

Supporting Information

Cobalt catalysed hydroboration of CO₂

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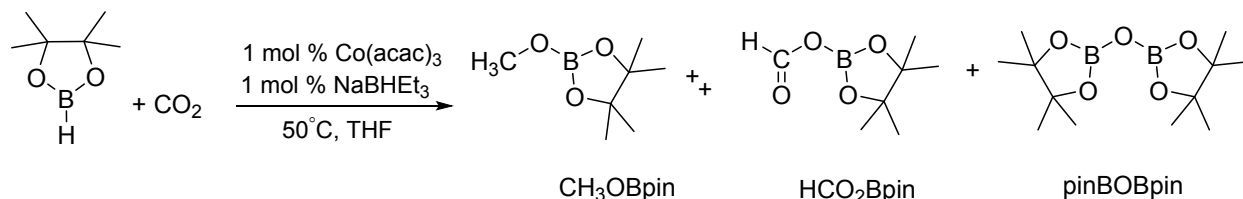
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General Considerations. All reagents were purchased from Sigma-Aldrich and Alfa-Aesar, and were used without further purification unless otherwise noted. All preparations were performed under an atmosphere of dry argon using Schlenk and glove box techniques unless otherwise noted. Solvents (Benzene- d_6 , Toluene- d_8) were dried over activated molecular sieves (4Å) prior to usage; THF- d_8 was dried and distilled over CaH_2 . ^1H , ^{11}B , and ^{13}C NMR spectra were recorded on a Jeol 400 MHz spectrometer at 300K unless otherwise noted. ^1H NMR spectra were referenced to the solvent residual peak (THF- d_8 , δ 3.58 ppm, Benzene- d_6 , δ 7.16 ppm, Toluene- d_8 , δ 2.08, Cyclohexane- d_{12} , δ 1.38 ppm, Dichloromethane- d_2 , δ 5.32 ppm and Chloroform- d δ 7.26 ppm). ^{13}C NMR were referenced to the solvent residual peak (THF- d_8 , δ 67.21 ppm). ^{11}B NMR were referenced to $\text{BF}_3 \cdot (\text{OEt})_2$ as external standard: HBPIn (THF- d_8 , δ 27.34 ppm and δ 28.7 ppm), HBCat (THF- d_8 , δ 23.7 ppm and δ 25.1 ppm), $\text{BH}_3 \cdot \text{S}(\text{Me})_2$ (THF- d_8 , δ - 21.3 ppm), B_2Pin_2 (THF- d_8 , δ 31.3 ppm).

General procedure for hydroboration of CO_2 with HBPIn



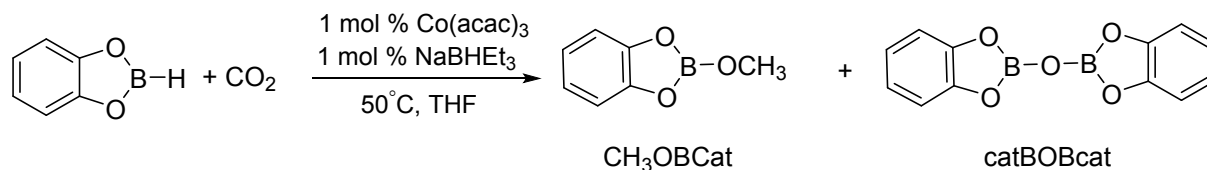
A pre-weighed oven dried shell vial was charged with 1 mol % $\text{Co}(\text{acac})_3$ (0.356 mg, 0.001 mmol). It was dissolved in 0.4 mL THF- d_8 , and transferred to an oven dried J-Young tube. 1 mol % NaBHET_3 (1 μL , 0.001 mmol, 1M in THF) was added and the reaction mixture turned into a clear light yellow solution after stirring for 1 minute. A separate pre-weighed vial was charged with HBPIn (12.8 mg, 0.1 mmol) and dissolved in THF- d_8 (0.3 mL); it was then transferred to the J-Young tube containing the reaction mixture. The reaction mixture was degassed by three cycles of freeze-pump-thaw, and backfilled with CO_2 for \sim 2 minutes. The J-Young NMR tube was then placed in a pre-heated oil bath at 50°C . The progress of the reaction was monitored by ^1H and ^{11}B over time. ^1H NMR yield was determined by adding mesitylene as internal standard.

HCO_2Bpin : ^1H NMR (400 MHz, THF- d_8): δ 8.29 (s, HCO_2Bpin); ^{11}B NMR (128.4 MHz, THF- d_8): δ 21.7 (s, br); ^{13}C NMR (100 MHz, THF- d_8): δ 159 ppm, 84.5 ppm.

pinBOBpin: ^1H NMR (400 MHz, THF- d_8): 1.18 (s, 24H); ^{11}B NMR (128.4 MHz, THF- d_8): δ 21.2 (s, br); ^{13}C NMR(100 MHz, THF- d_8): δ 83.15 ppm.

CH_3OBpin : ^1H NMR (400 MHz, THF- d_8): 3.50 (s, CH_3OBpin); ^{11}B NMR (128.4 MHz, THF- d_8): δ 22.03 (s, br).

General procedure for hydroboration of CO₂ with HBCat

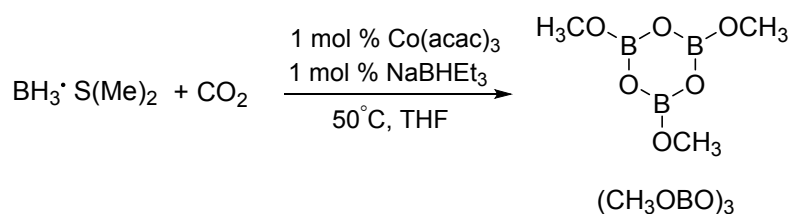


A pre-weighed oven dried shell vial was charged with 1 mol % Co(acac)₃ (0.356 mg, 0.001 mmol). It was dissolved in 0.4 mL THF-*d*₈, and transferred to an oven dried J-Young tube. 1 mol % NaHBET₃ (1 μL, 0.001 mmol, 1M in THF) was added and the reaction mixture turned into a clear light yellow solution after stirring for 1 minute. A separate pre-weighed vial was charged with HBCat (11.99 mg, 0.1 mmol) and dissolved in THF- *d*₈ (0.3 mL); it was then transferred to the J-Young tube containing the reaction mixture. The reaction mixture was degassed by three cycles of freeze-pump-thaw, and backfilled with CO₂ for ~ 2 minutes. The J-Young NMR tube was then placed in a pre-heated oil bath at 50°C. The progress of the reaction was monitored by ¹H and ¹¹B over time. ¹H NMR yield was determined by adding mesitylene as internal standard.

CH₃OBCat: ¹H NMR (400 MHz, THF- *d*₈): 3.78 (s, CH₃OBCat); ¹¹B NMR (128.4 MHz, THF- *d*₈): δ 23.4 (s, br); ¹³C NMR (100 MHz, THF- *d*₈): δ 53.3 ppm

CatBOBcat: ¹¹B NMR (128.4 MHz, THF- *d*₈): δ 17.7 (s, br); ¹³C NMR (100 MHz, THF- *d*₈): δ 150.2

General procedure for hydroboration of CO₂ with BH₃•S(Me)₂



A pre-weighed oven dried shell vial was charged with 1 mol % Co(acac)₃ (0.356 mg, 0.001 mmol). It was dissolved in 0.4 mL THF-*d*₈, and transferred to an oven dried J-Young tube. 1 mol % NaHBET₃ (1 μL, 0.001 mmol, 1M in THF) was added and the reaction mixture turned into a clear light yellow solution after stirring for 1 minute. A separate pre-weighed vial was charged with BH₃•S(Me)₂ (7.60 mg, 0.1 mmol) and dissolved in THF- *d*₈ (0.3 mL); it was then transferred to the J-Young tube containing the reaction mixture. The reaction mixture was degassed by three cycles of freeze-pump-thaw, and backfilled with CO₂ for ~ 2 minutes. The J-Young NMR tube was then placed in a pre-heated oil bath at 50°C. The progress of the reaction was monitored by ¹H and ¹¹B over time. ¹H NMR yield was determined by adding mesitylene as internal standard.

$(\text{CH}_3\text{OBO})_3$: ^1H NMR (400 MHz, THF- d_8): δ 3.54, (s, $(\text{CH}_3\text{OBO})_3$), ^{11}B NMR (128.4 MHz, THF- d_8): δ 19.3 ppm (s, br). ^{13}C NMR (100 MHz, THF- d_8): δ 51.3 ppm.

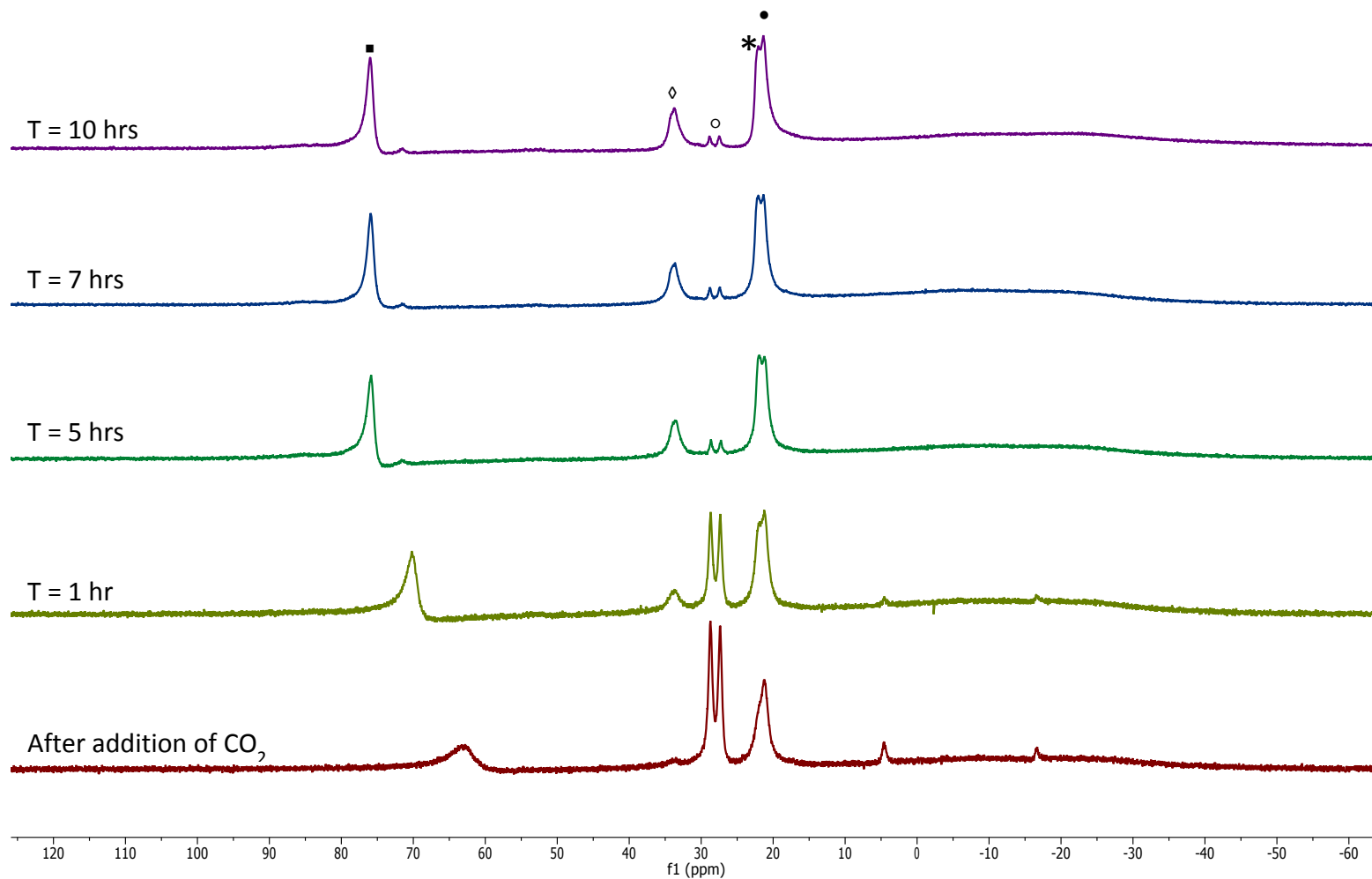


Figure S 1 ^{11}B NMR spectra for hydroboration of CO_2 with 10 mol % $\text{Co}(\text{acac})_3$, 10 mol % NaHBET_3 , and HBPIn (1.0 mmol) at various time intervals in THF. (■) represents the ^{11}B peak for BET_3 at 76 ppm, (*) represents the peak for CH_3OBPin at 22.03ppm, (●) represents the peak for pinBOBpin at 21.2 ppm, (○) represents the peak for unreacted HBPIn at 27.3 ppm and 28.7 ppm and (◇) represents the peak for unidentified boron species.

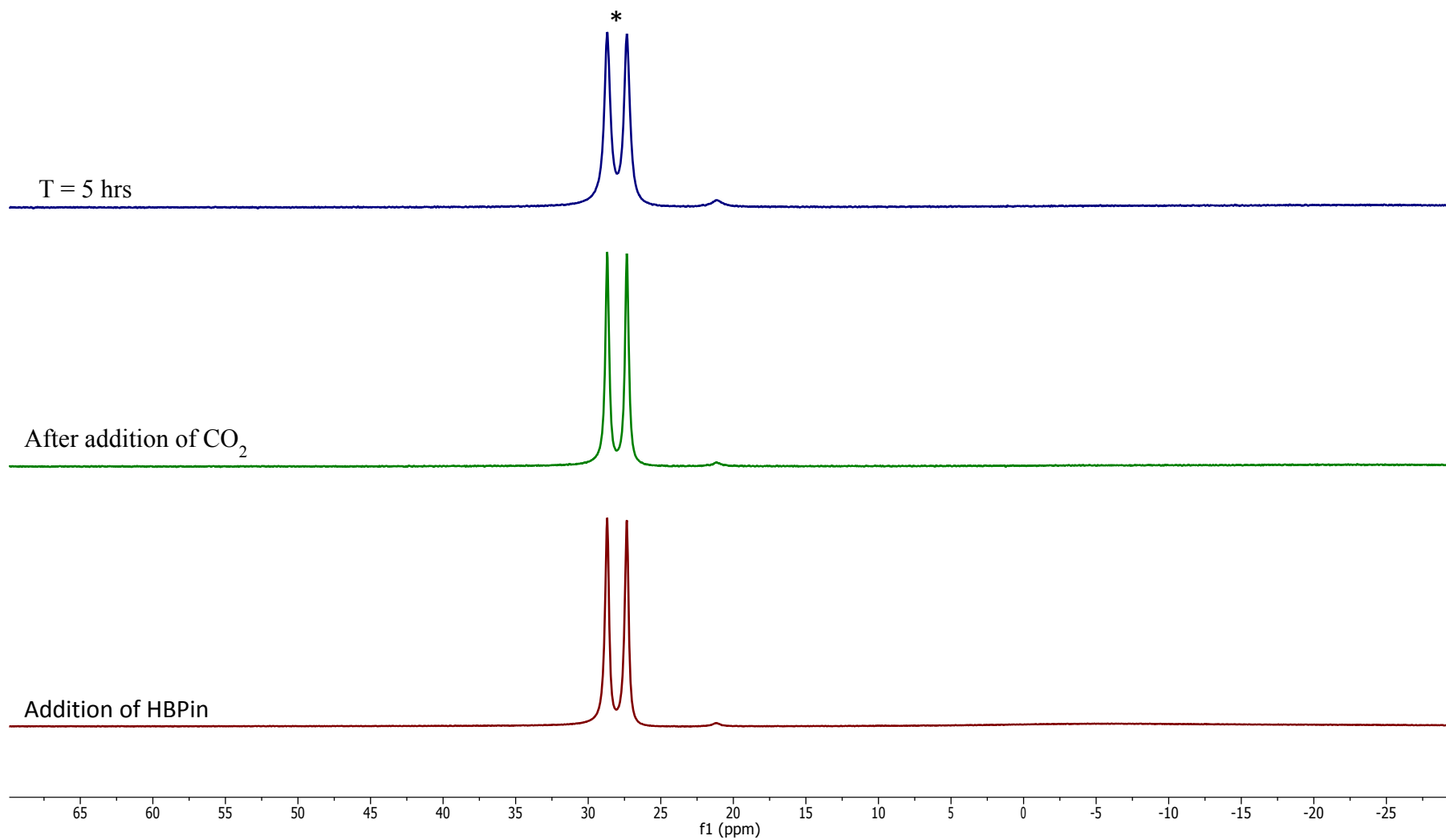


Figure S 2 ^{11}B NMR for hydroboration of CO_2 using 10 mol % $\text{Co}(\text{acac})_3$, and HBPIn (1.0 mmol) in THF. (*) represents the peak for HBPIn at 27.34 ppm and 28.7 ppm.

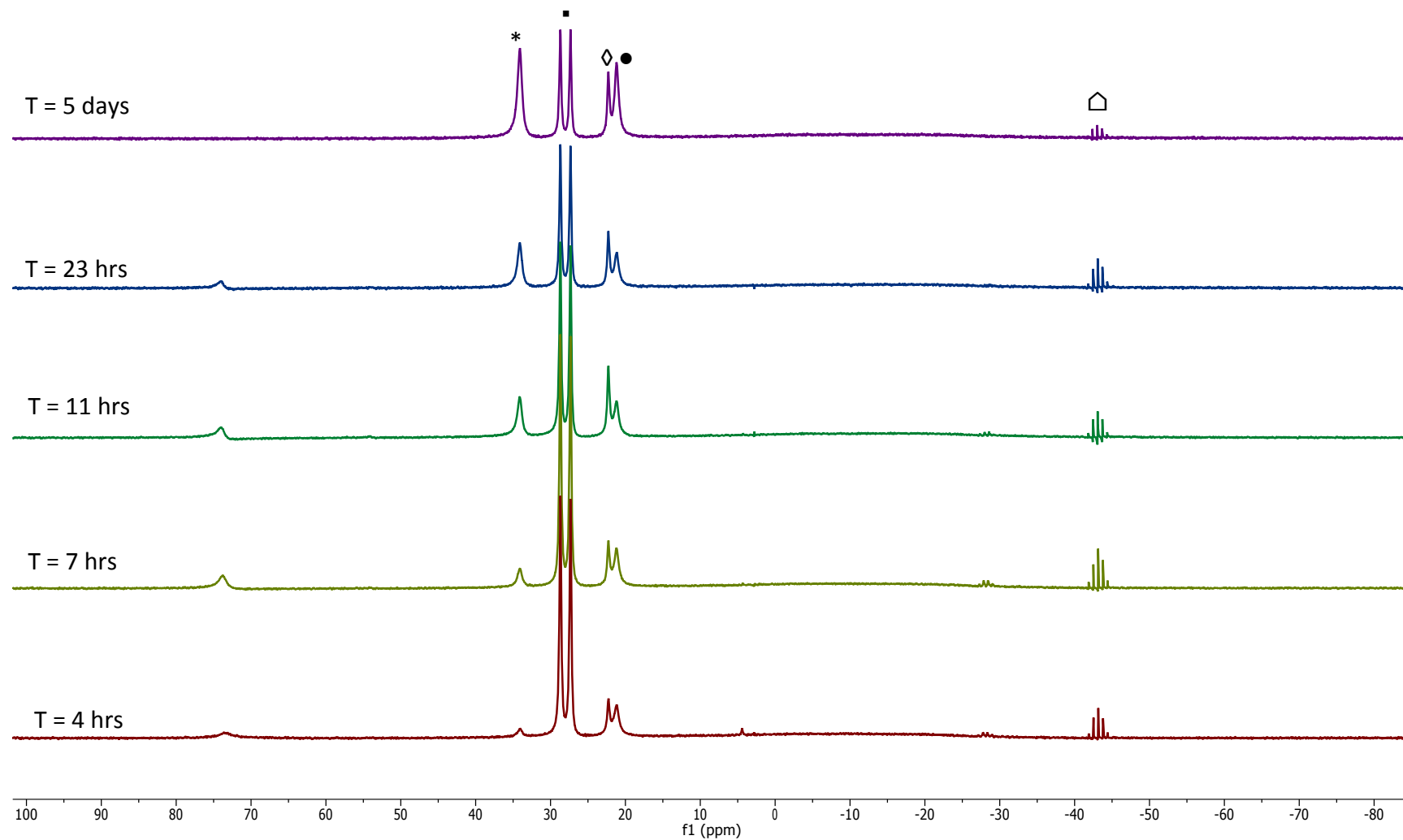


Figure S 3 ^{11}B NMR spectra for hydroboration of CO_2 with 10 mol % NaHBET_3 and HBPin (1.0 mmol) at various time intervals in $\text{THF-}d_8$. (■) represents the ^{11}B peak for HBPin at 27.4 and 28.7 ppm, (◇) represents the peak for $\text{CH}_3\text{-OBPin}$ at 22.3 ppm, (●) represents the peak for pinBOBpin at 21.2 ppm, (△) represents the peak for BH_4^- at -43.0 ppm, and (*) represents the peak for unidentified boron species.

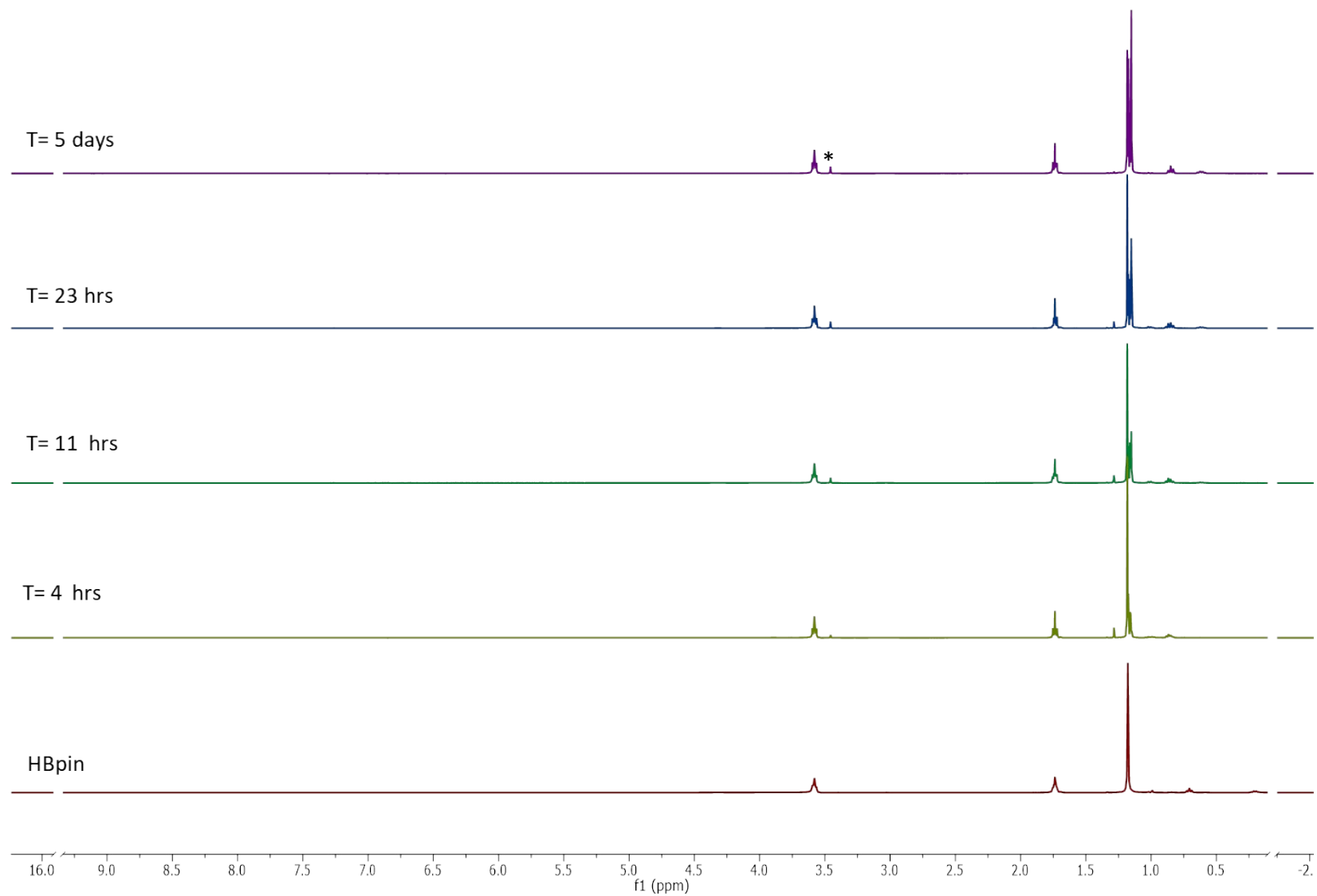


Figure S 4 ¹H NMR spectra for hydroboration of CO₂ with 10 mol % NaHBET₃, and HBpin (1.0 mmol) at various time intervals in THF-*d*₈. (*) represents the peak for CH₃-OBPin at 3.46 ppm.

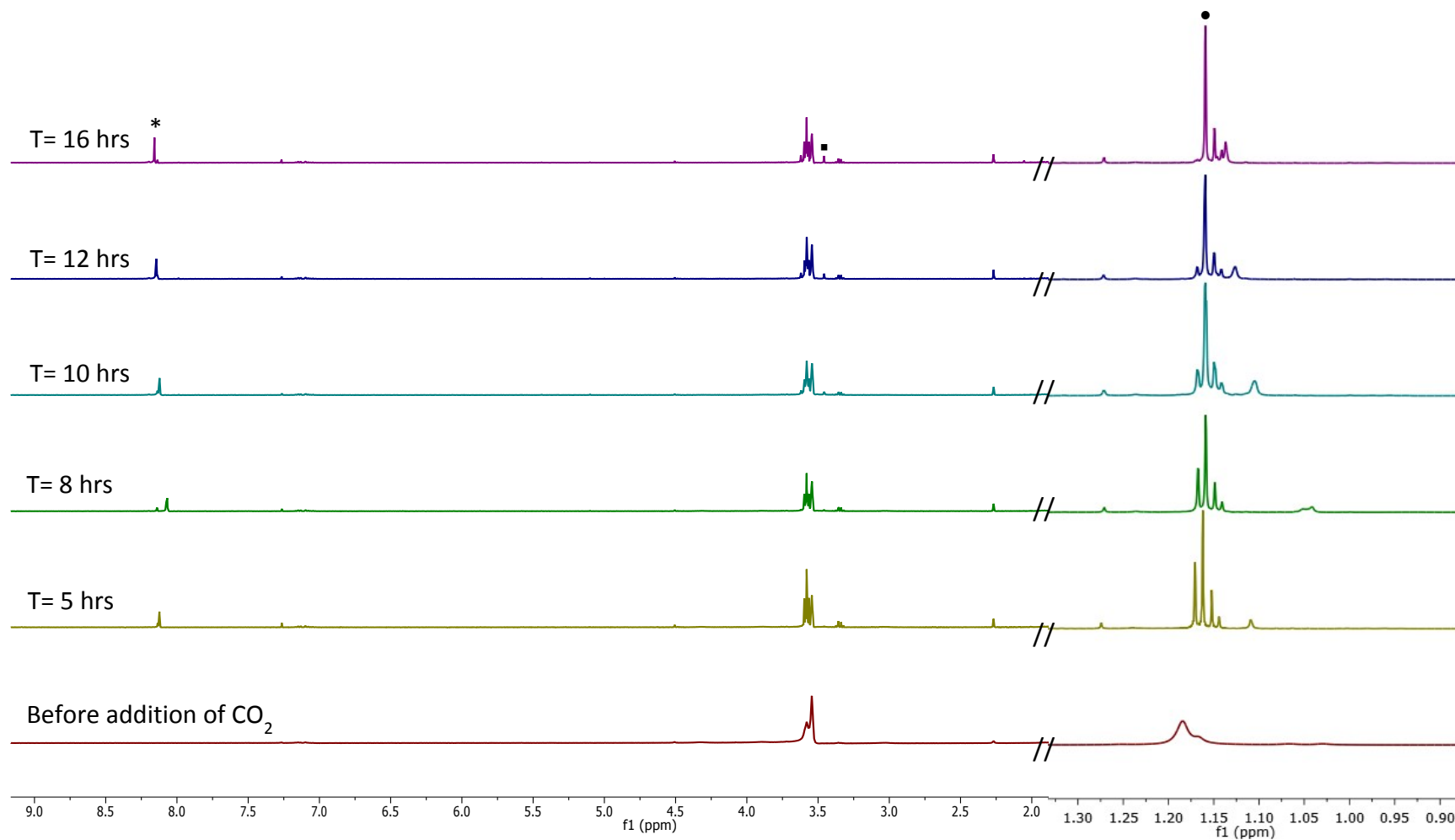


Figure S 5 ^1H NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and HBPIn (0.1 mmol) at various time intervals THF- d_8 . (▣) represents the ^1H peak for $\text{CH}_3\text{-OBPin}$ at 3.46ppm, (*) represents the peak for HCOOBPin at 8.32ppm and (●) represents the peak for pinBOBpin at 1.18 ppm.

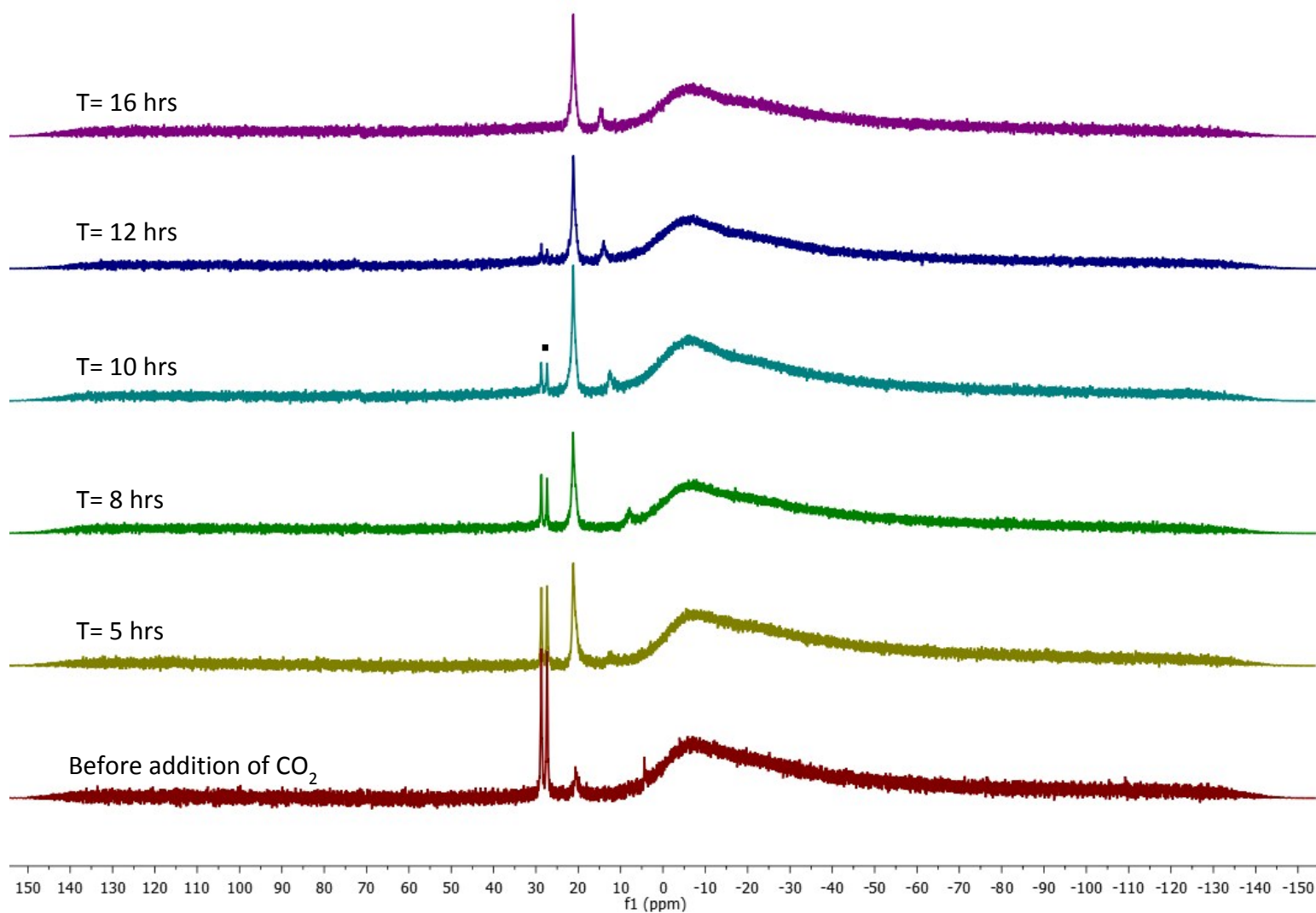


Figure S 6 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and HBPIn (0.1 mmol) at various time intervals in $\text{THF-}d_8$. The (▪) represents the peak for HBpin.

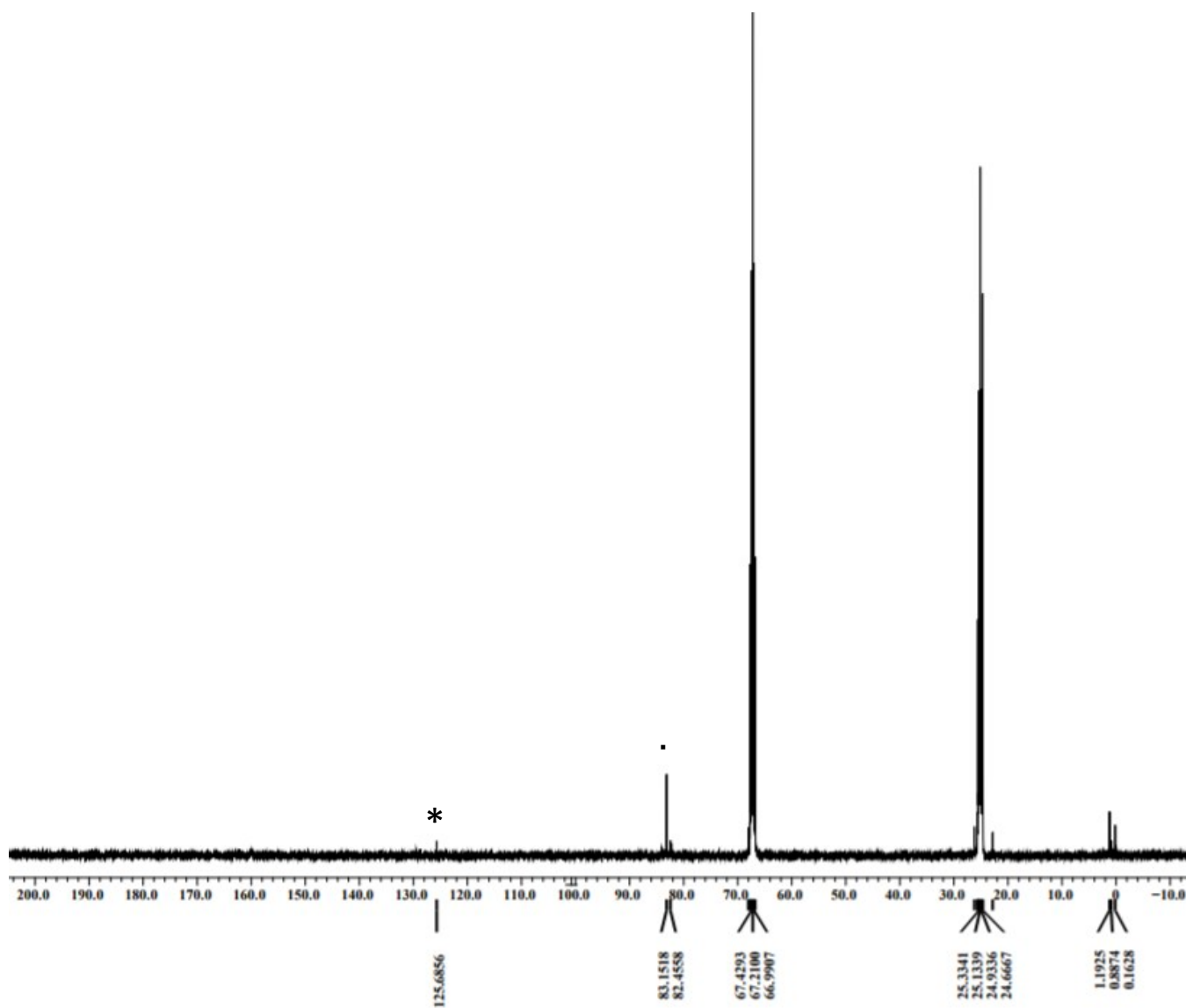


Figure S 7 ^{13}C NMR spectra after hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and HBpin (0.1 mmol) in $\text{THF-}d_8$. (*) represents the peak for CO_2 at 125.6 ppm, and (▪) represents the peak for pinBOBpin at 83.15 ppm.

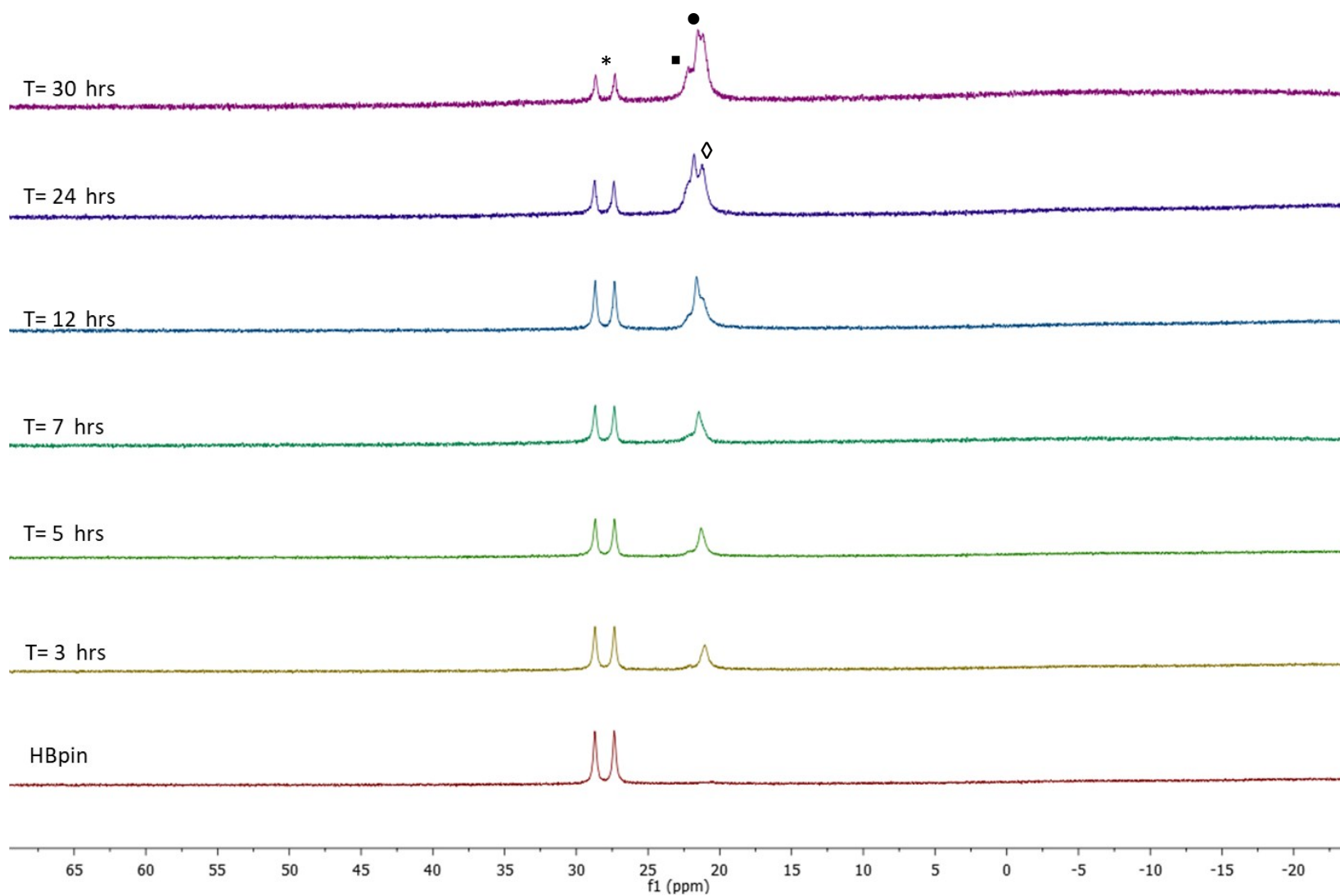


Figure S 8 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % NaHBet_3 , and HBpin (0.1 mmol) at various time intervals THF- d_8 . (*) represents the ^{11}B peak for HBpin at 27.34 ppm, (◻) represents the peak for $\text{CH}_3\text{-OBPin}$ at 22.23ppm, (◊) represents the broad peak for HCOOBPin at 21.8ppm, and (●) represents the peak for pinBOBpin at 21.2ppm.

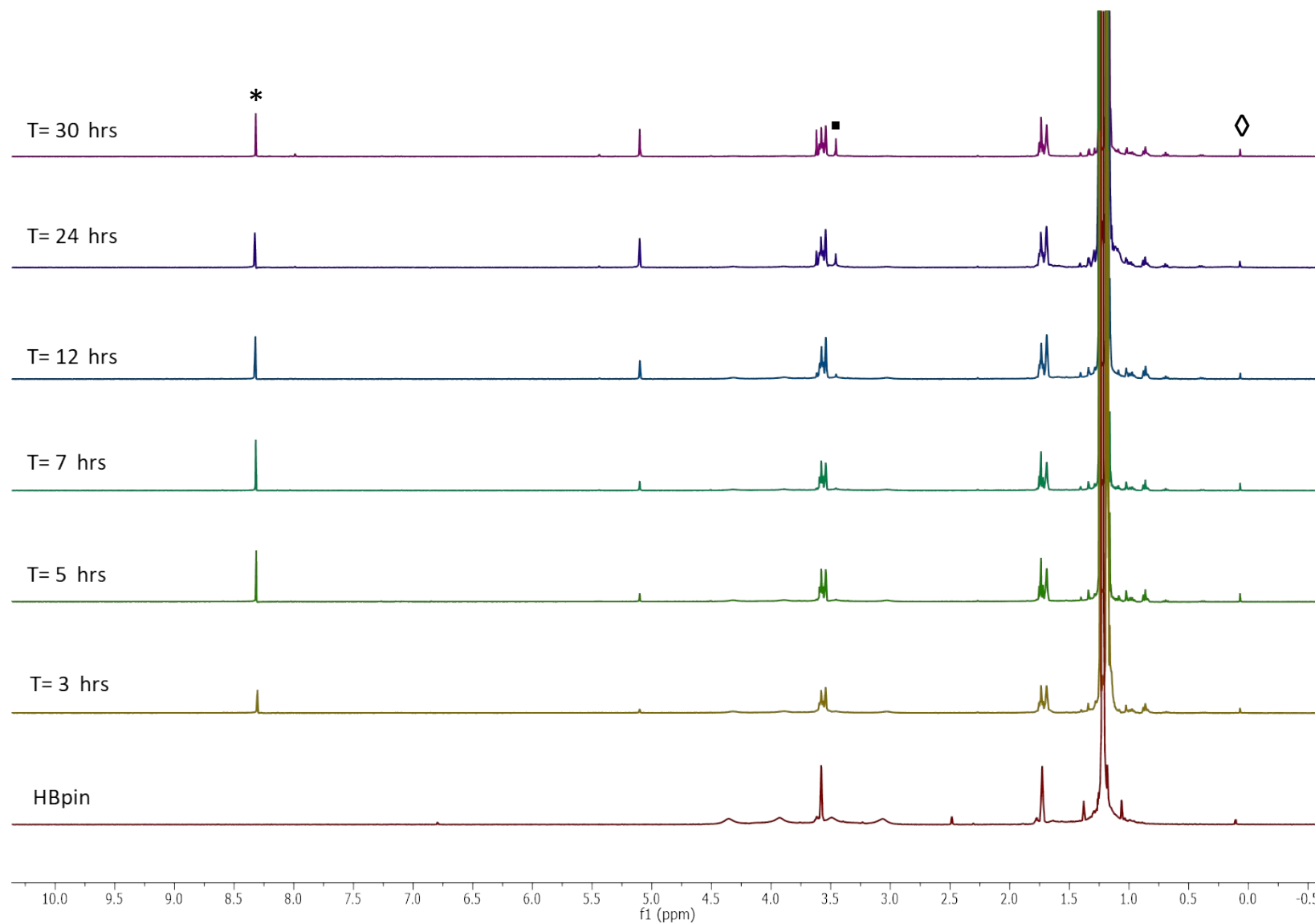


Figure S 9 ¹H NMR spectra for hydroboration of CO₂ with 1 mol % NaHBET₃, and HBpin (0.1 mmol) at various time intervals in THF-*d*₈. (▪) represents the ¹H peak for CH₃-OBPin at 3.46ppm, (*) represents the peak for HCOOBPin at 8.32ppm, (◊) represents the peak for grease.

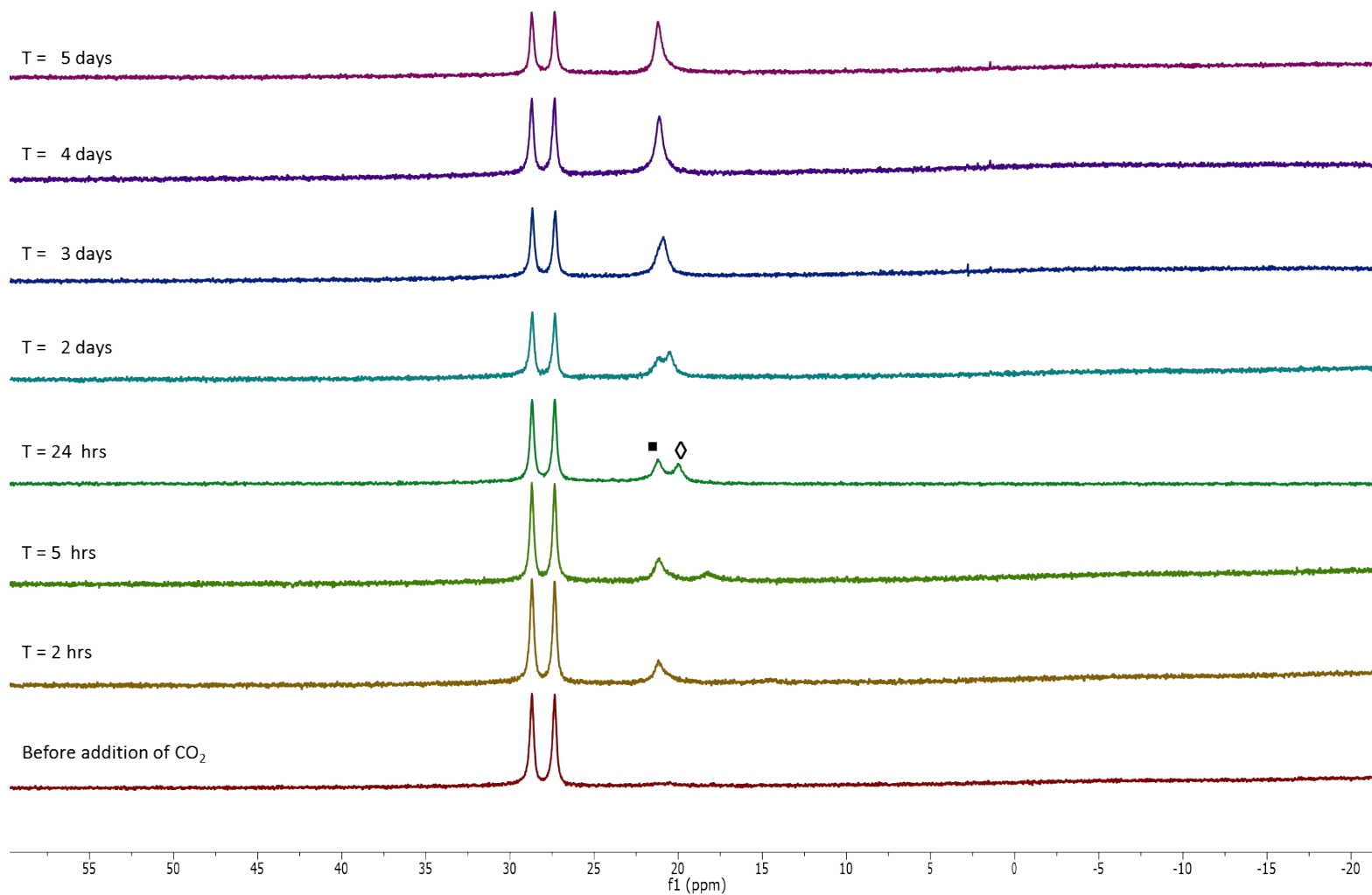


Figure S 10 ^{11}B NMR spectra for hydroboration of CO_2 with and HBpin (0.1 mmol) in the absence of $\text{Co}(\text{acac})_3$ and NaHBEt_3 at various time intervals THF- d_8 . (\blacksquare) represents the ^{11}B peak for pinBOBPin at 21.2ppm, (\blacklozenge) represents the broad peak for HCOOBPin at 20.5 ppm, and (*) represents the peak for HBpin.

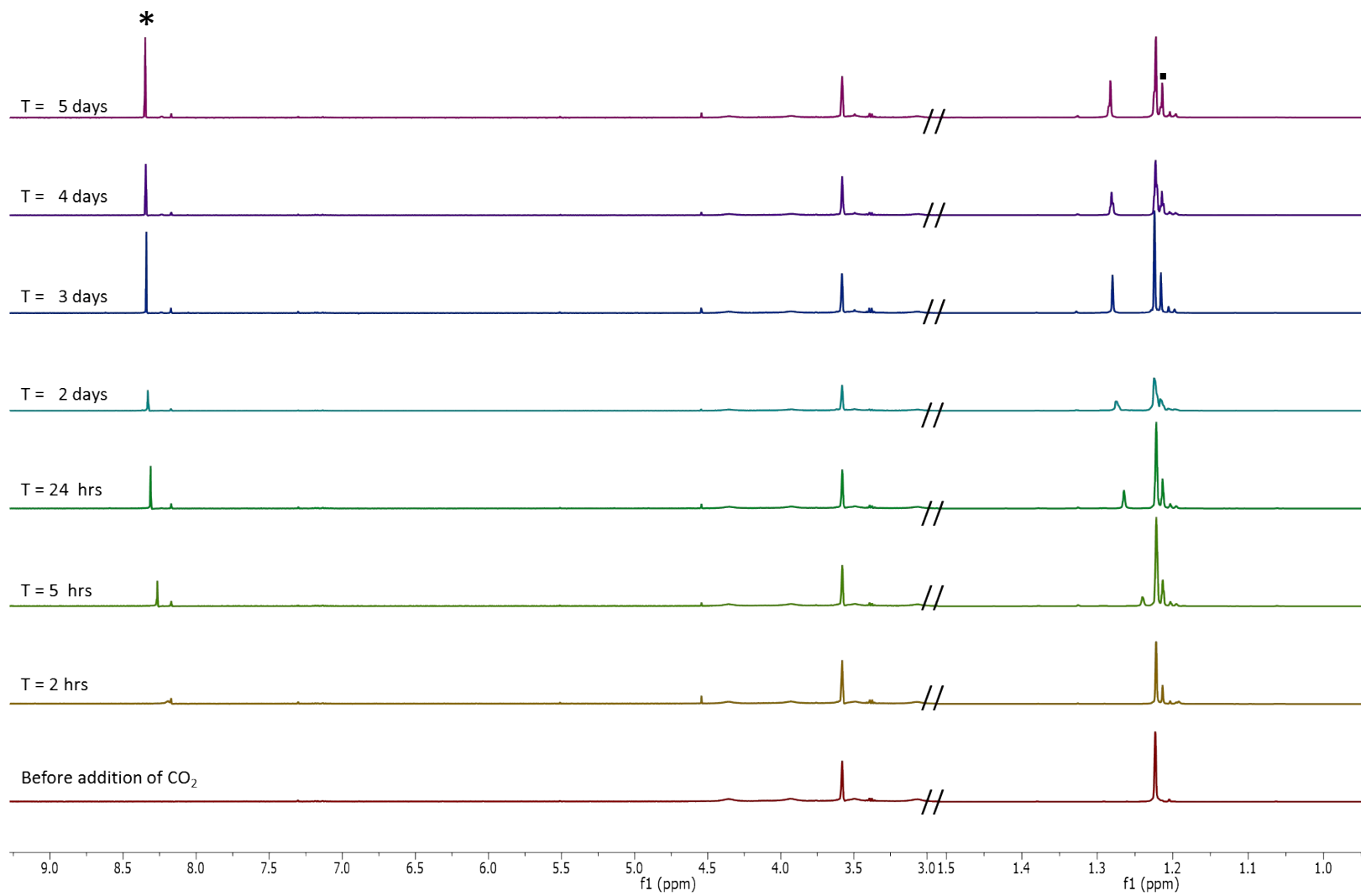


Figure S 11 ^1H NMR spectra for hydroboration of CO_2 with and HBpin (0.1 mmol) in the absence of $\text{Co}(\text{acac})_3$ and NaHBET_3 at various time intervals THF- d_8 . (•) represents the ^1H peak for pinBOBpin at 1.21ppm, and (*) represents the peak for HCOOBPin at 8.32ppm.

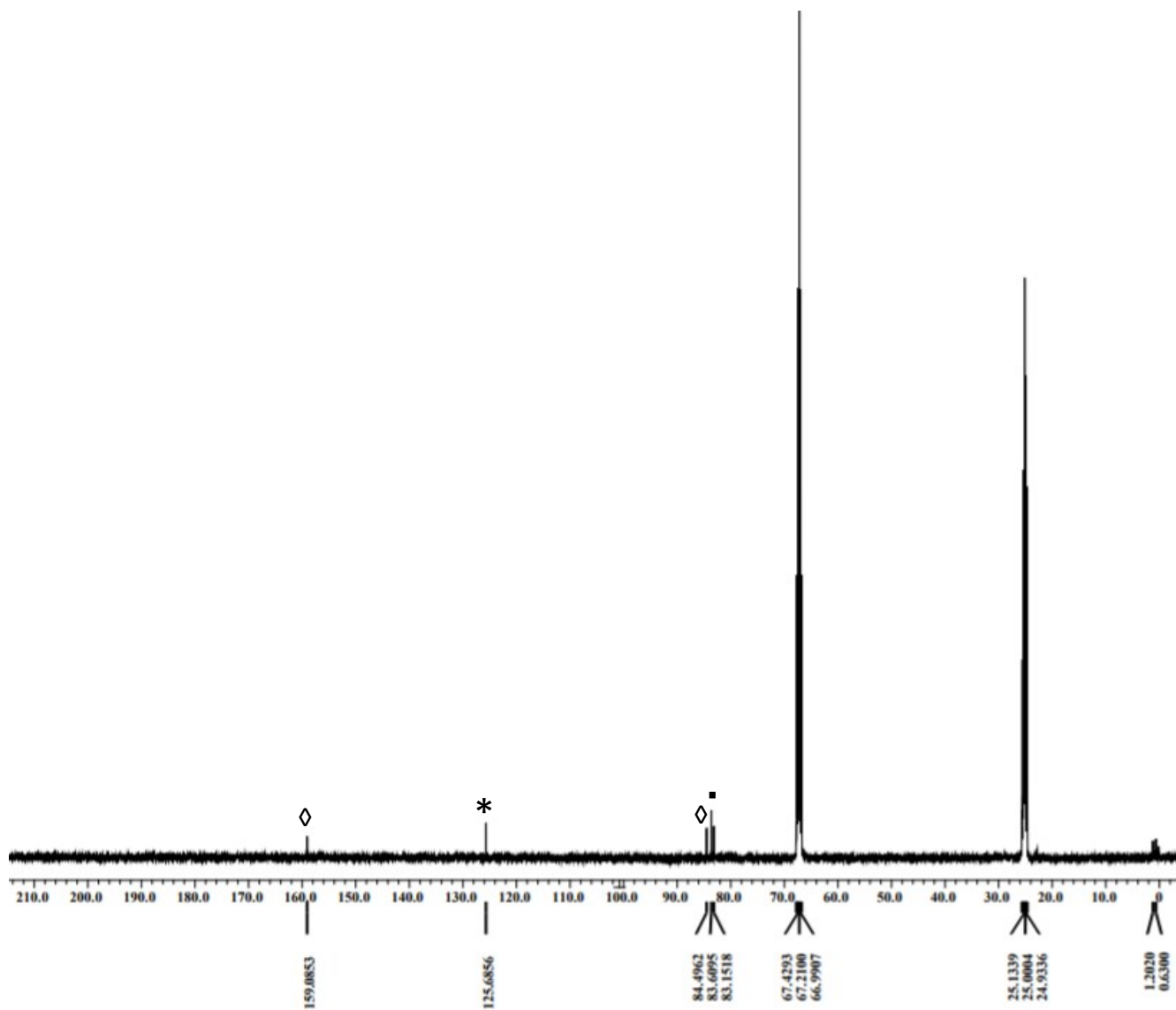


Figure S 12 ^{13}C NMR after hydroboration of CO_2 with HBpin (0.1mmol) in the absence of $\text{Co}(\text{acac})_3$ and NaHBEt_3 THF- d_8 . (\diamond)

represents the peak for HCOOBPin at 159 and 84.49ppm, (*) represents the peak for CO₂, and (•) represents the peak for pinBOBpin at 83.15 ppm.

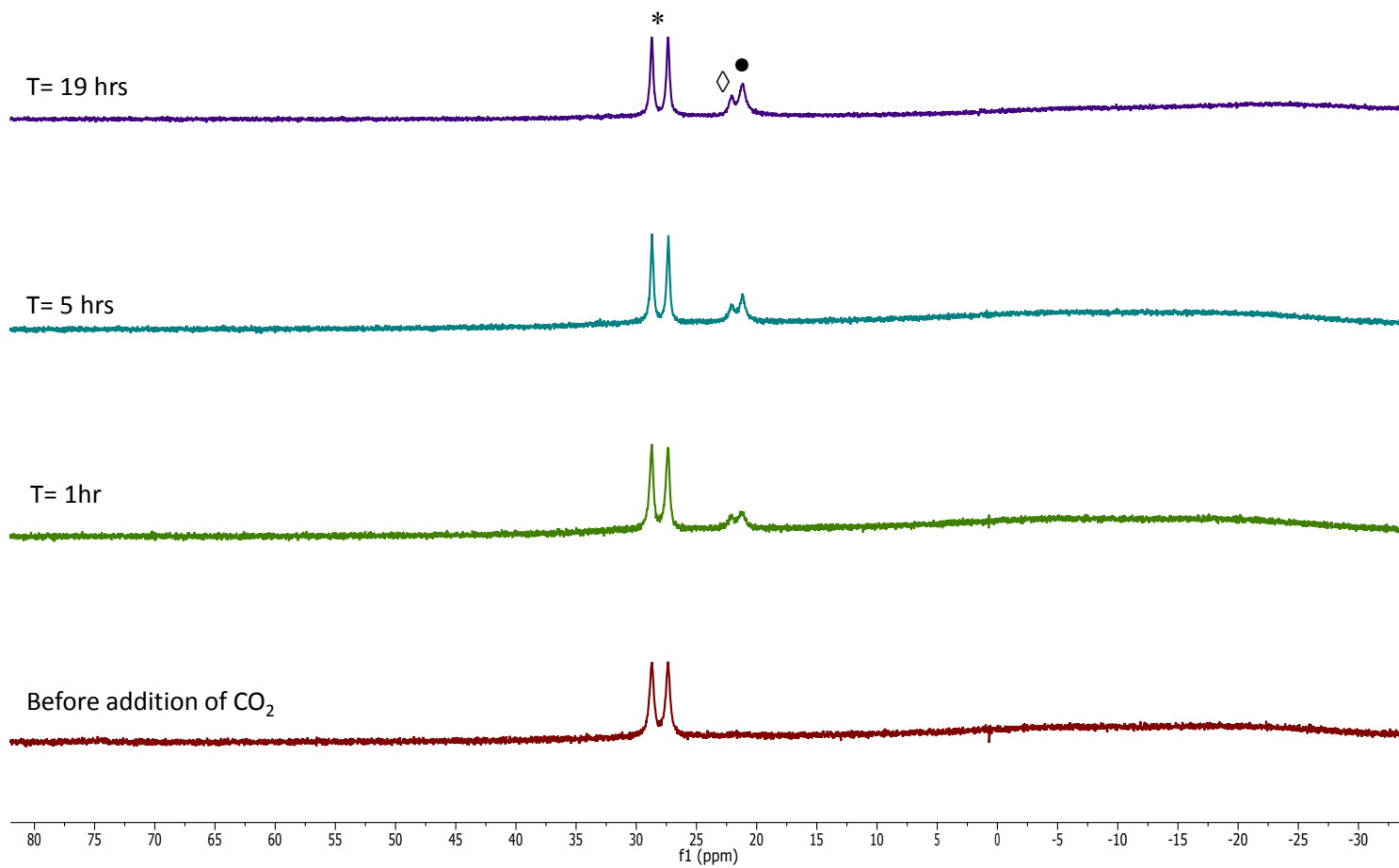


Figure S 13 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % CoBr_2 , 1 mol % NaHBET_3 , and HBPIn (0.1 mmol) at various time intervals in $\text{THF-}d_8$. (●) represents the ^{11}B peak for pinBOBpin at 21.2ppm, (◇) represents the broad peak for CH_3OBPin at 22.2 ppm, and (*) represents the peak for unreacted HBpin.

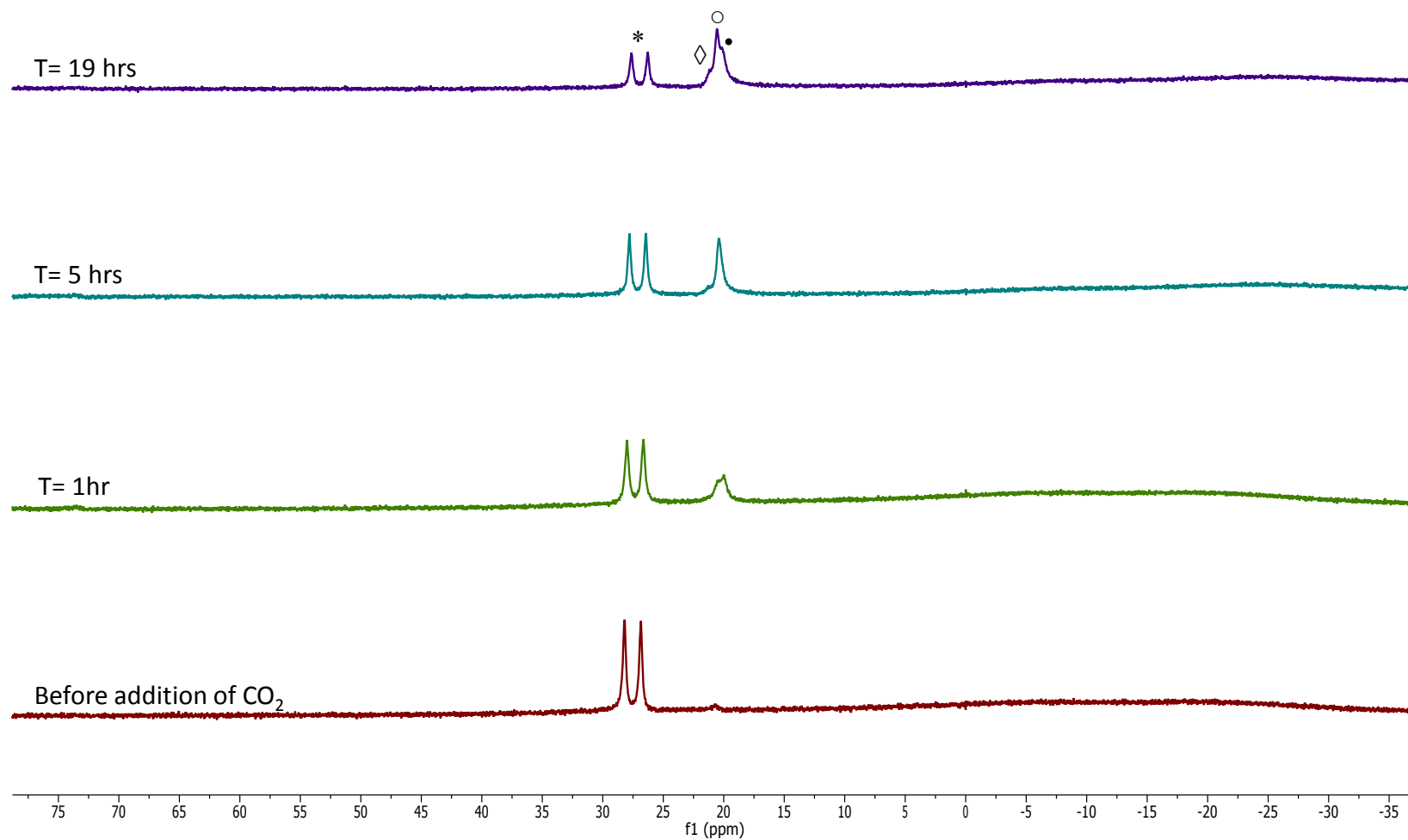


Figure S 14 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_2$, 1 mol % NaHBET_3 , and HBPin (0.1 mmol) at various time intervals in $\text{THF-}d_8$. (•) represents the ^{11}B peak for pinBOBpin at 21.2ppm, (◊) represents the broad peak for CH_3OBPin at 22.2 ppm, (◦) represents the peak for HCOOBpin at 21.7ppm and (*) represents the peak for unreacted HBPin.

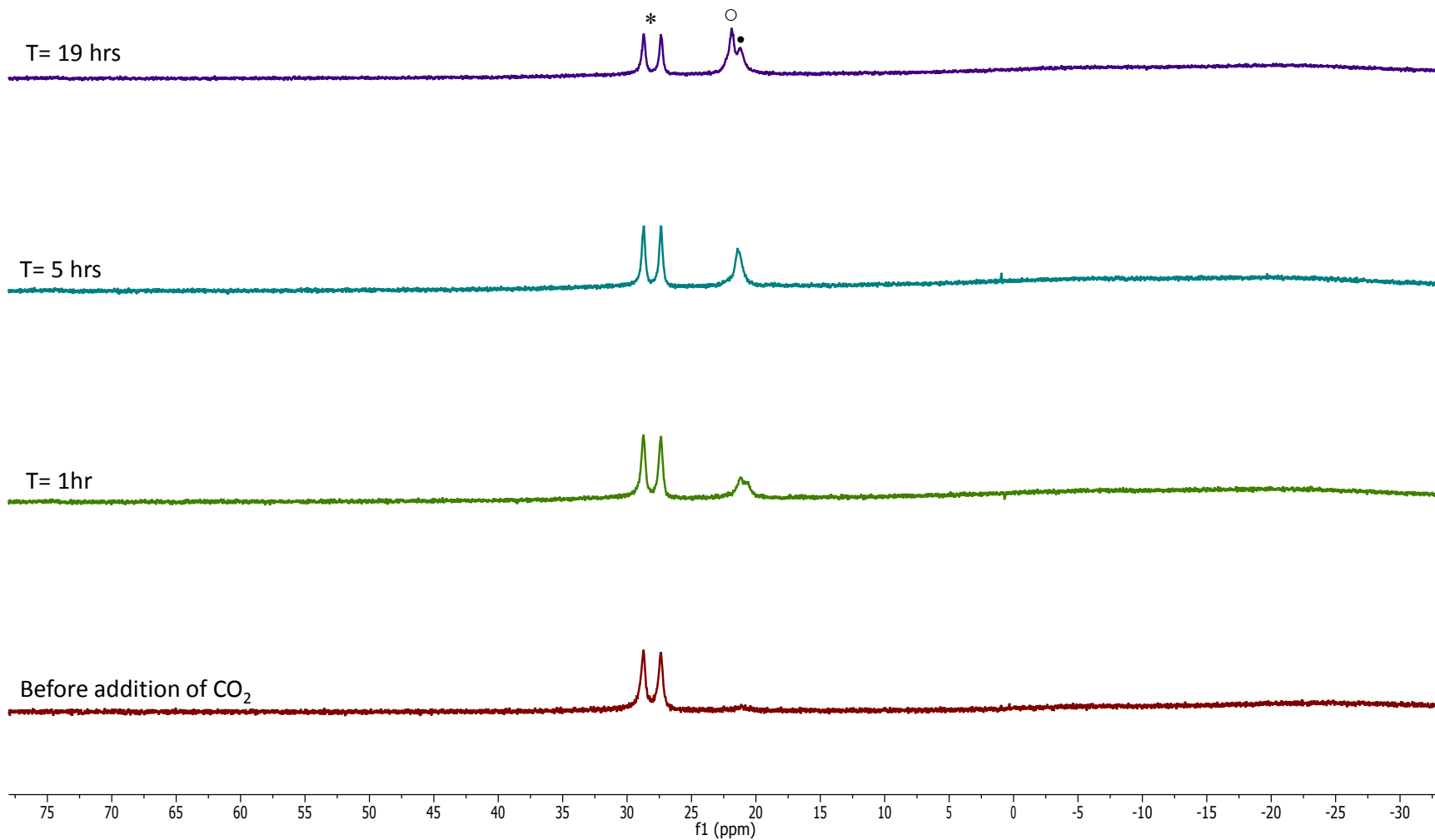


Figure S 15 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % Co(II) Benzoate, 1 mol % NaHBET_3 , and HBPIn (0.1 mmol) at various time intervals in $\text{THF-}d_8$. (•) represents the ^{11}B peak for pinBOBpin at 21.2ppm, (o) represents the peak for HCOOBpin at 21.7ppm and (*) represents the peak for unreacted HBpin.

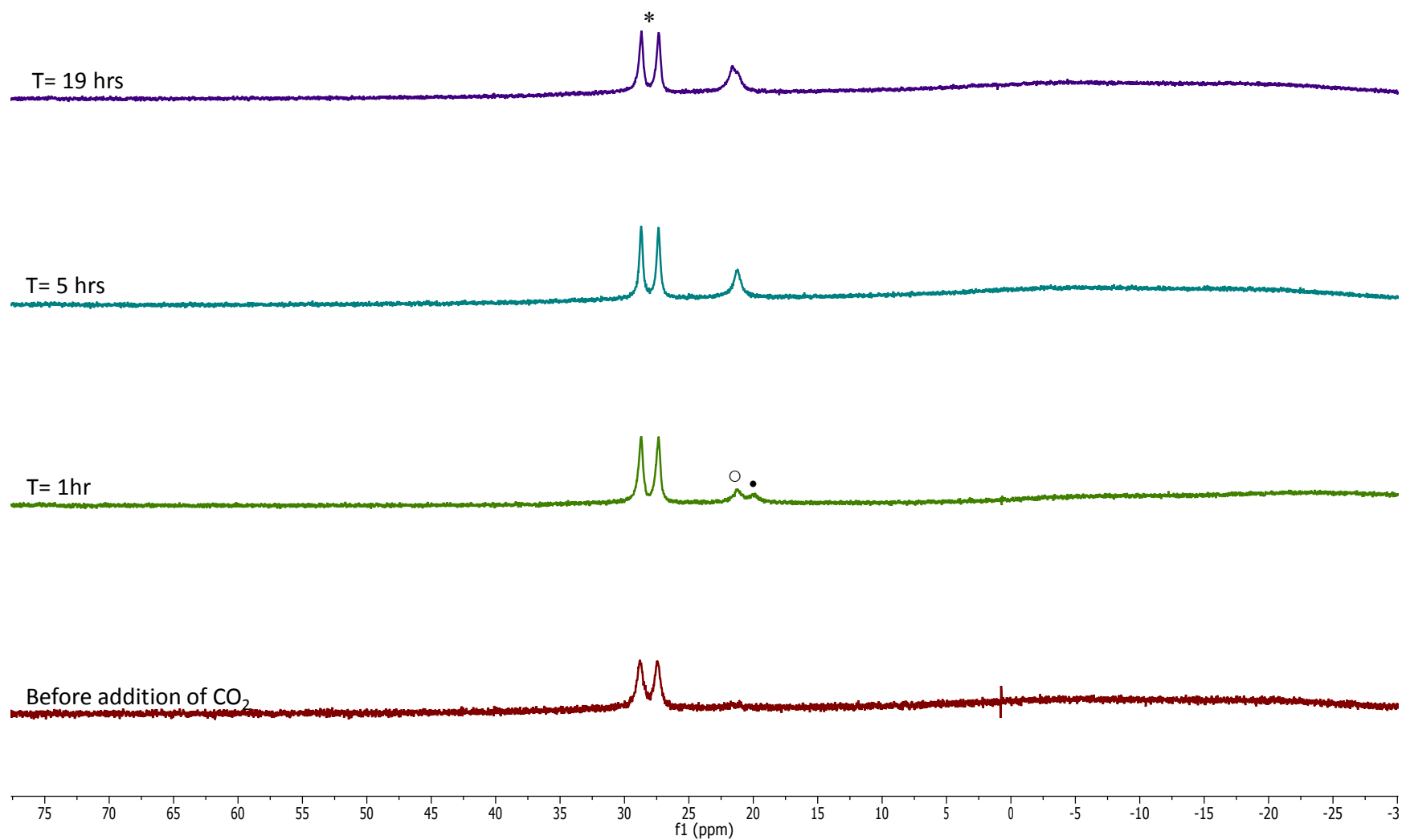


Figure S 16 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{TMHD})_3$, 1 mol % NaHBEt_3 , and HBPIn (0.1 mmol) at various time intervals in $\text{THF-}d_8$. (•) represents the ^{11}B peak for pinBOBpin at 21.2ppm, (o) represents the peak for HCOOBpin at 21.7ppm and (*) represents the peak for unreacted HBPIn.

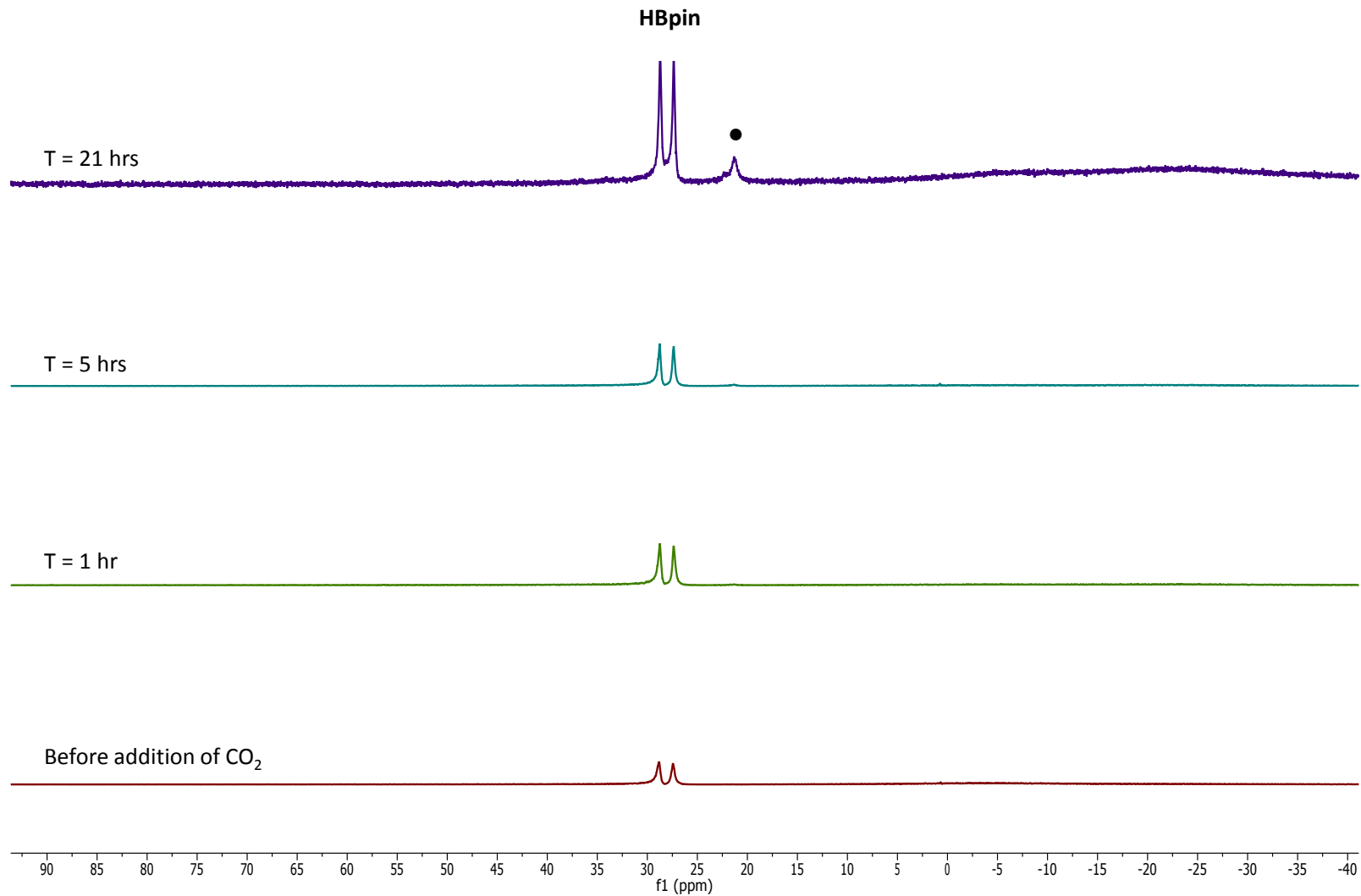


Figure S 17 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and HBPIn (0.1 mmol) at various time intervals in Toluene- d_8 . (●) represents the broad overlapped peak for pinBOBpin and HCOOBpin at 21.2 ppm.

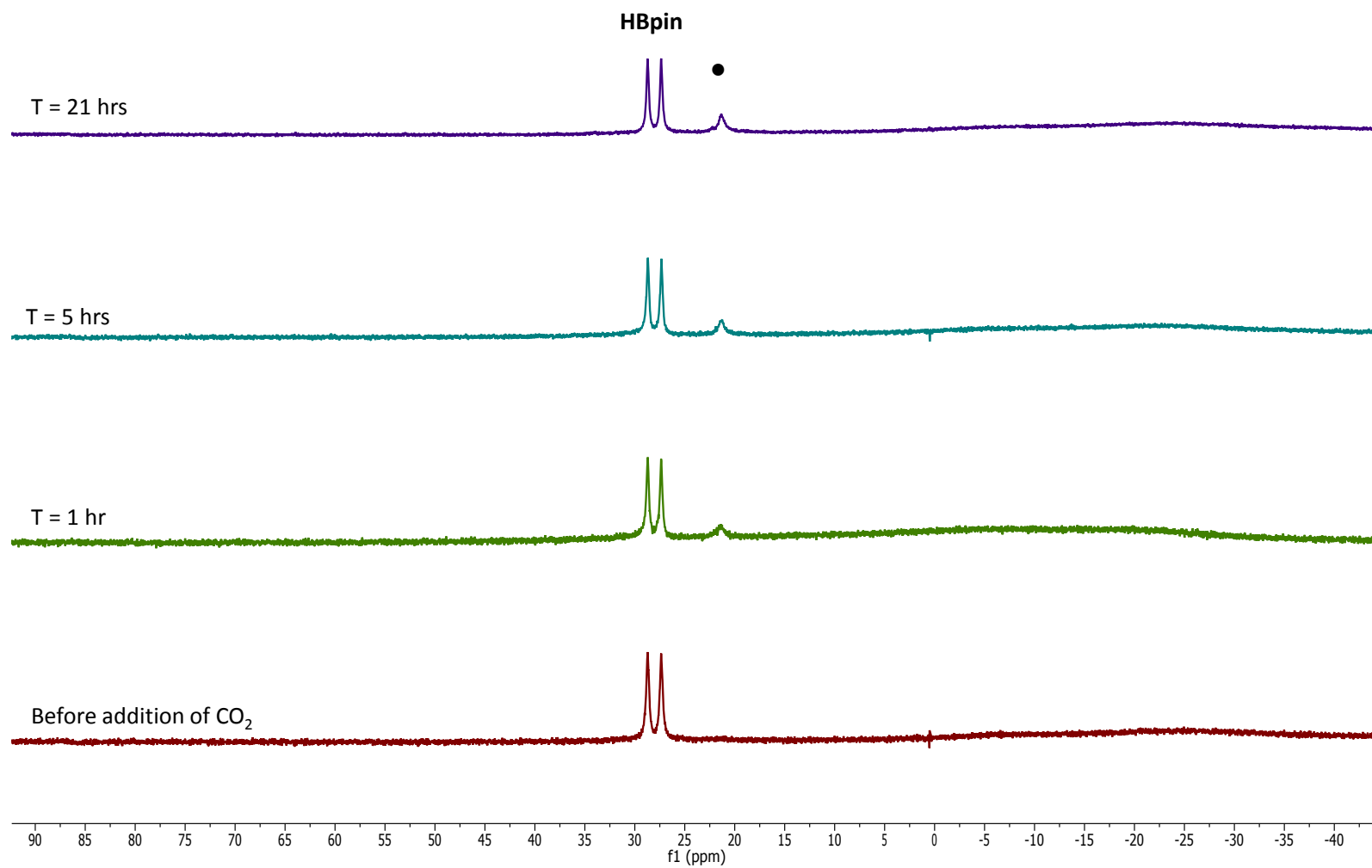


Figure S 18 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBEt_3 , and HBPin (0.1 mmol) at various time intervals in benzene- d_6 . (●) represents the broad peak for pinBOBpin at 21.4 ppm.

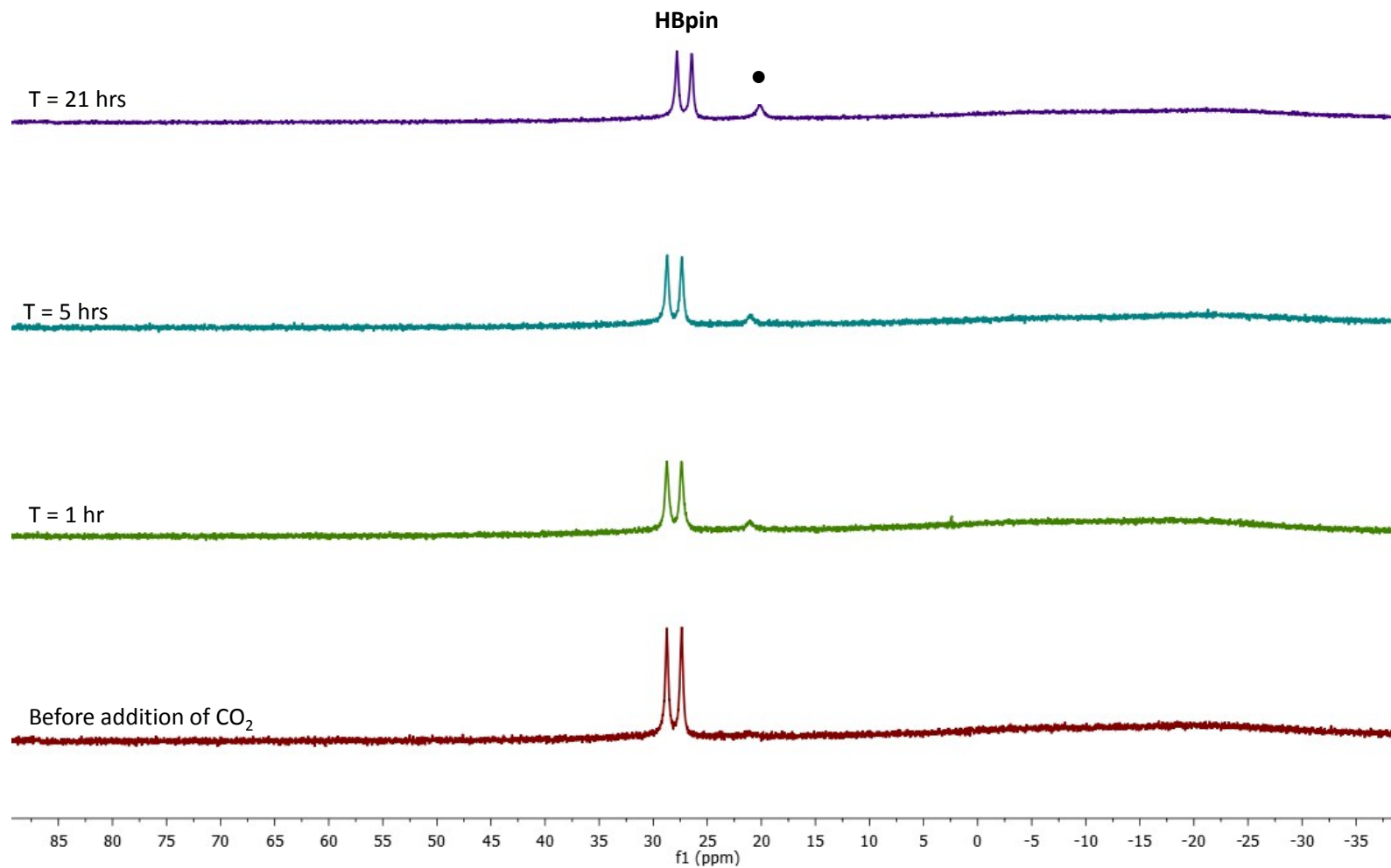


Figure S 19 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and HBPIn (0.1 mmol) at various time intervals in $\text{CD}_2\text{Cl}_2-d_2$. (●) represents the peaks for pinBOBpin at 21.1 ppm.

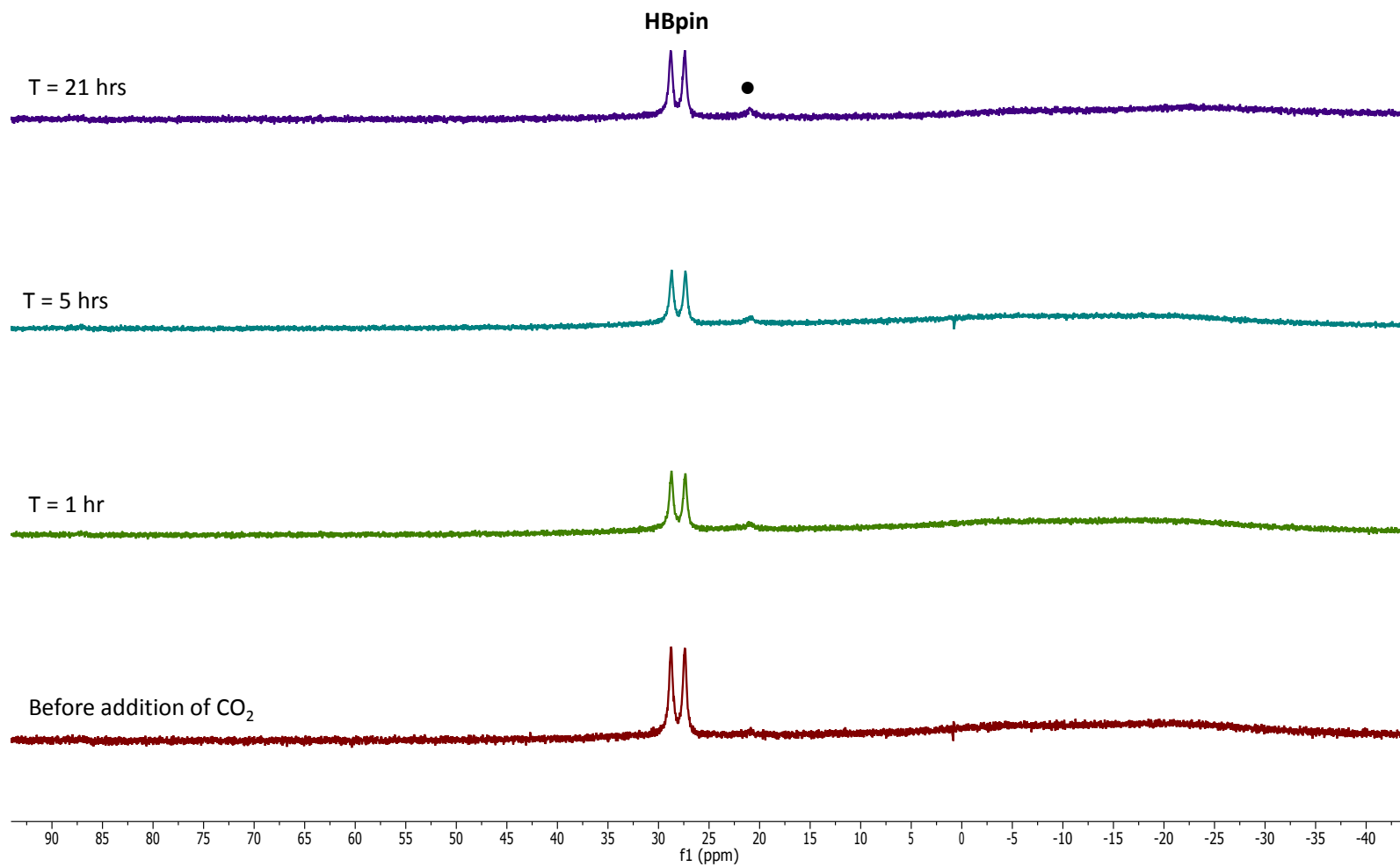


Figure S 20 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and HBPin (0.1 mmol) at various time intervals in CDCl_3 . (●) represents the peaks for trace amount of pinBOBpin at 21.0 ppm.

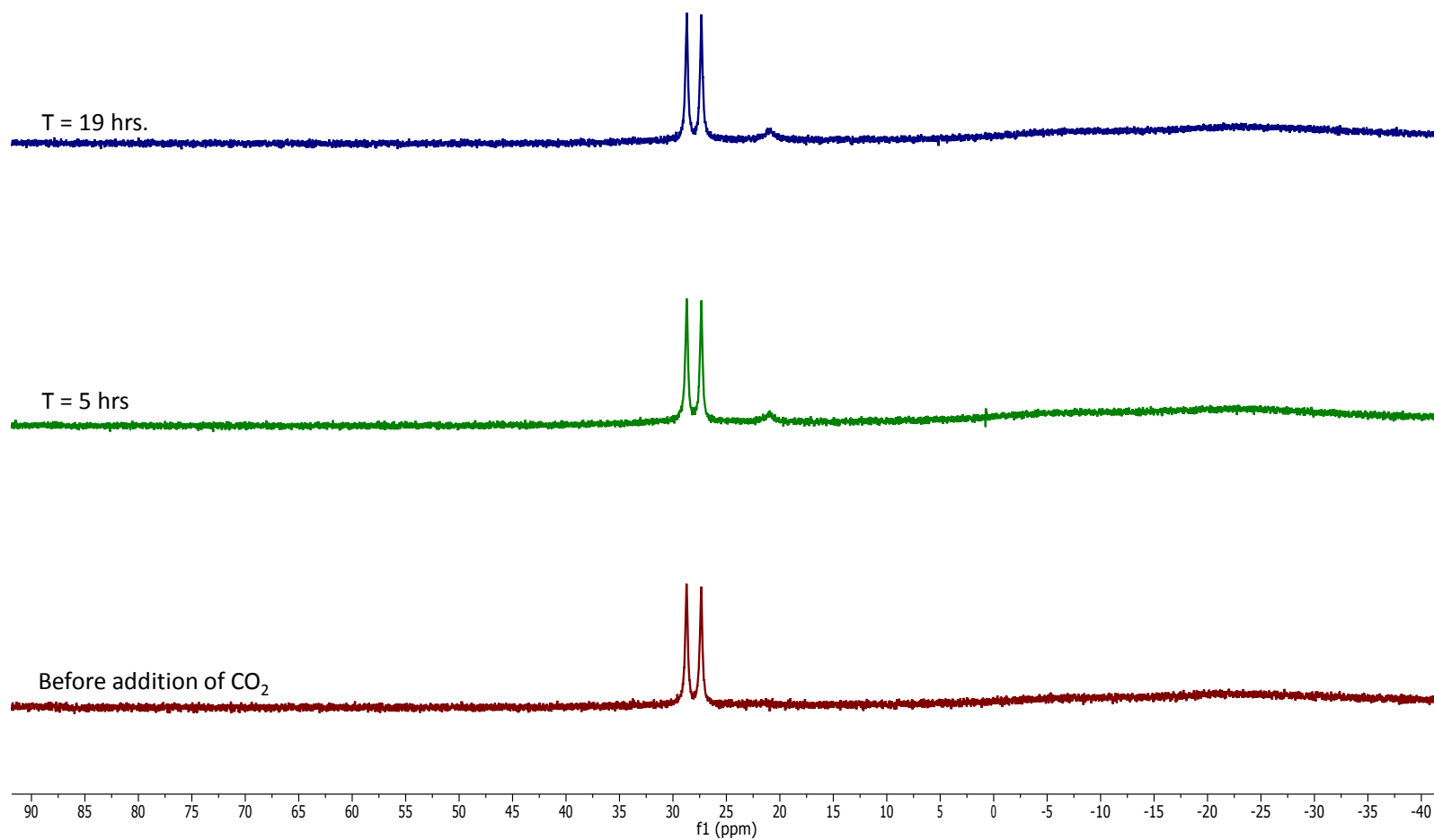


Figure S 21 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBet_3 , and HBPIn (0.1 mmol) at various time intervals in cyclohexane- d_{12} .

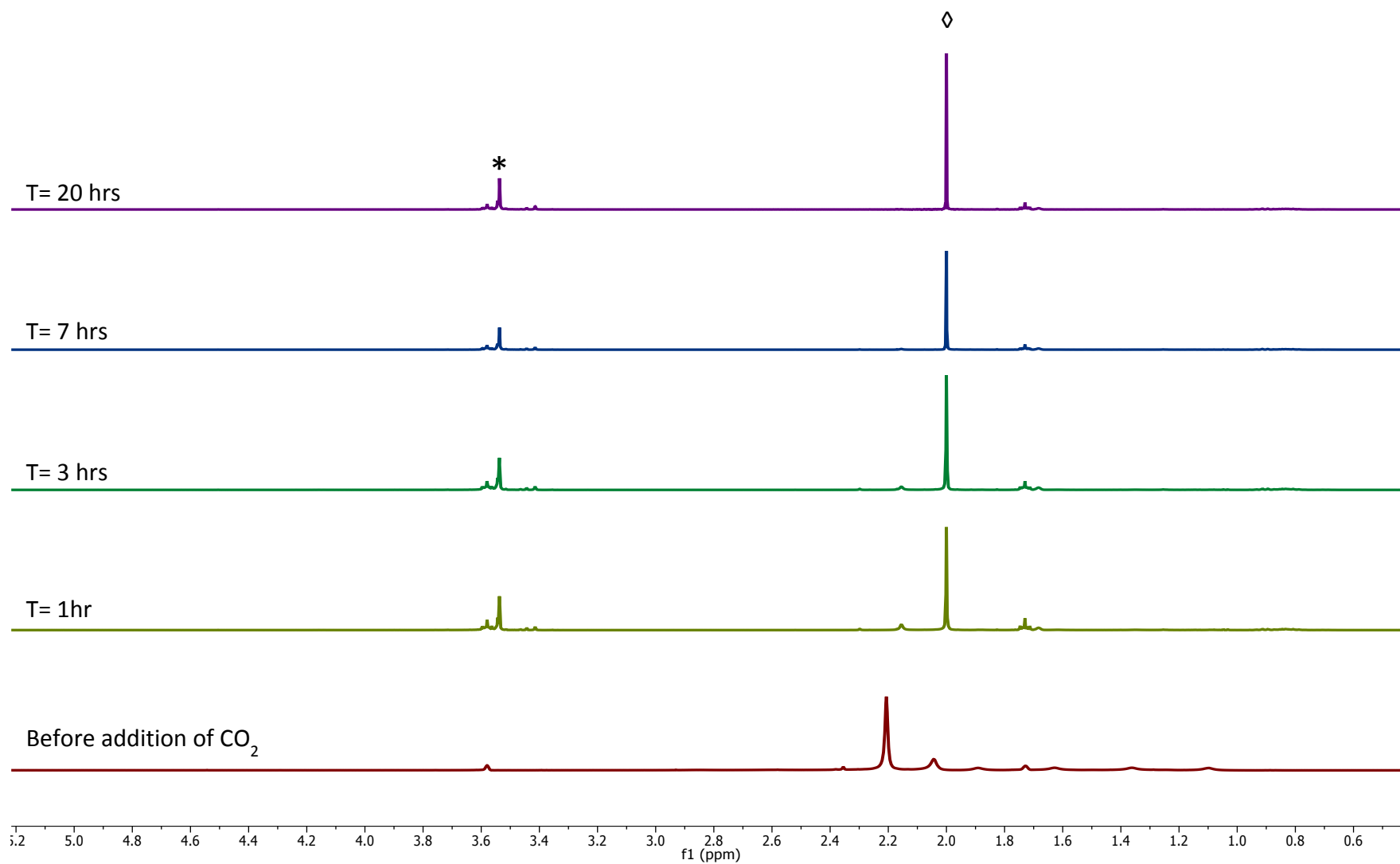


Figure S 22 ¹H NMR spectra for hydroboration of CO₂ with 1 mol % Co(acac)₃, 1 mol % NaHBet₃, and BH₃•S(Me)₂ (0.1 mmol) at various time intervals in THF-*d*₈. The (*) represents the ¹H peak for (CH₃OBO)₃ at 3.54 ppm and (◊) represents peak for free S(Me)₂ at 2.00 ppm.

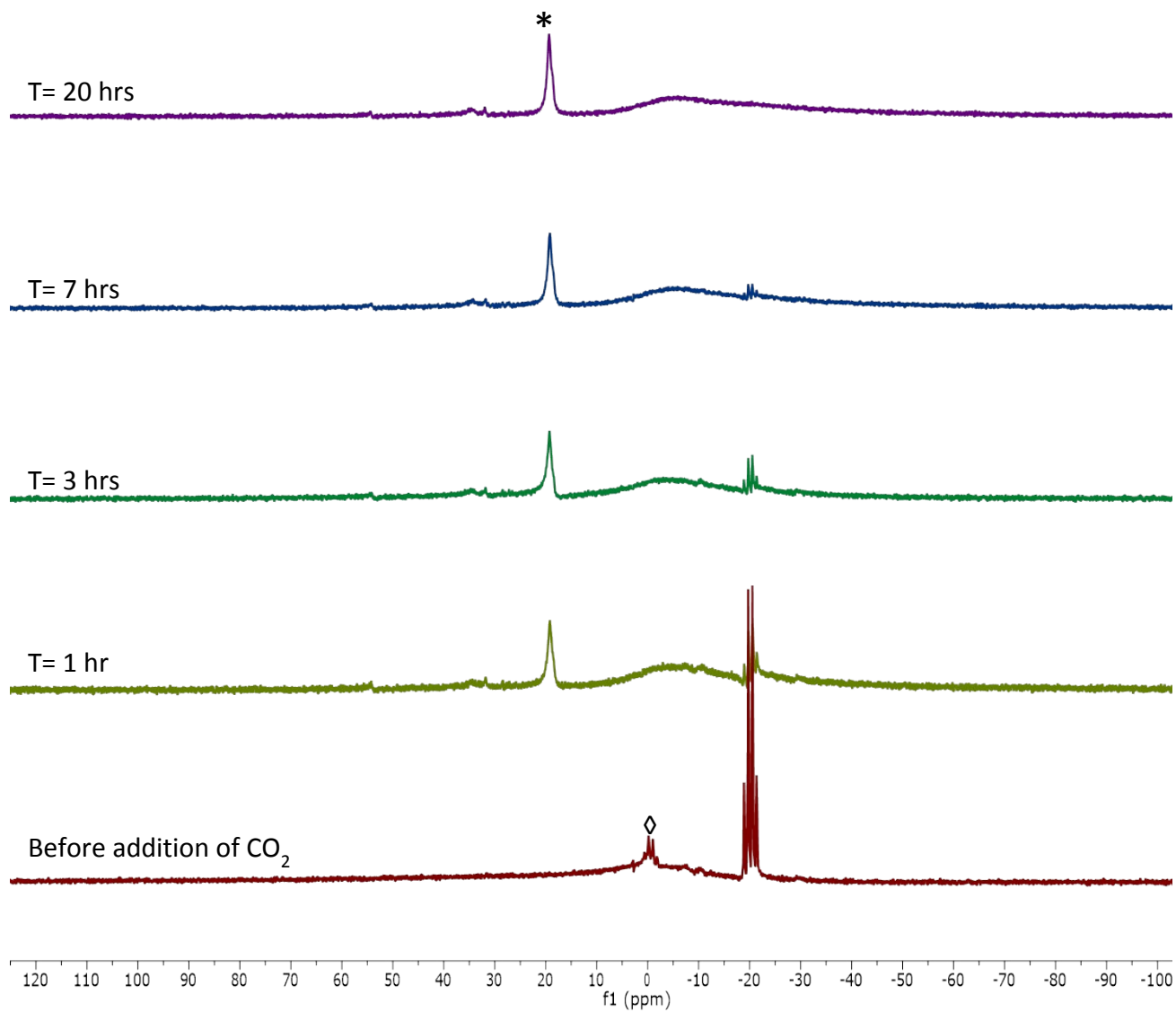


Figure S 23 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBEt_3 , and $\text{BH}_3\cdot\text{S}(\text{Me})_2$ (0.1 mmol) at

various time intervals THF- d_8 . The (*) represents the ^{11}B peak for $(\text{CH}_3\text{OBO})_3$ at 19.3 ppm, and (\diamond) represents the peak for $\text{BH}_3\cdot\text{THF}$ at -0.25ppm.

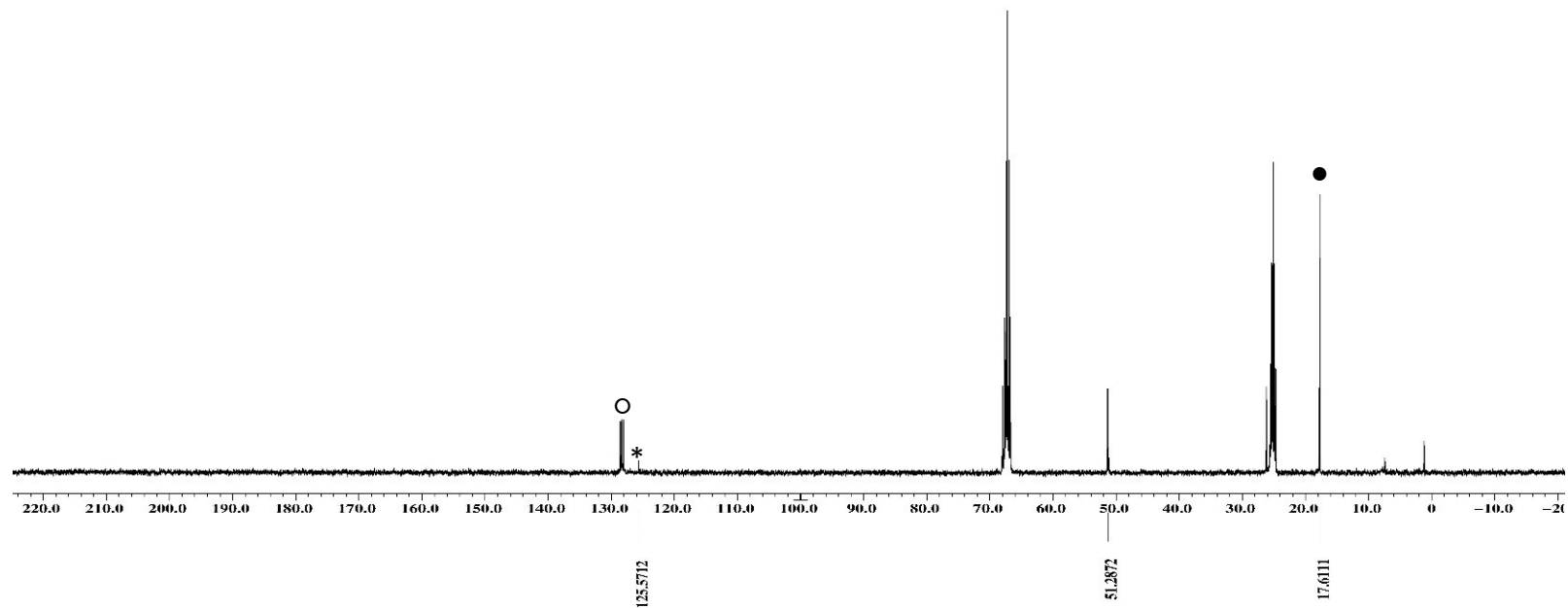


Figure S 24 ^{13}C NMR spectra after hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBET_3 , and $\text{BH}_3\cdot\text{S}(\text{Me})_2$ (0.1 mmol)

in THF- d_8 . The (\diamond) represents peak for $(\text{CH}_3\text{OBO})_3$ at 51.3ppm, (\bullet) represents the peak for $\text{S}(\text{Me})_2$ at 17.6ppm, (\circ) represents the peak for benzene- d_6 at 128.8ppm, and (*) represents the peak for CO_2 at 125ppm.

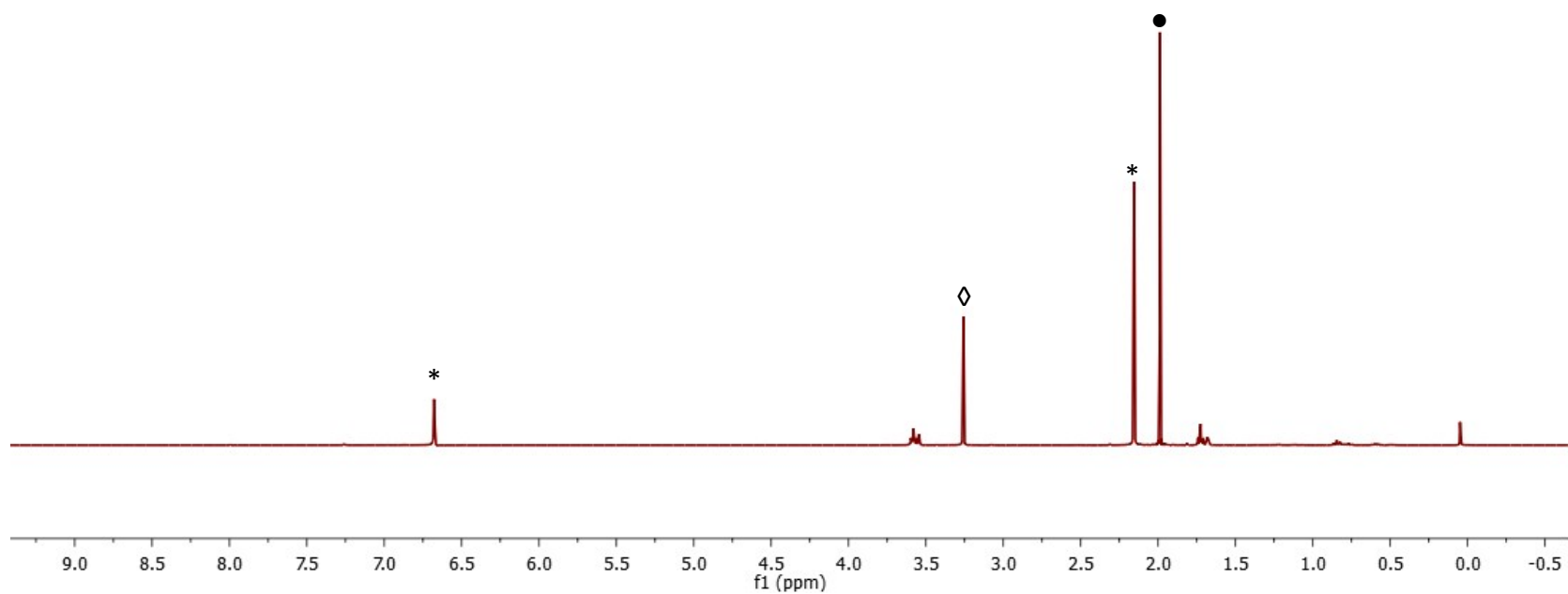


Figure S 25 ^1H NMR spectra in $\text{THF-}d_8$ after hydrolysis with $50\ \mu\text{L}$ of DCL in D_2O . The (\diamond) represents the peak for CH_3OD at 3.26 ppm, (\bullet) represents the peak for $\text{S}(\text{Me})_2$ at 1.99 ppm, and (*) represents the peak for mesitylene at 2.16 ppm, and 6.67 ppm.

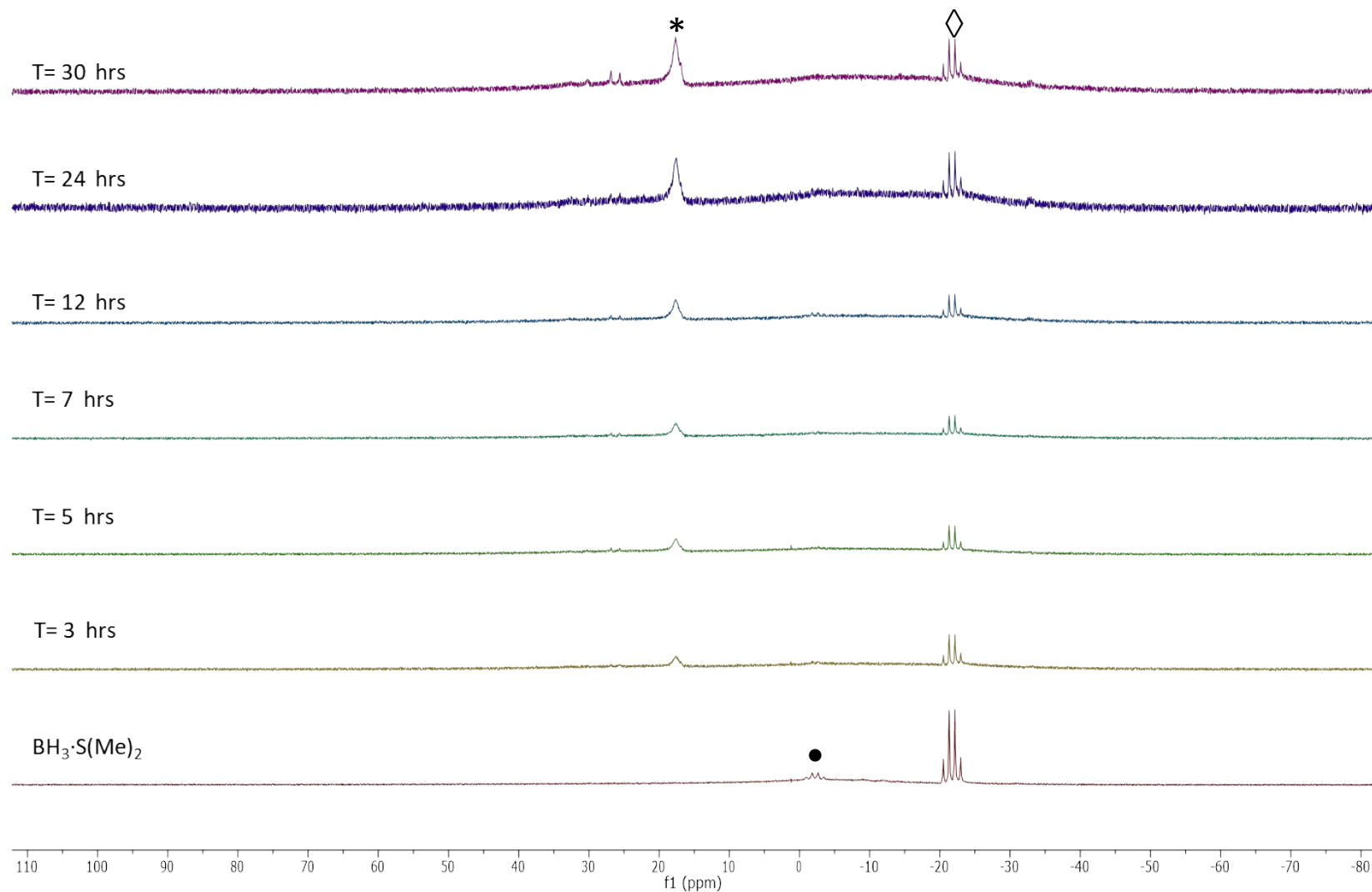
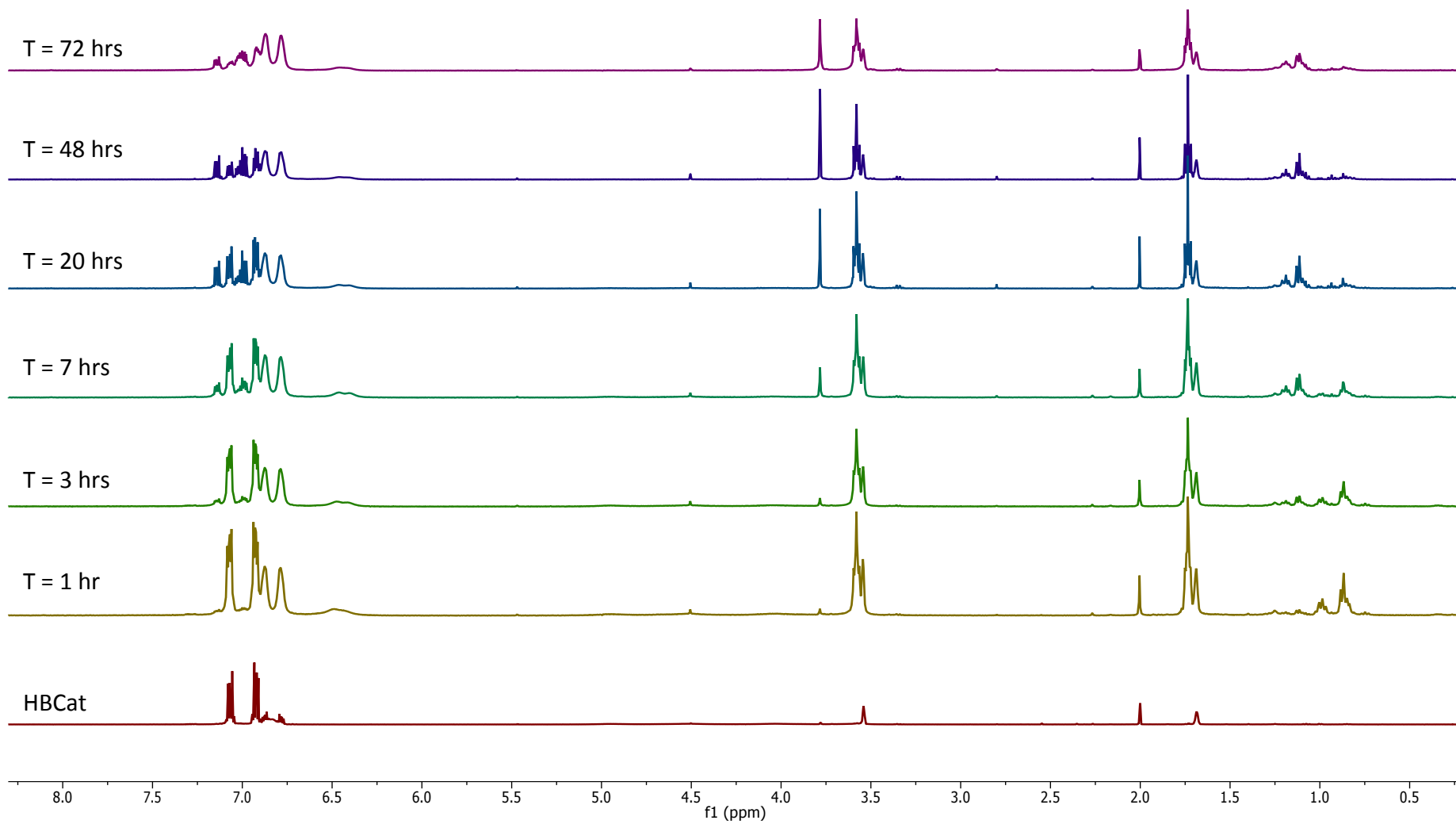


Figure S 26 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % NaHBET_3 , and $\text{BH}_3 \cdot \text{S}(\text{Me})_2$ (0.1 mmol) at various time intervals in THF. The (*) represents the ^{11}B peak for $(\text{CH}_3\text{OBO})_3$ at 19.3 ppm, (◇) represents the peak for unreacted $\text{BH}_3 \cdot \text{S}(\text{Me})_2$ at -21.3 ppm, and (●) represents the peak for $\text{BH}_3 \cdot \text{THF}$ at -0.25 ppm.



*

Figure S 27 ^1H NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBEt_3 , and HBCat (0.1 mmol) at various time intervals in $\text{THF-}d_8$. (*) represents the ^1H peak for CH_3OBCat at 3.78 ppm.

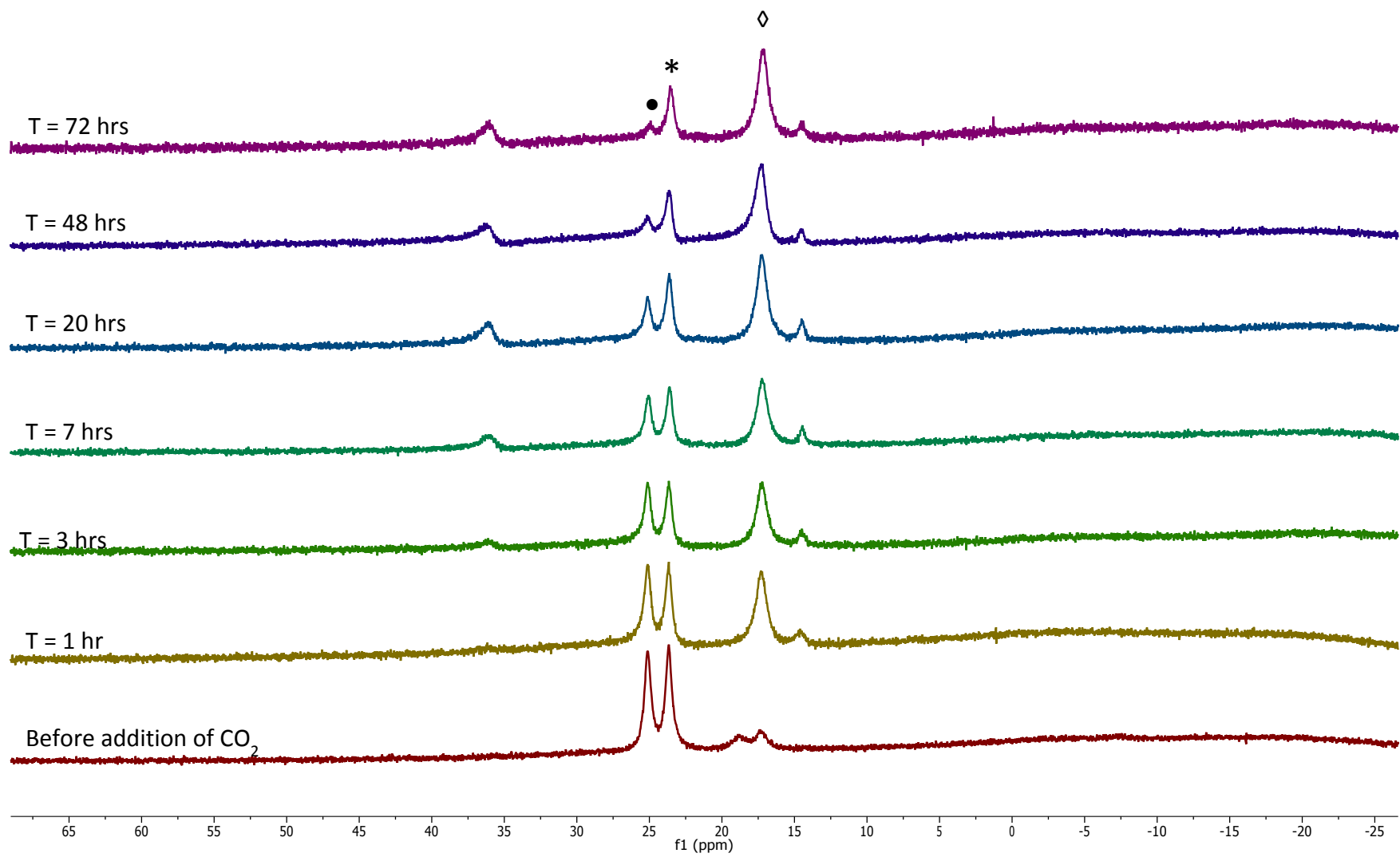


Figure S 28 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBEt_3 , HBCat (0.1 mmol) and CO_2 at various time intervals in $\text{THF-}d_8$. The (*) represents the ^{11}B peak for CH_3OBCat at 23.4ppm, (●) represents the peak for unreacted HBCat at 25.01ppm, and (◇) represents the peak for CatBOBCat at 17.1ppm.

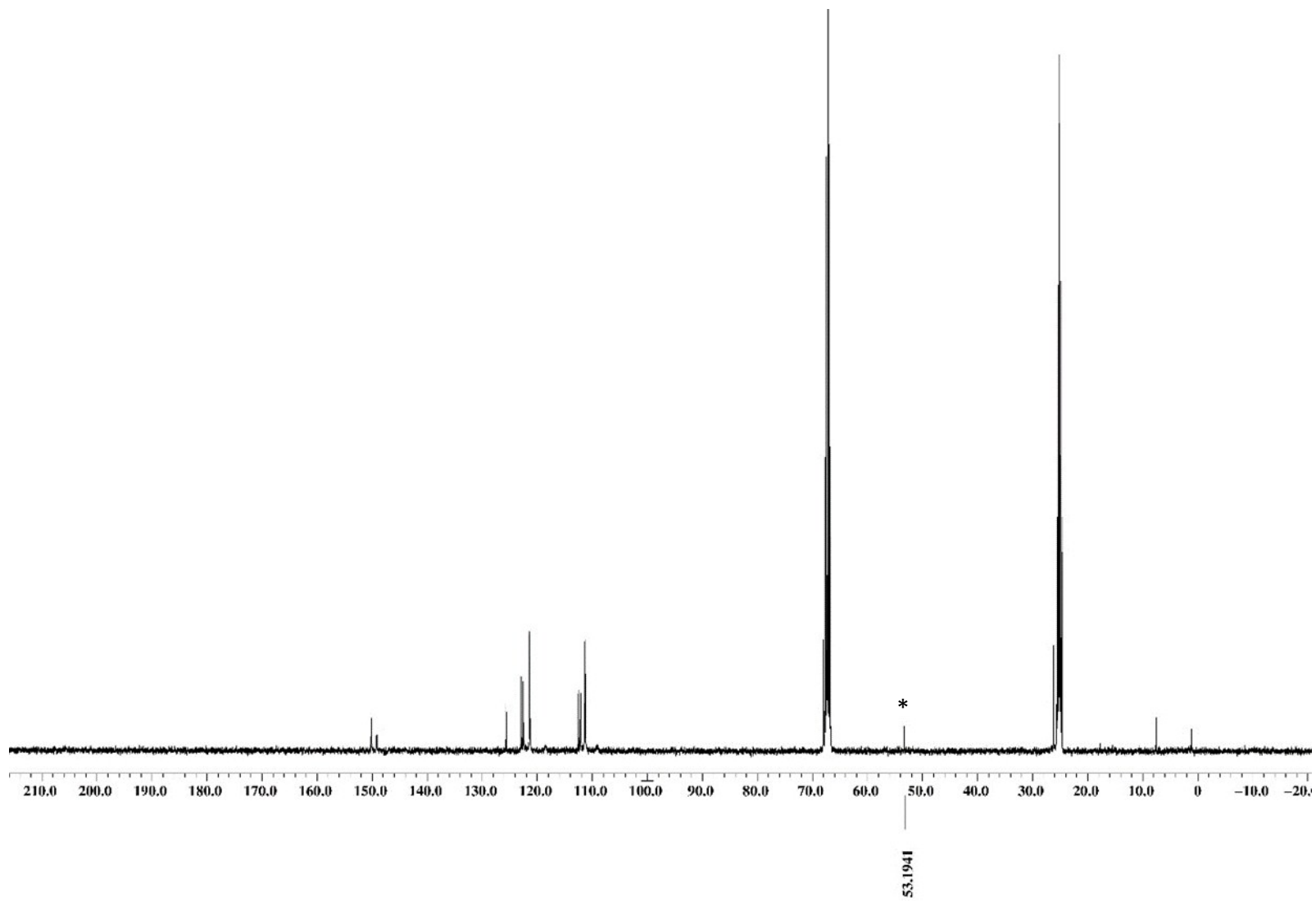


Figure S 29 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $\text{Co}(\text{acac})_3$, 1 mol % NaHBEt_3 , HBCat (0.1 mmol) and CO_2 at various time intervals in $\text{THF-}d_8$. (*) represents the ^{13}C peak for CH_3OBCat at 53.2ppm.

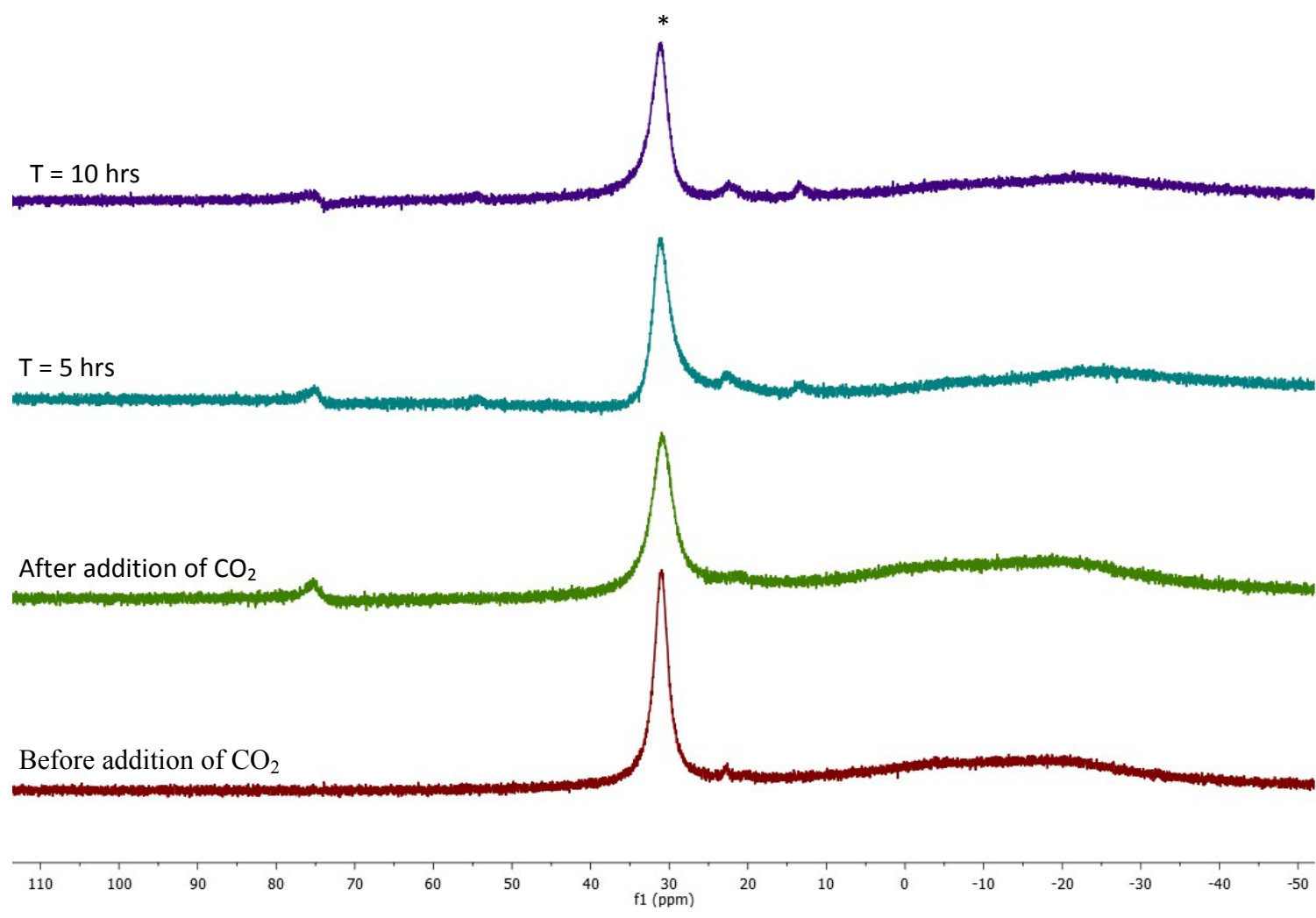


Figure S 30 ^{11}B NMR spectra for hydroboration of CO_2 with 10 mol % $\text{Co}(\text{acac})_3$, 10 mol % NaBHET_3 , and B_2Pin_2 (1.0 mmol) at various time intervals in THF. (*) represents the ^{11}B peak for B_2Pin_2 at 30.2 ppm.