

## Supporting Information

# Condensed-Phase Low Temperature Heterogeneous Hydrogenation of CO<sub>2</sub> to Methanol

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## 1. Standard procedure for the CO<sub>2</sub> hydrogenation

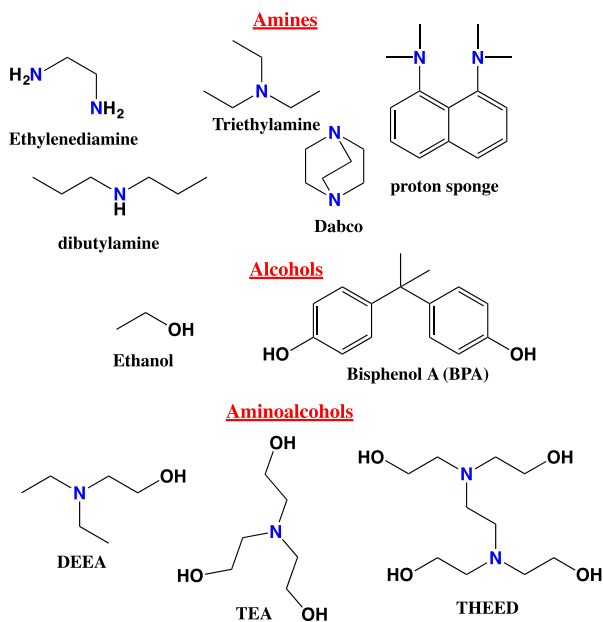
All materials were purchased from commercial suppliers and used without further purification.

300 mg of commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst from Syntex was activated under H<sub>2</sub> atmosphere (48 bar) at 125 °C in a stainless-steel reactor (8 mL). 48 bar was chosen as our previous studies have shown that this pressure of H<sub>2</sub> was able to fully reduce the catalyst in a previous study.<sup>1</sup> After 4h, the remaining H<sub>2</sub> pressure from the reactor was released and backfilled with H<sub>2</sub> at 125 °C and cooled to room temperature. The commercial black Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst's color changed to purple-black powder after the activation. The catalyst contains 55.7 wt.% Cu, 26.8 wt.% Zn, and 5.0 wt.% Al according to inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.

The above pre-activated catalyst was transferred to a 300 mL Parr reactor and a given amount of amine and alcohol were added to the reactor vessel and the reactor was sealed in a nitrogen glovebox. The reactor was first pressurized with 20 bar CO<sub>2</sub> and then additional 40 bar of H<sub>2</sub> was introduced (total pressure =60 bar). Then, the reactor was heated to 170 °C. After 24 h, the reactor was cooled to room temperature and then to -78 °C, the excess pressure was released slowly. 100 mg of 1,3,5-trimethoxybenzene was added as an internal standard to the reaction mixture (if necessary, DMSO or water was

added to get a homogeneous solution) and a small aliquot of the sample was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$ .

**Table S1: Initial Screening for the hydrogenation of  $\text{CO}_2$  to methanol**



Entry	Promoter	$\text{HCOO}^-$	$\text{HCOO}$	$\text{N-CHO}$	$\text{MeOH}$
		(%) <sup>a</sup>	R (%) <sup>a</sup>	(%) <sup>a</sup>	(%) <sup>a</sup>
1	Ethylenediamine	-	-	7%	-
2	Dibutylamine	-	-	2%	-
3	Ethylenediamine: EtOH	trace	3%	6%	-
4	THEED	-	-	-	-
5	TEA	-	-	-	-

<b>6</b>	DEEA	trace	trace	-	4%
<b>7</b>	NEt <sub>3</sub> :BPA	-	-	-	-
<b>8</b>	Proton sponge :EtOH	-	-	-	-

Standard reaction conditions: catalyst=Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (300 mg), CO<sub>2</sub>/H<sub>2</sub>=50 bar (1:2), amine (100 or 150 mmol), amine: alcohol=1:1, t=16h. Yield are based on <sup>1</sup>H NMR and they are calculated with respect to the amine.

## 2. Standard Procedure for carboxylation experiments

Reaction condition for carboxylation of methanol with tertiary amines and CO<sub>2</sub> :

Under an inert atmosphere, 0.0012 mol of amine was dissolved in 3.0 mL of methanol. The solution was syringed into the stainless-steel IR cell or in to a PEEK high pressure NMR cell<sup>1</sup> and charged with 10 bar CO<sub>2</sub> at room temperature. The NMR cells were agitated by vortex until equilibrium has been reached.

Reaction condition for carboxylation of various alcohols with NEt<sub>3</sub> and CO<sub>2</sub>:

Under an inert atmosphere, 0.0012 mol of NEt<sub>3</sub> was dissolved in 3.0 mL of alcohol. The solution was syringed in to a PEEK high pressure NMR cell<sup>2</sup> and charged with 10 bar CO<sub>2</sub> at room temperature.

Reaction condition for carboxylation of phenol with NEt<sub>3</sub> and CO<sub>2</sub>:

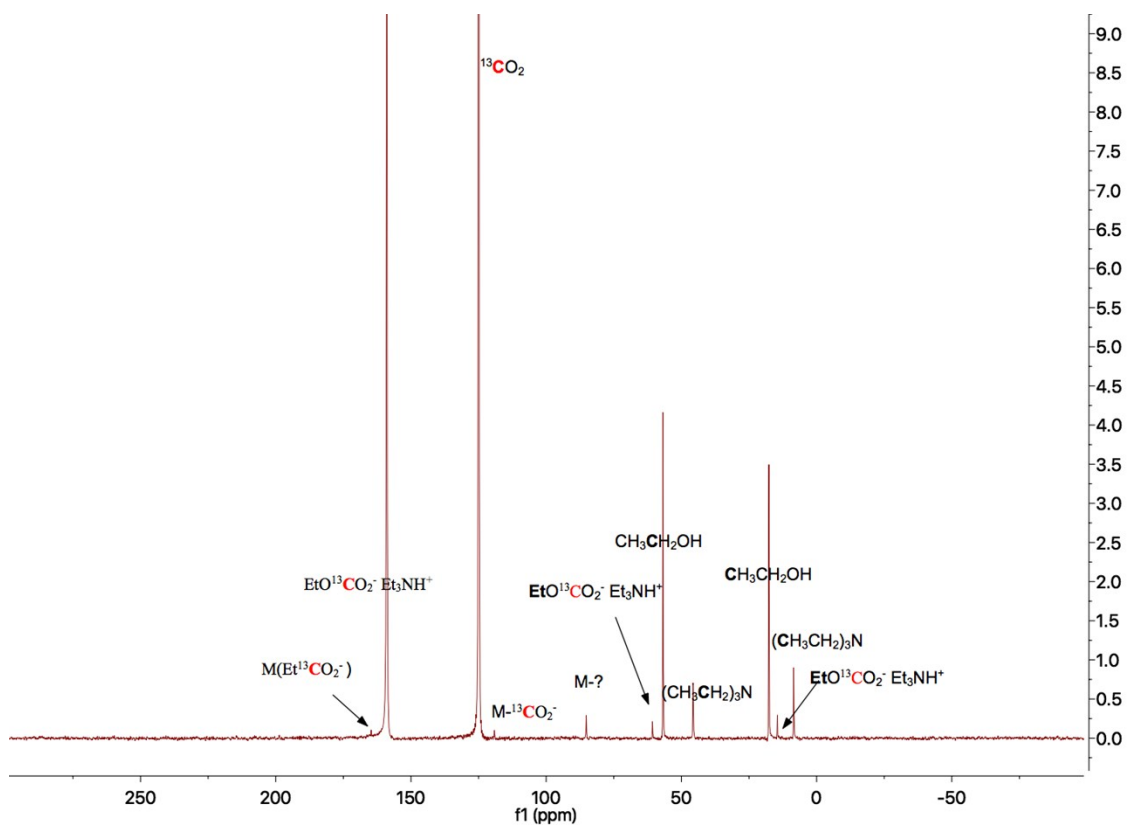
Under an inert atmosphere, 0.0012 mol of  $\text{NEt}_3$  and 0.0012 mol of phenol were dissolved in 3.0 mL of THF. The solution was syringed in to a PEEK high pressure NMR cell<sup>2</sup> and charged with 10 bar  $\text{CO}_2$  at room temperature.

### **3. Standard Procedure for *in situ* high pressure and high temperature MAS-NMR**

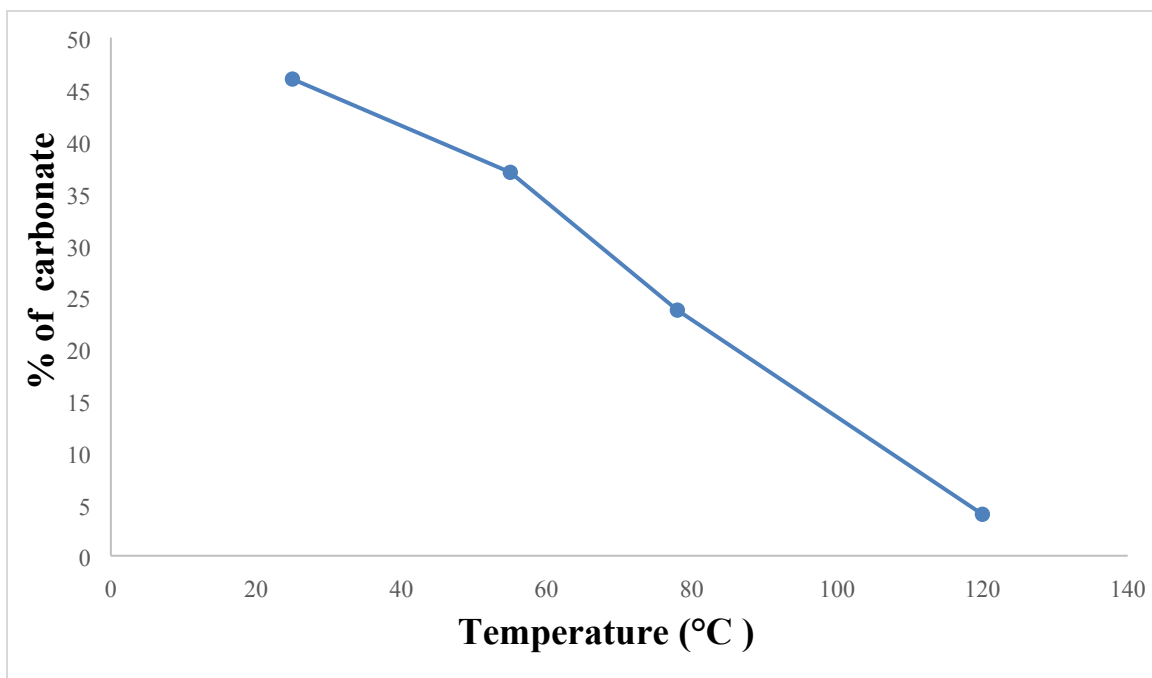
MAS-NMR experiments were performed on an Agilent-Varian VNMRS NMR spectrometer equipped with an 11.7 T magnet, operating at 125.7747 MHz for the  $^{13}\text{C}$  channel and 500.1822 MHz for  $^1\text{H}$  channel, and using a 5 mm homebuilt MAS double-resonance HX probe with a custom Pd-coated coil for increased sample magnetic homogeneity. The rotor was heated to various set temperatures and both  $^{13}\text{C}$  and  $^1\text{H}$  spectra were collected before further temperature elevation. All rotors were Varian/Agilent-style cavern rotors (Revolution NMR LLC), modified for high pressure samples as described previously.<sup>3</sup>

1:10  $\text{NEt}_3$ :EtOH mixture (0.09 mmol: 0.9 mmol) and 4.7 mg of pre-activated  $\text{Cu/ZnO/Al}_2\text{O}_3$  were transferred to a MAS NMR rotor in a  $\text{N}_2$  glovebox. The rotor was

charged with a 20 bar CO<sub>2</sub> at room temperature. Then the NMR of the initial reaction mixture was taken at 25 °C, which showed the formation of triethylammonium ethylcarbonate (EtOCO·Et<sub>3</sub>NH<sup>+</sup>) upon the reaction of free CO<sub>2</sub> with NEt<sub>3</sub> and ethanol (Figure S1). Subsequently the temperature is increased to 55, 78 and 120 °C. The percentage of EtOCO·Et<sub>3</sub>NH<sup>+</sup> with respect to total amine content vs temperature was plotted (Figure S2).

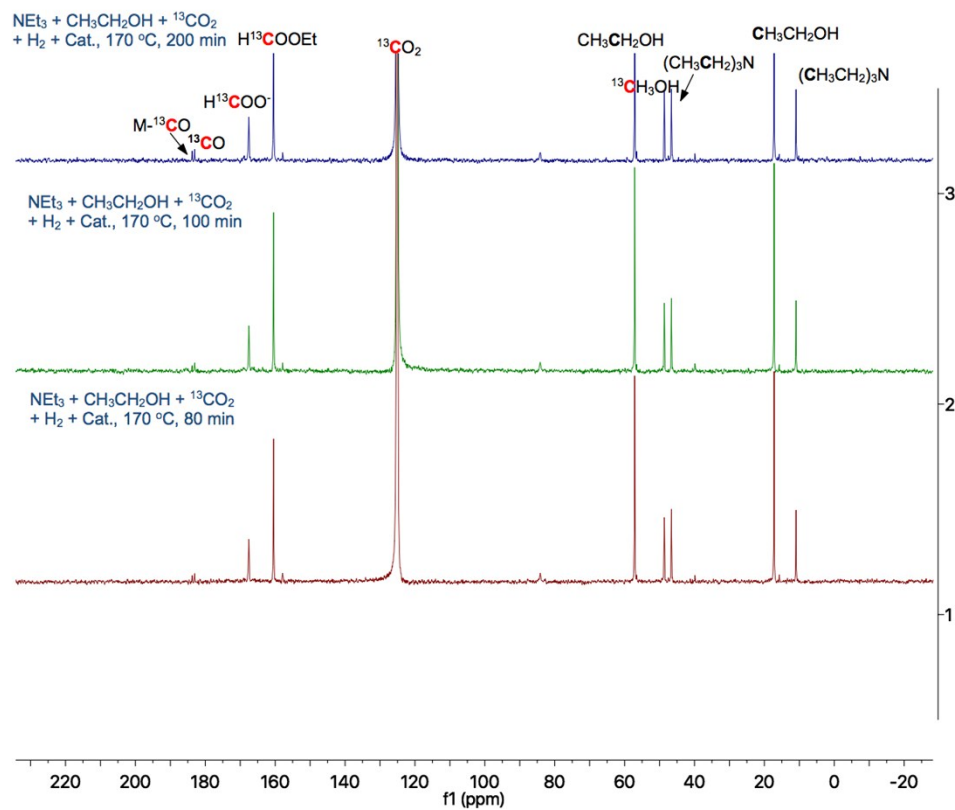


**Figure S1.** <sup>13</sup>C NMR of the reaction mixture under 20 bar CO<sub>2</sub> at 25 °C.



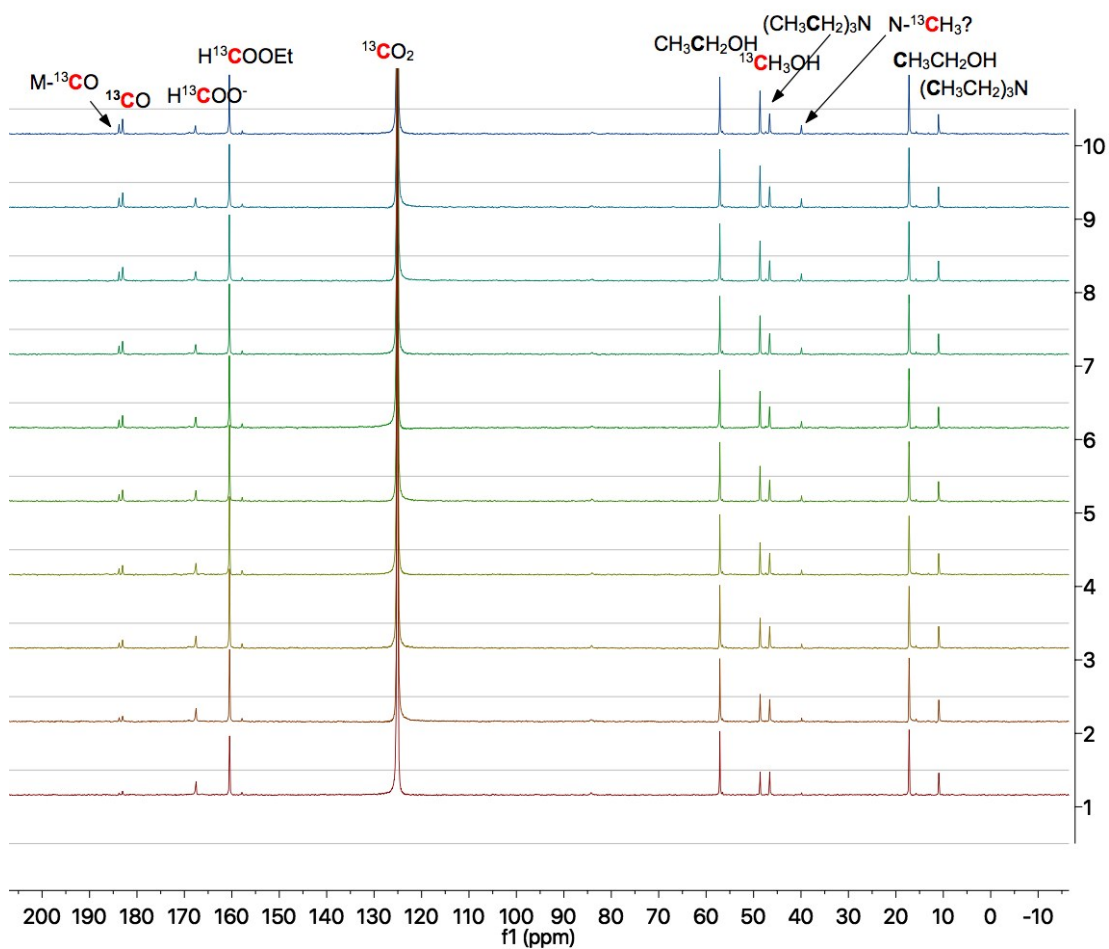
**Figure S2.** Percentage of  $\text{EtOCO}^-\text{Et}_3\text{NH}^+$  with respect to total amine content vs temperature

40 bar of hydrogen was introduced to the above mixture and the MAS rotor was heated at 170 °C for 8h - 1<sup>st</sup> hour (Figure 1), 2<sup>nd</sup> hour (Figure S3) and 3<sup>rd</sup>-8<sup>th</sup> hour (Figure S4).



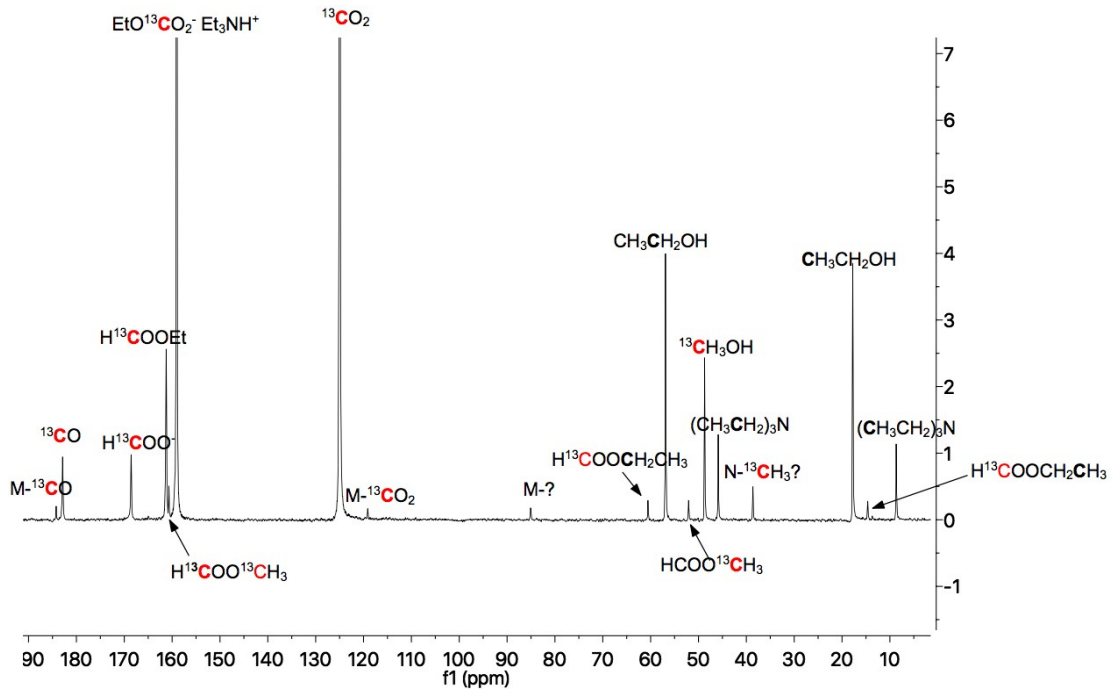
**Figure S3.** <sup>13</sup>C NMR of the reaction mixture under 60 bar 1:2 CO<sub>2</sub>: H<sub>2</sub> at 170 °C, 2-3h.



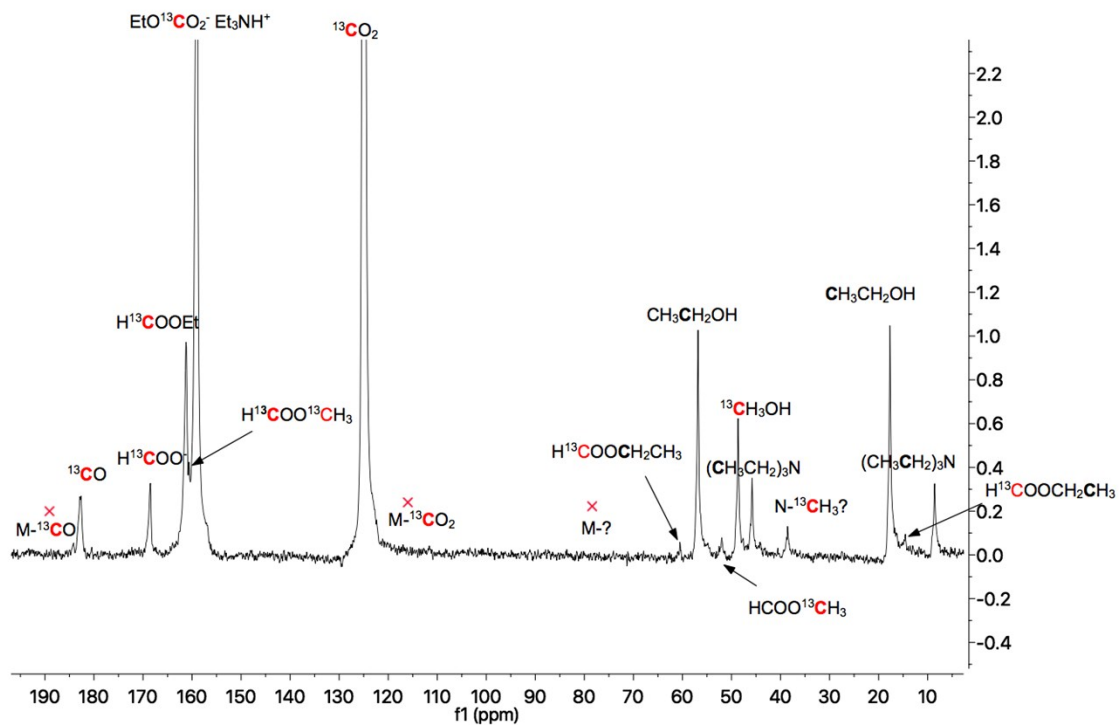


**Figure S4.**  $^{13}\text{C}$  NMR of the reaction mixture under 60 bar 1:2  $\text{CO}_2$ :  $\text{H}_2$  at 170 °C, 3-8h.

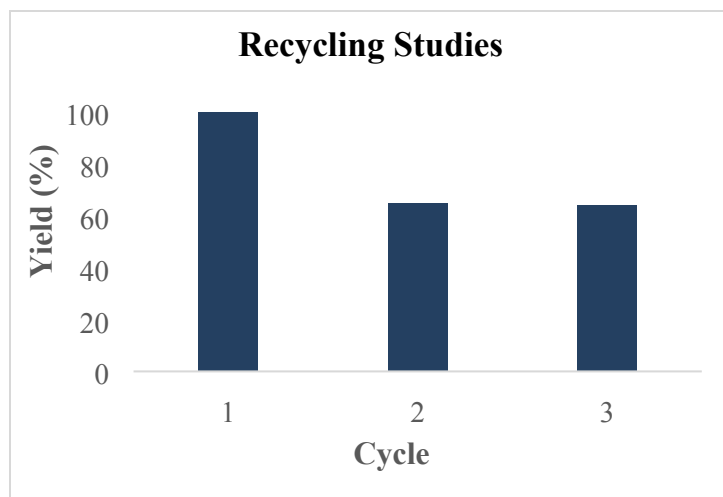
(a)



(b)



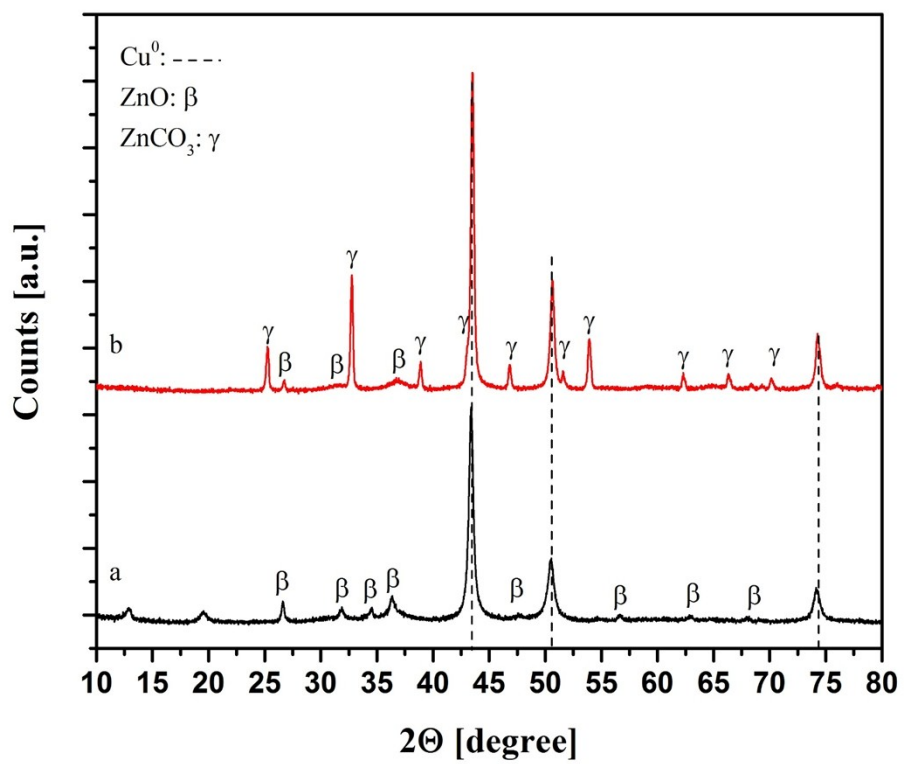
**Figure S5.**  $^{13}\text{C}$  NMR of the reaction mixture after cooling down to room temperature from  $170^\circ$  (a) spin (b) non-spin



**Figure S6.** Catalyst recycling study

#### **4. X-ray diffraction Study**

X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex II powder x-ray diffractometer with a Cu- $\alpha$  x-ray source operated at 30 kV and 15 mA with an amorphous glass sample holder. Prior to measurement, the fresh sample was ground and reduced at 125 °C for 4h under 48 bar H<sub>2</sub> atmosphere. The spent sample was collected and used as recovered. XRD patterns were collected from 10 to 80° 2 $\theta$  at a step size of 0.02 °2 $\theta$ /step. Peaks were analyzed and fit using the MDI Jade 9 software. Cu<sup>0</sup> crystallite size was calculated using the Scherer equation based on the 43.5° 2 $\theta$  peak. Cu dispersion was calculated from the Cu<sup>0</sup> particle size assuming hemispherical geometry using the formula  $D = 100/d$  where D represents the fractional dispersion and d is the Cu<sup>0</sup> particle size (in nm).<sup>4,5</sup>



**Figure S7.** XRD of the (a) pre-activated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, (b) spent Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst – after 3 recycling studies

## 5. Standard Procedure for *in situ* high-temperature MAS-NMR in the presence of 5 wt% Pd/ZnO

1:10 NEt<sub>3</sub>:EtOH mixture (0.09 mmol: 0.9 mmol) and 4 mg of pre-activated Pd/ZnO were transferred to a MAS NMR rotor in a N<sub>2</sub> glovebox. The rotor was charged with a 20 bar CO<sub>2</sub> and 40 bar of hydrogen at room temperature and the MAS rotor was heated at 170 °C for 15 h.

## 6. References

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