

Synthesis of a New Lariat Diaza Crown Ether Compounds

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ABSTRACT

New of lariat ether compounds were synthesized as cationic and molecular acceptors. Lariat ethers **7a** to **7b** were prepared by reaction of macrocyclic diamide **5** and phenols in the presence of paraformaldehyde by refluxed in dry toluene. The structures were characterized by FT-IR, ¹HNMR, ¹³CNMR and Mass spectrometry analyses.

KEYWORDS: Macrocyclic diamides, Mannich condensation, Aza-Crown ether, Liquid membrane transport

1. INTRODUCTION

Molecular devices and machines are chemical systems and therefore operate by means of chemical reactions that, broadly speaking, imply both electronic and nuclear rearrangements. In some cases, however, the function performed is essentially based on the transfer of electrons or electronic energy without substantial nuclear rearrangements. In other cases, the operation is based on the occurrence of more or less extensive nuclear displacements caused by electronic rearrangements. In principle, molecular machines can be designed starting from several kinds of molecular and supramolecular systems. [1]. Macrocyclic diamides and lariat ether compounds have wide applications in chemistry, medical, environmental, nano technology, biology, metal separation and transport, industrial and atomic energy uses. Crown ethers with functional donor groups in the side chain (lariat crown ethers) form, in many cases, stronger complexes with metal cations than their unsubstituted analogs and show highly selective complex formation. [2].

The progress of human civilization has always been related to the construction of novel devices and machines. Depending on their use, devices and machines can be very big or very small. The general trend in our 'knowledge age' is that of reducing the size and weight of the components employed as much as possible, particularly in the field of information technology. [3].

In the following years, supramolecular chemistry grew very rapidly and it became clear that the supramolecular bottom-up approach opens virtually unlimited possibilities concerning the design and construction of artificial molecular devices and machines. The function that could be performed by molecular devices and machines are various. They may be related to signal transfer (in the form of energy, electrons, protons, etc.), information processing (e.g. by molecular-level logic gates), energy conversion (e.g. conversion of light into an electrochemical potential or a chemical fuel), and a wide range of mechanical-like aspects (e.g. transportation of a cargo through a membrane). In an attempt to develop a set of molecular-level components for information processing, chemical species capable of mimicking the role of wires, switches, memories, sensors, antennas, plugsocket and extension cable systems, and logic gates at the nanoscale have been reported. [4]. A convenient method for the synthesis of mono- and polycyclic azacrown macrocycles containing aromatic fragments using the Mannich condensation of phenols and secondary diamines has been studied. Introducing aromatic fragments into the crown macrocyclic framework increases the rigidity of those ligands and improves their preorganization for binding particular ions or organic guest molecules. [5].

Transport of cations across an organic liquid membrane which separates two water phases has been extensively investigated. The synthetic macrocyclic compounds, such as crown ethers, are usually used as model carriers to mimic the naturally occurring antibiotic macrocycles which have been shown to alter the permeability of biological membranes to certain cations. Thus, they have important applications in both chemistry and biology to selective complexation of various metal cations. Nitrogen-oxygen mixed donor macrocycles can form stable complexes with both alkali and transition metal cations, therefore, they have received much attention as receptors for a range of cations. [6]. The Mannich reaction is known to be a powerful method for the functionalization of azacrown ethers with additional ligating units. [7]. The bottom-up design, construction, and operation of devices and machines on the molecular scale is a topic of great interest in nanoscience and a fascinating challenge for nanotechnology. Species made of interlocked molecular components are most attractive candidates for these purposes. [8].

2. Experimental

2.1. Preparation of compounds **7a** to **7b**

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The two new lariat ethers compounds are prepared according to the literature[17,18] following 2. Preparation of the compound 11-(2-hydroxy-3,4-dimethylbenzyl)-2,20-dimethyl-9,10,11,12,13,14-hexahydro-6H-dibenzo[b,e][1,7,4,10,13,16]dioxathiatriazacyclooctadecine-7,15(8H,16H)-dione(**7a**): To a solution of 1.35 g (45 mmol) of paraformaldehyde in 50 mL of CH₃OH was added 14.51g (33.8 mmol) of macrocyclic diamid compound 5. After standing for 45 min., CH₃OH was removed and to the residue was added 4.89g (40mmol) of 2,3-dimethylphenol and 150 ml of toluene. The mixture was stirred under reflux at 110°C for 36h. The solvent was evaporated by rotatory evaporation, and the yellow crystals of 1 was formed. The colorless crystals were obtained by recrystallization of compound from methanol. The resulting crystals were collected by filtration and dried, Yield 65%, mp.128-132°C. IR(KBr, cm⁻¹): 3393, 2924, 2860,1672,1498,1235,1055,873,797,665,650. ¹HNMR(500 MHz, CDCl₃) δ: 2.2(s, 3H), 2.24 (s, 3H), 2.32 (s, 3H), 2.79-2.85 (m, 4H), 3.4-3.58 (m, 4H), 4.49 (s,2H),4.57(s,2H), 4.71(s, 2H), 6.84 (d, 2H), 6.87 (s, 2 H), 6.92 (s, H), 7.09- 7.1 (d,2H) , 7.21 (s, H) , 7.49 (s, H) , 7.6 (s, H) ppm. ¹³CNMR(125 MHz,CDCl₃)δ: 168.43, 165.93, 153.65, 152, 136.35, 132.70, 132.61, 132, 129.74, 128.45, 127.67, 122.30, 115.13, 112.35, 67.96, 53.19, 52.15, 49.35, 44.82, 39.31, 38.87, 20.98, 20.85, 16.22 ppm. Preparation of the compound 11-(2-hydroxy-5-methylbenzyl)-2,20-dimethyl-9,10,11,12,13,14-hexahydro-6H-dibenzo[b,e][1,4,7,10,13,16]trioxatriazacyclooctadecine-7,15(8H,16H)-dione (**7b**): To a solution of 1.35 g (45 mmol) of paraformaldehyde in 50 mL of CH₃OH was added 14.51g(33.8mmol)of macrocyclic diamid compound 2, 20dimethyl-9,10,11,12,13,14hexahydro-6H-dibenzo[b,e][1,7,4,10,13,16] dioxathiatriazacyclooctadecine-7,15(8H,16H)-dione. After standing for 45 min., CH₃OH was removed and to the residue was added 4.89g (40mmol) of p-cresol and 150 ml of toluene. The mixture was stirred under reflux at 110°C for 36h. The solvent was evaporated by rotatory evaporation, and the yellow crystals of 2 formed. The colorless crystals were obtained by recrystallization of compound from methanol. The resulting crystals were collected by filtration and dried yield 58%, mp.119-123°C. IR(KBr,cm⁻¹):3470,3398,2927, 2856, 1659, 1533,1484,1451,1405,1360,1251,1078,1037,669,569,805. ¹HNMR (500 MHz,CDCl₃) δ: 2.19 (s, 3H), 2.22 (s, 3H), 2.26 (s, 3H), 2.79- 2.85 (m, 4H), 3.4-3.59 (m, 4H), 4.49(s,2H), 4.57(s, 2H), 4.62 (s, 2H), 6.82- 6.84 (d, 2H), 6.92(s, 2H,⁴J=1.75Hz), 6.97 (s, H), 7.09- 7.1(d, 2H,⁴J=1.82Hz), 7.2 (s, H), 7.295 (solvent), 7.50 (s, 2H), 7.6 (s, H) ppm. ¹³C NMR(125 MHz, CDCl₃)δ: 168.82, 168.48, 155.63, 154.67, 153.65, 136.34, 132.70, 132.62, 131.40, 130.81, 129.74, 122.3, 117.09, 114.03, 112.85, 112.36, 111.61, 67.95, 67.88, 53.17, 52.14, 49.33, 39.31, 38.88, 20.91, 20.98, 20.31, 19.18 ppm.

3. Result and Discussion

This paper describes the synthesis of lariat diaza crown ethers. The macrocyclic diamid compound 2,20-dimethyl-9,10,11,12,13,14-hexahydro-6H-dibenzo[b,e][1,7,4,10,13,16] dioxathiatriazacyclooctadecine

-7,15(8H,16H)-dione was prepared according to the literature [13,14,15,16] (Scheme 1). In this work, the reaction of aza crown ether (**5**) with phenol derivatives (**6a-e**) were afforded new aza crown ethers (**7a-e**) (Scheme 2). In fact, the Manich reaction of secondary amine in **5** with formalin (trimer of formaldehyde) in methanol and then reacted with phenol derivatives, was obtained **7a-e**. Our aim was attempt to developing the aza crown ether improvement through the connection of aromatic fragments (phenolic fragments) in to the aza crown macrocyclic structures. These phenolic units make it easier to modify the macrocyclic host with U.V. and/or fluorescent active groups, protonionizable fragments and functional groups.

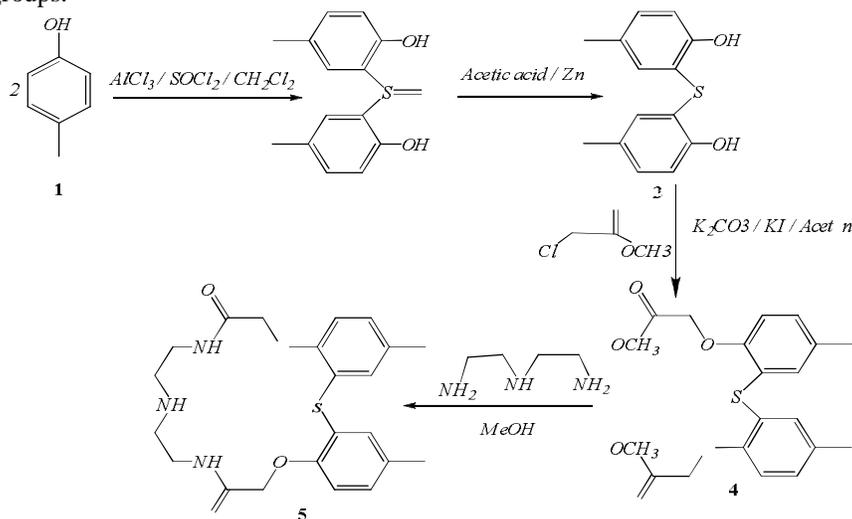


Figure 1. The synthetic route of macrocycle diamid compound

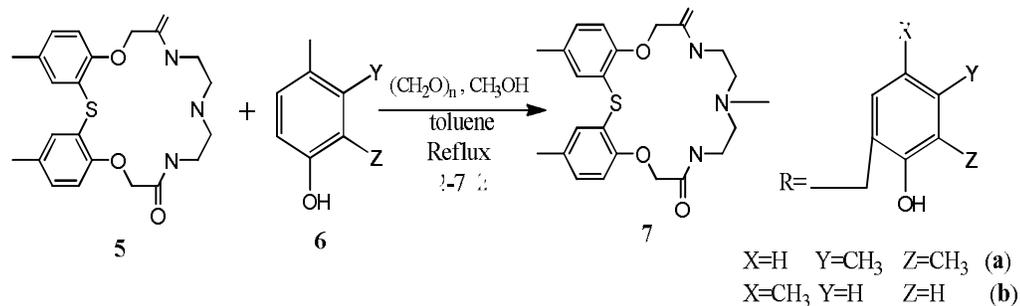
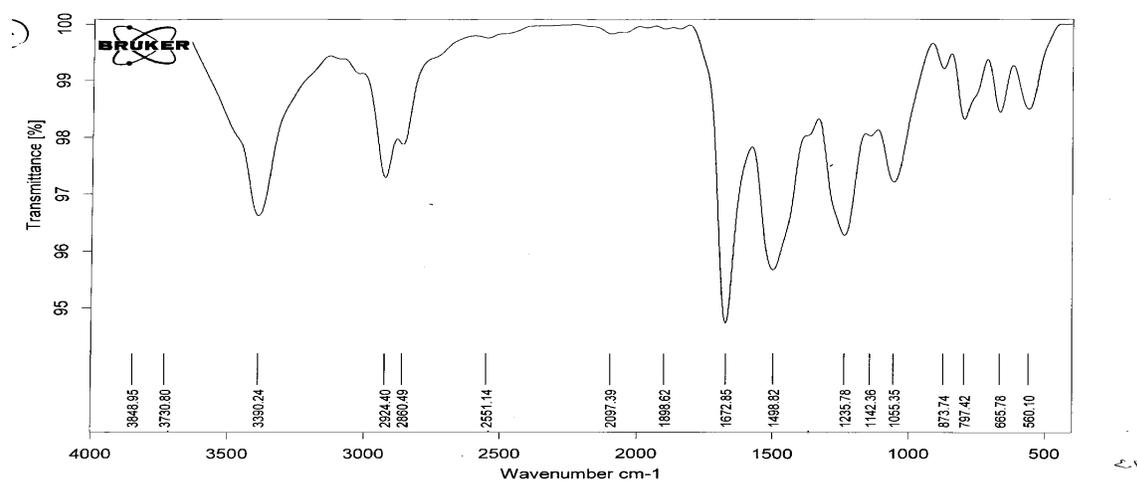


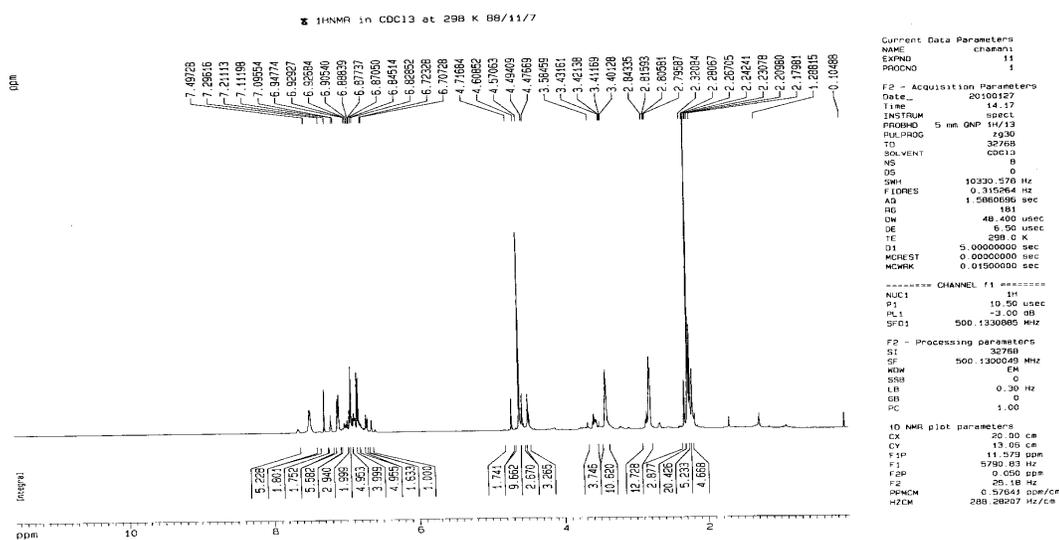
Figure 2. The synthetic route of lariat ethers compounds

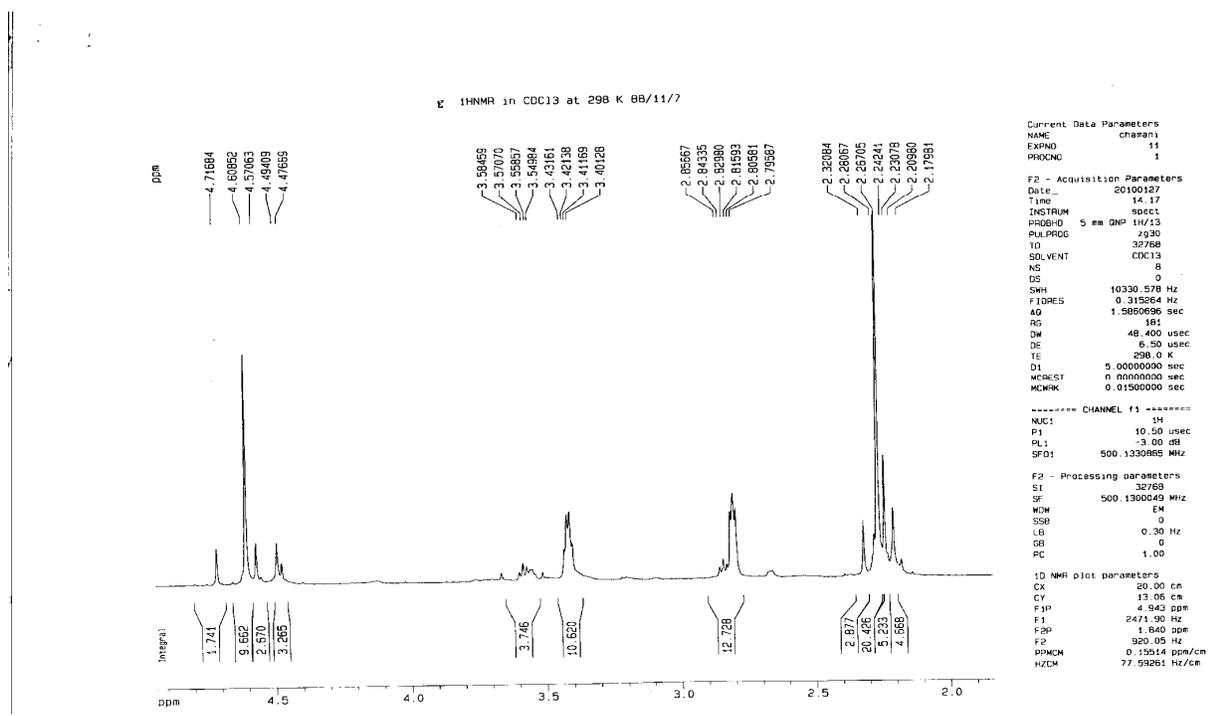
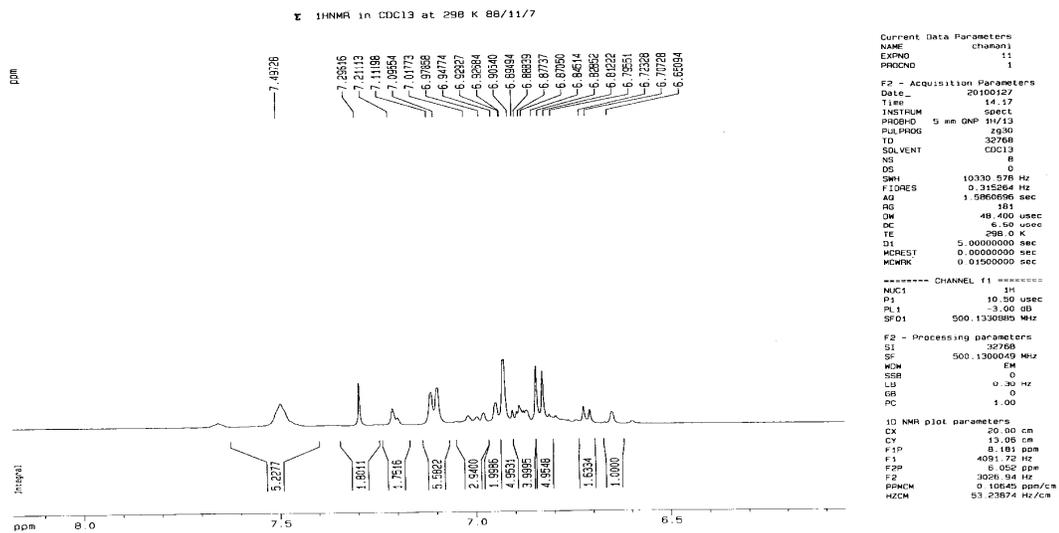
Supplementary Material

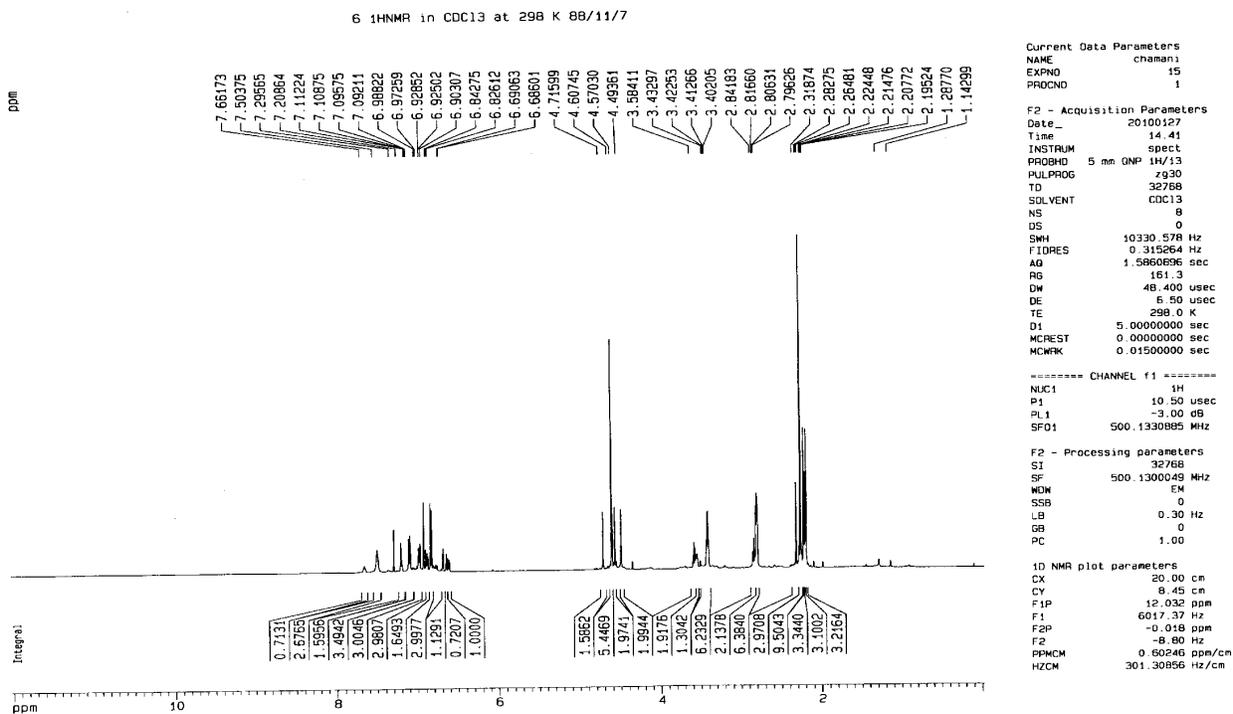
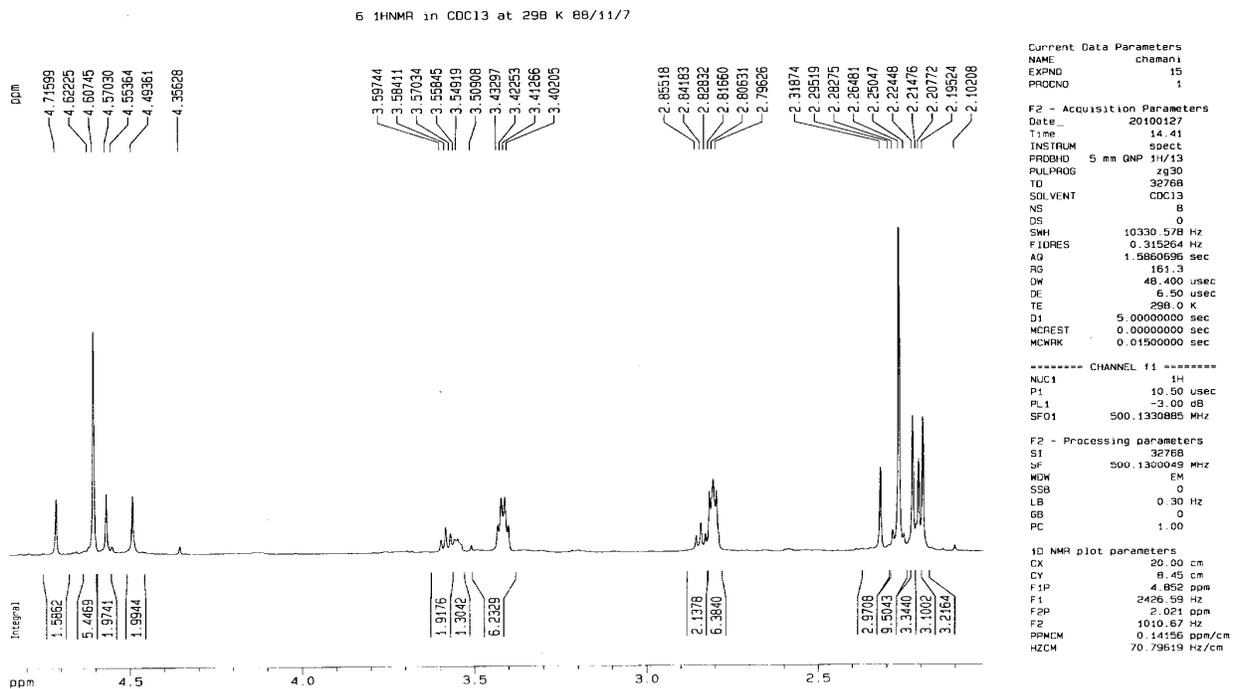
IR spectrum of 7a

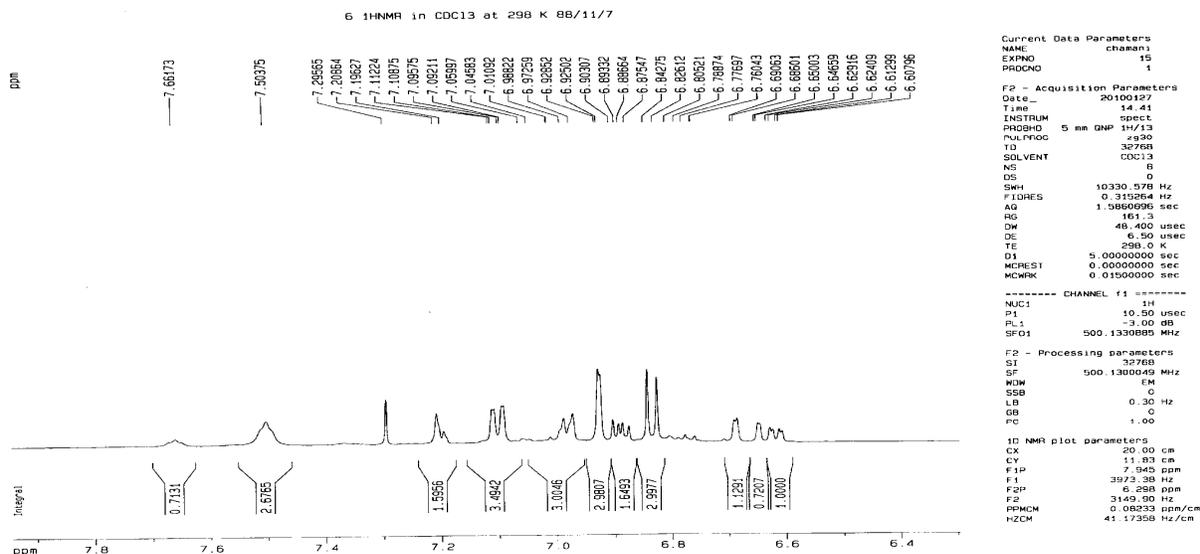


¹H NMR spectrum of 7a



Expanded ^1H NMR spectrum of **7a** (aliphatic region)Expanded ^1H NMR spectrum of **7a** (aromatic region) ^{13}C NMR spectrum of **7a**

Expanded ¹H NMR spectrum of **7b** (aliphatic region)Expanded ¹H NMR spectrum of **7b** (aromatic region)



¹³CNMR spectrum of 7b

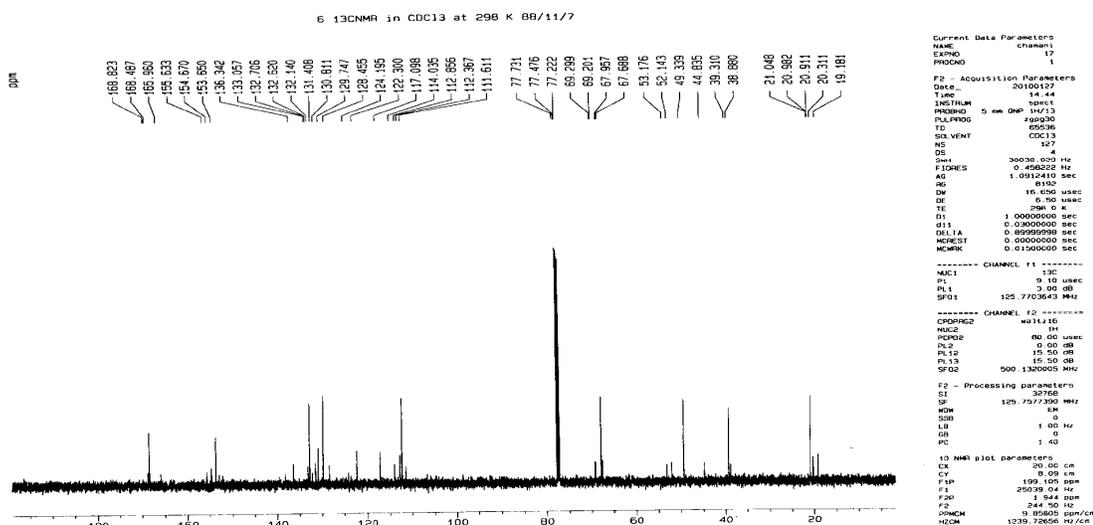


Figure 3. Supplementary Material

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