Supporting Information for:

"Chitosan Supported Ionic Liquid: A Recyclable Wet and Dry Catalyst for Direct Conversion of Aldehydes into Nitriles and Amides under Mild Conditions"

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Preparation of the CSMIL

At first, N-methyl imidazole (0.16 mol, 10 mL, 25 °C) was dropped very slowly into a mixture of 1,2- dichloroethane (0.32 mol, 25 mL, 25 °C) and acetone (25 mL) in a 100 mL three-necked flask. The reactants were magnetically stirred at reflux for 24 h. After filteration, the solid product was washed by acetone for four times and then dried under vacuum at 60 °C for 12 h (yeild: 80%, 23gr). Secondly, CS (4 g), 1-(2-chloroethyl)-3-methyl imidazolium chloride solution (10 g of 60 wt%) and isopropanol (30 mL) were added into a 100 mL three-necked flask. The reactants were magnetically stirred at 75 °C for 24 h. When the reaction was complete, the product was precipitated by the addition of ethanol into the reaction mixture, followed by filtration. Then, it was washed with anhydrous ethanol, and dried under vacuum at 80 °C for 24 h using phosphoric anhydride as a desiccant (yeild: 83%, 5 gr). The loading of ionic liquid in chitosan supported ionic liquid (CSIL) was 2.9 mmolg^{-1} determined by N and Cl elemental analysis with Elemental Analyzer. After preparation the CSIL, it was mixed with equimolar amounts of anhydrous $FeCl_3$ in the presence of anhydrouse ethanol at 30°C for 3 h, as a result a dark brown solid was obtained. The obtained catalyst was washed with small portions anhydrous ethanol, and dried under vacuum at 60 °C for 24h. The obtained catalyst should be stored at ambient and dry conditions.

Characterization of CSMIL

The CSMIL catalyst was characterized using some different microscopic and spectroscopic techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), FT-IR and Raman spectroscopies. To characterize the functionalized chitosan ionic liquid, first of all, we used the FT-IR spectrum. The FT-IR spectrum of native chitosan and functionalized chitosan ionic liquid sample is shown in Figure 1.

The results show that the band at about 3200–3500 cm^{-1}was attributed to the OH and NH stretching vibrations, and the band at about 1535-1658 cm^{-1} are related to the bending vibration absorption peak of N–H at about 1530-1660 cm^{-1}. Two absorption bands at ~897 and 1156 cm^{-1} are related to the chitosan structure. But, after functionalization, the bending vibration absorption peak of N–H at about 1530-1660 cm^{-1} was disappeared, which were assigned to the secondary amine. There are peaks at about 1145 cm^{-1}, which were assigned to the characteristic absorption of $N–CH_2$ in functionalized chitosan. There are three main peaks (CH_2: 1405-1465, 880-900, C=N stretching vibrations: 2215-2240, C=C stretching vibrations: 1585-1625) are related to imidazolium ionic liquid. In this spectra the two bands appearing at ~394 and 145 cm^{-1} can be assigned with certainty to the two predicted (Fe-Cl) bands. Previous works have shown that the iron-chloride stretches occur above 300 cm^{-1} and that the iron-chloride bending modes occur below 150 cm^{-1}.

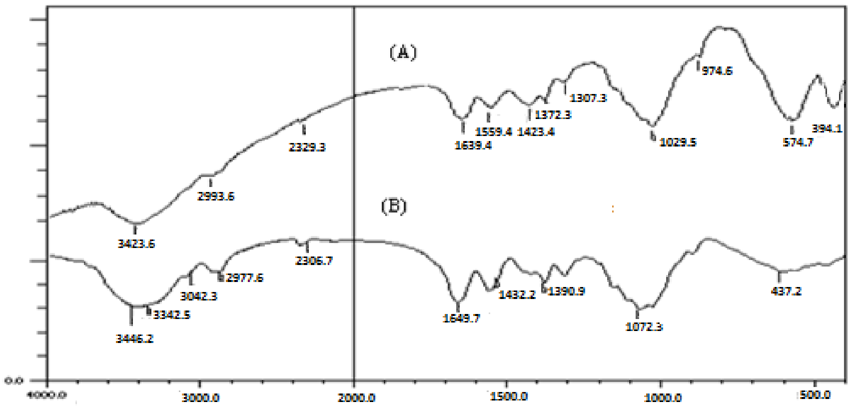


Figure 1. Comparison between FT-IR spectra of chitosan supported ionic liquid nanoparticles (A) and pure chitosan (B).

In this study, Dynamic light scattering (DLS) was used for particle size analyzing of the catalyst. The average diameter of CSMIL is evaluated to be about 80 nm which is shown in Figure 2. The histogram was proposed according to the results obtained from the SEM images. According to the SEM image (Figure 3, 4), the morphology of CSMIL is regularly spherical and arranged in an approximately good orderly manner with nano sized particles and its TEM pictures showed the average size of the particles entrapped in chitosan framework to be around 80–85 nm (Figure 5). Comparing the TEM of CS with CSMIL has shown an increase in the average particle size of chitosan after IL grafting.

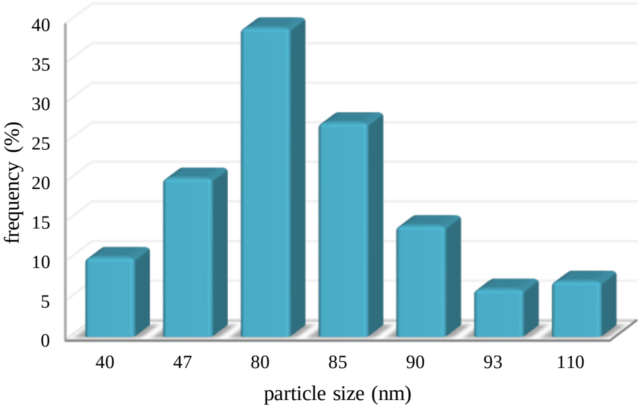


Figure 2. Histogram representing the size distribution of CSMIL.

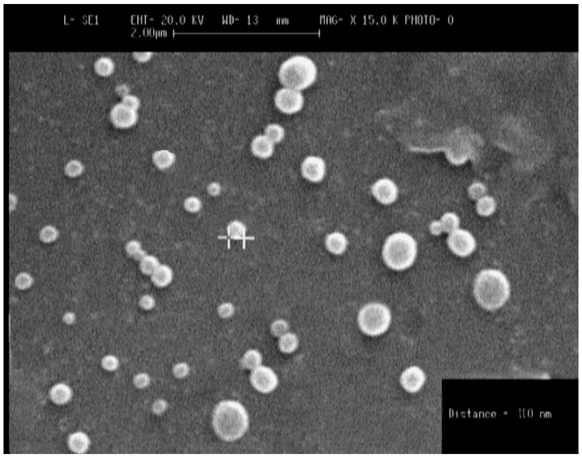


Figure 3. SEM image of CSMIL.

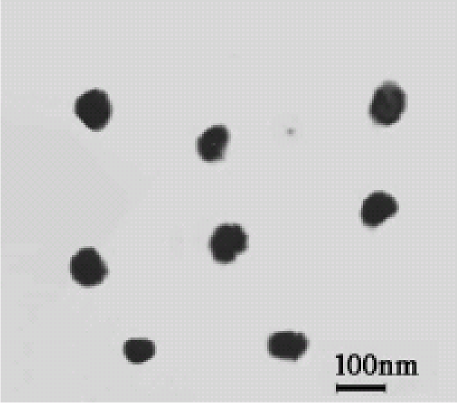


Figure 4. TEM image of chitosan.

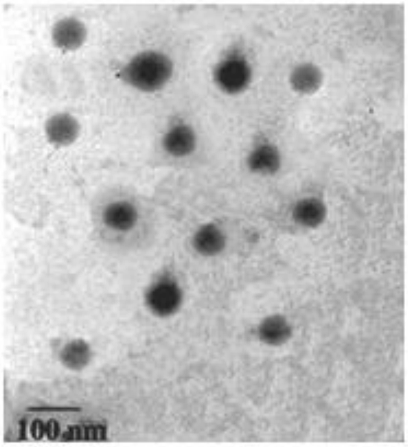


Figure 5. TEM image of CSMIL.

The field dependence of magnetic moment of catalyst was measured in the range of -10000 to 10000 Oe, and it showed a paramagnetic linear response similar to iron(III) chloride with 1-butyl-3-methylimidazolium chloride (Figure 6).

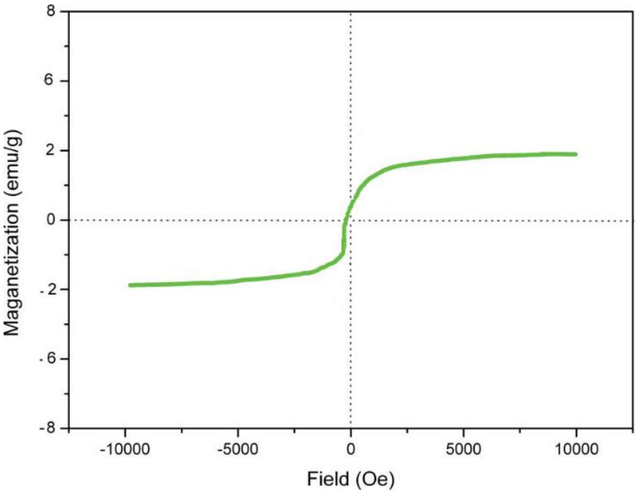


Figure 6. Field dependence of magnetic susceptibility of CSMIL catalyst at room temprature

Vibrational Raman spectra of CSMIL in the range 100–500 cm^{-1} show the previously observed symmetric Fe–Cl bond stretch vibrations of [$FeCl_4$] at ~113 and 331 cm^{-1}. This assignment provides further verification of the presence of the [$FeCl_4$] anion.

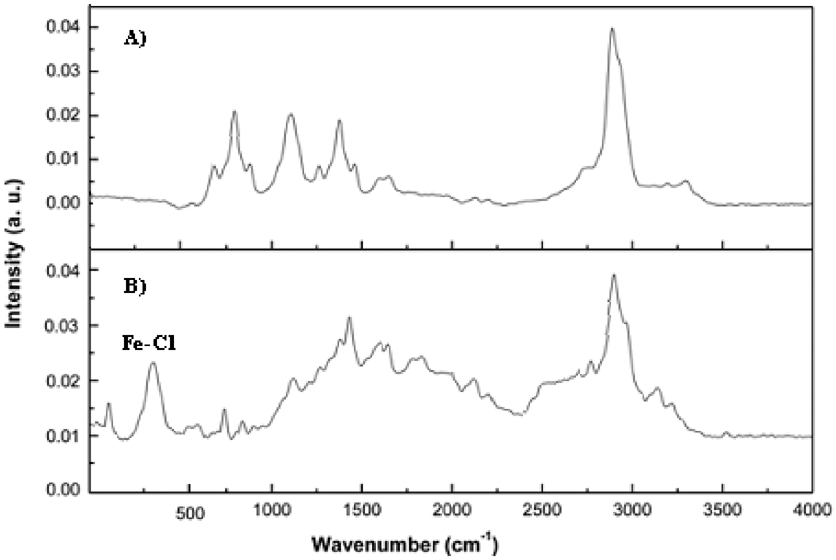


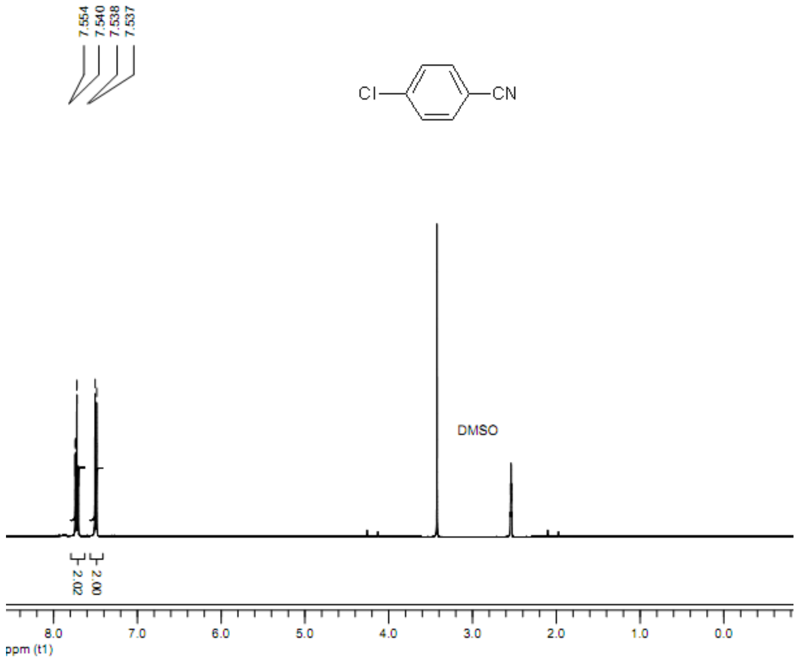
Figure 7. Vibrational Raman spectra of CS (A) and CSMIL (B)

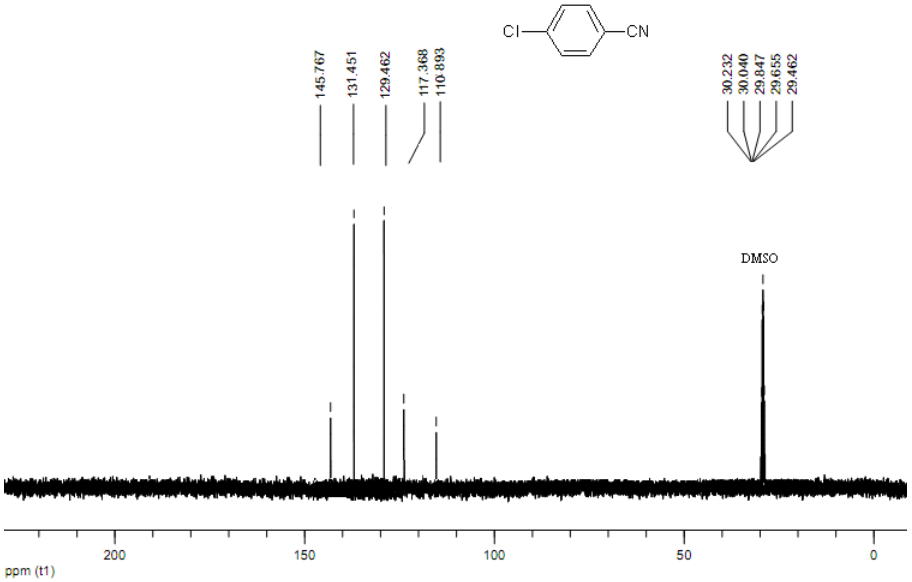
Raman showed structural change of chitosan after supporting ionic liquid and converting to CSMIL that all functional groups identified are presented inTable 1.

Table 1. Raman excitation frequencies for functional groups present in catalyst

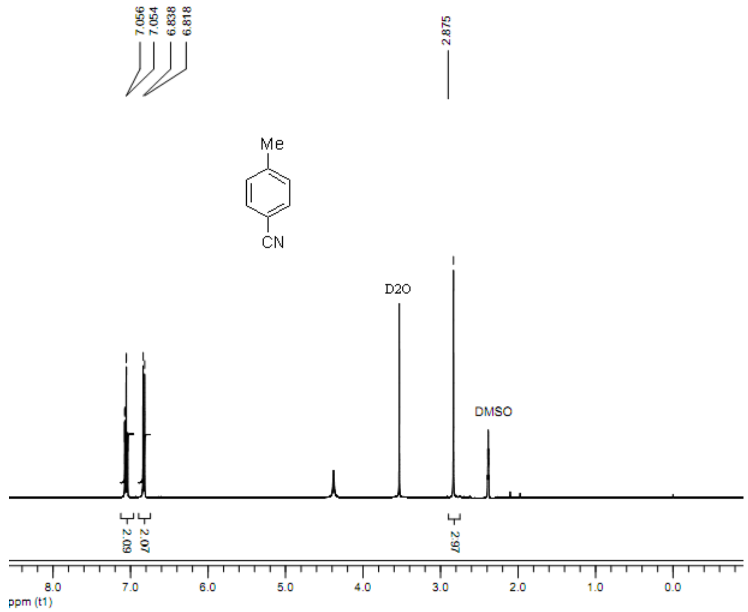
Group	Char. Freq. (cm^{-1})	Char. Freq. (cm^{-1})
1	Methylene: C-C, C-H	2850-2960
2	Amine: NH_2 (primary)	Pair of peaks, 3350 and 3270
3	Amine: NH (secondary)	3350-3310
4	Alchohol: C-OH	3600-3200
5	Ether: C-O-C	1100
6	N-C stretch vibration	791
7	Fe–Cl stretch	331, 113

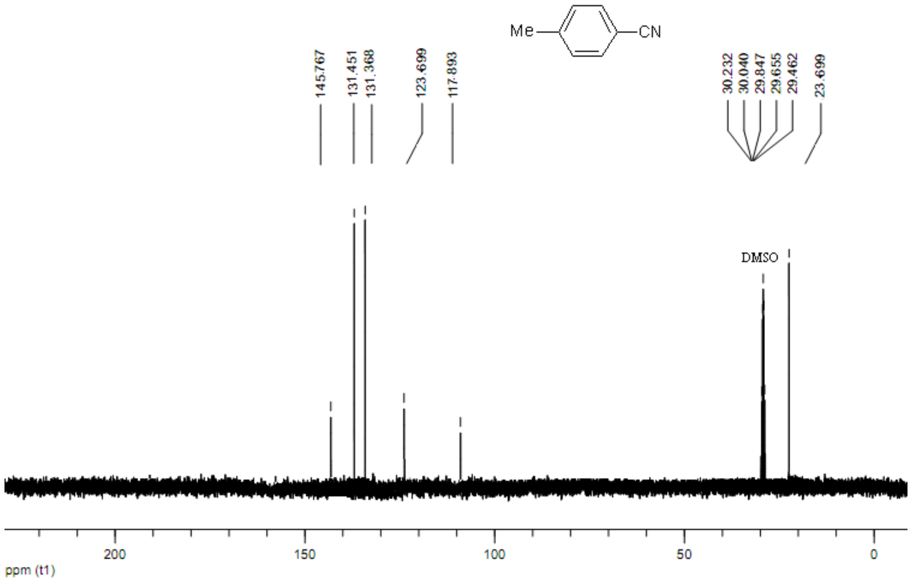
1)^{1}H NMR and ^{13}C NMR of compound 3b



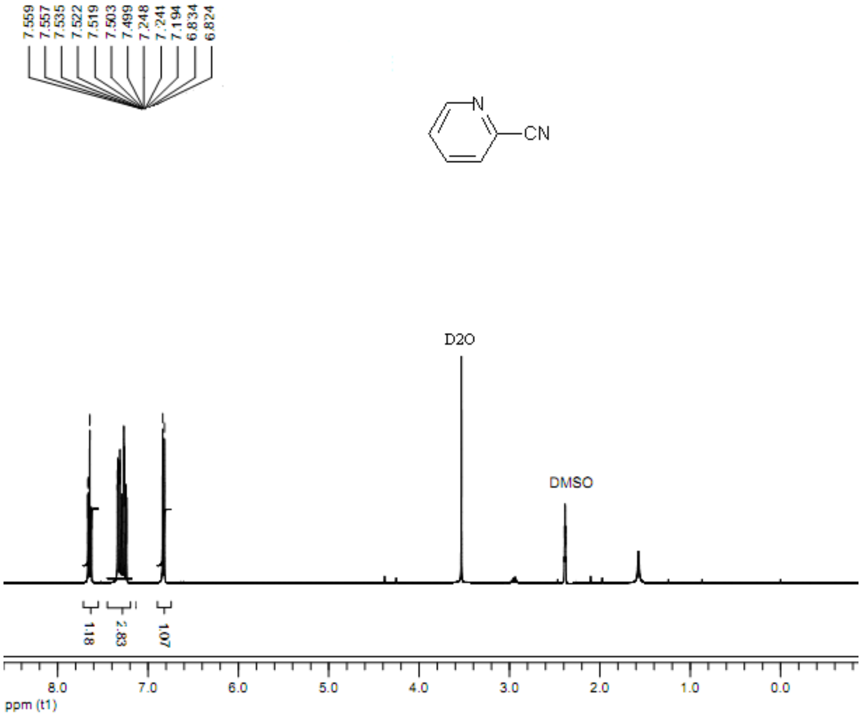


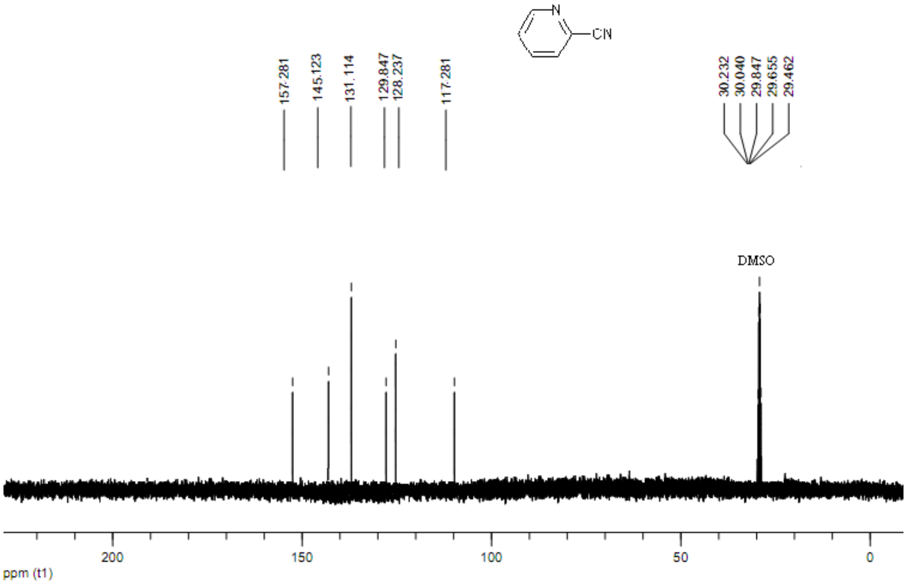
2)^{1}H NMR and ^{13}C NMR of compound 3d



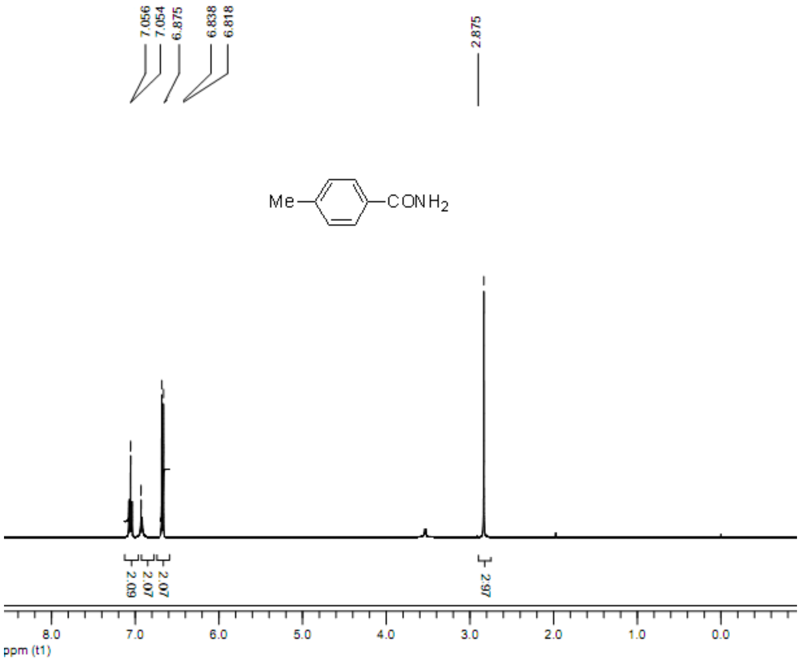


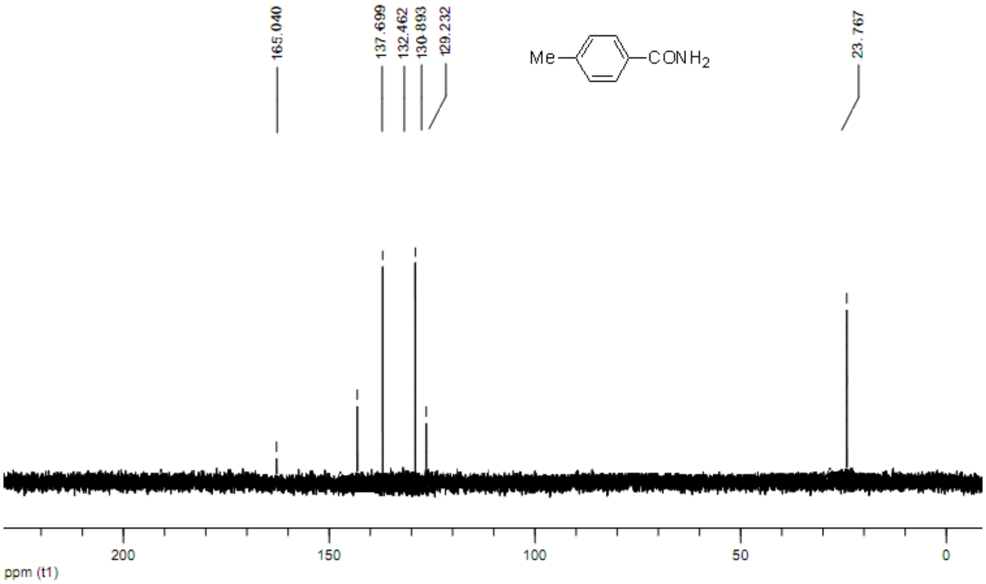
3)^{1}H NMR and ^{13}C NMR of compound 3k





4)1H NMR and 13C NMR of compound 4d





5)^{1}H NMR and ^{13}C NMR of compound 4g