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Meyer–Schuster-Type Rearrangement of Propargylic Alcohols into α-Selenoenals and -enones with Diselenides

Yong-Liang Ban, Long You, Kai-Wen Feng, Fei-Cen Ma, Xiao-Ling Jin, and Qiang Liu*

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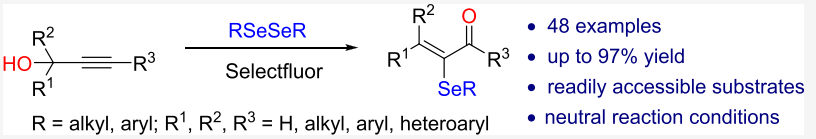


ABSTRACT: We describe a mild and broadly applicable protocol for the preparation of a diverse array of multisubstituted α-selenoenals and -enones from readily accessible propargylic alcohols and diselenides. The transformation proceeds via the Selectfluor-promoted selenirenium pathway, which enables selenenylation/rearrangement of a variety of propargylic alcohols. Gram-scale experiments showed the potential of this synergistic protocol for practical application.

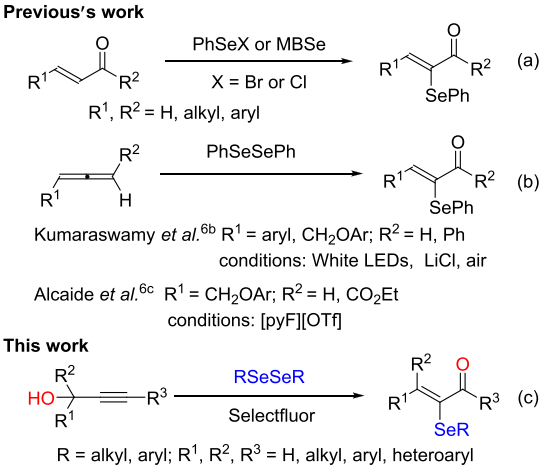
INTRODUCTION

Organoselenium compounds are of great importance because of their biological activities and physical as well as chemical properties.[1] The introduction of selenium groups into organic molecules, especially for natural building blocks, is of significant synthetic value.[2] Consequently, reactions that involve α-organoselenium motif incorporation with sustainable and green methods have attracted widespread concern.

α,β-Unsaturated carbonyls have received intensive investigations due to their synthetic versatility, prominent pharmacological and biological activities.[3] α-Selenoenals and -enones have immunomodulatory and antioxidant properties.[4] For example, 3-methyl-1-phenyl-2-(phenylseleno)oct-2-en-1-one could improve cellular integrity and exhibit superior NO scavenger activity.[4a] Modern approaches for the synthesis of α-selenoenals and -enones involve directly introduction of selenium groups into α,β-unsaturated carbonyls by using unstable phenylselenyl chloride (bromide) or presynthetic selenylating agents (Scheme 1a);[5] Due to stability and operational convenience, diselenides were used to prepare α-selenoenals and -enones as selenylating agents (Scheme 1b).[6] For instance, Kumaraswamy et al. established a visible-light-promoted selenofunctionalization of allenes with diphenyl diselenide for the generation of α-selenoenals and -enones.[6b] Recently, Alcaide and co-workers developed a 1-fluoropyridinium-involved oxidative strategy to synthesize α-phenylselenoenals from allenylmethyl aryl ethers and diphenyl diselenide.[6c] Although these methods have provided access to a range of simple nonhindered α-selenoenals and -enones, the development of mild and highly efficient methods for the production of multisubstituted α-selenoenals and -enones remains a significant challenge in organic synthesis.

The combination of N–F reagents and diselenides to generate electrophilic selenenium ions has been applied in selenenylation reactions.[7] However, studies using the *in situ* generated selenenium ions to attack propargylic alcohols of C–C triple bond (C≡C) are still very limited.[7a] The Meyer–Schuster rearrangement represents an atom-economical approach to the synthesis of α,β-unsaturated carbonyls from readily accessible propargylic alcohols.[8] Most recently, Lüdtke and co-workers established a Meyer–Schuster-type rearrangement reaction of propargylthioalkynes with *in situ* generated PhSeI for the production of α-selanyl-α, β-unsaturated

Scheme 1. Methodologies to Prepare α-Selenoenals and -enones



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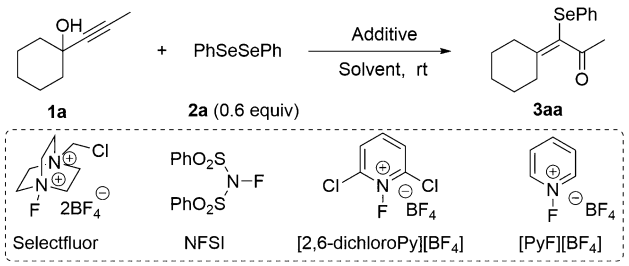
thioesters.[9] The rearrangement required presynthesis of PhSeI using 2 equiv of diselenides and I_2, and only electron-rich propargylthioalkynes were successfully explored as the substrates with the aid of Cs_2CO_3.

As a continuation of our studies on diselenide-mediated functionalization,[10] we recently harnessed selenium-π-acid,[7g] which is electrophilic interactions between selenenium and π bond, to develop an efficient strategy for the preparation of oxazole acetals.[10c] Consequently, we speculated that *in situ* generated PhSeX electrophilic species should attack the carbon−carbon triple bond of propargylic alcohols, which would undergo seleno-rearrangement to deliver α-selenoenals and -enones.[7e,11] Herein, we disclose the successful implementation of selenenylation/rearrangement of propargylic alcohols and present a broadly applicable protocol for the synthesis of multisubstituted α-selenoenals and -enones under neutral reaction conditions at room temperature.

RESULTS AND DISCUSSION

We started our preliminary investigation by reacting 1-(1-propynyl)cyclo-hexanol **1a** with diphenyl diselenide **2a** in the presence of 0.2 equiv of Selectfluor at rt. Gratifyingly, the corresponding α-selenoenone **3a** was isolated in 26% yield after 12 h (Table 1, entry 1). Screening of other N−F type

Table 1. Optimization of the Reaction Conditions[a]



entry	additives (equiv)	solvent	yield (%)
1	Selectfluor (0.2)	CH_3CN	26
2	NFSI (0.2)	CH_3CN	24
3	[2,6-dichloroPy][BF_4] (0.2)	CH_3CN	7
4	[PyF][BF_4] (0.2)	CH_3CN	18
5	Selectfluor (0.2)	CH_3OH	ND
6	Selectfluor (0.2)	H_2O	ND
7	Selectfluor (0.2)	acetone	5
8	Selectfluor (0.2)	DCM	18
9	Selectfluor (0.4)	CH_3CN	65
10	Selectfluor (0.6)	CH_3CN	95
11	Selectfluor (1.0)	CH_3CN	94
12		CH_3CN	ND
13[c]	Selectfluor (0.6)	CH_3CN	82

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.12 mmol), and additives in 2.0 mL of CH_3CN, the reaction mixture was stirred at rt for 12 h, unless otherwise noted. ND = not detected. [c]Under an argon atmosphere.

reagents including NFSI, [2,6-dichloroPy][BF_4] and [PyF][BF_4] suggested that Selectfluor is the optimal additive (entries 2−4). Subsequently, other solvents such as MeOH, H_2O, acetone and DCM were tested. CH_3CN is still the optional solvent (entries 5−8). Concerning the additive loading, 0.6 equiv of Selectfluor was found to be optimal (entries 9−11). Control experiments established that Selectfluor is essential for the reaction (entry 12); The presence of air has a beneficial effect on the reaction, which may be due to benzeneselenenic acid PhSeOH also as a selenenium electrophilic species, and PhSeOH generated from diphenyl diselenide in the air (entry 13).[12]

After establishing the optimized reaction conditions for selenofunctionalization of propargylic alcohols, the scope of the reaction was explored with different diselenides **2** (Scheme 2). A variety of diaryl diselenides was tolerated, thus efficiently transforming into the desired α-selenoenones **3ab**-**3af** in moderate to good yields. Several valuable functional groups such as methoxy (**2b**), fluoro (**2d**), cyano (**2e**), and trifluoro (**2f**) at different positions of diaryl diselenides were compatible. Importantly, dibenzyl and dialkyl diselenides were good reaction partners and provided α-selenoenones (**3ag**−**3ai**) in good yields.

Next, a diverse array of propargylic alcohols was employed as substrates to further broaden the scope of this reaction (Schemes 3 and 4). First, we tested alkynyl cyclohexanols with different substitutions, α-selenoenones **3ba**−**3fa** were formed in moderate to high yields. Moreover, adamantane-substituted propargylic alcohol **1g** was also tolerated in this reaction, furnishing the desired α-selenoenone **3ga** in 61% yield. Subsequently, several different sizes of cyclic propargylic alcohols also proceeded smoothly and furnished α-selenoenone derivatives **3ha**−**3ka** in excellent yields upon isolation. For phenyl and alkyl-substituted nonterminal propargylic alcohols, the corresponding products **3la** to **3pa** could be obtained in good yields with poor to excellent *Z*/*E* ratios. Moreover, *N*-methylisatin modificatory propargylic alcoholwas found to be successful and provided the desired α-selenoenone **3qa** with 81% yield, exclusively as the *Z*-isomer. Given the pharmaceutical relevance of selenium functional motifs, we further sought to showcase our novel procedure by selectively appending diphenyl diselenide **2a** onto theobromine as well as estrone derivatives; As expected, the corresponding α-selenoenones **3ra** and **3sa** were isolated in 95% and 43% yields although the former was obtained with a *Z*/*E* ratio of 1.0.

To further generalize the broad view of our current protocol, we next explored the substrate scope by employing various terminal propargylic alcohols **4** (Scheme 4). Different substituents in the *para*-position of the benzene ring of 1-phenylprop-2-yn-1-ols reacted efficiently under the typical reaction conditions to deliver the corresponding products **5aa**−**5fa** in poor to excellent yields. The structure of **5ba** was already unambiguously assigned by its single-crystal X-ray analysis (CCDC 2022161). This method exhibited high tolerance for bearing the hydroxyl group, giving rise to the desired α-selenoenal **5ca** in 97% yield. Moreover, when the β-naphthyl propargyl alcohol was used, α-selenoenal **5ga** was isolated in 60% yield with an excellent *Z*/*E* ratio. Afterward, terminal propargylic alcohols with phenyl and alkyl substitutions were tested under the standard reaction conditions, and the corresponding products of α-selenoenal **5ha**−**5ra** were isolated in good to high yields.

The seleno rearrangement proved to be scalable and could be run at gram-scale without significant impact on yield. For instance, the reaction between propargylic alcohol **1a** or **5j** (10 mmol) and diselenide **2a** (6 mmol) in the presence of Selectfluor (6 mmol) afforded the corresponding products in 94% and 77% isolated yields, respectively (Scheme 5a,b). Furthermore, α-selenoenal **5ja** could be transformed into

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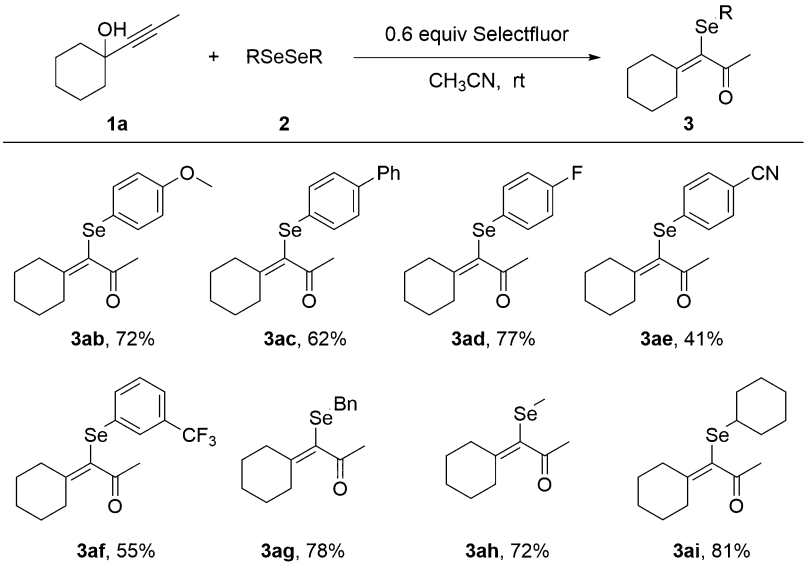
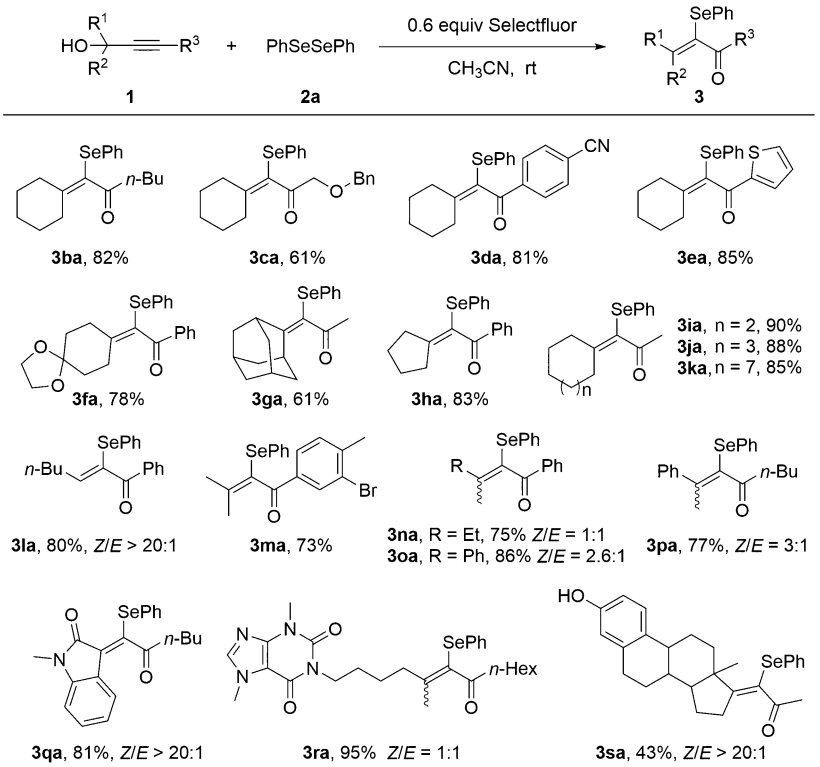
Scheme 2. Scope of Diselenides[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.12 mmol) and Selectfluor (0.12 mmol) in CH_3CN (2.0 mL), the reaction mixture was stirred at rt for 12 h.

Scheme 3. Scope of Nonterminal Propargylic Alcohols[a]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.12 mmol) and Selectfluor (0.12 mmol) in CH_3CN (2.0 mL), the reaction mixture was stirred at rt for 12 h.

selenoxide **6** with a yield of 95% upon treatment with H_2O_2 (Scheme 5c).[10b]

Having established the scope of the reaction, we turned our attention to preliminary mechanistic investigations (Scheme 6). First, typical radical scavengers (TEMPO or BHT) have no significant inhibition effect on the Selectfluor-promoted selenenylation/rearrangement (Scheme 6A). Unexpectedly, the seleno rearrangement of **1a** thoroughly inhibited, and 1-diphenyl-2-(phenylselanyl)ethan-1-ol **7** was obtained in 57% yield when 1,1-diphenylethylene (**DPE**) was introduced into the reaction (Scheme 6B). These results indicate that the involvement of any radical species may be ruled out and the reaction might produce $PhSe^+$ cation species from diphenyl diselenide **2a** and Selectfluor.[13]

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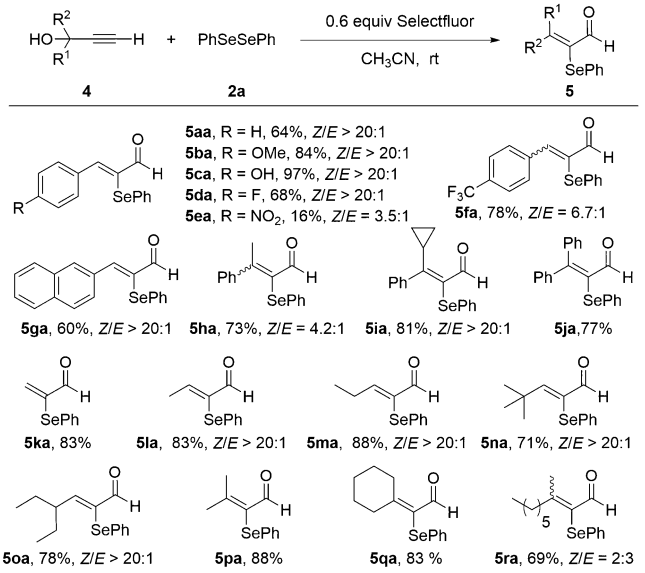
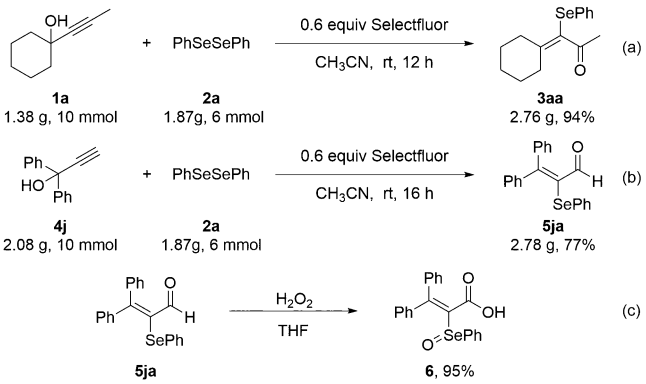
Scheme 4. Scope of Terminal Propargylic Alcohols[a]



[a]Reaction conditions: **4** (0.2 mmol), **2a** (0.12 mmol), and Selectfluor (0.12 mmol) in CH_3CN (2.0 mL), the reaction mixture was stirred at rt for 12 h.

Scheme 5. Gram-Scale Selenenylation/Rearrangement of 1a, 5j, and Derivatization of 5ja



Based on the mechanistic studies and previous reports,[6a,7,10c,14] a plausible mechanism for selenofunctionalization/rearrangement of propargylic alcohols is outlined in Scheme 6C. PhSeSePh is oxidized by Selectfluor to give electrophilic PhSeX species **I** and PhSeF. Subsequently, the electrophilic attack of $PhSe^+$ across the triple bond of **4b** generates intermediate **II**, which would instantly undergo an intramolecular hydroxyl attack to give oxetene intermediate **III**.[15] Due to oxetene III undergoing thermal conrotatory 4π electrocyclic ring-opening tends to rotate outward,[15d] the *p*-methoxyphenyl group should stay away from the carbonyl group during C−O bond cleavage of the strained oxetene **III**, resulting in the product **5ba**.

To further demonstrate the broad applicability of the selenenylation strategy, diverse substrates bearing alkyne moieties (**8**, **10** and **12**) were explored as shown in Scheme 7. The reactions occurred smoothly under identical conditions, giving the corresponding tandem selenenylation/cyclization products in 72% to 95% yields (**9**, **11**, and **13**). These results underscore the fact that the selenenylation using diselenide and Selectfluor indeed is powerful and thus represents a paradigm shift in selenenylation reactions.

CONCLUSIONS

We have disclosed a mild and highly efficient procedure for the synthesis of multisubstituted α-selenoenals and -enones from readily available propargylic alcohols and stable diselenides. The reaction proceeds via Selectfluor-promoted selenenylation and subsequent rearrangement. Moreover, the synergistic protocol is not restricted to propargylic alcohol but also applies to other substrates such as *o*-alkynylaniline and 2-alkynylphenols. Further applications aimed at broadening the strategy for other selenenylation/rearrangement reactions are currently underway.

EXPERIMENTAL SECTION

General Information and Methods. ^1H NMR, ^{13}C NMR, and ^{19}F NMR were recorded on a Bruker AM-400 MHz spectrometer (400, 100, and 376 MHz). Chemical shifts were reported in parts per million (δ) relative to $CDCl_3$ (7.26 ppm) or TMS (0.00 ppm) for ^1H NMR data and $CDCl_3$ (77.0 ppm) for ^{13}C NMR data or the peak of DMSO-d_6, defined at δ = 2.50 (^1H NMR) or δ = 39.5 (^{13}C NMR). Mass spectra were obtained on BrukerESQ6K4. The high-resolution mass spectra (HRMS) were measured on a TOF by ESI and performed on Bruker Daltonics APEXII 47e Specifications. The melting points were measured by WRX X-4B. Column chromatography was performed with silica gel (200−300 meshes). Thin-layer chromatography (TLC) was visualized using UV light. Unless otherwise noted, commercially available materials and all other reagents were used without further purification. Propargylic alcohols,[16] diselenides,[17] *o*-alkynylaniline,[18] and 2-alkynylphenols[19] were separately prepared by the previous reports.

General Procedure for the Synthesis of α-Selenoenals and -enones. A 10 mL reaction tube with a magnetic stirring bar was added propargylic alcohols (1.0 equiv, 0.2 mmol), diselenides **2** (0.6 equiv, 0.12 mmol), Selectfluor (0.6 equiv, 0.12 mmol), and CH_3CN (2 mL). The tube was equipped with a gas vent to allow air flow without solvent evaporation. Then, the reaction mixture was stirred at room temperature for 12 h. After completion of this reaction, the crude reaction mixture was purified by column chromatography on silica gel to give the corresponding product.

Gram-Scale Synthesis of 1a. A 100 mL round-bottom flask with a magnetic stirring bar was charged with diphenyl diselenide **2a** (1.87g, 6 mmol), Selectfluor (2.13g, 6 mmol) and 1-(prop-1-yn-1-yl)cyclohexan-1-ol **1a** (1.38g, 10 mmol) in CH_3CN (40 mL). The reaction mixture was stirred at room temperature, and the round-bottom flask was equipped with a gas vent to allow air flow without solvent evaporation. Then, the reaction was monitored after 12 h by TLC, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **3aa** in 94% yield (2.76 g).

Gram-Scale Synthesis of 4j. A 100 mL round-bottom flask with a magnetic stirring bar was added 1,1-diphenylprop-2-yn-1-ol **4j** (2.08g, 10 mmol), diphenyl diselenide **2a** (1.87g, 6 mmol), Selectfluor (2.13g, 6 mmol) and CH_3CN (40 mL). The round-bottom flask was equipped with a gas vent to allow air flow without solvent evaporation. Then, the reaction mixture was stirred at room temperature for 16 h. After completion of this reaction, the crude reaction mixture was purified by column chromatography on silica gel to give the desired product **5ja** in 77% yield (2.78 g).

Derivatization of 5ja. A mixture of α-selenoenal **5ja** (0.1 mmol) and 50% H_2O_2 (3 drops) in THF (2 mL) was stirred at room temperature until complete consumption of the starting material, as monitored by TLC. After the evaporation of the solvent, the residual crude product was purified by flash chromatography to give the desired product **6** in 95% yield.

*1-Cyclohexylidene-1-(phenylselanyl)propan-2-one (**3aa**):* yellow liquid, 55.6 mg (95% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−

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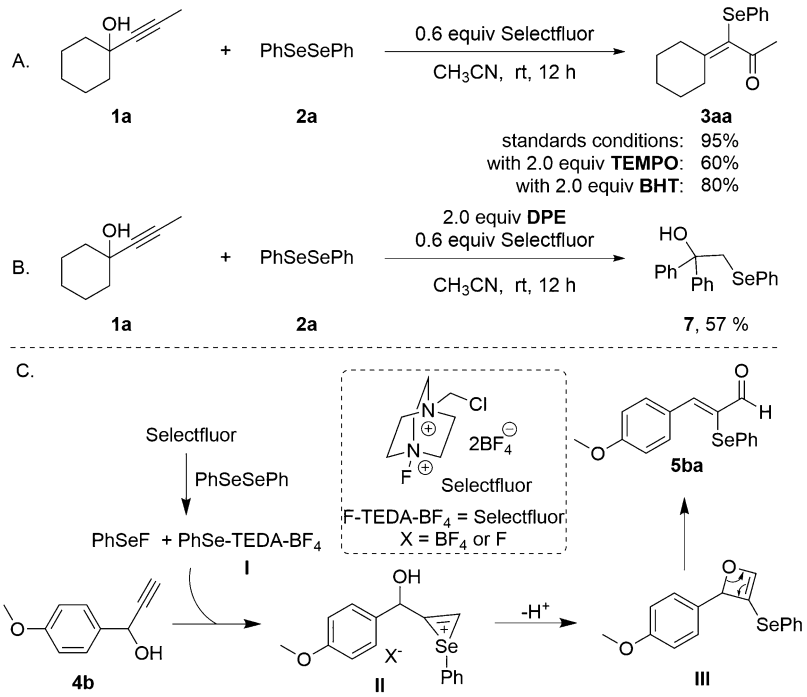
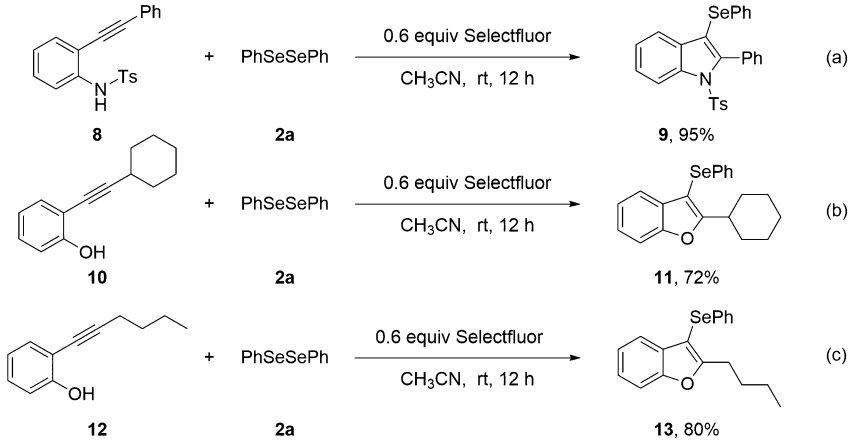
J. Org. Chem. 2021, 86, 5274−5283

Scheme 6. Control Experiments and Proposed Mechanism



Scheme 7. Selectfluor-Promoted Cyclization of *o*-Alkynylaniline and 2-Alkynylphenols



7.35 (m, 2H), 7.26−7.19 (m, 3H), 2.59 (t, J = 5.4 Hz, 2H), 2.41 (t, J = 5.6 Hz, 2H), 2.29 (s, 3H), 1.68−1.60 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9, 153.7, 130.8, 130.7, 129.2, 126.7, 123.8, 35.1, 33.3, 29.8, 28.4, 28.2, 26.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{19}OSe$ 295.0596, found 295.0593.

*1-Cyclohexylidene-1-((4-methoxyphenyl)selanyl)propan-2-one (**3ab**):* yellow liquid, 46.7 mg (72% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.58 (t, J = 5.4 Hz, 2H), 2.33 (t, J = 5.4 Hz, 2H), 2.24 (s, 3H), 1.67−1.58(m, 6H);$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.3, 159.1, 150.5, 133.9, 125.1, 120.0, 115.0, 55.2, 34.7, 33.3, 30.1, 28.3, 28.1, 26.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{21}O_2Se$ 325.0701, found 325.0700.

*1-([1,1′-Biphenyl]-4-ylselanyl)-1-cyclohexylidenepropan-2-one (**3ac**):* yellow liquid, 45.9 mg (62% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.50−7.47 (m, 2H), 7.45−7.41 (m, 4H), 7.36−7.32 (m, 1H), 2.63 (t, J = 5.8 Hz, 2H), 2.45 (t, J = 5.6 Hz, 2H), 2.34 (s, 3H), 1.69−1.62 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9, 153.9, 140.3, 139.7, 131.0, 129.9, 128.8, 127.9, 127.3, 126.9, 123.7, 35.1, 33.4, 29.8, 28.5, 28.2, 26.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{23}OSe$ 371.0909, found 371.0906.

*1-Cyclohexylidene-1-((4-fluorophenyl)selanyl)propan-2-one (**3ad**):* yellow liquid, 48.0 mg (77% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2H), 6.97−6.93 (m, 2H), 2.58 (t, J = 5.4 Hz, 2H), 2.38−2.35 (m, 2H), 2.27 (s, 3H), 1.65−1.58 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 201.8, 162.2 (d, J = 245.0 Hz), 152.6, 133.3 (d, J = 8.0 Hz), 124.9 (d, J = 3.0 Hz), 124.3, 116.5 (d, J = 22.0 Hz), 34.9, 33.3, 29.8, 28.4, 28.2, 26.2; ^{19}F NMR(376 MHz, $CDCl_3$) δ −114.97; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{17}FOSeNa$ 335.0321, found 335.0321.

*4-((1-Cyclohexylidene-2-oxopropyl)selanyl)benzonitrile (**3ae**):* yellow liquid, 25.9 mg (41% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50−7.47 (m, 2H), 7.42−7.40 (m, 2H), 2.57−2.54 (m, 2H), 2.46 (t, J = 6.0 Hz, 2H), 2.33 (s, 3H), 1.68−1.60 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.2, 157.3, 139.2, 132.5, 129.6, 121.8, 118.7, 109.7, 35.3, 33.4, 29.6, 28.5, 28.3, 26.1; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{18}NOSe$ 320.0548, found 320.0548.

*1-Cyclohexylidene-1-((4-(trifluoromethyl)phenyl)selanyl)propan-2-one (**3af**):* yellow liquid, 39.6 mg (55% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.38−7.32 (m, 1H), 2.58 (t, J = 5.6 Hz, 2H), 2.44 (t, J = 5.8 Hz, 2H), 2.31 (s, 3H), 1.71−1.58(m, 6H);$^{13}C\{^1H\}$ NMR (100 MHz,

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J. Org. Chem. 2021, 86, 5274−5283

$CDCl_3$) δ 201.4, 155.6, 133.3, 132.4, 131.5 (q, J = 32.0 Hz), 131.0 (q, J = 5.0 Hz), 129.6, 126.7 (q, J = 3.7 Hz), 123.7 (q, J = 271.3 Hz), 123.3 (q, J = 3.7 Hz), 122.7, 35.1, 33.4, 29.7, 28.5, 28.2, 26.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.83 (d, J = 3.8 Hz); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{17}F_3OSeNa$ 385.0289, found 385.0287.

*1-(Benzylselanyl)-1-cyclohexylidenepropan-2-one (**3ag**):* yellow liquid, 48.0 mg (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 4.4 Hz, 4H), 7.20−7.17 (m, 1H), 3.75 (s, 2H), 2.37 (s, 3H), 2.25−2.19 (m, 4H), 1.55−1.45 (m, 4H), 1.31−1.26 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 203.1, 151.0, 138.8, 129.1, 128.2, 126.7, 122.2, 33.8, 33.2, 31.3, 29.5, 28.1, 27.4, 26.1; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{20}OSeNa$ 331.0752, found 331.0751.

*1-Cyclohexylidene-1-(methylselanyl)propan-2-one (**3ah**):* yellow liquid, 33.4 mg (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49−2.43 (m, 2H), 2.38 (s, 3H), 2.26−2.21 (m, 2H), 1.99 (s, 3H), 1.65−1.53 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.9, 147.0, 123.6, 33.9, 33.1, 29.6, 28.1, 27.8, 26.2, 7.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{10}H_{17}OSe$ 233.0439, found 233.0441.

*1-Cyclohexylidene-1-(cyclohexylselanyl)propan-2-one (**3ai**):* yellow liquid, 48.6 mg (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96−2.89 (m, 1H), 2.52 (t, J = 5.6 Hz, 2H), 2.40 (s, 3H), 2.27 (t, J = 5.6 Hz, 2H), 1.98−1.92 (m, 2H), 1.72−1.70 (m, 2H), 1.61−1.54 (m, 7H), 1.49−1.40 (m, 2H), 1.35−1.23 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 203.6, 150.1, 122.9, 43.0, 34.3, 34.0, 33.2, 29.5, 28.4, 28.0, 26.7, 26.3, 25.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{25}OSe$ 301.1065, found 301.1066.

*1-Cyclohexylidene-1-(phenylselanyl)hexan-2-one (**3ba**):* yellow liquid, 55.1 mg (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.35 (m, 2H), 7.26−7.16 (m, 3H), 2.62−2.57 (m, 4H), 2.36 (t, J = 5.2 Hz, 2H), 1.62−1.59 (m, 6H), 1.48−1.42 (m, 2H), 1.24−1.19 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.6, 153.0, 130.9, 130.7, 129.2, 126.6, 123.4, 41.5, 34.9, 33.4, 28.4, 28.1, 26.22, 26.19, 22.2, 13.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{25}OSe$ 337.1065, found 337.1063.

*3-(Benzyloxy)-1-cyclohexylidene-1-(phenylselanyl)propan-2-one (**3ca**):* yellow liquid, 48.8 mg (61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 8H), 7.26−7.20 (m, 2H), 4.44 (s, 2H), 4.35 (s, 2H), 2.60 (t, J = 5.4 Hz, 2H), 2.42 (t, J = 5.4 Hz, 2H), 1.65−1.59 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.9, 156.4, 137.4, 130.8, 130.7, 129.3, 128.4, 127.9, 127.8, 126.9, 120.0, 74.1, 73.1, 35.1, 33.5, 28.5, 28.2, 26.2; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{22}H_{24}O_2SeNa$ 423.0834, found 423.0832.

*4-(2-Cyclohexylidene-2-(phenylselanyl)acetyl)benzonitrile (**3da**):* yellow liquid, 61.7 mg (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 5.2 Hz, 2H), 7.25−7.15 (m, 3H), 2.72 (t, J = 6.0 Hz, 2H), 2.26 (t, J = 5.8 Hz, 2H), 1.75−1.72 (m, 2H), 1.64−1.57 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.8, 153.4, 139.8, 132.6, 132.2, 129.5, 129.4, 129.1, 127.5, 119.5, 118.0, 115.9, 34.3, 33.9, 28.2, 28.1, 26.1; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{21}H_{19}NOSeNa$ 404.0524, found 404.0524.

*2-Cyclohexylidene-2-(phenylselanyl)-1-(thiophen-2-yl)ethan-1-one (**3ea**):* yellow liquid, 61.5 mg (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 4.8 Hz, 1H), 7.51 (d, J = 3.2 Hz, 1H), 7.46−7.44 (m, 2H), 7.22−7.15 (m, 3H), 7.03−7.01 (m, 1H), 2.67 (t, J = 6.0 Hz, 2H), 2.29 (d, J = 5.6 Hz, 2H), 1.71−1.65 (m, 2H), 1.61−1.54 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):δ 187.6, 151.7, 143.9, 134.3, 133.7, 132.5, 130.3, 128.9, 127.9, 127.2, 119.7, 34.1, 33.9, 28.0, 27.9, 26.1; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{19}OSSe$ 363.0316, found 363.0313.

*1-Phenyl-2-(phenylselanyl)-2-(1,4-dioxaspiro[4.5]decan-8-ylidene)ethan-1-one (**3fa**):* yellow solid, 64.7 mg (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 6.8 Hz, 1H), 7.39−7.35 (m, 4H), 7.24−7.09 (m, 3H), 4.07−3.85 (m, 4H), 2.87 (t, J = 6.4 Hz, 2H), 2.41 (t, J = 6.4 Hz, 2H), 1.83 (t, J = 6.6 Hz, 2H), 1.70 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.5, 148.5, 136.2, 133.2, 132.7, 129.8, 129.4, 129.1, 128.5, 127.4, 121.7, 108.0, 64.5, 35.5, 35.4, 30.9, 30.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{22}H_{23}O_3Se$ 415.0807, found 415.0807; mp 100−102 °C.

*1-((1R,3R,5R,7S)-Adamantan-2-ylidene)-1-(phenylselanyl)-propan-2-one (**3ga**):* yellow liquid, 42.1 mg (61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.2 Hz, 2H), 7.26−7.17 (m, 3H), 3.42−3.33 (m, 1H), 3.01−2.97 (m, 1H), 2.31 (s, 3H), 1.99−1.91 (m, 6H), 1.88−1.85 (m, 4H), 1.82−1.87 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.8, 162.2, 131.2, 130.5, 129.3, 126.5, 119.4, 39.5, 39.4, 37.9, 36.8, 36.6, 30.0, 27.7; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{23}OSe$ 347.0909, found 347.0909.

*2-Cyclopentylidene-1-phenyl-2-(phenylselanyl)ethan-1-one (**3ha**):* yellow liquid, 56.7 mg (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.74 (m, 2H), 7.50−7.46 (m, 1H), 7.48−7.34 (m, 4H), 7.16−7.14 (m, 3H), 2.62 (t, J = 5.8 Hz, 2H), 2.37 (t, J = 5.8 Hz, 2H), 1.77−1.73 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.1, 158.4, 136.5, 132.8, 132.5, 129.8, 129.2, 129.0, 128.3, 127.1, 119.0, 99.9, 35.2, 33.5, 27.3, 25.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{19}OSe$ 343.0596, found 343.0594.

*1-Cycloheptylidene-1-(phenylselanyl)propan-2-one (**3ia**):* yellow liquid, 55.4 mg (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 2H), 7.26−7.20 (m, 3H), 2.68−2.64 (m, 2H), 2.53−2.49 (m, 2H), 2.27 (s, 3H), 1.74−1.63 (m, 4H), 1.56−1.54 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.8, 155.0, 130.9, 130.6, 129.3, 127.0, 126.8, 36.4, 34.1, 30.0, 29.0, 28.6, 28.0, 27.0; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{21}OSe$ 309.0752, found 309.0751.

*1-Cyclooctylidene-1-(phenylselanyl)propan-2-one (**3ja**):* yellow liquid, 56.7 mg (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 2H), 7.26−7.20 (m, 3H), 2.62−2.59 (m, 2H), 2.48−2.45 (m, 2H), 2.27 (s, 3H), 1.77−1.72 (m, 4H), 1.55−1.48 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.7, 155.0, 131.4, 130.4, 129.3, 126.9, 126.8, 35.0, 34.2, 29.9, 28.0, 27.4, 26.2, 25.69, 25.66; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{23}OSe$ 323.0909, found 323.0907.

*1-Cyclododecylidene-1-(phenylselanyl)propan-2-one (**3ka**):* yellow liquid, 64.2 mg (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.32 (m, 2H), 7.24−7.15 (m, 3H), 2.54−2.50 (m, 2H), 2.34−2.27 (m, 2H), 2.26 (s, 3H), 1.65−1.60 (m, 2H), 1.57−1.50 (m, 2H), 1.45−1.32 (m, 14H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.4, 154.6, 130.64, 130.55, 129.1, 127.7, 126.6, 32.0, 30.1, 29.7, 25.9, 25.71, 25.65, 24.5, 23.8, 22.7, 22.6, 22.1, 21.7; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{21}H_{30}OSeNa$ 401.1354, found 401.1355.

*(Z)-1-Phenyl-2-(phenylselanyl)hept-2-en-1-one (**3la**):* yellow liquid, 55.0 mg (80%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.51−7.47 (m, 1H), 7.41−7.35 (m, 4H), 7.17−7.14 (m, 3H), 6.67 (t, J = 7.2 Hz, 1H), 2.51 (dd, J = 14.6, 7.4 Hz, 2H), 1.50−1.43 (m, 2H), 1.41−1.32 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.5, 149.1, 137.3, 136.9, 133.9, 132.7, 132.3, 129.7, 129.4, 129.0, 128.8, 128.1, 127.2, 32.2, 30.6, 22.4, 13.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{21}OSe$ 345.0752, found 345.0752.

*1-(3-Bromo-4-methylphenyl)-3-methyl-2-(phenylselanyl)but-2-en-1-one (**3ma**):* yellow liquid, 59.5 mg (73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.6 Hz, 1H), 7.61 (dd, J = 8.0, 1.6 Hz, 1H), 7.37−7.35 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.20−7.18 (m, 3H), 2.42 (s, 3H), 2.20 (s, 3H), 1.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.3, 144.9, 143.4, 137.4, 135.7, 133.1, 132.6, 130.7, 129.6, 129.0, 128.1, 127.3, 125.0, 122.9, 24.1, 23.2, 22.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{18}BrOSe$ 408.9701, found 408.9696.

*3-Methyl-1-phenyl-2-(phenylselanyl)pent-2-en-1-one (**3na**):* yellow liquid, 49.4 mg (75%), Z/E = 1:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.78 (m, 2H), 7.52−7.48 (m, 1H), 7.40−7.36 (m, 4H), 7.20−7.15 (m, 3H), 2.63 (dd, J = 15.2, 7.6 Hz, 1H), 2.23 (dd, J = 14.8, 7.6 Hz, 1H), 2.18 (s, 1.5H), 1.89 (s, 1.5H), 1.17 (t, J = 7.6 Hz, 1.5H), 1.07 (t, J = 7.6 Hz, 1.5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.6, 194.5, 149.2, 149.0, 136.2, 136.1, 132.90, 132.87, 132.6, 132.3, 129.71, 129.69, 129.3, 129.2, 128.92, 128.88, 128.30, 128.25, 127.2, 127.1, 123.0, 122.5, 30.7, 29.9, 20.9, 20.1, 13.0, 12.5; HRMS (ESI-

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J. Org. Chem. 2021, 86, 5274−5283

TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{18}OSeNa$ 353.0415, found 353.0413.

1,3-Diphenyl-2-(phenylselanyl)but-2-en-1-one (**3oa**): yellow liquid, 65.0 mg (86%), Z/E = 2.6:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.2 Hz, 0.54H), 7.71−7.62 (m, 1.46H), 7.53−7.41 (m, 3H), 7.39−7.32 (m, 1.39H), 7.27−7.06 (m, 8.43H), 2.51 (s, 2.14H), 2.13 (s, 0.82H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.5, 145.2, 141.3, 136.4, 136.1, 134.9, 133.8, 133.2, 132.6, 129.30, 129.26, 129.0, 128.7, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 24.6, 23.6; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{22}H_{19}OSe$ 379.0596, found 379.0593.

2-Phenyl-3-(phenylselanyl)oct-2-en-4-one (**3pa**): yellow liquid, 55.1 mg (77% yield), Z/E = 3:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.50 (m, 1.57H), 7.36−7.19 (m, 8.57H), 2.64 (t, J = 7.6 Hz, 0.45H), 2.39 (s, 2.25H), 2.19 (s, 0.70H), 1.97 (t, J = 7.4 Hz, 1.52H), 1.45−1.37 (m, 0.51H), 1.10−1.02 (m, 1.52H), 0.91−0.80 (m, 2.83H), 0.59 (t, J = 7.4 Hz, 2.26H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 205.0, 204.6, 145.3, 141.6, 132.9, 132.5, 131.1, 129.4, 129.21, 129.16, 128.4, 128.3, 128.1, 127.8, 127.7, 127.5, 127.33, 127.26, 42.7, 41.7, 26.0, 25.5, 25.1, 23.4, 22.2, 21.8, 13.8, 13.6; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{20}H_{23}OSe$ 359.0909, found 359.0904.

(Z)-1-Methyl-3-(2-oxo-1-(phenylselanyl)hexylidene)indolin-2-one (**3qa**): yellow liquid, 64.6 mg (81%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.47−7.43 (m, 1H), 7.39−7.30 (m, 3H), 7.14−7.10 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.19 (s, 3H), 2.64−2.03 (m, 2H), 1.32−1.16 (m, 2H), 1.10−1.01 (m, 2H), 0.73 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.3, 164.4, 151.8, 143.9, 137.7, 130.2, 129.5, 129.1, 124.2, 123.6, 122.1, 121.3, 108.0, 42.7, 25.9, 24.4, 21.8, 13.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{22}NO_2Se$ 400.0810, found 400.0810.

3,7-Dimethyl-1-(5-methyl-7-oxo-6-(phenylselanyl)tridec-5-en-1-yl)-3,7-dihydro-1H-purine-2,6-dione (**3ra**): yellow liquid, 103.4 mg (95%), Z/E = 1:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.34−7.29 (m, 2H), 7.24−7.15 (m, 3H), 4.02 (t, J = 7.4 Hz, 2H), 3.982, 3.977 (s, 3H), 3.573, 3.569 (s, 3H), 2.63−2.57 (m, 2H), 2.53 (t, J = 7.8 Hz, 1H), 2.32 (t, J = 7.6 Hz, 1H), 2.06 (s, 1.5H), 1.96 (s, 1.5H), 1.72−1.65 (m, 2H), 1.63−1.52 (m, 2H), 1.47−1.40 (m, 2H), 1.26−1.14 (m, 6H), 0.85−0.81 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.5, 204.0, 155.1, 151.3, 149.4, 149.2, 148.7, 141.4, 131.0, 130.7, 130.6, 130.5, 129.2, 129.1, 127.3, 127.0, 126.7, 126.6, 107.6, 41.7, 41.6, 41.0, 38.2, 36.1, 33.5, 31.4, 29.6, 28.69, 28.66, 27.91, 27.85, 26.0, 25.4, 24.0, 23.9, 22.5, 22.4, 20.6, 13.9; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{37}N_4O_3Se$ 545.2025, found 545.2025.

(Z)-1-(3-Hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta-[a]phenanthren-17-ylidene)-1-(phenylselanyl)propan-2-one (**3sa**): yellow solid, 39.9 mg (43%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 2H), 7.26−7.22 (m, 2H), 7.21−7.19 (m, 1H), 7.09 (d, J = 8.4 Hz, 1H), 6.62 (dd, J = 8.4, 2.8 Hz, 1H), 6.56 (d, J = 2.8 Hz, 1H), 5.61 (s, 1H), 2.84−79(m, 2H), 2.62−2.56 (m, 2H), 2.33 (s, 3H), 2.19−2.15 (m, 1H), 2.08−2.05 (m, 1H), 1.92−1.81 (m, 2H), 1.49−1.36 (m, 5H), 1.29−1.24 (m, 1H), 1.06 (s, 3H), 0.88−0.84 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.2, 164.1, 153.6, 137.9, 136.8, 132.0, 130.3, 130.2, 129.4, 129.0, 126.7, 126.4, 120.7, 115.2, 112.8, 55.1, 47.5, 43.3, 38.5, 34.8, 33.8, 29.7, 29.5, 27.4, 26.6, 23.3, 17.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{31}O_2Se$ 467.1484, found 467.1487; mp 114−116 °C.

(Z)-3-Phenyl-2-(phenylselanyl)acrylaldehyde (**5aa**): yellow liquid, 36.5 mg (64%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.00 (s, 1H), 7.86−7.83 (m, 2H), 7.43−7.38 (m, 5H), 7.21−7.18 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.3, 152.3, 134.2, 132.3, 131.9, 131.0, 130.8, 129.2, 128.5, 127.3; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{12}OSeNa$ 310.9946, found 310.9946.

(Z)-3-(4-Methoxyphenyl)-2-(phenylselanyl)acrylaldehyde (**5ba**): yellow solid, 53.4 mg (84%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.97−7.93 (m, 3H), 7.38−7.36 (m, 2H), 7.2−7.16 (m, 3H), 6.95−6.92 (m, 2H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.6, 162.0, 153.7, 135.8, 133.6, 131.4, 131.2, 130.9, 129.7, 129.2, 128.8, 126.9, 126.8, 114.0, 55.4; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{14}O_2SeNa$ 341.0051, found 341.0051; mp 77−79 °C.

(Z)-3-(4-Hydroxyphenyl)-2-(phenylselanyl)acrylaldehyde (**5ca**): yellow solid, 58.9 mg (97%), Z/E > 20:1; ^{1}H NMR(DMSO-d_6, 400 MHz):δ 10.41 (s, 1H), 9.49 (s, 1H), 8.26 (s, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.46−7.04 (m, 5H), 6.87 (d, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6):δ 191.8, 161.0, 157.3, 134.1, 130.3, 129.8, 129.3, 126.7, 126.4, 125.1, 115.7; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_2Se$ 305.0075, found 305.0073; mp 175−177 °C.

(Z)-3-(4-Fluorophenyl)-2-(phenylselanyl)acrylaldehyde (**5da**): yellow solid, 41.8 mg (68%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.96 (s, 1H), 7.90 (d, J = 5.2 Hz, 1H), 7.88 (d, J = 5.6 Hz, 1H), 7.39−7.36 (m, 2H), 7.24−7.16 (m, 3H), 7.15−7.06 (m, 2H);^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.3, 164.0 (d, J = 252.0 Hz), 151.1, 133.4, 133.3, 131.9 (d, J = 2.0 Hz), 131.8, 130.4 (d, J = 4.0 Hz), 129.3, 129.0, 127.4, 115.8, 115.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.47, −110.54; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{15}H_{11}FOSeNa$ 328.9851, found 328.9853; mp 82−84 °C.

3-(4-Nitrophenyl)-2-(phenylselanyl)acrylaldehyde (**5ea**):[6c] yellow liquid, 10.6 mg (16%), Z/E = 3.5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 0.22H), 9.52 (s, 0.78H), 8.25−8.17 (m, 2.08H), 7.99 (s, 0.77H), 7.89−7.85 (m, 1.55H), 7.72−7.64 (m, 0.44H), 7.49−7.42 (m, 0.58H), 7.40−7.33 (m, 1.93H), 7.24−7.15 (m, 2.26H), 7.10 (s, 0.22H);^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.7, 148.0, 146.3, 140.3, 137.0, 136.9, 132.8, 131.1, 130.2, 130.0, 129.5, 128.0, 127.8, 123.8, 123.5; MS (EI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}NO_3Se$ 334.0, found 334.0.

2-(Phenylselanyl)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde (**5fa**): yellow liquid, 55.5 mg (78%), Z/E = 6.7:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 0.13H), 9.51 (s, 0.87H), 8.00 (s, 0.90H), 7.86 (d, J = 8.0 Hz, 1.78H), 7.69−7.60 (m, 2.35H), 7.44−7.31 (m, 2.46H), 7.21−7.17 (m, 2.71H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.0, 188.4, 148.7, 142.1, 137.6, 136.8, 135.2, 132.5, 131.8 (q, J = 33.0 Hz), 130.7, 130.0, 129.6, 129.43, 129.35, 128.3, 127.7, 125.5 (q, J = 4.0 Hz), 125.3 (q, J = 4.0 Hz), 123.7 (q, J = 271 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.76, −62.92; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{11}F_3OSeNa$ 378.9819, found 378.9815.

(Z)-3-(Naphthalen-2-yl)-2-(phenylselanyl)acrylaldehyde (**5ga**): yellow liquid, 40.5 mg (60%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.63 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.64−7.53 (m, 3H), 7.50−7.42 (m, 1H), 7.32−7.30 (m, 2H), 7.11−7.05 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.9, 148.9, 136.5, 133.3, 132.7, 131.5, 131.1, 130.6, 129.0, 128.8, 128.6, 127.9, 127.3, 126.9, 126.3, 124.9, 123.7; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{14}OSeNa$ 361.0102, found 361.0102.

3-Phenyl-2-(phenylselanyl)but-2-enal (**5ha**): yellow liquid, 43.7 mg (73%), Z/E = 4.2:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 0.19H), 9.24 (s, 0.79H), 7.35−7.32 (m, 4H), 7.22−7.20 (m, 2H), 7.20−7.07 (m, 4H), 2.52, 2.50 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.3, 189.5, 167.6, 139.7, 133.6, 131.7, 131.3, 130.7, 129.3, 129.2, 129.1, 128.53, 128.48, 128.2, 126.9, 126.8, 126.7, 28.6, 23.0; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{14}OSeNa$ 325.0102, found 325.0103.

(Z)-3-Cyclopropyl-3-phenyl-2-(phenylselanyl)acrylaldehyde (**5ia**): yellow solid, 53.1 mg (81%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.39 (d, J = 6.8 Hz, 2H), 7.33−7.29 (m, 3H), 7.20−7.11 (m, 3H), 7.01 (dd, J = 6.6, 3.0 Hz, 2H), 2.81−2.75 (m, 1H), 0.89−0.79 (m, 2H), 0.49−0.45 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.1, 174.2, 134.3, 132.8, 131.1, 131.0, 129.1, 129.0, 128.5, 128.1, 126.6, 21.4, 8.2; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{18}H_{17}OSe$ 329.0439, found 329.0440; mp 72−74 °C.

3,3-Diphenyl-2-(phenylselanyl)acrylaldehyde (**5ja**): yellow liquid, 56.0 mg (77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.45−7.42 (m, 1H), 7.39−7.35 (m, 2H), 7.31−7.24 (m, 5H), 7.21−7.18 (m, 4H), 7.14−7.10 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.9, 166.1, 141.9, 139.4, 134.8, 132.3, 131.1, 130.9, 130.0,

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J. Org. Chem. 2021, 86, 5274−5283

129.6, 129.2, 128.9, 128.3, 127.9, 126.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{17}OSe$ 365.0439, found 365.0439.

*2-(Phenylselanyl)acrylaldehyde (**5ka**):* yellow liquid, 35.2 mg (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.63−7.60 (m, 2H), 7.42−7.36 (m, 3H), 6.54 (d, J = 1.2 Hz, 1H), 5.93 (d, J = 0.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.6, 146.5, 136.8, 132.2, 129.8, 129.2; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C_9H_8OSeNa 234.9633, found 234.9629.

*(Z)-2-(Phenylselanyl)but-2-enal (**5la**):* yellow liquid, 37.5 mg (83%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.41−7.33 (m, 3H), 7.24−7.20 (m, 3H), 2.20 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.7, 157.6, 137.3, 131.8, 129.5, 129.2, 127.0, 18.9; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{10}H_{10}OSeNa$ 248.9789, found 248.9787.

*(Z)-2-(Phenylselanyl)pent-2-enal (**5ma**):* yellow liquid, 42.2 mg (88%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.40 (m, 2H), 7.25−7.20 (m, 4H), 2.66−2.58 (m, 2H), 1.12 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.9, 163.8, 135.3, 131.8, 129.6, 129.2, 127.0, 26.3, 12.6; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{11}H_{12}OSeNa$ 262.9946, found 262.9946.

*(Z)-4,4-Dimethyl-2-(phenylselanyl)pent-2-enal (**5na**):* yellow liquid, 38.0 mg (71%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.38−7.35 (m, 3H), 7.25−7.20 (m, 3H), 1.37 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7, 170.3, 132.5, 131.4, 130.0, 129.2, 126.9, 35.4, 30.0; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{13}H_{16}OSeNa$ 291.0259, found 291.0258.

*(Z)-4-Ethyl-2-(phenylselanyl)hex-2-enal (**5oa**):* yellow liquid, 44.0 mg (78%), Z/E > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.41−7.38 (m, 2H), 7.23−7.21 (m, 3H), 6.98 (d, J = 10.4 Hz, 1H), 3.00−2.91 (m, 1H), 1.66−1.56 (m, 2H), 1.46−1.35 (m, 2H), 0.87 (t, J = 7.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.8, 166.5, 136.1, 131.9, 129.8, 129.1, 127.0, 45.9, 27.3, 11.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{14}H_{19}OSe$ 283.0596, found 283.0597.

*3-Methyl-2-(phenylselanyl)but-2-enal (**5pa**):* yellow liquid, 42.2 mg (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.33 (dd, J = 7.4, 1.6 Hz, 2H), 7.23−7.17 (m, 3H), 2.41 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.9, 164.8, 131.1, 130.7, 129.3, 129.2, 126.5, 28.9, 22.0; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{11}H_{12}OSeNa$ 262.9946, found 262.9942.

*2-Cyclohexylidene-2-(phenylselanyl)acetaldehyde (**5qa**):* yellow liquid, 46.3 mg (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.34−7.30 (m, 2H), 7.23−7.16 (m, 3H), 2.93−2.89 (m, 2H), 2.85−2.80 (m, 2H), 1.78−1.72 (m, 2H), 1.70−1.63 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.2, 172.1, 131.5, 130.7, 129.1, 127.3, 126.4, 38.7, 32.3, 28.9, 28.5, 26.2; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{14}H_{16}OSeNa$ 303.0259, found 303.0259.

*3-Methyl-2-(phenylselanyl)non-2-enal (**5ra**):* yellow liquid, 42.7 mg (69% yield), Z/E = 2:3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91, 9.87 (s, 1H), 7.33−7.29 (m, 2H), 7.21−7.17 (m, 3H), 2.79−2.66 (m, 2H), 2.39, 2.29 (s, 3H), 1.69−1.56 (m, 2H), 1.40−1.25 (m, 6H), 0.91−0.86 (m, 3H).HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{23}OSe$ 311.0909, found 311.0905.

(E)-3-Methyl-2-(phenylselanyl)non-2-enal: yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.33−7.28 (m, 2H), 7.23−7.16 (m, 3H), 2.79−2.75 (m, 2H), 2.29 (s, 3H), 1.62−1.55 (m, 2H), 1.38−1.27 (m, 6H), 0.91−0.88 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.2, 169.8, 131.2, 130.6, 129.8, 129.1, 126.5, 35.4, 31.5, 29.4, 29.2, 27.1, 22.5, 14.0.

(Z)-3-Methyl-2-(phenylselanyl)non-2-enal: yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.33−7.30 (m, 2H), 7.23−7.17 (m, 3H), 2.7−2.66 (m, 2H), 2.39 (s, 3H), 1.51−1.43 (m, 2H), 1.37−1.23 (m, 6H), 0.89−0.86 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.4, 168.3, 131.3, 130.7, 129.1, 128.9, 126.5, 42.2, 31.6, 29.3, 28.2, 22.5, 20.4, 14.0.

*3,3-Diphenyl-2-(phenylseleninyl)acrylic Acid (**6**):* white solid, 75.2 mg (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (brs, 1H), 7.88−7.69 (m, 2H), 7.67−7.51 (m, 4H), 7.50−7.44 (m, 2H), 7.43−7.32 (m, 3H), 7.28−7.15 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.0, 161.7, 139.0, 138.3, 138.0, 132.5, 131.1, 130.5, 130.4, 130.0, 129.6, 129.0, 128.4, 127.9, 127.4; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{17}O_3Se$ 397.0337, found 397.0331; mp 102−104 °C.

*1,1-Diphenyl-2-(phenylselanyl)ethan-1-ol (**7**):*[13a] yellow liquid, 48.4 mg (57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2H), 7.45−7.42 (m, 4H), 7.31−7.27 (m, 4H), 7.24 (dd, J = 1.2, 1.2 Hz, 1H), 7.23−7.20 (m, 4H), 3.87 (t, J = 4.4 Hz, 2H), 3.58 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.4, 133.0, 130.7, 129.2, 128.3, 127.30, 127.25, 126.0, 77.4, 44.7; MS (EI) m/z [M + Na]$^+$ calcd for $C_{20}H_{18}OSeNa$ 377.1, found 377.2.

*2-Phenyl-3-(phenylselanyl)-1-tosyl-1H-indole (**9**):* white solid, 95.2 mg (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 7.46−7.41 (m, 2H), 7.40−7.34 (m, 3H), 7.33−7.30 (m, 4H), 7.24 (dd, J = 7.4, 7.4 Hz, 1H), 7.07−6.99 (m, 5H), 6.96−6.89 (m, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.98, 144.95, 137.6, 135.0, 132.2, 131.9, 131.7, 131.0, 129.5, 129.30, 129.26, 129.1, 127.2, 127.0, 126.1, 125.8, 124.8, 121.3, 116.4, 110.6, 21.7; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{22}NO_2SSe$ 504.0531, found 504.0533; mp 169−171 °C.

*2-Cyclohexyl-3-(phenylselanyl)benzofuran (**11**):* yellow liquid, 51.2 mg (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 1H), 7.42 (dd, J = 7.6, 0.8 Hz, 1H), 7.26−7.22 (m, 3H), 7.20−7.17 (m, 1H), 7.16−7.11 (m, 3H), 3.25−3.17 (m, 1H), 2.04−1.70 (m, 7H), 1.42−1.24 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 154.3, 133.0, 132.0, 130.6, 129.3, 129.1, 129.0, 127.3, 126.0, 124.0, 123.0, 120.4, 111.0, 98.2, 37.1, 31.4, 26.2, 25.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{20}H_{21}OSe$ 357.0752, found 357.0753.

*2-Butyl-3-(phenylselanyl)benzofuran (**13**):*[20] yellow liquid, 52.8 mg (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.41 (m, 2H), 7.26−7.23 (m, 3H), 7.22−7.19 (m, 1H), 7.17−7.12 (m, 3H), 2.98 (t, J = 7.4 Hz, 2H), 1.75−1.67 (m, 2H), 1.40−1.31 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.8, 154.4, 131.8, 130.7, 129.12, 129.11, 126.0, 124.1, 123.1, 120.3, 110.9, 100.0, 30.4, 27.1, 22.3, 13.7; MS (EI, 70 eV) m/z (%) = 330 (63), 328 (32), 287 (41), 250 (38), 207 (100), 178 (38), 131 (38), 115 (10), 77(9).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00167.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of all products and X-ray crystal data (PDF)

Accession Codes

CCDC 2022161 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033

■ AUTHOR INFORMATION

Corresponding Author

Qiang Liu − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China;* orcid.org/0000-0001-8845-1874; Email: liuqiang@lzu.edu.cn

Authors

Yong-Liang Ban − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*

Long You − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*

Kai-Wen Feng − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*

Fei-Cen Ma − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*

Xiao-Ling Jin − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00167

Notes

The authors declare no competing financial interest.

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