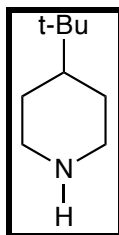


Supporting Information for

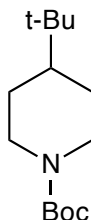
# Tin-Nitrogen ‘Anomeric’ Effect in $\alpha$ -Aminoorganostannanes

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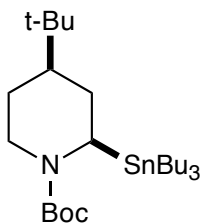


**4-t-Butylpiperidine.** To a 500 mL Parr bottle was added 10 g (74.7 mmol) of 4-t-butylpyridine, 200 mL of 95 % ethanol, 20 mL of chloroform and 0.5 g (2.2 mmol) of platinum dioxide. The heterogenous mixture was shaken under a 50 psi atmosphere of hydrogen for 2 days. The catalyst was gravity filtered, and the resulting colorless filtrate was concentrated in vacuo. The resulting white solid was dissolved in 100 mL of dichloromethane and washed with 100 mL of 2M aqueous potassium hydroxide. The aqueous layer was reextracted with 100 mL of dichloromethane. The combined organic extracts were dried ( $\text{MgSO}_4$ ) and concentrated in vacuo. The residue was distilled under reduced pressure to afford 8.4 g (80.5 %) of the amine as a colorless liquid: bp 61-64 °C, 5 torr;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.81 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 1.00-1.19 (m, 3H), 1.53 (bs, 1H, NH), 1.62 (d,  $J = 11.3$  Hz, 2H), 2.51 (t,  $J = 11.5$  Hz, 2H), 3.07 (d,  $J = 12.0$  Hz, 2H).



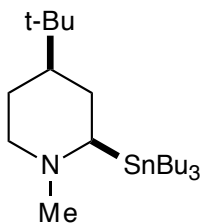
**N-Boc-4-t-butylpiperidine.** To a solution of 10 g (45.9 mmol) of di-t-butyl dicarbonate in 40 mL of THF at 0 °C was added a solution of 6.70 g (47.5 mmol) of 4-tertbutylpiperidine in 40 mL of THF over 20 min via addition funnel. The cold bath was removed allowing the mixture to gradually warm to rt where it was stirred for 12 h. The mixture was concentrated in vacuo, and the residue was purified by column chromatography over 50 g of flash silica [eluted with hexanes/ethyl acetate (5:1)] to afford 11.06 g (100 %) of the carbamate as a colorless oil: IR (neat) 1695  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.84 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 1.07-1.17 (m, 3H), 1.44 (s, 9H,  $(\text{CH}_3)_3\text{CO}$ ), 1.63 (d,  $J =$

9.8 Hz, 2H), 2.58 (bt, J = 11.1 Hz, 2H), 4,14 (bd, J = 9.8 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  27.2 (t), 27.6 (q), 28.8 (q), 32.5 (s), 45.0 (bt), 47.1 (d), 79.4 (s), 155.2 (s); mass calculated for  $\text{C}_{14}\text{H}_{28}\text{NO}_2$  ( $\text{MH}^+$ )  $m/z$  242, found  $m/z$  242.



**Cis-N-Boc-2-(tri-n-butylstannyl)-4-t-butylpiperidine.** To a stirred solution of 8.28 g (34.3 mmol) of N-BOC-4-tert-butylpiperidine in 80 mL of dry diethyl ether under nitrogen at -78 °C was added 6.0 g (51.5 mmol, 7.8 mL) of N,N'-tetramethylethylenediamine in one portion via syringe, and 37.2 mL (44.7 mmol) of a 1.2 M solution of sec-butyllithium in cyclohexane over 30 min via canula. The mixture turned yellow, then milky during the addition. The mixture was stirred for 5 h at -78 °C, and 17.9 g (55 mmol, 15 mL) of neat tri-n-butyltin chloride was added over 5 min via syringe. The cold bath was removed allowing the mixture to warm gradually to rt where it was stirred overnight. The mixture was diluted with 100 mL of ethyl acetate and washed with 100 mL of water. The aqueous layer was reextracted with two 100-mL portions of ethyl acetate. The combined organic extracts were dried ( $\text{MgSO}_4$ ) and concentrated in vacuo. The residue was purified by column chromatography over 250 g of flash silica [eluted with hexanes] to afford 11.1 g (61 %) of product as a colorless oil: IR (neat)  $1670\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.44-1.42 (m, 49 H), 1.51 (bd, J = 12.4 Hz, 1 H), 2.25 (bd, J = 12.2 Hz, 1H), 2.48 (bt, J = 11.3 Hz, 1H), 3.92 (bd, J = 12.1 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  12.3 (t), 14.2 (q), 27.7 (q), 27.9 (t), 28.0 (t), 28.8 (q), 29.7 (t), 32.0 (t), 32.7 (s), 46.7 (d), 48.0 (t), 50.0 (d), 79.4 (s), 156.4 (s); mass calculated for  $\text{C}_{26}\text{H}_{53}\text{NO}_2\text{Sn}$  ( $\text{MH}^+$  for Sn 119)  $m/z$  530, found  $m/z$  530.

Anal. Calcd. for  $\text{C}_{26}\text{H}_{53}\text{NO}_2\text{Sn}$ : C 58.87, H 10.07. Found C 58.71, H 9.98.



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**Cis-N-methyl-2-(tri-n-butylstannyl)-4-t-butylpiperidine (2).** To a stirred solution of 4.47 g (8.43 mmol) of cis-N-Boc-2-(tri-n-butylstannyl)-4-t-butylpiperidine in 50 mL of dry THF at 0 °C was added 7.19 g (50.6 mmol, 9.0 mL) of neat diisobutylaluminum hydride over 5 min via syringe. The mixture was heated to reflux for 60 h. The mixture was cooled to -78 °C, and 20 mL of methanol was added to quench the excess hydride. The mixture was treated with 50 mL of saturated aqueous potassium, sodium tartrate. The cold bath was removed allowing the mixture to warm to rt where it was stirred for 12 h. The layers of the resulting biphasic mixture were separated, and the aqueous layer was reextracted with three 50-mL portions of diethyl ether. The combined organic extracts were dried (MgSO<sub>4</sub>) and concentrated in vacuo. The residue was purified by column chromatography over 100 g of flash silica [eluted with hexanes/ethyl acetate (20:1) progressing to hexanes/ethyl acetate (5:1)] to afford 2.81 g (75 %) of amine **2** as a slightly yellow liquid: IR (neat) 1363 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 0.85-0.95 (m, 25 H), 1.22-1.56 (m, 14H), 1.60 (dt, J = 12.8, 2.82 Hz, 1H), 1.74 (dd, J = 12.9, 2.9 Hz, 1H), 1.80 (td, J = 11.6, 1.7 Hz, 1H), 2.05 (dd, J = 12.8, 2.2 Hz, 1H), 2.20 (s, 3H), 2.98 (dt, J = 11.0, 3.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 9.66 (t), 14.1 (q), 27.5 (t), 27.7 (q), 27.9 (t), 29.6 (t), 32.6 (t), 32.7 (s), 48.3 (d), 48.7 (q), 59.7 (d), 60.2 (t); exact mass calculated for C<sub>22</sub>H<sub>47</sub>NSn m/z 444, found m/z 444.

Anal. Calcd. for C<sub>22</sub>H<sub>47</sub>NSn: C 59.47, H 10.66, N 3.15. Found C 59.75, H 10.71, N 3.10.