Electronic Supplementary Material (ESI) for ChemComm.

# Supporting Information

## Mesoporous Imine-Based Organic Polymer: Catalyst-Free Synthesis in Water and Application in $CO_2$ Conversion

Xiaoxiao Yu,‡[a, b] Zhenzhen Yang,‡[a] Shien Guo[a, b] Zhenghui Liu,[a, b] Hongye Zhang,[a] Bo Yu,[a] Yanfei Zhao,[a] and Zhimin Liu*[a, b]

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China.

E-mail: liuzm@iccas.ac.cn

## Table of Contents

# 1. General experimental methods

## Materials

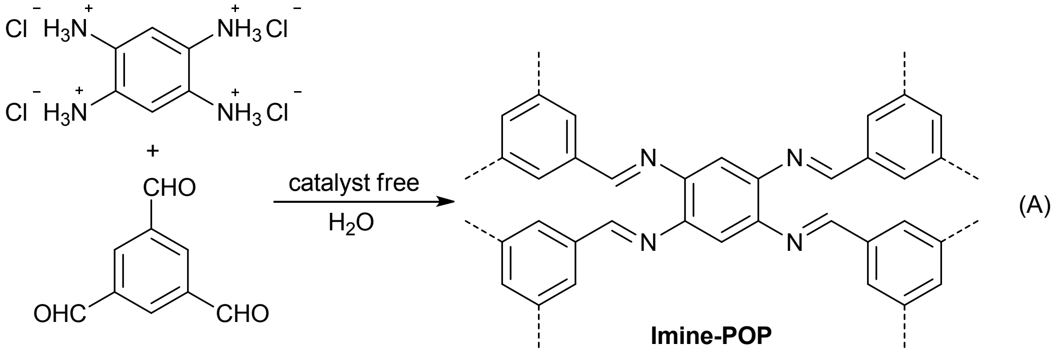
All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise.

## Instrumentation

Liquid $^{1}H$ and $^{13}C$ NMR spectra was recorded on Bruck 400 spectrometer. Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The $^{13}C$ CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 $cm^{-1}$. Gas sorption isotherms were obtained with Micromeritics TriStar II 3020 and Micromeritics ASAP 2020 M+C accelerated surface area and porosimetry analyzers at certain temperature. The samples were outgassed at 140 $^{o}C$ for 8 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi SU8020 microscope operated at an accelerating voltage of 15.0 kV. (HR) Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 and JEM-2100F instrument operated at 200 kV. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25 to 800 °C under air with a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of $\sim 3\times10^{-9}$ mbar (1 mbar = 100 Pa) using Al Ka as the excitation source (1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the $C_{1s}$ line at 284.8 eV from adventitious carbon. The XRD analysis was performed on a D/MAX-RC diffractometer operating at 30 kV and 100 mA with $Cu_{K\alpha}$ radiation. The reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a polar capillary column (HP-INNOWAX) (30 m × 0.25 mm × 0.25 μm). The column oven was temperature-programmed with a 2 min initial hold at 323 K, followed by the temperature increase to 538K at a rate of 20 K/min and kept at 538 K for 10 min. High purity nitrogen was used as a carrier gas.

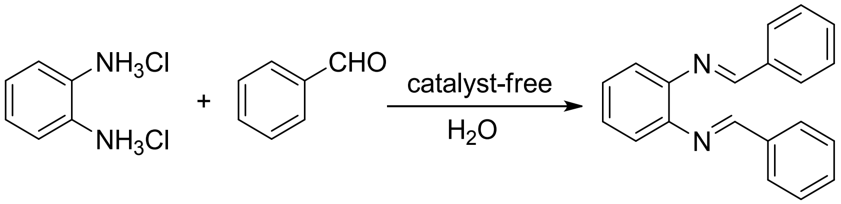
## 2. Synthetic procedures

### (1) Synthetic procedure for Imine-POP



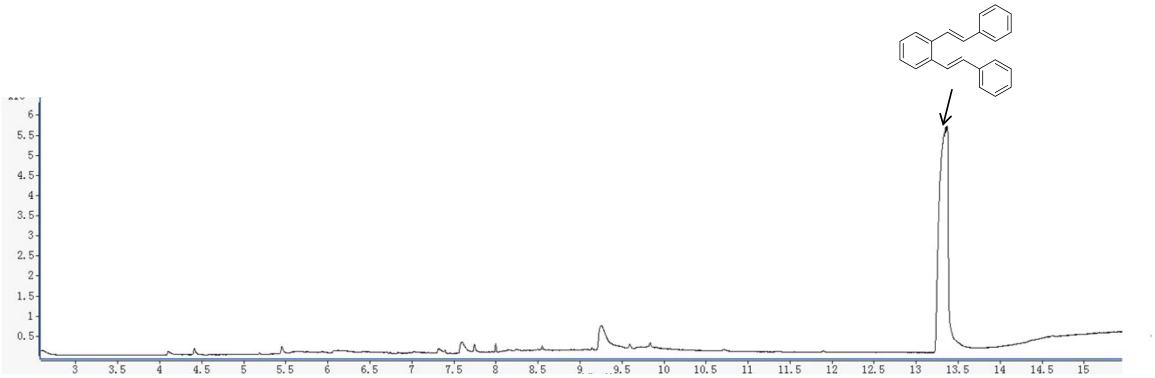
Typically, 1,2,4,5-benzenetetramine tetrahydrochloride (1 mmol), benzene-1,3,5-tricarbaldehyde (1.3 mmol) and $H_2O$ (50 mL) were added successively to a 100 mL autoclave with a Teflon inner tube. The mixture was stirred at 25 °C for 2 h and then 120 °C for 24 h. After cooling to room temperature, the solid was collected by filtration and washed by distilled water, tetrahydrofuran (THF) and ethanol (100 mL*3 for each liquid). After extracted in a Soxhlet extractor with methanol (70 mL), $H_2O$ (70 mL) and THF (70 mL) for 48 h, the sample was collected and dried in vacuum oven at 140 °C for 24 h. The sample, denoted as **Imine-POP,** was brown solid, and its yield was 85% .

### (2) Reaction of the monomers to produce N,N-dibenzylidenebenzene-1,2-diamine

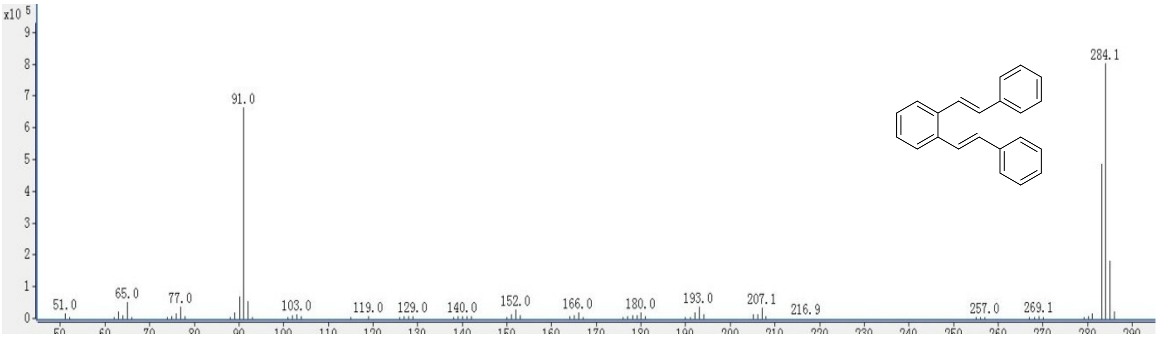


1,2-Benzenediamine dihydrochloride (1 mmol), benzaldehyde (2 mmol) and $H_2O$ (50 mL) were added successively to a 100 mL autoclave with a Teflon inner tube. The mixture was stirred at 25 °C for 2 h and then 120 °C for 24 h. After cooling to room temperature, the reaction system was extracted with chloroform (100 mL*2). The solvent was partly removed by rotary evaporation, and the residue was detected by GC-MS as shown below, indicating the formation of N,N-dibenzylidenebenzene-1,2-diamine.

**GC spectrum**



**MS spectrum**



### (3) Synthetic procedure for Imine-POP@Pd

To an $CH_2Cl_2$ (10 mL) dispersion of **Imine-POP** (0.1 g), 2 mL of $CH_2Cl_2$ solution of $Pd(OAc)_2$ (0.03 g, 0.13 mmol) was added under $N_2$ atmosphere and stirred for 12 h at room temperature. Then the solid was filtered, washed with dichloromethane (10*25 mL) and dried under vacuum at 60 $^oC$ for 24 h. The resultant sample was denoted as **Imine-POP@Pd**. The **$Al_2O_3$@Pd**, **$TiO_2$ @Pd** and **C@Pd** were prepared in the same way using various supports.

### (4) General procedure for the N-formylation reaction

Typically, amine (i.e., **1a-1n,** 1 mmol), **Imine-POP@Pd** (30 mg), $K_3PO_4$ (0.3 mmol) and DMI (4 mL) were successively added into a stainless steel autoclave with a Teflon tube (25 mL inner volume) under $N_2$ atmosphere. The autoclave was sealed and charged with $CO_2$ up to 3 MPa and then $H_2$ to total pressure of 6 MPa at room temperature. The autoclave was moved to an oil bath of 100 $^oC$ and stirred for 24 h. After reaction, the autoclave was cooled down to room temperature. The yield of **2a** was determined by GC using biphenyl as an internal standard, and the yields of **2b~2n** were determined by NMR using $CH_3NO_2$ as an internal standard and $CDCl_3$ as the solvent.

### (5) Isolation of the products

After reaction, the catalyst was removed by filtration,and the filtrate was collected into separating funnel. $H_2O$ ( 4 mL), which has good miscibility with DMI, and ethyl acetate (4 mL), which can solve the product well, were added into the separating funnel. The $H_2O$ layer was extracted by ethyl acetate (4 mL *5) and all the ethyl acetate solution of the product was gathered and dried by $Na_2SO_4$. The solvent was removed by rotary evaporateion and the pure product was obtained by column chromatography on silica gel using n-hexane/ethyl acetate as eluent.

**(6) Recycling of Imine-POP@Pd**

After reaction, the catalyst was separated by centrifugation, washed with dichloromethane, ethanol, deionized water, ethanol successively and then dried under vacuum at 60 $^oC$ for 24 h. The recycled catalyst was reused for the next run.

## 3. Supplementary Figure

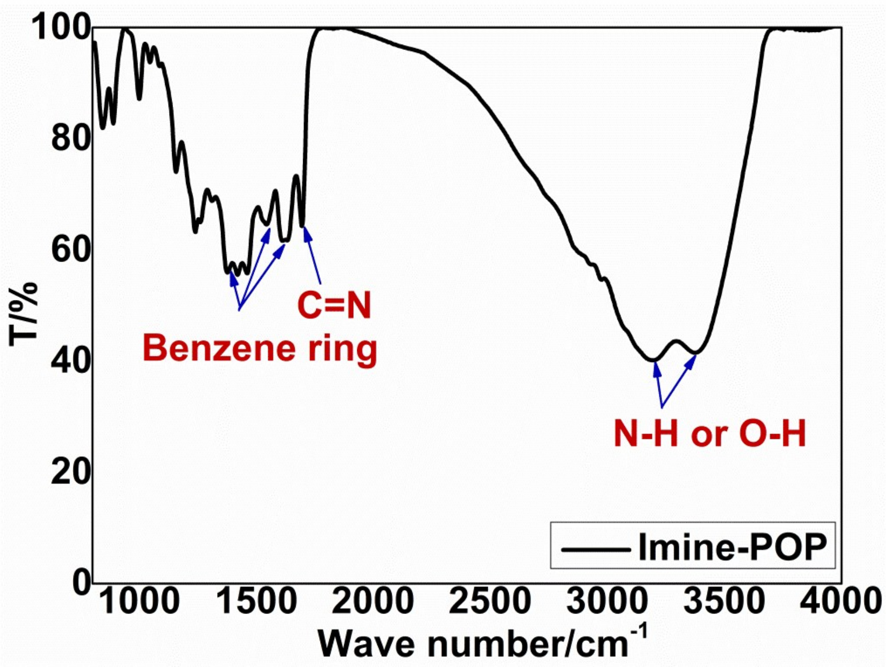


**Figure S1** FTIR spectrum of **Imine-POP.** The spectrum was recorded as KBr pellets.

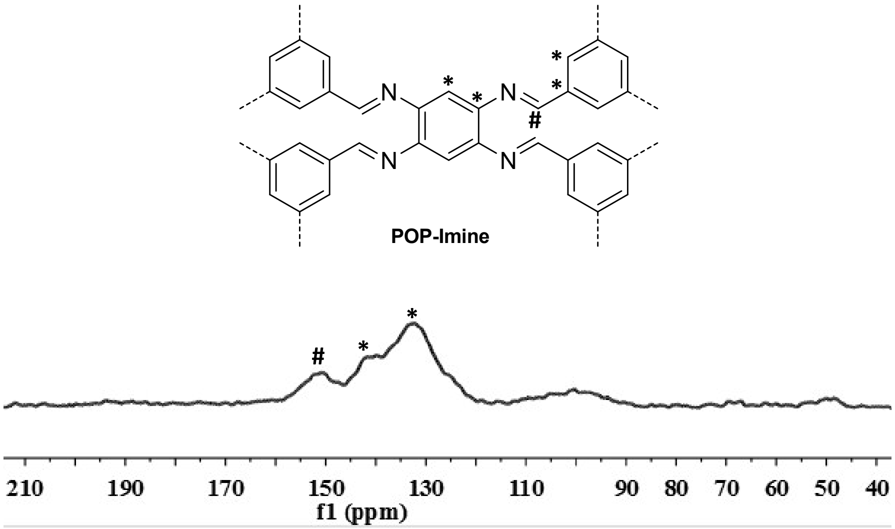


**Figure S2** CP/MAS $^{13}$C NMR spectrum for **Imine-POP**.

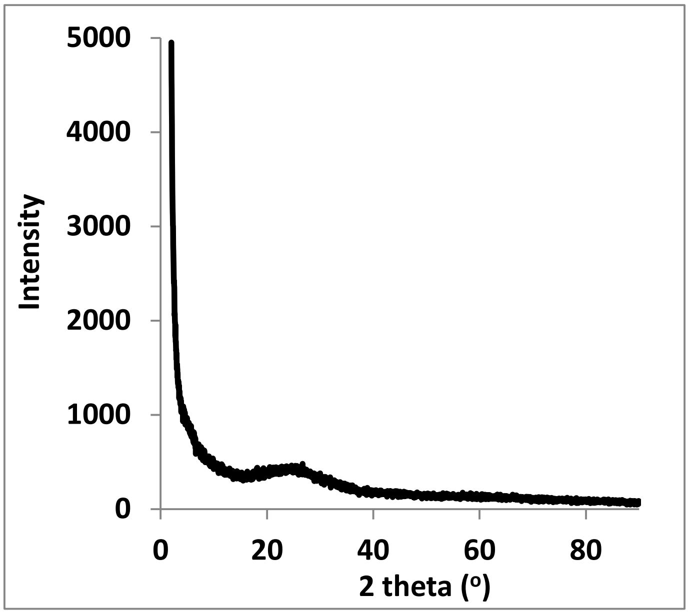


**Figure S3** PXRD-pattern of **Imine-POP.**

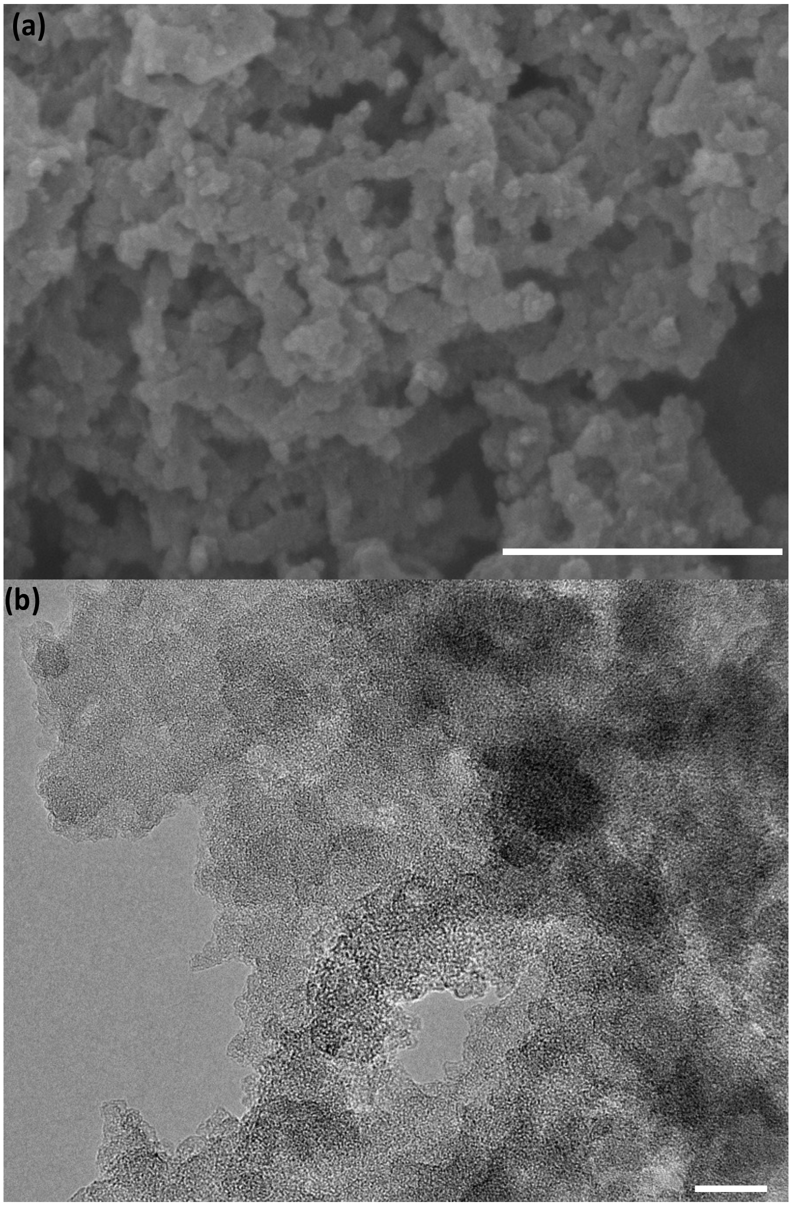


**Figure S4** (a) SEM and (b) TEM image of **Imine-POP**. Scale bar, (a) 300 nm, (b) 20 nm.

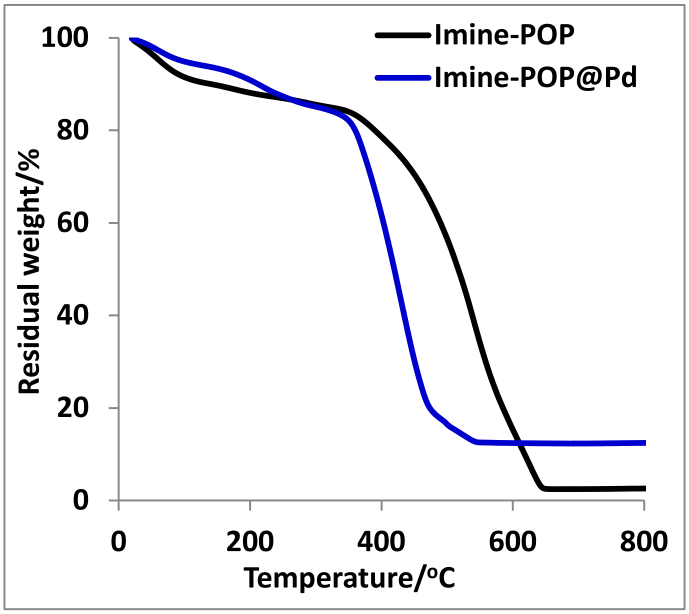


**Figure S5** TGA analysis on **Imine-POP** and **Imine-POP@Pd** in air, with a ramping rate of 10 °C min.

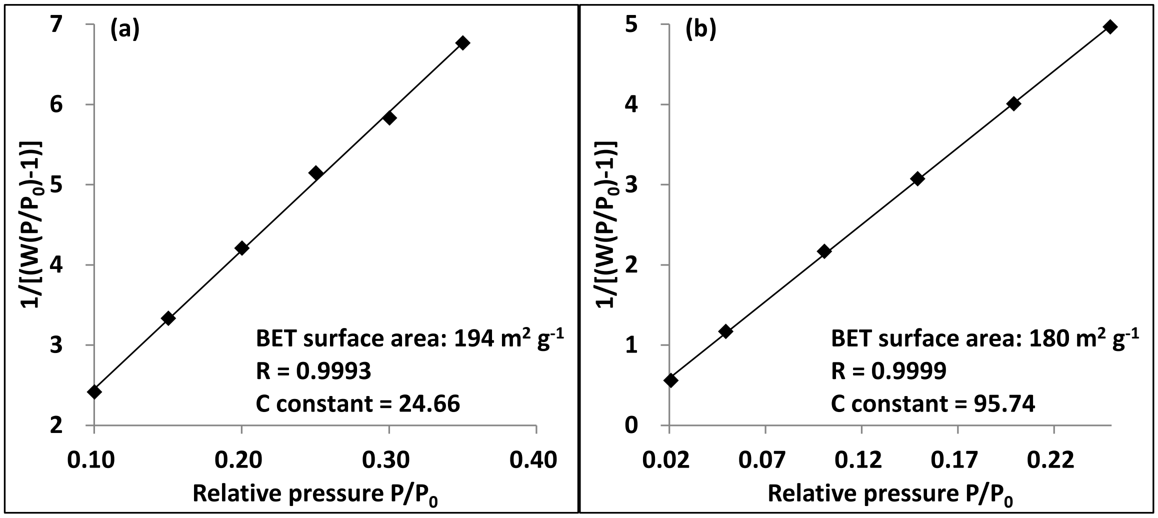


**Figure S6** BET plots of (a) **Imine-POP** and (b) **Imine-POP@Pd**.

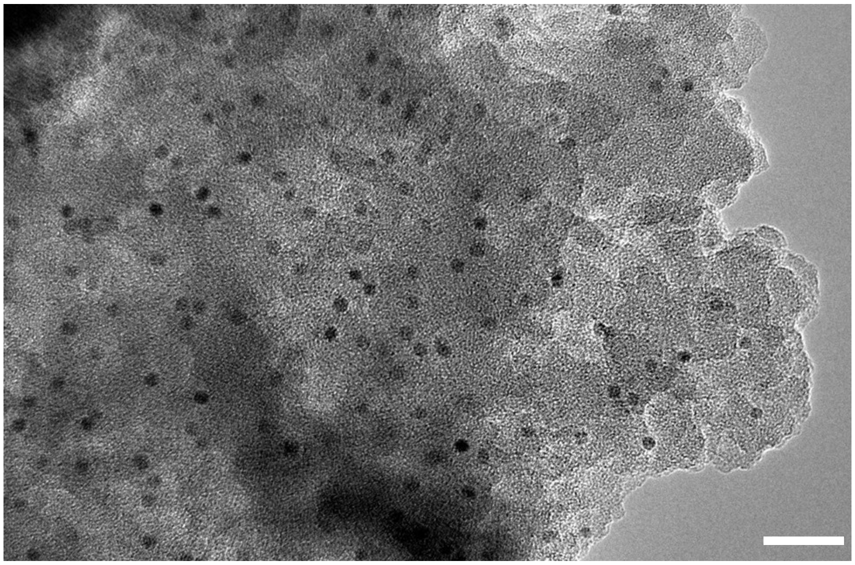


**Figure S7** (HR)TEM of **Imine-POP@Pd,** Scale bar 25 nm.

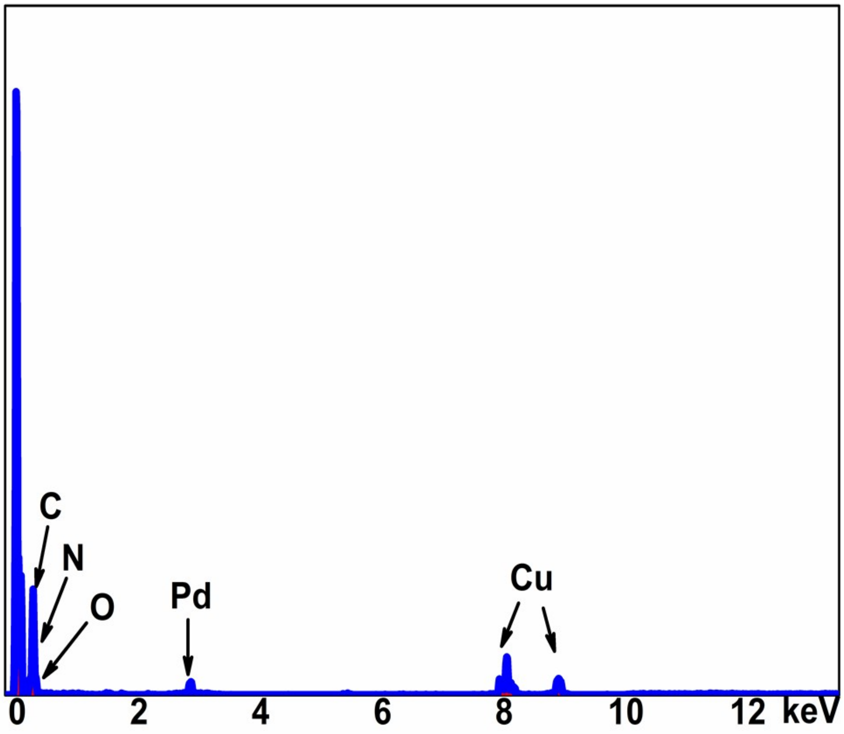


**Figure S8** EDS profile of **Imine-POP@Pd**

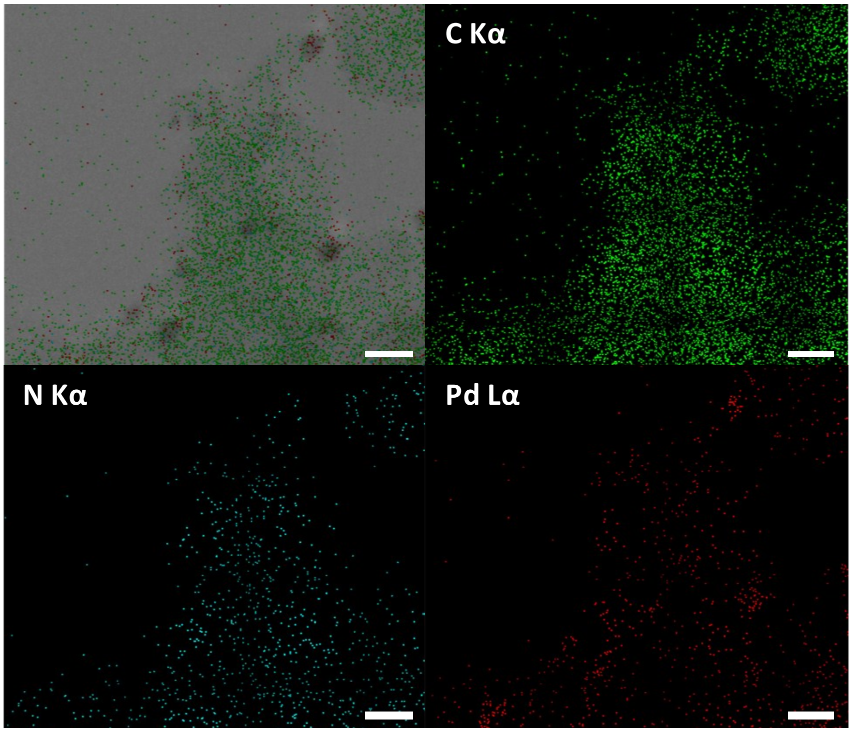


**Figure S9** Compositional EDS mapping of **Imine-POP@Pd** using scanning transmission electron microscopy. Scale bar 10 nm.

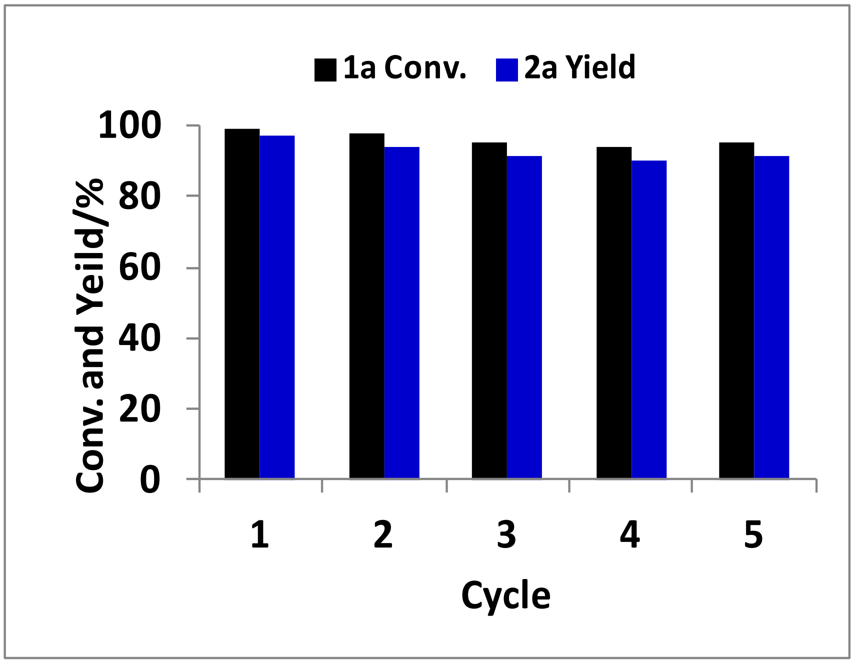
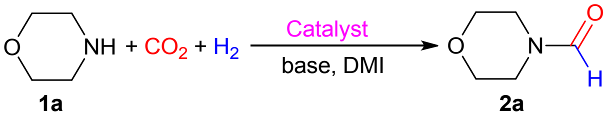


**Figure S10** Recyclability test of **Imine-POP@Pd**. Reaction conditions: morpholine, 1 mmol; **Imine-POP@Pd**, 30 mg (Pd 2.3 mol%); $K_3PO_4$, 0.3 mmol; $CO_2$, 3 MPa; $H_2$, 3 MPa; DMI, 4 mL; 100 $^{o}$C, 24 h. Conversion and yield were determined by GC using biphenyl as an internal standard.

**Table S1 Base and** catalyst screening[a]



| Entry | Base | Catalyst | Yield/%[b] |
|---|---|---|---|
| 1 | $K_3PO_4$ | **Imine-POP@Pd** | 97 |
| 2 | t-BuOK | **Imine-POP@Pd** | 59 |
| 3 | KOH | **Imine-POP@Pd** | 91 |
| 4 | $Cs_2CO_3$ | **Imine-POP@Pd** | 36 |
| 5 | DBU | **Imine-POP@Pd** | 23 |
| 6[c] | $K_3PO_4$ | **$Al_2O_3$@Pd** | 12 |
| 7[c] | $K_3PO_4$ | **$TiO_2$@Pd** | 87 |
| 8[c] | $K_3PO_4$ | **C@Pd** | 43 |
| 9[d] | $K_3PO_4$ | **Imine-POP@Pd** | 78 |
| 10[e] | $K_3PO_4$ | **Imine-POP@Pd** | 32 |
| 11[e] | $K_3PO_4$ | **Imine-POP@Pd** | 69 |

[a] Reaction condition: **1a**, 1 mmol; **Imine-POP@Pd**, 30 mg (Pd was 2.3 mol% based on **1a**); $K_3PO_4$, 0.3 mmol or other base 1 mmol; $CO_2$ 3 MPa, $H_2$ 3 MPa; DMI, 4 mL; 100 $^oC$, 24 h. [b] Determined by GC using biphenyl as the internal standard. [c] **Support@Pd** (Pd was 2.3 mol% based on **1a**). [d] The Pd content was 2.7 wt%, and the Pd loading was 2.3 mol% based on **1a**. [e] The Pd loading was 0.77 mol% (entry 10) and 1.53 mol% (entry 11).

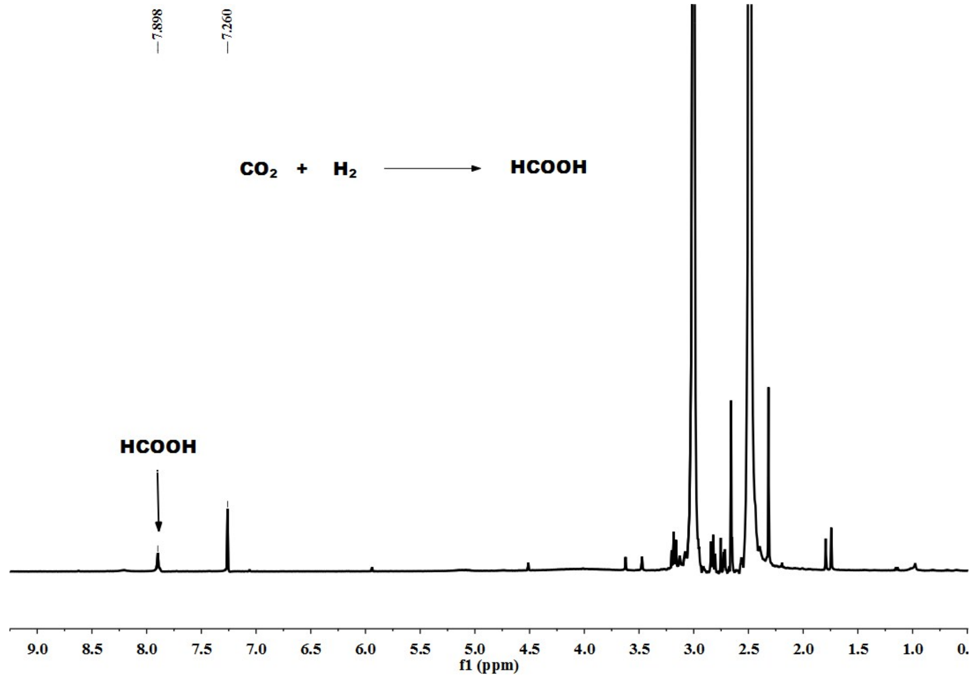
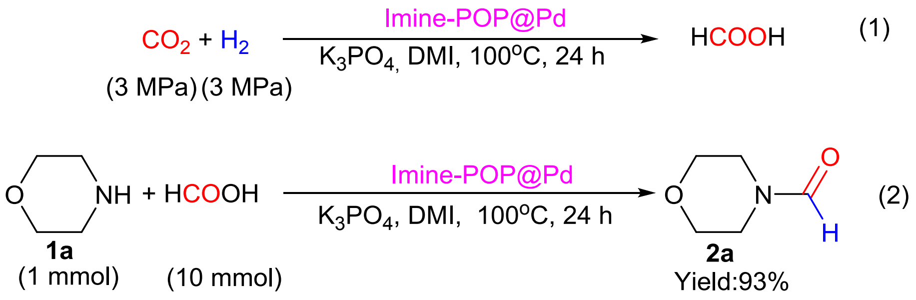
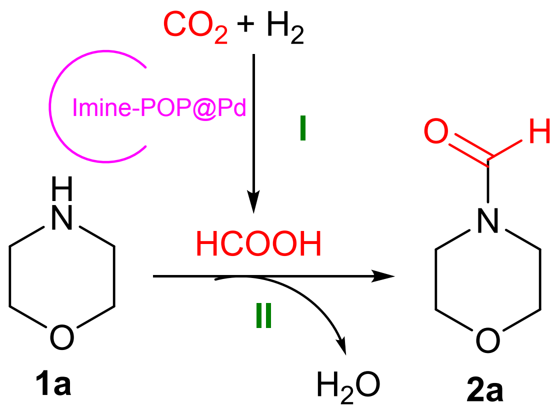


**Figure S11** The NMR spectrum of control experiment for mechanism study. Reaction conditions: **Imine-POP@Pd**, 30 mg (Pd 2.3 mol%); $K_3PO_4$, 0.3 mmol; $CO_2$, 3 MPa; $H_2$, 3 MPa; DMI, 4 mL; 100 °C, 24 h.



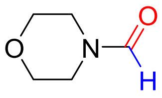
**Scheme S1** Control Experiment for Mechanism Study. (1) **Imine-POP@Pd** (Pd was 2.3 mol% based on 1a); $K_3PO_4$, 0.3 mmol; $CO_2$ 3 MPa, $H_2$ 3 MPa; DMI, 4 mL; 100 °C, 24 h. HCOOH was determined by NMR. (2) **1a**, 1 mmol; HCOOH 10 mmol, **Imine-POP@Pd** (Pd was 2.3 mol% based on 1a); $K_3PO_4$, 0.3 mmol; DMI, 4 mL; 100 °C, 24 h. The yield of **2a** was determined by GC using biphenyl as the internal standard.



**Scheme S2** Possible reaction mechanism for the **Imine-POP@Pd** catalyzed N-formylation reaction of amines with $CO_2/H_2$.

## 4. Determination of the product yields

The structure of **2a** was characterized by comparing the retention time with the authentic compound and GC-MS. The yield was determined by GC using biphenyl as the internal standard and calculated through the calibartion curves as shown below. For **2b-2n**, 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.



**2a**

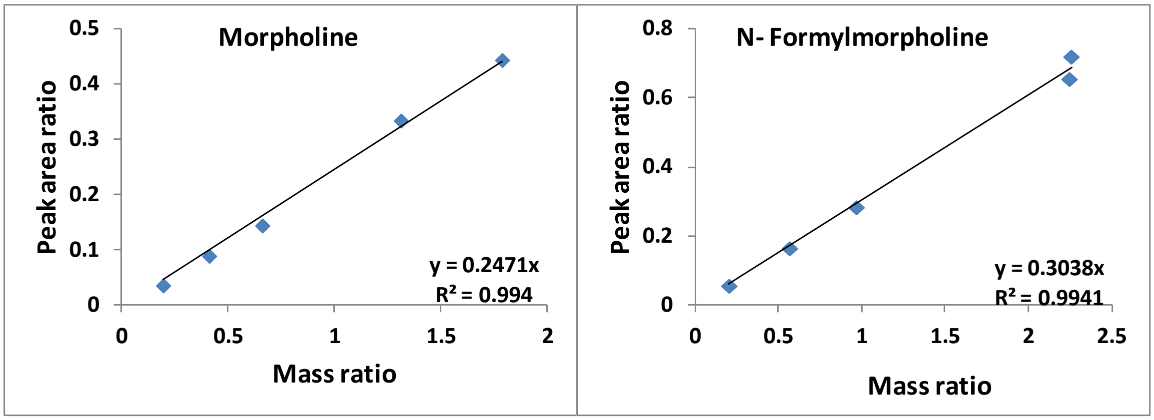


**Figure S12** Working Curves to determine concentrations of **morpholine and N-formylmorpholine**

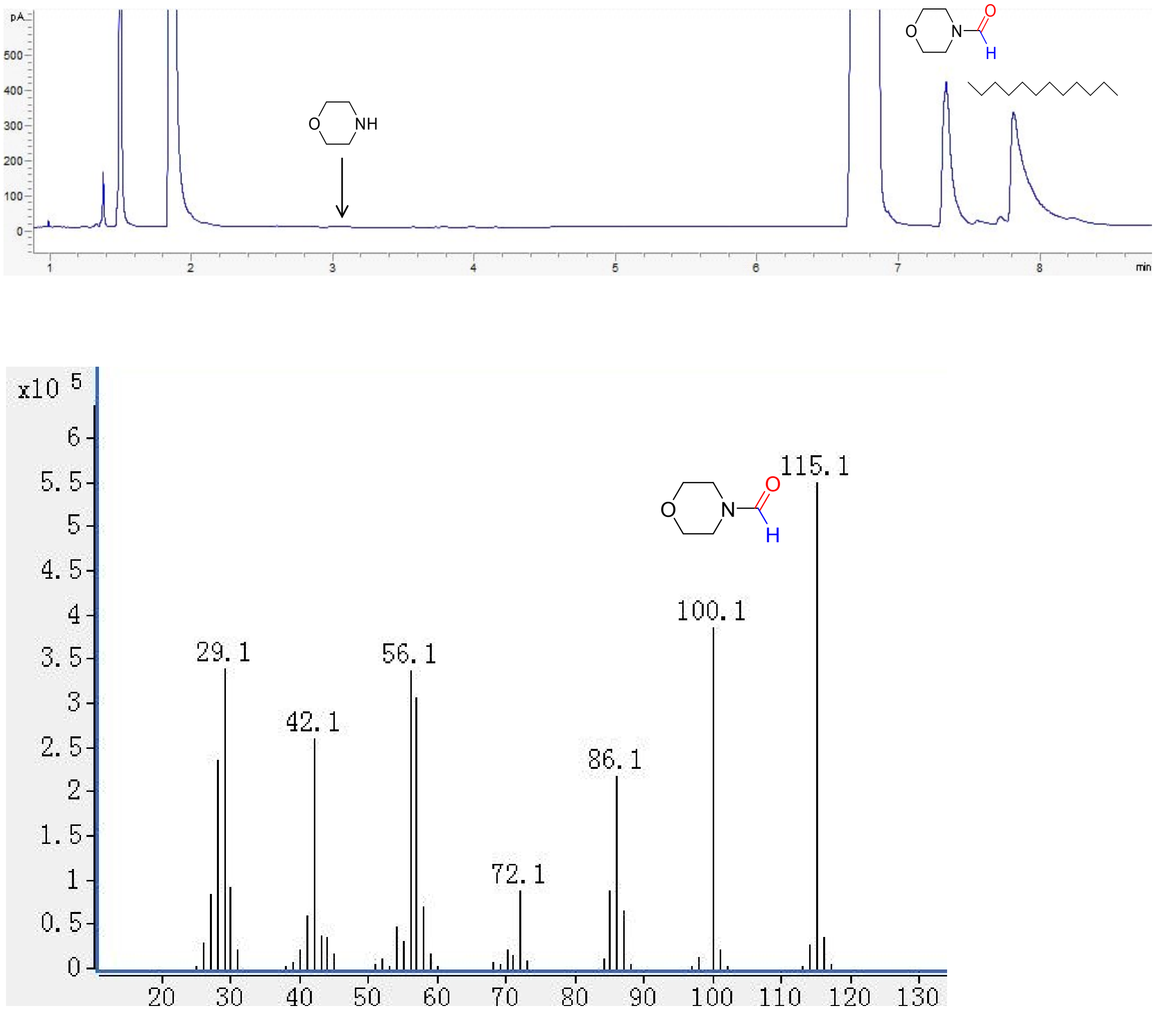
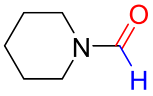


**Figure S13** GC spectra of reaction solution of morpholine **(1a)** reacting with $CO_2/H_2$ and MS spectrum of **2a.**



**2b**

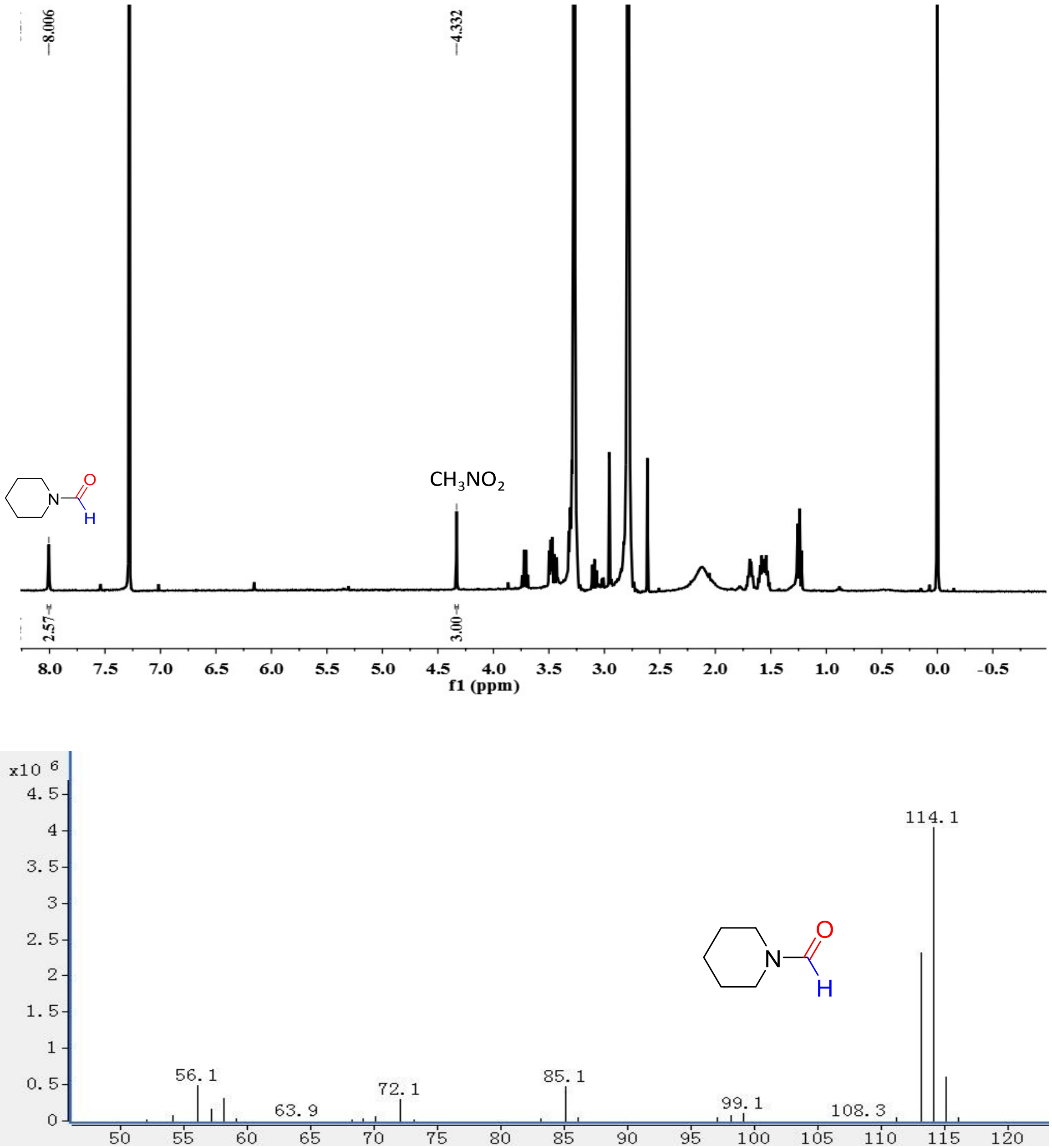
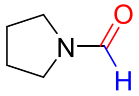


**Figure S14** NMR spectrum of reaction solution of **1b** reacting with CO$_2$/H$_2$ (**1b**: 0.0747 g; CH$_3$NO$_2$: 0.0190 g) and MS spectrum of **2b.**



**2c**

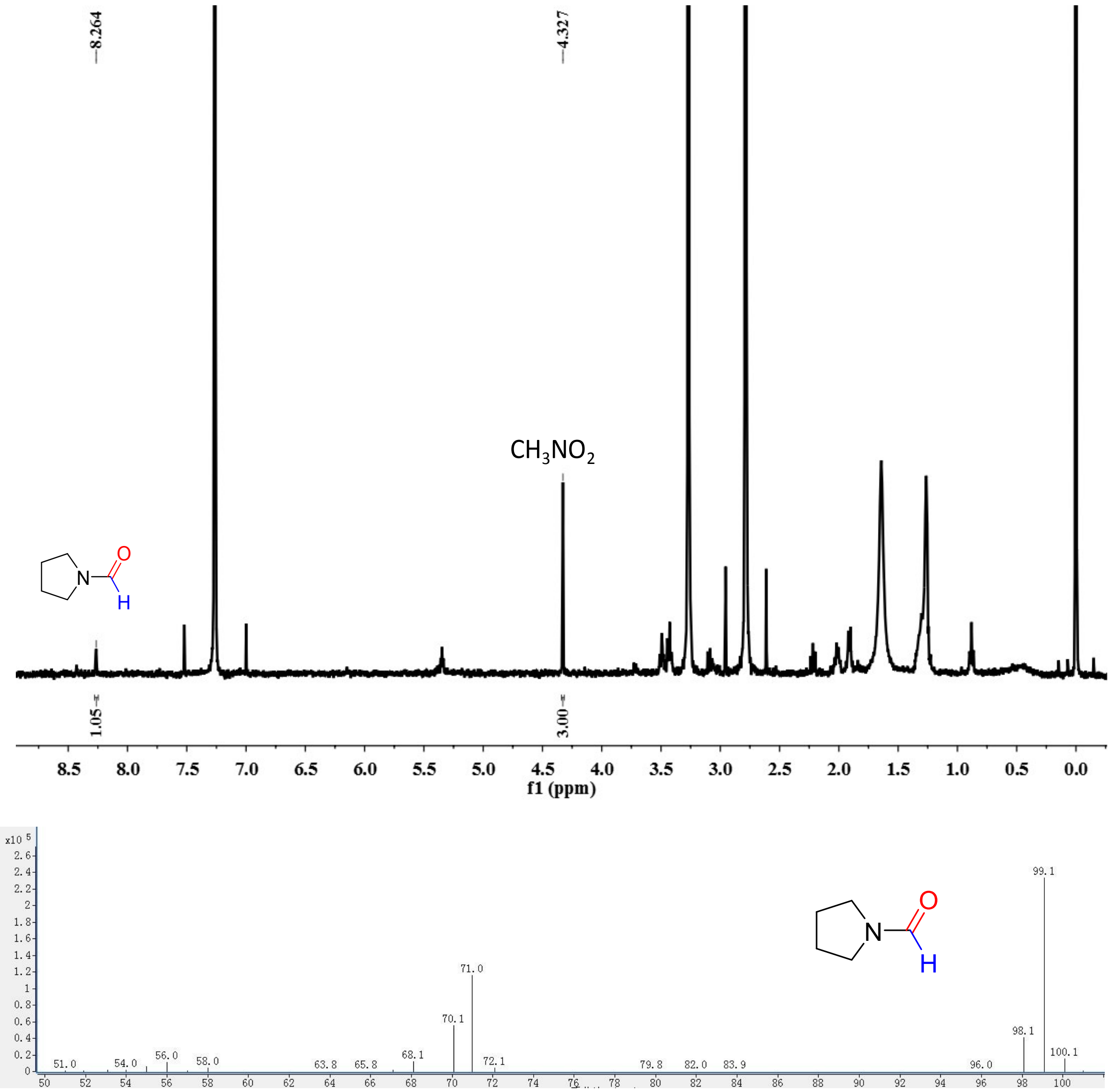
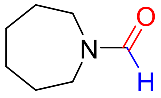


**Figure S15** NMR spectrum of reaction solution of **1c** reacting with $CO_2/H_2$ (**1c**: 0.0773 g; $CH_3NO_2$: 0.0584 g) and MS spectrum of **2c.**



**2d**

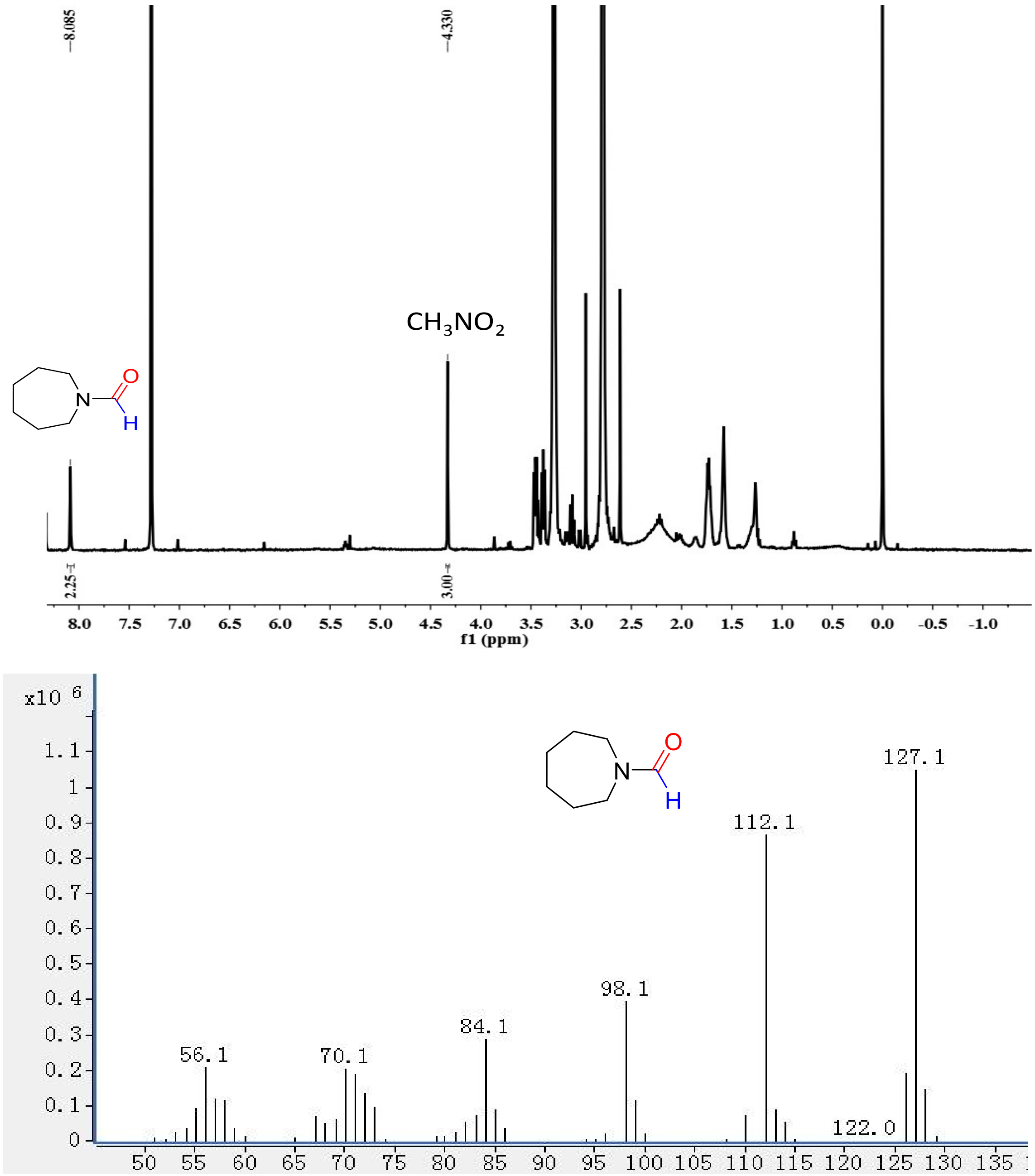
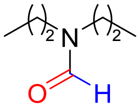
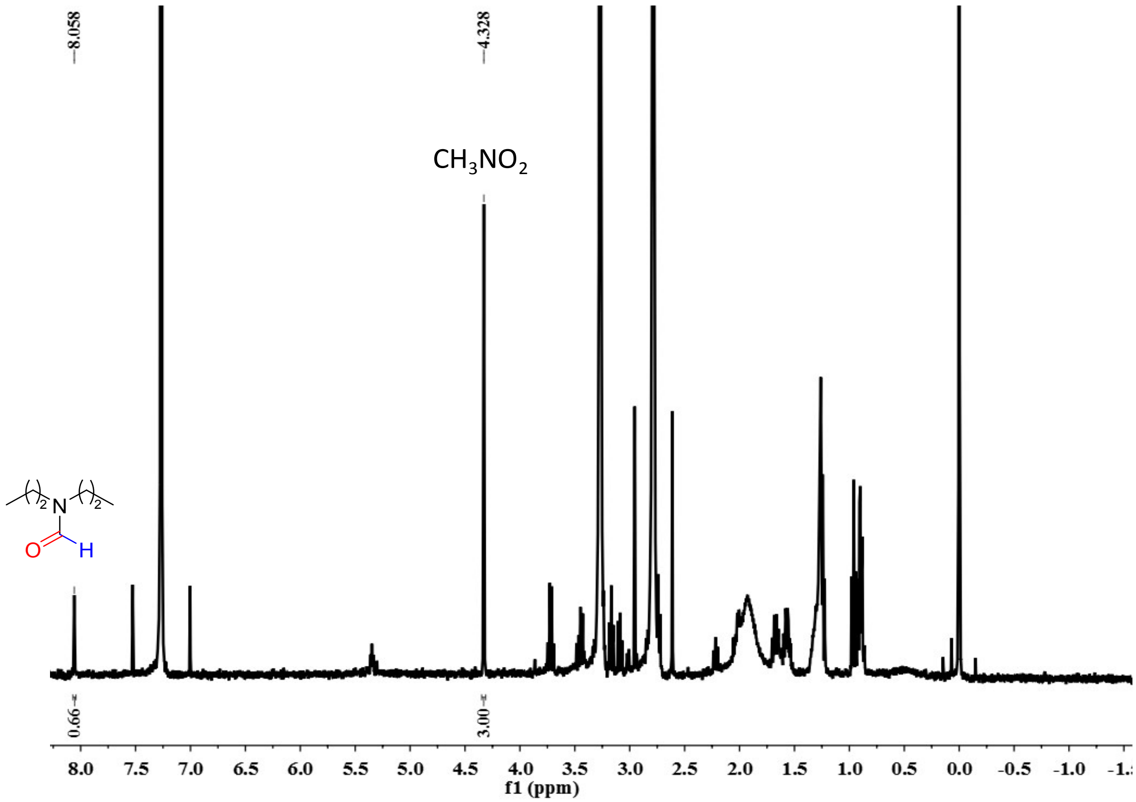


**Figure S16** NMR spectrum of reaction solution of **1d** reacting with $CO_2/H_2$ **(1d**: 0.1073 g; $CH_3NO_2$: 0.0245 g) and MS spectrum of **2d.**



**2e**



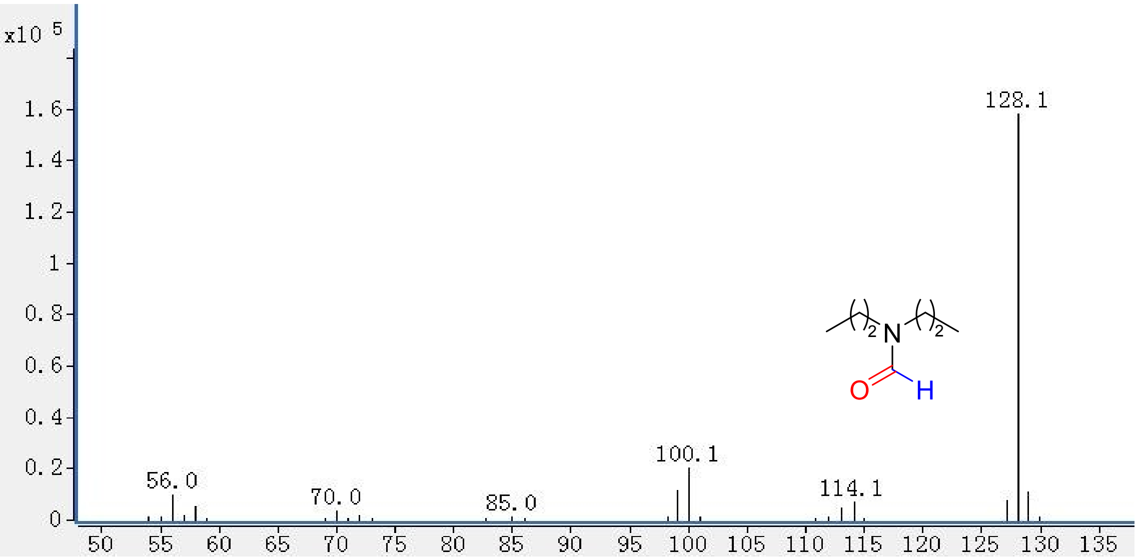
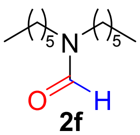


**Figure S17** NMR spectrum of reaction solution of **1e** reacting with $CO_2/H_2$ (**1e**: 0.0884 g; $CH_3NO_2$: 0.0563 g) and MS spectrum of **2e.**



**2f**

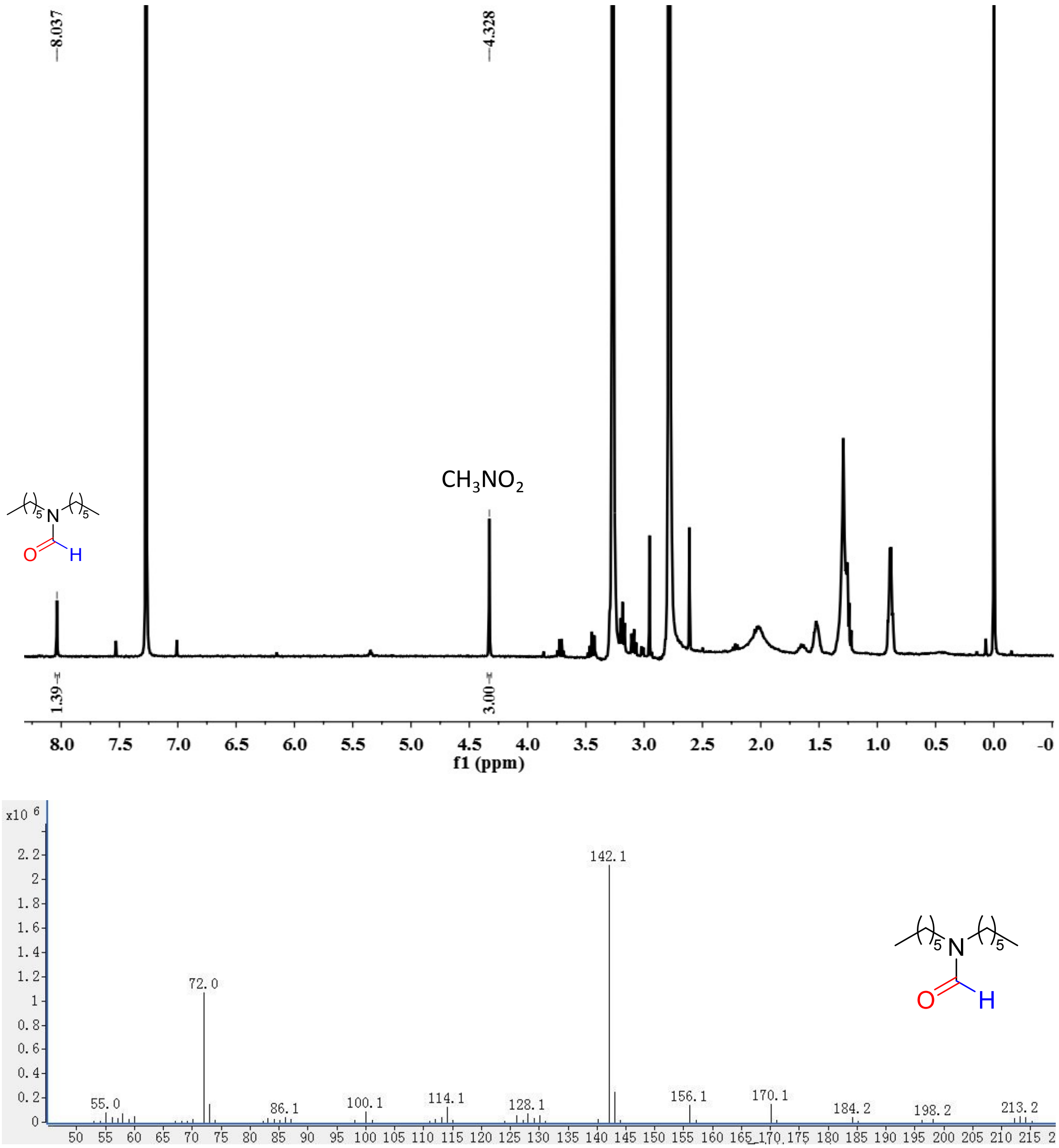
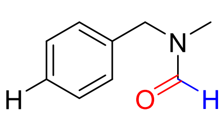


**Figure S18** NMR spectrum of reaction solution of **1f** reacting with CO$_2$/H$_2$ **(1f**: 0.1814 g; CH$_3$NO$_2$: 0.0360 g) and MS spectrum of **2f.**



**2g**

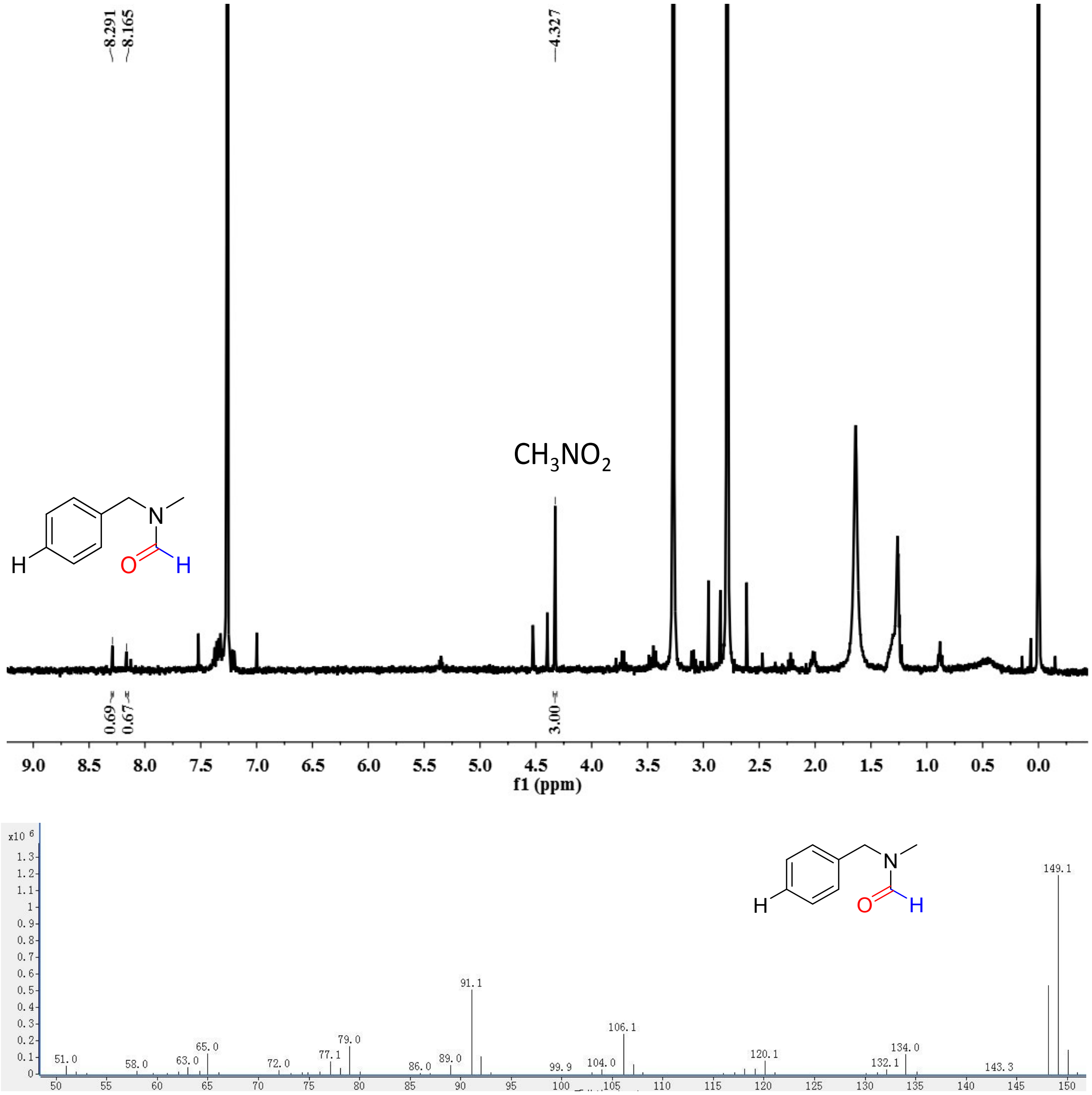
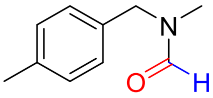
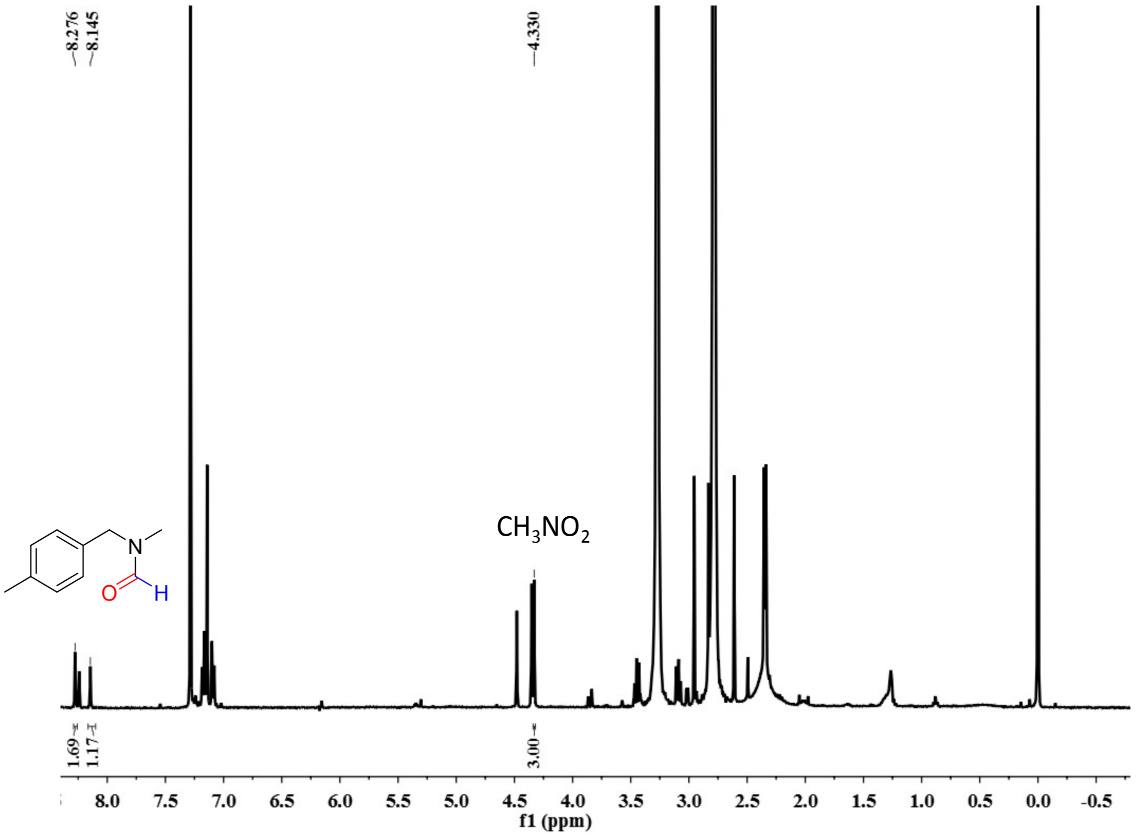


**Figure S19** NMR spectrum of reaction solution of **1g** reacting with $CO_2/H_2$ (**1g**: 0.1626 g; $CH_3NO_2$: 0.0590 g ) and MS spectrum of **2g.**



**2h**



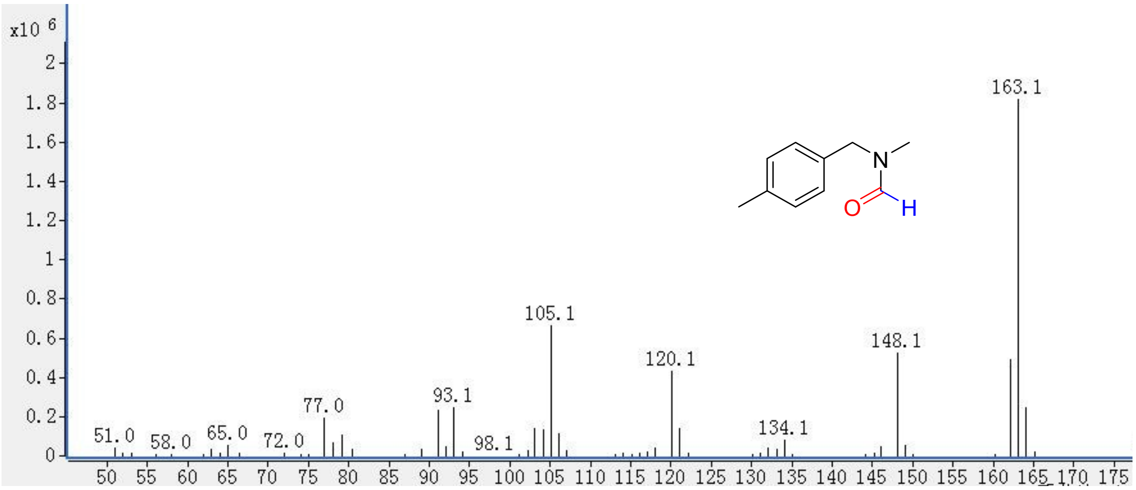
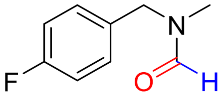
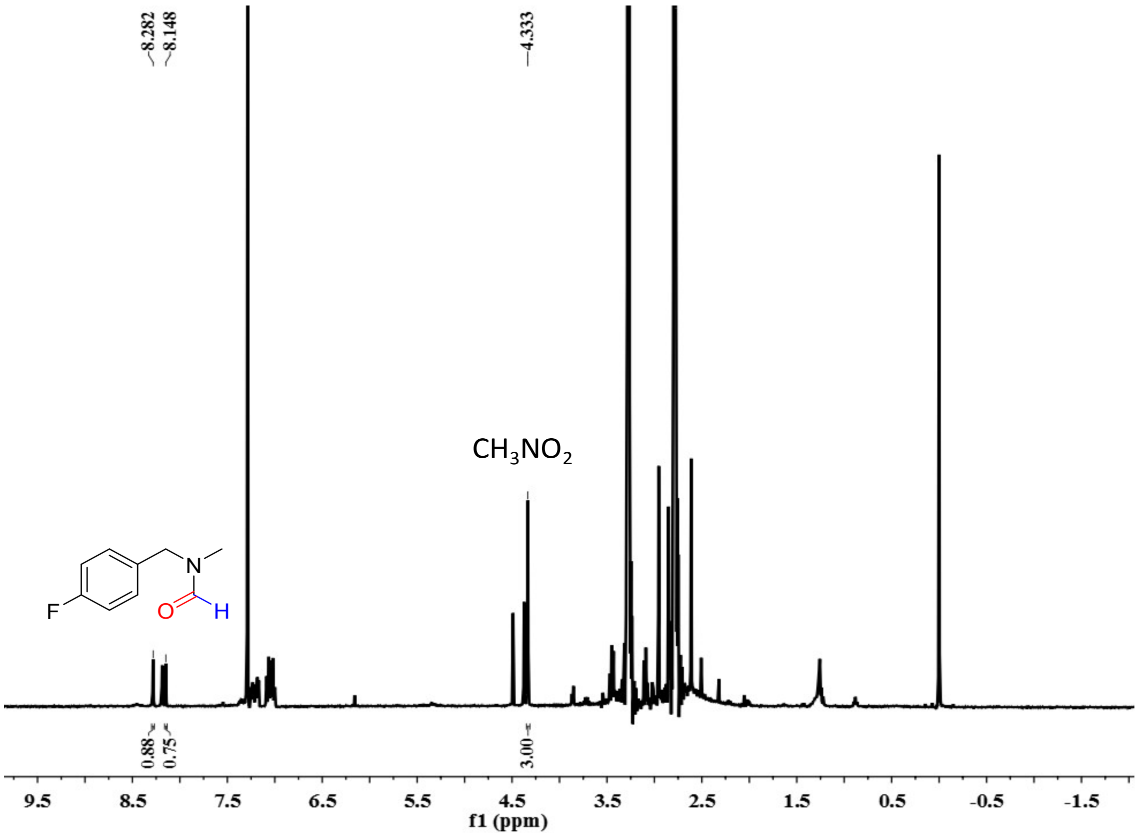


**Figure S20** NMR spectrum of reaction solution of **1h** reacting with CO$_2$/H$_2$ **(1h**: 0.1407 g; CH$_3$NO$_2$: 0.0157 g ) and MS spectrum of **2h.**



**2i**



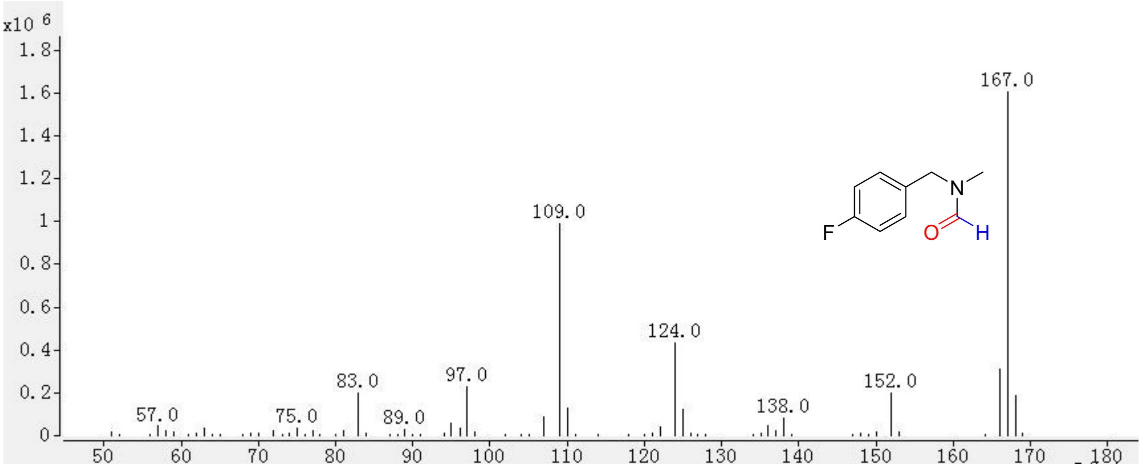
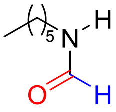
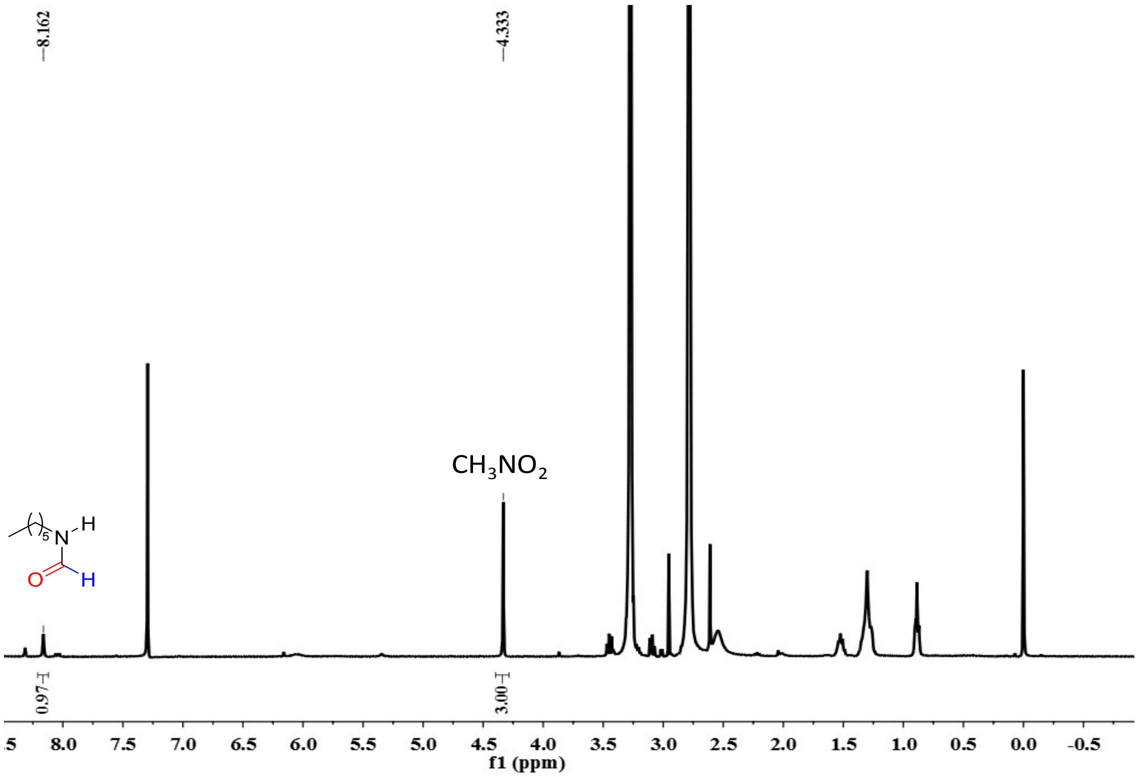


**Figure S21** NMR spectrum of reaction solution of **1i** reacting with CO$_2$/H$_2$ **(1i**: 0.1328 g; CH$_3$NO$_2$: 0.0272 g ) and MS spectrum of **2i.**



**2j**



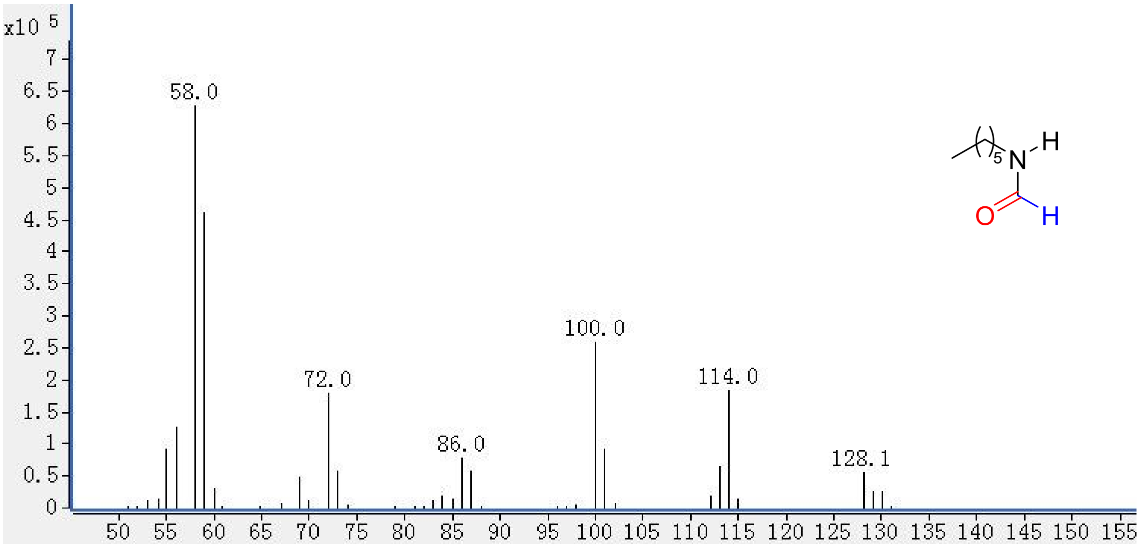
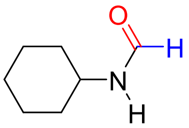


**Figure S22** NMR spectrum of reaction solution of **1j** reacting with $CO_2/H_2$ (**1j**: 0.1078 g; $CH_3NO_2$: 0.0424 g ) and MS spectrum of **2j.**



**2k**

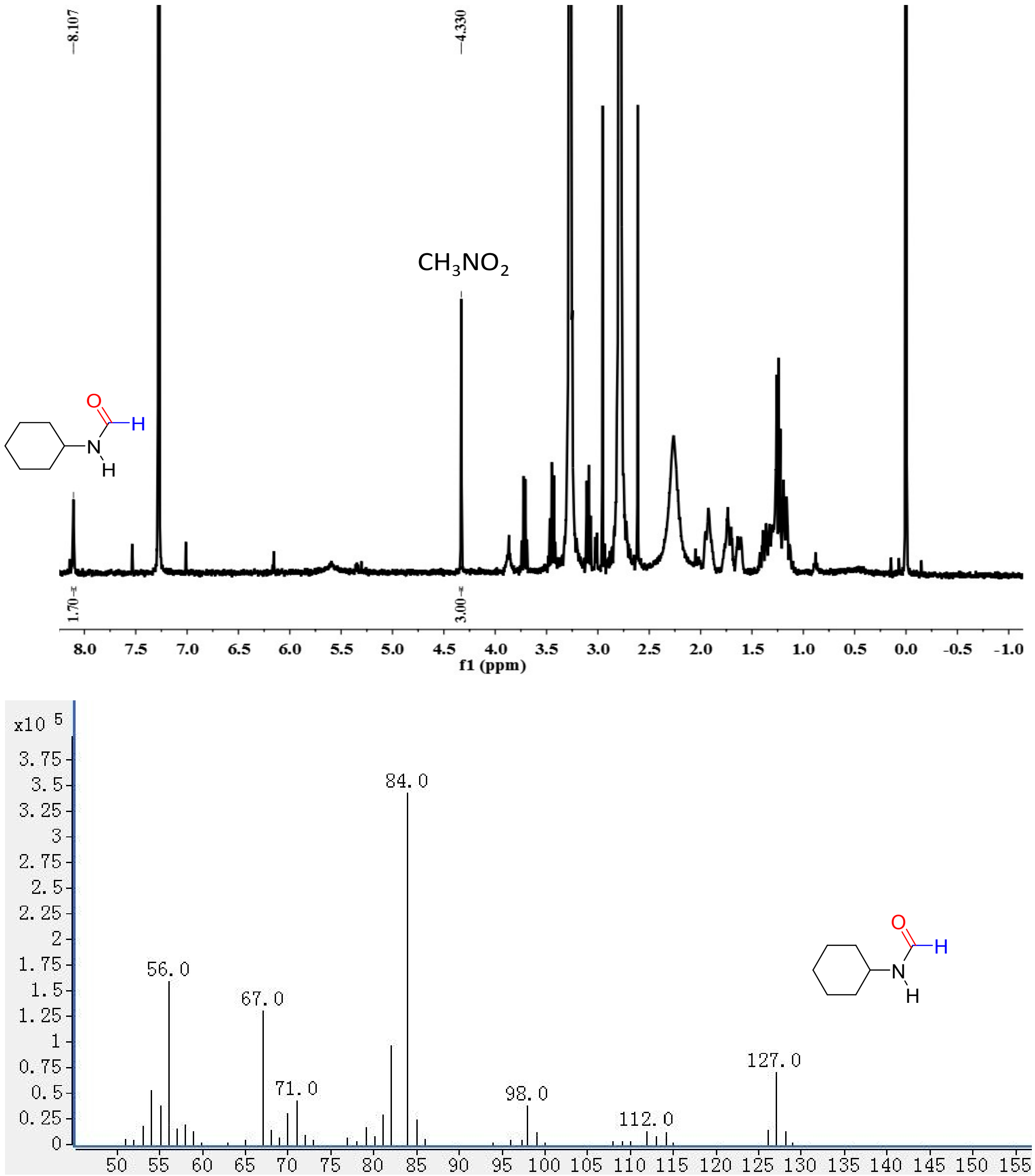
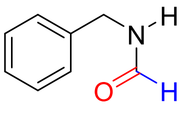


**Figure S23** NMR spectrum of reaction solution of **1k** reacting with $CO_2/H_2$ **(1k**:0.0992 g; $CH_3NO_2$: 0.0278 g ) and MS spectrum of **2k.**



**2l**

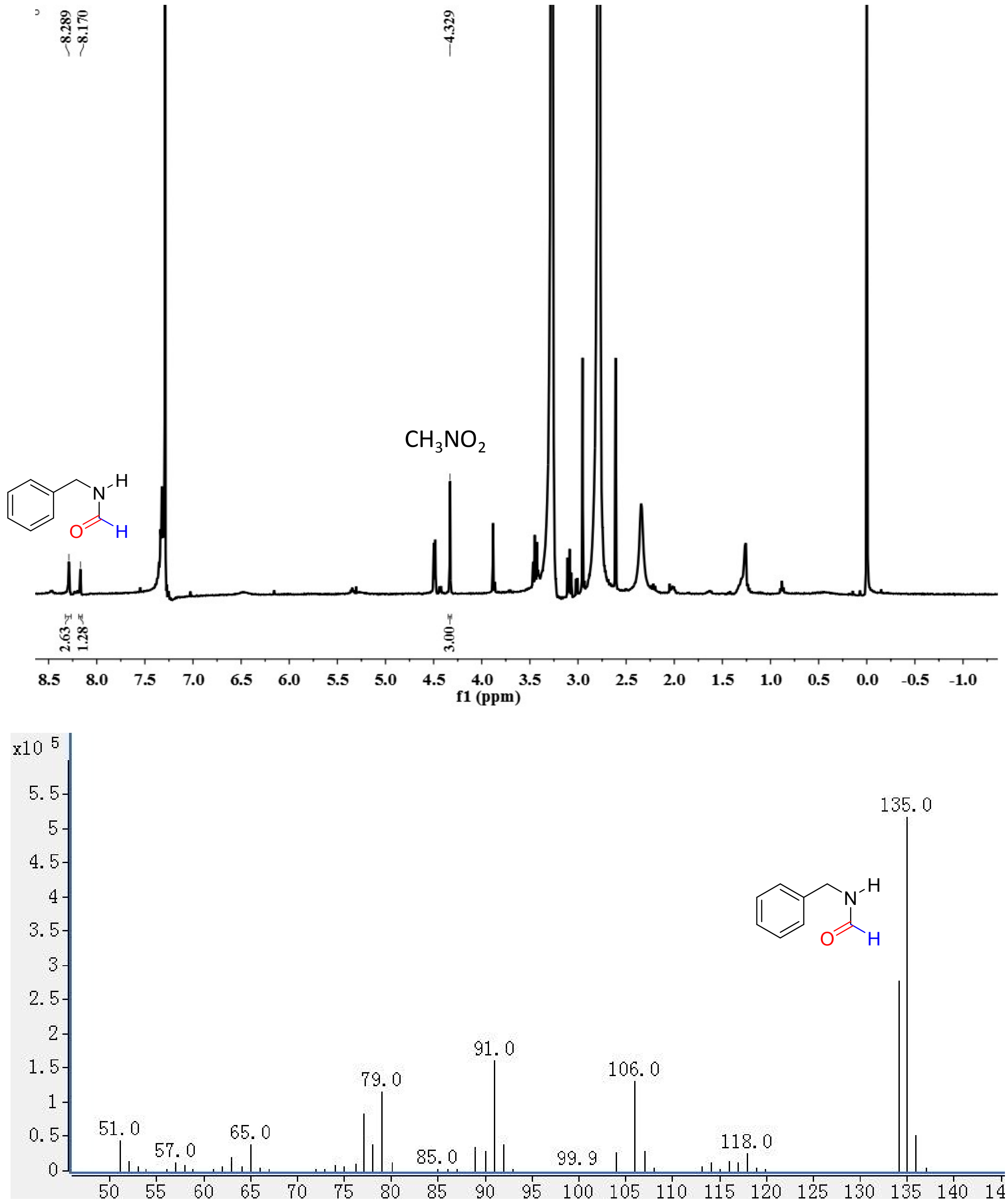
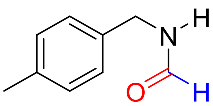
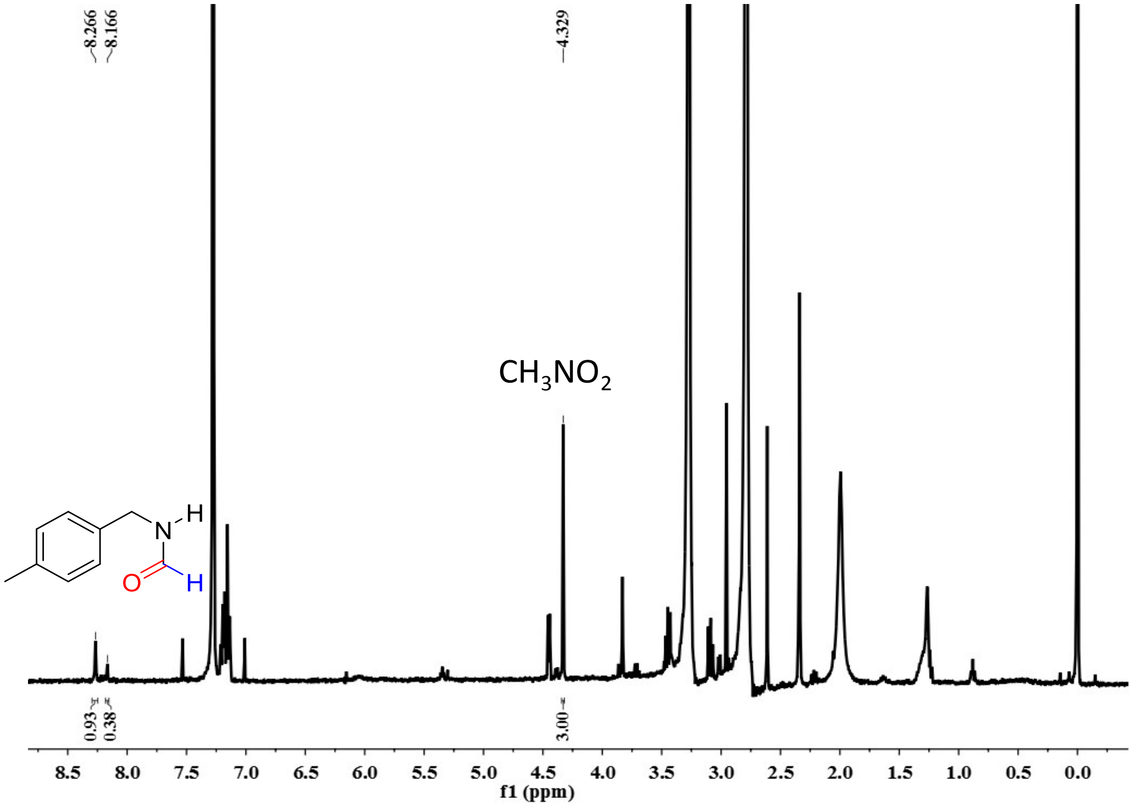


**Figure S24** NMR spectrum of reaction solution of **1l** reacting with $CO_2/H_2$ (**1l**:0.1329 g; $CH_3NO_2$: 0.0176 g) and MS spectrum of **2l.**



**2m**



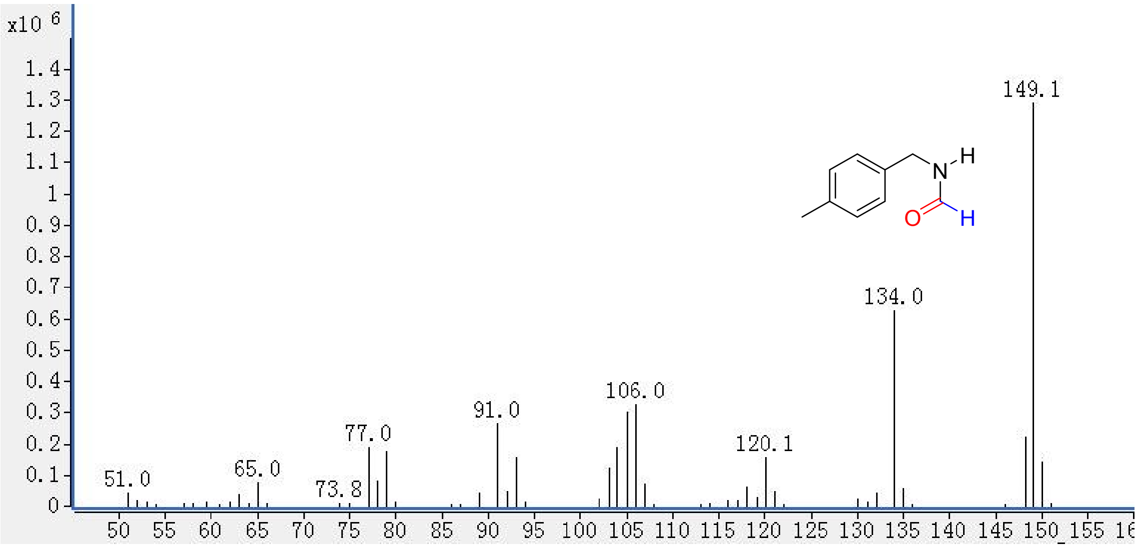
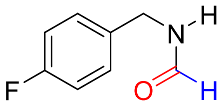


**Figure S25** NMR spectrum of reaction solution of **1m** reacting with $CO_2/H_2$ **(1m**:0.1168 g; $CH_3NO_2$: 0.0306 g) and MS spectrum of **2m.**



**2n**

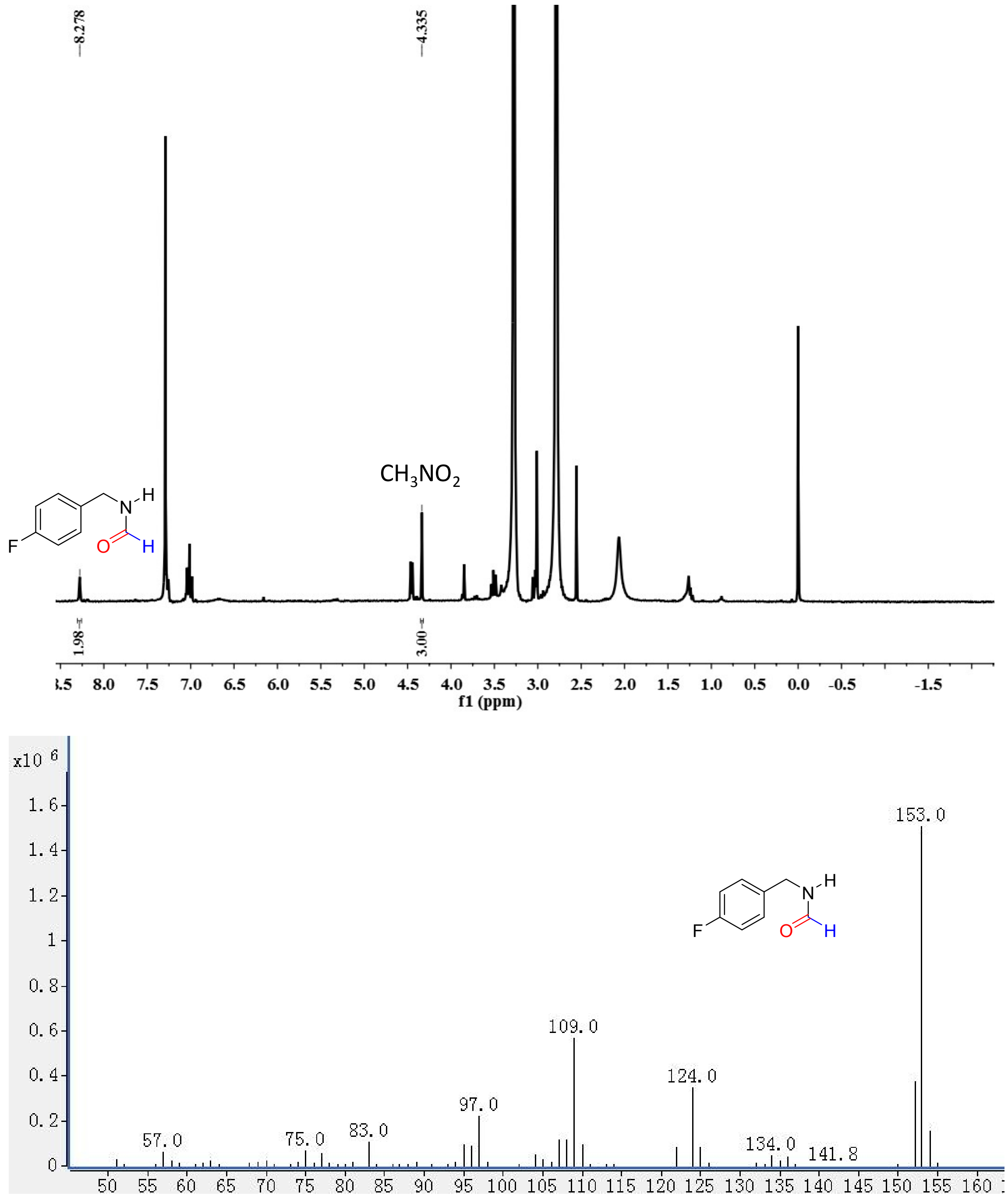
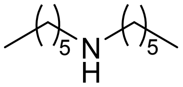
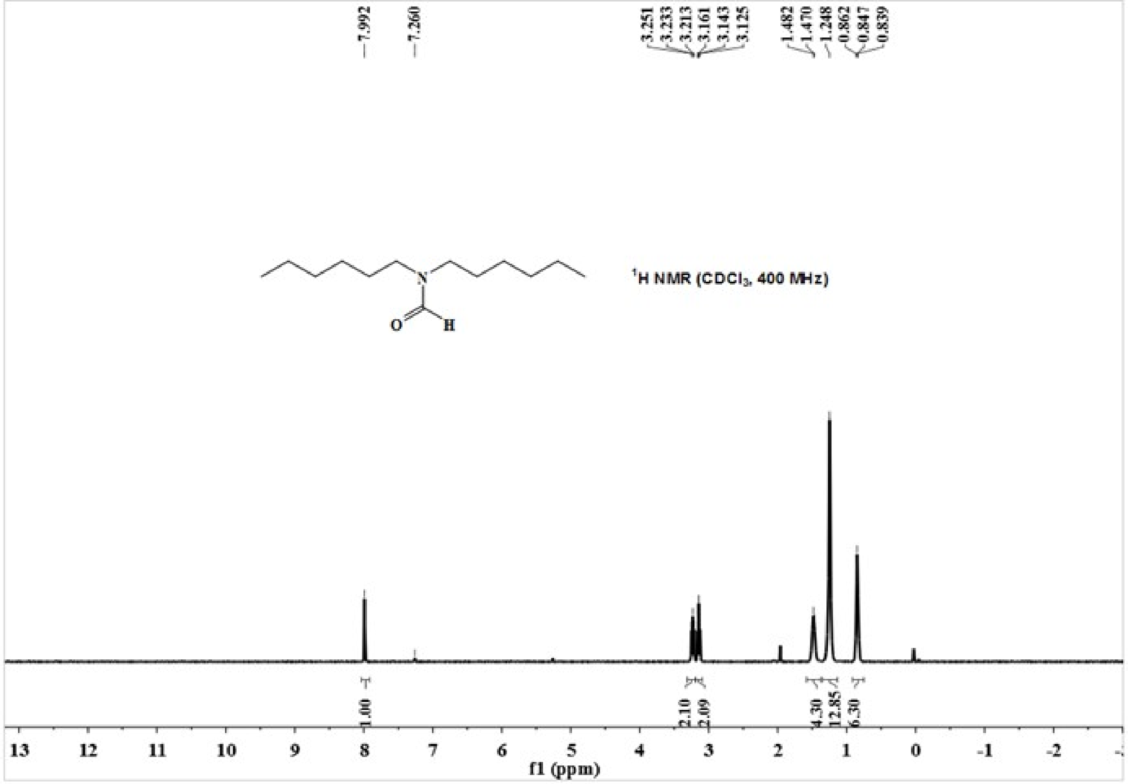


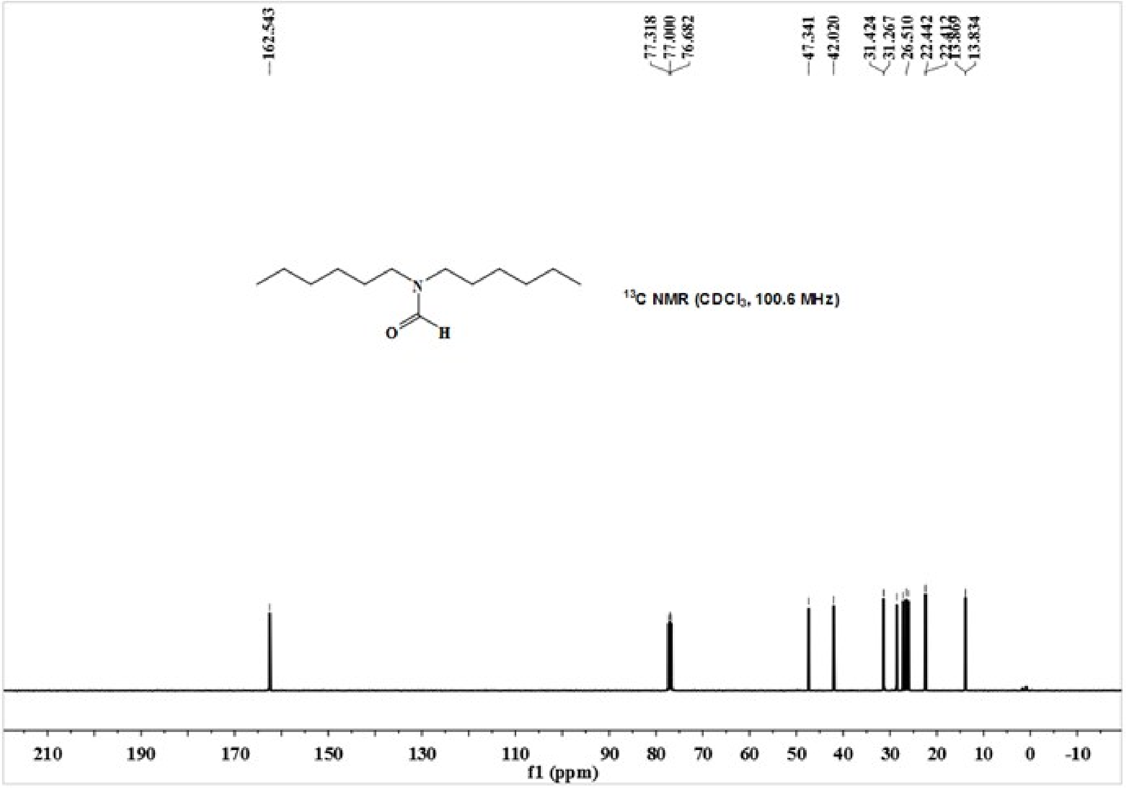
**Figure S26** NMR spectrum of reaction solution of **1n** reacting with CO$_2$/H$_2$ (**1n**:0.1309 g; CH$_3$NO$_2$: 0.0153 g ) and MS spectrum of **2n.**

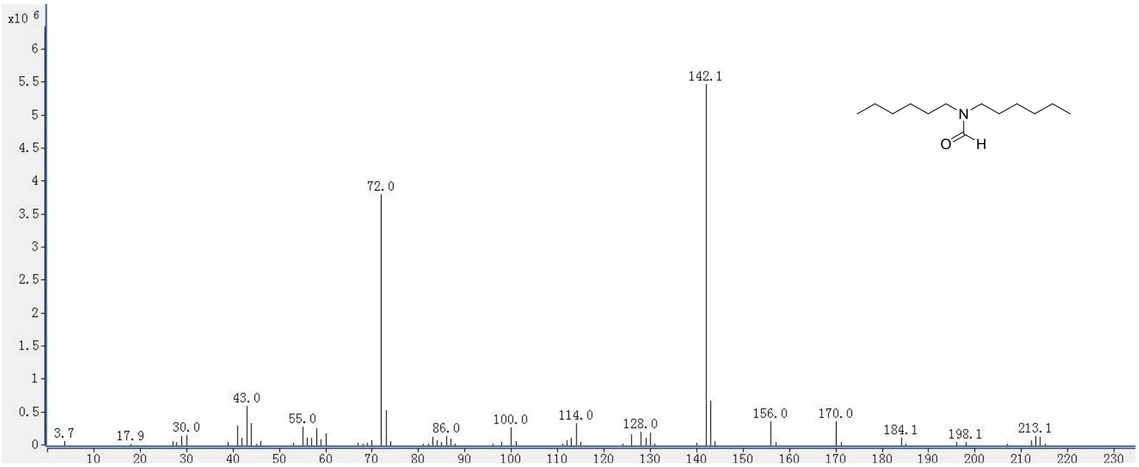
## 5. $^1$H and $^{13}$C NMR data of the isolated products

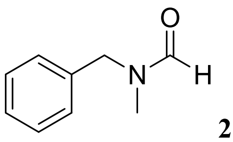


**2f**; N,N-dihexylformamide; Purification by column chromatography on silica gel using n-hexane/ ethyl acetate (50:1) as eluent. Light yellow liquid; $^1$H NMR ($CDCl_3$, 400 MHz) δ 0.84-0.86 (m, 6H), 1.25 (s, 12H), 1.47-1.48 (m, 4H), 3.14 (t, $^3J$ = 7.2 Hz, 2H), 3.23 (t, $^3J$ = 7.2 Hz, 2H), 7.99 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) δ 13.83, 13.87, 22.41, 22.44, 26.04, 26.51, 27.17, 28.54, 31.27, 31.42, 42.02, 47.34, 162.54. M ($C_{13}H_{27}NO$) = 213.2, EI-MS found 213.1 [M], 198.1 [M-$CH_3$], 184.1 [M-CHO].

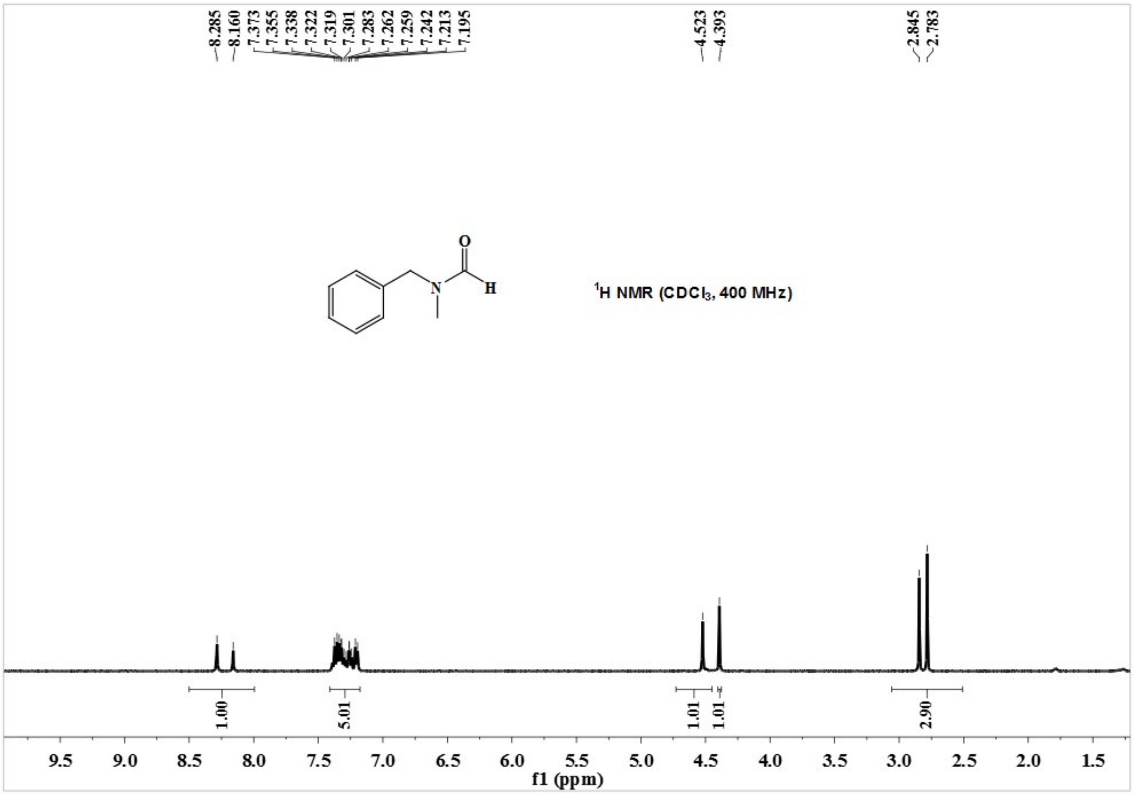


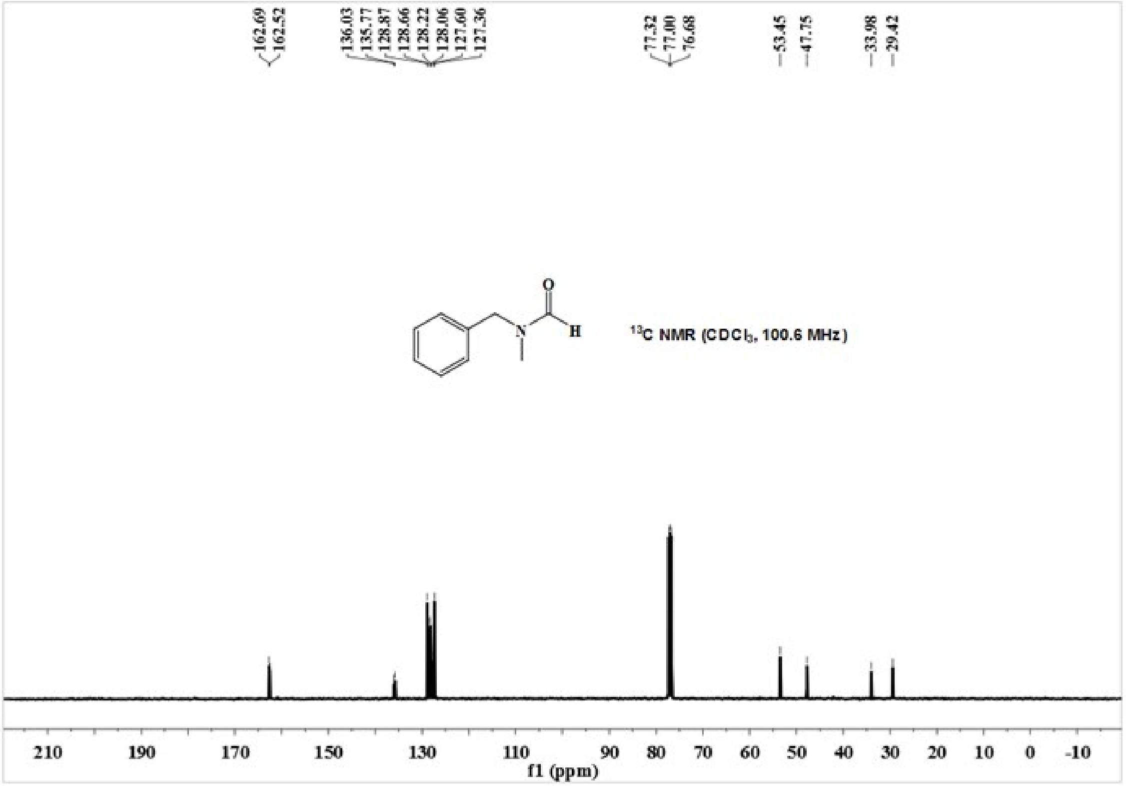


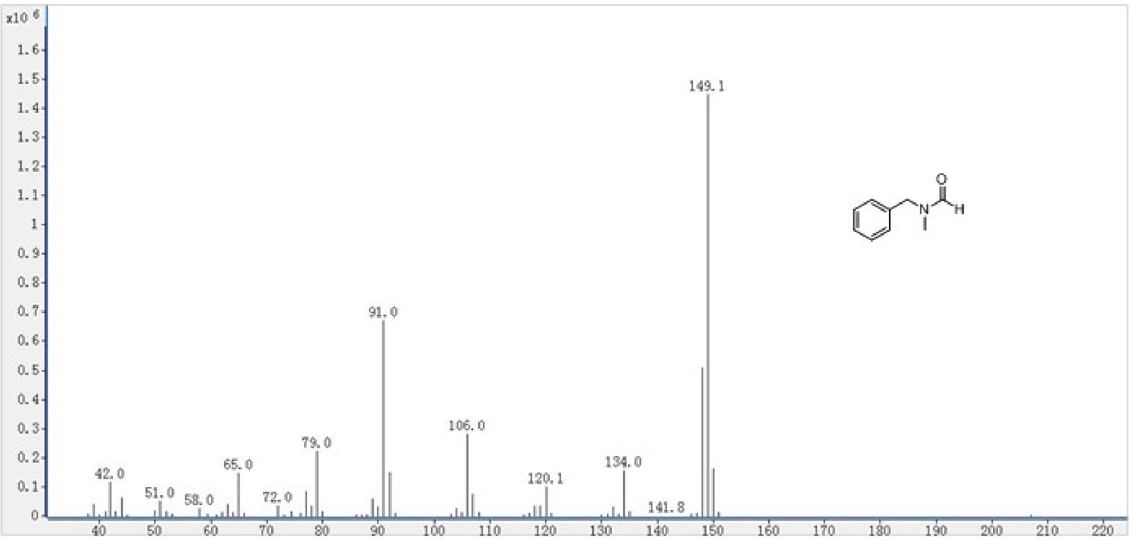


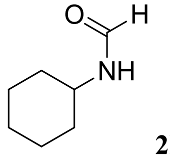


**2g**; N-methyl-N-benzylformamide; Purification by column chromatography on silica gel using n-hexane/ ethyl acetate (50:1) as eluent. Yellow liquid; $^{1}$H NMR (CDCl$_3$, 400 MHz) δ 2.78, 2.84 (s, 3H), 4.39 (s, 1H), 4.52 (s, 1H), 7.19-7.37 (m, 5H), 8.16, 8.28 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 29.42, 33.98, 47.75, 53.45, 127.36, 127.60, 128.06, 128.22, 128.66, 128.87, 135.77, 136.03, 162.52, 162.69. M (C$_9$H$_{11}$NO) = 149.1, EI-MS found 149.1 [M], 134.0 [M-CH$_3$], 120.1 [M-CHO].

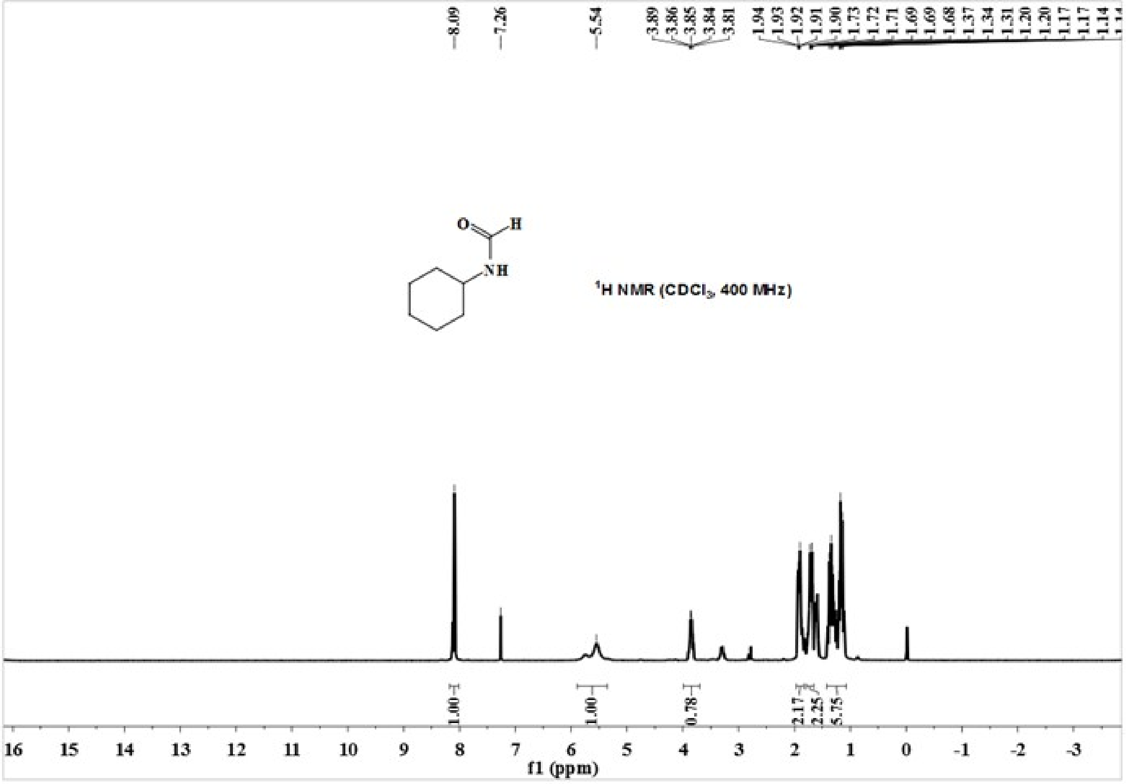

8.285
8.160
7.373
7.355
7.338
7.322
7.319
7.301
7.283
7.262
7.259
7.242
7.213
7.195
4.523
4.393
2.845
2.783
O
N
H
¹H NMR (CDCl₃, 400 MHz)
1.00
5.01
1.01
1.01
2.90
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

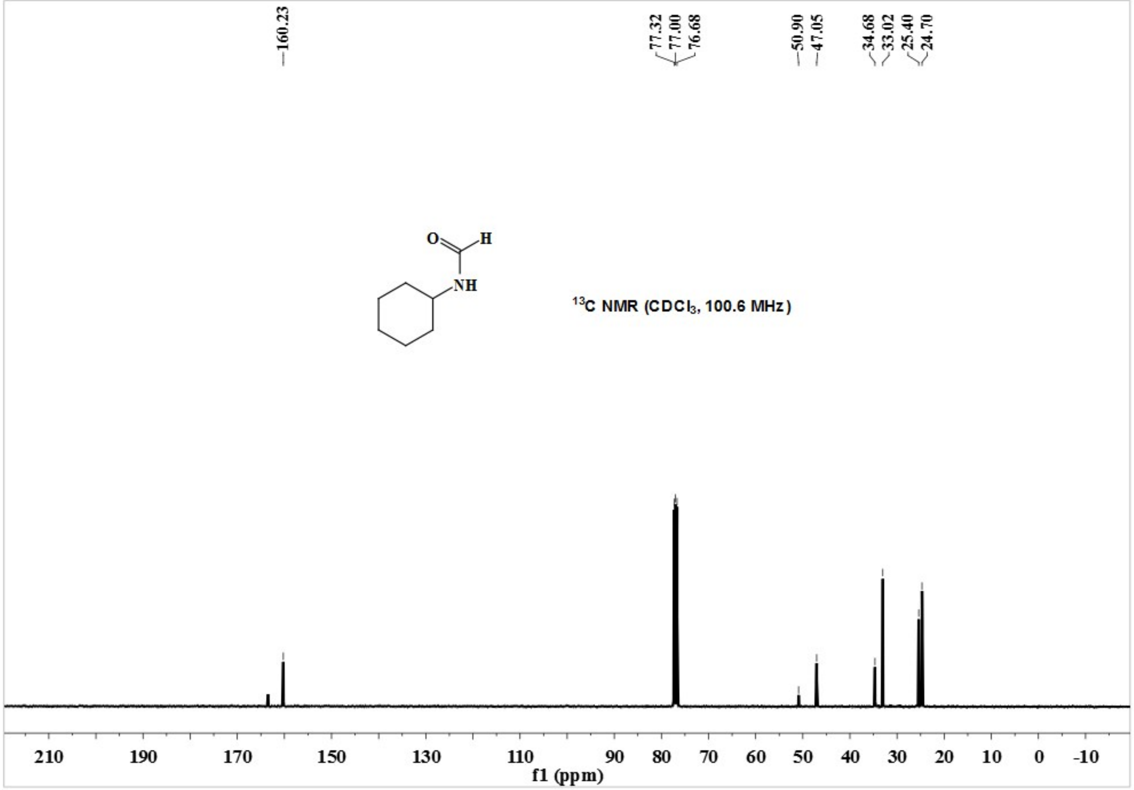

162.69
162.52
136.03
135.77
128.87
128.66
128.22
128.06
127.60
127.36
77.32
77.00
76.68
53.45
47.75
33.98
29.42
O
N
H
¹³C NMR (CDCl₃, 100.6 MHz)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

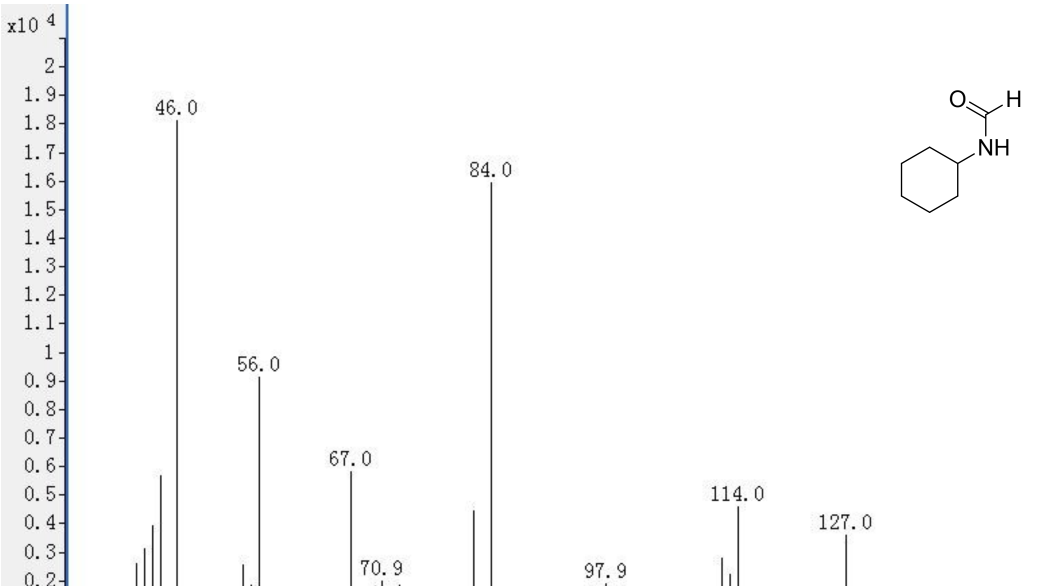


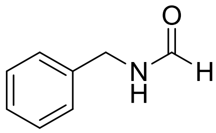


**2k**; N-cyclohexylformamide; Purification by column chromatography on silica gel using n-hexane/ ethyl acetate (20:1) as eluent. Colourless liquid; $^{1}$H NMR (CDCl$_3$, 400 MHz) δ 1.11-1.40 (m, 6H), 1.68-1.73 (m, 2H), 1.86-1.94 (m, 2H), 3.81-3.89 (m, 1H), 5.54 (s, 1H), 8.09 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 24.70, 25.40, 33.02, 34.68, 47.05, 50.90, 160.23. M ($C_7H_{13}NO$) = 127.1, EI-MS found 127.0 [M], 97.9 [M-CHO], 84.0 [M-NCHO].



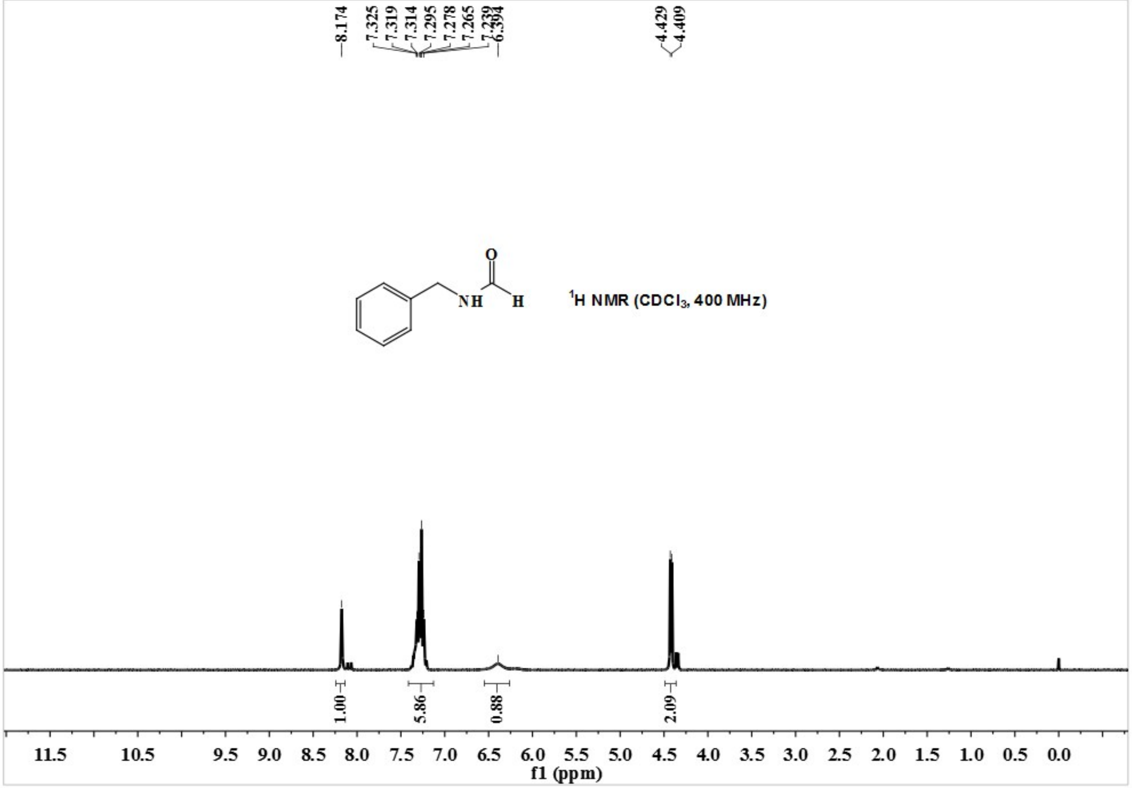


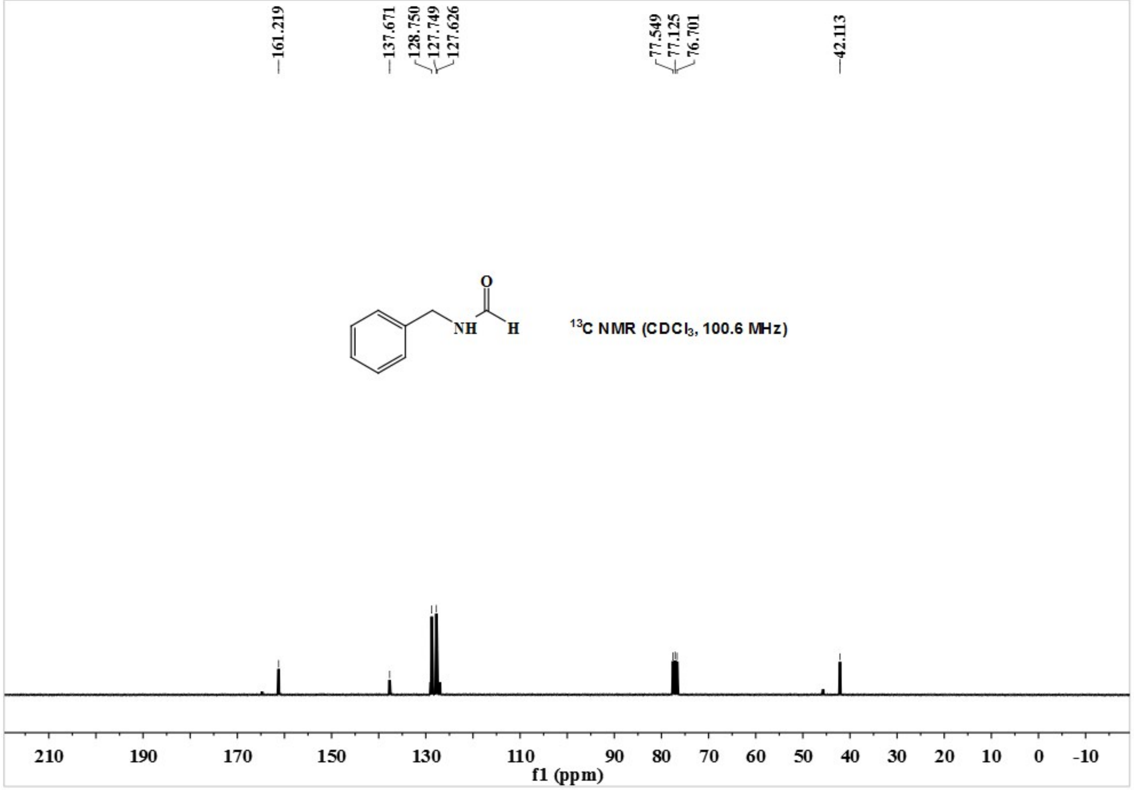


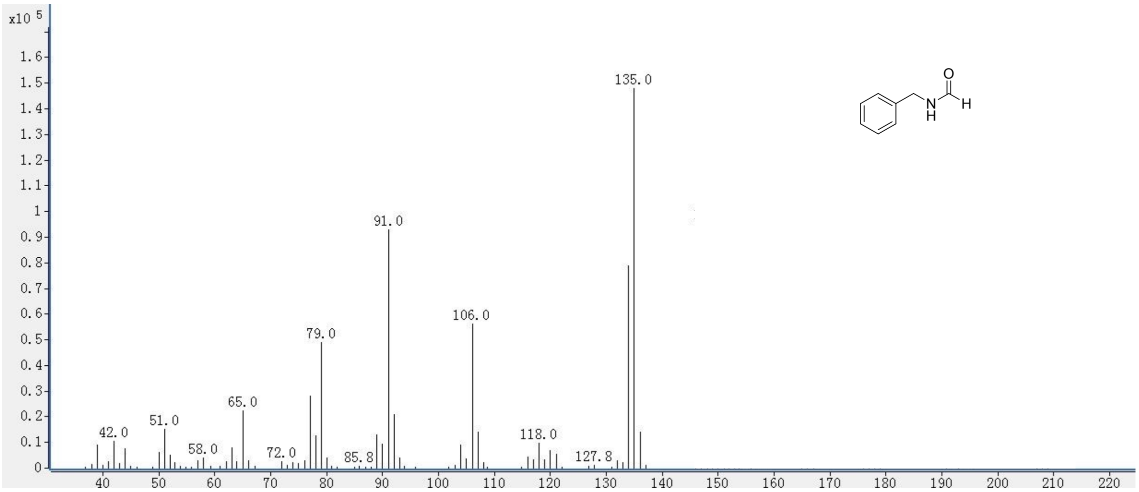


**2l**; N-benzylformamide; Purification by column chromatography on silica gel using n-hexane/ ethyl acetate (50:1) as eluent. Light yellow liquid; $^1$H NMR (CDCl$_3$, 400 MHz) δ 4.42 (d, $^3J$ = 8 Hz, 2H), 6.39 (s, 1H), 7.24-7.32 (m, 5H), 8.17 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ

42.11, 127.63, 127.75, 128.75, 137.67, 161.22. M ($C_8H_9NO$) = 135.1, EI-MS found 135.0 [M], 106.0 [M-CHO].






x10 5
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
135.0
91.0
106.0
79.0
65.0
51.0
42.0
118.0
58.0
72.0
85.8
127.8
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
O
H
N
H