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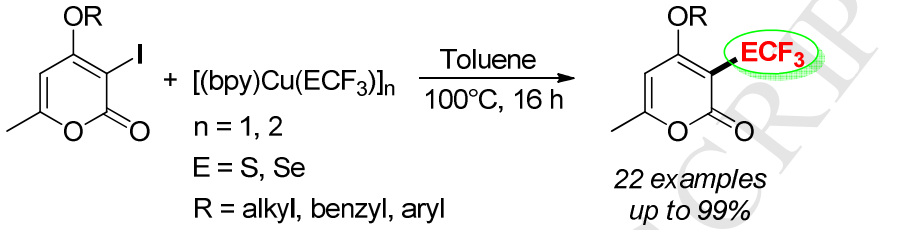

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Synthesis of trifluoromethylthiolated and trifluoromethylselenolated pyrones

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ABSTRACT

Trifluoromethylthiolation and trifluoromethylselenolation of 3- or 4-iodo(bromo)-2-pyrones with (bpy)$CuSCF_3$ and $[(bpy)CuSeCF_3]_2$ provide a convenient method for the synthesis of trifluoromethylthio(seleno)lated 4-alkoxy-, aryloxy-, and benzyloxy-2-pyrones in high yields.

1. Introduction

The synthesis of 2-pyrones and their derivatives has attracted much attention in the context of the biological activities of these compounds induced by the hetero-cyclic moiety.[1,2,3,4] These compounds display a wide range of biological activities such as cytotoxic, antibiotic and antifungal activity. Among them, compounds containing methyl or trifluoromethyl-substituted at C-3 position of the 2-pyrone moiety are privileged (Figure 1), as they are found in a large number of biologically and pharmaceutically active molecules that have a broad spectrum of properties. Further, they act as potential therapeutic agents for treatment of central nervous system disorders, and some exhibit fungicidal activity.[5,6,7,8] Consequently, the development of new practical methods for the synthesis of methyl- or trifluoromethyl-2-pyrone scaffold is of considerable interest.[9,10,11]

Trifluoromethylthiolated heterocycles are attracting growing interest in pharmaceutical and agricultural related research due to the unique properties of the trifluoromethylthio (SCF_3) group.[12,13,14,15,16] Because of its strong electron-withdrawing effects (Hammett constant: σ_m = 0.40 and σ_p = 0.50) and high lipophilicity (π_R = 1.44),[17,18,19] the introduction of SCF_3 group can influence the chemical, physical, and physiological properties of the resulting molecules. This realization has led to a rapid development of efficient and convenient trifluoromethylthiolation methods.[20,21,22,23,24] Among these, the use of trifluoromethylthiolating reagents for the SCF_3-functionalization of parent substrates play a pivotal role in this transformation. Examples of the transition-metal-catalyzed or metal-free trifluoromethylthiolation of organic halides,[25,26,27,28,29] boronic acids,[30,31,32] organometallic species,[33] C−H bonds,[34,35,36,37,38,39,40] alcohols,[41,42] and alkynes[43,44,45] with stable nucleophilic or electrophilic trifluoromethylthiolating reagents have recently been developed.

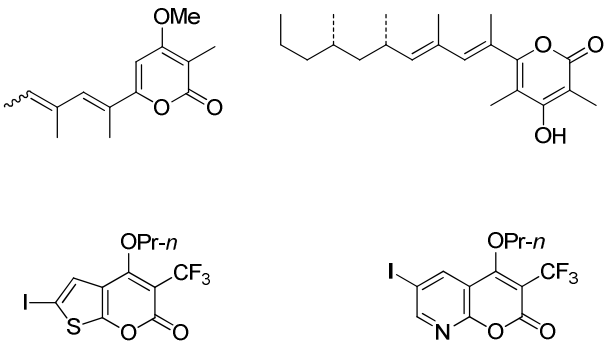

Figure 1. Bioactive 2-pyrone derivatives.

Recently, we reported the utilization of novel copper reagents (bpy)$CuSCF_3$ (**1a**) and $[(bpy)CuSeCF_3]_2$ (**1b**) for trifluoromethylthiolation[46] and trifluoromethylselenolation.[47] These copper reagents reacted with organic halides to provide the corresponding trifluoromethyl thio or selenoethers in good to excellent yields.[48,49,50,51,52]

In view of the aforementioned success, we planned to explore the possibility of introducing a

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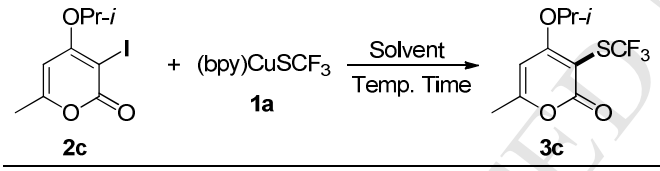
trifluoromethylthio(seleno) group into a pyrone ring through nucleophilic trifluoromethylthio(seleno)lation of the halogenated 2-pyrones with copper reagents **1a** and **1b**. We herein disclose our investigation into a synthetic strategy to trifluoromethylthio (seleno)lated pyrones.

2. Results and Discussion

In the preliminary studies, we chose 3-iodo-4-isopropoxy-6-methyl-2*H*-pyran-2-one (**2c**) as a model substrate to determine the reaction conditions (Table 1). The initial attempt was carried out using (bpy)$CuSCF_3$ (**1a**) as the trifluoromethylthiolating reagent in CH_3CN at 100 °C. Pleasingly, the desired trifluoromethylthiolated pyrones (**3c**) was obtained in 79% yield after 16 h (Table 1, Entry 1). A screening of solvents showed that DMSO, and DMF were inefficient (Table 1, Entries 2 and 3), whereas diglyme, THF, and dioxane gave better yields (Table 1, Entries 4-6). Toluene turned out to be the best solvent for this transformation (Table 1, Entry 7). Decreasing the reaction temperature from 100 °C to 80 °C led to a lower yield of product **3c** (68%; Table 1, Entry 8). Furthermore, a shorter reaction time (8 h) resulted in a slight decrease in the yield of **3c** (89%; Table 1, Entry 9). Therefore, we the conditions of using toluene as solvent with conventional heating at 100 °C for 16 h were adopted for the subsequent reactions.

Table 1
Optimization of trifluoromethylthiolation of 3-iodo-4-isopropoxy-6-methyl-2*H*-pyran-2-one (**2c**) [a]

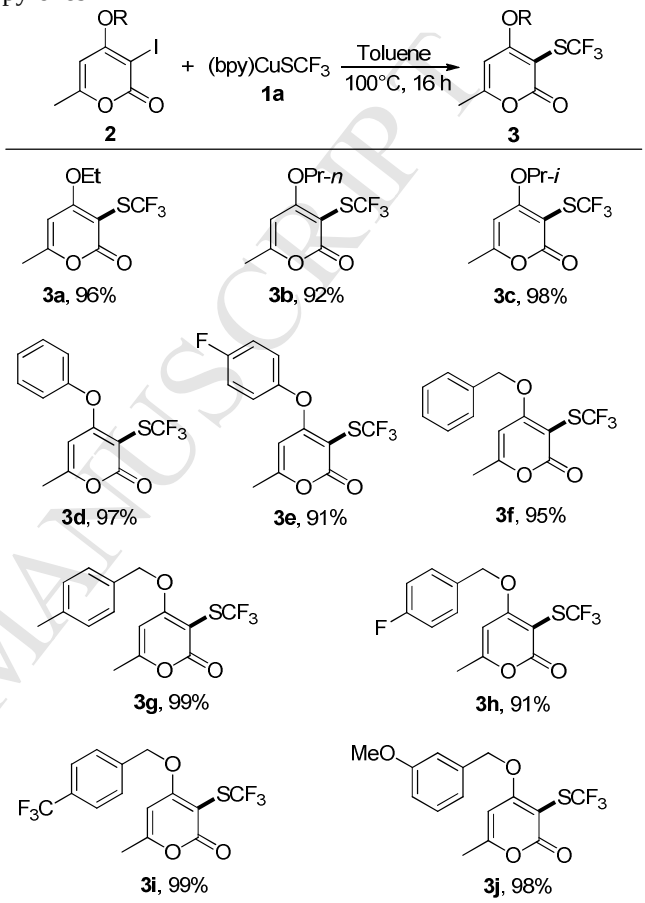


Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	CH_3CN	100	16	79
2	DMSO	100	16	trace
3	DMF	100	16	14
4	Diglyme	100	16	87
5	THF	100	16	91
6	Dioxane	100	16	85
7	Toluene	100	16	97
8	Toluene	80	16	68
9	Toluene	100	8	89

[a] Reaction conditions: **1a** (0.075 mmol), **2c** (0.050 mmol), solvent (1.2 mL), under N_2 atmosphere.
[b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

With the optimized conditions in hand, we investigated the scope of the transformation. As showed in Table 2, the 3-iodo-4-alkoxy-2-pyrones **2a**-**2c** were efficiently converted into the corresponding trifluoromethylthiolated pyrone derivatives, and the resulting products **3a**-**3c** were isolated in high yield (92-98%). Similarly, the use of 3-iodo-4-aryloxy-2-pyrones **2d** and **2e** as electrophile afforded the corresponding products **3d** and **3e** in high yields (97% and 91%, respectively) after isolation by column chromatography. Additionally, the reaction of 3-iodo-4-benzyloxy-2-pyrones **2f**-**2j** with **1a** led to the formation of the expected products **3f**-**3j** in excellent yields (91-99%).

Table 2
Substrate scope of trifluoromethylthiolation of 3-iodo-2-pyrones[a,b]



[a] Reaction conditions: **1a** (0.75 mmol), **2** (0.50 mmol), toluene (5 mL), 100 °C, 16 h, N_2.
[b] Yields shown are of isolated products.

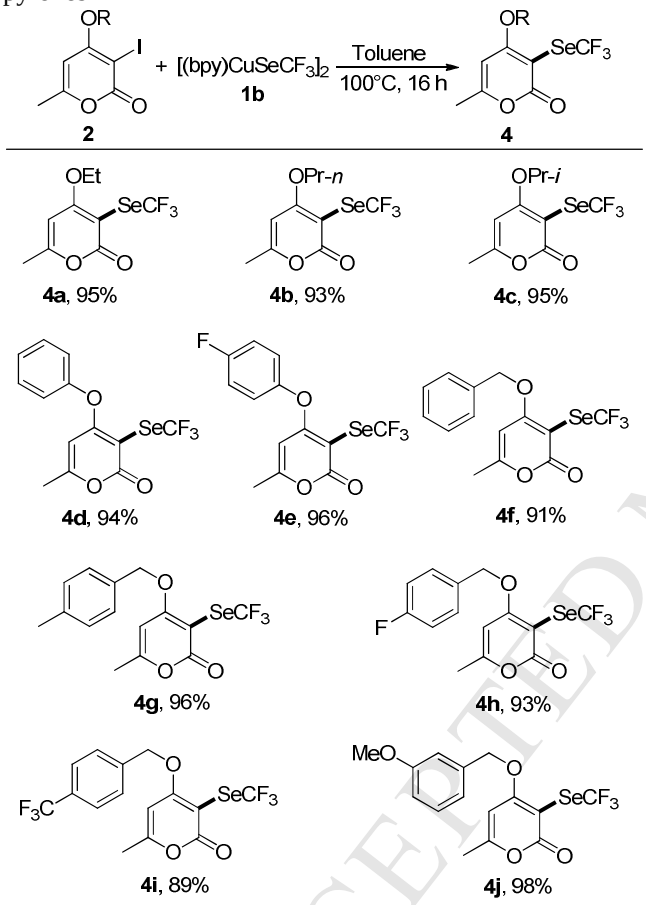
The trifluoromethylselenolation of 3-iodo-2-pyrones with $[(bpy)CuSeCF_3]_2$ (**1b**) was then investigated (Table 3). In most cases, the trifluoromethylselenolation proceeded smoothly to produce the desired trifluoromethylthiolated pyrones in excellent yields under the similar reaction conditions as those of **1a**.

Next, we extended the substrate scope of the reaction by conducting trifluoromethylthio(seleno)lation of 4-iodo-6-methyl-2*H*-pyran-2-one (**5a**) with **1a** or **1b** under the optimal conditions, to afford products **6a** and **6b** in 80% and 98% yields, respectively (Scheme 1).

To further investigate the substrate scope of this trifluoromethylthio(seleno)lation sequence, 4-bromo-2-pyrone was also explored. However, the trifluoromethylthiolation of 4-bromo-6-methyl-2*H*-pyran-2-one (**5b**) with **1a** gave the desired product **6a** in low yield (20%) under conditions used for the corresponding iodo starting material.[8] Taking into account the fact that trifluoromethylthiolation of organic

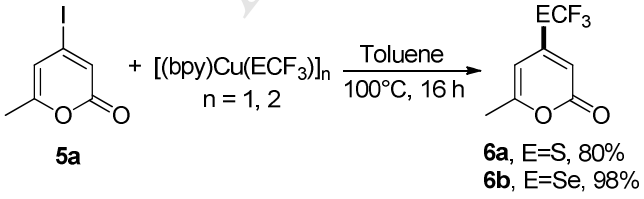
bromides has previously been carried out successfully in the synthesis of α-trifluoromethylthio-α,β-unsaturated carbonyl compounds with 2 equiv of CsF as an additive,[53] we decided to further optimize the reaction conditions by employing the same strategy. When the reaction was conducted in the presence of 2 equiv of CsF at 120 °C, indeed the yield of target compound **6a** was increased to 67%. The process was also found to be effective between 4-bromo-6-methyl-2*H*-pyran-2-one (**5b**) and **1b**, leading to the corresponding trifluoromethylselenolated pyrone **6b** in good yield (81%) (Scheme 2).

Table 3
Substrate scope of trifluoromethylselenolation of 3-iodo-2-pyrones[a,b]

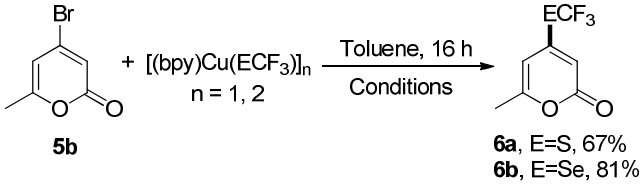


[a] Reaction conditions: **1b** (0.375 mmol), **2** (0.50 mmol), toluene (5 mL), 100 °C, 16 h, N_2.

[b] Yields shown are of isolated products.

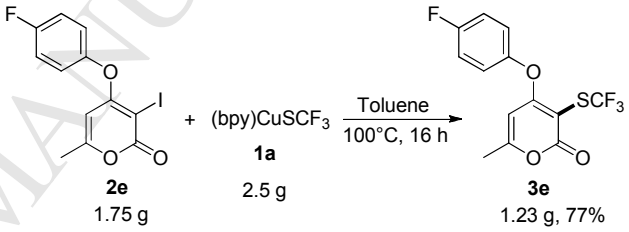


Scheme 1. Trifluoromethylthiolation and trifluoromethylselenolation of 4-iodo-6-methyl-2*H*-pyran-2-one (**5a**)



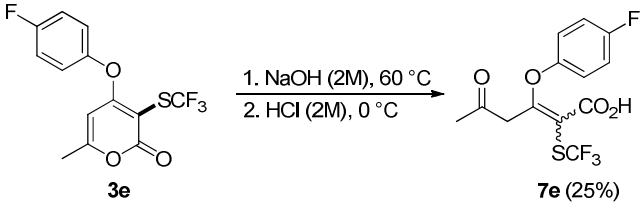
Scheme 2. Trifluoromethylthiolation and trifluoromethylselenolation of 6-methyl-3-bromo-2-pyrones (**5b**)

To demonstrate the scalability of this procedure, 1.75 g of 4-(4-fluorophenoxy)-3-iodo-6-methyl-2*H*-pyran-2-one (**2e**) was reacted with 2.5 g of **1a** in toluene at 100 °C for 16 h. The corresponding trifluoromethylthiolated pyrone **3e** was isolated in 1.23 g (77% yield, Scheme 3), indicating that the reaction can be scaled up without major difficulties.



Scheme 3. Scalability of the trifluoromethylthiolation of **2e**

To demonstrate the synthetic application of this methodology, ring-opening reaction of trifluoromethylthiolated pyrone **3e** was carried out at r.t., and the desired **7e** was obtained in 25% yield (Scheme 4). Thus, this method provided a new approach for the synthesis of novel SCF_3-substituted unsaturated carboxylic acids.



Scheme 4. Ring-opening reaction of **3e**

3. Conclusions

In summary, we have developed an efficient route to prepare trifluoromethylthio(seleno)lated pyrones by trifluoromethylthio(seleno)lation of 3- or 4-iodo(bromo)-2-pyrones with (bpy)$CuSCF_3$ (**1a**) and $[(bpy)CuSeCF_3]_2$ (**1b**). The reaction afforded good to excellent yields of a variety of trifluoromethylthio(seleno)lated 4-alkoxy-, aryloxy-, and

benzyloxy-2-pyrones. Investigations of this methodology to the synthesis of new trifluoromethylthio(seleno)lated heterocyclic derivatives are currently in progress in our laboratory.

4. Experimental

4.1 General experimental

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on Waters GCT-TOF at the Shanghai Institute of Organic Chemistry. The (bpy)$CuSCF_3$ (**1a**), [(bpy)$CuSeCF_3$]$_2$ (**1b**)[47], and 3-iodo-2-pyrones (**2**)[8,54] were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to *the purification handbook Purification of Laboratory Chemicals* prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

4.2 General procedure for trifluoromethylthiolation/trifluoromethylselenolation of 3-iodo-2-pyrones with (bpy)Cu(SCF_3)/[(bpy)Cu($SeCF_3$)]$_2$

3-Iodo-2-pyrones (**2**) (0.50 mmol), (bpy)Cu(SCF_3) (250 mg, 0.75 mmol, 1.5 equiv) or [(bpy)Cu($SeCF_3$)]$_2$ (280 mg, 0.375 mmol, 0.75 equiv) and toluene (5 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 16 hours. After cooled down to room temperature, the reaction mixture was filtered through a pad of celite. The filtrate was added water (3×10 mL) at 0 °C. The resulting mixture was extracted with Et_2O (3×15 mL), and the combined organic layers was washed with water, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation in an ice bath and the resulting product was purified by flash chromatography on silica gel using diethyl ether/*n*-pentane for elution.

*4.2.1 4-Ethoxy-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3a**).* Following the general procedure and workup, **3a** was isolated as a white solid in 96% yield (122 mg). M.p. 98.9-99.6 °C. R_f (diethyl ether) = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 1H), 4.29 (q, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 1.48 (t, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4 (s), 167.8 (s), 163.0 (s), 129.4 (q, *J* = 311.3 Hz), 95.7 (s), 87.2 (q, *J* = 2.0 Hz), 66.9 (s), 20.8 (s), 14.4(s). IR (KBr): ν 3105, 2923, 2853, 1698, 1636, 1505, 1454, 1323, 1219, 1102, 923, 751, 527 cm^{-1}. GC-MS m/z 254 (M^+). HRMS (EI) m/z: calcd. for $C_9H_9O_3F_3S$: 254.0225; found: 254.0224.

*4.2.2 6-Methyl-4-propoxy-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3b**).* Following the general procedure and workup, **3b** was isolated as a white solid in 92% yield (120 mg). M.p. 63.2-64.5 °C. R_f (diethyl ether) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 1H), 4.16 (t, *J* = 6.2 Hz, 2H), 2.33 (s, 3H), 1.92 – 1.81 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6 (s), 167.8 (s), 163.0 (s), 129.4 (q, *J* = 311.2 Hz), 95.8 (s), 87.2 (q, *J* = 2.0 Hz), 72.5 (s), 22.3 (s), 20.8(s), 10.0(s). IR (KBr): ν 2982, 2937, 1698, 1633, 1501, 1452, 1385, 1214, 1105, 898, 752, 531 cm^{-1}. GC-MS m/z 268 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_{11}O_3F_3S$: 268.0381; found: 268.0385.

*4.2.3 4-Isopropoxy-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3c**).* Following the general procedure and workup, **3c** was isolated as a white solid in 98% yield (131 mg). M.p. 119.3-120.3 °C. R_f (diethyl ether) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (s, 1H), 4.87 – 4.62 (m, 1H), 2.34 (s, 3H), 1.43 (d, *J* = 6.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6 (s), 167.4 (s), 163.2 (s), 129.8 (q, *J* = 311.2 Hz), 95.9 (s), 87.7 (q, *J* = 2.0 Hz), 74.4 (s), 22.0 (s), 20.8 (s). IR (KBr): ν 3098, 2988, 2924, 1702, 1633, 1507, 1453, 1318, 1215, 1094, 935, 765, 534 cm^{-1}. GC-MS m/z 268 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_{11}O_3F_3S$: 268.0381; found: 268.0386.

*4.2.4 6-Methyl-4-phenoxy-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3d**).* Following the general procedure and workup, **3d** was isolated as a white solid in 97% yield (148 mg). M.p. 99.1-99.8 °C. R_f (diethyl ether/*n*-pentane 1:1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.70 (s, 1H), 2.22 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (s), 167.2 (s), 162.7 (s), 152.7 (s), 130.4 (s), 126.8 (s), 122.2 (q, *J* = 335.7 Hz), 120.9 (s), 97.1 (s), 89.6 (q, *J* = 1.6 Hz), 67.9 (s), 25.6 (s), 20.5 (s). IR (KBr): ν 2924, 1725 , 1635, 1514, 1486, 1317, 1225, 1102, 915, 762, 695, 528 cm^{-1}. GC-MS m/z 302 (M^+). HRMS (EI) m/z: calcd. for $C_{13}H_9O_3F_3S$: 302.0225; found: 302.0218.

*4.2.5 4-(4-Fluorophenoxy)-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3e**).* Following the general procedure and workup, **3e** was isolated as a brown solid in 91% yield (145 mg). M.p. 123.7-124.8 °C. R_f (diethyl ether/*n*-pentane 1:1) = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 7.09 – 7.05 (m, 2H), 5.69 (s, 1H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.6 (s, 3F), -114.4 – -114.5 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6 (s), 168.0 (s), 162.2 (d, *J* = 53.4 Hz), 159.5 (s), 148.4 (d, *J* = 3.2 Hz), 129.3 (q, *J* = 311.3 Hz), 122.6 (s), 122.5 (s), 117.3 (s), 117.1 (s), 97.0 (s), 89.7 (q, *J* = 2.2 Hz), 20.6 (s). IR (KBr): ν 3099, 2923, 1725, 1636, 1523, 1500, 1319, 1202, 1132, 1103, 994, 847, 752, 540 cm^{-1}. GC-MS m/z 320 (M^+). HRMS (EI) m/z: calcd. for $C_{13}H_8O_3F_4S$: 320.0130; found: 320.0120.

*4.2.6 4-(Benzyloxy)-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3f**).* Following the general procedure and workup, **3f** was isolated as a pale yellow solid in 95% yield (150 mg). M.p. 112.5-113.5°C. R_f (diethyl ether) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 5H), 6.18 (s, 1H), 5.32 (s, 2H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (s), 162.9 (s), 134.1 (s), 129.4 (q, *J* = 311.4 Hz), 129.1 (s), 129.0 (s), 128.9 (s), 128.8 (s), 126.9 (s), 126.8 (s), 96.1 (s), 88.0 (q, *J* = 2.0 Hz), 72.2 (d, *J* = 1.5 Hz), 20.9 (s). IR (KBr): ν 3107, 1707, 1630, 1511, 1454, 1327, 1103, 904, 729, 691, 466 cm^{-1}. GC-MS m/z 316 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_{11}O_3F_3S$: 316.0381; found: 316.0387.

*4.2.7 6-Methyl-4-((4-methylbenzyl)oxy)-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3g**).* Following the general procedure and workup, **3g** was isolated as a pale yellow solid in 99% yield (160 mg). M.p. 118.6-119.3 °C. R_f

(diethyl ether) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 4H), 6.16 (s, 1H), 5.28 (s, 2H), 2.40 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3 (s), 167.7 (s), 162.9 (s), 138.9 (s), 131.1 (s), 129.7 (s), 129.5 (q, *J* = 311.4 Hz), 127.1 (s), 96.1 (s), 87.9 (q, *J* = 2.1 Hz), 72.2 (s), 21.2 (s), 20.9 (s). IR (KBr): ν 2924, 1700, 1635, 1503, 1324, 1211, 1114, 901, 765, 491 cm^{-1}. GC-MS m/z 330 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_{13}O_3F_3S$: 330.0538; found: 330.0546.

*4.2.8 4-((4-Fluorobenzyl)oxy)-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3h**).* Following the general procedure and workup, **3h** was isolated as a yellow solid in 91% yield (150 mg). M.p. 131.7-132.3°C. R_f (diethyl ether) = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.17 (s, 1H), 5.27 (s, 2H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5 (s, 3F), -112.24 – -112.34 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0 (s), 168.0 (s), 164.2 (s), 162.8 (s), 161.7 (s), 129.4 (q, *J* = 311.4 Hz), 129.0 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 21.8 Hz), 95.9 (s), 88.1 (q, *J* = 2.1 Hz), 71.5 (s), 20.9 (s). IR (KBr): ν 3073, 2920, 1720, 1628, 1509, 1402, 1327, 1104, 1070, 903, 750, 545 cm^{-1}. GC-MS m/z 334 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_{10}O_3F_4S$: 334.0287; found: 334.0293.

*4.2.9 6-Methyl-4-((4-(trifluoromethyl)benzyl)oxy)-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3i**).* Following the general procedure and workup, **3i** was isolated as a pale yellow solid in 99% yield (190 mg). M.p. 158.4-158.9 °C. R_f (diethyl ether) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 6.16 (s, 1H), 5.37 (s, 2H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.4 (s, 3F), -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8 (s), 168.3 (s), 162.6 (s), 138.0 (q, *J* = 1.3 Hz), 131.0 (q, *J* = 32.7 Hz), 127.0 (s), 126.0 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.3 Hz), 95.8 (s), 88.4 (q, *J* = 2.0 Hz), 71.1 (s), 30.3 (s), 21.0 (s). IR(KBr): ν 3105, 2925, 1716, 1629, 1513, 1322, 1153, 1106, 1064, 1005, 900, 823, 753, 592 cm^{-1}. GC-MS m/z 384 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_{10}O_3F_6S$: 384.0255; found: 384.0256.

*4.2.10 4-((3-Methoxybenzyl)oxy)-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (**3j**).* Following the general procedure and workup, **3j** was isolated as a pale yellow solid in 98% yield (167 mg). M.p. 96.3-96.9 °C. R_f (diethyl ether) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 1H), 7.06 – 6.78 (m, 3H), 6.15 (s, 1H), 5.30 (s, 2H), 3.83 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2 (s), 167.9 (s), 162.9 (s), 160.1 (s), 135.7 (s), 130.1 (s), 127.8 (q, *J* = 390.6), 118.7 (s), 114.6 (s), 111.9 (s), 96.1 (s), 88.1 (q, *J* = 2.0 Hz), 71.9 (s), 55.3 (s), 20.9 (s). IR (KBr): ν 3105, 2926, 2839,1699, 1634, 1504, 1449, 1321, 1272, 1108, 785, 753, 696 cm^{-1}. GC-MS m/z 346 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_{13}O_4F_3S$: 346.0487; found: 346.0499.

*4.2.11 4-Ethoxy-6-methyl-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4a**).* Following the general procedure and workup, **4a** was isolated as a white solid in 95% yield (143 mg). M.p. 97.8-99.3 °C. R_f (diethyl ether) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (s, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (s), 167.3 (s), 162.9 (s), 122.2 (q, *J* = 335.7 Hz), 95.4 (s), 87.4 (q, *J* = 1.4 Hz), 66.6 (s), 20.7 (s), 14.4 (s). IR (KBr): ν 3103, 2992, 2924, 1696, 1635, 1503, 1452, 1391, 1319, 1088, 910, 757, 734, 524 cm^{-1}. GC-MS m/z 301 (M^+). HRMS (EI) m/z: calcd. for $C_9H_9O_3F_3{}^{74}Se$: 295.9729; found: 295.9735.

*4.2.12 6-Methyl-4-propoxy-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4b**).* Following the general procedure and workup, **4b** was isolated as a white solid in 93% yield (146 mg). M.p. 66.2-67.2 °C. R_f (diethyl ether) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 4.15 (t, *J* = 6.2 Hz, 2H), 2.34 (s, 3H), 1.91 – 1.80 (dt, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3 (s), 167.4 (s), 163.0 (s), 122.2 (q, *J* = 335.7 Hz), 95.5 (s), 87.2 (q, *J* = 1.1 Hz), 72.3 (s), 22.3 (s), 20.7 (s), 10.2 (s). IR (KBr): ν 3094, 2974, 1697, 1631, 1510, 1453, 1380, 1324, 1213, 1085, 940, 757, 737, 531 cm^{-1}. GC-MS m/z 316 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_{11}O_3F_3{}^{74}Se$: 309.9885; found: 309.9883.

*4.2.13 4-Isopropoxy-6-methyl-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4c**).* Following the general procedure and workup, **4c** was isolated as a white solid in 95% yield (148 mg). M.p. 125.7-127.0 °C. R_f (diethyl ether) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H), 4.80 – 4.69 (m, 1H), 2.33 (s, 3H), 1.41 (d, *J* = 6.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (s), 167.0 (s), 163.1 (s), 122.2 (q, *J* = 335.6 Hz), 95.8 (s), 87.7 (q, *J* = 1.2 Hz), 74.2 (s), 22.1 (s), 20.7 (s). IR (KBr): ν 3097, 2988, 1696, 1631, 1507, 1453, 1316, 1214, 1120, 1089, 897, 757, 737, 532 cm^{-1}. GC-MS m/z 315 (M^+). HRMS (EI) m/z: calcd. for $C_{10}H_{11}O_3F_3{}^{74}Se$: 309.9885; found: 309.9877.

*4.2.14 6-Methyl-4-phenoxy-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4d**).* Following the general procedure and workup, **4d** was isolated as a pale yellow solid in 94% yield (158 mg). M.p. 101.8-102.8 °C. R_f (diethyl ether/*n*-pentane 1:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.39 – 7.32 (m, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 5.68 (s, 1H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (s), 167.3 (s), 162.8 (s), 152.8 (s), 130.5 (s), 126.9 (s), 122.2 (q, *J* = 335.7 Hz), 120.9 s), 97.1 (s), 89.6 (q, *J* = 1.6 Hz), 20.6 (s). IR (KBr): ν 3100, 2919, 1720, 1639, 1522, 1486, 1382, 1313, 1212, 1087, 991, 754, 687, 531 cm^{-1}. GC-MS m/z 349 (M^+). HRMS (EI) m/z: calcd. for $C_{13}H_9O_3F_3{}^{74}Se$: 343.9729; found: 343.9735.

*4.2.15 4-(4-Fluorophenoxy)-6-methyl-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4e**).* Following the general procedure and workup, **4e** was isolated as a pale yellow solid in 96% yield (176 mg). M.p. 123.0-124.2 °C. R_f (diethyl ether/*n*-pentane 1:1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 7.09 – 7.04 (m, 2H), 5.67 (s, 1H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.2 (s, 3F), -114.6 – -114.7 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (s), 167.6 (s), 162.3 (d, *J* = 64.2 Hz), 159.5 (s), 148.6 (d, *J* = 3.0 Hz), 122.6 (s), 122.5 (s), 122.2 (q, *J* = 335.6 Hz), 117.3 (s), 117.1 (s), 96.8 (s), 89.6 (q, *J* = 1.4 Hz), 20.6 (s). IR (KBr): ν 3097, 1719, 1636, 1521, 1499, 1444, 1381, 1312, 1201, 1130, 1086, 992, 846, 738, 537, 485 cm^{-1}. GC-MS m/z 367 (M^+). HRMS (EI) m/z: calcd. for $C_{13}H_8O_3F_4{}^{74}Se$: 361.9634; found: 361.9640.

*4.2.16 4-(Benzyloxy)-6-methyl-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4f**).* Following the general procedure and workup, **4f** was isolated as a white solid in 91% yield (165 mg). M.p. 107.7-108.6 °C. R_f (diethyl ether) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 5H), 6.18 (s, 1H), 5.31 (s, 2H), 2.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2 (s), 167.6 (s), 162.9 (s), 134.3 (s), 128.9 (s), 128.8 (s), 126.9 (s), 122.3 (q, *J* = 335.8 Hz), 95.9 (s), 87.8 (d, *J* = 1.2 Hz), 72.1 (s), 20.7 (s). IR (KBr): ν 3106, 1702, 1630, 1515, 1455, 1381, 1322, 1088, 1053, 999,

729, 691, 466 cm^{-1}. GC-MS m/z 363 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_{11}O_3F_3{}^{74}Se$: 357.9885; found: 357.9876.

*4.2.17 6-Methyl-4-((4-methylbenzyl)oxy)-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4g**).* Following the general procedure and workup, **4g** was isolated as a pale yellow solid in 96% yield (181 mg). M.p. 115.8-116.1 °C. R_f (diethyl ether) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.17 (s, 1H), 5.26 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2 (s), 167.5 (s), 162.9 (s), 138.9 (s), 131.2 (s), 129.6 (s), 127.1 (s), 122.3 (q, *J* = 335.9 Hz), 95.9 (s), 87.9 (q, *J* = 1.4 Hz), 72.2 (s), 21.2 (s), 20.8 (s). IR (KBr): ν 2922, 1709, 1635, 1511, 1444, 1378, 1318, 1209, 1090, 1002, 892, 810, 733, 493 cm^{-1}. GC-MS m/z 377 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_{13}O_3F_4{}^{74}Se$: 372.0042; found: 372.0058.

*4.2.18 4-((4-Fluorobenzyl)oxy)-6-methyl-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4h**).* Following the general procedure and workup, **4h** was isolated as a white solid in 93% yield (177 mg). M.p. 120.0-120.9 °C. R_f (diethyl ether) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.15 (s, 1H), 5.26 (s, 2H), 2.33 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.1 (s, 3F), -112.3 – -112.6 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9 (s), 167.7 (s), 164.1 (s), 162.8 (s), 161.6 (s), 129.9 (d, *J* = 3.3 Hz), 129.0 (d, *J* = 8.4 Hz), 122.2 (q, *J* = 335.7 Hz), 116.1 (s), 115.9 (s), 95.7 (s), 88.0 (q, *J* = 1.5 Hz), 71.4 (s), 20.8 (s). IR (KBr): ν 3106, 1702, 1630, 1515, 1455, 1381, 1322, 1088, 1000, 890, 729, 691, 574, 466 cm^{-1}. GC-MS m/z 381 (M^+). HRMS (EI) m/z: calcd. for $C_{14}H_{10}O_3F_4{}^{74}Se$: 375.9786; found: 375.9791.

*4.2.19 6-Methyl-4-((4-(trifluoromethyl)benzyl)oxy)-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4i**).* Following the general procedure and workup, **4i** was isolated as a white solid in 89% yield (190 mg). M.p. 167.8-168.3 °C. R_f (diethyl ether) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 6.14 (s, 1H), 5.36 (s, 2H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.0 (s, 3F), -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 (s), 167.9 (s), 162.6 (s), 138.2 (q, *J* = 1.2 Hz), 131.0 (q, *J* = 32.7 Hz), 127.0 (s), 125.9 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.2 Hz), 95.5 (s), 88.3 (q, *J* = 1.5 Hz), 71.0 (s), 20.8 (s). IR (KBr): ν 3103, 2923, 1709, 1629, 1514, 1381, 1319, 1223, 1055, 1000, 824, 755, 737, 526 cm^{-1}. GC-MS m/z 431 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_{10}O_3F_6{}^{74}Se$: 425.9759; found: 425.9750.

*4.2.20 4-((3-Methoxybenzyl)oxy)-6-methyl-3-((trifluoromethyl)selanyl)-2H-pyran-2-one (**4j**).* Following the general procedure and workup, **4j** was isolated as a pale yellow solid in 98% yield (190 mg). M.p. 100.1-101.4 °C. R_f (diethyl ether) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 1H), 6.99 – 6.86 (m, 3H), 6.14 (s, 1H), 5.29 (s, 2H), 3.83 (s, 3H), 2.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (s), 167.6 (s), 162.9 (s), 160.1 (s), 135.9 (s), 130.0 (s), 122.3 (q, *J* = 335.8 Hz), 118.8 (s), 114.5 (s), 112.0 (s), 95.8 (s), 87.9 (q, *J* = 1.3 Hz), 71.8 (s), 55.3 (s), 20.8 (s). IR (KBr): ν 2938, 2845, 1712, 1634, 1584, 1520, 1318, 1220, 1090, 1049, 1005, 892, 781, 753, 556 cm^{-1}. GC-MS m/z 393 (M^+). HRMS (EI) m/z: calcd. for $C_{15}H_{13}O_4F_3{}^{74}Se$: 387.9991 ; found: 388.0002.

*4.2.21 6-Methyl-4-((trifluoromethyl)thio)-2H-pyran-2-one (**6a**).* Following the general procedure and workup, **6a** was isolated as a pale yellow oil in 80% yield (84 mg). R_f (diethyl ether/*n*-pentane 1:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 1H), 6.04 (s, 1H), 2.28 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (s), 160.1 (s), 146.4 (q, *J* = 2.0 Hz), 128.1 (q, *J* = 309.9 Hz), 112.6 (q, *J* = 1.9 Hz), 103.7 (q, *J* = 1.8 Hz), 20.0 (s). IR (KBr): ν 3102, 2921, 1725, 1625, 1538, 1180, 1109, 739, 529 cm^{-1}. GC-MS m/z 210 (M^+). HRMS (EI) m/z: calcd. for $C_7H_5O_2F_3S$: 209.9962; Found: 209.9965.

*4.2.22 6-Methyl-4-((trifluoromethyl)selanyl)-2H-pyran-2-one (**6b**).* Following the general procedure and workup, **6b** was isolated as a pale yellow oil in 98% yield (125 mg). R_f (diethyl ether/*n*-pentane 1:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 6.14 (s, 1H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -32.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (s), 160.0 (s), 144.7 (q, *J* = 1.5 Hz), 121.9 (q, *J* = 333.1 Hz), 115.5 (q, *J* = 1.8 Hz), 105.9 (q, *J* = 1.6 Hz), 19.9 (s). IR (KBr): ν 3103, 2923, 1725, 1620, 1535, 1149, 1098, 737, 526 cm^{-1}. GC-MS m/z 257 (M^+). HRMS (EI) m/z: calcd. for $C_7H_5O_2F_3{}^{74}Se$: 251.9466; Found: 251.9470.

Procedure for Ring-opening reaction of 4-(4-Fluorophenoxy)-6-methyl-3-((trifluoromethyl)thio)-2H-pyran-2-one (3e)

A suspension of **3e** (200 mg, 0.625 mmol) in NaOH aqueous solution (2M, 40 mL) was stirred at 60 °C for 16 h. Upon cooling, the reaction mixture was filtered. The filterate was added dropwise of HCl aqueous solution (2M) to pH 4-5 at 0 °C. The mixture was extracted with EtOAc (3 × 20 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residues were purified by flash chromatography on silica gel using ethyl acetate/*n*-pentane (1:20) for elution.

*3-(4-fluorophenoxy)-5-oxo-2-((trifluoromethyl)thio)hex-2-enoic acid (**7e**).* Obtained as a yellow solid in 25% yield (40 mg, 0.12 mmol) with isomers. R_f (EtOAc/*n*-pentane 1:10) = 0.41. M.p. 60.7-61.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.18 – 7.08 (m, 2H), 7.04 – 6.97 (m, 2H), 3.73 (s, 2H), 2.44 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.36 (s), -43.20 (s), -43.93 (s), -115.68 – -115.79 (m), -116.02 – -116.13 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 (s), 171.5 (s), 161.7 (s), 159.2 (s), 148.8 (d, *J* = 2.9 Hz), 130.0 (q, *J* = 308.1 Hz), 129.4 (q, *J* = 312.1 Hz), 122.4 (d, *J* = 8.6 Hz), 121.8 (d, *J* = 8.6 Hz), 116.9 (d, *J* = 23.2 Hz), 116.8 (d, *J* = 23.8 Hz), 30.9 (s), 19.4 (s). IR (KBr): ν 3300, 2500, 2991, 1668, 1552, 1497, 1421, 1375, 1257, 1182, 1103, 842, 771, 752, 735, 523, 486 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{11}H_7O_3F_4S$ (M^+-$COCH_3$+H): 296.0130; found: 296.0136.

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Supplementary Material

Supplementary data associated with this article can be found, in the online version.

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