Supporting Information for

Copper-Catalyzed Radical 1, 2-Carbotrifluoromethylselenolation of Alkenes under Ambient Conditions

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Table of contents

1. General information	2		
 The synthesis of substrates, (Me₄N)SeCF₃ and L8 Typical procedure for Carbotrifluoromethylselenolation of Alkenes Typical procedure for Carbotrifluoromethylselenolation of Alkenes (Scope of Radical Precursors) 	3 5 20		
		5 Large Scale Reaction	27
		6. Mechanistic Study	27
7. References	30		
8. NMR spectra			

1. General information

All reactions were carried out under argon atmosphere using Schlenk techniques unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. **3a** and **3e** was purchased from J&K. **3b** was purchased from Admas. **3c** was purchased from TCI. **3d** was purchased from Macklin. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine, or basic KMnO4 indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ¹H NMR, 100 or 150 MHz for ¹³C NMR, and 376 MHz for ¹⁹F NMR, respectively, in CDCl₃ with tetramethylsilane (TMS) as an internal standard. (NMe4)SeCF₃ was synthesized according to the literature.¹ The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ¹H NMR were recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ¹³C NMR were reported in terms of chemical shift (δ , ppm). EPR spectra were recorded on Bruker EMX^{plus}-10/12. Mass spectrometric data were obtained using Bruker Apex IV RTMS.

2. The synthesis of substrates, (Me₄N)SeCF₃ and L8

Most of alkenes were purchased from commercial sources. The alkenes $1b^2$, $1c^3$, $1d^3$, $1e^4$, were synthesized according to the reported literature and the spectra were the same as that reported in literature.



(Me₄N)SeCF₃ was synthesized according to the reported literature.⁵

TMSCF₃ + Se + Me₄NF $(Me_4N)SeCF_3$ -78 °C to rt overnight, Ar

An oven-dried, 50-mL Schlenk flask equipped with a magnetic stirrer and a stopcock was flushed with Argon. To a suspension of (preferred) red selenium (1.58 g, 20.0 mmol) in 25 mL glyme, Me₃SiCF₃ (3.104 mL, 21.0 mmol) was added using an Eppendorf pipette. The reaction mixture was cooled to -78 °C using a dry ice bath. NMe₄F (1.86 g, 20.0 mmol) was added in one portion under a strong Argon flow and with vigorous stirring. The temperature was held for approximately 1 h and then allowed to warm to room temperature overnight. The color of the suspension changed during this period from dark red to gray. The solution was decanted and the remaining solid was dried in vacuo. The gray residue was extracted with two portions of 5 mL MeCN. The combined solution was moved solvent by reduced pressure distillation and (Me₄N)SeCF₃ was dried in vacuo in an average

yield of 60%. The spectra of 2 was the same as that reported in literature.

L8 was synthesized according to the reported literature.⁶



(1) Synthesis of 1-methylpyrrolidine-2-carboxylic acid.

A solution of pyrrolidine-2-carboxylic acid (5.4 g, 46.96 mmol), aqueous formaldehyde solution (37%-40%, 1 mL), catalytic CH₃COOH and Pd/C (1 g, 10% weight) in MeOH (100 mL) was stirred under H₂ (1 atm) for 2 h. The completion of reaction was monitored by LC-MS. The 1-methylpyrrolidine-2-carboxylic acid was removed by filtration, and the filtrate was concentrated to give 5.8 g of the desired product, which was directly used for the next step without further purification. (2) Synthesis of L8.

To a solution of 1-methylpyrrolidine-2-carboxylic acid (0.37 g, 2.9 mmol) in DCM (10.0 mL) at 0 °C was added isobutyl chloroformate (0.42 mL, 3.2 mmol) and triethylamine (0.45 mL, 3.2 mmol). After stirring for 20 min at 0 °C, aniline (0.95 g, 3.2 mmol) was added, and the reaction was warmed to rt and stirred overnight. The pure product (**L8**) was isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1) in an average yield of 35%.

The spectra of L8 was the same as that reported in literature.⁶

3. Typical procedure for Carbotrifluoromethylselenolation of Alkenes

$$R^{3}_{1} \sim R^{2} + (Me_{4}N)SeCF_{3} + ICF_{2}CO_{2}Et \xrightarrow{Cu_{2}O(10 \text{ mol}\%), L8(15 \text{ mol}\%)}{1,4\text{-dioxane, 48 h, rt, Ar}} \xrightarrow{SeCF_{3}} R^{1} \xrightarrow{CF_{2}CO_{2}Et} R^{3}_{R^{2}}$$

Into a 10 mL sealed tube were added alkene **1** (0.2 mmol), (Me₄N)SeCF₃ (66 mg, 0.3 mmol), ICF₂CO₂Et (150 mg, 0.6 mmol), Cu₂O (2.9 mg, 0.02 mmol), **L8** (11.6 mg, 0.03 mmol), Cs₂CO₃ (65 mg, 0.2 mmol) and anhydrous 1,4-dioxane (3 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 h. After the completion of reaction, the pure product was isolated by flash column chromatography.

ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (4)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **4** (81.1 mg, 90%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.68 – 7.53 (m, 4H), 7.54 – 7.34 (m, 5H), 4.91 (dd, J = 10.9, 4.1 Hz, 1H), 4.08 – 3.96 (m, 2H), 3.33 – 3.16 (m, 1H), 3.16 – 2.85 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.66 (s, 3F), -102.12 (dt, J = 264.5, 13.5 Hz, 1F), -105.87 (ddd, J = 264.5, 17.6, 14.7 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ²*J*_{C-F} = 32.0 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.0 Hz), 162.9 (C-F, ²*J*_{C-F} = 32.0 Hz), 141.4, 140.1, 136.8, 128.9, 128.1, 127.7, 127.6, 127.0, 127.8 (C-F, ¹*J*_{C-F} = 332.4 Hz), 124.5 (C-F, ¹*J*_{C-F} = 332.4 Hz), 121.2 (C-F, ¹*J*_{C-F} = 332.4 Hz), 117.9 (C-F, ¹*J*_{C-F} = 332.4 Hz), 116.9 (C-F, ¹*J*_{C-F} = 254.0 Hz), 114.44 (C-F, ¹*J*_{C-F} = 254.0 Hz), 114.42 (C-F, ¹*J*_{C-F} = 254.0 Hz), 111.9 (C-F, ¹*J*_{C-F} = 23.8 Hz), 41.7 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.4 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.7 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.4 (C-F, ²*J*_{C-F} = 23.8 Hz), 38.7, 13.7; HRMS (ESI) *m/z*: [M–H]⁻ Calcd for C19H16O2F5SE 451.0241; Found 451.0246.

ethyl 2,2-difluoro-4-(2-methoxyphenyl)-4-((trifluoromethyl)selanyl)butanoate (5)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **5** (71.2 mg, 88%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.34 – 7.29 (m, 1H), 7.27 – 7.16 (m, 3H), 5.07 (dd, J = 11.5, 3.3 Hz, 1H), 4.05 – 3.73 (m, 2H), 3.49 – 3.19 (m, 1H), 3.13 – 2.88 (m, 1H), 2.45 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -34.11 (s, 3F), -101.93 (dt, J = 262.7, 12.7 Hz, 1F), -106.64 (ddd, J = 262.6, 18.6, 14.9 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 162.9 (C-F, ²*J*_{C-F} = 32.1 Hz), 135.8, 135.1, 131.1, 128.4, 126.8, 126.6, 127.8 (C-F, ¹*J*_{C-F} = 332.7 Hz), 124.7 (C-F, ¹*J*_{C-F} = 332.7 Hz), 121.4 (C-F, ¹*J*_{C-F} = 332.7 Hz), 118.1 (C-F, ¹*J*_{C-F} = 332.7 Hz), 116.9 (C-F, ¹*J*_{C-F} = 254.1 Hz), 114.43 (C-F, ¹*J*_{C-F} = 254.1 Hz), 114.40 (C-F, ¹*J*_{C-F} = 254.1 Hz), 111.9 (C-F, ¹*J*_{C-F} = 254.1 Hz), 63.0, 42.0 (C-F, ²*J*_{C-F} = 23.7 Hz), 41.8 (C-F, ²*J*_{C-F} = 23.7 Hz), 41.5 (C-F, ²*J*_{C-F} = 23.7 Hz), 34.6, 19.1, 13.6; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₁₅O₃F₅NaSe 428.9999; Found 428.9996. ethyl 2,2-difluoro-4-(3-methoxyphenyl)-4-((trifluoromethyl)selanyl)butanoate (6)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **6** (70.6 mg, 86%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.28 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.89 – 6.81 (m, 2H), 4.80 (dd, J = 10.8, 4.1 Hz, 1H), 4.14 – 3.96 (m, 2H), 3.83 (s, 3H), 3.27 – 3.07 (m, 1H), 3.05 – 2.87 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.86 (s, 3F), -102.24 (dt, J = 264.7, 13.6 Hz, 1F), -105.95 (ddd, J = 264.8, 17.5, 14.8 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ² $J_{C-F} = 32.1$ Hz), 163.2 (C-F, ² $J_{C-F} = 32.1$ Hz), 162.8 (C-F, ² $J_{C-F} = 32.1$ Hz), 159.9, 139.4, 130.0, 127.8 (C-F, ¹ $J_{C-F} = 332.4$ Hz), 121.2 (C-F, ¹ $J_{C-F} = 332.4$ Hz), 119.8, 117.9 (C-F, ¹ $J_{C-F} = 332.4$

Hz), 116.9 (C-F, ${}^{1}J_{C-F} = 253.9$ Hz), 114.39 (C-F, ${}^{1}J_{C-F} = 253.9$ Hz), 114.37 (C-F, ${}^{1}J_{C-F} = 253.9$ Hz), 113.8, 113.4, 111.9 (C-F, ${}^{1}J_{C-F} = 253.9$ Hz), 63.0, 55.2, 42.0 (C-F, ${}^{2}J_{C-F} = 23.7$ Hz), 41.7 (C-F, ${}^{2}J_{C-F} = 23.7$ Hz), 41.5 (C-F, ${}^{2}J_{C-F} = 23.7$ Hz), 38.9, 13.6; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C14H15O3F5NaSe 428.9999; Found 428.9997.

ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)butanoate (7)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **7** (70.4 mg, 86%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.24 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 4.82 (dd, J = 11.0, 4.0 Hz, 1H), 4.14 – 3.95 (m, 2H), 3.79 (s, 3H), 3.25 – 3.04 (m, 1H), 3.02 – 2.77 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.78 (s, 3F), -102.07 (dt, J = 264.3, 13.4 Hz, 1F), -106.11 (ddd, J = 264.3, 18.0, 14.3 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 159.6, 129.5, 128.9, 127.9 (C-F, ¹*J*_{C-F} = 332.5 Hz), 124.6 (C-F, ¹*J*_{C-F} = 253.9 Hz), 114.46 (C-F, ¹*J*_{C-F} = 253.9 Hz), 114.44 (C-F, ¹*J*_{C-F} = 253.9 Hz), 114.3, 111.9 (C-F, ¹*J*_{C-F} = 253.9 Hz), 114.46 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.8 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.5 (C-F, ²*J*_{C-F} = 23.8 Hz), 38.7, 13.6; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₁₅O₃F₅NaSe 428.9999; Found 429.0002.





The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **8** (77.1 mg, 82%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.39 -7.31 (m, 2H), 7.31 -7.23 (m, 2H), 7.17 -7.09 m, 1H), 7.05 -6.98 (m, 2H), 6.97 -6.9 (m, 2H),

4.84 (dd, J = 10.8, 4.1 Hz, 1H), 4.18 – 3.96 (m, 2H), 3.26 – 3.04 (m, 1H), 3.04 – 2.79 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.69 (s, 3F), -102.47 (dt, J = 264.8, 13.8 Hz, 1F), -105.36 (dt, J = 264.8, 15.6 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm),163.5 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 162.9 (C-F, ²*J*_{C-F} = 32.1 Hz), 157.6, 156.4, 132.3, 129.9, 129.1, 123.8, 122.8 (q, J = 332.5 Hz),127.8 (C-F, ¹*J*_{C-F} = 332.5 Hz), 124.5 (C-F, ¹*J*_{C-F} = 332.5 Hz), 121.2 (C-F, ¹*J*_{C-F} = 332.5 Hz), 119.3, 118.7, 117.9 (C-F, ¹*J*_{C-F} = 332.5 Hz), 116.9 (C-F, ¹*J*_{C-F} = 253.9 Hz), 114.42 (C-F, ¹*J*_{C-F} = 253.9 Hz), 114.41 (C-F, ¹*J*_{C-F} = 253.9 Hz), 111.9 (C-F, ¹*J*_{C-F} = 253.9 Hz), 63.1, 41.9 (C-F, ²*J*_{C-F} = 23.7 Hz), 41.7 (C-F, ²*J*_{C-F} = 23.7 Hz), 41.4 (C-F, ²*J*_{C-F} = 23.7 Hz), 38.5 (C-F, ²*J*_{C-F} = 23.7 Hz), 13.7; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₇O₃F₅NaSe 491.0155; Found 491.0154.

ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (9)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **9** (72.3 mg, 83%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.37 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.83 (dd, J = 11.0, 3.9 Hz, 1H), 4.06 – 3.76 (m, 2H), 3.33 – 3.09 (m, 1H), 3.07 – 2.84 (m, 1H), 1.32 (s, 9H), 1.20 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.84 (s, 3F), -101.43 (dt, J = 264.1, 13.6 Hz, 1F), -106.61 (ddd, J = 264.1, 19.6, 13.7 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 162.9 (C-F, ²*J*_{C-F} = 32.1 Hz), 151.7, 134.4, 127.4, 127.9 (C-F, ¹*J*_{C-F} = 332.3 Hz), 125.9, 124.6 (C-F, ¹*J*_{C-F} = 332.3 Hz), 121.3 (C-F, ¹*J*_{C-F} = 332.3 Hz), 118.0 (C-F, ¹*J*_{C-F} = 332.3 Hz), 116.9 (C-F, ¹*J*_{C-F} = 253.8 Hz), 114.41 (C-F, ¹*J*_{C-F} = 253.8 Hz), 114.39 (C-F, ¹*J*_{C-F} = 23.9 Hz), 41.6 (C-F, ²*J*_{C-F} = 23.9 Hz), 41.9 (C-F, ²*J*_{C-F} = 23.9 Hz), 41.6 (C-F, ²*J*_{C-F} = 23.9 Hz),

38.7, 34.6, 31.1, 13.6; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₁O₂F₅NaSe 455.0519; Found 455.0518.

ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (10)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **10** (52.2 mg, 63%) as a colourless liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.35 – 7.23 (m, 4H), 4.80 (dd, J = 10.7, 4.2 Hz, 1H), 4.17 – 3.96 (m, 2H), 3.19 – 2.73 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.63 (s, 3F), -102.88 (dt, J = 265.4, 14.2 Hz, 1F), -105.34 (dt, J = 265.8, 15.8 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.4 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.8 (C-F, ² $J_{C-F} = 32.0$ Hz), 136.8, 134.4, 129.1, 129.0, 127.6 (C-F, ¹ $J_{C-F} = 332.5$ Hz), 124.3 (C-F, ¹ $J_{C-F} = 332.5$ Hz), 121.0 (C-F, ¹ $J_{C-F} = 332.5$ Hz), 117.7 (C-F, ¹ $J_{C-F} = 254.6$ Hz), 116.8 (C-F, ¹ $J_{C-F} = 254.6$ Hz), 114.3 (C-F, ¹ $J_{C-F} = 254.6$ Hz), 111.8 (C-F, ¹ $J_{C-F} = 254.6$ Hz), 63.2, 41.6 (C-F, ² $J_{C-F} = 23.6$ Hz), 41.4 (C-F, ² $J_{C-F} = 23.6$ Hz), 41.1 (C-F, ² $J_{C-F} = 23.6$ Hz), 38.1, 13.7; HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₃H₁₂O₂ClF₅NaSe 432.9503; Found 432.9503.

ethyl 4-(3-bromophenyl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (11)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **11** (74.1 mg, 81%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.53 – 7.48 (m, 1H), 7.48 – 7.42 (m, 1H), 7.32 – 7.18 (m, 2H), 4.78 (dd, J = 10.6, 4.3 Hz, 1H), 4.25 – 3.99 (m, 2H), 3.23 – 2.82 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) – 33.64 (s, 3F), -102.64 (dt, J = 265.8, 14.0 Hz, 1F), -105.48 (dt, J = 265.8, 15.9 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.4 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$ Hz), 162.7 (C-F, ² $J_{C-F} = 32.0$ Hz), 163.1 (C-F, ² $J_{C-F} = 32.0$

 $_{\rm F}$ = 32.0 Hz), 140.5, 131.7, 130.6, 130.5, 126.4, 122.8, 127.6 (C-F, $^{1}J_{\rm C-F}$ = 332.3 Hz), 124.3 (C-F, $^{1}J_{\rm C-F}$ = 332.3 Hz), 121.0 (C-F, $^{1}J_{\rm C-F}$ = 332.3 Hz), 117.7 (C-F, $^{1}J_{\rm C-F}$ = 332.3 Hz), 116.7 (C-F, $^{1}J_{\rm C-F}$ = 253.2 Hz), 114.2 (C-F, $^{1}J_{\rm C-F}$ = 253.2 Hz), 111.7 (C-F, $^{1}J_{\rm C-F}$ = 253.2 Hz), 63.2, 41.6 (C-F, $^{2}J_{\rm C-F}$ = 23.9 Hz), 41.4 (C-F, $^{2}J_{\rm C-F}$ = 23.9 Hz), 41.1 (C-F, $^{2}J_{\rm C-F}$ = 23.9 Hz), 38.0, 13.7; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₃H₁₂O₂BrF₅NaSe 476.8998; Found 476.8998.

ethyl 4-(3-cyanophenyl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (12)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **12** (67.3 mg, 84%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.69 – 7.65 (m, 1H), 7.64 – 7.58 (m, 2H), 7.49 (t, J = 7.8 Hz, 1H), 4.86 (dd, J = 10.3, 4.6 Hz, 1H), 4.25 – 4.12 (m, 2H), 3.16 – 2.84 (m, 2H), 1.31 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.46 (s, 3F), -103.91 – -104.44 (m, 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.3 (C-F, ²*J*_{C-F} = 31.9 Hz), 162.9 (C-F, ²*J*_{C-F} = 31.9 Hz), 162.6 (C-F, ²*J*_{C-F} = 31.9 Hz), 140.6, 132.1, 132.0, 131.1, 129.9, 127.4 (C-F, ¹*J*_{C-F} = 332.3 Hz), 124.1 (C-F, ¹*J*_{C-F} = 332.3 Hz), 120.8 (C-F, ¹*J*_{C-F} = 332.3 Hz), 118.0, 117.5 (C-F, ¹*J*_{C-F} = 332.3 Hz), 116.7 (C-F, ¹*J*_{C-F} = 253.6 Hz), 114.2 (C-F, ¹*J*_{C-F} = 253.6 Hz), 113.2, 111.7 (C-F, ¹*J*_{C-F} = 253.6 Hz), 63.4, 41.1 (C-F, ²*J*_{C-F} = 23.7 Hz), 40.8 (C-F, ²*J*_{C-F} = 23.7 Hz), 40.6 (C-F, ²*J*_{C-F} = 23.7 Hz), 37.6, 13.7; HRMS (ESI) *m*/*z*: [M+Na]⁺ Calcd for C₁₄H₁₂O₂NF₅NaSe 423.9846; Found 423.9848.

ethyl 2,2-difluoro-4-(4-nitrophenyl)-4-((trifluoromethyl)selanyl)butanoate (13)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **13** (74.1 mg, 88%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm)

8.22 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 4.91 (dd, J = 10.2, 4.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.24 – 2.78 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.41 (s, 3F), -104.03 – -104.49 (m, 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.3 (C-F, ²*J*_{C-F} = 31.9 Hz), 162.9 (C-F, ²*J*_{C-F} = 31.9 Hz), 162.6 (C-F, ²*J*_{C-F} = 31.9 Hz), 147.6, 146.2, 128.6, 124.2, 127.3 (C-F, ¹*J*_{C-F} = 332.5 Hz), 124.0 (C-F, ¹*J*_{C-F} = 332.5 Hz), 120.7 (C-F, ¹*J*_{C-F} = 332.5 Hz), 117.4 (C-F, ¹*J*_{C-F} = 332.5 Hz), 116.7 (C-F, ¹*J*_{C-F} = 253.8 Hz), 114.2 (C-F, ¹*J*_{C-F} = 253.8 Hz), 111.7 (C-F, ¹*J*_{C-F} = 253.8 Hz), 63.4, 41.0 (C-F, ²*J*_{C-F} = 23.6 Hz), 40.8 (C-F, ²*J*_{C-F} = 23.6 Hz), 40.5 (C-F, ²*J*_{C-F} = 23.6 Hz), 37.6, 13.7; HRMS (ESI) *m/z*: [M–H]⁻ Calcd for C₁₃H₁₁O₄NF₅Se 419.9779; Found 419.9778.

ethyl 2,2-difluoro-4-(naphthalen-2-yl)-4-((trifluoromethyl)selanyl)butanoate (14)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **14** (74.3 mg, 87%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.89 – 7.73 (m, 4H), 7.57 – 7.46 (m, 2H), 7.46 – 7.39 (m, 1H), 5.00 (dd, J = 10.8, 3.9 Hz, 1H), 3.81 (q, J = 7.1 Hz, 2H), 3.38 – 3.14 (m, 1H), 3.02 (qd, J = 14.6, 4.1 Hz, 1H), 1.08 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.65 (s, 3F), -101.97 (dt, J = 264.8, 13.4 Hz, 1F), -105.99 (ddd, J = 264.8, 17.2, 15.2 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 162.9 (C-F, ²*J*_{C-F} = 32.1 Hz), 135.1, 133.0, 133.0, 129.0, 127.9, 127.7, 126.8, 126.7, 125.0, 127.8 (C-F, ¹*J*_{C-F} = 332.0 Hz), 124.5 (C-F, ¹*J*_{C-F} = 332.0 Hz), 121.2 (C-F, ¹*J*_{C-F} = 332.0 Hz), 117.0 (C-F, ¹*J*_{C-F} = 254.1 Hz), 114.46 (C-F, ¹*J*_{C-F} = 254.1 Hz), 114.44 (C-F, ¹*J*_{C-F} = 254.1 Hz), 111.9 (C-F, ¹*J*_{C-F} = 254.1 Hz), 63.0, 41.8 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.5 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.3 (C-F, ²*J*_{C-F} = 23.8 Hz), 39.3, 13.5; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₁₅O₂F₅NaSe 449.0050; Found 449.0046.

ethyl 4-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (15)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **15** (80.4 mg, 95%) as a colourless liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 6.85 – 6.73 (m, 3H), 5.99 (s, 2H), 4.80 (dd, J = 10.9, 4.1 Hz, 1H), 4.24 – 4.03 (m, 2H), 3.23 – 3.01 (m, 1H), 3.01 – 2.77 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.79 (s, 3F), -102.62 (dt, J = 264.8, 13.9 Hz, 1F), -105.72 (ddd, J = 264.8, 16.4, 15.4 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 162.8 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 162.8 (C-F, ²*J*_{C-F} = 32.1 Hz), 148.0, 147.7, 131.5, 127.8 (C-F, ¹*J*_{C-F} = 332.5 Hz), 124.5 (C-F, ¹*J*_{C-F} = 332.5 Hz), 121.3, 121.2 (C-F, ¹*J*_{C-F} = 332.5 Hz), 117.9 (C-F, ¹*J*_{C-F} = 332.5 Hz), 116.9 (C-F, ¹*J*_{C-F} = 252.0 Hz), 114.39 (C-F, ¹*J*_{C-F} = 252.0 Hz), 114.38 (C-F, ¹*J*_{C-F} = 252.0 Hz), 111.9 (C-F, ¹*J*_{C-F} = 252.0 Hz), 108.4, 107.8, 101.4, 63.1, 42.0 (C-F, ²*J*_{C-F} = 23.7 Hz), 41.8 (C-F, ²*J*_{C-F} = 23.7 Hz), 41.5 (C-F, ²*J*_{C-F} = 23.7 Hz), 39.1, 13.7; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₁₃O₄F₅NaSe 442.9791; Found 442.9791.

cyclopenta[a]phenanthren-3-yl)-4-((trifluoromethyl)selanyl)butanoate (16)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford **16** (103.0 mg, 93%, dr = 1:1, major of the diastereomeric mixture) as a colourless liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.25 (d, J = 8.2 Hz, 1H + 1H), 7.11 – 7.05 (m, 1H + 1H), 7.05 – 7.00 (m, 1H + 1H), 4.77 (dd, J = 10.8, 4.0 Hz, 1H + 1H), 4.14 – 3.86 (m, 2H + 2H), 3.27 – 3.04 (m, 1H + 1H), 3.04 – 2.80 (m, 3H + 3H), 2.51 (dd, J = 18.7, 8.6 Hz, 1H + 1H), 2.45 – 2.33 (m, 1H + 1H), 2.32 – 2.22 (m, 1H + 1H), 2.21 – 1.87 (m, 4H + 4H), 1.77 – 1.33 (m, 6H + 6H), 1.22 (td, J) = 1.25 (td, J) =

J = 7.1, 1.0 Hz, 3H + 3H), 0.91 (s, 3H + 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.82 (s, 3F), -33.83 (s, 3F), -101.88 – -103.36 (m, 1F + 1F), -104.94 – -106.47 (m, 1F + 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 220.6, 163.60 (C-F, ²*J*_{C-F} = 32.2 Hz), 163.55 (C-F, ²*J*_{C-F} = 32.2 Hz), 163.27 (C-F, ²*J*_{C-F} F = 32.2 Hz), 163.23 (C-F, ²*J*_{C-F} = 32.2 Hz), 162.95 (C-F, ²*J*_{C-F} = 32.2 Hz), 162.91 (C-F, ²*J*_{C-F} = 32.2 Hz), 140.2, 137.28, 137.26, 135.1, 128.12, 128.05, 127.9 (C-F, ¹*J*_{C-F} = 332.5 Hz), 125.99, 125.97, 124.9, 124.7, 124.6 (C-F, ¹*J*_{C-F} = 332.5 Hz), 121.3 (C-F, ¹*J*_{C-F} = 332.5 Hz), 118.0 (C-F, ¹*J*_{C-F} = 332.5 Hz), 117.1 – 111.7 (m), 63.0, 50.5, 47.9, 44.3, 42.03 (C-F, ²*J*_{C-F} = 23.6 Hz), 41.97 (C-F, ²*J*_{C-F} = 23.6 Hz), 41.80 (C-F, ²*J*_{C-F} = 23.6 Hz), 41.73 (C-F, ²*J*_{C-F} = 23.6 Hz), 41.57 (C-F, ²*J*_{C-F} = 23.6 Hz), 41.50 (C-F, ²*J*_{C-F} = 23.6 Hz), 38.8, 37.9, 35.8, 31.5, 29.3, 29.2, 26.4, 26.3, 25.6, 21.5, 13.8, 13.7; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₂₉O₃F₅NaSe 575.1094; Found 575.1094.

ethyl 4-(benzofuran-3-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (17)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **17** (44.0 mg, 53%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.71 – 7.66 (m, 1H), 7.65 (s, 1H), 7.55 – 7.50 (m, 1H), 7.42 – 7.31 (m, 2H), 5.09 (dd, J = 10.8, 4.1 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.93 – 3.80 (m, 1H), 3.39 – 3.20 (m, 1H), 3.17 – 2.99 (m, 1H), 1.11 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.81 (s, 3F), -102.70 (dt, J = 265.1, 13.2 Hz, 1F), -106.29 (ddd, J = 265.1, 17.9, 14.5 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.4 (C-F, ²*J*C-F = 32.1 Hz), 163.1 (C-F, ²*J*C-F = 32.1 Hz), 162.8 (C-F, ²*J*C-F = 32.1 Hz), 155.6, 142.9, 127.6 (C-F, ¹*J*C-F = 332.2 Hz), 125.2, 125.1, 124.3 (C-F, ¹*J*C-F = 332.2 Hz), 123.1, 121.0 (C-F, ¹*J*C-F = 332.2 Hz), 119.9, 117.9, 117.7 (C-F, ¹*J*C-F = 332.2 Hz), 116.8 (C-F, ¹*J*C-F = 253.5 Hz), 114.33 (C-F, ¹*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F, ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F, ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F, ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F, ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F, ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F, ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F, ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F, ²*J*C-F = 253.5 Hz), 114.31 (C-F, ¹*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F, ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F, ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F), ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F), ²*J*C-F = 253.5 Hz), 114.31 (C-F), ¹*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F), ²*J*C-F = 253.5 Hz), 114.31 (C-F), ¹*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F), ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F), ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F), ²*J*C-F = 253.5 Hz), 112.0, 111.8 (C-F), ¹*J*C-F = 253.5 Hz), 63.1, 41.1 (C-F),

24.2 Hz), 40.8 (C-F, ${}^{2}J_{C-F} = 24.2$ Hz), 40.6 (C-F, ${}^{2}J_{C-F} = 24.2$ Hz), 28.9, 13.4; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₅H₁₃O₃F₅NaSe 438.9842; Found 438.9847.

ethyl 2,2-difluoro-4-(quinolin-3-yl)-4-((trifluoromethyl)selanyl)butanoate (18)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **18** (58.0 mg, 68%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 8.92 (d, J = 2.0 Hz, 1H), 8.15 – 8.03 (m, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.65 – 7.53 (m, 1H), 5.04 (dd, J = 10.6, 4.3 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 3.34 – 3.15 (m, 1H), 3.14 – 2.94 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.37 (s, 3F), -103.06 (dt, J = 266.2, 14.2 Hz, 3F), -104.94 (dt, J = 266.2, 15.6 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.4 (C-F, ²*J*_{C-F} = 31.9 Hz), 163.0 (C-F, ²*J*_{C-F} = 31.9 Hz), 162.7 (C-F, ²*J*_{C-F} = 31.9 Hz), 149.9, 147.7, 134.4, 131.3, 130.2, 129.3, 127.8, 127.6 (C-F, ¹*J*_{C-F} = 333.3 Hz), 127.5, 127.2, 124.2 (C-F, ¹*J*_{C-F} = 333.3 Hz), 120.9 (C-F, ¹*J*_{C-F} = 333.3 Hz), 117.6 (C-F, ¹*J*_{C-F} = 333.3 Hz), 116.8 (C-F, ¹*J*_{C-F} = 252.6 Hz), 114.3 (C-F, ¹*J*_{C-F} = 252.6 Hz), 111.8 (C-F, ¹*J*_{C-F} = 252.6 Hz), 63.3, 41.2 (C-F, ²*J*_{C-F} = 23.8 Hz), 41.0 (C-F, ²*J*_{C-F} = 23.8 Hz), 40.7 (C-F, ²*J*_{C-F} = 23.8 Hz), 36.1, 13.6; HRMS (ESI) *m*/*z*: [M+H]⁺ Calcd for C₁₆H₁₅O₂NF₅Se 428.0183; Found 428.0178.

ethyl 2,2-difluoro-4,4-diphenyl-4-((trifluoromethyl)selanyl)butanoate (19)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **19** (78.1 mg, 86%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.52 – 7.44 (m, 4H), 7.42 – 7.31 (m, 6H), 3.96 (q, J = 7.2 Hz, 2H), 3.86 (t, J = 14.7 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -32.56 (s, 3F), -98.75 (t, J = 14.7 Hz, 2F); ¹³C

NMR (101 MHz, CDCl₃) (ppm) 163.5 (C-F, ${}^{2}J_{C-F} = 32.3$ Hz), 163.2 (C-F, ${}^{2}J_{C-F} = 32.3$ Hz), 162.8 (C-F, ${}^{2}J_{C-F} = 32.3$ Hz), 141.2, 129.1, 128.0, 127.8 (C-F, ${}^{1}J_{C-F} = 334.3$ Hz), 124.5 (C-F, ${}^{1}J_{C-F} = 334.3$ Hz), 121.2 (C-F, ${}^{1}J_{C-F} = 334.3$ Hz), 117.8 (C-F, ${}^{1}J_{C-F} = 334.3$ Hz), 117.3 (C-F, ${}^{1}J_{C-F} = 254.3$ Hz), 114.8 (C-F, ${}^{1}J_{C-F} = 254.3$ Hz), 112.2 (C-F, ${}^{1}J_{C-F} = 254.3$ Hz), 63.0, 58.83 (C-F, ${}^{3}J_{C-F} = 2.6$ Hz), 59.80 (C-F, ${}^{3}J_{C-F} = 2.6$ Hz), 59.77 (C-F, ${}^{3}J_{C-F} = 2.6$ Hz), 46.6 (C-F, ${}^{2}J_{C-F} = 23.1$ Hz), 46.4 (C-F, ${}^{2}J_{C-F} = 23.1$ Hz), 46.2 (C-F, ${}^{2}J_{C-F} = 23.1$ Hz), 13.6; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₇O₂F₅NaSe 475.0206; Found 475.0206.

ethyl 2,2-difluoro-3-methyl-4-phenyl-4-((trifluoromethyl)selanyl)butanoate (20)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **20** (45.1 mg, 58%, dr = 14:1, major of the diastereomeric mixture) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.39 – 7.26 (m, 5H), 4.74 (d, J = 6.8 Hz, 1H), 4.16 – 3.97 (m, 2H), 3.11 – 2.76 (m, 1H), 1.32 (d, J = 7.0 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.55 (s, 3F), -106.90 (dd, J = 261.1, 12.5 Hz, 1F), -111.61 (dd, J = 261.2, 14.8 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.7 (C-F, ²*J*_{C-F} = 32.3 Hz), 163.4 (C-F, ²*J*_{C-F} = 32.3 Hz), 163.1 (C-F, ²*J*_{C-F} = 32.3 Hz), 140.0, 128.6, 128.5, 128.1, 127.3 (C-F, ¹*J*_{C-F} = 331.5 Hz), 120.7 (C-F, ¹*J*_{C-F} = 331.5 Hz), 118.4 (C-F, ¹*J*_{C-F} = 255.0 Hz), 117.4 (C-F, ¹*J*_{C-F} = 331.5 Hz), 115.90 (C-F, ¹*J*_{C-F} = 255.0 Hz), 115.89 (C-F, ¹*J*_{C-F} = 255.0 Hz), 113.4 (C-F, ¹*J*_{C-F} = 255.0 Hz), 13.7, 12.15 (C-F, ³*J*_{C-F} = 4.5 Hz), 12.10 (C-F, ³*J*_{C-F} = 4.5 Hz), 12.06 (C-F, ³*J*_{C-F} = 4.5 Hz); HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₄H₁₅O₂F₅NaSe 413.0050; Found 413.0047.

ethyl 2,2-difluoro-2-(2-phenyl-2-((trifluoromethyl)selanyl)cyclohexyl)acetate (21)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **21** (47.2 mg, 55%, dr > 20:1, major of the diastereomeric mixture) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.61 (d, J = 7.6 Hz, 2H), 7.34 – 7.20 (m, 3H), 3.96 – 3.82 (m, 1H), 3.82 – 3.70 (m, 1H), 3.49 – 3.34 m, 1H), 2.74 – 2.62 (m, 1H), 2.36 (d, J = 14.6 Hz, 1H), 2.30 – 2.12 (m, 2H), 2.02 – 1.93 (m, 1H), 1.91 – 1.77 (m, 1H), 1.77 – 1.66 (m, 1H), 1.66 – 1.51 (m, 1H), 1.16 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -31.35 (s, 3F), -95.85 (d, J = 266.1 Hz, 3F), -102.86 (dd, J = 266.1, 26.2 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.8 (C-F, ²*J*C-F = 32.6 Hz), 163.5 (C-F, ²*J*C-F = 32.6 Hz), 163.1 (C-F, ²*J*C-F = 32.6 Hz), 141.1, 129.0, 127.9, 127.6, 127.1 (C-F, ¹*J*C-F = 333.0 Hz), 123.8 (C-F, ¹*J*C-F = 333.0 Hz), 120.5 (C-F, ¹*J*C-F = 233.0 Hz), 118.8 (C-F, ¹*J*C-F = 266.6 Hz), 117.2 (C-F, ¹*J*C-F = 233.0 Hz), 20.6 (C-F, ³*J*C-F = 22.0 Hz), 46.1 (C-F, ²*J*C-F = 22.0 Hz), 31.84 (C-F, ³*J*C-F = 5.8 Hz), 31.79 (C-F, ³*J*C-F = 5.8 Hz), 23.55 (C-F, ³*J*C-F = 9.4 Hz), 23.46 (C-F, ³*J*C-F = 9.4 Hz), 22.6, 20.67 (C-F, ³*J*C-F = 0.9 Hz), 20.66 (C-F, ³*J*C-F = 0.9 Hz), 13.5; HRMS (ESI) *m*/z: [M+Na]⁺ Calcd for C₁₇H₁₉O₂F₅NaSe 453.0363; Found 453.0360.

ethyl 4-(9H-carbazol-9-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (22)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **22** (41.1 mg, 44%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 8.11 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.61 – 7.43 (m, 4H), 7.42 – 7.30 (m, 2H), 6.81 (dd,

J = 11.2, 3.6 Hz, 1H), 4.01 – 3.80 (m, 1H), 3.68 – 3.57 (m, 1H), 3.56 – 3.43 (m, 1H), 3.25 – 3.03 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -32.62(s, 3F), -102.33 (ddd, J = 268.9, 12.5, 10.0 Hz, 1F), -108.89 (ddd, J = 268.9, 20.8, 12.2 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 162.4 (C-F, ²*J*_{C-F} = 31.5 Hz), 162.1 (C-F, ²*J*_{C-F} = 31.5 Hz), 161.8 (C-F, ²*J*_{C-F} = 31.5 Hz), 139.6, 137.8, 126.7, 125.9, 125.3, 123.3, 127.8 (C-F, ¹*J*_{C-F} = 332.2 Hz), 124.5 (C-F, ¹*J*_{C-F} = 332.2 Hz), 121.1 (C-F, ¹*J*_{C-F} = 332.2 Hz), 117.8 (C-F, ¹*J*_{C-F} = 332.2 Hz), 121.2, 121.0, 120.9, 120.3, 116.3 (C-F, ¹*J*_{C-F} = 254.7 Hz), 111.3 (C-F, ¹*J*_{C-F} = 254.7 Hz), 111.4, 109.2, 63.1, 48.54 (C-F, ³*J*_{C-F} = 7.4 Hz), 48.47 (C-F, ³*J*_{C-F} = 7.4 Hz), 41.2 (C-F, ²*J*_{C-F} = 24.8 Hz), 41.0 (C-F, ²*J*_{C-F} = 24.8 Hz), 40.7 (C-F, ²*J*_{C-F} = 24.8 Hz), 13.2; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₆O₂NF₅NaSe 488.0159; Found 488.0154.

5-benzyl 1-ethyl 2,2-difluoro-4-((trifluoromethyl)selanyl)pentanedioate (23)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **23** (53.3 mg, 53%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.44 – 7.28 (m, 5H), 5.19 (d, J = 2.7 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.14 (dd, J = 10.5, 3.7 Hz, 1H), 3.23 – 3.01 (m, 1H), 2.88 – 2.61 (m, 1H), 1.34 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.37 (s, 3F), -105.44 – -105.85 (m, 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 170.0, 163.3 (C-F, ²*J*_{C-F} = 32.0 Hz), 163.0 (C-F, ²*J*_{C-F} = 32.0 Hz), 162.7 (C-F, ²*J*_{C-F} = 32.0 Hz), 134.7, 128.6, 128.3, 127.1 (C-F, ¹*J*_{C-F} = 332.2 Hz), 123.8 (C-F, ¹*J*_{C-F} = 332.2 Hz), 120.5 (C-F, ¹*J*_{C-F} = 332.2 Hz), 117.2 (C-F, ¹*J*_{C-F} = 332.2 Hz), 116.6 (C-F, ¹*J*_{C-F} = 252.9 Hz), 114.1 (C-F, ¹*J*_{C-F} = 252.9 Hz), 111.6 (C-F, ¹*J*_{C-F} = 24.0 Hz), 38.1 (C-F, ²*J*_{C-F} = 24.0 Hz), 37.8 (C-F, ²*J*_{C-F} = 24.0 Hz), 33.7, 13.8; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₅H₁₅O4F₅NaSe 456.9948; Found 456.9939.

ethyl (R, S)-4-(tert-butyl)-2,2-difluoro-6-((trifluoromethyl)selanyl)undeca-4,5-dienoate (24)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **24** (50.2 mg, 56%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 4.44 – 4.15 (m, 2H), 3.05 - 2.71 (m, 2H), 2.48 - 2.18 (m, 2H), 1.57 - 1.44 (m, 2H), 1.43 - 1.27 (m, 7H), 1.11 (s, 9H), 0.96 - 0.87 (m, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.27 (s, 3F), -100.91 (dt, J = 266.8, 13.9 Hz, 1F), -103.58 (ddd, J = 266.8, 18.1, 15.0 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 202.0, 163.8 (C-F, ${}^{2}J_{C-F} = 32.7$ Hz), 163.5 (C-F, ${}^{2}J_{C-F} = 32.7$ Hz), 163.1 (C-F, ${}^{2}J_{C-F} = 32.7$ Hz), 128.0 (C-F, ${}^{1}J_{C-F} = 333.9$ Hz), 124.7 (C-F, ${}^{1}J_{C-F} = 333.9$ Hz), 111.1 (C-F, ${}^{1}J_{C-F} = 333.9$ Hz), 117.6 (C-F, ${}^{1}J_{C-F} = 251.7$ Hz), 115.08 (C-F, ${}^{1}J_{C-F} = 251.7$ Hz), 115.06 (C-F, ${}^{1}J_{C-F} = 251.7$ Hz), 115.06 (C-F, ${}^{1}J_{C-F} = 5.2$ Hz), 105.40 (C-F, ${}^{3}J_{C-F} = 5.2$ Hz), 105.38 (C-F, ${}^{3}J_{C-F} = 5.2$ Hz), 105.40 (C-F, ${}^{3}J_{C-F} = 5.2$ Hz), 105.38 (C-F, ${}^{3}J_{C-F} = 24.3$ Hz), 32.9 (C-F, ${}^{2}J_{C-F} = 24.3$ Hz), 32.7 (C-F, ${}^{2}J_{C-F} = 24.3$ Hz), 31.2, 28.5, 27.8, 22.4, 13.9, 13.8; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₇O₂F₅NaSe 473.0989; Found 473.0985.



Using NMe₄SCF₃⁷ as the nucleophile: The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **25** (62.1 mg, 77%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.67 – 7.56 (m, 4H), 7.52 – 7.36 (m, 5H), 4.71 (dd, J = 9.6, 5.0 Hz, 1H), 4.15 – 3.97 (m, 2H), 3.16 – 2.77 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -40.25 (s, 3F), -102.25 (dt, J = 266.3, 13.9 Hz, 1F), -105.42 (ddd, J = 266.3, J = 266.3, J = 266.3

17.4, 14.3 Hz, 1F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 163.4 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.1 (C-F, ²*J*_{C-F} = 32.1 Hz), 163.2 (C-F, ²*J*_{C-F} = 32.1 Hz), 141.6, 140.1, 136.9, 134.5 (C-F, ¹*J*_{C-F} = 308.1 Hz), 131.4 (C-F, ¹*J*_{C-F} = 308.1 Hz), 128.9, 128.4 (C-F, ¹*J*_{C-F} = 308.1 Hz), 128.1, 127.7, 127.6, 127.0, 125.3 (C-F, ¹*J*_{C-F} = 308.1 Hz), 116.7 (C-F, ¹*J*_{C-F} = 253.5 Hz), 114.18 (C-F, ¹*J*_{C-F} = 253.5 Hz), 114.16 (C-F, ¹*J*_{C-F} = 253.5 Hz), 114.16 (C-F, ¹*J*_{C-F} = 253.5 Hz), 111.7 (C-F, ¹*J*_{C-F} = 253.5 Hz), 63.1, 43.9 – 42.3 (m), 41.5 (C-F, ²*J*_{C-F} = 23.9 Hz), 41.3 (C-F, ²*J*_{C-F} = 23.9 Hz), 41.1 (C-F, ²*J*_{C-F} = 23.9 Hz), 13.7; HRMS (ESI) *m*/*z*: [M+Na]⁺ Calcd for C₁₉H₁₇O₂F₅NaS 427.0762; Found 427.0763.

(1-([1,1'-biphenyl]-4-yl)-3,3-dichloro-4,4,4-trifluorobutyl)(trifluoromethyl)sulfane (26)



Using NMe₄SCF₃⁶ as the nucleophile: The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **26** (53.2 mg, 61%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.70 – 7.59 (m, 4H), 7.54 – 7.44 (m, 4H), 7.44 – 7.34 (m, 1H), 4.99 (dd, J = 8.7, 3.8 Hz, 1H), 3.20 (dd, J = 15.1, 8.7 Hz, 1H), 3.09 (dd, J = 15.1, 3.9 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -40.22 (s, 3F), -79.83 (s, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 141.6, 140.1, 137.6, 134.4 (C-F, ¹*J*_{C-F} = 309.4 Hz), 131.3 (C-F, ¹*J*_{C-F} = 309.4 Hz), 128.8, 128.3 (C-F, ¹*J*_{C-F} = 309.4 Hz), 128.2, 127.8, 127.7, 127.0, 126.2 (C-F, ¹*J*_{C-F} = 282.2 Hz), 125.2 (C-F, ¹*J*_{C-F} = 309.4 Hz), 123.4 (C-F, ¹*J*_{C-F} = 282.2 Hz), 127.6 (C-F, ¹*J*_{C-F} = 282.2 Hz), 117.8 (C-F, ¹*J*_{C-F} = 282.2 Hz), 83.7 (C-F, ²*J*_{C-F} = 35.1 Hz), 83.4 (C-F, ²*J*_{C-F} = 35.1 Hz), 83.0 (C-F, ²*J*_{C-F} = 35.1 Hz), 82.7 (C-F, ²*J*_{C-F} = 35.1 Hz), 46.3, 44.7; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₇H₁₃Cl₂F6 S 433.0014; Found 432.9992.

4. Typical procedure for Carbotrifluoromethylselenolation of Alkenes (Scope of Radical Precursors)



Into a 10 mL sealed tube were added alkene **1** (0.2 mmol), (NMe₄)SeCF₃ (66.6 mg, 0.3 mmol), other Radical Precursors (0.6 mmol), Cu₂O (2.9 mg, 0.02 mmol), **L8** (11.6 mg, 0.03 mmol), Cs₂CO₃ (65 mg, 0.2 mmol) and anhydrous 1,4-dioxane (3 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 h. After the completion of reaction, the pure product was isolated by flash column chromatography.

(1-([1,1'-biphenyl]-4-yl)-3,3,4,4,5,5,6,6,6-nonafluorohexyl)(trifluoromethyl)selane (27)



The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **27** (95.3 mg, 87%) as a white solid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.64 – 7.52 (m, 4H), 7.49 – 7.38 (m, 4H), 7.38 – 7.30 (m, 1H), 5.01 (dd, J = 10.6, 3.8 Hz, 1H), 3.29 - 3.10 (m, 1H), 3.10 - 2.90 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.9 (s, 3F), -81.0 (t, J = 9.3 Hz, 3F), -111.17 – -115.35 (m, 2F), -124.25 – -124.70 (m, 2F), -125.80 – -126.15 (m, 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 141.6, 140.1, 136.9, 128.8, 127.9, 127.7, 127.6, 127.0, 127.8 (C-F, ¹*J*C-F = 333.1 Hz), 124.5 (C-F, ¹*J*C-F = 333.1 Hz), 121.2 (C-F, ¹*J*C-F = 333.1 Hz), 117.9 (C-F, ¹*J*C-F = 333.1 Hz), 120.4 – 105.0 (m, 4C), 38.3 (C-F, ²*J*C-F = 20.9 Hz), 38.1 (C-F, ²*J*C-F = 20.9 Hz), 37.8 (C-F, ²*J*C-F = 20.9 Hz), 37.6; HRMS (ESI) *m/z*: [M–H]⁻ Calcd for C₁₉H₁₁F₁₂Se 546.9840; Found 546.9843.

(3,3,4,4,5,5,6,6,6-nonafluoro-1-(naphthalen-2-yl)hexyl)(trifluoromethyl)selane (28)



The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **28** (88.1 mg, 84%) as a white solid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.95 – 7.81 (m, 4H), 7.60 – 7.52 (m, 2H), 7.49 (dd, J = 8.5, 1.9 Hz, 1H), 5.18 (dd, J = 10.6, 3.9 Hz, 1H), 3.42 – 3.21 (m, 1H), 3.21 – 2.97 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.90 (s, 3F), -81.02 – -81.14 (m, 3F), - 111.23 – -115.07 (m, 2F), -124.25 – -124.60 (m, 2F), -125.82 – -126.18 (m, 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 135.3, 133.2, 133.1, 129.3, 128.0, 127.8, 127.7 (C-F, ¹*J*_{C-F} = 333.2 Hz), 126.8, 126.3, 124.5, 124.4 (C-F, ¹*J*_{C-F} = 333.2 Hz), 121.2 (C-F, ¹*J*_{C-F} = 333.2 Hz), 117.9 (C-F, ¹*J*_{C-F} = 333.2 Hz), 120.4 – 106.3 (m, 4C), 38.1, 38.0 (C-F, ²*J*_{C-F} = 20.9 Hz), 37.9 (C-F, ²*J*_{C-F} = 20.9 Hz), 37.8 (C-F, ²*J*_{C-F} = 20.9 Hz); HRMS (ESI) *m/z*: [M–H]⁻ Calcd for C₁₇H₉F₁₂Se 520.9683; Found 520.9681. (8R,9S,13S,14S)-13-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-((trifluoromethyl)selanyl)hexyl)-

6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (29)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **29** (93.0 mg, 72%, dr = 1:1, major of the diastereomeric mixture) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.27 (d, J = 8.1 Hz, 1H + 1H), 7.11 (d, J = 8.1 Hz, 1H + 1H), 7.05 (s, 1H + 1H), 4.91 (dd, J = 10.6, 3.7 Hz, 1H + 1H), 3.27 – 2.78 (m, 4H + 4H), 2.59 – 2.47 (m, 1H + 1H), 2.45 – 2.36 (m, 1H + 1H), 2.35 – 2.23 (m, 1H + 1H), 2.22 – 1.89 (m, 4H + 4H), 1.72 – 1.38 (m, 6H + 6H), 0.92 (s, 3H + 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -34.08 (s, 3F + 3F), -80.99 – -81.17 (m, 3F + 3F), -111.21 – -115.61 (m, 2F + 2F), -124.28 – -124.61 (m, 2F + 2F), -125.80

--126.15 (m, 2F + 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 220.6, 140.4, 137.5, 135.3, 135.2, 127.9 (C-F, ¹*J*_{C-F} = 332.1 Hz), 127.8, 127.6, 126.2, 124.6 (C-F, ¹*J*_{C-F} = 332.1 Hz), 124.3, 124.2, 121.3 (C-F, ¹*J*_{C-F} = 332.1 Hz), 118.0 (C-F, ¹*J*_{C-F} = 332.1 Hz), 120.2 - 105.3 (m), 50.5, 47.9, 44.3, 38.20 (t, J = 20.7), 38.33 (C-F, ²*J*_{C-F} = 20.7 Hz), 38.27 (C-F, ²*J*_{C-F} = 20.7 Hz), 38.11 (C-F, ²*J*_{C-F} = 20.7 Hz), 38.07 (C-F, ²*J*_{C-F} = 20.7 Hz), 37.9, 37.86 (C-F, ²*J*_{C-F} = 20.7 Hz), 37.80 (C-F, ²*J*_{C-F} = 20.7 Hz), 37.6, 35.8, 31.5, 29.2, 26.3, 25.5, 21.5, 13.8; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₅H₂₅OF₁₂Se 649.0874; Found 649.0885.

(1-([1,1'-biphenyl]-4-yl)-3,3-dichloro-4,4,4-trifluorobutyl)(trifluoromethyl)selane (30)



The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **30** (73.2 mg, 76%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.66 – 7.53 (m, 4H), 7.48 – 7.40 (m, 4H), 7.40 – 7.32 (m, 1H), 5.18 (dd, J = 10.0, 2.9 Hz, 1H), 3.37 (dd, J = 15.1, 10.0 Hz, 1H), 3.17 (dd, J = 15.1, 2.9 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.66 (s, 3F), -79.77 (s, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 141.4, 140.0, 137.4, 128.8, 128.1, 127.8, 127.7, 127.0, 127.9 (C-F, ¹*J*_{C-F} = 332.7 Hz), 126.2 (C-F, ¹*J*_{C-F} = 282.4 Hz), 124.6 (C-F, ¹*J*_{C-F} = 332.7 Hz), 123.4 (C-F, ¹*J*_{C-F} = 332.7 Hz), 121.3 (C-F, ¹*J*_{C-F} = 332.7 Hz), 120.6 (C-F, ¹*J*_{C-F} = 282.4 Hz), 118.0 (C-F, ¹*J*_{C-F} = 332.7 Hz), 117.8 (C-F, ¹*J*_{C-F} = 282.4 Hz), 84.3 (C-F, ²*J*_{C-F} = 35.0 Hz), 84.0 (C-F, ²*J*_{C-F} = 35.0 Hz), 83.6 (C-F, ²*J*_{C-F} = 35.0 Hz), 83.3 (C-F, ²*J*_{C-F} = 35.0 Hz), 46.6, 40.9; HRMS (ESI) *m*/*z*: [M–H]⁻ Calcd for C₁₇H₁₁Cl₂F₆Se 478.9313; Found 478.9311.

(3,3-dichloro-4,4,4-trifluoro-1-(naphthalen-2-yl)butyl)(trifluoromethyl)selane (31)



The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **31** (73.1 mg, 80%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.97 – 7.76 (m, 4H), 7.64 – 7.43 (m, 3H), 5.36 (dd, J = 10.0, 3.0 Hz, 1H), 3.50 (dd, J = 15.1, 10.0 Hz, 1H), 3.27 (dd, J = 15.1, 3.0 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.66 (s, 3F), -79.76 (s, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 135.8, 133.3, 133.1, 129.3, 128.0, 127.8, 126.9, 126.8, 126.7, 125.1, 127.9 (C-F, ¹J_{C-F} = 332.8 Hz), 124.6 (C-F, ¹J_{C-F} = 332.8 Hz), 121.3 (C-F, ¹J_{C-F} = 332.8 Hz), 118.0 (C-F, ¹J_{C-F} = 282.5 Hz), 123.4 (C-F, ¹J_{C-F} = 282.5 Hz), 120.6 (C-F, ¹J_{C-F} = 282.5 Hz), 117.8 (C-F, ¹J_{C-F} = 282.5 Hz), 84.4 (C-F, ²J_{C-F} = 35.1 Hz), 84.0 (C-F, ²J_{C-F} = 35.1 Hz), 83.3 (C-F, ²J_{C-F} = 35.1 Hz), 46.5, 41.5; HRMS (ESI) m/z: [M–H]⁻ Calcd for C₁₅H₉Cl₂F₆Se 452.9156; Found 452.9153.

3-(3,3-dichloro-4,4,4-trifluoro-1-((trifluoromethyl)selanyl)butyl)-14-methyl-

6,7,8,9,11,12,13,14,16,17-decahydro-15*H*-cyclopenta[*a*]phenanthren-15-one (32)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **32** (105.0 mg, 90%, dr = 1:1, diastereomeric mixture) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.29 (d, J = 8.0 Hz, 1H + 1H), 7.20 – 7.13 (m, 1H + 1H), 7.12 – 7.05 (m, 1H + 1H), 5.10 (dd, J = 9.9, 2.9 Hz, 1H + 1H), 3.36 (dd, J = 15.1, 9.9 Hz, 1H + 1H), 3.16 (dd, J = 15.1, 3.0 Hz, 1H + 1H), 3.00 – 2.86 (m, 2H + 2H), 2.53 (dd, J = 18.7, 8.6 Hz, 1H + 1H), 2.47 – 2.38 (m, 1H + 1H), 2.36 – 2.25 (m, 1H + 1H), 2.24 – 1.92 (m, 4H + 4H), 1.76 – 1.40 (m, 6H + 6H), 0.94 (s, 3H + 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.81 (s, 3F), -33.82 (s, 3F), -79.78 (s, 3F + 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 220.6, 140.3, 137.4, 135.8, 135.7, 128.2, 128.0, 126.1, 125.0, 124.8, 128.0 (C-F, ¹J_{C-F} = 332.9 Hz), 126.2 (C-F, ¹J_{C-F} = 282.2 Hz), 124.7 (C-F, ¹J_{C-F} = 332.9 Hz),

123.4 (C-F, ${}^{1}J_{C-F} = 282.2 \text{ Hz}$), 121.3 (C-F, ${}^{1}J_{C-F} = 332.9 \text{ Hz}$), 120.6 (C-F, ${}^{1}J_{C-F} = 282.2 \text{ Hz}$), 118.0 (C-F, ${}^{1}J_{C-F} = 332.9 \text{ Hz}$), 117.8 (C-F, ${}^{1}J_{C-F} = 282.2 \text{ Hz}$), 84.4 (C-F, ${}^{2}J_{C-F} = 34.9 \text{ Hz}$), 84.0 (C-F, ${}^{2}J_{C-F} = 34.9 \text{ Hz}$), 83.7 (C-F, ${}^{2}J_{C-F} = 34.9 \text{ Hz}$), 83.3 (C-F, ${}^{2}J_{C-F} = 34.9 \text{ Hz}$), 50.5, 47.9, 46.7, 46.6, 44.3, 41.0, 37.9, 35.8, 31.5, 29.2, 26.3, 25.5, 21.5, 13.8; HRMS (ESI) *m/z*: [M–H]⁻ Calcd for C₂₃H₂₃OCl₂F₆Se 579.0201; Found 579.0203.

tert-butyl 4-([1,1'-biphenyl]-4-yl)-2,2-dimethyl-4-((trifluoromethyl)selanyl)butanoate (33)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **33** (41.1 mg, 43%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.61 – 7.49 (m, 4H), 7.48 – 7.37 (m, 4H), 7.37 – 7.29 (m, 1H), 4.74 (dd, J = 9.1, 5.5 Hz, 1H), 2.61 – 2.31 (m, 2H), 1.36 (s, 9H), 1.15 (s, 3H), 1.01 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.71 (s, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 175.9, 140.8, 140.4, 140.0, 128.8, 128.3, 128.1 (C-F, ¹*J*_{C-F} = 332.2 Hz), 127.4, 127.4, 127.0, 124.8 (C-F, ¹*J*_{C-F} = 332.2 Hz), 121.5 (C-F, ¹*J*_{C-F} = 332.2 Hz) 118.2 (C-F, ¹*J*_{C-F} = 332.2 Hz), 80.5, 46.2, 44.2, 43.5, 27.8, 26.5, 25.3; HRMS (ESI) *m/z*: [M–H]⁻ Calcd for C₂₃H₂₆O₂F₃Se 471.1056; Found 471.1055.

tert-butyl 2,2-dimethyl-4-(naphthalen-2-yl)-4-((trifluoromethyl)selanyl)butanoate (34)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **34** (36.3 mg, 40%) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.84 – 7.76 (m, 3H), 7.74 (d, J = 1.3 Hz, 1H), 7.51 – 7.42 (m, 3H), 4.87 (t, J = 7.3 Hz, 1H), 2.51 (d, J = 7.3 Hz, 2H), 1.33 (s, 9H), 1.15 (s, 3H), 0.99 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.76

(s, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 175.9, 138.5, 133.2, 132.9, 128.7, 128.0 (C-F, ¹ $J_{C-F} = 332.3 \text{ Hz}$), 127.8, 127.6, 126.6, 126.4, 126.2, 125.6, 124.7 (C-F, ¹ $J_{C-F} = 332.3 \text{ Hz}$), 121.4 (C-F, ¹ $J_{C-F} = 332.3 \text{ Hz}$), 118.1 (C-F, ¹ $J_{C-F} = 332.3 \text{ Hz}$), 80.5, 46.0, 44.8, 43.6, 27.7, 26.7, 24.9; HRMS (ESI) *m*/*z*: [M+Na]⁺ Calcd for C₂₁H₂₅O₂F₃NaSe 469.0864; Found 469.0864.

tert-butyl-2,2-dimethyl-4-(14-methyl-15-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*cyclopenta[*a*]phenanthren-3-yl)-4-((trifluoromethyl)selanyl)butanoate (35)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **35** (35.4 mg, 31%, dr = 1:1, diastereomeric mixture) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.23 (d, J = 8.0 Hz, 1H + 1H), 7.15 – 7.08 (m, 1H + 1H), 7.07 – 6.99 (m, 1H + 1H), 4.69 – 4.61 (m, 1H + 1H), 3.00 – 2.81 (m, 2H + 2H), 2.59 – 2.37 (m, 4H + 4H), 2.36 – 2.23 (m, 1H + 1H), 2.23 – 1.88 (m, 4H + 4H), 1.73 – 1.42 (m, 6H + 6H), 1.37 (d, J = 3.8 Hz, 9H + 9H), 1.15 (s, 3H + 3H), 1.02 (d, J = 4.0 Hz, 3H + 3H), 0.93 (s, 3H + 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.82 (s, 3F), -33.82 (s, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 220.8, 176.0, 139.5, 138.1, 136.9, 136.8, 128.3, 128.2, 125.8.125.7, 125.1, 125.0, 128.2 (C-F, ¹ $_{JC-F}$ = 334.6 Hz), 121.6 (C-F, ¹ $_{JC-F}$ = 334.6 Hz), 117.8 (C-F, ¹ $_{JC-F}$ = 334.6 Hz), 80.3, 50.5, 47.9, 46.4, 46.3, 44.3, 43.5, 43.4, 38.0, 35.8, 31.5, 29.3, 27.7, 26.5, 26.4, 25.6, 25.3, 25.2, 21.5, 13.8; HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₉H₃₉O₃F₃NaSe 595.1909; Found 595.1912.



Into a 10 mL sealed tube were added alkene **1a** (18 mg, 0.1 mmol), (NMe4)SeCF₃ (33 mg, 0.15 mmol), **3e** (47.4 mg, 0.15 mmol), Cu₂O (1.43 mg, 0.01 mmol) , **L8** (5.8 mg, 0.015 mmol) and

anhydrous 1,4-dioxane (1.5 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 h. After the completion of reaction, The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **36** (13.5 mg, 34%) as a white solid.

(1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)(trifluoromethyl)selane (36)



The product mixture was purified by silica gel column chromatography (petroleum ether) to afford **36** (13.5 mg, 34%) as a white solid. ¹H NMR (400 MHz, CDCl₃) (ppm) 7.70 – 7.57 (m, 4H), 7.54 – 7.35 (m, 5H), 4.91 (dd, J = 10.7, 4.3 Hz, 1H), 3.32 – 3.13 (m, 1H), 3.16 – 2.87 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) -33.69 (s, 3F), -64.12 (t, J = 9.7 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 141.6, 140.1, 136.5, 128.8, 127.8, 127.7, 127.0, 129.3 (C-F, ¹*J*_{C-F} = 278.9 Hz), 127.8 (C-F, ¹*J*_{C-F} = 332.5 Hz), 126.6 (C-F, ¹*J*_{C-F} = 278.9 Hz), 124.5 (C-F, ¹*J*_{C-F} = 332.5 Hz), 123.8 (C-F, ¹*J*_{C-F} = 278.9 Hz), 121.2 (C-F, ¹*J*_{C-F} = 332.5 Hz), 121.0 (C-F, ¹*J*_{C-F} = 278.9 Hz), 117.9 (C-F, ¹*J*_{C-F} = 332.5 Hz), 41.7 (C-F, ²*J*_{C-F} = 28.6 Hz), 41.4 (C-F, ²*J*_{C-F} = 28.6 Hz), 41.1 (C-F, ²*J*_{C-F} = 28.6 Hz), 40.8 (C-F, ²*J*_{C-F} = 28.6 Hz), 38.5 (s); HRMS (ESI) *m/z*: [M-H]⁻ Calcd for C₁₆H₁₁F₆Se 396.9936; Found 396.9937.

5 Large Scale Reaction



Into a 100 mL Schlenk bottle were added alkene **1a** (0.54 g, 3.0 mmol), (Me4N)SeCF₃ (1.0 g, 4.5 mmol), ICF₂CO₂Et (2.25 g, 9.0 mmol), Cu₂O (43.0 mg, 0.3 mmol) , **L8** (175.0 mg, 0.45 mmol), Cs₂CO₃ (0.98 g, 3.0 mmol) and anhydrous 1,4-dioxane (45 mL) under argon atmosphere. The Schlenk bottle was sealed and the reaction mixture was stirred at room temperature for 72 h. After the completion of reaction, the pure product **4** was isolated by flash column chromatography (0.89 g, 66%).

6. Mechanistic Study



Into a 10 mL sealed tube were added alkene **1a** (18 mg, 0.1 mmol), **3c** or **3d** (0.3 mmol), Cu₂O (1.4 mg, 0.01 mmol) , **L8** (5.8 mg, 0.015 mmol), Cs₂CO₃ (33 mg, 0.1 mmol) and anhydrous 1,4-dioxane (1.5 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 h. But no conversion of alkene was observed.



Into a 10 mL sealed tube were added chloride⁸ or a similar bromide substrate (0.1 mmol), (NMe₄)SeCF₃ (33 mg, 0.15 mmol) and anhydrous 1,4-dioxane (1.5 mL) under argon atmosphere. The

tube was sealed and the reaction mixture was stirred at room temperature for 48 h. After the completion of reaction, the reaction system was added with PhCF₃ (0.1 mmol) as internal standard. The chloride substrate could not react with (Me₄N)SeCF₃ to generated the desired product **30**, but the bromide substrate reacted well with (Me₄N)SeCF₃ to provide the substitution product in 30% yield.



Into a 10 mL sealed tube were added radical clock substrate **37** (22 mg, 0.1 mmol), (NMe₄)SeCF₃ (33 mg, 0.15 mmol), ICF₂CO₂Et (75 mg, 0.3 mmol), Cu₂O (1.43 mg, 0.01 mmol), L8 (5.8 mg, 0.015 mmol), Cs₂CO₃ (33 mg, 0.1 mmol) and anhydrous 1,4-dioxane (1.5 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 h. After the completion of reaction, the pure product **38** was isolated by flash column chromatography.

ethyl (Z)-2,2-difluoro-4,7-diphenyl-7-((trifluoromethyl)selanyl)hept-4-enoate (38)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **38** (33.2 mg, 67%, mixture of Z/E = 1:10) as a slightly green liquid. ¹H NMR (400 MHz, CDCl₃) (major) (ppm) 7.35 (d, J = 4.2 Hz, 4H), 7.31 – 7.26 (m, 3H), 7.24 – 7.21 (m, 1H), 7.20 – 7.14 (m, 2H), 5.74 (t, J = 7.3 Hz, 1H), 4.66 (dd, J = 8.7, 6.8 Hz, 1H), 3.87 (q, J = 7.2 Hz, 2H), 3.33 – 3.20 (m, 2H), 3.13 – 3.04 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) (ppm) - 33.07 (s, 3F), -103.05 (dt, J = 38.5, 15.8 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃) (ppm) 164.0 (C-F, ²*J*_{C-F} = 32.5 Hz), 163.7 (C-F, ²*J*_{C-F} = 32.5 Hz), 163.3 (C-F, ²*J*_{C-F} = 32.5 Hz), 141.5, 139.7,132.93 (C-F, ³*J*_{C-F} = 4.1 Hz), 132.89 (C-F, ³*J*_{C-F} = 4.1 Hz), 132.85 (C-F, ³*J*_{C-F} = 4.1 Hz), 131.6, 128.9, 128.2, 128.1, 128.0 (C-F, ¹*J*_{C-F} = 331.6 Hz), 127.6, 127.5, 126.8, 124.7 (C-F, ¹*J*_{C-F} = 331.6 Hz), 121.4 (C-F, ¹*J*_{C-F} = 331.6 Hz), 118.1 (C-F, ¹*J*_{C-F} = 331.6 Hz), 117.4 (C-F, ¹*J*_{C-F} = 252.5 Hz), 114.9 (C-F, ¹*J*_{C-F} = 252.5 Hz), 112.4 (C-F, ¹*J*_{C-F} = 252.5 Hz), 112.4 (C-F, ¹*J*_{C-F} = 252.5 Hz), 112.4 (C-F, ¹*J*_{C-F} = 252.5 Hz), 12.4 (C-F, ¹*J*_{C-F} = 252.5 Hz), 112.4 (C-F, ¹*J*_{C-F} = 252.5 Hz), 62.7, 46.4, 36.3, 35.9 (C-F, ²*J*_{C-F} = 24.6 Hz), 35.7 (C-F, ²*J*_{C-F} = 252.5 Hz), 112.4 (C-F, ¹*J*_{C-F} = 252.5 Hz)

 $_{\rm F}$ = 24.6 Hz), 35.4 (C-F, $^2J_{\rm C-F}$ = 24.6 Hz), 13.6; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₂H₂₂F₅O₂Se 493.0700; Found 493.0690.



Into a 10 mL sealed tube were added alkene **1a** (18 mg, 0.1 mmol), (NMe₄)SeCF₃ (33 mg, 0.15 mmol,), ICF₂CO₂Et (75 mg, 0.3 mmol), Cu₂O (1.4 mg, 0.01 mmol) , **L8** (5.8 mg, 0.015 mmol), Cs₂CO₃ (33 mg, 0.1 mmol), TEMPO (47 mg, 0.3 mmol) and anhydrous 1,4-dioxane (1.5 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 h. After the completion of reaction, the reaction system was added with PhCF₃ (0.1 mmol) as internal standard, followed by direct fluorine spectrum to monitoring reaction system and high resolution mass of product **39**. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₃H₂₄F₂NO₃ 280.1719; Found 280.1713.



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8. NMR spectra

¹H NMR: (400 MHz, CDCl₃)



¹³C NMR: (101 MHz, CDCl₃)



¹⁹F NMR: (376 MHz, CDCl₃)





S34

¹³C NMR: (101 MHz, CDCl₃)



¹⁹F NMR: (376 MHz, CDCl₃)










S39




































































¹H NMR: (400 MHz, CDCl₃)



¹³C NMR: (101 MHz, CDCl₃)



¹⁹F NMR: (376 MHz, CDCl₃)





¹³C NMR: (101 MHz, CDCl₃)





¹H NMR: (400 MHz, CDCl₃)



¹³C NMR: (101 MHz, CDCl₃)



¹⁹F NMR: (376 MHz, CDCl₃)

