synthesized from **1a** (0.4 mmol) and **2j** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a light-yellow solid (69 mg, 47%): R_f = 0.49 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 − 7.47 (m, 2H), 7.47 − 7.40 (m, 2H), 7.36 − 7.31 (m, 2H), 7.25 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.15 − 7.09 (m, 2H), 7.09 − 7.05 (m, 1H), 7.03 (dd, *J* = 5.3, 3.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 2.89 − 2.81 (m, 2H), 2.51 − 2.43 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.4, 137.6, 136.6, 136.0, 134.5, 133.5, 132.0, 129.9, 128.6, 128.1, 127.7, 127.1, 126.6, 126.4, 125.2, 123.1,

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29.4, 28.6; HRMS (ESI) calcd for $C_{20}H_{17}SSe^+$ [M + H]$^+$ *m*/*z* 369.0211, found 369.0216.

Phenyl(1-(p-tolyl)-3,4-dihydronaphthalen-2-yl)selane (4): Synthesized from **1b** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 25/1 (*v*/*v*)], to give the product as a white solid (144 mg, 96%): R_f = 0.36 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 − 7.47 (m, 2H), 7.33 − 7.20 (m, 5H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 4.3 Hz, 2H), 7.07 − 7.00 (m, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 2.88 − 2.78 (m, 2H), 2.56 − 2.47 (m, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.3, 137.2, 137.1, 136.2, 134.9, 134.3, 131.9, 130.4, 129.8, 129.2, 129.0, 127.5, 127.1, 126.7, 126.4, 125.8, 30.6, 29.7, 21.4; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0785.

(1-(4-Fluorophenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (5): Synthesized from **1c** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)], to give the product as a colorless oil (142 mg, 93%): R_f = 0.44 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.33 − 7.18 (m, 5H), 7.19 − 7.09 (m, 4H), 7.05 (dt, *J* = 8.8, 4.4 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 2.89 − 2.78 (m, 2H), 2.56 − 2.45 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 247.5 Hz), 138.2, 136.0, 135.9 (d, *J* = 3.0 Hz), 134.9, 134.4, 132.7, 131.6 (d, *J* = 8.1 Hz), 130.0, 129.1, 127.7, 127.2, 126.9, 126.4, 125.5, 115.4 (d, *J* = 21.2 Hz), 30.6, 29.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.45; HRMS (ESI) calcd for $C_{22}H_{18}FSe^+$ [M + H]$^+$ *m*/*z* 381.0552, found 381.0544.

(1-(4-Chlorophenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (6): Synthesized from **1d** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)], to give the product as a white solid (147 mg, 93%): R_f = 0.38 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 124−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 − 7.46 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.24 (dd, *J* = 28.1, 6.9 Hz, 5H), 7.12 (d, *J* = 3.9 Hz, 2H), 7.05 (dd, *J* = 7.6, 4.2 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.67 − 2.38 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.4, 138.2, 135.8, 134.9, 134.4, 133.5, 132.7, 131.4, 129.9, 129.1, 128.7, 127.8, 127.3, 126.9, 126.5, 125.5, 30.6, 29.6; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0263.

(1-(4-Bromophenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (7): Synthesized from **1e** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (169 mg, 96%): R_f = 0.35 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.33 − 7.25 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 4.1 Hz, 2H), 7.05 (dt, *J* = 8.7, 4.3 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 2.87 − 2.79 (m, 2H), 2.55 − 2.47 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.9, 138.2, 135.7, 134.9, 134.4, 132.6, 131.7, 131.7, 129.9, 129.2, 127.8, 127.3, 127.0, 126.5, 125.5, 121.7, 30.6, 29.5; HRMS (ESI) calcd for $C_{22}H_{18}BrSe^+$ [M + H]$^+$ *m*/*z* 440.9752, found 440.9753.

(1-(4-Methoxyphenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (8): Synthesized from **1f** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)], to give the product as a white solid (144 mg, 92%): R_f = 0.62 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 141−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 − 7.46 (m, 2H), 7.27 (d, *J* = 3.9 Hz, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 4.1 Hz, 2H), 7.04 (dt, *J* = 8.5, 4.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.50 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.9, 138.8, 136.3, 134.9, 134.4, 132.3, 132.2, 131.2, 130.3, 129.0, 127.6, 127.1, 126.7, 126.4, 125.7, 113.8, 55.2, 30.5, 29.7; HRMS (ESI) calcd for $C_{23}H_{21}OSe^+$ [M + H]$^+$ *m*/*z* 393.0752, found 393.0757.

Ethyl 4-(2-(phenylselanyl)-3,4-dihydronaphthalen-1-yl)benzoate (9): Synthesized from **1g** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [hexane/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a light-yellow solid (150 mg, 86%): R_f = 0.36 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 91−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.31 − 7.27 (m, 3H), 7.13 (d, *J* = 4.2 Hz, 2H), 7.08 − 6.97 (m, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.94 − 2.78 (m, 2H), 2.65 − 2.46 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.5, 144.9, 138.7, 135.6, 134.8, 134.4, 132.5, 130.1, 129.9, 129.8, 129.7, 129.2, 127.8, 127.3, 127.0, 126.5, 125.6, 61.0, 30.7, 29.6, 14.4; HRMS (ESI) calcd for $C_{25}H_{23}O_2Se^+$ [M + H]$^+$ *m*/*z* 435.0858, found 435.0861.

Phenyl(1-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-2-yl)-selane (10): Synthesized from **1h** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (112 mg, 65%): R_f = 0.24 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.54 − 7.47 (m, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.33 − 7.25 (m, 3H), 7.13 (d, *J* = 4.1 Hz, 2H), 7.05 (dp, *J* = 7.5, 3.4 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 2.89 − 2.80 (m, 2H), 2.58 − 2.49 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.8, 138.3, 135.5, 134.8, 134.4, 132.9, 130.4, 129.73, 129.65 (d, *J* = 32.3 Hz), 129.2, 127.8, 127.4, 127.1, 126.5, 125.5, 125.4 (q, *J* = 4.0 Hz), 124.2 (d, *J* = 272.7 Hz), 30.7, 29.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.41; HRMS (ESI) calcd for $C_{23}H_{18}F_3Se^+$ [M + H]$^+$ *m*/*z* 431.0520, found 431.0517.

Phenyl(1-(m-tolyl)-3,4-dihydronaphthalen-2-yl)selane (11): Synthesized from **1i** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)], to give the product as a white solid (141 mg, 94%): R_f = 0.39 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 57−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 − 7.48 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.27 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 4.2 Hz, 2H), 7.05 (ddd, *J* = 12.6, 7.7, 2.7 Hz, 3H), 6.66 (d, *J* = 7.6 Hz, 1H), 2.88 − 2.79 (m, 2H), 2.55 − 2.47 (m, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.0, 139.4, 138.0, 136.2, 134.9, 134.4, 131.8, 130.5, 130.4, 129.0, 128.3, 128.3, 127.5, 127.1, 127.0, 126.7, 126.4, 125.8, 30.5, 29.7, 21.5; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0805.

(1-(3-Chlorophenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (12): Synthesized from **1j** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 25/1 (*v*/*v*)], to give the product as a colorless oil (143 mg, 91%): R_f = 0.33 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 − 7.47 (m, 2H), 7.40 − 7.33 (m, 2H), 7.28 (qd, *J* = 4.8, 1.8 Hz, 4H), 7.16 (ddd, *J* = 5.8, 3.1, 1.6 Hz, 1H), 7.14 − 7.10 (m, 2H), 7.09 − 7.02 (m, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 2.87 − 2.77 (m, 2H), 2.55 − 2.45 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.8, 138.0, 135.6, 134.8, 134.5, 134.3, 132.9, 130.0, 129.9, 129.7, 129.2, 128.3, 127.8, 127.7, 127.3, 127.0, 126.5, 125.5, 30.6, 29.5; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0256.

Phenyl(1-(3-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-2-yl)selane (13): Synthesized from **1k** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a colorless oil (127 mg, 74%): R_f = 0.19 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.61 − 7.53 (m, 2H), 7.53 − 7.44 (m, 3H), 7.28 (d, *J* = 6.7 Hz, 3H), 7.13 (d, *J* = 4.1 Hz, 2H), 7.06 (dq, *J* = 8.7, 3.8 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 2.90 − 2.80 (m, 2H), 2.59 − 2.48 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.8, 138.0, 135.6, 134.9, 134.5, 133.5, 133.3, 130.8 (q, *J* = 32.3 Hz), 129.7, 129.2, 128.9, 127.9, 127.3, 127.1, 126.9 (q, *J* = 4.0 Hz), 126.5, 124.1 (d, *J* = 272.7 Hz), 125.4, 124.4 (q, *J* = 4.0 Hz), 30.7, 29.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.42; HRMS (ESI) calcd for $C_{23}H_{18}F_3Se^+$ [M + H]$^+$ *m*/*z* 431.0520, found 431.0511.

Phenyl(1-(o-tolyl)-3,4-dihydronaphthalen-2-yl)selane (14): Synthesized from **1l** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)], to give the product as a light yellow oil (147 mg, 98%): R_f = 0.44 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 − 7.47 (m, 2H),

7.35 − 7.22 (m, 6H), 7.19 − 7.07 (m, 3H), 7.02 (td, *J* = 7.6, 2.0 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 2.98 − 2.79 (m, 2H), 2.54 − 2.46 (m, 2H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.3, 138.1, 136.5, 135.3, 134.6, 132.3, 130.2, 129.8, 129.1, 127.9, 127.7, 127.2, 126.7, 126.6, 126.0, 124.8, 30.0, 29.6, 19.4; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0804.

(1-(2-Chlorophenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (15): Synthesized from **1m** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)], to give the product as a colorless oil (141 mg, 89%): R_f = 0.42 (petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 − 7.53 (m, 2H), 7.53 − 7.47 (m, 1H), 7.39 − 7.31 (m, 2H), 7.27 (dd, *J* = 5.2, 2.1 Hz, 4H), 7.17 − 7.09 (m, 2H), 7.05 (ddd, *J* = 8.7, 5.9, 3.1 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 2.95 − 2.79 (m, 2H), 2.63 − 2.47 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.7, 137.3, 134.8, 134.6, 134.3, 133.9, 133.5, 131.9, 129.9, 129.7, 129.1, 129.1, 127.6, 127.3, 127.0, 126.9, 126.5, 124.8, 30.5, 29.5; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0244.

Methyl(2-(2-(phenylselanyl)-3,4-dihydronaphthalen-1-yl)phenyl)-sulfane (16): Synthesized from **1n** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)], to give the product as a yellow oil (146 mg, 90%): R_f = 0.08 (petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.40 (ddd, *J* = 7.9, 7.2, 1.6 Hz, 1H), 7.32 – 7.20 (m, 5H), 7.16 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.07 – 7.00 (m, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 2.96 – 2.78 (m, 2H), 2.62 – 2.45 (m, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.3, 138.1, 137.6, 134.8, 134.3, 134.0, 130.4, 130.2, 129.0, 128.4, 127.5, 127.3, 126.9, 126.5, 124.8, 124.6, 30.5, 29.5, 15.3; HRMS (ESI) calcd for $C_{23}H_{21}SSe^+$ [M + H]$^+$ *m*/*z* 409.0524, found 409.0529.

(3,4-Dihydro-[1,1'-binaphthalen]-2-yl)(phenyl)selane (17): Synthesized from **1o** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)], to give the product as a white solid (160 mg, 97%): R_f = 0.42 (petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)); mp 94−95 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.64 − 7.57 (m, 1H), 7.53 (dq, *J* = 6.9, 3.0, 2.4 Hz, 3H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.35 − 7.25 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.18 − 7.09 (m, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 1H), 3.09 − 2.94 (m, 2H), 2.67 (t, *J* = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.6, 137.2, 136.0, 134.5, 134.4, 134.2, 133.8, 131.8, 130.0, 129.0, 128.4, 128.1, 127.8, 127.7, 127.2, 126.8, 126.6, 126.3, 125.9, 125.6, 125.6, 30.5, 29.7; HRMS (ESI) calcd for $C_{26}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 413.0803, found 413.0807.

2-(2-(Phenylselanyl)-3,4-dihydronaphthalen-1-yl)thiophene (18): Synthesized from **1p** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (135 mg, 92%): R_f = 0.32 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 58−60 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 − 7.50 (m, 2H), 7.42 (d, *J* = 5.1 Hz, 1H), 7.34 − 7.24 (m, 3H), 7.15 − 7.05 (m, 4H), 7.04 − 7.00 (m, 1H), 6.90 − 6.84 (m, 1H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.57 − 2.40 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.4, 137.5, 136.1, 135.0, 134.4, 131.0, 129.8, 129.1, 128.6, 128.0, 127.1, 126.9, 126.5, 126.1, 125.4, 30.5, 29.3; HRMS (ESI) calcd for $C_{20}H_{17}SSe^+$ [M + H]$^+$ *m*/*z* 369.0211, found 369.0217.

3-(2-(Phenylselanyl)-3,4-dihydronaphthalen-1-yl)thiophene (19): Synthesized from **1q** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (133 mg, 90%): R_f = 0.34 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 67−68 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 − 7.49 (m, 2H), 7.39 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.28 (p, *J* = 3.1 Hz, 3H), 7.26 − 7.22 (m, 1H), 7.14 − 7.00 (m, 4H), 6.75 (d, *J* = 7.4 Hz, 1H), 2.86 − 2.75 (m, 2H), 2.52 − 2.43 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.8, 135.8, 134.8, 134.6, 133.8, 133.6, 130.0, 129.1, 129.0, 127.7, 127.1, 126.8, 126.4, 125.40, 125.35, 124.9, 30.5, 29.5; HRMS (ESI) calcd for $C_{20}H_{17}SSe^+$ [M + H]$^+$ *m*/*z* 369.0211, found 369.0214.

(7-Methyl-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (20): Synthesized from **1r** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (147 mg, 98%): R_f = 0.32 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 123−124 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.0, 2.5 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.27 (dd, *J* = 4.3, 2.4 Hz, 5H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 2.80 (t, *J* = 7.8 Hz, 2H), 2.55 − 2.46 (m, 2H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.2, 139.5, 135.9, 135.9, 134.3, 132.1, 131.9, 130.4, 129.9, 129.0, 128.4, 127.52, 127.48, 127.4, 127.1, 126.4, 30.8, 29.3, 21.2; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0805.

(7-Fluoro-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (21): Synthesized from **1s** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a colorless oil (148 mg, 98%): R_f = 0.39 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.49 − 7.37 (m, 3H), 7.31 − 7.25 (m, 5H), 7.05 (dd, *J* = 8.2, 5.8 Hz, 1H), 6.78 (td, *J* = 8.3, 2.7 Hz, 1H), 6.35 (dd, *J* = 10.5, 2.6 Hz, 1H), 2.78 (t, *J* = 7.9 Hz, 2H), 2.52 − 2.45 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 243.4 Hz), 139.4, 138.0 (d, *J* = 2.0 Hz), 137.8 (d, *J* = 8.1 Hz), 134.7, 134.1, 130.2 (d, *J* = 3.0 Hz), 129.8, 129.7, 129.1, 128.6, 128.1 (d, *J* = 8.1 Hz), 127.9, 127.8, 112.9 (d, *J* = 22.2 Hz), 112.5 (d, *J* = 23.2 Hz), 30.5, 28.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.06; HRMS (ESI) calcd for $C_{22}H_{17}FKSe^+$ [M + K]$^+$ *m*/*z* 419.0111, found 419.0112.

(7-Chloro-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (22): Synthesized from **1t** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)], to give the product as a white solid (152 mg, 96%): R_f = 0.52 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 93−95 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.32 − 7.23 (m, 5H), 7.09 − 7.00 (m, 2H), 6.61 (d, *J* = 1.8 Hz, 1H), 2.82 − 2.74 (m, 2H), 2.52 − 2.43 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.2, 137.7, 134.8, 134.3, 133.1, 132.1, 129.8, 129.7, 129.1, 128.7, 128.3, 127.9, 127.9, 126.3, 125.4, 30.2, 29.0; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0254.

(7-Methoxy-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (23): Synthesized from **1u** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)], to give the product as a white solid (151 mg, 96%): R_f = 0.56 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 76−77 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 − 7.48 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.40 − 7.34 (m, 1H), 7.30 − 7.21 (m, 5H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.65 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.24 (d, *J* = 2.6 Hz, 1H), 3.62 (s, 3H), 2.88 − 2.69 (m, 2H), 2.61 − 2.39 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.2, 139.9, 139.1, 137.1, 134.4, 133.0, 130.2, 129.9, 129.0, 128.4, 127.8, 127.61, 127.58, 127.1, 112.5, 111.1, 55.2, 30.9, 28.8; HRMS (ESI) calcd for $C_{23}H_{21}OSe^+$ [M + H]$^+$ *m*/*z* 393.0752, found 393.0752.

8-Phenyl-7-(phenylselanyl)-5,6-dihydronaphthalene-2-carbonitrile (24): Synthesized from **1v** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)], to give the product as a white solid (117 mg, 76%): R_f = 0.28 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 142−143 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 − 7.47 (m, 4H), 7.47 − 7.42 (m, 1H), 7.37 (dd, J = 7.7, 1.6 Hz, 1H), 7.35 − 7.27 (m, 3H), 7.27 − 7.23 (m, 2H), 7.19 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 1.4 Hz, 1H), 2.90 − 2.84 (m, 2H), 2.53 − 2.46 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.0, 138.6, 137.1, 136.4, 135.8, 135.2, 130.0, 129.7, 129.2, 129.1, 129.0, 128.5, 128.21, 127.9, 119.1, 110.3, 29.6; HRMS (ESI) calcd for $C_{23}H_{18}NSe^+$ [M + H]$^+$ *m*/*z* 388.0599, found 388.0596.

(6-Chloro-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (25): Synthesized from **1w** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [hexane/CH_2Cl_2, 50/1 (*v*/*v*)], to give the product as a white solid (86 mg, 54%): R_f = 0.41 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 − 7.47 (m, 2H), 7.47 − 7.41 (m, 2H), 7.41 − 7.35 (m, 1H), 7.31 − 7.21 (m, 5H), 7.09 (d, *J* = 2.0 Hz, 1H), 6.98 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 2.83 − 2.74 (m, 2H), 2.48 (dd, *J* = 8.7, 7.1 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.6, 138.1, 136.6, 134.6, 132.7, 132.0, 129.9, 129.8, 129.1, 128.5, 127.8, 127.7, 127.1, 126.9, 126.3, 30.2, 29.4; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0258.

(8-Chloro-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (25'): Synthesized from **1w** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [hexane/CH_2Cl_2, 50/1 (*v*/*v*)], to give the product as a light-yellow solid (37 mg, 23%): R_f = 0.37 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 − 7.51 (m, 2H), 7.42 − 7.27 (m, 8H), 7.13 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.09 − 7.01 (m, 2H), 2.72 (dd, *J* = 8.5, 6.0 Hz, 2H), 2.44 − 2.36 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 140.2, 137.4, 135.8, 135.1, 133.8, 131.7, 130.0, 129.9, 129.8, 129.1, 128.0, 127.8, 127.4, 127.1, 125.5, 31.2, 30.1; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0262.

(5-Methyl-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (26): Synthesized from **1x** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 25/1 (*v*/*v*)], to give the product as a white solid (140 mg, 93%): R_f = 0.31 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 − 7.48 (m, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.40 − 7.34 (m, 1H), 7.32 − 7.22 (m, 5H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 2.80 (t, *J* = 7.9 Hz, 2H), 2.52 (t, *J* = 7.9 Hz, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.5, 139.7, 136.0, 134.5, 134.3, 133.2, 131.4, 130.3, 129.9, 129.0, 128.9, 128.4, 127.5, 127.4, 125.7, 124.1, 30.2, 25.6, 19.6; HRMS (ESI) calcd for $C_{23}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 377.0803, found 377.0797.

(5-Chloro-1-phenyl-3,4-dihydronaphthalen-2-yl)(phenyl)selane (27): Synthesized from **1y** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 25/1 (*v*/*v*)], to give the product as a white solid (146 mg, 92%): R_f = 0.35 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 2H), 7.40 (dd, *J* = 8.4, 6.1 Hz, 1H), 7.34 − 7.22 (m, 5H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 3.00 − 2.93 (m, 2H), 2.55 − 2.45 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.8, 138.0, 137.9, 134.8, 133.7, 132.8, 132.4, 129.9, 129.6, 129.1, 128.6, 127.9, 127.7, 127.5, 126.9, 124.3, 29.6, 26.0; HRMS (ESI) calcd for $C_{22}H_{18}ClSe^+$ [M + H]$^+$ *m*/*z* 397.0257, found 397.0263.

Phenyl(1-phenyl-3,4-dihydrophenanthren-2-yl)selane (28): Synthesized from **1z** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 15/1 (*v*/*v*)], to give the product as a light-yellow solid (138 mg, 84%): R_f = 0.32 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.47 (t, *J* = 8.2 Hz, 3H), 7.41 (td, *J* = 7.3, 2.8 Hz, 2H), 7.30 (dt, *J* = 5.0, 2.6 Hz, 5H), 6.88 (d, *J* = 8.6 Hz, 1H), 3.30 − 3.21 (m, 2H), 2.71 − 2.60 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.4, 139.6, 134.4, 133.1, 132.6, 131.8, 131.0, 130.3, 130.1, 130.0, 129.1, 128.5, 127.7, 127.6, 126.12, 126.08, 125.2, 124.6, 123.5, 30.3, 24.9; HRMS (ESI) calcd for $C_{26}H_{21}Se^+$ [M + H]$^+$ *m*/*z* 413.0803, found 413.0797.

(7-Methyl-1-(4-nitrophenyl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (29): Synthesized from **1aa** (0.4 mmol) and **2a** (0.96 mmol) in 2 mL CH_2Cl_2 and Tf_2O (0.96 mmol) and Et_3N (3.2 mmol) were used. Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)], to give the product as a light-yellow solid (72 mg, 43%): R_f = 0.32 (petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)); mp 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 − 8.27 (m, 2H), 7.51 − 7.47 (m, 2H), 7.47 − 7.43 (m, 2H), 7.32 − 7.25 (m, 3H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 2.81 (t, *J* = 7.8 Hz, 2H), 2.57 − 2.49 (m, 2H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.3, 137.9, 136.1, 135.0, 134.3, 133.4, 131.8, 131.1, 129.5, 129.3, 127.9, 127.4, 126.0, 123.8, 31.0, 29.0, 21.1; HRMS (ESI) calcd for $C_{23}H_{20}NO_2Se^+$ [M + H]$^+$ *m*/*z* 422.0654, found 422.0664.

Phenyl(10-phenylphenanthren-9-yl)selane (30): Synthesized from **1ab** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 20/1 (*v*/*v*)], to give the product as a yellow oil (112 mg, 68%): R_f = 0.45 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (t, *J* = 8.8 Hz, 2H), 8.68 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.66 (tdd, *J* = 8.3, 5.5, 2.3 Hz, 2H), 7.55 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.50 − 7.44 (m, 2H), 7.42 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.26 (q, *J* = 2.8 Hz, 1H), 7.23 (q, *J* = 4.0, 3.0 Hz, 3H), 7.03 (s, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8, 142.0, 134.2, 132.9, 132.4, 132.2, 131.1, 130.7, 130.6, 129.7, 129.2, 128.91, 128.90, 127.9, 127.6, 127.4, 127.3, 127.0, 126.7, 125.5, 122.7, 122.6; HRMS (ESI) calcd for $C_{26}H_{19}Se^+$ [M + H]$^+$ *m*/*z* 411.0646, found 411.0654.

4-Phenyl-3-(phenylselanyl)-2H-chromene (31): Synthesized from **1ac** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 40/1 (*v*/*v*)], to give the product as a light-yellow solid (135 mg, 93%): R_f = 0.47 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 71−72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.49 − 7.38 (m, 3H), 7.32 − 7.26 (m, 5H), 7.14 (td, *J* = 8.0, 1.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.84 − 6.79 (m, 1H), 6.74 − 6.68 (m, 1H), 4.74 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.6, 138.3, 137.5, 133.5, 129.7, 129.4, 129.1, 128.6, 128.4, 128.1, 127.8, 126.2, 125.0, 122.5, 121.5, 115.9, 69.5; HRMS (ESI) calcd for $C_{21}H_{17}OSe^+$ [M + H]$^+$ *m*/*z* 365.0439, found 365.0429.

4-Phenyl-3-(phenylselanyl)-1-tosyl-1,2-dihydroquinoline (32): Synthesized from **1ad** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/ethyl acetate, 50/1 (*v*/*v*)], to give the product as a yellow solid (188 mg, 91%): R_f = 0.37 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 161−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.64 − 7.57 (m, 2H), 7.45 − 7.33 (m, 5H), 7.31 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.29 − 7.23 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 (td, *J* = 7.7, 1.2 Hz, 1H), 6.61 − 6.53 (m, 3H), 4.43 (s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.6, 137.6, 136.0, 135.92, 135.86, 135.7, 133.7, 132.0, 129.5, 129.3, 129.1, 128.9, 128.3, 127.8, 127.5, 127.0, 126.7, 126.2, 125.8, 125.5, 50.1, 21.4; HRMS (ESI) calcd for $C_{28}H_{24}NO_2SSe^+$ [M + H]$^+$ *m*/*z* 518.0687, found 518.0687.

4-Phenyl-3-(phenylselanyl)-2*H*-chromen-2-one (33): Synthesized from **1ae** (0.4 mmol) and **2a** (0.96 mmol) in 2 mL CH_2Cl_2 and Tf_2O (0.96 mmol) and Et_3N (3.2 mmol) were used. Purification by flash column chromatography [petroleum ether/ethyl acetate, 10/1 (*v*/*v*)], to give the product as a white solid (68 mg, 45%): R_f = 0.15 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.47 − 7.42 (m, 3H), 7.37 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.34 − 7.29 (m, 2H), 7.22 − 7.10 (m, 6H), 7.06 (dd, *J* = 8.0, 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.5, 158.9, 153.4, 136.2, 132.8, 132.0, 130.3, 129.0, 128.8, 128.5, 128.2, 127.9, 127.4, 124.2, 120.7, 120.5, 116.8; HRMS (ESI) calcd for $C_{21}H_{15}O_2Se^+$ [M + H]$^+$ *m*/*z* 379.0232, found 379.0240.

1-Methyl-4-phenyl-3-(phenylselanyl)quinolin-2(1H)-one (34): Synthesized from **1af** (0.4 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/ethyl acetate, 10/1 (*v*/*v*)], to give the product as a yellow oil (60 mg, 38%): R_f = 0.13 (petroleum ether/ethyl acetate, 5/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.43 − 7.35 (m, 4H), 7.27 (dt, *J* = 7.2, 2.4 Hz, 2H), 7.18 − 7.04 (m, 7H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 154.9, 139.8, 138.0, 132.1, 131.7, 130.8, 128.7, 128.6, 128.2, 128.0, 126.6, 126.2, 122.0, 121.4, 114.1, 30.8; HRMS (ESI) calcd for $C_{22}H_{18}NOSe^+$ [M + H]$^+$ *m*/*z* 392.0548, found 392.0542.

1,4-Bis(2-(phenylselanyl)-3,4-dihydronaphthalen-1-yl)benzene (35): Synthesized from **1ag** (0.2 mmol) and **2a** (0.48 mmol). Purification by flash column chromatography [petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)], to give the product as a white solid (94 mg, 73%): R_f = 0.46 (petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)); mp 221−222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 − 7.52 (m, 4H), 7.37 − 7.32 (m, 4H), 7.32 − 7.25 (m, 6H), 7.16 − 7.06 (m, 6H), 6.79 (d, *J* = 6.9 Hz, 2H), 2.86 (t, *J* = 7.7 Hz, 4H), 2.54 (td, *J* = 8.0, 7.3, 2.0 Hz, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.1, 138.9, 136.1, 134.9, 134.6, 132.3, 130.3, 130.0, 129.1, 127.6, 127.1, 126.7, 126.5, 125.8, 30.6, 29.7; HRMS (ESI) calcd for $C_{38}H_{31}Se_2^+$ [M + H]$^+$ *m*/*z* 647.0751, found 647.0756.

Procedure of large-scale synthesis: To a flame-dried Schlenk tube were added alkyne **1a** (4.0 mmol) and sulfoxide **2a** (4.8 mmol), and then they were dissolved with dichloromethane (20 mL) under a nitrogen atmosphere before being cooled to −78 °C (liquid N_2/ethyl acetate bath). Tf_2O (2.0 mL, 4.8 mmol) was added dropwise. After being stirred for 0.5 h, the mixture was warmed to room temperature and stirred for an additional 0.5 h, and then Et_3N (2.0 g, 20 mmol) was added dropwise at 0 °C. After being stirred for 2 h, the solution was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)] and afforded pure product (1.27 g, 88 %).

Procedure and characterization for transformations of products:

Phenyl(1-phenylnaphthalen-2-yl)selane (36): **3a** (0.5 mmol, 181 mg) was dissolved in CH_2Cl_2 (5 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (341 mg, 1.5 mmol) was added at room temperature. The brown mixture was stirred at room temperature for 12 h, and then concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography [petroleum ether/CH_2Cl_2, 30/1 (*v*/*v*)] to yield the corresponding product **36** as a white solid (171 mg, 95%): R_f = 0.43 (petroleum ether/CH_2Cl_2, 10/1 (*v*/*v*)); mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.50 (dtd, *J* = 8.7, 6.6, 4.9 Hz, 5H), 7.41 (td, *J* = 7.3, 6.8, 1.3 Hz, 2H), 7.35 (ddd, *J* = 8.1, 4.1, 1.6 Hz, 3H), 7.32 − 7.24 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.7, 139.6, 135.0, 133.1, 132.1, 131.0, 130.5, 130.2, 129.4, 128.5, 128.1, 127.91, 127.86, 127.8, 126.4, 126.1, 125.5; HRMS (ESI) calcd for $C_{22}H_{17}Se^+$ [M + H]$^+$ *m*/*z* 361.0490, found 361.0497.

4-Phenyl-3-(phenylseleninyl)-1,2-dihydronaphthalene (37): To a flame-dried 25 mL round-bottom flask was added **3a** (0.5 mmol, 181 mg) and dissolved in CH_2Cl_2 (5 mL) at 0 °C. A solution of *m*-CPBA (1.05 mmol, 107 mg, 85%) in CH_2Cl_2 (5 mL) was added dropwise to the cooled solution. The mixture was stirred for 0.5 h at 0 °C and then stirred at room temperature for an additional 2 h. Then the solvent was removed under reduced pressure and purified by flash column chromatography [CH_2Cl_2/CH_3OH, 30/1 (*v*/*v*)], to give **37** as a colorless oil (168 mg, 89%): R_f = 0.50 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 − 7.59 (m, 2H), 7.55 − 7.22 (m, 8H), 7.20 (td, *J* = 7.3, 1.0 Hz, 1H), 7.15 (d, *J* = 6.5 Hz, 1H), 7.08 (td, *J* = 7.6, 1.3 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 3.08 − 2.94 (m, 2H), 2.88 − 2.74 (m, 1H), 2.31 − 2.17 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.8, 142.3, 140.6, 136.4, 136.2, 134.3, 130.8, 129.3, 129.2, 128.7, 127.7, 127.3, 126.6, 126.3, 28.7, 19.1; HRMS (ESI) calcd for $C_{22}H_{19}OSe^+$ [M + H]$^+$ *m*/*z* 379.0596, found 379.0606.

1-Phenyl-2-(phenylseleninyl)naphthalene (38): To a flame-dried 25 mL round-bottom flask was added **36** (0.5 mmol, 180 mg) and dissolved in CH_2Cl_2 (5 mL) at 0 °C. A solution of *m*-CPBA (1.05 mmol, 107 mg, 85%) in CH_2Cl_2 (5 mL) was added dropwise to the cooled solution. The mixture was stirred for 0.5 h at 0 °C and then stirred at room temperature for an additional 2 h. Then the solvent was removed under reduced pressure and purified by flash column chromatography [CH_2Cl_2/CH_3OH, 30/1 (*v*/*v*)], to give **38** as a light-pink solid (160 mg, 85%): R_f = 0.48 (CH_2Cl_2/CH_3OH, 20/1 (*v*/*v*)); mp 148−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.7 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.95 − 7.88 (m, 1H), 7.65 − 7.58 (m, 1H), 7.58 − 7.50 (m, 4H), 7.42 (tdd, *J* = 7.3, 2.9, 0.9 Hz, 2H), 7.38 − 7.26 (m, 5H), 6.95 (d, *J* = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.9, 140.1, 139.4, 135.8, 134.5, 132.1, 131.2, 130.9, 130.3, 129.5, 129.2, 129.1, 128.8, 128.4, 128.3, 127.5, 127.0, 126.7, 126.4, 120.5; HRMS (ESI) calcd for $C_{22}H_{17}OSe^+$ [M + H]$^+$ *m*/*z* 377.0439, found 377.0433.

Diphenyl(1-phenylnaphthalen-2-yl)phosphane (39): To a flame-dried Schlenk tube was added **36** (0.2 mmol, 72 mg). The flask was evacuated and purged with nitrogen for three times. 1 mL THF was added under nitrogen atmosphere and the solution was cooled to -78 °C. *n*-BuLi (0.24 M in THF, 1 mL, 0.24 mmol) was added dropwise. The solution was stirred at -78 °C for 1 h and then Ph_2PCl (0.24 mmol, 53 mg) was added. The resulting solution was stirred at room temperature for 12 h. The reaction was quenched with water and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography [petroleum ether/ethyl acetate, 50/1 (*v*/*v*)], to give product **39** as a white solid (44 mg, 56%): R_f = 0.41 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 183−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.51 − 7.44 (m, 2H), 7.36 (q, *J* = 8.0, 6.9 Hz, 4H), 7.31 − 7.25 (m, 6H), 7.21 (ddd, *J* = 8.6, 6.4, 4.6 Hz, 5H), 7.15 (d, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8 (d, *J* = 31.3 Hz), 139.4 (d, *J* = 8.1 Hz), 138.0 (d, *J* = 13.1 Hz), 133.7 (d, *J* = 19.2 Hz), 137.6 (d, *J* = 27.3 Hz), 132.8 (d, *J* = 6.1 Hz), 130.8 (d, *J* = 2.0 Hz), 129.7, 128.32, 128.27, 127.8, 127.7, 127.6, 127.4, 127.0 (d, *J* = 2.0 Hz), 126.5, 126.2; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -13.70; HRMS (ESI) calcd for $C_{28}H_{22}P^+$ [M + H]$^+$ *m*/*z* 389.1454, found 389.1461.

Phenyl(1-phenylnaphthalen-2-yl)methanol (40): To a flame-dried Schlenk tube was added **36** (0.2 mmol, 72 mg). The flask was evacuated and purged with nitrogen for three times. 1 mL THF was added under nitrogen atmosphere and the solution was cooled to -78 °C. *n*-BuLi (0.24 M in THF, 1 mL, 0.24 mmol) was added dropwise. The solution was stirred at -78 °C for 1 h and then benzaldehyde (0.24 mmol, 25 mg) was added. The resulting solution was stirred at room temperature for 2 h. The reaction was quenched with water and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography [petroleum ether/ethyl acetate, 50/1 (*v*/*v*)], to give product **40** as a white solid (45 mg, 73%): R_f = 0.41 (petroleum ether/ethyl acetate, 20/1 (*v*/*v*)); mp 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 11.8, 8.4 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.56 − 7.50 (m, 1H), 7.49 − 7.38 (m, 5H), 7.37 − 7.32 (m, 1H), 7.29 − 7.17 (m, 6H), 7.17 − 7.13 (m, 1H), 5.85 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.7, 138.4, 138.2, 137.9, 132.8, 132.7, 130.8, 130.0, 128.5, 128.3, 128.2, 128.2, 127.8, 127.5, 127.1, 126.9, 126.5, 126.1, 125.9, 124.5, 72.8; HRMS (ESI) calcd for $C_{23}H_{18}NaO^+$ [M + Na]$^+$ *m*/*z* 333.1250, found 311.1252.

(1-([1,1'-Biphenyl]-4-yl)-3,4-dihydronaphthalen-2-yl)(phenyl)selane (41): To a flame-dried Schlenk tube was added **7** (0.3 mmol, 132 mg), phenylboronic acid (0.45 mmol, 55 mg), $[(C_6H_5)_3P]_2PdCl_2$ (6 mol %, 13 mg) and K_3PO_4 (0.6 mmol, 127mg). The flask was evacuated and purged with nitrogen for three times. 1.5 mL toluene was added under nitrogen atmosphere and the solution was stirred at 100 °C for 20 h. The reaction was quenched with water and extracted with ethyl acetate. Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography [petroleum ether CH_2Cl_2, 10/1 (*v*/*v*)], to give product **41** as a white solid (75 mg, 64%): R_f = 0.23 (petroleum ether/CH_2Cl_2, 5/1 (*v*/*v*)); mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 − 7.63 (m, 4H), 7.53 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 (dd, *J* = 7.4, 4.8 Hz, 3H), 7.27 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.12 (d, *J* = 4.3 Hz, 2H), 7.07 (ddt, *J* = 8.7, 5.7, 3.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.54 (dd, *J* = 9.0, 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.8, 140.2, 139.0, 136.1, 134.9, 134.4, 132.2, 130.4, 130.2, 129.1, 128.7, 127.6, 127.3, 127.2, 127.1, 126.8, 126.4, 125.8, 30.6, 29.7; HRMS (ESI) calcd for $C_{28}H_{23}Se^+$ [M + H]$^+$ *m*/*z* 439.0959, found 439.0951.

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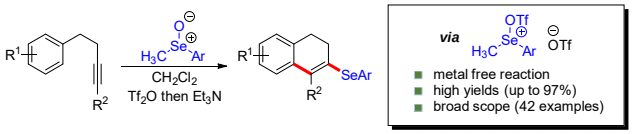

A metal-free, one-pot selenium mediated electrophilic cyclization reaction of alkynes and triflic anhydride-activated selenoxides was realized, giving selenium containing dihydronaphthalene products, including selenium-substituted phenanthrene, dihydroquinoline, 2*H*-chromene, and coumarin.