

Supporting Information

Catalytic Homogeneous Hydrogenation of CO to Methanol via Formamide

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Table of Contents

1. Materials and methods	S2
2. Standard procedure for amine carbonylation reaction (Table 1)	S2
2.1. Formation of 1a in the carbonylation reaction in ^1H NMR	S3
3. Standard procedure for the formamide hydrogenation reactions (Table 2)	S3
3.1. Representative spectra of hydrogenation reaction	S4
4. Standard procedure for sequential stepwise CO to methanol reactions (Table 3)	S5
4.1. Formation of methanol through sequential reaction in ^1H NMR	S6
5. Procedure for direct one-step CO hydrogenation to methanol (Table 4)	S7
5.1. Pressure profile of direct CO hydrogenation to methanol	S7
5.2. GC chromatogram of the unreacted gas mixture	S8
5.3. Methanol formation as observed from ^1H NMR	S8
6. Deactivation pathway of hydrogenation catalysts in presence of CO	S10
7. References	S10

1. Materials and methods

All experiments were carried out under an inert atmosphere (with N₂ or Ar) using standard Schlenk techniques. Complexes RuHCIPNP^{iPr}(CO) (**C-1**, Strem Chemicals, 97%), Ru-MACHO-BH (**C-2**, Strem Chemicals, 98%), Ru-MACHO (**C-3**, Strem Chemicals, 98%) were used as received without further purification. K₃PO₄, reagent grade, was purchased from Sigma-Aldrich and used without further purification. All catalysts including K₃PO₄ were weighed inside an argon filled glove box. The amines, piperidine (Sigma-Aldrich, 99%) and diethylenetriamine (DETA, Sigma-Aldrich, 99%) were sparged with N₂ for one hour prior to their use. The solvents, toluene (Drisolv), methanol (Drisolv) and ethanol (Drisolv.) were sparged with N₂ for 1 h prior to use. 1,3,5-trimethoxybenzene (TMB, Sigma-Aldrich, >99%) and DMSO-d₆ (CIL, D-99.9%) were used as received. ¹H and ¹³C NMR spectra were recorded on 400 MHz, Varian NMR spectrometers. ¹H and ¹³C NMR chemical shifts were determined relative to the residual solvent signals (DMSO-d₆) or internal standard (TMB). CO (Airgas, instrument grade 4.0), H₂ (Gilmore, ultra-high pure grade 5.0) were used without further purification. The gas mixtures were analyzed using a Thermo gas chromatograph (column: Supelco, Carboxen 1010 plot, 30 m x 0.53 mm) equipped with a TCD detector (CO detection limit: 0.099 v/v%).

Caution: Reactions are associated with CO and H₂ gas. They should be carefully handled inside proper fume hoods without any flame, spark or static electricity sources nearby.

2. Standard procedure for amine carbonylation reaction (Table 1)

K₃PO₄ (1 mmol), amine (piperidine (**1**)/DETA; NH content 10 mmol), and solvent (5 mL) were added in a nitrogen chamber to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. After pressurizing the reactor with CO to the desired pressure of 30 bar, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 5 min and then heated in a pre-heated oil bath to an internal temperature of 140 °C. After heating for a given amount of time, the reactor was cooled to RT. The gas mixture was carefully released inside a fume hood and the autoclave was then flushed with 40 bars of argon twice to remove any remaining CO inside. The reactor was then opened and a reaction solution containing white powders of K₃PO₄ was obtained. A known amount of TMB was added as an internal standard to the reaction mixture. This mixture was then analyzed by ¹H and ¹³C NMR with DMSO-d₆ as the deuterated solvent.

2.1. Formation of **1a** in the carbonylation reaction in ^1H NMR

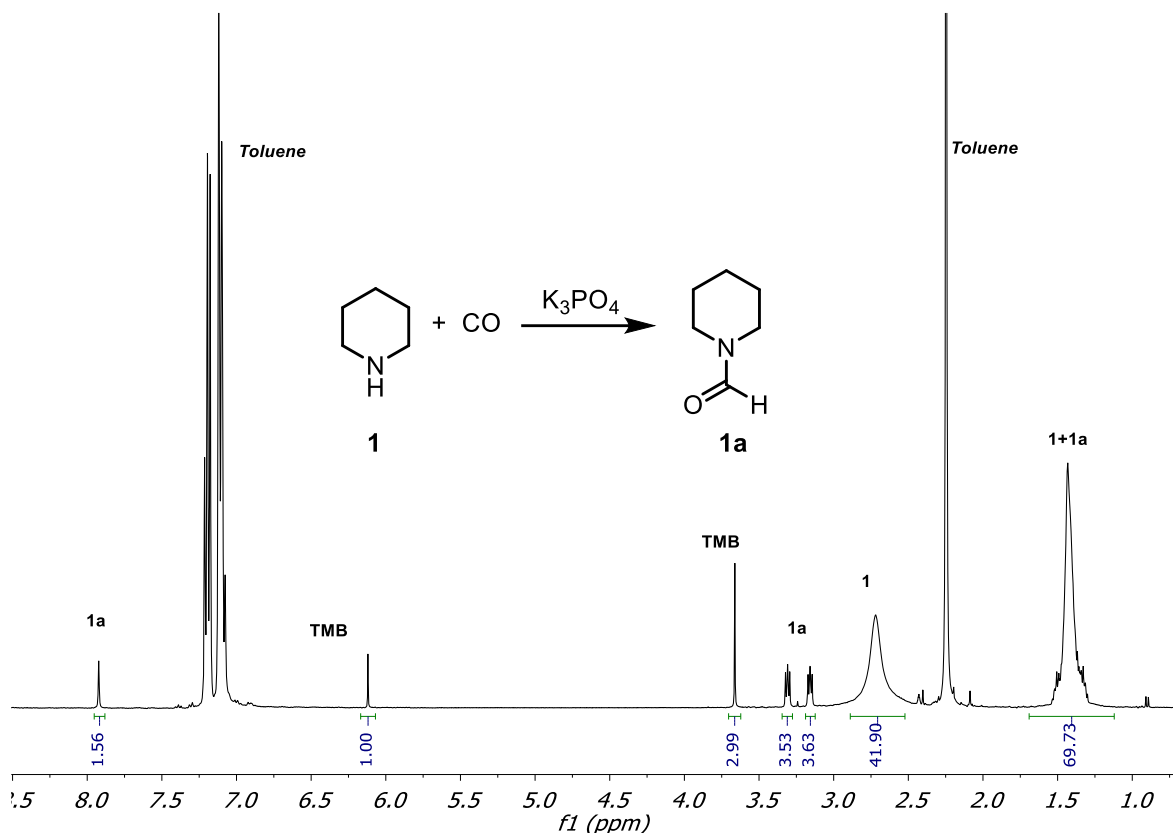
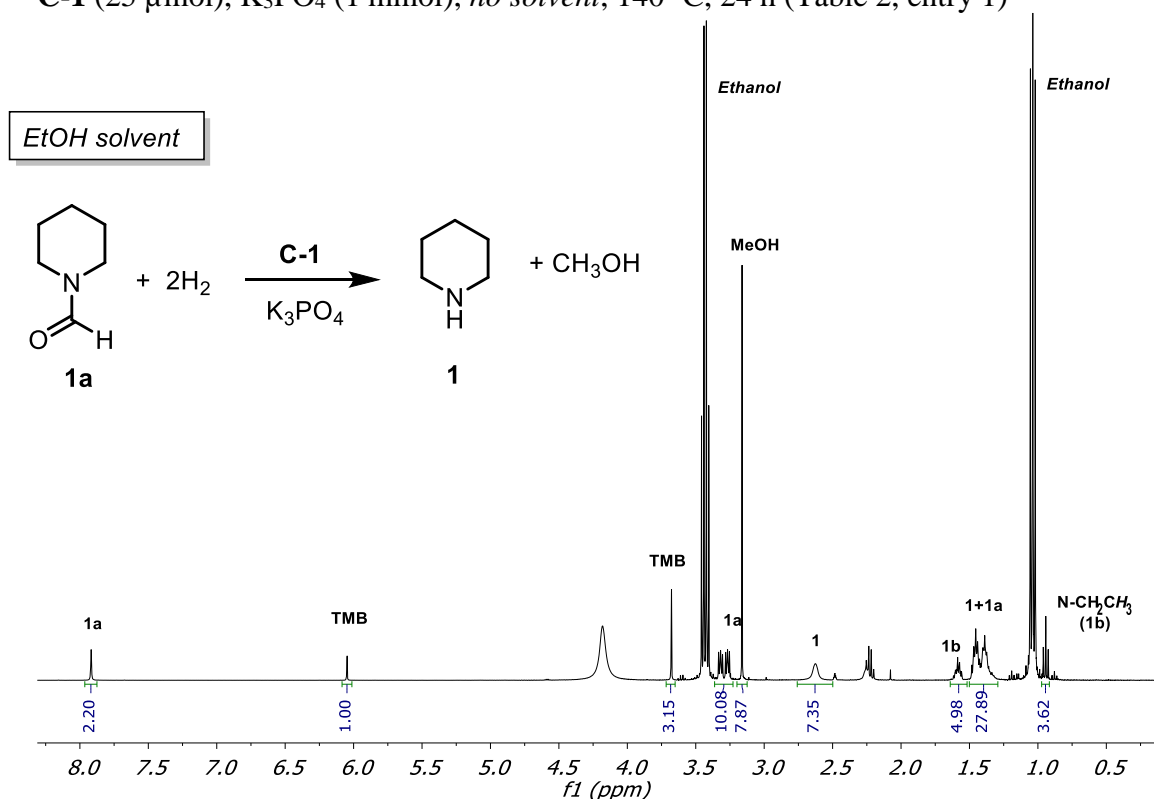
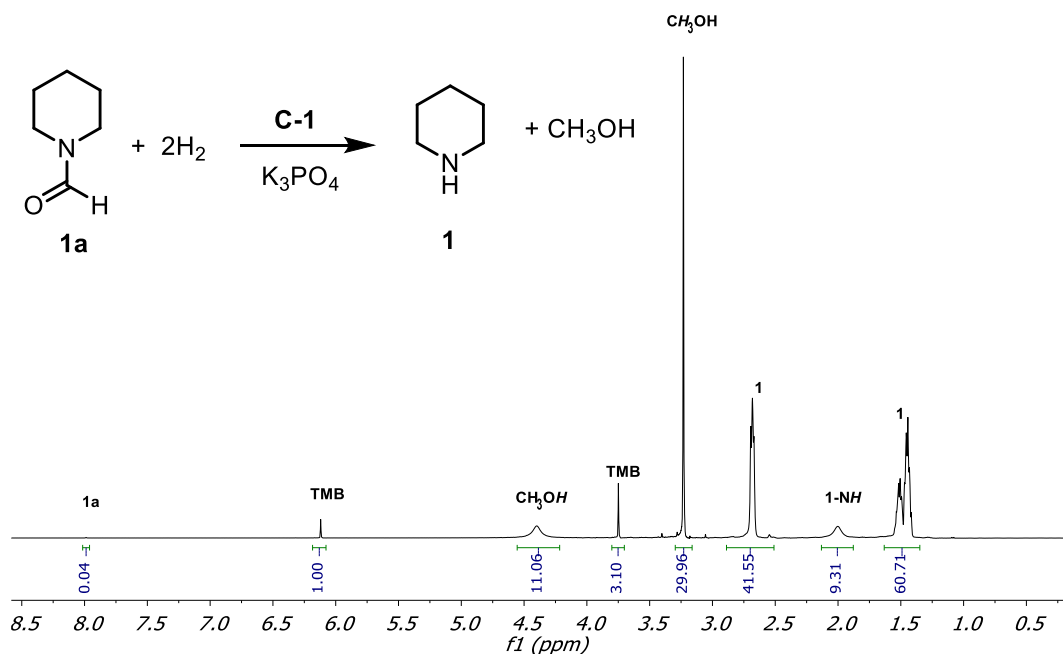


Figure S1. Formation of **1a** through carbonylation of **1**. Reaction conditions: **1** (10 mmol), CO (30 bar), K_3PO_4 (1 mmol), *no solvent*, 140 $^\circ\text{C}$, 24 h (Table 1, entry 1), Yield ~10%. 5 mL toluene was added during workup

3. Standard procedure for the formamide hydrogenation reactions (Table 2)

Catalyst **C-1** (25 μmol), K_3PO_4 (1 mmol), 1-formylpiperidine (**1a**, 10 mmol) and solvent (5mL) were added in a nitrogen chamber to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. After pressurizing the reactor with H_2 to a desired pressure, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 5 min and then heated in a pre-heated oil bath to an internal temperature of 140 $^\circ\text{C}$. After heating for a given amount of time, the reactor was cooled to RT. The reactor was then cooled in an ice bath for 30 min and the inside gases were slowly released. A clear solution was obtained upon opening the reaction vessel. A known amount of TMB was added as an internal standard to the reaction mixture. This mixture was then analyzed by ^1H and ^{13}C NMR with DMSO-d_6 as the deuterated solvent.

3.1. Representative spectra of hydrogenation reaction



4. Standard procedure for sequential stepwise CO to methanol reactions (Table 3)

In the first step, the amine carbonylation reaction was carried out in ethanol as a solvent. K_3PO_4 (1 mmol), amine (piperidine (**1**)/DETA; NH content 10 mmol), and the solvent (5 mL) were added in a nitrogen chamber to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. After pressurizing the reactor with CO to the desired pressure of 30 bar, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 5 min and then heated in a pre-heated oil bath to an internal temperature of 140 °C. After heating for a given amount of time, the reactor was cooled to RT. The gas mixture was carefully released inside a fume hood and the autoclave was then flushed with 40 bars of argon twice to remove any remaining CO inside. The reactor was then opened inside a N_2 chamber and the reaction solution was stirred for 15 minutes in N_2 atmosphere while keeping the vessel open to remove some of the dissolved CO.

Afterwards, the hydrogenation catalyst (**C-1/C-2/C-3**) and 15 mL of toluene were added to the reaction mixture inside the N_2 chamber. The reactor was then sealed and pressurized with H_2 to the desired pressure, the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 5 min and then heated in a pre-heated oil bath to an internal temperature of 140 °C. After heating for a given amount of time, the reactor was cooled to RT. The reactor was then cooled in an ice bath for 30 min and the inside gases were slowly released. A clear solution was obtained upon opening the reaction vessel. A known amount of TMB was added as an internal standard to the reaction mixture. This mixture was then analyzed by ^1H and ^{13}C NMR with DMSO-d_6 as the deuterated solvent.

4.1. Formation of methanol through sequential reaction in ^1H NMR

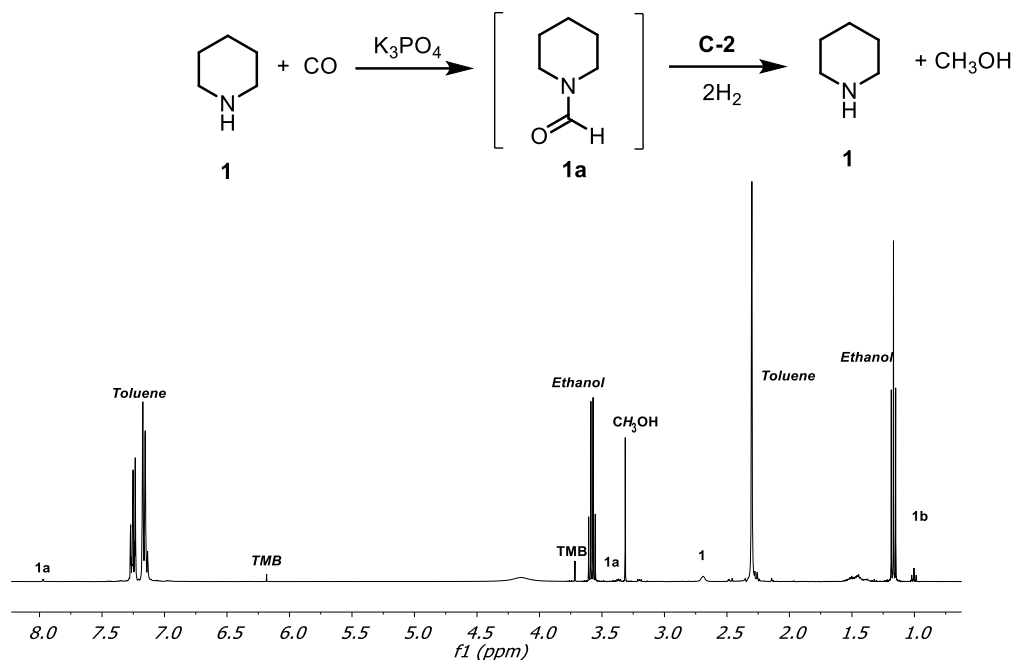


Figure S4. Sequential stepwise CO to methanol assisted by piperidine. Reaction conditions: Carbonylation step **1** (10 mmol), CO (30 bar), K_3PO_4 (1 mmol), ethanol (5 mL), 140 °C, 24 h. Hydrogenation step: toluene (15 mL), **C-2** (25 μmol), H_2 (60 bar), 140 °C, 24 h. (Table 3, entry 2)

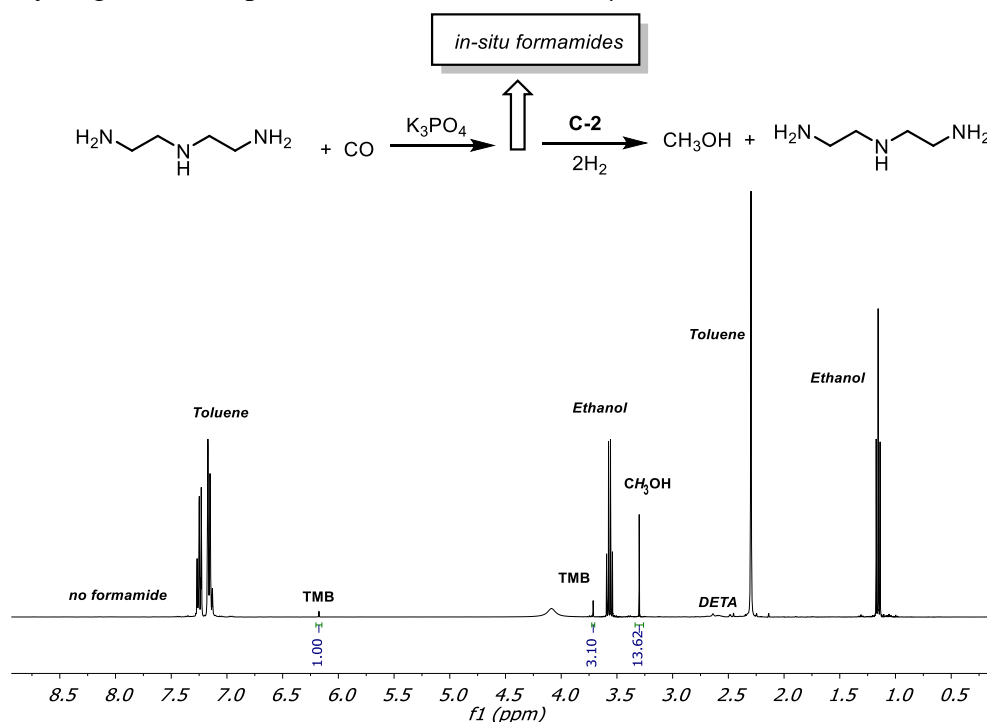


Figure S5. Sequential stepwise CO to methanol assisted by DETA. Reaction conditions: Carbonylation step DETA (3.33 mmol), CO (30 bar), K_3PO_4 (1 mmol), ethanol (5 mL), 140 °C, 36 h. Hydrogenation step: toluene (15 mL), **C-2** (25 μmol), H_2 (60 bar), 140 °C, 24 h. (Table 3, entry 3)

5. Procedure for direct one-step CO hydrogenation to methanol (Table 4)

C-2 (30 mg), K_3PO_4 (1 mmol), DETA (0.36 or 5 mL), and solvent (toluene/ethanol: 5 mL/5 mL) were added in a nitrogen chamber to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. Afterwards, the reactor was pressurized with the desired amount of CO (3 bar or 10 bar). Subsequently, after pressurizing the reactor with H_2 (70 bar), the LabVIEW 8.6 software was used to monitor and record the internal temperature and pressure of the reactor. The reaction mixture was stirred at room temperature (RT) for 5 min and then heated in a pre-heated oil bath to an internal temperature of 145 °C. After heating for a given amount of time (40 h or 1 week), the reactor was cooled to RT. The reactor was then cooled in an ice bath for 30 min. A sample of the gas was collected and analyzed through gas chromatography. The remaining gas mixture was carefully released inside a fume hood and the autoclave was then flushed with 40 bars of argon twice to remove any remaining CO inside. The reactor was then opened and a reaction solution containing white powders of K_3PO_4 was obtained. A known amount of TMB was added as an internal standard to the reaction mixture. This mixture was then analyzed by ^1H and ^{13}C NMR with DMSO-d_6 as the deuterated solvent.

5.1. Pressure profile of direct CO hydrogenation to methanol reaction

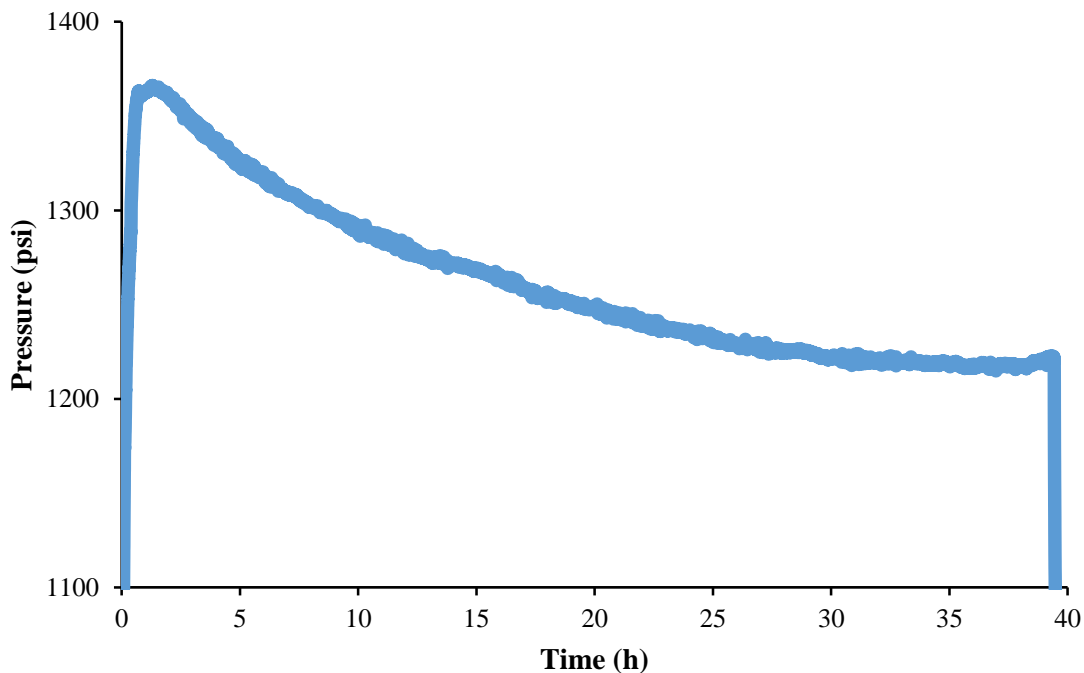


Figure S6. Continuous pressure-decrease observed during direct CO hydrogenation to methanol (Table 4, entry 1)

5.2. GC chromatogram of the unreacted gas mixture

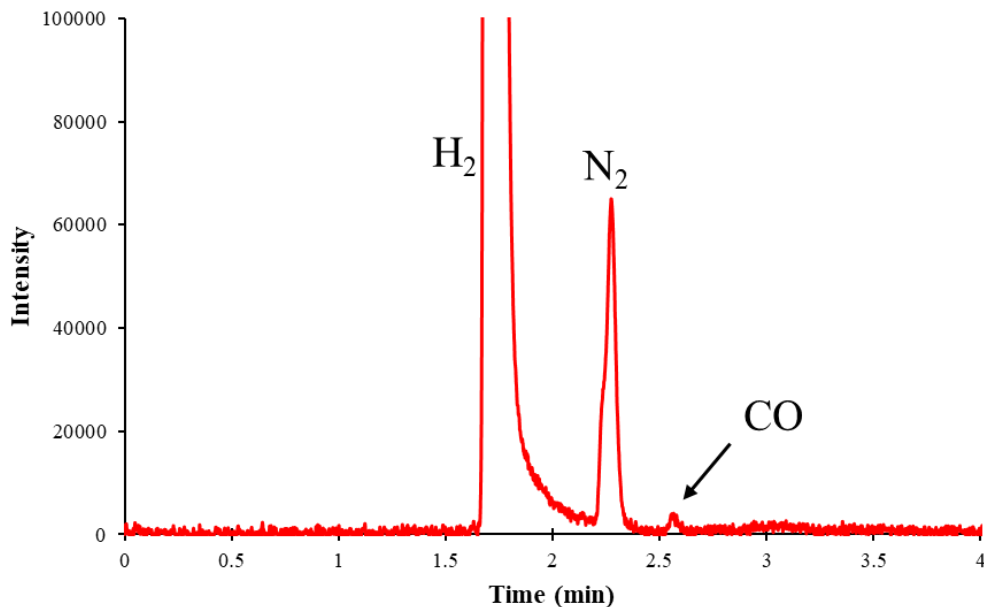


Figure S7. GC chromatogram of the unreacted gas mixture of Table 4, entry 1.

5.3. Methanol formation as observed from 1H NMR

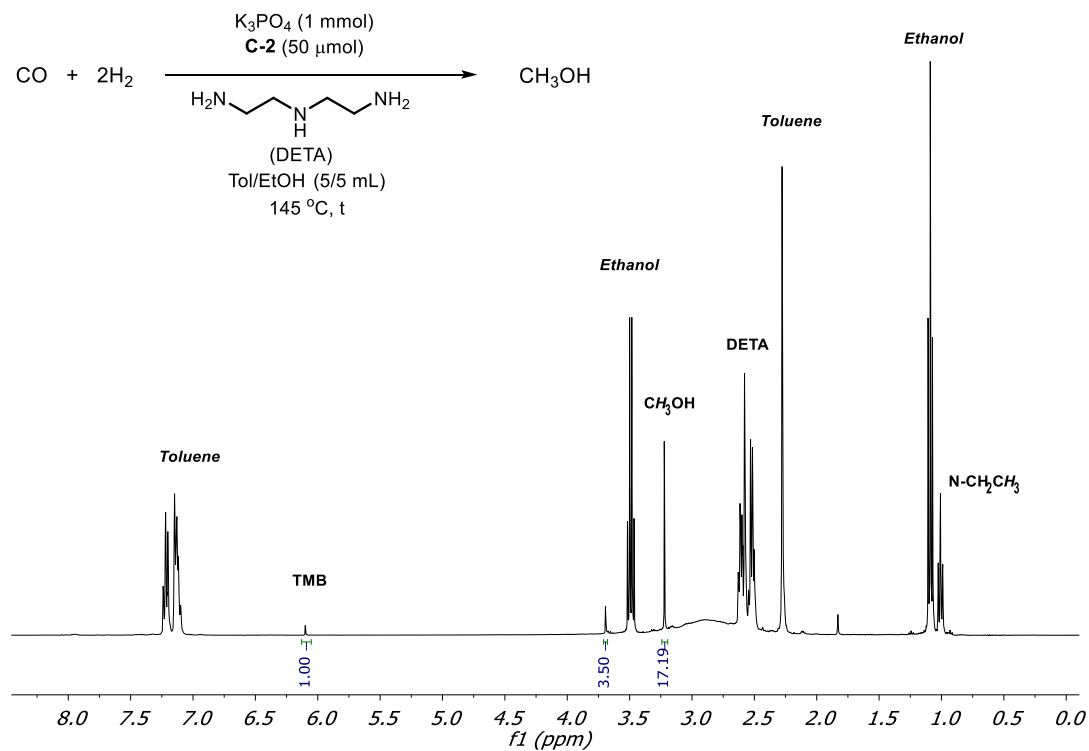


Figure S8. Direct CO to methanol in excess DETA. Reaction conditions: DETA (5 mL), **C-2** (50 μ mol), K_3PO_4 (1 mmol), Tol (5 mL), EtOH (5 mL), CO (3 bar), H_2 (70 bar), 145 $^{\circ}C$, 40 h. (Table 4, Entry 1)

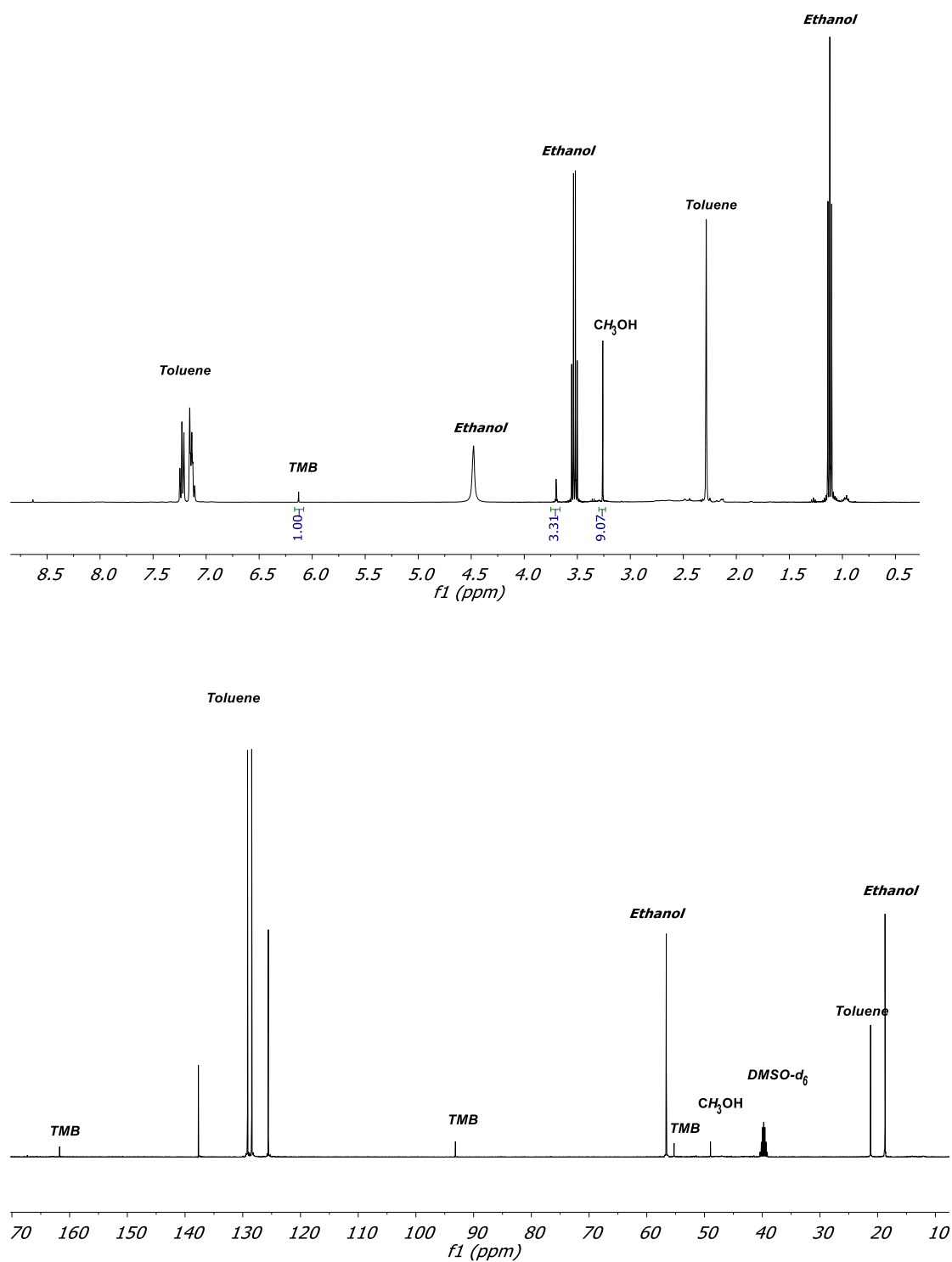
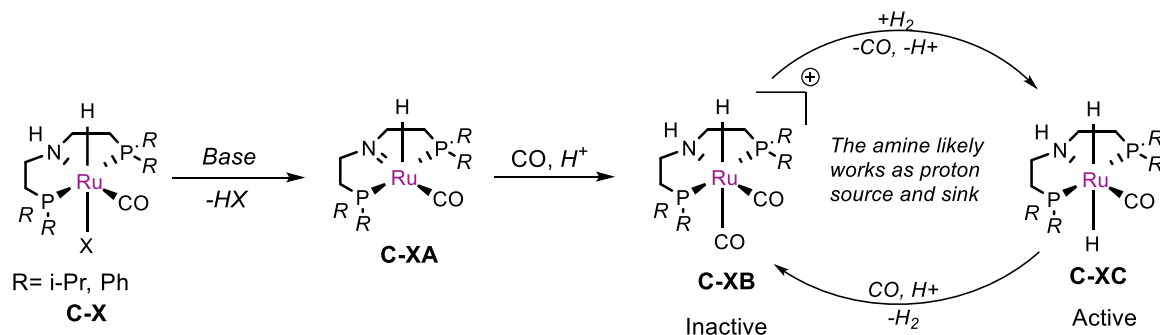


Figure S9. ¹H (top) and ¹³C NMR (bottom) of direct CO to methanol in lower DETA amount. Reaction conditions: DETA (360 μ L), **C-2** (50 μ mol), K₃PO₄ (1 mmol), Tol (5 mL), EtOH (5 mL), CO (3 bar), H₂ (70 bar), 145 $^{\circ}$ C, 168 h. (Table 4, Entry 3)

6. Deactivation pathway of hydrogenation catalysts in presence of CO

Scheme S1.



The deactivation pathway of the hydrogenation catalysts in the presence of CO is due to the formation of biscarbonyl monohydride complexes (**C-XB**) as shown in Scheme S1. The biscarbonyl complexes are unable to catalyze the hydrogenation of formamides to amine and methanol. However, the second axial carbonyl ligands of these complexes (**C-XB**) are labile. Depending on the H_2 pressure and the nature of R group (on the P atoms), the lability of the axial carbonyl changes. When R is an electron withdrawing group such as Ph, the lability of the axial CO increases and as a result the formation of catalytically active dihydride species **C-XC** is favored. Thus, complex **C-2** and **C-3** ($R = \text{Ph}$) can withstand higher concentration of CO and still catalyze the hydrogenation of formamides, as compared to **C-1** ($R = i\text{-Pr}$), which cannot. Please see reference 1 for a detailed account.

7. References

(1) Kar, S.; Sen, R.; Kothandaraman, J.; Goeppert, A.; Chowdhury, R.; Munoz, S. B.; Haiges, R.; Prakash, G. K. S., Mechanistic Insights into Ruthenium-Pincer-Catalyzed Amine-Assisted Homogeneous Hydrogenation of CO_2 to Methanol. *J. Am. Chem. Soc.* **2019**, *141*, 3160-3170.