Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Deuteration of boranes: catalysed versus *non-catalysed processes*

David J. Nelson, Jonathan B. Egbert and Steven P. Nolan*

EaStCHEM, School of Chemistry, University of St. Andrews, Purdie Building,

North Haugh, St. Andrews, Fife, KY16 9ST, Scotland.

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Experimental Details

General. All air-sensitive manipulations were carried out in an Argon-filled MBraun or Innovative Technologies glovebox; solutions of iridium complexes **8-10** are highly sensitive to oxygen. Dichloromethane-d_2 was dried overnight on calcium hydride, distilled, and degassed by freeze-pump-thaw cycles. Tetrahydrofuran-d_8 was dried overnight on sodium/benzophenone, distilled, and degassed by freeze-pump-thaw cycles. Tetrahydrofuran was obtained from an MBraun solvent purification system and degassed by purging with dry oxygen-free nitrogen. All boranes were obtained from commercial sources, except for BH_3·THF where both commercial and freshly-prepared borane was used (see the manuscript text). NMR analyses were conducted using either a Bruker AV300 (^{1}H obs. at 300 MHz; ^{11}B obs. at 96 MHz), a Bruker AV400 (^{1}H obs. at 400 MHz; ^{11}B obs. at 128 MHz) or a Bruker AV500 (^{2}H obs. at 77 MHz). Chemical shifts are in ppm, relative to tetramethylsilane (for ^{1}H), tetramethylsilane-d_{12} (for ^{2}H) or $Et_2O{\cdot}BF_3$ (for ^{11}B); coupling constants are in Hertz.

Deuteration Experiments. In a glovebox, the iridium complex (when used; typically *ca.* 1 to 2 mg) was weighed into a vial, and the borane (typically *ca.* 2 mmol) was weighed into a second vial. The borane was dissolved in solvent (0.5 mL CD_2Cl_2 for pinacolborane **2**, catecholborane **3**, and $Me_2S{\cdot}BH_3$ **5**; 2 mL THF for 9-BBN **4**; **1** was used as a 1 mol L^{-1} solution in THF; 2.5 mL CD_2Cl_2 for morpholine-borane **6** and *N*-methylmorpholine-borane **7**) and added to the iridium complex. The solution was then transferred to a *ca.* 100 mL flask fitted with valve, containing a stirrer bar. The valve was closed, the flask was removed from the glovebox and then connected to a Schlenk line. The solution was frozen and the flask was placed under vacuum. The flask was filled with D_2 and evacuated twice, before filling with D_2 to *ca.* 10 psi. The reaction was stirred for the specified time. Once this time had elapsed, the reactions of **2**, **3**, **5**, **6** and **7** were transferred to NMR tubes and analysed by ^{1}H and ^{11}B NMR spectroscopy. For **4**, the solvent was stripped under vacuum and a portion of the solid was dissolved in THF-d_8 and analysed by ^{1}H and ^{11}B NMR spectroscopy. For these reactions, the conversion was quantified by integrating the B-H peak *versus* other peaks on the ^{1}H NMR spectrum. For **1**, a portion of the reaction was transferred to an NMR tube, a small quantity (*ca.* 100 μL) of dry CD_2Cl_2 or THF-d_8 was added, and the sample was analysed by ^{1}H and ^{11}B NMR spectroscopy. Conversion was estimated in this case by inspection of the ^{11}B NMR spectrum; BH_3 exhibits a distinctive quartet resonance, while BD_3 manifests as a single broad signal (see spectra).

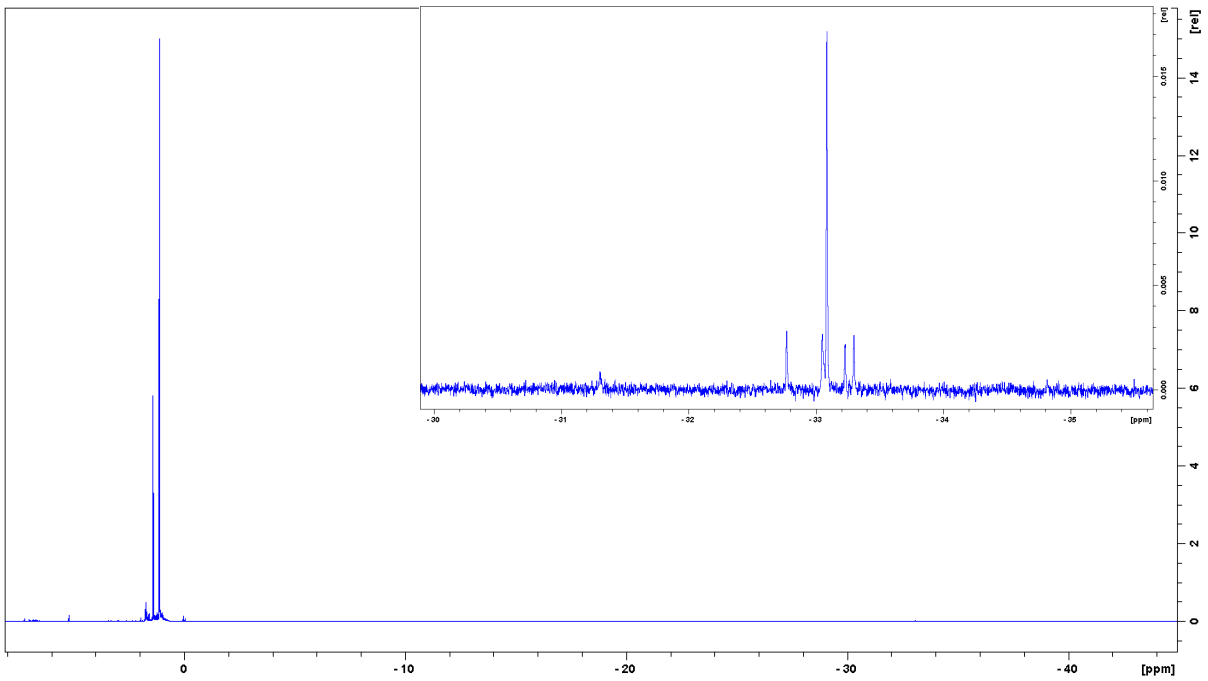
Sample ^{1}H and ^{11}B NMR Spectra

Where sample spectra are integrated, ½ of the B-H signal is often considered to avoid e.g. solvent peaks. In these cases, this is taken to represent 0.5 H and so the quoted conversions in the manuscript are correct.

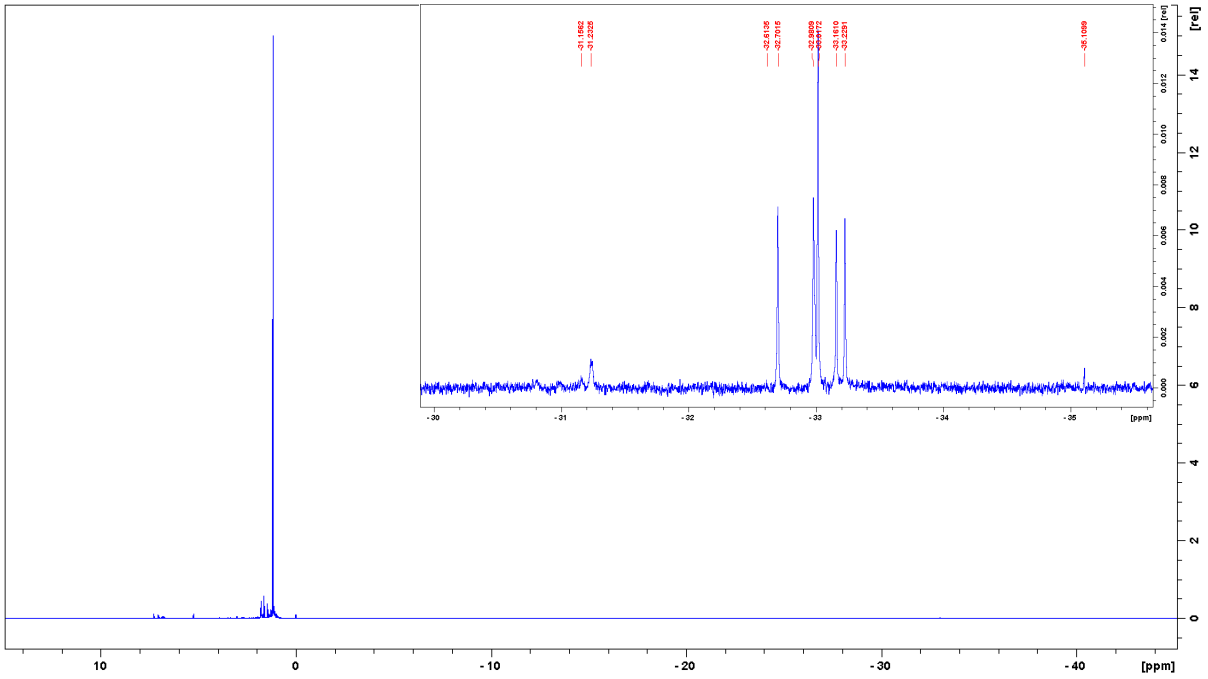
Pseudostoichiometric reactions

Ir-complex and *ca.* 3-5 equiv. of HBpin combined in CD_2Cl_2 and transferred to a J. Young NMR tube for analysis, in order to probe for interesting new complexes.

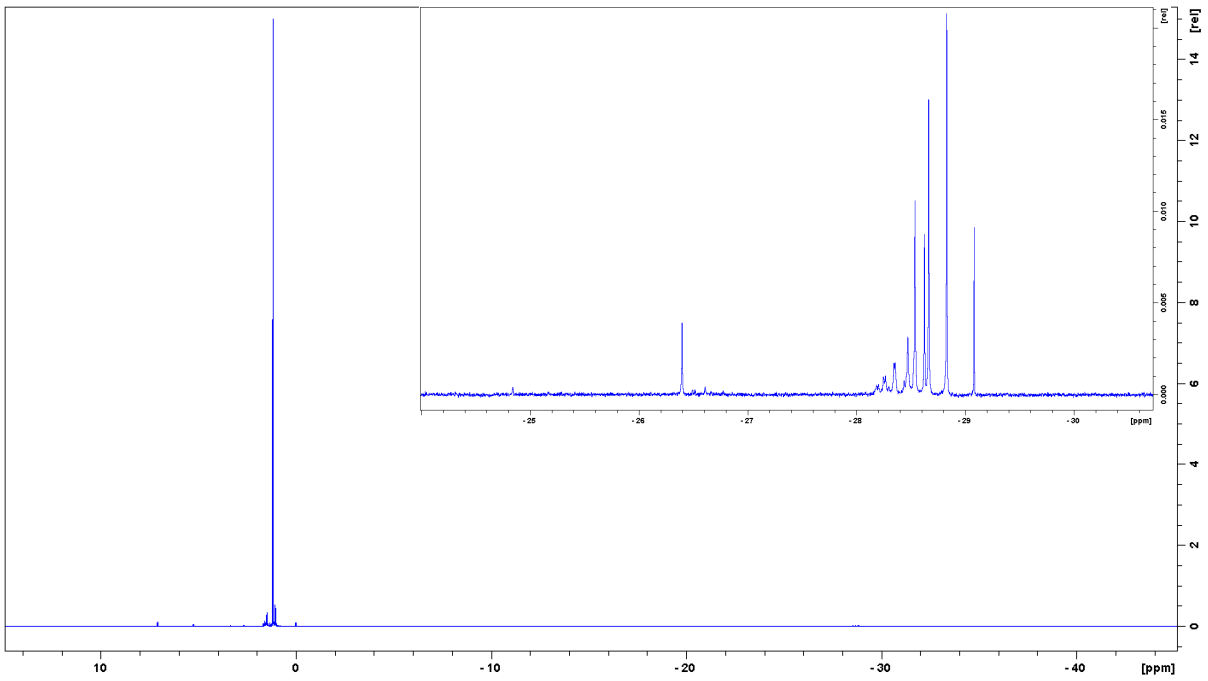
8 + HBpin



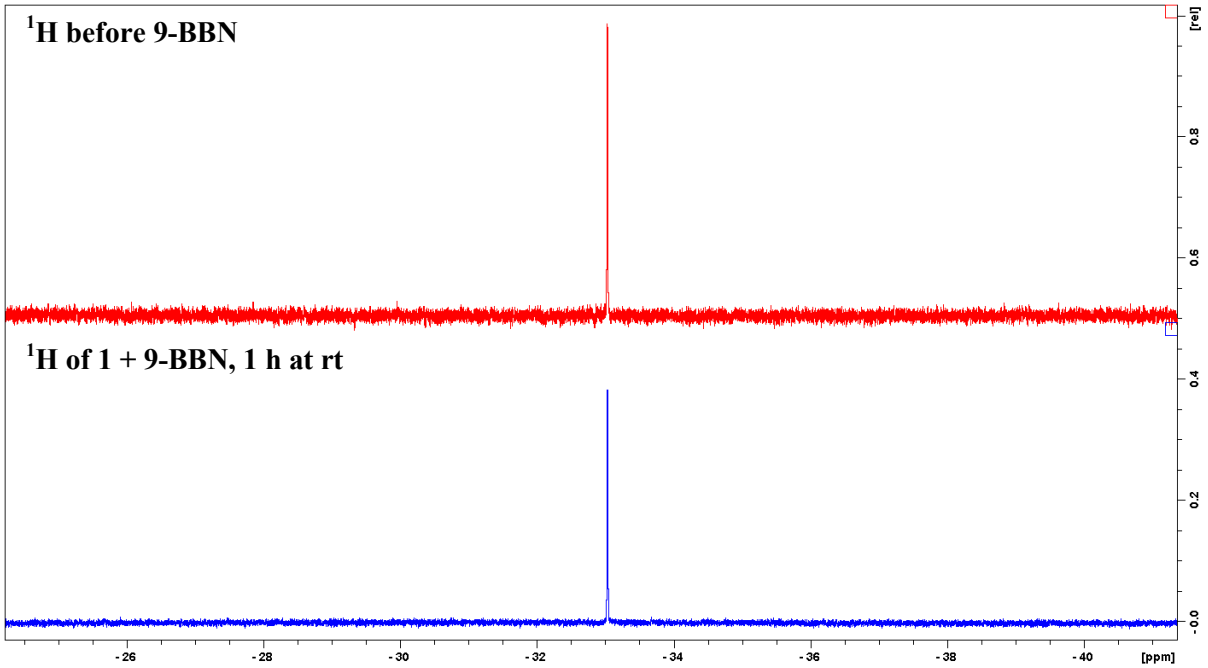
9 + HBpin



10 + HBpin

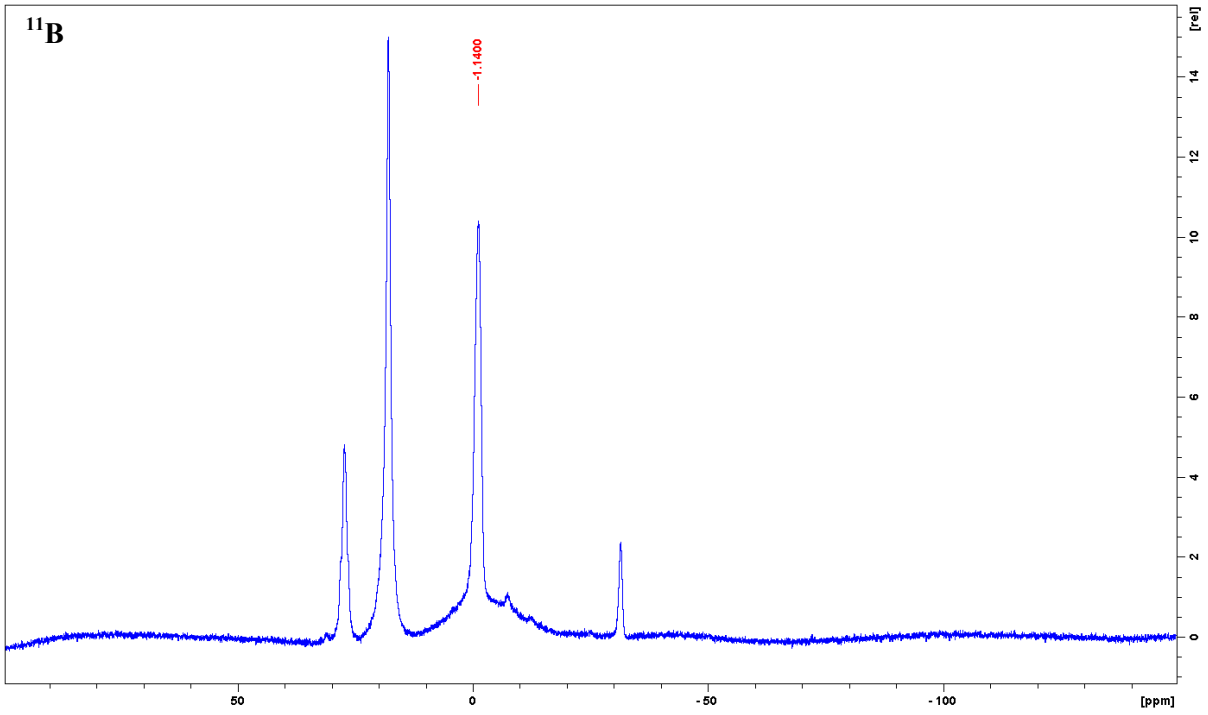


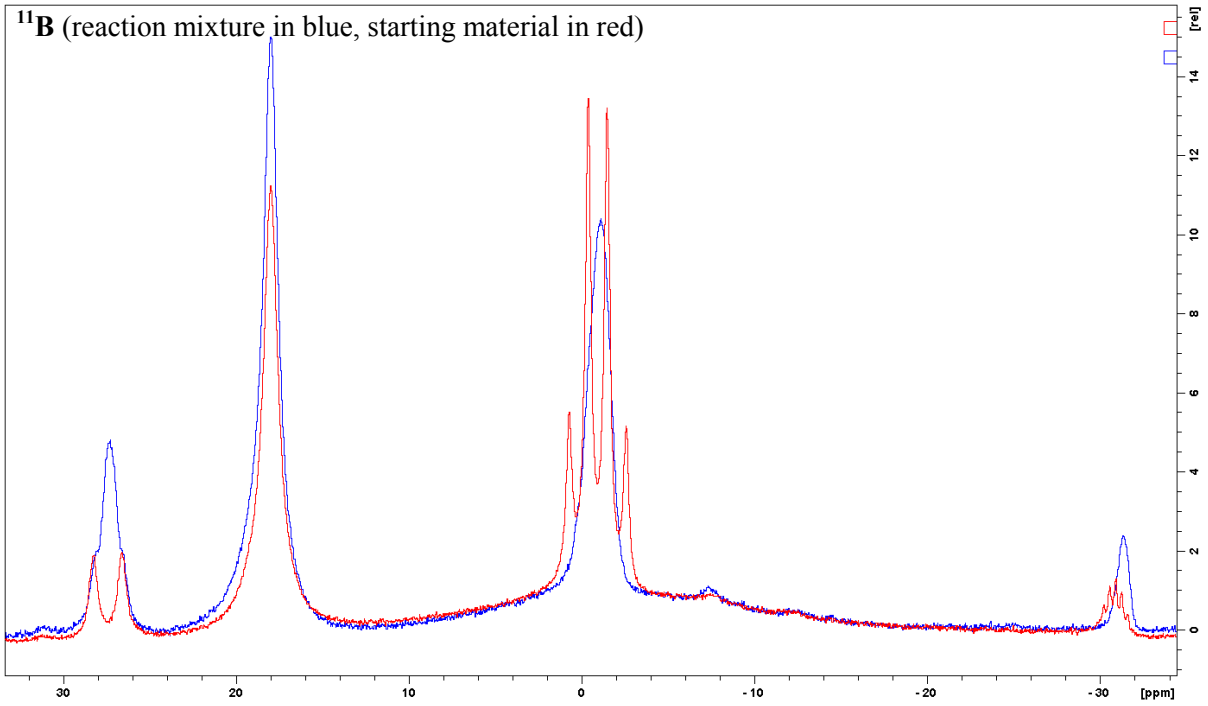
8 + 9-BBN



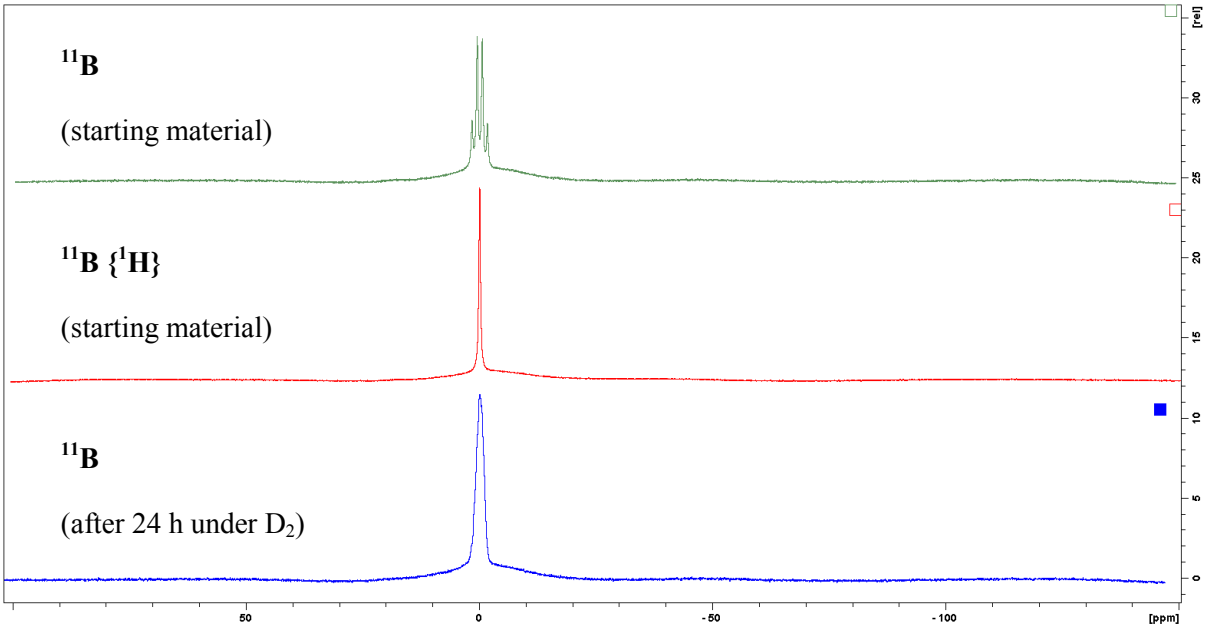
Preparative Reactions: Sample spectra from reactions carried out under D_2 in order to show that reaction has occurred.

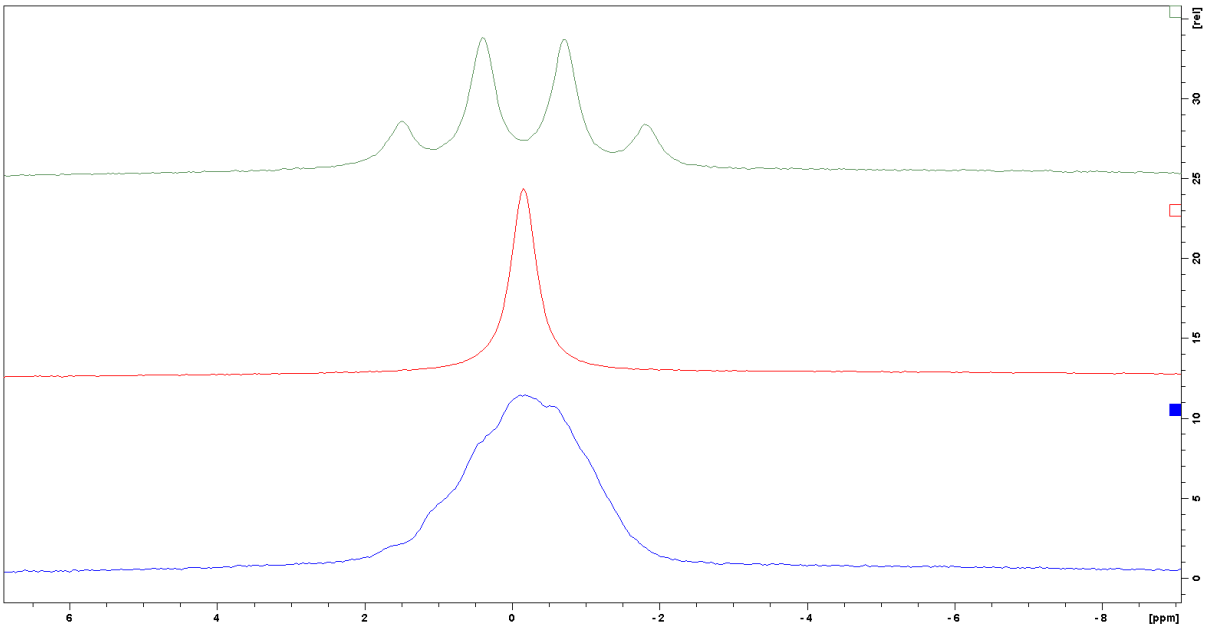
$THF.BH_3$ 1-d_3 (commercial material in THF) NB: Extra peaks are also present in a new, untouched bottle of commercial $THF\text{-}BH_3$, stored carefully in a glovebox at -40°C and only opened in an Argon-filled glovebox; one can be ascribed to B_2H_6.



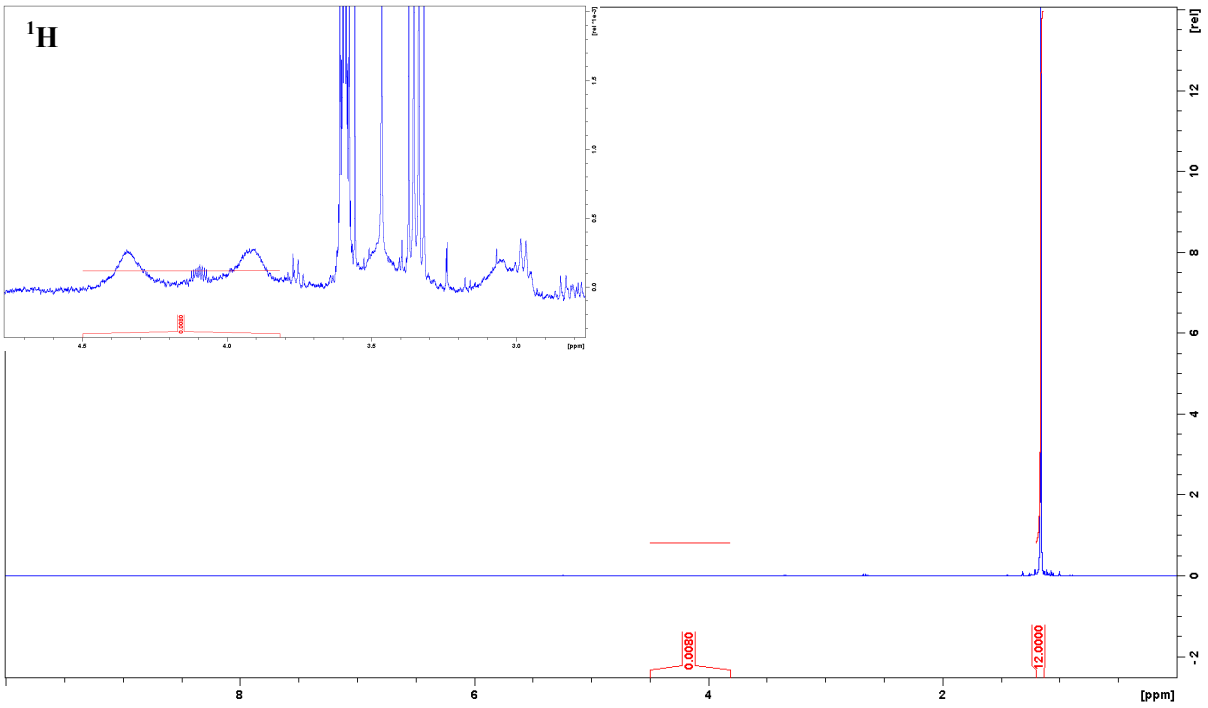


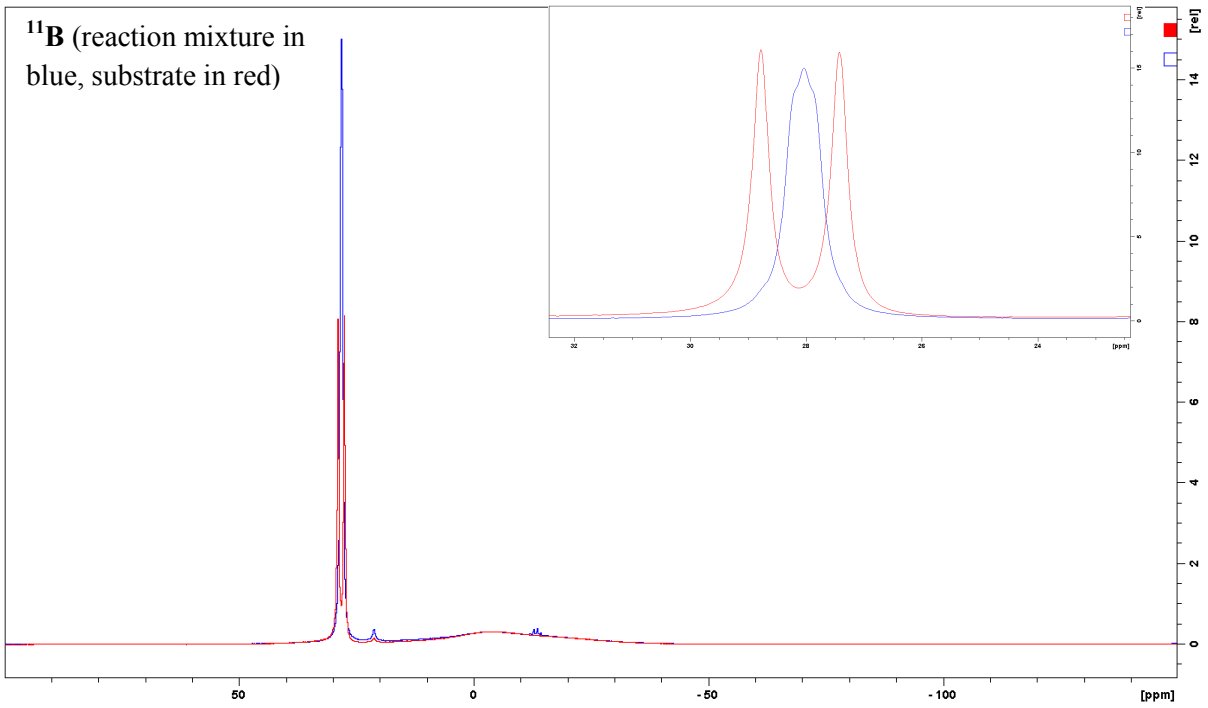
THF.BH_3 1-d_3 (freshly prepared in THF) A solution of BH_3·THF in THF was prepared according to the procedure of Brown (*Inorganic Chemistry*, 2000, **39**, 1795) and exposed to D_2 under the same reaction conditions as commercial material. ^{11}B NMR analysis confirmed that only BH_3 was present in the starting material; $^{11}B\{^1H\}$ analysis showed that the quartet structure arose from coupling to protons.

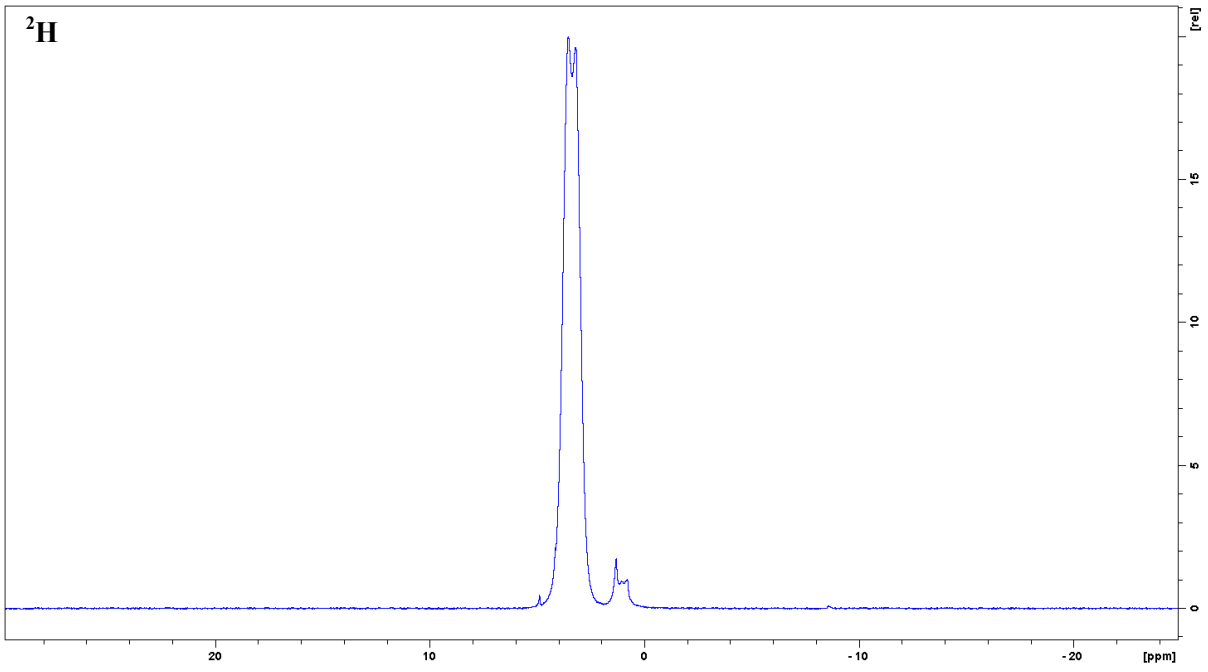




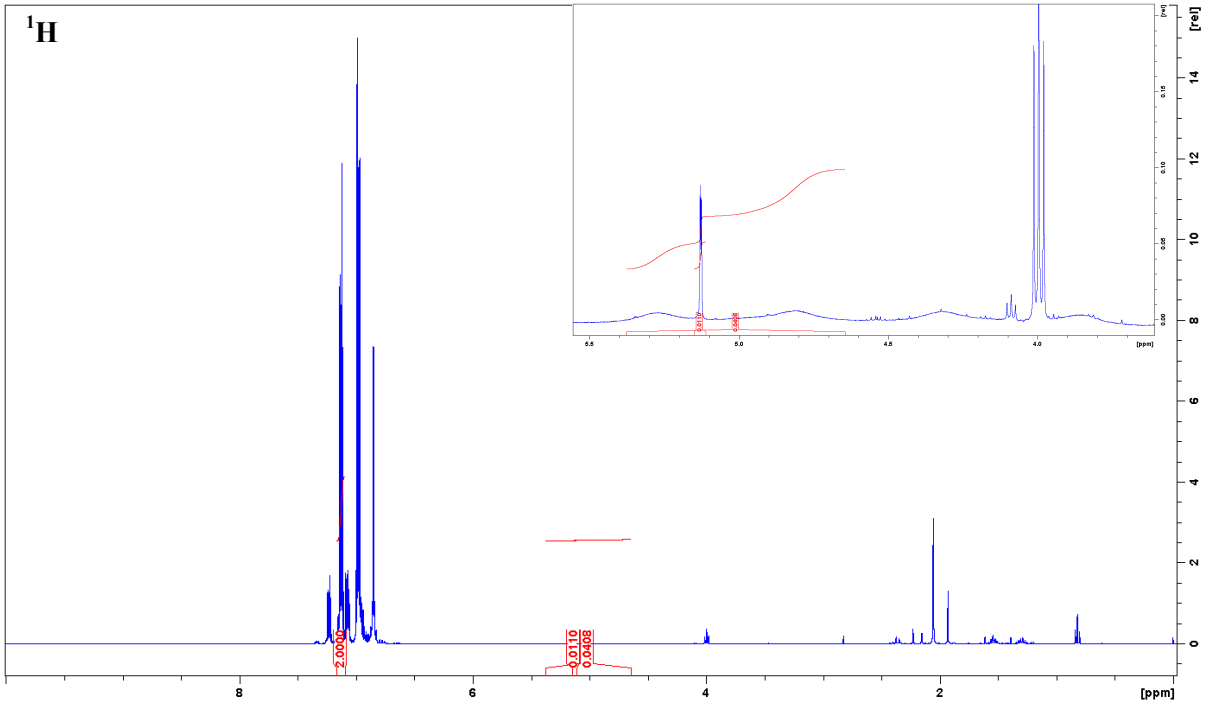
Pinacolborane 2-d_1 (with Ir, in CD_2Cl_2)

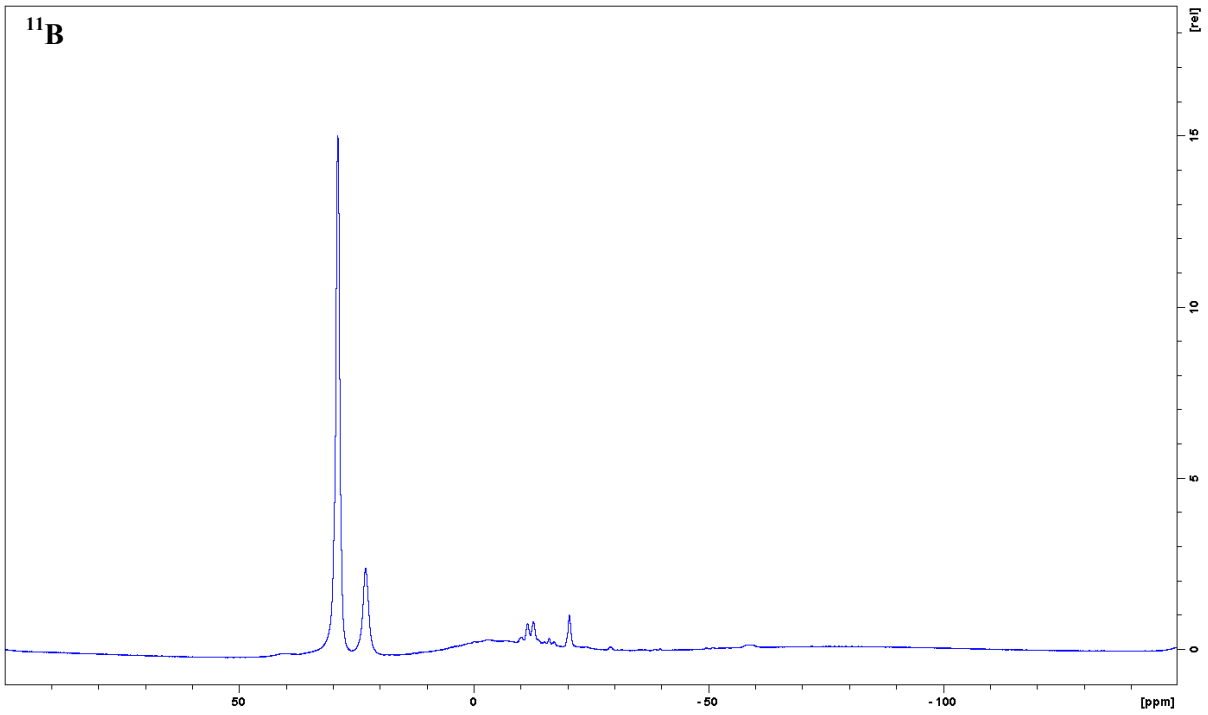




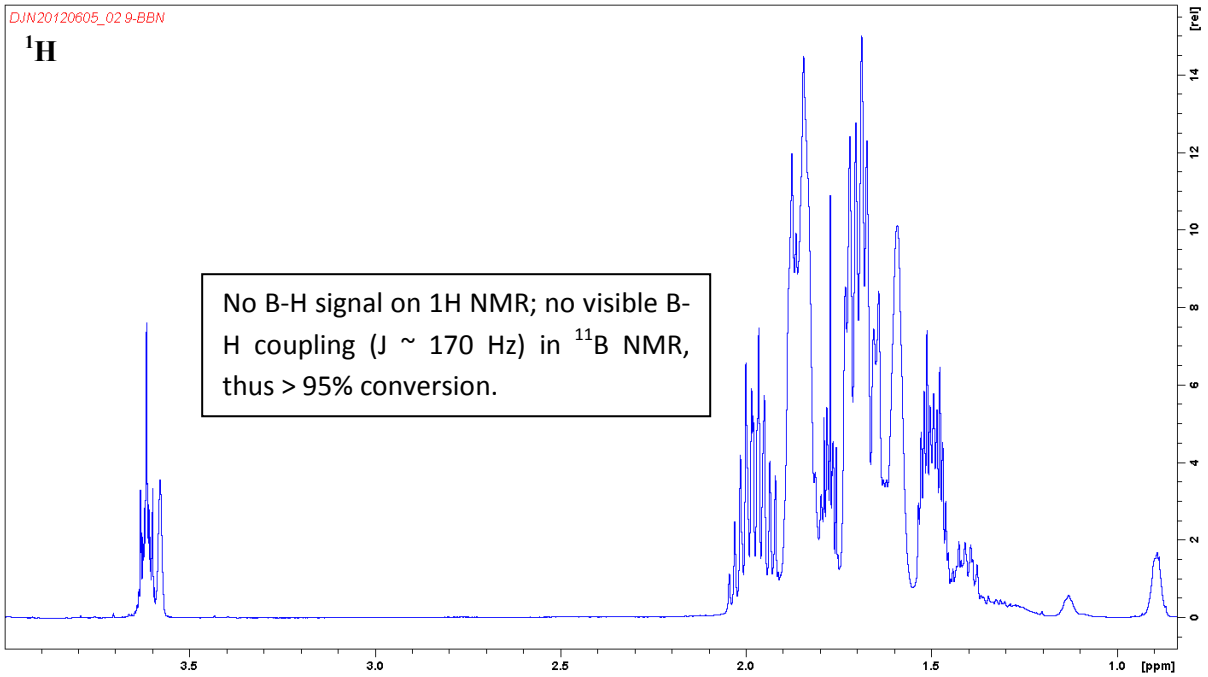


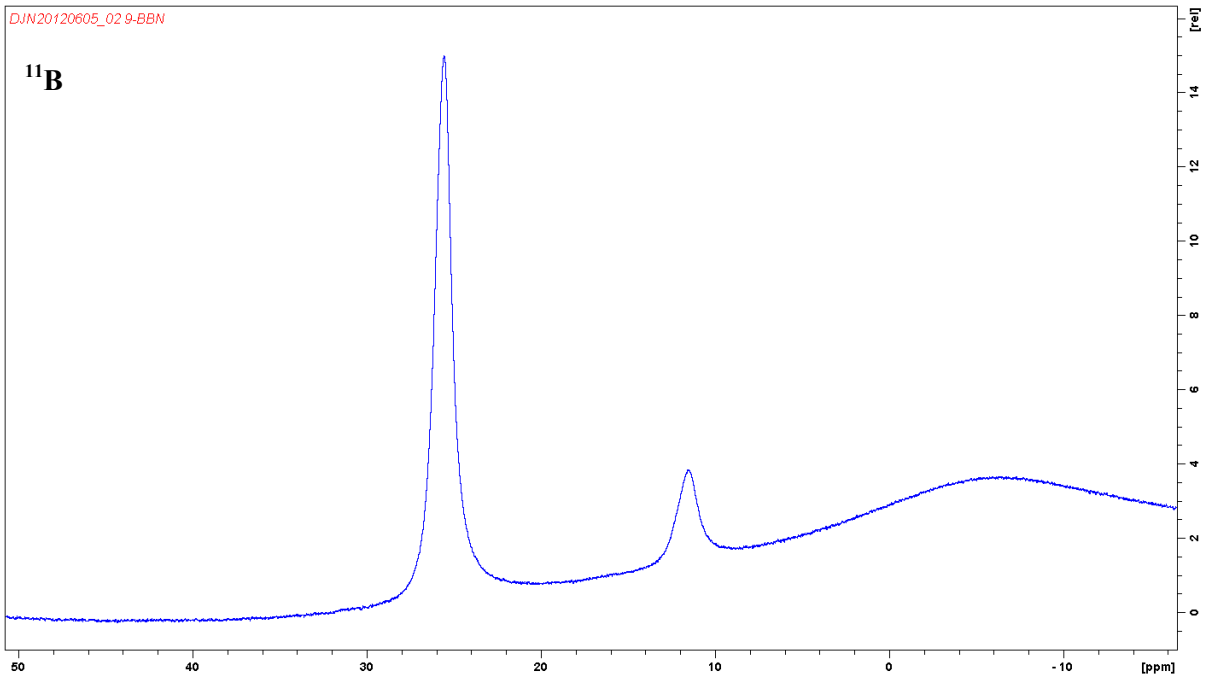
Catecholborane 3-d_1 (with Ir, in CD_2Cl_2)



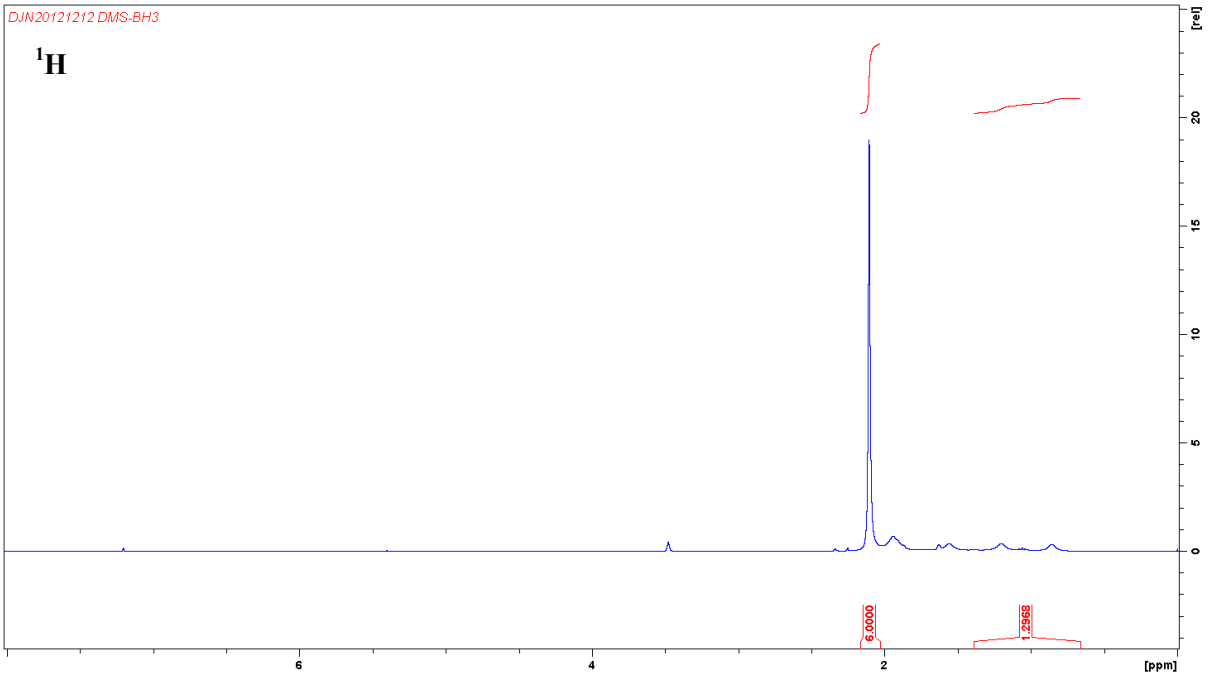


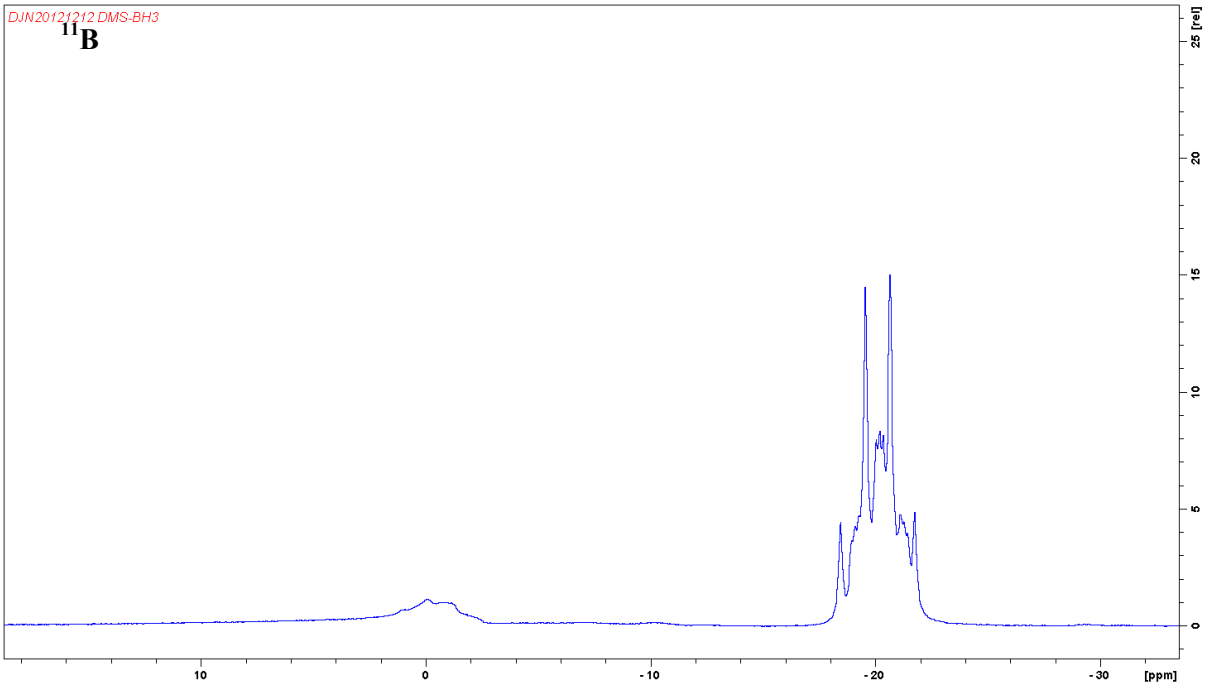
9-BBN 4-d_1 (in THF)



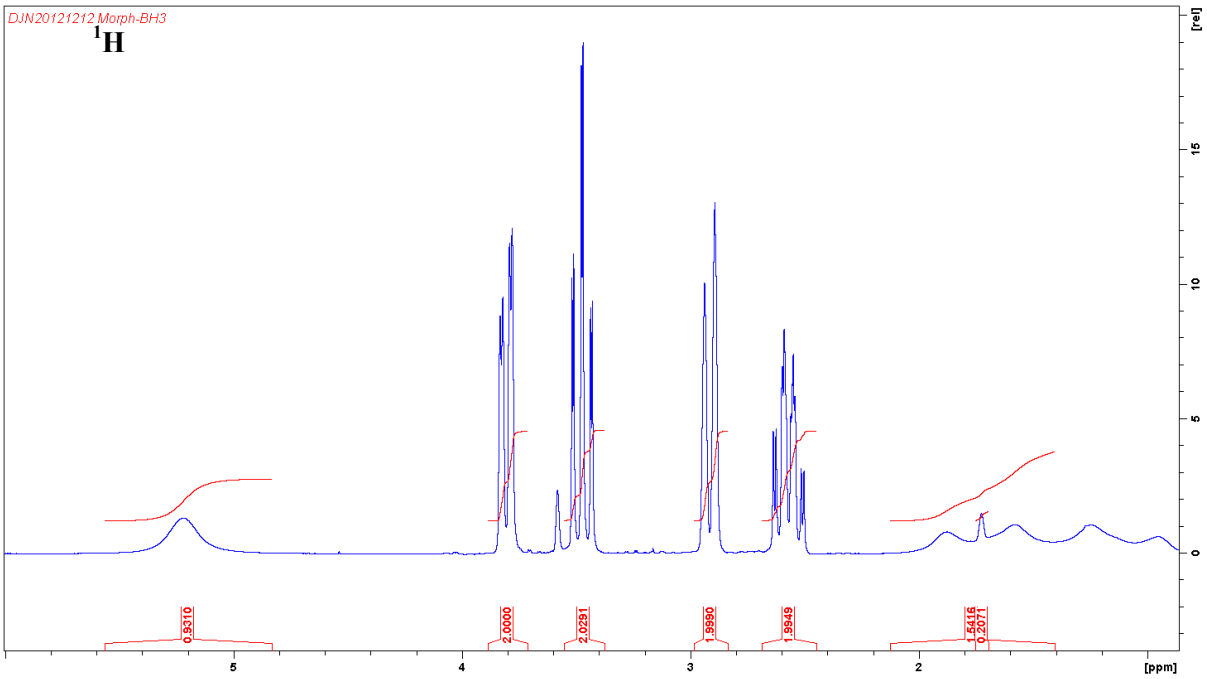


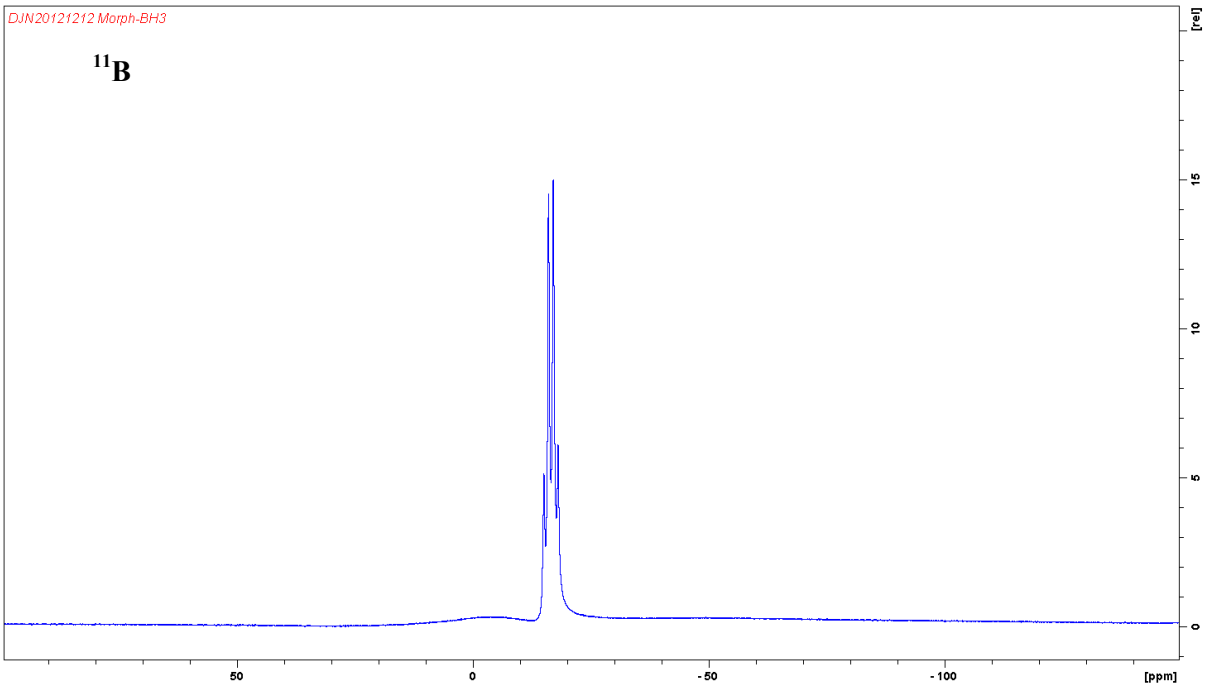
$DMS.BH_3$ 5 (in THF)



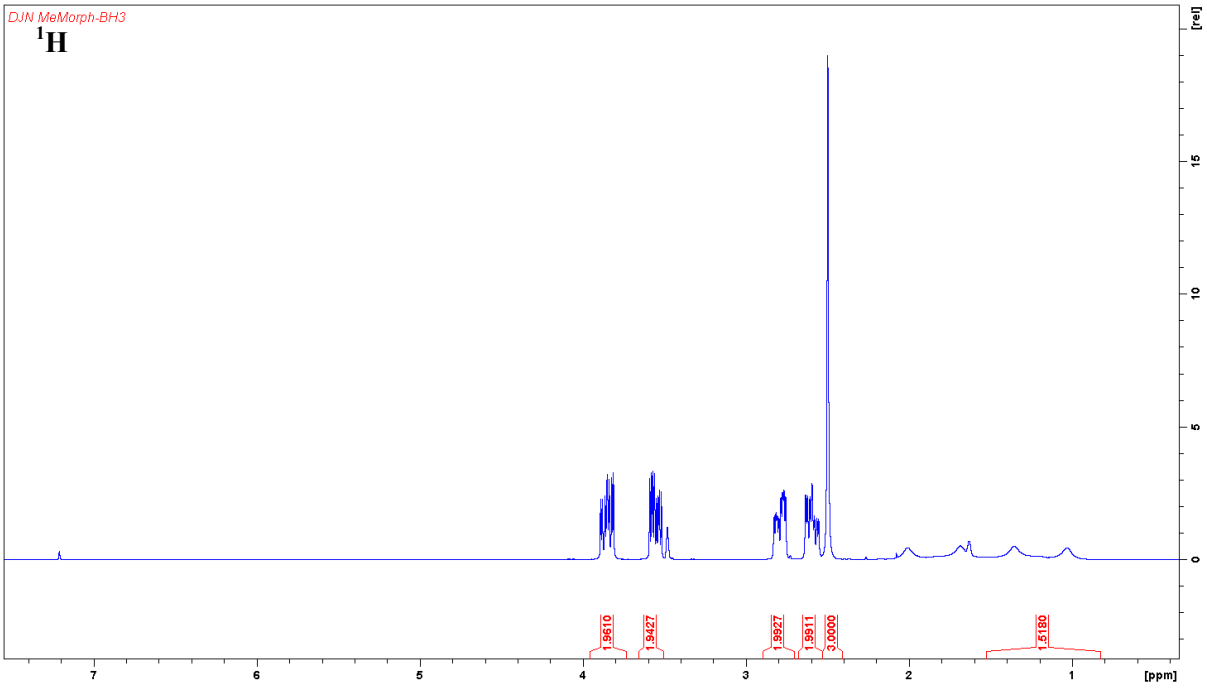


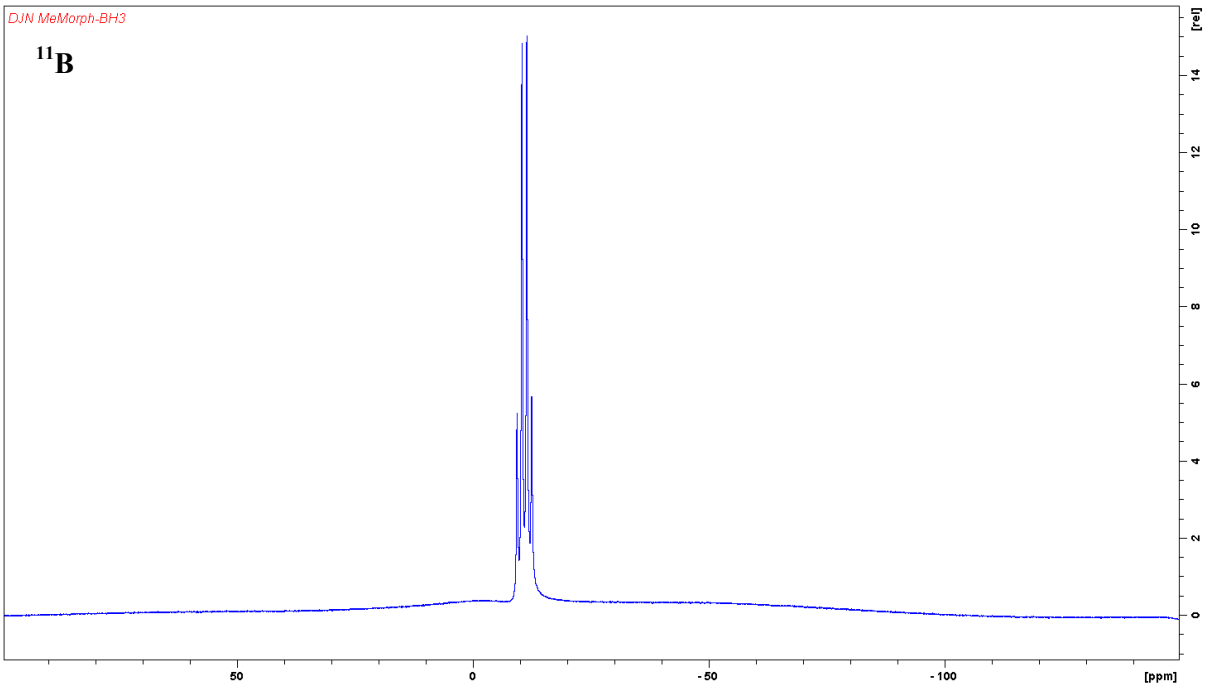
Morpholine-borane 6 (in THF)





N-methylmorpholine borane 7 (in THF)





Attempted deuteration of $NaBH_4$