Supporting Information

Difluorocarbene-derived trifluoromethylselenolation of benzyl halides

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1. General information

Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. $^1$H, $^{13}$C and $^{19}$F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (J) in Hz). Mass spectra were obtained on a GC-MS or LC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI mode.

2. Procedure for the preparation of 2

\[
\begin{align*}
\text{CuI, 2,2'-bpy,} & \\
\text{R-X + Ph$_3$P$^+$CF$_2$COO$^-$ + Se + CsF} & \\
\text{DMA, 70 °C, 1.5 h} & \\
\rightarrow & \\
\text{R-SeCF$_3$} & \\
\end{align*}
\]

Into a 10 mL sealed tube were added 1a (0.2 mmol, 49.4 mg), Ph$_3$P$^+$CF$_2$COO$^-$ (0.4 mmol, 142.4 mg), Se (1.2 mmol, 94.8 mg), CsF (0.6 mmol, 91.2 mg), CuI (0.6 mmol, 114.3 mg), 2,2'-bpy (0.4 mmol, 62.4 mg), $^n$Bu$_4$NCl (0.4 mmol, 111 mg), Ag$_2$CO$_3$ (0.04 mmol, 11.1 mg) and DMA (3 mL) under a N$_2$ atmosphere. The tube was sealed and the mixture was stirred at 70 °C for 1.5 h. After being cooled to room temperature, the mixture was filtrated. The solid was washed by DCM, and the combined organic phase was washed with water (20 mL × 3) to remove DMA. The organic phase was dried over Na$_2$SO$_4$. After the solvent was removed by concentration, the residue was subjected to flash column chromatography to afford the final product 2a.

![2a](image)

([(1,1'-biphenyl]-4-ylmethyl) (trifluoromethyl) selane; 71%; white solid; M. P.: 65 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58-7.54 (m, 4H), 7.45-7.39 (m, 4H), 7.34 (t, J = 6.8Hz, 1H), 4.28 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -34.41 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.8 (s), 140.5 (s), 135.1 (s), 130.6 (s), 129.5 (s), 128.8 (s), 127.6 (s), 127.1 (s) , 122.9 (q, J = 331.0 Hz), 28.9 (q, J = 1.3 Hz). IR (neat) ν = 1488, 1407, 1191, 1103, 842, 765, 738, 728, 662cm$^{-1}$; HRMS (EI) Calcd for C$_{14}$H$_{11}$F$_3$Se[M]$^+$: 310.0038, Found: 310.0051.

![2b](image)
(1,1'-biphenyl)-2-ylmethyl) (trifluoromethyl) selane; 41%; yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.38 (m, 4H), 7.34-7.31 (m, 4H), 7.24 (t, $J = 4.4$ Hz, 1H), 4.20 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.75 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.4 (s), 140.3 (s), 133.4 (s), 130.6 (s), 130.3 (s), 129.0 (s), 128.4 (s), 127.93 (s), 127.90 (s), 127.6 (s), 122.9 (q, $J = 331.0$ Hz), 27.3 (q, $J = 1.7$ Hz). IR (neat) $\tilde{\nu}$ = 3062, 1478, 1451, 1438, 1099, 762, 744, 702 cm$^{-1}$; HRMS (EI) Calcd for C$_{14}$H$_{11}$F$_3$Se[M]$^+$: 310.0038, Found: 310.0045.

![2c](image)

(4-chlorobenzyl) (trifluoromethyl) selane; 57%; slightly yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30-7.24 (m, 4H), 4.18 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.37 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.8 (s), 133.7 (s), 130.3 (s), 129.1 (s), 122.7 (q, $J = 331.4$ Hz), 28.3 (q, $J = 1.8$ Hz). IR (neat) $\tilde{\nu}$ = 2962, 1492, 1408, 1261, 1095, 864, 800, 739, 704 cm$^{-1}$; HRMS (EI) Calcd for C$_8$H$_6$ClF$_3$Se[M]$^+$: 267.9335, Found: 267.9330.

![2d](image)

(3,4-dichlorobenzyl) (trifluoromethyl) selane; 55%; slightly yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 2.1$ Hz, 1H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.16 (dd, $J = 8.2$, 2.1 Hz, 1H), 4.14 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.29 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 136.7 (s), 132.9 (s), 132.0 (s), 130.9 (s), 130.8 (s), 128.3 (s), 122.6 (q, $J = 331.5$ Hz), 27.7 (q, $J = 1.8$ Hz). IR (neat) $\tilde{\nu}$ = 1593, 1470, 1396, 1201, 1096, 1073, 1034, 891, 738 cm$^{-1}$; HRMS (EI) Calcd for C$_8$H$_6$ClF$_3$Se[M]$^+$: 301.8945, Found: 301.8957.

![2e](image)

(4-bromobenzyl) (trifluoromethyl) selane; 71%; white liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 4.16 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.36 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.3 (s), 132.0 (s), 130.7 (s), 122.5 (q, $J = 331.0$ Hz), 121.8 (s), 28.4 (q, $J = 1.7$ Hz). IR (neat) $\tilde{\nu}$ = 2960, 2925, 2853, 1590, 1488, 1420, 1403, 1261, 1097, 1012, 801, 477 cm$^{-1}$; HRMS (EI) Calcd for C$_8$H$_6$BrF$_3$Se[M]$^+$: 311.8830, Found: 311.8844.
(3,5-dibromobenzyl) (trifluoromethyl) selane; 81%; slightly yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (s, 1H), 7.42 (s, 2H), 4.12 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.29 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.3 (s), 133.5 (s), 130.8 (s), 123.2 (s), 122.4 (q, $J = 331.0$ Hz), 27.5 (s). IR (neat) $\nu = 1584, 1556, 1425, 1219, 1097, 1074, 858, 742, 684$ cm$^{-1}$; HRMS (EI) Calcd for C$_8$H$_5$Br$_2$F$_3$Se[M]$^+$: 389.7935, Found: 389.7932.

(2-iodobenzyl) (trifluoromethyl) selane; 43%; slightly yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 7.8$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.4$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 4.29 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.29 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.84 (s), 139.75 (s), 130.0 (s), 129.4 (s), 128.8 (s), 122.8 (q, $J = 331.9$ Hz), 100.6 (s), 34.8 (q, $J = 1.6$ Hz). IR (neat) $\nu = 2924, 1563, 1468, 1437, 1199, 1096, 754, 737, 718, 646$ cm$^{-1}$; HRMS (EI) Calcd for C$_8$H$_6$I$_7$F$_3$Se[M]$^+$: 359.8691, Found: 359.8695.

(trifluoromethyl) (4-(trifluoromethyl) benzyl) selane; 50%; slightly yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 4.24 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.39 (s, 3F), -62.73 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.6 (s), 130.0 (q, $J = 33.0$ Hz), 129.3 (s), 125.8 (q, $J = 3.8$ Hz), 124.0 (q, $J = 272.1$ Hz), 123.1 (q, $J = 333.0$ Hz), 28.3 (q, $J = 1.6$ Hz). IR (neat) $\nu = 1618, 1558, 1326, 1123, 1097, 1067, 1019, 848, 753, 739$ cm$^{-1}$; HRMS (EI) Calcd for C$_9$H$_6$F$_6$Se[M]$^+$: 301.9598, Found: 301.9592.

(naphthalen-2-ylmethyl) (trifluoromethyl) selane; 41%; white solid; M. P.: 48 °C;
$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83-7.78 (m, 4H), 7.52-7.43 (m, 3H), 4.41 (s, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.35 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 133.43 (s), 133.36 (s), 132.8 (s), 128.8 (s), 127.9 (s), 127.76 (s), 127.75 (s), 126.8 (s), 126.5 (s), 126.3 (s), 122.9 (q, $J = 331.4$ Hz), 29.6 (q, $J = 1.7$ Hz). IR (neat) $\nu$ = 1598, 1507, 1201, 1096, 966, 953, 867, 826, 751, 737, 480 cm$^{-1}$; HRMS (EI) Calcd for C$_{12}$H$_9$F$_3$Se[M]$^+$: 283.9881, Found: 283.9884.

![2j](image1.png)

(3-methoxybenzyl) (trifluoromethyl) selane$^1$; 71%; white liquid; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (t, $J = 7.9$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.85 (t, $J = 1.9$ Hz, 1H), 6.81 (dd, $J = 8.2$ Hz, 2.0 Hz, 1H), 4.21 (s, 2H), 3.80 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.53 (s, 3F).

![2k](image2.png)

(3,5-dimethoxybenzyl) (trifluoromethyl) selane; 50%; slightly yellow liquid; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.47 (d, $J = 2.2$ Hz, 2H), 6.35 (t, $J = 2.2$ Hz, 1H), 4.16 (s, 2H), 3.77 (s, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.57 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.1 (s), 138.2 (s), 122.9 (q, $J = 331.4$ Hz), 107.0 (s), 99.8 (s), 55.3 (s), 29.3 (q, $J = 1.7$ Hz). IR (neat) $\nu$ = 1608, 1598, 1464, 1430, 1325, 1207, 1158, 1099, 1066, 930, 737 cm$^{-1}$; HRMS (EI) Calcd for C$_{10}$H$_{11}$F$_3$O$_2$Se[M]$^+$: 293.9936, Found: 293.9944.

![2l](image3.png)

methylbenzyl) (trifluoromethyl) selane$^2$; 58%; slightly yellow liquid; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 4.22 (s, 2H), 2.33 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -34.50 (s, 3F).

![2m](image4.png)

(4-methoxybenzyl) (trifluoromethyl) selane; 45%; slightly yellow liquid; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (d, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 2H), 4.21 (s, 2H), 3.79
(s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -34.45 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.2 (s), 130.2 (s), 127.8 (s), 122.9 (q, $J = 333.2$ Hz), 114.3 (s), 55.3 (s), 28.8 (q, $J = 1.8$ Hz). IR (neat) ν = 2956, 1608, 1512, 1464, 1322, 1251, 1096, 1071, 1034, 737, 598 cm$^{-1}$; HRMS (EI) Calcd for C$_9$H$_9$F$_3$O$_7^{64}$Se[M$^+$]: 263.9830, Found: 263.9819.

\[
\text{SeCF}_3
\]

**2n**

cinnamyl(trifluoromethyl)selane$^3$; The yield determined by $^{19}$F NMR spectroscopy was 12%; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -33.86 (s, 3F).

\[
\text{SeCF}_3
\]

**2o**

phenethyl(trifluoromethyl)selane$^{1-2}$; The yield determined by $^{19}$F NMR spectroscopy was 20%; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -34.03 (s, 3F).

**3. The observation of [CuSeCF$_3$] intermediate**

\[
\begin{align*}
\text{CuI, Ag$_2$CO$_3$} & \quad \text{Ph$_3$P*CF$_2$CO$_2^-$ + Se + CsF} \quad \text{2,2'-bpy, $^{n}$Bu$_4$Cl} \\
\text{DMA, 70$^\circ$C, 0.5 h} & \quad \text{[CuSeCF$_3$]} \quad \text{2-PhC$_6$H$_4$CH$_2$Br} \quad \text{70$^\circ$C, 1 h} \\
\text{4-PhC$_6$H$_4$CH$_2$SeCF$_3$} & \quad 2a, 48%
\end{align*}
\]

Into a 10 mL sealed tube were added Ph$_3$P*CF$_2$CO$_2^-$ (0.4 mmol, 142.4 mg), Se (1.2 mmol, 94.8 mg), CsF (0.6 mmol, 91.2 mg), CuI (0.6 mmol, 114.3 mg), 2,2'-bpy (0.4 mmol, 62.4 mg), $^{n}$Bu$_4$NCl (0.4 mmol, 111 mg), Ag$_2$CO$_3$ (0.04 mmol, 11.1 mg) and DMA (3 mL) under a N$_2$ atmosphere. The tube was sealed and the mixture was stirred at 70 $^\circ$C for 0.5 h. $^{19}$F NMR analysis showed that [CuSeCF$_3$] complex was generated (0.2 mmol of PhCF$_3$ was used as an internal standard). The $^{19}$F NMR spectrum is shown as follows. The $^{19}$F NMR yield was quite low (10% based on Ph$_3$P*CF$_2$CO$_2^-$), because the complex decomposed during the process of collecting $^{19}$F NMR spectrum due to its instability. CuSeCF$_3$; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -26.37 (s, 3F)$^1$. 

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In order to prove that CuSeCF$_3$ is the key intermediate, substrate 1a was added after the complex was generated. The procedure is shown as follows.

Into a 10 mL sealed tube were added Ph$_3$P$^+$CF$_2$CO$_2^-$ (0.4 mmol, 142.4 mg), Se (1.2 mmol, 94.8 mg), CsF (0.6 mmol, 91.2 mg), CuI (0.6 mmol, 114.3 mg), 2,2'-bpy (0.4 mmol, 62.4 mg), $n$Bu$_4$NCl (0.4 mmol, 111 mg), Ag$_2$CO$_3$ (0.04 mmol, 11.1 mg) and DMA (3 mL) under a N$_2$ atmosphere. The tube was sealed and the mixture was stirred at 70 °C for 0.5 h. Substrate 1a (0.2 mmol, 49.4 mg) was added and the resulting mixture was stirred at 70 °C for 1 h. The $^{19}$F NMR analysis revealed that the desired product was obtained in 48% yield (0.2 mmol of PhCF$_3$ was used as an internal standard). The $^{19}$F NMR spectrum is shown as follows.
$[\text{CuSeCF}_3] \overset{4-\text{PhC}_6\text{H}_4\text{CH}_2\text{Br}}{\xrightarrow{70 \, ^\circ\text{C}, \, 1 \, \text{h}}} 4-\text{PhC}_6\text{H}_4\text{CH}_2\text{SeCF}_3$
4. References

5. Copies of $^{19}$F NMR, $^1$H NMR, and $^{13}$C NMR spectra

$^1$H NMR

$^{19}$F NMR

$^{13}$C NMR
$\text{Ph-\text{SeCF}_3}$

$\text{2a, }^{13}\text{C NMR}$

$\text{Ph-\text{SeCF}_3}$

$\text{2b, }^{19}\text{F NMR}$
2b, $^1$H NMR

2b, $^{13}$C NMR
$\text{Cl-}\text{SeCF}_3$  

$\text{2c, }^{19}\text{F NMR}$

$\text{Cl-}\text{SeCF}_3$  

$\text{2c }^{1}\text{H NMR}$
$2c, ^{13}C$ NMR

$2d, ^{19}F$ NMR
$\text{Br} - \text{SeCF}_3$

$2e, ^{19}\text{F NMR}$

$\text{Br} - \text{SeCF}_3$

$2e, ^1\text{H NMR}$
$\text{Br}_2\text{SeCF}_3$

$2e$, $^{13}$C NMR

$\text{Br}_2\text{SeCF}_3$

$2f$, $^{19}$F NMR
$2f$, $^1H$ NMR

$2f$, $^{13}C$ NMR
$^{19}$F NMR

$^1$H NMR
$^{13}C$ NMR

$^{19}F$ NMR

$^{15}I$ NMR
2h, $^1$H NMR

2h, $^{13}$C NMR
$2j. ^1H$ NMR

$2k. ^{19}F$ NMR
$^{19}$F NMR

$^1$H NMR
$2m, {^{19}}F\text{ NMR}$

$2m, {^1}H\text{ NMR}$
MeO-\(\text{SeCF}_3\)

2m, \(^{13}\text{C}\) NMR