

Reduction of CO₂ to Trimethoxyboroxine with BH₃ in THF

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Experimental Section

$^{13}\text{C}\{^1\text{H}\}$ NMR measurement of the reaction mixture.

To estimate the amount of the trimethoxyboroxine formed using $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, a calibration curve was prepared using the $^{13}\text{C}\{^1\text{H}\}$ integration intensity of the methoxy carbon signal relative to that of the methyl carbon signal of *p*-xylene which was added as an internal standard. Six THF solutions of different trimethoxyboroxine/*p*-xylene ratios ranging from 0.05 to 0.92 were prepared. A linear plot (correlation factor : $r^2 = 0.9982$) was obtained, when integration intensity ratio of the methoxy carbon signal of trimethoxyboroxine to the methyl carbon signal of *p*-xylene were correlated with the trimethoxyboroxine/*p*-xylene molar ratio.

After the reactions were stopped, a known amount of *p*-xylene was added to the reaction mixture, and the integration intensity ratio of the methoxy carbon signal of trimethoxyboroxine to the methyl carbon signal of *p*-xylene was determined on the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the solution. On the basis of the calibration curve, the intensity ratio was converted to the trimethoxyboroxine/*p*-xylene molar ratio, from which the amount of trimethoxyboroxine was obtained since the amount of *p*-xylene was known. The yields estimated by this method were almost consistent with those determined using the GC analysis of MeOH formed by hydrolysis of $(\text{MeOBO})_3$.

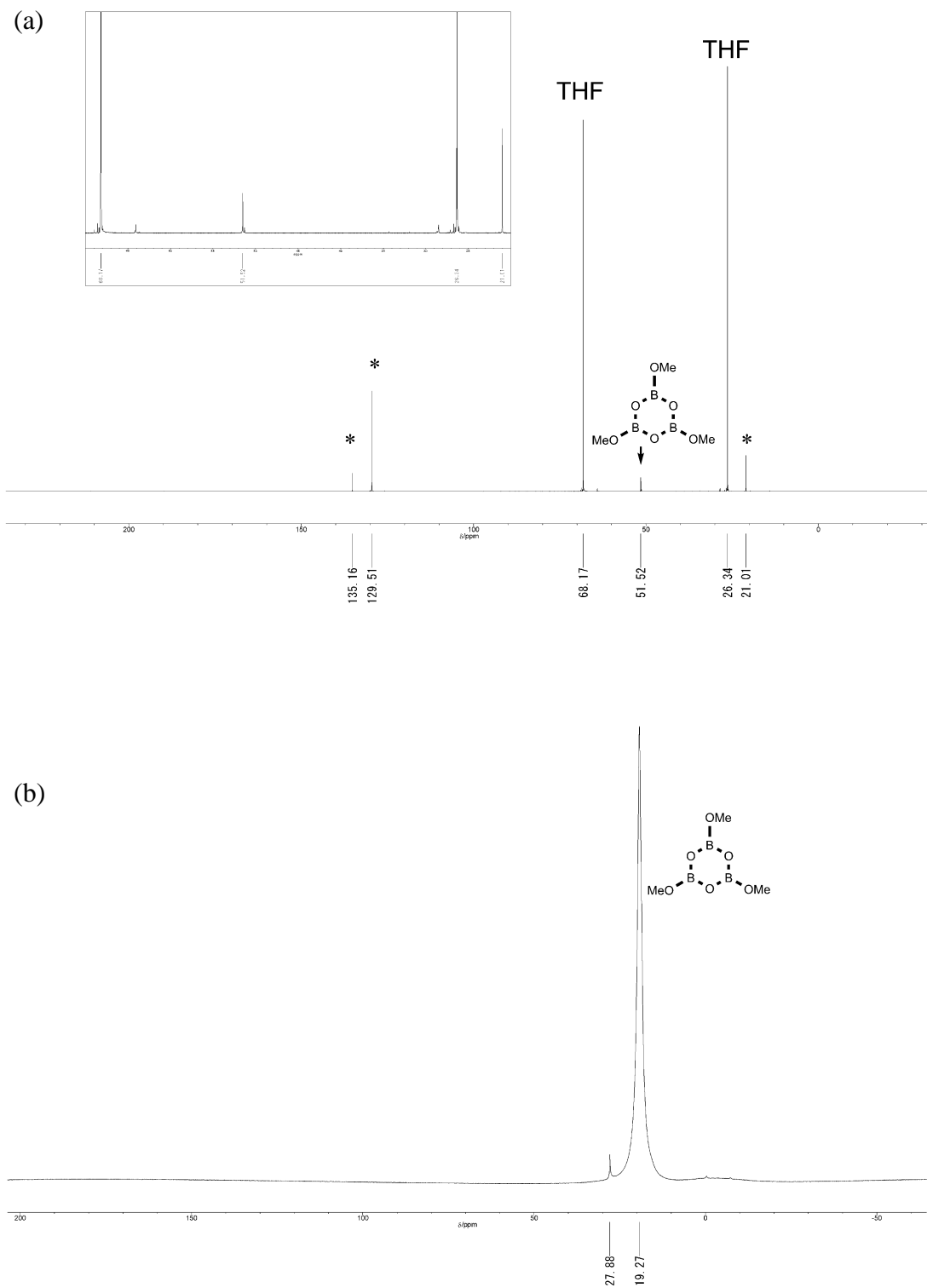


Figure S1. $^{13}\text{C}\{^1\text{H}\}$ (top) and $^{11}\text{B}\{^1\text{H}\}$ (bottom) NMR spectra of a reaction mixture obtained by the reaction of commercial $\text{BH}_3\cdot\text{THF}$ (Tokyo Chemical Industry) with CO_2 for 12 h. The signals with “*” are those of *p*-xylene added as an intensity standard. The inset of (a) is the magnification of 20 – 70 ppm.

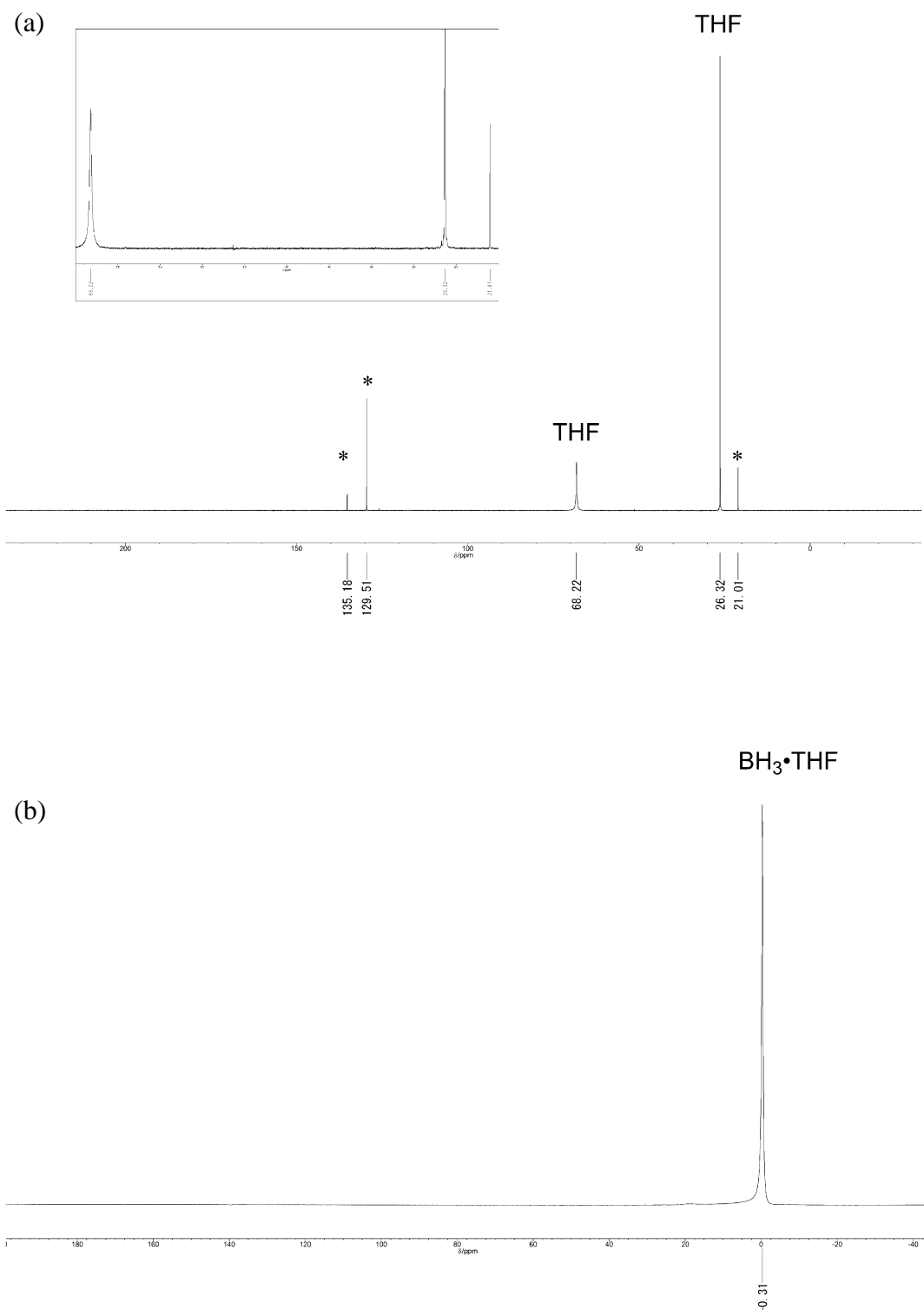


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ (top) and $^{11}\text{B}\{^1\text{H}\}$ (bottom) NMR spectra recorded after 12 h for the reaction of purified $\text{BH}_3\cdot\text{THF}$ with CO_2 . The signals with “*” are those of *p*-xylene added as an intensity standard. The inset of (a) is the magnification of 20 – 70 ppm.

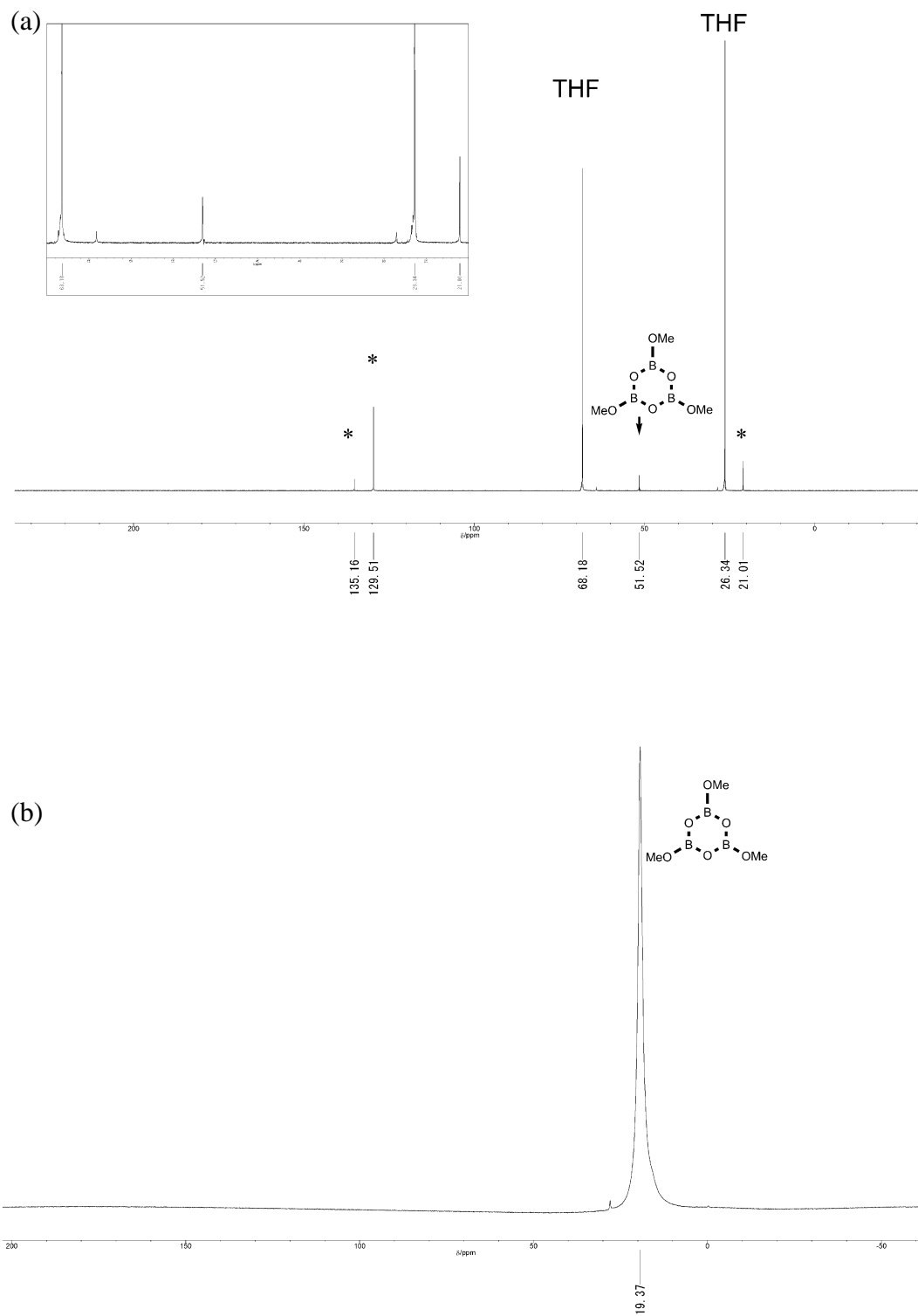


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ (top) and $^{11}\text{B}\{^1\text{H}\}$ (bottom) NMR spectra recorded after 12 h for the reaction of purified $\text{BH}_3 \cdot \text{THF}$ with CO_2 in the presence of NaBH_4 . The signals with “*” are those of *p*-xylene added as an intensity standard. The inset of (a) is the magnification of 20 – 70 ppm.

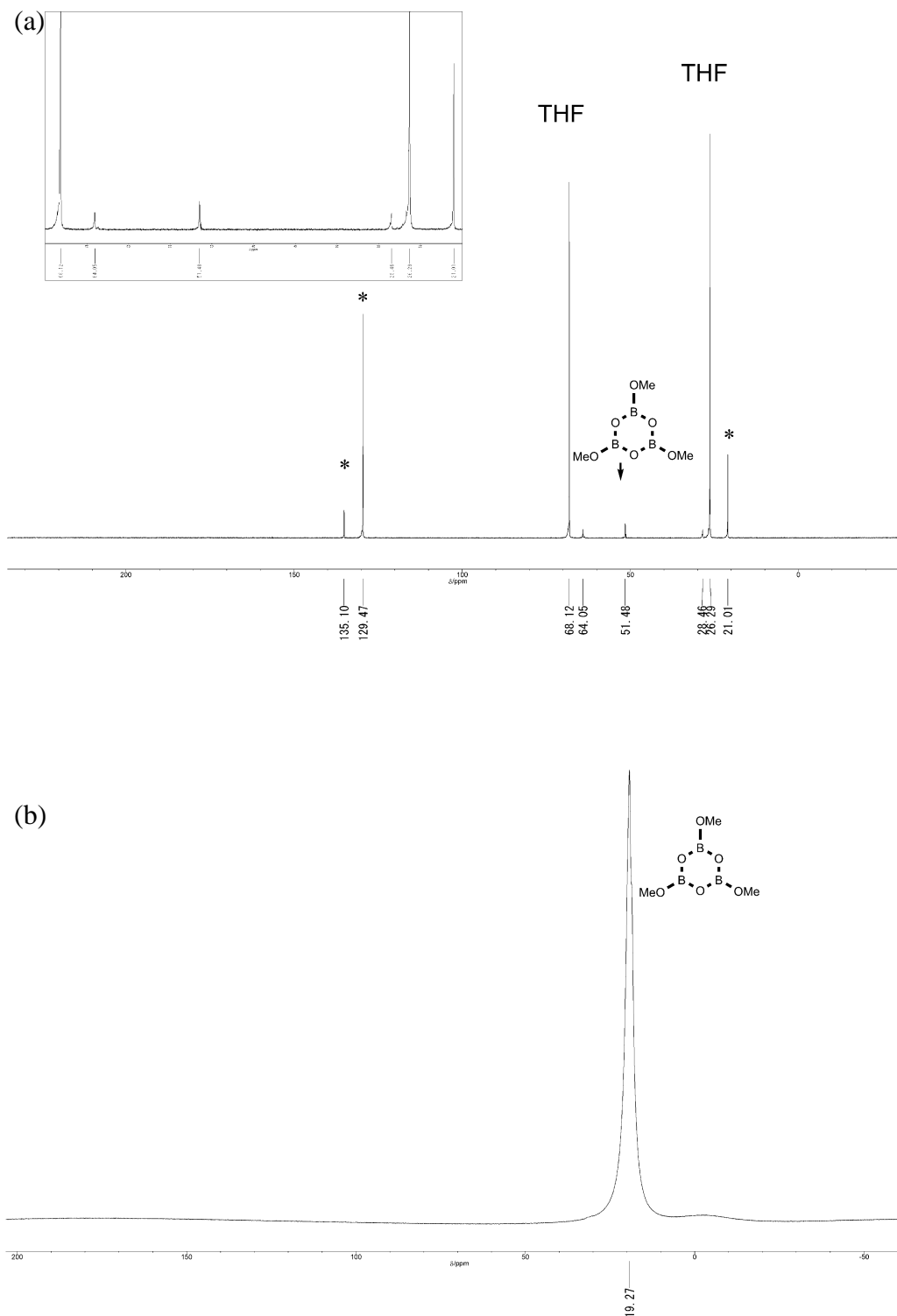


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ (top) and $^{11}\text{B}\{^1\text{H}\}$ (bottom) NMR spectra recorded after 12 h for the reaction of purified $\text{BH}_3 \cdot \text{THF}$ with CO_2 in the presence of HCOONa . The signals with “*” are those of *p*-xylene added as an intensity standard. The inset of (a) is the magnification of 20 – 70 ppm.

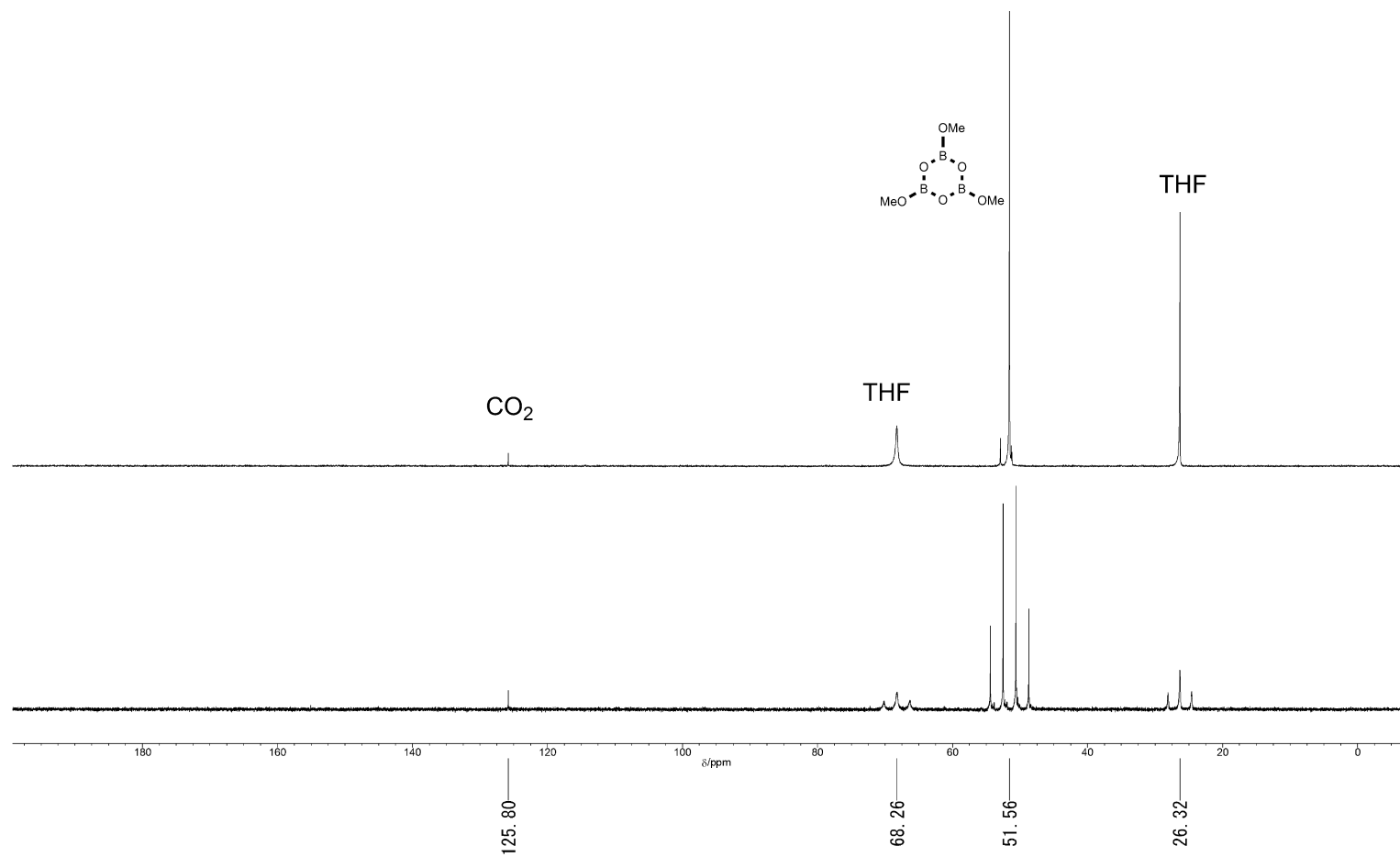


Figure S5. Proton-decoupled (top) and non-decoupled (bottom) ^{13}C NMR spectra recorded after 2.5 h for the reaction of commercial $\text{BH}_3 \cdot \text{THF}$ (Tokyo Chemical Industry) with $^{13}\text{CO}_2$.

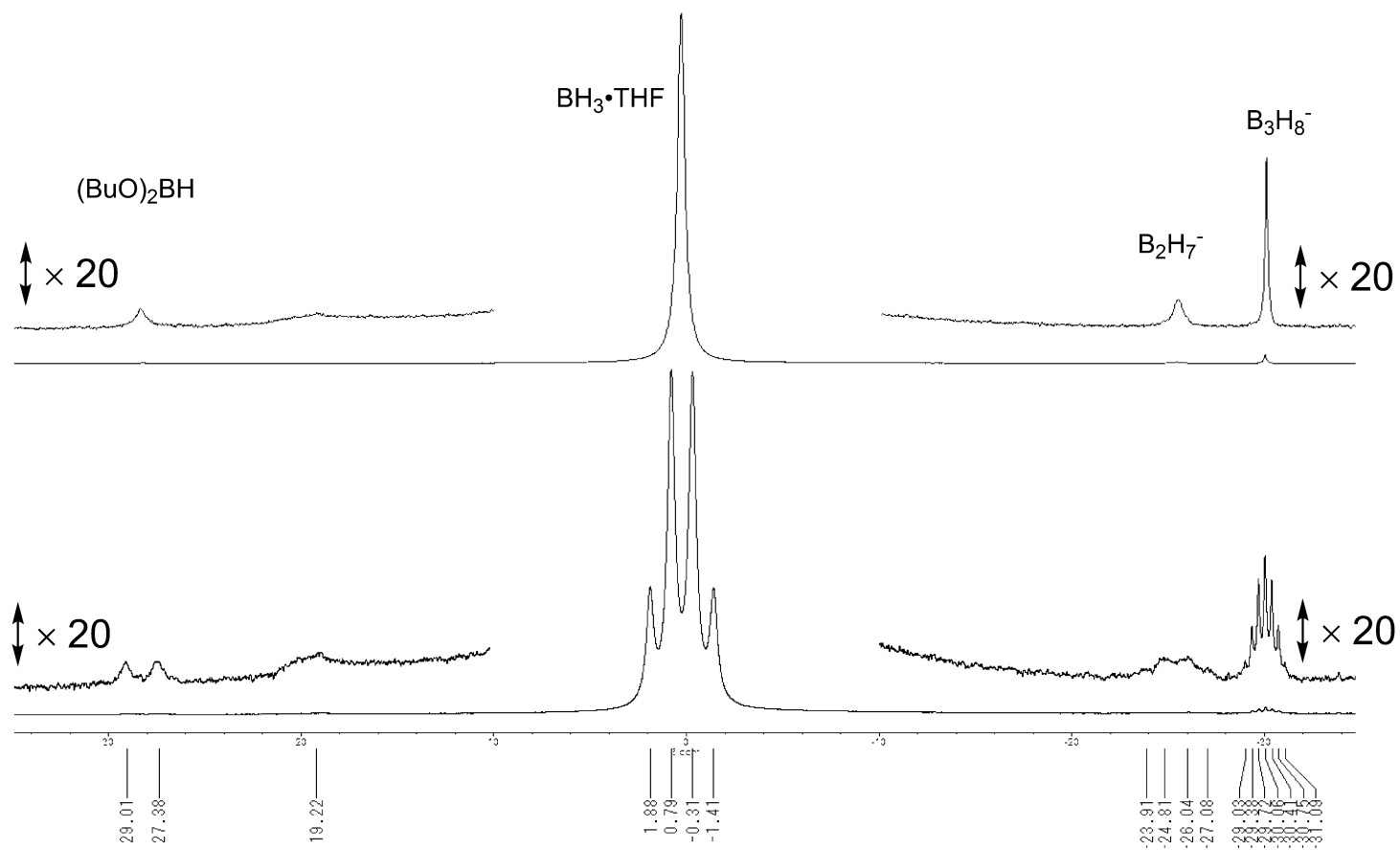


Figure S6. Proton-decoupled (top) and non-decoupled (bottom) ^{11}B NMR spectra of commercial $\text{BH}_3\cdot\text{THF}$ (Tokyo Chemical Industry).

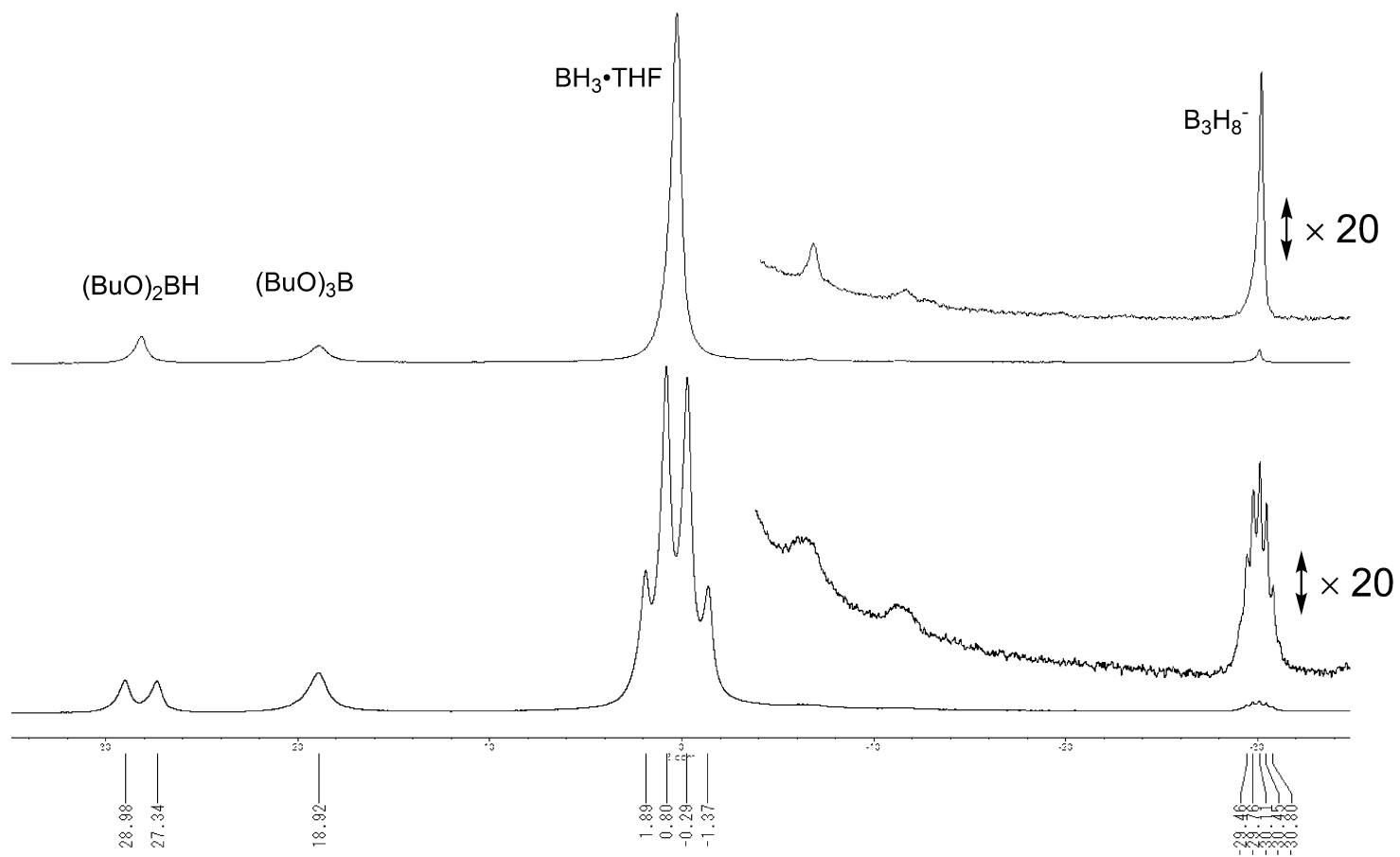


Figure S7. Proton-decoupled (top) and non-decoupled (bottom) ^{11}B NMR spectra of commercial $\text{BH}_3 \cdot \text{THF}$ (Aldrich).

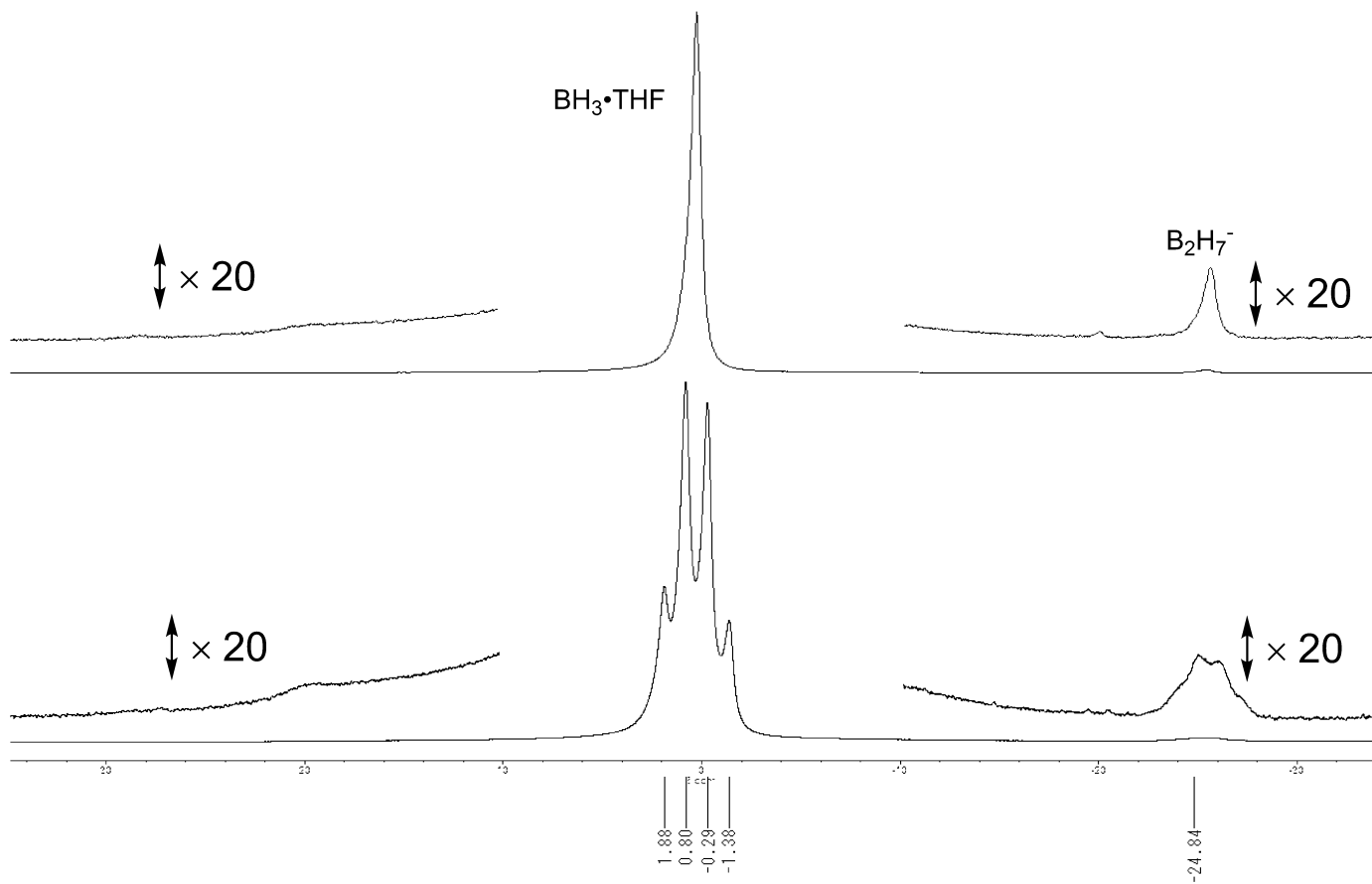


Figure S8. Proton-decoupled (top) and non-decoupled (bottom) ^{11}B NMR spectra of purified $\text{BH}_3\cdot\text{THF}$ to which 0.5 mol % of NaBH_4 was added. The BH_4^- is converted to B_2H_7^- by the reaction with BH_3 .