Hydrogen Activation Using A Novel Tribenzyltin Lewis Acid

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Supplementary Figure 1: $^1$H, $^{13}$C($^1$H) and $^{119}$Sn($^1$H) NMR spectra of BuSn in CDCl₃.
Supplementary Figure 2: $^1$H, $^{13}$C($^1$H), $^{19}$F and $^{119}$Sn($^1$H) NMR spectra of 1 in CDCl$_3$. 
Supplementary Figure 3: High resolution single mass analysis of 1.
Supplementary Figure 4: $^1$H [with insets showing the Bn$_3$SnH multiplicity and $^1J(^{117/119}$Sn-$^1$H) satellites], $^{13}$C($^1$H), $^{119}$Sn($^1$H) and $^{119}$Sn NMR spectra of an authentic sample of 2 in C$_6$D$_6$. 
**Supplementary Figure 5a:** $^1$H NMR spectra of (a) 1, (b) 1 and collidine and (c) after admission and activation of H$_2$ (4 bar) in C$_6$D$_6$. Insets show Bn$_3$SnH resonance and $^1$J($^{117/119}$Sn-$^1$H) satellites (generated *in situ*).
Supplementary Figure 5b: $^{119}$Sn$^1$H NMR spectra of (a) 1 and (b) 1 and collidine in C$_6$D$_6$. 
Supplementary Figure 6a: $^1$H NMR spectra of (a) 1 and 2, (b) after 60 hours at RT and (c) after 5 hours at 50 °C.
Supplementary Figure 6b: expanded $^1$H NMR spectra of (a) 1 and 2 [inset shows broad $\text{Bn}_3\text{SnH}$ resonance] and (b) after 90 min at RT.
Supplementary Figure 6c: $^{119}$Sn($^1$H) NMR spectra of (a) 1 and 2, (b) after 60 hours at RT and (c) after 5 hours at 50 ºC in C$_6$D$_6$. Peak at $\delta$ = +9.5 ppm is due to the presence of (Bn$_3$Sn)$_2$O formed from adventitious water (reported $\delta$ = +9.2 ppm in C$_6$D$_6$ [1]).
Supplementary Figure 7a: $^1$H NMR spectra of (a) 1, 2 and 2 equivalents of collidine, (b) after 60 hours at RT and (c) after 5 hours at 50 ºC. Insets show the growth of the [collidineH$^+$] resonance as decomposition progresses.
Supplementary Figure 7b: $^{119}$Sn($^1$H) NMR spectra of (a) 1, 2 and 2 equivalents of collidine, (b) after 60 hours at RT and (c) after 5 hours at 50 °C (c).
Supplementary Figure 9a: $^1$H NMR spectra for the hydrogenation of 3 in C$_6$D$_6$. 
Supplementary Figure 9b: $^{119}$Sn($^1$H) NMR spectra for the hydrogenation of 3 in C$_6$D$_6$. 
The X-ray crystal structure of 1

Crystal data for 1: C$_{22}$H$_{21}$F$_3$O$_3$Sn, $M = 541.14$, monoclinic, $P2_1$ (no. 4), $a = 19.5621(8)$, $b = 13.1989(3)$, $c = 20.0023(8)$ Å, $\beta = 119.081(5)^\circ$, $V = 4513.5(3)$ Å$^3$, $Z = 8$ [4 independent molecules], $D_c = 1.593$ g cm$^{-3}$, $\mu$(Mo-Ka) = 1.269 mm$^{-1}$, $T = 173$ K, colourless blocks, Agilent Xcalibur 3 E diffractometer; 13157 independent measured reflections ($R_{int} = 0.0257$), $F^2$ refinement,[2.3] $R_I$(obs) = 0.0295, $wR_F$(all) = 0.0617, 12005 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 56^\circ$], 1082 parameters. The absolute structure of 1 was determined by use of the Flack parameter [$x = −0.039(12)$]. CCDC 1534626.

The crystal of 1 that was studied was found to be a two component twin in a ca. 81:19 ratio, with the two lattices related by the twin law [−1.00 0.00 0.00 0.00 −1.00 0.00 0.99 0.00 1.00], and this was modelled at the refinement stage. The structure contains four independent “molecules” (1-A, 1-B, 1-C and 1-D) each of which forms an extended polymer along the crystallographic $b$ axis direction.

Supplementary Figure 10a: The structure of one (1-A) of the four independent “molecules” present in the crystal of 1 (50% probability ellipsoids). The atoms labelled with a prime at the end are related to those without the prime by action of the 2$_1$ screw axis.
Supplementary Figure 10b: The structure of one (1-B) of the four independent “molecules” present in the crystal of 1 (50% probability ellipsoids). The atoms labelled with a prime at the end are related to those without the prime by action of the 2₁ screw axis.

Supplementary Figure 10c: The structure of one (1-C) of the four independent “molecules” present in the crystal of 1 (50% probability ellipsoids). The atoms labelled with a prime at the end are related to those without the prime by action of the 2₁ screw axis.
**Supplementary Figure 10d:** The structure of one (1-D) of the four independent “molecules” present in the crystal of 1 (50% probability ellipsoids). The atoms labelled with a prime at the end are related to those without the prime by action of the 2₁ screw axis.
References

[1] A. Lyčka, J. Jirman and A. Koloničný. 1987. J. Organomet. Chem. 333, 305-315. (doi: 10.1016/S0022-328X(00)99807-3)

[2] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.

[3] SHELX-2013, G.M. Sheldrick, Acta Cryst., 2015, C71, 3-8. (doi: 10.1107/S2053229614024218)
