Supplementary Materials: NHI and NHC-Supported Al(III) Hydrides for Amine–Borane Dehydrocoupling Catalysis

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Contents

1. Catalysis

General procedure: 5 mol% of chosen catalyst (**1**-**6**, 0.012 mmol) and Me_2NHBH_3 (0.24 mmol) were dissolved in 0.5 mL of C_6D_6 and added to a Youngs Tap NMR tube. 1H and 11B NMR was recorded before being placed at the appropriate temperature and monitored over time until >80% consumption of Me_2NHBH_3.

Table S 1. Dehydrocoupling of Me_2NHBH_3 with 5 mol% Al(II) hydride catalysts **1**-**6**

					Product distribution				
Catalyst	**Temp/ °C**	**Time/ hr**	**Conversion[a] / %**	**TOF[b]/ hr^{-1}**	**A**	**B**	**C**	**D**	**Others**
1	80	34	90	0.53	76	2	-	6	-
2	80	34	84	0.49	85	5	-	-	-
3	50	65	80	0.25	70	-	-	6	4
4	50	26	92	0.74	76	-	-	9	7
5	50	65	93	0.29	66	-	-	9	18
6	50	40	92	0.46	72	-	-	8	15

Reaction conditions 5 mol% **1**-**6** (0.012 mmol), Me_2NHBH_3 (0.24 mmol), 0.5 mL C_6D_6. [a] conversion of Me_2NHBH_3 determined by ^{11}B NMR relative integrals; [b] TOF = (conversion/catalyst loading)/time

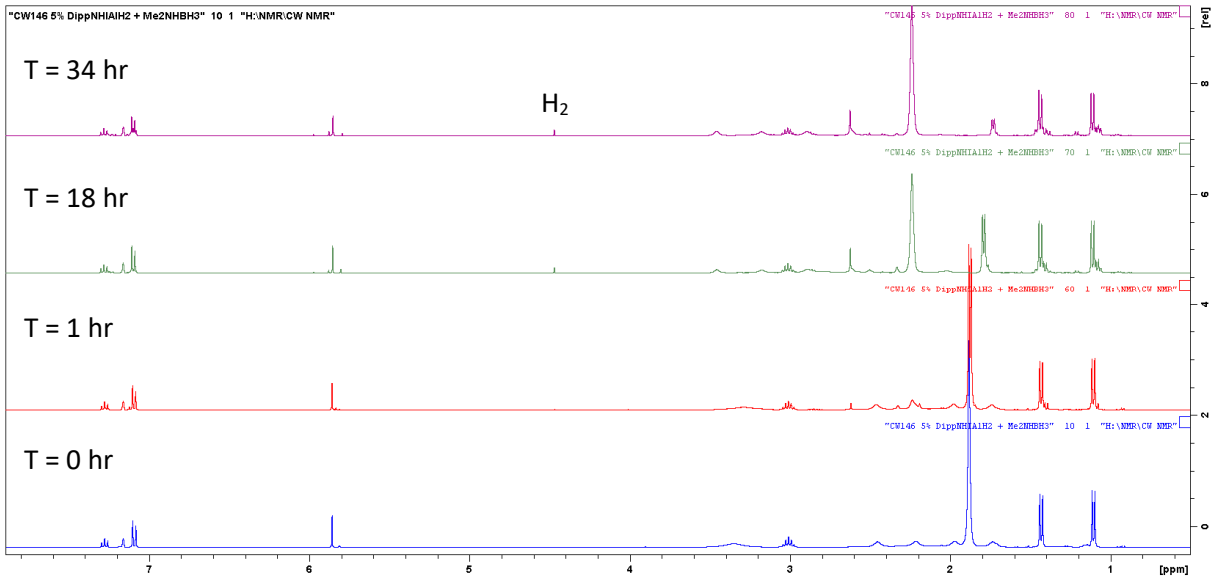

Figure S 1. Stacked ^{1}H NMR spectra for 5 mol% **1** with Me_2NBH_3 at 80 °C in C_6D_6

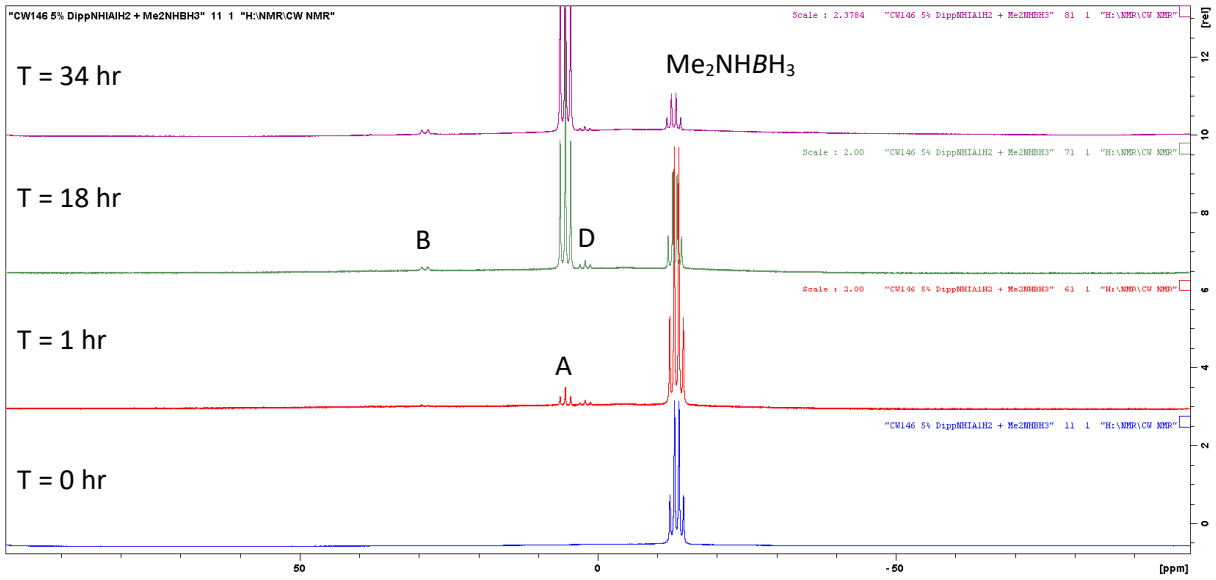

Figure S 2. Stacked ^{11}B NMR spectra for 5 mol% **1** with Me_2NBH_3 at 80 °C in C_6D_6

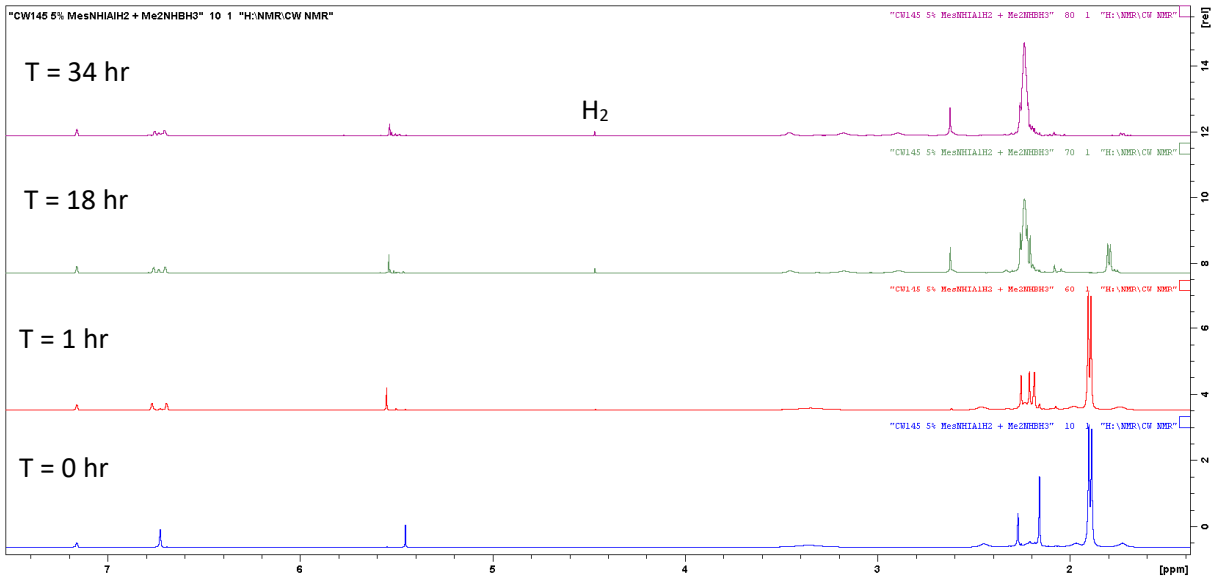

Figure S 3. Stacked ^{1}H NMR spectra for 5 mol% **2** with Me_2NBH_3 at 80 °C in C_6D_6

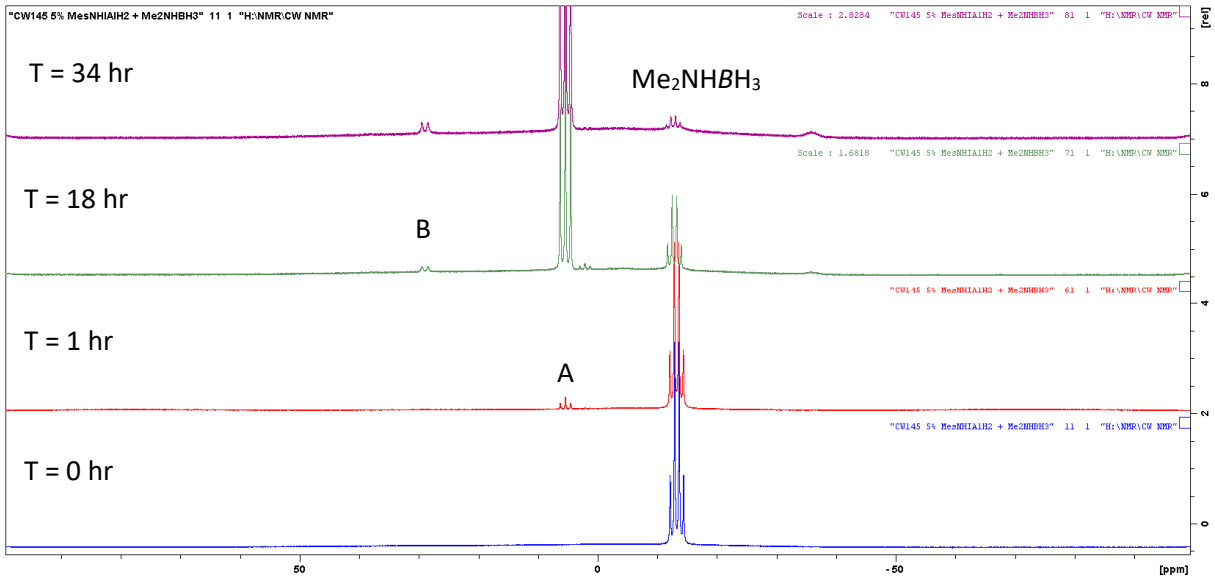

Figure S 4. Stacked ^{11}B NMR spectra for 5 mol% **2** with Me_2NBH_3 at 80 °C in C_6D_6

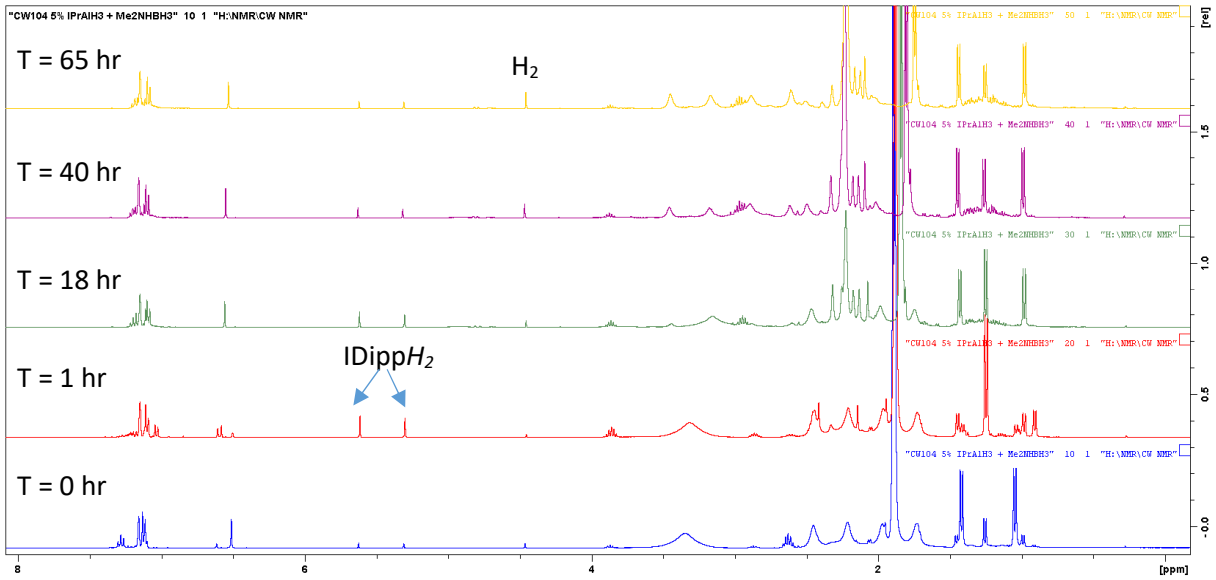

Figure S 5. Stacked ^{1}H NMR spectra for 5 mol% **3** with Me_2NBH_3 at 50 °C in C_6D_6

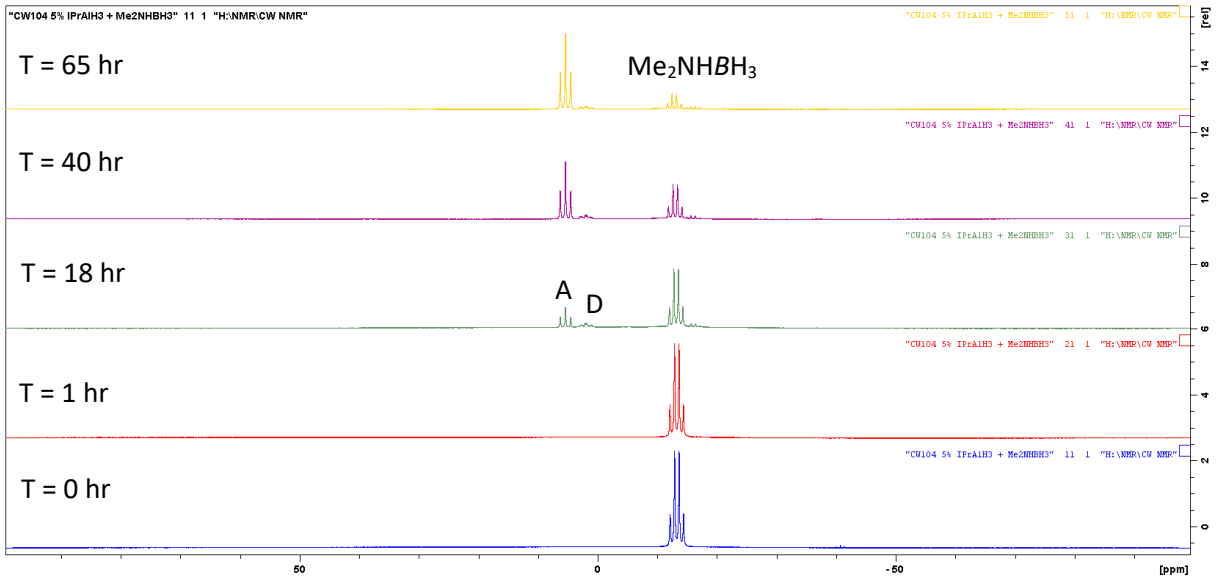

Figure S 6. Stacked ^{11}B NMR spectra for 5 mol% **3** with Me_2NBH_3 at 50 °C in C_6D_6

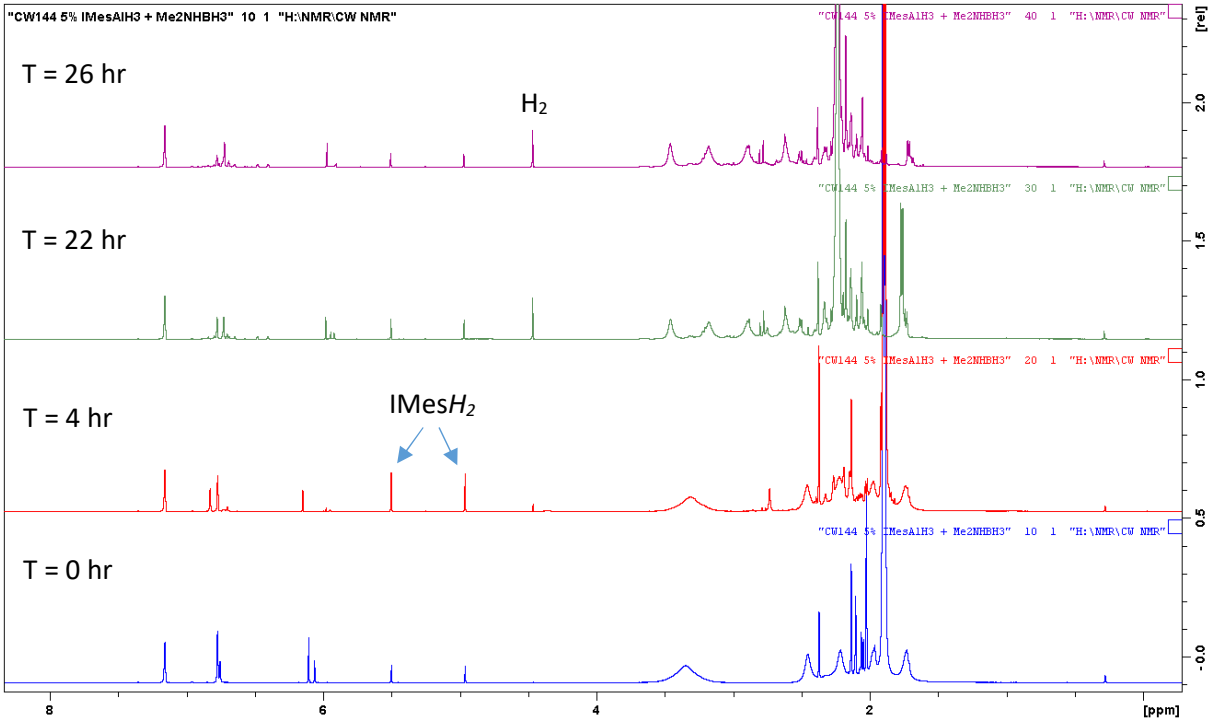

Figure S 7. Stacked ^{1}H NMR spectra for 5 mol% **4** with Me_2NBH_3 at 50 °C in C_6D_6

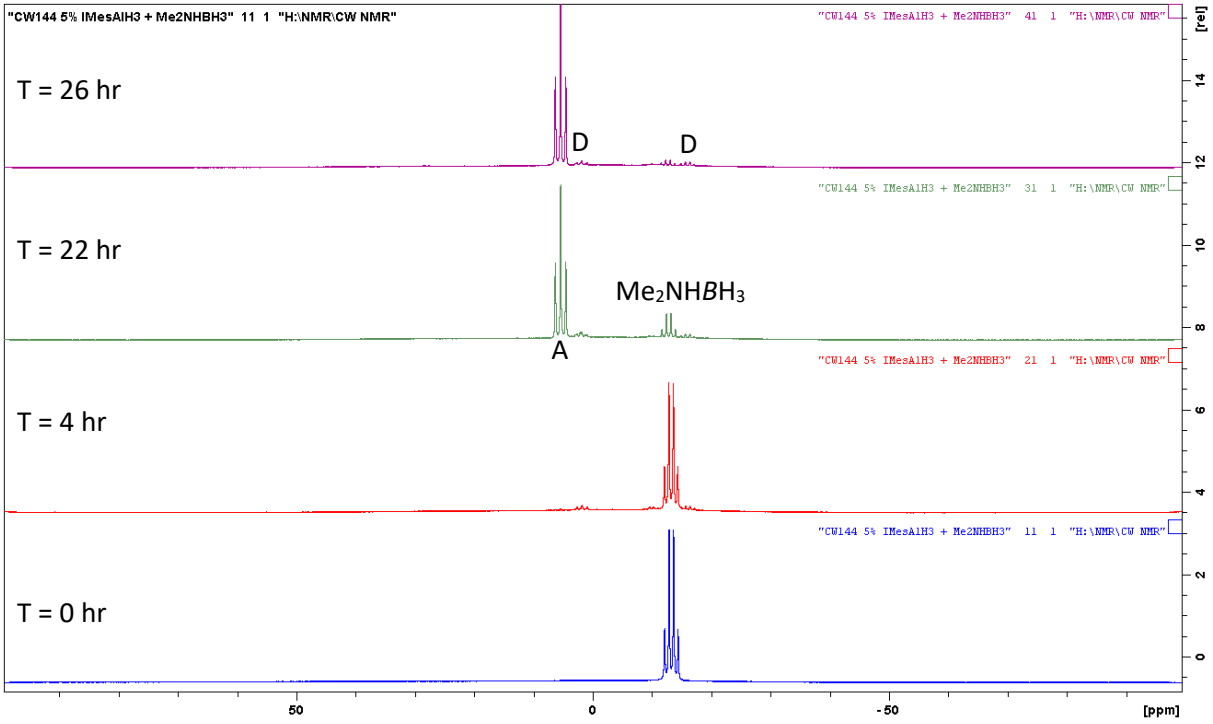

Figure S 8. Stacked ^{11}B NMR spectra for 5 mol% **4** with Me_2NBH_3 at 50 °C in C_6D_6

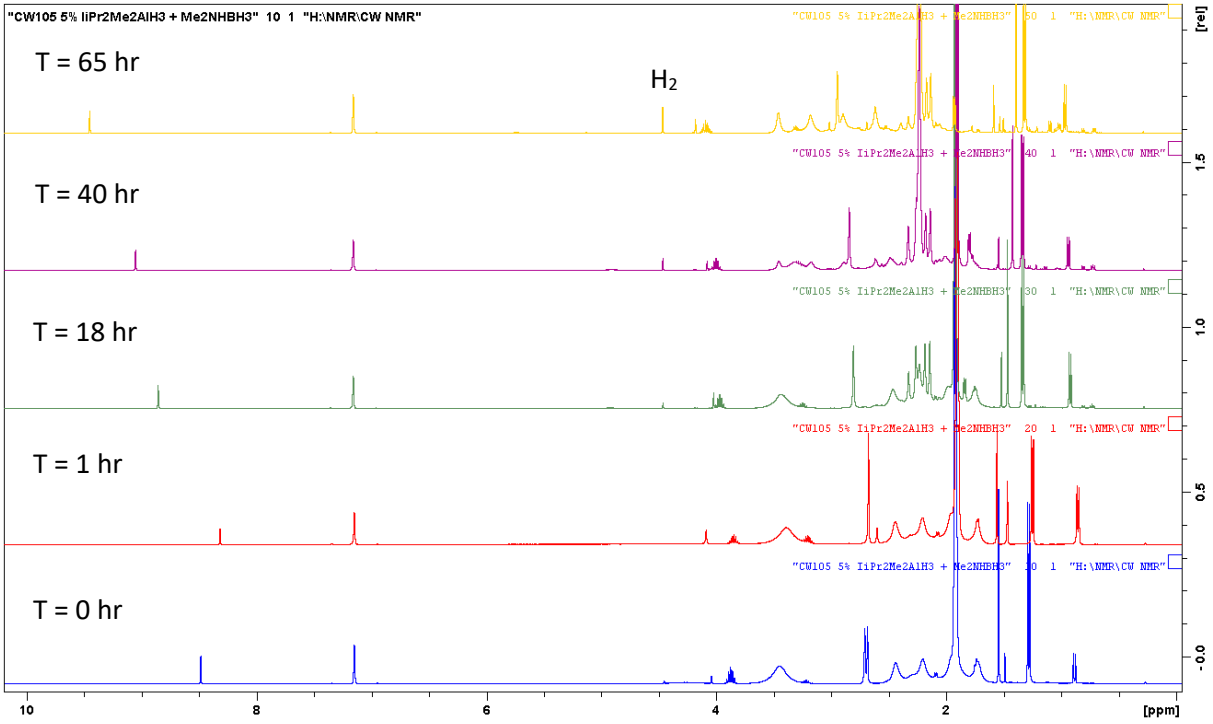

Figure S 9. Stacked ^{1}H NMR spectra for 5 mol% **5** with Me_2NBH_3 at 50 °C in C_6D_6

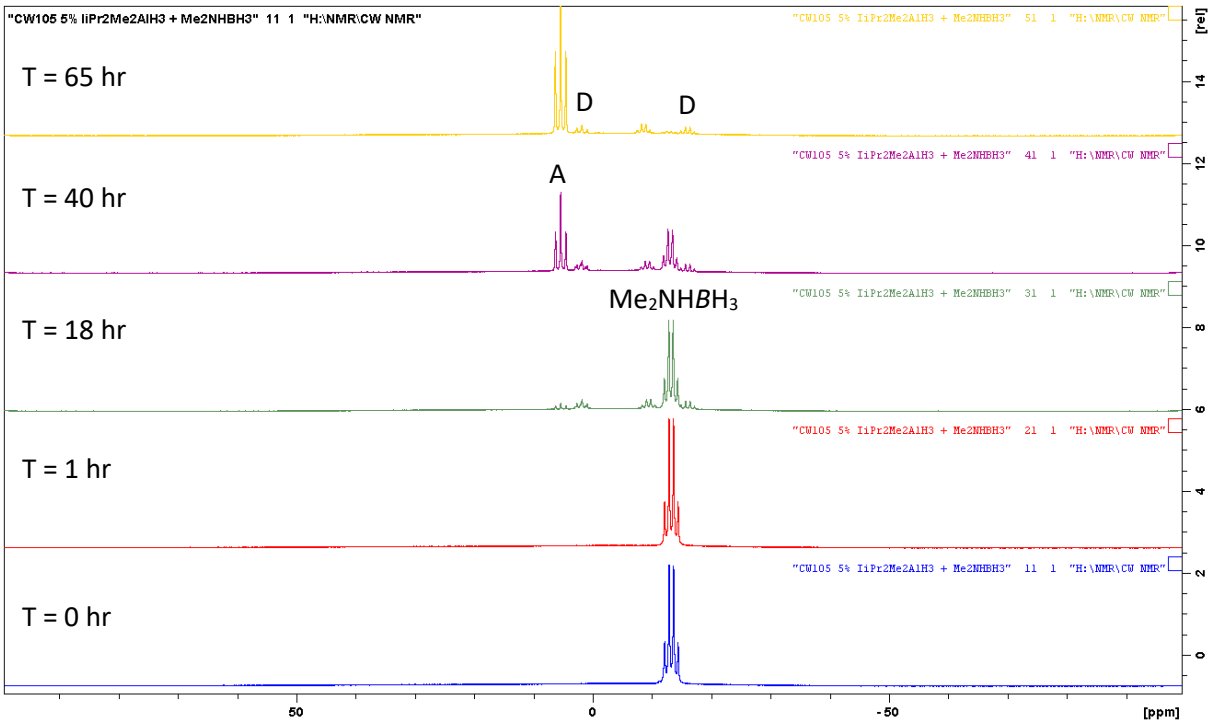

Figure S 10. Stacked ^{11}B NMR spectra for 5 mol% **5** with Me_2NBH_3 at 50 °C in C_6D_6

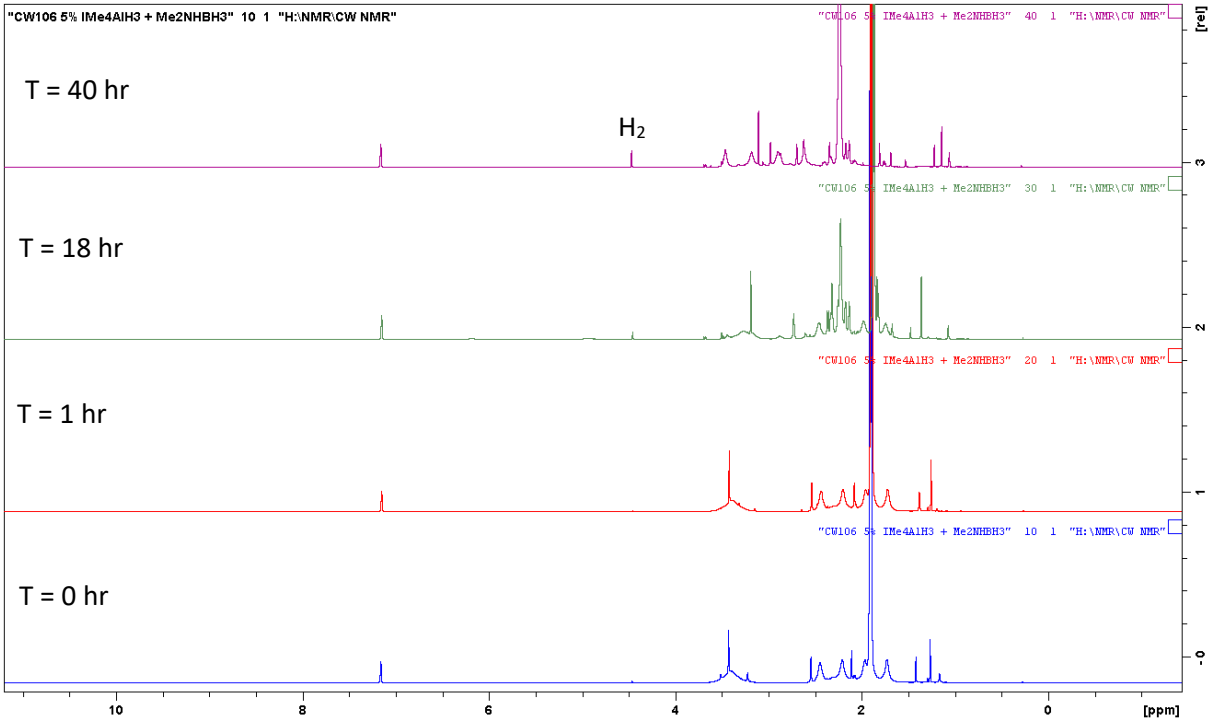

Figure S 11. Stacked ^{1}H NMR spectra for 5 mol% **6** with Me_2NBH_3 at 50 °C in C_6D_6

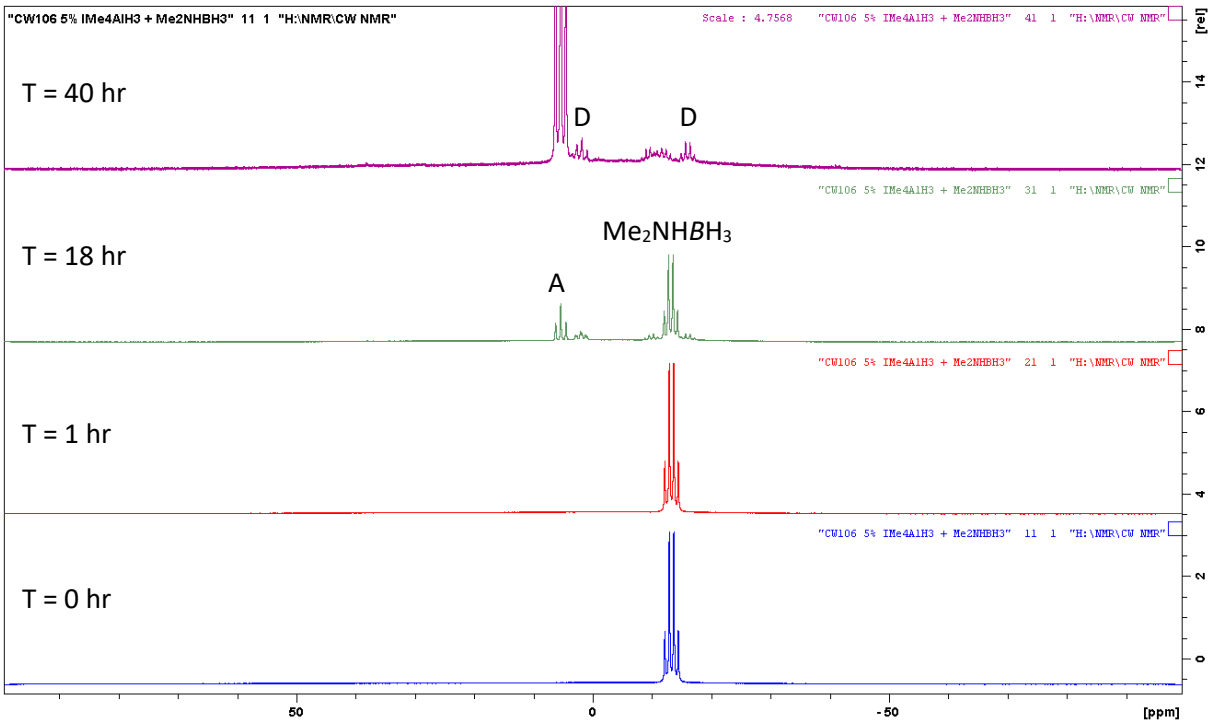

Figure S 12. Stacked ^{11}B NMR spectra for 5 mol% **6** with Me_2NBH_3 at 50 °C in C_6D_6

2. Mechanistic Studies

2.1. NHI Mechanism

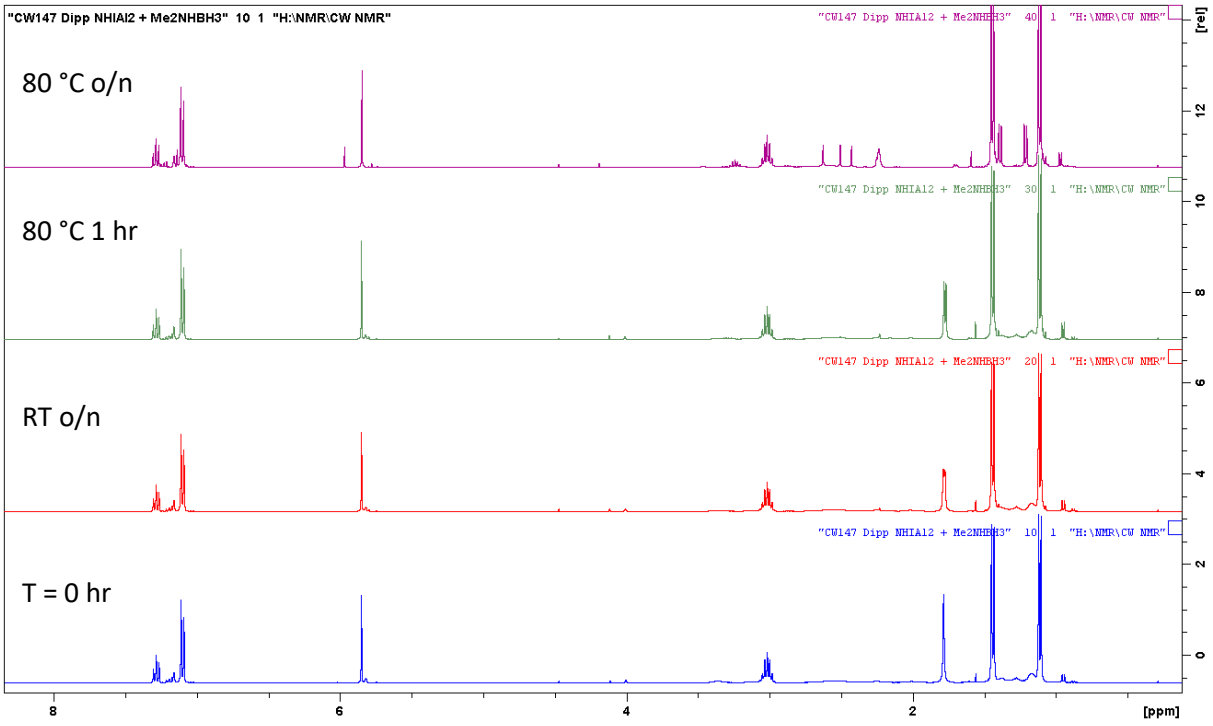

Figure S 13. Stacked ^{1}H NMR spectra for stoichiometric reaction between **1** and Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. At 80 °C o/n resulted in consumption of Me_2NHBH_3 with minor formation of compound **7.**

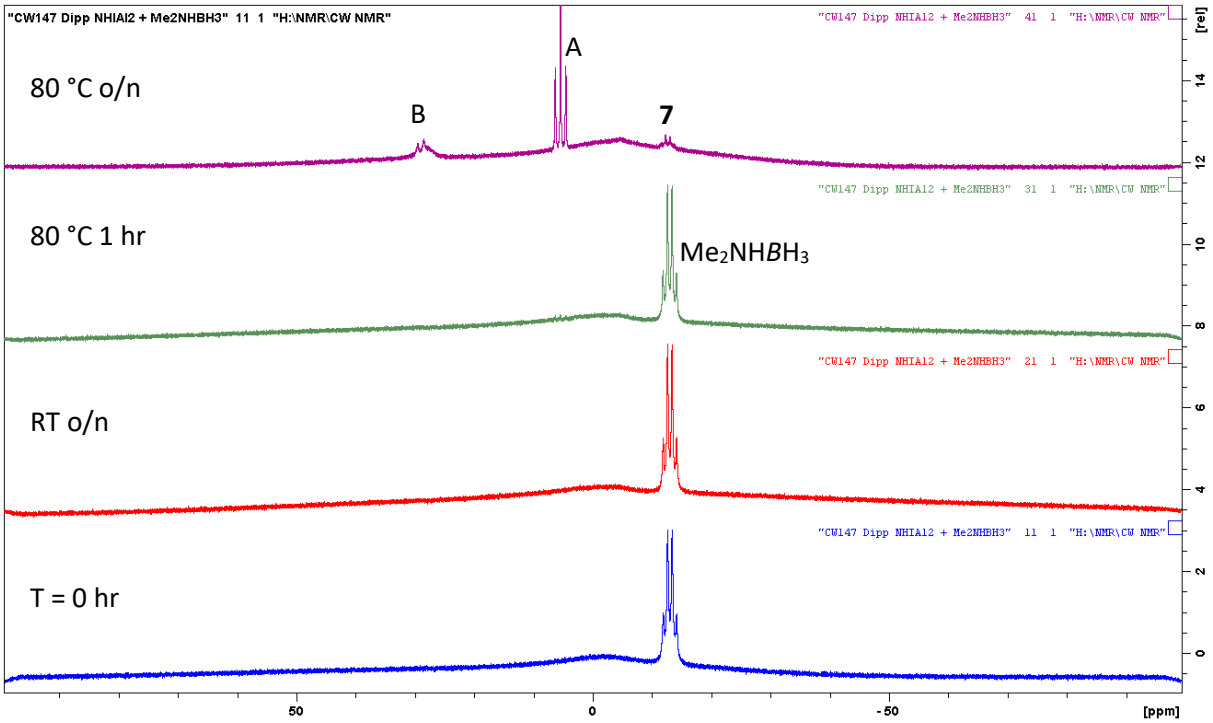

Figure S 14. Stacked ^{11}B NMR spectra for stoichiometric reaction between **1** and Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. At 80 °C o/n resulted in consumption of Me_2NHBH_3 with minor formation of compound **7.**

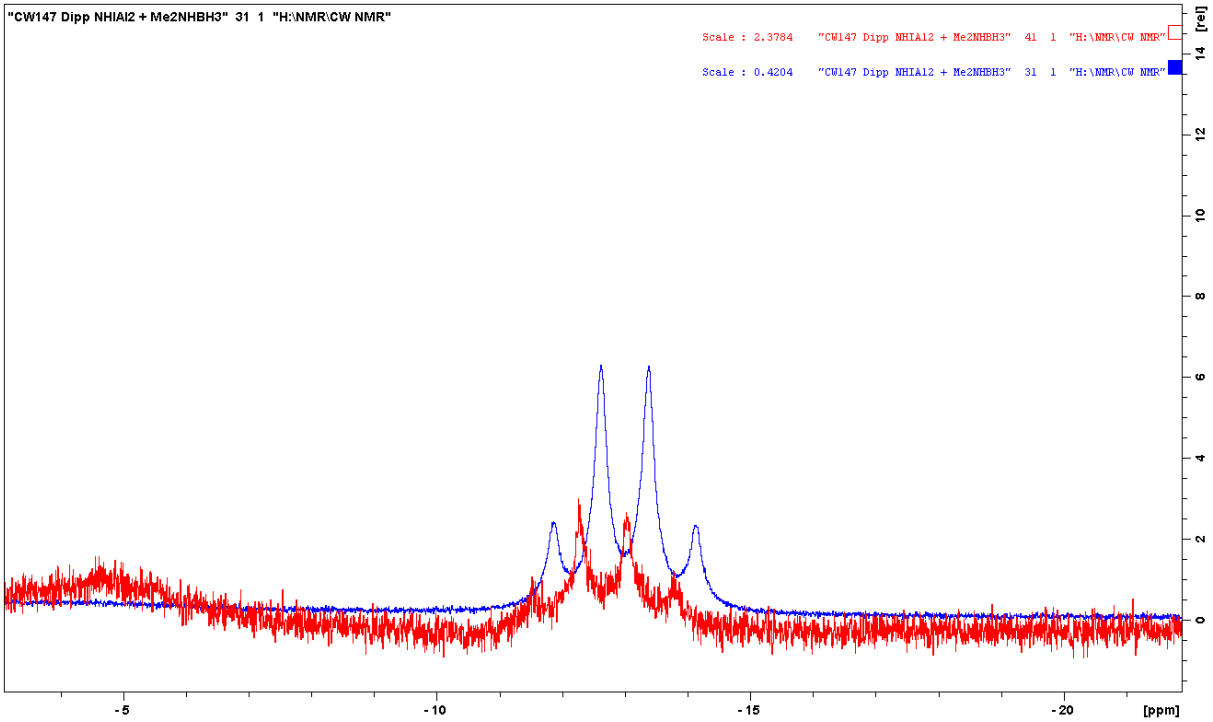

Figure S 15. Overlay of ^{11}B spectra depicting minor shift in consumption of Me_2NHBH_3 (blue spectrum) to formation of compound **7** (red spectrum).

2.2. NHC Mechanism

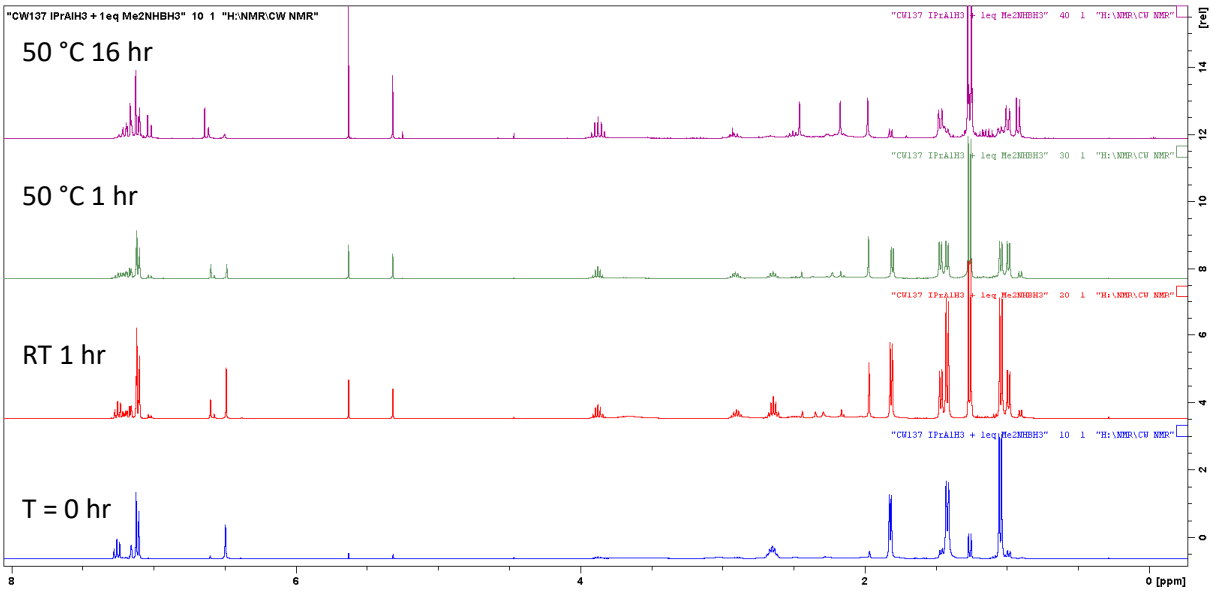

Figure S 16. Stacked ^1H NMR spectra for stoichiometric reaction between **3** and Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. At 50 °C o/n resulted in consumption of Me_2NHBH_3 with formation of compound **9.**

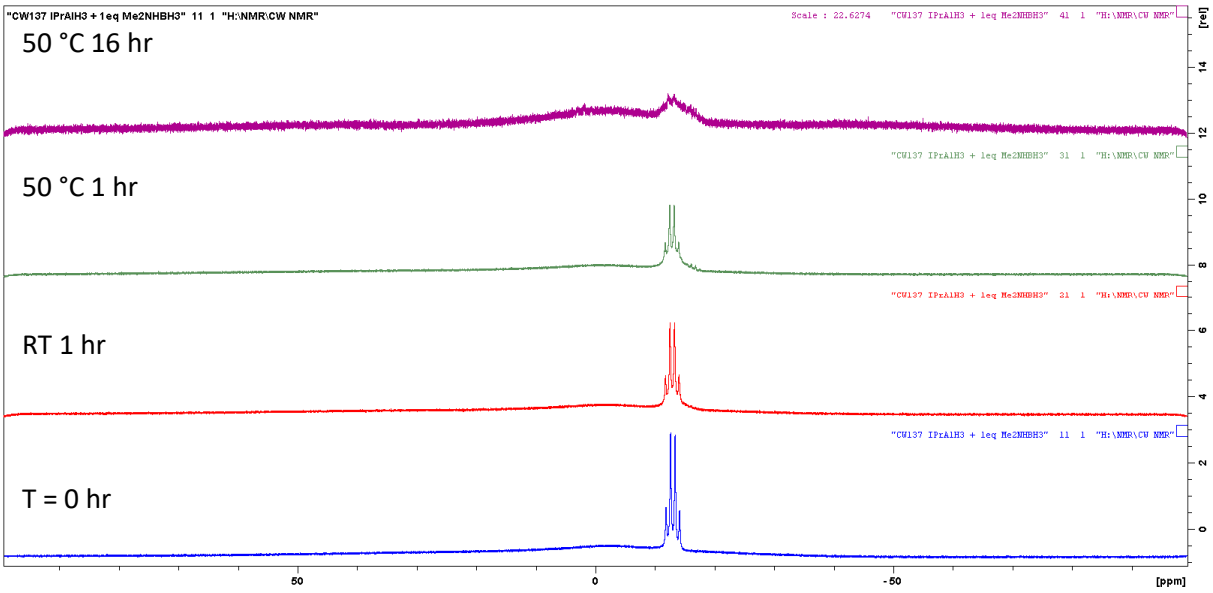

Figure S 17. Stacked ^{11}B NMR spectra for stoichiometric reaction between **3** and Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. At 50 °C o/n resulted in consumption of Me_2NHBH_3 with formation of compound **9.**

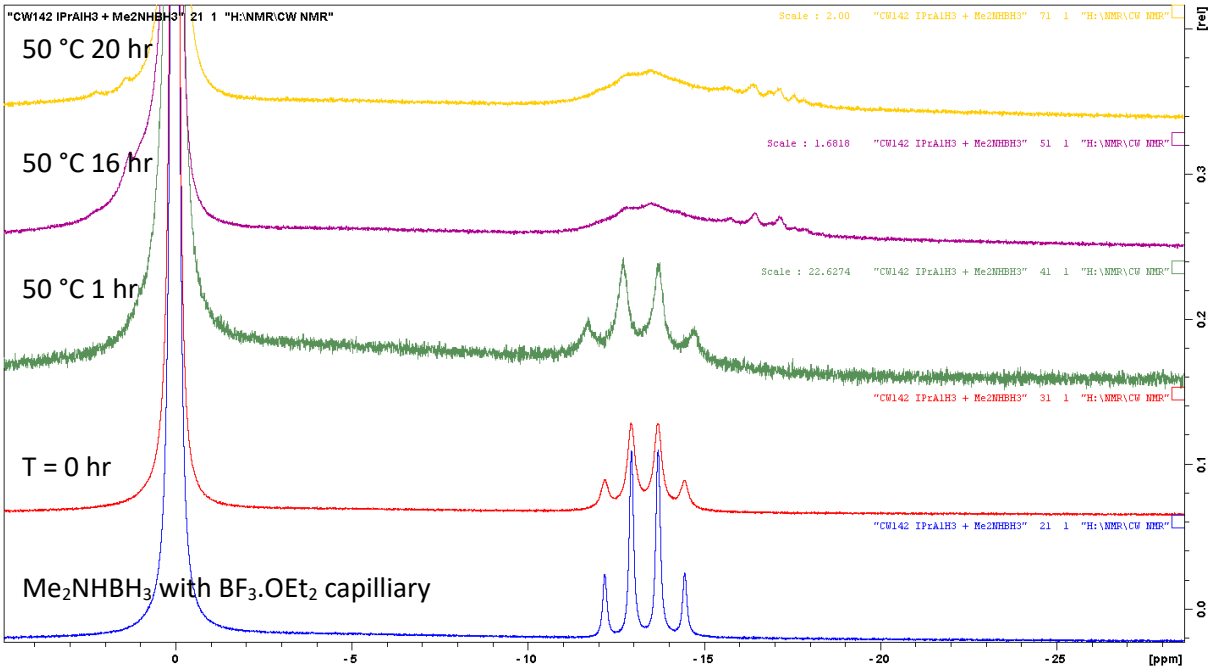

Figure S 18. Stacked ^{11}B NMR spectra (0 to -25 ppm, with BF_3OEt_2) for stoichiometric reaction between **3** and Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. 50 °C 1hr resulted in formation of compound **8** additional heating resulted formation of compound **9.**

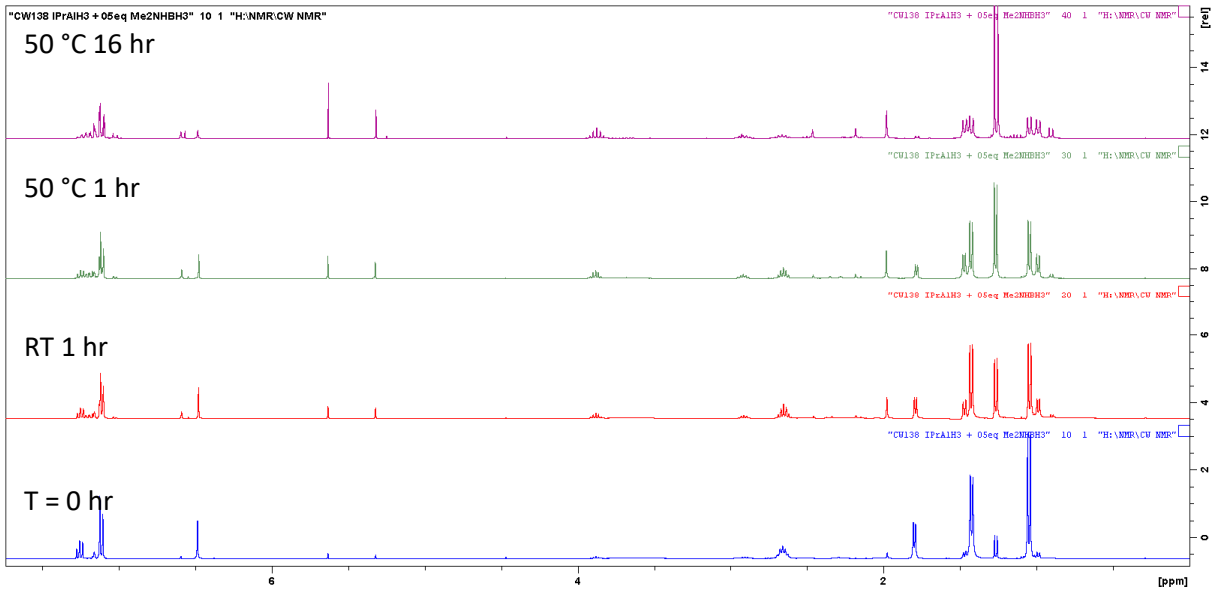

Figure S 19. Stacked ^{1}H NMR spectra for stoichiometric reaction between **3** and 0.5 eq. of Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. At 50 °C o/n resulted in consumption of Me_2NHBH_3 with formation of compound **9.**

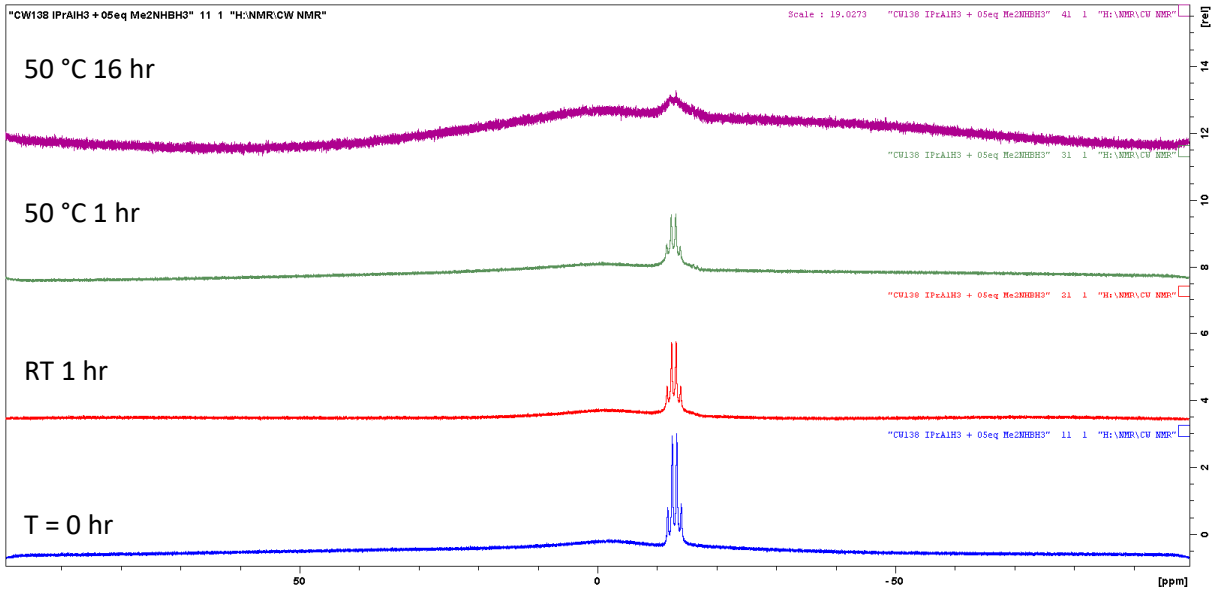

Figure S 20. Stacked ^{11}B NMR spectra for stoichiometric reaction between **3** and 0.5 eq. of Me_2NHBH_3 in C_6D_6. No reaction occurred at room temperature. At 50 °C o/n resulted in consumption of Me_2NHBH_3 with formation of compound **9.**

3. Data for compounds 8^{iPr} and 9

3.1 Compound 8^{iPr}

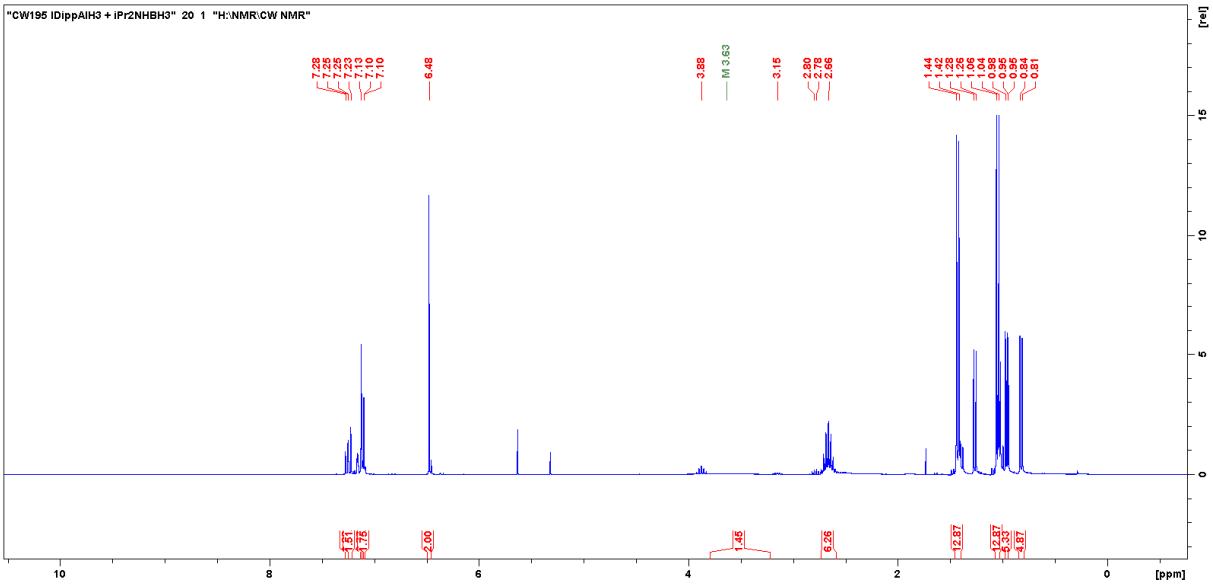

Figure S 21. ^{1}H NMR spectrum for compound $\mathbf{8^{iPr}}$ in C_6D_6. Small amount of $IDippH_2$ present after recrystallisation and additional washes.

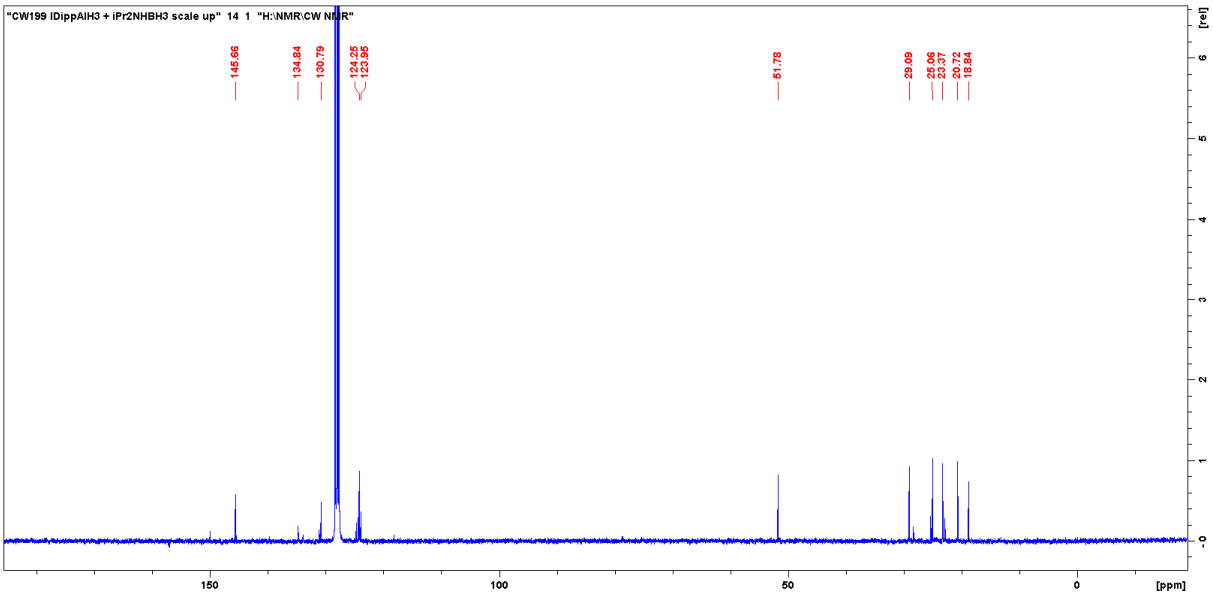

Figure S 22. ^{13}C NMR spectrum for compound $\mathbf{8^{iPr}}$ in C_6D_6. Small amount of $IDippH_2$ present after recrystallisation and additional washes.

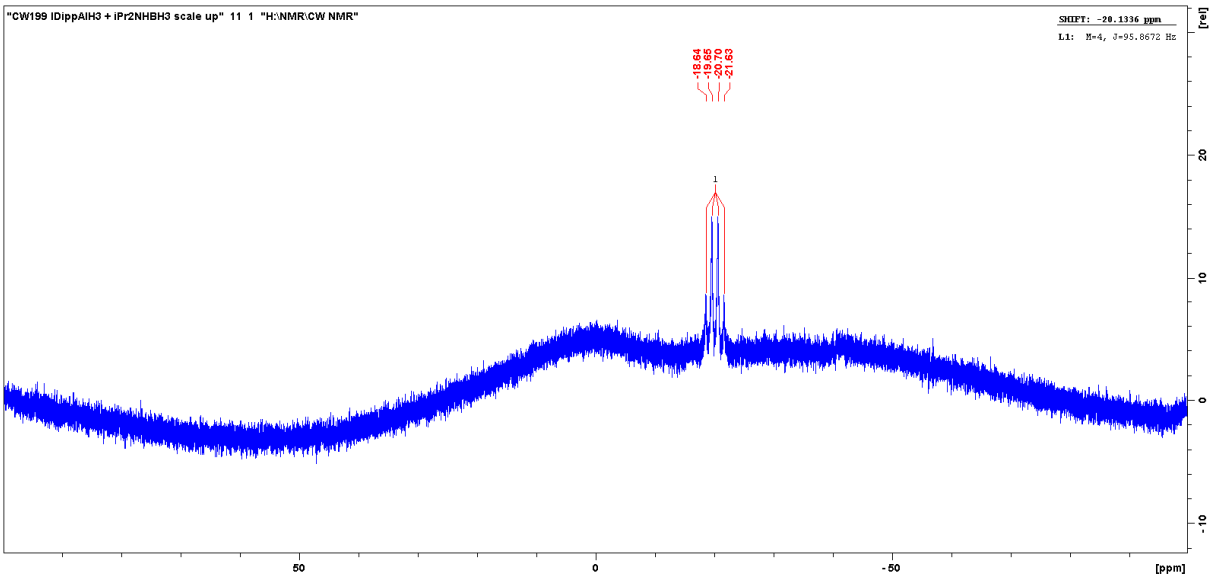

Figure S 23. ^{11}B NMR spectrum for compound **8^{iPr}** in C_6D_6. Small amount of IDippH$_2$ present after recrystallisation and additional washes.

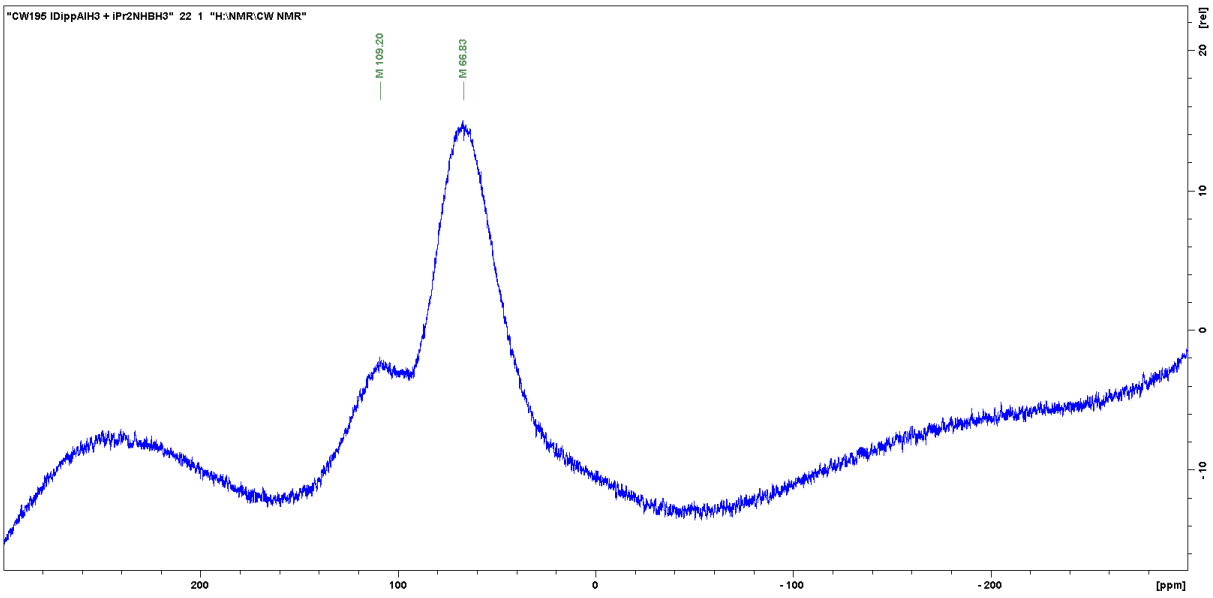

Figure S 24. ^{27}Al NMR spectrum for compound **8^{iPr}** in C_6D_6. Small amount of IDippH$_2$ present after recrystallisation and additional washes.

3.2 Compound ***9***

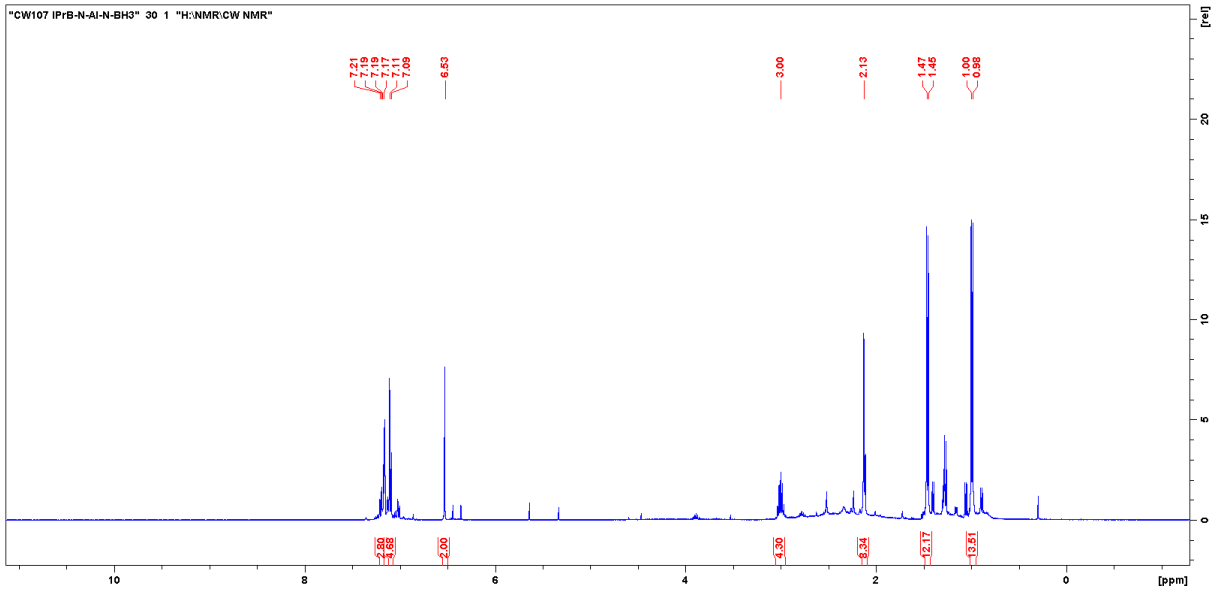

Figure S 25. ^{1}H NMR spectrum for compound **9** in C_6D_6. Small amount of $IDippH_2$ present after recrystallisation and additional washes.

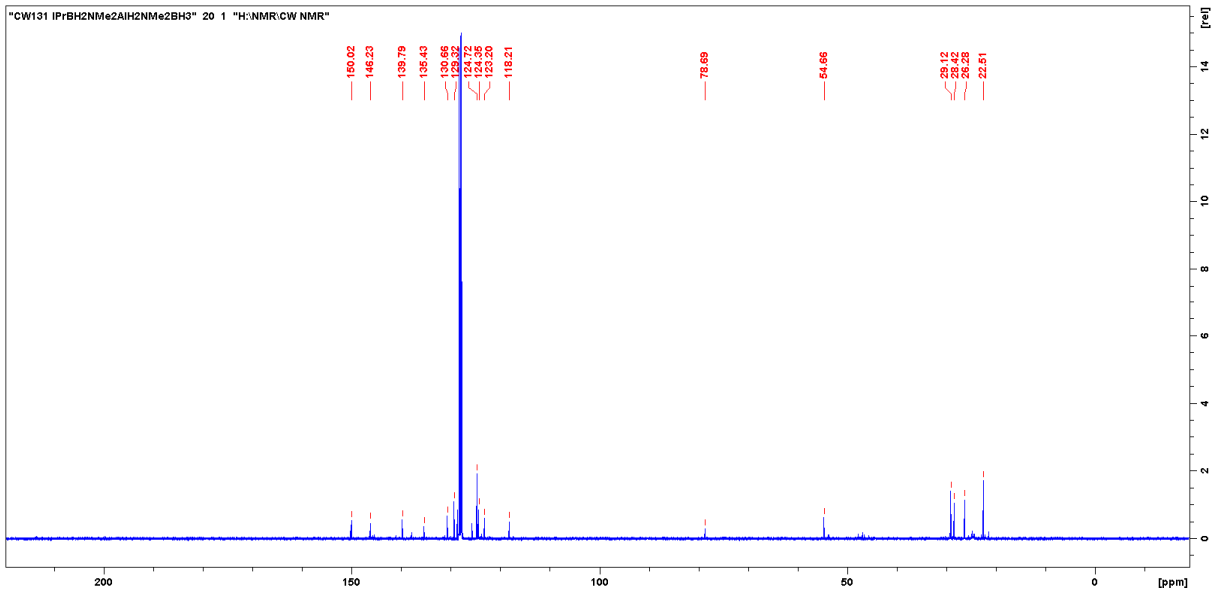

Figure S 26. $^{13}C\{^{1}H\}$ NMR spectrum for compound **9** in C_6D_6. Small amount of $IDippH_2$ present after recrystallisation and additional washes.

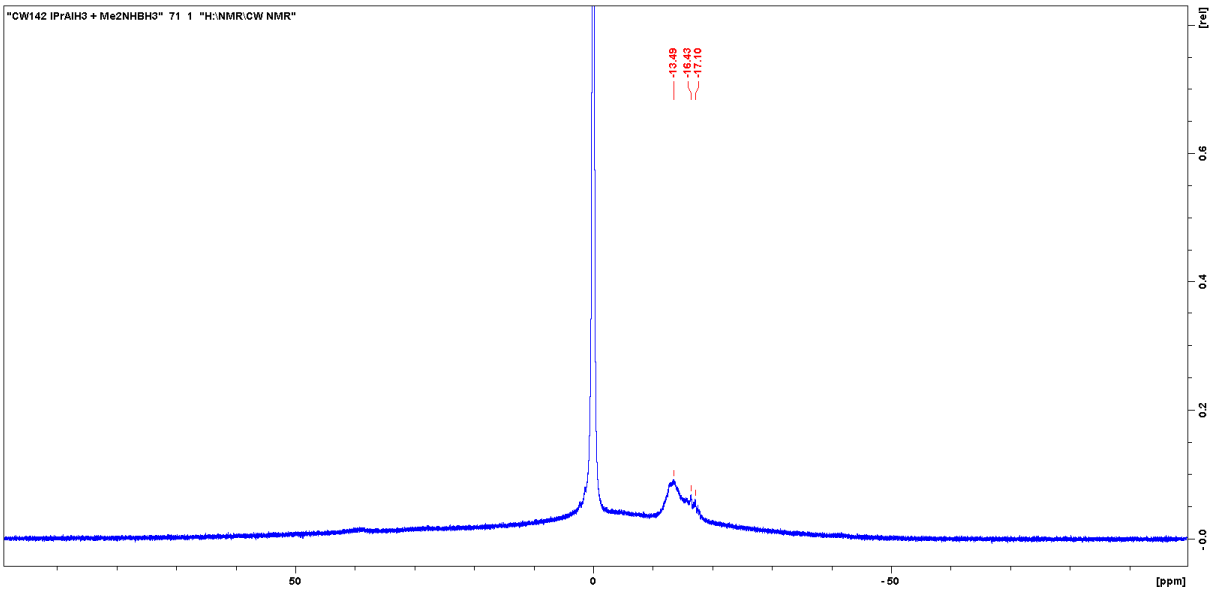

Figure S 27. ^{11}B NMR spectrum for compound **9** in C_6D_6, with $BF_3.OEt_2$ capillary (0.0 ppm).

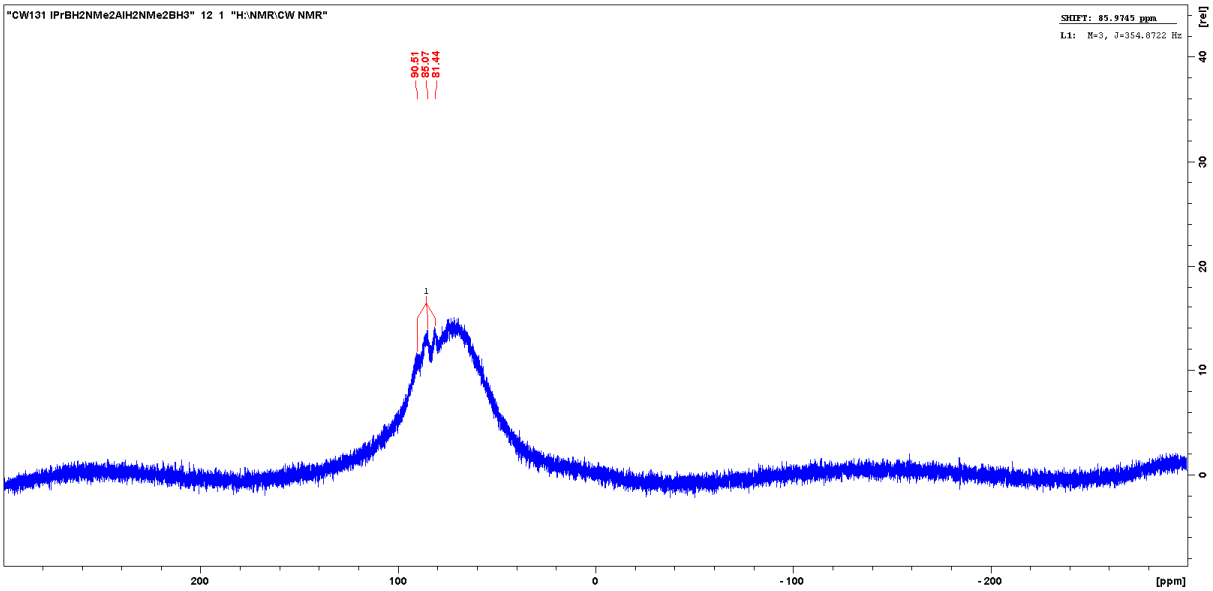

Figure S 28. ^{27}Al NMR spectrum for compound **9** in C_6D_6.

4. X-ray Data

General Information

Single crystal diffraction data were recorded on a Bruker D8 Venture system equipped with a Helios optic monochromator and a Mo TXS rotating anode (λ = 0.71073 Å). The data collection was performed by using the APEX III software package[S1] on single crystals coated with the perfluorinated ether Fomblin ® Y. The single crystal was picked on a micro sampler, transferred to the diffractometer and measured frozen under a stream of 100K nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[S2] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the APEX III software in conjunction with SHELXL-2014[S3] and SHELXLE.[S4] H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of

0.99 and 0.95 Å, respectively, and Uiso(H) = 1.2·Ueq(C); except for HB11, HB12, HA1, HA2, HB21, HB22, HB23, which could be located in the difference Fourier maps and were allowed to refine freely. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL weighting scheme.[S5] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S6] A split layer refinement was used for disordered groups and SIMU and DELU restraints were employed to stabilize the refinement of the layers. The images of the crystal structures were generated by Mercury.[S7] The CCDC number CCDC-1936588 (**9**) contains the supplementary crystallographic data for the structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

X-Ray Crystallographic Table

Table S 2. Crystal data and structural refinement parameters for compound **9**.

Compound	**9**
Molecular formula	**C31 H55 Al B2 N4**
Molecular weight	532.39
Temperature (K)	100
Wavelength (Å)	0.71073
Space group	P 1 21/c 1
a (Å)	10.135(9)
b (Å)	18.687(14)
c (Å)	19.155(15)
α °	90
β °	104.73(2)
γ °	90
Volume (Å^3)	3509(5)
Z	4
D_C (g cm^{-3})	1.008
μ (mm^{-1})	0.081
Index ranges	-12<=h<=12, -22<=k<=22, -23<=l<=23
Reflections collected	87849
Unique reflections	6558
Parameter varied	443
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.059
R_{int}	0.1319
R_1	0.0574
wR_2	0.1194
Largest diff. peak and hole (eÅ^3)	0.265 and -0.321

4. References

S1 *APEX suite of crystallographic software*, APEX 3 version 2015.5-2; Bruker AXS Inc.: Madison, Wisconsin, USA, **2015**.

S2 *SAINT*, Version 7.56a and *SADABS* Version 2008/1; Bruker AXS Inc.: Madison, Wisconsin, USA, **2008**.

S3 Sheldrick, G. M. *SHELXL-2014*, University of Göttingen, Göttingen, Germany, **2014**.

S4 Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Cryst.* **2011**, *44*, 1281-1284.

S5 Sheldrick, G. M. *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1998**.

S6 Wilson, A. J. C. *International Tables for Crystallography*, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199); Kluwer Academic Publishers: Dordrecht, The Netherlands, **1992**.

S7 Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.* **2008**, *41*, 466-470.