Supporting Information

ZnO nanoparticles catalyzed C–N bond-forming reactions: A highly efficient protocol to convert electron-deficient anilines to formanilides

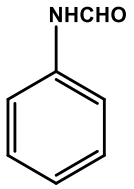
Tulan Chandra Saikia, Saddam Iraqui and Md. Harunar Rashid*

Department of Chemistry, Rajiv Gandhi University, Rono Hills, Doimukh 791 112, Arunachal Pradesh, India

*Corresponding author email: harunar.rashid@rgu.ac.in

Contents:

N-Phenylformamid (Table 2, Entry 1)

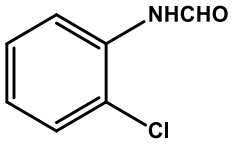


Brown solid; MP: 46-48 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 9.18 (s, 1H), 8.34 (s, 1H), 7.10-7.13 (d, 2H, J= 9 Hz), 7.29-7.38 (m, 2H), 7.55-7.58 (d, 2H, J=9Hz).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 163.12, 159.70, 136.72, 129.20, 125.43, 120.03, 118.63).

N-(2-chlorophenyl) formamide (Table 2, Entry 2)

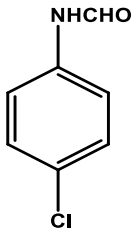


White solid; MP: 76-78 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C: δ 8.72 (d, 1H, j=12 Hz), 8.50 (s, 1H), 8.40 (d, 1H, j=9 Hz), 7.83 (s, 1H), 7.41 (m, 1H, j=9 Hz), 7.27 (m, 1H, j=6 Hz), 7.15 (m, 1H, j=6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 161.52, 158.90, 133.54, 130.20, 129.03, 127.71, 125.87, 125.05, 121.86, 118.57).

N-(4-chlorophenyl) formamide (Table 2, Entry 3)

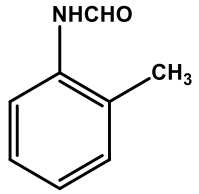


White solid; MP: 98-100 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C: δ 8.66 (d, 1H, j= 12Hz), 8.38 (s, 1H), 7.27 (m, 4H, j=12Hz).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 162.43, 158.94, 135.24, 130.62, 129.74, 129.03, 121.29, 119.95.

N-(2-methylphenyl) formamide (Table 2, Entry 4)

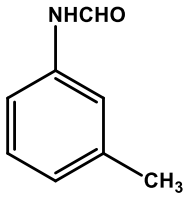


White solid; MP: 56-58 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.54 (s, 1H), 7.86 (d, 1H, j=12 Hz), 7.18 (m, 4H, j=12 Hz), 2.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C: δ 163.69, 159.36, 135.01, 131.23, 130.56, 129.81, 126.97, 125.43, 123.00, 120.66.

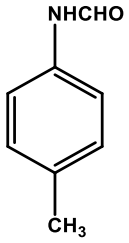
N-(3-methylphenyl) formamide (Table 2, Entry 5)



^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.56 (s, 1H), 8.20 (d, 1H), 7.63 (s, 1H) 7.03-7.19 (m, 2H), 6.77-6.86 (m, 2H), 2.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C: δ 162.92, 140.02, 136.56, 129.52, 125.94, 119.35, 115.83, 21.94.

N-(4-methylphenyl) formamide (Table 2, Entry 6)

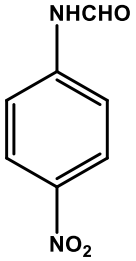


MP: 54 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.64 (s, 1H), 7.75 (s, 1H), 7.42-7.45 (s, 2H, J=9), 7.11-7.17 (t, 2H), 6.99-7.01 (d, 1H, 6Hz), 2.34 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 159.09, 135.23, 134.29, 130.01, 119.06, 20.98.

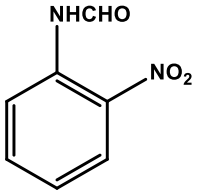
N-(4-nitrophenyl) formamide (Table 2, Entry 8)



Green solid; MP: 175-178 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.90 (d, 1H, j=12 Hz), 8.49 (s, 1H), 8.26 (t, 1H, j=12 Hz), 7.75 (d, 1H, j=12 Hz), 7.27 (s, 2H), 3.55 (s, 1H).

N-(2-nitrophenyl) formamide (Table 2, Entry 9)

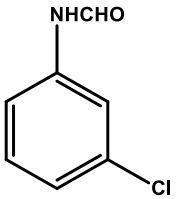


Yellow solid; MP: 110-116 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 10.35 (s, 1H), 8.82 (d, 1H, j=12Hz), 8.59 (s, 1H), 8.26 (d, 1H, j=12 Hz), 7.69 (t, 1H, j=12Hz), 7.27 (s,1H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 159.39, 136.05, 133.57, 125.78, 123.80, 122.63.

N-(3-chlorophenyl) formamide (Table 2, Entry 10)



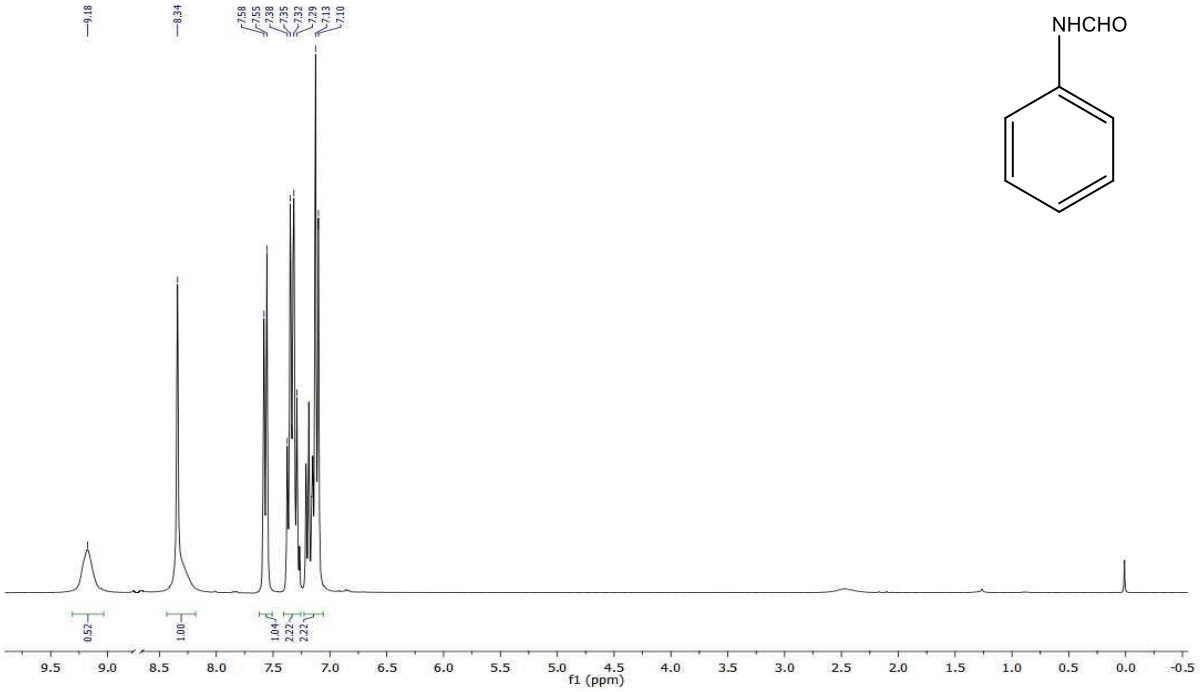
Yellow solid; MP: 50 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 9.06 (br. s, 1H), 8.70 (d, 1H, j=12 Hz), 8.37 (s, 1H), 8.12 (m, 1H, j=12 Hz), 7.67 (s, 1H), 7.20 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 162.72, 159.47, 137.88, 135.27, 134.55, 130.72, 130.01, 125.21, 124.78, 120.04, 118.57, 117.85, 116.53.

1H and 13C NMR of some synthesize product

FigureS1. ^{1}H and ^{13}C NMR spectrum of N-Phenyl formamide



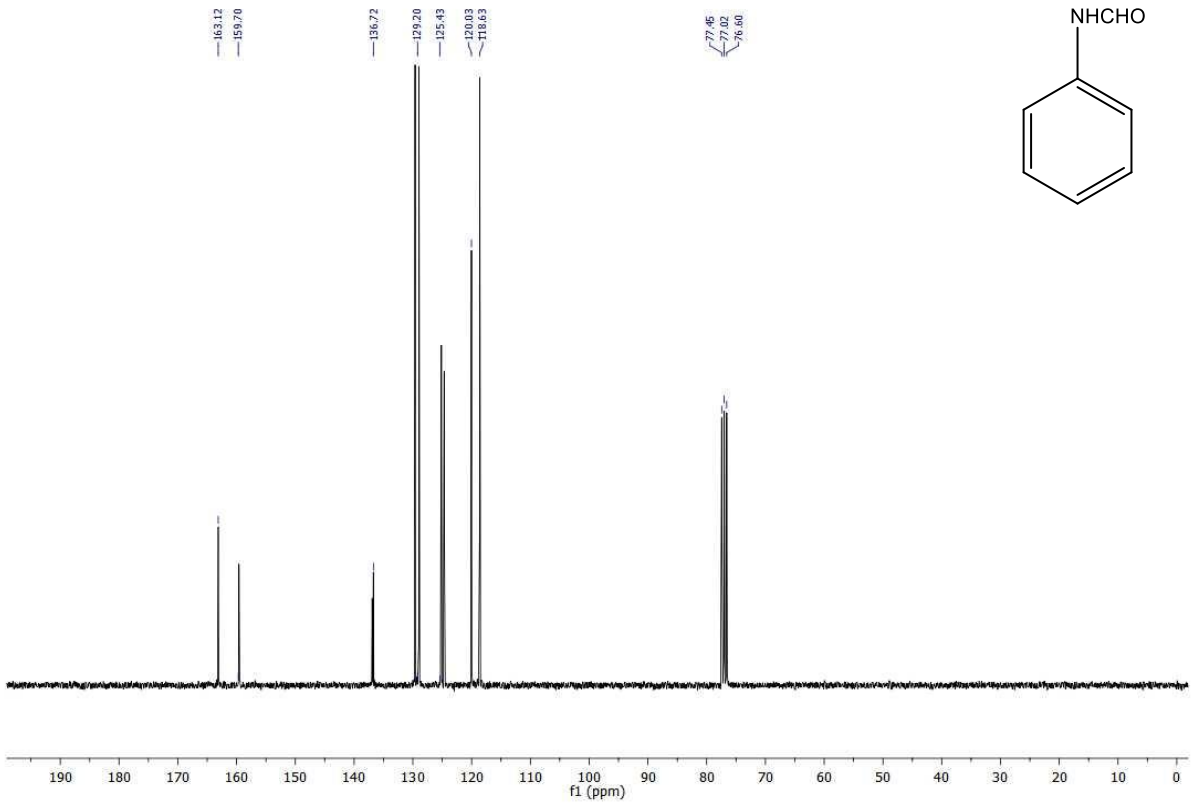
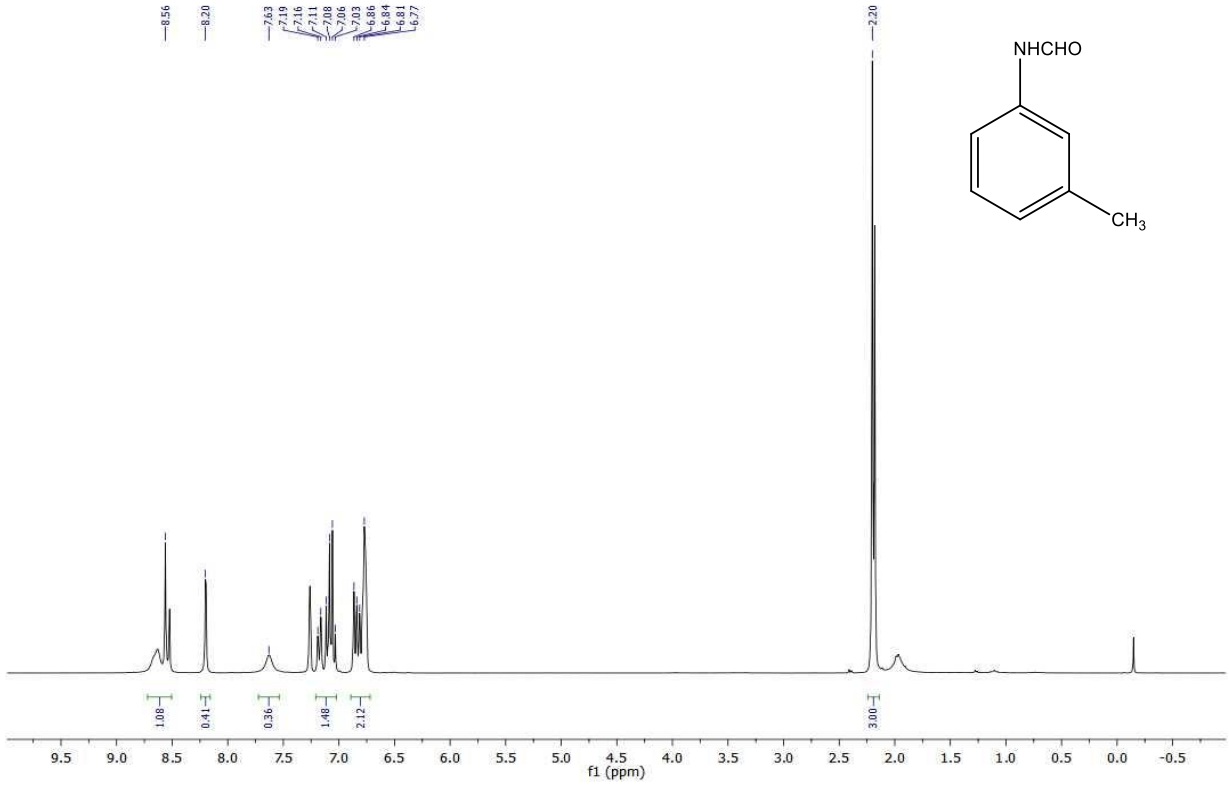


Figure S2. ^{1}H and ^{13}C NMR spectrum of *N-(3-methylphenyl) formamide.*



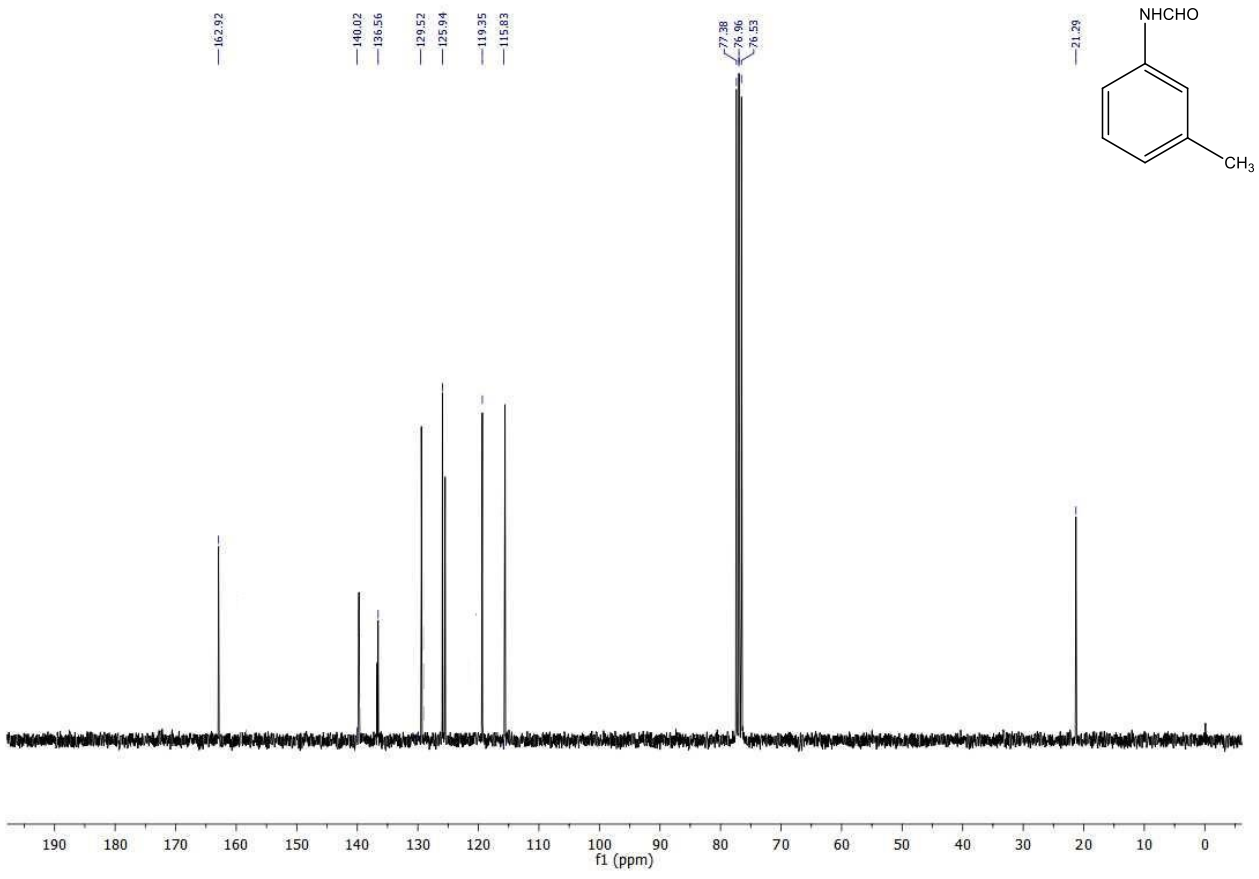
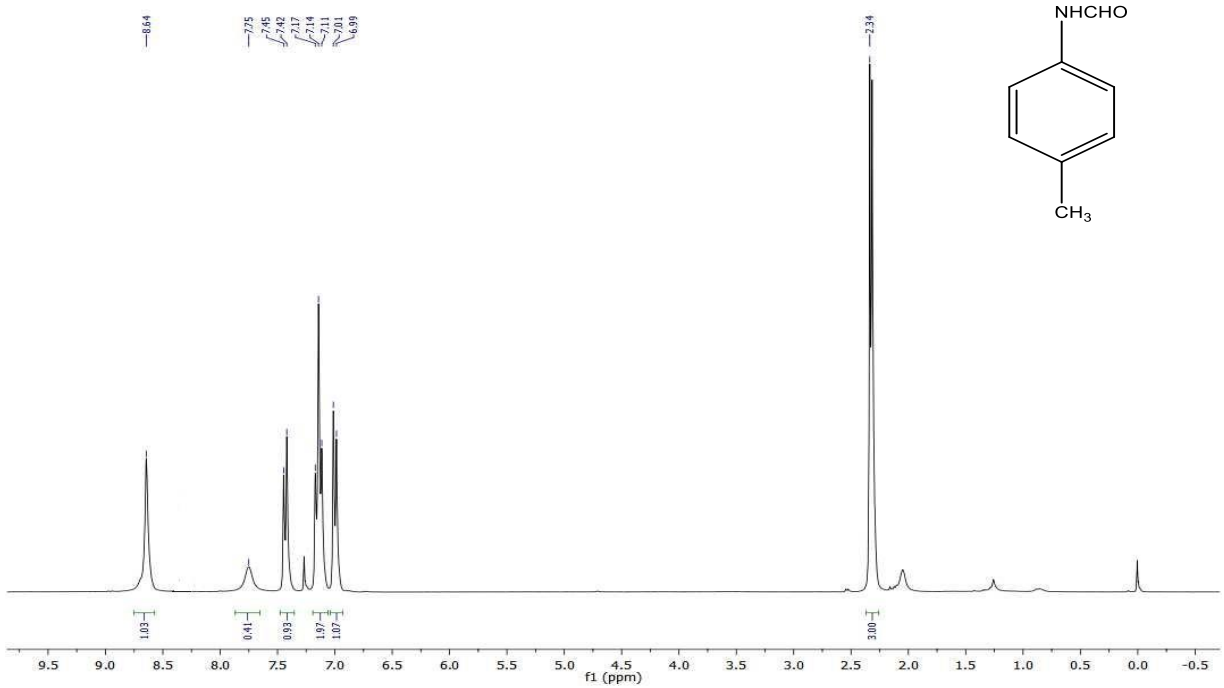


Figure S3. ^{1}H and ^{13}C NMR spectrum of *N-(4-methylphenyl) formamide*



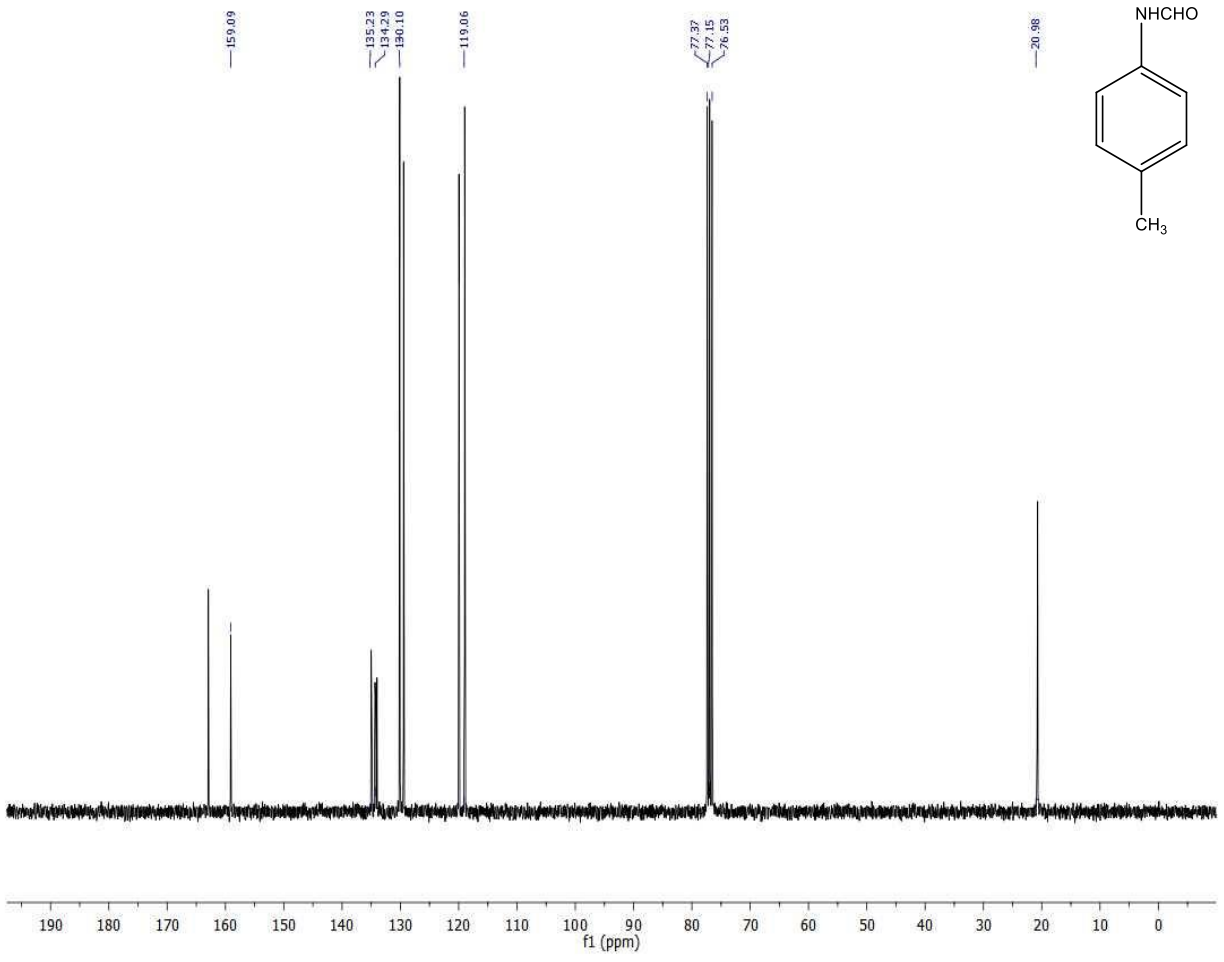
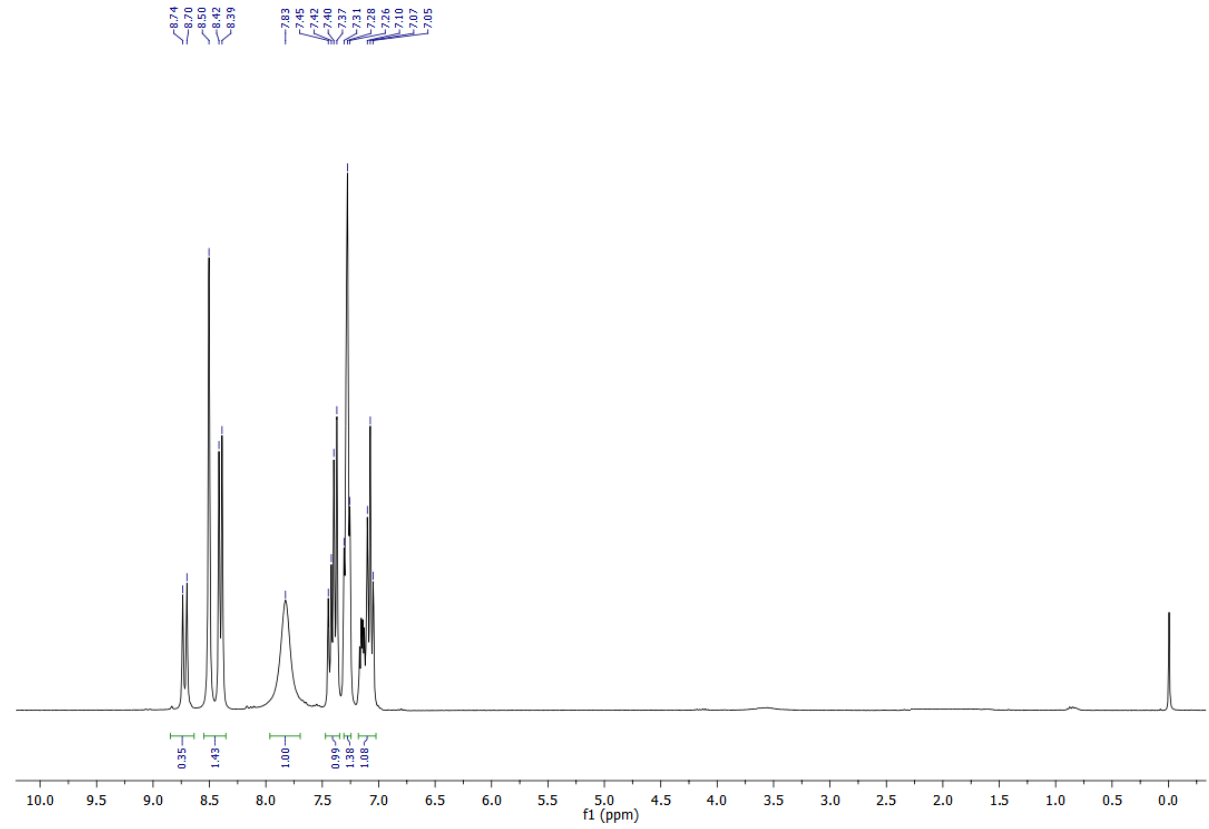


Figure S4. ^{1}H and ^{13}C NMR spectrum of*N-(2-chlorophenyl) formamide*



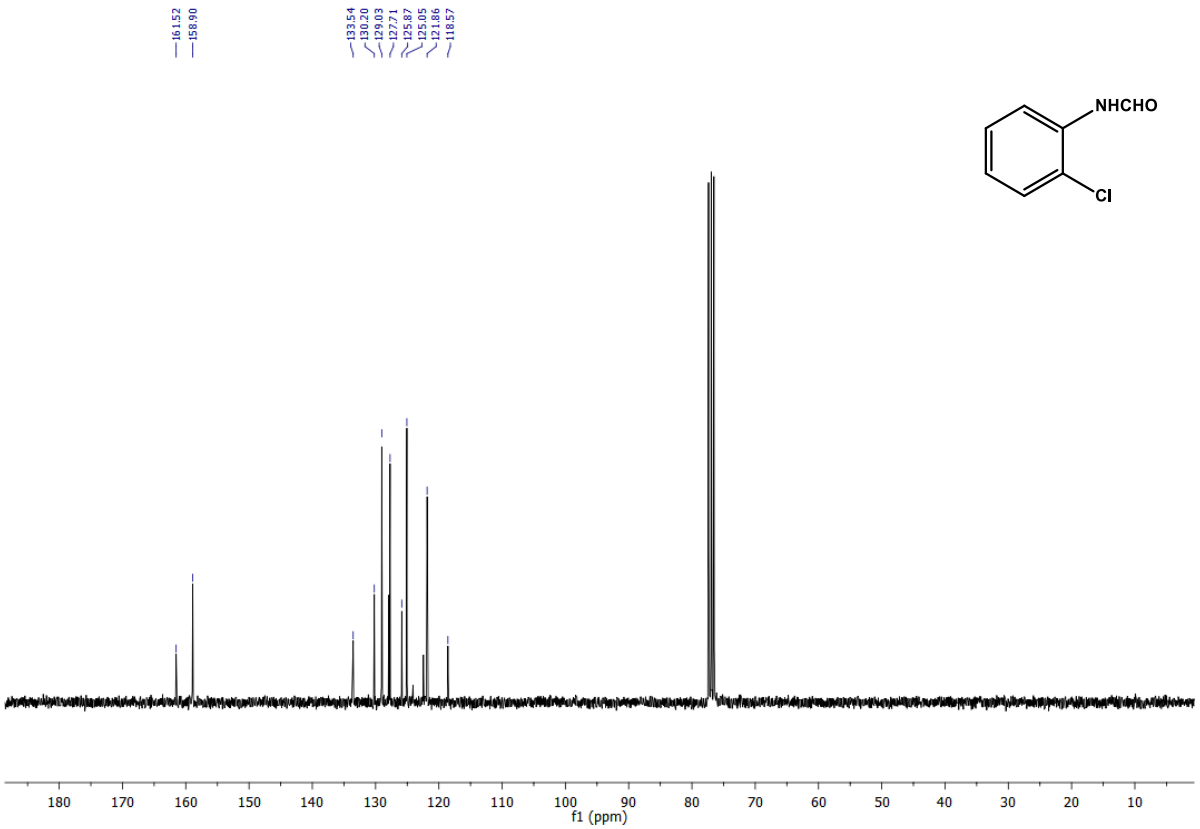
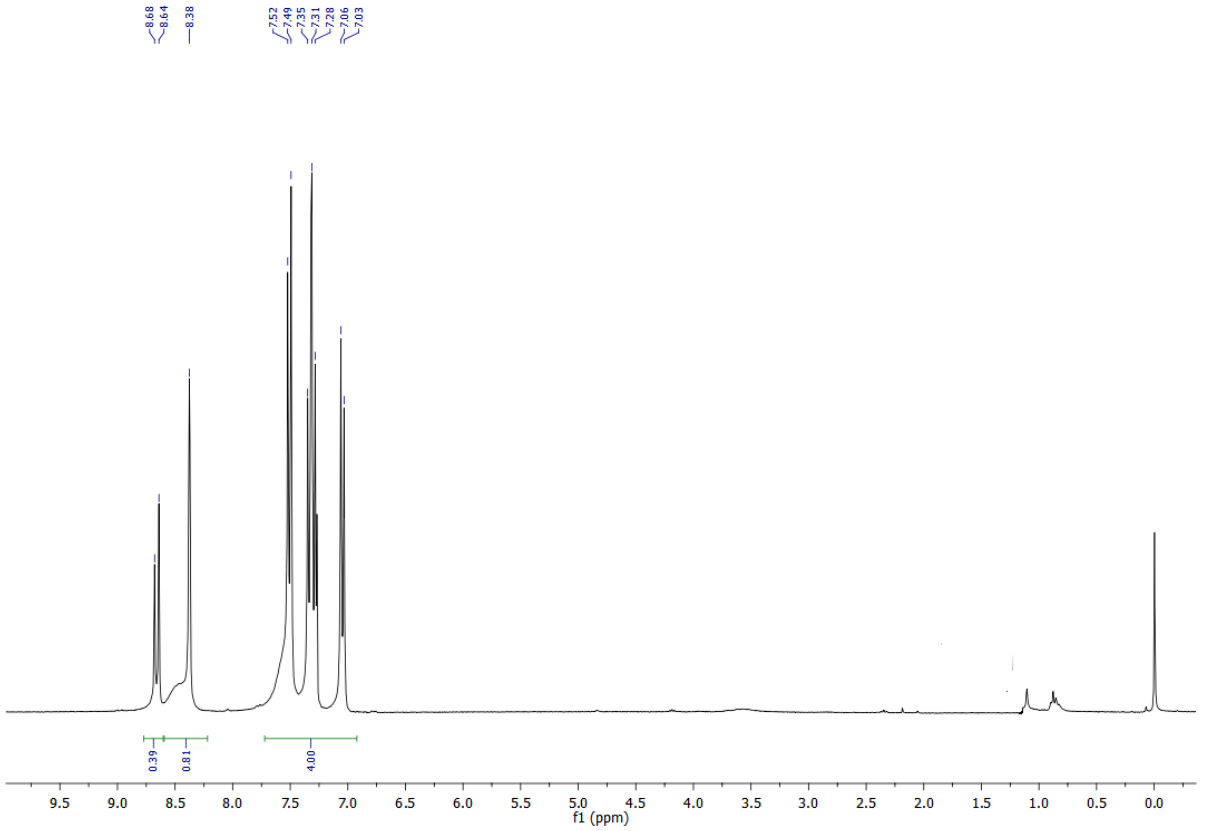


Figure S5. ^{1}H and ^{13}C NMR spectrum of *N-(4-chlorophenyl) formamide*



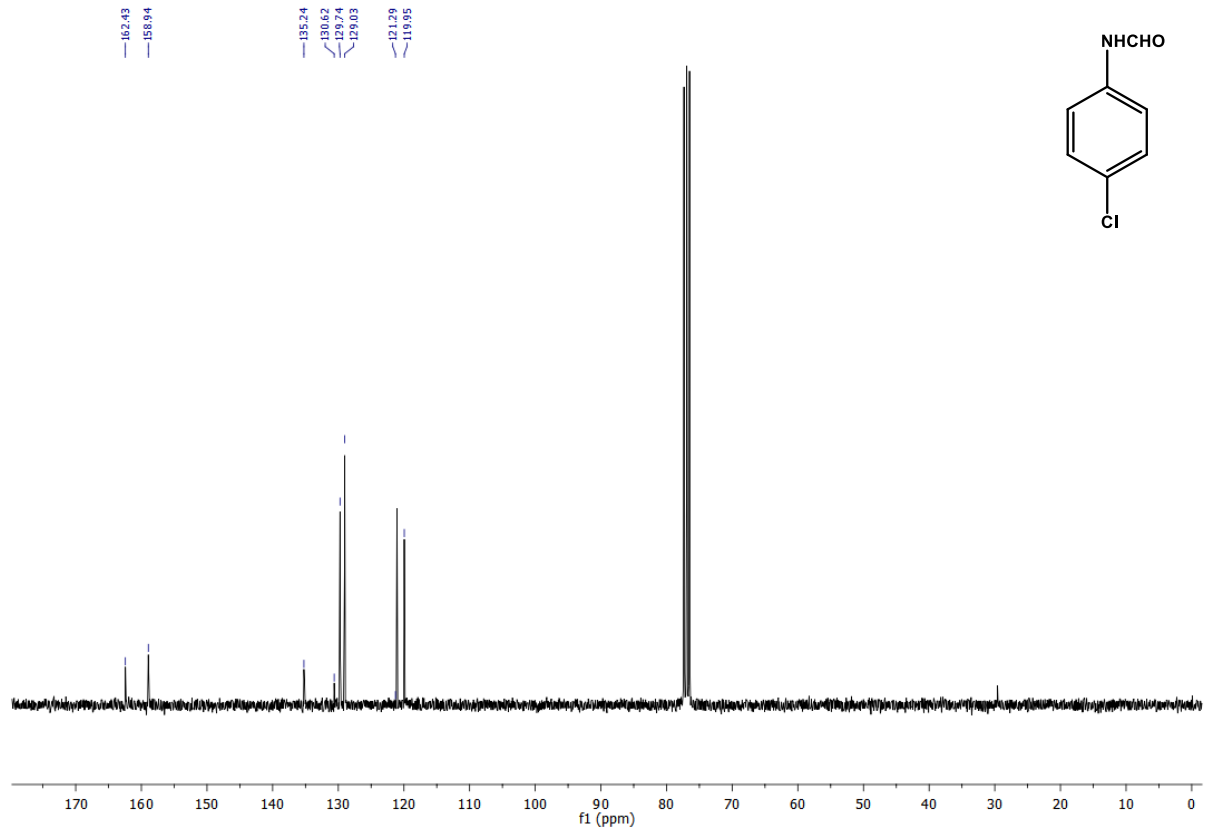


Figure S6. ^{1}H and ^{13}C NMR spectrum of *N-(2-methylphenyl) formamide*

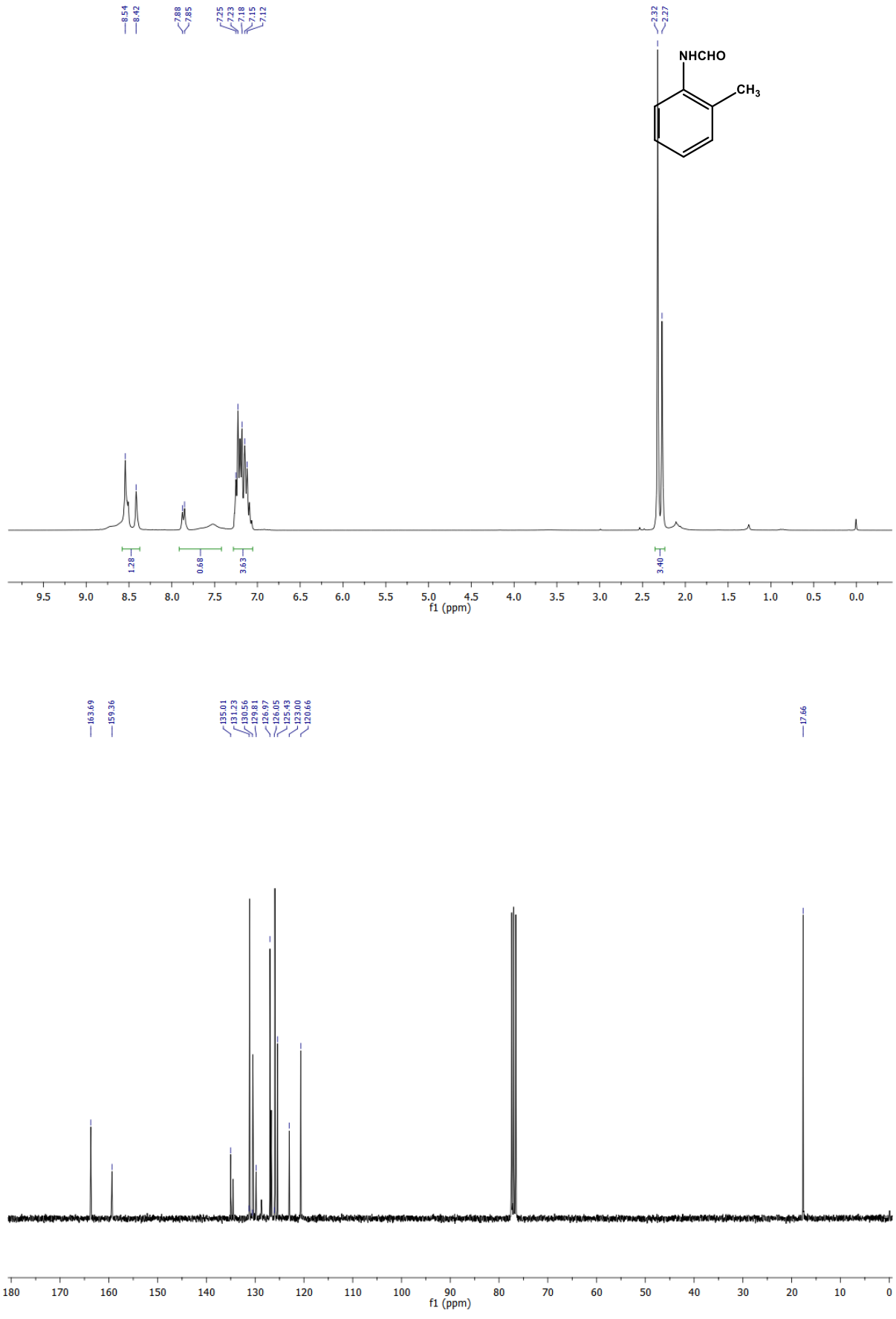


Figure S7. ^{1}H spectrum of *N-(4-nitrophenyl) formamide*

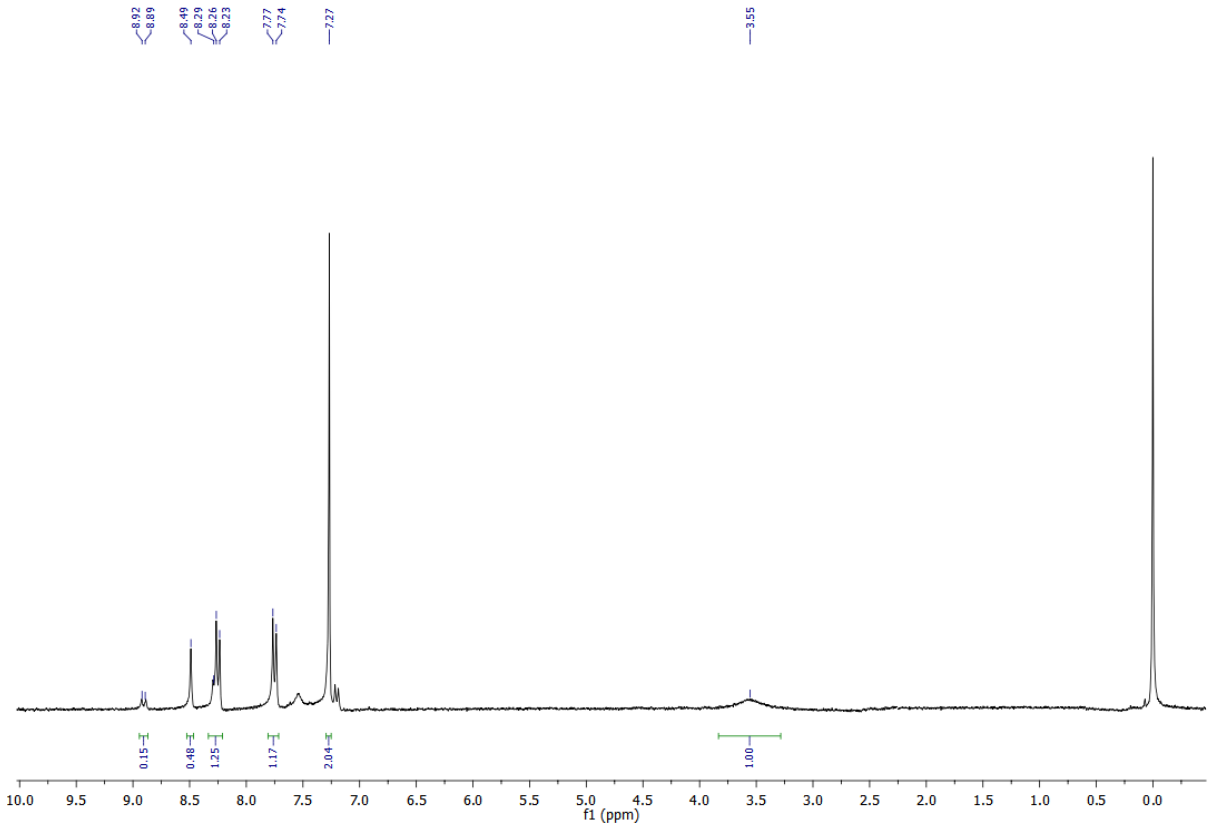


Figure S8. ^{1}H and ^{13}C NMR spectrum of *N-(2-nitrophenyl) formamide*

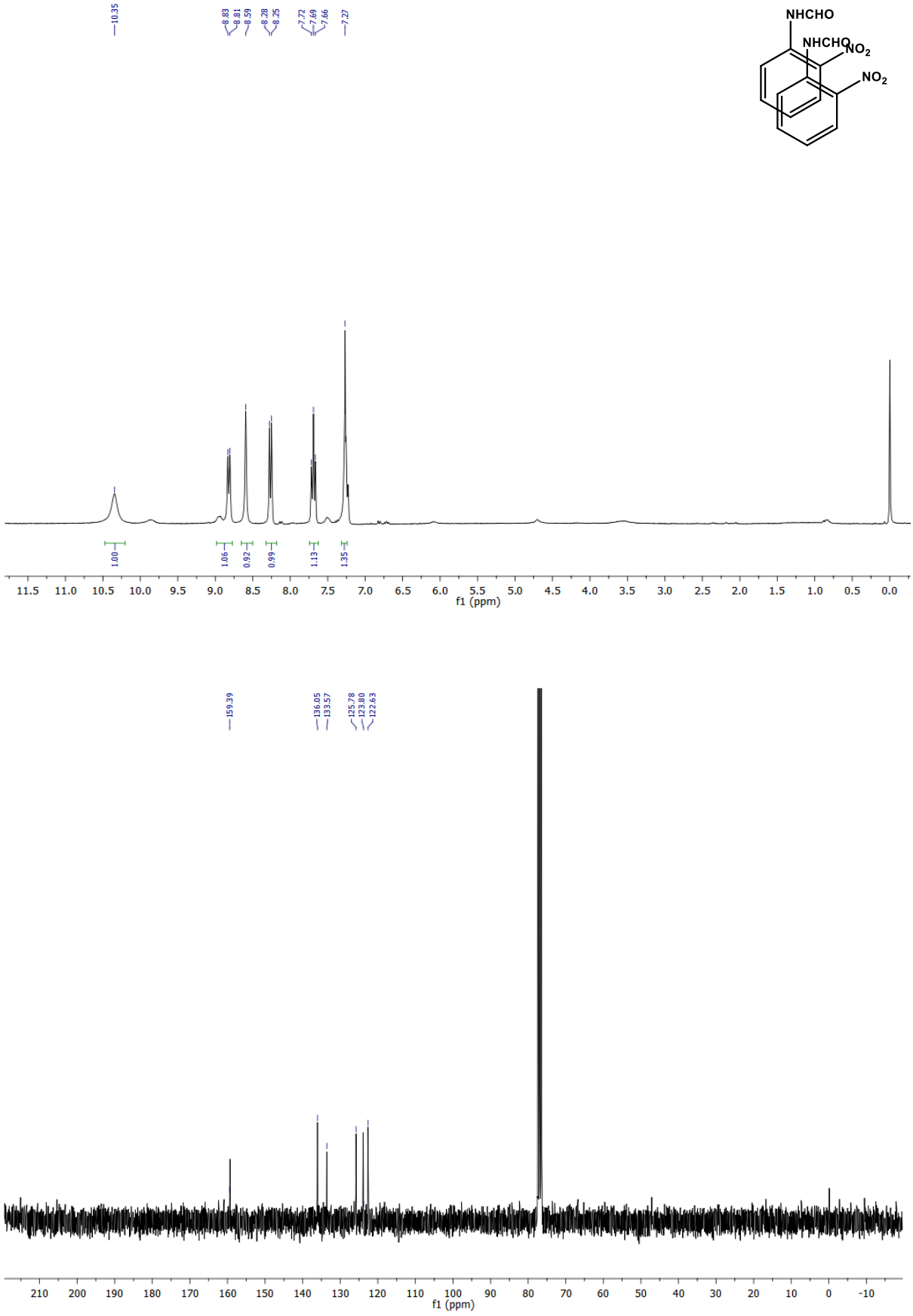
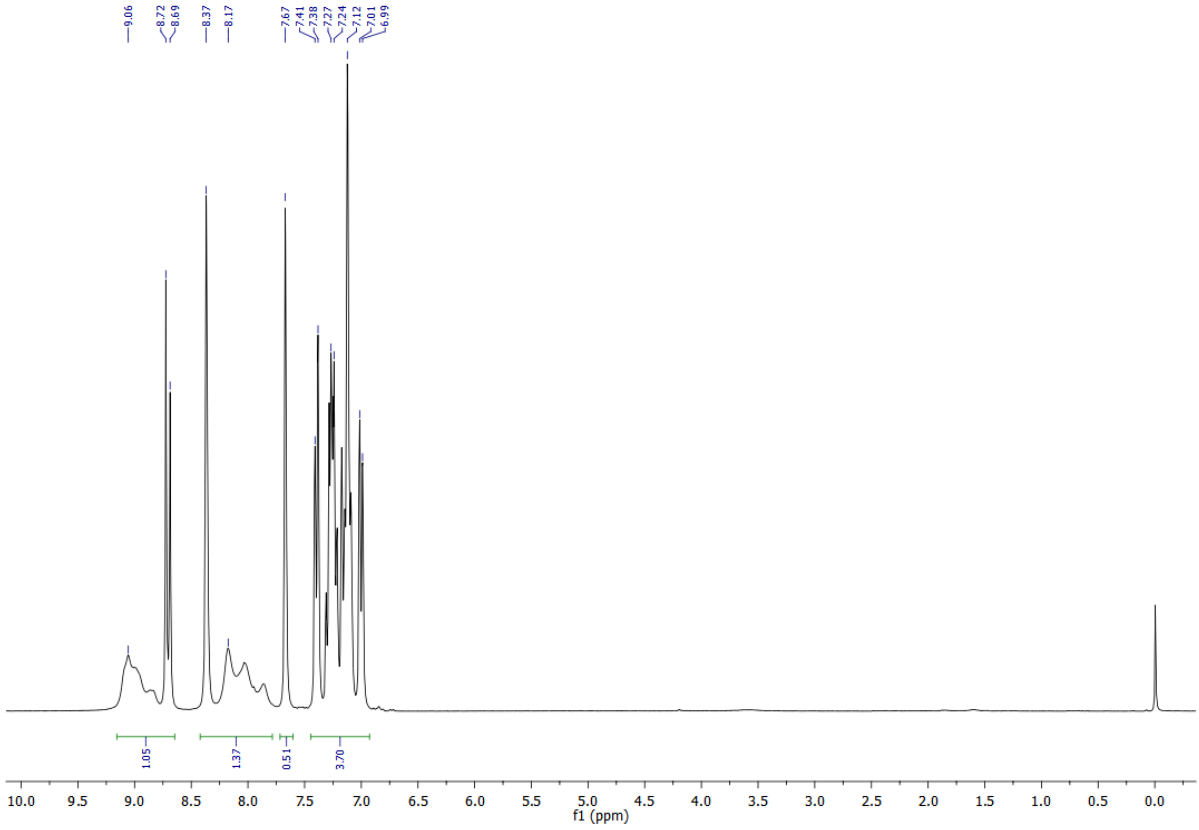
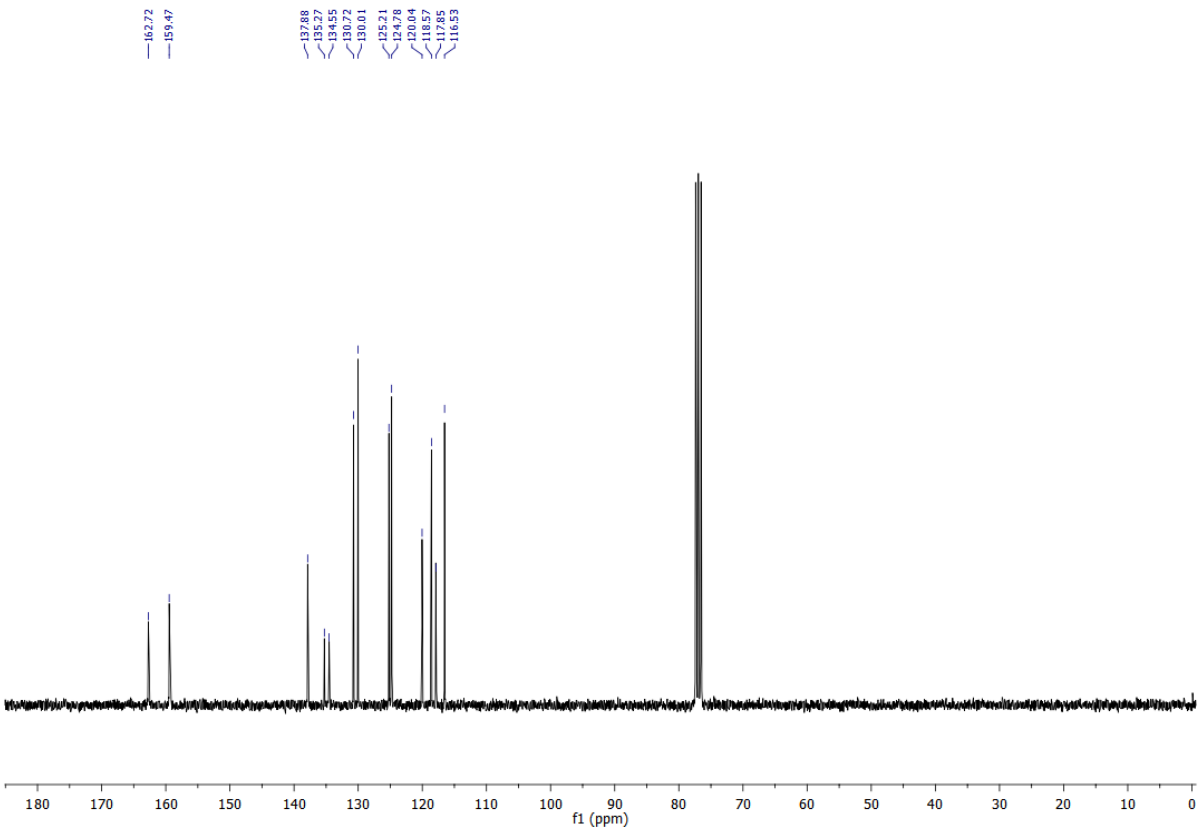


Figure S9. ^{1}H and ^{13}C NMR spectrum of *N-(3-chlorophenyl) formamide*





References.

1. Mona Hosseini Sarvari and Hashem Sharghi, ZnO as a New Catalyst for N-Formylation of Amines in Solvent-Free Conditions of Chemistry, *J. Org. Chem.* 2006, 71,6652-6654.
2. Che Chang Chong and Rei Kinjo, Hydrophosphination of CO_2 and Subsequent Formate Transfer in the 1,3,2-Diazaphospholene-Catalyzed N-Formylation of Amines, AngewandtaChemie,2015, 127, 12284-12288.
3. Leila Ma'mani, Mehdi Sheykhan, Akbar Heydari, Mohammad Faraji, YadollahYamini, Sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3nanocrystallites as a magnetically Brønsted acid for N-formylation of amines, Appl. Catal. A, 2010, 377, 64–69.