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PAPER

Chemoselective synthesis of highly substituted 1,2-allenyl ketones, furans, and 2-alkynyl ketones from reaction of lithium selenolates with 1-(1-alkynyl) cyclopropyl ketones and electrophiles†

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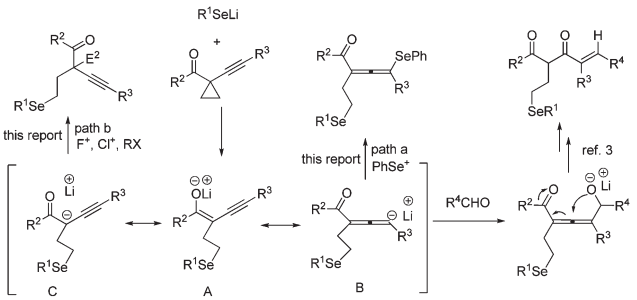
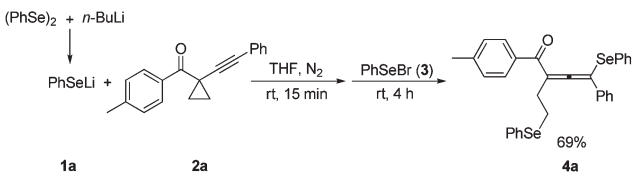
A homo-Michael addition reaction of lithium selenolates with 1-(1-alkynyl)cyclopropyl ketones and the subsequent reaction with electrophiles such as PhSeBr, NFSI and NCS is reported. Based on the nature of electrophiles, this reaction may afford highly substituted 1,2-allenyl ketones or furans ($E^+ = PhSe^+$) and 2-alkynyl ketones ($E^+ = F^+$, Cl^+, active halides) as the final products, respectively.

Introduction

The cleavage of cyclopropane ring is of great importance in organic chemistry due to its potential for the synthesis of various products, and therefore has attracted much attention during the past three decades.[1] 1-(1-Alkynyl)cyclopropyl ketone, containing both an alkyne and a cyclopropane unit, is a useful multifunctionalized building block.[2] Recently, Schmalz and Zhang,[2a] Zhang *et al.*,[2b,c] Zhang *et al.*,[2d,e] and Wang *et al.*[2f] have reported their facile strategies of using 1-(1-alkynyl)cyclopropyl ketones as readily available substrates for efficient construction of highly substituted furans and other cyclic compounds, respectively. Our group has also reported a novel synthesis of 4(*E*)-alken-1,3-diones from the three-component reaction of lithium selenolates with 1-(1-alkynyl)cyclopropyl ketones and aldehydes.[3] Since the homo-conjugate addition[4] of lithium selenolates to 1-(1-alkynyl) cyclopropyl ketones would form an alkynyl enolate intermediate **A**, which has two resonance structures **B** and **C**, we envisioned that when different electrophiles are used to capture these intermediates, it may form substituted 1,2-allenyl ketones[5] or 2-alkynyl ketones[6] as the expected products, depending on the nature of the electrophiles (Scheme 1).



Scheme 1 Previous work and our proposal.



Scheme 2

Results and discussion

Initially we used lithium phenylselenolate **1a** to react with 1-(phenylethynyl)cyclopropyl *p*-tolyl ketone **2a** for 15 min, then phenylselenyl bromide **3** was added. After reacting for additional 4 h, we were pleased to obtain 1,2-allenyl ketone **4a** in 69% yield exclusively (Scheme 2).

Further efforts was then made to optimize the conditions for this reaction, the results are summarized in Table 1. A solvent screening showed that anhydrous THF is the best (Table 1, entries 1–5). Surprisingly, when the amount of **3** was raised to 1.6 equiv, furan product **5a** was also formed and isolated in 19%

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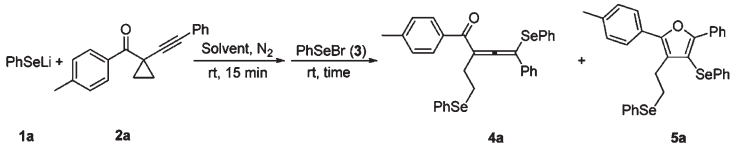
†Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra for **4**, **5**, **6**, and **8**, ^{19}F NMR spectra for **8a–j**, X-ray crystallographic data (CIF file), and an ORTEP drawing for **6a**. CCDC 821931. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25071c

‡Professor Huang passed away on March 6, 2010. He was fully in charge of this project. Professor Luling Wu is helping to finish all the projects with assistance from Professor Shengming Ma.

Table 1 Optimization of reaction conditions for the reaction of lithium phenylselenolate (**1a**), 1-(phenylethynyl)cyclopropyl *p*-tolyl ketone (**2a**) and phenylselenyl bromide (**3**)[a]



Entry	**1a** : **2a** : **3** (equiv)	Solvent	Time[b] (h)	Yield of **4a**[c] (%)	Yield of **5a**[c] (%)
1	1.0 : 1.0 : 1.0	THF	4	69	—
2	1.0 : 1.0 : 1.0	Et_2O	7	61	—
3	1.0 : 1.0 : 1.0	Toluene	6	62	—
4	1.0 : 1.0 : 1.0	Cyclohexane	11	52	—
5	1.0 : 1.0 : 1.0	1,4-Dioxane	4	66	—
6	**1.2** : **1.0** : **1.2**	THF	**7**	**76**	—
7	1.0 : 1.2 : 1.0	THF	7	68	—
8	1.2 : 1.0 : 1.4	THF	24	74	Trace
9	1.2 : 1.0 : 1.6	THF	24	52	19
10	1.2 : 1.0 : 1.8	THF	24	19	57
11	**1.2** : **1.0** : **2.0**	**THF**	**24**	**3**	**71**
12	1.2 : 1.0 : 2.2	THF	24	3	72

[a] Unless otherwise specified, the reaction was carried out using **1a** (0.6 mmol), **2a** (0.5 mmol), and **3** (0.6 mmol) in 4 mL of solvent at room temperature under a nitrogen atmosphere. [b] The reaction was monitored by TLC. [c] Isolated yields.

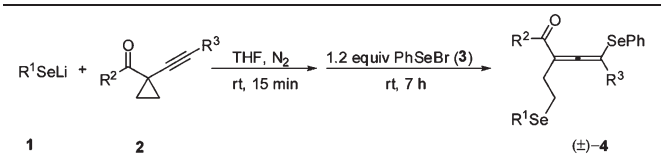
yield (Table 1, entry 9). After several attempts, we were pleased to define two sets of the optimal reaction conditions for the selective formation of **4a** and **5a**: at room temperature under a nitrogen atmosphere, the reaction of 1.2 equiv of **1a**, 1.0 equiv of **2a**, and 1.2 equiv of **3** in anhydrous THF for 7 h afforded 1,2-allenyl ketone **4a** as the sole product (Table 1, entry 6); the reaction of 1.2 equiv of **1a**, 1.0 equiv of **2a**, and 2.0 equiv of **3** in anhydrous THF for 24 h gave the highest yield of furan **5a** (Table 1, entry 11).

With the above optimized conditions in hand, the reaction of several lithium selenolates **1** and 1-(1-alkynyl)cyclopropyl ketones **2** followed by the addition of PhSeBr was investigated. As shown in Table 2, the yields of 1,2-allenyl ketones **4** ranged from 46% to 76%. Both lithium arylselenolate and alkylselenolate could be used, and the arylselenolate gave a much better result (Table 2, entries 1–2). With regard to the substrates **2**, no matter R^2 and R^3 are alkyl, aryl, or heteroaryl groups, all of them could afford the corresponding allenyl ketone products **4a** and **4c–i** in moderate yields (Table 2, entries 1 and 3–9).

At the meantime, we observed that the reaction with 2.0 equiv of PhSeBr afforded furans 5 as the products, the results are listed in Table 3. Compared with lithium phenylselenolate **1a**, lithium n-butylselenolate **1b** showed a much poorer reactivity in forming the corresponding furans (Table 3, entries 1–2). This reaction could tolerate various 1-(1-alkynyl)cyclopropyl ketones **2**: the R^2 and R^3 substituents could be alkyl, aryl, or heteraryl groups (Table 3, entries 1 and 3–10).

These reactions indicate that the excess amount of PhSeBr may catalyse or promote the transformation from allenyl ketones **4** to furans 5. Thus, we first applied 0.1 equiv of phenylselenyl bromide **3** to a solution of **4a** in THF. The reaction is catalytic, but slow: after 1 day, only 27% of **5a** was obtained with 29% of **4**a being recovered. By increasing the amount of **3** to 1.0 equiv, furan **5a** could be isolated in 63% yield (Scheme 3).

Table 2 Synthesis of various 1,2-allenyl ketones (**4**)[a]



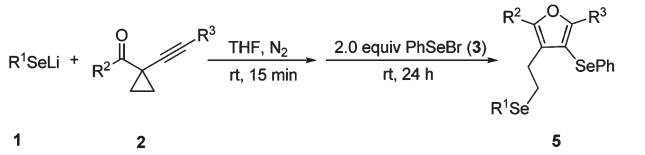
	1	**2**		
Entry	R^1	R^2	R^3	Yield of **4**[b] (%)
1	Ph (**1a**)	4-MeC_6H_4	Ph (**2a**)	76 (**4a**)
2	n-Bu (**1b**)	**2a**		46 (**4b**)
3	**1a**	4-$MeOC_6H_4$	Ph (**2b**)	68 (**4c**)
4	**1a**	4-FC_6H_4	Ph (**2c**)	59 (**4d**)
5	**1a**	2-Furyl	Ph (**2d**)	55 (**4e**)
6	**1a**	n-Pr	Ph (**2f**)	61 (**4f**)
7	**1a**	*t*-Bu	Ph (**2g**)	67 (**4g**)
8	**1a**	4-MeC_6H_4	n-Bu (**2h**)	65 (**4h**)
9	**1a**	i-Bu	n-Bu (**2i**)	64 (**4i**)

[a] The reaction was carried out using **1** (0.6 mmol), **2** (0.5 mmol), and **3** (0.6 mmol) in 4 mL of THF under a nitrogen atmosphere at room temperature for 7 h. [b] Isolated yields.

We proposed a mechanism to explain the formation of furan **5**. The allenyl moiety in ketone **4a** would interact with phenylselenyl bromide **3**, which would be followed by the attacking of the carbonyl group in **4a** to form intermediate **12** or **13**. Elimination of a phenylselenyl cation finally afforded furan product **5a** (Scheme 4). The higher loading of PhSeBr required indicates that the interaction between **3** and PhSeBr is rather slow.

As expected, when other electrophiles such as NIS, NBS and $CuCl_2$ were used instead of phenylselenyl bromide to react with **4a**, the corresponding halogen-substituted furans **6a–c** were formed, respectively (Scheme 5). The structure of

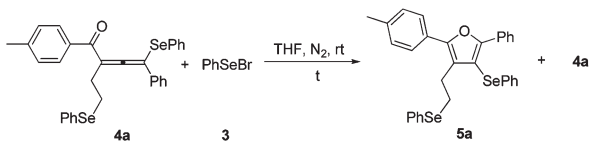
Table 3 Synthesis of various furans (**5**)[a]



1 2 5

Entry	1 R[1]	2 R[2]	2 R[3]	Yield of **5**[b] (%)
1	Ph (**1a**)	4-MeC$_6$H$_4$	Ph (**2a**)	71 (**5a**)
2	n-Bu (**1b**)	**2a**		46 (**4b**)
3	**1a**	4-MeOC$_6$H$_4$	Ph (**2b**)	65 (**5c**)
4	**1a**	4-FC$_6$H$_4$	Ph (**2c**)	58 (**5d**)
5	**1a**	2-Furyl	Ph (**2d**)	52 (**5e**)
6	**1a**	2-Thienyl	Ph (**2e**)	49 (**5f**)
7	**1a**	n-Pr	Ph (**2f**)	65 (**5g**)
8	**1a**	*t*-Bu	Ph (**2g**)	64 (**5h**)
9	**1a**	4-MeC$_6$H$_4$	n-Bu (**2h**)	68 (**5i**)
10	**1a**	i-Bu	n-Bu (**2i**)	51 (**5j**)

[a] The reaction was carried out using **1** (0.6 mmol), **2** (0.5 mmol), and **3** (1.0 mmol) in 4 mL of THF under a nitrogen atmosphere at room temperature for 24 h. [b] Isolated yields.



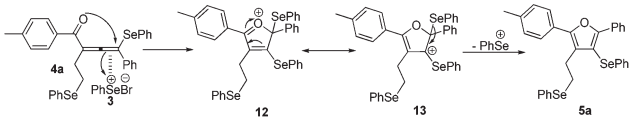
0.1 equiv	1d	27%	29% recovery
0.3 equiv	1d	54%	17% recovery
0.5 equiv	22h	51%	12% recovery
0.7 equiv	4 h	48%	10% recovery
1.0 equiv	0.5 h	63%	0% recovery

Scheme 3

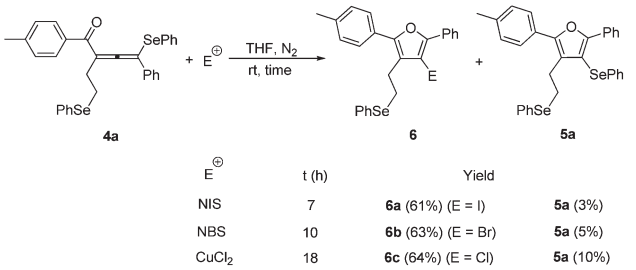
iodo-substituted furan **6a** was confirmed by its single-crystal X-ray diffraction analysis (Fig. 1).§

Fluorinated organic compounds are of current interest due to the rapidly increasing number of examples of these compounds with interesting and useful biological activities.[7] Thus, the reaction of lithium phenylselenolate **1a** with 1-(phenylethynyl) cyclopropyl *p*-tolyl ketone **2a** and Selectfluor (1-chloromethyl-4-fluoro-1,4-diazonia-bicyclo[2.2.2]octanebis-(tetrafluoroborate)) **7a** in anhydrous THF was studied. Unexpectedly, the reaction afforded fluoro-substituted 2-alkynyl ketone **8a** in 51% yield (Table 4, entry 1). We reasoned that this result maybe caused by the small size and hard nature of the F^+. Further study showed that the reaction in solvent such as Et_2O, toluene, and cyclohexane did not afford **8a** at all, while that in 1,4-dioxane

§ X-ray crystal data for **6a**: $C_{25}H_{21}IOSe$, $M = 543.28$, monoclinic, space group $P21/n$, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0368$, w$R_2 = 0.0816$, R indices (all data): $R_1 = 0.0564$, w$R_2 = 0.0921$, $a = 16.1185(6)$ Å, $b = 5.7251(2)$ Å, $c = 24.3065(9)$ Å, $\alpha = 90°$, $\beta = 106.365(4)°$, $\gamma = 90°$, $V = 2152.12(14)$ Å^3, $T = 293(2)$ K, $Z = 4$, reflections collected/unique: 9508/3928 ($R_{int} = 0.0326$), number of observations [$I > 2\sigma(I)$]: 2996, parameters: 262.



Scheme 4



E	t (h)	Yield	
NIS	7	**6a** (61%) (E = I)	**5a** (3%)
NBS	10	**6b** (63%) (E = Br)	**5a** (5%)
$CuCl_2$	18	**6c** (64%) (E = Cl)	**5a** (10%)

Scheme 5

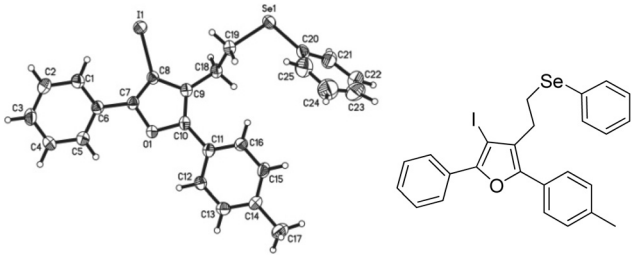


Fig. 1 ORTEP representation of furan **6a**.

afforded **8a** in 30% yield (Table 4, entries 2–5). The amount of **7a** did not have much influence on the reaction (Table 4, entries 1, 6, and 7). When **7a** was replaced with *N*-fluorodi(benzenesulfonyl) amine **7b**, the highest yield (57%) was observed when the reaction of 1.2 equiv of **1a**, 1.0 equiv of **2a**, and 1.2 equiv of **7b** in anhydrous THF was conducted at room temperature for 11 h (Table 4, entries 8–11). Thus, the reaction conditions presented in entry 9 of Table 4 were defined as the standard conditions for further study.

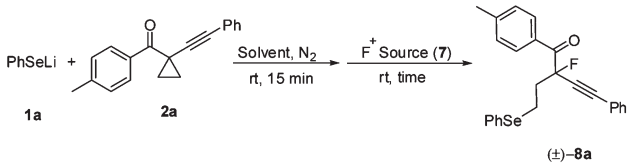
The reactions of organo lithium selenolates **1** and 1-(1-alkynyl)cyclopropyl ketones **2** with **7b** were then conducted by applying the standard reaction conditions. As listed in Table 5, lithium phenylselenolate **1a** gave a much better result than lithium n-butylselenolate **1b** (Table 5, entries 1–2). 1-(1-Alkynyl)cyclopropyl ketones **2** with alkyl, aryl, and heteroaryl substituents could all afford the corresponding fluoro-substituted 2-alkynyl ketones **8c–j** successfully, but when R^3 is an alkyl group, the yield was lower than when it is an aryl group (Table 5, entries 1 and 3–10).

Other electrophiles such as NCS, allylic bromide, and benzenyl bromide were also tested, and the result showed that they all followed path b to form the corresponding substituted 2-alkynyl ketones **8k–m** (Scheme 6).

Conclusions

In summary, we have developed an efficient method for the synthesis of highly substituted 1,2-allenyl ketones, furans, and 2-alkynyl ketones chemoselectively from readily available lithium

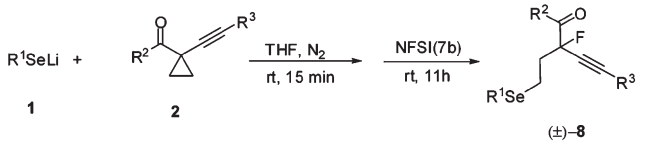
Table 4 Optimization of reaction conditions for the reaction of lithium phenylselenolate (**1a**), 1-(phenylethynyl)cyclopropyl *p*-tolyl ketone (**2a**) and F^+ source (**7**)[a]



Entry	**1a** : **2a** : **7** (equiv)	Solvent	Time[b] (h)	F^+ source **7**	Yield of **8a**[c] (%)
1	1.2 : 1.0 : 2.0	THF	8	Selectfluor (**7a**)	51
2	1.2 : 1.0 : 2.0	Et_2O	24	**7a**	—
3	1.2 : 1.0 : 2.0	Toluene	24	**7a**	—
4	1.2 : 1.0 : 2.0	Cyclohexane	24	**7a**	—
5	1.2 : 1.0 : 2.0	1,4-Dioxane	7	**7a**	30
6	1.2 : 1.0 : 1.6	THF	8	**7a**	45
7	1.2 : 1.0 : 2.4	THF	8	**7a**	48
8	1.2 : 1.0 : 1.0	THF	11	NFSI (**7b**)	51
9	**1.2** : **1.0** : **1.2**	**THF**	**11**	**7b**	**57**
10	1.2 : 1.0 : 1.4	THF	11	**7b**	54
11	1.2 : 1.0 : 1.6	THF	11	**7b**	50

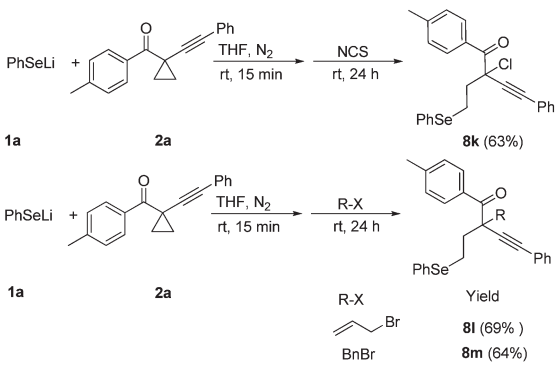
[a] Unless otherwise specified, the reaction was carried out using **1a** (0.6 mmol), **2a** (0.5 mmol), and **7** (0.6 mmol) in 4 mL of solvent at room temperature under a nitrogen atmosphere. [b] The reaction was monitored by TLC. [c] Isolated yields.

Table 5 Synthesis of various fluoro-substituted 2-alkynyl ketones (**8**)[a]



Entry	**1** R^1	**2** R^2	R^3	Yield of **8**[b] (%)
1	Ph (**1a**)	4-MeC_6H_4	Ph (**2a**)	57 (**8a**)
2	n-Bu (**1b**)	**2a**		42 (**8b**)
3	**1a**	4-$MeOC_6H_4$	Ph (**2b**)	52 (**8c**)
4	**1a**	4-FC_6H_4	Ph (**2c**)	49 (**8d**)
5	**1a**	2-Furyl	Ph (**2d**)	53 (**8e**)
6	**1a**	2-Thienyl	Ph (**2e**)	50 (**8f**)
7	**1a**	n-Pr	Ph (**2f**)	53 (**8g**)
8	**1a**	*t*-Bu	Ph (**2g**)	43 (**8h**)
9	**1a**	4-MeC_6H_4	n-Bu (**2h**)	43 (**8i**)
10	**1a**	i-Bu	n-Bu (**2i**)	33 (**8j**)

[a] The reaction was carried out using **1** (0.6 mmol), **2** (0.5 mmol), and **7b** (0.6 mmol) in 4 mL of THF under a nitrogen atmosphere at room temperature for 11 h. [b] Isolated yields.



Scheme 6

selenolates, 1-(1-alkynyl)cyclopropyl ketones, and electrophiles. The structures for the products are substrate-dependent. Further studies in this area are now in progress in our laboratory.

Experimental

General

THF was distilled from Na/benzophenone immediately prior to use. Petroleum ether refers to the fraction with the boiling point in the range 60–90 °C. All ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were measured in $CDCl_3$ with TMS as the internal standard, CF_3COOH was employed as external standard for the ^{19}F NMR measurement. Chemical shifts were expressed in ppm and *J* values were given in Hz. 1-(1-Alkynyl)cyclopropyl ketones were prepared according to the known procedure.[7] The other commercially available chemicals were purchased and used without further purification unless noted otherwise. Melting points were uncorrected.

General procedure for the synthesis of 1,2-allenyl ketones (4a–i). To a dried two-necked round-bottom flask (25 mL) were added diselenide (0.6 mmol, 1.2 equiv) and THF (2 mL) under a nitrogen atmosphere at room temperature. Then a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv) was added with a syringe to the reaction mixture to generate lithium selenolate **1** *in situ*. After 1–2 min, to the resulting reaction mixture was added a solution of 1-(1-alkynyl)cyclopropyl ketone **2** (0.5 mmol, 1.0 equiv) in 2 mL of THF at room temperature. The resulting reaction mixture was stirred for additional 15 min before phenylselenyl bromide (0.6 mmol, 1.2 equiv) was added. After being stirred for 7 h, the reaction was quenched

with H_2O and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether–ethyl acetate = 50 : 1) afforded the final product **4**.

*4-Phenyl-4-(phenylselenyl)-2-(2-(phenylselenyl)ethyl)-1-*p*-tolylbuta-2,3-dien-1-one (**4a**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4a** (218 mg, 76%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.2 Hz, 2H), 7.44 (d, J = 5.6 Hz, 2H), 7.15–7.31 (m, 9H), 7.01–7.09 (m, 4H), 2.69–2.99 (m, 4H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 192.9, 142.9, 135.4, 133.0, 132.9, 132.4, 130.0, 129.5, 129.1, 129.0, 128.8, 128.7, 128.3, 127.7, 126.7, 107.7, 100.5, 29.6, 25.4, 21.5; MS (EI, m/z): 574 (M^+); IR (ATR, neat, cm^{-1}): 1916, 1646, 1269, 756, 734, 689; HRMS (EI): m/z calcd for $C_{31}H_{26}OSe_2$ (M^+): 574.0314; Found: 574.0312.

*2-(2-(Butylselenyl)ethyl)-4-phenyl-4-(phenylselenyl)-1-*p*-tolylbuta-2,3-dien-1-one (**4b**).* The reaction of di(n-butyl) diselenide (163 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4b** (127 mg, 46%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.19–7.33 (m, 6H), 7.10–7.14 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 2.68–2.84 (m, 2H), 2.53–2.63 (m, 4H), 2.32 (s, 3H), 1.57–1.65 (m, 2H), 1.34–1.42 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 193.1, 143.0, 135.5, 133.0, 132.8, 129.7, 129.1, 128.8, 128.7, 128.7, 128.3, 127.7, 127.6, 107.9, 100.2, 32.5, 30.0, 23.8, 23.0, 21.5, 21.4, 13.6; MS (EI, m/z): 554 (M^+); IR (ATR, neat, cm^{-1}): 1916, 1647, 1268, 759, 736, 689; HRMS (EI): m/z calcd for $C_{29}H_{30}OSe_2$ (M^+): 554.0627; Found: 554.0623.

*1-(4-Methoxyphenyl)-4-phenyl-4-(phenylselenyl)-2-(2-(phenylselenyl)ethyl)buta-2,3-dien-1-one (**4c**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2b** (138 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4c** (201 mg, 68%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 7.2 Hz, 2H), 7.43–7.46 (m, 2H), 7.18–7.33 (m, 9H), 7.07–7.11 (m, 2H), 6.70 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 2.70–3.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 191.6, 163.0, 133.0, 132.7, 132.4, 131.1, 130.6, 130.0, 129.6, 129.2, 129.0, 128.7, 128.4, 127.7, 127.6, 126.7, 113.2, 107.4, 100.3, 55.3, 29.8, 25.4; MS (EI, m/z): 590 (M^+); IR (ATR, neat, cm^{-1}): 1916, 1642, 1251, 1025, 757, 735, 690; HRMS (EI): m/z calcd for $C_{31}H_{26}O_2Se_2$ (M^+): 590.0263; Found: 590.0272.

*1-(4-Fluorophenyl)-4-phenyl-4-(phenylselenyl)-2-(2-(phenylselenyl)ethyl)buta-2,3-dien-1-one (**4d**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2c** (132 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4d** (171 mg, 59%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.75 (m, 2H), 7.44–7.51 (m, 4H), 7.19–7.35 (m, 9H), 7.09–7.13 (m, 2H), 6.87–6.91 (m, 2H), 2.68–3.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 191.9, 165.1 (d, J = 252.1 Hz), 134.2 (d, J = 3.2 Hz), 133.1, 132.8, 132.5, 131.2 (d, J = 9.0 Hz), 129.9, 129.3, 129.2, 129.1, 128.8, 128.6, 128.0, 127.7, 126.9, 115.0 (d, J = 21.4 Hz), 107.8, 101.2, 29.5, 25.4; MS (EI, m/z): 578 (M^+); IR (ATR, neat, cm^{-1}): 1916, 1648, 1264, 759, 735, 689; HRMS (EI): m/z calcd for $C_{30}H_{23}FOSe_2$ (M^+): 578.0063; Found: 578.0078.

*1-(2-Furanyl)-4-phenyl-4-(phenylselenyl)-2-(2-(phenylselenyl)ethyl)buta-2,3-dien-1-one (**4e**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2d** (118 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4e** (151 mg, 55%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.49 (s, 1H), 7.31–7.42 (m, 7H), 7.18–7.24 (m, 5H), 7.12–7.16 (m, 2H), 6.37–6.38 (m, 1H), 2.70–2.89 (m, 3H), 2.51–2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 178.6, 151.6, 146.5, 134.2, 132.7, 132.3, 129.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.4, 127.7, 126.7, 118.4, 112.0, 107.8, 102.4, 29.3, 25.1; MS (EI, m/z): 550 (M^+); IR (ATR, neat, cm^{-1}): 1919, 1636, 1290, 759, 734, 689; HRMS (EI): m/z calcd for $C_{28}H_{22}O_2Se_2$ (M^+): 549.9950; Found: 549.9959.

*1-Phenyl-1-(phenylselenyl)-3-(2-(phenylselenyl)ethyl)hepta-1,2-dien-4-one (**4f**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2f** (106 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4f** (160 mg, 61%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 7.2 Hz, 2H), 7.17–7.40 (m, 11H), 2.72–2.85 (m, 2H), 2.57–2.64 (m, 1H), 2.39–2.49 (m, 3H), 1.48–1.57 (m, 2H), 0.82 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 199.9, 134.2, 132.8, 132.4, 130.0, 129.3, 129.1, 129.0, 128.8, 128.5, 128.4, 127.5, 126.7, 109.8, 101.8, 41.7, 28.2, 25.3, 17.8, 13.7; MS (EI, m/z): 526 (M^+); IR (ATR, neat, cm^{-1}): 1918, 1674, 1439, 1125, 735, 689; HRMS (EI): m/z calcd for $C_{27}H_{26}OSe_2$ (M^+): 526.0314; Found: 526.0318.

*2,2-Dimethyl-6-phenyl-6-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)hexa-4,5-dien-3-one (**4g**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2g** (113 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4g** (181 mg, 67%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 2H), 7.15–7.44 (m, 13H), 2.67–2.82 (m, 2H), 2.56–2.64 (m, 1H), 2.38–2.46 (m, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 205.0, 133.4, 132.7, 132.3, 130.0, 129.5, 129.2, 129.0, 128.8, 128.3, 128.0, 127.6, 126.7, 104.7, 99.8, 44.9, 30.7, 27.4, 25.4; MS (EI, m/z): 540 (M^+); IR (ATR, neat, cm^{-1}): 1913, 1663, 1475, 1108, 734, 689; HRMS (EI): m/z calcd for $C_{28}H_{28}OSe_2$ (M^+): 540.0471; Found: 540.0474.

*4-(Phenylselenyl)-2-(2-(phenylselenyl)ethyl)-1-*p*-tolylocta-2,3-dien-1-one (**4h**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2h** (120 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4h** (175 mg, 65%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.49

(d, J = 7.2 Hz, 2H), 7.13–7.28 (m, 10H), 2.84–2.97 (m, 2H), 2.60–2.74 (m, 2H), 2.40 (s, 3H), 2.23–2.26 (m, 2H), 1.40–1.45 (m, 2H), 1.14–1.20 (m, 2H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 194.2, 142.5, 135.9, 134.2, 132.4, 130.2, 129.1, 129.0, 128.9, 128.6, 128.6, 128.0, 126.7, 106.6, 99.5, 33.6, 30.3, 29.3, 25.7, 21.8, 21.6, 13.7; MS (EI, m/z): 554 (M^+); IR (ATR, neat, cm^{-1}): 1932, 1645, 1270, 830, 734, 689; HRMS (EI): m/z calcd for $C_{29}H_{30}OSe_2$ (M^+): 554.0627; Found: 554.0632.

2-Methyl-7-(phenylselenyl)-5-(2-(phenylselenyl)ethyl)undeca-5,6-dien-4-one ***(4i)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2i** (103 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (142 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **4i** (168 mg, 64%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 6.0 Hz, 2H), 7.21–7.29 (m, 6H), 2.68–2.82 (m, 2H), 2.25–2.52 (m, 6H), 2.02–2.09 (m, 1H), 1.53–1.60 (m, 2H), 1.34–1.39 (m, 2H), 0.85–0.92 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 200.6, 135.3, 132.3, 130.3, 129.2, 129.0, 128.6, 128.2, 126.7, 109.2, 100.8, 48.3, 33.7, 30.7, 27.9, 25.5, 25.4, 22.7, 22.6, 22.2, 13.8; MS (EI, m/z): 520 (M^+); IR (ATR, neat, cm^{-1}): 1933, 1670, 1472, 1021, 735, 690; HRMS (EI): m/z calcd for $C_{26}H_{32}OSe_2$ (M^+): 520.0784; Found: 520.0786.

General procedure for the synthesis of furans (5a–j). To a dried two-necked round-bottom flask (25 mL) were added diselenide (0.6 mmol, 1.2 equiv) and THF (2 mL) under a nitrogen atmosphere at room temperature. Then a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv) was added with a syringe to the reaction mixture to generate lithium selenolate **1** *in situ*. After 1–2 min, to the resulting reaction mixture was added a solution of 1-(1-alkynyl)cyclopropyl ketone **2** (0.5 mmol, 1.0 equiv) in 2 mL of THF at room temperature. The resulting reaction mixture was stirred for additional 15 min before phenylselenyl bromide (1.0 mmol, 2.0 equiv) was added. After being stirred for 24 h, the reaction was quenched with H_2O and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether–ethyl acetate = 50 : 1) afforded the final product **5**.

*2-Phenyl-3-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)-5-*p*-tolylfuran* ***(5a)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5a** (204 mg, 71%). Pale solid, mp 90–92 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 2H), 7.42–7.47 (m, 4H), 7.35 (t, J = 7.6 Hz, 2H), 7.10–7.29 (m, 11H), 3.03–3.07 (m, 2H), 2.91–2.95 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 148.9, 137.5, 133.2, 132.4, 130.3, 129.6, 129.4, 129.3, 128.9, 128.4, 128.3, 128.2, 127.9, 126.9, 126.5, 126.0, 125.4, 125.0, 106.8, 27.0, 26.6, 21.3; MS (EI, m/z): 574 (M^+); IR (ATR, neat, cm^{-1}): 1575, 1472, 1015, 765, 729, 684; HRMS (EI): m/z calcd for $C_{31}H_{26}OSe_2$ (M^+): 574.0314; Found: 574.0319.

*3-(2-(Butylselenyl)ethyl)-5-phenyl-4-(phenylselenyl)-2-*p*-tolylfuran* ***(5b)***. The reaction of di(n-butyl) diselenide (163 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5b** (86 mg, 31%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.14–7.31 (m, 8H), 3.02–3.06 (m, 2H), 2.60–2.64 (m, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.54–1.60 (m, 2H), 1.32–1.39 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 148.9, 137.6, 132.5, 130.4, 129.5, 129.4, 128.4, 128.3, 128.2, 128.1, 126.5, 126.0, 125.5, 125.3, 106.8, 32.8, 27.4, 23.7, 23.1, 22.5, 21.3,13.6; MS (EI, m/z): 554 (M^+); IR (ATR, neat, cm^{-1}): 1576, 1477, 818, 765, 733, 685; HRMS (EI): m/z calcd for $C_{29}H_{30}OSe_2$ (M^+): 554.0627; Found: 554.0624.

2-(4-Methoxyphenyl)-5-phenyl-4-(phenylselenyl)-3-(2-(phenylselenyl) ethyl)furan ***(5c)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2b** (138 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5c** (192 mg, 65%). Pale solid, mp 94–96 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 2H), 7.44–7.50 (m, 4H), 7.36 (t, J = 7.6 Hz, 2H), 7.12–7.29 (m, 9H), 6.86 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.01–3.05 (m, 2H), 2.91–2.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 154.0, 148.8, 133.3, 132.4, 130.3, 129.6, 129.3, 128.9, 128.4, 128.3, 128.1, 126.9, 126.4, 126.0, 124.1, 123.5, 114.1, 106.7, 55.3, 27.0, 26.7; MS (EI, m/z): 590 (M^+); IR (ATR, neat, cm^{-1}): 1577, 1474, 1065, 765, 733, 689; HRMS (EI): m/z calcd for $C_{31}H_{26}O_2Se_2$ (M^+): 590.0263; Found: 590.0264.

2-(4-Fluorophenyl)-5-phenyl-4-(phenylselenyl)-3-(2-(phenylselenyl)ethyl)furan ***(5d)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2c** (132 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5d** (167 mg, 58%). Pale solid, mp 93–95 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 2H), 7.46–7.49 (m, 4H), 7.36 (t, J = 7.6 Hz, 2H), 7.12–7.30 (m, 9H), 7.00 (t, J = 8.8 Hz, 2H), 3.00–3.05 (m, 2H), 2.89–2.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J = 246.5 Hz), 154.7, 147.9, 133.5, 132.2, 130.1, 129.4 (d, J = 9.4 Hz), 128.9, 128.5, 128.4, 127.4, 127.3, 127.1, 126.9 (d, J = 2.5 Hz), 126.5, 126.2, 125.3, 115.9, 115.7 (d, J = 21.6 Hz), 106.9, 27.0, 26.6; MS (EI, m/z): 578 (M^+); IR (ATR, neat, cm^{-1}): 1574, 1499, 1475, 1070, 838, 738, 689; HRMS (EI): m/z calcd for $C_{30}H_{23}FOSe_2$ (M^+): 578.0063; Found: 578.0072.

5-Phenyl-4-(phenylselenyl)-3-(2-(phenylselenyl)ethyl)-2,2'-bifuran ***(5e)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2d** (118 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5e** (143 mg, 52%). Pale solid, mp 55–57 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.45–7.47 (m, 2H), 7.28–7.39 (m, 4H), 7.13–7.23 (m, 8H), 6.54 (d, J = 3.6 Hz, 1H), 6.45–6.46 (m, 1H), 3.08–3.12 (m, 2H), 2.91–2.95 (m, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 154.4, 146.2, 142.1, 142.0, 132.7, 132.1, 130.0, 129.9, 129.4, 128.9, 128.5, 128.4, 128.3, 126.7, 126.5, 126.2, 125.4, 111.3, 106.6, 106.4, 26.7, 26.3; MS (EI, *m/z*): 550 (M^+); IR (ATR, neat, cm^{-1}): 1575, 1472, 1434, 1015, 765, 729, 684; HRMS (EI): *m/z* calcd for $C_{28}H_{22}O_2Se_2$ (M^+): 549.9950; Found: 549.9957.

*2-Phenyl-3-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)-5-(thiophen-2-yl)furan (**5f**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2e** (126 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5f** (139 mg, 49%). Pale solid, mp 96–98 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.43–7.45 (m, 2H), 7.32–7.36 (m, 2H), 7.10–7.28 (m, 11H), 6.96–6.98 (m, 1H), 3.02–3.06 (m, 2H), 2.87–2.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 145.0, 133.3, 132.6, 132.1, 129.9, 129.6, 129.3, 128.9, 128.5, 128.3, 127.6, 126.9, 126.4, 126.1, 124.9, 124.7, 123.4, 106.7, 26.8, 26.2; MS (EI, *m/z*): 566 (M^+); IR (ATR, neat, cm^{-1}): 1573, 1476, 1438, 1020, 766, 737, 684; HRMS (EI): *m/z* calcd for $C_{28}H_{22}OSSe_2$ (M^+): 565.9722; Found: 565.9721.

*2-Phenyl-3-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)-5-propylfuran (**5g**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2f** (106 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5g** (171 mg, 65%). Pale solid, mp 36–38 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.39–7.41 (m, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.11–7.27 (m, 9H), 2.91 (t, J = 7.2 Hz, 2H), 2.74 (t, J = 8.4 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 1.67–1.75 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 152.2, 132.7, 132.3, 130.6, 130.2, 129.3, 128.9, 128.3, 128.2, 127.8, 126.6, 126.2, 125.9, 123.6, 104.3, 28.6, 27.6, 25.8, 21.8, 13.8; MS (EI, *m/z*): 526 (M^+); IR (ATR, neat, cm^{-1}): 1575, 1476, 1436, 1069, 766, 737, 687; HRMS (EI): *m/z* calcd for $C_{27}H_{26}OSe_2$ (M^+): 526.0314; Found: 526.0324.

*2-Phenyl-3-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)-5-propylfuran (**5h**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2g** (113 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5h** (172 mg, 64%). Pale solid, mp 82–84 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.43–7.45 (m, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.11–7.26 (m, 9H), 2.84–2.91 (m, 4H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 152.8, 133.1, 132.7, 130.6, 129.8, 129.3, 128.9, 128.3, 128.2, 127.8, 126.8, 126.1, 125.9, 122.0, 105.6, 34.3, 29.7, 27.9, 26.7; MS (EI, *m/z*): 540 (M^+); IR (ATR, neat, cm^{-1}): 1573, 1478, 1440, 1110, 802, 737, 685; HRMS (EI): *m/z* calcd for $C_{28}H_{28}OSe_2$ (M^+): 540.0471; Found: 540.0477.

*2-Butyl-3-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)-5-*p*-tolylfuran (**5i**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2h** (120 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5i** (188 mg, 68%). Pale solid, mp 42–44 °C (petroleum ether–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.10–7.21 (m, 10H), 2.90–2.99 (m, 4H), 2.81 (t, J = 7.6 Hz, 2H), 2.34 (s, 3H), 1.59–1.67 (m, 2H), 1.31–1.39 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 148.2, 136.9, 133.0, 132.9, 129.7, 129.3, 129.1, 128.9, 128.5, 128.3, 126.8, 125.8, 125.1, 122.6, 106.6, 30.6, 27.1, 26.9, 26.6, 22.3, 21.2, 13.8; MS (EI, *m/z*): 554 (M^+); IR (ATR, neat, cm^{-1}): 1571, 1473, 1437, 1066, 823, 738, 690; HRMS (EI): *m/z* calcd for $C_{29}H_{30}O^{80}Se_2$ (M^+): 554.0627; Found: 554.0634.

*2-Butyl-5-isobutyl-3-(phenylselenyl)-4-(2-(phenylselenyl)ethyl)furan (**5j**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2i** (103 mg, 0.5 mmol, 1.0 equiv), and phenylselenyl bromide **3** (236 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **5j** (132 mg, 51%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.39 (m, 2H), 7.11–7.19 (m, 8H), 2.86–2.89 (m, 2H), 2.70 (t, J = 7.6 Hz, 2H), 2.61–2.66 (m, 2H), 2.37 (d, J = 6.8 Hz, 2H), 1.89–1.98 (m, 1H), 1.52–1.59 (m, 2H), 1.21–1.33 (m, 2H), 0.84–0.88 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 150.4, 133.3, 132.2, 130.3, 129.0, 128.9, 128.2, 126.5, 125.6, 121.7, 103.7, 35.5, 30.7, 28.2, 27.5, 26.7, 25.9, 22.3, 22.2, 13.7; MS (EI, *m/z*): 520 (M^+); IR (ATR, neat, cm^{-1}): 1578, 1476, 1437, 1065, 1021, 732, 689; HRMS (EI): *m/z* calcd for $C_{26}H_{32}OSe_2$ (M^+): 520.0784; Found: 520.0783.

Transformation of 4a into 5a. To a dried two-necked round-bottom flask (25 mL) were added **4a** (116 mg, 0.2 mmol, 1.0 equiv) and THF (4 mL) under a nitrogen atmosphere at room temperature. Then phenylselenyl bromide **3** (47 mg, 0.2 mmol, 1.0 equiv) was added and the reaction mixture was stirred for additional 0.5 h. When the reaction was complete, the reaction mixture was transferred to a pear-shaped flask. Evaporation and column chromatography on silica gel (eluent: petroleum ether–CH_2Cl_2 = 15 : 1) afforded **5a** (73 mg, 63%).

General procedure for the synthesis of halogen-substituted furans (6a–c). To a dried two-necked round-bottom flask (25 mL) were added **4a** (172 mg, 0.3 mmol, 1.0 equiv) and THF (4 mL) under a nitrogen atmosphere. Then electrophile (0.45 mmol, 1.5 equiv) was added and the reaction mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, the reaction mixture was transferred to a pear-shaped flask. Evaporation and column chromatography on silica gel (eluent: petroleum ether–CH_2Cl_2 = 15 : 1) afforded final product **6** and **5a**.

*3-Iodo-2-phenyl-4-(2-(phenylselenyl)ethyl)-5-*p*-tolylfuran (**6a**).* The reaction of **4a** (172 mg, 0.3 mmol, 1.0 equiv) and NIS (101 mg, 0.45 mmol, 1.5 equiv) in THF (4 mL) afforded **6a** (99 mg, 61%) and **5a** (5 mg, 3%). **6a**: Pale solid, mp 96–98 °C (petroleum ether–CH_2Cl_2 = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2H), 7.58 (s, 2H), 7.28–7.43 (m, 8H), 7.12 (d, J = 8.0 Hz, 2H), 3.04–3.09 (m, 4H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.9, 137.7, 133.7, 130.2, 129.4, 129.3, 129.0, 128.3, 128.1, 127.6, 127.2, 126.3, 125.5, 123.9, 70.4, 28.6, 26.1, 21.3; MS (EI, *m/z*): 544 (M^+); IR (ATR, neat,

cm^{-1}): 1501, 1477, 1440, 1109, 763, 732, 690; HRMS (EI): *m/z* calcd for $C_{25}H_{21}IOSe$ (M^+): 543.9802; Found: 543.9800.

*3-Bromo-2-phenyl-4-(2-(phenylselenyl)ethyl)-5-*p*-tolylfuran* ***(6b)***. The reaction of **4a** (172 mg, 0.3 mmol, 1.0 equiv) and NBS (80 mg, 0.45 mmol, 1.5 equiv) in THF (4 mL) afforded **6b** (94 mg, 63%) and **5a** (9 mg, 5%). **6b**: Pale solid, mp 72–74 °C (petroleum ether–CH_2Cl_2 = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.2 Hz, 2H), 7.55–7.57 (m, 2H), 7.39–7.43 (m, 4H), 7.26–7.32 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 3.02–3.13 (m, 4H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 147.0, 137.8, 133.5, 129.7, 129.5, 129.4, 129.0, 128.4, 127.8, 127.6, 127.2, 125.5, 125.4, 121.7, 101.1, 26.5, 25.9, 21.3; MS (EI, *m/z*): 496 (M^+); IR (ATR, neat, cm^{-1}): 1504, 1480, 1441, 1107, 817, 735, 689; HRMS (EI): *m/z* calcd for $C_{25}H_{21}BrOSe$ (M^+): 495.9941; Found: 495.9940.

*3-Chloro-2-phenyl-4-(2-(phenylselenyl)ethyl)-5-*p*-tolylfuran* ***(6c)***. The reaction of **4a** (172 mg, 0.3 mmol, 1.0 equiv) and $CuCl_2$ (61 mg, 0.45 mmol, 1.5 equiv) in THF (4 mL) afforded **6c** (87 mg, 64%) and **5a** (18 mg, 10%). **6c**: Pale solid, mp 104–106 °C (petroleum ether–CH_2Cl_2 = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.26–7.36 (m, 5H), 7.14–7.21 (m, 3H), 3.55 (t, J = 8.0 Hz, 2H), 3.15 (t, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 150.0, 138.0, 132.1, 10.2, 129.6, 129.4, 128.5, 128.4, 127.7, 126.5, 126.2, 125.7, 121.8, 106.7, 42.9, 29.2, 21.3; MS (EI, *m/z*): 452 (M^+); IR (ATR, neat, cm^{-1}): 1507, 1477, 1440, 1168, 817, 729, 683; HRMS (EI): *m/z* calcd for $C_{25}H_{21}ClOSe$ (M^+): 452.0446; Found: 452.0445.

General procedure for the synthesis of fluoro-substituted 2-alkynyl ketones (8a–j). To a dried two-necked round-bottom flask (25 mL) were added diselenide (0.6 mmol, 1.2 equiv) and THF (2 mL) under a nitrogen atmosphere at room temperature. Then a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv) was added with a syringe to the reaction mixture to generate lithium selenolate **1** *in situ*. After 1–2 min, to the resulting reaction mixture was added a solution of 1-(1-alkynyl)cyclopropyl ketone **2** (0.5 mmol, 1.0 equiv) in 2 mL of THF at room temperature. The resulting reaction mixture was stirred for additional 15 min before *N*-fluorodi(benzenesulfonyl) amine **7b** (0.6 mmol, 1.2 equiv) was added. After being stirred for 11 h, the reaction was quenched with H_2O and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether–ethyl acetate = 50 : 1) afforded the final product **8**.

*2-Fluoro-4-phenyl-2-(2-(phenylselenyl)ethyl)-1-*p*-tolylbut-3-yn-1-one* ***(8a)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8a** (124 mg, 57%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 6.4 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H), 7.23–7.36 (m, 8H), 3.22–3.29 (m, 1H), 3.08–3.16 (m, 1H), 2.62–2.77 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4 (d, J = 26.3 Hz), 144.8, 132.2, 131.8 (d, J = 2.8 Hz), 130.4, 130.3, 129.6, 129.5, 129.1, 129.0, 128.4, 126.9, 120.9, 93.6 (d, J = 183.3 Hz), 92.5 (d, J = 10.1 Hz), 83.9 (d, J = 29.2 Hz), 39.0 (d, J = 24.4 Hz), 21.7, 20.4 (d, J = 2.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.0; MS (EI, *m/z*): 436 (M^+); IR (ATR, neat, cm^{-1}): 2227, 1690, 1605, 1256, 754, 738, 689; HRMS (EI): *m/z* calcd for $C_{25}H_{21}FOSe$ (M^+): 436.0742; Found: 436.0747.

*2-(2-(Butylselenyl)ethyl)-2-fluoro-4-phenyl-1-*p*-tolylbut-3-yn-1-one* ***(8b)***. The reaction of di(n-butyl) diselenide (163 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8b** (87 mg, 42%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 6.8 Hz, 2H), 7.29–7.36 (m, 5H), 2.88–2.93 (m, 1H), 2.60–2.79 (m, 5H), 2.42 (s, 3H), 1.63–1.70 (m, 2H), 1.38–1.44 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (d, J = 27.0 Hz), 144.7, 131.8 (d, J = 3.4 Hz), 130.5 (d, J = 3.3 Hz), 130.4 (d, J = 5.0 Hz), 129.5, 129.1, 128.4, 121.0 (d, J = 4.2 Hz), 93.6 (d, J = 187.1 Hz), 92.3 (d, J = 9.8 Hz), 84.0 (d, J = 28.9 Hz), 39.5 (d, J = 23.7 Hz), 32.5, 23.8, 23.0, 21.7, 16.3 (d, J = 2.8 Hz), 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.2; MS (EI, *m/z*): 416 (M^+); IR (ATR, neat, cm^{-1}): 2228, 1690, 1606, 1257, 1021, 754, 689; HRMS (EI): *m/z* calcd for $C_{23}H_{25}FOSe$ (M^+): 416.1055; Found: 416.1049.

2-Fluoro-1-(4-methoxyphenyl)-4-phenyl-2-(2-(phenylselenyl)-ethyl)but-3-yn-1-one ***(8c)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2b** (138 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8c** (117 mg, 52%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.23–7.34 (m, 6H), 6.92 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.23–3.30 (m, 1H), 3.09–3.17 (m, 1H), 2.63–2.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1 (d, J = 26.7 Hz), 164.0, 132.7 (d, J = 4.7 Hz), 132.2, 131.8 (d, J = 2.0 Hz), 129.6, 129.5, 129.1, 128.4, 126.8, 125.7 (d, J = 3.2 Hz), 120.9 (d, J = 3.4 Hz), 113.6, 93.6 (d, J = 182.3 Hz), 92.4 (d, J = 10.2 Hz), 84.0 (d, J = 29.0 Hz), 55.4, 39.9 (d, J = 24.3 Hz), 20.4 (d, J = 2.2 Hz); ^{19}F NMR (376 MHz, CDCl3) δ −142.4; MS (EI, *m/z*): 452 (M^+); IR (ATR, neat, cm^{-1}): 2228, 1682, 1597, 1253, 1171, 736, 689; HRMS (EI): *m/z* calcd for $C_{25}H_{21}FO_2Se$ (M^+): 452.0691; Found: 452.0686.

2-Fluoro-1-(4-fluorophenyl)-4-phenyl-2-(2-(phenylselenyl)ethyl)-but-3-yn-1-one ***(8d)***. The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2c** (132 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8d** (108 mg, 49%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.27 (m, 2H), 7.51–7.53 (m, 2H), 7.23–7.40 (m, 8H), 7.11–7.15 (m, 2H), 3.22–3.29 (m, 1H), 3.09–3.16 (m, 1H), 2.64–2.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2 (d, J = 27.0 Hz), 166.0 (d, J = 255.7 Hz), 133.1 (q, J = 8.8 Hz), 132.3, 131.8 (d, J = 2.3 Hz), 129.7, 129.6, 129.3 (t, J = 3.5 Hz), 129.2, 128.4, 127.0, 120.7 (d, J = 4.0 Hz), 115.6 (d, J = 20.7 Hz), 93.5 (d, J = 182.6 Hz), 92.9 (d, J = 9.9 Hz), 83.5 (d, J = 29.0 Hz), 38.8 (d, J = 24.3 Hz), 20.4 (d, J = 2.7 Hz); ^{19}F NMR (376 MHz, CDCl3) δ −103.3, −142.8; MS (EI, *m/z*): 440 (M^+); IR (ATR, neat, cm^{-1}): 2228, 1694, 1596, 1238, 755, 735, 688; HRMS (EI): *m/z* calcd for $C_{24}H_{18}F_2OSe$ (M^+): 440.0491; Found: 440.0499.

*2-Fluoro-1-(2-furanyl)-4-phenyl-2-(2-(phenylselenyl)ethyl)but-3-yn-1-one (**8e**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2d** (118 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8e** (110 mg, 53%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.49–7.68 (m, 3H), 7.41 (d, J = 6.8 Hz, 2H), 7.22–7.37 (m, 6H), 6.56–6.57 (m, 1H), 3.19–3.26 (m, 1H), 3.06–3.13 (m, 1H), 2.61–2.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4 (d, J = 27.5 Hz), 148.4 (d, J = 2.8 Hz), 148.0, 132.3, 131.8 (d, J = 3.7 Hz), 129.5, 129.4, 129.1, 128.3, 126.9, 122.4 (d, J = 9.5 Hz), 120.7 (d, J = 3.5 Hz), 112.4, 93.4 (d, J = 183.5 Hz), 91.1 (d, J = 9.5 Hz), 83.2 (d, J = 29.2 Hz), 38.9 (d, J = 23.9 Hz), 20.1 (d, J = 2.4 Hz); ^{19}F NMR (376 MHz, CDCl3) δ −146.3; MS (EI, m/z): 412 (M^+); IR (ATR, neat, cm^{-1}): 2230, 1678, 1459, 1023, 757, 735, 689; HRMS (EI): m/z calcd for $C_{22}H_{17}FO_2Se$ (M^+): 412.0378; Found: 412.0374.

*2-Fluoro-4-phenyl-2-(2-(phenylselenyl)ethyl)-1-(thiophen-2-yl)-but-3-yn-1-one (**8f**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2e** (126 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8f** (107 mg, 50%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.72 (d, J = 4.8 Hz, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.24–7.37 (m, 6H), 7.16 (t, J = 4.4 Hz, 1H), 3.21–3.28 (m, 1H), 3.08–3.15 (m, 1H), 2.63–2.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2 (d, J = 28.5 Hz), 138.8 (d, J = 4.1 Hz), 135.6, 135.5, 132.3, 131.9 (d, J = 2.1 Hz), 129.5, 129.4, 129.2, 128.4, 127.0, 120.8 (d, J = 2.5 Hz), 94.0 (d, J = 183.3 Hz), 91.6 (d, J = 9.4 Hz), 83.5 (d, J = 28.3 Hz), 39.2 (d, J = 24.0 Hz), 20.2 (d, J = 2.0 Hz); ^{19}F NMR (376 MHz, CDCl3) δ −142.9; MS (EI, m/z): 428 (M^+); IR (ATR, neat, cm^{-1}): 2229, 1668, 1409, 1253, 755, 727, 688; HRMS (EI): m/z calcd for $C_{22}H_{17}FOSSe$ (M^+): 428.0149; Found: 428.0148.

*3-Fluoro-1-phenyl-3-(2-(phenylselenyl)ethyl)hept-1-yn-4-one (**8g**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2f** (106 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8g** (102 mg, 53%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.51 (m, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.23–7.37 (m, 6H), 3.13–3.20 (m, 1H), 2.98–3.05 (m, 1H), 2.66–2.79 (m, 2H), 2.39–2.55 (m, 2H), 1.62–1.72 (m, 2H), 0.95 (t, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6 (d, J = 28.2 Hz), 132.4, 131.9 (d, J = 3.1 Hz), 129.5, 129.4, 129.2, 128.4, 127.0, 120.8 (d, J = 3.6 Hz), 94.4 (d, J = 182.8 Hz), 90.3 (d, J = 9.8 Hz), 82.8 (d, J = 29.5 Hz), 38.8, 38.2 (d, J = 23.5 Hz), 20.3 (d, J = 2.1 Hz), 16.7 (d, J = 1.5 Hz), 13.5; ^{19}F NMR (376 MHz, CDCl3) δ −150.2; MS (EI, m/z): 388 (M^+); IR (ATR, neat, cm^{-1}): 2229, 1731, 1401, 1024, 755, 735, 689; HRMS (EI): m/z calcd for $C_{21}H_{21}FOSe$ (M^+): 388.0742; Found: 388.0746.

*4-Fluoro-2,2-dimethyl-6-phenyl-4-(2-(phenylselenyl)ethyl)hex-5-yn-3-one (**8h**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2g** (113 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8h** (86 mg, 43%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 6.8 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.24–7.35 (m, 6H), 3.12–3.19 (m, 1H), 2.95–3.02 (m, 1H), 2.48–2.58 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9 (d, J = 25.8 Hz), 132.2, 131.7 (d, J = 2.4 Hz), 129.6, 129.4, 129.1, 128.3, 126.9, 121.0 (d, J = 4.2 Hz), 96.0 (d, J = 187.3 Hz), 90.6 (d, J = 10.0 Hz), 83.5 (d, J = 28.0 Hz), 40.9 (d, J = 3.8 Hz), 39.8 (d, J = 23.9 Hz), 26.6 (d, J = 4.0 Hz), 20.3; ^{19}F NMR (376 MHz, CDCl3) δ −149.5; MS (EI, m/z): 402 (M^+); IR (ATR, neat, cm^{-1}): 2228, 1690, 1605, 1257, 801, 754, 689; HRMS (EI): m/z calcd for $C_{22}H_{23}FOSe$ (M^+): 402.0898; Found: 402.0891.

*2-Fluoro-2-(2-(phenylselenyl)ethyl)-1-*p*-tolyloct-3-yn-1-one (**8i**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2h** (120 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8i** (89 mg, 43%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.22–7.25 (m, 5H), 3.14–3.21 (m, 1H), 3.01–3.08 (m, 1H), 2.50–2.61 (m, 2H), 2.40 (s, 3H), 2.22–2.27 (m, 2H), 1.43–1.50 (m, 2H), 1.31–1.38 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9 (d, J = 27.4 Hz), 144.5, 132.2, 130.5 (d, J = 2.9 Hz), 130.4 (d, J = 4.1 Hz), 129.8, 129.1, 128.9, 126.8, 94.6 (d, J = 10.0 Hz), 93.5 (d, J = 181.8 Hz), 75.8 (d, J = 28.8 Hz), 39.0 (d, J = 25.3 Hz), 29.9 (d, J = 1.4 Hz), 21.8, 21.7, 20.5(d, J = 3.6 Hz), 18.5 (d, J = 3.4 Hz), 13.4; ^{19}F NMR (376 MHz, CDCl3) δ −142.3; MS (EI, m/z): 416 (M^+); IR (ATR, neat, cm^{-1}): 2235, 1690, 1606, 1260, 735, 690; HRMS (EI): m/z calcd for $C_{23}H_{25}FOSe$ (M^+): 416.1055; Found: 416.1057.

*5-Fluoro-2-methyl-5-(2-(phenylselenyl)ethyl)undec-6-yn-4-one (**8j**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2i** (103 mg, 0.5 mmol, 1.0 equiv), and **7b** (188 mg, 0.6 mmol, 1.2 equiv) in THF (4 mL) afforded **8j** (63 mg, 33%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.49 (m, 2H), 7.24–7.29 (m, 3H), 3.05–3.12 (m, 1H), 2.90–2.98 (m, 1H), 2.47–2.62 (m, 2H), 2.15–2.38 (m, 5H), 1.35–1.53 (m, 4H), 0.89–0.95 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5 (d, J = 28.2 Hz), 132.3, 129.6, 129.1, 127.0, 94.4 (d, J = 181.6 Hz), 92.3 (d, J = 10.3 Hz), 74.5 (d, J = 29.0 Hz), 45.6, 38.1 (d, J = 24.2 Hz), 30.0 (d, J = 1.9 Hz), 23.8, 22.4, 22.3, 21.9, 20.3 (d, J = 3.1 Hz), 18.4 (d, J = 3.6 Hz), 13.5; ^{19}F NMR (376 MHz, CDCl3) δ −149.4; MS (EI, m/z): 382 (M^+); IR (ATR, neat, cm^{-1}): 2237, 1731, 1464, 1364, 735, 690; HRMS (EI): m/z calcd for $C_{20}H_{27}FOSe$ (M^+): 382.1211; Found: 382.1205.

General procedure for the synthesis of substituted 2-alkynyl ketones (8k–m). To a dried two-necked round-bottom flask (25 mL) were added diselenide (0.6 mmol, 1.2 equiv) and THF (2 mL) under a nitrogen atmosphere at room temperature. Then a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv) was added with a syringe to the reaction mixture to generate lithium selenolate **1** *in situ*. After 1–2 min, to the resulting reaction mixture was added a solution of 1-(1-alkynyl)cyclopropyl ketone **2** (0.5 mmol, 1.0 equiv) in 2 mL of THF at room temperature. The resulting reaction mixture was stirred for additional 15 min before electrophile (1.0 mmol, 2.0 equiv) was added. After being stirred for 24 h, the reaction was quenched with H_2O and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with brine and dried over

Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether–ethyl acetate = 50 : 1) afforded the final product **8**.

*2-Chloro-4-phenyl-2-(2-(phenylselenyl)ethyl)-1-*p*-tolylbut-3-yn-1-one (**8k**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and NCS (133 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **8k** (142 mg, 63%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.24–7.37 (m, 10H), 3.26–3.31 (m, 2H), 2.67–2.86 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 144.5, 132.1, 131.7, 130.9, 130.1, 129.8, 129.5, 129.1, 128.7, 128.4, 126.8, 121.2, 91.8, 86.1, 64.5, 42.1, 22.0, 21.7; MS (EI, m/z): 452 (M^+); IR (ATR, neat, cm^{-1}): 2226, 16 878, 12 394, 1183, 755, 734, 688; HRMS (EI): m/z calcd for $C_{25}H_{21}ClOSe$ (M^+): 452.0446; Found: 452.0447.

*2-(Phenylethynyl)-2-(2-(phenylselenyl)ethyl)-1-*p*-tolylpent-4-en-1-one (c).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and allyl bromide (121 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **8l** (158 mg, 69%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 7.44–7.45 (m, 2H), 7.35–7.37 (m, 2H), 7.20–7.31 (m, 8H), 5.79–5.90 (m, 1H), 5.06–5.11 (m, 2H), 3.01–3.06 (m, 2H), 2.81–2.97 (m, 1H), 2.54–2.66 (m, 2H), 2.39 (s, 3H), 2.16–2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 143.4, 133.5, 132.8, 131.9, 131.4, 130.1, 129.8, 129.0, 128.7, 128.3, 126.5, 122.9, 119.0, 90.4, 88.0, 51.7, 43.1, 38.9, 22.3, 21.6; MS (EI, m/z): 458 (M^+); IR (ATR, neat, cm^{-1}): 1675, 1604, 1438, 1181, 7548, 734, 689; HRMS (EI): m/z calcd for $C_{28}H_{26}OSe$ (M^+): 458.1149; Found: 458.1154.

*2-Benzyl-4-phenyl-2-(2-(phenylselenyl)ethyl)-1-*p*-tolylbut-3-yn-1-one (**8m**).* The reaction of diphenyl diselenide (187 mg, 0.6 mmol, 1.2 equiv), a solution of n-BuLi in n-hexane (2.5 M, 0.24 mL, 0.6 mmol, 1.2 equiv), **2a** (130 mg, 0.5 mmol, 1.0 equiv), and benzyl bromide (171 mg, 1.0 mmol, 2.0 equiv) in THF (4 mL) afforded **8m** (163 mg, 64%). Liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 6.8 Hz, 2H), 7.27–7.30 (m, 5H), 7.20–7.22 (m, 8H), 7.12 (d, J = 8.4 Hz, 2H), 3.41 (d, J = 13.2 Hz, 1H), 3.09 (d, J = 13.2 Hz, 1H), 2.97–3.06 (m, 2H), 2.60–2.67 (m, 1H), 2.35 (s, 3H), 2.13–2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 143.1, 136.2, 134.3, 131.9, 131.2, 130.7, 130.1, 129.6, 129.0, 128.5, 128.3, 128.2, 127.9, 126.9, 126.6, 122.9, 90.7, 89.2, 53.9, 45.5, 40.2, 22.6, 21.6; MS (EI, m/z): 508 (M^+); IR (ATR, neat, cm^{-1}): 1673, 1604, 1439, 1180, 754, 734, 692; HRMS (EI): m/z calcd for $C_{32}H_{28}OSe$ (M^+): 508.1305; Found: 508.1306.

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