Supporting Information

for

Metal-free nucleophilic trifluoromethylselenolnation via an iodide-mediated umpolung reactivity of trifluoromethylselenotoluenesulfonate

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Synthesis of benzyl(trifluoromethyl)selane (3a)

\[
\text{Ph} - \text{SeCF}_3
\]

Colorless liquid
Eluent for flash chromatography: pentane 100%
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.36-7.27\) (massif, 5H), 4.25 (s, 2H).
\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta = -34.48\) (s, 3F).
Characterization data matched that reported in the literature[1].

Synthesis of [(1,1’-biphenyl)-4-ylmethyl](trifluoromethyl)selane (3c)

\[
\text{Ph} - \text{SeCF}_3
\]

White solid
Melting point: 70°C.
Eluent for flash chromatography: pentane 100%
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.61-7.54\) (massif, 4H), 7.47-7.32 (massif, 5H), 4.30 (s, 2H).
\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta = -34.38\) (s, 3F).
Characterization data matched that reported in the literature[2].

Synthesis of (4-fluorobenzyl)(trifluoromethyl)selane (3d)

\[
\text{F} - \text{Ph} - \text{SeCF}_3
\]

Colorless liquid
Eluent for flash chromatography: pentane 100%
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.31\) (m, 2H), 7.01 (m, 2H), 4.22 (s, 2H).
\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta = -34.38\) (s, 3F), -114.11 (tt, J = 8.5, 5.3 Hz, 1F).
Characterization data matched that reported in the literature[3].

Synthesis of (4-nitrobenzyl)(trifluoromethyl)selane (3e)

\[
\text{O}_2\text{N} - \text{Ph} - \text{SeCF}_3
\]

Yellow oil
Eluent for flash chromatography: pentane/Et\(_2\)O 8:2 to 7:3
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 8.20\) (m, 2H), 7.51 (m, 2H), 4.28 (s, 2H).
\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta = -34.11\) (s, 3F).
Characterization data matched that reported in the literature[4].
Synthesis of (3-methoxybenzyl)(trifluoromethyl)selane (3f)

![Chemical Structure](image)

Colorless liquid
Eluent for flash chromatography: pentane/Et₂O 97:3

\[^1\text{H}\text{ NMR (300 MHz, CDCl}_3\text{)} \delta = 7.24 (t, J = 8.0 Hz, 1H), 6.93 (m, 1H), 6.88 (t, J = 2.3 Hz, 1H), 6.82 (ddd, J = 7.9, 2.2, 0.9 Hz, 1H), 4.22 (s, 2H), 3.81 (s, 3H).\]

\[^{19}\text{F NMR (282 MHz, CDCl}_3\text{)} \delta = -34.50 (s, 3F).\]

Characterization data matched that reported in the literature[4].

Synthesis of 2-(((trifluoromethyl)selanyl)methyl)pyridine (3g)

![Chemical Structure](image)

Yellowish oil
Only 1 eq. of alkyl halide was used instead of 2 eq.
Saturated aqueous NaHCO₃ was used instead of water during work-up
Eluent for flash chromatography: pentane/Et₂O 8:2 to 7:3

\[^1\text{H}\text{ NMR (300 MHz, CDCl}_3\text{)} \delta = 8.55 (d, J = 4.9 Hz, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.20 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 4.37 (s, 2H).\]

\[^{19}\text{F NMR (282 MHz, CDCl}_3\text{)} \delta = -34.58 (s, 3F).\]

Characterization data matched that reported in the literature[5].

Synthesis of 2-nitro-5-(((trifluoromethyl)selanyl)methyl)furan (3h)

![Chemical Structure](image)

Brownish oil
Eluent for flash chromatography: pentane/Et₂O 8:2

\[^1\text{H}\text{ NMR (300 MHz, CDCl}_3\text{)} \delta = 7.27 (d, J = 3.7 Hz, 1H), 6.53 (d, J = 3.7 Hz, 1H), 4.20 (s, 2H).\]

\[^{19}\text{F NMR (282 MHz, CDCl}_3\text{)} \delta = -34.43 (s, 3F).\]

Characterization data matched that reported in the literature[5].
Synthesis of cinnamyl(trifluoromethyl)selane (3i)

![Structure of 3i](image)

Colorless liquid
Eluent for flash chromatography: pentane 100%
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.39-7.23 (massif, 5H), 6.58 (d, $J$ = 15.6 Hz, 1H), 6.33 (dt, $J$ = 15.5, 7.7 Hz, 1H), 3.84 (d, $J$ = 7.7 Hz, 2H).
$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ = -33.80 (s, 3F).
Characterization data matched that reported in the literature[4].

Synthesis of (3,7-dimethylocta-2,6-dienyl)(trifluoromethyl)selane (3j)

![Structure of 3j](image)

Colorless liquid
Eluent for flash chromatography: pentane 100%
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 5.37 (t, $J$ = 8.4 Hz, 1H), 5.08-5.03 (m, 1H), 3.69 (d, $J$ = 8.3 Hz, 2H), 2.14-2.00 (massif, 4H), 1.69 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H).
$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ = -34.03 (s, 3F).
Characterization data matched that reported in the literature[6].

Synthesis of (3-phenylprop-2-yn-1-yl)(trifluoromethyl)selane (3k)

![Structure of 3k](image)

Colorless liquid
Eluent for flash chromatography: pentane 100%
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.42 (m, 2H), 7.35-7.29 (massif, 4H), 3.91 (s, 2H).
$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ = -34.61 (s, 3F).
Characterization data matched that reported in the literature[4].
Synthesis of 1-phenyl-2-((trifluoromethyl)selanyl)ethan-1-one (3l)

Yellow oil
Eluent for flash chromatography: pentane/Et₂O 95:5

$^1$H NMR (300 MHz, CDCl₃) δ = 7.97 (m, 2H), 7.63 (t, J = 7.4, 1.2 Hz, 1H), 7.51 (m, 2H), 4.63 (s, 2H).

$^{19}$F NMR (282 MHz, CDCl₃) δ = -34.19 (s, 3F).

Characterization data matched that reported in the literature[4].

Synthesis of 2-(((1,1,2,2,2-pentafluoroethyl)selanyl)methyl)pyridine (4g)

Yellowish oil

Only 1 equiv of the alkyl halide was used instead of 2 equiv.
A saturated aqueous NaHCO₃ was used instead of water during work-up
Eluent for flash chromatography: pentane/Et₂O 8:2 to 7:3

$^1$H NMR (300 MHz, CDCl₃) δ = 8.55 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.20 (ddd, J = 7.6, 5.0, 1.2 Hz, 1H), 4.39 (s, 2H).

$^{19}$F NMR (282 MHz, CDCl₃) δ = -83.62 (t, J = 4.0 Hz, 3F), -91.92 (q, J = 4.2 Hz, 2F).

Characterization data matched that reported in the literature[5].

Synthesis of benzyl(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)selane (5a)

Yellowish oil
Eluent for flash chromatography: pentane 100%

$^1$H NMR (300 MHz, CDCl₃) δ = 7.37-7.27 (massif, 5H), 4.29 (s, 2H).

$^{19}$F NMR (282 MHz, CDCl₃) δ = -80.76 (tt, J = 10.0, 2.5 Hz, 3F), -86.73 (ddt, J = 17.5, 10.5, 3.5 Hz, 2F), -118.27 (m, 2F), -121.44 (m, 2F), -122.75 (m, 2F), -126.08 (m, 2F).

Characterization data matched that reported in the literature[7].
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NMR data:

![NMR Spectra](image)

3a
