

Supplementary Information for

**Structural and spectroscopic characterization
of potassium fluoroborohydrides**

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Experimental details

Ball milling. Commercial KBH_4 ($\geq 98\%$, Sigma Aldrich) and KBF_4 ($\geq 99.99\%$, Sigma Aldrich) powders were used to prepare mixtures in molar ratios 3:1 and 1:1. The mixtures were ground in a mortar and pestle for some minutes and after that milled in Spex 8000 M Mixer Mill for 10h. Stainless steel balls 10 mm in size with 40:1 ratio balls to powders were used. All handling and preparation of the mixtures took place in a glove box with continuously purified argon atmosphere where oxygen and moisture values were less than 1 ppm.

Powder X-ray diffraction. PXD was performed with Bruker AXS D8 Advance using $\text{Cu K}\alpha$ radiation ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54444 \text{ \AA}$). The samples were encapsulated airtight in 0.8 mm glass capillaries in the glove box. During the capillary preparation silicon powder ($\geq 99.999\%$; 1-5 micron; ABCR) was added to the sample as an internal standard. A LynxEyeTM strip-detector was used for data acquisition with step size of 0.02° in the 2Θ ranges of $20\text{--}65^\circ$ (sample **1**) and $20\text{--}90^\circ$ (sample **2**) at ambient temperature. The PXD data were analyzed according to the Rietveld method using the FullProf Suite software package. A pseudo-Voigt function with a simple mixing parameter was used to describe the Bragg peak profiles. The backgrounds were interpolated between manually selected background points (21 points for the 3:1 sample and 14 points for the 1:1 sample). Corrections for instrumental zeropoint offset and sample offset was determined from the positions of the silicon peaks.

Solid state NMR experiments. The experiments were performed at 11.7 T on a Bruker Avance III spectrometer using a 4.0 mm double resonance MAS probehead at room temperature. The MAS rate was 13 kHz for all experiments.

The ^1H spectra were obtained using 100 scans with a 10 second recycle delay. The ^{11}B spectra were obtained using 100 scans, 1 second recycle delay, and 1 microsecond long pulses, and the ^{19}F spectra were obtained using 100 scans, and 5 second recycle delay. The ^{11}B 3MQMAS experiment was carried out with a three pulse z-filtering sequence [1]. The spectra were acquired with 384 scans for each of the 200 experiments in the indirect dimension. The recycle delay was 1 s. $^1\text{H}\text{--}^{11}\text{B}$ CP, $^{19}\text{F}\text{--}^{11}\text{B}$ cross polarization (CP) spectra were acquired with 4000 scan, a recycle delay of 5 seconds and Hartmann-Hahn contact times of 500, 1500 and 200 microseconds. The α parameter is likely much less than 1 due to low rf-power levels used, the fast MAS rate and the likely low quadrupolar coupling strength of B in these samples.

The ^1H chemical shift is externally referred to TMS while pure KBH_4 and KBF_4 have been used for comparisons with synthesized materials.

All curve fittings were done using the MestReNova 8.1.1-11591 software with a mix of gaussian and lorentzian shapes.

Thermogravimetric experiments (TG). TG data was obtained with a STA449 F1 Jupiter instrument from NETZSCH. Samples of about 3 mg were measured in Al_2O_3 sample pans covered with pierced lids made of the same material. The experiments were conducted under flowing argon gas (50 ml/min) and with a heating rate of 2 $^\circ\text{C}/\text{min}$. The raw data was background corrected for sample holder effects by means of a correction file obtained under identical conditions.

Wet chemical synthesis. All operations were carried out in an Ar-filled glove box or with standard Schlenk techniques under Ar. All solvents were dried with either Na or CaH_2 and distilled. Potassium fluoride (Sigma-Aldrich, 0.43 g, 7.4 mmol) was ground to a powder with a mortar and pestle and placed in a 100 ml Schlenk flask. Dimethoxyethane (ca. 40 ml) was added via cannula and $\text{BH}_3\cdot\text{SMe}_2$ (Sigma-Aldrich, 1.0 ml, 10.5 mmol) was added via syringe. The resulting white slurry was then refluxed for 15 h. After cooling, the resulting white precipitate was isolated by filtration, washed with Et_2O (2 x 20 ml), and dried under vacuum. Yield: 0.45 g. The solid state ^{11}B NMR spectrum showed two resonances consistent with BF_4^- and BH_4^- tetrahedra. The solid state ^{19}F NMR spectrum showed several resonances; only that for KF (-133.0 ppm) and KBF_4 (-152.5 ppm) could be assigned. The PXRD data shows phases for KF, KBH_4 , and KBF_4 , in addition to reflections for other, unknown phases.

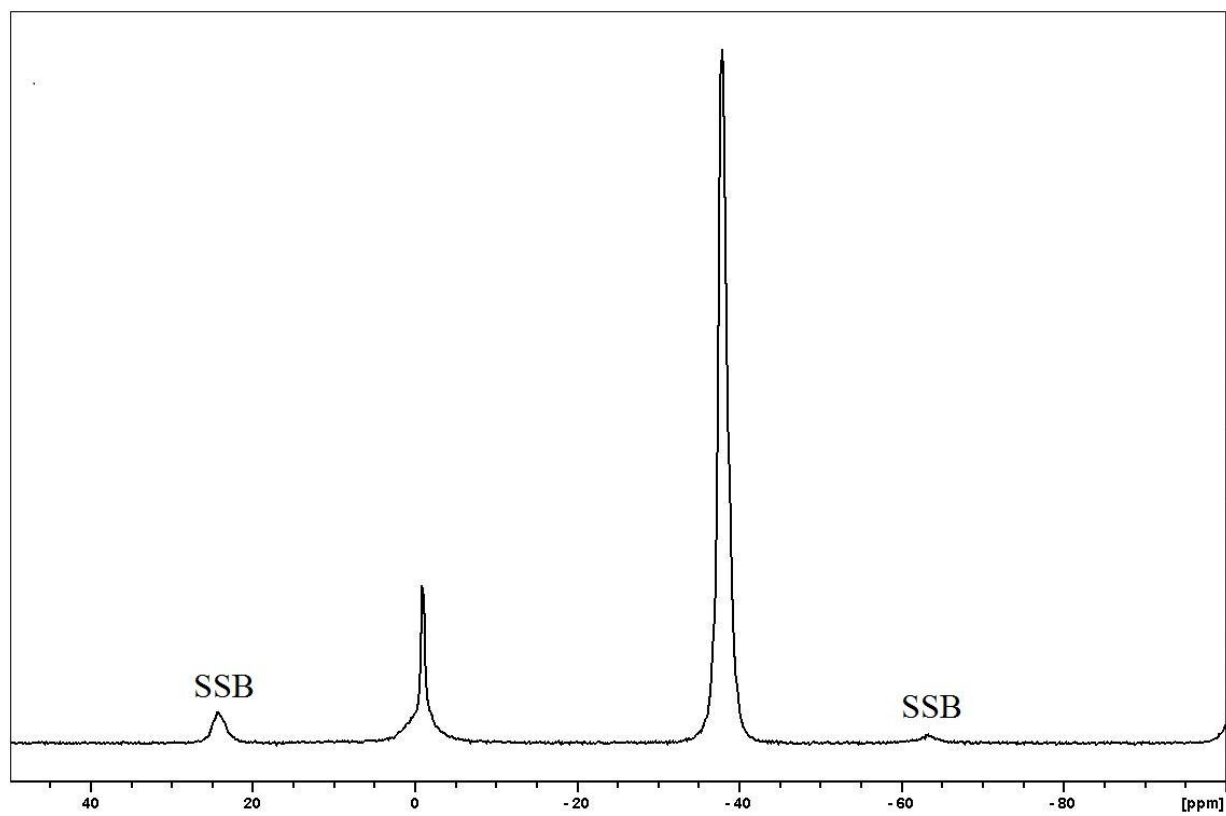


Figure 1S. Solid state ^{11}B NMR spectrum of **3**.

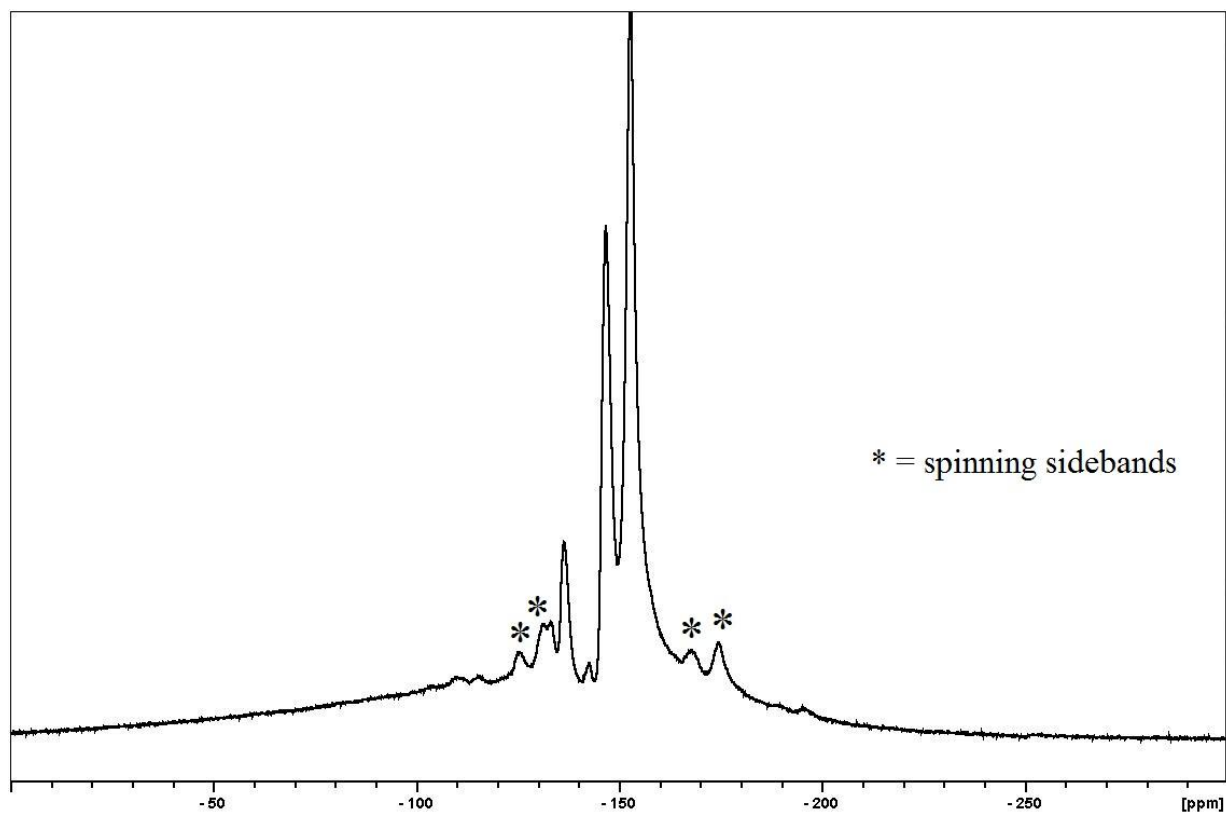


Figure 2S. Solid state ^{19}F NMR of **3**.

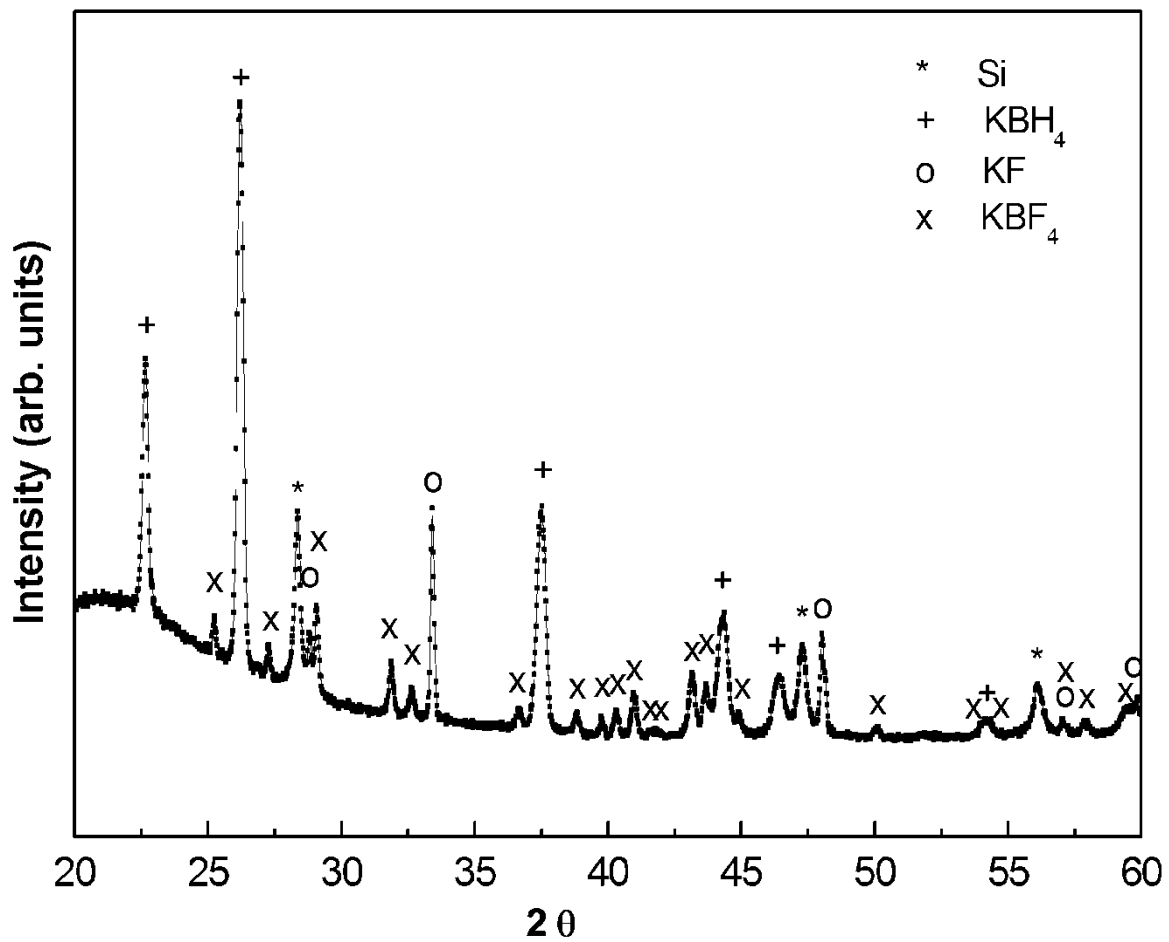


Figure 3S. PXRD of 3.

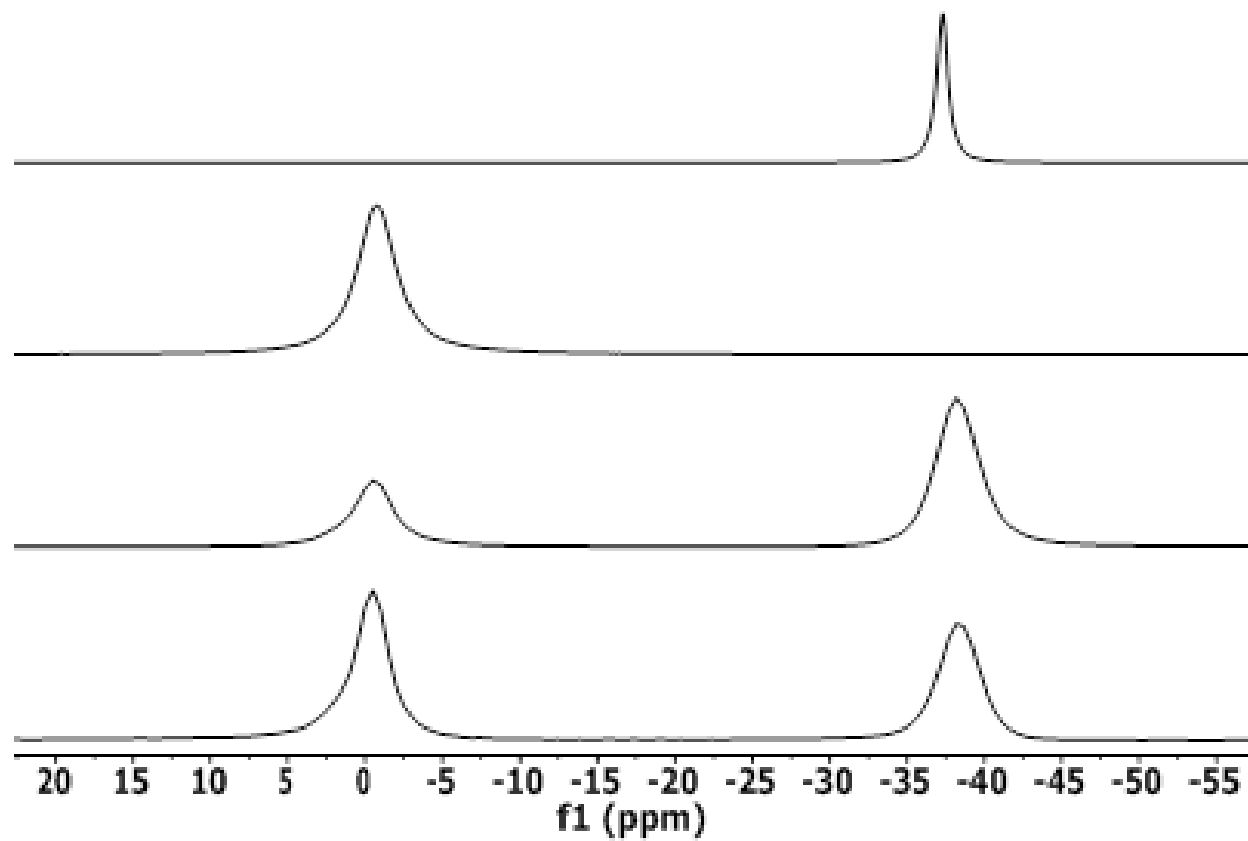


Figure 4S. Enlarged view of Figure 3 of the ^{11}B NMR spectra of KBH_4 , KBF_4 , **1**, and **2** (top to bottom).

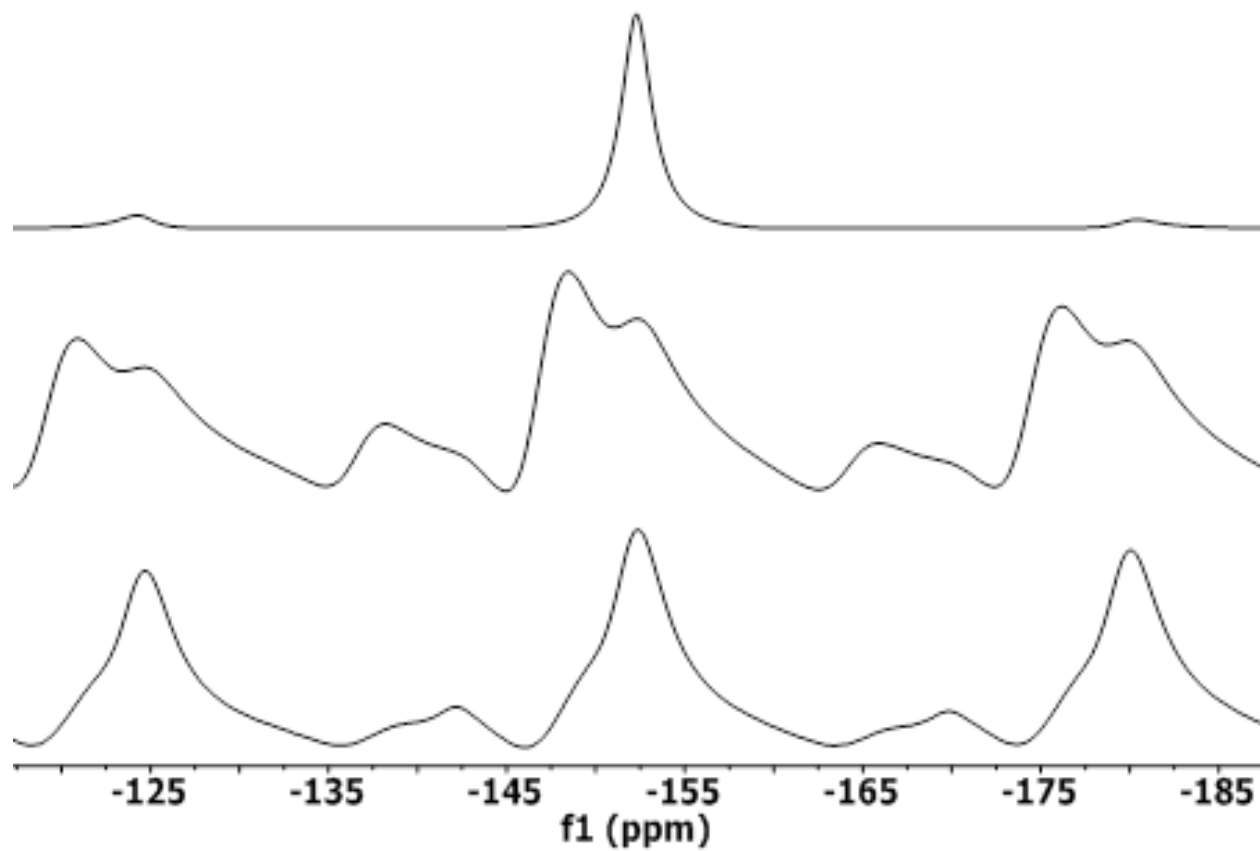


Figure 5S. Enlarged view of Figure 6 of the ^{19}F NMR spectra for KBF_4 , **1**, and **2** (top to bottom).

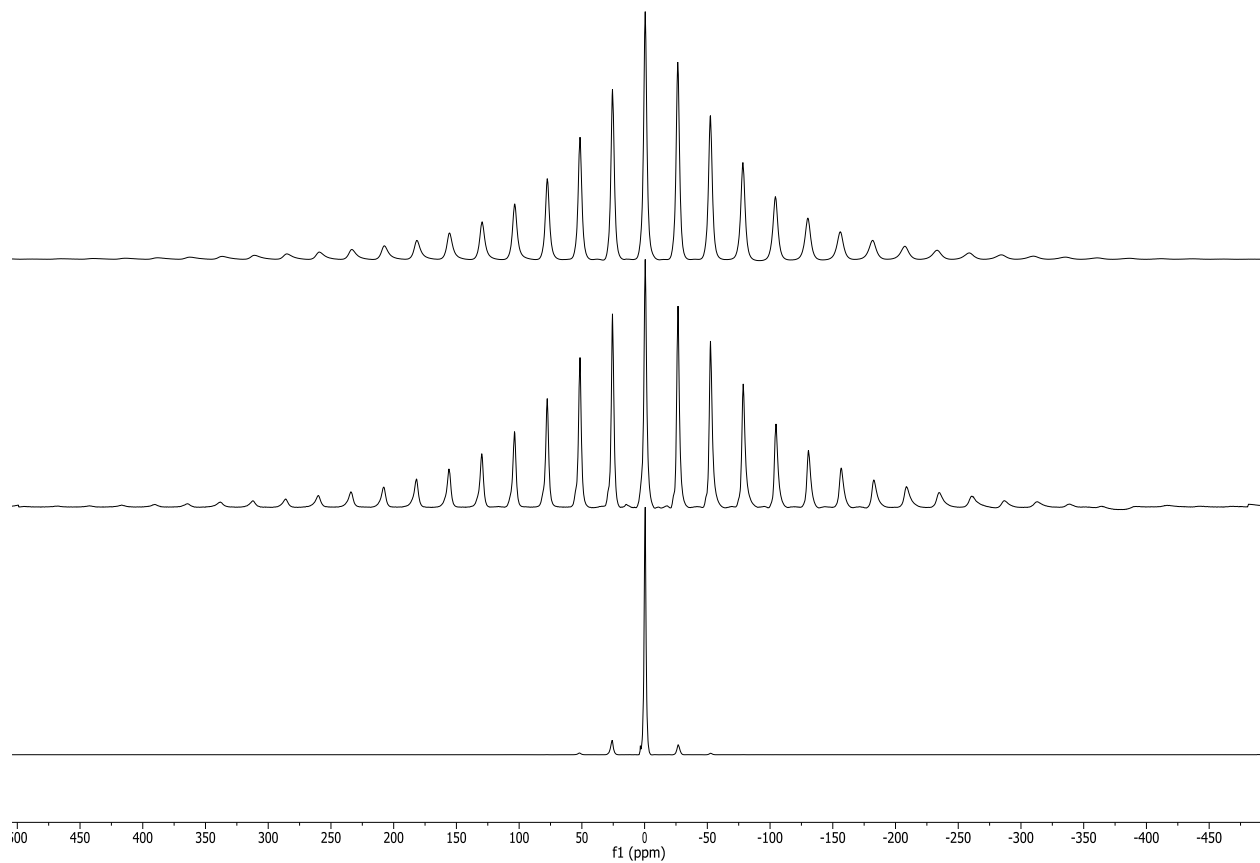


Figure 6S. ^1H NMR spectra for **1**, **2**, and **3** (top to bottom).

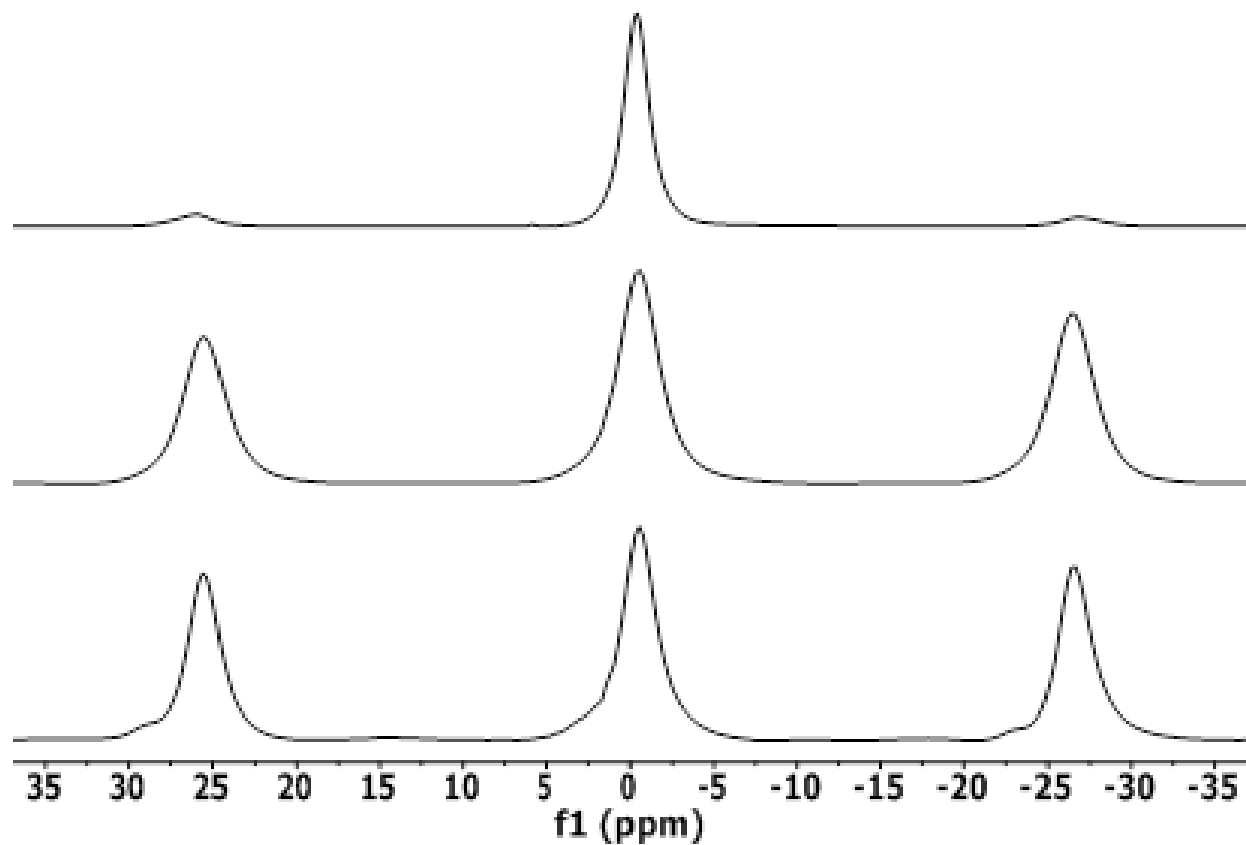


Figure7S. Enlarged view of the ^1H NMR spectra of KBH_4 , **1**, and **2** (top to bottom).

Footnotes

1. J. P. Amoureux, C. Fernandez, S. Steuernagel, *J. Magn. Res. Series A*, 1996, **123**, 116-118.