The Synthesis and Applications

of

Deuteriated Polypyridyl Ligands.

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I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of MSc. is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: Úna O'Dwyer ID No. 95970711

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The synthesis and applications of deuteriated polypyridyl ligands.

Una O' Dwyer.

Abstract.

This thesis describes the development of a new single-step method for the deuteriation of polypyridyl ligands and the possible applications of those deuteriated ligands.
Chapter 1 gives a summary of some of the deuteriation methods used previously and describes how ligand deuteriation may be used as a tool for the study of the excited states of Ru(II)polypyridyl ligands. Chapter 3 details the optimisation of the new deuteriation method to the synthesis of deuteriated 2,2'-bipyridyl (bpy), temperature and time variation studies revealed that the optimum reaction conditions for the synthesis of bpy-d_8 were 3 days at 200^0C, using 0.25g Pd/C per 3g bpy, the bpy deuteriated in this manner was calculated to be 95% deuteriated, it was also found that complete deuteriation may be obtained by repeating the procedure once with fresh D_2O and Pd/C. In this chapter we also see that the deuteriation method reported was successfuly applied to a whole range of (never previously deuteriated) pyridyl- and pyrazyl- triazole ligands. The temperature variation studies carried out on bpy indicated that it should be possible to achieve selective deuteration of bpy by carrying out the experiment with shorter reaction times, at lower temperatures and using less Pd/C. These milder conditions may also allow the deuteration of those compounds for which the previous conditions had proved too severe, eg. 3-(2,5'-dimethoxy-phenyl)-5-(pyridin-2-yl)-1,2,4-triazole. Chapter 4 shows some examples of how deuteriated polypyridyl ligands can be used both to obtain valuable information on the excited states, and to simplify the ^{1}Hnmr, of Ru(II)polypyridyl complexes.

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1. INTRODUCTION:

During the past few decades there has been intense interest and activity in studying the photochemistry and spectroscopy of Ru(II) polypyridyl complexes, [1] as the lowest excited states of these complexes are of considerable interest for their potential applications in cyclic photo-redox reactions, optic information storage systems and photo-chemical solar energy conversion devices. It is agreed in the literature [2], that the lowest excited states of $[Ru(bpy)_3]^{2+}$ and related compounds are classified as ^{3}MLCT states. [Fig. 1.1]

These MLCT states have several desirable features:

(1) they can be quite stable;

(2) there are adjacent oxidised and reduced forms, eg., $[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{+}$;

(3) their lifetimes can be sufficiently long to exploit with ease in chemical reactions;

(4) due to the huge number of stable Ru(II)-diimine complexes, it is possible to design supramolecular systems with user-defined photophysical properties.

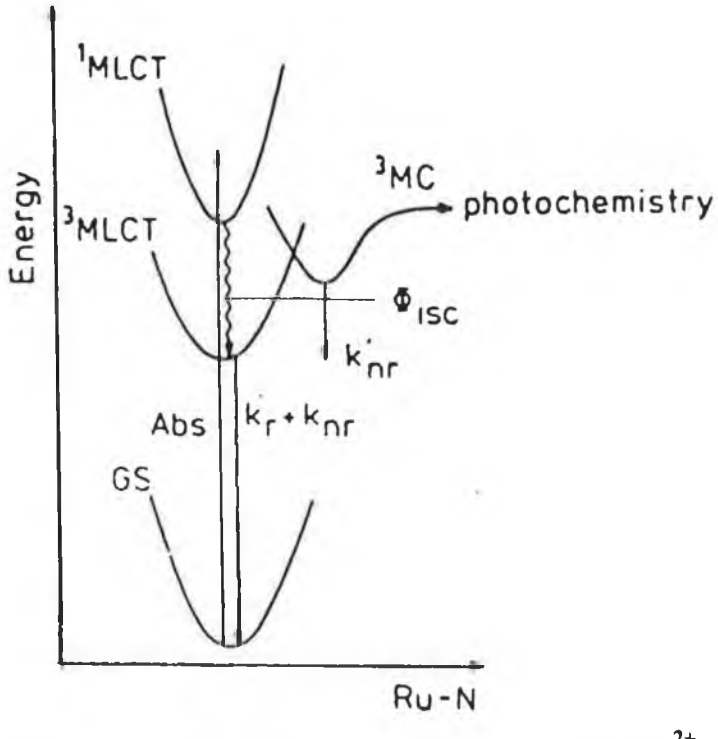


Figure 1.1 The Photophysical properties of $[Ru(bpy)_3]^{2+}$.

Currently much attention is being paid to the synthesis of polynuclear transition metal complexes [3-6] and as a result of the developement of the "complexes as metals" and "complexes as ligands" synthetic strategy, developed over the past few years mainly by the Balzani group, [7] multinuclear systems have been synthesised which show promise as devices capable of light induced directional electron and energy transfers. [Fig. 1.2] These polynuclear complexes exhibit intense visible absorption, they are luminescent in both fluid and rigid matrices and they exhibit rich photo- and electrochemistry.[7] In order to design and efficiently exploit this class of compounds for practical purposes a detailed understanding of the nature of the excited states is required.

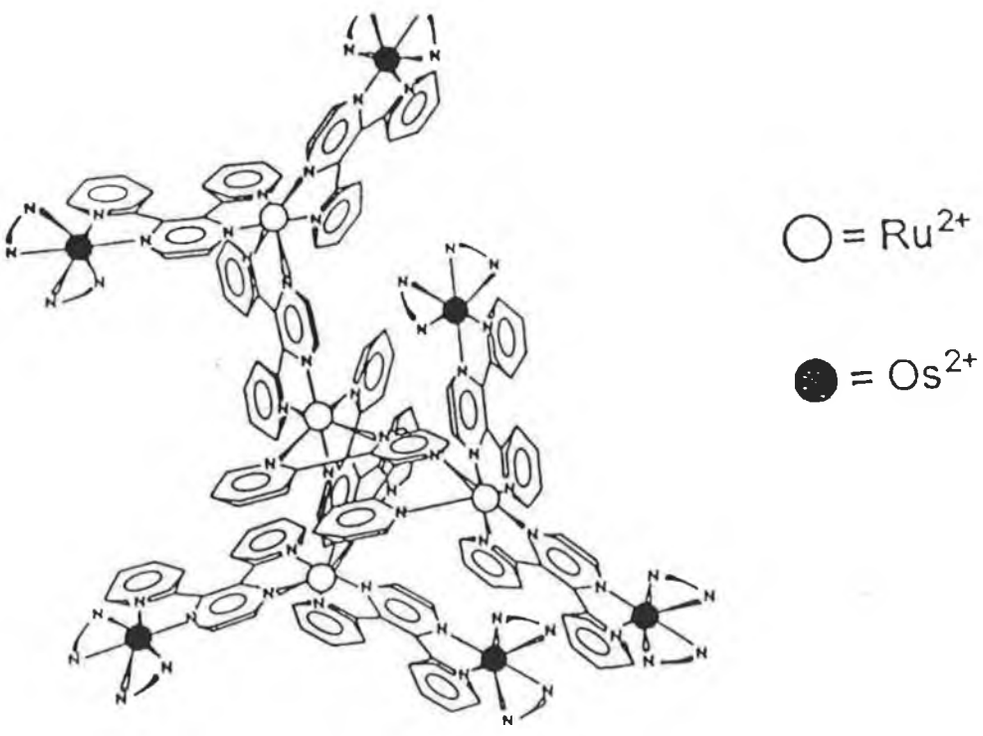


Figure 1.2 Structure of the $[Ru\{(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_2\}_3]^{20+}$ decanuclear complex.

Chapter 1

Introduction.

Deuteriation had been an important part of investigations into the excited states of organic compounds for many years, before its potential for use in coordination chemistry was revealed. One of the first reports of its use in inorganic chemistry was made in a paper by Van Houten and Watts in 1975, [8] in which they investigated the effect of ligand and solvent deuteriation on the excited state properties of $[Ru(bpy)_3]^{2+}$. Their studies revealed that deuteriation of the free ligand caused the measured luminescent lifetime, τ_m, to more than double, [Table 1.1]. The effect of ligand deuteriation was, however, mitigated in the complex, but a large isotope effect was then observed for the solvent causing the radiationless lifetime to almost double, while deuteriation of the ligand caused only a 20% increase. The effect of the solvent deuteriation was explained in terms of an excited state model involving partial charge transfer to solvent (CTTS).
In a subsequent paper Van Houten and Watts reported on the temperature dependence of the photophysical and photochemical properties of $[Ru(d_8\text{-bpy})_3]Cl_2$ and $[Ru(h_8\text{-bpy})_3]Cl_2$ in aqueous solution.[9] The model for temperature dependence employed by the authors possessed two terms to describe non-radiative decay, one they found to be strongly dependent on the deuteriation of ligands and solvent, and the other almost entirely independent. The independent term was attributed to the non-radiative decay from the d-d level. Since the d-d transition does not involve the bpys, and since it is a strongly internalised transition, solvent deuteriation should have little bearing.

Table 1.1 Measured lifetimes for the Tris(2,2'-bipyridyl)ruthenium(II) Complex Ion in Aqueous Solutions. [8]

Sample	Solvent	Temperature	τ_m
$[Ru(bpy)_3]Cl_2$	**H_2O**	298K	**0.58 μsec**
$[Ru(bpy\text{-}d_8)_3]Cl_2$	H_2O	298K	0.69 μsec
$[Ru(bpy)_3]Cl_2$	**D_2O**	298K	**1.02 μsec**
$Ru[(bpy\text{-}d_8)_3]Cl_2$	D_2O	298K	1.25 μsec
$[Ru(bpy)_3]Cl_2$	EtOH/MeOH 4:1,v/v	77 K	5.10 μsec
$[Ru(bpy\text{-}d_8)_3]Cl_2$	EtOH/MeOH 4:1,v/v	77 K	6.10 μsec
bpy - h_8	EtOH/MeOH 4:1,v/v	77 K	**0.97 sec**
bpy - d_8	EtOH/MeOH 4:1,v/v	77 K	**2.20 sec**

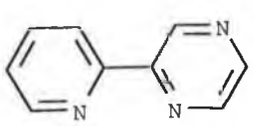
As stated above, the lowest excited states of $[Ru(bpy)_3]^{2+}$, (bpy=2,2'-bipyridyl), and related compounds are classified as ^{3}MLCT states, but the question of whether the excited electron is localised on one of the three bpy ligands, or delocalised over all three (indentical) bpy units, is still unresolved. Specific deuteriation experiments are being used to investigate this question and the two main research groups carrying out these investigations are, Yersin and co-workers and, Riesen and co-workers. Both groups have used highly resolved emission spectra of protonated, perdeuteriated, and partially deuteriated $[Ru(bpy)_3]^{2+}$ complexes doped into $[Zn(bpy)_3](ClO_4)$ as evidence of delocalisation and localisation respectively.

In the report by Yersin *et al.*, [10] the emission spectrum of $[Ru(bpy)_2(bpz)]^{2+}$, (bpz = 2,2'-bipyrazine), (which is a localised excitation from Ru d $\pi \rightarrow$ bpz π^* as the energy of the bpz π^* is considerably lower than that of the bpy), is compared to the emission spectra of the complexes containing the mixture of both perdeuteriated and protonated bpys. In the emission spectrum of $[Ru(bpy)_2(bpz)]^{2+}$, only ligand centred modes of bpz could be found, whereas, in contrast, for $[Ru(bpy)_2(bpy\text{-}d_8)]^{2+}$ the ligand centred vibrations of bpy-h_8 and bpy-d_8 accompany the same electronic origin. This is proof, according to Yersin *et al.*, that the excited state electron in $[Ru(bpy)_3]^{2+}$ is delocalised over all three bpy units.

Riesen *et al.*, [11] on the other hand discount this evidence, stating that their work confirms that the presence or absence of vibrational sidelines cannot be used, a priori, as evidence for localisation or delocalisation of ^{3}MLCT excitations. They claim that the question is better approached by detailed studies of electronic origins. In the excitation spectra of the series $[Ru(bpy)_{3-x}(bpy\text{-}d_8)_x]^{2+}$ (x = 0-3), in $[Zn(bpy)_3](ClO_4)_2$,they observed two sets of electronic ^{3}MLCT origins for the x = 1 and x = 2 systems. These were assigned as independent ^{3}MLCT transitions involving either the bpy-h_8 or the bpy-d_8 ligands. In order to confirm their assertion that the excited electron is localised on a single bpy ligand, they extended their study of deuteriation effects. In the series $[Ru(bpy\text{-}d_x)_3]^{2+}$ (x = 0,2,6,8), one set of origins was observed and the origins gradually shifted to higher energy with increasing deuteriation degree. The $[Ru(bpy)(bpy\text{-}d_8)_2]^{2+}$ complex was further deuteriated or protonated to $[Ru(bpy\text{-}d_2)(bpy\text{-}d_8)_2]^{2+}$ and $[Ru(bpy)(bpy\text{-}d_6)_2]^{2+}$, respectively. Transitions involving the bpy-d_2 and the bpy-d_6 ligand shifted to higher and lower energy, respectively, whereas transitions involving the bpy-d_8 or the bpy-h_8 ligand remained at the same energy as in the $[Ru(bpy)(bpy\text{-}d_8)_2]^{2+}$ complex. These results confirm, according to Riesen *et al.*, that the lowest excited ^{3}MLCT levels in $[Ru(bpy)_3]^{2+}$ systems are invariably localised.

Resonance Raman (rR) spectroscopy is another area where deuteriation of bipyridyls has proved important in the investigation into the localisation / delocalisation of the excited state. The results from this area are in agreement with those of Riesen *et al.* Examples come from the work of Kincaid *et al.*, [12-15] and others [16] which concur that the electron is localised on one bpy ligand ie., the excited state formulated as $[Ru^{III}(bpy)_2(bpy^{\cdot-})]^{2+}$. In order to achieve intensity enhancement, resonance Raman scattering employs exciting radiation at a wavelength within the absorption band of the species under investigation. Raman scattering studies of polypyridyl complexes invariably employ 347 or 353 nm laser pulses as source, and at these wavelengths there is strong absorption by the anions of bpy and related ligands. At low photon flux, the Raman spectrum observed is that of the ground state $[Ru(LL)_3]^{2+}$ molecules. Increasing the photon flux leads to a build up of moderate concentrations of the excited state species $[Ru(LL)_3]^{2+*}$. If the excited state species do contain polypyridyl anions as envisaged in the localised orbital descriptions of the excited state then one should be able to observe the Raman bands of the reduced ligand anion radicals, and indeed new Raman bands corresponding to the presence of $(LL^{\cdot-})$ species are readily observed.

Kincaid *et al.*, [17] have carried this study further and have, through deuteriation of the pyridine half of the asymmetric ligand 2-(2-pyridyl)pyrazine (pypz), [Fig. 1.3] shown that the excited electron is further localised in $[Ru(bpy)_2(pypz)]^{2+}$ to the pyrazine half of the pypz moiety.



Pyridylpyrazine

The study of deuteriation effects on measured lifetimes of excited states can provide insight into the precise mechanisms of nonradiative decay processes. There have been many reports, in organic chemistry, of observed increases in the triplet-state lifetimes upon perdeuteriation of for example, naphthalene [18] and benzene, [19] and more recently it has been revealed, by selective deuteriation studies, [20] that the triplet lifetime is dependent on the number and position of the deuterium substitution. [Table 1.2]

Table 1.2 ^{3}MLCT Lifetimes of Tris(2,2'-bipyridine)ruthenium(II) Complexes in Aqueous Solution. [20]

Complex	Lifetime, +/- 10ns
$[Ru(bpy)_3]^{2+}$	580
$[Ru(bpy\text{-}d_8)_3]^{2+}$	690
$[Ru(bpy\text{-}3,3'\text{-}d_2)_3]^{2+}$	580
$[Ru(bpy\text{-}6,6'\text{-}d_2)_3]^{2+}$	645
$[Ru(bpy\text{-}3,3',5,5'\text{-}d_4)_3]^{2+}$	655

The influence deuteriation has on the luminescent behaviour can be explained by relating it to the rate of non-radiative relaxation of the excited state, k_{nr}, which may be derived from the following equations;

$$\tau = k_r + k_{nr}\,, \quad \phi = k_r.\tau$$
$$k_{nr} = (1 / \tau_{77\,K}) - k_r$$

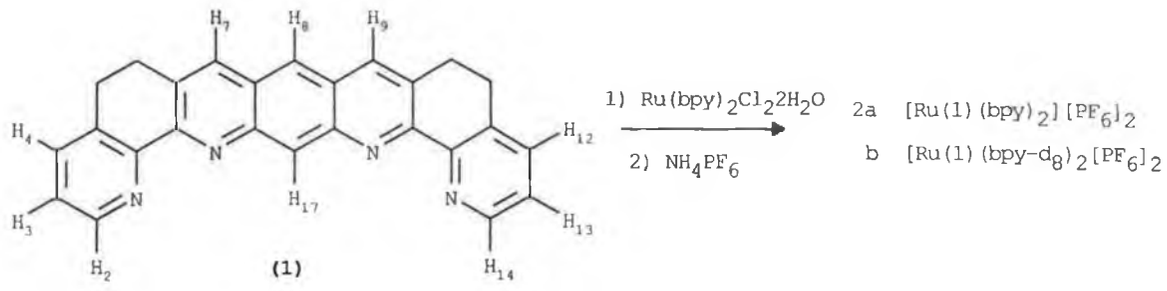
Where k_r = rate of radiative radiation, τ = lifetime of excited state, and ϕ = luminescent lifetime.

It has been shown previously, in work done by Tia Keyes of this laboratory, [21] that upon deuteriation of the bipyridyl ligand in mixed ligand Ru(II) polypyridyl complexes, there is a decrease in k_{nr}. This decrease is associated with the slower vibrational relaxation of the excited electron on the bipyridyl. This is explained in terms of the contribution of the bpy C-H stretch to the vibrational relaxation of the excited state of the complex.

According to Siebrand's theory of non-radiative transition, [22, 23] high energy anharmonic C-H stretching vibrations are the dominant promotional modes in non-radiative decay. This implies that the excited state lifetimes should increase upon deuteriation, as the energy of the C-D stretching vibration is 2250cm^{-1}, considerably lower than that of the C-H stretching vibration, which is 3000cm^{-1}.

In a subsequent report [24] Keyes *et al.*, also make the proposal that, in heteroleptic compounds, the emission lifetime may only increase upon deuteriation of a particular ligand, when the excited state is located on this ligand. Further investigation is needed in this area, as this would offer a simple means of determining the destination of the excited state electron in mixed ligand systems. Currently such elucidation requires a combination of acid-base, electrochemical and resonance raman spectroscopy.

Another very important motive behind the synthesis of deuteriated analogues, is the simplification of their ^1H nmr spectra - in the instances of asymmetric mononuclear complexes, up to sixteen non-equivalent protons may arise from the bipyridyl moieties, and in dinuclear complexes thirty two, making complete unambiguous structural assignment extremely difficult. Deuteriation of the bipyridyl results in the bipyridyl moiety appearing as low intensity singlet resonances in the ^1H nmr, thereby simplifying it to a large degree. One of the first examples of this can be seen in a report by Chirayil and Thummel [25] in which $Ru(bpy\text{-}d_8)_2Cl_2.2H_2O$ was used to prepare a mono-nuclear complex from a ligand with two equivalent bidentate sites: 5,6,10,11-tetra-hydro-16,18 diazadipyrido[2,3-a:3',2'-n]pentacene (**1**).



When the 16 signals due to the bpy protons were eliminated, the spectrum of the coordinated (**1**) (Fig 1.4), is easily interpreted, by comparison with previously established chemical shift values for ruthenium(II) complexes with bridged derivatives of 2,2'-bpy and 2,2'-biquinoline, nearly unambiguous assignments of the 10 remaining signals could be made.

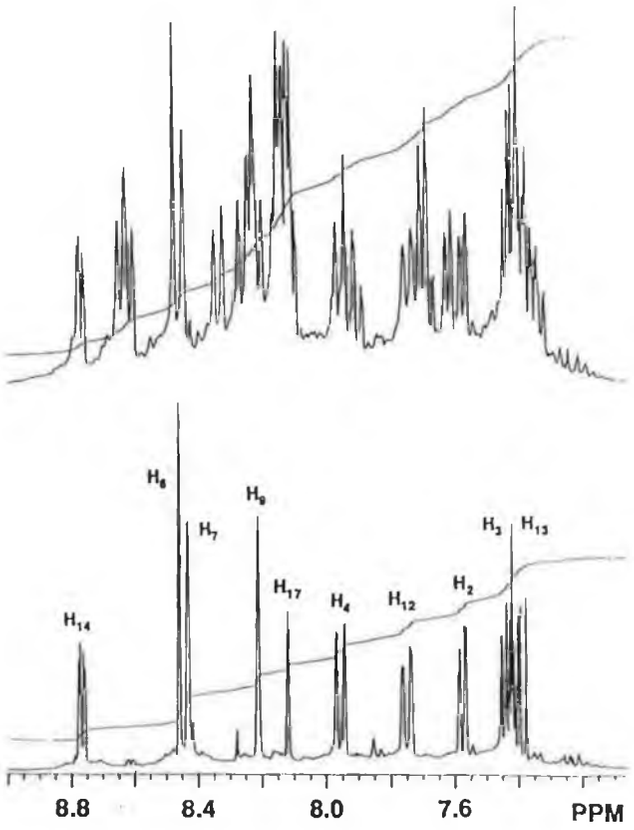
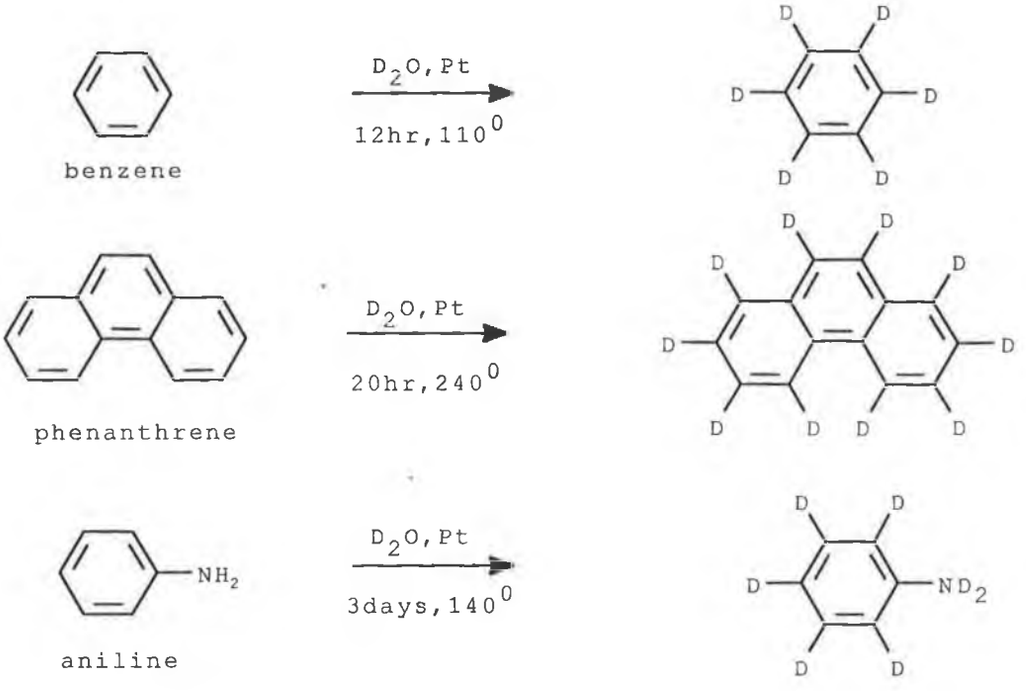


Figure 1.4 ^{1}Hnmr spectra of $[Ru(bpy)_2][PF_6]_2$ (top) and $[Ru(bpy\text{-}d_8)_2][PF_6]_2$ (bottom) recorded at 300 MHz in CD_3CN.

Ligand deuteriation as a tool for the investigation of excited states is a relatively under-exploited method, mainly due to the fact that until recently, the synthetic demands of producing deuteriated ligands were quite considerable. As was mentioned previously, deuteriation has been used in organic chemistry for many years, and the following section is a summary of some of the deuteriation methods previously used:

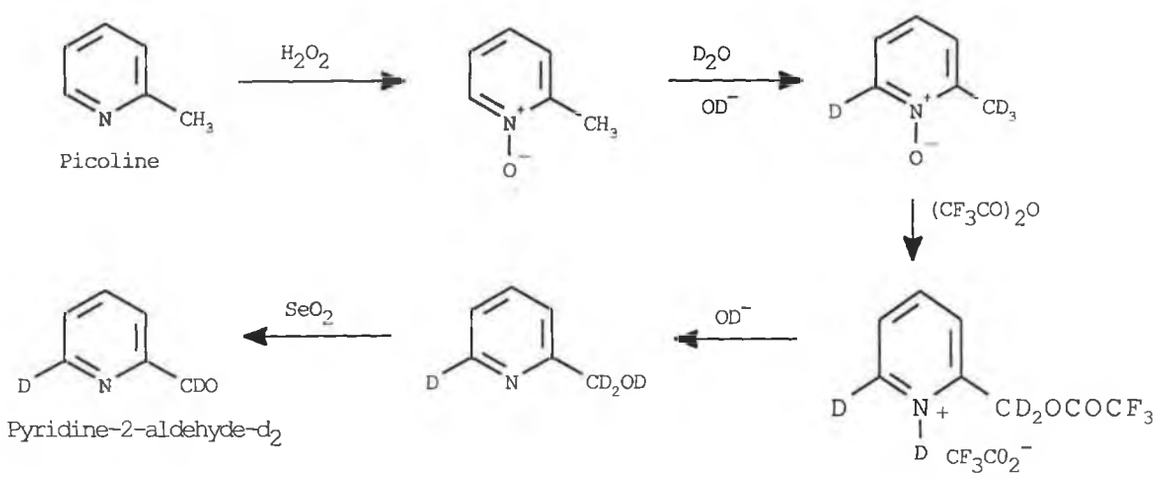
Benzene-d_6, [26] phenanthrene-d_{10}, [27] and aniline-d_7 [28] can all be synthesised using essentially the same deuteriation method, which involves heating the substrate along with D_2O and platinum black (prepared by reducing $PtO_2.H_2O$ with deuterium) in a sealed vessel.



The temperature and the reaction time vary depending on the substrate, as does the number of times the procedure has to be repeated to produce the desired deuteriated product. Thus benzene is heated at 110^0C for 12 hr, the procedure is repeated 3 times and the deuterium content after the final exchange is C_6D_6 = 95.24%, C_6D_5H = 3.96%. Phenanthrene is heated at 240^0C for 20 hr, the procedure is repeated 9 times and resulting

product is 95.5 mole% D_{10}, 4.4 mole% D_9, 0.1 mole% D_8. Aniline is heated at 140^0C for 3 days, the procedure is repeated 4 times and the product is estimated to be 99 atom% D.

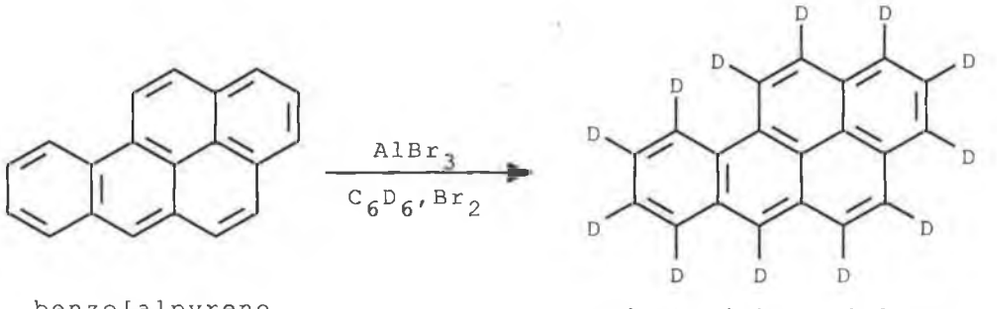
Pyridine [29] can be deuteriated by first reacting it with H_2O_2 to produce the N-oxide, then heating it in D_2O at 200^0C for 30hr in a monel bomb. After cooling the solvents are removed, the product is redissolved in D_2O and heated once more as above. The product obtained is pyridine 1-oxide-2,6-d_2 . The biggest advantage of this method is that it allows for selective deuteriation at the 2' and 6' position, but it requires the synthesis of the N-oxide which is a complicated procedure. This method can also be used to synthesise pyridine-2-aldehyde-d_2, [30] from picoline (as shown below).



Deuteriation of the N-oxide gives selective deuteriation, in this case of the 2'-position and of the methyl group. The deuteriated N-oxide is then reacted with triflouro-acetic acid and stirred overnight to produce 2-trifluoroacetatomethyl-pyridinium trifluoroacetate-d_4, which in turn is reacted with sodium ethoxide in D_2O and the solution heated at 60^0C for 18hr. Distillation yields 2-pyridylmethanol-d_4 which is heated along with dry dioxane and selenium dioxide at 80^0C for 4hr, after which the pyridine-2-aldehyde-d_2 is distilled off with a final yield of 94%.

An alternative to those methods involving exchange with heavy water in the presence of homogeneous or heterogeneous metal catalyst, is a method which uses organoaluminium dihalides, such as ethylaluminium dichloride, to catalyse very rapid exchange of hydrogen atoms between aromatic nuclei. An example of this is the synthesis of bromobenzene-d_5 ; [31] ethylaluminium dichloride (0.01g) is added by syringe to a mixture of perdeuteriobenzene ($0.2cm^3$) and bromobenzene ($0.2\ cm^3$) in a small serum-capped vial at room temperature. The reaction is terminated after a few minutes by the addition of excess water. Analysis of the quantitatively recovered bromobenzene shows that exchange equilibrium is reached at all five aromatic positions, whereas homogeneous and heterogeneous catalysis leads to exchange in only three positions in bromobenzene and a prolonged time at an elevated temperature is required. A wide range of compounds may be deuteriated using this technique, examples of which are, chlorobenzene, ethylbenzene, mesitylene and naphthalene. However, pyridine and many aromatic compounds substituted by electronegative groups (eg., anisole, benzaldehyde and aniline) fail to exchange under these conditions.

Using the above method perdeuteriobenzo-[a]pyrene may be synthesised, [32] but the reaction takes seven days at 90^0C, whereas if $AlBr_3$ is used as the catalyst, the same reaction takes only 6 hr (as shown below).



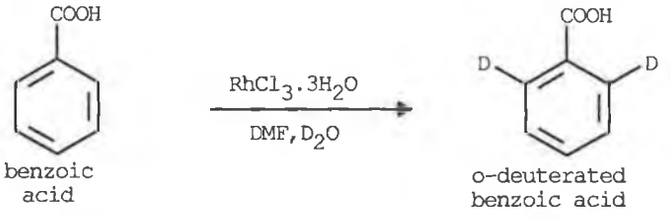
benzo[a]pyrene perdeuteriobenzo[a]pyrene

It is however, a more complicated procedure - $AlBr_3$ is added (in a dry box) to benzene-d_6 and pure bromine in a glass ampoule, the ampoule is then capped, removed from the dry box, cooled in dry ice/acetone and flame sealed. The sealed ampoule is then heated in an

oil-bath at 100^0C for 2 hr, the contents of the ampoule are then transferred to a second ampoule containing benzo[a]pyrene, the ampoule is sealed as before and heated in an oil-bath at 110^0C for 6 hr. After cooling, the benzene layer is removed and evaporated to dryness in *vacuo*, vacuum sublimation of the resulting residue yields benzo[a]pyrene which is 94.7 atom% deuterium. Using this procedure, perdeuteriated benz[a]anthracene, pyrene, chrysene, perylene, fluoranthene, carbazole and triphenylene may also be prepared. [32]

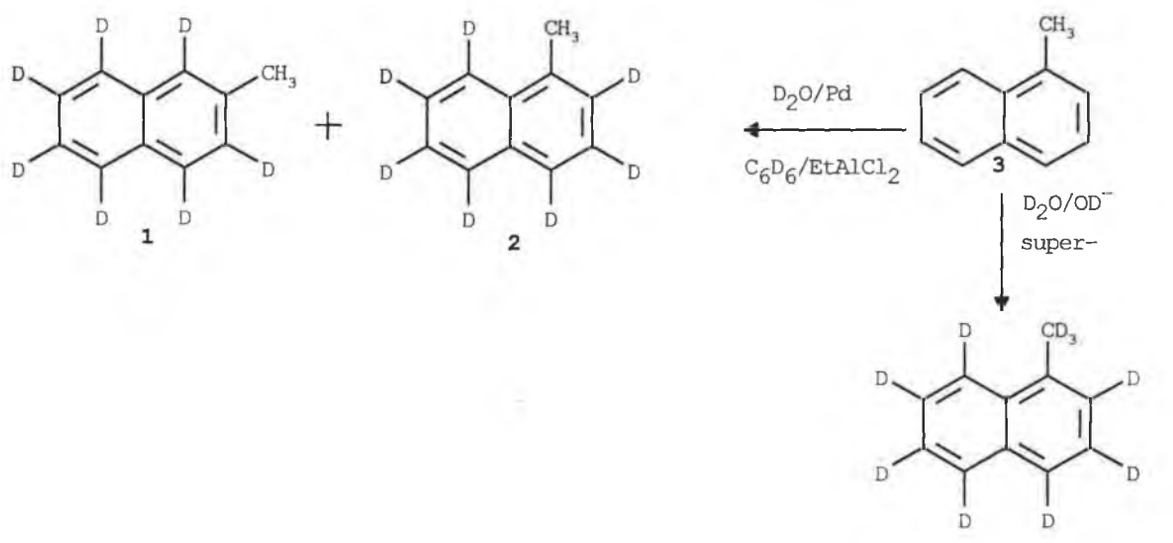
Another method for the deuteriation of polycyclic aromatic compounds, which claims to be faster and more convenient than than using deuteriohalides such as DBr and $AlBr_3$ or DF or DCl in CF_3COOD, is a technique which requires only BF_3 and D_2O [33]. The substrate is placed in a flask to which $D_2O.BF_3$ (prepared by blowing BF_3 gas into D_2O until a 1:1 molar solution is obtained), is added. A condenser is connected and the reaction mixture is stirred at room temperature. Naphthalene and phenanthrene exchanges are carried out at 90 and 105^0C, respectively, in fuming, slowly decomposing acid. After completion the organic layer is separated, washed twice with water, and dried over silica gel. This method can be used to deuteriate benzene, toluene, chlorobenzene, xylene, cumene, butylbenzene, tetralin, naphthalene and phenanthrene, but it can not be applied to deactivated benzenes ie., those containing electronegative groups.

Ortho-deuteriated aromatic carboxylic acids and β-deuterated α,β-unsaturated carboxylic acids may be prepared [34] with high regioselectivity by exchange deuteriation of the unlabelled acids in the presence of rhodium(III) chloride.



The substrate, along with rhodium(III) chloride, is dissolved in a mixture of N,N-dimethylformamide and deuterium oxide and heated at 110^0C for 18 hr. After deuteriation the labelled substrate is isolated by solvent extraction, labile deuterium removed by treatment with sodium bicarbonate solution followed by dilute hydrochloric acid, and the substrate purified, if necessary, by crystallisation from methanol or water.

Supercritical deuterium exchange (SDE), which proceeds in deuterium oxide above its triple point (374^0, 221bar), offers a new approach to the preparation of deuteriated arenes and heteroarenes (eg., phenanthrene, quinoxaline, aniline, acetophenone).[35]

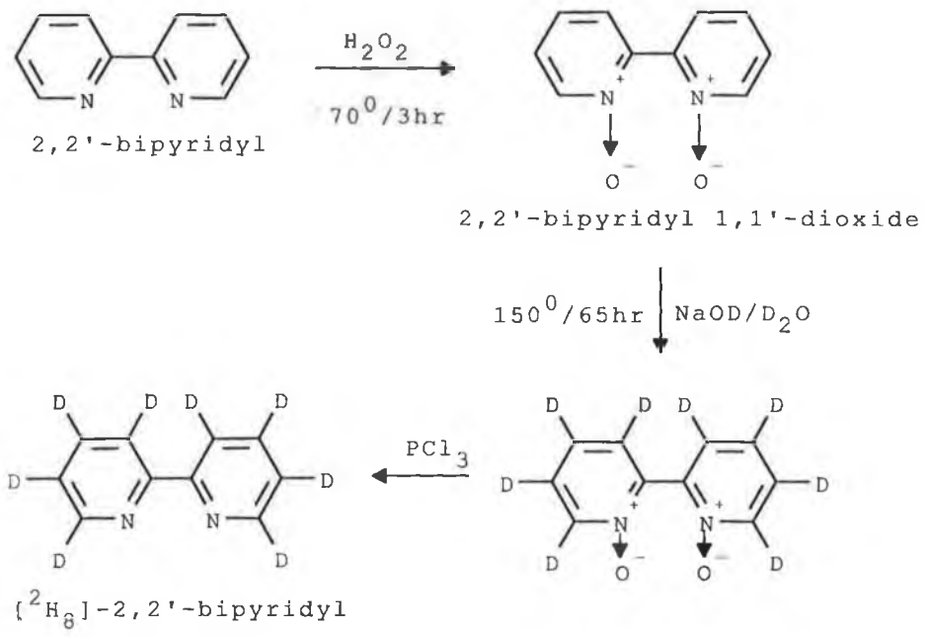


SDE has the advantages of short exchange times and relatively low costs. In these experiments the substrate is placed, along with deuterium oxide and sodium deuteroxide, in a $30cm^3$ Hastelloy-C reactor, the reactor is then purged with nitrogen and placed in a preheated furnace, reaction times vary from 1 to 24 hr depending on the substrate.

SDE is applicable to the preparation of both functionalised and non-functionalised aromatic substrates, and is particularly well suited for labeling alkylated polyaromatic hydrocarbons. SDE of 1-methylnaphthalene **3**, for example, produces 1-methylnaphthalene-d_{10} **4**, while ethyl aluminum dichloride and palladium catalysed exchanges produced mixtures of methylnaphthalene-d_7 isomers **1** and **2**. Application of SDE to functionalised and heterocyclic substrates is limited by the harsh conditions required to attain rapid isotopic equilibration, as well as substrate pyrolysis and other chemical side reactions. The reactions must be carried out under nitrogen as oxidation products are observed in the presence of air.

An alternative to ligand deuteriation is the synthesis of deuteriated complexes. It has been shown that the 3,3'-protons of $[Ru(bpy)_3]^{2+}$ are the most susceptible to hydrogen/deuterium exchange due to their slight acidity, promoted by steric strain. $[Ru(bpy\text{-}3,3'\text{-}d_2)_3]^{2+}$ may be prepared by reacting $[Ru(bpy)_3]^{2+}$ with $Na[OCD_3]$ in $(CD_3)_2SO$-CD_3OD solution at 35^0C, [36] greater than 95% deuteriation at the 3,3'-position being observed after 24 hr. Partial deuteriation at the 5,5'-position also occurs if the exchange reaction is extended - after 1 week, approximately 70% deuteriation was observed. $[Ru(bpy\text{-}6,6'\text{-}d_2)_3]Cl_2$ and $[Ru(bpy\text{-}d_8)_3]Cl_2$ can be prepared by reaction of $RuCl_3.3H_2O$ with bpy-6,6'-d_2 and bpy-d_8 respectively, [37] both of these deuteriated ligands are prepared from 2,2-bpy-N,N'-dioxide by the method proposed by Cook *et al.*, (see below) [38]. Deuteriation at the 6,6'-position was found to be complete (approx. 97%) after 18 hr, a longer exchange time (30 hr) produced significant amounts of species of higher deuterium content.

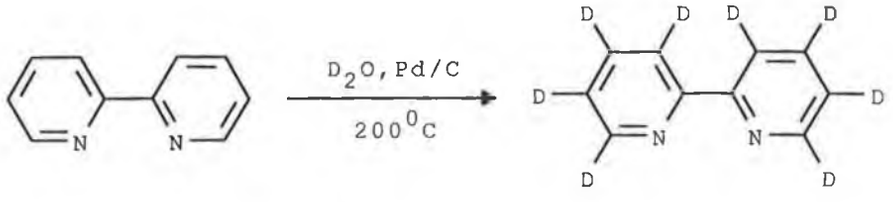
Until recently, the following method, proposed by Cooke *et al.*, [38] was the most convenient method for the deuteriation of 2,2'-bipyridyl (bpy):



The first step is the conversion of bpy into its N-oxide, which is achieved by dissolving the bpy in acetic acid and stirring the mixture at 60^0 for 1 hr, after which time H_2O_2 (35%) is added and the mixture left stirring for a further 3 hr. The volume is then reduced to a mininum under vacuum, the N-oxide crystallises out, and is redissolved in water and filtered to remove any remaining bpy. The solution is once again vacuum reduced and the 2,2'-bipyridyl 1,1'-dioxide which falls out of solution is recrystallised from ethanol/water. Treatment of this with NaOD-D_2O is then heated at 150^0C for 65hr in a sealed tube gives, from the filtered, concentrated, and cooled solution, [$^2H_8$]-2,2'-bipyridyl 1,1'-dioxide which separates as colourless needles. The material is dissolved in phosphorous trichloride and heated under reflux for 1.5hr. The cooled, neutralised (20% aqueous KOH) solution is extracted with ether. The extracts are dried ($MgSO_4$), the solvent evaporated, and [$^2H_8$]-2,2'-bipyridyl collected by sublimation of the residue. % Yield = 55%,- it should be noted that in practice the final yield is usually less than 55%.

The arduous and time consuming nature of this method, especially considering the low overall yield, has meant that although deuteriated bpy has great potential (as described previously), for use in both the simplification of ^{1}H nmr spectra, and the attainment of information about the excited states of Ru(II)polypyridyl complexes, there are very few reports of its use in these areas. In order to exploit this potential, therefore, a simpler and more efficient method of deuteriation is required.

Some preliminary work in this area has been done by Keyes of this laboratory, [21] who reported the following method: 2,2'-bipyridyl (bpy) was added to D_2O and the reaction mixture allowed to react in the presence of the H-D exchange catalyst Pd/C in a teflon-coated steel high pressure reactor at 200^0C for 8 days.



The contents of the reactor were then collected and filtered hot to remove the palladium catalyst and D_2O was removed under vacuum to obtain the product. The Pd/C catalyst was washed with acetone to remove any product present on its surface and the material obtained in this manner was recrystallised from hot water. The ^{1}Hnmr spectrum of the product obtained revealed four singlets, indicating >80% deuteriation. To achieve complete deuteriation, the same procedure was repeated with fresh D_2O for another week and the reaction mixture worked up as described above. The overall yield of the fully deuteriated product bpy-d_8 was >80%, and the material obtained was ^{1}Hnmr silent. Infrared spectroscopy showed bands at 2250-2295cm^{-1}, attributed to $\nu_{C\text{-}D}$ vibrations.

This was a significant improvement on the previous methods, allowing for a single-step, direct deuteriation of bpy. Chapter 3 details the optimisation of this method, and its application to other polypyridyl ligands. In chapter 4 we see some examples of how deuteriated ligands have been used in investigations of the excited states of Ru(II) poly-pyridyl complexes and in the deconvolution of their ^{1}Hnmr spectra. This section also details the synthesis of $[Ru(bpy)_2(3\text{-}(2,5\text{-dimethoxyphenyl})\text{-}5\text{-}(pyridin\text{-}2\text{-}yl)\text{-}1,2,4\text{-}triazole)]^{+} = [Ru(bpy)_2(L_1)]^{+}$, as this is the precursor to the hydroquinone-type complex $[Ru(bpy)_2(3\text{-}(2,5\text{-dihydroxyphenyl})\text{-}5\text{-}(pyridin\text{-}2\text{-}yl)\text{-}1,2,4\text{-}triazole)]^{2+} = [Ru(bpy)_2(HL_1)]^{2+}$. This complex is one of several aryl-substituted pyridyltriazole containing complexes currently under investigation, as it has been shown [21] that these complexes mimic some of the unit functions of the photosynthetic system, and it is hoped that further studies will provide a greater insight into the mechanistics of the photosynthetic process.

Chapter 2

Experimental.

2 . EXPERIMENTAL SECTION.

2.1 Instrumentation:

Nuclear Magnetic Resonance Spectroscopy.

Proton nuclear magnetic resonance (^{1}Hnmr) spectra were obtained using a Bruker AC 400MHz spectrometer. Measurements were carried out in $CDCl_3$-(99.8 atom % D) and $(CD_3)_2SO$-(99.5+atom % D) for the polypyridyl ligands, and acetonitrile-d_3-(99.5 atom % D) for the Ru(II) complexes.

Analytical HPLC.

Analytical cation exchange HPLC experiments were carried out using a Waters HPLC system, consisting of a model 6000A HPLC pump fitted with a 20μl injection loop, a Waters 990 photodiode array detector connected to a NEC APC III computer, and a μ-partisil SCX radical PAK cartridge mounted in a radical compression Z module.

The mobile phase used was 80:20 CH_3CN : H_2O containing 0.08M $LiClO_4$. The flow rate was 2.5 cm^3/ min^{-1}.

Luminescent Lifetime Measurements.

The lifetime measurements were carried out using a Q-switched Nd-YAG spectrum laser system. They were carried out in analytical grade acetonitrile at room temperature, (degassed by bubbling with Argon).

2.2 Experimental Procedures (Part 1).

Calculation of % deuteriation:

In order to explain how the % deuteriation of each sample was determined by analysis of its ^{1}Hnmr spectrum, the following is a detailed description of how the calculation was carried out from the ^{1}Hnmr spectrum of a sample of bpy after 4 days at 200^0C using 0.25g Pd/C.[Fig. 3.2]

Firstly the ^{1}Hnmr of undeuteriated 2,2'-bipyridyl was obtained [Fig. 3.1], by dissolving 6mg of bpy in $1cm^3$ of $CDCl_3$, and from this spectrum the ratio of the integration of the ligand peak (L) to the solvent peak (S) was determined, ie., the ratio of the relative number of hydrogens in the bpy sample compared to that in the deuteriated solvent. From the spectrum it can be seen that the ratio L/S = 10. [It must be noted that it is the overall % deuteriation of the ligand that is being calculated in these cases and so the value of L above is determined by calculating the average of all four ligand peak integrations, ie., in this case L = (1.00+1.02+1.03+1.04) ÷ 4 = 1.02 for the undeuteriated bpy [Fig. 3.1], and L = (1.00+1.01+1.00+0.98) ÷ 4 = 1.00 for the deuteriated bpy [Fig. 3.2]. In cases where it was necessary to obtain the % deuteriation of each ligand peak individually (see chapter 3), instead of using the average ligand peak integration, the calculation was simply carried out separately for the four individual ligand peaks.]

Then the ^{1}Hnmr spectrum of the deuteriated bpy was obtained by dissolving 12mg of deuteriated bpy in $1cm^3$ of $CDCl_3$. In this case the integration of the ligand peak must be divided by two in order to compare it with the corresponding peak in the spectrum of the undeuteriated bpy as 12mg was used instead of 6mg. The ratio of ligand to solvent peaks in this case therefore, L/S = 0.5. By comparing these two ratios it can be seen that, as the quantity of $CDCl_3$ is the same in both cases, the relative number of hydrogens present in the deuteriated sample is 20 times less than in the undeuteriated sample, so by making the

initial assumption that the undeuteriated sample was completely undeuteriated, ie., was 100% hydrogenated, it follows that the deuteriated sample has 20 times less hydrogens, ie. %H = 5, which means, therefore that the % deuteriation of the sample is 95%.

The individual % deuteriations were determined by taking the individual ligand peak integrations, and not, as described above, the average of all four ligand peaks. An example of the method used is given using the ^{1}Hnmr spectra shown in Fig. 3.1 and 3.3. From Fig 3.3 it can be seen that the ligand peak integration for the 3,3'-protons = 15.3, in order to compare this with the corresponding peak in the spectrum of the undeuteriated bpy shown in Fig. 3.1, this figure must be divided by two, (as 12mg bpy / 1 cm^3 $CDCl_3$ was used in this case). Therefore, the value of L = 7.7, the value of S = 1.7, the ratio of ligand to solvent peak, L/S = (7.7/1.7) = 4.5. By comparing this ratio with that of the undeuteriated bpy, (L/S = 10), it can be seen that the relative number of hydrogens present in the deuteriated sample is 2.2 times less than in the undeuteriated sample, the 3,3'-protons are, therefore 55% deuteriated.

Deuteriation of 2,2'-bipyridyl (bpy):

2,2'-bipyridyl (3g, 0.019mol) was added to 30cm^3 D_2O (deuteriation 99.9%) and the reaction mixture was allowed to react in the presence of the H-D exchange catalyst Pd/C (Aldrich, 10%Pd)(0.25g) in a teflon-coated steel high pressure reactor at 200^{0}C for 4 days. The contents of the reactor were then collected and filtered hot to remove the Pd catalyst and the Pd/C was washed with diethyl ether to remove any product present on it's surface. The D_2O was allowed to cool where upon the deuteriated bpy precipitated and was collected by vacuum filtration. Yield = (2.7g, 90%).
From the ^{1}Hnmr spectra the extent of deuteriation was calculated to be 95% (+/- 5%).
^{1}Hnmr ($CDCl_3$, ppm): 8.68 (s, 1H, H^6), 8.40 (s, 1H, H^3), 7.82 (s, 1H, H^4), 7.31 (s, 1H,H^5). [Fig. 3.1]
I.R. (KBr, cm^{-1}): 2366, 2267, 1551, 1522, 1329, 1283, 1242, 1027, 980, 817, 724, 660, 601, 578. [Fig 3.24]

The deuteriation of all the following polypyridyl ligands was carried out in essentially the same way as the deuteriation of bpy, with minor variations in the reaction time and the amount of Pd/C exchange catalyst used.

Deuteriation of 4,4'-dimethyl-2,2'-bipyridyl (dmbpy):

Dmbpy (3g, 0.016mol) was added to $30cm^3$ D_2O in the presence of 0.5g Pd/C. The reaction time was 4 days, after filtration the Pd/C was washed with acetone to remove any product remaining. The yield of deuteriated dmbpy was found to be quite low and after weighing of the Pd catalyst after filtration, it was ascertained that a considerable amount of the dmbpy was still present, but further extraction with acetone failed to remove the dmbpy. Soxhlet extraction with tetrachloromethane, in which dmbpy is soluble, also proved unsuccessful. Yield = (1.63g, 54%). From the ^{1}Hnmr the extent of deuteriation was calculated to be 98%.

^{1}Hnmr ($CDCl_3$, ppm): 8.51 (s, 1H, H^6), 8.19 (s, 1H, H^3), 7.11 (s, 1H, H^5), 2.38 (t, 3H, -CH_3). [Fig. 3.19]

I.R. (KBr, cm^{-1}): 2284, 2261, 1568, 1534, 1369, 1295, 966, 886, 830, 761, 654, 637. [Appendix Fig. 2]

Deuteriation of 1,10'-phenanthroline (phen):

Phen (3g, 0.016mol) was added to $30cm^3$ D_2O in the presence of 0.50g Pd/C. The reaction time was 6 days, after filtration the Pd/C was washed with acetone to remove any remaining product. On cooling of the D_2O the deuteriated phen rapidly precipitated. Yield = (2.7g, 90%). From the ^{1}Hnmr the extent of deuteriation was calculated to be 97%.

^{1}Hnmr ($CDCl_3$, ppm): 9.16 (s, 1H, $H^{2\&9}$), 8.23 (s, 1H, $H^{4\&7}$), 7.77 (s, 1H, $H^{5\&6}$), 7.61 (s, 1H, $H^{3\&8}$). [Appendix Fig. 4]

I.R. (KBr, cm^{-1}): 2258, 1642, 1555, 1468, 1335, 678, 642, 638, 606. [Appendix Fig. 6]

Deuteriation of 3-(pyridin-2-yl)-1,2,4-triazole (Hpytr):

Hpytr (3g, 0.02mol) was added to 30cm^3 D_2O in the presence of 0.5g Pd/C. The reaction time was 6 days, after filtration the Pd/C was washed with acetone. On cooling the deuteriated Hpytr precipitated and was collected in the usual manner, but it was very sticky and had to dried under vacuum overnight. Yield = (2.4g, 80%).
From the ^{1}Hnmr the extent of deuteriation was calculated to be 97%.
^{1}Hnmr ($CDCl_3$, ppm): 8.80 (s, 1H, pyridyl H^6), 8.27 (s, 1H, pyridyl H^3), 8.17 (s, 1H, triazole $H^{5'}$), 7.89 (s, 1H, pyridyl H^4), 7.42 (s, 1H, pyridyl H^5). [Fig. 3.21]
I.R. (KBr, cm^{-1}): 3143, 3064, 2942, 2838, 2270, 1574, 1550, 1446, 1330, 1220, 1135, 1007, 872, 665, 592. [Appendix Fig. 8]

Deuteriation of 3-(pyrazin-2-yl)-1,2,4-triazole (Hpztr):

Hpztr (3g, 0.02mol) was added to 30cm^3 of D_2O in the presence of 0.5g Pd/C.
The reaction time was 6 days, the Pd/C was washed with acetone and the deuteriated Hpztr that precipitated upon cooling of the D_2O was dried under vacuum overnight.
Yield = (2.4g, 80%). From the ^{1}Hnmr the extent of deuteriation was calculated to be 98%.
^{1}Hnmr $(CD_3)_2SO$, ppm) : 9.41 (s, 1H, pyrazyl H^6), 9.29 (s, 1H, pyrazyl H^3), 8.80 (d, 2H, triazole $H^{5'}$ & pyrazyl H^5). [Appendix Fig. 10]
I.R. (KBr, cm^{-1}): 3056, 2951, 2834, 2812, 2757, 2362, 2279, 1447, 1347, 1330, 1252, 1175, 1014, 975, 875, 681, 598. [Appendix Fig. 12]

Deuteriation of 3,5 bis(pyridin-2-yl)-1,2,4-triazole (Hbpt):

Hbpt (2.0g, 0.007mol) was added to 20cm^3 of D_2O in the presence of 0.33g Pd/C. The reaction time was 6 days, the Pd/C was washed several times with hot ethanol to remove any remaining deuteriated Hbpt. Also after filtration the D_2O was distilled to remove any deuteriated Hbpt which remained in solution, but the yield was still quite low. Yield = (1.28g, 64%). From the ^{1}Hnmr the extent of deuteriation was calculated to be 95%.
^{1}Hnmr ($(CD_3)_2SO$, ppm): 8.71 (s, 1H, H^6), 8.16 (s, 1H, H^3), 7.98 (s, 1H, H^4) , 7.49 (s, 1H, H^5). [Appendix Fig. 14]
I.R. (KBr, cm^{-1}): 3053, 2940, 2851, 2798, 2371, 2258, 1576, 1552, 1451, 1327, 1303, 1155, 1125, 1000, 923, 822, 704, 603. [Appendix Fig. 16]

Deuteriation of 3,5 bis(pyrazin-2-yl)-1,2,4-triazole (Hbpzt):

Hbpzt (1.5g, 0.005mol) was added to 15cm^3 of D_2O in the presence of 0.25g Pd/C. The reaction time was 6 days, the Pd/C was washed several times with hot ethanol to remove any remaining deuteriated Hbpzt and as above distillation of the D_2O after filtration was carried out, but the resulting yield was still low. Yield = (0.73g, 49%).
From the ^{1}Hnmr the extent of deuteriation was calculated to be 93%.
^{1}Hnmr ($(CD_3)_2SO$, ppm): 9.36 (s, 1H, H^6), 8.78 (d, 2H, H^3 & H^5). [Appendix Fig. 18]
I.R. (KBr, cm^{-1}): 3043, 2922, 2837, 2735, 2644, 2564, 2291, 2268, 1522, 1448, 1300, 1271, 1242, 1180, 1123, 986, 861, 753, 616, 542. [Appendix Fig. 20]

Deuteriation of 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4'-triazole (Hppt):

Hppt (1.5g, 0.005mol) was added to 15cm^3 of D_2O in the presence of 0.25g Pd/C. The reaction time was 6 days, the Pd/C was washed with hot ethanol to try to remove any deuteriated product remaining but as the yield was still low it was concluded that the

deuteriated Hppt had stayed in solution. Distillation of the D_2O after filtration however yielded only a minute quantity of product. Yield = (0.55g, 37%).

From the ^{1}Hnmr the extent of deuteriation was calculated to be 96%.

^{1}Hnmr ($(CD_3)_2SO$, ppm): 9.35 (s, 1H, pyrazine H^3), 8.78 (s, 1H, pyridyl H^6), 8.74 (d, 2H, pyrazine H^6 & H^5), 8.20 (s, 1H, pyridyl H^3), 8.03 (s, 1H, pyridyl H^4), 7.56 (s, pyridyl H^5). [Appendix Fig. 22]

I.R. (KBr, cm^{-1}): 3040, 2934, 2828, 2266, 2207, 2134, 1546,1427, 1354, 1249, 1176, 1123, 978, 879, 826, 680, 575. [Appendix Fig. 24]

Deuteriation of dipyrido[3,2-*a*:2,'3'-*c*]phenazine(dppz):

Dppz (0.3g, 0.00mol) was added to 15cm^3 of D_2O in the presence of 0.08g Pd/C. The reaction time was 6 days, upon cooling the deuteriated dppz precipitated, the Pd/C was washed with dichloromethane to remove any remaining deuteriated dppz. Yield = (0.283g, 94%). From the ^{1}Hnmr the extent of deuteriation was calculated to be 97%.

^{1}Hnmr ($CDCl_3$, ppm): 9.56 (s, 1H, $H^{6\&9}$), 8.35 (s,1H, $H^{2\&13}$). [Fig. 3.23]

I.R. (KBr, cm^{-1}): 2263, 1551, 1521, 1454, 1380, 1292, 1139, 979, 928, 816, 578. [Appendix Fig. 26]

Deuteriation of [3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole] = [L_1]:

L_1 (1.5g, 0.005mol) was added to 15cm^3 of D_2O in the presence of 0.25g Pd/C. The reaction time was 6 days, isolation of the product was not possible as the ligand had decomposed leaving a black 'sludge' at the bottom of the reaction vessel.

Deuteriation of [3-(3,4-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole] = [L_6]:

L_6 (1.5g, 0.005mol) was added to 15cm^3 of D_2O in the presence of 0.25g Pd/C. The reaction time was 6 days, isolation of the product was not possible as the ligand had decomposed leaving a black 'sludge' at the bottom of the reaction vessel.

2.3 Experimental Procedures (Part 2).

Synthesis of [Ru(bpy)$_2$(3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole)]$^+$ = [Ru(bpy)$_2$(L_1)]$^+$[21]:

All of the following synthetic steps, with exception of the step 2, were carried out according to procedures detailed in the PhD Thesis of Tia Keyes. [21]

Step 1 Synthesis of pyridine-2-carboximidehydrazide [21]:

2-Cyanopyridine (0.20mol, 21g) was melted and dissolved in 60cm^3 of ethanol, an excess of hydrazine monohydrate (0.24mol, 11.6cm^3) was added and the solution was stirred overnight and then stored at 4^{0}C for three days. The product crystallised as white needles and was collected by vacuum filtration, and washed twice with diethyl ether to remove any unreacted cyanopyridine. The product was stored under vacuum to avoid decomposition. Yield = (0.12mol, 60%).

^{1}Hnmr ($CDCl_3$, ppm) 8.44 (d, 1H, H_6), 7.96 (d, 1H, H^3), 7.63 (t, 1H, H^4), 7.20 (t, 1H, H^3), 5.32 (s, 2H, N-N-H_2), 4.48 (s, 2H, N-H_2). [Appendix Fig. 27]

Step 2 Synthesis of 2,5-dimethoxybenzoyl-chloride [39]:

Prior to carrying out the reaction, a short-path distillation apparatus was set-up which was connected to a vacuum line. 2,5-Dimethoxybenzoic acid (0.02 mol, 3.66g), previously dried in a desiccator was placed in a 25cm^3 round bottomed flask and phosphorous

pentachloride (0.02mol, 4.58g) was added. The short-path distillation apparatus was then connected to the neck of the flask, and the mixture stirred until reaction was complete, as judged by no more vapour observed emerging from the end of the tube. The vacuum was then turned on slowly, and the temperature of the silicon bath was slowly raised to around 150^0C, at which point the phosphorusoxychloride, which was a by-product of the reaction was collected. The temperature of the silicon-bath was then raised to maximum, and the acidchloride was distilled over. Due to the high boiling point of the acidchloride (bp=290^0), distillation, even under vacuum proved very difficult and it was necessary to turn off the water to the condenser and insulate the whole apparatus in order to avoid crystallisation of the acid chloride. However, it was sometimes necessary to use a hair-drier to get the acidchloride from the condenser into the receiving flask. Due to the unstable nature of the acidchloride, the amount of product required for the next step (0.01mol, 2.00g) was weighed out, still in its liquid form, and used immediately.

Step 3 Synthesis of Acylamidrazone. [21]

Pyridine-2-carboximidehydrazide (0.01mol, 1.36g) and triethylamine (0.015mol, 1.5g) were placed in a 250cm^3 round bottomed flask to which 30cm^3 of dried THF was added. The solution was vigorously stirred and cooled down to 0^0C with an ice-bath. 2,5-Dimethoxybenzoylchloride (0.01mol, 2.00g) was dissolved in 10cm^3 of dried THF and added slowly to mixture in the flask. The reaction was exothermic and white vapours evolved from the mixture. The solution turned opaque after the first few drops were added and a white /yellow solid precipitated. When the addition was complete, the solution was refluxed for approximately 5 minutes, the solution was allowed to cool and was then reduced to half by means of a rotary evaporator. The same amount of water was then added and the flask was stored at 4^0C overnight. The white precipitate was collected by filtration and washed twice with 25cm^3 water and then dried under vacuum to remove any residual water. The melting point was very broad between 120^0 and 140^0C. Yield = (7.5mmol, 75%).

^{1}Hnmr ($(CD_3)_2SO$, ppm): 10.13 (s, 1H, ^{1}N-H), 8.59 (d, 1H, H^6), 8.15 (d, 1H, H^3), 7.90 (t, 1H, H^4), 7.48 (t, 1H, H^5), 7.12 (d, 1H, $H^{3''}$), 7.06 (m, 2H, $H^{6''}$ & $H^{4''}$), 6.73 (s, 2H, $^4NH_2$), 3.80 (s, 3H, OME), 3.75 (s, 3H, OMe). [Appendix Fig 28]

Step 4 Synthesis of 3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole(L_1)[21]:

The acylamidrazone was placed in a small round bottomed flask and a minimum amount of ethylene glycol was added, the mixture was then refluxed at 220^{0}C for approximately three hours. The flask was then removed from the heat and allowed to cool slowly. When room temperature was reached the flask was placed in the fridge overnight. If at this point the compound had not precipitated, the process was initiated by scratching, which caused the precipitation of a yellow-white solid which was collected by vacuum filtration and washed thoroughly with 2 x 30cm^3 of water and 25cm^3 ether. The cyclised ligand was dried overnight in a desiccator. Overall yield = (0.005mol, 60%), m.p.=150-160^{0}C. The ^{1}Hnmr data in $(CD_3)_2SO$ is listed below, cyclisation was complete if the peaks at around 10ppm and below 7ppm have disappeared. Recrystallisation of the cyclised ligand was carried out in ethanol.

^{1}Hnmr ($(CD_3)_2SO$, ppm): 8.68 (d, 1H, H^6), 8.15 (d, 1H, H^3), 7.94 (t, 1H, H^4), 7.71 (d, 1H, $H^{6''}$), 7.12 (t, 1H, H^5), 7.06 (d, 1H, $H^{3''}$), 6.73 (d, 1H, $H^{4''}$), 3.92 (s, 3H, OME), 3.78 (s, 3H, OMe), [Appendix Fig. 29]

Step 5 Synthesis of [Ru(bpy)$_2$(3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole)]$^+$ = [Ru(bpy)$_2$(L_1)]$^+$[21]:

This complex was synthesised according to a method described in the Ph.D thesis of Tia Keyes. [21] (3-(2,5-Dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole) (0.35g, 1.27 mmol) was heated to reflux in 50cm^3 of ethanol / water (1:1 v/v). When the ligand had fully dissolved $[Ru(bpy)_2Cl_2].2H_2O$ (0.66g, 1.27 mmol), was added slowly to the

refluxing solution. The apparatus was then covered in aluminium foil to avoid photo-induced reactions, and the mixture refluxed for 5 hr. After the solution had cooled down the whole reaction mixture was filtered and the volume reduced to ca. 15cm^3, to which several drops of concentrated NH_4PF_6 were added. The flask was kept at 4^{0}C overnight. The dark red precipitate was collected by filtration and purified by recrystallisation from acetone/water (1:1 v/v). Due to the structural complexity of this complex, the ^{1}Hnmr spectrum was obtained in CD_3CN at high pH , as the deprotonated complex yields a more finely structured spectrum. Yield = (0.63g, 59%). The ^{1}Hnmr spectrum was very highly structured. [Fig. 4.9]
HPLC: peak at 2.46 min. [Appendix Fig. 30]

Step 6 Synthesis of [Ru(bpy-d_8)$_2$(3-(2,5-dimethoxyphenyl)-5(-pyridin-2-yl))-1,2,4-triazole)]$^+$ = [Ru(bpy-d_8)$_2$(L_1)]$^+$:

This complex was synthesised in exactly the same manner as the undeuteriated complex, using [Ru(bpy-d_8)$_2$$Cl_2$].2$H_2O$ in place of [Ru(bpy)$_2$$Cl_2$].2$H_2O$. Yield = (0.59g, 55%). ^{1}Hnmr (CH_3CN, ppm): 8.43 (d, 1H, pyridyl H^3), 8.06 (t, 1H, pyridyl H^4), 7.63 (d, 1H, pyridyl H^6), 7.50 (s, 1H, H$^{6'}$), 7.36 (t, 1H, pyridyl H^5), 7.07 (d, 2H, H$^{3'}$ & H$^{4'}$), 3.80 (s, 3H, OMe), 3.71 (s, 3H, OMe). [Fig 4.10]
HPLC: peak at 2.23 min. [Appendix Fig. 31]

The following complexes are discussed in chapter 4; [Ru(bpy)$_2$(pztr)]$^+$, (pztr = (3-(pyrazin-2-yl)-1,2,4-triazole)), [Ru(bpy)$_2$(ppt)]$^+$, (ppt = (3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole)[40], [Ru(bpy)$_2$(3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4'-triazole)]$^+$ = [Ru(bpy)$_2$(L_1)]$^+$, and [Ru(phen)$_2$(3-(3,4-dimethoxy-phenyl)-5-(pyridin-2-yl)-1,2,4-triazole)]$^+$ = [Ru(phen)$_2$(L_6)]$^+$ [41]. All complexes were prepared by standard procedures as reported in the literature.

Chapter 3

Deuteriation of polypyridyl ligands.

3. Deuteriation of 2,2'-bipyridyl and other polypyridyl ligands.

3.1 *Introduction.*

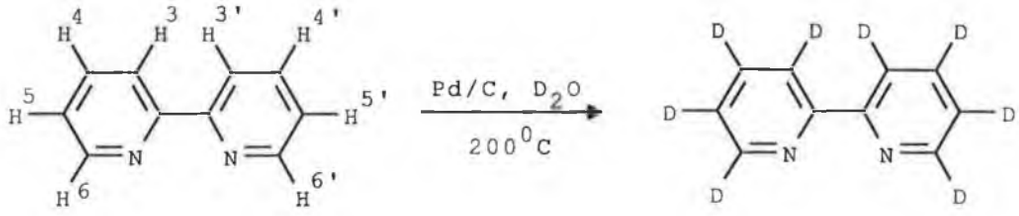
Ru(II) polypyridyl complexes are currently provoking a huge amount of interest, this interest being largely due to their potential utility as components in energy conversion devices. For this potential to be fully realised, it will be necessary to have a thorough, and in-depth knowledge of the excited states of these compounds. As described previously in chapter 1, substitution of the polypyridyl ligands with their deuteriated analogues can reveal valuable information on the nature and location of their excited states. [10-17] Deuteriation has also proved to be very useful in the deconvolution of the ^{1}Hnmr spectra of these complexes, which are otherwise extremely difficult to interpret due to the presence of a large number of bpy protons. [25]

Despite the obvious applications of deuteriated polypyridyl ligands, the time-consuming and expensive nature of their synthesis has, so far, restricted their use. The deuteriation method proposed by Keyes [21], decribed in the Introduction, is a significant improvement on previous methods as it offers a simple, single-step procedure for the synthesis of deuteriated bpy. Further development of this method and investigation into its possible application to other polypyridyl ligands is therefore of obvious importance.

The main aim of this work was to improve upon the Keyes *et al.*,[21] deuteriation method for 2,2-bipyridyl (bpy) described previously, in order to achieve this it was neccessary to optimise the reaction conditions. The first part of this section details the optimisation studies carried out on the reaction time and temperature and on the quantity of Pd/C exchange catalyst. The second part describes the application of the method to other polypyridyl ligands.

3.2 *Optimisation of the Reaction Time.*

In the report by Keyes *et al.*, [21] the reaction time required to deuteriate 3g bpy in 30 cm^3 D_2O in the presence of 0.5g Pd/C at 200^0C, as shown below, was 8 days.



It was decided to see what effect halving both the reaction time and the amount of Pd/C would have on the % deuteriation of the bpy, this experiment revealed that reducing the reaction time from 8 days to 4 days, and the amount of Pd/C catalyst from 0.50g to 0.25g, had no adverse effect on the % deuteriation, which from ^{1}Hnmr was calculated to be approximately 96%. [Figure 3.2]

In order to obtain more detailed information on the progression of deuteriation, it was decided to obtain a sample of deuteriated bpy after 1, 2, 3 and 4 days. Due to the highly hydroscopic nature of D_2O exposure to air had to be kept to a minimum, it was, therefore not possible to work-up the reaction in the usual manner (ie. filtration etc.), so the samples were simply obtained by cooling the reaction vessel to a sufficiently low temperature to allow a sample to be taken with a glass rod, after which the reaction vessel was quickly resealed and replaced in the oven at 200^0C. These precautions proved inadequate however, as can be clearly seen from an examination of the ^{1}Hnmr spectra of the samples, [Fig. 3.3-3.6].

Table 3.1 % Deuteriation values for 2,2'-bipyridyl at 200^{0}C, using 0.25g Pd/C per 3g bpy in 30 cm^3 D_2O, at a various reaction times monitored by sampling.

Reaction time/days	6,6-protons % d	3,3'-protons % d	4,4'-protons % d	5,5'-protons % d	Overall % d
1	97	55	88	93	83
2	96	51	91	95	84
3	96	60	92	95	86
4	96	62	92	95	86

The spectra show that after day 1 there is no significant increase in %d of bpy and the expected 96% overall deuteriation after day 4, is not achieved. The results indicate that opening of the reaction vessel, even for such a short length of time, slows down the rate of deuteriation considerably. Despite the inaccuracy of the data obtained from the ^{1}Hnmr spectra , the experiments did reveal that the first position to be deuteriated is H6,6', followed by H5,5' and H4,4' with the H3,3' position being considerably slower. [Table 3.1]

As the above experiment had shown that it was not possible to open the reaction vessel without interfering with the rate of deuteriation, the only way to obtain accurate data was to carry out four separate experiments with four separate reaction times of 1, 2, 3 and 4 days. [Table 3.2]

Table 3.2 % Deuteriation values for 2,2'-bipyridyl at 200^{0}C, using 0.25g Pd/C per 3g bpy in 30 cm^3 D_2O, at various reaction times.

Reaction time/days	6,6'-protons % d	3,3'-protons % d	4,4'-protons % d	5,5'-protons % d	Overall % d
1	97	55	88	93	83
2	96	86	95	95	93
3	95	94	95	95	95
4	96	95	96	96	96
6	95	95	95	95	95
3 * 2	99	99	99	99	99

The ^{1}Hnmr spectra show that after day 1, [Fig. 3.3] both the signal at 8.66pm due to the 6,6'-protons, and that at 7.28ppm due to the 5,5'-protons have collapsed to singlets, due to the fact that the protons at both positions have been exchanged and are therefore, no longer being split by each other. The 5,5'-signal is broad as it is still experiencing some splitting from the unexchanged protons at the 4,4'-position. The triplet of doublets at 7.80ppm due to the 4,4'-protons is still present but the signal has decreased considerably by comparison with the same signal in the spectrum of undeuteriated bpy. The signal at 8.36ppm due to the 3,3'-protons is still strong, but H/D exchange of the 4,4'-protons has reduced the splitting, with the result that the signal is practically a singlet. Comparison of the integration of each peak with the corresponding integration in the spectrum of undeuteriated bpy, [Fig. 3.1] shows that the ratio of H6,6' : H3,3' : H4,4' : H5,5' changes from 1:1:1:1 for undeuteriated bpy to 1:15:4:2 for the sample after 1 day. The ^{1}Hnmr spectra of the samples after 2, 3, and 4 days [Fig. 3.7, 3.8 and 3.2] show that as deuteriation progresses the remaining splitting disappears and the integration of the peaks due to the 4,4'- and 3,3'-protons gets smaller, with the integration of all peaks being 1 after 3 days. After day 1, H6,6' and H5,5' were already >90% deuteriated, H4,4' was >80% deuteriated, while H3,3' was only 50% deuteriated. After day 2, H6,6', H5,5' and

H4,4' were all >/= 95% deuteriated, while H3,3' was still only 86% deuteriated. By day 3, 95% deuteriation had been reached at all positions.

It appears that, once approximately 95% deuteriation was achieved at a position, the % deuteriation at that position ceased to increase with time. This can be seen clearly from the results of the experiments carried out for 4 and 6 days, [Table 3.2][Fig. 3.2 and 3.9] as there is no significant improvement, at any of the positions, over the results from day 3. If, however after 3 days the Pd/C and D_2O were removed and the procedure was repeated with fresh Pd/C and D_2O for a further 3 days [Table 3.2][Fig. 3.10] the % deuteriation increases from 95% to 99%.

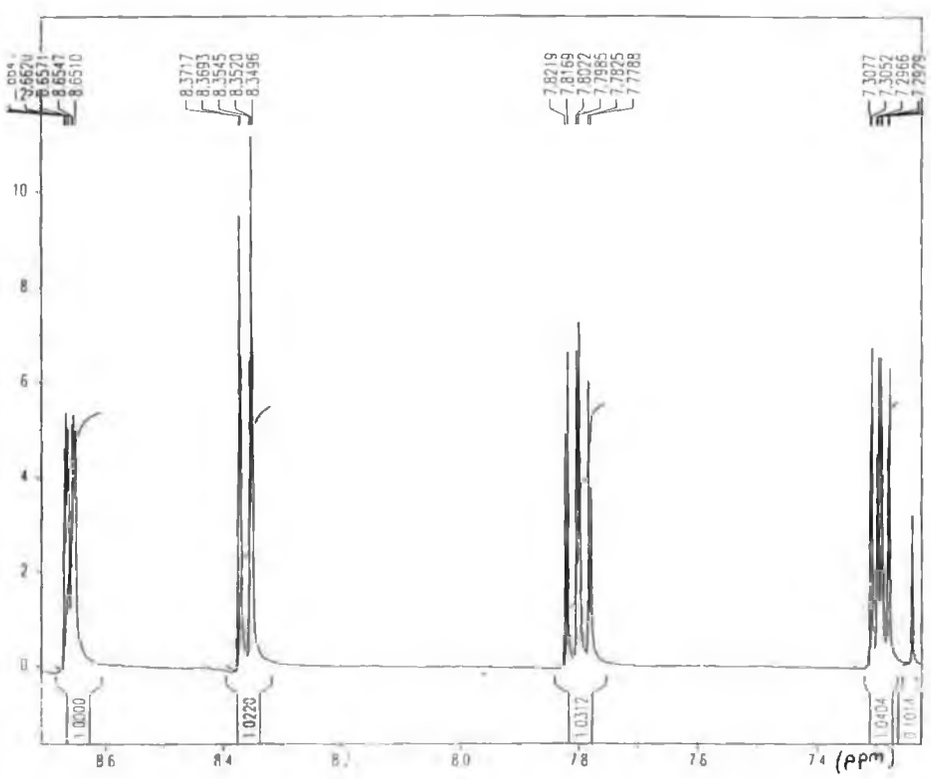


Figure 3.1 ^{1}Hnmr of 2,2'-bipyridyl (bpy-h_8).

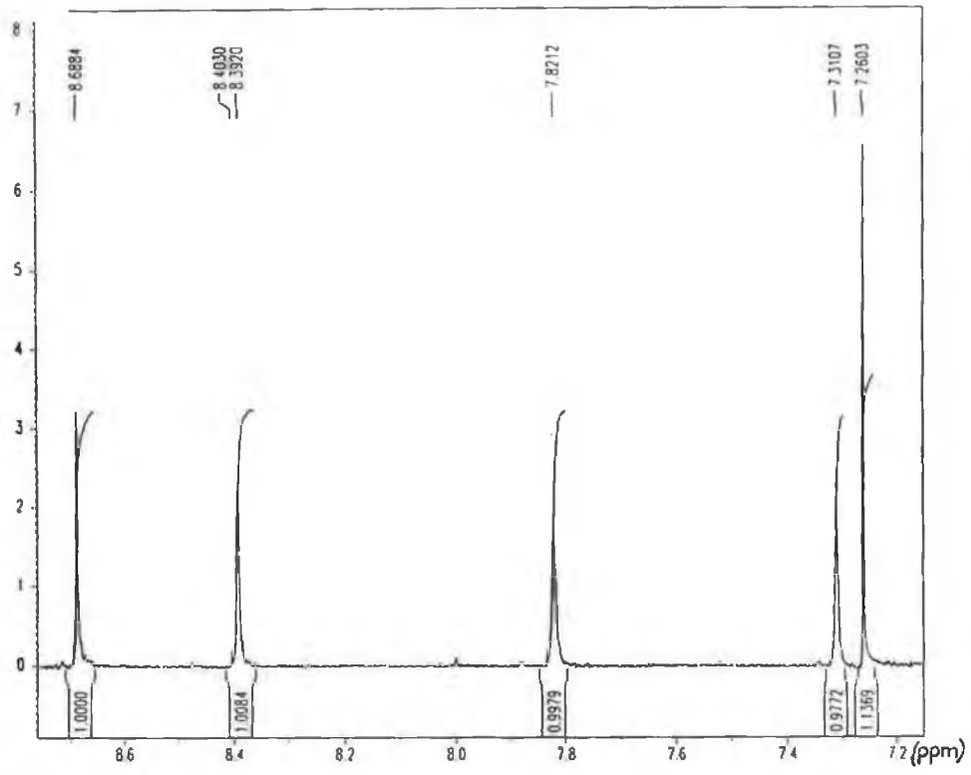


Figure 3.2 ^{1}Hnmr of bpy after 4 days at 200^{0}C using 0.25g Pd/C - (96%d).

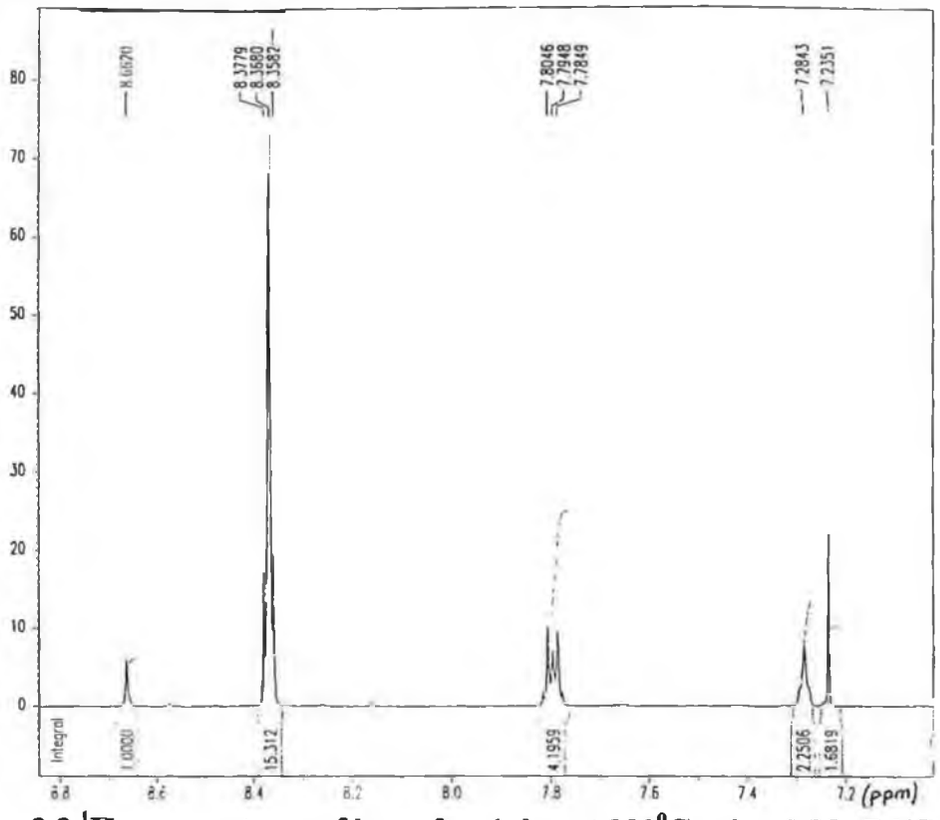


Figure 3.3 ^{1}Hnmr spectrum of bpy after 1 day at 200^{0}C using 0.25g Pd/C - (83%d).

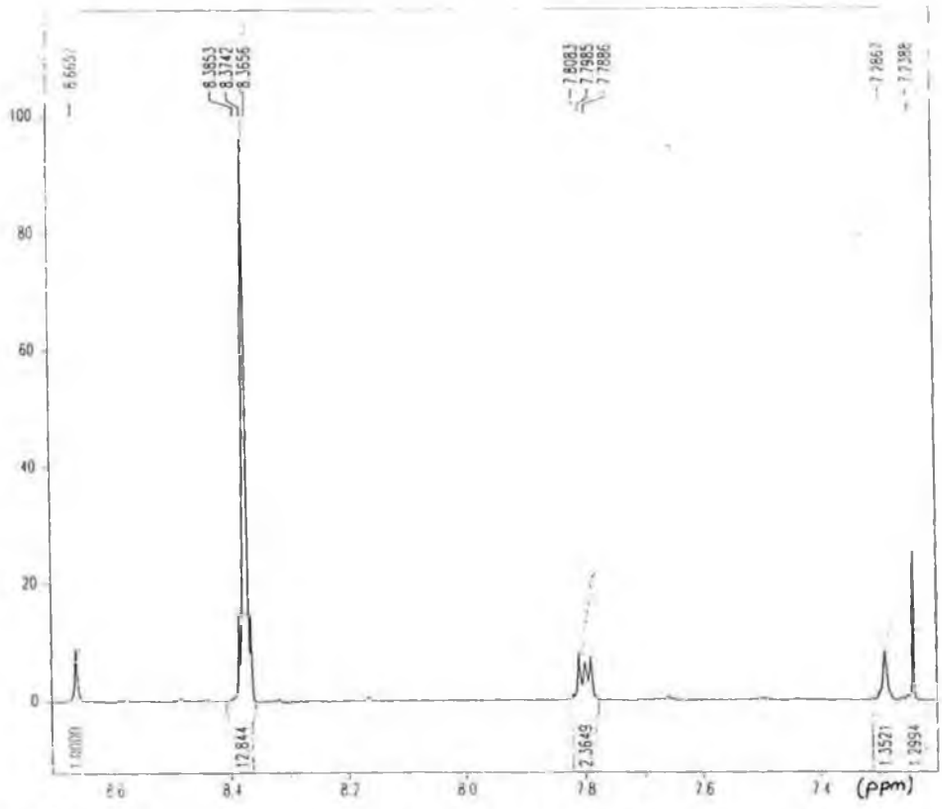


Figure 3.4 ^{1}Hnmr spectrum of bpy after 2 days at 200^{0}C using 0.25g Pd/C - (84%d).

(after reaction vessel had been opened)

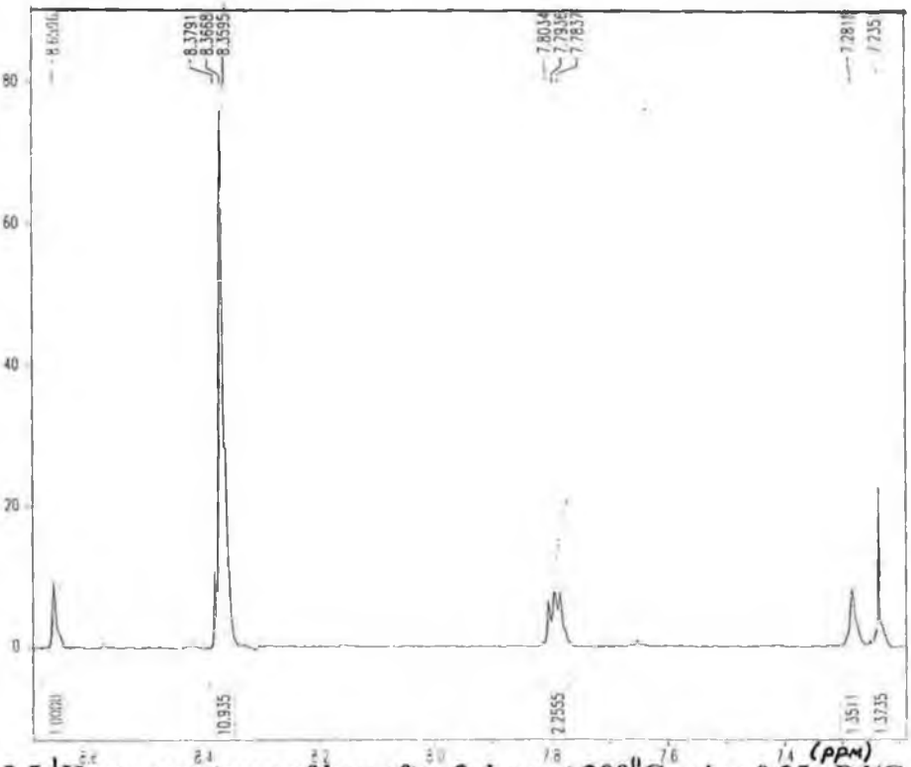


Figure 3.5 ^{1}Hnmr spectrum of bpy after 3 days at 200^{0}C using 0.25g Pd/C - (86%d).

(after reaction vessel had been opened).

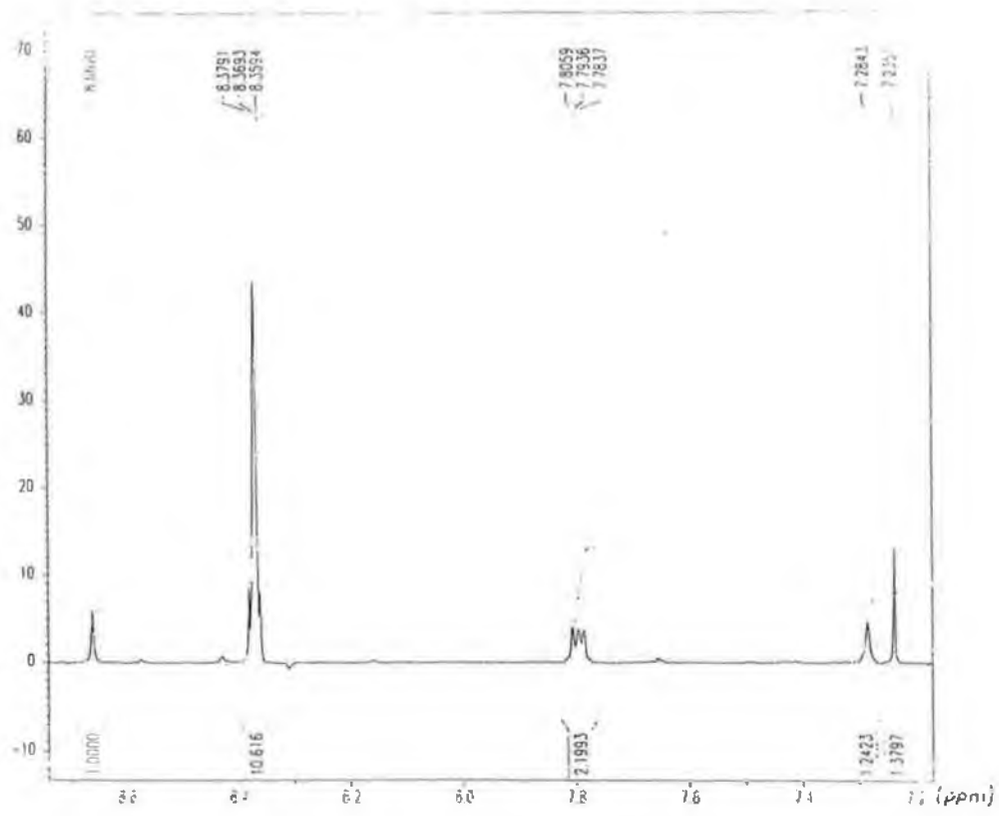


Figure 3.6 ^{1}Hnmr spectrum of bpy after 4 days at 200^{0}C using 0.25g Pd/C - (86%d).

(after reaction vessel had been opened)

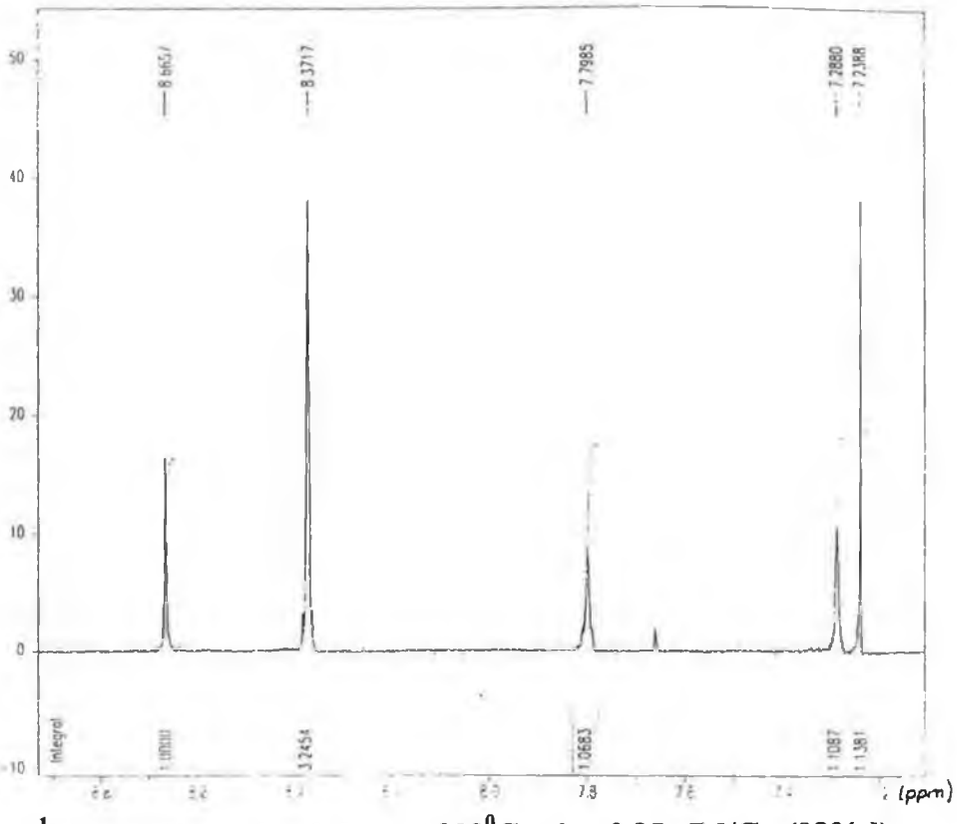


Figure 3.7 ^{1}Hnmr of bpy after 2 days at 200^{0}C using 0.25g Pd/C - (93%d).

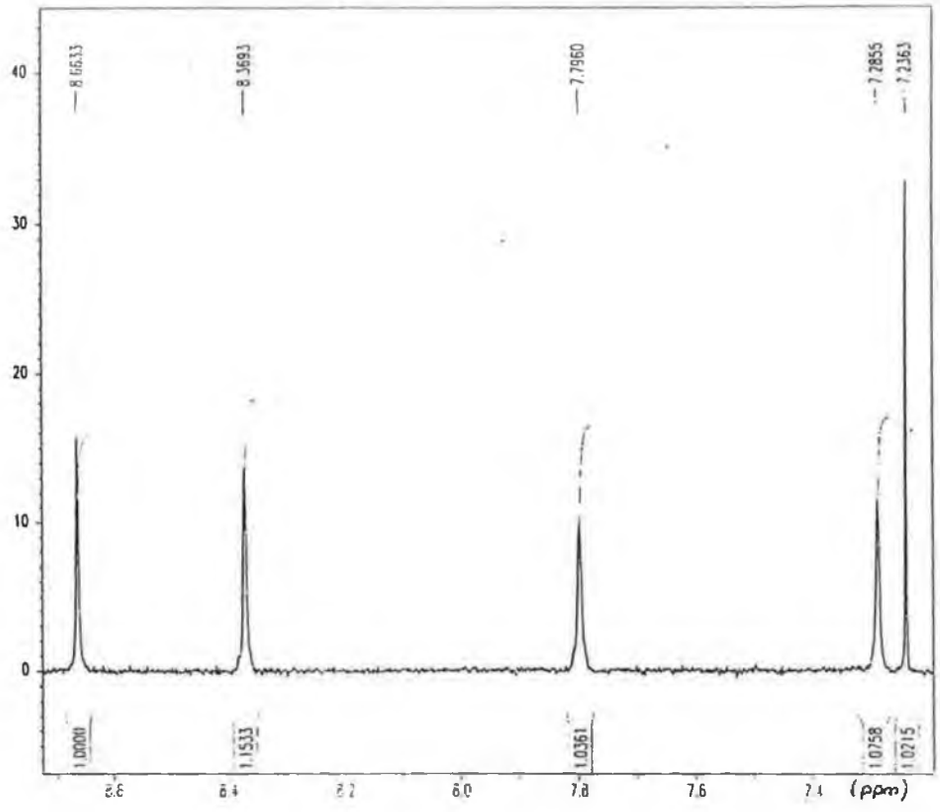


Figure 3.8 ^{1}Hnmr of bpy after 3 days at 200^{0}C using 0.25g Pd/C - (95%d).

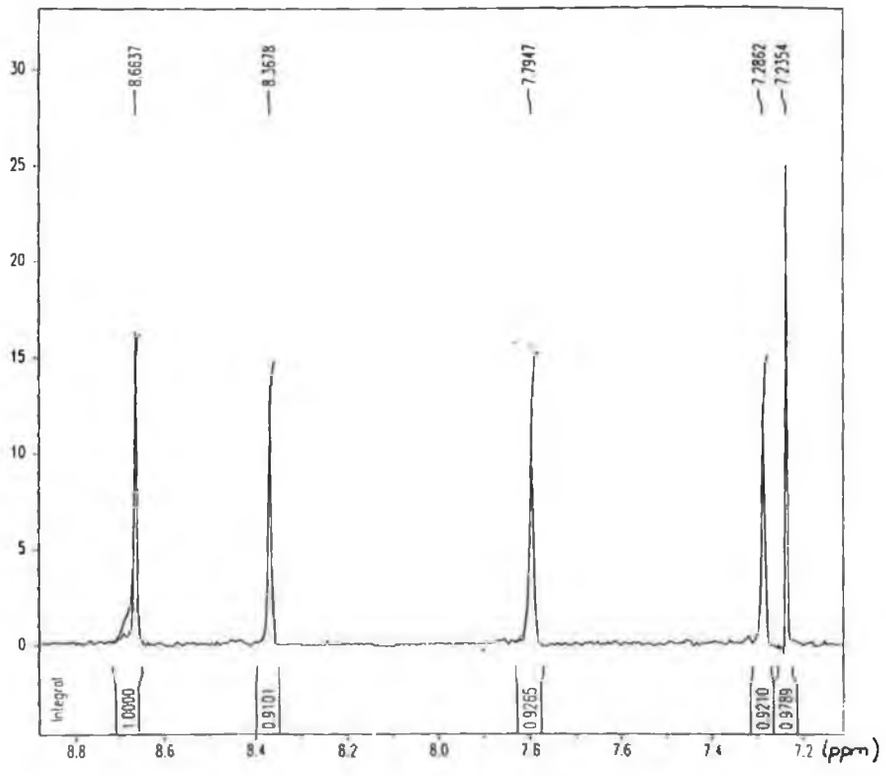


Figure 3.9 ^{1}Hnmr of bpy after 6 days at 200^{0}C using 0.25g Pd/C - (95%d).

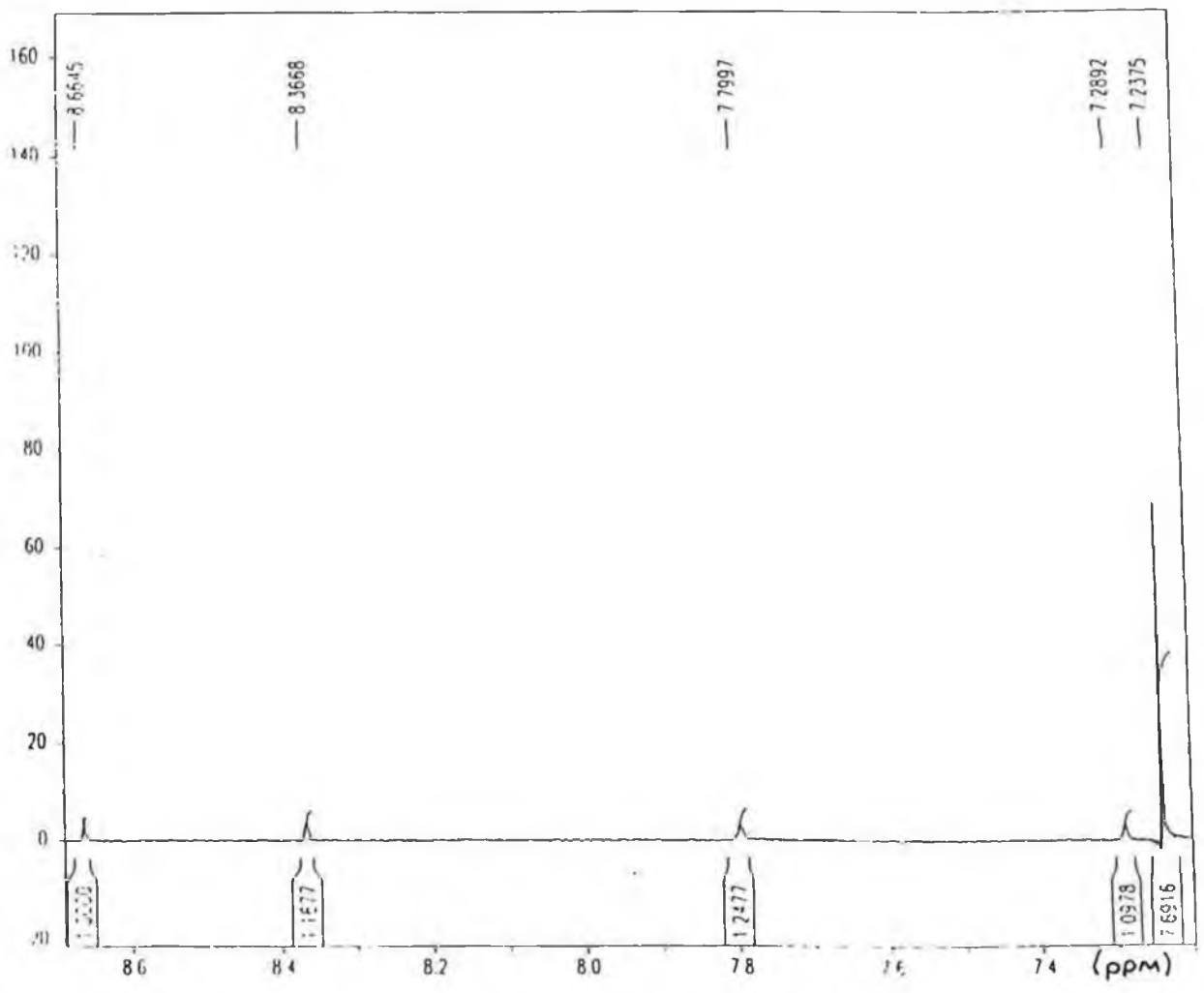


Figure 3.10 ^{1}Hnmr of bpy after 3x2 days at 200^{0}C using 0.25g Pd/C - (99%d).

3.3 *Optimisation of the Reaction Temperature.*

Having ascertained the optimum reaction time, the next condition under investigation was the reaction temperature. It was decided to carry out the reaction for 3 days using 0.25g Pd/C at 200^0, 180^0, 160^0, and 140^0C to see how the rate of deuteriation varied with decreasing temperature.[Table 3.3]

Table 3.3 % Deuteriation values for 2,2'-bipyridyl after 3 days, using 0.25g Pd/C per 3g bpy in 30 cm^3 D_2O, at various temperatures.

Temp/ ^{0} C	6,6'-protons % d	3,3'-protons % d	4,4'-protons % d	5,5'-protons % d	Overall % d
200	96	95	96	96	96
180	97	84	96	96	93
160	97	41	65	81	71
140	23	0	0	0	0

Figure 3.11 shows the ^{1}Hnmr spectrum of bpy after 3 days at 180^0C, it is clear that only the 3,3' position has been affected significantly by the decrease in temperature, the integration of this peak is no longer equivalent to the other three ligand peak integrations, the relative number of hydrogens at the 3,3' position is now approximately four times greater than at the other three positions. All four peaks, although they have broadened slightly compared with the corresponding peaks in the ^{1}Hnmr spectrum of bpy after 3 days at 200^0C, [Fig. 3.8] remain unsplit, illustrating the fact that the extent of deuteriation at the 6,6', 5,5', and 4,4' positions is unaffected by the change in temperature.

Figure 3.12 shows the ^{1}Hnmr spectrum of bpy after 3 days at 160^0C, this spectrum shows a considerable deterioration in the efficiency of hydrogen/deuterium exchange at all but

the 6,6' position, this deterioration is shown both by the changes in the integrations of the three peaks, and by the fact that the peaks are now split, due to the increase in the number of hydrogens present at each position. The integration is no longer equal at all three positions, the relative number of hydrogens is now greatest at the 3,3' position, (17.26) followed by the 4,4', (10.27) and 5,5' position, (5.54), this data would seem to back up the trend revealed previously in the time dependent studies.

Figure 3.13 shows the ^{1}Hnmr spectrum of bpy after 3 days at 140^{0}C, which is, essentially the spectrum of undeuteriated bpy, all peaks are now split, and the integrations, of all but the peak due to the 6,6' protons, are once again approximately equivalent, the integration of the 6,6' is 1.4 times less than that of the other three peaks, indicating that deuteriation is still taking place at this position.

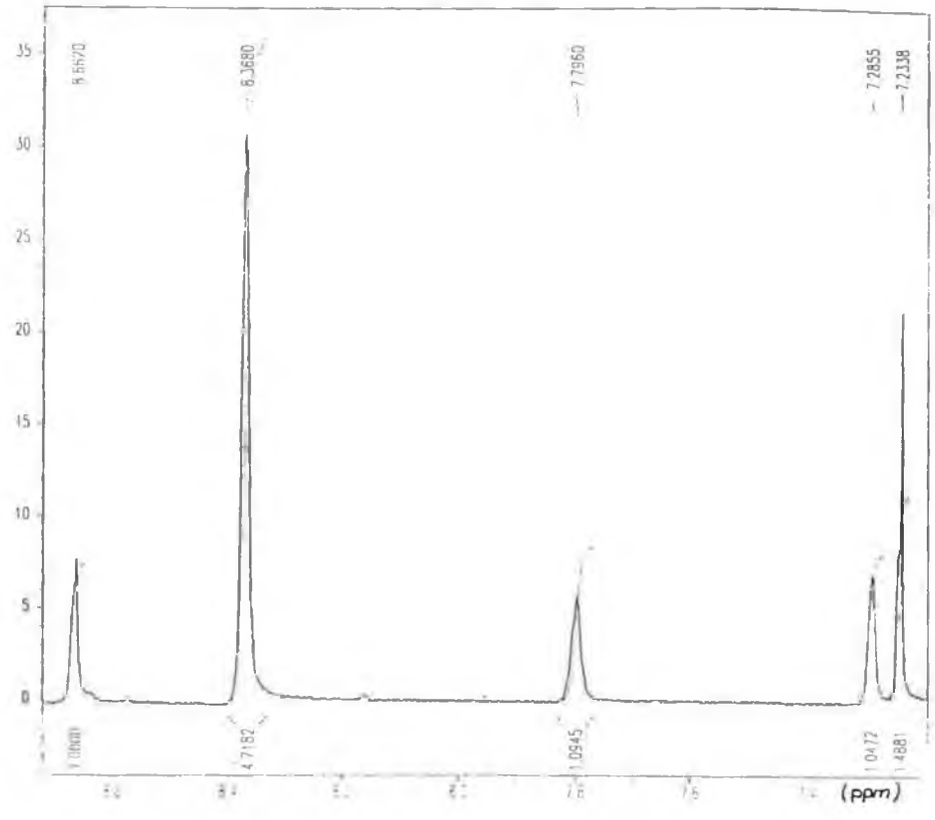


Figure 3.11 ^{1}Hnmr of bpy after 3 days at 180^{0}C using 0.25g Pd/C - (93%d).

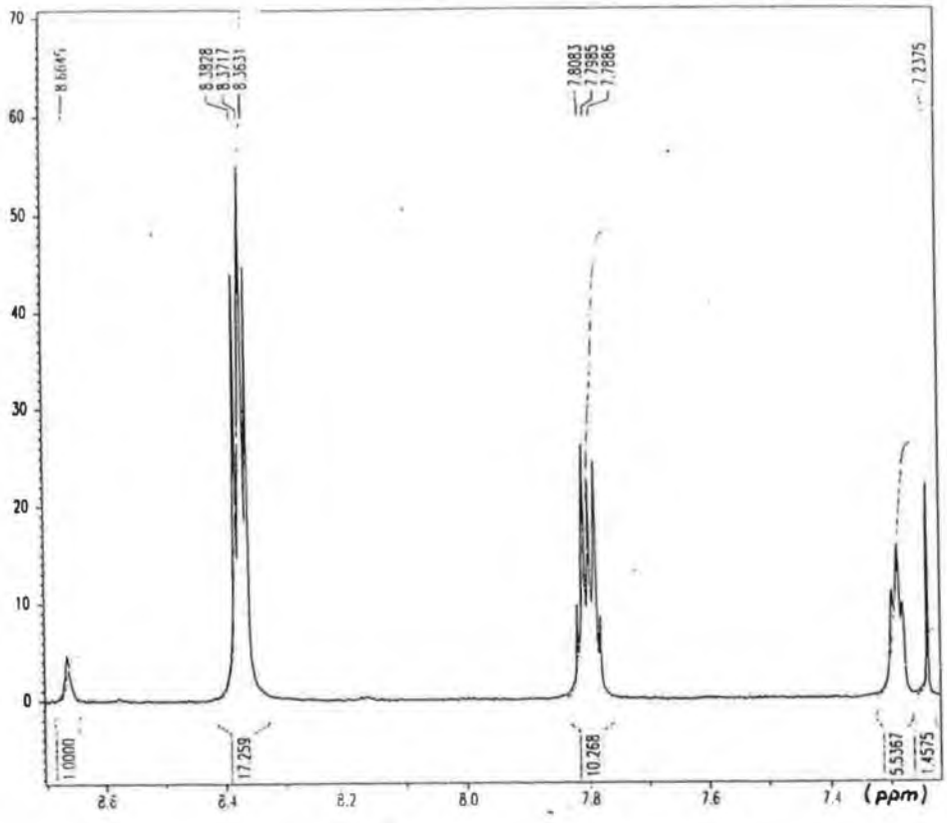


Figure 3.12 ^{1}Hnmr of bpy after 3 days at 160^{0}C using 0.25g Pd/C - (71%d).

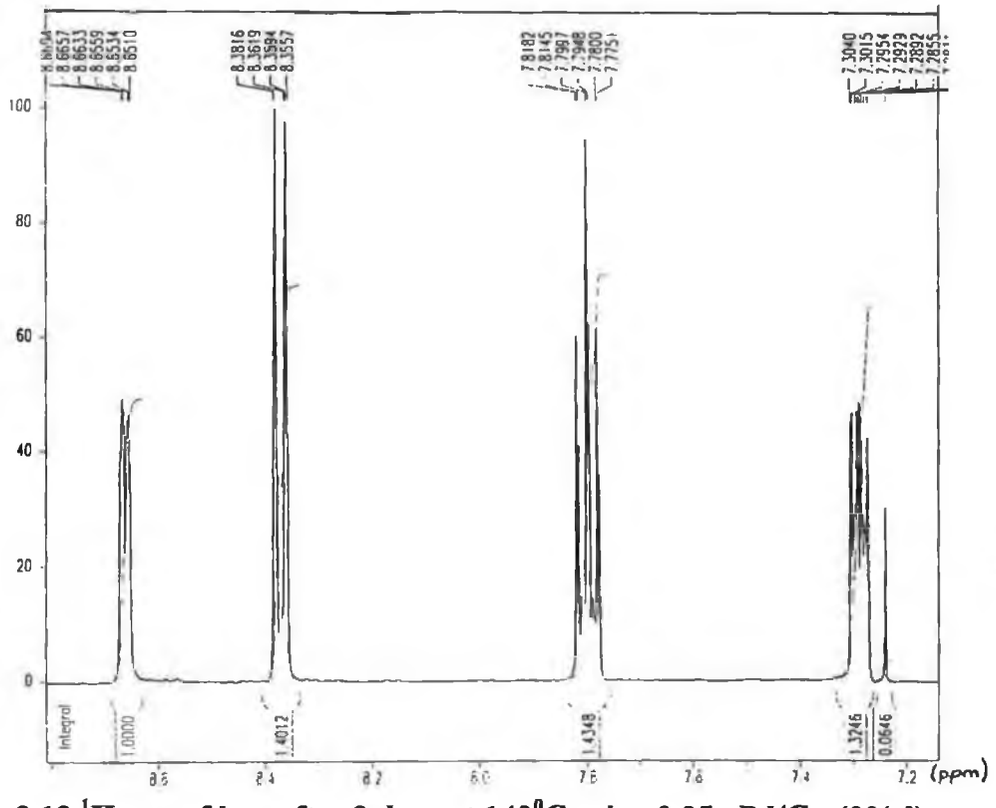


Figure 3.13 ^{1}Hnmr of bpy after 3 days at 140^{0}C using 0.25g Pd/C - (0%d).

These studies have shown that at 200^0C there was no significant difference in the final % deuteriation when the amount of Pd/C was reduced from 0.50g (per 3g bpy), to 0.25g, [Fig 3.14] but it was unknown whether this would change if the reaction was carried at lower temperatures. So the above temperature variation experiments were repeated using 0.5g Pd/C per 3g bpy.[Table 3.4]

Table 3.4 % Deuteriation values for 2,2'-bipyridyl after 3 days, using 0.50g Pd/C per 3g bpy in 30 cm^3 D_2O, at various temperatures.

Temp/ ^{0} C (0.50g Pd/C)	**6,6'-protons % d**	**3,3'-protons % d**	**4,4'-protons % d**	**5,5'-protons % d**	**Overall % d**
200	98	98	98	98	98
180	97	97	97	97	97
160	97	96	97	97	97
140	83	39	44	55	55

On examination of the ^{1}Hnmr spectra [Fig. 3.14-3.17], it can be seen that there is no appreciable change, in either the integration, or the splitting of the ligand peaks at any position, in any of the spectra, until the temperature was lowered to 140^0C, at which point there was a significant drop in % deuteriation at all four positions. This drop is illustrated by the appearance of splitting, and an increase in the ligand peak to solvent peak ratio at all positions.[Fig. 3.17] Although there is no splitting at the 6,6' position, the peak is considerably broader than the corresponding peak in the previous three spectra ,[Fig. 3.14-3.16], the same order is again observed in the rate of deuteriation, as was described above.

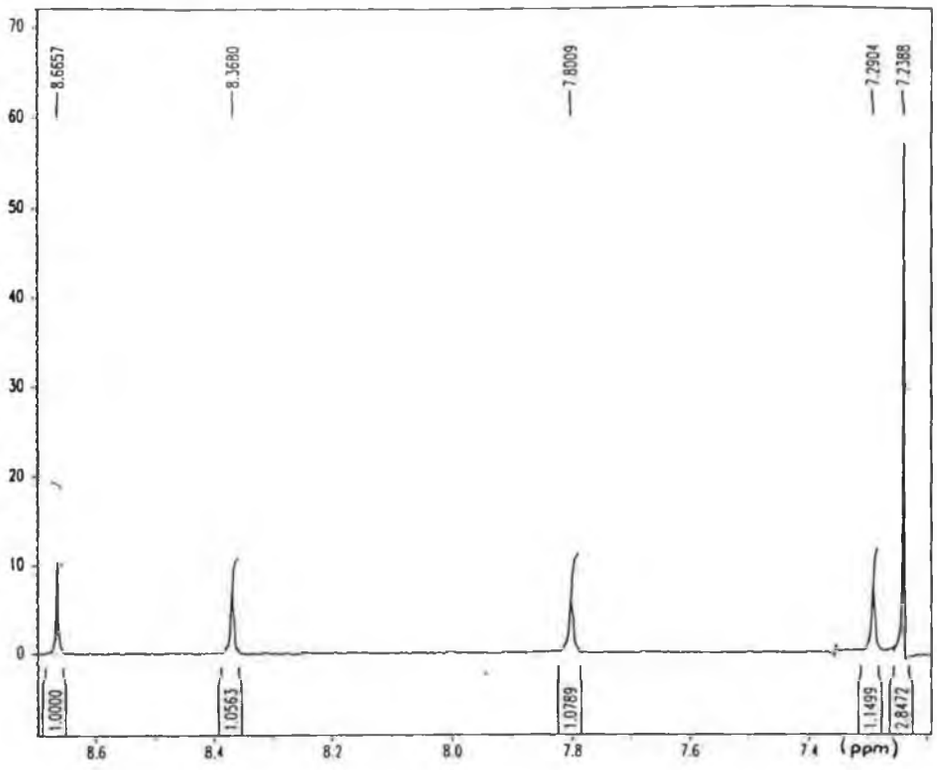


Figure 3.14 ^{1}Hnmr of bpy after 3 days at 200^{0}C using 0.5g Pd/C - (98%d).

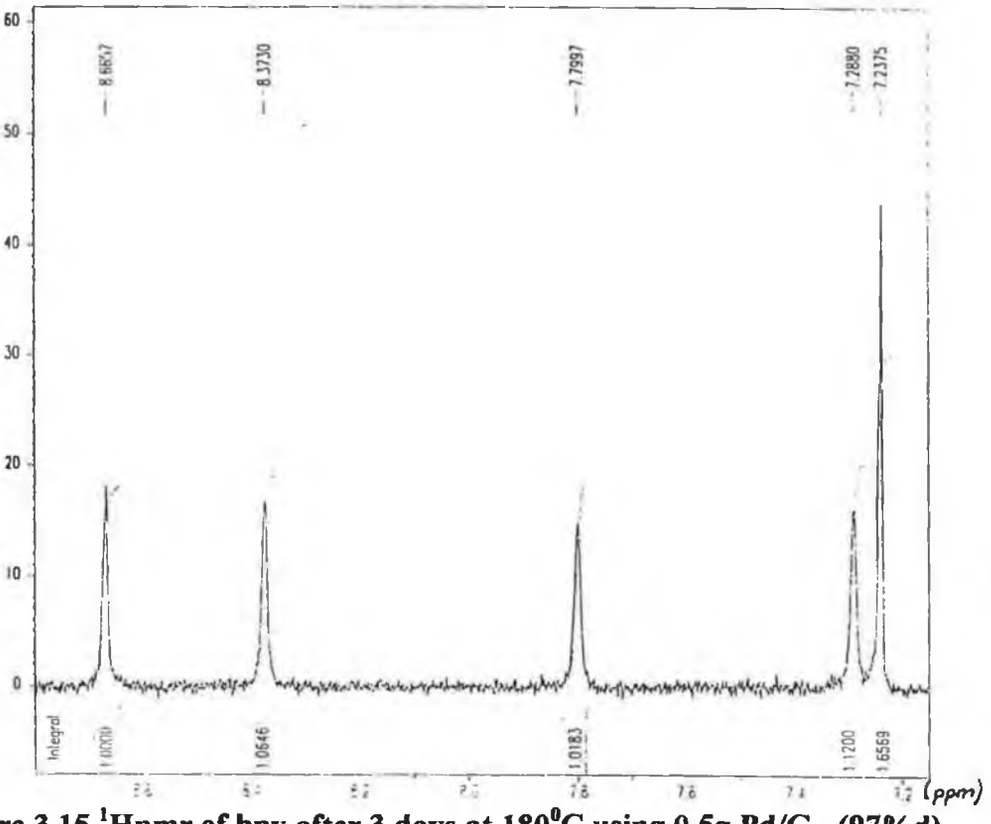


Figure 3.15 ^{1}Hnmr of bpy after 3 days at 180^{0}C using 0.5g Pd/C - (97%d).

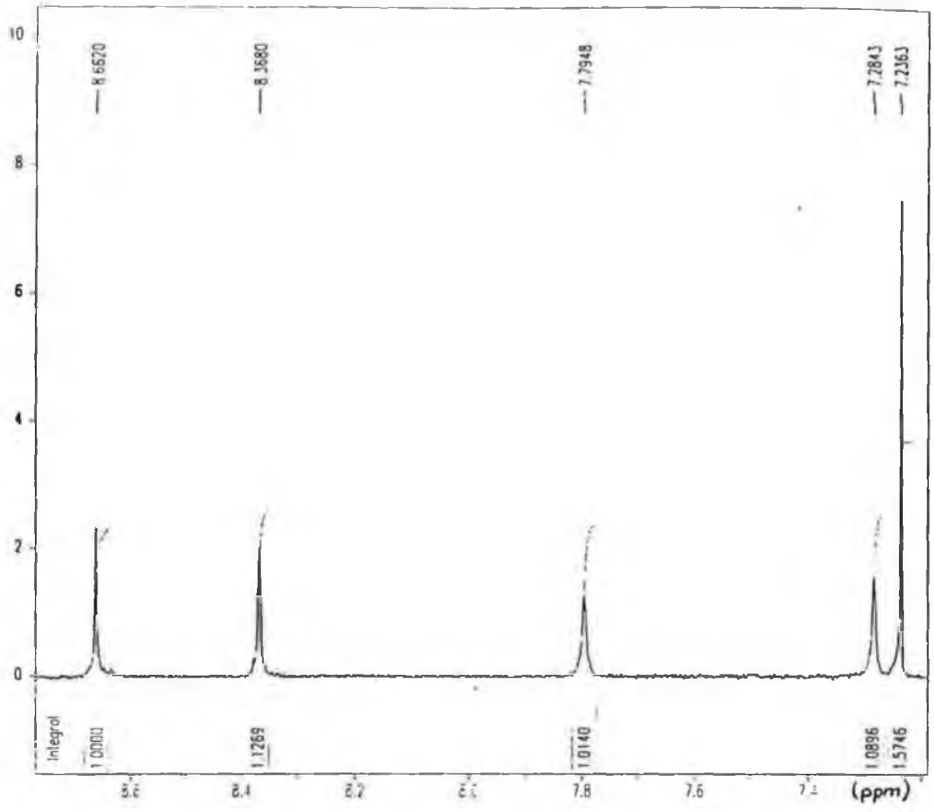


Figure 3.16 ^{1}Hnmr of bpy after 3 days at 160^{0}C using 0.5g Pd/C - (97%d).

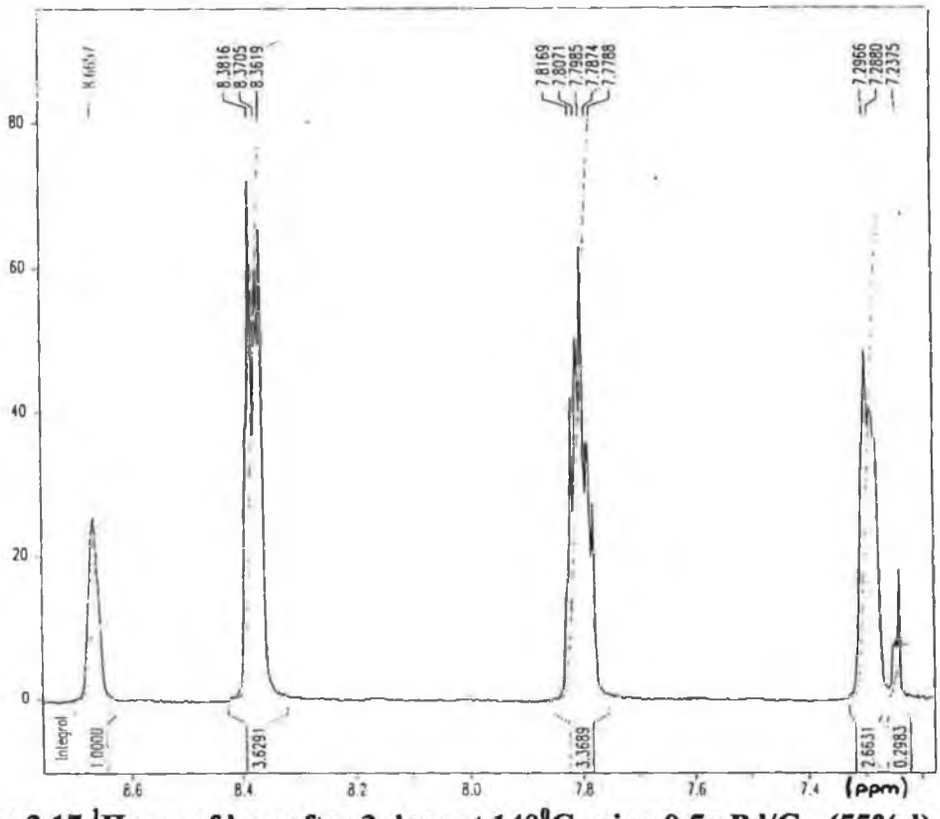


Figure 3.17 ^{1}Hnmr of bpy after 3 days at 140^{0}C using 0.5g Pd/C - (55%d).

Analysis of the data obtained from both the bpy time and temperature variation studies leads to the conclusion that the optimum reaction conditions for the synthesis of perdeuteriated bpy are, 3 days at 200^0C using 0.25g Pd/C per 3g bpy. The temperature variation studies revealed that at temperatures lower than 200^0C the quantity of Pd/C catalyst used had a significant effect on the overall % deuteriation of the bpy, but it had no effect on the rate of H-D exchange at the H6,6' position until the temperature was lowered to 140^0C. This coupled with the fact that >95% deuteriation had occurred at the H6,6' position after only 1 day, suggests the possibility that selective deuteriation of this position could be achieved by reducing both the reaction time and the quantity of Pd/C, and by carrying out the reaction at lower temperatures.

The ease with which the H6,6'-protons of free bpy are deuteriated, is interesting, as it is the H3,3'-protons which are most readily exchanged in $[Ru(bpy)_3]^{2+}$ [36]. This latter result has been explained by assuming that the steric strain they experience causes them to be slightly acidic. In fact when $[Ru(bpy)_3]^{2+}$ is reacted with $Na[OCD_3]$ in $(CD_3)_2SO$-CD_3OD, the H3,3'-protons are so susceptible to exchange that selective deuteriation at this position is achieved after after 24hrs at 35^0C.

Knowing the order in which deuteriation occurs at each position, it should also be possible, by careful manipulation of the reaction conditions, to synthesise d_2-, d_4-, and d_6-bpy, using the deuteriation method reported in this work. Some work has already been done in this area by Riesen et al., [11] who have reported selective deuteriation of bpy at the H6,6' position by using essentially the same method - 2g bpy, $20cm^3$ D_2O at 210^0C, but with no Pd/C, and a reduced reaction time of 31hours. Prior to this, bpy-6,6'-d_2 had been prepared by heating the corresponding N-oxide in D_2O at 170^0C for 18 hr. [37] In recent years Kincaid *et al.*, have published several papers [15, 20 and 42] in which they have reported the preparation of the following selectively deuteriated $[Ru(bpy)_3]^{2+}$ complexes; $[Ru(bpy\text{-}3,3'\text{-}d_2)_3]^{2+}$, $[Ru(bpy\text{-}4,4'\text{-}d_2)_3]^{2+}$, $[Ru(bpy\text{-}5,5'\text{-}d_2)_3]^{2+}$, $[Ru(bpy\text{-}6,6'\text{-}d_2)_3]^{2+}$, $[Ru(bpy\text{-}3,3',4,4'\text{-}d_4)_3]^{2+}$, $[Ru(bpy\text{-}3,3',5,5'\text{-}d_4)_3]^{2+}$, $[Ru(bpy\text{-}3,3',6,6'\text{-}d_4)_3]^{2+}$, $[Ru(bpy\text{-}4,4',5,5',6,6'\text{-}d_6)_3]^{2+}$ and $[Ru(bpy\text{-}d_8)_3]^{2+}$.

$[Ru(bpy\text{-}4,4'\text{-}d_2)_3]^{2+}$ [42] was prepared from the corresponding 4,4'-dibromo-bpy analogue via zinc dust reduction in D_2SO_4 / D_2O solution. The 3,3',4,4'- and 3,3',6,6'-tetradeuteriated analogues (from the corresponding di-deuteriated analogues) were generated via exchange of the 3,3'-protons with a 1/10 (v/v) solution of 0.10 M NaOD in D_2O and $(CD_3)_2SO$. The 4,4',5,5',6,6'-heaxadeuterio derivative was prepared from the perdeuteriated complex by the same procedure with the natural abundance reagents.

The excited state lifetimes for the nine deuteriated analogues of $[Ru(bpy)_3]^{2+}$ and the parent complex, obtained by Kincaid *et al.*, [43] showed a general increase of the lifetime and a decrease in the nonradiative decay rates with the number of deuterons. The results obtained for the isotopomers possessing the same number of deuterons at different positions revealed that deuteriation at positions 3 and 4 induces smaller increases in the lifetime of the excited state than does deuteriation at the 5 and 6 positions. These results provide evidence that such studies may be of substantial value in probing nonradiative relaxation processes in these systems in that they are consistant with the "active H atom" theory of Robbins and Thomson [44] which proposes that increased electron density in the region of the atoms whose vibrations act as promoting modes should lead to greater efficiency of radiationless decay. The information provided by these studies is of obvious significance, but at present the only methods available for selective deuteriation are synthetically demanding and all involve the deuteriation of the tris(2,2'-bpy) complex. The deuteriation method reported here would be far more straightforward and would produce selectively deuteriated bpy which could be incorporated into any complex, thus providing an even greater variety of compounds for analysis.

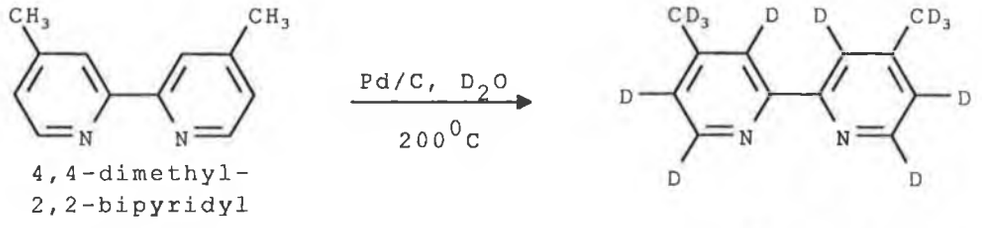
3.4 *Application of deuteriation method to other polypyridyl ligands:*

The method reported, by Keyes, [21] had never been applied to ligands other than bpy. In these experiments the conditions used were those used by Keyes for bpy and further studies are required to determine the optimum conditions for each individual ligand. Table 3.5 briefly details the ligands which were successfully deuteriated using this method, *ie.*, 3g ligand was added to 30 cm^3 D_2O in the presence of 0.5g Pd/C exchange catalyst and the mixture was heated at 200^0C for either 4 or 6 days. The % deuteriation of each ligand was calculated from its ^{1}Hnmr, as described previously (experimental section).

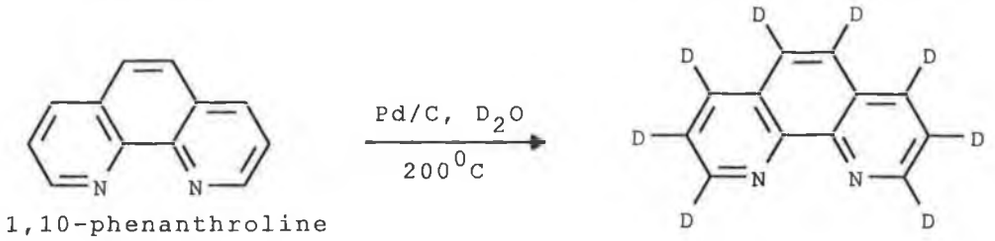
Table 3.5. % Deuteriation and Yield values for all polypyridyl ligands successfully deuteriated using the new single-step deuteriation method.

Ligand	Time / Days	% Deuteriation	% Yield
2,2'-bipyridyl	4	97	90
4,4'-dimethyl -2,2'-bipyridyl	4	98	54
1,10-phenanthroline	4	98	90
3-(pyridin-2-yl)-1,2,4-triazole	6	98	80
3-(pyrazin-2-yl)-1,2,4-triazole	6	97	80
3,5-bis(pyridin-2-yl)-1,2,4-triazole	6	95	49
3,5-bis(pyrazin-2-yl)-1,2,4-triazole	6	93	64
3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4'-triazole	6	96	37
dipyrido[3,2-*a*:2',3'-*c*] -phenazine	6	97	94

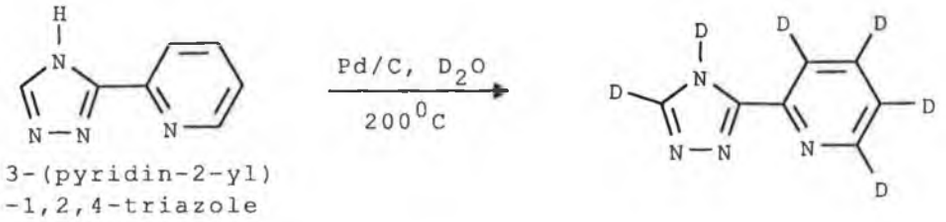
Scheme 1 Reaction schemes for all the polypyridyl ligands deuteriated using the method reported above.



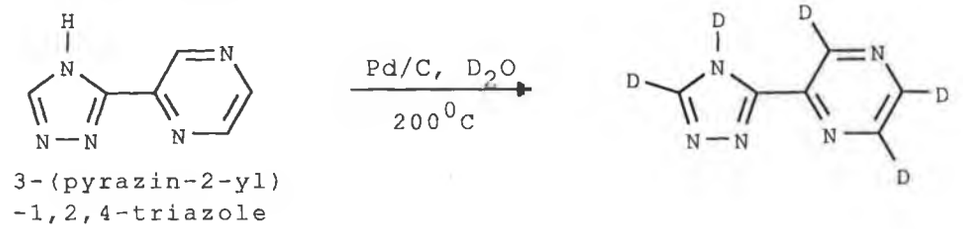
4,4-dimethyl-
2,2-bipyridyl



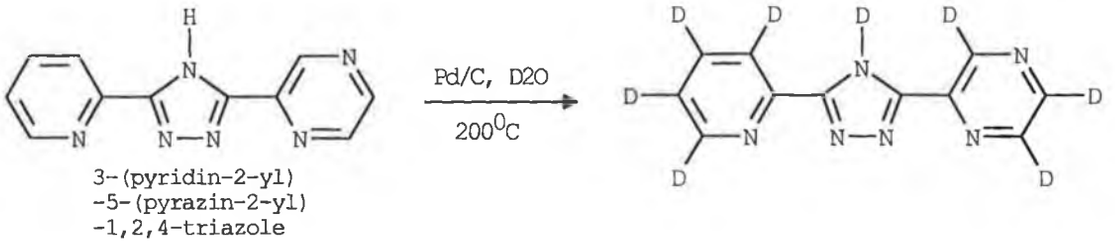
1,10-phenanthroline



3-(pyridin-2-yl)
-1,2,4-triazole

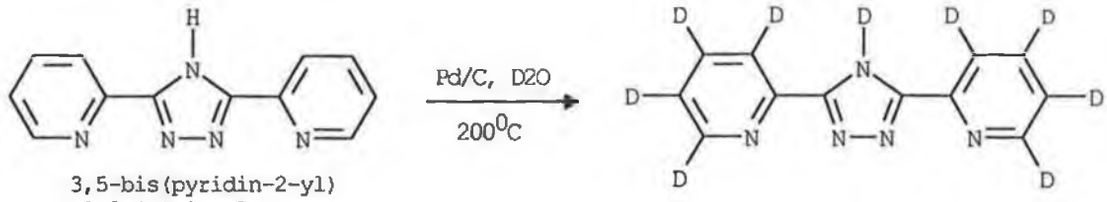


3-(pyrazin-2-yl)
-1,2,4-triazole

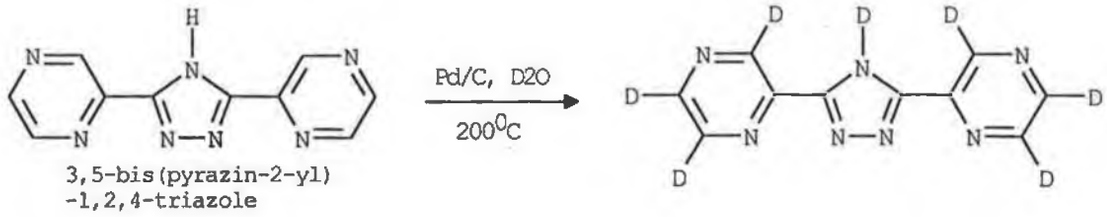


3-(pyridin-2-yl)
-5-(pyrazin-2-yl)
-1,2,4-triazole

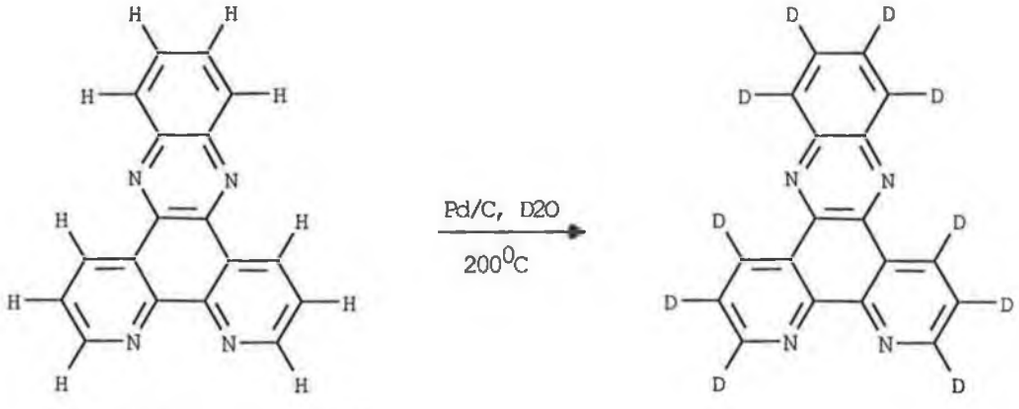
Scheme 1-cont'd. Reaction schemes for all the polpyridyl ligands deuteriated using the method reported above.



3,5-bis(pyridin-2-yl)
-1,2,4-triazole

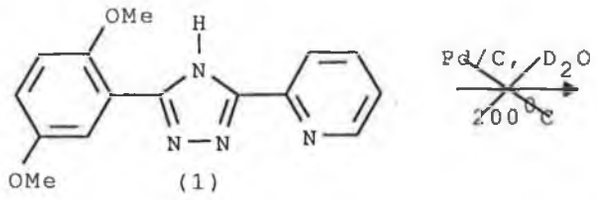


3,5-bis(pyrazin-2-yl)
-1,2,4-triazole

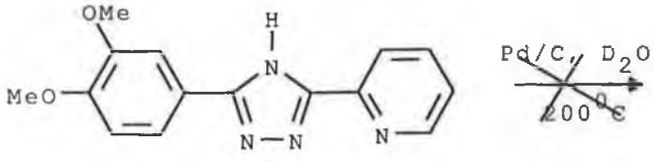


dipyrido [3,2-*a* : 2',3'-*c*]
-phenazine

The method was found to be unsuitable for the deuteriation of (3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl))-1,2,4-triazole (**1**), and (3-(3,4-dimethoxyphenyl)-5-(pyridin-2-yl))-1,2,4-triazole (**2**), both of which decomposed under these conditions.



(1)



(2)

Although only preliminary studies were carried out on all the other polypyridyl ligands, closer examination of their ^{1}Hnmr spectra does reveal some interesting information; The signal due to the three protons of the methyl group in 4,4'-dimethyl-2,2'-bipyridyl (dmbpy), can be seen at 2.41 ppm in the ^{1}Hnmr spectrum of undeuteriated dmbpy [Fig. 3.18], and at 2.38 ppm in the spectrum of deuteriated dmby [Fig. 3.19]. The fact that the integration of this peak is approximately equal to 3 times that of the ring protons in both spectra, is evidence that the methyl group protons were exchanged with approximately the same efficiency as the ring protons.

After 4 days at 200^{0}C (using 0.5g Pd/C per 3g dmbpy in 30 cm^{3} D_2O), the extent of deuteriation of the 6,6'- and 5,5- protons was roughly the same, exchange at the 3,3' position, as in the case of bpy, was slightly slower. The presence of the two methyl groups had a detrimental effect on the yield, which was reduced from 90% for bpy to 54% for dmby. The Pd/C was weighed afer the experiment and it was deduced that rather

than precipitating upon cooling, a large quantity of the dmbpy had stuck to the Pd/C, although several attempts were made to extract the dmbpy, using several different solvents and even employing soxhlet extraction, all efforts proved futile and only a few more mgs of dmbpy were extracted. Despite this problem the dmbpy which was obtained was 98% deuteriated, proving that although the reaction conditions may need to be adjusted, the overall method was very well suited for the deuteriation of dmbpy.

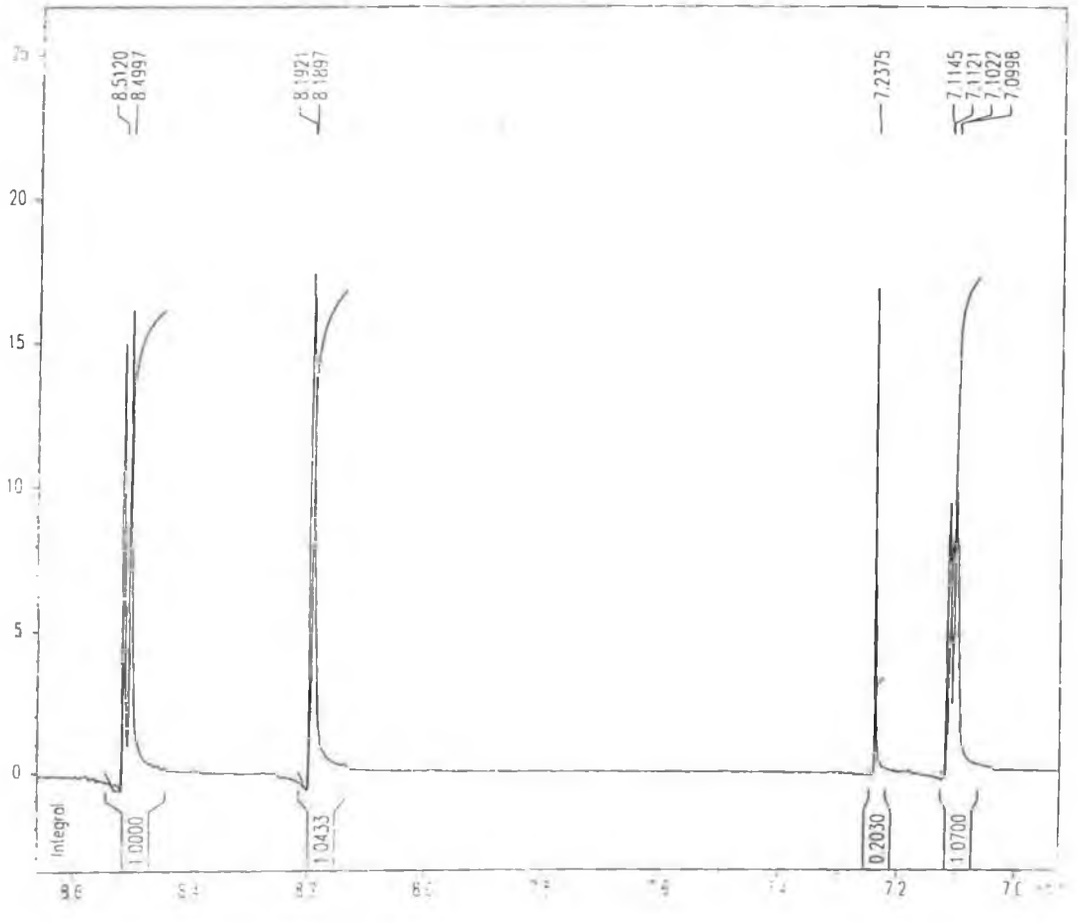


Figure 3.18(a) ^{1}Hnmr spectrum of 4,4-dimethyl-2,2'-bipyridyl in $CDCl_3$ - aromatic region.

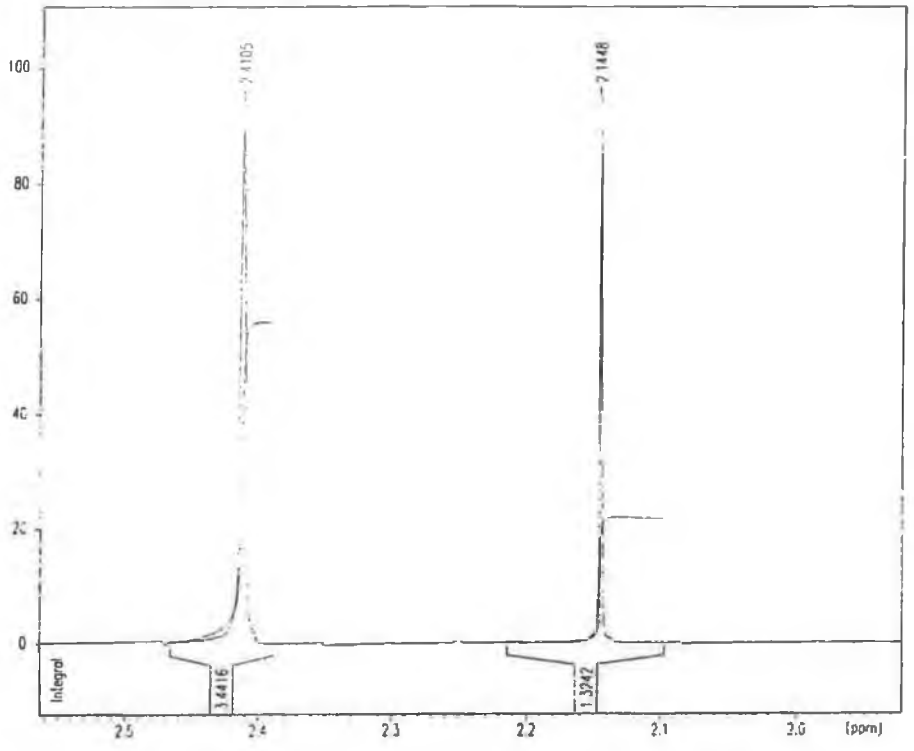


Figure 3.18(b) ^{1}Hnmr spectrum of 4,4-dimethyl-2,2'-bipyridyl in $CDCl_3$ - aliphatic region.

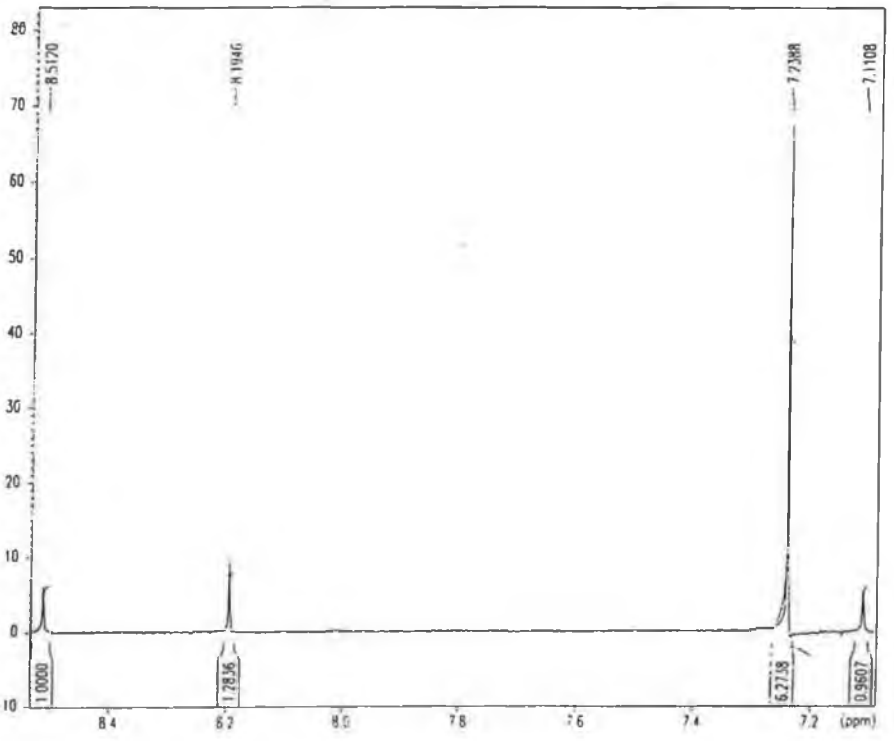


Figure 3.19(a) ^{1}Hnmr spectrum of deuteriated 4,4-dimethyl-2,2'-bipyridyl in $CDCl_3$ - aromatic region.

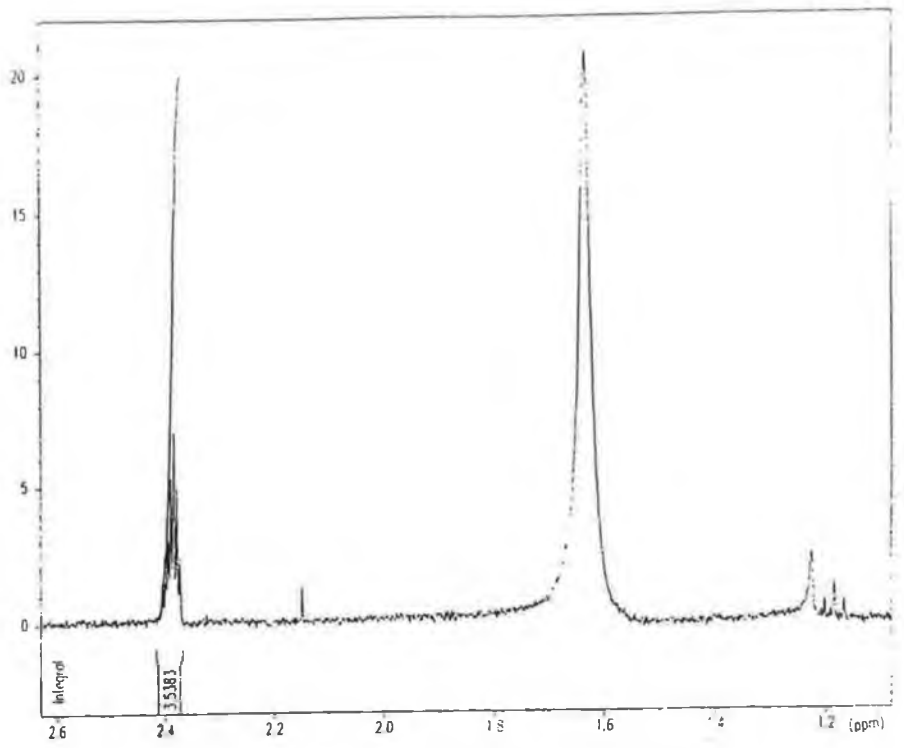


Figure 3.19(b) ^{1}Hnmr spectrum of deuteriated 4,4-dimethyl-2,2'-bipyridyl in $CDCl_3$ - aliphatic region.

1,10-phenanthroline (phen) was very successfully deuteriated using this method, with % deuteriation and % yield values equal to those obtained for bpy. After 4 days at 200^{0}C (using 0.5g Pd/C per 3g phen in 30cm^3 D_2O), all four peaks had reached > 95 deuteriation.

In the ^{1}Hnmr spectrum of deuteriated 3-(pyridin-2-yl)-1,2,4-triazole (Hpytr) (after 6 days at 200^{0}C using 0.5g Pd/C per 3g Hpytr in 30 cm^3 D_2O), [Fig. 3.20 and 3.21]the peak due to H^5 of the triazole has a negligible integration, with approximately 100% deuteriation occurring at this position. While the exchange of the pyridyl protons was slightly less efficient, >95% deuteriation was still achieved at all four positions. Some difficulty was encountered in the isolation of the final product as some of the deuteriated Hpytr remained stuck to the Pd/C resulting in the slightly lower yield of 80%, as in the case of dmby above, the reaction conditions need to be altered to suit this particular ligand, but the % deuteriation obtained shows that this method can be very successfully applied to the deuteriation Hpytr.

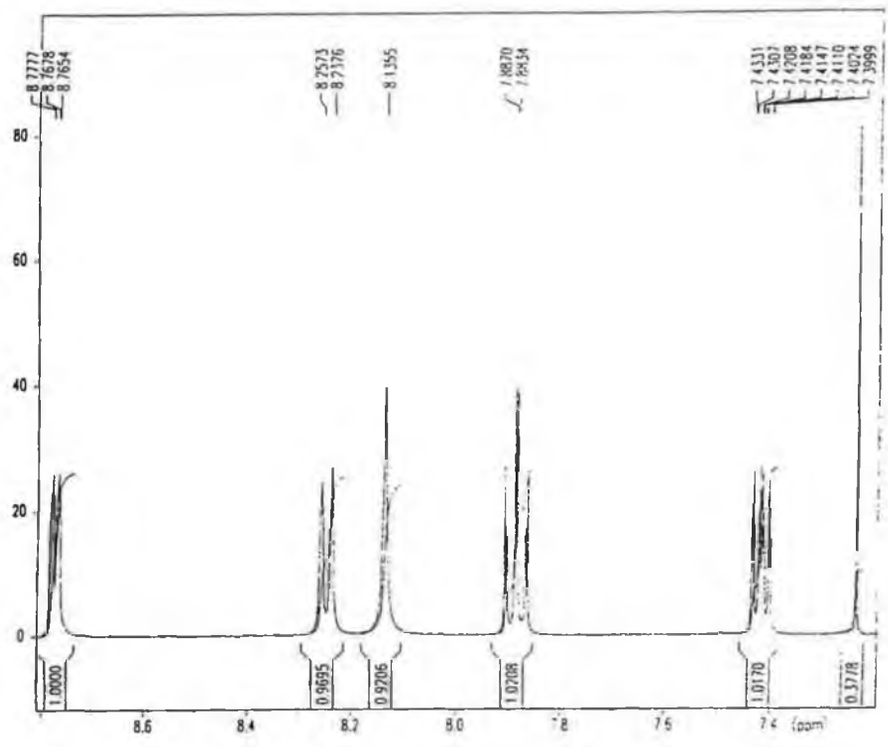


Figure 3.20 ^{1}Hnmr spectrum of 3-(pyridin-2-yl)-1,2,4-triazole in $CDCl_3$.

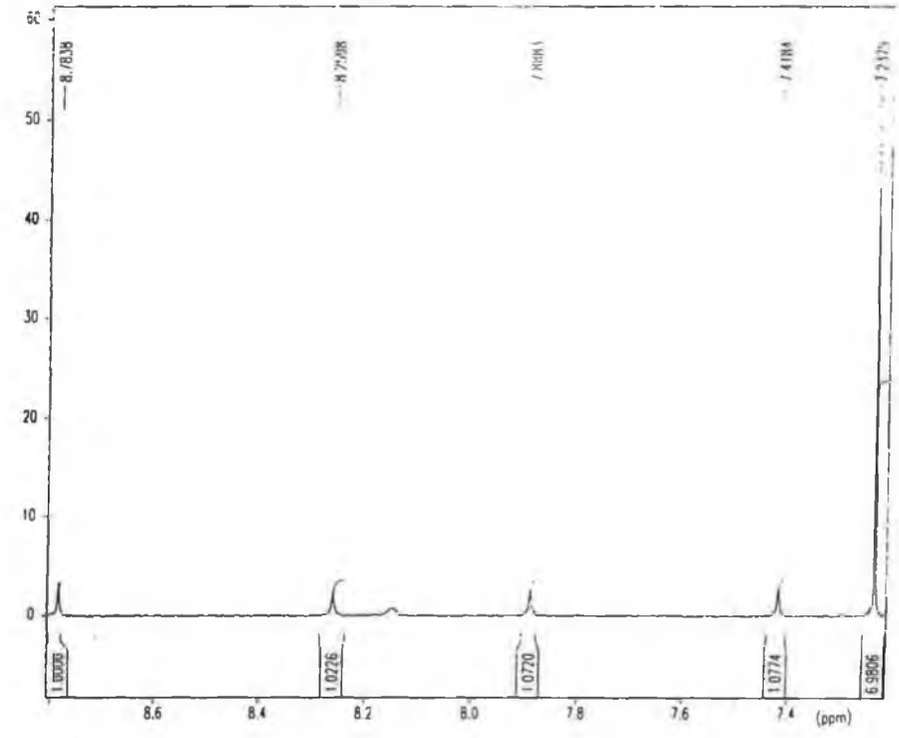


Figure 3.21 ^{1}Hnmr spectrum of deuteriaied 3-(pyridin-2-yl)-1,2,4'-triazole in $CDCl_3$.

From the ligand peak integrations in the ^{1}Hnmr spectrum of 3-(pyrazin-2-yl)-1,2,4-triazole (Hpztr) (after 6 days at 200^{0}C using 0.25g Pd/C per 1.5g Hpztr in 15 cm^{3} D_2O), it can be seen that there is little or no difference, at this stage, in the rates of deuteriation, with >95 % deuteriation having been achieved at all positions. The yield of deuteriated Hpztr was 80%, due to the same difficulties in isolation as encountered for Hpytr, indictating that optimisation of the reaction conditions is necessary in order to tailor this method to suit the triazole-type ligands, this is further illustrated by the low yields obtained for all of the following ligands; 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt), 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (Hbpzt), and 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole (Hppt).

From the ^{1}Hnmr spectrum of deuteriated Hbpt (after 6 days at 200^{0}C using 0.25g Pd/C per 1.5g Hbpt in 15 cm^{3} D_2O), it can be seen that the integration of the peak at 8.17 ppm, due to the 3,3'- protons, is approximately 14 times that of the other three peaks, it appears that the presence of the triazole ring impedes the rate of exchange at this position on the pyridine ring, as it is also this position which has the slowest rate of exchange in Hppt (after 6 days at 200^{0}C using 0.25g Pd/C per 1.5g Hppt in 15 cm^{3} D_2O), and although this position was slow to exchange in bpy, > 95 % deuteriation had been achieved after 4 days at 200^{0}C. Despite the low yields obtained, the overall % deuteriation values of all the ligands listed above were >95%.

Dipyrido[3,2-*a*:2',3'-*c*] -phenazine (dppz) proved to be very well suited to this method of deuteriation, with a yield of 94% and a deuteriation of 97%, in fact the ^{1}Hnmr of deuteriated dppz (after 6 days at 200^{0}C using 0.08g Pd/C per 0.3g dppz in 15 cm^{3} D_2O), [Fig. 3.22 & 3.23] shows that three of the five ligand peaks present in the spectrum of undeuteriated dppz have all but disappeared, indicating that complete deuteriation was achieved at these positions. The two peaks remaining are due to $H^{6\&9}$ and $H^{2\&13}$, with the integration of the $H^{6\&9}$ protons being 5 times that of the $H^{2\&13}$.

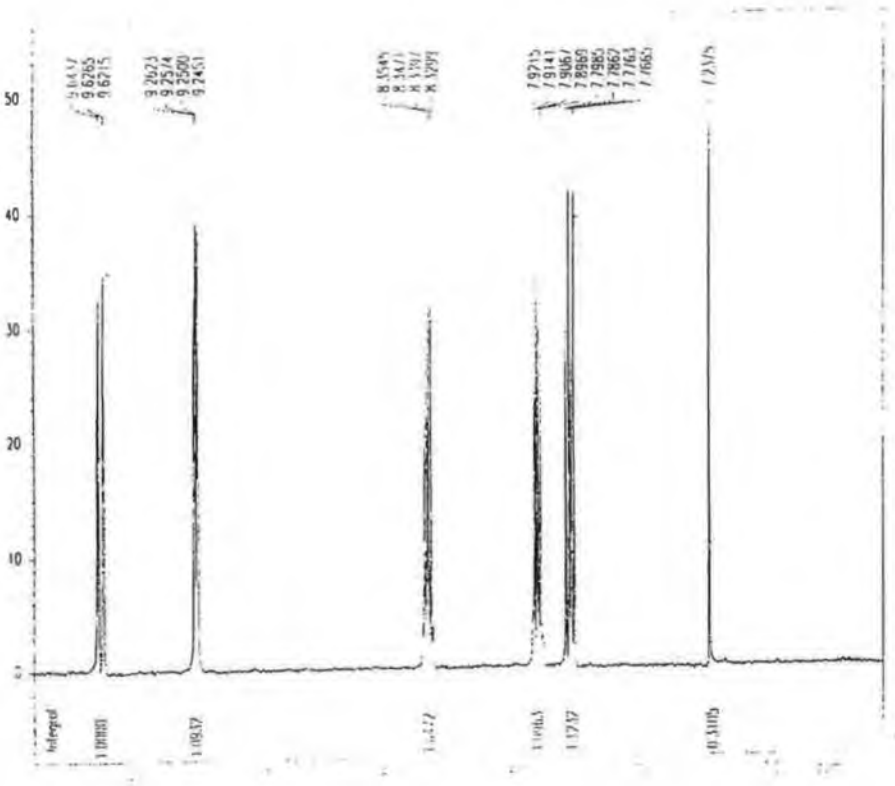


Figure 3.22 ^{1}Hnmr spectrum of dipyrido[3,2-*a*:2,'3'-*c*]phenazine in $CDCl_3$.

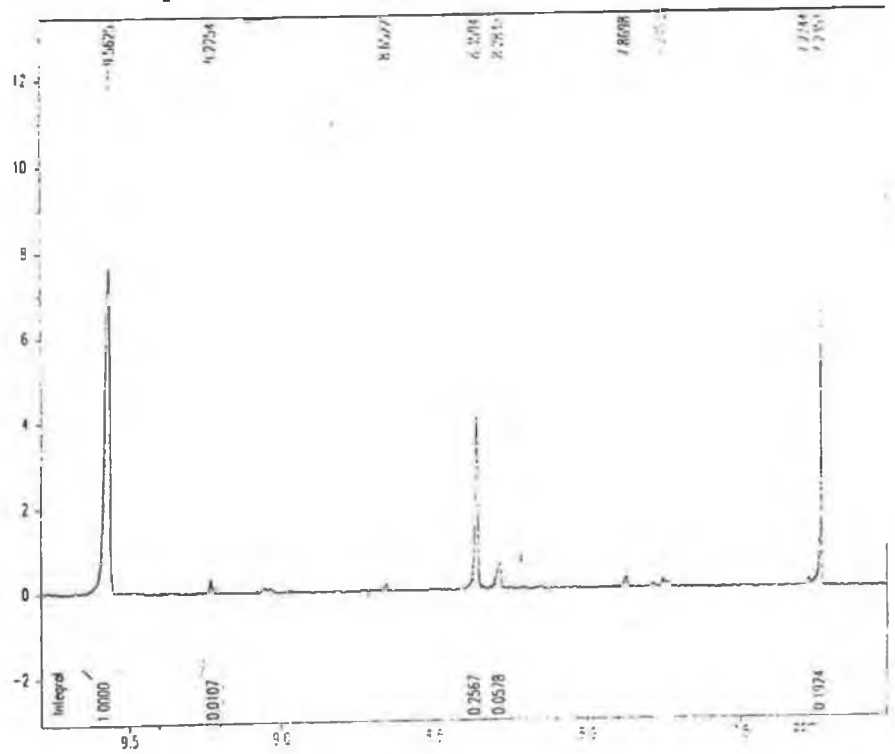


Figure 3.23 ^{1}Hnmr spectrum of deuteriated dipyrido[3,2-*a*:2,'3'-*c*]phenazine in $CDCl_3$.

As mentioned previously, there were some ligands for which this method was not suited, eg., (3-(2,5-dimethoxyphenyl)-(5-pyridin-2-yl))-1,2,4-triazole. The problems experienced with these ligands may be due to the fact that the high temperature (200^0C) required for the synthesis of bpy- d_8 is too extreme for these ligands, causing them to decompose. The temperature variation studies on bpy show that when the quantity of Pd/C was increased to 0.5g, there was no decrease in the rate of H-D exchange until the temperature was reduced to 140^0C, so by using larger quantities of Pd/C it might be possible to carry out the deuteriation of these ligands at lower temperatures, thereby reducing the likelihood of the ligands decomposing.

I.R. spectra of all the ligands and their deuteriated analogues were obtained. Taking 2,2'-bipyridyl as an example, [Fig. 3.24] it can clearly be seen that upon deuteriation, the C-H stretching vibration at 3059 cm^{-1} is replaced by C-D stretching vibration which appears much lower at 2265 cm^{-1}. In addition all the peaks in the 1500 - 500 cm^{-1} range are shifted to slightly lower wavenumbers, a list of those shifts is given in Table 3.6.

Table 3.6 I.R. Frequency shifts upon deuteriation of 2,2'-bipyridyl.

Undeuteriated 2,2'-bipyridyl Wavenumber / cm^{-1}.	Deuteriated 2,2'-bipyridyl Wavenumber / cm^{-1}.
3059	2264.5
1582 , 1558.5	1546.5 , 1522.5
1457.5 , 1415.8	1333 , 1285.5
1250	1244
1089.7 , 1042.5 , 989	1024.5 , 982.9 , 959
757.2	728
624	579.5

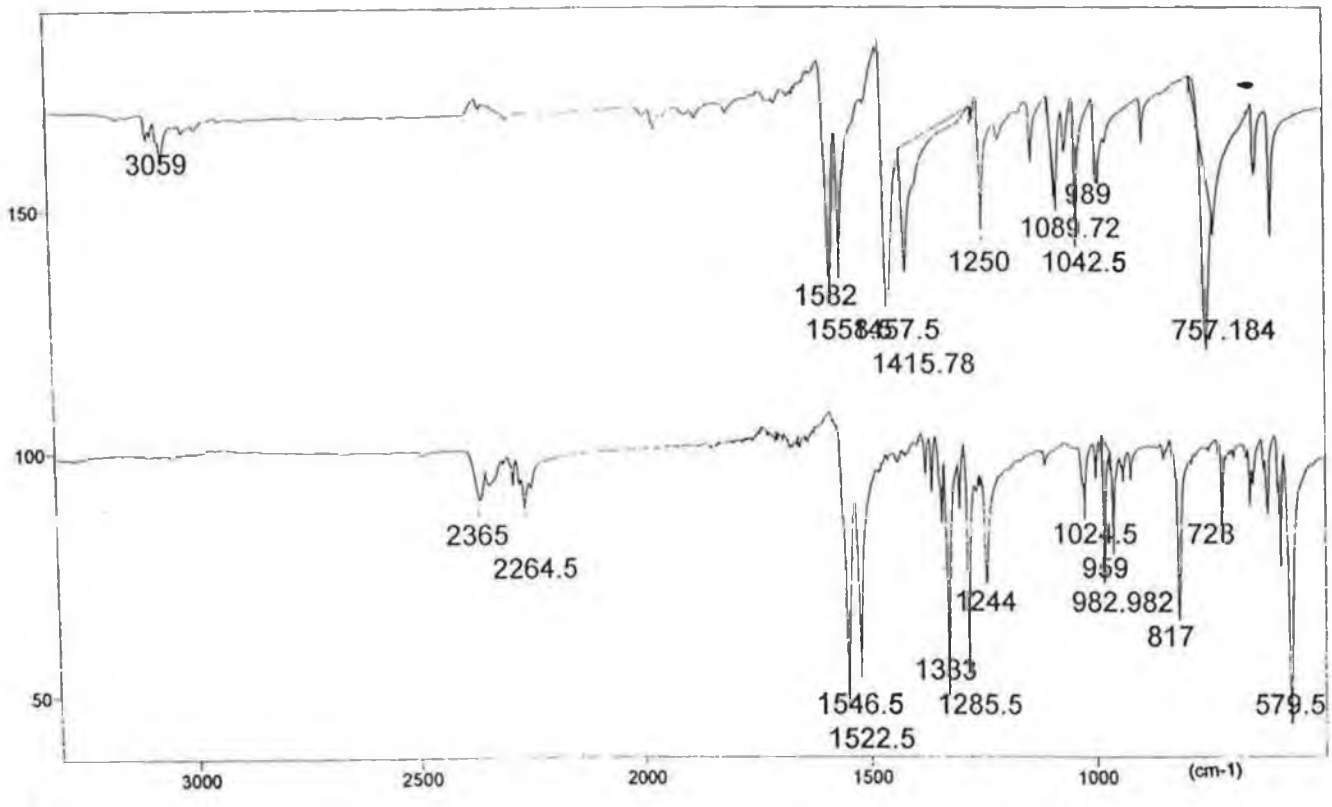


Figure 3.24 I.R. Spectrum of 2,2'-bipyridyl (top) and 2,2'-bipyridyl-d_8 (bottom).

Analysis of the I.R. spectra of the other polypyridyl ligands, reveals similar shifts in frequencies to those listed above for 2,2'-bipyridyl.

^{1}Hnmr and I.R. spectra of all the ligands listed in Table 3.5 above are given in chapter 4 and in the Appendix.

3.5 *Conclusion.*

Given the wide range of potential applications for deuteriated polypyridyl ligands in supramolecular devices, and the difficulties involved in their synthesis, the results revealed by these studies are quite significant. The deuteriation method reported above is remarkably simple, the bpy is heated in D_2O in the presence of Pd/C exchange catalyst, after which it is cooled and filtered. By comparison with previous bpy deuteriation methods, this method clearly offers a simpler, faster, and more efficient route to the synthesis of perdeuteriated 2,2'-bipyridyl.

Prior to the development of this method, the most direct route for the synthesis of deuteriated bpy [33] involved several complicated steps, the first of which was the conversion of bpy into its N-oxide (which is a very laborious procedure), followed by the deuteriation of the N-oxide after which the bpy-d_8 1,1'-dioxide must be converted back to bpy and the solution neutralised, extracted several times with ether and dried. The yield of bpy-d_8 obtained with this method is less than 55%, as compared to 90% achieved with method reported above.

The optimisation studies carried out on bpy have revealed that with careful control of the reaction time and temperature and of the amount of Pd/C catalyst used, the method reported could potentially be used for the preparation of selectively deuteriated bpy.

In all of the deuteriation methods reported in the introduction section for the deuteriation of other compounds besides bpy, (see chapter 1) it was necessary to carry out the deuteriation procedure several times in order to obtain a sufficiently high % deuteriation, thereby reducing the final % yield of the experiment considerably and significantly increasing the time required for the synthesis. Using the method reported, >95% deuteriation was achieved in a single run, for all ligands tested. As in the case of bpy complete deuteriation can be achieved by repeating the procedure once with fresh Pd/C and D_2O.

As described in the introduction, deuteriation is not a new technique and has been used in both organic and inorganic chemistry for many years, but to our knowledge the polypyridyl ligands deuteriated in these studies, with the exception of bpy, have never previously been deuteriated. The success of these experiments on pyridyl- and pyrazine-triazole containing compounds has shown that the method reported is suitable, not just for bpy-type ligands, but for a whole range of other compounds.

Chapter 4

Applications of deuteriated polypyridyl ligands.

4. Applications of deuteriated compounds:

4.1 *Introduction.*

As stated previously, (section 1.1) Ru(II) polypyridyl complexes possess unique photophysical and electrochemical properties which make them the ideal subjects for the on-going investigations into the design of supramolecular systems with user-defined photophysical properties. Although $[Ru(bpy)_3]^{2+}$ represents a significant step towards an ideal solar sensitiser, its restricted visible absorbance range and its lack of photochemical stability mar its usefulness as a sensitiser. It has been shown that the excited state properties of Ru(II) polypyridyl complexes may be altered by substituting another ligand for a bipyridyl ligand.

With this in mind, the Vos research group has been experimenting with a number of complexes in which one of the bipyridyls has been replaced by a 1,2,4-triazole containing ligand.[39, 40] Because of their strong σ-donating ability, the triazole ligands possess π^* levels of much higher energy than bipyridyl, and as a result in mixed ligand complexes containing both bipyridyl and triazole, the excited state is always based on the bipyridyl ligand. The magnitudes of σ - and π - donating properties of these ligands can be modified by the introduction of substituents onto the triazole ligand. Another important property of triazoles is their acid/base chemistry - the uncoordinated nitrogen of the triazole ring can undergo protonation and deprotonation, which has a profound effect on the π - acceptor and σ - donor properties of the ligand.

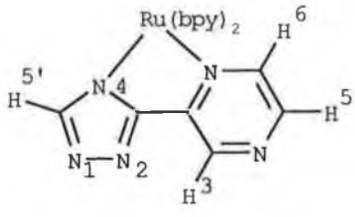
The negative charge produced on deprotonation of the triazole ring has proved to be very effective in promoting both electron transfer processes and interaction between metal centres in bridging ligands such as Hbpt, Hppt and Hpztr. In particular in the synthesis of multinuclear complexes, very complicated ^{1}Hnmr spectra are obtained, which make a definite identification of the species prepared difficult. Even more so since for the triazole ring coordination to the N^2 or N^4 atom yields significantly different compounds. In the

next set of examples the use of deuteriation of ligands for simplifying these problems will be highlighted.

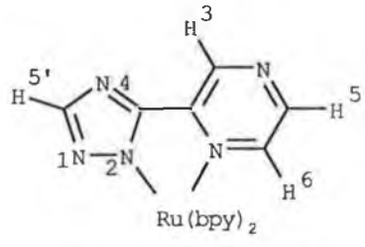
The following complexes are currently being studied - $[Ru(bpy)_2(pztr)]^+$, (Hpztr = (3-(pyrazin-2-yl)-1,2,4-triazole)), $[Ru(bpy)_2(ppt)]^+$, (Hppt = (3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole)[34], $[Ru(bpy)_2$(3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4'-triazole)$]^+ = [Ru(bpy)_2(L_1)]^+$, and $[Ru(phen)_2$(3-(3,4-dimethoxy-phenyl)-5-(pyridin-2-yl)-1,2,4-triazole)$]^+ = [Ru(phen)_2(L_6)]^+$ [35]. The effects of deuteriation on ^{1}Hnmr and excited state properties are discussed.

4.2 *^{1}Hnmr Spectra of Pyrazine-triazole containing complexes.*

The reaction of Hpztr with $Ru(bpy)_2Cl_2.2H_2O$, yields two coordination isomers as shown below.



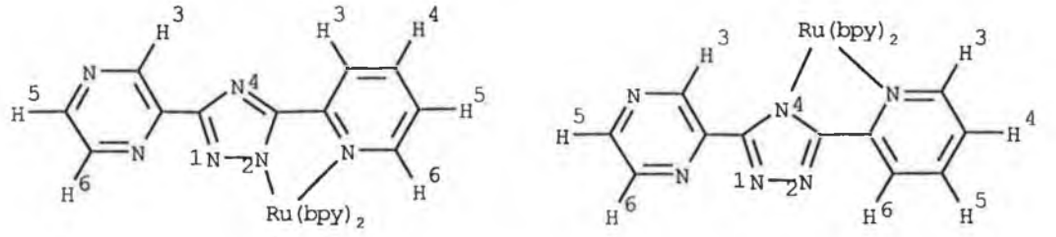
Isomer 1 - N_4bound

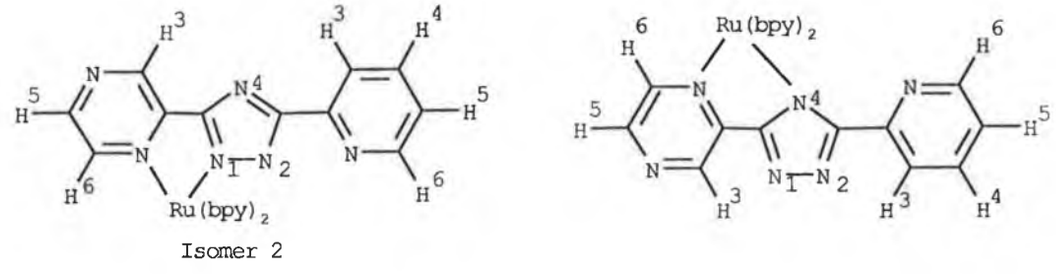


Isomer 2 - N_2bound

The two coordination isomers of $[Ru(bpy)_2(pztr)]^+[PF_6]^-_{11/2}$.

While for $[Ru(bpy)_2(ppt)]^+$ four coordination isomers are possible, in practice the synthesis of the mononuclear complex yields only two coordination isomers - denoted isomer 1 and isomer 2 below;





The four possible coordination isomers of $[Ru(bpy)_2(ppt)]^+[PF_6]^-_2$.

As the ^{1}Hnmr spectra of the two isomers of both complexes are significantly different due to the effect of the different binding sites of $Ru(bpy)_2$, ^{1}Hnmr has proved to be a very useful technique in the elucidation of their structures. [34] The ^{1}Hnmr spectra of these complexes are however quite complicated, especially when mixtures of isomers are obtained. The use of deuteriated bipyridyl is expected to simplify these spectra since it eliminates the bpy signals from the spectra and so greatly facilitates the interpretation of shifts observed for the triazole based ligand. Figures 4.1 - 4.8 below show the ^{1}Hnmr spectra obtained for these complexes. [40]

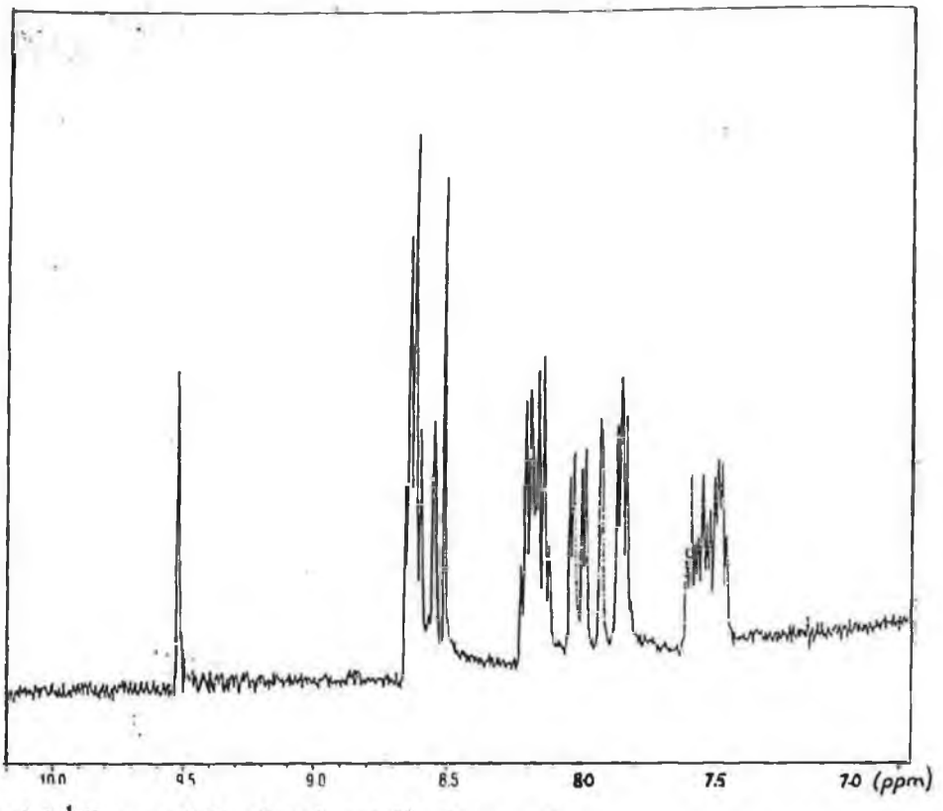


Figure 4.1 ^{1}Hnmr of $[Ru(bpy)_2pztr]^{+}$ - Isomer 1

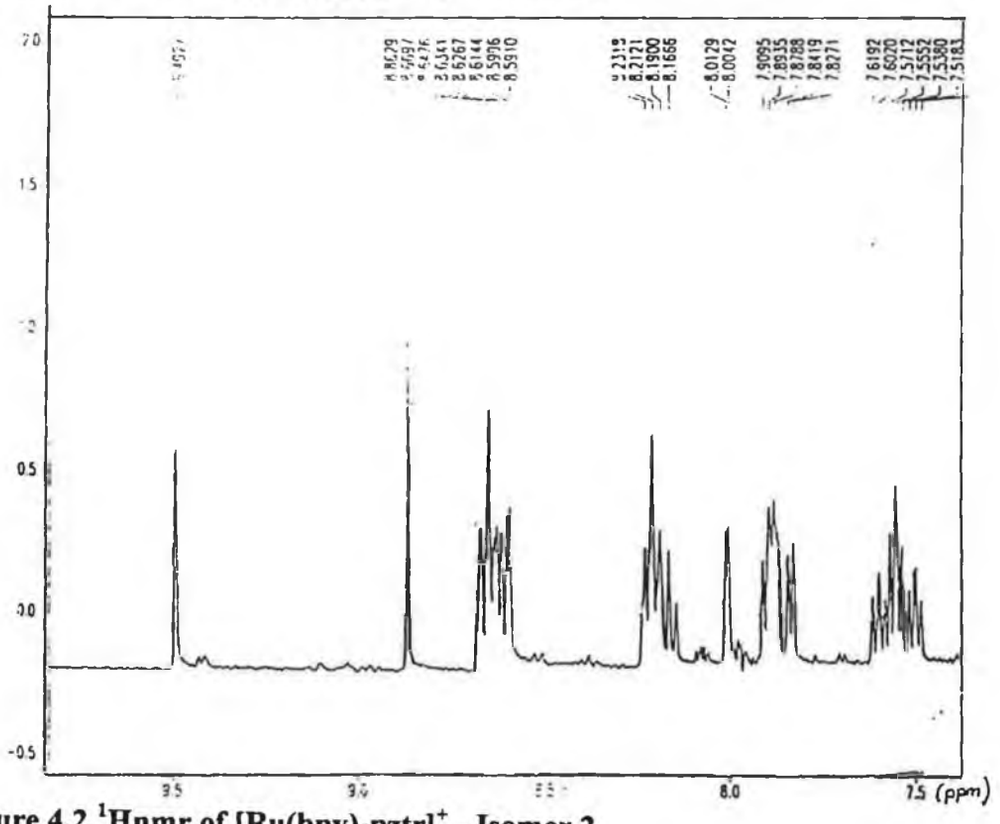


Figure 4.2 ^{1}Hnmr of $[Ru(bpy)_2pztr]^{+}$ - Isomer 2

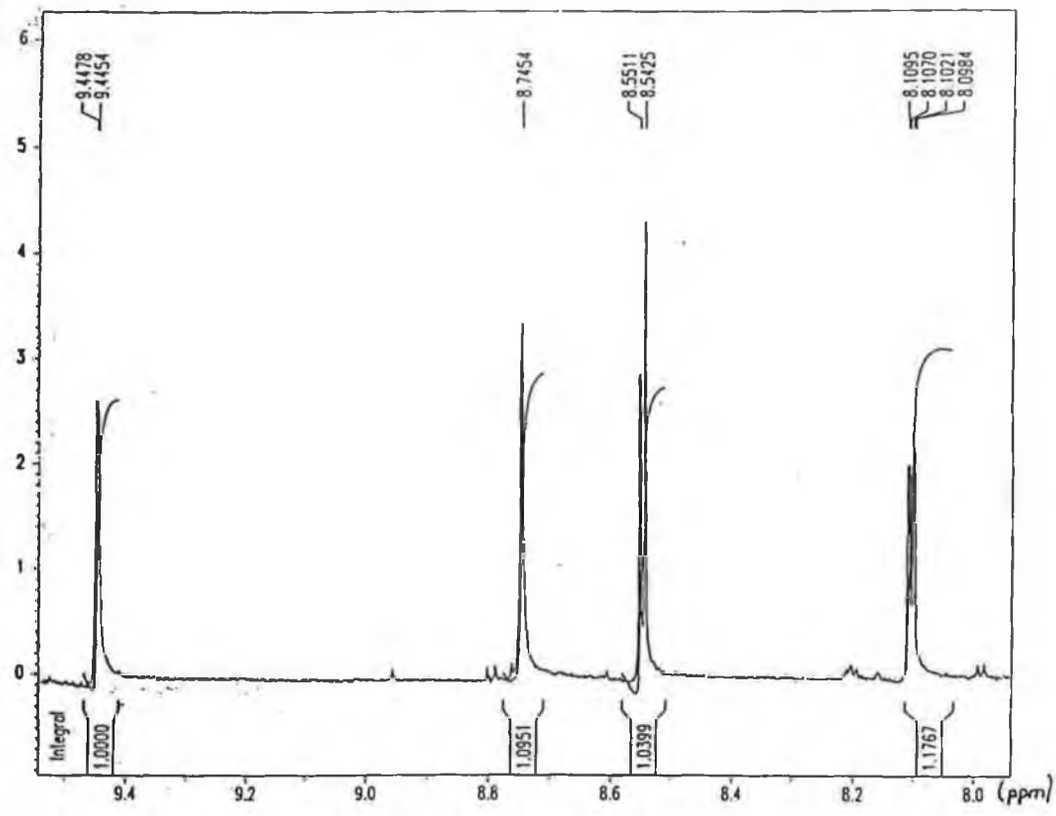


Figure 4.3 ^{1}Hnmr of [Ru(bpy-d_8)$_2$pztr]$^{+}$ - Isomer 1

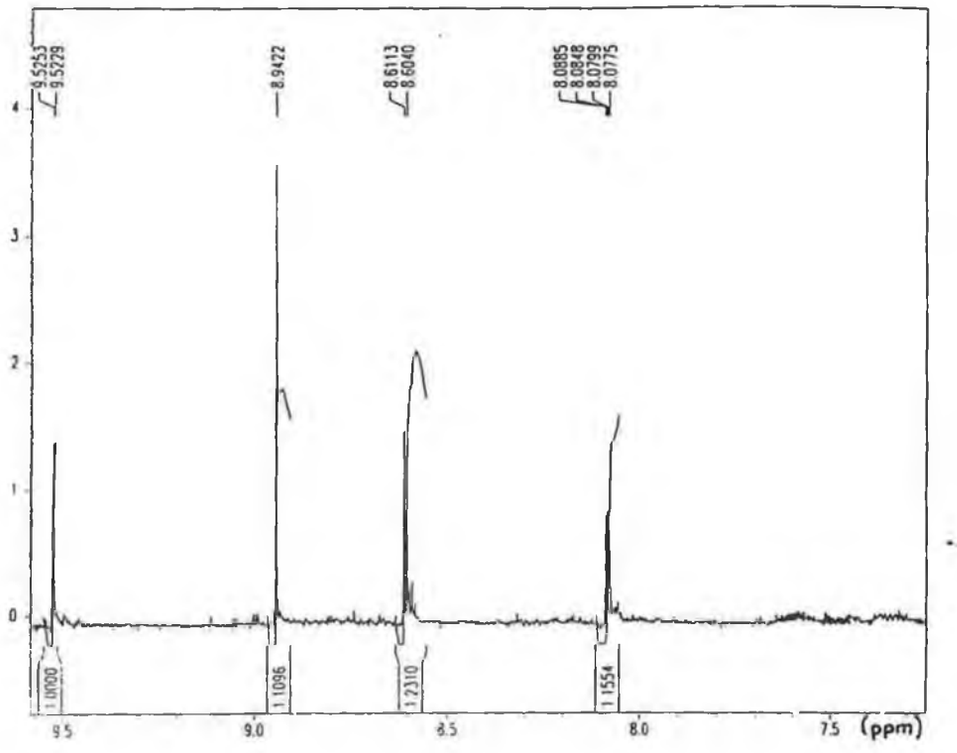


Figure 4.4 ^{1}Hnmr of [Ru(bpy-d_8)$_2$pztr]$^{+}$ - Isomer 2

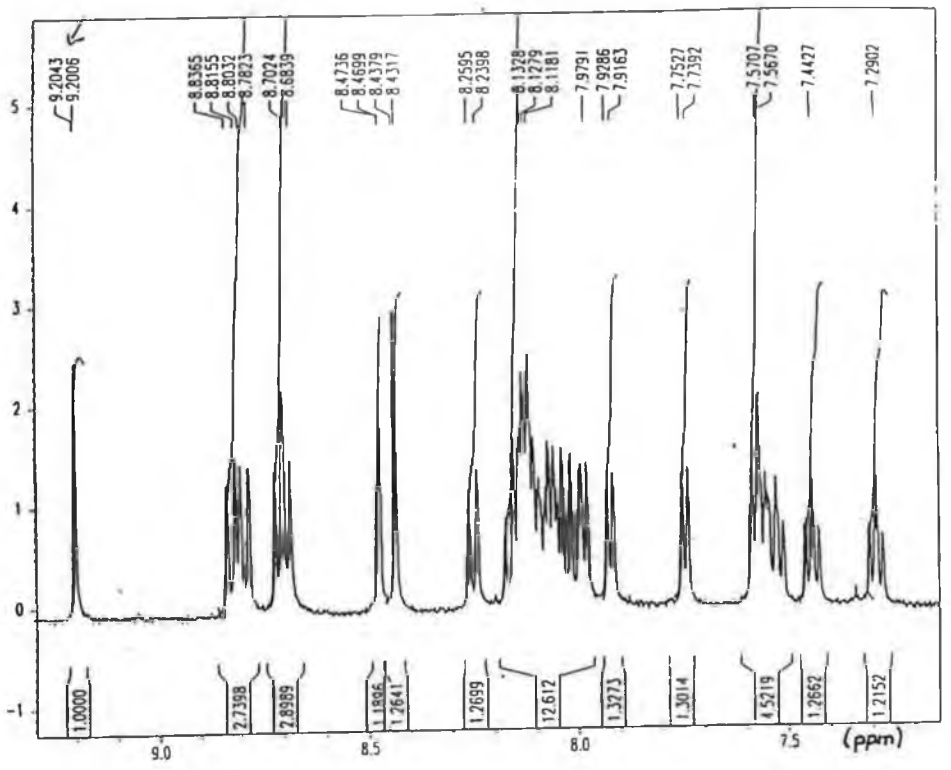


Figure 4.5 ^{1}Hnmr of $[Ru(bpy)_2ppt]^{+}$ - Isomer 1

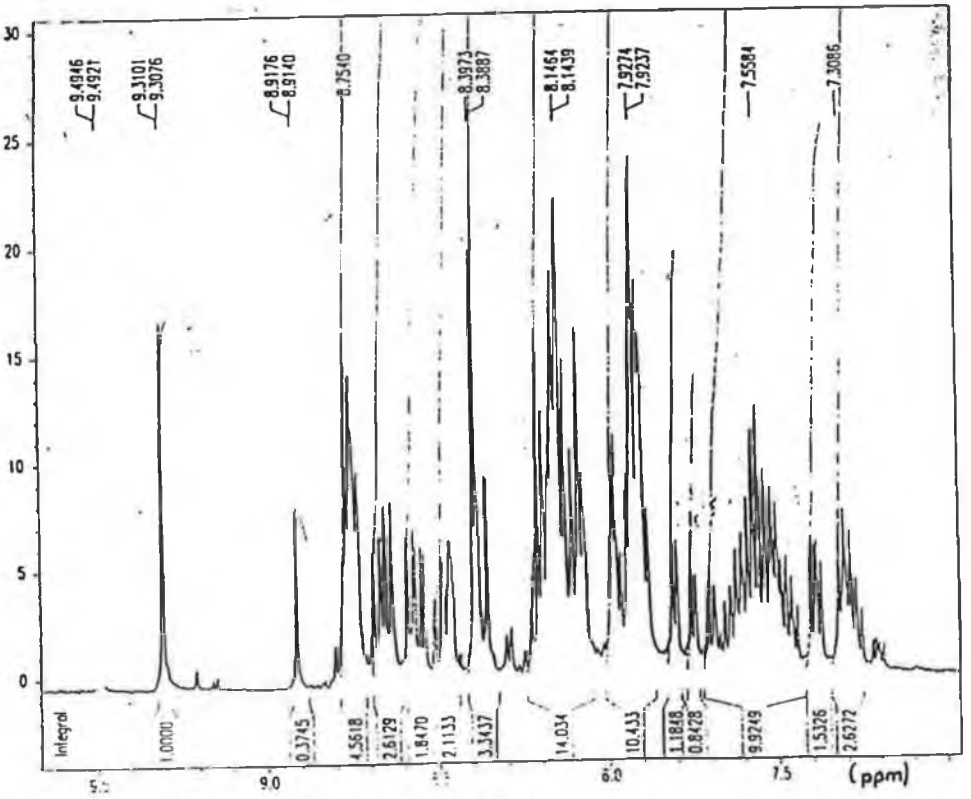


Figure 4.6 ^{1}Hnmr of $[Ru(bpy)_2ppt]^{+}$ - Isomer 2

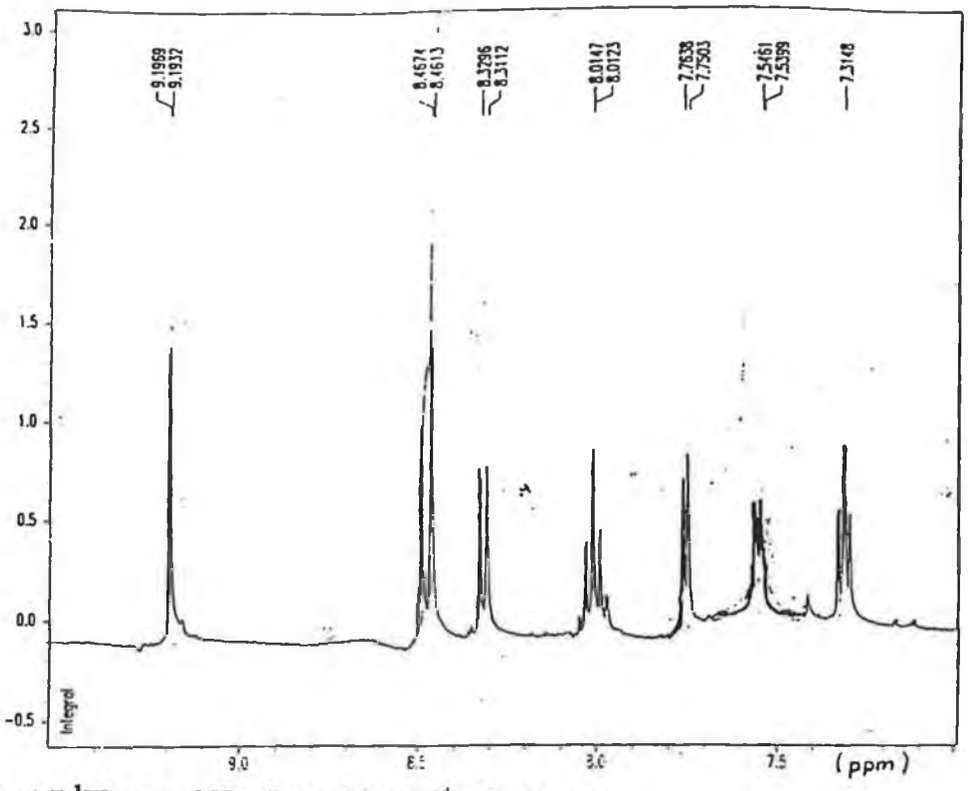


Figure 4.7 ^{1}Hnmr of [Ru(bpy-d_8)$_2$ppt]$^{+}$ - Isomer 1

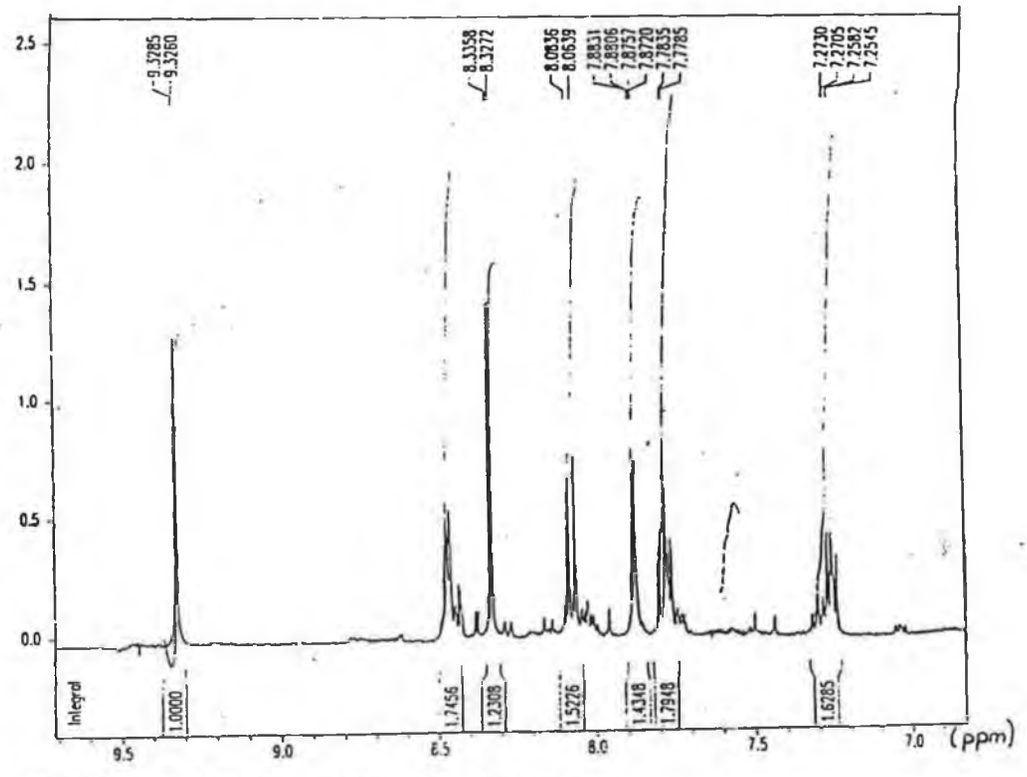


Figure 4.8 ^{1}Hnmr of [Ru(bpy-d_8)$_2$ppt]$^{+}$ - Isomer 2

On examination of the ^{1}Hnmr spectra of $[Ru(bpy)_2(pztr)]^+$ - Isomer 1 and 2 [Fig 4.1 and 4.2], the only peak that can be unambiguously assigned in either spectrum is the peak at 9.5ppm which is due to H_3 of the pyrazine, all the other ligand peaks are obscured by bpy resonances, whereas in the ^{1}Hnmr spectra of $[Ru(bpy\text{-}d_8)_2(pztr)]^+$ [Fig. 4.3 and 4.4], the only peaks present are those due to the pyrazine-triazole. Interpretation of these spectra enables us to differentiate between the two isomers, as structural models reveal that when the triazole is bound via N_4, as is the case in isomer 1, the $H_{5'}$ proton is shielded by the bpy ring and its signal is therefore shifted upfield, but for the N_2 bound isomer (ie., isomer 2), there is no such effect - see table 4.1 below. In the ^{1}Hnmr spectrum of the free ligand, although the doublets at 8.65 ppm and 8.24 ppm have been assigned as H_5 and H_6 respectively, it is not really possible to distinguish between the two signals as they are both doublets coupled to one another appearing at very similar positions in the spectrum. This changes however, upon formation of the complex as the proximity of the bpy ring to the H_6 and H_5 protons has a shielding effect on them and thus the signals are shifted upfield, (this effect is the same for both isomers), but it is the doublet due to the H_6 - protons which experiences the biggest shift as it is this position which is closest to the bpy ring.

Table 4.1 ^{1}Hnmr signal assignments for the triazole ligand Hpztr in both coordination isomers of $[Ru(bpy\text{-}d_8)_2(pztr)]^+$.

Compound	H_3	H_5	H_6	$H_{5'}$
Hpztr ligand	9.47(s)	8.71(d)	8.65(d)	8.24(s)
$[Ru(bpy\text{-}d_8)_2(pztr)]^+$ Isomer 1	9.44(s)	8.55(d)	8.10(d)	8.74(s)
$[Ru(bpy\text{-}d_8)_2(pztr)]^+$ Isomer 2	9.52(s)	8.60(d)	8.07(d)	8.94(s)

Due to the asymmetric nature of the Hppt ligand, its ^{1}Hnmr spectrum is very complicated, as signals due to both the pyridine and the pyrazine ring protons are present. It was

therefore necessary to obtain a COSY ^{1}Hnmr of Hppt to in order to correctly assign all of the signals. [40] Although the Hppt ligand contains four possible coordination sites, prior studies on the more symmetric ligands bpt and bpzt showed no evidence for coordination via the N_4 of the triazole, and the synthesis of $[Ru(bpy)_2(ppt)]^+$ yields two isomers (shown above). Isomer 1 has been assigned to coordinate via N_2 of the triazole and N of the pyridine ring. Isomer 2 has been assigned to coordinate via N_1 of the triazole and N of the pyrazine ring.

The ^{1}Hnmr spectra of the these two coordination isomers [Fig. 4.5 and 4.6] are obviously, even harder to interpret than the ^{1}Hnmr spectrum of the free Hppt ligand, due to the presence of many bpy protons, this difficulty is overcome by the use bpy-d_8 which simplifies the spectra enormously.[Fig. 4.7 and 4.8] The shielding effect of the bpy ring on the H_5 and H_6 protons of Hpztr described previously is also seen upon formation of the $[Ru(bpy)_2(ppt)]^+$ complex. In this case it is possible to distinguish between the two isomers by interpretation of their ^{1}Hnmr spectra [Fig 4.7 and 4.8], due to the fact that in the case of isomer 1, it is the pyridine H_6 and H_5 - protons that are closest to the bpy ring and so it is these two signals which will be most significantly shifted upfield in the ^{1}Hnmr spectrum of Isomer 1, (relative to the corresponding signals in the ^{1}Hnmr spectrum of the free ligand), whereas in the spectrum of isomer 2 it is the signals due to the pyrazine H_6 and H_5 -protons which experience the greatest shift. [Table 4.2]

Table 4.2 ^{1}Hnmr signal assignments for triazole ligand Hppt in both coordination isomers of $[Ru(bpy\text{-}d_8)_2(ppt)]^+$. [40]

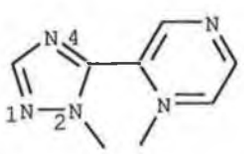
Compound		H_3	H_4	H_5	H_6
Hppt ligand	**pz**	9.33(s)	-----	8.72(d)	8.72(d)
	py	8.17(d)	8.01(t)	7.54(t)	8.77(d)
$[Ru(bpy\text{-}d_8)_2(ppt)]^+$	**pz**	9.19(s)	-----	8.46(d)	8.32(d)
Isomer 1	**py**	7.75(d)	8.01(t)	7.31(t)	7.56(d)
$[Ru(bpy\text{-}d_8)_2(ppt)]^+$	**pz**	9.32(s)	-----	8.32(d)	
Isomer 2	**py**	8.08(d)	7.59(m)	7.25(m)	

4.3 *The application of deuteriation in the investigation into the excited state properties of ruthenium polypyridyl complexes.*

The increase in the luminescent lifetime of $[Ru(bpy)_3]^{2+}$ upon deuteriation of the bpy ligands has been well documented (see chapter 1), but to date no systematic study of the effect of selective deuteriation on the lifetimes of mixed ligand ruthenium polypyridyl complexes has ever been carried out. This is most likely as a result of the difficulties involved in the synthesis of deuteriated polypyridyl ligands. The deuteriation method reported here has effectively done away with these difficulties.

Keyes *et al.*, [19] previously made the proposal that the emission lifetime may only increase upon deuteriation of a particular ligand when the excited state is located on that ligand, in a recent study they have used partial deuteriation techniques in order to consider this issue in more detail.[41] Although not part of this thesis, the following study does illustrate how deuteriated polypyridyl ligands (synthesised according to the method reported), can be used to obtain valuable information into the excited state properties of these complexes.

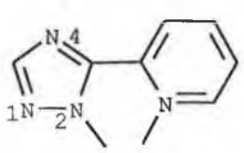
The emission behaviour of a series of complexes of the type $[Ru(bpy)_2(L)]^{n+}$ where L is 3-(pyridin-2-yl)-1,2,4-triazole (Hpytr) or 3-(pyrazin-2-yl)-1,2,4-triazole (Hpztr) has been investigated.



Ru(bpy)$_2$

[Ru(bpy)$_2$(pztr)]$^+$

Isomer 2



Ru(bpy)$_2$

[Ru(bpy)$_2$(pztr)]$^+$

Isomer 2

In both sets of complexes the triazole ring can be protonated and this protonation has a significant effect on the excited state properties of the compounds. As described previously for Hpztr, synthesis of these complexes yields two isomers as the metal centre

may be coordinated via either N^4 or N^2 of the triazole ring giving isomer 1 or 2 respectively. This study concentrated on isomer 2 (*ie.*, N^2 bound) of both the pyridyltriazole and the pyrazyltriazole complexes. The emission lifetimes obtained for compounds with various degrees of deuteriation are given in Table 4.3 below.

Table 4.3 Emission Lifetime data *

Complex	Lifetime / ns Isomer 2	Complex	Lifetime / ns Isomer 2
$[Ru(bpy)_2(pztr)]^+$	228	$[Ru(bpy)_2(pytr)]^+$	145
$[Ru(bpy)_2(Hpztr)]^{2+}$	230	$[Ru(bpy)_2(Hpytr)]^{2+}$	-
$[Ru(bpy\text{-}d_8)_2(pztr)]^+$	266	$[Ru(bpy\text{-}d_8)_2(pytr)]^+$	251
$[Ru(bpy\text{-}d_8)_2(Hpztr)]^{2+}$	230	$[Ru(bpy\text{-}d_8)_2(Hpytr)]^{2+}$	-
$[Ru(bpy)_2(pztr\text{-}d_4)]^+$	210	$[Ru(bpy)_2(pytr\text{-}d_5)]^+$	142
$[Ru(bpy)_2(Hpztr\text{-}d_4)]^{2+}$	467	$[Ru(bpy)_2(Hpytr\text{-}d_5)]^{2+}$	-
$[Ru(bpy\text{-}d_8)_2(pztr\text{-}d_4)]^+$	300	$[Ru(bpy\text{-}d_8)_2(pytr\text{-}d_5)]^+$	-

* All measurements were carried out at room temperature under nitrogen atmosphere in CH_3CN degassed with argon, experimental error = +/- 10%.

- Lifetimes for the Hpytr complexes are too short (<20 ns) to be measured with the laser system available.

The data above are in agreement with previous studies [48] which have shown that for the pyridyltriazole complexes the excited state emission is firmly bpy based. The emission data for the deprotonated species show that on deuteriation of bpy there was a significant increase in the luminescent lifetime, whereas deuteriation of pytr had no effect at all on the lifetime. Lifetimes for the protonated species were too short to be measured because on protonation the electron density of the triazole ring is reduced. This stabilises the t_{2g} orbitals and reduces the energy of the d-d / ^{3}MC orbitals, making population of them possible at room temperature. As non-radiative decay may take place by population of

these orbitals, this results in a decrease in luminescent lifetime. The emission behaviour observed for the pyridyltriazole complexes was therefore, the behaviour which had previously been postulated *ie.*, that deuteriation will only affect the lifetime if the emision is based on the deuteriated ligand.

On the basis of excited state pKa measurements, backed-up by excited state resonance Raman spectra, it had been postulated [47] that for the protonated pyrazyltriazole complex the excited state is based on the pyrazyl ligand, while for the deprotonated species the excited state is bpy based. The emission data in Table 4.3 for the pyrazyltriazole complexes shows that there was no dramatic decrease in emission lifetime observed on protonation, neither was there any increase in lifetime on deuteriation of bpy, but deuteriation of pytr lead to a doubling of emission lifetime, this data directly supports the switching of the emitting state from bpy to pyrazyl upon protonation of the triazole ring.

It is proposed above that the excited state of the deprotonated pyrazyltriazole complex is bpy based, in which case a significant increase in lifetime is expected upon deuteriation of bpy. However the data in Table 4.3 shows that although there was a slight increase in lifetime, it was nothing compared to the increase observed for the pyridyltriazole complex, nor was there any increase upon deuteriation of pztr. Detailed temperature dependence studies were carried out in order to try to rationalise this behaviour, and it was found that for the deprotonated complex $[Ru(bpy)_2(pztr)]^+$, in the temperature range 120-250 K, the emission is resolved into two distinct bands of intensity ratio 1:2 at 600 nm and 700 nm respectively. At 120 K a single emission peak was observed at 700 nm, upon increasing the temperature the second signal was then observed at 600 nm, therefore at higher energy. This was not observed for the protonated complex, nor for the analogous complexes based on pyridyltriazole. The excited state lifetime at 250 K, was monitored separately at 700 nm and 600 nm and at 700 nm a single exponential decay was observed with a lifetime of 280 ns, while at 600 nm a longer lived lifetime of 1 μs was observed. This excited state lifetime data corroborates the dual nature of the emission

process above 120 K. Excitation spectra obtained of each of the emissions were sufficiently similar to suggest that both states are based on MLCT emissions. At 90 K both lifetime and emission data show only one emission site, the formation of two individual emitting sites only occurred at temperatures above 120 K.

The explanation suggested for the behaviour observed for $[Ru(bpy)_2(pztr)]^+$, is that in the temperature range 120-250 K there is a thermal population of a higher lying pyrazine state which may transfer its energy to the lower bpy state, this energy transfer process is itself temperature activated and is ineffecient below 120 K. Although this theory was by no means proven conclusively, the presence of two closely linked excited states might account for the fact that there was no marked increase in the emission lifetime of the $[Ru(bpy)_2(pztr)]^+$ complex on deuteriation of bpy. If there is an equilibrium between two triplet states based on different ligands, the deuteriation of one of these ligands is not going to have the same effect as when the excited states in question are non-coupled. These results have also shown that for this particular complex deuteriation cannot be used to identify the emitting ligand. [47]

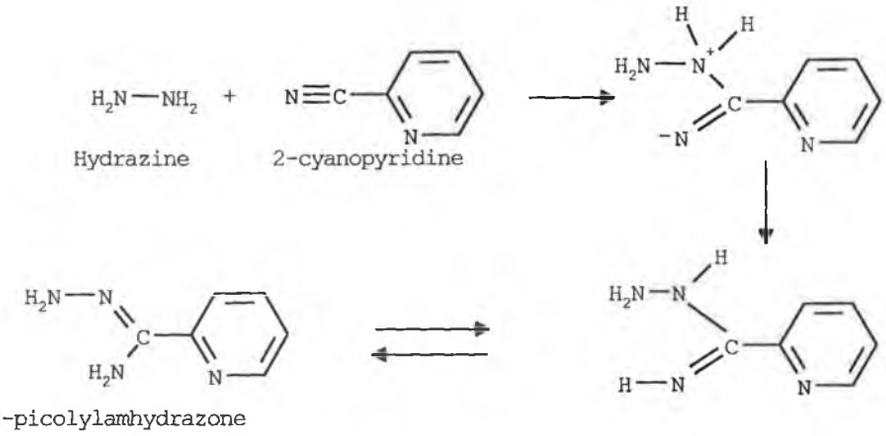
4.4 *Aryl-substituted pyridyltriazole containing complexes.*

Quinones and hydroquinones play an important role in electron transport chains in mitochondrial reactions and in both electron and proton transport in plant and bacterial photosynthesis. In an effort to try to copy these reactions abiotically, a series of aryl-substituted pyridyltriazole ligands and their subsequent complexes was synthesised by Keyes *et al.*[21] The results of studies carried out on these complexes revealed that on a considerably simpler level, these complexes mimic some of the unit functions of the photosynthetic system and therefore require more investigation as they may provide valuable information on the mechanistics of the photosynthetic process.

$[Ru(bpy)_2(3\text{-}(2,5\text{-dimethoxyphenyl})\text{-}5(\text{-pyridin-2-yl})\text{-}1,2,4\text{-triazole})]^+PF_6^-$ was synthesised as part of the on going study of these complexes, as it is a precursor to the hydroquinone complex $[Ru(bpy)_2(3\text{-}(2,5\text{-dihydroxyphenyl})\text{-}5(\text{-pyridin-2-yl})\text{-}1,2,4\text{-triazole})]^+PF_6^-$, which is formed upon removal of the two methyl protecting groups. The dimethoxyl complex was synthesised according to the method described in the experimental section [21]. The synthesis was carried out in several stages, the following is a description of the reaction mechanisms involved.

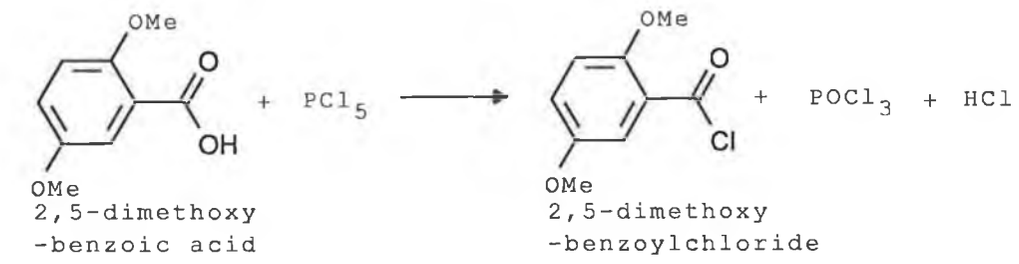
4.4.1 Synthesis of pyridine-2-carboximidehydrazide [21]

The first step is the preparation of 2-picolylamhydrazone and can best be described as a nucleophilic attack by hydrazine on 2-cyanopyridine. It is a relatively simple synthetic procedure but it takes three days and the final yield was estimated to be only 60%. 2-picolylamhydrazone is extremely moisture sensitive and must be stored under vacuum immediately on isolation to prevent decomposition. The product was characterised by ^{1}Hnmr (see experimental section), the two doublets and two triplets due to the pyridine protons can be seen between 8.5 and 7.0 ppm and the singlets due to the two NH_2 groups appear at 5.32 and 4.48 ppm.



4.4.2 Synthesis of 2,5-dimethoxybenzoylchloride. [39]

The second step in the ligand synthesis was the preparation of the corresponding acid chloride by reacting 2,5-dimethoxybenzoic acid with phosphoruspentachloride. Due to the high boiling point of this acidchloride (bp=290^{0}C), distillation, even under vacuum, proved very difficult as the whole distillation apparatus had to be insulated and the water to the condenser turned off, to prevent the acidchloride crystallising out before it reached the receiving flask. When this did happen the acidchloride was reheated using a hairdrier. The 2,5-dimethoxybenzoylchloride synthesised was very unstable and had to be used immediately, to prevent its conversion back to the carboxylic acid, so it was not possible to carry out any kind of characterisation. This reaction also produces two quite noxious by-products - phosphorus oxychloride and hydrogen chloride gas, which necessitate that the reaction be carried out in the fumehood.



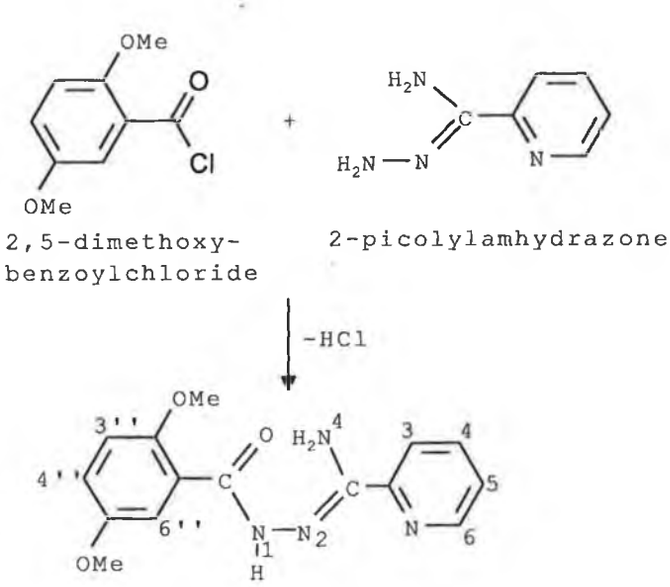
2,5-dimethoxy -benzoic acid

2,5-dimethoxy -benzoylchloride

4.4.3 Synthesis of Acylamidrazone [21].

2-Picolylamhydrazone and 2,5-dimethoxybenzoylchloride were then reacted together to produce the intermediate which is the precursor for the L_1 ligand. During the course of the reaction HCl gas was evolved. This step worked well in general, but it is absolutely imperative that all glassware is completely dry and that the THF used is also thoroughly dry as any water present at this stage will immediately react with the acidchloride and convert it back to the carboxylic acid.

The product was characterised by ^{1}Hnmr (see experimental section), the signal at 5.32 ppm in the ^{1}Hnmr spectrum of 2-picolylamhydrazone due to the ^{1}N-H_2 protons has been replaced by the signal at 10.13 ppm due to the ^{1}N-H proton, the ^{4}N-H_2 signal now appears much further downfield at 6.73 ppm due to the large deshielding effect of the adjacent carboxy group. The two doublets and two triplets due to the pyridine protons have been shifted downfield relative to their previous positions, the signals at 7.12 and 7.06 ppm are due to the three benzyl protons and the two singlets at 3.80 and 3.75 ppm both have an integration of 3 and are due to the two methyl group protons.

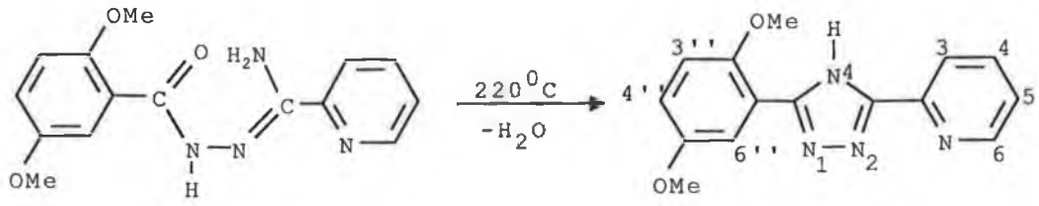


Acylamidrazone

4.4.4 Synthesis of 3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole(L_1) [21].

This reaction is essentially a modified imine formation - the cyclisation is carried out by refluxing the intermediate at 200^{0}C for approximately 3 hr. in ethylene glycol. This reaction was attempted many times before it was carried out successfully, the main problem was that too much ethylene glycol was used and so after refluxing the product did not precipitate on cooling. It was found that the best results were achieved by using the minimum volume of ethylene glycol possible. Several trials were also needed to

ascertain how long it was necessary to reflux the solution in order to achieve cyclisation. Thus if the solution was heated for too long thermal decomposition occurred, but equally if the solution was not heated for long enough, cyclisation did not take place. The yield of 60% was not particularly good, mainly due to the difficulties described above in isolating the ligand from the ethylene glycol solution. The product was characterised by ^{1}Hnmr (see experimental section), cyclisation was complete when the peak at around 10 ppm due to the ^{1}N-H proton and the peak below 7 ppm due to ^{4}N-H_2 were no longer present, all other signals appeared at approximately the same position as in the ^{1}Hnmr spectrum of the acylamidrazone.



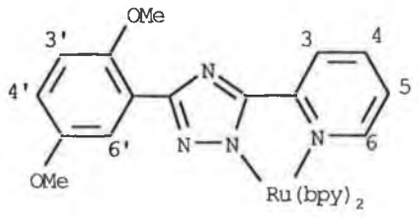
Acylamidrazone

3-(2,5-dimethoxyphenyl)
-5-(pyridin-2-yl)
-1,2,4-triazole

4.4.5 Synthesis of $[Ru(bpy)_2(3\text{-}(2,5\text{-dimethoxyphenyl})\text{-}5\text{-}(pyridin\text{-}2\text{-}yl)\text{-}1,2,4\text{-}triazole)]^{+}[PF_6]^{-}$ [21].

$[Ru(bpy)_2(3\text{-}(2,5\text{-dimethoxyphenyl})\text{-}5\text{-}(pyridin\text{-}2\text{-}yl)\text{-}1,2,4\text{-}triazole)]^{+} = [Ru(bpy)_2(L_1)]^{+}$ was synthesised according to a method reported previously by Tia Keyes [19], with no alterations. After recrystallisation in acetone/water the final yield of $[Ru(bpy)_2(L_1)]^{+}$ was 59%, it was characterised by HPLC and ^{1}Hnmr (see Appendix). The ^{1}Hnmr of $[Ru(bpy)_2(L_1)]^{+}$ was obtained in acetonitrile at high pH which causes deprotonation as this simplifies the spectrum to a certain extent [Fig. 4.9]. The spectrum is still highly structured, as the bpy resonances obscure those of the heteroligand making assignment of the signals very difficult. This problem is solved by using bpy-d_8, as this eliminates the

bpy signals from the spectrum. [Fig. 4.10] $[Ru(bpy\text{-}d_8)_2(L_1)]^+$ was synthesised by exactly the same method as $[Ru(bpy)_2(L_1)]^+$, the final yield was 55%. ^{1}Hnmr peak assignments are given in Table 4.4.



$[Ru(bpy)_2(L_1)]^+$.

Table 4.4 ^{1}Hnmr signal assignments for $[Ru(bpy\text{-}d_8)_2(L_1)]^+$ in $(CD_3)_2SO$.

Shift in ppm	Signal	Integration	Assignment
8.43	doublet	1	H_3
8.06	triplet	1	H_4
7.63	doublet	1	H_6
7.50	singlet	1	$H_{6'}$
7.36	triplet	1	H_5
7.07	doublet	2	$H_{3'\&4'}$

As described previously the excited state of $[Ru(bpy)_2(L_1)]^+$ is bpy based and so it is expected that deuteriation of the bpy ligands will result in an increase in the luminescent lifetime. Preliminary lifetime studies have shown that there is an increase from 79 ns for $[Ru(bpy)_2(L_1)]^+$ to 542 ns for $[Ru(bpy\text{-}d_8)_2(L_1)]^+$, see Fig. 4.11 and 4.12.

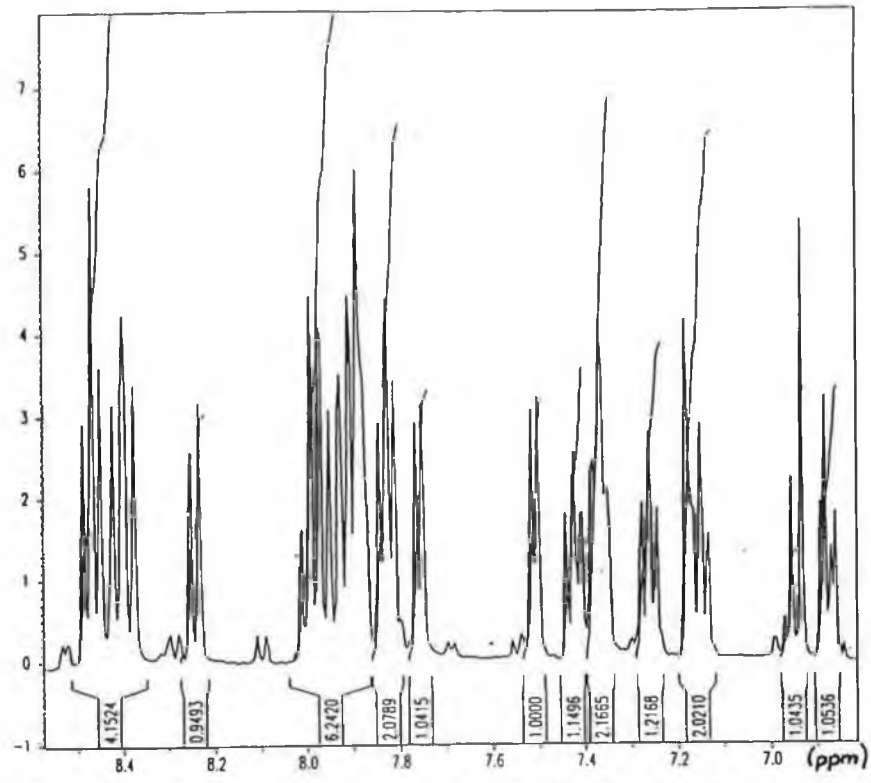


Figure 4.9 ^{1}Hnmr of deprotonated $[Ru(bpy)_2(L_1)]^{+}$ in CH_3CN.

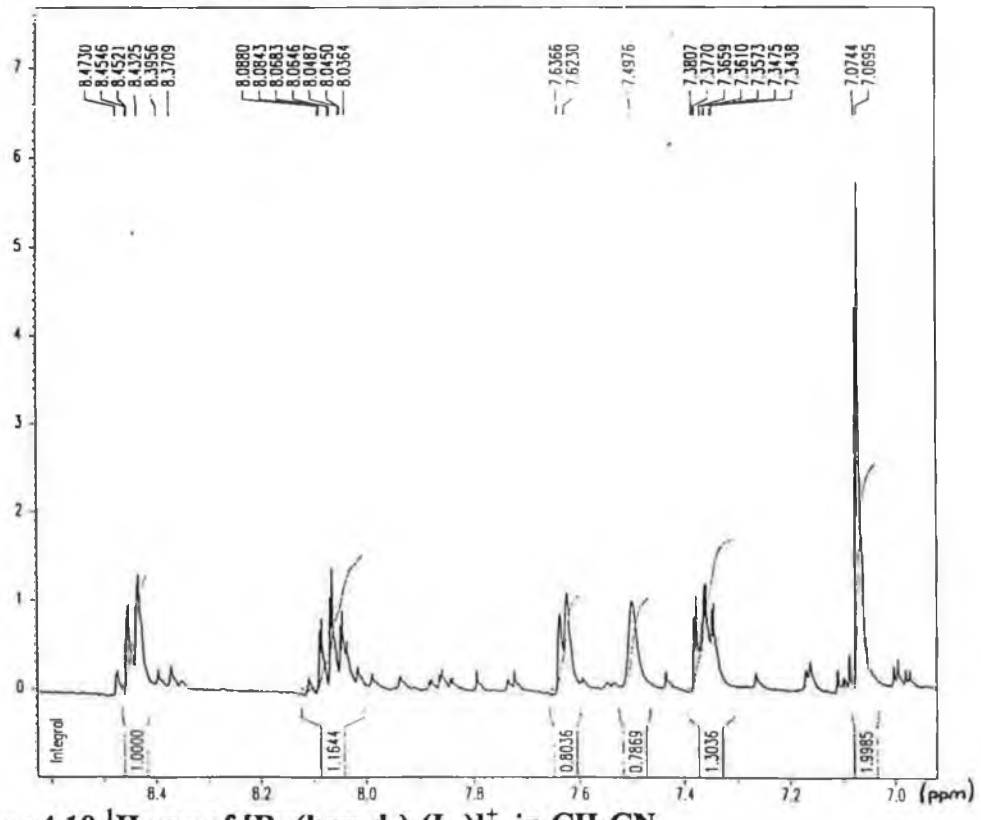


Figure 4.10 ^{1}Hnmr of $[Ru(bpy\text{-}d_8)_2(L_1)]^{+}$ in CH_3CN.

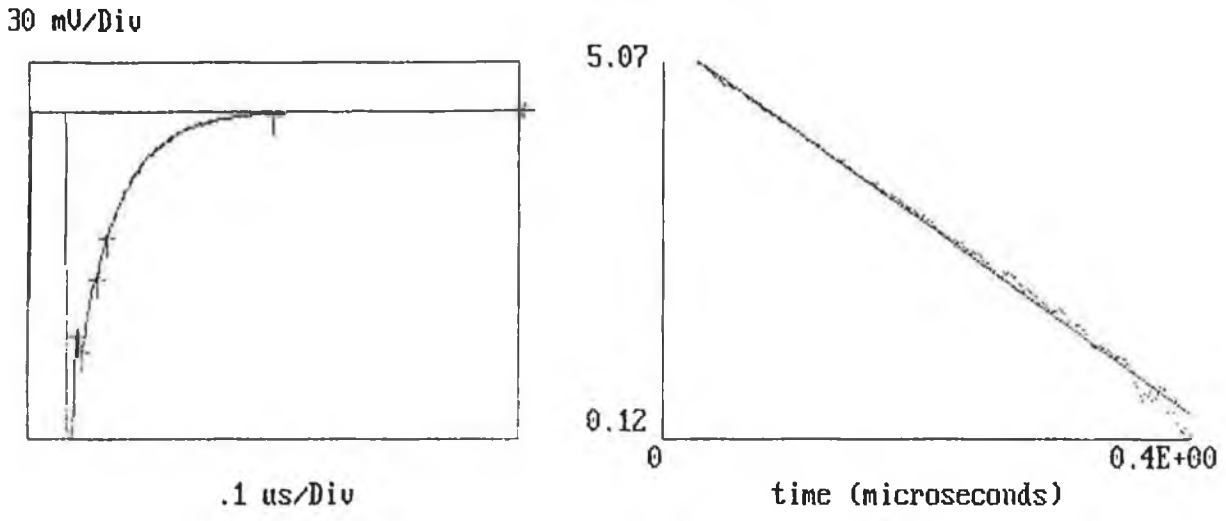


Figure 4.11 Luminescent lifetime data for $[Ru(bpy)_2(L_1)]^+$.

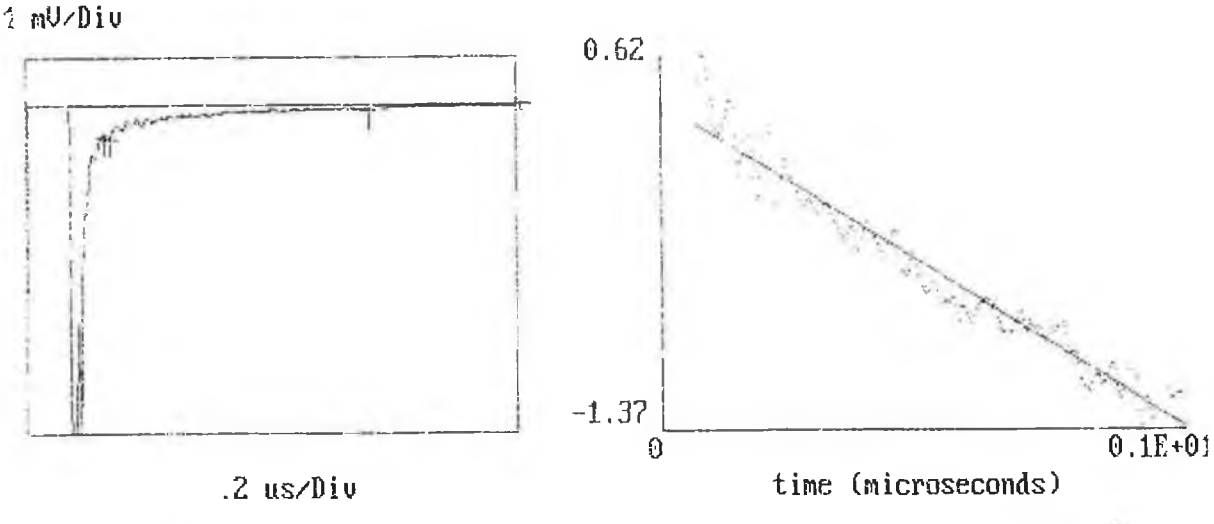
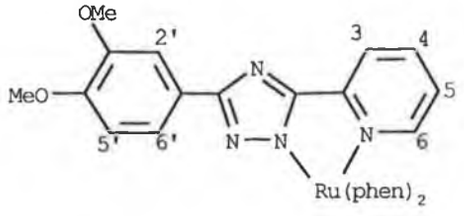


Figure 4.12 Luminescent lifetime data for $[Ru(bpy\text{-}d_8)_2(L_1)]^+$.

Work is also being carried out on another very similar complex- $[Ru(phen)_2$ (3-(3,4-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole)$]^+$ = $[Ru(phen)_2(L_6)]^+$, (phen = 1,10'-phenanthroline). [41]



$[Ru(phen)_2(L_6)]^+$

Once again deuteriation is used to aid in the interpretation of the ^{1}Hnmr spectra, in this case phen-d_{10} is used, see Fig 4.11 and 4.12. Although the phen peaks are still somewhat visible, it is now possible to assign the signals as follows; [Table 4.5]

Table 4.5 ^{1}Hnmr signal assignments for $[Ru(phen\text{-}d_{10})_2(L_6)]^+$ in $(CD_3)_2SO$. [41]

Shift in ppm	Signal	Integration	Assignment
8.37	doublet	1	H_3
8.02	triplet	1	H_4
7.56	doublet	1	H_6
7.45	doublet	1	$H_{6'}$
7.43	singlet	1	$H_{2'}$
7.22	triplet	1	H_5
6.99	doublet	1	$H_{5'}$

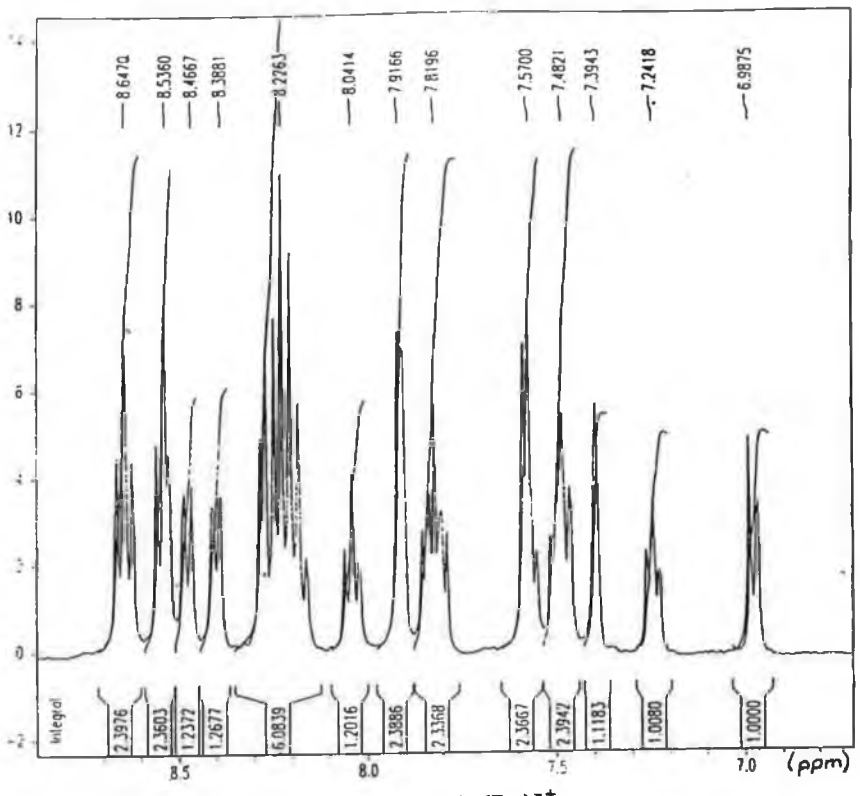


Figure 4.13 ^{1}Hnmr spectrum of $[Ru(phen)_2(L_6)]^{+}$.

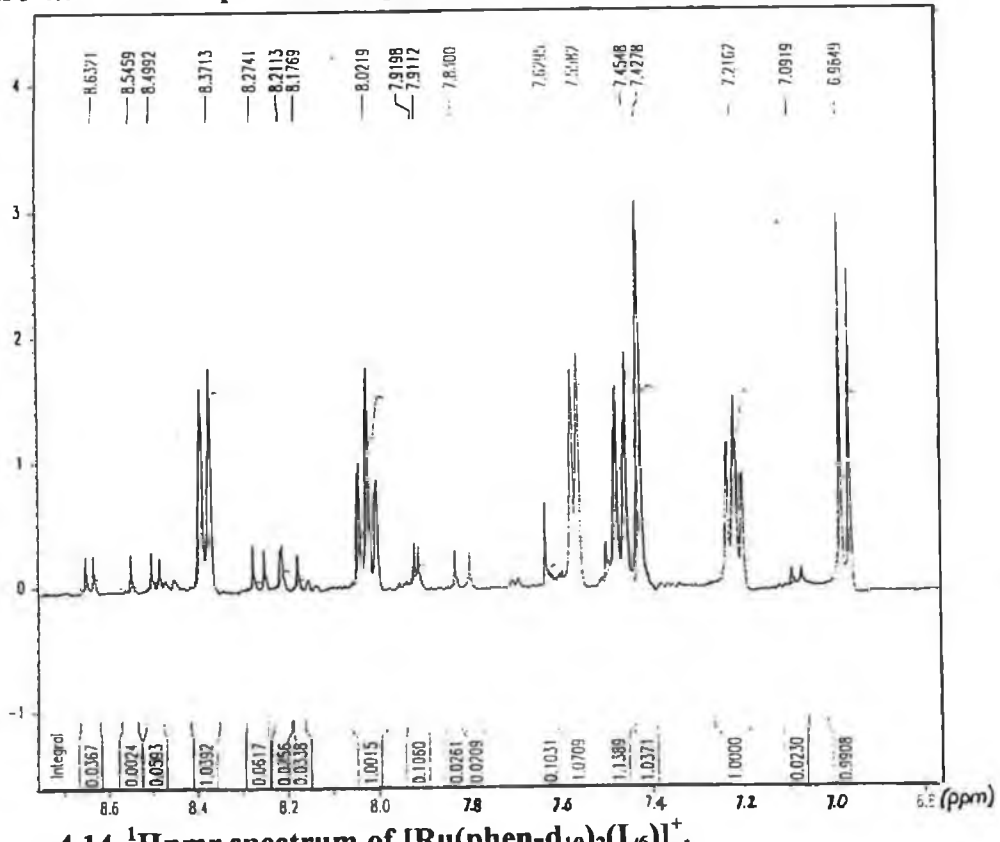


Figure 4.14 ^{1}Hnmr spectrum of $[Ru(phen\text{-}d_{10})_2(L_6)]^{+}$.

4.5 *Conclusion.*

Ruthenium polypyridyl complexes possess some very useful excited state properties which make them ideal for incorporation into supramolecular devices. However, a thorough understanding of the nature of their excited states is needed before we can begin to design supramolecular systems with user-defined photophysical properties. Deuteriation has proven to be a very valuable technique, both in the investigations into the excited states of these compounds and, (by the simplification of their ^{1}Hnmr spectra) in their structural elucidation. However, the laborious and time-consuming nature of the synthetic routes previously available for the synthesis of deuteriated compounds has prevented its wide-scale use and there are to date, relatively few examples of this technique in the literature.

The deuteriation method reported in these studies provides a much simpler, far more efficient route to the preparation of perdeuteriated bpy. Temperature and time optimisation studies on bipyridyl showed that >95% deuteriation was achieved after only 3 days and complete deuteriation was obtained by repeating the procedure, just once, with fresh D_2O and Pd/C. Whereas with previous methods yields were low [33], the yields obtained using this method were consistently equal to or above 90%. The optimisation studies also revealed that with some variations of the reaction conditions, it may be possible to prepare bpy-d_2, -d_4 and -d_6. The deuteriation method reported was also very successfully applied to both pyridyl- and pyrazyl-triazole containing ligands and >95% deuteriation was achieved for all ligands. The problems encountered in the isolation of dmbpy, Hbpt, Hbpzt and Hppt, due to their adherence to the Pd/C catalyst, and the failure of the reported method to deuteriate (3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl))-1,2,4-triazole and (3-(3,4-dimethoxyphenyl)-5-(pyridin-2-yl))-1,2,4-triazole, have shown that the reaction conditions are not ideally suited to these ligands and that further studies are required in these areas. Nevertheless, it is clear that the simplicity, efficiency and versatility of the deuteriation method reported will allow for the more general application of deuteriated compounds in future investigations of ruthenium polypyridyl complexes.

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Appendix

List of Figures:

Figure 1. I.R. of 4,4'-dimethyl-2,2'-bipyridyl (dmbpy) in $CDCl_3$ - KBr disc.

Figure 2. I.R. of deuteriated dmbpy in $CDCl_3$ - KBr disc.

Figure 3. ^{1}Hnmr of 1,10'-phenanthroline (phen) in $CDCl_3$ - 6.0mg phen / 1 cm^3 $CDCl_3$.

Figure 4. ^{1}Hnmr of phen, after 6 days at 200^0C in 30 cm^3 D_2O, using 0.50g Pd/C / 3g phen, in $CDCl_3$ - 12.0 mg phen / 1 cm^3 $CDCl_3$.

Figure 5. I.R. of phen - KBr disc

Figure 6. I.R. of phen, after 6 days at 200^0C in 30 cm^3 D_2O, using 0.50g Pd/C / 3g phen - KBr disc.

Figure 7. I.R. of 3-(pyridin-2-yl)-1,2,4-triazole (pytr) - KBr disc.

Figure 8. I.R. of pytr after 6 days at 200^0C in 30 cm^3 D_2O, using 0.50g Pd/C / 3g pztr - KBr disc.

Figure 9. ^{1}Hnmr of 3-(pyrazin-2-yl)-1,2,4-triazole (pztr) in $(CD_3)_2SO$ - 6.0mg pztr / 1 cm^3 $(CD_3)_2SO$.

Figure 10. ^{1}Hnmr of pztr, after 6 days at 200^0C in 30 cm^3 D_2O, using 0.50g Pd/C / 3g pztr, in $(CD_3)_2SO$ - 12.0 mg pytr / 1 cm^3 $(CD_3)_2SO$.

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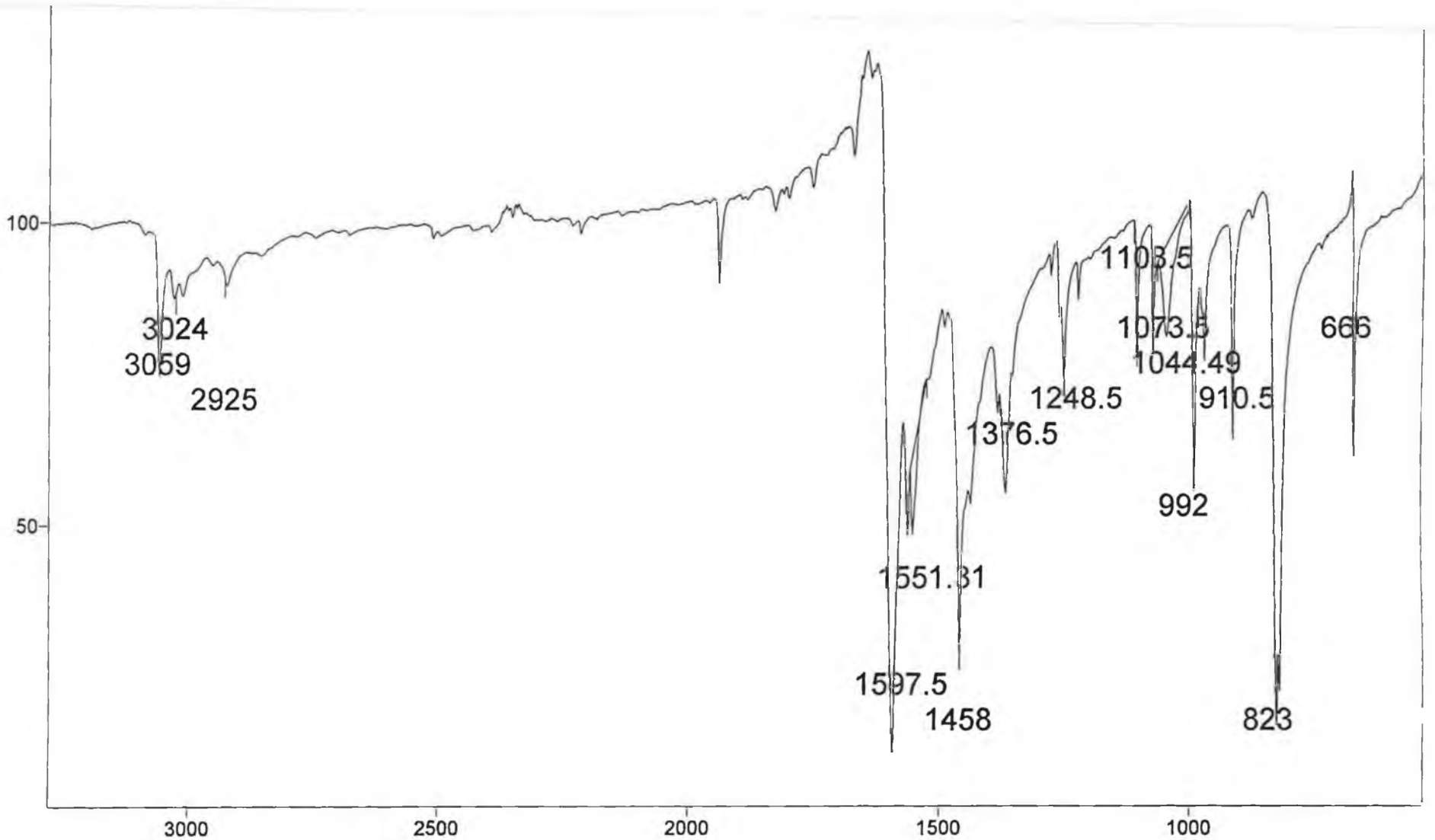


Figure 1. I.R. spectrum of 4,4'-dimethyl-2,2'-bipyridyl.

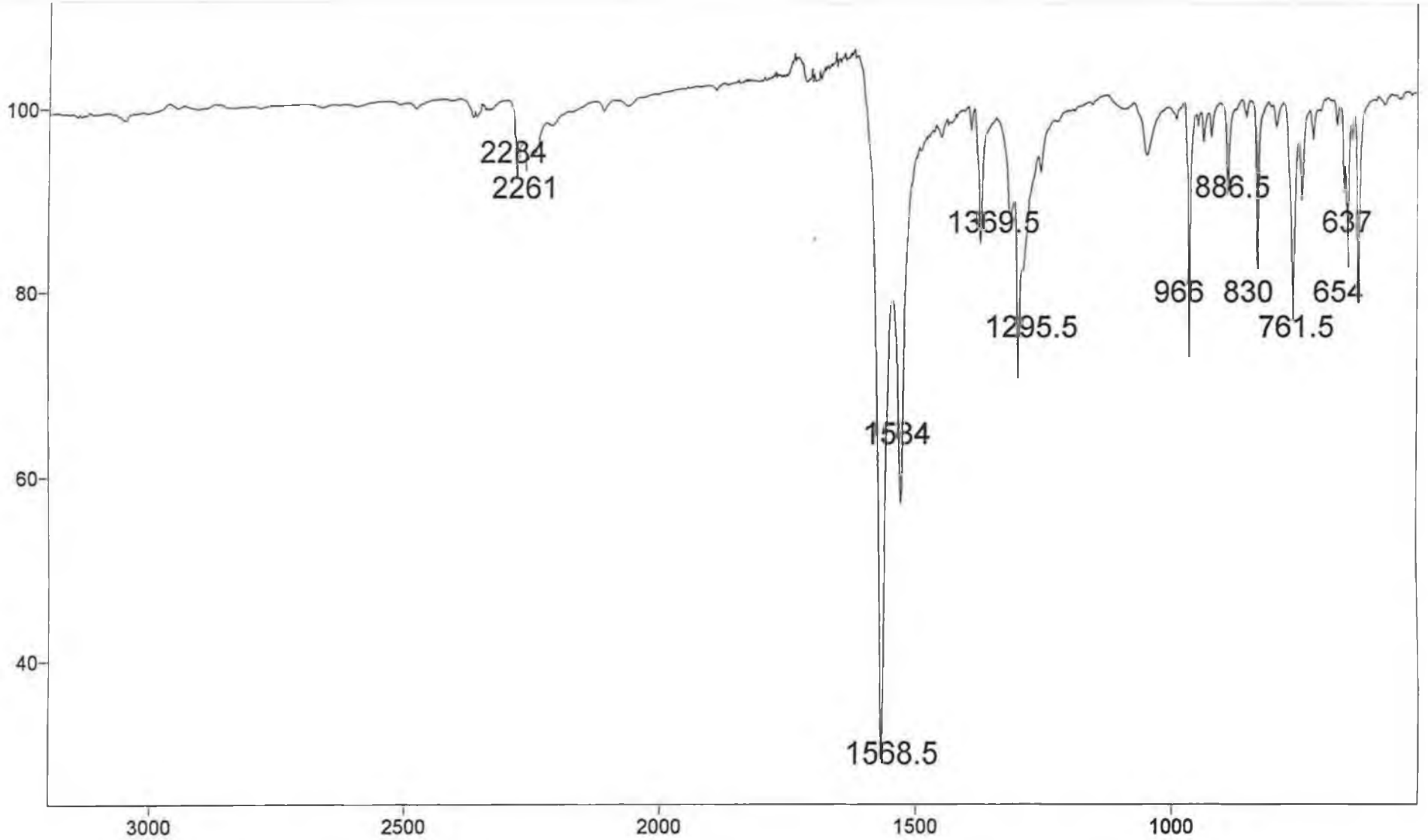


Figure 2. I.R. spectrum of deuteriated 4,4'-dimethyl-2,2'-bipyridyl.

Figure 3. **^{1}Hnmr spectrum of 1,10'-phenanthroline in $CDCl_3$.**

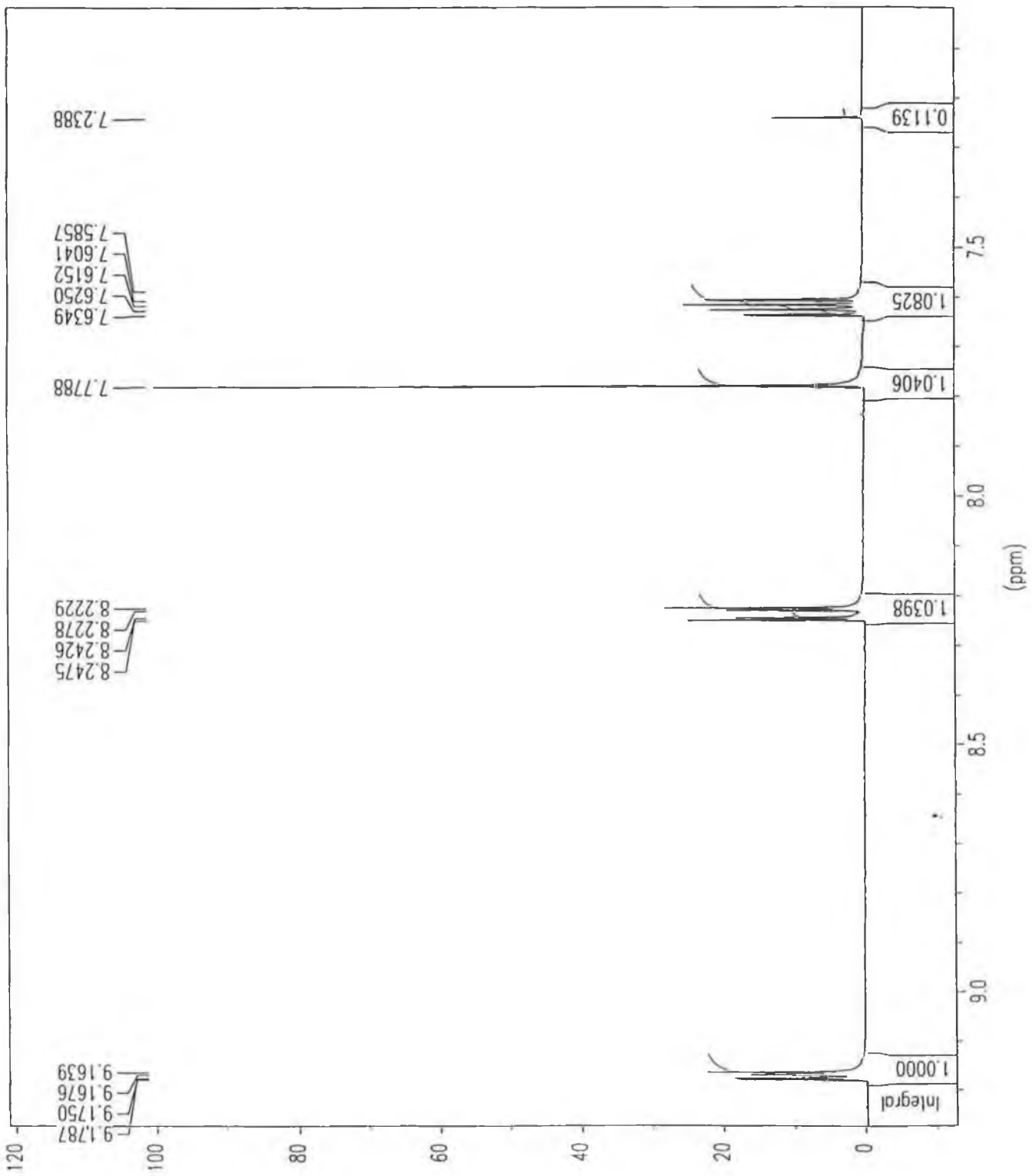
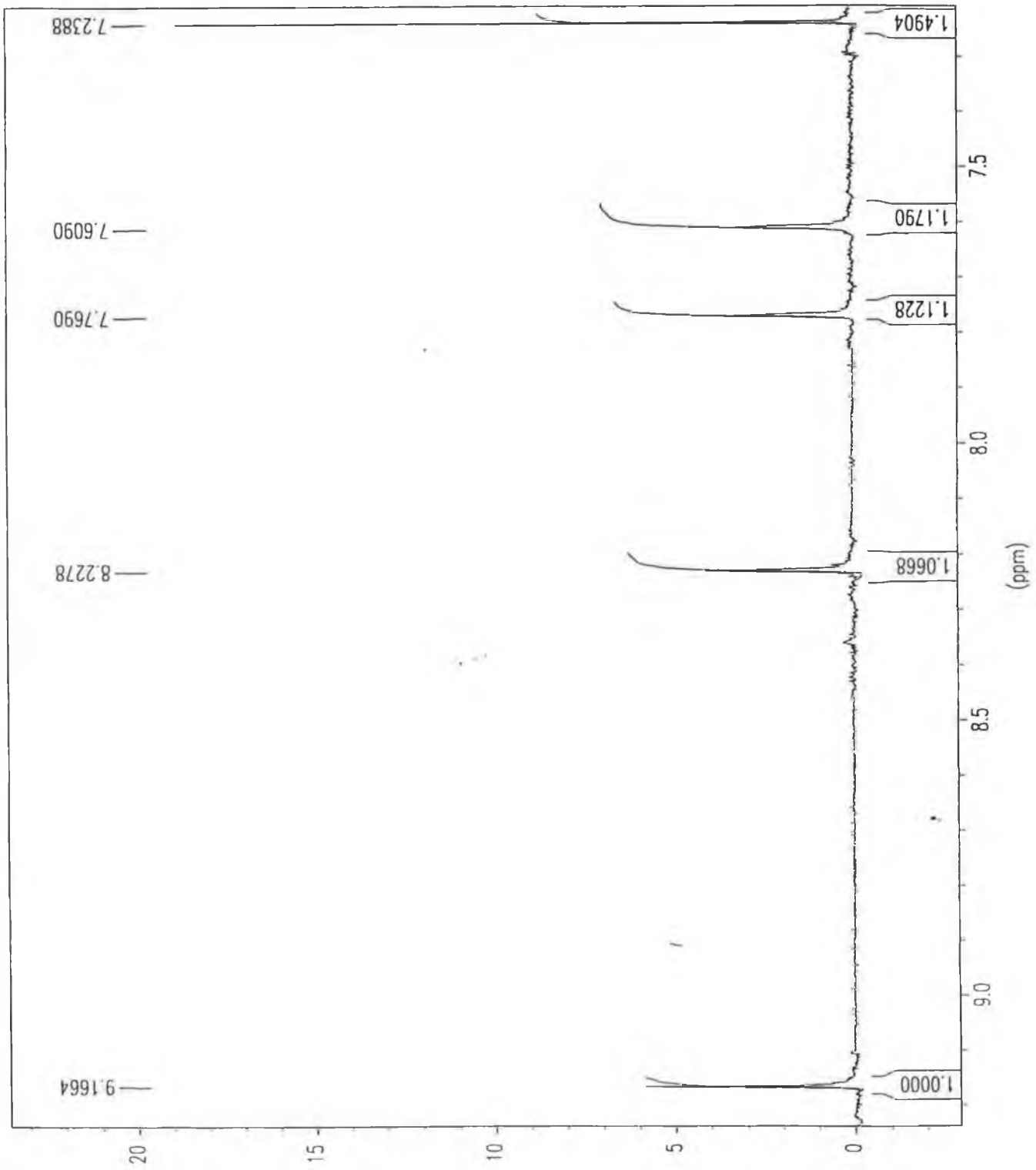


Figure 4. **^{1}Hnmr spectrum of deuteriated 1,10'-phenanthroline in $CDCl_3$.**



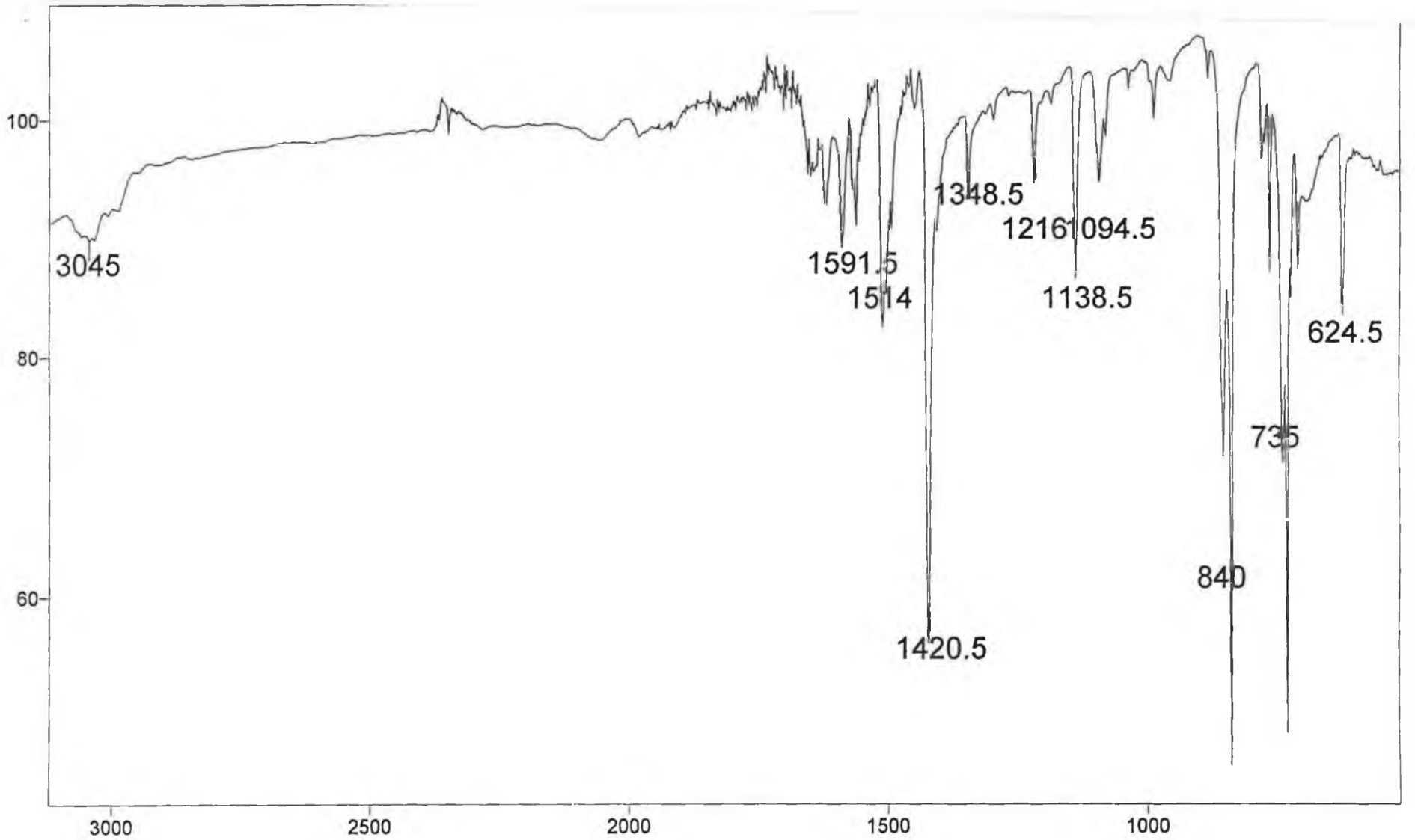
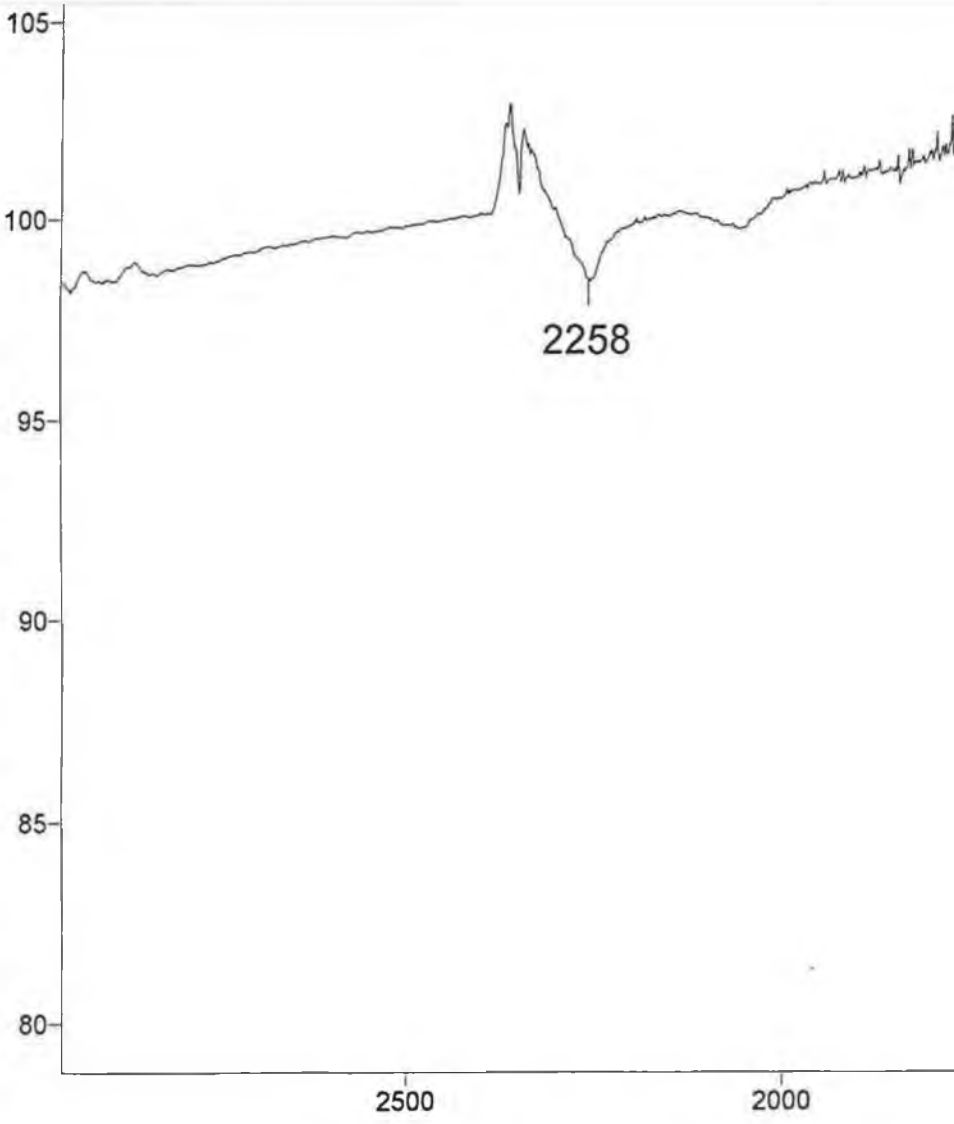


Figure 5. I.R. spectrum of 1,10'-phenanthroline.



Transmittance / Wavenumber (cm-1)

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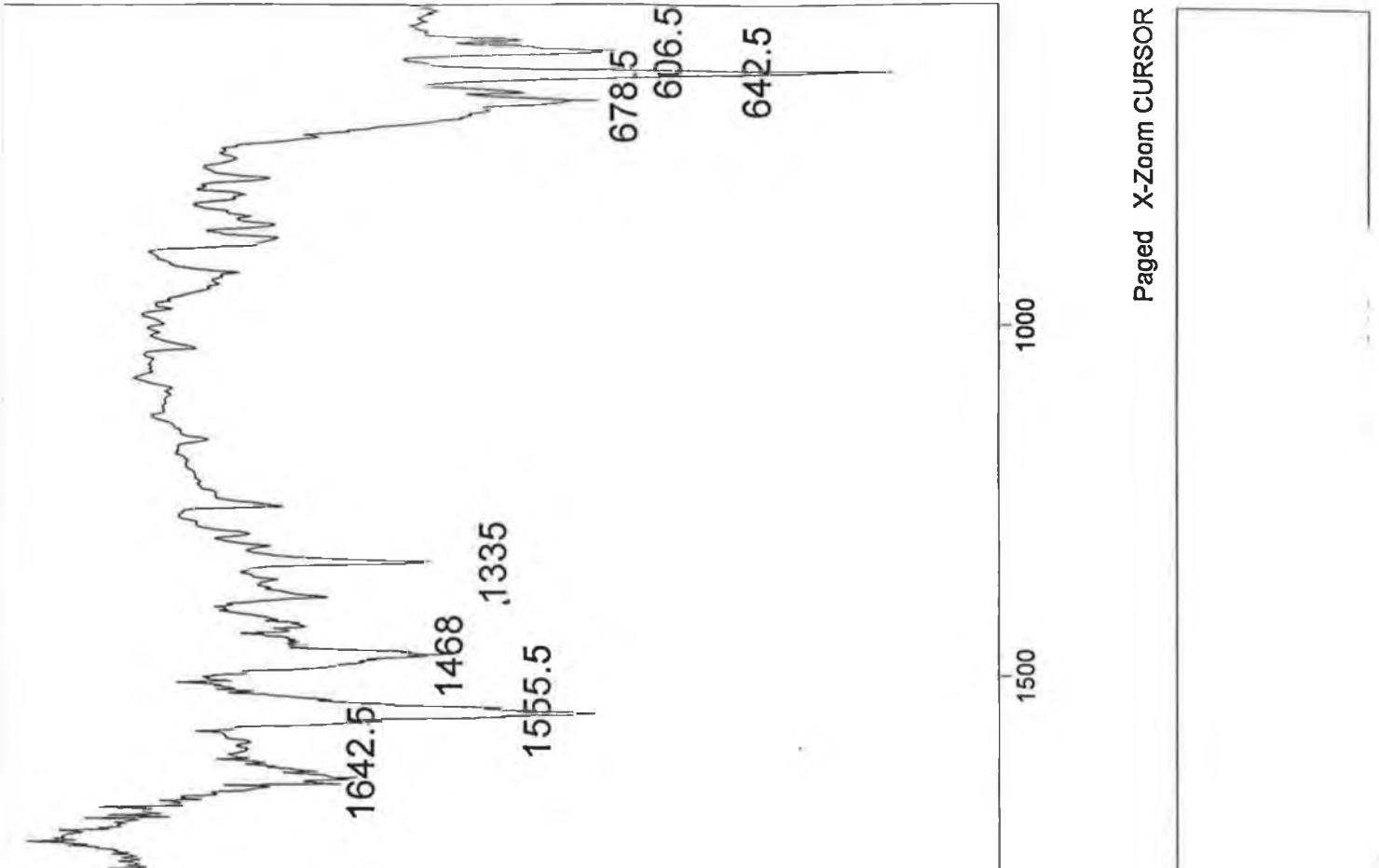
File # 4 : D-PHEN

Figure 6. I.R. spectrum of deuteriated 1,10'-phenanthroline.



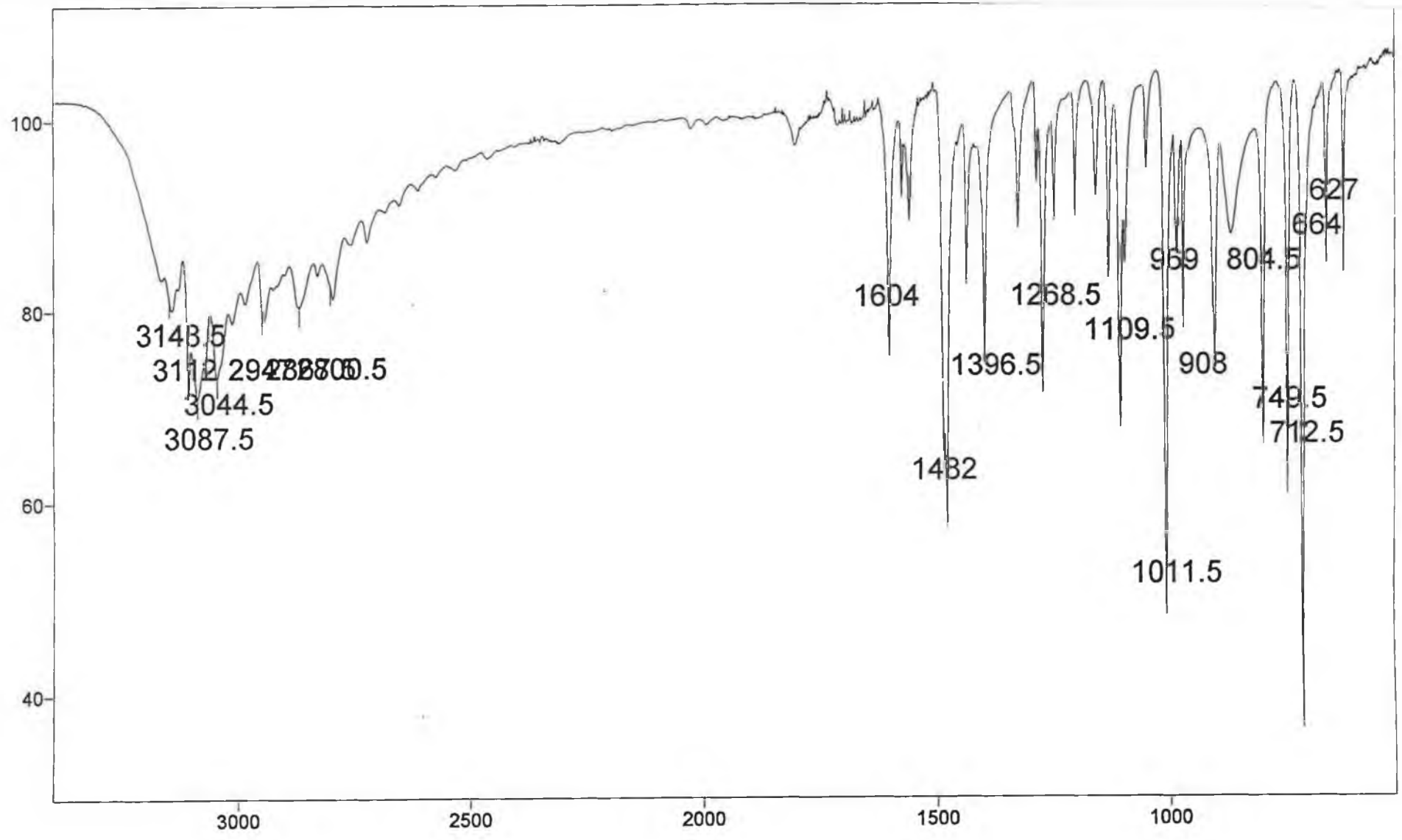


Figure 7. I.R. of 3-(pyridin-2-yl)-1,2,4'-triazole.

Transmittance / Wavenumber (cm-1)

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File # 6 : PYTR

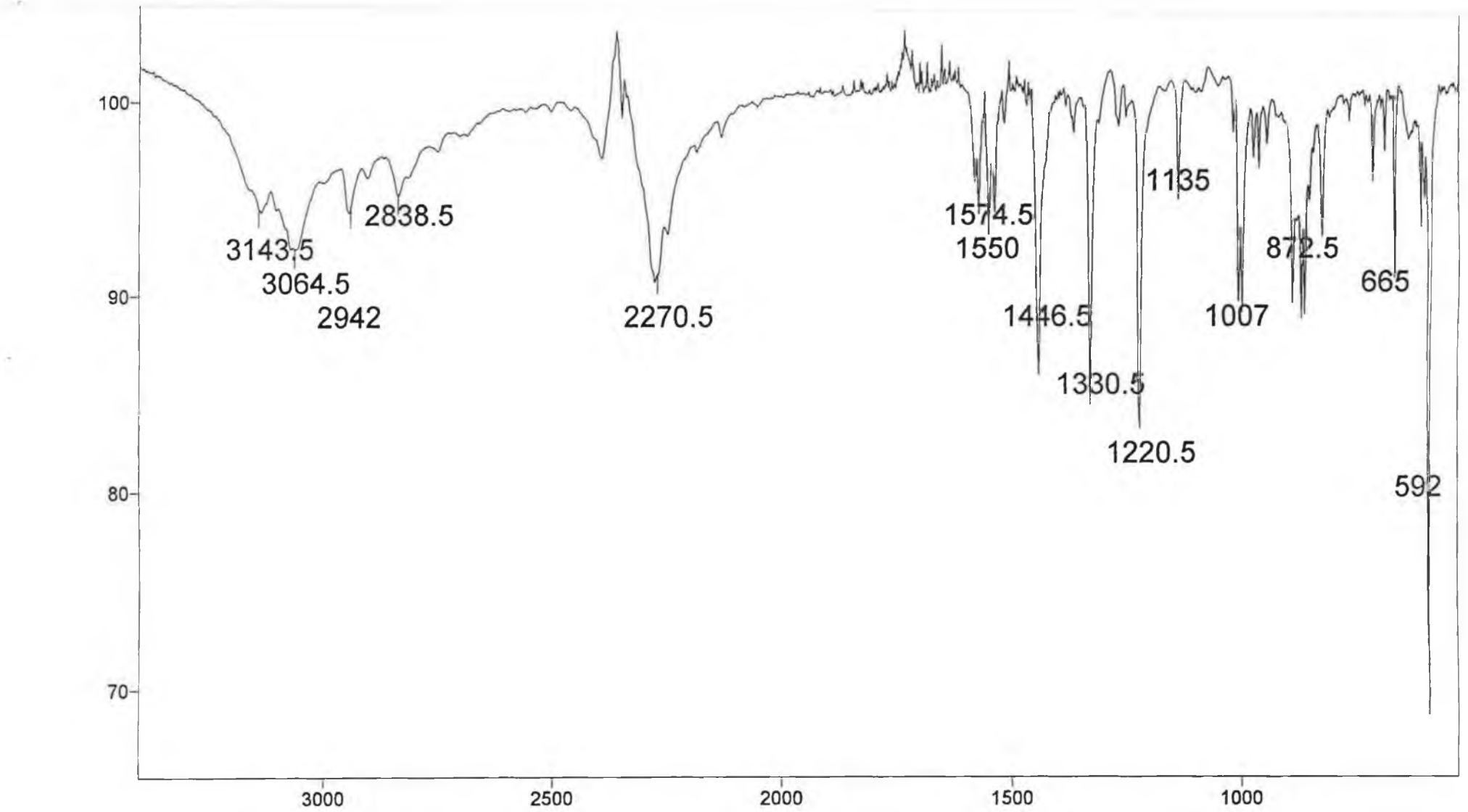
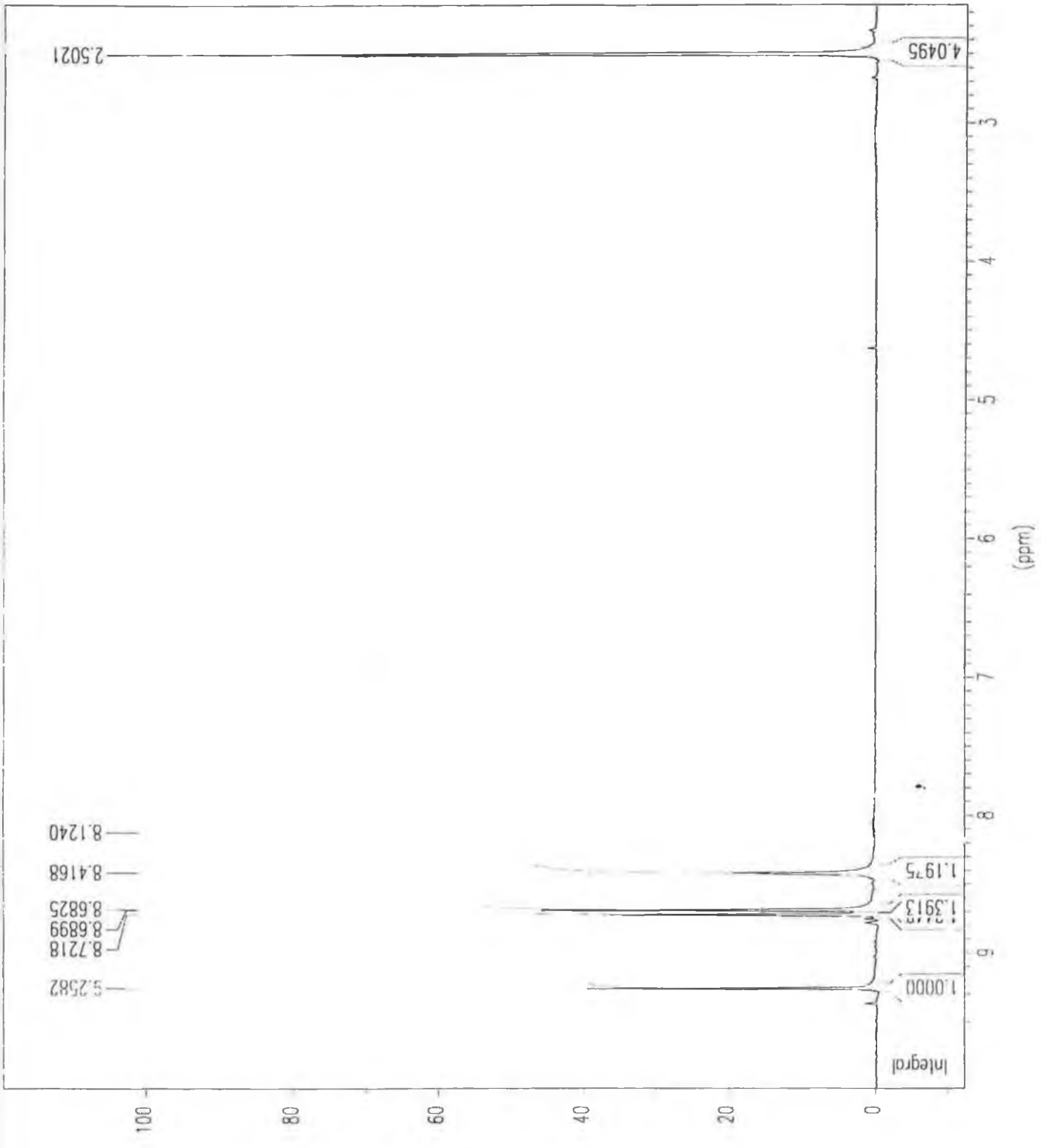


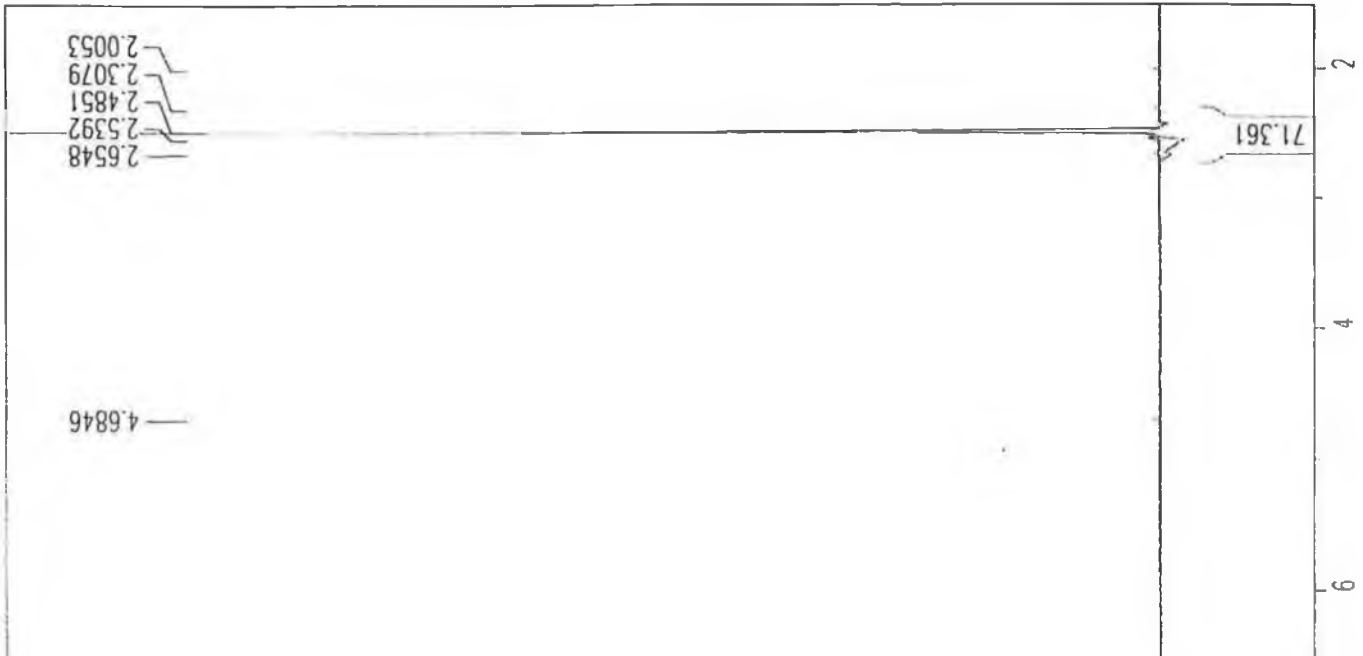
Figure 8. I.R. of deuteriated 3-(pyridin-2-yl)-1,2,4'-triazole.

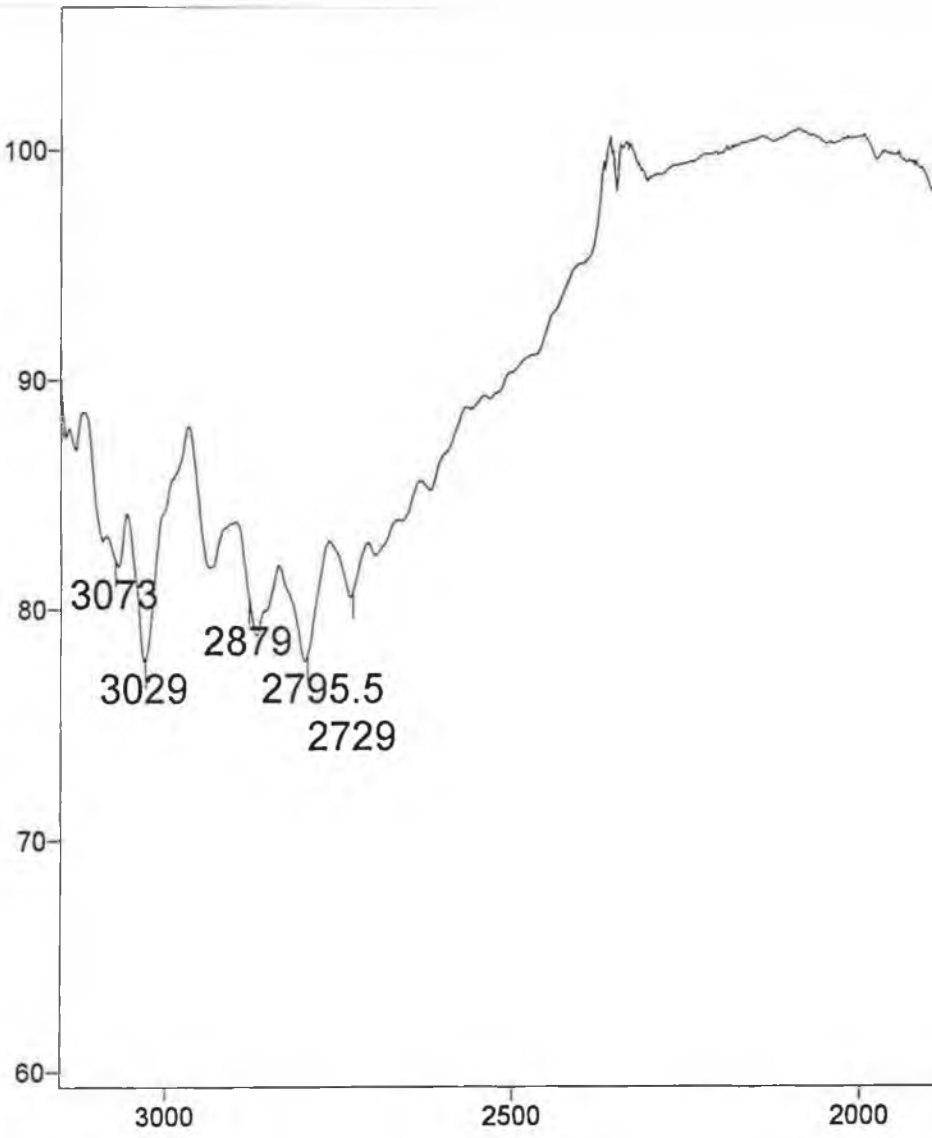
Figure 2 **^{1}Hnmr spectrum of 3-(pyrazin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$.**



11.5686
11.5416
11.4678
9.4109
9.2879
8.8057
8.7934
120
100
80
60
40
20
0
Integral
315.51
1.0000
0.9984
2.0348
12
10
8
(ppm)

Figure 10. **^{1}Hnmr spectrum of deuteriated 3-(pyrazin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$.**





Transmittance / Wavenumber (cm-1)

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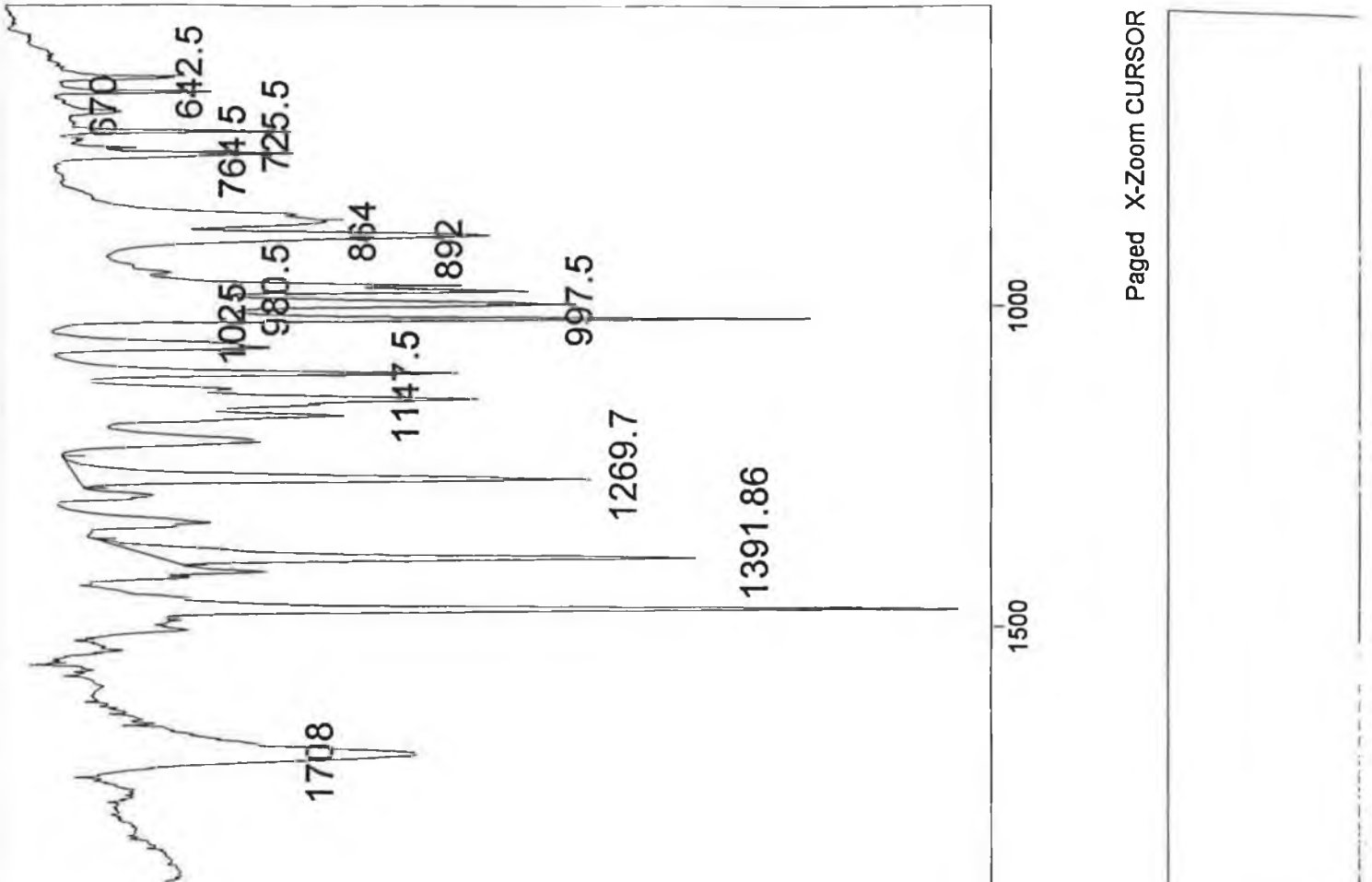
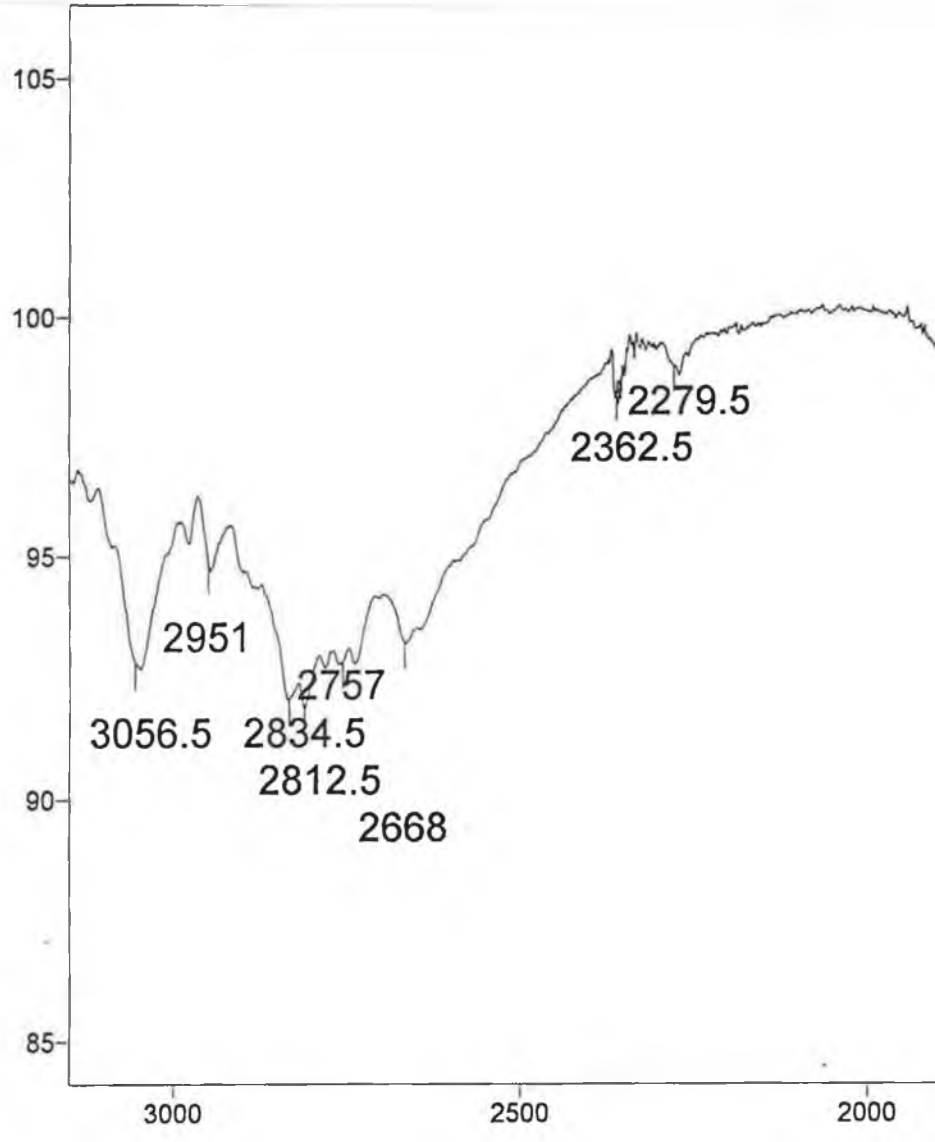
File # 3 : PZTR

Figure 11. I.R. spectrum of 3-(pyrazin-2-yl)-1,2,4'-triazole.





Transmittance / Wavenumber (cm-1)

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File # 4 : D-PZTR

Figure 12. I.R. spectrum of deuteriated 3-(pyrazin-2-yl)-1,2,4'-triazole.

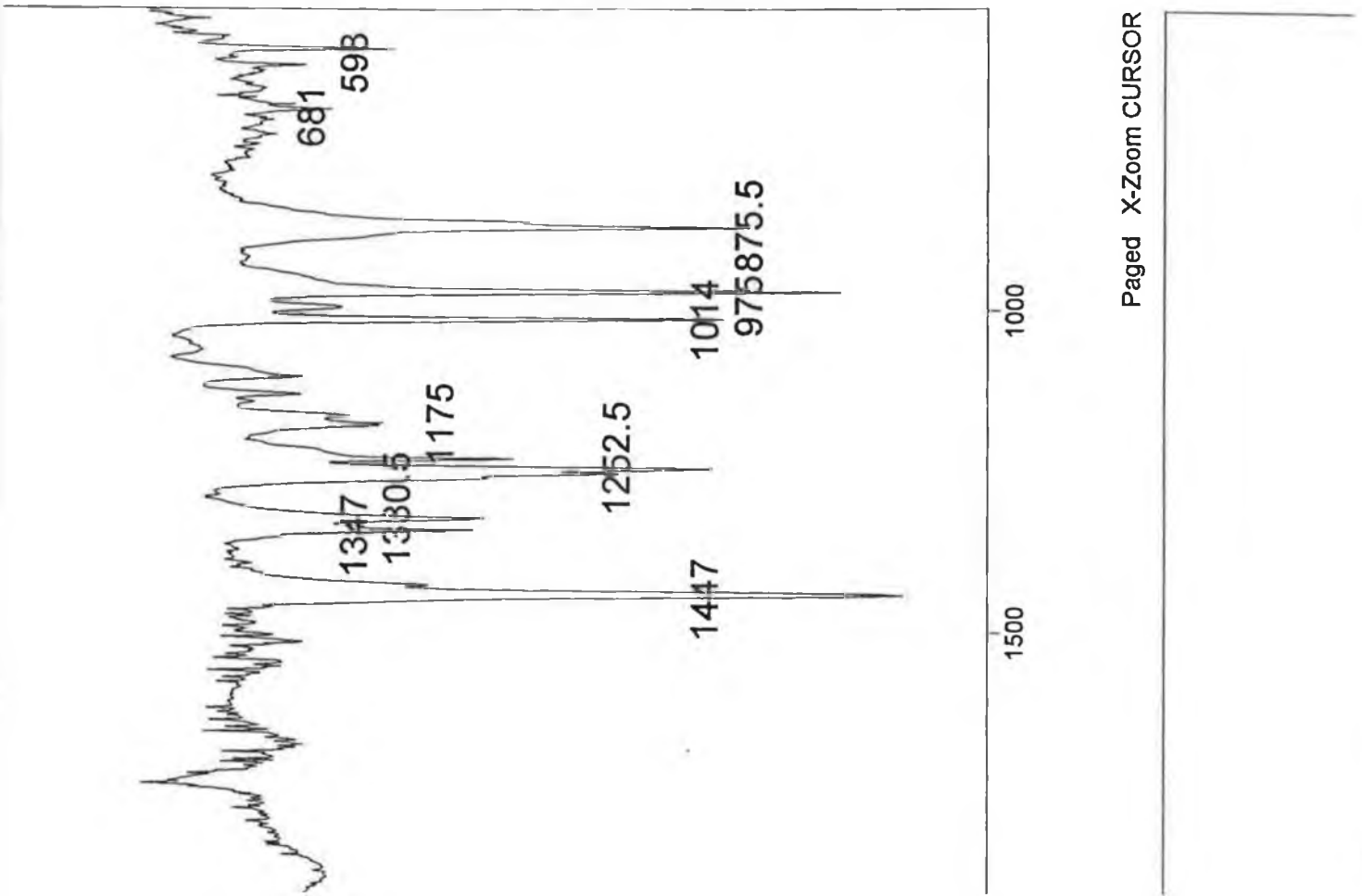


Figure 13(a). ^{1}Hnmr spectrum of 3,5 bis-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ -aromatic region.

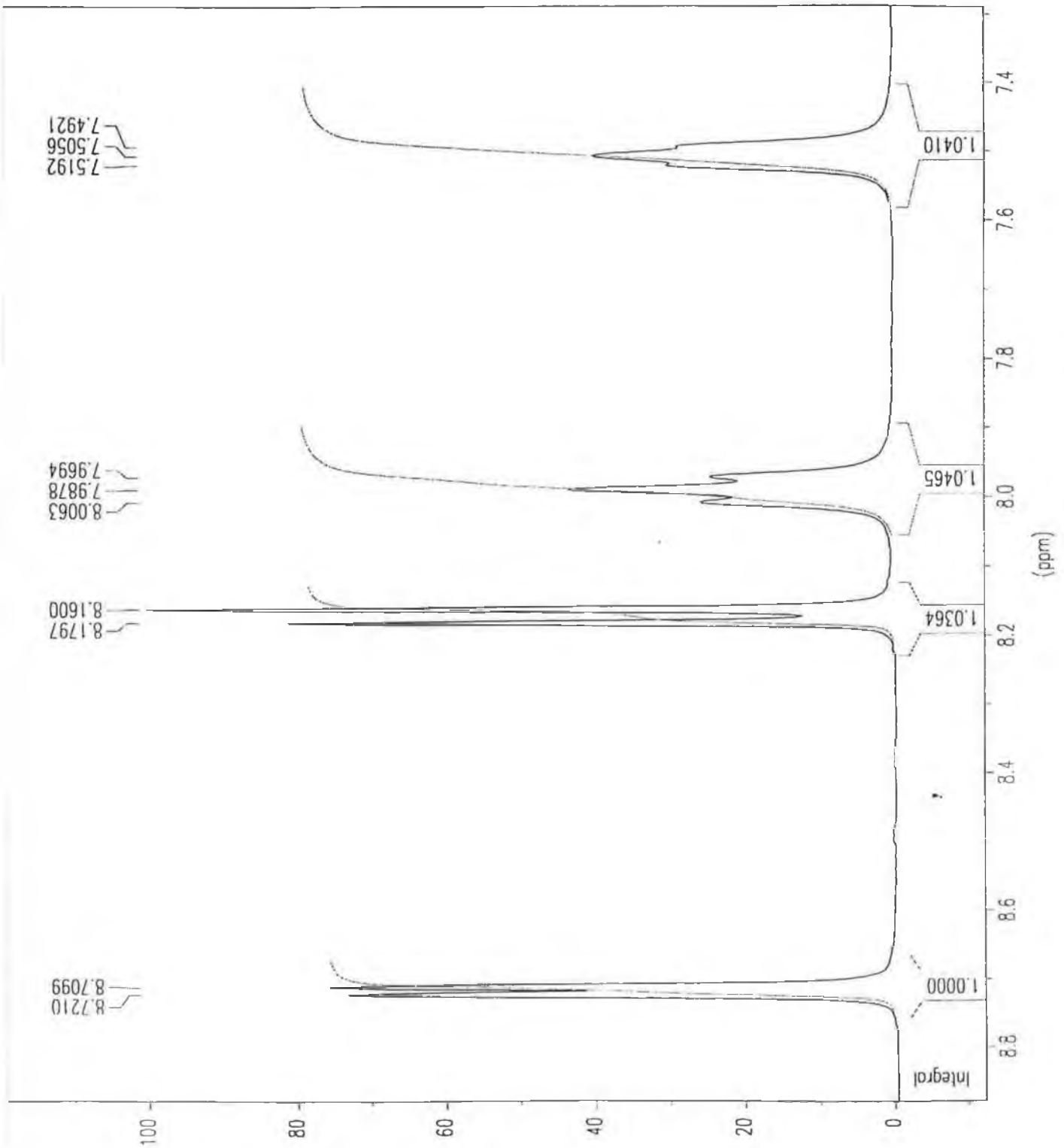


Figure 13(b). ^{1}Hnmr spectrum of 3,5 bis-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ -aliphatic region.

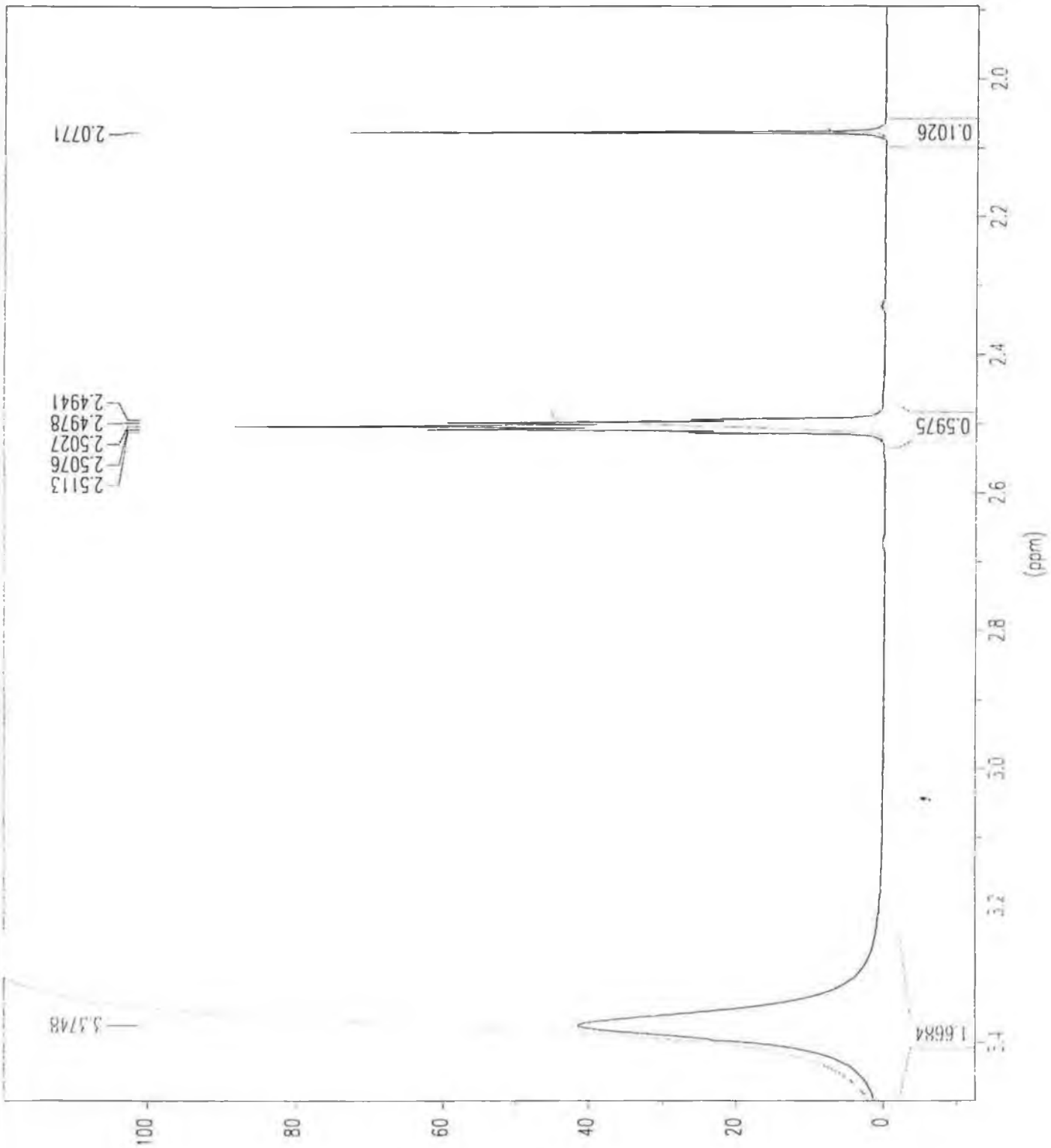


Figure 14(a). ^{1}Hnmr spectrum of deuteriated 3,5 bis-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aromatic region.

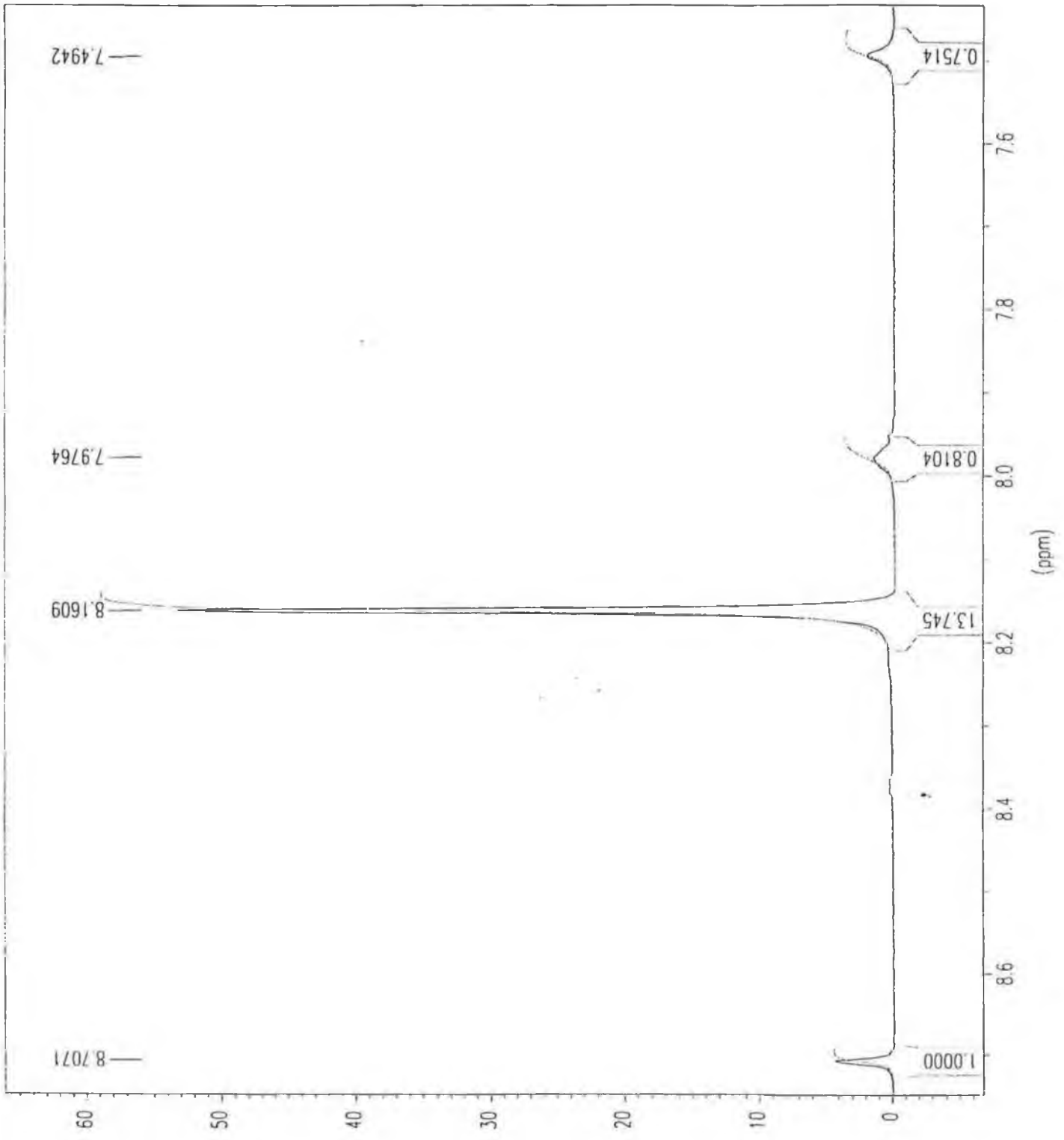
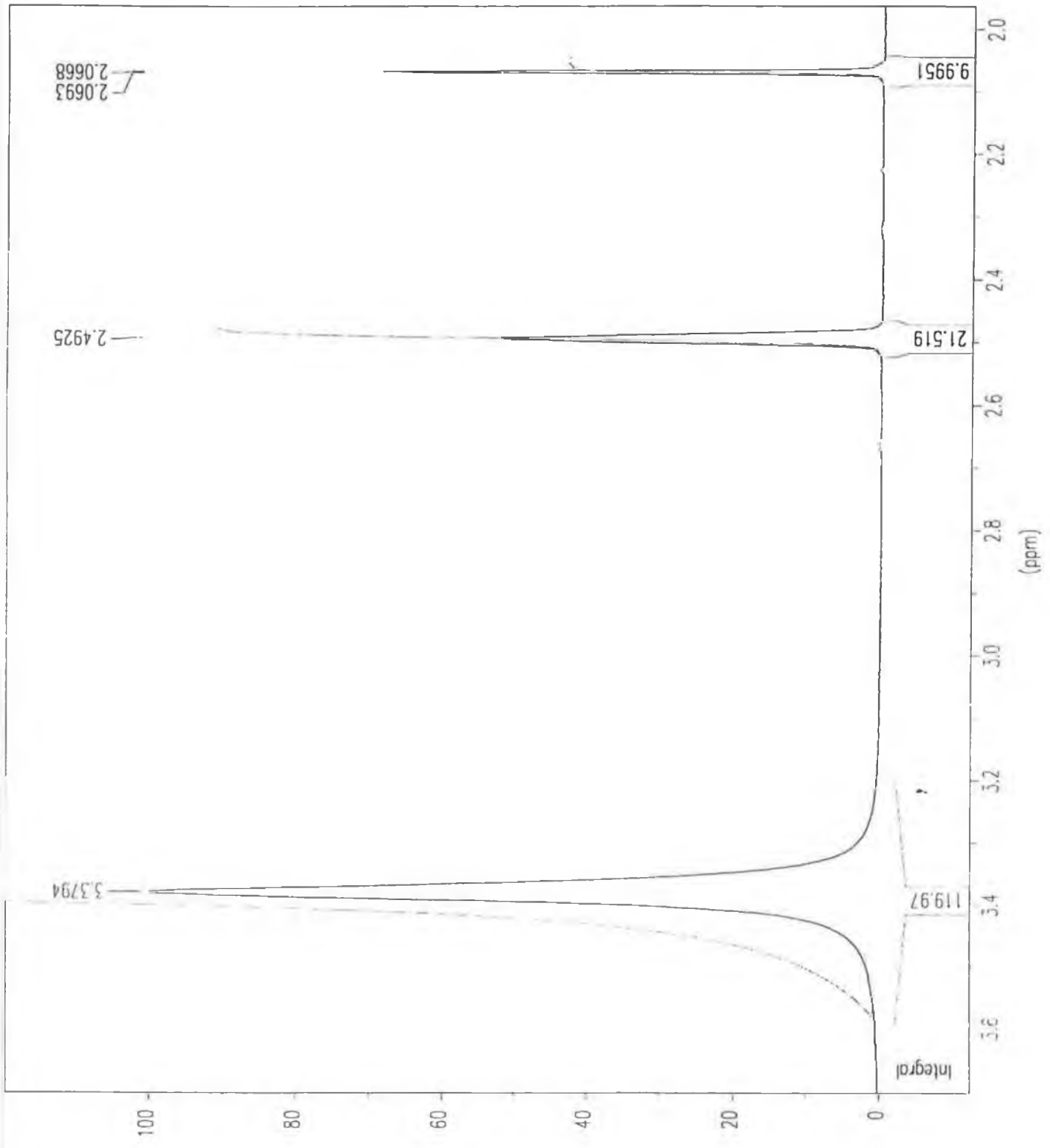


Figure 14(b). ^{1}Hnmr spectrum of deuteriated 3,5 bis-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aliphatic region.



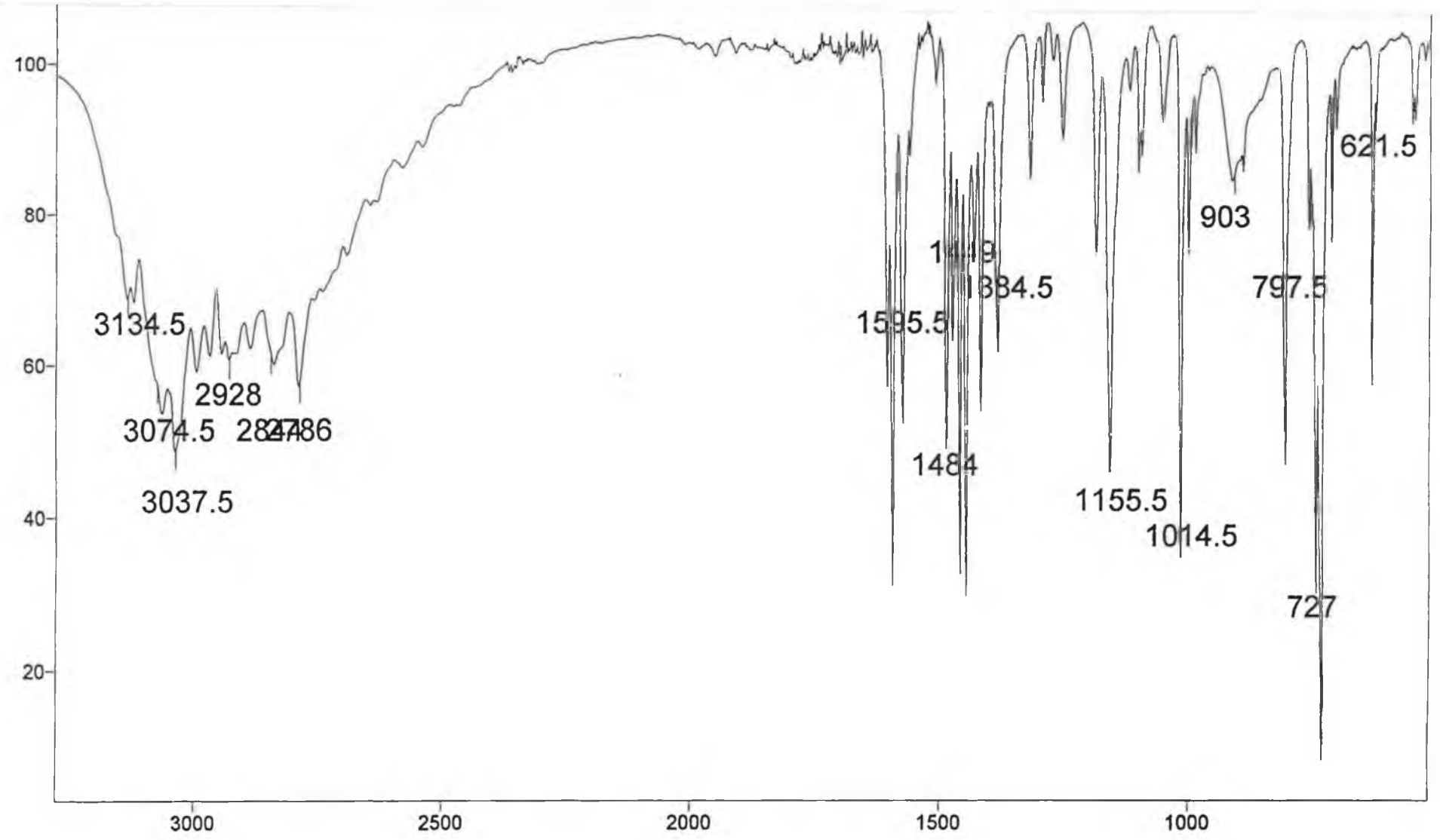


Figure 15. I.R. spectrum of 3,5bis-(pyridin-2-yl)-1,2,4'-triazole.

Transmittance / Wavenumber (cm-1)

Paged X-Zoom CURSOR

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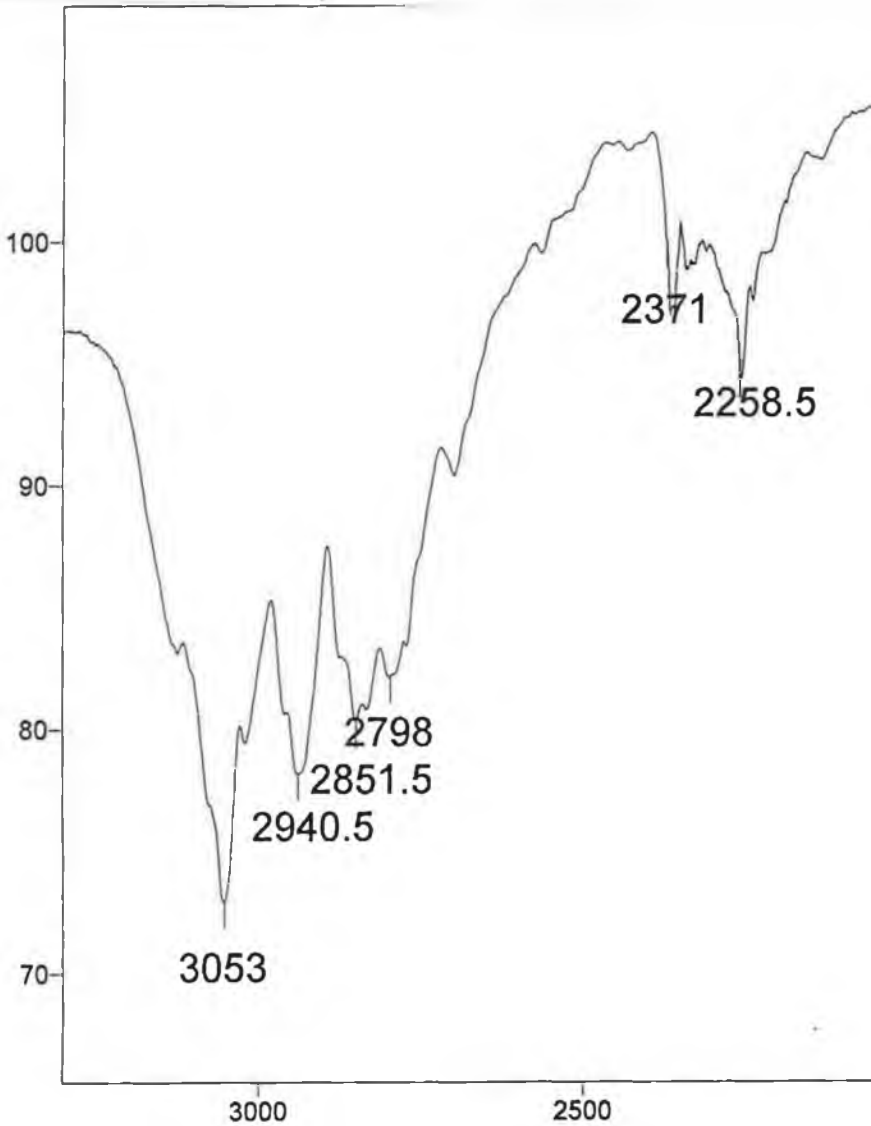
File # 7 : BPT



Transmittance / Wavenumber (cm-1)

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File # 6 : D-BPT

Figure 16. I.R. spectrum of deuteriated 3,5bis-(pyridin-2-yl)-1,2,4'-triazole.

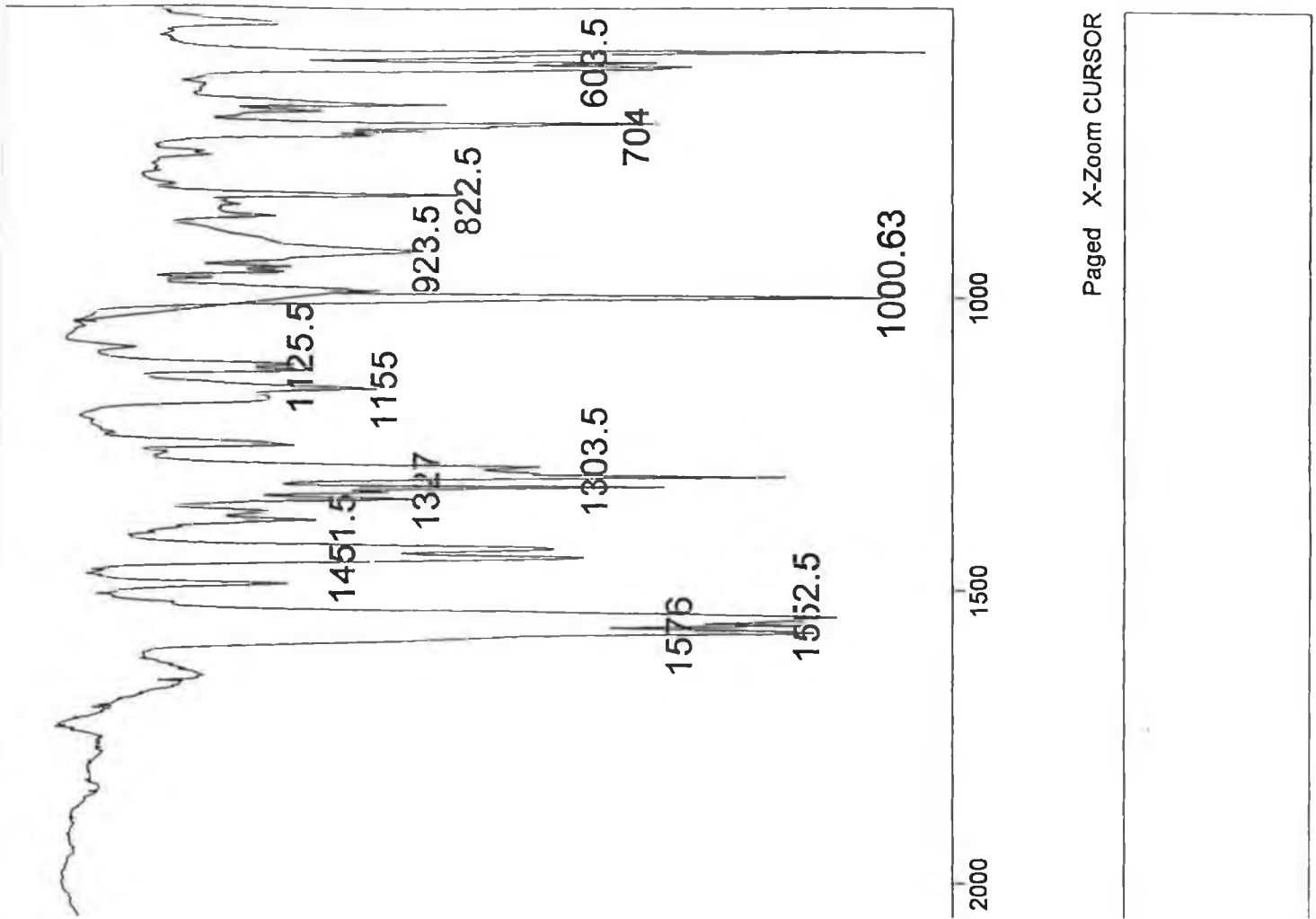


Figure 17(a). ^{1}Hnmr spectrum of 3,5 bis-(pyrazin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aromatic region.

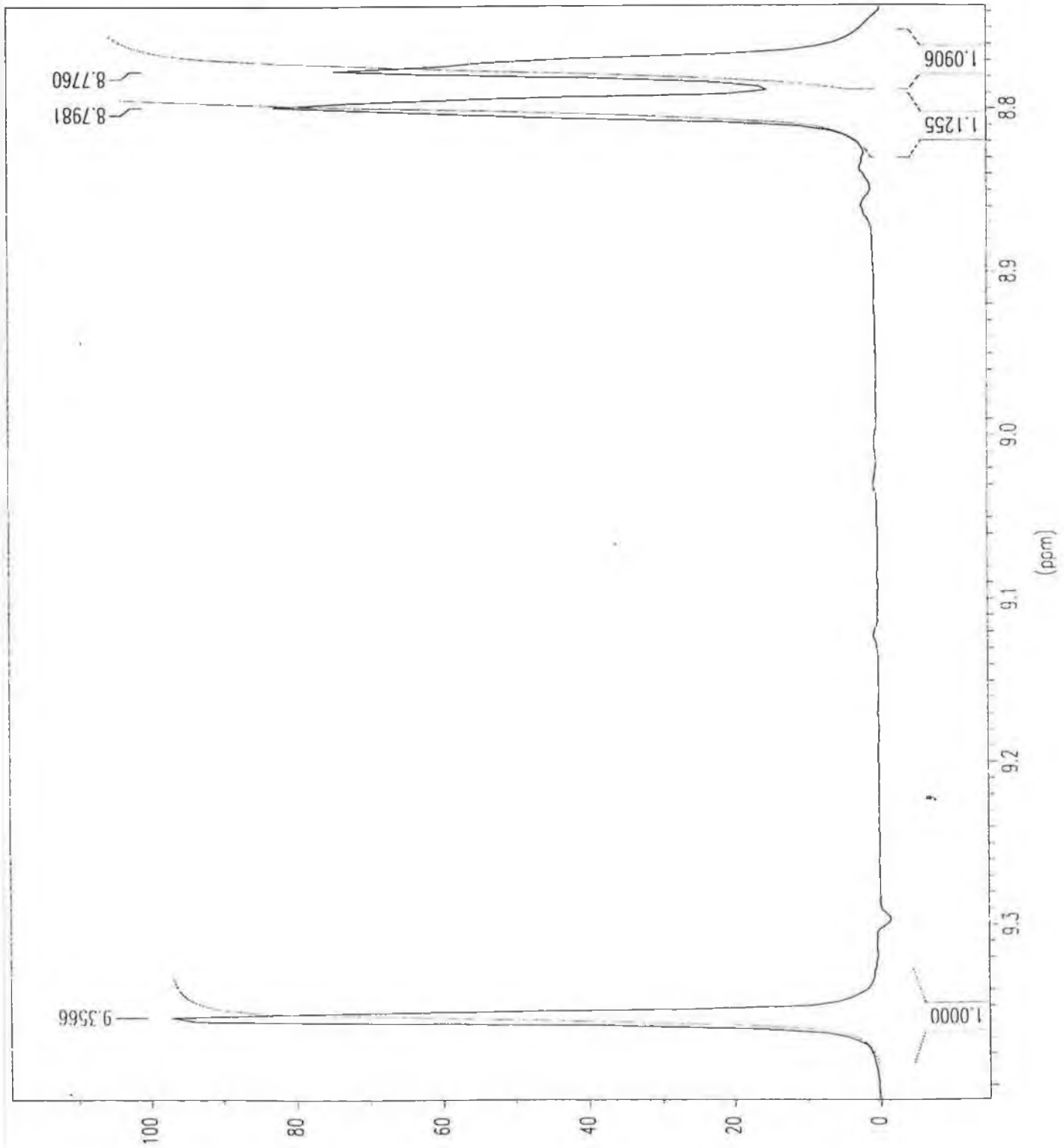


Figure 17(b). ^{1}Hnmr spectrum of 3,5 bis-(pyrazin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aliphatic region.

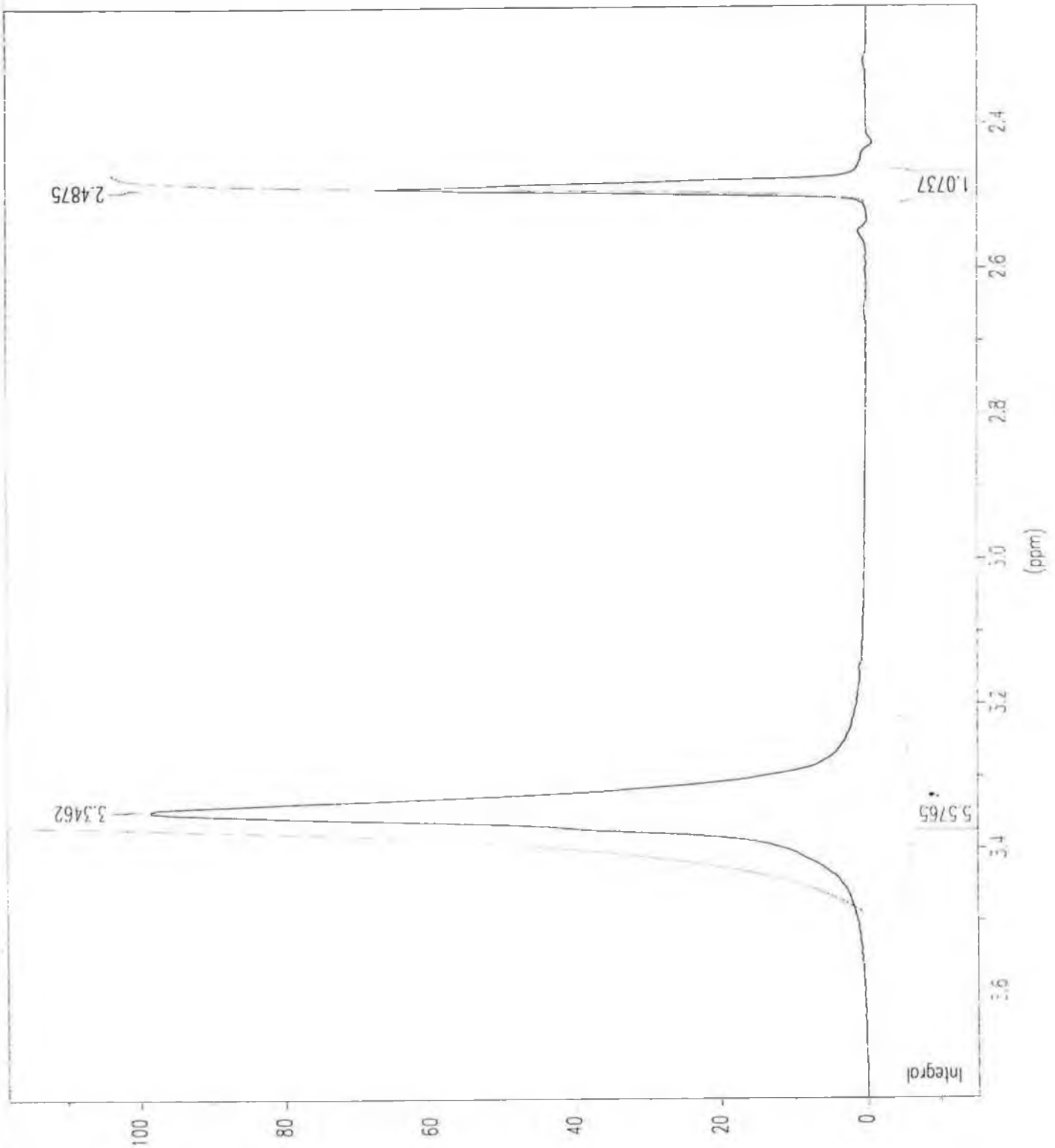


Figure 18(a). ^{1}Hnmr spectrum of deuteriated 3,5 bis-(pyrazin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aromatic region.

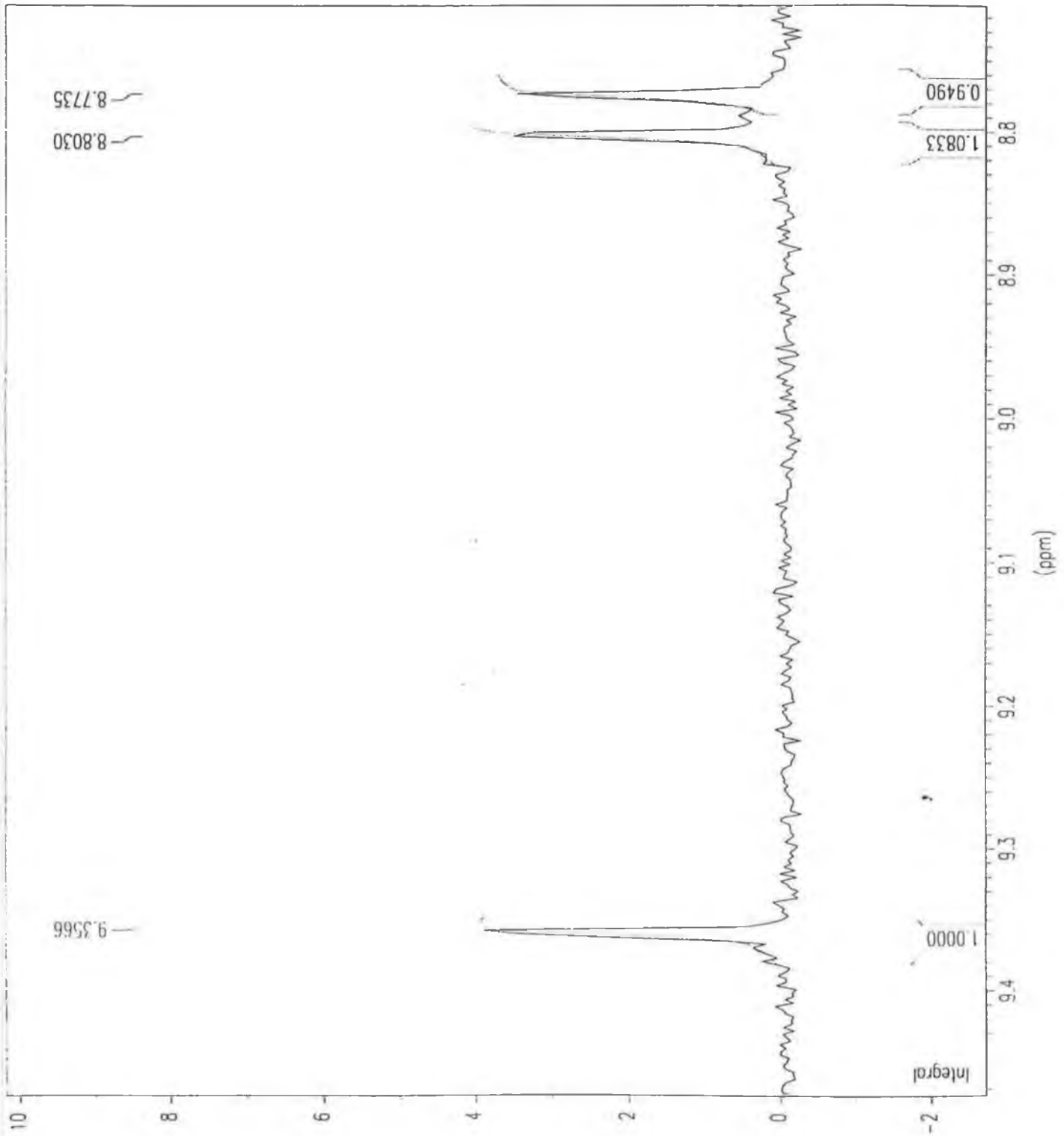
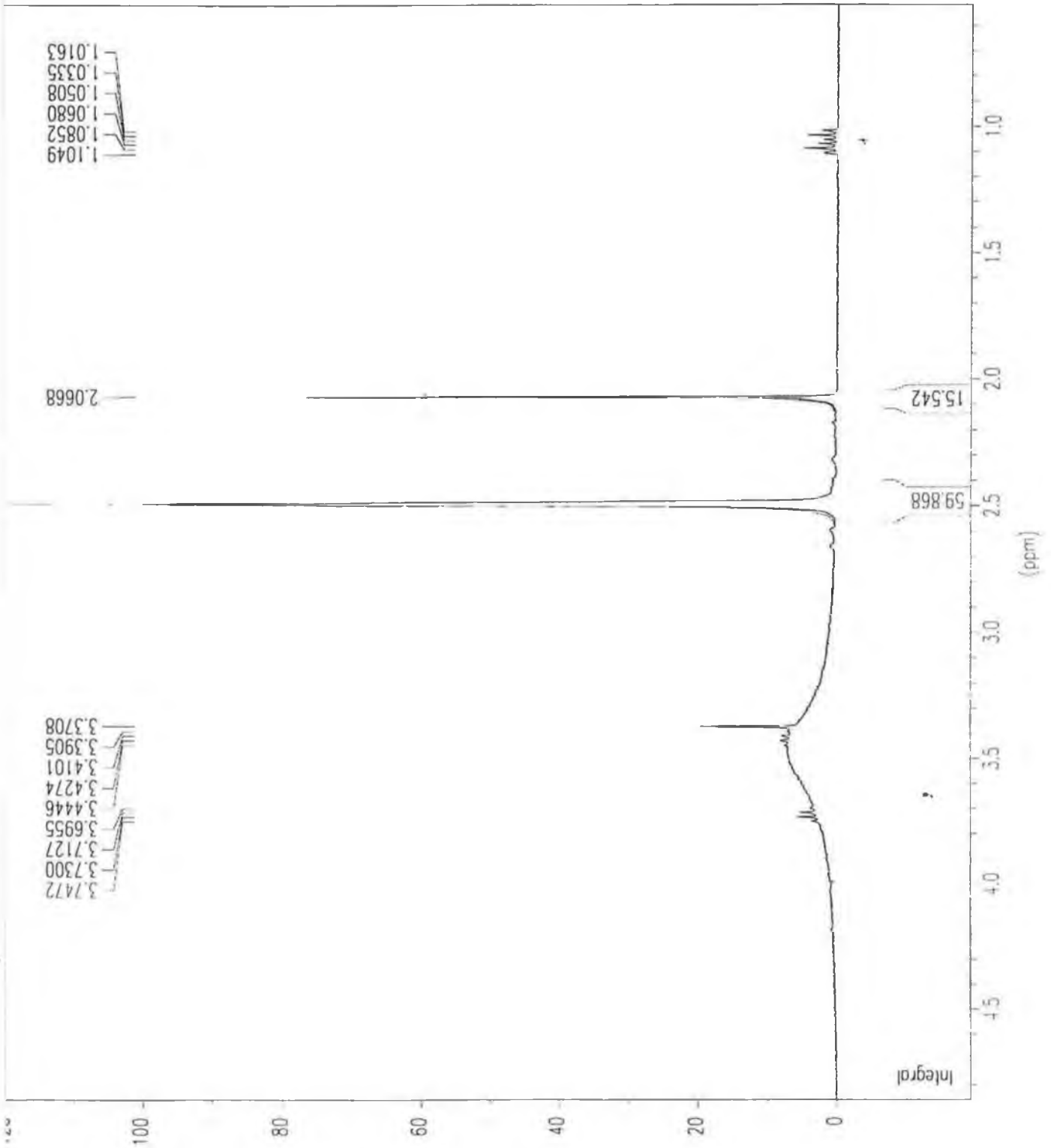


Figure 18(b). ^{1}Hnmr spectrum of deuteriated 3,5 bis-(pyrazin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aliphatic region.



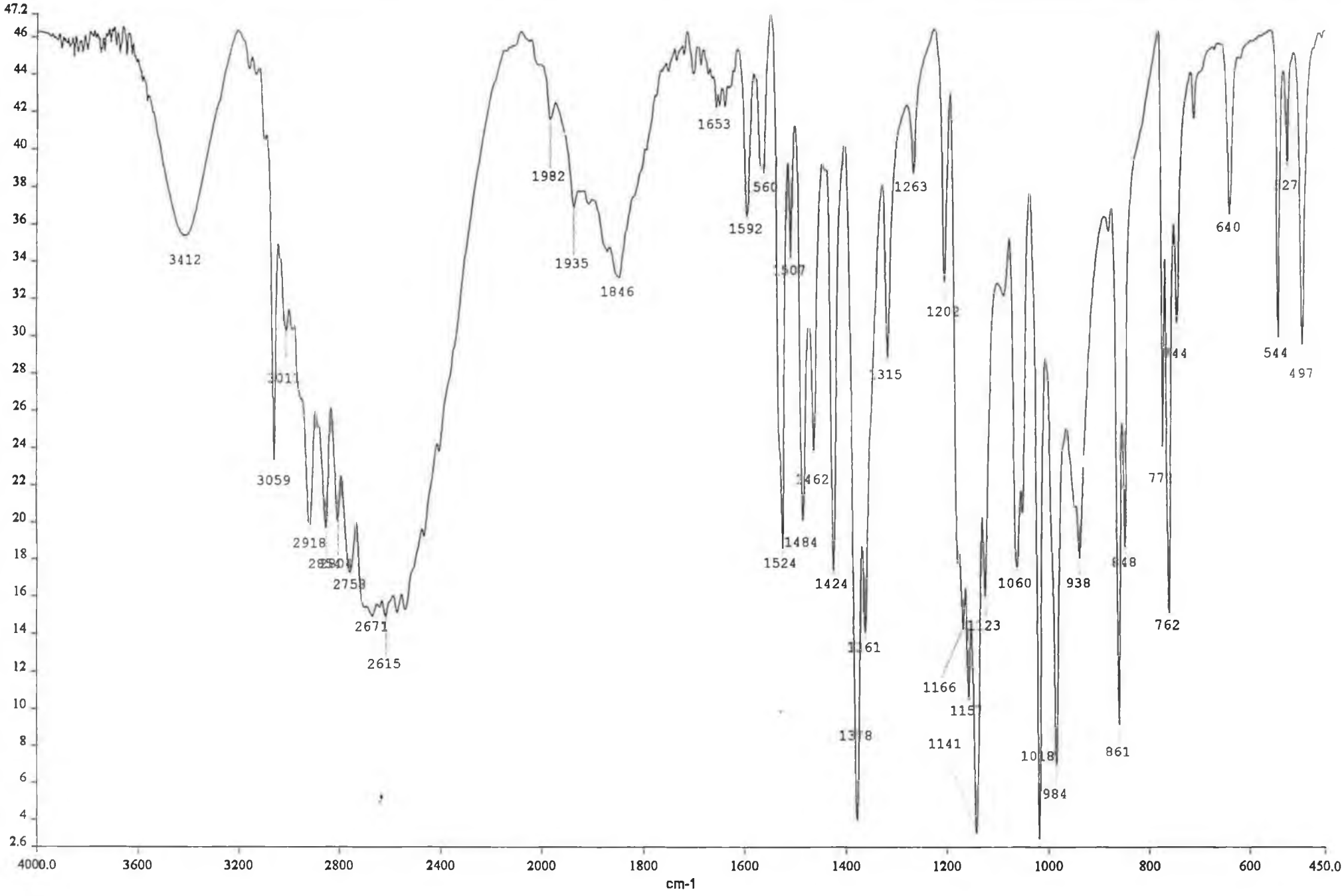
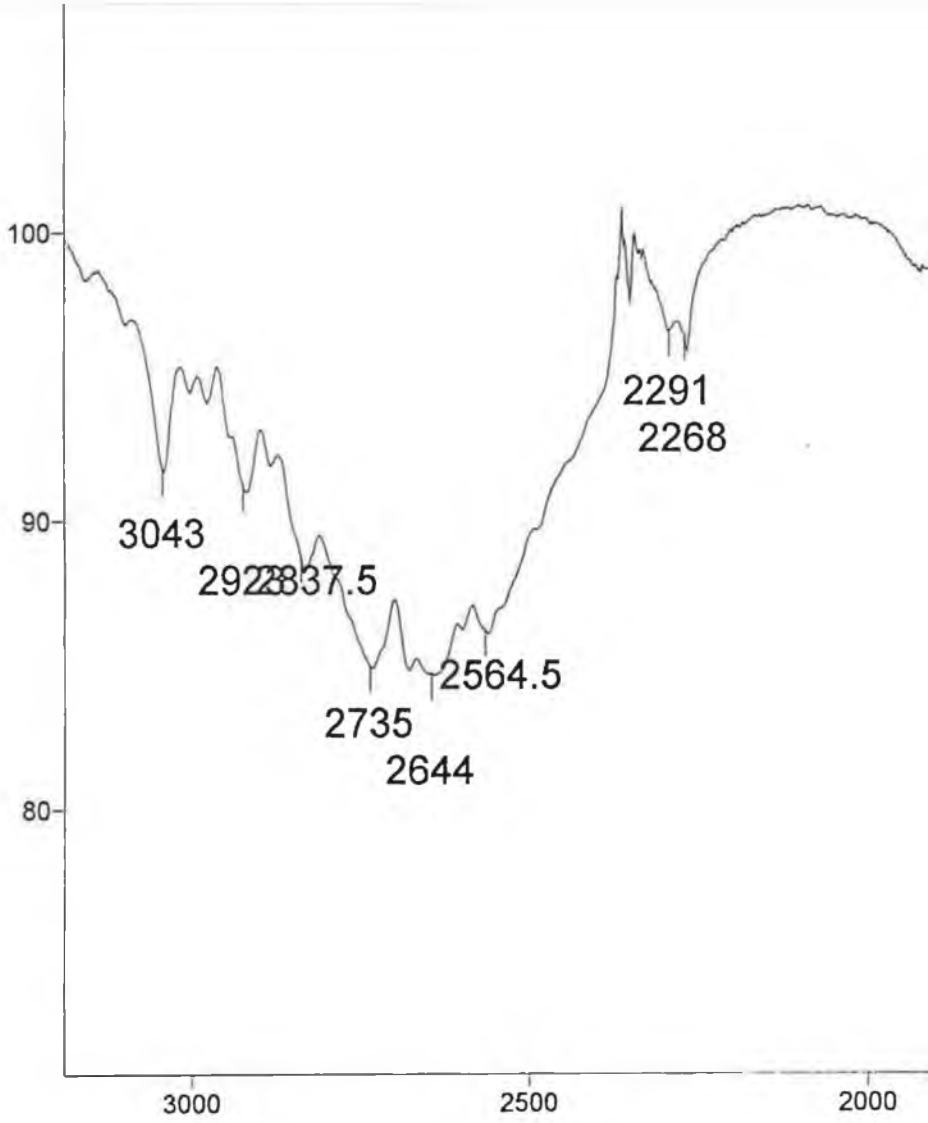


Figure 19. I.R. spectrum of 3,5bis-(pyrazin-2-yl)-1,2,4'-triazole.



Transmittance / Wavenumber (cm-1)

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File # 2 : D-BPZTR

Figure 20. I.R. spectrum of deuteriated 3,5bis-(pyrazin-2-yl)-1,2,4'-triazole.

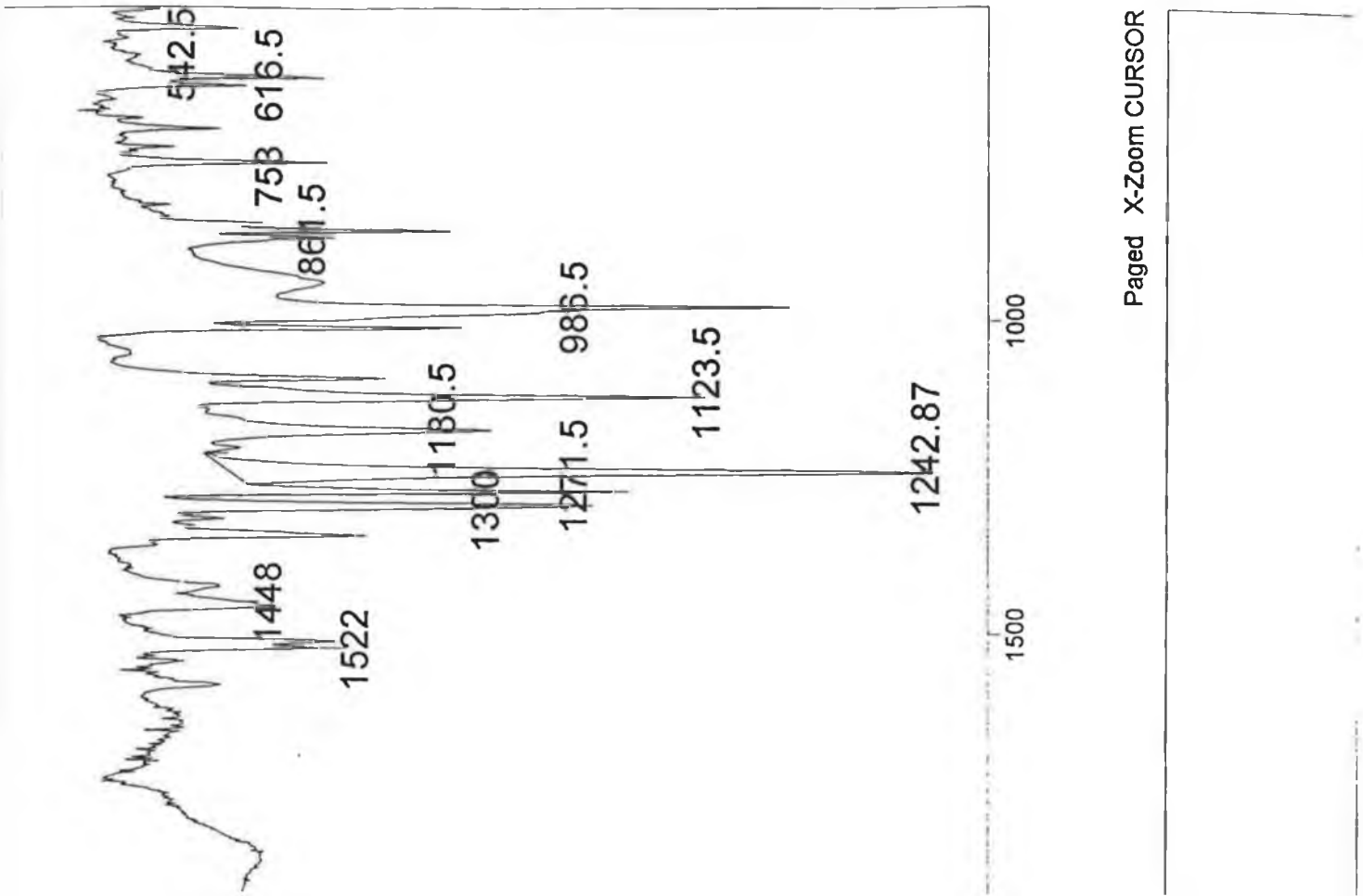


Figure 21(a). ^{1}Hnmr spectrum of 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aromatic region.

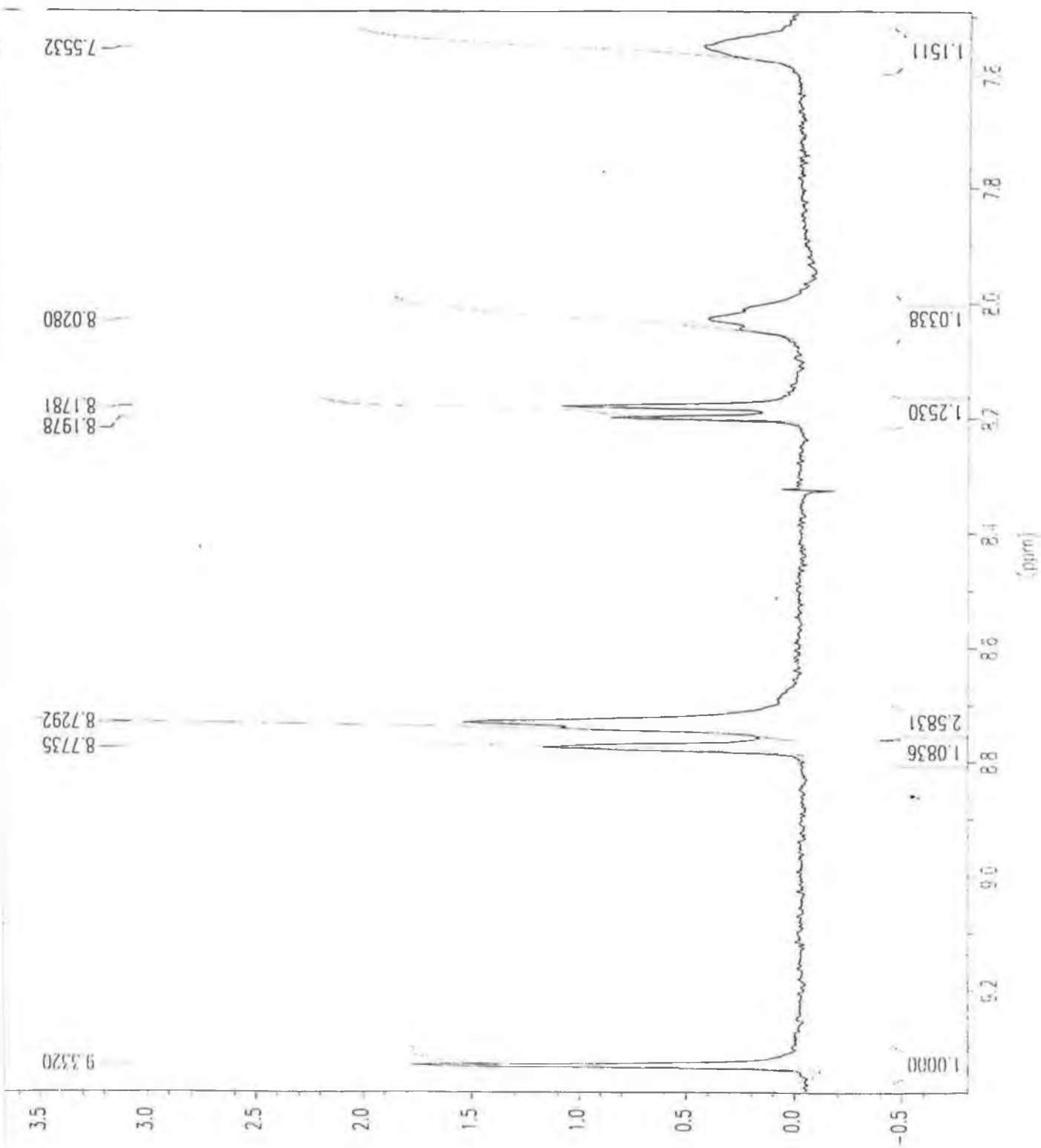


Figure 21(b). ^{1}Hnmr spectrum of 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aliphatic region.

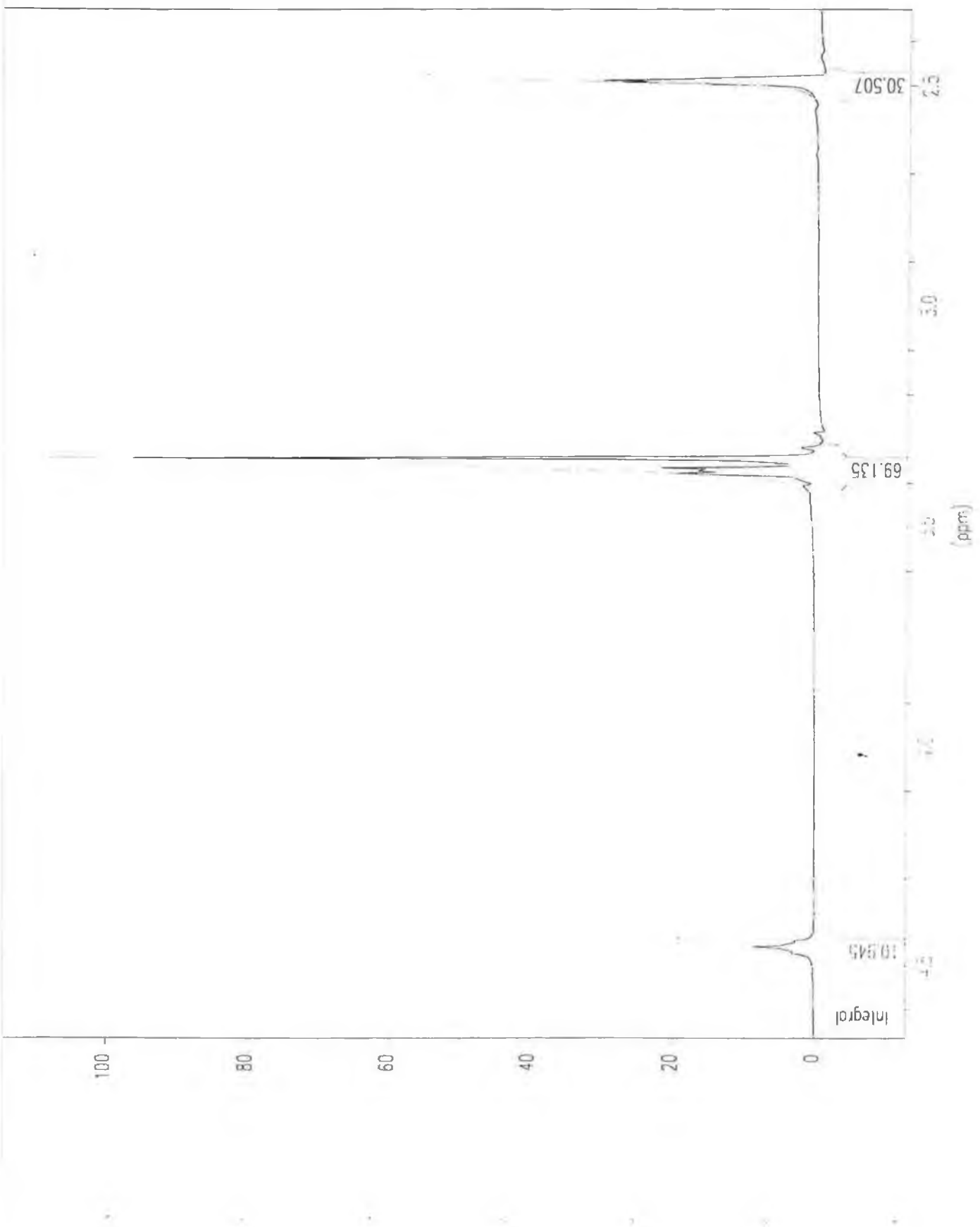


Figure 22(a). ^{1}Hnmr spectrum of deuteriated 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aromatic region.

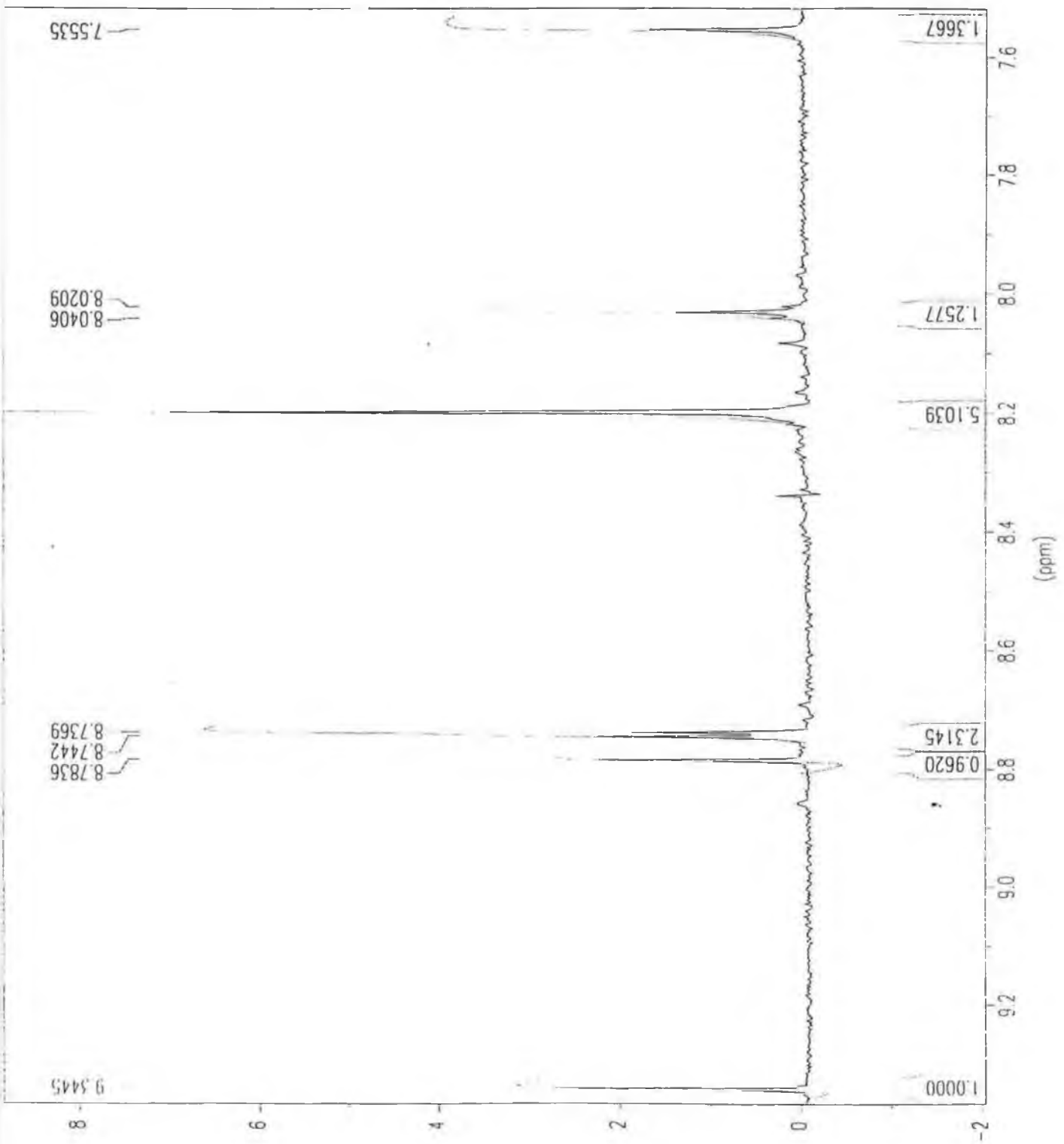
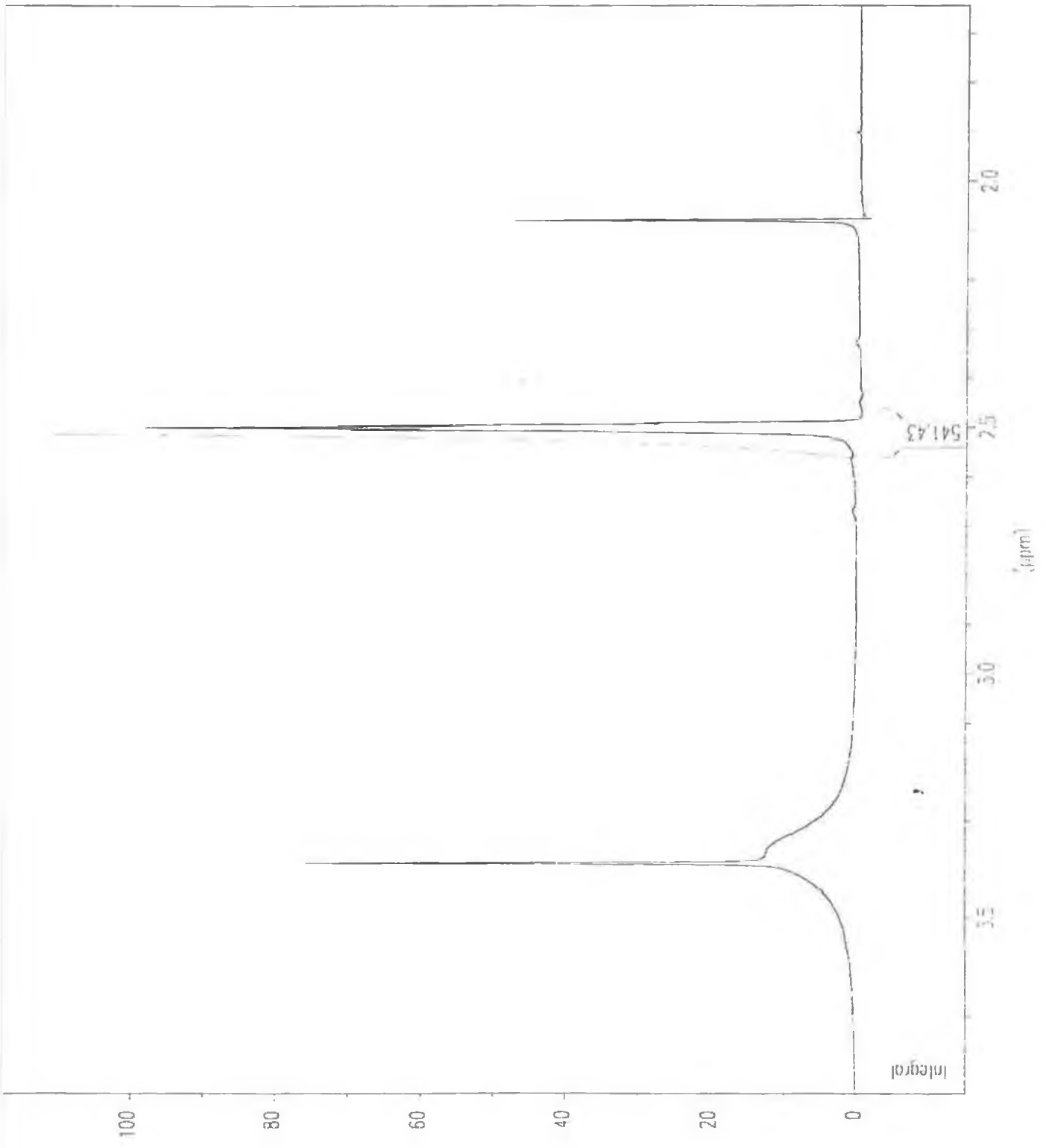
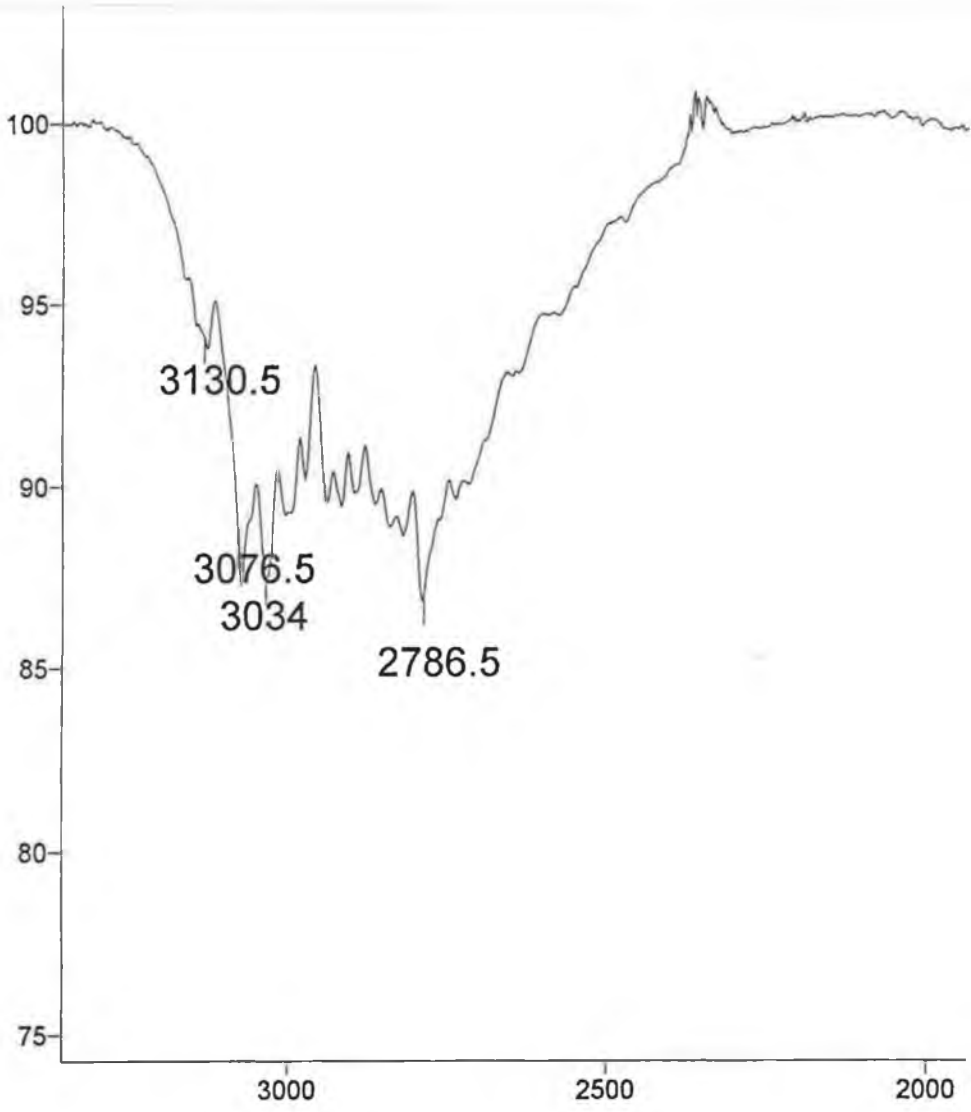


Figure 22(b). ^{1}Hnmr spectrum of deuteriated 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole in $(CD_3)_2SO$ - aliphatic region.





Transmittance / Wavenumber (cm-1)

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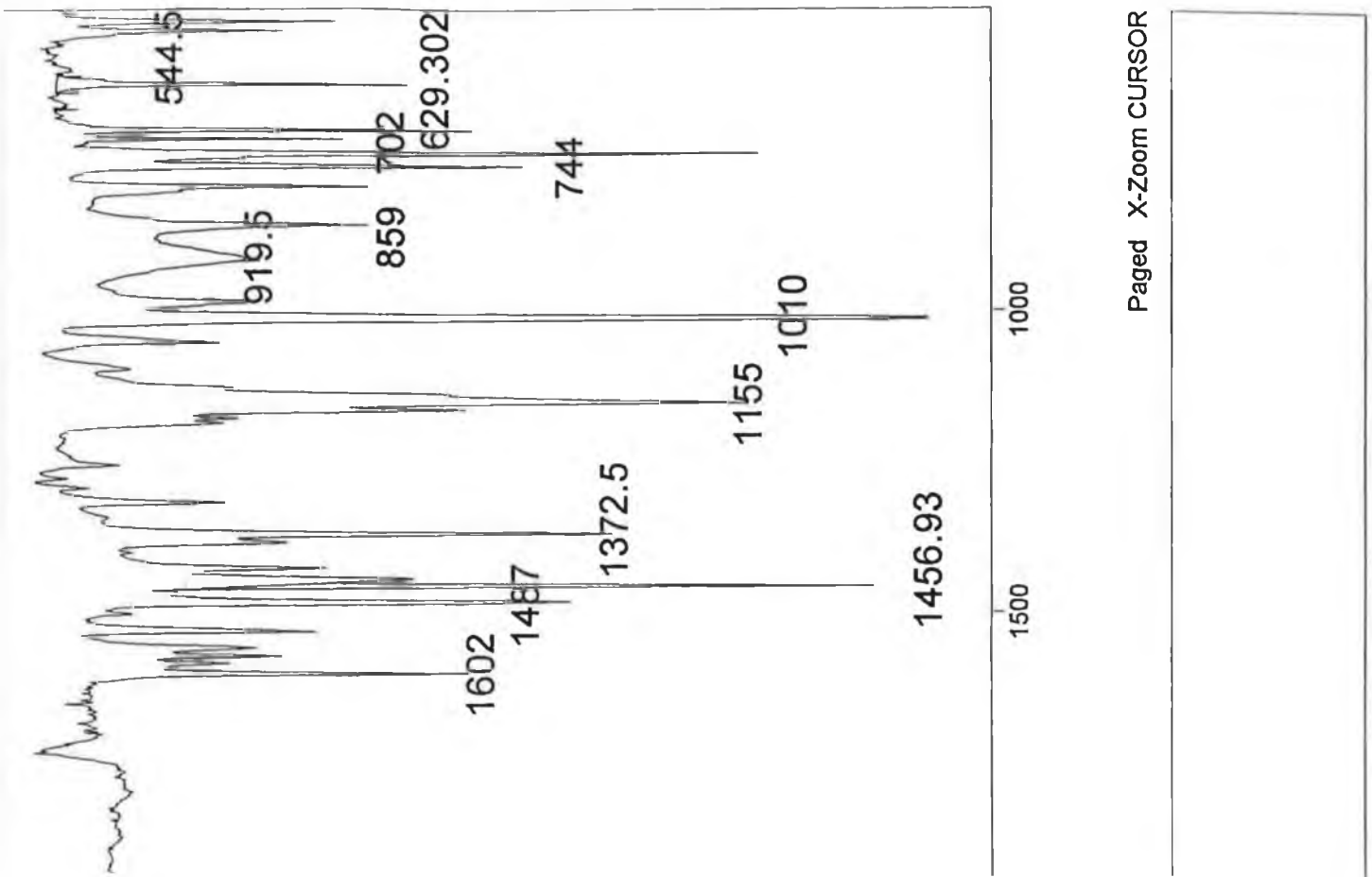
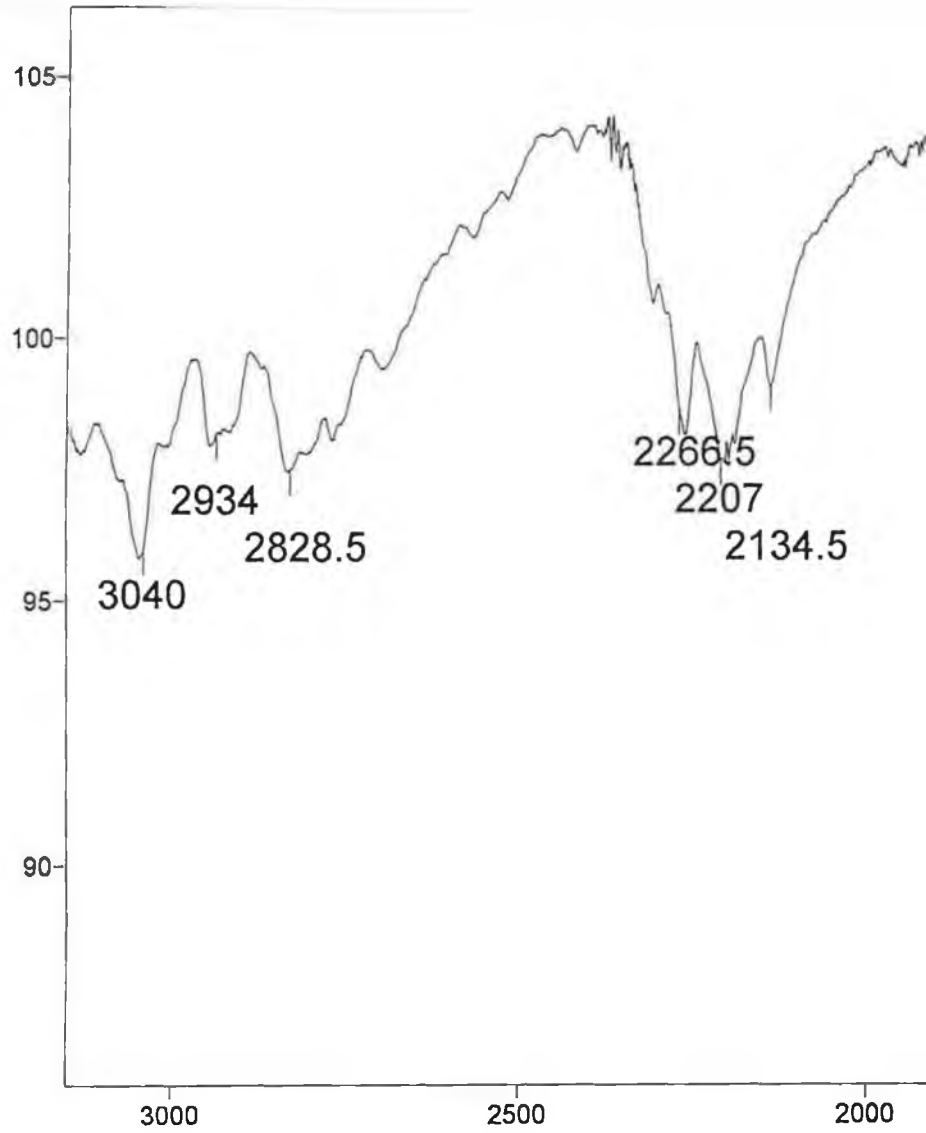
File # 5 : PPT

Figure 23. I.R. spectrum of 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4'-triazole.





Transmittance / Wavenumber (cm-1)

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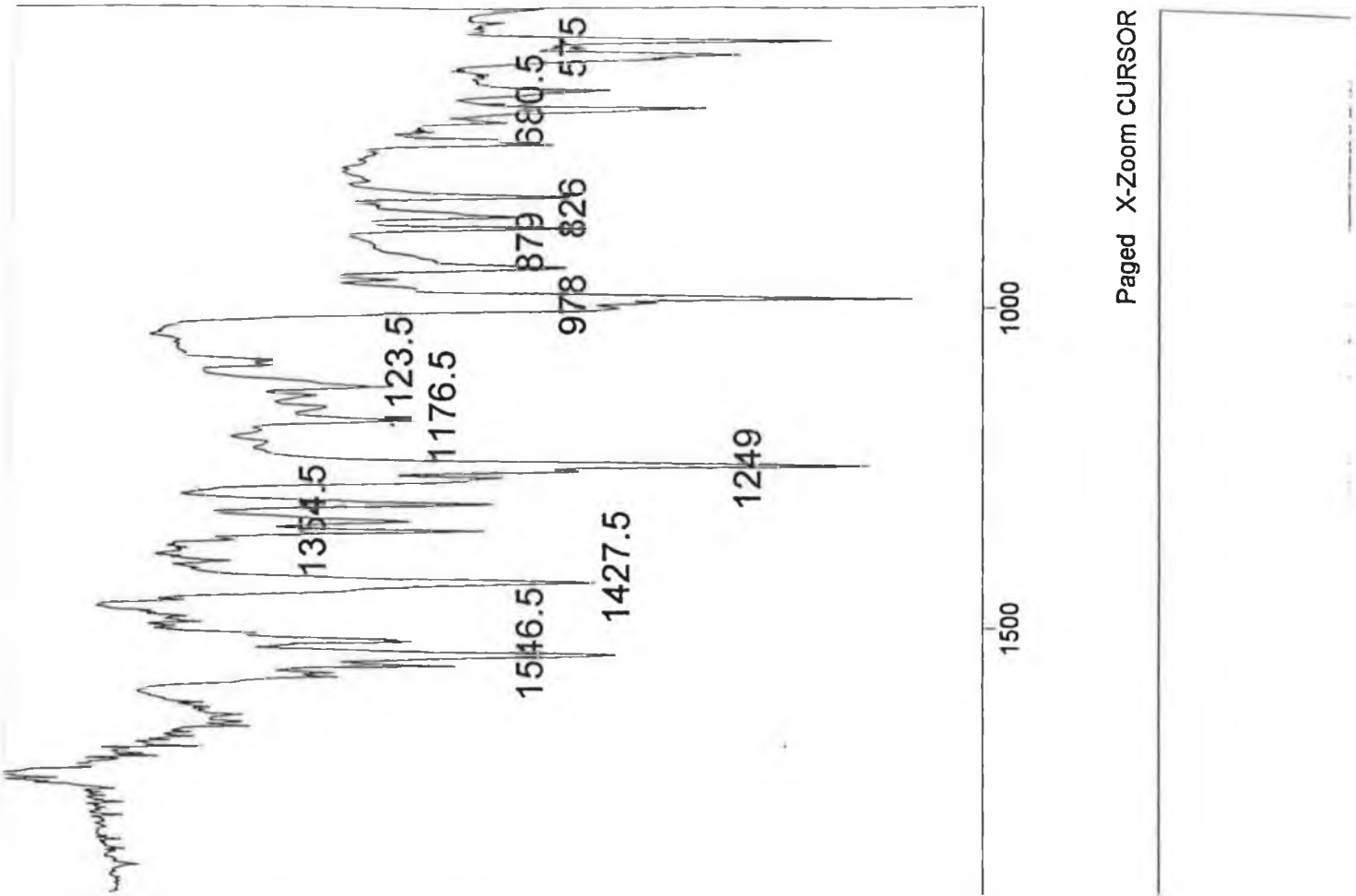
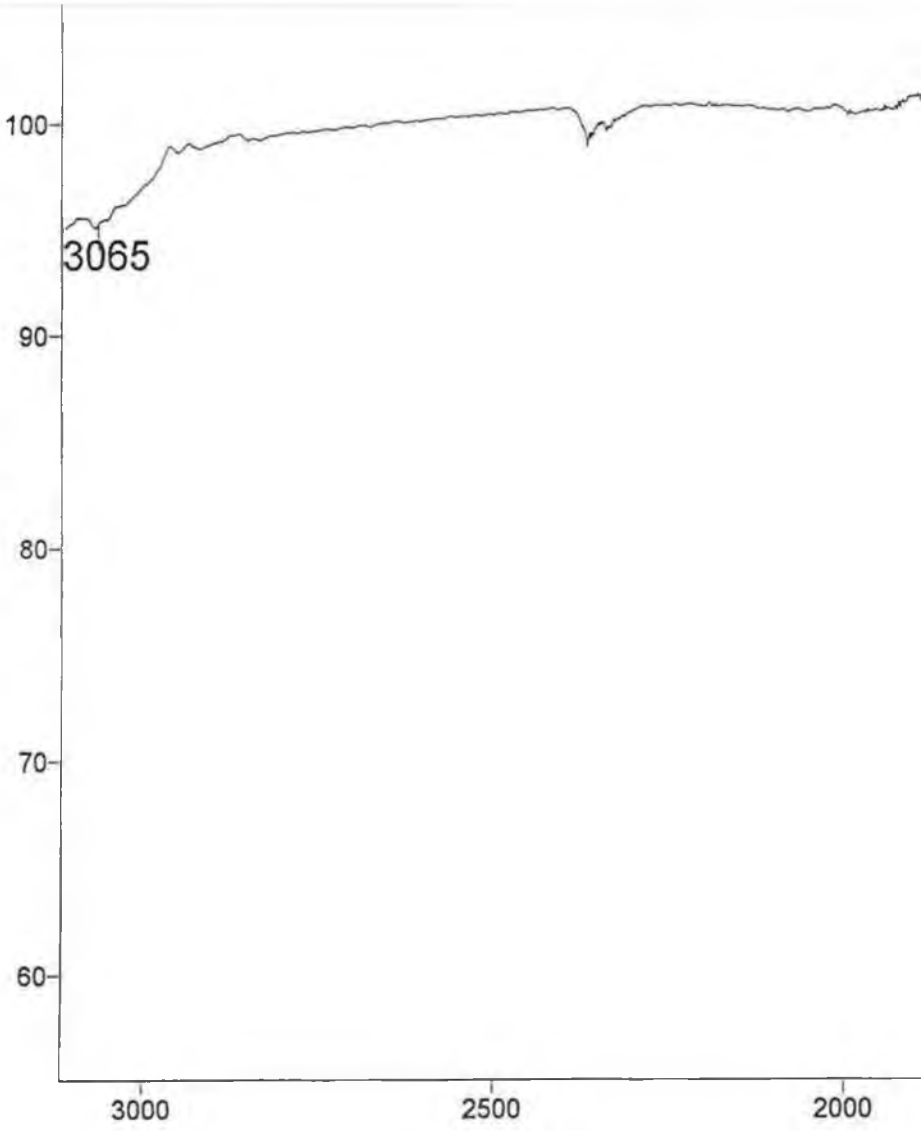
File # 6 : D-PPT

Figure 24. I.R. spectrum of deuteriated 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4'-triazole.





Transmittance / Wavenumber (cm-1)

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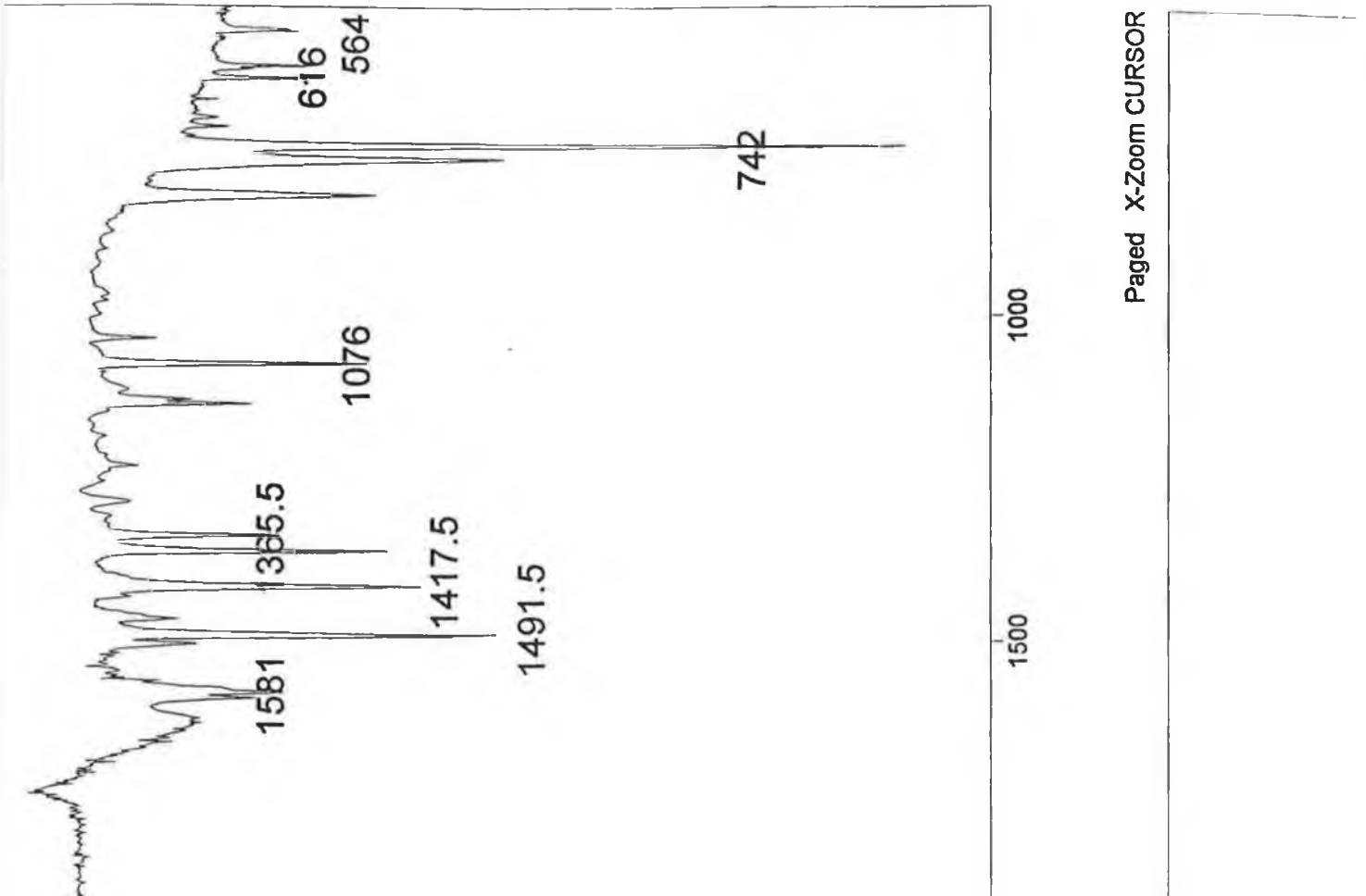
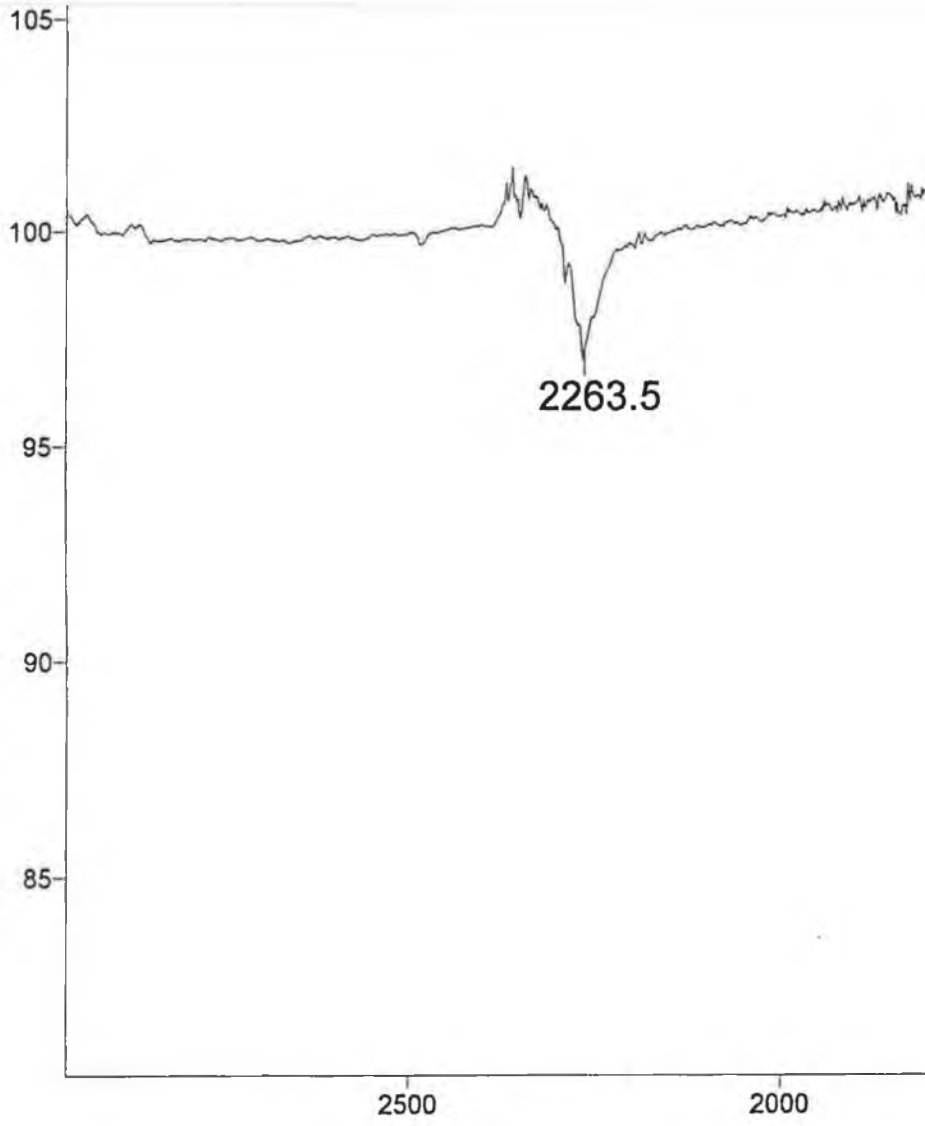
File # 4 : DPPZ

Figure 8.2. dipyrido[3,2-a:2,'3-c]phenazine

Figure 25. I.R. spectrum of dipyrido[3,2-*a*:2,'3'-*c*]phenazine.





Transmittance / Wavenumber (cm-1)

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File # 4 : D-DPPZ

Figure 8.3. deuteriated dipyrido[3,2-a:2,'3-c]phenazine

Figure 26. I.R. spectrum of deuteriated dipyrido[3,2-*a*:2,'3'-*c*]phenazine.

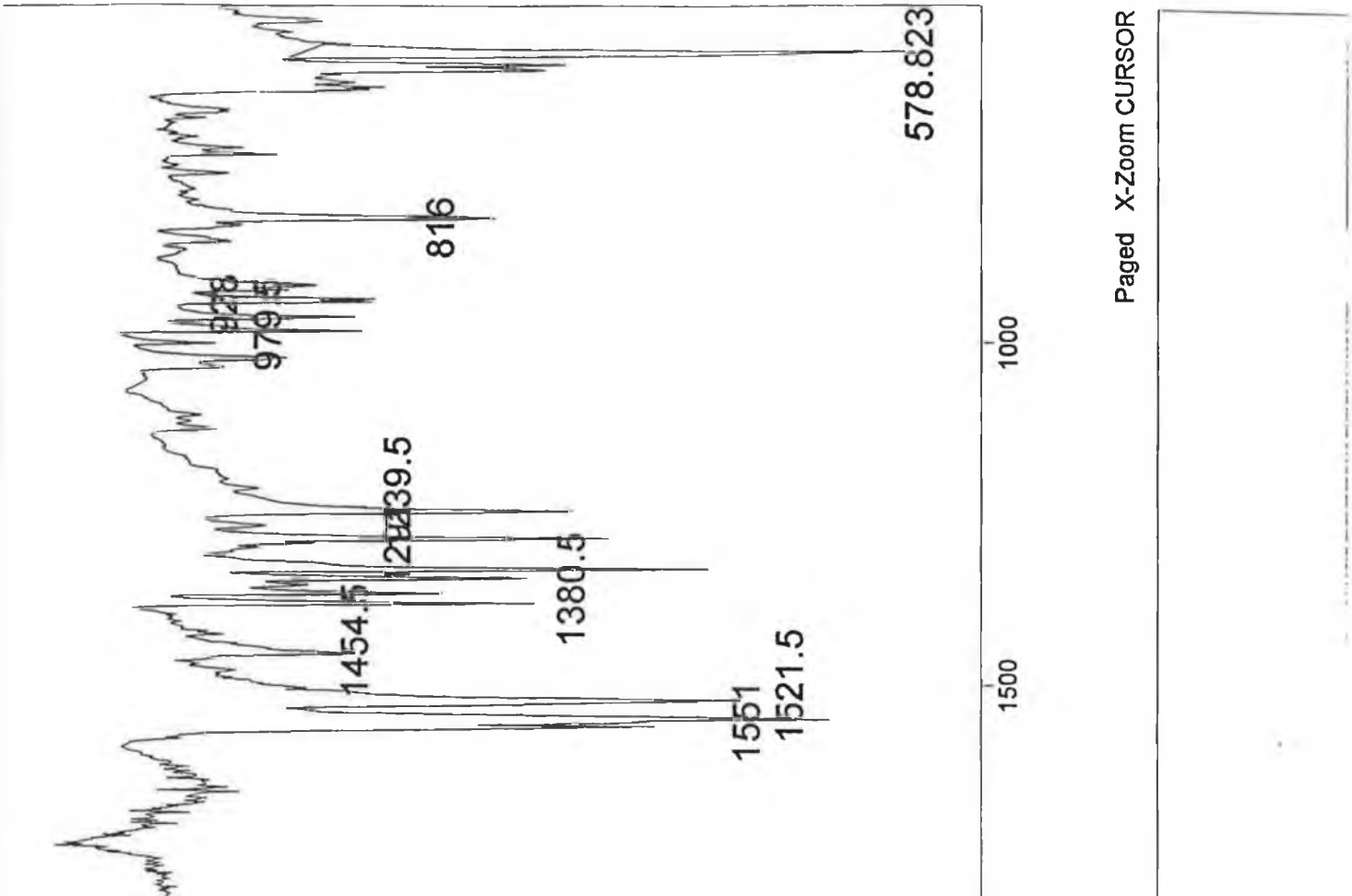


Figure 27.\ ^{1}Hnmr of 2-picolylamhydrazone in $(CD_3)_2SO$.

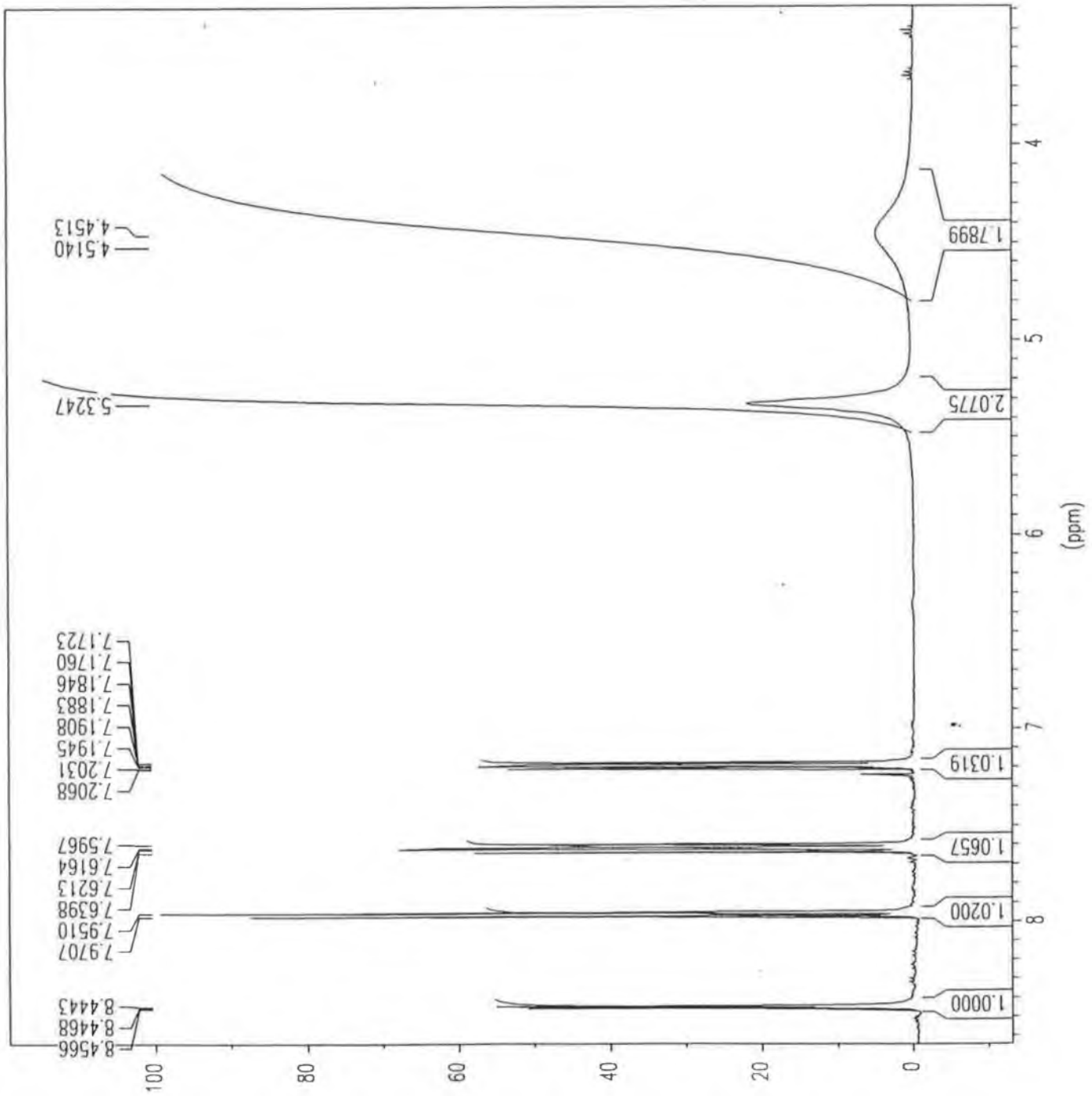


Figure 28. (a) ^{1}Hnmr of acylamidrazone in $(CD_3)_2SO$ - aromatic region.

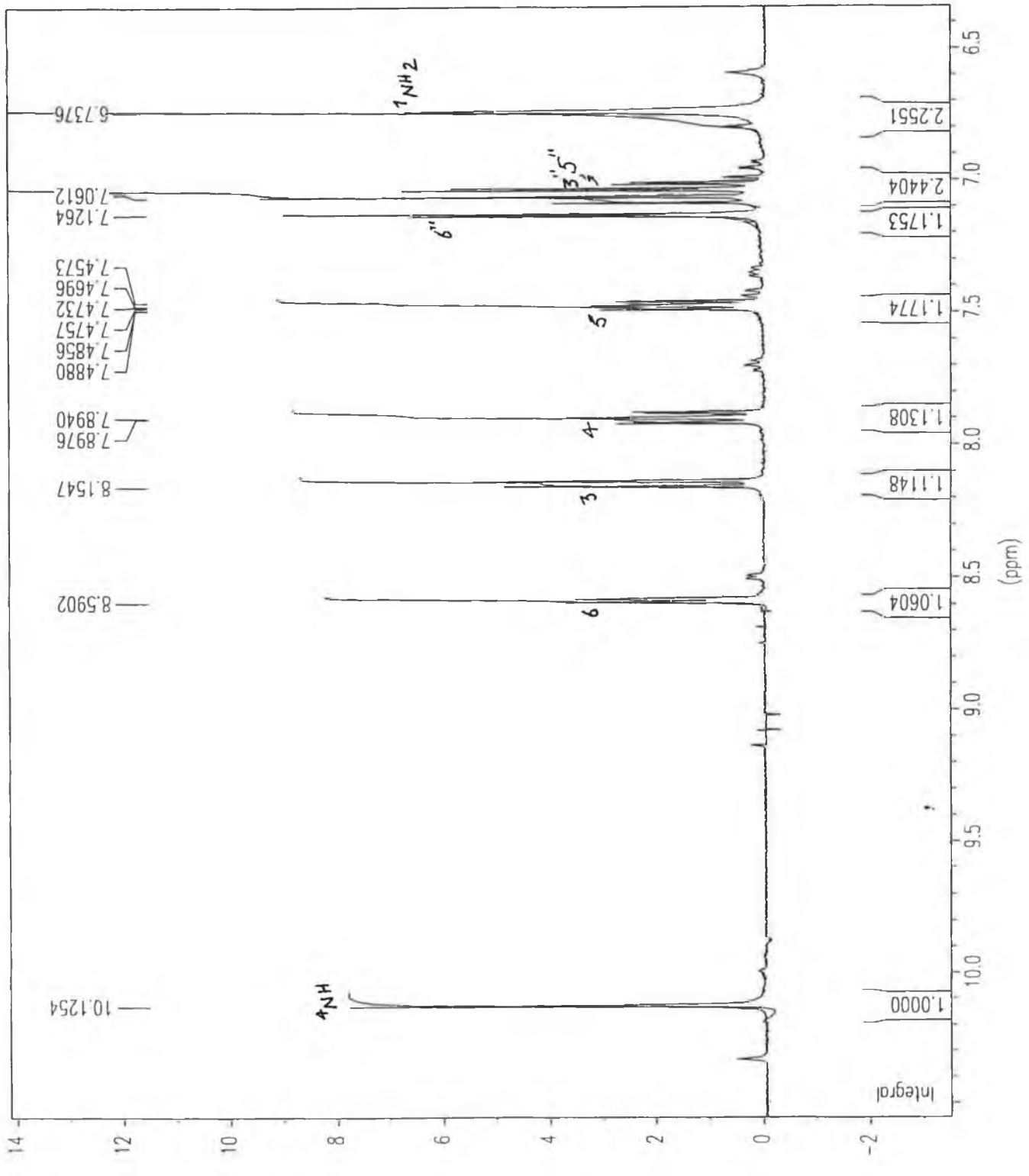


Figure 28. (b) ^{1}Hnmr of acylamidrazone in $(CD_3)_2SO$ - aliphatic region.

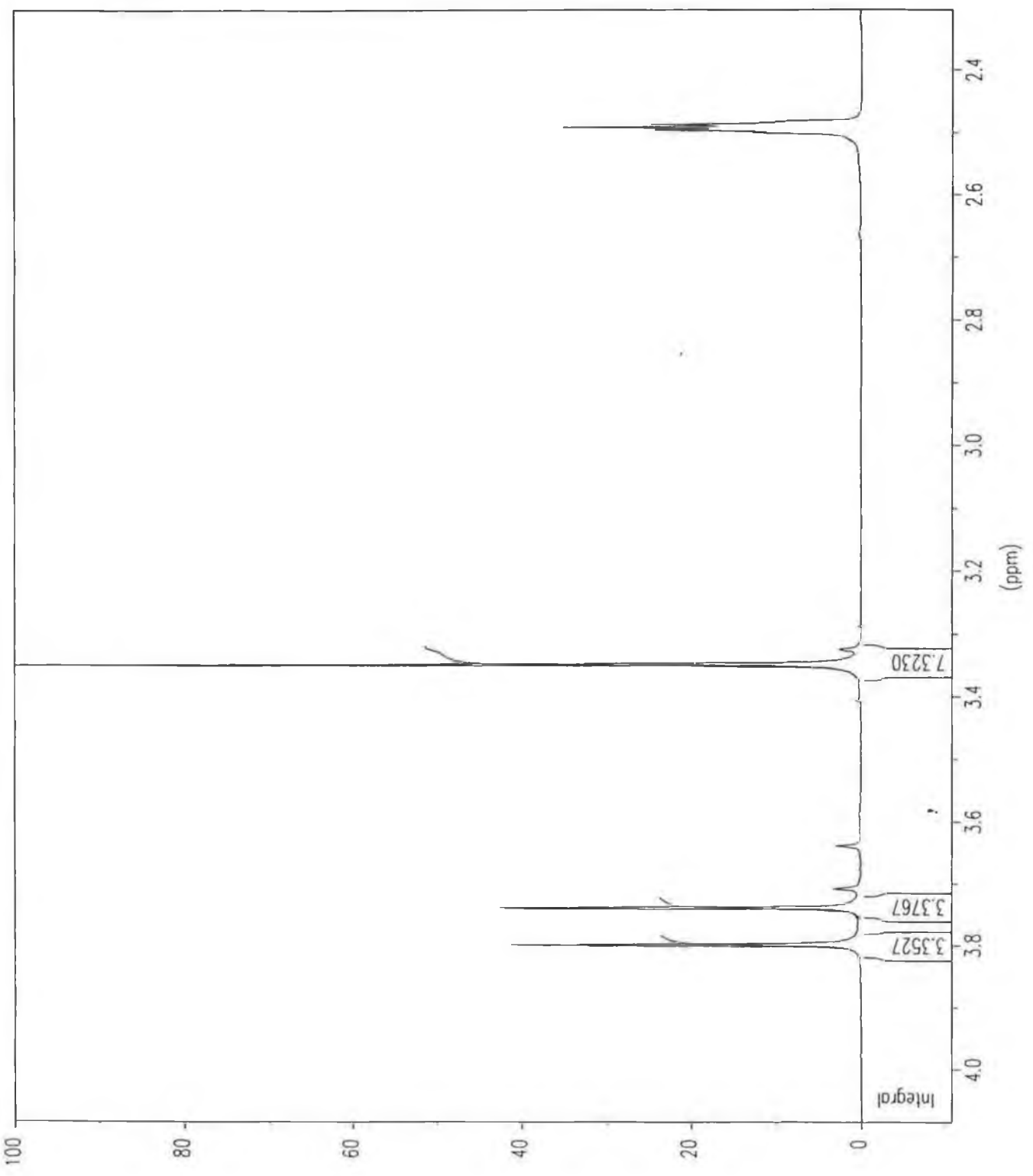


Figure 29. (a) ^{1}Hnmr of 3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole (L_1) in $(CD_3)_2SO$ - aromatic region.

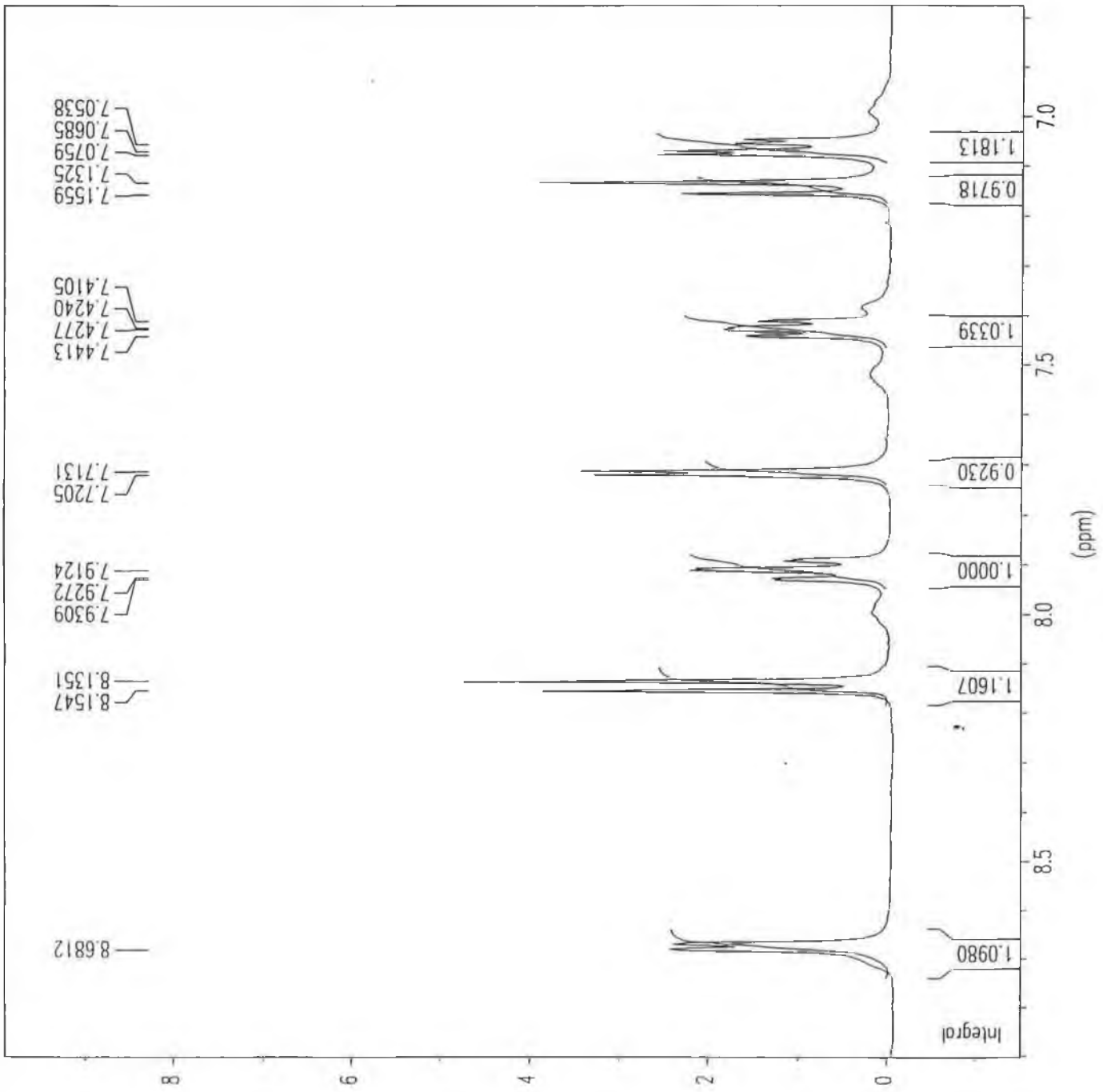
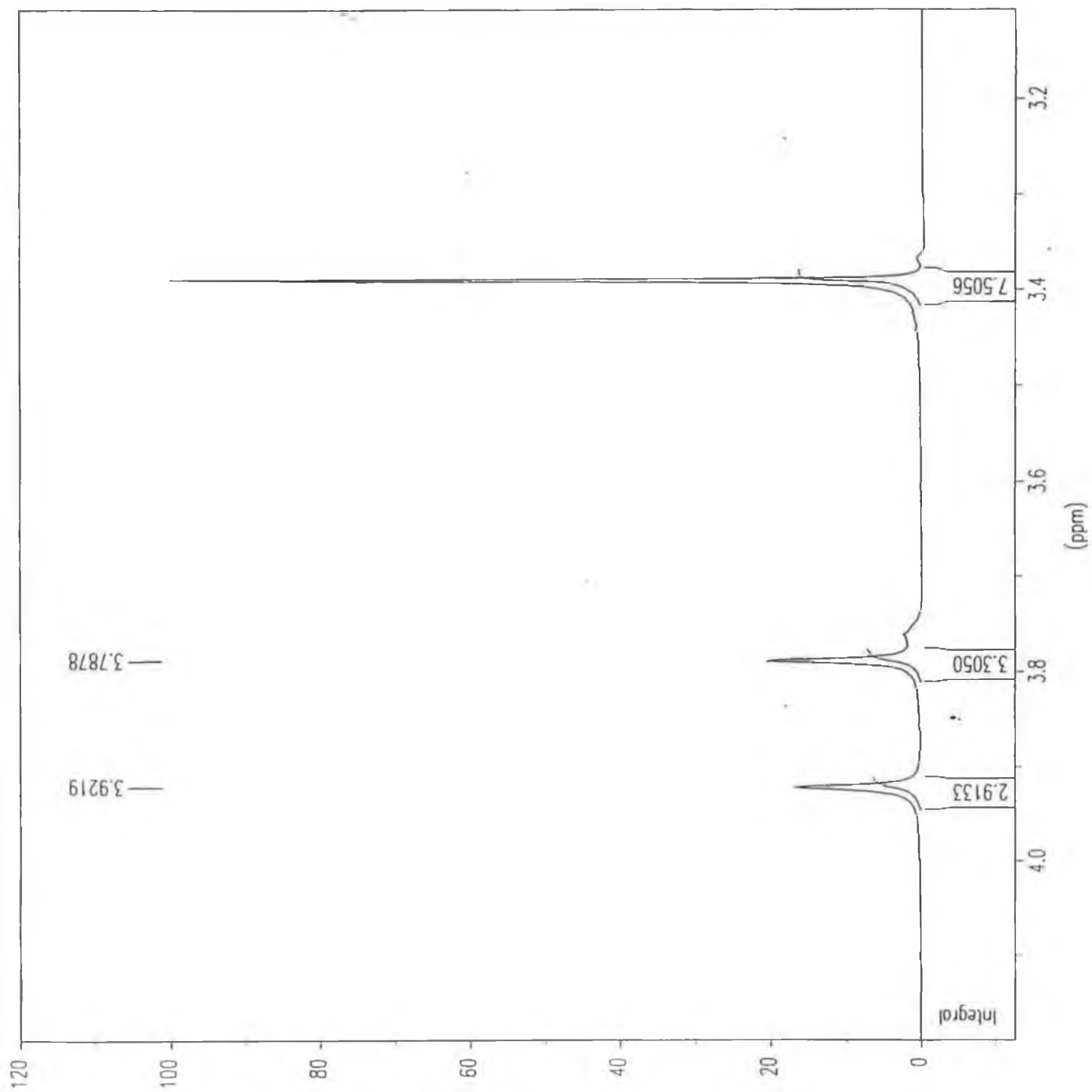
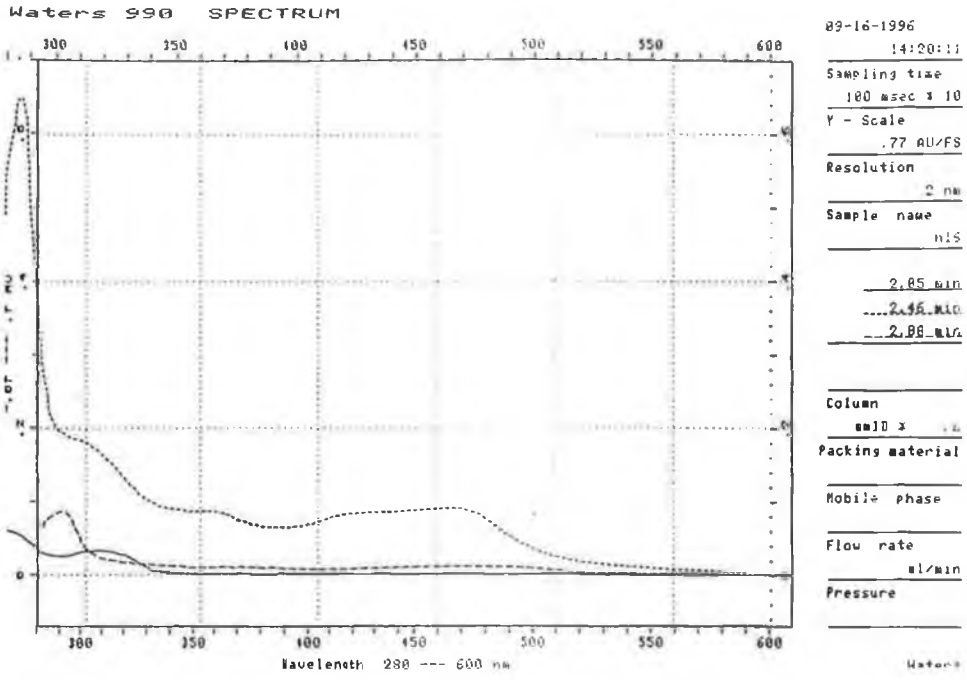


Figure 29. (b) ^{1}Hnmr of 3-(2,5-dimethoxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole (L_1) in $(CD_3)_2SO$ - aliphatic region.

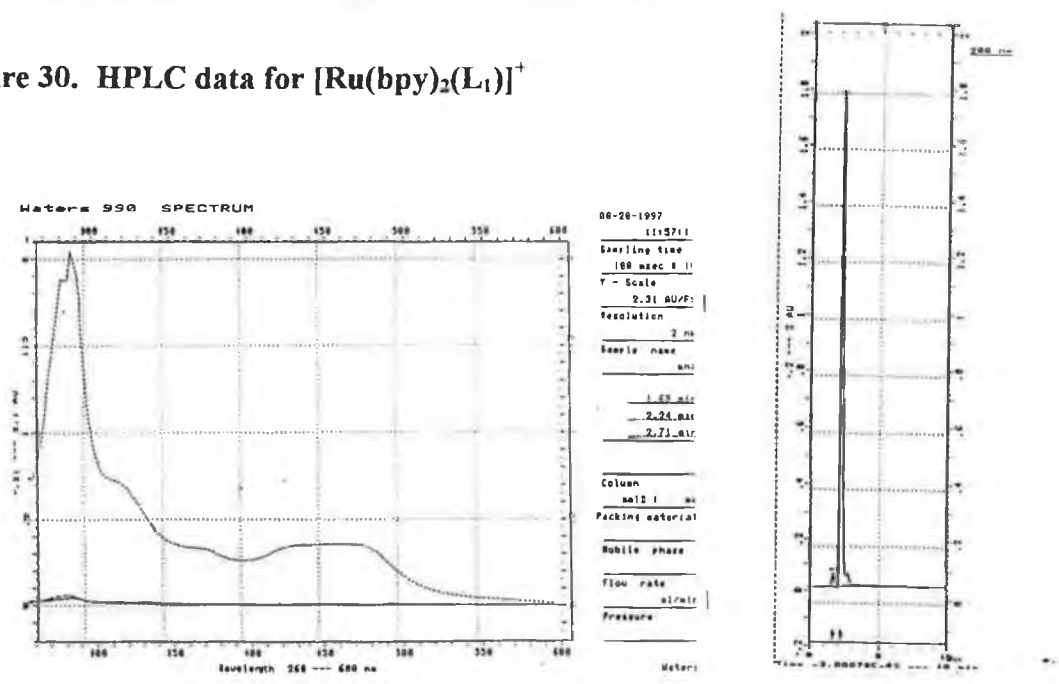




280 nm

No.	R.time [min]	height [AU]	left [min]	right [min]	area [AU*min]	area [%]	mark
1	2.46	0.4904	1.67	4.19	0.174657	98.220	
2	2.88	0.0179	2.72	3.07	0.003166	1.780	TA

Figure 30. HPLC data for $[Ru(bpy)_2(L_1)]^+$



280 nm

No.	R.time [min]	height [AU]	left [min]	right [min]	area [AU*min]	area [%]	mark
1	1.67	0.0473	1.16	2.02	0.012969	3.570	
2	2.23	1.7280	1.95	8.67	0.350258	96.430	

Figure 31. HPLC data for $[Ru(bpy\text{-}d_8)_2(L_1)]^+$