Electronic Supplementary Information

Reactivity and Catalytic Activity of *tert*-Butoxy-Aluminium Hydride Reagents

Robert J. Less,* Hayley R. Simmonds and Dominic S. Wright*

General Experimental Details of NMR Spectroscopic Studies

NMR spectra were obtained in deuterated NMR solvents (d_6-benzene, d_8-toluene, d_8-thf) which had been dried over a sodium mirror. A Bruker 500 MHz TCI Cryoprobe Spectrometer was used and all spectra are recorded at +25°C. The frequencies of the nuclei and external reference standards are as follows: ^{1}H – 500.20 MHz, (Me_4Si, $CDCl_3$, 1%), ^{11}B – 160.48 MHz, ($BF_3{\cdot}Et_2O$, $CDCl_3$), ^{27}Al – 130.35 MHz, ($Al(NO_3)_3$, D_2O, 1.1M), ^{7}Li – 194.40 MHz, (LiCl, D_2O, 9.7M).

In situ NMR spectroscopic studies in THF and toluene were undertaken using Wilmad 528pp tubes fitted with Youngs' tap adaptors, which allowed the attachment of the tube to a vacuum line during the course of reactions. During reactions evolved H_2 gas was therefore allowed to escape from the reaction system. The time intervals at which the spectra were recorded for catalytic studies using 10 mol% of the reagents involved are given on the appropriate spectra. In each case a series of spectra for the corresponding 1:1 reactions accompany the catalytic studies for comparison.

1. NMR Spectra of Aluminium Hydride Precursors 1, 2, 3 and 4

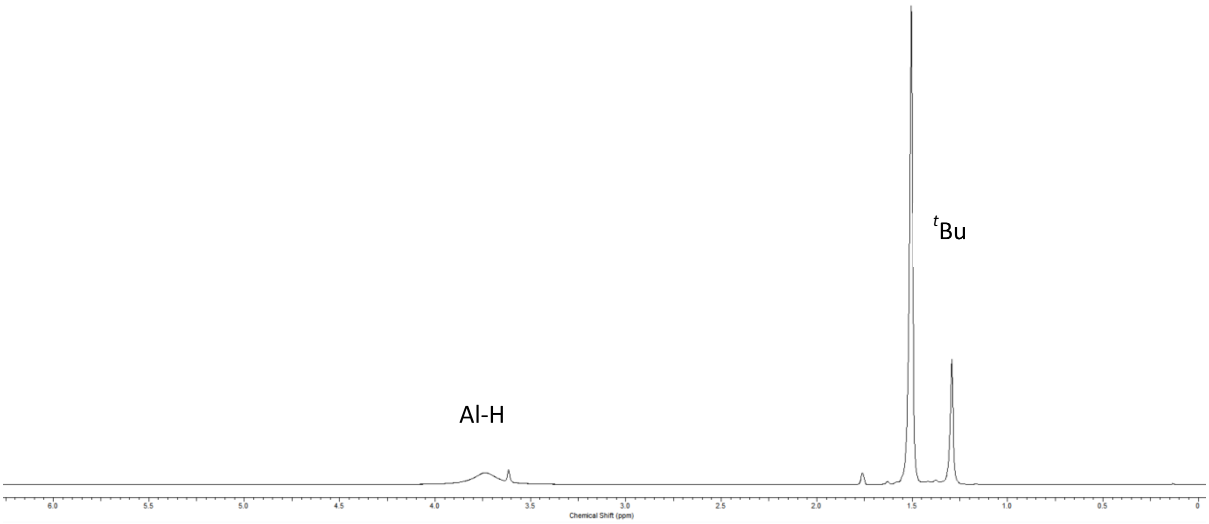

Figure 1.1 ^{1}H NMR Spectrum of ^{t}BuOAlH$_2$ (**1**) in D$_8$-THF.

Note: In the original paper (reference 11) the NMR spectra of **1** were obtained in D$_6$-benzene). The observation of two ^{t}Bu resonances in THF here can be tentatively ascribed to the presence of solvated monomer [(^{t}BuO)AlH$_2$.THF] (δ 1.50) and *intact* dimer [H$_2$Al(μ-O^{t}Bu)]$_2$ (δ1.30), on the basis of the observed chemical shift in the ^{1}H NMR spectrum of **1** in D$_6$-benzene (see below).

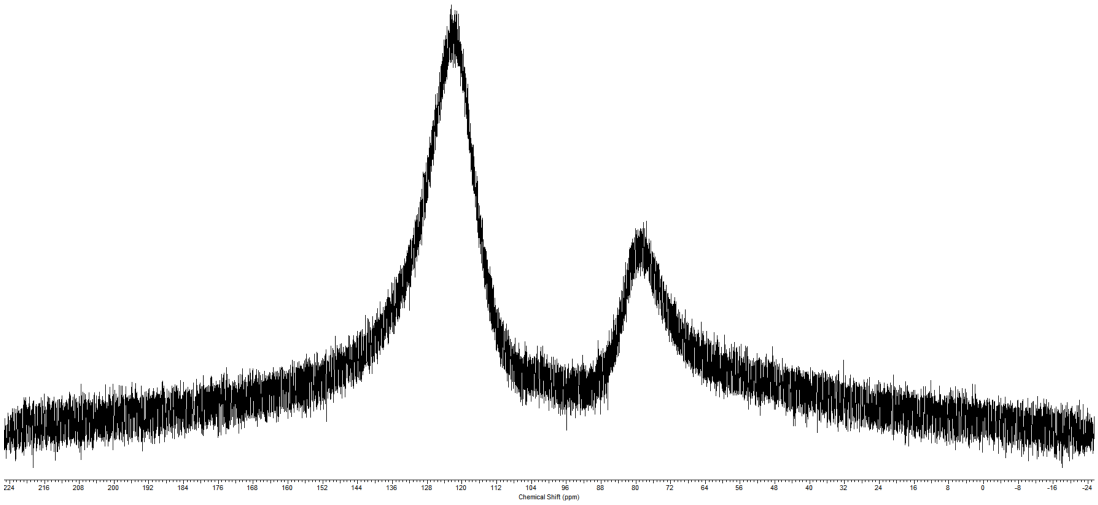

Figure 1.2 ^{27}Al (H-coupled) in D$_8$-THF (the peak at 75 ppm is that for glass).

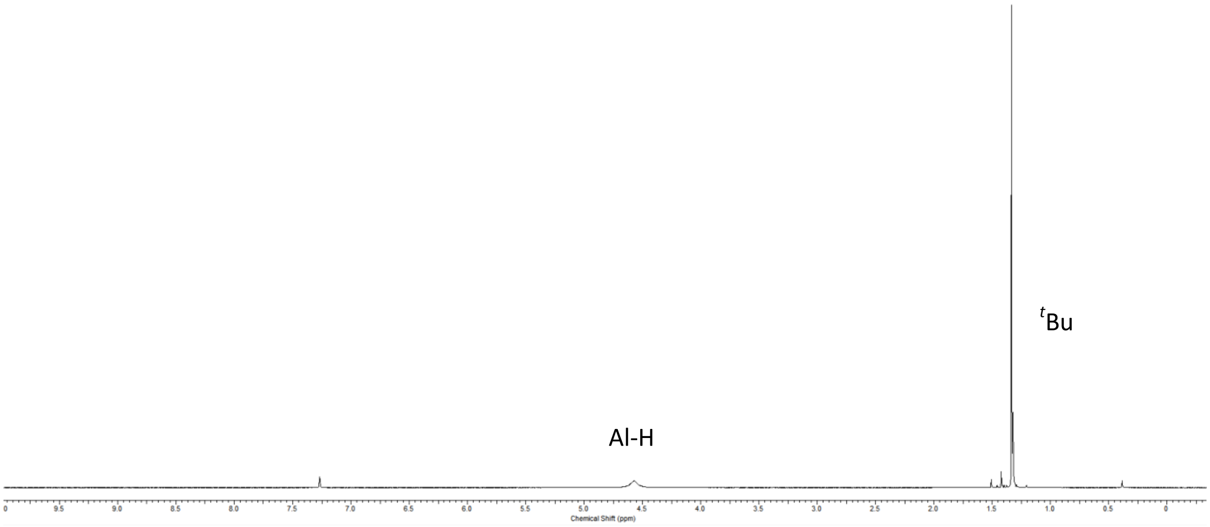

Figure 1.3 ^{1}H NMR Spectrum of ^{t}BuOAlH$_2$ (**1**) in D$_6$-benzene.
Note: The ^{1}H NMR spectrum is identical to that reported in reference 11 in the same solvent.

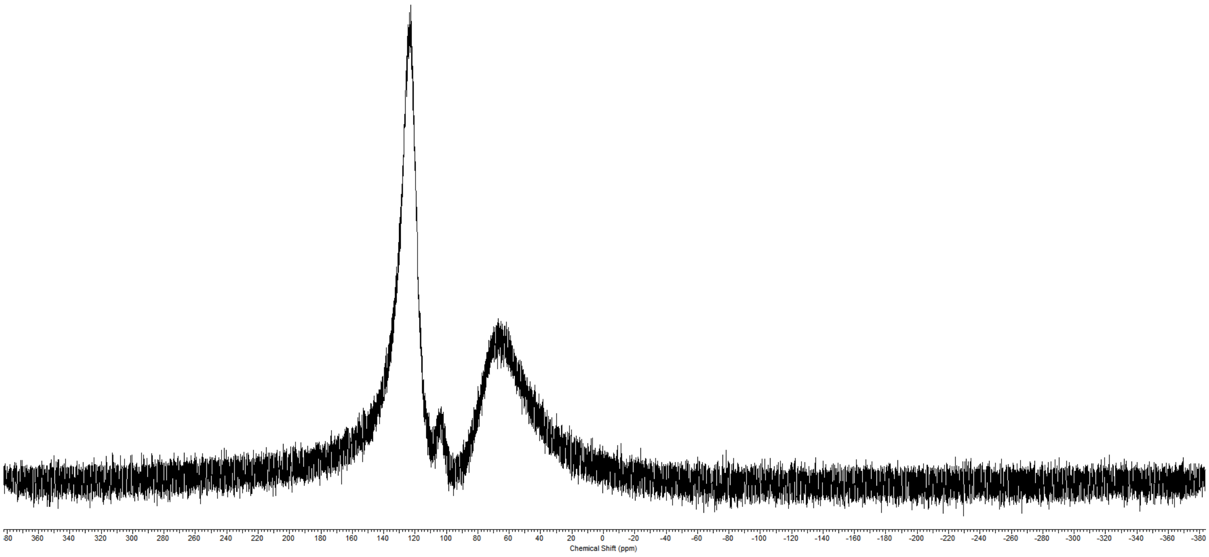

Figure 1.4 ^{27}Al (H-coupled) (the peak at 75 ppm is that for glass).

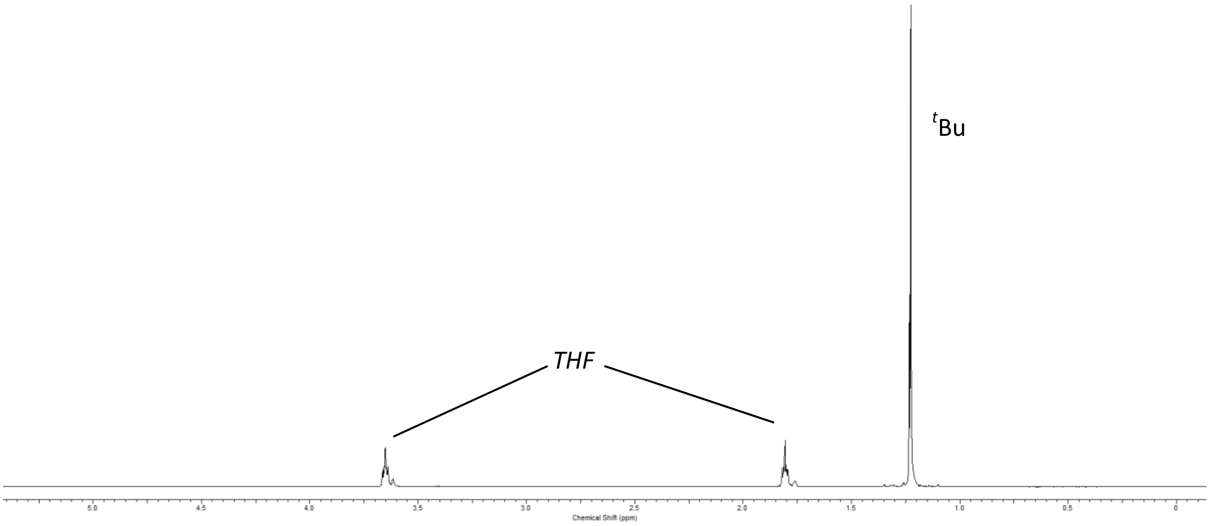

Figure 1.5 ^{1}H NMR Spectrum of (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**) in D$_8$-THF

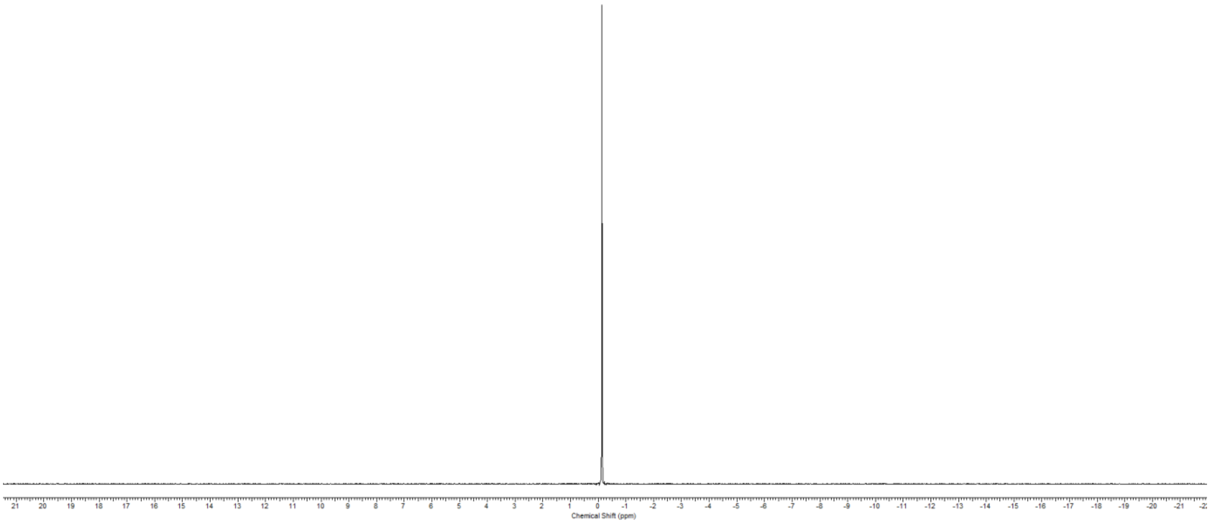

Figure 1.6 ^{7}Li NMR Spectrum of (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**) in D$_8$-THF

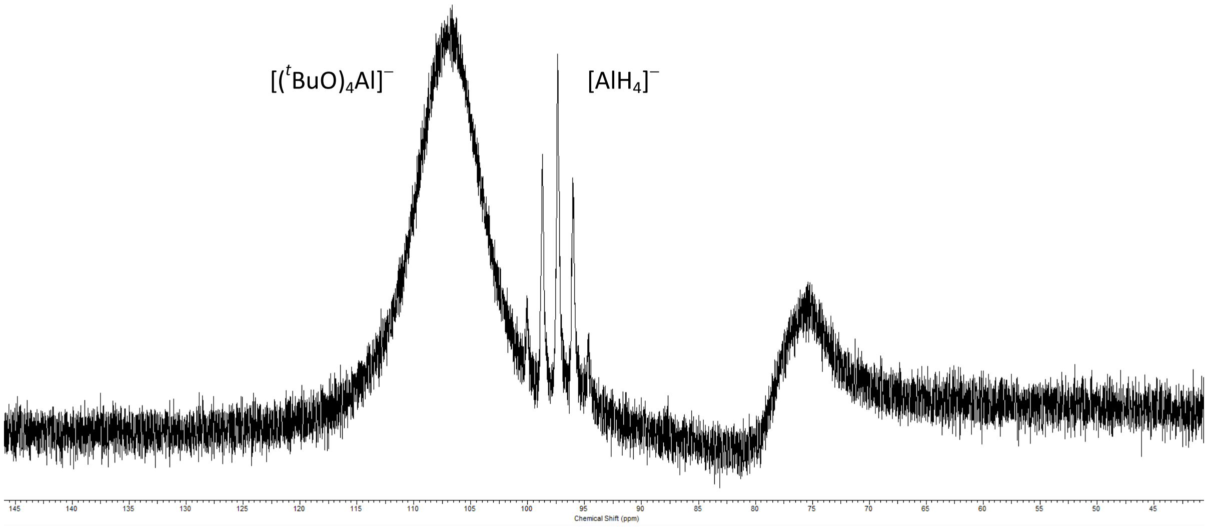

Figure 1.7 ^{27}Al NMR Spectrum of (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**) in D$_8$-THF (the peak at 75ppm is that for glass).

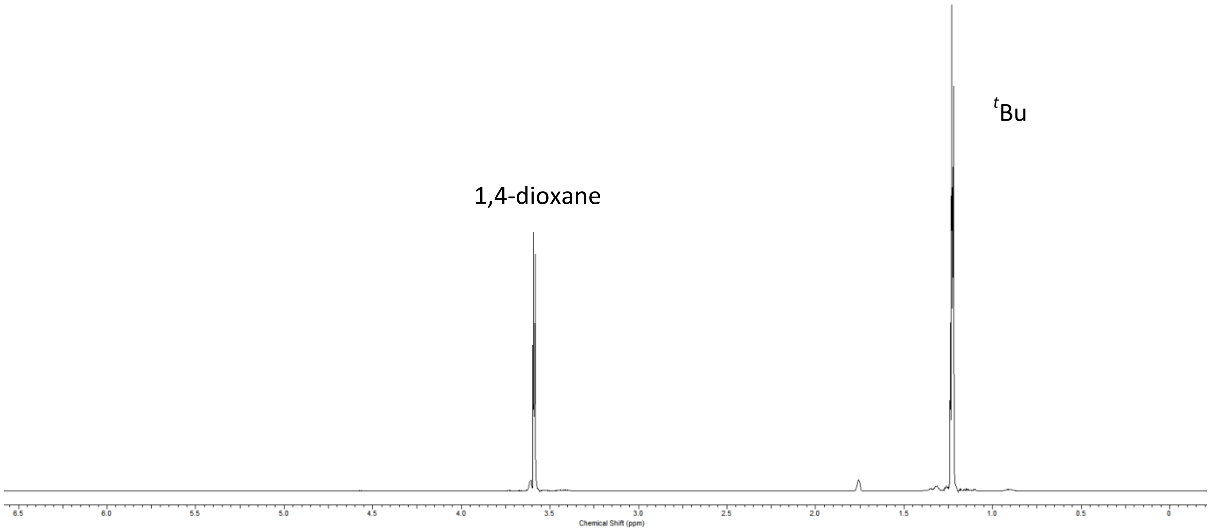

Figure 1.8 ^{1}H NMR Spectrum of (1,4-dioxane)Li(^{t}BuO)$_2$AlH$_2$ (**4**) in D$_8$-THF.

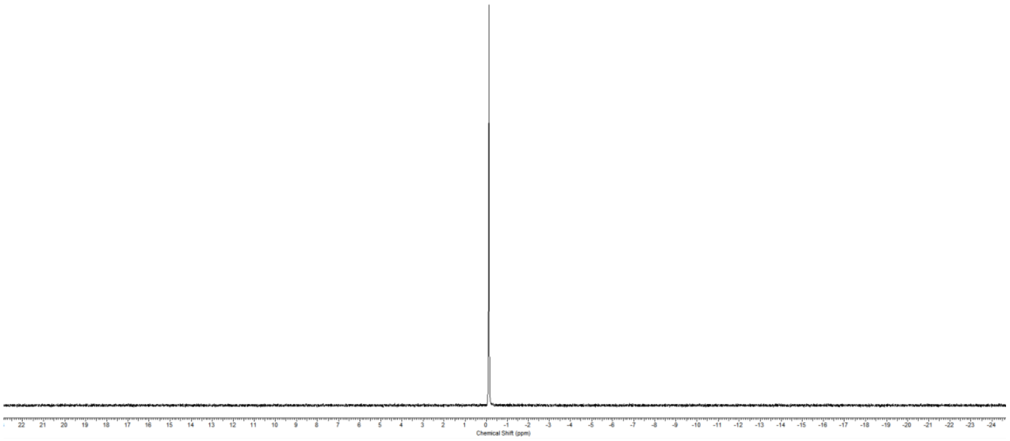

Figure 1.9 ^{7}Li NMR Spectrum of (1,4-dioxane)Li(^{t}BuO)$_2$AlH$_2$ (**4**) in D$_8$-THF.

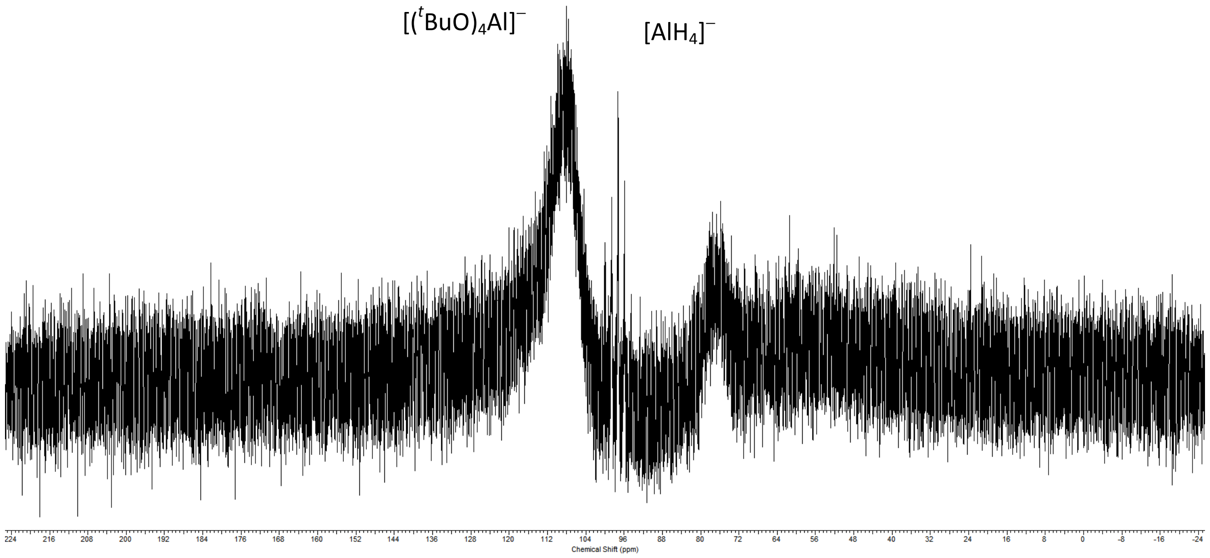

Figure 1.10 ^{27}Al NMR Spectrum of (1,4-dioxane)Li(^{t}BuO)$_2$AlH$_2$ (**4**) in D$_8$-THF (the peak at 75ppm is that for glass).

Note: The spectra for **3** and **4** are almost identical in THF, the only difference being that the ^{1}H spectrum of the latter contains the 1,4-dioxane resonance. The $^1J_{\text{Al-H}}$ coupling constants for the AlH_4^- ion (δ 97 ppm) are also identical to one decimal place and are consistent with the reported Al-H coupling in AlH_4^- of 170 – 173 Hz (reference 19 in the paper).

2. NMR Spectra of the Reaction Products 5 and 6

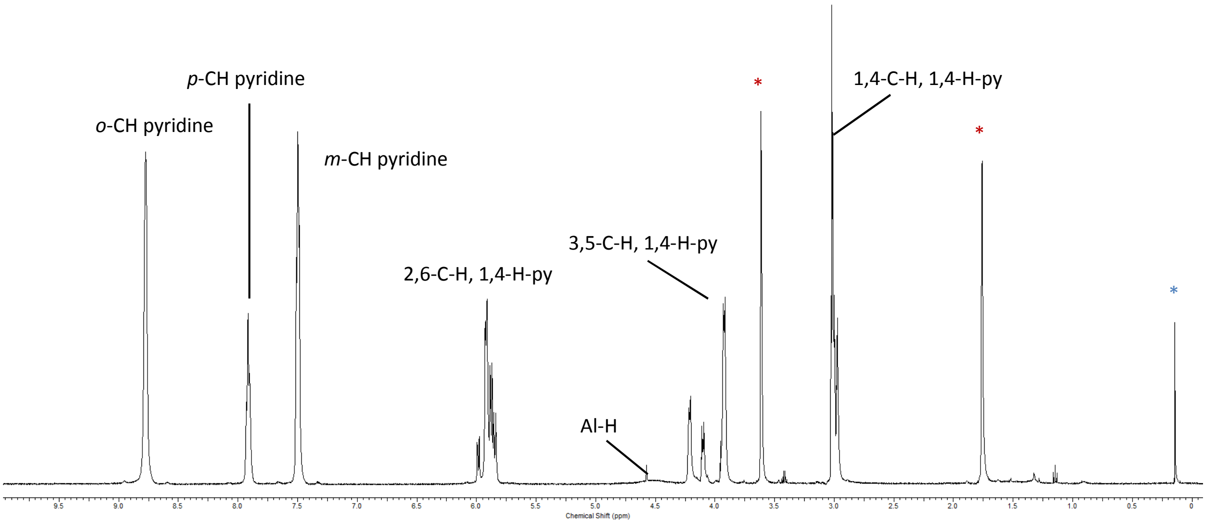

Figure 2.1 ^{1}H NMR Spectrum of [(1,4-H-pyrid-1-yl)$_4$Al]$^-$[(pyridine)$_4$AlH$_2$]$^+$ (**5**) in D$_8$-THF (THF peaks solvent peaks are marked *, vacuum grease *).

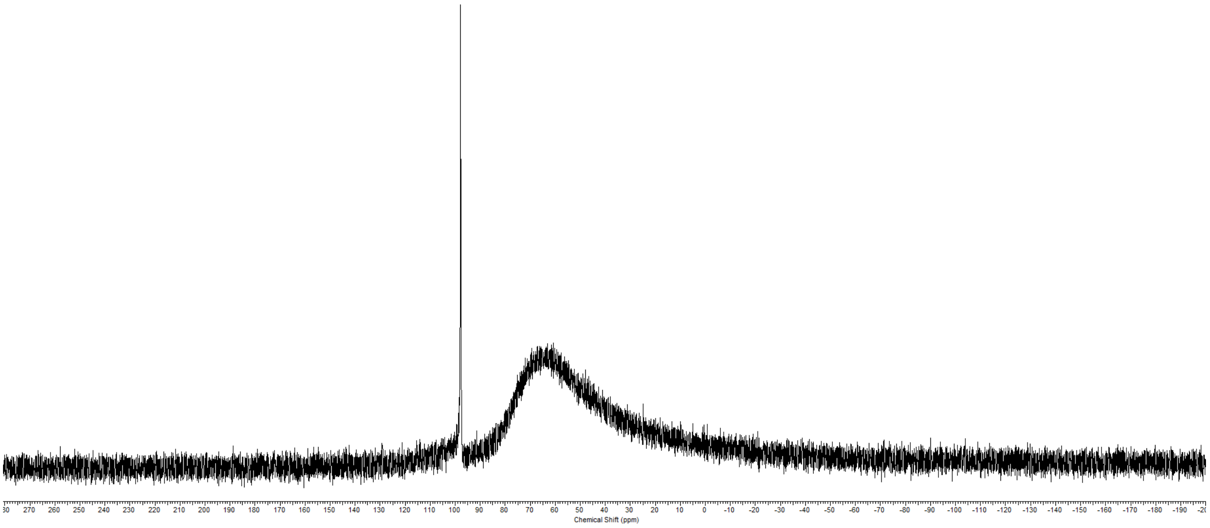

Figure 2.2 ^{27}Al NMR (H-decoupled) of [(1,4-H-pyrid-1-yl)$_4$Al]$^-$[(pyridine)$_4$AlH$_2$]$^+$ (**5**) in D$_8$-THF (the peak at 75 ppm is that for glass).

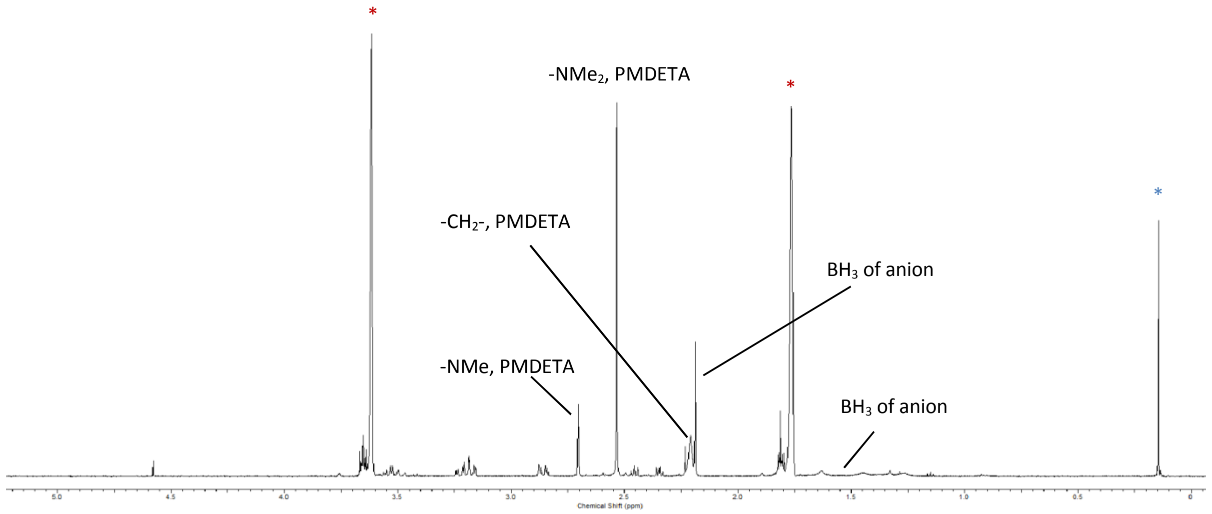

Figure 2.3 ^{1}H NMR Spectrum of $[(PMDETA)AlH_2]^+[(H_3B)_2(NMe_2)]^-$ (**6**) in D_8-THF (THF peaks solvent peaks are marked *, vacuum grease *).

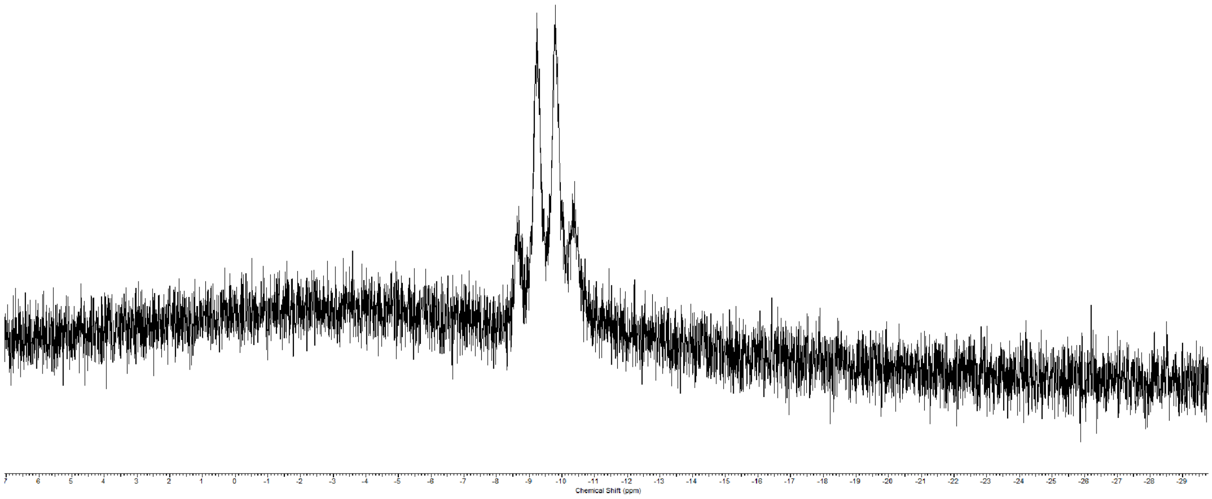

Figure 2.4 ^{11}B NMR Spectrum of $[(PMDETA)AlH_2]^+[(H_3B)_2(NMe_2)]^-$ (**6**) in D_8-THF.

3. *In situ* ^{11}B NMR Spectroscopic Studies of Catalytic and Stoichiometric Reactions of 1, 2, 3 and 4 with Me_2NHBH_3.

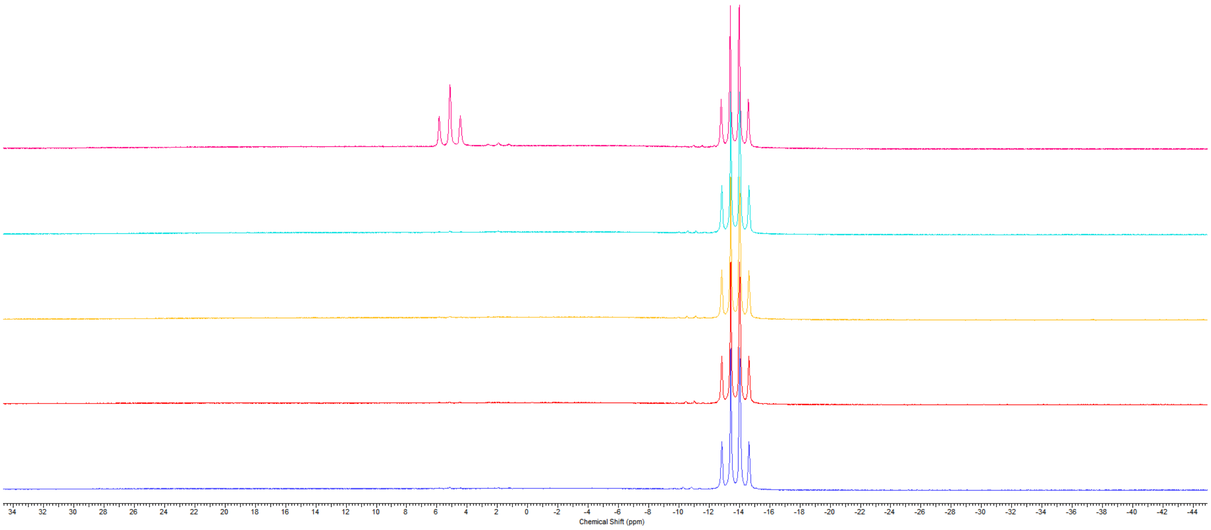

Figure 3.1 $^{t}BuOAlH_2$ (**1**) (10 mol% loading) + Me_2NHBH_3 in D_8-THF. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours and after heating overnight.

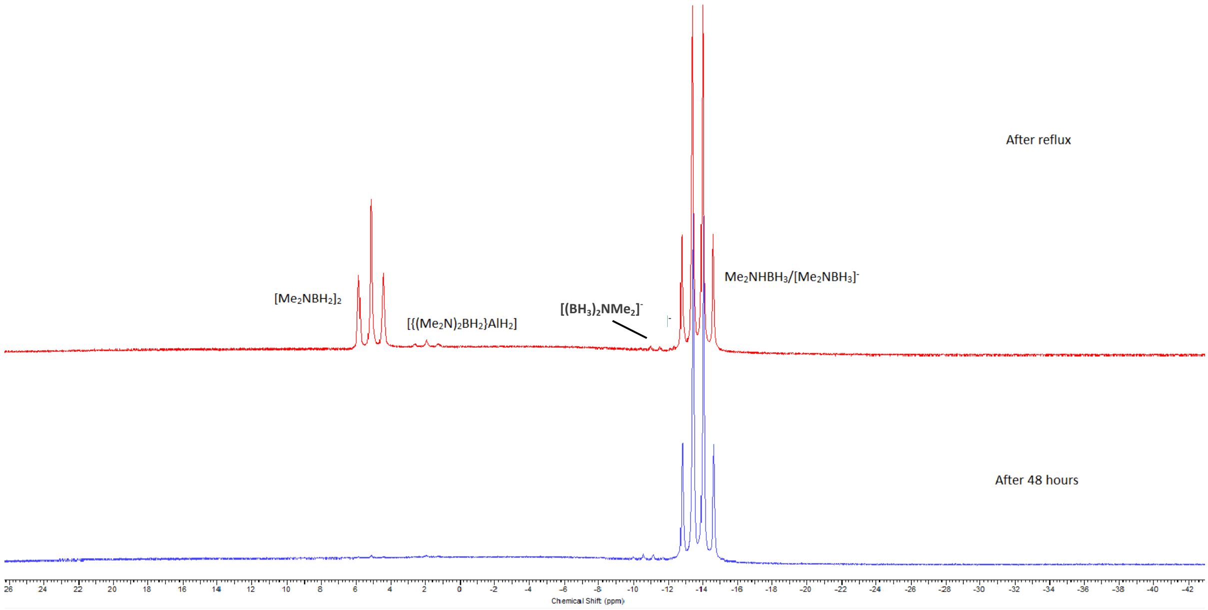

Figure 3.2 Comparison of the spectra taken after 48 hours and after heating overnight (taken from Figure 3.1).

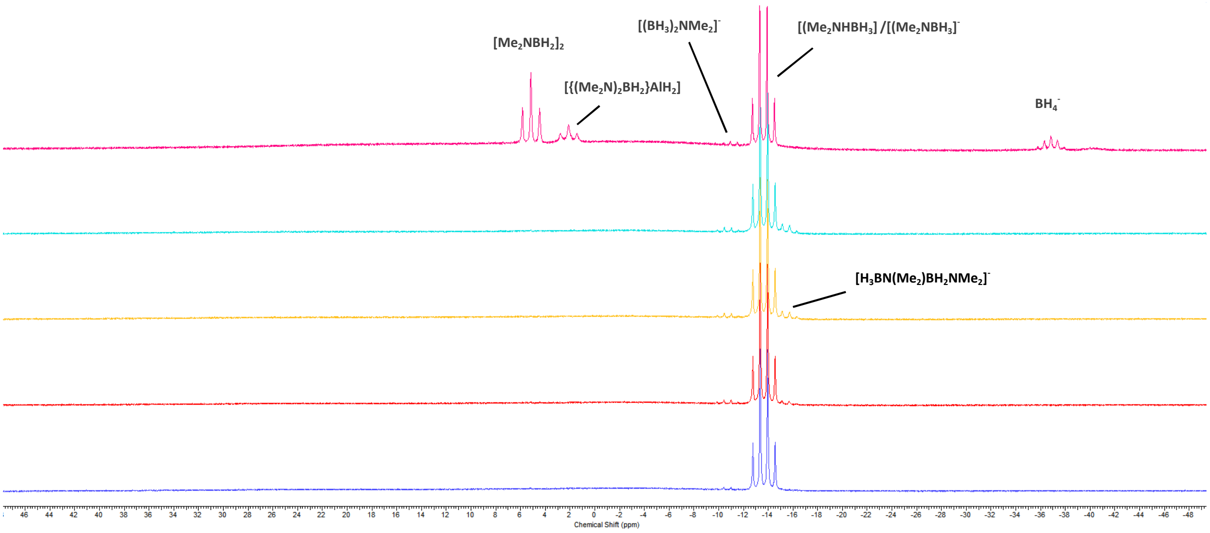

Figure 3.3 1 :1 Reaction of ^{t}BuOAlH$_2$ (**1**) + Me$_2$NHBH$_3$ in D$_8$-THF. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours and after heating overnight.

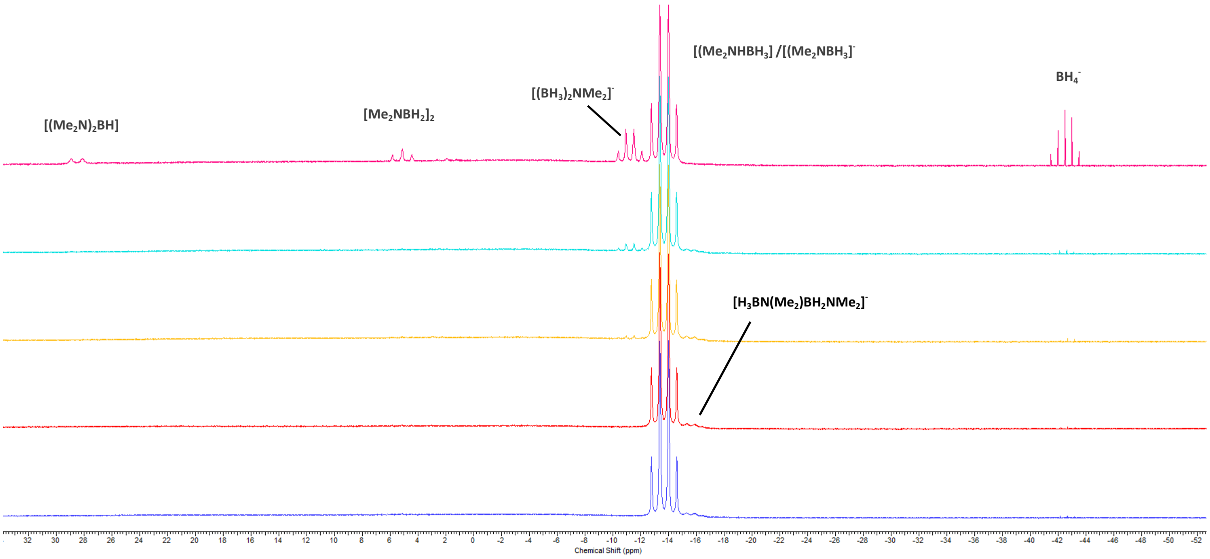

Figure 3.4 (^{t}BuO)$_2$AlH (**2**) + Me$_2$NHBH$_3$ (10 mol% loading) in D$_8$-THF. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours and after heating overnight.

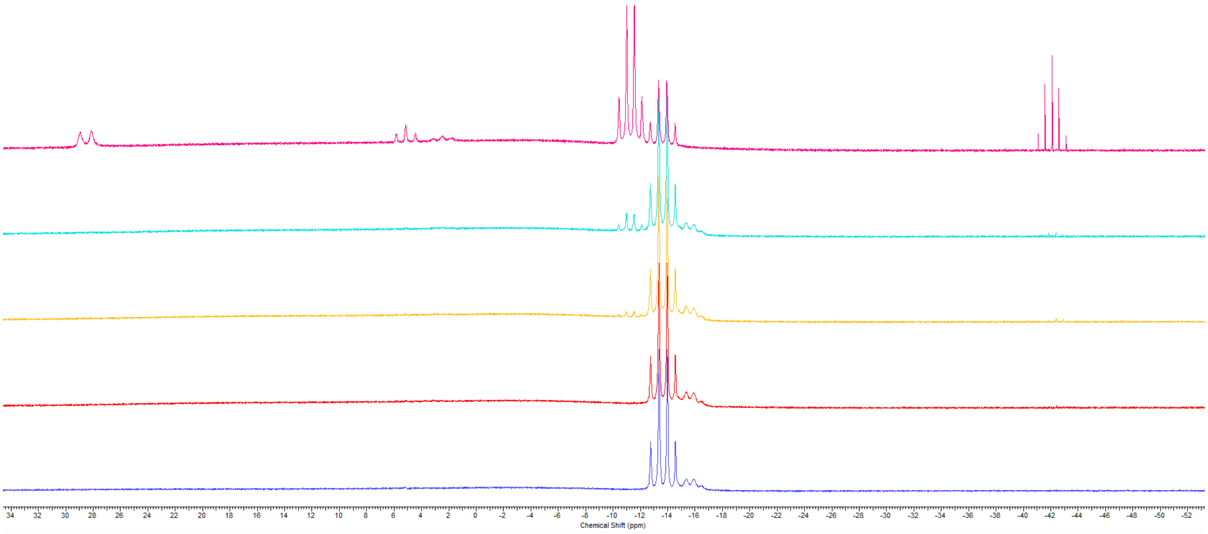

Figure 3. 5 1 :1 Reaction of (^{t}BuO)$_2$AlH (**2**) + Me$_2$NHBH$_3$ in D$_8$-THF. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours and after heating overnight.

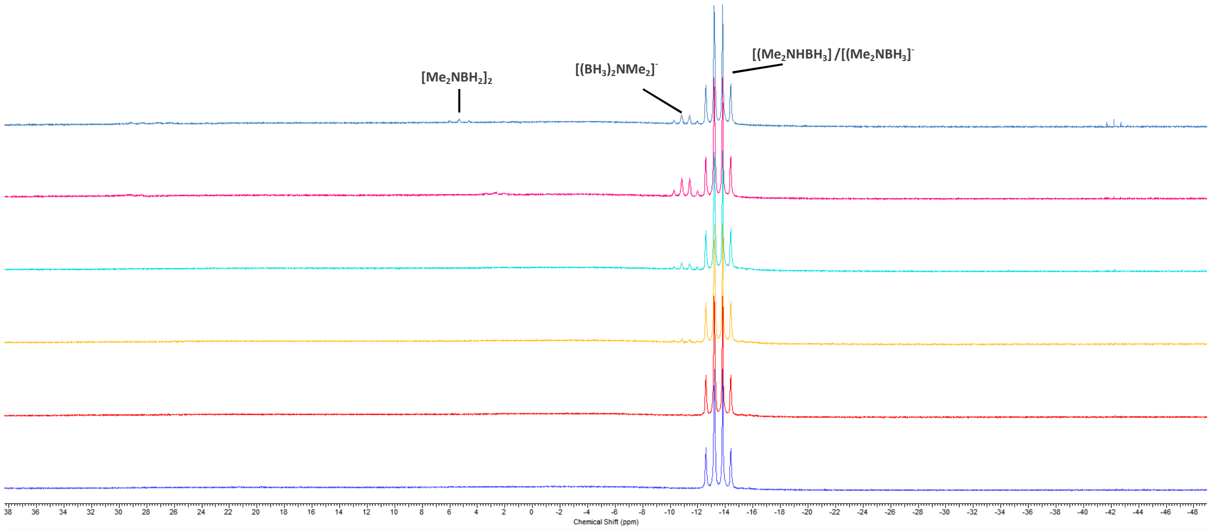

Figure 3.6 (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**) (10 mol% loading) + Me_2NHBH_3 in D_8-THF. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours, 168 hours and after heating overnight.

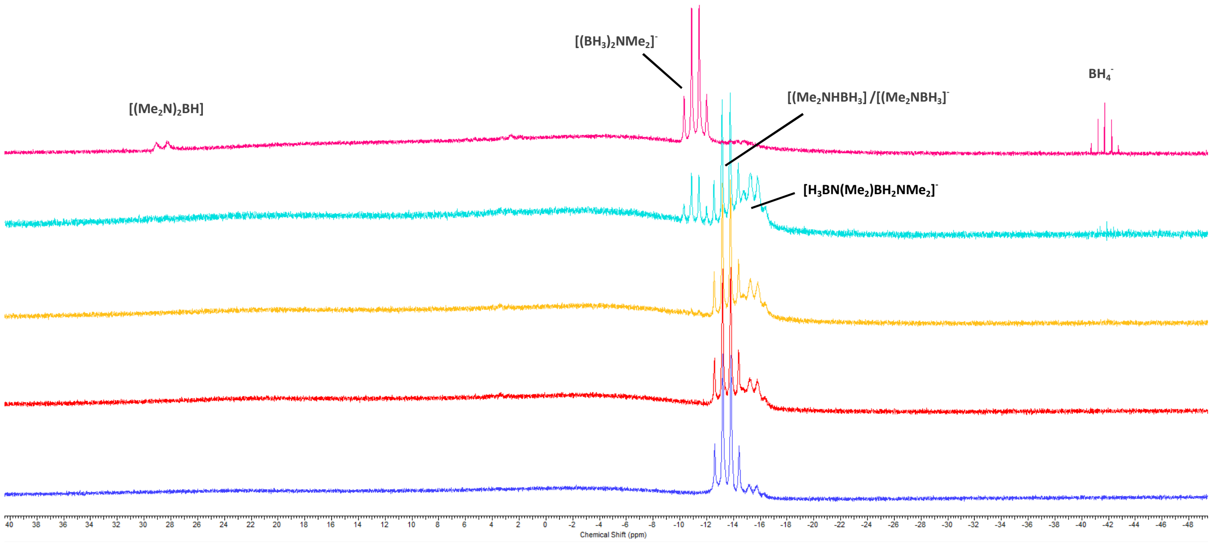

Figure 3.7 1 :1 Reaction of (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**) (10 mol% loading) + Me_2NHBH_3 in D_8-THF. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 144 hours and after heating overnight.

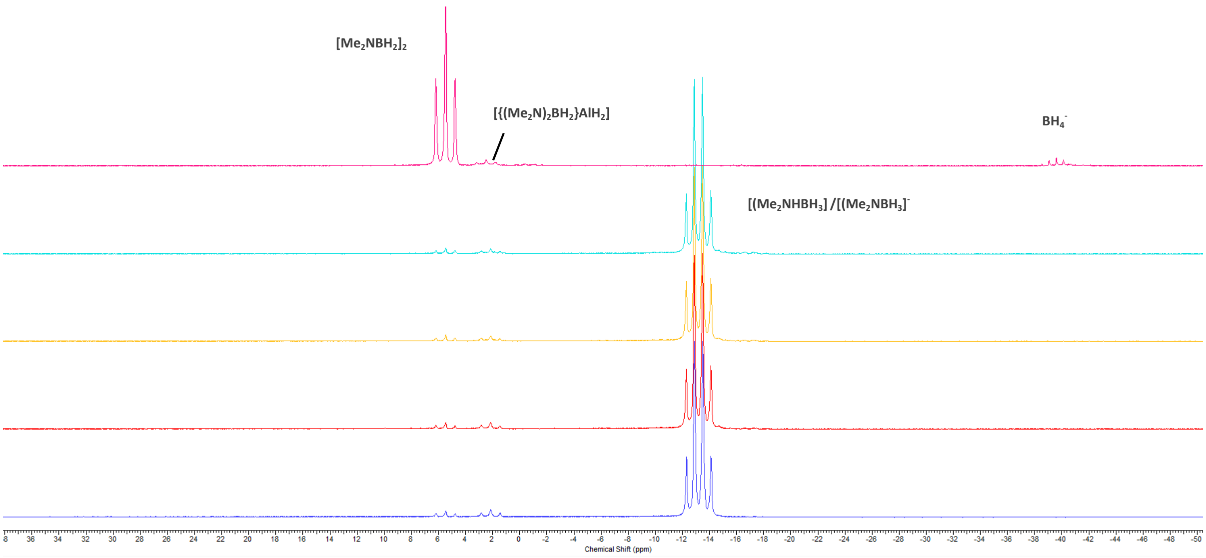

Figure 3.8 ^{t}BuOAlH$_2$ (**1**) (10 mol% loading) + Me$_2$NHBH$_3$ in D$_8$-toluene. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours and after heating overnight.

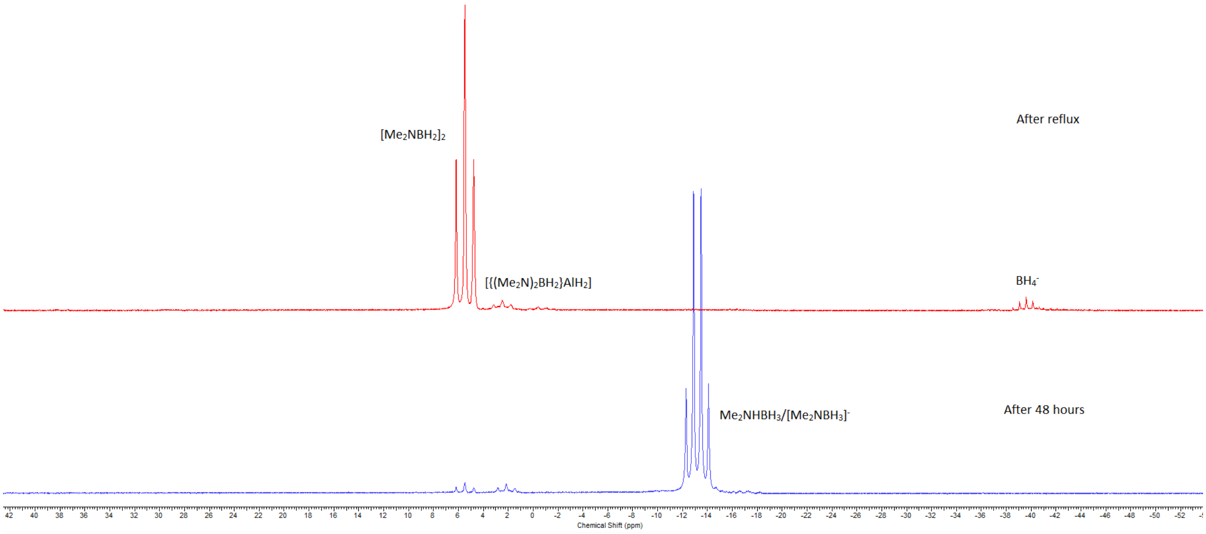

Figure 3.9 Comparison of the spectra taken after 48 hours and after heating overnight (taken from Figure 3.8).

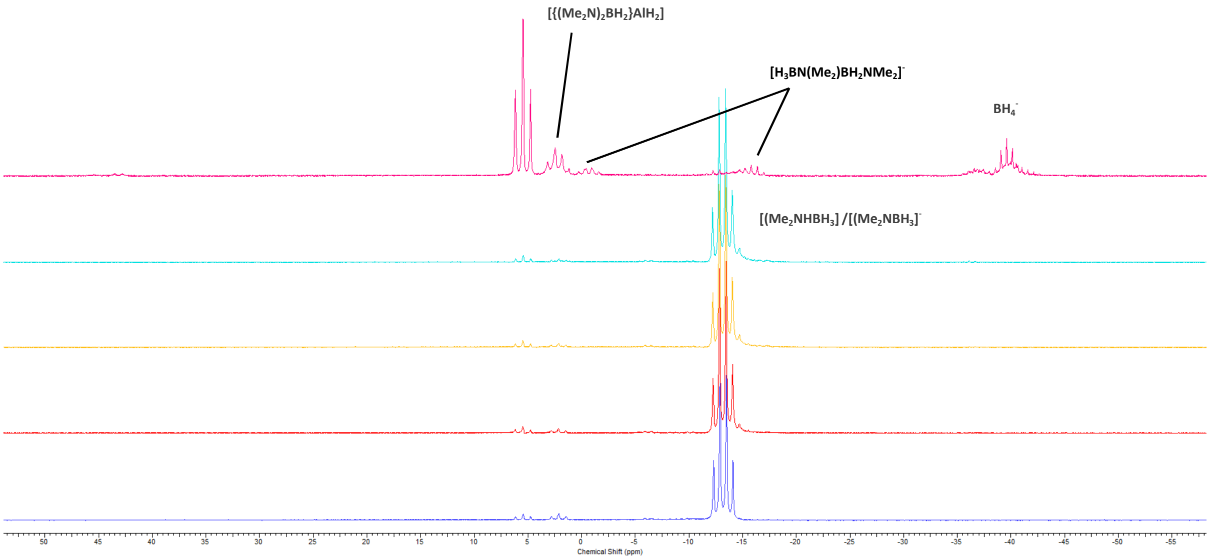

Figure 3.10 1 :1 Reaction of $^{t}BuOAlH_2$ (**1**) + Me_2NHBH_3 in D_8-toluene. Spectra taken at t = (from bottom to top) 0 hours, 24 hours, 48 hours, 72 hours and after heating overnight.

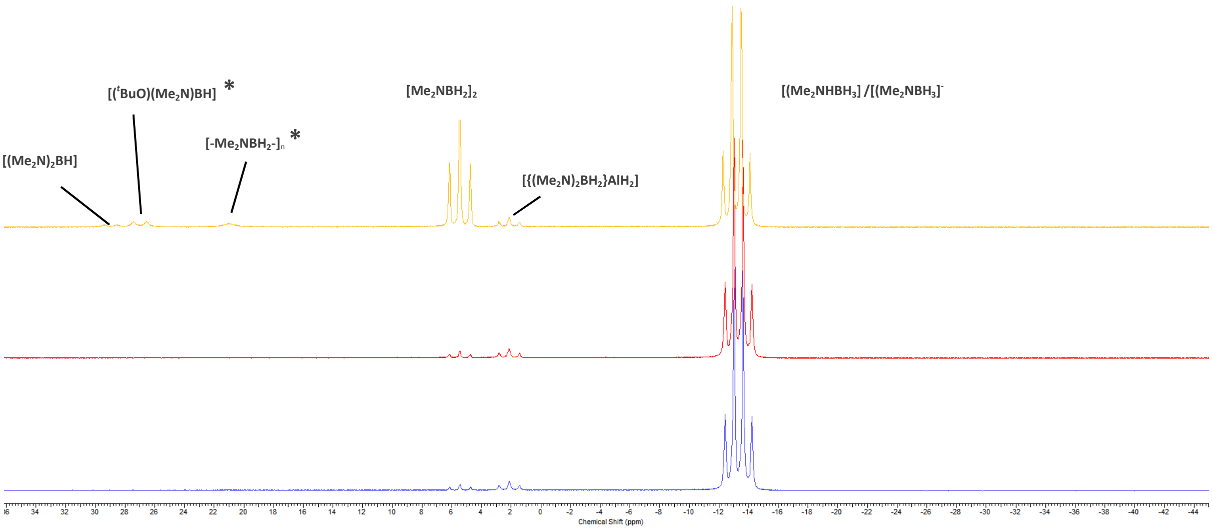

Figure 3.11 $(^{t}BuO)_2AlH$ (**2**) + Me_2NHBH_3 (10 mol% loading) in D_8-toluene. Spectra taken at t = (from bottom to top) 0 hours, 72 hours and after heating overnight.

Notes –

The broad peak at *ca.* δ22 was assigned on the basis of previous studies to the polymer/oligomer $[-BH_2NMe_2-]_n$ (see K. A. Erickson, D. S. Wright, R. Waterman, *J. Organomet. Chem.*, in press and references therein).

The doublet at δ26.8 ($^{1}J_{BH}$ = 128 Hz) was assigned to the assymetric chain product $[(^{t}BuO)(Me_2N)BH]$ (see P. Belham, M. S. Hill, G. Kociok-Köhn, D. J. Liprot, *Chem. Commun.*, 2013, **49**, 1960). This species results from the nucleophilic addition of a ^{t}BuO-Al group onto a the B-atom of $[Me_2N{=}BH_2]$ (see Scheme 5 of the paper).

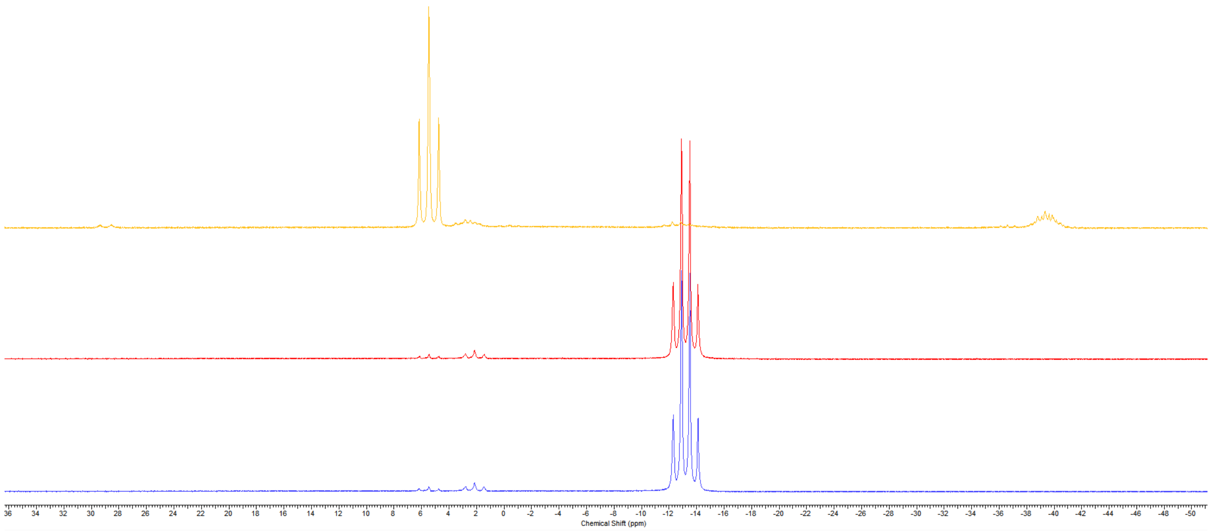

Figure 3.12 1 :1 Reaction of $(^tBuO)_2AlH$ (**2**) + Me_2NHBH_3 in D_8-toluene. Spectra taken at t = (from bottom to top) 0 hours, 72 hours and after heating overnight.

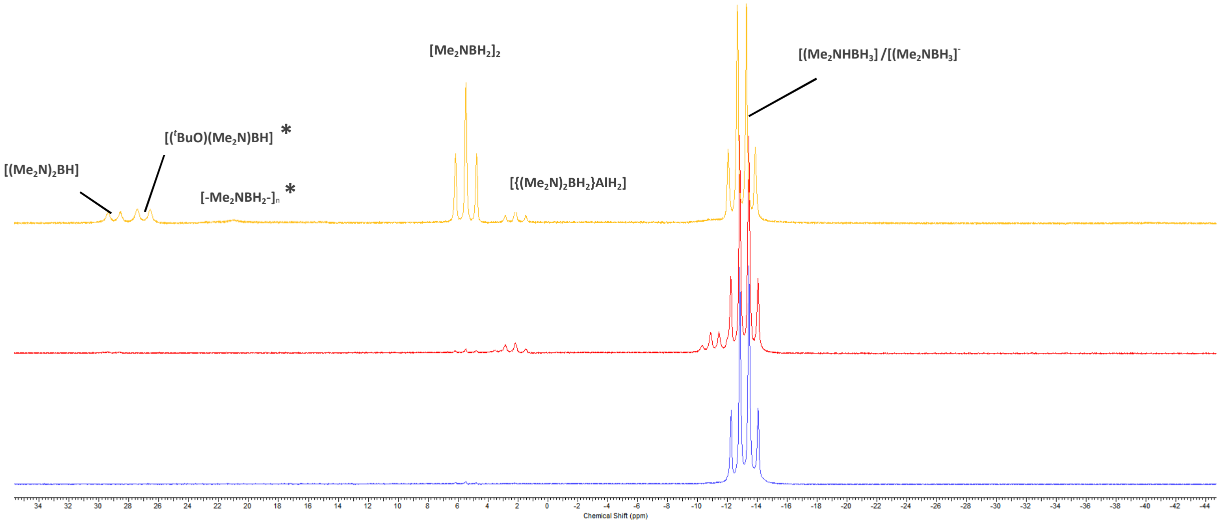

Figure 3.13 $(THF)Li[(^tBuO)_2AlH_2]$ (**3**) (10 mol% loading) + Me_2NHBH_3 in D_8-toluene. Spectra taken at t = (from bottom to top) 0 hours, 72 hours and after heating overnight (* see notes to Figure 3.11).

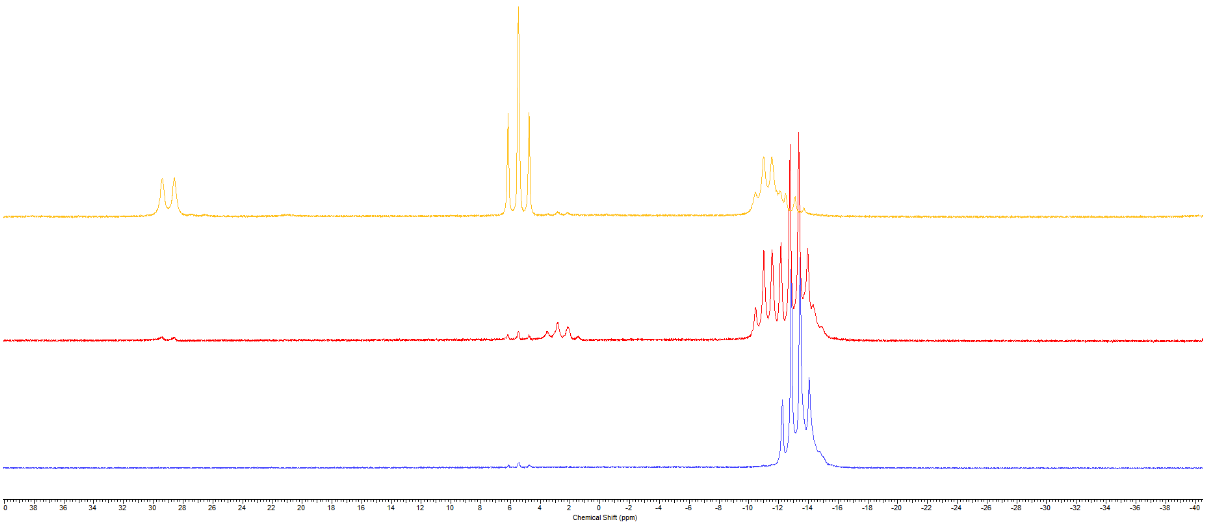

Figure 3.14 1 :1 Reaction of (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**) + Me_2NHBH_3 in D$_8$-toluene. Spectra taken at t = (from bottom to top) 0 hours, 72 hours and after heating overnight.

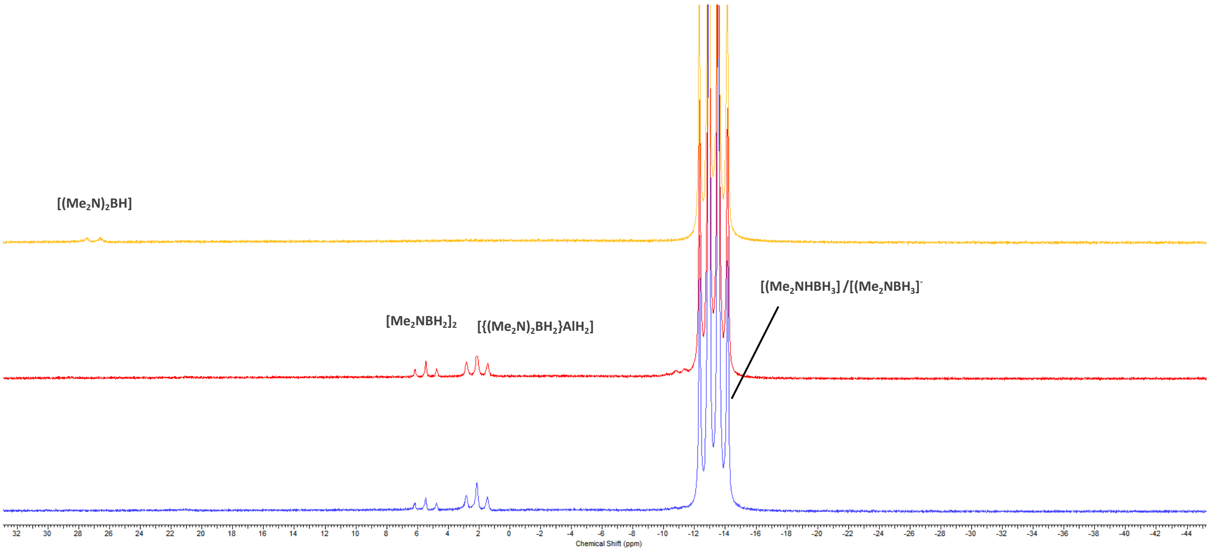

Figure 3.15 (1,4-dioxane)Li[(^{t}BuO)$_2$AlH$_2$] (**4**) (10 mol% loading) + Me_2NHBH_3 in D$_8$-toluene. Spectra taken at t = (from bottom to top) 0 hours, 72 hours and after heating overnight.

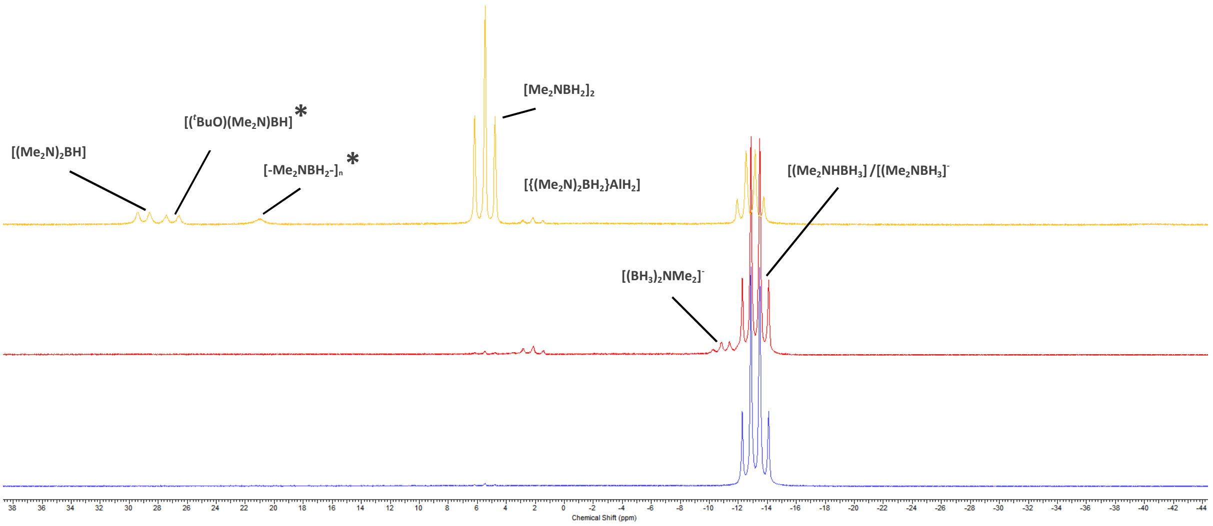

Figure 3.16 1 :1 Reaction of (1,4-dioxane)Li[(^{t}BuO)$_2$AlH$_2$] (**4**) + Me$_2$NHBH$_3$ in D$_8$-toluene. Spectra taken at t = (from bottom to top) 0 hours, 72 hours and after heating overnight (* see notes to Figure 3.11).

4. Study of Recation of (^{t}BuO)AlH$_2$ with D$_5$-pyridine

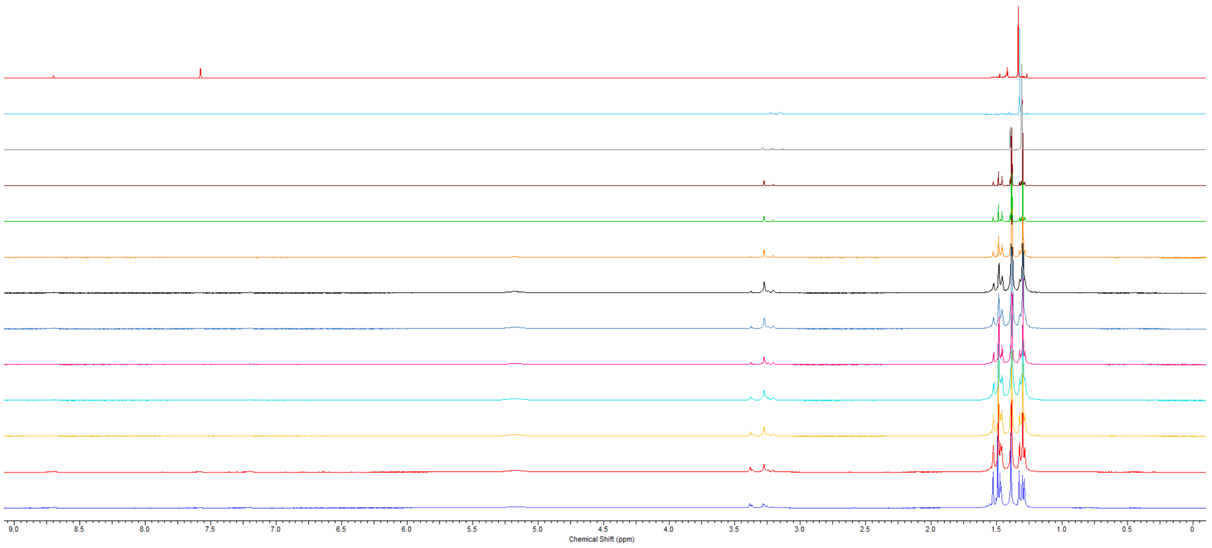

Figure 4.1 ^{1}H NMR Spectrum of the Reaction of 1 with D5-pyridine. The whole spectrum, showing the change in alkyl region over time. Spectra taken at t = (from bottom to top) 0 mins, 4 mins, 8 mins, 12 mins, 16 mins, 20 mins, 24 mins, 30 mins, 36 mins, 42 mins, 24 hours, 48 hours and after heating overnight.

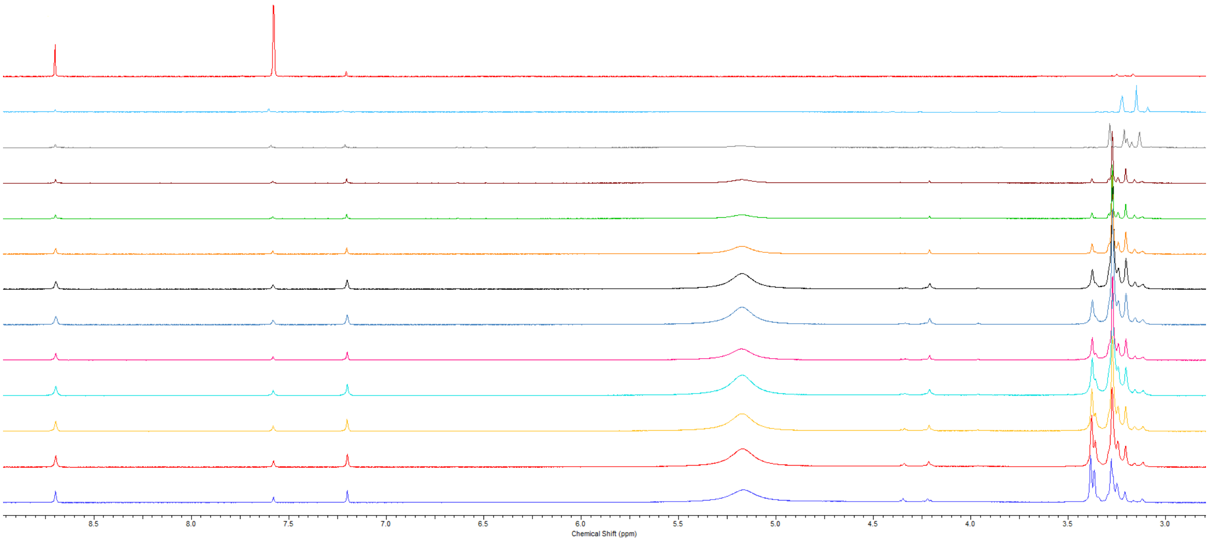

Figure 5.2 Expansion of the spectrum shown in Figure 5.1 (cropped to show the 3.0 – 9.0 ppm region). Visible is a hydride peak at 5.17 ppm which disappears after longer reaction periods. Also visible are the deuterated pyridine peaks, with the *ortho*-proton appearing furthest downfield and the *meta*-proton appearing furthest upfield. The *ortho*:*para*:*meta* ratio at t=0 is 2:1:2, as expected, and over time an exchange reaction occurs.