Supplementary Information for

Surefire generation of stannylpotassium: highly reactive stannyl anions and applications

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1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere or in Glovebox (MBRAUN MB 150-BG UNIlab). The O_2/H_2O Analyzer monitored the oxygen and moisture concentrations in the glovebox atmosphere to ensure both were always maintained at H_2O 0.3 ppm> and O_2 0.6 ppm>. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^1H, 500 MHz; ^{13}C, 125 MHz; ^{19}F, 470 MHz; ^{119}Sn, 186 MHz) spectrometer using residual chloroform (^1H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.16) as an internal standard, and tetramethylstannane (^{119}Sn, δ = 0) as an external standard (solvent: $CDCl_3$). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GL Science), 30 m × 0.25 mm, film 0.25 μm; Flow rate: 1.89 mL/min; Injector temperature: 250 °C; Oven temperature: 100 °C to 250 °C at 20 °C/min, hold at 250 °C for 10 min; FID temperature: 250 °C). High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer or a JEOL JMS-T100GCV spectrometer. Preparative recycling gel permeation chromatography was performed with JAI LC-9201 equipped with JAI GEL-1H and -2H columns (chloroform or toluene as an eluent). Unless otherwise noted, commercially available reagents were used without purification, and products were purified by column chromatography using 10% w/w anhydrous potassium carbonate-silica (Merck Kieselgel 60). Column chromatography on florisil was carried out using KANTO CHEMICAL 16231-08. THF was distilled from sodium/benzophenone ketyl.

2. Synthesis of silylstannanes

2.1 Synthesis of trimethyl(dimethylphenylsilyl)stannane (1a)

A round-bottom flask equipped with a magnetic stirring bar was flame-dried. To a solution of naphthalene (128 mg, 1.0 mmol) in THF (20 mL), were added lithium clippings (416 mg, 60 mmol). The resulting mixture turned dark green and was stirred at room temperature for 1 h under an argon atmosphere. Then trimethyltin chloride (3.98 mL, 20 mmol) was added dropwise and the mixture was stirred at room temperature for 3 h. The resulting solution was added via a cannula into a stirred solution of chlorodimethylphenylsilane (3.7 ml, 22 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight, followed by extraction with hexane. The organic phase was washed with brine and dried over Na_2SO_4. The crude product was purified by Kugelrohr distillation under reduced pressure to provide trimethyl(dimethylphenylsilyl)stannane (**1a**) as a colorless oil (5.21 g, 87%)

Trimethyl(dimethylphenylsilyl)stannane (1a)[1]

$PhMe_2Si-SnMe_3$

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.50 (s, 6H), 7.31 – 7.40 (m, 3H), 7.42 – 7.52 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ -11.77, -1.21, 127.88, 128.57, 133.60, 140.06.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -123.34.

2.2 Synthesis of tributyl(trimethylsilyl)stannane (1b)

Tributyl(trimethylsilyl)stannane (**1b**)[2] was prepared according to the literature procedure and was obtained as a colorless oil in 86% yield.

Tributyl(trimethylsilyl)stannane (1b)

$TMS-SnBu_3$

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.78 – 0.94 (m, 15H), 1.23 – 1.37 (m, 6H), 1.40 – 1.54 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 1.47, 7.82, 13.72, 27.57, 30.29.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -121.76.

3. Confirmation of the generation of stannylpotassium species

3.1 Synthesis of $KSnMe_3$•18-crown-6 (2a)

In an argon-filled glovebox, $PhMe_2Si–SnMe_3$ (**1a**, 186.5 mg, 0.624 mmol), 18-crown-6 (166.0 mg, 0.628 mmol) and *t*-BuOK (70.0 mg, 0.624 mmol) were mixed in THF (4 mL). The reaction mixture was stirred for 5 min and kept at room temperature for 2 h. After the removal of the solvent, the reaction mixture was recrystallized from THF/hexane two-layer system at room temperature. The supernatant was decanted, and the resulting white precipitate was washed with hexane (2 mL × 3). Consequently, drying the white precipitate under a vacuum resulted in the isolation of the compound (**2a**, 262.0 mg, 0.561 mmol, 90%).

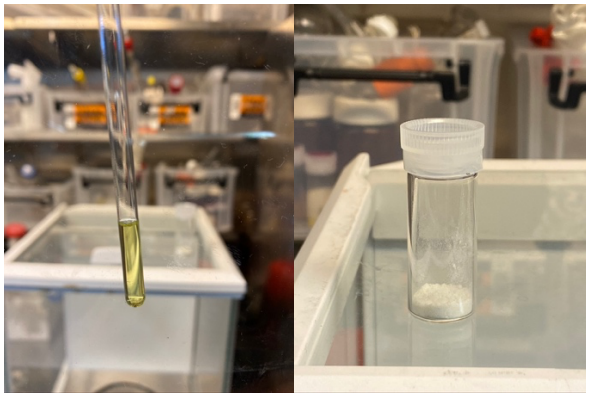


Figure S1. Pictures of 2a (left: THF-d_8 solution, right: solid-state)

3.2 Stannylation of 1-iodonaphthalene (3m) with 2a

In an argon-filled glovebox, a flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with $KSnMe_3$•18-crown-6 (**2a**) (102.8 mg, 0.22 mmol) and THF (0.67 mL). The Schlenk tube was taken from the glovebox, and then 1-iodonaphtalene (**3m**) (40.8 mg, 0.2 mmol) was added to the mixture. The resulting mixture was stirred at 30 °C for 1 h and was diluted with hexane. The organic solution was filtered through a celite pad and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (hexane as an eluent) to give **4am** (50.9 mg, 61%).

3.3 Synthesis of $KSnMe_3$ (2a')

A round-bottom flask equipped with a magnetic stirring bar was flame-dried. $PhMe_2Si–SnMe_3$ (**1a**, 1.471 g, 4.92 mmol) and *t*-BuOK (1 M in THF, 4.92 mL, 4.92 mmol) were mixed in THF (16 mL). The reaction mixture was stirred for 10 min and then the solvent was removed. The resulting white precipitate was brought into an argon-filled glovebox and washed with hexane (5 mL × 3). Consequently, drying the white precipitate under a vacuum resulted in the isolation of the compound (**2a'**, 726.9 mg, 3.59 mmol, 73%).

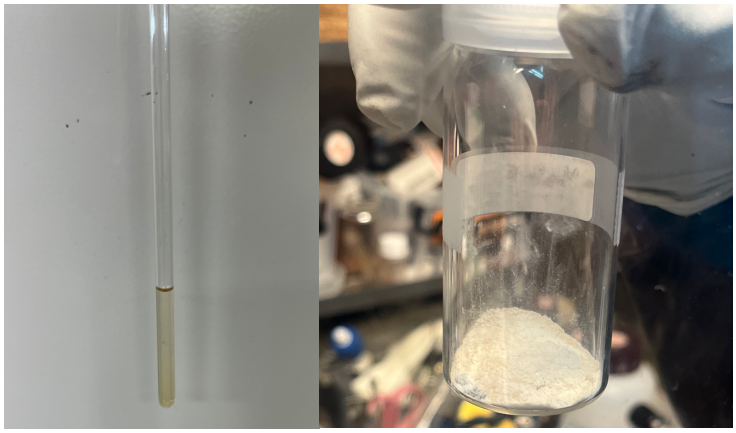


Figure S2. Pictures of 2a' (left: THF-d_8 solution, right: solid-state)

White solid, isolated yield 73%

^{1}H NMR (500 MHz, THF-d_8) δ -0.43 (s, 9H).

^{13}C NMR (126 MHz, THF-d_8) δ -1.35.

^{119}Sn NMR (186 MHz, THF-d_8) δ -175.71.

3.4 Synthesis of $KSnBu_3$ (2b)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with tributyl(trimethylsilyl)stannane (**1b**) (72.7mg, 0.20 mmol) and *t*-BuOK (1 M in THF, 0.20 mL, 0.20 mmol) were mixed in THF (0.67 mL). The reaction mixture was stirred for 10 min and then removed the solvent. The resulting yellow oil was brought into an argon-filled glove box, dissolved in THF-d_8 (0.45 ml), and analyzed by ^{119}Sn NMR.

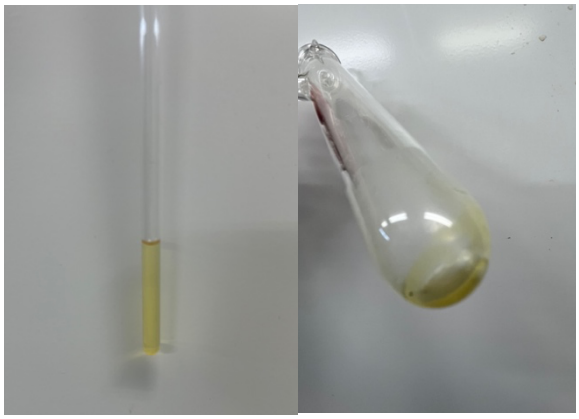


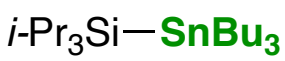
Figure S3. Pictures of 2b (left: THF-d_8 solution, right: neat)

3.5 Generation and capture of 2b

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with tributyl(trimethylsilyl)stannane (72.7 mg, 0.2 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.20 mL, 0.20 mmol). The reaction mixture was stirred for 1 min and triisopropylsilyl chloride (38.6 mg, 0.2 mmol) was added. The resulting mixture was stirred at 30 °C for 1 h and was diluted with hexane. The organic solution was filtered through a celite pad and concentrated by

rotary evaporation. The crude material was purified by GPC to give tributyl(triisopropylsilyl)stannane (**1c**) (34.9 mg, 39%).

Tributyl(triisopropylsilyl)stannane (1c)



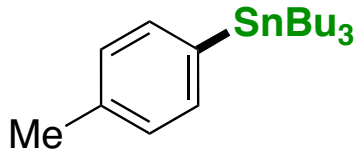
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 – 0.96 (m, 15H), 1.08 (d, J = 7.3 Hz, 18H), 1.16 – 1.26 (m, 3H), 1.32 (h, J = 7.3 Hz, 6H), 1.41 – 1.53 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 9.16, 13.47, 13.60, 20.15, 27.76, 30.09.
^{119}Sn NMR (186 MHz, $CDCl_3$) δ -125.92.
HRMS (FI) Calcd for $C_{17}H_{39}SiSn$: $[M\text{-}C_4H_9]^+$, 391.18375. Found: m/z 391.18339.

4. Stannylation of aryl halides with silylstannanes: a general procedure

A flame-dried schlenk tube equipped with a magnetic stirring bar was charged with silylstannane (0.22 mmol), aryl halides (0.20 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.22 mL, 0.22 mmol). The resulting mixture was stirred at 30 °C for 1 h and was diluted with hexane. The organic solution was filtered through a celite pad and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (hexane as an eluent) to give a stannylation product.

4-Iodo-*N*,*N*-dimethylaniline (**3i**),[3] 2,4,6-triisopropyliodobezene (**3u**),[4] 2'-iodo-1,1':3',1''-terphenyl (**3v**),[5] (1's,3's)-2'-iodo-2,2'',6,6''-tetraisopropyl-1,1':3',1''-terphenyl (**3w**),[6] ethyl 2-[(1-bromo-2-naphthalenyl)oxy]acetate (**6f**)[7] and 1-bromo-2-(but-3-enyl) benzene (**6h**)[8] were prepared according to literature procedures.

Tributyl(*p*-tolyl)stannane (4bb)[9]



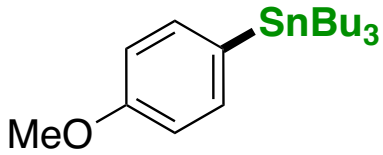
Colorless oil, isolated yield 78%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.95 – 1.13 (m, 6H), 1.27 – 1.40 (m, 6H), 1.44 – 1.63 (m, 6H), 2.34 (s, 3H), 7.16 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.51, 13.68, 21.38, 27.41, 29.10, 128.91, 136.52, 137.62, 137.86.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -43.18.

Tributyl(4-methoxyphenyl)stannane (4bc)[10]



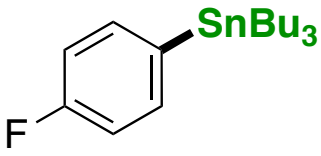
Colorless oil, isolated yield 89%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 – 0.94 (m, 9H), 0.94 – 1.12 (m, 6H), 1.34 (h, J = 7.3 Hz, 6H), 1.46 – 1.65 (m, 6H), 3.81 (s, 3H), 6.92 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.57, 13.70, 27.40, 29.11, 54.93, 113.89, 131.98, 137.49, 159.66.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -41.74.

Tributyl(4-fluorophenyl)stannane (4bd)[10]



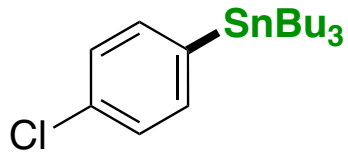
Colorless oil, isolated yield 73%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 9H), 0.96 – 1.12 (m, 6H), 1.32 (h, J = 7.3 Hz, 6H), 1.43 – 1.62 (m, 6H), 7.04 (dd, J = 9.7, 8.4 Hz, 2H), 7.35 – 7.48 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.64, 13.66, 27.35, 29.05, 115.10 (d, J = 19.0 Hz), 136.68 (d, J = 4.3 Hz), 137.82 (d, J = 6.7 Hz), 163.20 (d, J = 246.2 Hz).

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -40.22 (d, J = 7.9 Hz).

Tributyl(4-chlorophenyl)stannane (4be)[11]



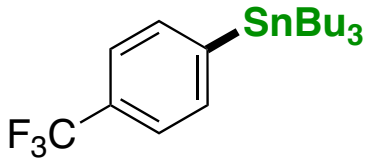
Colorless oil, isolated yield 76%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.97 – 1.13 (m, 6H), 1.33 (h, J = 7.3 Hz, 6H), 1.42 – 1.63 (m, 6H), 7.30 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.62, 13.64, 27.32, 29.02, 128.07, 134.28, 137.59, 140.02.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -39.79.

Tributyl(4-trifluoromethylphenyl)stannane (4bf)[11]



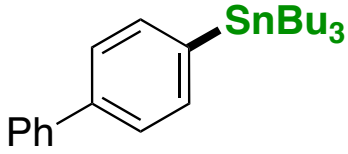
Colorless oil, isolated yield 77%

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.98 – 1.19 (m, 6H), 1.27 – 1.41 (m, 6H), 1.43 – 1.64 (m, 6H), 7.50 – 7.66 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.64, 13.62, 27.33, 29.01, 124.13 (q, J = 3.7 Hz), 124.40 (d, J = 272.0 Hz), 130.02 (q, J = 32.1 Hz), 136.59, 147.65.

^{119}Sn NMR (149 MHz, $CDCl_3$) δ -40.72.

[1,1'-Biphenyl]-4-yltributylstannane (4bg)[9]



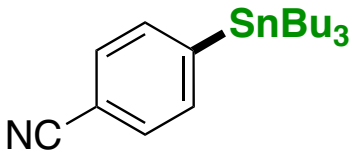
Colorless oil, isolated yield 88%

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 9H), 1.03 – 1.21 (m, 6H), 1.33 – 1.44 (m, 6H), 1.50 – 1.71 (m, 6H), 7.33 – 7.39 (m, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.55 – 7.66 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 9.63, 13.73, 27.44, 29.15, 126.64, 127.12, 127.19, 128.74,

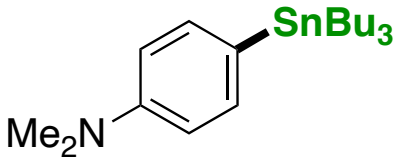
136.92, 140.76, 140.87, 141.32.
^{119}Sn NMR (149 MHz, $CDCl_3$) δ -42.66.

4-(Tributylstannyl)benzonitrile (4bh)[11]



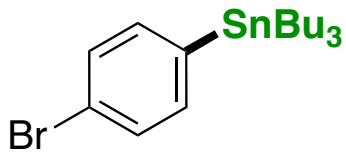
Colorless oil, isolated yield 79%
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 9H), 1.01 – 1.18 (m, 6H), 1.32 (h, J = 7.1 Hz, 6H), 1.42 – 1.60 (m, 6H), 7.53 – 7.62 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 9.72, 13.63, 27.29, 28.96, 111.54, 119.25, 130.71, 136.88, 150.34.
^{119}Sn NMR (186 MHz, $CDCl_3$) δ -38.40.

Tributyl(4-*N*,*N*-dimethylaminophenyl)stannane (4bi)[12]



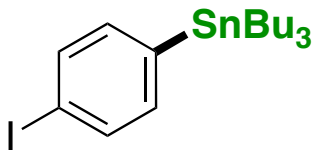
Colorless oil, isolated yield 75%
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.94 – 1.09 (m, 6H), 1.34 (h, J = 7.3 Hz, 6H), 1.46 – 1.61 (m, 6H), 2.95 (s, 6H), 6.76 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 9.52, 13.71, 27.44, 29.15, 40.34, 112.65, 126.45, 137.23, 150.46.
^{119}Sn NMR (186 MHz, $CDCl_3$) δ -42.80.

Tributyl(4-bromophenyl)stannane (4bj)[11]



Colorless oil, isolated yield 64%
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.97 – 1.14 (m, 6H), 1.33 (h, J = 7.3 Hz, 6H), 1.43 – 1.63 (m, 6H), 7.32 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 9.61, 13.67, 27.34, 29.03, 122.75, 130.91, 137.85, 140.62.
^{119}Sn NMR (186 MHz, $CDCl_3$) δ -39.22.

Tributyl(4-iodophenyl)stannane (4bk)



Colorless oil, isolated yield 80%

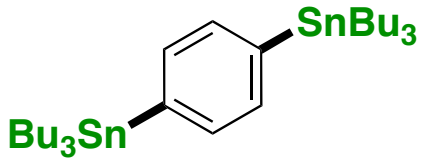
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 9H), 0.96 – 1.13 (m, 6H), 1.27 – 1.41 (m, 6H), 1.43 – 1.62 (m, 6H), 7.19 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.59, 13.67, 27.34, 29.02, 94.77, 136.85, 138.08, 141.31.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -38.78.

HRMS (FI) Calcd for $C_{14}H_{22}ISn$: $[M\text{-}C_4H_9]^+$, 436.97827. Found: m/z 436.97724.

1,4-Bis(tributylstannyl)benzene (4bl)[13]



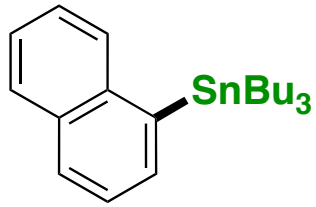
Colorless oil, isolated yield 88%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 18H), 0.98 – 1.13 (m, 12H), 1.35 (h, J = 7.4 Hz, 12H), 1.47 – 1.65 (m, 12H), 7.42 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.51, 13.69, 27.43, 29.13, 136.13, 141.54.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -45.25.

Tributyl(naphthalene-1-yl)stannane (4bm)[9]



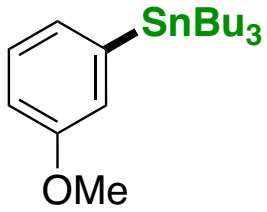
Colorless oil, isolated yield 81%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 9H), 1.15 – 1.31 (m, 6H), 1.32 – 1.43 (m, 6H), 1.51 – 1.69 (m, 6H), 7.42 – 7.55 (m, 3H), 7.59 – 7.73 (m, 1H), 7.76 – 7.91 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 10.40, 13.68, 27.40, 29.21, 125.33, 125.64, 125.83, 127.89, 128.43, 128.91, 130.18, 133.67, 135.12, 139.01, 142.94.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -40.13.

Tributyl(3-methoxyphenyl)stannane (4bn)[11]



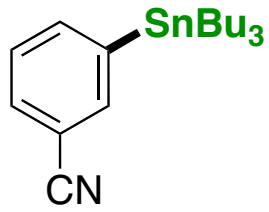
Colorless oil, isolated yield 77%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.9 Hz, 9H), 0.97 – 1.15 (m, 6H), 1.27 – 1.41 (m, 6H), 1.46 – 1.66 (m, 6H), 3.82 (d, J = 1.1 Hz, 3H), 6.85 (dd, J = 8.2, 2.8 Hz, 1H), 6.97 – 7.11 (m, 2H), 7.23 – 7.33 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.59, 13.69, 27.39, 29.08, 55.03, 112.93, 122.08, 128.73, 128.79, 143.48, 158.88.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -41.48.

3-(Tributylstannyl)benzonitrile (4bo)[9]



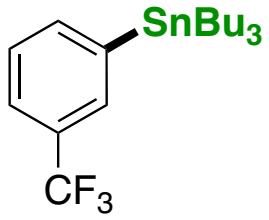
Colorless oil, isolated yield 89%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (td, J = 7.3, 1.1 Hz, 9H), 1.00 – 1.18 (m, 6H), 1.27 – 1.39 (m, 6H), 1.43 – 1.63 (m, 6H), 7.36 – 7.43 (m, 1H), 7.57 (dq, J = 7.7, 1.5 Hz, 1H), 7.62 – 7.77 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.73, 13.63, 27.29, 28.95, 112.07, 119.51, 128.11, 131.43, 139.63, 140.51, 144.17.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -37.34.

Tributyl(3-trifluoromethylphenyl)stannane (4bp)[9]



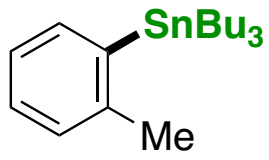
Colorless oil, isolated yield 75%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 1.01 – 1.18 (m, 6H), 1.34 (h, J = 6.9 Hz, 6H), 1.44 – 1.64 (m, 6H), 7.42 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.58 – 7.66 (m, 1H), 7.69 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.65, 13.61, 27.30, 28.99, 124.67 (q, J = 4.0 Hz), 127.85, 132.51 (q, J = 3.7 Hz), 139.73, 143.43.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -39.14.

Tributyl(*o*-tolyl)stannane (4bq)[11]



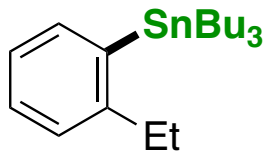
Colorless oil, isolated yield 63%

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.98 – 1.18 (m, 6H), 1.28 – 1.40 (m, 6H), 1.47 – 1.56 (m, 6H), 2.40 (s, 3H), 7.11 – 7.25 (m, 3H), 7.39 (d, J = 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 9.99, 13.66, 25.01, 27.41, 29.16, 124.84, 128.26, 128.84, 136.50, 142.01, 144.62.

^{119}Sn NMR (149 MHz, $CDCl_3$) δ -41.85.

Tributyl(2-ethylphenyl)stannane (4br)[14]



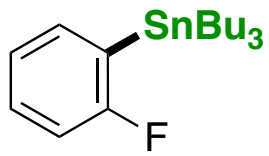
Colorless oil, isolated yield 74%

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 9H), 0.96 – 1.15 (m, 6H), 1.23 (t, J = 7.6 Hz, 3H), 1.33 (m,6H), 1.44 – 1.60 (m, 6H), 2.62 (q, J = 7.6 Hz, 2H), 7.14 (td, J = 7.1, 1.8 Hz, 1H), 7.20 – 7.31 (m, 3H), 7.38 (d, J = 7.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 10.28, 13.66, 16.45, 27.41, 29.14, 32.16, 77.21, 125.11, 127.23, 128.41, 136.61, 141.46, 150.90.

^{119}Sn NMR (149 MHz, $CDCl_3$) δ -43.08.

Tributyl(2-fluorophenyl)stannane (4bs)[12]



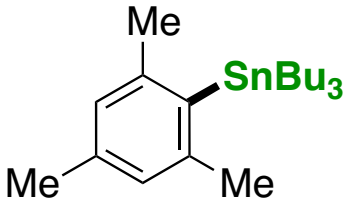
Colorless oil, isolated yield 69%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 9H), 1.03 – 1.21 (m, 6H), 1.35 (h, J = 7.3 Hz, 6H), 1.44 – 1.65 (m, 6H), 7.00 (t, J = 6.9 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.27 – 7.35 (m, 1H), 7.40 (ddd, J = 7.1, 3.9, 1.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.86, 13.66, 27.29, 29.00, 114.16 (d, J = 28.1 Hz), 124.05 (d, J = 2.8 Hz), 126.87 (d, J = 46.2 Hz), 130.21 (d, J = 7.6 Hz), 137.26 (d, J = 15.4 Hz), 167.32 (d, J = 234.2 Hz).

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -38.58 (d, J = 35.5 Hz).

Tributyl(mesityl)stannane (4bt)[15]



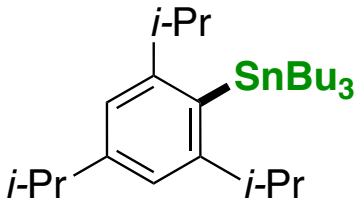
Colorless oil, isolated yield 71%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 9H), 1.02 – 1.20 (m, 6H), 1.37 (h, J = 7.3 Hz, 6H), 1.45 – 1.64 (m, 6H), 2.29 (s, 3H), 2.40 (s, 5H), 6.87 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 12.51, 13.67, 20.96, 25.58, 27.49, 29.22, 77.24, 127.62, 137.87, 138.34, 145.22.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -50.09.

Tributyl(2,4,6-triisopropylphenyl)stannane (4bu)



Colorless oil, isolated yield 82%

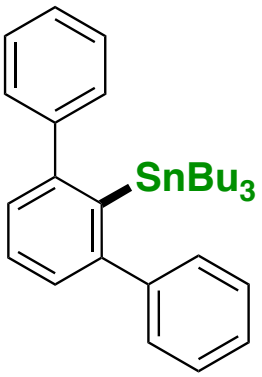
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 9H), 1.01 – 1.16 (m, 6H), 1.26 (d, J = 6.8 Hz, 12H), 1.28 (d, J = 7.0 Hz, 6H), 1.37 (h, J = 7.2 Hz, 6H), 1.46 – 1.62 (m, 6H), 2.83 – 2.95 (m, 3H), 7.02 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 13.00, 13.66, 23.98, 25.32, 27.52, 29.26, 34.11, 36.84, 120.98, 138.15, 148.81, 155.92.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -63.78.

HRMS (FI) Calcd for $C_{23}H_{41}Sn$: $[M\text{-}C_4H_9]^+$, 437.22247. Found: m/z 437.22291.

[1,1':3',1''-Terphenyl]-2'-yltributylstannane (4bv)



White solid, isolated yield 64%

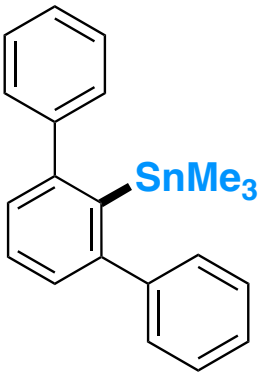
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.10 – 0.32 (m, 6H), 0.71 – 0.81 (m, 9H), 0.98 – 1.22 (m, 12H), 7.32 – 7.50 (m, 13H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 12.07, 13.56, 27.16, 28.96, 127.16, 127.81, 128.32, 129.40, 141.71, 146.00, 151.56.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -40.82.

HRMS (FI) Calcd for $C_{26}H_{31}Sn$: $[M\text{-}C_4H_9]^+$, 463.14422. Found: m/z 463.14497.

[1,1':3',1''-Terphenyl]-2'-yltrimethylstannane (4av)



White solid, isolated yield 90%

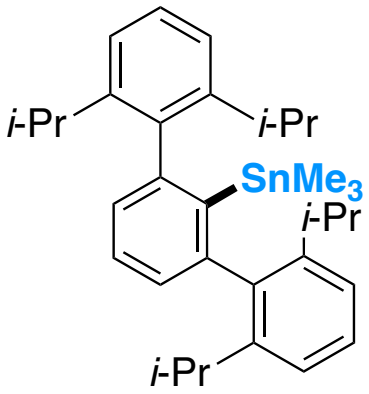
^{1}H NMR (500 MHz, $CDCl_3$) δ -0.43 (s, 9H), 7.35 – 7.51 (m, 13H).

^{13}C NMR (126 MHz, $CDCl_3$) δ -5.86, 127.30, 127.74, 128.14, 128.45, 129.40, 141.90, 145.77, 151.43.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -34.21.

HRMS (FI) Calcd for $C_{20}H_{19}Sn$: $[M\text{-}CH_3]^+$, 379.05032. Found: m/z 379.05011.

Trimethyl((1's,3's)-2,2'',6,6''-tetraisopropyl-[1,1':3',1''-terphenyl]-2'-yl)stannane (4aw)[16]



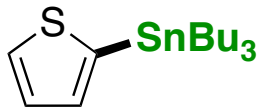
White solid, isolated yield 73%

^{1}H NMR (500 MHz, $CDCl_3$) δ -0.55 (s, 9H), 1.09 (d, J = 6.8 Hz, 12H), 1.24 (d, J = 6.9 Hz, 12H), 2.73 (p, J = 6.7 Hz, 4H), 7.13 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.8 Hz, 4H), 7.28 – 7.42 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ -6.53, 22.83, 25.75, 30.37, 122.71, 126.68, 128.12, 129.14, 141.64, 142.21, 146.86, 147.76.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -54.27.

Tributyl(thien-2-yl)stannane (7ba)[10]



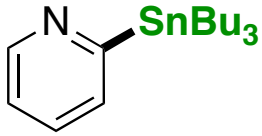
Colorless oil, isolated yield 73%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 9H), 1.02 – 1.20 (m, 6H), 1.35 (dq, J = 14.5, 7.3 Hz, 6H), 1.49 – 1.67 (m, 6H), 7.21 (dd, J = 3.2, 0.8 Hz, 1H), 7.24 – 7.30 (m, 1H), 7.66 (dd, J = 4.7, 0.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 10.79, 13.64, 27.24, 28.94, 127.80, 130.55, 135.15, 136.16.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -39.75.

2-(Tributylstannyl)pyridine (7bb)[10]



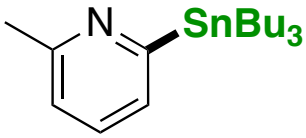
Colorless oil, isolated yield 49%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 9H), 1.01 – 1.20 (m, 6H), 1.25 – 1.39 (m, 6H), 1.45 – 1.64 (m, 6H), 7.02 – 7.17 (m, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.44 – 7.51 (m, 1H), 8.73 (d, J = 4.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.73, 13.67, 27.33, 29.06, 121.96, 132.34, 133.22, 150.51, 174.07.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -63.43.

2-Methyl-6-(tributylstannyl)pyridine (7bc)[17]



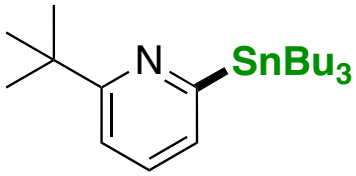
Colorless oil, isolated yield 64%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 9H), 1.02 – 1.19 (m, 6H), 1.33 (h, J = 7.3 Hz, 6H), 1.48 – 1.66 (m, 6H), 2.54 (s, 3H), 6.95 (dd, J = 7.9, 1.2 Hz, 1H), 7.18 (d, J = 8.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 9.81, 13.70, 24.96, 27.34, 29.08, 121.52, 129.39, 133.29, 158.59, 173.04.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -66.32.

2-*tert*-Butyl-6-(tributylstannyl)pyridine (7bd)



Colorless oil, isolated yield 66%

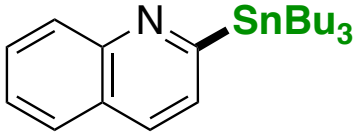
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 9H), 0.99 – 1.16 (m, 6H), 1.27 – 1.40 (m, 15H), 1.51 – 1.69 (m, 6H), 7.12 (dd, J = 8.0, 1.2 Hz, 1H), 7.17 (dd, J = 7.2, 1.2 Hz, 1H), 7.36 – 7.45 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 10.40, 14.13, 27.73, 29.52, 30.56, 37.99, 117.19, 129.44, 133.59, 169.17, 172.71.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -69.22.

HRMS (FI) Calcd for $C_{17}H_{30}NSn$: $[M\text{-}C_4H_9]^+$, 368.13947. Found: m/z 368.13974.

2-(Tributylstannyl)quinoline (7be)



Colorless oil, isolated yield 68%

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 9H), 1.12 – 1.30 (m, 6H), 1.37 (h, J = 7.5 Hz, 6H), 1.53 – 1.73 (m, 6H), 7.45 – 7.54 (m, 2H), 7.64 – 7.71 (m, 1H), 7.75 (d, J = 9.5 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 10.06, 13.73, 27.38, 29.14, 125.82, 125.91, 127.14, 127.80, 128.61, 128.70, 132.04, 149.35, 177.04.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -65.04.

HRMS (FI) Calcd for $C_{17}H_{25}NSn$: $[M\text{-}C_4H_9]^+$, 363.10035. Found: m/z 363.10056.

5. Mechanistic studies

5.1 Formation of *tert*-butyl dimethylphenylsilyl ether (8)

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with trimethyl(dimetylphenylsilyl)stannane (**1a**) (65.8 mg, 0.22 mmol), 2'-iodo-2,2",6,6"-tetraisopropyl-1,1':3',1"-terphenyl (**3w**) (105.0 mg, 0.20 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.22 mL, 0.22 mmol). The resulting mixture was stirred at 30 °C for 1 h and was diluted with hexane. The organic solution was filtered through celite pad and concentrated by rotary evaporation. Tthe crude material was purified by GPC to give *tert*-butyl dimethylphenylsilyl ether (**8**) (21.2 mg, 51%).

tert-Butyl dimethylphenylsilyl ether (8)[18]

$PhMe_2Si—Ot\text{-}Bu$

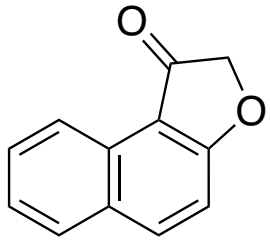
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.38 (s, 6H), 1.25 (s, 9H), 7.31 – 7.39 (m, 3H), 7.56 – 7.65 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 1.39, 32.06, 72.76, 127.61, 129.03, 133.33, 140.58.

5.2 Reaction with 6f

In an argon-filled glovebox, a flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with $KSnMe_3$ (**2a'**) (40.6 mg, 0.22 mmol), THF (0.67 mL). The Schlenk tube was taken from the glovebox, and ethyl 2-[(1-bromo-2-naphthalenyl)oxy]acetate (**6f**) (61.8 mg, 0.2 mmol) was added to the mixture. The resulting mixture was stirred at 30 °C for 1 h and was diluted with $CHCl_3$. The organic solution was filtered through celite pad and concentrated by rotary evaporation. The crude material was purified by GPC to give naphtho[2,1-*b*]furan-1(2*H*)-one (**9**) (3.7 mg, 10%) as a white solid.

Naphtho[2,1-*b*]furan-1(2*H*)-one (9)[19]



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 (s, 2H), 7.28 (d, J = 9.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 8.77 (d, J = 8.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 75.52, 113.31, 114.00, 123.15, 125.47, 128.48, 129.11, 129.17, 129.90, 139.87, 199.37.

5.3 Reaction conducted in THF-d_8

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with tributyl(trimethylsilyl)stannane (**1b**) (39.9mg, 0.11 mmol), 2,4,6-tri-*tert*-butylphenyl bromide (**6g**) (32.5 mg, 0.10 mmol), THF-d_8 (0.5 mL) and *t*-BuOK (12.34 mg, 0.11 mmol). The resulting mixture was stirred at 30 °C for 1 h and was diluted with EtOAc. The organic solution was filtered through celite pad and concentrated by rotary evaporation. The deuterium incorporation ratio (52% D) and the yield (24%) of 2,4,6-tri-*tert*-butylbenzene (**10**) was determined by ^{1}H NMR analysis of the crude reaction mixture. The presence of the deuterium on the benzene ring was also confirmed by ^{2}D NMR analysis.

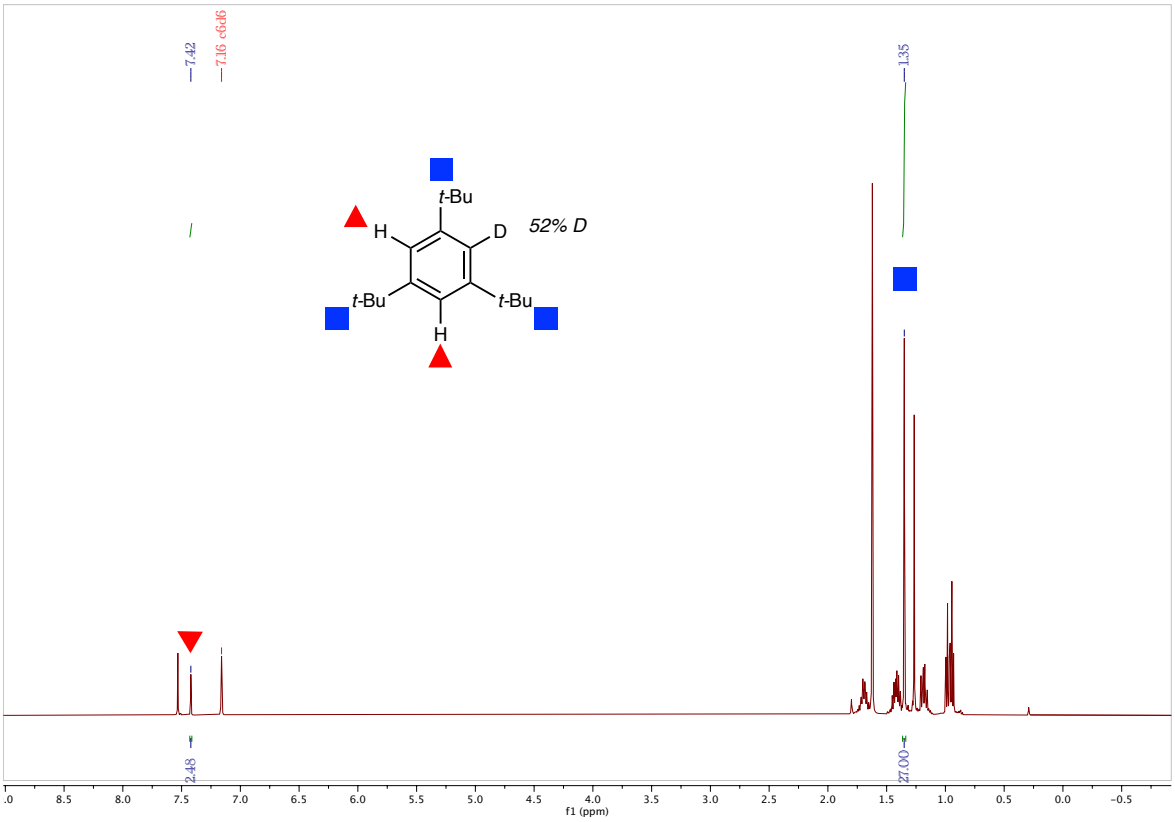


Figure S4. ^{1}H NMR of 10 in benzene-d_6

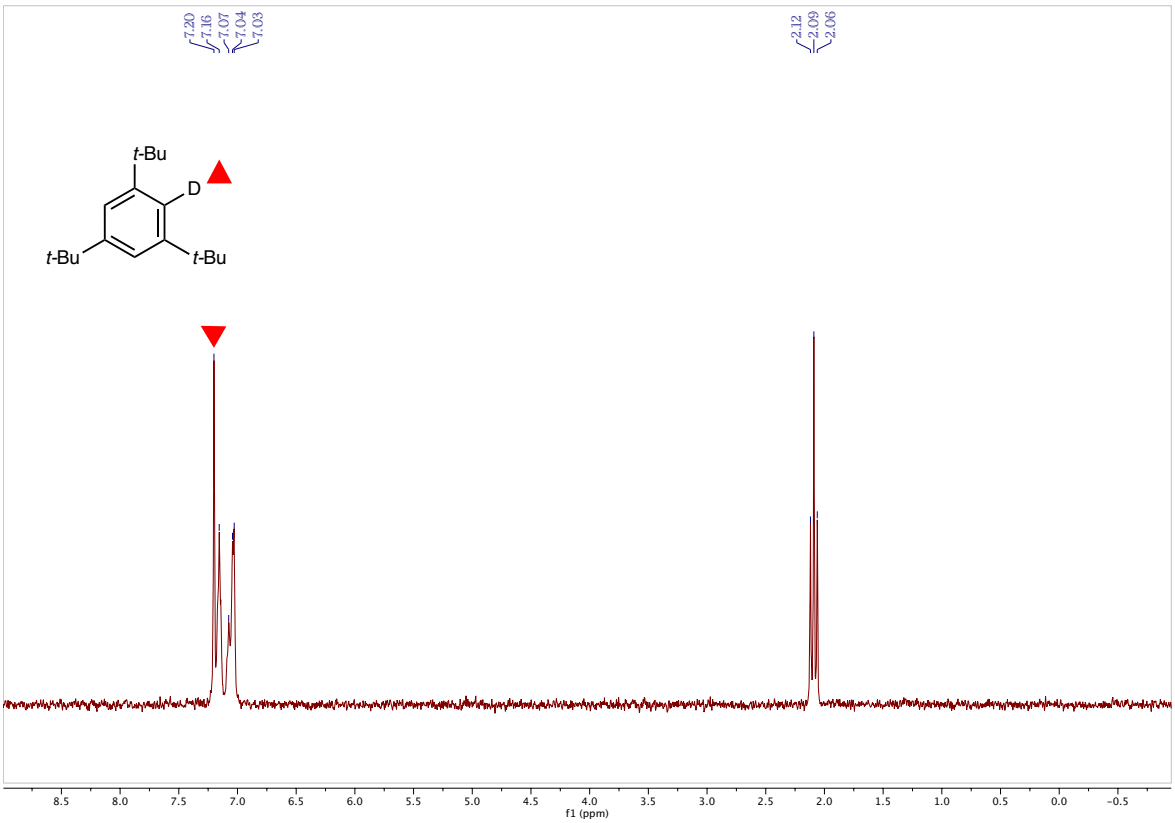


Figure S5. ^{2}D NMR of 10 in toluene

5.4 Confirmation of tin-based by-products in the reaction of 6g

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with tributyl(trimethylsilyl)stannane (**1b**) (79.8 mg, 0.22 mmol), 2,4,6-tri-*tert*-butylphenyl bromide (**6g**) (65.1 mg, 0.20 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.22 mL, 0.22 mmol). The resulting mixture was stirred at 30 °C for 1 h and analyzed by ^{119}Sn NMR, confirming the formation of Bu_3SnO*t*-Bu (62.19 ppm) and $Bu_3SnSnBu_3$ (-84.27 ppm).

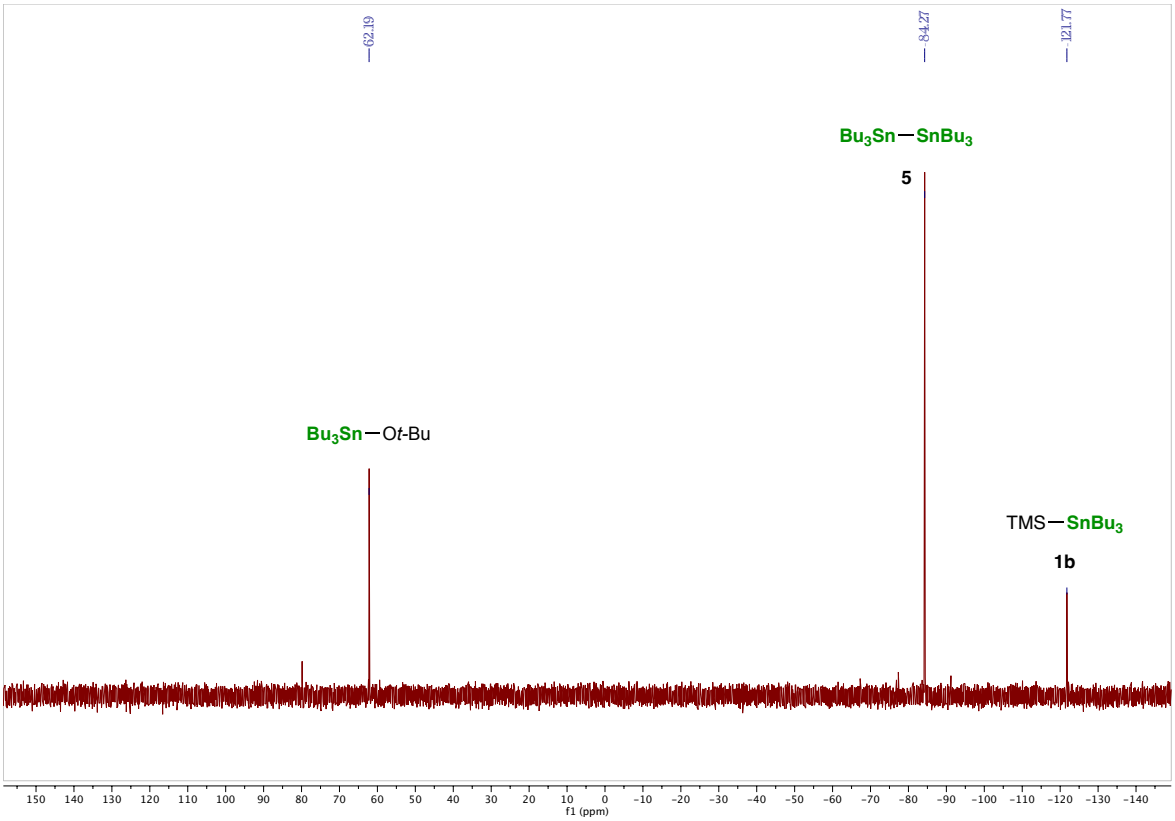


Figure S6. ^{119}Sn NMR of tin-based by-products

The formation of Bu_3SnO*t*-Bu from Bu_3SnBr and *t*-BuOK was verified as follows: A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with Bu_3SnBr (73.9 mg, 0.20 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.20 mL, 0.20 mmol). The resulting mixture was stirred at 30 °C for 1 h and was analyzed by ^{119}Sn NMR.

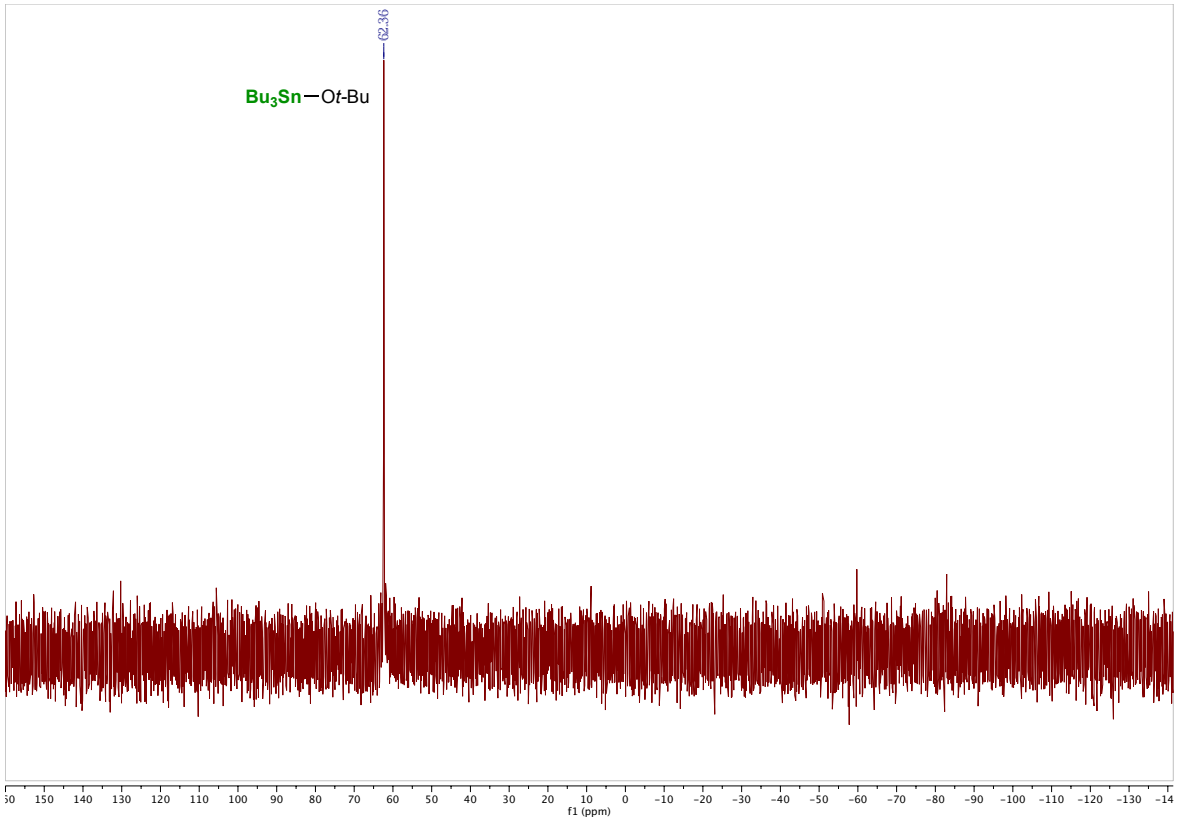


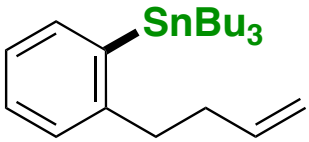
Figure S7. ^{119}Sn NMR of Bu_3SnO*t*-Bu (from Bu_3SnBr and *t*-BuOK)

6. Control experiments

6.1 Radical clock experiment

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with tributyl(trimethylsilyl)stannane (**1b**) (79.9 mg, 0.22 mmol), 1-bromo-2-(but-3-enyl)benzene (**6h**) (42.2 mg, 0.20 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.22 mL, 0.22 mmol). The resulting mixture was stirred at 30 °C for 1 h and was diluted with hexane. The organic solution was filtered through celite pad and concentrated by rotary evaporation. The crude material was purified by GPC to give tributyl(2-(but-3-en-1-yl)phenyl)stannane (**6bh**) (32.1 mg, 38%).

(2-(But-3-en-1-yl)phenyl)tributylstannane (6bh)



^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 9H), 0.99 – 1.17 (m, 6H), 1.34 (h, J = 7.3 Hz, 6H), 1.47 – 1.60 (m, 6H), 2.30 – 2.41 (m, 2H), 2.62 – 2.76 (m, 2H), 4.96 – 5.16 (m, 2H), 5.91 (ddt, J = 16.8, 10.3, 6.5 Hz, 1H), 7.13 – 7.20 (m, 1H), 7.20 – 7.31 (m, 2H), 7.40 (d, J = 8.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 10.36, 13.67, 27.43, 29.15, 36.41, 38.60, 114.85, 125.33, 127.95, 128.32, 136.77, 138.08, 141.79, 148.65.

^{119}Sn NMR (186 MHz, $CDCl_3$) δ -41.61.

HRMS (FI) Calcd for $C_{18}H_{29}Sn$: $[M\text{-}C_4H_9]^+$, 365.12857. Found: m/z 365.12860.

6.2 Stannylation reaction in the presence of a radical scavenger

A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with tributyl(trimethylsilyl)stannane (**1b**) (79.9 mg, 0.22 mmol), 1-iodonaphthalane (**3m**) (50.8 mg, 0.20 mmol), 9,10-dihydroanthracene (36.1 mg, 0.2 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.22 mL, 0.22 mmol). The resulting mixture was stirred at 30 °C for 1 h and was diluted with hexane. The organic solution was filtered through celite pad and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (hexane as an eluent) to give tributyl(naphthalene-1-yl)stannane (**4bm**) (49.8 mg, 59%).

6.3 Stannylation reaction conducted under dark conditions

A flame-dried Schlenk tube equipped with a magnetic stirring bar and covered with aluminum foil was charged with tributyl(trimethylsilyl)stannane (**1b**) (79.9 mg, 0.22 mmol), 1-iodonaphthalane (**3m**) (50.8 mg, 0.20 mmol), THF (0.67 mL) and *t*-BuOK (1 M in THF, 0.22 mL, 0.22 mmol). The resulting mixture was stirred at 30 °C for 1 h. The yield of tributyl(naphthalene-1-yl)stannane (**4bm**) (86%) was determined by ^{119}Sn NMR analysis of the

crude reaction mixture.

7. Computational Details

DFT calculation

Gas-phase theoretical calculations were conducted using the Gaussian16 program.[20] Geometry optimization was carried out without symmetry constraints using the hybrid range-separated density function, ω-B97XD, and the basis set was employed for def2-svp. The same manner of optimization obtained NBO ver. 3.1 analysis result. The wave function for AIM analysis was obtained from the Gaussian16 program using the level of theory. The NBO result and molecular graph for AIM were drawn using Avogadro. The bond critical point for (1, 1) was calculated by use of AIM2000[21] These results were illustrated by use of Avogadro program. [22,23]

Me_3Sn–Li

SCF Energy –341.4908096593 a.u.

C	1.69847726	-1.21917638	-0.00000000
C	0.10602070	1.23861095	1.66825757
C	0.10602070	1.23861095	-1.66825757
Sn	-0.38539471	-0.09371278	0.00000000
H	1.95880909	-1.81593162	-0.89743036
H	2.40674384	-0.38422663	-0.00000000
H	1.95880909	-1.81593162	0.89743036
H	-0.66786123	2.00620993	1.79450408
H	0.19045452	0.69102876	2.61481810
H	1.05950637	1.74734666	1.47328458
H	-0.66786123	2.00620993	-1.79450408
H	1.05950637	1.74734666	-1.47328458
H	0.19045452	0.69102876	-2.61481810
Li	0.10602070	-2.57857170	0.00000000

Me_3Sn–K

SCF Energy –2372.725906417 a.u.

C	1.80382987	-0.38643282	0.00000000
C	-0.02916812	1.84797591	1.66845781
C	-0.02916812	1.84797591	-1.66845781
K	-0.02916812	-2.77299590	0.00000000
Sn	-0.33373678	0.43455320	0.00000000
H	2.05678870	-0.98452187	-0.89993357
H	2.50310634	0.46542025	0.00000000
H	2.05678870	-0.98452187	0.89993357
H	-0.90950236	2.49736864	1.79942220
H	0.14083667	1.31638466	2.61870657

H	0.84435952	2.48913242	1.46588748
H	-0.90950236	2.49736864	-1.79942220
H	0.84435952	2.48913242	-1.46588748
H	0.14083667	1.31638466	-2.61870657

NBO Calculation date

Me_3Sn–Li

1. (1.98729) BD (1) C 1 - Sn 4
   (81.58%) 0.9032* C 1 s(25.32%)p 2.95(74.68%)d 0.00(0.00%)
   -0.0000 -0.5019 0.0356 0.0008 0.8152
   -0.0673 -0.0071 -0.2781 -0.0166 -0.0043
   0.0000 0.0000 0.0000 -0.0024 0.0000
   -0.0000 -0.0032 0.0035
   (18.42%) 0.4292* Sn 4 s(10.41%)p 8.61(89.59%)
   -0.3224 -0.0116 -0.8294 -0.0098 0.4536
   0.0459 -0.0000 -0.0000
2. (1.99233) BD (1) C 1 - H 5
   (61.09%) 0.7816* C 1 s(24.53%)p 3.07(75.39%)d 0.00(0.08%)
   0.0000 0.4951 0.0116 -0.0020 0.1400
   0.0117 0.0152 -0.4843 -0.0047 0.0042
   -0.7057 -0.0379 -0.0005 -0.0053 -0.0100
   0.0225 -0.0093 0.0092
   (38.91%) 0.6238* H 5 s(100.00%)
   1.0000 -0.0002
3. (1.99513) BD (1) C 1 - H 6
   (64.39%) 0.8024* C 1 s(25.54%)p 2.91(74.41%)d 0.00(0.06%)
   0.0001 0.5046 0.0270 0.0042 0.5398
   0.0067 0.0129 0.6726 0.0059 -0.0034
   0.0000 0.0000 0.0000 0.0209 0.0000
   -0.0000 0.0024 -0.0107
   (35.61%) 0.5967* H 6 s(100.00%)
   1.0000 0.0028
4. (1.99233) BD (1) C 1 - H 7
   (61.09%) 0.7816* C 1 s(24.53%)p 3.07(75.39%)d 0.00(0.08%)
   0.0000 0.4951 0.0116 -0.0020 0.1400
   0.0117 0.0152 -0.4843 -0.0047 0.0042
   0.7057 0.0379 0.0005 -0.0053 0.0100
   -0.0225 -0.0093 0.0092
   (38.91%) 0.6238* H 7 s(100.00%)

1.0000 -0.0002

5. (1.98048) BD (1) C 2 - Sn 4

(75.03%) 0.8662* C 2 s(23.79%)p 3.20(76.20%)d 0.00(0.01%)

-0.0002 -0.4869 0.0280 0.0082 0.1980

-0.0094 -0.0053 0.5432 -0.0325 -0.0061

0.6520 -0.0373 -0.0043 -0.0034 -0.0036

-0.0092 0.0032 -0.0036

(24.97%) 0.4997* Sn 4 s(28.34%)p 2.53(71.66%)

-0.5318 -0.0254 -0.0469 0.0076 -0.4627

-0.0156 -0.7063 -0.0345

6. (1.99517) BD (1) C 2 - H 8

(62.35%) 0.7896* C 2 s(25.06%)p 2.99(74.88%)d 0.00(0.07%)

0.0000 0.5004 0.0120 0.0020 -0.6375

-0.0137 0.0002 0.5785 0.0137 0.0056

0.0855 0.0047 0.0077 -0.0219 -0.0051

0.0039 0.0005 -0.0119

(37.65%) 0.6136* H 8 s(100.00%)

1.0000 -0.0001

7. (1.99539) BD (1) C 2 - H 9

(62.11%) 0.7881* C 2 s(25.29%)p 2.95(74.64%)d 0.00(0.07%)

-0.0000 0.5027 0.0129 0.0029 0.0798

0.0016 -0.0004 -0.4547 -0.0096 0.0055

0.7299 0.0193 0.0076 -0.0027 0.0034

-0.0184 -0.0041 0.0169

(37.89%) 0.6155* H 9 s(100.00%)

1.0000 -0.0000

8. (1.99631) BD (1) C 2 - H 10

(62.18%) 0.7885* C 2 s(25.80%)p 2.87(74.13%)d 0.00(0.06%)

-0.0000 0.5078 0.0118 -0.0012 0.7393

0.0177 -0.0002 0.4022 0.0113 0.0054

-0.1800 0.0004 0.0073 0.0188 -0.0049

-0.0033 0.0100 -0.0122

(37.82%) 0.6150* H 10 s(100.00%)

1.0000 0.0030

9. (1.98048) BD (1) C 3 - Sn 4

(75.03%) 0.8662* C 3 s(23.79%)p 3.20(76.20%)d 0.00(0.01%)

-0.0002 -0.4869 0.0280 0.0082 0.1980

-0.0094 -0.0053 0.5432 -0.0325 -0.0061

-0.6520 0.0373 0.0043 -0.0034 0.0036

0.0092 0.0032 -0.0036

(24.97%) 0.4997* Sn 4 s(28.34%)p 2.53(71.66%)

-0.5318 -0.0254 -0.0469 0.0076 -0.4627

-0.0156 0.7063 0.0345

10. (1.99517) BD (1) C 3 - H 11

(62.35%) 0.7896* C 3 s(25.06%)p 2.99(74.88%)d 0.00(0.07%)

0.0000 0.5004 0.0120 0.0020 -0.6375

-0.0137 0.0002 0.5785 0.0137 0.0056

-0.0855 -0.0047 -0.0077 -0.0219 0.0051

-0.0039 0.0005 -0.0119

(37.65%) 0.6136* H 11 s(100.00%)

1.0000 -0.0001

11. (1.99631) BD (1) C 3 - H 12

(62.18%) 0.7885* C 3 s(25.80%)p 2.87(74.13%)d 0.00(0.06%)

-0.0000 0.5078 0.0118 -0.0012 0.7393

0.0177 -0.0002 0.4022 0.0113 0.0054

0.1800 -0.0004 -0.0073 0.0188 0.0049

0.0033 0.0100 -0.0122

(37.82%) 0.6150* H 12 s(100.00%)

1.0000 0.0030

12. (1.99539) BD (1) C 3 - H 13

(62.11%) 0.7881* C 3 s(25.29%)p 2.95(74.64%)d 0.00(0.07%)

0.0000 -0.5027 -0.0129 -0.0029 -0.0798

-0.0016 0.0004 0.4547 0.0096 -0.0055

0.7299 0.0193 0.0076 0.0027 0.0034

-0.0184 0.0041 -0.0169

(37.89%) 0.6155* H 13 s(100.00%)

-1.0000 0.0000

13. (1.86570) BD (1) Sn 4 - Li 14

(90.74%) 0.9526* Sn 4 s(33.05%)p 2.03(66.95%)

0.5744 -0.0233 -0.5524 0.0305 -0.6028

0.0104 0.0000 0.0000

(9.26%) 0.3043* Li 14 s(87.86%)p 0.13(11.33%)d 0.01(0.80%)

-0.0008 0.9373 0.0053 -0.0022 -0.2705

-0.0024 0.0034 0.2002 -0.0034 0.0073

0.0000 0.0000 0.0000 -0.0570 0.0000

0.0000 -0.0468 -0.0510

Me_3Sn–K

1. (1.98297) BD (1) C 1 - Sn 5
   (80.43%) 0.8968* C 1 s(26.75%)p 2.74(73.25%) d 0.00 (0.00%)
   -0.0002 -0.5166 0.0238 0.0016 0.8164
   -0.0604 -0.0097 -0.2496 0.0002 0.0011
   -0.0000 -0.0000 -0.0000 -0.0004 -0.0000
   0.0000 -0.0014 0.0001
   (19.57%) 0.4424* Sn 5 s(9.12%)p 9.97 (90.88%)
   -0.3010 -0.0237 -0.8932 -0.0362 0.3258
   0.0591 -0.0000 -0.0000
2. (1.99574) BD (1) C 1 - H 6
   (60.24%) 0.7762* C 1 s(23.93%)p 3.18(75.99%)d 0.00(0.08%)
   0.0000 0.4891 0.0117 0.0014 0.1618
   0.0057 0.0101 -0.4839 -0.0054 -0.0019
   -0.7059 -0.0331 -0.0007 -0.0078 -0.0111
   0.0210 -0.0081 0.0100
   (39.76%) 0.6305* H 6 s(100.00%)
   1.0000 -0.0001
3. (1.99708) BD (1) C 1 - H 7
   (63.18%) 0.7949* C 1 s(25.27%)p 2.96(74.67%)d 0.00(0.07%)
   0.0001 0.5025 0.0106 -0.0008 0.5276
   0.0075 0.0116 0.6841 0.0109 -0.0011
   0.0000 0.0000 0.0000 0.0232 0.0000
   -0.0000 0.0017 -0.0115
   (36.82%) 0.6068* H 7 s(100.00%)
   1.0000 0.0039
4. (1.99574) BD (1) C 1 - H 8
   (60.24%) 0.7762* C 1 s(23.93%)p 3.18(75.99%)d 0.00(0.08%)
   0.0000 0.4891 0.0117 0.0014 0.1618
   0.0057 0.0101 -0.4839 -0.0054 -0.0019
   0.7059 0.0331 0.0007 -0.0078 0.0111
   -0.0210 -0.0081 0.0100
   (39.76%) 0.6305* H 8 s(100.00%)
   1.0000 -0.0001
5. (1.97696) BD (1) C 2 - Sn 5
   (76.60%) 0.8752* C 2 s(24.95%)p 3.01(75.05%)d 0.00(0.00%)
   -0.0003 -0.4988 0.0178 0.0193 0.1292
   -0.0080 0.0010 0.5613 -0.0367 -0.0016
   0.6449 -0.0371 -0.0081 -0.0006 -0.0017

-0.0050 0.0022 -0.0022

(23.40%) 0.4838* Sn 5 s(15.00%)p 5.67(85.00%)

-0.3864 -0.0265 -0.0845 0.0228 -0.5849

-0.0164 -0.7041 -0.0648

6. (1.99574) BD (1) C 2 - H 9

(62.00%) 0.7874* C 2 s(24.88%)p 3.02(75.06%)d 0.00(0.07%)

0.0000 0.4986 0.0070 0.0087 -0.6995

-0.0176 0.0011 0.5030 0.0120 0.0065

0.0881 0.0021 0.0084 -0.0213 -0.0061

0.0041 0.0050 -0.0116

(38.00%) 0.6165* H 9 s(100.00%)

1.0000 -0.0001

7. (1.99568) BD (1) C 2 - H 10

(61.64%) 0.7851* C 2 s(24.86%)p 3.02(75.07%)d 0.00(0.07%)

0.0000 0.4985 0.0069 0.0095 0.1354

0.0031 0.0000 -0.4346 -0.0119 0.0070

0.7368 0.0191 0.0076 -0.0034 0.0058

-0.0174 -0.0031 0.0178

(38.36%) 0.6193* H 10 s(100.00%)

1.0000 -0.0000

8. (1.99679) BD (1) C 2 - H 11

(61.96%) 0.7872* C 2 s(25.24%)p 2.96(74.69%)d 0.00(0.07%)

-0.0000 0.5023 0.0096 0.0061 0.6886

0.0163 -0.0002 0.4910 0.0126 0.0067

-0.1764 -0.0026 0.0077 0.0210 -0.0041

-0.0037 0.0053 -0.0126

(38.04%) 0.6167* H 11 s(100.00%)

1.0000 0.0038

9. (1.97696) BD (1) C 3 - Sn 5

(76.60%) 0.8752* C 3 s(24.95%)p 3.01(75.05%)d 0.00(0.00%)

-0.0003 -0.4988 0.0178 0.0193 0.1292

-0.0080 0.0010 0.5613 -0.0367 -0.0016

-0.6449 0.0371 0.0081 -0.0006 0.0017

0.0050 0.0022 -0.0022

(23.40%) 0.4838* Sn 5 s(15.00%)p 5.67(85.00%)

-0.3864 -0.0265 -0.0845 0.0228 -0.5849

-0.0164 0.7041 0.0648

10. (1.99574) BD (1) C 3 - H 12

(62.00%) 0.7874* C 3 s(24.88%)p 3.02(75.06%)d 0.00(0.07%)

0.0000 0.4986 0.0070 0.0087 -0.6995
-0.0176 0.0011 0.5030 0.0120 0.0065
-0.0881 -0.0021 -0.0084 -0.0213 0.0061
-0.0041 0.0050 -0.0116

(38.00%) 0.6165* H 12 s(100.00%)
1.0000 -0.0001

11. (1.99679) BD (1) C 3 - H 13

(61.96%) 0.7872* C 3 s(25.24%)p 2.96(74.69%)d 0.00(0.07%)
-0.0000 0.5023 0.0096 0.0061 0.6886
0.0163 -0.0002 0.4910 0.0126 0.0067
0.1764 0.0026 -0.0077 0.0210 0.0041
0.0037 0.0053 -0.0126

(38.04%) 0.6167* H 13 s(100.00%)
1.0000 0.0038

12. (1.99568) BD (1) C 3 - H 14

(61.64%) 0.7851* C 3 s(24.86%)p 3.02(75.07%)d 0.00(0.07%)
-0.0000 -0.4985 -0.0069 -0.0095 -0.1354
-0.0031 -0.0000 0.4346 0.0119 -0.0070
0.7368 0.0191 0.0076 0.0034 0.0058
-0.0174 0.0031 -0.0178

(38.36%) 0.6193* H 14 s(100.00%)

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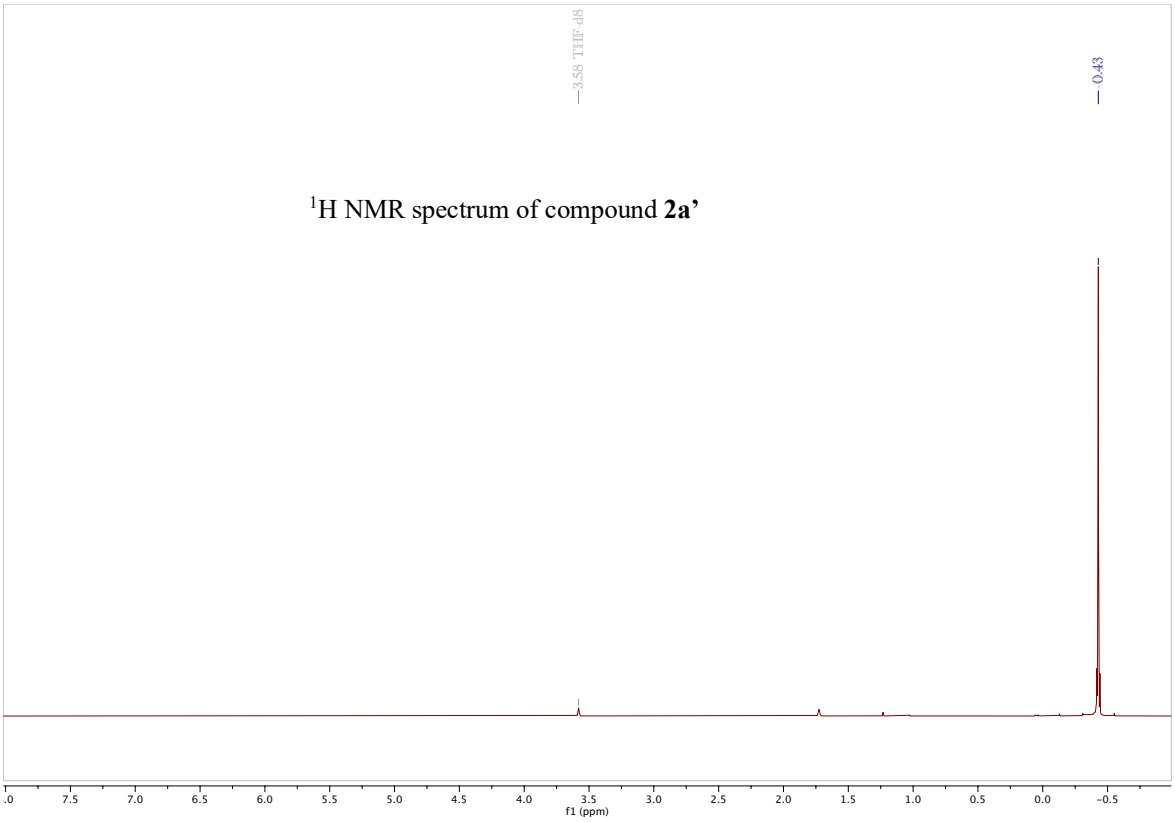
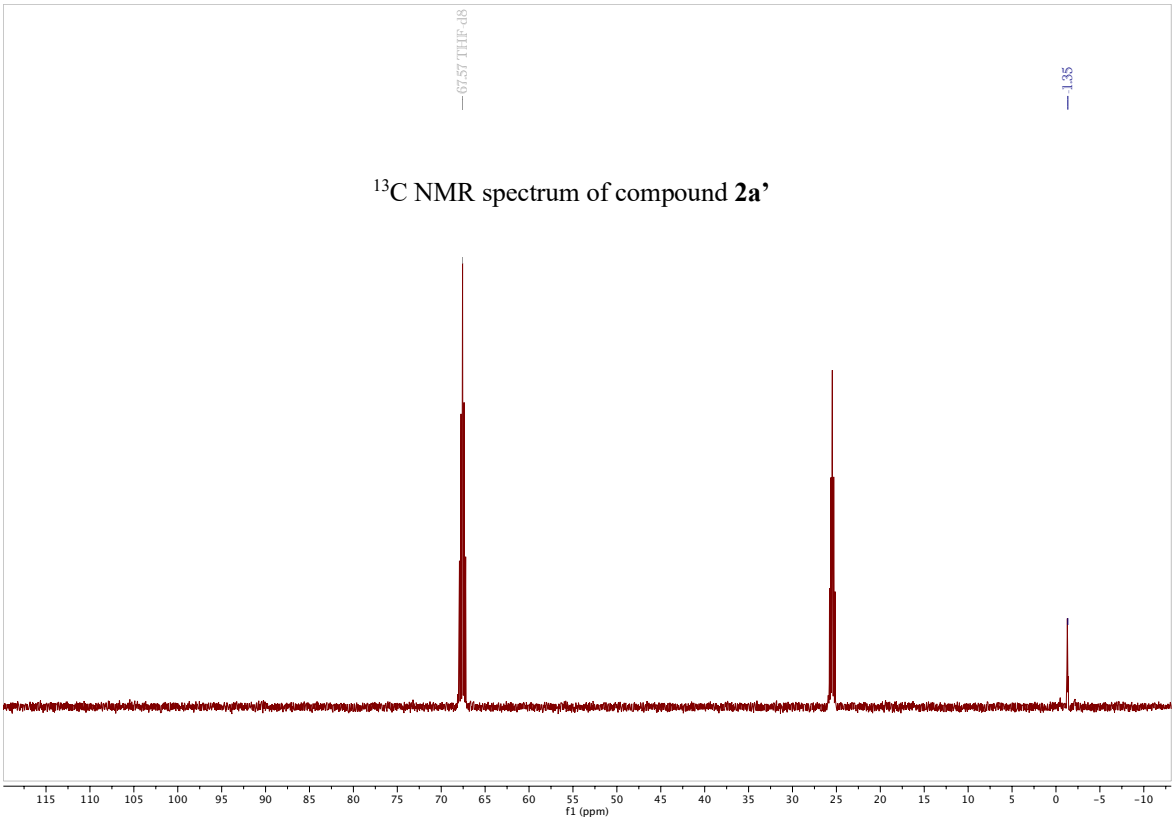
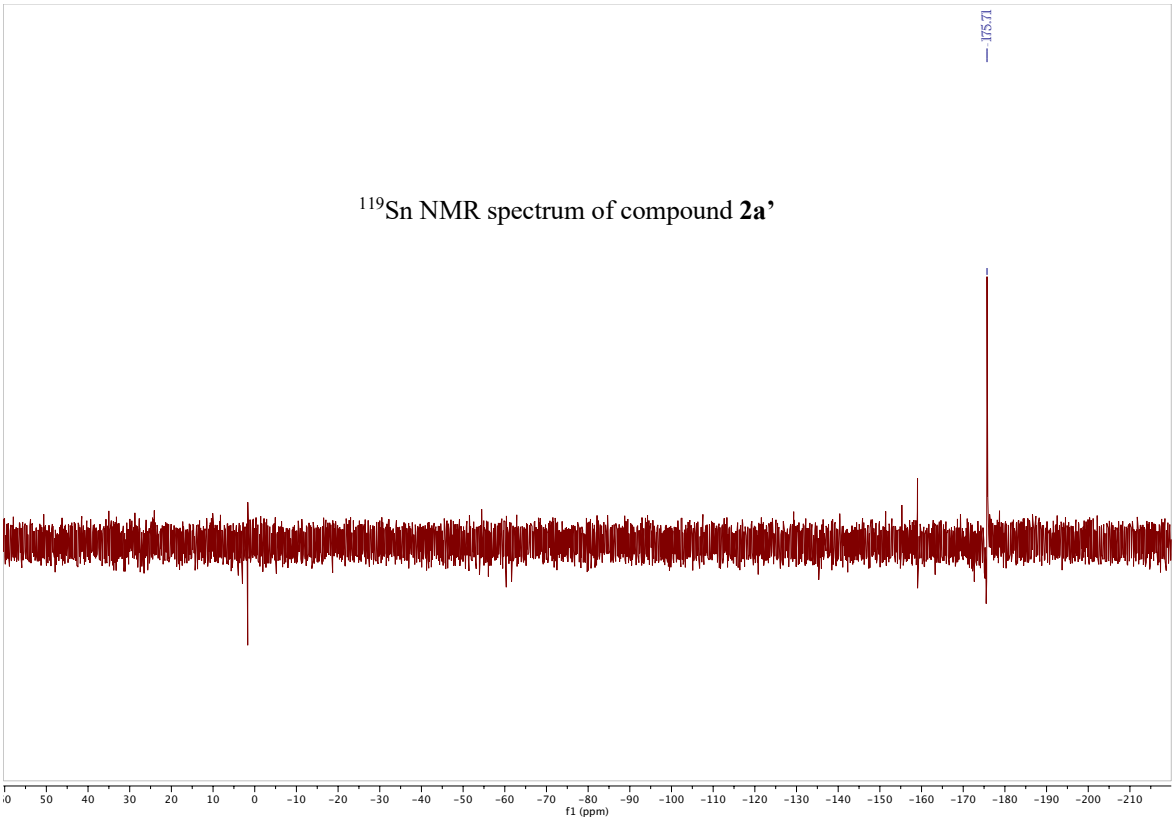
9. NMR spectra



^{1}H NMR spectrum of compound **2a'**

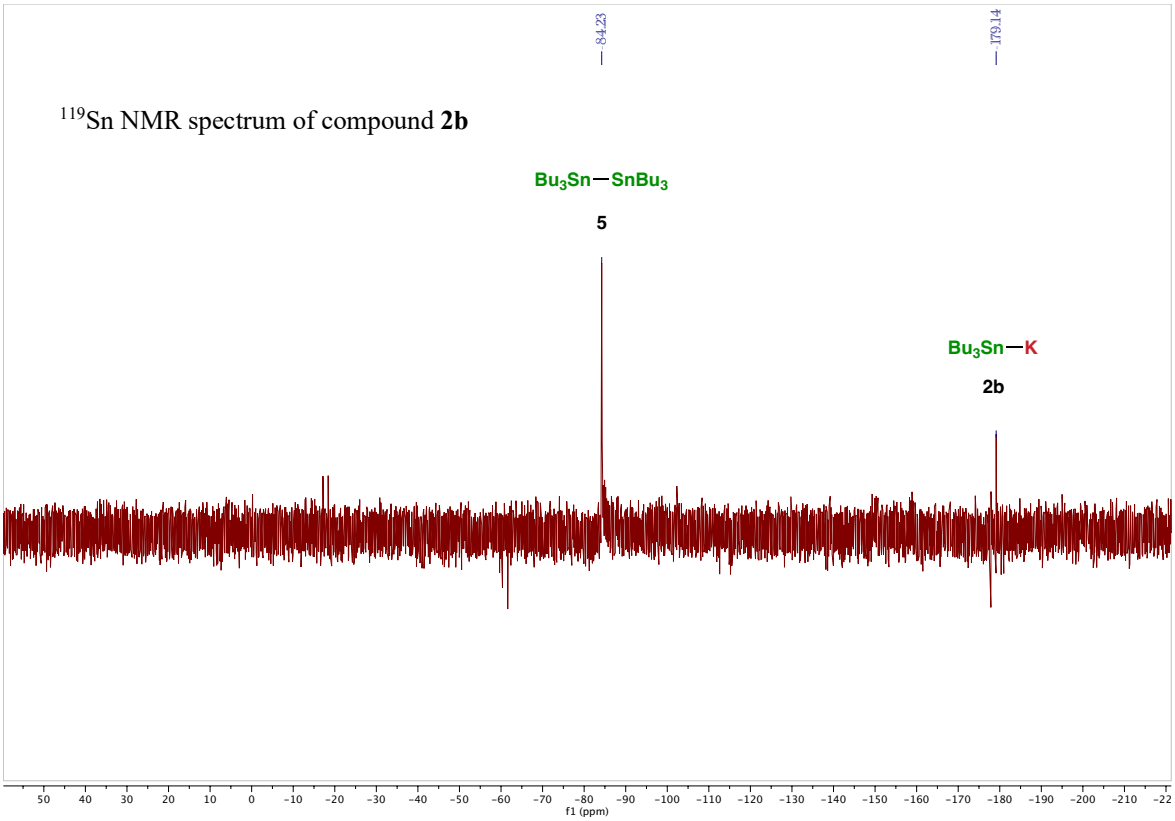


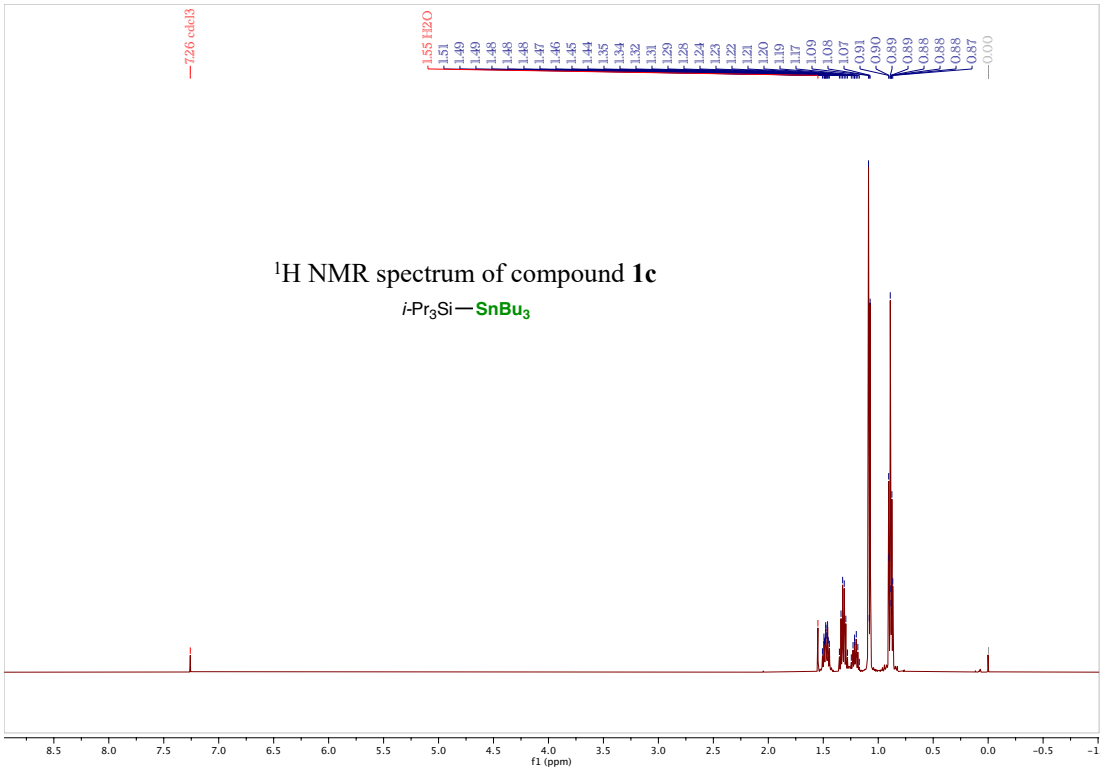
^{13}C NMR spectrum of compound **2a'**



^{119}Sn NMR spectrum of compound **2a'**

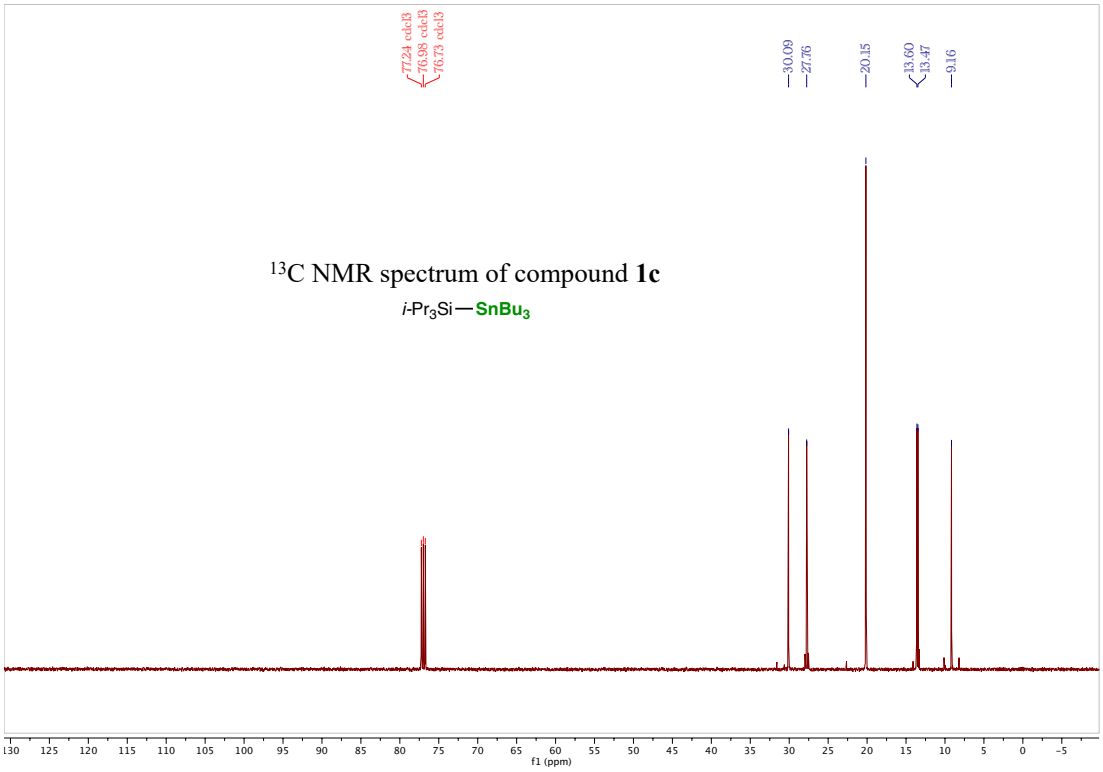
^{119}Sn NMR spectrum of compound **2b**





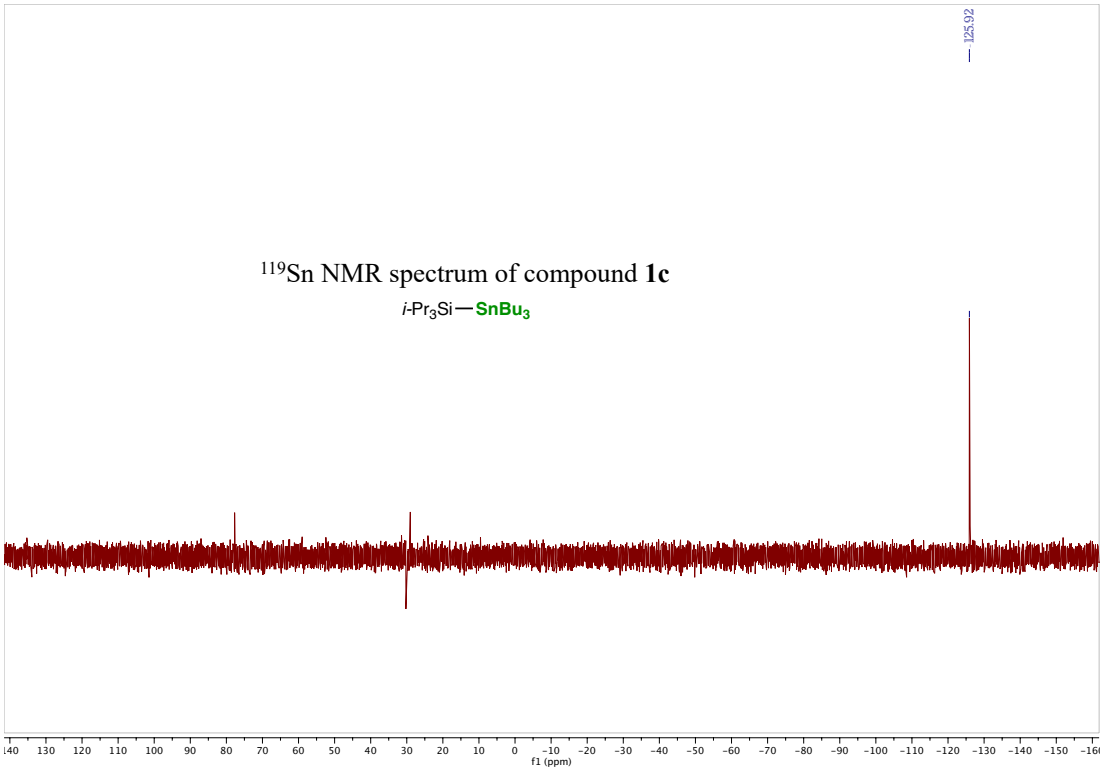
^{1}H NMR spectrum of compound **1c**

i-Pr_3Si—$SnBu_3$



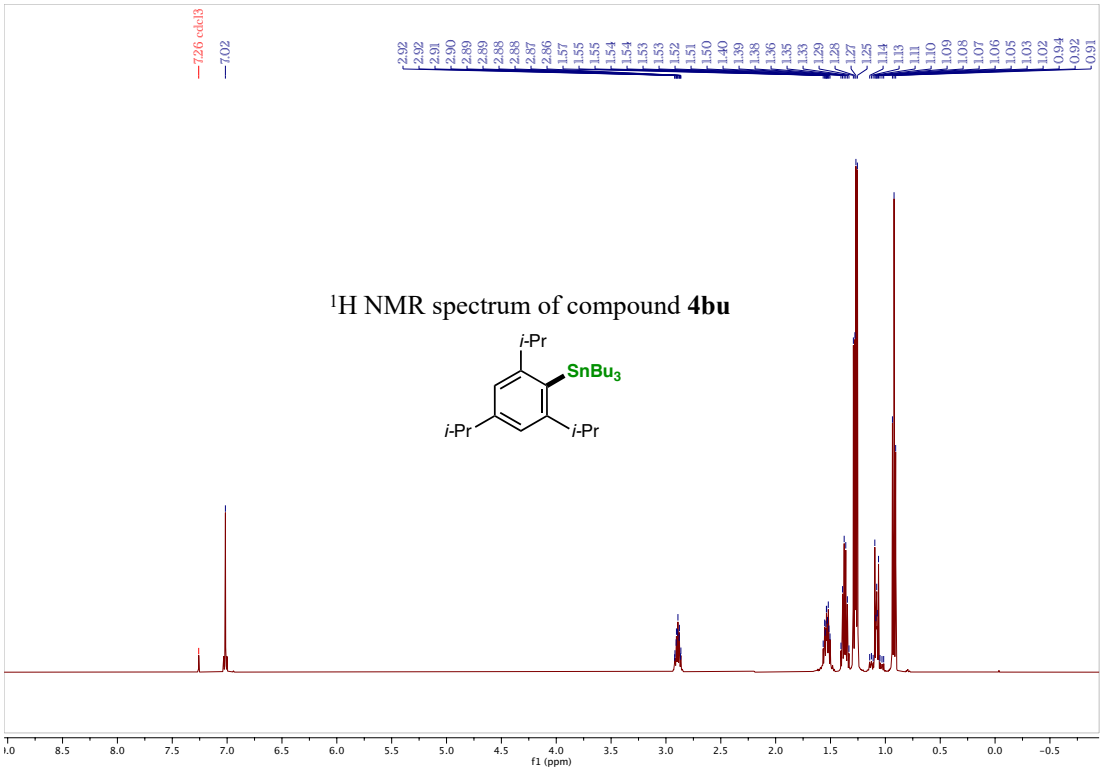
^{13}C NMR spectrum of compound **1c**

i-Pr_3Si—$SnBu_3$

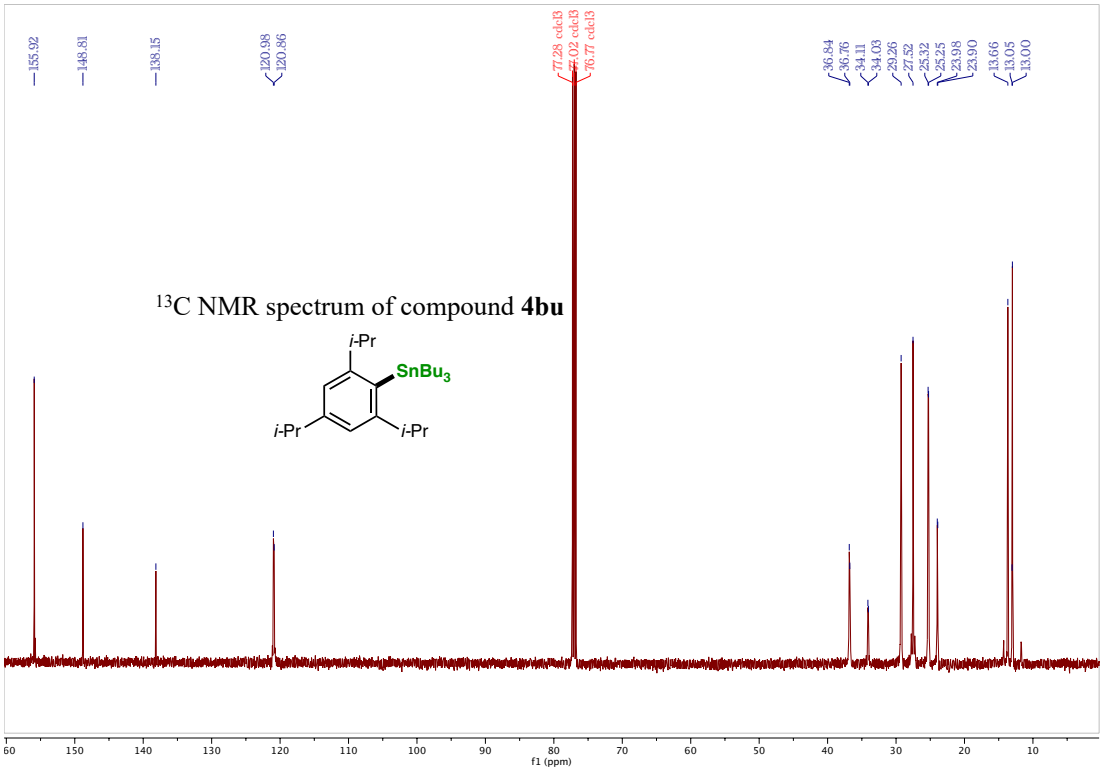


^{119}Sn NMR spectrum of compound **1c**

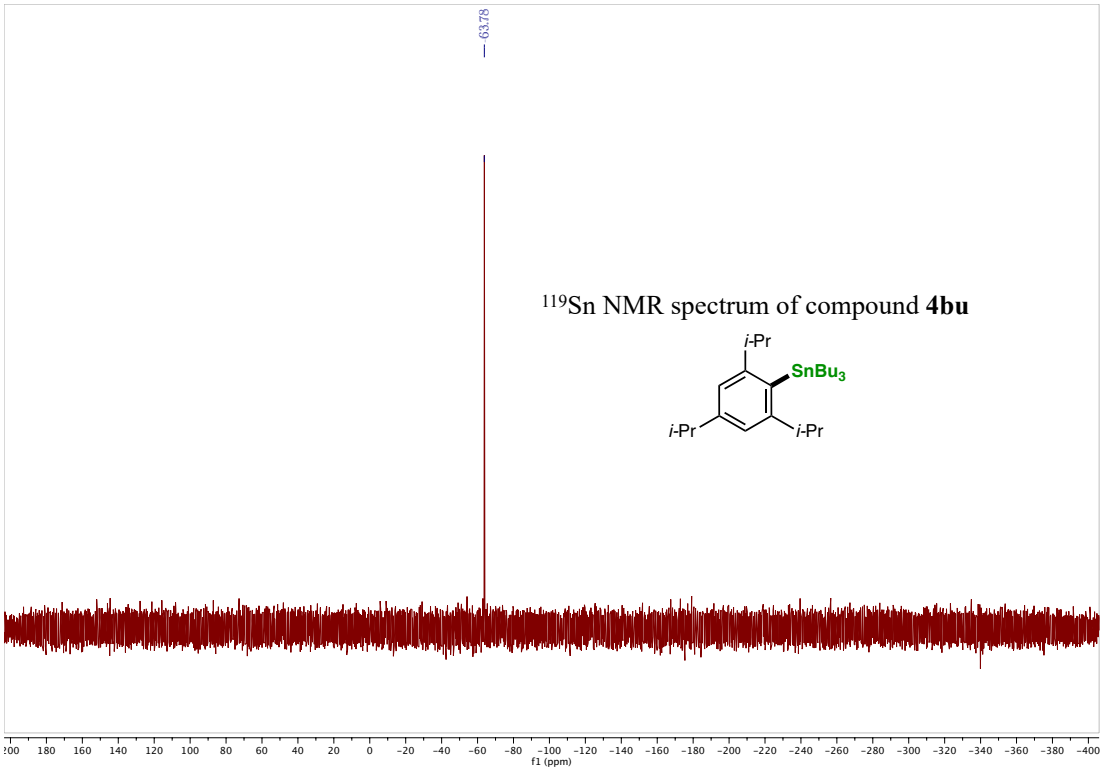
i-Pr_3Si—**$SnBu_3$**



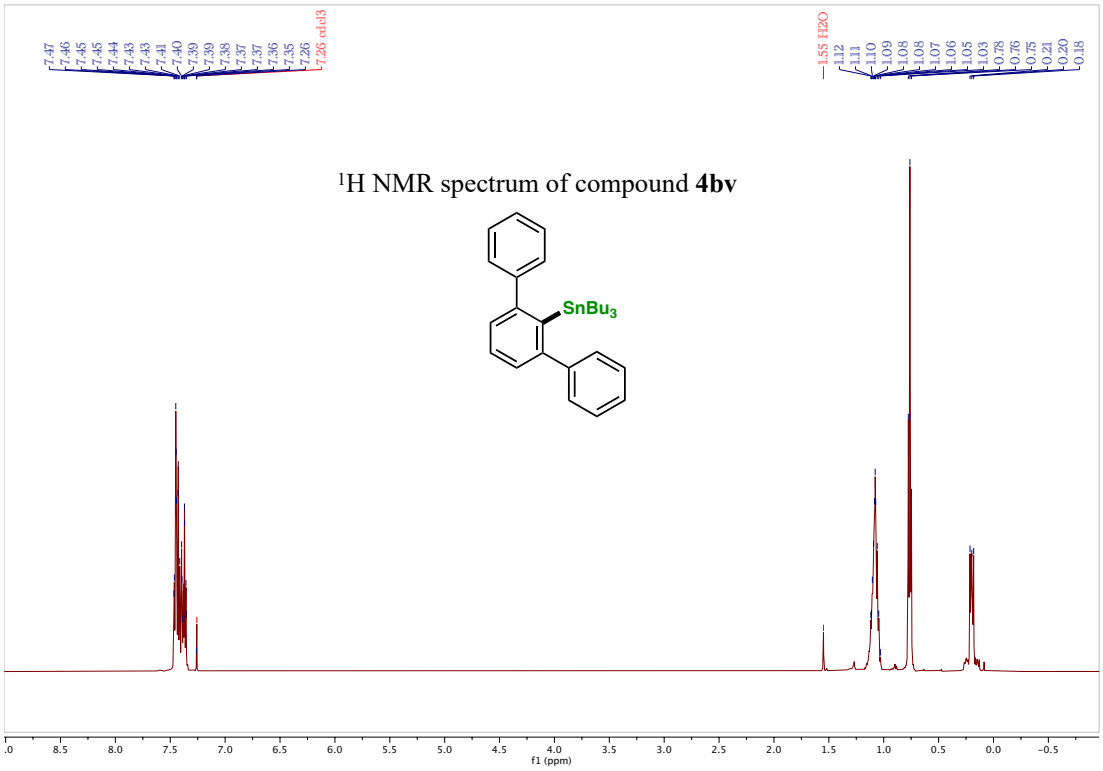
^{1}H NMR spectrum of compound **4bu**



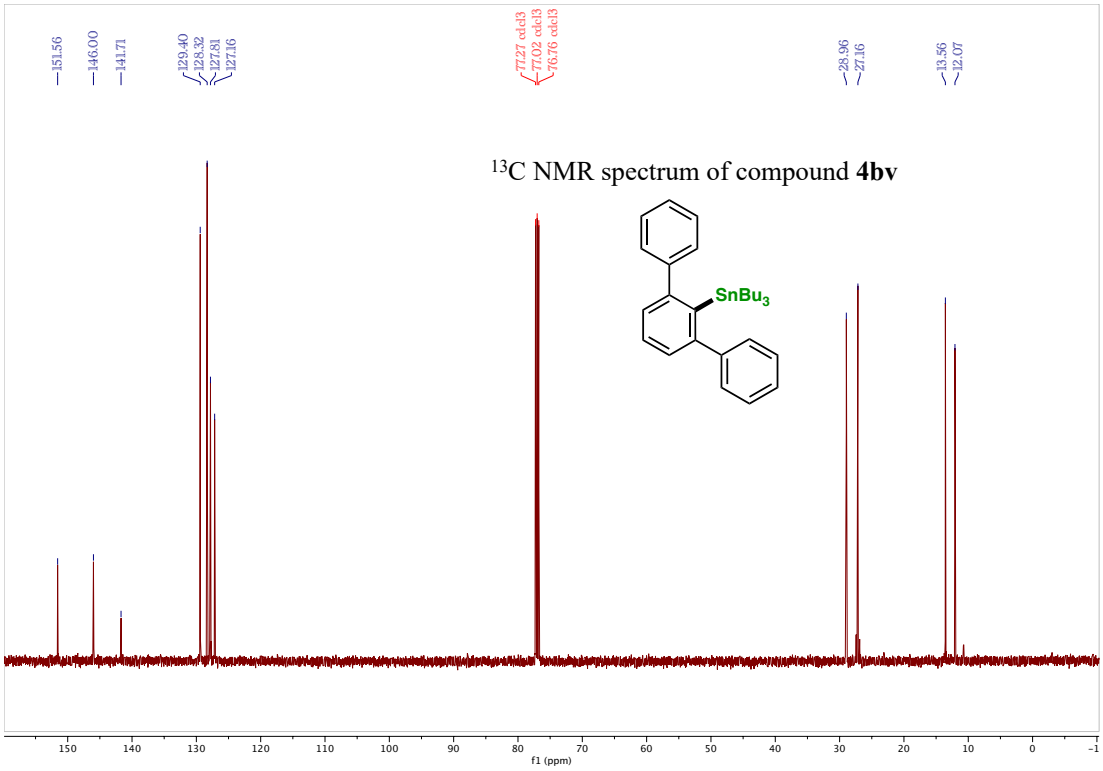
^{13}C NMR spectrum of compound **4bu**



^{119}Sn NMR spectrum of compound **4bu**

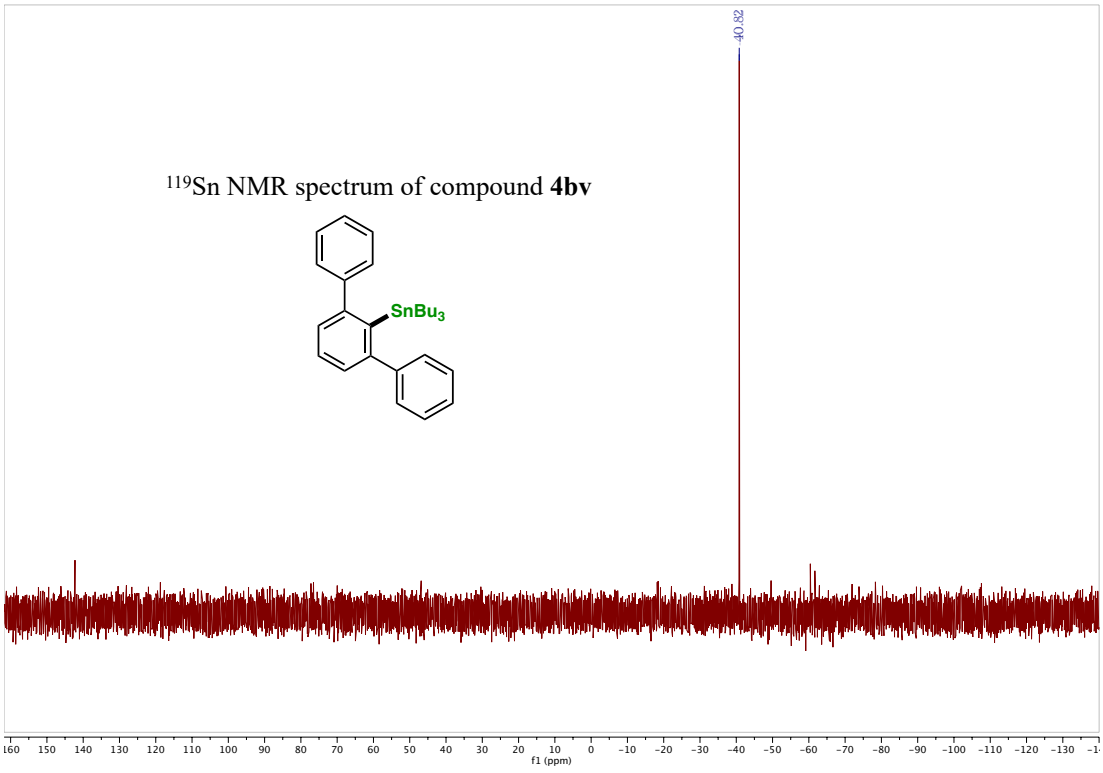


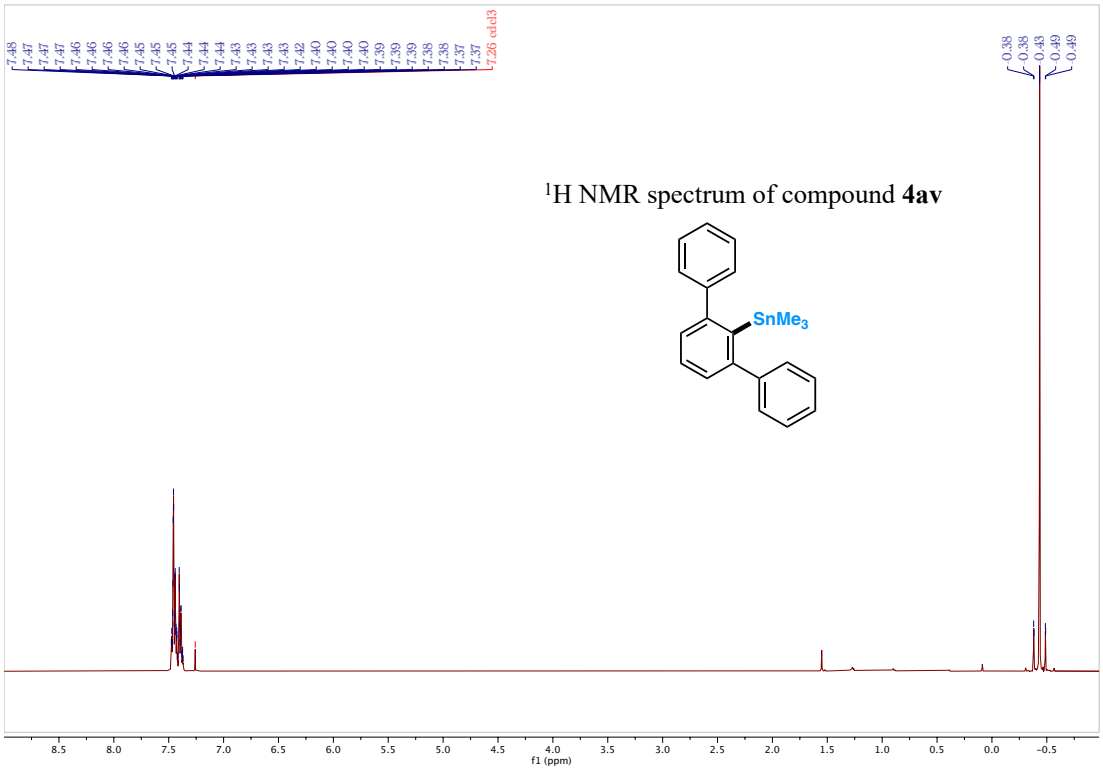
^{1}H NMR spectrum of compound **4bv**



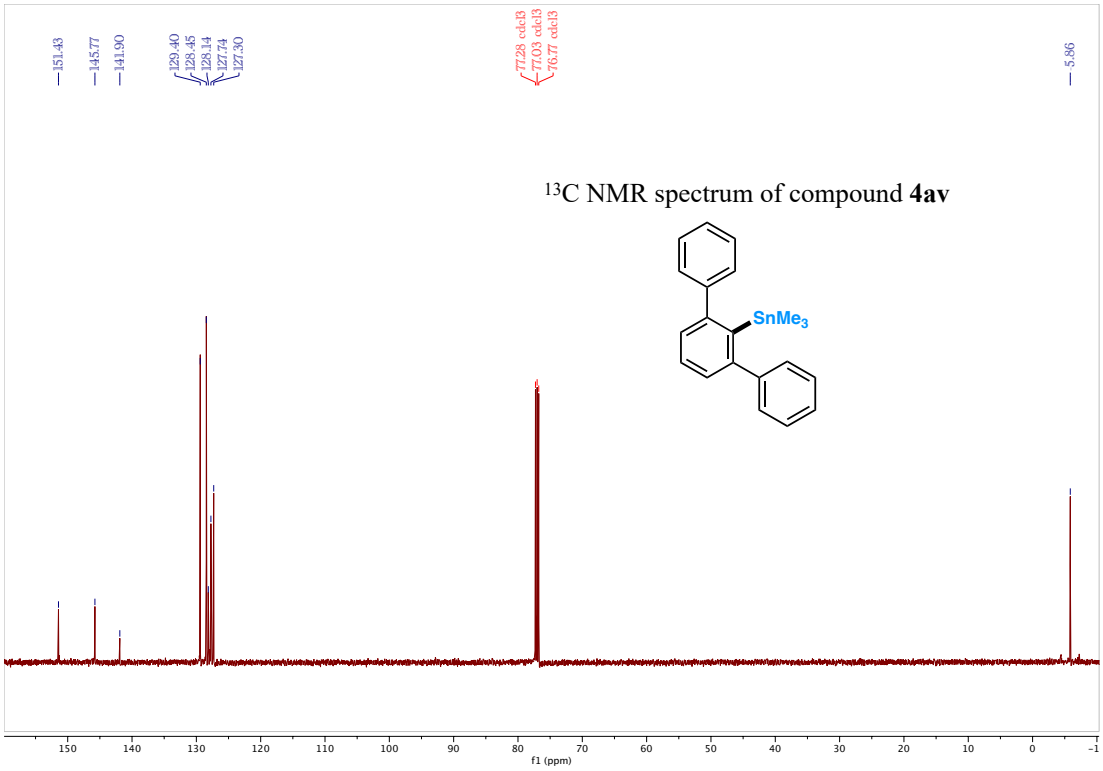
^{13}C NMR spectrum of compound **4bv**

^{119}Sn NMR spectrum of compound **4bv**



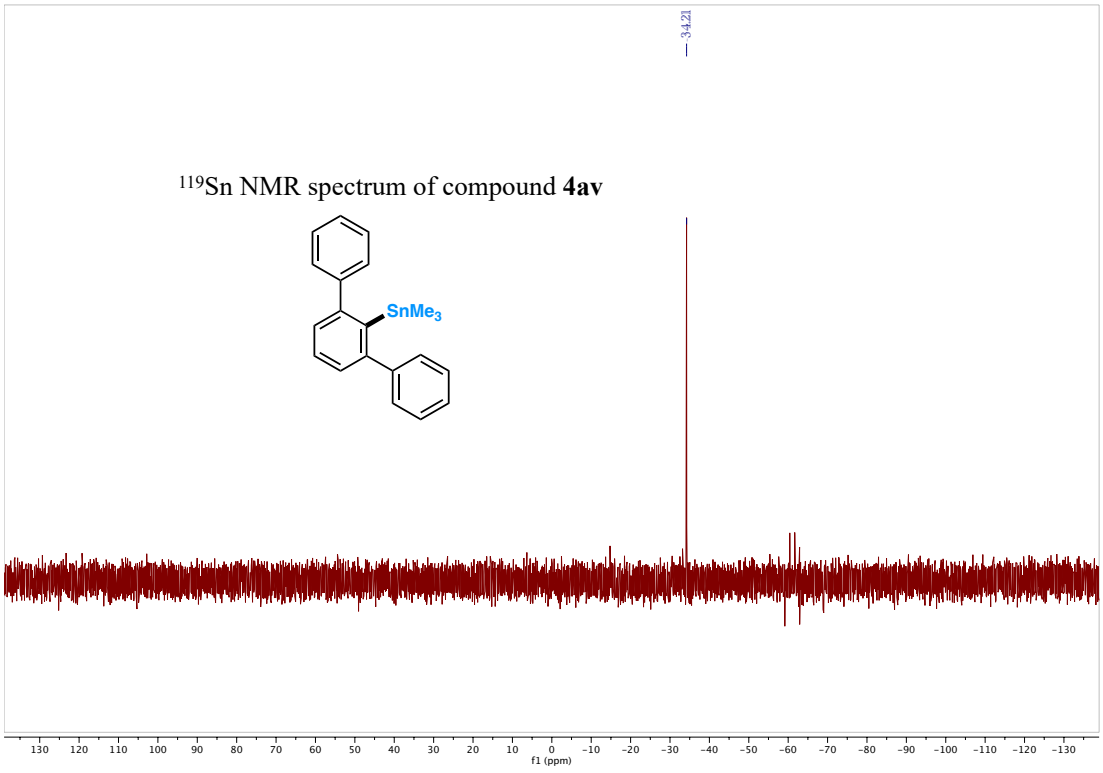


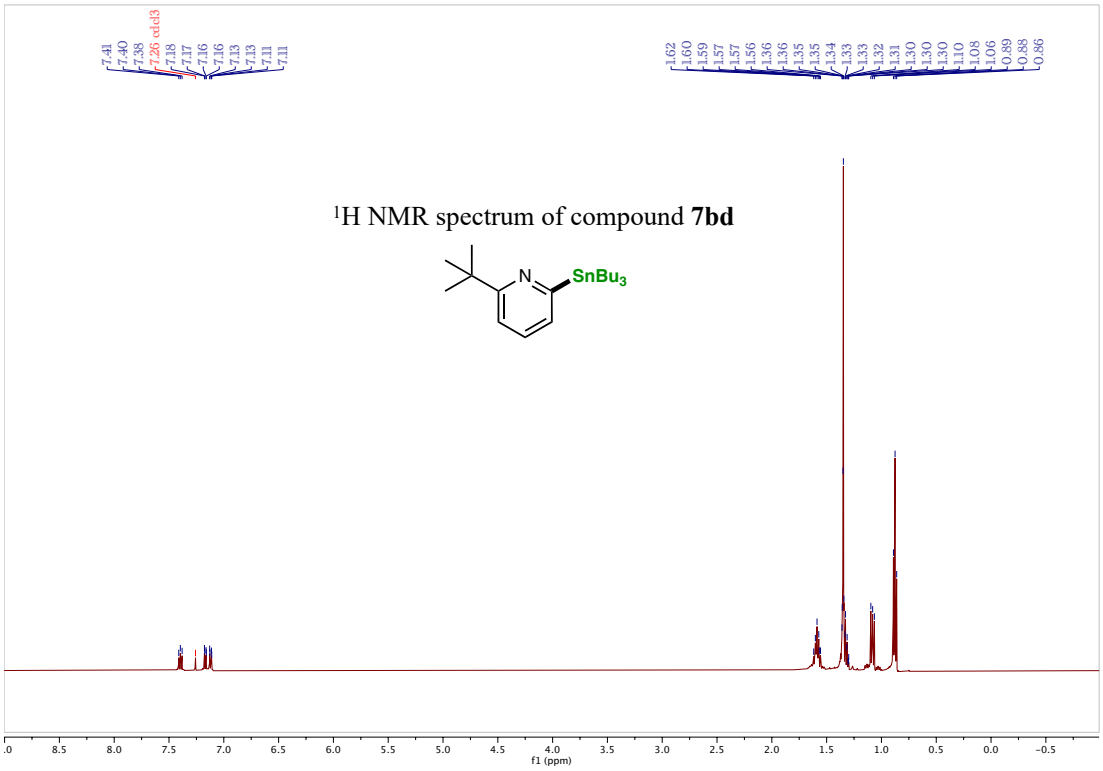
^{1}H NMR spectrum of compound **4av**



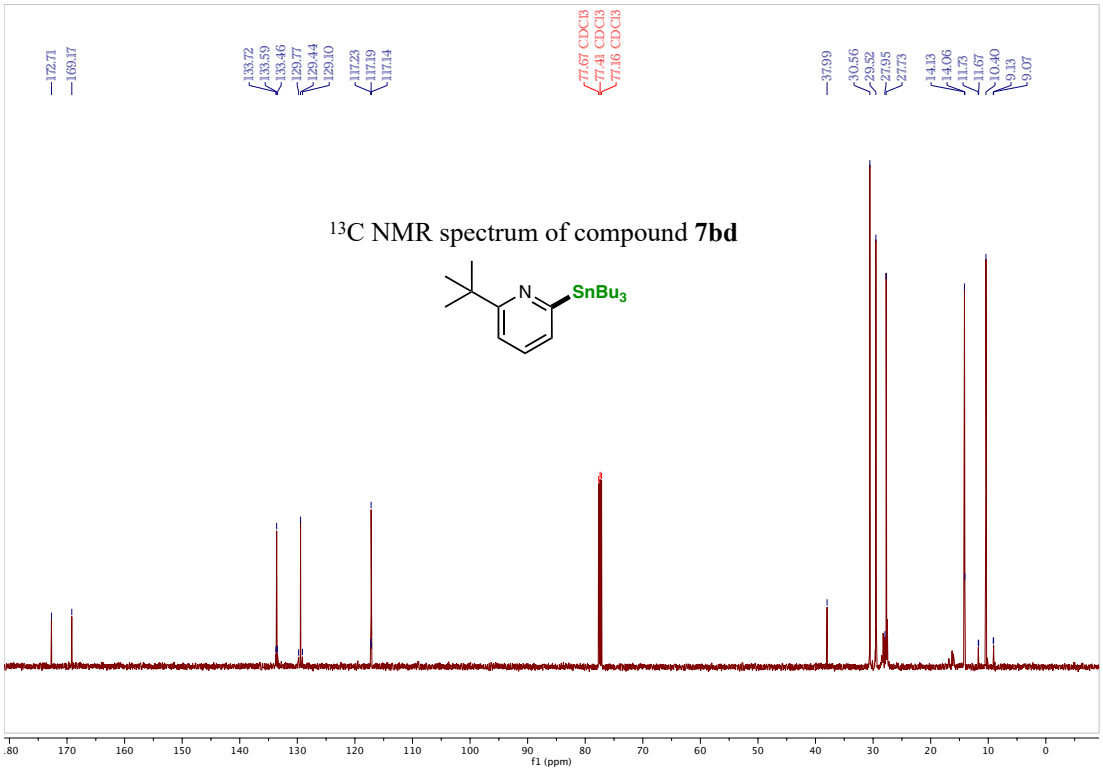
^{13}C NMR spectrum of compound **4av**

^{119}Sn NMR spectrum of compound **4av**

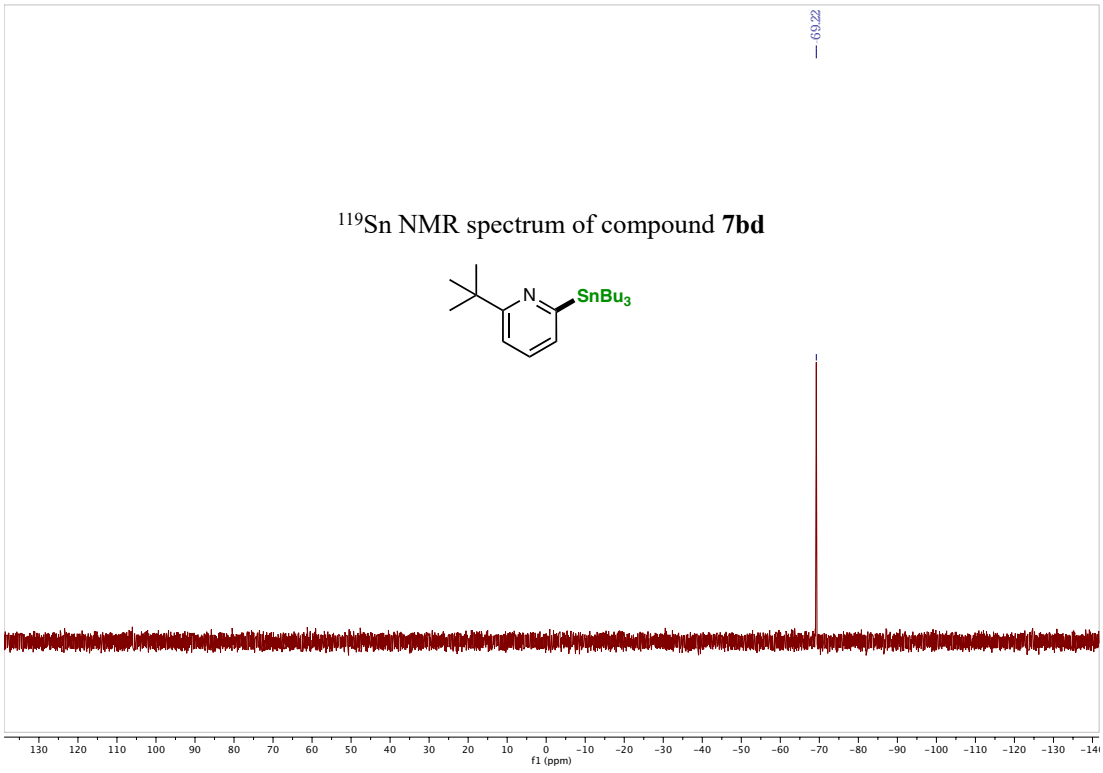




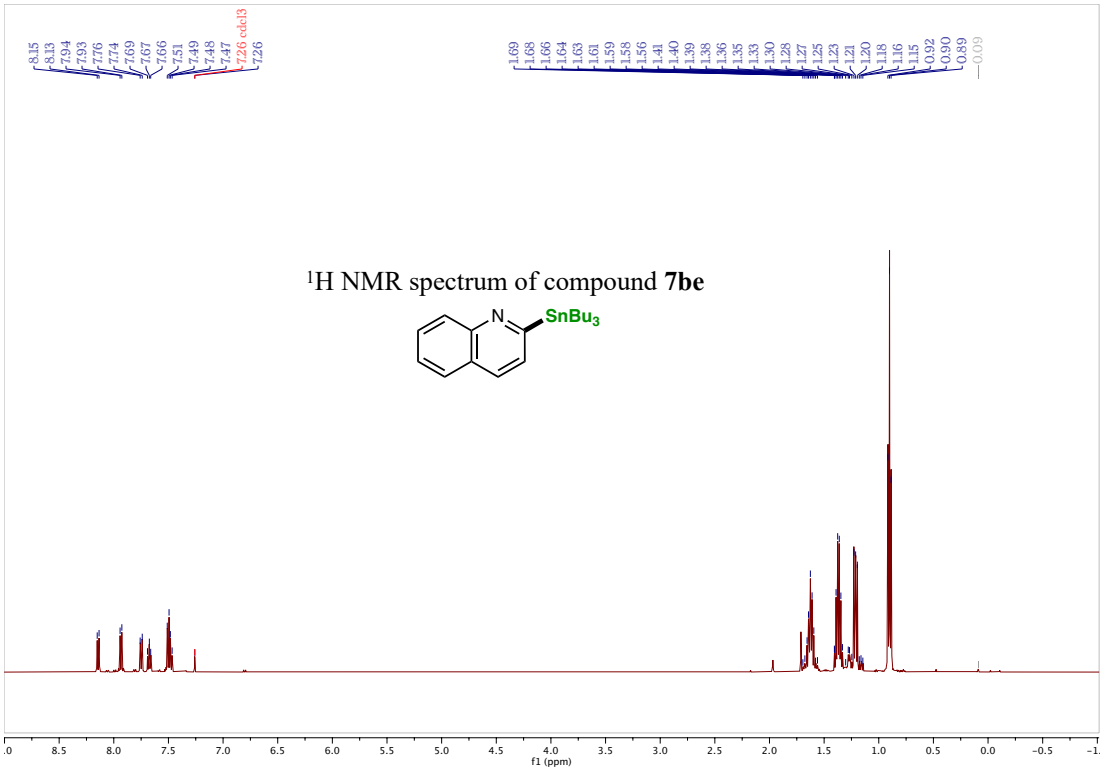
^{1}H NMR spectrum of compound **7bd**



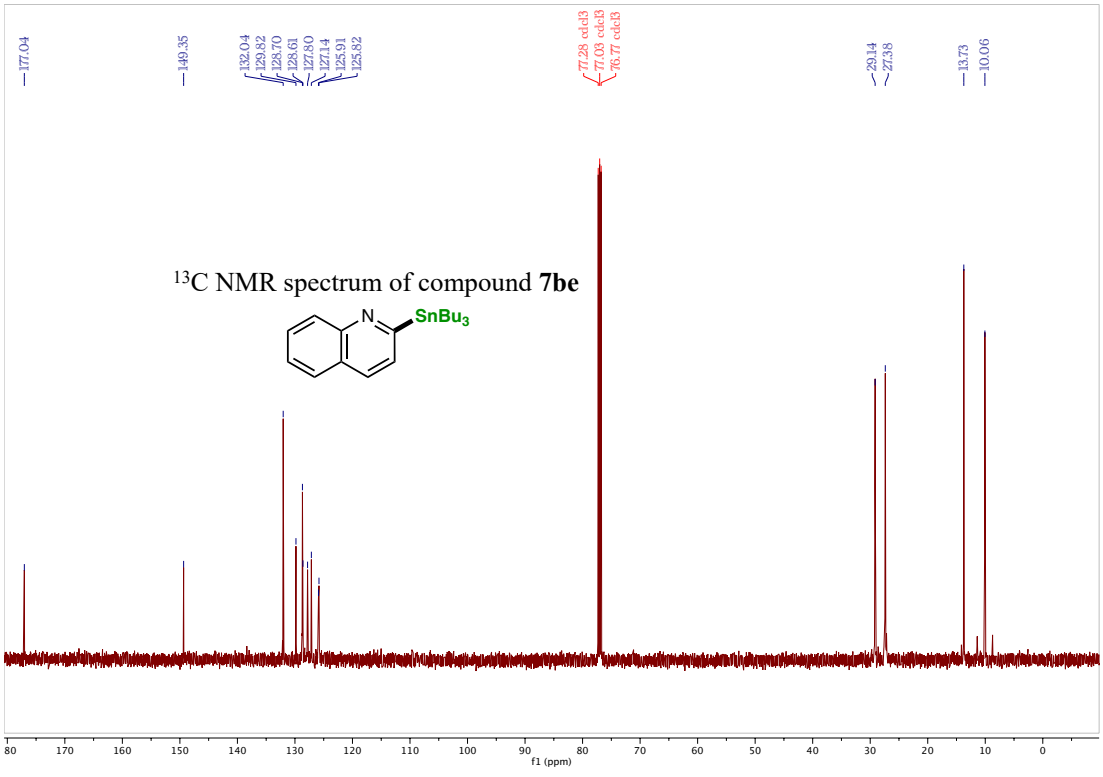
^{13}C NMR spectrum of compound **7bd**



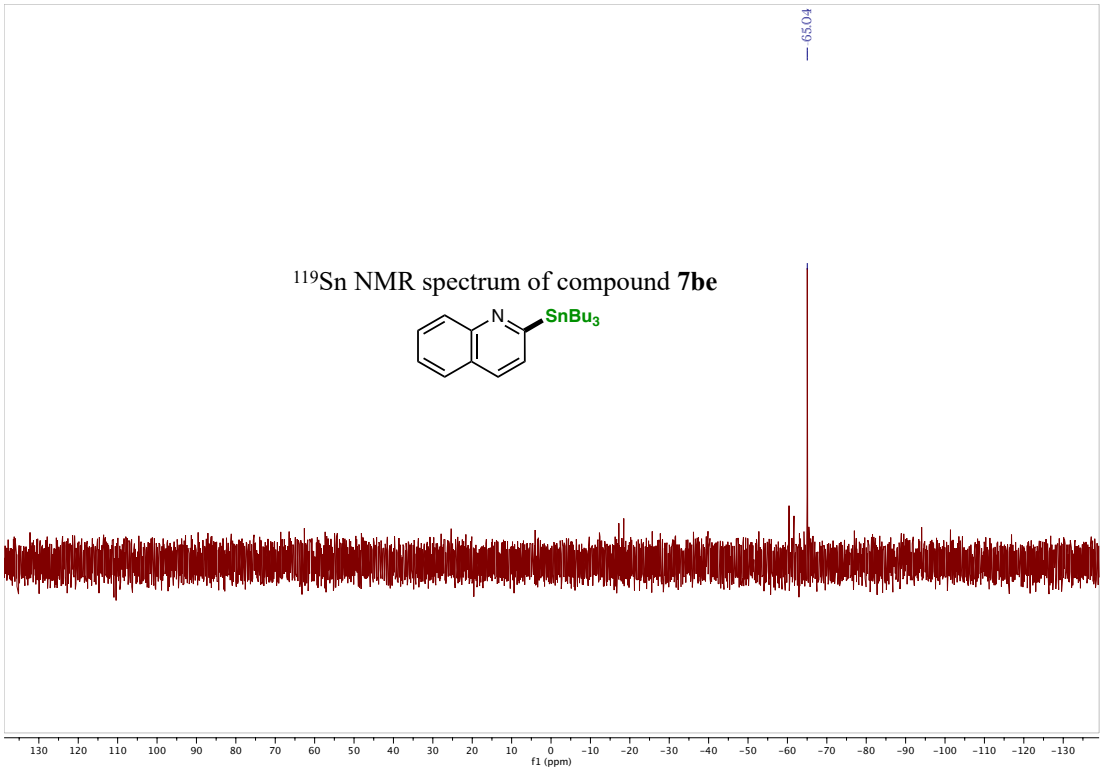
^{119}Sn NMR spectrum of compound **7bd**



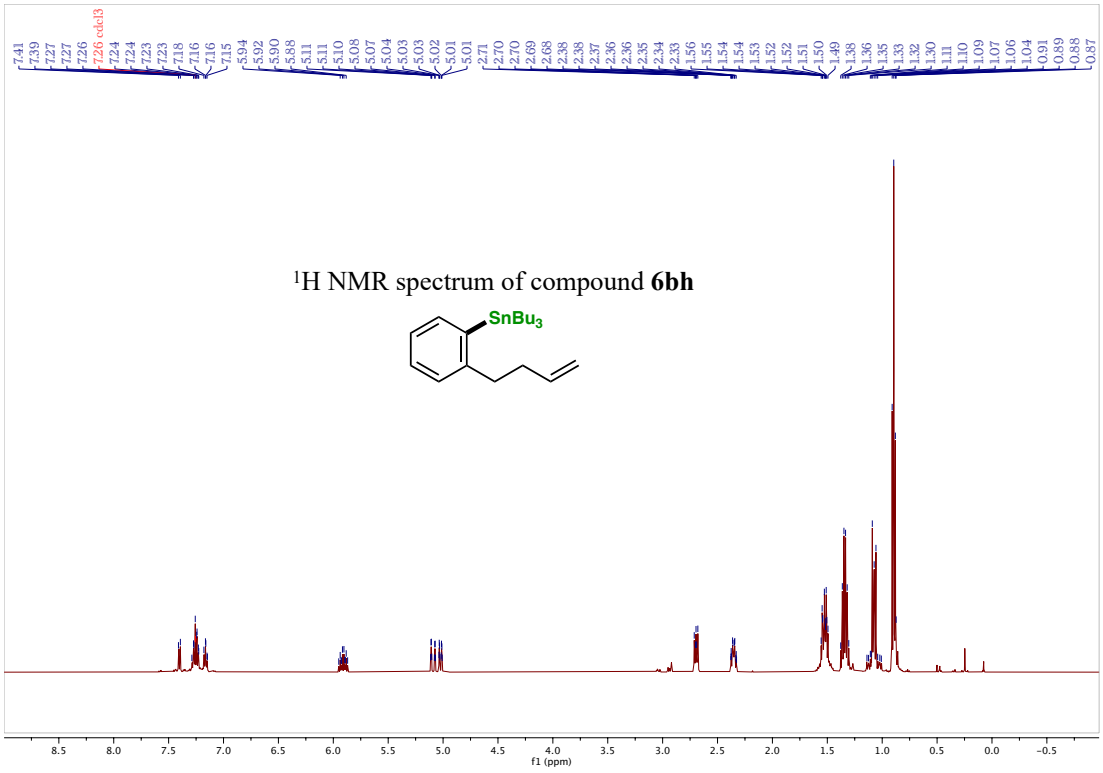
^{1}H NMR spectrum of compound **7be**



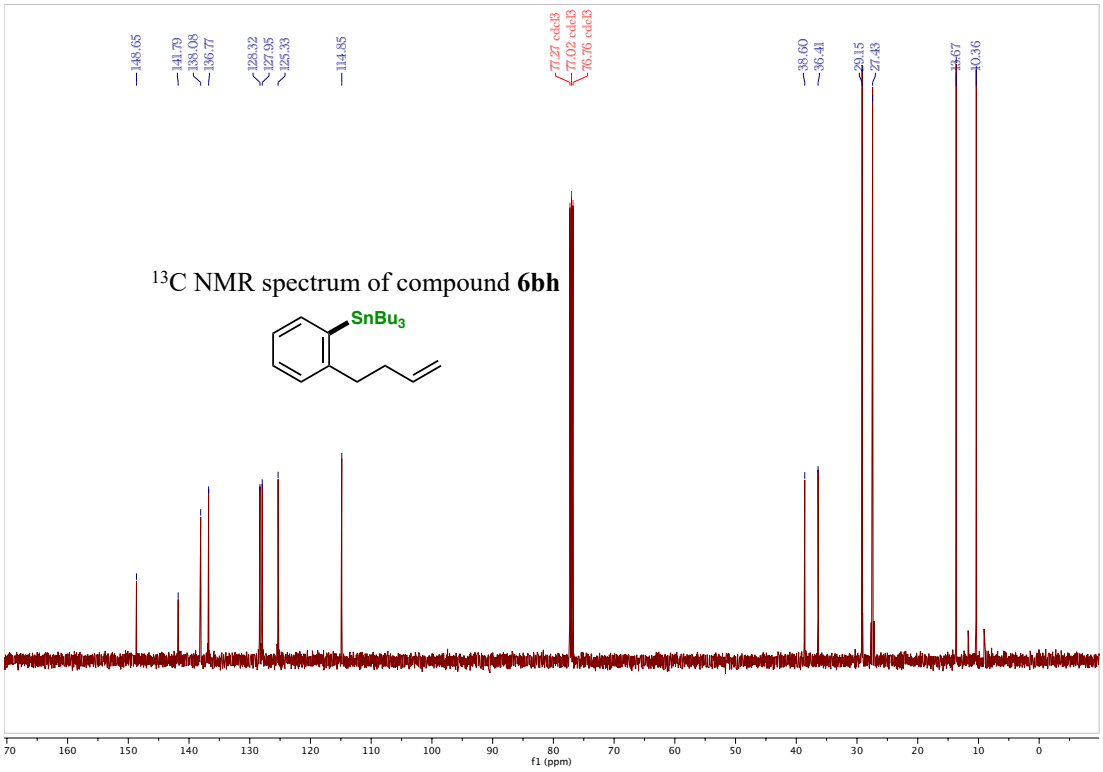
^{13}C NMR spectrum of compound **7be**



^{119}Sn NMR spectrum of compound **7be**



^{1}H NMR spectrum of compound **6bh**



^{13}C NMR spectrum of compound **6bh**

^{119}Sn NMR spectrum of compound **6bh**