Supporting Information
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Supporting Information

Synthesis of Aryl Stannanes from Silyl Triflates via Aryne Intermediates

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General
All reactions were carried out in oven-dried glassware (80 °C) under an atmosphere of nitrogen or argon. Dried solvents were distilled before use: THF was distilled from LiAlH₄ or sodium/benzophenone. The products were purified by flash chromatography on silica gel columns (Macherey-Nagel 60, 0.063-0.2 mm). Mixtures of ethyl acetate and hexane or petrolether were generally used as eluents. Analytical TLC was performed on precoated silica gel plates (Macherey-Nagel, Polygram® SIL G/UV254). Visualization was accomplished with UV-light and KMnO₄ solution. ¹H and ¹³C NMR spectra were recorded with a Bruker AC-400 [400 MHz (¹H) and 100 MHz (¹³C)] spectrometer in CDCl₃. Chemical shifts are reported in ppm (δ) with respect to TMS, and CHCl₃ was used as the internal standard (¹H: δ = 7.26 ppm, ¹³C: δ = 77.0 ppm). Integrals are in accordance with assignments; coupling constants are given in Hz. All ¹³C spectra are proton-decoupled. For detailed peak assignments 2D spectra were measured. Mass spectra were recorded with a Finnigan MAT 95 spectrometer using CI or EI technique. For microwave irradiation a CEM discover microwave was used (200 Watt, air cooling, 10 ml vial). The temperatures quoted in microwave reactions are those measured by the CEM’s internal vertically-focused IR sensor and indicate the equilibrated cavity temperature.

General procedure for ortho-trialkylsilylaryl triflates: A mixture of ortho-bromohydroxyarene (2.00 g, 11.6 mmol) and HMDS (4.8 ml, 23 mmol) in THF (4 ml) was
refluxed for 90 min. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH₃ and unreacted HMDS. After ¹H NMR confirmation of the quantitative formation of the corresponding silyl ether, the crude product was dissolved in THF (15 ml), the solution was cooled to -100 °C and n-BuLi (1.6 M in hexane, 14 ml, 23 mmol) was added drop wise. The mixture was stirred for 20 min while the temperature reached to -80 °C. Then the mixture was again cooled to -100 °C, Tf₂O (4.0 ml, 23 mmol) was added drop wise, and stirring was continued for 20 min while the temperature reached to -80 °C. Cold sat. aq. NaHCO₃ was added, the phases were separated and the aqueous layer was extracted with Et₂O. The combined organic layers were dried with Na₂SO₄, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography (silica, hexane/EtOAc) afforded silyl triflate 1a as a colorless oil (3.25 g, 94%).

**Analytical data of aryl silyl triflates 1**

2-(Trimethylsilyl)phenyl trifluoromethanesulfonate 1a:

![](image)

¹H NMR (400 MHz, CDCl₃): δ = 0.37 (s, 9 H, Si(CH₃)₃), 7.32-7.37 (m, 2 H, Ar), 7.44 (ddd, J = 8.0, 7.2, 1.8 Hz, 1 H, Ar), 7.54 (dd, J = 7.2, 1.8 Hz, 1 H, Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = -0.9 [q, Si(CH₃)₃], 118.5 (q, J = 320 Hz, CF₃), 119.5, 127.5, 131.2, 132.5, 136.3, 155.1 (4 d, 2 s, Ar) ppm. HRMS (CI): Calcd. for C₉H₁₀F₃O₃SiS [M-CH₃]⁺: 283.0067. Found: 283.0101.

4-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1b:

![](image)

¹H NMR (400 MHz, CDCl₃): δ = 0.37 [s, 9 H, Si(CH₃)₃], 3.82 (s, OCH₃), 6.90 (dd, J = 9.1, 3.2 Hz, 1 H, 5-H), 7.01 (d, J = 3.2 Hz, 1 H, 3-H), 7.25 (d, J = 9.1 Hz, 1 H, 6-H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = -0.9 [q, Si(CH₃)₃], 55.6 (q, OCH₃), 113.7 (d, Ar), 118.5 (q, J = 320 Hz, CF₃), 120.8, 121.5, 134.2, 148.3, 158.1 (2 d, 3 s, Ar) ppm. HRMS (CI): Calcd. for C₁₀H₁₂F₃O₄SiS [M-CH₃]⁺: 313.0172. Found: 313.0148.

5-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1c:

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.35 [s, 9 H, Si(CH$_3$)$_3$], 3.83 (s, 3 H, OCH$_3$), 6.88 (d, $J$ = 2.4 Hz, 1 H, 6-H), 6.90 (dd, $J$ = 8.0, 2.4 Hz, 1 H, 4-H), 7.43 (d, $J$ = 8.0 Hz, 1 H, 3-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = -0.8 [q, Si(CH$_3$)$_3$], 55.5 (q, OCH$_3$), 106.2 (d, Ar), 113.1 (d, Ar), 118.5 (q, $J$ = 318 Hz, CF$_3$), 123.0, 136.7, 155.7, 161.9 (1 d, 3 s, Ar) ppm. HRMS (CI): Calcd for C$_{10}$H$_{12}$O$_4$F$_3$SiS [M$-$CH$_3$]$^+$: 313.0172. Found: 313.0169.

4-Methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1d:

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.38 [s, 9 H, Si(CH$_3$)$_3$], 2.38 (s, 3 H, CH$_3$), 7.22 (s, 2 H, Ar), 7.31 (s, 1 H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = -0.8 [q, Si(CH$_3$)$_3$], 20.8 (q, CH$_3$), 118.5 (q, $J$ = 320 Hz, CF$_3$), 119.3, 131.7, 132.2, 136.7, 137.2, 153.1 (3 d, 3 s, Ar) ppm. HRMS (CI): Calcd. for C$_{10}$H$_{12}$F$_3$O$_3$SiS [M$-$CH$_3$]$^+$: 297.0223. Found: 297.0219.

2,4-Dimethyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1e:

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.39 [s, 9 H, Si(CH$_3$)$_3$], 2.34 (s, 3 H, CH$_3$), 2.35 (s, 3 H, CH$_3$), 7.10 (br. s, 1 H, Ar), 7.18 (br. s, 1 H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 0.1 [q, Si(CH$_3$)$_3$], 17.2 (q, CH$_3$), 20.7 (q, CH$_3$), 118.7 (q, $J$ = 320 Hz, CF$_3$), 130.9 (s, Ar), 134.3 (s, Ar), 134.3 (d, Ar), 135.0 (d, Ar), 137.6 (s, Ar), 149.1 (s, Ar) ppm. HRMS (CI): Calcd. for C$_{11}$H$_{14}$F$_3$O$_3$SiS [M$-$CH$_3$]$^+$: 311.0380. Found: 311.0345.

2,4-Di-tert-butyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1f:

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.36 [s, 9 H, Si(CH$_3$)$_3$], 1.33 [s, 9 H, C(CH$_3$)$_3$], 1.43 [s, 9 H, C(CH$_3$)$_3$], 7.38 (d, $J$ = 2.6 Hz, 1 H, Ar), 7.53 (d, $J$ = 2.6 Hz, 1 H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 1.0 [q, Si(CH$_3$)$_3$], 31.3, 32.0 [2 q, C(CH$_3$)$_3$], 34.6, 36.4 [2 s, C(CH$_3$)$_3$],
118.5 (q, J = 320 Hz, CF₃), 128.9, 132.0 (2 d, Ar), 135.4, 142.4, 145.6, 149.5 (4 s, Ar) ppm. HRMS (CI): Calcd for C₁₇H₂₆O₃F₃SiS [M-CH₃]⁺: 395.1319. Found: 395.1301.

3-(Trimethylsilyl)-1,1'biphenyl-2-yl trifluoromethanesulfonate 1g:

\[
\begin{array}{c}
\text{Ph} \\
\text{OTf} \\
\text{SiMe₃}
\end{array}
\]

¹H NMR (400 MHz, CDCl₃): δ = 0.46 [s, 9 H, Si(CH₃)₃], 7.34-7.46 (m, 7 H, Ar), 7.55-7.59 (m, 1 H, Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 0.2 [q, Si(CH₃)₃], 118.0 (q, J = 321 Hz, CF₃), 128.0, 128.1, 128.3, 129.6, 133.6, 135.8, 135.9, 136.3, 136.9, 149.7 (6 d, 4 s, Ar) ppm. HRMS (CI): Calcd. for C₁₆H₁₇O₃F₃S [M⁺]: 374.0614. Found: 374.0579.

2,4-Dichloro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1h:

\[
\begin{array}{c}
\text{Cl} \\
\text{OTf} \\
\text{SiMe₃}
\end{array}
\]

¹H NMR (400 MHz, CDCl₃): δ = 0.41 [s, 9 H, Si(CH₃)₃], 7.38 (d, J = 2.6 Hz, 1 H, Ar), 7.51 (d, J = 2.6 Hz, 1 H, Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = -0.3 [q, Si(CH₃)₃], 118.6 (q, J = 321 Hz, CF₃), 128.4 (s, Ar), 131.9 (d, Ar), 134.4 (s, Ar), 134.5 (d, Ar), 139.4 (s, Ar), 146.6 (s, Ar) ppm. HRMS (CI): Calcd. for C₉H₈Cl₂F₃O₃SSi [M⁺]: 350.9287. Found: 350.9346.

1-(Trimethylsilyl)-2-naphthyl trifluoromethanesulfonate 1i:

\[
\begin{array}{c}
\text{SiMe₃} \\
\text{OTf}
\end{array}
\]

¹H NMR (400 MHz, CDCl₃): δ = 0.59 [s, 9 H, Si(CH₃)₃], 7.41 (d, J = 9.1 Hz, 1 H, Ar), 7.51-7.60 (m, 2 H, Ar), 7.85-7.93 (m, 2 H, Ar), 8.22 (d, J = 8.1 Hz, 1 H, Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 2.2 [q, Si(CH₃)₃], 118.7 (q, J = 321 Hz, CF₃), 119.1, 126.3, 126.7, 128.8, 129.0, 129.2, 132.36, 132.41, 137.6, 152.5 (6 d, 4 s, Ar) ppm. HRMS (CI): Calcd. for C₁₃H₁₂F₃O₃SSi [M-CH₃]⁺: 333.0223. Found: 333.0198.

Analytical data of aryl stannanes 2

Tributyl(phenyl)stannane 2a:

\[ \delta = 0.92 (t, J = 7.2 \text{ Hz}, 9 \text{ H}, \text{CH}_3), 0.99-1.18 (m, 6 \text{ H}, \text{CH}_2), 1.37 (\text{sext}, J = 7.2 \text{ Hz}, 6 \text{ H}, \text{CH}_2), 1.47-1.68 (m, 6 \text{ H}, \text{CH}_2), 7.28-7.38 (m, 3 \text{ H}, \text{Ar}), 7.42-7.56 (m, 2 \text{ H}, \text{Ar}) \text{ ppm}. \]

\[ \delta = 9.5, 13.7, 27.4, 29.1 (q, 3 \text{ t}, \text{CH}_3, \text{CH}_2), 127.9, 136.5, 142.0 \text{ ppm}. \]

\[ \delta = \text{Calcd. for } C_{14}H_{23}^{120}\text{Sn [M-Bu]^{+}}: 311.0816. \text{ Found: 311.0963}. \]

\[ \delta = -42.5 \text{ ppm}. \]

\[ \delta = -40.4 \text{ ppm}. \]

\[ \delta = -40.6 \text{ ppm}. \text{ HRMS (CI): Calcd. for } C_{15}H_{25}O^{120}\text{Sn [M-Bu]^{+}}: 341.0922. \text{ Found: 341.0907}. \]

\[ \delta = -42.9 \text{ ppm}. \]

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Compound 2d* (minor): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.91 (t, $J$ = 7.3 Hz, 9 H, CH$_3$), 0.97-1.16 (m, 6 H, CH$_2$), 1.30-1.41 (m, 6 H, CH$_2$), 1.47-1.66 (m, 6 H, CH$_2$), 2.36 (s, 3 H, CH$_3$), 7.17 (d, $J$ = 7.0 Hz, 2 H, Ar), 7.38 (d, $J$ = 7.0 Hz, 2 H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 9.5, 13.7 (q, t, CH$_3$, CH$_2$), 21.4 (q, Ar-CH$_3$), 27.4, 29.1 (2 t, CH$_2$), 128.8, 136.4 (2 d, Ar), 137.6, 137.9 (2 s, Ar) ppm. $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta$ = -42.1 ppm. HRMS (Cl): Calcd. for C$_{15}$H$_{25}$ $^{120}$Sn[M-Bu]$^+$: 325.0973. Found: 325.0979.

**Tributyl(3,5-dimethylphenyl)stannane 2e and tributyl(2,4-dimethylphenyl)stannane 2e*:**

![Diagram](image)

Compound 2e (major): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.80-0.94 (m, 9 H, CH$_3$), 1.03-1.10 (m, 6 H, CH$_2$), 1.25-1.42 (m, 6 H, CH$_2$), 1.45-1.60 (m, 6 H, CH$_2$), 2.33 (s, 6 H, Ar-CH$_3$), 6.96 (s, 1 H, 4-H), 7.09 (s, 2 H, 2-H, 6-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 9.5, 13.6 (q, t, CH$_3$, CH$_2$), 21.4 (q, Ar-CH$_3$), 27.4, 29.1 (2 t, CH$_2$) 129.8 (d, C-4), 134.1 (d, C-2, C-6), 137.0 (s, C-3, C-5), 138.0 (s, C-1). $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta$ = -43.3 ppm.

Compound 2e* (minor): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.80-0.94 (m, 9 H, CH$_3$), 0.96-1.02 (m, 6 H, CH$_2$), 1.25-1.42 (m, 6 H, CH$_2$), 1.45-1.60 (m, 6 H, CH$_2$), 2.33 (s, 3 H, Ar-CH$_3$), 2.38 (s, 3 H, Ar-CH$_3$), 6.94-7.10 (m, 2 H, 3-H, 5-H), 7.31 (d, $J$ = 7.2 Hz, H-6) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 10.0, 13.7, 21.2, 24.9, 27.5, 29.2 (3 q, 3 t, CH$_3$, CH$_2$), 125.7, 130.0, 136.5, 137.9, 141.6, 144.6 (3 d, 3 s, Ar) ppm. $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta$ = -40.3 ppm. HRMS (Cl): Calcd. for C$_{16}$H$_{25}$ $^{120}$Sn[M-Bu-2 H]$^+$: 337.0973. Found: 337.0968.

**Tributyl(3,5-ditert-butylphenyl)stannane 2f:**

![Diagram](image)

Compound 2f: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.87-0.92 (m, 9 H, CH$_3$), 1.05-1.12 (m, 6 H, CH$_2$), 1.34 (s, 18 H, t-Bu), 1.40-1.58 (m, 6 H, CH$_2$), 7.20-7.25 (m, 2 H, 2-H, 6-H), 7.40-7.50 (m, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 10.0, 13.7, 27.5, 29.1 (q, 3 t, CH$_3$, CH$_2$), 36.7 (s, C(CH$_3$_)$_3$), 31.3 (q, C(CH$_3$_)$_3$), 122.3 (d, C-4), 127.6 (d, C-2, C-6), 137.6 (s, C-1), 150.1 (s, C-3, C-5) ppm. $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta$ = -36.8 ppm. HRMS (Cl): Calcd. for C$_{22}$H$_{39}$ $^{120}$Sn[M-Bu]$^+$: 423.2068. Found: 423.2065.

1,1'-Biphenyl-3-yl(tributyl)stannane 2g and 1,1'-biphenyl-2-yl(tributyl)stannane 2g*: 

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Compound 2g (major): $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.90$ (t, $J = 7.2$ Hz, 9 H, CH$_3$), 1.00-1.18 (m, 6 H, CH$_2$), 1.30-1.40 (m, 6 H, CH$_2$), 1.52-1.63 (m, 6 H, CH$_2$), 7.30-7.47 (m, 5 H, Ar), 7.48-7.54 (m, 1 H, Ar), 7.57-7.62 (m, 2 H, Ar), 7.66 (br s, 1 H, Ar), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 9.6, 13.7, 27.4, 29.1$ (q, 3 t, CH$_3$, CH$_2$), 127.1 (d, Ar), 127.3 (d, Ar), 128.1 (d, Ar), 128.7 (d, Ar), 135.4, 140.6, 141.8, 142.6 (d, 3 s, Ar) ppm. $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta = -40.9$ ppm.

Compound 2g' (minor): $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.65-0.84$ (m, 6 H, CH$_2$), 0.85 (t, $J = 7.2$ Hz, 9 H, CH$_3$), 1.18-1.32 (m, 6 H, CH$_2$), 1.32-1.45 (m, 6 H, CH$_2$), 7.30-7.45 (m, 8 H, Ar), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 10.7, 13.6, 27.3, 29.0$ (q, 3 t, CH$_3$, CH$_2$), 128.0 (d, Ar), 128.1 (d, Ar), 128.7 (d, Ar), 137.0, 142.0, 145.7, 150.4 (d, 3 s, Ar) ppm. $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta = -37.9$ ppm. HRMS (CI): Calcd for C$_{20}$H$_{27}$Sn [M-Bu]$^+$: 387.1129. Found: 387.1022.

Tributyl(3,5-dichlorophenyl)stannane 2h and tributyl(2,4-dichlorophenyl)stannane 2h':

Compound 2h (major): $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.85$ (d, $J = 2.0$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 10.6, 13.6, 27.3, 29.0$ (q, 3 t, CH$_3$, CH$_2$), 128.0 (d, C-4), 133.8 (d, C-2, C-6), 134.7 (s, C-3, C-5), 141.2 (s, C-1) ppm. $^{119}$Sn-NMR (149 MHz, CDCl$_3$): $\delta = -28.9$ ppm.

Compound 2h' (minor): $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.85$ (d, $J = 2.0$ Hz, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 9.9, 13.6, 27.3, 29.0$ (q, 3 t, CH$_3$, CH$_2$), 126.3, 128.2, 135.1, 138.1, 143.1, 146.5 (3 d, 3 s, Ar) ppm. $^{119}$Sn-NMR (149.2 MHz, CDCl$_3$): $\delta = -32.1$ ppm.

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