Supporting Information

Cobalt catalyzed hydroboration of CO_2

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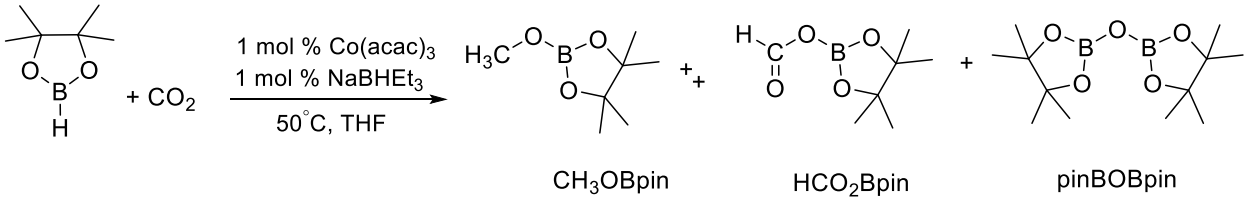
Contents

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 (4**Å)** prior to usage; THF-*d*8 was dried and distilled over CaH_2. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a Jeol 400 MHz spectrometer at 300K unless otherwise noted. ^{1}H 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 $BF_3{\cdot}(OEt)_2$ 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), $BH_3{\cdot}S(Me)_2$ (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



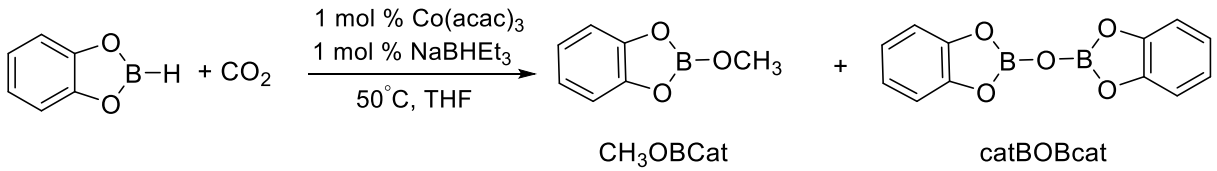
A pre-weighed oven dried shell vial was charged with 1 mol % $Co(acac)_3$ (0.356 mg, 0.001 mmol). It was dissolved in 0.4 mL THF-d_8, and transferred to an oven dried J-Young tube. 1 mol % $NaHBEt_3$ (1µL, 0.001 mmol, 1M in THF) was added and the reaction mixture turned into a clear light yellow solution 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 ~ 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 ^{1}H and ^{11}B over time. ^{1}H NMR yield was determined by adding mesitylene as internal standard.

HCO_2Bpin: ^{1}H NMR (400 MHz, THF- *d*8): δ 8.29 (s, *H*CO_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: ^{1}H 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: ^{1}H NMR (400 MHz, THF- *d*8): 3.50 (s, C*H*$_3$OBpin); ^{11}B NMR (128.4 MHz, THF-d*8*): δ 22.03 (s, br).

General procedure for hydroboration of CO_2 with HBCat



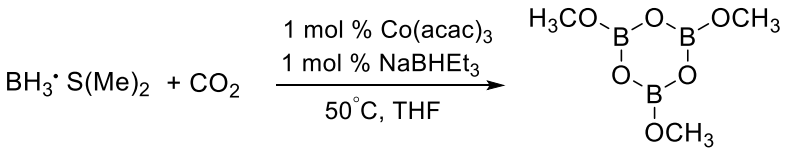
CH_3OBCat catBOBcat

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 % $NaHBEt_3$ (1µL, 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 CO_2 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 ^{11}B over time. ^1H NMR yield was determined by adding mesitylene as internal standard.

CH_3OBCat: ^1H NMR (400 MHz, THF- *d*8): 3.78 (s, C*H*$_3$OBCat); ^{11}B NMR (128.4 MHz, THF-*d*8): δ 23.4 (s, br); ^{13}C NMR (100 MHz, THF- *d*8): δ 53.3 ppm

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

General procedure for hydroboration of CO_2 with BH_3•S(Me)$_2$



$(CH_3OBO)_3$

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 % $NaHBEt_3$ (1µL, 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 BH_3•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 CO_2 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 ^{11}B over time. ^1H NMR yield was determined by adding mesitylene as internal standard.

$(CH_3OBO)_3$: ^1H NMR (400 MHz, THF-d*8*): δ 3.54, (s, (C*H*$_3$OBO)$_3$), ^{11}B NMR (128.4 MHz, THF-d*8*): δ 19.3ppm (s, br). ^{13}C NMR (100 MHz, THF-d*8*): δ 51.3 ppm.

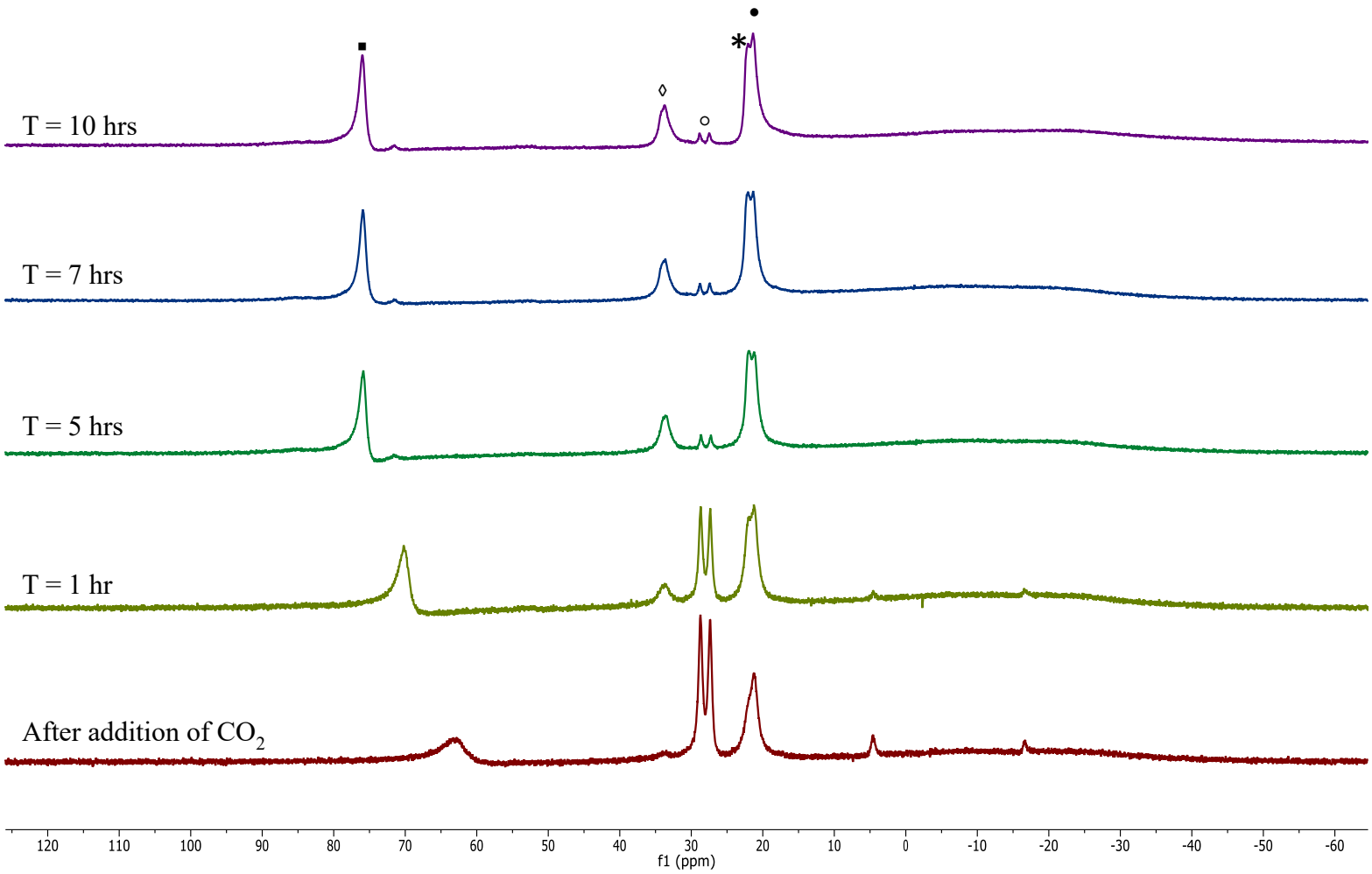


Figure S 1 ^{11}B NMR spectra for hydroboration of CO_2 with 10 mol % $Co(acac)_3$,10 mol % $NaHBEt_3$, and HBPin (1.0 mmol) at various time intervals in THF. (▪) represents the ^{11}B peak for BEt_3 at 76 ppm, (*) represents the peak for CH_3OBPin at 22.03 ppm, (●) represents the peak for pinBOBpin 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.

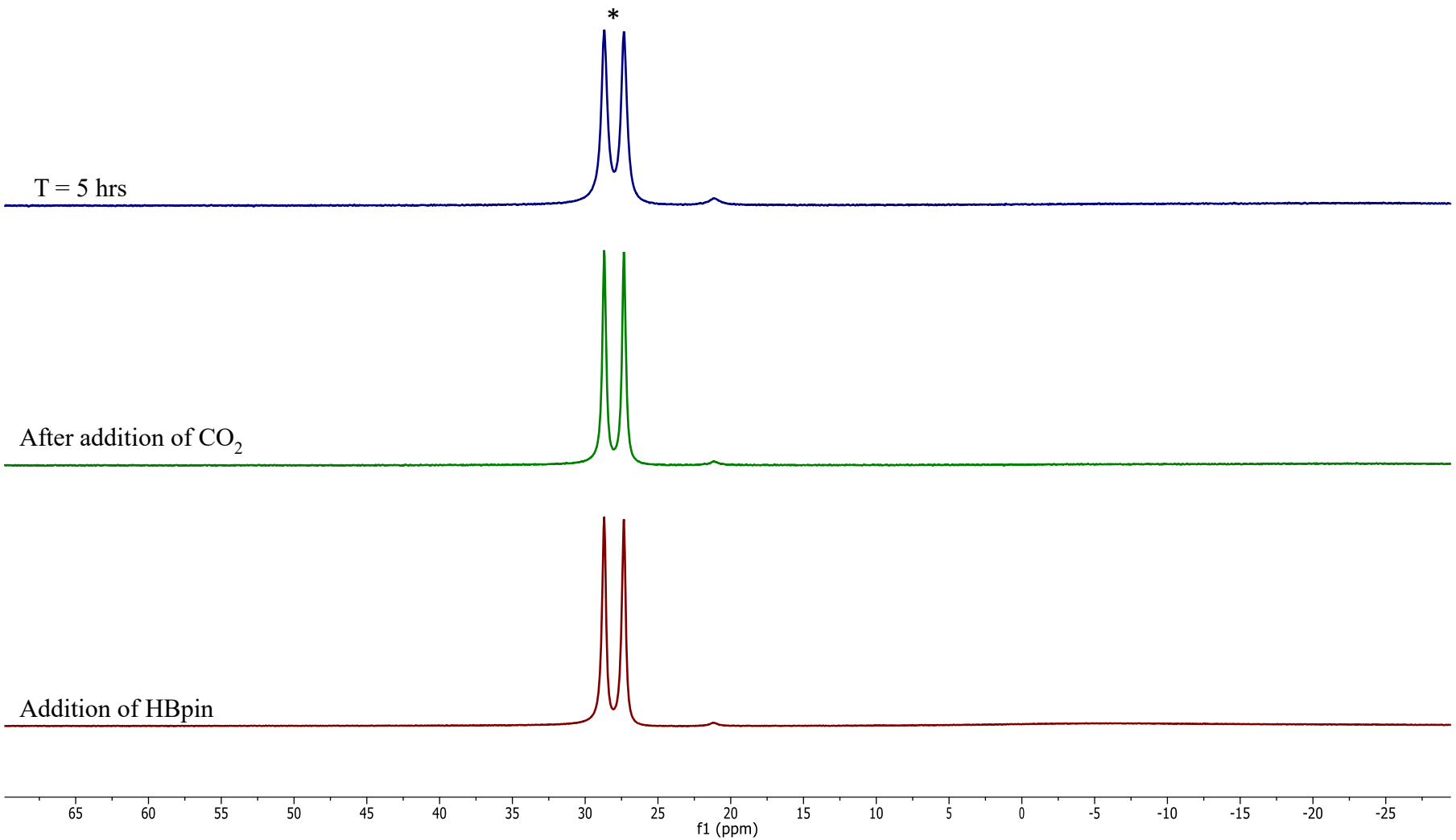


Figure S 2 ^{11}B NMR for hydroboration of CO_2 using 10 mol % $Co(acac)_3$, and HBPin (1.0 mmol) in THF. (*) represents the peak for HBpin at 27.34 ppm and 28.7 ppm.

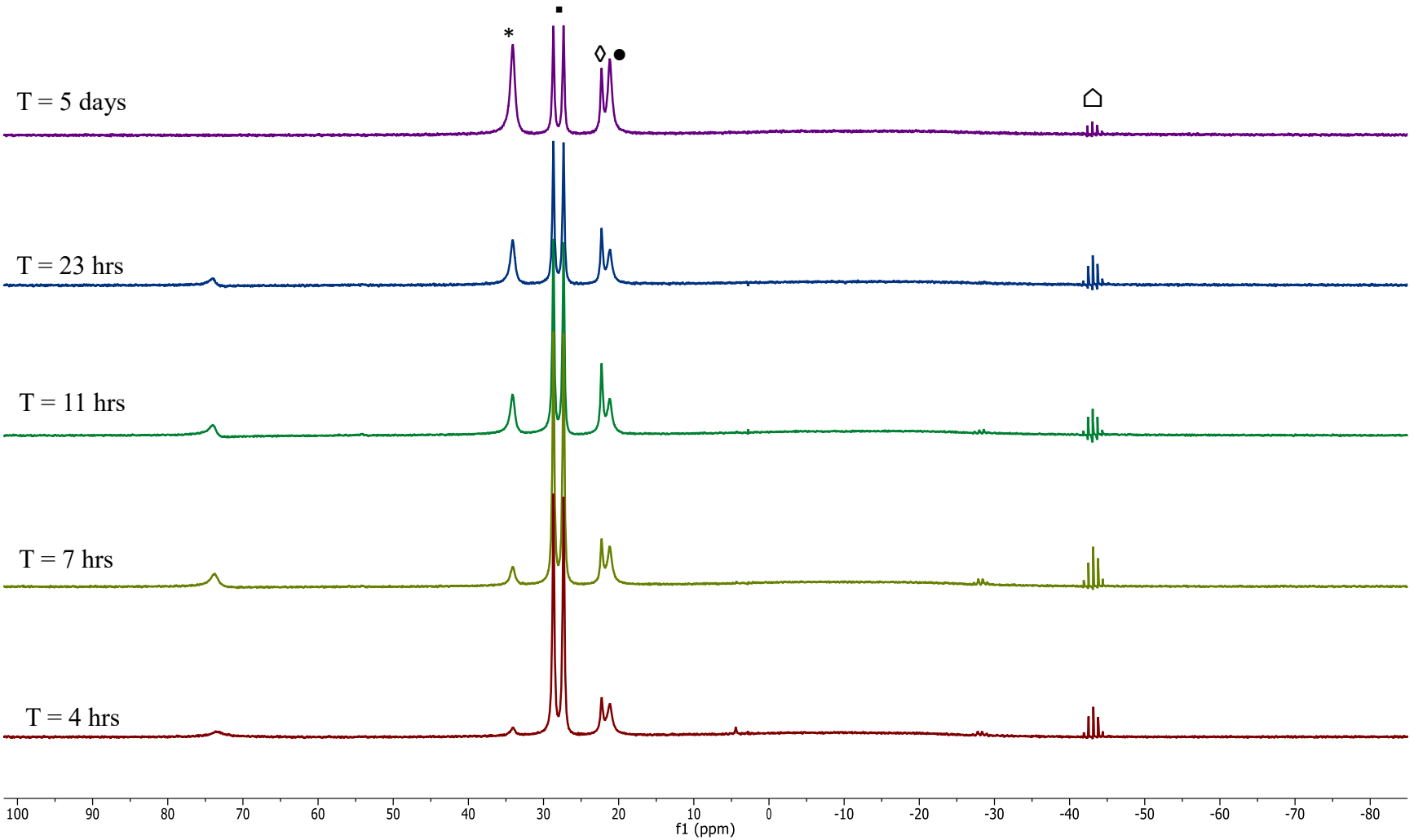


Figure S 3 ^{11}B NMR spectra for hydroboration of CO_2 with 10 mol % $NaHBEt_3$, and HBpin (1.0 mmol) at various time intervals in THF-d_8. (▪) represents the ^{11}B peak for HBPin at 27.4 and 28.7 ppm, (◊) represents the peak for CH_3-OBPin at 22.3 ppm, (●) represents the peak for pinBOBpin at 21.2 ppm, (⌂) represents the peak for BH_4^- at -43.0 ppm, and (*) represents the peak for unidentified boron species.

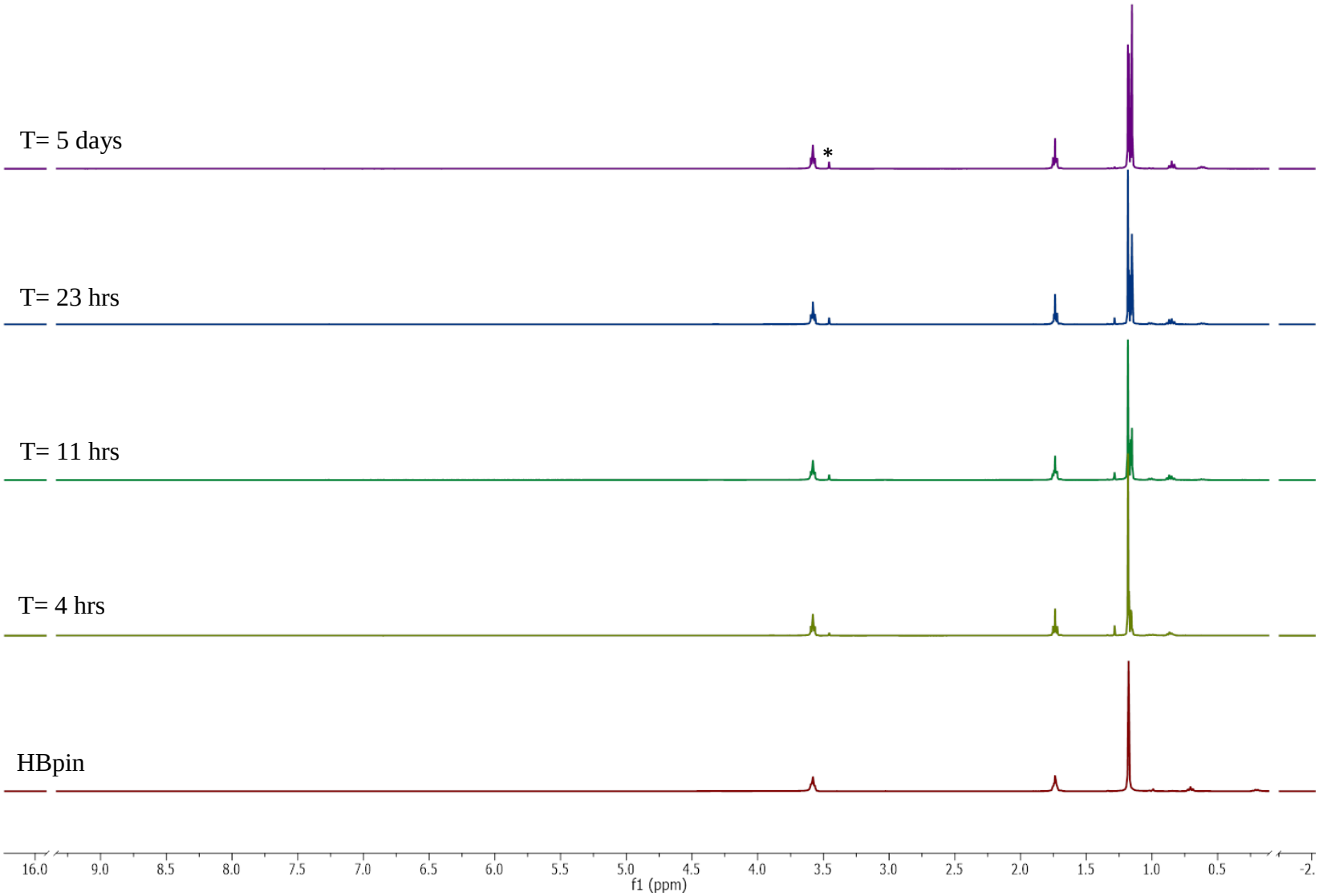


Figure S 4 ^{1}H NMR spectra for hydroboration of CO_2 with 10 mol % $NaHBEt_3$, and HBpin (1.0 mmol) at various time intervals in THF-d_8. (*) represents the peak for CH_3-OBPin at 3.46 ppm.

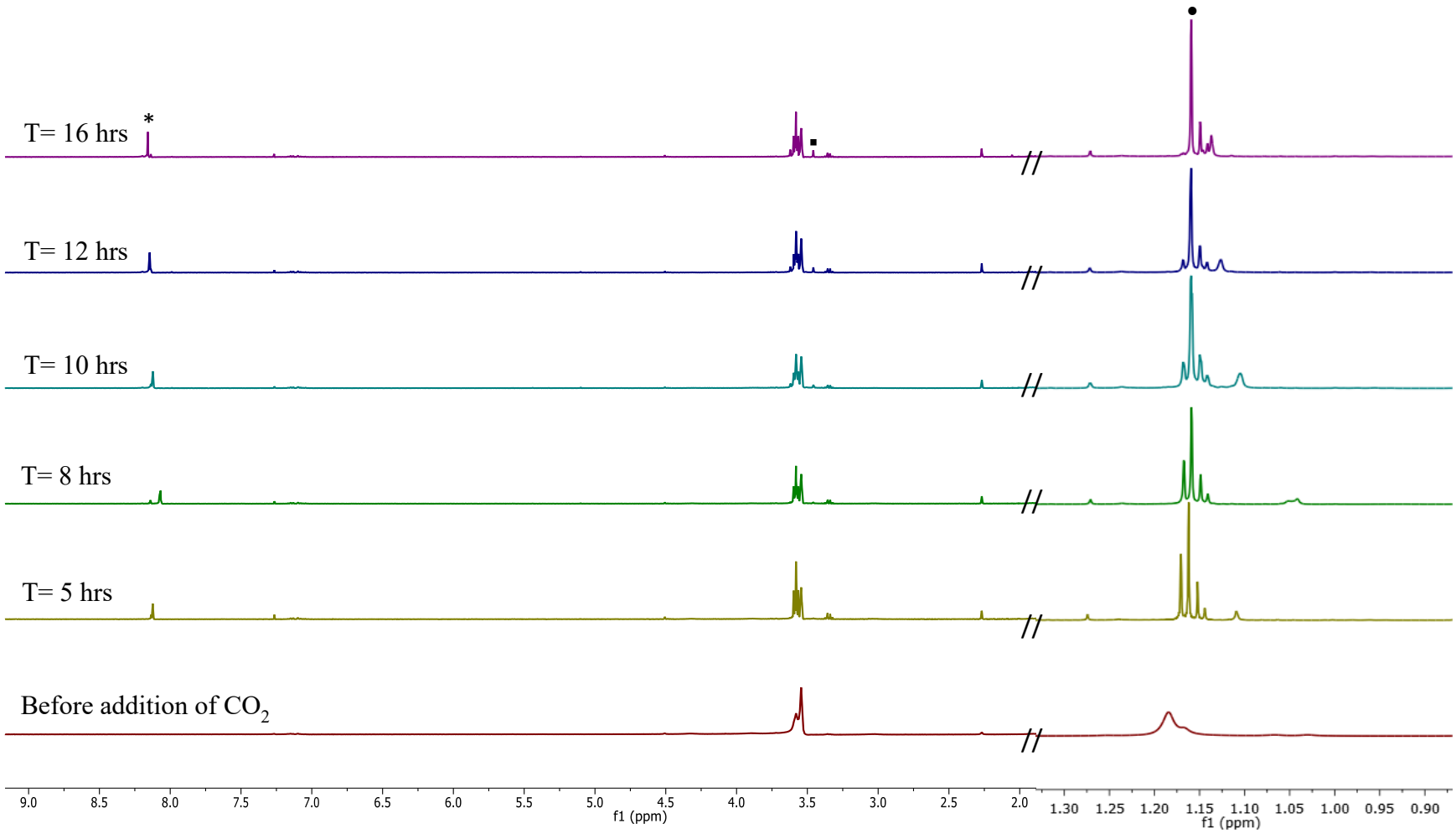


Figure S 5 ^{1}H NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals THF-d_8. (▪) represents the ^{1}H peak for CH_3-OBPin at 3.46 ppm, (*) represents the peak for *H*COOBPin at 8.32 ppm and (•) represents the peak for pinBOBpin at 1.18 ppm.

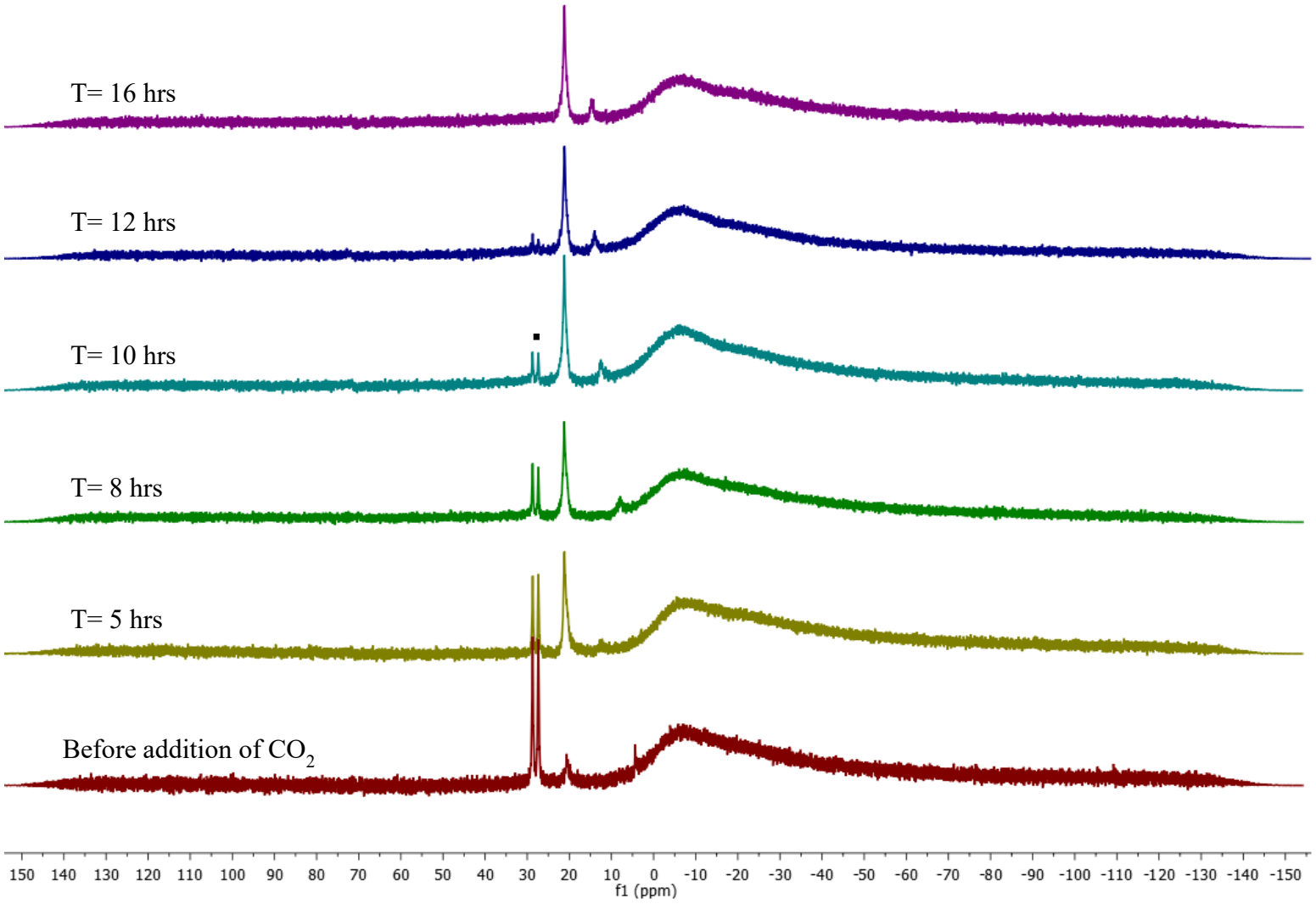


Figure S 6 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in THF-d_8. The (▪) represents the peak for HBpin.

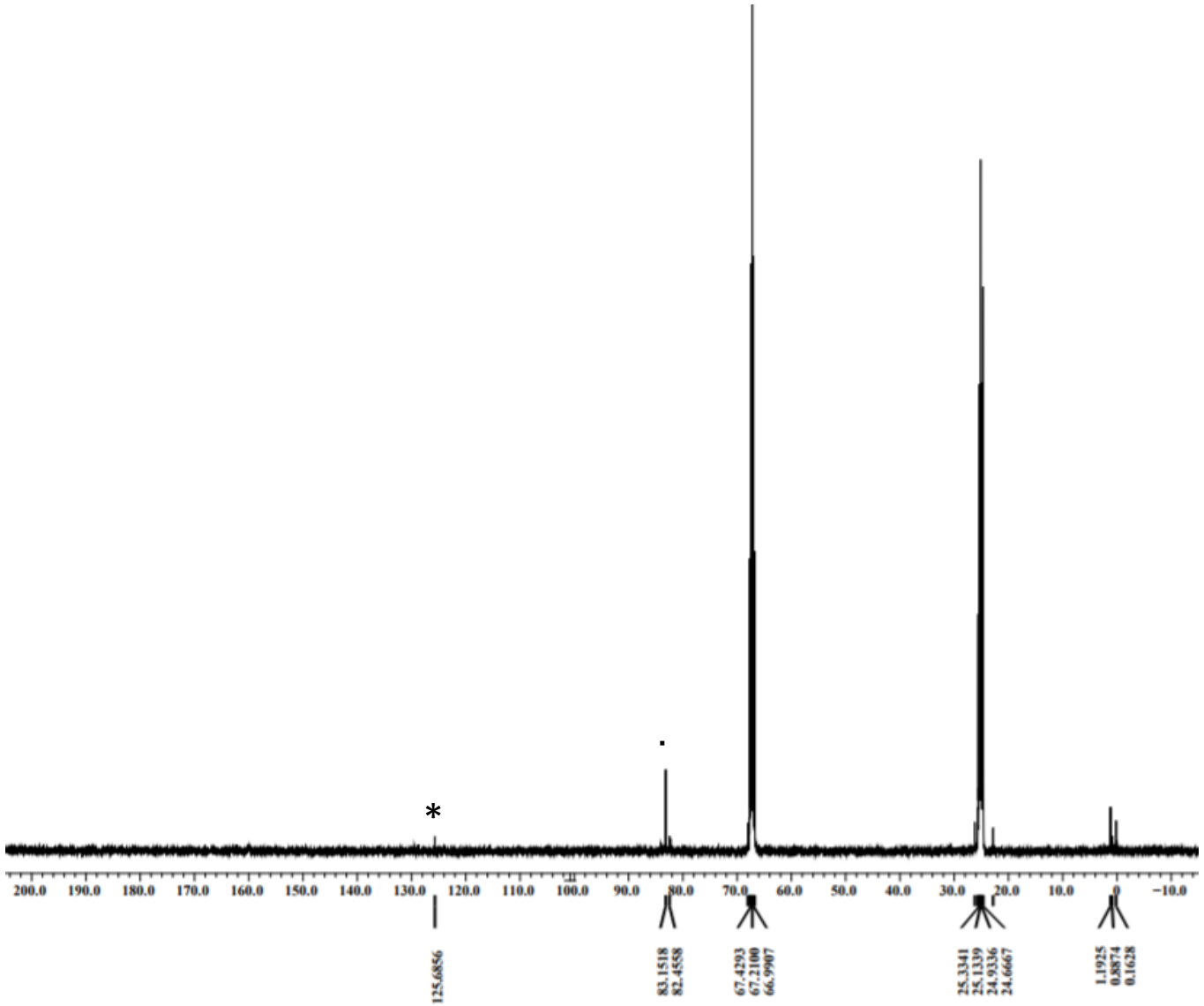


Figure S 7 ^{13}C NMR spectra after hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, and HBpin (0.1 mmol) in THF-d_8. (*) represents the peak for CO_2 at 125.6 ppm, and (▪) represents the peak for pinBOBpin at 83.15 ppm.

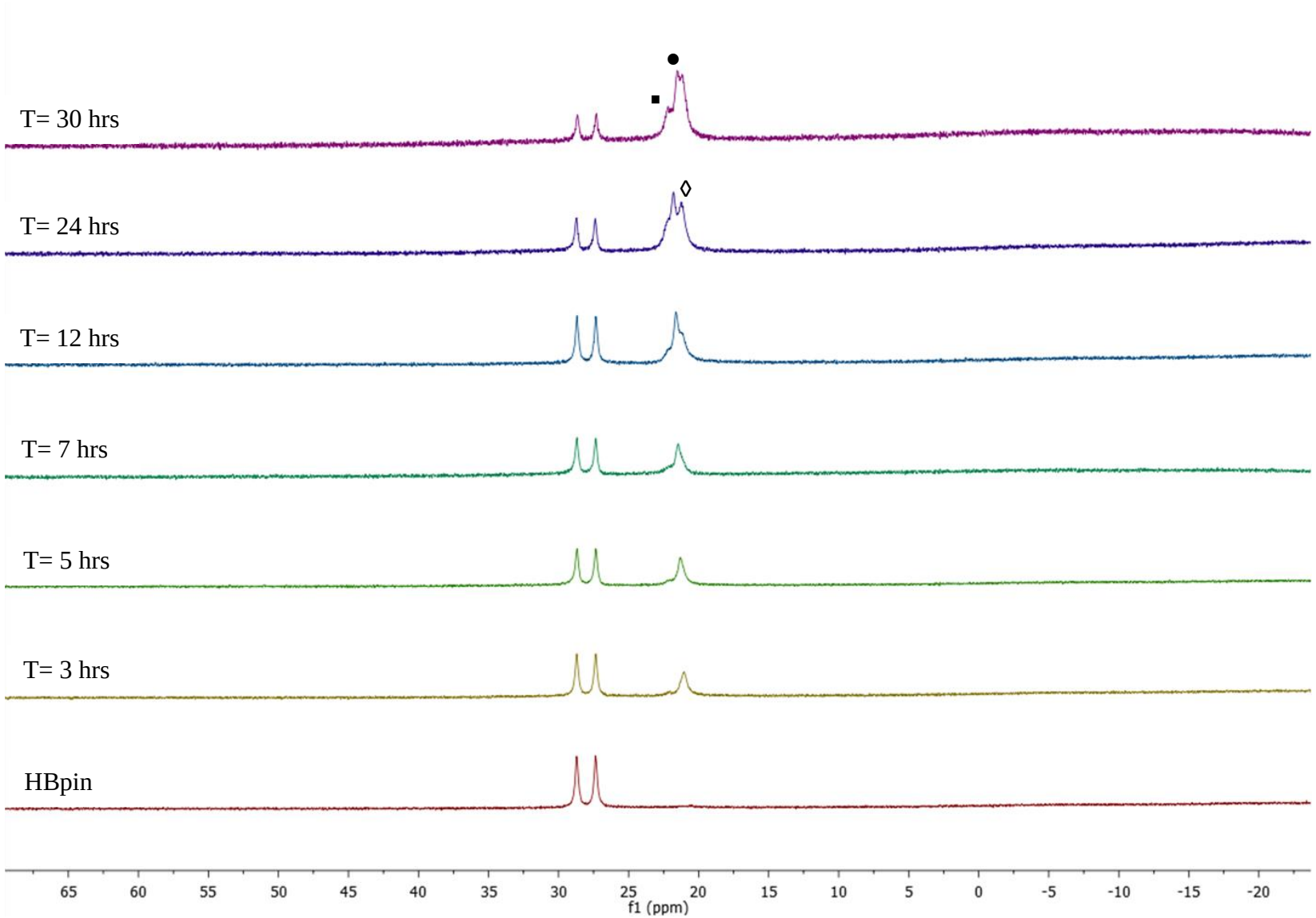


Figure S 8 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $NaHBEt_3$, and HBpin (0.1 mmol) at various time intervals THF-d_8. (*) represents the ^{11}B peak for HBpin at 27.34 ppm, (▪) represents the peak for CH_3-OBPin at 22.23 ppm, (◊) represents the broad peak for HCOOBPin at 21.8 ppm, and (●) represents the peak for pinBOBpin at 21.2 ppm.

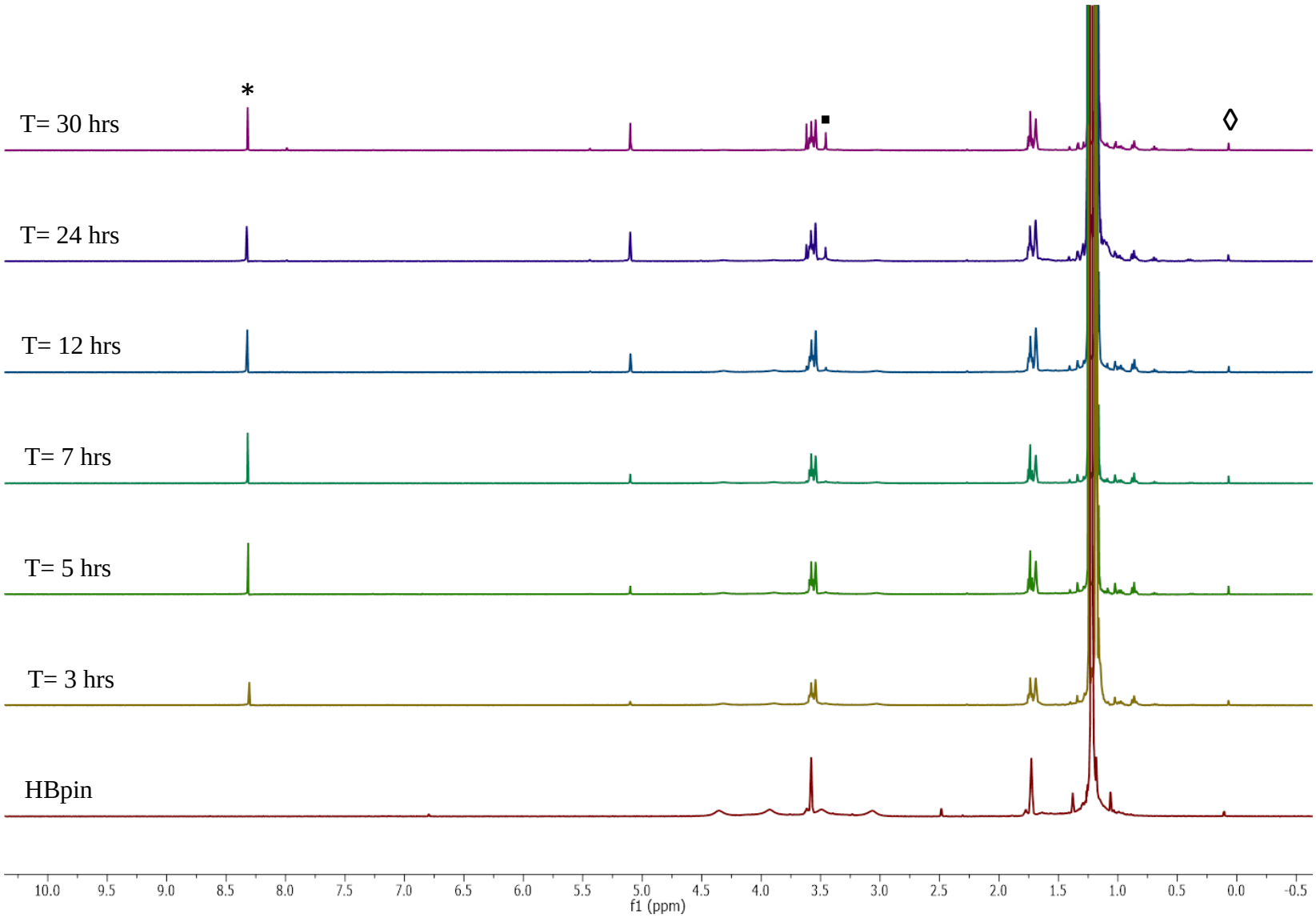


Figure S 9 ^{1}H NMR spectra for hydroboration of CO_2 with 1 mol % $NaHBEt_3$, and HBpin (0.1 mmol) at various time intervals in THF-d_8. (▪) represents the ^{1}H peak for CH_3-OBPin at 3.46 ppm, (*) represents the peak for HCOOBPin at 8.32 ppm, (◊) represents the peak for grease.

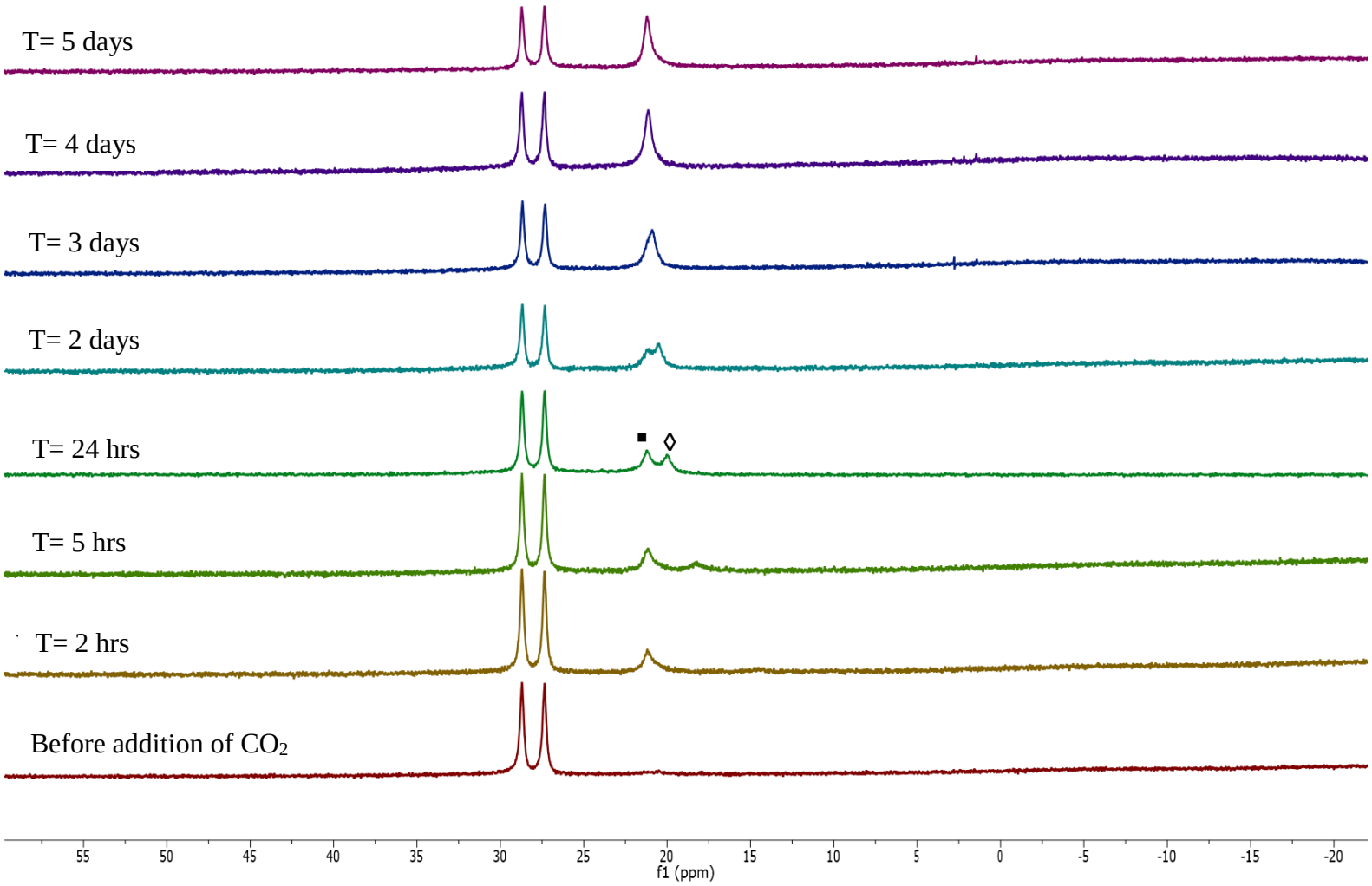


Figure S 10 ^{11}B NMR spectra for hydroboration of CO_2 with and HBpin (0.1 mmol) in the absence of $Co(acac)_3$ and $NaHBEt_3$ at various time intervals THF-d_8. (▪) represents the ^{11}B peak for pinBOBpin at 21.2ppm, (◊) represents the broad peak for HCOOBPin at 20.5 ppm, and (*) represents the peak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

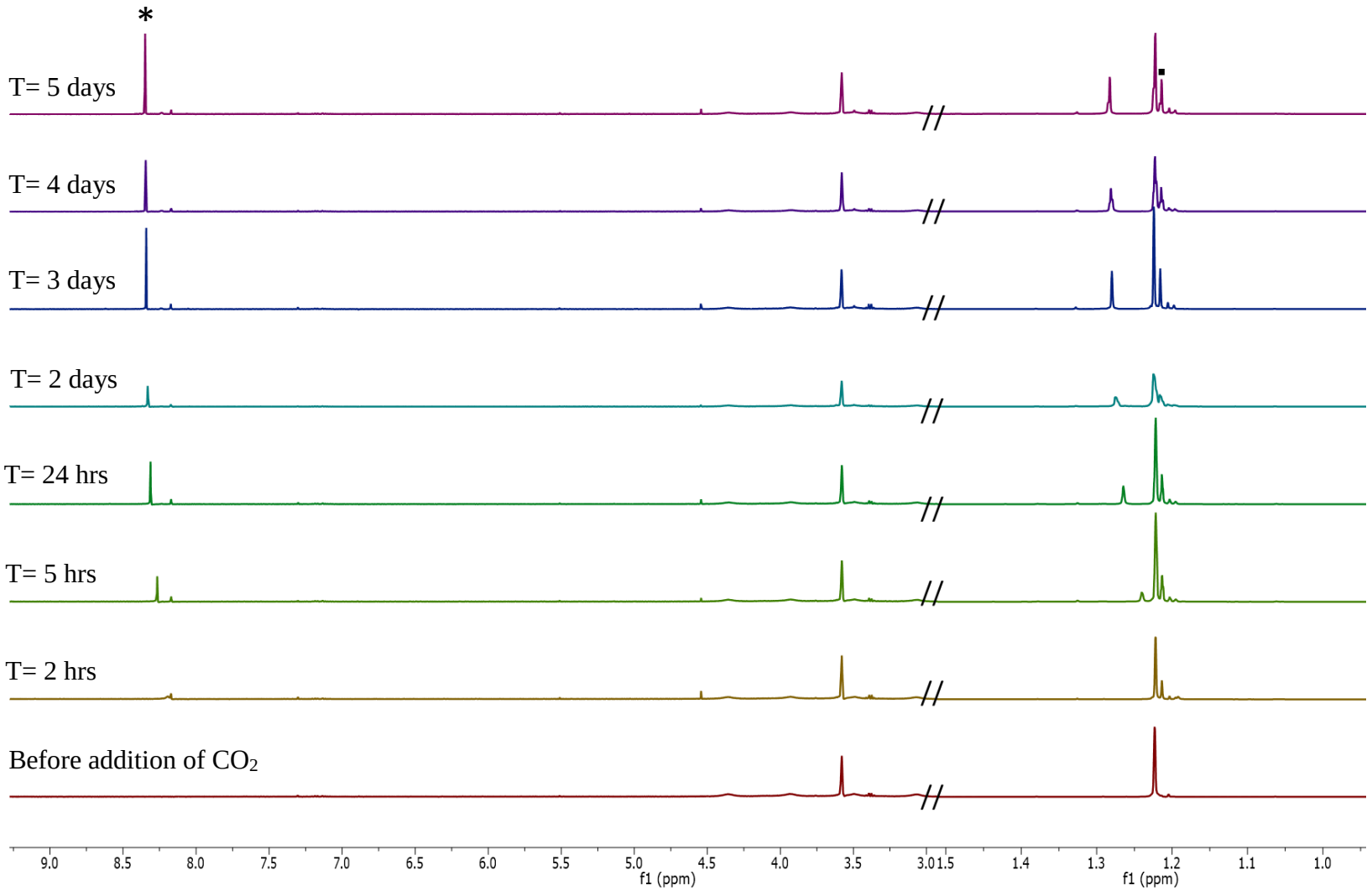


Figure S 11 ^{1}H NMR spectra for hydroboration of CO_2 with and HBpin (0.1 mmol) in the absence of $Co(acac)_3$ and $NaHBEt_3$ at various time intervals THF-d_8. (▪) represents the ^{1}H peak for pinBOBpin at 1.21 ppm, and (*) represents the peak for HCOOBPin at 8.32 ppm.

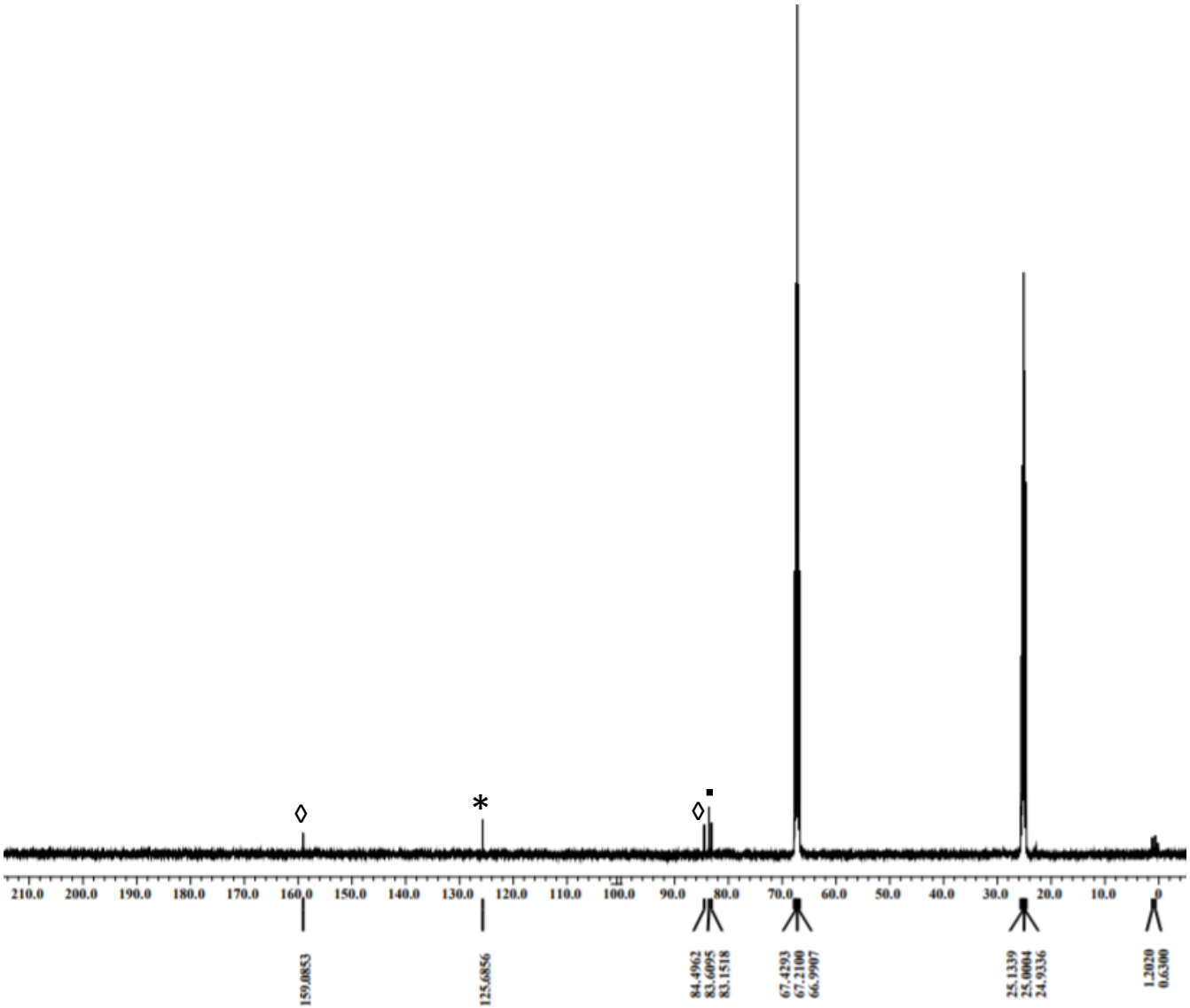


Figure S 12 ^{13}C NMR after hydroboration of CO_2 with HBpin (0.1mmol) in the absence of $Co(acac)_3$ and $NaHBEt_3$ THF-d_8. (◊) represents the peak for HCOOBPin at 159 ppm and 84.49 ppm, (*) represents the peak for CO_2, and (▪) represents the peak for pinBOBpin at 83.15 ppm.

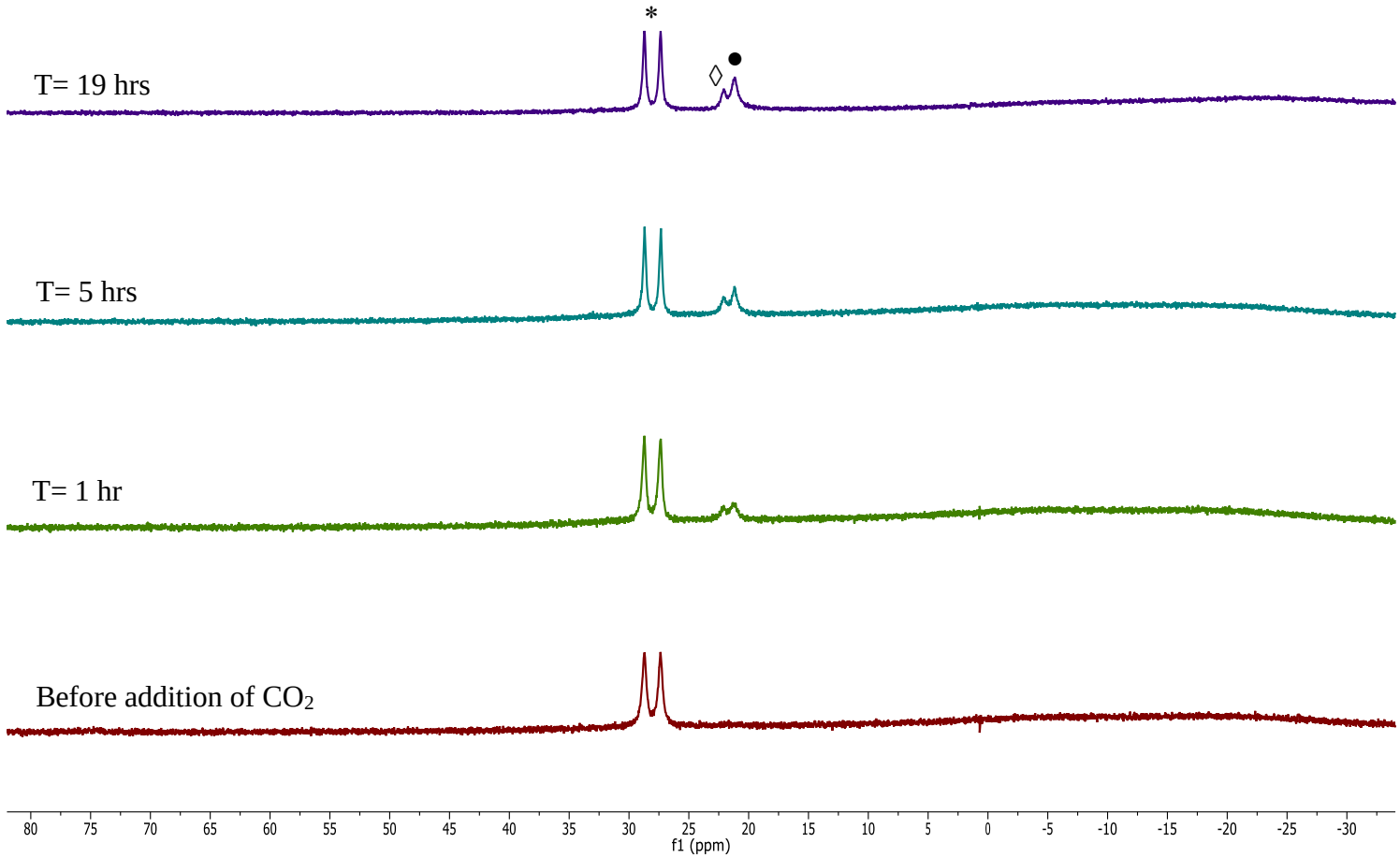


Figure S 13 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $CoBr_2$, 1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in THF-d_8. (●) represents the ^{11}B peak for pinBOBpin at 21.2 ppm, (◊) represents the broad peak for CH_3OBPin at 22.2 ppm, and (*) represents the peak for unreacted HBpin.

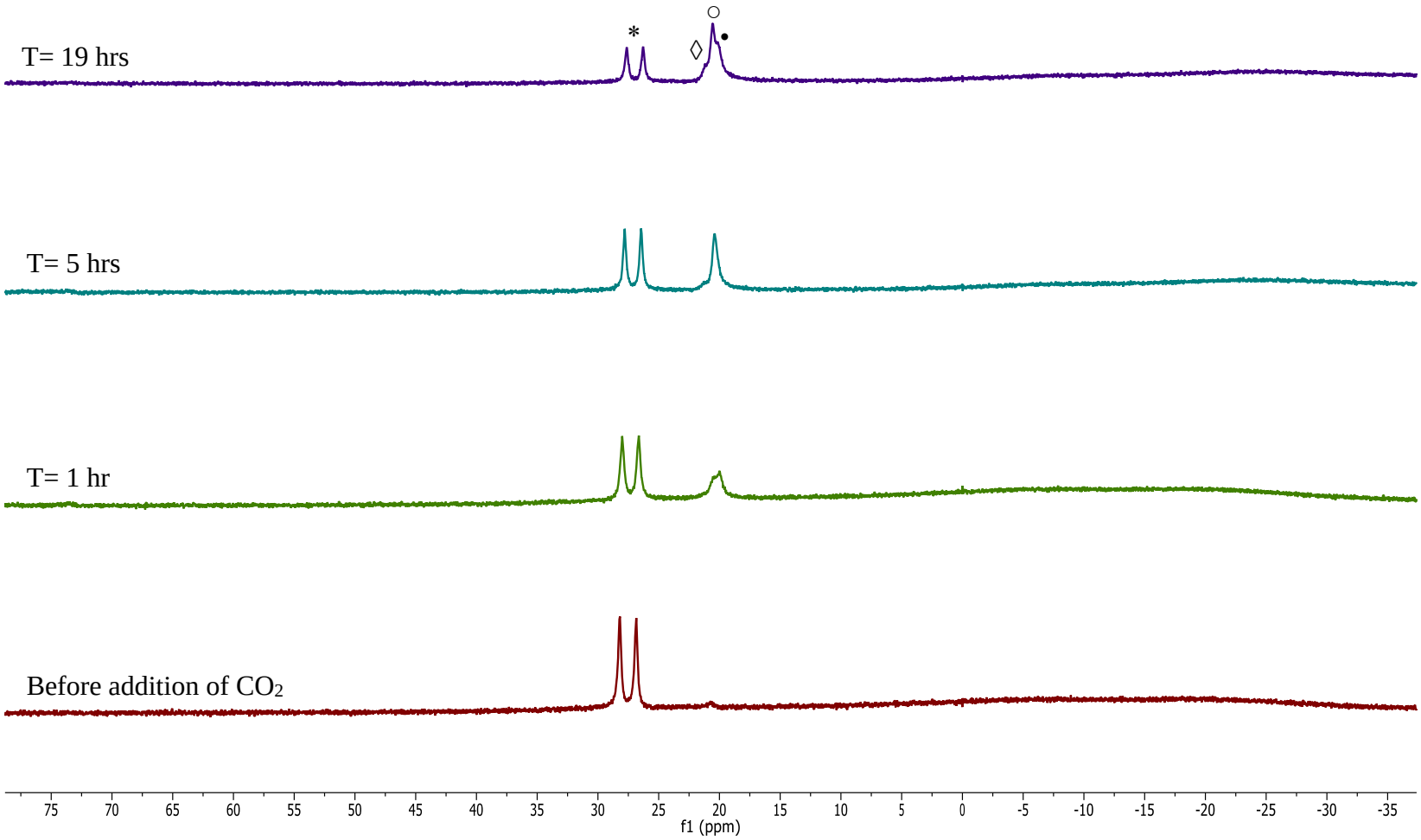


Figure S 14 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_2$, 1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in THF-d_8. (•) represents the ^{11}B peak for pinBOBpin at 21.2 ppm, (◊) represents the broad peak for CH_3OBPin at 22.2 ppm, (○) represents the peak for HCOOBpin at 21.7 ppm and (*) represents the peak for unreacted HBpin.

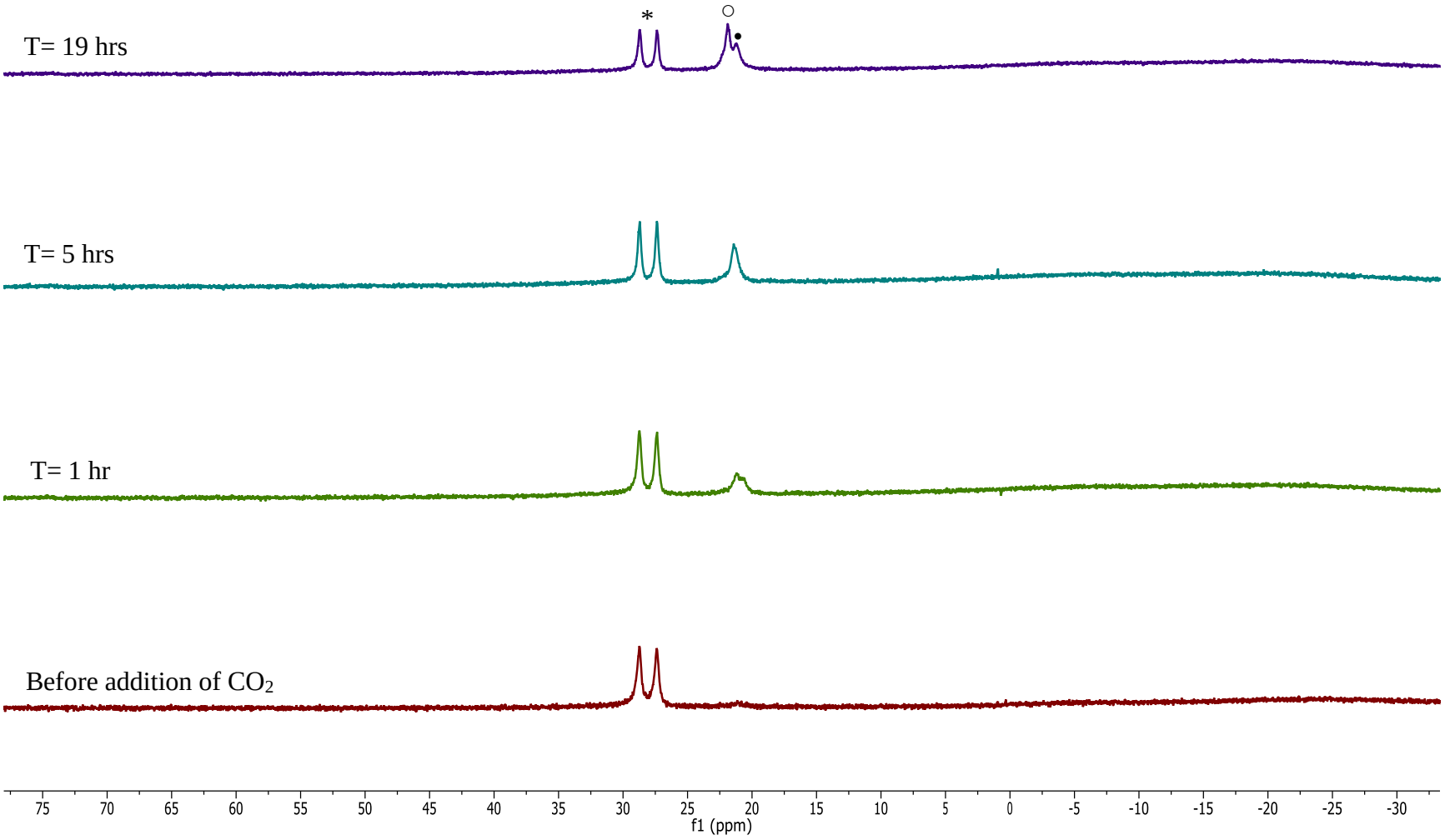


Figure S 15 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % Co(II) Benzoate, 1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in THF-d_8. (•) represents the ^{11}B peak for pinBOBpin at 21.2 ppm, (○) represents the peak for HCOOBpin at 21.7 ppm and (*) represents the peak for unreacted HBpin.

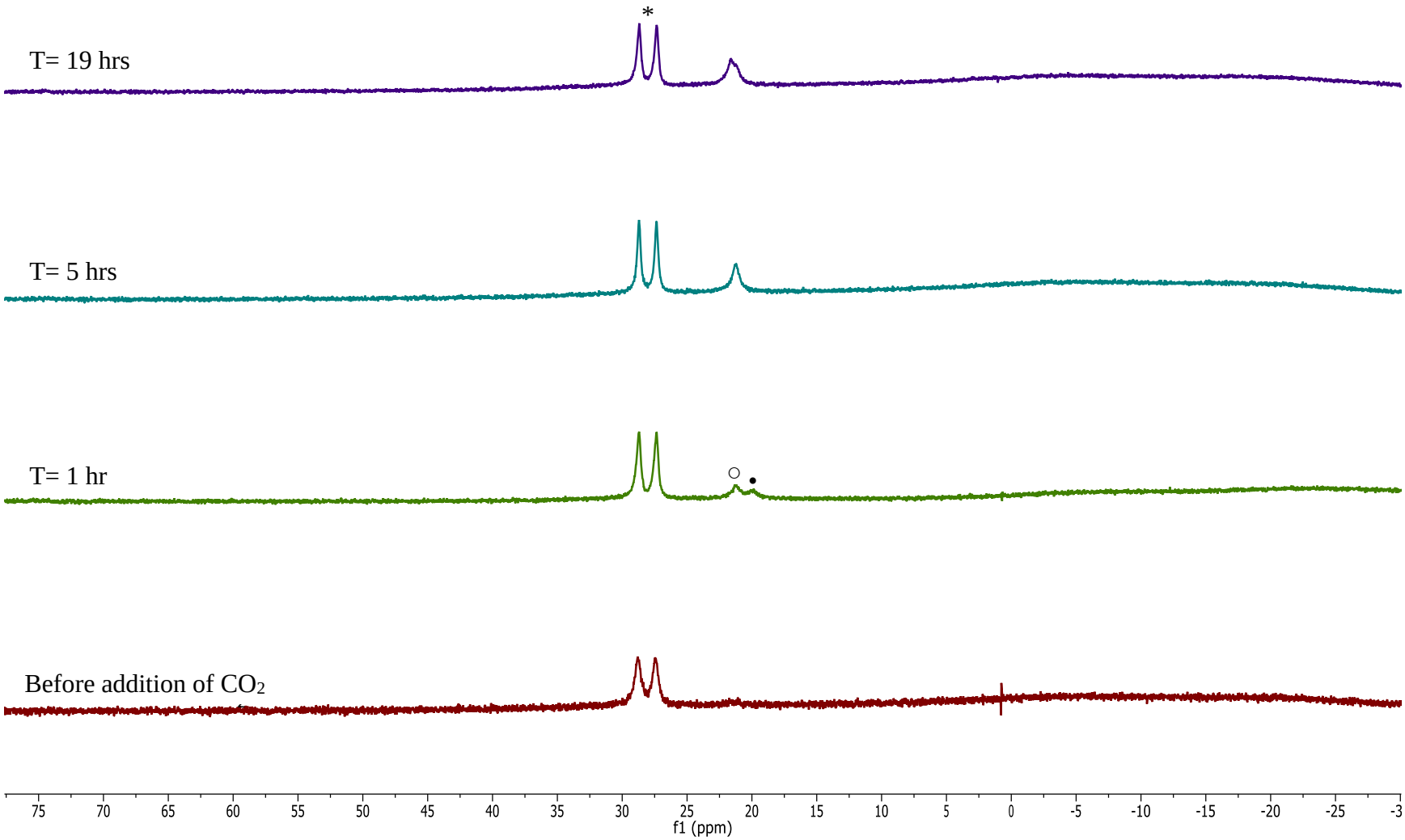


Figure S 16 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(TMHD)_3$, 1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in THF-d_8. (•) represents the ^{11}B peak for pinBOBpin at 21.2 ppm, (○) represents the peak for HCOOBpin at 21.7 ppm and (*) represents the peak for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

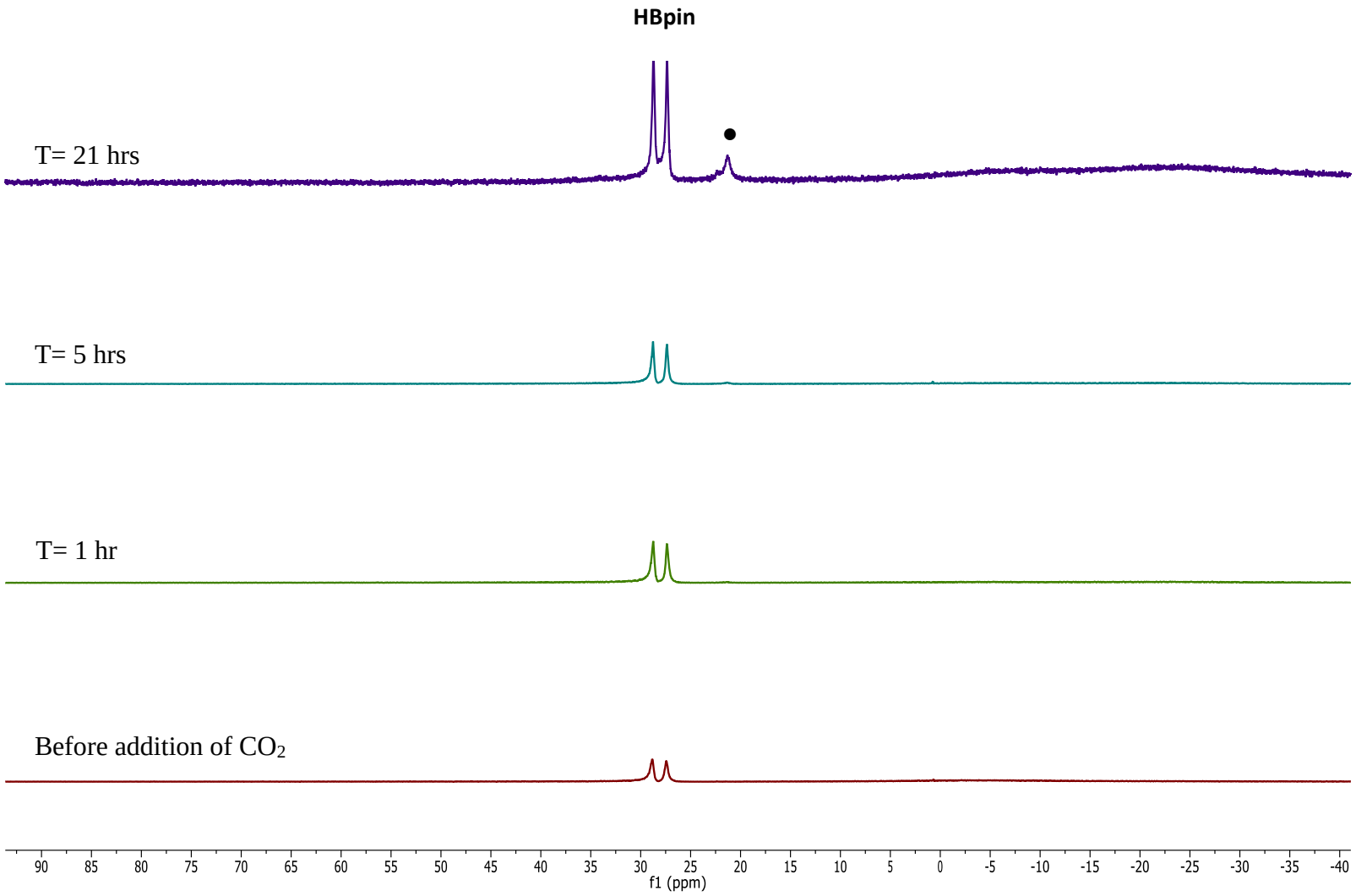


Figure S 17 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in Toluene-d_8. (●) represents the broad overlapped peak for pinBOBpin and HCOOBpin at 21.2 ppm.

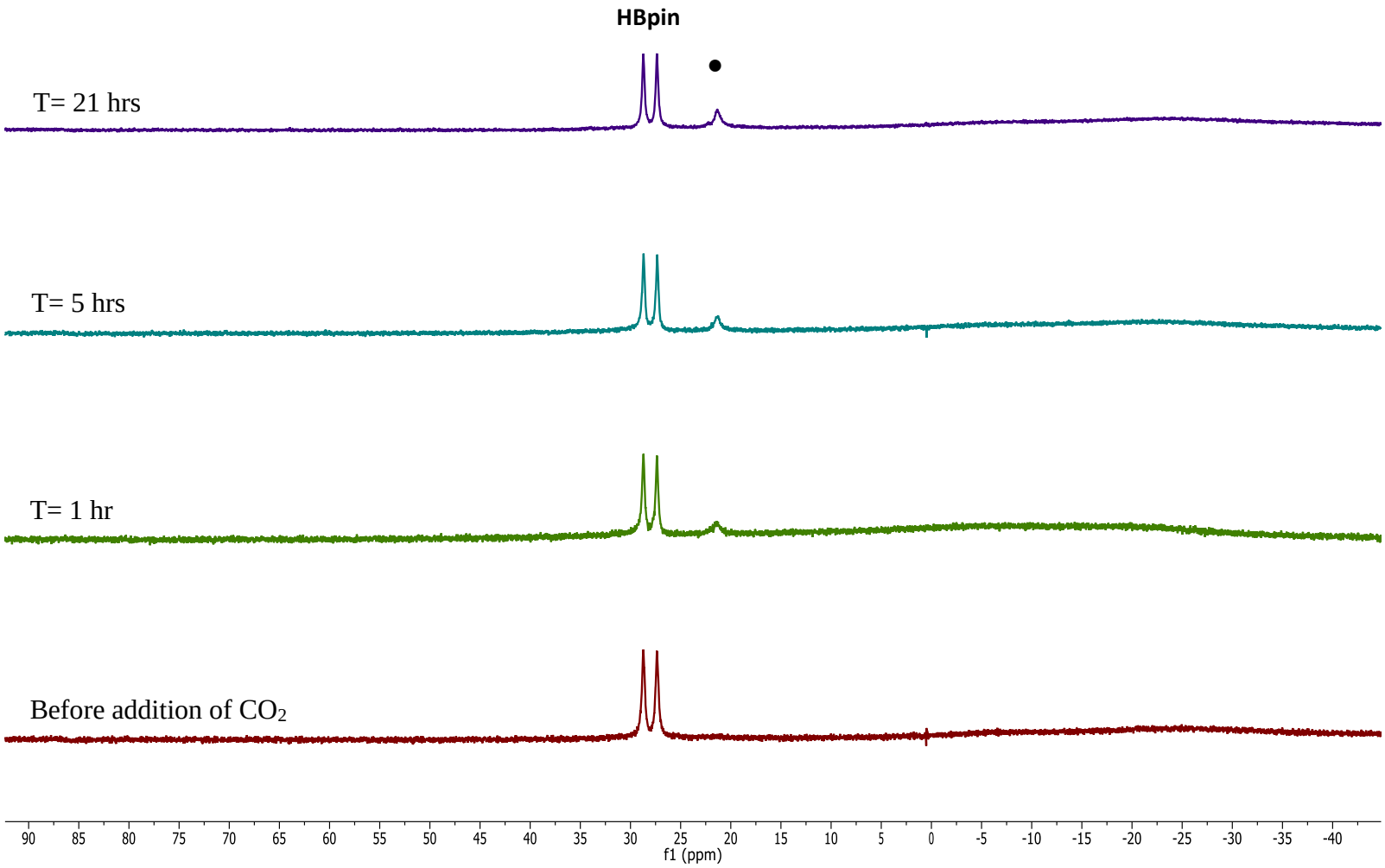


Figure S 18 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in benzene-d_6. (●) represents the broad peak for pinBOBpin at 21.4 ppm.

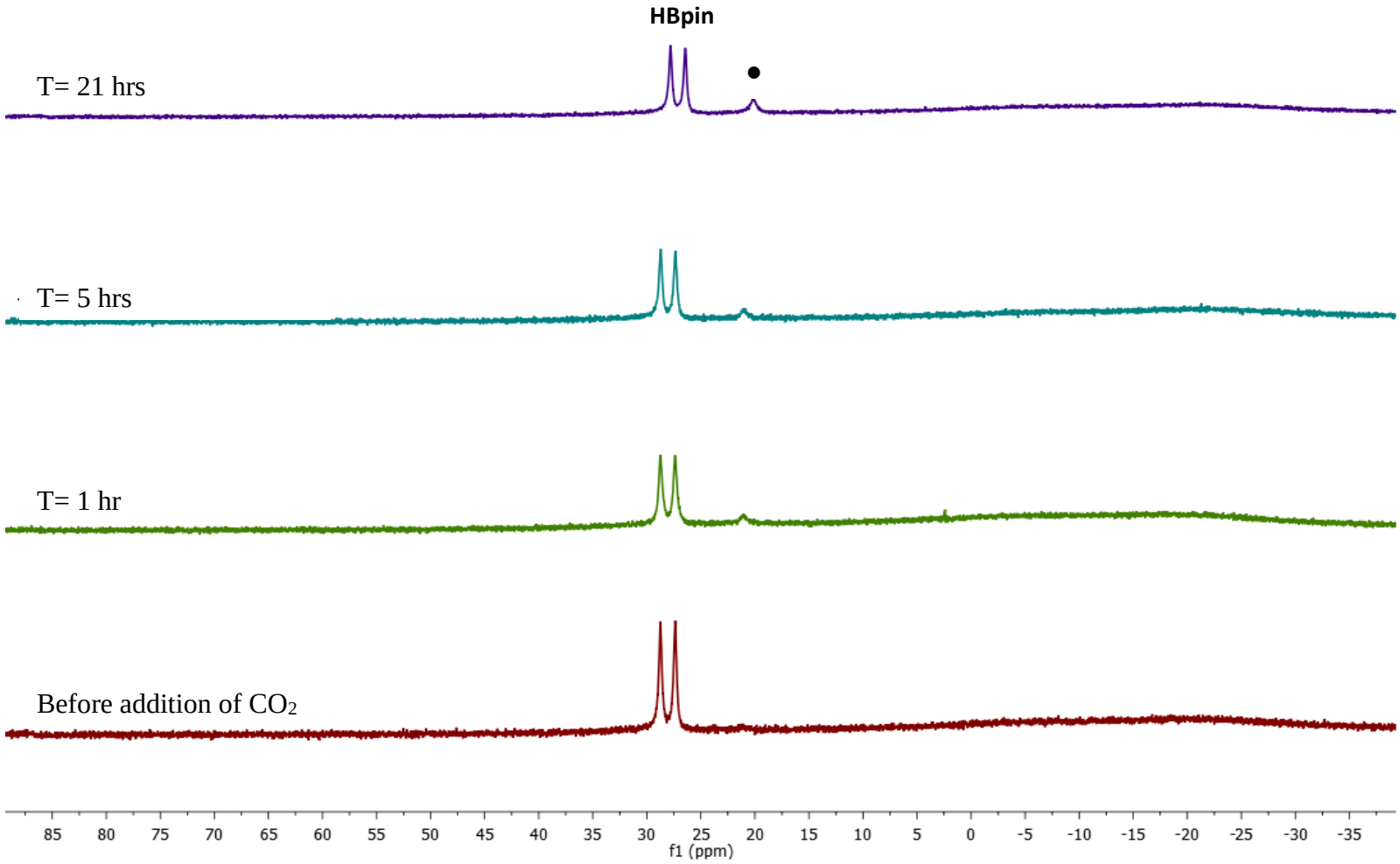


Figure S 19 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in CD_2Cl_2-d_2. (●) represents the peaks for pinBOBpin at 21.1 ppm.

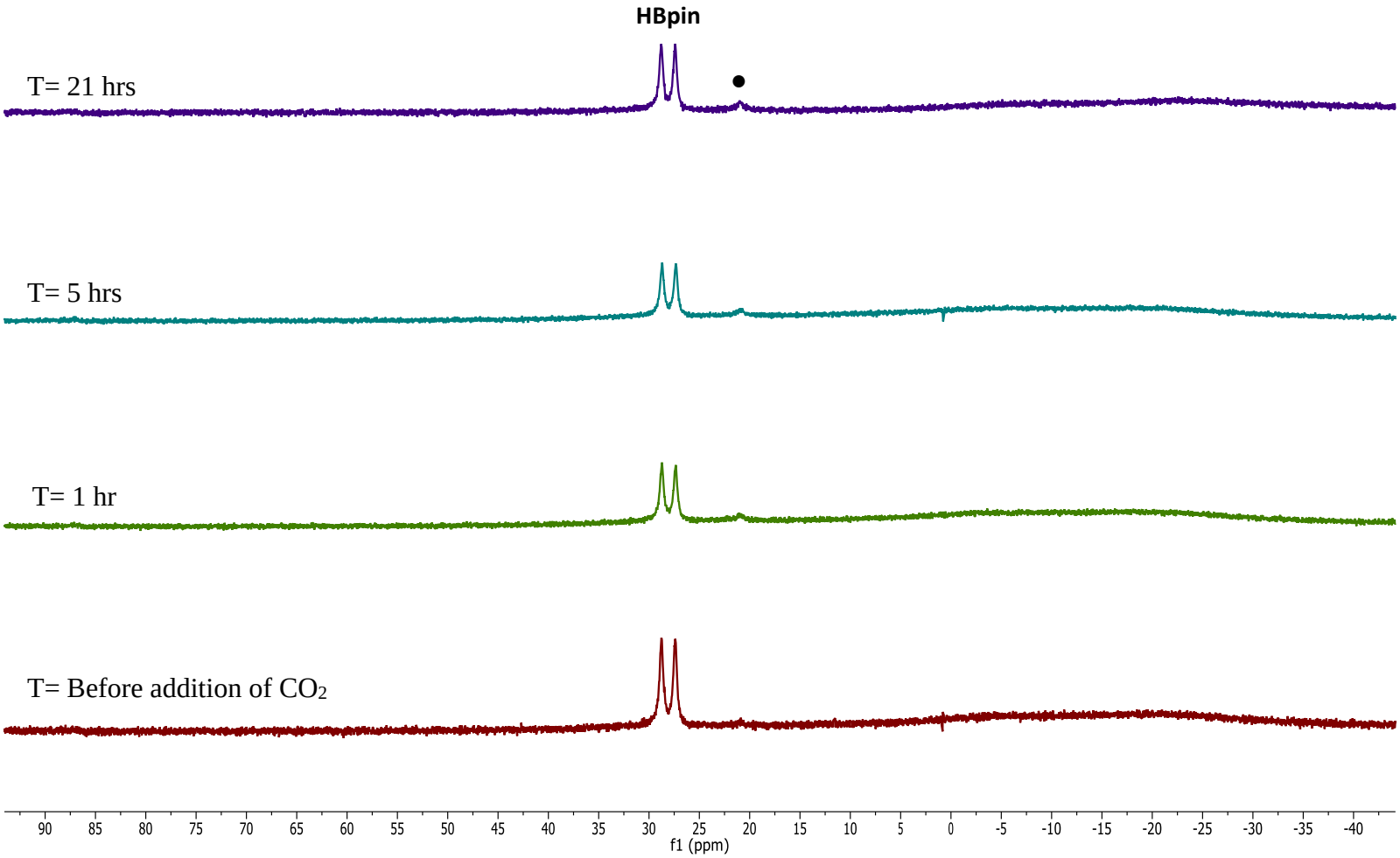


Figure S 20 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in $CDCl_3$. (●) represents the peaks for trace amount of pinBOBpin at 21.0 ppm.

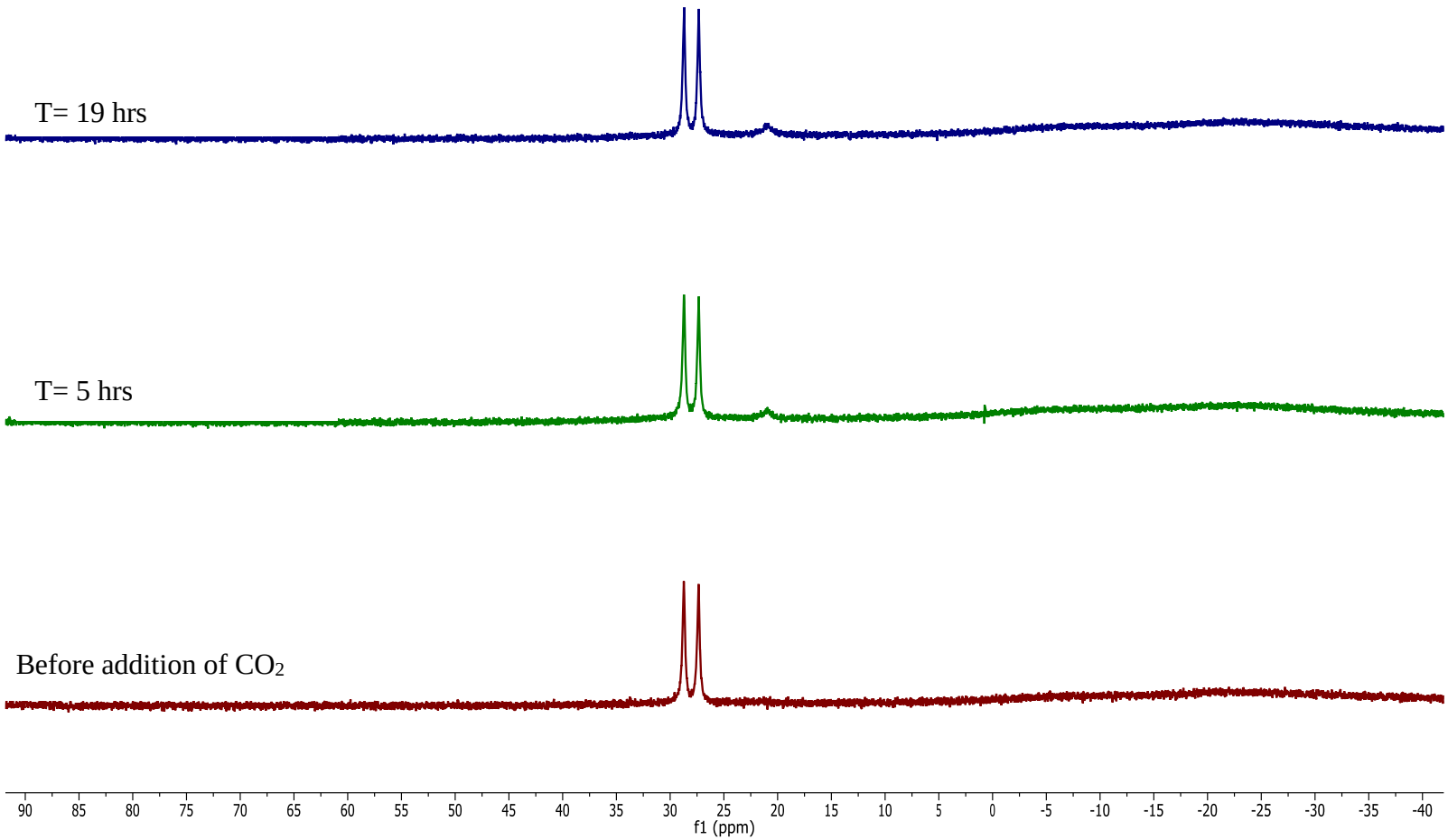


Figure S 21 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$,1 mol % $NaHBEt_3$, and HBPin (0.1 mmol) at various time intervals in cyclohexane-d_{12}.

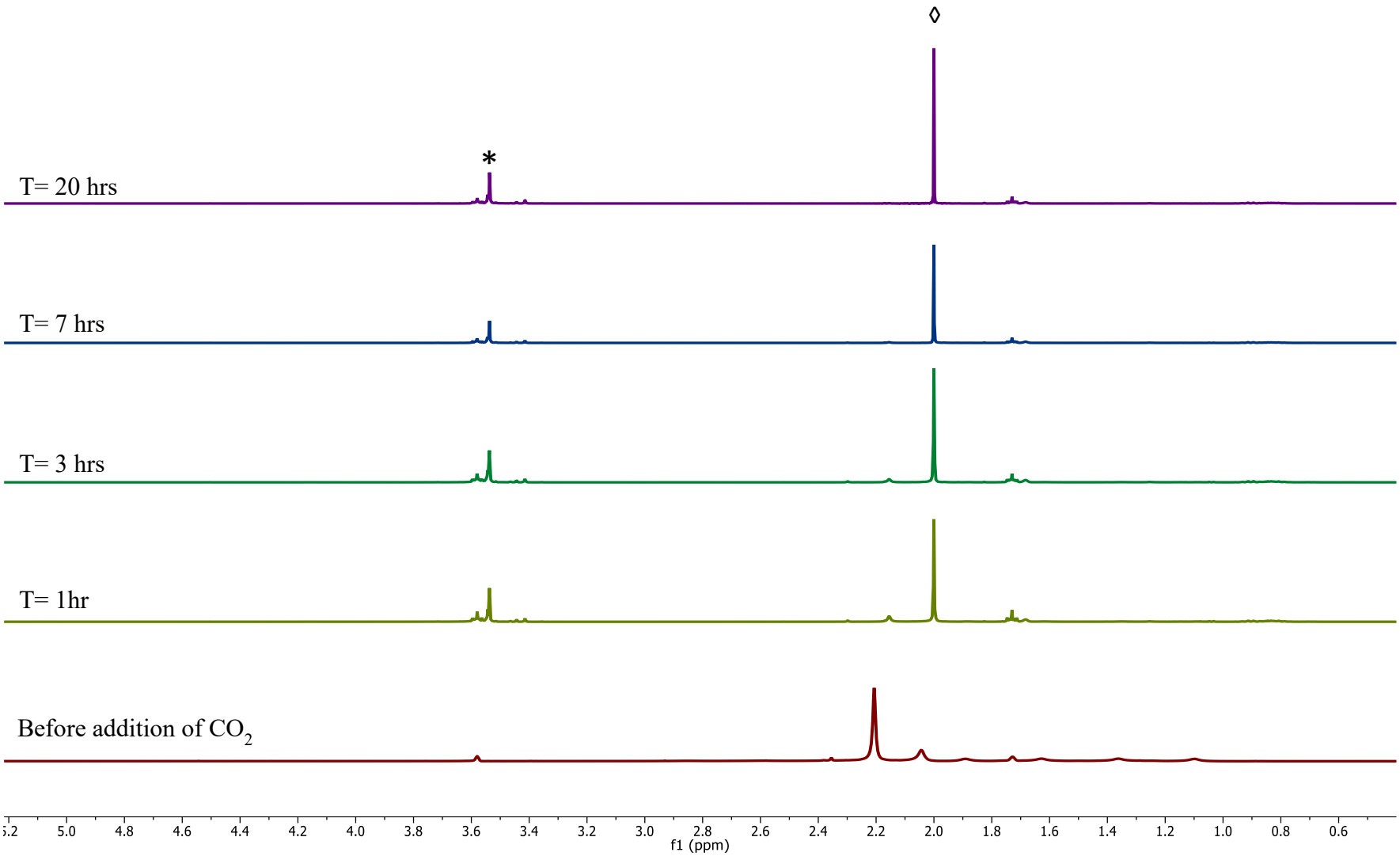


Figure S 22 ^{1}H NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, and BH_3•$S(Me)_2$ (0.1 mmol) at various time intervals in THF-d_8. The (*) represents the ^{1}H peak for $(CH_3OBO)_3$ at 3.54 ppm and (◊) represents peak for free $S(Me)_2$ at 2.00 ppm.

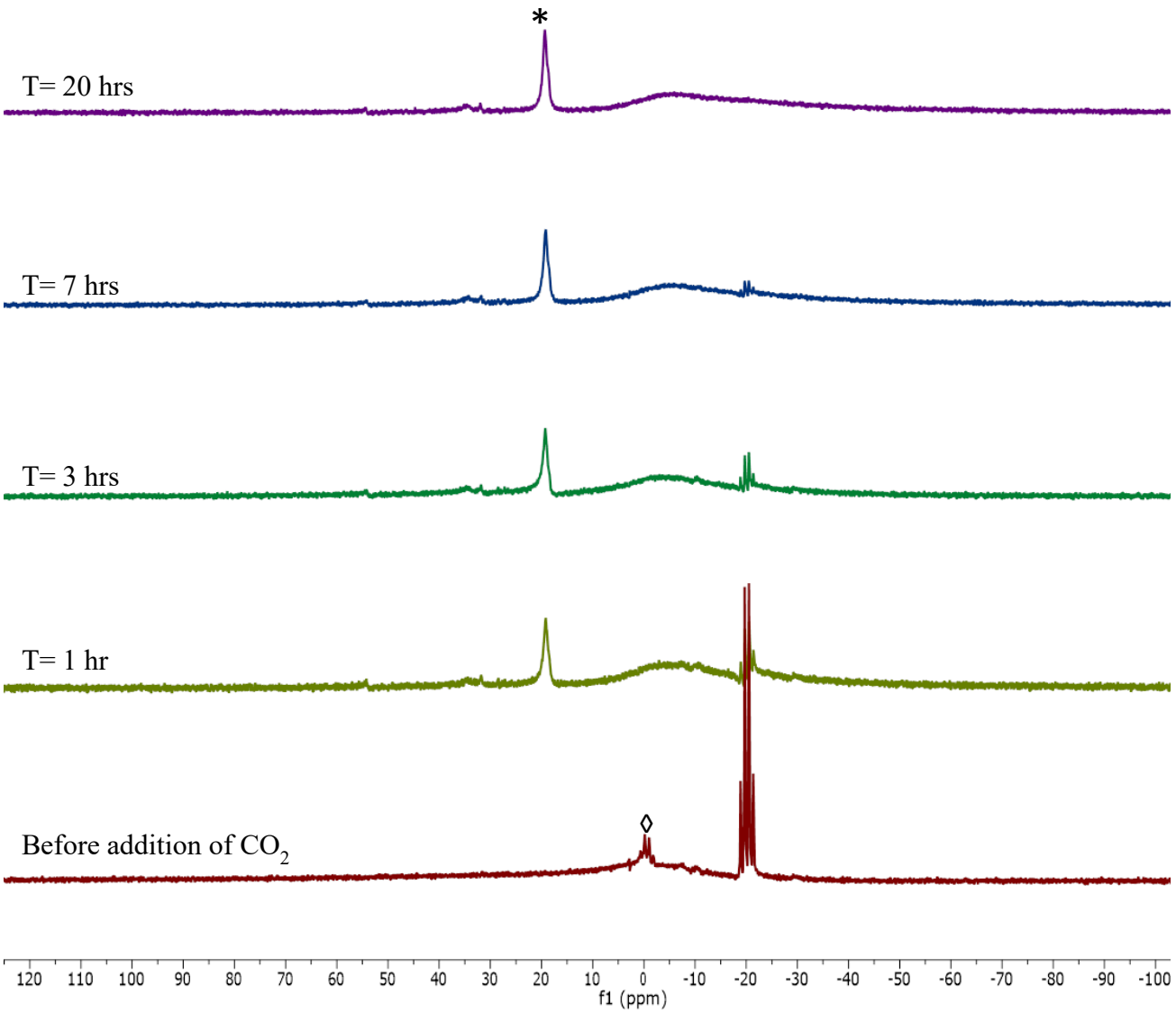


Figure S 23 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, and BH_3•$S(Me)_2$ (0.1 mmol) at various time intervals THF-d_8. The (*) represents the ^{11}B peak for $(CH_3OBO)_3$ at 19.3 ppm, and (◊) represents the peak for BH_3•THF at -0.25 ppm.

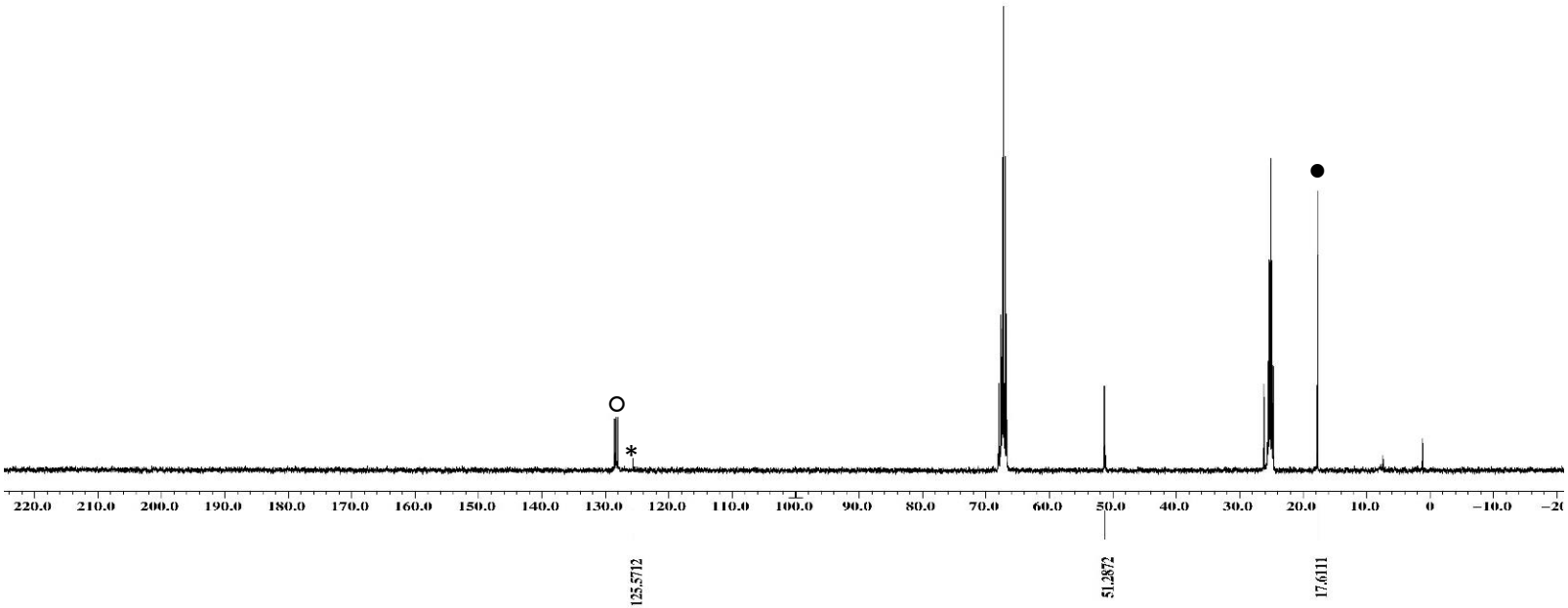


Figure S 24 ^{13}C NMR spectra after hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, and BH_3•$S(Me)_2$ (0.1 mmol) in THF-d_8 . The (◊) represents peak for $(CH_3OBO)_3$ at 51.3 ppm, (●) represents the peak for $S(Me)_2$ at 17.6 ppm,(○) represents the peak for benzene-d_6 at 128.8 ppm, and (*) represents the peak for CO_2 at 125 ppm.

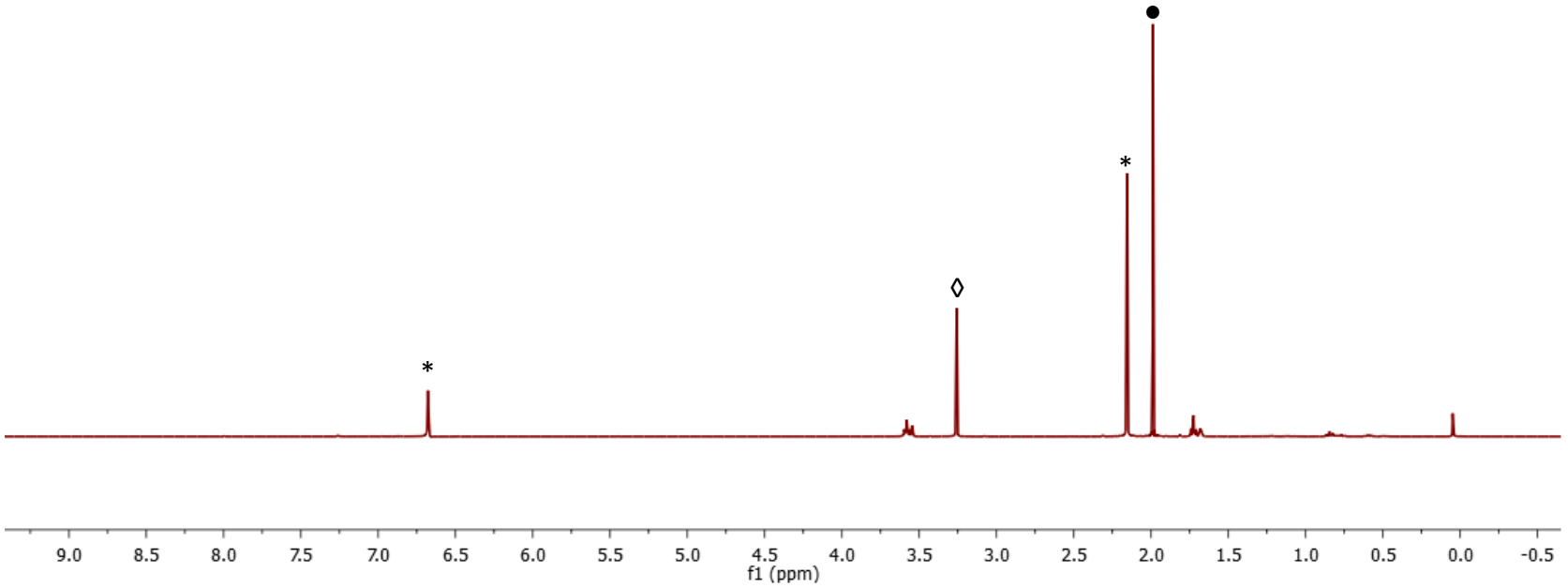


Figure S 25 ^{1}H NMR spectra in THF-d_8 after hydrolysis with 50 µL of DCL in D_2O.The (◊) represents the peak for CH_3OD at 3.26 ppm, (●) represents the peak for $S(Me)_2$ at 1.99 ppm, and (*) represents the peak for mesitylene at 2.16 ppm, and 6.67 ppm.

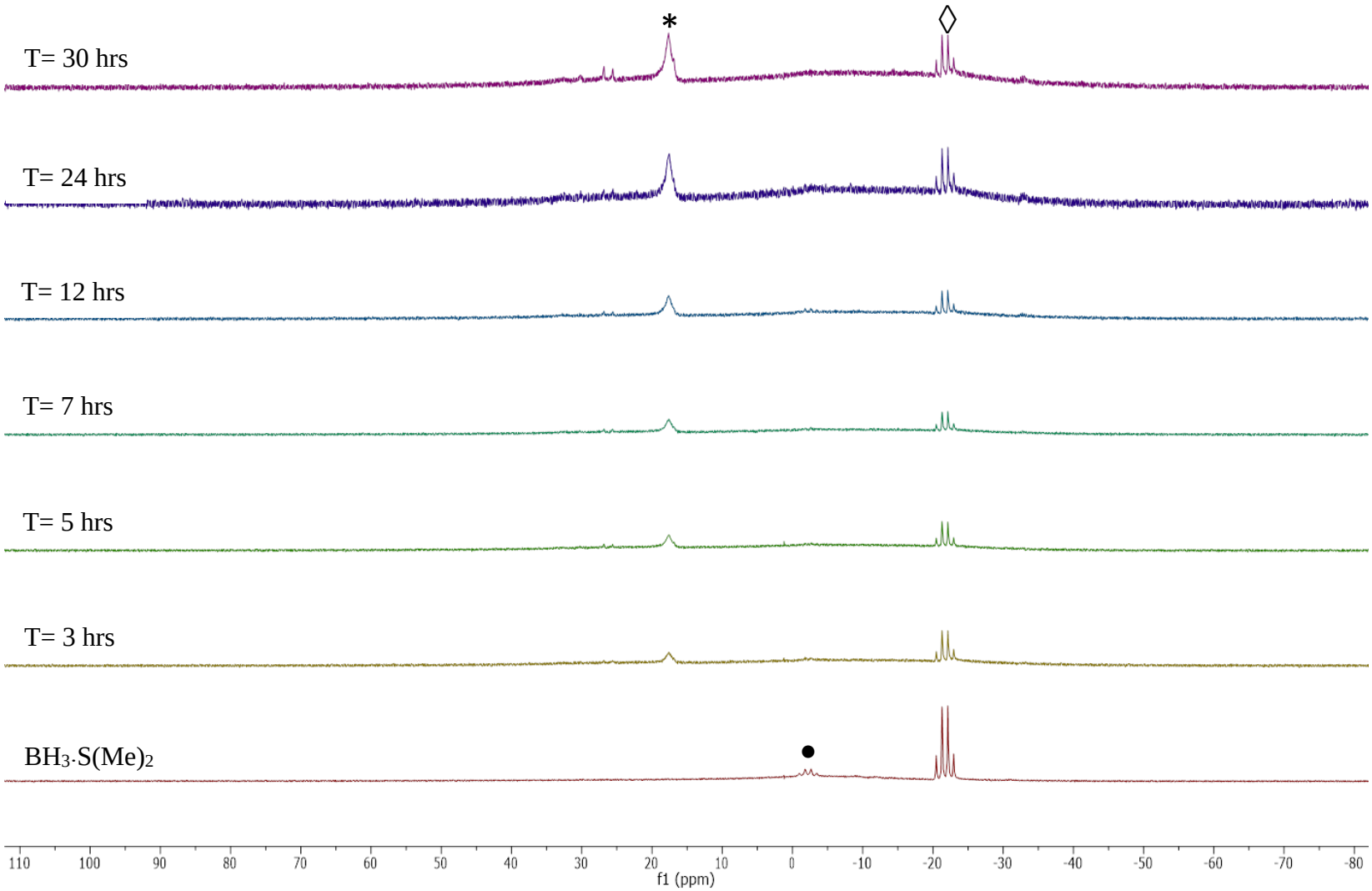


Figure S 26 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $NaHBEt_3$, and BH_3•$S(Me)_2$ (0.1 mmol) at various time intervals in THF. The (*) represents the ^{11}B peak for $(CH_3OBO)_3$ at 19.3 ppm, (◊) represents the peak for unreacted BH_3•$S(Me)_2$ at -21.3 ppm, and (●) represents the peak for BH_3•THF at -0.25 ppm.

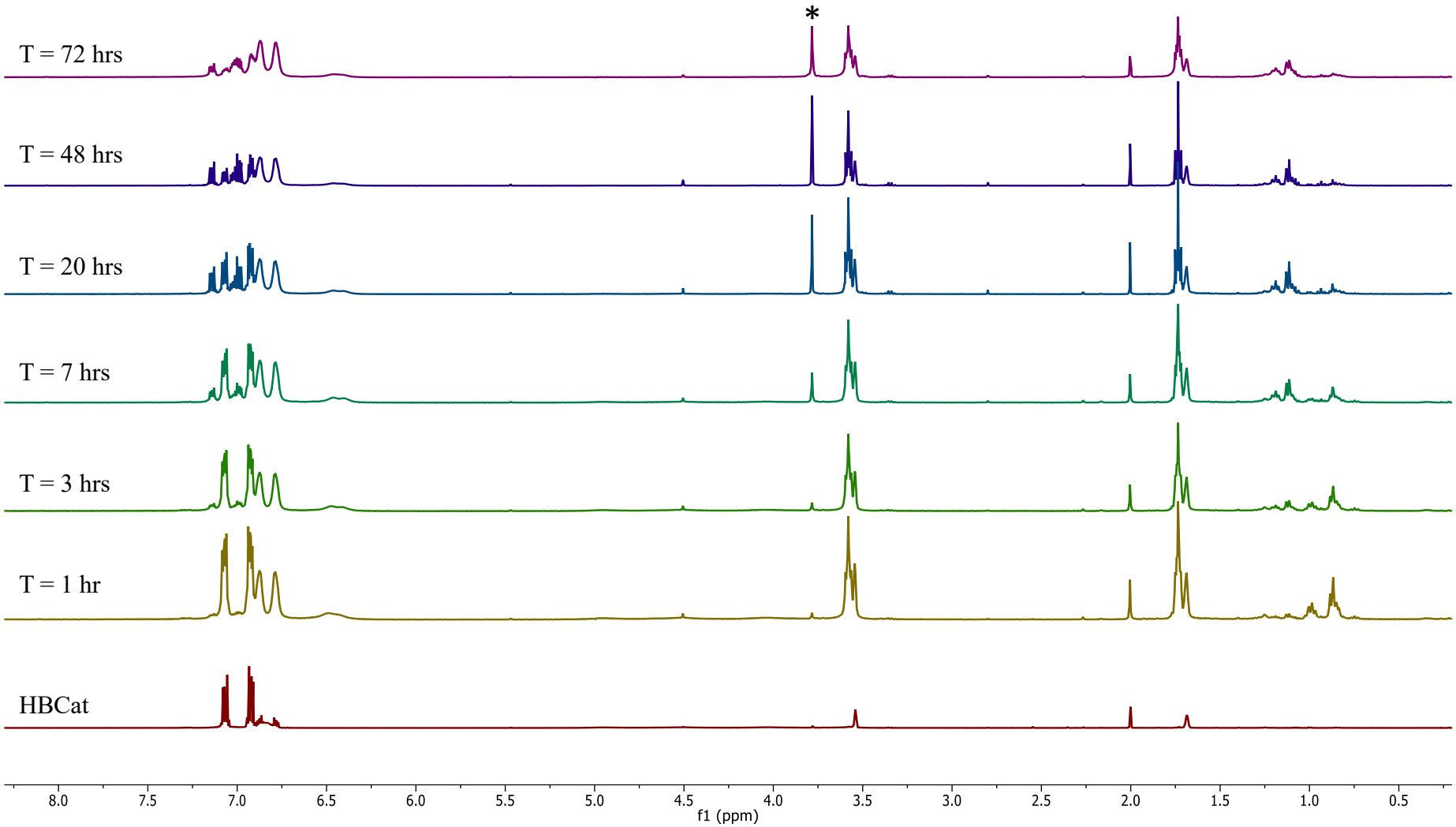


Figure S 27 ^{1}H NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, and HBCat (0.1 mmol) at various time intervals in THF-d_8. (*) represents the ^{1}H peak for CH_3OBCat at 3.78 ppm.

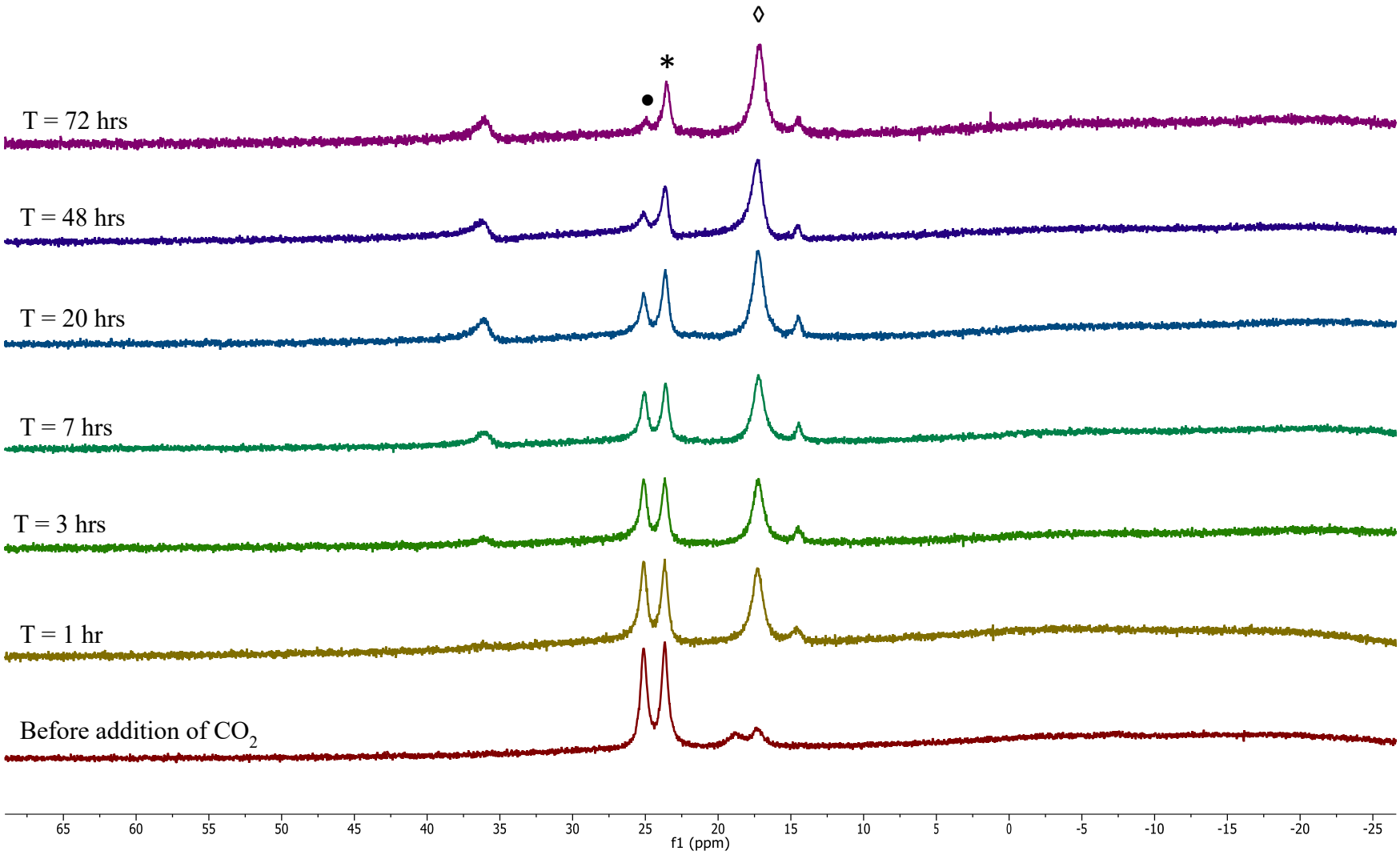


Figure S 28 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, HBCat (0.1 mmol) and CO_2 at various time intervals in THF-d_8. The (*) represents the ^{11}B peak for CH_3OBCat at 23.4ppm, (●) represents the peak for unreacted HBCat at 25.01ppm, and (◊) represents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

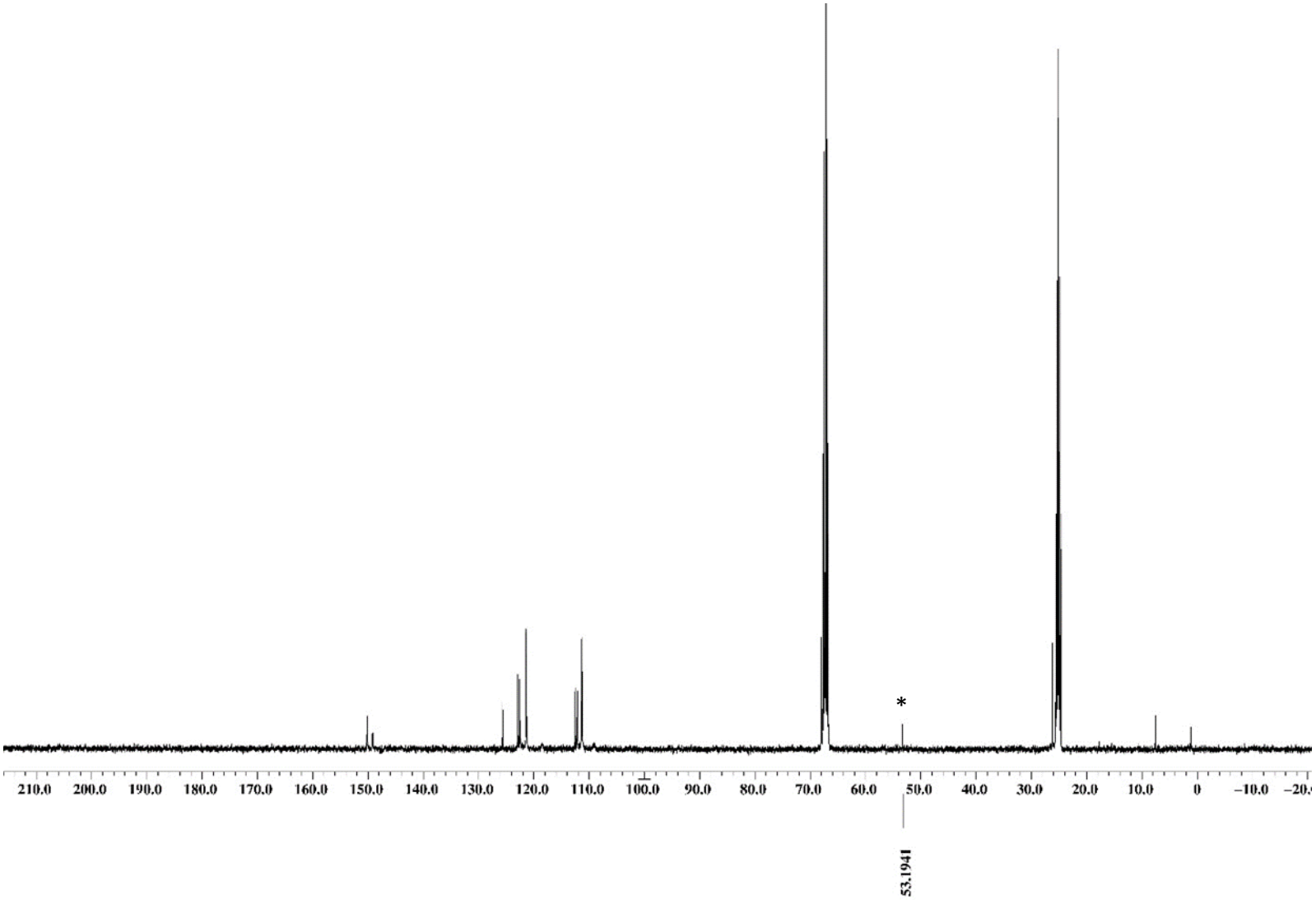


Figure S 29 ^{11}B NMR spectra for hydroboration of CO_2 with 1 mol % $Co(acac)_3$, 1 mol % $NaHBEt_3$, HBCat (0.1 mmol) and CO_2 at various time intervals in THF-d_8. (*) represents the ^{13}C peak for CH_3OBCat at 53.2 ppm.

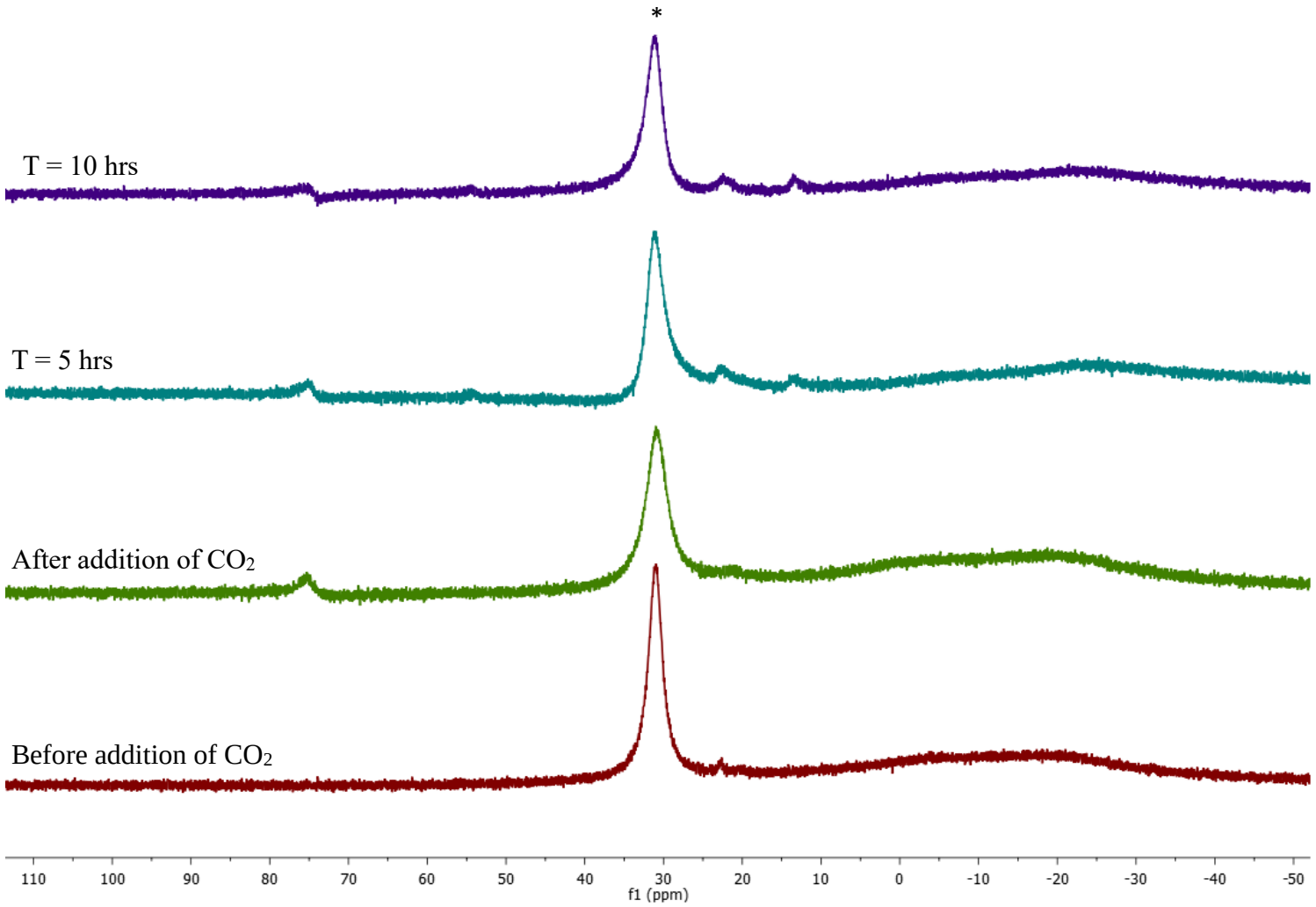


Figure S 30 ^{11}B NMR spectra for hydroboration of CO_2 with 10 mol % $Co(acac)_3$, 10 mol % $NaBHEt_3$, and B_2Pin_2 (1.0 mmol) at various time intervals in THF. (*) represents the ^{11}B peak for B_2Pin_2 at 30.2 ppm.