Supporting Information

Hydroxyl Group Regulated Nano-Pd/C Catalyst Generation via In-situ Reduction of $Pd(NH_3)_xCl_y/C$ for N-Formylation of Amine with CO_2/H_2

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I. General Information and Experimental Section

All solvents and chemicals were obtained commercially and were used as received.

NMR spectra were measured using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). All spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Mass spectra were in general recorded on an HP 6890/5973 GC-MS.

X-ray diffraction (XRD)

XRD patterns of samples were obtained on a STADI P automated transmission diffractometer instrument equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation (40 KV and 40 mA) was used as the X-ray source. The precipitated particles were dried in air and pressed on a glass slide for analysis.

Transmission Electron Microscopy (TEM)

For the prepared catalysts, the particle dispersion was diluted by ethanol, and then 10 μL of dispersion was cast on the TEM grids with a micro-pipet. TEM images were obtained on a Tecnai G2 F30 S-Twin operating at 300 kV.

X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Mg anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar+ ion-gun. All spectra were recorded using non-monochromatic Mg Kα (1253.6 eV) radiation.

BET and ICP-AES analysis

Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Pd content of the catalyst was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

Typical procedure for carbon support preparation

The carbon materials were prepared via sol-gel polymerization of resorcinol and formaldehyde with Na_2CO_3 as a catalyst. First, a wet RF gel was prepared by polymerization of resorcinol and formaldehyde at 80 ^oC using a hydrothermal method. Then, the wet RF gel was mixed with KOH or another base and heated at 800 ^oC under a nitrogen flow. Next the carbonized sample was washed with deionized water to remove the base, and the carbon material was obtained. A series of carbon materials was prepared using this method by varying the type of base. The carbon materials that were not treated with a base are denoted C-none. C-KOH (C-0), C-NaOH, C-K_2CO_3, C-Na_2CO_3, C-K_3PO_4 were prepared using various bases (that is, KOH, NaOH, K_2CO_3, Na_2CO_3, K_3PO_4 respectively) with a fixed ratio of wet RF gel to base (that is, 1 : 1).

The oxidation process was carried out by adding 40 mL of nitric acid (14.5 M, 65% HNO_3) to 4.0 g C-KOH placed in a round-bottom flask. The mixture was heated at 25 ^oC, 50 ^oC, 80 ^oC or 110 ^oC on hot plate with constant stirring for 1 h, then washed with distilled water to neutral, decanted and the solid sample was dried at 110 ^oC in air. The carbon materials that were not treated with a nitric acid are denoted C-0 (C-KOH). C-1, C-2, C-3 and C-4 were prepared at different temperatures (that is 25 ^oC, 50 ^oC, 80 ^oC or 110 ^oC).

Typical procedure for carbon supported nano-Pd catalyst preparation

0.25 g C-KOH-3 and 0.08 mL H_2PdCl_4 (aqueous solution, 29.93 mg/mL) were added into 10 mL aqueous solution of ammonia (1 mol/L). After further stirring for 24 h at r.t., the water was removed under vacuum. It was dried at 80 °C in air for 6 h and then reduced under hydrogen flow at 200 °C for 2 h. The resulting catalyst samples were denoted as Pd/C-3.

Typical procedure for formylation of amines by CO_2 hydrogenation

1.0 mmol amines, 50 mg catalyst and 2 mL methanol were added into a 100 mL autoclave equipped with magnetic stirrer. The autoclave was sealed and exchanged with CO_2 for 2 times and reacted at 130 ^oC under 1 MPa CO_2 and 3 MPa H_2 for 24 h.

Then it was cooled to room temperature. 10 mL ethanol was added to dissolve the reaction mixture and the product was detected by HP 6890/5973 GC-MS. The GC-yield was determined by GC-FID using biphenyl as internal standard and the isolated yields were obtained by flash column chromatography.

Purification Procedure:

The crude products were subjected to silica gel column chromatography (60, 230-400 mesh supplied by Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd). Eluting with~75mL of dichloromethane, followed by 300:1 (dichloromethane: Methanol).

Typical procedure for formylation of amines by CO_2 and H_2

1.0 mmol piperidine 50 mg catalyst Pd/C-3 (1wt% Pd, 0.47 mol% Pd to 1a), 2 mL methanol, 130 ^oC and 0.5 mmol KOH were added in to an 100 mL autoclave. It was then exchanged with 1/3 MPa CO_2/H_2. The reaction was reacted at 130°C for 24 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 70 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

Table S1. Surface Oxygenated Groups by Boehm Titration

Sample	carboxylic acid (umol/g)	Lactone (umol/g)	Phenol (umol/g)
C-0	0	203	208
C-1	119	193	119
C-2	188	248	293
C-3	382	317	332
C-4	2599	997	808

Table S2. The K/C atomic ratio in XPS

Sample	K/C atomic ratio	Catalyst	Piperidine yield (%)
C-0	0.00663	Pd/C-0	13
C-1	0.00466	Pd/C-1	11
C-2	0.00609	Pd/C-2	17
C-3	0.00335	Pd/C-3	19
C-4	0.00204	Pd/C-4	16

Ⅱ.Characterization results of catalysts

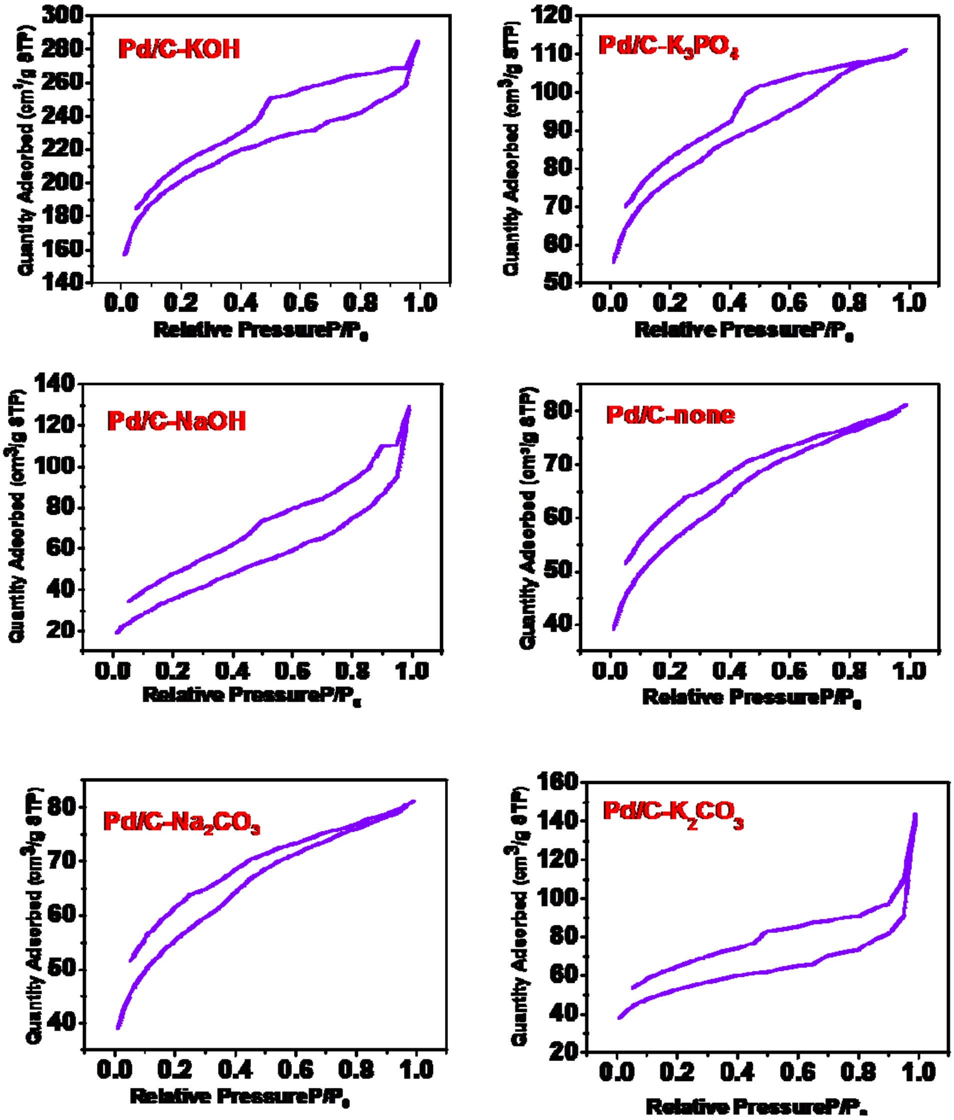


Fig. S1. BET pictures for Pd/C-K_2CO_3, Pd/C-NaOH, Pd/C-none, Pd/C-K_3PO_4, Pd/C-KOH and Pd/C-Na_2CO_3.

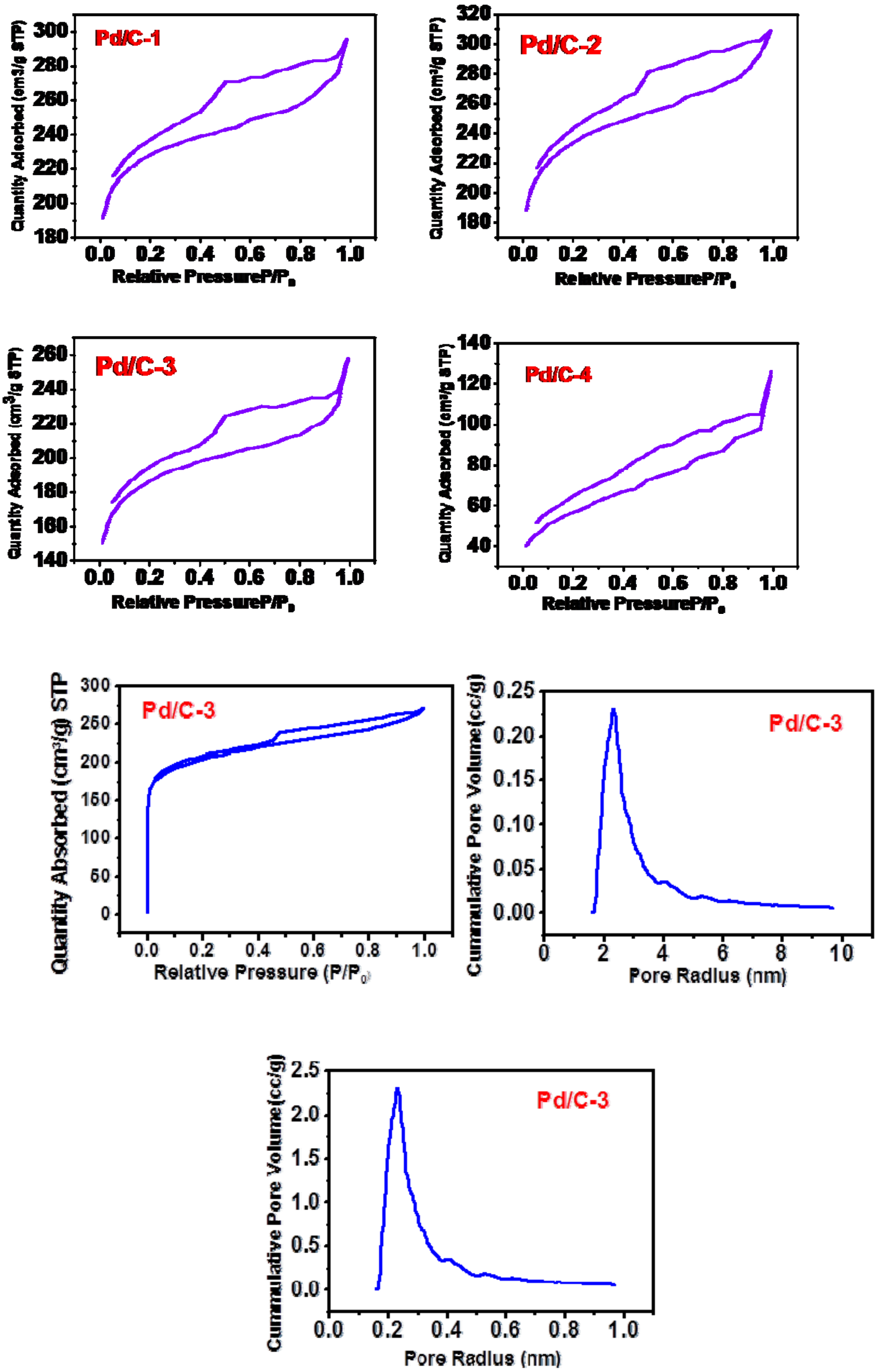
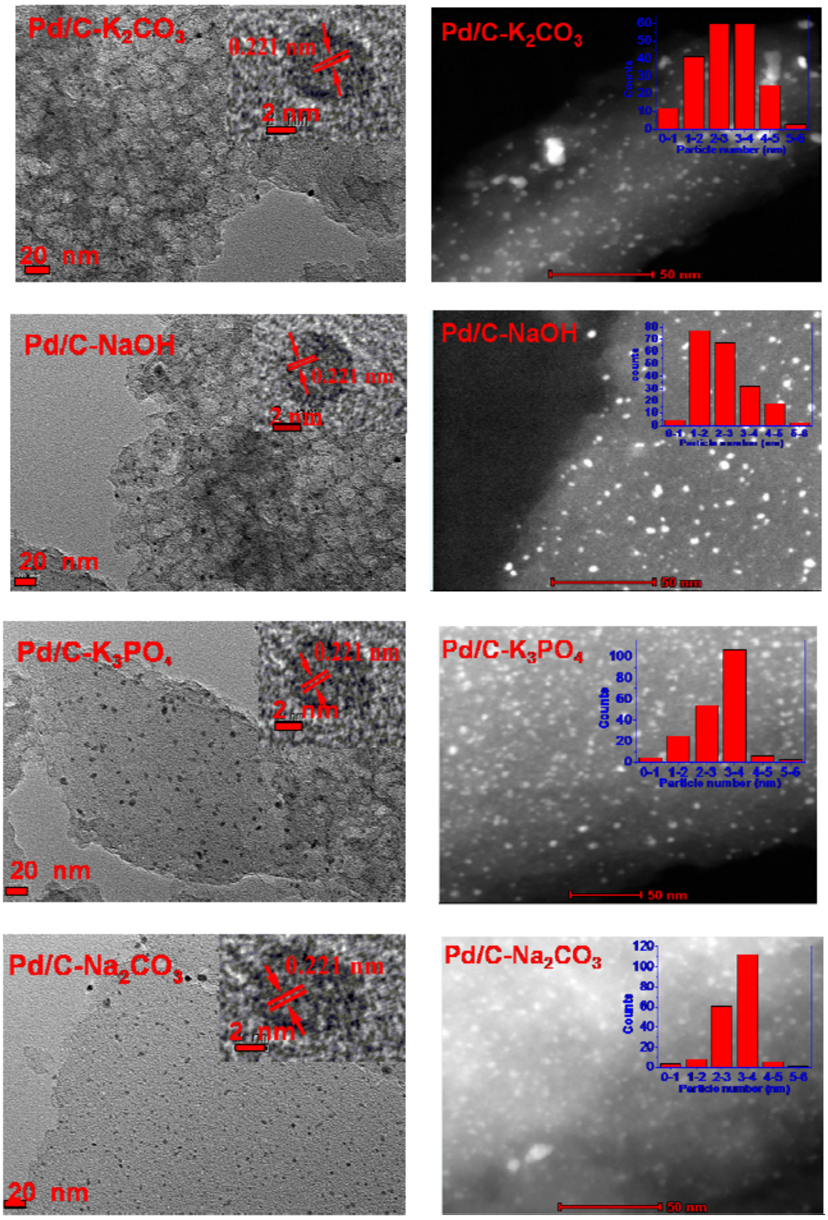


Fig. S2. BET pictures for Pd/C-1, Pd/C-2, Pd/C-3, Pd/C-4.


Pd/C-K2CO3
0.221 nm
2 nm
20 nm
Pd/C-K2CO3
Counts
Particle number (nm)
50 nm
Pd/C-NaOH
0.221 nm
2 nm
20 nm
Pd/C-NaOH
Particle number (nm)
50 nm
Pd/C-K3PO4
0.221 nm
2 nm
20 nm
Pd/C-K3PO4
Counts
Particle number (nm)
50 nm
Pd/C-Na2CO3
0.221 nm
2 nm
20 nm
Pd/C-Na2CO3
Counts
Particle number (nm)
50 nm

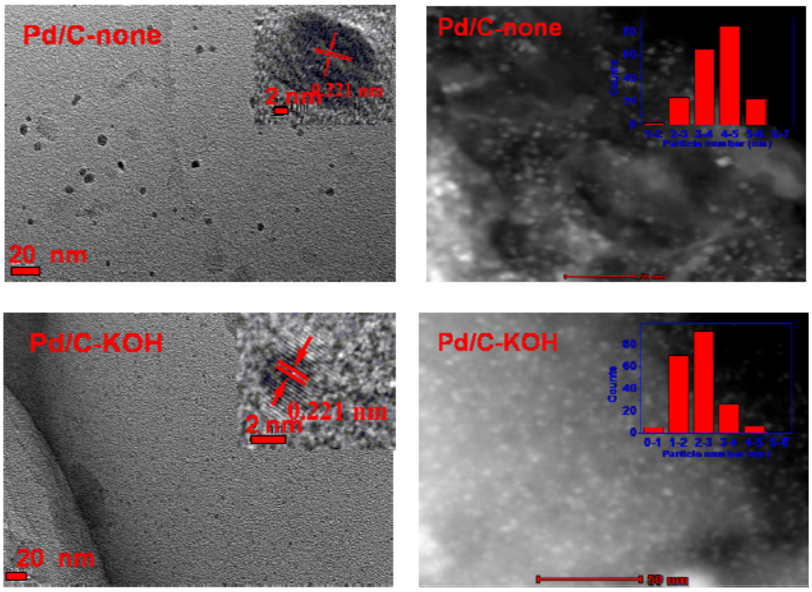
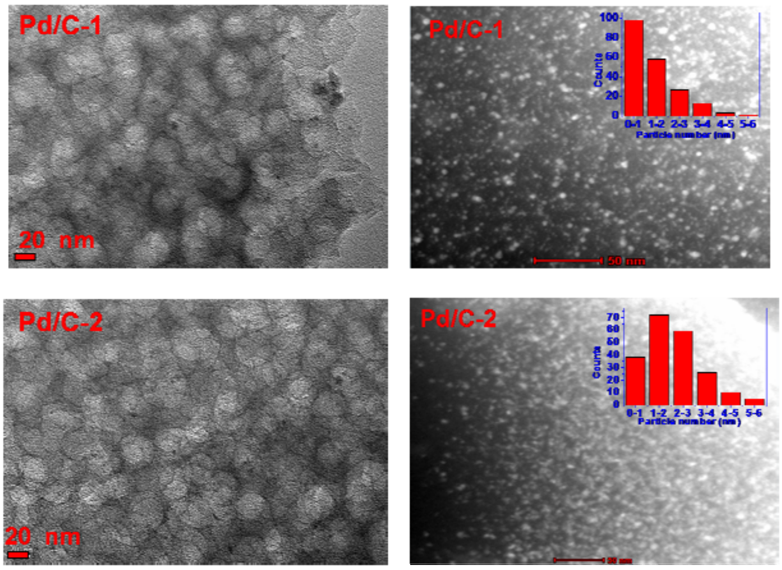


Fig. S3. TEM and HADDF-STEM images for Pd/C-K_2CO_3, Pd/C-NaOH, Pd/C-none, Pd/C-K_3PO_4, Pd/C-KOH and Pd/C-Na_2CO_3.



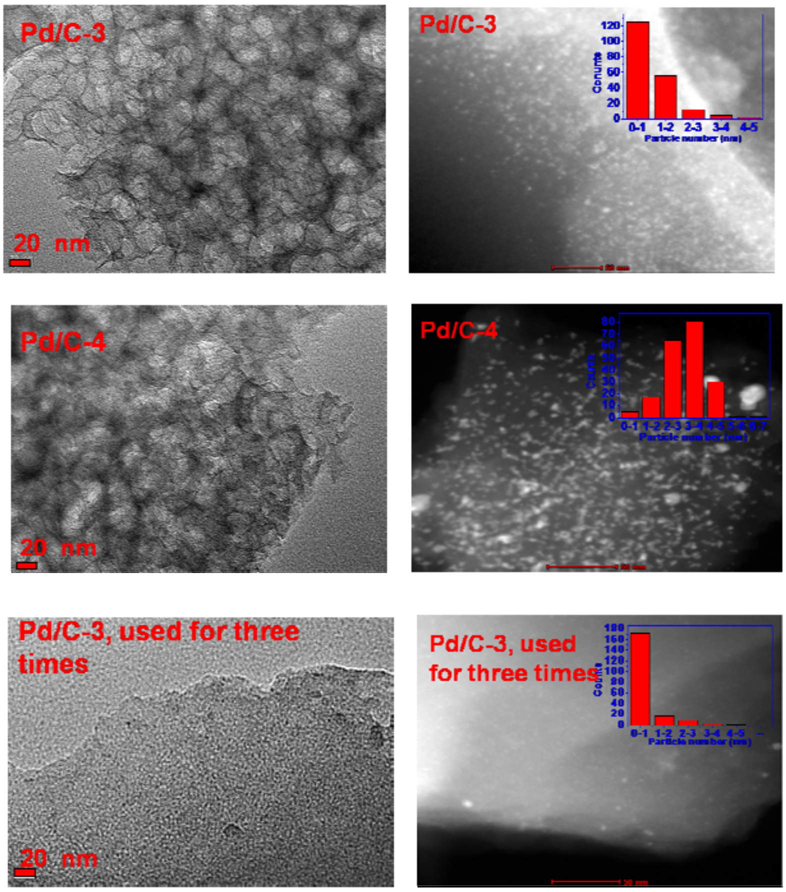


Fig. S4. TEM and HADDF-STEM pictures for Pd/C-1, Pd/C-2, Pd/C-3, Pd/C-4, Pd/C-3 and used for three times.

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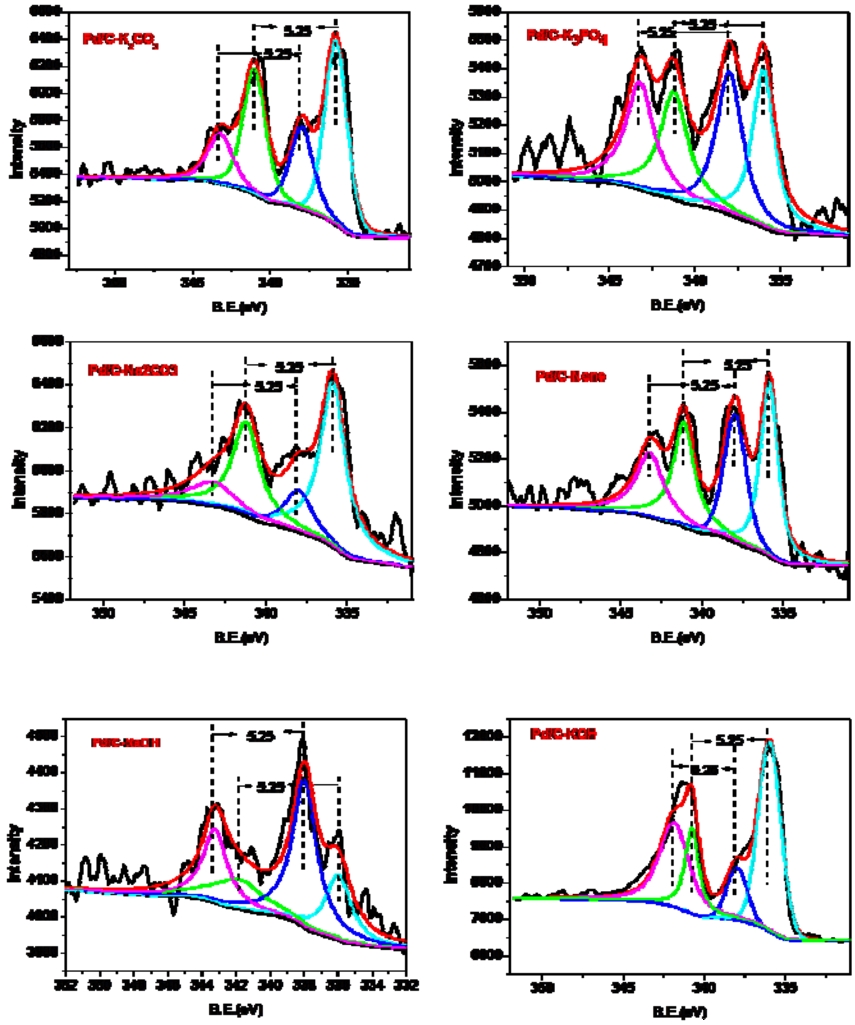


Fig. S5. XPS pictures for Pd/C-K_2CO_3, Pd/C-NaOH, Pd/C-none, Pd/C-K_3PO_4, Pd/C-KOH and Pd/C-Na_2CO_3.

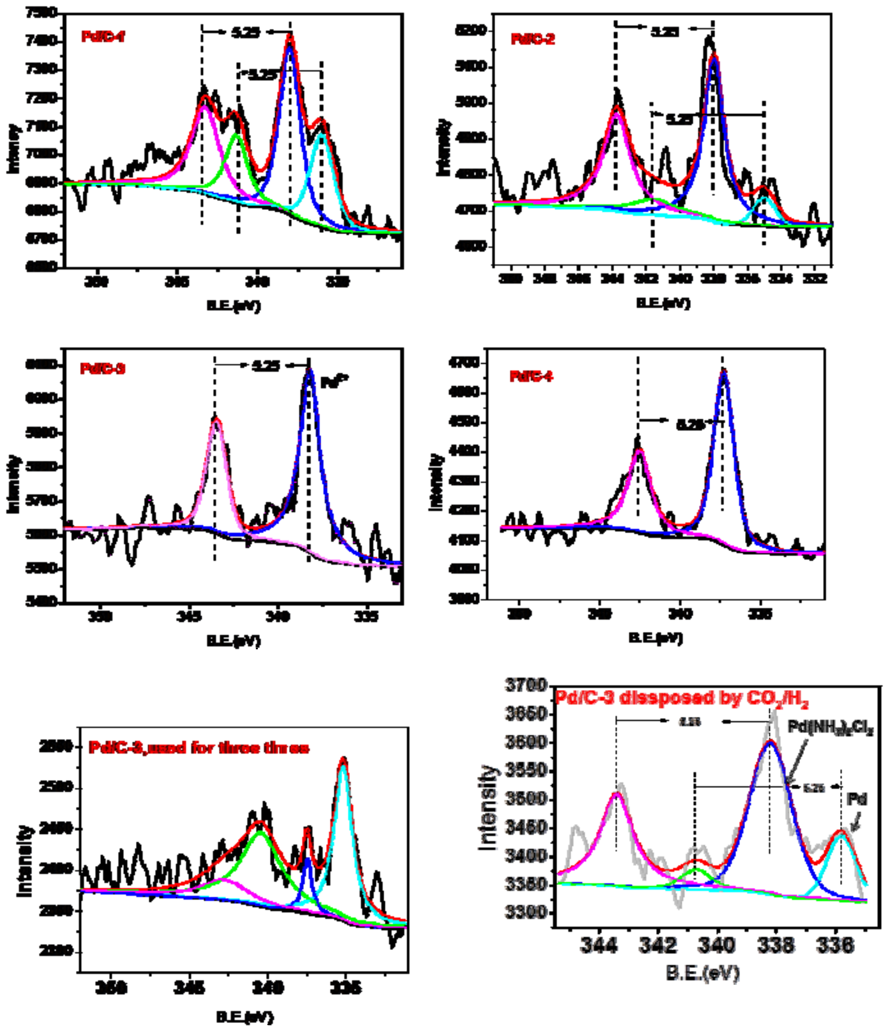


Fig. S6. XPS pictures for Pd/C-1, Pd/C-2, Pd/C-3, Pd/C-4, Pd/C-3 used for three times, and Pd/C-3 submitted to $CO_2 + H_2$

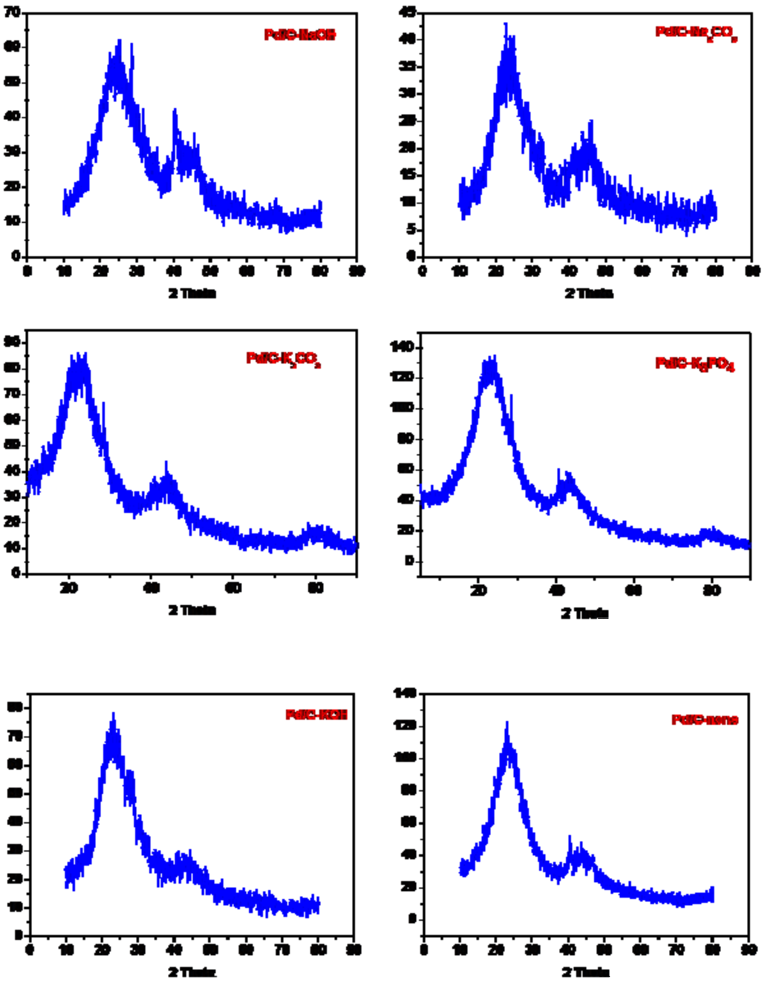


Fig. S7. XRD pictures for Pd/C-K_2CO_3, Pd/C-NaOH, Pd/C-none, Pd/C-K_3PO_4, Pd/C-KOH and Pd/C-Na_2CO_3.

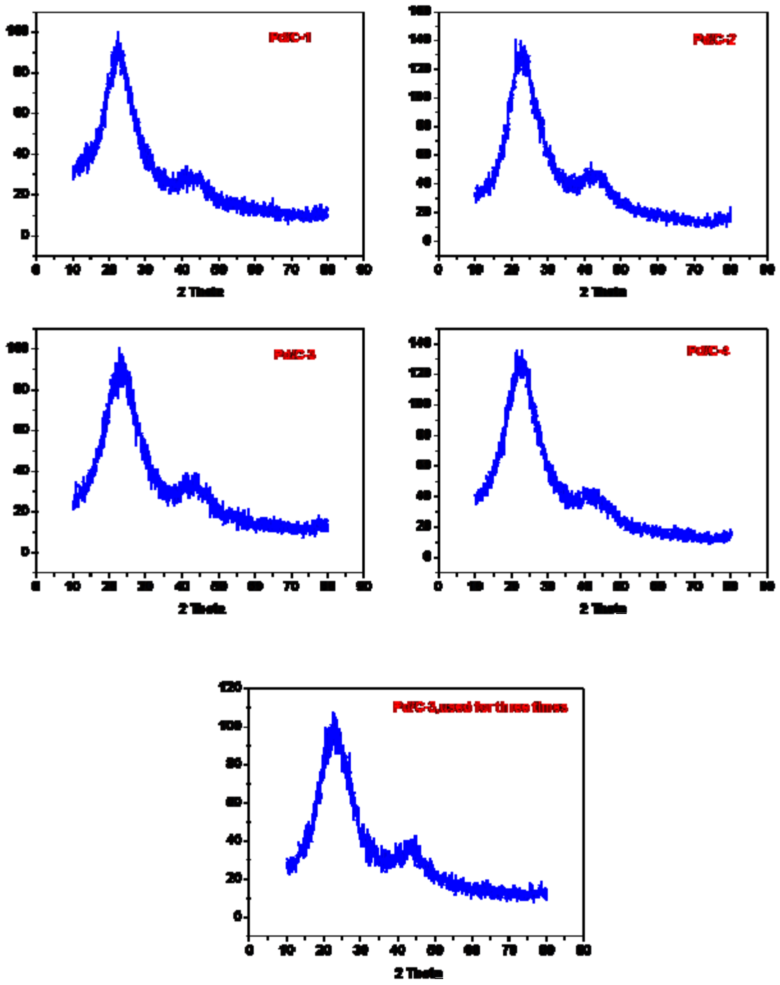


Fig. S 8.XRD pictures for Pd/C-1, Pd/C-2, Pd/C-3, Pd/C-4 and Pd/C-3 and used for three times.

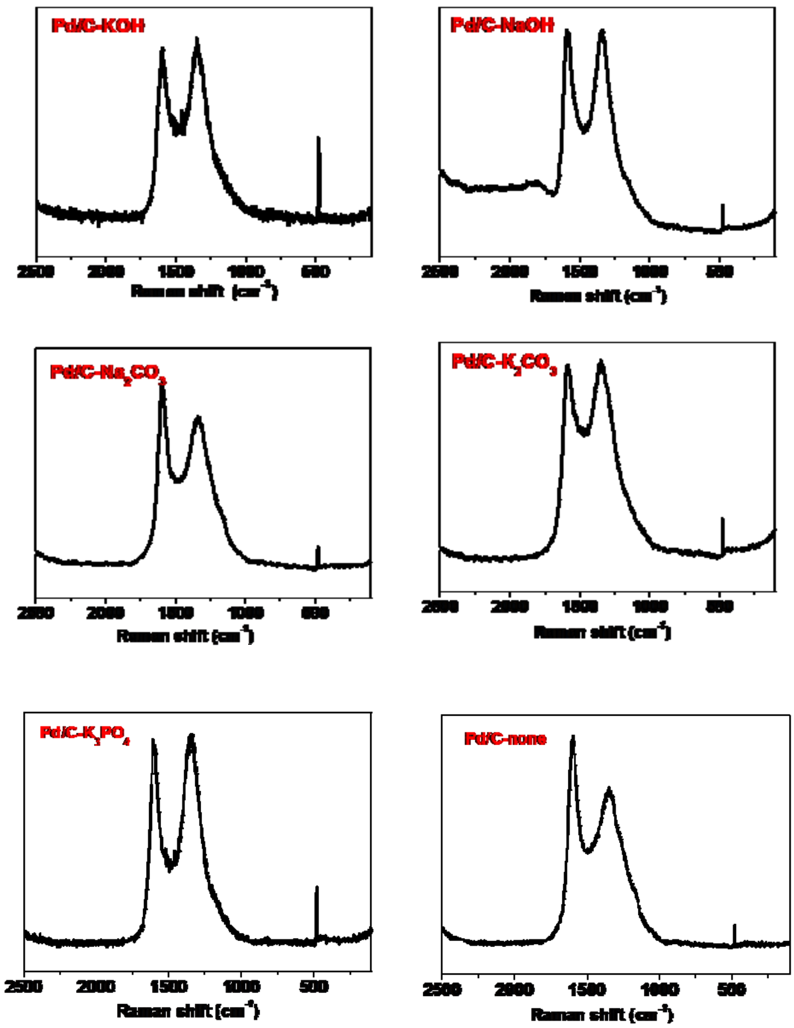


Fig. S9. Raman pictures for Pd/C-K_2CO_3, Pd/C-NaOH, Pd/C-none, Pd/C-K_3PO_4, Pd/C-KOH and Pd/C-Na_2CO_3.

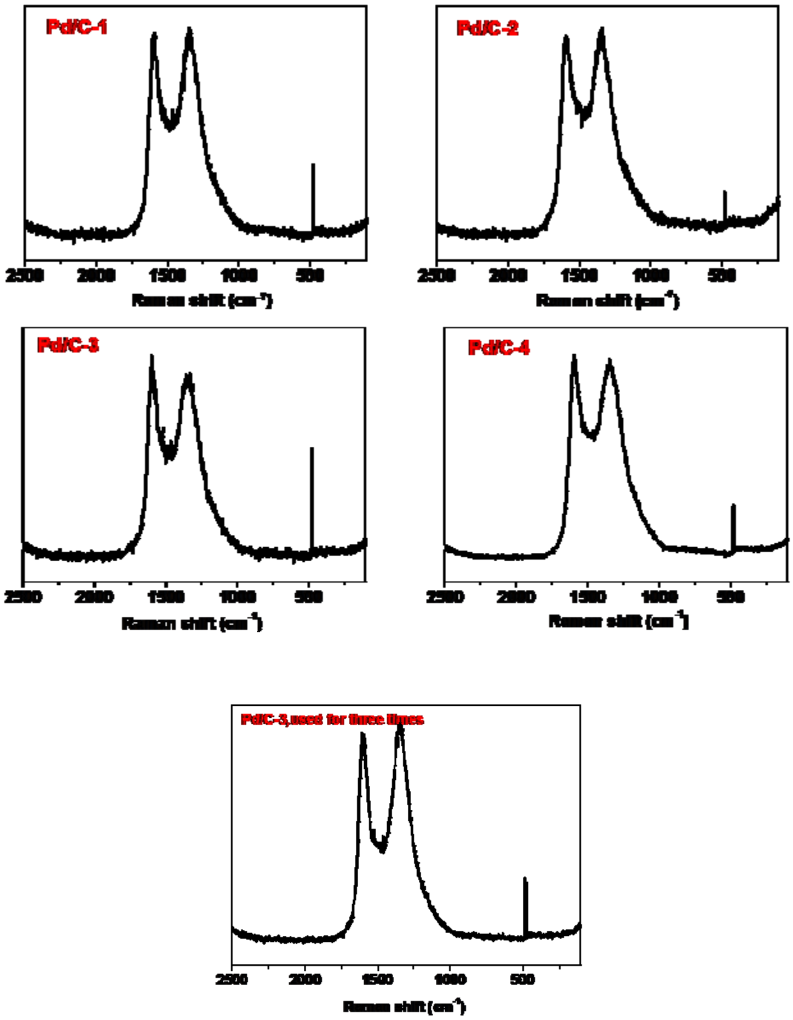


Fig. S10. Raman pictures for Pd/C-1, Pd/C-2, Pd/C-3, Pd/C-4, Pd/C-3 and used for three times.

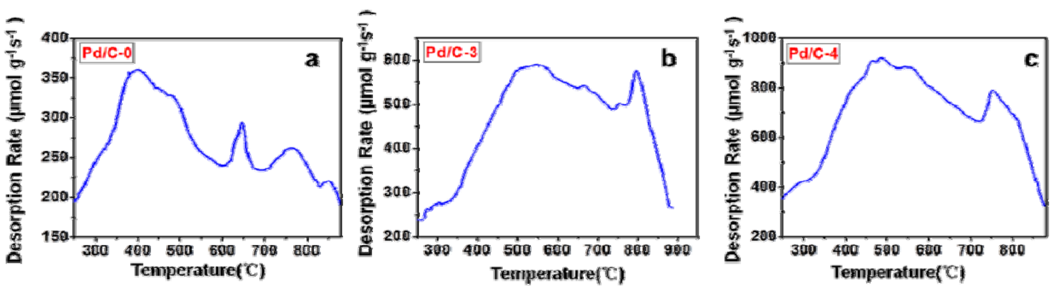


Fig. S11. CO_2-TPD profiles of a) Pd/C-0, b) Pd/C-3, c)Pd/C-4

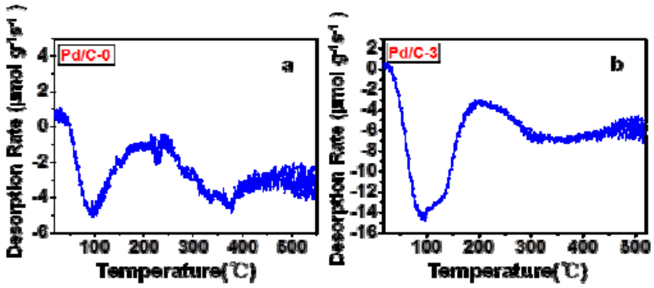


Fig. S12. NH_3-TPD profiles of a) Pd/C-0, b) Pd/C-3, c)Pd/C-4

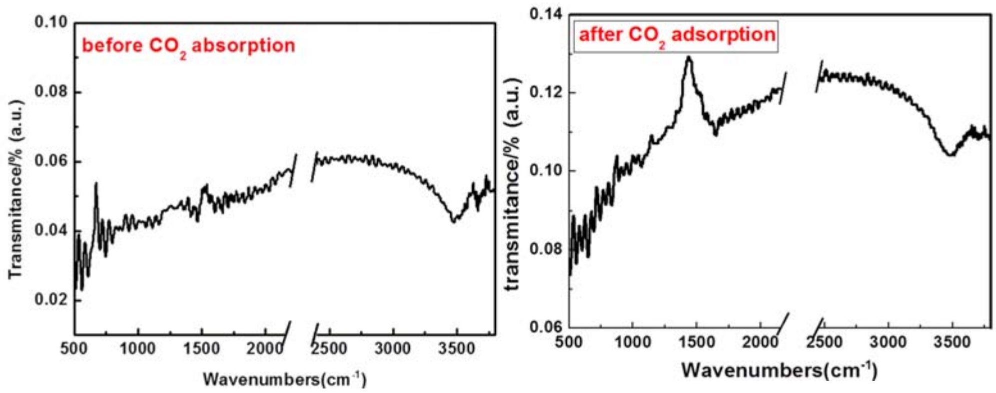
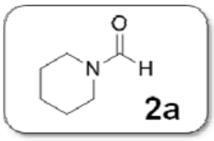
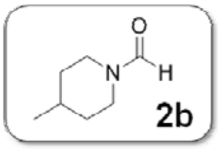


Fig. S13. CO_2 adsorption tests

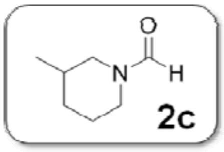
III.Characterization data for products



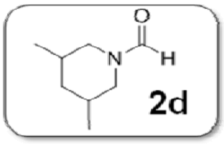
N-Formylpiperidine (2a): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 85 mg, 93% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 3.52–3.41 (m, 2H), 3.37–3.27 (m, 2H), 1.69 (td, J = 6.5, 2.1 Hz, 2H), 1.61–1.52 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.83, 46.84, 40.63, 26.57, 25.07, 24.70.



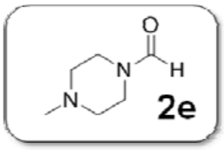
1-methylpiperidine-4-carbaldehyde (2b): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 93 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.56 (d, J = 4.1 Hz, 2H), 3.42–3.37 (m, 2H), 2.52–2.33 (m, 5H), 2.33–2.30 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.72, 55.28, 54.11, 46.03, 45.43, 39.74.



3-methylpiperidine-1-carbaldehyde (2c): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 97 mg, 73% yield. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.94 (d, J = 4.8 Hz, 1H), 4.15–3.94 (m, 1H), 3.55 (dd, J = 10.2, 2.8 Hz, 1H), 2.77–2.60 (m, 1H), 1.82 (dd, J = 13.1, 3.6 Hz, 1H), 1.7 –1.60 (m, 1H), 1.59–1.23 (m, 3H), 1.2 –1.13 (m, 1H), 0.89 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.99, 162.93, 54.41, 48.01, 47.63, 41.21, 34.04, 34.01, 33.26, 32.03, 26.95, 25.47, 19.12, 18.82.

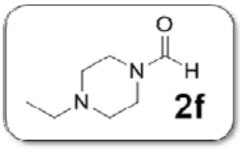


3,5-dimethylpiperidine-1-carbaldehyde (2d) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil,108mg, 84% yield. **^{1}H NMR** (400 MHz, CD_3OD) δ 8.07 (s, 1H), 4.40–4.20 (m, 1H), 3.76–3.62 (m, 1H), 2.69 (t, J = 12.2 Hz, 1H), 2.22 (t, J = 12.2 Hz, 1H), 1.92 (d, J = 13.2 Hz, 1H), 1.67–1.43 (m, 2H), 1.01 (dd, J = 6.6, 1.9 Hz, 6H), 0.97–0.86 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.30, 52.59, 46.16, 41.94, 32.17, 30.76, 17.80, 17.50.

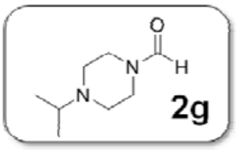


1-Formyl-4-methylpiperazine (2e) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 123 mg, 69% yield. **^{1}H NMR**

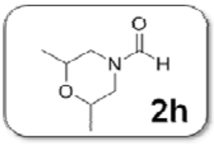
(400 MHz, CD_3OD) δ 8.02 (s, 1H), 3.58–3.51 (m, 2H), 3.49–3.43 (m, 2H), 2.51–2.44 (m, 2H), 2.43–2.39 (m, 2H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.09, 56.26, 55.10, 46.36, 46.11, 40.52.



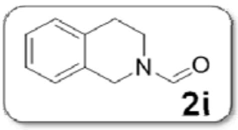
4-ethylpiperazine-1-carbaldehyde (2f) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 142 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.57 (s, 2H), 3.40 (dd, *J* = 6.7, 3.1 Hz, 2H), 2.47–2.38 (m, 6H), 1.09 (dd, *J* = 8.3, 6.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.70, 53.17, 52.25, 51.95, 45.58, 39.91, 11.82–11.21.



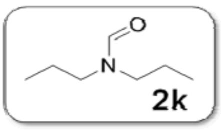
4-isopropylpiperazine-1-carbaldehyde (2g) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 165 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.56 (s, 2H), 3.38 (d, *J* = 3.9 Hz, 2H), 2.82–2.71 (m, 1H), 2.54–2.43 (m, 4H), 1.05 (dd, *J* = 6.5, 1.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.66, 54.67, 49.11, 47.87, 46.02, 40.34, 18.24.



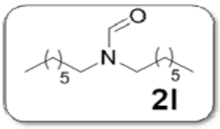
2,6-dimethylmorpholine-4-carbaldehyde (2h) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 142mg, 89% yield. **^{1}H NMR** (400 MHz, CD_3OD) δ 8.04 (s, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.17 (d, *J* = 13.0 Hz, 1H), 3.64–3.49 (m, 2H), 2.84 (dd, *J* = 13.2, 11.1 Hz, 1H), 2.42 (dd, *J* = 12.9, 10.9 Hz, 1H), 1.18 (dd, *J* = 6.1, 3.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.21, 74.11, 73.11, 52.47, 46.93, 19.18, 18.88.



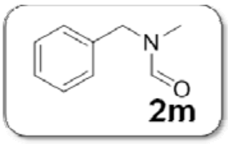
N-Formyl-1,2,3,4-tetrahydroisoquinoline(2i) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 165 mg, 83% yield.**^{1}H NMR** (400 MHz, CD_3OD) δ 8.18 (dd, *J* = 19.3, 3.1 Hz, 1H), 7.24–6.90 (m, 4H), 4.63–4.47 (m, 2H), 3.71–3.58 (m, 2H), 2.85 (dd, *J* = 11.2, 5.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.93, 163.45, 135.56, 135.14, 133.96, 132.82, 129.98, 128.07, 127.74, 127.67, 127.53, 126.98, 48.26, 44.51, 43.15, 39.25–39.16, 30.54–30.12, 28.79.



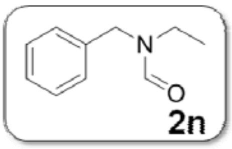
N,N-dipropylformamide (2k) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil,143 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 3.26 (dd, *J* = 8.3, 6.9 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 1.68–1.44 (m, 4H), 0.96 – 0.84 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.82, 49.17, 43.75, 21.81, 20.52, 11.31, 10.91.


2l

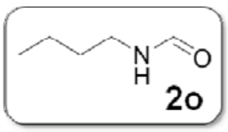
N,N-diheptylformamide: The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 212 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 3.33–3.24 (m, 2H), 3.19 (t, *J* = 7.1 Hz, 2H), 1.53 (s, 4H), 1.29 (s, 20H), 0.89 (dd, *J* = 6.3, 4.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.66, 47.46, 42.14, 31.77, 31.73, 29.30, 29.20, 29.15, 28.68, 27.32, 26.96, 26.48, 22.61, 14.04.


2m

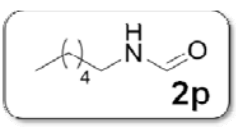
N-benzyl-N-methylformamide(2m): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 153 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.34 (dd, *J* = 14.1, 7.5 Hz, 5H), 4.38 (s, 2H), 2.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.79, 162.62, 136.03, 135.77, 128.91, 128.70, 128.25, 128.11, 127.65–127.62, 127.41 (s), 53.48, 47.76, 34.00–32.94, 29.45.


2n

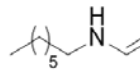
N-benzyl-N-ethyl-formamide(2n): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 161 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.20–7.12 (m, 4H), 4.69 (s, 2H), 3.65 (t, *J* = 5.9 Hz, 2H), 2.92–2.86 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.69, 161.18, 134.48, 133.57, 132.27, 131.81, 129.23, 128.94, 127.14 , 126.78, 126.67, 126.52, 125.91, 47.35, 43.27, 42.35, 38.03, 29.77, 27.96.


2o

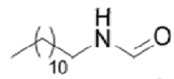
N-butylformamide (2o) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil,98 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 6.05 (s, 1H), 3.35–3.24 (m, 2H), 1.51 (dd, *J* = 14.9, 7.3 Hz, 2H), 1.37 (dd, *J* = 14.8, 7.5 Hz, 2H), 0.93 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.76, 161.35, 41.51, 37.89, 33.21, 31.51, 19.97, 19.51, 13.65, 13.54.


2p

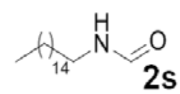
N-hexylformamide (2p) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 112 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 5.82 (s, 1H), 3.29 (td, J = 7.5, 1.8 Hz, 2H), 1.55–1.49 (m, 2H), 1.30 (s, 6H), 0.89 (d, J = 1.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.19, 38.20, 31.39, 29.47, 26.49, 22.51, 13.95.


2q

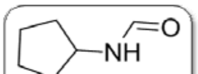
N-heptylformamide (2q) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 131 mg, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 5.84 (s, 1H), 3.29 (d, J = 6.2 Hz, 2H), 1.54–1.51 (m, 2H), 1.29 (d, J = 10.0 Hz, 8H), 0.90–0.86 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.23, 38.21, 31.71, 29.50, 28.89, 26.79, 22.55, 14.03.


2r

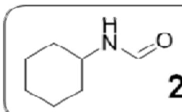
N-decylformamide(2r) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the White solid, 187 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 5.68 (s, 1H), 3.31 (m, J = 13.4, 6.7 Hz, 2H), 1.56–1.51 (m, 2H), 1.27 (s, 18H), 0.89 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.15, 65.32, 38.16–37.69, 31.90, 29.52, 29.32, 29.23, 26.84, 22.67, 14.08, 11.09.


2s

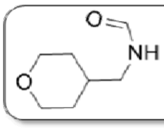
N-heptadecylformamide (2s) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the White solid, 237 mg, 83% yield.**^{1}H NMR** (400 MHz, CD_3OD) δ 7.96 (s, 1H), 3.15 (t, J = 7.0 Hz, 2H), 1.45 (d, J = 6.8 Hz, 2H), 1.25 (d, J = 12.2 Hz, 26H), 0.85 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.68, 38.99, 33.07, 30.77, 30.70, 30.67, 30.47, 30.36, 27.94, 23.73, 14.43.


2t

N-cyclopentylformamide (2t) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 111 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 5.80 (s, 1H), 4.64–3.93 (m, 1H), 1.99 (dd, J = 7.8, 3.7 Hz, 2H), 1.79–1.55 (m, 4H), 1.42 (dd, J = 12.4, 6.3 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.82, 49.97, 33.07, 23.66.

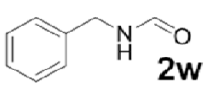

2u

N-cyclohexylformamide (2u) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 126 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 6.60 (s, 1H), 3.93–3.64 (m, 1H), 1.90 (d, *J* = 12.2 Hz, 2H), 1.72 (d, *J* = 13.5 Hz, 2H), 1.65–1.27 (m, 4H), 1.20 (d, *J* = 11.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.79, 160.62, 51.13, 47.03, 34.52, 32.83, 25.35, 24.71.



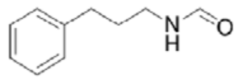
2v

N-((tetrahydro-2H-pyran-4-yl)methyl)formamide (2v): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 139 mg, 78% yield. **^{1}H NMR** (400 MHz, CD_3OD) δ 8.05 (s, 1H), 3.92 (dd, *J* = 10.9, 4.3 Hz, 2H), 3.35 (dd, *J* = 11.7, 1.8 Hz, 2H), 3.11 (d, *J* = 6.8 Hz, 2H), 1.82–1.67 (m, 1H), 1.62 (dd, *J* = 13.1, 1.6 Hz, 2H), 1.27 (qd, *J* = 12.1, 4.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.84, 68.59, 44.54, 36.34, 31.66.



2w

N-benzylformamide(2w) : The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 134 mg, 91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.38–7.26 (m, 3H), 7.21 (d, *J* = 11.1 Hz, 2H), 7.02–6.47 (m, 1H), 4.38 (d, *J* = 5.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.33–159.38, 137.71, 128.71, 127.69, 127.56, 42.05.



2x

N-(3-phenylpropyl) formamide (2x): The title compound was prepared according to the general procedure and purified by columnchromatography to give the yellow oil, 168mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.30 (dd, *J* = 11.9, 4.4 Hz, 2H), 7.2–7.17 (m, 3H), 5.77 (s, 1H), 3.35 (q, *J* = 6.7 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.88 (dd, *J* = 14.8, 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.26, 141.19, 128.52, 128.36, 126.11, 37.83, 33.19, 31.12.

Ⅳ.NMR spectra of all products

Figure S14. ^{1}HNMR of **2a**

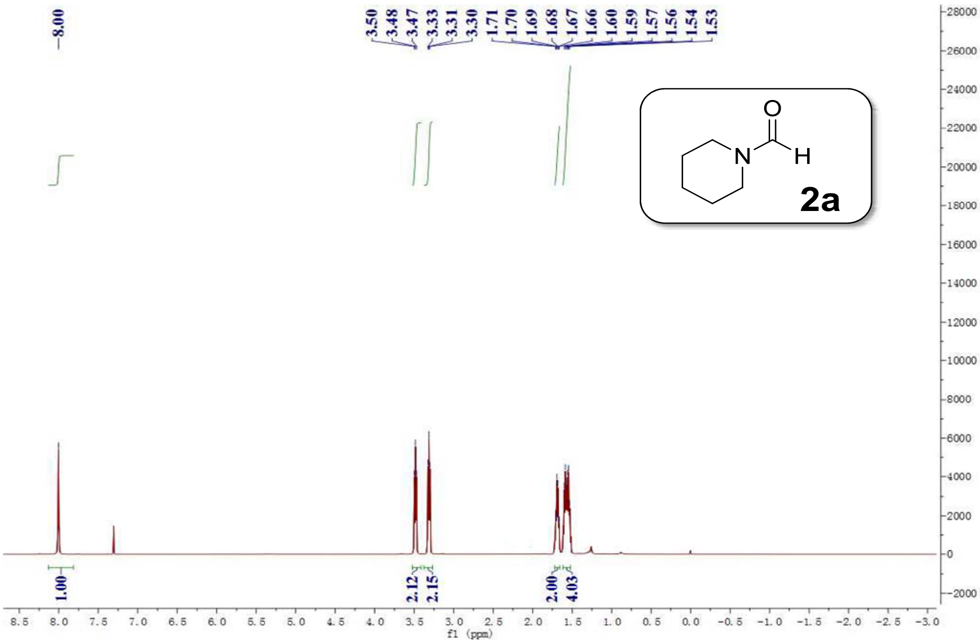


Figure S15. ^{13}CNMR of **2a**

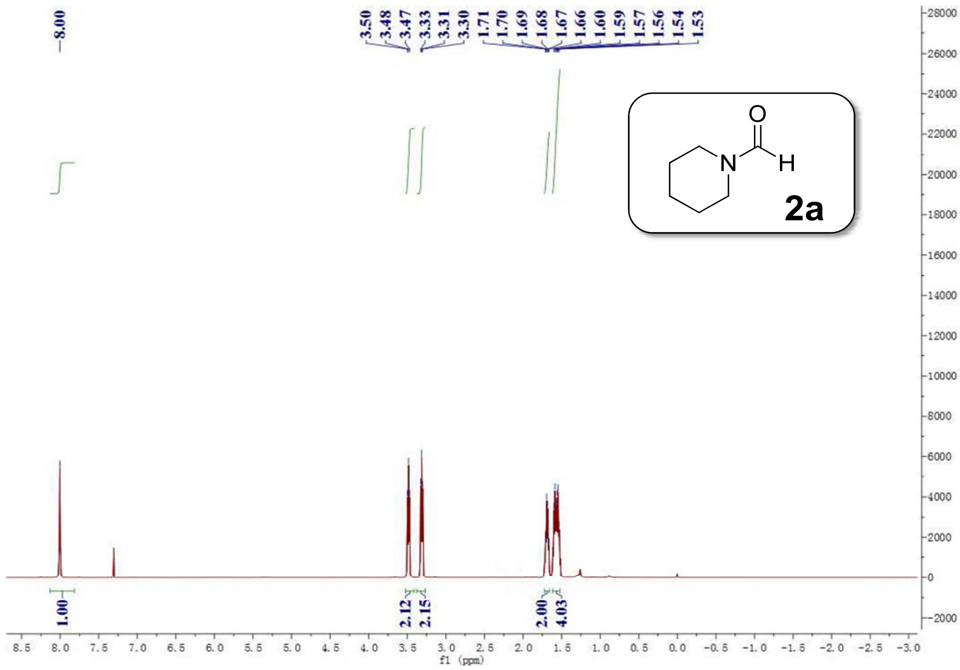


Figure S16. ^{1}HNMR of **2b**

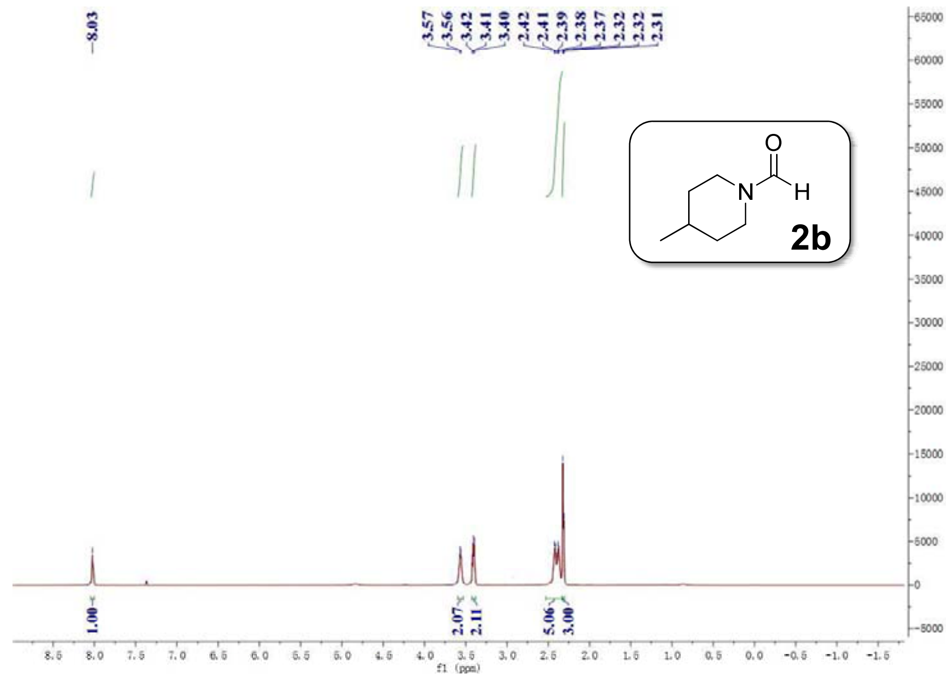


Figure S17. ^{13}CNMR of **2b**

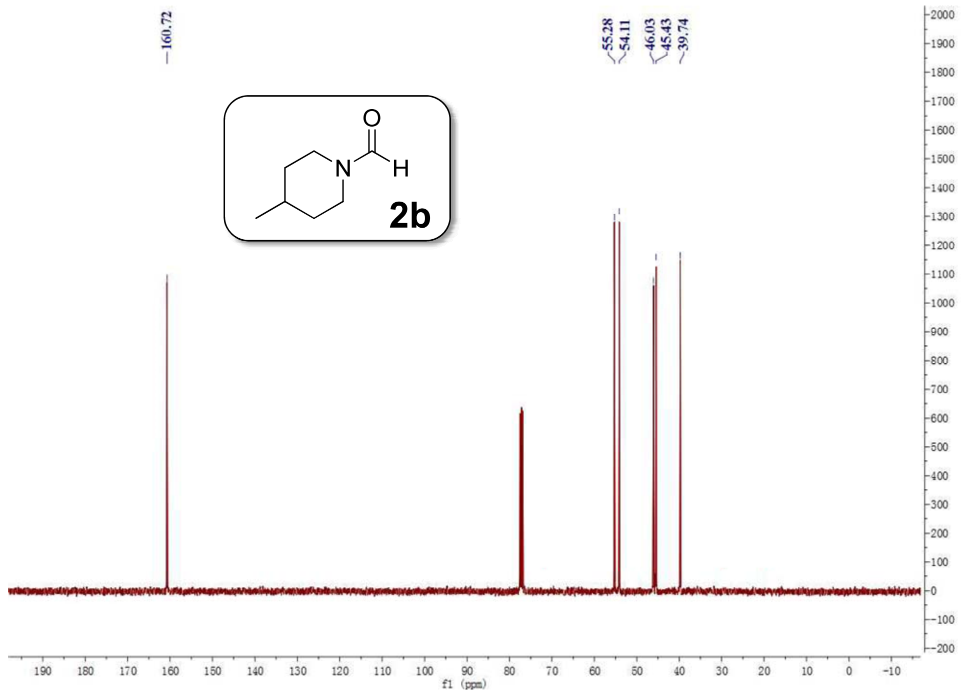


Figure S18. ^{1}HNMR of **2c**

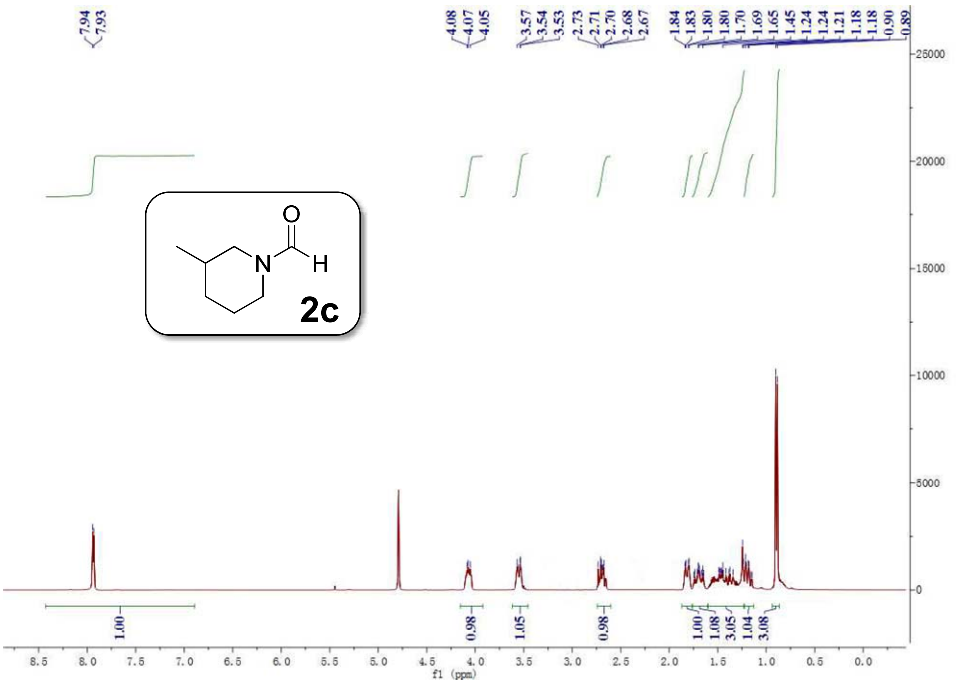


Figure S19. ^{13}CNMR of **2c**

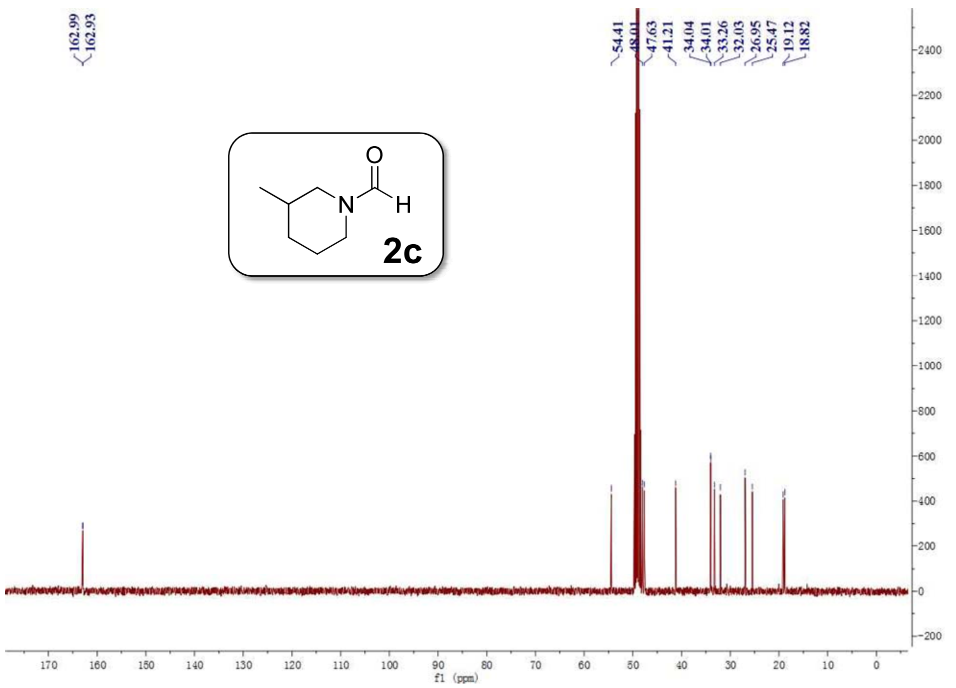


Figure S20. ^{1}HNMR of **2d**

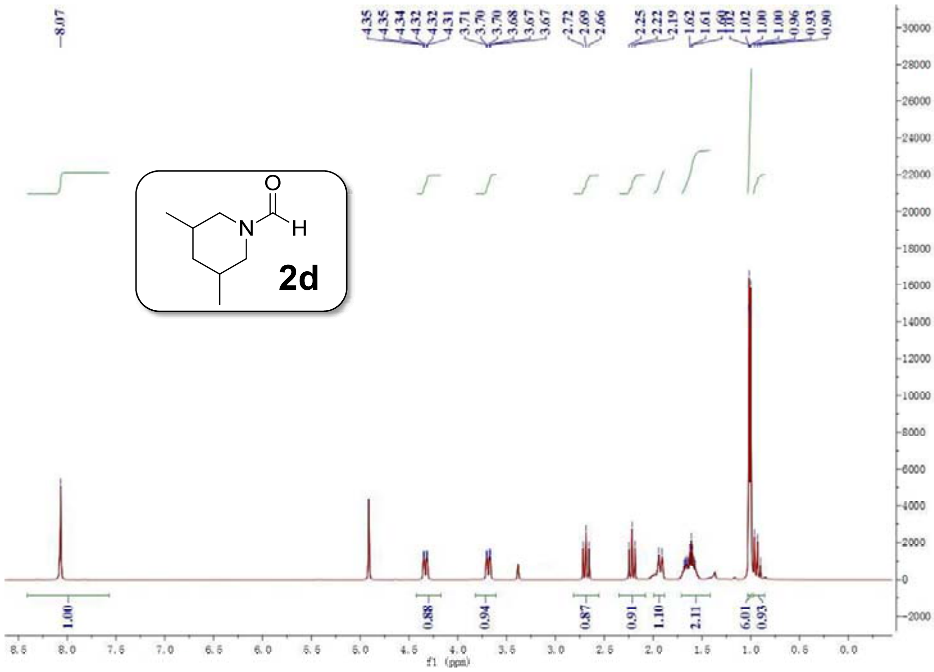


Figure S21. ^{13}CNMR of **2d**

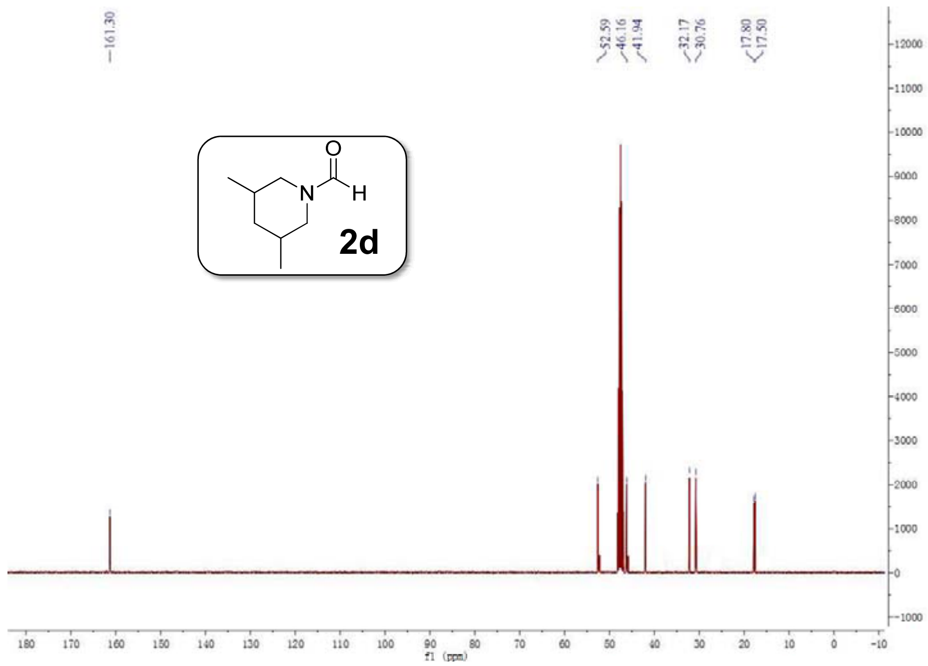


Figure S22. ^{1}HNMR of **2e**

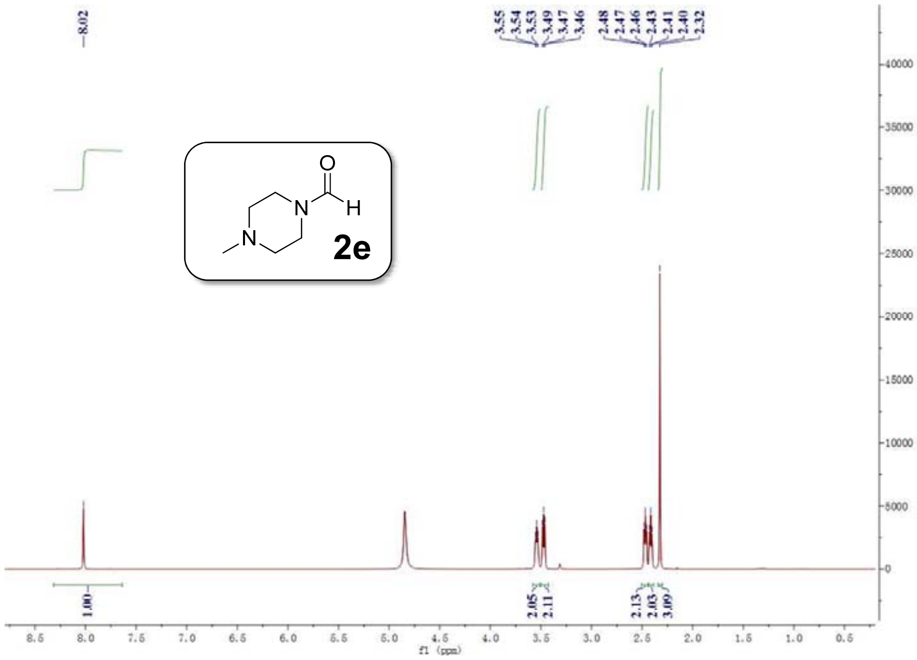


Figure S23. ^{13}CNMR of **2e**

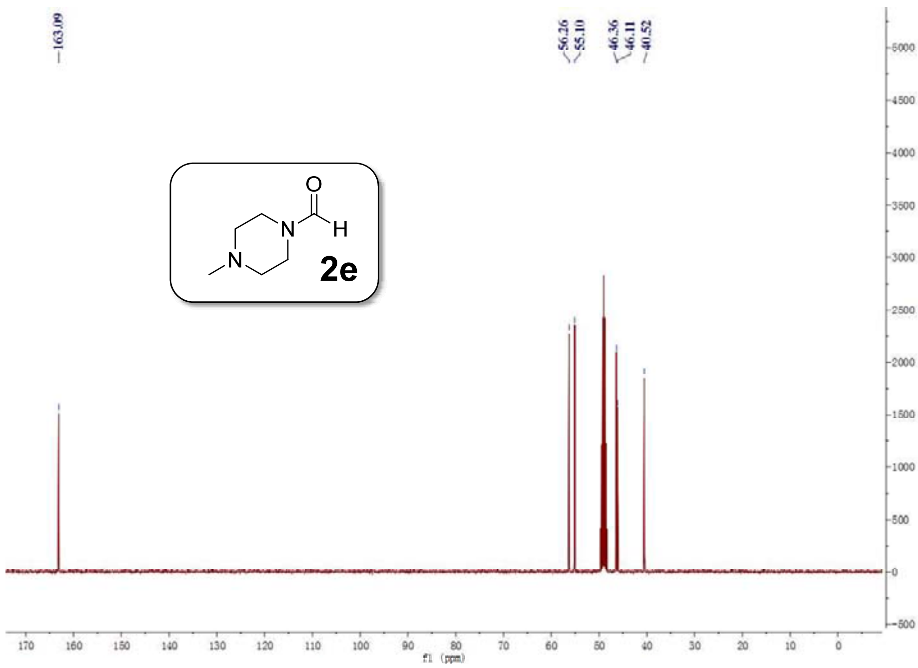


Figure S24. ^{1}HNMR of **2f**

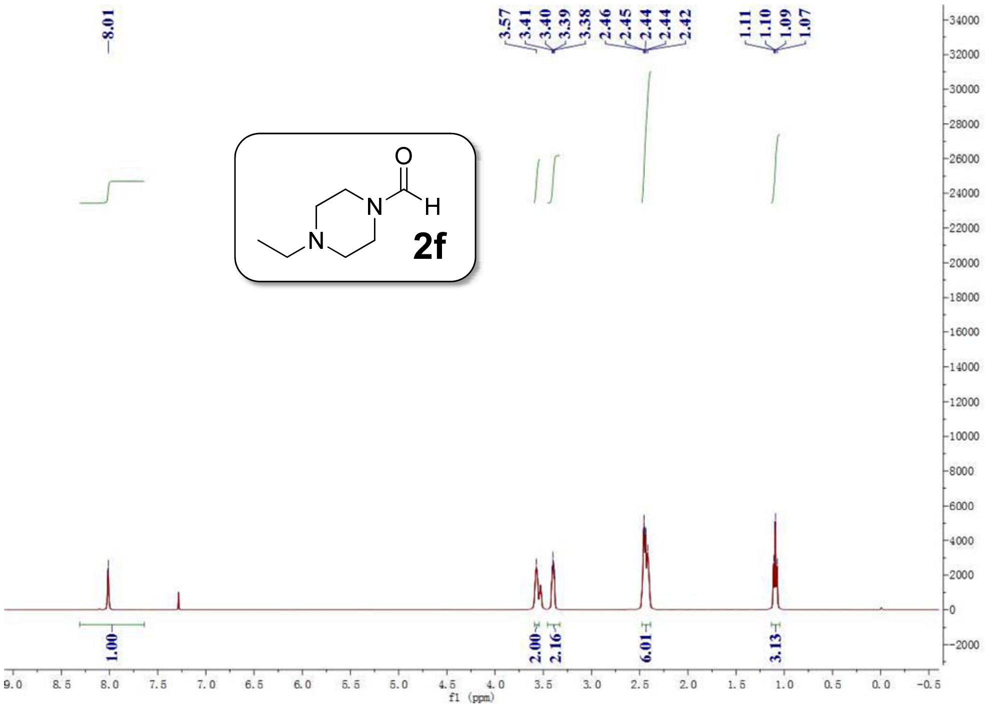


Figure S25. ^{13}CNMR of **2f**

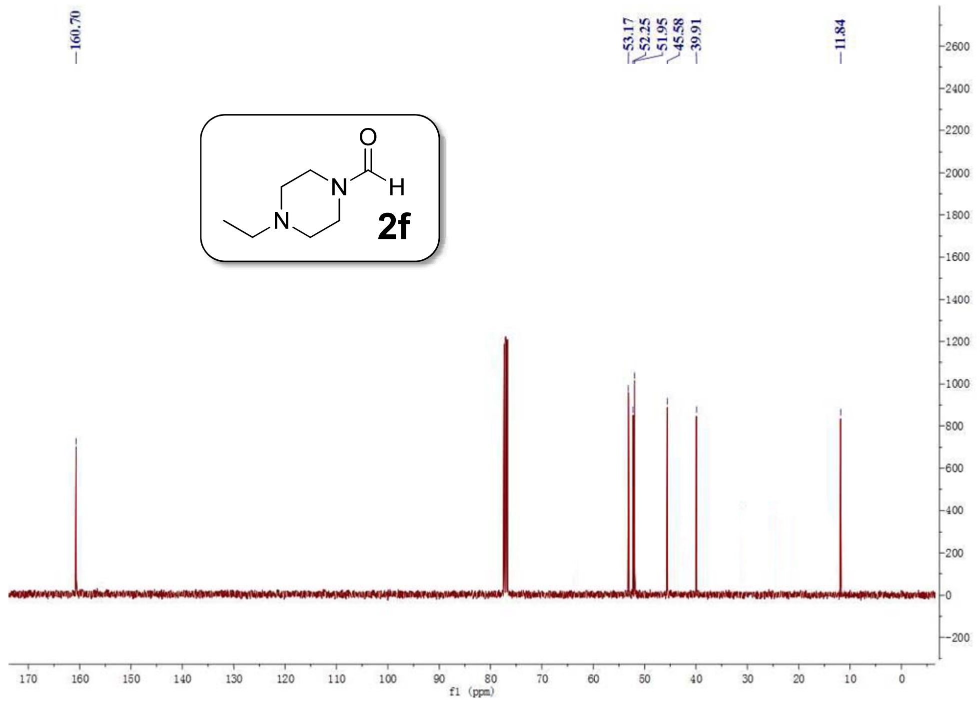


Figure S26. ^{1}HNMR of **2g**

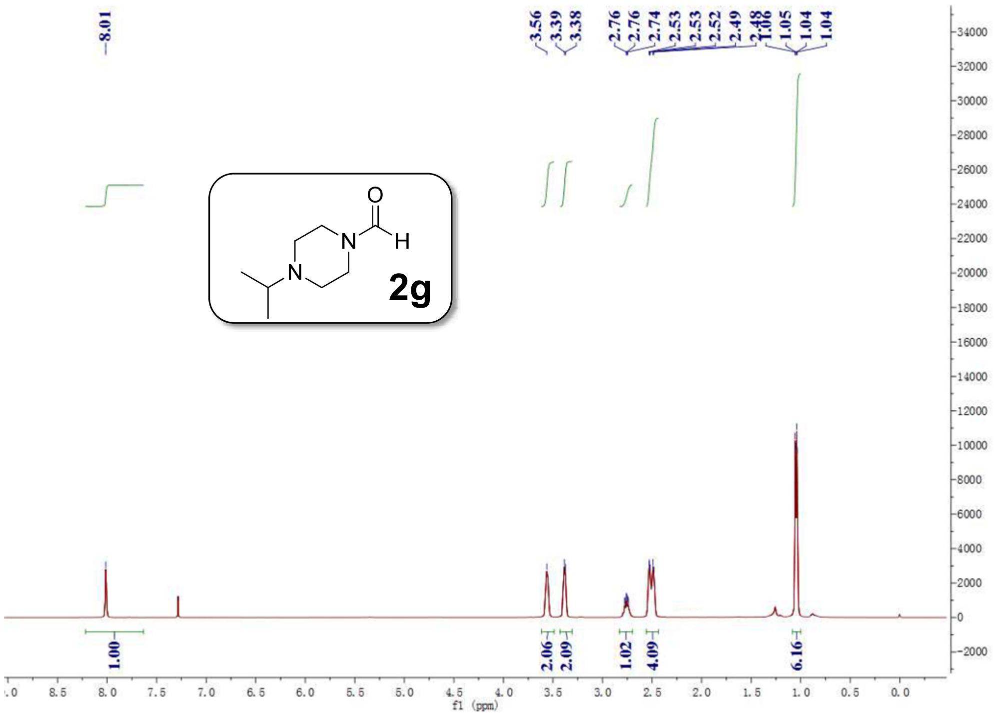


Figure S27. ^{13}CNMR of **2g**

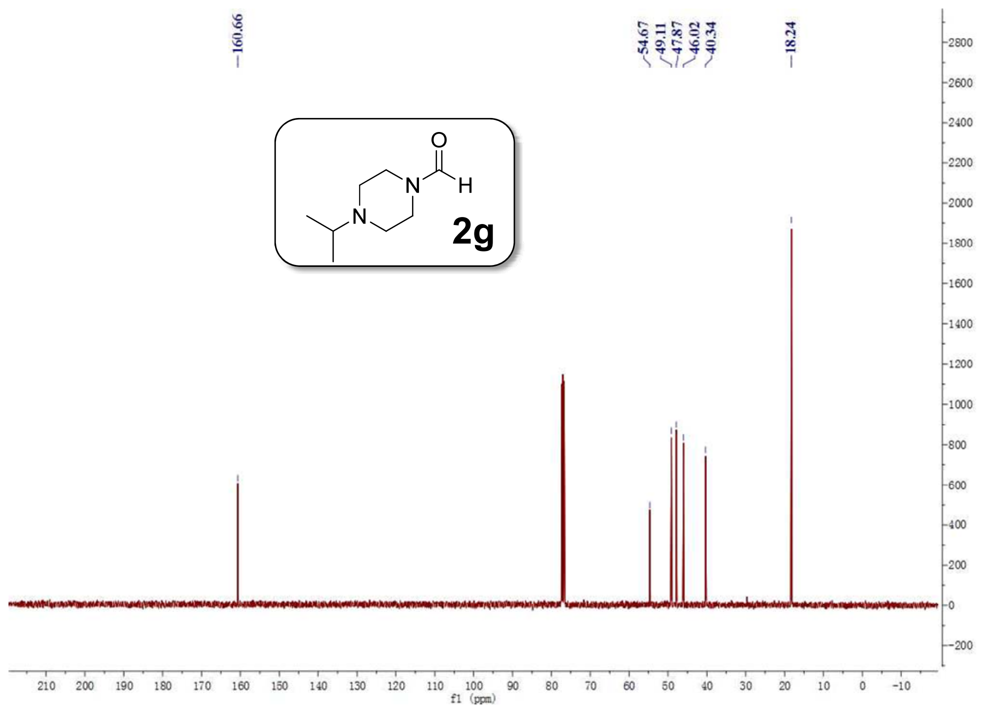


Figure S28. ^{1}HNMR of **2h**

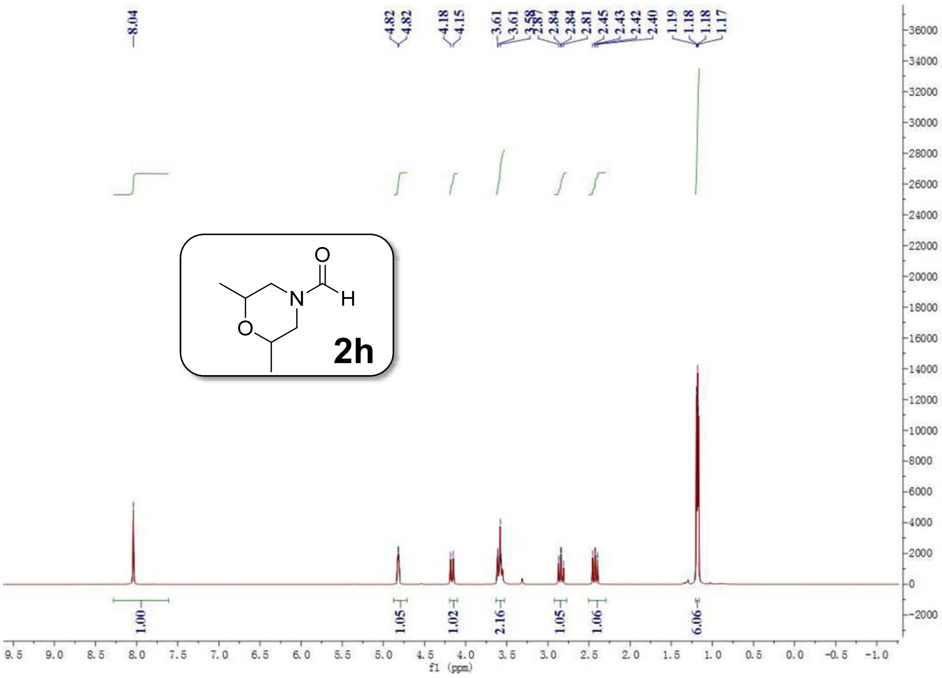


Figure S29. ^{13}CNMR of **2h**

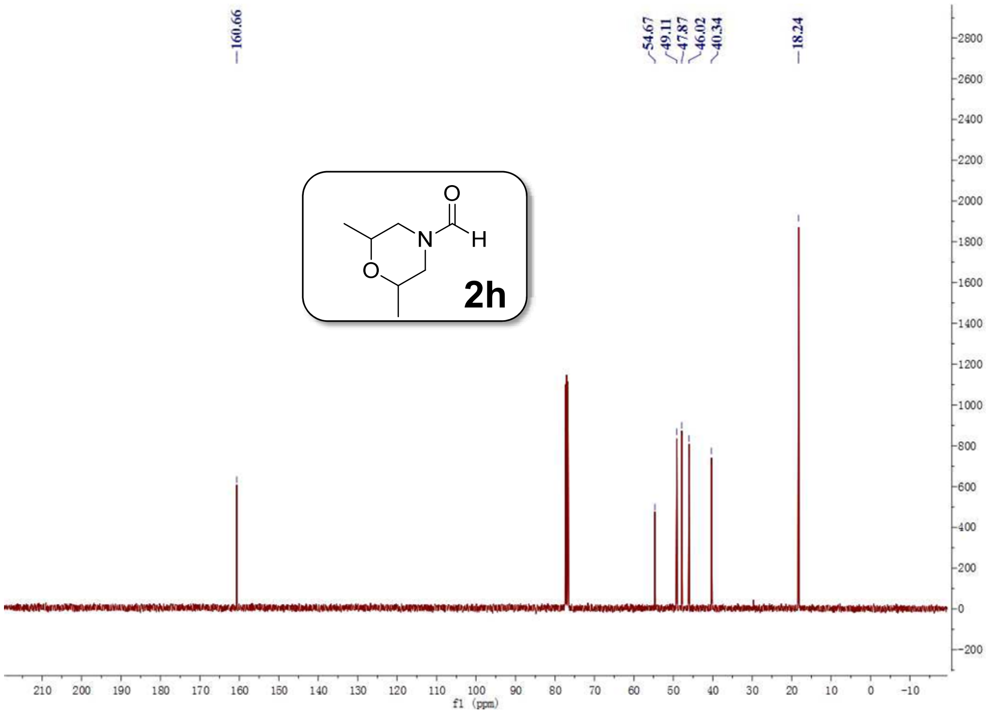


Figure S30. ^{1}HNMR of **2i**

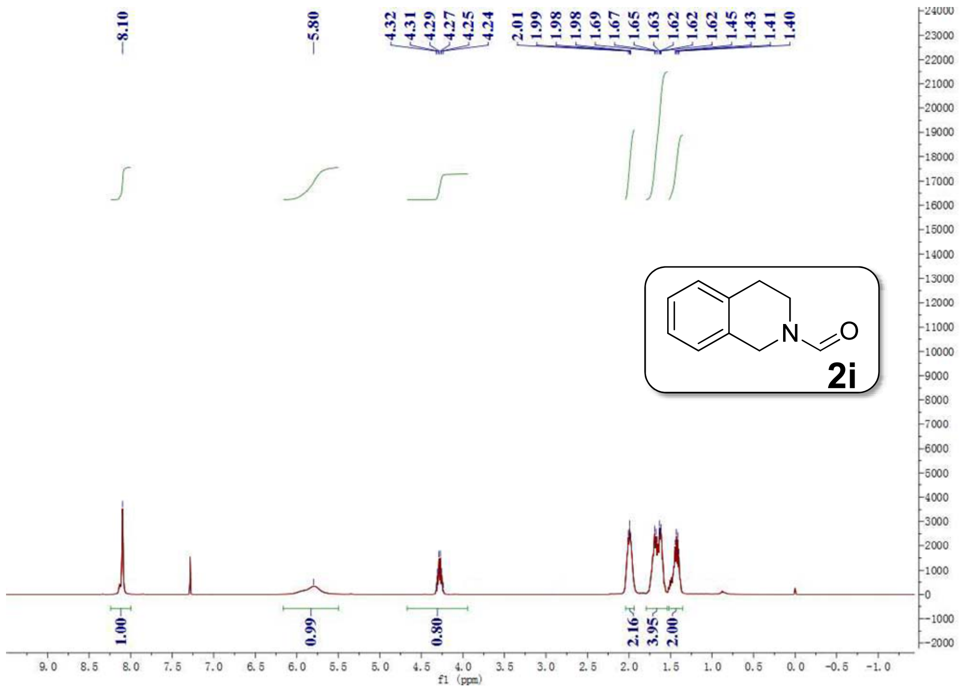


Figure S31. ^{13}CNMR of **2i**

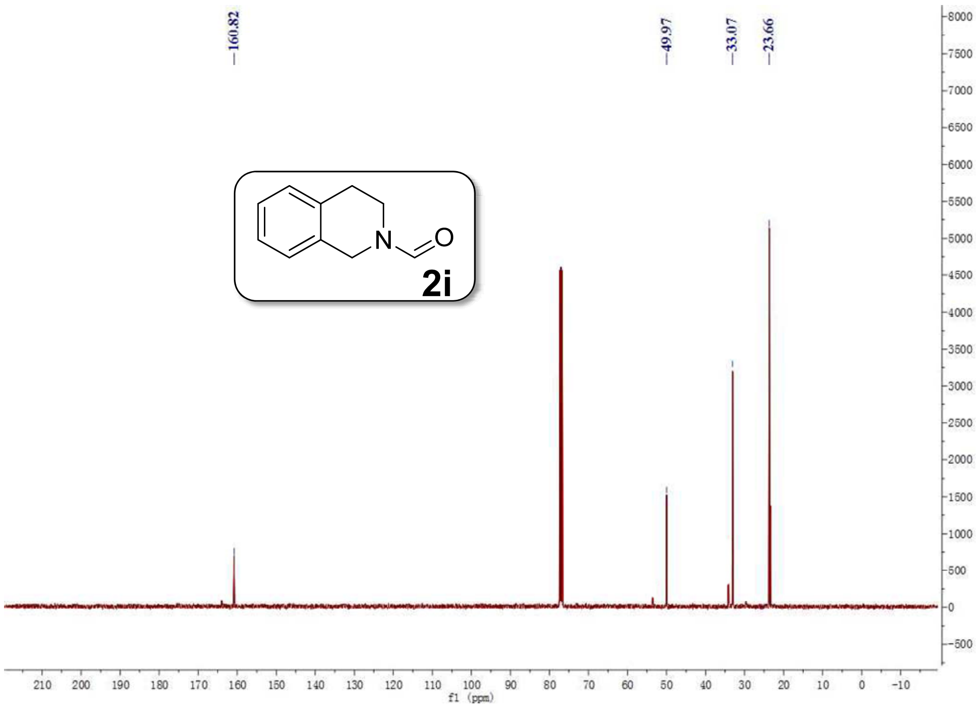


Figure S32. ^{1}HNMR of **2k**

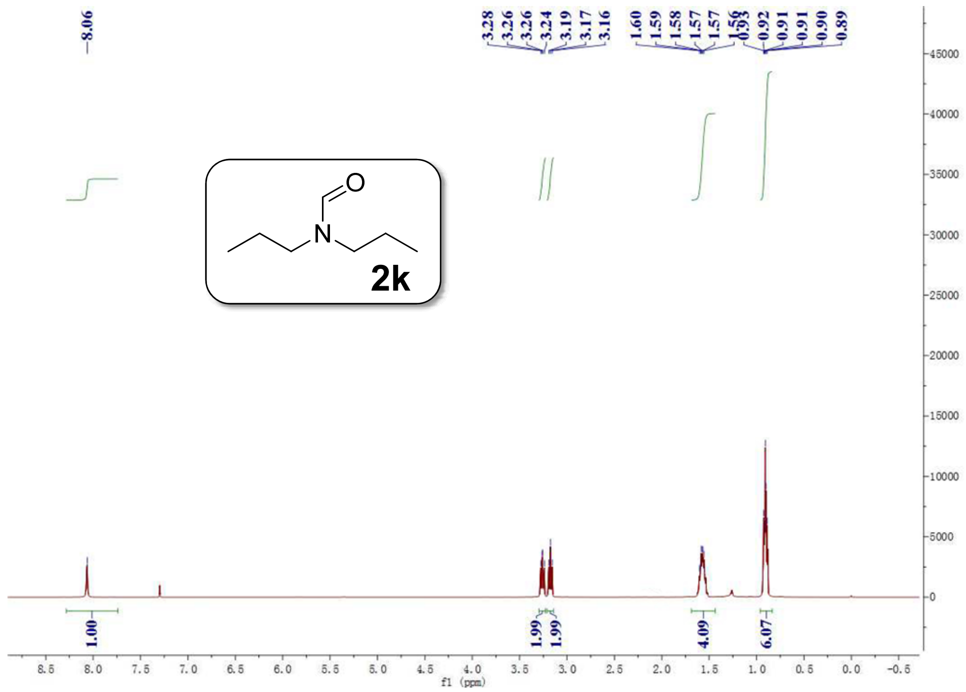


Figure S33. ^{13}CNMR of **2k**

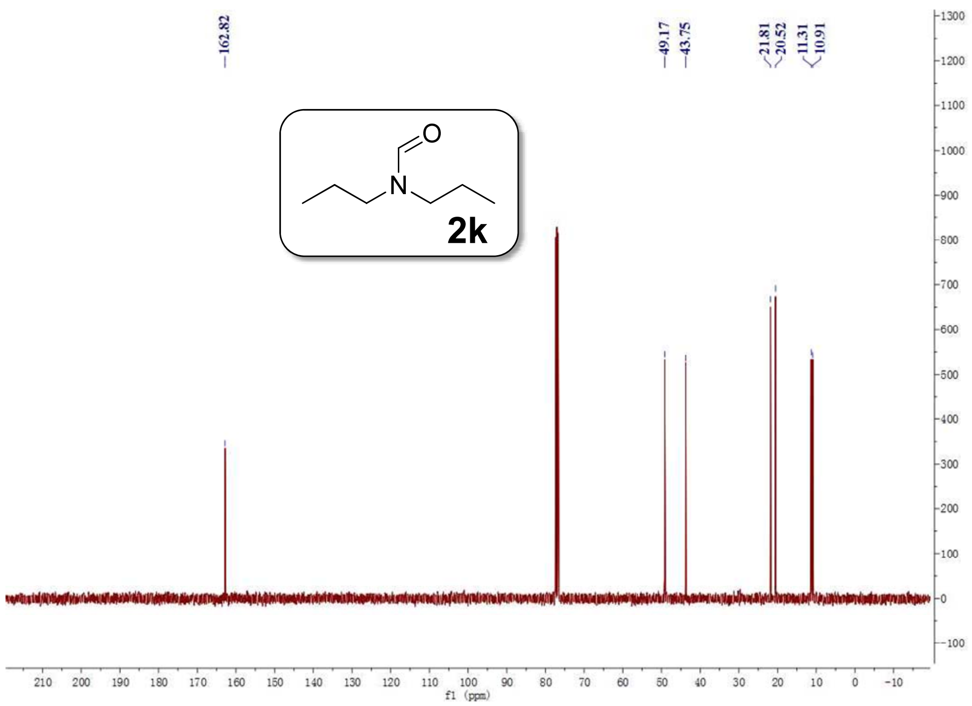


Figure S34. ^{1}HNMR of **2l**

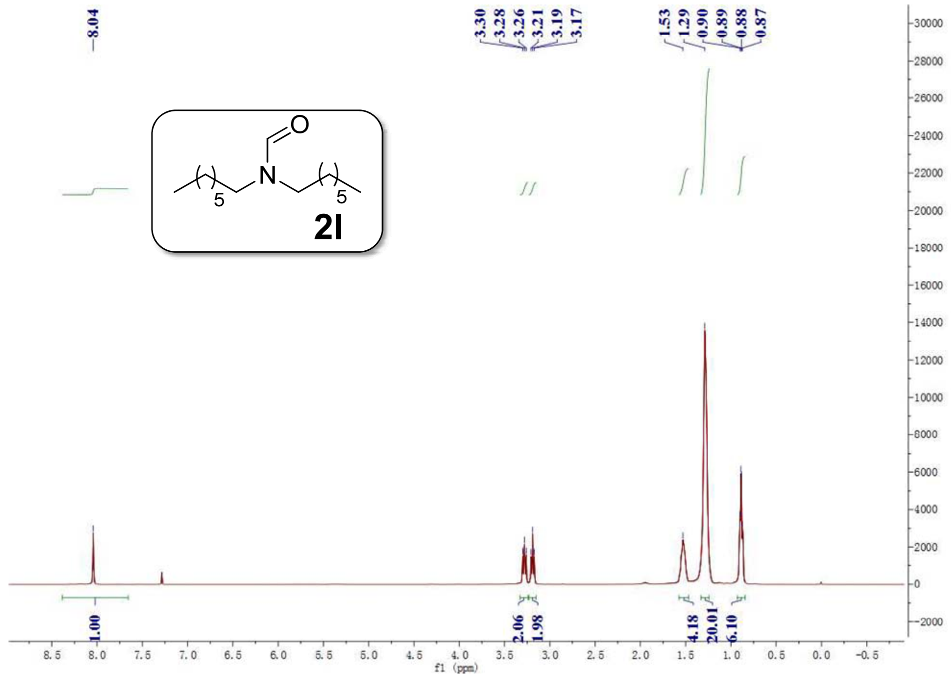


Figure S35. ^{13}CNMR of **2l**

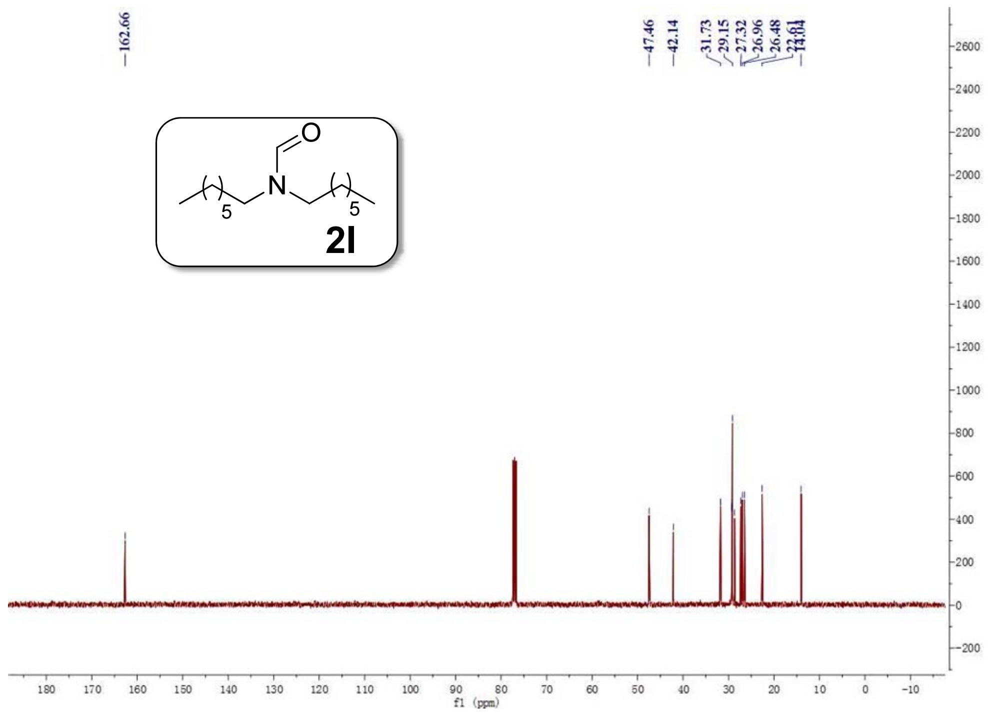


Figure S36. ^{1}HNMR of **2m**

Figure S37. ^{13}CNMR of **2m**

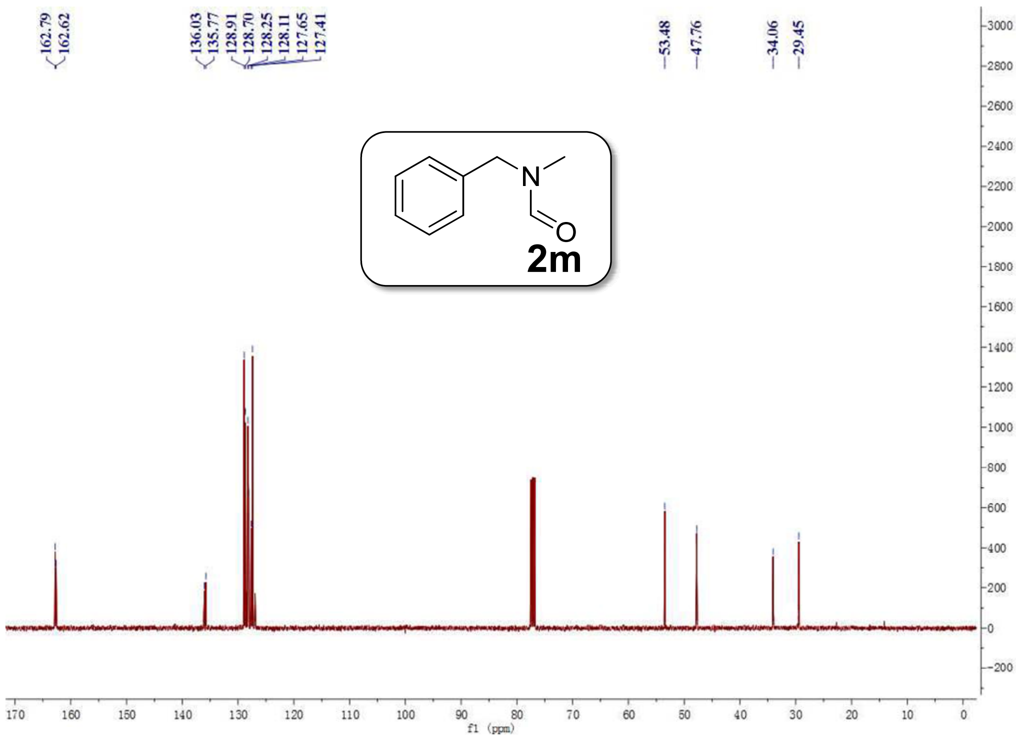


Figure S38. ^{1}HNMR of **2n**

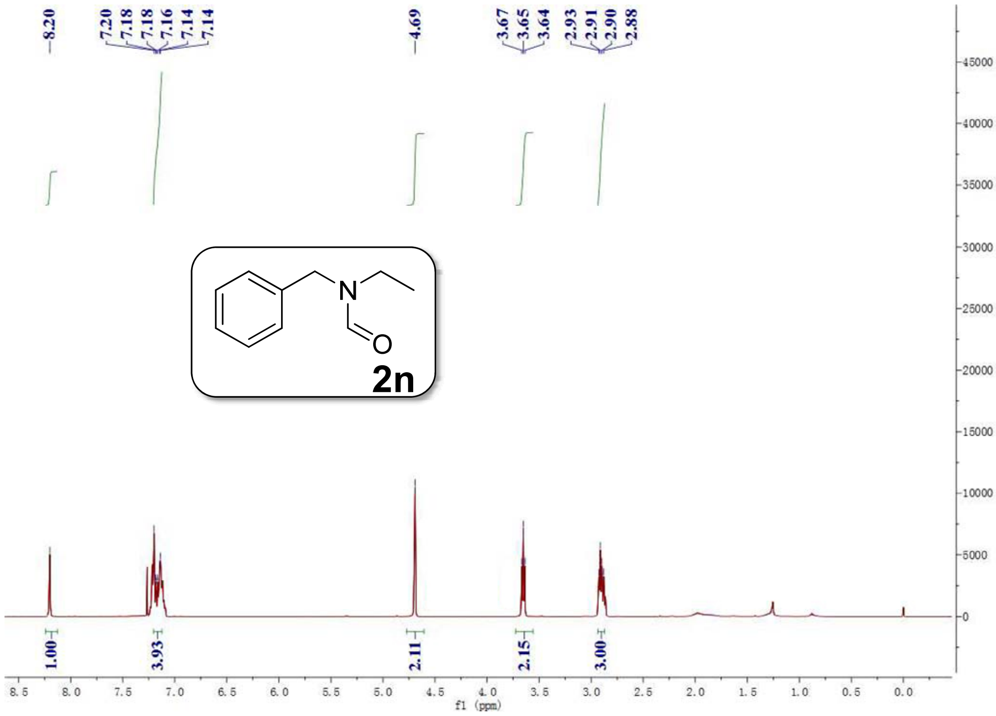


Figure S39. ^{13}CNMR of **2n**

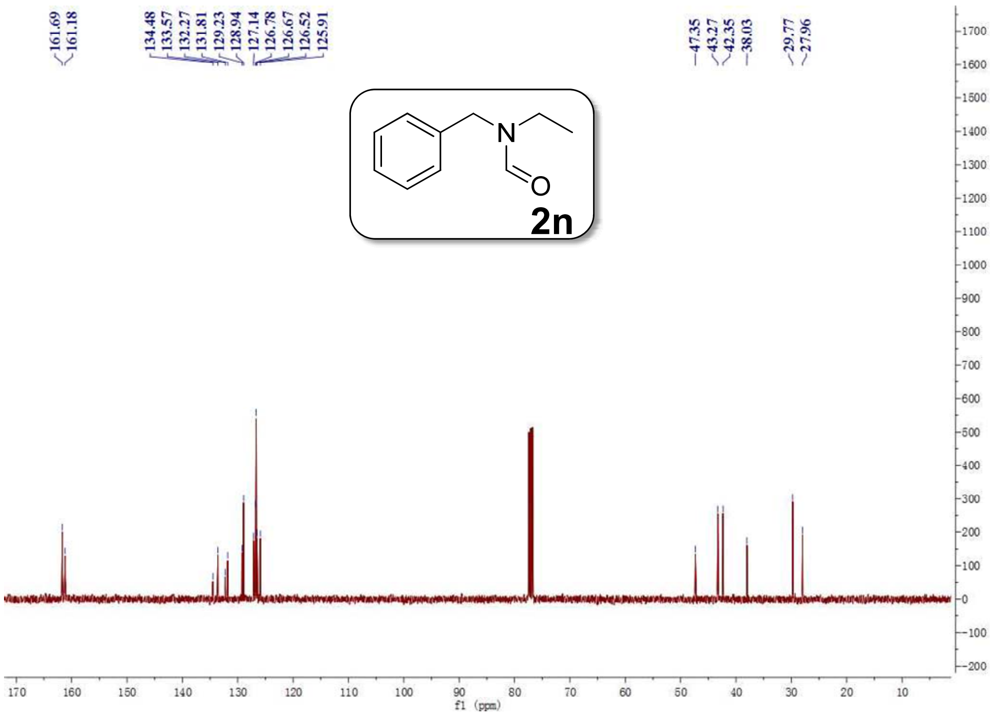


Figure S40. ^{1}HNMR of **2o**

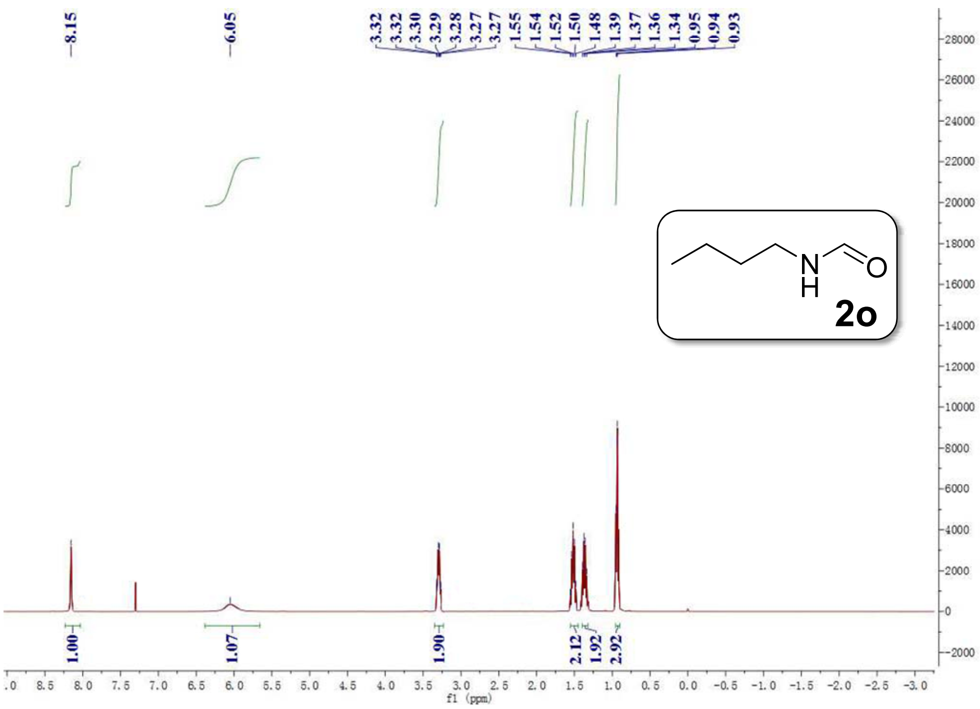


Figure S41. ^{13}CNMR of **2o**

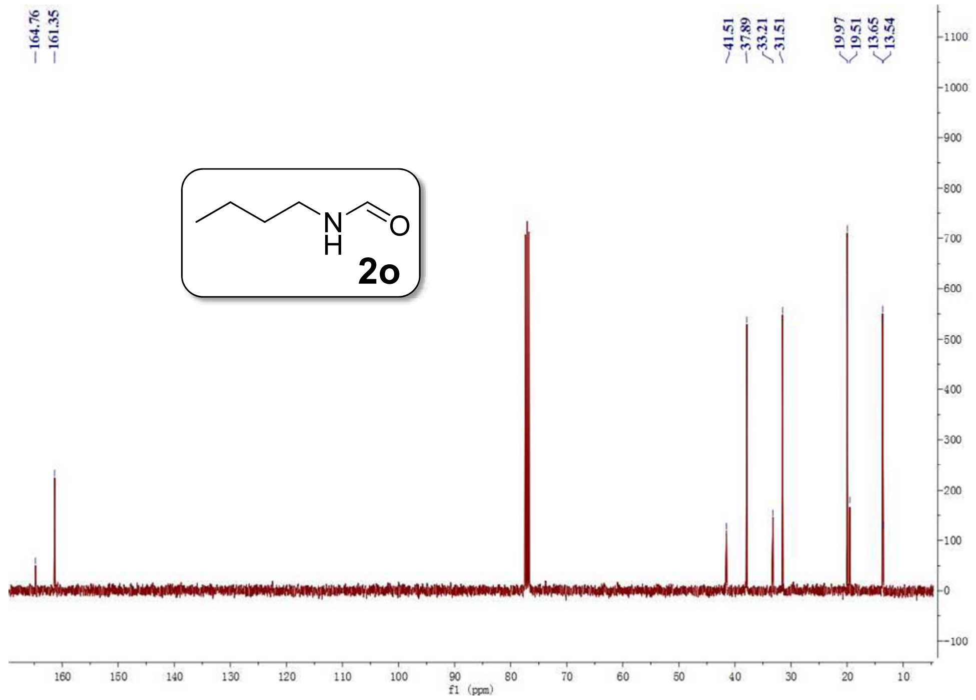


Figure S42. ^{1}HNMR of **2p**

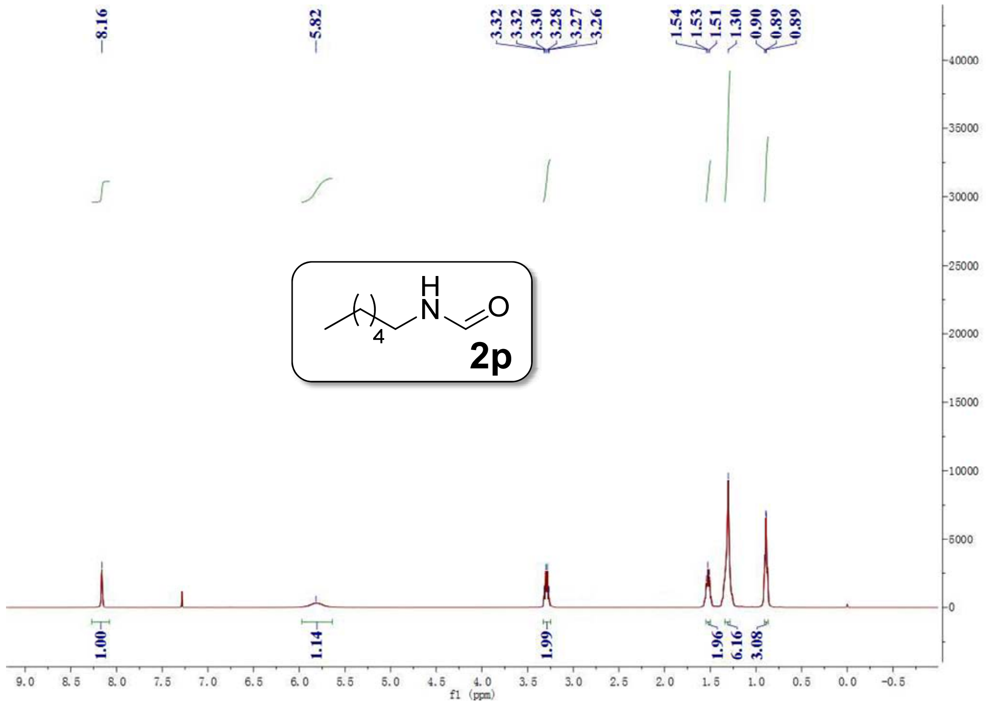


Figure S43. ^{13}CNMR of **2p**

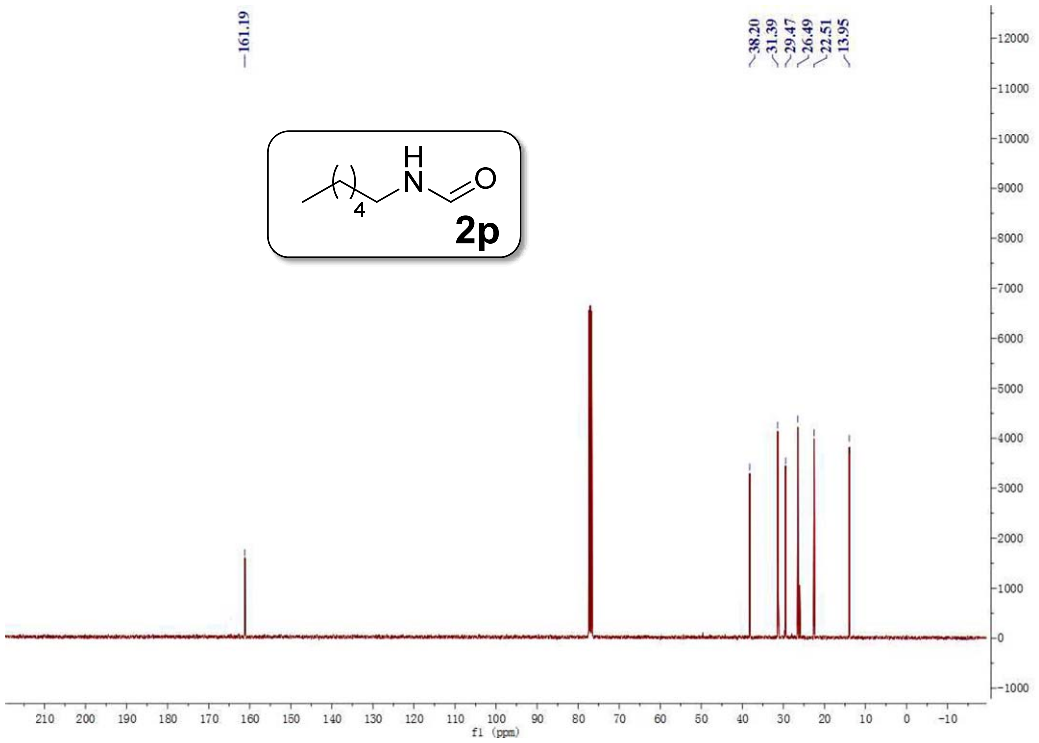


Figure S44. ^{1}HNMR of **2q**

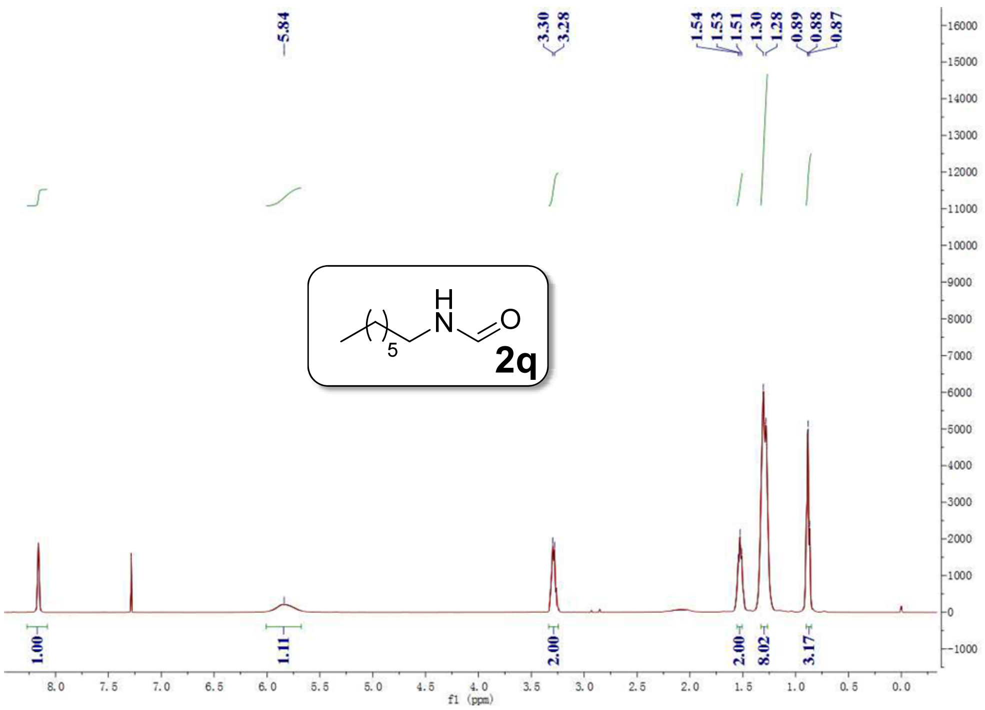


Figure S45. ^{13}CNMR of **2q**

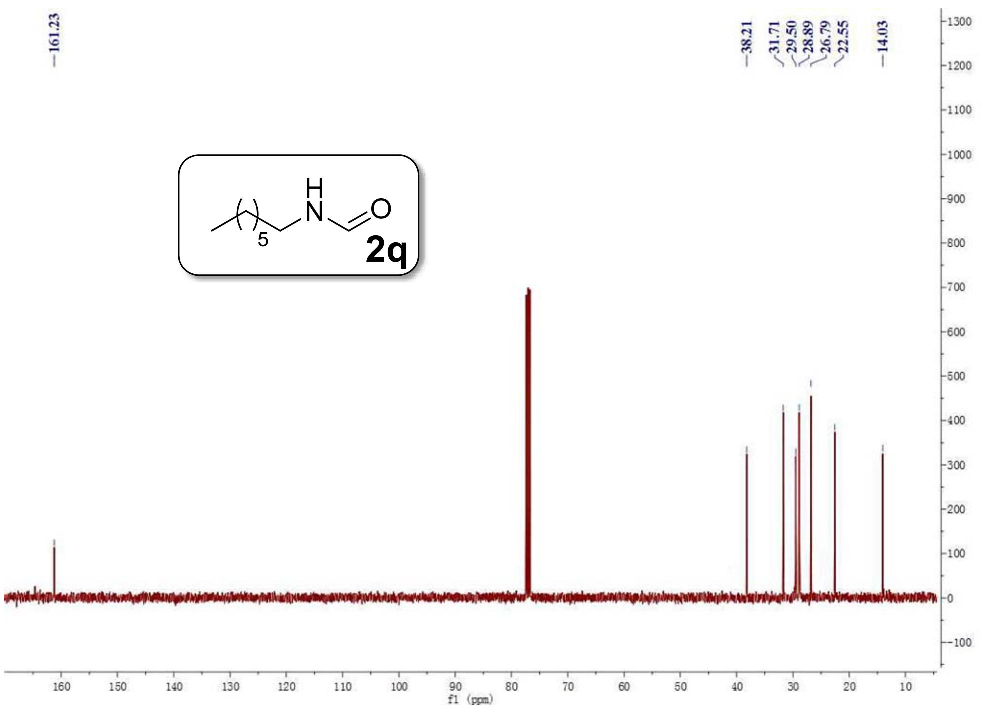


Figure S46. ^{1}HNMR of **2r**

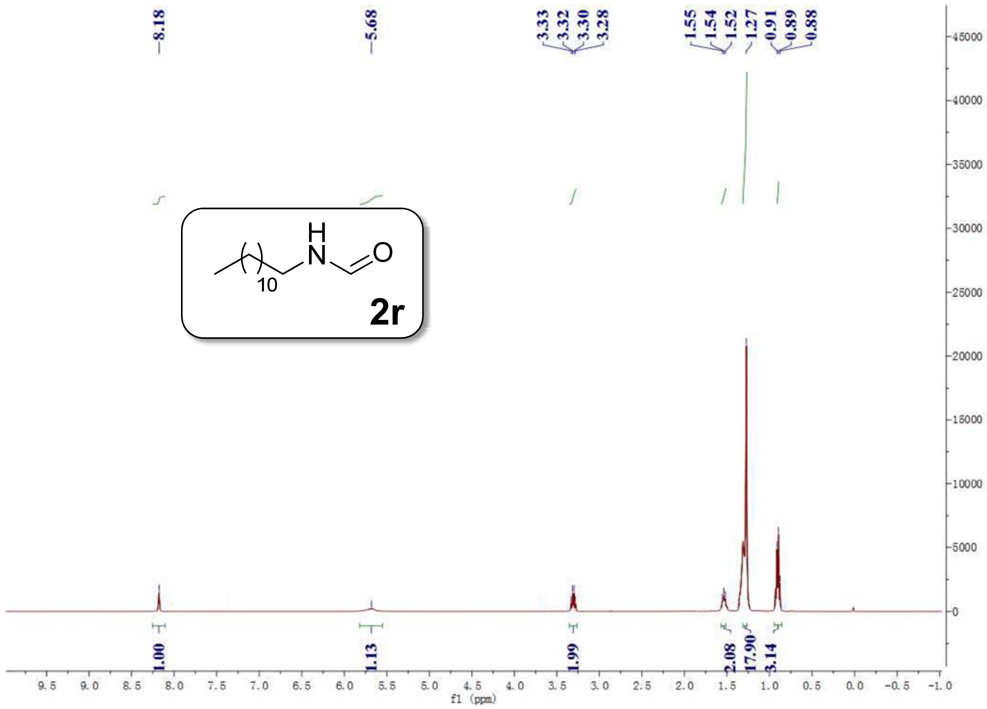


Figure S47. ^{13}CNMR of **2r**

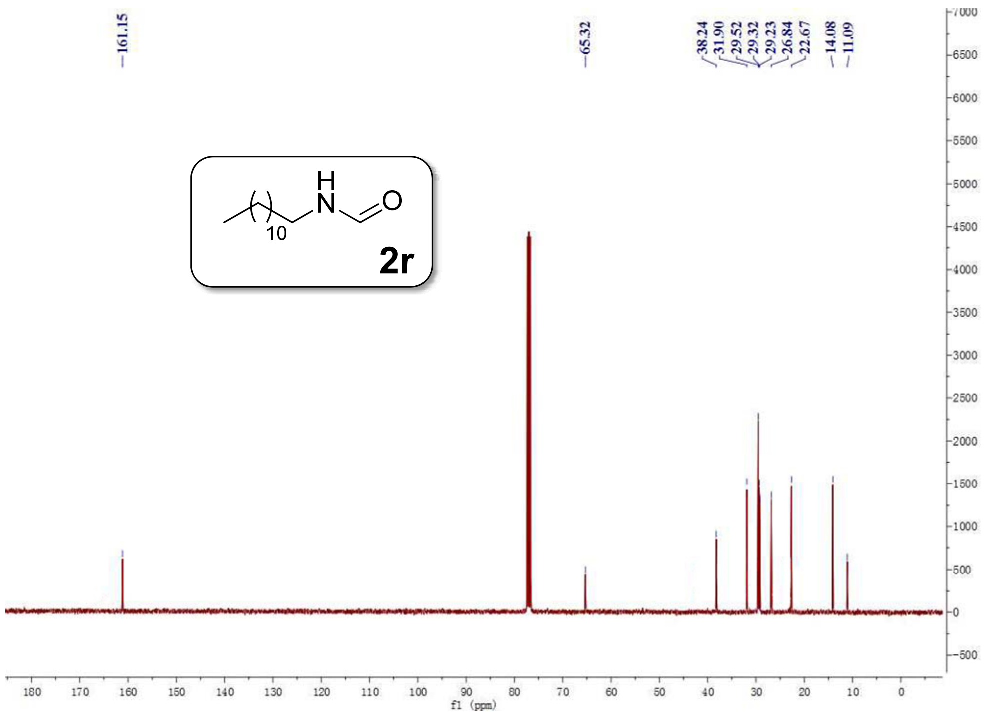


Figure S48. ^{1}HNMR of **2s**

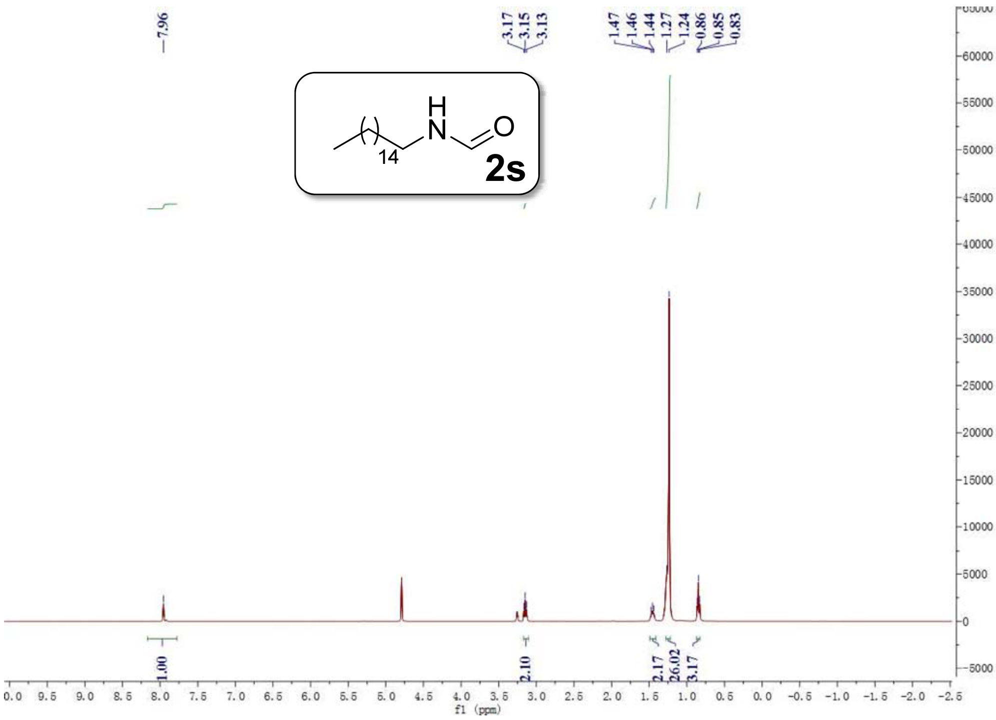


Figure S49. ^{13}CNMR of **2s**

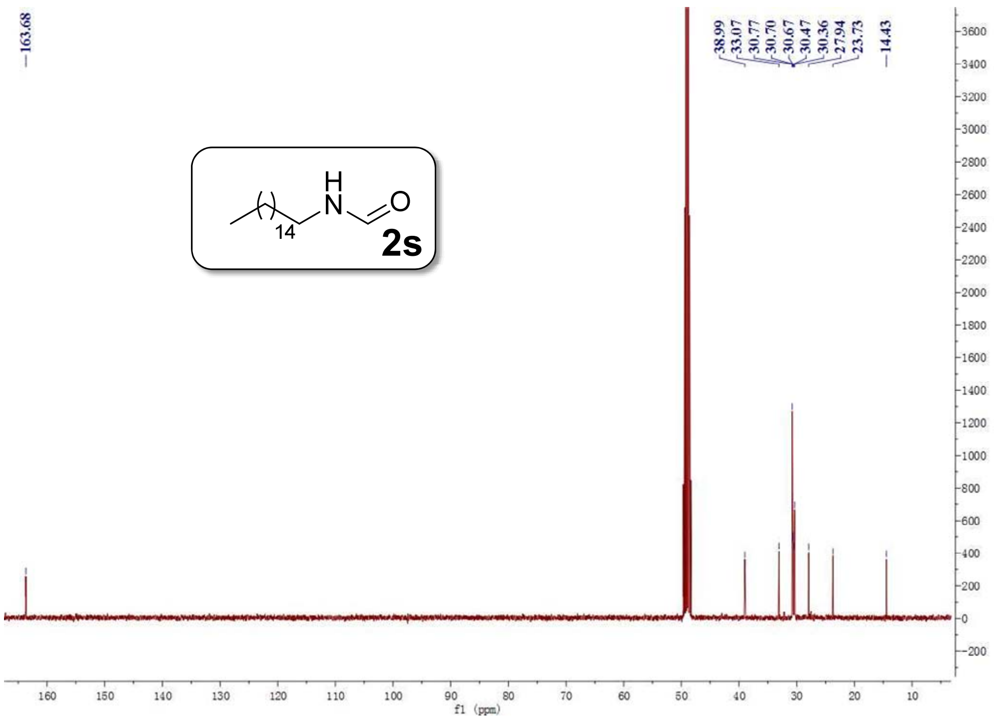


Figure S50. ^{1}HNMR of **2t**

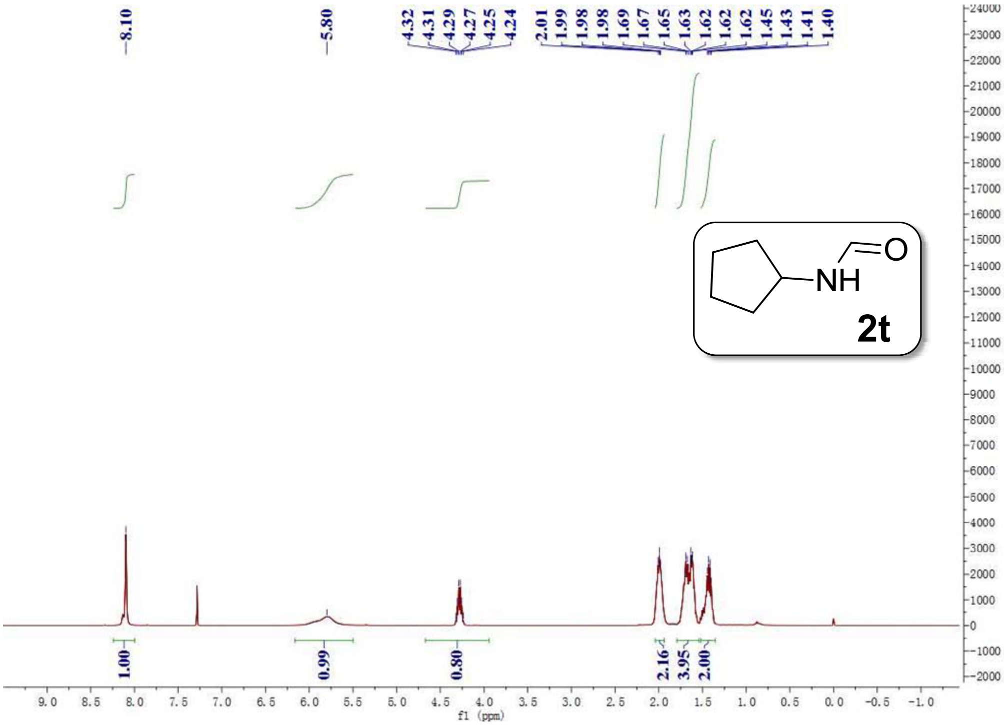


Figure S51. ^{13}CNMR of **2t**

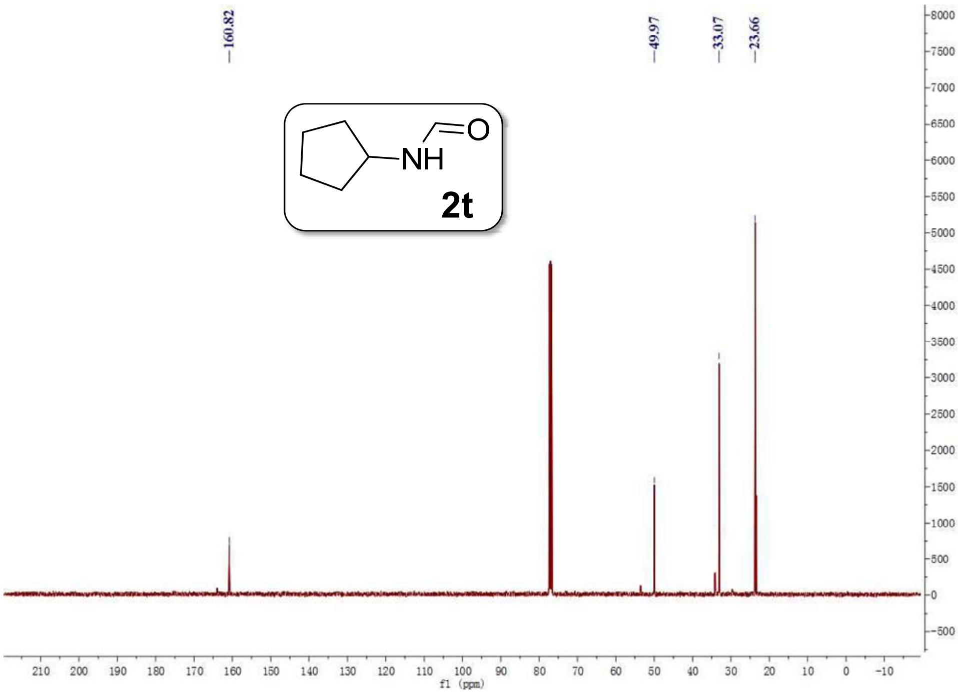


Figure S52. ^{1}HNMR of **2u**

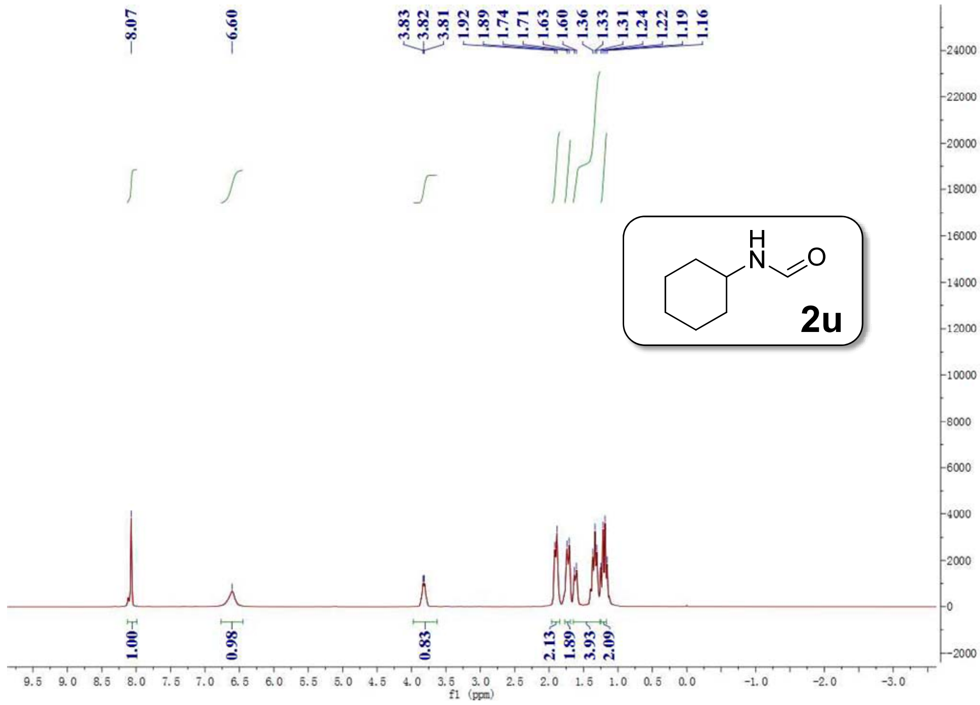


Figure S53. ^{13}CNMR of **2u**

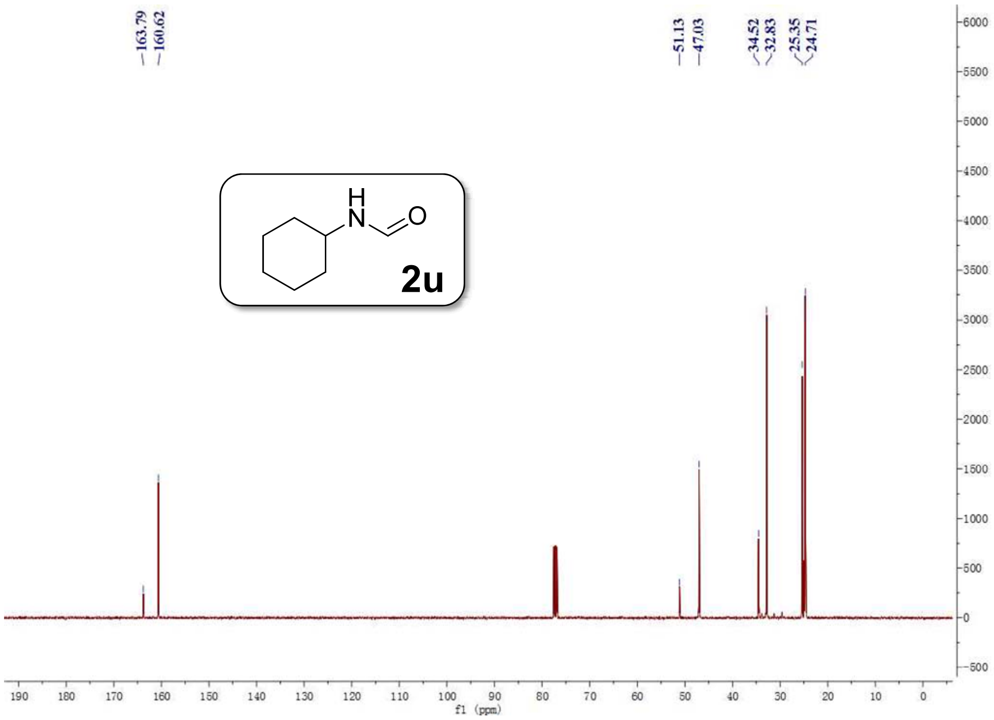


Figure S54. ^{1}HNMR of **2v**

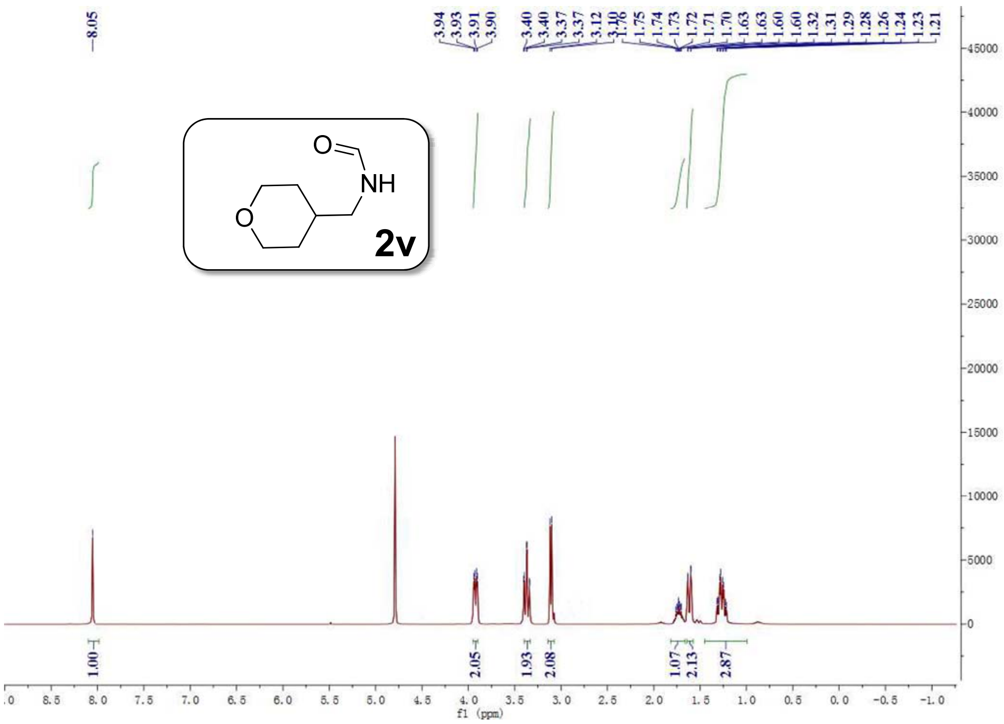


Figure S55. ^{13}CNMR of **2v**

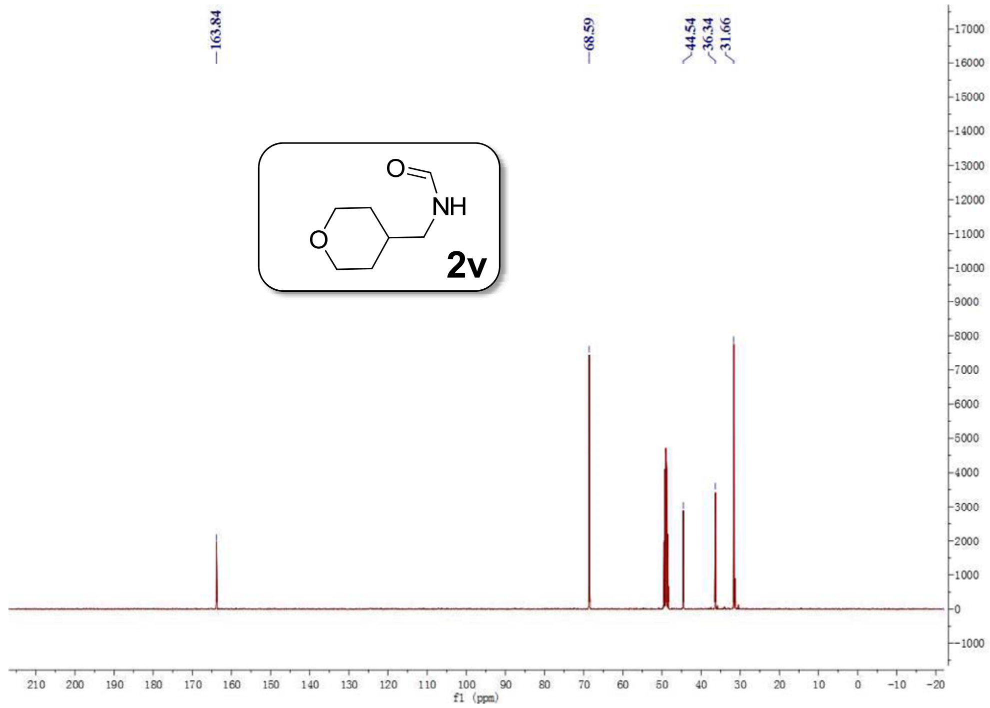


Figure S56. ^{1}HNMR of **2w**

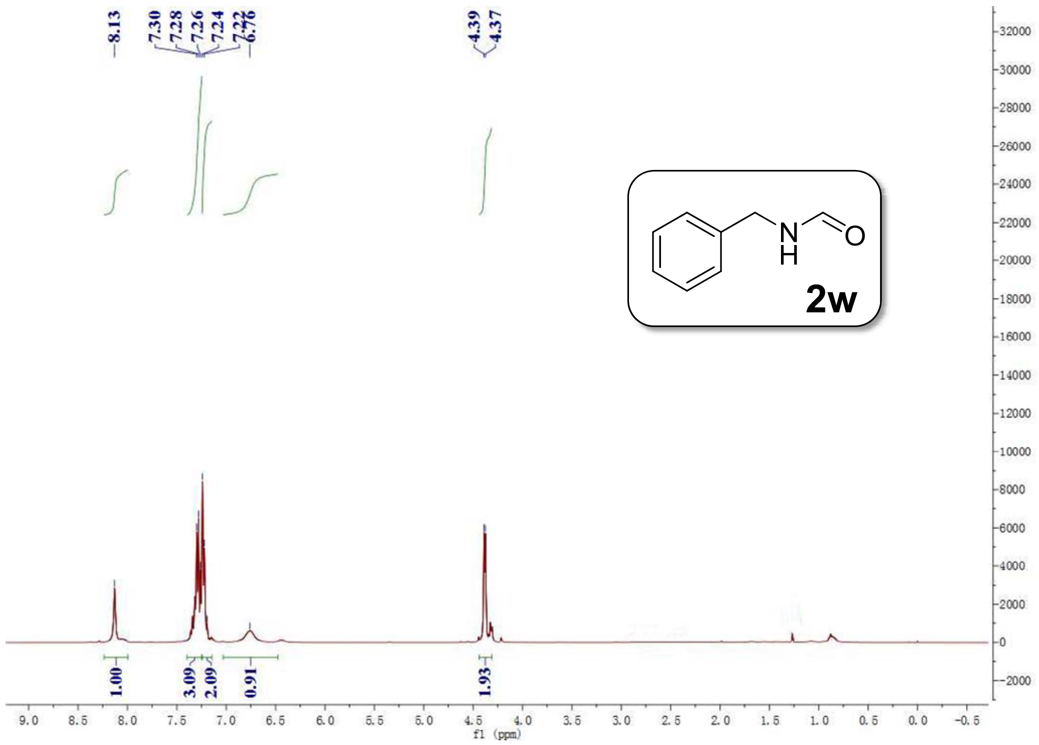


Figure S57. ^{13}CNMR of **2w**

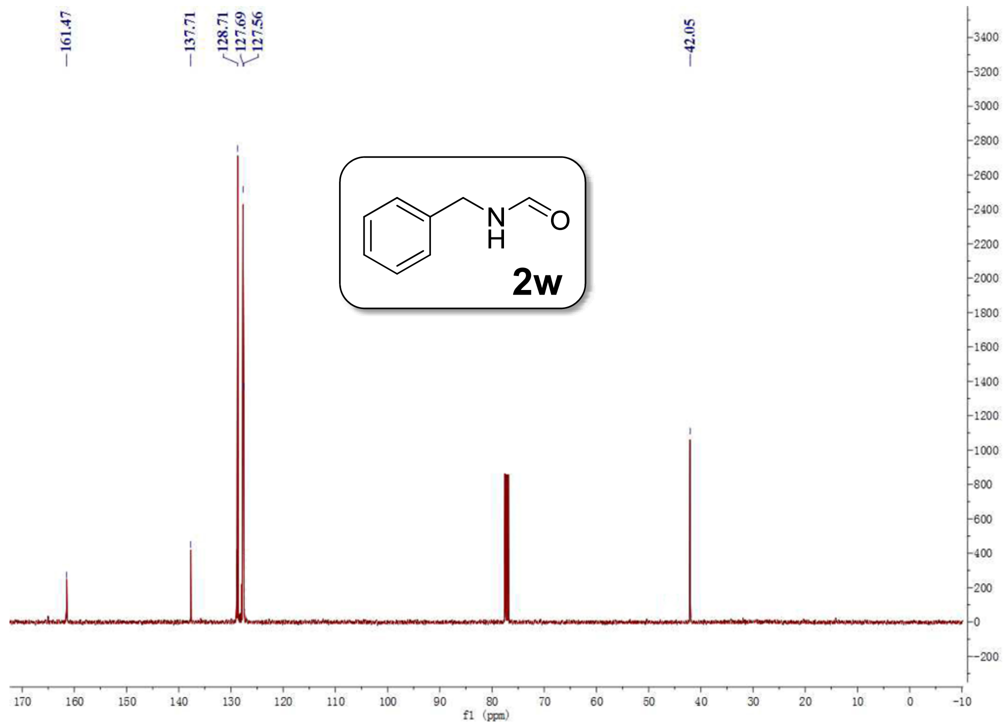


Figure S58. ^{1}HNMR of **2x**

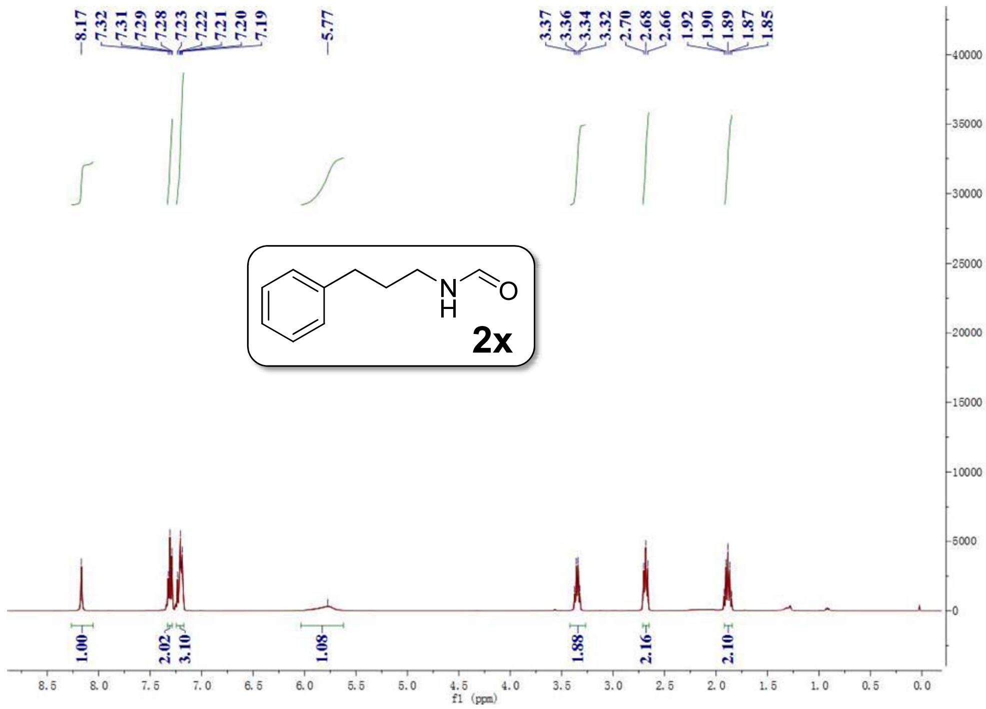


Figure S59. ^{13}CNMR of **2x**