Electronic Supporting Information

Formation of a Unique 'Unsupported' Hydridic Sn(II) Stannate

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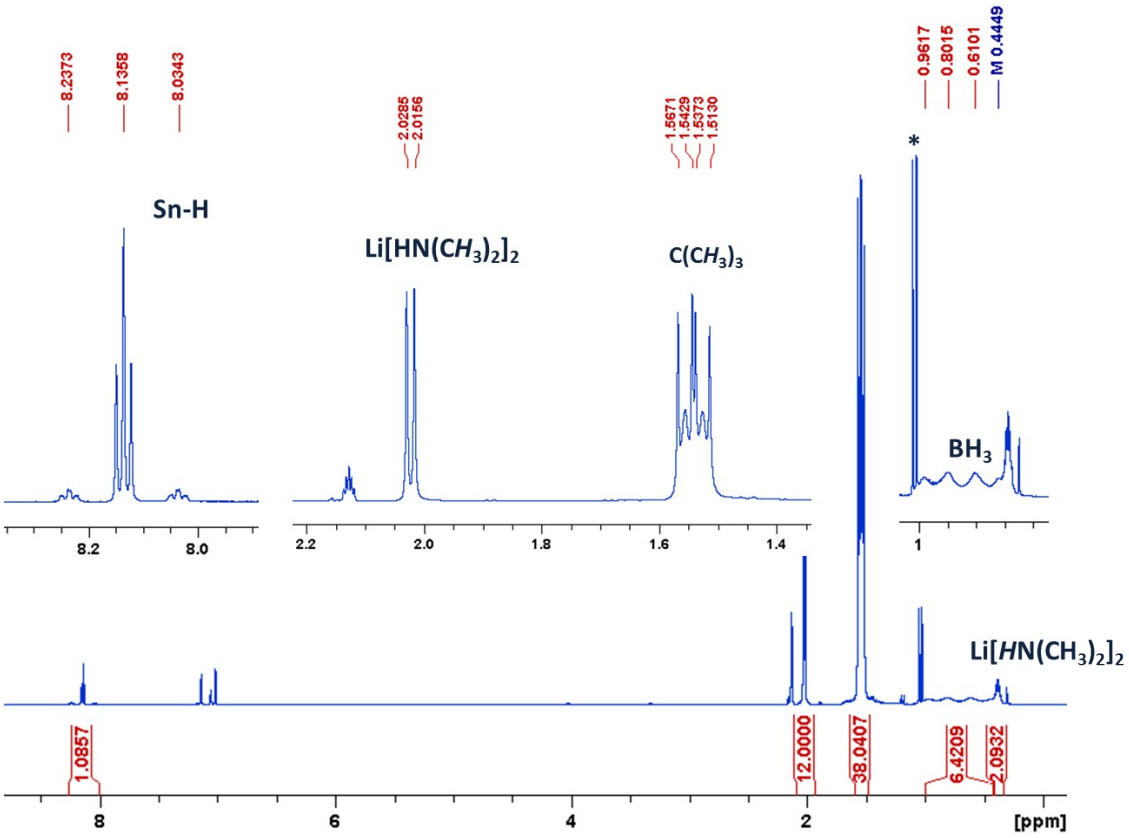

Figure S1. ^{1}H NMR (298K, d_8-toluene, 500 MHz) spectrum for crystals of **1**. Asterisk (*)is [^{t}Bu$_2$PH·BH$_3$].

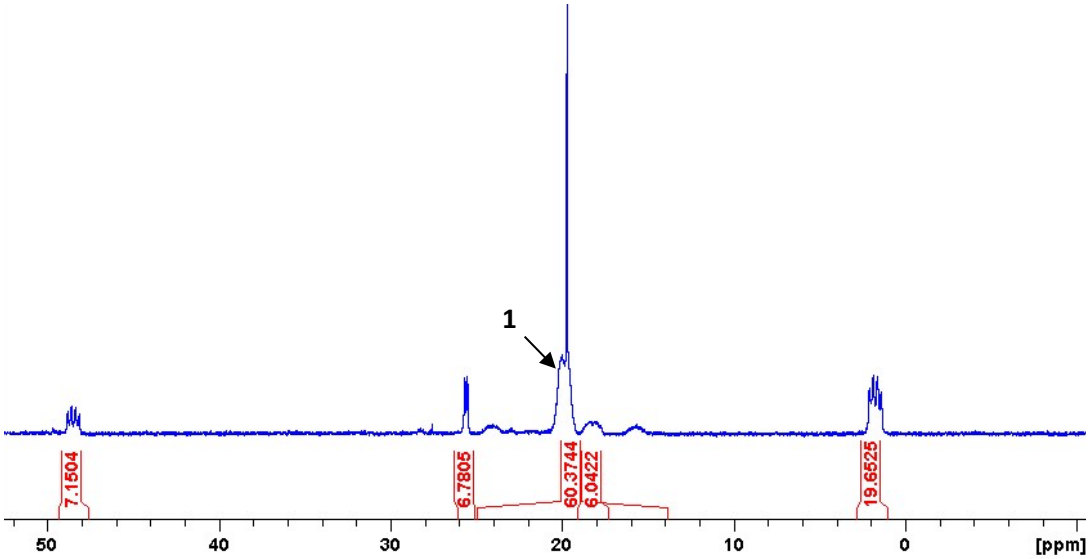

Figure S2. $^{31}P\{^{1}H\}$ NMR (298K, d_8-toluene, 202.47 MHz) in situ NMR spectrum a 1 : 1 reaction of the original $Sn(NMe_2)_2$ used with $^{t}Bu_2PHBH_3$, after storage at room temperature in a J. Young NMR tube under N_2.

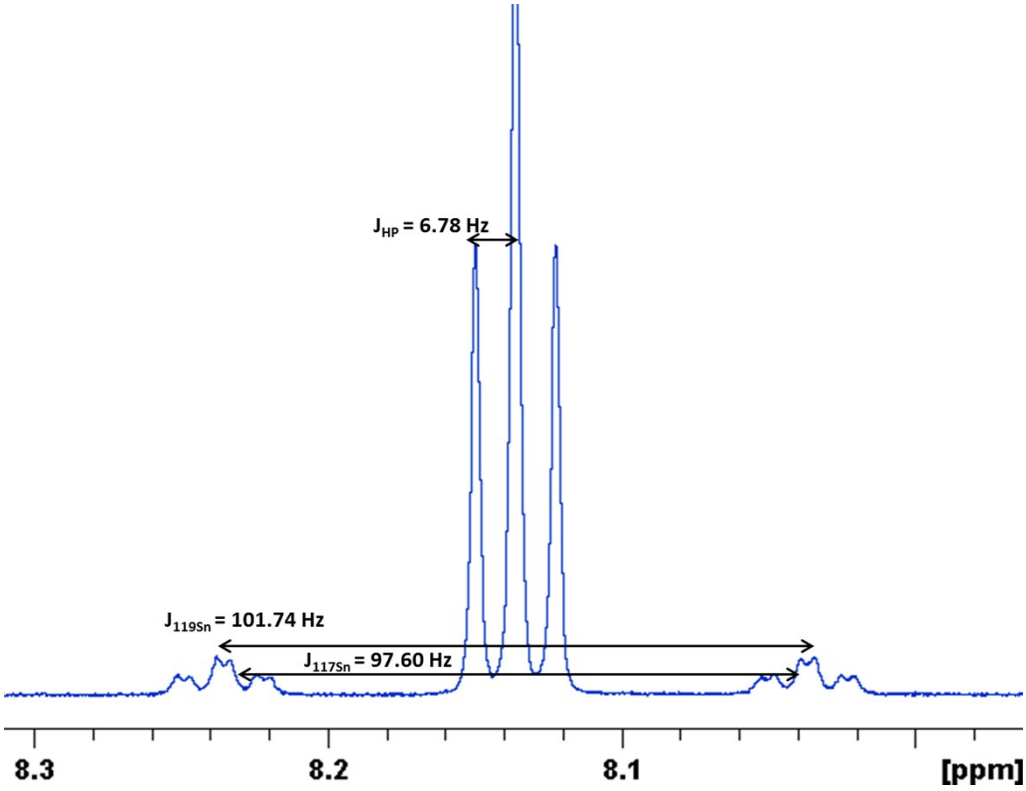

Figure S3. ^{1}H NMR (298K, d_8-toluene, 500 MHz) spectrum for crystals of **1** showing the hydride resonance and the satellites due to ^{119}Sn and ^{117}Sn coupling, J_{117Sn} / J_{119Sn} = 0.959. The signal appears as a triplet due to $^{2}J_{P\text{-}H}$ as confirmed by $^{31}P\text{-}^{1}H$ HMBC (see Fig S6) and $^{1}H\{^{31}P\}$ experiments (Figure S4a).

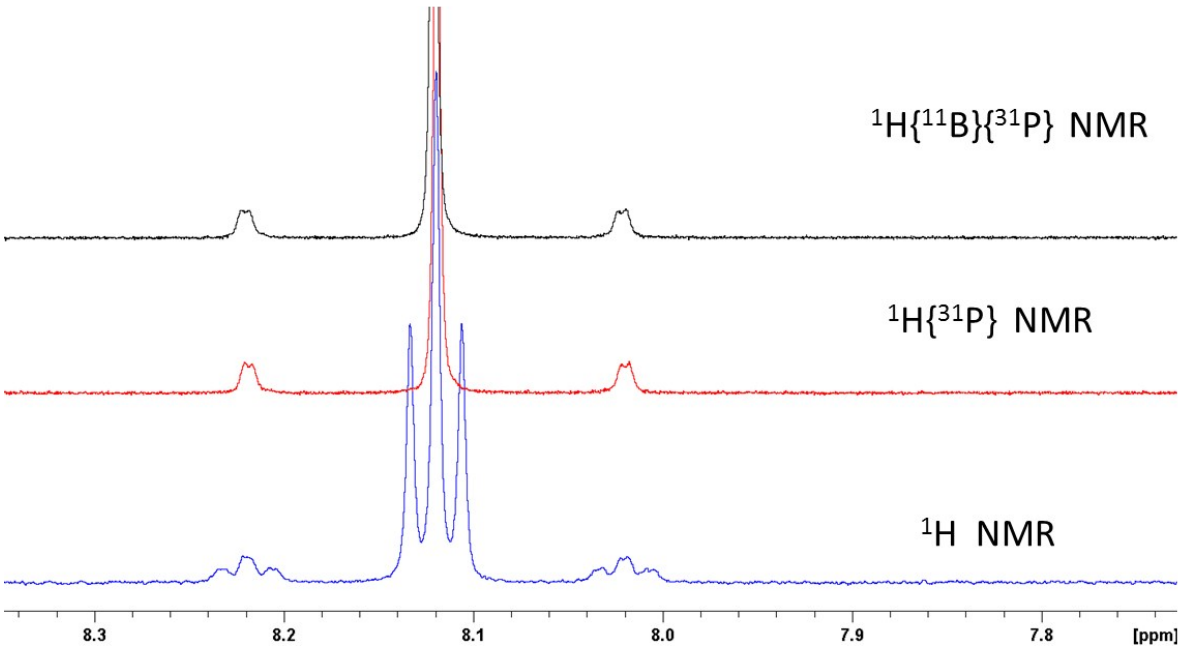

Figure S4a. From bottom to top: ^{1}H NMR, $^{1}H\{^{31}P\}$ NMR and $^{1}H\{^{11}B\}\{^{31}P\}$ (298K, d_8-toluene, 500 MHz) spectra for crystals of **1**, showing that the hydride signal is coupling with two phosphorus atoms (see also ^{1}H-^{31}P HMBC experiment, Figure S5).

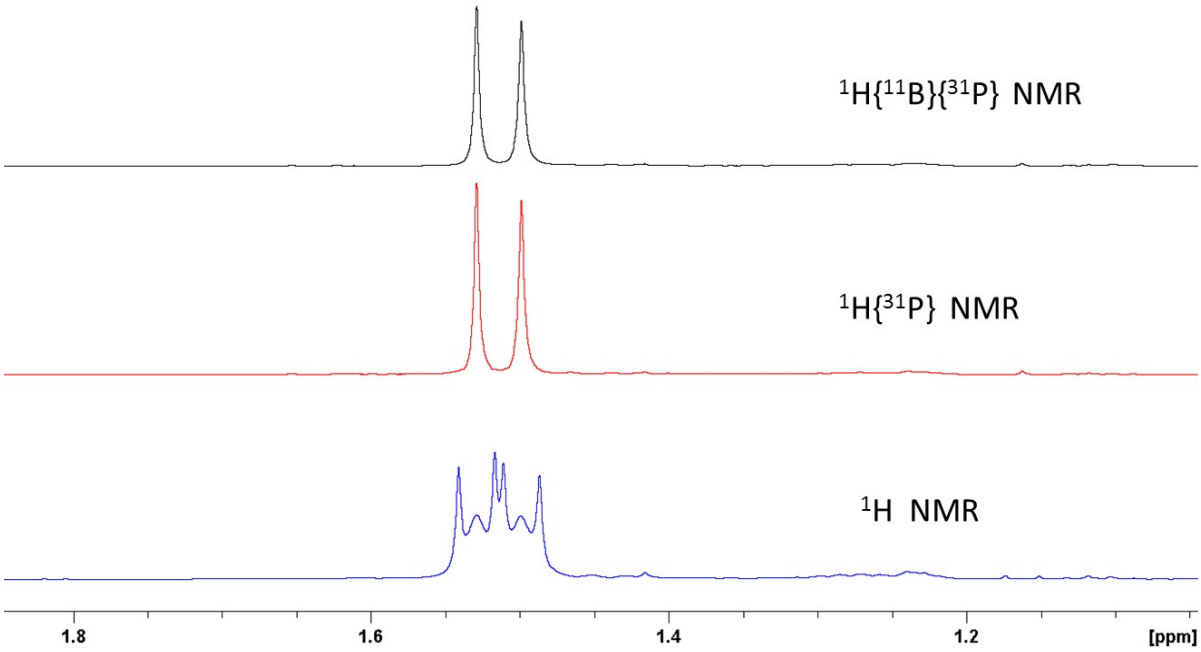

Figure S4b. From bottom to top: ^{1}H NMR, $^{1}H\{^{31}P\}$ NMR and $^{1}H\{^{11}B\}\{^{31}P\}$ (298K, d_8-toluene, 500 MHz) spectra showing the ^{t}Bu resonance for crystals of **1**, showing the complex coupling pattern due to phosphorus coupling. The two singlets in the $^{1}H\{^{31}P\}$ NMR spectrum show two different environments for the ^{t}Bu protons.

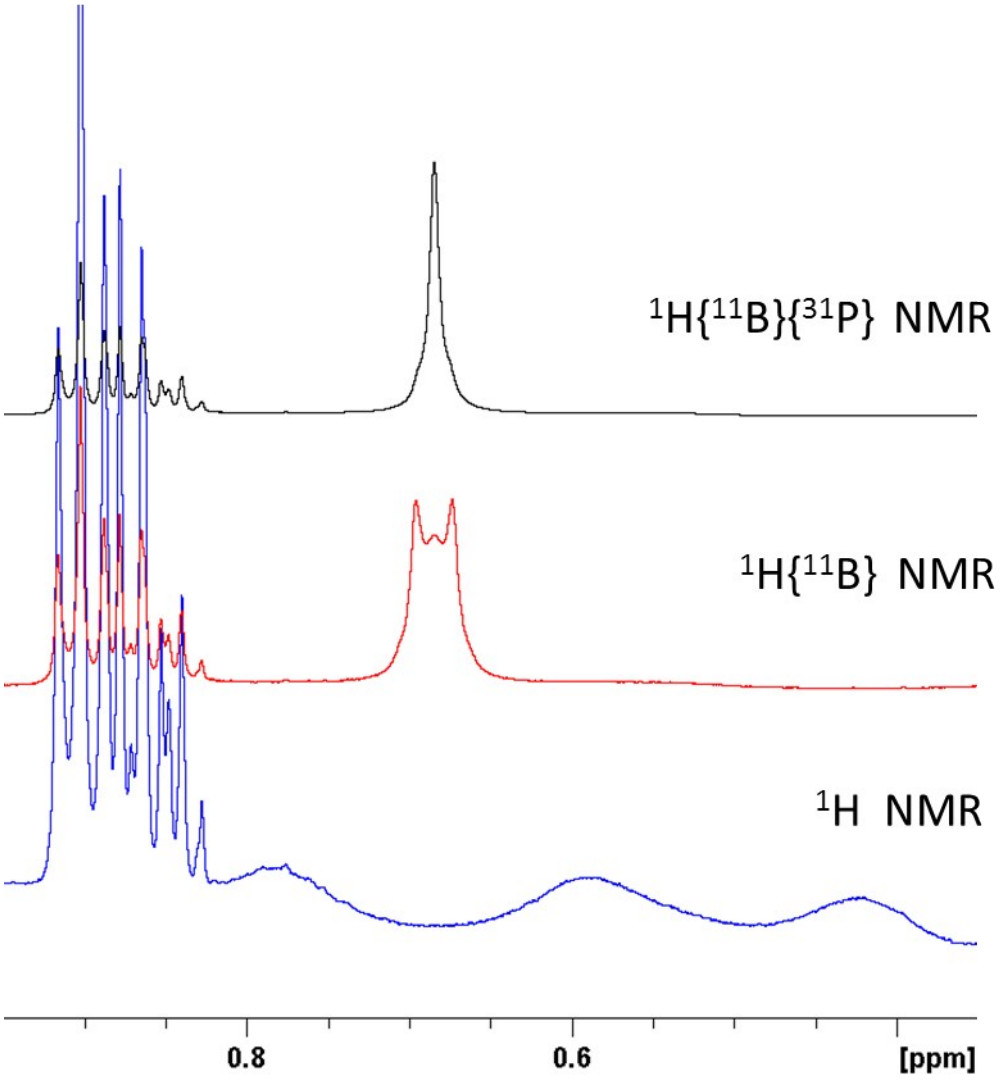

Figure S4c. From bottom to top: ^{1}H NMR, $^{1}H\{^{11}B\}$ NMR and $^{1}H\{^{11}B\}\{^{31}P\}$ (298K, d_8-toluene, 500 MHz) spectra showing the P-BH_3 resonance for crystals of **1**, confirming the P-BH_3 linkage. Signals at around 0.85-0.90 ppm are due to decomposition and residual hexane.

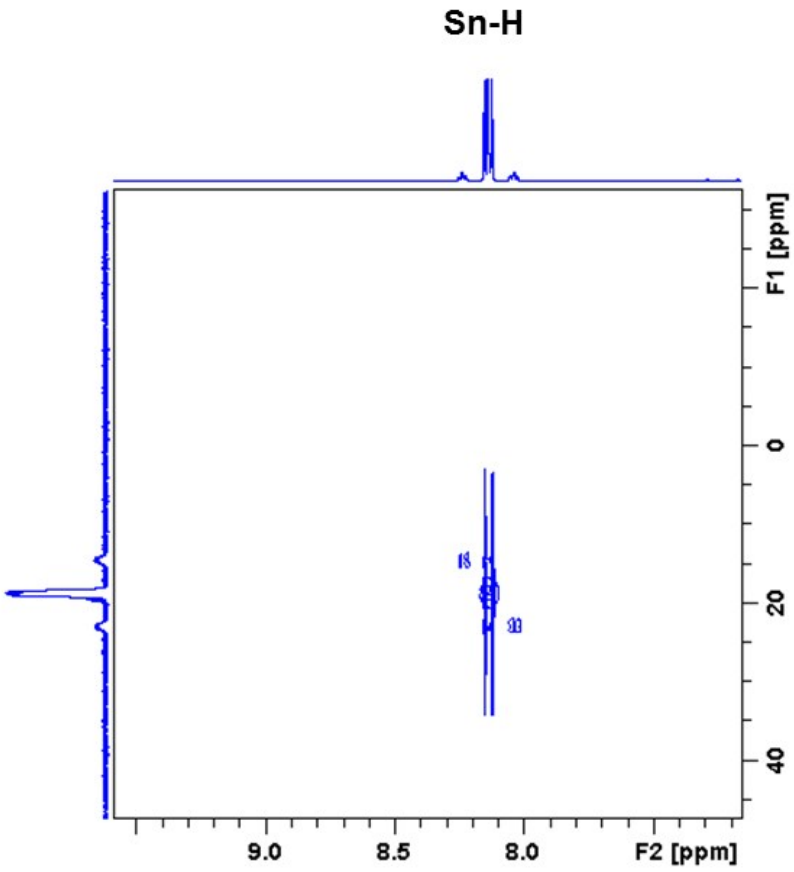

Figure S5. ^{1}H ^{31}P HMBC NMR (298K, d_8-toluene, 500 MHz) spectrum for crystals of **1** showing the coupling of the hydride signal to phosphorus.

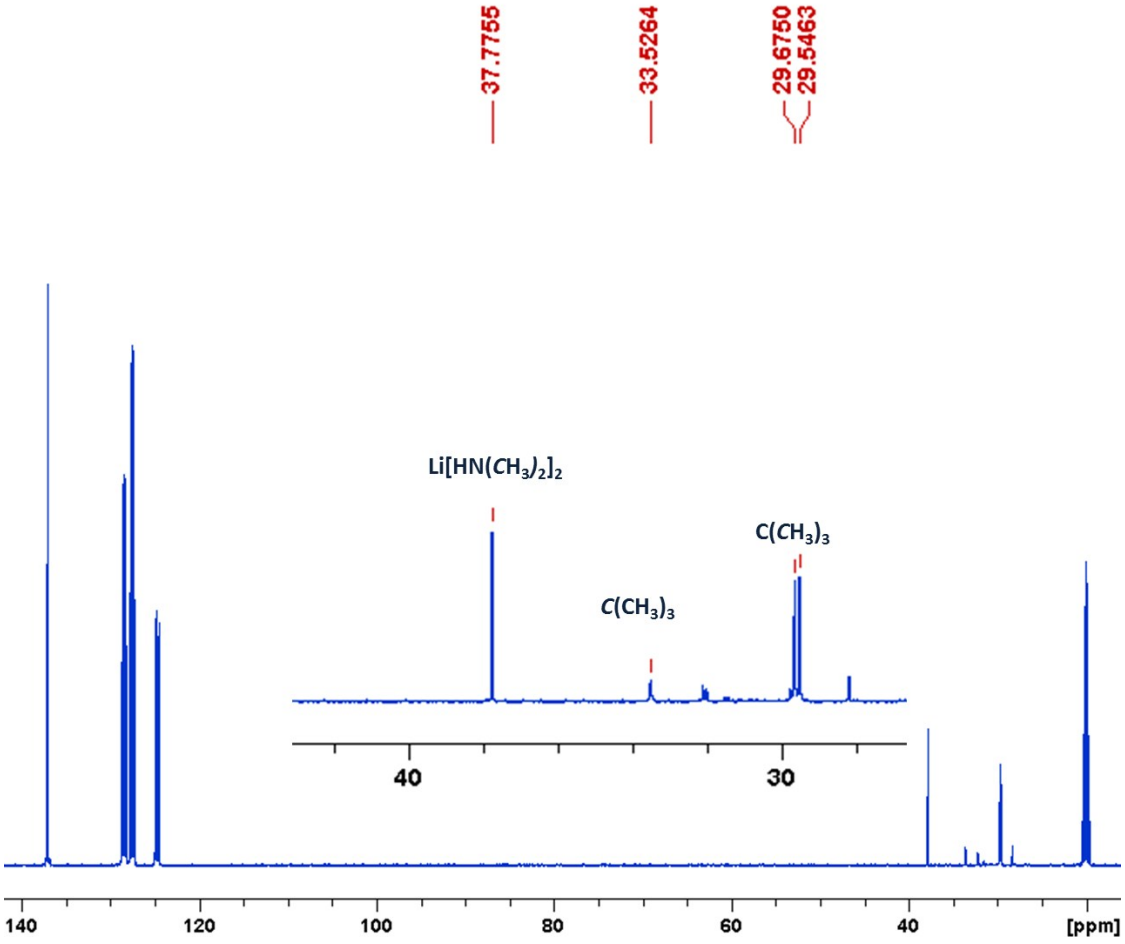

Figure S6. ^{13}C NMR (298K, d_8-toluene, 125.65 MHz) spectrum for crystals of **1**. Toluene solvent signals at 140-120 ppm.

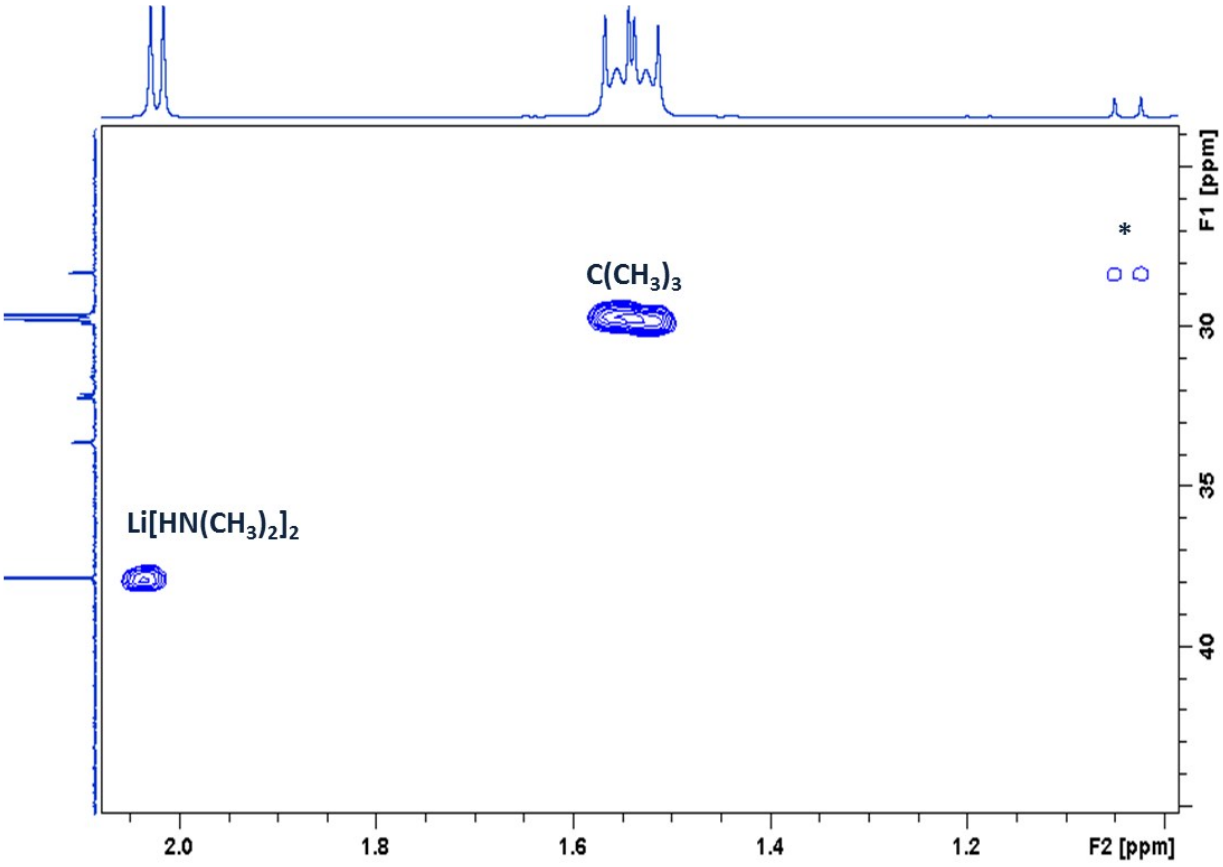

Figure S7. ^{1}H ^{13}C HSQC NMR (298K, d_8-toluene, 500 MHz) spectrum for crystals of **1**. . Asterisk (*) is [$^{t}Bu_2PH{\cdot}BH_3$].

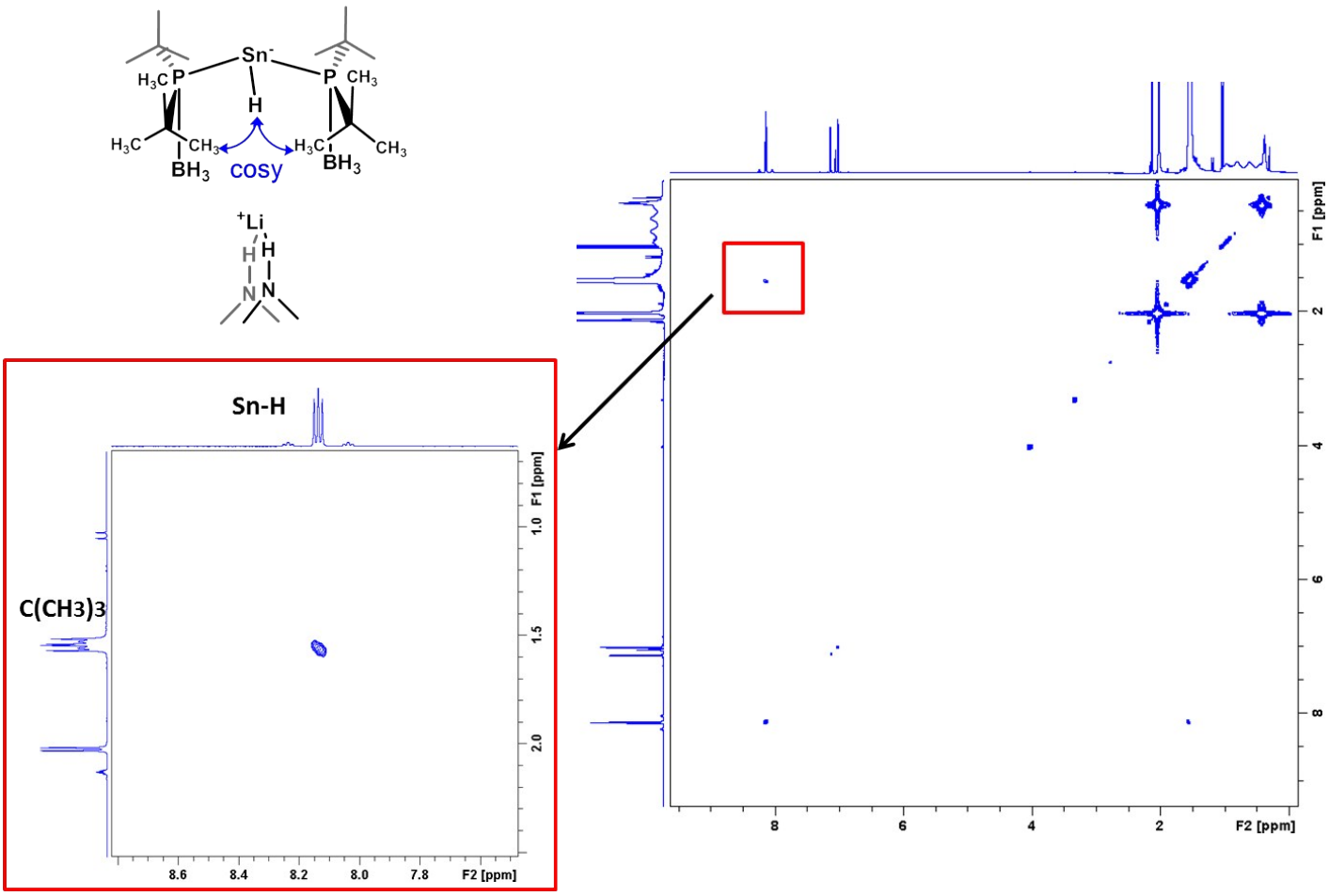

Figure S8. ^{1}H ^{1}H COSY NMR (298K, d_8-toluene, 500 MHz) spectrum for crystals of **1**. Showing that the hydride is only weakly coupled to the ^{t}Bu groups and appear as a triplet due to coupling to two phosphorus atoms (see Fig S4a and S5).

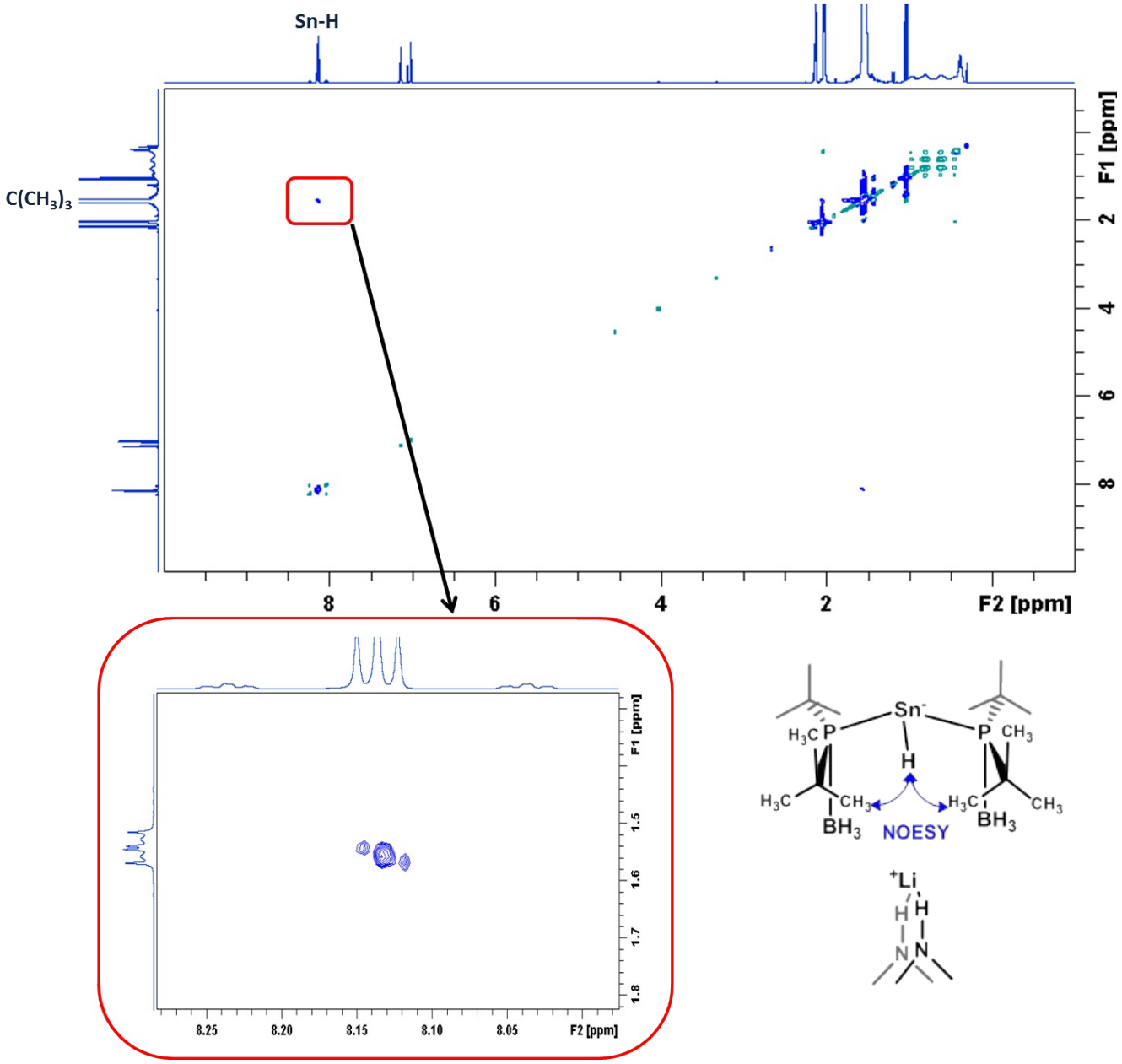

Figure S9. ^{1}H ^{1}H NOESY NMR (298K, d_8-toluene, 500 MHz) spectrum for crystals of **1**, showing that hydride is in near proximity to the ^{t}Bu groups.

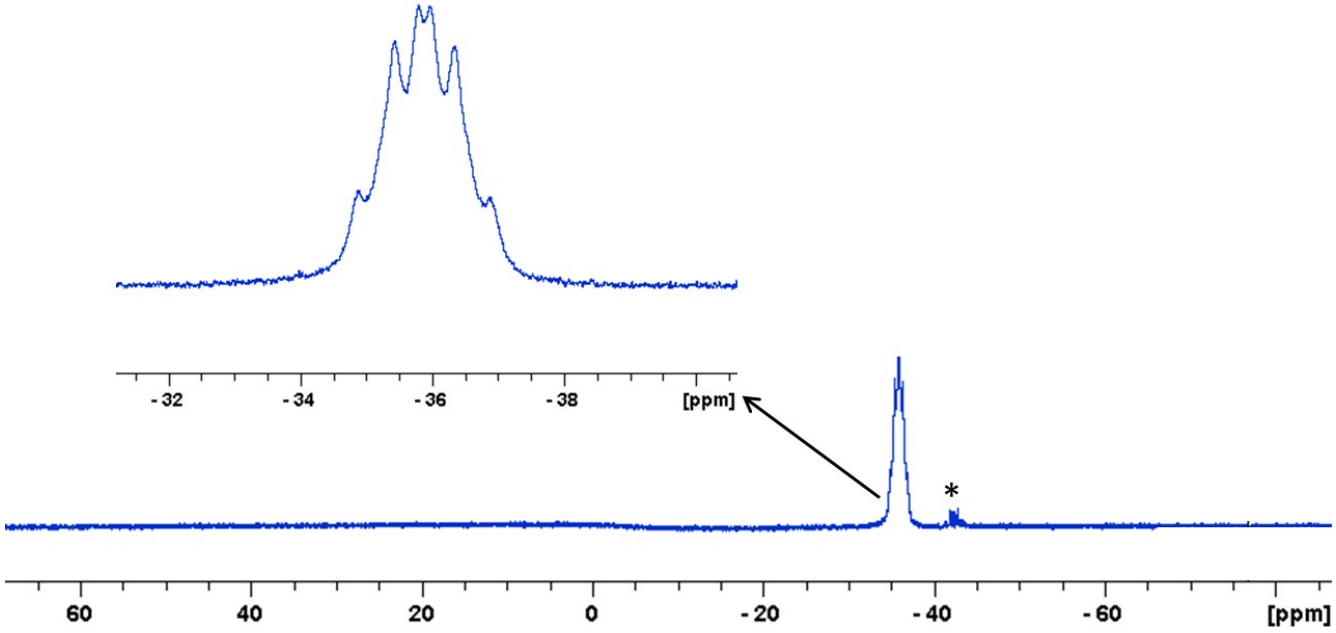

Figure S10. ^{11}B NMR (298K, d_8-toluene, 160.35 MHz) spectrum for crystals of **1**. Asterisk (*) is [$^{t}Bu_2PH{\cdot}BH_3$].

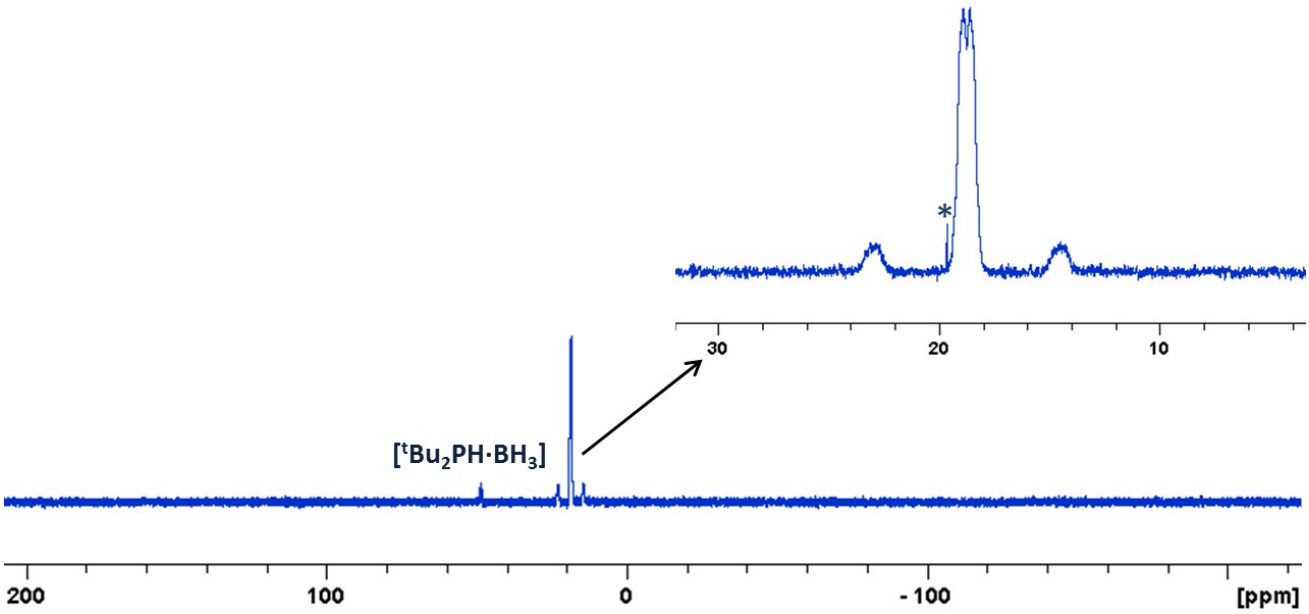

Figure S11. $^{31}P\{^{1}H\}$ NMR (298K, d_8-toluene, 202.47 MHz) spectrum for crystals of 1. Asterisk (*) is $^{t}Bu_2PH$.

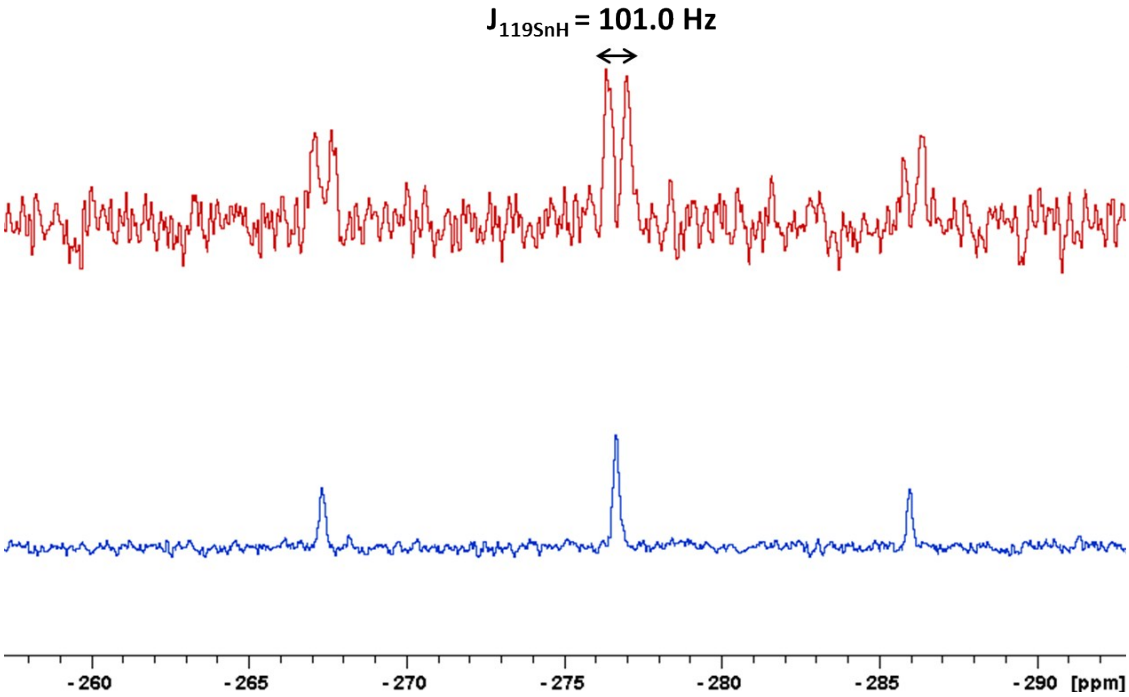

Figure S12. ^{119}Sn {^{1}H} and ^{119}Sn NMR NMR (298K, d_8-toluene, 186.53 MHz) spectra for crystals of **1**.

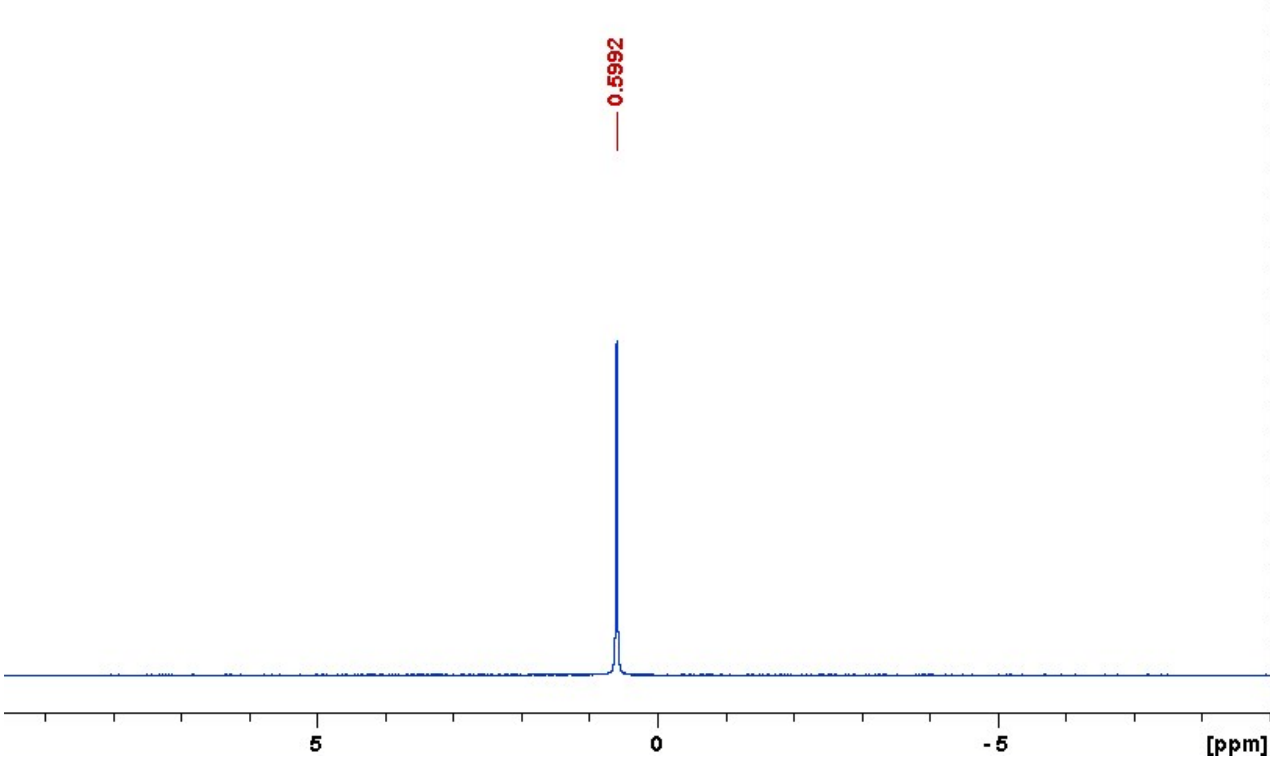

Figure S13. ^{7}Li NMR (298K, d_8-toluene, 194.32 MHz) spectrum for crystals of **1**.

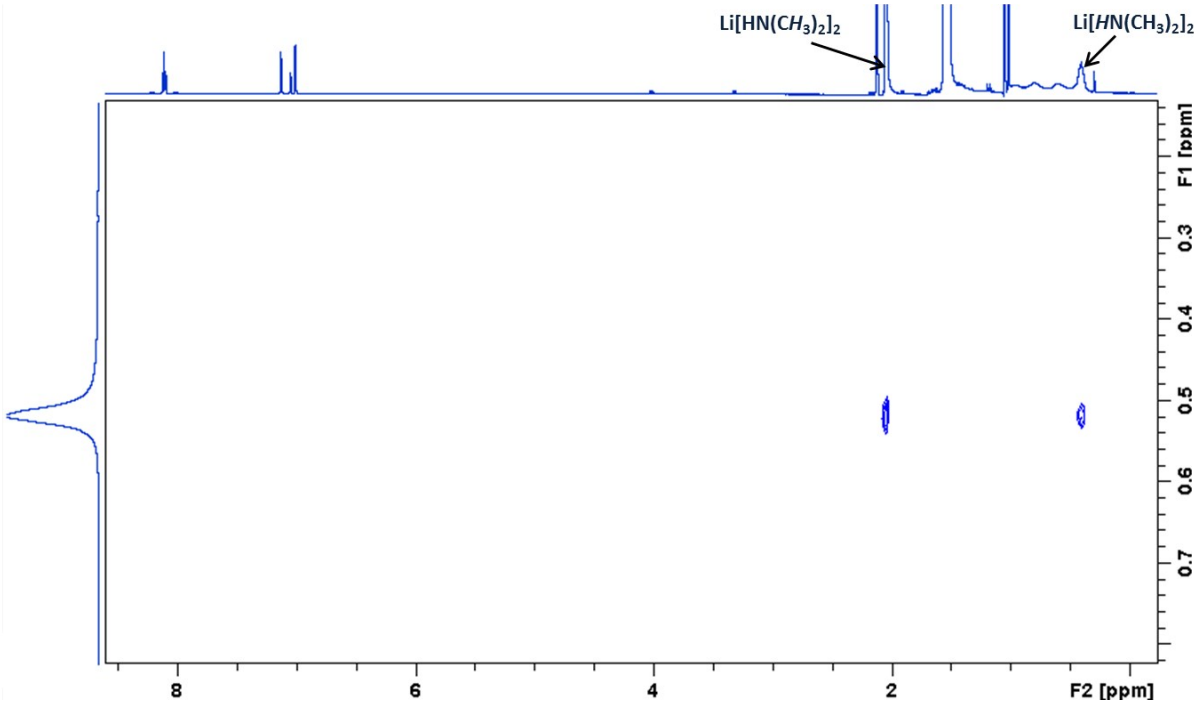

Figure S14. ^{1}H ^{7}Li HOESY NMR (298K, d_8-toluene, 194.32 MHz) spectrum for crystals of **1**

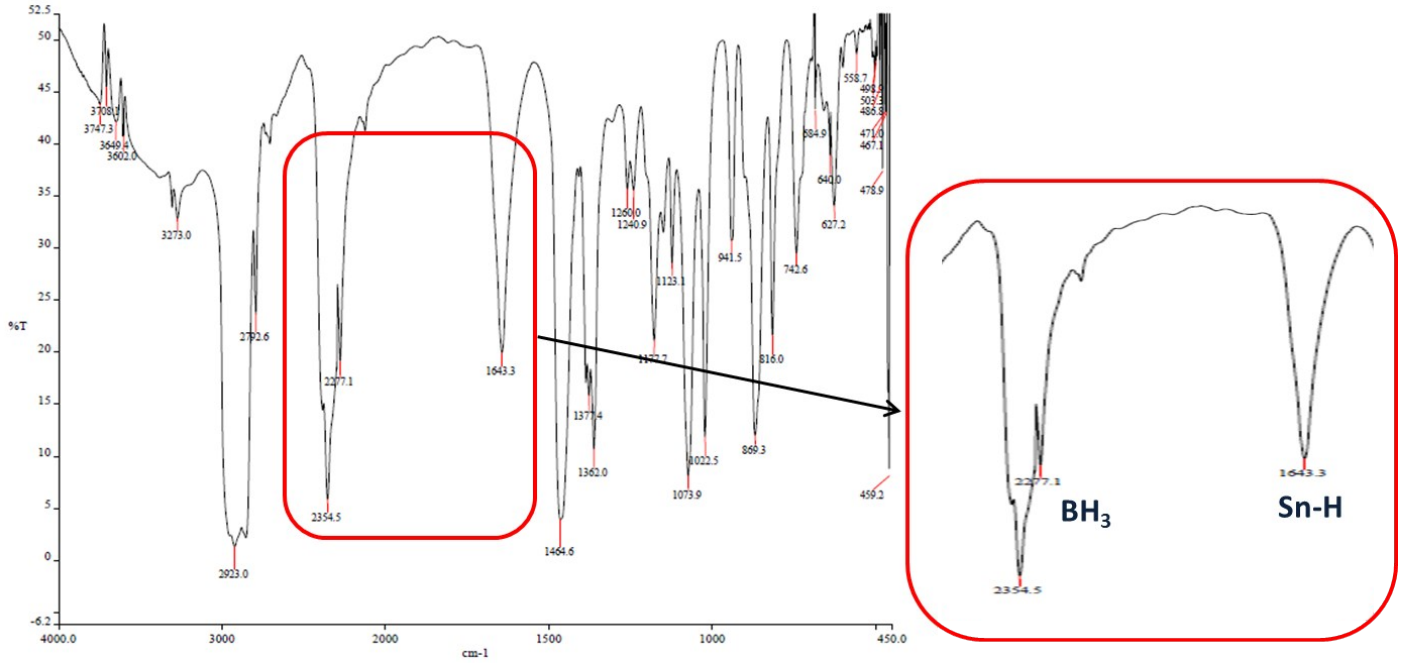

Figure S15. IR (Nujol, cm^{-1}) 2390.0, 2354.5, 2277.1 (BH_3) 1643.3 (Sn-H)