Supporting Information

Highly Efficient Conversion of CO_2 to N-Formamides Catalyzed by a Noble-Metal-Free Aluminum-based MOF under Mild Conditions

Zhi-Qiang Wang,[#ab] Cheng-Hua Deng,[#c] Xiao Liu[b]* and Wen-Min Wang[bd]*

[a]Basic Sciences Depart, Shanxi Agricultural University, Jinzhong, 030800, P.R. China.

[b]Department of Chemistry and Key Laboratory of Advanced Energy Material Chemistry (MOE), College of Chemistry, Nankai University, Tianjin 300071, P. R. China.

[c]Bernal Institute, Department of Chemical Sciences, University of Limerick, Limerick V94 T9PX, Ireland.

[d]College of Chemistry and Materials, Taiyuan Normal University, Jinzhong, 030619, China.

*Correspondence to: lx@nankai.edu.cn; wangwenmin0506@126.com.

[#]ZQW and CHD contributed equally to this work.

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Experimental Section

General Information. Unless otherwise noted, all manipulations were performed under a dry argon or carbon dioxide atmosphere using Schlenk-line techniques. All the reagents employed were commercially available and used without further purification, Aluminum(III) chloride ($AlCl_3 \cdot 6H_2O$, Aladdin, 99%), 3,5-pyrridinedicarboxylic acid (Hpydc, Aladdin, 98%), Sodium hydroxide (NaOH, Aladdin, 98%), $PhSiH_3$ (Energy Chemical, 99%), 1,8-diazabicyclo[5.4.0]undec-7ene (DBU, Energy Chemical, 99%), Et_3N (Energy Chemical, 99.5%), Cs_2CO_3 (Energy Chemical, 99.99%), K_2CO_3 (Energy Chemical, 99.99%), $(C_2H_5O)_3SiH$ (Energy Chemical, 98%). Superdry DME, THF, CH_3OH and CH_3CN (Energy Chemical, 98%) with molecular sieves were used without further purification. The substrates are commercially purchased from Energy Chemical and require no further purification.

NMR spectra were recorded on a Bruker Ascend-400 spectrometer (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz; $CDCl_3$). Data were reported in the following order: chemical shift in ppm (multiplicity was indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)). Power X-ray diffraction (PXRD) was tested on an Ultima IV X-ray diffractometer using Cu Kα radiation in the 2θ range of 3-50° (λ = 0.154178 nm). Morphologies of samples were characterized by scanning electron microscope (SEM, ZEISS, MERLIN Compact).

Synthesis of CAU-10pydc. The metal precursor solution was first obtained by mixing 7.0 g (29 mmol) of $AlCl_3 \cdot 6H_2O$ in 20 mL of deionized water, followed by its dropwise addition into the linker solution prepared by dissolving 5.0 g (30 mmol) of Hpydc and 3.6 g (90 mmol) of NaOH in 60 mL of deionized water. The reaction solution after stirring for 10 min at room temperature was elevated and maintained at 120 °C for 12 h under reflux conditions. The white crystallites of CAU-10pydc formed after hydrothermal reflux synthesis were separated by filtration, and the purification was individually performed at room temperature for 3 h with 150 mL of deionized water and 150 mL of EtOH. After that, the filtered CAU-10pydc precipitate was dried at 150 °C for 12 h in a convection oven. The weight of the recovered sample was 5.58 g (reaction yield: 92%, based on Al).

General Experimental Procedures for 2a-k *via* Formylation of 1a–k. In a 10 mL Schlenk tube, a mixture of N-methylaniline (**1**) (1.0 mmol, 1.0 equiv.), $PhSiH_3$ (1.5 mmol, 1.5 equiv.), and CAU-10pydc (30 mg) were added in 2 mL anhydrous CH_3CN. Once added, the Schlenk tube was placed at atmospheric pressure of CO_2 (1 atm) and stirred for 12 h at 25°C. Then, the system was evaporated under the reduced pressure directly. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product **2**.

Experimental Procedures for the Recyclability Test of CAU-10pydc. The CAU-10pydc catalyst was recovered in the solid residue after centrifugation and separation from the organic layer containing the product. The solid residue was washed with methanol and H_2O, then respectively soaked in methanol for 5 h. The solid residue

containing recovered catalyst was directly used as recycled catalyst in the subsequent runs.

DFT Calculations. DFT calculations were then performed to optimize the geometry and calculate the Gibbs free energy of the reaction on the Gaussian 16 program[1] with the B3LYP functional.[2] The geometry optimization and transit state search were performed using the def2-svp basis set for all atoms. Single point energies were calculated at the B3LYP/def2tzvp level on optimized geometries.[3]

General Characterizations and Potential Mechanism

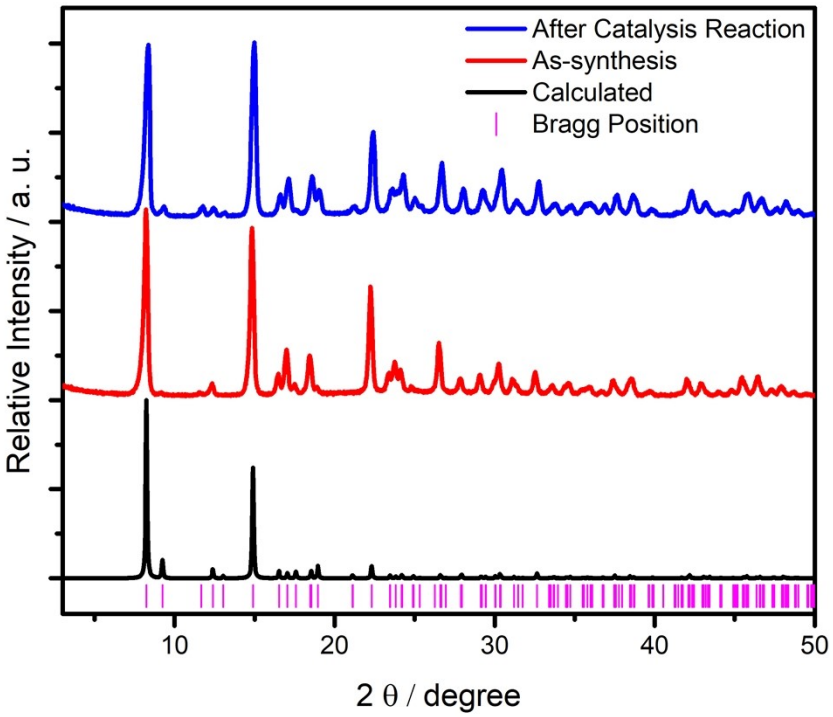


Figure S1. PXRD patterns of **CAU-10pydc**.

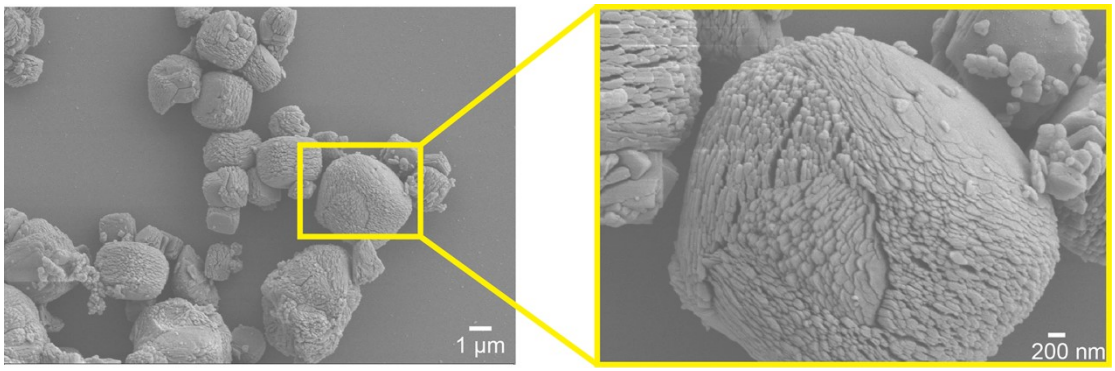
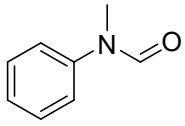


Figure S2. SEM images of **CAU-10pydc** (1 µm and 200 nm) after 5 cycles of **1a** to **2a** catalytic reaction.

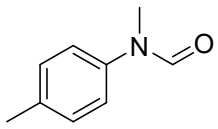
NMR Spectra



N-methyl-N-phenylformamide (2a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.39-7.43 (t, *J*=8Hz, 2H), 7.25-7.29 (m, 1H), 7.16-7.18 (d, *J*=8Hz, 2H), 3.31 (s, 3H);

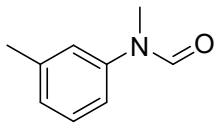
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.34, 142.20, 129.63, 122.35, 77.48, 77.16, 76.84, 32.03.



N-methyl-N-(p-tolyl)formamide (2b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.19-7.21 (d, *J*=8Hz, 2H), 7.04-7.06 (d, *J*=8Hz, 2H), 3.28 (s, 3H), 2.36 (s, 3H);

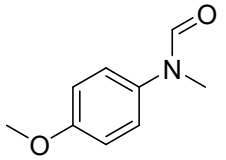
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.51, 139.80, 136.50, 130.26, 122.68, 77.48, 77.16, 76.84, 32.35, 20.98.



N-methyl-N-(m-tolyl)formamide (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.28-7.32 (t, *J*=8Hz, 1H), 7.09-7.11 (d, *J*=8Hz, 1H), 6.97-6.99 (d, *J*=8Hz, 2H), 3.31 (s, 3H), 2.40 (s, 3H);

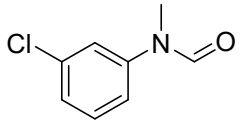
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.46, 142.22, 139.76, 129.47, 127.27, 123.18, 119.54, 77.48, 77.16, 76.84, 32.16, 21.49.



N-(4-methoxyphenyl)-N-methylformamide (2d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32(s, 1H), 7.07-7.09 (d, *J*=8Hz, 2H), 6.90-6.92 (d, *J*=8Hz, 2H), 3.81 (s, 3H), 3.25 (s, 3H);

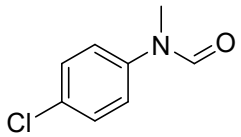
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56, 158.38, 135.33, 124.75, 114.85, 77.48, 77.16, 76.84, 55.64, 32.79.



N-(3-chlorophenyl)-N-methylformamide (2e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.34-7.38 (t, *J*=8Hz, 1H), 7.26-7.28 (d, *J*=8Hz, 1H), 7.20 (s, 1H), 7.08-7.10 (d, *J*=8Hz,1H), 3.33 (s, 3H);

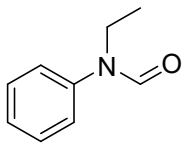
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 143.42, 135.33, 130.69, 126.44, 122.30, 120.13, 77.48, 77.16, 76.84, 31.98.



N-(4-chlorophenyl)-N-methylformamide (2f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.35-7.38 (d, *J*=12Hz, 2H), 7.10-7.12 (d, *J*=8Hz, 2H), 3.29 (s, 3H);

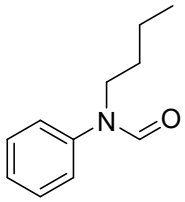
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.00, 140.73, 131.97, 129.74, 123.08, 77.44, 77.12, 76.81, 32.04.



N-ethyl-N-phenylformamide (2g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.39-7.43 (t, *J*=8Hz, 2H), 7.28-7.32 (t, *J*=8Hz, 1H), 7.16-7.17 (d, *J*=4Hz, 2H), 3.83-3.89 (m, 2H), 1.14-1.18 (t, *J*=8Hz, 3H);

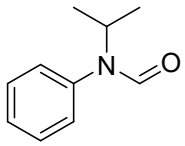
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.17, 140.94, 129.75, 126.99, 124.39, 77.48, 77.16, 76.84, 40.21, 13.17.



N-phenyl-N-propylformamide (2h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.39-7.43 (t, *J*=8Hz, 2H), 7.27-7.31 (t, *J*=8Hz, 1H), 7.16-7.18 (d, *J*=8Hz, 2H), 3.79-3.83 (t, *J*=8Hz, 2H), 1.47-1.55 (m, 2H), 1.28-1.36 (m, 2H), 0.87-0.90 (t, *J*=8Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.48, 141.18, 129.75, 126.94, 124.37, 77.48, 77.16, 76.84, 44.85, 29.81, 20.13, 13.83.



N-isopropyl-N-phenylformamide (2i)

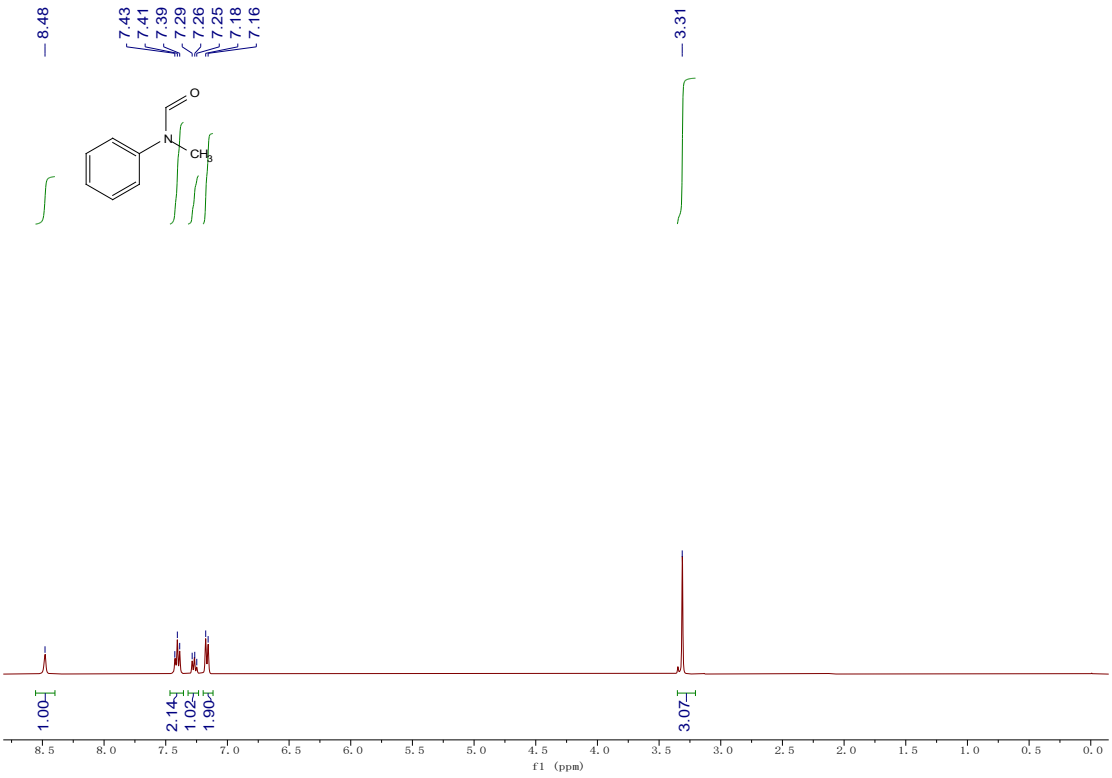
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.38-7.43 (m, 3H), 7.15-7.17 (d, *J*=8Hz, 2H), 4.77-4.83 (m, 1H), 1.19-1.20 (d, *J*=8Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.67, 138.48, 129.35, 129.07, 128.26, 77.48, 77.16, 76.84, 45.87, 21.03.

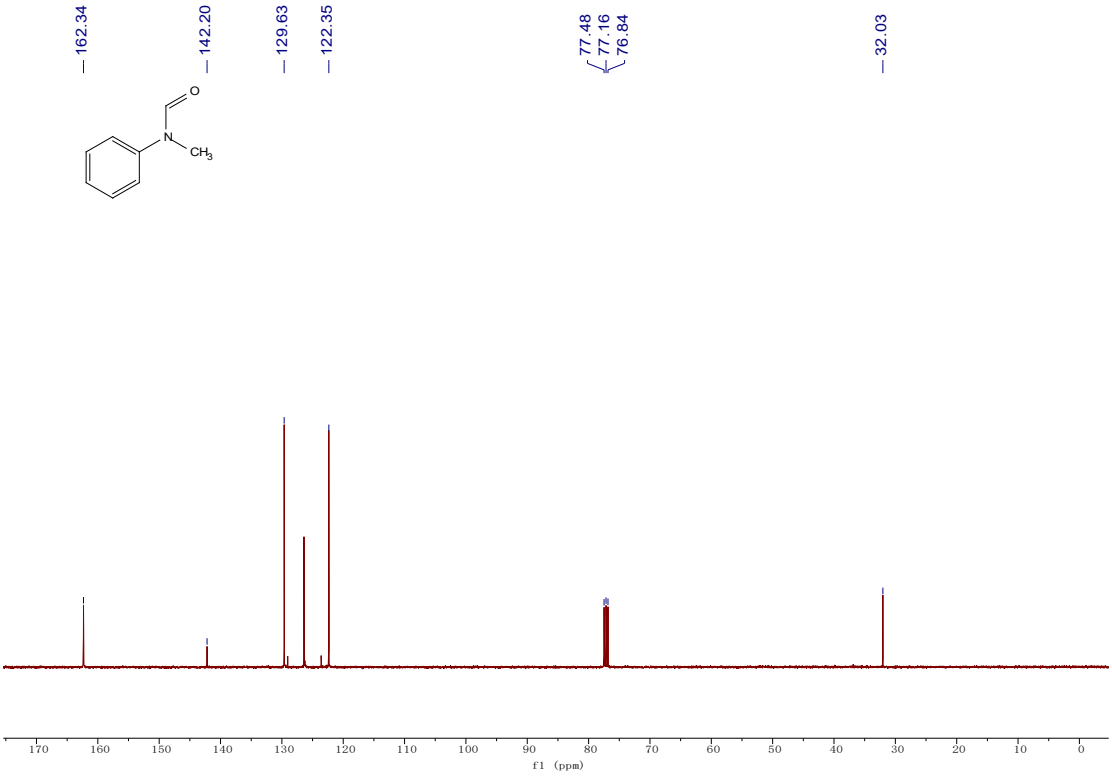
^{1}H NMR and ^{13}C NMR Spectra

N-methyl-N-phenylformamide **(2a)**

^{1}H NMR (400 MHz, $CDCl_3$)

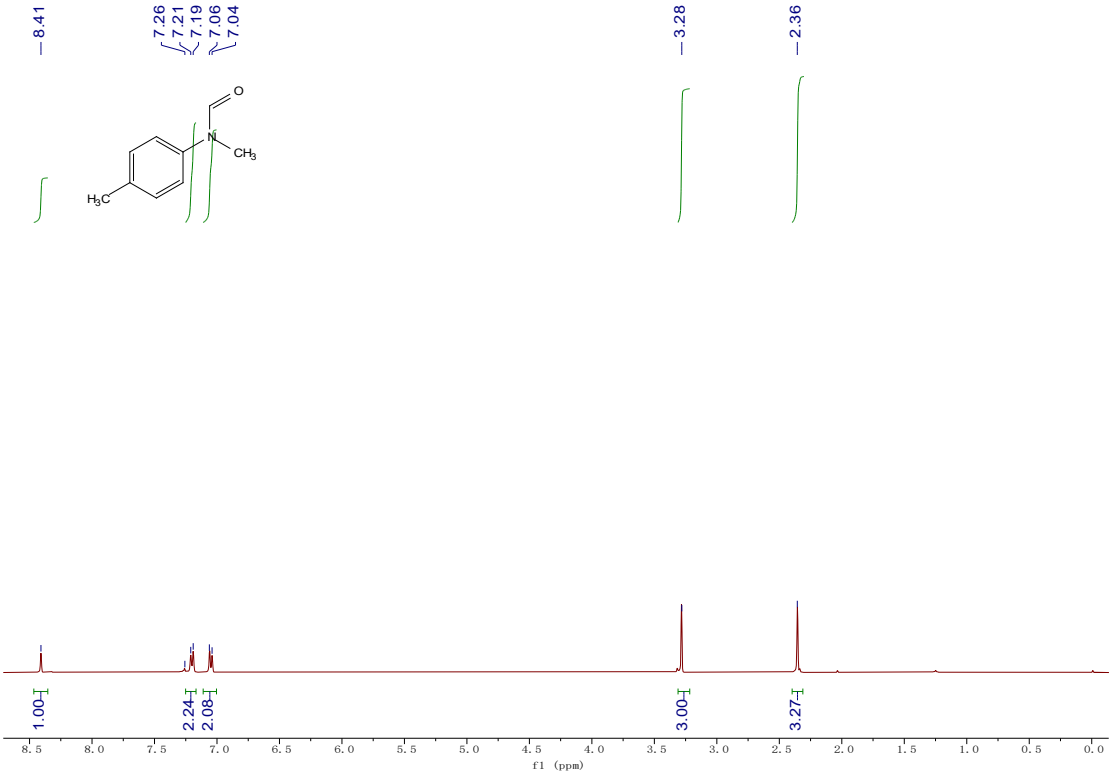


^{13}C NMR (101 MHz, $CDCl_3$)

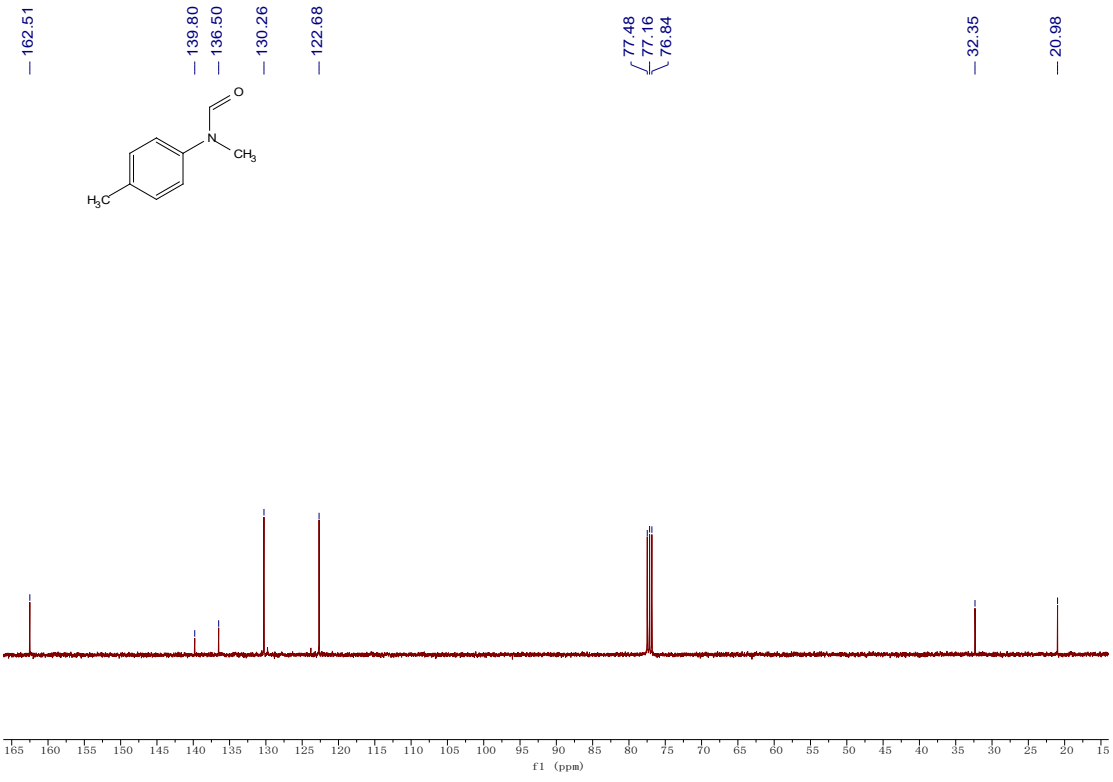


N-methyl-N-(p-tolyl)formamide **(2b)**

^{1}H NMR (400 MHz, $CDCl_3$)

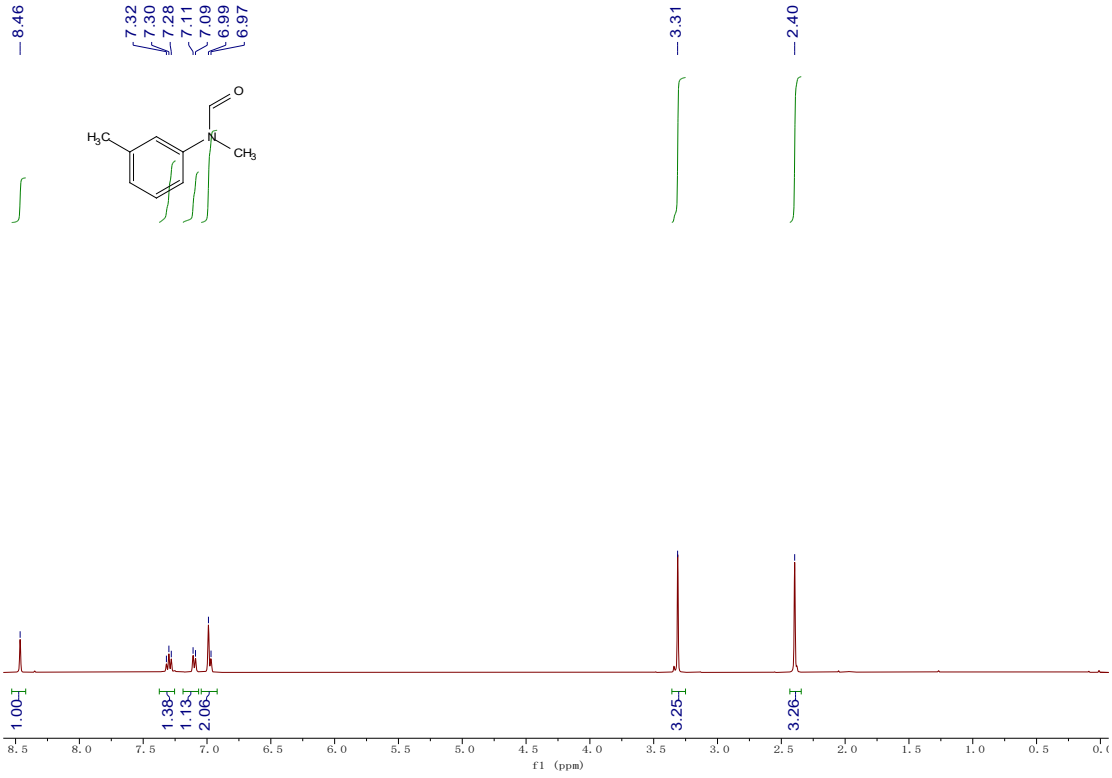


^{13}C NMR (101 MHz, $CDCl_3$)



N-methyl-N-(m-tolyl)formamide **(2c)**

^{1}H NMR (400 MHz, $CDCl_3$)



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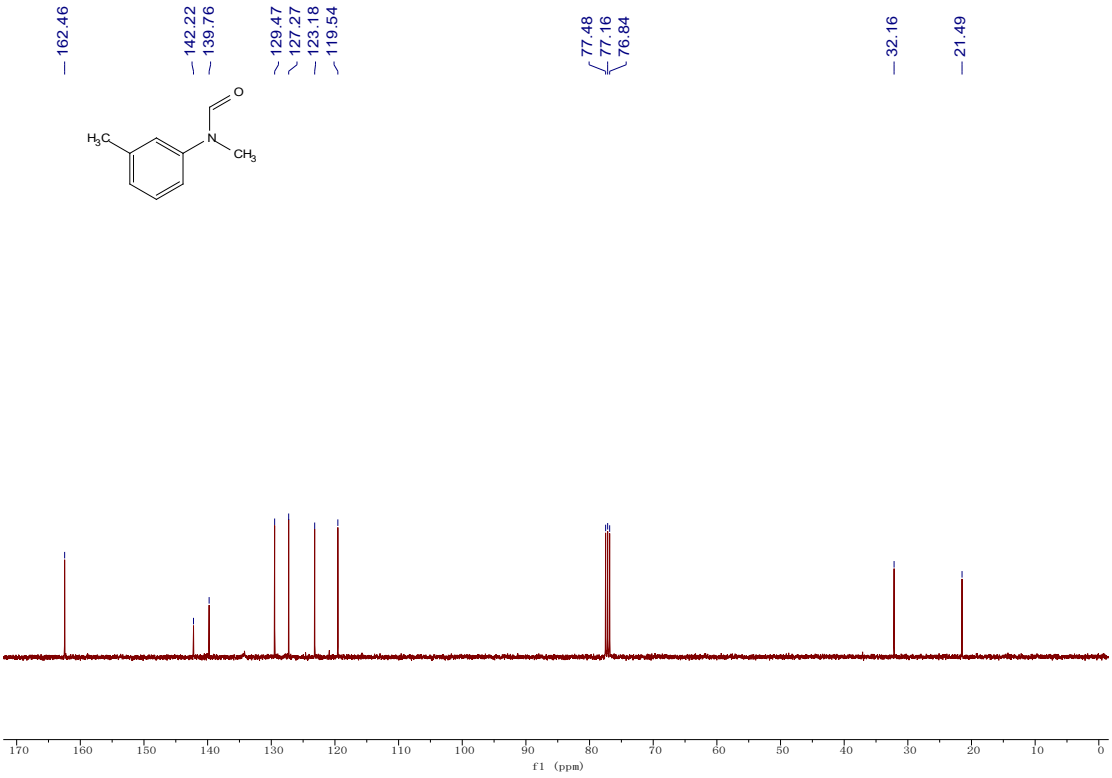

N-(4-methoxyphenyl)-N-methylformamide **(2d)**

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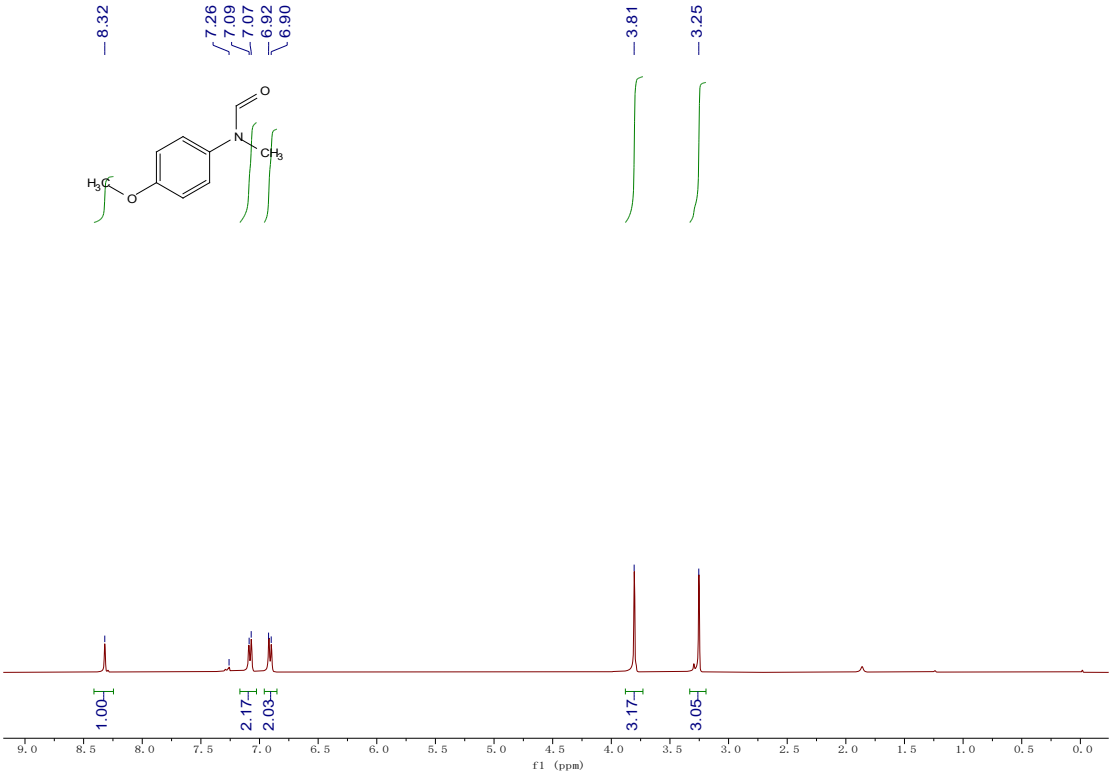
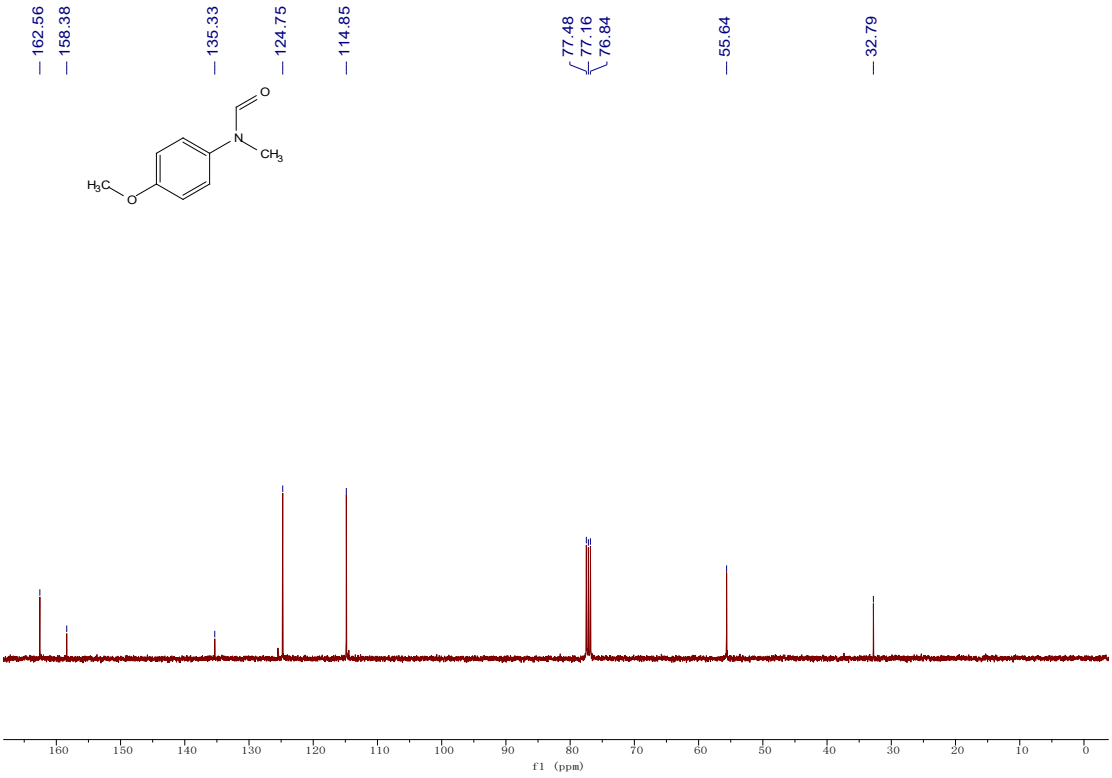
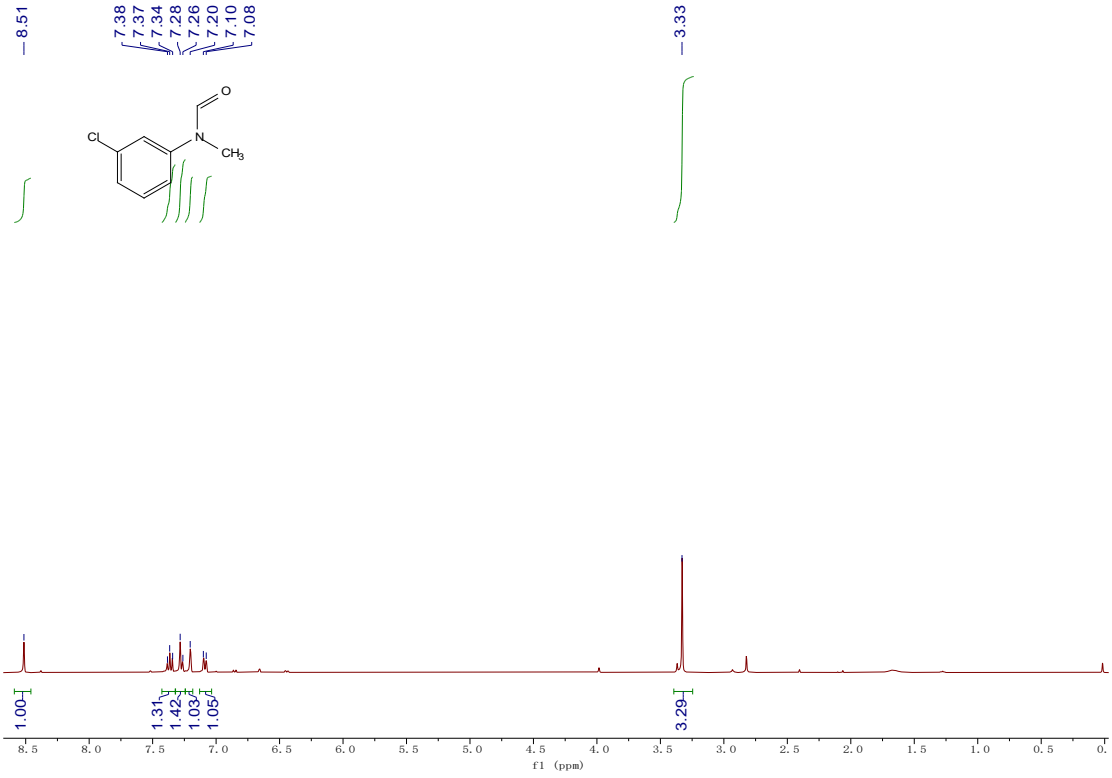


^{13}C NMR (101 MHz, $CDCl_3$)

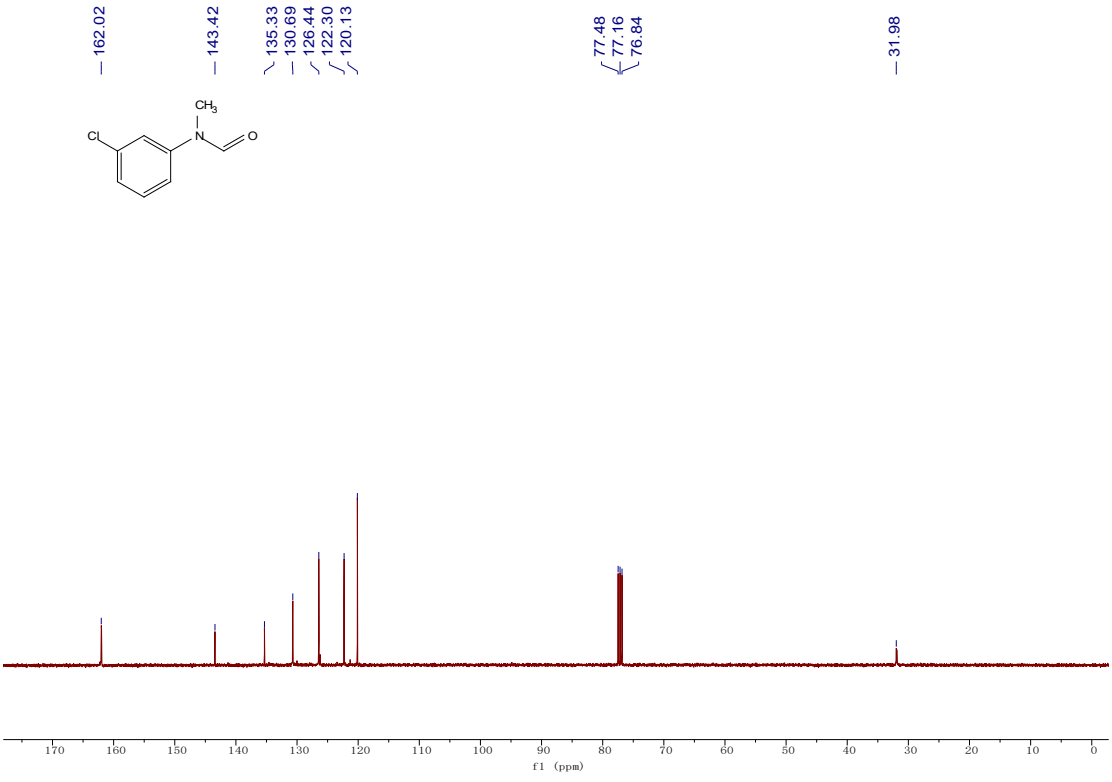


N-(3-chlorophenyl)-N-methylformamide **(2e)**

^{1}H NMR (400 MHz, $CDCl_3$)

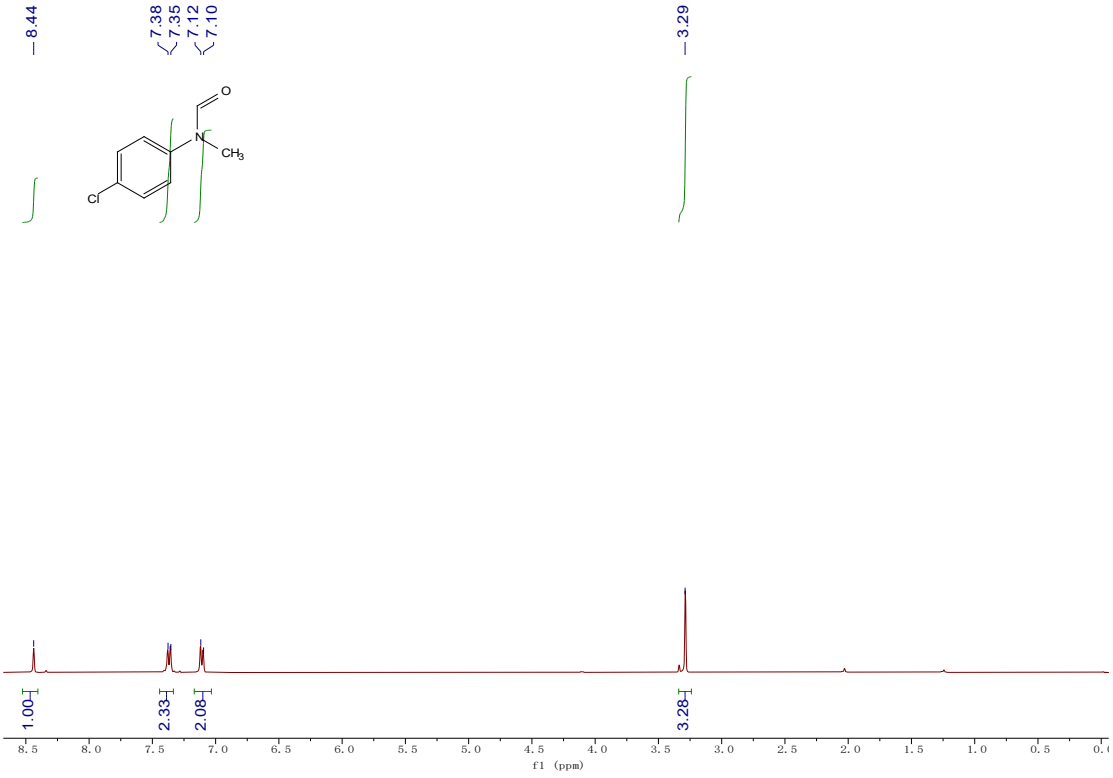


^{13}C NMR (101 MHz, $CDCl_3$)



N-(4-chlorophenyl)-N-methylformamide **(2f)**

^{1}H NMR (400 MHz, $CDCl_3$)



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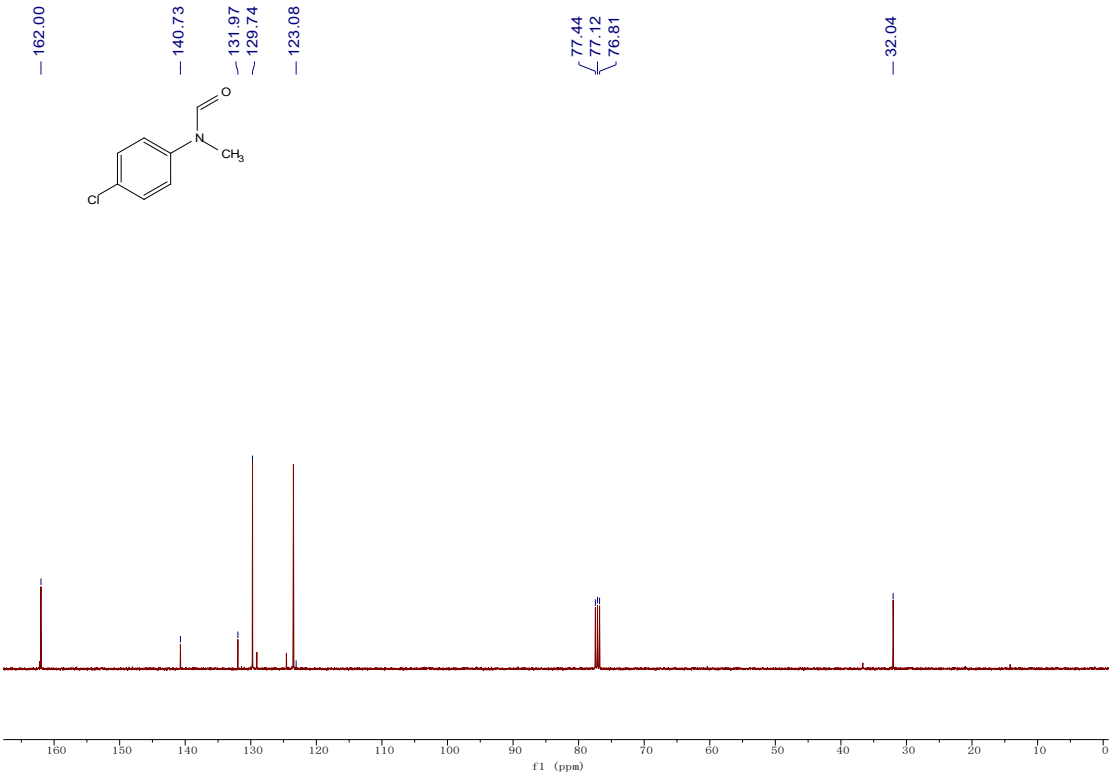
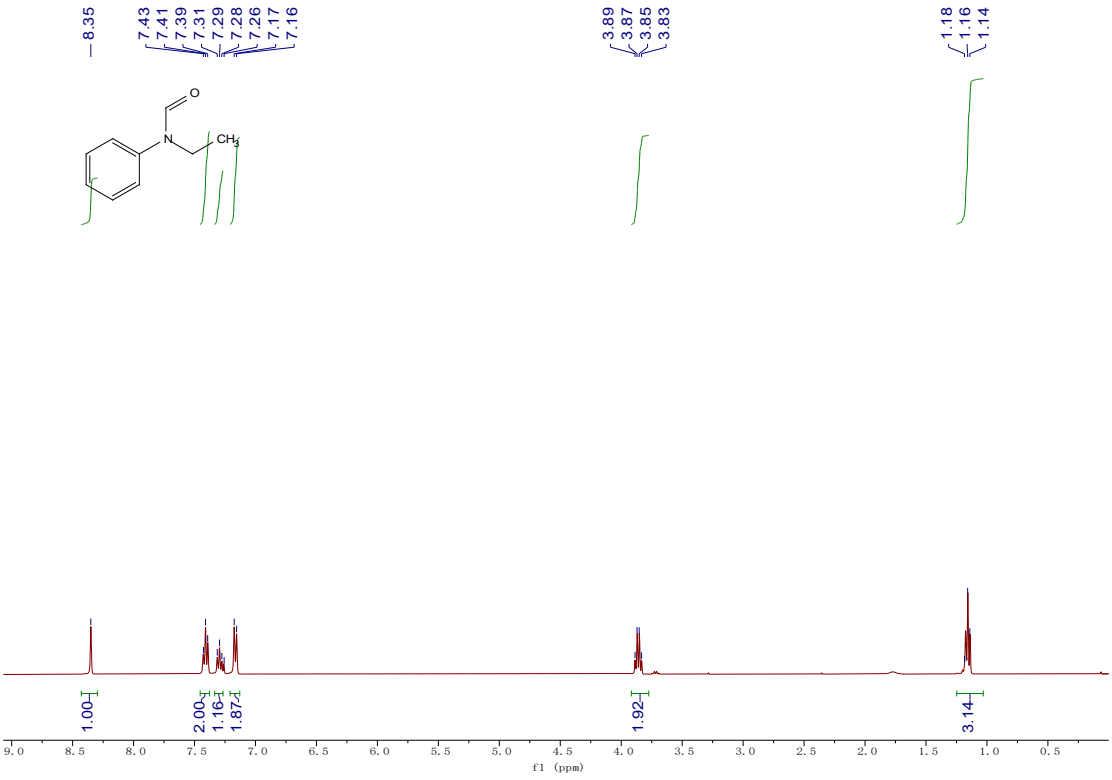


N-ethyl-N-phenylformamide **(2g)**

^{1}H NMR (400 MHz, $CDCl_3$)



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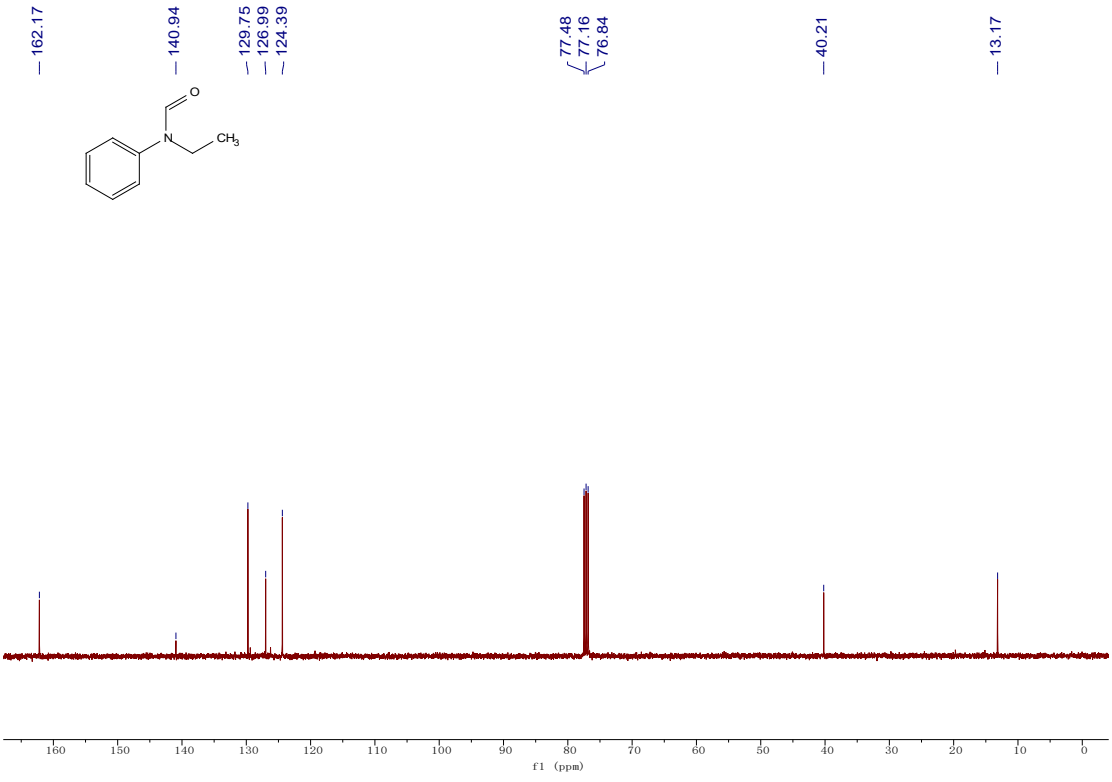
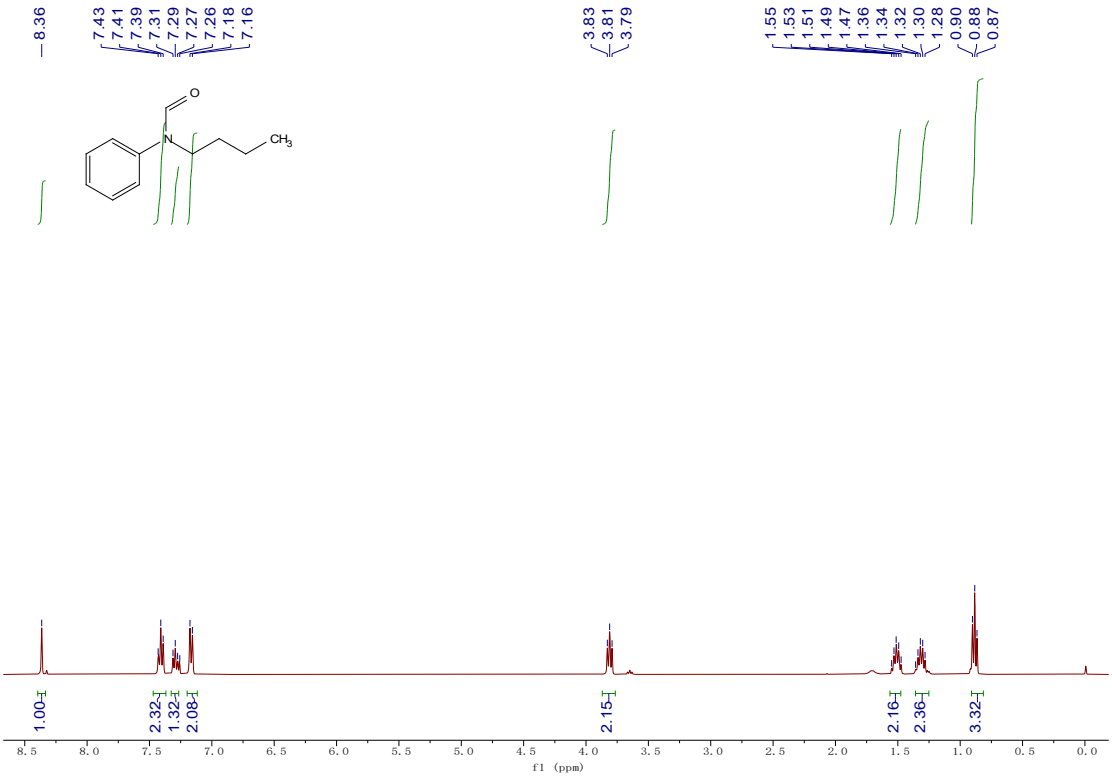


N-phenyl-N-propylformamide **(2h)**

^{1}H NMR (400 MHz, $CDCl_3$)



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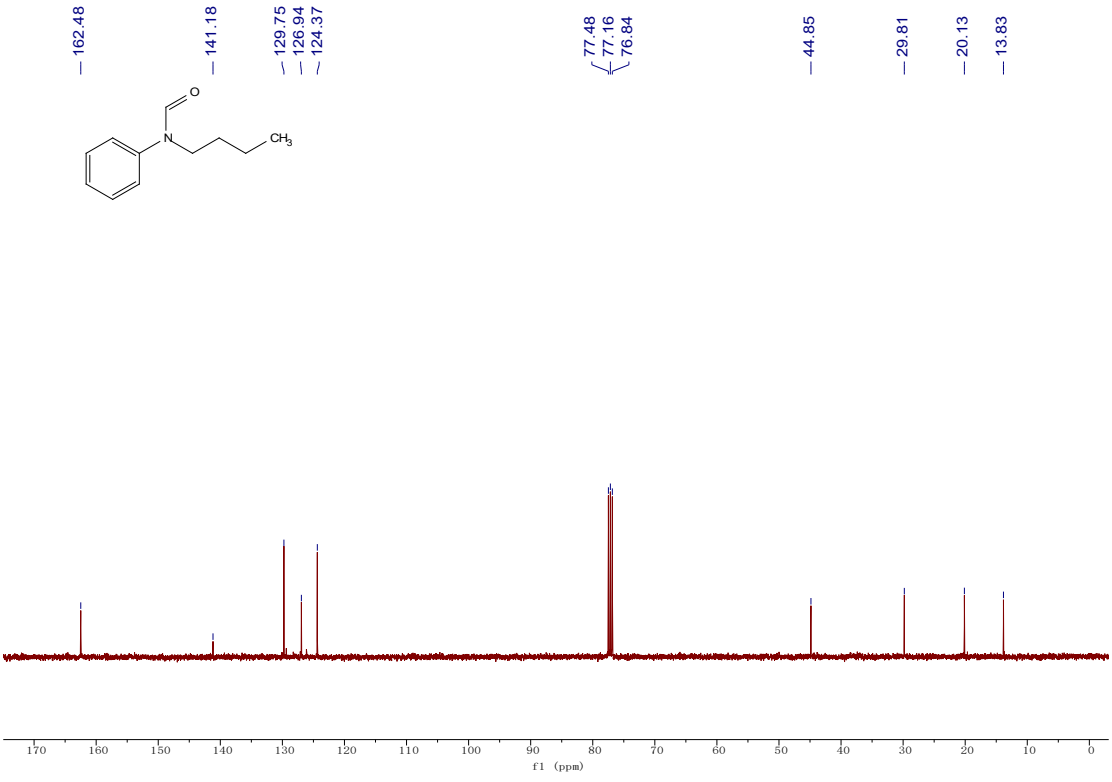
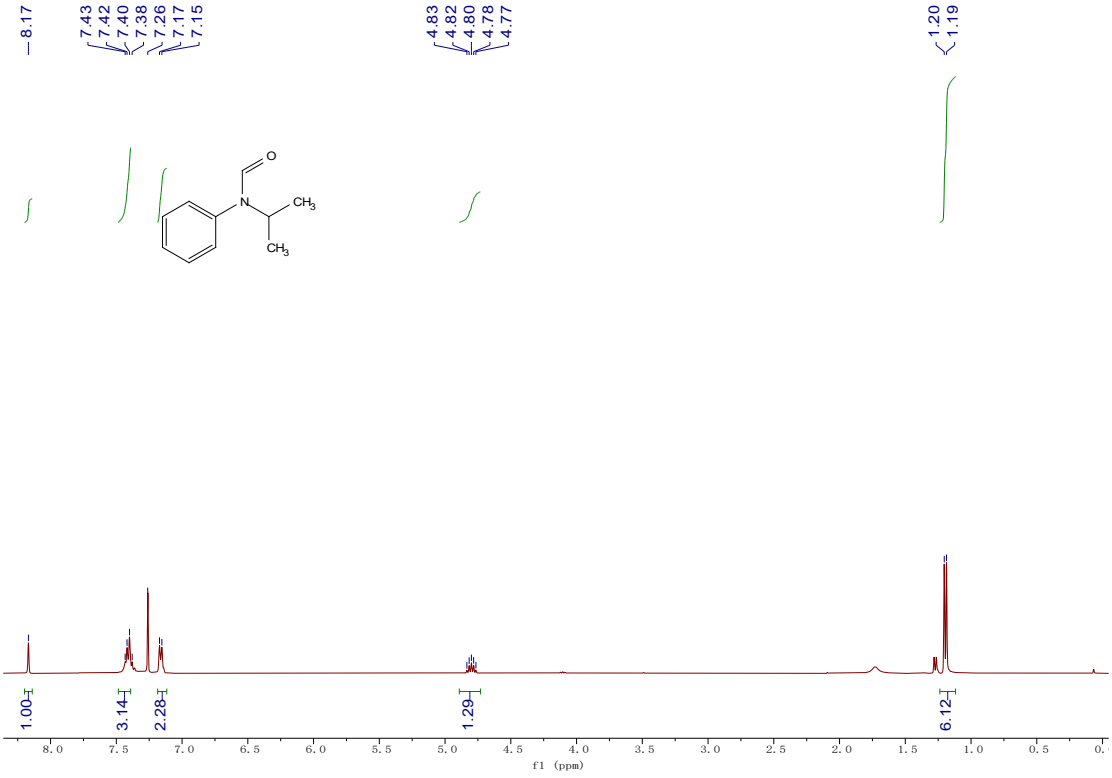


N-isopropyl-N-phenylformamide **(2i)**

^{1}H NMR (400 MHz, $CDCl_3$)



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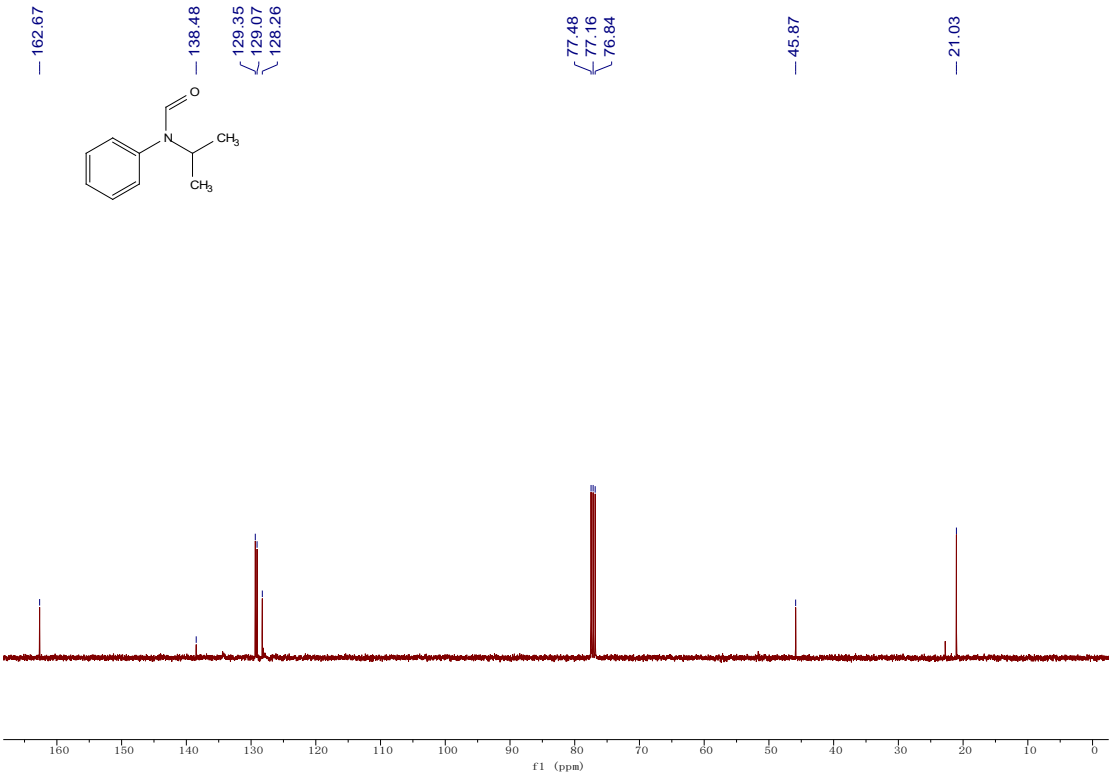

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(2) A. D Becke. *Phys. Rev. A*, **1988**, *38*, 3098-3100.
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