Supporting Information for:

Lewis Base Activation of Borane-Dimethylsulfide into Strongly Reducing Ion Pairs for the Transformation of Carbon Dioxide to Methoxyboranes

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1. Synthetic procedures

a. General Procedures.

Unless otherwise specified, manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Catalytic reactions were carried out in a sealed J-Young NMR tube, in which case NMR conversions are indicated, or in standard flame-dried Schlenk glassware. All solvents were distilled from Na/benzophenone, benzene-d_6 was purified by vacuum distillation from Na/K alloy, dichloromethane-d_2 was dried over 4Å Molecular sieves. Proton Sponge, DBU, TBD, terpyridine and borane-dimethylsulfide were purchased from Sigma-Aldrich and used as provided.

NMR spectra were recorded on an Agilent Technologies NMR spectrometer at 500 MHz (^{1}H), 125.76 MHz (^{13}C), 202.46 MHz (^{31}P), 160.46 MHz (^{11}B), and on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.58 MHz (^{13}C), 161.92 MHz (^{31}P). ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. ^{11}B{^{1}H} was calibrated using an external reference of $B(OMe)_3$ (set at +18.1 relative to BF_3 etherate solution). Multiplicities are reported as singlet (s), broad signal (br) doublet (d), triplet (t), quadruplet (q), quintuplet (qt) nontuplet (n), multiplet (m). Chemical shifts are reported in ppm.

b. General method for the hydroboration of carbon dioxide.

0.01 mmol of base catalyst was dissolved in *ca.* 0.4 mL of benzene-d_6 or dichloromethane-d_2 containing an internal standard of hexamethylbenzene. The BH_3•SMe_2 was added to the solution and the mixture was introduced in a J-Young NMR tube. The J-young NMR tube was frozen in a liquid nitrogen bath and its atmosphere was removed under vacuum after which the headspace was filled with CO_2. The reaction was then followed by NMR spectroscopy. Yields are reported using ^{1}H NMR spectroscopy according to the integration of the $[MeOBO]_n$ moieties at 3.36 ppm and compared to that of the internal standard.

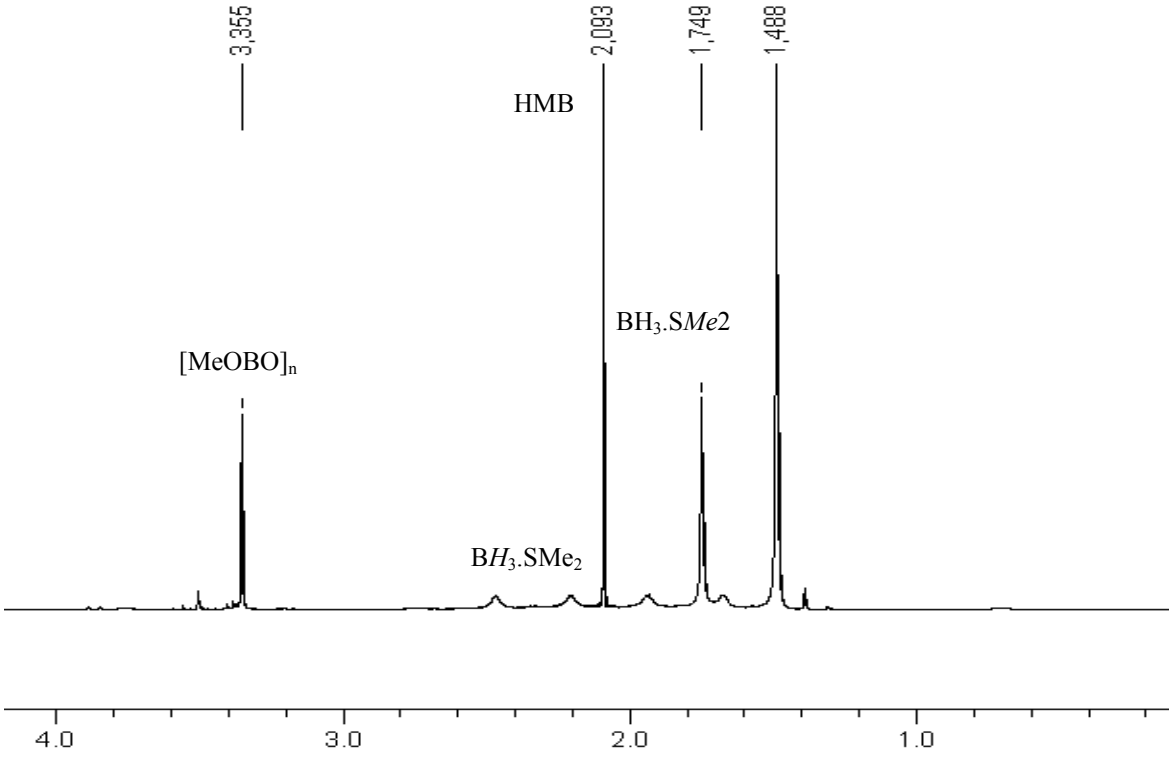

Figure S1**.** Typical ^{1}H NMR spectrum of the catalyzed reduction of carbon dioxide by $BH_3.SMe_2$ catalyzed. Experiment with TBD (500MHz, benzene-d_6).

c. Synthesis and characterization of boronium salts.

[PS(BH_2)][BH_4] (2-BH_4). 300 mg of proton sponge (1.40 mmol) were dissolved in 20 mL of diethylether. To this solution was added 0.3 mL (3.1 mmol) of $BH_3.SMe_2$. The resulting mixture was stirred for 16 hours at room temperature after which the volatiles were removed *in vacuo* to afford colourless crystals, which were rinsed with hexanes. 291 mg (86%) of **2-BH_4** were collected in this manner. The spectral data are consistent with those of the [PS(BH_2)]$^+$ and [BH_4]$^-$ which were reported previously.[i] ^{1}H NMR (500 MHz, dichloromethane-d_2): 8.23 (d, 2H, $^1J_{H-H}$ = 7.7 Hz, *p*-PS), 8.08 (d, 2H, $^1J_{H-H}$ = 8.4 Hz, *o*-PS), 7.78 (dd, 2H, $^1J_{H-H}$ = *ca* 8 Hz, *m*-PS), 3.48 (s, 12H, NMe_2), -0.06 (q, 4H, $^1J_{B-H}$ = 81.4 Hz, BH_4), the BH_2 was not located; $^{13}C\{^1H\}$ (101 MHz, dichloromethane-d_2): 140.2 (s, C_{quat}), 135.8 (s, C_{quat}), 130.9 (s, *o*-PS), 127.5 (s, *p*-PS), 121.3 (s, *m*-PS), 56.5 (s, NMe_2), one quaternary signal was not located; ^{11}B (160.46 MHz, dichloromethane-d_2): 1.7 (br , BH_2), -38.4 (qt, $^1J_{B-H}$ = 81.4 Hz, BH_4).

[PS(BH_2)][B_3H_8] (2-B_3H_8). 300 mg of proton sponge (1.40 mmol) were dissolved in 30 mL of toluene. To this solution was added 1.3 mL (14 mmol) of $BH_3.SMe_2$. The resulting mixture was stirred for 16 hours at 80°C. The resulting yellow suspension was filtered and the residue was rinsed twice with toluene to afford a yellow powder (194 mg. (52%). The spectral data are consistent with those of the [PS(BH_2)]$^+$ and [BH_4]$^-$ which were reported previously.[ii] ^{1}H NMR: (400 MHz, dichloromethane-d_2): 8.11 (d, 2H, $^1J_{H-H}$ = 8.2 Hz, *p*-PS), 8.03 (d, 2H, $^1J_{H-H}$ = 7.8 Hz, *o*-PS), 7.79 (dd, 2H, $^1J_{H-H}$ = *ca* 8 Hz, *m*-PS), 3.48 (s, 12H, NMe_2), 0.17 (br m, B_3H_8); $^{13}C\{^1H\}$ (101 MHz, dichloromethane-d_2): 140.1 (s,

C_{quat}), 136.0 (s, C_{quat}), 131.2 (s, *o*-PS), 127.5 (s, *p*-PS), 120.7 (s, *m*-PS), 56.5 (s, NMe_2), one quaternary signal was not located; ^{11}B (160.46 MHz, dichloromethane-d_2): 1.5 (br m , BH_2), -30.0 (n, $^1J_{B-H}$ = 81.4 Hz, B_3H_8).

$(PS(BH_2)])_2[B_{12}H_{12}]$ (2-$B_{12}H_{12}$). 2.1 mg (0.01 mmol) of proton sponge was dissolved with 38 mg (50 equiv, 0.5 mmol) of $BH_3.SMe_2$ in benzene-d_6 and transferred to a J-Young NMR tube. The tube was frozen in liquid nitrogen and put under vacuum. Its atmosphere was then replaced with carbon dioxide. The reaction mixture was heated at 70 °C for 20 hours. A single crop of crystals suitable for X-ray diffraction study was collected at the bottom of the tube at the end of the reaction.

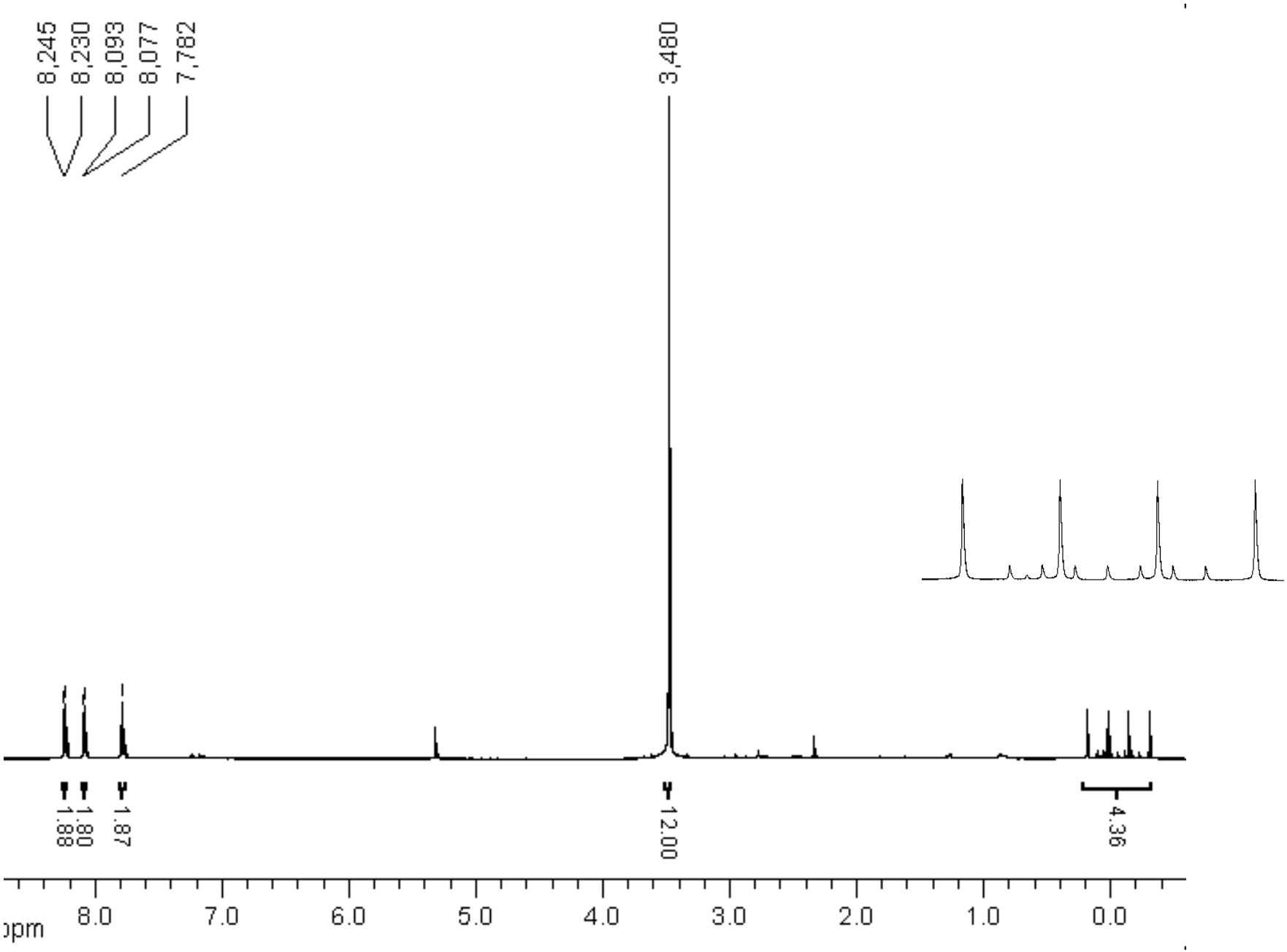

Figure S2. ^{1}H NMR spectrum (500 MHz, dichloromethane-d_2) of **2-BH$_4$**

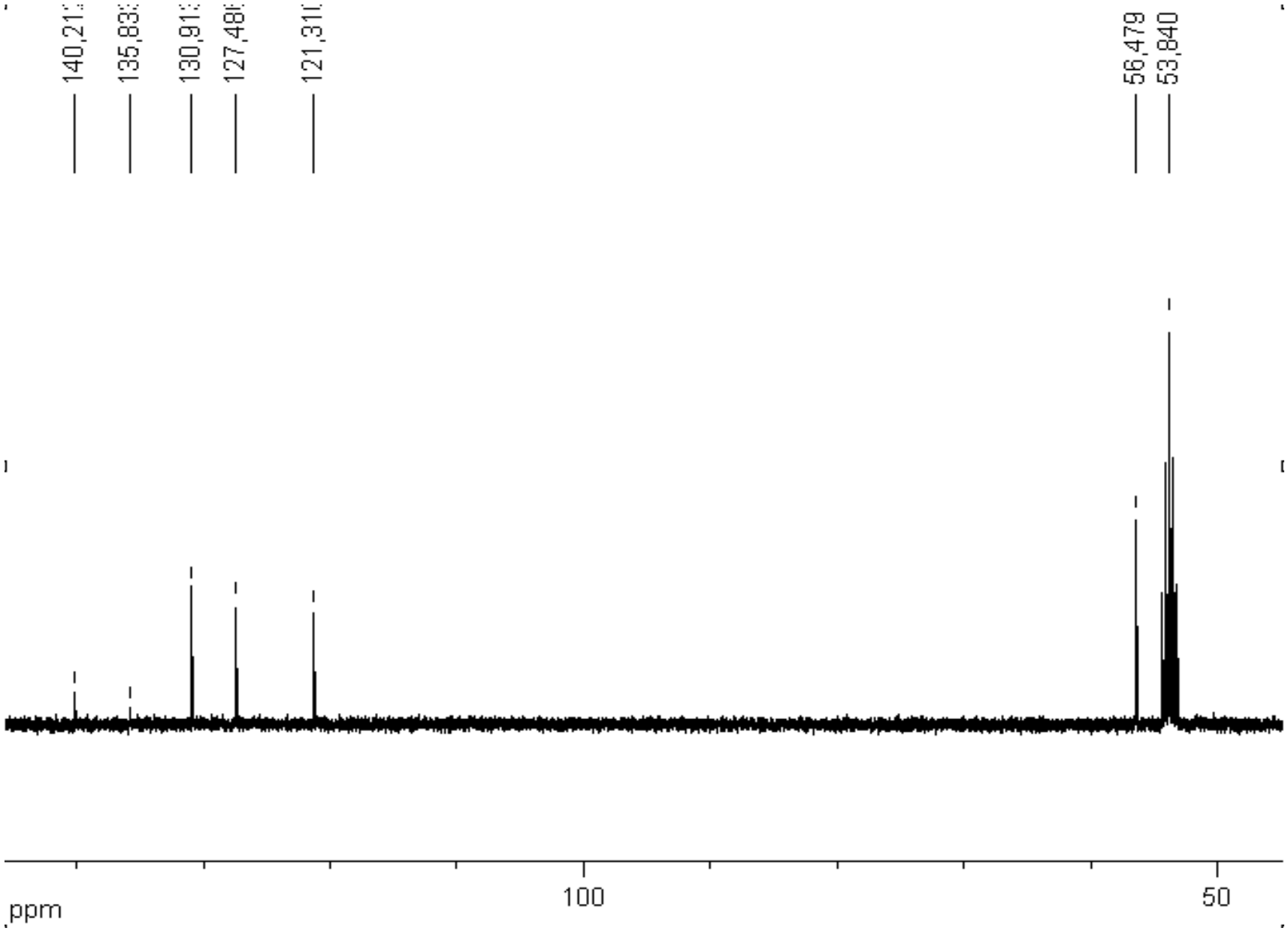

Figure S3. ^{13}C NMR spectrum (101 MHz, dichloromethane-d_2) of **2-BH$_4$**

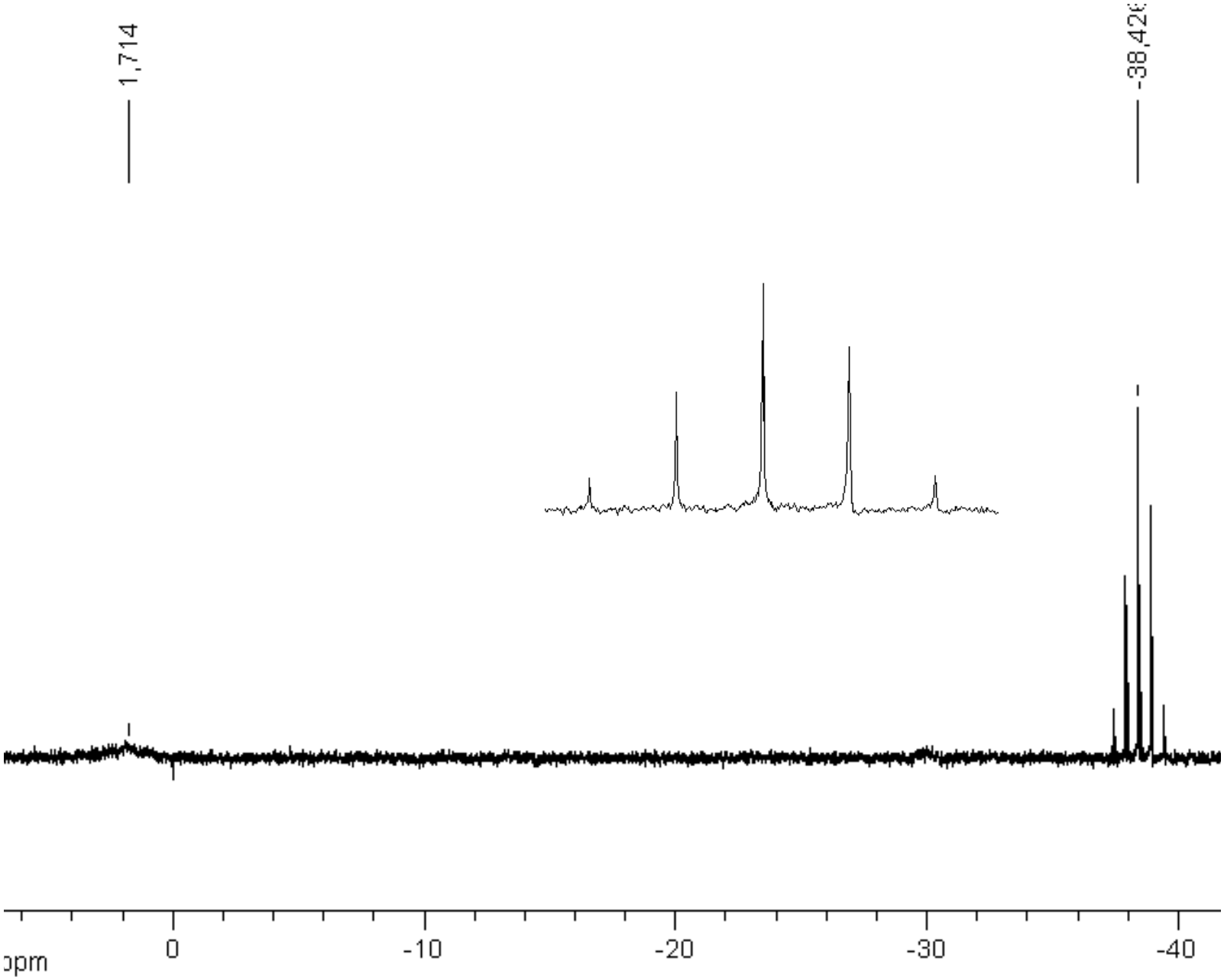

Figure S4. ^{11}B NMR spectrum (160.46 MHz, dichloromethane-d_2) of **2-BH$_4$**

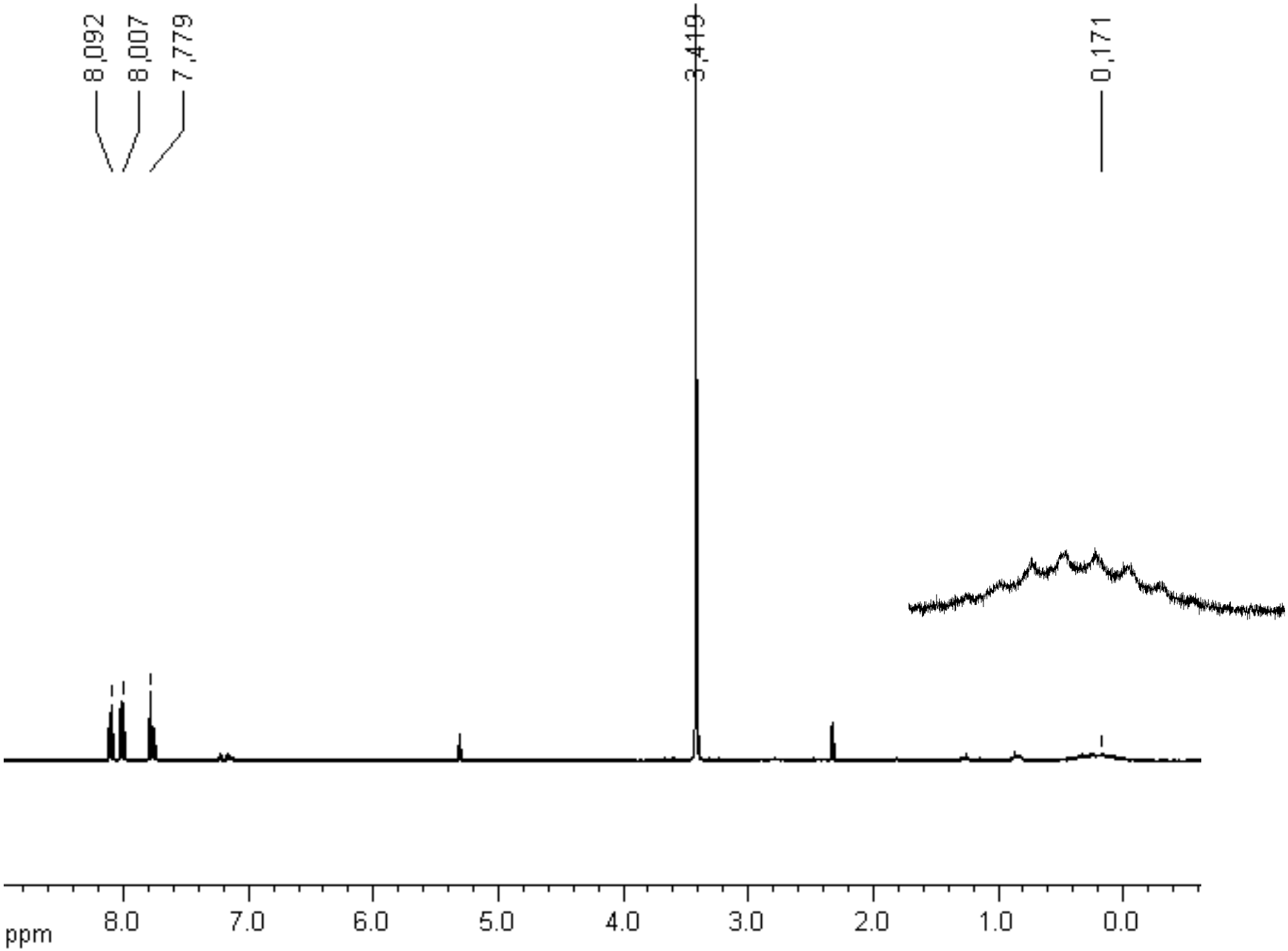

Figure S5. ^{1}H NMR spectrum (500 MHz, dichloromethane-d_2) of **2-B_3H_8**

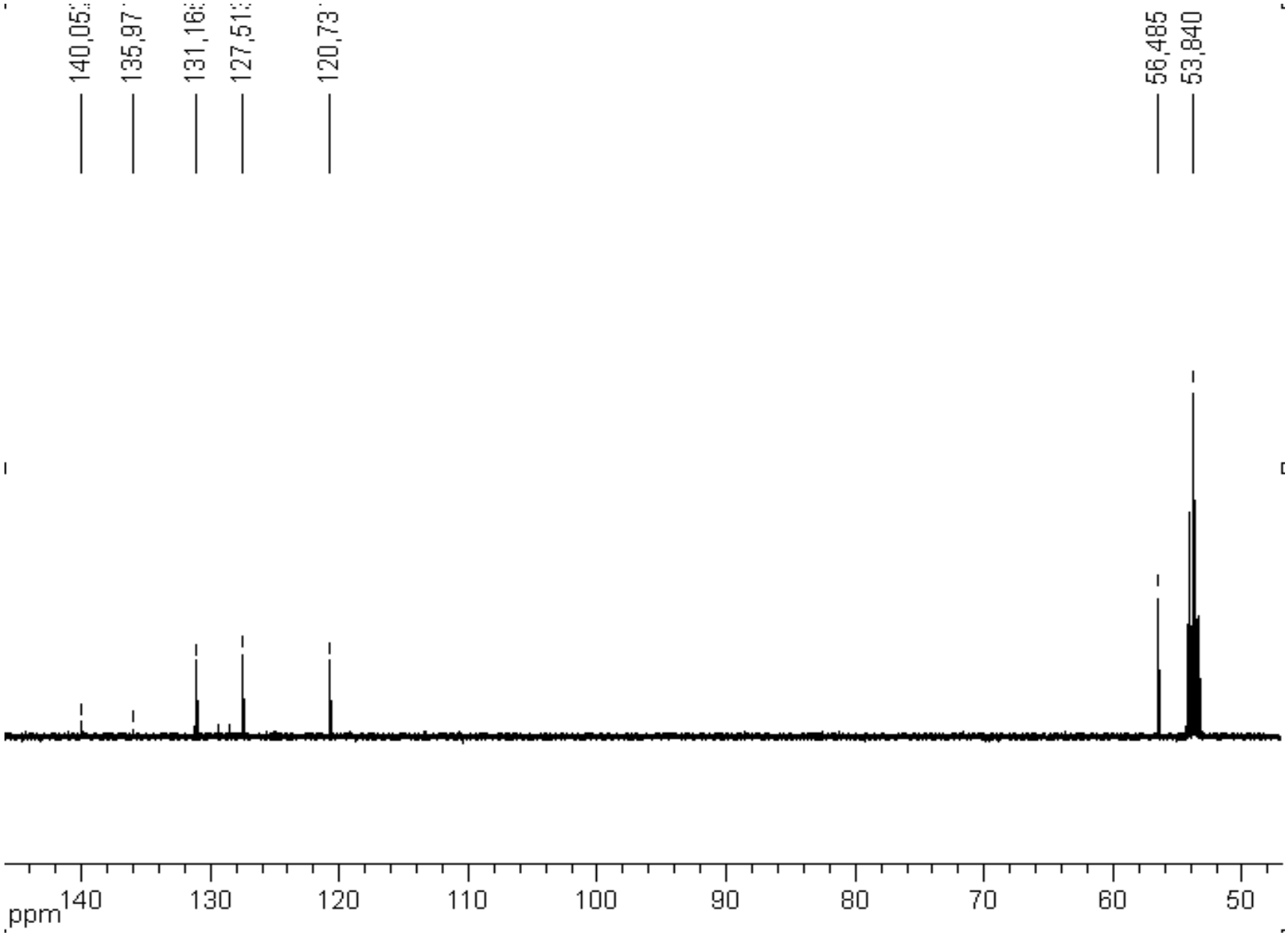

Figure S6. ^{13}C NMR spectrum (101 MHz, dichloromethane-d_2) of **2-B_3H_8**

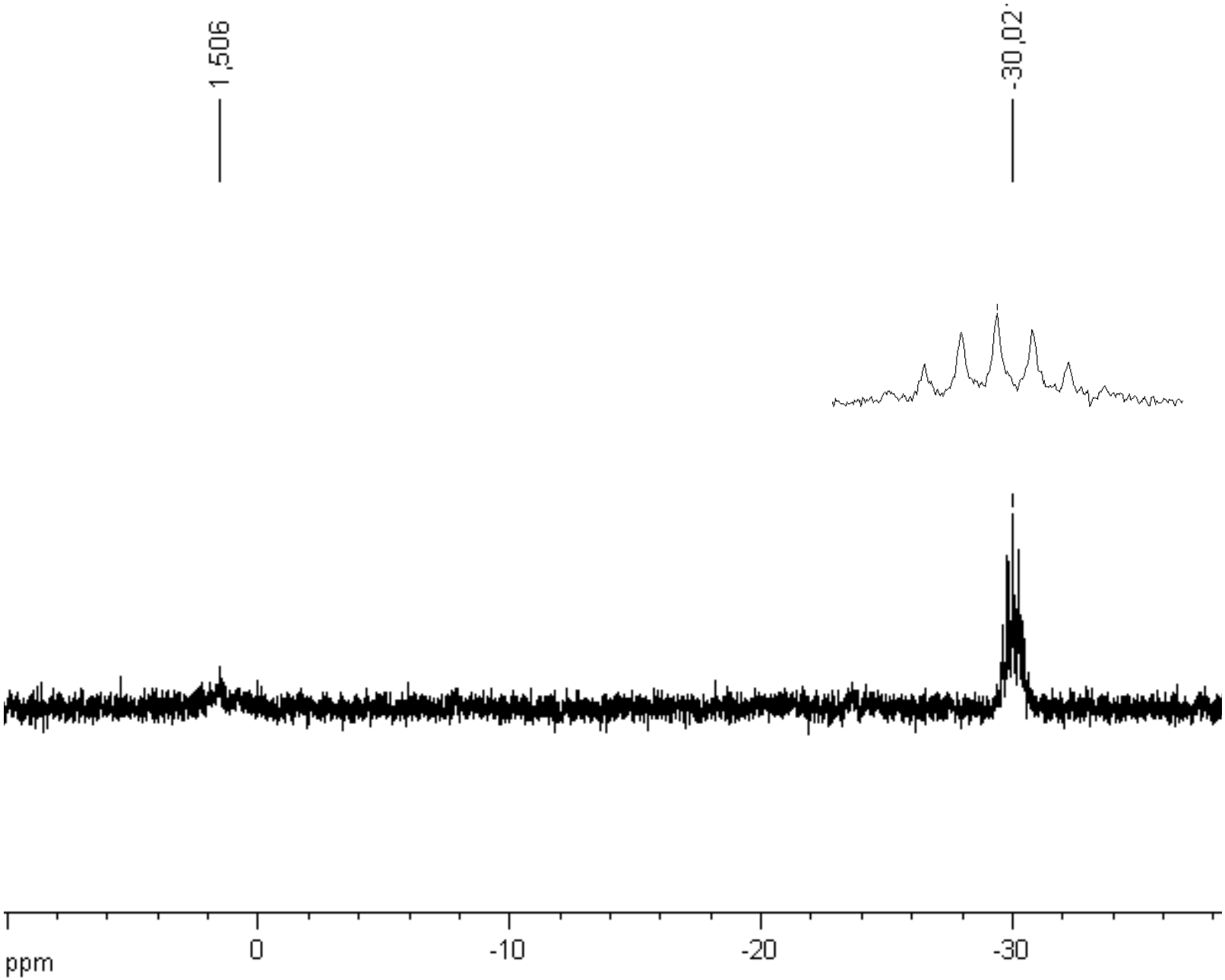

Figure S7. ^{11}B NMR spectrum (500 MHz, dichloromethane-d_2) of **2-B_3H_8**

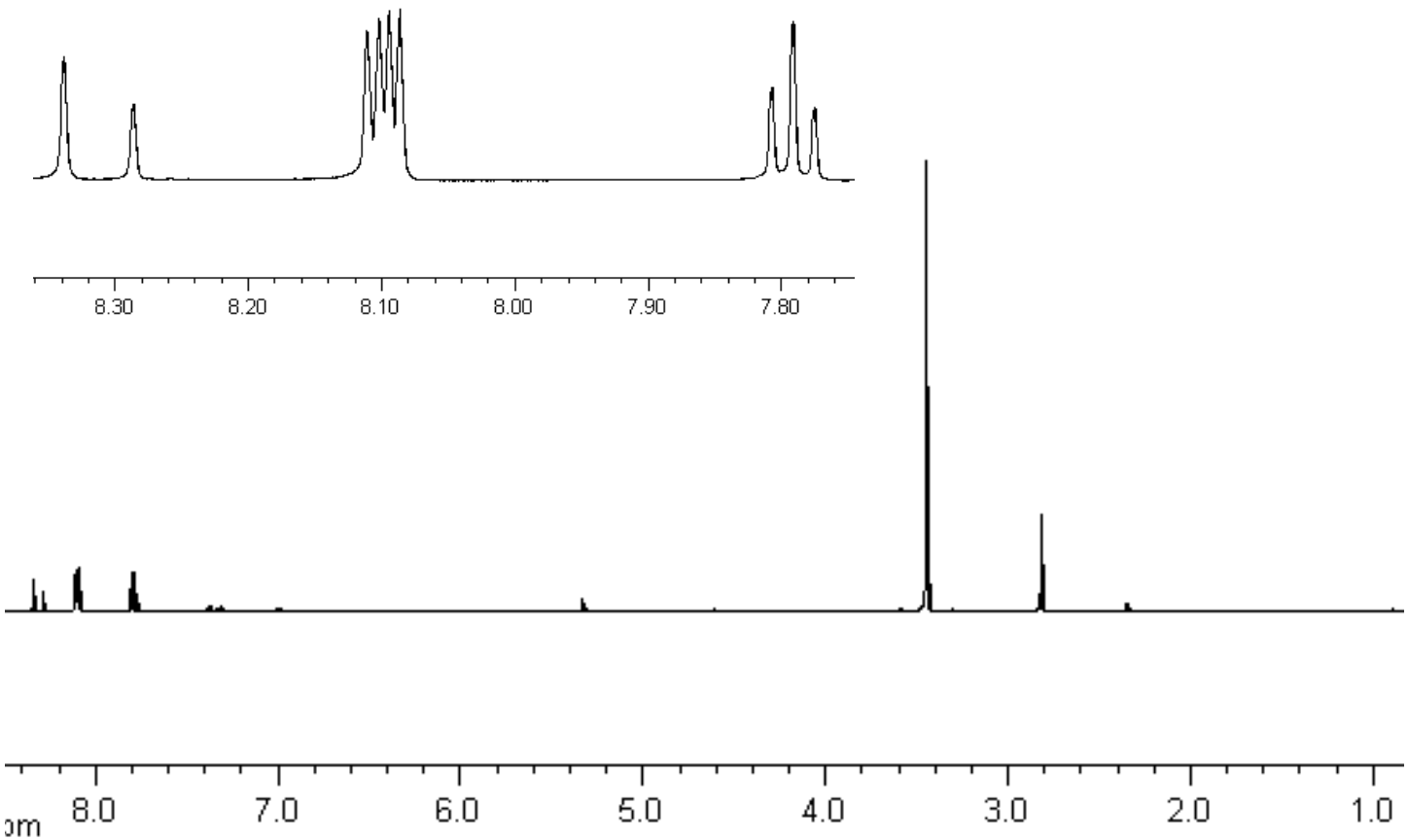

Figure S8. ^{1}H NMR spectrum (500 MHz, dichloromethane-d_2) of the reaction of **2-BH$_4$** with CO_2

Crystallographic details

A crystal of suitable size was obtained from the reaction of PS with 25 equiv of $BH_3.SMe_2$ and CO_2 in benzene-d_6. It was mounted on CryoLoops with Paratone-N and optically aligned on a Bruker SMART APEX-II X-ray diffractometer with 1K CCD detector using a digital camera. Initial intensity measurements were performed using a fine-focused sealed tube, graphite-monochromated, X-ray source (Mo $K\alpha$, λ = 0.71073 Å) at 50 kV and 30 mA. Standard APEX-II[iii] software package was used for determining the unit cells, generating the data collection strategy, and controlling data collection. SAINT[iv] was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using SCALE (SADABS[v,vi]). The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with SHELX-97[vii] in the SHELXTL6.14 package. All of the H atoms (on C atoms) were generated geometrically and refined in riding mode. Crystallographic information for all crystals summarized in Table S1. Atomic coordinates and additional structural information are in the .cif file provided. The CCDC number is 1009675.

Table S1. Crystal data and structure refinement for $[PS(BH_2)]_2[B_{12}H_{12}]$

Empirical formula	C14 H26 B7 N2	
Formula weight	298.04	
Temperature	150(2) K	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6172(11) Å	α = 96.336(2) °
	b = 9.7108(11) Å	β = 109.264(2) °
	c = 10.0025(12) Å	γ = 102.874(2) °
Volume	842.34(17) $Å^3$	
Z	2	
Density (calculated)	1.175 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	318	
Crystal size	0.22 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.196 to 26.445°.	
Index ranges	-12<=h<=12, -12<=k<=12, -12<=l<=12	
Reflections collected	7763	
Independent reflections	3464 [R(int) = 0.0262]	
Completeness to theta = 25.242°	99.9 %	
Max. and min. transmission	0.998 and 0.993	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3464 / 0 / 244	
Goodness-of-fit on F^2	1.022	

Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1273
R indices (all data)	R1 = 0.0774, wR2 = 0.1424
Largest diff. peak and hole	0.269 and -0.166 e.Å^{-3}

References

[i] P. C. Keller and J. V. Rund, *Inorg. Chem*,. 1979, **18**, 3197-3199.

[ii] J. D. Woollins, *Inorganic Experiments, 3rd Revised Edition*, Wiley-VCH, 2010, Weinheim, 405-408.

[iii] *APEX2*; Bruker AXS Inc.: Madison, WI, 2007.

[iv] *SAINT*; Bruker AXS Inc.: Madison, WI, 2007.

[v] Sheldrick, G. M. *SADABS*; Bruker AXS Inc.: Madison, WI, 2007.

[vi]Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

[vii] Spek, A. L. Acta Cryst. **2009**, *D65*, 148-155.