Electronic Supplementary Material (ESI) for Green Chemistry.

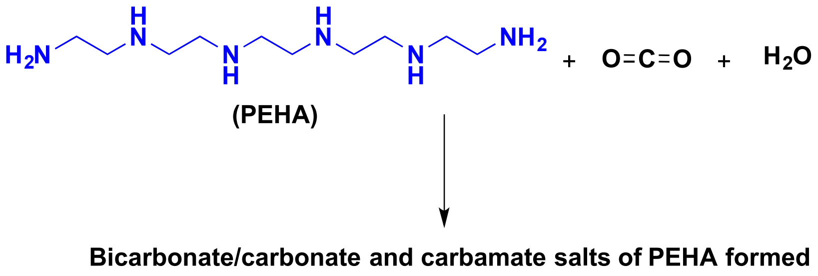
Supporting Information

CO_2 Capture by Amines in Aqueous Media and its Subsequent Conversion to Formate With Reusable Ruthenium and Iron Catalysts

Jotheeswari Kothandaraman, Alain Goeppert, Miklos Czaun, George A. Olah and G. K. Surya Prakash**

I. CO_2 capture of different amines in water

1. PEHA with CO_2 in water



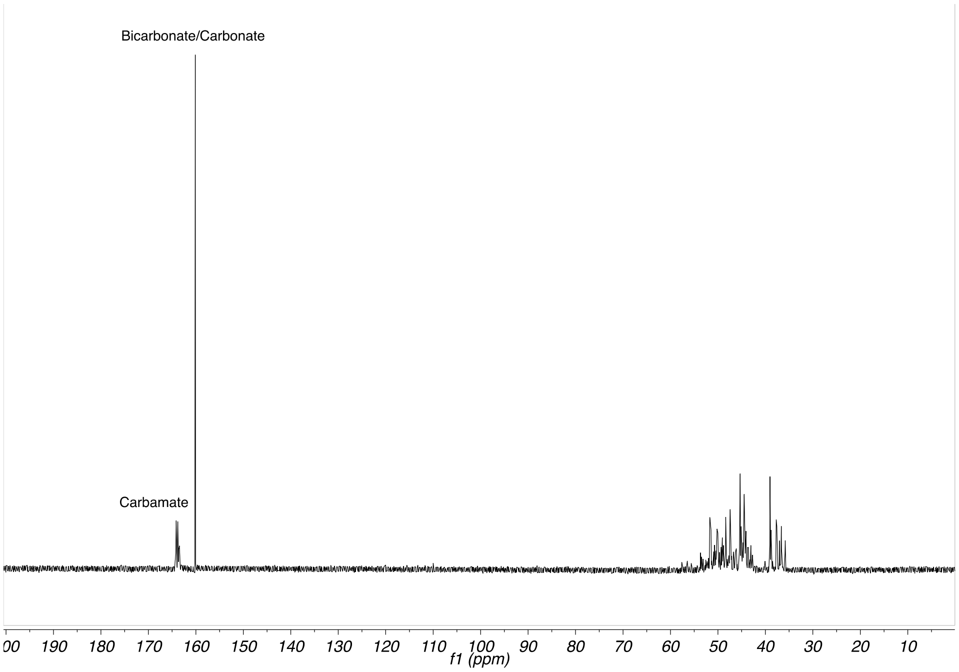
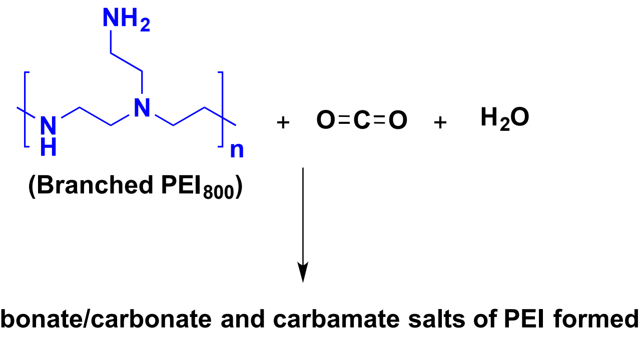


Fig. S1 ^{13}C NMR spectrum of PEHA-CO_2-H_2O in D_2O

2. Branched PEI$_{800}$ with CO$_2$ in water



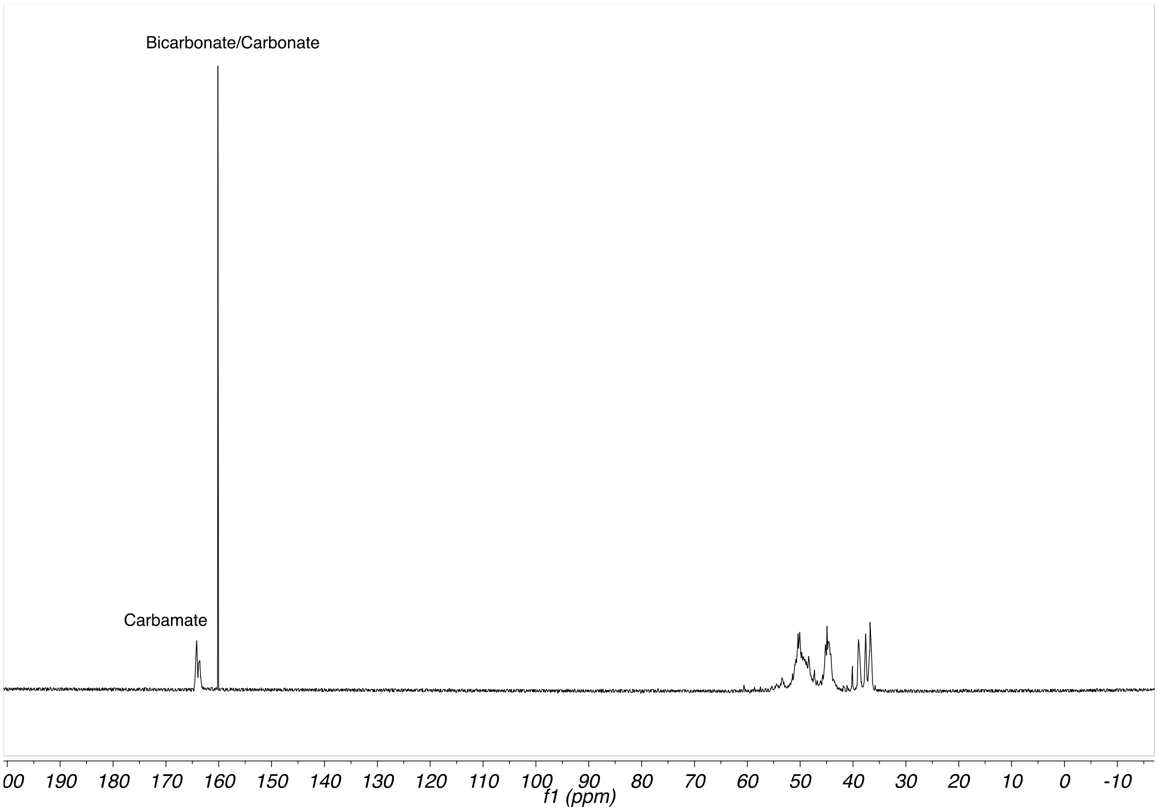
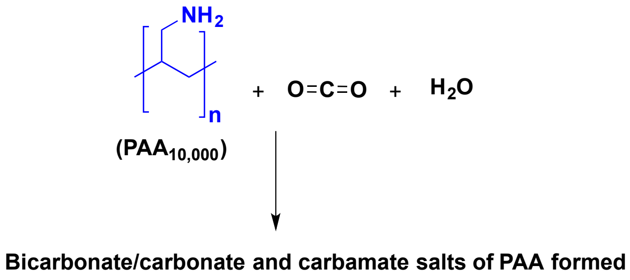


Fig. S2 ^{13}C NMR spectrum of branched PEI$_{800}$-CO$_2$-H$_2$O in D$_2$O

3. PAA$_{10,000}$ with CO$_2$ in water



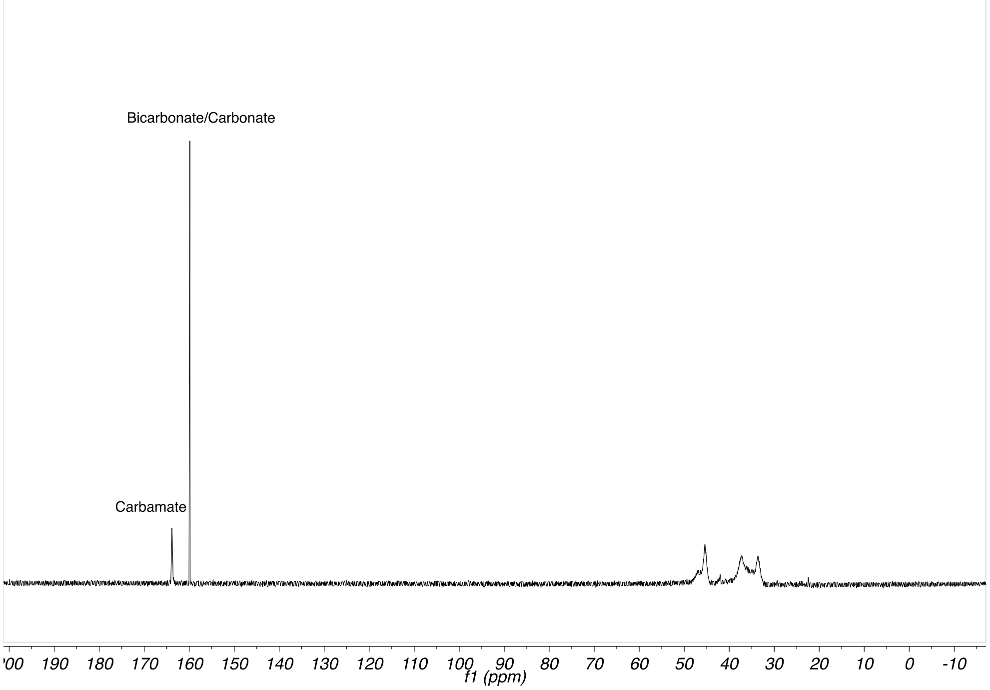
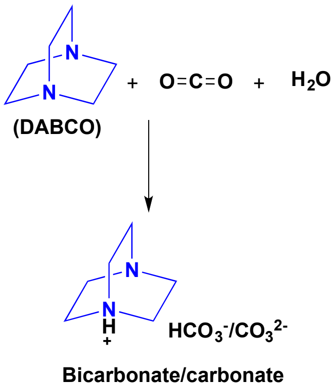


Fig. S3 ^{13}C NMR spectrum of PAA$_{10,000}$-CO$_2$-H$_2$O in D$_2$O

4. DABCO with CO_2 in water



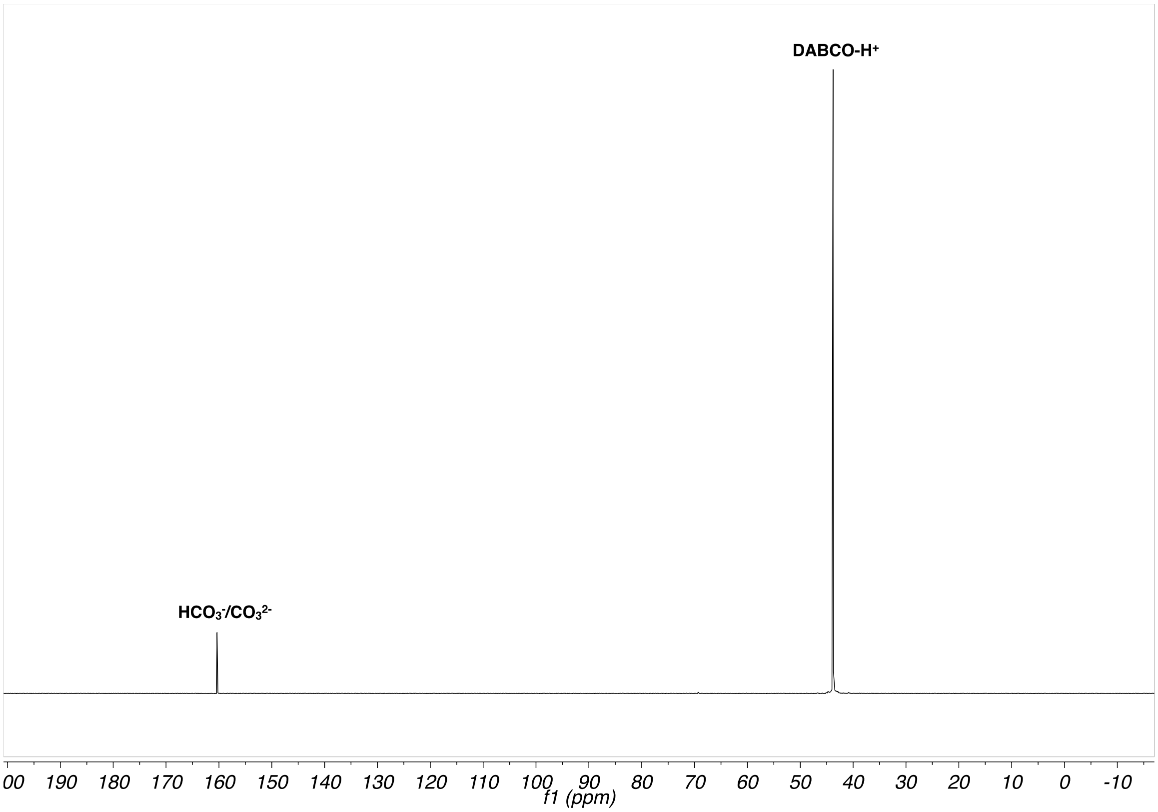
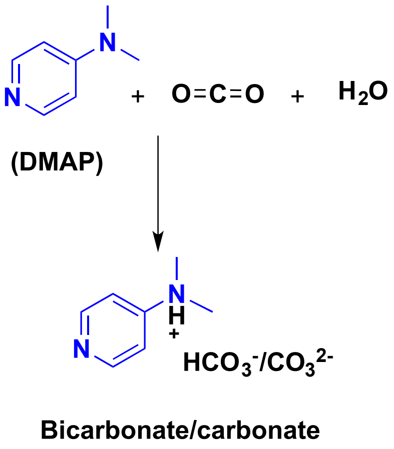


Fig. S4 ^{13}C NMR spectrum of DABCO-CO_2-H_2O in D_2O

5. DMAP with CO_2 in water



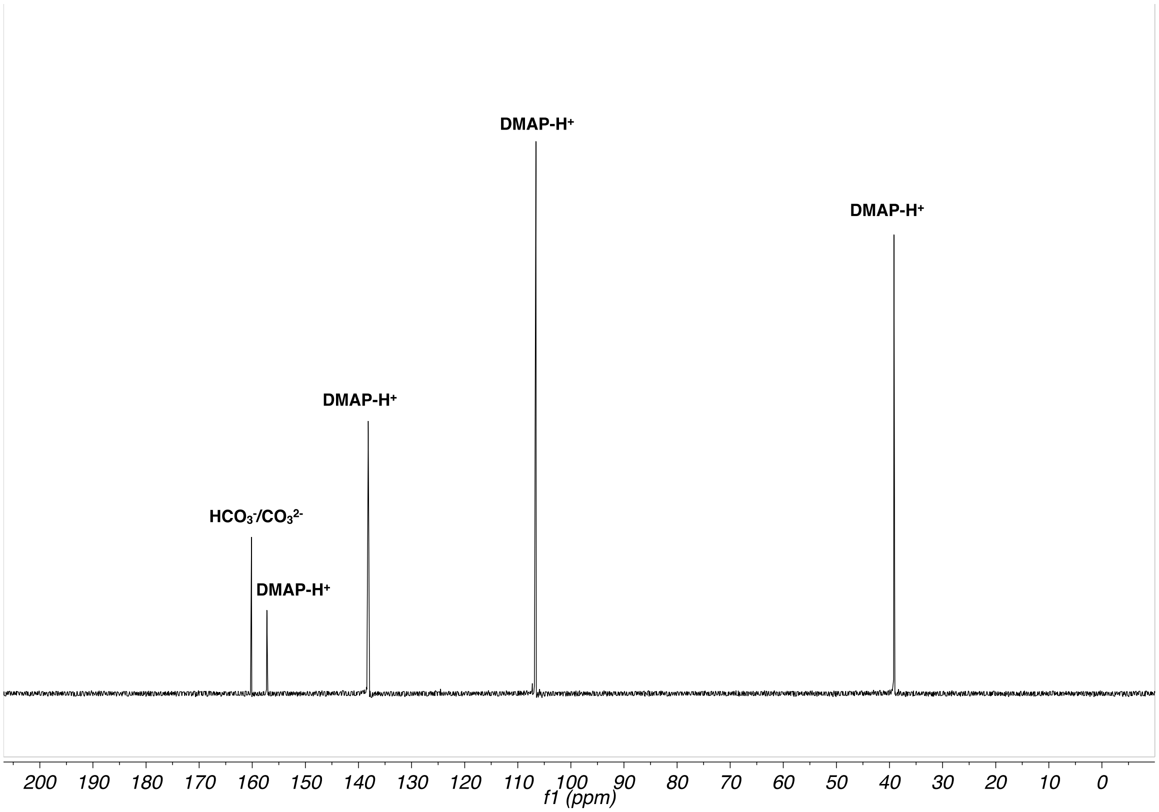
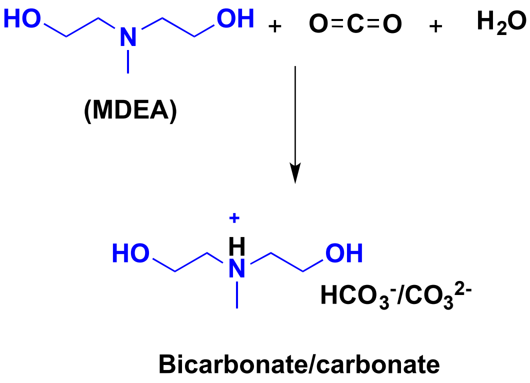


Fig. S5 ^{13}C NMR spectrum of DMAP-CO_2-H_2O in D_2O

6. MDEA with CO_2 in water



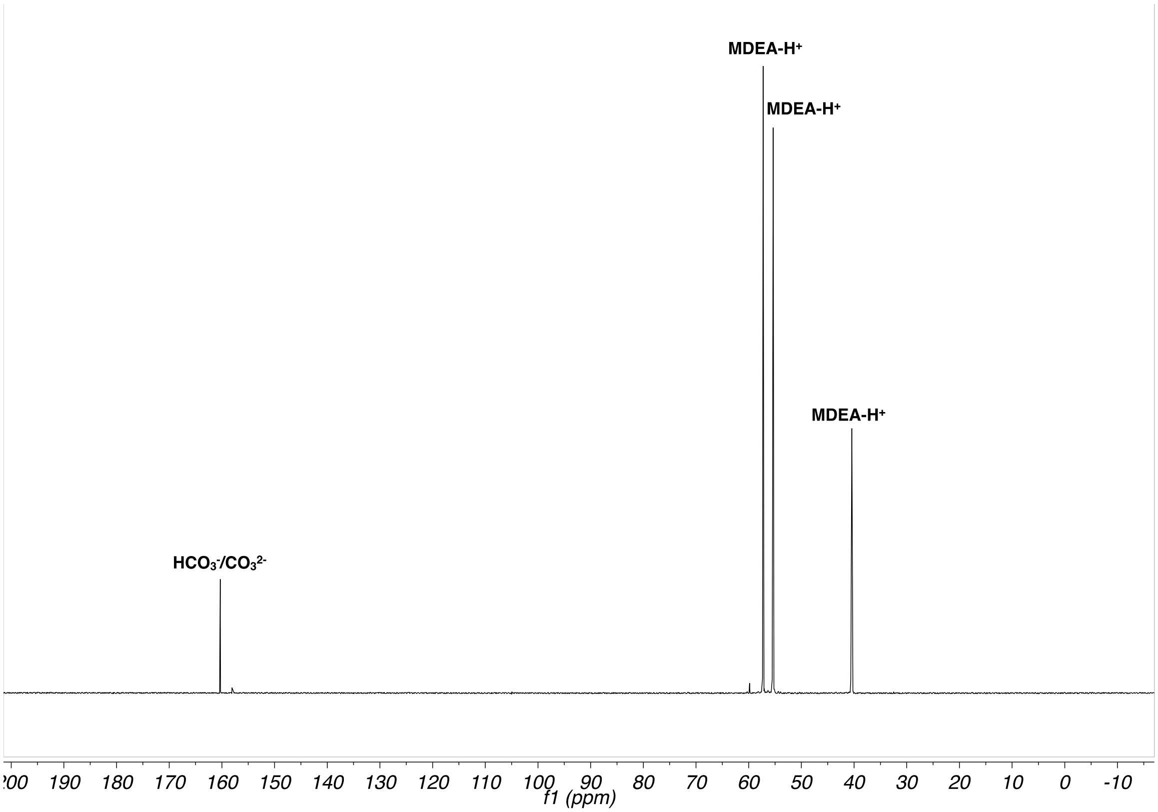
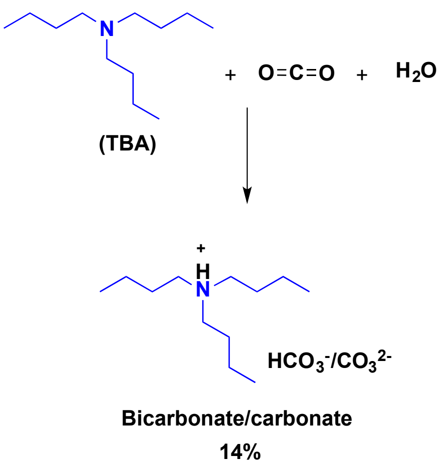


Fig. S6 ^{13}C NMR spectrum of MDEA-CO_2-H_2O in D_2O.

7. TBA with CO_2 in water



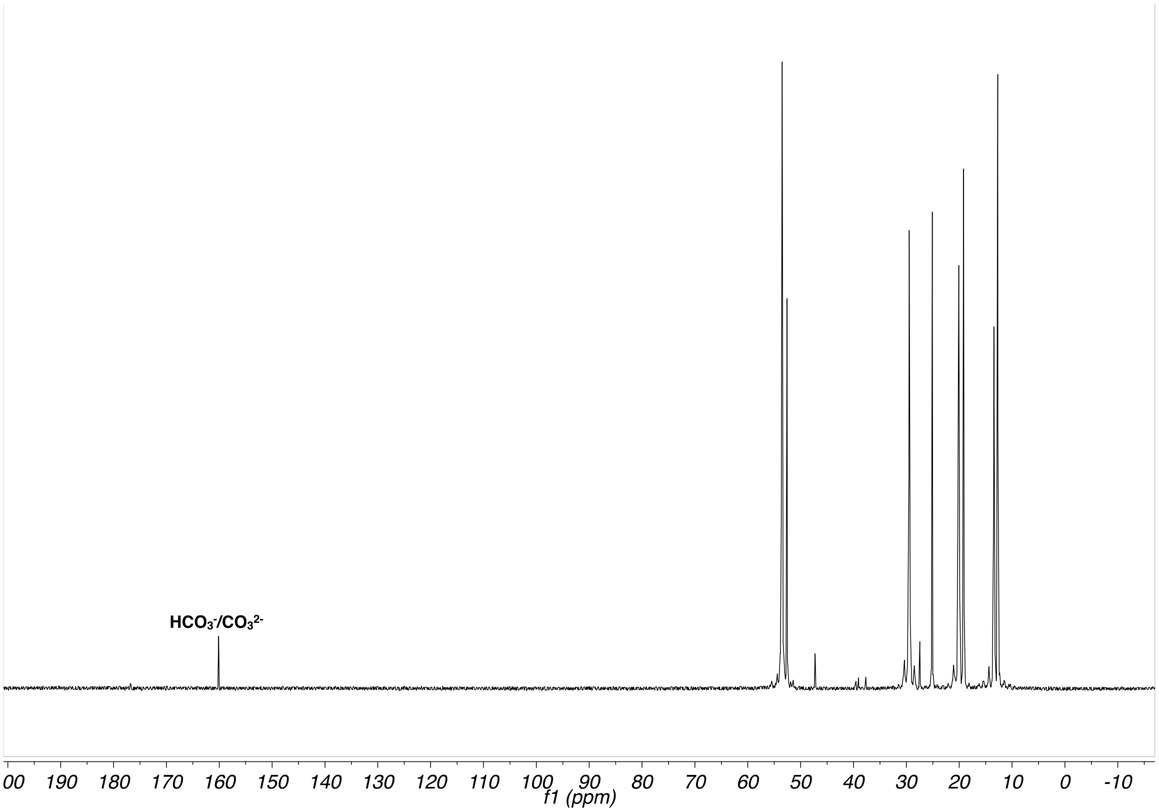
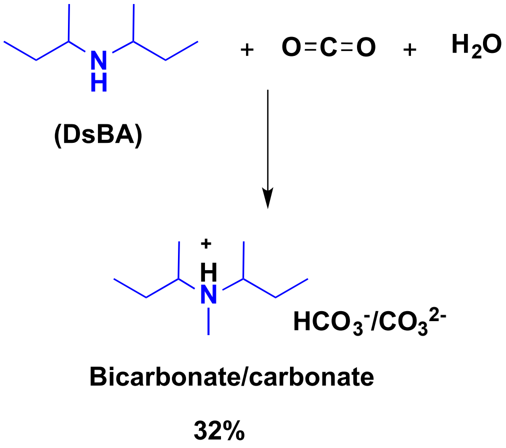


Fig. S7 ^{13}C NMR spectrum of TBA-CO_2-H_2O in D_2O. Biphasic mixture was obtained after adding H_2O to TBA. After 30 min of CO_2 capture, again biphasic reaction mixture remained. ^{13}C NMR of the reaction mixture was taken in D_2O

8. DsBA with CO_2 in water



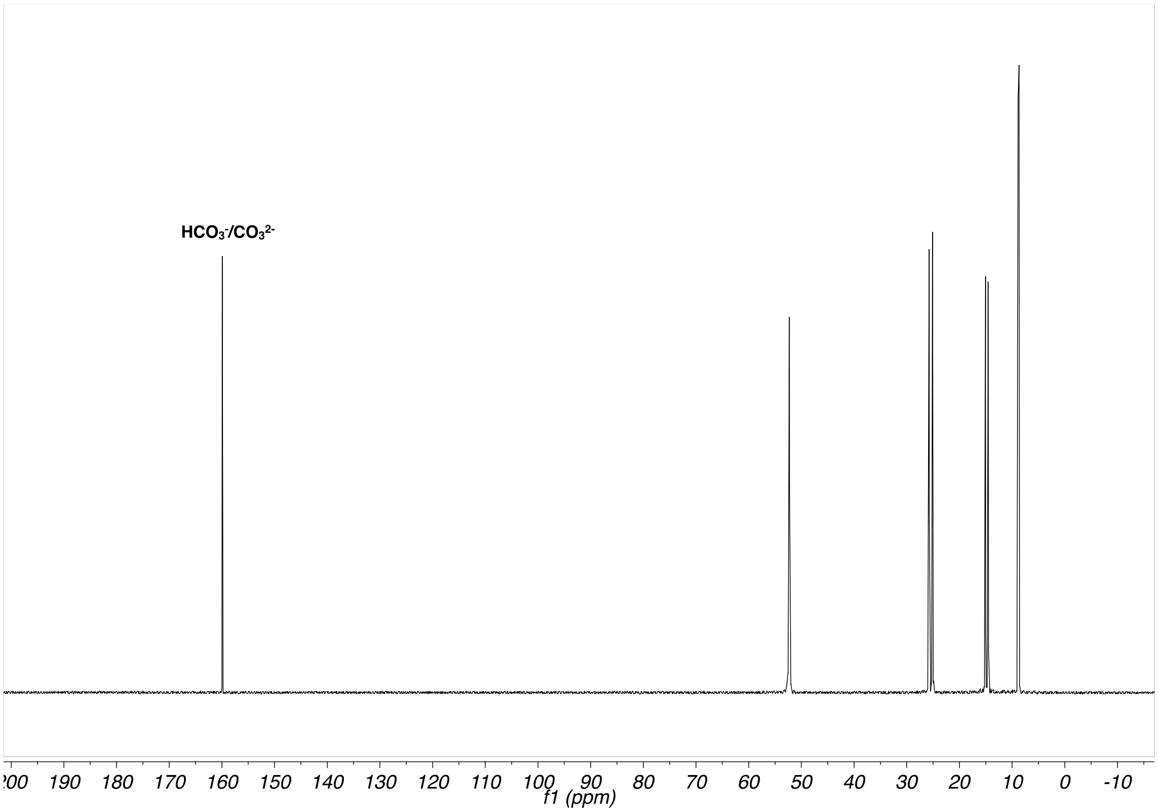
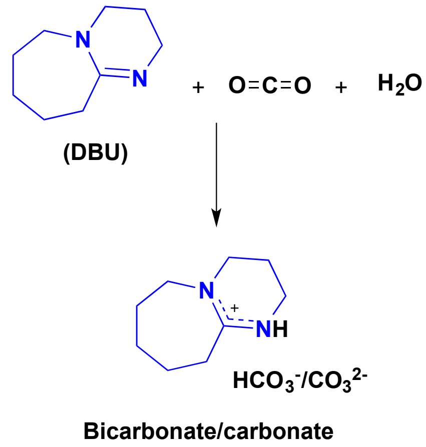


Fig. S8 ^{13}C NMR spectrum of DsBA-CO_2-H_2O in D_2O. Biphasic mixture was obtained after adding H_2O to TBA. After 30 min of CO_2 capture, again biphasic reaction mixture remained. ^{13}C NMR of the reaction mixture was taken in D_2O

9. DBU with CO_2 in water



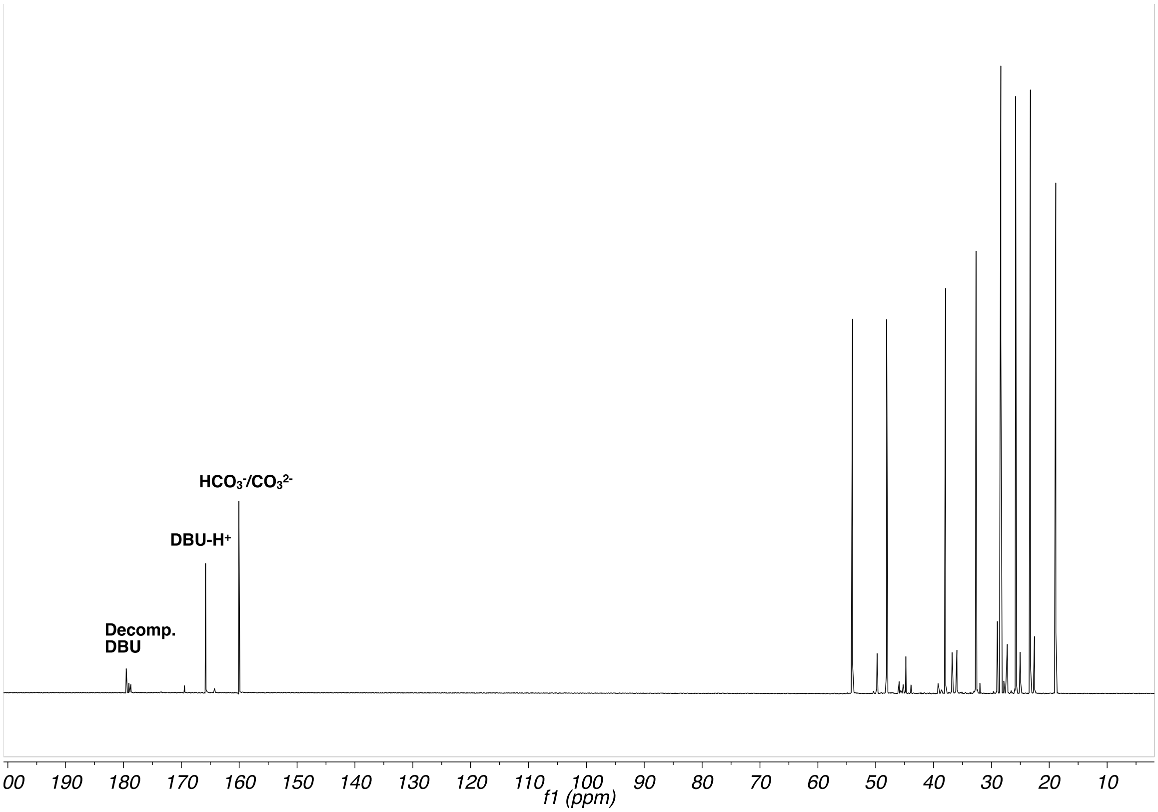
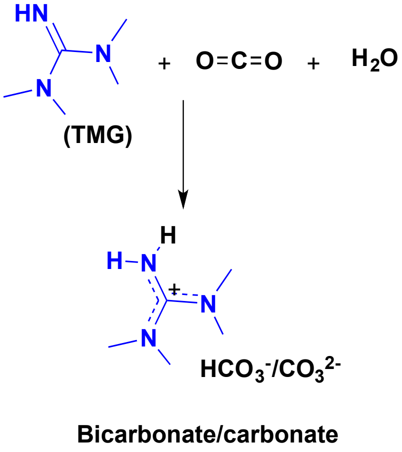


Fig. S9 ^{13}C NMR spectrum of DBU-CO_2-H_2O in D_2O.

10. TMG with CO_2 in water



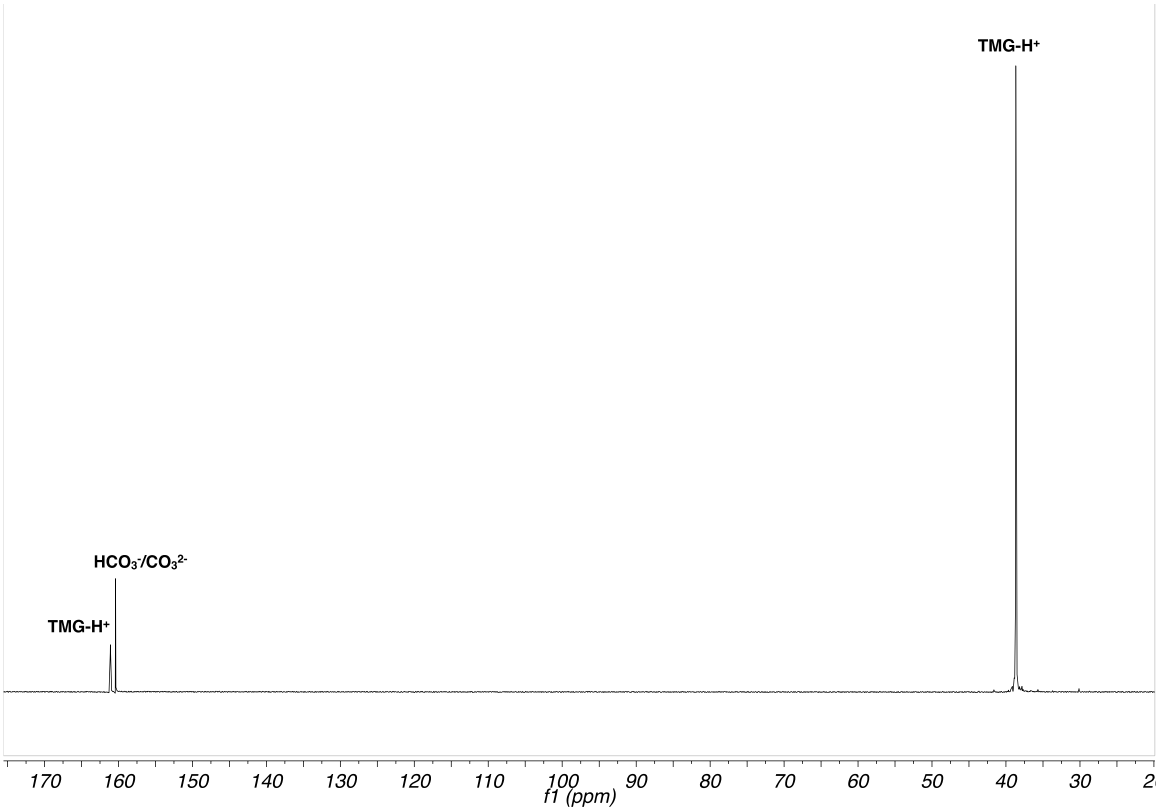
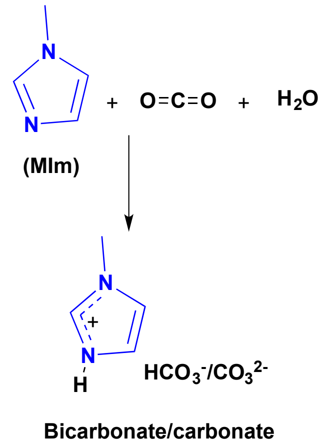


Fig. S10 ^{13}C NMR spectrum of TMG-CO_2-H_2O in D_2O.

11. MIm with CO_2 in water



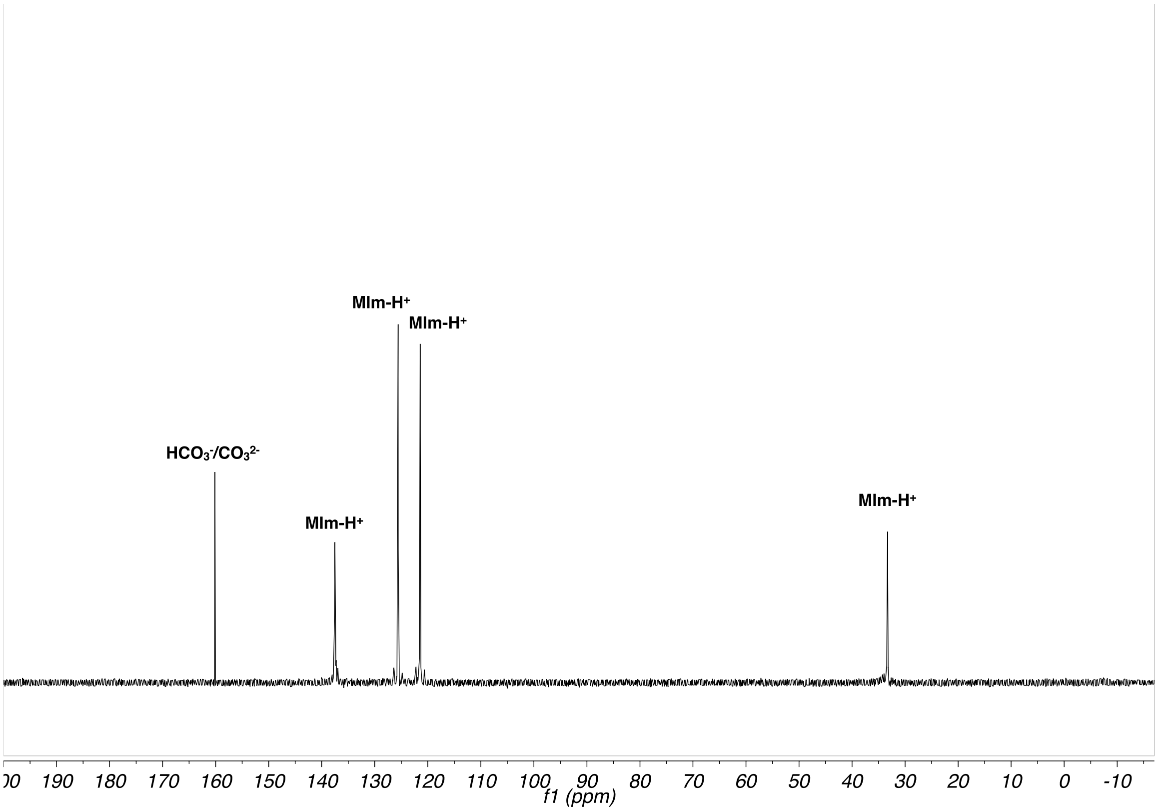


Fig. S11 ^{13}C NMR spectrum of MIm-CO_2-H_2O in D_2O

II. Synthesis of $FeBr_2PNP^{iPr}(CO)$ and $FeHBrPNP^{iPr}(CO)$

Complexes $FeBr_2[PNP^{iPr}]CO$ and $FeHBr[PNP^{iPr}]CO$ were prepared following the literature procedure. [1]

1) Synthesis of $FeBr_2PNP^{iPr}(CO)$

Anhydrous $FeBr_2$ (510mg, 2.36 mmol) was weighed in to a two-necked 100 mL schlenk flask charged with a stir bar in an argon glove box. 30 mL of degassed dry THF was introduced to the flask under nitrogen atmosphere. To the above solution, 9 mL of PNP^{iPr} (10 wt% in THF) was added and stirred at room temperature under nitrogen atmosphere for 10-15 min to get a off-white precipitate. The flask was frozen using liquid nitrogen, subjected to vacuum, backfilled with CO (1 atm) and slowly thawed to RT. The mixture was stirred for 2 h to get a dark blue solution. The solvent was evaporated under vacuum at RT to obtain a blue powder, which was dissolved in minimum amount of THF and filtered through a short pad of celite. The filtrate was concentrated under vacuum and the resulting blue solid was further washed with pentane and dried in vacuum to get 1.24 g (95%) of product as a blue solid. NMR (^1H, ^{31}P and ^{13}C) of the solid was recorded in a 500 MHz Varian spectrometer. The spectroscopic data is consistent with the literature report. [1,2]

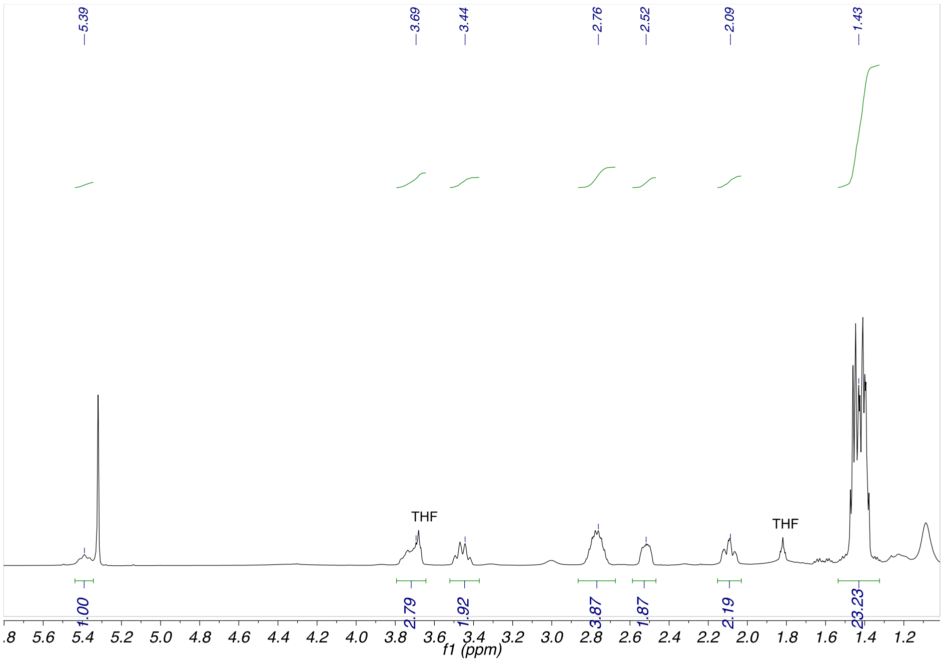


Fig. S12 ^1H NMR of $FeBr_2PNP^{iPr}(CO)$ in CD_2Cl_2.

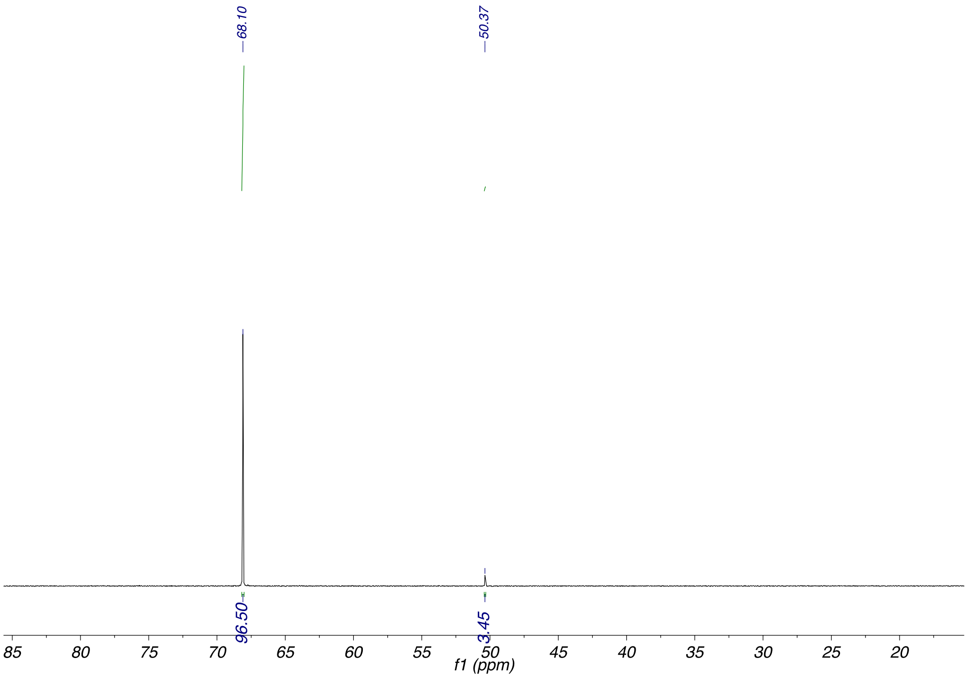


Fig. S13 ^{31}P NMR of FeBr$_2$PNP$^{i\mathrm{Pr}}$(CO) in CD$_2$Cl$_2$.

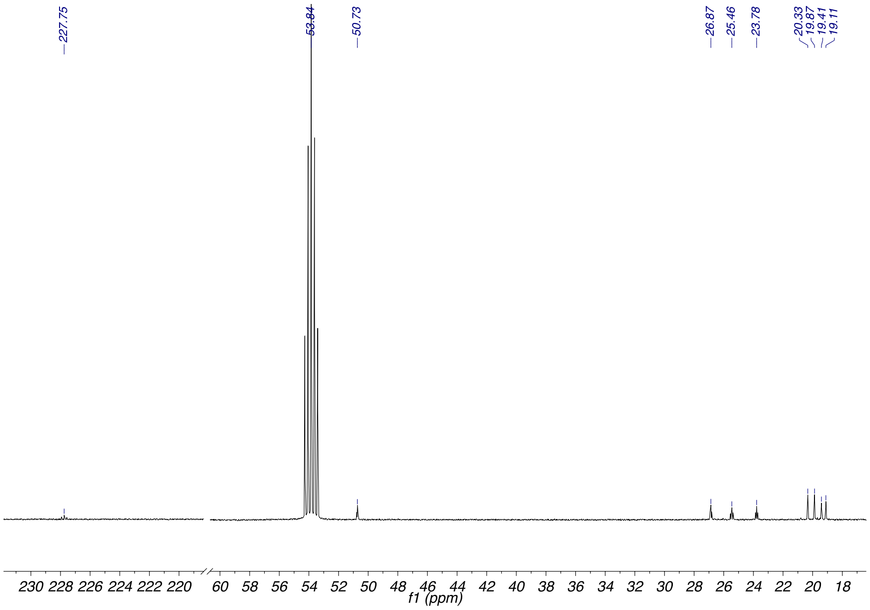


Fig. S14 ^{13}C NMR of FeBr$_2$PNP$^{i\mathrm{Pr}}$(CO) in CD$_2$Cl$_2$.

2) Synthesis of **FeHBr[PNP^{iPr}]CO, 4**

710 mg (1.29 mmol) of $FeBr_2PNP^{iPr}$(CO) and 50 mg $NaBH_4$ were added to a schlenk flask equipped with a stir bar in an Ar glovebox. 60 mL dry ethanol was introduced in to the solution at 0 °C to give a green solution, which changed its color to a homogenous orange solution in 20 min. The mixture was stirred at room temperature for 16 h. Ethanol was removed under vacuum to give an orange powder, which was dissolved in toluene and filtered through a short pad of celite to give an orange solution. The solvent was pumped off under vacuum and washed with hexane to give FeHBr[PNP^{iPr}]CO (402 mg, 0.855 mmol) as orange solid in 66% yield. NMR (^{1}H, ^{31}P and ^{13}C) of the solid was recorded in a 500 MHz spectrometer.
A major isomer with a hydride peak at -22.7 ppm (83%) and a minor isomer at –22.5 ppm (17%) were obtained. The spectroscopic data is consistent with the literature report.[2]

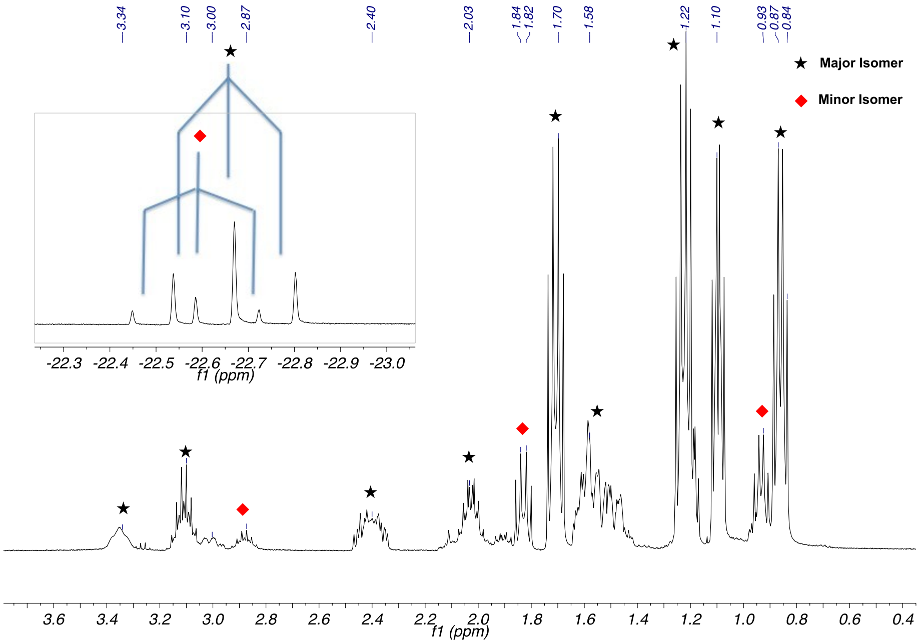


Fig. S15 ^{1}H NMR of FeHBrPNP^{iPr}(CO) in C_6D_6.

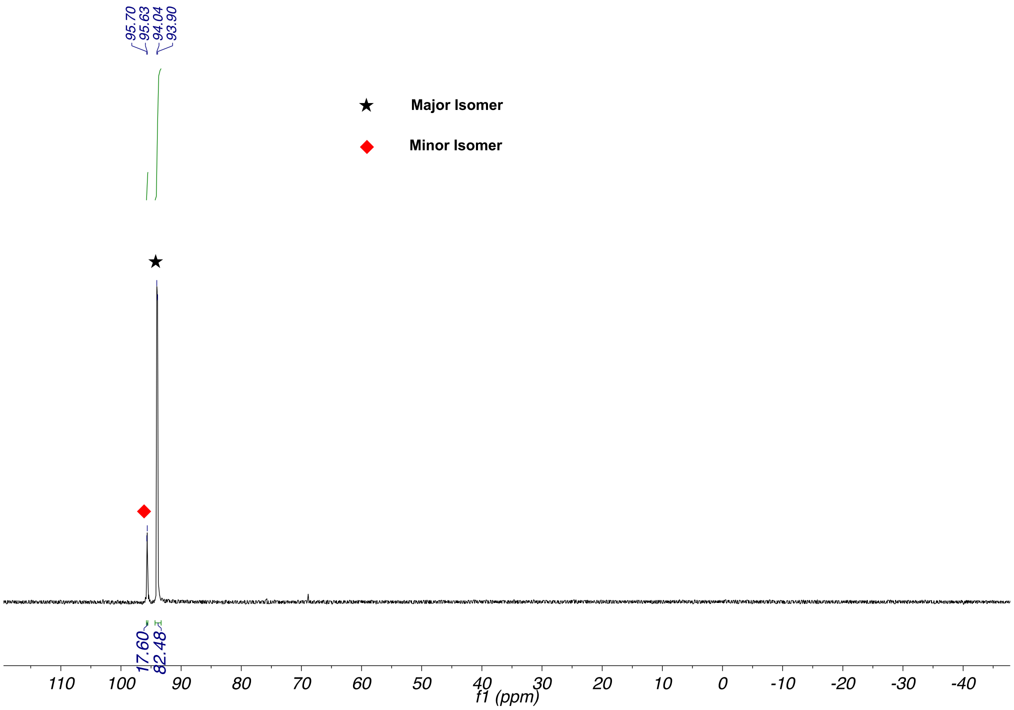


Fig. S16 ^{31}P NMR of FeHBrPNP$^{i\mathrm{Pr}}$(CO) in C_6D_6.

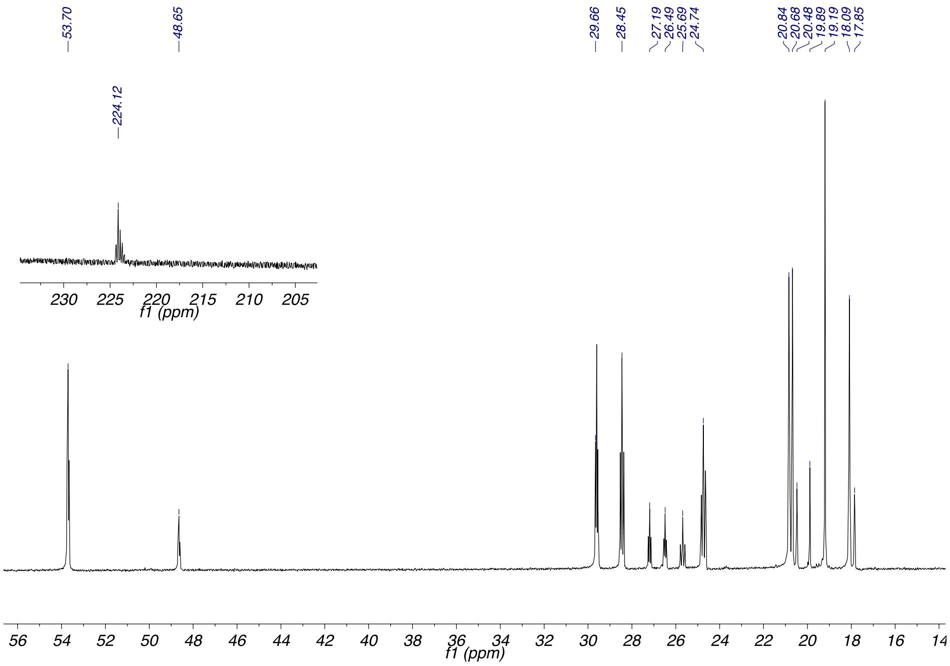


Fig. S17 ^{13}C NMR of FeHBrPNP$^{i\mathrm{Pr}}$(CO) in C_6D_6. Only signals corresponding to the major isomer was clearly visible in the ^{13}C NMR.

III. Hydrogenation of captured CO_2 to formate

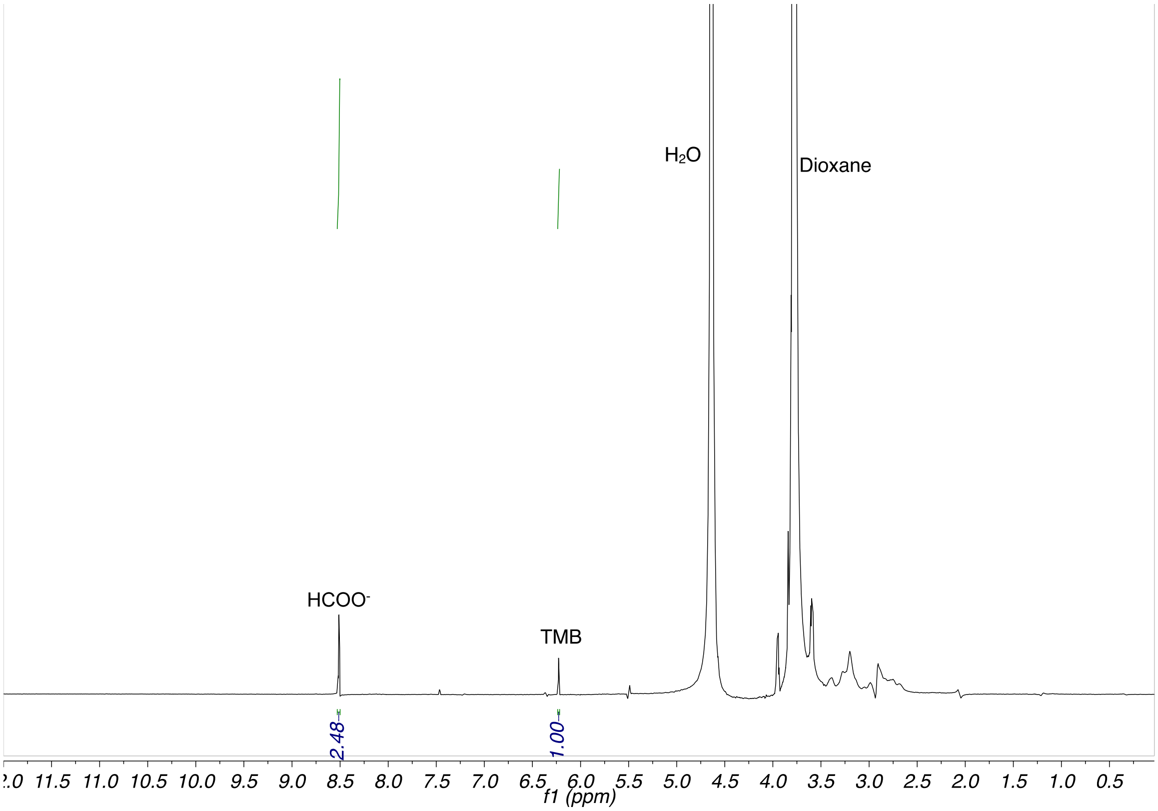


Fig. S18 ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of PEHA with 75 bar 3:1 H_2/CO_2 mixture at 70 °C using catalyst **1** in D_2O. 100mg trimethoxybenzene was added as internal standard.

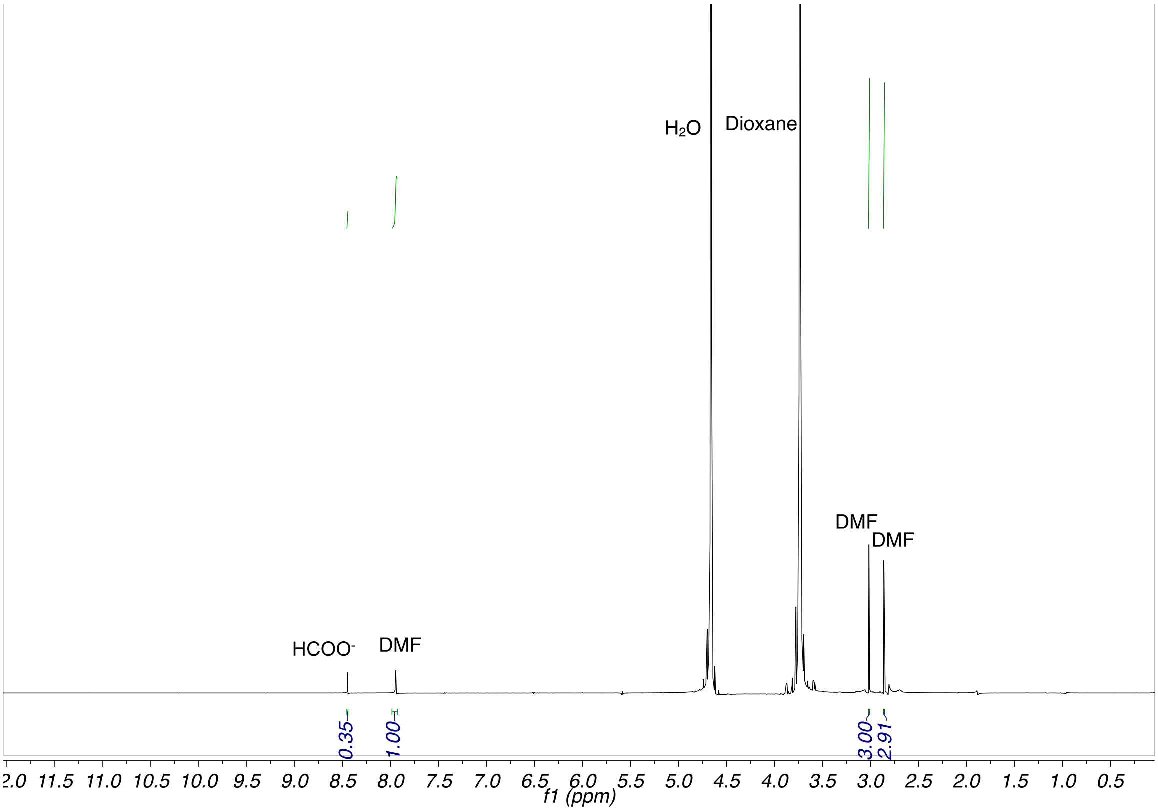


Fig. S19 ^{1}H NMR spectrum of the reaction mixture obtained after the hydrogenation of bi(carbonate) and carbamate salts of PEI_{800} with 50 bar H_2 using catalyst **1** in D_2O at 70 °C. 0.9 g DMF added as internal standard.

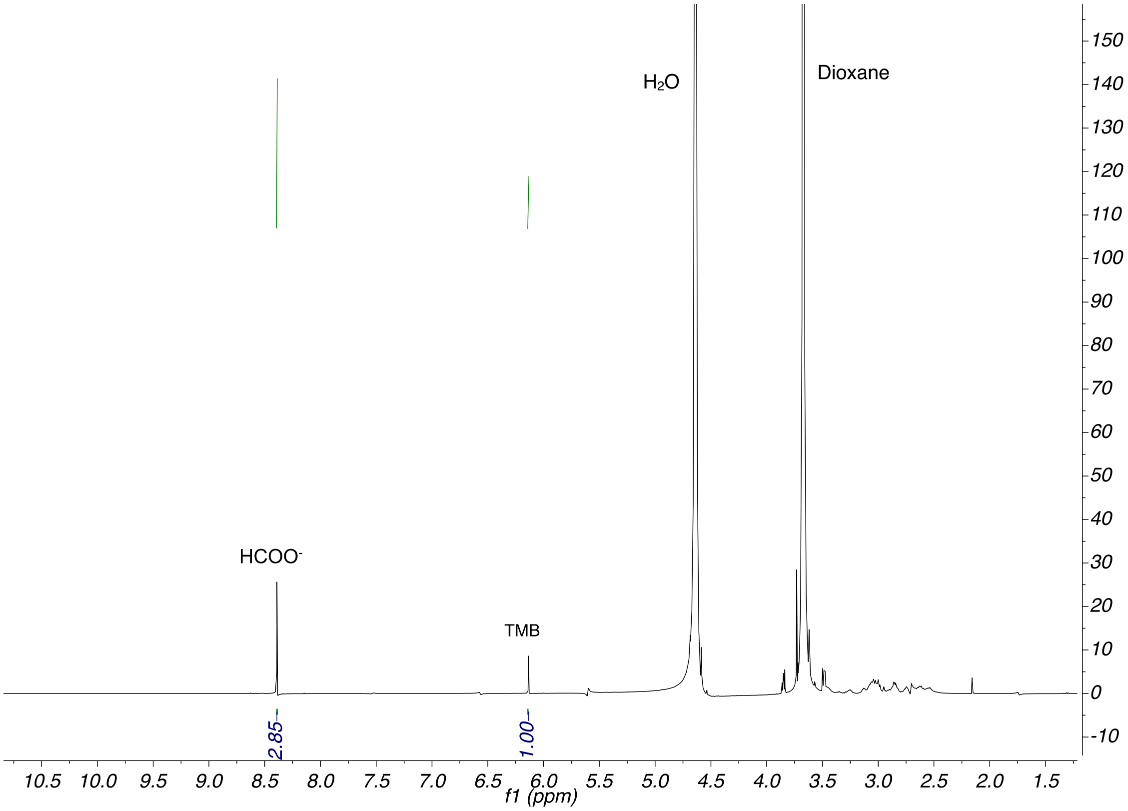


Fig. S20 ^{1}H NMR spectrum of the reaction mixture obtained after the hydrogenation of bi(carbonate) and carbamate salts of PEHA with 80 bar H_2 using catalyst **4** in D_2O at 50 °C. 100 mg trimethoxybenzene was added as internal standard.

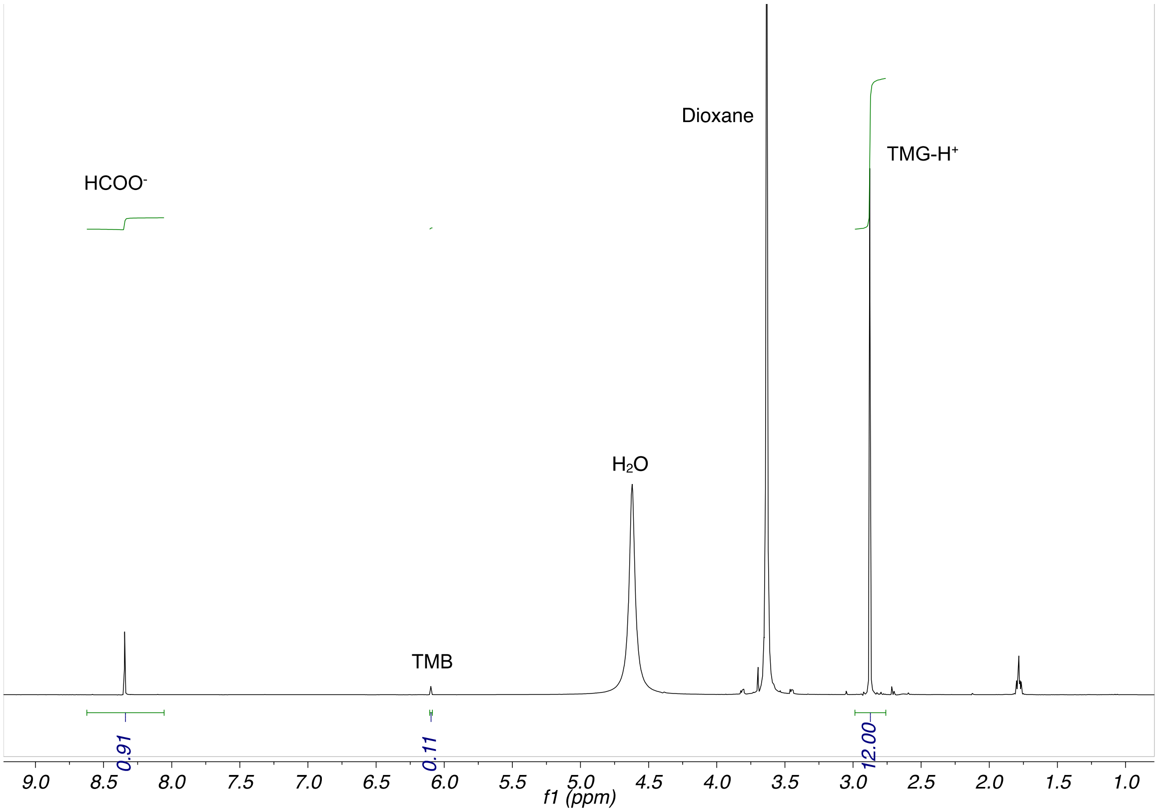


Fig. S21 ^{1}H NMR spectrum of the reaction mixture obtained after the hydrogenation of bicarbonate salts of TMG with 50 bar H_2 using catalyst **1** in D_2O at 55 °C using 2 µmol of catalyst **1**. 100 mg trimethoxybenzene was added as internal standard.

IV. Recycling studies in biphasic conditions

Fig. S22 H_2O and 2-MeTHF biphasic reaction mixture obtained with DABCO and catalyst **1** (Ru-PNP). DABCO stayed in the aqueous layer (lower layer) and the catalyst **1** remained in the organic layer (upper layer). Organic layer was reused for subsequent cycles.

Fig. S23 The product, formate salt of DABCO, obtained as white solid after the removal of water from the aqueous layer using lyophilizer.

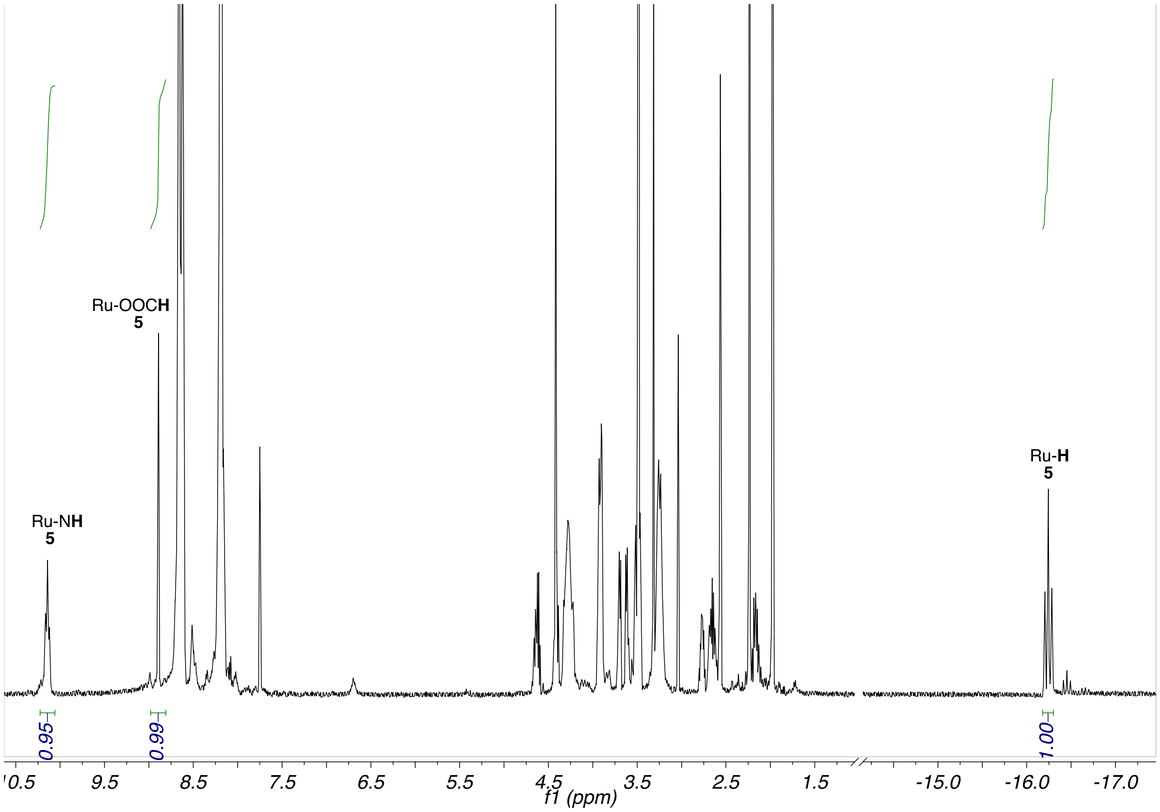


Fig. S24 ^{1}H NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **1** in THF-d_8.

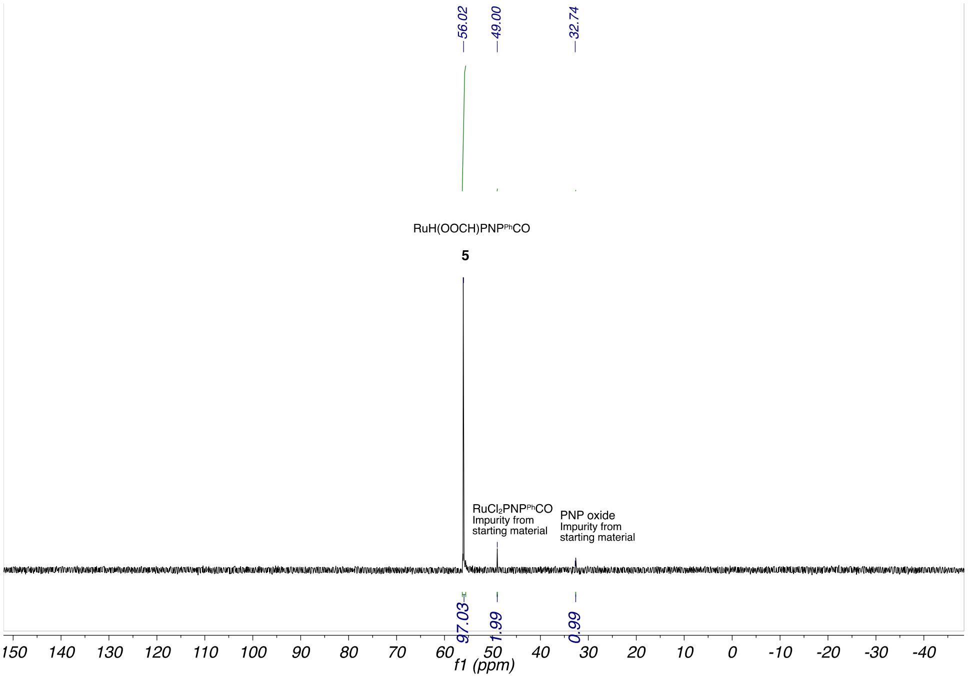


Fig. S25 ^{31}P NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **1** in THF-d$_8$.

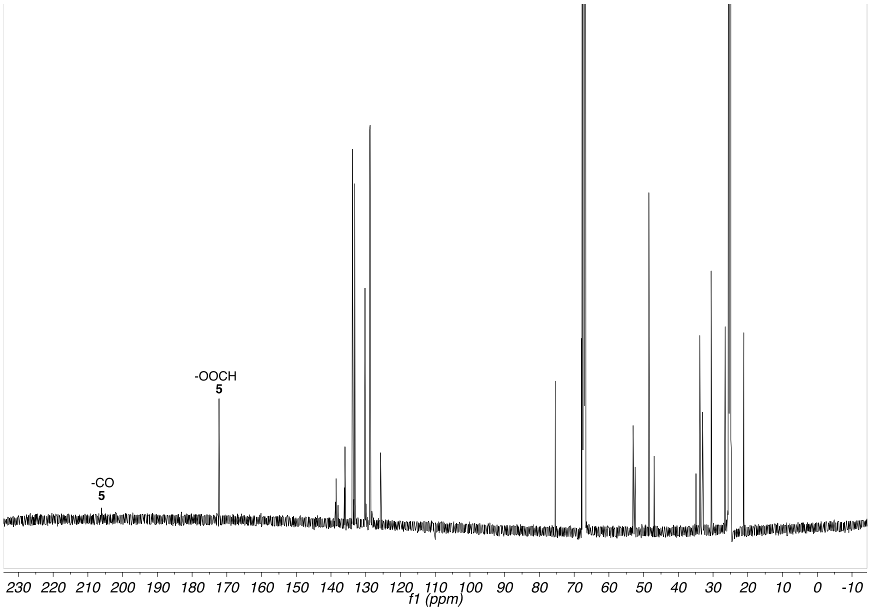


Fig. S26 ^{13}C NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **1** in THF

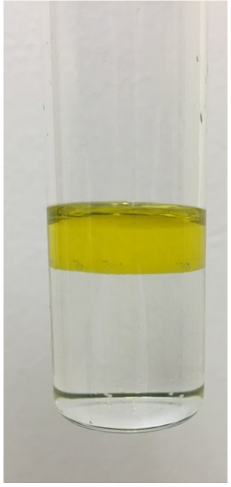


Fig. S27 H_2O and 2-MeTHF biphasic reaction mixture obtained with DABCO and catalyst **4** (Fe-PNP). DABCO stayed in the aqueous layer (colorless lower layer) and the catalyst **4** remained in the organic layer (yellow upper layer). Organic layer was reused for subsequent cycles.

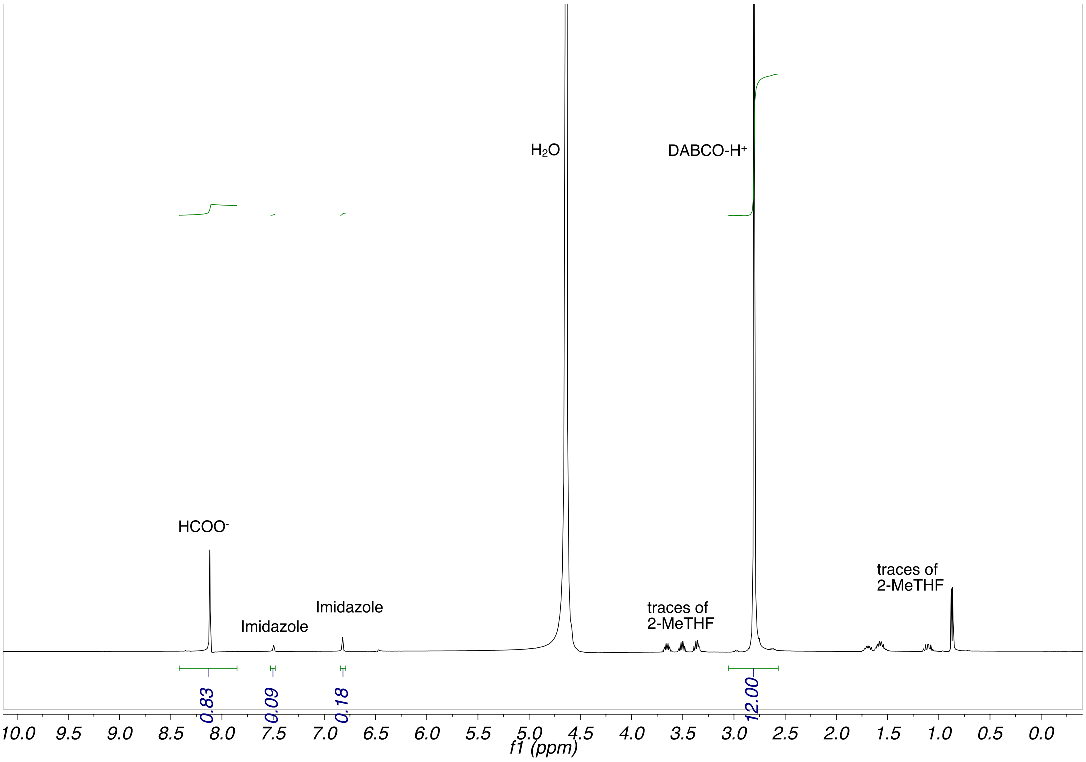


Fig. S28 ^1H NMR spectrum of the aqueous layer after the hydrogenation of bicarbonate salts of DABCO with 50 bar H_2 using catalyst **4** in D_2O (with 100 mg imidazole as internal standard).

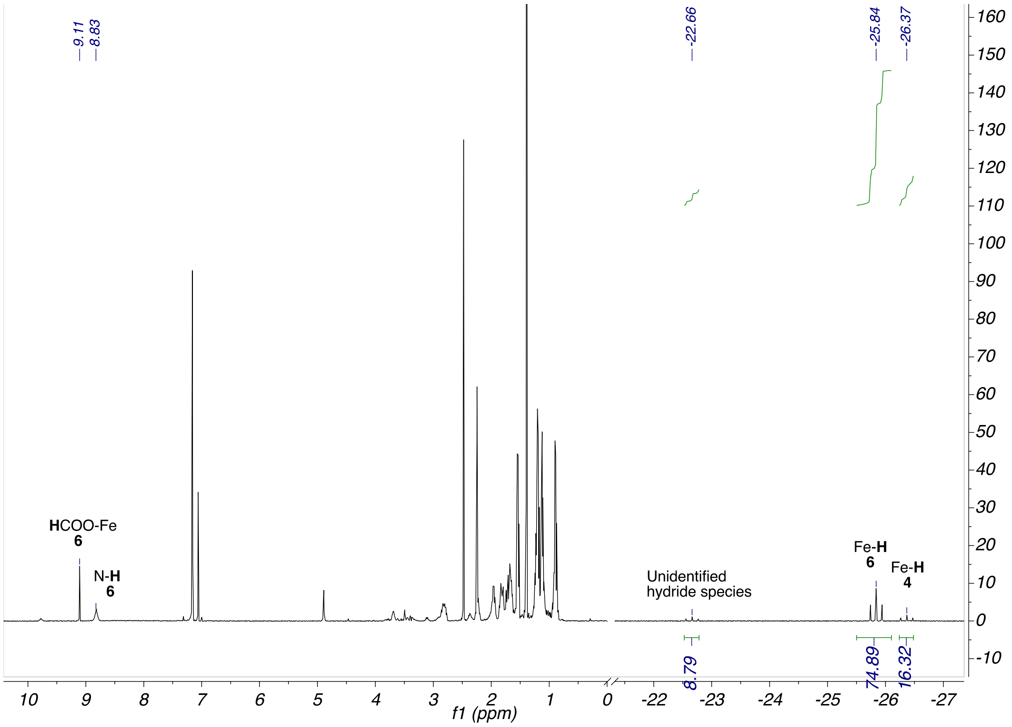


Fig. S29 ^{1}H NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **4** in C_6D_6.

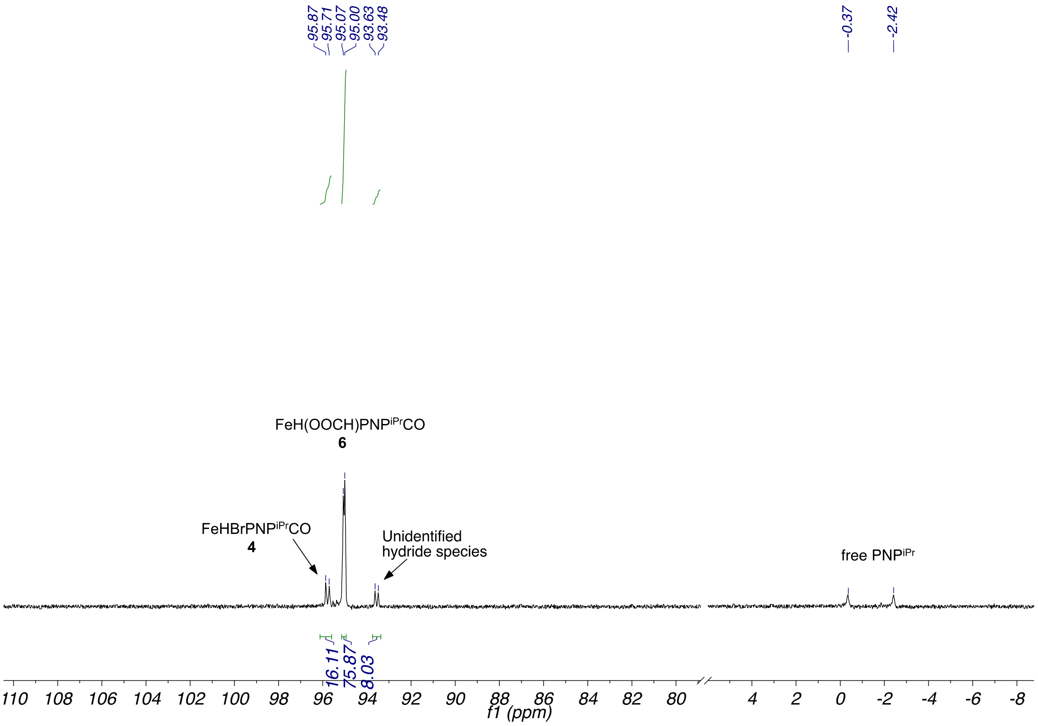


Fig. S30 ^{31}P NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **4** in C_6D_6.

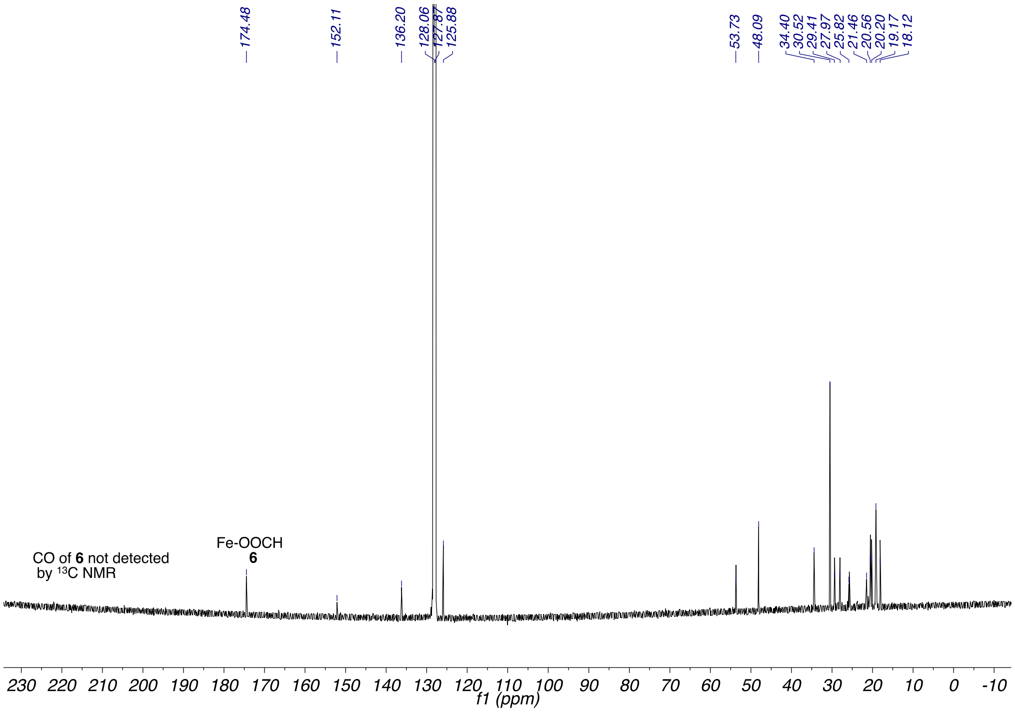


Fig. S31 ^{13}C NMR spectrum of the organic layer of the biphasic reaction mixture after the evaporation of Me-THF using catalyst **4** in C_6D_6.

V. References

1. S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause and H. Guan, *J. Am. Chem. Soc.*, 2014, **136**, 7869–7872.
2. E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H. J. Drexler, W. Baumann, H. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 14162–14166.