

# Determination of Coupling Signs $^1J(^{119}\text{Sn}, ^{15}\text{N})$ and $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ in Trimethylstannylamines

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The  $^{15}\text{N}$ -labelled trimethylstannylamines **1** - **3** [(Me<sub>3</sub>Sn)<sub>3</sub>N, (Me<sub>3</sub>Sn)<sub>2</sub>NPh, (Me<sub>3</sub>Sn)<sub>2</sub>N-BC<sub>8</sub>H<sub>14</sub> (BC<sub>8</sub>H<sub>14</sub> = 9-borabicyclo[3.3.0]nonyl) and the non-labelled **4**, Me<sub>3</sub>Sn-N(BC<sub>8</sub>H<sub>14</sub>)<sub>2</sub>, were prepared and studied by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{119}\text{Sn}$  NMR. The  $^{15}\text{N}$  ultrahigh resolution NMR spectra of **1** revealed otherwise unobserved parameters such as  $^2J(^{15}\text{N}, \text{Sn}, ^{13}\text{C})$  and the isotope induced chemical shift  $^2\Delta^{12/13}\text{C}(^{15}\text{N})$ .  $^{119}\text{Sn}$  NMR spectra of **1**, recorded under similar conditions, also show new parameters such as  $^3J(^{119}\text{Sn}, \text{N}, \text{Sn}, ^{13}\text{C})$  which are not resolved in the non-labelled derivative. By using various types of two-dimensional heteronuclear shift correlations, absolute coupling signs of  $^1J(^{119}\text{Sn}, ^{15}\text{N})$  (all < 0) in **1** - **3** were determined. By the same techniques it proved possible to confirm the negative sign of  $^2J(\text{Sn}, \text{Sn})$  (-195.4 Hz) in **1**. In contrast, the coupling constants  $^2J(\text{Sn}, \text{Sn})$  for **2** (+71.7) and **3** (+62.0) possess a positive sign. This sign inversion, observed here for the first time for apparently similar compounds, demonstrates the enormous influence of substituents on the nature of the lone pair of electrons at the nitrogen atom. It also shows that these experiments for sign determinations of coupling constants are necessary in order to interpret these data correctly.

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