Electronic Supplementary Material (ESI) for RSC Advances.

An efficient copper catalyzed formylation of amines utilizing CO_2 and hydrogen

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1. Materials

High purity carbon dioxide (99.99%) and hydrogen compressed cylinders were purchased from Sigma-Gases India. $CuCl_2$ (99.99%), dimethylamine (40 wt% in water), diethylamine (99.5%), N-methylaniline (98%), piperidine (99%), 4-methylpiperidine (96%), pyrrolidine (99.5%), piperazine (99%) and morpholine (99%) were procured from Sigma Aldrich. Dehydrated ethanol and glycine were indented from MERCK India. All chemicals were used as received and no further purification was done.

2. Experimental Techniques used

FTIR spectrum of the synthesized catalyst was recorded on Perkin–Elmer spectrum RX-1 IR spectrophotometer in the wavelength range of 4000-400 cm^{-1}. X-ray photoelectron spectroscopy (XPS, JPS-9010TRX, JEOL Ltd.) measurements were carried out using thin films of developed catalyst deposited on carbon tape. All XPS measurements were executed using a MgKα line as the X-ray source. The structural and phase properties of synthesized materials was characterized by X-ray diffraction pattern using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K_α radiation (λ= 0.15418 nm) with a scan rate 10°/min. The analysis was done by taking samples in glass slide and drying. Thermal degradation pattern (TGA) for evaluation of chemical nature of material was obtained on a thermal analyzer TA-SDT Q-600 between temperature range was 50 °C to 700 °C with heating rate was 10 °C/min under nitrogen flow. The ^1H NMR spectra were recorded on a Bruker Avance 500 Spectrometer in $CDCl_3$ as a standard and the chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. All reaction is performed in a 15ml Parr reactor connected with Teledyne ISCO D-SERIES Syringe pump to inject the carbon dioxide and hydrogen gasses (Fig. S1)

Fig. S1: Experimental set-up for formylation reactions

3. Experimental procedure for the synthesis of trans-*bis*-(glycinato)copper(II) complex

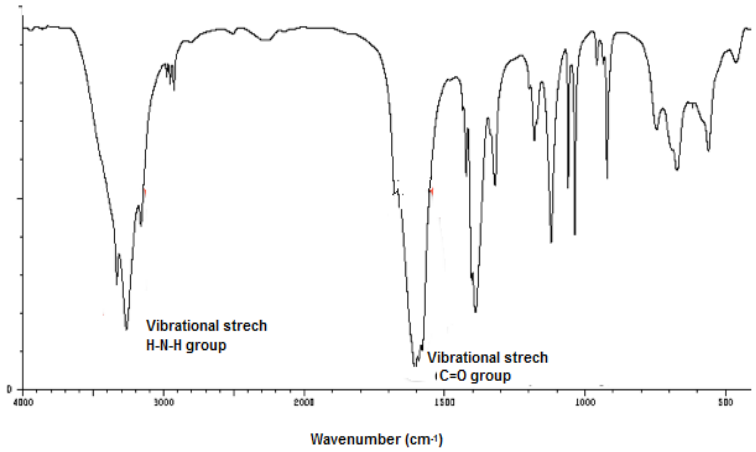
Copper (II) chloride and glycine were added in a 1:2 molar ratio in 15 ml dehydrated ethanol and the mixture was magnetically stirred for 15 minutes at room temperature. Then the solution was transferred into 25 mL stainless-steel autoclave lined with Teflon, which was sealed and maintained at 100 °C for 3h. The resulting deep blue product was separated *via* centrifugation and washed thoroughly with ethanol and dried at 200 °C for 4 h to get the *trans*-$Cu(gly)_2$ complex (48% yield).

4. Typical experimental procedure for formylation of amines

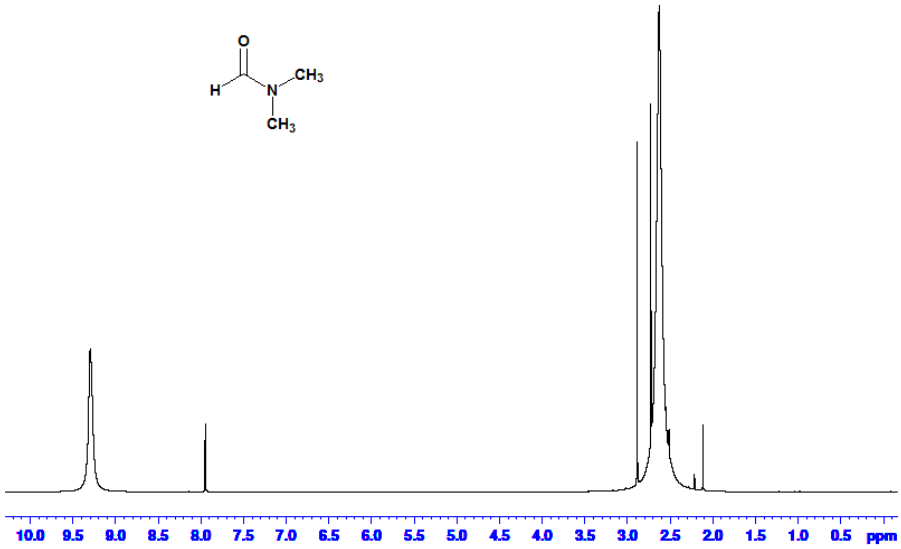
In a typical reaction, catalyst (0.1 g) and diethylamine (5 ml), were charged into the 15 ml high pressure reactor without using any additional solvent. The reactor was sealed and purged with carbon dioxide to replace all others gases. Reactor is then charged with CO_2 and H_2 in desired molar ratio (1.25) with the help of syringe pump (D series) maintaining 50 bar pressure

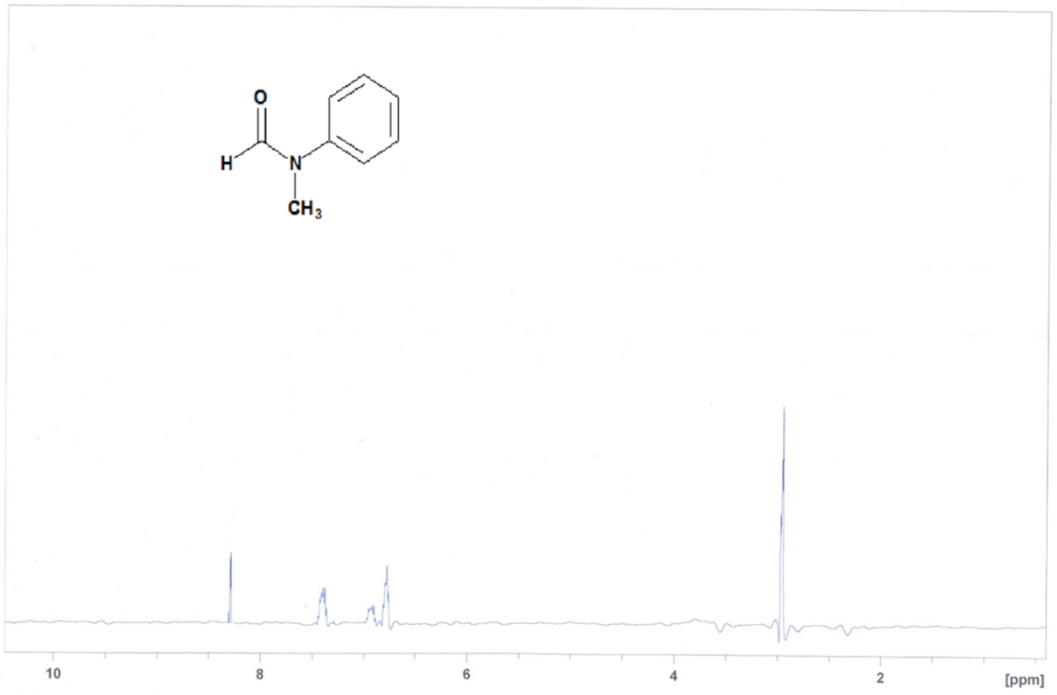
of the reaction vessel. The reaction mixture was stirred for 4 h at 85 °C. After this, the reactor was placed into ice water and un-reacted gases were released slowly passing through a cold trap containing ethanol. After depressurization, the reaction mixture in the reactor was transferred in a beaker and the catalyst was separated by filtration. Reaction mixture was then analyzed by GC equipped with a flame-ionized detector and a capillary column. The crude product was obtained in almost quantitative yield (95 %). To study the reusability of the catalyst, the recovered $Cu(gly)_2$ complex was washed using ethanol and then dried under vacuum for 2 h at 50 °C before reuse.

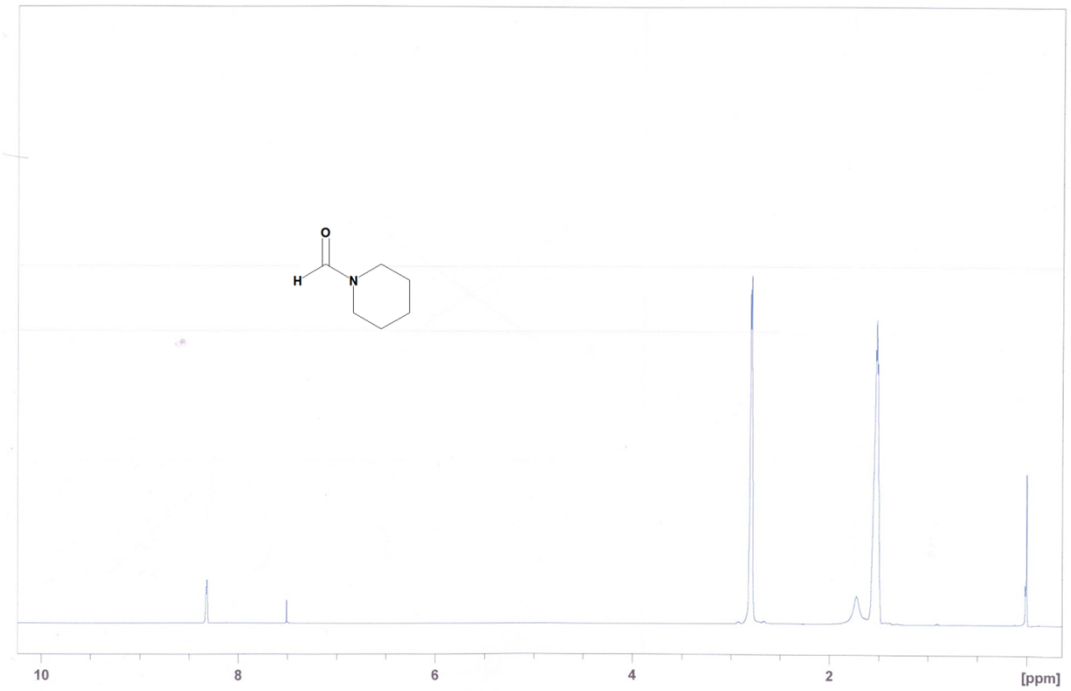
5. FT-IR spectra of *bis*-(glycinato)copper(II) complex



6. ^{1}H- NMR spectra of Products



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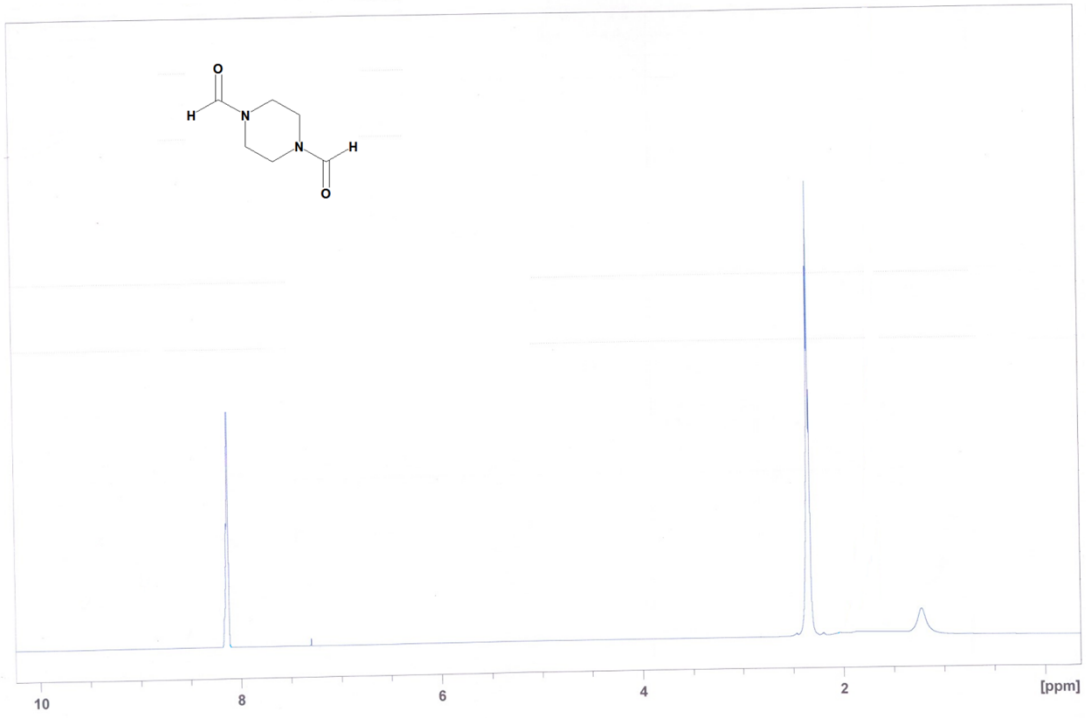
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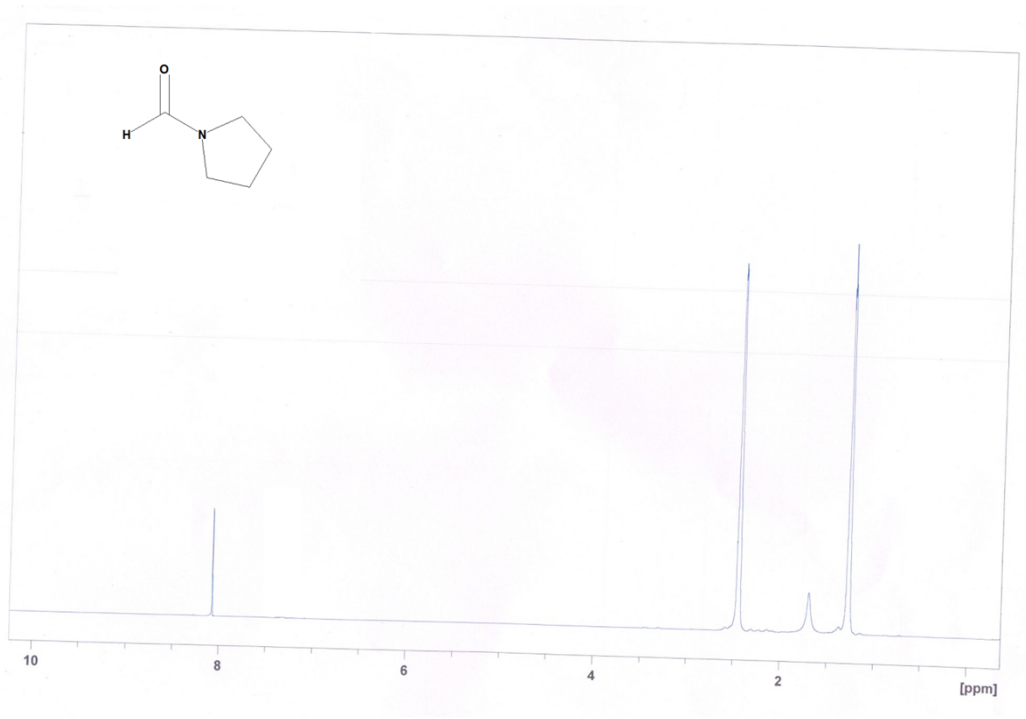
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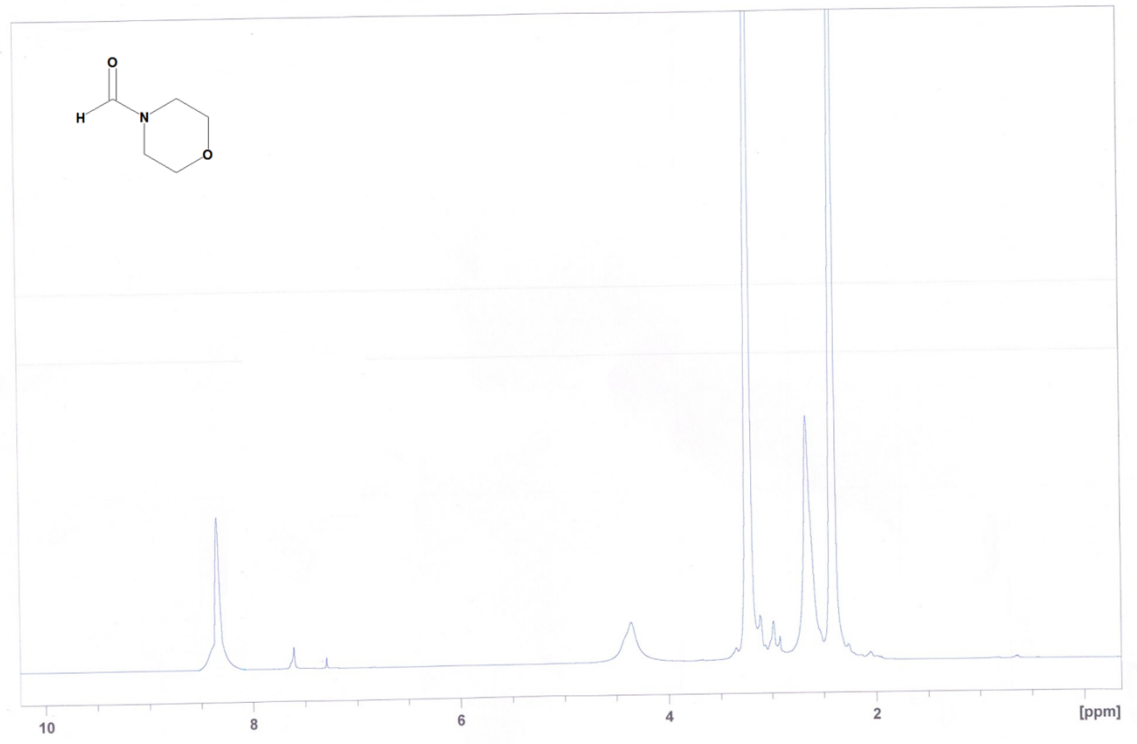
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