Supporting Information

Expeditious Trifluoromethylthiolation and Trifluoromethylselenolation of Alkynyl(phenyl)iodoniums by [XCF$_3$]$^-$ (X = S, Se) Anions

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1. General considerations

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in CDCl$_3$ on a 500 or 400 MHz (for $^1$H), 471 or 376 MHz (for $^{19}$F), and 126 or 100 MHz (for $^{13}$C) spectrometer. All chemical shifts were reported in ppm relative to TMS ($^1$H NMR, 0 ppm) and PhCF$_3$ ($^{19}$F NMR, –63.5 ppm) as an internal or external standard. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of product were determined by using the corresponding pure compound as the external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Koser’s reagent$^1$ and alkynyl(phenyl)iodonium tosylates$^2$ were synthesized according to the literatures. Solvents were dried before use according to the literature.$^3$ Other reagents in this study were all purchased from commercial sources and used without further purification.

2. Screening the optimized reaction conditions

Table 1 Trifluoromethylthiolation of 1a by [Me$_4$N][SCF$_3$] at different reactant ratio$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>x (equiv)</th>
<th>Yield (2a, %)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>85 (83)</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>78 (74)</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>86</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1a (0.1 mmol) / [Me$_4$N][SCF$_3$] (0.05, 0.1, 0.12, 0.15, 0.2, or 0.4 mmol) / CH$_3$CN (2 mL) / r.t. / N$_2$ / overnight.

$^b$Yields were determined by HPLC.
using ([1,1’-biphenyl]-4-ylethynyl)(trifluoromethyl)sulfane (2a) as the external standard (t_\text{R} = 6.081 \text{ min}, \lambda_{\text{max}} = 278.4 \text{ nm}, \text{methanol/water} = 90 : 10 (v / v)). The isolated yield is depicted in the parentheses.

Table 2 Screening the reaction time for the reaction of 1a with [Me_4N][SCF_3]^a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (min)</th>
<th>Yield (2a, %)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
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<td>78</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>85</td>
</tr>
</tbody>
</table>

^a Reaction conditions: 1a (0.1 mmol) / [Me_4N][SCF_3] (0.1 mmol) / CH_3CN (2 mL) / r.t. / N_2. ^b Yields were determined by HPLC using ([1,1’-biphenyl]-4-ylethynyl)(trifluoromethyl)sulfane (2a) as the external standard (t_\text{R} = 6.081 \text{ min}, \lambda_{\text{max}} = 278.4 \text{ nm}, \text{methanol/water} = 90 : 10 (v / v)).

Table 3 The effects of temperature on the reaction of 1a with [Me_4N][SCF_3]^a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Yield (2a, %)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>r.t.</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>81</td>
</tr>
</tbody>
</table>

^a Reaction conditions: 1a (0.1 mmol) / [Me_4N][SCF_3] (0.1 mmol) / CH_3CN (2 mL) / r.t. / N_2. ^b Yields were determined by HPLC using ([1,1’-biphenyl]-4-ylethynyl)(trifluoromethyl)sulfane (2a) as the external standard (t_\text{R} = 6.081 \text{ min}, \lambda_{\text{max}} = 278.4 \text{ nm}, \text{methanol/water} = 90 : 10 (v / v)).
Table 4 The solvent effects on the reaction of 1a with [Me₄N][SCF₃]¹

\[
\begin{array}{ccc}
\text{Entry} & \text{Solvent} & \text{Yield (2a, %)}^b \\
1 & \text{CH₃CN} & 85 \\
2 & \text{THF} & 46 \\
3 & \text{DMF} & 42 \\
4 & \text{DMSO} & 60 \\
5 & \text{DCE} & 50 \\
6 & \text{DCM} & 80 \\
\end{array}
\]

¹ Reaction conditions: 1a (0.1 mmol) / [Me₄N][SCF₃] (0.1 mmol) / solvent (2 mL) / r.t. / N₂.  
b Yields were determined by HPLC using ([1,1'-biphenyl]-4-ylethynyl) (trifluoromethyl)sulfane (2a) as the external standard (tᵣ = 6.081 min, λₘₐₓ = 278.4 nm, methanol/water = 90 : 10 (v/v)).

Table 5 The concentration effects of reactants on the reaction of 1a with [Me₄N][SCF₃]¹

\[
\begin{array}{ccc}
\text{Entry} & y (\text{mL}) & \text{Yield (2a, %)}^b \\
1 & 0.5 & 75 \\
2 & 1 & 74 \\
3 & 2 & 85 \\
4 & 4 & 77 \\
\end{array}
\]

¹ Reaction conditions: 1a (0.1 mmol) / [Me₄N][SCF₃] (0.1 mmol) / CH₃CN (y mL) / r.t. / N₂.  
b Yields were determined by HPLC using ([1,1'-biphenyl]-4-ylethynyl)
(trifluoromethyl)sulfane (2a) as the external standard ($t_R = 6.081$ min, $\lambda_{max} = 278.4$ nm, methanol/water = 90 : 10 (v / v)).

3. Synthesis of Koser’s reagent (PhI(OH)OTs)$^1$

A solution of toluenesulfonic acid monohydrate (7.6 g, 40 mmol) in CH$_3$CN (70 mL) was added to a suspension of iodobenzene diacetate (6.4 g, 20 mmol) in CH$_3$CN (40 mL) with vigorous stirring. The yellow color soon disappeared as a white precipitate was formed. The mixture was kept stirring at room temperature for another 30 min. The resulting solid was collected, washed with acetone and ether, and dried in vacuum to give 5.8 g of the title compound (80% yield).

4. General procedures for the preparation of alkynyl(phenyl)iodonium tosylates$^2$

**Procedure A:**$^{2a}$ An oven-dried tube (30 mL) was charged with Koser’s reagent (0.9 g, 2.3 mmol), terminal alkyne (4.6 mmol), allochroic silica gel (1.0 g), and CH$_2$Cl$_2$ (10 mL) in a glovebox with vigorous stirring. After 15 h (at room temperature), the solvent was removed and the residue was redissolved in a minimum amount of CH$_2$Cl$_2$. Then diethyl ether was added dropwise with stirring. The precipitates were filtered, washed with diethyl ether, and dried in vacuum to give the title compound.

**Procedure B:**$^{2b}$ To a suspension of iodosobenzene (PhIO, 550 mg, 2.5 mmol) and 1-(trimethylsilyl)-1-alkyne (2.5 mmol) in CHCl$_3$ (5 mL) was slowly added BF$_3$•OEt$_2$ (2.5 mmol) at 0°C. The mixture was reacted at room temperature for 4 h and recooled to 0 °C. Then a solution of sodium $p$-toluenesulfonate (1.94 g, 10 mmol) in water (10 mL) was added dropwise with vigorous stirring. After 10 minutes, the reaction mixture was extracted with CHCl$_3$ (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated. The sticky residue was redissolved in a minimum amount of CHCl$_3$ and diethyl ether was added. The precipitates (solid) were filtered, washed with diethyl ether, and dried in vacuum to give the title compound.
5. General procedure for the trifluoromethylthiolation and trifluoromethylselenolation of alkynyl(phenyl)iodonium tosylates

An oven-dried tube (10 mL) was charged with alkynyl(phenyl)iodonium tosylate (0.2 mmol), [Me₄N][XCF₃] (X = S or Se, 0.2 mmol), and CH₃CN (4 mL) in a glovebox with vigorous stirring. After 5 or 10 minutes (at room temperature), the reaction mixture was quenched by water and extracted with dichloromethane (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated to dryness. The residue was purified by flash column chromatography using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the desired product.

![Structural formula of 2a](image)

(1,1'-Biphenyl)-4-ylethynyl)(trifluoromethyl)sulfane (2a). White crystal, 46.2 mg, 83% yield, petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.61-7.58 (m, 6H), 7.47 (t, J = 7.0 Hz, 2H), 7.39 (t, J = 7.0 Hz, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ -43.3 (s, 3F).

![Structural formula of 2b](image)

(Phenylethynyl)(trifluoromethyl)sulfane (2b). Light yellow oil, 21.0 mg, 52% yield, petroleum ether as eluent for column chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.48 (m, 2H), 7.40-7.33 (m, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -43.6 (s, 3F).
(p-Tolylenyl)(trifluoromethyl)sulfane (2c). Light yellow oil, 34.6 mg, 80% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.37 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -43.8 (s, 3F).

(m-Tolylenyl)(trifluoromethyl)sulfane (2d). Light yellow oil, 28.5 mg, 66% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32-7.18 (m, 4H), 2.34 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -43.7 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 138.2, 132.6, 130.4, 129.1, 128.3, 121.8, 120.7 (q, $J = 337.1$ Hz), 107.4, 61.3 (q, $J = 2.8$ Hz), 21.2. IR (KBr): 2923, 2825, 1646, 1466, 1421, 1381, 1260, 1445, 1096, 968, 802, 722, 648 cm$^{-1}$. HRMS-EI (m/z) calcd. for C$_{10}$H$_7$F$_3$S: 216.0221, found: 216.0225.

((4-Propylphenyl)ethynyl)(trifluoromethyl)sulfane (2e). Light yellow oil, 37.1 mg, 76% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.60 (t, $J = 7.2$ Hz, 2H), 1.64 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -43.8 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 145.0, 132.3, 128.7, 128.2 (q, $J = 313$ Hz), 118.8, 101.6, 65.8 (q, $J = 4.2$ Hz), 38.0, 24.2, 13.7. IR (KBr): 3030, 2962, 2931, 2873, 2177,
1606, 1508, 1466, 1411, 1380, 1158, 1104, 1019, 835, 798, 757 cm$^{-1}$. HRMS-EI (m/z) calcd. for C$_{12}$H$_{11}$F$_{3}$S: 244.0534, found: 244.0528.

$(2$-Ethylphenyl$)$ethynyl(trifluoromethyl)sulfane (2f). Light yellow oil, 35.9 mg, 78% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 2.80 (q, $J = 7.5$ Hz, 2H), 1.24 (t, $J = 7.5$ Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -43.8 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.4, 132.6, 129.9, 128.2, 128.2 (q, $J = 313.0$ Hz), 125.8, 120.7, 100.2, 69.6 (q, $J = 3.0$ Hz), 27.7, 15.3. IR (KBr): 2965, 2920, 2850, 2175, 1655, 1631, 1482, 1468, 1260, 1159, 1103, 1015, 866, 803, 756 cm$^{-1}$. HRMS-EI (m/z) calcd. for C$_{11}$H$_{9}$F$_{3}$S: 230.0377, found: 230.0376.

$((4$-Methoxyphenyl$)$ethynyl(trifluoromethyl)sulfane (2g). Light yellow oil, 32.0 mg, 69% yield, petroleum ether / dichloromethane = 6 : 1 (v / v) as eluents for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.5$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 2H), 3.83 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -44.1 (s, 3F).

$((2$-Methoxyphenyl$)$ethynyl(trifluoromethyl)sulfane (2h). Light yellow solid, 30.2 mg, 65% yield, petroleum ether as eluent for column chromatography. M.p.: 46-48 °C.
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 6.94-6.88 (m, 2H), 3.89 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -43.8 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 160.8, 134.2, 131.3, 128.2 (q, $J = 313$ Hz), 120.5, 110.9, 110.9, 97.9, 70.2 (q, $J = 4.3$ Hz), 55.9. IR (KBr): 2962, 2920, 2840, 2178, 1596, 1575, 1491, 1464, 1434, 1282, 1261, 1160, 1102, 1047, 1024, 801, 751 cm$^{-1}$. HRMS-EI (m/z) calcd. for C$_{10}$H$_7$F$_3$OS: 232.0170, found: 232.0178.

SCF$_3$EtO$_2$i ((4-Ethoxyphenyl)ethynyl)(trifluoromethyl)sulfane (2i). Light yellow solid, 36.4 mg, 74% yield, petroleum ether / dichloromethane = 6 : 1 (v / v) as eluents for column chromatography. M.p.: 48-50 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.5$ Hz, 2H), 6.85 (d, $J = 8.5$ Hz, 2H), 4.05 (q, $J = 7.0$ Hz, 2H), 1.43 (t, $J = 7.0$ Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -44.1 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$): δ 160.3, 134.4, 128.2 (q, $J = 313.1$ Hz), 114.6, 113.3, 101.6, 65.0 (q, $J = 4.3$ Hz), 63.6, 14.7. IR (KBr): 2991, 2935, 2168, 1603, 1563, 1509, 1474, 1392, 1296, 1257, 1160, 1113, 1044, 922, 837, 826, 807, 792, 755 cm$^{-1}$. HRMS-EI (m/z) calcd. for C$_{11}$H$_9$F$_3$OS: 246.0326, found: 246.0318.

$\text{SCF}_3\begin{array}{c} \text{Cl} \\ \text{EtO} \end{array} \quad \text{2i}$

$((4\text{-Ethoxyphenyl})\text{ethyl})\text{(trifluoromethyl)sulfane (2i)}$. Yellow oil, 31.2 mg, 66% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -43.4 (s, 3F).

SCF$_3$Cl$_2$j ((4-Chlorophenyl)ethynyl)(trifluoromethyl)sulfane (2j). Yellow oil, 31.2 mg, 66% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -43.4 (s, 3F).
((4-Bromophenyl)ethynyl)(trifluoromethyl)sulfane (2k). Light yellow solid, 30.9 mg, 55% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -43.4 (s, 3F).

1-(4-(2-(Trifluoromethylthio)ethynyl)phenyl)ethanone (2l). Brown oil, 32.7 mg, 67% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents for isolation by preparative TLC (silica gel). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 2.61 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -43.2 (s, 3F).

Methyl 4-(((trifluoromethyl)thio)ethynyl)benzoate (2m). Colorless oil, 35.9 mg, 69% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 3.93 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -43.2 (s, 3F).

Oct-1-yn-1-yl(trifluoromethyl)sulfane (2n). Light yellow oil, 12.5 mg, 30% yield, hexane as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.37 (t, $J$ S10
= 7.0 Hz, 2H), 1.55 (m, 2H), 1.42-1.26 (m, 6H), 0.89 (t, J = 6.5 Hz, 3H). \(^{19}\text{F} \text{NMR} \ (471 \text{ MHz, } \text{CDCl}_3) \ \delta \ -44.4 \ (s, \ 3\text{F}). \(^{13}\text{C} \text{NMR} \ (126 \text{ MHz, } \text{CDCl}_3) \ \delta \ 128.5 \ (q, \ J = 312.1 \text{ Hz}), \ 104.0, \ 56.8 \ (q, \ J = 4.4 \text{ Hz}), \ 31.2, \ 28.4, \ 28.0, \ 22.5, \ 20.2, \ 14.0. \ \text{IR} \ (\text{KBr}): \ 2956, \ 2924, \ 2854, \ 1462, \ 1377, \ 1260, \ 1159, \ 1107, \ 1018, \ 800 \text{ cm}^{-1}. \ \text{HRMS-ESI} \ (m/z) \ \text{calcd. for } [\text{C}_9\text{H}_{14}\text{F}_3\text{S}]^+ ([\text{M} + \text{H}]^+) \ : \ 211.0768, \ \text{found: } 211.0773.

\[
\text{Dec-1-yne-1-yl(trifluoromethyl)sulfane (2o).}^{9} \text{ Light yellow oil, 24.0 mg, 50\% yield, hexane as eluent for column chromatography.}^{1}\text{H NMR} \ (500 \text{ MHz, } \text{CDCl}_3) \ \delta \ 2.37 \ (t, \ J = 7.0 \text{ Hz, } 2\text{H}), \ 1.55 \ (m, \ 2\text{H}), \ 1.40-1.26 \ (m, \ 10\text{H}), \ 0.89 \ (t, \ J = 6.5 \text{ Hz, } 3\text{H}). \ \text{^{19}F NMR} \ (471 \text{ MHz, } \text{CDCl}_3) \ \delta \ -44.4 \ (s, \ 3\text{F}).
\]

\[
\begin{align*}
\text{(1,1'-Biphenyl)-4-yneyl(trifluoromethyl)selane (3a).}^{10} \text{ White solid, 52.0 mg, 80\% yield, petroleum ether as eluent for column chromatography.}^{1}\text{H NMR} \ (500 \text{ MHz, } \text{CDCl}_3) \ \delta \ 7.61-7.56 \ (m, \ 6\text{H}), \ 7.47 \ (t, \ J = 7.6 \text{ Hz, } 2\text{H}), \ 7.39 \ (t, \ J = 7.6 \text{ Hz, } 1\text{H}). \ \text{^{19}F NMR} \ (471 \text{ MHz, } \text{CDCl}_3) \ \delta \ -36.1 \ (s, \ 3\text{F}).
\end{align*}
\]

\[
\begin{align*}
\text{(Phenylethyneyl)(trifluoromethyl)selane (3b).}^{10} \text{ Light yellow oil, 25.4 mg, 51\% yield, petroleum ether as eluent for column chromatography.}^{1}\text{H NMR} \ (400 \text{ MHz, } \text{CDCl}_3) \ \delta \ 7.51-7.48 \ (m, \ 2\text{H}), \ 7.38-7.33 \ (m, \ 3\text{H}). \ \text{^{19}F NMR} \ (376 \text{ MHz, } \text{CDCl}_3) \ \delta \ -36.2 \ (s, \ 3\text{F}).
\end{align*}
\]
(p-Tolylethynyl)(trifluoromethyl)selane (3c). Yellow solid, 43.7 mg, 83% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J$ = 8.0 Hz, 2H), 7.15 (d, $J$ = 8.0 Hz, 2H), 2.37 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.3 (s, 3F).

(m-Tolylethynyl)(trifluoromethyl)selane (3d). Light yellow oil, 36.3 mg, 69% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32-7.18 (m, 4H), 2.34 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.2 (s, 3F).

((4-Propylphenyl)ethynyl)(trifluoromethyl)selane (3e). Light yellow solid, 33.8 mg, 58% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 2.60 (t, $J$ = 7.2 Hz, 2H), 1.64 (m, 2H), 0.93 (t, $J$ = 7.2 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.3 (s, 3F).

(o-Tolylethynyl)(trifluoromethyl)selane (3f'). Light yellow oil, 31.6 mg, 60% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.44 (d, J = 7.6 Hz, 1H), 7.29-7.22 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 2.45 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.4 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.0, 132.1, 129.6, 129.4, 125.6, 121.9, 120.8 (q, J = 336.9 Hz), 106.3, 65.2 (q, J = 3.0 Hz), 20.5. IR (KBr): 2960, 2924, 2853, 1659, 1635, 1466, 1419, 1381, 1262, 1098, 1021, 867, 802, 703 cm$^{-1}$. HRMS-EI (m/z) calcd. For [C$_{10}$H$_7$F$_3$Se]: 257.9725, found: 257.9716.

![3g](image)

((4-Methoxyphenyl)ethynyl)(trifluoromethyl)selane (3g). Light yellow oil, 34.6 mg, 62% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -36.5 (s, 3F).

![3h](image)

((2-Methoxyphenyl)ethynyl)(trifluoromethyl)selane (3h). Light yellow solid, 31.8 mg, 57% yield, petroleum ether as eluent for column chromatography. M.p.: 47-49 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (m, 1H), 7.35 (m, 1H), 6.95-6.88 (m, 2H), 3.89 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -36.3 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.6, 134.1, 131.1, 120.7 (q, J = 336.9 Hz), 120.5, 111.3, 110.8, 103.7, 65.3 (q, J = 3.0 Hz), 55.9. IR (KBr): 2969, 2923, 2844, 2161, 1639, 1596, 1575, 1490, 1464, 1433, 1287, 1254, 1138, 1105, 1045, 1015, 940, 848, 802, 750 cm$^{-1}$. HRMS-ESI (m/z) calcd. for[C$_{10}$H$_8$F$_3$OSe]$^+$ ([M + H]$^+$): 280.9687, found: 280.9688.

![3j](image)
((4-Chlorophenyl)ethynyl)(trifluoromethyl)selane (3j). Light yellow solid, 45.4 mg, 80% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -35.9 (s, 3F).

((4-Bromophenyl)ethynyl)(trifluoromethyl)selane (3k). Light yellow solid, 40.7 mg, 62% yield, petroleum ether as eluent for column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -35.6 (s, 3F).

1-(4-(((Trifluoromethyl)selanyl)ethynyl)phenyl)ethanone (3l). Light yellow oil, 39.0 mg, 67% yield, petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluents for column chromatography. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 2.60 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -35.7 (s, 3F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.1, 137.1, 131.8, 128.3, 126.6, 120.6 (q, $J = 337.0$ Hz), 106.4, 65.8 (q, $J = 2.8$ Hz), 26.6. IR (KBr): 3007, 2927, 2856, 2168, 1687, 1601, 1559, 1428, 1404, 1361, 1264, 1092, 1017, 957, 836, 741, 704, 591 cm$^{-1}$. HRMS-ESI (m/z) calcd. for [C$_{11}$H$_8$F$_3$OSe]$^+$ ([M + H]$^+$): 292.9692, found: 292.9686.
Methyl 4-(trifluoromethylseleno)ethynylbenzoate (3m). White solid, 54.7 mg, 89% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents for column chromatography. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.02 (d, \(J = 8.0\) Hz, 2H), 7.54 (d, \(J = 8.0\) Hz, 2H), 3.93 (s, 3H). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -35.5 (s, 3F).

Oct-1-yn-1-yl(trifluoromethyl)selane (3n). Light yellow oil, 7.0 mg, 14% yield, hexane as eluent for column chromatography. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.42 (t, \(J = 7.0\) Hz, 2H), 1.55 (m, 2H), 1.42-1.26 (m, 6H), 0.89 (t, \(J = 7.0\) Hz, 3H). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -37.0 (s, 3F).

Dec-1-yn-1-yl(trifluoromethyl)selane (3o). Light yellow oil, 20.1 mg, 35% yield, hexane as eluent for column chromatography. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.42 (t, \(J = 7.0\) Hz, 2H), 1.55 (m, 2H), 1.40-1.28 (m, 10H), 0.89 (t, \(J = 6.5\) Hz, 3H). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -37.0 (s, 3F). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 120.7 (q, \(J = 336.0\) Hz), 109.5, 51.1 (q, \(J = 2.6\) Hz), 31.8, 29.1, 29.0, 28.7, 28.2, 22.6, 20.5, 14.1. IR (KBr): 2956, 2929, 2857, 2189, 1466, 1429, 1378, 1326, 1155, 1097, 741 cm\(^{-1}\). HRMS-ESI (m/z) calcd. for [C\(_{11}\)H\(_{18}\)F\(_3\)Se]\(^+\) ([M + H]\(^+\)): 287.0526, found: 287.0517.

Reference:


6. One-pot synthesis of 2b (or 3b) from 4b and [Me₄N][SCF₃] (or [Me₄N][SeCF₃])

An oven-dried round-bottom flask (50 mL) was charged with Koser's reagent (1.17 g, 3 mmol), phenylacetylene (4b, 0.82 g, 8 mmol), [Me₄N][XCF₃] (X = S or Se, 2 mmol), allochroic silica gel (1.0 g), and CH₂Cl₂ (15 mL) in a nitrogen-filled glovebox with vigorous stirring. The mixture was reacted at room temperature overnight, quenched by water, and extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated to dryness. The residue was purified by column chromatography using petroleum ether as eluent to give the desired product (2b, 0.102 g, 0.50 mmol, 25% yield, or 3b, 0.112 g, 0.45 mmol, 22% yield).

7. Stepwise one-pot synthesis of 2b, 3b, or 3j from 4b and [Me₄N][XCF₃] (X = S or Se) or Se₈/ TMSCF₃/ [Me₄N]F and 1j.

An oven-dried tube (20 mL) was charged with Koser’s reagent (0.293 g, 0.75 mmol), phenylacetylene (4b, 0.204 g, 2.0 mmol), allochroic silica gel (0.25 g), and CH₂Cl₂ (3.5 mL) with vigorous stirring in a nitrogen-filled glovebox. After 15 h, a solution of [Me₄N][XCF₃] (X = S or Se, 0.5 mmol) in CH₃CN (2 mL) was added. The mixture was kept reacting at room temperature for another 15 min and quenched with water. PhCF₃ (19.9 mg (0.136 mmol) or 31.9 mg (0.218 mmol)) was added to the
reaction mixture of 2b or 3b as an internal standard to determine the $^{19}$F yield, respectively.

Under a nitrogen atmosphere, TMSCF$_3$ (0.75 mL, 5 mmol) and [Me$_4$N]F (0.230 g, 2.4 mmol) were added into a suspension of selenium (0.190 g, 2.4 mmol) in DMF (5 mL) at -40 °C. After 10 min, the mixture was warmed to room temperature for 30 min, and a solution of 1j (0.510 g, 1.0 mmol) in CH$_3$CN (2.5 mL) was added. The resulting mixture was kept reacting at room temperature for another 12 h (till 1j was entirely consumed) and quenched with water. PhCF$_3$ (18.7 mg, 0.128 mmol) was added to the reaction mixture as an internal standard to determine the $^{19}$F yield of 3j.

**Figure 1.** $^{19}$F NMR spectrum of the reaction mixture of Koser’s reagent, 4b, and [Me$_4$N][SCF$_3$] in CH$_2$Cl$_2$ (**equation 1**):
Figure 2. $^{19}$F NMR spectrum of the reaction mixture of Koser’s reagent, 4b, and [Me$_4$N][SeCF$_3$] in CH$_2$Cl$_2$ (equation 2):

$$
\begin{align*}
\text{SeCF}_3 & \rightarrow \text{CF}_3 \\
\end{align*}
$$

Figure 3. $^{19}$F NMR spectrum of the reaction mixture of equation 3:

$$
\begin{align*}
\text{SeCF}_3 & \rightarrow \text{CF}_3 \\
\end{align*}
$$
8. Metal-free trifluoromethylthiolation and trifluoromethylselenolation of 5 by [Me₄N][XCF₃] (X = S, Se)

In a nitrogen-filled glovebox, an oven-dried tube (10 mL) was charged with (phenylethynyl)benziodoxol(on)e (5, 70 mg, 0.2 mmol), [Me₄N][XCF₃] (X = S or Se, 0.2 mmol), and CH₃CN (4 mL) at room temperature with stirring. After 45 min, the reaction mixture was quenched by water. PhCF₃ (18.1 mg (0.124 mmol) or 17.1 mg (0.117 mmol)) was added as an internal standard to determine the ¹⁹F yield of 2b or 3b, respectively.

**Figure 4.** ¹⁹F NMR spectrum of the reaction mixture of 5 and [Me₄N][SCF₃] in CH₃CN:
Figure 5. $^{19}$F NMR spectrum of the reaction mixture of 5 and [Me$_4$N][SeCF$_3$] in CH$_3$CN:
9. NMR spectra of 2 and 3.

\[ \text{Ph}^- \text{SCF}_3^- \]

\( ^1 \text{H NMR (500 MHz, CDCl}_3 \)\)

\[ \text{Ph}^- \text{SCF}_3^- \]

\( ^19 \text{F NMR (471 MHz, CDCl}_3 \)\)
2b

$^1$H NMR (400 MHz, CDCl$_3$)

2b

$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{19}$F NMR (376 MHz, CDCl$_3$)
$^{13}$C NMR (126 MHz, CDCl₃)

$^1$H NMR (400 MHz, CDCl₃)
$^{19}$F NMR (376 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
**S28**

**SCF-32f**

**2f**

$^1$H NMR (500 MHz, CDCl$_3$)

![NMR Spectrum](image)

$^1$H NMR (500 MHz, CDCl$_3$)

**19F NMR (471 MHz, CDCl$_3$)**

![NMR Spectrum](image)

$^{19}$F NMR (471 MHz, CDCl$_3$)
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (471MHz, CDCl$_3$)

$^{13}$C NMR (126MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
$\text{EtO} \quad \equiv \quad \text{SCF}_{3}$

2i

$^\text{13}C$ NMR (126 MHz, CDCl$_3$)

$\text{Cl}$

$\equiv \quad \text{SCF}_{3}$

2j

$^\text{1}H$ NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{19}F$ NMR (376 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
\[ \text{MeO}_2C\] \vphantom{\text{CF}_3} \\rightleftharpoons \text{SCF}_3 \]

**2m**

\(^{19}\text{F NMR} (471 \text{ MHz, CDCl}_3)\)

**2n**

\(^{1}\text{H NMR} (500 \text{ MHz, CDCl}_3)\)
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{19}F$ NMR (471 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{19}$F NMR (471 MHz, CDCl$_3$)
$\text{SeCF}_3$

3b

$^1\text{H NMR (400 MHz, CDCl}_3)$

$\text{SeCF}_3$

3b

$^{19}\text{F NMR (376 MHz, CDCl}_3)$
$\text{SeCF}_3$

$3c$

$^1H$ NMR (400 MHz, CDCl$_3$)

$^19F$ NMR (376 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{19}F$ NMR (376 MHz, CDCl$_3$)
\[ 3e \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3) \]

\[ 3e \]

\[ ^19\text{F NMR (376 MHz, CDCl}_3) \]
3f'<br>
^1H NMR (400 MHz, CDCl_3)

3f'<br>
^19F NMR (376MHz, CDCl_3)
$\text{SeCF}_3$

$3f$

$^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$

$\text{MeO}$

$3g$

$^1\text{H NMR (500 MHz, CDCl}_3\text{)}$
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^1$H NMR (400MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
\[ \text{Cl} \quad 3j \quad \text{SeCF}_3 \]

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \]

\[ \text{Cl} \quad 3j \quad \text{SeCF}_3 \]

\[ \text{F NMR (376 MHz, CDCl}_3 \text{)} \]
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{19}F$ NMR (376 MHz, CDCl$_3$)
$\text{SeCF}_3\text{O}_3\text{I}$

$^1\text{H NMR (500 MHz, CDCl}_3)$

$^1\text{H NMR (500 MHz, CDCl}_3)$

$^{19}\text{F NMR (471 MHz, CDCl}_3)$
SeCF₃

3I

¹³C NMR (126 MHz, CDCl₃)

MeO₂C

3m

¹H NMR (500 MHz, CDCl₃)
$\text{MeO}_2\text{C} \quad \text{3m}$

$^{19}\text{F} \text{ NMR (471 MHz, } \text{CDCl}_3)$

$\text{3n}$

$^1\text{H} \text{ NMR (500 MHz, } \text{CDCl}_3)$
\[ \text{SeCF}_3 \]

\(3n\)

\(^{19}\text{F NMR (471 MHz, CDCl}_3\)}

\[ \text{SeCF}_3 \]

\(3o\)

\(^{1}\text{H NMR (500 MHz, CDCl}_3\)}
$^{19}$F NMR (471 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)