

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Non-Extractive Spectrophotometric Determination of Copper in Alloys Samples Using 2,4-Dihydroxyacetophenone acetoxyhydrazone

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ABSTRACT

A very simple, highly selective and non-extractive spectrophotometric method for the trace amounts of copper(II) has been developed. 2,4-Dihydroxyacetophenone acetoxyhydrazone(DAAH) has been proposed as a new analytical reagent for the direct non-extractive spectrophotometric determination of copper(II). The reagent reacts with copper(II) in acidic medium(pH 4.0) to form a pale yellow coloured 1: 1 (M : L) complex. The reaction is instantaneous and the complex shows maximum absorbance at 370 nm. The molar absorptivity and Sandell's sensitivity are found to be $1.02 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.623 \mu\text{g cm}^{-2}$ respectively. The system obeys Beer's law in the range, 0.2- 2.0 $\mu\text{g/ml}$ of copper(II). The method is highly selective for copper and successfully used for determination of copper in alloys.

Key words: Spectrophotometric determination, 2,4-dihydroxyacetophenone acetoxyhydrazone, Alloy and steel samples.

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INTRODUCTION

Hydrazones are potential and interesting analytical reagents [1-3]. These reagents are frequently used for the spectrophotometric determination of metal ions. However, 2,4-dihydroxyacetophenone acetylhydrazone (DAAH) is not so far used for the spectrophotometric determination of copper. Therefore, it is of interest to develop spectrophotometric method for the determination of copper using DAAH. Copper is widely utilized in electrical industries and in making industrially useful alloys. Hence determination of copper in alloys has been regarded as an interesting research activity. In the light of the above, and in continuation of our previous work [4-6], herein we report synthesis, characterization and spectrophotometric properties of DAAH. The developed DAAH method is applied for the determination of copper(II) in alloys.

MATERIALS AND METHODS

Materials

2,4-Dihydroxyacetophenone and acetohydrazide were procured from Merck, India. Ethanol of AR grade, Merck and used as received. Solvent like N,N-dimethylformamide used after distillation.

Synthesis of reagent 2,4-Dihydroxyacetophenone acetylhydrazone(DAAH)

2,4-Dihydroxyacetophenone (1.52 g, 0.01 mol, dissolved in 5 ml of ethanol) and acetohydrazide (0.74 g, 0.01 mol dissolved in 3 ml of ethanol) were mixed in a clean round bottom flask. Suitable quantity(10 ml) of ethanol was added to the reaction mixture and refluxed with stirring for 3 hrs. The pale brown coloured product was separated out on cooling. It was collected by filtration, washed several times with hot water. This compound was recrystallized from methanol and dried in vacuum. The yield was found to be 78 % ; m.p. 243 – 245°C. The reaction route for the synthesis is shown in Fig 1.

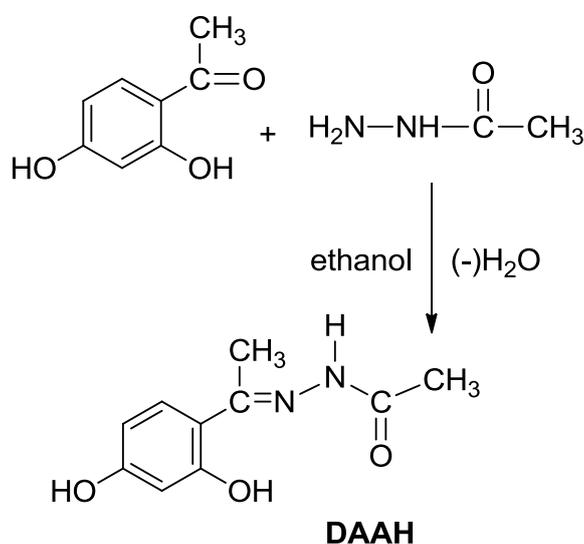


Figure 1: Synthesis of ligand (DAAH)

Preparation of reagent solution

The reagent solution (0.01M) was prepared by dissolving 0.052gm of the compound in 10 ml of dimethylformamide (DMF) in 25-ml volumetric flask. The reagent solution was found to be stable for 10 hrs.

Preparation of copper(II) solution

A 1×10^{-2} M stock solution of divalent copper was prepared by dissolving requisite quantity (0.20 g) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in doubly distilled water containing few drops of glacial CH_3COOH and made

up to mark in 100- ml volumetric flask. The stock solution was standardised gravimetrically [7]. Dilute solutions were prepared from this stock solution. Solutions of large number of inorganic ions, complexing agents were prepared from their analaR grade (or) equivalent grade water soluble salts.

Procedure

An aliquot of the solution containing copper in optimum concentration range, 10ml of buffer solution (pH 4.0) and 1ml of 0.01 M reagent solution were combined in 25ml volumetric standard flask and resulting solution was diluted to the mark with distilled water. The absorbance of the solution was measured at 370 nm against reagent (DAAH) blank. The measured absorbance was used to compute the amount of copper from predetermined calibration plot.

Preparation of Alloy sample

100 mg of alloy sample was dissolved in aquaregia and evaporated on hot water bath to dryness. The residue was dissolved in minimum amount of dilute hydrochloric acid and transferred into 50 ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

Apparatus

A Perkin – Elmer (Lambda 25), UV – Visible spectrophotometer equipped with 1.0- cm (path length) quartz cell and ELICO model LI- 610 pH meter were used in the present study.

RESULTS AND DISCUSSION

Characterization of reagent 2,4-Dihydroxyacetophenone acetylhydrazone (DAAH)

The newly synthesized reagent 2,4-Dihydroxyacetophenone acetylhydrazone (DAAH) is characterized using IR, NMR and Mass spectral data.

IR spectra

Infrared spectrum shows sharp strong peak at 3461 cm^{-1} may be assigned for the stretching vibrations of -OH and 3235 cm^{-1} may be assigned for the stretching of secondary -NH groups. The sharp peaks appeared at 1662 cm^{-1} may be assigned for stretching vibrations of amide -C=O group. The band at 1627 cm^{-1} may be assigned for plane bending vibration of -NH group, band at 1581 cm^{-1} may be assigned for stretching vibration of azomethine -C=N group, band at 1451 cm^{-1} may be assigned for asymmetric bending vibration of -CH group, band at 1296 cm^{-1} may be assigned for stretching vibration of -CN group, band at 1269 cm^{-1} may be assigned for stretching vibration of -CN group (coupled), band appeared at 751 cm^{-1} is assigned for oop bending of aromatic -CH group and band at 695 cm^{-1} may be assigned for stretching vibrations of -OCN deformation.

^1H – NMR spectra

The ^1H – NMR spectrum of DAAH (in $\text{DMSO}-d_6$) showed signals at (δ ppm) 2.02, 2.26, 6.25, 7.36, 9.80 and 10.76 due to -CH_3 protons, acetyl [-COCH_3] protons, phenyl protons, imine protons, p-phenolic and o-phenolic protons respectively.

Mass spectra

Mass spectrum (Fig. 2) of DAAH shows signal at m/z 208 due to the formation of molecular ion. The peaks observed at m/z values of 193 and 165 are due to the loss of -CH_3 and -COCH_3 radicals respectively.

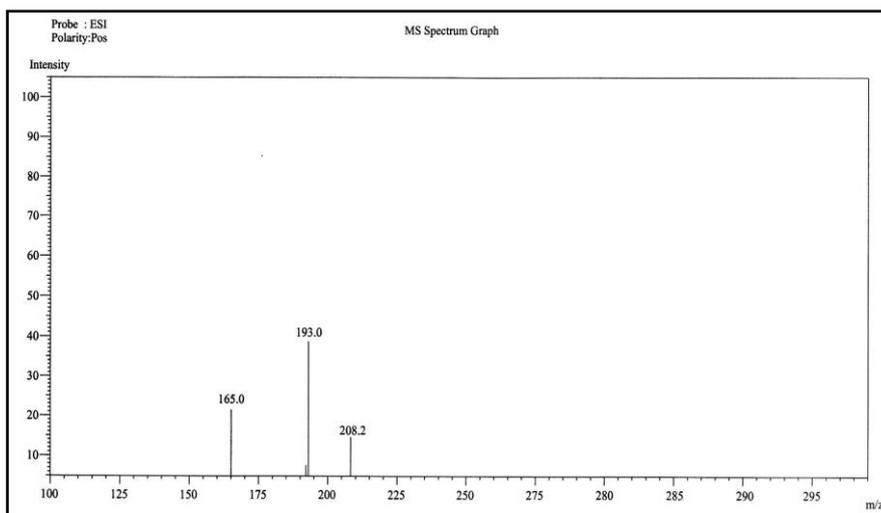


Figure 2: Mass spectrum of DAAH

UV-Visible spectra

Absorption spectra (Fig 3) of 2×10^{-5} M DAAH solution at different pH values were recorded and pKa values were determined spectrophotometrically using Phillip and Merritt method [8]. The bathochromic shift from 295 – 365 nm indicates that in solution on increasing pH the >C=O group of the reagent (DAAH) is enolised and dissociated. The values of DAAH are 5.4 (pK₁) and 8.5 (pK₂) respectively. The pK₁ and pK₂ values are presumably due to keto – enol tautomerism and deprotonation of -NH group respectively.

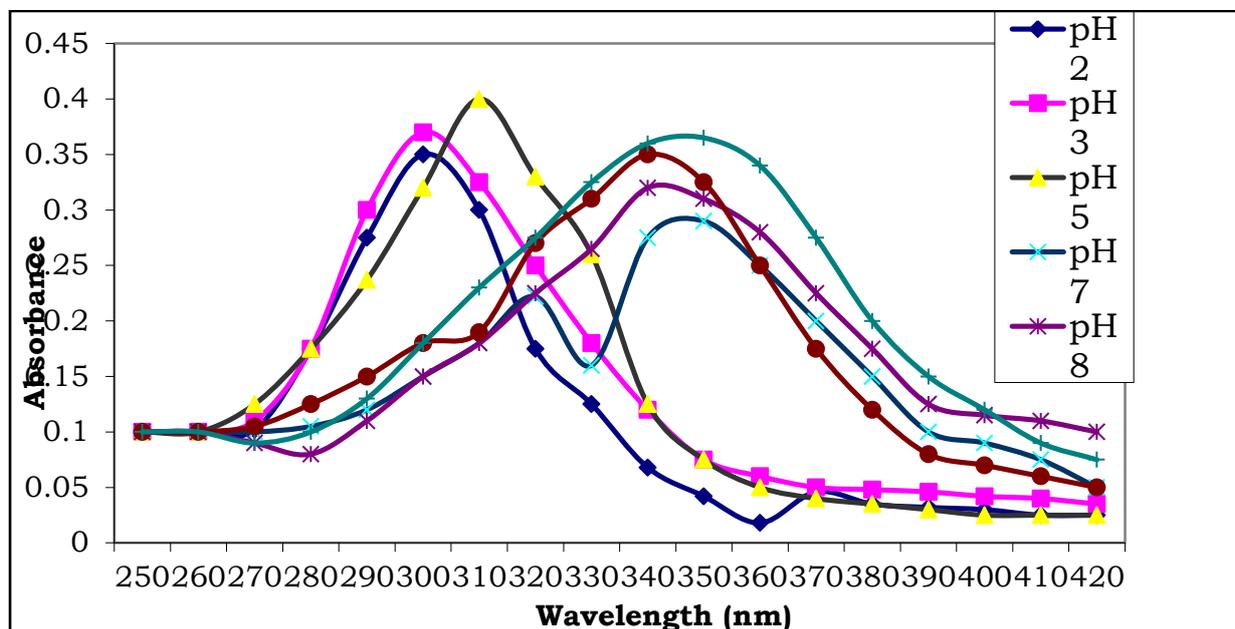


Figure 3: Absorption spectra of 2×10^{-5} M at different pH values

Effect of reagent concentration

The data (Table 1) indicate that a 10- fold molar excess of reagent is sufficient for full colour development.

Table 1: Effect of reagent (DAAH) concentration on the absorbance of the complex.

Cu(II) : DAAH	Absorbance at 370 nm
1: 05	0.460
1:10	0.470
1:20	0.484
1:40	0.492
1:60	0.500

Effect of time

The absorbance of Cu(II) – DAAH complex was measured at different time intervals to ascertain the time stability of the complex .The absorbance of the Cu(II) complex was measured at 370 nm. The colour development is instantaneous and the absorbance of the complex remains constant for 3 hrs and there after showed gradual decrease in intensity with increasing time.

Effect of pH

The effect of pH on the colour intensity of Cu(II) – DAAH complex is studied . A plot between absorbance at of the complex at 370 nm and pH is shown in Fig 4. The graph indicates that the complex shows maximum and constant absorbance in the pH range 3.5 – 4.5. Hence, buffer solution of pH 4.0 is chosen for subsequent studies.

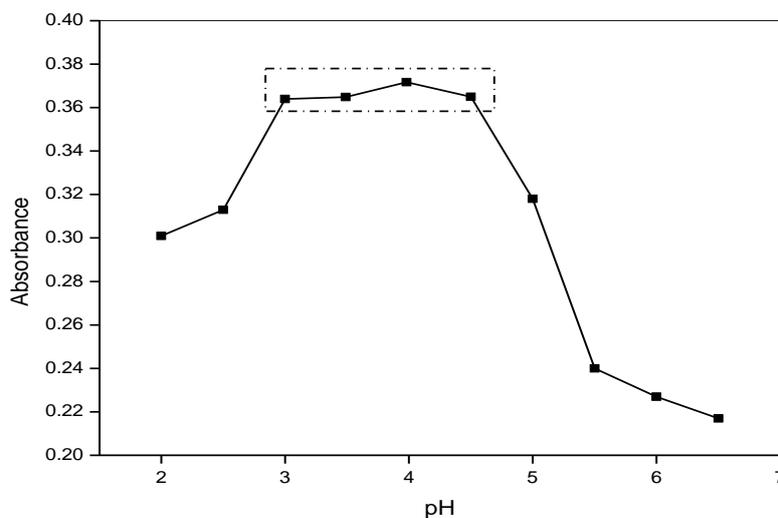


Figure 4: Effect of pH on the absorbance of Cu(II)-DAAH complex

Adherence to Beers law, Molar absorptivity, and Sandell’s sensitivity

The system obeys Beer’s law in the range of 0.2 - 2.0 µg/ml of copper (II). The calibration plot is shown in Fig 5. Molar absorptivity and Sandell’s sensitivity of the method are found to be $1.02 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.623 \text{ µg} \cdot \text{cm}^{-2}$ respectively.

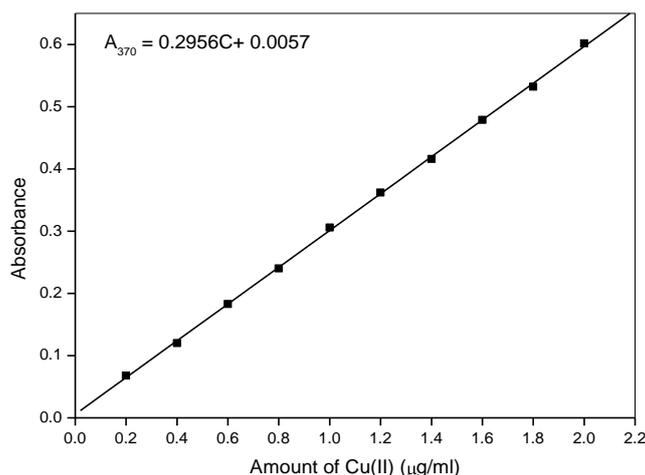


Figure 5: Calibration plot for copper determination

Precision

The precision of the method was checked by ten replicate analysis of sample each containing 2.12 ppm of copper. The standard deviation and relative standard deviation are found to be ± 0.0059 and $\pm 1.75\%$ respectively.

Effect of foreign ions

The validity of the method was assessed by investigating the effect of various cations and anions on the determination of copper(II). The amount of foreign ion which brings about a change in absorbance by $\pm 2\%$ was taken as its tolerance limit and results are given in Table 2.

Table 2: Tolerance limit of foreign ions in the determination of 1.27 µg/ml of copper

Ion added	Tolerance limit	Ion added	Tolerance limit
EDTA	615	Mg ⁺²	28
Tartarate	595	Zn ⁺²	26
Citrate	326	Ni ⁺²	24
Sulphate	307	Mn ⁺²	22
Iodide	252	Mo ⁺²	19
Bromide	240	Fe ⁺²	11
Thiourea	152	Hg ⁺²	8 ^a
Chloride	142	Co ⁺²	2.3
Nitrate	124	Ag ⁺¹	2.2
Flouride	76	Cu ⁺²	1.9
Phosphate	30	Al ⁺³	0.5
Oxalate	18	Fe ⁺³	0.4 ^b
Ascorbate	10	Pt ⁺⁴	0.08

^amasked with 200 mg/ml of iodide.

^bmasked with 450 mg/ml of cyanide.

Larger amounts of Hg(II) and Fe(III) do not interfere in the presence of masking agents. Interference of molybdenum(IV) and iron(III) are masked with iodide and cyanide respectively.

Determination of composition of the complex

The composition of the complex (M : L = 1 : 1) was determined by Job's continuous variation method and molar ratio method. The plots are shown in Fig 6 and Fig 7.

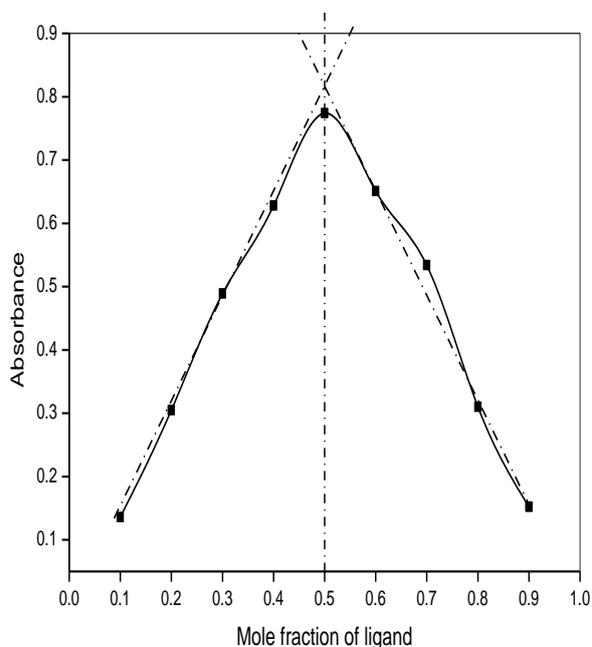


Figure 6. Job's curve

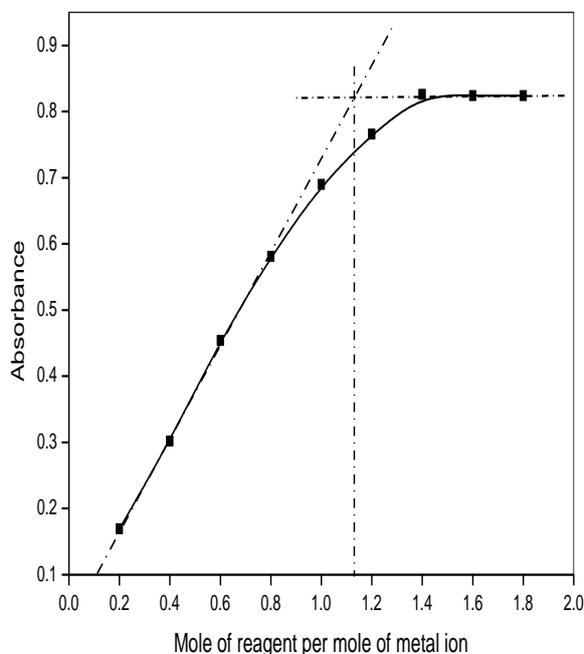


Figure 7 Molar ratio plot.

Table 3: Physico – Chemical and Analytical Characteristics of Cu(II) Complex with DAAH

Characteristics	Cu(II) – DAAH
λ_{max} (nm)	370
pH – range (optimum)	3.0 – 4.5
Mean absorbance	0.230±0.0005
Mole of reagent required per mole of metal ion for full color development	5 fold
Time stability of the complex (h)	2
Beers law validity range (µg/ml)	0.2 – 2.0
Molar absorptivity (L mol ⁻¹ cm ⁻¹)	1.02 x 10 ⁴
Specific absorptivity (ml g ⁻¹ cm ⁻¹)	0.160
Sandell's sensitivity (µg/cm ²)	0.623
Composition of the complex as obtained from Jobs and Molar ratio method (M : L)	1 : 1
Stability constant of the complex	1.08 x 10 ⁵
Standard deviation in the determination of 2.12 µg/ml of Pd(II)	0.0059
Relative standard deviation	1.75
Detection limit (µg ml ⁻¹)	0.0523
Determination limit (µg ml ⁻¹)	0.156

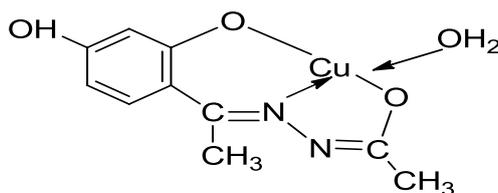


Figure 8: The proposed structure of Cu-DAAH

Respectively, The dissociation constant (α) and concentration (c) of the reagent at intersecting point were used in the calculation of stability constant of the complex. Stability constant of the complex 1: 1 (M : L) complex is given by $1-\alpha/4\alpha^3c^2$. The predicted structure of Cu(II) – DAAH is given in Fig 8. Various physico-chemical and analytical characteristics of copper complex are summarized in Table 3.

APPLICATIONS

The amount of copper present in synthetic samples whose composition corresponding BAS -106 and monel metal was determined by the developed method, by taking a known aliquot of the sample solution in a 25 ml standard flask containing 10 ml of buffer solution, 2.5 ml of N,N-dimethyl formamide and reagent [1.0ml of 1×10^{-2} M DAAH] solution and made up to the mark with distilled water. The absorbance of the complex was measured at 370 nm against the reagent blank prepared under the similar experimental conditions. The absorbance values were referred to the predetermined calibration plot to compute the amount of the metal ion in alloy samples and the data is given in Table 4.

Table 4: Determination of Copper in Certified Reference Materials

Name of the certified reference material	Amount of copper (%)		
	Certified Found ^a Value	%Error	
BAS-106 ^b	4.10	4.13	0.73
Monel metal ^c	30.00	30.07	2.20

^a Average of five determinations, ^b BAS-106 - Ni 1.93%, Cu 4.1%, Fe 0.43%, Mn 0.2% & Mg 1.61%.

^c Monel metal - Cu 30%, Ni 67%, Fe 3%.

CONCLUSION

A comparison of spectrophotometric methods [9 - 14] for the determination copper is given in Table 5. The data suggest that the present method seems to rank among the sensitive methods.

Table 1 : Comparison of Spectrophotometric Methods For The Determination of Copper (II)

Name of the Reference reagent	λ_{\max} (nm)	pH range	Determination ($\mu\text{g/ml}$)	$\epsilon \times 10^4$ ($\text{L mol}^{-1} \text{cm}^{-1}$)	
Eosin- Perindopril	535	-	-	6.55×10^3	9
Ramipril	535	-	-	4.00×10^3	
3-{2-[2-(2-hydroxy imino-1-Methyl-propylidene amino)-(ethylamino)-ethyl-imino]-butan-2-one oxime	570	alkaline	-	0.16×10^4	10
1-phenyl-1-hydrazonyl-2-oximino propane-1,2-dione	345	9.4	-	0.35×10^3	11
Acetophenone-p-chloro phenyl thiosemicarbazone	-	4.0-9.0	0.25-6.35	5.5×10^3	12
Cefixime	336	-	1.015-8.122	8.29×10^3	13
[N-(o-hydroxy benzylidene)-4-methylaniline] arbazone	-	5.8-6.8	1.0-20.0	0.89×10^3	14
2,4-Dihydroxyacetophenone Acetoylhydrazone(DAAH)	370	4.0	0.2-2.0	1.0×10^4	PM

PM-Present method

The present method is simple, rapid and more sensitive than other reported methods for determination of copper. It is successfully applied for the determination of copper in alloy samples.

ACKNOWLEDGEMENT

The authors thank UGC and DST, New Delhi for providing equipment facility under UGC-SAP and DST-FIST programmes respectively. The authors also thank M. Subbalakshmi of IICT, Hyderabad for her help in recording IR and NMR spectra of reagent sample.

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