Amine Formylation via Carbon Dioxide Recycling Catalyzed by a Simple and Efficient Heterogeneous Palladium Catalyst

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1. Experimental

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.

TPR measurement:

50 mg of catalyst was placed in a quartz tube, and it was heated up to 350 °C under 20 mL/min O_2 flow (10 °C/min) and maintained 100 min. The sample was cooled to room temperature and purged with highly pure Ar for 1 h. Then it was reduced with 5% H_2 (balanced with N_2) with the increasing of the temperature to 350 °C (10 °C /min). The amount of hydrogen uptake was monitored on-line by a TCD detector and recorded as a function of temperature.

Typical procedure for Al_2O_3-nanorods (NR) preparation

Typically, 10 mmol $AlCl_3$ was dissolved in 30 mL distilled water and 10 mmol BMImCl was added afterwards. Following with the addition of 50 mL $(NH_4)_2CO_3$ solution, the mixture were stirred for 30 min to form a milk-white solution. Then, the resulting precursor solution was transferred into a Teflon-lined stainless autoclave. After being hydrothermal treated at 120 °C for 12 h, the reaction mixture was cooled to room temperature, centrifuged, and washed with 40 mL distilled water and ethanol. The white solid sample was dried at 60 °C under vaccum for 3 h and calcined at 600 °C for 2 h to obtain the final Al_2O_3 nano-rods sample (Al_2O_3-NR).

Typical procedure for catalyst preparation

Reductive Deposition (RD) method: Suitable amount of H_2PdCl_4 (8 mg) were added into 50 mL distilled water and 400 mg Al_2O_3 nano-rods was added to the solution under stirring. A freshly prepared solution of $NaBH_4$ (0.1 M, 20 mL) was then added under stirring to form a dark solution. After the mixture was further stirred for 3 h at 30 °C, it was centrifuged and washed by water, dried at 120 °C for 4 h and calcined at 350 °C for 4 h in air. A grey solid sample was obtained and denoted as Pd/Al_2O_3-NR-RD. Pd/α-Al_2O_3-RD and Pd/γ-Al_2O_3-RD were prepared with the same procedure.

Deposition Precipitation (DP) method: Suitable amount of H_2PdCl_4 (8 mg) were added into 50 mL distilled water and 400 mg Al_2O_3 nano-rods was added to the solution under stirring. A freshly prepared solution of $NaCO_3$ (0.05 M, 20 mL) was then added to form a dark solution. After the reaction mixture was stirred for another 3 h at 30 °C, it was centrifuged and washed by water, dried at 120 °C for 4 h and calcined at 350 °C for 4 h in air. A grey solid sample was obtained and denoted as Pd/Al_2O_3-NR-DP.

Impregnation (IP) method: Suitable amount of H_2PdCl_4 (8 mg) were added into 5 mL distilled water and 400 mg Al_2O_3 nano-rods was added to the solution under stirring. After the reaction mixture was stirred for another 3 h at 30 ^oC, it was dried at 60 ^oC for 2 h under vacuum and calcined at 350 ^oC for 4 h in air. A grey solid sample was obtained and denoted as Pd/Al_2O_3-NR-IP.

Typical procedure for formylation of amines by CO_2 hydrogenation

1.0 mmol amines, 50 mg catalyst and 3 mL octane 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 2 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.

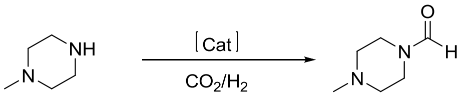
Table S1. BET results of the studied catalysts

Catalysts	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Pd/α-Al_2O_3 - RD	154.2	0.72	134.9
Pd/γ-Al_2O_3 - RD	281.6	0.48	57.2
Pd/Al_2O_3-NR- RD	177.8	0.93	213.4
Pd/Al_2O_3-NR-DP	247.8	1.07	145.4
Pd/Al_2O_3-NR-IP	208.3	0.78	137.7

Table S2. Palladium loading, H_2 chemisorption and peak temperature results for the studied catalysts

Catalysts	Pd (wt%)	H_2 consumption	Peak temperature
Pd/α-Al_2O_3-RD	0.47	9.5 $\mu molg_{cat}^{-1}$	45 ^oC
Pd/γ-Al_2O -RD	0.55	15 $\mu molg_{cat}^{-1}$	70 ^oC
Pd/Al_2O_3-NR-RD	0.53	13 $\mu molg_{cat}^{-1}$	47 ^oC
Pd/Al_2O_3-NR-DP	0.59	15 $\mu molg_{cat}^{-1}$)	65 ^oC
Pd/Al_2O_3-NR-IP	0.85	45 $\mu molg_{cat}^{-1}$	112 ^oC

Table S3. Reaction conditions optimization with 1-methylpiperazine formylation by CO_2/H_2 as model reaction[a]



ntry	Catalysts	Solvents	CO_2:H_2/ MPa	Yield (%)[b]
1	----	Octane	1:2	0
2	Al_2O_3-NR	Octane	1:2	0
3	Pd/Al_2O_3-NR-RD	Octane	1:2	89
4	Pd/Al_2O_3-NR-IP	Octane	1:2	2
5	Pd/Al_2O_3-NR-DP	Octane	1:2	4
6	Pt/Al_2O_3-NR-RD	Octane	1:2	54
7	Rh/Al_2O_3-NR-RD	Octane	1:2	29
8	Ru/Al_2O_3-NR-RD	Octane	1:2	10
9	Pd/α-Al_2O_3-RD	Octane	1:2	36
10	Pd/γ-Al_2O_3-RD	Octane	1:2	53
11	Pd/Al_2O_3-NR-RD	Octane	1:1	52
12	Pd/Al_2O_3-NR-RD	Octane	1:3	96
13	Pd/Al_2O_3-NR-RD	Octane	2:2	90
14	Pd/Al_2O_3-NR-RD	Octane	2:1	45
15	Pd/Al_2O_3-NR-RD	Octane	3:1	52
16	Pd/Al_2O_3-NR-RD	Toluene	1:2	38
17	Pd/Al_2O_3-NR-RD	Xylene	1:2	43
18	Pd/Al_2O_3-NR-RD	Dioxane	1:2	30
19	Pd/Al_2O_3-NR-RD	THF	1:2	46
20[c]	Pd/Al_2O_3-NR-RD	Octane	1:2	46
21[d]	Pd/Al_2O_3-NR-RD	Octane	1:2	93
22[e]	Pd/Al_2O_3-NR-RD	Octane	1:2	96
23[f]	Pd/Al_2O_3-NR-RD	Octane	1:2	83

[a] 1 mmol (100 mg) 1-methylpiperazine, 50 mg catalyst, 3 mL solvent, 130 °C, 16 h; [b] Determined by GC-FID using biphenyl as standard material; [c] 120 °C; [d] 140 °C; [e] Reaction time: 24 h; [f] Yield at the 3rd run.

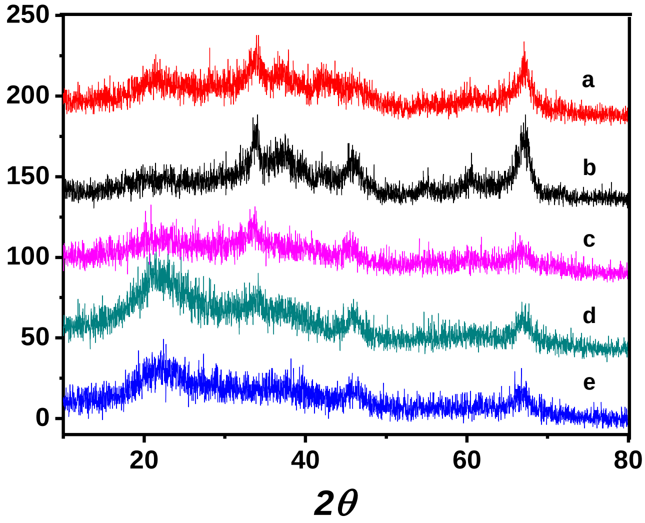


Fig. S1. XRD diffraction patterns for a) Pd/α-Al_2O_3 -RD, b) Pd/ γ -Al_2O_3 -RD, c) Pd/Al_2O_3-NR-RD, d) Pd/Al_2O_3-NR-DP and e) Pd/Al_2O_3-NR-IP.

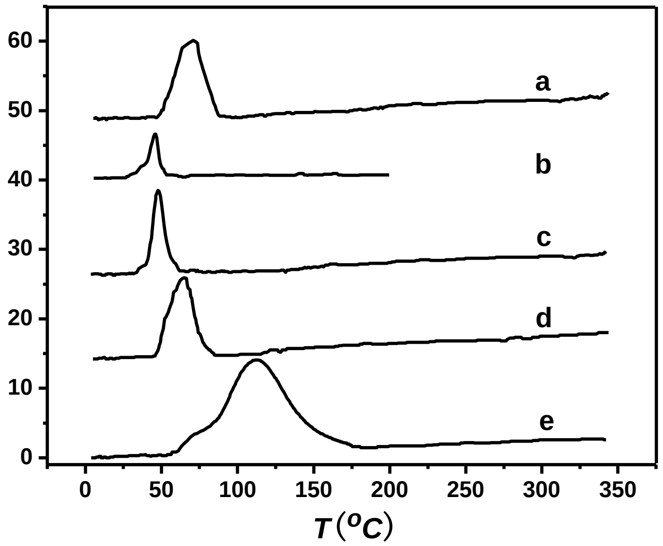


Fig. S2. TPR profile for a) Pd/α-Al_2O_3-RD, b) Pd/γ-Al_2O_3 -RD, c) Pd/Al_2O_3-NR-RD, d) Pd/Al_2O_3-NR-DP and e) Pd/Al_2O_3-NR-IP.

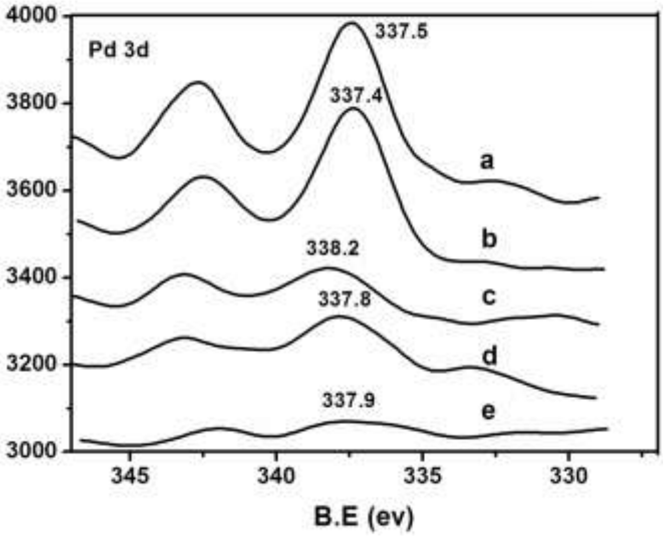


Fig. S3. XPS profile for a) Pd/α-Al_2O_3 -RD, b) Pd/γ-Al_2O_3 -RD, c) Pd/Al_2O_3-NR-RD, d) Pd/Al_2O_3-NR-DP and e) Pd/Al_2O_3-NR-IP.

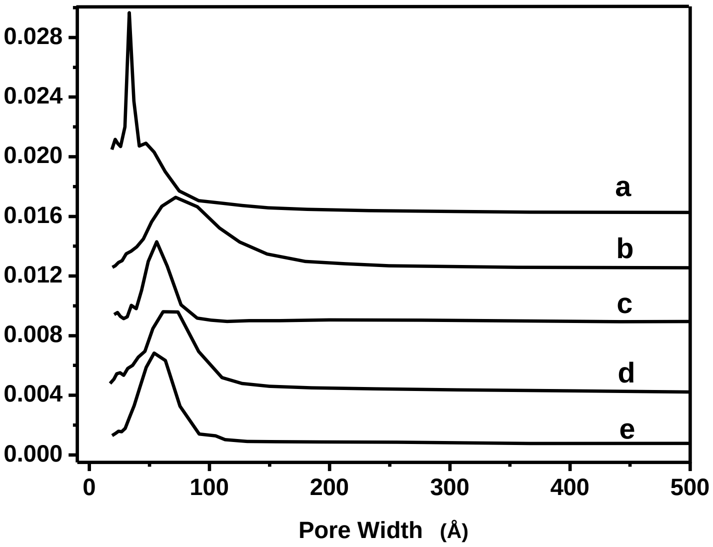


Fig. S4. BET profile for a) Pd/α-Al_2O_3 -RD, b) Pd/γ-Al_2O_3 -RD, c) Pd/Al_2O_3-NR-RD, d) Pd/Al_2O_3-NR-DP and e) Pd/Al_2O_3-NR-IP.

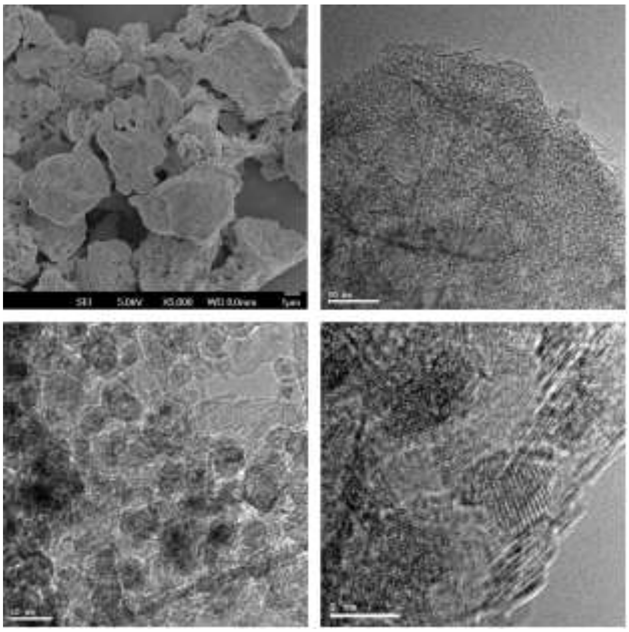


Fig. S5. SEM and TEM pictures for Pd/γ-Al_2O_3-RD.

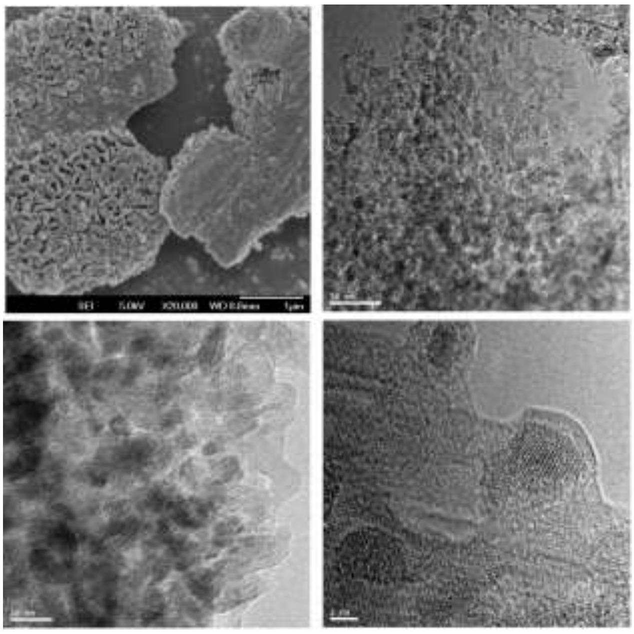


Fig. S6. SEM and TEM pictures for Pd/α-Al_2O_3-RD.

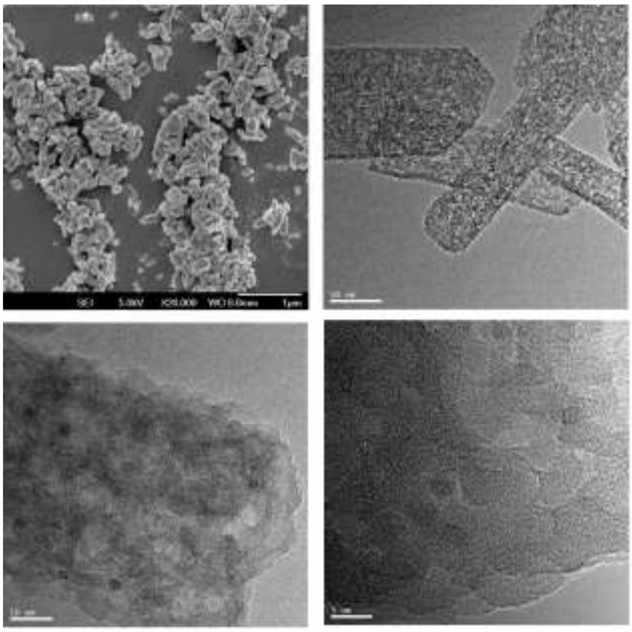


Fig. S7. SEM and TEM pictures for Pd/ Pd/Al_2O_3-NR-DP.

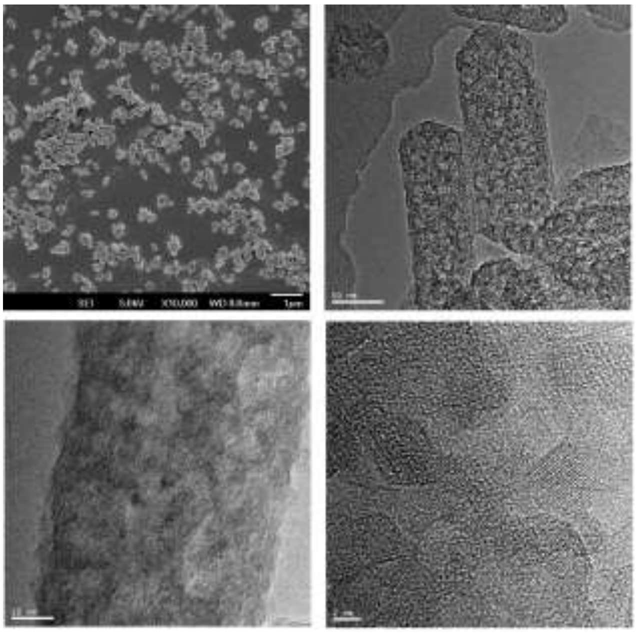
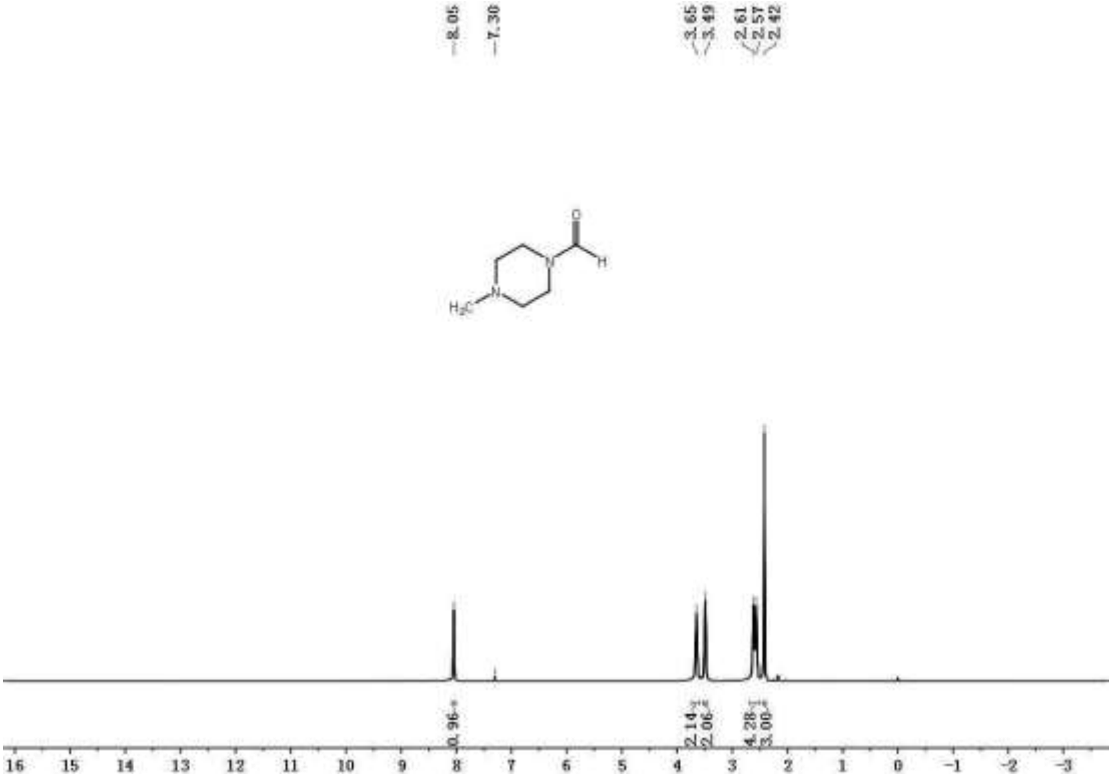
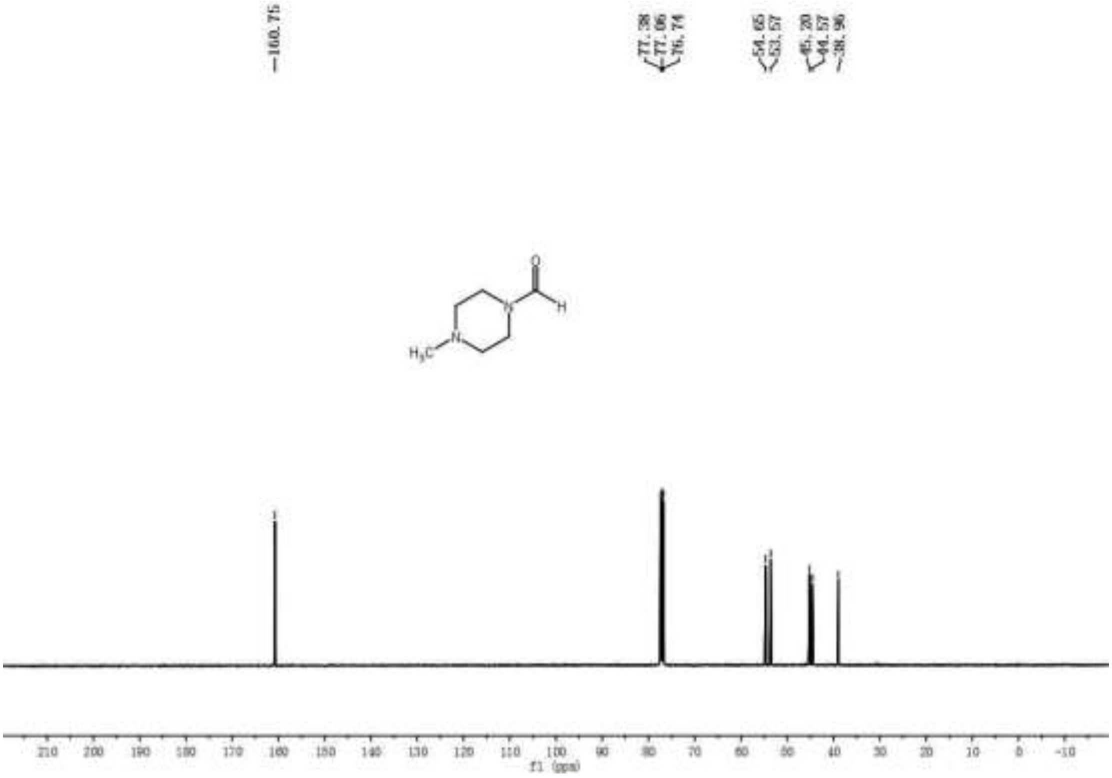
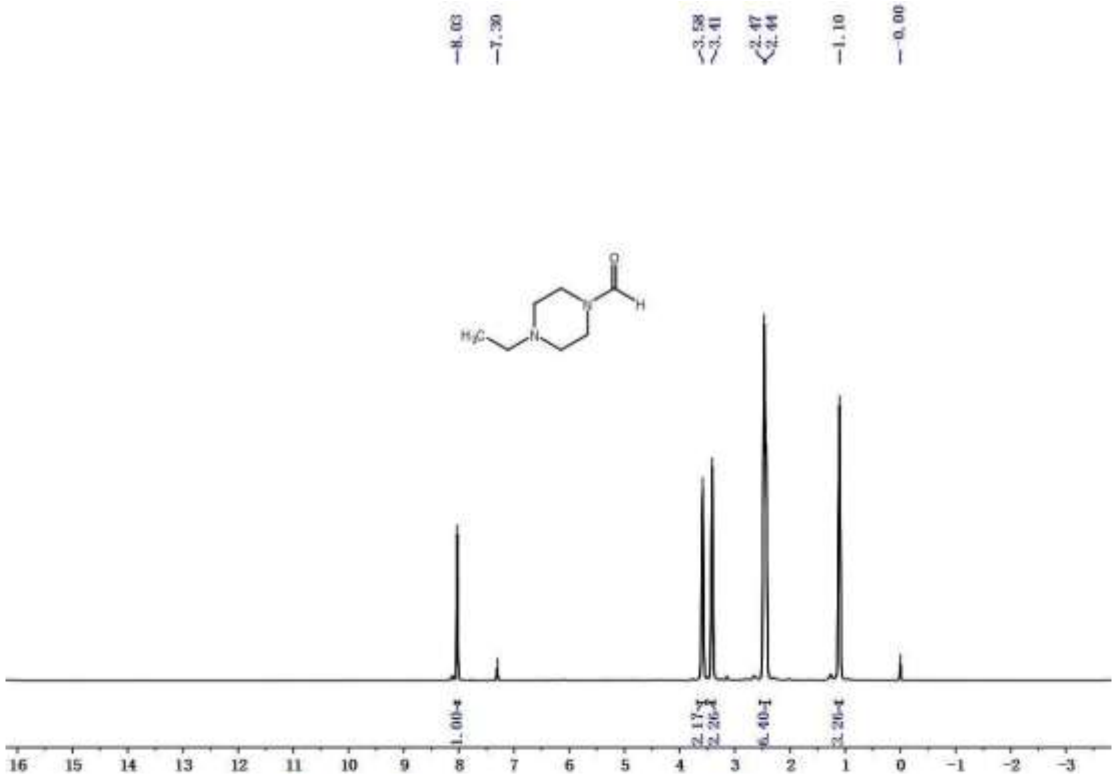


Fig. S8. SEM and TEM pictures for Pd/Al_2O_3-NR-IP.

^{1}H and ^{13}C NMR spectra of the products



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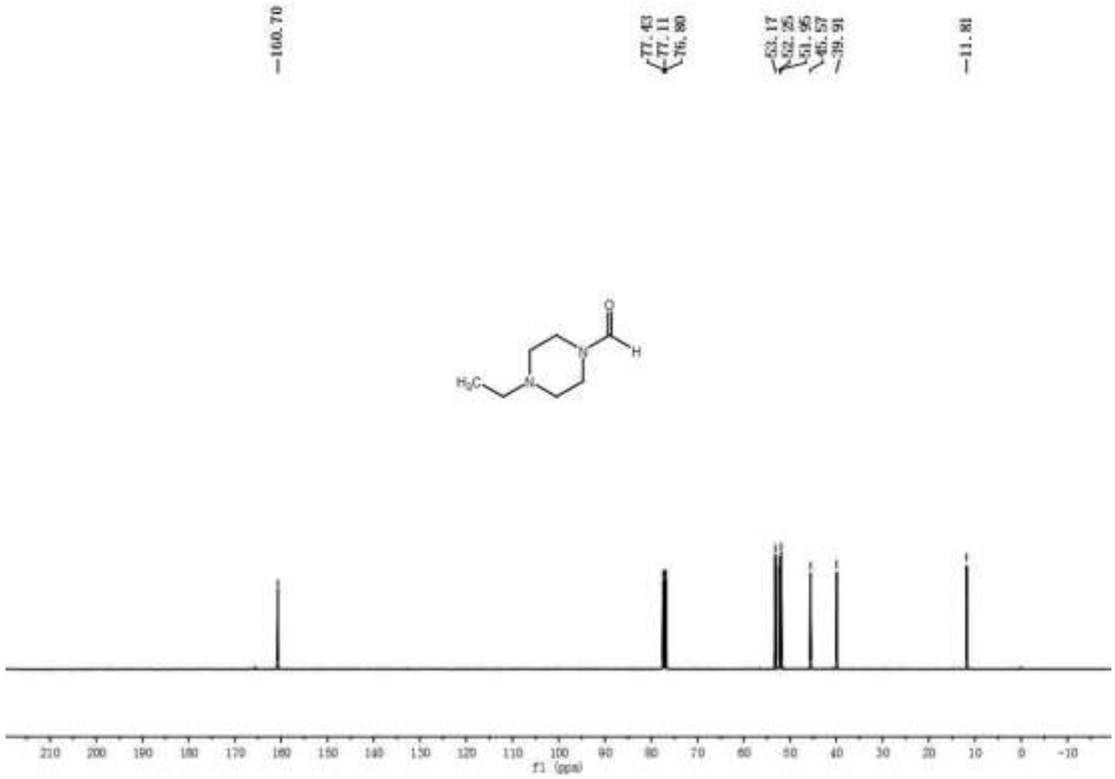
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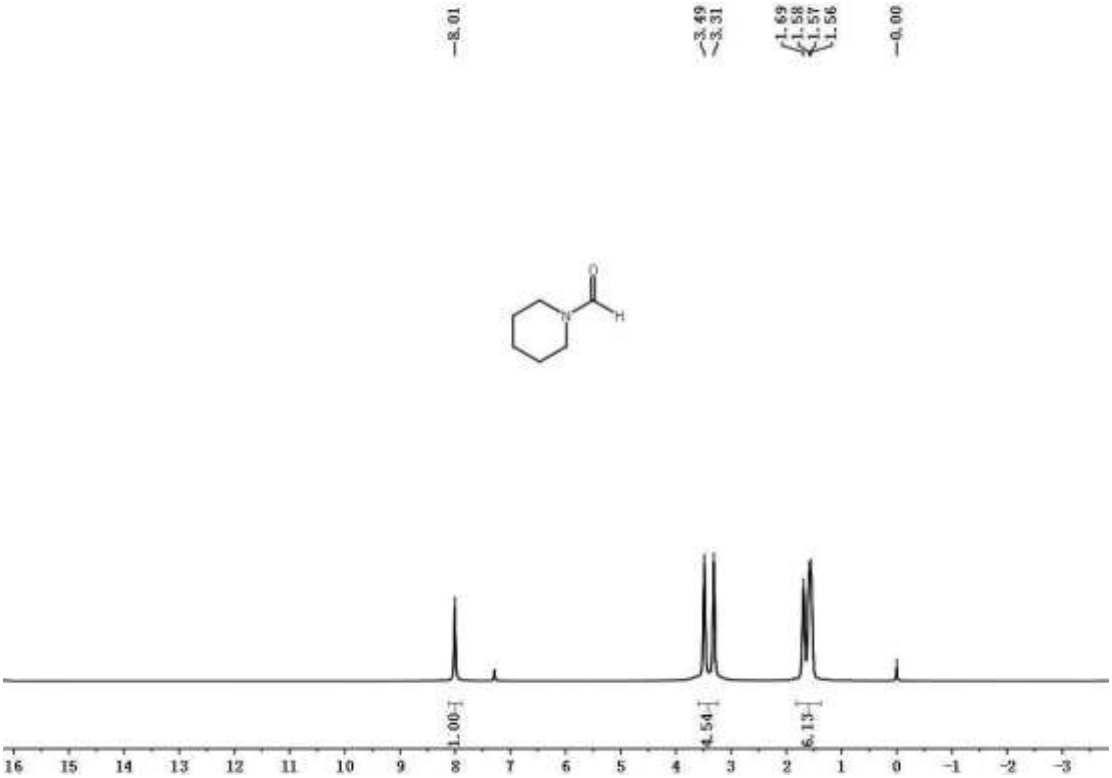
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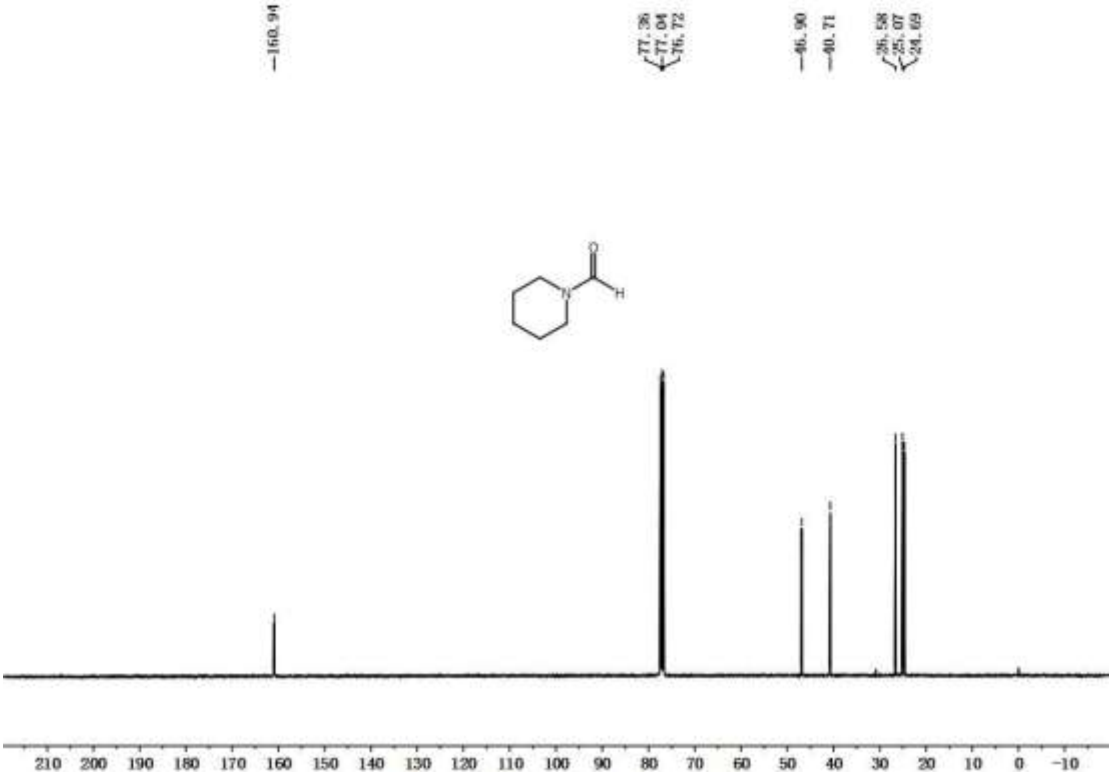
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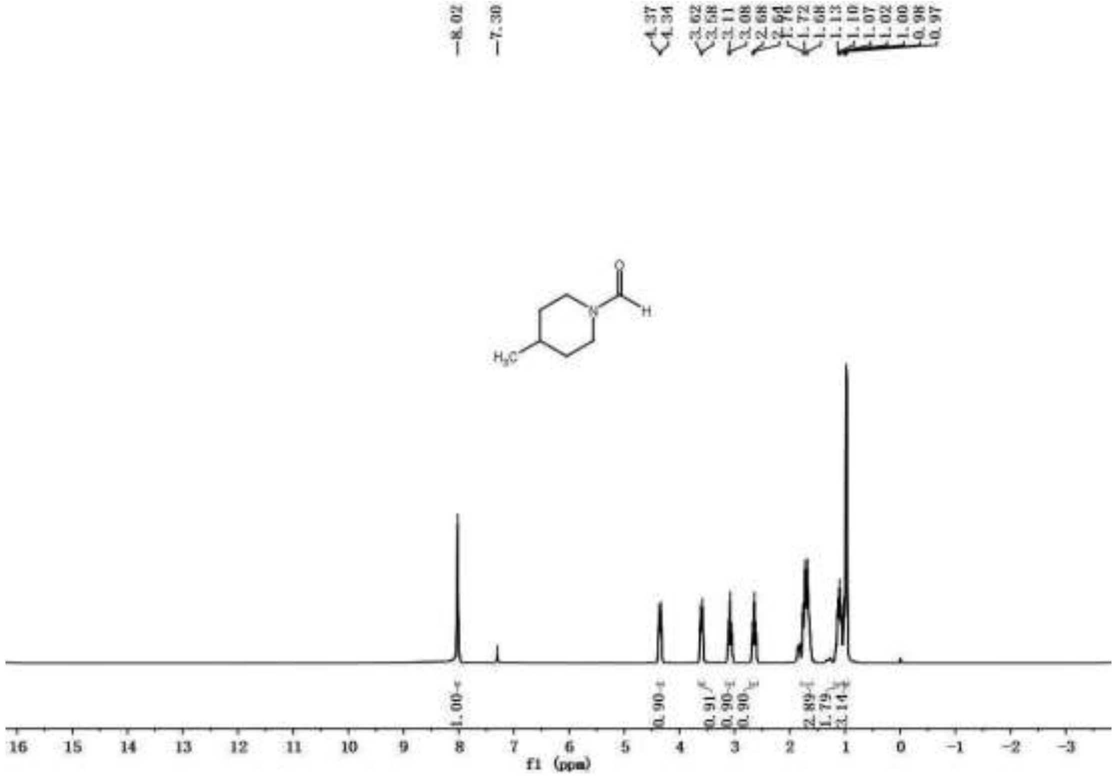
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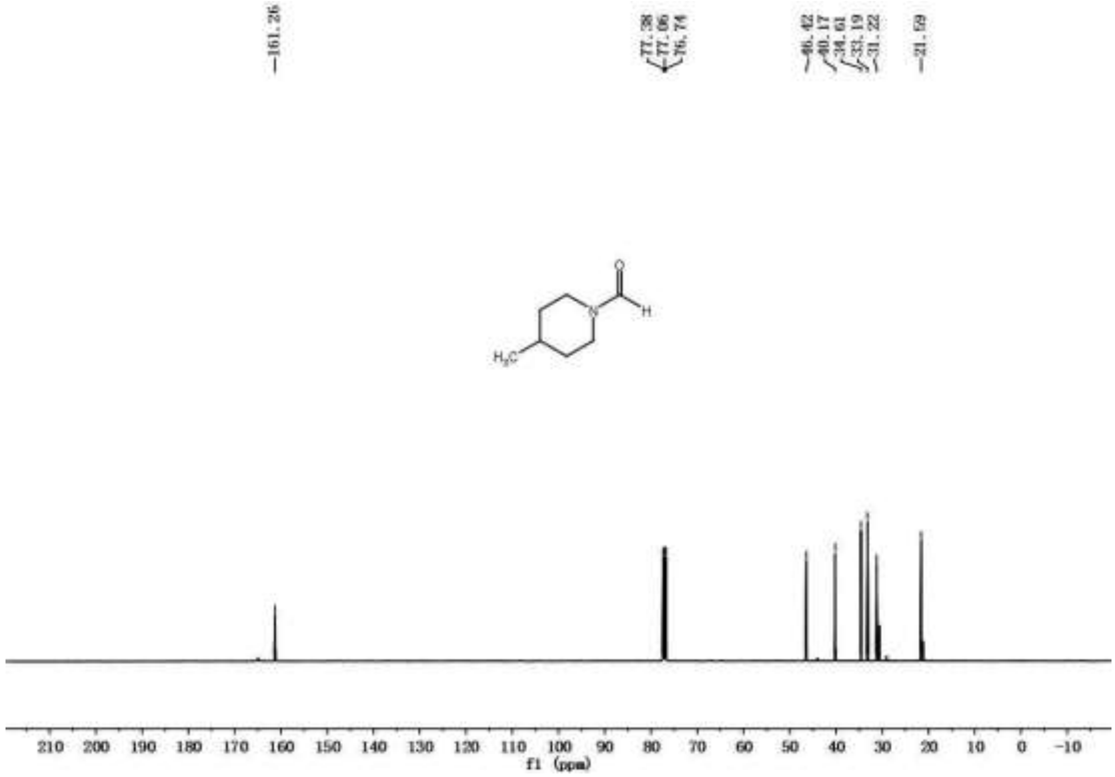
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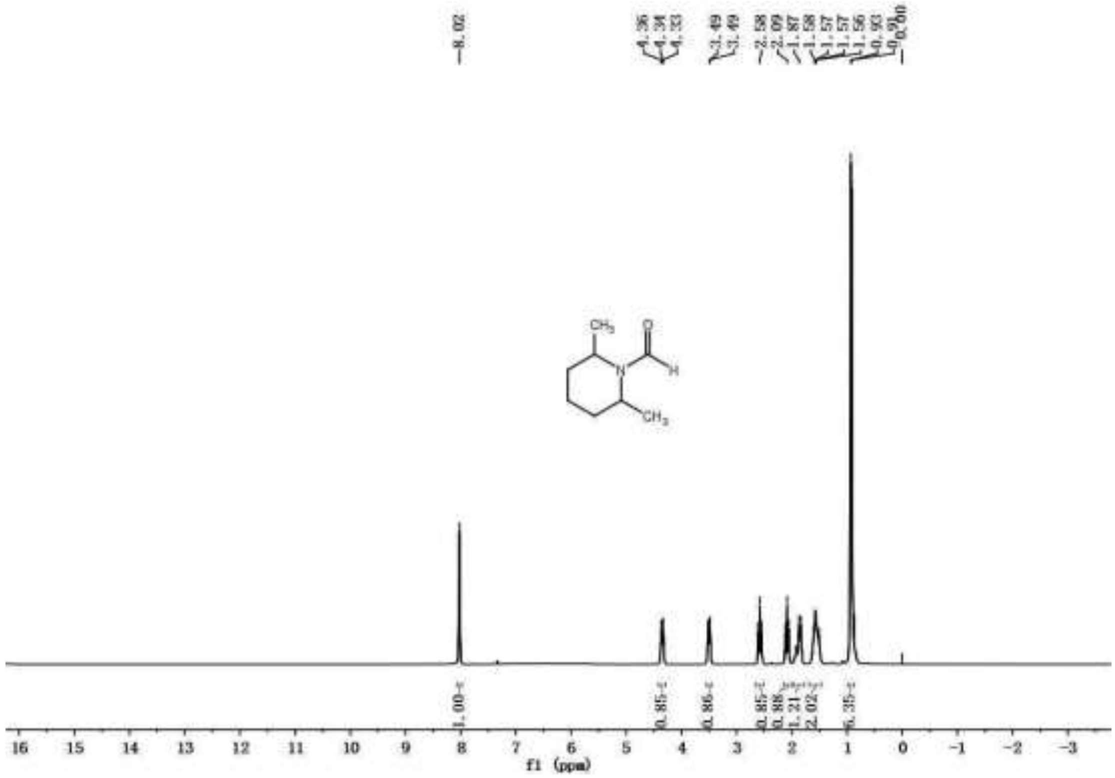
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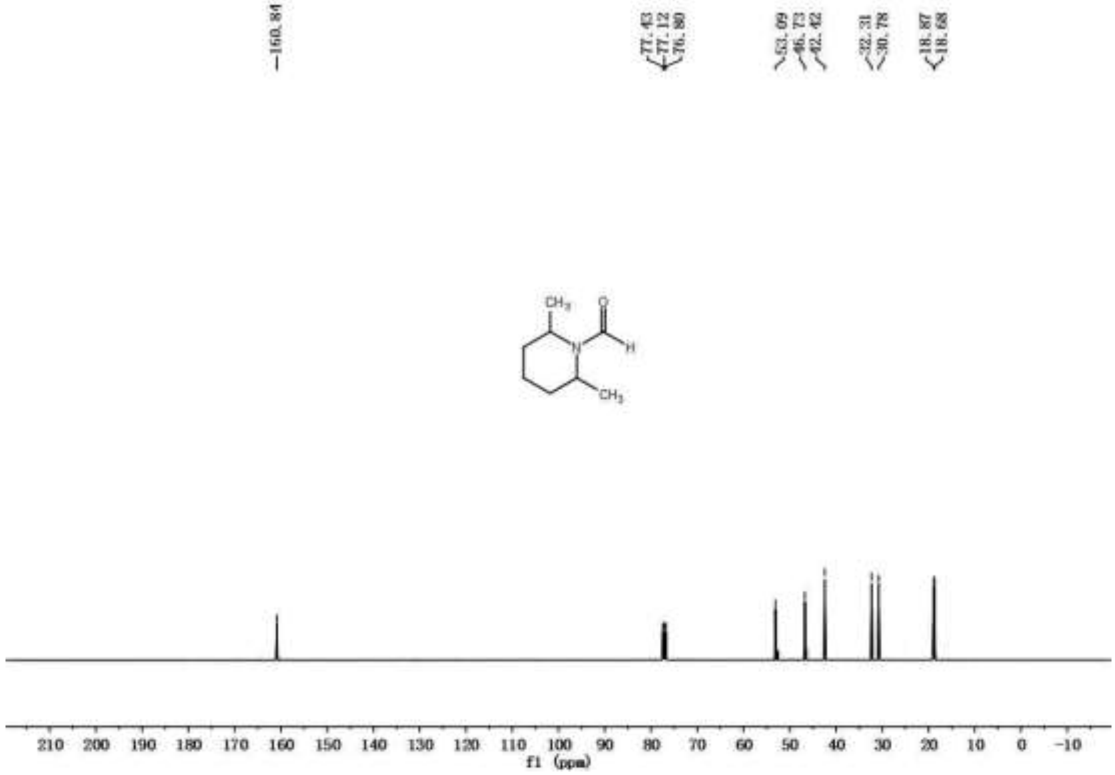
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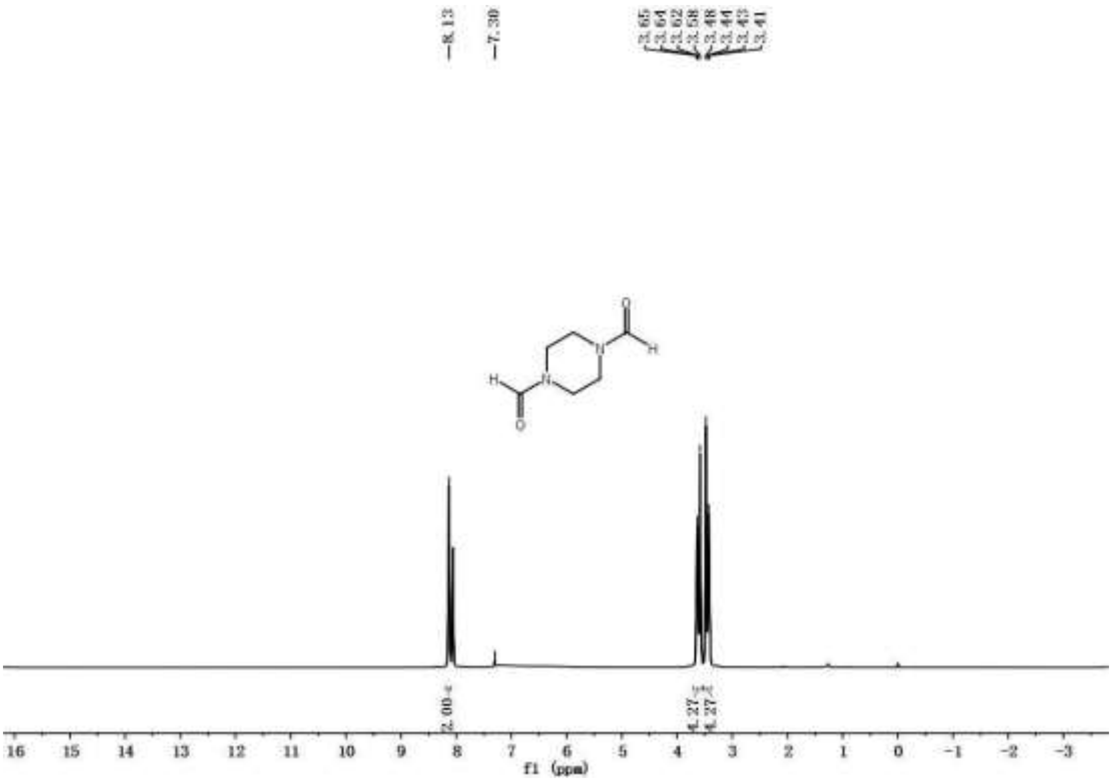
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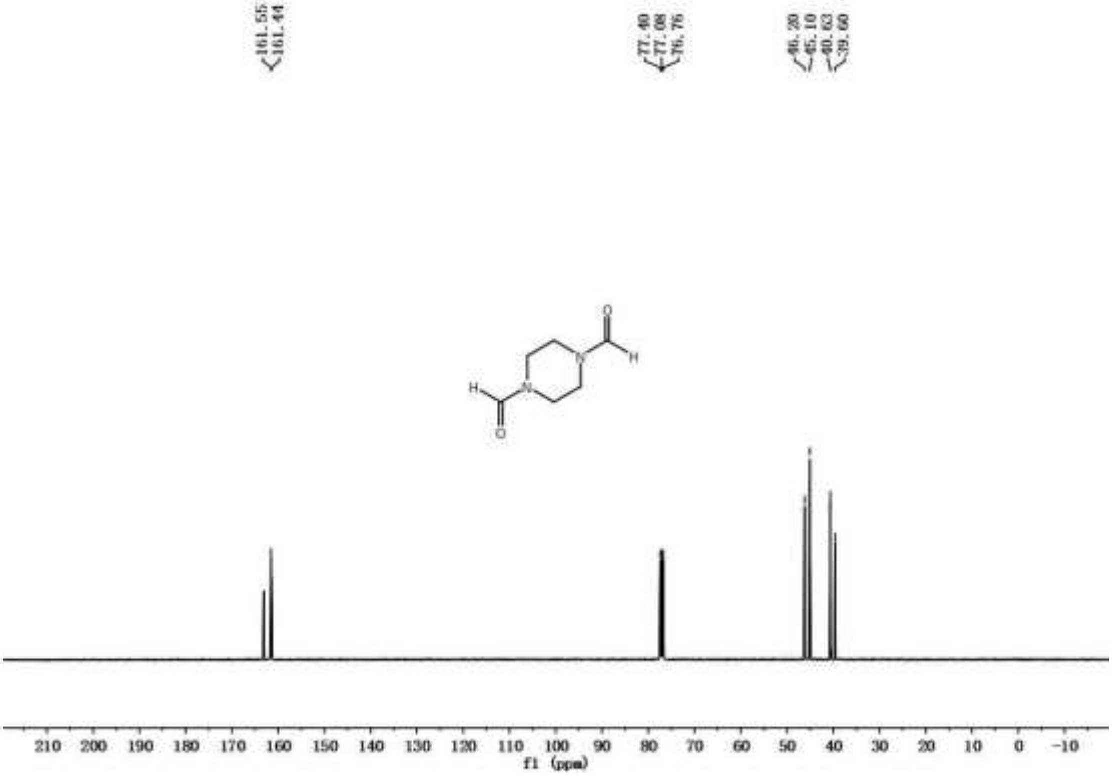
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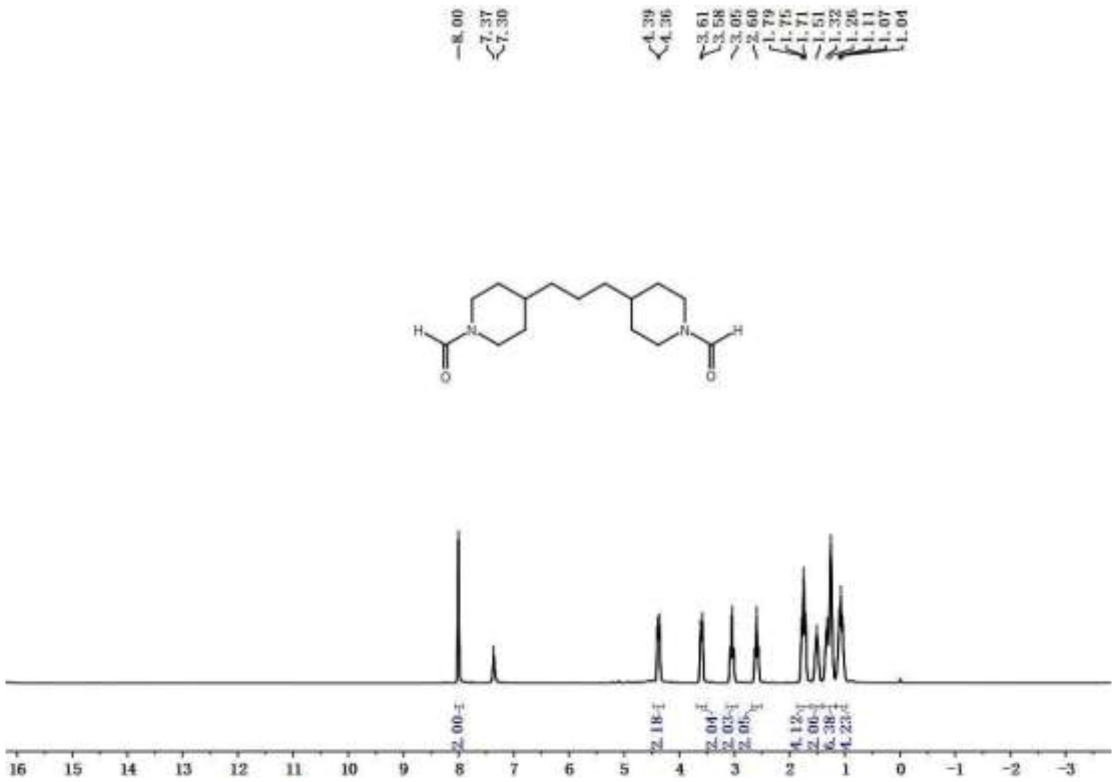
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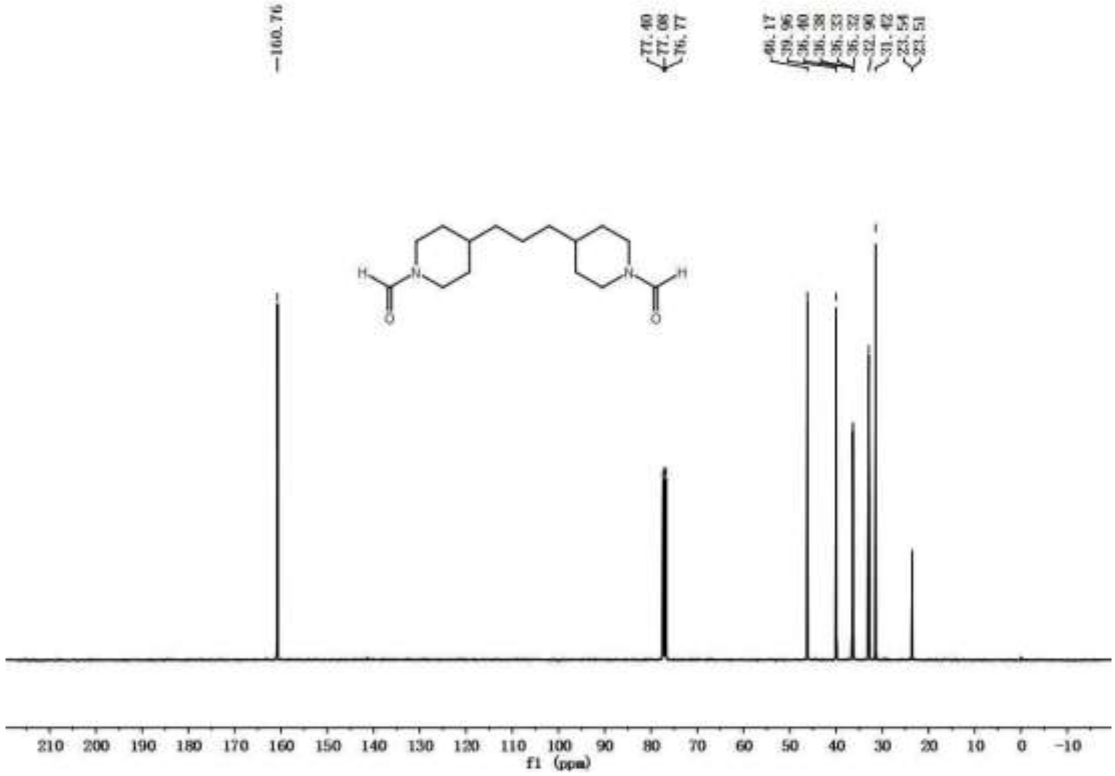
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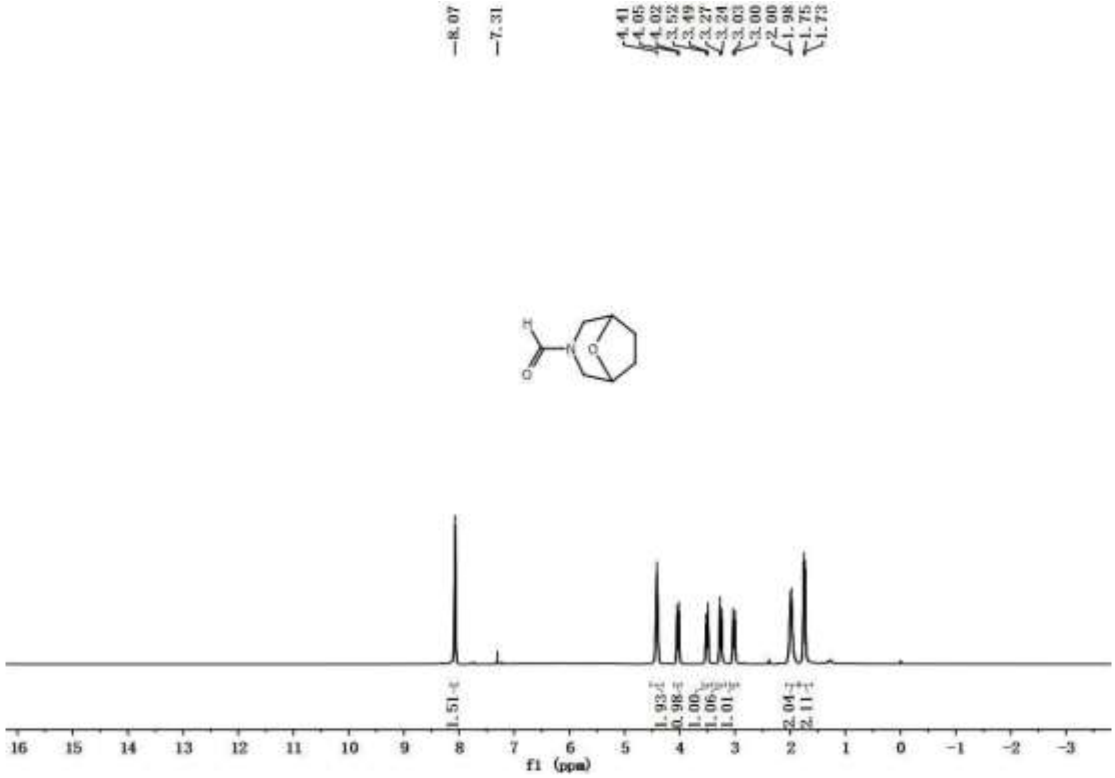
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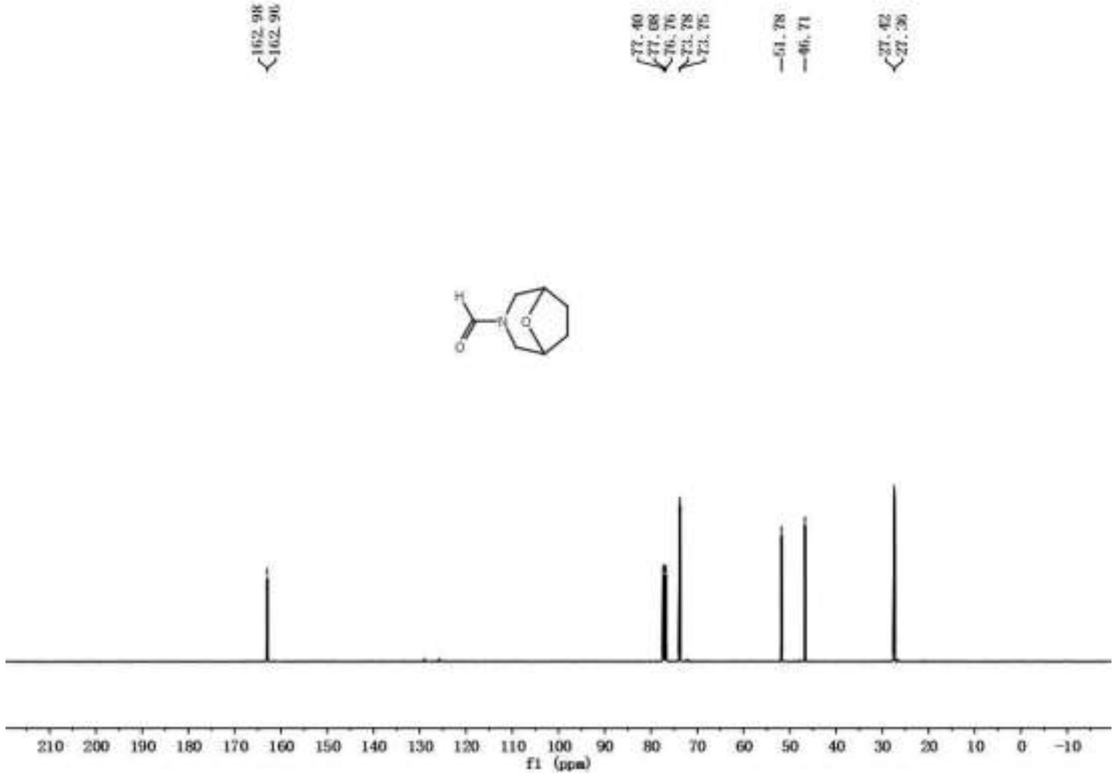
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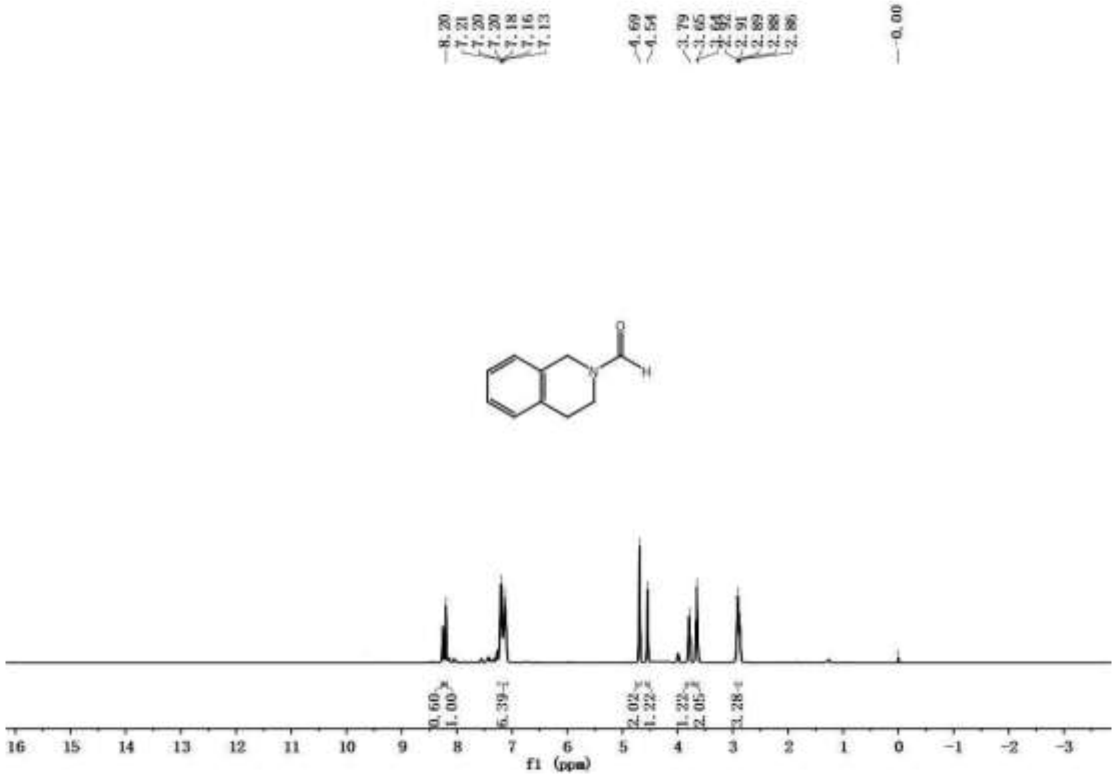
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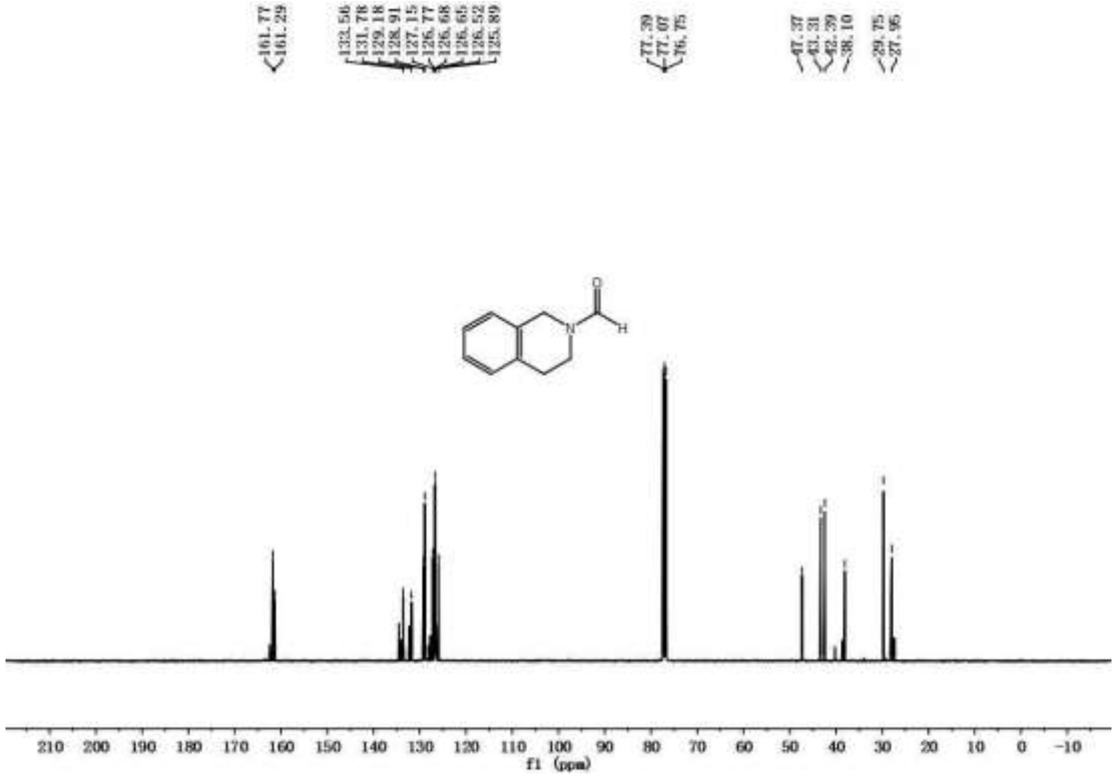
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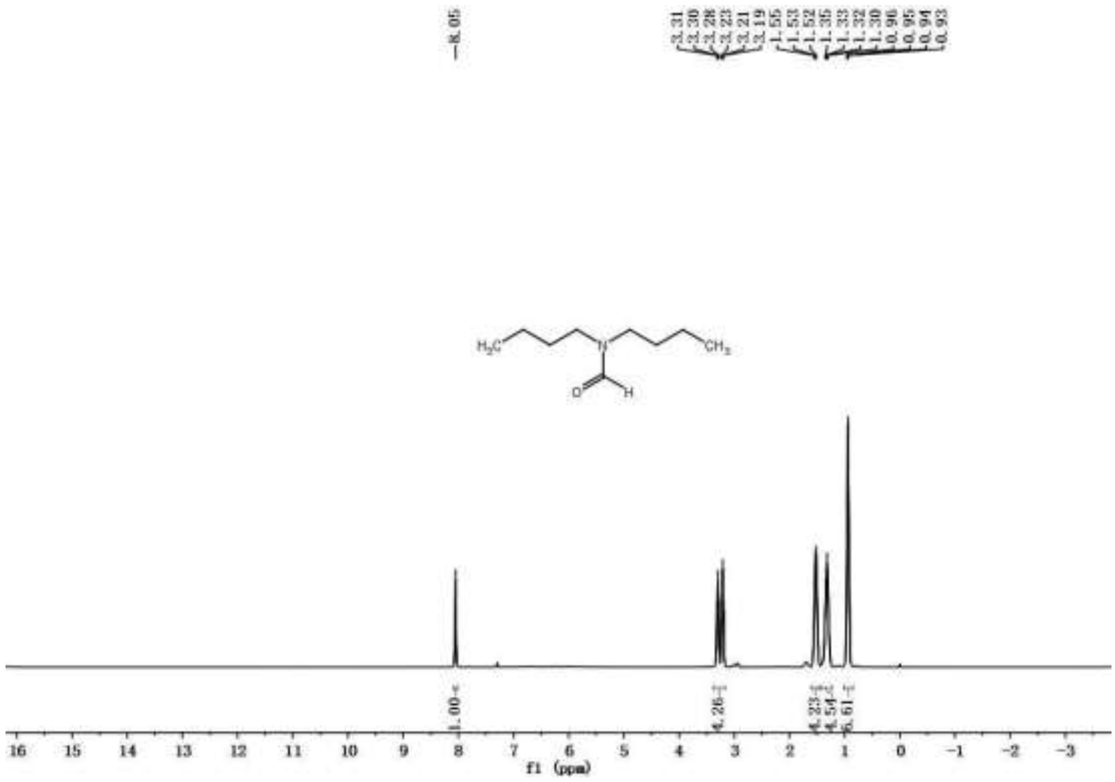
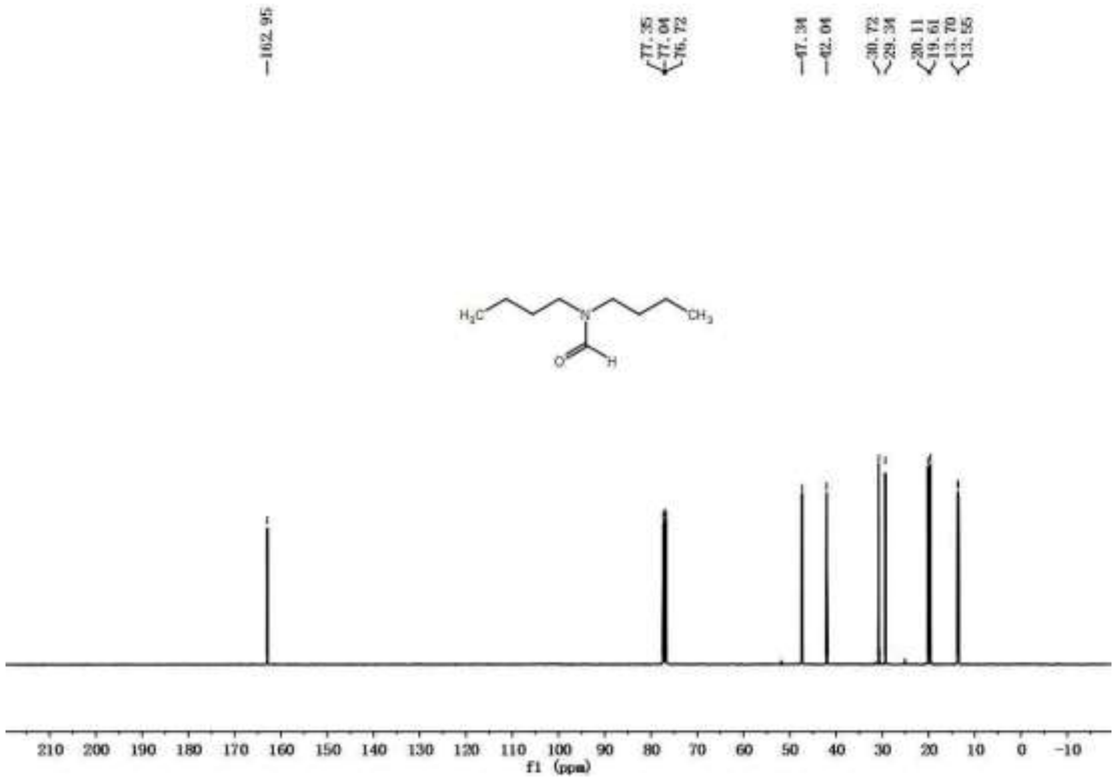
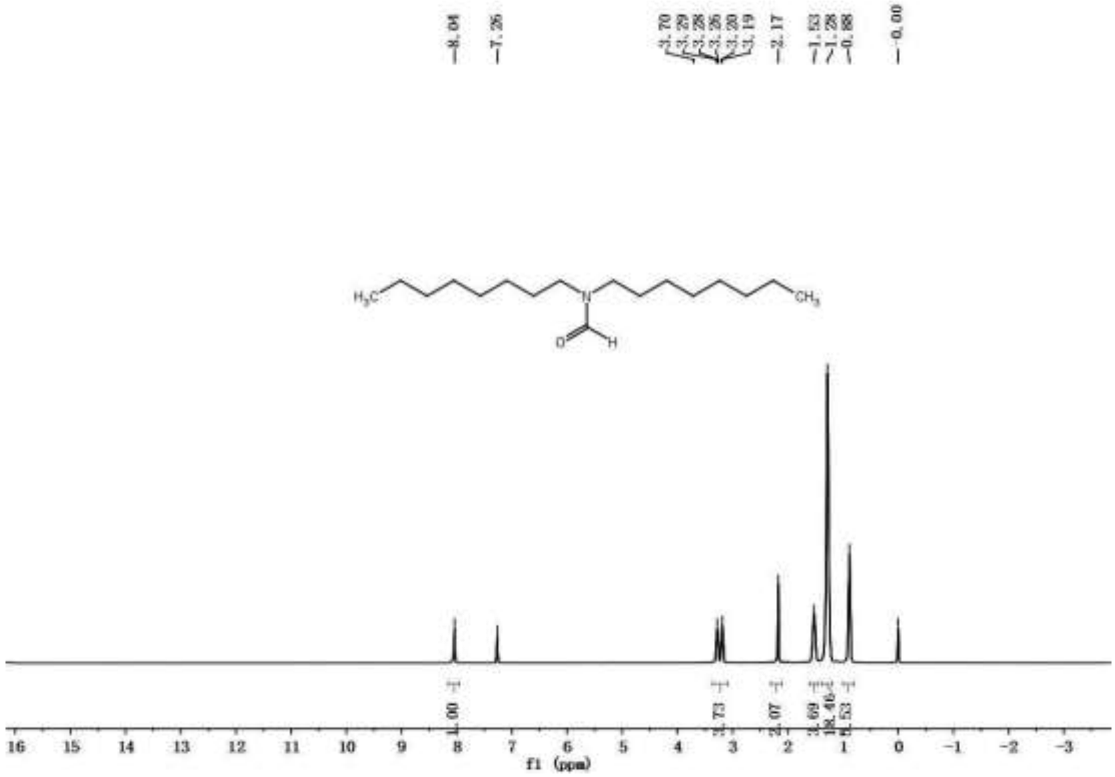
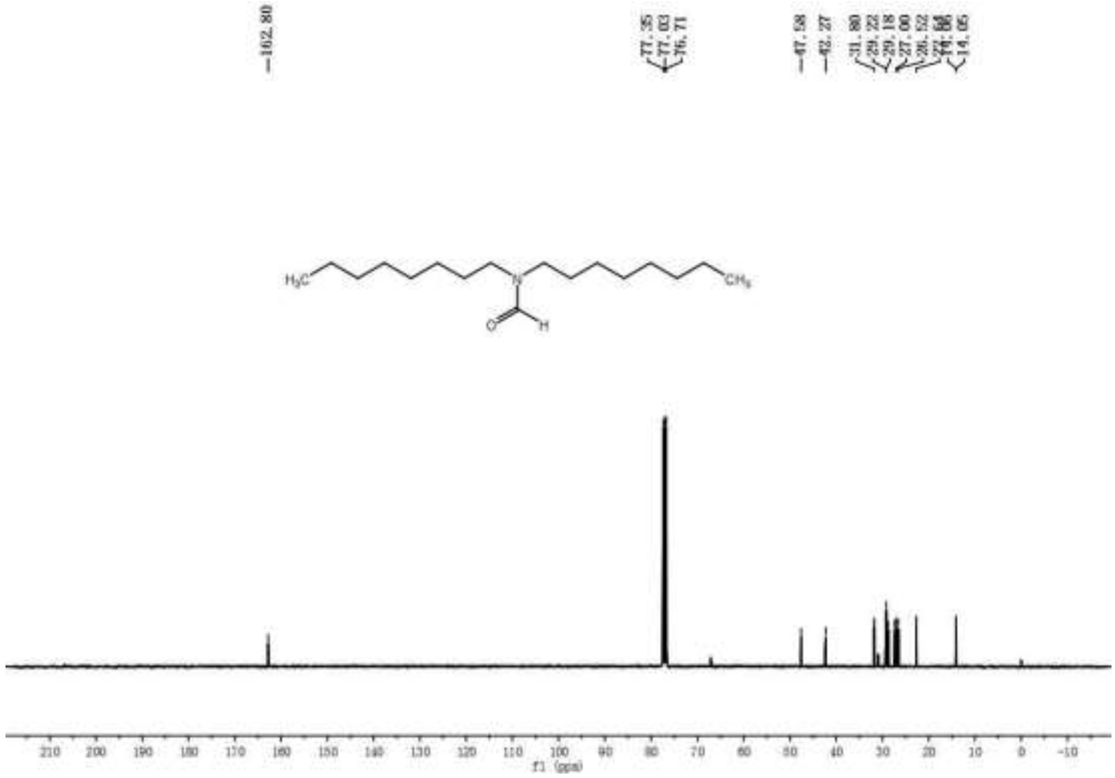
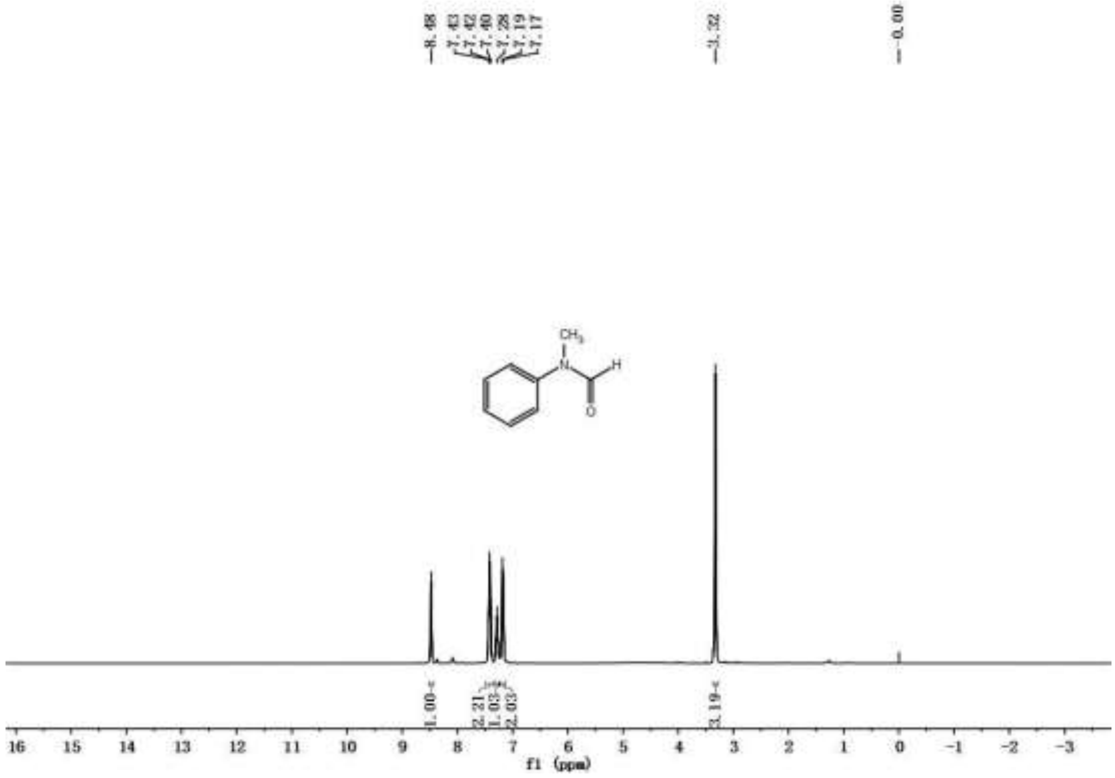
f1 (ppm)

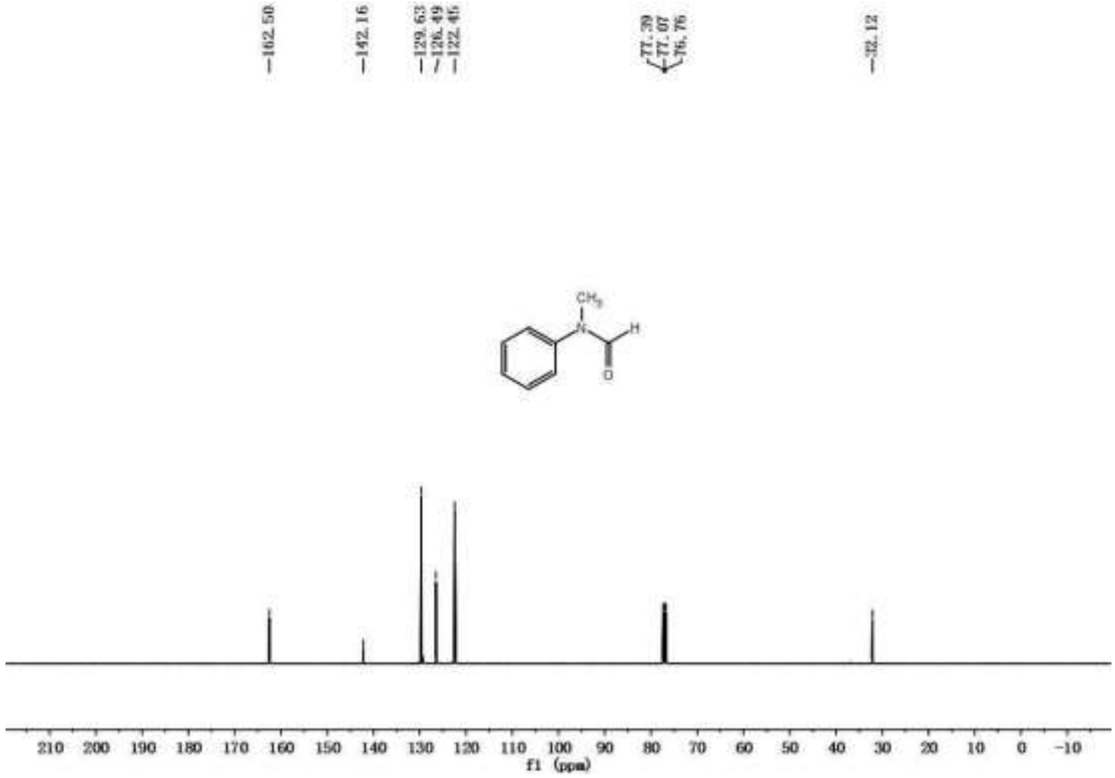

8.05
3.31
3.30
3.28
3.23
3.21
3.19
1.55
1.53
1.52
1.35
1.33
1.32
1.30
0.96
0.95
0.94
0.93
H_3C
N
CH_3
O
H
1.00
4.26
4.23
4.54
6.61
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


162.95
77.35
77.04
76.72
47.34
42.04
30.72
29.34
20.11
19.61
13.70
13.55
H_3C
N
CH_3
O
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.04
7.26
3.30
3.29
3.28
3.26
3.20
3.19
2.17
1.53
1.28
0.88
0.00
H_3C
N
O
H
CH_3
1.00
3.73
2.07
3.69
18.46
5.53
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)


162.80
77.35
77.03
76.71
47.58
42.27
31.80
29.22
29.18
27.60
26.52
14.05
H_3C
N
O
H
CH_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.48
7.43
7.42
7.40
7.28
7.19
7.17
3.32
0.00
CH3
N
H
O
1.00
2.21
1.03
2.03
3.19
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


162.50
142.16
129.63
126.49
122.45
77.39
77.07
76.76
32.12
CH3
N
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)