Supporting Information for

Palladium-Catalyzed Tandem Synthesis of
2-Trifluoromethylthio(seleno)-Substituted Benzofused Heterocycles

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General information

$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra were recorded using Bruker AVIII 400 spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as the external standard and low field is positive. Coupling constants ($J$) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: $^1$H NMR (chloroform $\delta$ 7.26) and $^{13}$C NMR (chloroform $\delta$ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on Waters GCT-TOF. (bpy)CuSCF$_3$ (1a)$^{1,2}$ [(bpy)CuSeCF$_3$]$_2$ (1b)$^3$ and 2-(2,2-dibromovinyl)phenols,$^4$ 2-(gem-dibromovinyl)thiophenol,$^4$ and gem-dibromovinylaniline$^5$ were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using silica gel 60.
General procedure of palladium-catalyzed synthesis 2-trifluoromethylthiobenzofused heterocycles

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added (bpy)CuSCF\(_3\) (320 mg, 1.0 mmol, 2.0 equiv), dibromovinyl phenols, thiophenols, or anilines (0.50 mmol, 1.0 equiv), Et\(_3\)N (2.0 mmol, 4.0 equiv), Pd\(_2\)(dba)\(_3\) (22.8 mg, 0.025 mmol, 5.0 mol%), P(o-Tol)\(_3\) (22.8 mg, 0.075 mmol, 15 mol%), and CH\(_3\)CN (5.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The reaction mixture was filtered through a layer of Celite, eluted with n-pentane. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with n-pentane/dichloromethane or n-pentane/diethyl ether.
General procedure of palladium-catalyzed synthesis 2-trifluoromethylseleno-benzofused heterocycles

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added \([\text{bpy}]\text{CuSeCF}_3\)\(^2\) (368 mg, 0.50 mmol, 1.0 equiv), dibromovinyl phenols, thiophenols, or anilines (0.50 mmol, 1.0 equiv), Et\(_3\)N (2.0 mmol, 4.0 equiv), \(\text{Pd}_2(\text{dba})_3\) (22.8 mg, 0.025 mmol, 5.0 mol%), \(\text{P(\text{o-Tol})_3}\) (22.8 mg, 0.075 mmol, 15 mol%), and CH\(_3\)CN (5.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The reaction mixture was filtered through a layer of Celite, eluted with \(n\)-pentane. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with \(n\)-pentane/dichloromethane or \(n\)-pentane/diethyl ether.
Scalability of the trifluoromethylthiolation reaction of 2g with 1a

\[
\begin{align*}
\begin{array}{c}
\text{MeO} & \text{OH} & \text{Br} \\
2g & 1.5 \text{ g} & 4.90 \text{ mol} \\
\end{array}
& \begin{array}{c}
\text{MeO} & \text{SCF}_3 \\
3g & 0.69 \text{ g} & 57\% \\
\end{array}
\end{align*}
\]

In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar were added [(bpy)CuSCF\(_3\)] (1a) (3.15 g, 9.8 mmol, 2.0 equiv), 2-(2,2-dibromovinyl)-5-methoxyphenol (2g) (4.90 mmol, 1.0 equiv), Et\(_3\)N (19.6 mmol, 1.98 g, 4.0 equiv), Pd\(_2\)(dba)\(_3\) (224 mg, 0.25 mmol, 5 mmol%), P(o-Tol)\(_3\) (224 mg, 0.75 mmol, 15 mmol%), and CH\(_3\)CN (25.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was diluted with n-pentane (50 × 3 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO\(_4\), and filtered. The residue obtained was purified by column chromatography on silica gel with n-pentane/diethyl ether to give 0.69 g of product 3g (57% yield).
Scalability of the trifluoromethylselenolation reaction of 2g with 1b

![Reaction Diagram]

In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar were added [(bpy)CuSeCF₃]₂ (1b) (3.60 g, 4.9 mmol, 1.0 equiv), 2-(2,2-dibromovinyl)-5-methoxyphenol (2g) (4.90 mmol, 1.0 equiv), Et₃N (19.6 mmol, 1.98 g, 4.0 equiv), Pd₂(dba)₃ (224 mg, 0.25 mmol, 5 mmol%), P(o-Tol)₃ (224 mg, 0.75 mmol, 15 mmol%), and CH₃CN (25.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was diluted with n-pentane (50 × 3 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO₄, and filtered. The residue obtained was purified by column chromatography on silica gel with n-pentane/diethyl ether to give 1.19 g of product 6g (82% yield).
Mechanistic exploratory experiment

a) Procedure of the synthesis 2-bromobenzofuran 9.4

\[
\begin{align*}
\text{2a} & \quad \text{Br} \quad \text{Br} \\
& \xrightarrow{\text{Pd}_2(\text{dba})_3 (5.0 \text{ mol\%}), \text{P}(\text{o-Tol})_3 (15 \text{ mol\%})} \quad \text{Et}_3\text{N, CH}_3\text{CN} \\
& \quad 60 \, ^\circ\text{C}, 24 \text{ h} \\
& \xrightarrow{} \quad \text{9, 37\%}
\end{align*}
\]

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added 2a (82.8 mg, 0.30 mmol, 1.0 equiv), Et₃N (1.2 mmol, 4.0 equiv), Pd₂(dba)₃ (13.5 mg, 0.075 mmol, 5.0 mmol%), P(o-Tol)₃ (13.5 mg, 0.225 mmol, 15 mmol%), and CH₃CN (5.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 60 °C for 24 h. The tube was removed from the oil bath and cooled to room temperature. The reaction mixture was filtered through a layer of Celite. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with n-pentane to give 22 mg of product 2-bromobenzofuran 9 (37% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.34 – 7.22 (m, 2H), 6.76 (s, 1H). GC-MS m/z 195 (M⁺).

b) Reaction of 2-bromobenzofuran (9) with 1a under palladium-catalyzed conditions.

\[
\begin{align*}
\text{9} & \quad \text{Br} \\
& \xrightarrow{(bpy)\text{CuSCF}_3 \text{ (65 mg, 0.20 mmol, 2.0 equiv)}, \text{Et}_3\text{N (40.4 mg, 0.40 mmol, 4.0 equiv), Pd}_2(\text{dba})_3 (4.5 mg, 0.025 mmol, 5 mmol%), P(o-Tol)_3 (4.5 mg, 0.075 mmol, 15 mmol%), and CH}_3\text{CN (1.0 mL)}} \quad \text{100 °C, 24 h} \\
& \xrightarrow{} \quad \text{3a, 87%}
\end{align*}
\]

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added (bpy)CuSCF₃ (1a) (65 mg, 0.20 mmol, 2.0 equiv), 9 (19.6 mg, 0.10 mmol, 1.0 equiv), Et₃N (40.4 mg, 0.40 mmol, 4.0 equiv), Pd₂(dba)₃ (4.5 mg, 0.025 mmol, 5 mmol%), P(o-Tol)₃ (4.5 mg, 0.075 mmol, 15 mmol%), and CH₃CN (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The reaction mixture was filtered through a layer of Celite. The mixture solution was analyzed by GC/MS and ¹⁹F NMR spectroscopy. The yield of the
2-((trifluoromethyl)thio)benzofuran 3a was calculated to be 87%.

c) Reaction of 2-bromobenzofuran (9) with 1a without palladium-catalyzed conditions.

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added (bpy)CuSCF$_3$ (1a) (65 mg, 0.20 mmol, 2.0 equiv), 9 (19.6 mg, 0.10 mmol, 1.0 equiv), Et$_3$N (40.4 mg, 0.40 mmol, 4.0 equiv), and CH$_3$CN (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The reaction mixture was filtered through a layer of Celite. The mixture solution was analyzed by GC/MS and $^{19}$F NMR spectroscopy. The yield of the 2-((trifluoromethyl)thio)benzofuran 3a was calculated to be 86%.

d) Reaction of 2-(2,2-dibromovinyl)phenol (2a) with 1a without palladium-catalyzed conditions.

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added (bpy)CuSCF$_3$ (1a) (65 mg, 0.20 mmol, 2.0 equiv), 2a (27.8 mg, 0.10 mmol, 1.0 equiv), Et$_3$N (40.4 mg, 0.40 mmol, 4.0 equiv), and CH$_3$CN (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The reaction mixture was filtered through a layer of Celite. The mixture solution was analyzed by GC/MS and $^{19}$F NMR spectroscopy. The yield of the 2-((trifluoromethyl)thio)benzofuran 3a was calculated to be 9%.

e) Reaction of 2-(2,2-dibromovinyl)phenol (2a) with 1a without palladium-catalyzed conditions, using Cs$_2$CO$_3$ as a base in DMF.
In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added (bpy)CuSCF$_3$ (1a) (65 mg, 0.20 mmol, 2.0 equiv), 2a (27.8 mg, 0.10 mmol, 1.0 equiv), Cs$_2$CO$_3$ (130.4 mg, 0.40 mmol, 4.0 equiv), and DMF (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 100 °C for 24 h. The reaction mixture was filtered through a layer of Celite. The mixture solution was analyzed by GC/MS and $^{19}$F NMR spectroscopy. No 3a was detected by $^{19}$F NMR spectroscopy.
Proposed reaction mechanism
Data for compounds 3–8

2-((Trifluoromethyl)thio)benzofuran (3a)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 3a as a pale yellow oil in 68% yield (66 mg). Rf (n-pentane) = 0.89. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (dd, $J = 8.2$, 0.8 Hz, 1H), 7.54 (dd, $J = 8.4$, 0.7 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.33 – 7.24 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -42.4 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.5 (s), 138.6 (q, $J = 3.0$ Hz), 128.0 (q, $J = 311.8$ Hz), 127.6 (s), 126.8 (s), 123.6 (s), 121.7 (s), 119.9 (q, $J = 1.2$ Hz), 111.8 (s). IR (ATR): $\nu$ 2927, 1534, 1443, 1342, 1255, 1148, 1105, 1059, 927, 882, 823, 750, 637, 438 cm$^{-1}$. GC-MS m/z 218 (M$^+$). HR-MS (EI) m/z: calcd. for C$_9$H$_5$OF$_3$S: 218.0013; found: 218.0017.

5-Methyl-2-((trifluoromethyl)thio)benzofuran (3b)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 3b as a pale yellow oil in 52% yield (60 mg). Rf (n-pentane) = 0.74. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48 – 7.40 (m, 2H), 7.25 (dd, $J = 8.5$, 1.3 Hz, 1H), 7.23 (d, $J = 0.8$ Hz, 1H), 2.48 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -42.5 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 156.0 (s), 138.4 (q, $J = 2.9$ Hz), 133.1 (s), 128.2 (s), 128.0 (q, $J = 311.8$ Hz), 127.7 (s), 121.3 (s), 119.6 (q, $J = 1.1$ Hz), 111.3 (s), 21.3 (s). IR (ATR): $\nu$ 2925, 1537, 1452, 1327, 1193, 1134, 1100, 1060, 922, 873, 799, 756, 640, 585, 462, 429 cm$^{-1}$. GC-MS m/z 232 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{10}$H$_7$OF$_3$S: 232.0170; found: 232.0178.
Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 3c as a pale yellow solid in 57% yield (66 mg). mp: 37-38 °C. Rf (n-pentane) = 0.77. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.50 – 7.45 (m, 1H), 7.29 (s, 1H), 7.27 – 7.21 (m, 2H), 2.58 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -42.5 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 156.7 (s), 138.1 (q, $J$ = 2.9 Hz), 128.0 (q, $J$ = 311.8 Hz), 127.5 (s), 127.2 (s), 123.6 (s), 122.2 (s), 120.2 (q, $J$ = 1.2 Hz), 119.0 (s), 15.0 (s). IR (ATR): ν 2927, 1539, 1483, 1450, 1304, 1227, 1178, 1143, 1106, 1057, 921, 852, 744, 637, 528, 461 cm$^{-1}$. GC-MS m/z 232 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{10}$H$_7$OF$_3$S: 232.0170; found: 232.0166.

$^{7}$-Methyl-2-((trifluoromethyl)thio)benzofuran (3c)

$^{7}$-(tert-Butyl)-2-((trifluoromethyl)thio)benzofuran (3d)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 3d as a pale yellow oil in 60% yield (82 mg). Rf (n-pentane) = 0.80. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52 (dd, $J$ = 7.7, 1.3 Hz, 1H), 7.36 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.31 – 7.23 (m, 2H), 1.57 (s, 9H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -42.6 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 156.0 (s), 137.5 (q, $J$ = 2.9 Hz), 135.5 (s), 128.2 (s), 128.1 (q, $J$ = 311.8 Hz), 123.5 (s), 123.2 (s), 119.6 (q, $J$ = 1.2 Hz), 119.5 (s), 34.4 (s), 29.7 (s). IR (ATR): ν 2961, 2872, 1541, 1483, 1406, 1365, 1143, 1102, 1071, 1057, 924, 829, 746, 640, 540, 468, 443 cm$^{-1}$. GC-MS m/z 274 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{13}$H$_{13}$OF$_3$S: 274.0639; found: 274.0627.
5-Phenyl-2-((trifluoromethyl)thio)benzofuran (3e)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 3e as a pale yellow solid in 65% yield (95 mg). mp: 49-51°C. Rᵋ (n-pentane) = 0.45. ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 1.2 Hz, 1H), 7.71–7.60 (m, 4H), 7.55–7.47 (m, 2H), 7.45–7.38 (m, 1H), 7.36 (d, J = 0.7 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -42.3 (s, 3F). ¹³C NMR (101 MHz, CDCl₃): δ 157.1 (s), 141.0 (s), 139.2 (q, J = 2.9 Hz), 137.4 (s), 128.9 (s), 128.8 (s), 128.0 (q, J = 311.9 Hz), 127.5 (s), 127.3 (s), 123.9 (s), 120.1 (q, J = 1.2 Hz), 120.0 (s), 118.6 (s), 112.0 (s), 111.0 (s), 108.5 (s). IR (ATR): ν 2958, 1599, 1539, 1450, 1313, 1143, 1101, 1058, 929, 882, 813, 758, 695, 519, 438 cm⁻¹. GC-MS m/z 293 (M⁺). HR-MS (EI) m/z: calcd. for C₁₅H₉OF₃S: 294.0326; found: 294.0324.

5-Methoxy-2-((trifluoromethyl)thio)benzofuran (3f)

Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 3f as a colorless solid in 44% yield (54 mg). mp: 36-39°C. Rᵋ (diethyl ether/n-pentane 1:10) = 0.90. ¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.10–7.01 (m, 2H), 3.87 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ -42.5 (s, 3F). ¹³C NMR (101 MHz, CDCl₃): δ 156.3 (s), 152.7 (s), 128.1 (s), 128.0 (q, J = 311.8 Hz), 119.9 (q, J = 1.2 Hz), 116.3 (s), 112.5 (s), 111.4 (s), 103.1 (s), 55.9 (s). IR (KBr): 2939, 1618, 1533, 1464, 1295, 1207, 1148, 1107, 1065, 903, 845, 732, 643 cm⁻¹. GC-MS: m/z 248 (M⁺). HR-MS (EI) m/z: calcd. for C₁₀H₇O₂F₃S: 248.0119; found: 248.0115.

6-Methoxy-2-((trifluoromethyl)thio)benzofuran (3g)

Following the general procedure and workup, and purification by column
chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 3g as a pale yellow solid in 64% yield (79 mg). mp: 36-39 °C. R_f (diethyl ether/n-pentane 1:10) = 0.87. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.50 (d, \(J = 8.8\) Hz, 1H), 7.23 (d, \(J = 0.80\) Hz, 1H), 7.06 (d, \(J = 2.0\) Hz, 1H), 6.95 (dd, \(J = 8.6, 2.0\) Hz, 1H), 3.89 (s, 3H). \(^19\)F NMR (376 MHz, CDCl₃): \(\delta\) -43.0 (s, 3F). \(^13\)C NMR (101 MHz, CDCl₃): \(\delta\) 159.8 (s), 158.8 (s), 136.8 (q, \(J = 2.8\) Hz), 128.0 (t, \(J = 313.3\) Hz), 121.9 (s), 120.9 (s), 120.2 (q, \(J = 1.2\) Hz), 113.5 (s), 95.5 (s), 55.7 (s). IR (ATR): α 2923, 1622, 1493, 1438, 1299, 1277, 1144, 1101, 1054, 1027, 954, 834, 755, 537, 466, 439 cm⁻¹. GC-MS m/z 248 (M⁺). HR-MS (EI) m/z: calcd. for C₁₀H₇O₂F₃S: 248.0119; found: 248.0126.

[Image of 7-Methoxy-2-((trifluoromethyl)thio)benzofuran (3h)]

Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 3h as a pale yellow solid in 56% yield (69 mg). mp: 54-56 °C. R_f (diethyl ether/n-pentane 1:10) = 0.88. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.30 (s, 1H), 7.26 – 7.22 (m, 2H), 6.98 – 6.87 (m, 1H), 4.05 (s, 3H). \(^19\)F NMR (376 MHz, CDCl₃): \(\delta\) -42.4 (s, 3F). \(^13\)C NMR (101 MHz, CDCl₃): \(\delta\) 147.2 (s), 145.5 (s), 138.8 (q, \(J = 3.0\) Hz), 129.2 (s), 128.0 (q, \(J = 311.8\) Hz), 124.2 (s), 120.3 (q, \(J = 1.1\) Hz), 113.6 (s), 108.4 (s), 56.2 (s). IR (ATR): α 2918, 2848, 1619, 1592, 1485, 1426, 1315, 1275, 1148, 1114, 1094, 1052, 967, 829, 774, 730, 638, 463 cm⁻¹. GC-MS m/z 248 (M⁺). HR-MS (EI) m/z: calcd. for C₁₀H₇O₂F₃S: 248.0119; found: 248.0120.

[Image of Methyl 2-((trifluoromethyl)thio)benzofuran-5-carboxylate (3i)]
Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 3i as a yellow solid in 32% yield (44 mg). mp: 60-63 °C. \( R_f \) (diethyl ether/n-pentane 1:10) = 0.75. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.39 (d, \( J = 1.2 \) Hz, 1H), 8.16 (dd, \( J = 8.8, 1.6 \) Hz, 1H), 7.60 (d, \( J = 8.8 \) Hz, 1H), 7.37 (s, 1H), 3.98 (s, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -42.0 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 166.7 (s), 159.7 (s), 140.5 (q, \( J = 2.8 \)), 128.2 (s), 127.8 (q, \( J = 311.9 \) Hz), 127.5 (s), 126.0 (s), 124.2 (s), 120.2 (q, \( J = 1.1 \) Hz), 111.8 (s), 52.3 (s). IR (ATR): 2955, 1717, 1616, 1459, 1309, 1266, 1243, 1157, 1119, 1057, 985, 908, 767, 639, 521, 467, 428 cm\(^{-1}\). GC-MS: \( m/z \) 276 (M\(^+\)). HR-MS (EI) \( m/z \): calcd. for C\(_{11}\)H\(_7\)O\(_3\)F\(_3\)S: 276.0068; found: 276.0063.

\[
\begin{array}{c}
\text{F} \\
\text{SCF}_3
\end{array}
\]

**6-Fluoro-2-((trifluoromethyl)thio)benzofuran (3j)**

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 3j as a pale yellow oil in 57% yield (67 mg). \( R_f \) (n-pentane) = 0.63. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.51 (dd, \( J = 8.9, 2.8 \) Hz, 1H), 7.36 – 7.23 (m, 2H), 7.18 (tt, \( J = 8.8, 2.4 \) Hz, 1H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -42.2 (s, 3F), -119.2 (t, \( J = 8.3 \) Hz, 1F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 159.3 (d, \( J = 240.6 \) Hz), 153.8 (s), 140.5 (q, \( J = 2.9 \) Hz), 128.2 (d, \( J = 10.9 \) Hz), 127.9 (q, \( J = 311.5 \) Hz), 119.7 (m), 114.9 (d, \( J = 26.6 \) Hz), 112.7 (d, \( J = 9.4 \) Hz), 107.0 (d, \( J = 25.1 \) Hz). IR (ATR): \( \tilde{\nu} \) 3015, 1678, 1501, 1470, 1415, 1267, 1190, 1156, 987, 930, 767, 678, 539, 427 cm\(^{-1}\). GC-MS \( m/z \) 236 (M\(^+\)). HR-MS (EI) \( m/z \): calcd. for C\(_9\)H\(_4\)OF\(_4\)S: 235.9919; found: 235.9924.

\[
\begin{array}{c}
\text{Cl} \\
\text{SCF}_3
\end{array}
\]

**5-Chloro-2-((trifluoromethyl)thio)benzofuran (3k)**

Following the general procedure and workup, and purification by column
chromatography (silica gel, \textit{n}-pentane) gave final product 3k as a pale yellow oil in 53\% yield (61 mg). \textit{R}_{f} (\textit{n}-pentane) = 0.65. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.62 (d, \( J = 2.1 \) Hz, 1H), 7.49 (d, \( J = 8.9 \) Hz, 1H), 7.40 (dd, \( J = 8.8, 2.1 \) Hz, 1H), 7.25 (d, \( J = 0.8 \) Hz, 1H). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \( \delta \) -42.1 (s, 3F). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \( \delta \) 155.8 (s), 140.4 (q, \( J = 2.9 \) Hz), 129.3 (s), 128.8 (s), 127.9 (q, \( J = 311.9 \) Hz), 127.1 (s), 121.2 (s), 119.1 (q, \( J = 1.2 \) Hz), 112.9 (s). IR (ATR): v 2925, 1532, 1437, 1257, 1144, 1099, 1059, 929, 907, 807, 803, 757, 694, 641, 585, 493, 426 cm\textsuperscript{-1}. GC-MS m/z 251 (M\textsuperscript{+}). HR-MS (EI) m/z: calcd. for C\textsubscript{9}H\textsubscript{4}OF\textsubscript{3}SCl: 251.9623; found: 251.9630.

5-(Phenylethynyl)-2-((trifluoromethyl)thio)benzofuran (3l)

Following the general procedure and workup, and purification by column chromatography (silica gel, \textit{n}-pentane) gave final product 3l as a pale yellow solid in 51\% yield (81 mg). mp: 77-78 °C. \textit{R}_{f} (\textit{n}-pentane) = 0.37. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.84 (d, \( J = 0.9 \) Hz, 1H), 7.66 – 7.52 (m, 5H), 7.40 – 7.36 (m, 2H), 7.30 (s, 1H). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \( \delta \) -42.1 (s, 3F). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \( \delta \) 156.9 (s), 139.8 (q, \( J = 2.8 \) Hz), 131.6 (s), 130.4 (s), 128.4 (s), 128.3 (s), 127.9 (q, \( J = 311.9 \) Hz), 127.8 (s), 125.0 (s), 123.1 (s), 119.6 (s), 118.9 (s), 112.0 (s), 111.1 (s), 108.2 (s), 88.9 (s), 88.8 (s). IR (ATR): v 3061, 1597, 1536, 1491, 1454, 1442, 1251, 1168, 1146, 1110, 1061, 922, 884, 811, 754, 689, 643, 612, 534, 489 cm\textsuperscript{-1}. GC-MS m/z 318 (M\textsuperscript{+}). HR-MS (EI) m/z: calcd. for C\textsubscript{17}H\textsubscript{9}OF\textsubscript{3}S: 318.0326; found: 318.0330.

2-((Trifluoromethyl)thio)naphtho[1,2-b]furan (3m)

Following the general procedure and workup, and purification by column chromatography (silica gel, \textit{n}-pentane) gave final product 3m as a pale yellow solid in
54% yield (72 mg). mp: 78-80 °C. $R_f$ (n-pentane) = 0.35. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J$ = 8.7 Hz, 1H), 7.98 (d, $J$ = 8.2 Hz, 1H), 7.86 (d, $J$ = 9.0 Hz, 1H), 7.78 (d, $J$ = 0.8 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.61 – 7.52 (m, 1H). $^19$F NMR (376 MHz, CDCl$_3$): $\delta$ -42.8 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 155.9 (s), 137.1 (q, $J$ = 2.9 Hz), 130.3 (s), 128.9 (s), 128.1 (s), 128.0 (q, $J$ = 301.7 Hz), 127.3 (s), 127.2 (s), 125.3 (s), 123.4 (s), 123.3 (s), 119.0 (q, $J$ = 1.2 Hz), 112.4 (s). IR (ATR): $\nu$ 3102, 1629, 1586, 1443, 1388, 1158, 1142, 1115, 1084, 987, 903, 804, 723, 628, 517, 484, 462 cm$^{-1}$. GC-MS m/z 268 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{13}$H$_7$OF$_3$S: 268.0170; found: 268.0165.
2-((Trifluoromethyl)thio)benzo[b]thiophene (4a)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 4a as a pale yellow oil in 42% yield (49 mg). $R_f$ (n-pentane) = 0.89. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 – 7.81 (m, 2H), 7.71 (s, 1H), 7.51 – 7.39 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -43.8 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 144.0 (s), 138.9 (s), 136.4 ($q$, $J = 0.9$ Hz), 128.5 ($q$, $J = 310.7$ Hz), 126.2 (s), 125.0 (s), 124.5 (s), 122.7 ($q$, $J = 2.4$ Hz), 122.1 (s). IR (ATR): v 3075, 1469, 1457, 1420, 1325, 1246, 1136, 1101, 973, 861, 836, 744, 724, 598, 567, 504, 429 cm$^{-1}$. GC-MS m/z 233 ($M^+$). HR-MS (EI) m/z: calcd. for C$_9$H$_5$F$_3$S$_2$: 233.9785; found: 233.9786.

4-Chloro-2-((trifluoromethyl)thio)benzo[b]thiophene (4b)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 4b as a pale yellow solid in 86% yield (115 mg). mp: 36-38 °C. $R_f$ (n-pentane) = 0.75. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (s, 1H), 7.74 ($d$, $J = 7.9$ Hz, 1H), 7.46 – 7.34 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -43.5 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 144.9 (s), 137.4 (s), 134.5 ($q$, $J = 1.0$ Hz), 129.5 (s), 128.4 ($q$, $J = 310.9$ Hz), 126.9 (s), 125.0 (s), 124.1 ($q$, $J = 2.6$ Hz), 120.6 (s). IR (ATR): v 3086, 1590, 1547, 1440, 1405, 1324, 1199, 1137, 1097, 982, 847, 805, 767, 722, 625, 572, 500, 454 cm$^{-1}$. GC-MS m/z 267 ($M^+$). HR-MS (EI) m/z: calcd. for C$_9$H$_4$F$_3$S$_2$Cl: 267.9395; found: 267.9389.
Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 5a as a pale yellow oil in 46% yield (59 mg). $R_f$ (diethyl ether/n-pentane 1:10) = 0.77. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (t, $J = 9.0$ Hz, 2H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.08 (s, 1H), 5.96 – 4.43 (m, 1H), 1.69 (d, $J = 7.0$ Hz, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -44.0 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.8 (s), 128.3 (q, $J = 311.0$ Hz), 127.7 (s), 123.6 (s), 121.9 (s), 120.0 (s), 117.8 (q, $J = 2.4$ Hz), 115.8 (q, $J = 8.5$ Hz), 112.4 (s), 47.9 (s), 21.2 (s). IR (ATR): v 2982, 1613, 1506, 1441, 1403, 1371, 1314, 1230, 1129, 1099, 1035, 903, 796, 751, 734, 633, 618, 546, 477, 430 cm$^{-1}$. GC-MS m/z 258 (M$^+$). HR-MS (El) m/z: calcd. for C$_{12}$H$_{12}$NF$_3$S: 259.0643; found: 259.0632.
Following the general procedure and workup, and purification by column chromatography (silica gel, \(n\)-pentane) gave final product 6a as a pale yellow oil in 90% yield (119 mg). \(R_t\) (\(n\)-pentane) = 0.89. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.66 (d, \(J = 7.8\) Hz, 1H), 7.59 (d, \(J = 8.3\) Hz, 1H), 7.42 (t, \(J = 7.8\) Hz, 1H), 7.37 – 7.21 (m, 2H). \(^1\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -35.4 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 158.0 (s), 136.3 (q, \(J = 1.8\) Hz), 127.9 (s), 126.3 (s), 123.4 (s), 121.7 (q, \(J = 335.8\) Hz), 121.4 (s), 120.6 (q, \(J = 1.2\) Hz), 111.7 (s). IR (ATR): \(\nu\) 2927, 1527, 1440, 1341, 1251, 1143, 1096, 1047, 918, 880, 819, 748, 739, 615, 428 cm\(^{-1}\). GC-MS m/z 265 (M\(^+\)). HR-MS (EI) m/z: calcd. for C\(_9\)H\(_5\)F\(_3\)O\(_74\)Se: 259.9517; found: 259.9521.

**5-Methyl-2-((trifluoromethyl)selanyl)benzofuran (6b)**

Following the general procedure and workup, and purification by column chromatography (silica gel, \(n\)-pentane) gave final product 6b as a pale yellow solid in 51% yield (71 mg). mp: 46-47 °C. \(R_t\) (\(n\)-pentane) = 0.73. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.47 (d, \(J = 8.5\) Hz, 1H), 7.43 (s, 1H), 7.27 – 7.19 (m, 2H), 2.49 (s, 3H). \(^1\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -35.5 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 156.6 (s), 136.2 (q, \(J = 2.0\) Hz), 133.0 (s), 128.0 (s), 127.7 (s), 121.7 (q, \(J = 335.8\) Hz), 121.0 (s), 120.4 (q, \(J = 1.1\) Hz), 111.2 (s), 21.3 (s). IR (ATR): \(\nu\) 2910, 1470, 1428, 1267, 1190, 1094, 970, 818, 750, 737, 648, 570, 431 cm\(^{-1}\). GC-MS m/z 280 (M\(^+\)). HR-MS (EI) m/z: calcd. for C\(_{10}\)H\(_7\)F\(_3\)O\(_74\)Se: 273.9674; found: 273.9682.
7-Methyl-2-((trifluoromethyl)selanyl)benzofuran (6c)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 6c as a pale yellow solid in 52% yield (73 mg). mp: 43-45 °C. $R_f$ (n-pentane) = 0.80. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52 – 7.43 (m, 1H), 7.28 (d, $J = 1.7$ Hz, 1H), 7.25 – 7.19 (m, 2H), 2.59 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -35.5 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 157.3 (s), 135.9 (q, $J = 2.0$ Hz), 127.4 (s), 127.0 (s), 123.5 (s), 122.0 (s), 121.7 (q, $J = 33.5$ Hz), 120.8 (q, $J = 1.2$ Hz), 118.8 (s), 15.0 (s). IR (ATR): ν 3063, 2925, 1533, 1480, 1301, 1222, 1174, 1141, 1098, 1050, 825, 739, 650, 621, 516, 448 cm$^{-1}$. GC-MS m/z 280 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{10}$H$_7$OF$_3$Se: 273.9674; found: 273.9664.

![SeCF$_3$](image)

6-Methyl-2-((trifluoromethyl)selanyl)benzofuran (6c')

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 6c' as a pale yellow solid in 57% yield (80 mg). mp: 46-47 °C. $R_f$ (n-pentane) = 0.80. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52 (d, $J = 8.0$ Hz, 1H), 7.39 (s, 1H), 7.25 (s, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 2.53 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -35.6 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 158.5 (s), 136.9 (s), 135.4 (q, $J = 2.0$ Hz), 125.4 (s), 125.0 (s), 121.7 (q, $J = 33.7$ Hz), 120.9 (s), 120.6 (d, $J = 1.1$ Hz), 111.8 (s), 21.8 (s). IR (ATR): ν 2910, 1470, 1428, 1267, 1190, 1094, 970, 818, 750, 737, 648, 570, 431 cm$^{-1}$. GC-MS m/z 280 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{10}$H$_7$OF$_3$Se: 273.9674; found: 273.9664.

![SeCF$_3$ and tert-Butyl](image)

7-(tert-Butyl)-2-((trifluoromethyl)selanyl)benzofuran (6d)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 6d as a pale yellow oil in 84%
yield (136 mg). \( R_f \) (n-pentane) = 0.75. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.51 (d, \( J = 7.6 \) Hz, 1H), 7.32 (d, \( J = 7.4 \) Hz, 1H), 7.30 – 7.21 (m, 2H), 1.56 (s, 9H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -35.5 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 156.6 (s), 135.3 (s), 135.2 (q, \( J = 1.9 \) Hz), 128.4 (s), 123.4 (s), 122.8 (s), 121.7 (q, \( J = 335.8 \) Hz), 120.4 (q, \( J = 1.0 \) Hz), 119.3 (s), 34.4 (s), 29.7 (s). IR (ATR): \( \nu \) 2957, 2871, 1534, 1482, 1406, 1364, 1275, 1143, 1095, 853, 737, 650 cm\(^{-1}\). GC-MS m/z 321 (M\(^+\)). HR-MS (El) m/z: calcd. for C\(_{13}\)H\(_{13}\)OF\(_3\)Se: 316.0143; found: 316.0149.

5-Methoxy-2-(((trifluoromethyl)selanyl)benzofuran (6f)

Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 6f as a pale yellow solid in 93% yield (137 mg). mp: 45-47 °C. \( R_f \) (diethyl ether/n-pentane 1:10) = 0.87. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.47 (d, \( J = 8.9 \) Hz, 1H), 7.22 (s, 1H), 7.12 – 6.97 (m, 2H), 3.88 (s, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -35.4 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 156.3 (s), 153.2 (s), 136.7 (q, \( J = 1.9 \) Hz), 128.3 (s), 121.7 (q, \( J = 335.9 \) Hz), 120.6 (s), 115.8 (s), 112.3 (s), 103.0 (s), 55.9 (s). IR (ATR): \( \nu \) 3104, 1618, 1470, 1339, 1276, 1208, 1150, 1097, 970, 848, 649, 431 cm\(^{-1}\). GC-MS m/z 296 (M\(^+\)). HR-MS (El) m/z: calcd. for C\(_{10}\)H\(_7\)O\(_2\)F\(_3\)Se: 289.9623; found: 289.9621.

6-Methoxy-2-(((trifluoromethyl)selanyl)benzofuran (6g)

Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 6g as a pale yellow solid in 90% yield (133 mg). mp: 40-44 °C. \( R_f \) (diethyl ether/n-pentane 1:10) = 0.83. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.50 (d, \( J = 8.6 \) Hz, 1H), 7.22 (s, 1H),
7.09 (s, 1H), 6.95 (d, $J = 8.6$ Hz, 1H), 3.89 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -36.0 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.5 (s), 159.3 (s), 134.5 (q, $J = 1.8$ Hz), 121.7 (q, $J = 336.2$ Hz), 121.6 (s), 121.2 (s), 120.9 (q, $J = 1.2$ Hz), 113.3 (s), 95.5 (s), 55.7 (s). IR (ATR): v 2927, 1615, 1527, 1461, 1433, 1295, 1233, 1204, 1142, 1093, 1052, 904, 737, 649, 431 cm$^{-1}$. GC-MS m/z 296 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{10}$H$_7$O$_2$F$_3$Se: 289.9623; found: 289.9618.

7-Methoxy-2-((trifluoromethyl)selanyl)benzofuran (6h)

Following the general procedure and workup, and purification by column chromatography (silica gel, diethyl ether/n-pentane 1:10) gave final product 6h as a pale yellow solid in 92% yield (134 mg). mp: 62-65 °C. $R_f$ (diethyl ether/n-pentane 1:10) = 0.69. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.28 (s, 1H), 7.26 – 7.20 (m, 2H), 6.90 (t, $J = 4.0$ Hz, 1H), 4.05 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -35.4 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 147.8 (s), 145.4 (s), 136.4 (q, $J = 2.1$ Hz), 129.5 (s), 124.2 (s), 121.7 (q, $J = 335.8$ Hz), 121.0 (q, $J = 1.1$ Hz), 113.5 (s), 108.1 (s), 56.1 (s). IR (ATR): v 2939, 2841, 1620, 1591, 1481, 1424, 1312, 1272, 1142, 1092, 1045, 908, 825, 729, 649, 628, 534 cm$^{-1}$. GC-MS m/z 296 (M$^+$). HR-MS (EI) m/z: calcd. for C$_{10}$H$_7$O$_2$F$_3$Se: 289.9623; found: 289.9626.

6-Fluoro-2-((trifluoromethyl)selanyl)benzofuran (6j)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 6j as a pale yellow oil in 85% yield (120 mg). $R_f$ (n-pentane) = 0.65. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 – 7.47 (m, 1H), 7.30 (d, $J = 8.2$ Hz, 1H), 7.26 (s, 1H), 7.15 (t, $J = 9.1$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -35.1 (s, 3F), -119.4 (td, $J = 8.1$, 4.0 Hz, 1F). $^{13}$C NMR (101 MHz,
CDCl₃: δ 159.3 (d, J = 243.0 Hz), 154.3 (s), 138.2 (q, J = 2.0 Hz), 128.5 (d, J = 10.7 Hz), 121.7 (q, J = 335.7 Hz), 120.4 (m), 114.4 (d, J = 26.6 Hz), 112.5 (d, J = 9.5 Hz), 106.7 (d, J = 25.0 Hz). IR (ATR): ν 2926, 1624, 1598, 1530, 1456, 1443, 1336, 1286, 1182, 1133, 1090, 1048, 914, 860, 802, 759, 595, 433 cm⁻¹. GC-MS m/z 283 (M⁺). HR-MS (EI) m/z: calcd. for C₉H₄OF₄Se: 277.9423; found: 277.9430.

5-Chloro-2-((trifluoromethyl)selanyl)benzofuran (6k)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 6k as a pale yellow oil in 90% yield (135 mg). Rᵣ (n-pentane) = 0.68. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (s, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.23 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -35.0 (s, 3F). ¹³C NMR (101 MHz, CDCl₃): δ 156.3 (s), 138.0 (q, J = 2.2 Hz), 129.1 (s), 129.0 (s), 126.6 (q, J = 2.7 Hz), 121.6 (q, J = 335.8 Hz), 120.9 (s), 119.9 (q, J = 1.2 Hz), 112.7 (s). IR (ATR): ν 3105, 1524, 1434, 1321, 1254, 1143, 1091, 1050, 922, 870, 802, 739, 697, 583, 465 cm⁻¹. GC-MS m/z 299 (M⁺). GC-MS m/z 299 (M⁺). HR-MS (EI) m/z: calcd. for C₉H₄OF₃Cl₇⁴Se: 293.9128; found: 293.9122.

2-((Trifluoromethyl)selanyl)naphtho[2,1-b]furan (6l)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 6l as a pale yellow solid in 89% yield (140 mg). mp: 90-92 °C. Rᵣ (n-pentane) = 0.38. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.76 (s, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -35.7 (s, 3F). ¹³C NMR (101 MHz, CDCl₃): δ 156.4
(s), 134.8 (q, J = 2.0 Hz), 130.3 (s), 128.9 (s), 127.6 (s), 127.3 (s), 127.1 (s), 125.2 (s),
123.5 (s), 123.4 (s), 121.8 (q, J = 336.2 Hz), 119.8 (q, J = 1.2 Hz), 112.3 (s). IR
(ATR): ν 3113, 2925, 1746, 1627, 1531, 1441, 1385, 1248, 1162, 1132, 1101, 1066,
985, 804, 736, 649, 513, 472 cm⁻¹. GC-MS m/z 315 (M⁺). HR-MS (EI) m/z: calcd. for
C₁₃H₇OF₃⁷⁴Se: 309.9674; found: 309.9675.
2-((Trifluoromethyl)selanyl)benzo[b]thiophene (7a)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 7a as a pale yellow oil in 75% yield (106 mg). \(R_f\) (n-pentane) = 0.85. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.93 – 7.83 (m, 2H), 7.73 (s, 1H), 7.54 – 7.36 (m, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -36.8 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 144.8 (s), 139.5 (s), 136.8 (q, \(J = 0.8\) Hz), 125.9 (s), 124.9 (s), 124.2 (s), 121.9 (s), 121.8 (q, \(J = 335.1\) Hz), 117.9 (q, \(J = 1.7\) Hz). IR (ATR): \(\nu\) 3060, 2235, 1456, 1421, 1140, 1096, 903, 762, 724, 649, 556, 471, 417 cm\(^{-1}\). GC-MS \(m/z\) 282 (M\(^+\)). HR-MS (EI) \(m/z\): calcd. for \(C_9H_5F_3S^{74}\)Se: 275.9289; found: 275.9291.
5-Fluoro-1-isopropyl-2-((trifluoromethyl)selanyl)-1H-indole (8a)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 8a as a colorless oil liquid in 25% yield (40 mg). $R_f$ (n-pentane) = 0.93. $^1$H NMR (400 MHz, CDCl₃) δ 7.62 – 7.55 (m, 1H), 7.31 (d, $J = 9.2$ Hz, 1H), 7.06 (t, $J = 9.1$ Hz, 1H), 6.99 (s, 1H), 5.32 – 5.17 (m, 1H), 1.67 (s, 3H), 1.66 (s, 3H). $^{19}$F NMR (376 MHz, CDCl₃) δ -36.8 (s, 3F), -124.06 (td, $J = 8.5$, 3.9 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl₃) δ 157.6 (d, $J = 236.9$ Hz), 133.2 (s), 128.6 (d, $J = 10.1$ Hz), 121.7 (q, $J = 335.9$ Hz), 118.6 (q, $J = 0.7$ Hz), 115.9 (d, $J = 4.8$ Hz), 113.0 (d, $J = 9.3$ Hz), 112.2 (d, $J = 26.4$ Hz), 106.0 (d, $J = 22.9$ Hz), 49.7 (s), 21.2 (s). IR (ATR): ν 3048, 2984, 2937, 2252, 1621, 1508, 1439, 1268, 1143, 1094, 904, 728 cm⁻¹. GC-MS m/z 324 (M⁺). HR-MS (EI) m/z: calcd. for C₁₂H₁₁F₄N₇⁴Se: 319.0053; found: 319.0051.

5-Chloro-1-isopropyl-2-((trifluoromethyl)selanyl)-1H-indole (8b)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 8b as a colorless oil liquid in 16% yield (27 mg). $R_f$ (n-pentane) = 0.92. $^1$H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.58 (d, $J = 8.9$ Hz, 1H), 7.24 (d, $J = 8.9$ Hz, 1H), 6.98 (s, 1H), 5.30 – 5.17 (m, 1H), 1.67 (s, 3H), 1.65 (s, 3H). $^{19}$F NMR (376 MHz, CDCl₃) δ -36.8 (s, 3F). $^{13}$C NMR (101 MHz, CDCl₃) δ 134.8 (s), 129.3 (s), 125.8 (s), 123.7 (s), 121.6 (q, $J = 335.9$ Hz), 120.9 (s), 118.6 (q, $J = 2.0$ Hz), 115.6 (s), 113.2 (s), 49.7 (s), 21.2 (s). IR (ATR): ν 3047, 2984, 2935, 2253, 1495, 1434, 1335, 1221, 1095, 903, 724 cm⁻¹. GC-MS m/z 340 (M⁺). HR-MS (EI) m/z: calcd. for C₁₂H₁₁ClF₃N⁷⁴Se: 334.9757; found: 334.9752.
6-Chloro-1-isopropyl-2-((trifluoromethyl)selanyl)-1H-indole (8c)

Following the general procedure and workup, and purification by column chromatography (silica gel, n-pentane) gave final product 8c as a colorless oil liquid in 19% yield (32 mg). \( R_f \) (n-pentane) = 0.93. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.65 (s, 1H), 7.58 (d, \( J = 8.3 \) Hz, 1H), 7.14 (d, \( J = 8.4 \) Hz, 1H), 7.02 (s, 1H), 5.23 (dt, \( J = 13.6, 6.8 \) Hz, 1H), 1.67 (s, 3H), 1.65 (s, 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -36.9 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 136.7 (s), 129.4 (s), 126.9 (s), 122.5 (s), 121.6 (q, \( J = 336.2 \) Hz), 120.8 (s), 118.0 (q, \( J = 1.4 \) Hz), 116.4 (s), 112.0 (s), 49.6 (s), 21.1 (s). IR (ATR): v 3047, 2984, 2935, 1608, 1467, 1391, 1346, 1311, 1140, 1091, 922, 815, 738 cm\(^{-1}\). GC-MS m/z 340 (M\(^+\)). HR-MS (EI) m/z: calcd. for C\(_{12}\)H\(_{11}\)ClF\(_3\)N\(^7\)Se: 334.9757; found: 334.9753.
Crystal structure analyses.

The suitable crystals of 3i (CCDC 1914199) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.
ORTEP diagrams

ORTEP diagram of compound 3i. Thermal ellipsoids are drawn at 40% probability.
References:


(6) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.
Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

$^1$H NMR spectrum of 3a in CDCl$_3$

$^{19}$F NMR spectrum of 3a in CDCl$_3$
$^{13}$C NMR spectrum of 3a in CDCl$_3$

$^1$H NMR spectrum of 3b in CDCl$_3$
$^{19}$F NMR spectrum of 3b in CDCl$_3$

$^{13}$C NMR spectrum of 3b in CDCl$_3$
$^1\text{H NMR}$ spectrum of 3c in CDCl$_3$

$^{19}\text{F NMR}$ spectrum of 3c in CDCl$_3$
$^{13}$C NMR spectrum of 3c in CDCl$_3$

$^1$H NMR spectrum of 3d in CDCl$_3$
$^{19}$F NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
$^1$H NMR spectrum of 3e in CDCl$_3$

$^{19}$F NMR spectrum of 3e in CDCl$_3$
$^{13}$C NMR spectrum of $3e$ in CDCl$_3$

$^1$H NMR spectrum of $3f$ in CDCl$_3$
$^{19}$F NMR spectrum of 3f in CDCl$_3$

$^{13}$C NMR spectrum of 3f in CDCl$_3$
$^1$H NMR spectrum of 3g in CDCl$_3$

$^{19}$F NMR spectrum of 3g in CDCl$_3$
$^{13}$C NMR spectrum of 3g in CDCl$_3$

$^1$H NMR spectrum of 3h in CDCl$_3$
$^{19}$F NMR spectrum of 3h in CDCl$_3$

$^{13}$C NMR spectrum of 3h in CDCl$_3$
$^1\text{H NMR}$ spectrum of $3i$ in CDCl$_3$

$^{19}\text{F NMR}$ spectrum of $3i$ in CDCl$_3$
\(^{13}\)C NMR spectrum of 3i in CDCl\(_3\)

\(^1\)H NMR spectrum of 3j in CDCl\(_3\)
$^{19}$F NMR spectrum of 3j in CDCl$_3$

$^{13}$C NMR spectrum of 3j in CDCl$_3$
$^1$H NMR spectrum of 3k in CDCl$_3$

$^{19}$F NMR spectrum of 3k in CDCl$_3$
$^{13}\text{C NMR}$ spectrum of 3k in CDCl$_3$

$^1\text{H NMR}$ spectrum of 3l in CDCl$_3$
$^{19}\text{F NMR}$ spectrum of 3l in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of 3l in CDCl$_3$
$^1$H NMR spectrum of 3m in CDCl$_3$

$^{19}$F NMR spectrum of 3m in CDCl$_3$
$^{13}$C NMR spectrum of 3m in CDCl$_3$

$^1$H NMR spectrum of 4a in CDCl$_3$
$^{19}$F NMR spectrum of 4a in CDCl$_3$

$^{13}$C NMR spectrum of 4a in CDCl$_3$
$^1$H NMR spectrum of 4b in CDCl$_3$

$^{19}$F NMR spectrum of 4b in CDCl$_3$
$^{13}$C NMR spectrum of 4b in CDCl$_3$

$^1$H NMR spectrum of 5a in CDCl$_3$
$^{19}\text{F NMR}$ spectrum of 5a in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of 5a in CDCl$_3$
$^1$H NMR spectrum of 6a in CDCl$_3$

$^{19}$F NMR spectrum of 6a in CDCl$_3$
$^{13}$C NMR spectrum of 6a in CDCl$_3$

$^1$H NMR spectrum of 6b in CDCl$_3$
$^{19}$F NMR spectrum of 6b in CDCl$_3$

$^{13}$C NMR spectrum of 6b in CDCl$_3$
$^1$H NMR spectrum of 6c in CDCl$_3$

![H NMR spectrum of 6c in CDCl$_3$]

$^{19}$F NMR spectrum of 6c in CDCl$_3$

![F NMR spectrum of 6c in CDCl$_3$]
$^{13}$C NMR spectrum of $6c$ in CDCl$_3$

$^1$H NMR spectrum of $6c'$ in CDCl$_3$
$^{19}$F NMR spectrum of 6c' in CDCl$_3$

$^{13}$C NMR spectrum of 6c' in CDCl$_3$
$^1$H NMR spectrum of 6d in CDCl$_3$

$^{19}$F NMR spectrum of 6d in CDCl$_3$
$^{13}$C NMR spectrum of 6d in CDCl$_3$

$^1$H NMR spectrum of 6f in CDCl$_3$
$^{19}$F NMR spectrum of 6f in CDCl$_3$

$^{13}$C NMR spectrum of 6f in CDCl$_3$
$^{1}H$ NMR spectrum of 6g in CDCl$_3$

$^{19}F$ NMR spectrum of 6g in CDCl$_3$
$^{13}$C NMR spectrum of $6g$ in CDCl$_3$

$^1$H NMR spectrum of $6h$ in CDCl$_3$
$^{19}$F NMR spectrum of 6h in CDCl$_3$

$^{13}$C NMR spectrum of 6h in CDCl$_3$
$^1$H NMR spectrum of 6j in CDCl$_3$

$^{19}$F NMR spectrum of 6j in CDCl$_3$
$^{13}$C NMR spectrum of 6j in CDCl$_3$

$^1$H NMR spectrum of 6k in CDCl$_3$
**$^{19}\text{F NMR}$ spectrum of $6k$ in CDCl$_3$**

![19F NMR spectrum](image)

**$^{13}\text{C NMR}$ spectrum of $6k$ in CDCl$_3$**

![13C NMR spectrum](image)
$^1\text{H NMR}$ spectrum of 6l in CDCl$_3$

$^{19}\text{F NMR}$ spectrum of 6l in CDCl$_3$
$^{13}$C NMR spectrum of 6l in CDCl$_3$

$^1$H NMR spectrum of 7a in CDCl$_3$
$^{19}$F NMR spectrum of 7a in CDCl$_3$

$^{13}$C NMR spectrum of 7a in CDCl$_3$
$^1$H NMR spectrum of 8a in CDCl$_3$

$^{19}$F NMR spectrum of 8a in CDCl$_3$
$^{13}$C NMR spectrum of 8a in CDCl$_3$

$^1$H NMR spectrum of 8b in CDCl$_3$
$^{19}$F NMR spectrum of 8b in CDCl$_3$

$^{13}$C NMR spectrum of 8b in CDCl$_3$
$^1$H NMR spectrum of 8c in CDCl$_3$

$^{19}$F NMR spectrum of 8c in CDCl$_3$
$^{13}$C NMR spectrum of 8e in CDCl$_3$