

**Oxidized Graphitic Carbon Nitride as Sustainable Metal-free Catalyst for  
Hydrogen Transfer Reactions under Mild Conditions**

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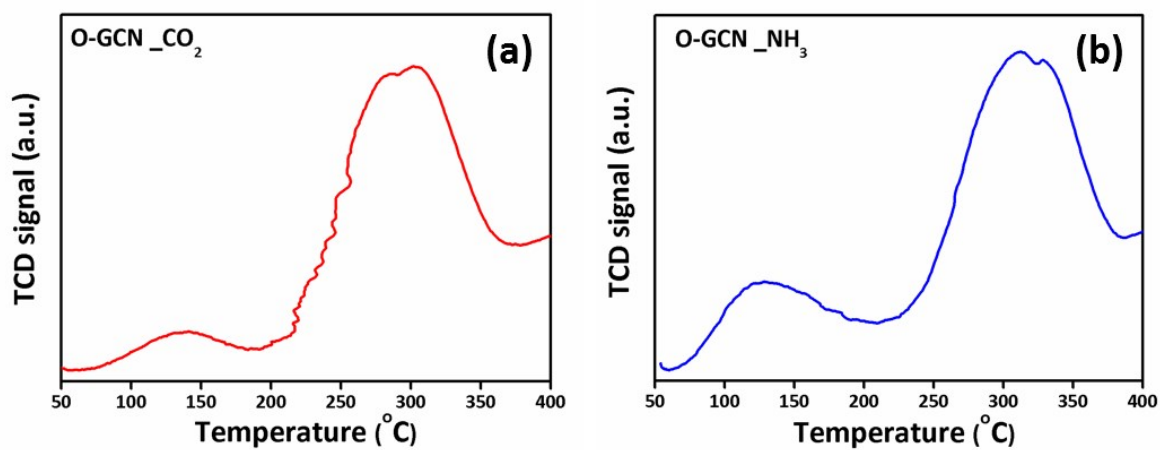
Sl. No.	Contents	Page No.
1	<b>S1.</b> Materials characterization	S2
2	<b>Table S1.</b> Atomic percentage of elements in O-GCN catalyst from XPS analysis	S3
3	<b>Figure S1.</b> CO <sub>2</sub> and NH <sub>3</sub> TPD measurement of O-GCN nanosheets	S4
4	<b>S2.</b> Product yield calculation	S5
5	<b>S3.</b> Calculation of number of active sites and turnover number (TON)	S6
6	<b>S4.</b> Green chemistry metrics calculations	S7-S8
7	<b>Table S2.</b> Summary of green metrics parameters for model reaction	S9
8	<b>Table S3.</b> Optimization Table for variation in catalyst amount	S10
9	<b>S5.</b> Mechanistic study	S11-S12
10	<b>Figure S2.</b> NMR spectra of the compounds	S13-S30

## S1. Materials characterization

The detailed characterization of catalysts was performed by using various instruments. The powder X-ray diffraction data was collected using a Rigaku SmartLab 9 kW rotating anode X-ray diffractometer in a Bragg–Brentano configuration using a Cu-sealed tube (Cu K $\alpha$  X-rays of 0.1541 nm) operating at 45 kV and 100 mA. The measurements were performed in the scattering  $2\theta$  range from  $10^\circ$  to  $80^\circ$  with a scan rate of  $2^\circ$  per min and a step size of  $0.02^\circ$ . Raman spectroscopy measurements were done on Horiba LabRAM high resolution instrument using 785 nm laser excitation. FT-IR measurements were done on Agilent K8002AA Cary 660 instrument. Thermogravimetric analysis (TGA) was performed using a PerkinElmer Pyris 1 instrument. The samples were heated under a nitrogen atmosphere from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  with the heating rate of  $10^\circ\text{C min}^{-1}$  at a flow rate of  $20\text{ mL min}^{-1}$ . The morphological analysis was done using a scanning electron microscope (SEM) FEI Nova SEM-450 and transmission electron microscope (TEM) FEI Tecnai G2 20 S-twin microscope operating at 200 kV. Energy dispersive X-ray spectra (EDAX) and elemental mapping data were also obtained by using the same TEM instrument. The X-ray photoelectron spectroscopy (XPS) measurements were done using Thermo Scientific NEXSA photoemission spectrometer using Al-K $\alpha$  (1486.6 eV) X-ray radiation. The XPS data were acquired with a spot size  $400\ \mu\text{m}$  having a standard lens mode. The obtained data from the instrument were plotted and deconvoluted using Avantage software. The Brunauer–Emmett–Teller (BET) specific surface area was measured on Quanta chrome Autosorb-iQ-MP-XR system at 77 K. The temperature-programmed desorption (TPD) study was done using CHEMBET™ TPR/TPD, QUANTACHROME. NMR spectra were measured using a JEOL-USA (JNMECX500) spectrometer in DMSO- $d_6$  using TMS (tetramethyl silane) as an internal standard. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts in NMR is reported in ppm relative to 2.50 and 39.50 of the DMSO- $d_6$  solvent as the standard. The coupling constant “J” was calculated in Hz. All  $^1\text{H}$ -NMR spectra were recorded at 500 MHz frequency, wherein  $^{13}\text{C}$ -NMR spectra were recorded at 125 MHz frequency.

**Table S1.** Atomic percentage of elements in O-GCN catalyst from XPS analysis.

<b>Sl. No.</b>	<b>Elements</b>	<b>Binding energy (eV)</b>	<b>Atomic percentage</b>
1	C 1s	289.30	43.00
2	N 1s	400.12	52.68
3	O 1s	532.50	4.32



**Figure S1.** (a) CO<sub>2</sub> TPD measurement of O-GCN nanosheets and (b) NH<sub>3</sub> TPD measurement of O-GCN nanosheets.

## S2. Product yield calculation:

The product yield was calculated after purification of the product using column chromatography. The yield of the product was calculated by using the following formula:

$$\text{Yield (\%)} = \frac{\text{Actual yield (in mg)}}{\text{Theoretical yield (in mg)}} \times 100$$

Herein, theoretical yield = Molecular weight of product  $\times$  mmol of reactants (Theoretical yield is the 100 % yield)

### S3. Detailed calculation of number of active sites and turnover number (TON)

The term active site is referred to effective sites for a particular heterogeneous catalytic reaction. The number of active sites can be used to describe an ensemble of sites at which a catalytic reaction takes place.

The effectiveness of the catalyst is expressed in the catalytic reaction system as turnover number (TON). TON is a unit less measure and can be calculated as below:

$$TON = \frac{(\%conversion) \times N_{\text{moles of reactants}}}{N_{\text{moles of catalyst}}}$$

From the TPD analysis it was found that the amount of acidic sites present in O-GCN nanosheets are 0.059 mmol g<sup>-1</sup> and basic sites are 0.051 mmol g<sup>-1</sup>. Since the active sites are acidic, therefore only the moles corresponding to the acidic sites will account for TON calculations.

According to TPD analysis, 1 g of catalyst = 0.059 mmol of active sites.

Therefore, 1 mg of catalyst contains  $5.9 \times 10^{-5}$  mmol of active sites.

Since, 20 mg of catalyst is used in the catalytic reaction.

Therefore, for 20 mg of catalyst contains  $1.18 \times 10^{-3}$  mmol of active sites.

For the model reaction involving 4-chlorobenzaldehyde, TON can be calculated as below:

$$TON = \frac{92 \times 1}{118 \times 10^{-3}}$$

$$TON = 77576$$

Similarly, TON for all the reactions was calculated and is given in Table 2 in main manuscript.

#### S4. Green metrics calculations

Green chemistry metrics calculations were performed for the developed catalytic hydrogen transfer reaction of carbonyl compounds to study the environmental impact and sustainability of the reaction. The important parameters for a Green and sustainable reaction have been discussed in detail.

**(1) Environmental factor (E-factor):** E-factor is a popular Green chemistry metrics which defines the ratio of mass of waste to mass of product. It tells us about how much waste formed is generated in a chemical process. For an ideal Green chemical reaction, E-factor should be 0. Higher the E-factor means more amount of waste is generated which can have a detrimental impact on environment.

$$E - factor = (mass\ of\ waste)/(mass\ of\ product)$$

$$Mass\ of\ waste = Total\ mass\ of\ raw\ materials - Total\ mass\ of\ product$$

The E- Factor calculated for our model reaction was found to 0.087.

**(2) Atom economy (AE):** AE of a reaction describes the total number of atoms resides in the product from the starting materials. It is considered as an important parameter to determine the efficiency of a reaction. The ideal value of AE factor is 100%.

$$AE = Mol.\ wt.\ of\ product / \Sigma(Mol.\ wt.\ of\ stoichiometric\ reactants) \times 100$$

AE calculated for the model reaction was found to be 100% as all atoms from the starting materials still resides in the product.

**(3) Mass intensity (MI):** MI is the total mass involves in process divided by the mass of product. Lower the mass intensity value, lower will be the cost and the process will be more sustainable.

$$MI = (Total\ mass\ in\ process) / (Mass\ of\ product)$$

MI value calculated for the model reaction was 1.087.

**(4) Process mass intensity (PMI):** PMI is the total mass used in a chemical process including the mass of the solvents used divided by the mass of product.

$$PMI = [Total\ mass\ in\ process\ (including\ solvent)] / [Mass\ of\ product]$$

The solvent used in the model reaction was 2-propanol which is itself a green solvent and the PMI value was calculated to be 2.016.

**(5) Reaction mass efficiency (RME):** Reaction mass efficiency is defined as the mass of product divided by the sum of total mass of stoichiometric reactants. RME measures the “cleanness” of a chemical reaction. Values of RME range from 0-100%.

$$RME (\%) = \text{mass of product} / \Sigma(\text{mass of stoichiometric reactants}) \times 100$$

RME value for the model reaction was found to be 91.99%. Higher value of RME is considered better for an ideal green chemical reaction.

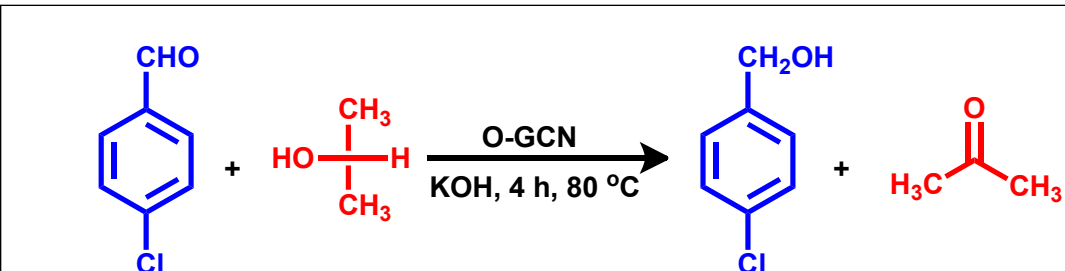
**(6) Carbon economy (CE):** CE is the measure of the carbon content in product with respect to the carbon content in reactant.

$$CE (\%) = [\text{Total carbon in product}] / [\text{Total carbon in reactant}] \times 100$$

CE for the model reaction was found to be 100% which indicates that the carbon content in reactant and the product remain unchanged.



**Table S2.** Summary of green metrics parameters calculated for the model reaction.

 <p style="text-align: center;"> <span style="margin-right: 100px;">4-chlorobenzaldehyde</span> <span style="margin-right: 100px;">2-propanol</span> <span style="margin-right: 100px;">4-chlorobenzyl alcohol</span> <span>Acetone</span> </p>		
Sl. No.	Green metric parameters	Calculated values
1	Environmental factor (E-factor)	0.087
2	Atom economy (AE)	100%
3	Mass intensity (MI)	1.087
4	Process mass intensity (PMI)	2.016
5	Reaction mass efficiency (RME)	92%
6	Carbon economy (CE)	100%

**Table S3.** Optimization of catalyst amount for model reaction involving 4-chlorobenzaldehyde

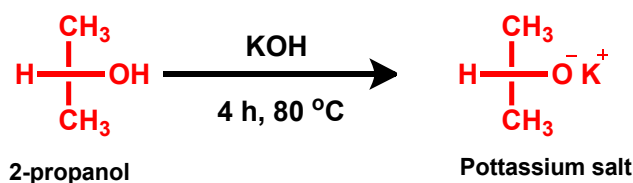
<b>Sl. No.</b>	<b>Catalyst</b>	<b>Amount of catalyst (mg)</b>	<b>Temperature (°C)</b>	<b>Time (h)</b>	<b>Yield (%)</b>
1	O-GCN	10	60	8	56
2	O-GCN	20	60	8	78
3	O-GCN	30	60	8	82
4	O-GCN	20	80	4	92
5	O-GCN	30	80	4	92

## S5. Mechanistic Study

The detailed mechanistic study was done by performing several control reactions as mentioned below.

### (i) Reaction of 2-propanol with KOH without O-GCN catalyst

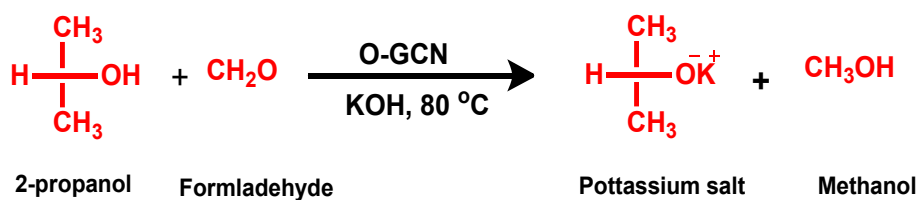
The reaction of 2-propanol with KOH was carried out under the model reaction conditions, i.e. at 80 °C for 4 hours. After the completion of reaction, NMR of crude reaction mixture was recorded and it was found that the reaction results in the formation of potassium salt with 2-propanol. The NMR signal for O-H proton was missing in the formed product, which clearly indicates proton abstraction and the formation of potassium salt of 2-propanol. No other product was observed in the reaction mixture.



Furthermore to confirm the formation of potassium salt the reaction mixture was extracted with  $\text{CHCl}_3/\text{H}_2\text{O}$  which again resulted in formation of 2-propanol, which was confirmed by NMR spectra.

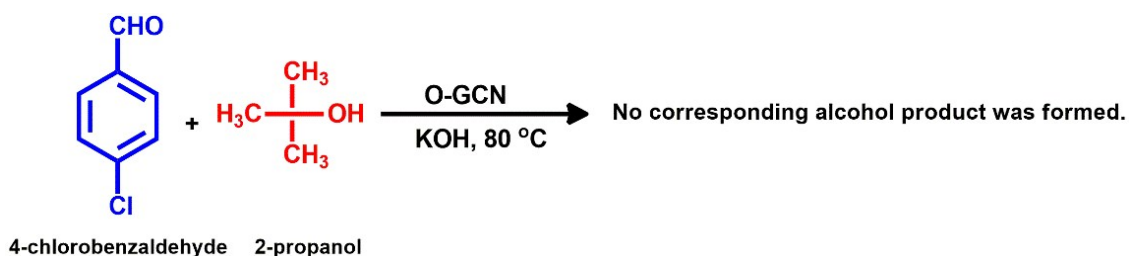
### (ii) Reaction of 2-propanol with KOH and O-GCN catalyst

Further the reaction of 2-propanol with KOH was carried out in presence O-GCN catalyst. The reaction again resulted in the formation of potassium salt with 2-propanol, which was confirmed by NMR. In order to examine the next step of the proposed mechanism, formaldehyde was added to the same reaction mixture and allowed to react. The reaction mixture was analyzed using NMR. It was observed that on addition of carbonyl substrate (i.e. hydrogen acceptor), the second hydrogen was also released from the potassium salt of 2-propanol resulting in the formation of the corresponding alcohol. Alcohol formation was confirmed via NMR spectra. This confirms that carbonyl substrate triggers the concerted hydrogen transfer step in the proposed mechanism.



### (iii) Reaction with tert-butyl alcohol

In order to confirm transfer hydrogenation, a non-hydrogen donor alcohol was used instead of 2-propanol. The model reaction was carried out in presence of tert-butyl alcohol and O-GCN catalyst for 4 hours at 80°C. The reaction showed no formation of alcohol product which confirms that the hydrogen is coming from 2-propanol and not from KOH.



### (iv) Reaction with K<sub>2</sub>CO<sub>3</sub>

The model reaction was carried out using K<sub>2</sub>CO<sub>3</sub> as base and O-GCN catalyst for 4 hours at 80°C. The reaction resulted in corresponding alcohol product but the yield obtained (72%) was comparatively less as compared to KOH (92%). This can be attributed to the reason that K<sub>2</sub>CO<sub>3</sub> is a weaker base than KOH.

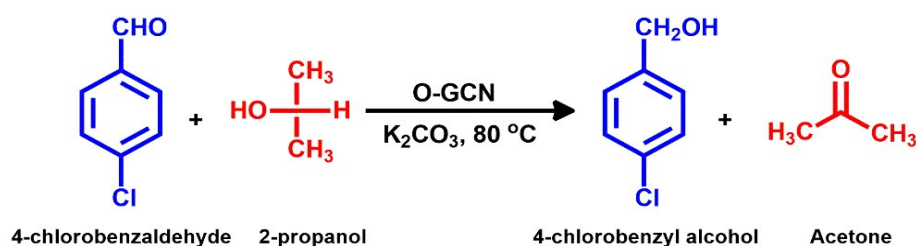
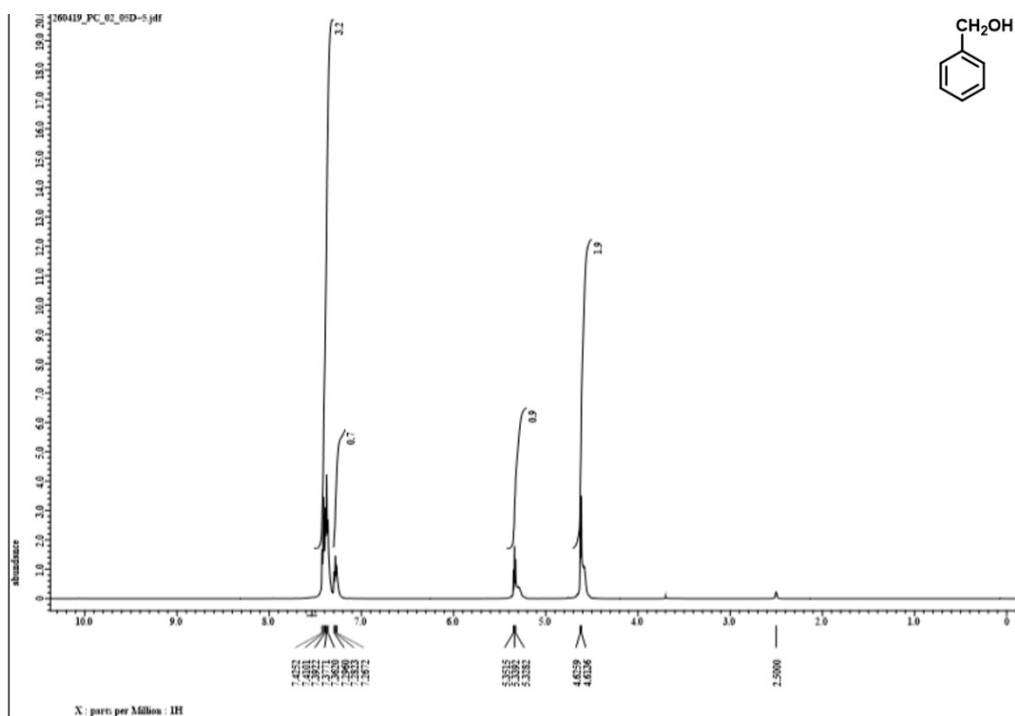
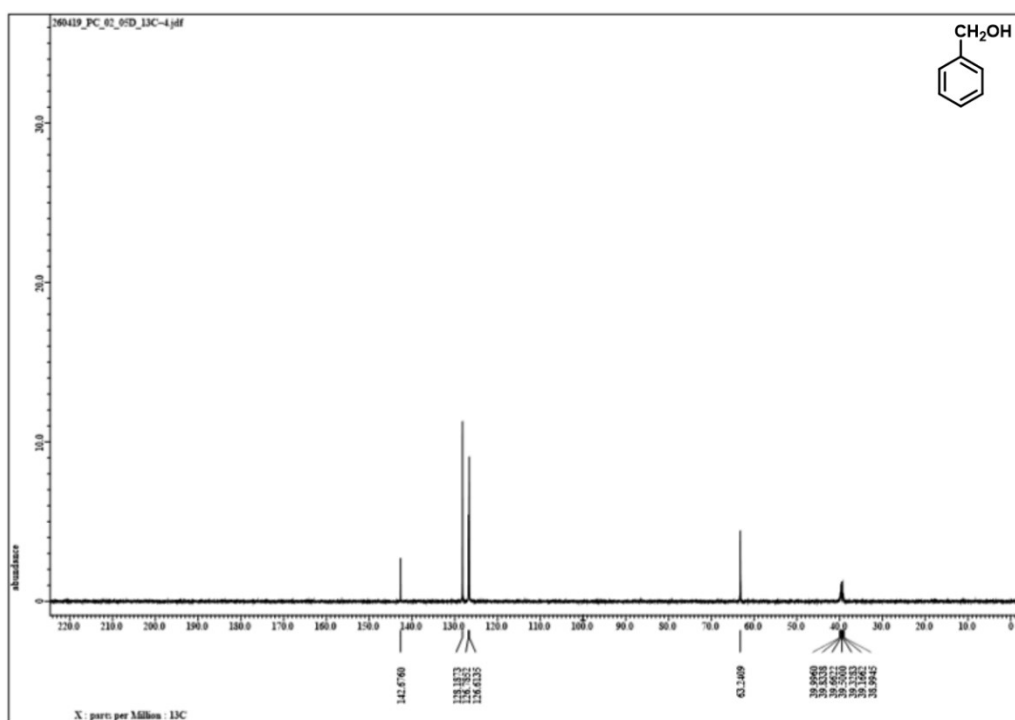


Figure S2. NMR spectra of the compounds

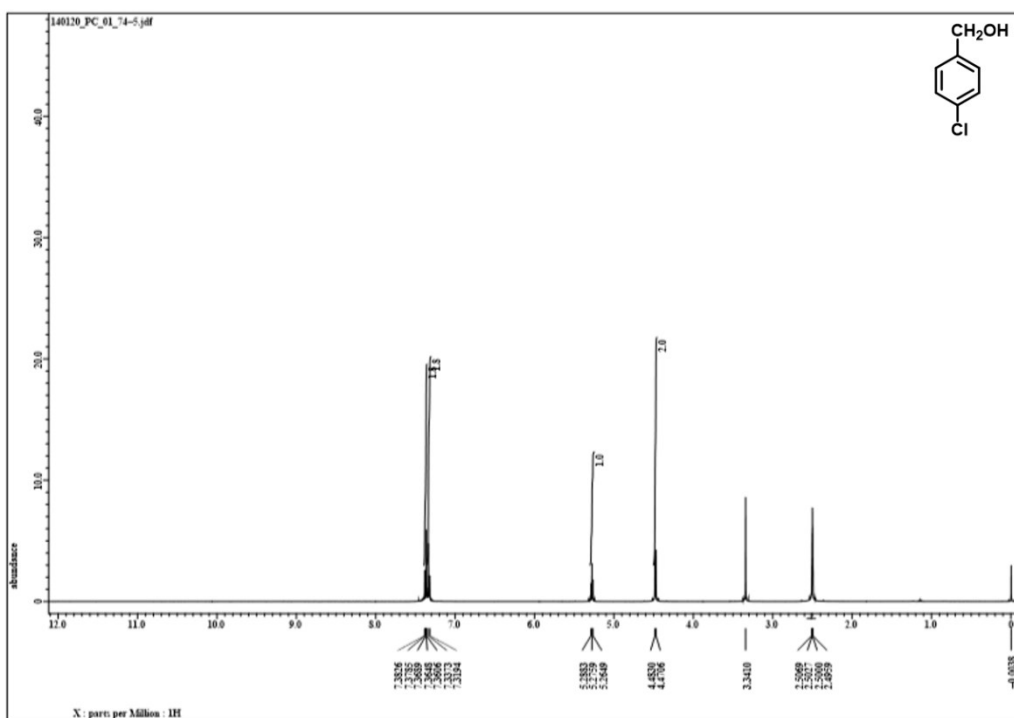
<sup>1</sup>H-NMR spectra of Phenylmethanol (3a) [500 MHz, DMSO-d<sub>6</sub>]



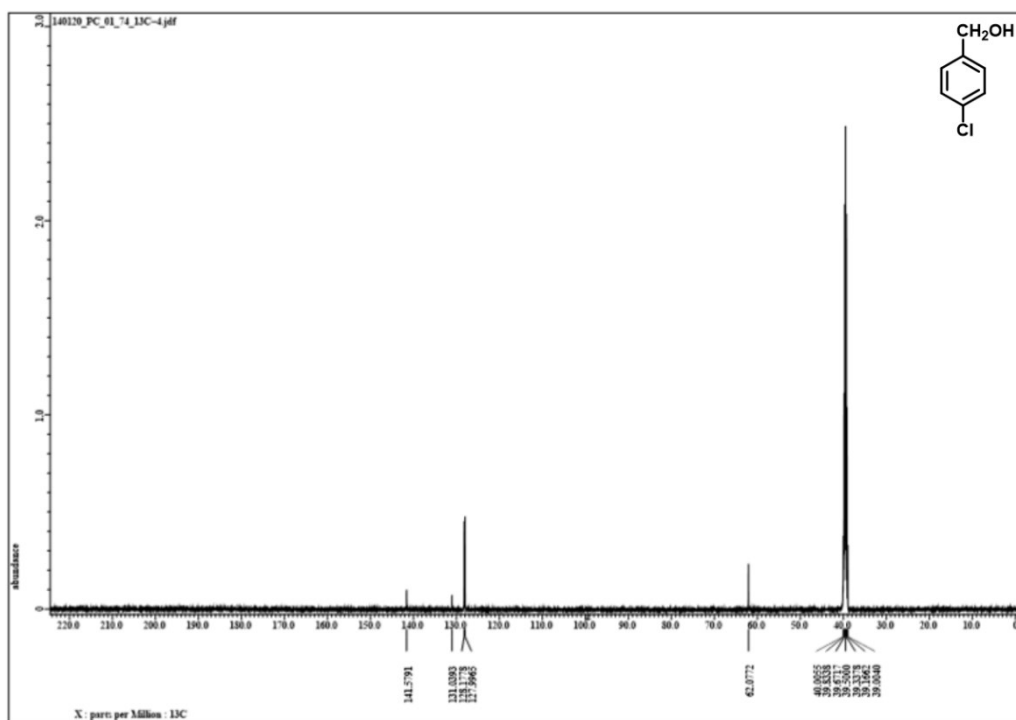
<sup>13</sup>C-NMR spectra of Phenylmethanol (3a) [125 MHz, DMSO-d<sub>6</sub>]



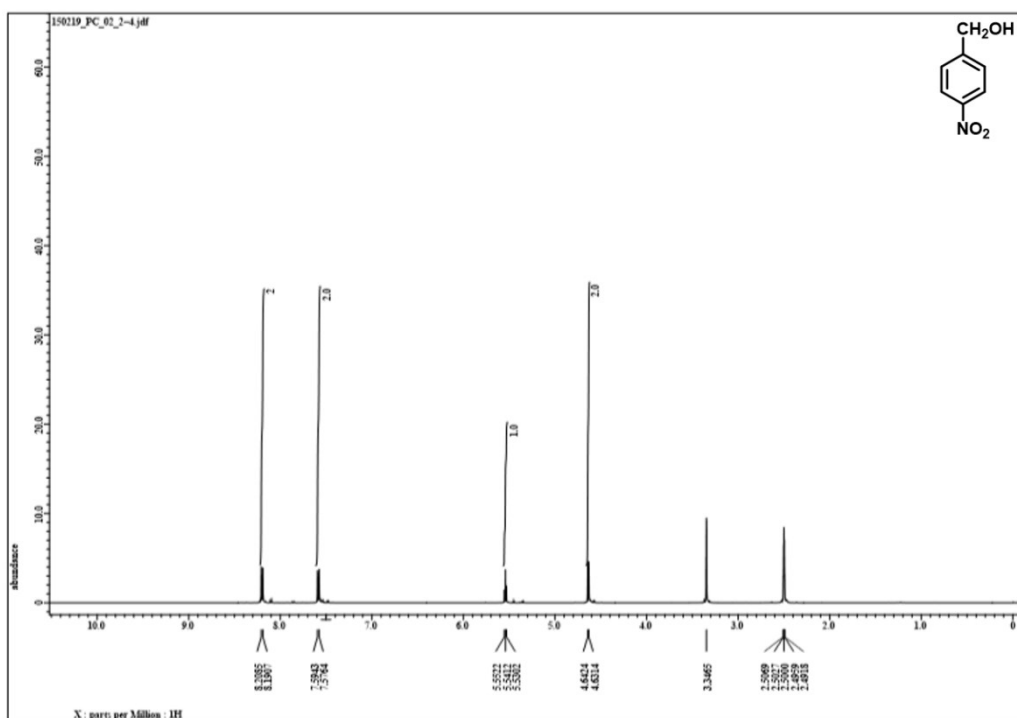
**<sup>1</sup>H-NMR spectra of (4-chlorophenyl)methanol (3b) [500 MHz, DMSO-d<sub>6</sub>]**



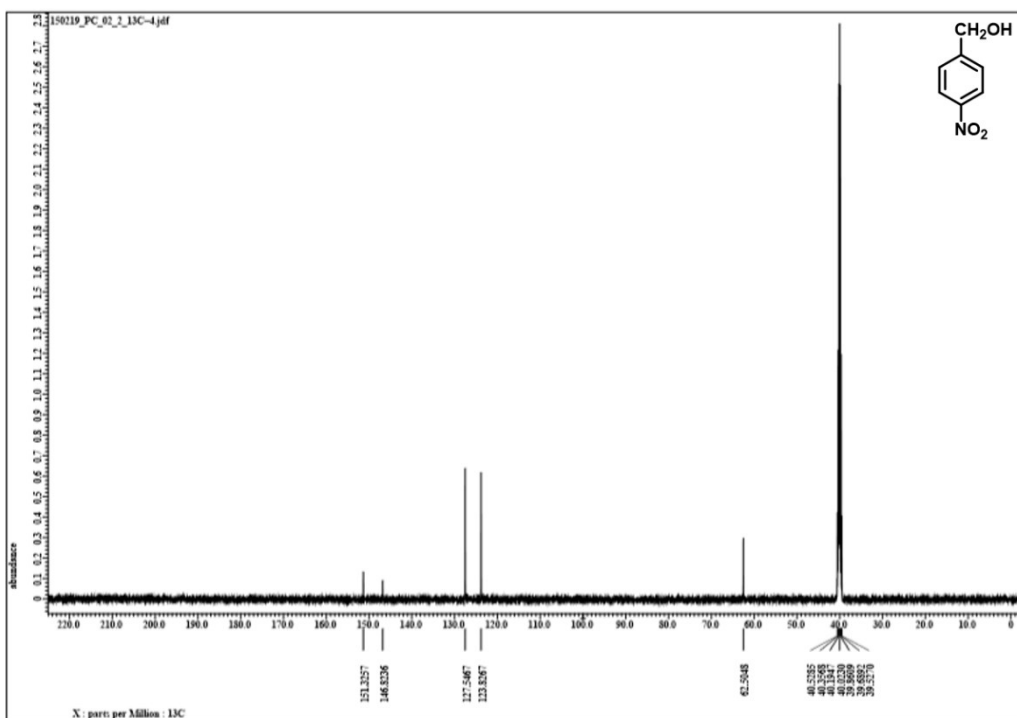
**<sup>13</sup>C-NMR spectra of (4-chlorophenyl)methanol (3b) [125 MHz, DMSO-d<sub>6</sub>]**



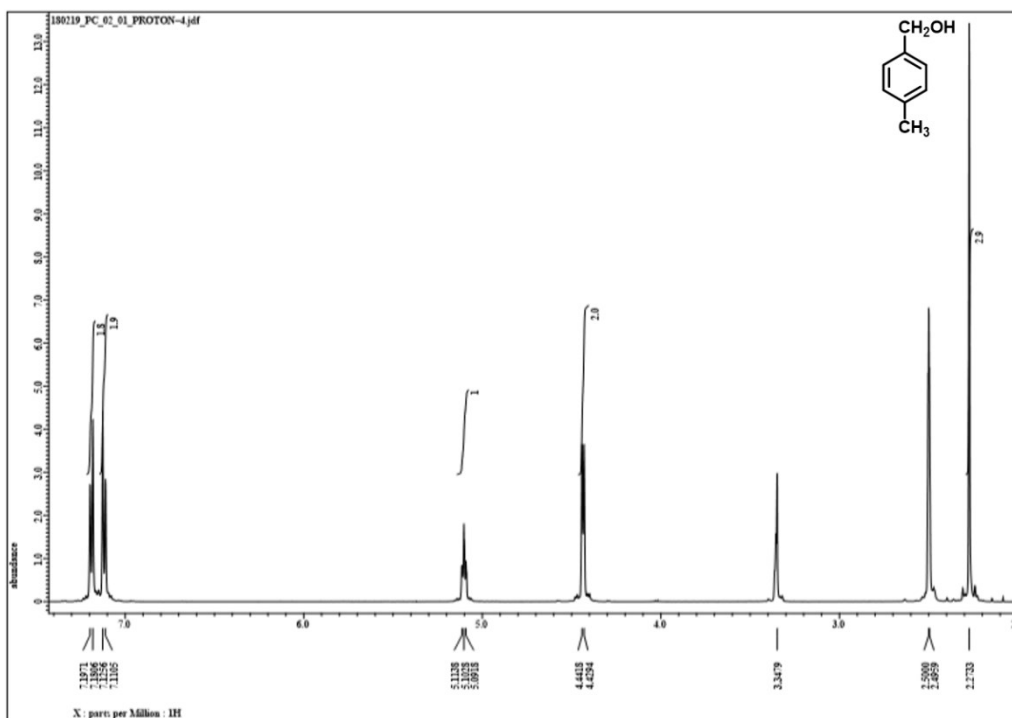
**<sup>1</sup>H-NMR spectra of (4-nitrophenyl)methanol (3c) [500 MHz, DMSO-d<sub>6</sub>]**



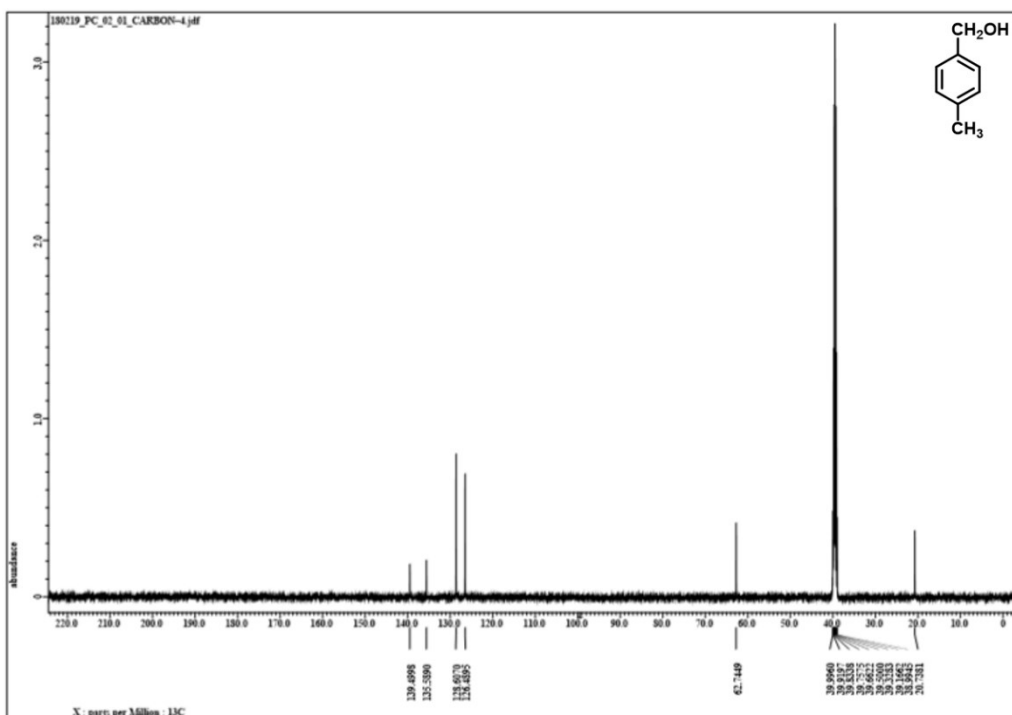
**<sup>13</sup>C-NMR spectra of (4-nitrophenyl)methanol (3c) [125 MHz, DMSO-d<sub>6</sub>]**



### <sup>1</sup>H-NMR spectra of p-tolylmethanol (3d) [500 MHz, DMSO-d<sub>6</sub>]

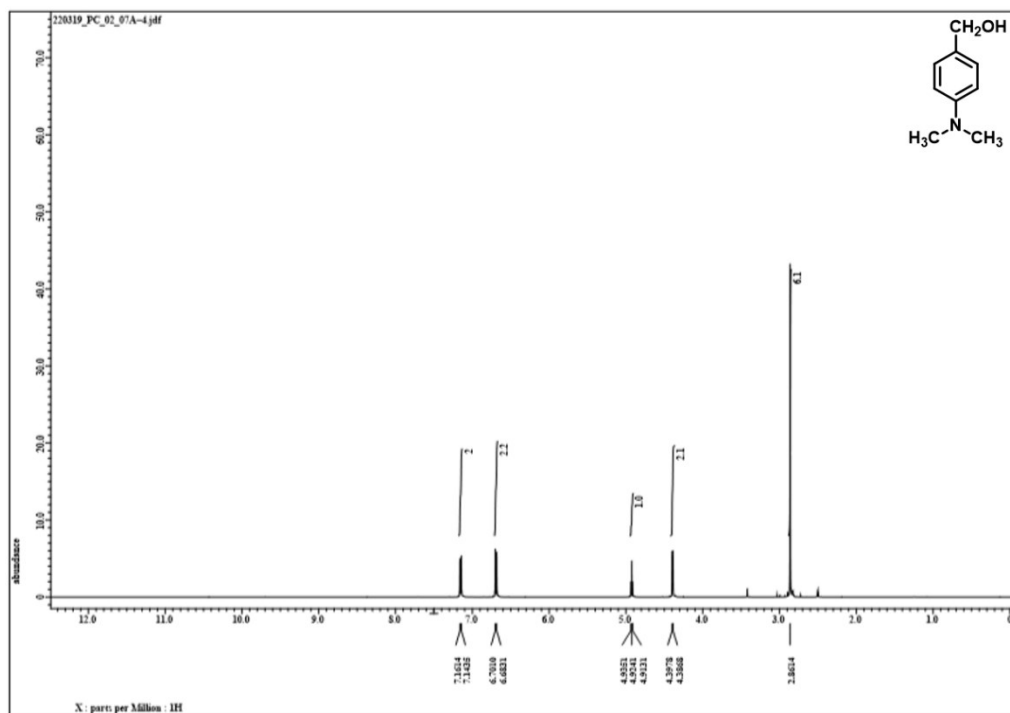


### <sup>13</sup>C-NMR spectra of p-tolylmethanol (3d) [125 MHz, DMSO-d<sub>6</sub>]

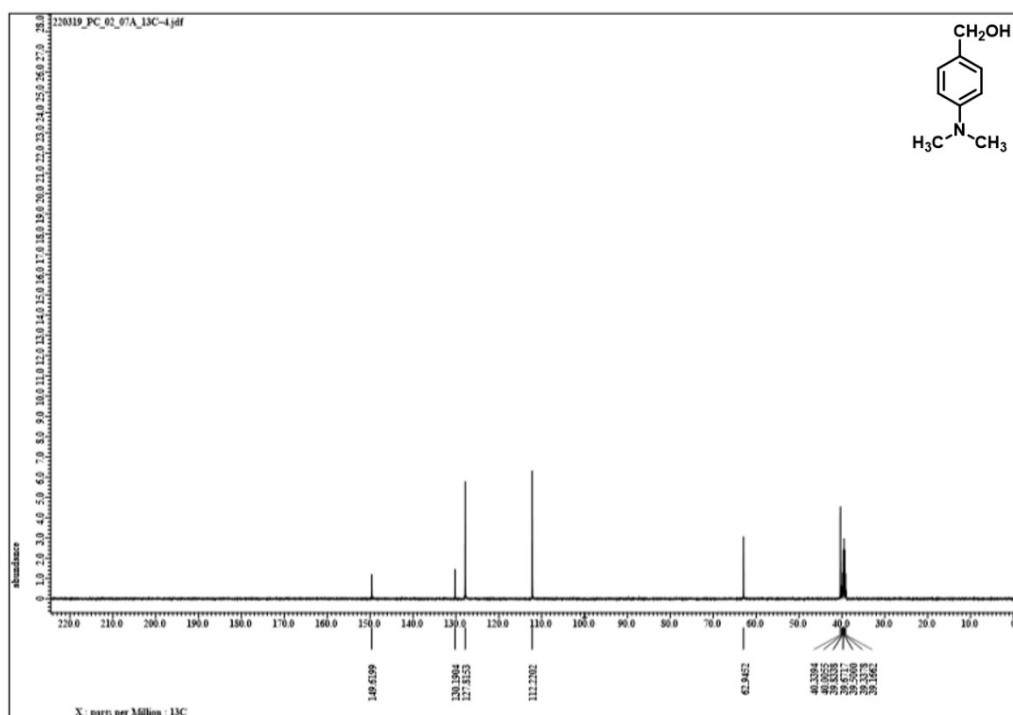




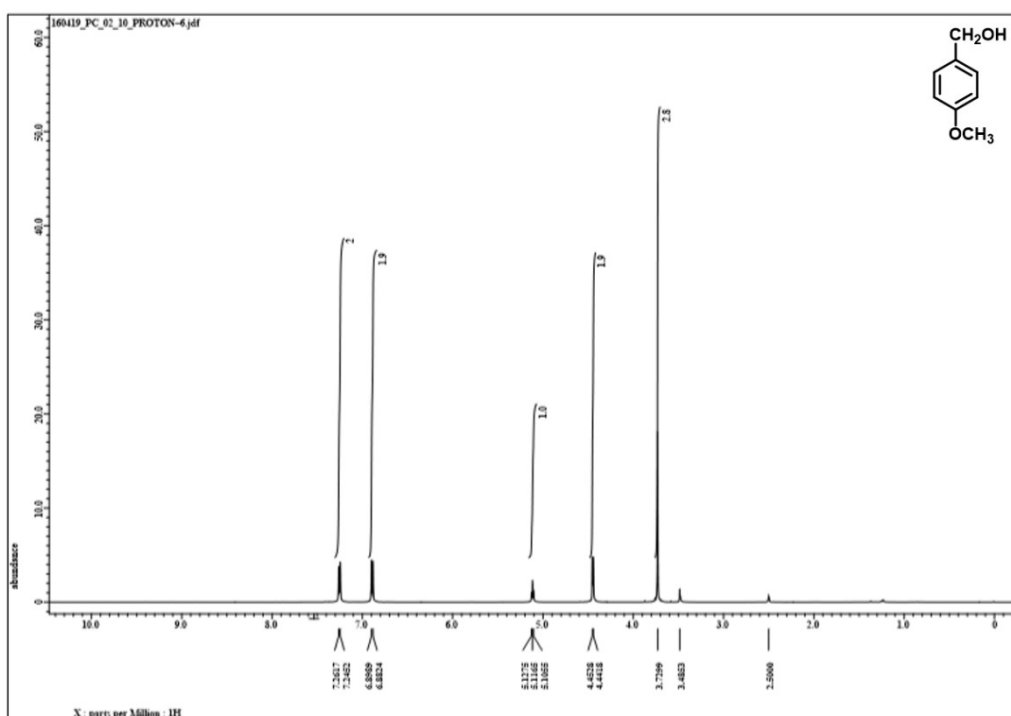
**<sup>1</sup>H-NMR spectra of (4-(dimethylamino)phenyl)methanol (3e) [500 MHz, DMSO-d<sub>6</sub>]**



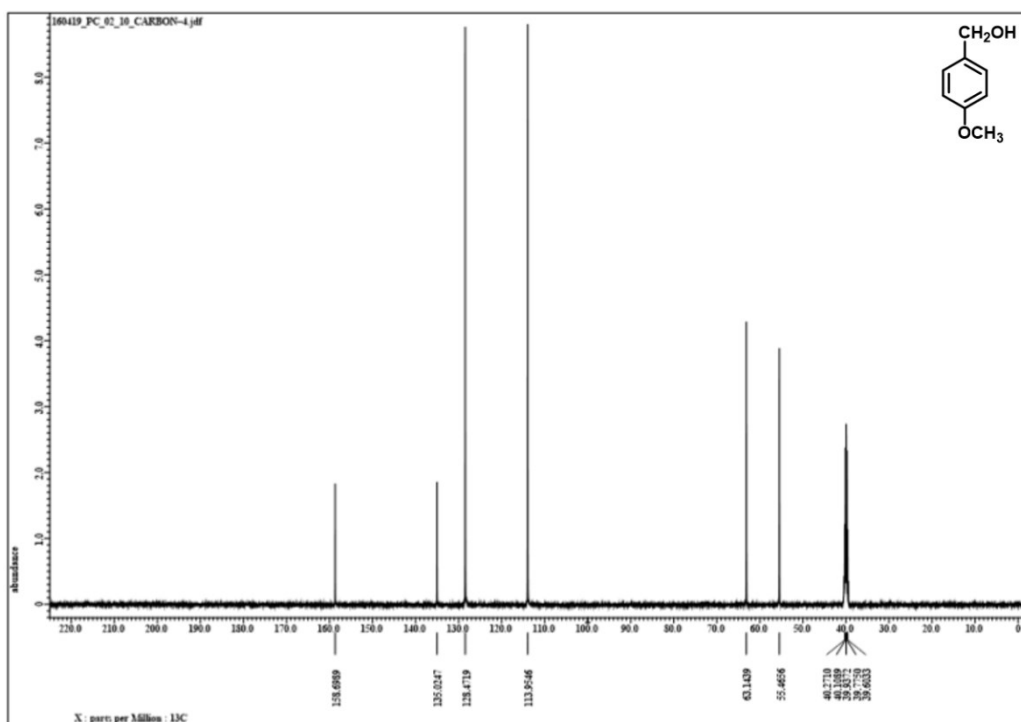
**<sup>13</sup>C-NMR spectra of (4-(dimethylamino)phenyl)methanol (3e) [125 MHz, DMSO-d<sub>6</sub>]**



**<sup>1</sup>H-NMR spectra of (4-methoxyphenyl)methanol (3f) [500 MHz, DMSO-d<sub>6</sub>]**

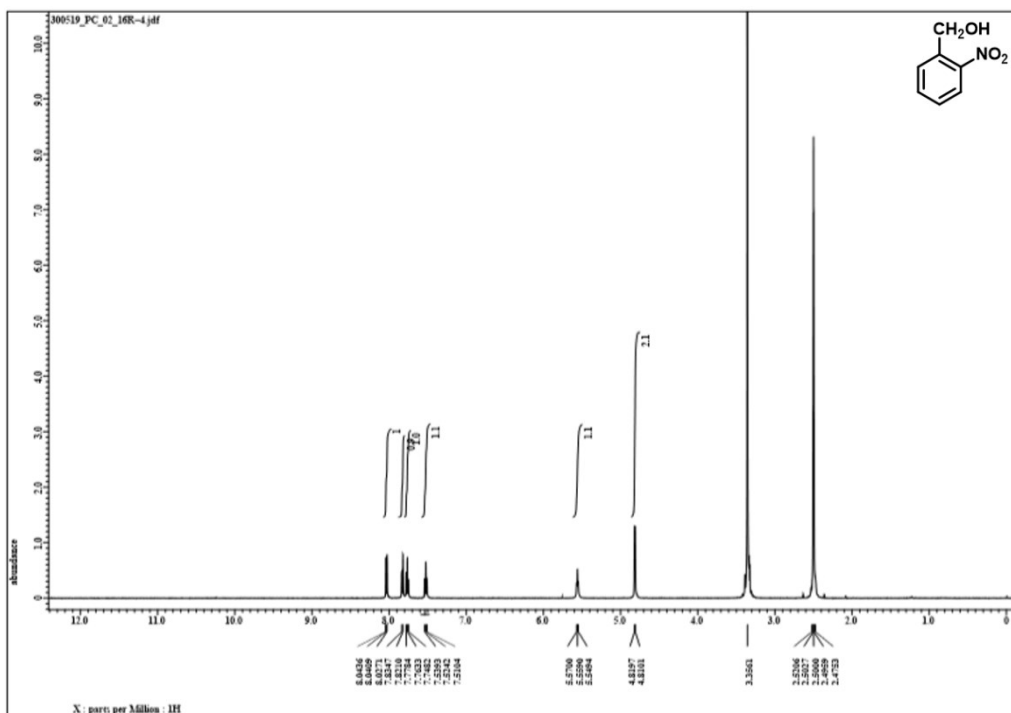


**<sup>13</sup>C-NMR spectra of (4-methoxyphenyl)methanol (3f) [125 MHz, DMSO-d<sub>6</sub>]**

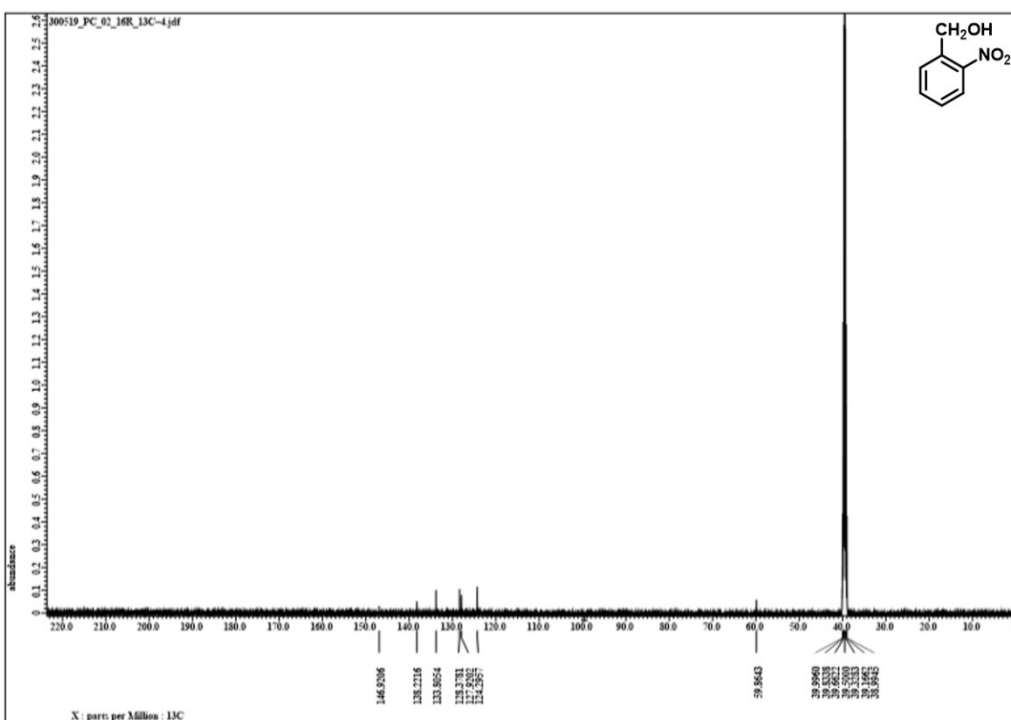




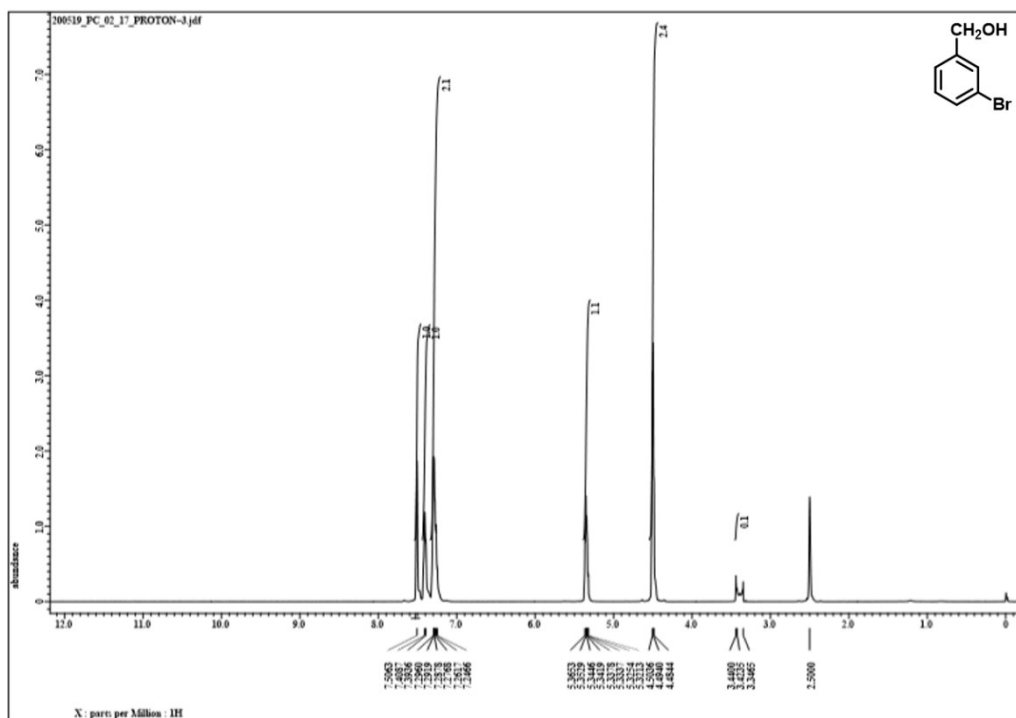
<sup>1</sup>H-NMR spectra of (2-nitrophenyl)methanol (3h) [500 MHz, DMSO-d<sub>6</sub>]



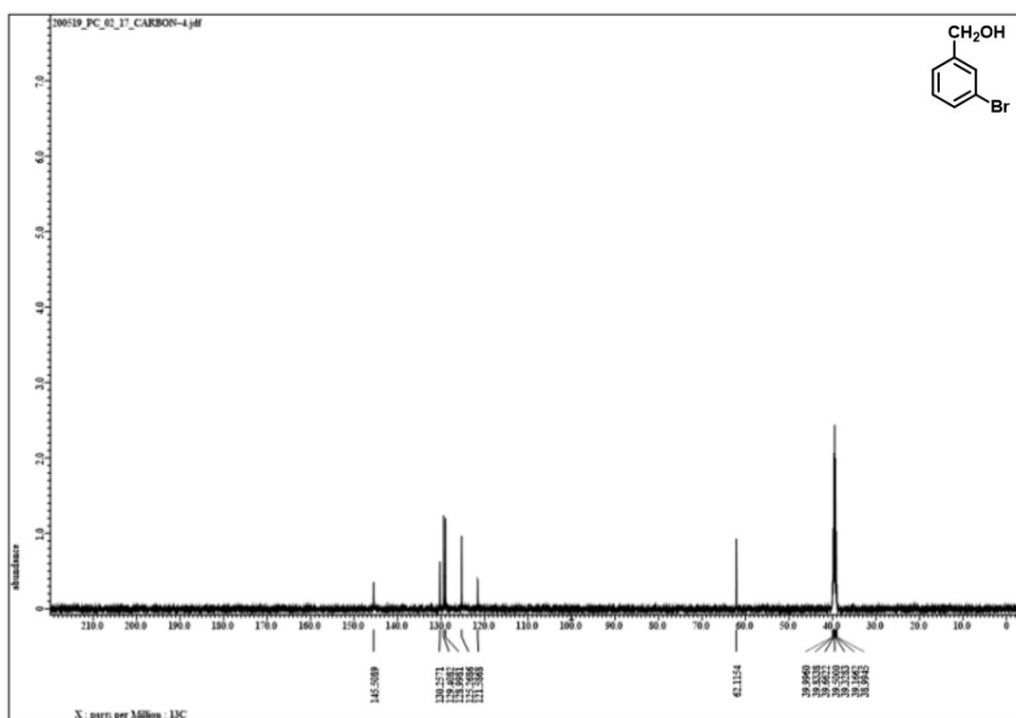
<sup>13</sup>C-NMR spectra of (2-nitrophenyl)methanol (3h) [125 MHz, DMSO-d<sub>6</sub>]



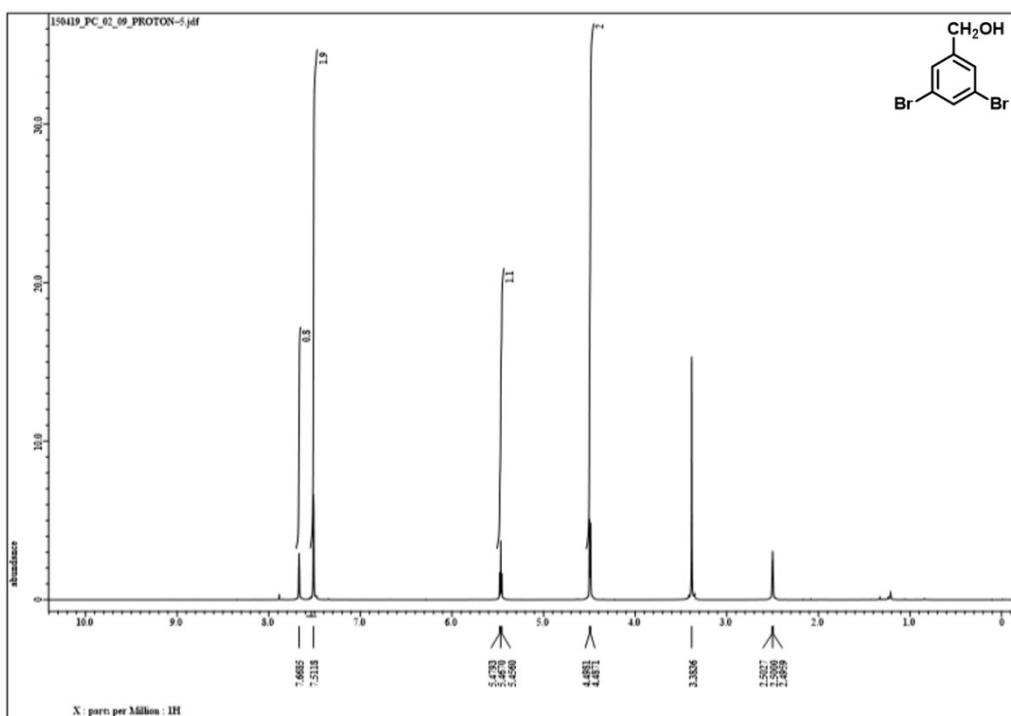
### <sup>1</sup>H-NMR spectra of (3-bromophenyl)methanol (3i) [500 MHz, DMSO-d<sub>6</sub>]



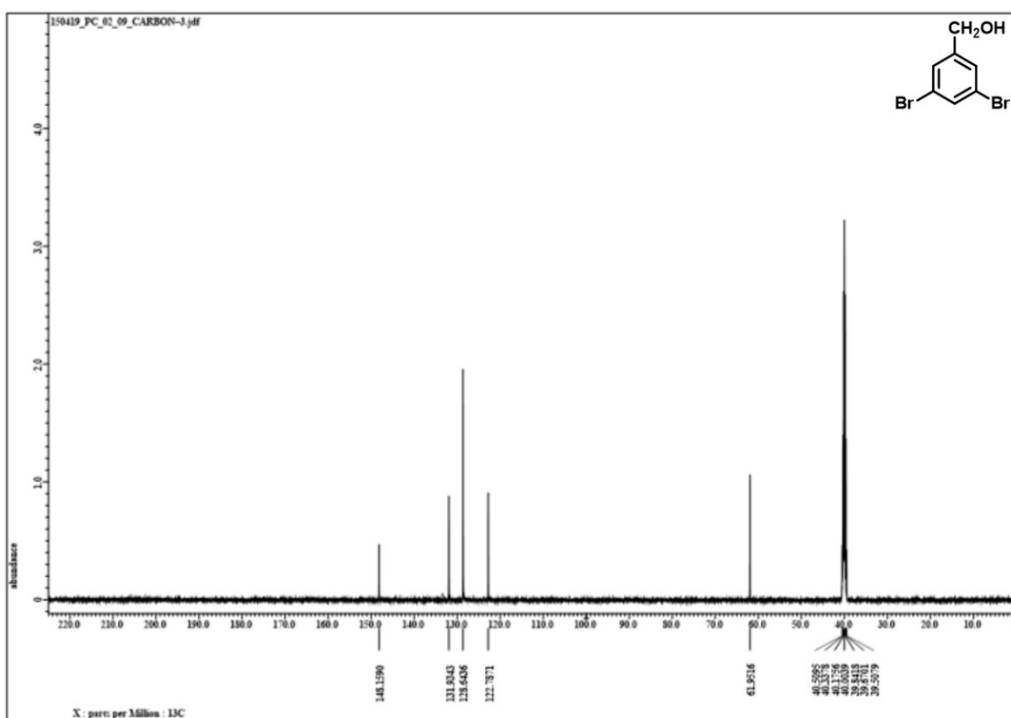
### <sup>13</sup>C-NMR spectra of (3-bromophenyl)methanol (3i) [125 MHz, DMSO-d<sub>6</sub>]



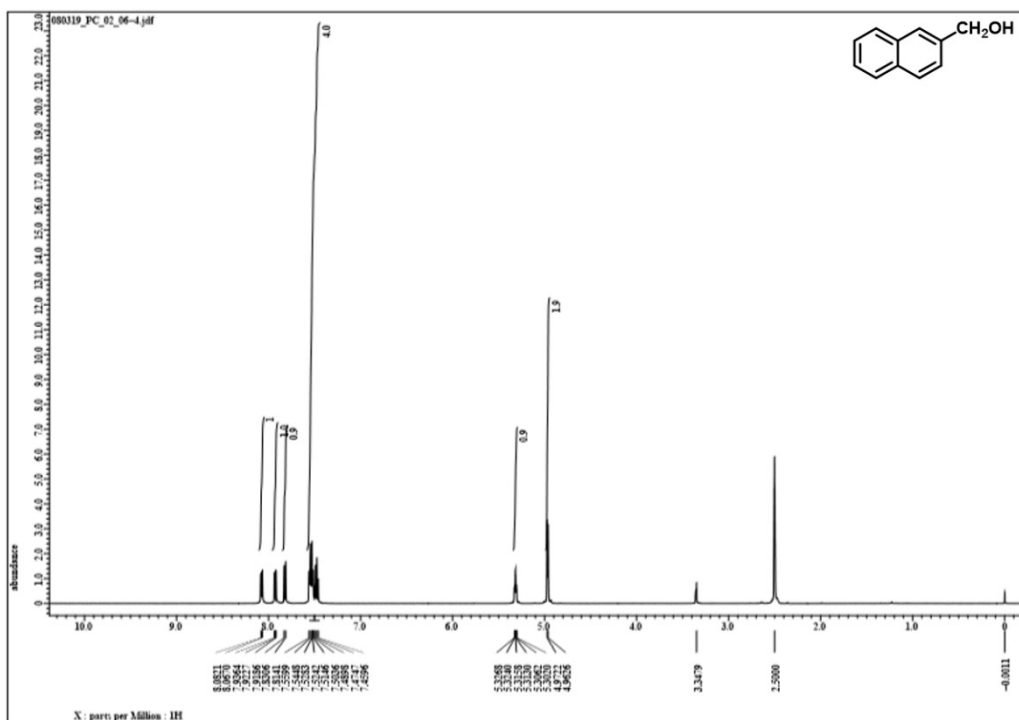
**<sup>1</sup>H-NMR spectra of (3,5-dibromophenyl)methanol (3j) [500 MHz, DMSO-d<sub>6</sub>]**



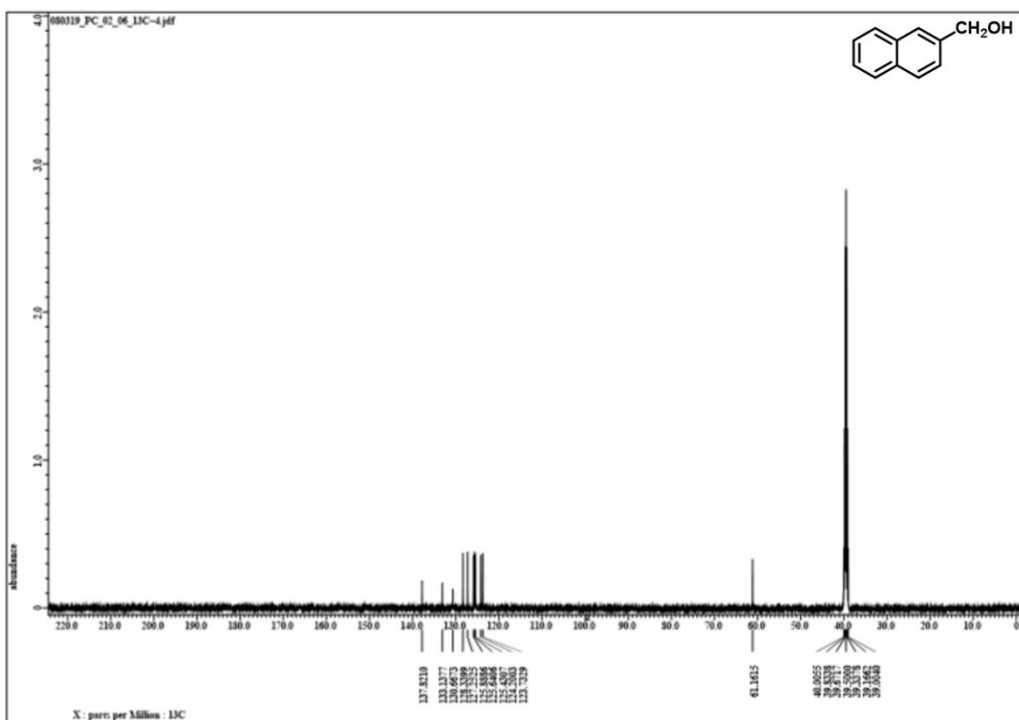
**<sup>13</sup>C-NMR spectra of (3,5-dibromophenyl)methanol (3j) [125 MHz, DMSO-d<sub>6</sub>]**



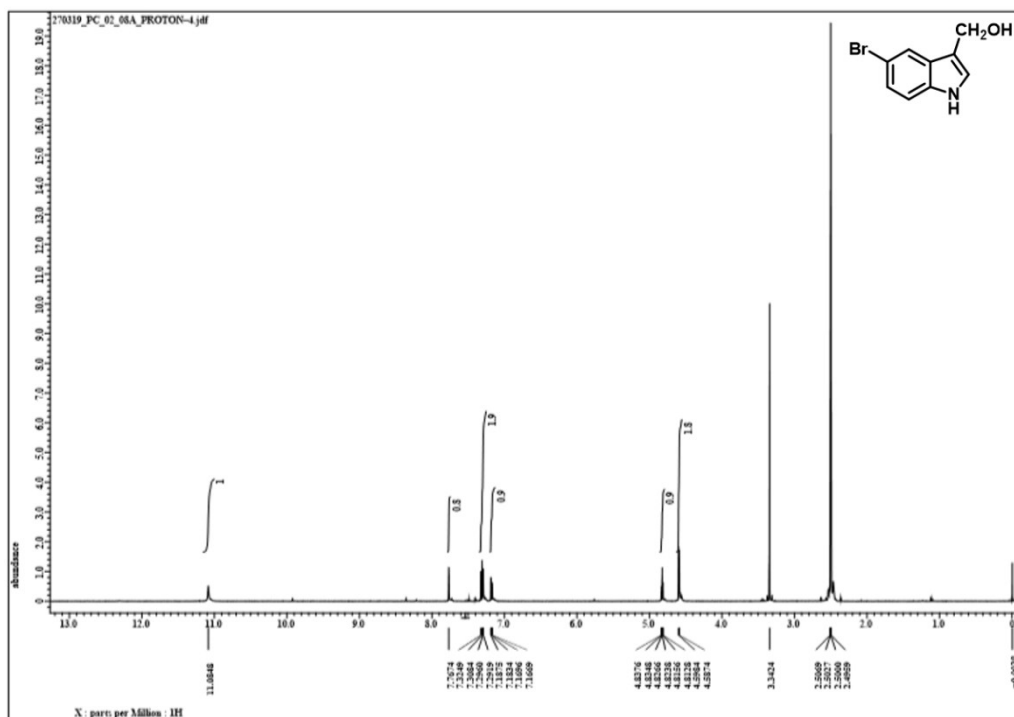
**<sup>1</sup>H-NMR spectra of Naphthalen-2-ylmethanol (3k) [500 MHz, DMSO-d<sub>6</sub>]**



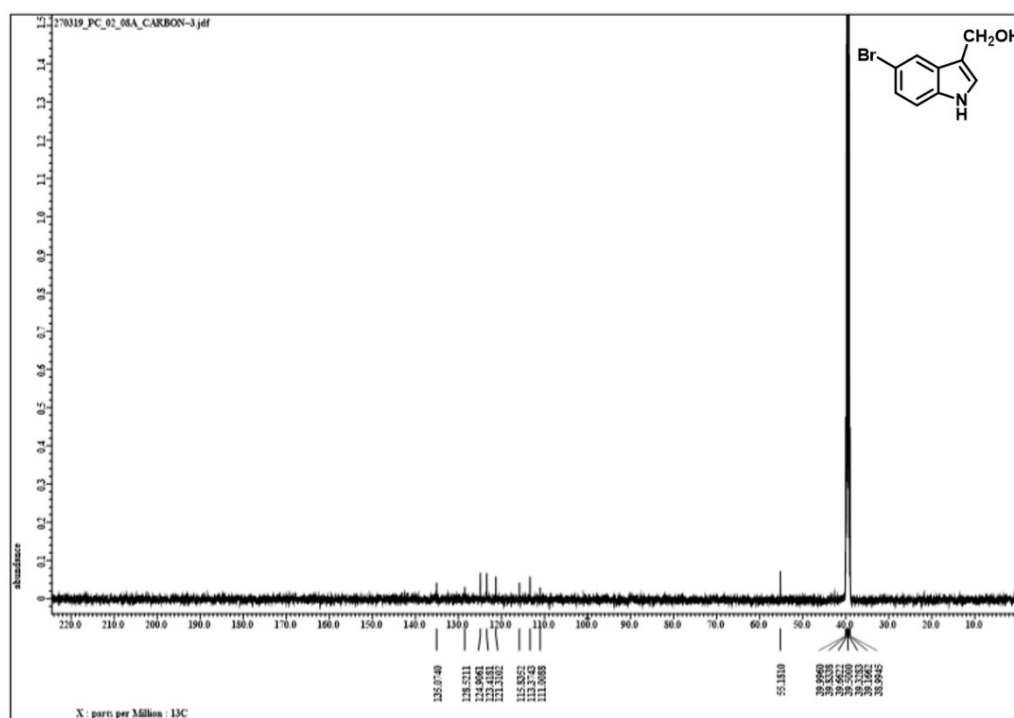
**<sup>13</sup>C-NMR spectra of Naphthalen-2-ylmethanol (3k) [125 MHz, DMSO-d<sub>6</sub>]**



**<sup>1</sup>H-NMR spectra of (5-bromo-1H-indol-3-yl)methanol (3I) [500 MHz, DMSO-d<sub>6</sub>]**

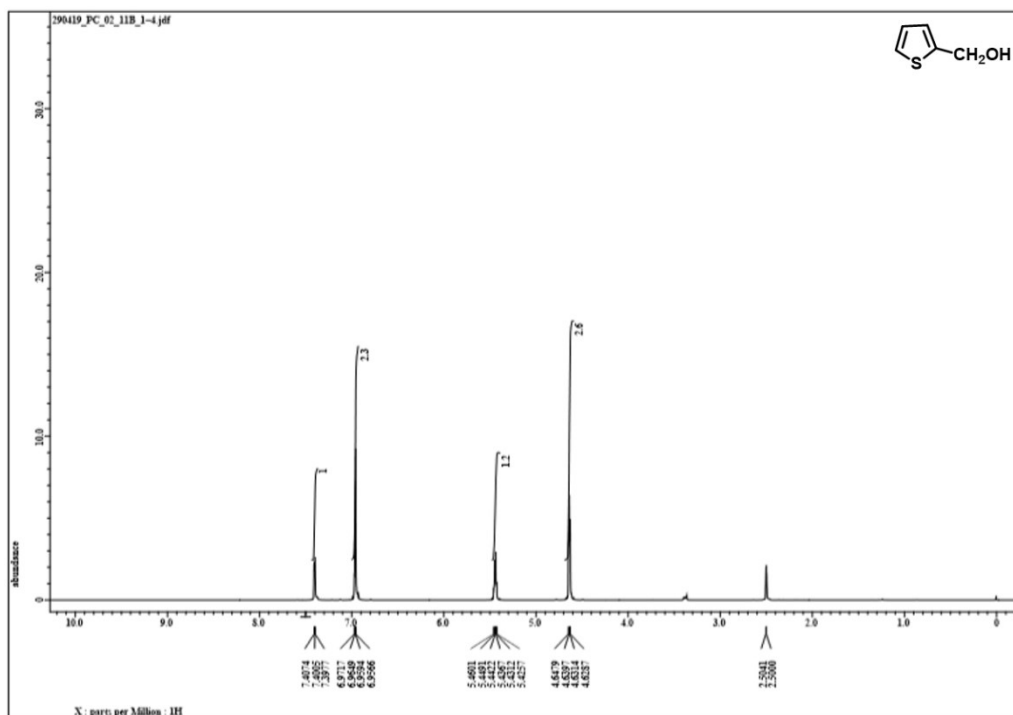


**<sup>13</sup>C-NMR spectra of (5-bromo-1H-indol-3-yl)methanol (3I) [125 MHz, DMSO-d<sub>6</sub>]**

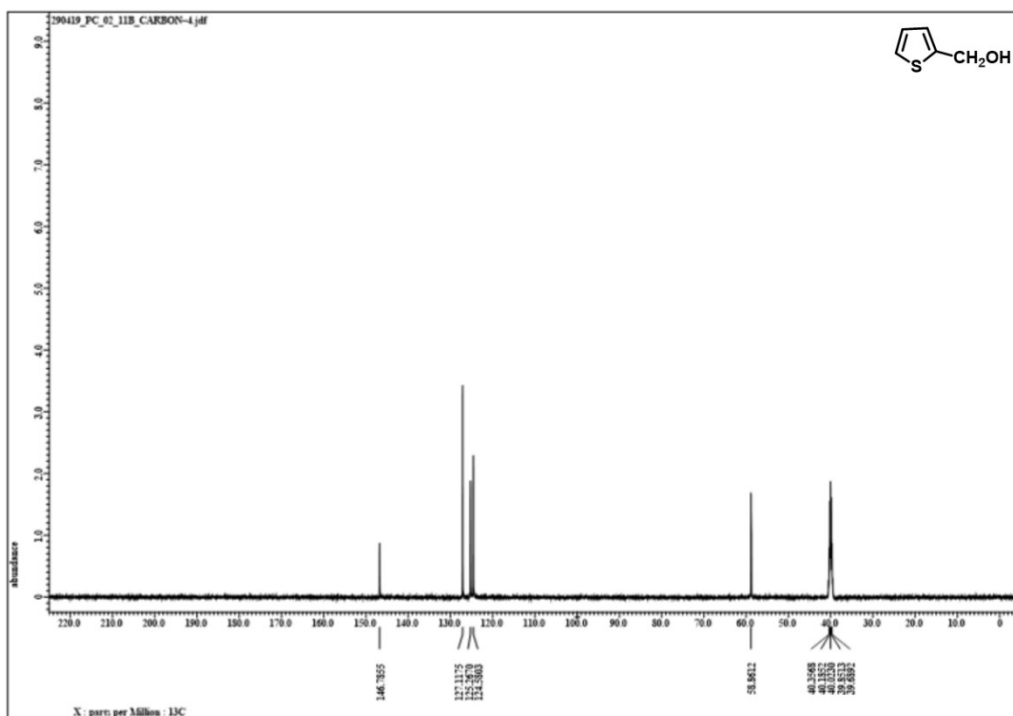




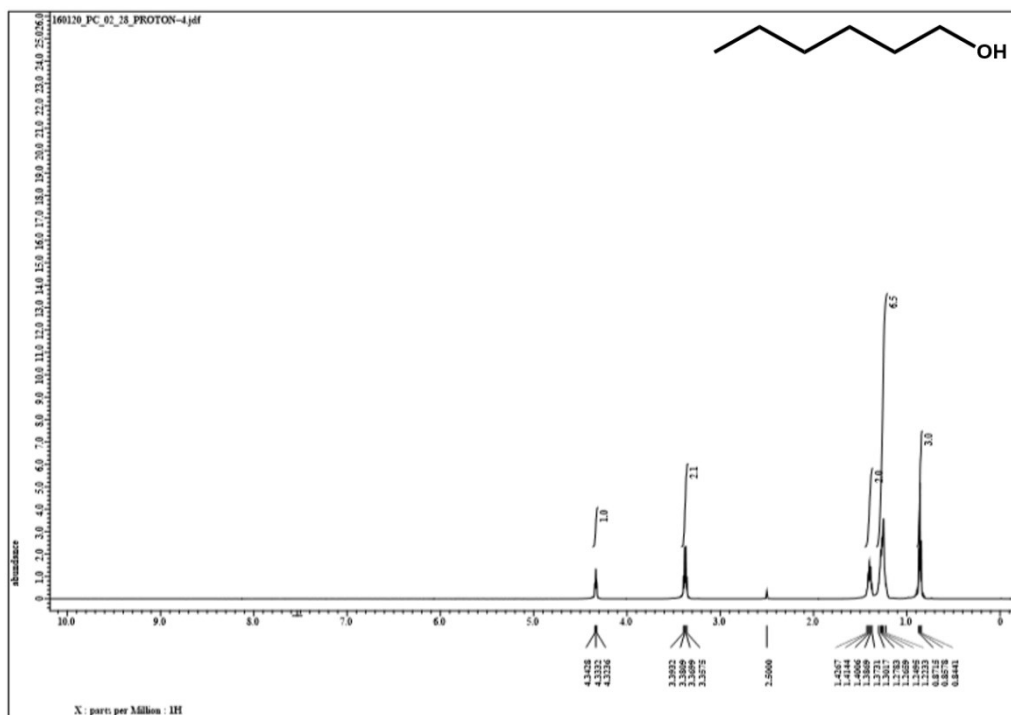
### <sup>1</sup>H-NMR spectra of Thiophen-2-ylmethanol (3m) [500 MHz, DMSO-d<sub>6</sub>]



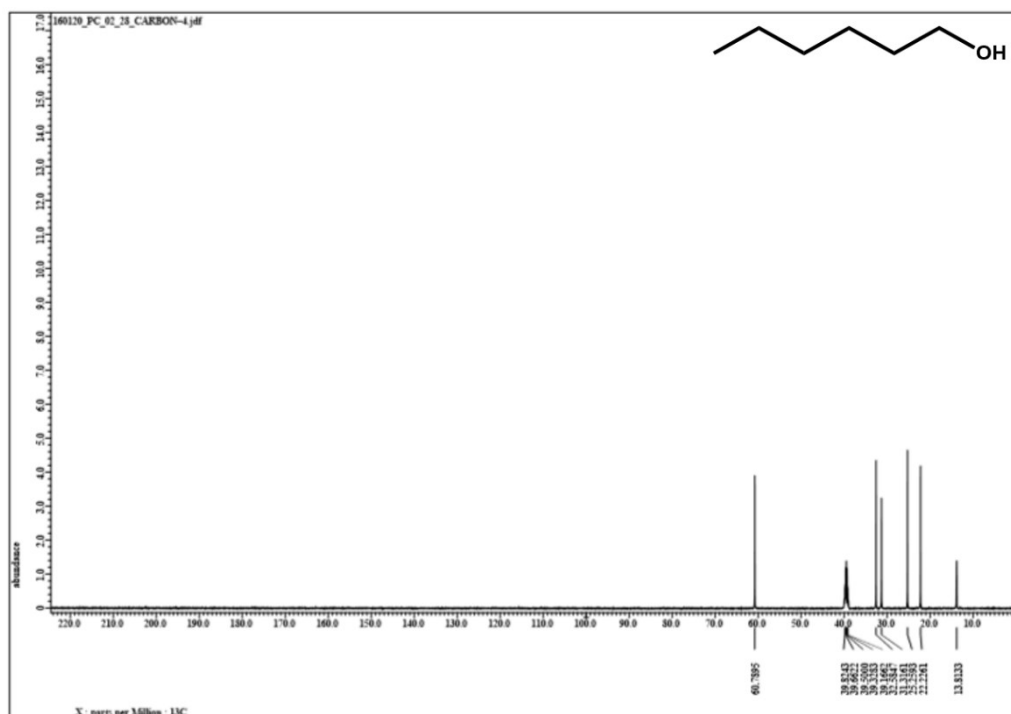
### <sup>13</sup>C-NMR spectra of Thiophen-2-ylmethanol (3m) [125 MHz, DMSO-d<sub>6</sub>]



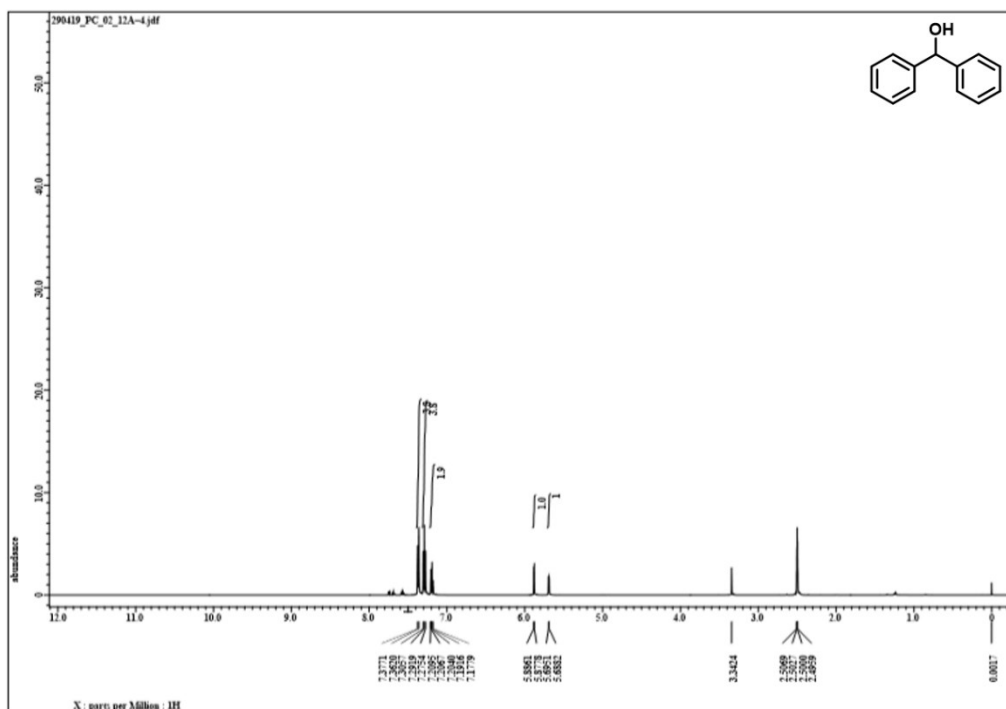
### <sup>1</sup>H-NMR spectra of Hexan-1-ol (3n) [500 MHz, DMSO-d<sub>6</sub>]



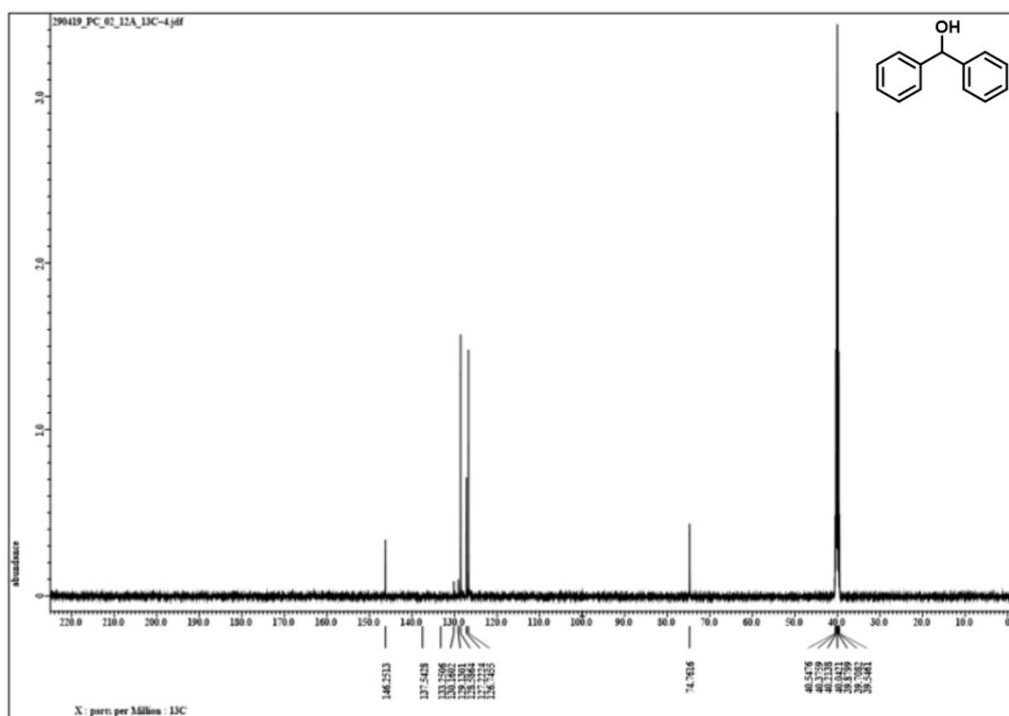
### <sup>13</sup>C-NMR spectra of Hexan-1-ol (3n) [125 MHz, DMSO-d<sub>6</sub>]



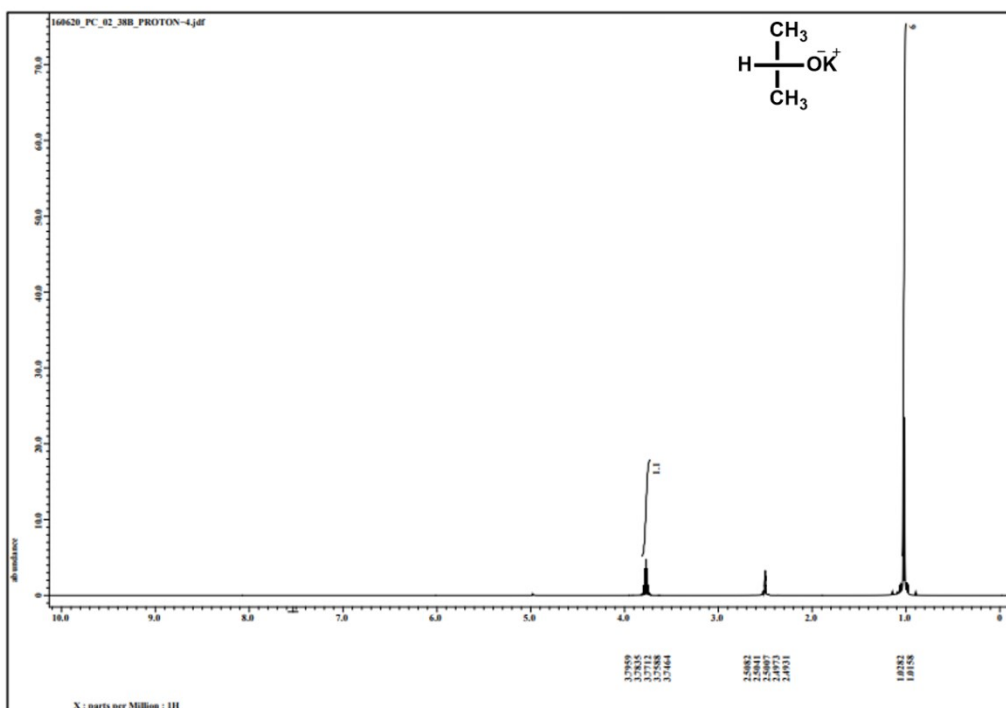
### <sup>1</sup>H-NMR spectra of Diphenylmethanol (3o) [500 MHz, DMSO-d<sub>6</sub>]



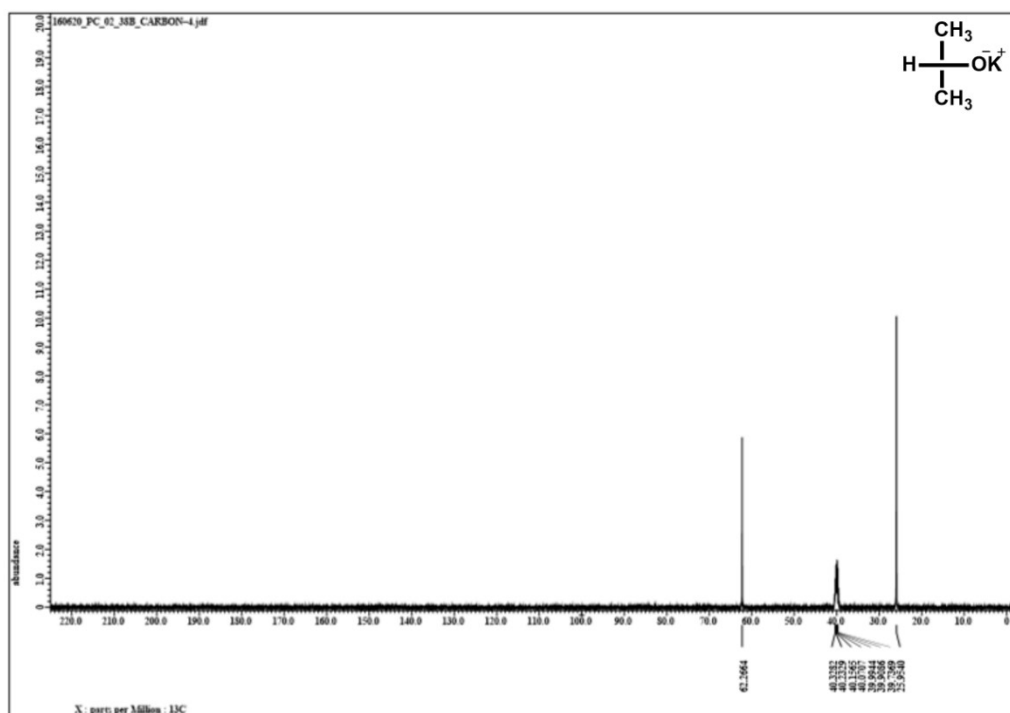
### <sup>13</sup>C-NMR spectra of Diphenylmethanol (3o) [125 MHz, DMSO-d<sub>6</sub>]



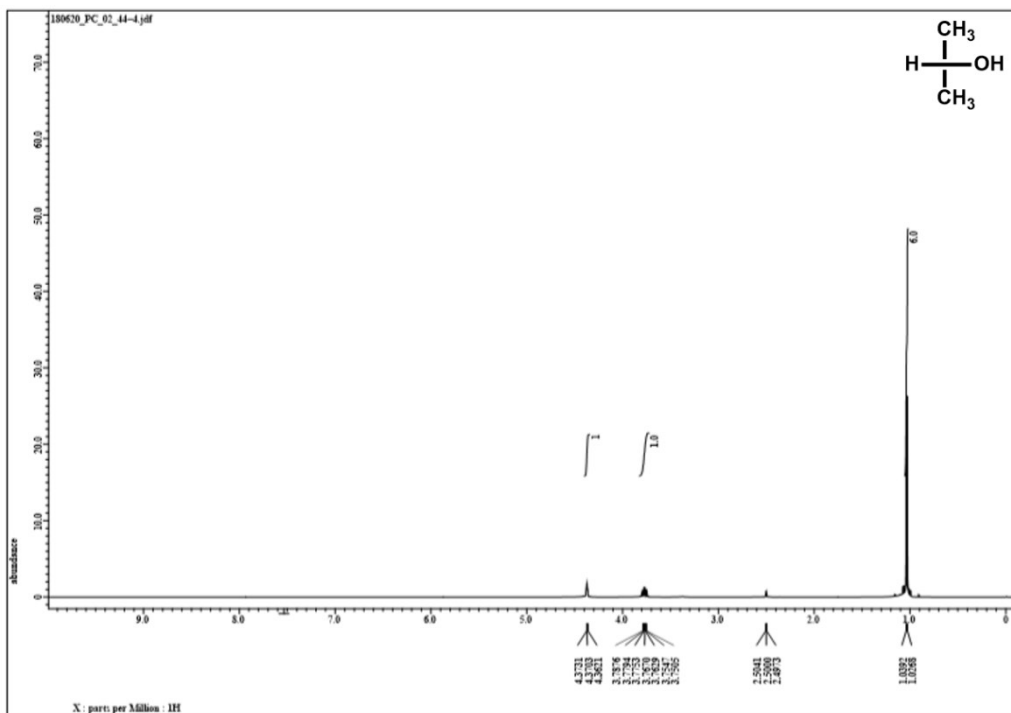
**<sup>1</sup>H NMR spectra of crude reaction mixture (S5 (i) ) [500 MHz, DMSO-d<sub>6</sub>]**



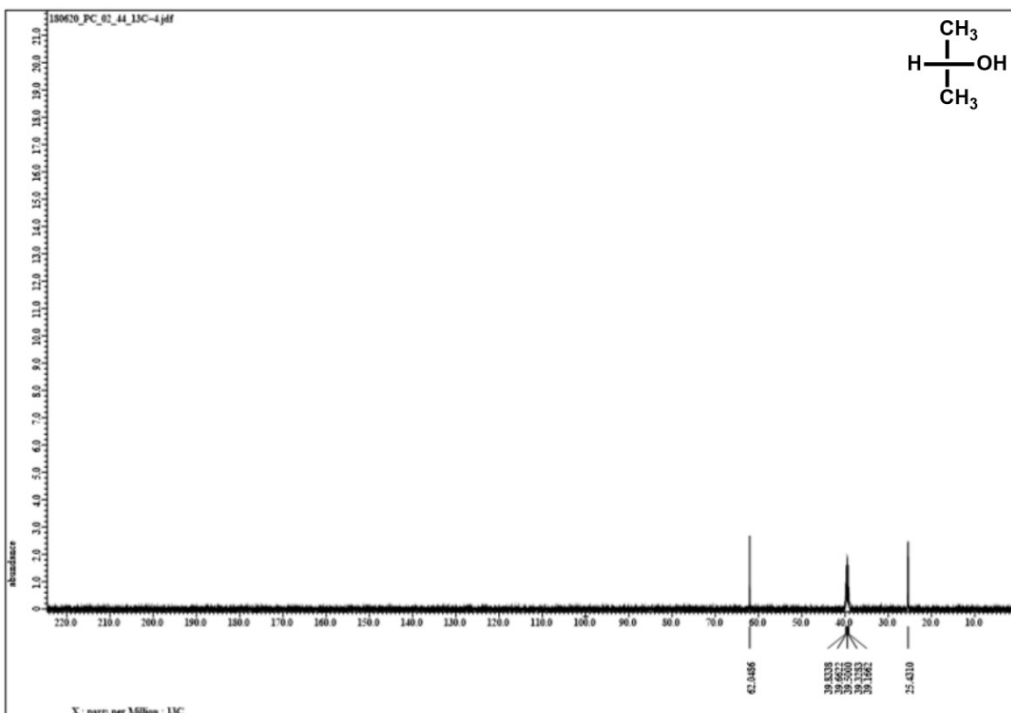
**<sup>13</sup>C NMR spectra of crude reaction mixture (S5 (i) ) [125 MHz, DMSO-d<sub>6</sub>]**



**<sup>1</sup>H NMR spectra of reaction mixture extracted with CHCl<sub>3</sub>/ H<sub>2</sub>O with (S5 (i))**  
**[500 MHz, DMSO-d<sub>6</sub>]**

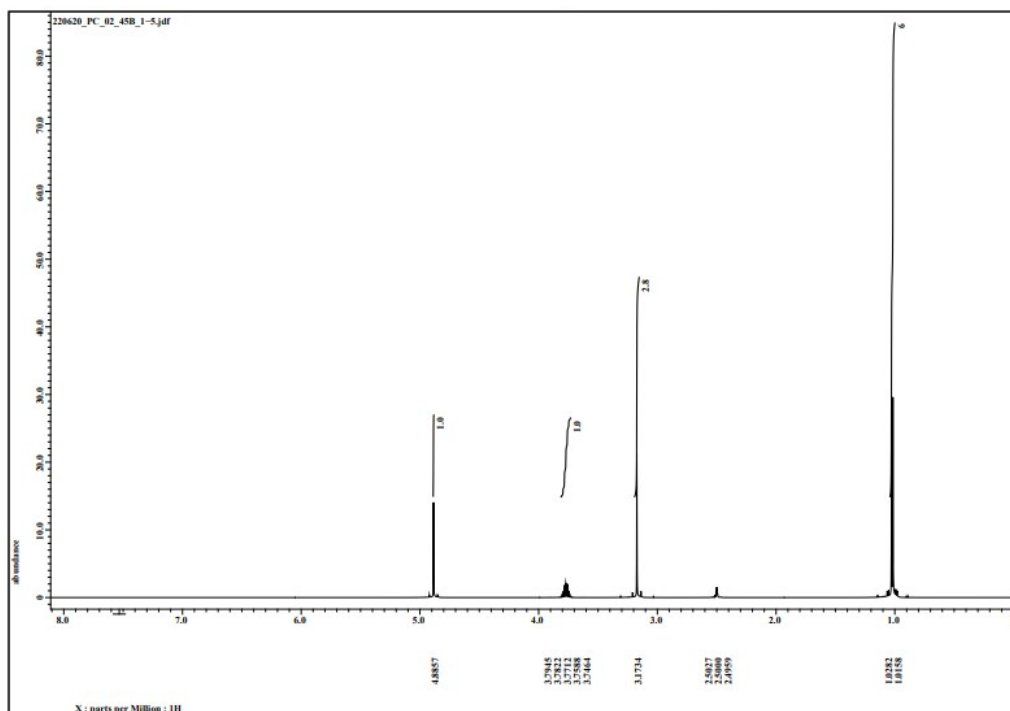


**<sup>13</sup>C NMR spectra of reaction mixture extracted with CHCl<sub>3</sub>/ H<sub>2</sub>O (S5 (i))**  
**[125 MHz, DMSO-d<sub>6</sub>]**



**<sup>1</sup>H NMR spectra of reaction mixture with O-GCN catalyst and formaldehyde (S5 (ii))**

**[500 MHz, DMSO-d<sub>6</sub>]**



**<sup>13</sup>C NMR spectra of reaction mixture with O-GCN catalyst and formaldehyde (S5 (ii))**

**[125 MHz, DMSO-d<sub>6</sub>]**

