

## Supporting Information for:

### Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

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**General Procedures.** All reactions were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene- $d_6$  was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze-pump-thaw cycles. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs' type column system (*I*), produced by Innovative Technology.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{19}\text{F}\{^1\text{H}\}$ , and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei.  $^1\text{H}$  NMR spectra were referenced to residual protons ( $\text{C}_6\text{D}_6$ ,  $\delta$  7.15,  $\text{CDCl}_3$ ,  $\delta$  7.24) with respect to tetramethylsilane at  $\delta$  0.00.  $^{13}\text{C}\{^1\text{H}\}$  spectra were referenced relative to solvent resonances ( $\text{C}_6\text{D}_6$ ,  $\delta$  128.0).  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra were referenced to an external sample of 80 %  $\text{CCl}_3\text{F}$  in  $\text{CDCl}_3$  at  $\delta$  0.0.  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra were referenced to an external sample of  $\text{SnMe}_4$  at  $\delta$  0.0.  $\text{C}_6\text{D}_6$  was purchased from Cambridge Isotope Laboratory. The compounds pentafluorobenzene, 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrafluorobenzene, 1,3,5-, 1,2,4-, and 1,2,3-trifluorobenzene, 1,2-, 1,3-, and 1,4-difluorobenzene, fluorobenzene, 2,3,5,6-tetrafluoropyridine, tributyl(vinyl)tin, and  $\text{Me}_6\text{Sn}_2$  were purchased from Aldrich. The compounds *cis*-

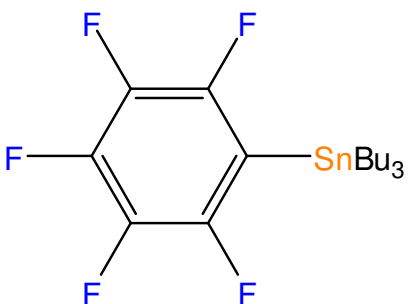
tributyl(1-propenyl)tin and *cis-trans*-tributyl(1-propenyl)tin were purchased from Alfa Aesar. The compounds  $P^iPr_3$ ,  $PEt_3$ ,  $PCy_3$ , and  $P^tBu_3$  were purchased from Strem Chemicals. The compounds  $MeNC_5H_4N^iPr$  (2),  $Me_3Sn(vinyl)$  (3),  $Ni(COD)_2$  (4),  $Pt(COD)_2$  (5),  $Pt(PCy_3)_2$  (6),  $C_6F_5D$  (7) and  $C_6F_4HD$  (8) were prepared by literature procedures. High Resolution Mass Spectroscopy was performed at McMaster University, Hamilton, Ontario, Canada. Note the method used for HRMS was positive-ion electron impact (EI), this is a high impact method and the loss of a butyl group for compounds **1-22** can be expected as EI often brings about the loss of R from  $R_3SnR'$ .(9, 10)

It should be noted that for reactions where a single product was obtained, passing the crude mixture through a silica plug and removal of volatiles in vacuo was sufficient in purifying the resulting oil as confirmed by  $^1H$ ,  $^{19}F\{^1H\}$ , and  $^{31}P\{^1H\}$  NMR spectroscopy. This technique suitably removed all of the nitrogen donor or  $P^iPr_3$ , and COD. In the reactions where multiple products were obtained, such as in the synthesis of the di- or tri-substituted products, further purification by a  $C_{18}$  reverse-phase silica column was used to separate the mono-substituted product from the di- or tri-substituted products. The mono-substituted products elute from the column first through numerous methanol washes; subsequent washes with toluene suitably removed the di- and tri-substituted products from the column. Removal of the volatiles in vacuo resulted in pure products as confirmed by  $^1H$  and  $^{19}F\{^1H\}$  NMR spectroscopy.

**Synthesis of tributyl(2,3,4,5,6-pentafluorophenyl)stannane, 1.** A solution of pentafluorobenzene (0.187 g, 1.11 mmol) and tributyl(vinyl)tin (0.176 g, 0.555 mmol) in 0.6 g of  $C_6D_6$  was added to  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and  $Ni(COD)_2$  (0.004 g, 0.017 mmol). The solution was heated at 35 °C for 1 h. The reaction mixture was

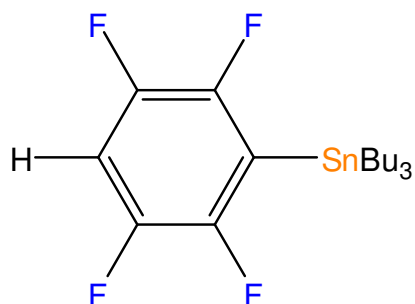
filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy; isolated 0.178 g, 70 % yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.88 (t, 9H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.0$  Hz); 1.16 (m with Sn satellites, 6H,  $\text{SnCH}_2$ ,  $^2J_{\text{HSn}} = 54.0$  Hz,  $^3J_{\text{HH}} = 8.3$  Hz); 1.31 (dt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.7$  Hz,  $^3J_{\text{HH}} = 7.2$  Hz); 1.51 (tt, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.5$  Hz,  $^3J_{\text{HH}} = 7.7$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -121.3 (AA'MM'N second order with Sn satellites, 2F, 2,6-Ar-F,  $^3J_{\text{FSn}} = 7.7$  Hz); -153.0 (tt with Sn satellites, 1F, 4-Ar-F,  $^3J_{\text{FF}} = 19.9$  Hz,  $^4J_{\text{FF}} = 1.8$  Hz,  $^5J_{\text{FSn}} = 7.4$  Hz); -160.7 (AA'MM'N second order, 2F, 3,5-Ar-F).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  11.7 (t with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 359$  Hz,  $^1J_{\text{CSn}(117)} = 343$  Hz,  $^4J_{\text{CF}} = 2.0$  Hz); 13.7 (s,  $\text{CH}_3$ ); 27.5 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}(119)} = 65.9$  Hz,  $^2J_{\text{CSn}(117)} = 63.1$  Hz); 29.2 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 21.3$  Hz); 110.9 (t, 1-Ar-C,  $^2J_{\text{CF}} = 53.7$  Hz); 137.2 (dm, Ar-C,  $^1J_{\text{CF}} = 254.9$  Hz); 141.7 (dm, Ar-C,  $^1J_{\text{CF}} = 251.1$  Hz); 149.0 (dm, Ar-C,  $^1J_{\text{CF}} = 234.1$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 111.96 MHz):  $\delta$  -18.05 (ttd,  $^3J_{\text{SnF}} = 7.7$  Hz,  $^4J_{\text{SnF}} = 2.0$  Hz,  $^5J_{\text{SnF}} = 7.2$  Hz). Calcd for  $\text{C}_{18}\text{H}_{27}\text{F}_5\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_8]$ , 401.0351. Found:  $m/z$  401.0346.

**Alternate synthesis of tributyl(2,3,4,5,6-pentafluorophenyl)stannane, 1.** A solution of pentafluorobenzene (0.057 g, 0.335 mmol) in toluene was added to a mixture of tributyl(vinyl)tin (0.106 g, 0.335 mmol),  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol), and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution is heated at 80 °C for 3 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (98 % yield by NMR spectroscopy).



**Synthesis of tributyl(2,3,5,6-tetrafluorophenyl)stannane, 2.** To a solution of 1,2,4,5-tetrafluorobenzene (0.417 g, 2.76 mmol) and tributyl(vinyl)tin (0.176 g, 0.55 mmol) in 0.6 g of  $C_6D_6$  was added  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and  $Ni(COD)_2$  (0.004 g, 0.0167 mmol). The solution was heated at 35 °C for 30 min, filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300.13 MHz):  $\delta$  0.86 (t, 9H,  $CH_3$ ,  $^3J_{HH} = 7.4$  Hz); 1.19 (m with Sn satellites, 6H,  $SnCH_2$ ,  $^2J_{HSn} = 54.5$  Hz,  $^3J_{HH} = 7.8$  Hz); 1.30 (qd, 6H,  $SnCH_2CH_2CH_2$ ,  $^3J_{HH} = 7.5$  Hz,  $^3J_{HH} = 7.4$  Hz); 1.52 (tt, 6H,  $SnCH_2CH_2$ ,  $^3J_{HH} = 7.8$  Hz,  $^3J_{HH} = 7.5$  Hz); 6.37 (tt, 1H, 4-Ar-H,  $^3J_{HF} = 9.3$  Hz,  $^4J_{HF} = 7.5$  Hz).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 282.40 MHz):  $\delta$  -122.4 (AA'MM' second order, 2F, 2,6-Ar-F,  $^3J_{SnF} = 6.0$  Hz); -138.4 (AA'MM' second order, 2F, 3,5-Ar-F,  $^4J_{SnF} = 0.4$  Hz).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 75.47 MHz):  $\delta$  11.5 (s with Sn satellites,  $SnCH_2$ ,  $^1J_{CSn(119)} = 359$  Hz,  $^1J_{CSn(117)} = 343$  Hz); 13.8 (s,  $CH_3$ ); 27.5 (s with Sn satellites,  $SnCH_2CH_2$ ,  $^2J_{CSn} = 64.4$  Hz); 29.2 (s with Sn satellites,  $SnCH_2CH_2CH_2$ ,  $^3J_{CSn} = 20.5$  Hz); 107.2 (t, 4-Ar-C,  $^2J_{CF} = 23.0$  Hz); 118.7 (tt, 1-Ar-C,  $^2J_{CF} = 48.7$  Hz,  $^3J_{CF} = 3.4$  Hz); 145.8 (dm, 2,6-Ar-C,  $^1J_{CF} = 255.9$  Hz); 149.1 (dm, 3,5-Ar-C,  $^1J_{CF} = 235.1$  Hz).  $^{119}Sn\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 111.96 MHz):  $\delta$  -21.5 (t,  $^3J_{SnF} = 6.0$  Hz). Calcd for  $C_{18}H_{28}F_4Sn$ :  $[M^+ - C_4H_9]$ , 383.0445. Found: m/z 383.0445.

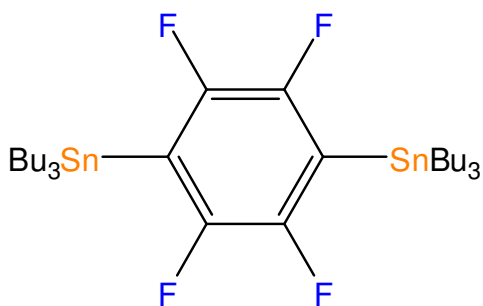
**Alternate synthesis of tributyl(2,3,5,6-tetrafluorophenyl)stannane, 2.** A solution of 1,2,4,5-tetrafluorobenzene (0.250 g, 1.7 mmol) in toluene was added to a mixture of tributyl(vinyl)tin (0.106 g, 0.335 mmol),  $P^iPr_3$  (0.0054 g, 0.033 mmol), and  $Ni(COD)_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 10 min. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (93 % yield by NMR spectroscopy, 7 % of **3**).



**Synthesis of 2,3,5,6-tetrafluorophenyl-1,4-bis(tributylstannane), 3.** To a solution of 1,2,4,5-tetrafluorobenzene (0.083 g, 0.55 mmol) and tributyl(vinyl)tin (0.440 g, 1.39 mmol) in 0.6 g of  $C_6D_6$  was added  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and  $Ni(COD)_2$  (0.004 g, 0.017 mmol). The solution was heated to 45 °C for 6 h, filtered through silica and the solvent removed, leaving a colourless oil. (85 % yield by NMR spectroscopy, 11% of **2**).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300.13 MHz):  $\delta$  0.85 (t, 9H,  $CH_3$ ,  $^3J_{HH} = 7.4$  Hz); 1.20 (m with Sn satellites, 6H,  $SnCH_2$ ,  $^2J_{HSn} = 51.6$  Hz,  $^3J_{HH} = 8.2$  Hz); 1.30 (qt, 6H,  $SnCH_2CH_2CH_2$ ,  $^3J_{HH} = 7.5$  Hz,  $^3J_{HH} = 7.2$  Hz); 1.54 (tt, 6H,  $SnCH_2CH_2$ ,  $^3J_{HH} = 7.9$  Hz,  $^3J_{HH} = 7.5$  Hz).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 282.40 MHz):  $\delta$  -112.3 (s with second order Sn satellites  $A_2A'_2$ , 4F, 2,3,5,6-Ar-F,  $^3J_{SnF} = 5.0$  Hz).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 75.47 MHz):  $\delta$  11.1 (s with Sn satellites,  $SnCH_2$ ,  $^1J_{CSn(119)} = 359$  Hz,  $^1J_{CSn(117)} = 343$  Hz); 13.4 (s,  $CH_3$ ); 27.2 (s with Sn satellites,  $SnCH_2CH_2$ ,  $^1J_{CSn} = 63.8$  Hz); 28.9 (s with Sn

satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 20.7 \text{ Hz}$ ); 119.1 (pentet, 1,3-Ar-C,  $^2J_{\text{CF}} = 60.4 \text{ Hz}$ ,  $^3J_{\text{CF}} = 21.7 \text{ Hz}$ ); 148.7 (dm, 2,3,5,6-Ar-C,  $^1J_{\text{CF}} = 244.9 \text{ Hz}$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 111.96 MHz):  $\delta$  -21.3 (AA'X<sub>2</sub>X'<sub>2</sub> second order,  $^3J_{\text{SnF}} = 5.0 \text{ Hz}$ ). Calcd for  $\text{C}_{30}\text{H}_{54}\text{F}_4\text{Sn}_2$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 673.1501. Found:  $m/z$  673.1518.

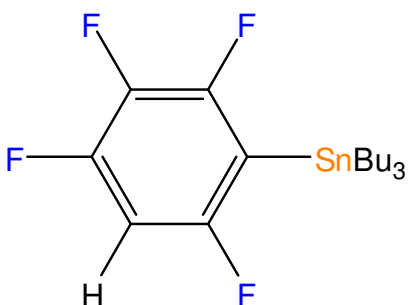
**Alternate synthesis of 2,3,5,6-tetrafluorophenyl-1,4-bis(tributylstannane), 3.** A solution of 1,2,4,5-tetrafluorobenzene (0.051 g, 0.335 mmol) and tributyl(vinyl)tin (0.265 g, 0.835 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 8 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (99 % yield by NMR spectroscopy).



**Synthesis of tributyl(2,3,4,6-tetrafluorophenyl)stannane, 4.** To a solution of 1,2,3,5-tetrafluorobenzene (0.417 g, 2.76 mmol) and tributyl(vinyl)tin (0.176 g, 0.55 mmol) in 0.6 g of  $\text{C}_6\text{D}_6$  was added  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.005 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.004 g, 0.017 mmol). The solution was heated to 35 °C for 40 min, filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy; isolated 0.200 g, 82 % yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.88 (t, 9H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.3 \text{ Hz}$ ); 1.18 (m with Sn satellites, 6H,  $\text{SnCH}_2$ ,  $^2J_{\text{HSn}} = 7.3 \text{ Hz}$ ,  $^3J_{\text{HH}} = 8.7 \text{ Hz}$ ); 1.32 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.3 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.7 \text{ Hz}$ ); 1.55 (tt, 6H,  $\text{SnCH}_2\text{CH}_2$ ,

$^3J_{\text{HH}} = 8.7 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.6 \text{ Hz}$ ); 6.17 (dddd, 1H, 5-Ar-H,  $^3J_{\text{HF}} = 10.8$ ,  $^3J_{\text{HF}} = 6.0 \text{ Hz}$ ,  $^4J_{\text{HF}} = 4.7 \text{ Hz}$ ,  $^5J_{\text{HF}} = 2.4 \text{ Hz}$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -96.2 (td with Sn satellites, 1F, 6-Ar-F,  $^3J_{\text{FSn}} = 3.5 \text{ Hz}$ ,  $^4J_{\text{FF}} = 3.5 \text{ Hz}$ ,  $^5J_{\text{FF}} = 13.0 \text{ Hz}$ ); -115.2 (ddd with Sn satellites, 1F, 4-Ar-F,  $^3J_{\text{FF}} = 26.8 \text{ Hz}$ ,  $^4J_{\text{FF}} = 7.0 \text{ Hz}$ ,  $^4J_{\text{FF}} = 3.5 \text{ Hz}$ ,  $^5J_{\text{FSn}} = 2.2 \text{ Hz}$ ); -132.3 (ddd with Sn satellites, 1F, 2-Ar-F,  $^3J_{\text{FSn}} = 3.6 \text{ Hz}$ ,  $^3J_{\text{FF}} = 20.1 \text{ Hz}$ ,  $^4J_{\text{FF}} = 7.0 \text{ Hz}$ ,  $^4J_{\text{FF}} = 3.5 \text{ Hz}$ ); -165.9 (ddd with Sn satellites, 1F, 3-Ar-F,  $^3J_{\text{FF}} = 20.1 \text{ Hz}$ ,  $^3J_{\text{FF}} = 26.8 \text{ Hz}$ ,  $^4J_{\text{FSn}} = 4.1 \text{ Hz}$ ,  $^5J_{\text{FF}} = 13.0 \text{ Hz}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  11.4 (t with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 362 \text{ Hz}$ ,  $^1J_{\text{CSn}(117)} = 345 \text{ Hz}$ ,  $^4J_{\text{CF}} = 1.9 \text{ Hz}$ ); 13.8 (s,  $\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}(119)} = 65 \text{ Hz}$ ,  $^2J_{\text{CSn}(117)} = 62 \text{ Hz}$ ); 29.3 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 20.8 \text{ Hz}$ ); 100.7 (ddm, 5-Ar-C,  $^2J_{\text{CF}} = 35.9 \text{ Hz}$ ,  $^2J_{\text{CF}} = 20.9 \text{ Hz}$ ); 111.0 (tm, 1-Ar-C,  $^2J_{\text{CF}} = 50.7 \text{ Hz}$ ); 137.3 (dm, Ar-C,  $^1J_{\text{CF}} = 251.9 \text{ Hz}$ ); 151.9 (dm, Ar-C,  $^1J_{\text{CF}} = 238.7 \text{ Hz}$ ); 155.0 (dm, Ar-C,  $^1J_{\text{CF}} = 220.5 \text{ Hz}$ ); 161.2 (dm, Ar-C,  $^1J_{\text{CF}} = 234.1 \text{ Hz}$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 111.96 MHz):  $\delta$  -26.6 (dddd,  $^3J_{\text{SnF}} = 3.6 \text{ Hz}$ ,  $^3J_{\text{SnF}} = 3.6 \text{ Hz}$ ,  $^4J_{\text{SnF}} = 4.4 \text{ Hz}$ ,  $^2J_{\text{SnF}} = 2.8 \text{ Hz}$ ). Calcd for  $\text{C}_{18}\text{H}_{28}\text{F}_4\text{Sn}$ : M+, 440.1149. Found: m/z 440.1148.

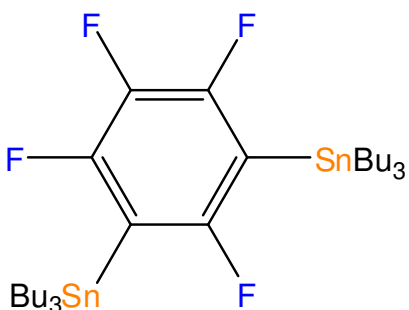
**Alternate synthesis of tributyl(2,3,4,6-tetrafluorophenyl)stannane, 4.** A solution of 1,2,3,5-tetrafluorobenzene (0.151 g, 1.01 mmol) and tributyl(vinyl)tin (0.106 g, 0.335 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 30 min. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (90 % yield by NMR spectroscopy, 10 % of **5**).



**Synthesis of 2,4,5,6-tetrafluorophenyl-1,3-bis(tributylstannane), 5.** To a solution of 1,2,3,5-tetrafluorobenzene (0.083 g, 0.55 mmol) and tributyl(vinyl)tin (0.440 g, 1.39 mmol) in 0.6 g of  $C_6D_6$  was added  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and  $Ni(COD)_2$  (0.004 g, 0.0167 mmol). The solution was heated to 40 °C for 18 h, filtered through silica and the solvent was removed, leaving a colourless oil. (84 % yield by NMR spectroscopy, 12 % of **4**).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300.13 MHz):  $\delta$  0.89 (t, 9H,  $CH_3$ ,  $^3J_{HH} = 7.3$  Hz); 1.23 (m, 6H,  $SnCH_2$ ,  $^3J_{HH} = 8.6$  Hz); 1.34 (qd, 6H,  $SnCH_2CH_2CH_2$ ,  $^3J_{HH} = 7.3$  Hz,  $^3J_{HH} = 7.5$  Hz); 1.58 (tt, 6H,  $SnCH_2CH_2$ ,  $^3J_{HH} = 7.6$  Hz,  $^3J_{HH} = 8.6$  Hz).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 282.40 MHz):  $\delta$  -77.5 (d, 1F, 2-Ar-F,  $^5J_{FF} = 15.2$  Hz); -115.9 (d, 2F, 4,6-Ar-F,  $^3J_{FF} = 25.3$  Hz); -165.7 (td with Sn satellites, 1F, 5-Ar-F,  $^3J_{FF} = 25.3$  Hz,  $^4J_{FSn} = 3.1$  Hz,  $^5J_{FF} = 15.2$  Hz).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 75.47 MHz):  $\delta$  11.2 (s with Sn satellites,  $SnCH_2$ ,  $^1J_{CSn(119)} = 358$  Hz,  $^1J_{CSn(117)} = 342$  Hz); 13.5 (s,  $CH_3$ ); 27.2 (s with Sn satellites,  $SnCH_2CH_2$ ,  $^2J_{CSn(119)} = 64$  Hz,  $^2J_{CSn(117)} = 62$  Hz); 29.0 (s with Sn satellites,  $SnCH_2CH_2CH_2$ ,  $^3J_{CSn} = 20.7$  Hz); 110.0 (ddm, 1,3-Ar-C,  $^2J_{CF} = 50.5$  Hz,  $^2J_{CF} = 64.2$  Hz); 137.3 (dm, Ar-C,  $^1J_{CF} = 262.8$  Hz); 155.6 (dm, Ar-C,  $^1J_{CF} = 237.0$  Hz); 164.9 (dm, Ar-C,  $^1J_{CF} = 237.8$  Hz).  $^{119}Sn\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 111.96 MHz):  $\delta$  -28.7 (m AA'XX'YZ second order,  $^4J_{SnSn} = 3.1$  Hz). Calcd for  $C_{30}H_{54}F_4Sn_2$ :  $[M^+ - C_4H_9]$ , 673.1501. Found: m/z 673.1502.



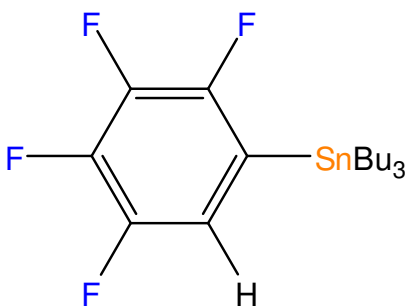
**Alternate synthesis of 2,4,5,6-tetrafluorophenyl-1,3-bis(tributylstannane), 5.** A solution of 1,2,3,5-tetrafluorobenzene (0.051 g, 0.335 mmol) and tributyl(vinyl)tin (0.265 g, 0.835 mmol) in toluene was added to a mixture of  $P^iPr_3$  (0.0054 g, 0.033 mmol) and  $Ni(COD)_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 12 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (99 % yield by NMR spectroscopy).



**Synthesis of tributyl(2,3,4,5-tetrafluorophenyl)stannane, 6.** To a solution of 1,2,3,4-tetrafluorobenzene (0.417 g, 2.776 mmol) and tributyl(vinyl)tin (0.176 g, 0.55 mmol) in 0.6 g of  $C_6D_6$  was added  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and  $Ni(COD)_2$  (0.004 g, 0.017 mmol). The solution was heated to 45 °C for 12 h, filtered through silica and the solvent was removed, leaving a colourless oil. (38 % yield by NMR spectroscopy).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300.13 MHz):  $\delta$  0.90 (t, 9H,  $CH_3$ ,  $^3J_{HH} = 7.4$  Hz); 1.10 (m with Sn satellites, 6H,  $SnCH_2$ ,  $^2J_{HSn} = 48.1$  Hz,  $^3J_{HH} = 8.4$  Hz); 1.31 (qt, 6H,  $SnCH_2CH_2CH_2$ ,  $^3J_{HH} = 7.4$  Hz,  $^3J_{HH} = 7.7$  Hz); 1.52 (tt, 6H,  $SnCH_2CH_2$ ,  $^3J_{HH} = 8.5$  Hz,  $^3J_{HH} = 7.7$  Hz); 6.70 (dddd with Sn satellites, 1H, 6-Ar-H,  $^3J_{HSn} = 21.0$  Hz,  $^3J_{HF} = 8.1$ ,  $^4J_{HF} = 2.3$  Hz,  $^4J_{HF} = 2.3$  Hz,  $^5J_{HF} = 8.1$  Hz).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 282.40 MHz):  $\delta$  -120.6 (ddd, 1F, 2-Ar-F,  $^3J_{FF} = 27.5$  Hz,  $^5J_{FF} = 16.0$  Hz,  $^4J_{FF} = 3.0$  Hz,  $^3J_{SnF} = 14.3$  Hz); -139.4 (ddd, 1F, 5-Ar-F,  $^3J_{FF} = 19.5$  Hz,  $^4J_{FF} = 16.0$  Hz,  $^5J_{FF} = 1.8$  Hz); -155.5 (ddd, 1F, 3-Ar-F,  $^3J_{FF} = 27.5$

Hz,  $^3J_{\text{FF}} = 19.5$  Hz,  $^4J_{\text{FF}} = 1.8$  Hz);  $-155.8$  (ddd, 1F, 4-Ar-F,  $^3J_{\text{FF}} = 19.5$  Hz,  $^3J_{\text{FF}} = 19.5$  Hz,  $^4J_{\text{FF}} = 3.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.4 (s with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{SnC}(119)} = 356$  Hz,  $^1J_{\text{SnC}(117)} = 339$  Hz); 13.8 (s,  $\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 60.1$  Hz); 29.2 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 19.5$  Hz); 116.4 (td, 6-Ar-C,  $^2J_{\text{CF}} = 16.3$  Hz,  $^3J_{\text{CF}} = 4.8$  Hz); 122.9 (d with Sn satellites, 1-Ar-C,  $^2J_{\text{CF}} = 46.9$  Hz,  $^1J_{\text{CSn}} = 257.9$  Hz); 140.4 (dm, Ar-C,  $^1J_{\text{CF}} = 260.1$  Hz); 141.1 (dm, Ar-C,  $^1J_{\text{CF}} = 259.4$  Hz); 148.1 (ddd, Ar-C,  $^1J_{\text{CF}} = 252.5$  Hz,  $^2J_{\text{CF}} = 10.5$  Hz,  $^3J_{\text{CF}} = 2.5$  Hz); 150.8 (dd, Ar-C,  $^1J_{\text{CF}} = 231.2$  Hz,  $^2J_{\text{CF}} = 6.1$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 111.96 MHz):  $\delta$   $-25.7$  (dddd,  $^3J_{\text{SnF}} = 15.2$  Hz,  $^4J_{\text{SnF}} = 11.0$  Hz,  $^4J_{\text{SnF}} = 5.0$  Hz,  $^5J_{\text{SnF}} = 7.0$  Hz). Calcd for  $\text{C}_{18}\text{H}_{28}\text{F}_4\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$  383.0445. Found:  $m/z$  383.0437.

**Alternate synthesis of tributyl(2,3,4,5-tetrafluorophenyl)stannane, 6.** A solution of 1,2,3,4-tetrafluorobenzene (0.252 g, 1.67 mmol) and tributyl(vinyl)tin (0.106 g, 0.335 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 4 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy).

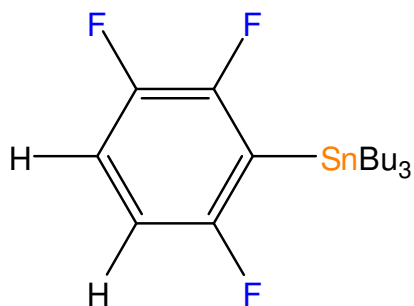


**Synthesis of tributyl(2,3,6-trifluorophenyl)stannane, 7.** To a solution of 1,2,4-trifluorobenzene (0.220 g, 1.67 mmol) and tributyl(vinyl)tin (0.176 g, 0.55 mmol) in 0.6

g of C<sub>6</sub>D<sub>6</sub> was added MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr (0.005 g, 0.033 mmol) and Ni(COD)<sub>2</sub> (0.004 g, 0.017 mmol). The solution was heated to 35 °C for 7 h, filtered through silica and the solvent was removed, leaving a colourless oil. (98 % yield by NMR spectroscopy). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.13 MHz): δ 0.86 (t, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz); 1.19 (m with Sn satellites, 6H, SnCH<sub>2</sub>, <sup>2</sup>J<sub>HSn</sub> = 55.0 Hz, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz); 1.30 (qt, 6H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz); 1.54 (tt, 6H, SnCH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz); 6.40 (dddd, 1H, 4-Ar-H, <sup>3</sup>J<sub>HF</sub> = 9.1, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz, <sup>4</sup>J<sub>HF</sub> = 2.8 Hz, <sup>4</sup>J<sub>HF</sub> = 1.6 Hz); 6.63 (ddd, 1H, 5-Ar-H, <sup>3</sup>J<sub>HF</sub> = 5.3 Hz, <sup>3</sup>J<sub>HH</sub> = 5.3 Hz, <sup>4</sup>J<sub>HF</sub> = 9.1 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 282.40 MHz): δ -98.5 (dd with Sn satellites, 1F, 6-Ar-F, <sup>4</sup>J<sub>FF</sub> = 17.8 Hz, <sup>5</sup>J<sub>FF</sub> = 1.6 Hz, <sup>3</sup>J<sub>SnF</sub> = 7.8 Hz); -116.6 (dd with Sn satellites, 1F, 3-Ar-F, <sup>3</sup>J<sub>FF</sub> = 26.8 Hz, <sup>5</sup>J<sub>FF</sub> = 1.6 Hz, <sup>3</sup>J<sub>SnF</sub> = 5.5 Hz); -143.2 (dd with Sn satellites, 1F, 2-Ar-F, <sup>3</sup>J<sub>FF</sub> = 26.8 Hz, <sup>4</sup>J<sub>FF</sub> = 17.8 Hz, <sup>3</sup>J<sub>SnF</sub> = 7.4 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 75.47 MHz): δ 10.0 (t with Sn satellites, SnCH<sub>2</sub>, <sup>1</sup>J<sub>CSn(119)</sub> = 360 Hz, <sup>1</sup>J<sub>CSn(117)</sub> = 344 Hz, <sup>4</sup>J<sub>CF</sub> = 1.8 Hz); 12.4 (s, CH<sub>3</sub>); 26.2 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>, <sup>2</sup>J<sub>CSn(119)</sub> = 65 Hz, <sup>2</sup>J<sub>CSn(117)</sub> = 62 Hz); 27.9 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>CSn</sub> = 20.8 Hz); 109.2 (td, 4-Ar-C, <sup>2</sup>J<sub>CF</sub> = 32.1 Hz, <sup>3</sup>J<sub>CF</sub> = 4.3 Hz); 115.4 (ddd, 1-Ar-C, <sup>2</sup>J<sub>CF</sub> = 52.9 Hz, <sup>2</sup>J<sub>CF</sub> = 45.8 Hz, <sup>3</sup>J<sub>CF</sub> = 3.5 Hz); 116.9 (dd, 5-Ar-C, <sup>2</sup>J<sub>CF</sub> = 20.3 Hz, <sup>3</sup>J<sub>CF</sub> = 9.8 Hz); 146.0 (ddd, 6-Ar-C, <sup>1</sup>J<sub>CF</sub> = 248.3 Hz, <sup>3</sup>J<sub>CF</sub> = 18.7 Hz, <sup>4</sup>J<sub>CF</sub> = 3.9 Hz); 152.8 (ddd, 2-Ar-C, <sup>1</sup>J<sub>CF</sub> = 237.2 Hz, <sup>2</sup>J<sub>CF</sub> = 20.1 Hz, <sup>3</sup>J<sub>CF</sub> = 12.3 Hz); 161.0 (ddd, 3-Ar-C, <sup>1</sup>J<sub>CF</sub> = 233.6 Hz, <sup>2</sup>J<sub>CF</sub> = 16.8 Hz, <sup>4</sup>J<sub>CF</sub> = 2.3 Hz). <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 111.96 MHz): δ -28.7 (ddd, <sup>3</sup>J<sub>SnF</sub> = 7.8 Hz, <sup>3</sup>J<sub>SnF</sub> = 7.4, <sup>4</sup>J<sub>SnF</sub> = 5.6 Hz). Calcd for C<sub>18</sub>H<sub>29</sub>F<sub>3</sub>Sn: [M+ - C<sub>4</sub>H<sub>9</sub>], 365.0539. Found: m/z 365.0537.

**Alternate synthesis of tributyl(2,3,6-trifluorophenyl)stannane, 7.** A solution of 1,2,4-trifluorobenzene (0.192 g, 1.456 mmol) and tributyl(vinyl)tin (0.115 g, 0.36 mmol) in

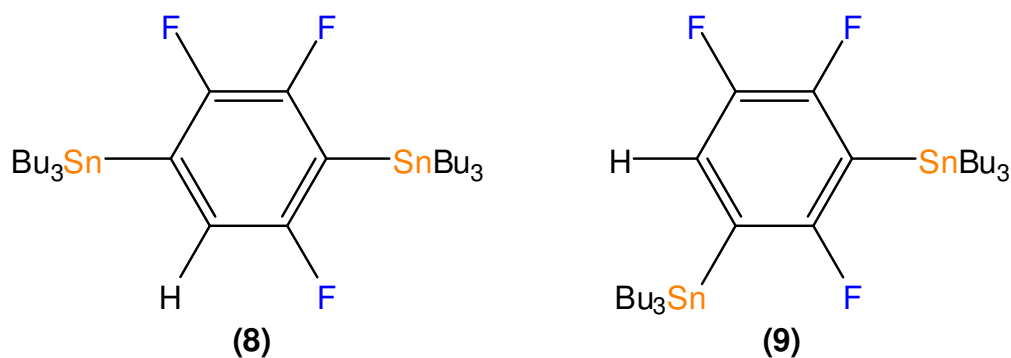
toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 1 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (98 % yield by NMR spectroscopy).



**Synthesis of 2,3,6-trifluorophenyl-1,4-bis(tributylstannane), 8.** A solution of 1,2,4-trifluorobenzene (0.048 g, 0.364 mmol) and tributyl(vinyl)tin (0.288 g, 0.910 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 48 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (50 % yield by NMR spectroscopy, 40 % of **7** and  $\text{Bu}_6\text{Sn}_2$ , 5 % of 2,4,5-trifluorophenyl-1,3-bis(tributylstannane), **9**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.84 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$  Hz); 1.09 (m with Sn satellites, 6H,  $\text{SnCH}_2$ ,  $^2J_{\text{HSn}} = 51.2$  Hz,  $^3J_{\text{HH}} = 7.4$  Hz); 1.29 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.1$  Hz,  $^3J_{\text{HH}} = 7.4$  Hz); 1.55 (tt with Sn satellites, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.1$  Hz,  $^3J_{\text{HH}} = 7.4$  Hz,  $^3J_{\text{HSn}} = 3.1$  Hz); 6.35 (m, 1H, 6-Ar-H).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -99.2 (dd with Sn satellites, 1F, 5-Ar-F,  $^4J_{\text{FF}} = 22.1$  Hz,  $^5J_{\text{FF}} = 0.9$  Hz,  $^3J_{\text{SnF}} = 9.8$  Hz); -115.7 (dd with Sn satellites, 1F, 2-Ar-F,  $^3J_{\text{FF}} = 33.4$  Hz,  $^5J_{\text{FF}} = 0.9$  Hz,  $^3J_{\text{SnF}} = 20.6$  Hz); -124.6 (dd with Sn satellites,

1F, 3-Ar-F,  $^3J_{\text{FF}} = 33.4$  Hz,  $^4J_{\text{FF}} = 22.1$  Hz,  $^3J_{\text{FSn}(119)} = 21.5$  Hz,  $^3J_{\text{FSn}(117)} = 9.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.5 (s with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 354$  Hz,  $^1J_{\text{CSn}(117)} = 338$  Hz); 11.5 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 60.5$  Hz); 29.3 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 20.4$  Hz); 116.9 (ddd, 4-Ar-C,  $^2J_{\text{CF}} = 27.6$  Hz,  $^3J_{\text{CF}} = 14.5$  Hz,  $^4J_{\text{CF}} = 4.7$  Hz); 117.6 (dd, 1-Ar-C,  $^2J_{\text{CF}} = 46.2$  Hz,  $^3J_{\text{CF}} = 2.5$  Hz); 132.6 (d, 6-Ar-C,  $^2J_{\text{CF}} = 44.8$  Hz), 151.0 (ddd, 5-Ar-C,  $^1J_{\text{CF}} = 233$  Hz,  $^3J_{\text{CF}} = 15.8$  Hz,  $^4J_{\text{CF}} = 3.2$  Hz); 153.8 (ddd, 2-Ar-C,  $^1J_{\text{CF}} = 244.8$  Hz,  $^2J_{\text{CF}} = 19.7$  Hz,  $^3J_{\text{CF}} = 17.1$  Hz); 162.9 (dd, 3-Ar-C,  $^1J_{\text{CF}} = 238.3$  Hz,  $^2J_{\text{CF}} = 14.5$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -30.5 (virtual quartet, 1Sn,  $^3J_{\text{SnF}} = 9.3$  Hz,  $^3J_{\text{SnF}} = 8.6$ ); -31.2 (m, 1Sn,  $^3J_{\text{SnF}} = 21.32$  Hz,  $^3J_{\text{SnF}} = 11.44$ ). Calcd for  $\text{C}_{30}\text{H}_{55}\text{F}_3\text{Sn}_2$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 655.1596. Found:  $m/z$  655.1594.

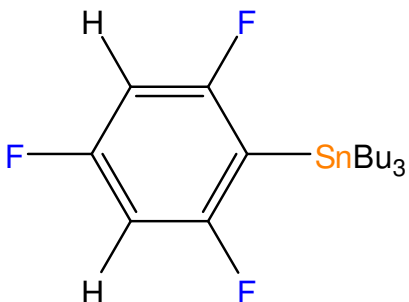
**2,4,5-trifluorophenyl-1,3-bis(tributylstannane), 9.**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  6.32 (m, 1H, 6-Ar-F).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -78.9 (dd with Sn satellites, 1F, 2-Ar-F,  $^5J_{\text{FF}} = 19.8$  Hz,  $^4J_{\text{FF}} = 3.6$  Hz,  $^3J_{\text{SnF}} = 14.7$  Hz); -116.7 (dd with Sn satellites, 1F, 4-Ar-F,  $^3J_{\text{FF}} = 24.4$  Hz,  $^5J_{\text{FF}} = 19.5$  Hz); -143.5 (dd with Sn satellites, 1F, 5-Ar-F,  $^3J_{\text{FF}} = 24.4$  Hz,  $^5J_{\text{FF}} = 19.8$  Hz,  $^4J_{\text{SnF}} = 3.6$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -29.9 (m, 1Sn, 3-Ar-Sn,  $^3J_{\text{SnF}} = 9.7$  Hz,  $^3J_{\text{SnF}} = 7.3$ ); -34.3 (m, 1Sn, 1-Ar-Sn). Calcd for  $\text{C}_{30}\text{H}_{55}\text{F}_3\text{Sn}_2$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 655.1596. Found:  $m/z$  655.1594.



**Synthesis of tributyl(2,4,6-trifluorophenyl)stannane, 10.** To a solution of 1,3,5-trifluorobenzene (0.147 g, 1.11 mmol) and tributyl(vinyl)tin (0.176 g, 0.55 mmol) in 0.6 g of  $C_6D_6$  was added  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and  $Ni(COD)_2$  (0.004 g, 0.017 mmol). The solution was heated to 40 °C for 4 h, filtered through silica and the solvent was removed, leaving a colourless oil. (91 % yield by NMR spectroscopy; isolated 0.167 g, 83 % yield).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300.13 MHz):  $\delta$  0.87 (t, 9H,  $CH_3$ ,  $^3J_{HH} = 7.3$  Hz); 1.18 (m with Sn satellites, 6H,  $SnCH_2$ ,  $^3J_{HSn} = 53.4$  Hz,  $^3J_{HH} = 8.7$  Hz); 1.31 (qt, 6H,  $SnCH_2CH_2CH_2$ ,  $^3J_{HH} = 7.6$  Hz,  $^3J_{HH} = 7.3$  Hz); 1.54 (tt, 6H,  $SnCH_2CH_2$ ,  $^3J_{HH} = 8.9$  Hz,  $^3J_{HH} = 7.5$  Hz); 6.34 (AA'XYY' second order, 2H, 3,5-Ar-H,  $^3J_{HF} = 9.1$ ,  $^3J_{HF} = 5.9$  Hz).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 282.40 MHz):  $\delta$  -90.3 (d, 2F, 2,6-Ar-F,  $^4J_{FF} = 8.2$  Hz,  $^3J_{FSn} = 8.5$  Hz); -108.7 (t with Sn satellites, 1F, 4-Ar-F,  $^4J_{FF} = 8.2$  Hz,  $^5J_{SnF} = 3.1$  Hz).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 75.47 MHz):  $\delta$  11.2 (t with Sn satellites,  $SnCH_2$ ,  $^1J_{CSn(119)} = 361$  Hz,  $^1J_{CSn(117)} = 349$  Hz  $^4J_{CF} = 1.7$  Hz); 13.8 (s,  $CH_3$ ); 27.6 (s with Sn satellites,  $SnCH_2CH_2$ ,  $^2J_{CSn(119)} = 64$  Hz,  $^2J_{CSn(117)} = 62$  Hz); 29.4 (s with Sn satellites,  $SnCH_2CH_2CH_2$ ,  $^3J_{CSn} = 20.7$  Hz); 99.7 (ddd, 3,5-Ar-C,  $^2J_{CF} = 33.6$  Hz,  $^2J_{CF} = 24.6$  Hz,  $^4J_{CF} = 5.0$  Hz); 109.1 (td, 1-Ar-C,  $^2J_{CF} = 51.0$  Hz,  $^4J_{CF} = 4.2$  Hz,  $^1J_{CSn} = 239.3$  Hz); 164.9 (dt, 4-Ar-C,  $^1J_{CF} = 248.2$  Hz,  $^3J_{CF} = 14.6$  Hz); 168.1 (ddd, 2,6-Ar-C,  $^1J_{CF} = 237.7$  Hz,

$^3J_{\text{CF}} = 23.7 \text{ Hz}$ ,  $^3J_{\text{CF}} = 14.7 \text{ Hz}$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ,  $111.96 \text{ MHz}$ ):  $\delta -31.0$  (td,  $^3J_{\text{SnF}} = 8.9 \text{ Hz}$ ,  $^5J_{\text{SnF}} = 3.1 \text{ Hz}$ ). Calcd for  $\text{C}_{18}\text{H}_{29}\text{F}_3\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ ,  $365.0539$ . Found:  $m/z$   $365.0519$ .

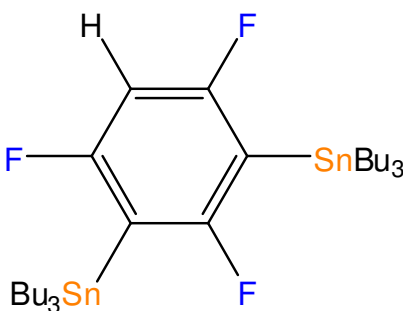
**Alternate synthesis of tributyl(2,4,6-trifluorophenyl)stannane, 10.** A solution of 1,3,5-trifluorobenzene (0.144 g, 1.092 mmol) and tributyl(vinyl)tin (0.106 g, 0.364 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at  $80^\circ\text{C}$  for 30 min. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (83 % yield by NMR spectroscopy, 17 % of **11**).



**Synthesis of 2,4,6-trifluorophenyl-1,3-bis(tributylstannane), 11.** To a solution of 1,3,5-trifluorobenzene (0.061 g, 0.47 mmol) and tributyl(vinyl)tin (0.296 g, 0.93 mmol) in 0.6 g of  $\text{C}_6\text{D}_6$  was added  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.007 g, 0.047 mmol) and  $\text{Ni}(\text{COD})_2$  (0.006 g, 0.023 mmol). The solution was heated to  $40^\circ\text{C}$  for 18 h, filtered through silica and the solvent was removed, leaving a colourless oil. (38 % yield by NMR spectroscopy, 55 % of **10**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ,  $300.13 \text{ MHz}$ ):  $\delta$  0.90 (t, 18H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.2 \text{ Hz}$ ); 1.27 (m with Sn satellites, 12H,  $\text{SnCH}_2$ ,  $^3J_{\text{HH}} = 8.4 \text{ Hz}$ ); 1.36 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.2 \text{ Hz}$ ); 1.62 (tt, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.6 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.3 \text{ Hz}$ ); 6.50 (td with Sn satellites, 1H, 5-Ar-H,  $^3J_{\text{HF}} = 8.6$ ,  $^5J_{\text{HF}} = 2.8 \text{ Hz}$ ,  $^4J_{\text{SnF}} = 6.9 \text{ Hz}$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR

(C<sub>6</sub>D<sub>6</sub>, 25 °C, 282.40 MHz):  $\delta$  -71.0 (t with Sn satellites, 1F, 2-Ar-F,  $^4J_{\text{FF}} = 2.5$  Hz,  $^3J_{\text{FSn}} = 5$  Hz); -90.7 (d with Sn satellites, 2F, 4,6-Ar-F,  $^4J_{\text{FF}} = 2.4$  Hz,  $^3J_{\text{SnF}} = 8$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 75.47 MHz):  $\delta$  11.3 (br s with Sn satellites, SnCH<sub>2</sub>,  $^1J_{\text{CSn}(119)} = 367$  Hz,  $^1J_{\text{CSn}(117)} = 348$  Hz); 13.8 (s, CH<sub>3</sub>); 27.5 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>,  $^2J_{\text{CSn}} = 64$  Hz); 29.4 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>,  $^3J_{\text{CSn}} = 21$  Hz); 99.5 (td, 5-Ar-C,  $^2J_{\text{CF}} = 31.7$  Hz,  $^4J_{\text{CF}} = 5.7$  Hz); 108.3 (dd, 1,3-Ar-C,  $^2J_{\text{CF}} = 60.0$  Hz,  $^2J_{\text{CF}} = 53.3$  Hz); 169.5 (ddd, 4,6-Ar-C,  $^1J_{\text{CF}} = 238.3$  Hz,  $^3J_{\text{CF}} = 22.2$  Hz,  $^3J_{\text{CF}} = 14.6$  Hz); 172.5 (dt, 2-Ar-C,  $^1J_{\text{CF}} = 228.5$  Hz,  $^3J_{\text{CF}} = 23.2$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 111.96 MHz):  $\delta$  -31.5 (virtual quartet,  $^3J_{\text{SnF}} = 6.4$  Hz,  $^5J_{\text{SnF}} = 5.8$  Hz).

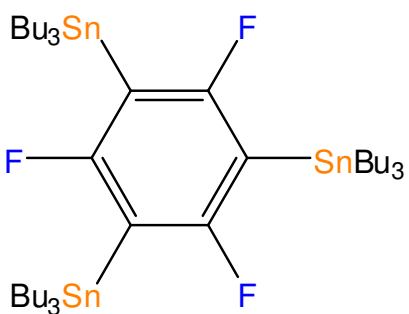
**Alternate synthesis of 2,4,6-trifluorophenyl-1,3-bis(tributylstannane), 11.** A solution of 1,3,5-trifluorobenzene (0.048 g, 0.364 mmol) and tributyl(vinyl)tin (0.288 g, 0.910 mmol) in toluene was added to a mixture of P<sup>*i*</sup>Pr<sub>3</sub> (0.0058 g, 0.036 mmol) and Ni(COD)<sub>2</sub> (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 12 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (45 % yield by NMR spectroscopy, 50 % yield **12**, 2 % yield **10**).



**Synthesis of 2,4,6-trifluorophenyl-1,3,5-tris(tributylstannane), 12.** A solution of 1,3,5-trifluorobenzene (0.048 g, 0.364 mmol) and tributyl(vinyl)tin (0.404 g, 1.27 mmol) in

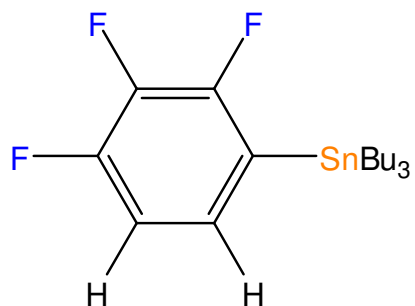


toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy, 5 % of **11**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.93 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 6.5$  Hz); 1.26 (m, 6H,  $\text{SnCH}_2$ ,  $^3J_{\text{HH}} = 8.1$  Hz); 1.38 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.7$  Hz,  $^3J_{\text{HH}} = 6.5$  Hz); 1.65 (m, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.7$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -73.0 (s with Sn satellites, 3F,  $^3J_{\text{FSn}} = 44.2$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  11.4 (s with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 360.9$  Hz,  $^1J_{\text{CSn}(117)} = 341.3$  Hz); 13.9 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 64$  Hz); 29.4 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 22$  Hz); 107.4 (td with Sn satellites, 1,3,5-Ar-C,  $^2J_{\text{CF}} = 57.75$  Hz,  $^4J_{\text{CF}} = 3.17$  Hz,  $J_{\text{CSn}} = 252$  Hz); 174.2 (d with Sn satellites, 2,4,6-Ar-C,  $J_{\text{CF}} = 228.08$  Hz,  $^2J_{\text{CSn}} = 22.92$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 111.96 MHz):  $\delta$  -32.2 (m,  $^3J_{\text{SnF}} = 7.28$  Hz,  $^5J_{\text{SnF}} = 1.4$  Hz).

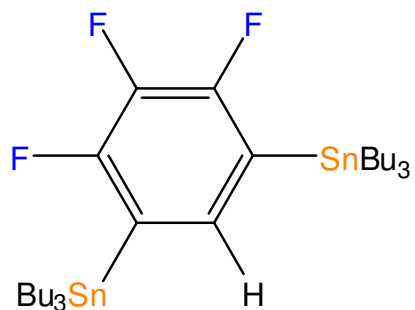


**Synthesis of tributyl(2,3,4-trifluorophenyl)stannane, 13.** A solution of 1,2,3-trifluorobenzene (0.192 g, 1.456 mmol) and tributyl(vinyl)tin (0.115 g, 0.36 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 48 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (50 % yield

by NMR spectroscopy, 30 % of **14**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.86 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.5$  Hz); 1.06 (m with Sn satellites, 6H,  $\text{SnCH}_2$ ,  $^3J_{\text{HH}} = 7.8$  Hz,  $^3J_{\text{HSn}} = 51.6$  Hz); 1.31 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 11.4$  Hz,  $^3J_{\text{HH}} = 7.1$  Hz); 1.52 (tt, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 11.4$  Hz,  $^3J_{\text{HH}} = 7.8$  Hz); 6.58 (m, 1H, 6-Ar-H,  $^4J_{\text{HF}} = 2.1$ ,  $^3J_{\text{HH}} = 7.0$  Hz); 6.75 (m, 1H, 5-Ar-H,  $^3J_{\text{HF}} = 6.4$ ,  $^3J_{\text{HH}} = 7.0$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -117.1 (dd with Sn satellites, 1F, 2-Ar-F,  $^3J_{\text{FF}} = 27.48$ ,  $^4J_{\text{FF}} = 8.1$  Hz,  $^3J_{\text{FSn}} = 27.8$  Hz); -135.9 (dd, 1F, 4-Ar-F,  $^3J_{\text{FF}} = 19.51$ ,  $^4J_{\text{FF}} = 8.1$  Hz); -161.7 (dd with Sn satellites, 1F, 3-Ar-F,  $^3J_{\text{FF}} = 27.48$ ,  $^4J_{\text{FF}} = 8.1$  Hz,  $^3J_{\text{FSn}} = 12.2$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.3 (s with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 354.4$  Hz,  $^1J_{\text{CSn}(117)} = 338.3$  Hz); 13.9 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 65.7$  Hz); 29.3 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 20$  Hz); 113.4 (d with Sn satellites, 1-Ar-C,  $^2J_{\text{CF}} = 16$  Hz,  $^2J_{\text{CSn}} = 53.7$  Hz); 124.2 (dm, 5-Ar-C,  $^2J_{\text{CF}} = 44.5$  Hz,  $^3J_{\text{CF}} = 5.6$  Hz); 130.3 (dm, 6-Ar-C,  $^3J_{\text{CF}} = 17.6$  Hz,  $^4J_{\text{CF}} = 6.4$  Hz); 140.1 (ddd, 3-Ar-C,  $^1J_{\text{CF}} = 242.2$  Hz,  $^2J_{\text{CF}} = 12.0$  Hz,  $^2J_{\text{CF}} = 7.2$  Hz); 152.2 (ddd, 2-Ar-C,  $^1J_{\text{CF}} = 242.9$  Hz,  $^2J_{\text{CF}} = 13.6$  Hz,  $^3J_{\text{CF}} = 4$  Hz); 155.4 (dm, 4-Ar-C,  $^1J_{\text{CF}} = 227.7$  Hz,  $^3J_{\text{CF}} = 5.6$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -31.8 (ddd,  $^3J_{\text{SnF}} = 20.72$  Hz,  $^4J_{\text{SnF}} = 12.24$  Hz,  $^5J_{\text{SnF}} = 3.59$  Hz). Calcd for  $\text{C}_{18}\text{H}_{29}\text{F}_3\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 365.0539. Found:  $m/z$  365.0534.



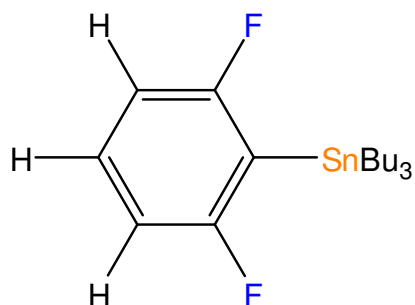
**Synthesis of 2,3,4-trifluorophenyl-1,5-bis(tributylstannane), 14.** A solution of 1,2,3-trifluorobenzene (0.048 g, 0.364 mmol) and tributyl(vinyl)tin (0.288 g, 0.910 mmol) in toluene was added to a mixture of  $P^iPr_3$  (0.0058 g, 0.036 mmol) and  $Ni(COD)_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (30 % yield by NMR spectroscopy, 40 % of **13** and  $Bu_6Sn_2$ ).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300.13 MHz):  $\delta$  0.91 (t, 9H,  $SnCH_2CH_2CH_2CH_3$ ,  $^3J_{HH} = 7.3$  Hz); 1.18 (m, 6H,  $SnCH_2$ ,  $^3J_{HH} = 8.1$  Hz); 1.36 (m, 6H,  $SnCH_2CH_2CH_2$ ); 1.59 (m, 6H,  $SnCH_2CH_2$ ); 7.31 (m with Sn satellites, 6-Ar-H,  $^4J_{HF} = 2.6$ ,  $^3J_{HSn} = 32.9$  Hz).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 282.40 MHz):  $\delta$  -118.0 (d with Sn satellites, 2F, 2,4-Ar-F,  $^3J_{FF} = 25.9$ ,  $^3J_{FSn} = 17.4$  Hz); -161.6 (t with Sn satellites, 1F, 3-Ar-F,  $^3J_{FF} = 25.9$ ,  $^3J_{FSn} = 9.93$  Hz).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 75.47 MHz):  $\delta$  10.4 (s with Sn satellites,  $SnCH_2$ ,  $^1J_{CSn(119)} = 353.1$  Hz,  $^1J_{CSn(117)} = 335.2$  Hz); 13.8 (s,  $SnCH_2CH_2CH_2CH_3$ ); 27.7 (s with Sn satellites,  $SnCH_2CH_2$ ,  $^2J_{CSn} = 60.2$  Hz); 29.4 (s with Sn satellites,  $SnCH_2CH_2CH_2$ ,  $^3J_{CSn} = 22$  Hz); 125.0 (dd with Sn satellites, 6-Ar-C,  $^3J_{CF} = 4.6$  Hz,  $^2J_{CSn} = 44.2$  Hz); 137.3 (td with Sn satellites, 1,5-Ar-C,  $^2J_{CF} = 16.1$  Hz,  $^3J_{CF} = 8.4$  Hz,  $J_{CSn} = 131.1$  Hz); 152.2 (ddd, 2,4-Ar-C,  $^1J_{CF} = 244.5$  Hz,  $^2J_{CF} = 12.3$  Hz,  $^3J_{CF} = 8.2$  Hz); 156.0 (ddd, 3-Ar-C,  $^1J_{CF} = 236.5$  Hz,  $^2J_{CF} = 11.6$  Hz,  $^3J_{CF} = 7.5$  Hz).  $^{119}Sn\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 186.49 MHz):  $\delta$  -33.4 (m AA'XX'Y second order,  $^3J_{CF} = 10.64$  Hz,  $^4J_{SnSn} = 5.7$  Hz).



**Synthesis of tributyl(2,6-difluorophenyl)stannane, 15.** To a solution of 1,3-difluorobenzene (0.180 g, 1.58 mmol) and tributyl(vinyl)tin (0.500 g, 1.58 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub> was added MeNC<sub>5</sub>H<sub>4</sub>N<sup>i</sup>Pr (0.010 g, 0.063 mmol) and Ni(COD)<sub>2</sub> (0.009 g, 0.0315 mmol). The solution was allowed to react for 12 h at 37 °C, filtered through silica and the solvent was removed, leaving a colourless oil. (30 % yield by NMR spectroscopy, 30 % Bu<sub>6</sub>Sn<sub>2</sub>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.13 MHz): δ 0.84 (t, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz); 1.20 (m with Sn satellites, 6H, SnCH<sub>2</sub>, <sup>2</sup>J<sub>HSn</sub> = 53.5 Hz, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz); 1.32 (qt, 6H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz); 1.55 (tt, 6H, SnCH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 8.6 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz); 6.57 (dd, 2H, 3,5-Ar-H, <sup>3</sup>J<sub>HF</sub> = 6.3, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz); 6.78 (tt, 1H, 4-Ar-H, <sup>3</sup>J<sub>HH</sub> = 8.0, <sup>4</sup>J<sub>HF</sub> = 7.1 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 282.40 MHz): δ -92.1 (s with Sn satellites, 2F, 2,6-Ar-F, <sup>3</sup>J<sub>FSn</sub> = 14.5 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 75.47 MHz): δ 11.2 (s with Sn satellites, SnCH<sub>2</sub>, <sup>1</sup>J<sub>CSn(119)</sub> = 360 Hz, <sup>1</sup>J<sub>CSn(117)</sub> = 344 Hz); 13.9 (s, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 27.6 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>, <sup>2</sup>J<sub>CSn(119)</sub> = 64 Hz, <sup>2</sup>J<sub>CSn(117)</sub> = 61 Hz); 29.4 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>CSn</sub> = 21 Hz); 110.2 (dd with Sn satellites, 3,5-Ar-C, <sup>2</sup>J<sub>CF</sub> = 28.2 Hz, <sup>4</sup>J<sub>CF</sub> = 3.7 Hz, <sup>3</sup>J<sub>CSn</sub> = 13 Hz); 114.0 (t, 1-Ar-C, <sup>2</sup>J<sub>CF</sub> = 49.8 Hz); 131.8 (t, 4-Ar-C, <sup>3</sup>J<sub>CF</sub> = 9.2 Hz); 168.2 (dd with Sn satellites, 2,6-Ar-C, <sup>1</sup>J<sub>CF</sub> = 237.2 Hz, <sup>3</sup>J<sub>CF</sub> = 19.2 Hz, <sup>2</sup>J<sub>CSn</sub> = 4 Hz). <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C,

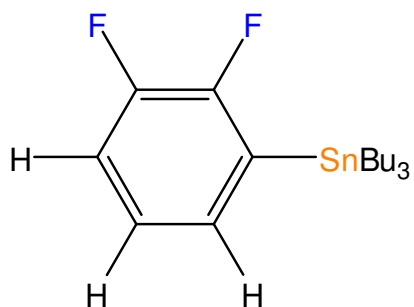
111.96 MHz):  $\delta$  -33.1 (t,  $^3J_{\text{SnF}} = 15.0$  Hz). Calcd for  $\text{C}_{18}\text{H}_{30}\text{F}_2\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 345.0477. Found:  $m/z$  345.0482.

**Alternate synthesis of tributyl(2,6-difluorophenyl)stannane, 15.** A solution of 1,3-difluorobenzene (0.100 g, 0.88 mmol) and tributyl(vinyl)tin (0.231 g, 0.73 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.012 g, 0.073 mmol) and  $\text{Ni}(\text{COD})_2$  (0.01 g, 0.036 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (90 % yield by NMR spectroscopy).



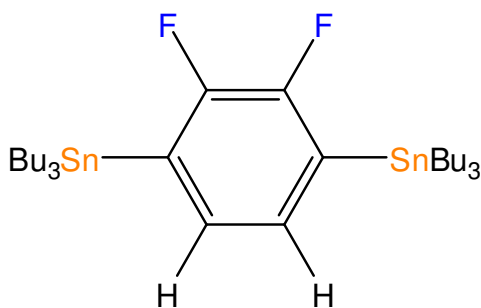
**Synthesis of tributyl(2,3-difluorophenyl)stannane, 16.** A solution of 1,2-difluorobenzene (0.381 g, 3.34 mmol) and tributyl(vinyl)tin (0.106 g, 0.335 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (92 % yield by NMR spectroscopy, 2 % of **17**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.84 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.7$  Hz); 1.08 (m with satellites, 6H,  $\text{SnCH}_2$ ,  $^2J_{\text{HSn}} = 51.9$  Hz,  $^3J_{\text{HH}} = 8.8$  Hz); 1.29 (m, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ); 1.52 (tt, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.8$  Hz,  $^3J_{\text{HH}} = 6.8$  Hz); 6.75 (m, 1H, 5-Ar-H,  $^3J_{\text{HH}} = 7.8$  Hz,  $^4J_{\text{HF}} = 4.1$  Hz). 6.82 (ddm, 1H, 4-Ar-H,  $^3J_{\text{HF}} = 9.4$  Hz,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HF}} = 4.1$  Hz), 7.08 (d with Sn satellites, 1H, 6-Ar-H,

$^3J_{\text{HH}} = 7.3$  Hz,  $^3J_{\text{HSn}} = 22.7$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -119.8 (d with Sn satellites, 1F, 2-Ar-F,  $^3J_{\text{FF}} = 28.5$  Hz,  $^3J_{\text{FSn}} = 28.4$  Hz); -138.1 (d with Sn satellites, 1F, 3-Ar-F,  $^3J_{\text{FF}} = 28.5$  Hz,  $^4J_{\text{FSn}} = 17.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.3 (s,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 353.5$  Hz,  $^1J_{\text{CSn}(117)} = 335.9$  Hz); 13.8 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 52.7$  Hz); 29.3 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 22.9$  Hz); 117.78 (d, 6-Ar-C,  $^3J_{\text{CF}} = 17.56$  Hz); 123.3 (s, 5-Ar-C); 130.2 (d, 4-Ar-C,  $^2J_{\text{CF}} = 41.7$  Hz); 131.7 (d, 1-Ar-C,  $^3J_{\text{CF}} = 13.17$  Hz); 150.7 (dd, 3-Ar-C,  $^1J_{\text{CF}} = 254.68$  Hz,  $^2J_{\text{CF}} = 21.96$  Hz); 154.7 (dd, 2-Ar-C,  $^1J_{\text{CF}} = 234.92$  Hz,  $^2J_{\text{CF}} = 21.96$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -34.2 (dd,  $^3J_{\text{SnF}} = 30.6$  Hz,  $^4J_{\text{SnF}} = 18.1$  Hz). Calcd for  $\text{C}_{18}\text{H}_{30}\text{F}_2\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 347.0633. Found:  $m/z$  347.0641.



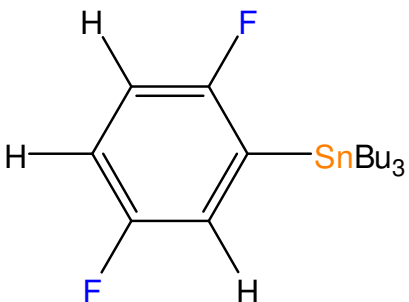
**Synthesis of 2,3-difluorophenyl-1,4-bis(tributylstannane), 17.** A solution of 1,2-difluorobenzene (0.042 g, 0.364 mmol) and tributyl(vinyl)tin (0.288 g, 0.910 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (25 % yield by NMR spectroscopy, 50 % of **16** and  $\text{Bu}_6\text{Sn}_2$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.87 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.2$  Hz); 1.15 (m with satellites, 6H,  $\text{SnCH}_2$ ,

$^2J_{\text{HSn}} = 57.2$  Hz,  $^3J_{\text{HH}} = 8.5$  Hz); 1.33 (m, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ); 1.58 (m, 6H,  $\text{SnCH}_2\text{CH}_2$ ); 7.23 (s with Sn satellites, 5,6-Ar-H,  $^3J_{\text{HSn}} = 12.7$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -118.8 (s with Sn satellites, 2F, 2,3-Ar-F,  $^3J_{\text{FSn}} = 28.3$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.5 (s,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 352.09$  Hz,  $^1J_{\text{CSn}(117)} = 336.0$  Hz); 13.8 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.6 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 53.2$  Hz); 29.5 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 24.1$  Hz); 125.3 (m, 1,4-Ar-C); 132.3 (dd, 5,6-Ar-C,  $^3J_{\text{CF}} = 8.29$  Hz,  $^4J_{\text{CF}} = 7.25$  Hz); 154.6 (d with Sn satellites, 2,3-Ar-C,  $^1J_{\text{CF}} = 243.9$  Hz,  $^2J_{\text{CSn}} = 19.25$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -35.1 (t,  $^3J_{\text{SnF}} = 29.2$  Hz).  $\text{C}_{30}\text{H}_{56}\text{F}_2\text{Sn}_2$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ . Found: m/z.



**Synthesis of tributyl(2,5-difluorophenyl)stannane, 18.** A solution of 1,4-difluorobenzene (0.381 g, 3.34 mmol) and tributyl(vinyl)tin (0.106 g, 0.335 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (90 % yield by NMR spectroscopy, 10 % of **19**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.85 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.1$  Hz); 1.07 (m with satellites, 6H,  $\text{SnCH}_2$ ,  $^2J_{\text{HSn}} = 50.6$  Hz,  $^3J_{\text{HH}} = 8.0$  Hz); 1.31 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.1$  Hz,  $^3J_{\text{HH}} = 6.6$  Hz); 1.53 (tt, 6H,

$\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 8.0 \text{ Hz}$ ,  $^3J_{\text{HH}} = 7.1 \text{ Hz}$ ); 6.64 (m, 3,4-Ar-H,  $^3J_{\text{HF}} = 8.1 \text{ Hz}$ ,  $^3J_{\text{HH}} = 6.6 \text{ Hz}$ ,  $^4J_{\text{HH}} = 4.7 \text{ Hz}$ ); 7.1 (dddd, 6-Ar-H,  $^5J_{\text{HH}} = 8 \text{ Hz}$ ,  $^3J_{\text{HF}} = 7.2 \text{ Hz}$ ,  $^3J_{\text{HH}} = 4.7 \text{ Hz}$ ,  $^4J_{\text{HF}} = 1.9 \text{ Hz}$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -101.3 (d with Sn satellites, 1F, 2-Ar-F,  $^5J_{\text{FF}} = 20.7 \text{ Hz}$ ,  $^3J_{\text{FSn}} = 26.2 \text{ Hz}$ ), -120.7 (d with Sn satellites, 1F, 5-Ar-F,  $^5J_{\text{FF}} = 20.7 \text{ Hz}$ ,  $^3J_{\text{FSn}} = 8.7 \text{ Hz}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.2 (s with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 354.4 \text{ Hz}$ ,  $^1J_{\text{CSn}(117)} = 339.6 \text{ Hz}$ ); 13.8 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.7 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 50.3 \text{ Hz}$ ); 29.3 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 21.6 \text{ Hz}$ ); 115.5 (dd with Sn satellites, 4-Ar-C,  $^2J_{\text{CF}} = 32.3 \text{ Hz}$ ,  $^3J_{\text{CF}} = 7.9 \text{ Hz}$ ,  $^4J_{\text{CSn}} = 27.1 \text{ Hz}$ ); 117.0 (dd, 1-Ar-C,  $^2J_{\text{CF}} = 24.3 \text{ Hz}$ ,  $^3J_{\text{CF}} = 9.4 \text{ Hz}$ ); 123.1 (dd with Sn satellites, 6-Ar-C,  $^2J_{\text{CF}} = 20.8 \text{ Hz}$ ,  $^3J_{\text{CF}} = 16.1 \text{ Hz}$ ,  $^2J_{\text{CSn}} = 16.9 \text{ Hz}$ ); 129.5 (dd, 3-Ar-C,  $^2J_{\text{CF}} = 50.6 \text{ Hz}$ ,  $^3J_{\text{CF}} = 4.7 \text{ Hz}$ ); 159.7 (d, 5-Ar-C,  $^1J_{\text{CF}} = 247.3 \text{ Hz}$ ); 163.5 (d, 2-Ar-C,  $^1J_{\text{CF}} = 229.7 \text{ Hz}$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -35.0 (dd,  $^3J_{\text{SnF}} = 26.98 \text{ Hz}$ ,  $^4J_{\text{SnF}} = 9.0 \text{ Hz}$ ). Calcd for  $\text{C}_{18}\text{H}_{30}\text{F}_2\text{Sn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 347.0633. Found:  $m/z$  347.0633.



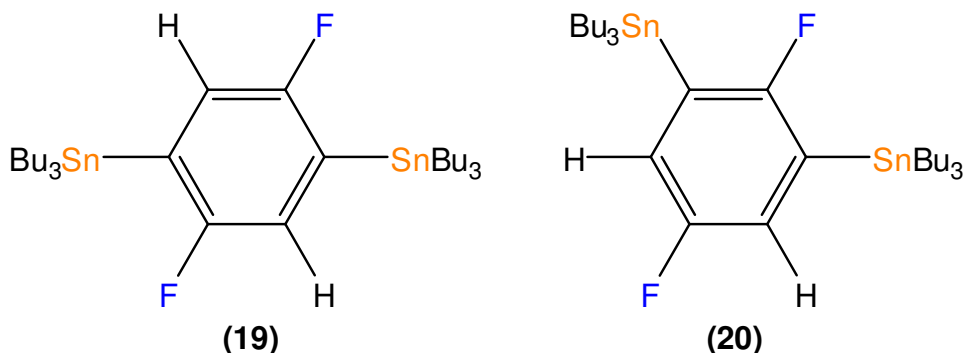
**Synthesis of 2,5-difluorophenyl-1,4-bis(tributylstannane), 19.** A solution of 1,4-difluorobenzene (0.042 g, 0.364 mmol) and tributyl(vinyl)tin (0.288 g, 0.910 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0058 g, 0.036 mmol) and  $\text{Ni}(\text{COD})_2$  (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was



filtered through silica and the solvent was removed, leaving a colourless oil. (10 % yield by NMR spectroscopy, 70 % of **18** and Bu<sub>6</sub>Sn<sub>2</sub>, 10 % of 2,5-difluorophenyl-1,3-bis(tributylstannane), **20**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.13 MHz): δ 0.85 (t, 9H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz); 1.09 (m, 6H, SnCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz); 1.3 (m, 6H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.55 (m, 6H, SnCH<sub>2</sub>CH<sub>2</sub>); 6.95 (dd second order with Sn satellites, 2H, 3,6-Ar-H, <sup>3</sup>J<sub>HF</sub> = 5.7 Hz, <sup>4</sup>J<sub>HF</sub> = 3.4 Hz, <sup>3</sup>J<sub>HSn</sub> = 17.8 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 282.40 MHz): δ -102.2 (s with Sn satellites, 2F, 2,5-Ar-F, <sup>3</sup>J<sub>FSn</sub> = 19.37 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 75.47 MHz): δ 10.2 (s with Sn satellites, SnCH<sub>2</sub>, <sup>1</sup>J<sub>CSn(119)</sub> = 355.7 Hz, <sup>1</sup>J<sub>CSn(117)</sub> = 335.9 Hz); 13.8 (s, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 27.6 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>, <sup>2</sup>J<sub>CSn</sub> = 61.5 Hz); 29.4 (s, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 117.0 (dd, 1-Ar-C, <sup>2</sup>J<sub>CF</sub> = 24.2 Hz, <sup>3</sup>J<sub>CF</sub> = 8.8 Hz); 123.4 (dd, 3,6-Ar-C, <sup>2</sup>J<sub>CF</sub> = 21.96 Hz, <sup>3</sup>J<sub>CF</sub> = 17.56 Hz); 159.7 (d, 2,5-Ar-C, <sup>1</sup>J<sub>CF</sub> = 245.9 Hz). <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 186.49 MHz): δ -35.9 (t, <sup>3</sup>J<sub>SnF</sub> = 20.0 Hz).

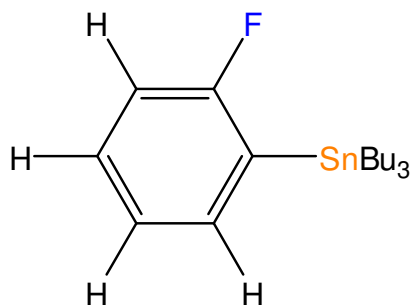
**2,5-difluorophenyl-1,3-bis(tributylstannane), 20.** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 300.13 MHz): δ 0.85 (t, 9H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz); 1.11 (m, 6H, SnCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz); 1.2 (m, 6H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.55 (m, 6H, SnCH<sub>2</sub>CH<sub>2</sub>); 7.21 (dd with Sn satellites, 2H, 4,6-Ar-H, <sup>3</sup>J<sub>HF</sub> = 6.5 Hz, <sup>4</sup>J<sub>HF</sub> = 3.4 Hz, <sup>3</sup>J<sub>HSn</sub> = 31.0 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 282.40 MHz): δ -82.3 (d with Sn satellites, 1F, 2-Ar-F, <sup>5</sup>J<sub>FF</sub> = 24.2 Hz, <sup>3</sup>J<sub>FSn</sub> = 17.3 Hz), -121.2 (d with Sn satellites, 1F, 5-Ar-F, <sup>5</sup>J<sub>FF</sub> = 24.2 Hz, <sup>3</sup>J<sub>FSn</sub> = 7.9 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 75.47 MHz): δ 11.6 (s with Sn satellites, SnCH<sub>2</sub>, <sup>1</sup>J<sub>CSn</sub> = 357.9 Hz); 14.3 (s, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 27.7 (s with Sn satellites, SnCH<sub>2</sub>CH<sub>2</sub>, <sup>2</sup>J<sub>CSn</sub> = 63.7 Hz); 29.5 (s, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 115.5 (dd, 1-Ar-C, <sup>2</sup>J<sub>CF</sub> = 32.9 Hz, <sup>3</sup>J<sub>CF</sub> = 8.8 Hz); 122.1 (dd, 3,6-Ar-C, <sup>2</sup>J<sub>CF</sub> = 21.96 Hz, <sup>3</sup>J<sub>CF</sub> = 19.76 Hz); 161.0 (d, 2-Ar-C, <sup>1</sup>J<sub>CF</sub> = 241.4 Hz); 163.5 (d, 2-

Ar-C,  $^1J_{\text{CF}} = 228.2$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta -35.6$  (dd,  $^3J_{\text{SnF}} = 17.8$  Hz,  $^4J_{\text{SnF}} = 7.2$  Hz).



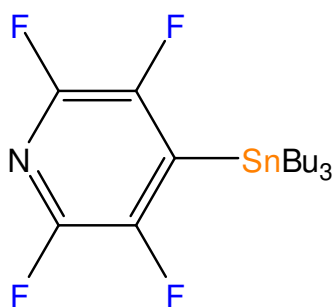
**Synthesis of tributyl(2-fluorophenyl)stannane, 21.** A solution of fluorobenzene (0.321 g, 3.34 mmol) and tributyl(vinyl)tin (0.106 g, 0.334 mmol) in toluene was added to a mixture of  $\text{P}^i\text{Pr}_3$  (0.0054 g, 0.033 mmol) and  $\text{Ni}(\text{COD})_2$  (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (15 % yield by NMR spectroscopy).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.92 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.7$  Hz); 1.15 (m with satellites, 6H,  $\text{SnCH}_2$ ,  $^2J_{\text{HSn}} = 58.2$  Hz,  $^3J_{\text{HH}} = 8.2$  Hz); 1.35 (m, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ); 1.6 (m, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.3$  Hz,  $^3J_{\text{HH}} = 8.2$  Hz); 6.89 (dd, 1H, 3-Ar-H,  $^3J_{\text{HH}} = 7.3$ ,  $^3J_{\text{HF}} = 8.2$  Hz); 7.28 (m, 1H, 6-Ar-H,  $^3J_{\text{HH}} = 7.3$ ,  $^4J_{\text{HF}} = 6.8$  Hz); 7.37 and 7.39 (dd, 2H, 4,5-Ar-H,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HF}} = 4.5$  Hz,  $^5J_{\text{HF}} = 2.1$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta -93.7$  (s with Sn satellites,  $^3J_{\text{FSn}} = 36$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  10.2 (s with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 353.4$  Hz,  $^1J_{\text{CSn}(117)} = 337.2$  Hz); 13.9 (s,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.7 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}} = 53.4$  Hz); 29.5 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 21.1$  Hz); 114.6 (d, 1-Ar-C,  $^2J_{\text{CF}} = 27.8$  Hz); 124.5 (d with Sn satellites, 6-Ar-C,  $^3J_{\text{CF}} = 2.4$  Hz,

$^2J_{\text{CSn}} = 34.52$  Hz); 128.8 (s, 4-Ar-C); 130.67 (d, 5-Ar-C,  $^4J_{\text{CF}} = 7.7$  Hz); 137.5 (d, 3-Ar-C,  $^2J_{\text{CF}} = 15.1$  Hz); 167.9 (d, 2-Ar-C,  $^1J_{\text{CF}} = 234.5$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 186.49 MHz):  $\delta$  -37.4 (d,  $^3J_{\text{SnF}} = 36.35$  Hz). Calcd for  $\text{C}_{18}\text{H}_{31}\text{FSn}$ :  $[\text{M}^+ - \text{C}_4\text{H}_9]$ , 329.0728. Found:  $m/z$  329.0742.

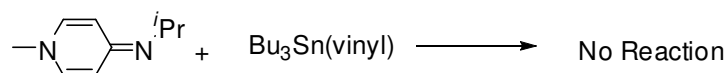


**Synthesis of tributyl(2,3,5,6-tetrafluoropyridyl)stannane, 22.** A solution of 2,3,5,6-tetrafluoropyridine (0.110 g, 0.73 mmol) in toluene was added to a mixture of tributyl(vinyl)tin (0.231 g, 0.73 mmol),  $\text{P}^i\text{Pr}_3$  (0.0116 g, 0.073 mmol), and  $\text{Ni}(\text{COD})_2$  (0.01 g, 0.036 mmol). The solution was heated at 80 °C for 2 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a pale orange oil. (98 % yield by NMR spectroscopy; isolated 0.277 g, 87 %).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.89 (t, 9H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 6.6$  Hz); 1.17 (m, 6H,  $\text{SnCH}_2$ ,  $^3J_{\text{HH}} = 7.7$  Hz); 1.29 (qt, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 6.9$  Hz,  $^3J_{\text{HH}} = 6.6$  Hz); 1.49 (tt, 6H,  $\text{SnCH}_2\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.7$  Hz,  $^3J_{\text{HH}} = 6.6$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $\delta$  -93.5 (AA'MM' second order, 2F, 2,6-Ar-F); -125.4 (AA'MM' second order, 2F, 2,6-Ar-F).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 75.47 MHz):  $\delta$  11.6 (t with Sn satellites,  $\text{SnCH}_2$ ,  $^1J_{\text{CSn}(119)} = 359.7$  Hz,  $^1J_{\text{CSn}(117)} = 341.6$  Hz,  $^4J_{\text{CF}} = 1.8$  Hz); 13.7 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $^4J_{\text{CSn}} = 2.7$  Hz); 27.4 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2$ ,  $^2J_{\text{CSn}(119)} = 66.8$  Hz,  $^2J_{\text{CSn}(117)} = 63.3$  Hz); 29.0 (s with Sn satellites,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ,  $^3J_{\text{CSn}} = 21.1$  Hz);

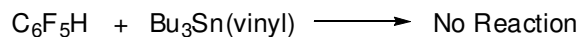
118.4 (tm, 1-Ar-C,  $^2J_{\text{CF}} = 21.1$  Hz); 143.7 (dddd second order, 2,6-Ar-C,  $^1J_{\text{CF}} = 234.5$  Hz,  $J = 24.1, 10.3, 1.7$  Hz); 145.3 (dm second order, 3,5-Ar-C,  $^1J_{\text{CF}} = 244.8$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 111.95 MHz):  $\delta -19.3$  (tt,  $^3J_{\text{SnF}} = 11.26$  Hz,  $^4J_{\text{SnF}} = 7.0$  Hz). Calcd for  $\text{C}_{17}\text{H}_{27}\text{F}_4\text{NSn}$ :  $[\text{M} + - \text{C}_4\text{H}_9]$ , 384.0397. Found:  $m/z$  384.0387.



**Reaction of  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A colourless solution of tributyl(vinyl)tin (0.010 g, 0.033 mmol) and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.005 g, 0.033 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was allowed to react overnight at room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR spectroscopy, and only starting materials were observed.

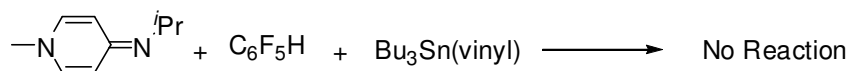


**Reaction of  $\text{C}_6\text{F}_5\text{H}$  and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A colourless solution of tributyl(vinyl)tin (0.010 g, 0.031 mmol) and  $\text{C}_6\text{F}_5\text{H}$  (0.005 g, 0.031 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was allowed to react overnight at 100 °C. The reaction mixture was analyzed by  $^1\text{H}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, and only starting materials were observed.



**Reaction of  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$ ,  $\text{C}_6\text{F}_5\text{H}$ , and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A colourless solution of tributyl(vinyl)tin (0.021 g, 0.067 mmol),  $\text{C}_6\text{F}_5\text{H}$  (0.011 g, 0.067 mmol) and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.010 g, 0.067 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was allowed to react overnight at

100 °C. The reaction mixture was analyzed by  $^1\text{H}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, and only starting materials were observed.



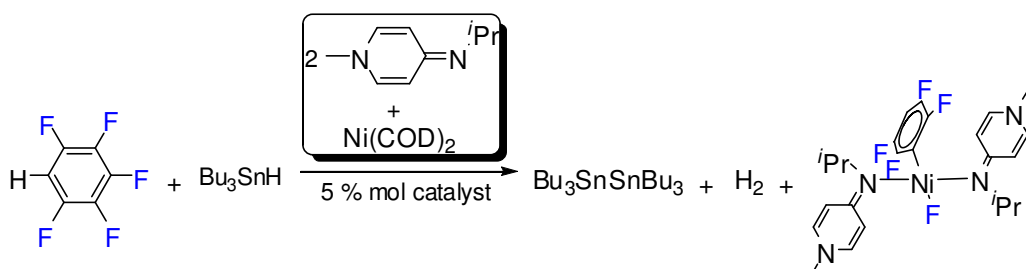
**Reaction of  $\text{Ni(COD)}_2$ ,  $\text{C}_6\text{F}_5\text{H}$ , and  $\text{Bu}_3\text{Sn(vinyl)}$ .** A bright orange solution of tributyl(vinyl)tin (0.115 g, 0.364 mmol),  $\text{C}_6\text{F}_5\text{H}$  (0.061 mg, 0.364 mmol), and  $\text{Ni(COD)}_2$  (0.005 g, 0.018 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was allowed to react overnight at 50 °C. The reaction mixture was analyzed by  $^1\text{H}$  and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectroscopy, there was free COD present at  $\delta$  2.10 and 5.50 and no remaining  $\text{Ni(COD)}_2$ . There was also a small amount of remaining tributyl(vinyl)tin, however, the major product was hexabutylditin with a 3 % impurity of the conversion to **1**.

**Reaction of  $\text{C}_6\text{F}_5\text{H}$ ,  $\text{Bu}_3\text{Sn(vinyl)}$ , Hg, and 10 % catalyst loading of  $\text{Ni(COD)}_2$  and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$ .** A dark golden yellow solution of tributyl(vinyl)tin (0.053 g, 0.167 mmol),  $\text{C}_6\text{F}_5\text{H}$  (0.028 g, 0.167 mmol), Hg (0.500 g, 2.49 mmol),  $\text{Ni(COD)}_2$  (0.004 g, 0.0167 mmol), and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.005 mg, 0.033 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was allowed to react for 30 min.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz):  $-121.3$  (AA'MM'N second order with satellites, 2F, 1,5–Ar–F,  $^3J_{\text{FSn}} = 7.7$  Hz);  $-153.0$  (tt with satellites, 1F, 3–Ar–F,  $^3J_{\text{FF}} = 19.9$  Hz,  $^4J_{\text{FF}} = 1.8$  Hz,  $^5J_{\text{FSn}} = 7.4$  Hz);  $-160.7$  (AA'MM'N second order, 2F, 2,4–Ar–F).

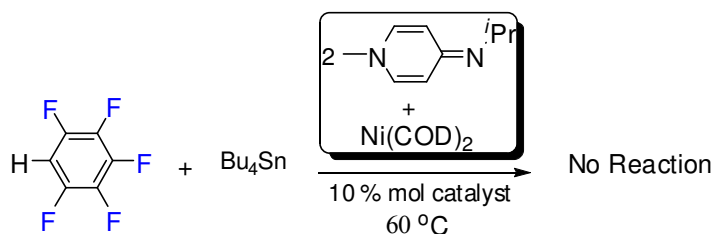
After 30 min the desired product is formed, which indicates that  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  and nickel are directly involved in the reaction, but nickel metal is not.

**Reaction of  $\text{C}_6\text{F}_5\text{H}$ ,  $\text{Bu}_3\text{SnH}$ , and 5 % catalyst loading of  $\text{Ni(COD)}_2$  and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$ .** A solution of  $\text{C}_6\text{F}_5\text{H}$  (0.056 g, 0.33 mmol),  $\text{Bu}_3\text{SnH}$  (0.097 g, 0.33

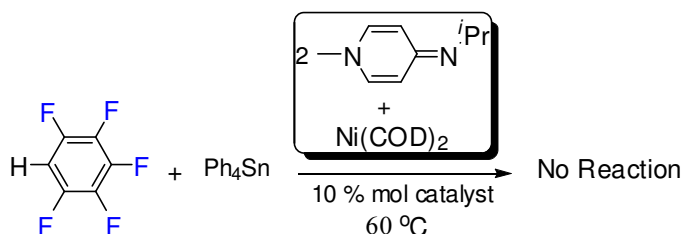
mmol) in 1 mL of  $C_6D_6$  was mixed with  $Ni(COD)_2$  (0.005 g, 0.0167 mmol) and  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol). Upon addition of all components,  $H_2$  was vigorously released forming  $Bu_3SnSnBu_3$  and a precipitate. The precipitate was dissolved in  $CD_2Cl_2$  and confirmed by  $^1H$  and  $^{19}F\{^1H\}$  NMR spectroscopy to be  $trans-(MeNC_5H_4N^iPr)_2NiF(2,2',3,3'-C_6F_4H)$  which is the expected C–F activation complex. This reaction was also performed analogously with  $Ni(COD)_2$  and triisopropylphosphine as the ligand and provided hexabutylditin and various activation products.



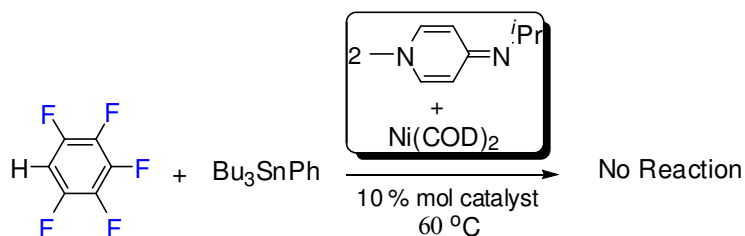
**Reaction of  $C_6F_5H$ ,  $Bu_4Sn$ , and 10 % catalyst loading of  $Ni(COD)_2$  and  $MeNC_5H_4N^iPr$ .** A solution of  $C_6F_5H$  (0.028 g, 0.167 mmol),  $Bu_4Sn$  (0.058 g, 0.167 mmol) in 1 mL of  $C_6D_6$  was mixed with  $Ni(COD)_2$  (0.004 g, 0.0167 mmol) and  $MeNC_5H_4N^iPr$  (0.005 g, 0.033 mmol) and allowed to react for 1 day at 60 °C. No significant reaction was observed by  $^1H$  and  $^{19}F\{^1H\}$  NMR spectroscopy. This reaction was also performed stoichiometrically at room temperature with  $Ni(COD)_2$  and triisopropylphosphine as the ligand and provided the same results.



**Reaction of C<sub>6</sub>F<sub>5</sub>H, Ph<sub>4</sub>Sn, and 10 % catalyst loading of Ni(COD)<sub>2</sub> and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr.** A solution of C<sub>6</sub>F<sub>5</sub>H (0.028 g, 0.167 mmol), Ph<sub>4</sub>Sn (0.071 g, 0.167 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub> was mixed with Ni(COD)<sub>2</sub> (0.004 g, 0.0167 mmol) and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr (0.005 g, 0.033 mmol) and allowed to react for 1 day at 60 °C. No significant reaction was observed by <sup>1</sup>H and <sup>19</sup>F{<sup>1</sup>H} NMR spectroscopy. This reaction was also performed stoichiometrically at room temperature with Ni(COD)<sub>2</sub> and triisopropylphosphine as the ligand and provided the same results.



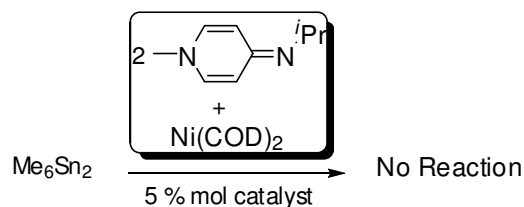
**Reaction of C<sub>6</sub>F<sub>5</sub>H, Bu<sub>3</sub>SnPh, and 10 % catalyst loading of Ni(COD)<sub>2</sub> and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr.** A solution of C<sub>6</sub>F<sub>5</sub>H (0.028 g, 0.167 mmol), Bu<sub>3</sub>SnPh (0.061 g, 0.167 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub> was mixed with Ni(COD)<sub>2</sub> (0.004 g, 0.0167 mmol) and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr (0.005 g, 0.033 mmol) and allowed to react for 1 day at 60 °C. No significant reaction was observed by <sup>1</sup>H and <sup>19</sup>F{<sup>1</sup>H} NMR spectroscopy.



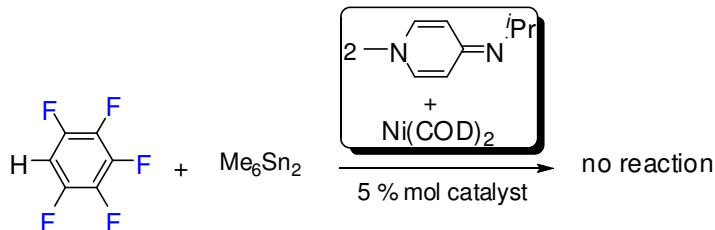
**Reaction of 5 % catalyst loading of MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr and Ni(COD)<sub>2</sub> with Me<sub>6</sub>Sn<sub>2</sub>.**

A solution of Me<sub>6</sub>Sn<sub>2</sub> (0.109 g, 0.333 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub> was mixed with Ni(COD)<sub>2</sub> (0.004 g, 0.0167 mmol) and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr (0.005 g, 0.033 mmol) and allowed to react

for 1 h at room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR spectroscopy, only starting materials were observed.



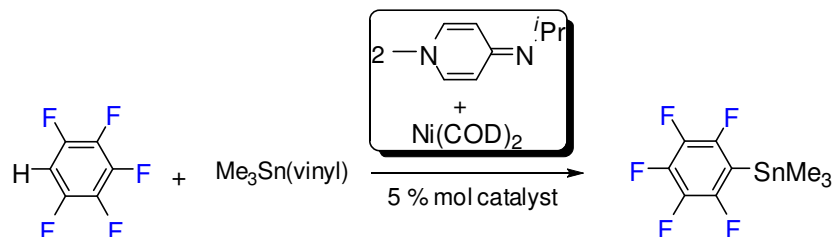
**Reaction of 5 % catalyst loading of  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  and  $\text{Ni}(\text{COD})_2$  with  $\text{Me}_6\text{Sn}_2$  and  $\text{C}_6\text{F}_5\text{H}$ .** A solution of  $\text{Me}_6\text{Sn}_2$  (0.109 g, 0.333 mmol) and  $\text{C}_6\text{F}_5\text{H}$  (0.060 g, 0.333 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was mixed with  $\text{Ni}(\text{COD})_2$  (0.004 g, 0.0167 mmol) and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.005 g, 0.033 mmol) and allowed to react for 1 h at room temperature. The reaction mixture was analyzed by  $^1\text{H}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, there was no observed reaction.



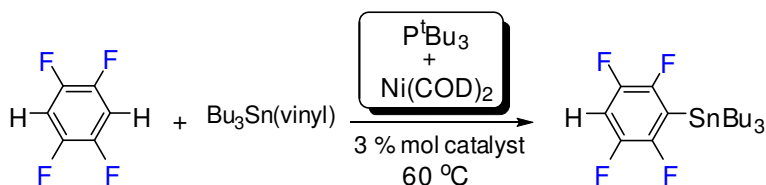
**Reaction of 5 % catalyst loading of  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  and  $\text{Ni}(\text{COD})_2$  with  $\text{C}_6\text{F}_5\text{H}$  and  $\text{Me}_3\text{Sn}(\text{vinyl})$ .** A solution of  $\text{C}_6\text{F}_5\text{H}$  (0.169 g, 1.00 mmol) and  $\text{Me}_3\text{Sn}(\text{vinyl})$  (0.250 g, 1.00 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was mixed with  $\text{Ni}(\text{COD})_2$  (0.014 g, 0.050 mmol) and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.015 g, 0.101 mmol) and allowed to react for 48 h at 50 °C. The reaction mixture was analyzed by  $^1\text{H}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, which indicated a 90 % conversion to the desired product by NMR spectroscopy, trimethyl(2,3,4,5,6-pentafluorophenyl)tin, with respect to  $\text{C}_6\text{F}_5\text{H}$ . This reaction was also performed analogously with  $\text{Ni}(\text{COD})_2$  and triisopropylphosphine as the ligand yielding the same



results after heating at 50 °C for 24 h.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300.13 MHz):  $\delta$  0.35 (s with satellites, 9H,  $\text{CH}_3$ ,  $^2J_{\text{Hsn}} = 58.6$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 282.40 MHz): –122.5 (AA'MM'X second order, 2F, 2,6–Ar–F,  $^3J_{\text{FF}} = 15.8$  Hz); –153.9 (t, 1F, 4–Ar–F,  $^3J_{\text{FF}} = 19.6$  Hz); –161.5 (AA'MM'X second order, 2F, 3,5–Ar–F,  $^3J_{\text{FF}} = 15.8$  Hz,  $^3J_{\text{FF}} = 19.6$  Hz).

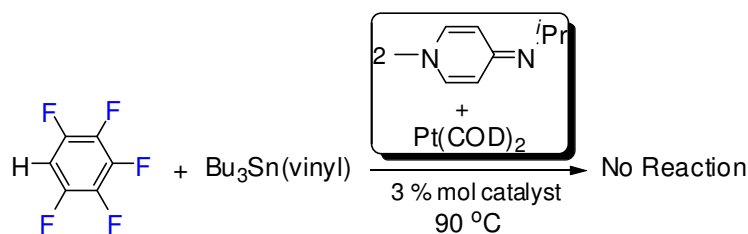


**Reaction of 3 % catalyst loading of  $\text{P}^t\text{Bu}_3$  and  $\text{Ni}(\text{COD})_2$  with 1,2,4,5– $\text{C}_6\text{F}_4\text{H}_2$  and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A solution of 1,2,4,5– $\text{C}_6\text{F}_4\text{H}_2$  (0.250 g, 1.67 mmol) and tributyl(vinyl)tin (0.176 g, 0.555 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was mixed with  $\text{Ni}(\text{COD})_2$  (0.004 g, 0.0167 mmol) and  $\text{P}^t\text{Bu}_3$  (0.005 g, 0.033 mmol) and allowed to react overnight at 60 °C. The reaction mixture was analyzed by  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, which indicated a 42 % conversion to the desired product **2**, with respect to remaining 1,2,4,5– $\text{C}_6\text{F}_4\text{H}_2$ .

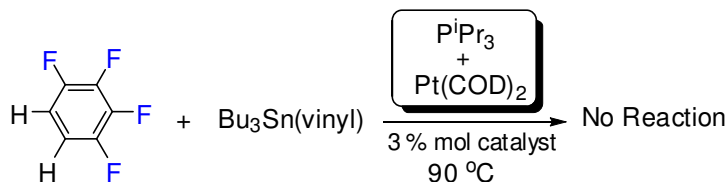


**Reaction of 3 % catalyst loading of  $\text{Pt}(\text{COD})_2$  and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  with  $\text{C}_6\text{F}_5\text{H}$  and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A solution of  $\text{C}_6\text{F}_5\text{H}$  (0.094 g, 0.555 mmol) and tributyl(vinyl)tin (0.176 g, 0.555 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was mixed with  $\text{Pt}(\text{COD})_2$  (0.007 g, 0.0167 mmol) and  $\text{MeNC}_5\text{H}_4\text{N}^i\text{Pr}$  (0.005 g, 0.033 mmol) and allowed to react overnight at 90 °C. The

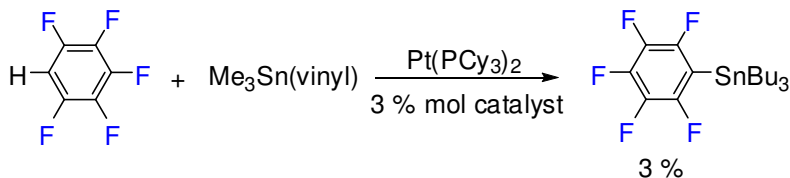
reaction mixture was analyzed by  $^1\text{H}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, the desired activation product was not observed.



**Reaction of 3 % catalyst loading of  $\text{Pt}(\text{COD})_2$  and  $\text{P}^i\text{Pr}_3$  with 1,2,3,4- $\text{C}_6\text{F}_4\text{H}_2$  and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A solution of 1,2,3,4- $\text{C}_6\text{F}_4\text{H}_2$  (0.083 g, 0.555 mmol) and tributyl(vinyl)tin (0.176 g, 0.555 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was mixed with  $\text{Pt}(\text{COD})_2$  (0.007 g, 0.0167 mmol) and  $\text{P}^i\text{Pr}_3$  (0.005 g, 0.033 mmol) and allowed to react overnight at  $90\text{ }^\circ\text{C}$ . The reaction mixture was analyzed by  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, the desired activation product was not observed.

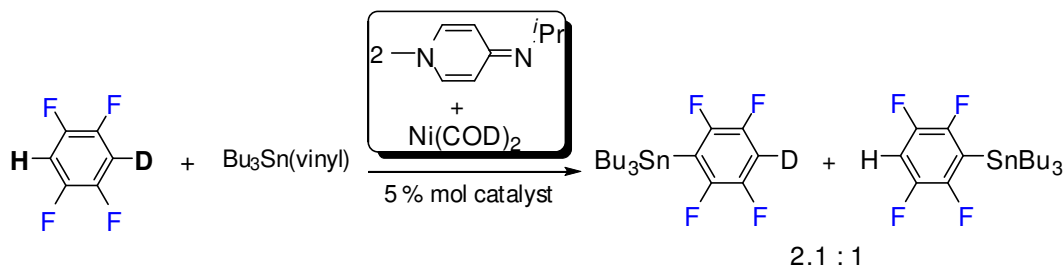


**Reaction of 3 % catalyst loading of  $\text{Pt}(\text{PCy}_3)_2$  with  $\text{C}_6\text{F}_5\text{H}$  and  $\text{Bu}_3\text{Sn}(\text{vinyl})$ .** A solution of  $\text{C}_6\text{F}_5\text{H}$  (0.056 g, 0.333 mmol) and tributyl(vinyl)tin (0.106 g, 0.333 mmol) in 1 mL of  $\text{C}_6\text{D}_6$  was mixed with  $\text{Pt}(\text{PCy}_3)_2$  (0.013 g, 0.0167 mmol) and allowed to react overnight at  $90\text{ }^\circ\text{C}$ . The reaction mixture was analyzed by  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectroscopy, only about 3 % conversion to the desired product **1** was observed by NMR with respect to remaining  $\text{C}_6\text{F}_5\text{H}$ .



## Deuterium Labelling Studies

**Reaction of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>HD, Bu<sub>3</sub>Sn(vinyl), and 5 % catalyst loading of Ni(COD)<sub>2</sub> and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr.** A solution of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>HD (0.050 g, 0.33 mmol), tributyl(vinyl)tin (0.106 g, 0.33 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub> was mixed with Ni(COD)<sub>2</sub> (0.005 g, 0.0167 mmol) and **1** (0.005 g, 0.033 mmol). The <sup>19</sup>F{<sup>1</sup>H} NMR spectra of the reaction mixture was recorded within 5 min of the initiation of the reaction in order to determine the initial deuterium isotope effect for C–H vs. C–D activation. Activation of hydrogen over deuterium can be confirmed by a ~0.3 ppm shift of any *ortho* fluorine adjacent to the remaining deuterium in the product and the isotope effect can be determined through integration. Oxidative addition is favored for C–H over C–D bonds, and the integrals of the peaks were found to be in a 2.1:1 at 298 K. <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 282.40 MHz): –122.2 (AA'BB' second order, 2,4–Ar–F); –138.1 (AA'BB' second order, 1,4–Ar–F); –138.4 (AA'BB' second order, 1,4–Ar–F).

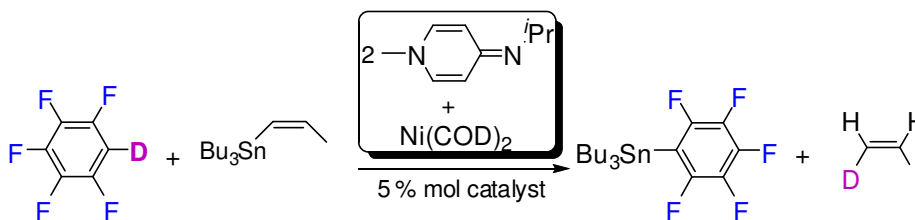


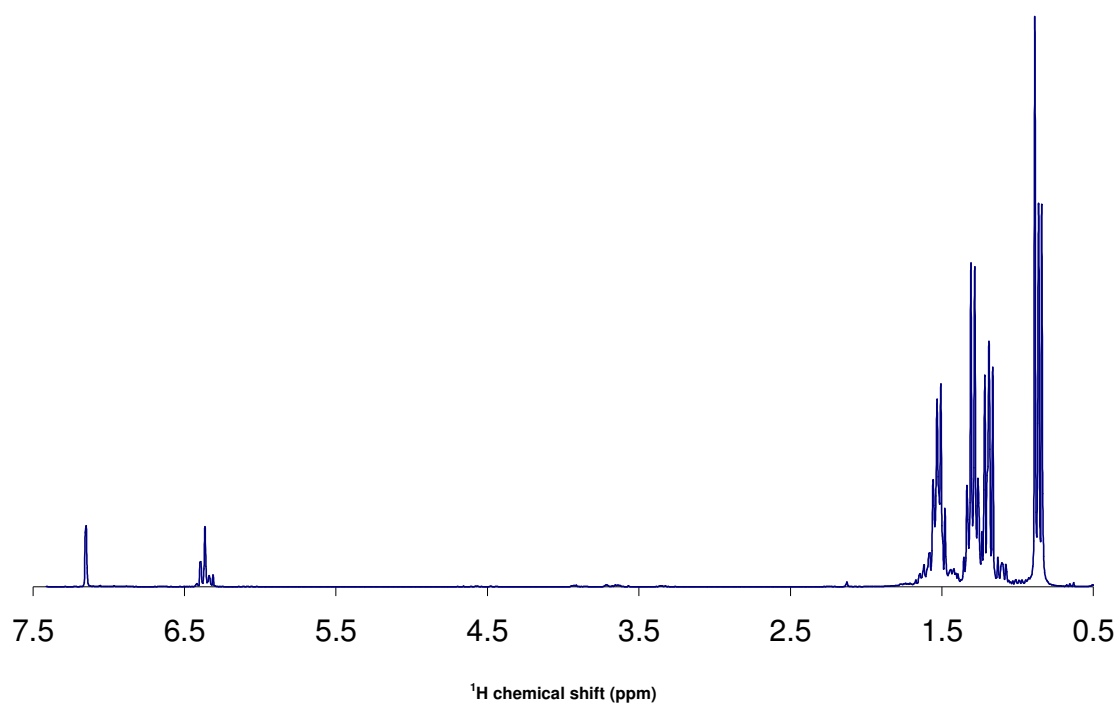
**Reaction of C<sub>6</sub>F<sub>5</sub>D, *cis*-Bu<sub>3</sub>Sn(propene), and 5 % catalyst loadings of Ni(COD)<sub>2</sub> and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr.** A solution of C<sub>6</sub>F<sub>5</sub>D (0.056 g, 0.33 mmol), *cis*-Bu<sub>3</sub>Sn(propene) (0.110

g, 0.33 mmol) in 1 mL of C<sub>6</sub>D<sub>6</sub> was mixed with Ni(COD)<sub>2</sub> (0.005 g, 0.0167 mmol) and MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr (0.005 g, 0.033 mmol). The reaction mixture was allowed to react overnight at room temperature. The resultant deuterium labeled propene was vacuum transferred to a J. Young tube containing CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR spectroscopy. This reaction was also performed analogously with triisopropylphosphine in lieu of the MeNC<sub>5</sub>H<sub>4</sub>N<sup>*i*</sup>Pr ligand at 10 mol % catalyst loading.

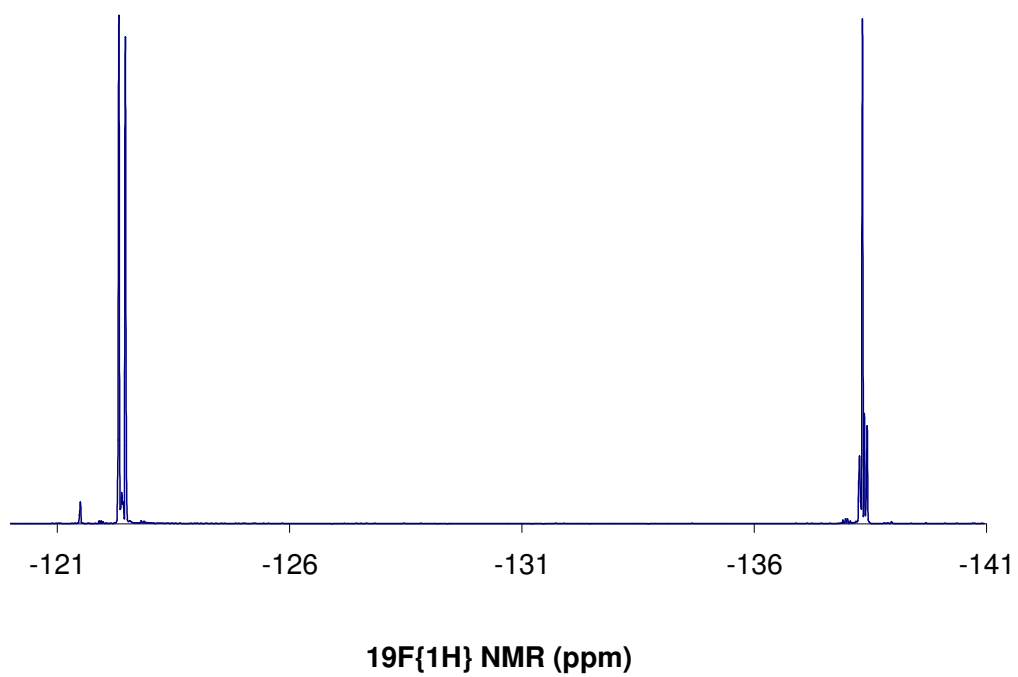
**Experimental chemical shifts and coupling constants of propene-*d*<sub>1</sub> CDCl<sub>3</sub>. (11)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 300.13 MHz): δ 1.79 (dd, CH<sub>3</sub>, <sup>3</sup>*J*<sub>HH</sub> = 6.78 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz); 5.08 (second order, H, <sup>3</sup>*J*<sub>HH</sub> = 16.72 Hz, <sup>4</sup>*J*<sub>HH</sub> = 2.05 Hz); 5.90 (dqt, H, <sup>3</sup>*J*<sub>HH</sub> = 17.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 6.50 Hz, <sup>3</sup>*J*<sub>HD</sub> = 1.6 Hz).





**Figure 1.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ .



**Figure 2.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ .

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