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Electronic Supplementary Information

Pyridine-functionalized organic porous polymers: applications in efficient CO_2 adsorption and conversion

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1. General experimental methods

Materials

All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise. 2,6-di(9H-carbazol-9-yl)pyridine (**CarPy**), **CarPy-CMP** were prepared following procedures reported in the literature (Chem. Commun. 2016, 10.1039/C1036CC09374D.). Preparation of **CarPy-CMP@Ru** was shown below. Ru/C (5 wt%) was purchased from Shanxi Rock New Materials Co. Ltd.

Instrumentation

Liquid ^{1}H NMR spectra was recorded in $CDCl_3$ using the residual $CHCl_3$ as internal reference (7.26 ppm) on Bruck 400 spectrometer. Liquid ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ using the residual $CHCl_3$ as internal reference (77.0 ppm). 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 120 ^{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. (HR) Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 and JEM-2011F instrument operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of ~3×10^{-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 content of Fe or Ru was determined by ICP-AES (VISTA-MPX). The reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a nonpolar capillary column (DB-5) (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) Synthesis of Car-CMP-1@Ru

Ref.: *Angew. Chem. Int. Ed.* 2014, **53**, 8645-8648.

Take the synthesis of **Car-CMP-1@Ru** as a typical example: 100 mg of **Car-CMP-1** were initially dispersed in 100 mL EtOH solution of $RuCl_3{\cdot}3H_2O$ (6.5 mg) to form a uniform suspensionvia tip sonication (500 W, 20 kHz, 38% amplitude power output) for 4 min and then stir for 2 h at room temperature. The mixture was dried under vacuum at 60 °C for 2 h, then put into a quartz tube and heated to 300 °C under H_2 atmosphere and maintained for 2 h.

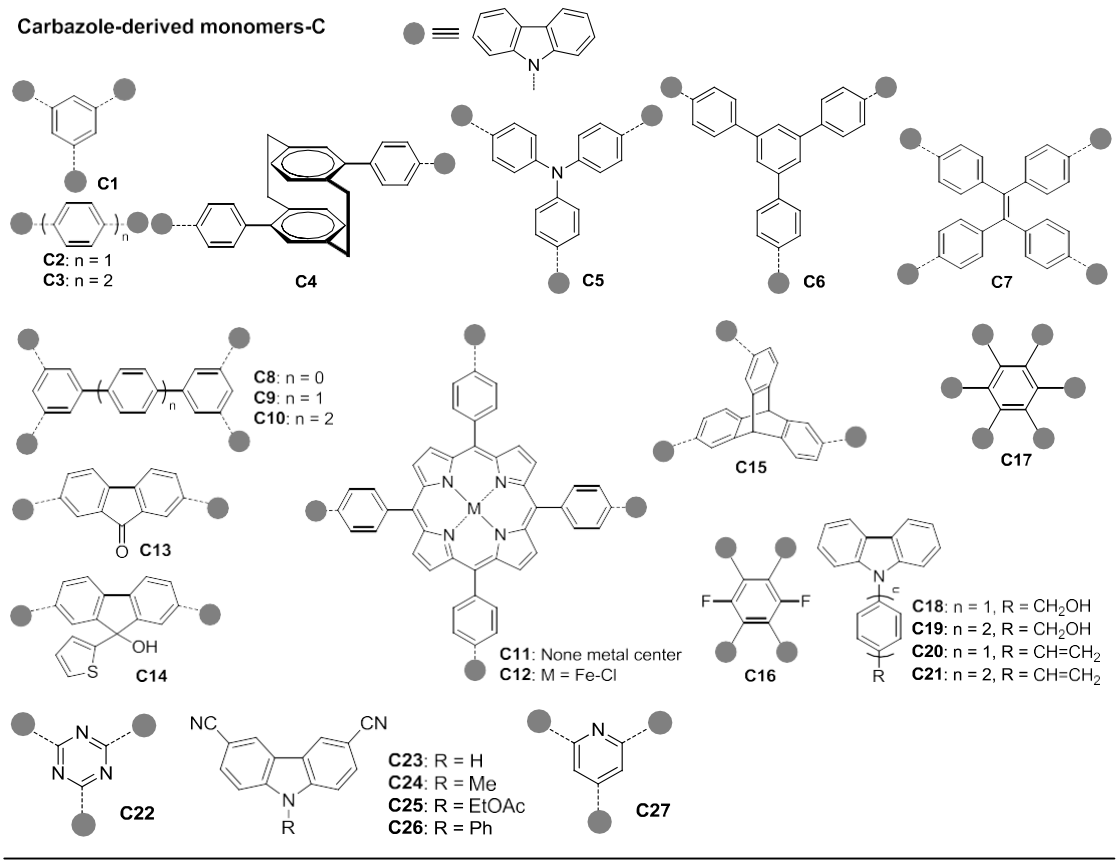
(2) Typical procedures for the formylation of morpholine

For a typital procedure, in a glovebox, **Car-CMP-1@Ru** (20 mg), morpholine (1 mmol) and MeOH (3 mL) was added successively into a stainless steel autoclave with a Teflon tube (25 mL

inner volume). CO_2 (4 MPa) and then H_2 was charged in the reactor untill the total pressure reached 8 MPa at room temperature. The autoclave was stirred at 130 ^oC for 24 h. After reaction, the autoclave was cooling to 0 ^oC then the excess of gas was vented slowly. Dodecane (internal standard) and CH_2Cl_2 (5 mL) was added, stirred vigorously and centrifuged. The upper liquid was analyzed by GC. For catalyst recycling, the catalyst was recycled by filtration, washed with CH_2Cl_2 and EtOH, and then dried under vacuum at 140 ^oC for 24 h, followed by being reused for the next run. For the substrate scope investigation, the products were isolated by column chromatography on silica gel (eluent: petroleum and dichloromethane) and identified by NMR spectra.

Table S1. CO_2 Adsorption capacities of CMPs derived from various carbazole monomers (273 K, 1 atm)

Entry	Monomer	BET surface areas/m^2 g^{-1}	CO_2 capacity /mg g^{-1}	Reference
1	**C1**	2220	212	*J. Am. Chem. Soc.* **2012**, *134*, 6084.
2	**C2**	510	78	*Small* **2014**, *10*, 308.
3	**C3**	630	84	*Small* **2014**, *10*, 308.
4	**C4**	660	90	*Small* **2014**, *10*, 308.
5	**C5**	1050	118	*Small* **2014**, *10*, 308.
6	**C6**	980	115	*Small* **2014**, *10*, 308.
7	**C7**	1430	132	*Small* **2014**, *10*, 308.
8	**C8**	1610	165	*Macromolecules* **2014**, *47*, 5926.
9	**C9**	2440	182	*Macromolecules* **2014**, *47*, 5926.
10	**C10**	1110	148	*Macromolecules* **2014**, *47*, 5926.
11	**C11**	1320	138	*Polym. Chem.* **2014**, *5*, 3081.
12	**C12**	1180	121	*Polym. Chem.* **2014**, *5*, 3081.
13	**C13**	611	89	*J. Mater. Chem. A* **2014**, *2*, 1877.
14	**C14**	1222	145	*J. Mater. Chem. A* **2014**, *2*, 1877.
15	**C15**	893	125	*Chem.-Asian J.* **2016**, *11*, 294.
16	**C16**	1109	160	*Polymer* **2015**, *70*, 52.
17	**C17**	790	94	*Polymer* **2015**, *70*, 52.
18	**C18**	780	103	*Polym. Chem.* **2015**, *6*, 2478.
19	**C19**	700	110	*Polym. Chem.* **2015**, *6*, 2478.
20	**C20**	1040	151	*Polym. Chem.* **2015**, *6*, 2478.
21	**C21**	1130	167	*Polym. Chem.* **2015**, *6*, 2478.
22	**C22**	840	162	*J. Mater. Chem. A* **2014**, *2*, 13422.
23	**C23**	982	106	*J. Mater. Chem. A* **2014**, *2*, 7795. *Macromolecules* **2014**, *47*, 2875.
24	**C24**	952	118	*J. Mater. Chem. A* **2014**, *2*, 7795.
25	**C25**	965	123	*J. Mater. Chem. A* **2014**, *2*, 7795.
26	**C26**	1187	132	*J. Mater. Chem. A* **2014**, *2*, 7795.
27	**C27**	1647	245	*Chem. Commun.* **2016**, *52*, 4454.



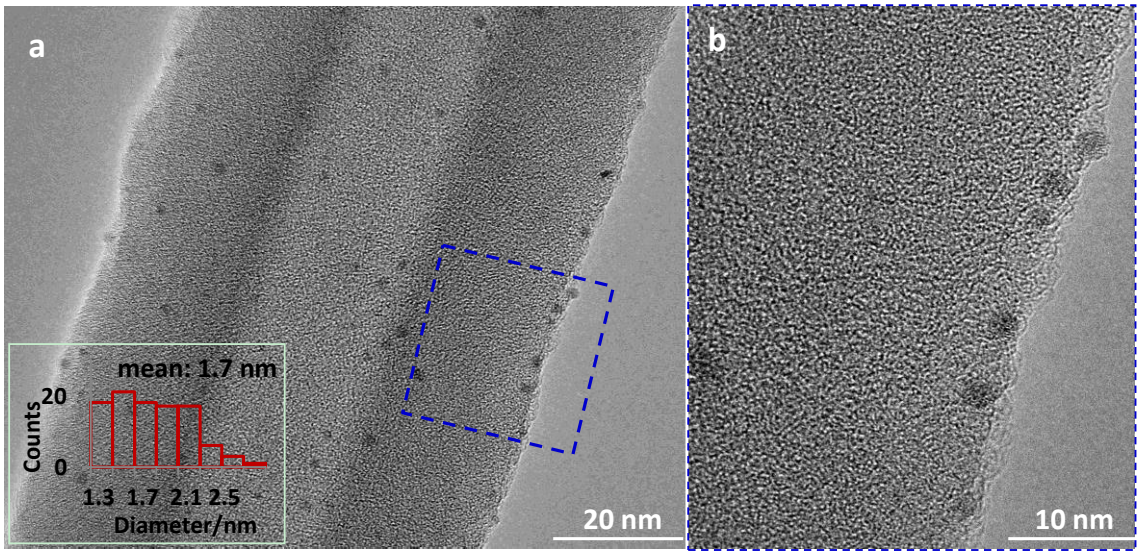


Figure S1 (HR)TEM images of **CarPy-CMP@Ru**. Map of Ru^0 particle sizes distribution was obtained by counting 100 particles. b was the magnified section within the blue dashed line square in a.

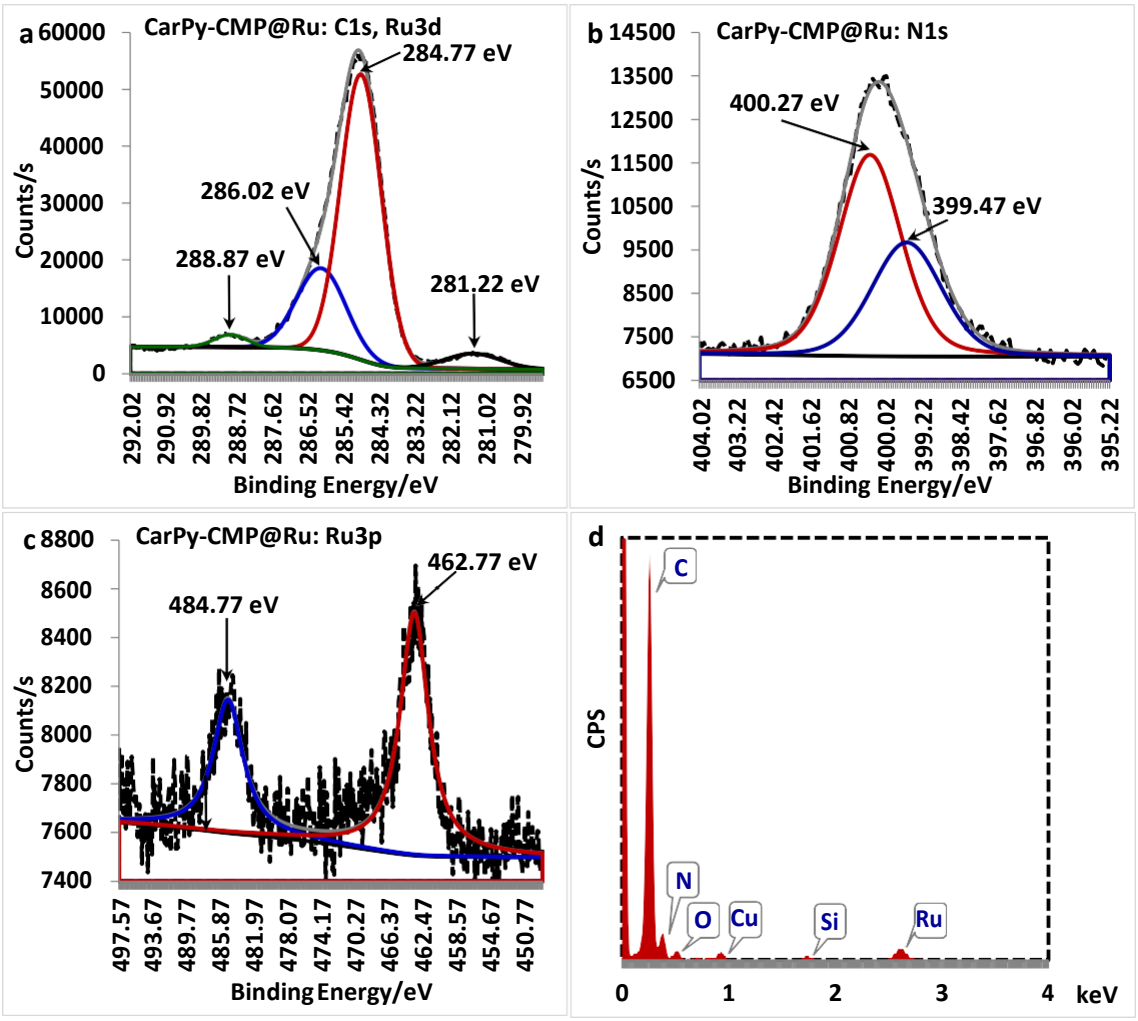


Figure S2 a, b, c) XPS spectra of C1s, N1s, Ru3d and Ru3p for **CarPy-CMP@Ru**. d) EDS profile of **CarPy-CMP@Ru**.

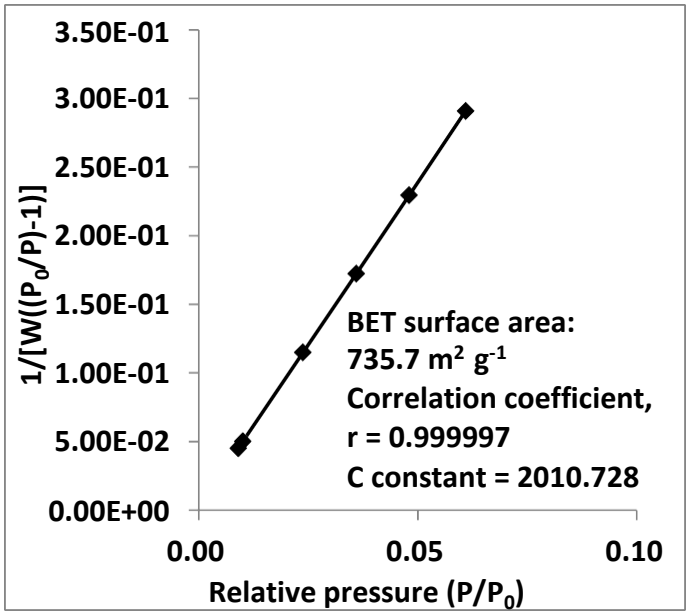


Figure S3 BET plot of **CarPy-CMP@Ru**.

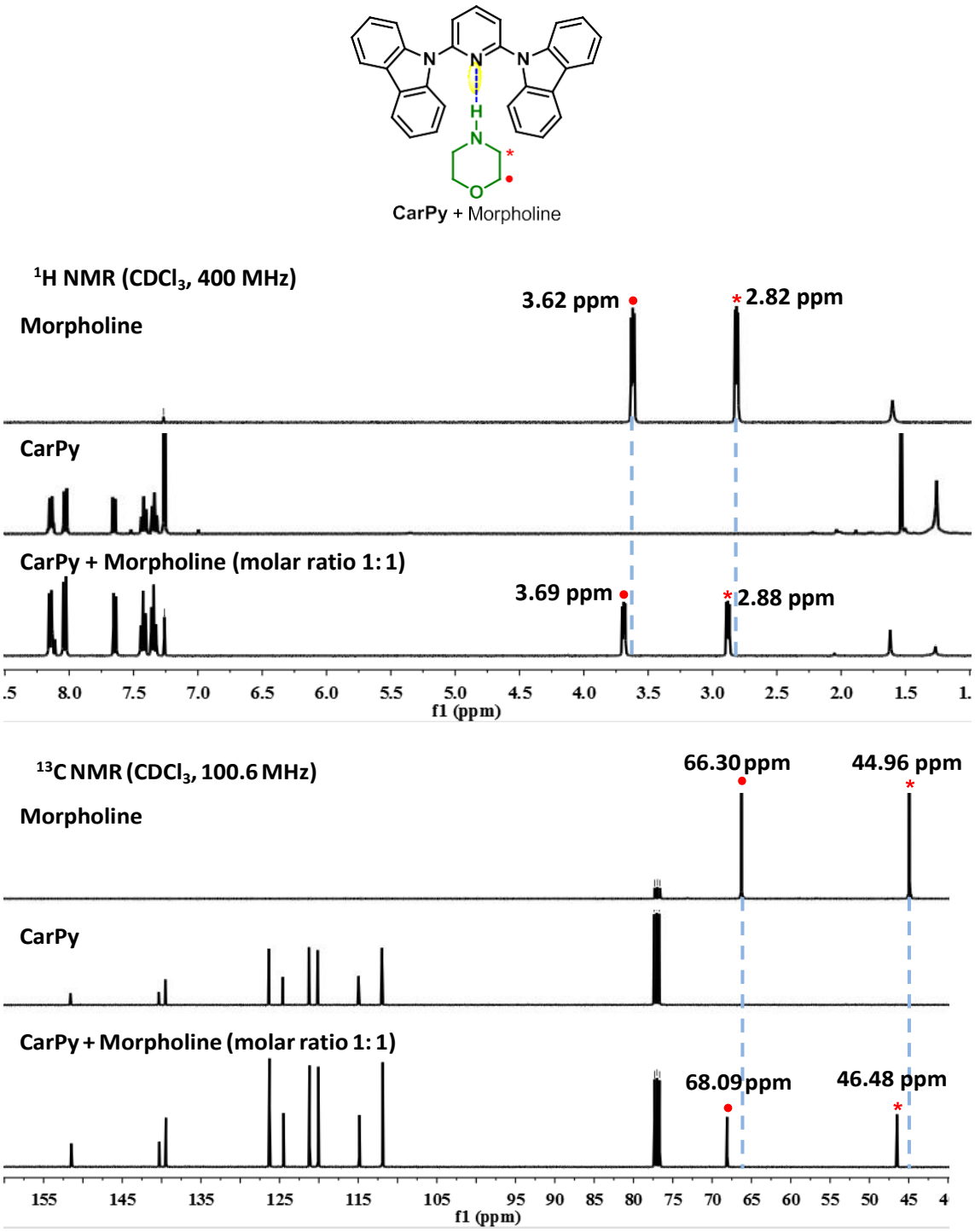


Figure S4 ^{1}H and ^{13}C NMR of morpholine and monomer CarPy, and their mixtures (molar ratio 1:1).

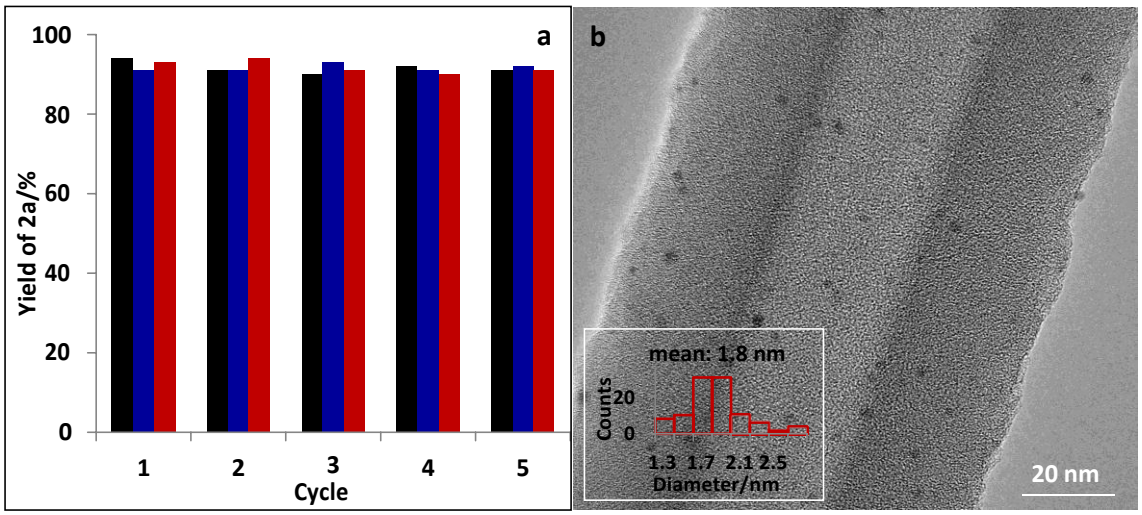
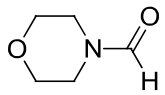


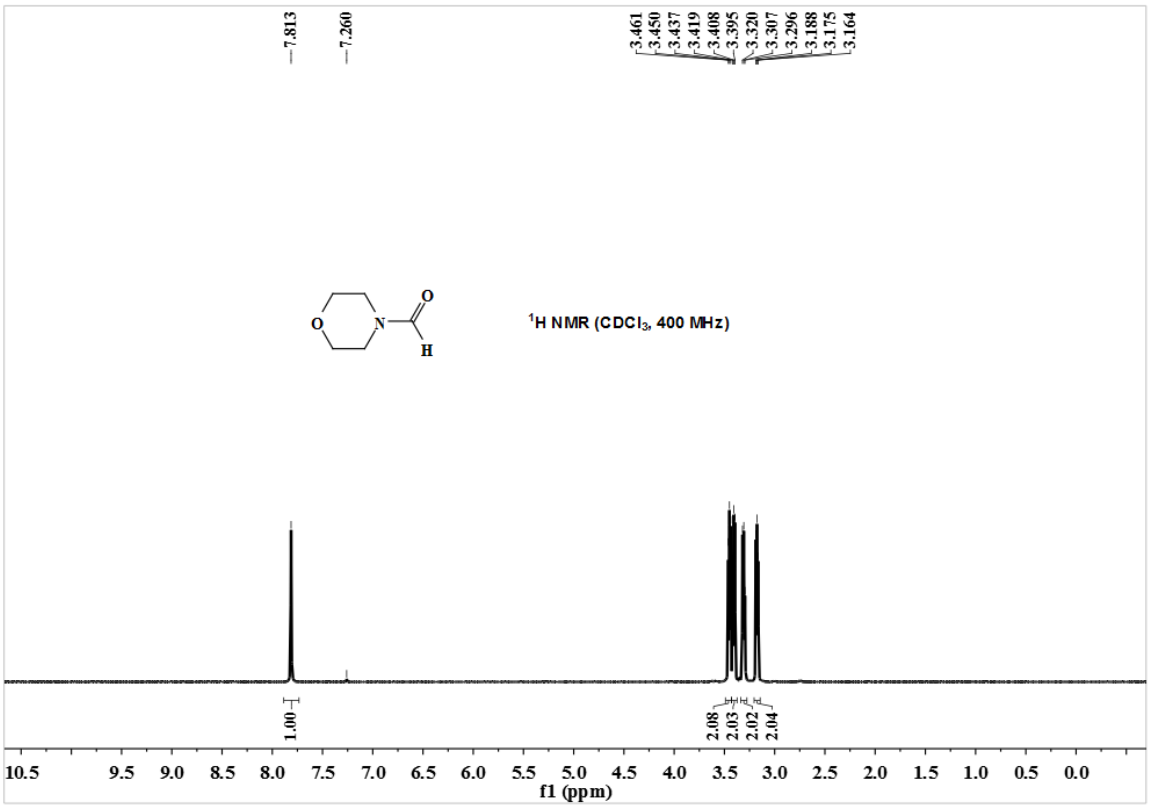
Figure S5 a) Recyclability test of **Car-CMP-1@Ru** for formylation of morpholine (**1a**) with CO_2/H_2. Three parallel experiment has been done for each cycle. Reaction conditions: **1a** 1 mmol, catalyst loading 0.5 mol% Ru based on **1a**, MeOH 3 mL, CO_2 pressure 4 MPa, total pressure (CO_2 + H_2) 8 MPa, 130 ^{o}C, 24 h. The yield of morpholine-4-carbaldehyde (**2a**) was determined by GC using dodecane as an internal standard. b) TEM images of **Car-CMP-1@Ru**. Map of Ru^0 particle sizes distribution was obtained by counting 100 particles.

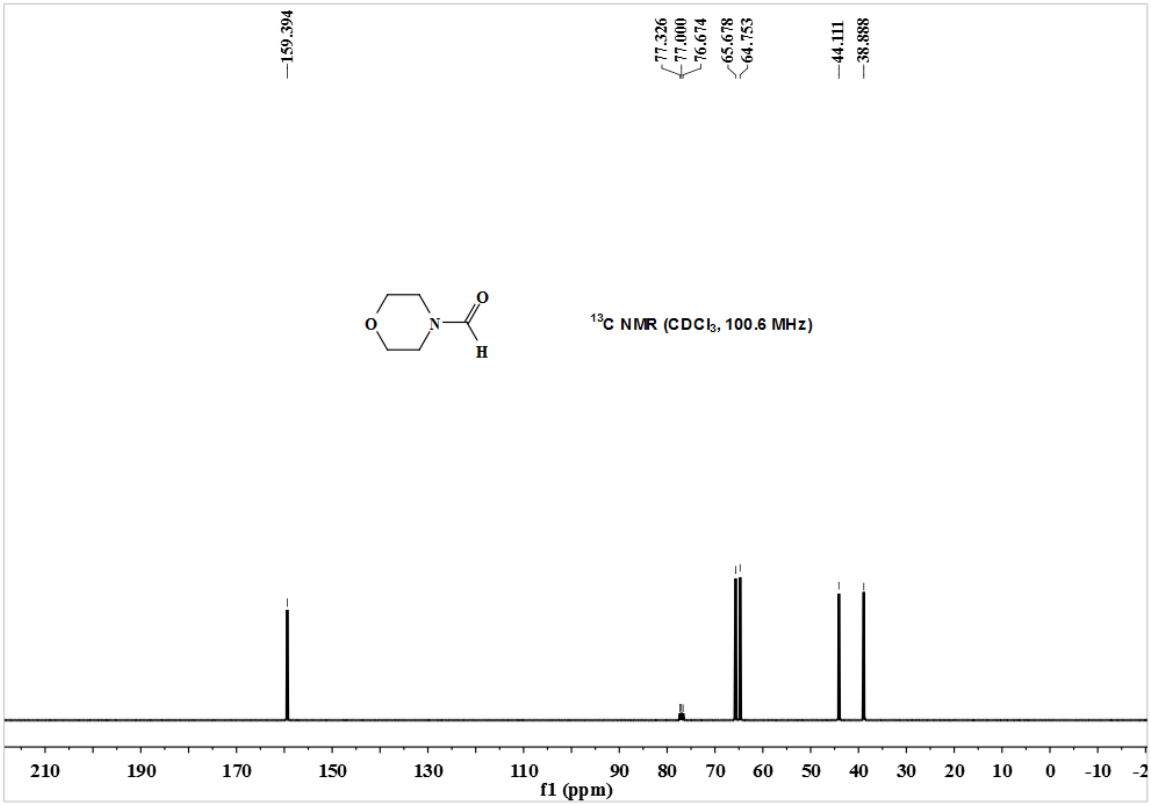
3. NMR characterization of the formamides

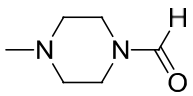


^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.17 (t, ^{3}J = 5.2 Hz, 2H), 3.31 (t, ^{3}J = 5.2 Hz, 2H), 3.41 (t, ^{3}J = 4.4 Hz, 2H), 3.45 (t, ^{3}J = 4.4 Hz, 2H), 7.81 (s, 1H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 38.89, 44.11, 64.75, 65.68, 159.39.



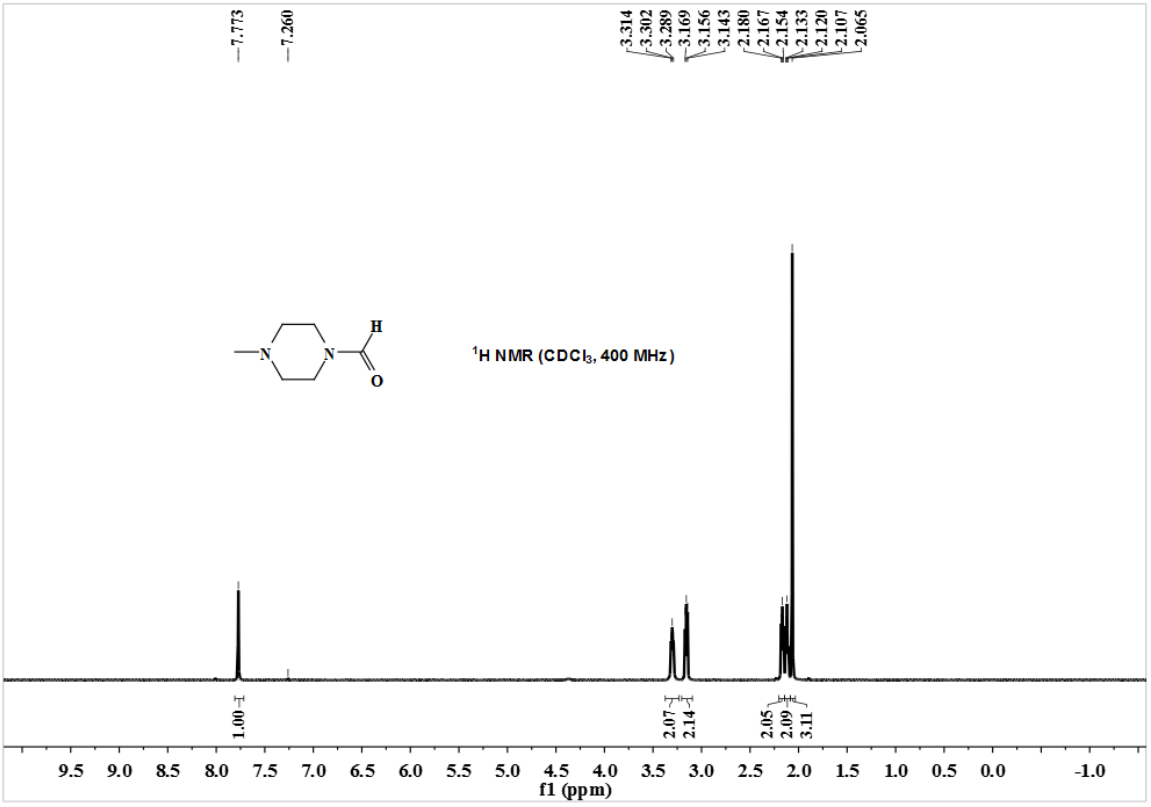


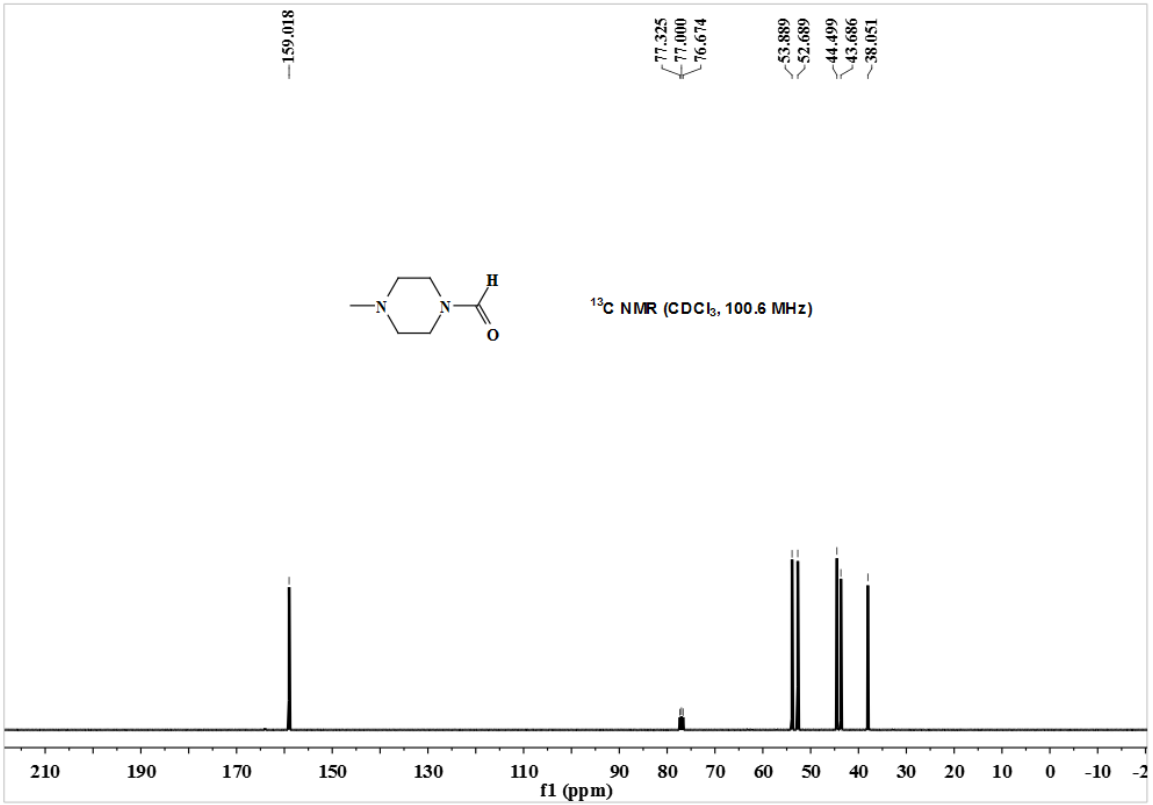


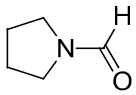
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.06 (s, 3H), 2.12 (t, ^{3}J = 5.2 Hz, 2H), 2.17 (t, ^{3}J = 5.2 Hz, 2 H), 3.16 (t,

^{3}J = 5.2 Hz, 2H), 3.30 (t, ^{3}J = 4.8 Hz, 2H), 7.77 (s, 1H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 38.05, 43.69, 44.50, 52.69, 53.89, 159.02.

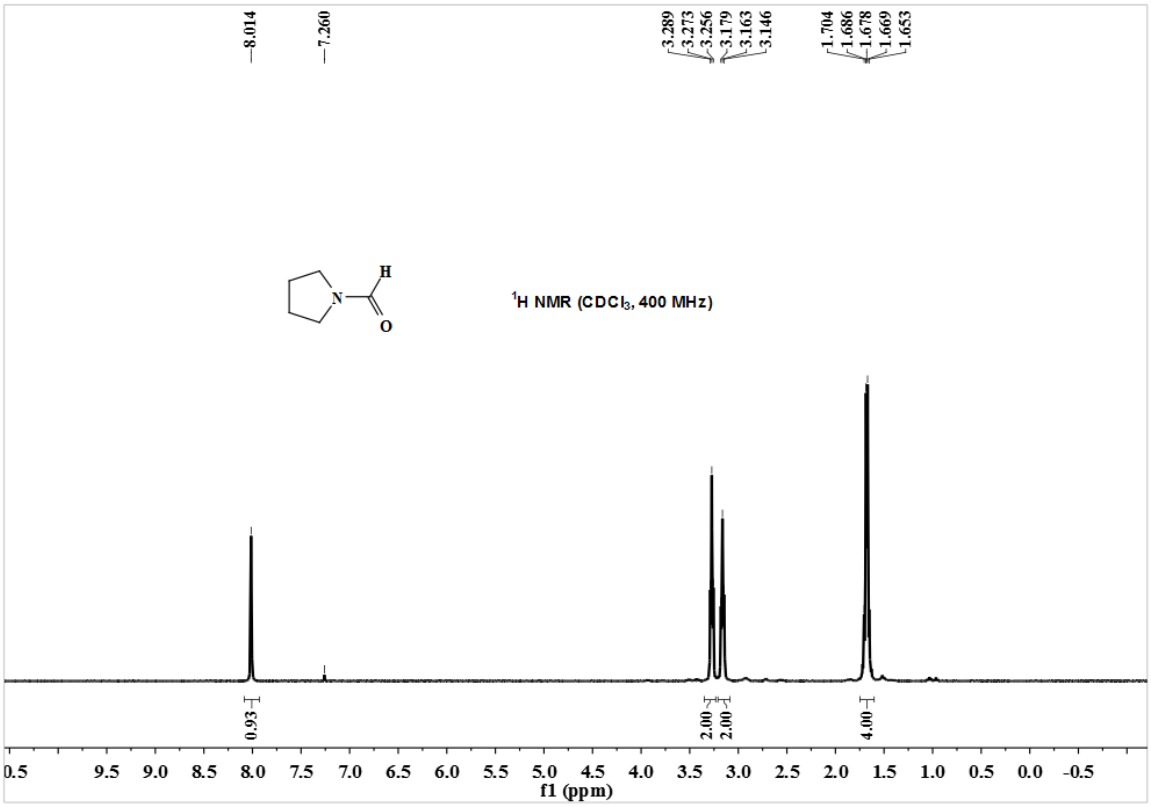


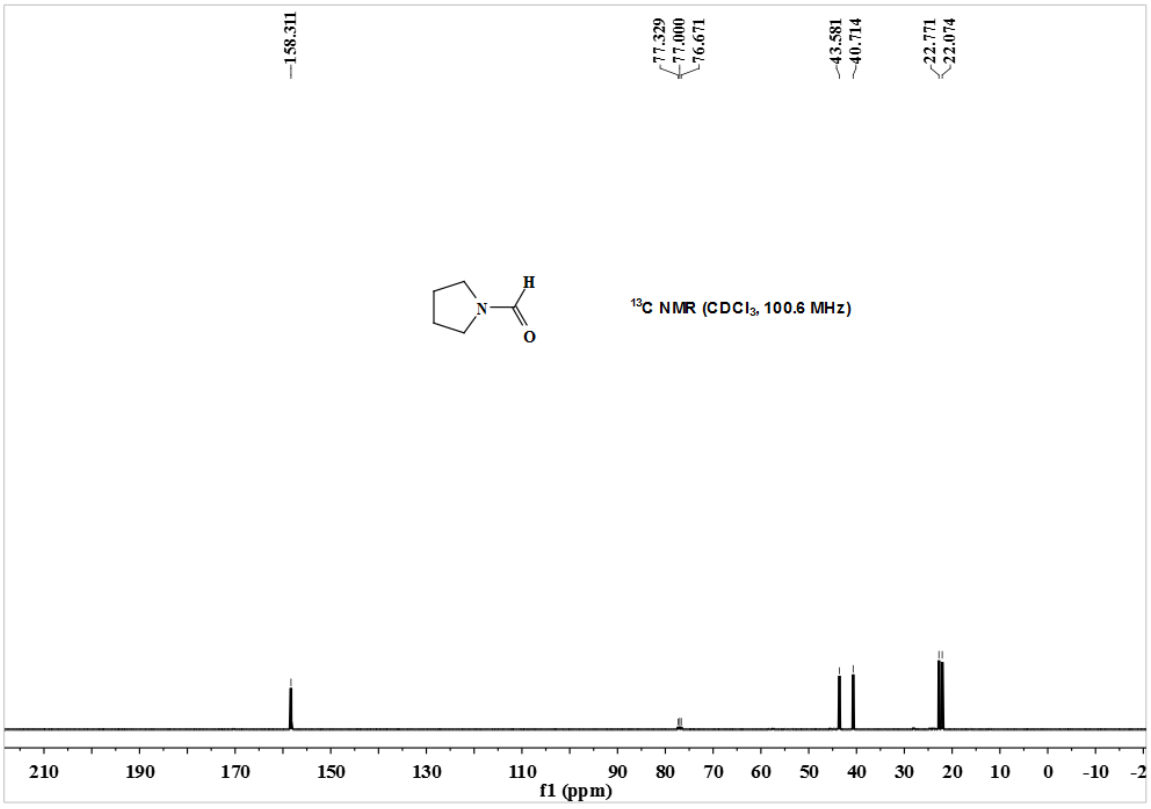


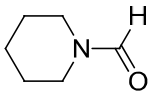


^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65-1.70 (m, 4H), 3.16 (t, ^{3}J = 6.4 Hz, 2H), 3.27 (t, ^{3}J = 6.4 Hz, 2 H), 8.01 (s, 1H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.07, 22.77, 40.71, 43.58, 158.31.

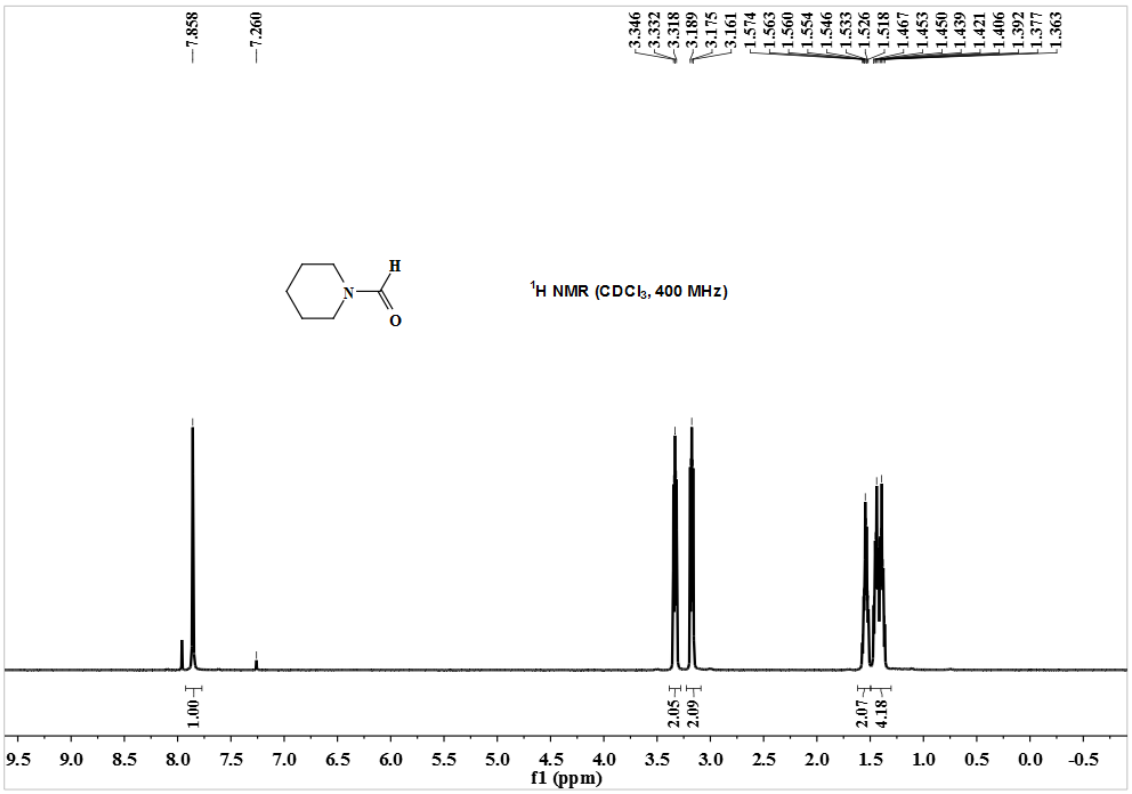


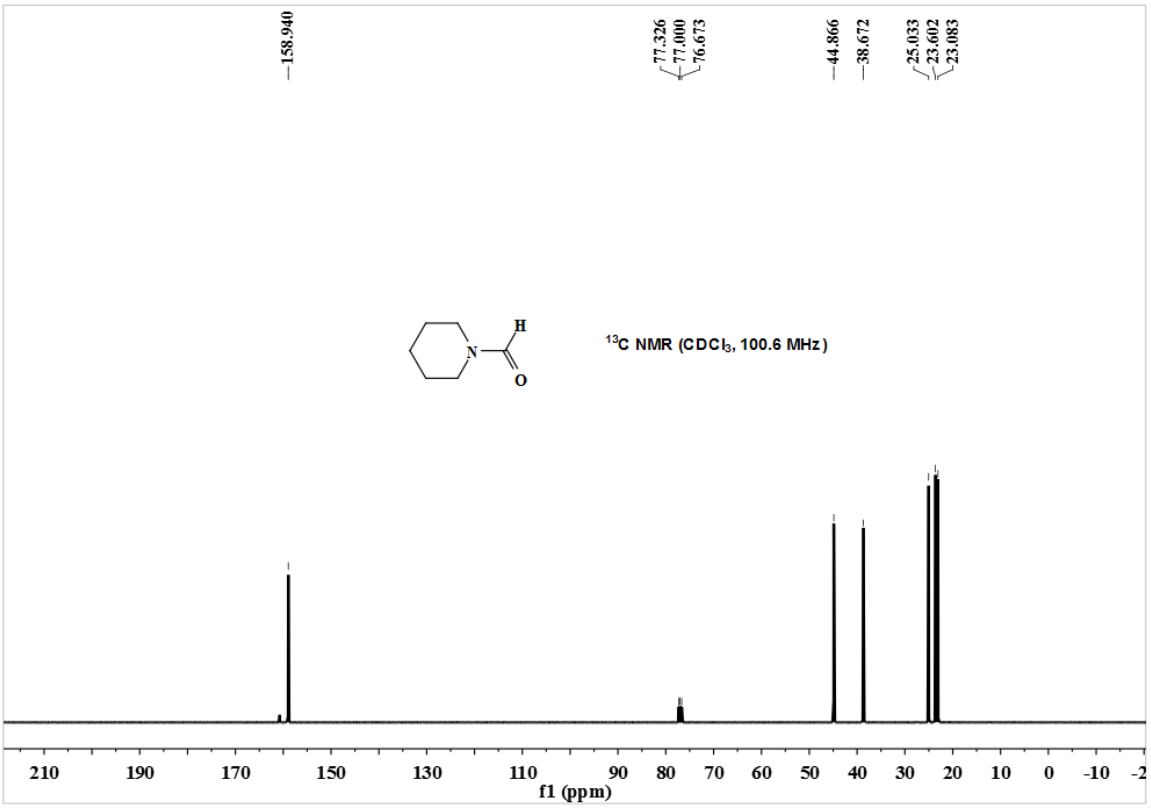


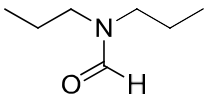


^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36-1.47 (m, 4H), 1.52-1.57 (m, 2H), 3.17 (t, ^{3}J = 5.6 Hz, 2H), 3.33 (t, ^{3}J = 5.6 Hz, 2 H), 7.86 (s, 1H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 23.08, 23.60, 25.03, 38.67, 44.87, 158.94.

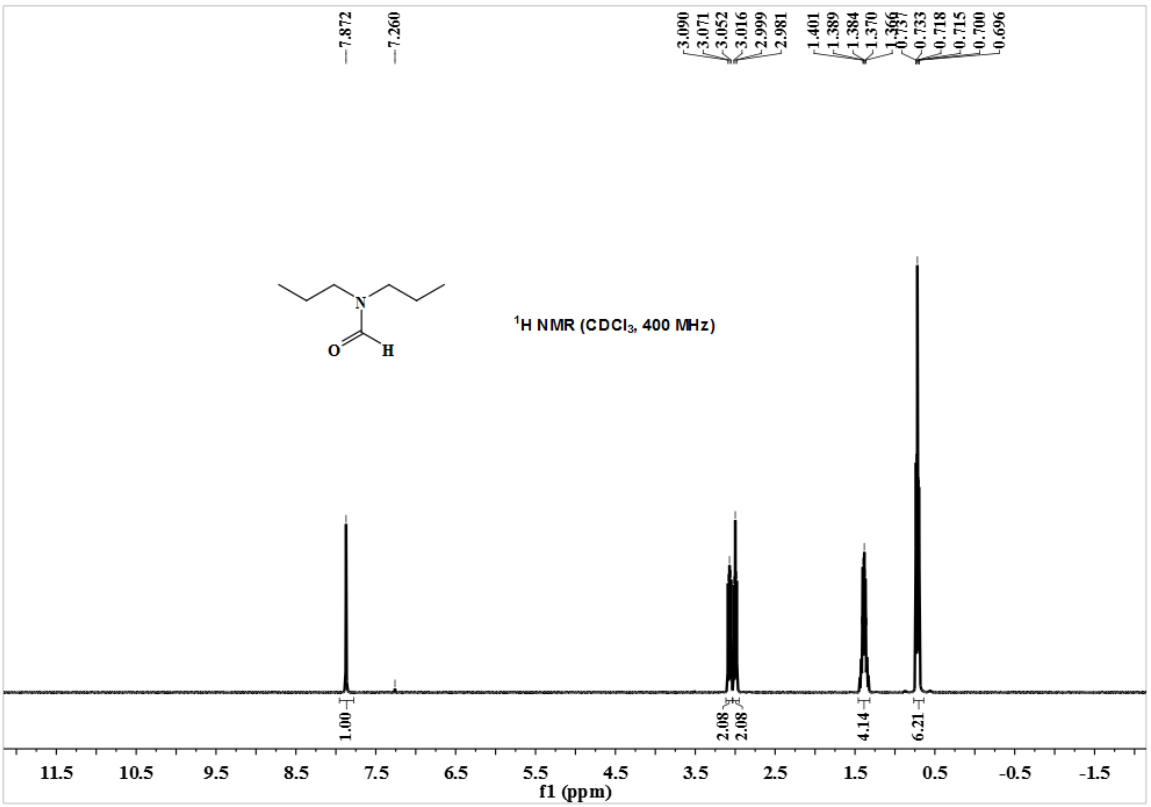






^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.70-0.74 (m, 6H), 1.33-1.44 (m, 4H), 3.00 (t, ^{3}J = 6.8 Hz, 2H), 3.07 (t, ^{3}J = 7.6 Hz, 2H), 7.87 (s, 1H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 9.41, 9.85, 19.22, 20.50, 42.23, 47.55, 161.15.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3.071
3.052
3.016
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2.981
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1.389
1.384
1.370
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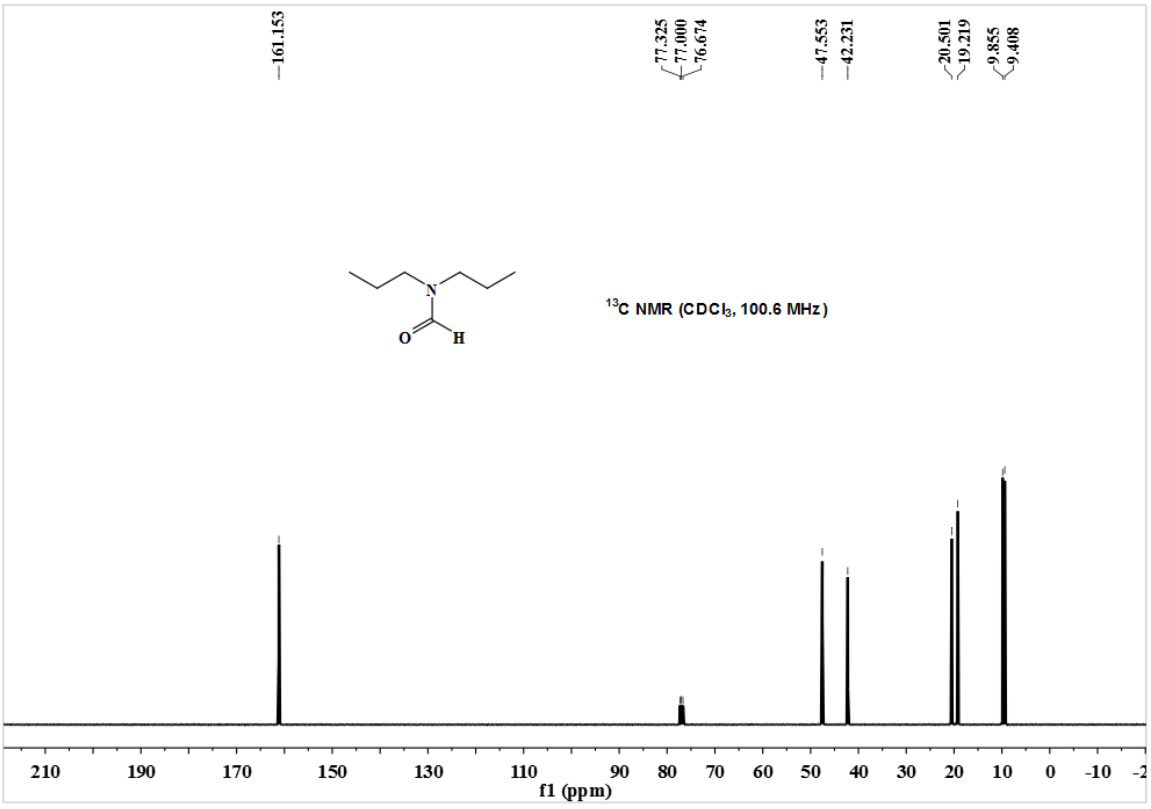
0.718
0.715
0.700
0.696
^{1}H NMR (CDCl$_3$, 400 MHz)
1.00
2.08
2.08
4.14
6.21
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)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47.553
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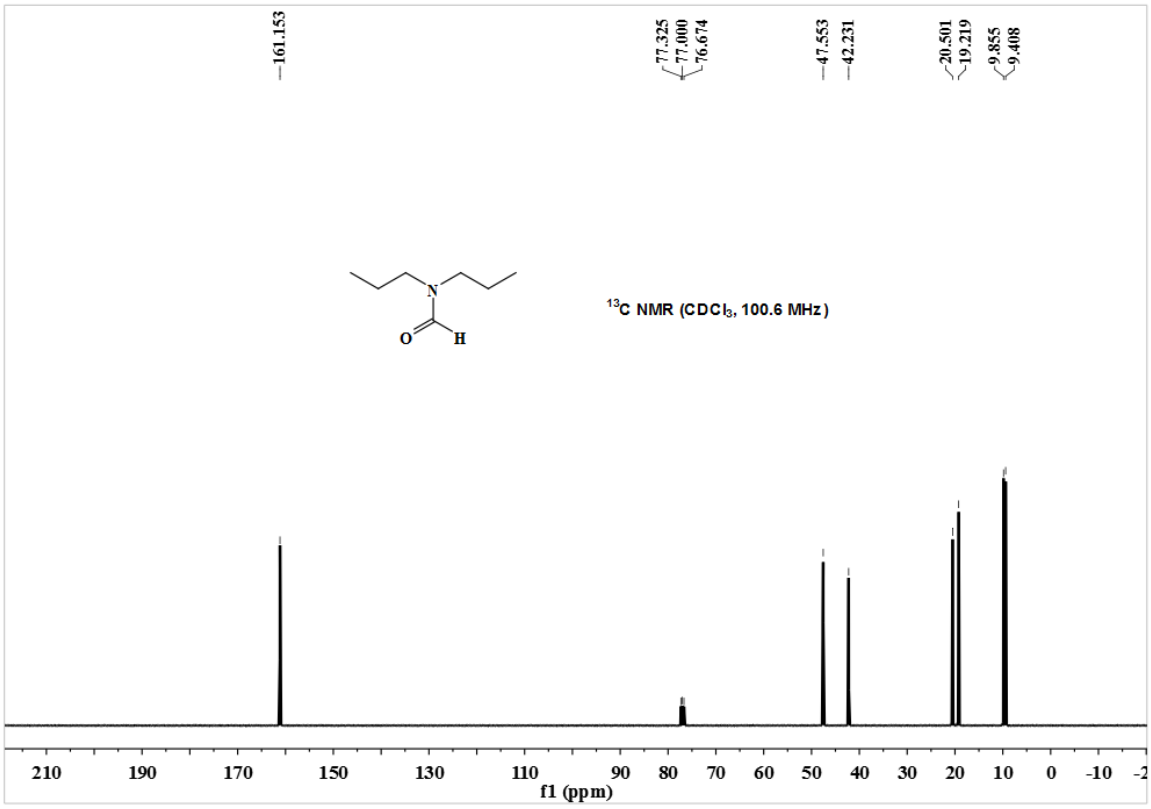
f1 (ppm)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N
O
H
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210
190
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90
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70
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30
20
10
0
-10
f1 (ppm)