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Copper-catalyzed *ipso*-selenation of aromatic carboxylic acids†

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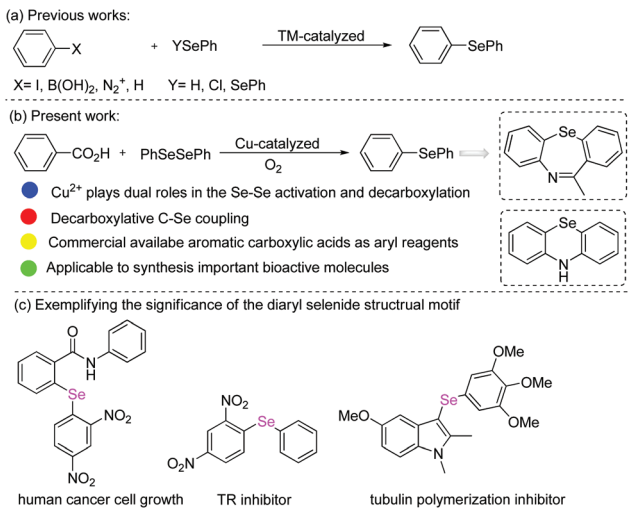
The copper-catalyzed decarboxylative selenation of aromatic carboxylic acids with diselenide is reported. This transformation tolerated a diverse set of functional groups on the substrates, including pentafluorobenzoic acid and heteroaromatic acids, delivering diaryl and methyl aryl selenides in good to excellent yields. Mechanistic studies indicated that the copper catalyst is essential in the activation of the Se–Se bond and the decarboxylation of aromatic acids. The utility of the products has been demonstrated in the facile synthesis of 10*H*-phenoselenazine and 11-methyldibenzo-(*b*,*f*)-1,4-selenazepine.

Introduction

The C–Se bond is an important motif in pharmaceutical and biologically active compounds.[1] For example, diaryl selenides have been used in several applications, such as human cancer cell growth inhibitors,[2a] TR inhibitors[2a] and tubulin polymerization inhibitors[2b] (Scheme 1c). Additionally, aryl selenides serve as spectroscopic tools for neuro-biological applications,[3a] but they also function as key intermediates in the synthesis of aryl selenones[3b] and selenoxides.[3c] Therefore, developing an efficient and practical method for the synthesis of these useful compounds is highly attractive.

Over the last few decades, the formation of transition-metal catalyzed C–Se bonds *via* the cross-coupling of aryl halides or boronic acid with selenols or diselenides has emerged as an important tool for the rapid construction of aryl selenides (Scheme 1a).[4] However, one of the drawbacks among these methods is that they require prefunctionalized substrates. Subsequently, the regio-selective C–H selenation of arenes with diselenides has been achieved under transition-metal catalysis with a directing group on the substrates.[5] Furthermore, the metal-free radical selenation of aryl diazonium ions with diphenyl diselenides has been reported.[6] Despite these transformations representing significant advancements toward the formation of a new C–Se bond, there is still an urgent need to utilize the easily accessible substrates to construct the complex selenium-containing compounds through an efficient and versatile protocol, which remains a great challenge. In addition, a structurally diverse, readily-available, and bench-stable starting material is preferred, among which aromatic carboxylic acids are good candidates.[7] In our previous studies on copper-catalyzed arylselenation reactions, we showed that PhSeCu intermediates could be intercepted by nucleophiles such as indoles and azoles to allow the C3-phenylselenation of indoles[8a] and 3-arylselanyl-azoles,[8b] respectively, or could react with electrophilic epoxides to give β-hydroxy phenylselenides.[8c] We envisioned that the PhSeCu intermediate generated *in situ* could also react with aromatic carboxylic acids to afford the de-



Scheme 1 Representative aryl selenides and oxidative decarboxylative C–Se coupling.

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carboxylative C–Se coupling products. Recently, Hoover and co-workers reported the copper-catalyzed decarboxylative thiolation to synthesize aryl sulfides.[7h] Here, we report the copper-catalyzed oxidative decarboxylative selenation of aromatic carboxylic acids with diselenides, affording the diaryl selenides and methyl aryl selenides. The key features of this transformation are the use of oxygen as the oxidant and the dual roles of the copper catalyst. The utility of this method was also demonstrated in the facile synthesis of 10*H*-phenoselenazine[9a] and 11-methyldibenzo-(*b*,*f*)-1,4-selenazepine.[9b]

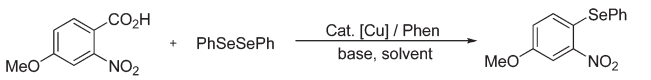
The potential issues in such transformations include the deactivation of the copper species by excess selenium compounds,[10] the copper-catalyzed protodecarboxylation of the aromatic acids[11] or homo-coupling.[12] To address these problems, our strategy was to identify a suitable bidentate ligand to modify the steric environment and electron density on the copper, resulting in the formation of a copper intermediate that could favor coordination to the selenide and aryl groups. In addition, we reasoned that the "hardness" of high valent copper might alleviate the problem of catalyst poisoning.

Results and discussion

At the onset of this project, we chose the reaction between 4-methoxy-2-nitrobenzoic acid and diphenyl diselenide as the model system for screening a variety of reaction parameters. As shown in Table 1, we observed that the choice of the copper catalyst had a considerable impact on the reaction outcome. When Cu(I) salts (entries 1–3) were used as catalysts, the selenation did not proceed at all. In contrast, when Cu(II) salts were used, 4-methoxy-2-nitrobenzoic acid was smoothly converted into the desired product (entries 4–6); further exploration confirmed that $Cu(OAc)_2$ was the most efficient catalyst. The poor activities of the Cu(I) salts are likely due to the selenide compounds, which act as "soft" ligands, binding strongly to the low valent copper species and causing catalyst deactivation. K_2CO_3 was found to be the optimal base among all the bases examined, namely, Li_2CO_3, Na_2CO_3 and Cs_2CO_3 (entries 7–9). It is worth noting that the efficiency of the reaction was dependent on their cations, probably because the bases were involved in the activation of the Se–Se bond of the starting material and were required to promote anion exchange of the benzoate with the copper catalyst to trigger the reaction. Subsequent investigation on the effect of different solvents found that when the reaction was conducted in a polar solvent, such as DMF or DMSO, or a weakly coordinating solvent, such as THF (entries 10–12), only the protodecarboxylation by-product 3-nitroanisole was observed. It is believed that coordinating solvents interfere with the selenation process by competing with the benzoate anion or selenium atom at the copper center. Control experiments indicated that the combination of copper and a ligand with a weak base was required for the decarboxylative C–Se coupling reaction (entries 14–16).

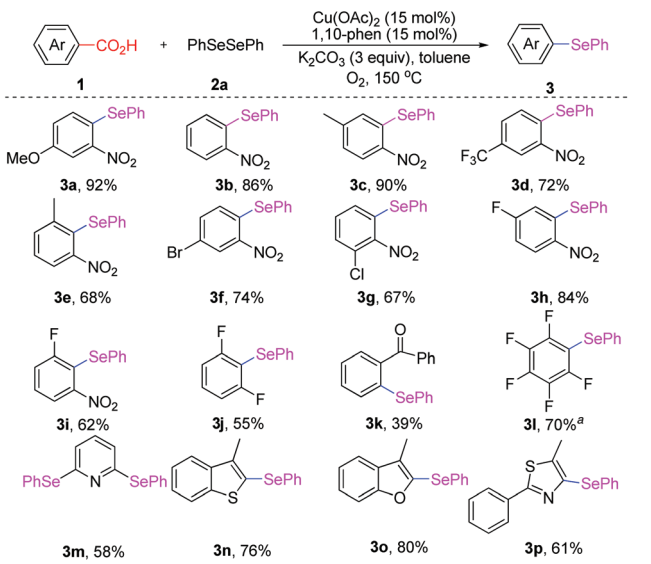
With the optimal conditions in hand, we examined the scope of aromatic benzoic acids **1** (Scheme 2). Both electron-donating (**3a**, **3c**) and electron-withdrawing (**3d**) groups on the benzene ring of the aryl acid were well tolerated and afforded the corresponding C–Se coupling products in good to excellent yields. Sterically hindered substrates also provided the desired

Table 1 Optimization of the reaction conditions[a]



Entry	[Cu]	Base	Solvent	Yield[b], %
1	CuI	K_2CO_3	Toluene	0
2	CuBr	K_2CO_3	Toluene	0
3	CuCl	K_2CO_3	Toluene	0
4	$Cu(OAc)_2$	K_2CO_3	Toluene	92
5	$CuBr_2$	K_2CO_3	Toluene	45
6	$CuCl_2$	K_2CO_3	Toluene	78
7	$Cu(OAc)_2$	Li_2CO_3	Toluene	21
8	$Cu(OAc)_2$	Na_2CO_3	Toluene	65
9	$Cu(OAc)_2$	Cs_2CO_3	Toluene	34
10	$Cu(OAc)_2$	K_2CO_3	DMF	0
11	$Cu(OAc)_2$	K_2CO_3	DMSO	0
12	$Cu(OAc)_2$	K_2CO_3	THF	0
13[c]	$Cu(OAc)_2$	K_2CO_3	Toluene	17
14	—	K_2CO_3	Toluene	0
15[d]	$Cu(OAc)_2$	K_2CO_3	Toluene	0
16	$Cu(OAc)_2$	—	Toluene	0

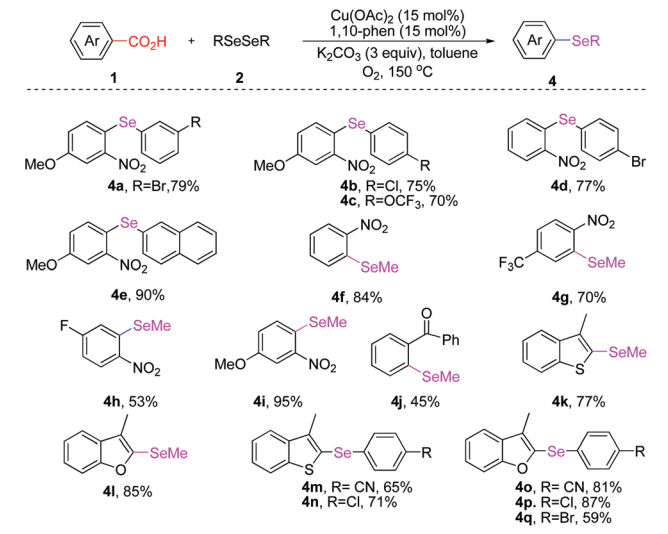
[a] Reaction conditions unless stated otherwise: **1a** (0.2 mmol), **2a** (0.3 mmol), [Cu] (15 mmol %), phen (15 mmol %), base (0.6 mmol), solvent (2.0 mL), under O_2, 150 °C, 24 h. [b] Isolated yield. [c] Under N_2. [d] In the absence of the phen ligand.



Scheme 2 The scope of aryl acids. Reaction conditions unless specified otherwise: aryl acid (0.2 mmol), diphenyl diselenide (0.3 mmol), $Cu(OAc)_2$ (15 mmol %), phen (15 mmol %) and K_2CO_3 (0.6 mmol) in toluene (2 mL) were stirred at 150 °C for 24 h under 1 atm of O_2, isolated yield. [a] Pentafluorobenzoic acid (0.4 mmol), diphenyl diselenide (0.2 mmol).

products **3e** and **3i** in good yields. Moreover, halogen substituted 2-nitrobenzoic acids were smoothly converted to the selenation products (**3f**, **3g**, **3h**) with diphenyl diselenide, which provides an opportunity for further late-stage derivatization of selenium-containing compounds. In addition, 2-benzoylbenzoic acid (**3k**) was tolerated, although the yield was relatively lower. It is worth noting that decarboxylative selenation is sensitive to the electronic effects of the substituents on the *ortho* benzoic acids, and when 2-chlorobenzoic acid, *o*-toluic acid or *o*-anisic acid was subjected to the optimal reaction conditions, the desired products were not observed. However, the difluoro substituted benzoic acid could be converted to the difluoro-substituted diaryl selenide (**3j**). When pentafluorobenzoic acid was employed under the standard reaction conditions, only the chemoselective selenation product (**3l**) was obtained in good yield, and the by-product from S_NAr substitution was not detected. Interestingly, in the case of picolinic acid *N*-oxide, *ortho*-diselenated product **3m** was obtained, which suggested that the reaction works through both decarboxylative and *ortho* C–H selenation mechanisms. To our delight, benzofuran-2-carboxylic acid, benzo[*b*]thiophene-2-carboxylic acid and thiazole-5-carboxylic acid were tolerated in this reaction and gave the desired products in high selectivities and good yields (**3n**, **3o**, **3p**).

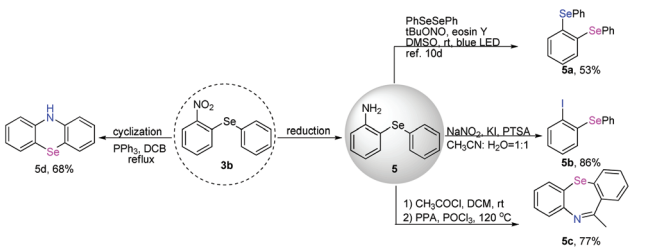
Next, we examined the scope of diselenide **2** (Scheme 3). Diaryl diselenides containing either *meta* or *para* substituents on the benzene ring were found to be efficient coupling partners and gave the corresponding selenation products. The reaction conditions are compatible with common functional groups such as bromide (**4a**, **4d**), chloride (**4b**), methoxymethyl (**4e**) and trifluoromethoxy (**4c**). It was exciting to discover that dimethyl diselenide was also an active selenating agent, and, accordingly, various aromatic carboxylic acids have been converted into aryl methyl selenides (**4f–4l**) *via* the reaction with dimethyl diselenide. Furthermore, a high selectivity for the arylselenation of benzo[*b*]thiophene (**4m**, **4n**) and benzofuran (**4o–4q**) was still achieved even when the substituents on the substrates were changed.



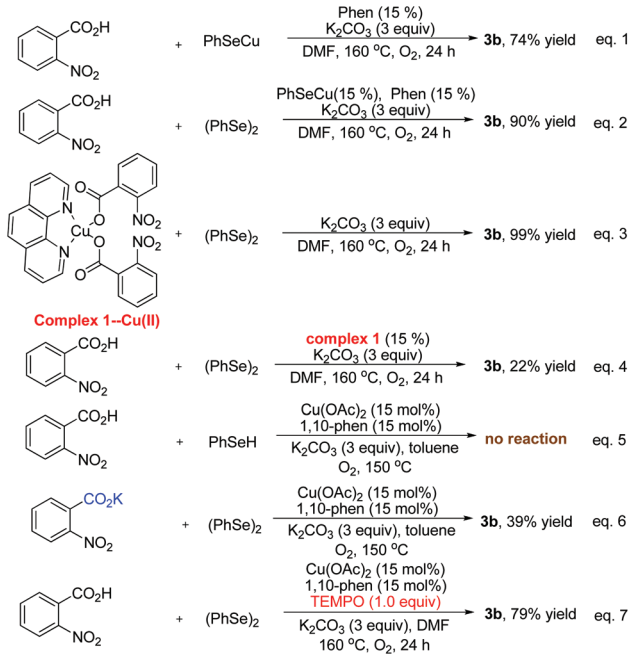
Scheme 3 The scope of diselenides. Reaction conditions unless specified otherwise: aryl acid (0.2 mmol), diselenide (0.3 mmol), $Cu(OAc)_2$ (15 mmol %), phen (15 mmol %) and K_2CO_3 (0.6 mmol) in toluene (2 mL) were stirred at 150 °C for 24 h under 1 atm of O_2, with an isolated yield.

The application of our method is shown in Scheme 4. The phenylselenation product **3b** was smoothly transformed into 10*H*-phenoselenazine **5d** in 68% yield by a PPh_3-mediated reductive cyclization reaction.[13] Furthermore, the nitro group was then converted into an amine, giving the substituted diphenyl selenide. The presence of a primary amino group as a versatile synthetic handle is an advantage. When 2-(phenylselanyl)aniline was treated with diphenyl diselenide under photo-catalytic conditions, the corresponding 1,2-bis(phenylselanyl)benzene (**5a**) was generated with 53% yield.[6b] For the classical Sandmeyer reaction, the diazotization of **5** with $NaNO_2$ followed by the reaction with KI gave (2-iodophenyl)(phenyl)selane (**5b**) with 86% yield. In addition, the biologically active 11-methyldibenzo-(*b*,*f*)-1,4-selenazepine (**5c**) was synthesized from **5** with 77% yield.[14]

To further understand the mechanism, the PhSeCu intermediate[15] and the copper(II) benzoate complex[16] were synthesized according to the literature. Firstly, we conducted the stoichiometric reaction of 2-nitrobenzoic acid with PhSeCu under our optimized reaction conditions, which afforded the desired product **3b** with 74% yield (eqn (1)). As shown in eqn (2) (Scheme 5), PhSeCu is a chemically competent intermediate, which is consistent with our tentative hypothesis. Strikingly, the stoichiometric reaction of complex **1** with diphenyl diselenide led to a decarboxylative cross-coupling product with almost quantitative yield (eqn (3)). However, when complex **1** was used catalytically, the yield of **3b** decreased to 22% (eqn (4)). These data indicated that copper(II) played dual roles in Se–Se activation and decarboxylation, both key steps to generate the selenide–copper complex, followed by decarboxylation to generate the *ipso*-selenation product. Additionally, the nature of the original selenide source affected the reaction outcome (eqn (5)). When the selenation reaction was attempted using benzeneselenol, no product was observed. Most likely, PhSeH has strong proclivity for copper catalyst deactivation. Finally, potassium 2-nitrobenzoate could be smoothly converted into product **3b** with diphenyl diselenide (eqn (6)), which suggested that the base plays a critical role in deprotonating the aryl acids and forming the copper(II) benzo-



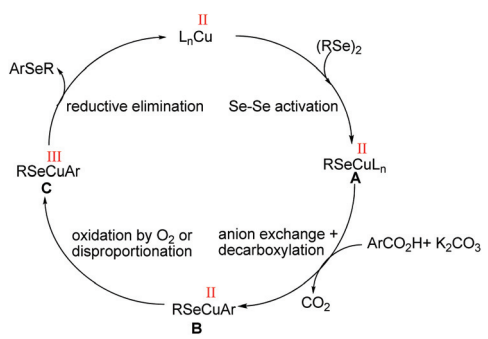
Scheme 4 Derivatization of the selenation product **3b**.



Scheme 5 Preliminary mechanism investigation.

ate complex. Finally, we performed a radical clock experiment by adding 3.0 equiv. of radical scavengers (eqn (7)), for example TEMPO did not significantly alter the efficiency of the oxidative decarboxylative selenation process, which suggested that a single electron transfer mechanism could be excluded.

Based on the above results and previous literature reports, we proposed a mechanism to explain the reaction of benzoic acid and diselenide (Scheme 6). The initial Se–Se activation of diselenide produced Se–Cu intermediate **A**. Then, the aromatic carboxylate was transferred to the copper center by base-promoted anion exchange, which would be followed by decarboxylation to generate organocopper species **B**. Then, copper(III) **C** [17] was formed either by disproportionation with another Cu(II) species or by oxidation with O_2. Finally, reductive elimination could afford the desired selenation product and regenerate the copper catalyst to complete the catalytic cycle.



Scheme 6 Proposed catalytic cycle.

Conclusions

In summary, a protocol for the copper-catalyzed decarboxylative selenation of aromatic carboxylic acids with diselenide has been developed. This protocol enables a variety of aromatic carboxylic acids to be converted to diaryl selenides or aryl methyl selenides under aerobic reaction conditions. In particular, the selenation products could easily be transformed into valuable selenium-containing azaheterocycles. Further study on the utility of the current strategy for late-stage functionalization of pharmaceuticals and the expansion of the scope is currently underway in our laboratory.

Experimental

General remarks

Diaryl diselenides1 were prepared according to the reported procedures.[18] The ^{1}H and ^{13}C spectra of the known compounds were in accordance with those described in the literature. All other reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros, and Meyer and were used without further purification. Toluene was distilled from Na under nitrogen and stored under nitrogen. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 MHz) spectra were recorded in $CDCl_3$ solutions using a Bruker AVANCE 500 spectrometer. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. The analysis of the crude reaction mixture was carried out on the Varian 4000 GC/MS and 1200 LC. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300–400 m).

General procedure for the copper-catalyzed decarboxylative selenation of aromatic carboxylic acids with diselenide

A 25 mL Schlenk tube equipped with a stir bar was charged with 2-nitrobenzoic acid (0.2 mmol), diphenyl diselenide (0.3 mmol), $Cu(OAc)_2$ (15 mol%), 1,10-phen (15 mol%), K_2CO_3 (0.6 mmol) and 2 mL toluene. The tube was fitted with a rubber septum, then it was evacuated and refilled with dioxygen three times, and then the septum was replaced by a Teflon screwcap under an oxygen flow. The reaction mixture was stirred at 150 °C for 24 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether and filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (20 mL) and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

Characterization data of compounds 3, 4 and 5

(4-Methoxy-2-nitrophenyl)(phenyl)selane (3a). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (56.8 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 2.8 Hz, 1H), 7.69–7.67 (m, 2H), 7.50–7.47 (m, 1H), 7.45–7.42 (m, 2H), 6.93 (dd, J = 9.0, 2.8 Hz,

1H), 6.86 (d, J = 9.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 146.1, 137.3, 131.1, 130.0, 129.7, 128.5, 126.1, 122.2, 109.3, 55.9. HRMS (TIC): calcd for $C_{13}H_{11}NO_3Se$ $[M + H]^+$ 309.9977, found 309.9976.

(2-Nitrophenyl)(phenyl)selane[7h] (3b). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (47.9 mg, 86% yield), mp 79–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 1H), 7.70–7.69 (m, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.31–7.24 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.6, 137.4, 135.8, 133.6, 130.3, 130.1, 129.9, 128.2, 126.0, 125.7. HRMS (TIC): calcd for $C_{12}H_9NO_2Se$ $[M + H]^+$ 279.9872, found 279.9870.

(5-Methyl-2-nitrophenyl)(phenyl)selane (3c). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (52.7 mg, 90% yield), mp 100–101 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.4 Hz, 1H), 7.71–7.69 (m, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.05 (d, J = 8.4 Hz, 1H), 6.74 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.0, 143.6, 137.4, 135.8, 130.3, 130.0, 129.8, 128.2, 126.8, 126.0, 21.6. HRMS (TIC): calcd for $C_{13}H_{11}NO_2Se$ $[M + H]^+$ 294.0028, found 294.0027.

(2-Nitro-4-(trifluoromethyl)phenyl)(phenyl)selane (3d). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (49.9 mg, 72% yield), mp 79–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.71–7.69 (m, 2H), 7.57–7.54 (m, 1H), 7.51–7.48 (m, 3H), 7.13 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$):δ 145.2, 141.3, 137.3, 131.2, 130.4, 129.4 (d, J_F = 3.3 Hz), 128.4 (q, J_F = 34.4 Hz), 127.4, 126.9, 123.0 (d, J_F = 272.2 Hz), 123.2 (q, J_F = 4.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.8 (s, 3F). HRMS (TIC): calcd for $C_{13}H_8F_3NO_2Se$ $[M + H]^+$ 347.9745, found 347.9744.

(2-Methyl-6-nitrophenyl)(phenyl)selane (3e). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (39.8 mg, 68% yield), mp 107–108 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.58 (m, 1H), 7.42–7.36 (m, 2H), 7.26–7.20 (m, 5H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 133.7, 131.3, 129.4, 129.1, 127.2, 124.2, 121.1, 23.9. HRMS (TIC): calcd for $C_{13}H_{11}NO_2Se$ $[M + H]^+$ 294.0028, found 294.0027.

(4-Bromo-2-nitrophenyl)(phenyl)selane (3f). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (52.8 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 2.1 Hz, 1H), 7.70–7.68 (m, 2H), 7.54–7.51 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 8.7, 2.1 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.9, 137.4, 136.5, 135.1, 131.6, 130.2, 130.1, 128.7, 127.7, 118.8. HRMS (TIC): calcd for $C_{12}H_8BrNO_2Se$ $[M + H]^+$ 357.8977, found 357.8978.

(3-Chloro-2-nitrophenyl)(phenyl)selane (3g). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (41.9 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.59 (m, 2H), 7.43–7.40 (m, 1H), 7.38–7.33 (m, 3H), 7.18 (t, J = 8.0 Hz, 1H), 7.14 (dd, J = 8.0, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.6, 131.7, 131.2, 129.9, 129.4, 129.3, 129.0, 128.2, 126.5. HRMS (TIC): calcd for $C_{12}H_8ClNO_2Se$ $[M + H]^+$ 313.9482, found 313.9484.

(5-Fluoro-2-nitrophenyl)(phenyl)selane (3h). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (49.8 mg, 84% yield), mp 92–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (dd, J = 9.1, 5.1 Hz, 1H), 7.71 (m, 2H), 7.56–7.53 (m, 1H), 7.51–7.48 (m, 2H), 6.97–6.93 (m, 1H), 6.62 (dd, J = 9.4, 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3 (d, J_F = 257.6 Hz), 141.8, 139.9 (d, J_F = 8.7 Hz), 137.4, 130.4, 128.7 (d, J_F = 10.4 Hz), 127.7, 116.6 (d, J_F = 26.9 Hz), 113.4, 113.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −102.6 (s, 1F). HRMS (TIC): calcd for $C_{12}H_8FNO_2Se$ $[M + H]^+$ 297.9777, found 297.9775.

(2-Fluoro-6-nitrophenyl)(phenyl)selane (3i). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (36.8 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.41–7.37 (m, 1H), 7.33–7.27 (m, 3H), 7.20 (t, J = 8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5 (d, J_F = 251.2 Hz), 152.4, 133.5, 129.9 (q, J_F = 3.8 Hz), 129.3, 129.2, 129.0 (d, J_F = 9.0 Hz), 128.4, 120.3 (d, J_F = 25.7 Hz), 116.9 (d, J_F = 24.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ −93.8 (s, 1F). HRMS (TIC): calcd for $C_{12}H_8FNO_2Se$ $[M + H]^+$ 297.9777, found 297.9776.

(2,6-Difluorophenyl)(phenyl)selane (3j). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (29.7 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.42 (m, 2H), 7.36–7.30 (m, 1H), 7.23–7.22 (m, 3H), 6.96–6.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2 (d, J_F = 247.1 Hz), 163.1 (d, J_F = 247.1 Hz), 131.9, 131.5, 131.3 (t, J_F = 10.0 Hz), 130.0, 129.2, 127.3, 111.6 (q, J_F = 5.3 Hz), 105.8 (t, J_F = 26.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ −98.5 (s, 2F). HRMS (TIC): calcd for $C_{12}H_8F_2Se$ $[M + H]^+$ 270.9832, found 270.9833.

Phenyl(2-(phenylselanyl)phenyl)methanone (3k). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (26.4 mg, 39% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 7.4 Hz, 2H), 7.64 (d, J = 6.6 Hz, 2H), 7.58–7.57 (m, 2H), 7.49–7.46 (m, 2H), 7.39–7.34 (m, 3H), 7.27–7.19 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.6, 137.7, 137.5, 137.0, 136.1, 132.6, 131.8, 131.6, 131.5, 130.1, 129.5, 128.5, 128.3, 125.0. HRMS (TIC): calcd for $C_{19}H_{14}OSe$ $[M + H]^+$ 339.0283, found 339.0284.

(Perfluorophenyl)(phenyl)selane (3l). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (45.4 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.52 (m, 2H), 7.32–7.25 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1–148.0 (m), 146.2–146.0 (m), 143.0–142.8 (m), 140.9–140.8 (m), 138.7–138.4 (m), 136.6–136.3 (m), 133.4, 129.5, 128.5, 103.7–103.2 (m). ^{19}F NMR (470 MHz, $CDCl_3$): δ −126.0 (d, J_F = 26.5 Hz, 2F), −151.5 (t, J_F = 21.3 Hz, 1F), −160.0–160.1 (m, 2F). HRMS (TIC): calcd for $C_{19}H_{14}OSe$ $[M + H]^+$ 324.9550, found 324.9551.

2,6-Dipheylselanylpyridine (3m). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (47.2 mg, 58% yield), mp 178–179 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 7.3 Hz, 4H), 7.51–7.48 (m, 2H), 7.45–7.42 (m, 4H), 6.72 (t, J = 7.8 Hz, 1H), 6.40 (d, J = 7.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 137.4, 130.1, 129.9,

126.2, 125.5, 120.2. HRMS (TIC): calcd for $C_{17}H_{13}NOSe_2$ $[M + H]^+$ 391.9451, found 391.9455.

3-Methyl-2-(phenylselanyl)benzo[*b*]thiophene (3n). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (46.2 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.35–7.34 (m, 2H), 7.32–7.29 (m, 1H), 7.25–7.20 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 140.5, 130.8, 130.5, 129.4, 129.1, 126.9, 125.2, 124.7, 122.5, 119.7, 111.3, 9.9. HRMS (TIC): calcd for $C_{15}H_{12}SSe$ $[M + H]^+$ 304.9898, found 304.9897.

3-Methyl-2-(phenylselanyl)benzofuran (3o). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (46.1 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.35–7.33 (m, 2H), 7.31–7.28 (m, 1H), 7.24–7.23 (m, 1H), 7.21–7.18 (m, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 140.6, 130.8, 130.5, 129.4, 129.2, 126.9, 125.2, 124.7, 122.5, 119.7, 111.3, 9.9. HRMS (TIC): calcd for $C_{15}H_{12}OSe$ $[M + H]^+$ 289.0126, found 289.0124.

4-Methyl-2-phenyl-5-(phenylselanyl)thiazole (3p). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (40.3 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91–7.89 (m, 2H), 7.43–7.41 (m, 3H), 7.32–7.30 (m, 2H), 7.25–7.19 (m, 3H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 159.8, 133.3, 132.3, 130.3, 129.9, 129.4, 129.0, 126.9, 126.4, 113.3, 16.7. HRMS (TIC): calcd for $C_{12}H_{19}NSSe$ $[M + H]^+$ 332.0007, found 332.0009.

(3-Bromophenyl)(4-methoxy-2-nitrophenyl)selane (4a). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (61.1 mg, 79% yield), mp 115–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 2.7 Hz, 1H), 7.81–7.80 (m, 1H), 7.77–7.56 (m, 1H), 7.37–7.32 (m, 2H), 6.98 (dd, J = 9.0, 2.8 Hz, 1H), 6.81 (d, J = 8.9 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 146.4, 139.1, 133.8, 131.7, 131.6, 131.4, 130.9, 128.6, 124.3, 122.4, 109.4, 55.9. HRMS (TIC): calcd for $C_{13}H_{10}BrNO_3Se$ $[M + H]^+$ 387.9082, found 387.9080.

(4-Chlorophenyl)(4-methoxy-2-nitrophenyl)selane (4b). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (51.4 mg, 75% yield), mp 97–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 2.7 Hz, 1H), 7.62–7.61 (m, 2H), 7.42–7.40 (m, 2H), 6.96 (dd, J = 9.0, 2.9 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 146.2, 138.6, 136.3, 130.9, 130.3, 126.7, 125.4, 122.3, 109.3, 55.9. HRMS (TIC): calcd for $C_{13}H_{10}ClNO_3Se$ $[M + H]^+$ 343.9587, found 343.9588.

(4-Methoxy-2-nitrophenyl)(4-(trifluoromethoxy)phenyl)selane (4c). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (55.0 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 7.9 Hz, 1H), 6.98 (d, J = 8.7 Hz, 1H), 6.85 (d, J = 8.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 150.4, 146.3, 138.9, 132.6, 132.1, 130.9, 126.8, 125.1, 122.3, 122.2, 120.3 (q, J_F = 257.9), 109.5, 55.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ −57.7 (s, 3F). HRMS (TIC): calcd for $C_{14}H_{10}F_3NO_3Se$ $[M + H]^+$ 377.9851, found 377.9852.

(4-Bromophenyl)(2-nitrophenyl)selane (4d). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (55.0 mg, 77% yield), mp 115–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (dd, J = 8.1, 1.5 Hz, 1H), 7.60–7.56 (m, 4H), 7.36–7.28 (m, 2H), 6.97 (dd, J = 8.0, 1.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.6, 138.9, 135.2, 133.8, 133.3, 130.1, 127.1, 126.2, 126.0, 124.9. HRMS (TIC): calcd for $C_{12}H_8BrNO_2Se$ $[M + H]^+$ 357.8977, found 357.8976.

(4-Methoxy-2-nitrophenyl)(naphthalen-1-yl)selane (4e). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (64.6 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 1H), 8.05 (dd, J = 6.9 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.84 (s, 1H), 7.55–7.47 (m, 3H), 6.75–6.73 (m, 1H), 6.57 (d, J = 8.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 146.1, 137.7, 135.2, 134.3, 131.4, 131.0, 128.8, 128.1, 127.6, 127.5, 126.3, 125.6, 122.2, 109.4, 55.8. HRMS (TIC): calcd for $C_{17}H_{13}NO_3Se$ $[M + H]^+$ 360.0134, found 360.0133.

Methyl (2-nitrophenyl)selane (4f). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (36.5 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.55–7.33 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.5, 134.4, 133.6, 128.4, 126.3, 125.1, 7.3. HRMS (TIC): calcd for $C_7H_7NO_2Se$ $[M + H]^+$ 217.9715, found 217.9717.

Methyl (2-nitro-4-(trifluoromethyl)phenyl)selane (4g). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (40.0 mg, 70% yield), mp 80–81 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.2, 139.9, 129.5 (q, J_F = 3.2 Hz), 129.3, 128.0 (q, J_F = 34.3 Hz), 123.0 (d, J_F = 270.3 Hz), 123.5 (q, J_F = 4.0 Hz), 7.80. ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.7 (s, 3F). HRMS (TIC): calcd for $C_8H_6F_3NO_2Se$ $[M + H]^+$ 285.9589, found 285.9591.

(5-Fluoro-2-nitrophenyl)(methyl)selane (4h). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (24.9 mg, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39–8.36 (m, 1H), 7.14 (d, J = 9.2 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (q, J_F = 258.0 Hz), 142.7, 138.4 (q, J_F = 8.9 Hz), 129.0 (d, J_F = 10.4 Hz), 115.1 (q, J_F = 26.0 Hz), 112.6 (q, J_F = 23.6.0 Hz), 7.83. ^{19}F NMR (470 MHz, $CDCl_3$): δ −102.9 (s, 1F). HRMS (TIC): calcd for $C_7H_6FNO_2Se$ $[M + H]^+$ 235.9621, found 235.9623.

(4-Methoxy-2-nitrophenyl)(methyl)selane (4i). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (46.9 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 2.8 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 7.18 (dd, J = 8.9, 2.8 Hz, 1H), 3.88 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 146.9, 129.1, 124.7, 122.3, 109.7, 55.9, 7.3. HRMS (TIC): calcd for $C_8H_6F_3NO_2Se$ $[M + H]^+$ 285.9821, found 285.9823.

(2-(Methylselanyl)phenyl)(phenyl)methanone (4j). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (24.8 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77–7.75 (m, 2H), 7.59–7.52 (m, 3H),

7.48–7.43 (m, 3H), 7.24 (t, J = 7.5 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8, 137.8, 136.3, 132.5, 131.7, 131.6, 130.0, 129.5, 128.3, 124.7, 124.5, 7.24. HRMS (TIC): calcd for $C_{14}H_{12}OSe$ $[M + H]^+$ 277.0126, found 277.0124.

3-Methyl-2-(methylselanyl)benzo[*b*]thiophene (4k). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (37.2 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.36–7.28 (m, 2H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7, 139.9, 135.6, 124.3, 124.1, 123.1, 121.9, 121.8, 13.7, 10.3. HRMS (TIC): calcd for $C_{10}H_{10}SSe$ $[M + H]^+$ 242.9741, found 242.9743.

3-Methyl-2-(methylselanyl)benzofuran (4l). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (38.4 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.41 (m, 2H), 7.26–7.20 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 141.4, 129.5, 124.3, 122.3, 121.1, 119.1, 110.8, 9.6, 8.1. HRMS (TIC): calcd for $C_{10}H_{10}OSe$ $[M + H]^+$ 226.9970, found 226.9971.

4-(3-Methylbenzo[*b*]thiophen-2-ylselanyl)benzonitrile (4m). Following the general procedure, using petroleum ether as the eluant afforded a yellow solid (42.7 mg, 65% yield), mp 125–126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.78 (m, 2H), 7.43–7.43 (m, 4H), 7.28–7.27 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.9, 140.5, 140.4, 139.3, 132.5, 128.9, 125.7, 124.5, 122.9, 122.2, 118.9, 118.6, 109.8, 13.9. HRMS (TIC): calcd for $C_{16}H_{11}NSSe$ $[M + H]^+$ 329.9850, found 329.9851.

2-(4-Chlorophenylselanyl)-3-methylbenzo[*b*]thiophene (4n). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (48.0 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.39–7.33 (m, 2H), 7.23 (d, J = 7.7 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6, 139.6, 138.8, 133.0, 131.6, 130.4, 129.4, 125.2, 124.3, 122.7, 122.1, 121.4, 13.9. HRMS (TIC): calcd for $C_{15}H_{11}ClSSe$ $[M + H]^+$ 338.9508, found 338.9510.

4-(3-Methylbenzofuran-2-ylselanyl)benzonitrile (4o). Following the general procedure, using petroleum ether as the eluant afforded a yellow liquid (50.7 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.57 (m, 1H), 7.49–7.45 (m, 3H), 7.38–7.35 (m, 1H), 7.33–7.28 (m, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 138.9, 132.6, 129.5, 128.8, 126.4, 125.8, 122.9, 119.9, 118.5, 111.4, 110.2, 9.9. HRMS (TIC): calcd for $C_{16}H_{11}NOSe$ $[M + H]^+$ 314.0079, found 314.0077.

2-(4-Chlorophenylselanyl)-3-methylbenzofuran (4p). Following the general procedure, using petroleum ether as the eluant afforded a colorless liquid (56.0 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.33–7.30 (m, 1H), 7.28–7.25 (m, 3H), 7.17 (d, J = 8.3 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 140.0, 133.2, 131.8, 129.5, 129.0, 128.9, 125.4, 124.9, 122.7, 119.8, 111.4, 9.9. HRMS (TIC): calcd for $C_{15}H_{11}BrOSe$ $[M + H]^+$ 366.9231, found 366.9230.

2-(4-Bromophenylselanyl)-3-methylbenzofuran (4q). Following the general procedure, using petroleum ether as the eluant afforded a colorless liquid (43.2 mg, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.33–7.30 (m, 3H), 7.26–7.25 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 139.9, 132.4, 132.0, 129.8, 129.0, 125.4, 124.9, 122.6, 121.2, 119.8, 111.3, 9.9. HRMS (TIC): calcd for $C_{15}H_{11}BrOSe$ $[M + H]^+$ 366.9231, found 366.9230.

1,2-Bis(phenylselanyl)benzene[6b] (5a). To an 25 mL Schlenk reaction tube charged with 2-(phenylselanyl)aniline (0.5 mmol), diphenyl diselenide (1.0 mmol), *t*BuONO (1.1 mmol), eosin Y (0.01 mmol) and 2 ml DMSO was stirred under blue-LED light at room temperature for 2 hours (TLC) and the product was extracted with ethyl acetate. The extract was washed with water (10 mL) and brine (10 mL). Then the organic phase was dried over Na_2SO_4 and evaporated to leave the crude product, and the crude product was extracted with EtOAc and purified by flash chromatography (petroleum ether) to obtain a yellow solid (41.3 mg, 53% yield), mp 90–91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–7.51 (m, 4H), 7.31–7.31 (m, 6H), 7.20–7.18 (m, 2H), 7.06–7.04 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9, 134.1, 134.0, 133.0, 130.7, 129.5, 127.9, 127.9. HRMS (TIC): calcd for $C_8H_{14}Se_2$ $[M + H]^+$ 390.9499, found 390.9498.

(2-Iodophenyl)(phenyl)selane[19] (5b). A 25 mL Schlenk tube equipped with a stir bar was charged with *p*-TsOH·H_2O (1.5 mmol), 2-(phenylselanyl) aniline (0.5 mmol) and MeCN (2.0 mL). The resulting suspension of amine salt was cooled to 5–10 °C and to this was added, gradually, a solution of $NaNO_2$ (1.0 mmol) and KI (1.25 mmol) in H_2O (0.3 mL). The reaction mixture was stirred for 10 min, then allowed to cool to room temperature and stirred for 30 min. The crude product was extracted with EtOAc and purified by flash chromatography (petroleum ether) to obtain a brown solid (61.9 mg, 86% yield), mp 76–77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.3 Hz, 2H), 7.45–7.36 (m, 3H), 7.11 (t, J = 7.4 Hz, 1H), 6.89–6.83 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 139.4, 135.8, 130.4, 130.3, 129.9, 128.8, 128.7, 127.5, 99.6. HRMS (TIC): calcd for $C_{15}H_{11}BrOSe$ $[M + H]^+$ 360.8987, found 360.8988.

11-Methyldibenzo-(*b*,*f*)-1,4-selenazepine (5c). A 25 mL Schlenk tube equipped with a stir bar was charged with 2-(phenylselanyl)aniline (0.5 mmol), and acetyl chloride (1.5 mmol) was added slowly to the solution, and then the temperature was increased spontaneously to ambient temperature, and monitored by TLC. Then, water (20 mL) was added to the mixture. The organic layer was washed with brine (1 × 30 mL), dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. Polyphosphoric acid (PPA) (2.0 g) and phosphorus oxychloride (1.5 mmol) were added to the residue. The reaction mixture was heated at 120 °C for 3 h and poured into ice-cold water, then treated with aqueous ammonia and extracted with CH_2Cl_2 (3 × 10 mL), dried with anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was extracted with EtOAc and purified by flash chromatography (petroleum ether : EtOAc = 2 : 98) to obtain a colorless solid (42.0 mg, 77% yield), mp 125–126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98–7.97

(m, 1H), 7.56 (d, J = 7.4 Hz, 1H), 7.29–7.23 (m, 3H), 6.99–6.98 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.8, 149.5, 139.2, 138.1, 134.3, 132.8, 131.9, 131.5, 128.8, 124.9, 119.0, 114.8, 113.6, 27.1. HRMS (TIC): calcd for $C_{14}H_{11}NSe$ $[M + H]^+$ 274.0130, found 274.0129.

10*H*-Phenoselenazine[20] (5d). A 25 mL Schlenk tube equipped with a stir bar was charged with 2-(phenylselanyl) aniline (0.5 mmol), triphenylphosphine (1.25 mmol) and 2 mL 1,2-dichlorobenzene. The tube was fitted with a rubber septum, and then it was evacuated and refilled with N_2 three times, then the septum was replaced by a Teflon screwcap under a N_2 flow. The reaction mixture was stirred at 180 °C for 24 h. The crude product was extracted with EtOAc and purified by flash chromatography (petroleum ether : EtOAc = 2 : 98) to obtain a colorless solid (33.6 mg, 68% yield), mp 194–195 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.09 (d, J = 7.5 Hz, 2H), 7.03 (t, J = 7.7 Hz, 2H), 6.78–6.75 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.1, 128.8, 127.8, 122.1, 115.1, 111.5. HRMS (TIC): calcd for $C_{12}H_9NSe$ $[M + H]^+$ 247.9973, found 247.9972.

Conflicts of interest

The authors declare no competing financial interest.

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