Supporting Information for

Alkynyl Trifluoromethyl Selenides Synthesis via

Oxidative Trifluoromethylselenolation of Terminal Alkynes

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**General Information:** $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra were recorded using a 400 spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as the external standard and low field is positive. Coupling constants ($J$) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: $^1$H NMR (chloroform δ 7.26) and $^{13}$C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on GCT-TOF. $[(bpy)Cu(SeCF_3)]_2$ was prepared according to the published procedures.\(^1\) Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures\(^2\) prior to use. Column chromatography purifications were performed by flash chromatography using silica gel 60.

**General procedure for trifluoromethylselenolation of terminal alkynes with $[(bpy)Cu(SeCF_3)]_2$:** Terminal alkynes $2$ (0.30 mmol), $[(bpy)Cu(SeCF_3)]_2$ $1$ (132 mg, 0.18 mmol), DMP (255 mg, 0.60 mmol, 2.0 equiv), KF (52 mg, 0.90 mmol, 3.0 equiv), and DMF (2.5 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 25 ºC for 16 hours. The reaction mixture was filtered through a pad of celite. The filtrate was added water (30 mL) at 0 ºC. The resulting mixture was extracted with Et$_2$O (3×15 mL), and the combined organic layers was washed with water, and then dried over MgSO$_4$. The solvent was removed by rotary evaporation in an ice bath and the resulting product was purified by column chromatography on silica gel with pentane/Et$_2$O.

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Data for compounds 3

(Phenylethynyl)(trifluoromethyl)selane (3a)

Obtained as a pale yellow oil in 74% yield (55 mg). $R_f$ (n-pentane) = 0.76. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 – 7.51 (m, 2H), 7.44 – 7.33 (m, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.2 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 132.0 (s), 129.5 (s), 128.4 (s), 120.7 (q, $J = 336.3$ Hz), 122.0 (s), 107.2 (d, $J = 1.1$ Hz), 61.8 (q, $J = 3.1$ Hz). IR (KBr): ν 2928, 2852, 2169, 1489, 1443, 1154, 1098, 755, 689, 532 cm$^{-1}$. GC-MS m/z 249 (M$^+$). HRMS (EI) m/z: Calcd. for C$_9$H$_5$F$_3$Se: 243.9568; Found: 243.9566.

(p-Tolylethynyl)(trifluoromethyl)selane (3b)

Obtained as a yellow solid in 87% yield (69 mg). M.p: 40–41 °C. $R_f$ (n-pentane) = 0.72. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.1$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 2.40 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.3 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.0 (s), 132.1 (s), 129.2 (s), 120.7 (q, $J = 336.3$ Hz), 119.0 (s), 107.4 (d, $J = 1.3$ Hz), 60.9 (q, $J = 3.1$ Hz), 21.6 (s). IR (KBr): ν 2951, 1683, 1558, 1508, 1154, 1072, 1047, 917, 816, 741 cm$^{-1}$. GC-MS m/z 263 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{10}$H$_7$F$_3$Se: 257.9725; Found: 257.9731.

(m-Tolylethynyl)(trifluoromethyl)selane (3c)

Obtained as a yellow oil in 81% yield (64 mg). $R_f$ (n-pentane) = 0.71. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.20 (m, 4H), 2.37 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.2 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.2 (s), 132.6 (s), 130.4 (s), 129.1 (s),
128.3 (s), 121.8 (s), 120.5 (q, \( J = 336.3 \) Hz), 107.4 (d, \( J = 1.1 \) Hz), 61.3 (q, \( J = 3.1 \) Hz), 21.2 (s). IR (KBr): \( \nu = 2925, 2855, 1600, 1483, 1155, 1096, 784, 741, 689, 442 \) cm\(^{-1}\). GC-MS m/z 263 (M\(^+\)). HRMS (EI) m/z: Calcd. for C\(_{10}\)H\(_7\)F\(_3\)Se: 257.9725; Found: 257.9728.

((4-Ethylphenyl)ethynyl)(trifluoromethyl)selane (3d)

Obtained as a yellow solid in 87% yield (72 mg). M.p: 31–32 °C. \( R_f \) (n-pentane) = 0.64. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.45 \) (d, \( J = 8.1 \) Hz, 2H), 7.21 (d, \( J = 8.1 \) Hz, 2H), 2.70 (q, \( J = 7.6 \) Hz, 2H), 1.27 (t, \( J = 7.6 \) Hz, 3H). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta = -36.4 \) (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 146.2 \) (s), 132.2 (s), 128.0 (s), 120.7 (q, \( J = 336.4 \) Hz), 119.2 (s), 107.5 (d, \( J = 0.7 \) Hz), 60.9 (q, \( J = 3.1 \) Hz), 28.9 (s), 15.3 (s). IR (KBr): \( \nu = 3031, 2936, 2166, 1508, 1154, 1093, 1019, 932, 741 \) cm\(^{-1}\). GC-MS m/z 277 (M\(^+\)). HRMS (EI) m/z: Calcd. for C\(_{11}\)H\(_9\)F\(_3\)Se: 271.9881; Found: 271.9886.

((4-Propylphenyl)ethynyl)(trifluoromethyl)selane (3e)

Obtained as a white solid in 84% yield (73 mg). M.p: 31–32 °C. \( R_f \) (n-pentane) = 0.70. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.44 \) (d, \( J = 8.2 \) Hz, 2H), 7.19 (d, \( J = 8.2 \) Hz, 2H), 2.68 – 2.57 (m, 2H), 1.73 – 1.61 (m, 2H), 0.97 (t, \( J = 7.3 \) Hz, 3H). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta = -36.4 \) (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 144.7 \) (s), 132.1 (s), 128.6 (s), 120.7 (q, \( J = 336.4 \) Hz), 119.2 (s), 107.5 (d, \( J = 1.3 \) Hz), 60.9 (q, \( J = 3.1 \) Hz), 38.0 (s), 24.3 (s), 13.7 (s). IR (KBr): \( \nu = 2974, 1686, 1561, 1508, 1459, 1157, 1094, 1051, 741 \) cm\(^{-1}\). GC-MS m/z 291 (M\(^+\)). HRMS (EI) m/z: Calcd. for C\(_{12}\)H\(_{11}\)F\(_3\)Se: 286.0038; Found: 286.0031.
((4-Butylphenyl)ethynyl)(trifluoromethyl)selane (3f)

Obtained as a yellow oil in 81% yield (74 mg). $R_t$ (n-pentane) = 0.69. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 2.70 – 2.57 (m, 2H), 1.68 – 1.53 (m, 2H), 1.45 – 1.30 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.4 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 145.0 (s), 132.1 (s), 128.6 (s), 120.7 (q, $J = 336.0$ Hz), 119.1 (s), 107.4 (d, $J = 1.3$ Hz), 60.9 (q, $J = 3.1$ Hz), 35.7 (s), 33.3 (s), 22.3 (s), 13.9 (s). IR (KBr): ν 2959, 2932, 2860, 2166, 1507, 1156, 1094, 828, 741, 537 cm$^{-1}$. GC-MS m/z 305 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{13}$H$_{13}$F$_3$Se: 300.0194; Found: 300.0200.

((4-Pentylphenyl)ethynyl)(trifluoromethyl)selane (3g)

Obtained as a yellow oil in 78% yield (75 mg). $R_t$ (n-pentane) = 0.80. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 8.3$ Hz, 2H), 2.71 – 2.52 (m, 2H), 1.74 – 1.50 (m, 2H), 1.45 – 1.30 (m, 4H), 0.92 (t, $J = 6.9$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.4 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 145.0 (s), 132.1 (s), 128.6 (s), 120.7 (q, $J = 336.0$ Hz), 119.2 (s), 107.5 (d, $J = 1.1$ Hz), 60.9 (q, $J = 3.1$ Hz), 35.9 (s), 31.4 (s), 30.9 (s), 22.5 (s), 14.0 (s). IR (KBr): ν 2958, 2935, 2859, 2161, 1508, 1151, 1104, 831, 740, 541 cm$^{-1}$. GC-MS m/z 320 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{14}$H$_{15}$F$_3$Se: 314.0351; Found: 314.0356.

([1,1'-Biphenyl]-4-ylyethynyl)(trifluoromethyl)selane (3h)

Obtained as a yellow solid in 74% yield (74 mg). M.p: 53–54 °C. $R_t$ (n-pentane) =
0.79. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.50 (m, 6H), 7.44 (t, $J = 7.4$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.1 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.3 (s), 140.1 (s), 132.6 (s), 129.0 (s), 128.0 (s), 127.1 (s), 120.9 (s), 120.8 (q, $J = 336.5$ Hz), 107.2 (d, $J = 1.1$ Hz), 62.5 (q, $J = 3.1$ Hz). IR (KBr): ν 2951, 1558, 1404, 1147, 1108, 1082, 841, 764, 741, 693 cm$^{-1}$. GC-MS m/z 326 (M$^+$+H).

HRMS (EI) m/z: Calcd. for C$_{15}$H$_9$F$_3$Se: 319.9881; Found: 319.9882.

![Chemical Structure](attachment:image.png)

((4-Methoxyphenyl)vinyl)(trifluoromethyl)selane (3i)

Obtained as a yellow oil in 81% yield (68 mg). $R_f$ (n-pentane) = 0.49. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 3.85 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.5 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.7 (s), 134.1 (s), 120.7 (q, $J = 336.5$ Hz), 114.1 (s), 107.3 (d, $J = 1.2$ Hz), 60.2 (q, $J = 3.2$ Hz), 55.3 (s). IR (KBr): ν 2952, 1605, 1509, 1294, 1252, 1152, 1106, 832, 741, 669 cm$^{-1}$. GC-MS m/z 279 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{10}$H$_7$OF$_3$Se: 273.9674; Found: 273.9670.

![Chemical Structure](attachment:image.png)

((4-Ethoxyphenyl)vinyl)(trifluoromethyl)selane (3j)

Obtained as a white solid in 73% yield (64 mg). M.p: 61–62 °C. $R_f$ (n-pentane) = 0.46. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.07 (q, $J = 7.0$ Hz, 2H), 1.45 (t, $J = 7.0$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.6 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.1 (s), 134.1 (s), 120.7 (q, $J = 336.5$ Hz), 114.5 (s), 113.8 (s), 107.4 (d, $J = 0.6$ Hz), 63.6 (s), 60.1 (q, $J = 3.1$ Hz), 14.7 (s). IR (KBr): ν 2990, 2935, 2156, 1602, 1508, 1475, 1258, 1149, 1116, 840 cm$^{-1}$. GC-MS m/z 293 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{11}$H$_9$OF$_3$Se: 287.9830; Found:
((4-Pentyloxy)phenyl)ethynyl)(trifluoromethyl)selane (3k)

Obtained as a yellow solid in 79% yield (79 mg). M.p: 37–38 °C. $R_f$ (n-pentane) = 0.64. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.9$ Hz, 2H), 6.88 (d, $J = 8.9$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 1.90 – 1.72 (m, 2H), 1.54 – 1.34 (m, 4H), 0.96 (t, $J = 7.1$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.6 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.3 (s), 134.1 (s), 120.7 (q, $J = 336.5$ Hz), 114.6 (s), 113.8 (s), 107.5 (d, $J = 1.2$ Hz), 68.2 (s), 60.0 (q, $J = 3.2$ Hz), 28.8 (s), 28.2 (s), 22.4 (s), 14.0 (s). IR (KBr): $\nu$ 2936, 2862, 2156, 1602, 1508, 1259, 1151, 1125, 1108, 837 cm$^{-1}$. GC-MS m/z 335 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{14}$H$_{15}$OF$_3$Se: 330.0300; Found: 330.0302.

(Trifluoromethyl)((4-(trifluoromethyl)phenyl)ethynyl)selane (3l)

Obtained as a yellow oil in 68% yield (67 mg). $R_f$ (n-pentane) = 0.69. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.52 (m, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -35.8 (s, 3F), -63.1 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 132.0 (s), 131.0 (q, $J = 32.9$ Hz), 125.4 (q, $J = 3.8$ Hz), 125.1 (s), 122.4 (s), 120.6 (q, $J = 336.2$ Hz), 105.7 (s), 65.0 (q, $J = 3.0$ Hz). IR (KBr): $\nu$ 2946, 1615, 1324, 1163, 1091, 1067, 1017, 742, 642, 597 cm$^{-1}$. GC-MS m/z 317 (M$^+$). HRMS (EI) m/z: Calcd. for C$_{10}$H$_4$F$_6$Se$^{74}$: 311.9442; Found: 311.9439.

((4-Fluorophenyl)ethynyl)(trifluoromethyl)selane (3m)
Obtained as a yellow oil in 71% yield (59 mg). \( R_f \) (n-pentane) = 0.75. \(^1\)H NMR (400 MHz, CDCl\(_3\) \( \delta \) 7.51 (dd, \( J = 8.2, 5.8 \) Hz, 2H), 7.07 (t, \( J = 8.6 \) Hz, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\) \( \delta \) -36.2 (s, 3F), -108.4 – -108.5 (m, 1F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\) \( \delta \) 163.2 (d, \( J = 252.5 \) Hz), 134.3 (d, \( J = 8.6 \) Hz), 120.7 (q, \( J = 336.2 \) Hz), 118.1 (d, \( J = 3.6 \) Hz), 115.8 (d, \( J = 22.2 \) Hz), 106.1 (d, \( J = 1.0 \) Hz), 61.7 (q, \( J = 3.2 \) Hz). IR (KBr): \( \nu \) 2929, 2854, 2170, 1601, 1507, 1237, 1157, 1090, 836, 771 cm\(^{-1}\). GC-MS m/z 267 (\( M^+ \)). HRMS (EI) m/z: Calcd. for C\(_9\)H\(_4\)F\(_4\)Se: 261.9474; Found: 261.9472.

\[
\begin{align*}
\text{(2-Fluorophenyl)ethynyl(trifluoromethyl)selane (3n)}
\end{align*}
\]

Obtained as a pale yellow oil in 77% yield (62 mg). \( R_f \) (n-pentane) = 0.60. \(^1\)H NMR (400 MHz, CDCl\(_3\) \( \delta \) 7.50 (t, \( J = 6.7 \) Hz, 1H), 7.44- 7.34 (m, 1H), 7.21 – 7.08 (m, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\) \( \delta \) -35.9 (s, 3F), -108.8 – -108.9 (m, 1F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\) \( \delta \) 163.0 (d, \( J = 254.5 \) Hz), 133.8 (s), 131.4 (d, \( J = 8.1 \) Hz), 124.1 (d, \( J = 3.8 \) Hz), 120.7 (q, \( J = 336.4 \) Hz), 115.7 (d, \( J = 21.2 \) Hz), 110.7 (d, \( J = 15.6 \) Hz), 100.5 (s), 67.2 (q, \( J = 3.2 \) Hz). IR (KBr): \( \nu \) 2927, 2853, 2174, 1491, 1247, 1160, 1098, 779, 756, 742 cm\(^{-1}\). GC-MS m/z 267 (\( M^+ \)). HRMS (EI) m/z: Calcd. for C\(_9\)H\(_4\) F\(_4\)Se: 261.9474; Found: 261.9478.

\[
\begin{align*}
\text{(4-Chlorophenyl)ethynyl(trifluoromethyl)selane (3o)}
\end{align*}
\]

Obtained as a pale yellow solid in 82% yield (70 mg). M.p: 30–31 °C. \( R_f \) (n-pentane) = 0.80. \(^1\)H NMR (400 MHz, CDCl\(_3\) \( \delta \) 7.44 (d, \( J = 8.3 \) Hz, 2H), 7.35 (d, \( J = 8.3 \) Hz, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\) \( \delta \) -35.9 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\) \( \delta \) 135.7 (s), 133.2 (s), 128.9 (s), 122.3 (q, \( J = 336.4 \) Hz), 120.5 (s), 106.0 (d, \( J = 1.1 \) Hz), 63.1 (q, \( J = 3.1 \) Hz). IR (KBr): \( \nu \) 2952, 2913, 1686, 1655, 1560, 1509, 1155, 1070,
943, 828 cm⁻¹. GC-MS m/z 283 (M⁺). HRMS (EI) m/z: Calcd. for C₉H₄F₃Cl⁷⁴Se: 277.9178; Found: 277.9177.

![Structure of 3p](image)

**((4-Bromophenyl)ethynyl)(trifluoromethyl)selane (3p)**

Obtained as a pale yellow solid in 76% yield (75 mg). M.p: 38–39 °C. Rᵣ(n-pentane) = 0.80. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -35.9 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 133.4 (s), 131.8 (s), 124.0 (s), 120.9 (s), 120.6 (q, J = 336.4 Hz), 106.1 (d, J = 1.1 Hz), 63.3 (q, J = 3.1 Hz). IR (KBr): ν 2951, 1584, 1486, 1156, 1085, 1011, 823, 741, 650 cm⁻¹. GC-MS m/z 327 (M⁺). HRMS (EI) m/z: Calcd. for C₉H₄F₃⁷⁴SeBr: 321.8673; Found: 321.8665.

![Structure of 3q](image)

**((3-Bromophenyl)ethynyl)(trifluoromethyl)selane (3q)**

Obtained as a pale yellow oil in 75% yield (74 mg). Rᵣ(n-pentane) = 0.68. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -35.8 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 134.6 (s), 132.6 (s), 130.6 (s), 129.9 (s), 123.9 (s), 122.3 (s), 120.6 (q, J = 336.5 Hz), 105.5 (d, J = 1.1 Hz), 63.7 (q, J = 3.1 Hz). IR (KBr): ν 1585, 1561, 1471, 1157, 1095, 867, 782, 742, 679, 437 cm⁻¹. GC-MS m/z 327 (M⁺). HRMS (EI) m/z: Calcd. for C₉H₄F₃⁷⁴SeBr: 321.8673; Found: 321.8669.

![Structure of 3r](image)

**2-((Trifluoromethylselanyl)ethynyl)pyridine (3r)**
Obtained as a sepia oil in 73% yield (55 mg). $R_f$ (n-pentane/diethyl ether 1:1) = 0.52. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (d, $J = 4.7$ Hz, 1H), 7.70 (t, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 6.2$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -35.3 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.2 (s), 142.1 (s), 136.3 (s), 127.3 (s), 123.7 (s), 120.6 (q, $J = 336.5$ Hz), 106.4 (d, $J = 1.0$ Hz), 63.3 (q, $J = 3.0$ Hz). IR (KBr): $\nu$ 2952, 2913, 1581, 1460, 1427, 1151, 1095, 777, 740 cm$^{-1}$. GC-MS m/z 250 (M$^+$). HRMS (EI) m/z: Calcd. for C$_8$H$_4$NF$_3$Se: 244.9521; Found: 244.9522.

![3s](image)

3-((Trifluoromethylselanyl)ethynyl)pyridine (3s)

Obtained as a sepia oil in 67% yield (50 mg). $R_f$ (n-pentane/diethyl ether 1:1) = 0.60. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (s, 1H), 8.60 (d, $J = 4.8$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.34 – 7.26 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -35.7 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.5 (s), 149.7 (s), 138.9 (s), 123.1 (s), 120.6 (q, $J = 336.4$ Hz), 119.2 (s), 103.8 (d, $J = 1.1$ Hz), 66.0 (q, $J = 3.0$ Hz). IR (KBr): $\nu$ 2952, 1563, 1475, 1408, 1155, 1094, 1022, 804, 741, 703 cm$^{-1}$. GC-MS m/z 250 (M$^+$). HRMS (EI) m/z: Calcd. for C$_8$H$_4$NF$_3$Se: 244.9521; Found: 244.9517.

![3t](image)

2-((Trifluoromethylselanyl)ethynyl)thiophene (3t)

Obtained as a yellow oil in 72% yield (55 mg). $R_f$ (n-pentane/diethyl ether 5:1) = 0.79. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.35 (m, 2H), 7.05 (t, $J = 3.6$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.2 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.8 (s), 129.7 (s), 127.2 (s), 121.9 (s), 120.6 (q, $J = 337.0$ Hz), 100.4 (d, $J = 1.1$ Hz), 66.8 (q, $J = 3.1$ Hz). IR (KBr): $\nu$ 2926, 2854, 2153, 1418, 1157, 1096, 855, 835, 741, 705 cm$^{-1}$. GC-MS m/z 255 (M$^+$). HRMS (EI) m/z: Calcd. for C$_7$H$_3$F$_3$S$_2$Se: 249.9132; Found:
3-((Trifluoromethylselanyl)ethynyl)thiophene (3u)

Obtained as a yellow oil in 74% yield (57 mg). $R_f$ (n-pentane) = 0.70. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (s, 1H), 7.36 – 7.29 (m, 1H), 7.20 (d, $J = 4.2$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -36.2 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 131.5 (s), 130.0 (s), 125.7 (s), 121.2 (s), 120.6 (q, $J = 337.0$ Hz), 102.2 (s), 61.7 (q, $J = 3.0$ Hz). IR (KBr): ν 2952, 2161, 1358, 1155, 1091, 949, 872, 783, 741, 625 cm$^{-1}$. GC-MS m/z 255 (M$^+$). HRMS (EI) m/z: Calcd. for C$_7$H$_3$F$_3$S$^{74}$Se: 249.9132; Found: 249.9130.

Oct-1-yn-1-yl(trifluoromethyl)selane (3v)

Obtained as a yellow oil in 57% yield (44 mg). $R_f$ (n-pentane) = 0.47. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.45 (t, $J = 7.0$ Hz, 2H), 1.66 – 1.51 (m, 2H), 1.49 – 1.21 (m, 6H), 0.92 (t, $J = 6.5$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -37.0 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 120.7 (q, $J = 335.6$ Hz), 109.5 (d, $J = 1.0$ Hz), 51.1 (q, $J = 3.1$ Hz), 31.2 (s), 28.4 (s), 28.2 (s), 22.5 (s), 20.5 (s), 14.0 (s). IR (KBr): ν 2959, 2933, 2861, 2190, 1467, 1380, 1326, 1156, 1097, 741 cm$^{-1}$. GC-MS m/z 257 (M$^+$). HRMS (EI) m/z: Calcd. for C$_9$H$_{13}$F$_3$ $^{74}$Se: 252.0194; Found: 252.0189.
Procedure for gram scale reaction for synthesis of \((p\text{-tolylethynyl})(\text{trifluoromethyl})\text{selane (3b)}\): 4-Ethynyltoluene (2b) (1.04 g, 9.0 mmol), \([(\text{bpy})\text{Cu(SeCF}_3\text{)}]_2\) 1 (3.98 g, 5.4 mmol, 0.60 equiv), DMP (7.63 g, 18 mmol, 2.0 equiv), KF (1.57 g, 27 mmol, 3.0 equiv), and DMF (25 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 25 °C for 16 hours. The reaction mixture was filtered through a pad of celite. The filtrate was added water (30 mL) at 0 °C. The resulting mixture was extracted with Et\(_2\)O (3×20 mL), and the combined organic layers was washed with water, and then dried over MgSO\(_4\). The solvent was removed by rotary evaporation in an ice bath and the resulting product was purified by column chromatography on silica gel with pentane/Et\(_2\)O. Compound 3b was obtained in 84% yield (1.99 g).

Procedure for the trifluoromethylselenolation of 1 with 4-ethynyltoluene (2b) in the presence of 1.0 equiv TEMPO: 4-Ethynyltoluene (2b) (11.6 mg, 0.10 mmol), \([(\text{bpy})\text{Cu(SeCF}_3\text{)}]_2\) 1 (44.1 mg, 0.060 mmol), DMP (84.8 mg, 0.20 mmol, 2.0 equiv), KF (17.4 mg, 0.30 mmol, 3.0 equiv), TEMPO (15.6 mg, 0.10 mmol), and DMF (2.5 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 25 °C for 16 hours. The tube was removed from the oil bath and cooled to room temperature, and then 10 μL (trifluoromethoxy)benzene was added as an internal standard. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by \(^{19}\text{F NMR and GC-MS. The yield of the (p-tolylethynyl)(trifluoromethyl)selane (3b)}\) was calculated to be 65%.
Experiments for Mechanistic Investigations

(1) Procedure for reaction of [(bpy)Cu(SeCF$_3$)$_2$] (I) with Dess–Martin periodinane in the presence of KF.

$[(bpy)Cu(SeCF_3)_2]_2 + \text{DMP, r.t.} \rightarrow \underbrace{[(bpy)Cu^{II}(SeCF_3)(L)]}_{\text{Intermediate I}}$

$[(bpy)Cu(SeCF_3)_2]_2$ (I) (44 mg, 0.060 mmol), DMP (85 mg, 0.20 mmol), KF (17.4 mg, 0.30 mmol), and PhOCF$_3$ (10 $\mu$L) as internal standard were weighed into a vial and dissolved in 2.0 mL of DMF. The contents of the vial were agitated and then transferred to an NMR tube. The NMR tube was agitated for 10 min and the $^{19}$F NMR spectrum was acquired. The yield of the intermediate I was calculated to be 75% based on I.

![NMR spectrum of intermediate I](image)
(2). Procedure for reaction of intermediate I with 4-ethynyltoluene (2b).

\[
\text{Intermediate I} \quad \text{[bpy]Cu}^{II} \text{(SeCF}_3\text{)(L)}} + 2b \quad \xrightarrow{[\text{Cu}, \text{KF}, \text{DMF}, \text{r.t.}]} \quad 3b
\]

4-Ethynyltoluene (2b) (11.6 mg, 0.10 mmol) was then added to the above intermediate I solution. The resulting mixture was measured by $^{19}$F NMR at regular intervals at 25 °C until the yield did not change. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by GC-MS. The yield of the (p-tolylethynyl)(trifluoromethyl)selane (3b) was calculated to be 82% based on 2b.

Addition of substrate (1-ethyl-1-methylbenzene)

Time = 10 min

Intermediate I
XPS of intermediate I

Total acquisition time 2 mins 16.0 secs
Number of Scans 1
Source Gun Type Al K Alpha
Spot Size 500 µm
Lens Mode Standard
Analyser Mode CAE : Pass Energy 100.0 eV
Energy Step Size 1.000 eV
Number of Energy Steps 1361
Copies of $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR Spectra for Compounds 3a–v

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

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

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

![$^{13}$C NMR spectrum of 3b in CDCl$_3$]

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

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

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

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

![13C NMR spectrum of 3d in CDCl$_3$](image)

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

![$^{19}$F NMR spectrum of 3d in CDCl$_3$](image)
$^1$H NMR spectrum of 3e in CDCl$_3$

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

![F NMR spectrum of 3e in CDCl$_3$]

$^1\text{H NMR}$ spectrum of 3f in CDCl$_3$

![H NMR spectrum of 3f in CDCl$_3$]
$^{13}\text{C NMR}$ spectrum of 3f in CDCl$_3$

![13C NMR spectrum of 3f in CDCl$_3$](image)

$^{19}\text{F NMR}$ spectrum of 3f in CDCl$_3$

![19F NMR spectrum of 3f in CDCl$_3$](image)
$^{1}H$ NMR spectrum of 3g in CDCl$_3$

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

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

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

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

\(^{1}\text{H NMR}\) spectrum of 3j in CDCl\(_3\)
$^{13}$C NMR spectrum of 3j in CDCl$_3$

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

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

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

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

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

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

![13C NMR spectrum of 3n in CDCl3]

$^{19}$F NMR spectrum of 3n in CDCl$_3$

![19F NMR spectrum of 3n in CDCl3]
$^1$H NMR spectrum of 3o in CDCl$_3$ 

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

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

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

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

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

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

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

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

![H NMR spectrum](image)

$^{13}\text{C NMR}$ spectrum of 3u in CDCl$_3$

![C NMR spectrum](image)
$^{19}$F NMR spectrum of 3u in CDCl$_3$

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

$^{19}$F NMR spectrum of 3v in CDCl$_3$