Supplementary Materials

Highly efficient heterogeneous Pd@POPs catalyst for the N-formylation of amine and CO_2

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1. Characterization of catalyst

N_2 adsorption isotherms were obtained by N_2 physisorptions measurements using a Quantachrome Autosorb-1 at 77 K. About 25 mg samples were employed for each test. The powder samples were outgassed for 10 h at 393 K before the measurements. The specific surface areas were calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) method. The pore size distribution curves were obtained from the adsorption branches using the non-local density functional theory (NLDFT) method.

Transmission electron microscopy (TEM) images were obtained using a JEM-2100 with an accelerating voltage of 200 kV. The point resolution was 0.23 nm while the linear resolution was 0.14 nm. Scanning electron microscopy (SEM) was performed using a JSM-7800F with an accelerating voltage of 0.01-30 kV. The resolution of the secondary electron image was 0.8 nm at 15 kV and 1.2 nm at 1 kV while the resolution of the backscatter electron image was 1.5 nm at 15 kV.

Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449F3), the samples were heated at the rate of 10 K/min from room temperature up to 923 K in a flow of nitrogen. 6.95 mg of the powder sample was employed. The gas flow of the protective gas (N_2) was fixed at 20 ml/min, and the gas flow of the carrier gas (N_2) was also fixed at 20 ml/min.

Solid-state ^{31}P MAS NMR experiments were carried out on a Bruker Avance III spectrometer (9.4 T) equipped with 4 mm HXY probes in double resonance mode at a

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frequency of 162 MHz. The experiments were carried out at a magic angle spinning rate of 13 kHz and a delay of 3 s. Solid-state ^{31}P NMR chemical shifts were referenced to $(NH_4)_2HPO_4$. And ^{13}C MAS NMR spectra were recorded at a magic angle spinning rate of 13 kHz and a delay of 1.5 s. Solid-state ^{13}C NMR chemical shifts were referenced to CH of adamantane. About 35 mg of powder samples were filled in the ZrO_2 sample cell when testing.

X-ray photoelectron spectroscopy spectrum were conducted using KRATOS, Axis Ultra^{DLD} with the Al Kα irradiation (hv is 1486.6 eV) for X-ray sources, and the spectrometer binding energy was calibrated through the reference C 1s (284.6 eV). The pressure of the vacuum chamber was kept lower than 9.8×10^{-10} mbar when testing while a step size of 0.05/0.10 eV was employed.

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2. Supplementary Figure

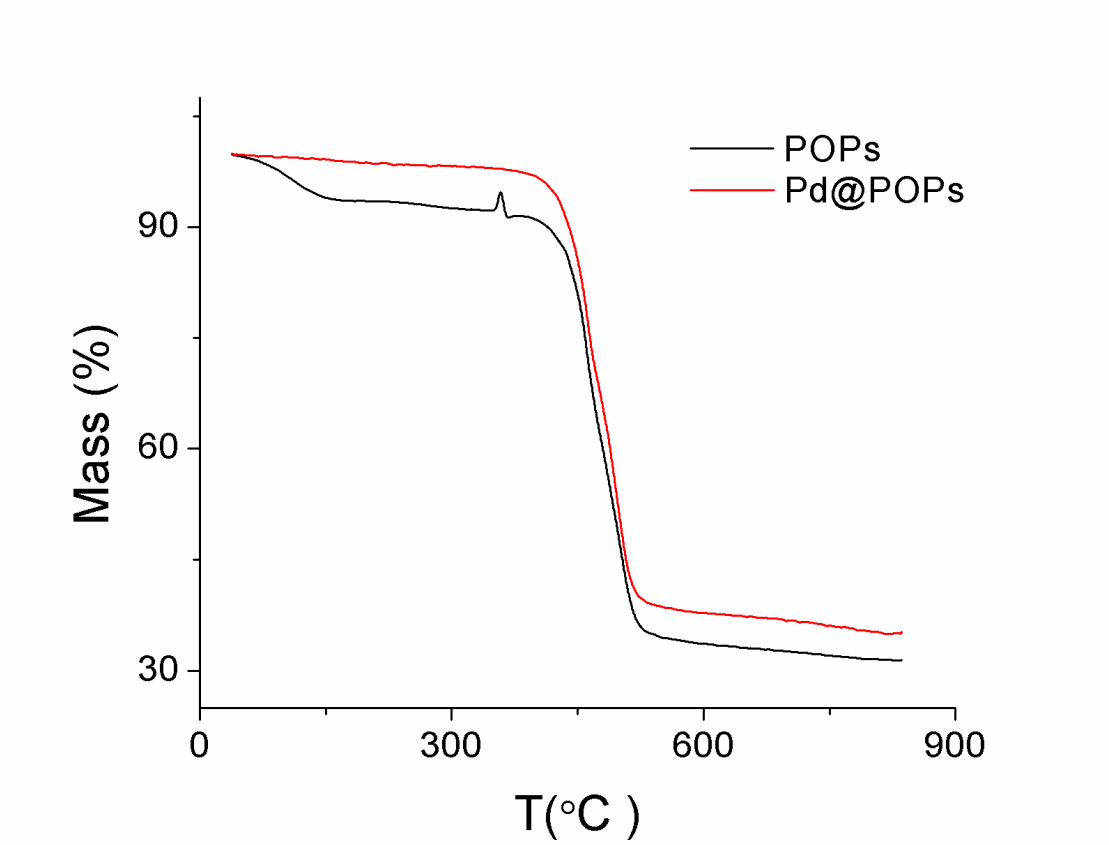

Figure S1 TG curves of POPs (black) and Pd@POPs (red).

2. Determination of the product yields

The structure of 1a was characterized by comparing the retention time with the authentic compound and GC-MS. The yield was determined by GC using toluene as the internal standard. For 2b-9b, NMR yields were given. The ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of the reaction mixture and MS spectra of the product were shown below.

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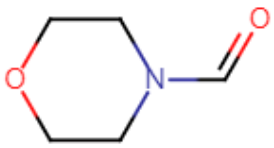


1b

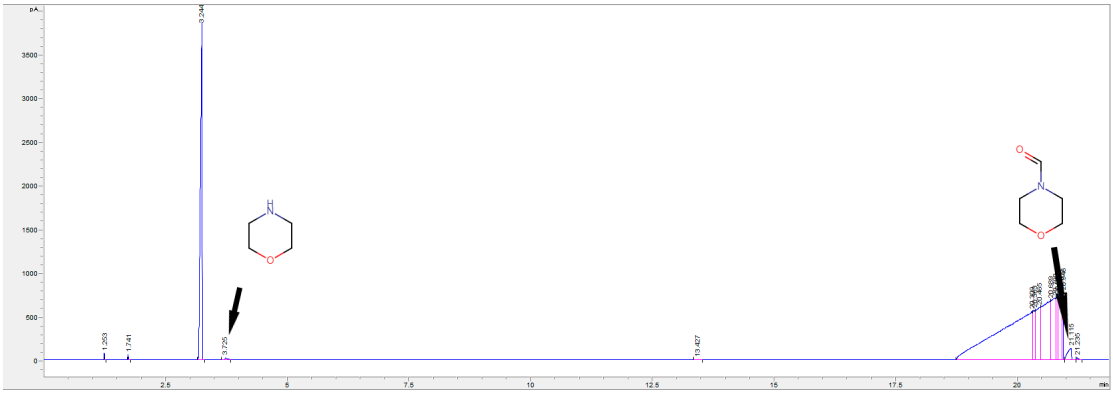
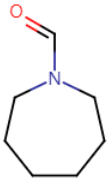


Figure S2 GC spectra of reaction solution of morpholine (1a) reacting with CO_2/H_2.



2b

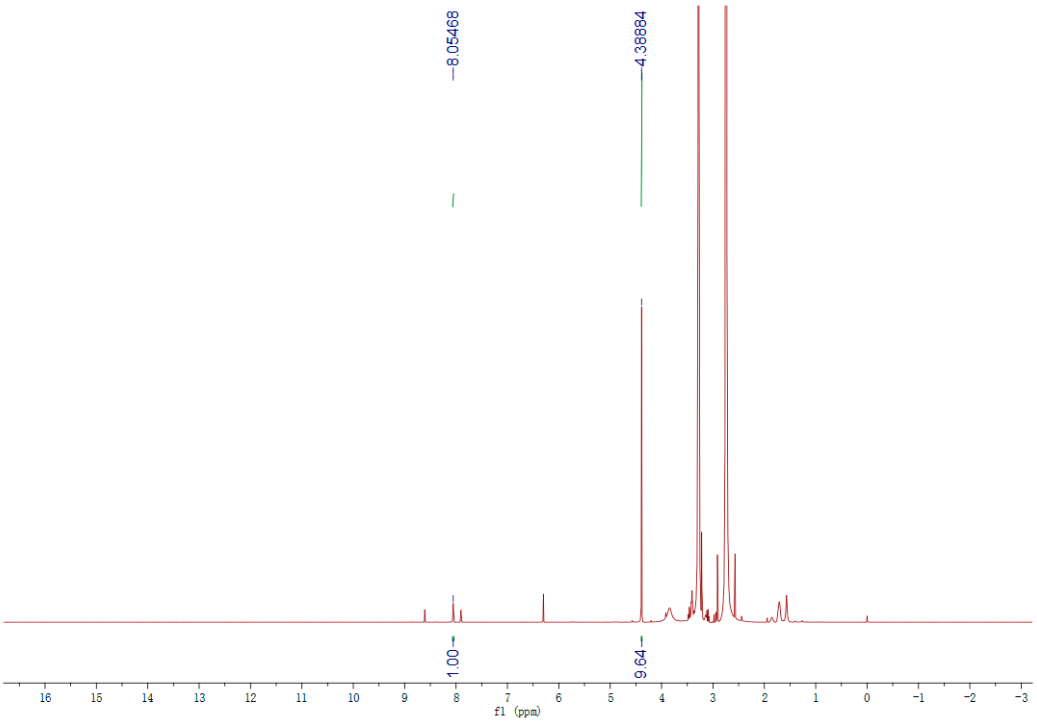


Figure S3 NMR spectrum of reaction solution of 2a reacting with CO_2/H_2 (CH_3NO_2: 0.0174 g).

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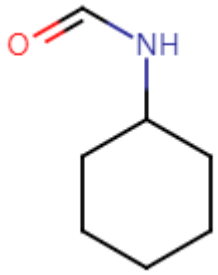

3b

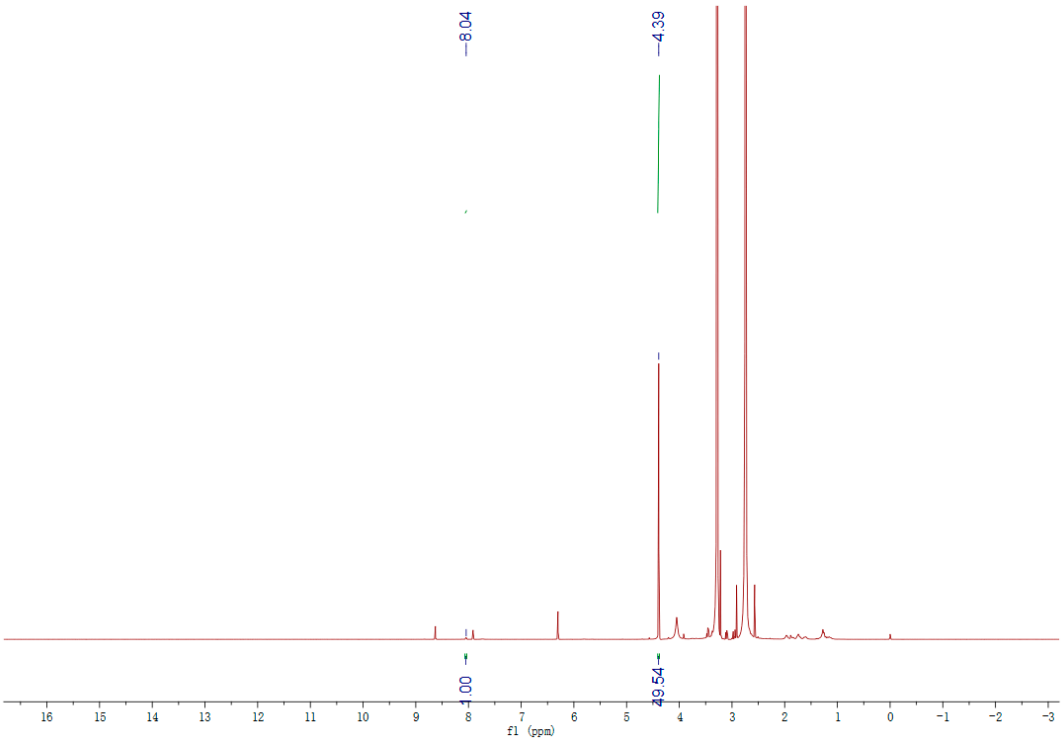

Figure S4 NMR spectrum of reaction solution of 3a reacting with CO_2/H_2 (CH_3NO_2: 0.0184 g).

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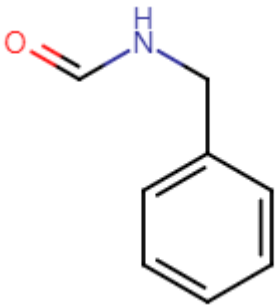

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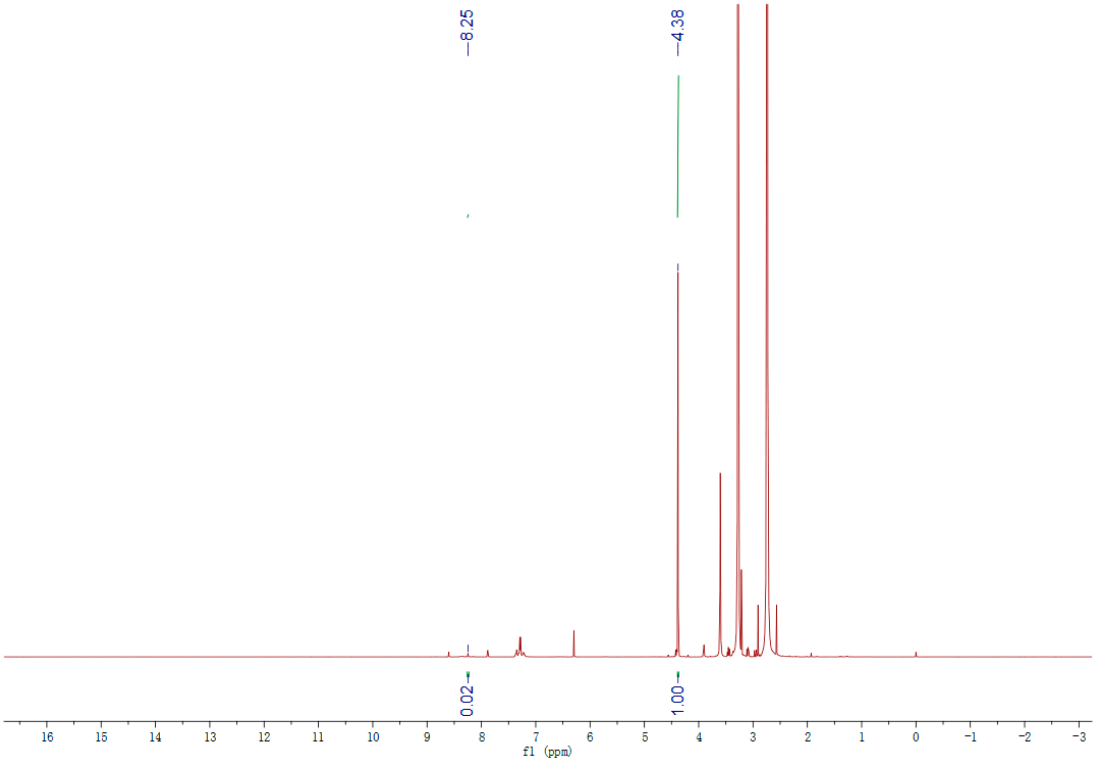

Figure S5 NMR spectrum of reaction solution of 4a reacting with CO_2/H_2 (CH_3NO_2: 0.0248 g).

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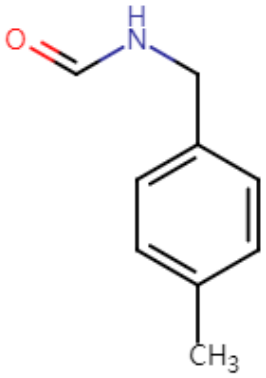

5b

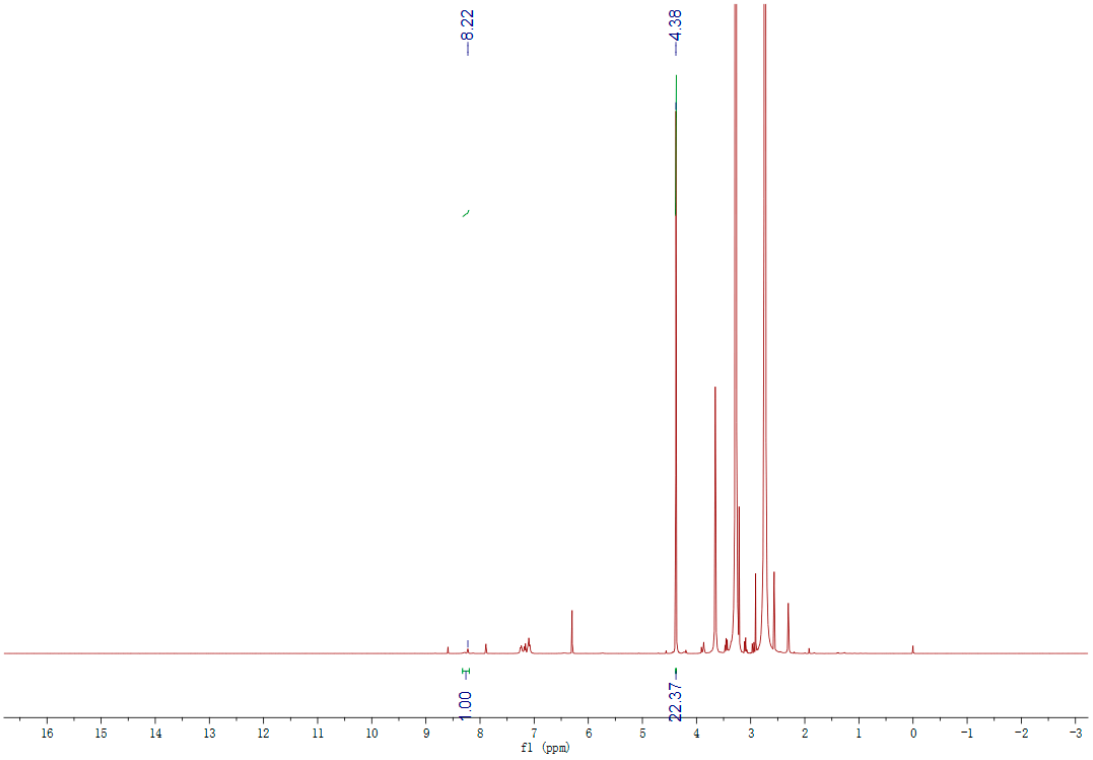

Figure S6 NMR spectrum of reaction solution of 5a reacting with CO_2/H_2 (CH_3NO_2: 0.0233 g).

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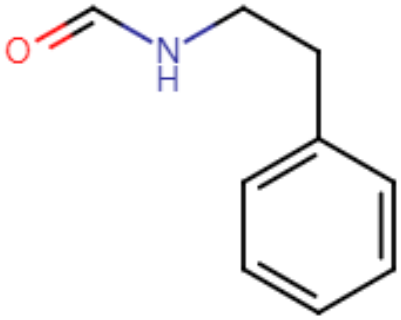

6b

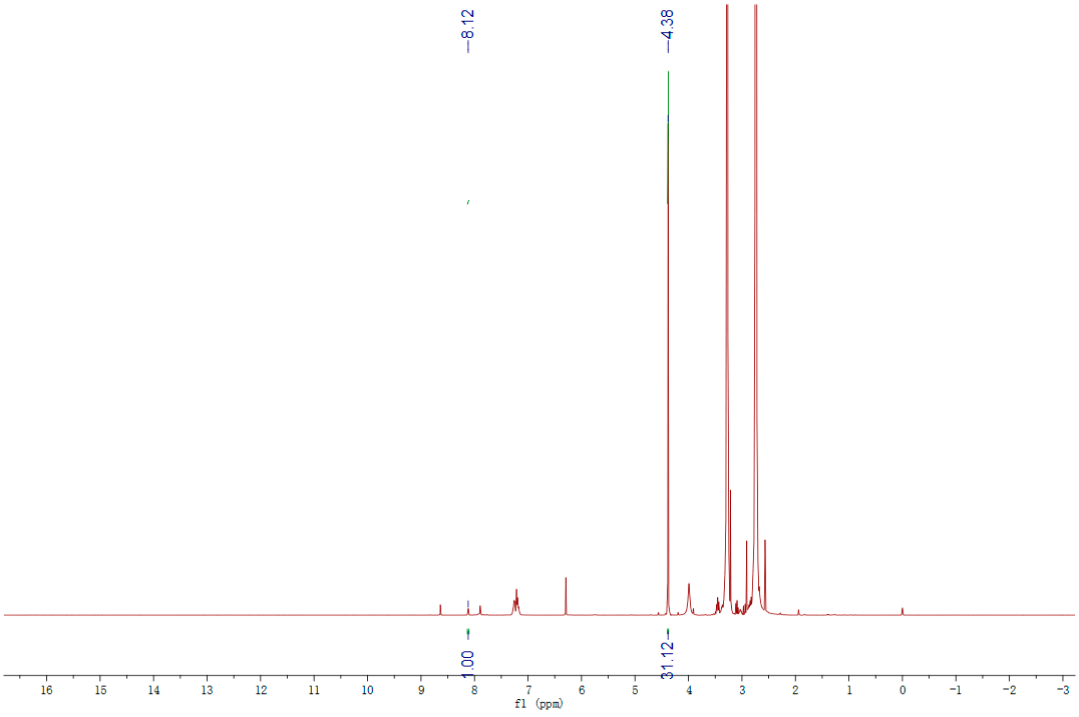

Figure S7 NMR spectrum of reaction solution of 6a reacting with CO_2/H_2 (CH_3NO_2: 0.0227g).

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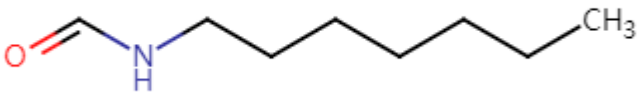

7b

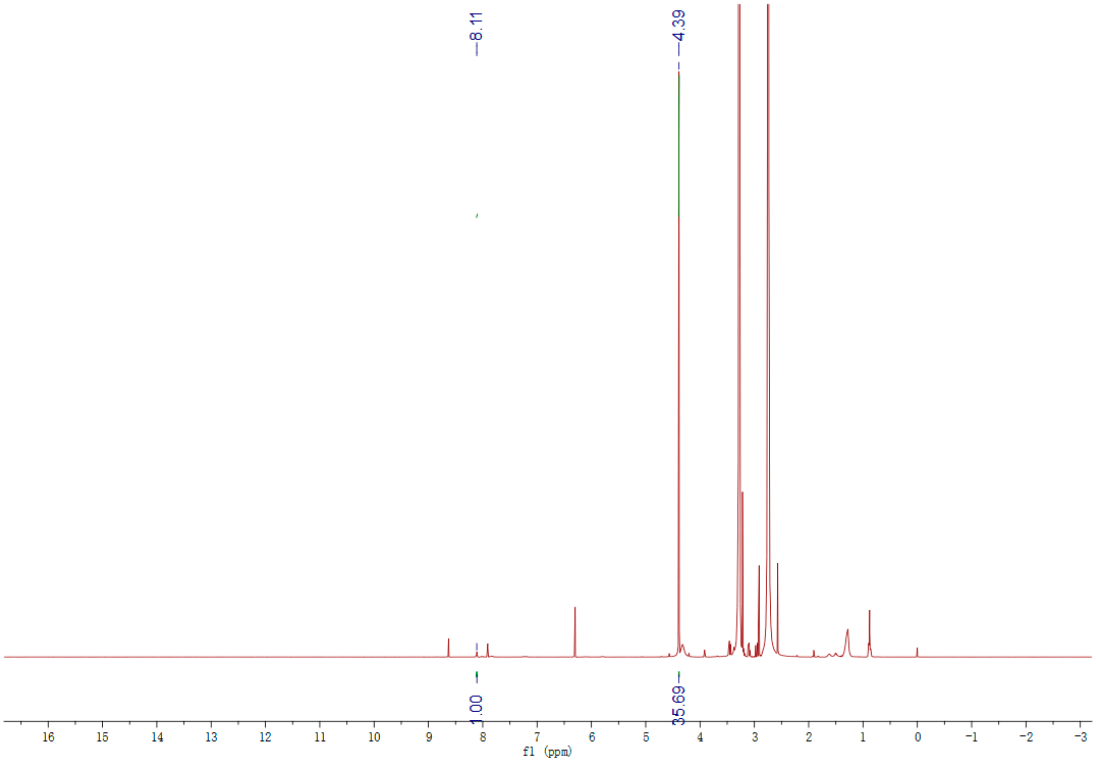

Figure S8 NMR spectrum of reaction solution of 7a reacting with CO_2/H_2 (CH_3NO_2: 0.0235 g).

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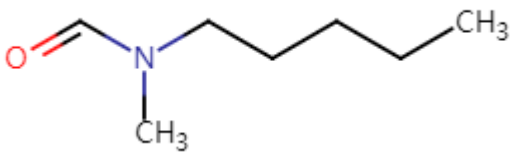

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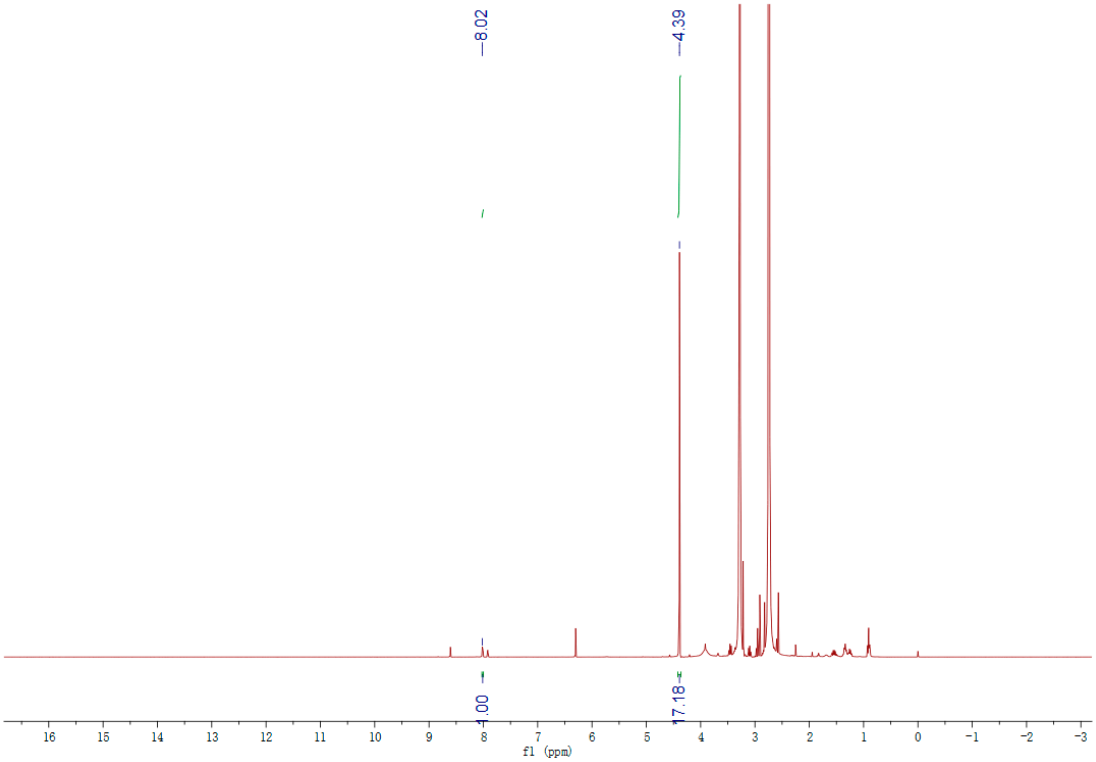

Figure S9 NMR spectrum of reaction solution of 8a reacting with CO_2/H_2 (CH_3NO_2: 0.0214 g).

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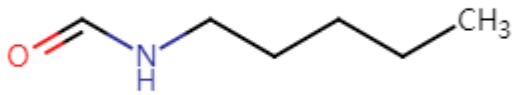

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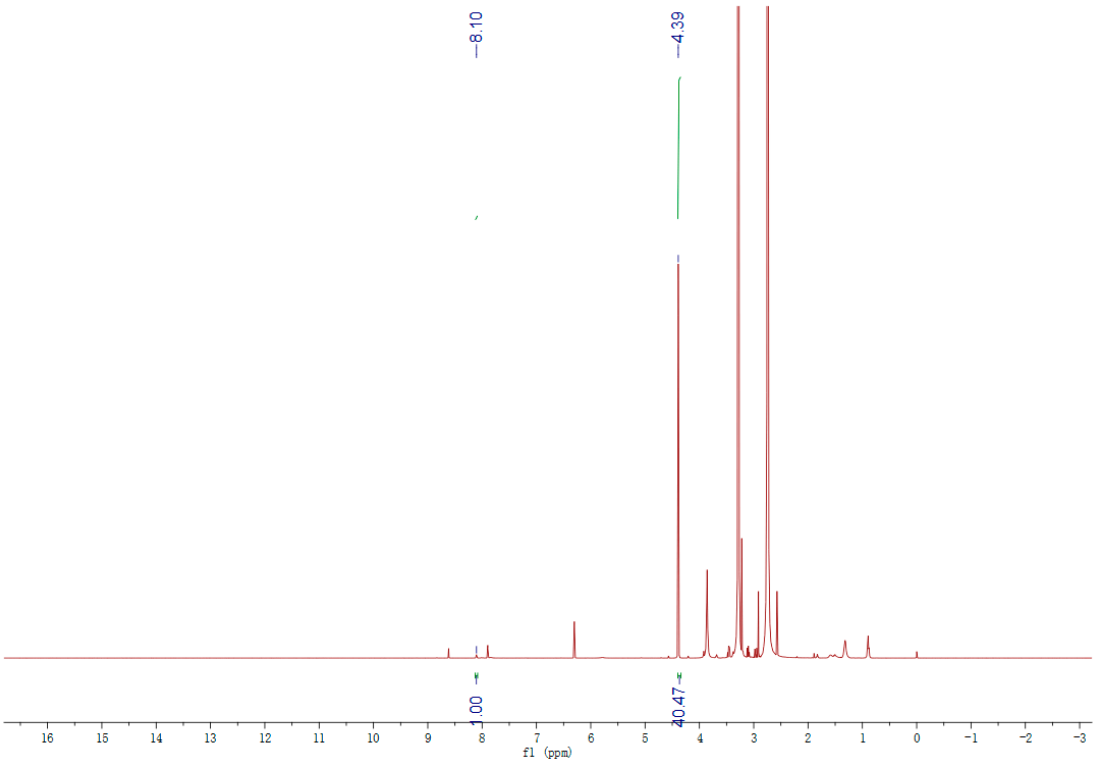

Figure S10 NMR spectrum of reaction solution of 9a reacting with CO_2/H_2 (CH_3NO_2: 0.0235 g).

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