Supporting Information

Zn (II) @ TFP-DAQ COF: An efficient mesoporous catalyst for the synthesis of N-methylated amine and carbamate through chemical fixation of CO_2

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Materials

1,3,5-Triformylphloroglucinol (TFP) was prepared from hexamethylenetetramine, dried phloroglucinol and trifluoroacetic acid using the previously reported literature procedure [1]. 2,6-diaminoanthraquinone (DAQ), Hexamethylene triamine, *p*-toluenesulfonic acid (PTSA),all the amines were purchased from Sigma Aldrich, India. Anhydrous $ZnCl_2$ and N,N-dimethylacetamide, Polymethylhydrosiloxane (PMHS) were obtained from TCI, India. All the solvents were brought from Marck, India and were used without further purification.

2.2. Synthetic procedure for TFP- DAQ COF :

Solid state mixing of chemicals were involved for Synthesis of TFP-DAQ COF by reacting 1,3,5-triformylphloroglucinol (TFP) (63 mg, 0.3 mmol) and DAQ (0.321mg,1.34 mmol) using 7.5 mmol of *p*-toluenesulfonic acid (PTSA). PTSA and DAQ were mixed in a mortar-pestle and homogeneously grinded for 10 minutes. 0.9 mmol of TFP was added to the reaction mixture followed by further grinding of 15 minutes. Few drops of water based on requirement were added to make the mixture viscous. Then the COF precursors was taken in a Teflon-lined steel autoclave and heated at 60 ^{0}C for first 6 h followed by 90 ^{0}C for another 10 h in static condition.

The resulting TFP- DAQ COF was washed for 4-5 times using *N,N*-dimethylacetamide (DMAc) and then with excess acetone to remove the residues of the starting materials . The material was dried under vacuum for 12 h at room temperature to obtain the as-synthesized TFP-DAQ COF.

Instrumentation

Absorption spectroscopy: UV-Vis absorption spectrum of the catalyst was recorded on SHIMADZU, UV-2600 UV-Vis spectrometer with a standard 1 cm x 1 cm cuvette.

NMR Spectra: ^{1}H Proton nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm).

PXRD: The PXRD analysis was performed by using an X-raydiffractometer (BRUKER, Powder X-Ray eco D8 ADVANCE) equipped with Ni-filtered Cu Kα (λ= 0.15406 nm) radiation.

IR Spectra: The FTIR spectra of the materials were recorded from a Perkin-Elmer spectrophotometer (FT-IR 783) on KBr pellets.

SEM: FESEM images of the catalyst were acquired by using Scanning Electron Microscope (SEM) [JEOL JSM IT 300].

TEM: Transmission Electron Microscope (TEM) [JEOL JEM 2100] was used obtain the morphological information of the sample.

TGA: The thermal stability of the COF material was analyzed by a Thermogravimetric Analyzer [SDT Q600 V20.9 Build 20].

BET: The N_2 adsorption-desorption analysis of TFPG-DAAQ COF sample was conducted by using a BET Surface Analyzer [QUANTACHROME ASIQCOV602-5].

XPS: The XPS analysis was conducted by using the instrument: Thermo Fisher Scientific Pvt. Ltd.,UK; model:ESCALAB Xi+.

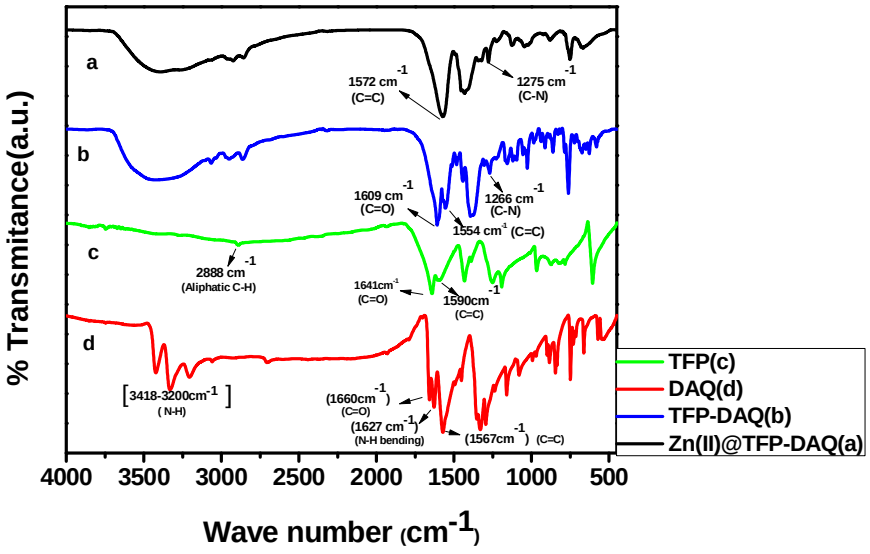


Figure S1. FTIR spectra of the TFP, DAQ, TFP- DAQ COF and Zn (II) @ TFP- DAQ COF catalyst.

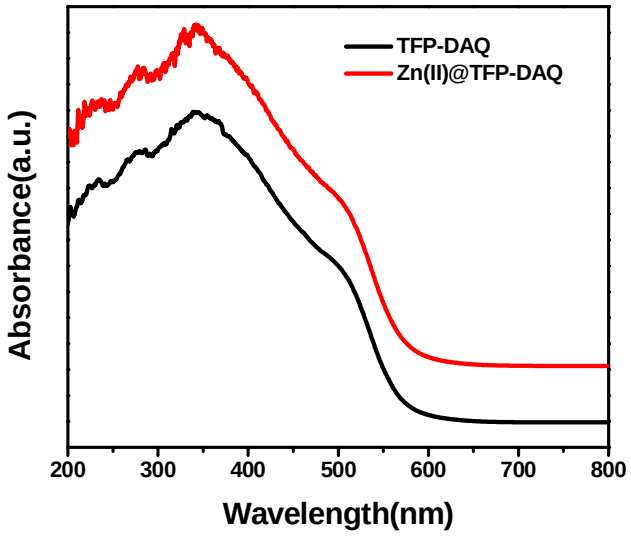


Figure S2. UV-vis spectra of the TFP- DAQ COF and Zn (II) @ TFP- DAQ COF samples.

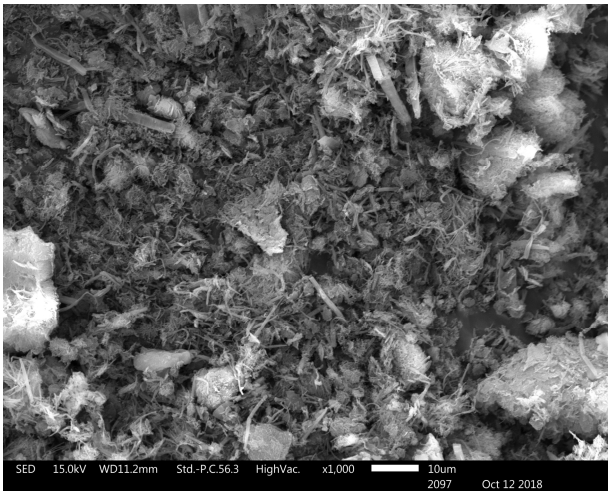


Figure S3. FESEM image of reused Zn (II) @ TFP- DAQ COF sample.

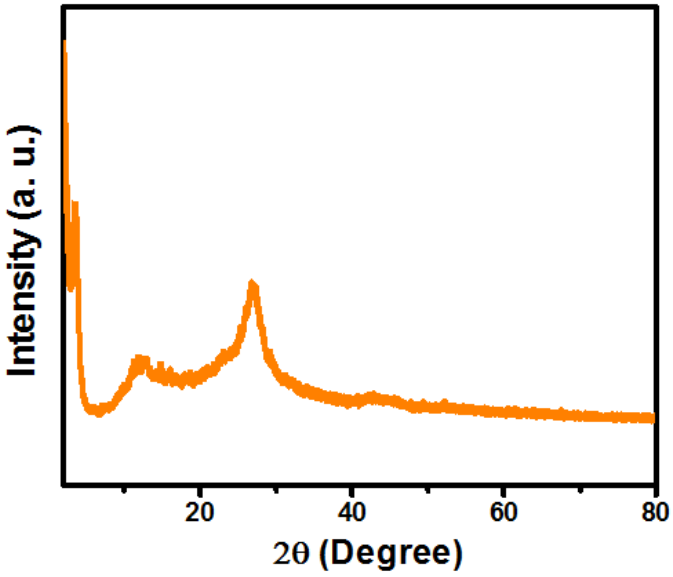


Figure S4. PXRD pattern of reused Zn (II) @ TFP- DAQ COF sample.

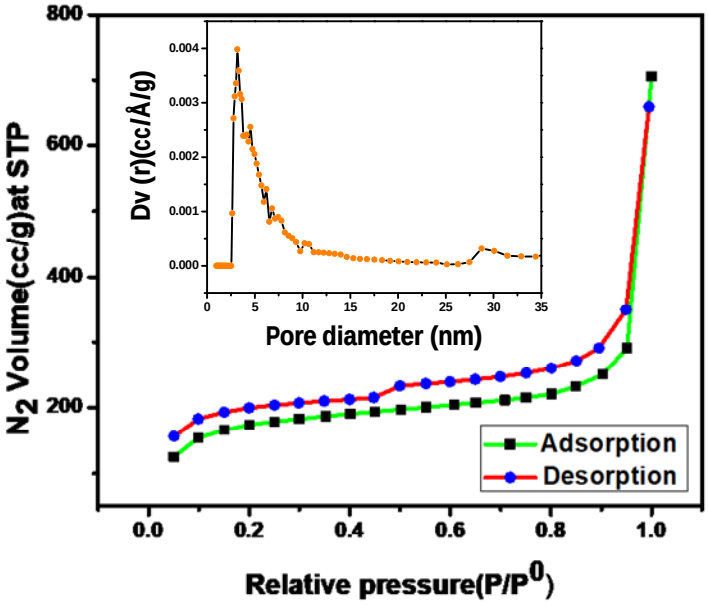


Figure S5. N_2 adsorption–desorption isotherm of reused Zn (II) @ TFP- DAQ COF at 77 K. Pore size distribution plot (inset).

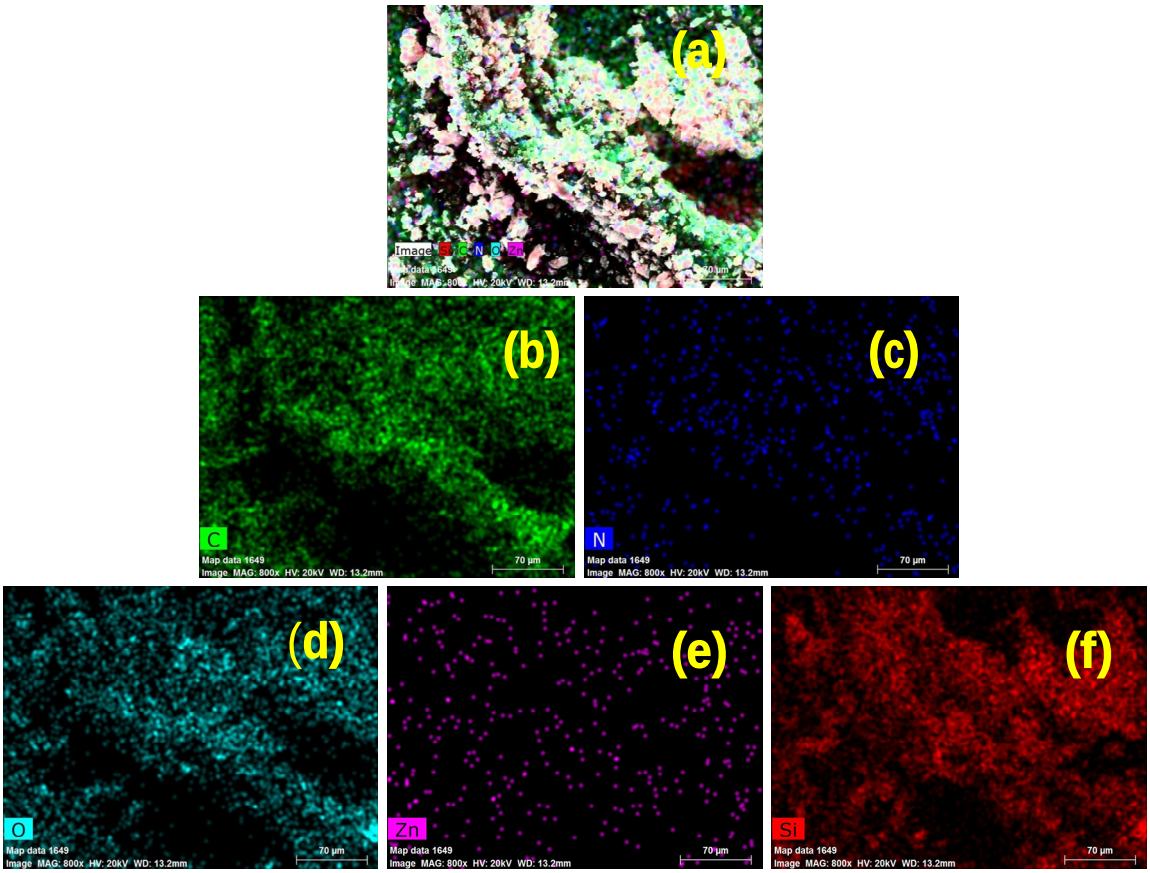


Figure S6. EDS mapping images of reused Zn (II) @ TFP- DAQ COF sample.

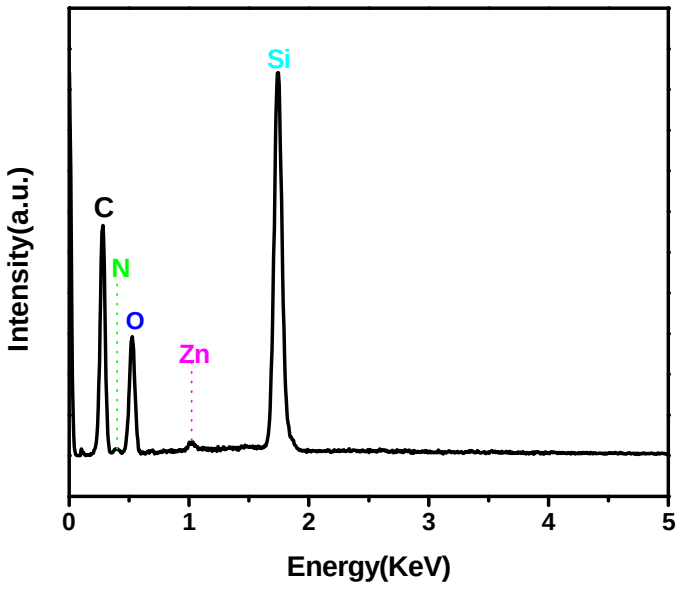
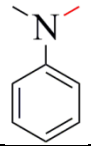
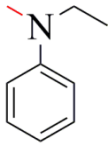
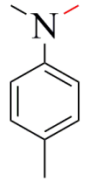
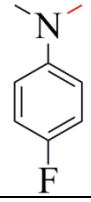
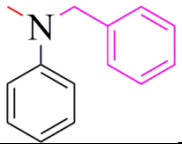
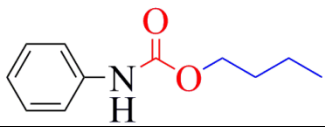
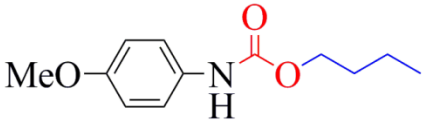
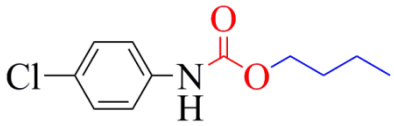
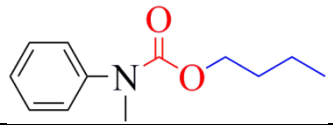
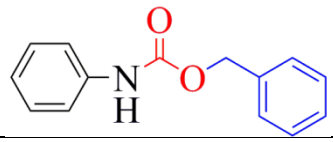
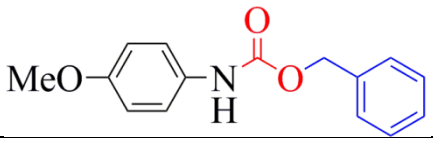
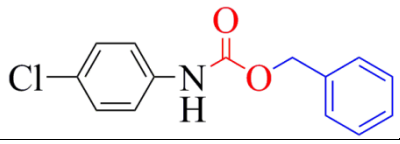
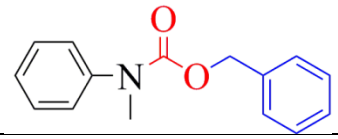


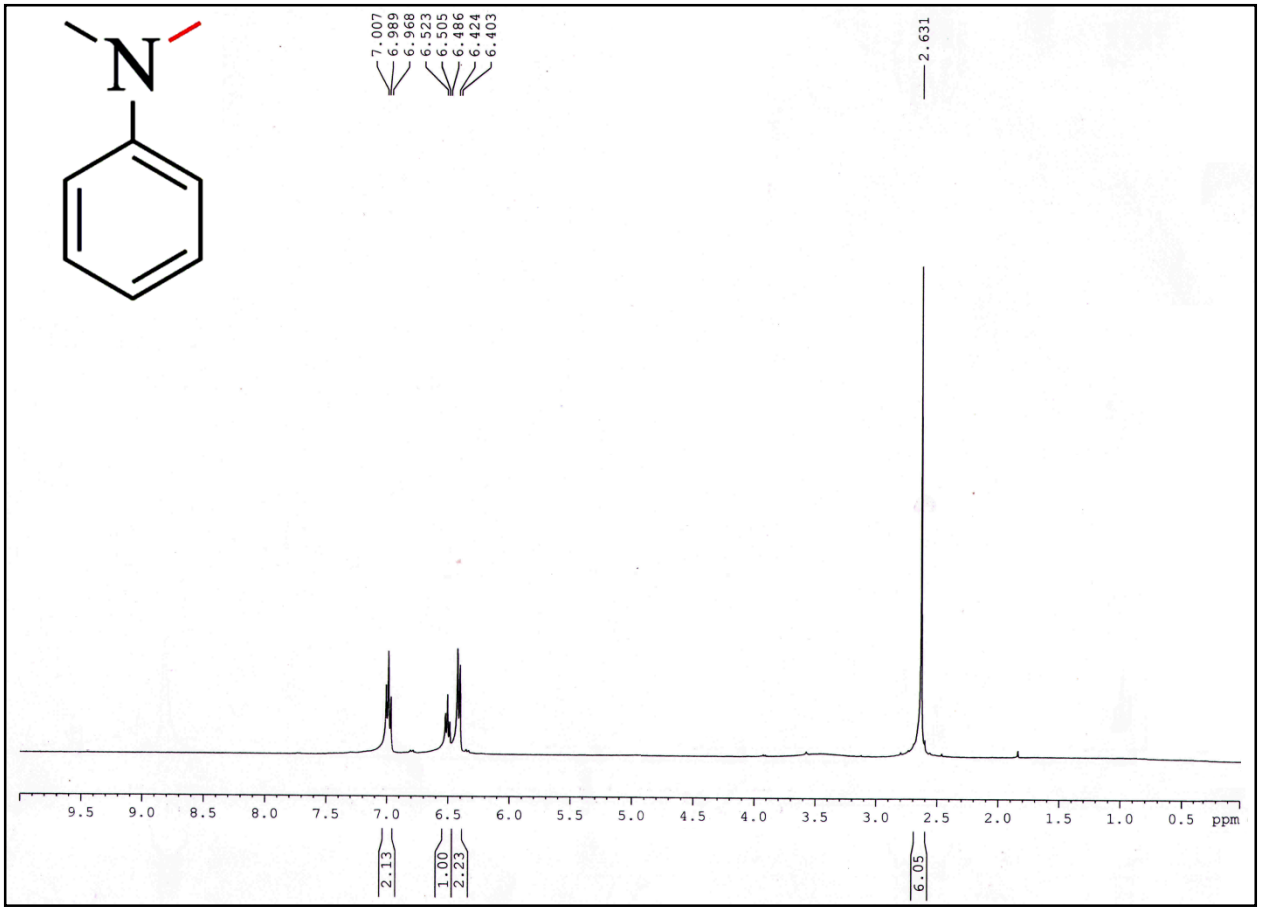
Figure S7. EDAX pattern of reused Zn (II) @ TFP- DAQ COF sample.

^{1}H NMR data of isolated products:

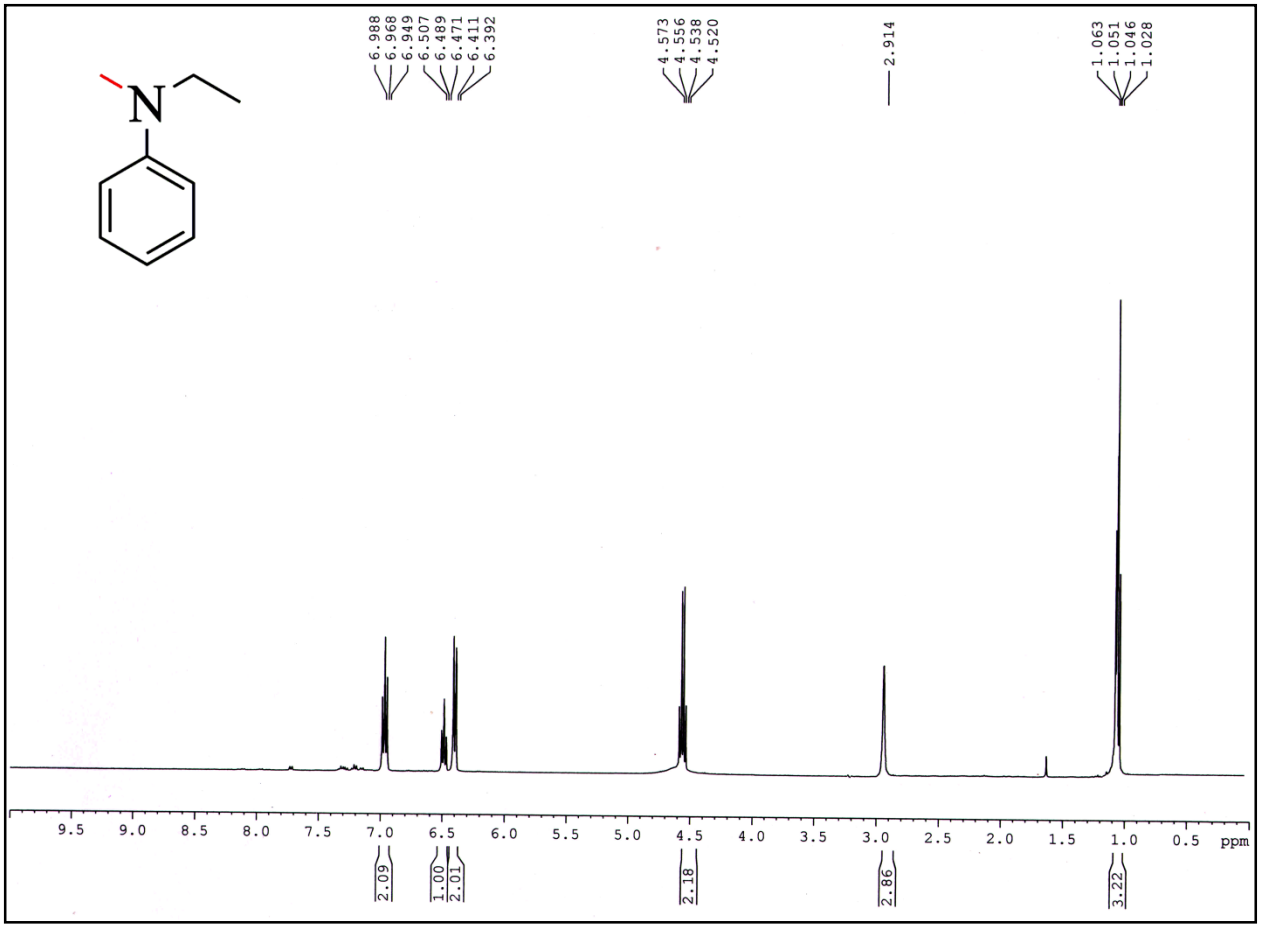
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.63 (s, 6H), 6.40 (d, *J* = 8.4 Hz, 2H), 6.48 (t, *J* = 7.6 Hz, 7.2 Hz, 1H), 6.96 (t, *J* = 8.4 Hz, 7.2 Hz, 2H) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.10 (dd, *J* = 5.2 Hz, 7.2 Hz, 3H), 2.91 (s, 3H), 4.52 (dd, *J* = 7.2 Hz, 14.2 Hz, 2H), 6.39 (d, *J* = 7.6 Hz, 8.0 Hz, 2H), 6.47 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 2H) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.10 (s, 3 H), 2.62 (s, 3 H), 6.59 (d, *J* = 8.4 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2H) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.80 (s, 6H), 6.60 (d, *J* = 8.4 Hz, 2 H), 4.29-4.36 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 2 H) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.10 (s, 3H), 4.25 (s, 2H), 6.56 (d, *J* = 8.4 Hz, 2 H), 6.67 (t, *J* = 7.2 Hz, 2 H), 7.11 (t, *J* = 7.6 Hz, 2 H), 7.28 (dd, *J* = 7.6 Hz, 14.2 Hz) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.86-0.89 (m, 3H), 1.30-1.37 (m, 2H), 1.48-1.54 (m, 2H), 3.00-3.04 (m, 2H), 6.48-6.62 (m, 3H), 7.06-7.11 (m, 2H), 8.53 (brs, -NH) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.81-0.89 (m, 3H), 1.32-1.37 (m, 2H), 1.49-1.53 (m, 2H), 2.97-3.01 (m, 2H), 3.66 (s, 3H), 6.51 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 6.8 Hz, 2H), 8.05 (brs, -NH) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.85-0.89 (m, 3H), 1.31-1.38 (m, 2H), 1.46-1.54 (m, 2H), 2.96-3.00 (m, 2H), 4.09 (brs, -NH), 6.41 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H) ppm.

	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.81-0.89 (m, 3H), 1.20-1.29 (m, 2H), 1.44-1.50 (m, 2H), 2.83 (s, 3H), 3.19-3.23 (m, 2H), 6.58-6.64 (m, 3H), 7.13-7.17 (m, 2H) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.58 (s, 2H), 6.60-6.67 (m, 2H), 7.06-7.26 (m, 8H), 8.60 (brs, -NH).
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.65 (s, 3H), 4.47 (s, 2H), 6.61-6.69 (m, 3H), 7.15-7.26 (m, 6H), 8.15 (brs, -NH) ppm.
	1H NMR (400 MHz, CDCl3) δ 4.54 (s, 2H), 5.58 (brs, -NH), 6.55-7.28 (m, 9H) ppm.
	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.43 (s, 3H), 4.42 (s, 2H), 6.96-7.50 (m, 10H) ppm.

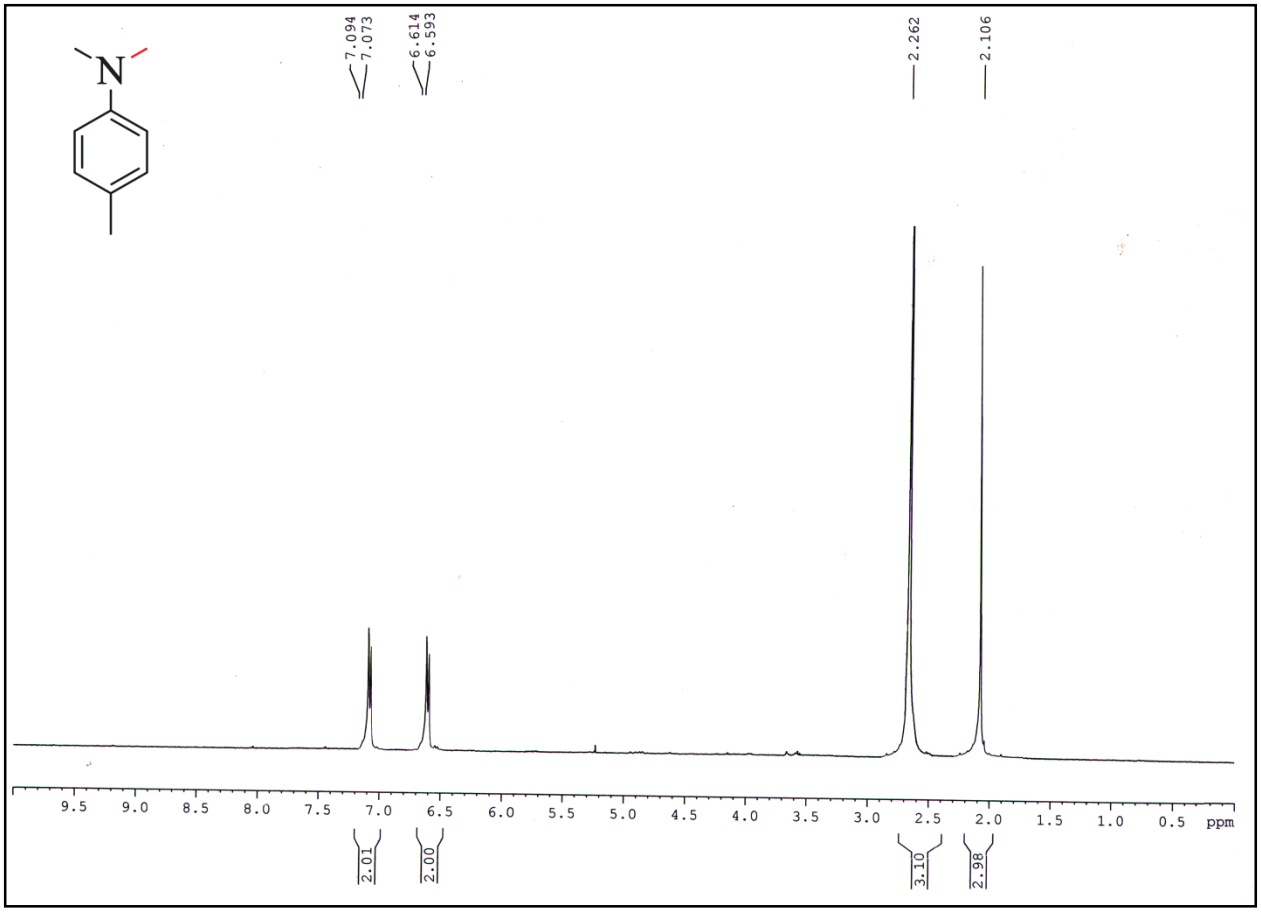
^{1}H NMR of N,N-dimethylaniline



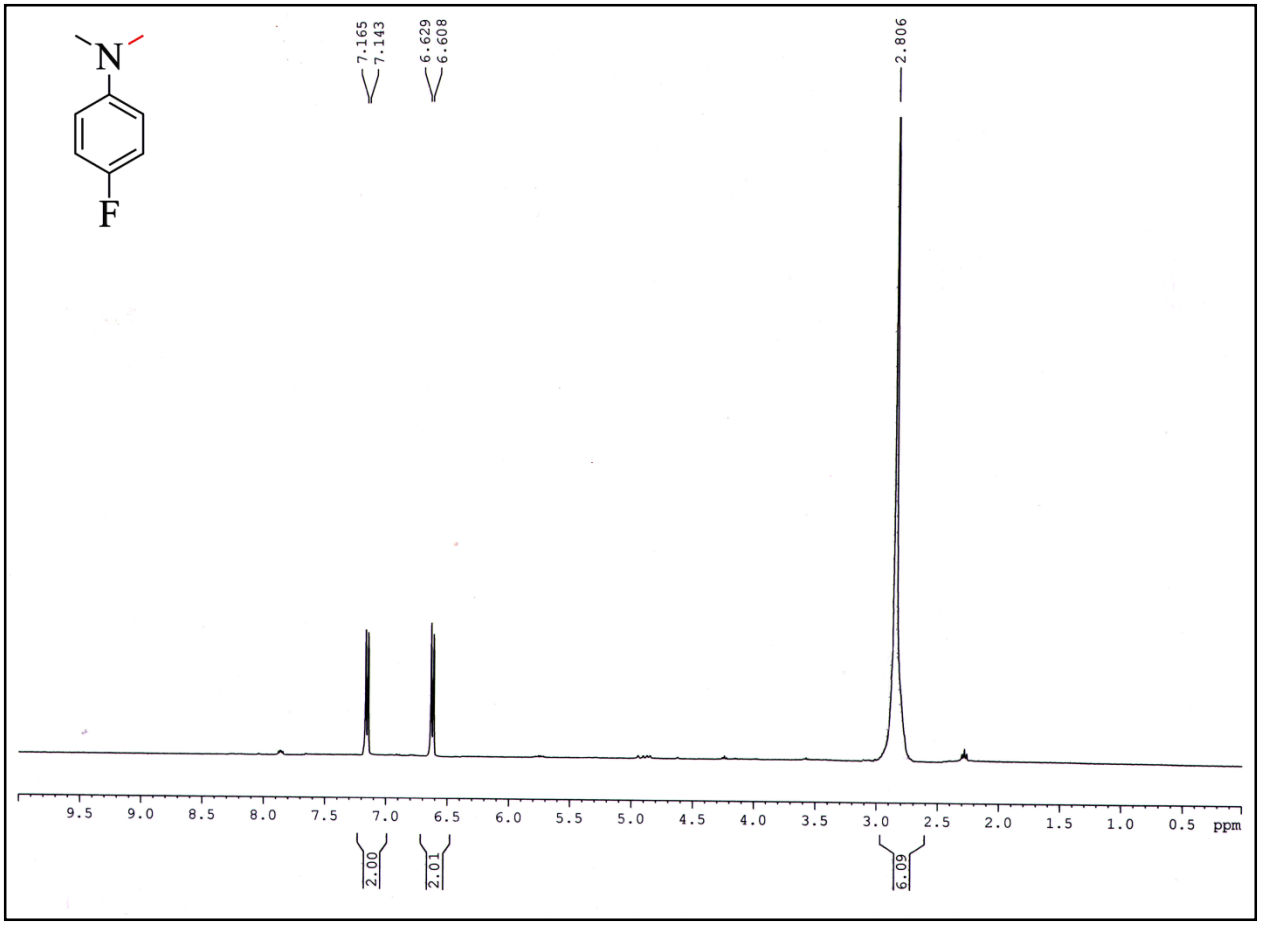
^{1}H NMR of N-ethyl-N-methylaniline.



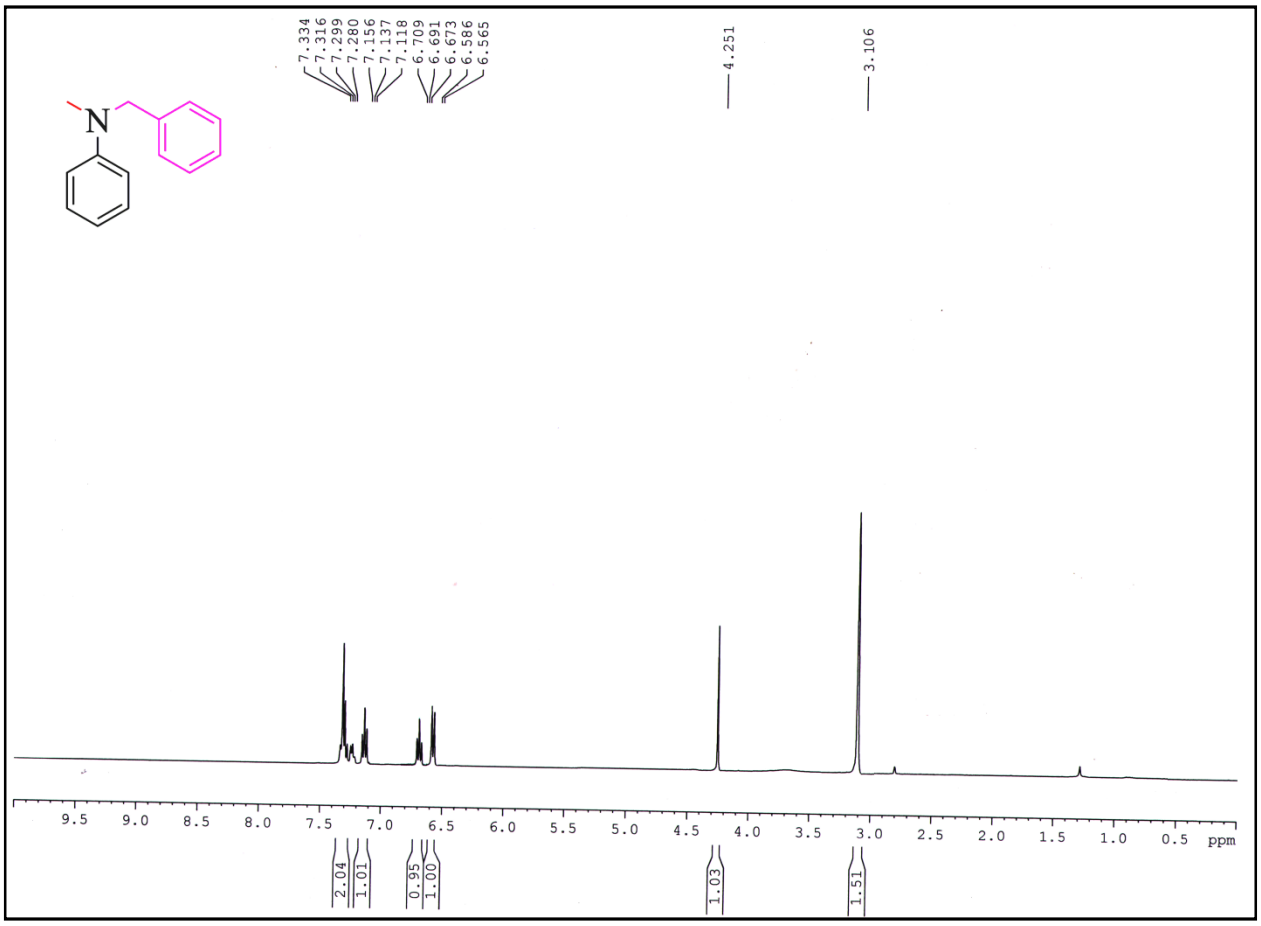
^{1}H NMR of N,N,4-trimethylaniline



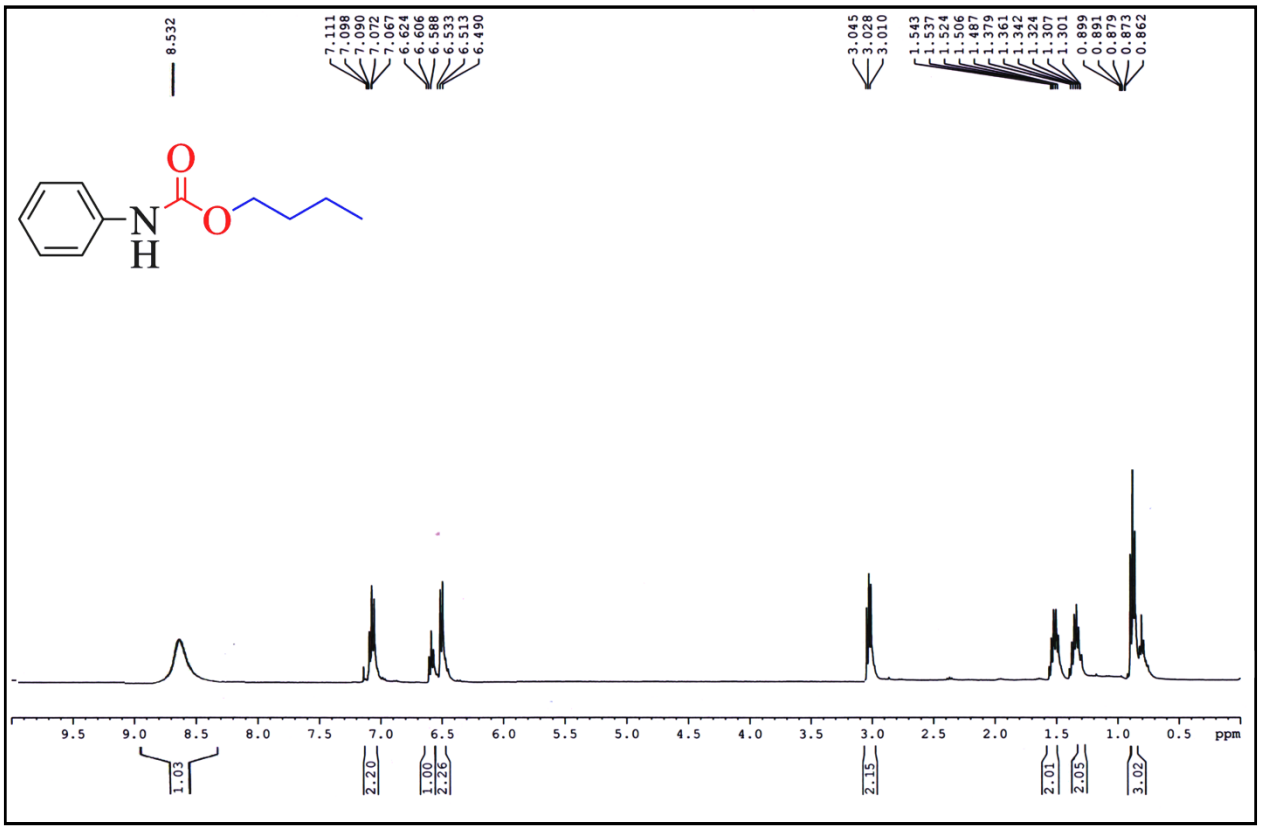
^{1}H NMR of 4-fluoro-N,N-dimethylaniline


N
F
7.165
7.143
6.629
6.608
2.806
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.01
6.09

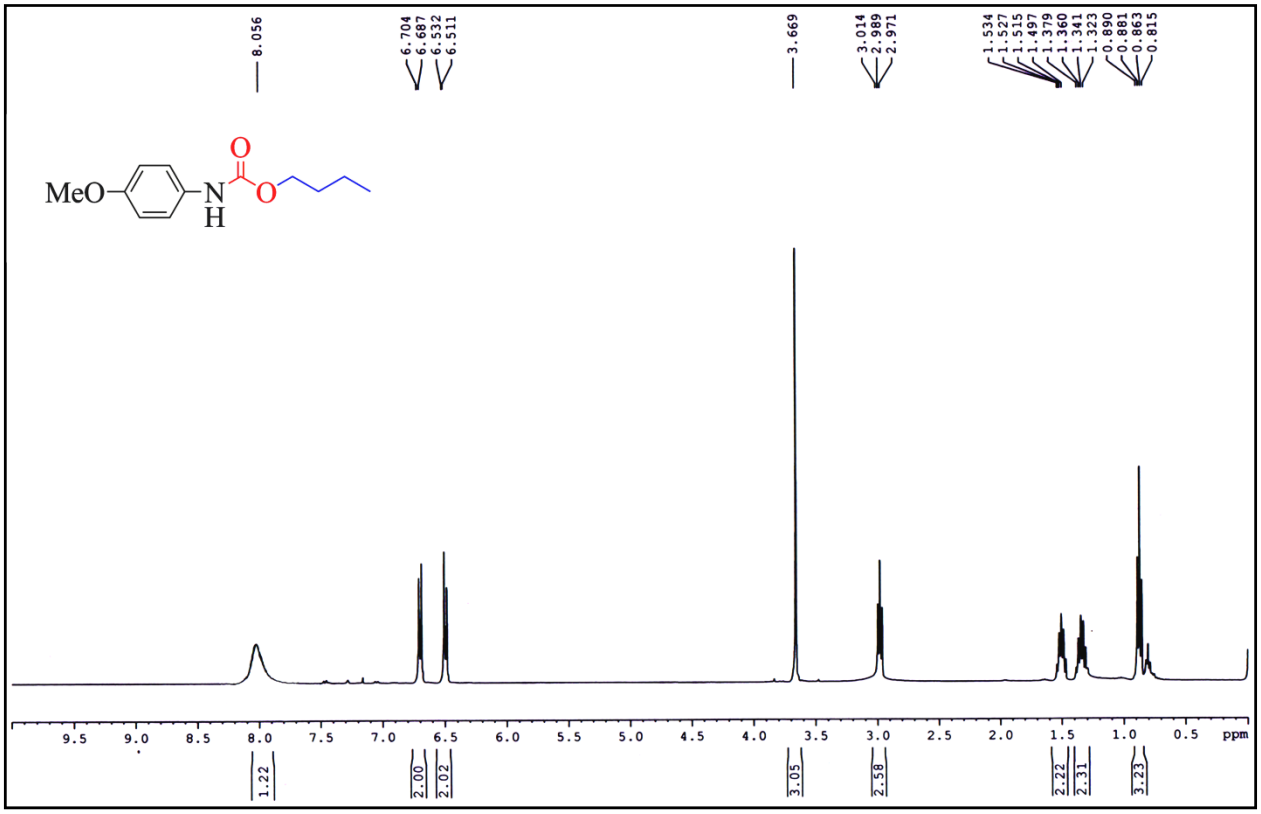
^{1}H NMR of N-benzyl-N-methylaniline



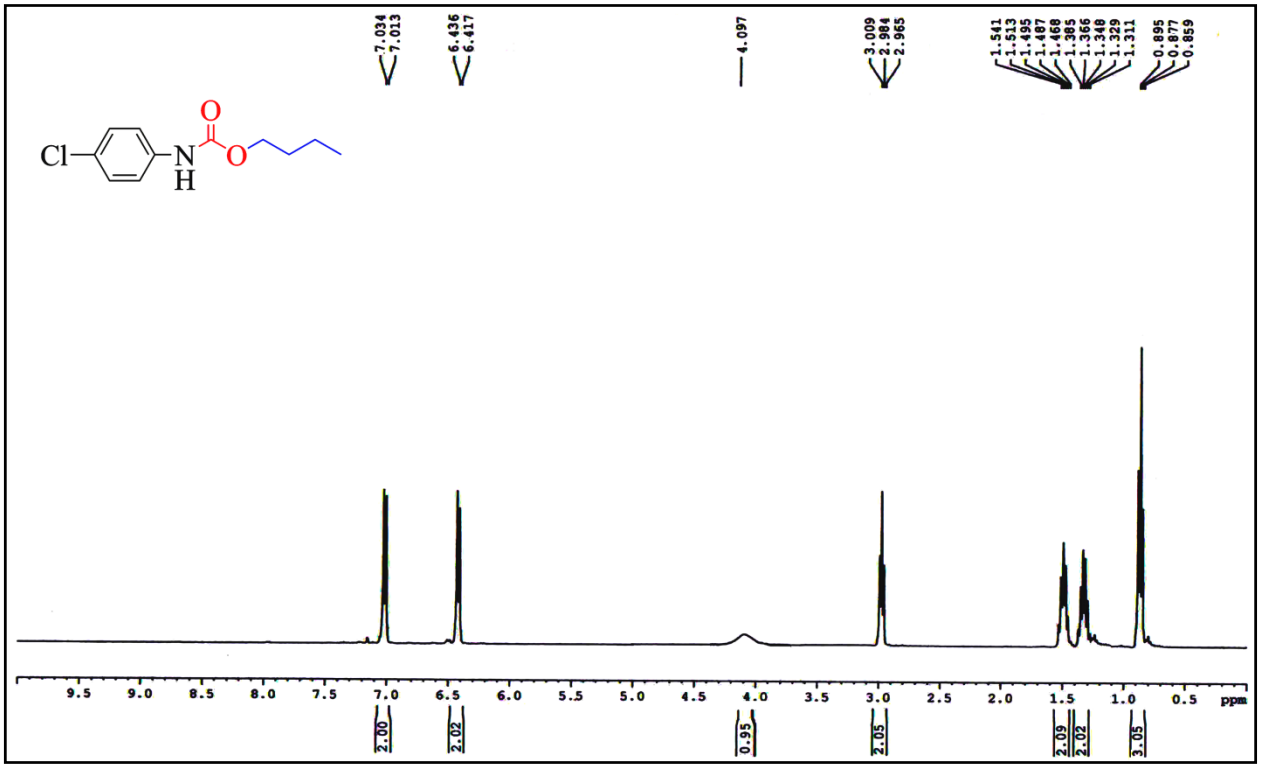
^{1}H NMR of butyl phenylcarbamate



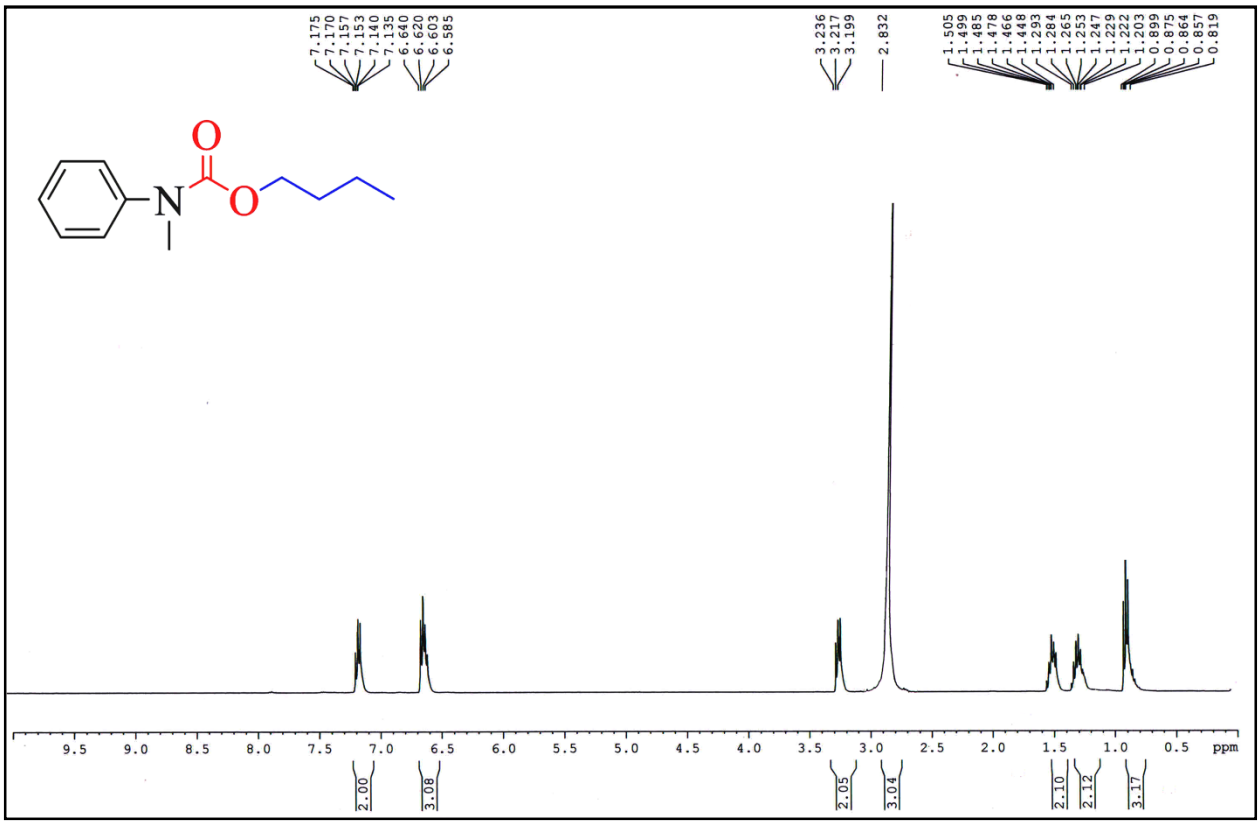
^{1}H NMR of butyl 4-methoxyphenylcarbamate



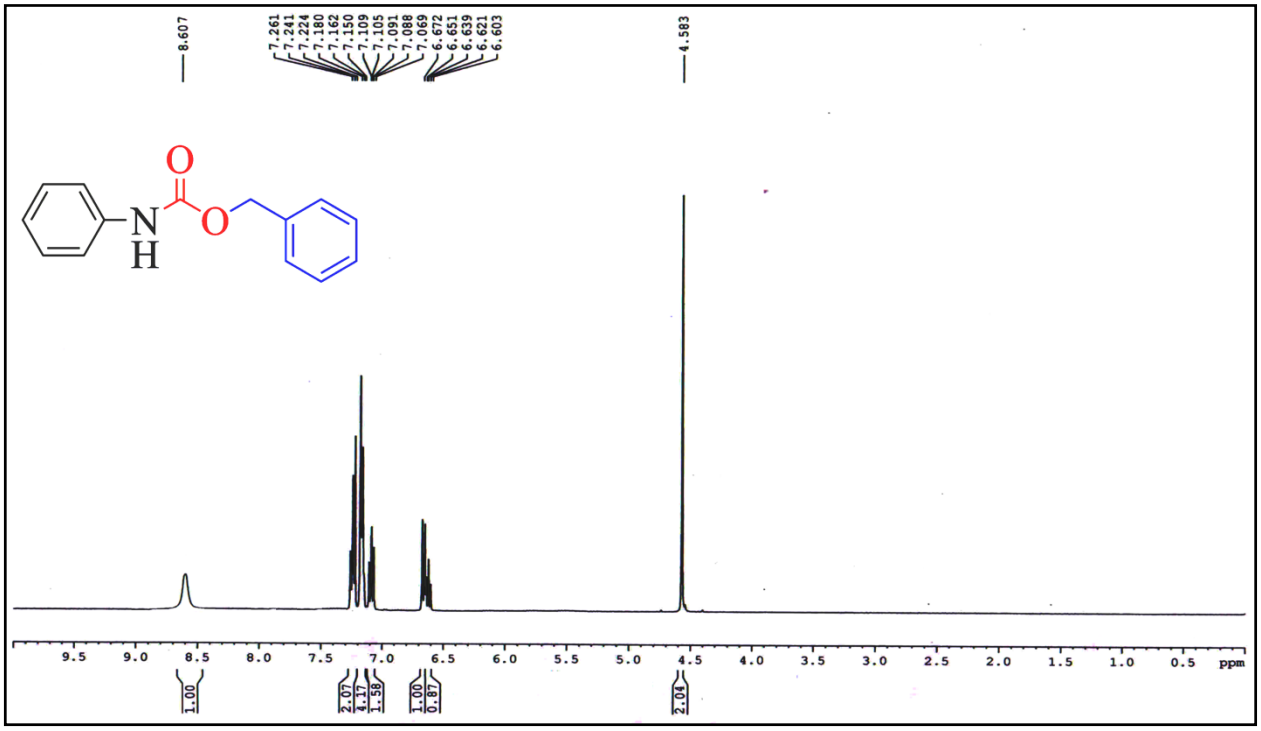
^{1}H NMR of butyl 4-chlorophenylcarbamate



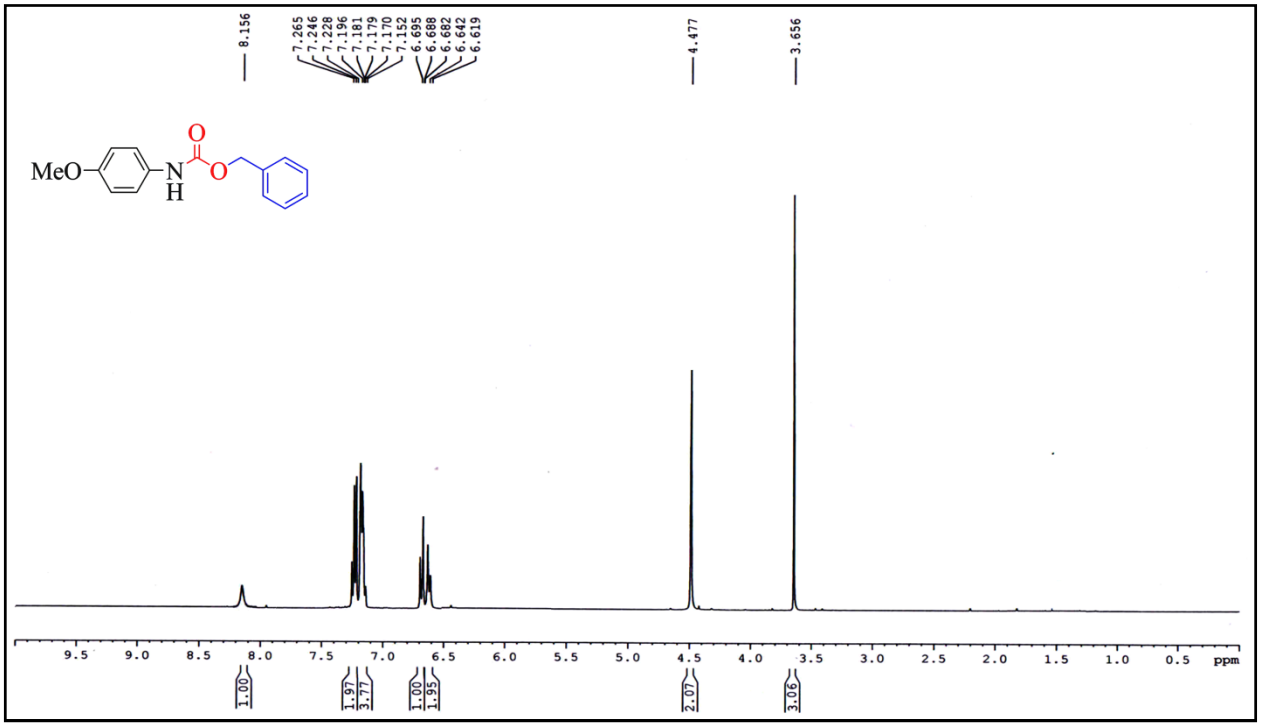
^{1}H NMR of butyl methyl(phenyl)carbamate



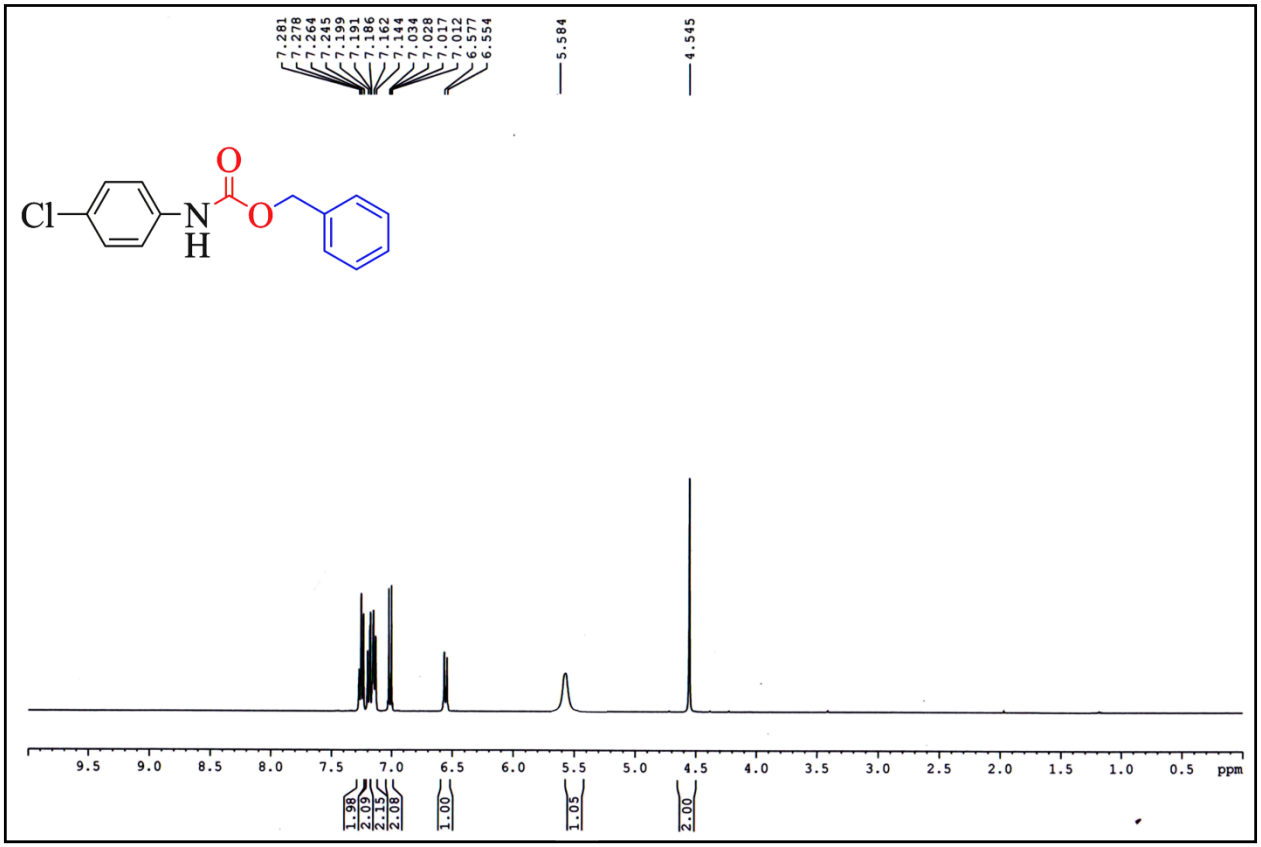
^{1}H NMR of benzyl phenylcarbamate



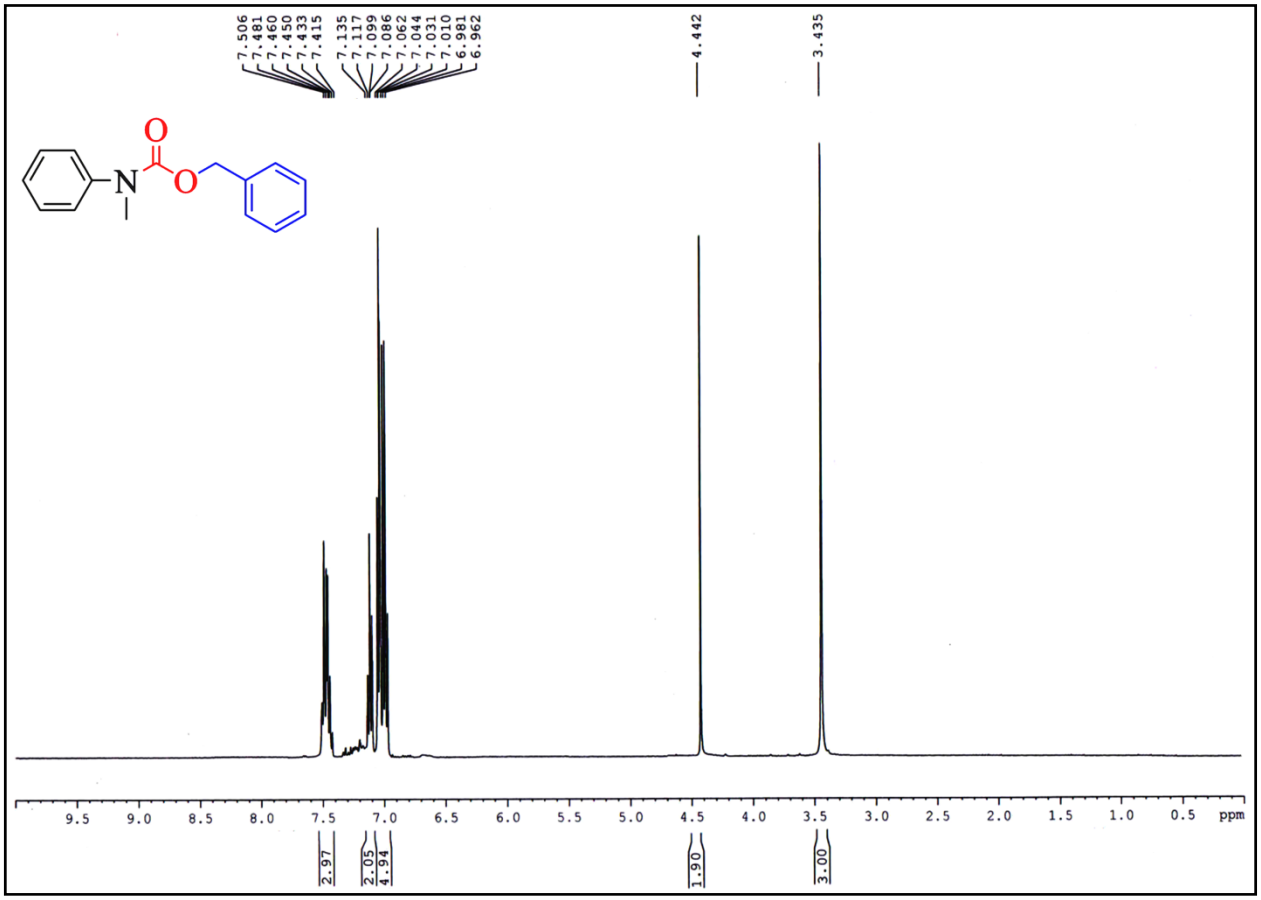
^{1}H NMR of benzyl 4-methoxyphenylcarbamate



^{1}H NMR of benzyl 4-chlorophenylcarbamate



^{1}H NMR of benzyl methyl(phenyl)carbamate



References:

[1] J. H. Chong, M. Sauer, B. O. Patrick, M. J. MacLachlan, *Org. Lett.*, 2003, **21**, 3823-3826.