Supplementary information

Ru/ceria-Catalyzed Direct Formylation of Amines and CO to Produce Formamides

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Experimental section

All chemicals were of analytical grade and used as purchased without further purification. Most of chemicals were purchased from J&K Chemicals and Aladdin Chemicals.

General catalyst preparation. Ceria powder was prepared by a precipitation method. Briefly, 5.0 g of Ce $(NO_3)_3.6H_2O$ was dissolved in 100 mL of Millipore-purified water (>18 MΩ-cm^{-1}, MilliQ-UV, Millipore Co., Bedford, MA), and the solution was adjusted to pH = 11.0 by the addition of NH_4OH (3.4 M) under magnetic stirring at room temperature. The resulting gel mixture was washed with water, dried in an oven at 115 °C for 12 h, and calcined at 500° C in air for 4 h.

The 2.0Ru/ceria catalyst was prepared by wet impregnation method. Powder ceria was slowly stirred in an aqueous solution of $RuCl_3$ containing 0.1 g of Ru for 20 h. The slurry was then dried and calcined at 200 °C in air overnight. The dried solid sample was reduced at 350 °C in a hydrogen flow (25 mL min^{-1}) for 4 h. The same impregnation procedure was employed for the other noble metals (Au, Pt, Pd and Rh) supported ceria catalysts and other materials supported Ru catalysts.

To obtain ceria of different morphologies, Ce $(NO_3)_3{\cdot}6H_2O$ was used as the cerium source. The preparation of different morphologies of ceria samples was previously reported by our group and other groups.[1]

Characterization of Catalysts.

Thermogravimetry analysis (TGA) data were collected over a NETZSCH STA 409 PC/PG thermobalance from 40 ^{o}C to 700 ^{o}C at a ramping rate of 10 ^{o}C min^{-1} in an air flow (30 mL min^{-1}).

Fourier transform infrared spectroscopy (FT-IR) was collected on a Bruker Tensor 27 instrument to obtain information of in situ adsorption of CO and/or *n*-butylamine on catalysts. The catalyst sample was pressed into a self-supporting disk (13 mm diameter) and placed in a homemade IR quartz cell attached to a closed glass-circulation system. Prior to CO or *n*-butylamine adsorption, the sample disk was pretreated at 350 °C for 1h in H_2 (30 mL·min^{-1}) and then cooled to room temperature. CO gas was supplied from a cylinder. *n*-Butylamine was introduced into the cell by flowing Ar gas into a bubbler containing pure *n*-butylamine. The flowing gas was switched to Ar (50 mL min^{-1}) upon cooling to room temperature, at which IR spectra were collected.

Catalytic reactions in batch reactor and product analysis. Benzylamine (1.5 mmol), catalyst (50 mg), methanol (2.0 mL), and a magnetic stir bar were loaded into a Teflon-lined autoclave reactor. Carbon monoxide was supplied from a cylinder and charged into the reactor to a desired pressure (0.1-0.9 MPa). The reactor was then sealed and placed in a preheated red copper mantle at the desired temperature. Products were analyzed by gas chromatography (GC, Agilent 7890) and gas chromatography–mass spectrometry (GC−MS) using an Agilent 7890A/5975C instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter).

Amine conversion and formamide selectivity were determined by GC. Product yield was calculated by multiplying amine conversion by formamide selectivity.

Catalytic reaction in the fixed-bed reactor. The catalyst powder was pressed into pellet under 15 MPa and crushed to small particles (14-25 mesh), which was then loaded in a vertical reactor heated by an electric furnace. DMA gas was carried into the reactor by CO/N_2 stream flowing through a DMA-containing bubbler. Products and unreacted DMA were collected in a cold trap and were analyzed by a gas chromatography (GC). The effluent gas was monitored by an online GC.

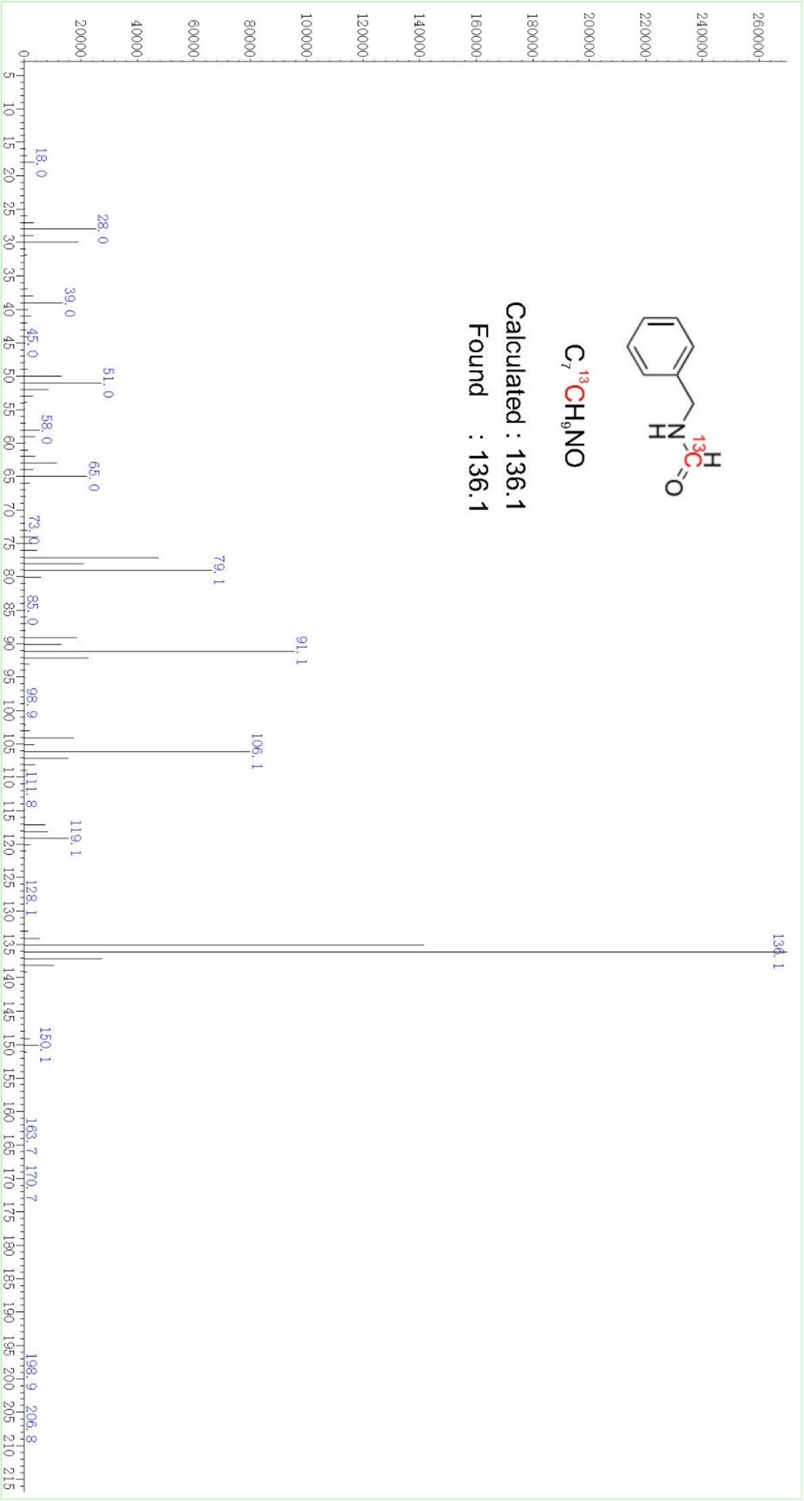

Figure S1. Mass spectrum of Ph-CH_2-NH-^{13}CHO.

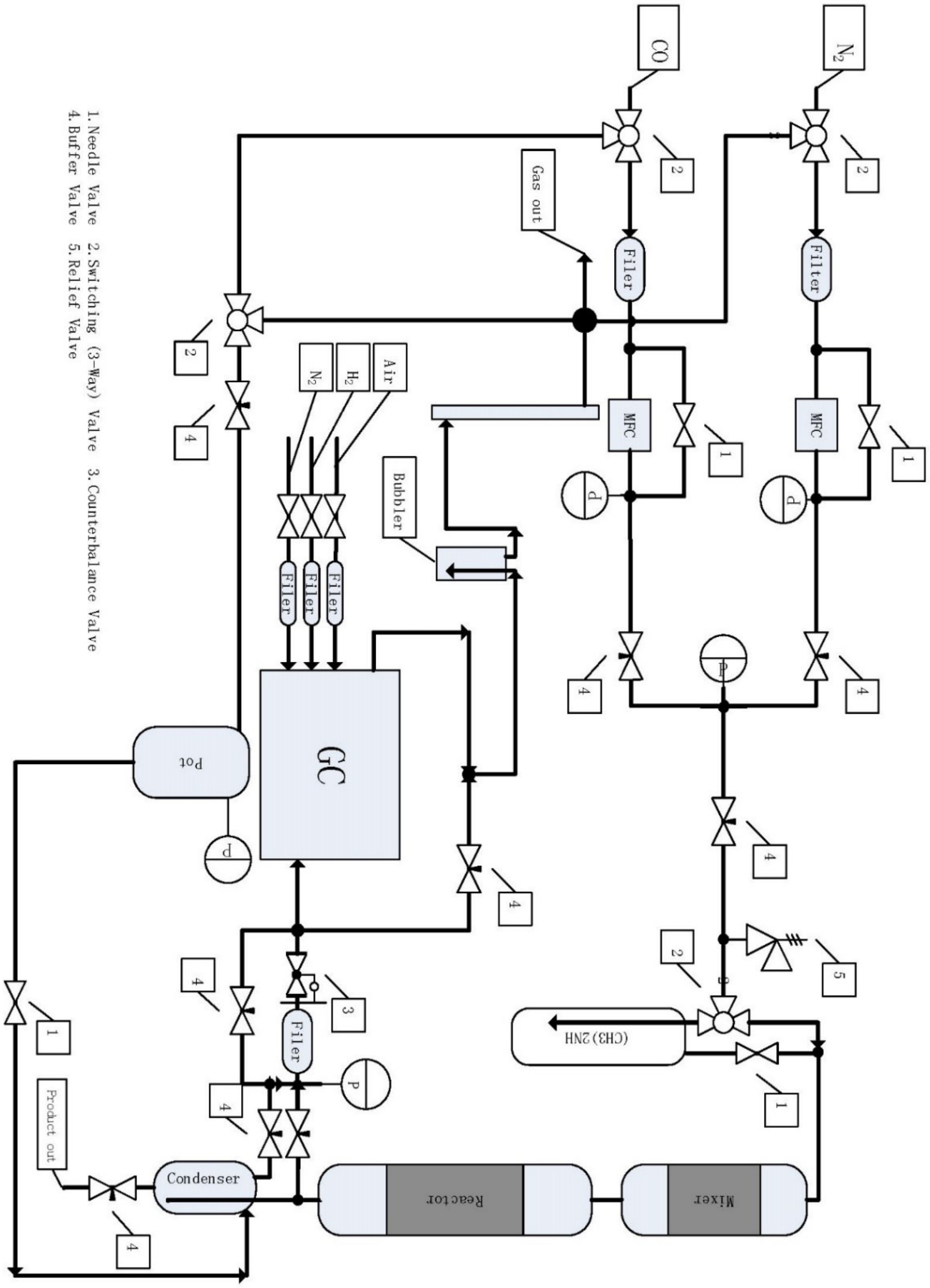

Figure S2. The fixed-bed reaction system.

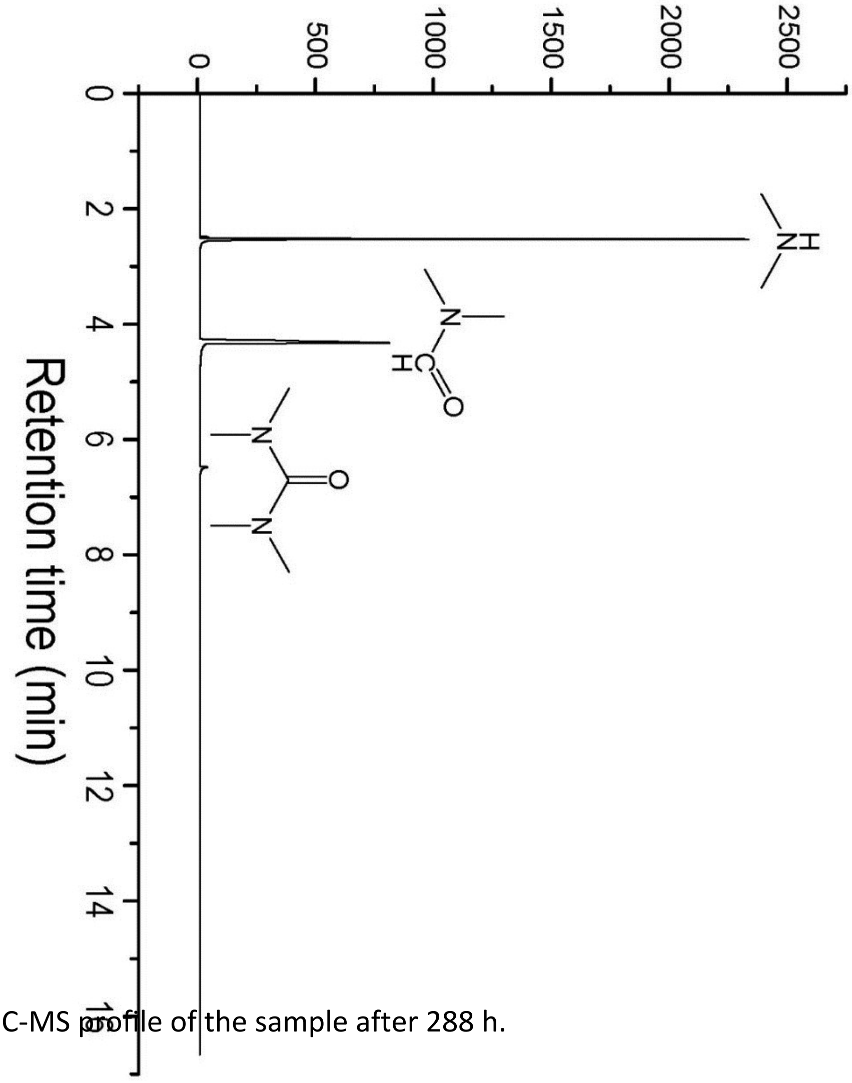

Figure S3. GC-MS profile of the sample after 288 h.

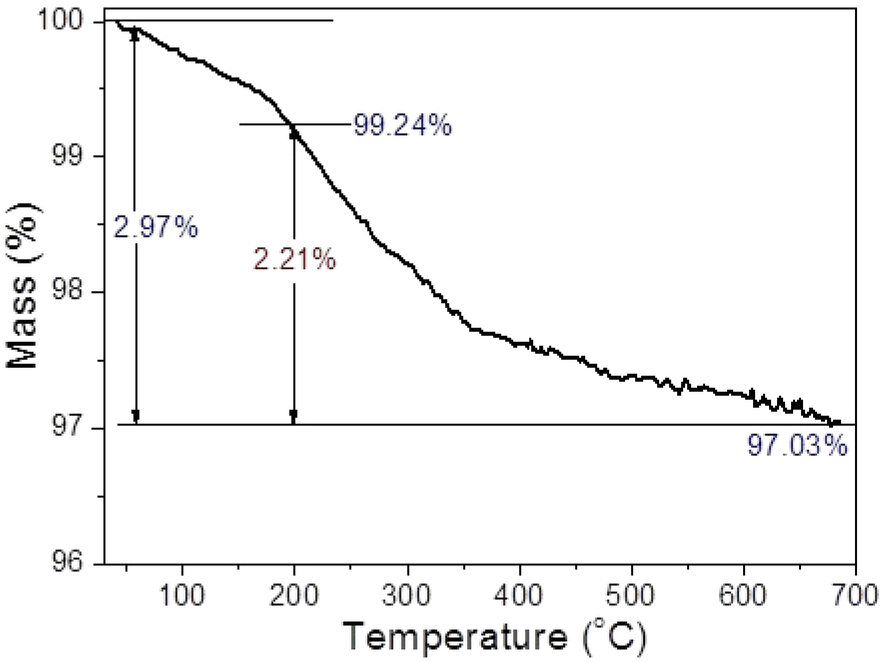

Figure S4. TGA of the used catalyst in the fixed bed reactor. Reaction conditions: about 50 mg of sample was placed in the TGA crucible, flowing gas: 30 mL min^{-1} dry air, temperature was programmed at a speed of 10 ^{o}C min^{-1}. The rough 2.2% weight loss from 200 ^{o}C was caused by the deposited carbon combustion.

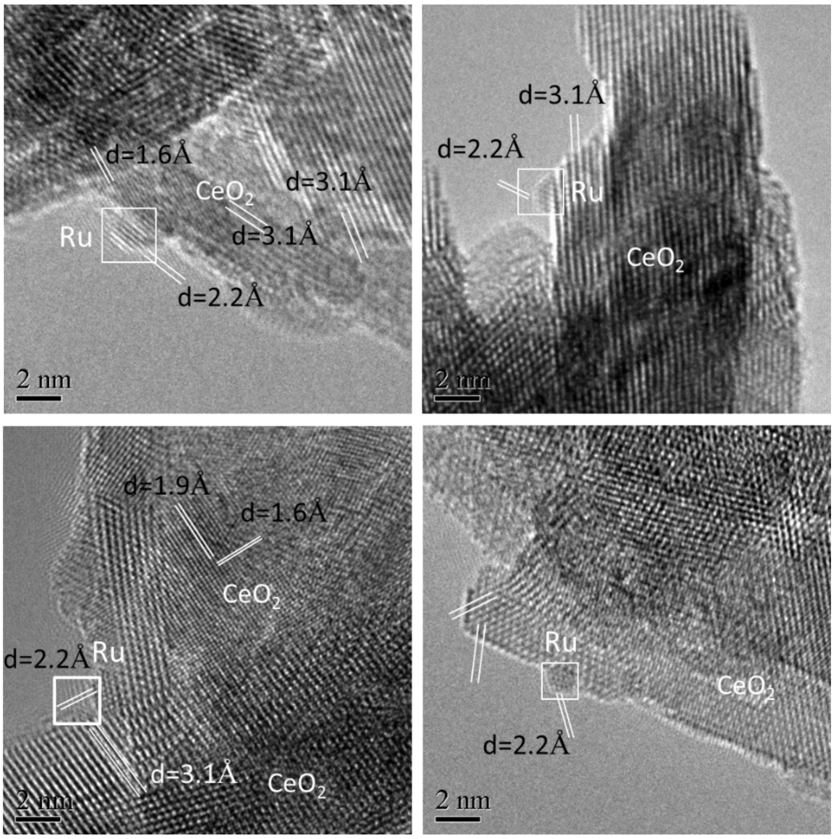

Figure S5. HR-TEM images of Ru/ceria.

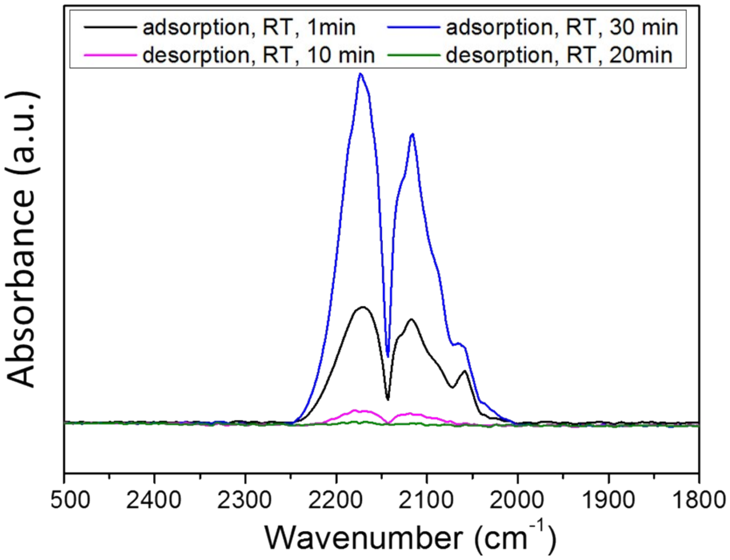

Figure S6. FT-IR spectra recorded after admission of CO and desorption at RT on Ru/ceria after calcination at 500 ^{o}C in air.

After CO adsorbed on Ru/ceria after calcination at 500 ^{o}C, the bands observed are from free CO molecules and no new remarkable band or band shift was found. With increasing in desorption time at room temperature, the bands disappeared completely, indicating that there was no chemical interaction between the Ru catalyst and CO. That could be the reason that Ru/ceria could not catalyze the formylation reaction efficiently after calcination at 500 ^{o}C.

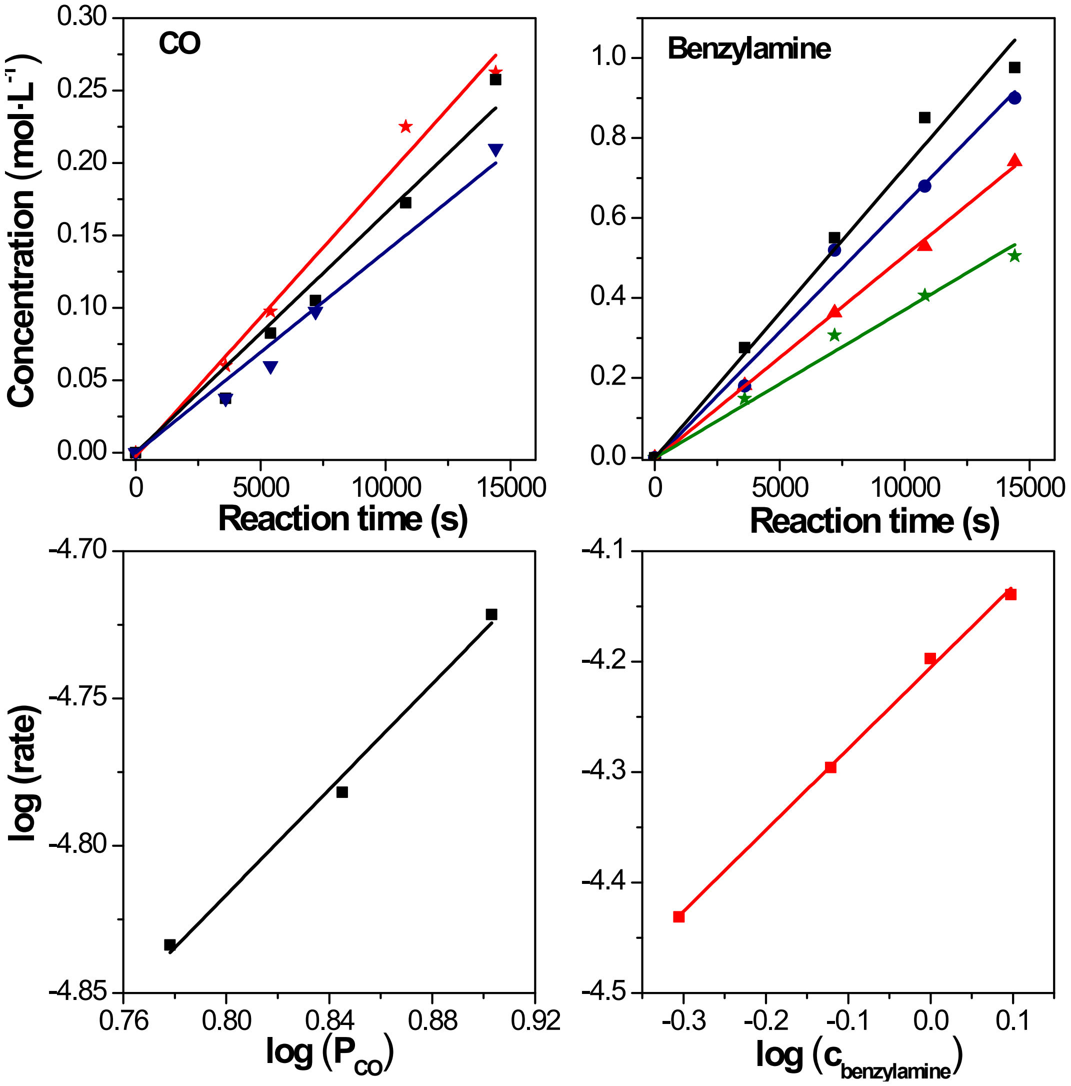

Figure S7. Dependence of the reaction rates on the pressure of CO or concentration of benzylamine.

Reference

(1) (a) Mai, H.-X.; Sun, L.-D.; Zhang, Y.-W.; Si, R.; Feng, W.; Zhang, H.-P.; Liu, H.-C.; Yan, C.-H. *J. Phys. Chem. B* **2005**, *109*, 24380(b) Wang, Y.; Wang, F.; Song, Q.; Xin, Q.; Xu, S.; Xu, J. *J. Am. Chem. Soc.* **2012**, *135*, 1506.