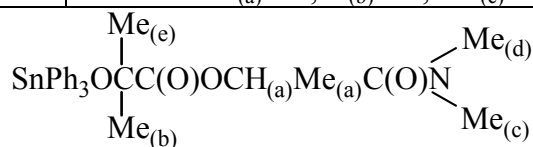


# Supplementary Information

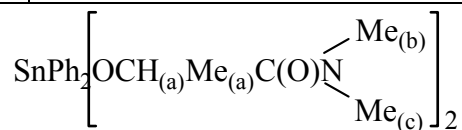
NOE Difference Spectroscopy:



Irradiated signal	Enhanced signal(s) (%)
Me <sub>(a)</sub>	Me <sub>(c)</sub> 0.5, Me <sub>(d)</sub> 0.6
Me <sub>(b)</sub>	-
Me <sub>(c)</sub>	H <sub>(a)</sub> 7.2
Me <sub>(d)</sub>	H <sub>(a)</sub> 5.4
H <sub>(a)</sub>	Me <sub>(c)</sub> 0.6, Me <sub>(d)</sub> 0.6, <i>o</i> -H 0.1
H <sub>(b)</sub>	-
<i>o</i> -H	H <sub>(a)</sub> 2.4, H <sub>(b)</sub> 1.8, Me <sub>(c)</sub> 0.4, Me <sub>(d)</sub> 0.4



Irradiated signal	Enhanced signal(s) (%)
Me <sub>(a)</sub>	Me <sub>(b)</sub> 0.3, Me <sub>(c)</sub> 0.3, Me <sub>(d)</sub> 0.3, Me <sub>(e)</sub> 0.2
Me <sub>(b)</sub>	Me <sub>(a)</sub> 0.5, Me <sub>(e)</sub> 1.9
Me <sub>(c)</sub>	H <sub>(a)</sub> 3.9
Me <sub>(d)</sub>	H <sub>(a)</sub> 3.0, Me <sub>(a)</sub> 0.9
Me <sub>(e)</sub>	Me <sub>(a)</sub> 0.4, Me <sub>(b)</sub> 0.07, Me <sub>(c)</sub> 0.4, Me <sub>(d)</sub> 0.3, Me <sub>(e)</sub> 0.03
H <sub>(a)</sub>	Me <sub>(c)</sub> 0.6, Me <sub>(d)</sub> 0.6, <i>o</i> -H 0.1
<i>o</i> -H	-
<i>m</i> -H	-



Irradiated signal	Enhanced signal(s) (%)
Me <sub>(a)</sub>	Me <sub>(b)</sub> 1.1, Me <sub>(c)</sub> 0.6, H <sub>(a)</sub> 5.1, <i>o</i> -H 0.05
Me <sub>(b)</sub>	Me <sub>(a)</sub> 3.0
Me <sub>(c)</sub>	Me <sub>(a)</sub> 2.8, <i>m</i> -H 0.1
H <sub>(a)</sub>	<i>o</i> -H 0.1
<i>o</i> -H	Me <sub>(a)</sub> 0.6, Me <sub>(c)</sub> 0.2, H <sub>(a)</sub> 1.2
<i>m</i> -H	-
<i>p</i> -H	-

**Synthesis and Characterization of Ar<sub>3</sub>SnX and Ph<sub>2</sub>SnX<sub>2</sub> where X = NMe<sub>2</sub>, OMe, OPr<sup>i</sup>, OCH(CF<sub>3</sub>)<sub>2</sub>, OBU<sup>t</sup>, OPh, and PPh<sub>2</sub>.**

All liquid alcohols and diphenylphosphine were dried over activated molecular sieves. Phenol was used as received.

*Dimethylamidotriphenyltin(IV)* Chlorotriphenyltin(IV) (1.45 g, 3.76 mmol) dissolved in THF (10 mL) was added to a stirred THF (20 mL) solution of lithium dimethylamide (0.20 g, 3.92 mmol). The slightly pale yellow solution was heated at 60° C for 20 h after which time the THF was removed under vacuum and the off white residue was extracted with hexanes (50 mL) and filtered from suspended lithium chloride. The clear solution was pumped to dryness to yield a white solid that was recrystallized from hexanes at -20° C giving 1.38 g (93 %) of the title complex. IR (Nujol), cm<sup>-1</sup>: 3064 m, 2766 m, 1480 m, 1428 ms, 1332 w, 1302 w, 1260 w, 1237 w, 1167 m, 1075 s, 1061 w, 1021 w, 996 m, 946 s, 727 vs, 698 vs, 659 w, 525 w, 446 s. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): δ 2.94 (s, NMe<sub>2</sub>, 6H, <sup>119/117</sup>Sn satellites *J*<sub>SnH</sub> 44 Hz), 7.17 (m, *m*- and *p*-H, 9H), 7.63 (d, *o*-H, 6H, <sup>119/117</sup>Sn satellites *J*<sub>SnH</sub> <sup>117</sup>Sn 53, <sup>119</sup>Sn 43 Hz). <sup>119</sup>Sn NMR (149 MHz, benzene-*d*<sub>6</sub>): δ -86 (s).

*Bis(dimethylamido)diphenyltin(IV)* Dichlorodiphenyltin(IV) (2.18 g, 6.34 mmol) dissolved in THF (20 mL) was added to a stirred THF (20 mL) solution of lithium dimethylamide (0.71 g, 13.94 mmol). The slightly orange solution was heated at 60 °C for 15 h after which time the THF was removed under vacuum and the off-white, sticky residue was extracted with hexanes (50 mL) and filtered from the lithium chloride and excess lithium dimethylamide. The orange solution was pumped to dryness to yield an orange oil that was distilled under vacuum to give 1.87 g (82 %) of a colorless oil. <sup>1</sup>H

NMR (500 MHz, benzene- $d_6$ ):  $\delta$  2.96 (s, NMe<sub>2</sub>, 12H, <sup>119/117</sup>Sn satellites  $J_{\text{SnH}}$  <sup>117</sup>Sn 44, <sup>119</sup>Sn 43 Hz), 7.18 (m, *m*- and *p*-H, 6H), 7.61 (dd, *o*-H, 4H  $J_{\text{HH}}$  7.6 and 1.6 Hz; <sup>119/117</sup>Sn satellites  $J_{\text{SnH}}$  <sup>117</sup>Sn 61, <sup>119</sup>Sn 47 Hz). <sup>119</sup>Sn NMR (187 MHz, benzene- $d_6$ ):  $\delta$  -79 (s).

*Dimethylamidotris(2-methylbenzo)tin(IV)* Chlorotris(2-methylbenzo)tin(IV) (1.50 g, 3.52 mmol) dissolved in THF (15 mL) was added to a stirred THF (15 mL) solution of lithium dimethylamide (0.20 g, 3.92 mmol). The colorless solution was heated at 50° C for 72 h after which time the solvent was removed under vacuum giving an off-white semi-solid residue which was extracted with benzene (50 mL). The white suspension was filtered from the pale yellow solution and the benzene was removed giving a pale yellow semi-solid which was recrystallized from hexane to afford a white solid 0.78 g (51 %). IR (Nujol), cm<sup>-1</sup>: 3054 m, 2771 w, 1584 m, 1559 m, 1279 w, 1265 m, 1243 w, 1202 m, 1169 s, 1117 s, 1066 w, 951 vs, 795 m, 745 vs, 697 w. <sup>1</sup>H NMR (500 MHz, benzene- $d_6$ ):  $\delta$  2.35 (s, Me aryl, 9H, <sup>119/117</sup>Sn satellites  $J_{\text{SnH}}$  6.4 Hz), 2.86 (s, NMe<sub>2</sub>, 6H, <sup>119/117</sup>Sn satellites  $J_{\text{SnH}}$  <sup>117</sup>Sn 44, <sup>119</sup>Sn 42 Hz), 7.10 (m, *m*- and *p*-H, 9H), 7.68 (dd, *o*-H, 3H,  $J_{\text{HH}}$  7.3 and 1.3 Hz, <sup>119/117</sup>Sn satellites  $J_{\text{SnH}}$  <sup>117</sup>Sn 64, <sup>119</sup>Sn 49 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, benzene- $d_6$ ): 24.88 (s, Me aryl, <sup>119/117</sup>Sn satellites  $J_{\text{SnC}}$  28 Hz), 44.43 (s, NMe<sub>2</sub>), 126.16 (s, *m*-C <sup>119/117</sup>Sn satellites  $J_{\text{SnC}}$  55 Hz), 129.82 (s, *m*\*-C <sup>119/117</sup>Sn satellites  $J_{\text{SnC}}$  11 Hz), 130.05 (s, *p*-C), 137.38 (s, *o*-C <sup>119/117</sup>Sn satellites  $J_{\text{SnC}}$  42 Hz) 140.23 (s, *ipso*-C), 144.98 (s, *o*-C\*, <sup>119/117</sup>Sn satellites  $J_{\text{SnC}}$  36 Hz) \*denotes Me side of phenyl ring. <sup>119</sup>Sn NMR (149 MHz, benzene- $d_6$ ):  $\delta$  -67 (s).

*tert*-Butoxytriphenyltin(IV) Excess *tert*-butanol (2.78 g, 37.6 mmol) was added to a hexane (20 mL) solution/suspension of dimethylamidotriphenyltin(IV) (1.48 g, 3.76 mmol). After stirring at room temperature for 12 h the colorless solution was filtered to

remove a small amount of precipitate. The hexanes were removed giving a white crystalline powder 1.42 g (89 %) that was heated (60 °C) under vacuum for 30 mins. Anal. Calcd for C<sub>18</sub>H<sub>24</sub>OSn: C, 62.45; H, 5.72. Found: C, 61.66; H, 5.72. IR (Nujol), cm<sup>-1</sup>: 3053 w, 1479 m, 1430 m, 1359 m, 1332 w, 1303 w, 1261 w, 1230 w, 1190 br s, 1075 s, 1022 m, 996 m, 964 vs, 774 m, 729 vs, 697 vs, 661 m, 582 m, 467 m, 447 s, 438 m. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): δ 1.38 (s, Bu<sup>t</sup>O, 9H), 7.15 (m, *m*- and *p*-H, 9H), 7.73 (d, *o*-H, 6H, <sup>119/117</sup>Sn satellites *J*<sub>SnH</sub> <sup>117</sup>Sn 53, <sup>119</sup>Sn 43 Hz). <sup>119</sup>Sn NMR (149 MHz, benzene-*d*<sub>6</sub>): δ -114 (s).

*iso*-Propoxytriphenyltin(IV) Excess *iso*-propanol (0.15 g, 2.54 mmol) was added to a hexane (10 mL) solution of dimethylamidotriphenyltin(IV) (0.10 g, 0.254 mmol). After stirring at room temperature for 12 h the colorless solution was concentrated and stored at -20° C where a white crystalline material 75 mg (72 %) formed which was separated from the solution and dried under vacuum to give the title complex. Anal. Calcd for C<sub>21</sub>H<sub>22</sub>OSn: C, 61.66; H, 5.42. Found: C, 61.13; H, 5.15. IR (Nujol), cm<sup>-1</sup>: 3063 w, 1479 m, 1429 m, 1332 w, 1302 w, 1261 w, 1191 w, 1156 w, 1117m, 1076 s, 1023 m, 996 m, 973 m, 836 w, 729 vs, 697 vs, 660 w, 607 w, 447 s, 375 m. <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>): δ 1.28 (d, Me, 6H), 4.30 (sept., CHMe<sub>2</sub>, 1H), 7.17 (m, *m*- and *p*-H, 9H), 7.65 (d, *o*-H, 6H, <sup>119/117</sup>Sn satellites *J*<sub>SnH</sub> <sup>117</sup>Sn 57, <sup>119</sup>Sn 46 Hz). <sup>119</sup>Sn NMR (149 MHz, benzene-*d*<sub>6</sub>): δ -95 (s).

*Methoxytriphenyltin(IV)* Excess methanol (0.12 g, 4.00 mmol) was added to a hexane (20 mL) solution/suspension of dimethylamidotriphenyltin(IV) (0.80 g, 2.03 mmol). After stirring at room temperature for 12 h the colorless solution was filtered to remove a small amount of precipitate. The hexanes were removed giving a white crystalline

powder 0.85 g (87 %) that was heated (60 °C) under vacuum for 30 mins.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ):  $\delta$  3.92 (s, MeO, 9H), 7.17 (m, *m*- and *p*-H, 9H), 7.62 (m, *o*-H, 6H).  $^{119}\text{Sn}$  NMR (149 MHz, benzene- $d_6$ ):  $\delta$  -82 (s).

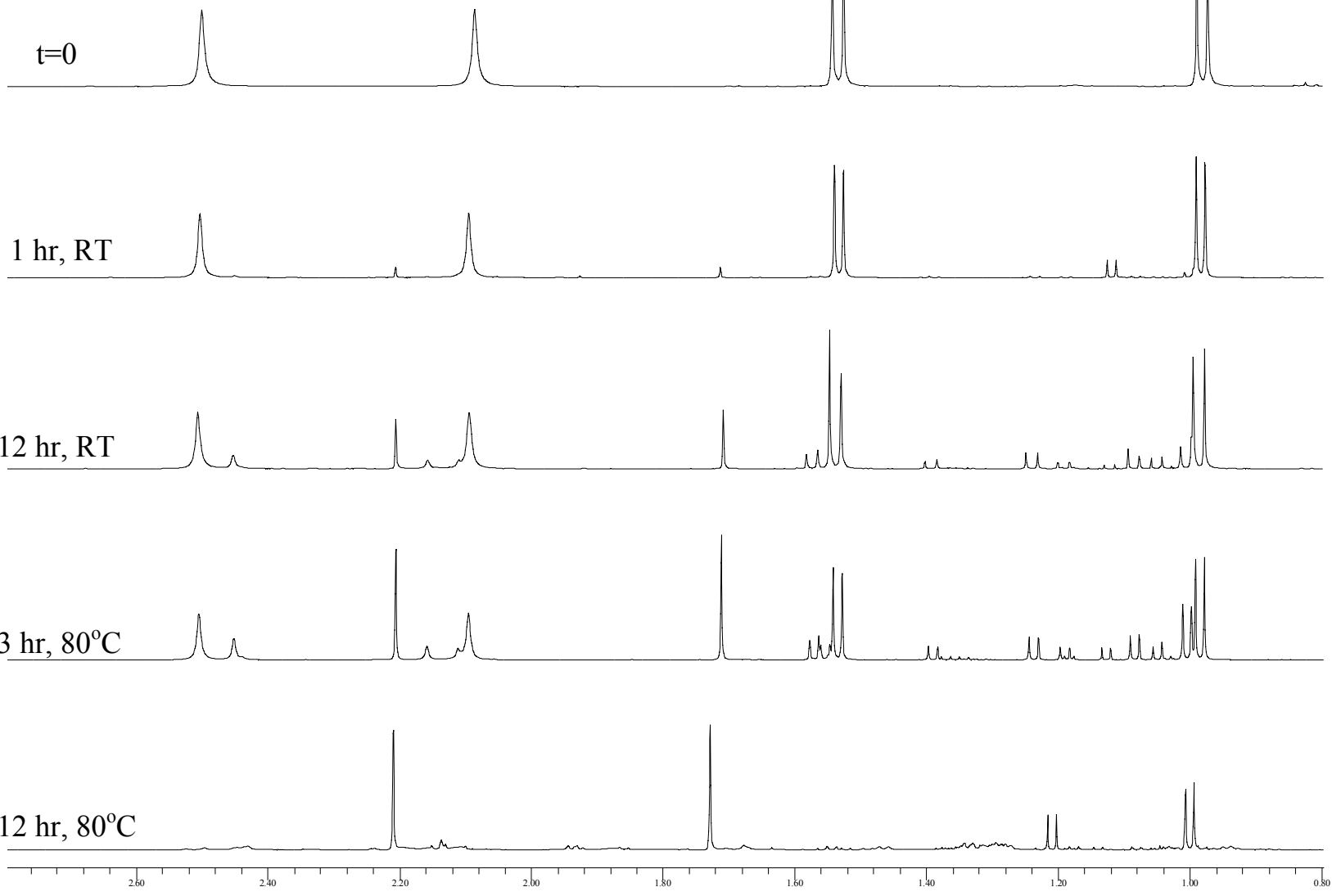
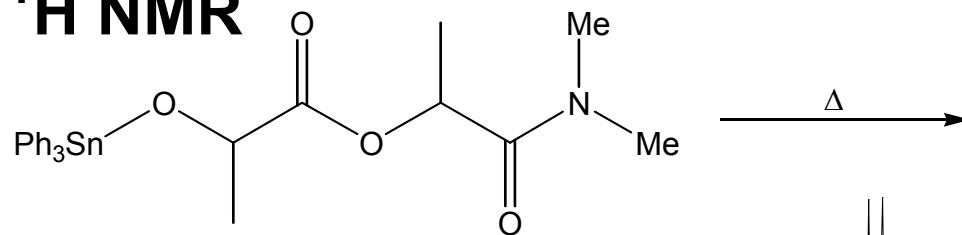
*Phenoxytriphenyltin(IV)* Phenol (0.19 g, 2.00 mmol) was added to a hexane (20 mL) solution/suspension of dimethylamidotriphenyltin(IV) (0.80 g, 2.03 mmol). After stirring at room temperature for 12 h the colorless solution was filtered to remove a small amount of precipitate. The hexanes were removed giving a white crystalline powder 0.72 g (81 %) that was heated (60 °C) under vacuum for 30 mins and recrystallized from benzene.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ):  $\delta$  6.72 (tt, *p*-H in PhO, 1H,  $J_{\text{HH}}$  7.1 and 2.6 Hz), 7.05 (dd, *m*-H in PhO, 2H,  $J_{\text{HH}}$  13.8 and 7.0 Hz), 7.09-7.11 (m, *o*-H in PhO, and *m*- and *p*-H in Ph), 7.61 (m, *o*-H, 6H).  $^{119}\text{Sn}$  NMR (149 MHz, benzene- $d_6$ ):  $\delta$  -98 (s).

*Bis(trifluoromethyl)iso-propoxytriphenyltin(IV)* Bis(trifluoromethyl)isopropanol (0.67 g, 4.00 mmol) was added to a hexane (20 mL) solution/suspension of dimethylamidotriphenyltin(IV) (0.80 g, 2.03 mmol). After stirring at room temperature for 12 h the colorless solution was filtered to remove a small amount of precipitate. The hexanes were removed giving a white crystalline powder 0.91 g (87 %) that was heated (60 °C) under vacuum for 30 mins and recrystallized from benzene.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ):  $\delta$  4.41 (sept,  $\text{CH}(\text{CF}_3)_2$   $J_{\text{HF}}$  5.9 Hz), 7.12 (m, *m*- and *p*-H), 7.52 (m, *o*-H, 6H).  $^{119}\text{Sn}$  NMR (149 MHz, benzene- $d_6$ ):  $\delta$  -54 (s).

*Diphenylphosphidotriphenyltin(IV)* Diphenylphosphine (0.26 g, 1.40 mmol) was added to a hexane (20 mL) solution/suspension of dimethylamidotriphenyltin(IV) (0.50 g, 1.27 mmol). After stirring at 60° C for 12 h a white precipitate formed which was filtered off and washed with hexane and dried under vacuum to give a white crystalline powder 0.52

g (77 %).  $^1\text{H}$  NMR (500 MHz, benzene- $d_6$ ):  $\delta$  6.92 (m, , *m*- and *p*-H on  $\text{PPh}_2$ , 6H), 7.09 (m, , *m*- and *p*-H on  $\text{SnPh}_3$ , 9H), 7.46 (m, *o*-H on  $\text{SnPh}_3$ , 6H), 7.62 (m, *o*-H on  $\text{PPh}_2$ , 4H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, benzene- $d_6$ ): -55.2 (s,  $^{119/117}\text{Sn}$  satellites  $J_{\text{SnP}}$   $^{117}\text{Sn}$  715,  $^{119}\text{Sn}$  683 Hz).  $^{31}\text{P}$  NMR (202 MHz, benzene- $d_6$ ): -55.2 (pent,  $J_{\text{PH}}$  7.4 Hz, coupling to four *o*-H protons  $^{119/117}\text{Sn}$  satellites two overlapping pentets).  $^{119}\text{Sn}$  NMR (149 MHz, benzene- $d_6$ ):  $\delta$  -123 (d,  $J_{\text{SnP}}$   $^{119}\text{Sn}$  719 Hz).

# <sup>1</sup>H NMR



$^1\text{H}$  NMR spectrum in benzene- $d_6$  of  $\text{Ph}_3\text{Sn}(\text{OCMe}_2\text{C}(\text{O})\text{OCHMeC}(\text{O})\text{ONMe}_2)$ .

