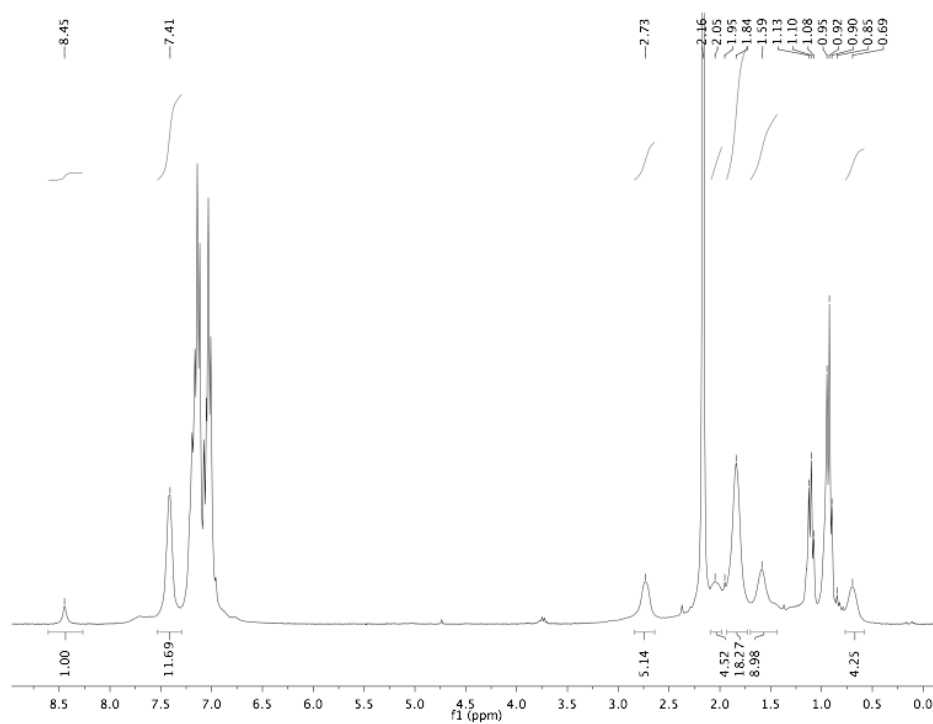


# Trialkylborane-Assisted CO<sub>2</sub> Reduction by Late Transition Metals

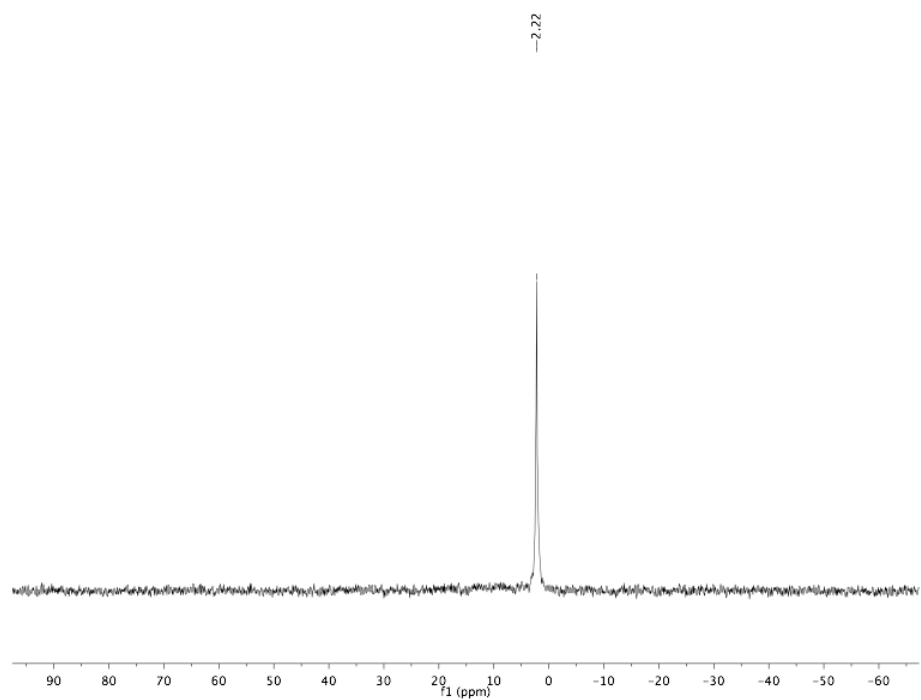
Alexander J. M. Miller, Jay A. Labinger,\* and John E. Bercaw\*

## Supporting Information

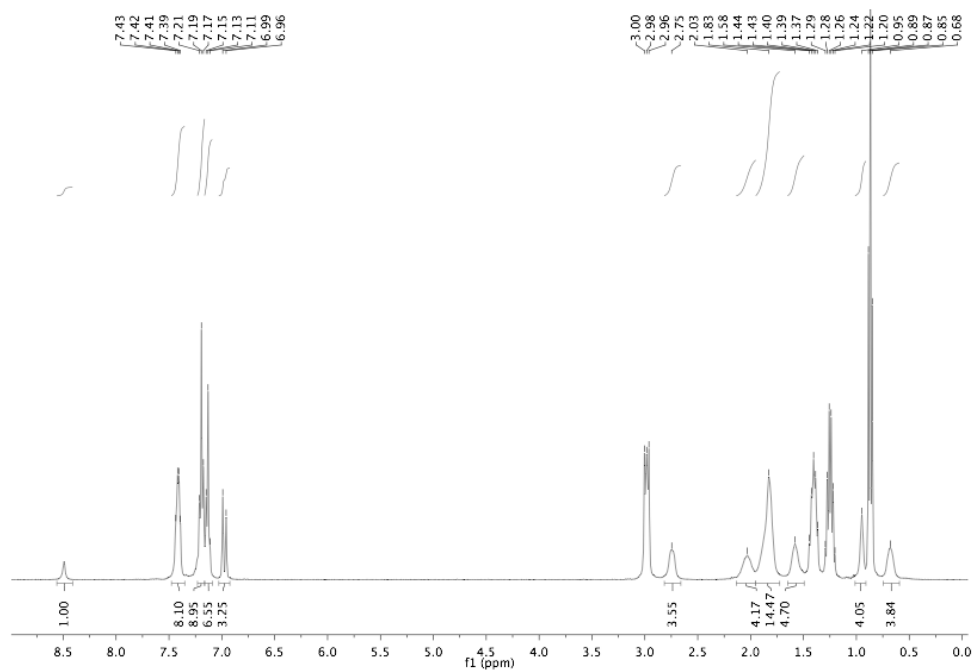
NMR spectra to accompany Experimental Section.



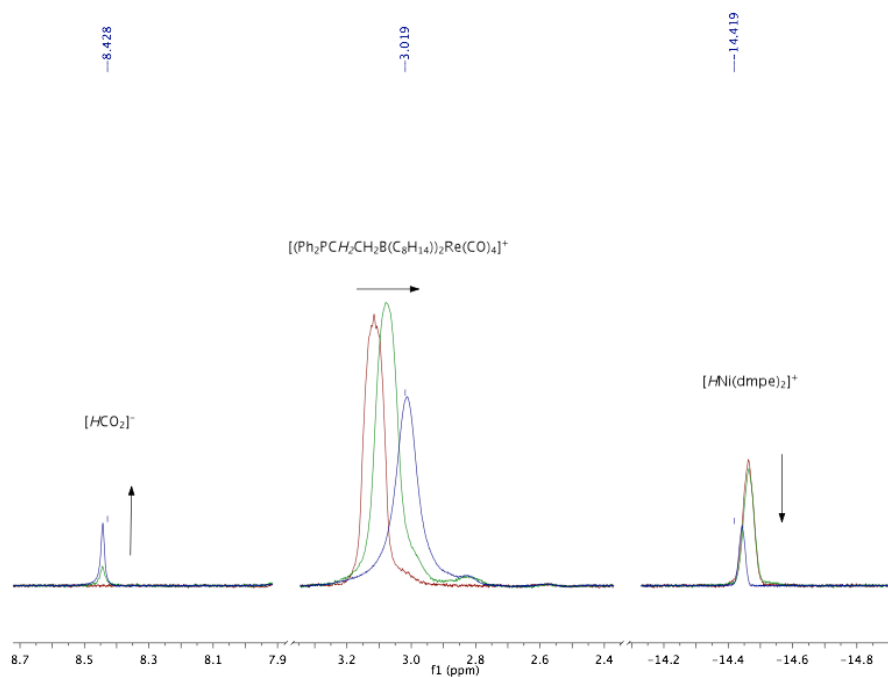
**Figure S1.** Reaction of **2** with CO<sub>2</sub>: <sup>1</sup>H NMR of **1**•(HCO<sub>2</sub>).



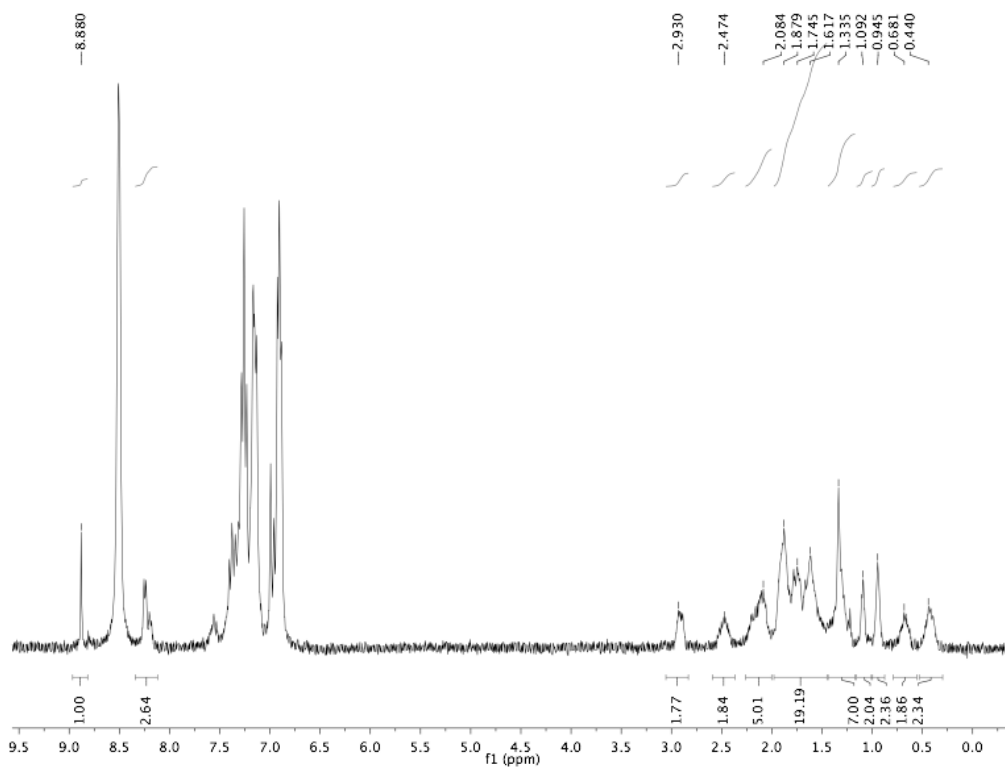
**Figure S2.** Reaction of **2** with  $\text{CO}_2$ :  $^{31}\text{P}\{^1\text{H}\}$  NMR of **1**•( $\text{HCO}_2$ ).



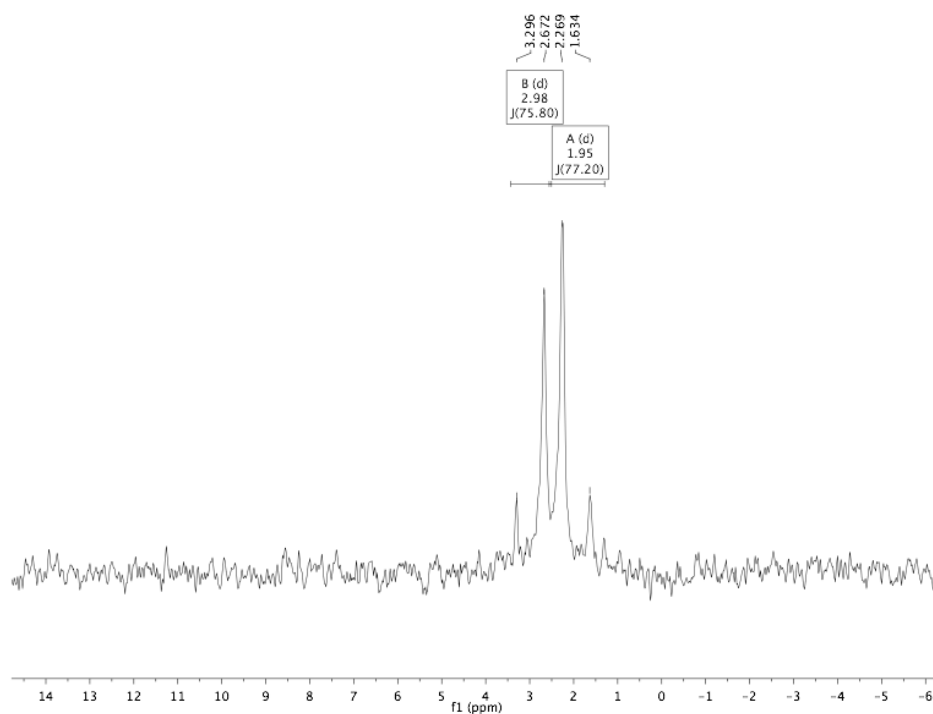
**Figure S3.** Reaction of **[1]** $[\text{BF}_4]$  with  $[\text{Bu}_4\text{N}][\text{HCO}_2]$ :  $^1\text{H}$  NMR of **1**•( $\text{HCO}_2$ ).



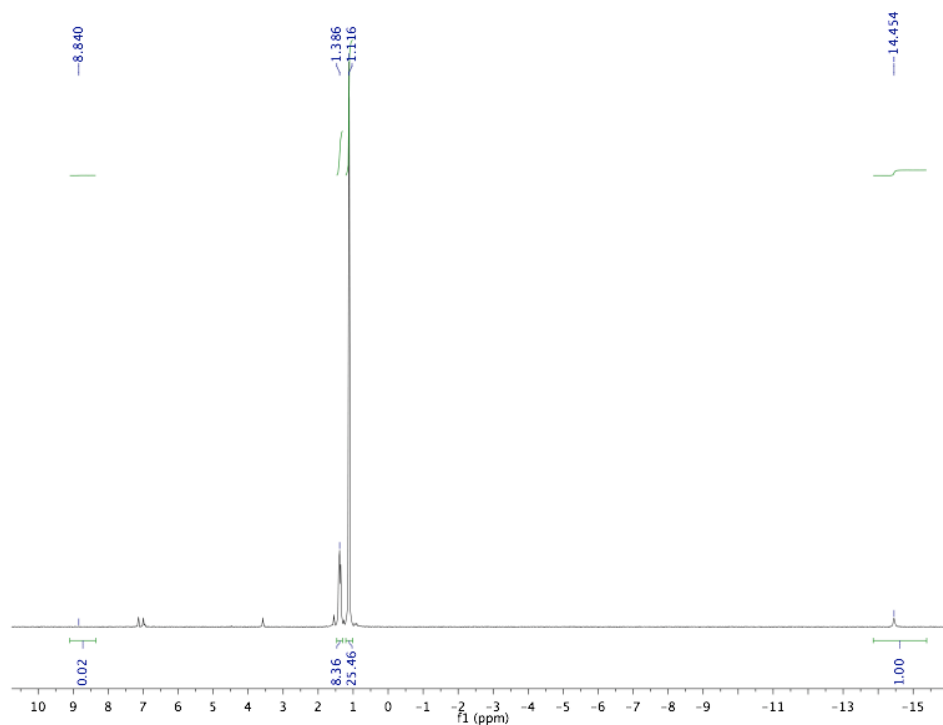
**Figure S4.** Reaction of  $[1][\text{BF}_4]$  and  $[\text{HNi}(\text{dmpe})_2][\text{PF}_6]$  with  $\text{CO}_2$  in  $\text{C}_6\text{D}_5\text{Cl}$ : Time course ( $^1\text{H}$  NMR excerpts).



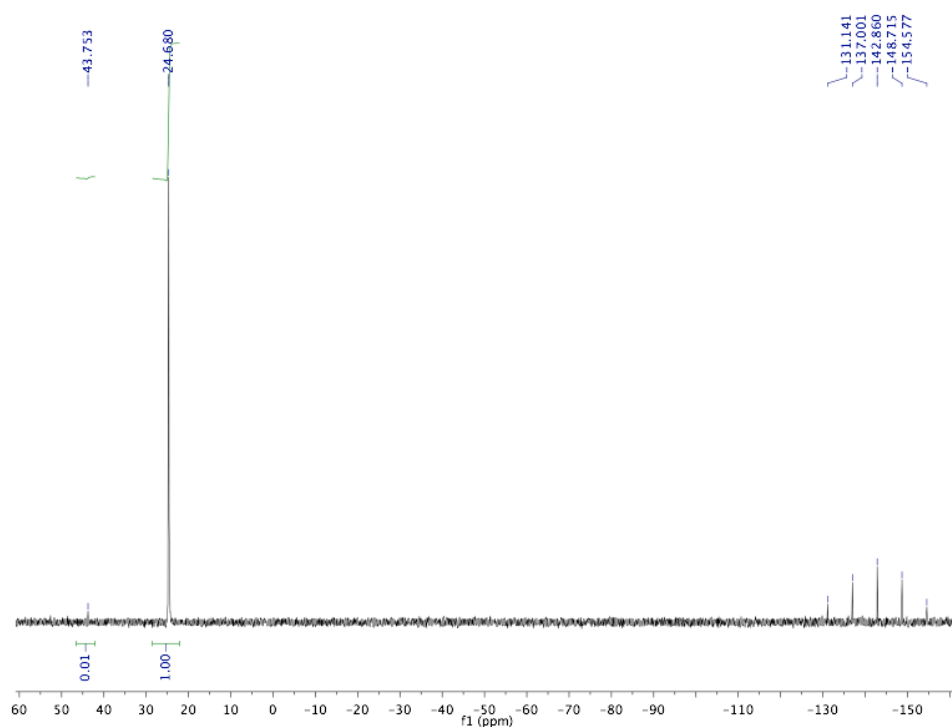
**Figure S5.** Reaction of  $[1][\text{BF}_4]$  and  $[\text{HNi}(\text{dmpe})_2][\text{PF}_6]$  with  $\text{CO}_2$  in  $\text{C}_6\text{D}_5\text{Cl}$ :  $^1\text{H}$  NMR of  $1 \cdot (\text{HCO}_2)(\text{pyridine})$ .



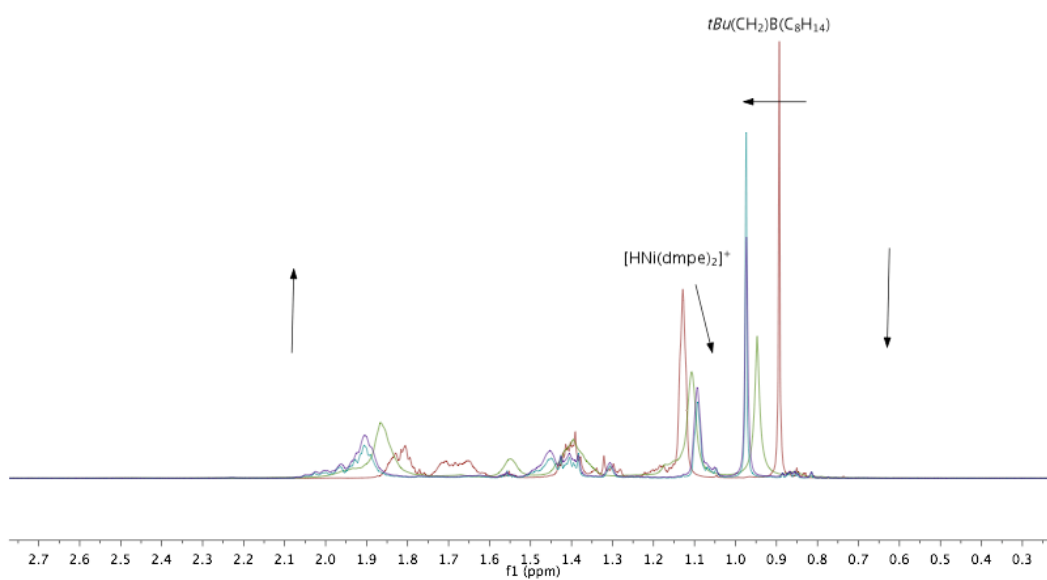
**Figure S6.** Reaction of  $[1][BF_4]$  and  $[HNi(dmpe)_2][PF_6]$  with  $CO_2$  in  $C_6D_5Cl$ :  $^{31}P\{^1H\}$  NMR of  $1\bullet(HCO_2)(pyridine)$ .



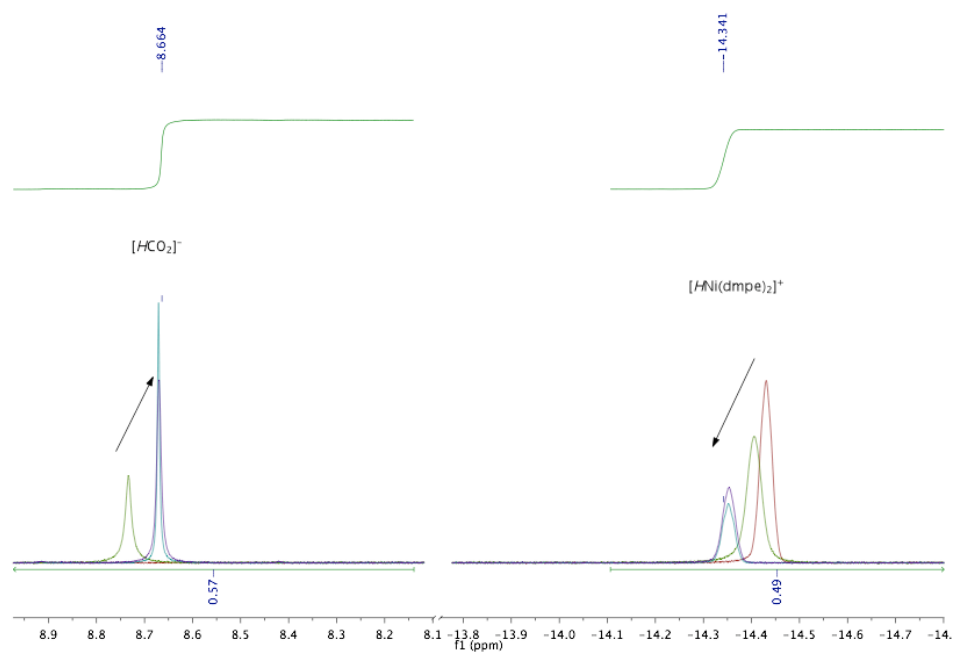
**Figure S7.** Reaction of  $[HNi(dmpe)_2][PF_6]$  with  $CO_2$  in  $C_6D_5Cl$  ( $^1H$  NMR). Spectrum shows almost entirely unreacted Ni hydride, with trace formate.



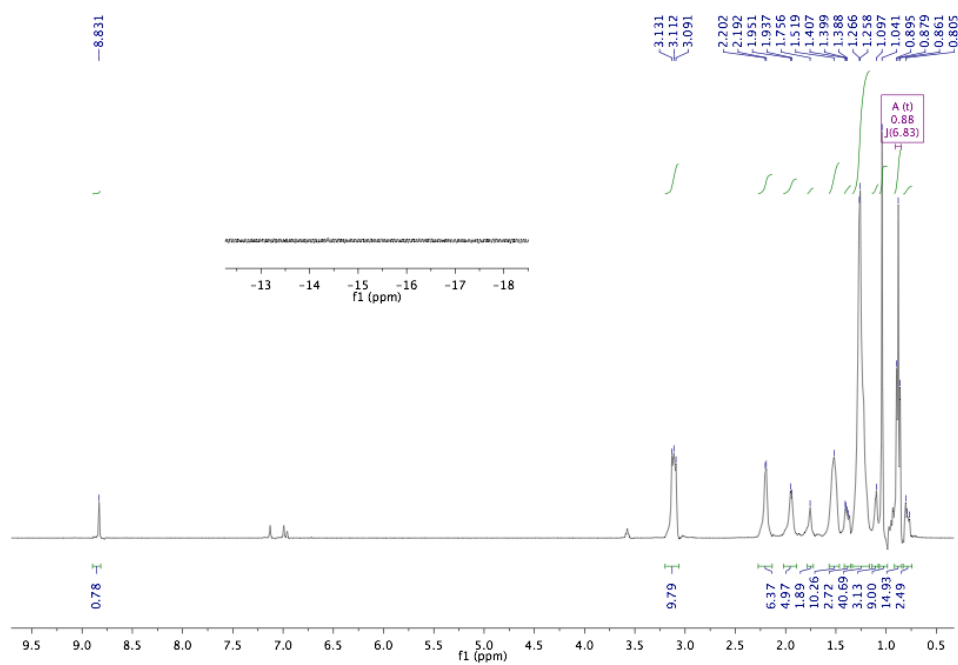
**Figure S8.** Reaction of  $[\text{HNi}(\text{dmpe})_2][\text{PF}_6]$  ( $\delta$  24.68) with  $\text{CO}_2$  in  $\text{C}_6\text{D}_5\text{Cl}$  ( $^{31}\text{P}$  NMR).



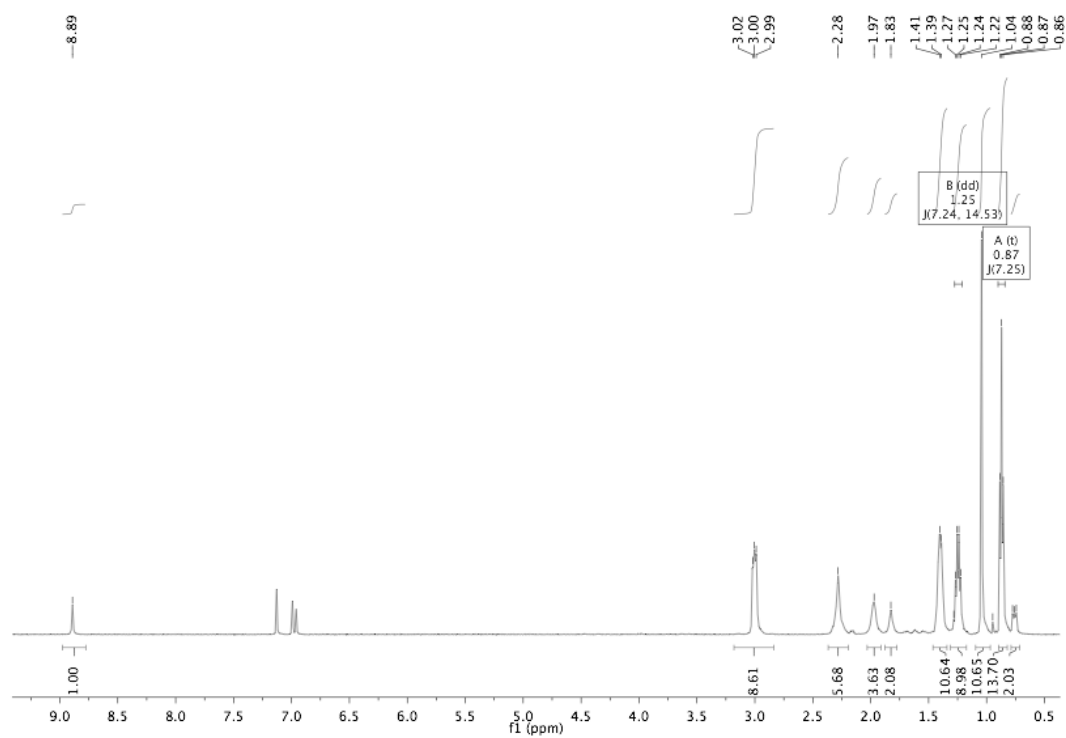
**Figure S9.** Reaction of  $[\text{HNi}(\text{dmpe})_2][\text{PF}_6]$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$ : Time course ( $^1\text{H}$  NMR alkyl region).



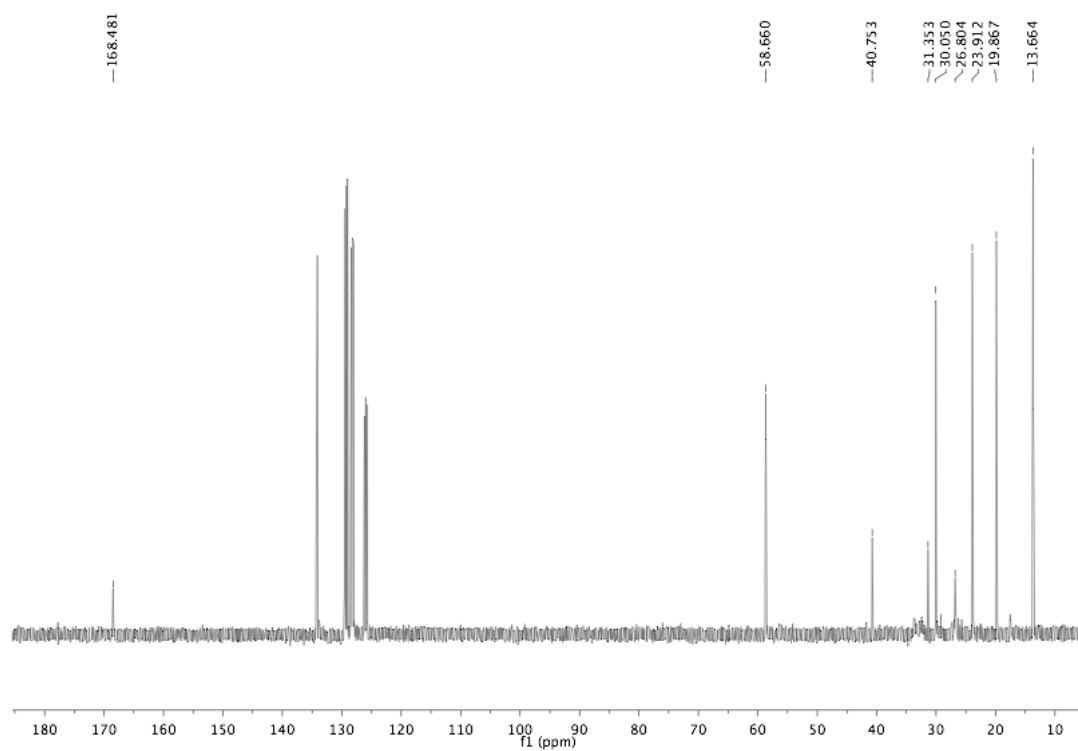
**Figure S10.** Reaction of  $[\text{HNi}(\text{dmpe})_2][\text{PF}_6]$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$ : Time course ( $^1\text{H}$  NMR formate and hydride region).



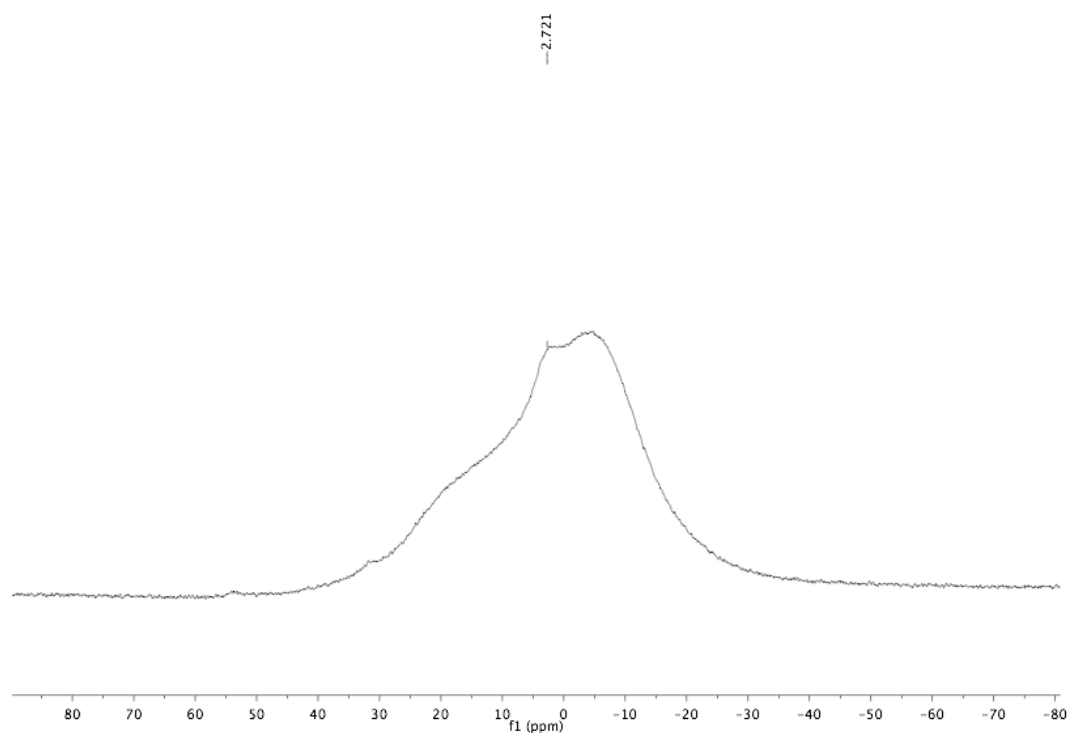
**Figure S11.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$ :  $^1\text{H}$  NMR after addition of  $[\text{hept}_4\text{N}][\text{Br}]$  (inset shows hydride region).



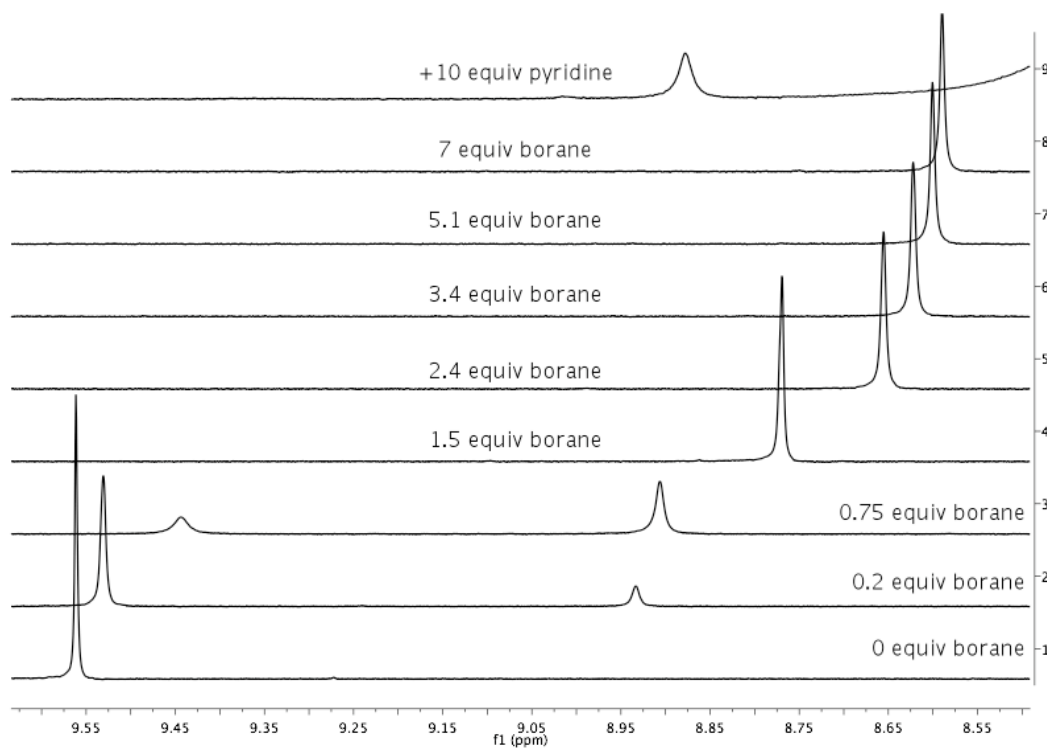
**Figure S12.** Reaction of  $[\text{Bu}_4\text{N}][\text{HCO}_2]$  with  ${}^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  in  $\text{C}_6\text{D}_5\text{Cl}$ :  ${}^1\text{H}$  NMR of  $[\text{Bu}_4\text{N}][\text{HCO}_2\text{BR}_3]$ .



**Figure S13.** Reaction of  $[\text{Bu}_4\text{N}][\text{HCO}_2]$  with  ${}^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  in  $\text{C}_6\text{D}_5\text{Cl}$ :  ${}^{13}\text{C}\{{}^1\text{H}\}$  NMR of  $[\text{Bu}_4\text{N}][\text{HCO}_2\text{BR}_3]$ .

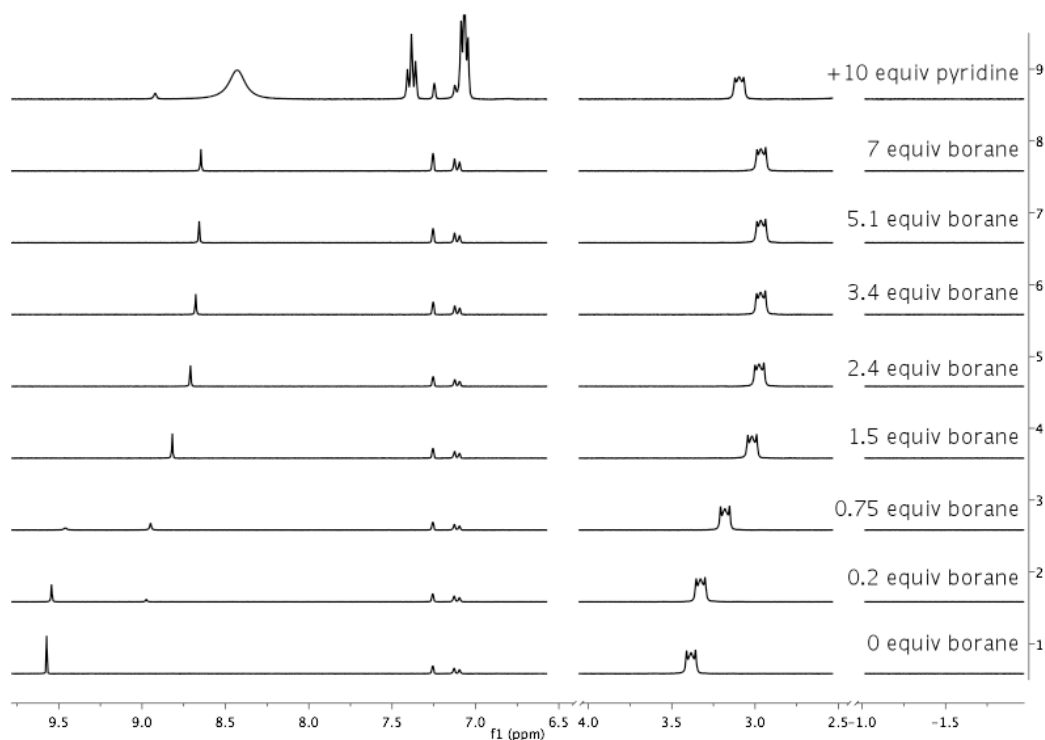


**Figure S14.** Reaction of  $[\text{Bu}_4\text{N}][\text{HCO}_2]$  with  ${}^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  in  $\text{C}_6\text{D}_5\text{Cl}$ :  ${}^{11}\text{B}$  NMR of  $[\text{Bu}_4\text{N}][\text{HCO}_2\text{BR}_3]$ .

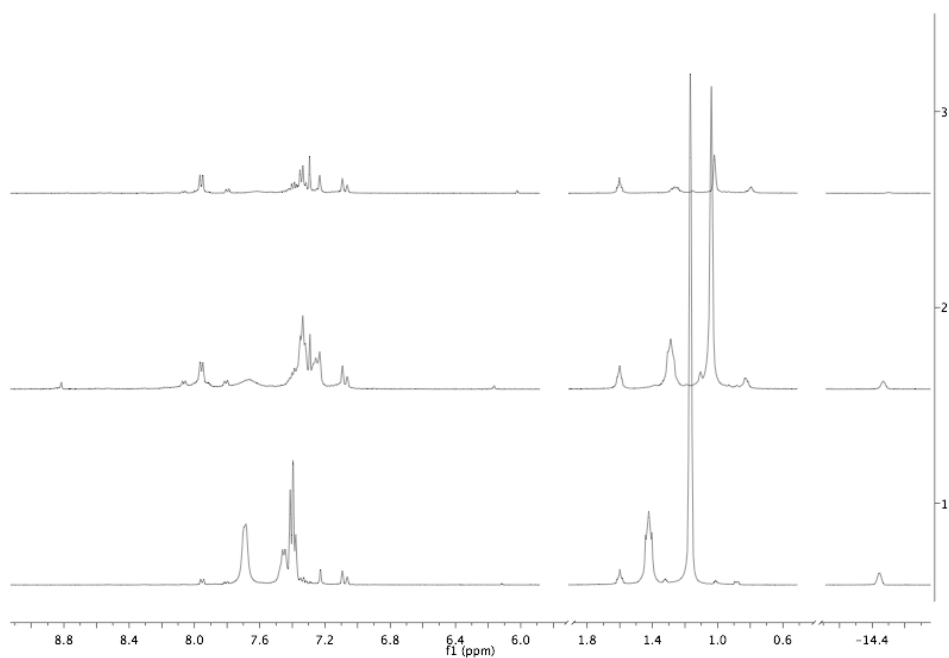


**Figure S15.** Titration of  $[\text{Bu}_4\text{N}][\text{HCO}_2]$  with  ${}^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  in  $\text{C}_6\text{D}_5\text{Cl}$  (formate region).

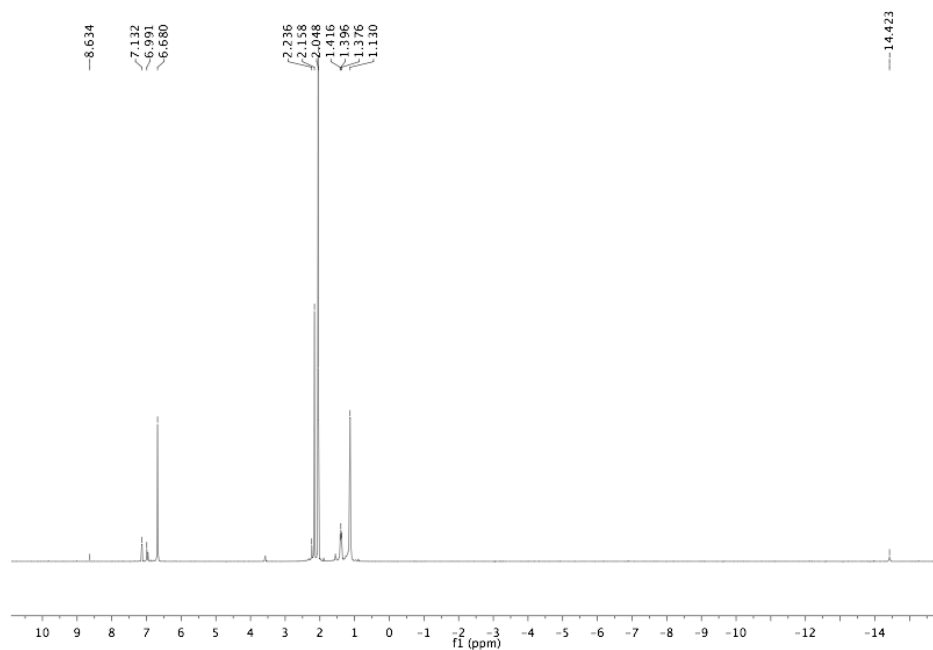




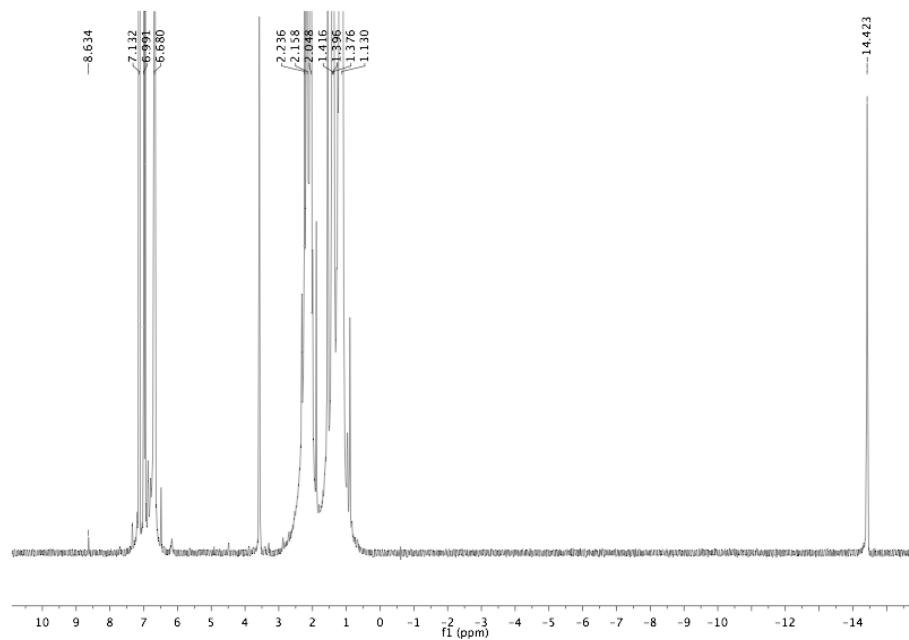
**Figure S16.** Titration of  $[\text{Bu}_4\text{N}][\text{HCO}_2]$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  in  $\text{C}_6\text{D}_5\text{Cl}$  (alkyl region omitted).



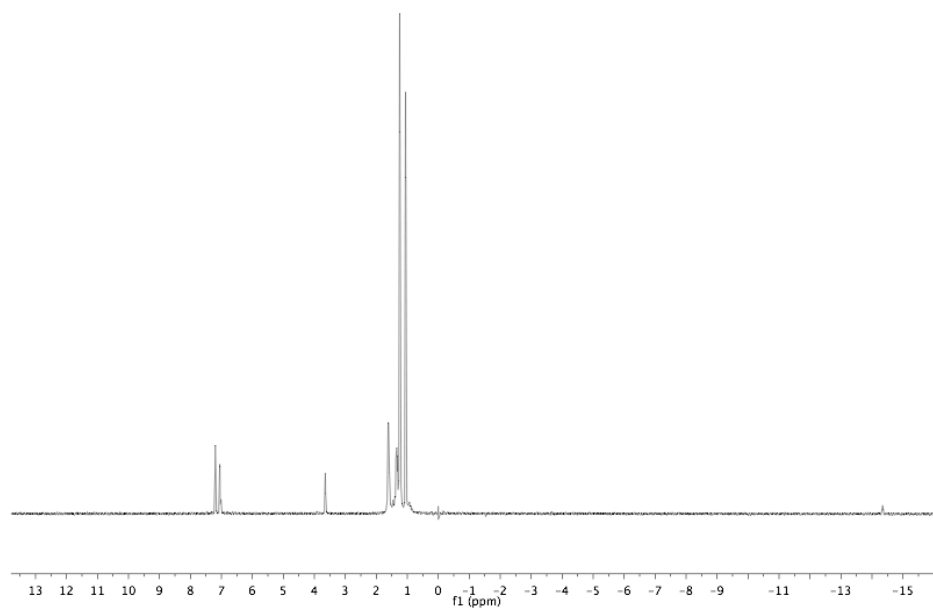
**Figure S17.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  and  $\text{BPh}_3$  before  $\text{CO}_2$  addition (bottom); 5 hours after addition (middle); 2 days after addition (top).



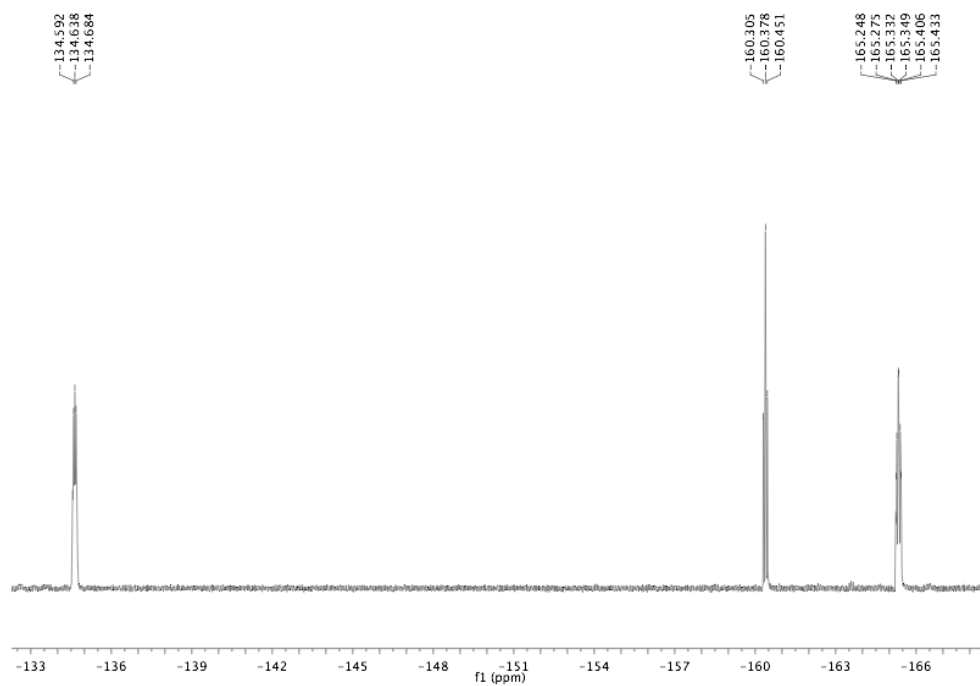
**Figure S18.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$ ,  $\text{BMes}_3$ , and  $\text{CO}_2$ :  $^1\text{H}$  NMR.



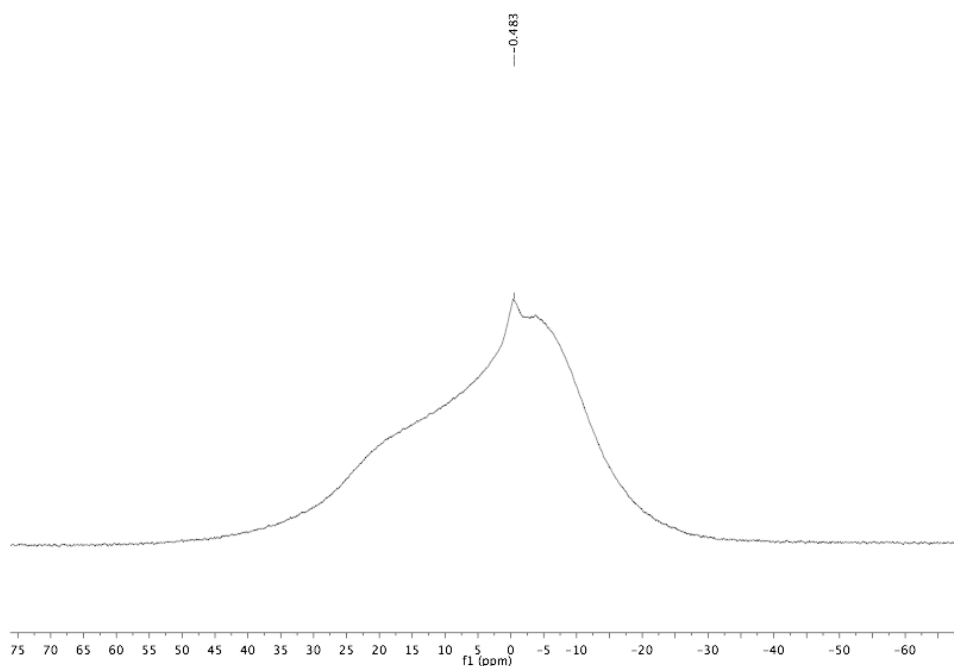
**Figure S19.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$ ,  $\text{BMes}_3$ , and  $\text{CO}_2$ :  $^1\text{H}$  NMR (blow-up).



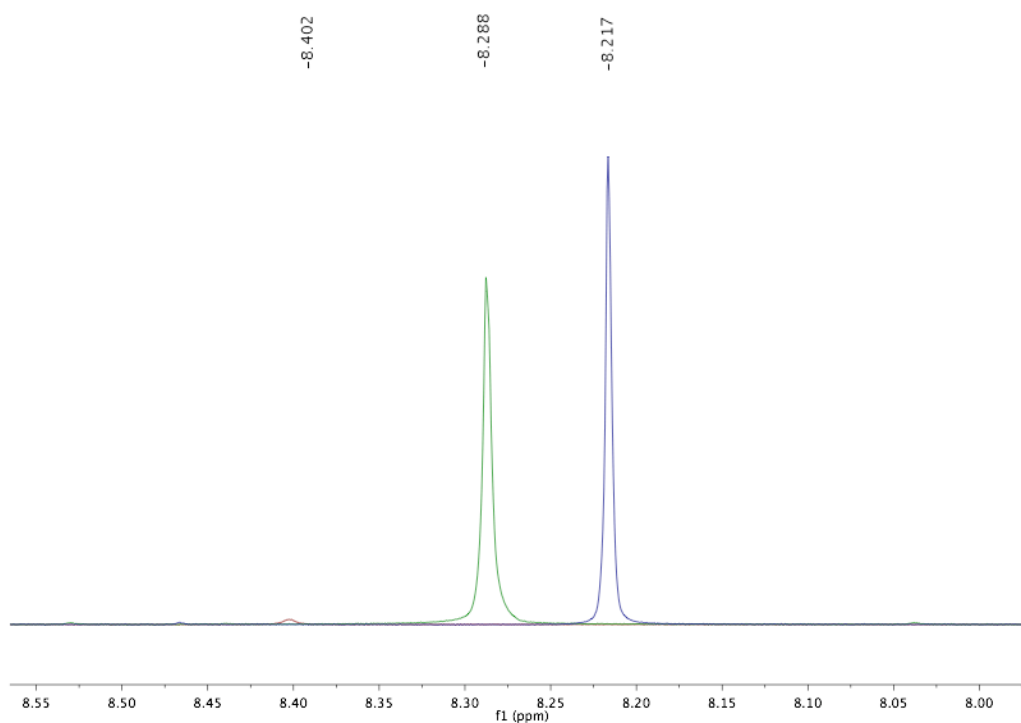
**Figure S20.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{CO}_2$ :  $^1\text{H}$  NMR.



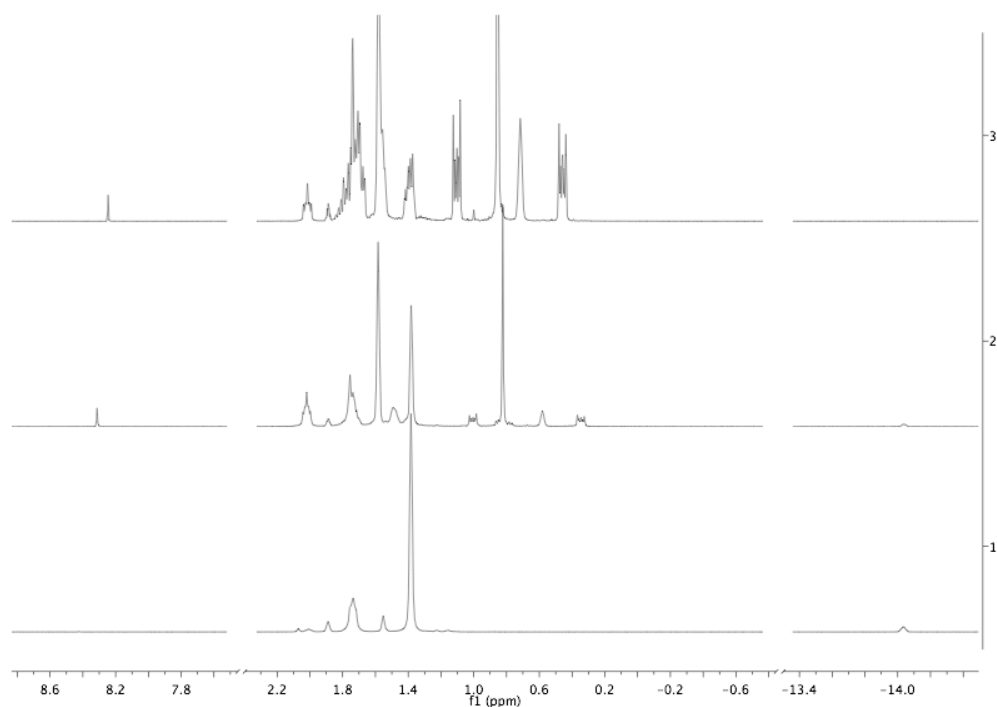
**Figure S21.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{CO}_2$ :  $^{19}\text{F}$  NMR.



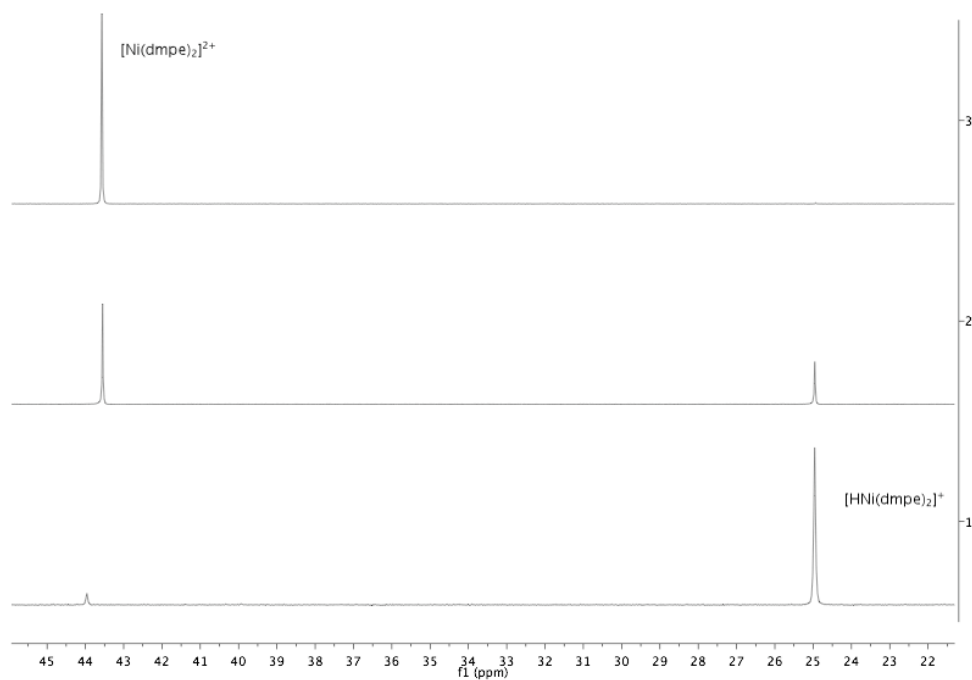
**Figure S22.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{CO}_2$ :  $^{11}\text{B}$  NMR.



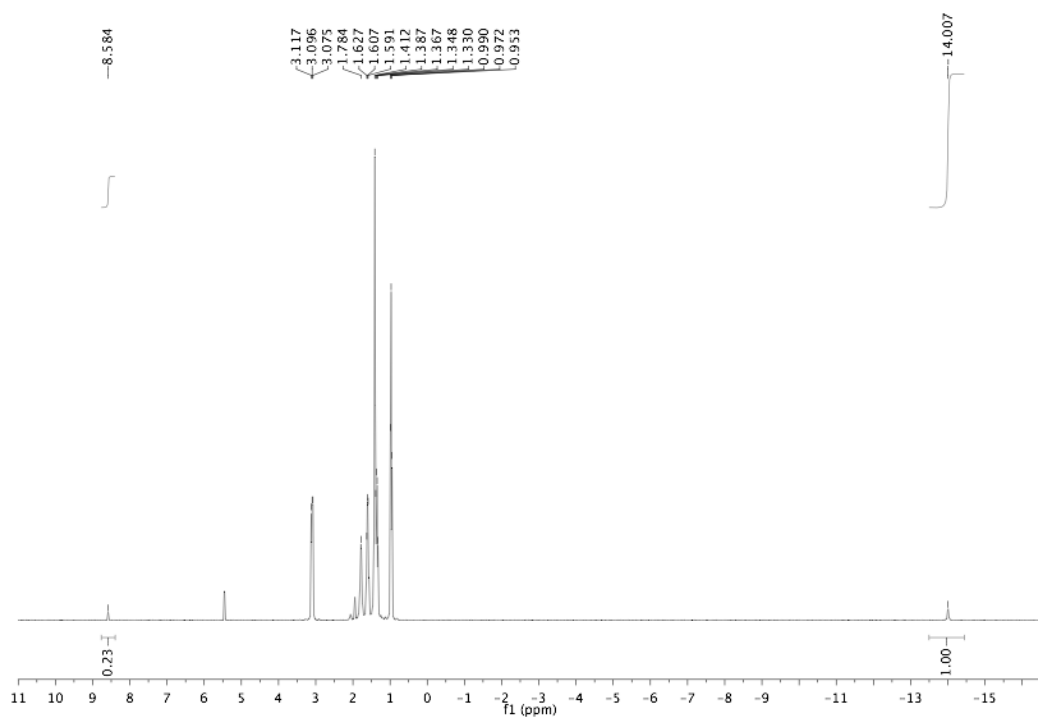
**Figure S23.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$  in MeCN: Overlay ( $^1\text{H}$  NMR, formate region) of reactions at equilibrium with 0 (red), 1 (green) and 10 (blue) equiv  $^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$ .



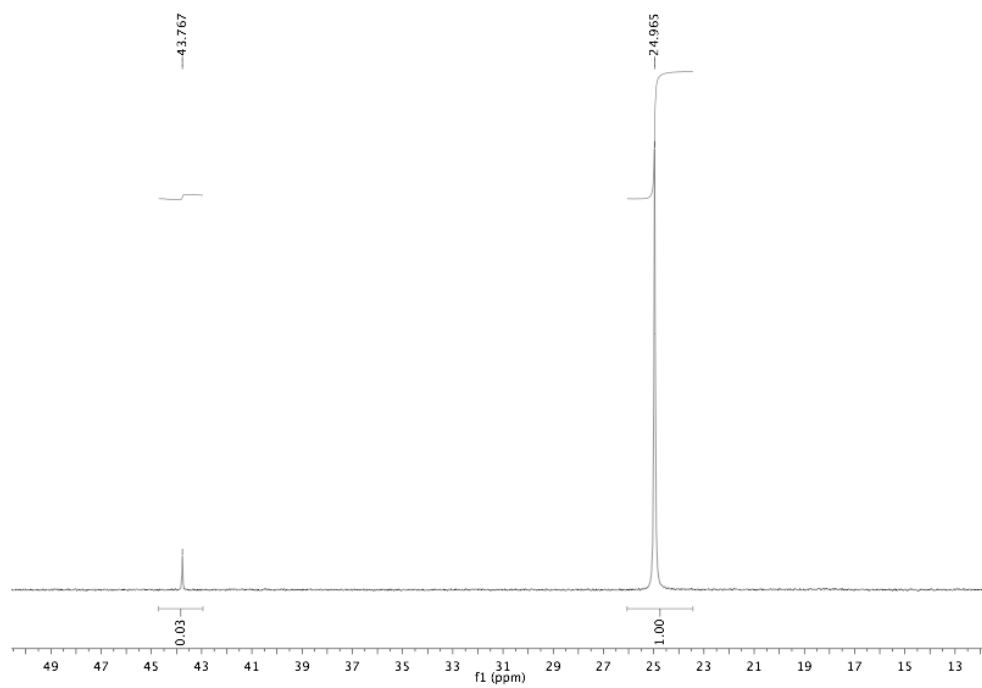
**Figure S24.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$  in MeCN: Comparison ( $^1\text{H}$  NMR) of reactions at equilibrium with 0 (bottom), 1 (middle) and 10 (top) equiv  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$ .



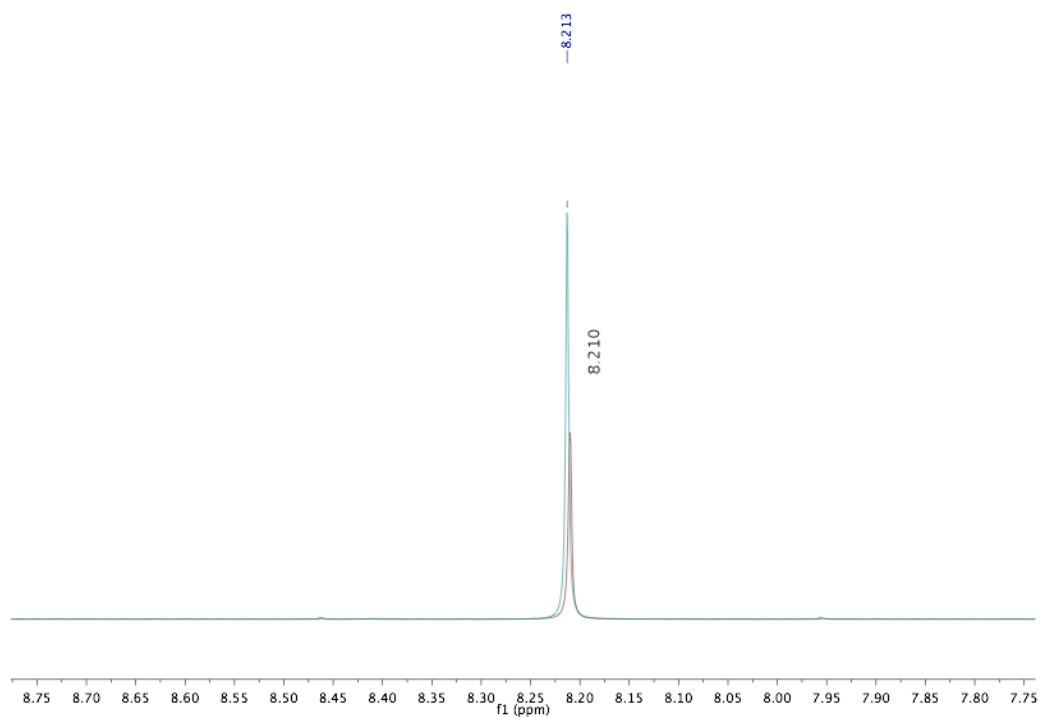
**Figure S25.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$  in MeCN: Comparison ( $^{31}\text{P}\{^1\text{H}\}$  NMR) of reactions at equilibrium with 0 (bottom), 1 (middle) and 10 (top) equiv  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$ .



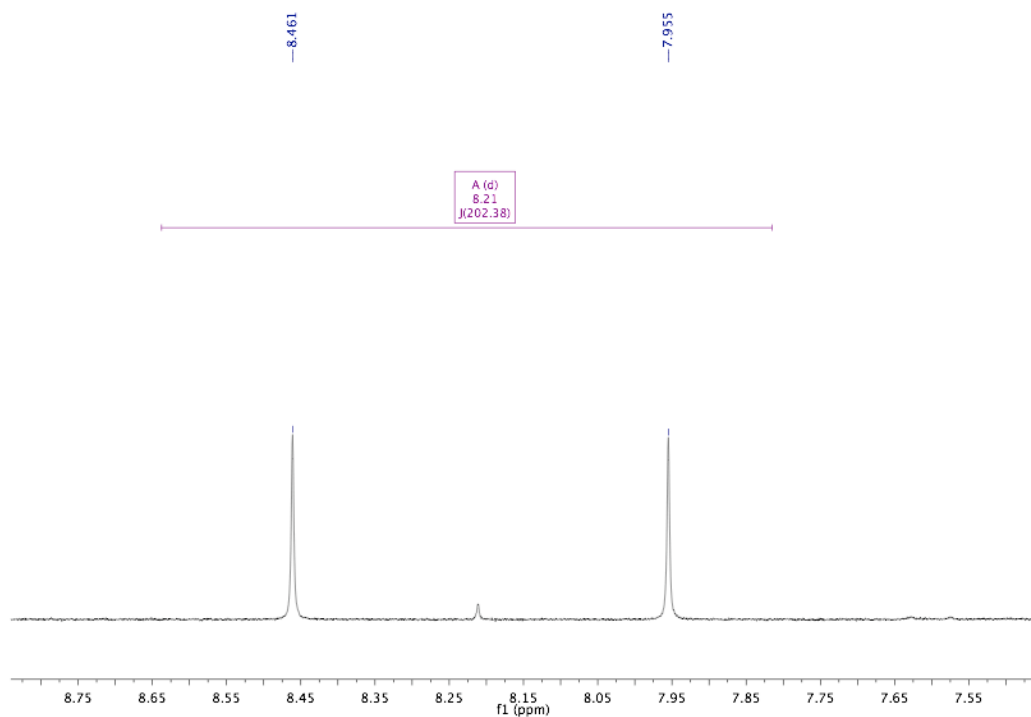
**Figure S26.** Reaction of  $[\text{Ni}(\text{dmpe})_2][\text{PF}_6]_2$  with  $[\text{Bu}_4\text{N}][\text{HCO}_2]$ :  $^1\text{H}$  NMR.



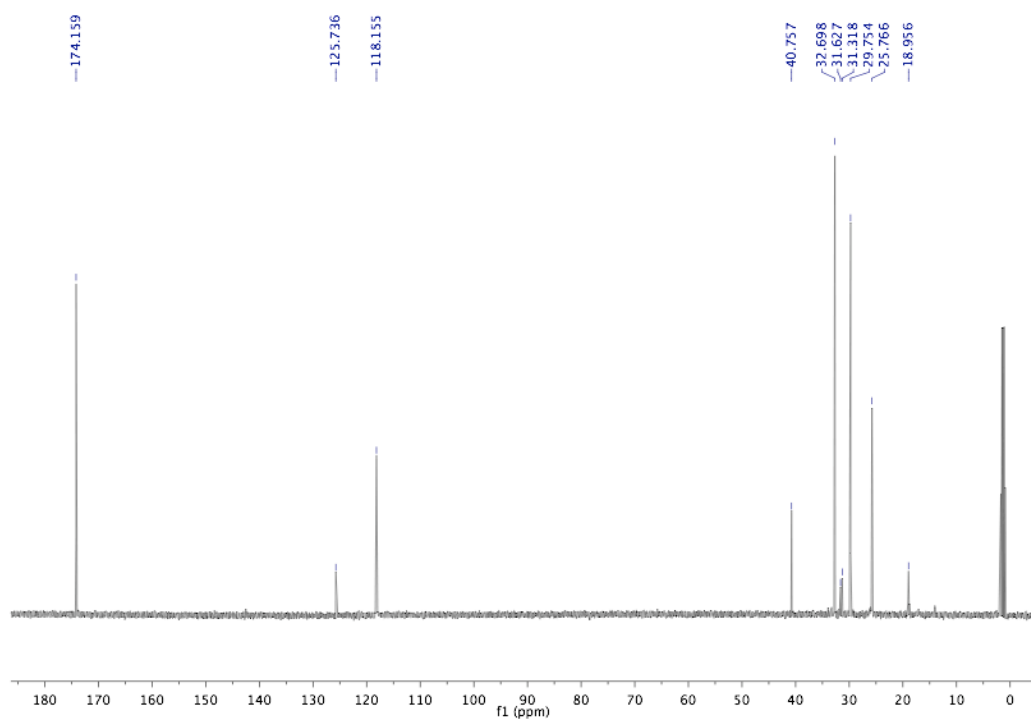
**Figure S27.** Reaction of  $[\text{Ni}(\text{dmpe})_2][\text{PF}_6]_2$  with  $[\text{Bu}_4\text{N}][\text{HCO}_2]$ :  $^{31}\text{P}\{^1\text{H}\}$  NMR.



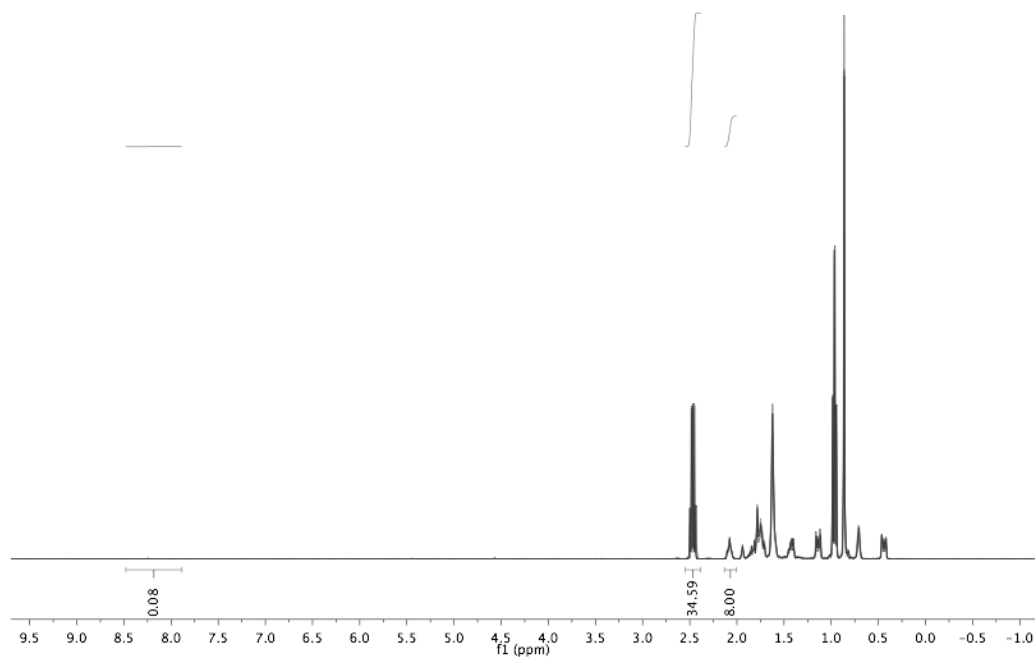
**Figure S28.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $\text{CO}_2$ :  $^1\text{H}$  NMR (formate region) before (red) and after (blue) addition of  $[\text{Bu}_4\text{N}][\text{HCO}_2]$ .



**Figure S29.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $^t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $^{13}\text{CO}_2$ :  $^1\text{H}$  NMR (formate region) after 12 hours.

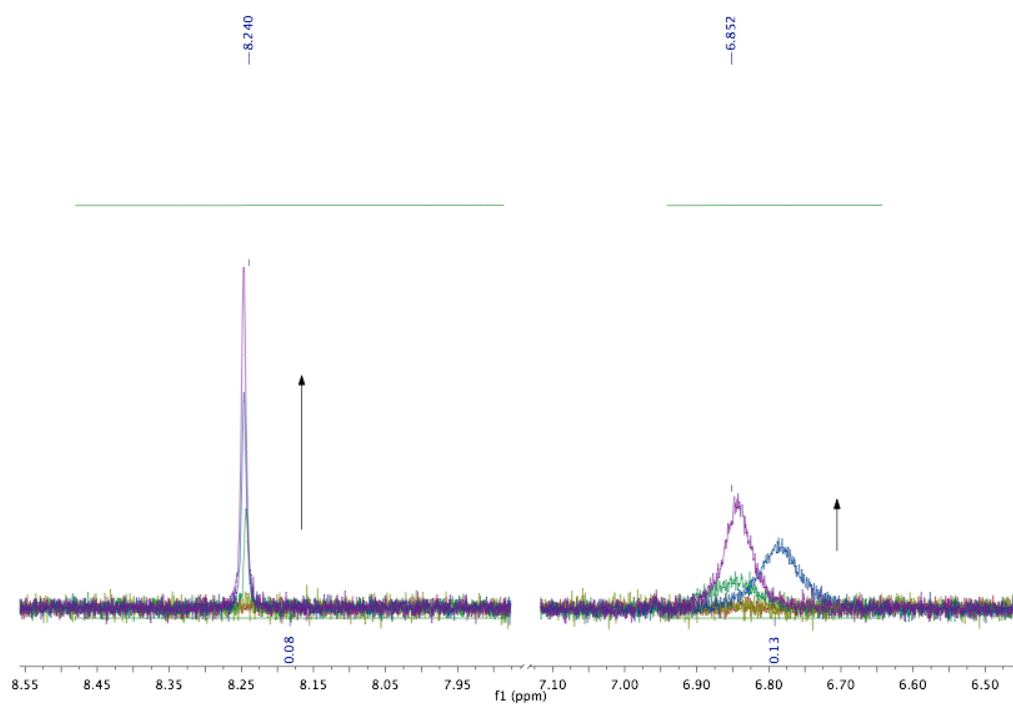


**Figure S30.** Reaction of  $[\text{HNi}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$  and  $^{13}\text{CO}_2$ :  $^{13}\text{C}\{^1\text{H}\}$  NMR after 12 hours.

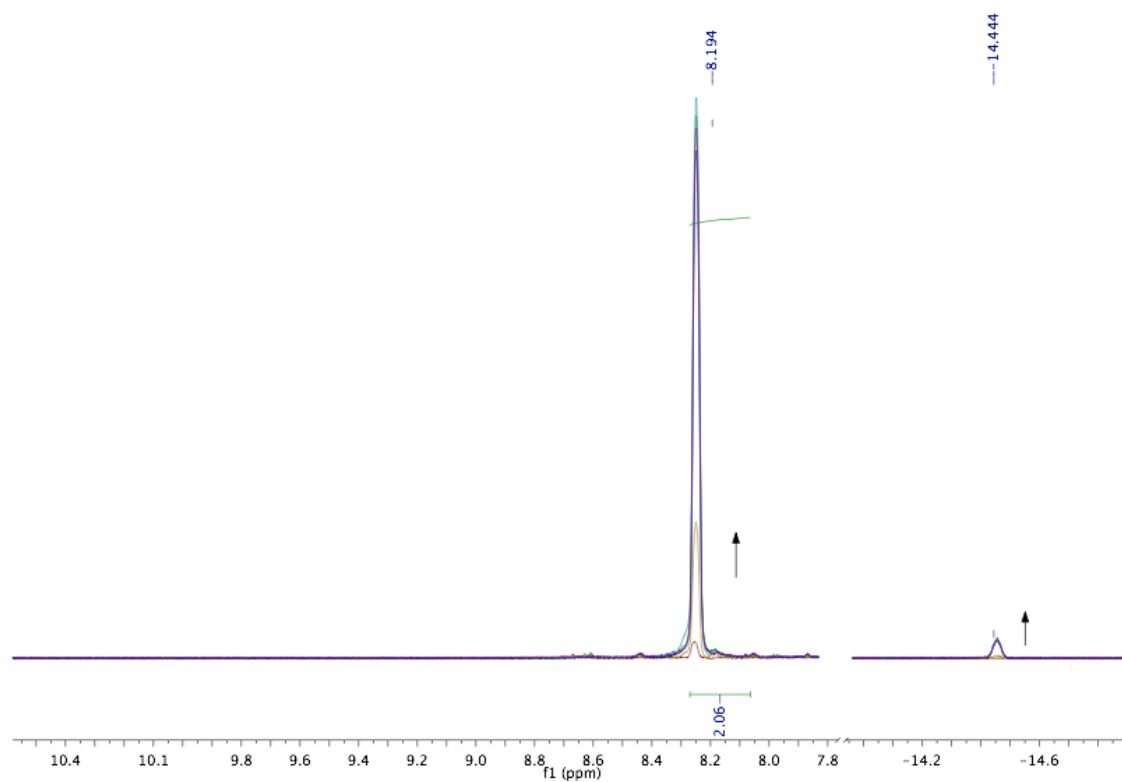


**Figure S31.** Attempted catalysis in  $\text{CD}_3\text{CN}$ :  $^1\text{H}$  NMR time course (over 3 days).

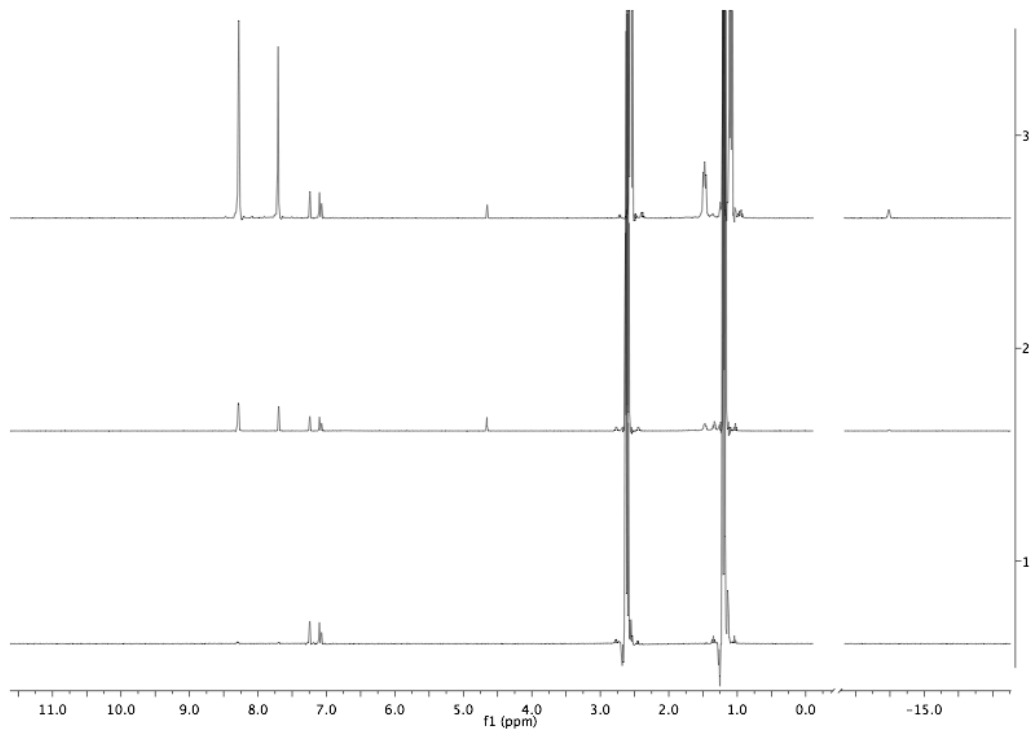




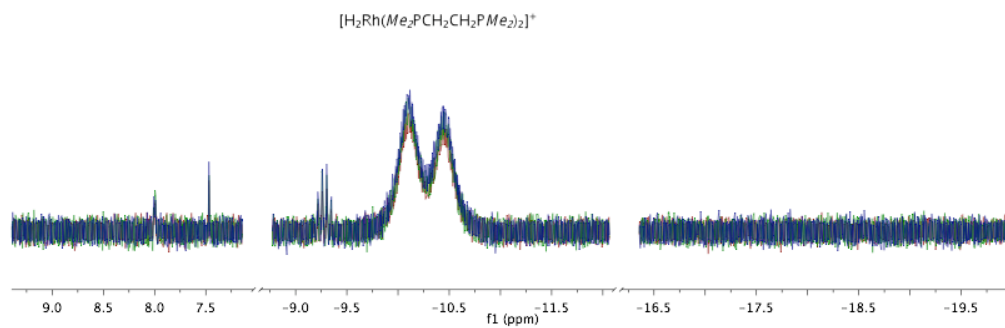
**Figure S32.** Attempted catalysis in  $\text{CD}_3\text{CN}$ :  $^1\text{H}$  NMR time course (over 3 days).



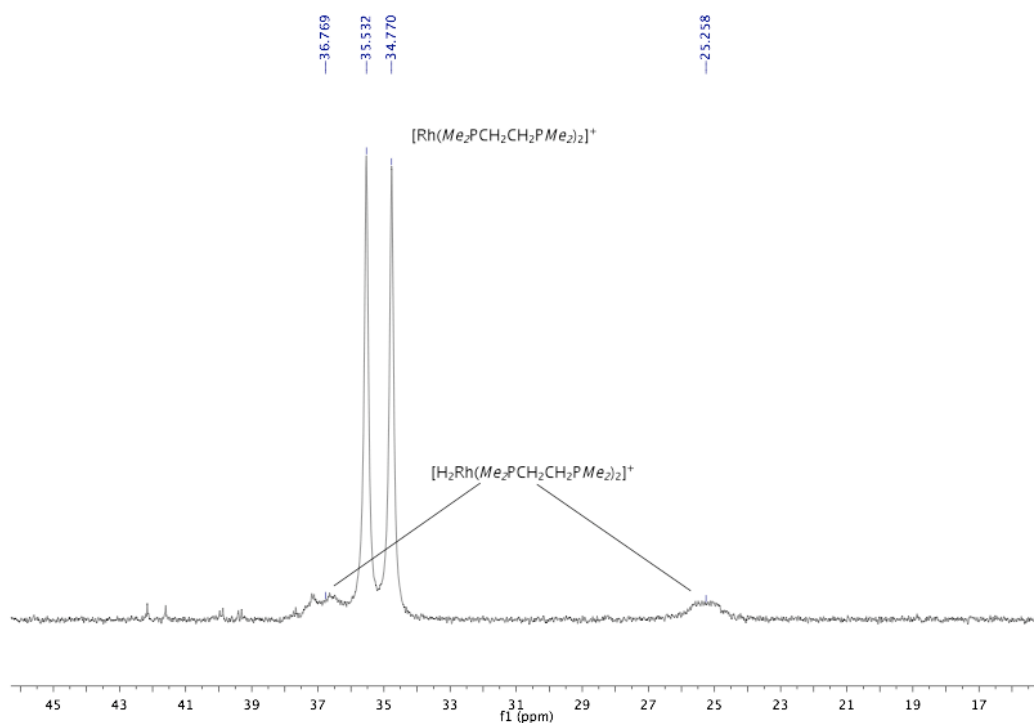
**Figure S33.** Attempted catalysis in  $\text{C}_6\text{D}_5\text{Cl}$ :  $^1\text{H}$  NMR time course.



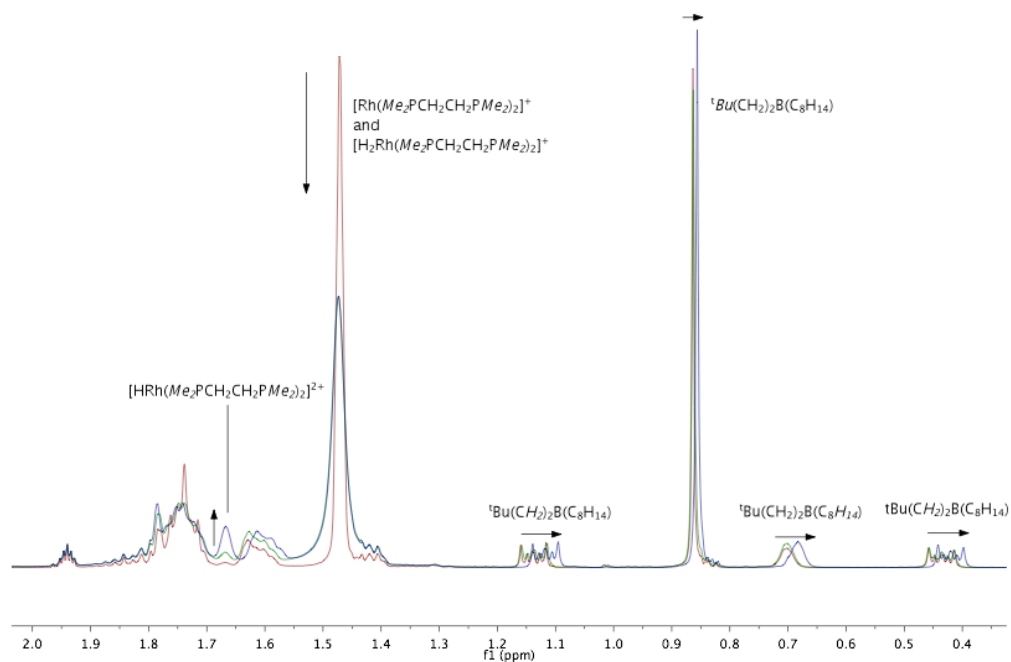
**Figure S34.** H<sub>2</sub> cleavage by [Ni(dmpe)<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>]<sub>2</sub>: <sup>1</sup>H NMR time course (excess NEt<sub>3</sub> cut off) before H<sub>2</sub> addition (bottom), 30 minutes after H<sub>2</sub> addition (middle), and 12 hours after H<sub>2</sub> addition (top).



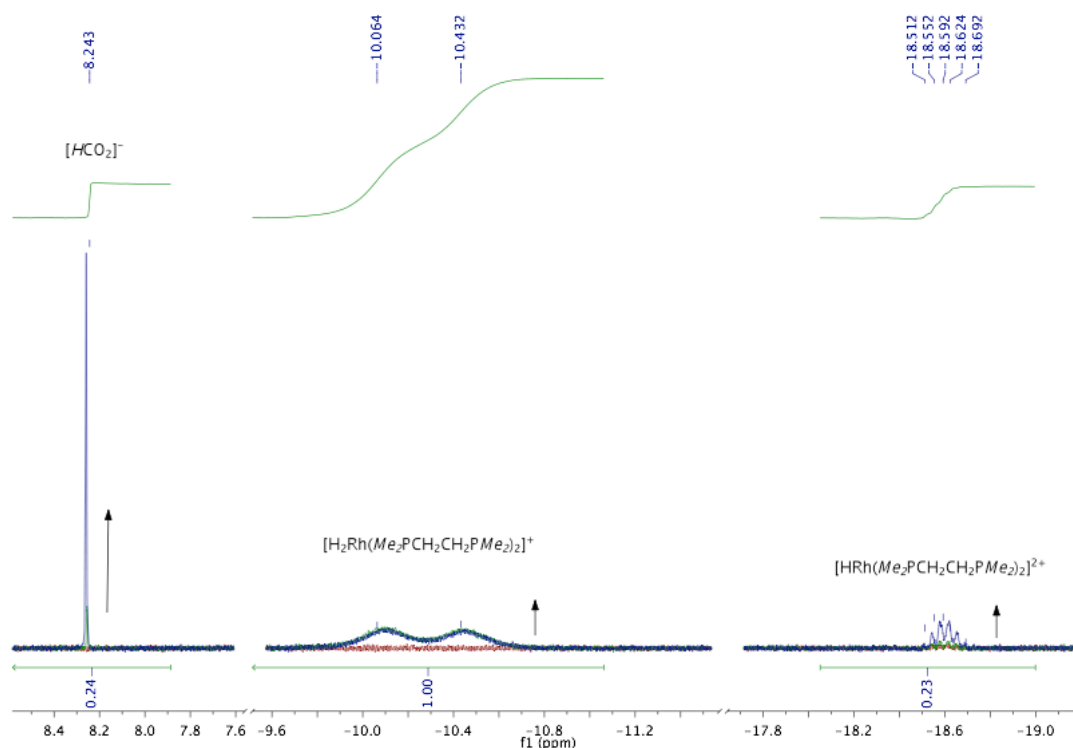
**Figure S35.** Reaction of [Rh(dmpe)<sub>2</sub>]<sup>+</sup> with CO<sub>2</sub> and H<sub>2</sub>: <sup>1</sup>H NMR overlay (formate and hydride regions), after 3 hours (red), 24 hours (green), 4 days (blue).



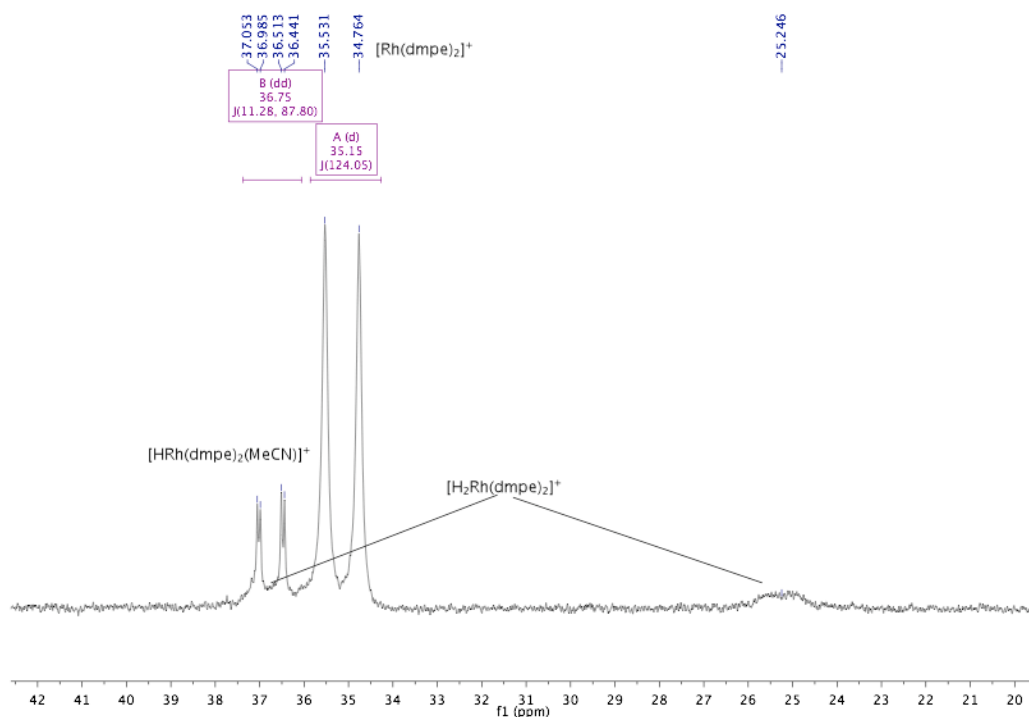
**Figure S36.** Reaction of  $[\text{Rh}(\text{dmpe})_2]^+$  with  $\text{CO}_2$  and  $\text{H}_2$ :  $^{31}\text{P}\{^1\text{H}\}$  NMR after 24 hours.



**Figure S37.** Reaction of  $[\text{Rh}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$ ,  $\text{CO}_2$  and  $\text{H}_2$ :  $^1\text{H}$  NMR time course (aliphatic region); red: before  $\text{H}_2/\text{CO}_2$  addition. green, 1.5 hrs after  $\text{H}_2/\text{CO}_2$  addition. yellow, 18 hrs after  $\text{H}_2/\text{CO}_2$  addition.



**Figure S38.** Reaction of  $[\text{Rh}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$ ,  $\text{CO}_2$  and  $\text{H}_2$ :  $^1\text{H}$  NMR time course (formate and hydride regions); red: before  $\text{H}_2/\text{CO}_2$  addition. green, 1.5 hrs after  $\text{H}_2/\text{CO}_2$  addition. yellow, 18 hrs after  $\text{H}_2/\text{CO}_2$  addition.



**Figure S39.** Reaction of  $[\text{Rh}(\text{dmpe})_2]^+$  with  $t\text{Bu}(\text{CH}_2)_2\text{B}(\text{C}_8\text{H}_{14})$ ,  $\text{CO}_2$  and  $\text{H}_2$ :  $^{31}\text{P}$  NMR (partially decoupled) after 18 hours.