Metal-free Regioselective Fluoroalkylfluoroalkylselenolation of

Unactivated Alkenes: Incorporation of Two Photoinduced Process

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1. General information

Unless stated otherwise, all reactions were carried out under an argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC). Column chromatography purifications were carried out using silica gel GF254. ¹H NMR, ¹⁹F NMR, ¹³C NMR, and ³¹P NMR spectra were recorded on Bruker instrument (300MHz, 282MHz, 75MHz or 125MHz and 131MHz) spectrometer in CDCl₃. ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm, ¹⁹F NMR chemical shifts were determined relative to CFCl₃ (δ 0.0 ppm) as inter standard. Data for ¹H NMR, ¹⁹F NMR, and ¹³C NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad, q = quartet, coupling constant (s) in Hz, integration). Data for, ³¹P NMR is reported in terms of chemical shift (δ , ppm). High resolution mass spectra (HRMS) were obtained by ESI and EI ionization source. Gas chromatography-mass analysis was carried out on an Agilent Technologies 7890B GC system with an Agilent 5973C VL MSD and a HP-5MS column (0.25 mm × 30 M, film: 0.25 µm). Liquid chromatography-mass analysis was carried out on an Agilent Technologies C6100 system with an Agilent DAD717C MSD.

Materials: Commercial grade reagents and solvents were purchased from Energy-Chemical, Innochem, TCI, aladin, adamas-beta, Ark Pharm and used as received without further purifications. The preparation of **3a**, **3b** and alkenes were accomplished following the reported procedures.¹⁻³

2. General procedure for fluoroalkylfluoroalkylselenolation of unactivated alkenes.

2.1 General procedure

To an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added alkenes 1 (0.2 mmol), **3** (0.3 mmol, 1.5 equiv), Eosin Y (5 mmol %) and Et₃N (0.2 mmol, 1.0 equiv). Then, air was withdrawn and backfilled with Ar (three times). **2** (0.4 mmol, 2.0 equiv), DMSO (2.0 mL), and H₂O (0.6 mmol, 3 equiv) were added by syringe. Thereafter, the test tube was transferred to a blue light photoreactor (18 W, see Scheme S1 for details), where it was irradiated for 4 h. Then, the reaction was quenched with water (2 mL), extracted with ethyl acetate (3×2 mL), the combined organic layer was dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (cyclohexane/ ethyl acetate, 20:1 to 5:1) to afford the product.



Scheme S1. Placement of blue light around quartz test tube.

Instructions on placement of light source: One 18 W blue light LED annular tubes was placed in the 1L petri dish and the inside diameter is 12 cm.

2.2 General procedure of scale-up experiment



To an oven-dried 25 mL quartz test tube with a magnetic stirring bar was added alkene **1a** (4 mmol), **3a** (6 mmol, 1.5 equiv), Eosin Y (5 mmol %) and Et₃N (4 mmol, 1.0 equiv). Then, air was withdrawn and backfilled with Ar (three times). **2a** (8 mmol, 2.0 equiv), DMSO (20 mL), and H₂O (12 mmol, 3 equiv) were added by syringe. Thereafter, the test tube was transferred to a blue light photoreactor (18 W, see Scheme S1 for details), where it was irradiated for 4 h. Then, the reaction was quenched with water (20 mL), extracted with ethyl acetate (3×20 mL), the combined organic layer was dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (cyclohexane/ ethyl acetate, 20:1 to 10:1) to afford the product.

Unsuccessful substrates:



Some alkenes such as styrene and internal alkenes were not suitable for current condition.

2.3 Optimization of reaction conditions



Table S1. Light sources screening

^a Unless otherwise noted, the reactions were carried out in 0.1 mmol scale, Eosin Y (5 mol %), DMSO (1.0 mL) were used. The reaction mixtures were irradiated with indicated light sourse at room temperature for 12 h. Yields reffered to isolated yields.

Table	S2.	Solvents	screening
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H ₃ CO	0 0 1a	+ CF ₃ SO ₂ CI + 2a 2.0 equiv	TsSeCF ₃ 3a 1.5 equiv	18 W blue LED Eosin Y (5 mol %) Ar, rt, solvent, 12 h	3 ^{CO} 4a	SeCF ₃
Entry			Solver	nt	Yie	ld [%] ^a
1			DMSC)		25
2			DMF			20
3			DMA	2		17
4			CH ₂ Cl	2	t	trace
5			CH ₃ CI	N	t	trace
6			THF		t	trace
7			aceton	e	t	trace
8			toluen	e	t	trace

^a Unless otherwise noted, the reactions were carried out in 0.1 mmol scale, Eosin Y (5 mol %), DMSO (1.0 mL) were used. The reaction mixtures were irradiated with indicated light sourse at room temperature for 12 h. Yields reffered to isolated yields.

Table S3. Photocatalyst screening.

H ₃ CO 1a	$D^{(1)} + CF_3SO_2CI + TsSeCF_3 \xrightarrow{photocatalyst (}{18 W blue}$ $H_2O 3.0 eq$ 2a 2.0 equiv 3a 1.5 equiv Ar, rt, DMSC	5 mol %) O LED uiv $0, 12 h H_3CO$ $4a$ CF_3
Entry	photocatalyst	Yield [%] ^a
1	Ru(bpy)₃Cl₂ · 6H₂O	14
2	<i>fac</i> -Ir(ppy) ₃	24
3	lr(ppy) ₂ (dtppy)PF ₆	22
4	lr(dF-CF ₃ -ppy) ₂ (dtppy)PF ₆	20
5	Mes-Acr ⁺ ClO ₄ -	38
6	Eosin Y	56
7	Fluorescein	34
8	4-CzTPN	40

^a Unless otherwise noted, the reactions were carried out in 0.1 mmol scale, indicated photocatalyst (5 mol %), H_2O (0.3 mmol), DMSO (1.0 mL) were used. The reaction mixtures were irradiated with 18 W blue LED at room temperature for 12 h. Yields reffered to isolated yields.



Table S4. Bases screening.

\langle			T-0-05	Eosin Y(5 mol % 18 W blue LED)	
H ₃ CO	1a	2a 2.0 equiv 3a	1.5 equiv	base 1.0 equiv H ₂ O 3.0 equiv Ar, rt, DMSO, 12 h	H ₃ CO	O CF3 SeCF3 4a
Entry	Base	Yield [%]	а	Entry	Base	Yield [%] ^a
1	NaHCO ₃	48		8	K ₃ PO ₄	36
2	K ₂ HPO ₄	44		9	LiO ^t Bu	74
3	KHCO ₃	45		10	KO ^t Bu	65
4	NaOAc	46		11	Cs ₂ CO ₃	64
5	Na ₂ CO ₃	50		12	Et ₃ N	76
6	K ₂ CO ₃	52		13	DIPEA	60
7	Na ₃ PO ₄	35		14	DBU	40

^a Unless otherwise noted, the reactions were carried out in 0.1 mmol scale, Eosin Y (5 mol %), H₂O (0.3 mmol), indicated base (0.1 mmol), DMSO (1.0 mL) were used. The reaction mixtures were irradiated with 18 W blue LED at room temperature for 12 h. Yields reffered to isolated yields.

Table S5. Reaction time screening.

				Eosin Y(5 mol %) 18 W blue LED		
H ₃ CO	1a	2a 2.0 equiv	3a 1.5 equiv	Et ₃ N 1.0 equiv H ₂ O 3.0 equiv Ar, rt, DMSO, time	H ₃ CO	SeCF ₃
Entry			Time (h)		Yield [%] ^a
1			2			84
2			4			86
3			6			81
4			8			76
5			12			73

^a Unless otherwise noted, the reactions were carried out in 0.1 mmol scale, Eosin Y (5 mol %), H_2O (0.3 mmol), Et₃N (0.1 mmol), DMSO (1.0 mL) were used. The reaction mixtures were irradiated with 18 W blue LED at room temperature for indicated time. Yields reffered to isolated yields.

3. Mechanistic study

3.1 Redox potentials

The redox potential of Eosin Y in the ground state is $EY/EY^{-} = -1.06$ V vs SCE, the excited triplet state of Eosin Y was estimated to be ${}^{3}EY^{*}/EY^{-} = +0.83$ V vs SCE,⁴ and the redox potential of the oxidation of the excited state is $EY^{*+/3}EY^{*} = -1.1$ V vs SCE.⁵

The oxidation potential of CF₃SO₂Cl is -0.18 V vs SCE.⁶

TsSeCF₃ **3a** was found to be easily reduced in DMSO at a potential close to -0.90 V. No anodic peak potential could be observed up to oxidation of solvent/electrolyte for **3a** (onset at + 1.65 V for CH₃CN, + 1.40 V for DMF, + 0.85 V for DMSO and + 1.35 V for THF).⁷

3.2 Control experiments

Under the standard conditions, without light and in the dark environment, no difunctionalized product could be observed (eqn 1); In the absence of photocatalyst Eosin Y, no desired product could be detected (eqn 2).



We choose tert-butyl hydroperoxide (TBHP) as the oxidant instead of Eosin Y catalyzed photoredox cycle to produce \cdot CF₃ under 18 W blue LED irradiation, the reaction was completed within 1 h with 67% yield (eqn 3). In addition, this reaction did not proceed under dark condition (eqn 4).

(3)
$$\begin{array}{c} 18 \text{ W blue LED} \\ \hline \textbf{TBHP (3.0 equiv)} \\ 1g \quad (2.0 equiv) \quad 3a \quad \begin{array}{c} 18 \text{ W blue LED} \\ \hline \textbf{TBHP (3.0 equiv)} \\ H_2O (3.0 equiv) \\ \text{Ar, rt, DMSO, 1 h} \quad \begin{array}{c} \hline \textbf{GCF}_3 \\ \hline \textbf{SeCF}_3 \\ 4g, 67\% \end{array}$$



3.3 Detection of CF₃SeSeCF₃

For spectroscopic investigations of CF₃SeSeCF₃, see: C. J. Marsden, *J. Fluorine Chem.* 1975, 5, 401.





Figure S1. ¹⁹F NMR and GC-MS of CF₃SeSeCF₃.

3.4 Replacing TsSeCF₃ with CF₃SeSeCF₃ experiment.



To an oven-dried 10 mL quartz test tube with a magnetic stirring bar, TsSeCF₃ **3a** (0.3 mmol) and 2.0 mL DMSO were added, air was withdrawn and backfilled with Ar (three times). The reaction mixture was irradiated under 18 W blue LED for 2 hours till **3a** was fully converted to CF₃SeSeCF₃ determined by ¹⁹F NMR. Then **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv), Eosin Y (5 mol%), Et₃N (0.2 mmol, 1.0 equiv) and H₂O (0.6 mmol, 3.0 equiv) were added by syringe. Thereafter, the test tube was transferred to a blue light photoreactor, where it was irradiated for 4 h. Then, the reaction was quenched with water (2 mL), extracted with ethyl acetate (3×2 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (cyclohexane/ ethyl acetate, 20:1 to 10:1) to afford the product.

3.5 Radical trapping and radical clock experiments.

When the radical scavenger TEMPO (2,2,6,6-tetromethyl-1-piperidinyloxy, 2.0 equiv) was added under the standard conditions, the reaction was completely suppressed, and the radical trapping product $^{n}C_{4}F_{9}$ -TEMPO was observed in ^{19}F NMR and detected by LC-MS. The radical clock experiment with *N*-diallyl-4-methylbenzenesulfonamide **1w** led to the formation of the cyclization product **6** in 60% yield. These results suggesting that the $^{n}C_{4}F_{9}$ radical was likely generated in situ in the presence of Eosin Y catalyst through a single electron-transfer process.





Figure S2. ¹⁹F NMR of C₄F₉SO₂Cl and ⁿC₄F₉-TEMPO.

3.6 Stern-Volmer fluorescence quenching study

Emission spectra of Eosin Y were recorded with a HITACHI spectrofluorophotometer F-7000 using a 10⁻⁴M degassed DMSO solution of the Eosin Y catalyst. Emission intensities were recorded by using a HITACHI spectrofluorophotometer F-7000.

DMSO was degassed with a stream of argon for 30 min, 60 mL of 10^{-4} M stock solution of the Eosin Y catalyst in DMSO were prepared. For each experiment 2 mL of the resulting solution were put in a sealable 10 mm quartz cuvette equipped. Et₃N, **1a**, TsSeCF₃ **3a** and CF₃SO₂Cl **2a** each was used to prepare a 3 mL of 2.5×10^{-2} M solution of these quenchers. Then, the latter solution was added by aliquots into the solution of pure Eosin Y in the sealable cuvette. All solutions were excited at 420 nm and the fluorescence emission spectra were recorded.



Figure S3. Stern–Volmer experiment for the emission quenching of Eosin Y (2 × 10⁻⁴ M) in DMSO by various concentration of quencher: Et₃N, 1a, TsSeCF₃ 3a and CF₃SO₂Cl 2a.

Quenching experiment of Eosin Y with Et₃N, **1a** and **3a** have been conducted, Et₃N did not quench the excited state of Eosin Y at 420 nm in DMSO, whereas alkene 1a and TsSeCF₃ **3a** showed much weaker quenching efficiency than **2a**. We observed that reagent **3a** would quantitatively convert to CF₃SeSeCF₃ under light in DMSO within 1 hour. Furthermore, as mentioned above, compared with TsSeCF₃ (-0.90 V vs SCE), CF₃SO₂Cl (-0.18 V vs SCE) is much easier to be reduced than TsSeCF₃. Moreover, replacing CF₃SeSeCF₃ with TsSeCF₃ led to slightly decreased in yield (78%). Taking these experiment results into account, a different quenching cycle was not likely happened in this transformation.

3.7 Determination of quantum yield

1g + CF_3SO_2Na + **3a** + TBHP $\xrightarrow{420 \text{ nm hv}}$ **4g** 2.0 equiv 2.0 equiv Ar, rt, DMSO, 1h

To an oven-dried 25 mL quartz test round-bottom flask with a magnetic stirring bar was added allylbenzene (1.0 mmol), TsSeCF₃ (1.5 mmol, 1.5 equiv), CF₃SO₂Na (2.0 mmol, 2.0 equiv) and TBHP (2.0 mmol, 2.0 equiv) .Then, air was withdrawn and backfilled with Ar (three times). DMSO (10 mL) and H₂O (3.0 mmol, 3 equiv) was added by syringe. The reaction mixture was stirred and irradiated ($\lambda = 420$ nm, PLS-LED100B) for 3600 s (60 min). After irradiation, the solution was measured the unit area photon flux (TBQ - 5 photosynthetic active radiation meter, TRM-SCY).

And the yield of formed product was determined by ¹H NMR based on a mesitylene standard. The quantum yield is calculated using the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot S \cdot t}$$

Where, Φ is quantum yield, S (m²) is the irradiation area, and t (s) is the photoreaction time. Experiment: 118.18 mg of allylbenzene, 454.74 mg of TsSeCF₃, 32.40 mg of Eosin Y, 148 µL of Et₃N, and 54 µL of H₂O, after 3600 s, the unit area photon flux was 40.2 µmol·s⁻¹·m⁻² (average of five experiments), the irradiation area was 4.31×10^{-4} m², and the product yield was 55%.

Sample quantum yield calculation:

$$\Phi = \frac{1 \times 10^3 \times 0.55}{40.2 \times 4.31 \times 10^4 \times 3600} = 8.8$$



Scheme S2. Placement of TBQ - 5 photosynthetic active radiation meter and TRM-SCY

3.8 "Light/Dark" experiment:

To an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added allylbenzene (0.4 mmol), TsSeCF₃ (0.6 mmol, 1.5 equiv), CF₃SO₂Na (2.0 equiv), TBHP (2.0 equiv), and mesitylene (0.4 mmol) as internal standard. Then, air was withdrawn and backfilled with Ar (three times). DMSO (4 mL) and H₂O (1.2 mmol, 3 equiv) was added by syringe. Thereafter, the reaction was alternatively irradiated with a blue light photoreactor (18 W, see Scheme S1 for details) and kept in the dark in a five-minute interval. The yield was determined by ¹H NMR.

We observed that product formation occurred only during periods of constant irradiation. The study of quantum yield measurements and "light/dark" experiments for radical chain reactions, see: M. A. Cismesia and T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426.



Figure S4. "Light/Dark" experiment.













4. X-ray structure of 4h



4h, CCDC: 1974072

Bond precision:	C-C = 0.0073 A	Wavelength=1.54184	
Cell:	a=10.4389(2) alpha=90 293 K Calculated 3113.27(11) P 21/n -P 2yn	b=21.5791(4) beta=109.581(2)	c=14.6690(3) gamma=90
Temperature:			
Reported			

Volume		
Space group	3113.26(11)	
Hall group		
P 1 21/n 1		
-P 2yn		
	2(C13 H9 F6 N O2	
Moiety formula C13	Se)	
H9 F6 N O2 Se	C26 H18 F12 N2 O4	
	Se2	
Sum formula		
Mr		
Dx,g cm-3		
Z		
Mu (mm-1)		
F000	C13 H9 F6 N O2 Se	
F000'		
h,k,lmax		
Nref		
Tmin,Tmax		
Tmin'		
404.17		
1.725		
8		
3.968	808.34	
1584.0	1.725	
1583.84	4	
12,25,17	3.968	
5505	1584.0	
0.514,0.621		
0.466		
12,25,17		
5495		
0.015,1.000		
Correction method= #		
Reported T Limits:		
Tmin=0.015		
Tmax=1.000		
AbsCorr = MULTI-		
SCAN		
Data completeness=	Theta(max) = $66.5/3$	
0.998		
R(reflections)=	wR2(reflections)=	
0.0574(4530)	0.1635(5495)	
S = 1.036	Npar= 415	

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

PLAT234_ALERT_4_C Large Hirshfeld Difference C24 --C25 . 0.16 Ang. PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds 0.00727 Ang. PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 40 Ang**3 PLAT906_ALERT_3_C Large K Value in the Analysis of Variance 4.353 Check PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.595 10 Report PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 2 Note PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 2 Report PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ... 2.00 Check PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 1 Report PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 1 Report PLAT199_ALERT_1_G Reported _cell_measurement_temperature (K) 293 Check PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature (K) 293 Check PLAT242_ALERT_2_G Low MainMol Ueq as Compared to Neighbors of C12 Check PLAT242_ALERT_2_G Low MainMol Ueq as Compared to Neighbors of C25 Check PLAT242_ALERT_2_G Low MainMol Ueq as Compared to Neighbors of C26 Check PLAT242_ALERT_2_G Low MainMol Ueq as Compared to Neighbors of C26 Check PLAT242_ALERT_2_G Low MainMol Ueq as Compared to Neighbors of C26 Check PLAT242_ALERT_2_G Low MainMol Ueq as Compared to Neighbors of C26 Check PLAT242_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2 Note C13 H9 F6 N O2 Se

9 ALERT type 2 Indicator that the structure model may be wrong or deficient

5 ALERT type 3 Indicator that the structure quality may be low

6 ALERT type 4 Improvement, methodology, query or suggestion

0 ALERT type 5 Informative message, check

5. Characterization of products



12,12,12-trifluoro-10-((trifluoromethyl)selanyl)dodecyl 4-methoxybenzoate (4a): colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 3.68-3.46 (m, 1H), 2.93-2.48 (m, 2H), 1.93-1.68 (m, 4H), 1.47-1.18 (m, 12H). ¹⁹F NMR (282 MHz, CDCl₃) -33.18 (s), -64.28 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 166.60, 163.37, 131.67, 125.91 (q, $J_{C-F} = 276.8$ Hz), 123.07, 122.88 (q, $J_{C-F} = 329.0$ Hz), 113.68, 64.92, 55.55, 40.78 (q, $J_{C-F} = 28.1$ Hz), 37.16, 34.78, 29.49, 29.42 29.34, 29.07, 28.88, 27.32, 26.14.

HRMS (ESI): C₂₁H₂₈F₆O₃Se+Na⁺ Calcd: 545.1001, Found: 545.1006.



(4,4,4-trifluoro-1-phenylbutan-2-yl)(trifluoromethyl)selane (4b): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.40-7.28 (m, 3H), 7.21 (d, *J* = 6.8 Hz, 2H), 3.90-3.72 (m, 1H), 3.31-3.09 (m, 2H), 2.76-2.60 (m, 2H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.20 (s), -63.69 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 137.10, 129.33, 128.97, 127.62, 125.82 (q, *J*_{C-F} = 276.7 Hz), 122.88 (q, *J*_{C-F} = 328.4 Hz), 41.35, 39.28 (q, *J*_{C-F} = 29.2 Hz), 37.34.

HRMS (EI): C₁₁H₁₀F₆Se⁺ Calcd: 335.9852, Found: 335.9856.

(1,1,1-trifluoro-6-phenoxyhexan-3-yl)(trifluoromethyl)selane (4c): colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.02-6.79 (m, 3H), 4.00 (t, *J* = 5.2 Hz, 2H), 3.72-3.55 (m, 1H), 2.97-2.55 (m, 2H), 2.24-1.82 (m, 4H). ¹⁹F NMR (282 MHz, CDCl₃) δ -33.02 (s), -64.20 (s). ¹³C NMR (75 MHz, CDCl₃) δ 158.81, 129.64, 125.87 (q, *J*_{C-F} = 274.7 Hz), 122.68 (q, *J*_{C-F} = 328.9 Hz), 121.02, 114.54, 66.82, 40.97 (q, *J*_{C-F} = 28.1 Hz), 36.92, 31.81, 27.37. HRMS (EI): Cl₃H₁₄F₆OSe⁺ Calcd: 380.0114, Found: 380.0120.

(1,1,1-trifluoro-6-(4-fluorophenoxy)hexan-3-yl)(trifluoromethyl)selane (4d): colorless oil. **¹H NMR** (300 MHz, CDCl₃) δ 6.97 (t, *J* = 8.6 Hz, 2H), 6.88-6.76 (m, 2H), 3.96 (t, *J* = 5.5 Hz, 2H), 3.73-3.56 (m, 1H), 2.94-2.59 (m, 2H), 2.27-1.79 (m, 4H). ¹⁹F NMR (282 MHz, CDCl₃) δ -33.01 (s), -64.20 (s), -124.35 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 157.46 (d, J_{C-F} = 237.0 Hz), 154.95 (d, J_{C-F} = 2.1 Hz), 125.86 (q, J_{C-F} = 276.9 Hz), 122.82 (q, J_{C-F} = 329.1 Hz), 115.90 (d, J_{C-F} = 25 Hz), 115.42 (d, J_{C-F} = 7.9 Hz), 67.58, 41.01 (q, J_{C-F} = 28.1 Hz), 36.88, 31.76, 27.37.

HRMS (EI): C₁₃H₁₃F₇OSe⁺ Calcd: 398.0020, Found: 398.0022.



(1,1,1-trifluoro-6-(4-iodophenoxy)hexan-3-yl)(trifluoromethyl)selane (4e): colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.96 (t, *J* = 5.4 Hz, 2H), 3.52-3.70 (m, 1H), 2.94-2.56 (m, 2H), 2.20-1.83 (m, 4H). ¹⁹F NMR (282 MHz, CDCl₃) δ -33.00 (s), -64.20 (s). ¹³C NMR (75 MHz, CDCl₃) δ 158.71, 138.39, 125.84 (q, *J*_{C-F} = 276.7 Hz), 122.80 (q, *J*_{C-F} = 329.0 Hz), 116.95, 83.09, 67.05, 40.98 (q, *J*_{C-F} = 28.1 Hz), 36.83, 31.70, 27.25. HRMS (EI): C₁₃H₁₃F₆IOSe⁺ Calcd: 505.9080, Found: 505.9072.



(1,1,1-trifluoro-6-(4-nitrophenoxy)hexan-3-yl)(trifluoromethyl)selane (4f): colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 8.21 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H), 4.11 (t, J = 4.8 Hz, 2H), 3.74-3.56 (m, 1H), 2.99-2.56 (m, 2H), 2.24-2.07 (m, 2H), 2.04-1.87 (m, 2H). ¹⁹F NMR (282 MHz, CDCl₃) δ -32.94 (s), -64.19 (s). ¹³C NMR (75 MHz, CDCl₃) δ 163.82, 141.79, 126.11, 125.81 (q, J_{C-F} = 276.7 Hz), 122.76 (q, J_{C-F}

 $= 329.2 \text{ Hz}, 114.50, 67.80, 41.04 (q, J_{C-F} = 28.1 \text{ Hz}), 36.70, 31.55, 27.14.$

HRMS (ESI): $C_{13}H_{13}F_6NO_3Se+Na^+$ Calcd: 447.9857, Found: 447.9854.

H₃CO

(1,1,1-trifluoro-6-(4-methoxyphenoxy)hexan-3-yl)(trifluoromethyl)selane (4g): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 6.83 (s, 4H), 3.95 (t, *J* = 5.5 Hz, 2H), 3.77 (s, 3H), 3.71-3.58 (m,

1H), 2.95-2.54 (m, 2H), 2.18-1.81 (m, 4H).

 ^{19}F NMR (282 MHz, CDCl₃) δ -33.03 (s), -64.20 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 154.07, 152.97, 125.87 (q, $J_{C-F} = 276.7$ Hz), 122.84 (q, $J_{C-F} = 328.3$ Hz), 115.54, 114.80, 67.62, 55.86, 40.98 (q, $J_{C-F} = 28.4$ Hz), 36.91, 31.83, 27.44.

HRMS (EI): C₁₄H₁₆F₆O₂Se⁺ Calcd: 410.0220, Found:410.0213.



2-(4,4,4-trifluoro-2-((trifluoromethyl)selanyl)butyl)isoindoline-1,3-dione (4h): colorless solid, mp: 35-37 °C.

¹**H NMR** (300 MHz, CDCl₃) δ 7.89 (d, *J* = 3.2 Hz, 2H), 7.79 (d, *J* = 2.9 Hz, 2H), 4.08 (d, *J* = 7.1 Hz, 2H), 4.05-3.89 (m, 1H), 2.96-2.63 (m, 2H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -33.08 (s), -64.08 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 168.04, 134.61, 131.71, 125.58 (q, *J*_{C-F} = 276.1 Hz), 123.85, 122.52 (q, *J*_{C-F} = 329.4 Hz), 41.85, 38.83 (q, *J*_{C-F} = 29.3 Hz), 34.34.

HRMS (ESI): C₁₃H₉F₆NO₂Se+H⁺ Calcd: 427.9595, Found: 427.9583.



N,4-dimethyl-N-(6,6,6-trifluoro-4-((trifluoromethyl)selanyl)hexyl)benzenesulfonamide (4i): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.68-3.47 (m, 1H), 3.18-2.89 (m, 2H), 2.86-2.54 (m, 5H), 2.43 (s, 3H), 2.11-1.92 (m, 1H), 1.91-1.72 (m, 2H), 1.72-1.59 (m, 1H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -32.98 (s), -64.18 (s).

¹³C NMR (75 MHz, CDCl₃) δ 143.62., 134.46, 129.88, 127.54, 125.81 (q, $J_{C-F} = 276.7$ Hz), 122.77 (q, $J_{C-F} = 329.3$ Hz), 49.34, 41.13 (q, $J_{C-F} = 27.83$ Hz), 36.77, 34.83, 31.82, 25.53, 21.65. HRMS (ESI): C₁₅H₁₉F₆NO₂SSe+Na⁺ Calcd: 494.0098, Found: 494.0097.



12,12,12-trifluoro-10-((trifluoromethyl)selanyl)dodecyl 4-methylbenzenesulfonate (4j): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.64-3.47 (m, 1H), 2.96-2.52 (m, 2H), 2.45 (s, 3H), 1.98-1.70 (m, 2H), 1.70-1.59 (m, 2H), 1.24 (s, 12H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.18 (s), -64.28 (s).

¹³**C NMR** (125 MHz, CDCl₃) δ 144.78, 133.38, 129.94, 128.03, 125.92 (q, *J*_{C-F} = 276.6 Hz), 122.88 (q, *J*_{C-F} = 328.8 Hz), 70.79, 40.86, (q, *J*_{C-F} = 27.9 Hz), 37.16, 34.80, 29.34, 29.26, 29.01, 28.98, 28.94, 27.31, 25.44, 21.76.

HRMS (ESI): C₂₀H₂₈F₆O₃SSe+Na⁺ Calcd: 565.0721, Found: 565.0718.



12,12,12-trifluoro-10-((trifluoromethyl)selanyl)dodecyl diphenylphosphinate (4k): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.81 (dd, *J* = 12.0, 7.7 Hz, 4H), 7.58-7.39 (m, 6H), 4.02 (q, *J* = 6.5 Hz, 2H), 3.68-3.47 (m, 1H), 2.92-2.53 (m, 2H), 1.92-1.67 (m, 4H), 1.53-1.23 (m, 12H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -33.19 (s), -64.28 (s).

³¹**P NMR** (121 MHz, CDCl₃) δ 31.16 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 132.75, 132.23, 132.19, 131.84, 131.71, 130.93, 128.72, 128.55, 125.91 (q, *J*_{C-F} = 276.6 Hz), 122.88 (q, *J*_{C-F} = 328.7 Hz), 65.07, 40.81 (q, *J*_{C-F} = 27.9 Hz), 37.16, 34.80, 30.71, 29.45, 29.33, 29.20, 29.05, 27.33, 25.71.

HRMS (ESI): C₂₅H₃₁F₆O₂PSe+Na⁺ Calcd: 611.1025, Found: 611.1018.



2-(((7,7,7-trifluoro-5-((trifluoromethyl)selanyl)heptyl)oxy)methyl)pyridine (4l): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 8.56 (d, *J* = 4.1 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.23-7.12 (m, 1H), 4.63 (s, 2H), 3.58 (t, *J* = 5.9 Hz, 3H), 2.90-2.52 (m, 2H), 2.00-1.78 (m, 2H), 1.71-1.49 (m, 4H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.13 (s), -64.27 (s).

¹³C NMR (75 MHz, CDCl₃) δ 158.72, 149.22, 136.77, 125.87 (q, J_{C-F} = 276.6 Hz), 122.83 (q, J_{C-F} = 328.9 Hz), 122.48, 121.42, 73.98, 70.57, 40.78 (q, J_{C-F} = 27.9 Hz), 37.02, 34.66, 29.19, 24.23. HRMS (ESI): C₁₄H₁₇F₆NOSe+Na⁺ Calcd: 432.0272, Found: 432.0273.



5,5,5-trifluoro-3-((trifluoromethyl)selanyl)pentyl picolinate (4m): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 8.78 (d, *J* = 4.5 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.87 (td, *J* = 7.7, 1.3 Hz, 1H), 7.51 (dd, *J* = 7.0, 5.3 Hz, 1H), 4.74-4.49 (m, 2H), 3.84-3.65 (m, 1H), 3.00-2.69 (m, 2H), 2.62-2.43 (m, 1H), 2.38-2.17 (m, 1H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -33.22 (s), -64.10 (s).

¹³C NMR (75 MHz, CDCl₃) δ 165.05, 150.18, 147.71, 137.24, 127.29, 124.81 (q, $J_{C-F} = 276.3$ Hz), 122.74 (q, $J_{C-F} = 329.2$ Hz), 125.31, 63.14, 40.75 (q, $J_{C-F} = 27.8$ Hz), 33.66, 33.23. HRMS (ESI): $C_{12}H_{11}F_6NO_2Se+Na^+$ Calcd: 417.9752, Found: 417.9750.



4-methoxyphenyl 6,6,6-trifluoro-4-((trifluoromethyl)selanyl)hexanoate (4n): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 6.99 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 3.76-3.58 (m, 1H), 2.98-2.61 (m, 4H), 2.53-2.33 (m, 1H), 2.20-1.88 (m, 1H). ¹⁹**F NMR** (282 MHz, CDCl₃) δ -32.88 (s), -64.05 (s).

¹³C NMR (75 MHz, CDCl₃) δ 171.30, 157.51, 144.05, 125.76 (q, J_{C-F} = 276.7 Hz), 122.71 (q, J_{C-F} = 329.2 Hz), 122.30, 114.65, 55.74, 41.48 (q, J_{C-F} = 28.3 Hz), 36.40, 32.28, 29.89. HRMS (ESI): C₁₄H₁₄F₆O₃Se+Na⁺ Calcd: 446.9905, Found: 446.9898.

12,12,12-trifluoro-10-((trifluoromethyl)selanyl)dodecyl acetate (40): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 4.05 (t, *J* = 6.6 Hz, 2H), 3.67-3.47 (m, 1H), 2.92-2.50 (m, 2H), 2.05 (s, 3H), 1.96-1.71 (m, 2H), 1.61 (s, 2H), 1.30 (s, 12H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -33.18 (s), -64.28 (s).

¹³C NMR (125 MHz, CDCl₃) δ 171.42, 125.93 (q, $J_{C-F} = 276.7$ Hz), 122.89 (q, $J_{C-F} = 328.8$ Hz), 64.76, 40.83 (q, $J_{C-F} = 29.0$ Hz), 37.17, 34.82, 29.47, 29.34, 29.30, 29.06, 28.72, 27.33, 26.00, 21.16. HRMS (ESI): C₁₅H₂₄F₆O₂Se+Na⁺ Calcd: 453.0738, Found: 453.0738.



3-methylbut-2-en-1-yl 6,6,6-trifluoro-4-((trifluoromethyl)selanyl)hexanoate (4p): colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 5.34 (t, J = 7.2 Hz, 1H), 4.60 (d, J = 7.3 Hz, 2H), 3.65-3.55 (m, 1H), 2.88-2.57 (m, 4H), 2.34-2.27 (m, 1H), 2.04-1.94 (m, 1H), 1.77 (s, 3H), 1.71 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃) δ -32.96 (s), -64.13 (s). ¹³C NMR (75 MHz, CDCl₃) δ 172.25, 139.76, 125.78 (q, J_{C-F} = 276.5 Hz), 122.71 (q, J_{C-F} = 328.5 Hz), 118.37, 61.86, 41.35 (q, J_{C-F} = 28.4 Hz), 36.46, 32.32, 30.07, 25.89, 18.13. HRMS (ESI): C₁₂H₁₆F₆O₂Se+Na⁺ Calcd: 409.0112, Found: 409.0108.

HO HO CF_3 SeCF₃

12,12,12-trifluoro-10-((trifluoromethyl)selanyl)dodecan-1-ol (4q): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 3.70-3.52 (m, 3H), 2.88-2.50 (m, 2H), 1.93-1.71 (m, 2H), 1.60-1.49 (m, 3H), 1.35-1.27 (m, 11H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.18 (s), -64.28 (s).

¹³C NMR (125 MHz, CDCl₃) δ 125.93 (q, $J_{C-F} = 276.7$ Hz), 122.89 (q, $J_{C-F} = 328.7$ Hz), 63.19, 40.83 (q, $J_{C-F} = 28.1$ Hz), 37.17, 34.82, 32.90, 29.56, 29.47, 29.36, 29.07, 27.33, 25.84.

HRMS (ESI): C₁₃H₂₂F₆OSe+Na⁺ Calcd: 411.0633, Found: 411.0620.

2-(10,10,10-trifluoro-8-((trifluoromethyl)selanyl)decyl)oxirane (4r): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 3.80 (s, 1H), 3.64 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.61-3.53 (m, 1H), 3.48 (dd, *J* = 11.0, 7.1 Hz, 1H), 2.92-2.52 (m, 2H), 2.17 (s, 1H), 1.94-1.73 (m, 2H), 1.46 (s, 4H), 1.35 (s, 7H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.16 (s), -64.28 (s).

¹³C NMR (75 MHz, CDCl₃) δ 125.90 (q, J_{C-F} = 276.8 Hz), 122.88 (q, J_{C-F} = 326.6 Hz), 71.50, 71.12, 50.71, 40.82 (q, J_{C-F} = 28.0 Hz), 37.12, 34.75, 34.23, 29.31, 28.96, 27.26, 25.53. HRMS (EI): C₁₃H₂₀F₆OSe⁺ Calcd: 386.0584, Found: 386.0587.



(8S,9S,10R,13S,14S,17S)-5,5,5-trifluoro-3-((trifluoromethyl)selanyl)pentyl 10,13-dimethyl-3oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-17carboxylate (4s): colorless oil, d.r. = 1.5 : 1

¹**H NMR** (300 MHz, CDCl₃) δ 5.73 (s, 1H), 4.35-4.20 (m, 2H), 3.69 (s, 1H), 2.95-2.63 (m, 2H), 2.45-2.25 (m, 6H), 2.15-1.98 (m, 4H), 1.90-1.80 (m, 2H), 1.77-1.56 (m, 5H), 1.42-1.31 (m, 3H), 1.19 (s, 3H), 1.04-0.92 (m, 2H), 0.72 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.06/-33.25 (s), -64.20/-64.22(s)

¹³**C NMR** (125 MHz, CDCl₃) δ 199.66, 173.72/173.71, 171.11, 125.77 (q, $J_{C-F} = 276.8$ Hz), 124.10, 122.74 (q, $J_{C-F} = 329.1$ Hz), 61.34/61.25, 55.44, 55.30/55.26, 53.81, 44.12/44.07, 41.10 (q, $J_{C-F} = 28.4$ Hz)/41.03 (q, $J_{C-F} = 28.1$ Hz), 38.74, 38.25, 35.86, 35.84, 34.09, 33.91/33.85, 33.44/33.32, 32.92, 32.04, 24.53, 23.74/23.71, 20.98/20.97, 17.51, 13.61/13.59.

HRMS (ESI): C₂₆H₃₄F₆O₃Se+Na⁺ Calcd: 611.1471, Found: 611.1456.



N-butyl-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)-N-(7,7,7-trifluoro-5-((trifluoromethyl)selanyl)heptyl)benzenesulfonamide (4t): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 7.78 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.13 (dd, J = 22.1, 8.1 Hz, 4H), 6.75 (s, 1H), 3.60-3.45 (m, 1H), 3.17-3.02 (m, 4H), 2.88-2.54 (m, 2H), 2.38 (s, 3H), 1.95-1.72 (m, 2H), 1.54-1.40 (m, 4H), 1.38-1.27 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). ¹⁹**F NMR** (282 MHz, CDCl₃) δ -33.10 (s), -62.96 (s), -64.24 (s).

¹³**C NMR** (125 MHz, CDCl₃) δ 145.39, 144.24 (q, J_{C-F} = 38.3 Hz), 142.44, 139.95, 139.53, 129.87, 128.85, 128.18, 125.84 (q, J_{C-F} = 276.8 Hz), 125.82, 125.70, 122.81 (q, J_{C-F} = 329.0 Hz), 122.27, 120.13, 106.37, 48.41, 48.03, 40.85 (q, J_{C-F} = 28.0 Hz), 36.89, 34.39, 30.83, 28.38, 24.59, 21.45, 20.04, 13.78.

HRMS (ESI): C₂₉H₃₂F₉N₃O₂SSe+Na⁺ Calcd: 760.1130, Found: 760.1124.



(8R,9S,13S,14S)-13-methyl-3-((7,7,7-trifluoro-5-((trifluoromethyl)selanyl)heptyl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (4u): colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.20 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 1H), 6.64 (s, 1H), 3.94 (d, *J* = 5.8 Hz, 2H), 3.69-3.51 (m, 1H), 3.04-2.58 (m, 4H), 2.51 (dd, *J* = 18.0, 8.1 Hz, 1H), 2.44-2.34 (m, 1H), 2.31-2.20 (m, 1H), 2.19-1.90 (m, 5H), 1.90-1.69 (m, 4H), 1.64-1.44 (m, 7H), 0.91 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.09 (s), -64.23 (s).

¹³C NMR (125 MHz, CDCl₃) δ 221.14, 157.06, 137.93, 132.27, 126.50, 125.85 (q, J_{C-F} = 276.8 Hz), 122.82 (q, J_{C-F} = 328.9 Hz), 114.70, 112.23, 67.42, 50.56, 48.17, 44.13, 40.79 (q, J_{C-F} = 28.0 Hz), 38.52, 37.03, 36.03, 34.65, 31.73, 29.80, 28.84, 26.70, 26.07, 24.26, 21.74, 14.00. HRMS (ESI): C₂₆H₃₂F₆O₂Se+Na⁺ Calcd: 593.1365, Found: 593.1363.



(2R,3S,5R,6S)-2-(acetoxymethyl)-6-((7,7,7-trifluoro-5-

((trifluoromethyl)selanyl)heptyl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4v): colorless oil, d.r. = 1.1 : 1

¹**H NMR** (300 MHz, CDCl₃) δ 5.40 (s, 1H), 5.27-5.15 (m, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.50 (t, *J* = 6.4 Hz, 1H), 4.25-3.98 (m, 4H), 3.92 (t, *J* = 6.5 Hz, 1H), 3.82-3.61 (m, 2H), 2.95-2.63 (m, 2H), 2.37-2.17 (m, 3H), 2.06 (s, 8H), 1.99 (s, 4H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.34/-33.72 (s), -64.10/-64.33 (s).

¹³**C NMR** (125 MHz, CDCl₃) δ 170.50/170.48, 170.35/170.33, 170.22, 169.42/169.41, 125.85 (q, $J_{C-F} = 276.6 \text{ Hz}$)/125.80 (q, $J_{C-F} = 276.6 \text{ Hz}$), 122.94 (q, $J_{C-F} = 329.3 \text{ Hz}$)/122.86 (q, $J_{C-F} = 329.3 \text{ Hz}$), 101.14/100.75, 71.00/70.98, 70.91/70.89, 68.75, 67.11/67.10, 66.29, 61.41/64.37, 40.65 (q, $J_{C-F} = 28.1 \text{ Hz}$)/40.25 (q, $J_{C-F} = 28.1 \text{ Hz}$), 34.55, 34.28, 33.49, 33.10, 29.83, 20.75/20.67, 20.71, 20.69/20.62.

HRMS (EI): C₂₂H₃₀F₆O₁₀Se⁺ Calcd: 648.0908, Found: 648.0910.

4-methoxyphenyl 6,6,6-trichloro-4-((trifluoromethyl)selanyl)hexanoate (5a): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 6.99 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.93-3.80 (m, 1H), 3.78 (s, 3H), 3.50 (dd, *J* = 15.7, 4.0 Hz, 1H), 3.22 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.85 (t, *J* = 6.7 Hz, 2H), 2.70-2.55 (m, 1H), 2.27-2.07 (m, 1H).

¹⁹F NMR (282 MHz, CDCl₃) δ -31.51 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 171.30, 157.47, 144.04, 122.77 (q, *J*_{C-F} = 329.6 Hz), 122.31, 114.62, 97.49, 60.90, 55.70, 40.50, 32.50, 31.12.

HRMS (ESI): C₁₄H₁₄Cl₃F₃O₃Se+Na⁺ Calcd: 494.9011, Found: 494.9005.



(4,4,4-trichloro-1-phenylbutan-2-yl)(trifluoromethyl)selane (5b): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.40-7.18 (m, 5H), 3.95 (dt, *J* = 12.3, 6.0 Hz, 1H), 3.45 (dd, *J* = 14.5, 6.2 Hz, 1H), 3.37-3.21 (m, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -32.17 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 137.56, 129.54, 128.86, 127.51, 122.97 (q, *J*_{C-F} = 329.7 Hz), 97.76, 59.07, 42.32, 41.85.

HRMS (EI): C₁₁H₁₀Cl₃F₃Se⁺ Calcd: 383.8965, Found: 383.8950.



12,12.trichloro-10-((trifluoromethyl)selanyl)dodecyl 4-methoxybenzoate (5c): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 8.00 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.86 (s, 3H), 3.80-3.65 (m, 1H), 3.39 (dd, J = 15.6, 4.1 Hz, 1H), 3.19 (dd, J = 15.7, 7.0 Hz, 1H), 2.17-1.84 (m, 2H), 1.81-1.67 (m, 2H), 1.54-1.27 (m, 12H).

¹⁹F NMR (282 MHz, CDCl₃) δ -32.46 (s).

¹³C NMR (125 MHz, CDCl₃) δ 166.60, 163.40, 131.67, 123.10, 122.97 (q, *J*_{C-F} = 329.3 Hz), 113.70, 97.92, 64.92, 60.38, 55.55, 41.44, 35.97, 29.52, 29.41, 29.35, 29.10, 28.90, 27.44, 26.15. HRMS (ESI): C₂₁H₂₈Cl₃F₃O₃Se+Na⁺ Calcd: 593.0108, Found: 593.0099.



(6,6,7,7,8,8,9,9,9-nonafluoro-1-(4-nitrophenoxy)nonan-4-yl)(trifluoromethyl)selane (5d): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 8.21 (d, *J* = 9.1 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 4.12 (d, *J* = 5.3 Hz, 2H), 3.88-3.68 (m, 1H), 2.99-2.49 (m, 2H), 2.28-1.88 (m, 4H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -32.99 (s), -81.48 (t, J = 9.6 Hz), -112.07—115.38 (m), -124.96 (d, J = 5.3 Hz), -126.34 (dd, J = 23.7, 12.5 Hz).

¹³**C NMR** (125 MHz, CDCl₃) δ 163.83, 141.81, 126.09, 122.77 (q, *J*_{C-F} = 329.4 Hz), 114.49, 67.78, 37.89 (t, *J*_{C-F} = 20.7 Hz), 35.90, 32.23, 27.24.

HRMS (ESI): C₁₆H₁₃F₁₂NO₃Se+Na⁺ Calcd: 597.9762, Found: 597.9758.



12,12,13,13,14,14,15,15,15-nonafluoro-10-((trifluoromethyl)selanyl)pentadecyl methoxybenzoate (5e): colorless oil.

¹**H** NMR (300 MHz, CDCl₃) δ 8.00 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.85 (s, 3H), 3.78-3.62 (m, 1H), 2.92-2.39 (m, 2H), 2.03-1.66 (m, 4H), 1.58-1.28 (m, 12H). ¹⁹**F** NMR (282 MHz, CDCl₃) δ -33.27 (s), -81.56 (t, J = 9.6 Hz), -112.19—115.54 (m), -12.06 (dd, J = 12.0, 6.8 Hz), -126.40 (t, J = 11.6 Hz).

4-

¹³**C NMR** (75 MHz, CDCl₃) δ 166.57, 163.38, 131.66, 123.08, 122.89 (q, *J*_{C-F} = 328.4 Hz), 113.66, 64.90, 55.49, 53.48, 38.79, 37.58 (t, *J*_{C-F} = 21.8 Hz), 36.34, 35.45, 29.49, 29.34, 29.06, 28.88, 27.41, 26.14.

HRMS (ESI): C₂₄H₂₈F₁₂O₃Se+Na⁺ Calcd: 695.0905, Found: 695.0894.



4-methoxyphenyl 6,6,7,7,8,8,9,9,9-nonafluoro-4-((trifluoromethyl)selanyl)nonanoate (5f): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.00 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.94-3.64 (m, 4H), 3.03-2.56 (m, 4H), 2.53-2.31 (m, 1H), 2.23-1.98 (m, 1H).

¹⁹**F NMR** (282 MHz, CDCl₃) δ -32.92 (s), -81.47 (d, J = 9.5 Hz), -112.07—115.01 (m), -124.96 (d, J = 8.7 Hz), -126.34 (s).

¹³**C NMR** (75 MHz, CDCl₃) δ 171.27, 157.52, 144.04, 122.30, 114.64, 55.73, 38.33 (t, *J*_{C-F} = 20.3 Hz), 35.58, 32.42, 30.93, 30.54.

HRMS (ESI): C₁₇H₁₄F₁₂O₃Se+Na⁺ Calcd: 596.9809, Found: 596.9801.



13-ethoxy-12,12-difluoro-13-oxo-10-((trifluoromethyl)selanyl)tridecyl4-methoxybenzoate(5g): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.43-4.12 (m, 5H), 3.86 (s, 3H), 3.03-2.59 (m, 2H), 1.88-1.61 (m, 4H), 1.49-1.27 (m, 15H).

¹⁹F NMR (282 MHz, CDCl₃) δ -33.09 (s), -102.10—103.31 (m), -106.45—107.85 (m). ¹³C NMR (75 MHz, CDCl₃) δ 166.60, 163.37, 131.67, 123.09, 113.68, 64.93, 63.39, 55.56, 45.46 (t, *J*_{C-F} = 23.3 Hz), 40.55, 29.61, 29.53, 29.43, 29.36, 28.89, 28.63, 27.34, 26.16, 23.51, 14.05. HRMS (ESI): C₂₄H₃₃F₅O₅Se+Na⁺ Calcd: 599.1307, Found: 599.1297.



H₃CO

12,12,12-trifluoro-10-((perfluoropropyl)selanyl)dodecyl 4-methoxybenzoate (5h): colorless oil. ¹**H NMR** (300 MHz, CDCl₃) δ 8.00 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 4.28 (t, J = 6.7Hz, 2H), 4.16-4.03 (m, 1H), 3.86 (s, 3H), 2.84-2.41 (m, 2H), 1.86-1.65 (m, 4H), 1.48-1.29 (m, 12H). ¹⁹**F NMR** (282 MHz, CDCl₃) δ -64.32 (s), -80.16 (t, J = 9.2 Hz), -86.99 (s), -123.20 (s).

¹³C NMR (75 MHz, CDCl₃) δ 166.60, 163.39, 131.67, 125.83 (q, J_{C-F} = 276.8 Hz), 123.09, 113.68, 64.92, 55.53, 41.09 (q, *J*_{C-F} = 28.1 Hz), 36.67, 35.03, 29.85, 29.49, 29.35, 29.11, 28.89, 27.24, 26.15. HRMS (ESI): C₂₃H₂₈F₁₀O₃Se+Na⁺ Calcd: 645.0937, Found: 645.0916.



12,12,13,13,14,14,15,15,15-nonafluoro-10-((perfluoropropyl)selanyl)pentadecyl 4methoxybenzoate (5i): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.36-4.17 (m, 3H), 3.86 (s, 3H), 2.81-2.36 (m, 2H), 1.92-1.66 (m, 4H), 1.48-1.28 (m, 12H).

¹⁹F NMR (282 MHz, CDCl₃) δ -80.17 (t, J = 9.3 Hz), -81.51 (t, J = 9.5 Hz), -87.11 (s), -113.94— 114.05 (m), -123.21 (s), -125.05 (d, J = 9.0 Hz), -126.39 (t, J = 11.4 Hz).

¹³C NMR (75 MHz, CDCl₃) δ 166.60, 163.42, 131.68, 123.14, 113.71, 64.92, 55.55, 53.50, 39.46 $(t, J_{C-F} = 20.9 \text{ Hz}), 38.83, 29.85, 29.52, 29.45, 29.36, 28.96, 28.91, 26.17, 26.07.$

HRMS (ESI): C₂₆H₂₈F₁₆O₃Se+Na⁺ Calcd: 795.0840, Found: 795.0893.

1-tosyl-3-(2,2,2-trifluoroethyl)-4-(((trifluoromethyl)selanyl)methyl)pyrrolidine (6): colorless oil.

¹**H NMR** (300 MHz, CDCl₃) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 3.60-3.47 (m, 1H), 3.46-3.32 (m, 2H), 3.11 (t, J = 9.1 Hz, 1H), 2.96 (d, J = 12.6 Hz, 1H), 2.58-2.40 (m, 5H), 2.31-2.14(m, 2H), 2.07-1.97 (m, 1H).

¹⁹F NMR (282 MHz, CDCl₃) δ -34.51 (s), -65.45 (s).

¹³C NMR (75 MHz, CDCl₃) δ 144.26, 133.44, 130.11, 127.47, 126.24 (q, *J*_{C-F} = 273.79 Hz), 122.21 $(q, J_{C-F} = 327.11 \text{ Hz}), 52.07, 50.64, 41.55, 36.09, 32.24 (q, J_{C-F} = 29.00 \text{ Hz}), 23.53, 21.68.$ **HRMS (ESI)**: C₁₅H₁₇F₆NO₂SSe+Na⁺ Calcd: 491.9941, Found: 491.9937.

6. Copies of NMR spectra









S33



Sect² Sec

F

4d ¹H NMR (300MHz, CDCI₃)








138.39 131.37 122.68 122.69 123.99 123.99 123.99 116.22

83.09 77.58 77.16 76.74 67.05 41.56 41.18 40.81 40.81 40.44 736.83 70 727.25

SeCF₃ CF₃ 4e ¹³C NMR (75MHz, CDCl₃)

















0+ CF3 SeCF3 H₃C²



4k ³¹P NMR (121MHz, CDCI₃)

CF3 SeCF3







4m ¹H NMR (300MHz, CDCI₃)













4p ¹H NMR (300MHz, CDCI₃)









4r ¹H NMR (300MHz, CDCI₃)







<-64.20 -64.22

4s ¹⁹F NMR (282MHz, CDCI₃)













H₃CO、 SeCF₃

5a ¹⁹F NMR (282MHz, CDCI₃)
























5h ¹H NMR (300MHz, CDCI₃)







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7. References

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