

**THE RING CLOSURE REACTIONS OF
AMIDOXIMES
WITH PHENYLBORONIC ACID**

MUHARREM AKCAN

2007

**THE RING CLOSURE REACTIONS OF
AMIDOXIMES
WITH PHENYLBORONIC ACID**

by

MUHARREM AKCAN

**THESIS SUBMITTED TO
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THE DEPARTMENT OF
CHEMISTRY**

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Approval of the Graduate School of Natural and Applied Sciences.

Prof. Dr. Nihat ÇELEBİ
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Mahmut ACIMIŞ
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Sciences.

Prof. Dr. Yaşar DÜRÜST
Supervisor

Examining Committee Members

1. **Prof. Dr. Yaşar DÜRÜST**
2. **Prof. Dr. Çetin BOZKURT**
3. **Doç. Dr. Mustafa KÜÇÜKİSLAMOĞLU**

ABSTRACT

THE RING CLOSURE REACTIONS OF

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AKCAN, Muharrem

M.Sc., Department of Chemistry

Supervisor: Prof. Dr. Yaşar DÜRÜST

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The aim of this work is the synthesis of 3,4,5-trisubstituted-4,5-dihydro-1,2,4,5-oxadiazaborole heterocycles by the cyclodehydration reactions of mono and *N*-substituted amidoximes with phenylboronic acid. They have been reported to have hypotensive, cardiac, and central nervous system depressant activities. For this purpose, first, amidoximes as starting compounds were synthesized according to the literature procedures. The amidoximes were then reacted with phenylboronic acid to give 3,4,5-trisubstituted-4,5-dihydro-1,2,4,5-oxadiazaborole heterocycles.

All of the compounds newly synthesized were identified by means of spectral measurements (IR, NMR, MS, X-Ray) and physical constants (e.g. melting points, *R_f* values) and in this regard, this work is an important contribution to the synthetic organic chemistry.

Keywords: Amidoxime, Phenylboronic acid, Cyclodehydration reaction, Oxadiazaborole, Spectroscopy, Hammett constant, Substituent effect.

ÖZET

AMİDOKSİMLERİN FENİLBORONİK ASİT İLE HALKA KAPANMA REAKSİYONLARI

AKCAN, Muharrem

Yüksek Lisans Tezi , Kimya Bölümü

Tez Danışmanı : Prof. Dr. Yaşar DÜRÜST

Ocak 2007, 176 sayfa

Bu çalışmanın amacı yeni 3,4,5-trisubstitue-4,5-dihidro-1,2,4,5-oksadiazaborol heterohalkalarının bazı amidoksimlerin fenilboronik asit ile birlikte halkadehidrasyon reaksiyonları ile sentezlenmesidir. Bu amaçla, öncelikle literatürdeki yöntemlere göre amidoksimler sentezlenmiştir. Daha sonra, amidoksimler, 3,4,5-trisubstitue-4,5-dihidro-1,2,4,5-oksadiazaborol heterohalkalarının sentezi için fenilboronik asit ile reaksiyona sokulmuşlardır.

Yeni bileşiklerin yapıları spektroskopik ölçümler (IR, NMR, Kütle ve X-Işını Spektrumları) ve fiziksel sabitler (erime noktası, Rf değerleri) yardımıyla aydınlatılmıştır.

Anahtar Kelimeler: Amidoksim, Fenilboronik asit, Halka dehidrasyonu Reaksiyonları, Oksadiazaborol, Spektroskopi, Hammett Sabiti, Substituent Etkisi.

TO MY PARENTS

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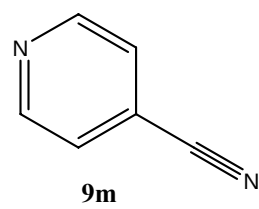
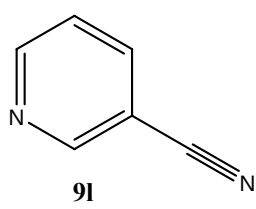
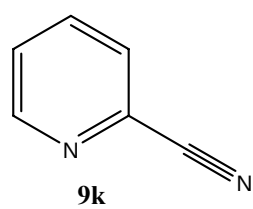
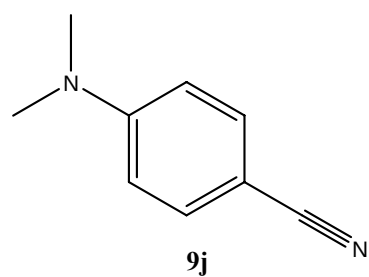
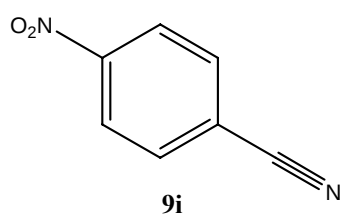
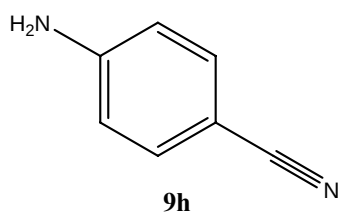
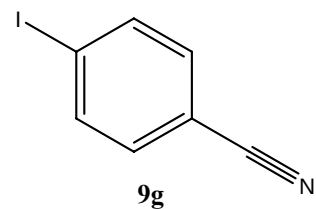
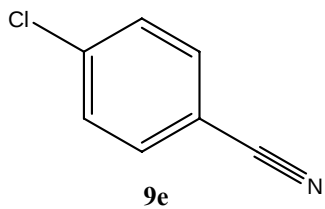
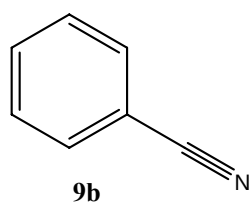
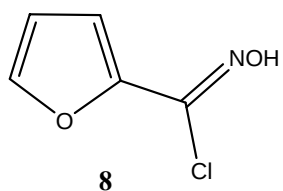
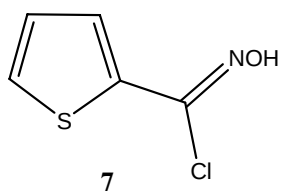
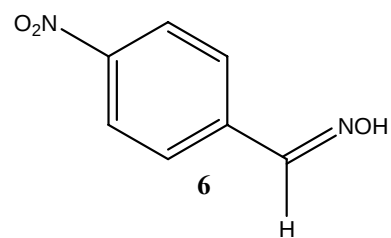
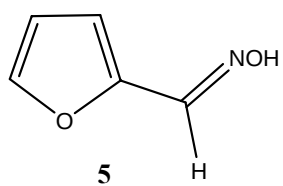
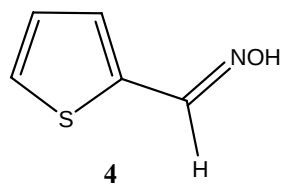
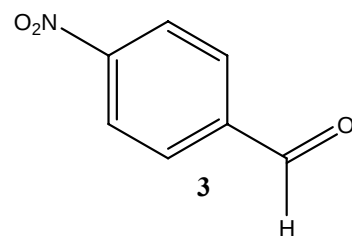
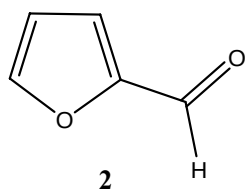
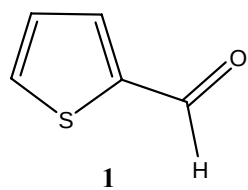
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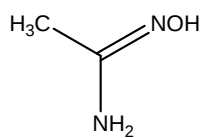
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LIST OF SYMBOLS AND ABBREVIATIONS

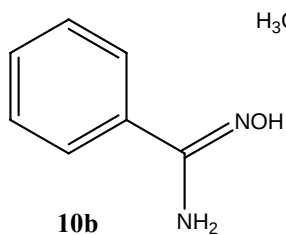
NH₂OH.HCl	: Hydroxylamine hydrochloride
NaCH₃COO.3H₂O	: Sodium acetate trihydrate
KBr	: Potassium bromide
Na₂SO₄	: Sodium sulfate
Et₃N	: Triethyl amine
NCS	: <i>N</i> -Chlorosuccinimide
DMF	: <i>N,N</i> -Dimethylformamide
PB	: Petroleum Benzine
EtOAc	: Ethyl acetate
NH₃	: Ammonia
TLC	: Thin Layer Chromatography
Δ	: Heat
GC-MS	: Gas Chromatography-Mass Spectroscopy
IR	: Infra Red
NMR	: Nuclear Magnetic Resonance
R_f	: Retention Factor
M.p.	: Melting Point

FORMULAE

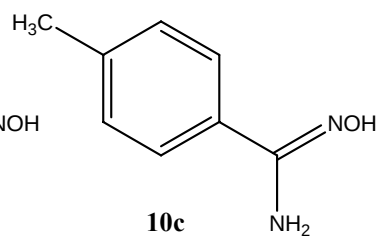




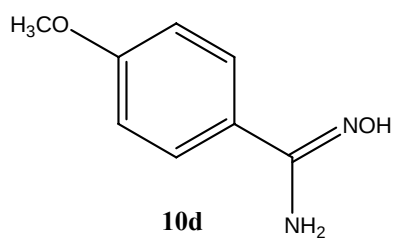
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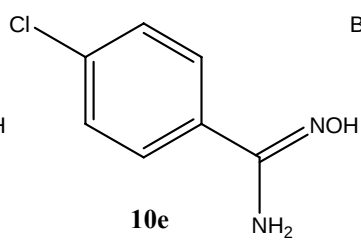
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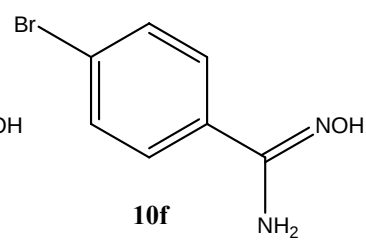
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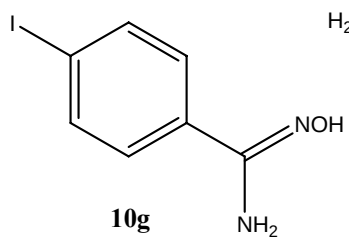
10d



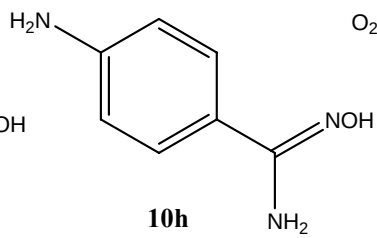
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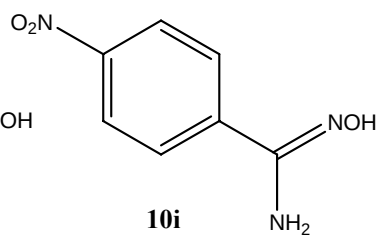
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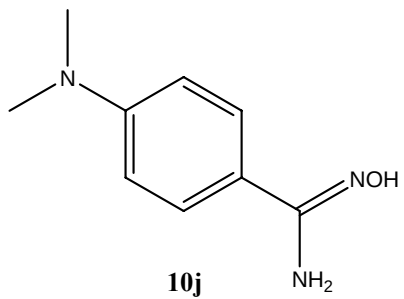
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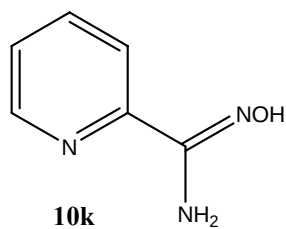
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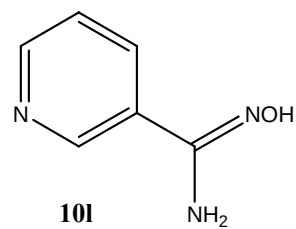
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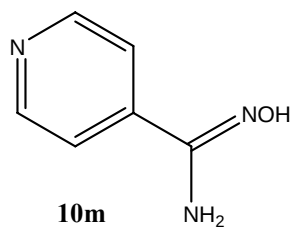
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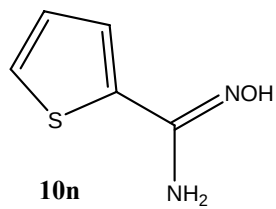
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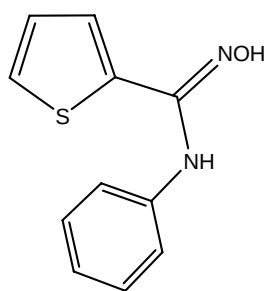
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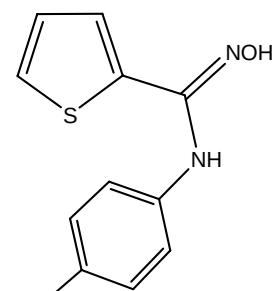
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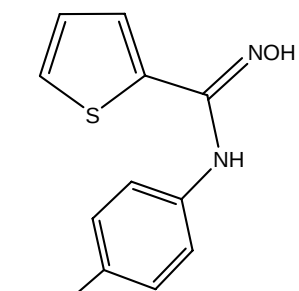
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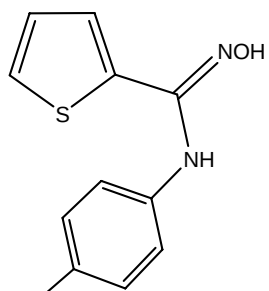
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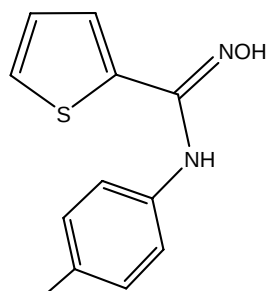
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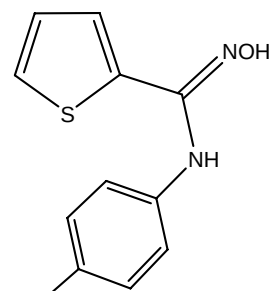
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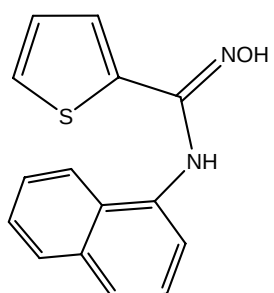
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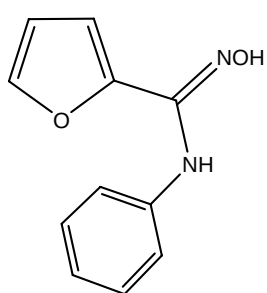
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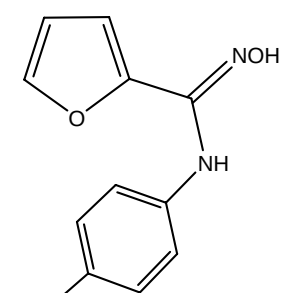
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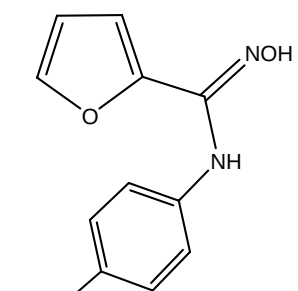
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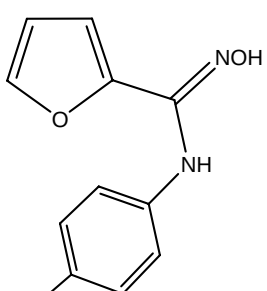
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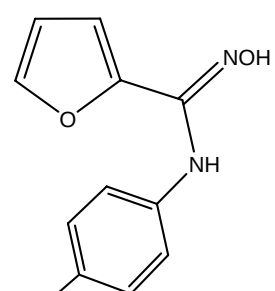
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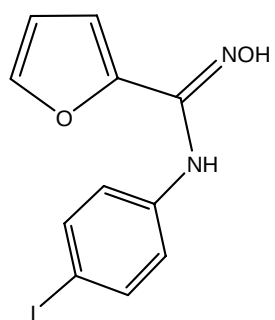
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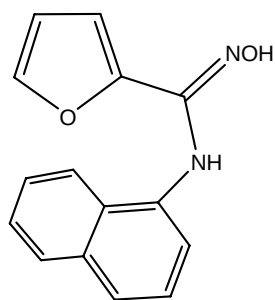
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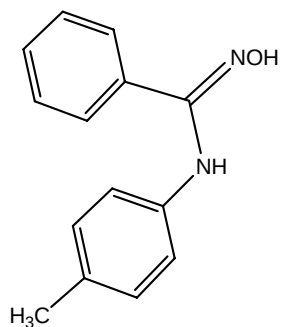
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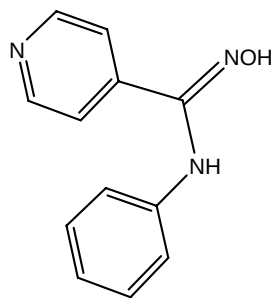
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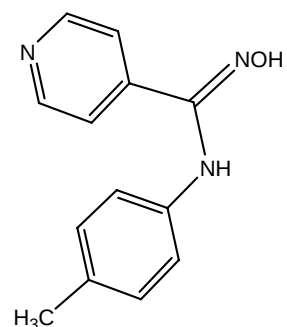
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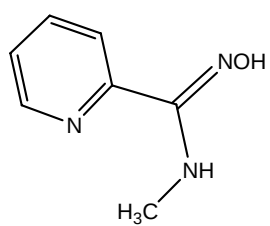
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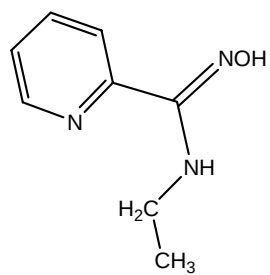
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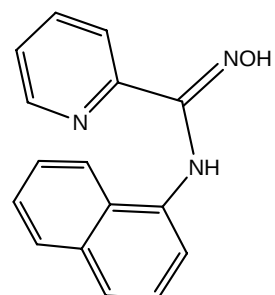
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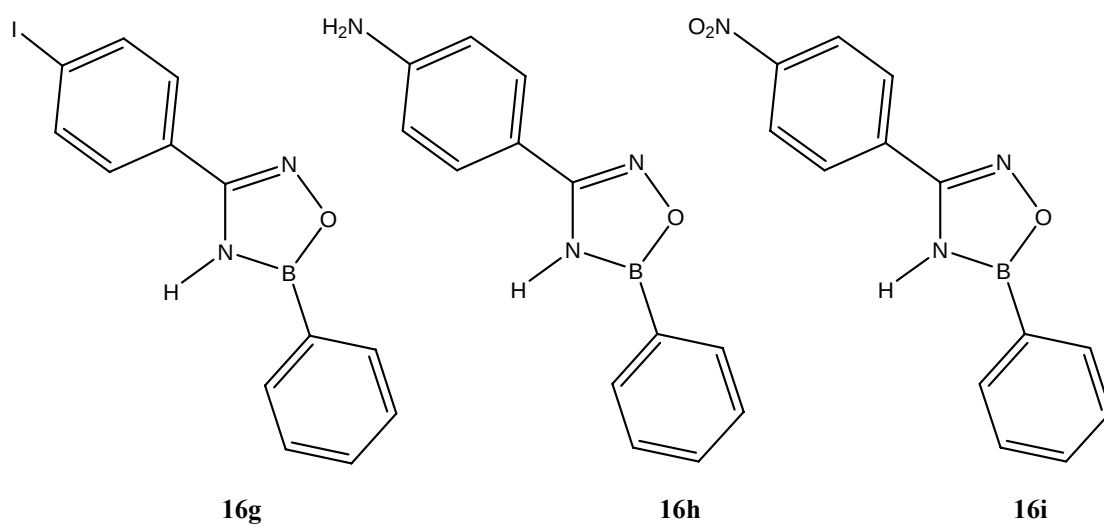
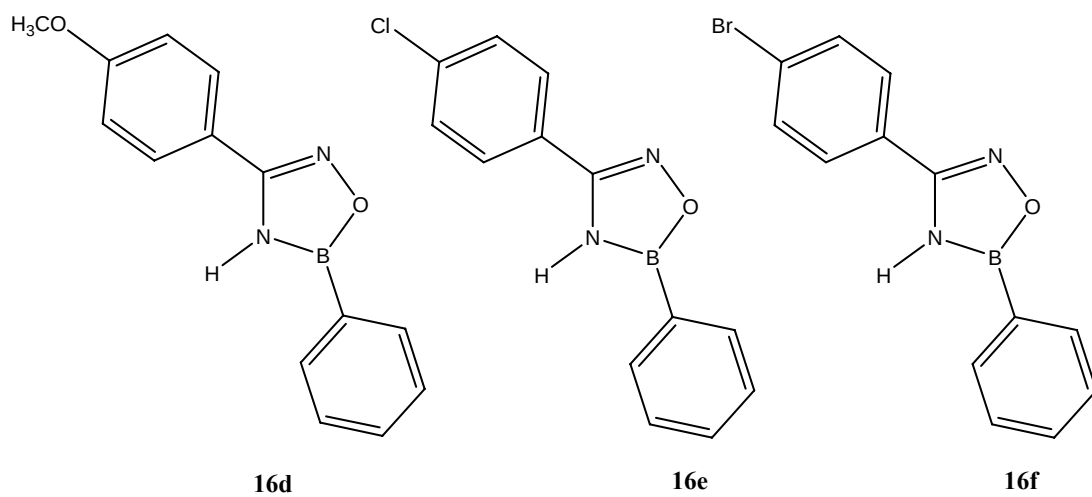
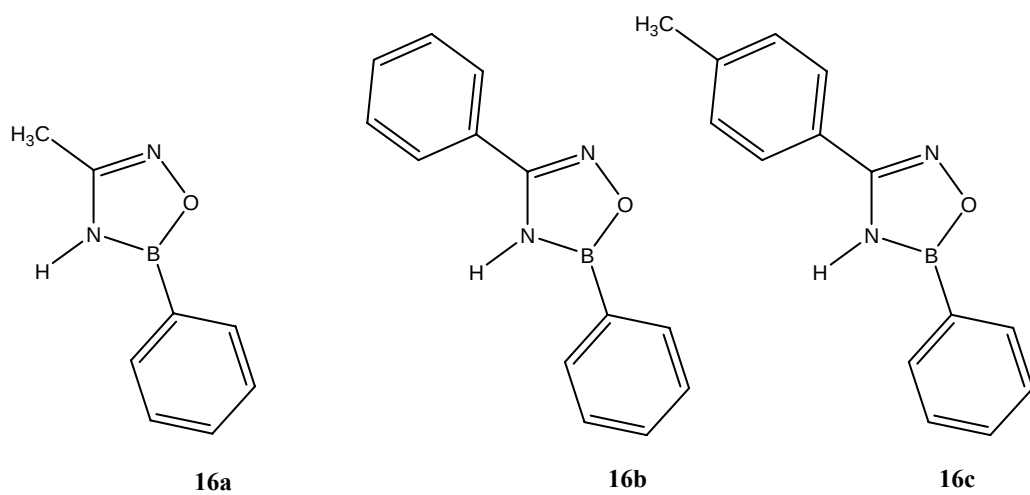
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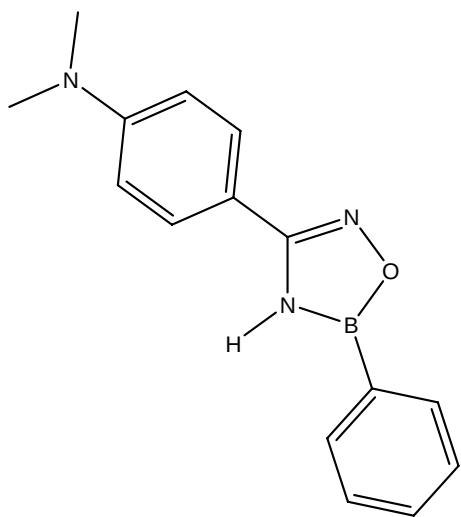


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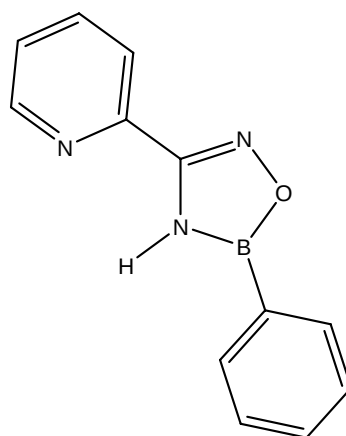


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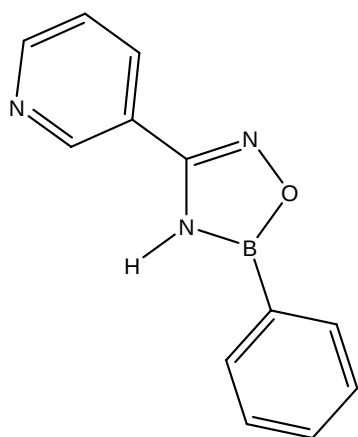




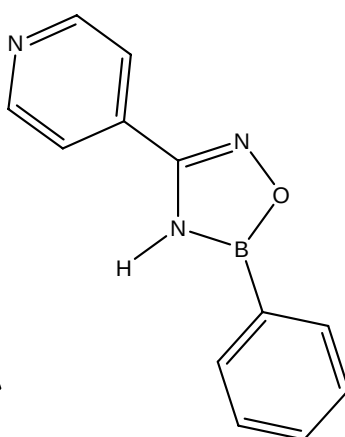
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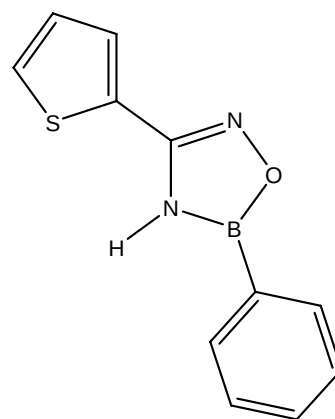
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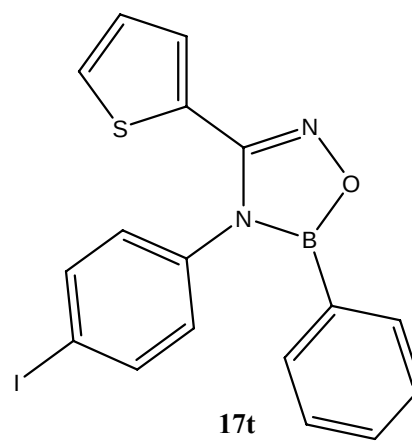
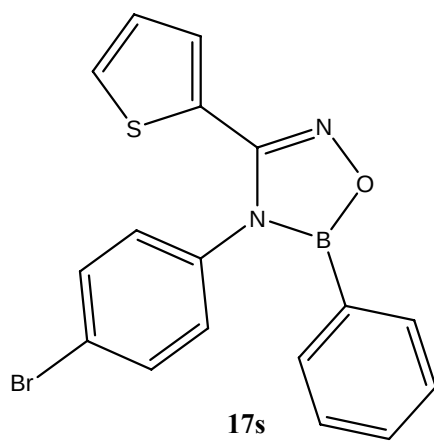
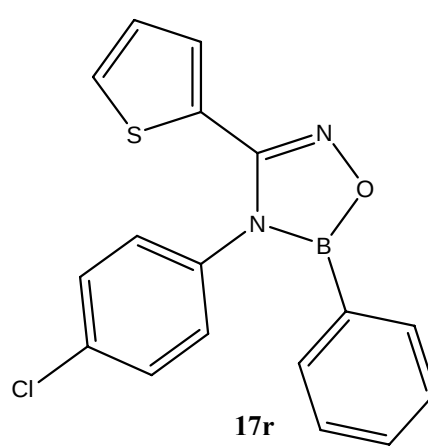
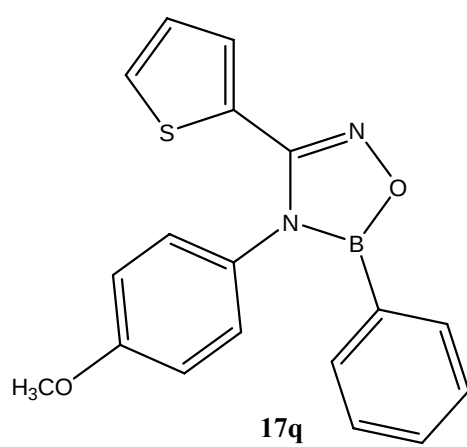
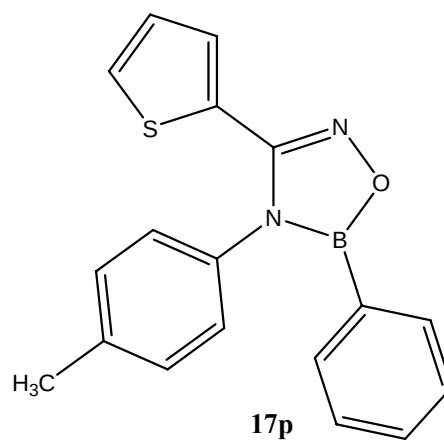
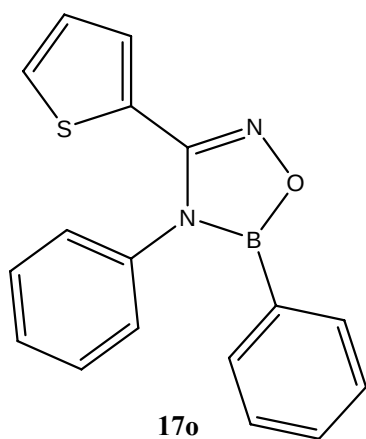
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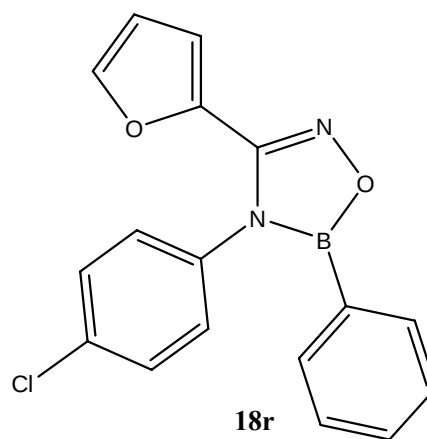
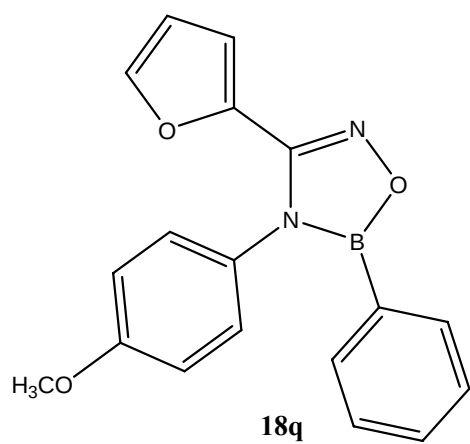
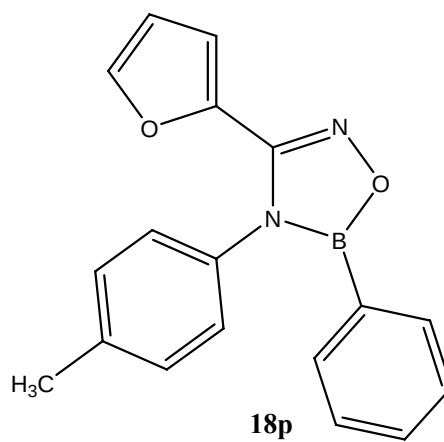
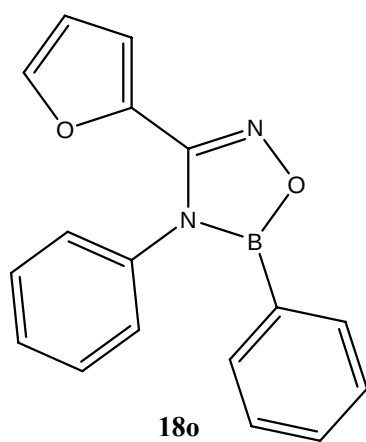
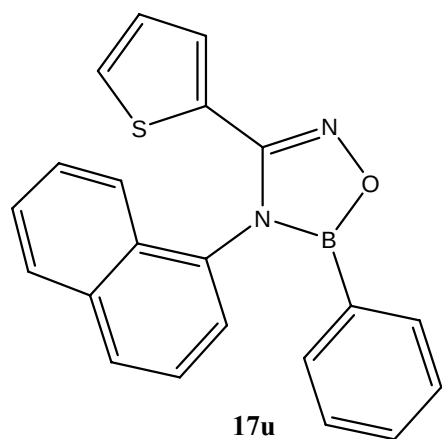


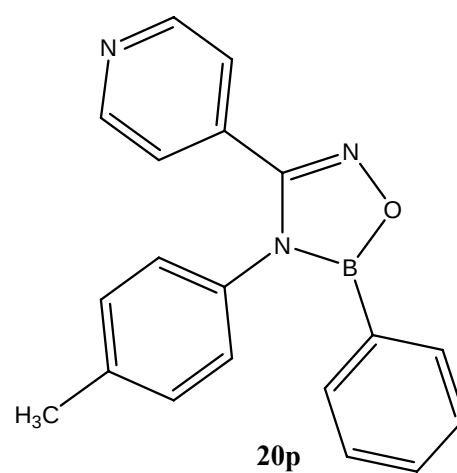
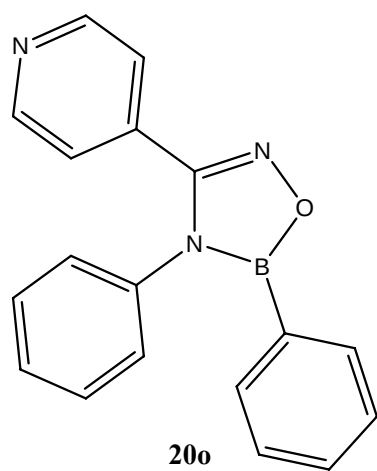
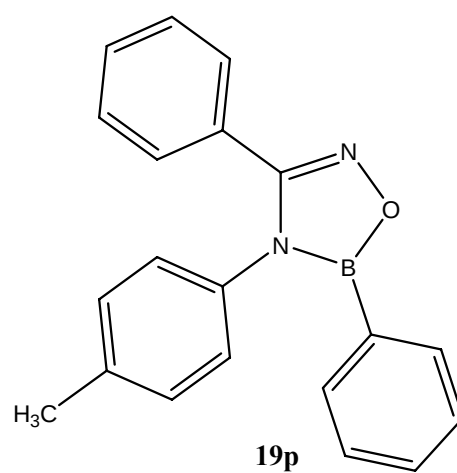
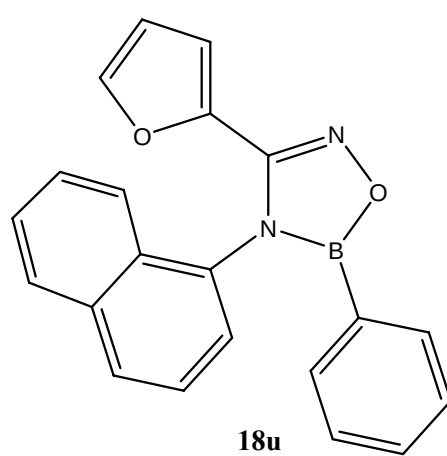
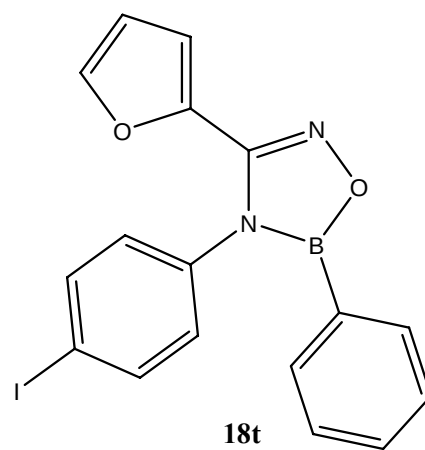
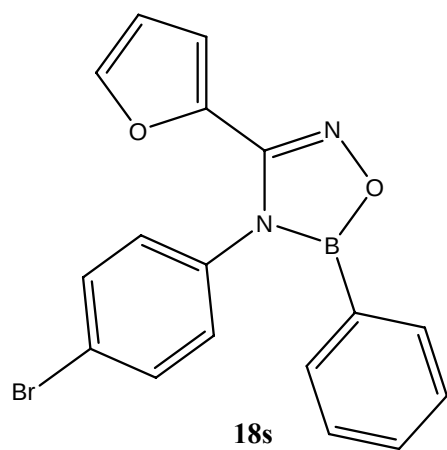
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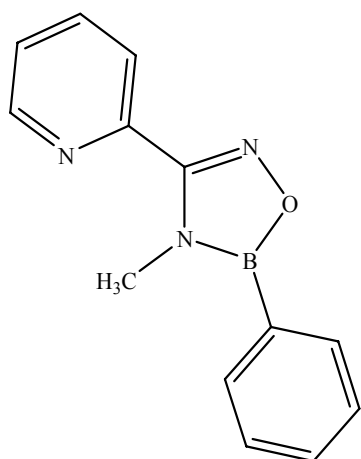


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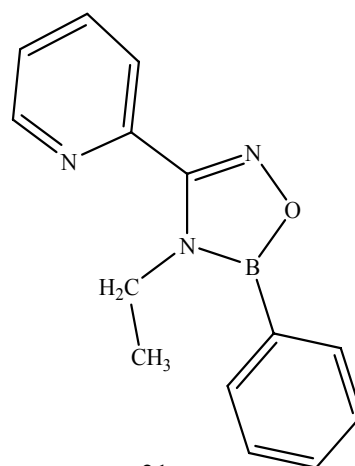




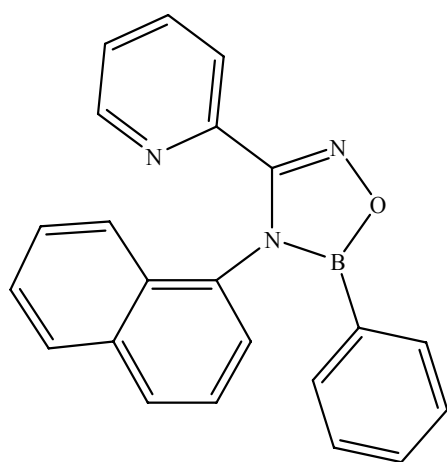




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CHAPTER I

INTRODUCTION

1.1. AMIDOXIMES

Amidoximes are the important class of compounds bearing both a hydroxyimino and an amino function at the same carbon atom and have been used for the synthesis of a variety of valuable compounds.

In 1873, Lossen and Schifferdecker [1] prepared the first amidoxime by reacting hydrogen cyanide with hydroxylamine. The compound is called as “isuretin” as shown below.

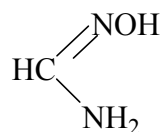


Figure 1: Structure of isuretin

The name “amidoxime” was first used by Tiemann [2] who prepared two related compounds mandelamidoxime and benzamidoxime in 1884 by reacting hydroxylamine with benzaldehyde and benzonitrile respectively.

During the last years more amidoximes have been tested for pharmacological properties and have been found to be bactericidal and fungicidal [3], local anaesthetics and fibrinogen receptor antagonists [4].

1.1.1. Synthesis of Amidoximes

1.1.1.1. Action of Hydroxylamine on Nitriles

The preparation of amidoximes from nitriles by the action of hydroxylamine was first studied by Tiemann and Krüger [2].

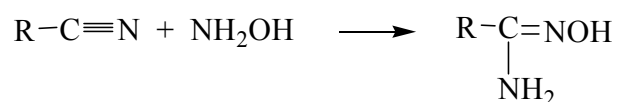


Figure 2: Action of hydroxylamine on nitriles

Addition of the equivalent amount of nitrile in ethanol to hydroxylamine whose hydrochloride part was liberated by sodium carbonate yields amidoximes at 60-80 °C during a few hours.

Amidoximes with highest yields were obtained when a 15% excess of a solution of hydroxylamine in butanol was used [5].

1.1.1.2. Action of Hydroxylamine on Amidine Hydrochlorides and Iminoethers

Action of hydroxylamine on amidine hydrochlorides and iminoethers was first studied by Pinner [6] who synthesized benzamidoxime by treating benzamidine hydrochloride with hydroxylamine.

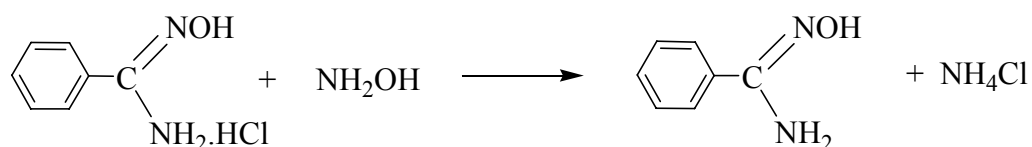


Figure 3: Synthesis of benzamidoxime

Benzamidoxime was also prepared by the action of hydroxylamine on phenyl benzimidate by Pinner [6] and Lossen [7].

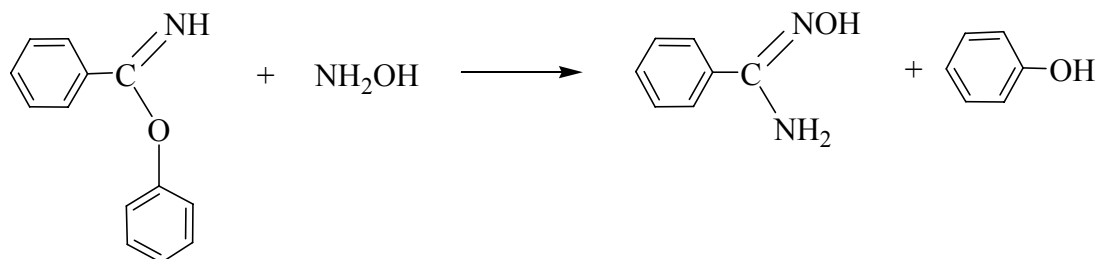


Figure 4: Synthesis of benzamidoxime

1.1.1.3. Action of Hydroxylamine on Amides and Thioamides

The procedure for the synthesis of amidoximes from amides and thioamides is same as from nitriles. By this method some aromatic amidoximes have been prepared [8-11].



Figure 5: Action of hydroxylamine on thioamides

The preparation of amidoximes from amides and hydroxylamine has only been reported by Schiff [12] and Durio and Dugone [13].

1.1.1.4. Action of Ammonia on Oximinoethers and Hydroximic Acid Chlorides

In 1889, benzamidoxime was prepared by heating benzhydroxamic acid and alcoholic solution of ammonia in a pressure bottle for 8 h at 175 °C by Lossen [14].

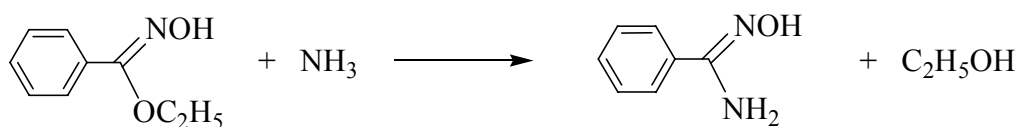


Figure 6: Action of ammonia on oximinoethers

Chlorination of aldoximes forms hydroximic acid chlorides. The reactions of these chlorides with ammonia yield amidoximes [15, 16].

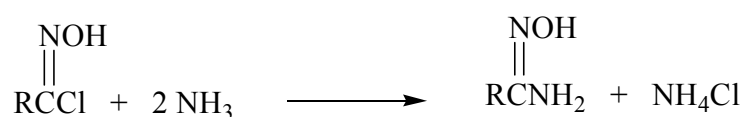


Figure 7: Action of ammonia on hydroximic acid chlorides

1.1.1.5. Reduction of Oxyamidoximes, Nitrosolic and Nitrolic Acids

Ley and Ulrich [17] prepared benzoxyamidoxime by reacting phenyl hydroxymoyl chloride with hydroxylamine. The reduction of the product with sulfurdioxide yields benzamidoxime.

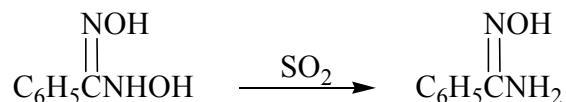


Figure 8: Reduction of oxyamidoximes with sulfurdioxide

The reduction of nitrosolic and nitrolic acids with hydrogen sulfide and hydrogen gases respectively gives amidoximes. Wieland and Bauer [18] prepared benzamidoxime by reducing benzonitrosolic acid with hydrogen sulfide.

1.1.2. Physical Properties of Amidoximes

The amidoximes are colorless crystalline compounds which can be decomposed by heating over their melting points. Aryl amidoximes which are insoluble in water and soluble in alcohols and some organic solvents are more stable than aliphatic amidoximes. The first member of aliphatic series is soluble in water but their solubilities decrease with increasing molecular weight.

The amidoximes are O-H acids, not N-H acids as is brought out by the appreciably higher pK_{HA} of *O*-methyl derivative of benzamidoxime whose pK_{HA} value is 26.0. The pK_{HA} value of benzamidoxime is 23.0 [19].

Tautomerism, conformation, and configuration are important characteristics associated with amidoximes. Considerable work has been done since 1960 in determining these properties for simple amidoximes such as benzamidoximes, formamidoxime, and *N,N*-dimethylacetamidoxime. These studies indicate that there is a major configurational difference between unsubstituted amidoximes (I) or their *N*-alkyl analogues (II) and the *N,N*-dialkyl derivatives (III).

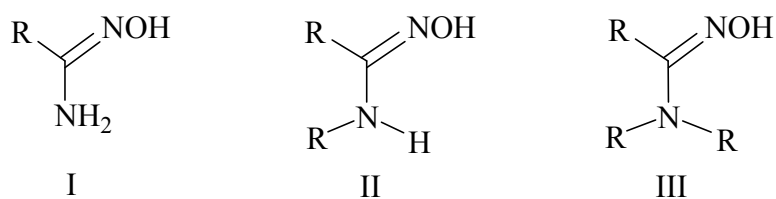


Figure 9: Amidoximes

Tiemann recognized that the amidoximes may be present in two tautomeric forms.

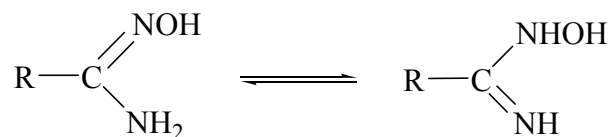


Figure 10: Tautomeric forms of amidoximes

Infrared and nuclear magnetic resonance spectroscopy established that amidoximes and their *O*-acyl derivatives exist in solutions in the amino oxime form [20]. The infrared spectra of amidoximes shows two well defined absorption bands: the first is a doublet at 3484-3412 cm⁻¹ and 3378-3300 cm⁻¹, assigned to the two NH₂ stretching modes; the second between 1680 and 1644 cm⁻¹ to the C=N stretching. The OH stretching band of the NOH group is very broad and has its maximum at approximately 3125 cm⁻¹.

1.1.3. Reactions of Amidoximes

1.1.3.1. Oxidation

The oxidation of benzamidoxime with some oxidizing agents such as potassium ferricyanide, chlorine or bromine in acetic acid, and iodine in aqueous bicarbonate yield a product which corresponds to an aminodihydrooxadiazole.

Iodine in sodium hydroxide yields benzonitrile with benzamidoxime. The oxidation of oxamidedioxime studied by Holleman [21] failed to yield any defined product.

To investigate deoxygenation of nitrosoazomethine derivatives as a method for the generation of azomethine nitrenes, a preparation of nitroso compounds by the oxidation and dehydrogenation of secondary amidoximes has been studied by Boyer and Frints [22] in 1968.

1.1.3.2. Reduction

The reduction of benzamidoxime with sodium amalgam [23, 24] produces ammonia and benzaldoxime with a yield of only 10 to 12%; most of the amidoxime remains unchanged.

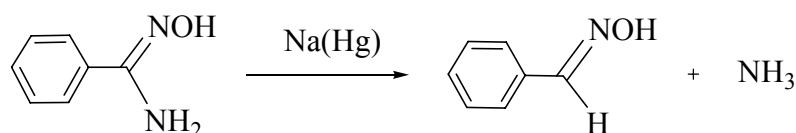


Figure 11: The reduction of benzamidoxime

Zinc and hydrochloric acid do not reduce amidoximes. Therefore this reagent reduces p-nitrobenzamidoxime to p-aminobenzamidoxime [25].

When *N*-substituted amidoximes are reduced on a palladium charcoal catalyst under 10 to 20 atm of hydrogen [26], only 3 moles of hydrogen are taken up; there is evidence that both nitrogen atoms are still present in the reaction product but the structure of these substances has not yet been established.

Amidines can be prepared by reduction of the corresponding amidoximes [27, 28] in the presence of Raney nickel at 30 atm. and 60-80 °C.

1.1.3.3. O-Alkylation

When sodium salts of amidoximes which obtained from sodium alcoholate, treated with aliphatic halogen compounds, *O*-alkyl ethers are yield.

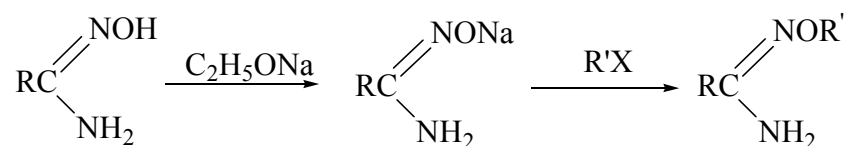


Figure 12: *O*-Alkylation of amidoximes

Instead of sodium ethoxide, potassium or sodium hydroxide in aqueous alcoholic solution can be used [29].

1.1.3.4. Acylation

Acylation of amidoximes can be achieved on both oxygen and the amino nitrogen atoms. In fact acylation always occurs on the oxygen, unless the hydroxyimino function is substituted. *O*-acylated amidoximes can be prepared by acid chlorides or anhydrides.

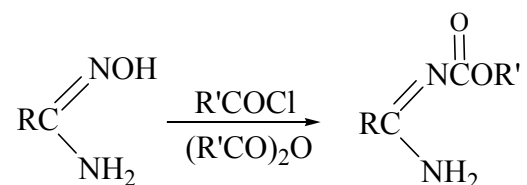


Figure 13: Acylation of amidoximes

Instead of acid anhydrides and chlorides, other reagents have been used, such as ketene, mixed carboxylic-carbonic anhydrides, carboxylic acid azides, and thioacetic acid [30].

O-Acylated amidoximes also have been prepared from acylated hydroximic acid chlorides and ammonia.

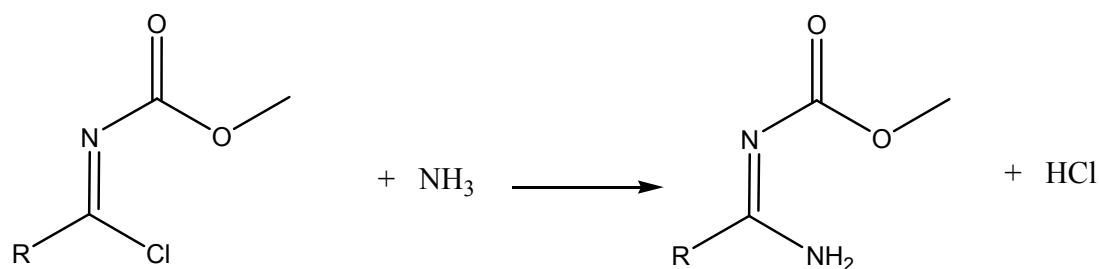


Figure 14: Reactions of acylated hydroximic acid chlorides with ammonia

N-Acylated amidoximes have been described by Ponzio and his collaborators who studied the acylation of two isomers α and β of 1-phenyl-2-aminoglyoxime corresponds to the structures I and II respectively. On acylation, the amidoxime group of the former is *N*-acylated, while the latter undergoes *O*-acylation. In order to prove this point, cyclization with aqueous alkali is performed, which leads to a furazan III in the first case and to an oxadiazole ring IV in the second [31, 32].

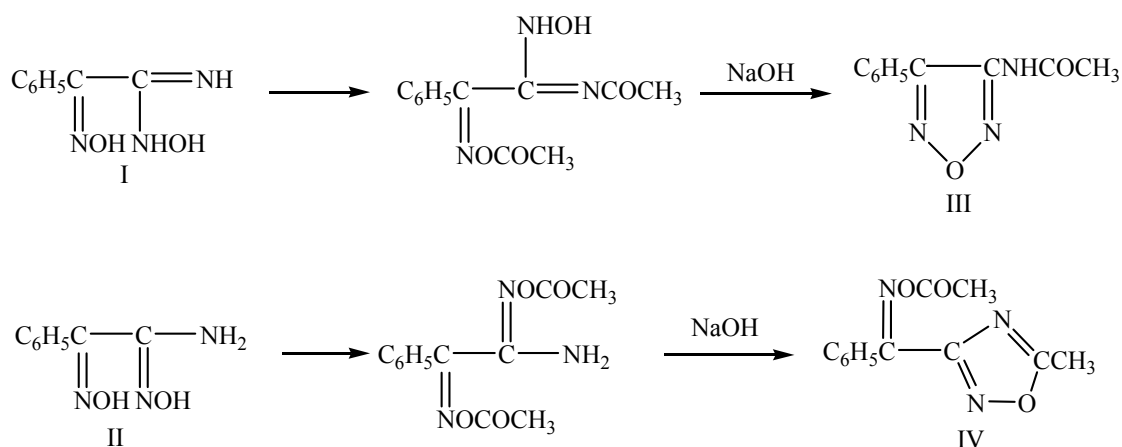


Figure 15: Cyclization with aqueous alkali

1.1.3.5. *N*-Substitution

1.1.3.5.1. Action of an Amine on Hydroximic Acid Halides

N-substituted amidoximes can be prepared by reaction of hydroximic acid chlorides with primary and secondary, aliphatic and aromatic amines. This is the usual way of preparing *N*-substituted amidoximes and the reaction is carried out in absolute ethanol or in ether at room temperature and an excess of amine is used to neutralize the hydroximic acid halide formed.

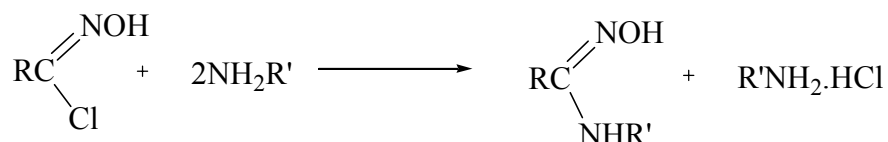


Figure 16: Action of an amine on hydroximic acid chloride

1.1.3.5.2. Action of Hydroxyl Amine on *N*-substituted Thioamides

The yields are less than in the case of unsubstituted thioamides [33, 34, 35].

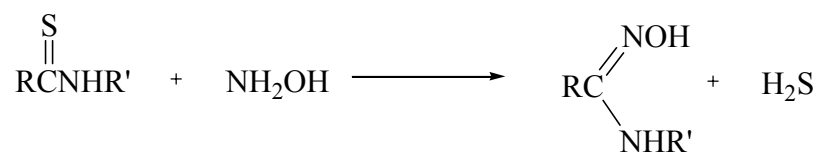


Figure 17: Action of hydroxyl amine on *N*-substituted thioamides

1.1.3.5.3. Action of Amines on Glyoxime Peroxides

N-substituted aminoglyoximes can be prepared by reacting amines with glyoxime peroxides [36-38].

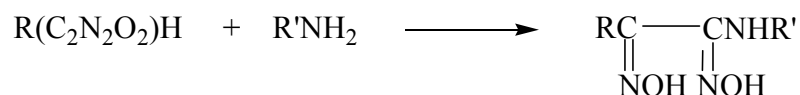


Figure 18: Action of amines on glyoxime peroxides

1.1.3.5.4. Action of Aniline on Amidoximes

The reaction of acetamidoxime and formamidoxime hydrochloride at 80-90 °C was resulted with the formation of the corresponding *N*-substituted amidoximes and the evolution of ammonia [39, 40].

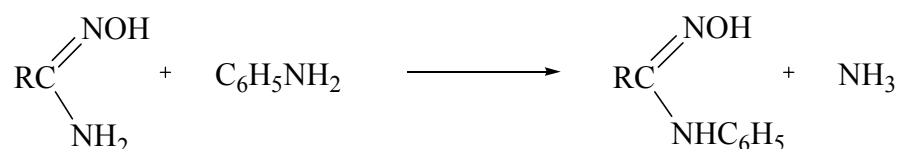


Figure 19: Action of aniline on amidoximes

1.2.3.5.5. Action of Isocyanates and Isothiocyanates

According to Tiemann [23] cyanic acid and phenyl isocyanate react with benzamidoxime to yield ureide or phenylureide oximes. In the case of *O*-alkyl amidoximes, isocyanates can evidently yield only ureide oximes [41-43].

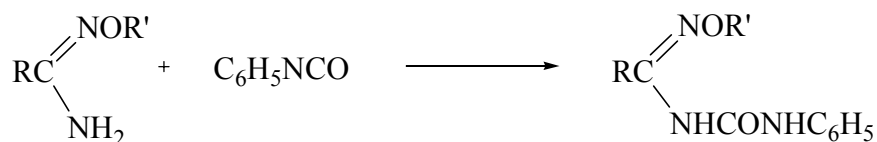


Figure 20: Action of isocyanates

Benzanilidoxime hydrochloride is reported to react with potassium cyanate [33]. The formula proposed for the reaction product is that of a ureide oxime but the compound is completely insoluble in alkali and therefore it is more probable that the correct structure is that of a carbamate.

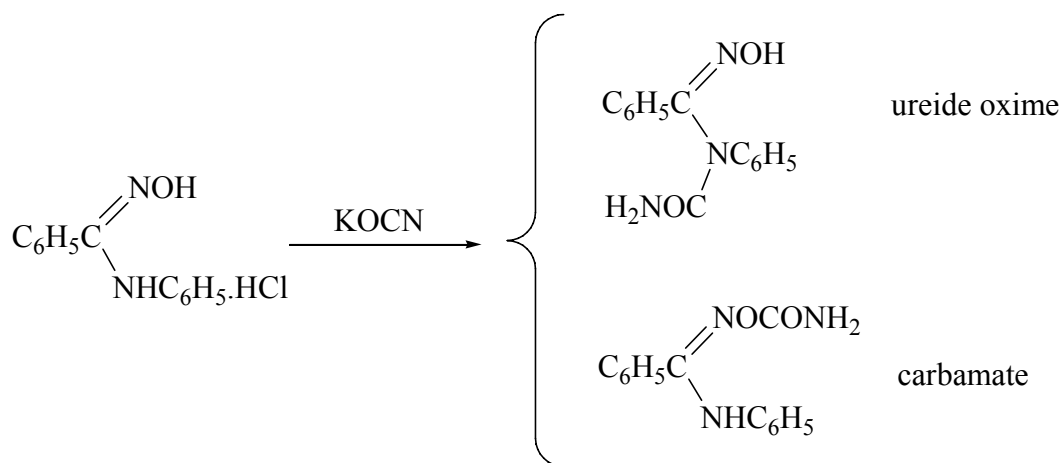


Figure 21: Action of potassium cyanates

When phenyl isothiocyanate and benzanilidoxime react in equimolar amounts and the reaction is carried out at room temperature, benzoylphenylthiourea oxime is formed [44, 45].

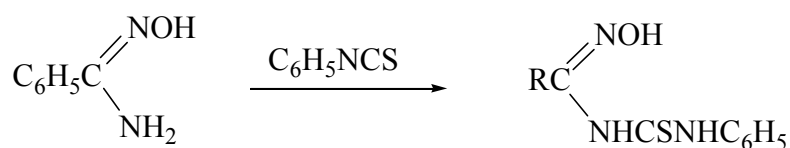


Figure 22: Action of isothiocyanates

1.2. BORONIC ACIDS

Boronic acids are boron containing organic compounds that possess one alkyl substituent (i.e., a C–B bond) and two hydroxyl groups. The sp^2 -hybridized boron atom possesses a vacant p orbital. These compounds are derived synthetically from primary sources of boron such as boric acid, H_3BO_3 which is made by the acidification of borax with carbondioxide.

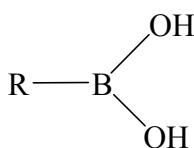


Figure 23: Structure of a boronic acid

1.2.1. Structure and Properties of Boronic Acids

Most boronic acids exist as white crystalline solids that can be handled in air without special precautions. The reactivity and properties of boronic acids is highly dependent on the nature of the carbon group (R) directly bonded to boron. Boronic acids are classified in subtypes such as alkyl-, alkenyl-, alkynyl-, and aryl- boronic acids.

When treated as an independent substituent, the prefix borono is employed to name the boronyl group. The five and six membered cyclic boronic esters are named as dioxaborolanes and dioxaborinanes. The corresponding nitrogen analogues are called diazaborolidines and diazaborinanes, and the mixed nitrogen-oxygen heterocycles are denoted by the prefix oxaza. Unsaturated heterocycles are named as boroles according to IUPAC RB-1-1 rules [46] for heterocycles.

Retting and Trother reported the X-ray crystal structure of phenylboronic acid in 1977 [47]. The crystals are orthorhombic and each asymmetric unit consists of two distinct molecules, bound through a pair of O—H···O hydrogen bonds. The benzene ring is coplanar with the CBO₂ plane.

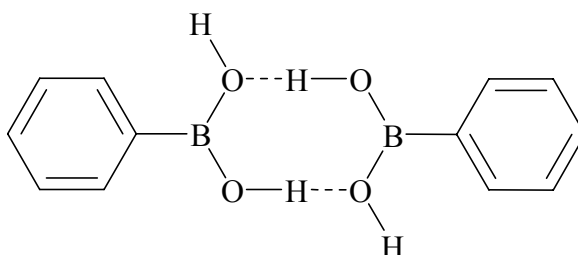


Figure 24: Dimeric unit showing hydrogen bonding

Despite the presence of two hydroxyl groups, the acidic character of most boronic acids is not that of a Bronsted acid, but usually that of a Lewis acid.

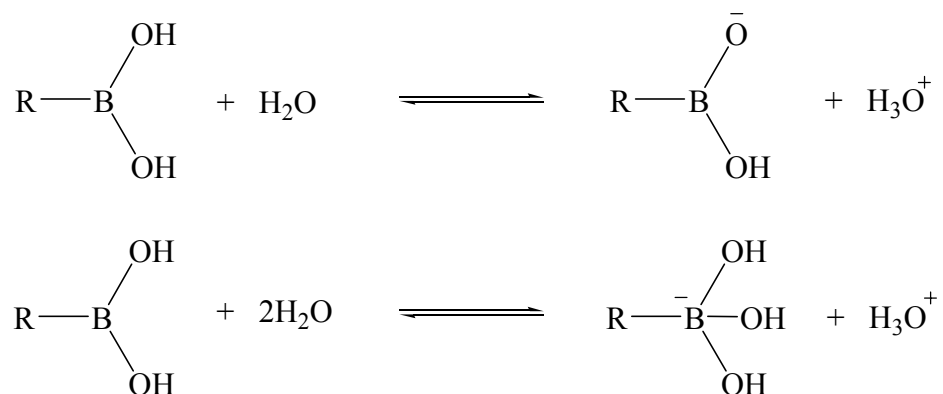


Figure 25: Ionization equilibrium of boronic acids in water.

The acidic character of boronic acids in water had been measured by electrochemical methods [48, 49]. Phenylboronic acid with a pKa of 8.8 in water [50] has a comparable acidity to a phenol. It is slightly more acidic than boric acid (pKa = 9.2).

1.2.2. Synthesis of Boronic Acids

Aryl boronic acids can be synthesized by the reaction of a hard organometallic intermediate (i.e., lithium or magnesium) with a borate ester at low temperature.

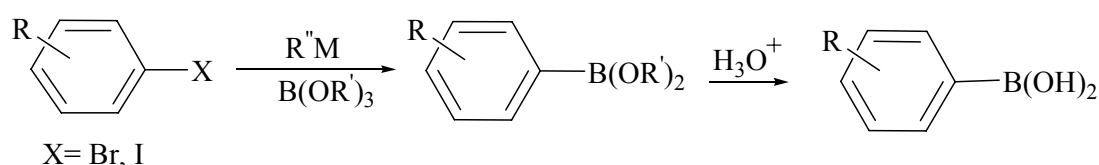


Figure 26: Synthesis of boronic acids

Johnson and co-workers developed the first practical and popular method for preparing phenylboronic acid and other arylboronic acids in which phenylmagnesium bromide is added to a solution of tri-n-butylborate at -70 °C [51]. Another methods are the transmetallation of aryl silanes and stannanes [52] and direct boronylation by transition metal catalyzed aromatic C–H functionalization [53].

Alkenylboronic acids and alkynylboronic acids can be synthesized in a similar way to arylboronic acids from alkenyl- and alkynylmetal species respectively [54, 55].

Alkylboronic acids can be synthesized from the trapping of organomagnesium and organolithium intermediates with borates. For example, methylboronic acid esters are made using the condensation of methyllithium and triisopropylborate [56].

1.2.3. Overview of the Reactions of Boronic Acid Derivatives

1.2.3.1. Oxidation

In 1930, A.D. Ainley and F. Challaenger was first reported the oxidation of arylboronic acids and esters with alkaline hydrogen peroxide to produce the corresponding phenols [57].

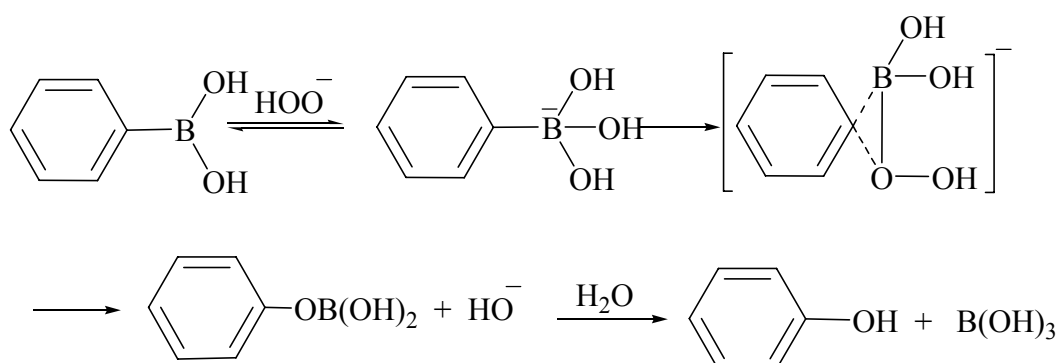


Figure 27: Oxidation of phenylboronic acid

The oxidation of alkyl- and alkenyl- boronic acid derivatives leads to alcohols or aldehydes and ketones respectively [58-60].

1.2.3.2. Amination

Aryl azides can be accessed from arylboronic acids via *in situ* generated aryllead intermediates [61].

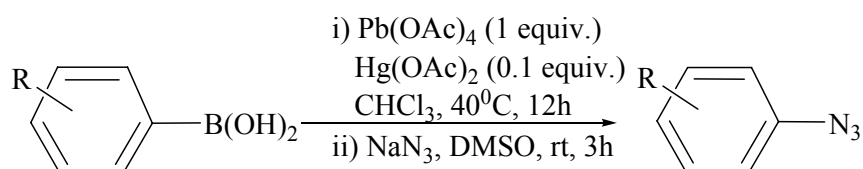


Figure 28: Oxidative amination of boronic acid derivatives

1.2.3.3. Halogenation

N-bromo and *N*-iodosuccinimides convert arylboronic acids into the corresponding aryl halides in good yields. Cuprous chloride and bromide provide the corresponding *ipso*-substituted phenyl halides from phenylboronic acid [57].

The use of 1,3-dibromo-5,5-dimethylhydantoin (DMDMH) under catalysis by sodium methoxide was shown to be an efficient bromo deboronation method for arylboronic acids when acetonitrile is used as solvent [62].

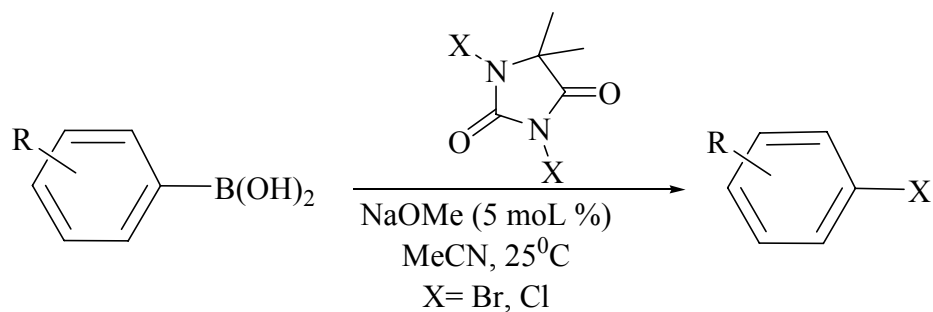


Figure 29: Halogenation of arylboronic acids

1.2.3.4. Suzuki Coupling

In 1979 Miyaura and Suzuki reported that a Pd(0)-catalyzed coupling between alkenyl boranes and aryl halide, in the presence of a base provide arylated alkene products in high yields [63].

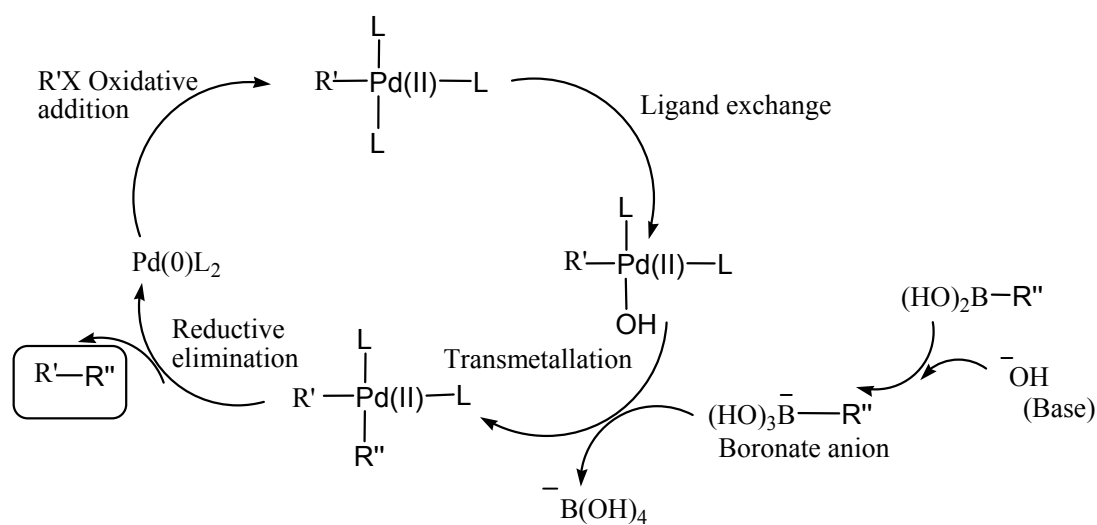


Figure 30: Mechanism for the Suzuki cross-coupling reaction

1.3. 1,2,4,5-OXADIAZABOROLES

The 1,2,4,5-oxadiazaborole heterocycles can be synthesized by the cyclodehydration reactions of amidoximes with a boronic acid with a general formula RB(OH)_2 in a hydrocarbon solvent like xylene or toluene by removing the formed water.

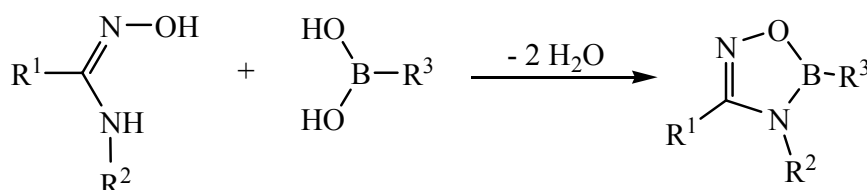


Figure 31: Synthesis of the 3,4,5-Trisubstituted-4,5-dihydro-1,2,4,5-oxadiazaborole heterocycles

The oxadiazaborole heterocycles have central depressant activity and are useful in psychotherapy. They are also cardioactive and are useful as hypotensive agents [64].

The crystal and molecular structural studies of oxadiazaborole heterocycles was first studied by Eric S. Raper [65] for 3-methyl-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole in 1978. The structure was determined from X-Ray data by direct methods. Both rings in the molecule are planar and dihedral angle between them is 4.5° . Bond lengths, as well as bond order calculations, show that all bonds in the heterocyclic ring have significant π characters. The B–N, B–O and C–N distances are all significantly shorter than those reported by Retting and Trotter for saturated, five membered, oxazaborolidine rings thus confirming the aromatic character of this oxadiazaborole system. The extensive delocalization of the $p\pi$ electrons in the

oxadiazaborole moiety may be rationalized in terms of the canonical forms shown in figure. The largest contributor is expected to be form I.

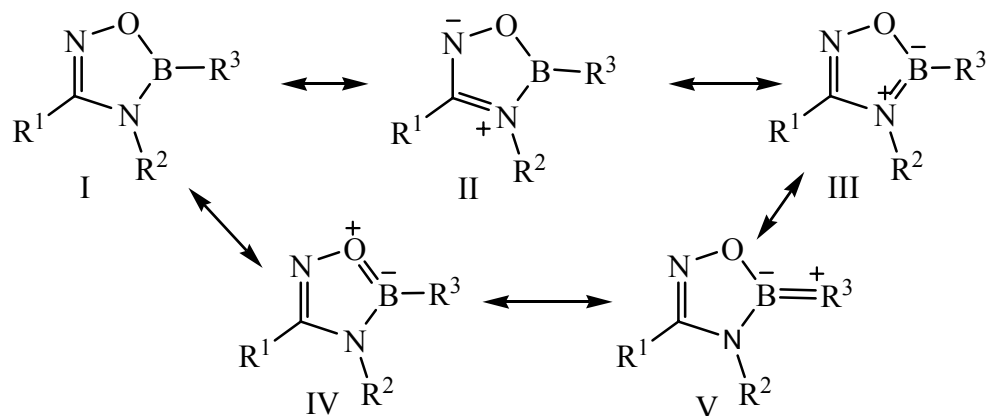


Figure 32: Canonical forms of the molecule

The molecules are linked by N-H-----N hydrogen bonds to form extended chains.

CHAPTER II

EXPERIMENTAL

Aldehydes, nitriles, *N*-chlorosuccinimide and primary amines were purchased from Merck and Fluka. Phenylboronic acid was purchased from Aldrich. ^1H and ^{13}C -NMR spectra were recorded on BRUKER and VARIAN spectrometers (300 and 400 MHz for ^1H ; 75 and 100 MHz for ^{13}C). IR spectra were recorded on a JASCO 430 FT/IR instrument (KBr pellet). Mass spectra were run on Agilent GC 6890 instrument with MS 5975 mass detector. Melting points were determined on a Meltemp apparatus and uncorrected. Flash column chromatography was performed on Silica Gel (Merck, 230-400 Mesh ASTM). TLC was done using precoated plates with fluorescent indicator (Merck 5735). The stain solutions of permanganate, *p*-anisaldehyde and iodine were used for visualization of the TLC spots.

Thiophene-2-carboxaldehyde oxime (4):

To a solution of thiophene-2-carbaldehyde (**1**) (5.00 g, 45.0 mmol) in 20 ml of ethanol, a mixture of $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ (12.5 g, 90.0 mmol) and $\text{NH}_2\text{OH} \cdot \text{HCl}$ (6.25 g, 90.0 mmol) prepared by dissolving separately in a minimum amount of water was added and the mixture was heated under reflux for 5h. Ethanol was evaporated under the reduced pressure, then crude product was filtered, and crystallized from 30% ethanol-water mixture as light yellow needles.

Yield: 4.4 g, 77%

M.p. : 130-132 $^{\circ}\text{C}$ (Lit⁶⁶: 130-133 $^{\circ}\text{C}$)

Rf : 0.76 (Eluant: Hexane:Ethyl acetate; 4:1)

IR (KBr, ν : cm^{-1}): 3126 and 2836 (broad, NOH, H-bonded), 1631 (C=N)

Thiophene-2-hydroximoyl chloride (7):

To a stirred solution of thiophene-2-carbaldehyde oxime (**4**) (3.00 g, 24.0 mmol) in *N,N*-dimethyl formamide (DMF) (15 mL) at room temperature, *N*-chlorosuccinimide (6.30 g, 48.0 mmol) was added in portions over 15 min. The reaction mixture was stirred for 2 days. The solution was poured into ice-water (60 mL) mixture and extracted with diethyl ether (2x50 mL), washed with brine and dried over anhydrous sodium sulphate, Na_2SO_4 , and finally evaporated under reduced pressure to give the thiophene-2-hydroximoyl chloride (**7**). The product was used without further purification to obtain the *N*-substituted thiophene-2-carboxamidoximes.

Yield: 3.2 g, 85%

M.p. : 99-102 $^{\circ}\text{C}$ (Lit⁶⁷: 102 $^{\circ}\text{C}$)

Rf : 0.72 (Eluant: Hexane:Ethyl acetate; 4:1)

IR (KBr, ν : cm^{-1}): 3197 and 2985 broad, (NOH), 1597 (C=N)

Furan-2-carbaldehyde oxime (5):

To a solution of furan-2-carbaldehyde (**2**) (5.00 g, 52.0 mmol) in 20 ml of ethanol, a mixture of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (6.94 g, 100 mmol) and $\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ (13.9 g, 100 mmol) prepared by dissolving separately in a minimum amount of water was added and the mixture was heated under reflux for 5h. Ethanol was evaporated under

the reduced pressure, then crude product was filtered, and crystallized from 30% ethanol-water mixture as light yellow needles.

Yield: 3.4 g, 60%

M.p. : 86-88 °C

R_f : 0.67 (Eluant: Hexane:Ethyl acetate; 4:1)

IR (KBr, ν : cm⁻¹): 3164 and 2862 (broad, NOH, H-bonded), 1644 (C=N)

Furan-2-hydroximoyl chloride (8):

To a stirred solution of furan-2-carbaldehyde oxime (**5**) (2.00 g, 18.0 mmol) in *N,N*-dimethyl formamide (15 mL) at room temperature, *N*-chlorosuccinimide (4.80 g, 36.0 mmol) was added in portions over 15 min. The reaction mixture was stirred for 2 days. The solution was poured into ice-water (60 mL) mixture and extracted with diethyl ether (2x50 mL), washed with brine and dried over anhydrous Na₂SO₄ and finally evaporated under reduced pressure to give the furan-2-hydroximoyl chloride (**8**). The product was used without further purification to obtain the *N*-substituted furan-2-carboxamidoximes.

Yield: quantitative

M.p. : oily

R_f : 0.68 (Eluant: Hexane:Ethyl acetate; 4:1)

IR (KBr, ν : cm⁻¹): 3236 and 3132 broad, (NOH), 1654 (C=N)

***p*-Nitrobenzaldehyde oxime (6) :**

To a solution of *p*-nitrobenzaldehyde (**3**) (2.00 g, 13.2 mmol) in 20 ml of ethanol, a mixture of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1.84 g, 26.4 mmol) and $\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ (3.66 g, 26.4 mmol) prepared by dissolving separately in a minimum amount of water was added and the mixture was heated under reflux for 5h. Ethanol was evaporated under the reduced pressure, crude product was filtered, and crystallized from 30% ethanol-water mixture as light yellow crystals.

Yield: 1.98 g, 90%

M.p. : 182-184 °C

R_f : 0.81 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, ν : cm^{-1}): 3296 (broad, NOH, H-bonded, 1605 (C=N)

***p*-Nitrobenzonitrile (9i) :**

The mixture of *p*-nitrobenzaldehyde oxime (**6**) (1.50 g, 9.00 mmol) and phthalic anhydride (1.60 g, 0.11 mmol) in a beaker was heated in a sand bath at about 150 – 160 °C for ten minutes. After dehydration of all *p*-nitrobenzaldehyde, the crude product was dissolved in dichloromethane and 30 mL 5 % NH_3 solution was added. The mixture was extracted, washed with water and brine solution and dried with anhydrous Na_2SO_4 . After evaporation of the solvent under the reduced pressure yellow product was get.

Yield: 0.80 g, 61 %

M.p. : 146-147 °C

R_f : (Eluant: Hexane:Ethyl acetate; 2:1)

IR (KBr, ν : cm⁻¹): 2234 (C $\equiv$ N)

Benzamidoxime (10b):

To a solution of benzonitrile (**9b**) (3.82 g, 37.0 mmol) and triethylamine, Et₃N (101 g, 56.7 mmol) in 100 mL ethanol, NH₂OH.HCl (4.05 g, 56.7 mmol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with anhydrous Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was crystallized from benzene.

Yield: 3 g, 60 %

M.p. : 72-74 °C

R_f : 0.57 (Eluant: Hexane:Ethyl acetate; 2:1)

IR (KBr, ν : cm⁻¹): 3452 (N-H), 1648 (C=N)

***p*-Chlorobenzamidoxime (10e) :**

To a solution of *p*-Chlorobenzonitrile (**9e**) (2.77 g, 20.0 mmol) and Et₃N (4.08 g, 40.0 mmol) in 100 mL ethanol, NH₂OH.HCl (2.76 g, 40.0 mmol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude

product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 3.20 g, 94 %

M.p. : 130-132 °C

R_f : 0.60 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, v: cm⁻¹): 3451 (N–H), 1651 (C=N)

***p*-Iodobenzamidoxime (10g):**

To a solution of *p*-Iodobenzonitrile (**9g**) (0.61 g, 2.64 mmol) and Et₃N (0.53 g, 5.92 mmol) in 100 mL ethanol, NH₂OH.HCl (0.36 g, 5.92 mmol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 0.40 g, 60 %

M.p. : 148-150 °C

R_f : 0.56 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, v: cm⁻¹): 3481 (N–H), 1660 (C=N)

***p*-Aminobenzamidoxime (10h) :**

To a solution of *p*-aminobenzonitrile (**9h**) (1.00 g, 8.46 mmol) and Et₃N (1.58 g, 15.6 mmol) in 100 mL ethanol, NH₂OH.HCl (1.15 g, 169 mmol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 1.02 g, 80 %

M.p. : 156-157 °C

R_f : 0.20 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, ν: cm⁻¹): 3463 (N–H), 1652 (C=N)

***p*-Nitrobenzamidoxime (10i) :**

To a solution of *p*-nitrobenzonitrile (**9i**) (0.79 g, 5.36 mmol) and Et₃N (1.00 g, 11.0 mmol) in 100 mL ethanol, NH₂OH.HCl (0.70 g, 11.0mmol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 20 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with anhydrous Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 0.83 g, 86 %

M.p. : 148-150 °C

R_f : 0.71 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, ν : cm⁻¹): 3463 (N-H), 3184 (broad, NOH, H-bonded), 1661 (C=N)

***p*-N,N-dimethylaminobenzamidoxime (10j)**

To a solution of *p*-(N,N-dimethylamino)benzonitrile (**9j**) (1.00 g, 6.84 mmol) and Et₃N (1.38 g, 13.6 mmol) in 100 mL ethanol, NH₂OH.HCl (0.95 g, 13.6 mmol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with anhydrous Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 0.95 g, 78 %

M.p. : 153-154 °C

R_f : 0.15 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, ν : cm⁻¹): 3497 (N-H), 3234 (broad, NOH, H-bonded), 1655 (C=N)

Pyridine-2-carboxamidoxime (10k):

To a solution of pyridine-2-carbonitrile (**9k**) (0.68 g, 0.006 mol) and Et₃N (1.32 g, 0.013 mol) in 100 mL ethanol, NH₂OH.HCl (0.89 g, 0.013 mol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude

product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 0.60 g, 66 %

M.p. : 114-116 °C

R_f : 0.34 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, v: cm⁻¹): 3466 (N-H), 1647 (C=N)

Pyridine-3-carboxamidoxime (10l):

To a solution of pyridine-3-carbonitrile (**9l**) (1.01 g, 0.009 mol) and Et₃N (1.96 g, 0.01 mol) in 100 mL ethanol, NH₂OH.HCl (1.33 g, 0.01 mol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 0.24 g, 20 %

M.p. : 127-128 °C

R_f : 0.16 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, v: cm⁻¹): 3420 (N-H), 1646 (C=N)

Pyridine-4-carboxamidoxime (10m)

To a solution of pyridine-4-carbonitrile (**9m**) (2.20 g, 0.02 mol) and triethylamine, Et₃N (4.228 g, 0.04 mol) in 100 mL ethanol, NH₂OH.HCl (2.90 g, 0.04 mol) was added slowly by stirring until all NH₂OH.HCl was dissolved. The mixture was stirred under reflux for 24 hours. Solvent was evaporated under the reduced pressure and the crude product was extracted with ethyl acetate:water (25mL:25mL)x4. Combined organics was washed with brine solution and dried with Na₂SO₄. Solvent was evaporated under the reduced pressure and the product was used without purification to obtain oxadiazaboroles.

Yield: 1.25 g, 45 %

M.p. :198-199.5 °C

R_f : 0.08 (Eluant: Hexane:Ethyl acetate; 1:2)

IR (KBr, ν: cm⁻¹): 3348 (N–H), 1647 (C=N)

***N*-Phenylthiophene-2-carboxamidoxime (11o):**

To a solution of thiophene-2-hydroximoyl chloride (**7**) (0.98 g, 6.06 mmol) in chloroform (20 mL) was added dropwise aniline (1.13 g, 12.1 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate; 1:3) to give *N*-Phenylthiophene-2-carboxamidoxime (**11o**).

Yield: 0.78 g, 65 %

M.p. : 131-133 °C

R_f : 0.42 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm^{-1}): 3368 (N–H), 3204–3099 (broad, NOH), 1630 (C=N)

N-p-Tolylthiophene-2-carboxamidoxime (11p):

To a solution of thiophene-2-hydroximoyl chloride (**7**) (0.90 g, 5.57 mmol) in chloroform (20 mL) was added dropwise *p*-toluidine (1.20 g, 11.0 mol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate;1:3) to give *N-p*-Tolylthiophene-2-carboxamidoxime (**11p**).

Yield: 0.72 g, 60 %

M.p. : 154-156 °C

R_f : 0.54 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm^{-1}): 3360 (N–H), 3163–3101 (broad, NOH), 1629 (C=N)

N-(p-Methoxyphenyl)thiophene-2-carboxamidoxime (11q):

To a solution of thiophene-2-hydroximoyl chloride (**7**) (1.00 g, 6.19 mmol) in chloroform (20 mL) was added dropwise *p*-methoxy aniline (1.48 g, 12.0 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate;1:3) to give *N-(p*-Methoxyphenyl)thiophene-2-carboxamidoxime (**11q**).

Yield: 0.96 g, 65 %

M.p. : 180-183 °C

R_f : 0.15 (Eluant: Hexane:Ethyl acetate; 3:2)

IR (KBr, ν : cm⁻¹): 3342 (N-H), 3200–3106 (broad, NOH), 1631 (C=N)

***N*-(*p*-Chlorophenyl)thiophene-2-carboxamidoxime (11r):**

To a solution of thiophene-2-hydroximoyl chloride (**7**) (0.96 g, 5.97 mmol) in chloroform (20 mL) was added dropwise *p*-chloro aniline (1.53 g, 12.0 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate;1:3) to give *N*-(*p*-Chlorophenyl)thiophene-2-carboxamidoxime (**11r**).

Yield: 1.10 g, 73 %

M.p. : 97-99 °C

R_f : 0.50 (Eluant: Hexane:Ethyl acetate; 3: 2)

IR (KBr, ν : cm⁻¹): 3382 (N-H), 3215 (broad, NOH), 1626 (C=N)

***N*-(*p*-Bromophenyl)thiophene-2-carboxamidoxime (11s):**

To a solution of thiophene-2-hydroximoyl chloride (**7**) (1.00 g, 6.19 mmol) in chloroform (20 mL) was added dropwise *p*-bromo aniline (2.13 g, 12.4 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography

(eluant: hexane:ethyl acetate;1:3) to give *N*-(*p*-Bromophenyl)thiophene-2-carboxamidoxime (**11s**).

Yield: 1.54 g, 84 %

M.p. : 143-145 °C

R_f : 0.61 (Eluant: Hexane:Ethyl acetate; 3:2)

IR (KBr, ν : cm⁻¹): 3387 (N–H), 3235 (broad, NOH), 1630 (C=N)

***N*-(*p*-Iodophenyl)thiophene-2-carboxamidoxime (**11t**):**

To a solution of thiophene-2-hydroximoyl chloride (**7**) (0.63 g, 3.89 mmol) in chloroform (20 mL) was added dropwise *p*-iodo aniline (1.70 g, 7.78 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate;1:3) to give *N*-(*p*-Iodophenyl)thiophene-2-carboxamidoxime (**11t**).

Yield: 0.69 g, 50 %

M.p. : 141-144 °C

R_f : 0.50 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm⁻¹): 3394 (N–H), 3217 (broad, NOH), 1636 (C=N)

***N*-(1-Naphthyl)thiophene-2-carboxamidoxime (**11u**):**

To a solution of thiophene-2-hydroximoyl chloride (**7**) (1.00 g, 6.19 mmol) in chloroform (20 mL) was added dropwise 1-naphthyl amine (1.77 g, 12.0 mmol) in

chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate;1:3) to give *N*-(1-Naphthyl)thiophene-2-carboxamidoxime (**11u**).

Yield: 0.39 g, 65 %

M.p. : 168-170 °C

R_f : 0.44 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm⁻¹): 3381 (N-H), 3224-3103 (broad, NOH), 1632 (C=N)

***N*-Phenylfuran-2-carboxamidoxime (12o):**

To a solution of furan-2-hydroximoyl chloride (**8**) (0.86 g, 5.91 mmol) in chloroform (20 mL) was added dropwise aniline (1.12 g, 12.0 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N*-phenylfuran-2-carboxamidoxime (**12o**).

Yield: 0.24 g, 20 %

M.p. : 147-149 °C

R_f : 0.29 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm⁻¹): 3384 (N-H), 3119-2945 (broad NOH), 1627 (C=N)

N-p-Tolylfuran-2-carboxamidoxime (12p):

To a solution of furan-2-hydroximoyl chloride (**8**) (0.85 g, 5.84 mmol) in chloroform (20 mL) was added dropwise *p*-toluidine (1.25 g, 11.6 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N-p*-Tolylfuran-2-carboxamidoxime (**12p**).

Yield: 0.48 g, 40 %

M.p. : 157-159 °C

R_f : 0.23 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm⁻¹): 3384 (N-H), 3089-2970 (broad, NOH), 1624 (C=N)

N-(p-Methoxyphenyl)furan-2-carboxamidoxime (12q):

To a solution of furan-2-hydroximoyl chloride (**8**) (0.87 g, 5.98 mmol) in chloroform (20 mL) was added dropwise *p*-methoxy aniline (1.25 g, 12.0 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N*-(*p*-methoxyphenyl)furan-2-carboxamidoxime (**12q**).

Yield: 0.31 g, 22%

M.p. : 141-143 °C

R_f : 0.32 (Eluant: Hexane:Ethyl acetate; 3:2)

IR (KBr, ν : cm⁻¹): 3363 (N-H), 3191-3155 (broad, NOH), 1641 (C=N)

***N*-(*p*-Chlorophenyl)furan-2-carboxamidoxime (12r):**

To a solution of furan-2-hydroximoyl chloride (**8**) (0.90 g, 6.18 mmol) in chloroform (20 mL) was added dropwise *p*-chloro aniline (1.57 g, 12.0 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N*-(*p*-chlorophenyl)furan-2-carboxamidoxime (**12r**).

Yield: 0.40 g, 30 %

M.p. : 142-144 °C

R_f : 0.29 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm⁻¹): 3382 (N-H), 3127-3094 (broad, NOH), 1622 (C=N)

***N*-(*p*-Bromophenyl)furan-2-carboxamidoxime (12s):**

To a solution of furan-2-hydroximoyl chloride (**8**) (0.85 g, 5.84 mmol) in chloroform (20 mL) was added dropwise *p*-bromo aniline (2.01 g, 11.7 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N*-(*p*-bromophenyl)furan-2-carboxamidoxime (**12s**).

Yield: 0.73 g, 44 %

M.p. : 163-164 °C

R_f : 0.66 (Eluant: Hexane:Ethyl acetate; 3 :1)

IR (KBr, ν : cm⁻¹): 3382 (N-H), 3087-2970 (broad, NOH), 1625 (C=N)

***N*-(*p*-Iodophenyl)furan-2-carboxamidoxime (**12t**):**

To a solution of furan-2-hydroximoyl chloride (**8**) (0.85 g, 5.84 mmol) in chloroform (20 mL) was added dropwise *p*-iodo aniline (2.56 g, 11.6 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N*-(*p*-iodophenyl)furan-2-carboxamidoxime (**12t**).

Yield: 0.50 g, 26 %

M.p. : 165-167 °C

R_f : 0.58 (Eluant: Hexane:Ethyl acetate; 3:1)

IR (KBr, ν : cm⁻¹): 3385 (N–H), 3082-2962 (broad, NOH), 1627 (C=N)

***N*-(1-Naphthyl) furan-2-carboxamidoxime (**12u**):**

To a solution of furan-2-hydroximoyl chloride (**8**) (0.90 g, 6.18 mmol) in chloroform (20 mL) was added dropwise 1-naphthyl amine (1.57 g, 12.0 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under the reduced pressure. The impure product was crystallized from hexane:ethyl acetate (3:1) to give *N*-(1-naphthyl)furan-2-carboxamidoxime (**12u**).

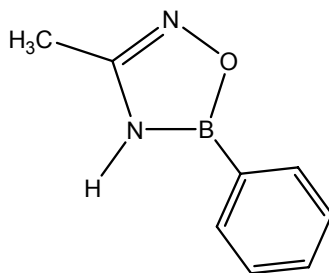
Yield: 0.40 g, 30%

M.p. : 128-129 °C

R_f : 0.49 (Eluant: Hexane:Ethyl acetate; 3:2)

IR (KBr, ν : cm⁻¹): 3365 (N–H), 3143 (broad, NOH), 1636 (C=N)

3-methyl-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16a):



A mixture of acetamidoxime (**10a**) (100 mg, 1.35 mmol) and phenylboronic acid (164 mg, 1.35 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-petroleum ether mixture.

Yield : 233 mg (85 %)

M.p : 163-165 °C

Rf : 0.02 (Eluant: Hexane:Ethyl acetate; 2:1)

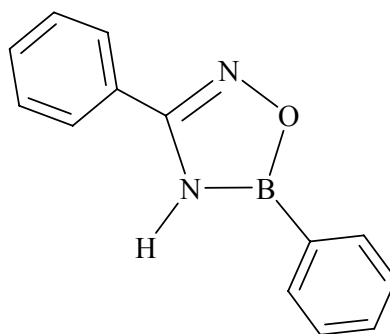
IR (KBr, ν : cm^{-1}): 3195 (N-H), 1605 (C=N), 1421 (B-N), 834, 697

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 8.92 (1H, s N-H), 7.63-7.61 (2H, d, J =7.6 Hz), 7.27-7.1 (3H, m), 2.13 (3H, s)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 158.28, 134.03, 130.94, 128.20, 11.77

MS (m/z , %): 160 (M^+ , 100), 119 (16), 104 (8), 91 (8), 77 (24), 51 (8).

3,5-diphenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16b):



A mixture of benzamidoxime (**10b**) (136 mg, 1.0 mmol) and phenylboronic acid (130 mg, 1.0 mmol) in benzene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane.

Yield : 128 mg (65 %)

M.p : 154-156 °C

Rf : 0.24 (Eluant: Hexane:Ethyl acetate; 1:2)

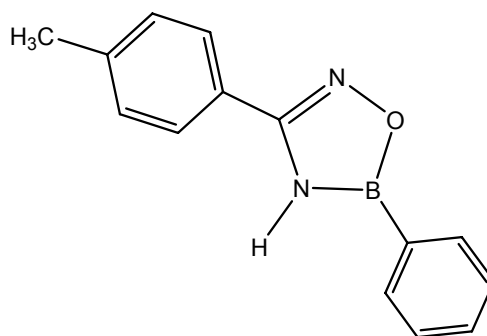
IR (KBr, ν : cm^{-1}): 3423, 3388 (N-H), 3045, 1603 (C=N), 1419 (B-N), 1202, 1071, 692

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz) : 9.55 (1H, s), 7.32-7.84 (10H, m)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz) : 159.88, 134.28, 133.61, 130.67, 129.26, 128.50, 127.60, 126.55, 125.66

MS (m/z , %): 222 (M^+ , 100), 118 (39), 104 (13), 91 (14), 77 (18), 51 (9).

5-phenyl-3-*p*-tolyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16c):



A mixture of *p*-toluenecarboxamidoxime (**10c**) (200 mg, 1.33 mmol) and phenylboronic acid (162 mg, 1.33 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 166 mg (54 %)

M.p : 154-156 °C

Rf : 0.32 (Eluant: Hexane:Ethyl acetate; 1:2)

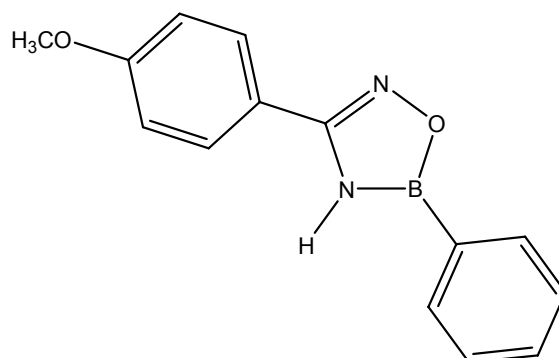
IR (KBr, ν : cm^{-1}): 3391 (N–H), 1601 (C=N), 1439(B–N), 1200, 1070

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 9.47 (1H, s, NH), 7.79-7.77 (2H, dd, J = 5 Hz), 7.69-7.65 (2H, d, J = 6 Hz), 7.29-7.21 (3H, m), 7.08-7.05 (2H, d, J = 9.4 Hz), 2.21 (3H, s)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 160.00, 140.91, 134.28, 131.04, 129.55, 128.19, 126.62, 124.301, 21.59

MS (m/z , %): 236 (M^+ , 100), 132 (31), 118 (15), 104 (8), 91 (15), 77 (8).

3-(*p*-methoxyphenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16d):



A mixture of *p*-methoxyphenyl carboxamidoxime (**10d**) (212 mg, 1.27 mmol) and phenylboronic acid (155 mg, 1.27 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 190 mg (60 %)

M.p : 182-184 °C

Rf : 0.43 (Eluant: Hexane:Ethyl acetate; 1:2)

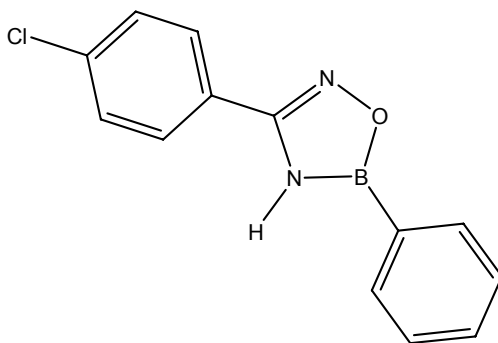
IR (KBr, ν : cm^{-1}): 3208 (N–H), 1613 (C=N), 1437(B–N), 1254, 1180, 1024

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 9.25 (1H, s, NH), 7.95-7.87 (4H, m), 7.48- 7.35 (3H, m), 6.98-6.95 (2H, d, $J = 9$ Hz), 3.92 (3H, s)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 159.88, 159.65, 134.31, 131.08, 128.28, 128.25, 119.64, 114.30, 55.56

MS (m/z , %): 252 (M^+ , 100), 148 (51), 133 (75), 105 (16), 90 (5), 77 (14), 63 (5), 51 (7).

3-(*p*-chlorophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16e):



A mixture of *p*-chlorobenzamidoxime (**10e**) (200 mg, 1.17 mmol) and phenylboronic acid (143 mg, 1.17 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from toluene.

Yield : 143 mg (96 %)

M.p : 214-216 °C

Rf : 0.70 (Eluant: PB:Ethyl acetate; 1:2)

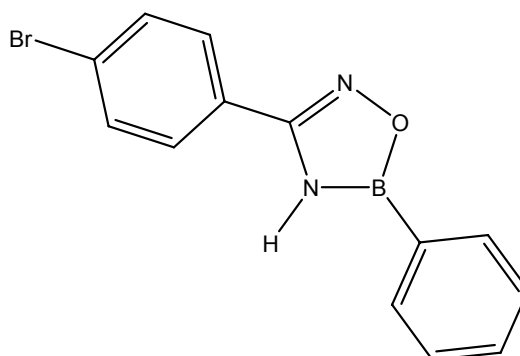
IR (KBr, ν : cm^{-1}): 3391 (N–H), 1602 (C=N), 1446(B–N), 1097

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 9.81 (1H, s, NH), 7.96-7.94 (4H, d, J = 8.5 Hz), 7.50-7.40 (5H, m)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 159.11, 136.55, 134.25, 131.14, 129.08, 128.21, 128.1, 125.84

MS (m/z , %): 256(M^+ , 100), 152 (76), 138 (11), 125 (24), 111 (11), 90 (11), 77 (14), 51 (11).

3-(*p*-bromophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16f):



A mixture of *p*-bromobenzamidoxime (**10f**) (303 mg, 1.41 mmol) and phenylboronic acid (172 mg, 1.41 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethylacetate mixture.

Yield : 278 mg (66 %)

M.p : 217-219 °C

R_f : 0.82 (Eluant: Hexane:Ethyl acetate; 1:2)

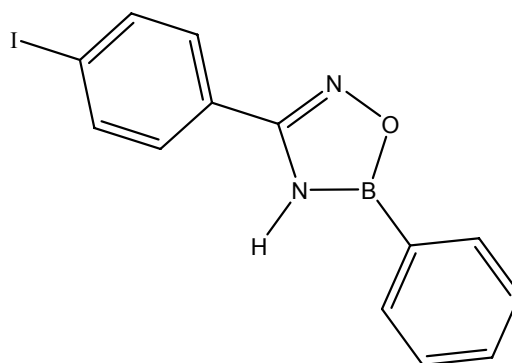
IR (KBr, ν: cm⁻¹): 3338 (N–H), 1600 (C=N), 1439(B–N), 1199

¹H NMR, δ_H (CDCl₃+DMSO-d₆, 300 MHz): 9.88 (1H, s, NH), 7.96-7.85 (4H, m), 7.63-7.55 (2H, m), 7.52-7.41 (3H, m)

¹³C NMR, δ_C (CDCl₃+DMSO-d₆, 75 MHz): 159.14, 134.21, 131.99, 131.10, 128.28, 128.17, 126.28, 124.87

MS (m/z, %): 302 (M⁺, 100), 196 (44), 117 (9), 102 (9), 90 (24), 77 (16), 51 (9).

3-(*p*-iodophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16g):



A mixture of *p*-iodobenzamidoxime (**10g**) (200 mg, 0.76 mmol) and phenylboronic acid (93 mg, 0.76 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-petroleum ether mixture.

Yield : 150 mg (60 %)

M.p : 219-221 °C

R_f : 0.70 (Eluant: Hexane:Ethyl acetate; 1:2)

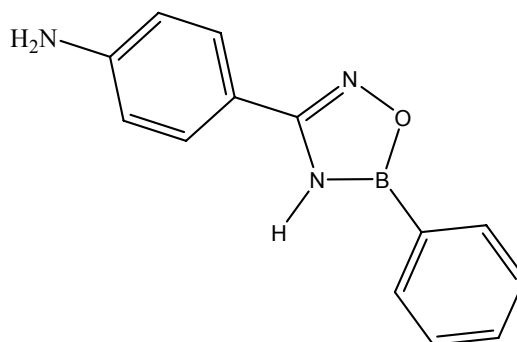
IR (KBr, ν: cm⁻¹): 3383 (N–H), 1599 (C=N), 1440(B–N)

¹H NMR, δ_H (CDCl₃+DMSO-d₆, 300 MHz): 9.81 (1H, s, NH), 7.94 (2H, d, *J* = 7.3 Hz), 7.82 (2H, d, *J* = 8.2 Hz), 7.74 (2H, d, *J* = 7.9 Hz), 7.49-7.41 (3H, m)

¹³C NMR, δ_C (CDCl₃+DMSO-d₆, 75 MHz): 159.30, 137.97, 134.26, 131.14, 128.33, 128.21, 126.82, 97.04

MS (m/z, %): 348 (M⁺, 100), 244 (21), 174 (5), 117 (8), 90 (17), 77 (8).

3-(*p*-aminophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16h):



A mixture of *p*-aminobenzamidoxime (**10h**) (150 mg, 1.0 mmol) and phenylboronic acid (121 mg, 1.0 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from toluene.

Yield : 152 mg (65 %)

M.p : 156-158 °C

Rf : 0.42 (Eluant: Hexane:Ethyl acetate; 1:2)

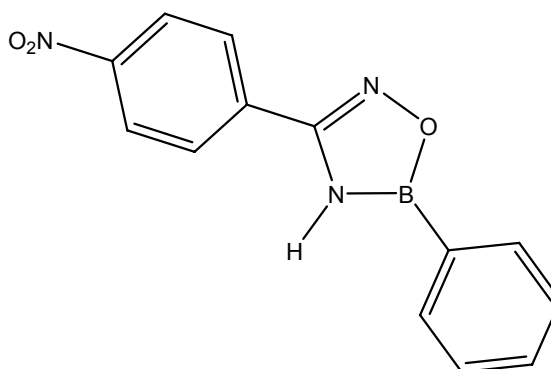
IR (KBr, ν : cm^{-1}): 3400 (NH_2), 3319 (N–H), 1607 (C=N), 1445(B–N), 1441, 1276

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 9.35 (1H, s, NH), 7.94 (2H, dd, J = 6.8 Hz), 7.73 (2H, d, J = 8.2 Hz), 7.48-7.40 (3H, m), 6.73 (2H, d, J = 8 Hz), 4.34 (2H, s, NH_2)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 160.03, 149.48, 134.25, 130.93, 128.16, 128.13, 116.16, 114.60

MS (m/z , %): 237 (M^+ , 100), 133 (65), 118 (11), 106 (18).

3-(*p*-nitrophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16i):



A mixture of *p*-nitrobenzamidoxime (**10i**) (250 mg, 1.38 mmol) and phenylboronic acid (168 mg, 1.38 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from toluene.

Yield : 198 mg (54 %)

M.p : 228-230 °C

Rf : 0.74 (Eluant: Hexane:Ethyl acetate; 1:2)

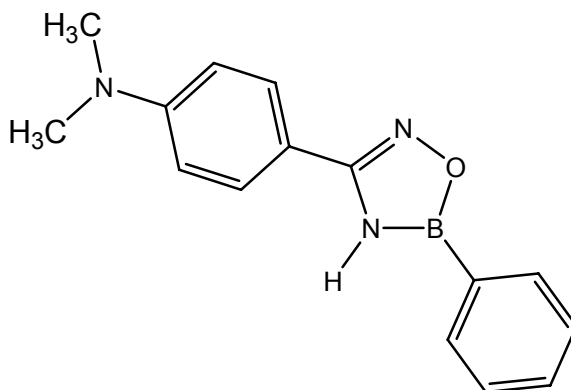
IR (KBr, ν : cm^{-1}): 3405 (N–H), 1601 (C=N), 1517, 1444 (B–N), 1421, 1402, 1356

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 10.09 (1H, s, NH), 8.33 (2H, d, $J = 8.2$ Hz), 8.25 (2H, d, $J = 8.2$ Hz), 7.96 (2H, d, $J = 7.4$ Hz), 7.47 (3H, m)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 158.40, 134.28, 133.41, 131.33, 128.27, 127.70, 124.05

MS (m/z , %): 267 (M^+ , 100), 237 (6), 221 (8), 133 (8), 117 (8), 105 (12), 90 (17), 77 (14), 63 (5), 51 (5).

3-(*p*-*N,N*-dimethylaminophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole
(16j)



A mixture of *p*-(*N,N*-dimethylamino)benzamidoxime (**10j**) (180 mg, 1.00 mmol) and phenylboronic acid (122 mg, 1.00 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from toluene.

Yield : 180 mg (68 %)

M.p : 161-162 °C

Rf : 0.16 (Eluant: Hexane:Ethyl acetate; 1:2)

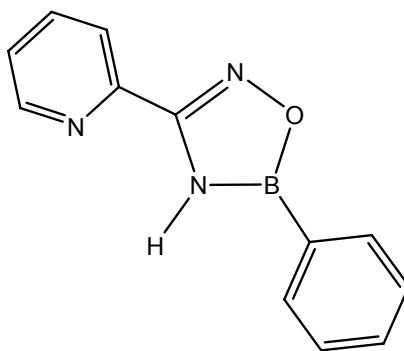
IR (KBr, ν : cm^{-1}): 3258 (broad N–H), 1613 (C=N), 1524, 1439(B–N), 1365, 1205

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 9.30 (1H, s), 7.91-6.65 (9H, m), 2.95 (6H, s)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 159.98, 152.11, 151.34, 134.37, 131.53, 130.61, 128.72, 127.84, 126.71, 120.81, 113.54, 112.03, 40.29, 40.10

MS (m/z , %): 265 (M^+ , 100), 161(15), 145 (10), 132 (5).

3-(2-pyridyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16k):



A mixture of pyridine-2-carboxamidoxime (**10k**) (200 mg, 1.45 mmol) and phenylboronic acid (178 mg, 1.45 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-hexane mixture.

Yield : 179 mg (55 %)

M.p : 158-159 °C

R_f : 0.36 (Eluant: Hexane:Ethyl acetate; 1:2)

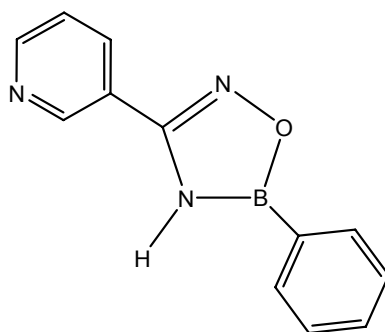
IR (KBr, ν: cm⁻¹): 3345 (N–H), 1603 (C=N), 1457, 1421(B–N)

¹H NMR, δ_H (CDCl₃+DMSO-d₆, 300 MHz): 8.66 (1H, dt, *J* = 4.7 Hz), 8.37 (1H, broad s, NH), 8.19 (1H, dd, *J* = 7.9 Hz), 7.90-7.80 (4H, m), 7.54-7.36 (5H, m)

¹³C NMR, δ_C (CDCl₃+DMSO-d₆, 75 MHz): 159.55, 149.48, 145.54, 137.39, 134.28, 131.52, 128.51, 125.57, 121.84

MS (m/z, %): 223 (M⁺, 100), 191 (8), 105 (94), 78 (27), 51 (14).

3-(3-pyridyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16l):



A mixture of pyridine-3-carboxamidoxime (**10l**) (150 mg, 1.09 mmol) and phenylboronic acid (133 mg, 1.09 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethylacetate mixture.

Yield : 87mg (58 %)

M.p : 236-237 °C

Rf : 0.08 (Eluant: Hexane:Ethyl acetate; 1:2)

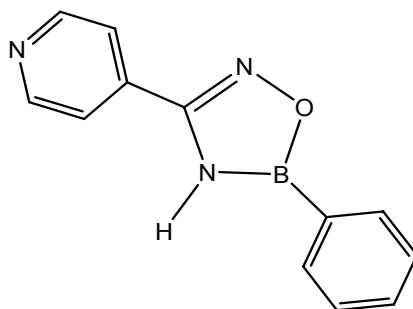
IR (KBr, ν : cm^{-1}): 3197 (N–H), 1603 (C=N), 1442(B–N), 1029

^1H NMR, δ_{H} ($\text{CDCl}_3 + \text{DMSO-d}_6$, 300 MHz): 10.19 (1H, s, NH), 9.23 (1H, d, J : 2 Hz), 8.71 (1H, dt, J = 3.5 Hz), 8.33 (1H, d, J = 5.5 Hz), 7.95 (2H, d, J = 6.4 Hz), 7.49-7.42 (3H, m)

^{13}C NMR, δ_{C} ($\text{CDCl}_3 + \text{DMSO-d}_6$, 75 MHz): 157.77, 151.37, 147.67, 134.14, 134.01, 131.11, 128.14, 123.65, 123.53

MS (m/z , %): 223 (M^+ , 100), 119 (18), 105 (23), 92 (14), 77 (14), 51 (9),

3-(4-pyridyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (16m):



A mixture of pyridine-4-carboxamidoxime (**10m**) (200 mg, 1.45 mmol) and phenylboronic acid (178 mg, 1.45 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-hexane mixture.

Yield : 128 mg (54 %)

M.p : 216-218 °C

Rf : 0.27 (Eluant: PB:Ethyl acetate; 1:2)

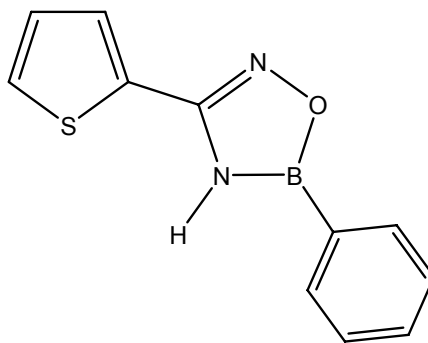
IR (KBr, ν : cm^{-1}): 3148 (N-H), 1602 (C=N), 1542, 1501, 1450(B-N)

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 10.04 (1H, s, NH), 8.75 (2H, d, J = 5.8 Hz), 7.95 (2H, dd, J = 9.2 Hz), 7.92 (2H, dd, J = 2.9 Hz), 7.53-7.42 (3H, m)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 158.30, 150.55, 134.86, 134.30, 131.33, 128.28, 120.71

MS (m/z , %): 223 (M^+ , 100), 119 (18), 105 (23), 92 (12), 77 (12), 51 (8).

5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (16n):



A mixture of thiophene-2-carboxamidoxime (**10n**) (200 mg, 1.4 mmol) and phenylboronic acid (171 mg, 1.4 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-petroleum ether mixture.

Yield : 172 mg (65 %)

M.p : 187.5-189.5 °C

R_f : 0.24 (Eluant: Hexane:Ethyl acetate; 3:2)

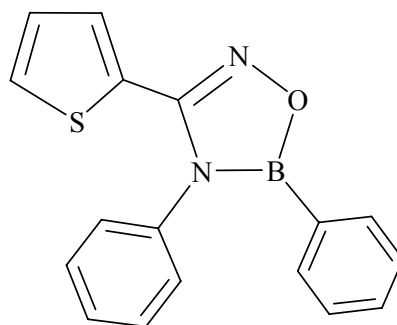
IR (KBr, ν: cm⁻¹): 3255 (N-H), 1602 (C=N), 1421(B-N)

¹H NMR, δ_H (CDCl₃+DMSO-d₆, 300 MHz): 9.67 (1H, s, N-H), 7.58 (1H, d, *J* = 3.5 Hz), 7.76 (2H, d, *J* = 7.4 Hz), 7.33-7.18 (4H, m), 6.94 (1H, t)

¹³C NMR, δ_C (CDCl₃+DMSO-d₆, 75 MHz): 156.04, 134.28, 131.19, 128.68, 128.60, 128.44, 128.24, 127.67

MS (m/z, %): 228 (M⁺, 100), 124 (60), 97 (21), 77 (7), 51 (4).

4,5-diphenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (17o):



A mixture of *N*-Phenylthiophene-2-carboxamidoxime (**11o**) (150 mg, 0.68 mmol) and phenylboronic acid (92 mg, 0.76 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethylacetate mixture.

Yield : 140 mg (67 %)

M.p : 164-166 °C

R_f : 0.41 (Eluant: Hexane:Ethyl acetate; 3:2)

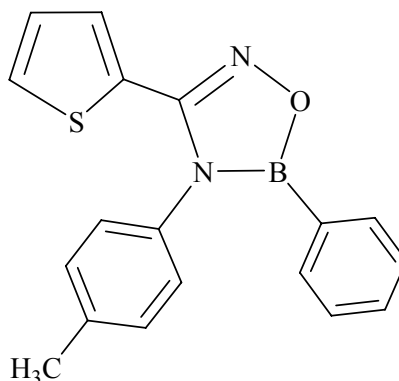
IR (KBr, ν: cm⁻¹): 1601 (C=N), 1498, 1452, 1372 (B-N), 1109,

¹H NMR, δ_H (CDCl₃, 300 MHz): 7.53-7.49 (5H, m), 7.40-7.38 (2H, m), 7.34-7.24 (4H, m), 6.70 (1H, dd, *J* = 4.10 Hz, 2.05 Hz), 6.53 (1H, dd, *J* = 4.10 Hz, 2.05 Hz)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 155.51, 136.92, 134.36, 134.01, 131.44, 130.30, 129.64, 129.05, 128.68, 128.29, 126.68, 125.49

MS (m/z, %): 338 (M⁺+34, 100), 234 (15), 179 (20), 103 (11), 91 (7), 77 (15), 51 (6).

5-phenyl-3-(2-thienyl)-4-*p*-tolyl-4,5-dihydro-1,2,4,5-oxadiazaborole (17p):



A mixture of *N-p*-Tolylthiophene-2-carboxamidoxime (**11p**) (250 mg, 1.07 mmol) and phenylboronic acid (131 mg, 1.07 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane.

Yield : 153 mg (45 %)

M.p : 222-224 °C

R_f : 0.54 (Eluant: Hexane:Ethyl acetate; 3:2)

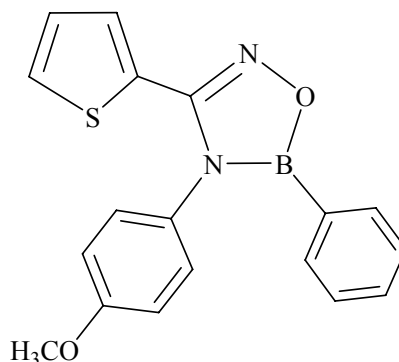
IR (KBr, ν: cm⁻¹): 1599 (C=N), 1514, 1445, 1371 (B-N), 1111, 1024

¹H NMR, δ_H (CDCl₃, 300 MHz): 7.54 (2H, d, *J* = 7.91 Hz), 7.43- 7.17 (8H, m), 6.92- 6.89 (1H, m), 6.82 (1H, d, *J* = 3.51 Hz), 2.46 (3H, s)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 139.03, 134.55, 134.38, 131.26, 130.71, 129.58, 128.87, 128.44, 128.22, 127.45, 126.93, 21.59

MS (m/z, %): 318 (M⁺, 100), 214 (15), 193 (23), 116 (7), 105 (8), 91 (5), 77 (8).

4-(*p*-methoxyphenyl)-5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (17q):



A mixture of *N*-(*p*-methoxyphenyl)thiophene-2-carboxamidoxime (**11q**) (100 mg, 4.03 mmol) and phenylboronic acid (49 mg, 4.03 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethylacetate mixture.

Yield : 94 mg (70 %)

M.p : 161-163 °C

R_f : 0.15 (Eluant: Hexane:Ethyl acetate; 3:2)

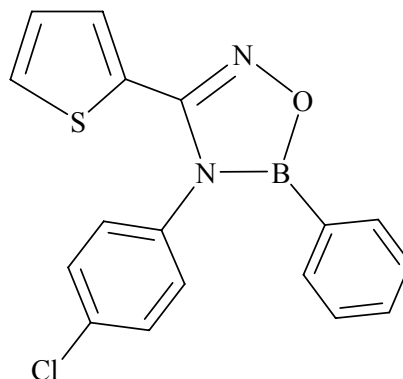
IR (KBr, ν: cm⁻¹): 3066-2937 (CH₃), 1610 (C=N), 1515, 1370 (B-N), 1256, 1030

¹H NMR, δ_H (CDCl₃, 300 MHz): 7.55 (4H, d, *J* = 7.32 Hz), 7.40-7.21 (4H, m), 7.00-6.86 (4H, m), 3.89 (3H, s)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 159.86, 156.70, 134.38, 131.30, 129.79, 129.59, 128.96, 128.26, 127.49, 126.92, 115.15, 55.79

MS (m/z, %): 334 (M⁺, 100), 230 (6), 216 (25), 209 (30), 194 (12), 121 (15), 77 (9).

4-(*p*-chlorophenyl)-5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (17r):



A mixture of *N*-(*p*-chlorophenyl)thiophene-2-carboxamidoxime (**11r**) (300 mg, 1.2 mmol) and phenylboronic acid (146 mg, 1.2 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane.

Yield : 304 mg (75 %)

M.p : 158-160 °C

Rf : 0.50 (Eluant: Hexane:Ethyl acetate; 3:2)

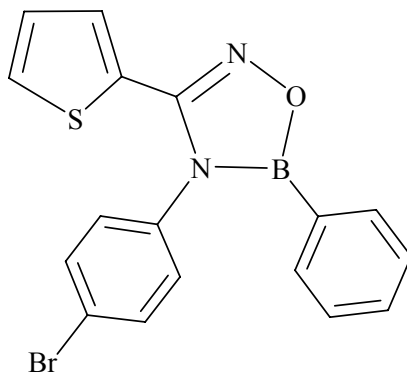
IR (KBr, ν : cm^{-1}): 1600 (C=N), 1525, 1493, 1449, 1370 (B-N), 1093

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.49-7.40 (6H, m), 7.31-7.25 (4H, m), 6.66 (1H, dd, $J = 50$ Hz, 1.76 Hz), 6.58 (1H, dd, $J = 3.9$ Hz, 1.46 Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 155.23, 135.51, 135.23, 134.31, 131.61, 130.54, 129.96, 129.19, 128.40, 126.81, 125.08

MS (m/z , %): 372 ($\text{M}^+ + 34$, 100), 268 (14), 233 (9), 213 (26), 137 (15), 125 (11), 96 (12), 77 (14), 51 (5).

4-(*p*-bromophenyl)-5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (17s):



A mixture of *N*-(*p*-bromophenyl)thiophene-2-carboxamidoxime (**11s**) (150 mg, 0.5 mmol) and phenylboronic acid (68 mg, 0.5 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 144 mg (75 %)

M.p : 177-179 °C

Rf : 0.61 (Eluant: Hexane:Ethyl acetate; 3:2)

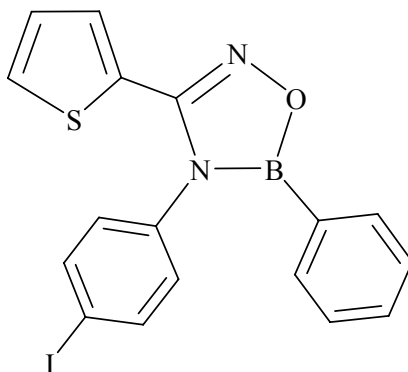
IR (KBr, ν : cm^{-1}): 1602 (C=N), 1568, 1510, 1488, 1455, 1366 (B-N)

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.65 (1H, d, $J = 0.88$ Hz), 7.63 (1H, m), 7.49-7.26 (6H, m), 7.22 (1H, d, $J = 0.88$ Hz), 7.20 (1H, m), 6.74 (1H, dd, $J = 2.34$ Hz, 1.17 Hz), 6.56 (1H, dd, $J = 2.34$ Hz, 1.17 Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 155.15, 136.04, 134.32, 133.53, 131.62, 130.28, 129.21, 128.41, 126.84, 125.07, 123.23

MS (m/z , %): 418 ($\text{M}^+ + 34$, 100), 314 (12), 257 (14), 181 (8), 169 (8), 143 (12), 102 (18), 90 (12), 77 (15), 63 (8), 51 (8).

4-(*p*-iodophenyl)-5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (17t):



A mixture of *N*-(*p*-iodophenyl)thiophene-2-carboxamidoxime (**11t**) (200 mg, 0.58 mmol) and phenylboronic acid (78 mg, 0.64 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 129 mg (52 %)

M.p : 184-186 °C

Rf : 0.50 (Eluant: Hexane:Ethyl acetate; 3:2)

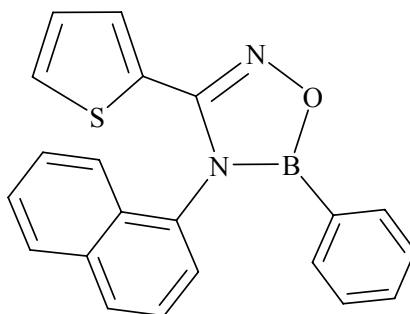
IR (KBr, ν : cm^{-1}): 1605 (C=N), 1597, 1508, 1485, 1455, 1368 (B-N)

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.83 (2H, d, $J = 7.6$ Hz), 7.49-7.25 (6H, m), 7.07 (2H, d, $J = 7.6$ Hz), 6.74 (1H, d, $J = 3.5$ Hz), 6.55 (1H, d, $J = 3.4$ Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 155.10, 139.49, 136.72, 134.32, 134.27, 131.62, 130.49, 129.23, 128.41, 126.86, 125.05, 94.76

MS (m/z , %): 464 ($\text{M}^+ + 34$, 100), 360 (12), 305 (26), 229 (7), 198 (7), 151 (9), 102 (15), 90 (17), 77 (11), 63 (7).

4-(1-naphthyl)-5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (17u):



A mixture of *N*-(1-naphthyl)thiophene-2-carboxamidoxime (**11u**) (150 mg, 0.55 mmol) and phenylboronic acid (75 mg, 0.61 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 92 mg (46 %)

M.p : 132-134 °C

R_f : 0.54 (Eluant: Hexane:Ethyl acetate; 3:2)

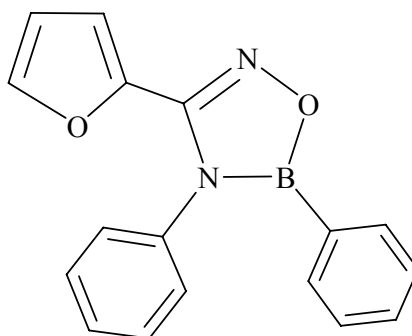
IR (KBr, ν : cm^{-1}): 3054 (C–H), 1599 (C=N), 1508, 1452, 1407, 1369 (B–N)

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 8.06 (1H, d, $J = 7.9$ Hz), 8.00 (1H, d, $J = 7.9$ Hz), 7.74- 7.16 (11H, m), 6.53 (1H, dd, $J = 1.76$ Hz, 0.88 Hz), 6.39 (1H, dd, $J = 1.76$ Hz, 0.88 Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 156.11, 134.57, 134.22, 133.89, 133.13, 131.48, 131.11, 130.19, 128.90, 128.68, 128.28, 128.24, 127.46, 126.79, 126.62, 125.99, 125.23, 122.52

MS (m/z , %): 388 ($\text{M}^+ + 34$, 100), 249 (26), 229 (69), 153 (25), 140 (18), 126 (11), 115 (12), 77(9), 51 (5).

3-(2-furyl)-4,5-diphenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18o):



A mixture of *N*-phenyl furan-2-carboxamidoxime (**12o**) (150 mg, 0.74 mmol) and phenylboronic acid (90 mg, 0.74 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-petroleum ether mixture.

Yield : 105 mg (50 %)

M.p : 114-116 °C

Rf : 0.29 (Eluant: Hexane:Ethyl acetate; 3:1)

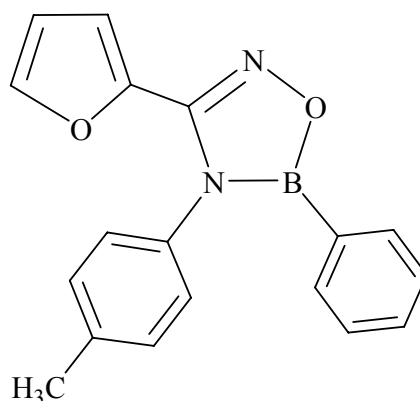
IR (KBr, ν : cm^{-1}): 1598 (C=N), 1534, 1498, 1484, 1375 (B-N), 1024

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.52- 7.23 (11H, m), 6.07 (1H, dd, $J = 2.34$ Hz, 1.17 Hz), 5.87 (1H, dd, $J = 3.66$ Hz, 1.17 Hz, 0.88 Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 152.63, 140.20, 139.68, 136.99, 134.40, 131.45, 130.15, 129.20, 128.30, 128.27, 115.70, 108.22

MS (m/z , %): 322 ($\text{M}^+ + 34$, 100), 285 (15), 258 (31), 179 (18), 166 (35), 154 (44), 128 (15), 103 (35), 77 (34), 64 (10), 51 (13).

3-(2-furyl)-5-phenyl-4-*p*-tolyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18p):



A mixture of *N-p*-tolyl furan-2-carboxamidoxime (**12p**) (100 mg, 0.46 mmol) and phenylboronic acid (56 mg, 0.46 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from benzene-petroleum ether mixture.

Yield : 83 mg (60 %)

M.p : 167-168 °C

R_f : 0.23 (Eluant: Hexane:Ethyl acetate; 3:1)

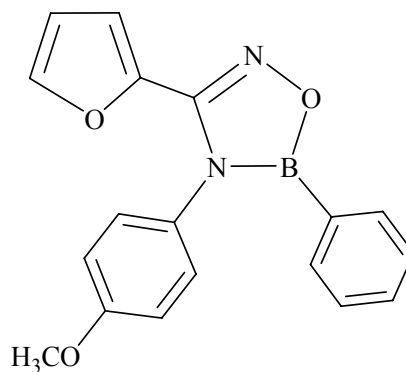
IR (KBr, ν: cm⁻¹): 3153, 3052, 1611 (C=N), 1515, 1485, 1376 (B-N), 1138, 1028

¹H NMR, δ_H (CDCl₃, 300 MHz): 7.53 (2H, d, *J* = 7.32 Hz), 7.41-7.26 (5H, m), 7.19 (2H, d, *J* = 7.32 Hz), 7.03 (1H, d, *J* = 8.50 Hz), 6.77 (1H, d, *J* = 8.20 Hz), 2.46 (3H, s)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 134.41, 131.37, 130.71, 129.74, 128.23, 128.01, 115.65, 108.15, 21.52

MS (m/z, %): 336 (M⁺+34, 100), 299 (15), 271 (10), 192 (23), 180 (23), 168 (54), 142 (8), 127 (7), 116 (28), 104 (10), 90 (15), 77 (20), 65 (8), 51 (8).

3-(2-furyl)-4-(*p*-methoxyphenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18q):



A mixture of *N*-(*p*-methoxyphenyl)furan-2-carboxamidoxime (**12q**) (150 mg, 0.64 mmol) and phenylboronic acid (78 mg, 0.64 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 133 mg (65 %)

M.p : 145-147 °C

R_f : 0.32 (Eluant: Hexane:Ethyl acetate; 3:1)

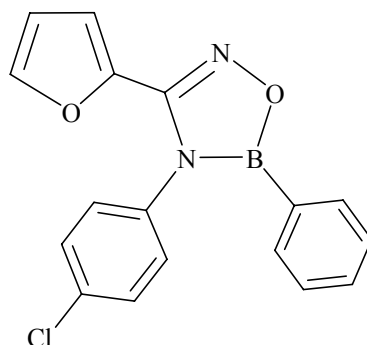
IR (KBr, ν: cm⁻¹): 3127-2839 (CH₃), 1612 (C=N), 1516, 1489, 1375 (B-N), 1251, 1023

¹H NMR, δ_H (CDCl₃, 300 MHz): 7.45-6.90 (10H, m), 6.00 (1H, dd, *J* = 3.52 Hz, 1.76 Hz), 5.70 (1H, dd, *J* = 3.52 Hz, 1.76 Hz), 3.81 (3H, s)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 159.91, 152.92, 140.36, 139.62, 134.40, 131.43, 129.49, 129.34, 128.28, 115.71, 108.26, 55.83

MS (m/z, %): 352 (M⁺+34, 100), 209 (27), 194 (16), 184 (30), 133 (21), 121 (10), 103 (11), 90 (13), 77 (15).

4-(*p*-chlorophenyl)-3-(2-furyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18r):



A mixture of *N*-(*p*-chlorophenyl)furan-2-carboxamidoxime (**12r**) (200 mg, 0.84 mmol) and phenylboronic acid (103 mg, 0.84 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-dichloroethane mixture.

Yield : 116 mg (43 %)

M.p : 131-133 °C

Rf : 0.29 (Eluant: Hexane:Ethyl acetate; 3:1)

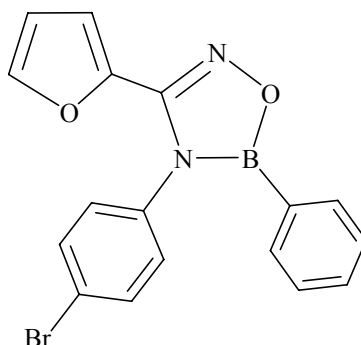
IR (KBr, ν : cm^{-1}): 1611 (C=N), 1530, 1496, 1373 (B-N), 1021

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.49- 7.26 (10H, m), 6.12 (1H, dd, $J = 3.33$ Hz, 1.76 Hz, 1.46), 5.98 (1H, dd, $J = 3.52$ Hz, 1.76 Hz, 1.46 Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 152.38, 139.88, 135.60, 135.03, 134.36, 131.63, 130.36, 129.65, 128.39, 115.91, 108.33

MS (m/z , %): 356 ($\text{M}^+ + 34$, 100), 319 (7), 293 (15), 257 (12), 213 (25), 200 (25), 189 (38), 162 (9), 137 (40), 102 (25), 77 (20), 64 (8), 51(9).

4-(*p*-bromophenyl)-3-(2-furyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18s):



A mixture of *N*-(*p*-bromophenyl)furan-2-carboxamidoxime (**12s**) (150 mg, 0.53 mmol) and phenylboronic acid (78 mg, 0.64 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 151 mg (72 %)

M.p : 166-168 °C

Rf : 0.66 (Eluant: Hexane:Ethyl acetate; 3:2)

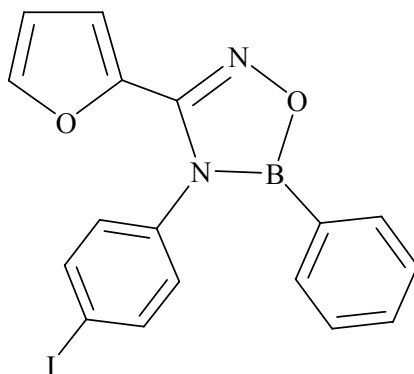
IR (KBr, ν : cm^{-1}): 1610 (C=N), 1530, 1492, 1374 (B-N), 1020

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.65 (10H, m), 6.13 (1H, d, $J = 3.22$ Hz), 5.99 (1H, dd, $J = 1.76$ Hz, 0.88 Hz)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 152.30, 139.92, 139.84, 136.12, 134.37, 133.35, 131.64, 129.96, 128.40, 123.08, 115.90, 108.33

MS (m/z , %): 402 ($\text{M}^+ + 34$, 100), 257 (29), 244 (15), 232 (26), 181 (18), 154 (8), 127 (15), 102 (40), 90 (12), 77 (26), 63 (9), 51 (9).

3-(2-furyl)-4-(*p*-iodophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18t):



A mixture of *N*-(*p*-iodophenyl)furan-2-carboxamidoxime (**12t**) (150 mg, 0.45 mmol) and phenylboronic acid (67 mg, 0.55 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 141 mg (75 %)

M.p : 203-205 °C

R_f : 0.58 (Eluant: Hexane:Ethyl acetate; 3:2)

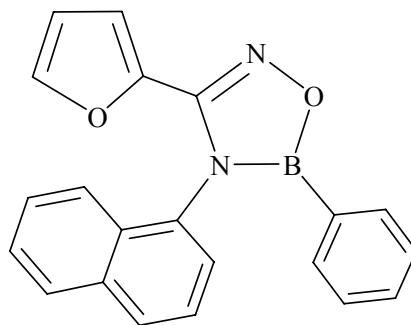
IR (KBr, ν: cm⁻¹): 1605 (C=N), 1532, 1490, 1375 (B-N)

¹H NMR, δ_H (CDCl₃, 300 MHz): 7.83 (1H, d, *J* = 1.17 Hz), 7.81 (1H, s), 7.50-7.24 (6H, m), 7.08 (1H, d, *J* = 1.17 Hz), 7.06 (1H, s), 6.13 (1H, dd, *J* = 2.34 Hz, 1.17 Hz), 5.99 (1H, dd, *J* = 2.34 Hz, 1.17 Hz)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 152.27, 139.93, 139.83, 139.31, 136.81, 134.37, 131.63, 130.16, 128.39, 115.92, 108.32, 94.45

MS (m/z, %): 448 (M⁺+34, 100), 305 (20), 292 (23), 280 (39), 257 (23), 229 (16), 203 (7), 189 (9), 154 (11), 127 (16), 102 (41), 90 (16), 77 (19), 63 (13), 51(9).

3-(2-furyl)-4-(1-naphthyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (18u):



A mixture of *N*-(1-naphthyl)furan-2-carboxamidoxime (**12u**) (150 mg, 0.59 mmol) and phenylboronic acid (72 mg, 0.59 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-dichloroethane mixture.

Yield : 79 mg (40 %)

M.p : 148-150 °C

Rf : 0.49 (Eluant: Hexane:Ethyl acetate; 3:2)

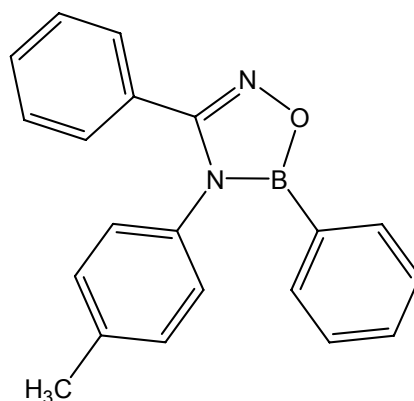
IR (KBr, ν : cm^{-1}): 3047, 1603 (C=N), 1527, 1484, 1371 (B-N), 1209, 1143, 1018

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 8.03 (1H, d, $J = 8.03$ Hz), 7.98 (1H, d, $J = 8.03$ Hz), 7.69- 7.12 (11H, m), 5.87 (1H, s), 5.39 (1H, s)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 153.08, 140.00, 139.55, 134.49, 134.26, 133.24, 131.50, 130.79, 129.86, 128.79, 128.26, 125.15, 127.41, 126.27, 125.93, 122.52, 115.32, 108.23

MS (m/z , %): 372 ($\text{M}^+ + 34$, 69), 336 (92), 308 (42), 292 (15), 259 (34), 233 (48), 216 (54), 204 (100), 189 (15), 178 (17), 153 (54), 140 (34), 126 (29), 115 (23), 77 (18), 51 (8).

3,5-diphenyl-4-*p*-tolyl-4,5-dihydro-1,2,4,5-oxadiazaborole (19p):



A mixture of *N-p*-tolyl benzamidoxime (**13p**) (150 mg, 0.66 mmol) and phenylboronic acid (81 mg, 0.66 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 265 mg (85 %)

M.p : 243-245 °C

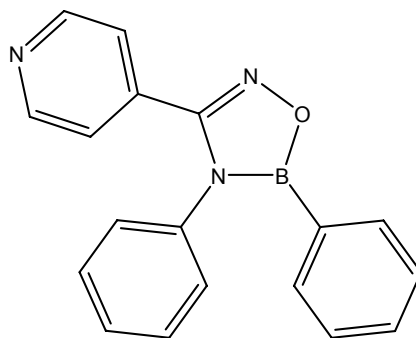
Rf : 0.51 (Eluant: Hexane:Ethyl acetate; 2:1)

IR (KBr, ν : cm^{-1}): 3039, 1600 (C=N), 1514, 1373 (B-N)

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 7.75-6.69 (14H, m), 2.46 (3H, s)

MS (m/z , %) : 312 (M^+ , 100), 297 (8), 208 (15), 193 (29), 104 (9), 91 (12), 77 (15).

3-(4-pyridyl)-4-5-diphenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (20o):



A mixture of *N*-phenyl pyridine-4-carboxamidoxime (**14o**) (110 mg, 0.52 mmol) and phenylboronic acid (63 mg, 0.52 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-ethyl acetate mixture.

Yield : 65 mg (42 %)

M.p : 213-215 °C

R_f : 0.08 (Eluant: Hexane:Ethyl acetate; 2:1)

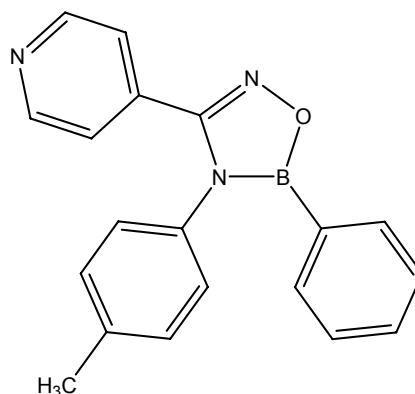
IR (KBr, ν: cm⁻¹): 1598 (C=N), 1521, 1499, 1412, 1373 (B-N), 700

¹H NMR, δ_H (CDCl₃+DMSO-d₆, 300 MHz): 8.22 (1H, d, *J* = 5.86 Hz), 8.18 (1H, d, *J* = 5.56 Hz), 7.49 (1H, d, *J* = 7.33 Hz), 7.24-6.56 (10H, m), 6.33 (1H, d, *J* = 7.62 Hz)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 149.92, 149.35, 134.20, 134.01, 131.24, 129.94, 128.82, 128.09, 127.57, 127.44, 122.90, 122.40, 120.74

MS (m/z, %): 299(M⁺, 100), 222 (8), 195 (11), 179 (31), 118 (8), 91 (11), 77 (15), 51 (9).

3-(4-pyridyl)-5-phenyl-4-(*p*-tolyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (20p):



A mixture of *N*-(*p*-tolyl)pyridine-4-carboxamidoxime (**14p**) (96 mg, 0.42 mmol) and phenylboronic acid (51 mg, 0.42 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-dichloroethane mixture.

Yield : 105 mg (80 %)

M.p : 234-236 °C

Rf : 0.18 (Eluant: Hexane:Ethyl acetate; 1:2)

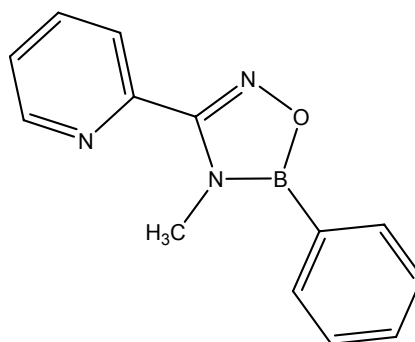
IR (KBr, ν : cm^{-1}): 2924, 1653 ((C=N), 1599, 1516, 1375 (B-N), 823

^1H NMR, δ_{H} (CDCl_3 +DMSO- d_6 , 300 MHz): 8.46-6.61 (13H, m), 2.16 (3H,s)

^{13}C NMR, δ_{C} (CDCl_3 +DMSO- d_6 , 75 MHz): 149.85, 148.37, 138.56, 134.45, 130.80, 130.20, 129.32, 128.58, 127.57, 122.45, 120.94, 20.68

MS (m/z , %): 313 (M^+ , 100), 298 (7), 208 (10), 193 (23), 104 (7), 91(9), 77 (8), 51(6).

4-methyl-3-(2-pyridyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (21v):



A mixture of *N*-methyl pyridine-2-carboxamidoxime (**15v**) (150 mg, 0.99 mmol) and phenylboronic acid (121 mg, 0.99 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-petroleum ether mixture.

Yield : 65 mg (28 %)

M.p : 76-77 °C

R_f : 0.18 (Eluant: Hexane:Ethyl acetate; 1:3)

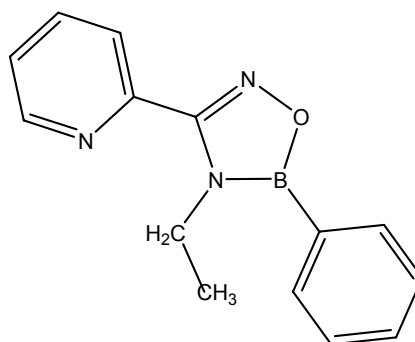
IR (KBr, ν: cm⁻¹): 3055, 1587 (C=N), 1541, 1483, 1390 (B=N), 694

¹H NMR, δ_H (CDCl₃, 300 MHz): 8.78-7.44 (9H, m), 3.67 (3H, s)

¹³C NMR, δ_C (CDCl₃, 75 MHz): 160.05, 149.24, 147.50, 137.07, 133.88, 130.72, 128.27, 124.76, 124.73, 31.43

MS (m/z, %): 236 (100), 160 (9), 133 (25), 105 (100), 78 (29), 51(10).

4-ethyl-3-(2-pyridyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (21w):



A mixture of *N*-ethyl pyridine-2-carboxamidoxime (**15w**) (80 mg, 0.48 mmol) and phenylboronic acid (59 mg, 0.48 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-petroleum ether mixture.

Yield : 66 mg (63 %)

M.p : 82-83 °C

Rf : 0.11 (Eluant: Hexane:Ethyl acetate; 2:1)

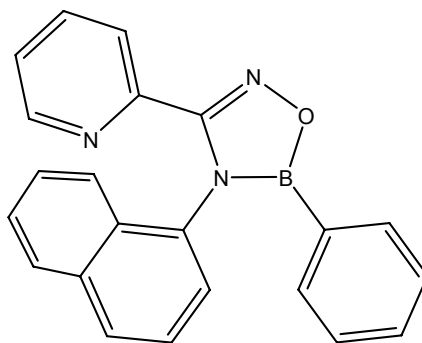
IR (KBr, ν : cm^{-1}): 3061-2972, 1587 (C=N), 1543, 1482, 1420 (B-N), 1298, 706

^1H NMR, δ_{H} (CDCl_3 , 300 MHz): 8.73- 8.71 (1H, m), 7.96-7.79 (4H, m), 7.51-7.45 (4H, m), 4.18 (2H, q), 1.26 (3H, t)

^{13}C NMR, δ_{C} (CDCl_3 , 75 MHz): 160.07, 149.54, 147.74, 137.29, 133.94, 130.95, 128.53, 124.96, 124.89, 38.40, 17.85

MS (m/z , %): 250 (M^+ , 54), 236 (8), 174 (52), 147 (31), 105 (100), 78 (40), 51 (11).

4-(1-naphthyl)-3-(2-pyridyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (21u):



A mixture of *N*-(1-naphthyl)pyridine-2-carboxamidoxime (**15u**) (74 mg, 0.28 mmol) and phenylboronic acid (34 mg, 0.28 mmol) in toluene (10 mL) was refluxed under inert atmosphere with molecular sieves (4Å) over night. After extracted with acetone, filtered and the solvents was evaporated under the reduced pressure. The product was crystallized from hexane-petroleum ether mixture.

Yield : 50 mg (51 %)

M.p : 181-182 °C

Rf : 0.31 (Eluant: Hexane:Ethyl acetate; 1:3)

IR (KBr, ν : cm^{-1}): 3057, 1600 (C=N), 1551, 1473, 1371 (B-N), 1151, 777

^1H NMR, δ_{H} (DMSO- d_6 , 300 MHz): 8.20-7.08 (16H, m)

^{13}C NMR, δ_{C} (DMSO- d_6 , 75 MHz): 190.68, 160.30, 149.25, 146.18, 136.33, 134.13, 134.10, 134.08, 131.07, 130.85, 128.44, 128.36, 128.29, 127.97, 127.10, 126.46, 125.87, 125.41, 124.37, 124.12, 122.71

MS (m/z , %): 349 (100), 318 (11), 272 (19), 244 (27), 229 (10), 141 (27), 115 (8), 78 (9).

CHAPTER III

RESULTS AND DISCUSSION

The ring closure reactions of amidoximes with phenylboronic acid give 3,4,5-trisubstituted-4,5-dihydro-1,2,4,5-oxadiazaboroles. They have been reported to have hypotensive, cardiac, and central nervous system depressant activities [64]. To our best knowledge of literature survey based on the electronic databases; Science Finder Scholar, Web of Science, Science Direct, Beilstein Crossfire Commander, there are only a few examples for cyclodehydration reactions of amidoximes with phenyl boronic acid. For this reason, we are focused, in this study, to obtain oxadiazaborole heterocycles starting from both *N*-unsubstituted amidoximes and *N*-substituted amidoximes bearing thiophene, furan and pyridine rings which might have an effect themselves to enhance the biological activities of the title compounds [65, 68-74].

The present research work is basically consisted of four parts. In the first part of the study, *N*-unsubstituted and *N*-substituted amidoximes were synthesized according to the literature procedures [75-81]. They were purified by flash column chromatography and recrystallized from appropriate solvents.

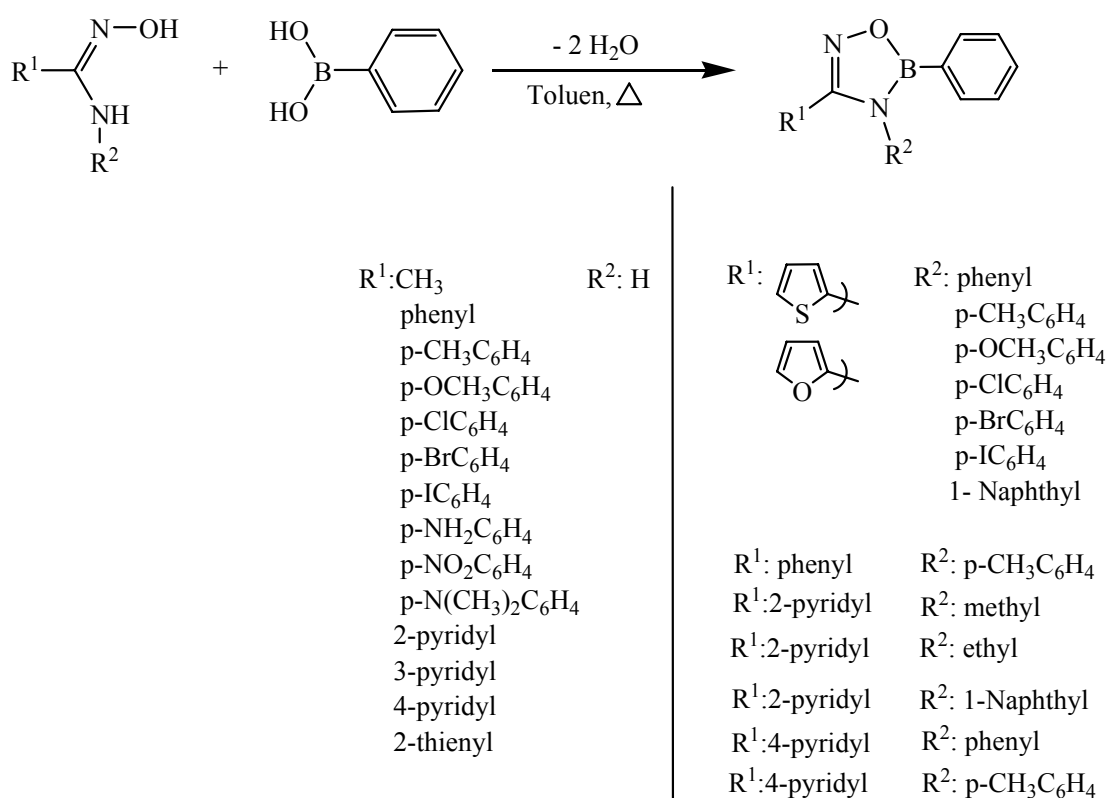
In the second part, the pure monoamidoximes and *N*-substituted amidoximes were reacted with phenylboronic acid in the presence of molecular sieves (4 Å) at the reflux temperature of toluene to give corresponding 1,2,4,5-oxadiazaboroles.

In the third part, we investigated and interpreted the electron impact mass spectral fragmentations of the title oxadiazaboroles.

The part 4 of the work involves in the investigation of the substituent effect on the both iminic carbon chemical shifts $\delta_{C=N}$ and NH proton chemical δ_{N-H} shifts and

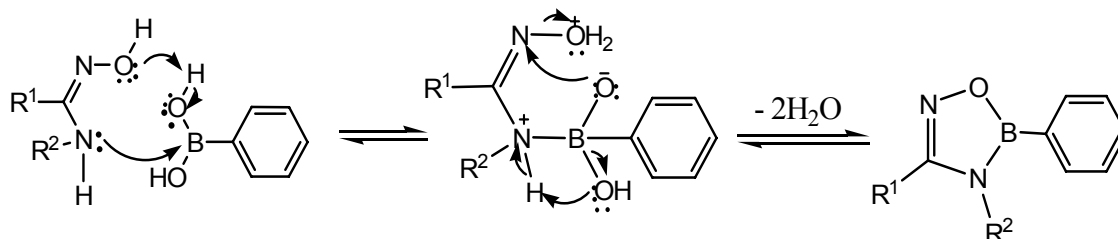
it is concluded that a good correlation exist between Hammett σ_p constants [82] and related NMR chemical shift values.

All the new oxadiazaborole heterocycles are crystalline compounds and have narrow range melting points. They were also checked by thin layer chromatography for purity. After crystallization from the appropriate solvents the heterocycles were identified based on the spectroscopic and physical data (IR, NMR, MS, X-Ray, m.p., Rf). Although *N*-unsubstituted amidoximes gave high yielded (80-95 %) heterocycles (R^1 : H), *N*-substituted amidoximes were obtained in moderate yields (50-70 %). An account for this would be considered as the steric hindrance of the substituents on the nitrogen atom (R^2).



Scheme 1: The synthesis and structures of oxadiazaboroles

The proposed reaction mechanism for the cyclodehydration reactions of amidoximes with phenylboronic acid is shown below.



Scheme 2: Proposed reaction mechanism for the transformation of amidoximes into oxadiazaboroles

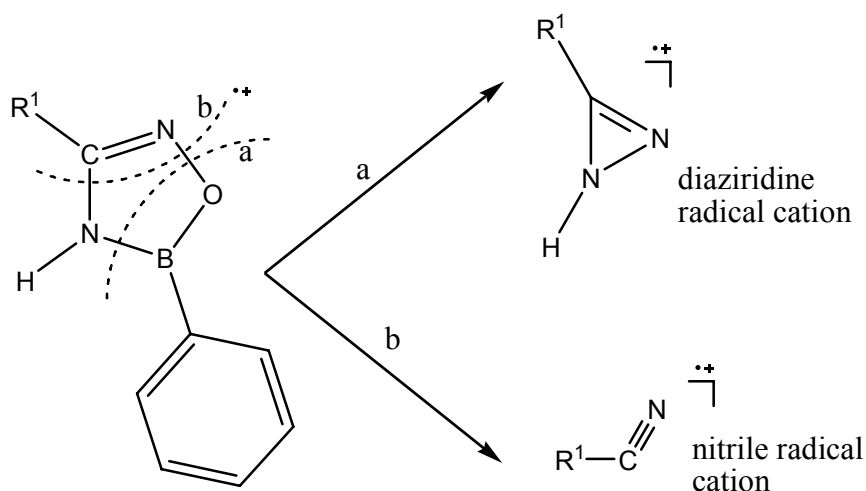
The disappearance of the broad hydrogen-bonded NOH absorption of the starting amidoxime and arising of the B–N absorption signal in the IR spectra around $1450\text{--}1350\text{ cm}^{-1}$ is accepted as the proof of the title compounds [73]. The peaks between $1613\text{--}1599\text{ cm}^{-1}$ are due to the C=N bond. The heterocycles synthesized from the *N*-unsubstituted amidoximes have N–H bond peaks around $3424\text{--}3148\text{ cm}^{-1}$ which show broadening that indicate the presence of H–bonding. In addition, in the ^1H -NMR spectra the N–H chemical shifts appeared at around 10.19–8.66 ppm in DMSO- d_6 but not there in the case of CDCl_3 as solvent.

In the ^{13}C -NMR spectra, the chemical shift values of the iminic carbons were observed at about 160 ppm. An interesting difference in the chemical shift position of the *ipso* carbons where an iodine is attached was found to appear at more upfield region about 95 ppm in comparison to the non iodine-bonded cases.

The mass spectral measurement of the heterocycles prepared from *N*-unsubstituted amidoximes on a GC-MS instrument showed that the most abundant

ions are the molecular ions. These base peaks appear with an abundance of 100 %.

The mass spectral fragmentations of the compounds **16a-16n** is shown below.



Scheme 3: The mass spectral fragmentations of the compounds **16a-16n**

The mass spectral study of heterocycles prepared from *N*-substituted amidoximes shows interesting features. The main peaks of heterocycles appear as $m/z \text{ M}^+ + 34$ amu except for **17p**, **17q**, **19p**, **20o**, **20p**, **21u**, **21v** and **21w**. It is assumed that the excess 34 amu might be due to the two O–H groups bonded to the boron atom because of its electron deficiency or nitrogen atom. However, a detailed high resolution mass spectral study should be carry out to clarify this.

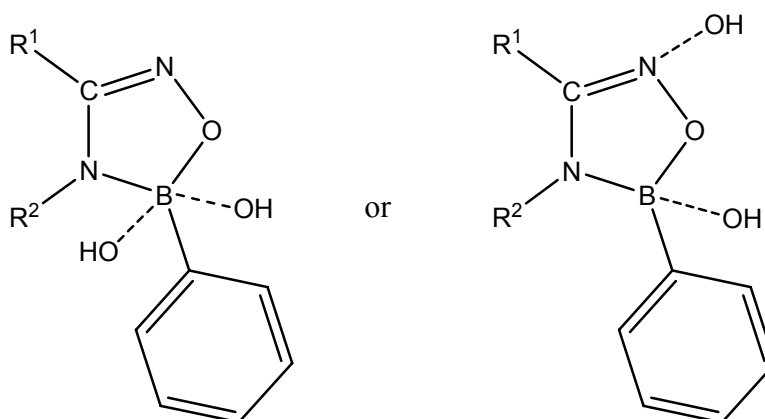
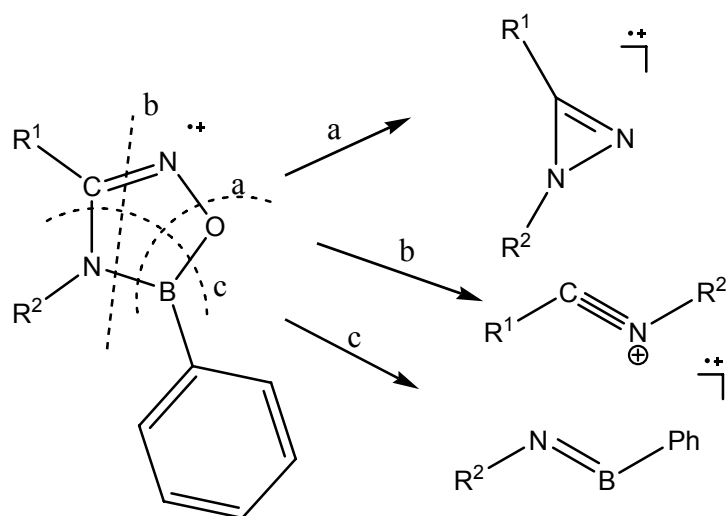


Figure 33: O–H groups bonded to the nitrogen atom and electron deficient boron atom.

The mass fragmentations of the compounds **17o-17u**, **18o-18u**, **20o**, **20p**, **21v**, **21w** and **21u** is shown below.



Scheme 4: The mass fragmentations of the compounds **17o-17u**, **18o-18u**, **20o**, **20p**, **21v**, **21w** and **21u**

In order to perform a correlation between Hammett sigma constants and carbon NMR shifts of the imino carbons (Table 1) of the oxadiazaboroles synthesized from monoamidoximes and phenylboronic acid, a plot between $\delta_{C=N}$ and σ_p constants was constructed. The graph is in accord with the theoretical expectations depending on the substituents (i.e. electron withdrawing and electron releasing groups) on the C-substituted phenyl ring (Figure 34). Thus, electron releasing groups cause C=N carbon chemical shifts to appear at lower field region while the electron withdrawing groups makes this higher in comparison to first ones.

In addition, a correlation between δ_{N-H} values and Hammett σ_p constants was also observed when these values are plotted (Figure 35). Again the graph is matched with the theoretically expected behaviour of the substituents on the C-substituted phenyl ring.

σ_p values	δ_{N-H} (ppm)	$\delta_{C=N}$ (ppm)	Substituents
-0.83	9.30	159.98	p-N(CH ₃) ₂
-0.66	9.35	160.03	p-NH ₂
-0.24	9.25	159.80	p-OCH ₃
-0.16	9.47	160.00	p-CH ₃
0	10.1	159.88	phenyl
0.18	9.81	159.30	p-I
0.22	9.81	159.11	p-Cl
0.23	9.88	159.14	p-Br
0.78	10.09	158.40	p-NO ₂

Table 1: σ_p , δ_{N-H} (ppm) and $\delta_{C=N}$ (ppm) values of the substituents.

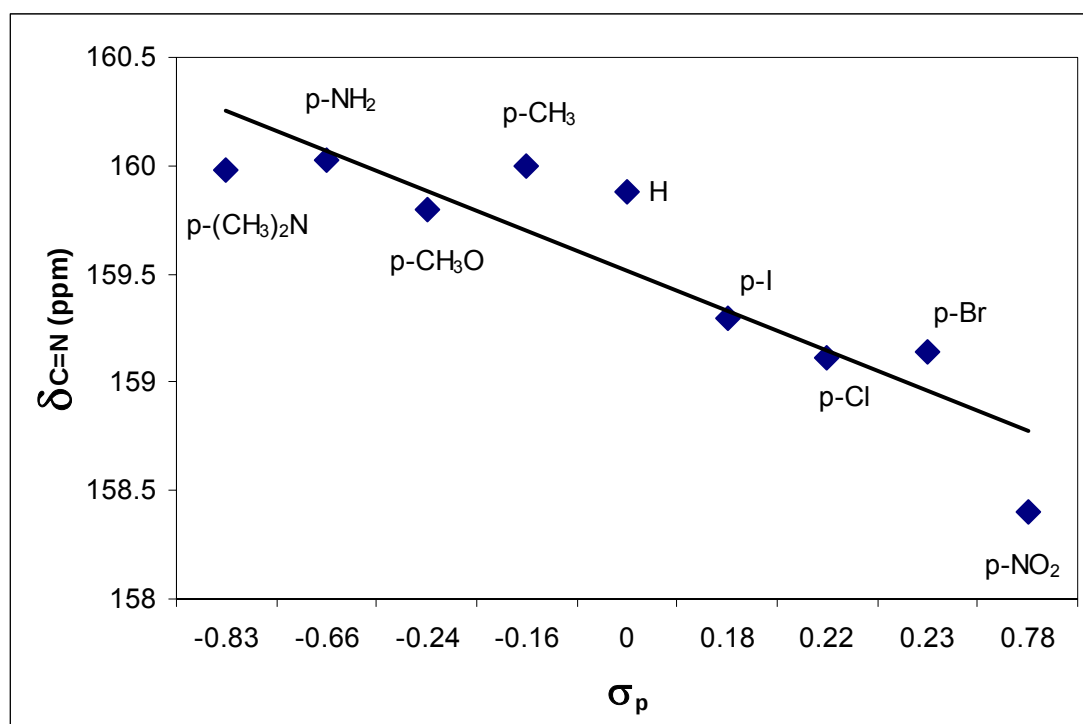


Figure 34: Plot of Hammett σ_p constants versus $\delta_{C=N}$ (ppm)

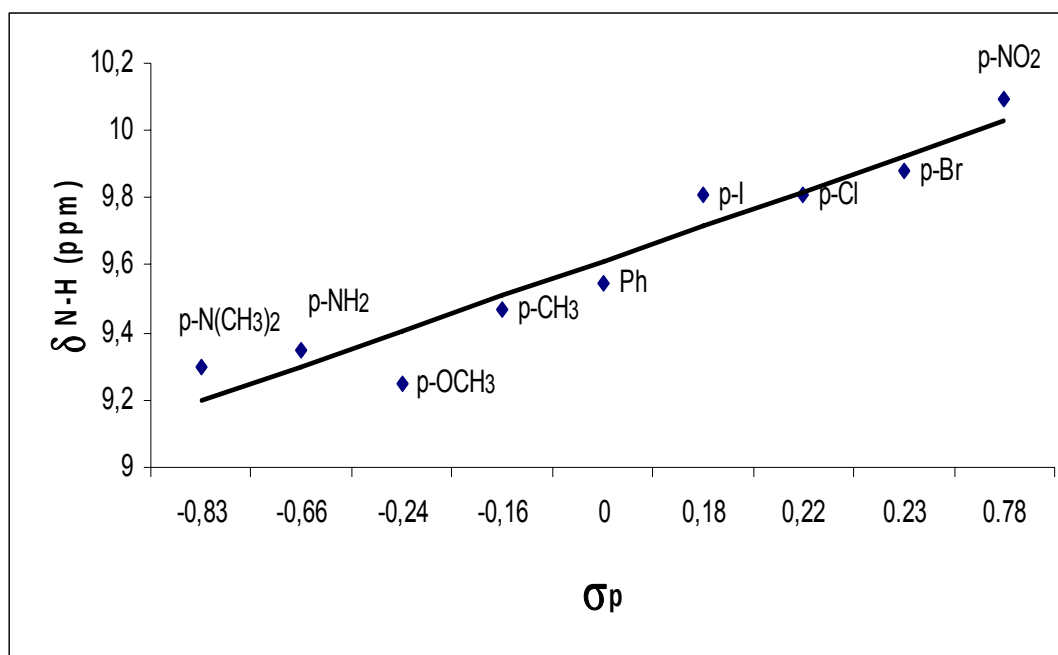


Figure 35: Plot of Hammett σ_p constants versus δ_{N-H} (ppm)

CHAPTER IV

CONCLUSION

In summary, this study presents a good protocol to synthesize the new 1,2,4,5-oxadiazaboroles, both *N*-substituted and unsubstituted ones in high yields. The mass spectral fragmentation routes of these heterocyclic rings are also interpreted. In addition, in order to see how substituents on the phenyl ring (on C-3 of oxadiazaborole ring) effect the carbon and proton NMR chemical shifts on the basis of Hammett σ_p constants, an investigation is performed.

REFERENCES

- [1] W. Lossen and P. Schifferdecker, *Ann. Chem.*, **1873**, 166, 295.
- [2] F. Tiemann, *Ber.*, **1884**, 17, 126.
- [3] T. Bandiera, F. M. Albini, E. Albini, *J. Heterocyclic Chem.* **1987**, 24, 1597.
- [4] K. Sindelar, Z. Sedivy, M. Hrubantova, M. Valchar, J. Metysava, and M. Protiva, *Collect. Czech. Chem. Commun.*, **1988**, 53, 381.
- [5] R. Lenaers, F. Eloy, and C. Moussebois, *Helv. Chim. Acta*, **1962**, 45, 441.
- [6] A. Pinner, *Ber.*, **1884**, 17, 184.
- [7] W. Lossen, *Ber.*, **1884**, 17, 1587.
- [8] O. Goldbeck, *Ber.*, **1891**, 24, 3658.
- [9] R. N. Hurd and G. De La Mater, *Chem. Revs.* **1961**, 61, 66.
- [10] A. Spilker, *Ber.*, **1889**, 22, 2767.
- [11] F. Tiemann, *Ber.*, **1886**, 19, 1668.
- [12] H. Schiff, *Ann.*, **1902**, 321, 357.
- [13] E. Durio, and S. Dugone, *Gazz. Chim. Ital.*, **1936**, 66, 139.
- [14] W. Lossen, *Ann.*, **1889**, 252, 214.
- [15] A. Werner, and C. Bloch, *Ber.*, **1899**, 32, 1975.
- [16] A. Werner, and H. Buss, *Ber.*, **1894**, 27, 2193.
- [17] H. Ley and M. Ulrich, *Ber.*, **1914**, 47, 2941.
- [18] H. Wieland and H. Bauer, *Ber.*, **1906**, 39, 1480.
- [19] G. F. Bordwell and Guo-Zhen Jif, *J. Org. Chem.* **1992**, 57, 3019-3025.
- [20] L. Bauer, C.N.V. Nambury, and C.L. Bell, *Tetrahedron*, **1964**, 20, 165.
- [21] A. F. Holleman, *Rec. Trav. Chim.*, **1894**, 13, 80.
- [22] J. H. Boyera, P. J. A. Frints, *J. Org. Chem.*, **1968**, 4554-4556.

- [23] F. Tiemann, and P. Kruger, *Ber.*, **1884**, 17, 1685.
- [24] F. Tiemann, and E. Niigeli, *Ber.*, **1885**, 18, 1086.
- [25] J. Weise, *Ber.*, **1889**, 22, 2418.
- [26] J. La Rocca, W. Hartung, and N. Levin, *J. Am. Pharm. Assoc*, **1951**, 40, 140.
- [27] H. J. Barber and A. D. Self, British Patent 551,445 (Feb. 23, 1943); U.S. Patent 2,375,611 (May 8, 1945); *Chem. Abstracts*, **1945**, 39, 3544.
- [28] N. Buu-Hoi, M. Welsch, N. Xuong, K. Thang, *Esperientia*, **1954**, 10, 169.
- [29] A. Werner, *Ber.*, **1892**, 25, 27.
- [30] F. Eloy, R. Lenaers and C. Moussebois, *Helv. Chim. Acta*, **1962**, 45, 437
- [31] G. Ponzio, *Gazz. Chim. Ital.*, **1930**, 60, 886.
- [32] G. Ponzio and E. Durio, *Gazz. Chim. Ital.*, **1930**, 60, 436.
- [33] G. Muller, *Ber.*, **1886**, 19, 1669.
- [34] G. Muller, *Ber.*, **1889**, 22, 2401.
- [35] J. Stieglitz, *Ber.*, **1889**, 22, 3148.
- [36] G. Longo and G. Randone, *Gazz. Chim. Ital.*, **1936**, 66, 145.
- [37] G. Ponzio and L. Avogadro, *Gazz. Chim. Ital.*, **1923**, 53, 305.
- [38] G. Ponzio and L. Avogadro, *Gazz. Chim. Ital.*, **1927**, 57, 124.
- [39] J. Nef, *Ann.*, **1891**, 280, 294.
- [40] E. Nordmann, *Ber.*, **1884**, 17, 2746.
- [41] F. Gross, *Ber.*, **1885**, 18, 2477.
- [42] P. Knudsen, *Ber.*, **1885**, 18, 2482.
- [43] H. Wolff, *Ber.*, **1889**, 22, 2395.
- [44] H. Koch, *Ber.*, **1891**, 24, 394.
- [45] P. Kruger, *Ber.*, **1885**, 18, 1053.
- [46] W. H. Powel, *Pure Appl. Chem.*, **1983**, 55, 409-416.

- [47] S. J. Rettig, J. Trotter, *Can. J. Chem.* **1977**, *55*, 3071–3075.
- [48] G. E. K. Branch, D. L. Yabroff, B. Bettmann, *J. Am. Chem. Soc.* **1934**, *56*, 937–941.
- [49] B. Bettman, G. E. K. Branch, D. L. Yabroff, *J. Am. Chem. Soc.* **1934**, *56*, 1865–1870.
- [50] P. R. Westmark, S. J. Gardiner, B. D. Smith, *J. Am. Chem. Soc.* **1996**, *118*, 11093–11100.
- [51] F. R. Bean, J. R. Johnson, *J. Am. Chem. Soc.* **1932**, *54*, 4415–4425.
- [52] T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508–7510.
- [53] H. Tamura, H. Yamazaki, H. Sato, S. Sakaki, *J. Am. Chem. Soc.* **2003**, *125*, 16114–16126.
- [54] H. A. Dieck, R. F. Heck, *J. Org. Chem.* **1975**, *40*, 1083–1090.
- [55] D. S. Matteson, K. Peacock, *J. Org. Chem.* **1963**, *28*, 369–371.
- [56] H. C. Brown, T. E. Cole, *Organometallics*, **1983**, *2*, 1316–1319.
- [57] A. D. Ainley, F. Challenger, *J. Chem. Soc.* **1930**, 2171–2180.
- [58] H. R. Snyder, J. A. Kuck, J. R. Johnson, *J. Am. Chem. Soc.* **1938**, *60*, 105–111.
- [59] H. C. Brown, D. Basavaiah, S. U. Kulkarni, H. D. Lee, E. Negishi, J. Katz, *J. Org. Chem.* **1986**, *51*, 5270–5276.
- [60] H. C. Brown, D. Basavaiah, S. U. Kulkarni, *J. Org. Chem.* **1982**, *47*, 3808–3810.
- [61] M.-L. Huber, J. T. Pinhey, *J. Chem. Soc., Perkin Trans.* **1990**, 721–722.
- [62] W. Ni, H. Fang, G. Springsteen, B. Wang, *J. Org. Chem.* **2004**, *69*, 1999–2007.
- [63] N. Miyaura, A. Suzuki, *J. Chem. Soc., Chem. Commun.* **1979**, 866–867.
- [64] E. J. Pribyl, H. L. Yale, *Bernstein Jack. (Olin Mathieson Corp.)*. Patent No: US 313772, **1964**.

- [65] E. S. Raper, *Acta Cryst.* B34, **1978**, 3281-3284.
- [66] Y. Iwakura, K. Uno, S. Shiraishi, T. Hongu, *Bull. Chem. Soc.*, **1968**, 41, 2954-2959.
- [67] S. G. Tandon, S. C. Bhattacharya, *Anal. Chem.*, **1960**, 32, 194-196.
- [68] J. Lessel, G. Herfs, *Pharmazie*, **2000**, 55(1), 22-26.
- [69] H. Möhrle, J. Lessel, *Archiv der Pharmazie*, **1991**, 324(6), 367-372.
- [70] R. H. Cragg, T. J. Miller, *J. Chem. Soc. Dalton Trans.* **1982**, 907-909.
- [71] L. Nigam, V. D. Gupta, R. C. Mehrotra, *Syn. React. Inorg. Met.* **1980**, 10 (5), 491-507.
- [72] A. B. Goel, V. D. Gupta, *J. Indian Chem. Soc.* **1977**, 54 (6), 581-585.
- [73] A. B. Goel, V. D. Gupta, *J. Organomet. Chem.* **1974**, 77 (2), 183-188.
- [74] H. L. Yale, *J. Heterocyclic Chem.*, **1971**, 8 (2), 205-208.
- [75] H. A. Oskooie, M. M. Heravi, Z. Jaddi, *Phosphorus, Sulfur and Silicon*, **2005**, 180, 1993-1996.
- [76] K. Niknam, B. Karami, A. R. Kiasat, *Bull. Korean Chem. Soc.*, **2005**, 26, 6, 975-978.
- [77] N. Iranpoor, H. Firouzabadi, G. Aghapour, *Synth. Commun.*, **2002**, 32, 16, 2535-2541.
- [78] S. Chandrasekhar, K. Gopalaiah, *Tetrahedron Lett.*, **2001**, 42, 45, 8123-8125.
- [79] T. L. Ho, C. M. Wong, *Synth. Commun.*, **1975**, 5, 4, 299-304.
- [80] Y. Dürüst, C. Altuğ, F. Kılıç, *Phosphorus, Sulfur and Silicon*, **2007** (in press), 182, 2.
- [81] N. Dürüst, Y. Dürüst, İ. Meriç, *Turk J. Chem.*, **2002**, 26, 833-838.
- [82] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.*, **1991**, 97, 165-195.

APPENDICES

APPENDIX A.

The IR spectra of amidoximes (**10a-n**, **11o-u**, **12o-u**, **13p**, **14o**, **14p**, **15v**, **15w** and **15u**) and 3,4,5-trisubstituted-4,5-dihydro-1,2,4,5-oxadiazaboroles (**16a-n**, **17o-u**, **18o-u**, **19p**, **20o**, **20p**, **21v**, **21w** and **21u**), the ^1H -NMR, ^{13}C -NMR and mass spectra of 3,4,5-trisubstituted-4,5-dihydro-1,2,4,5-oxadiazaboroles (**16a-n**, **17o-u**, **18o-u**, **19p**, **20o**, **20p**, **21v**, **21w** and **21u**) and the X-Ray patterns of **16c**, **16l**, **16n** and **21w**.

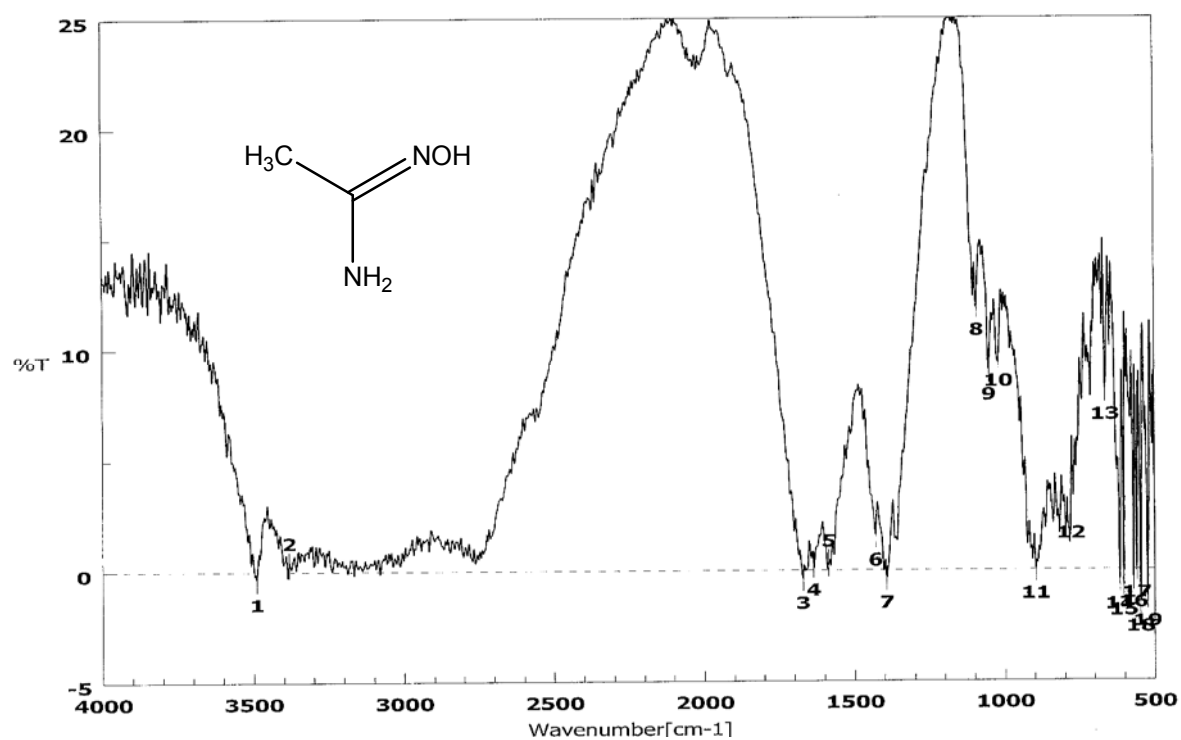


Figure 36: The IR spectrum of 10a

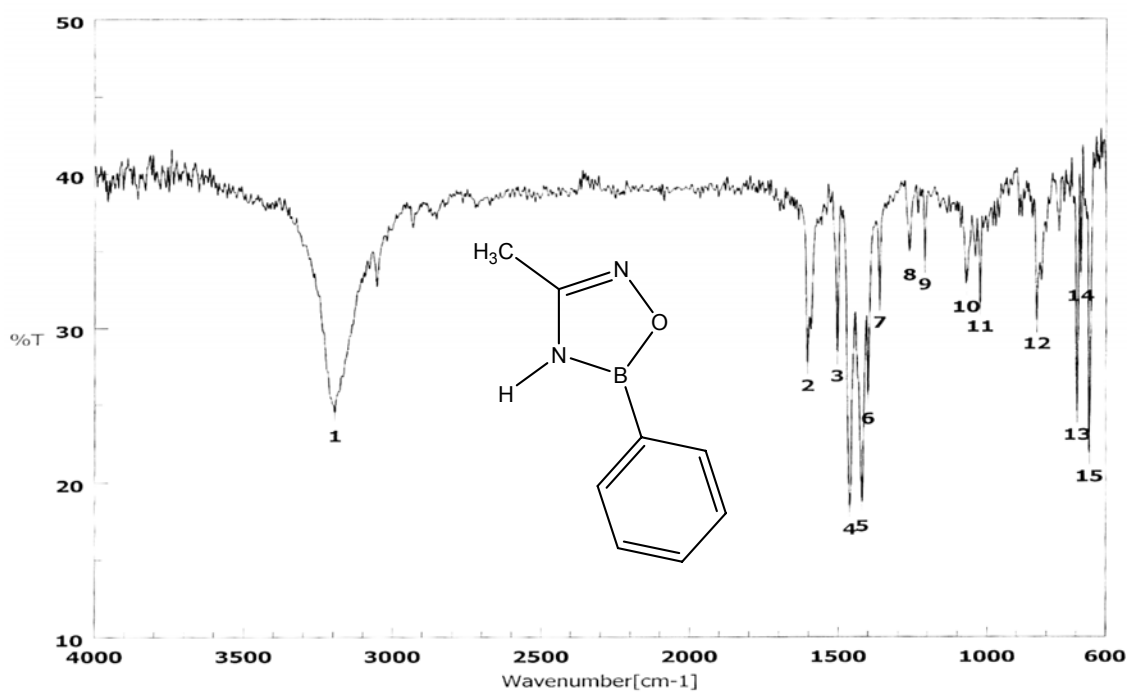


Figure 37A: The IR spectrum of 16a

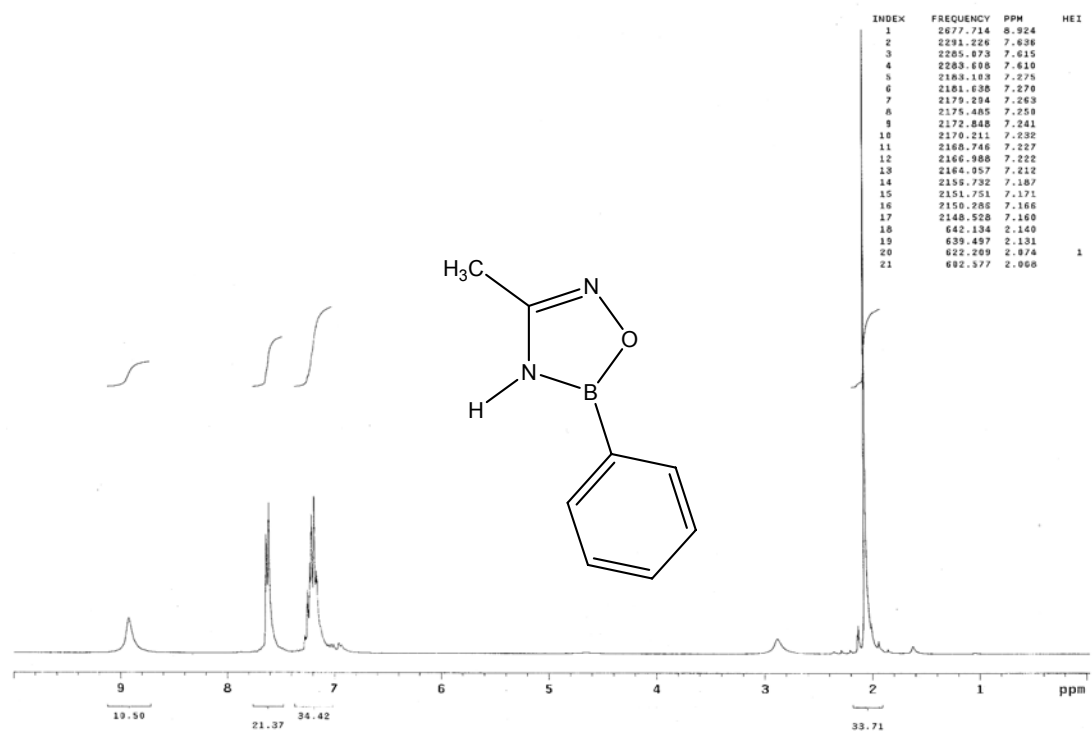


Figure 37B: The ^1H -NMR spectrum of **16a**

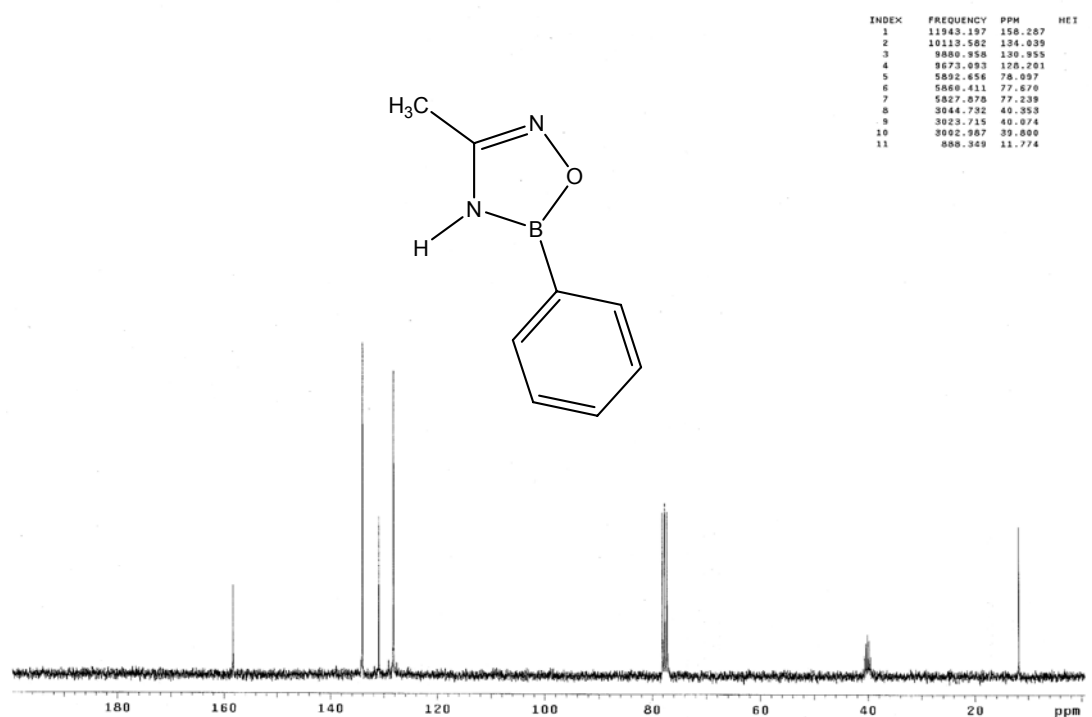


Figure 37C: The ^{13}C -NMR spectrum of **16a**

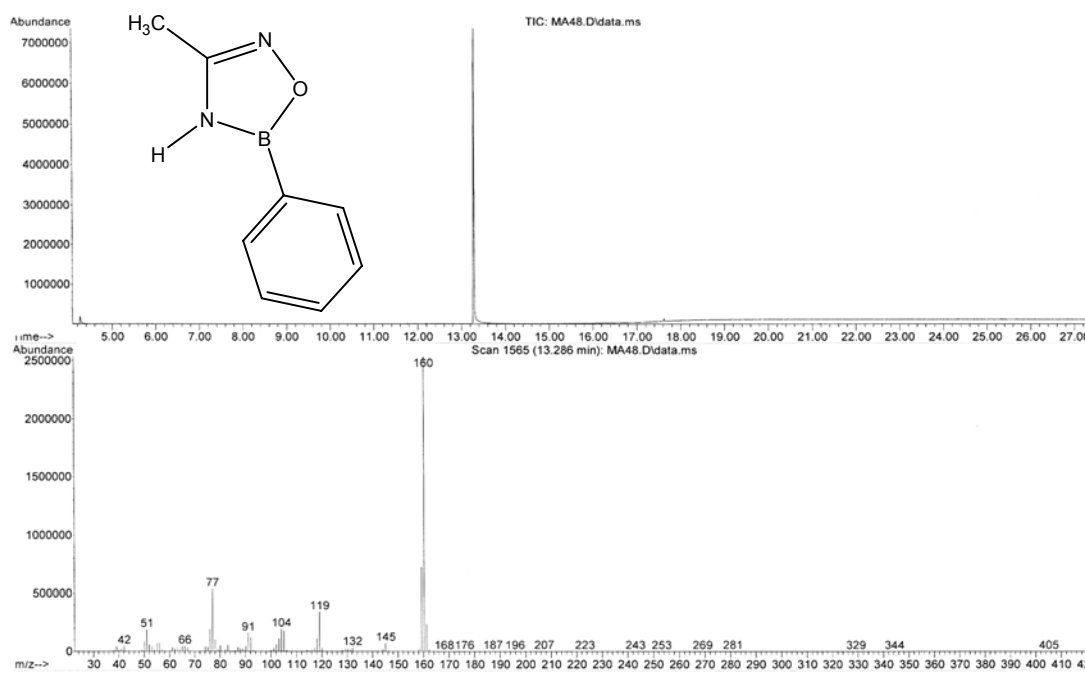


Figure 37D: The mass spectrum of **16a**

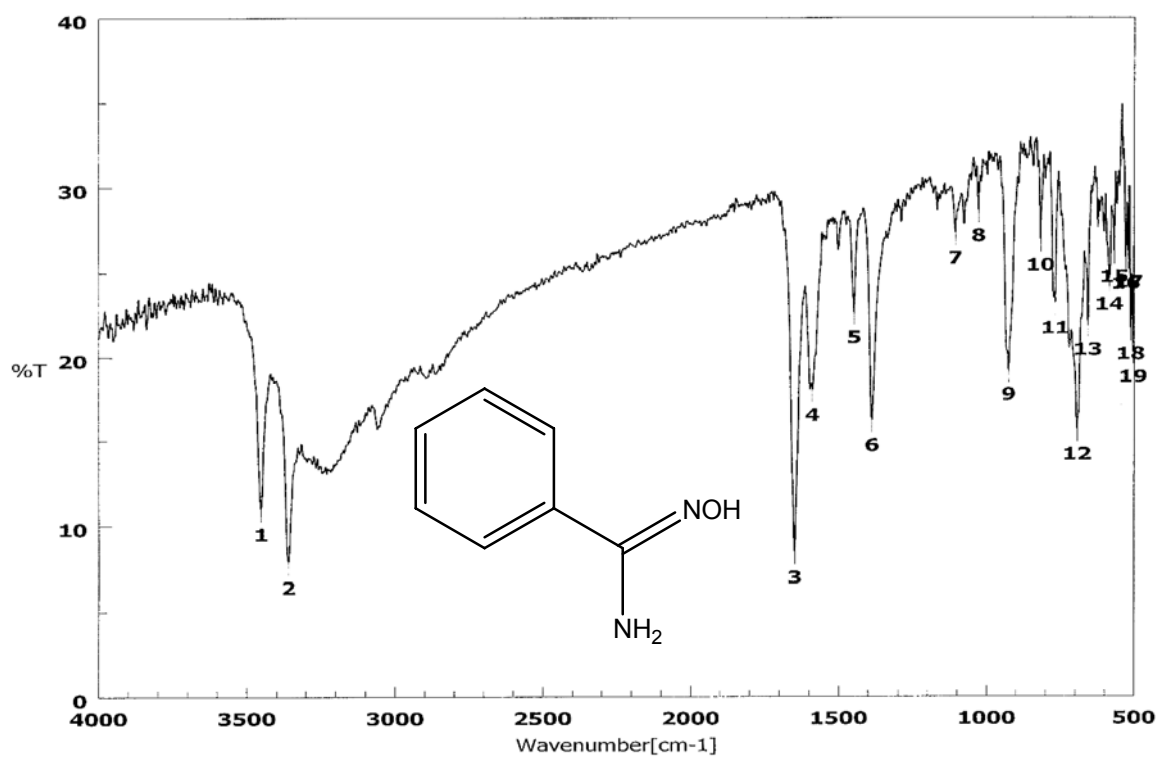


Figure 38: The IR spectrum of **10b**

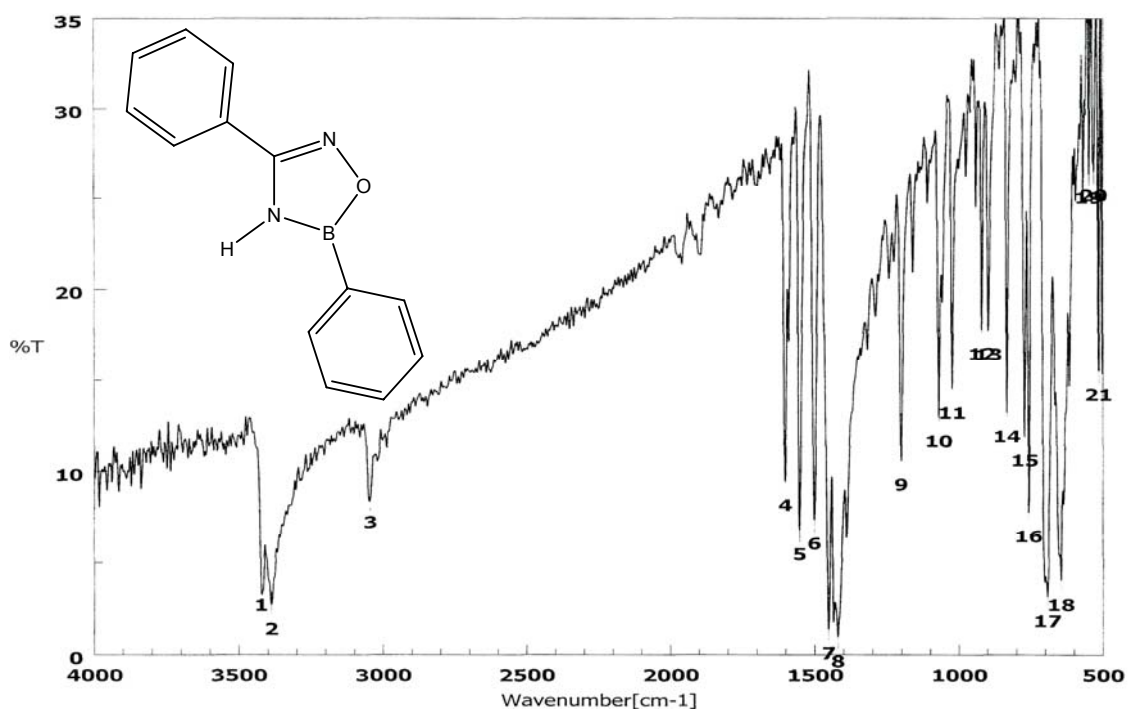


Figure 39A: The IR spectrum of **16b**

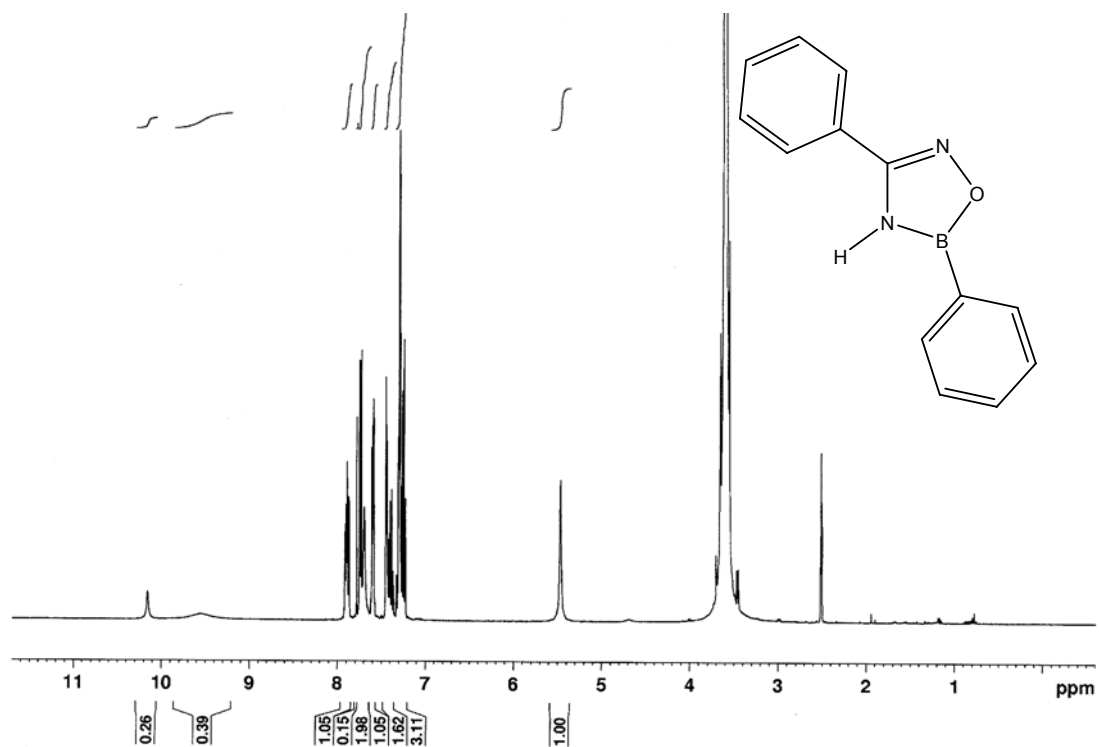


Figure 39B: The ^1H -NMR spectrum of **16b**

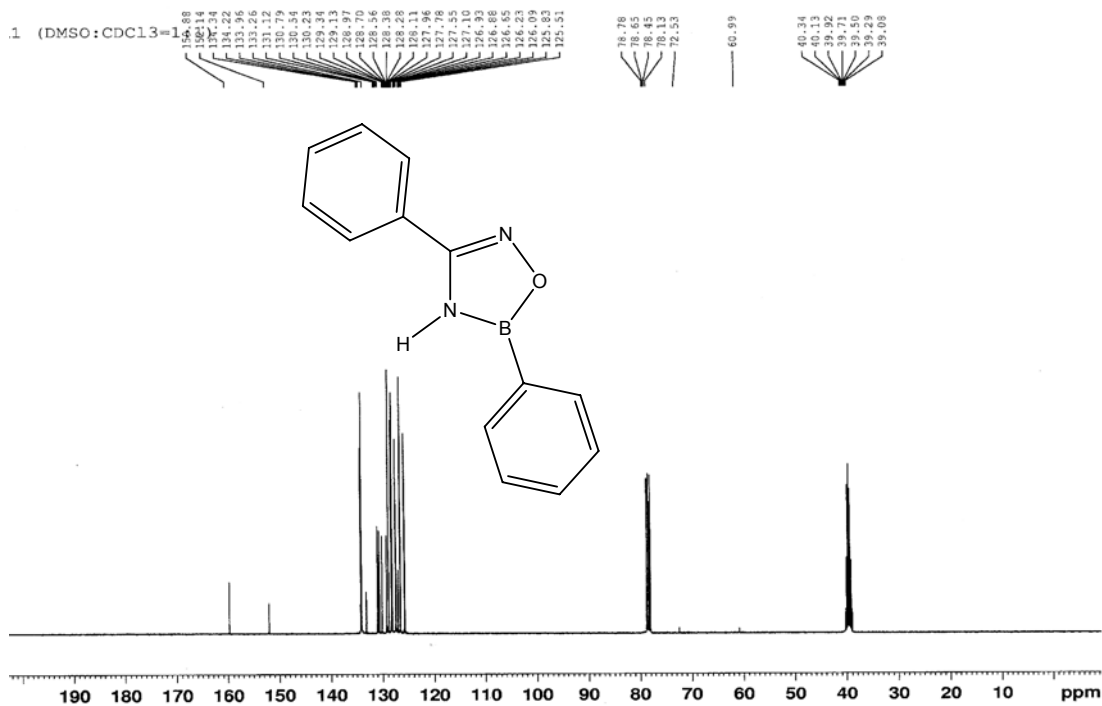


Figure 39C: The ^{13}C -NMR spectrum of **16b**

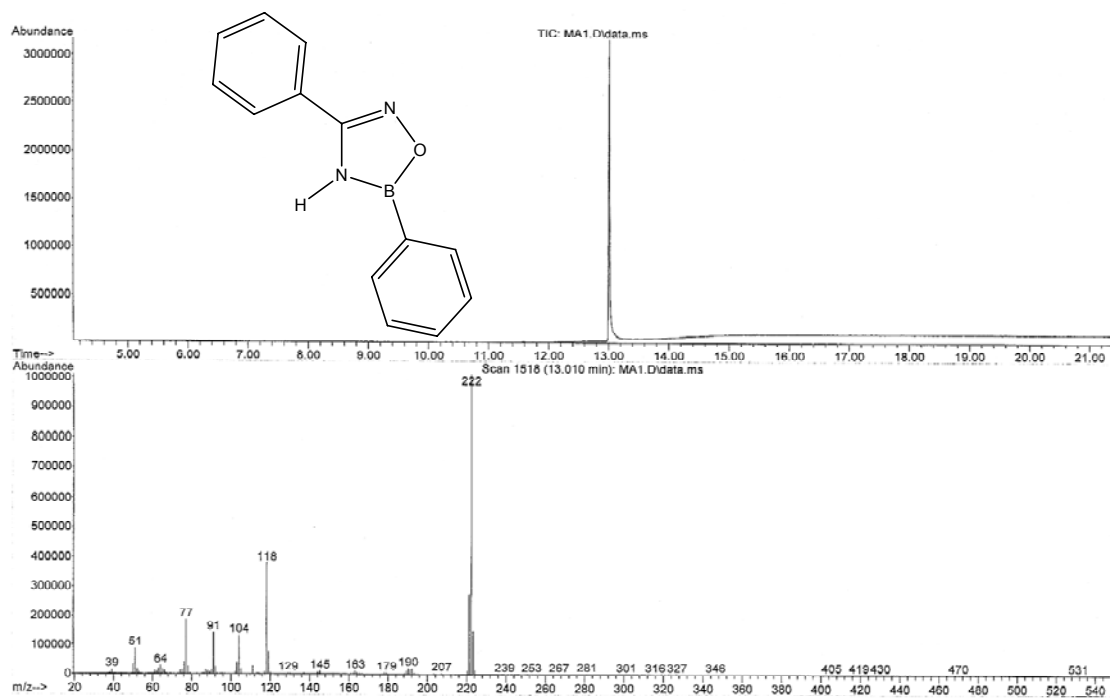


Figure 39D: The mass spectrum of **16b**

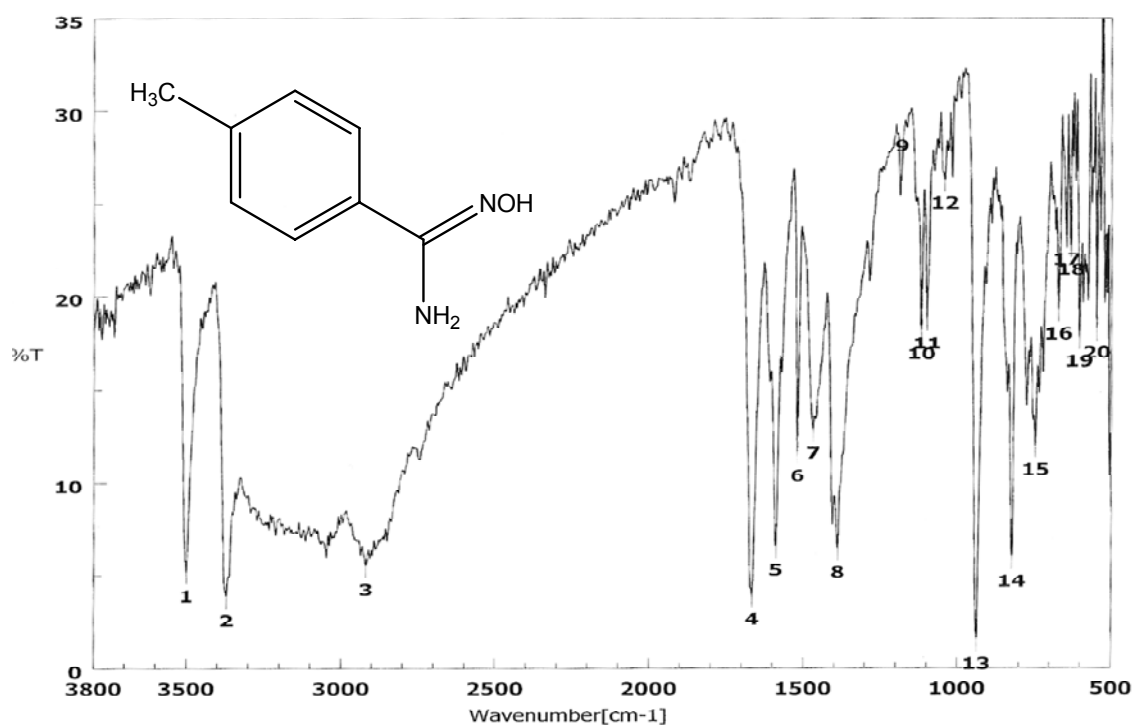


Figure 40: The IR spectrum of **10c**

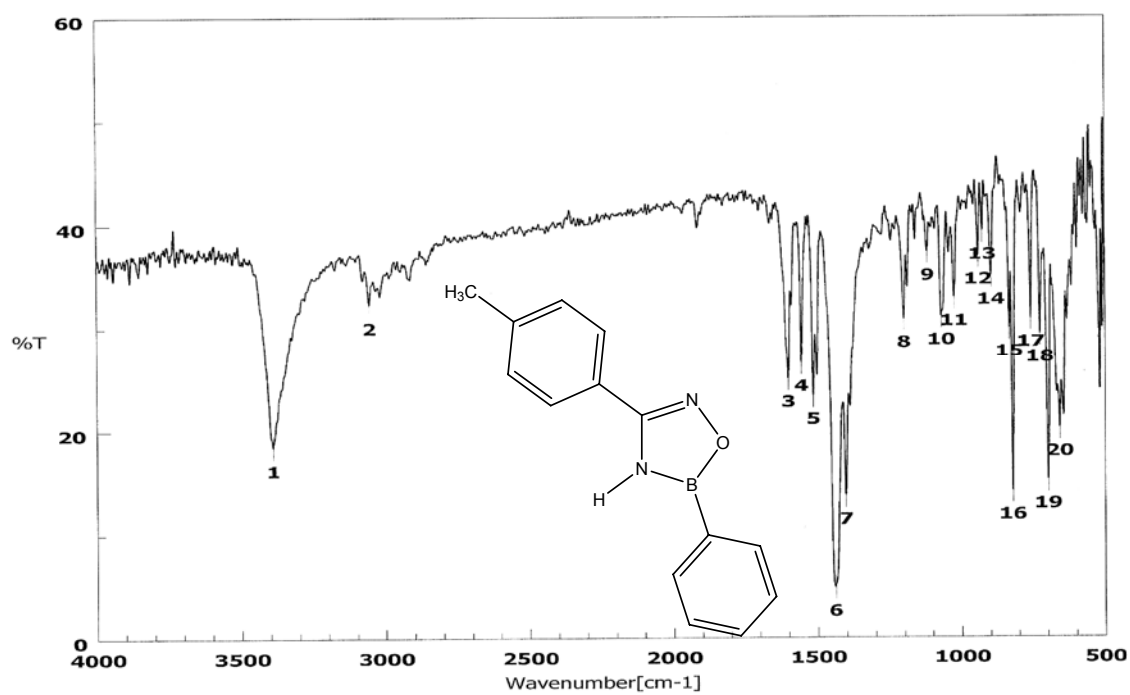


Figure 41A: The IR spectrum of **16c**

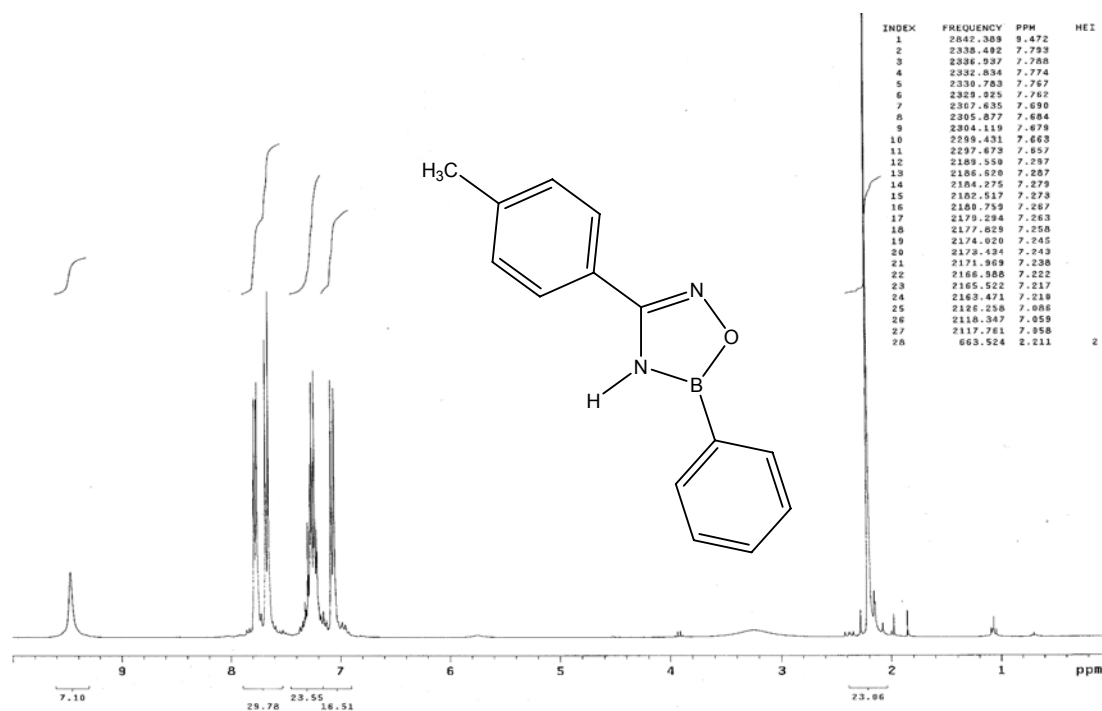


Figure 41B: The ^1H -NMR spectrum of **16c**

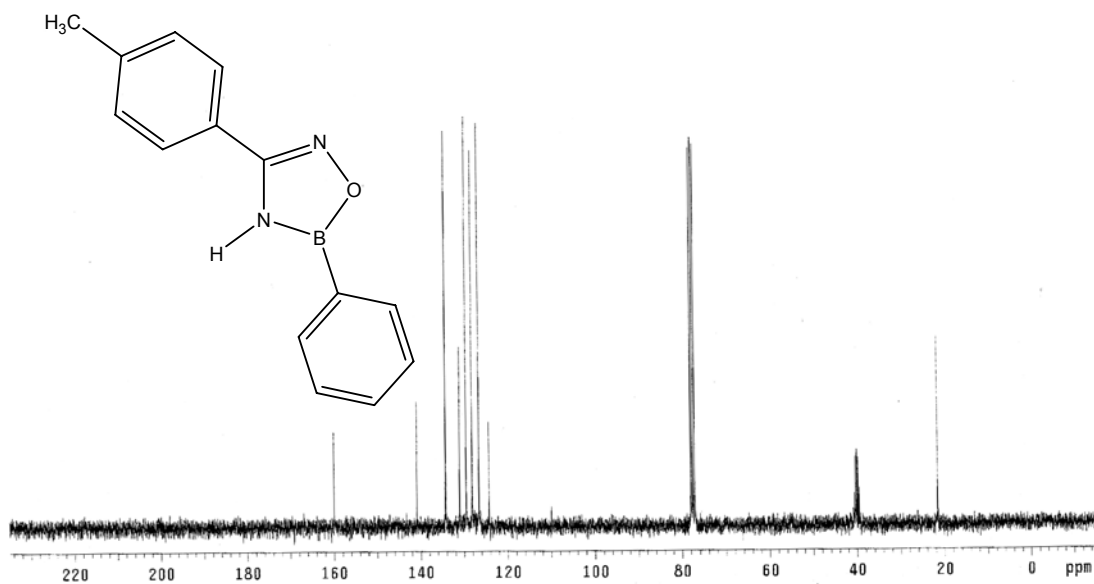


Figure 41C: The ^{13}C -NMR spectrum of **16c**

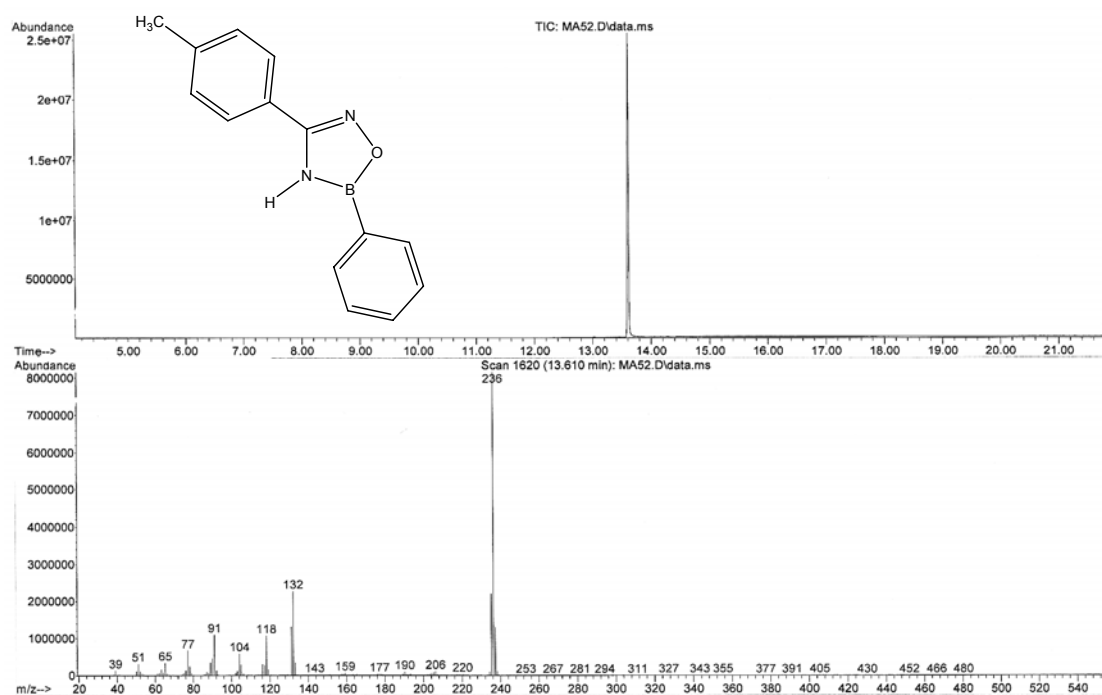


Figure 41D: The mass spectrum of **16c**

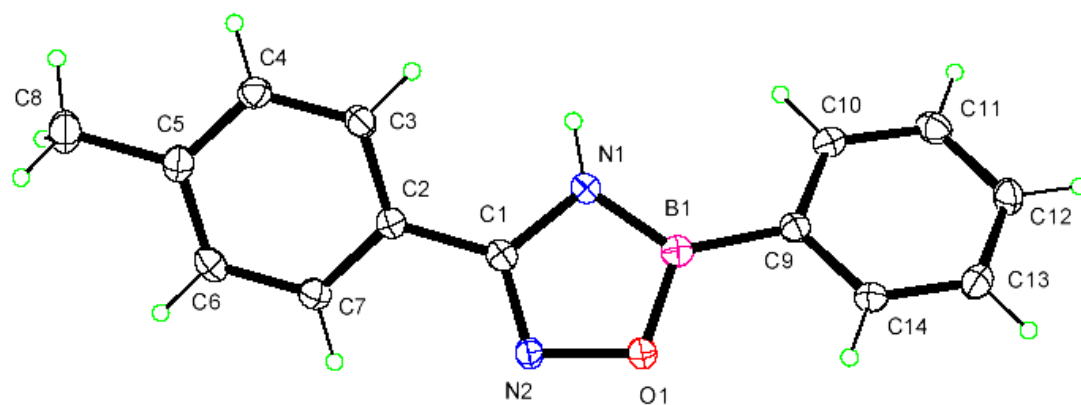


Figure 41E: The X-Ray pattern of **16c**

Crystal data

$C_{14}H_{13}BN_2O$	D_m not measured
$M_r = 236.07$	Mo K_α radiation
Monoclinic	$\lambda = 0.71073 \text{ \AA}$
$P2_1/n$	Cell parameters from 2936 reflections
$a = 5.5346 (10) \text{ \AA}$	$\theta = 2.5\text{--}29.1^\circ$
$b = 18.142(4) \text{ \AA}$	$\mu = 0.082 \text{ mm}^{-1}$
$c = 12.163 (2) \text{ \AA}$	$T = 90 \text{ K}$
$\beta = 99.327 (12)^\circ$	Lath
$V = 1205.1 (12) \text{ \AA}^3$	Colorless
$Z = 4$	$0.40 \times 0.17 \times 0.03 \text{ mm}$
$D_x = 1.301 \text{ Mg m}^{-3}$	Crystal source: local laboratory

Data collection

KappaCCD (with Oxford Cryostream)	$I > 2\sigma(I)$
diffractometer	$R_{\text{int}} = 0.035$
ω scans with κ offsets	$\theta_{\text{max}} = 29.1^\circ$
Absorption correction: none	$h = -7 \rightarrow 7$
15031 measured reflections	$k = -20 \rightarrow 24$
3239 independent reflections	$l = -16 \rightarrow 16$
2385 reflections with	intensity decay: $< 2 \%$

Table 2: Crystal data of **16c**

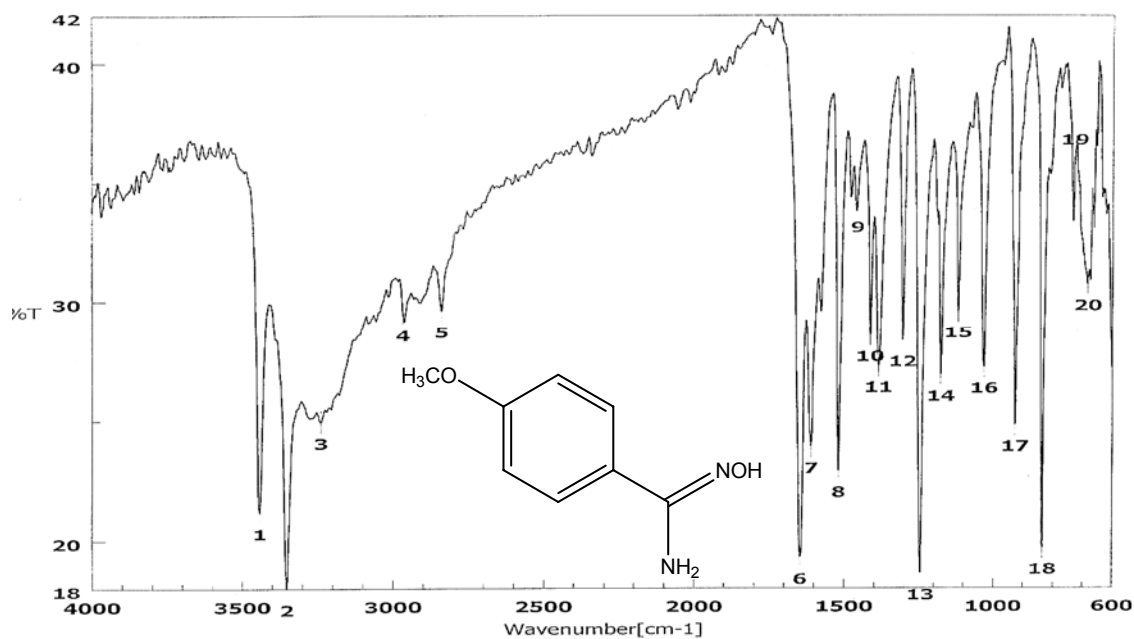


Figure 42: The IR spectrum of **10d**

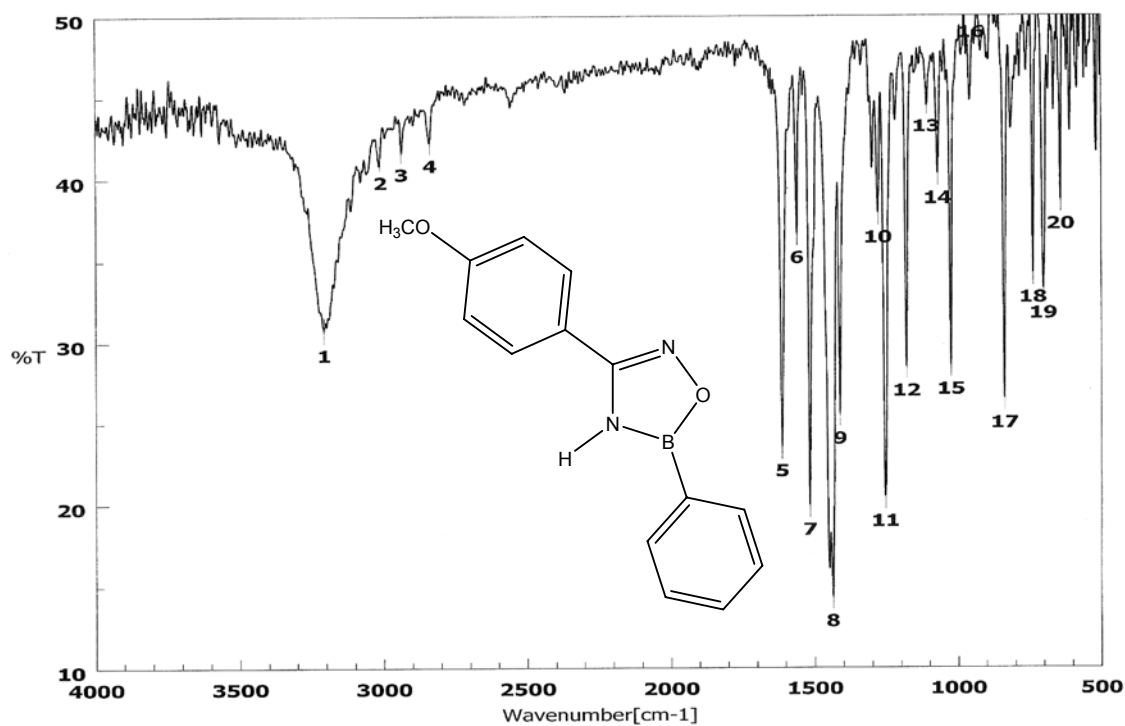


Figure 43A: The IR spectrum of **16d**

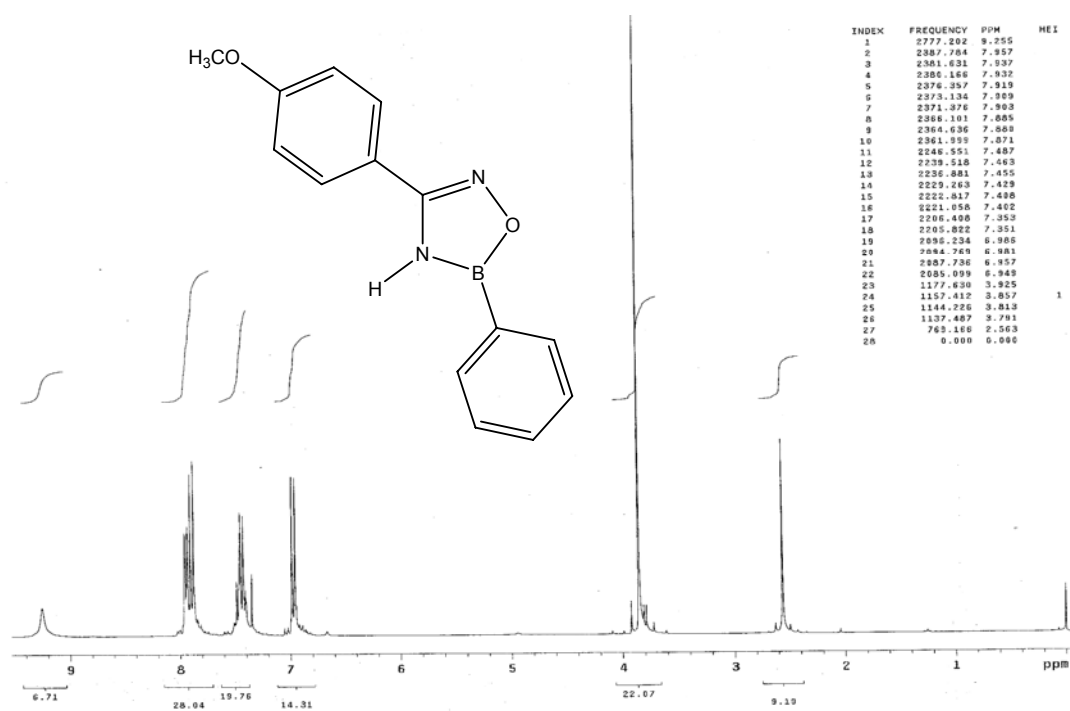


Figure 43B: The ^1H -NMR spectrum of **16d**

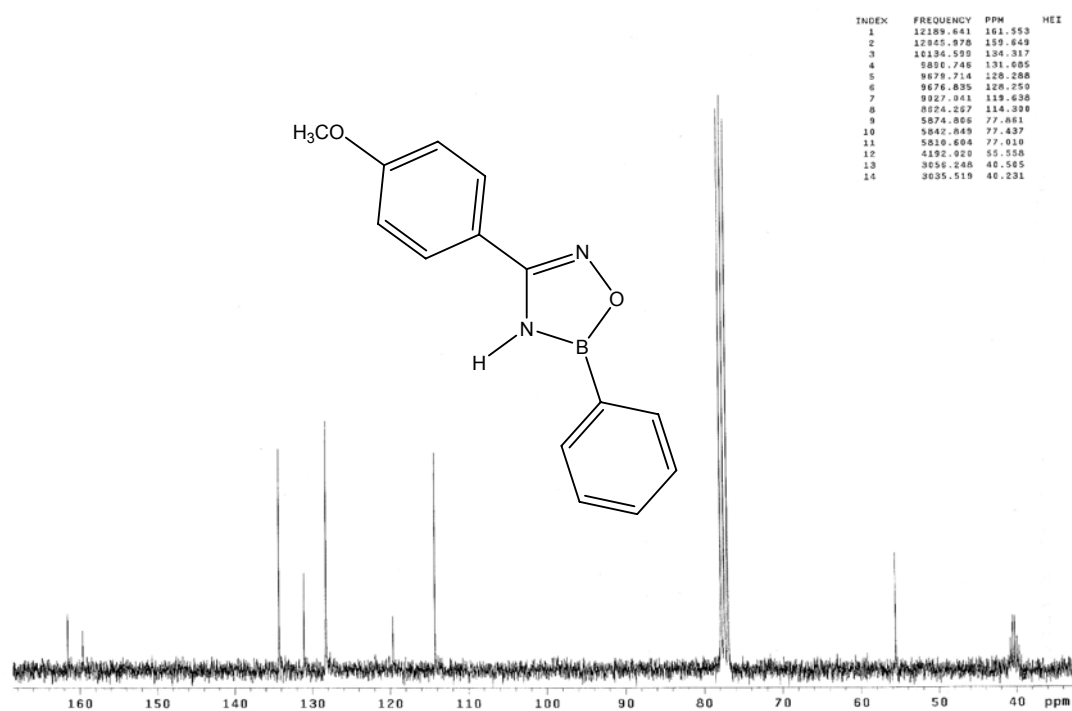


Figure 43C: The ^{13}C -NMR spectrum of **16d**

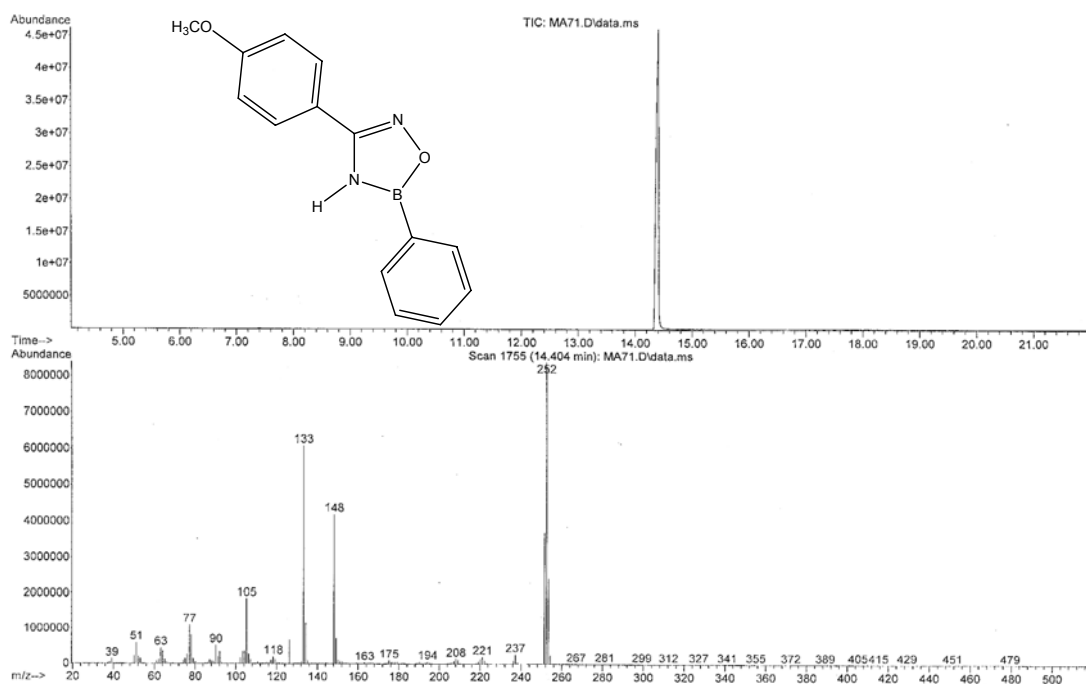


Figure 43D: The mass spectrum of **16d**

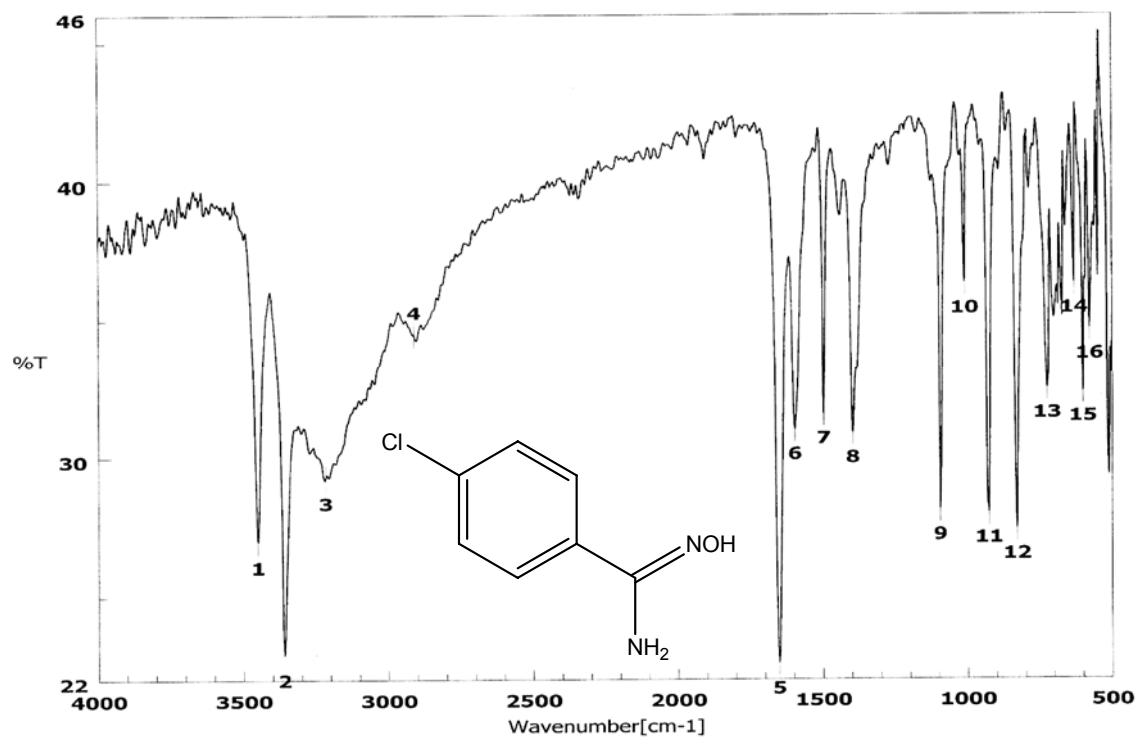


Figure 44: The IR spectrum of **10e**

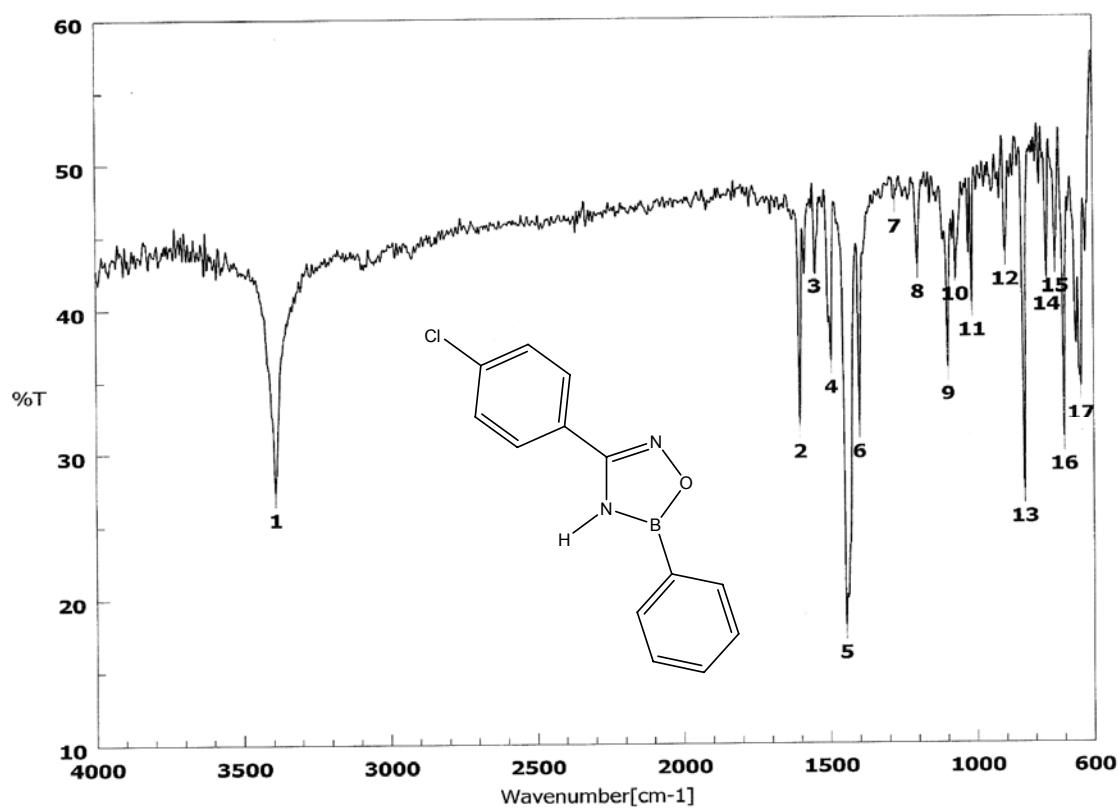


Figure 45A: The IR spectrum of **16e**

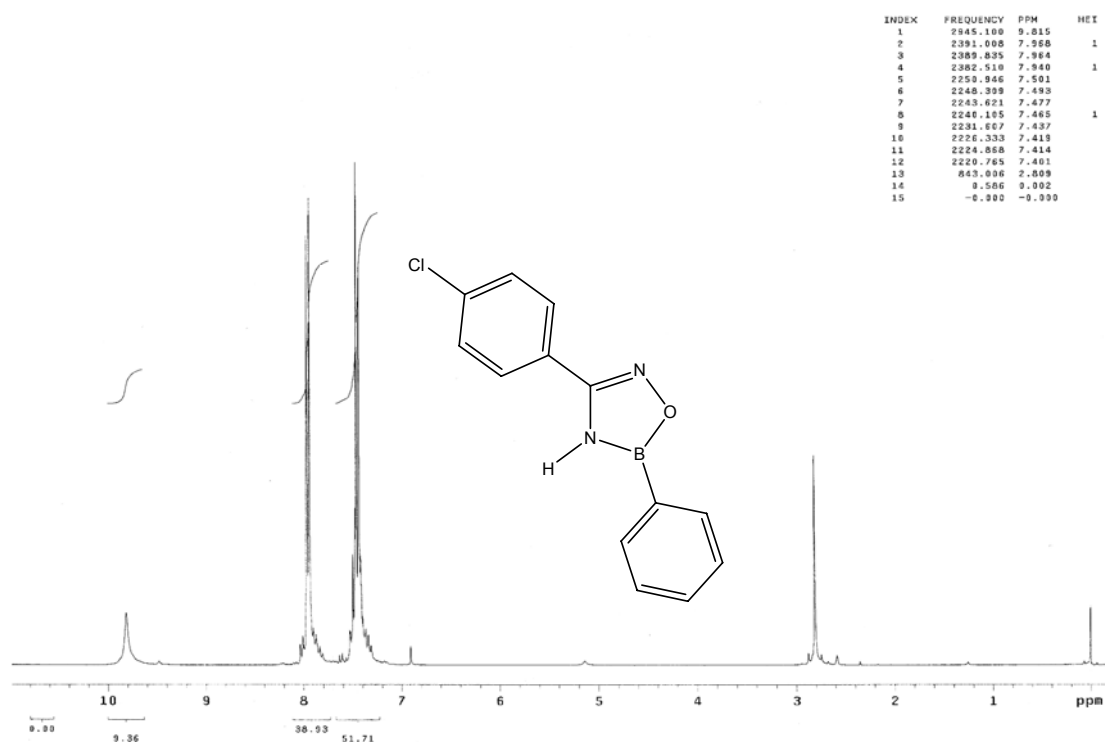


Figure 45B: The ^1H -NMR spectrum of **16e**

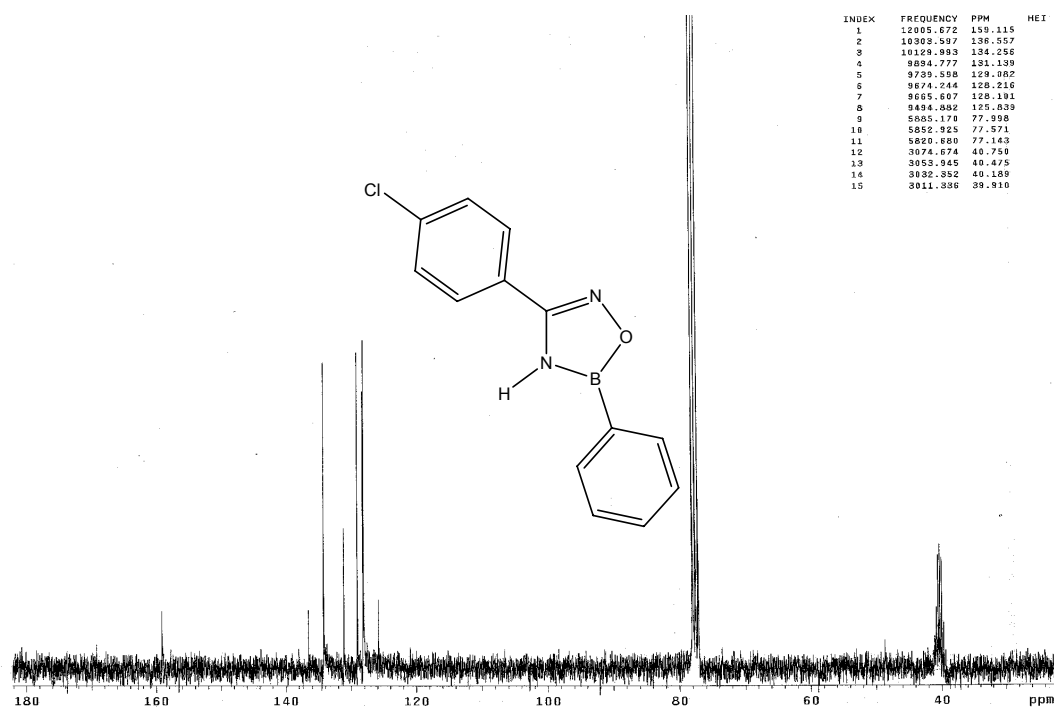


Figure 45C: The ^{13}C -NMR spectrum of **16e**

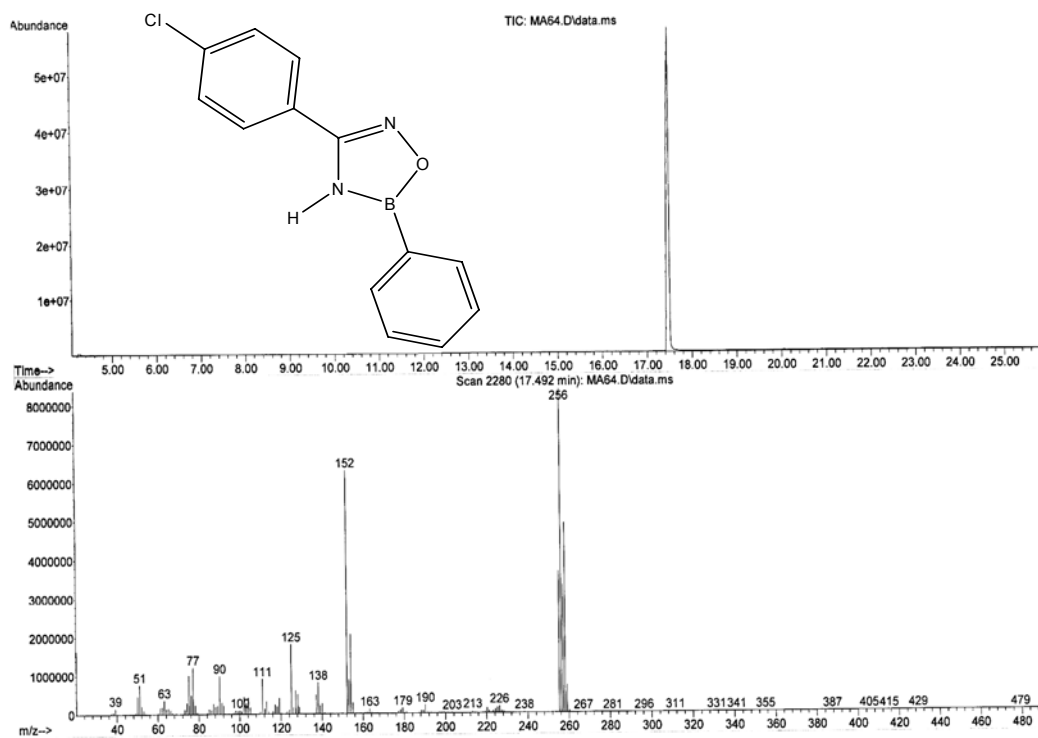


Figure 45D: The mass spectrum of **16e**

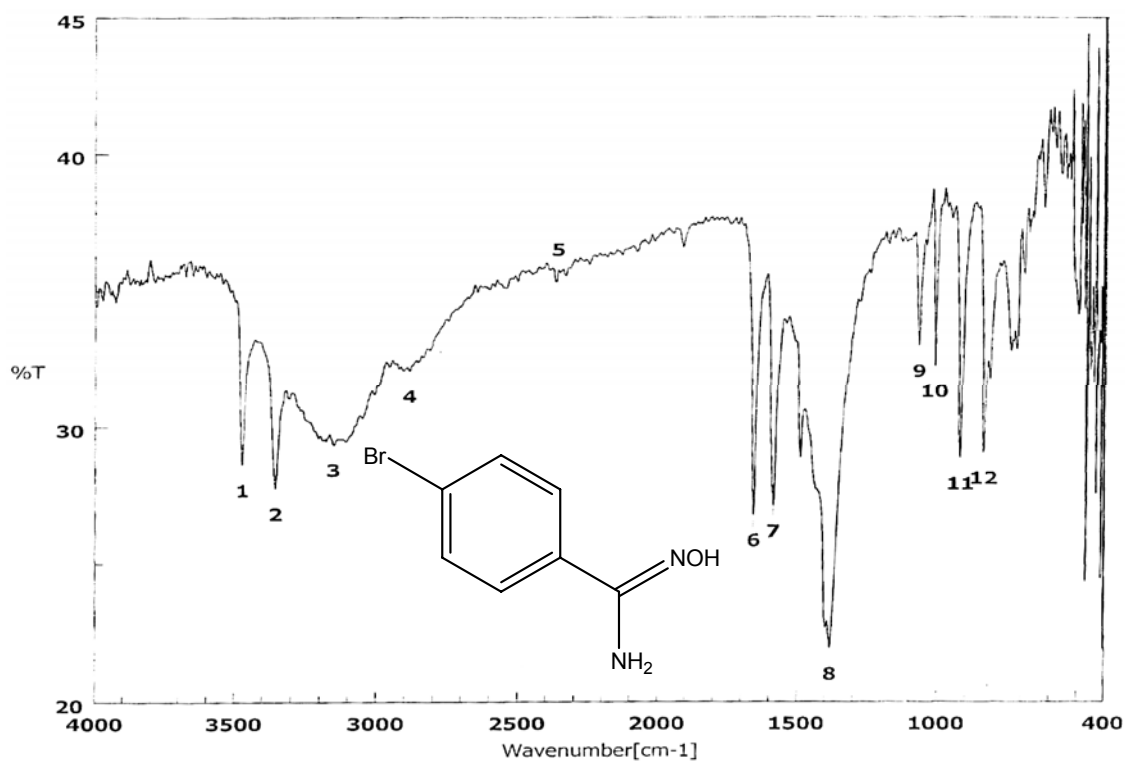


Figure 46: The IR spectrum of **10f**

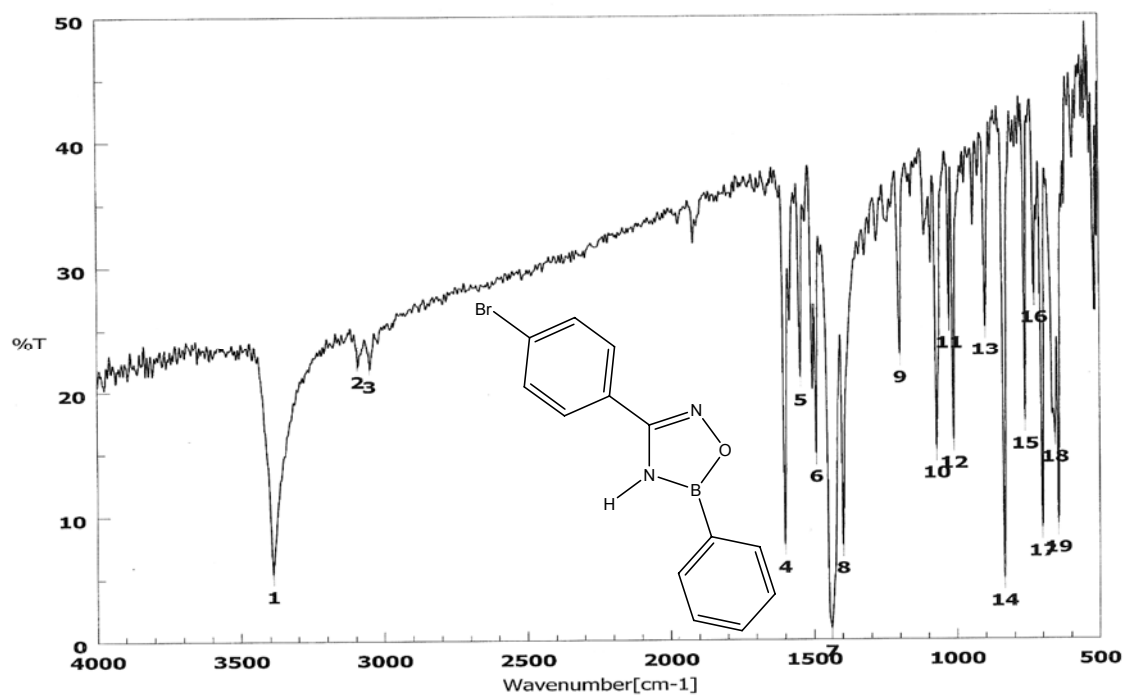


Figure 47A: The IR spectrum of **16f**

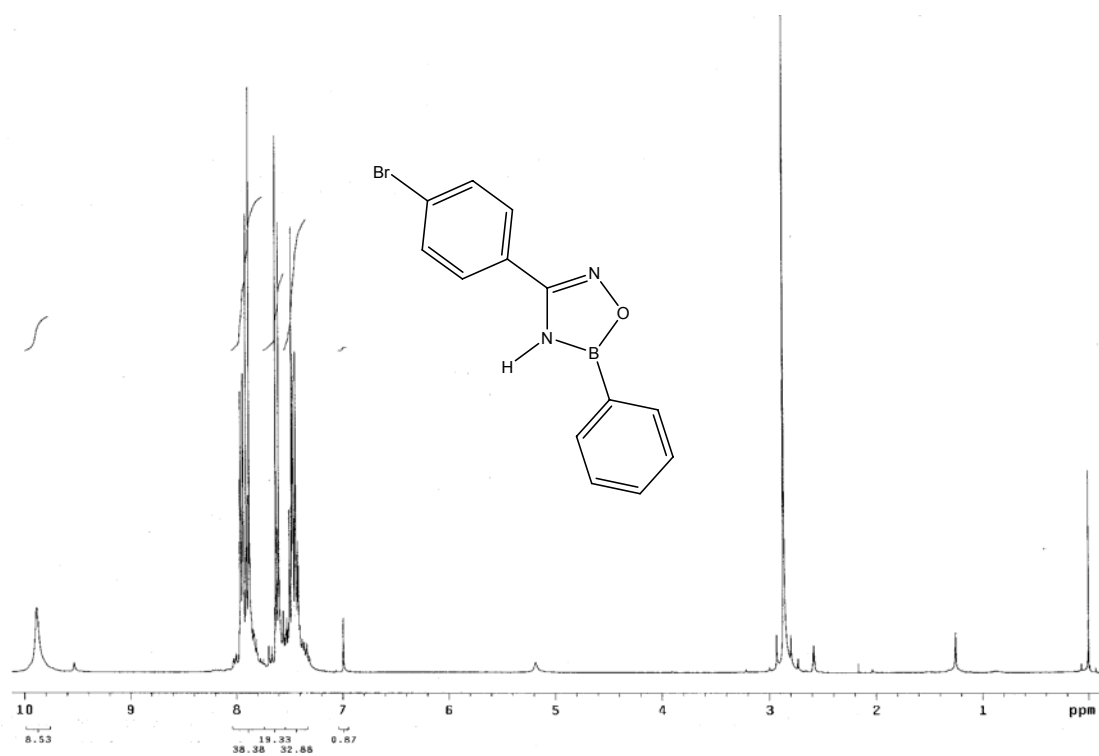


Figure 47B: The ¹H-NMR spectrum of **16f**

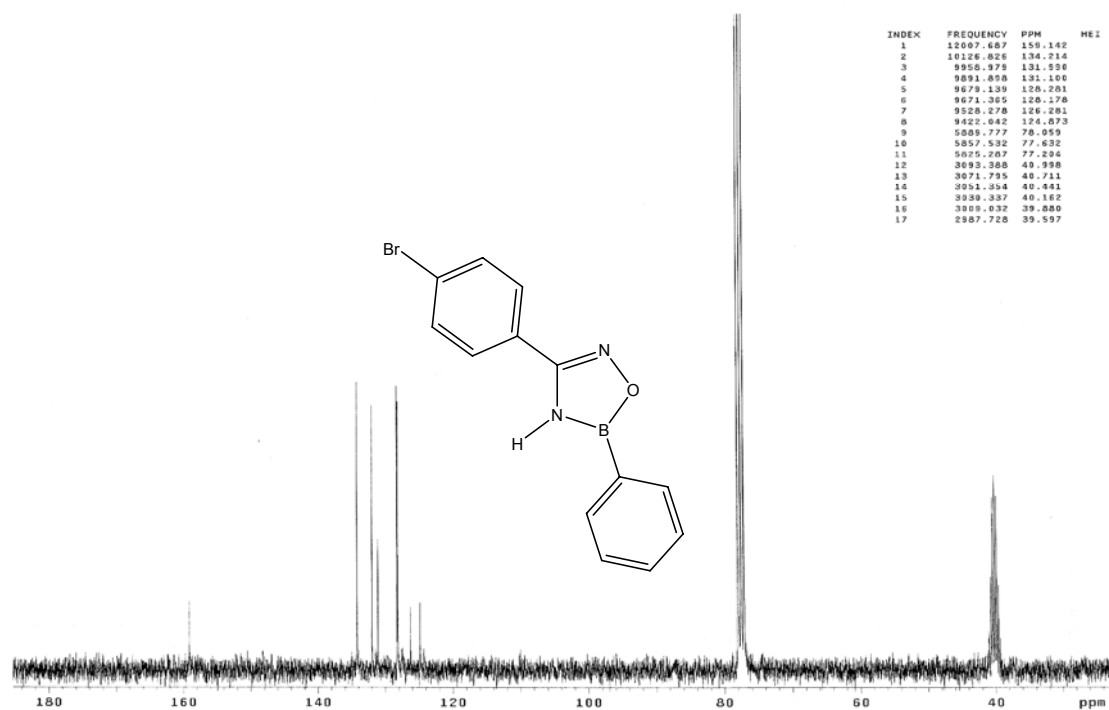


Figure 47C: The ¹³C-NMR spectrum of **16f**

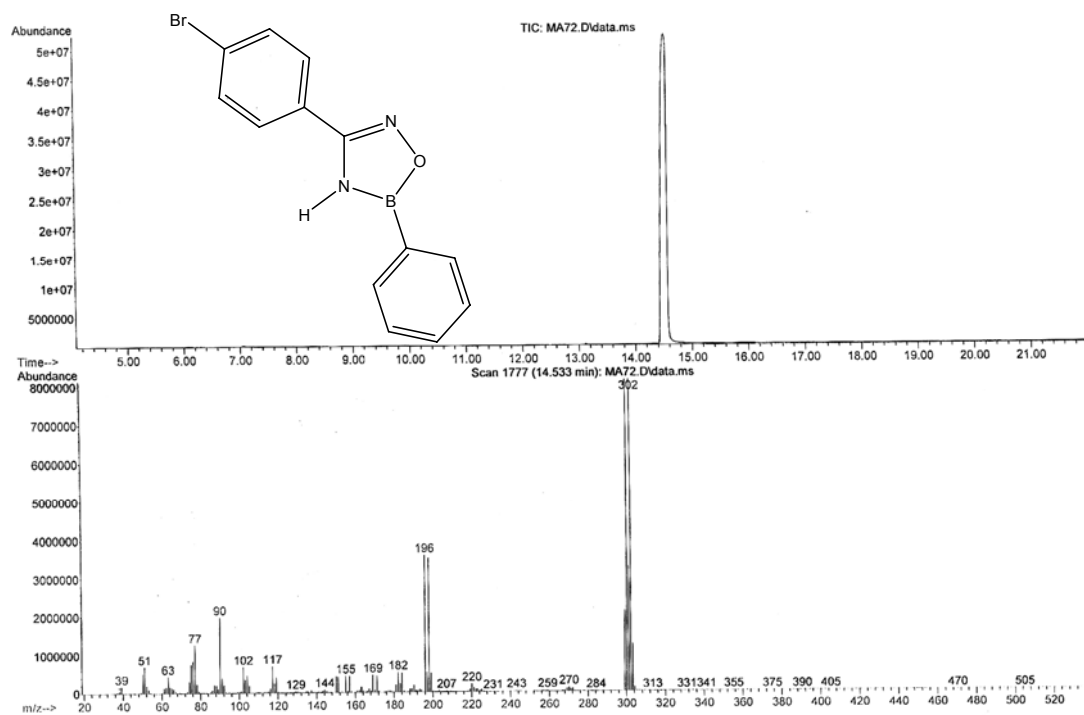


Figure 47D: The mass spectrum of 16f

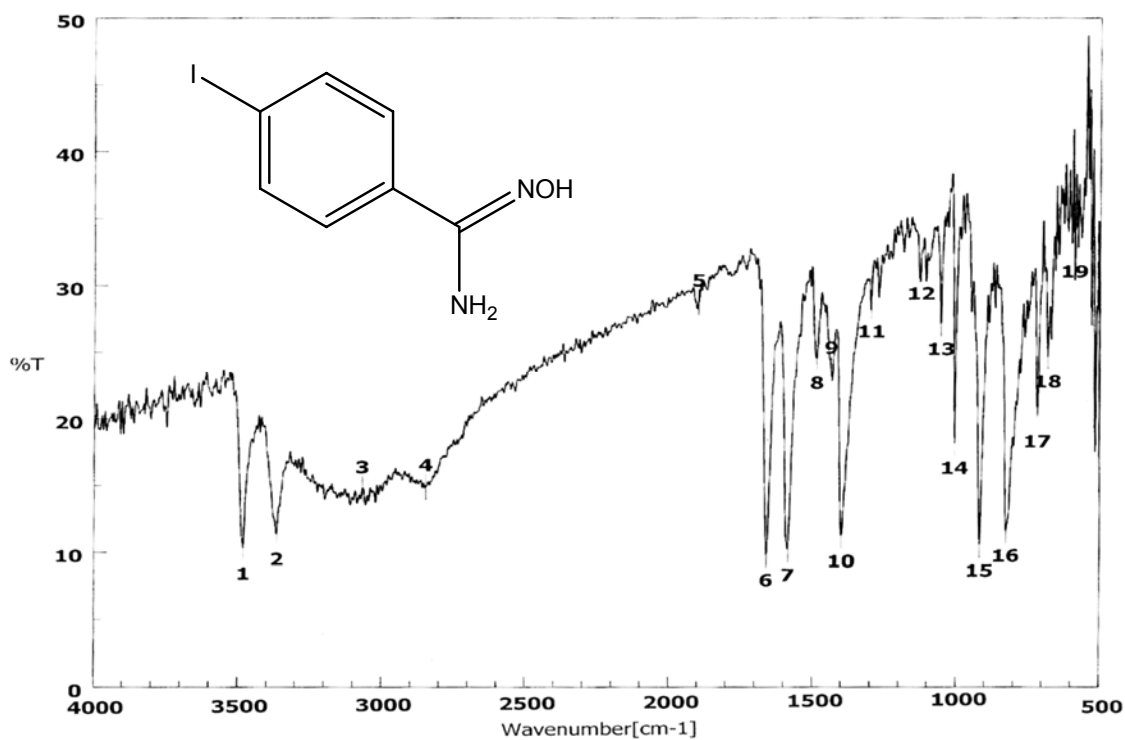


Figure 48: The IR spectrum of 10g

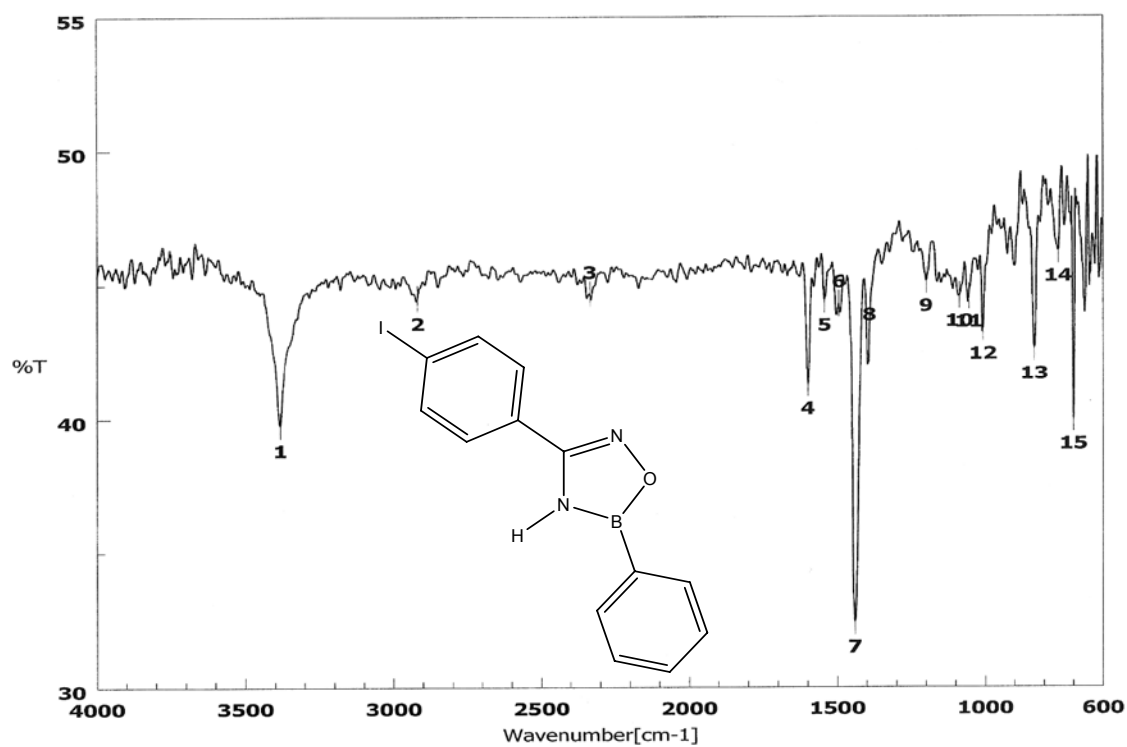


Figure 49A: The IR spectrum of 16g

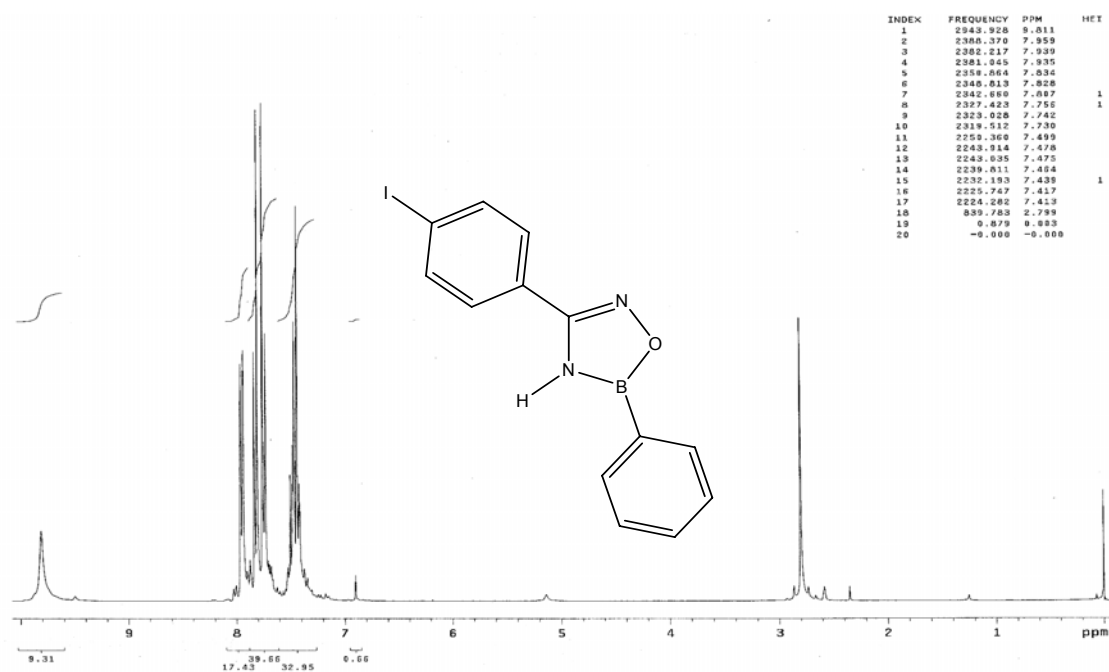


Figure 49B: The ¹H-NMR spectrum of 16g

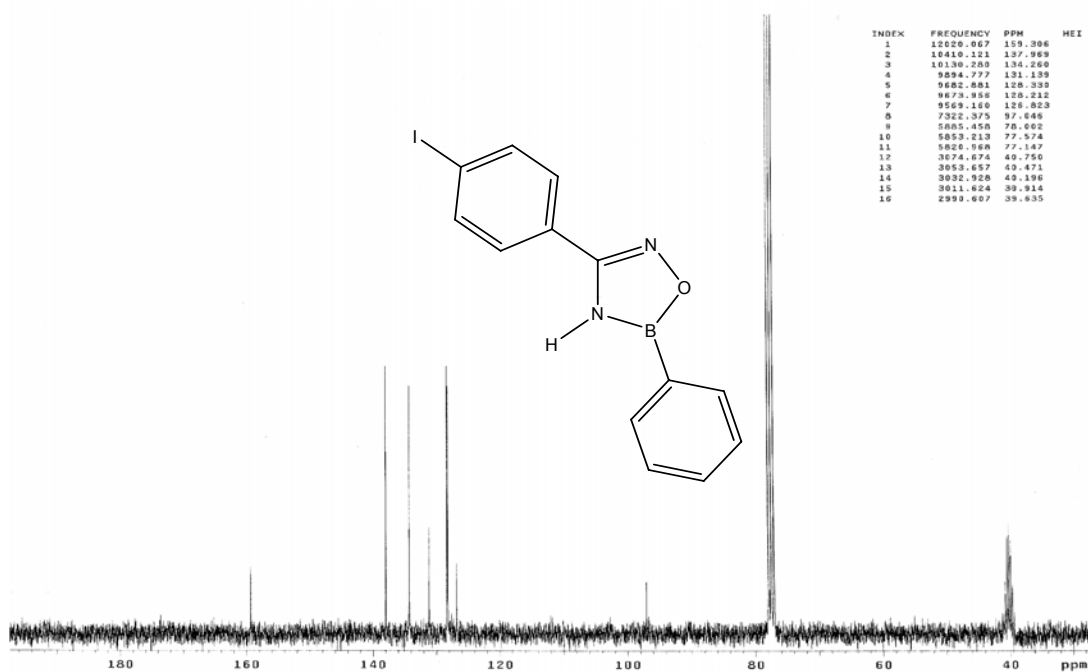


Figure 49C: The ^{13}C -NMR spectrum of **16g**

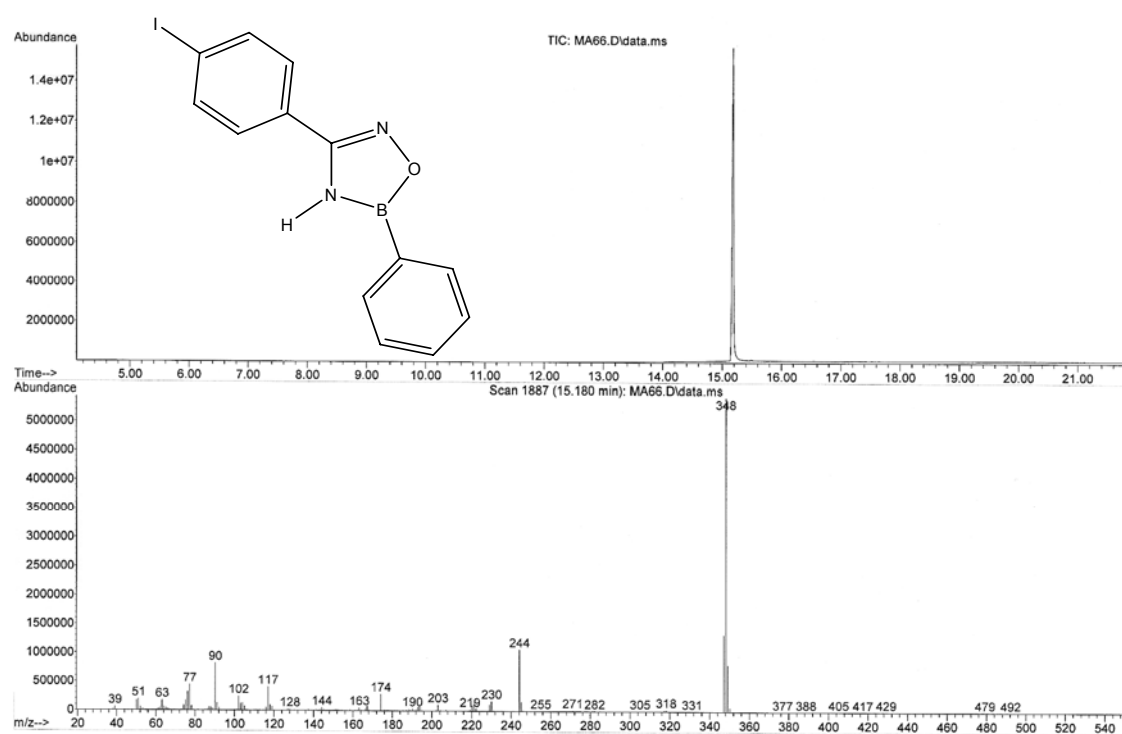


Figure 49D: The mass spectrum of **16g**

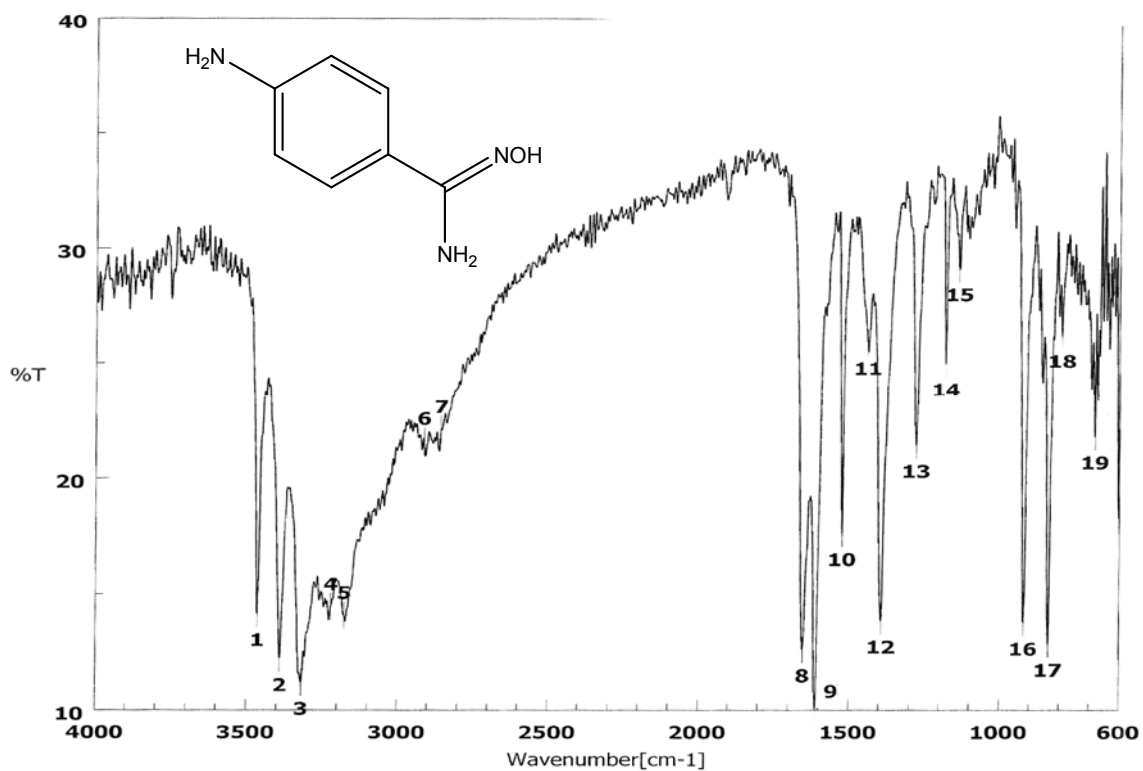


Figure 50: The IR spectrum of **10h**

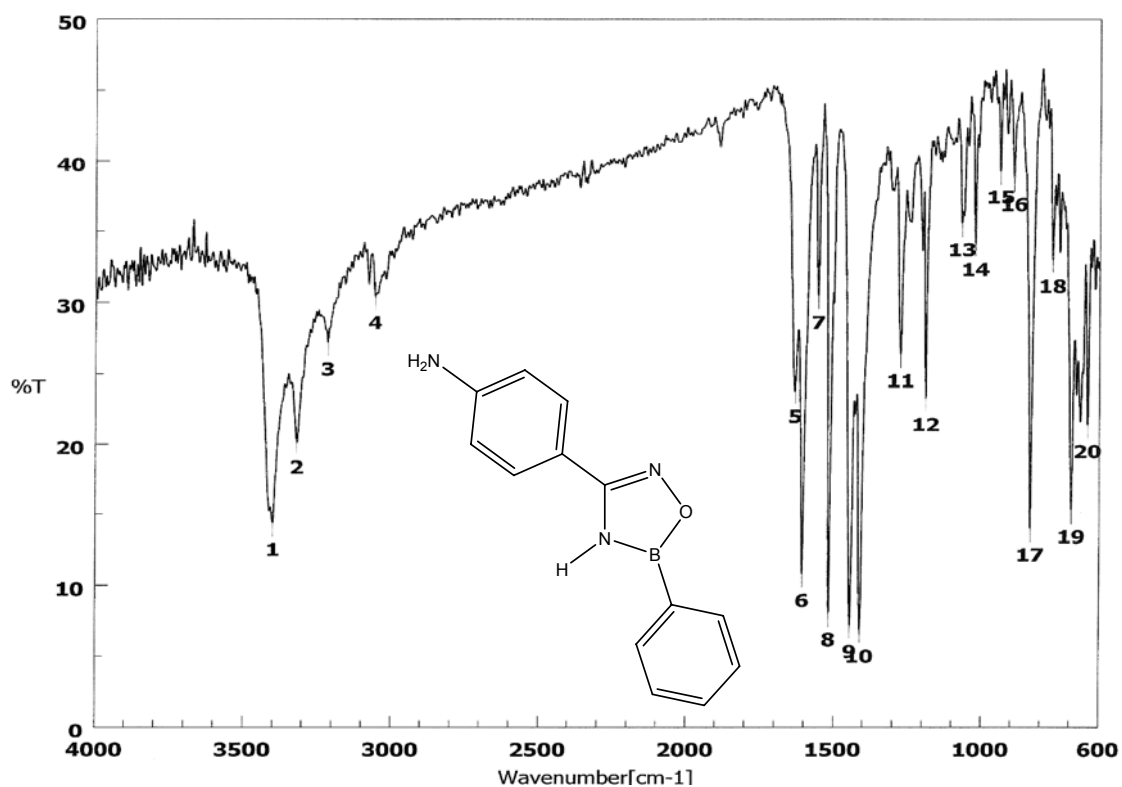


Figure 51A: The IR spectrum of **16h**

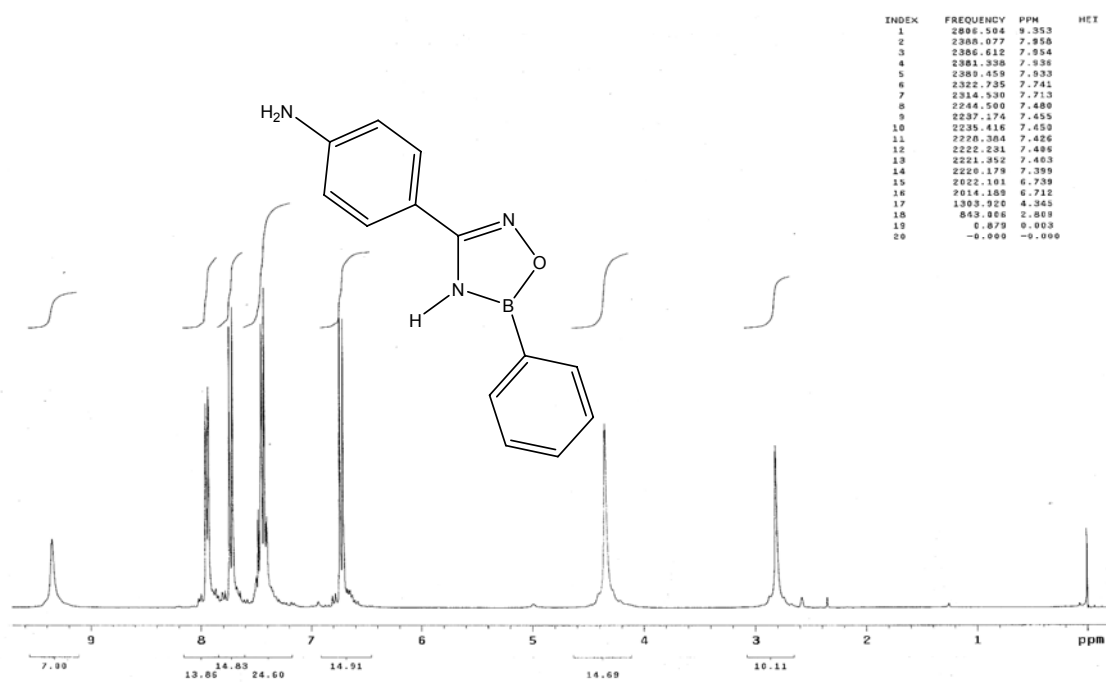


Figure 51B: The ^1H -NMR spectrum of **16h**

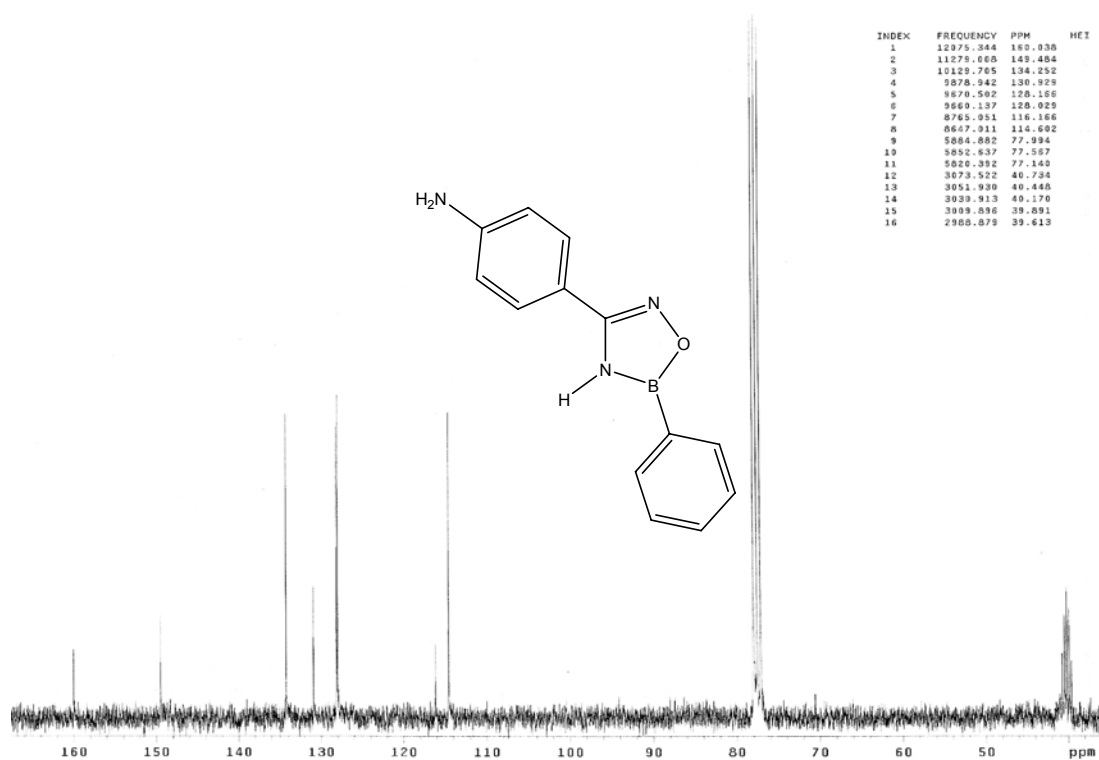


Figure 51C: The ^{13}C -NMR spectrum of **16h**

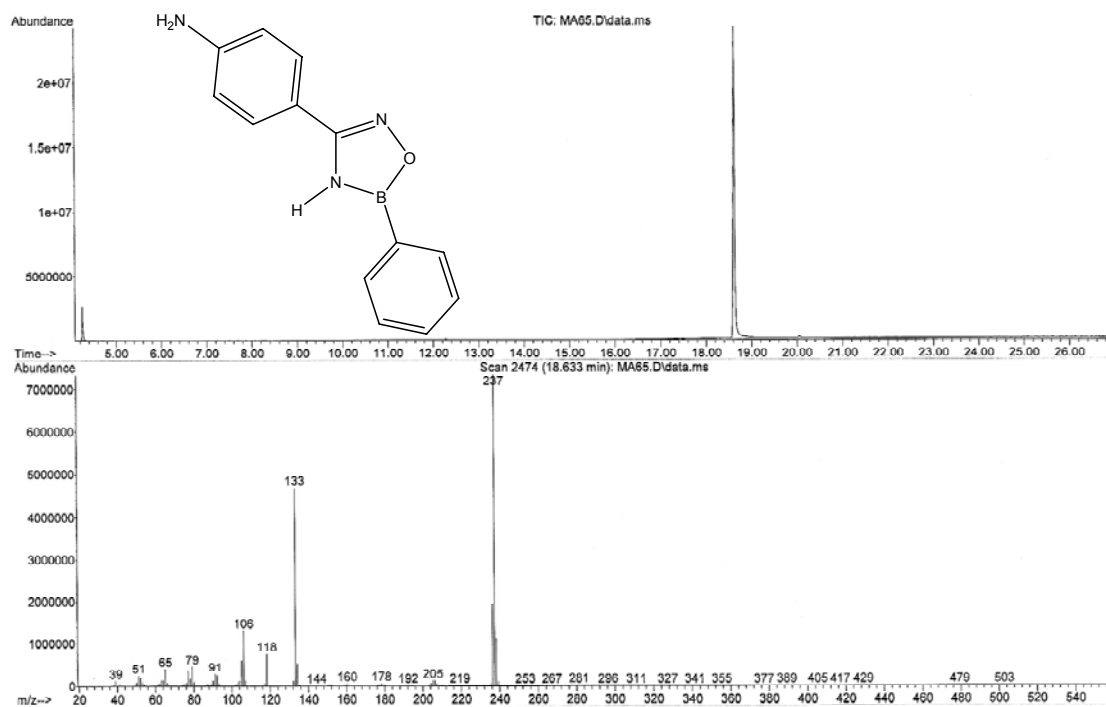


Figure 51D: The mass spectrum of **16h**

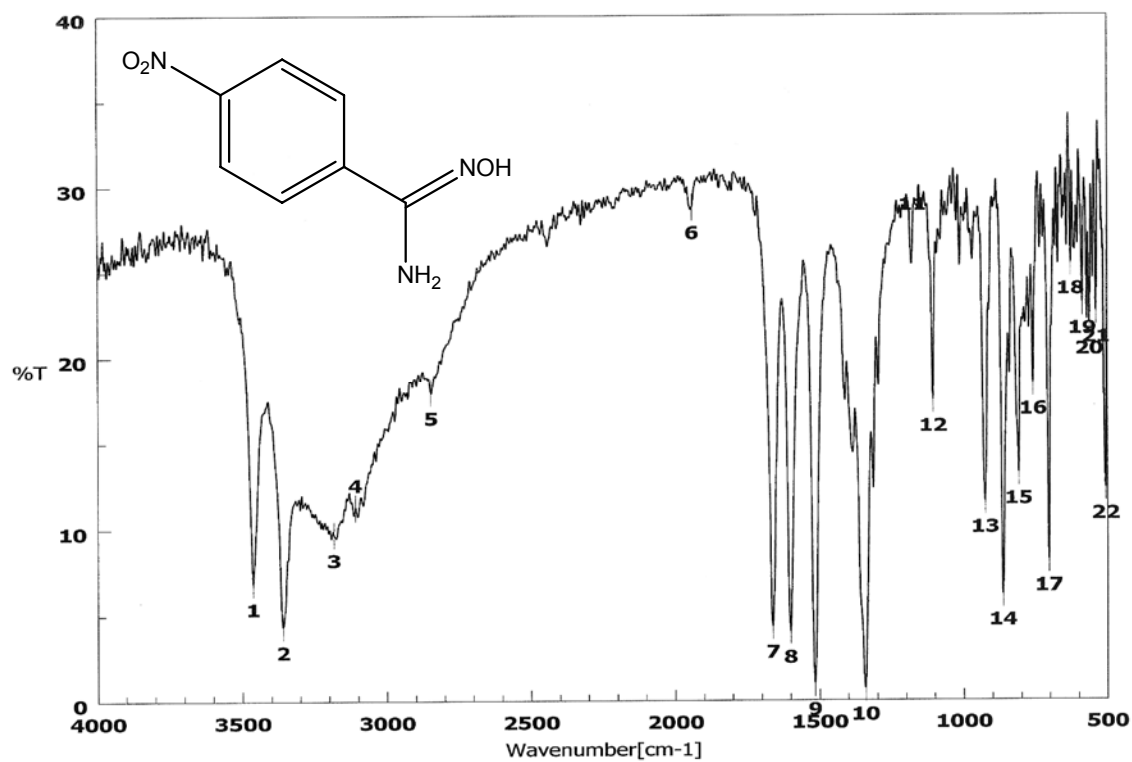


Figure 52: The IR spectrum of **10i**

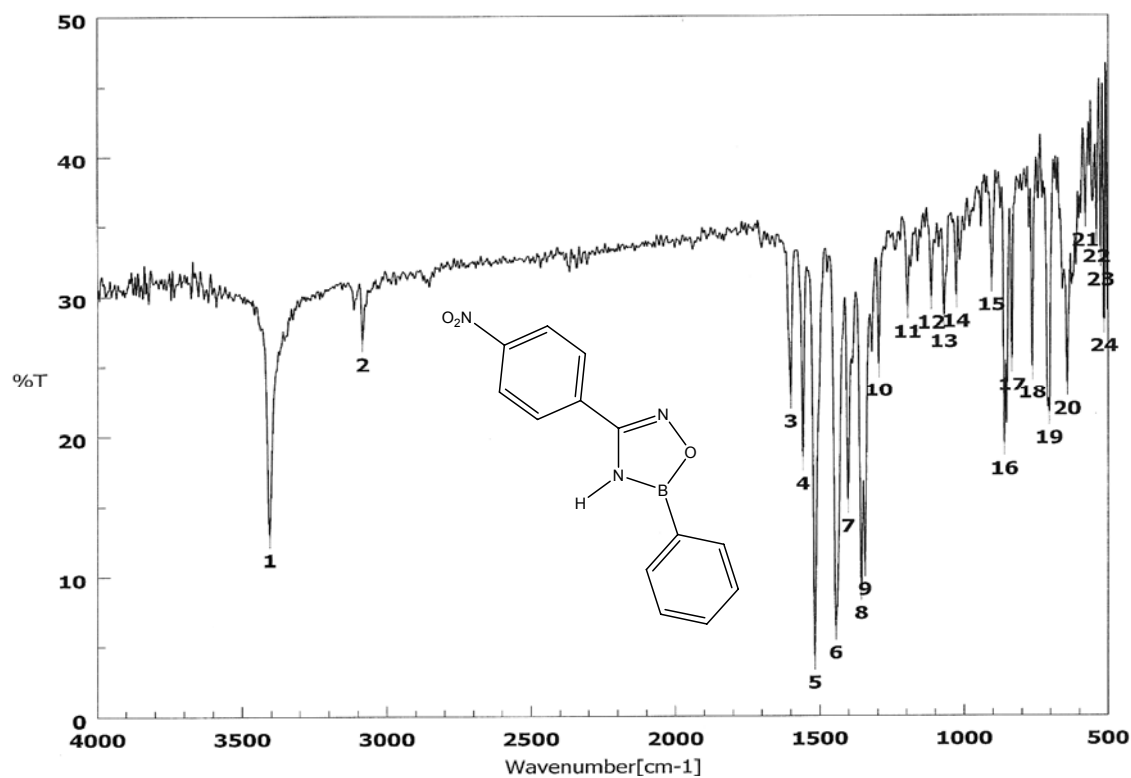


Figure 53A: The IR spectrum of **16i**

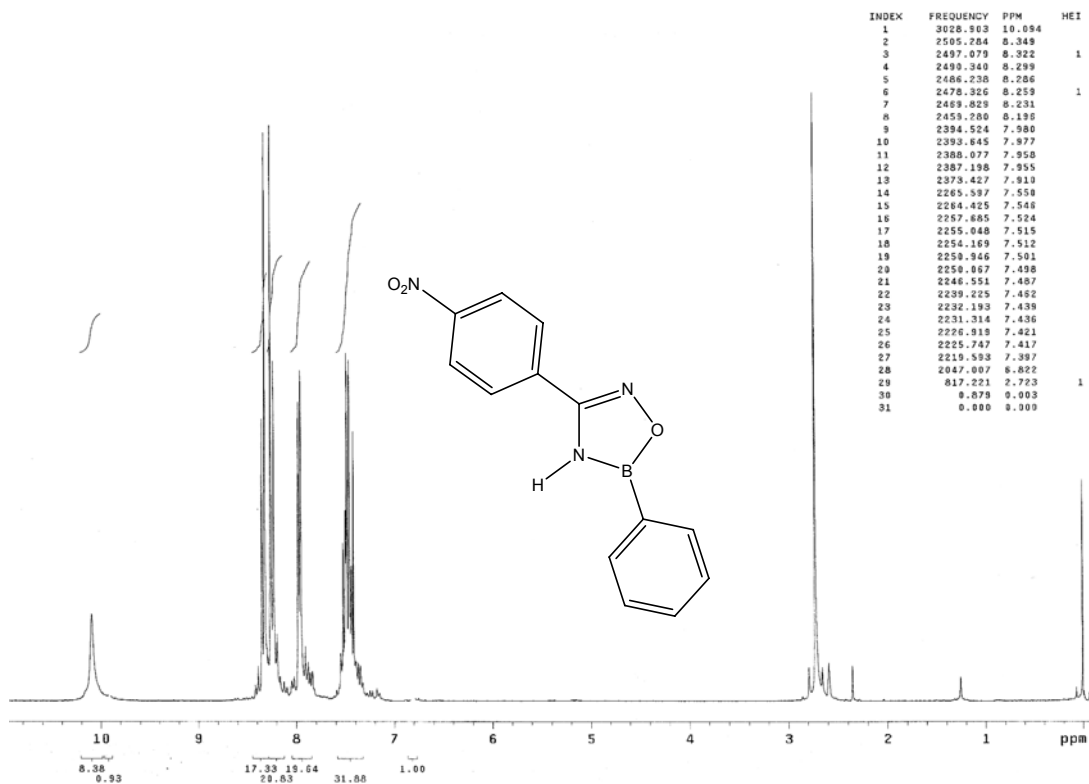


Figure 53B: The ^1H -NMR spectrum of **16i**

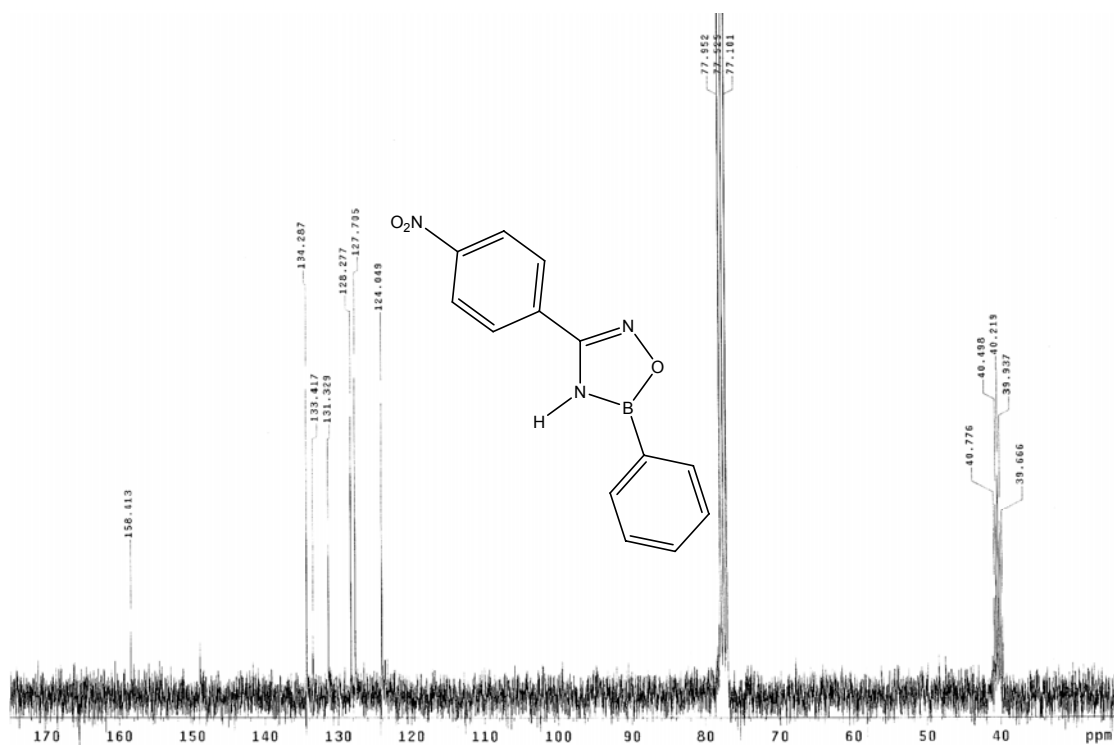


Figure 53C: The ¹³C-NMR spectrum of **16i**

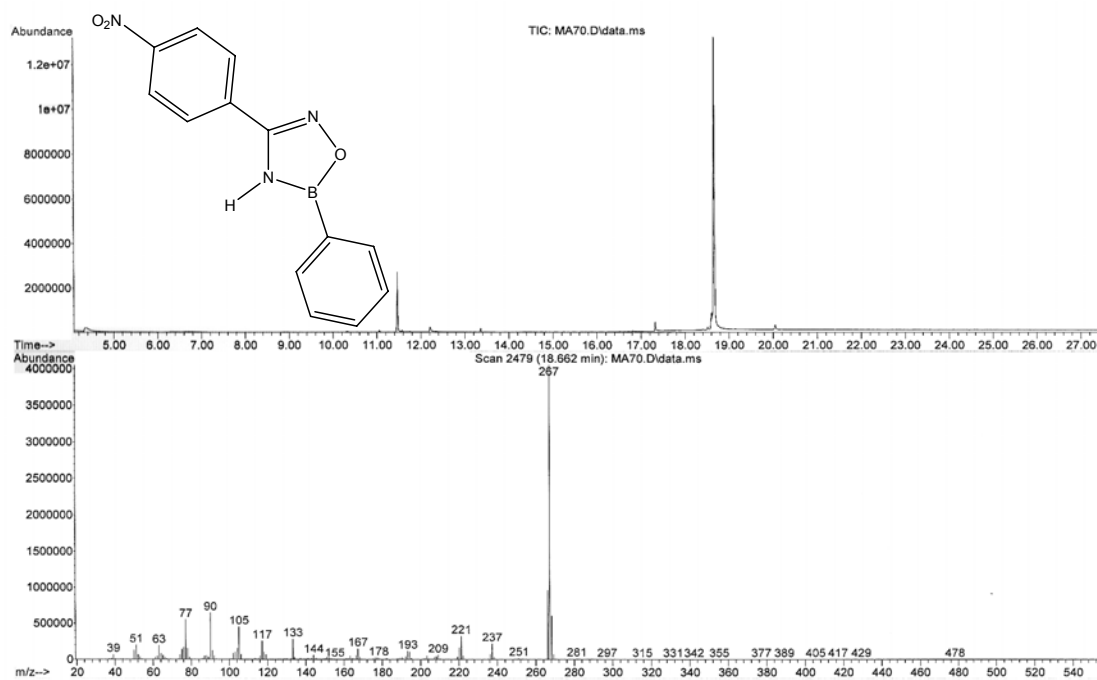


Figure 53D: The mass spectrum of **16i**

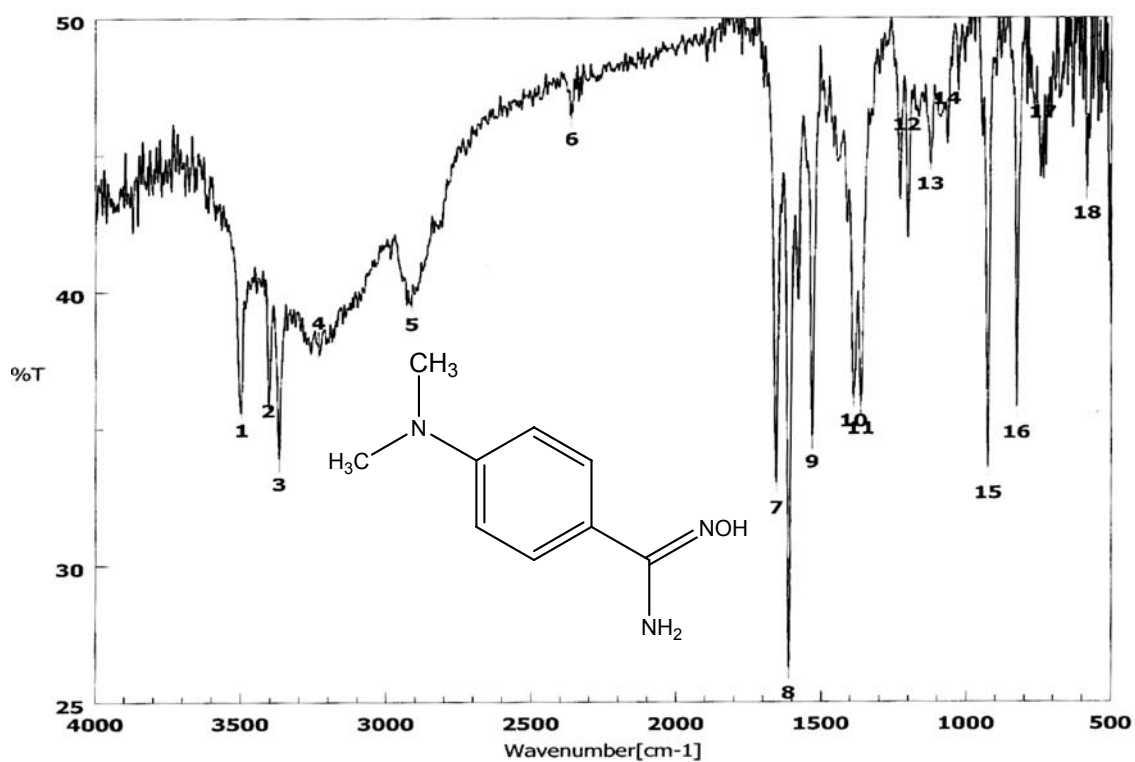


Figure 54: The IR spectrum of **10j**

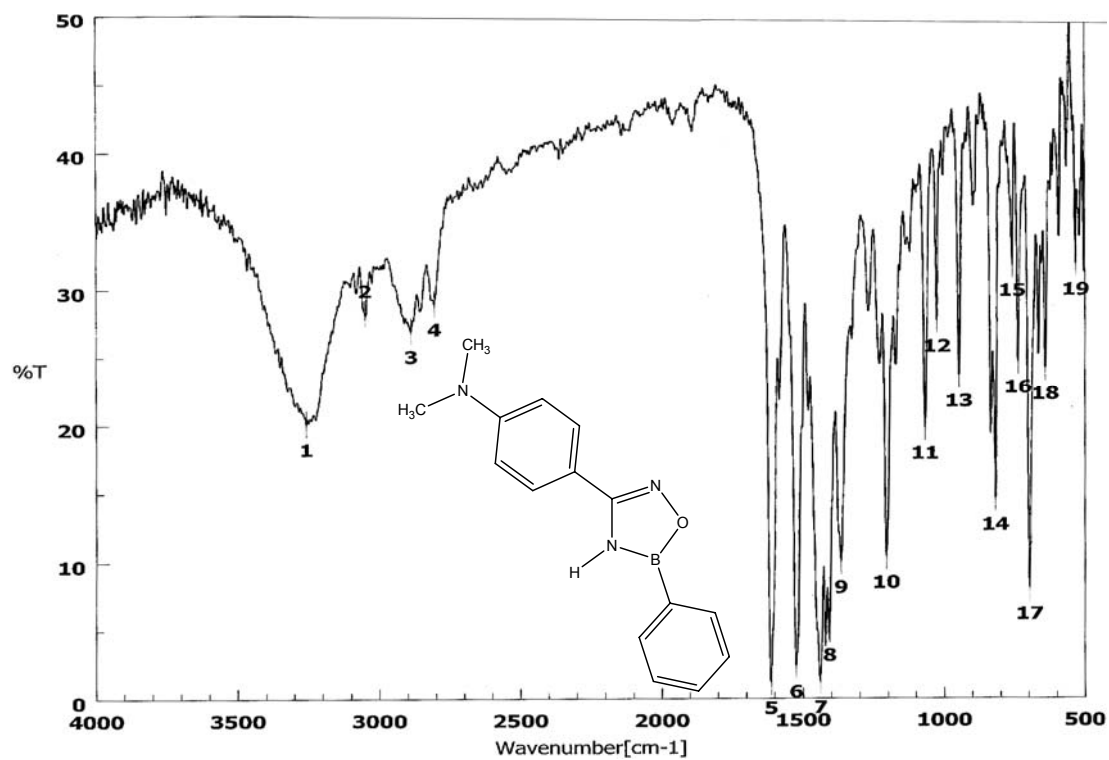


Figure 55A: The IR spectrum of **16j**

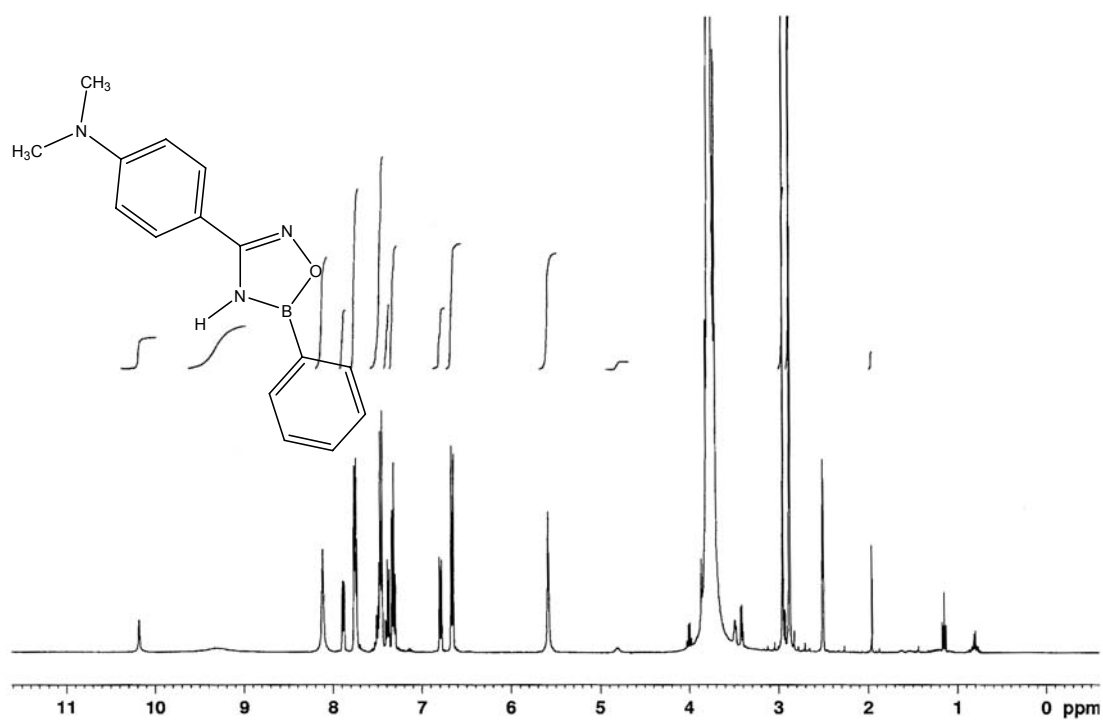


Figure 55B: The ¹H-NMR spectrum of **16j**

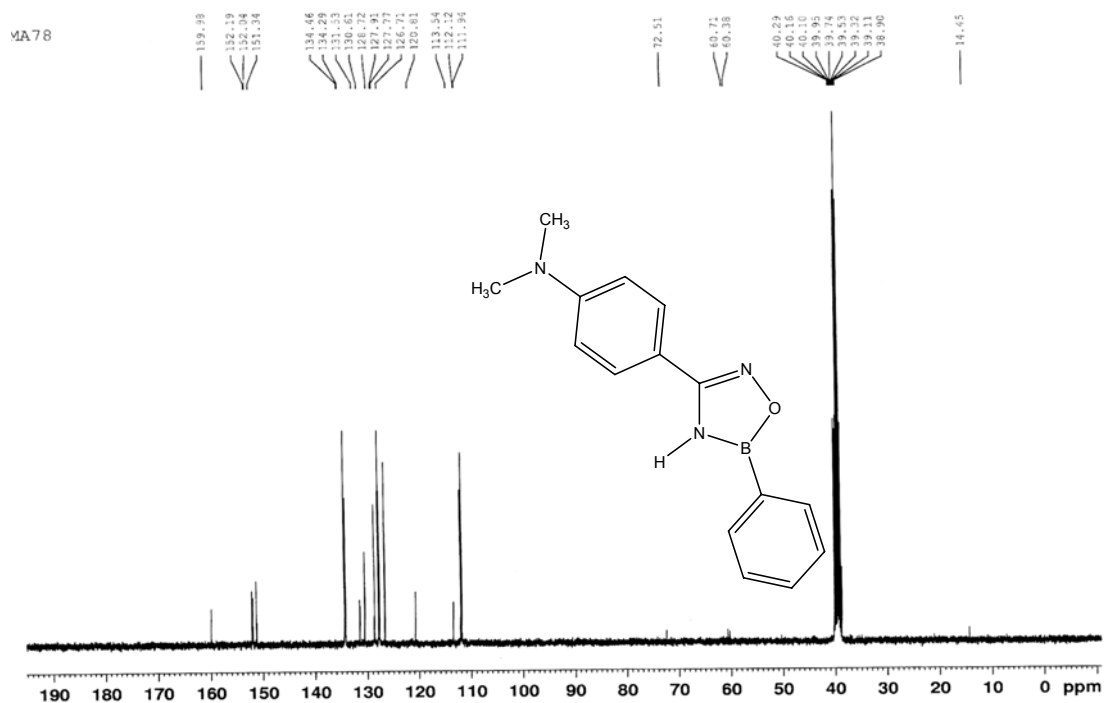


Figure 55C: The ¹³C-NMR spectrum of **16j**

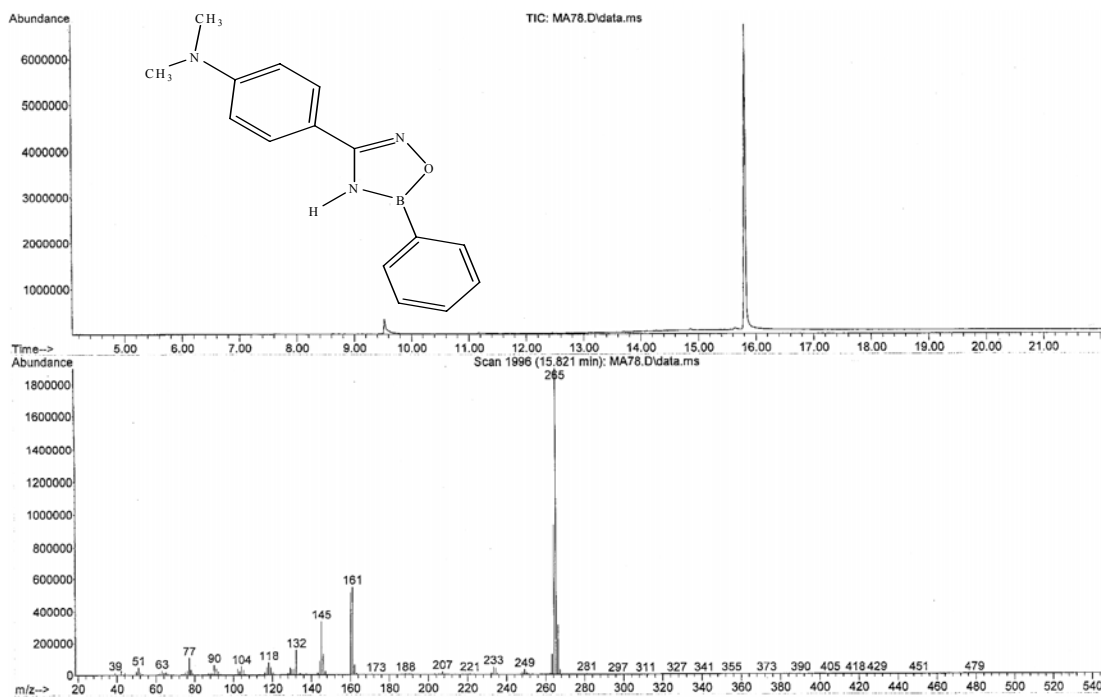


Figure 55D: The mass spectrum of **16j**

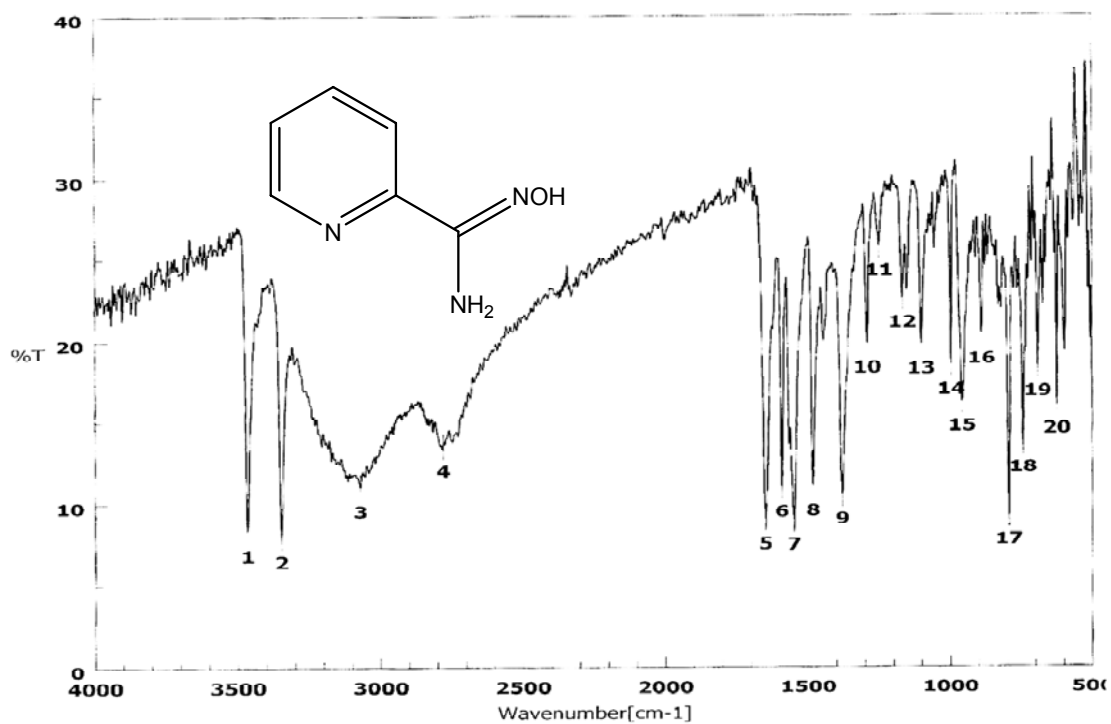


Figure 56: The IR spectrum of **10k**

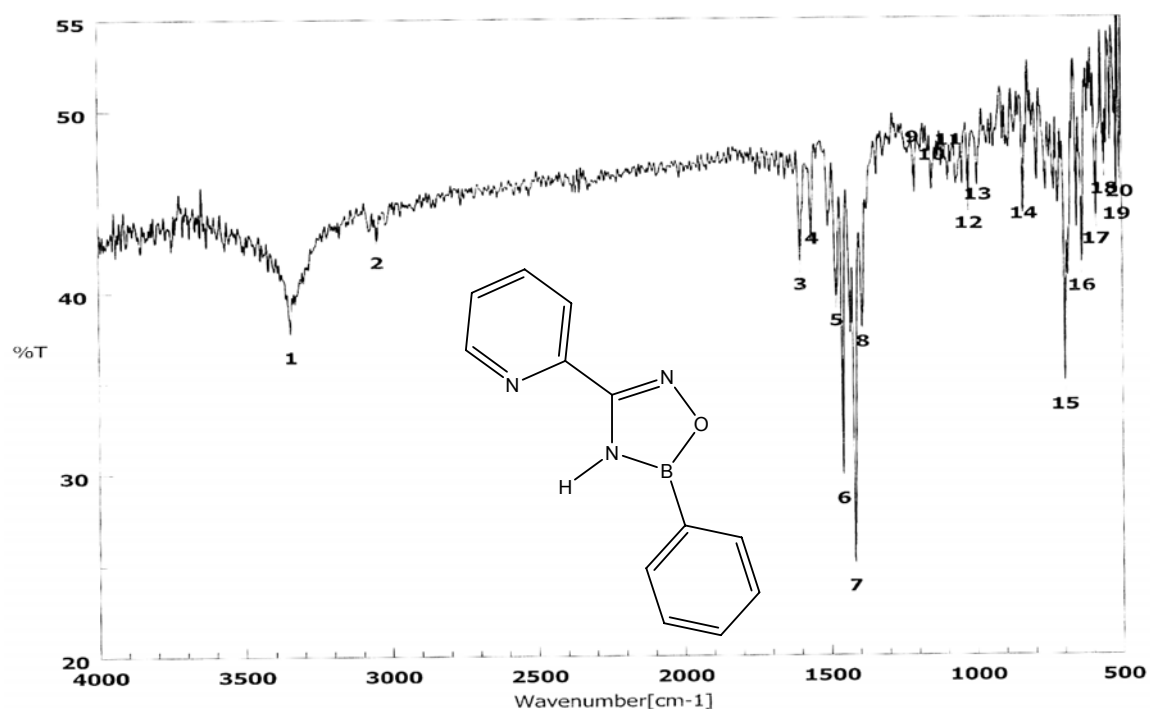


Figure 57A: The IR spectrum of **16k**

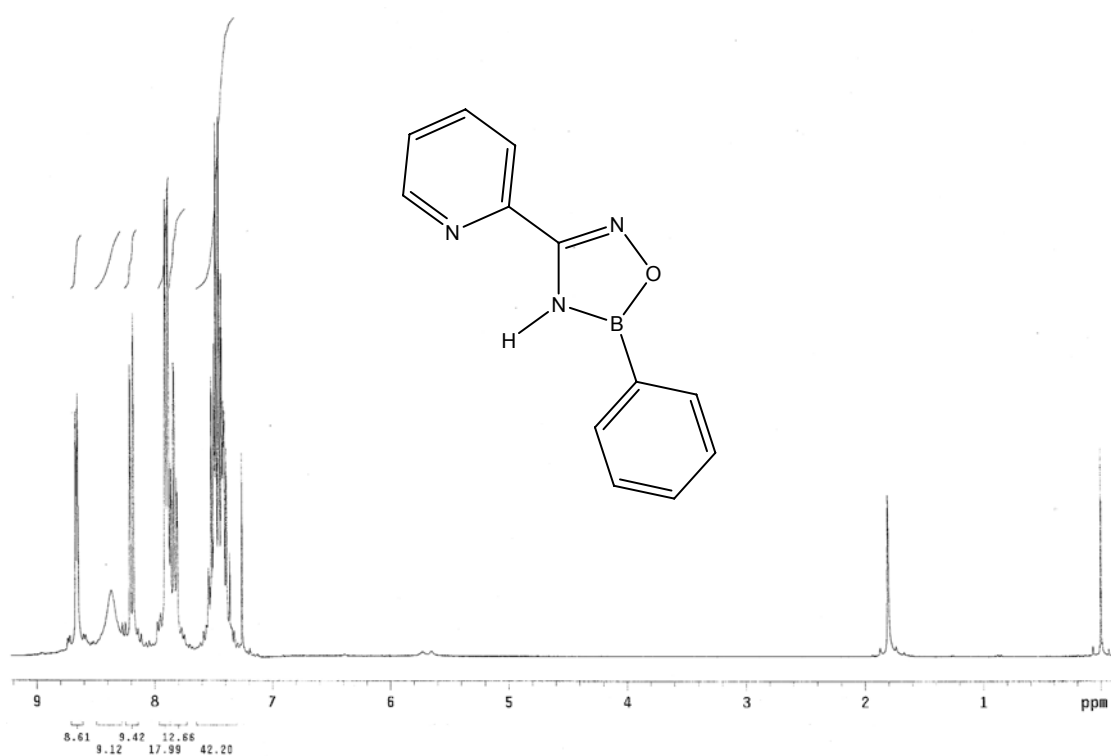


Figure 57B: The ^1H -NMR spectrum of **16k**

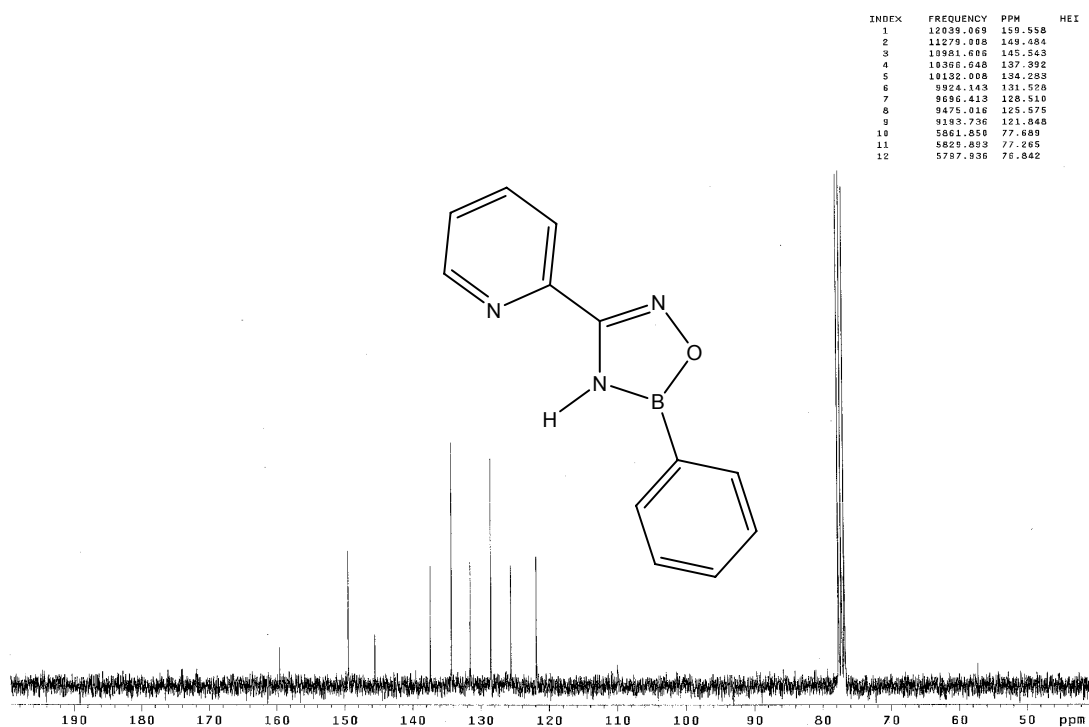


Figure 57C: The ^{13}C -NMR spectrum of **16k**

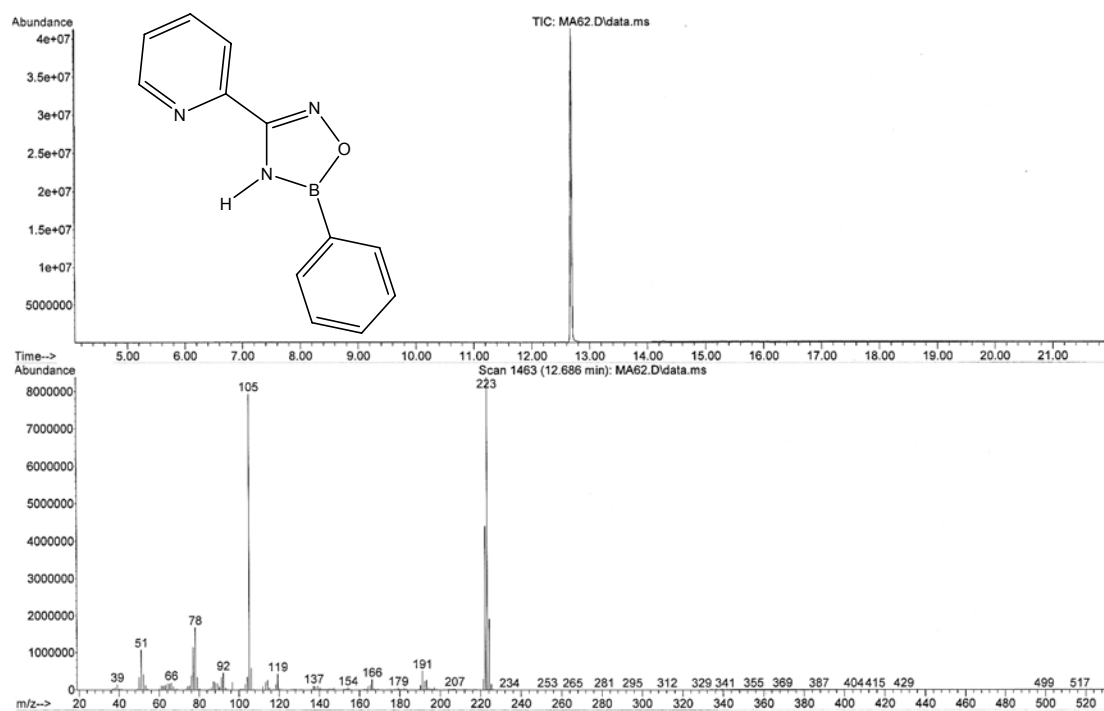


Figure 57D: The mass spectrum of **16k**

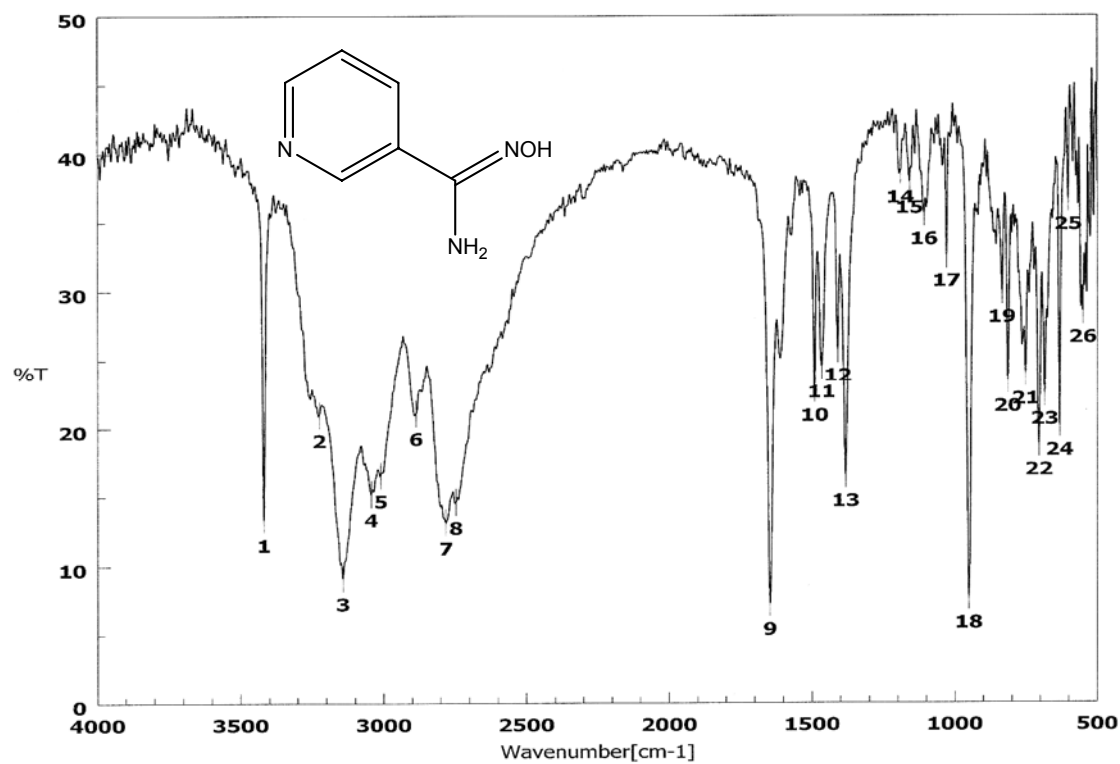


Figure 58: The IR spectrum of **10l**

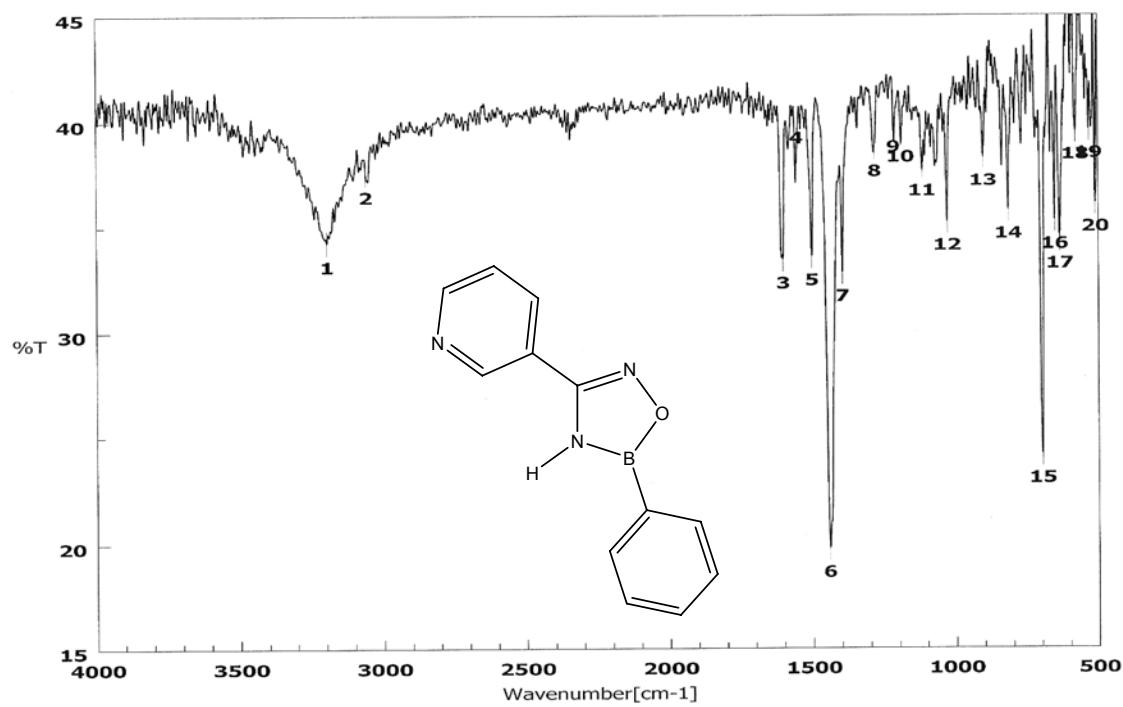


Figure 59A: The IR spectrum of **16l**

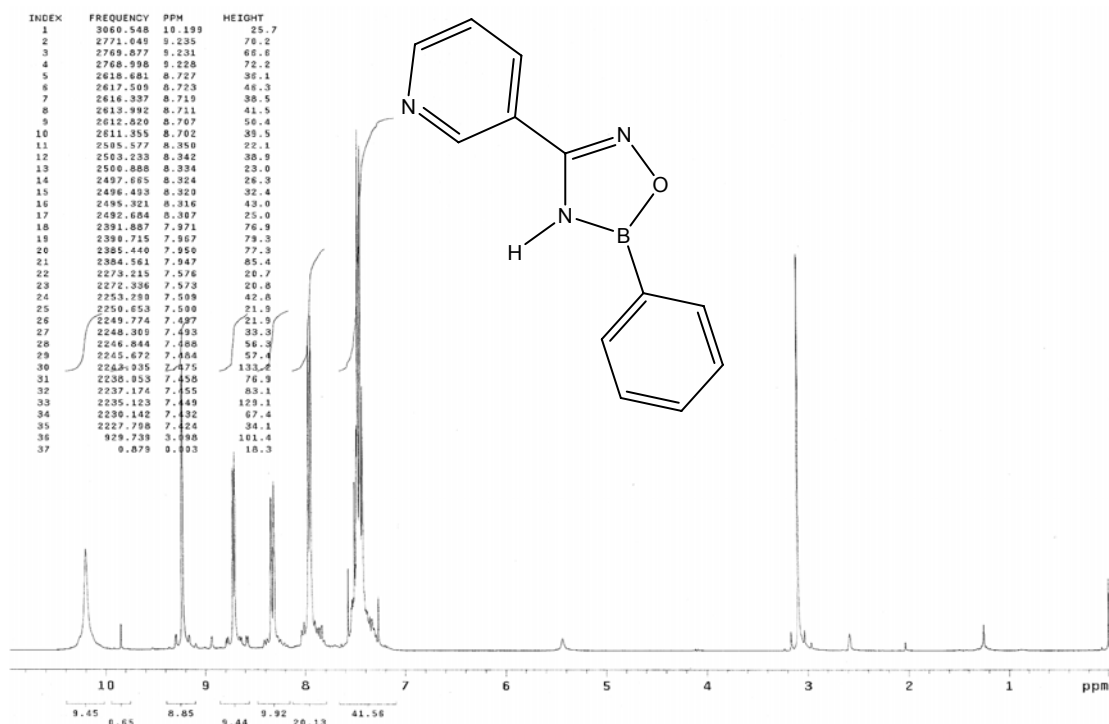


Figure 59B: The ^1H -NMR spectrum of **16l**

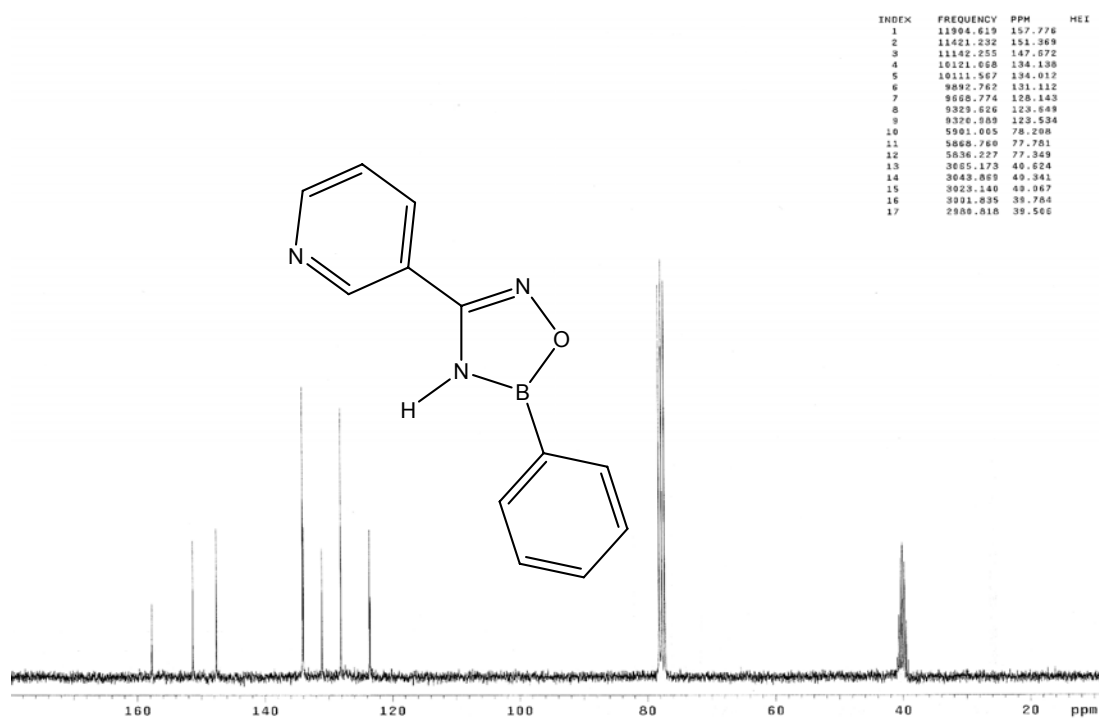


Figure 59C: The ^{13}C -NMR spectrum of **16l**

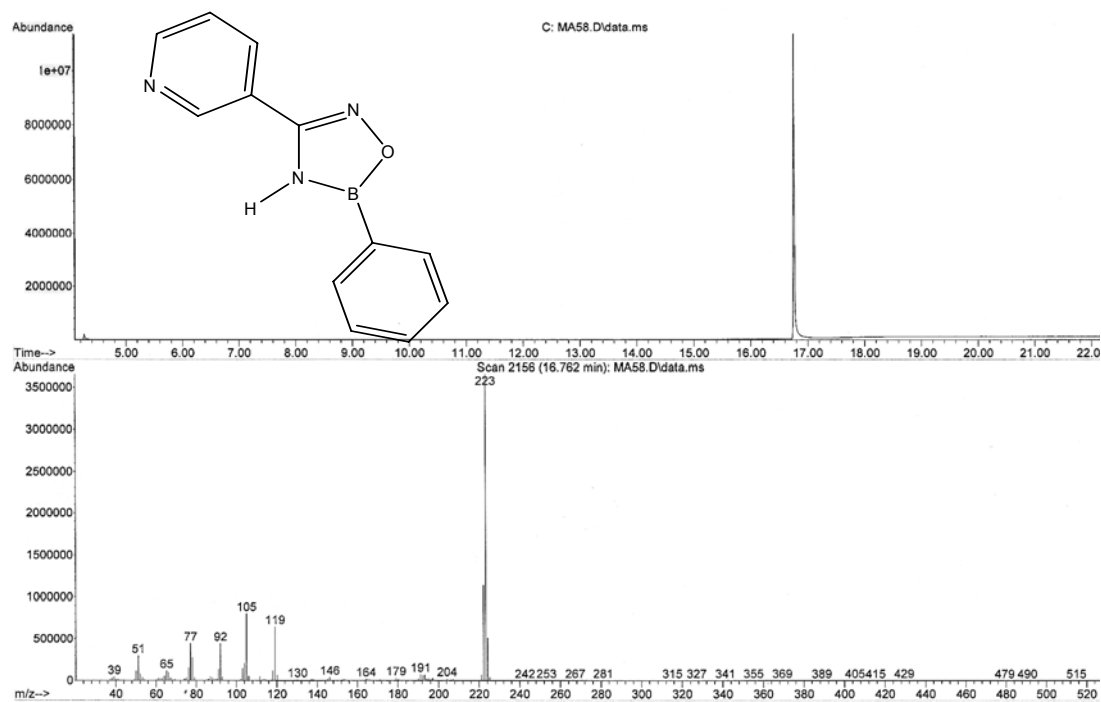


Figure 59D: The mass spectrum of **16l**

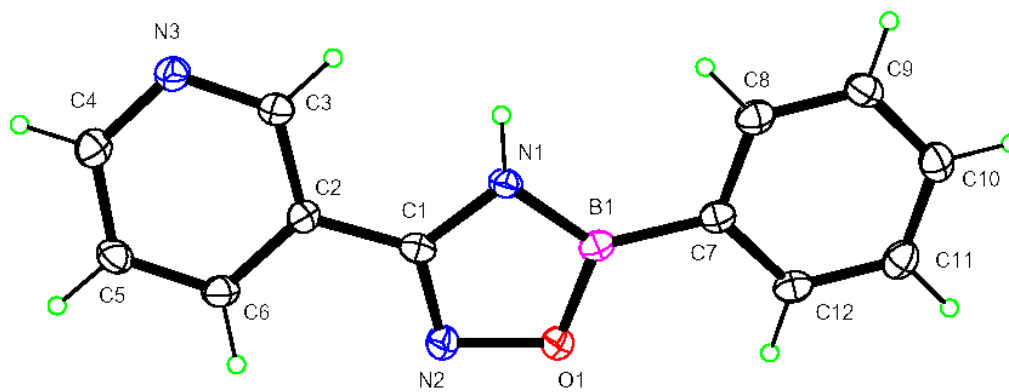


Figure 59E: The X-Ray pattern of **16l**

Crystal data

$C_{12}H_{10}BN_3O$	Dm not measured
$M_r = 223.04$	Mo $K\alpha$ radiation
Orthorhombic	$\lambda = 0.71073 \text{ \AA}$
$P2_12_12_1$	Cell parameters from 1266 reflections
$a = 5.3091 (12) \text{ \AA}$	$\theta = 2.5\text{--}26.3^\circ$
$b = 13.217 (4) \text{ \AA}$	$\mu = 0.089 \text{ mm}^{-1}$
$c = 15.593 (6) \text{ \AA}$	$T = 90 \text{ K}$
$V = 1094.2 (6) \text{ \AA}^3$	Needle
$Z = 4$	Colorless
$D_x = 1.354 \text{ Mg m}^{-3}$	$0.40 \times 0.05 \times 0.04 \text{ mm}$
	Crystal source: local laborator

Data collection

KappaCCD (with Oxford Cryostream)	$I > 2\sigma(I)$
diffractometer	$R_{\text{int}} = 0.031$
ω scans with κ offsets	$\theta_{\text{max}} = 26.4^\circ$
Absorption correction: none	$h = -6 \rightarrow 6$
6418 measured reflections	$k = -16 \rightarrow 16$
1314 independent reflections	$l = -19 \rightarrow 19$
1108 reflections with	intensity decay: $<2\%$

Table 3: Crystall data of **16l**

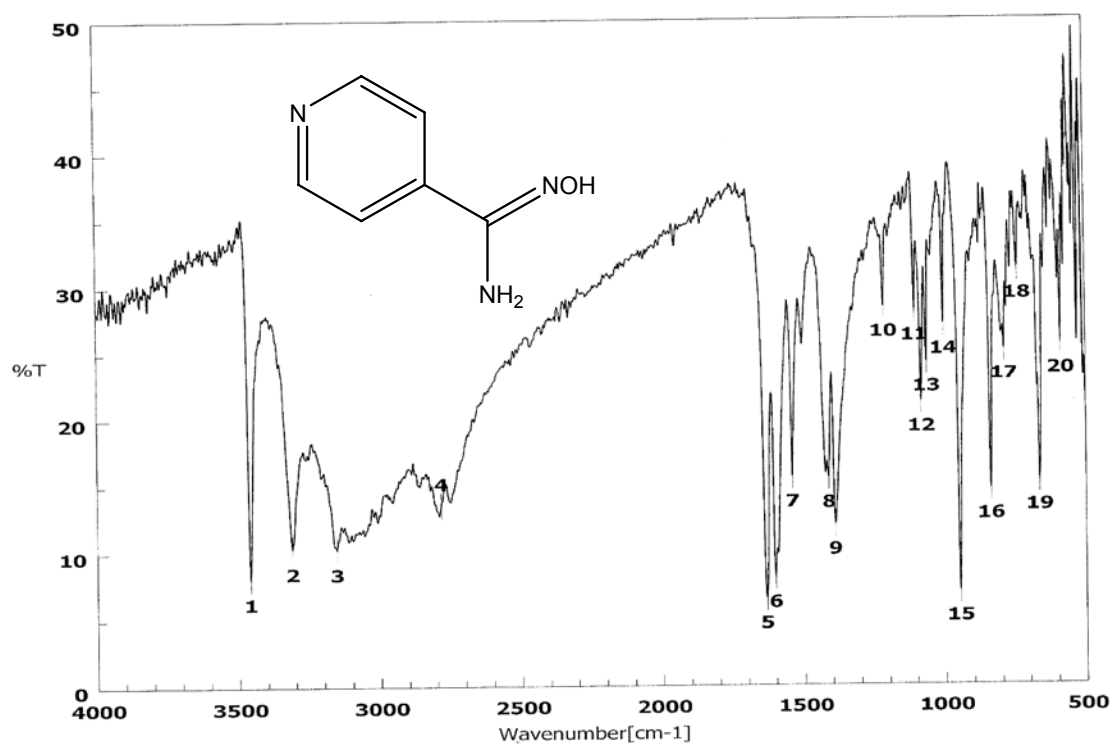


Figure 60: The IR spectrum of 10m

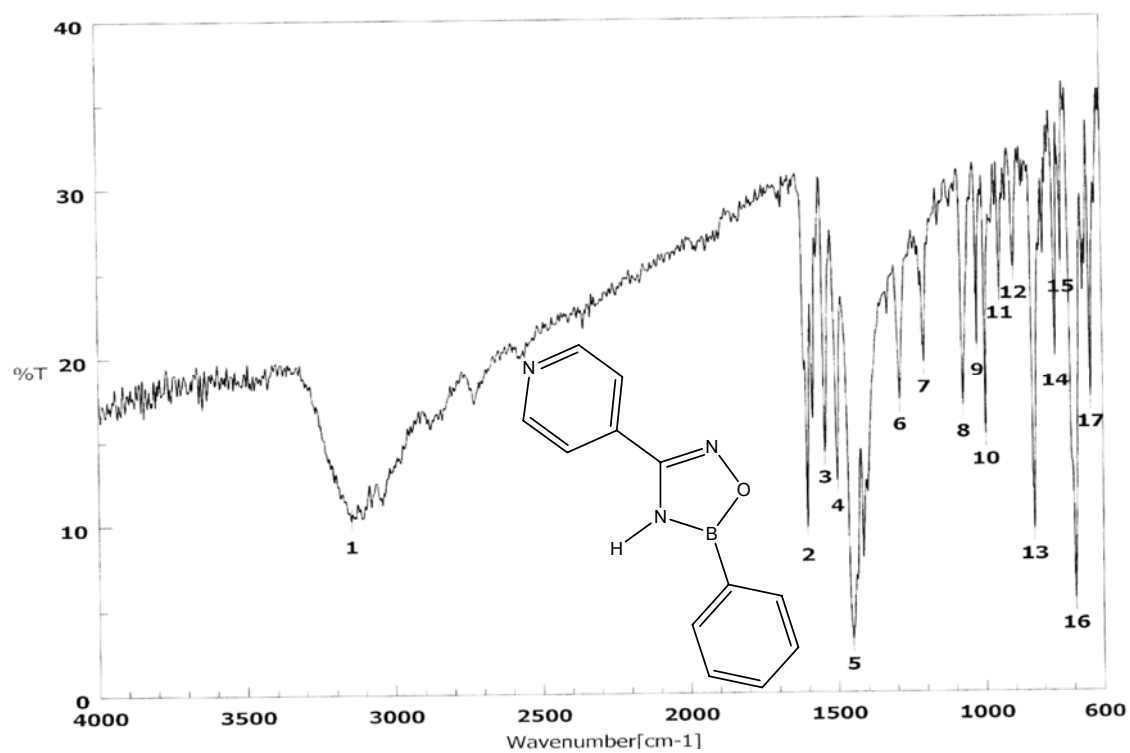


Figure 61A: The IR spectrum of 16m

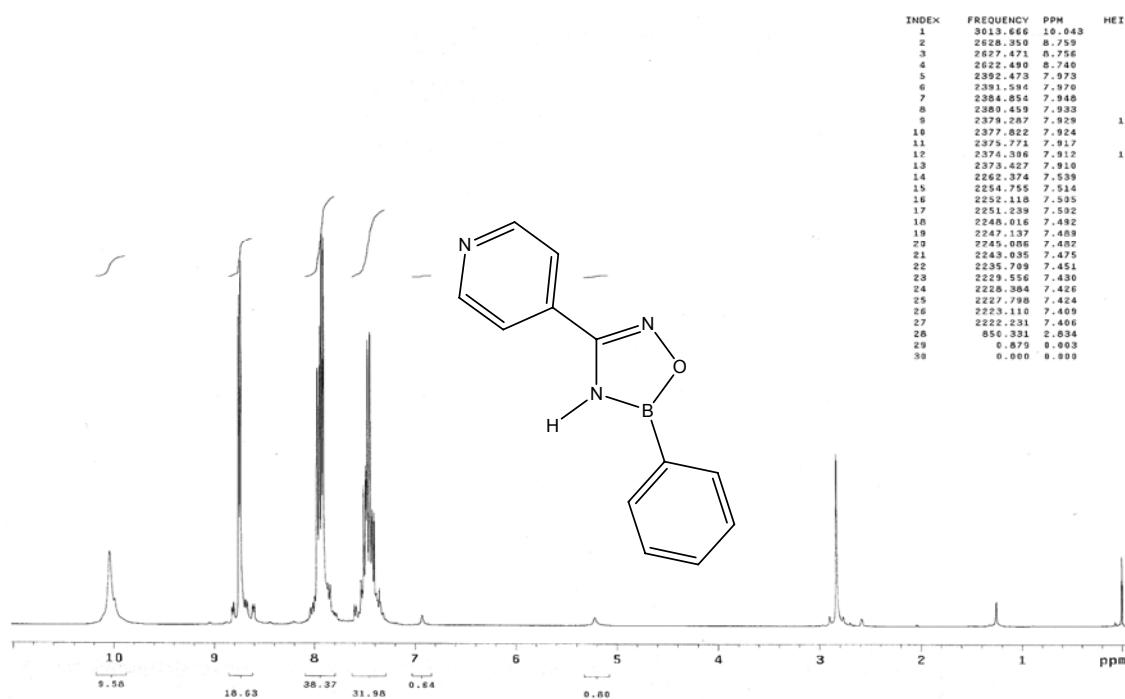


Figure 61B: The ^1H -NMR spectrum of **16m**

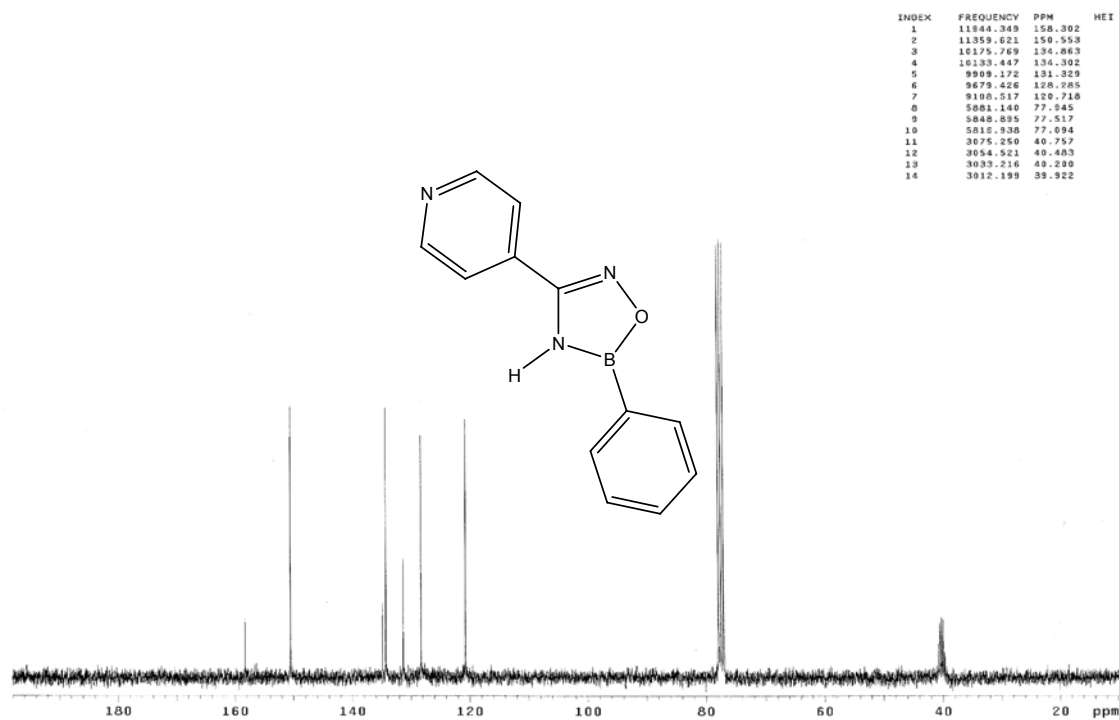


Figure 61C: The ^{13}C -NMR spectrum of **16m**

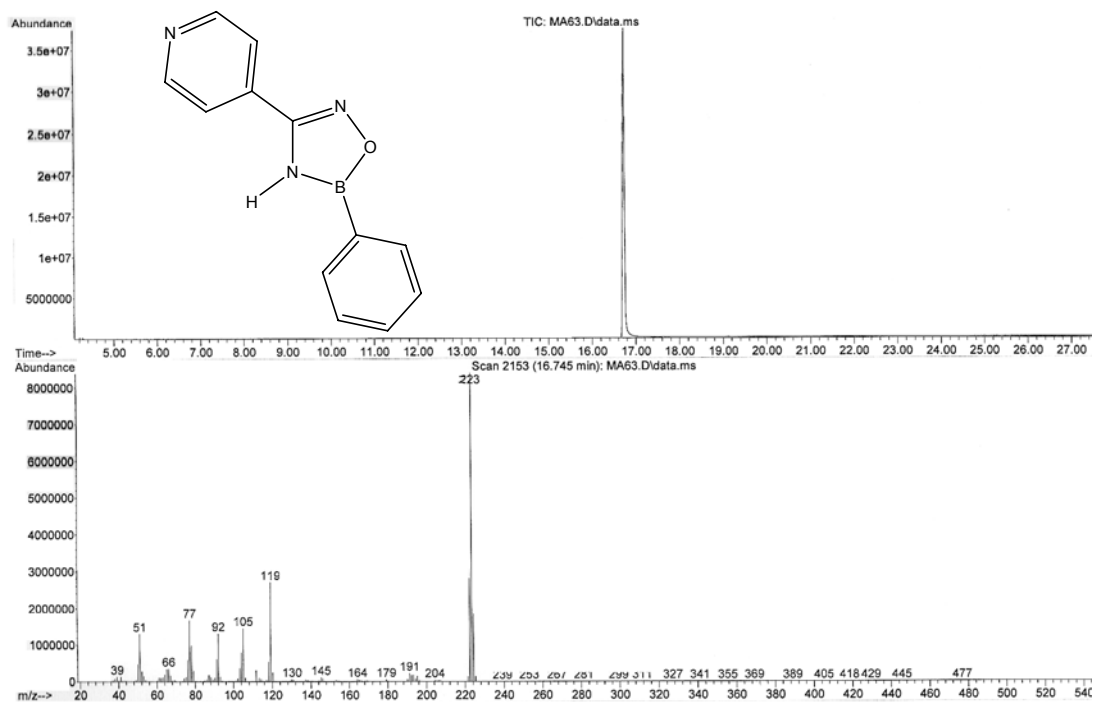


Figure 61D: The mass spectrum of **16m**

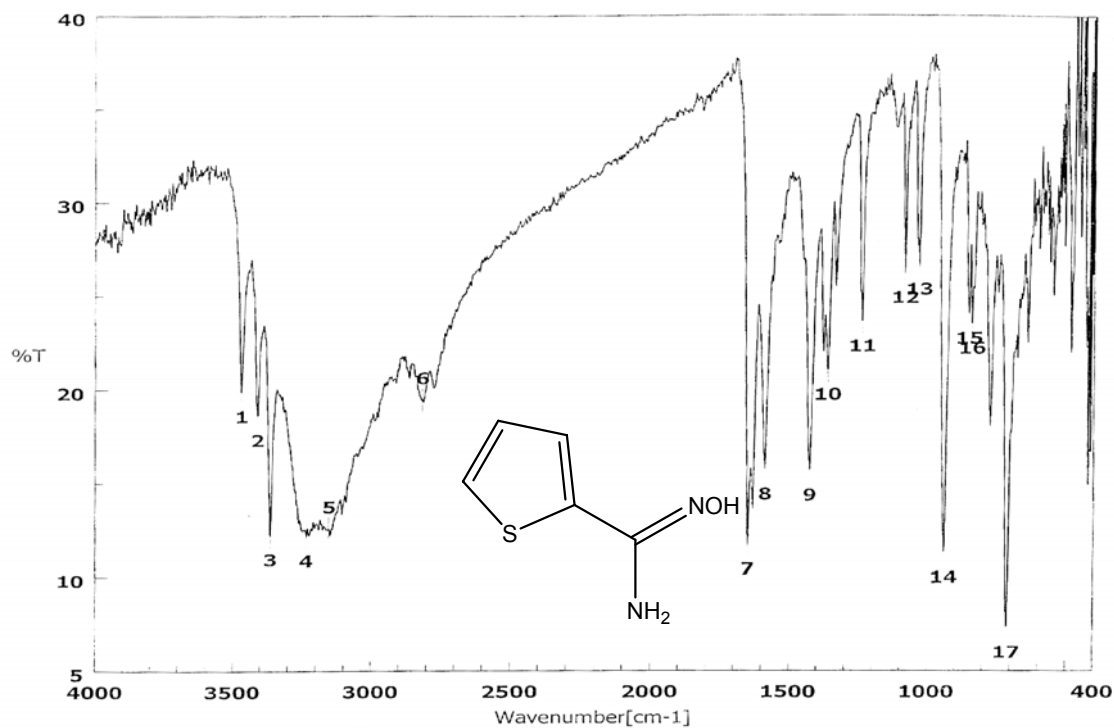


Figure 62: The IR spectrum of **10n**

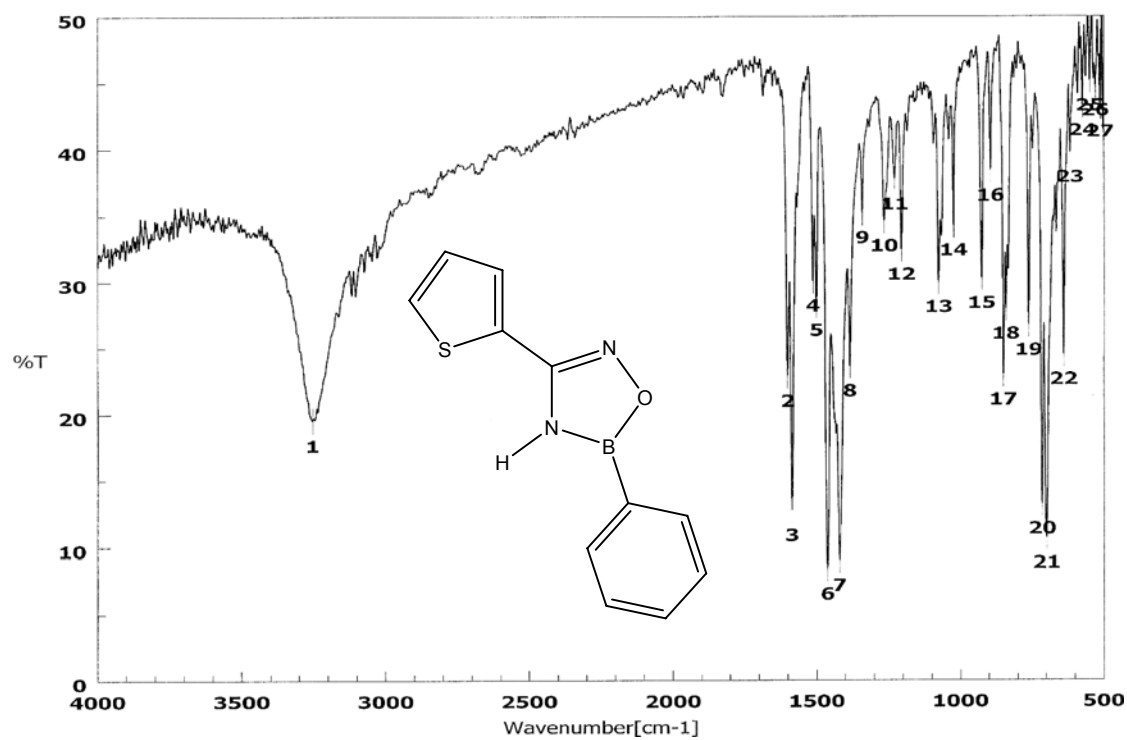


Figure 63A: The IR spectrum of **16n**

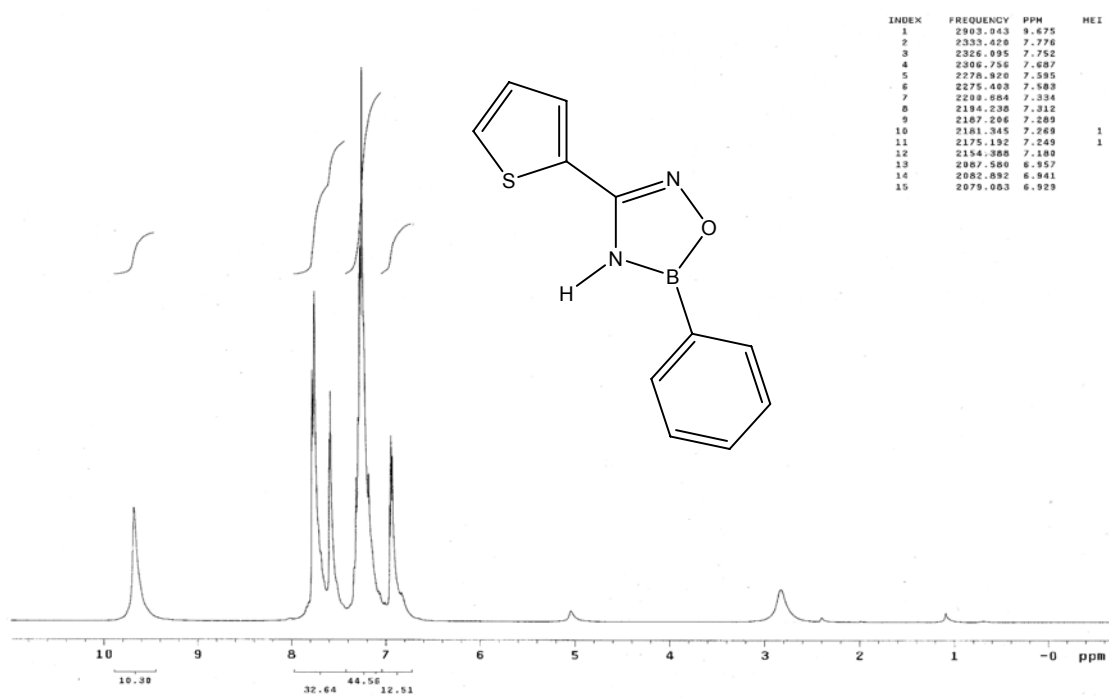


Figure 63B: The ^1H -NMR spectrum of **16n**

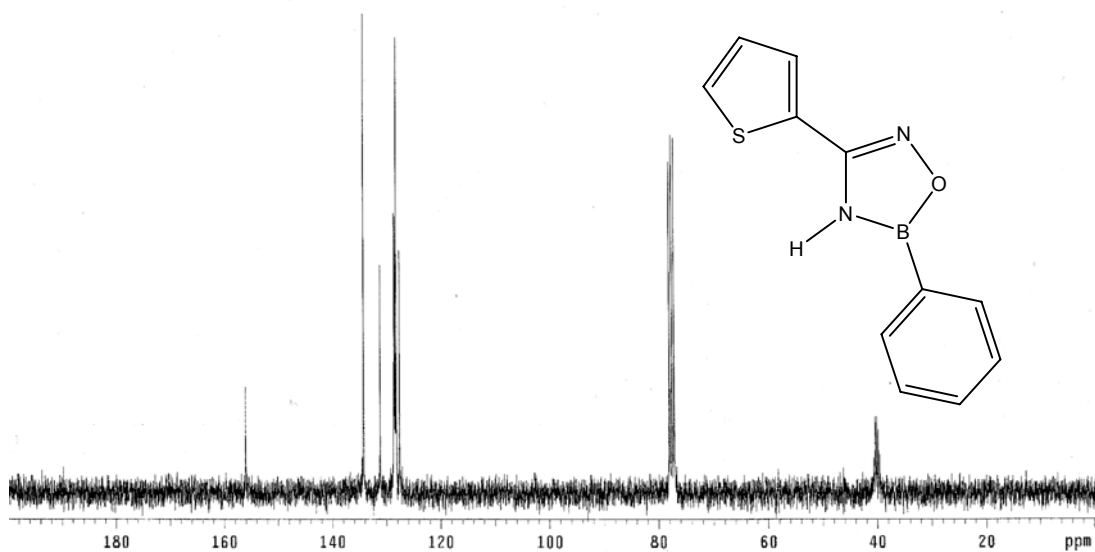


Figure 63C: The ^{13}C -NMR spectrum of **16n**



Figure 63D: The mass spectrum of **16n**

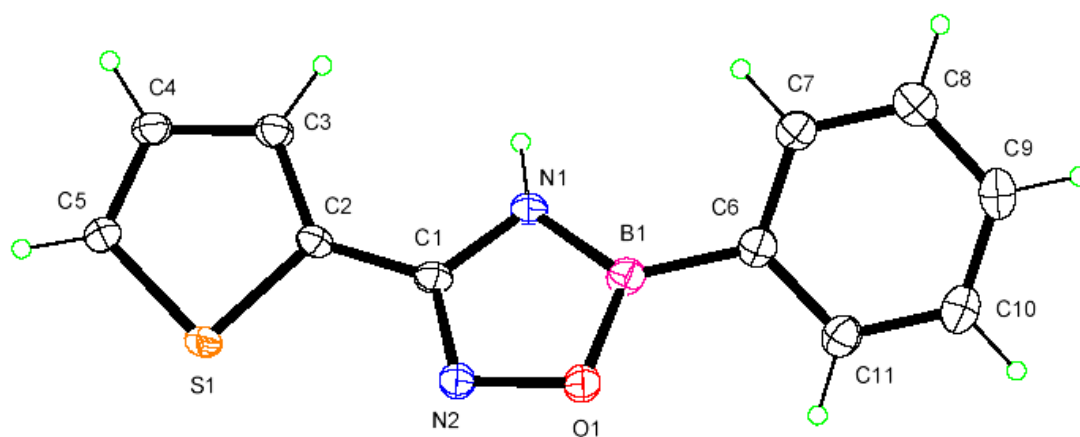


Figure 63E: The X-Ray pattern of **16n**

Crystal data

$C_{11}H_9BN_2O$

$M_r = 228.07$

Orthorhombic

$Pca2_1$

$a = 19.545 (3) \text{ \AA}$

$b = 5.4482 (10) \text{ \AA}$

$c = 10.1282 (14) \text{ \AA}$

$V = 1078.5 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.405 \text{ Mg m}^{-3}$

D_m not measured

Mo K_α radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2259 reflections

$\theta = 2.5\text{--}33.1^\circ$

$\mu = 0.275 \text{ mm}^{-1}$

$T = 90 \text{ K}$

Lath

Colorless

$0.40 \times 0.10 \times 0.05 \text{ mm}$

Crystal source: local laboratory

Data collection

KappaCCD (with Oxford Cryostream)	3734 independent reflections
diffractometer	3301 reflections with $I > 2\sigma(I)$
ω scans with κ offsets	$R_{\text{int}} = 0.057$
Absorption correction: multi-scan Denzo and Scalepack (otwinowski and Minor, 1997)	$\theta_{\text{max}} = 32.9^\circ$ $h = -29 \rightarrow 29$ $k = -8 \rightarrow 8$ $l = -15 \rightarrow 15$
$T_{\text{min}} = 0.898$, $T_{\text{max}} = 0.986$	intensity decay: $< 2\%$
14020 measured reflections	

Table 4: Crystal data and refinement of **16n**

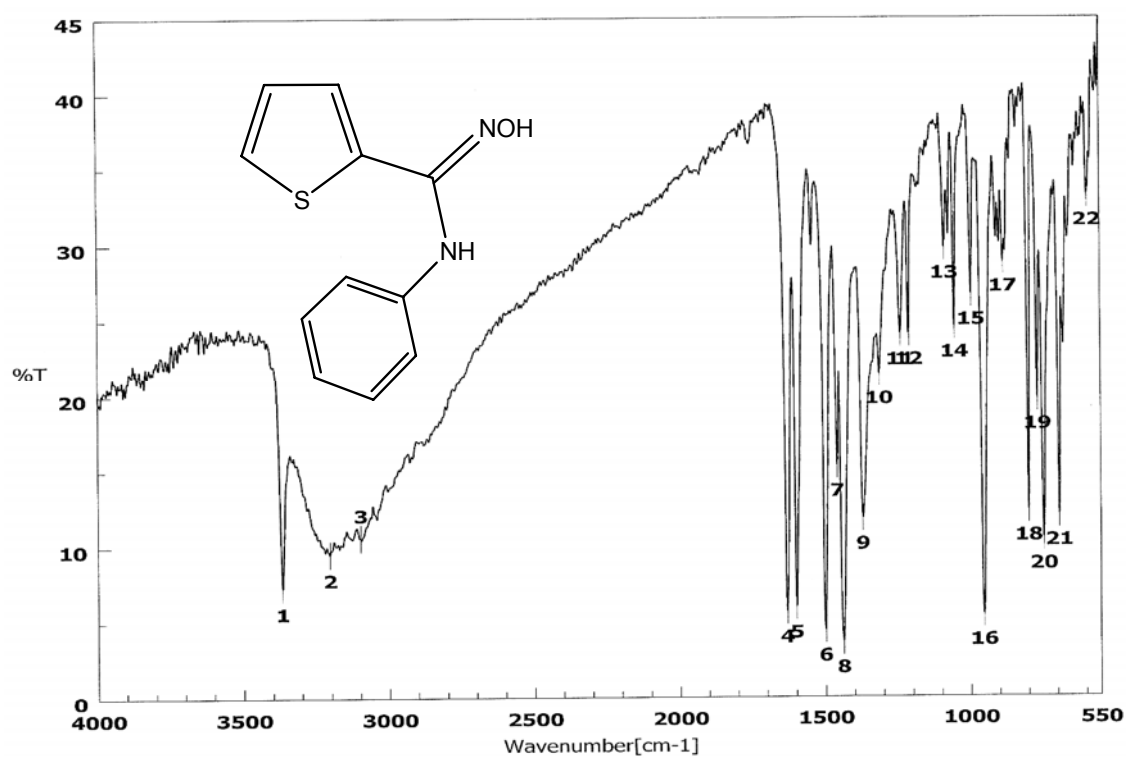


Figure 64: The IR spectrum of 11o

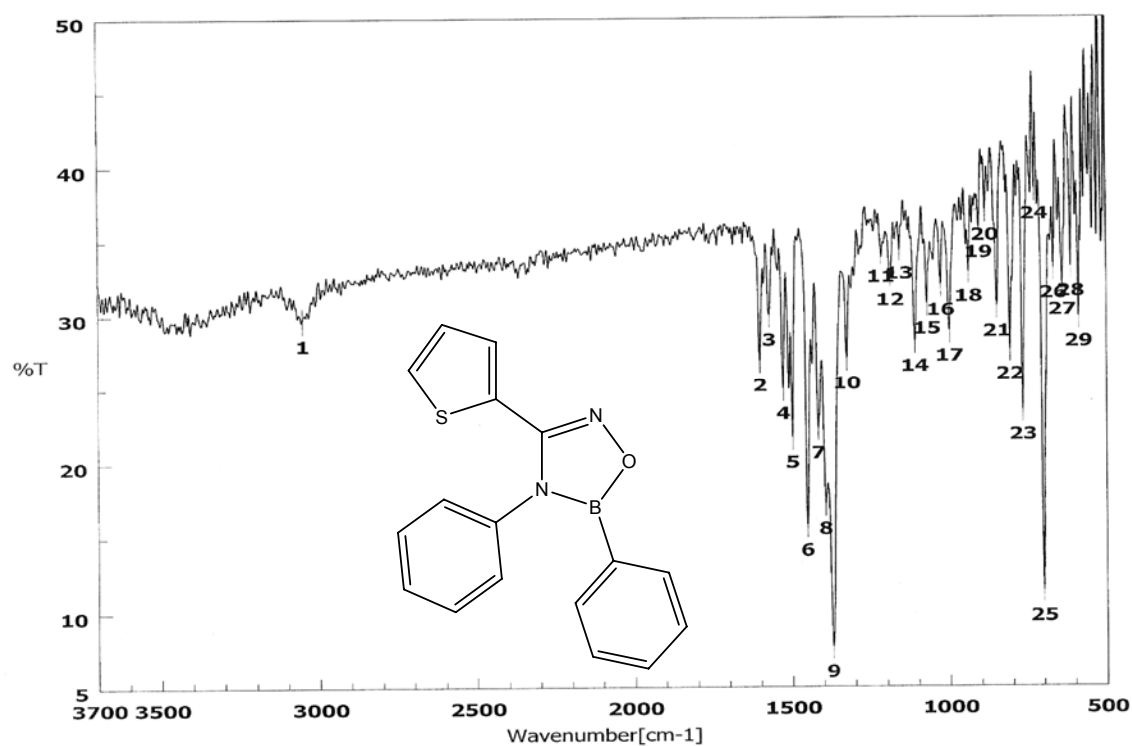


Figure 65A: The IR spectrum of 17o

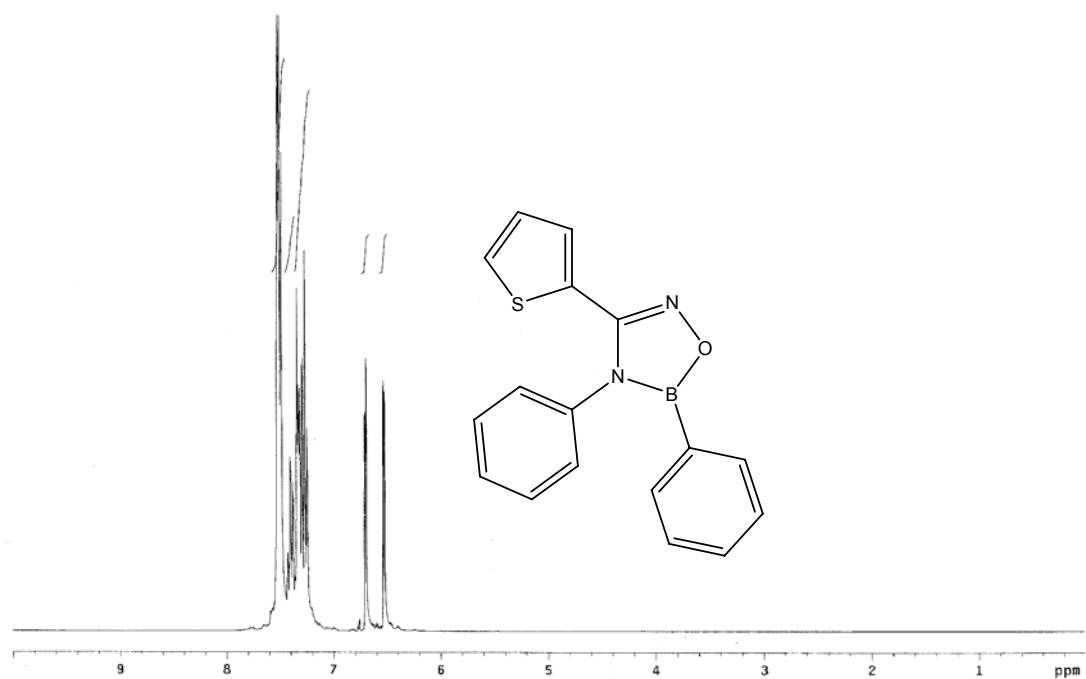


Figure 65B: The ^1H -NMR spectrum of **17o**

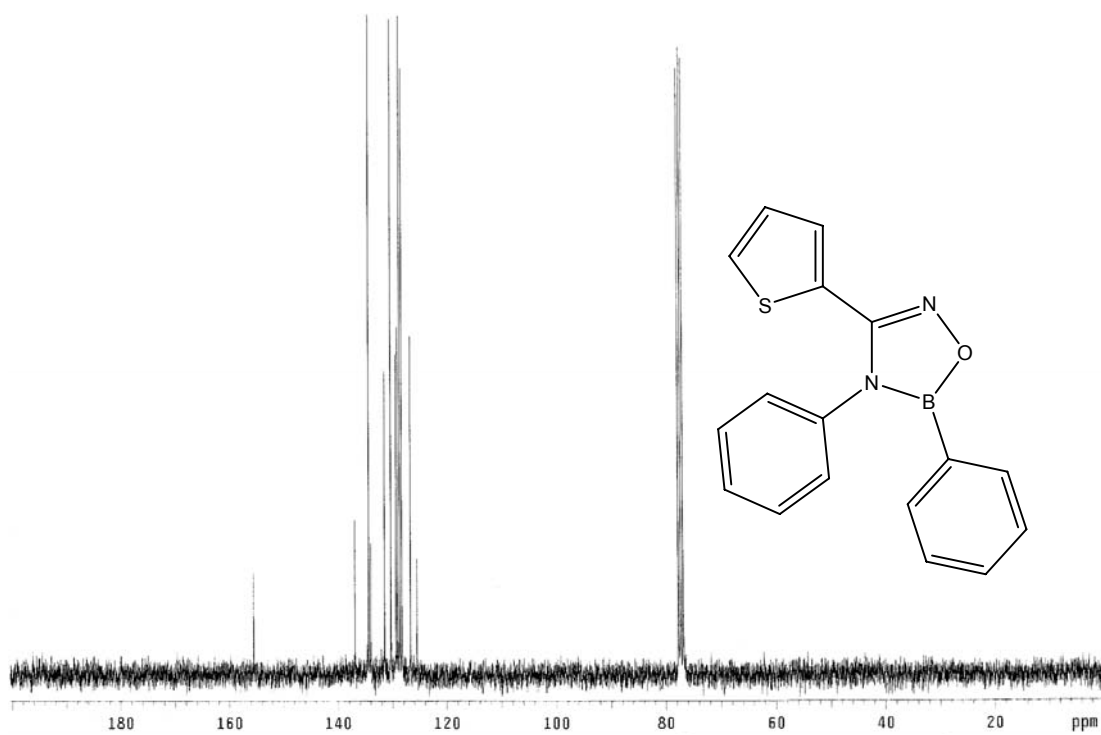


Figure 65C: The ^{13}C -NMR spectrum of **17o**

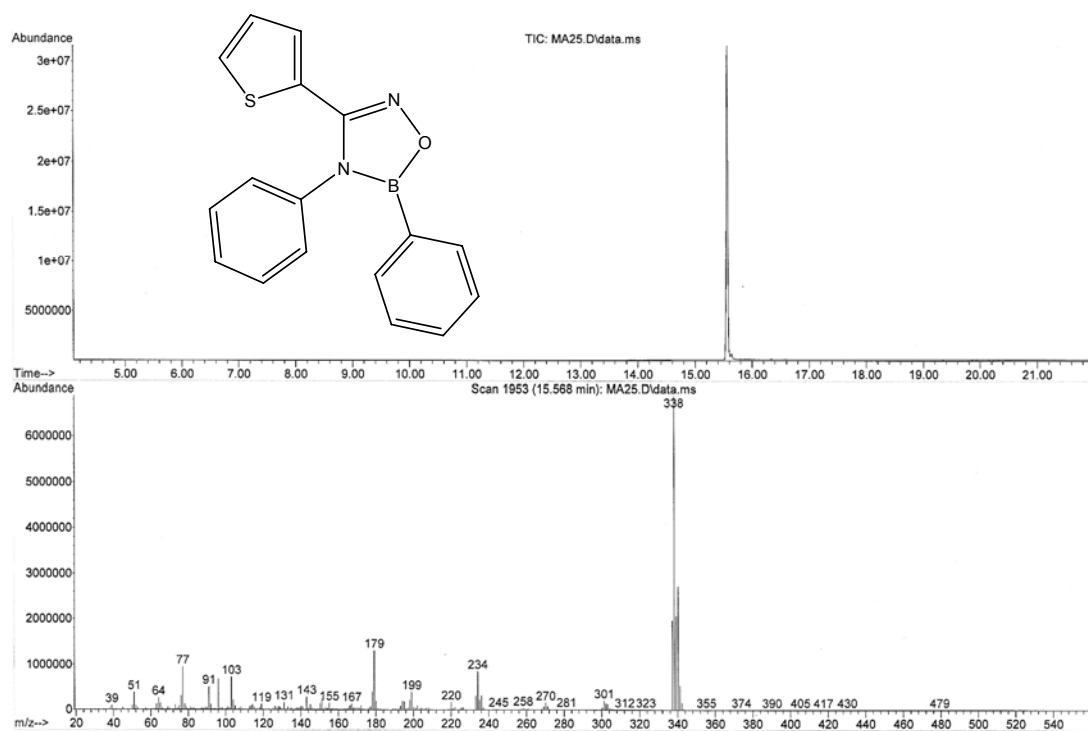


Figure 65D: The mass spectrum of **17o**

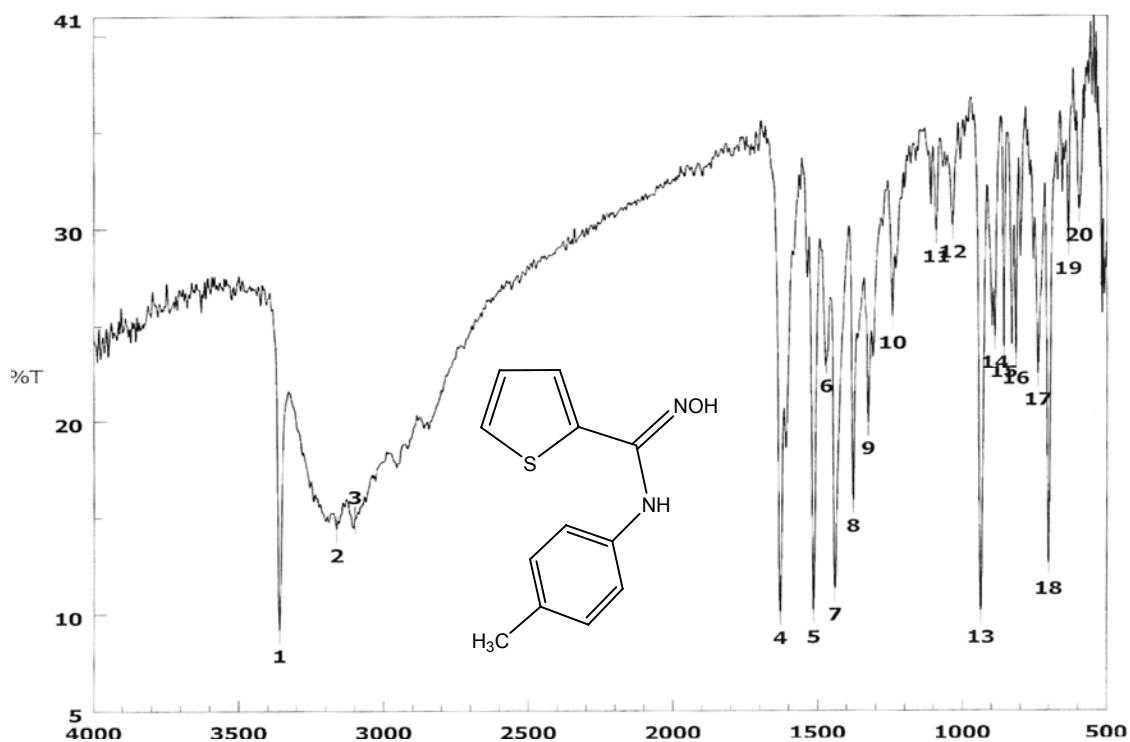


Figure 66: The IR spectrum of **11p**

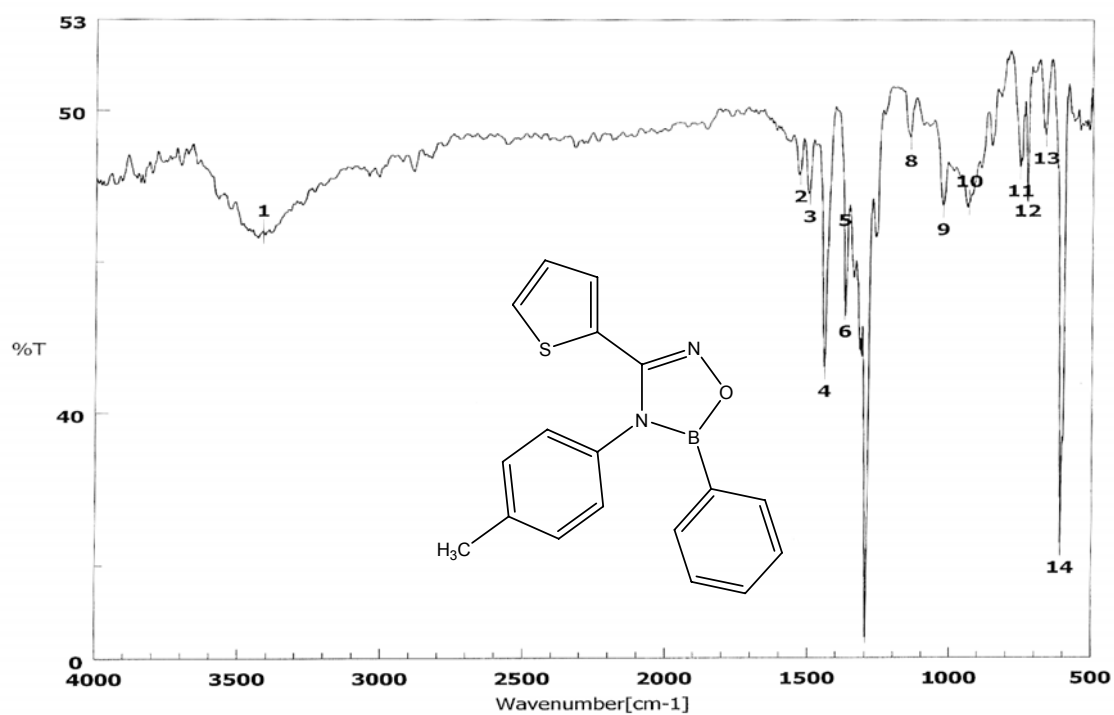


Figure 67A: The IR spectrum of **17p**

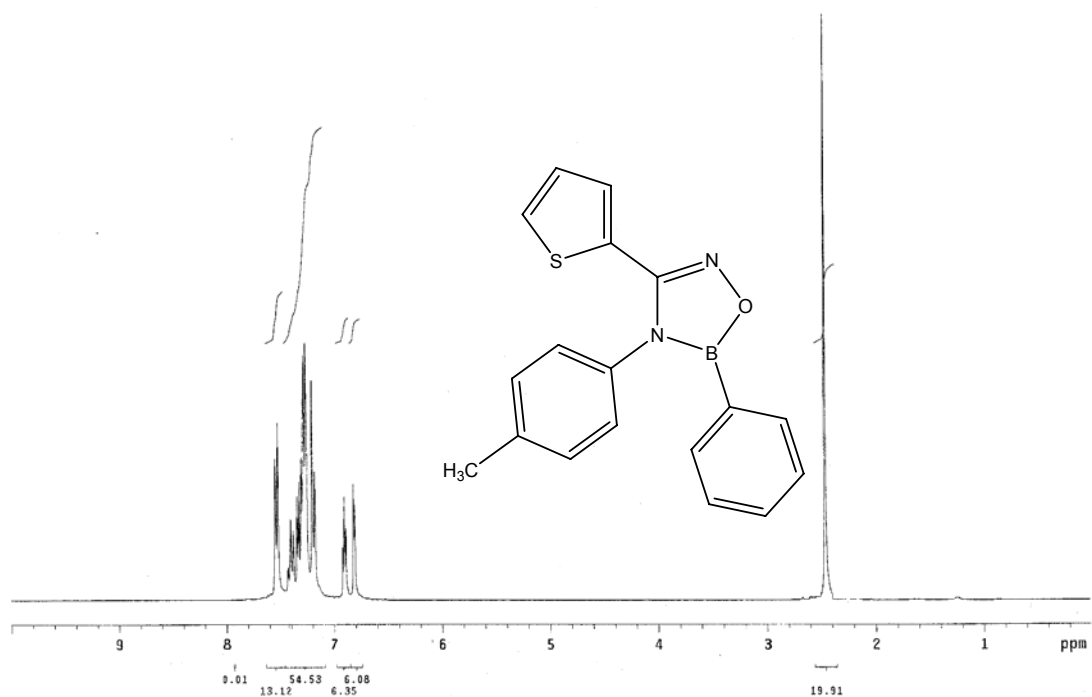


Figure 67B: The ¹H-NMR spectrum of **17p**

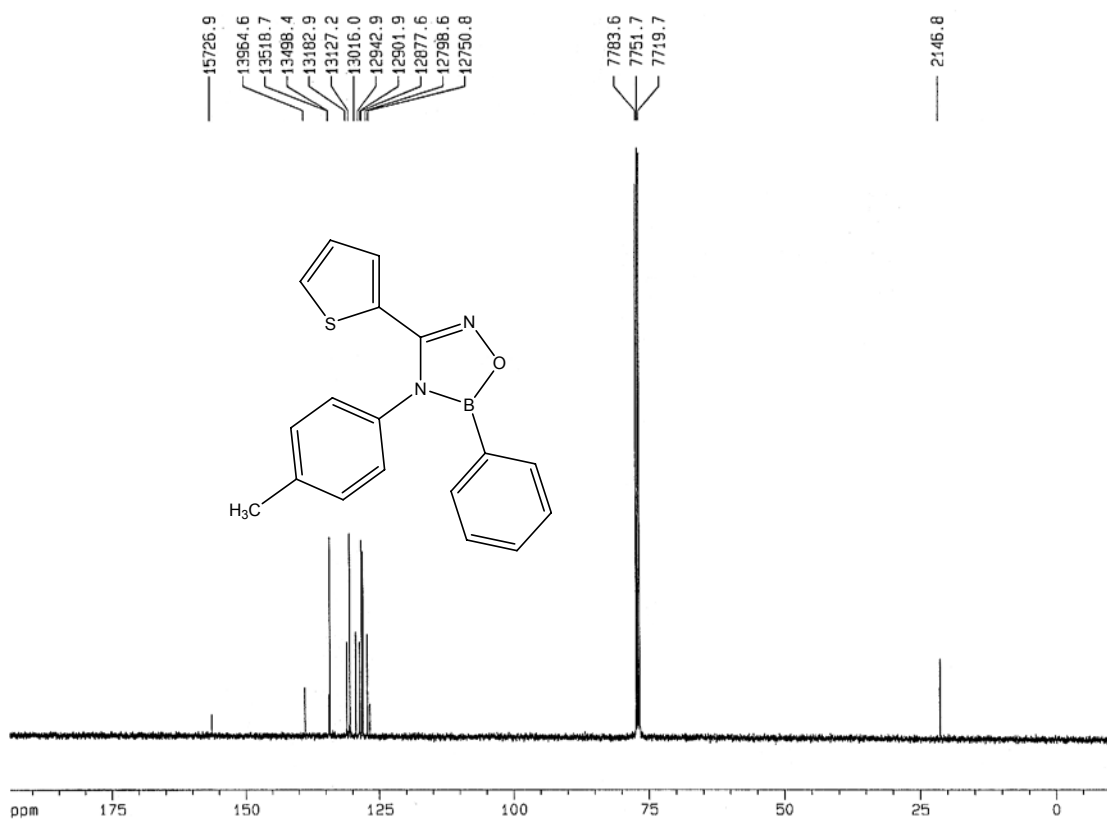


Figure 67C: The ¹³C-NMR spectrum of 17p

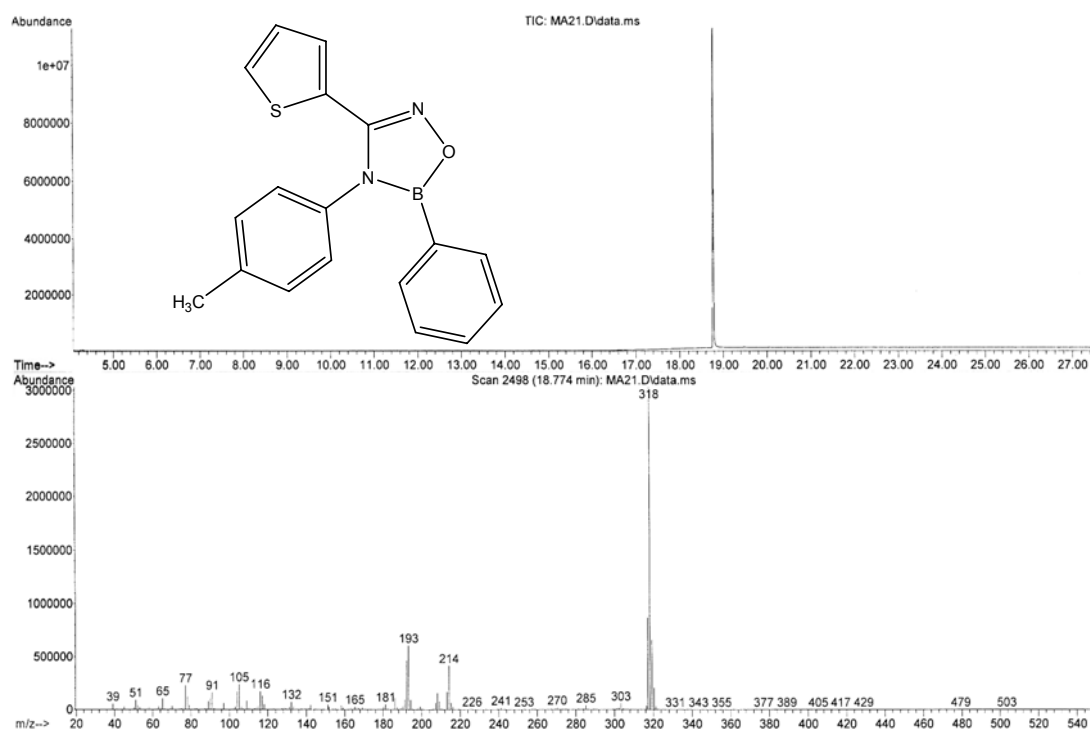


Figure 67D: The mass spectrum of 17p

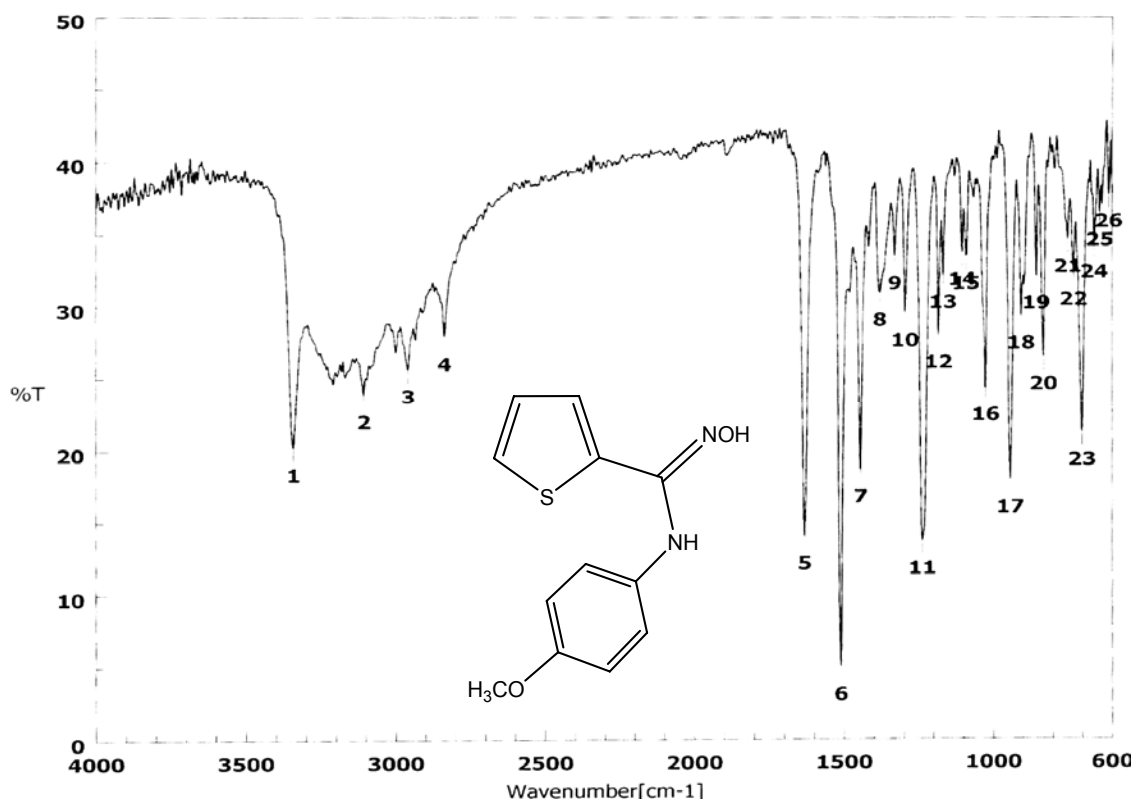


Figure 68: The IR spectrum of **11q**

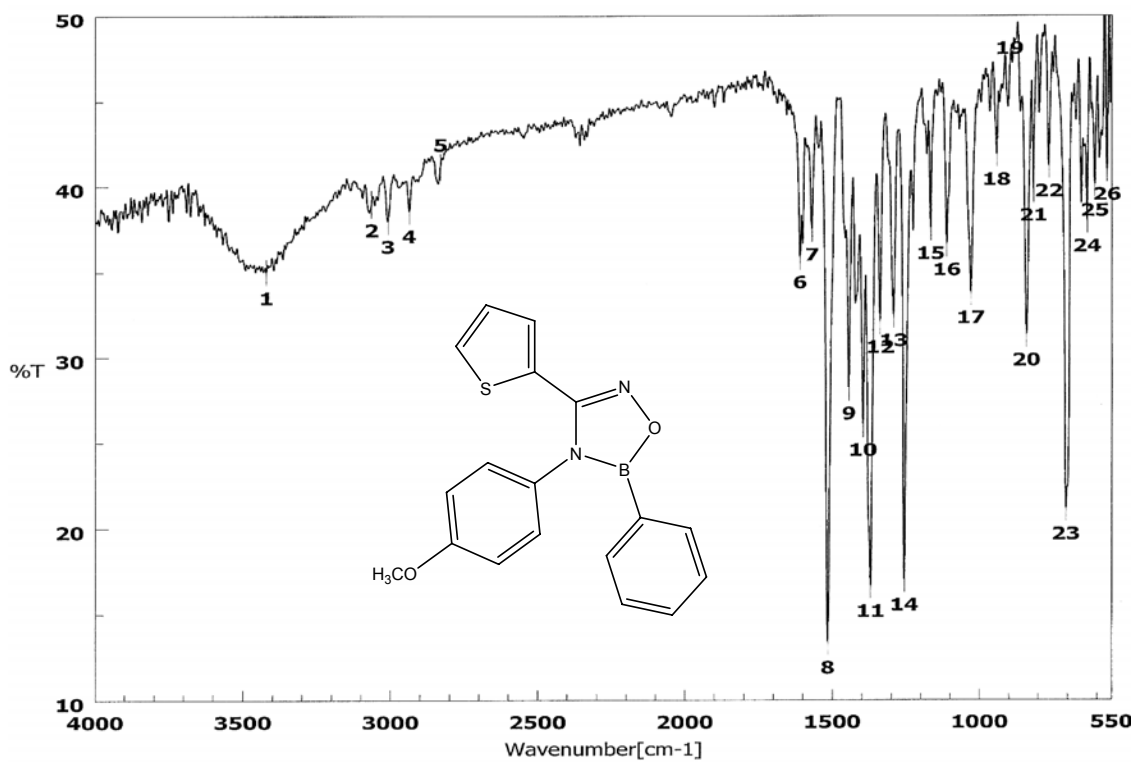


Figure 69A: The IR spectrum of **17q**

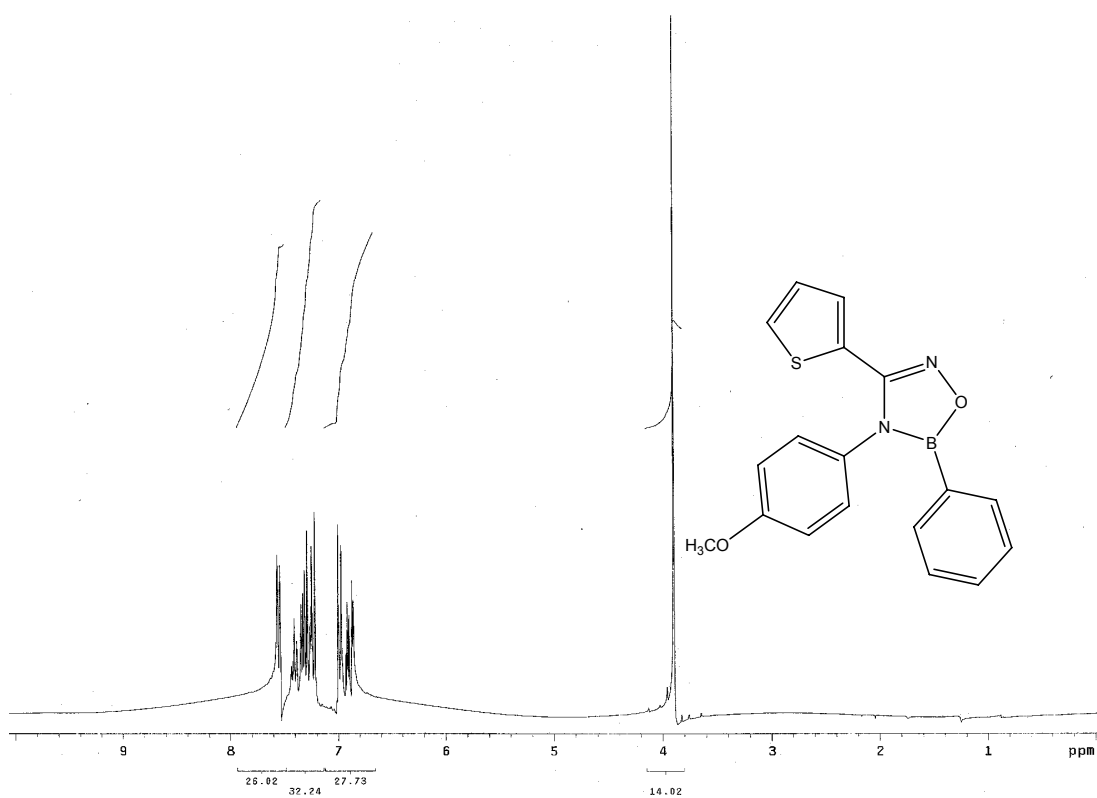


Figure 69B: The ^1H -NMR spectrum of **17q**

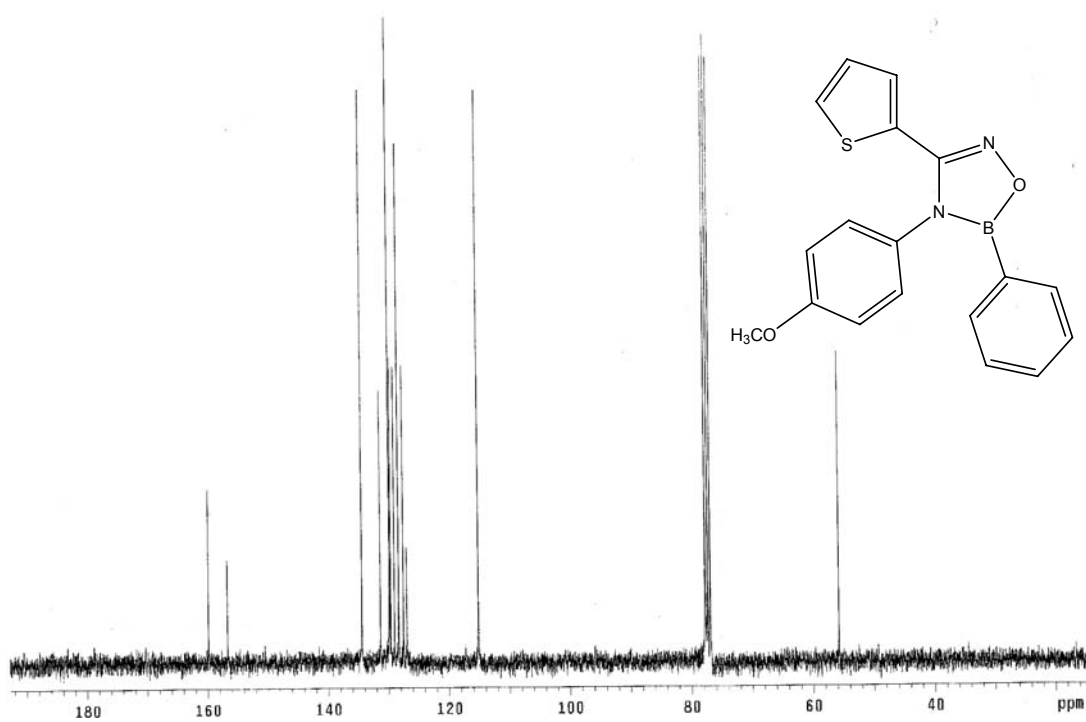


Figure 69C: The ^{13}C -NMR spectrum of **17q**

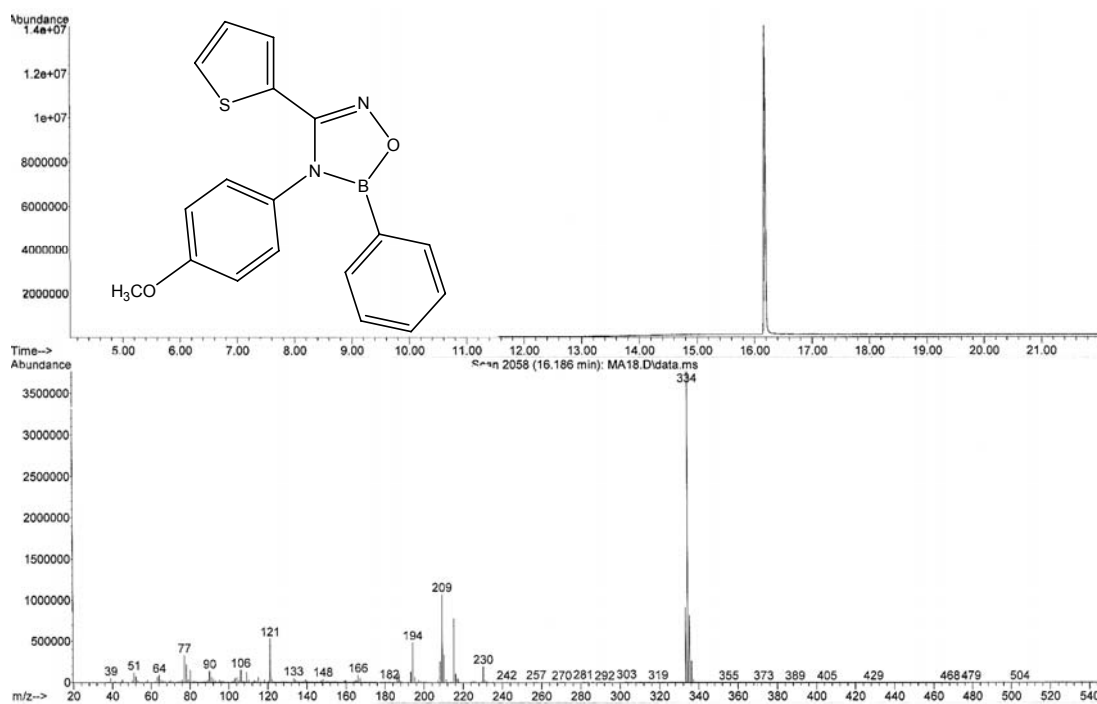


Figure 69D: The mass spectrum of 17q

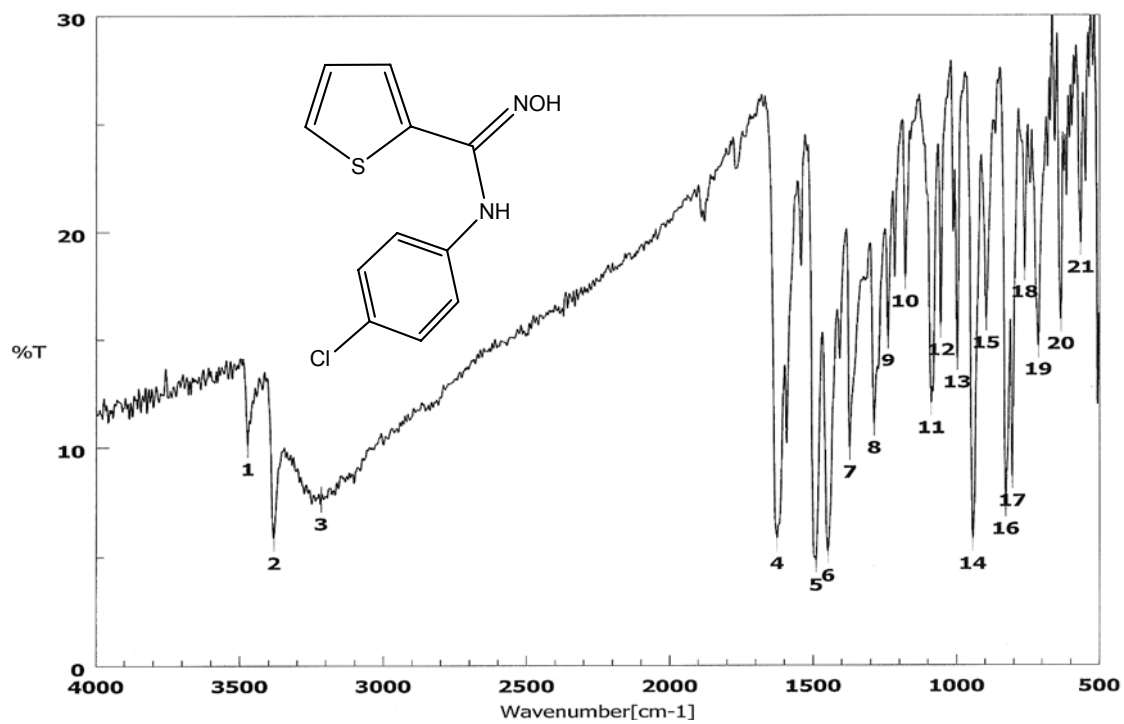


Figure 70: The IR spectrum of 11r

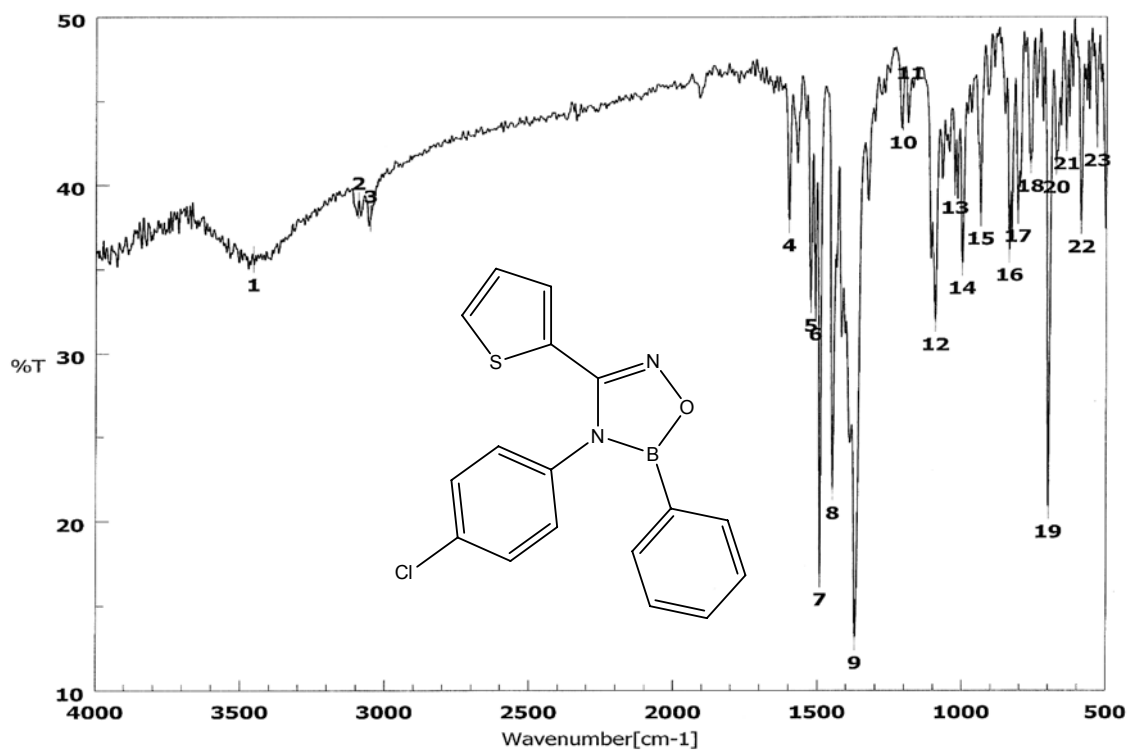


Figure 71A: The IR spectrum of **17r**

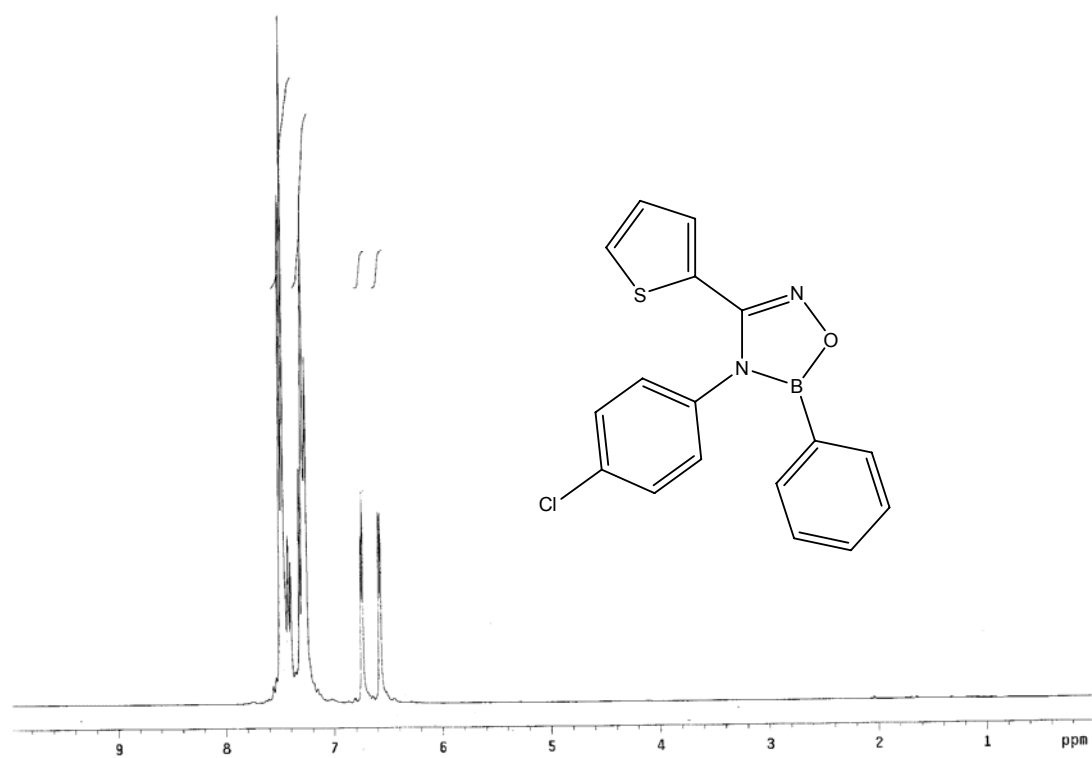


Figure 71B: The ¹H-NMR spectrum of **17r**

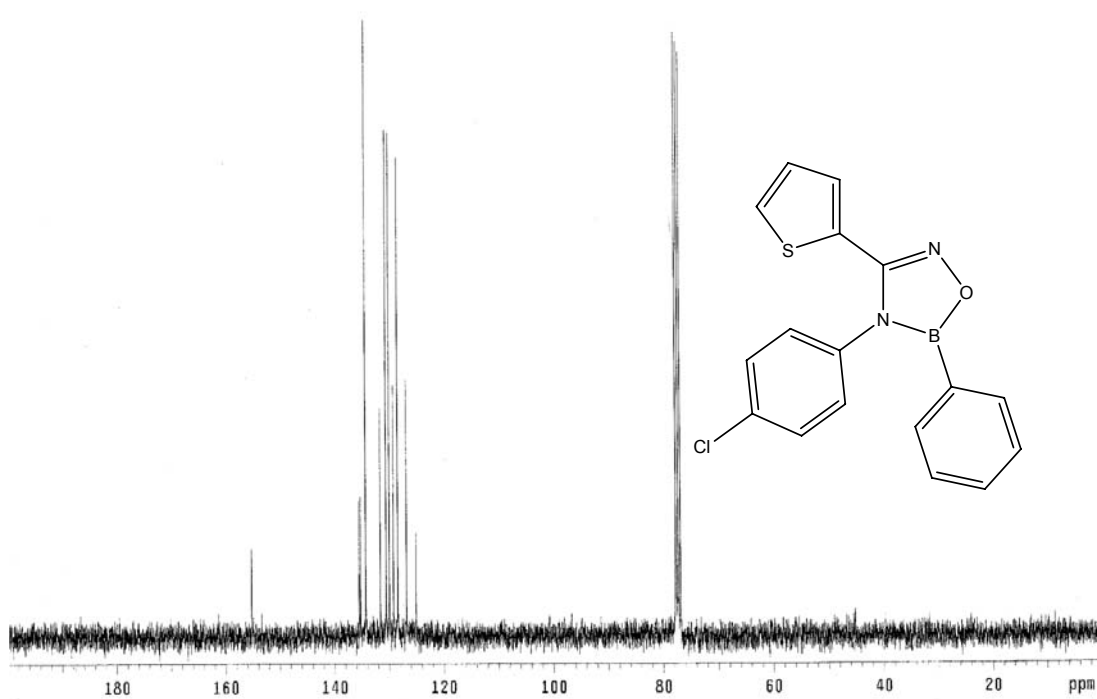


Figure 71C: The ^{13}C -NMR spectrum of **17r**

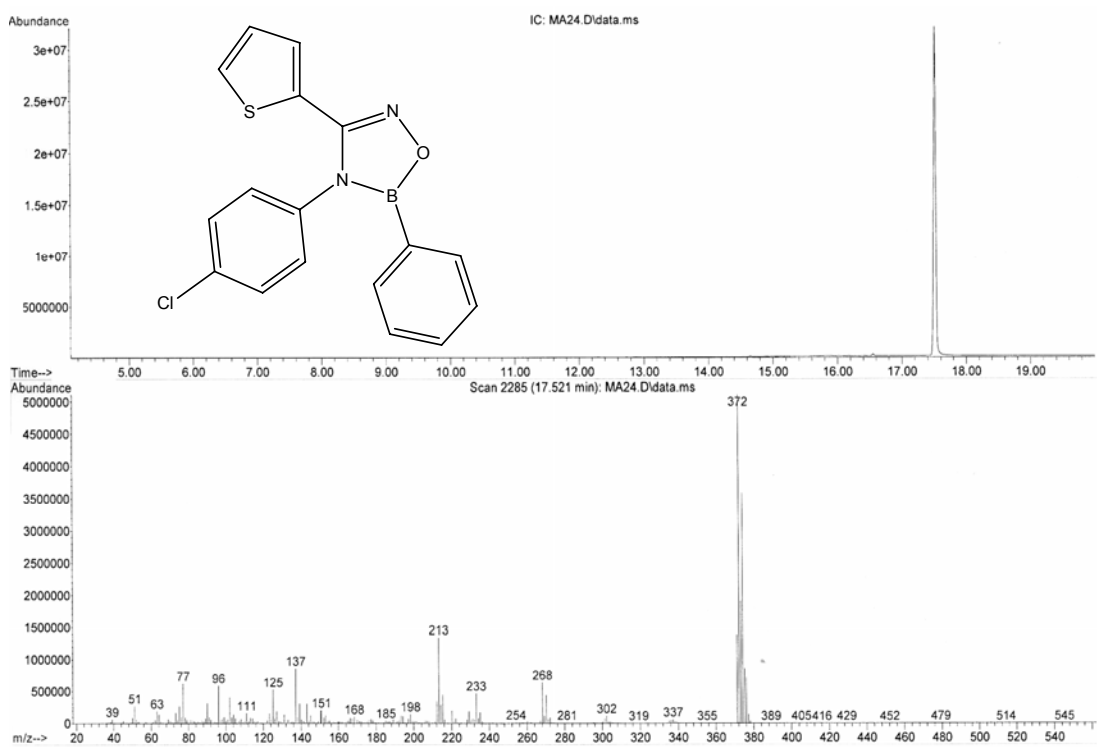


Figure 71D: The mass spectrum of **17r**

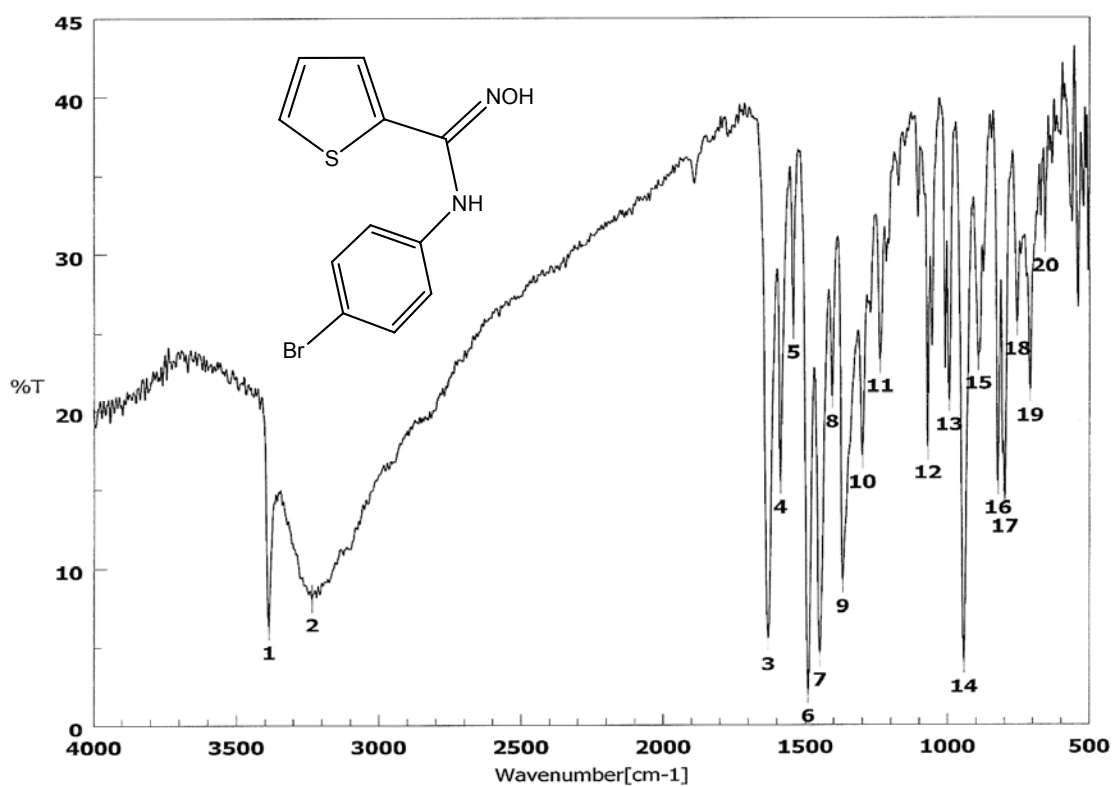


Figure 72: The IR spectrum of **11s**

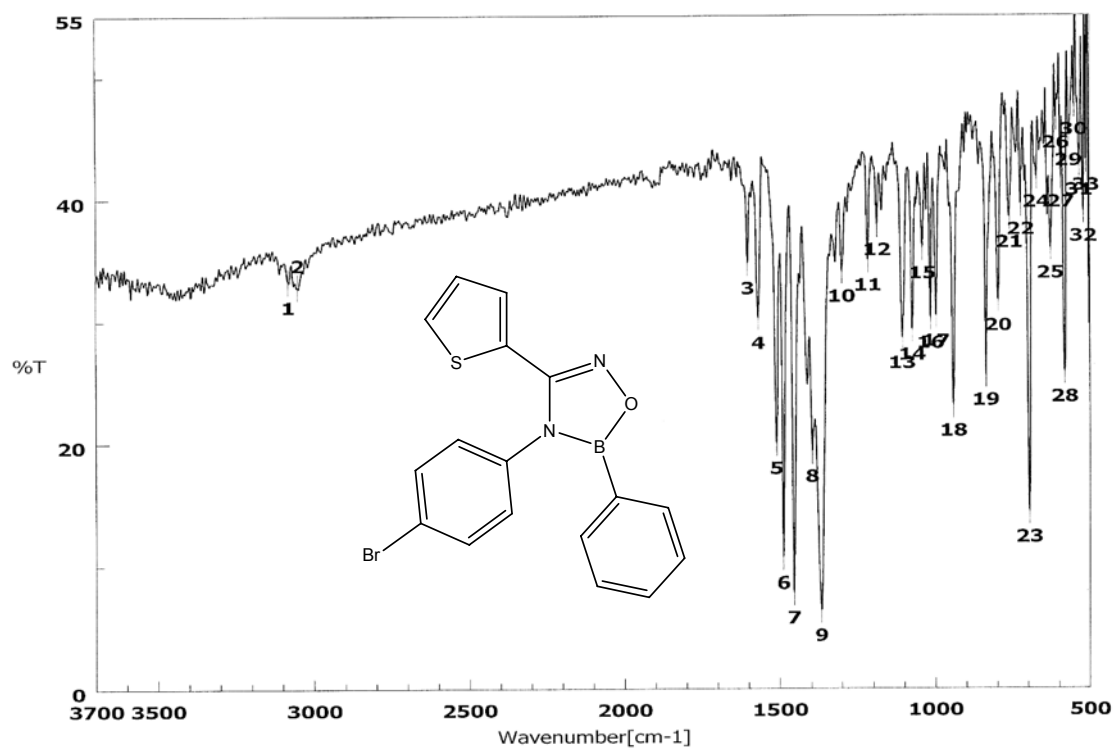


Figure 73A: The IR spectrum of **17s**

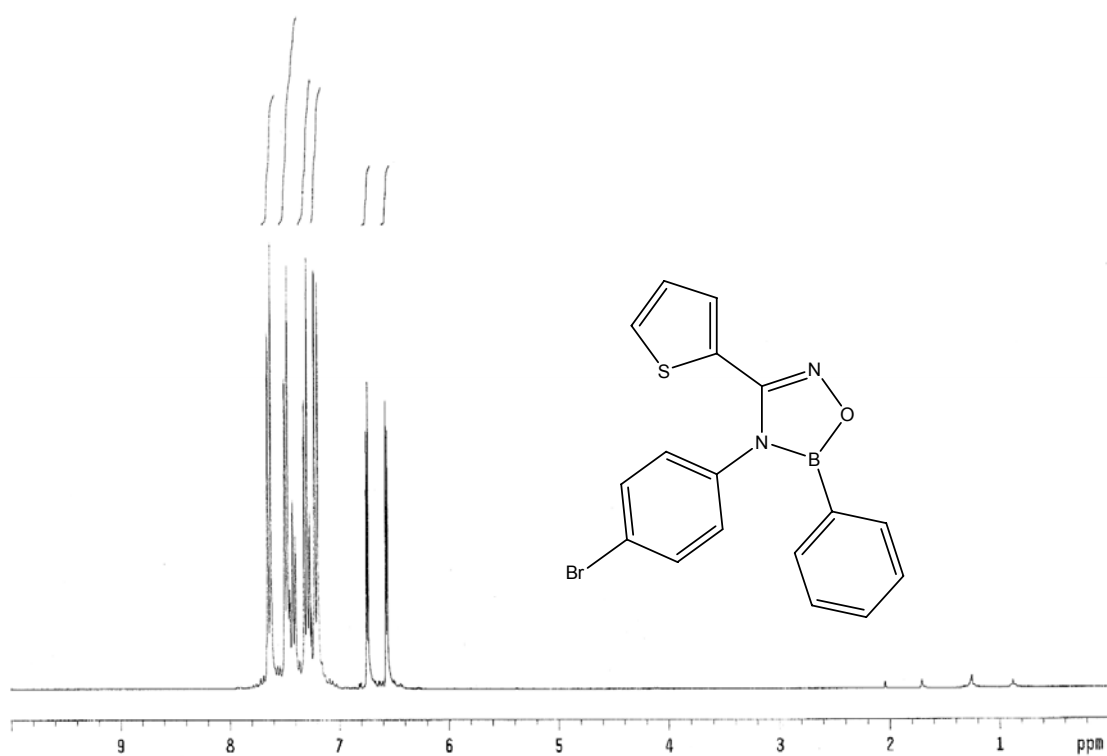


Figure 73B: The ^1H -NMR spectrum of **17s**

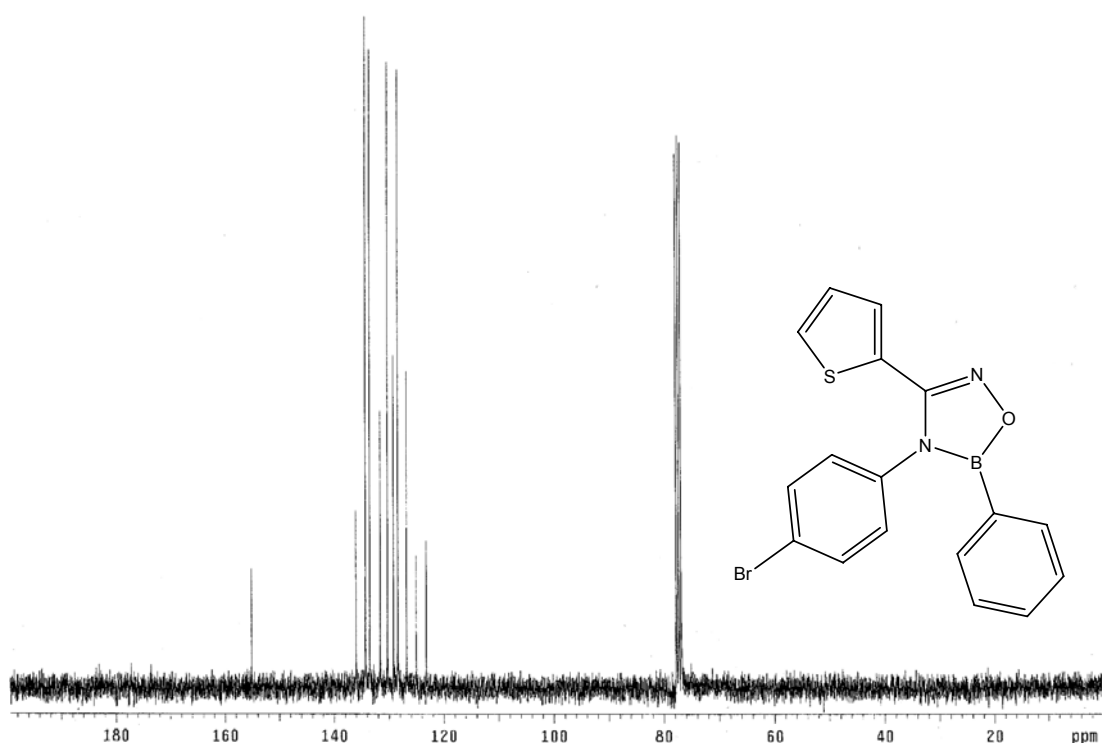


Figure 73C: The ^{13}C -NMR spectrum of **17s**

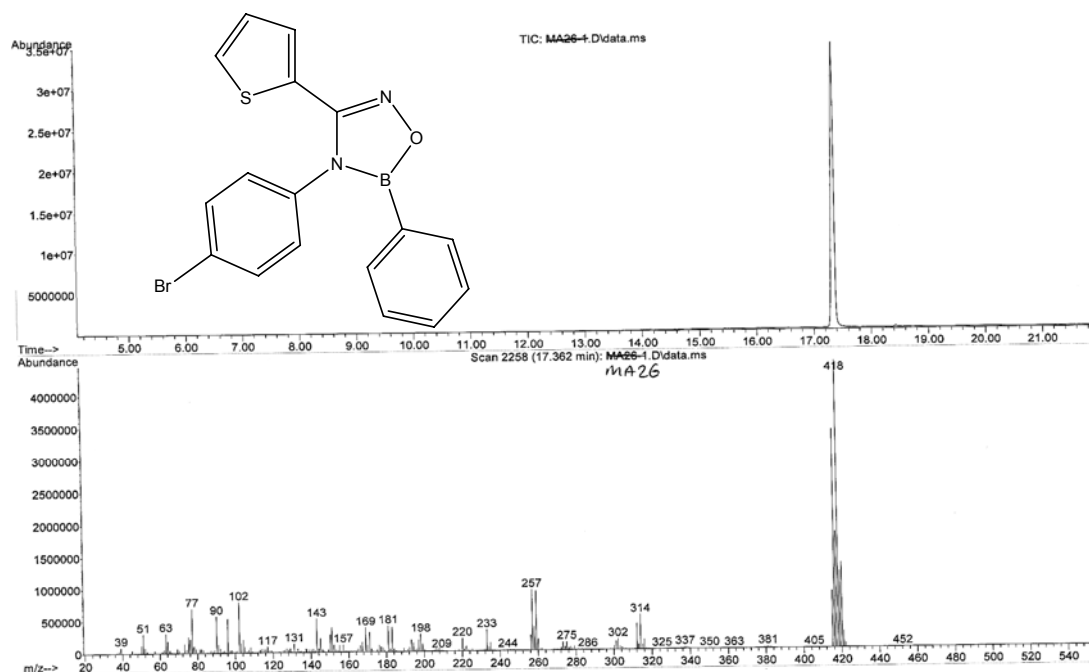


Figure 73D: The mass spectrum of 17s

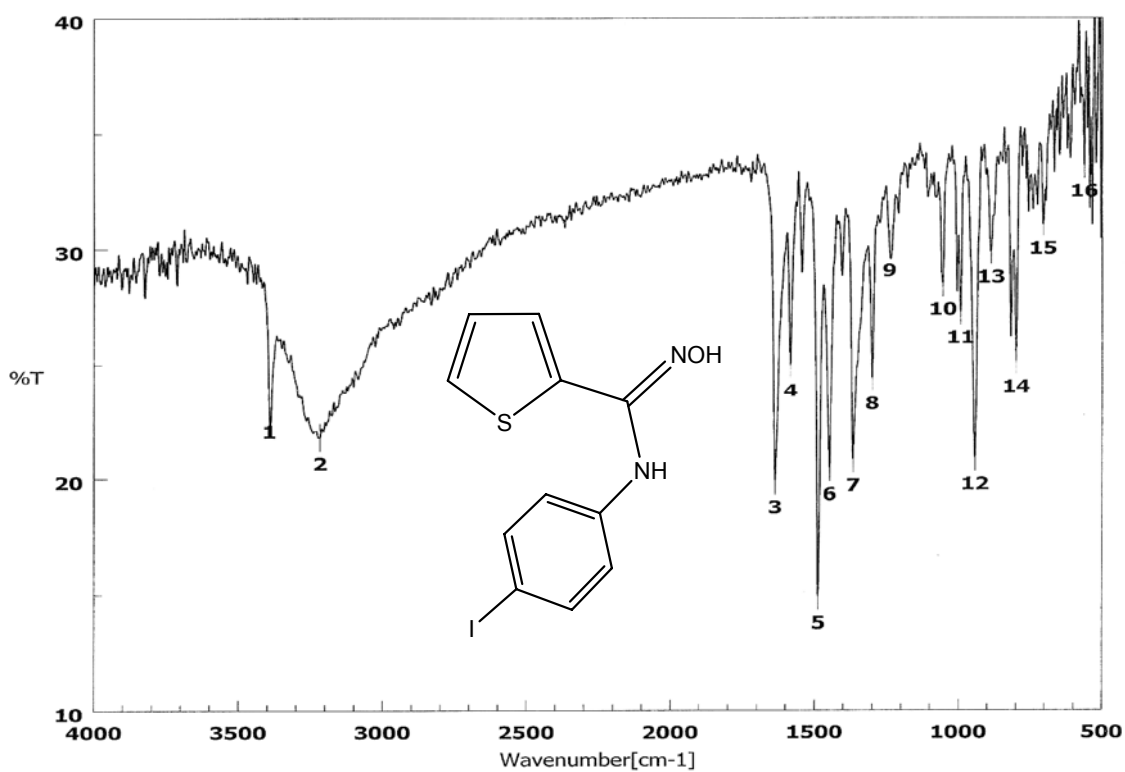


Figure 74: The IR spectrum of 11t

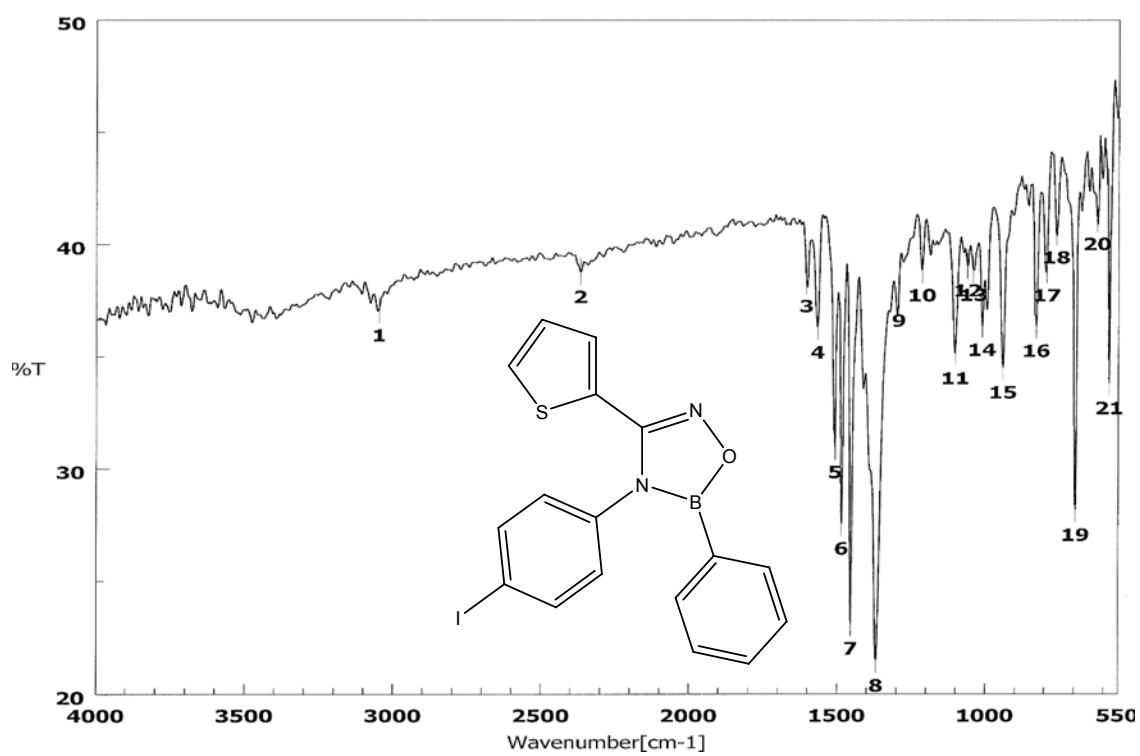


Figure 75A: The IR spectrum of **17t**

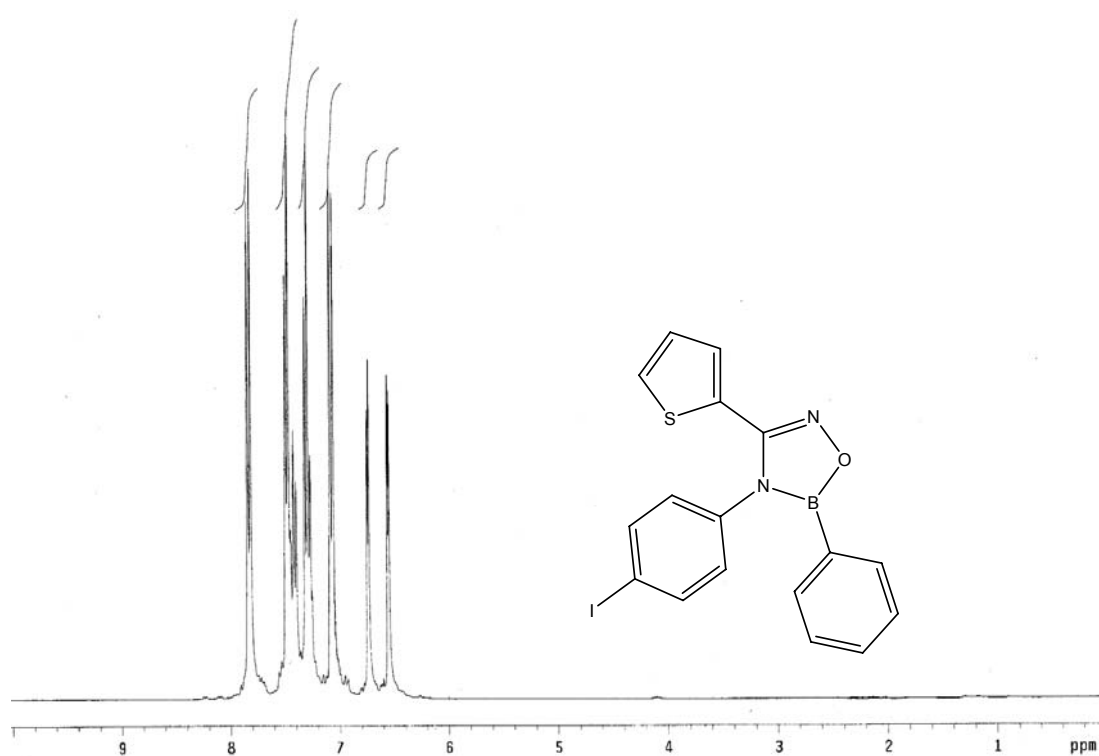


Figure 75B: The ¹H-NMR spectrum of **17t**

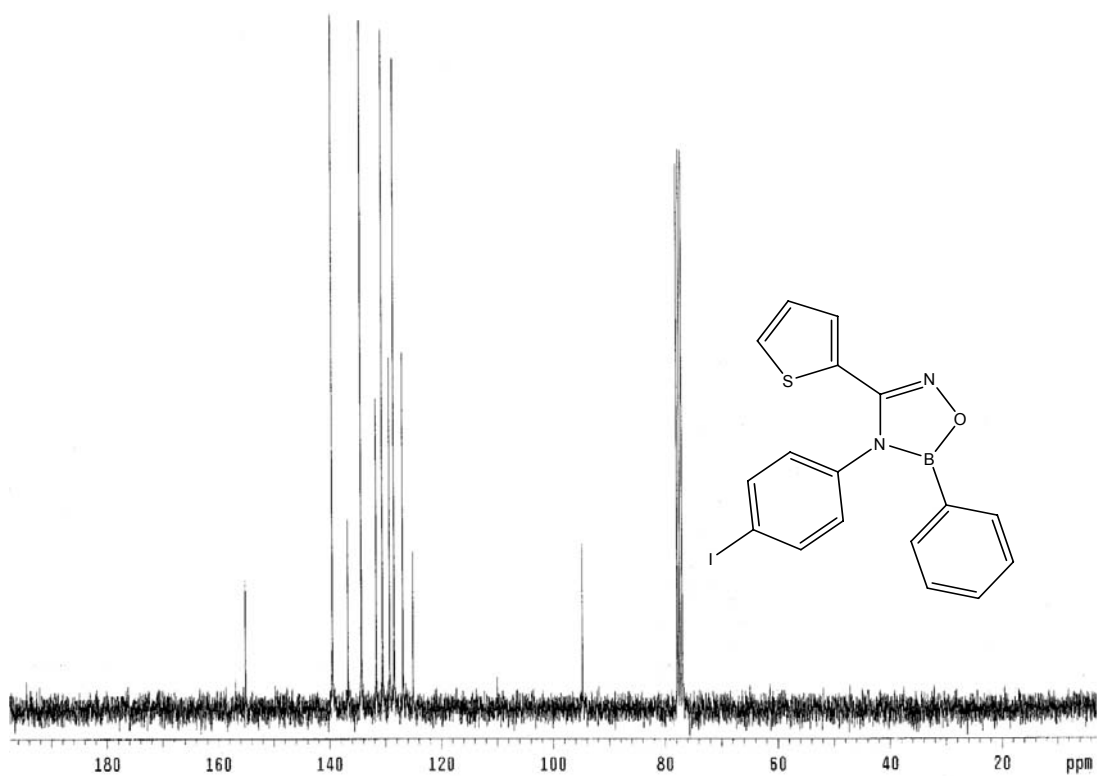


Figure 75C: The ^{13}C -NMR spectrum of **17t**

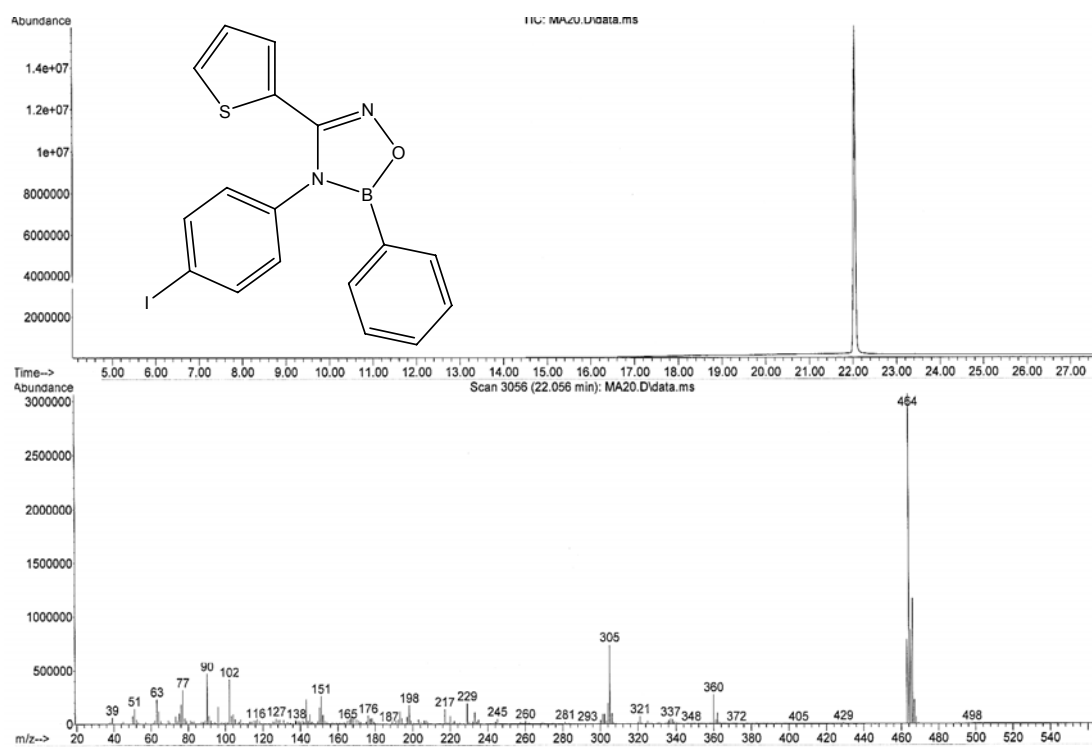


Figure 75D: The mass spectrum of **17t**

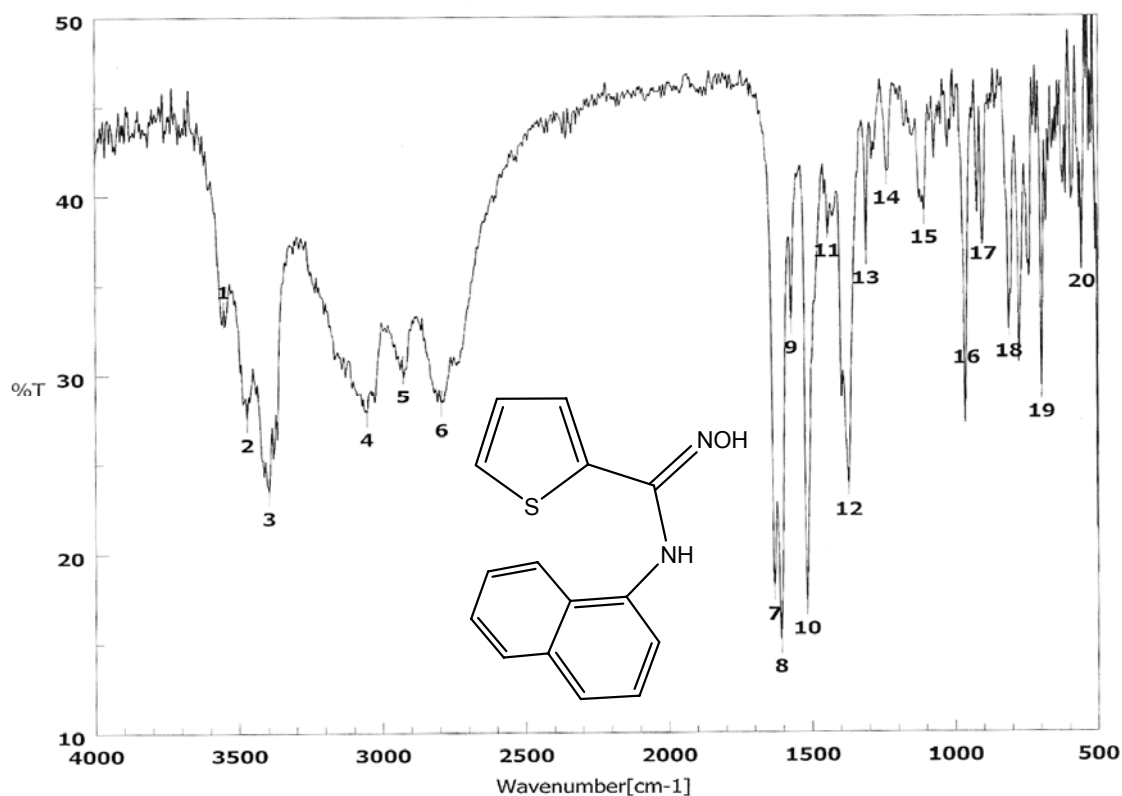


Figure 76: The IR spectrum of 11u

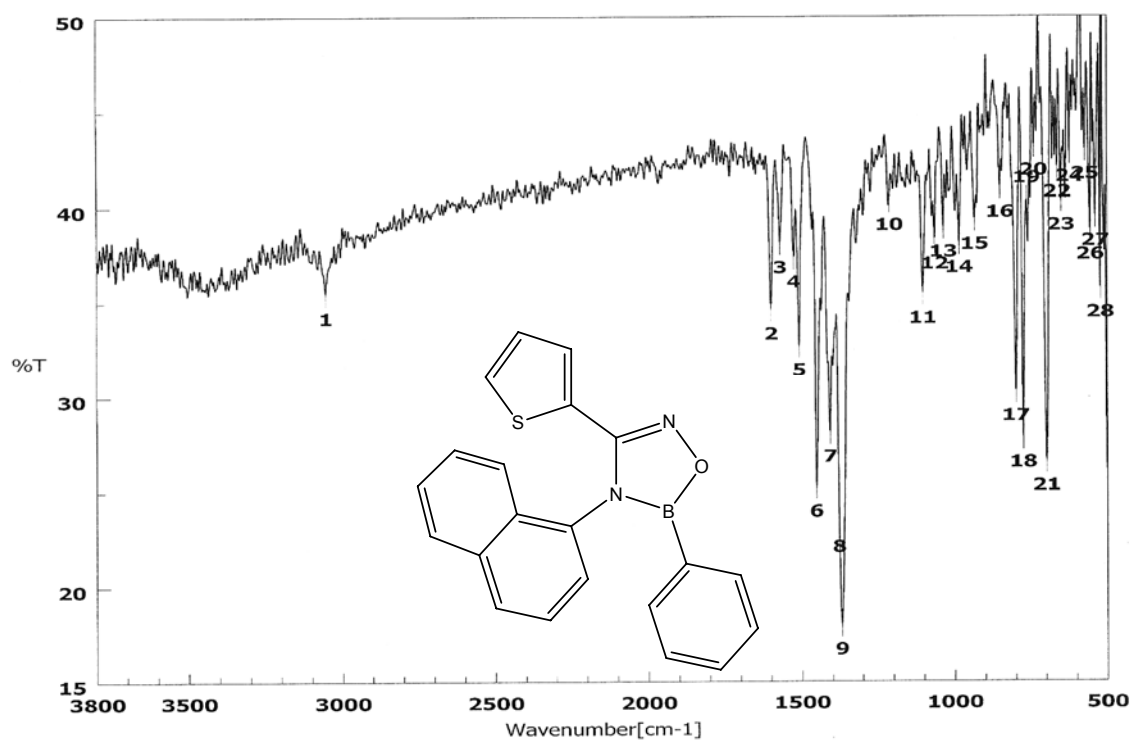


Figure 77A: The IR spectrum of 17u

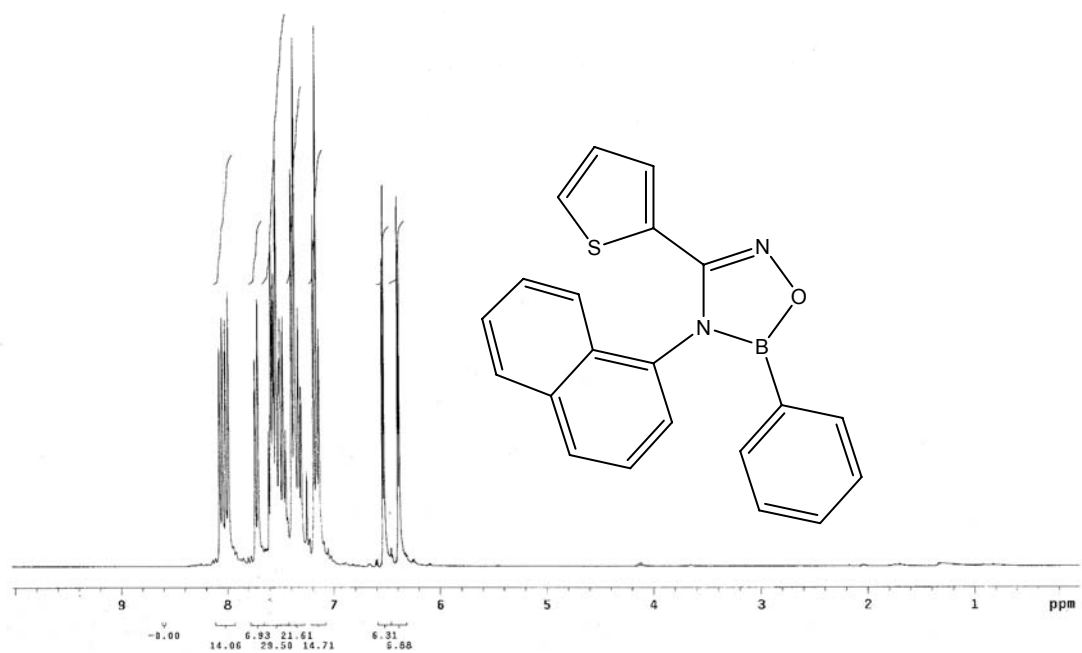


Figure 77B: The ^1H -NMR spectrum of **17u**

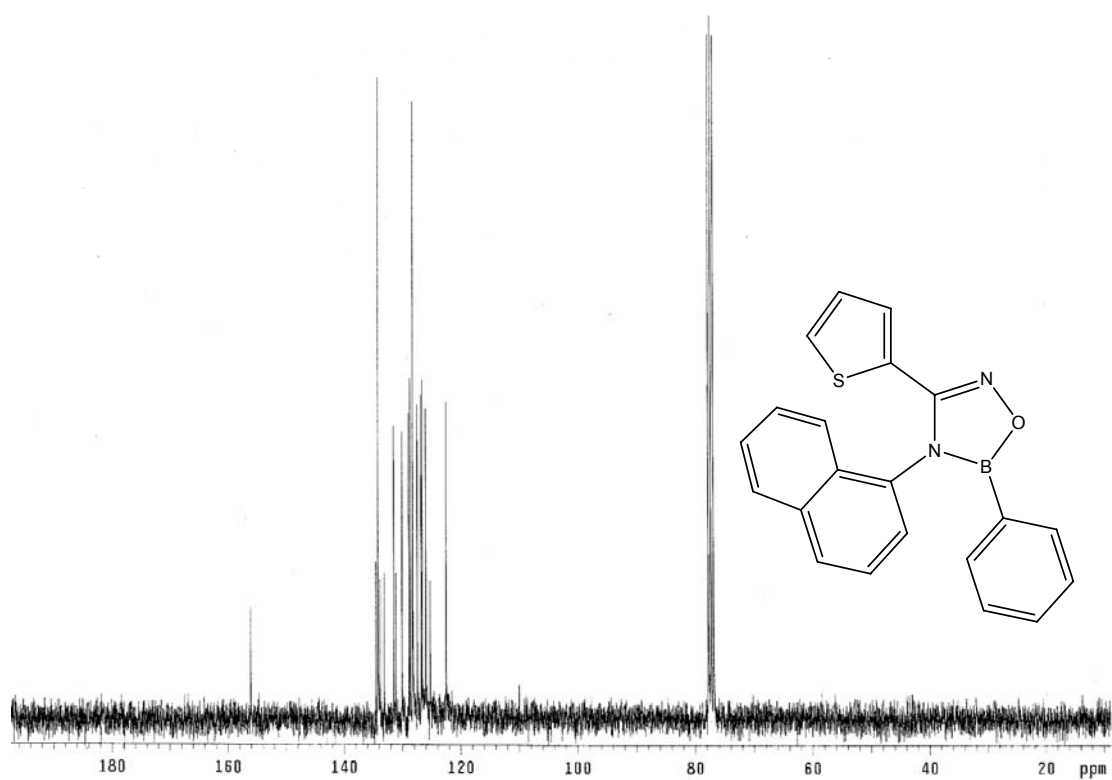


Figure 77C: The ^{13}C -NMR spectrum of **17u**

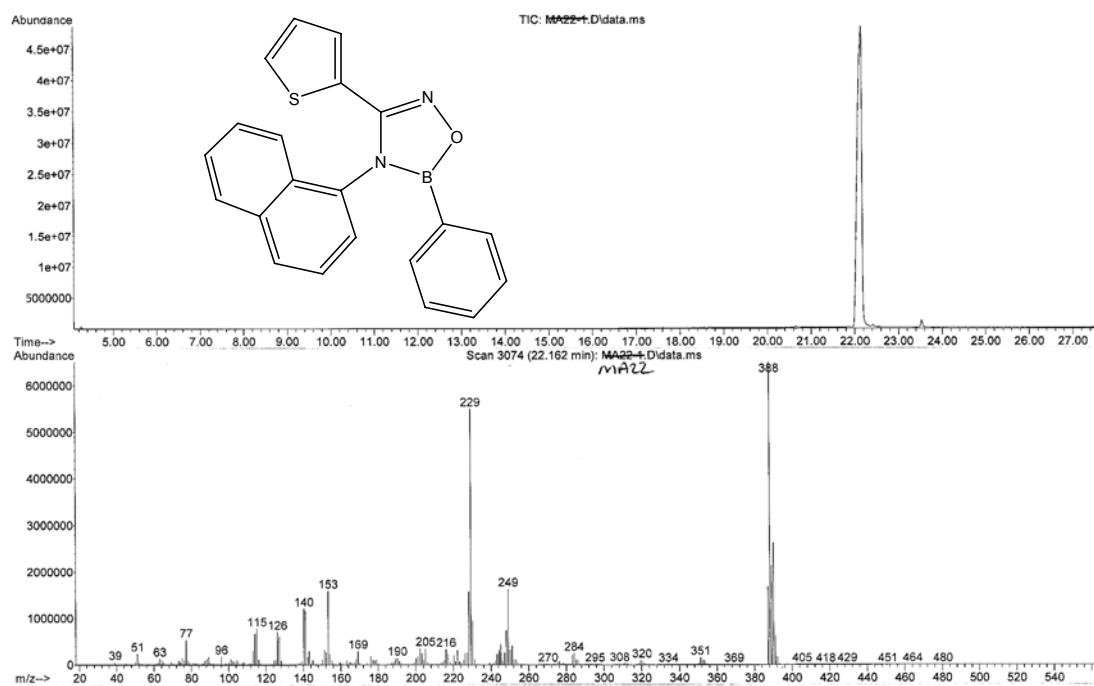


Figure 77D: The mass spectrum of 17u

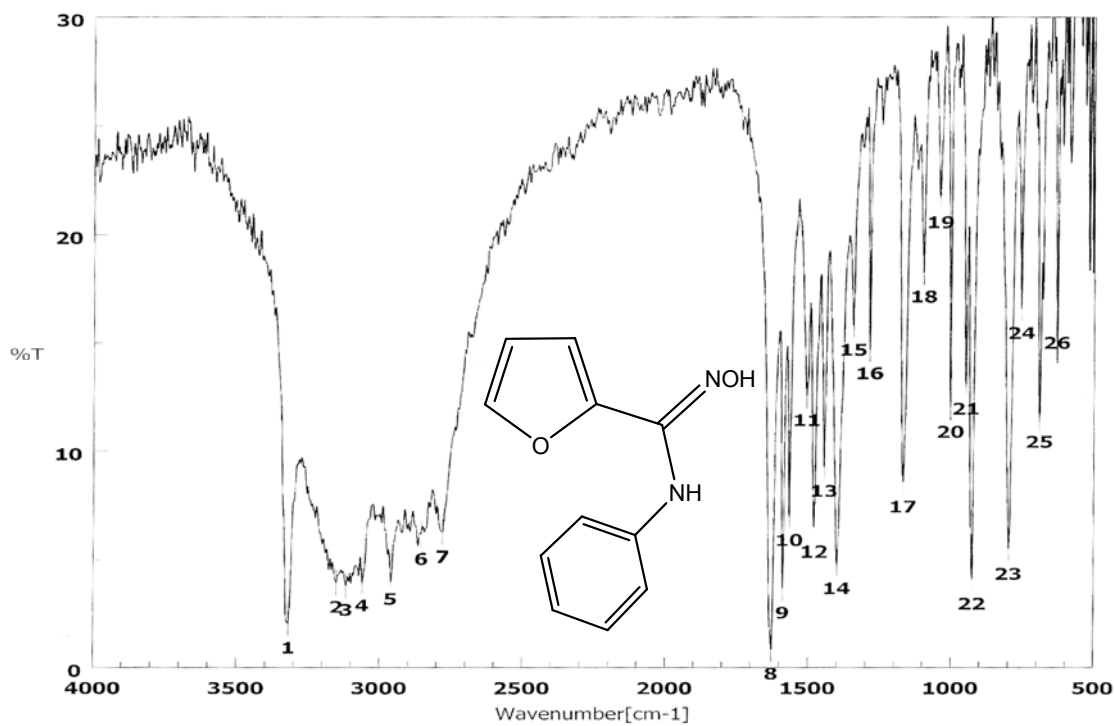


Figure 78: The IR spectrum of 12o

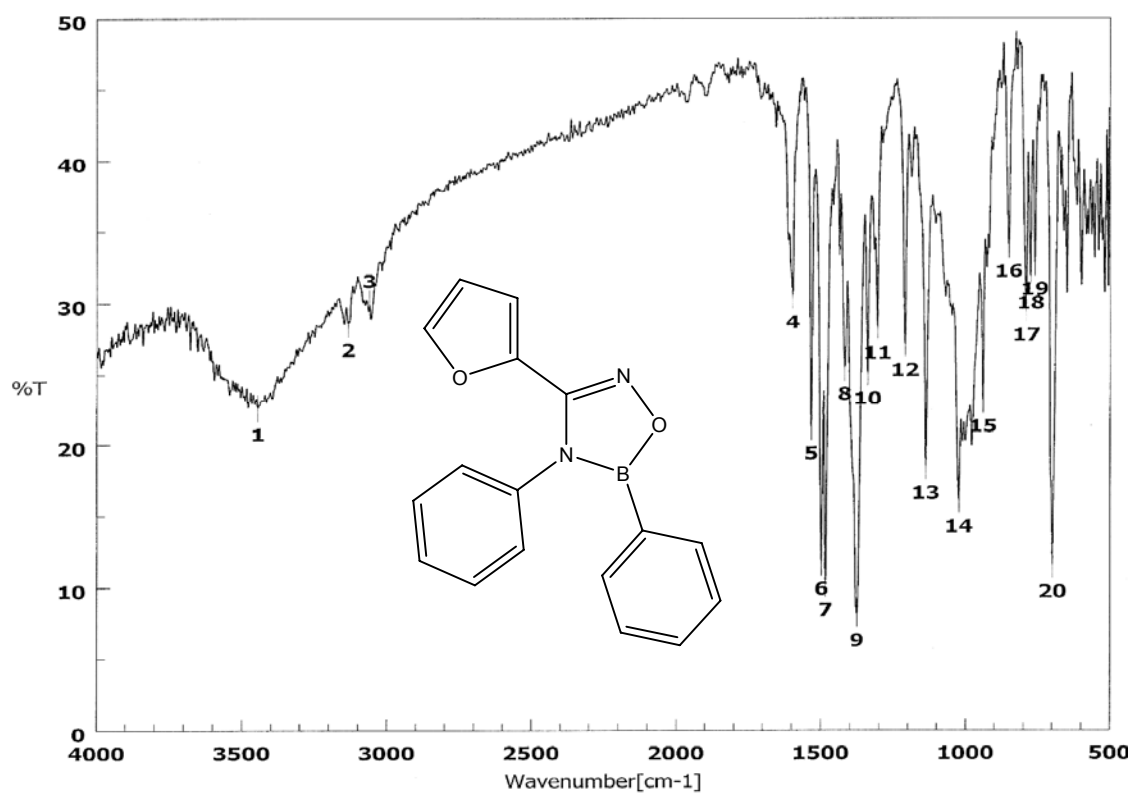


Figure 79A: The IR spectrum of **18o**

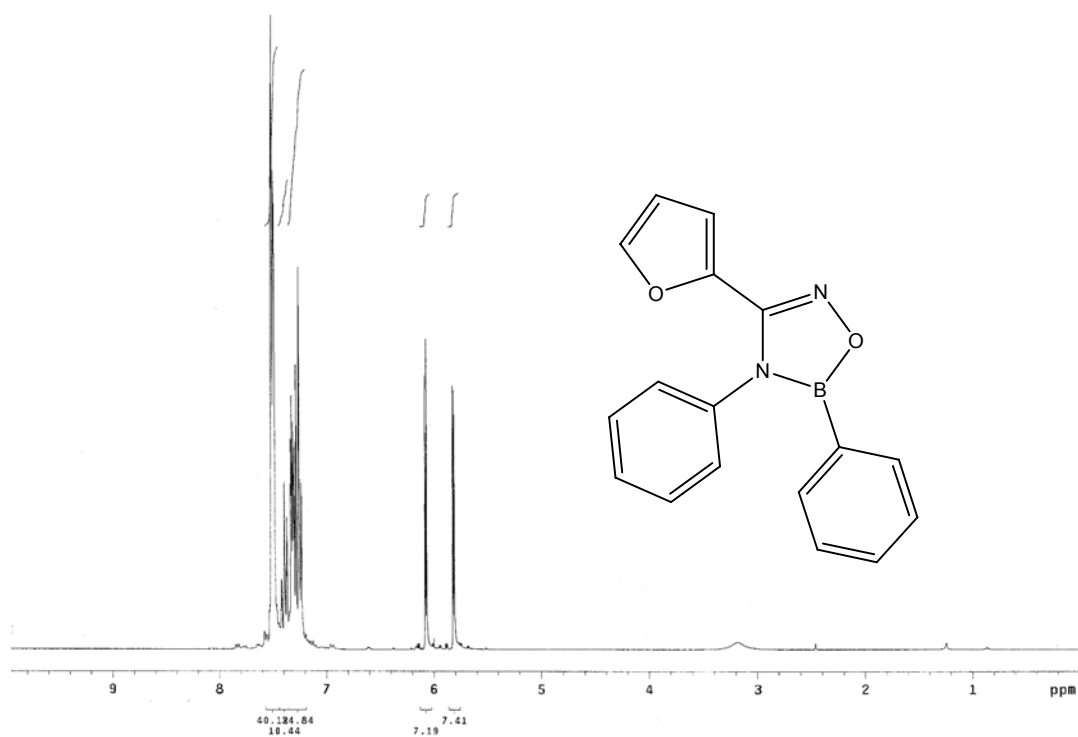


Figure 79B: The ^1H -NMR spectrum of **18o**

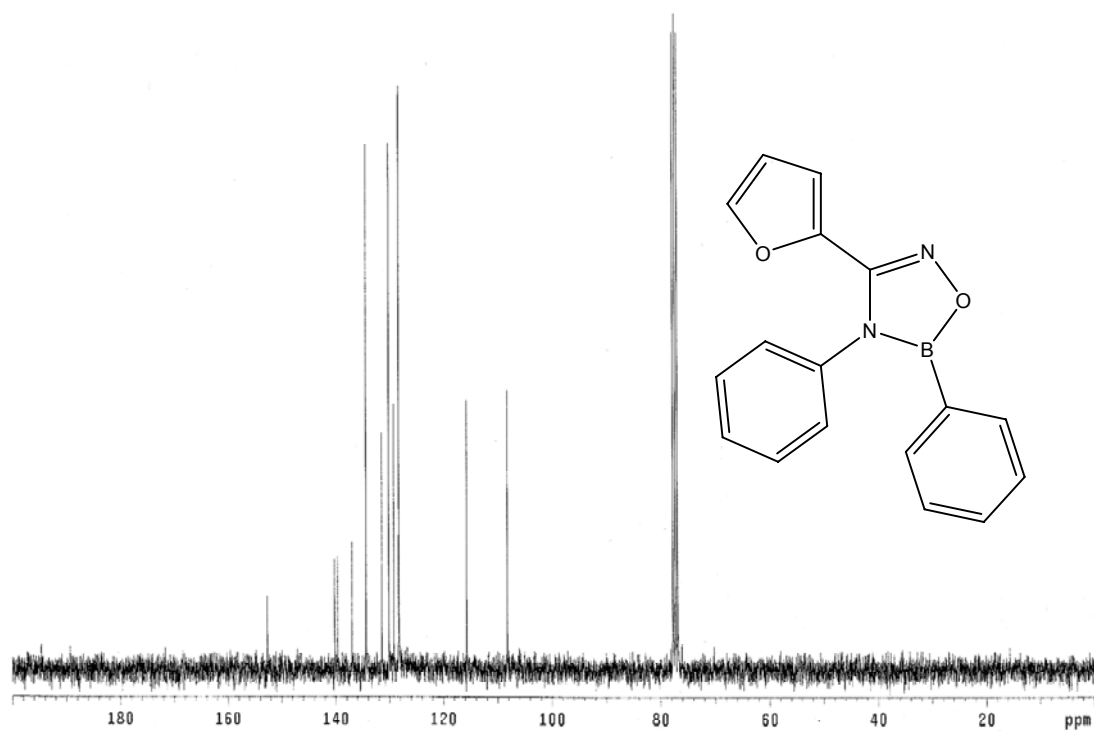


Figure 79C: The ^{13}C -NMR spectrum of **18o**

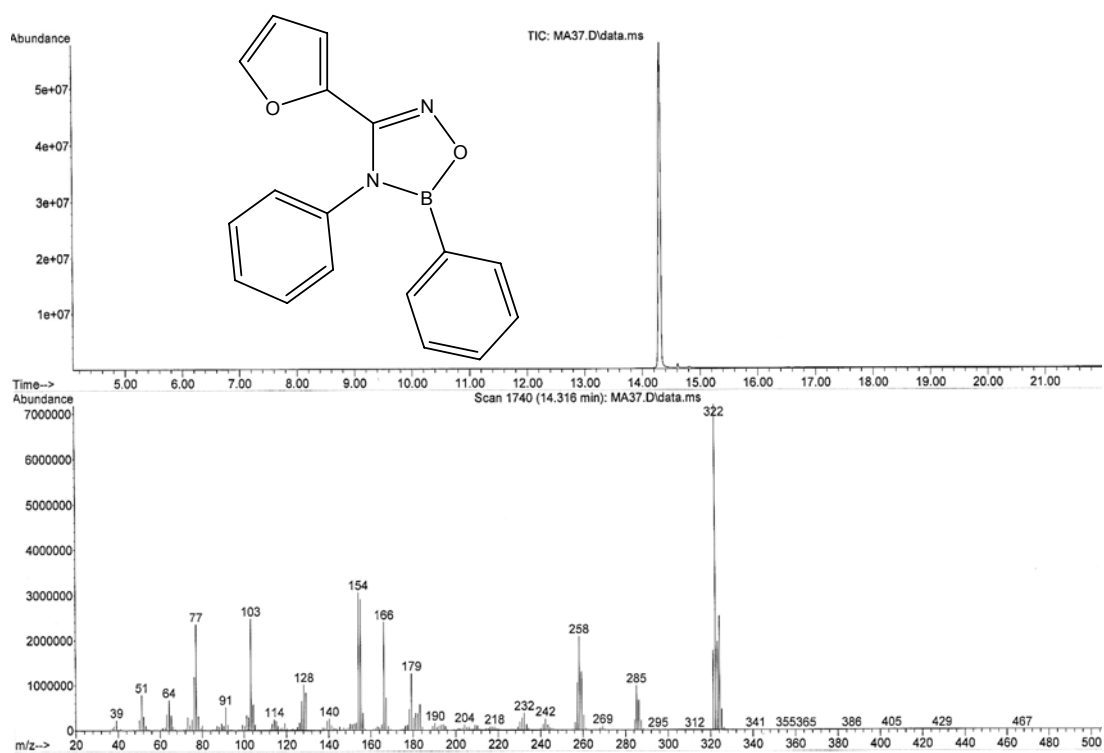


Figure 79D: The mass spectrum of **18o**

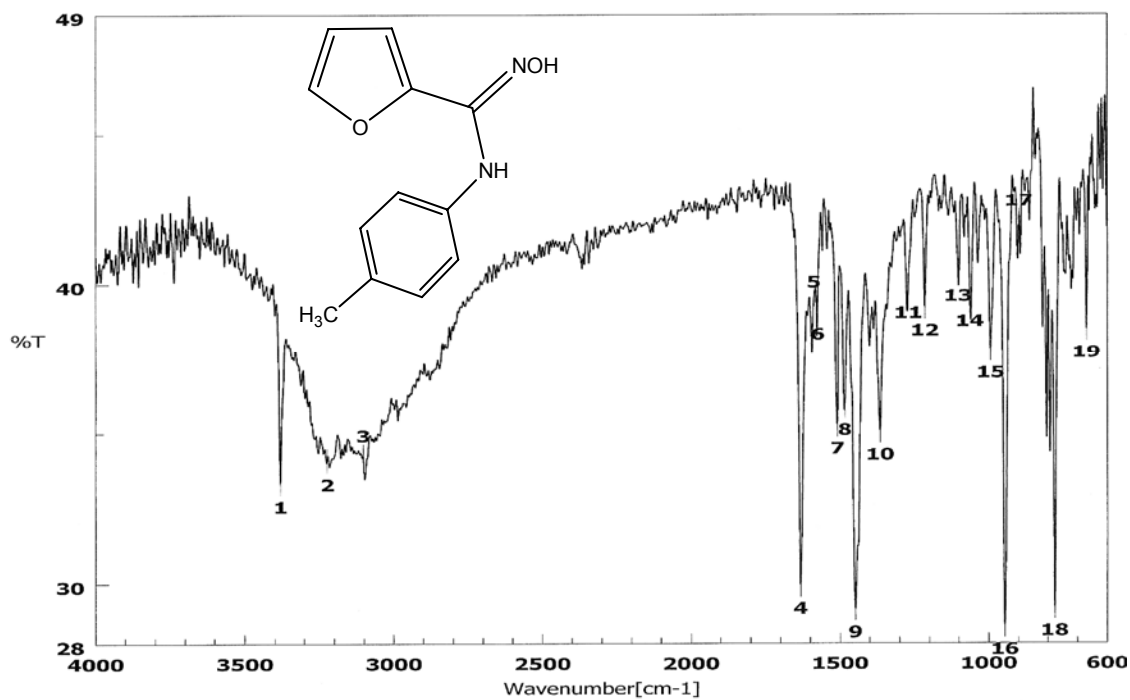


Figure 80: The IR spectrum of **12p**

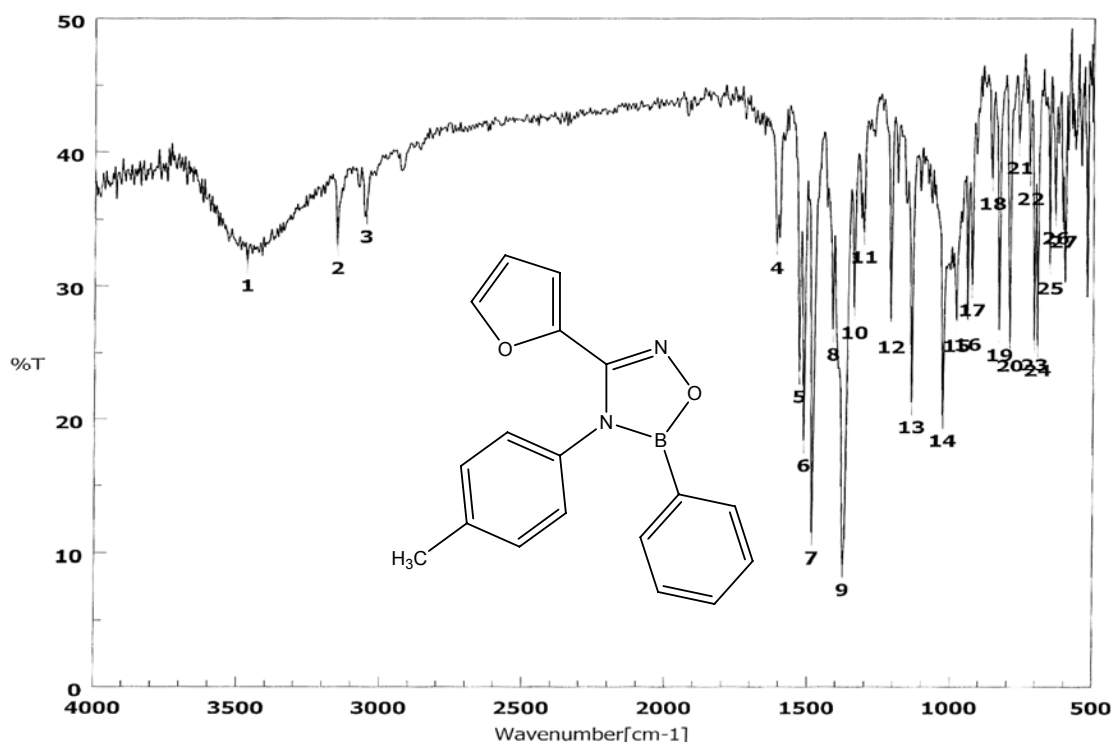


Figure 81A: The IR spectrum of **18p**

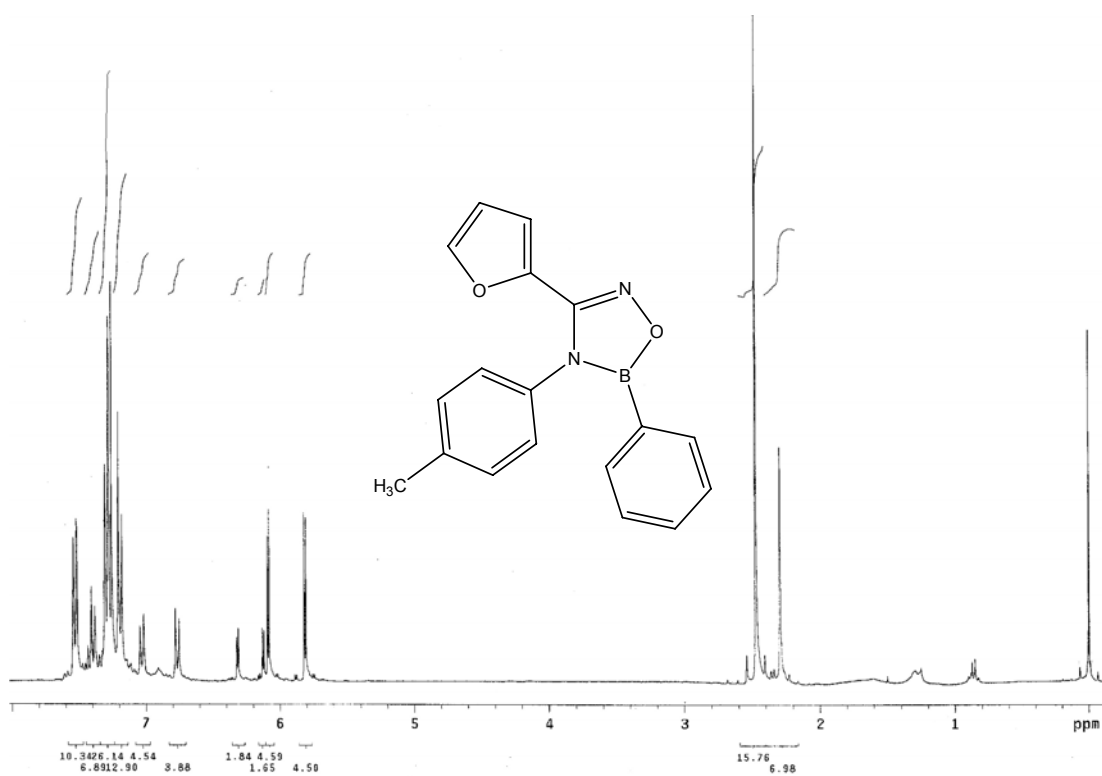


Figure 81B: The ¹H-NMR spectrum of **18p**

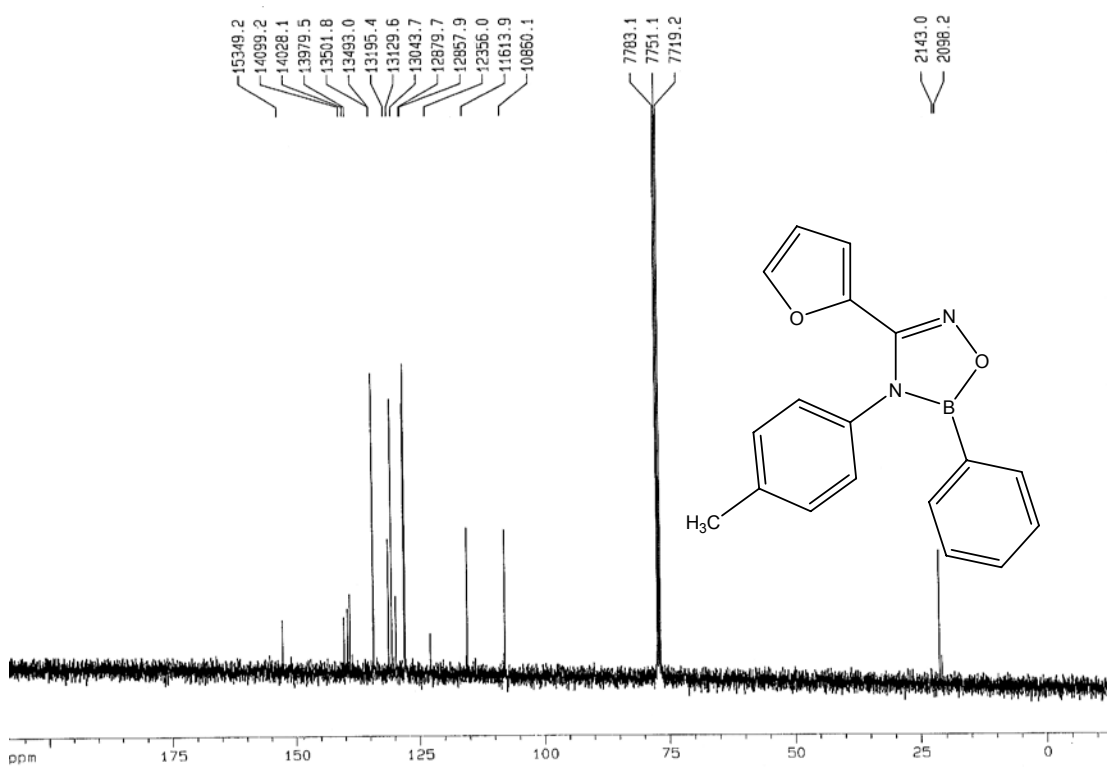


Figure 81C: The ¹³C-NMR spectrum of **18p**

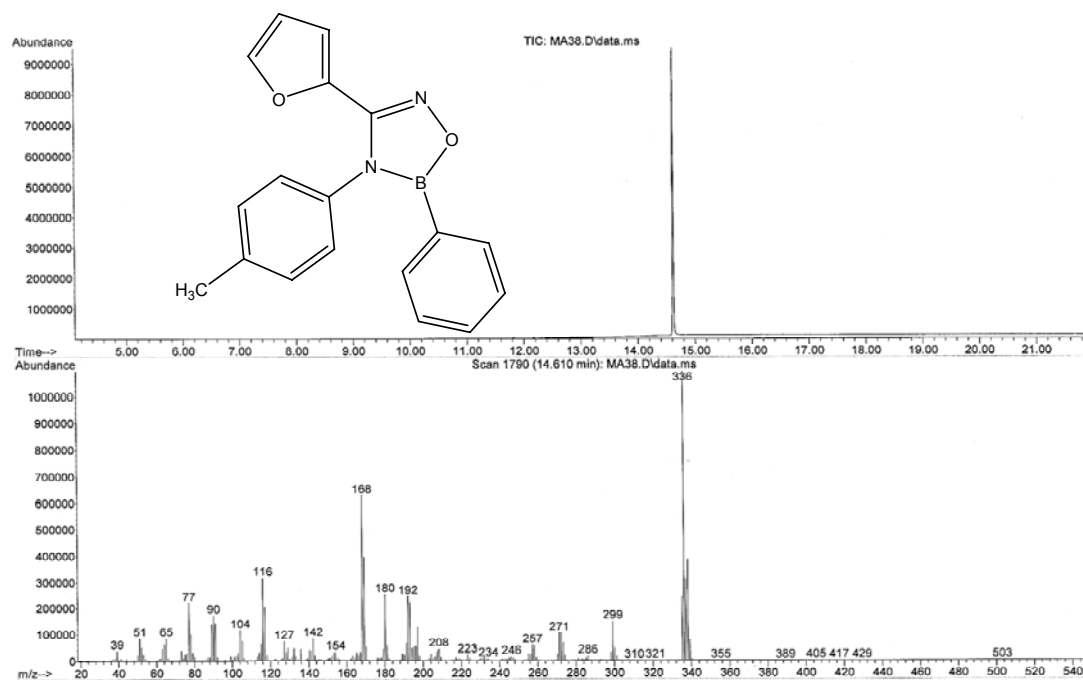


Figure 81D: The mass spectrum of **18p**

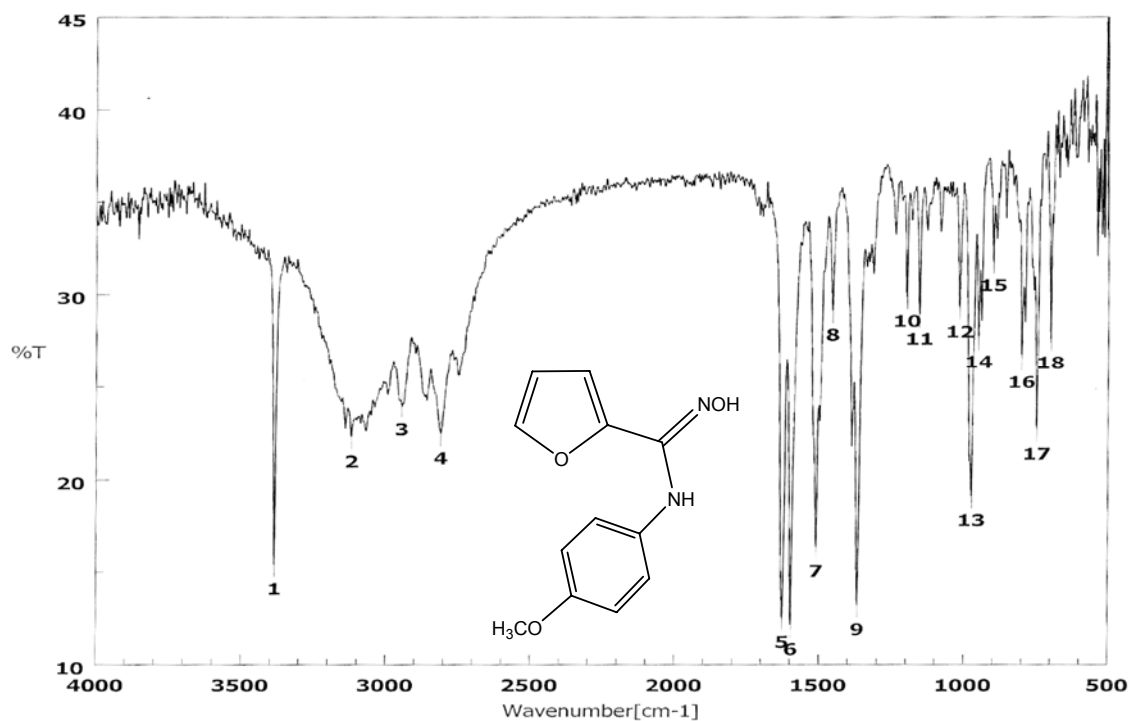


Figure 82: The IR spectrum of **12q**

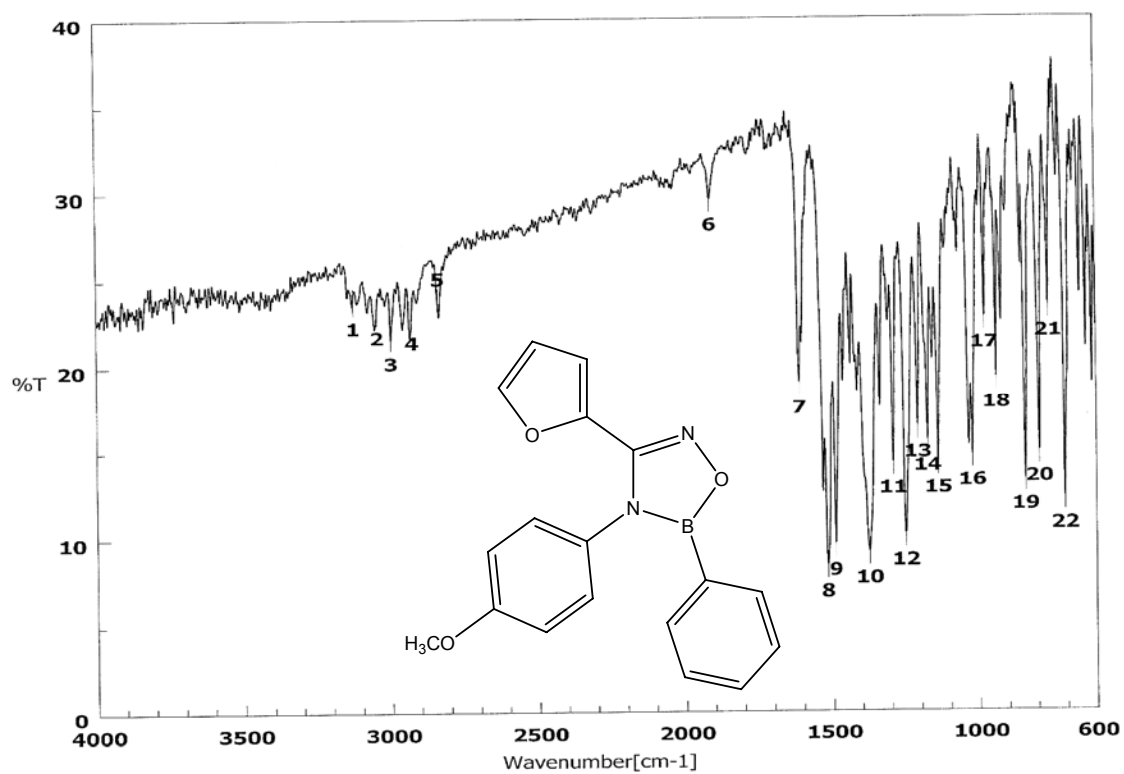


Figure 83A: The IR spectrum of **18q**

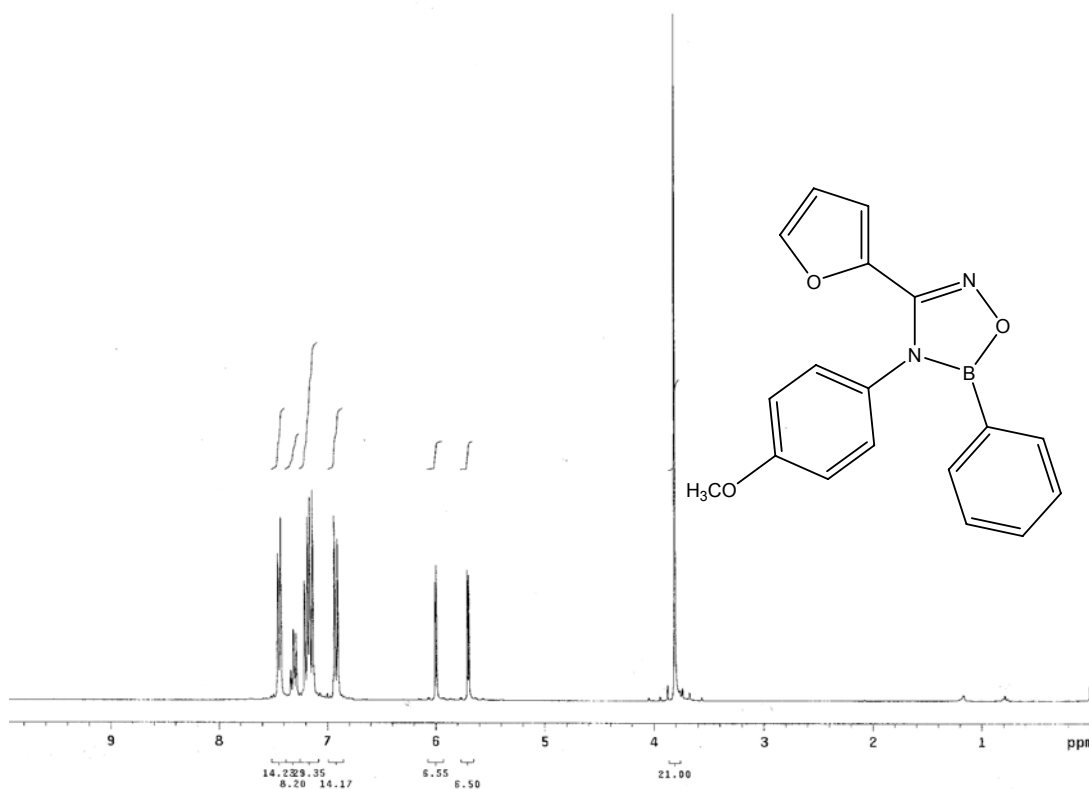


Figure 83B: The ¹H-NMR spectrum of **18q**

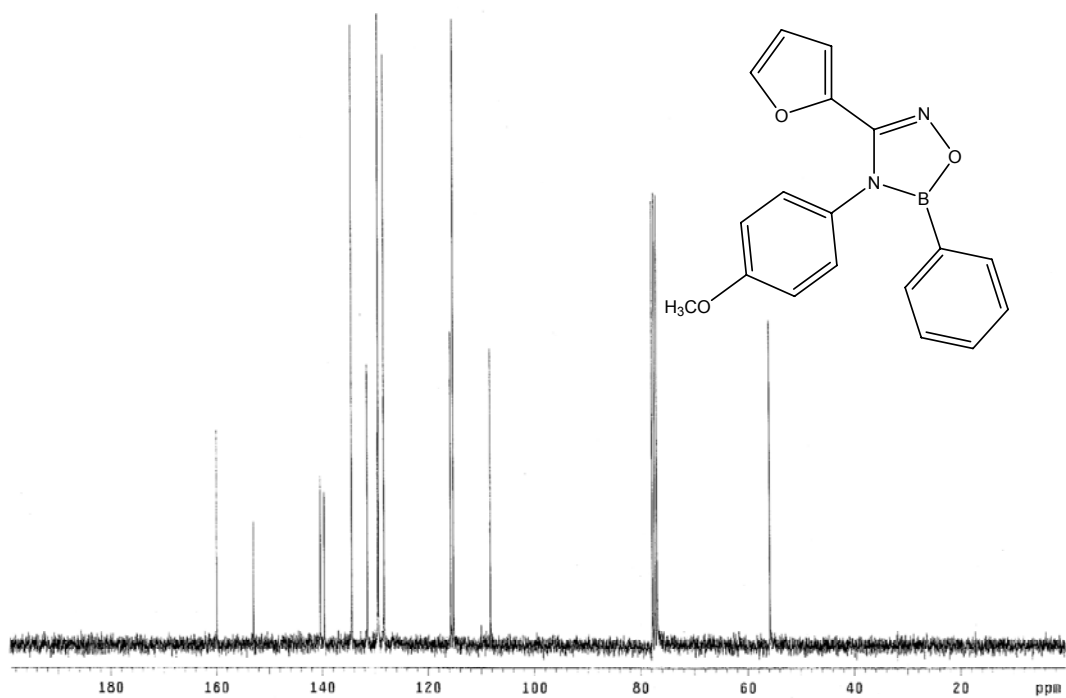


Figure 83C: The ^{13}C -NMR spectrum of **18q**

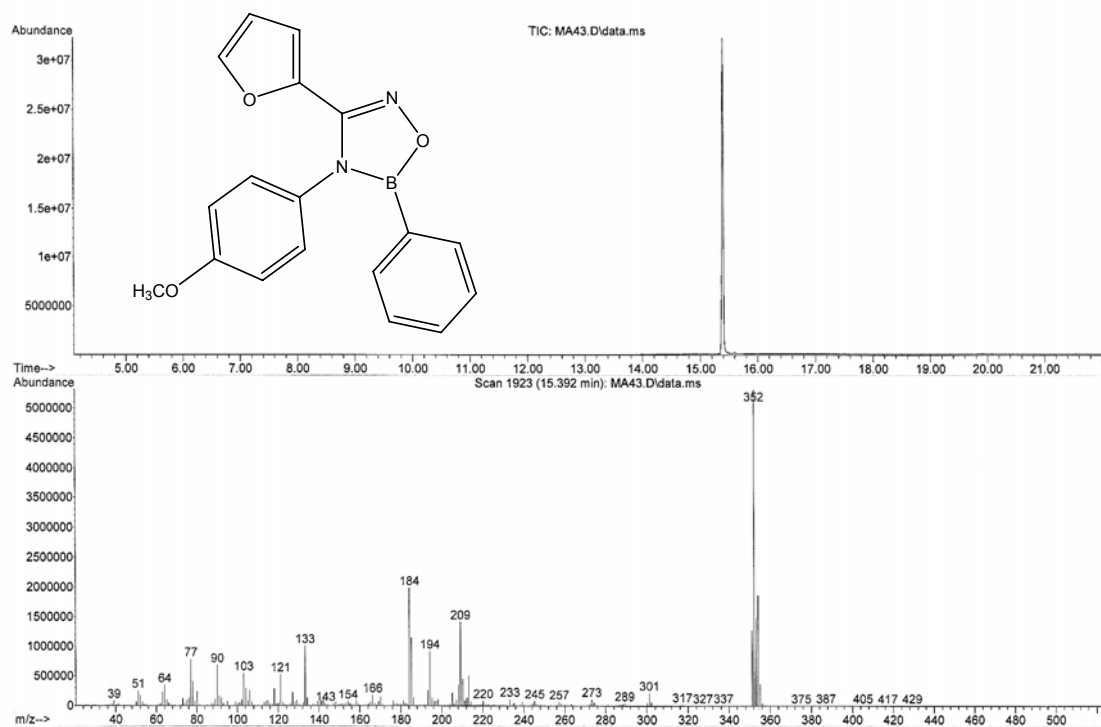


Figure 83D: The mass spectrum of **18q**

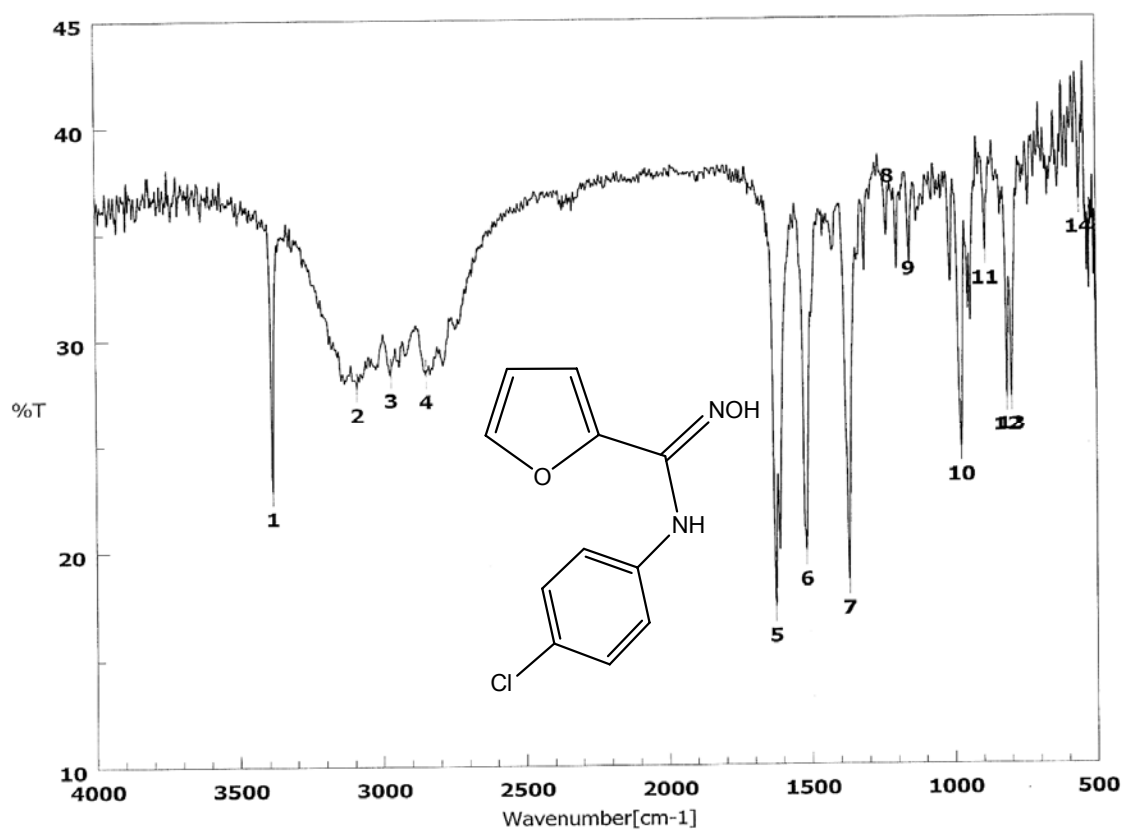


Figure 84: The IR spectrum of **12r**

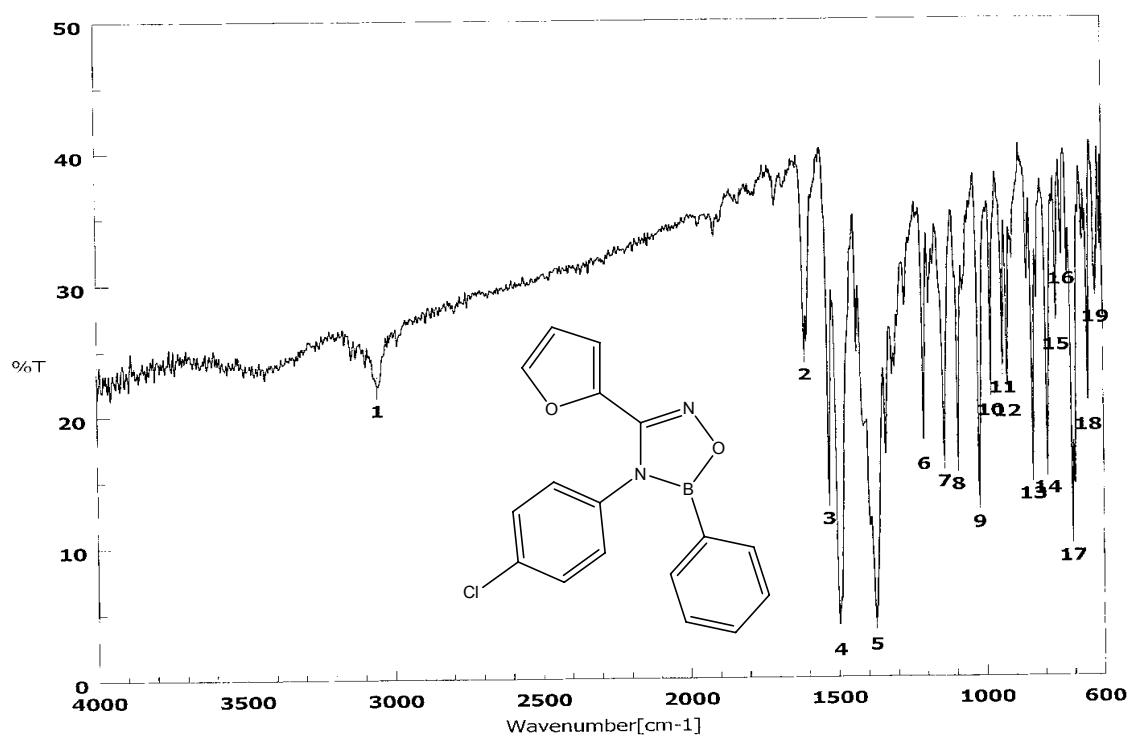


Figure 85A: The IR spectrum of **18r**

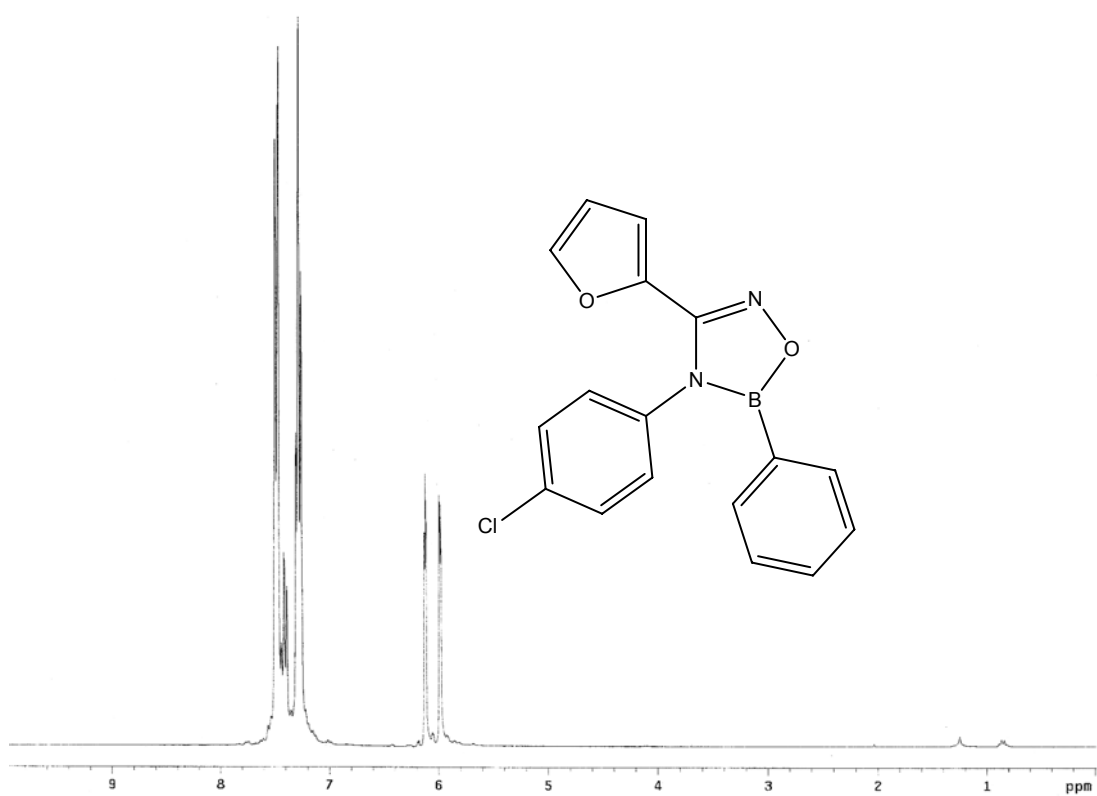


Figure 85B: The ^1H -NMR spectrum of **18r**

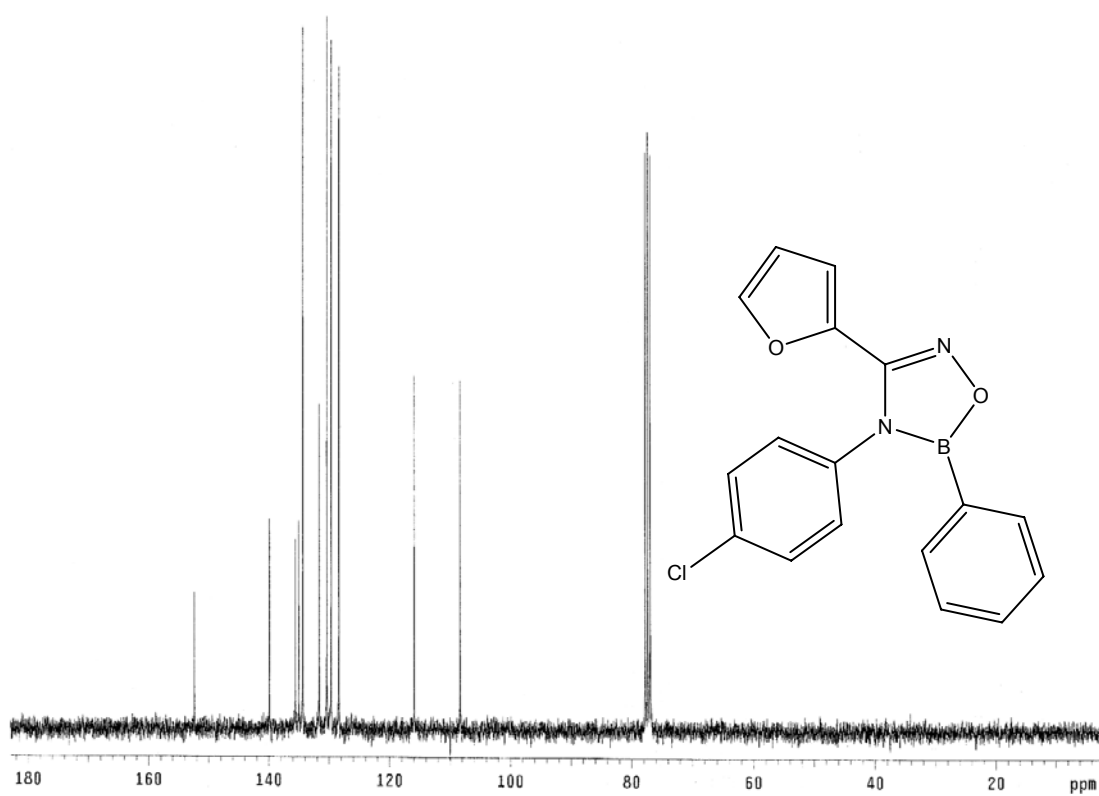


Figure 85C: The ^{13}C -NMR spectrum of **18r**

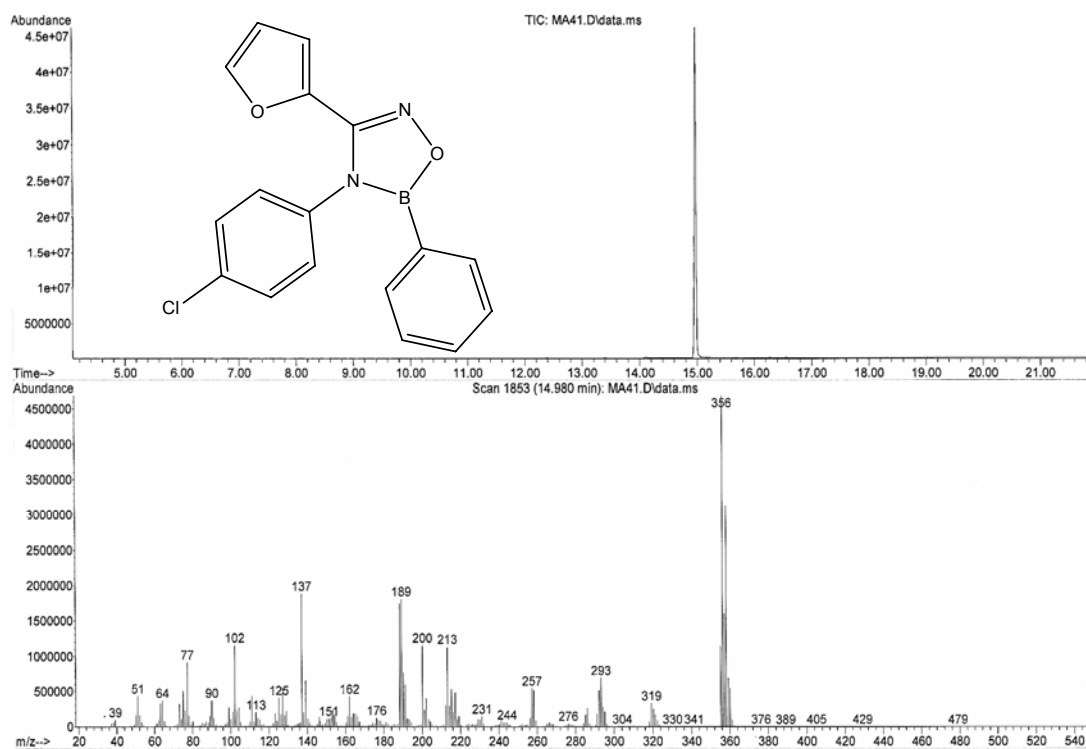


Figure 85D: The mass spectrum of **18r**

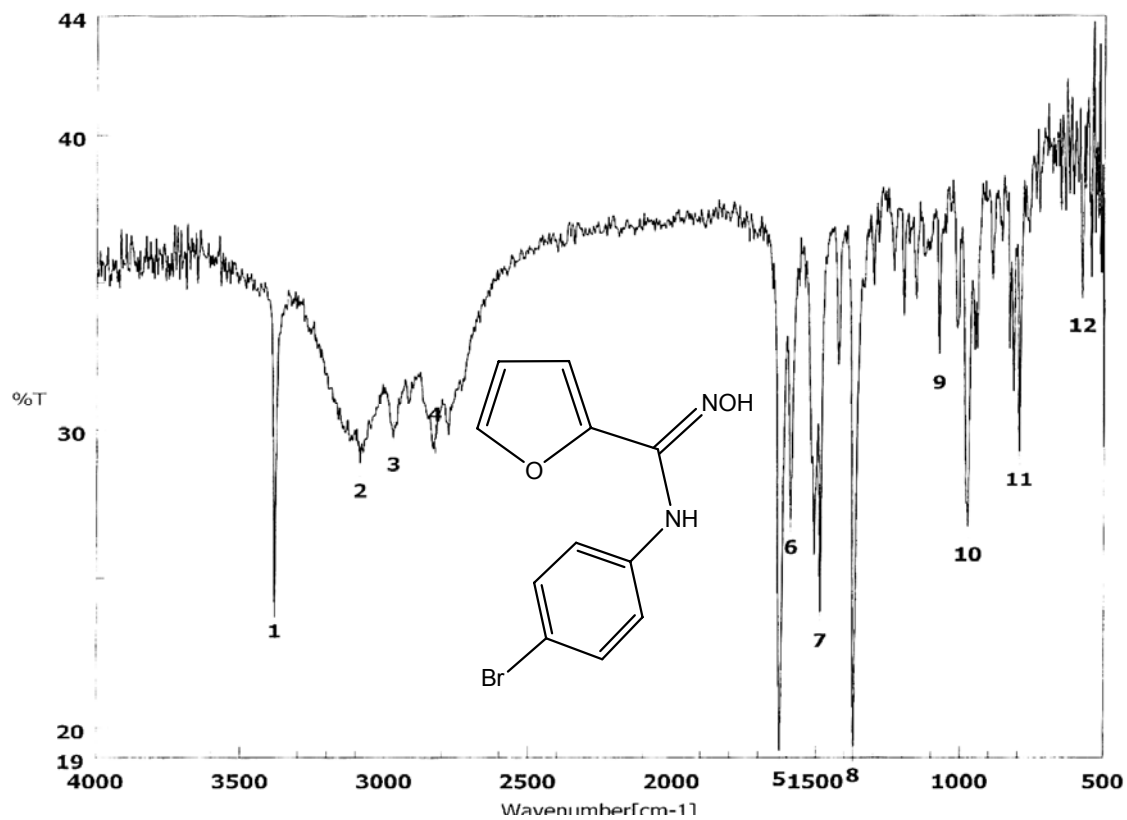


Figure 86: The IR spectrum of **12s**

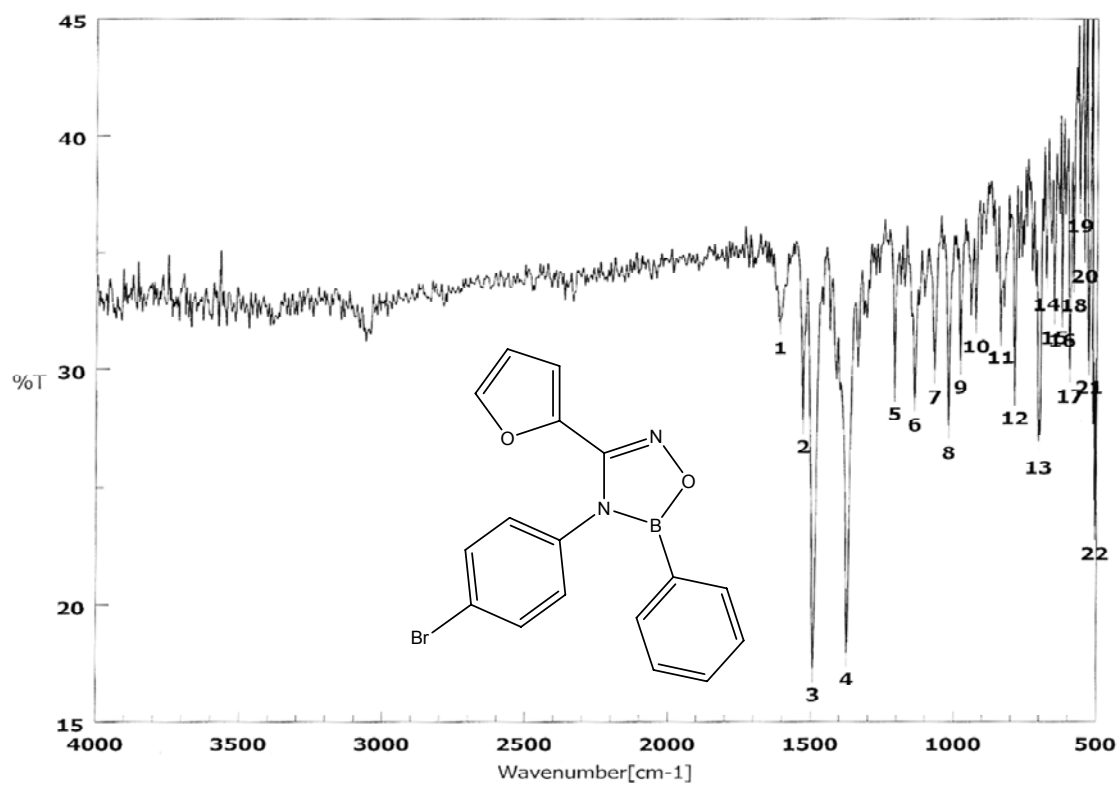


Figure 87A: The IR spectrum of **18s**

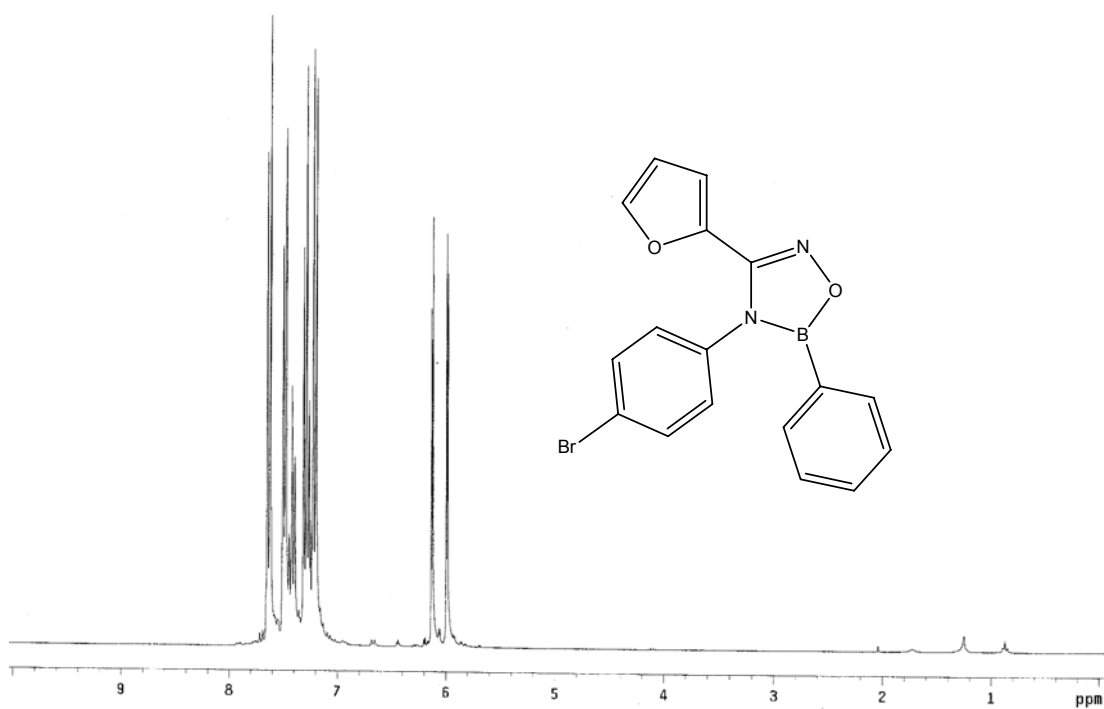


Figure 87B: The ¹H-NMR spectrum of **18s**

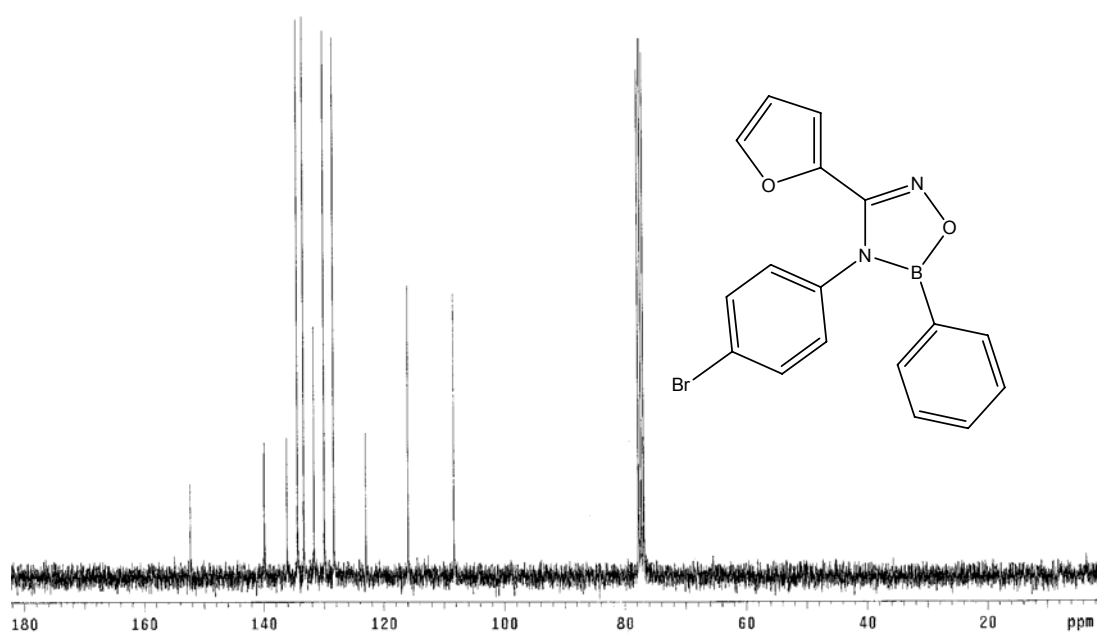


Figure 87C: The ^{13}C -NMR spectrum of **18s**

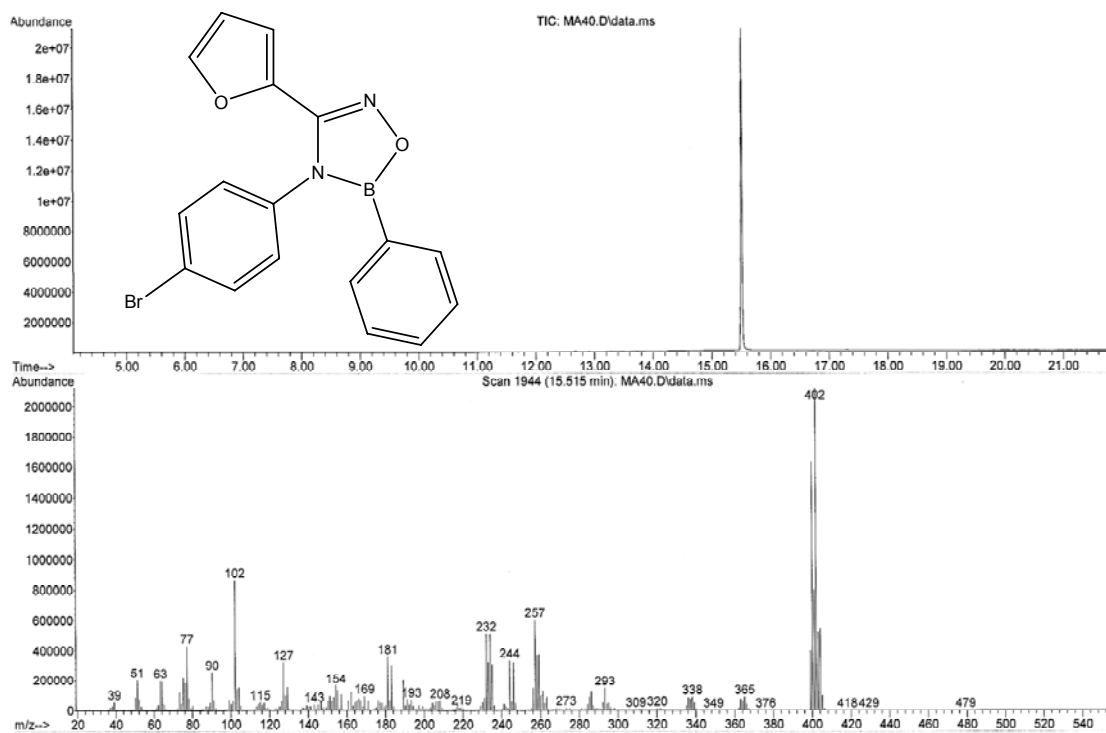


Figure 87D: The mass spectrum of **18s**

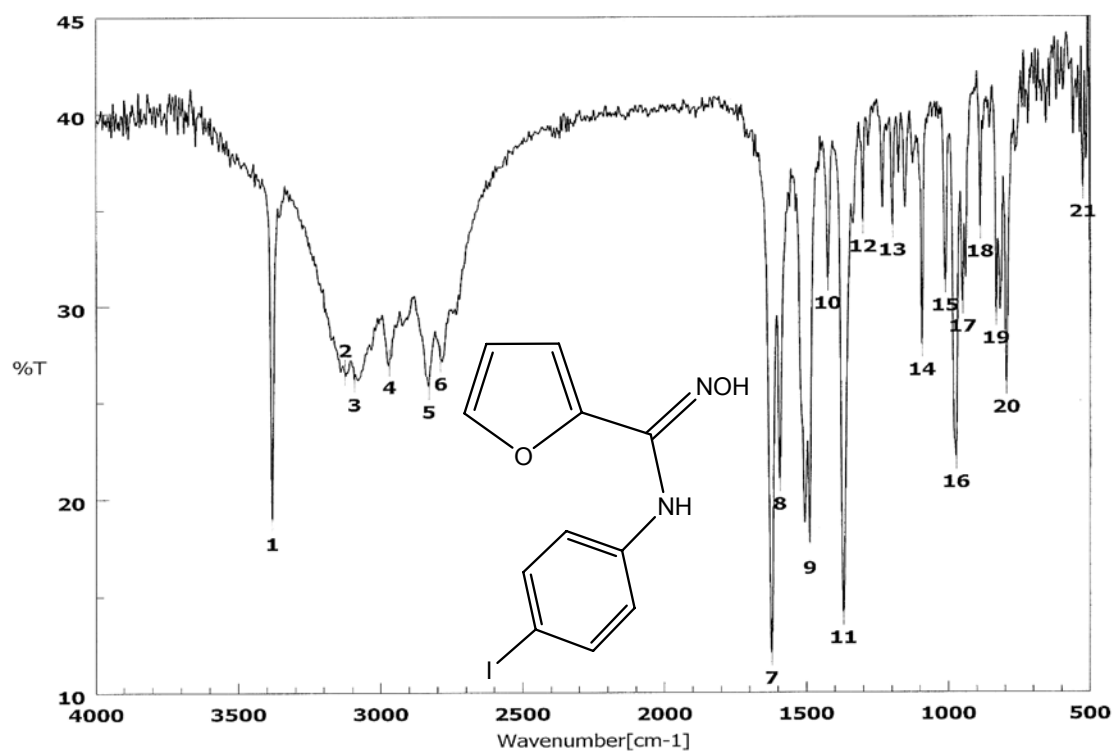


Figure 88: The IR spectrum of **12t**

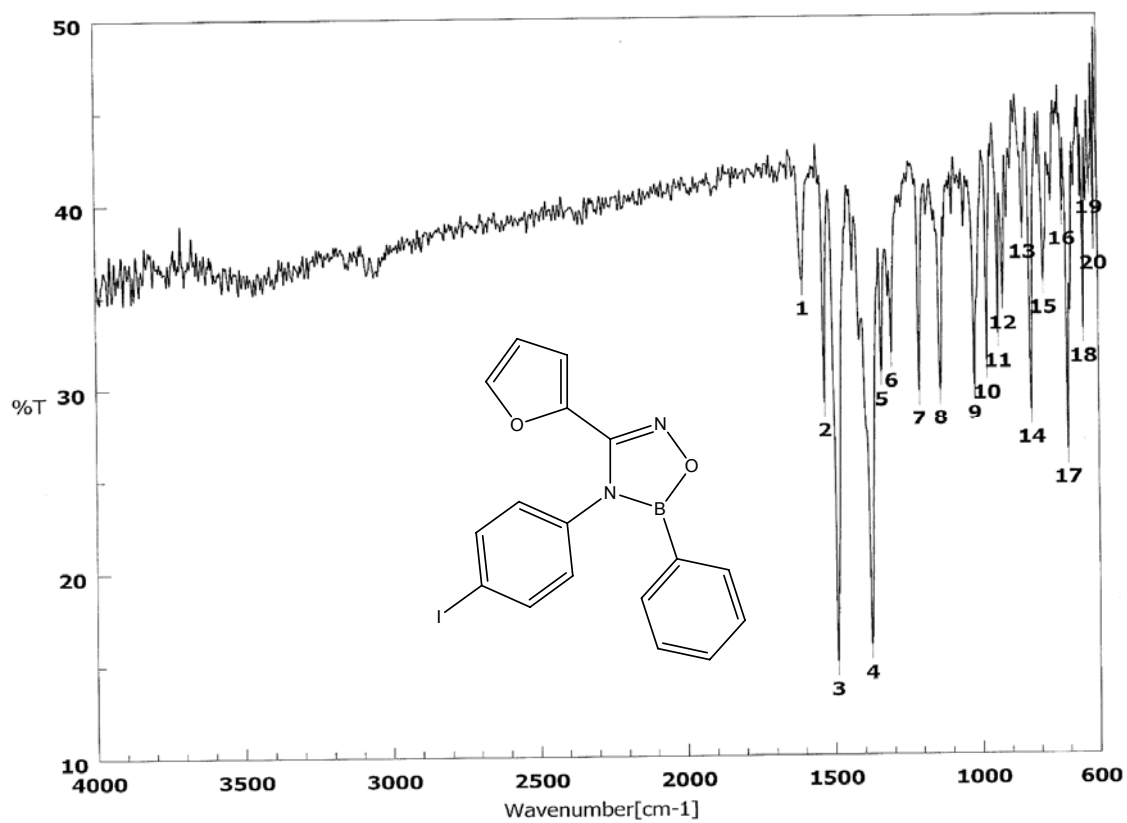


Figure 89A: The IR spectrum of **18t**

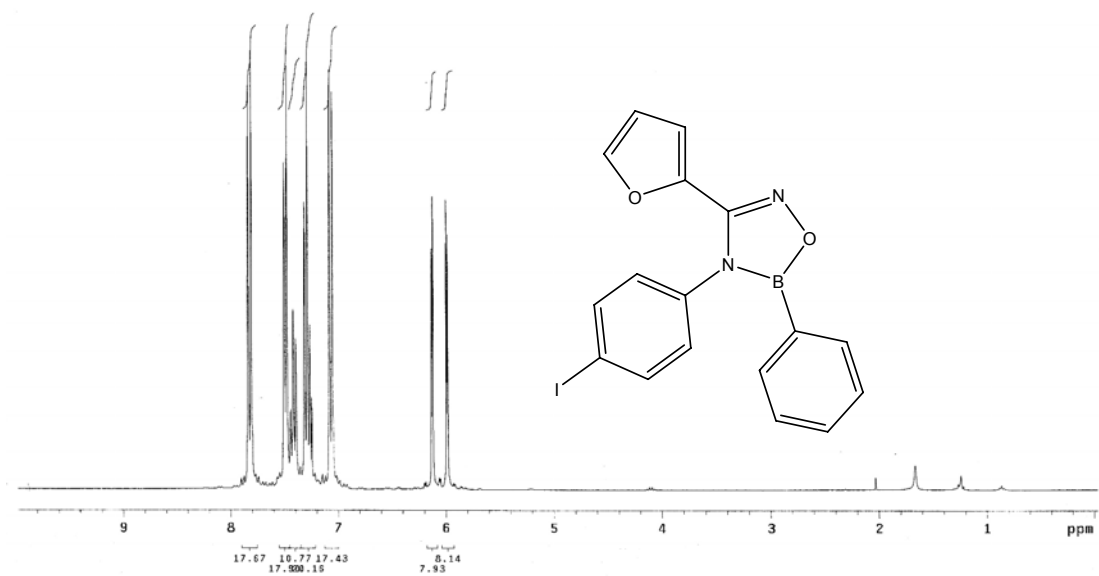


Figure 89B: The ^1H -NMR spectrum of **18t**

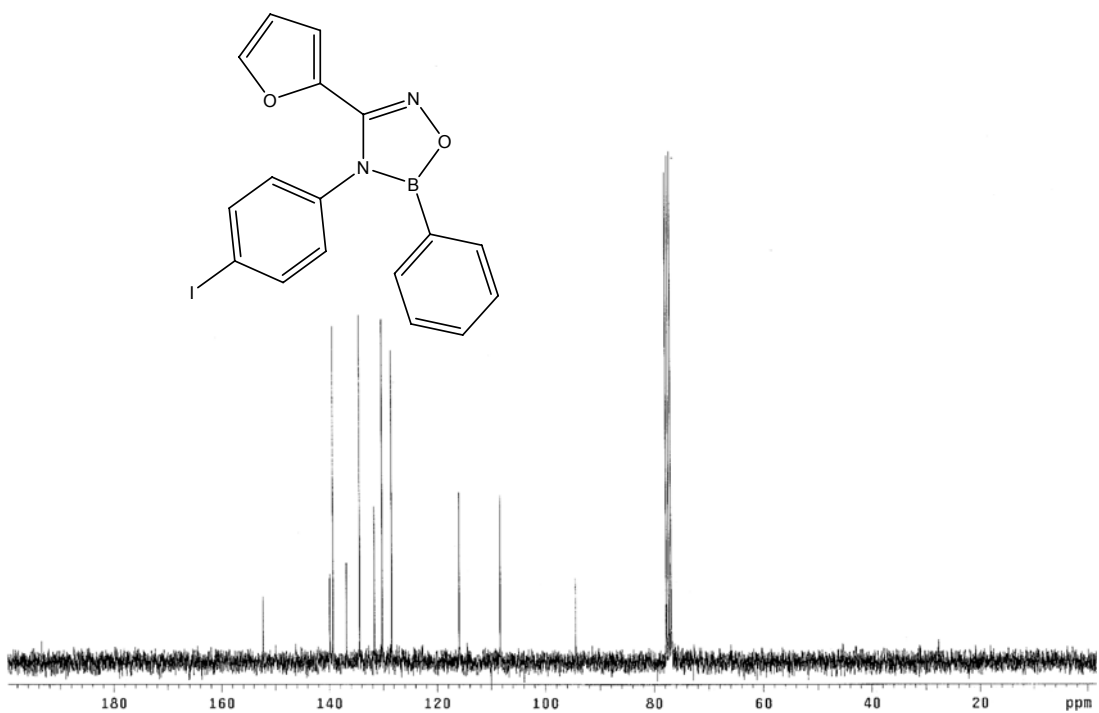


Figure 89C: The ^{13}C -NMR spectrum of **18t**

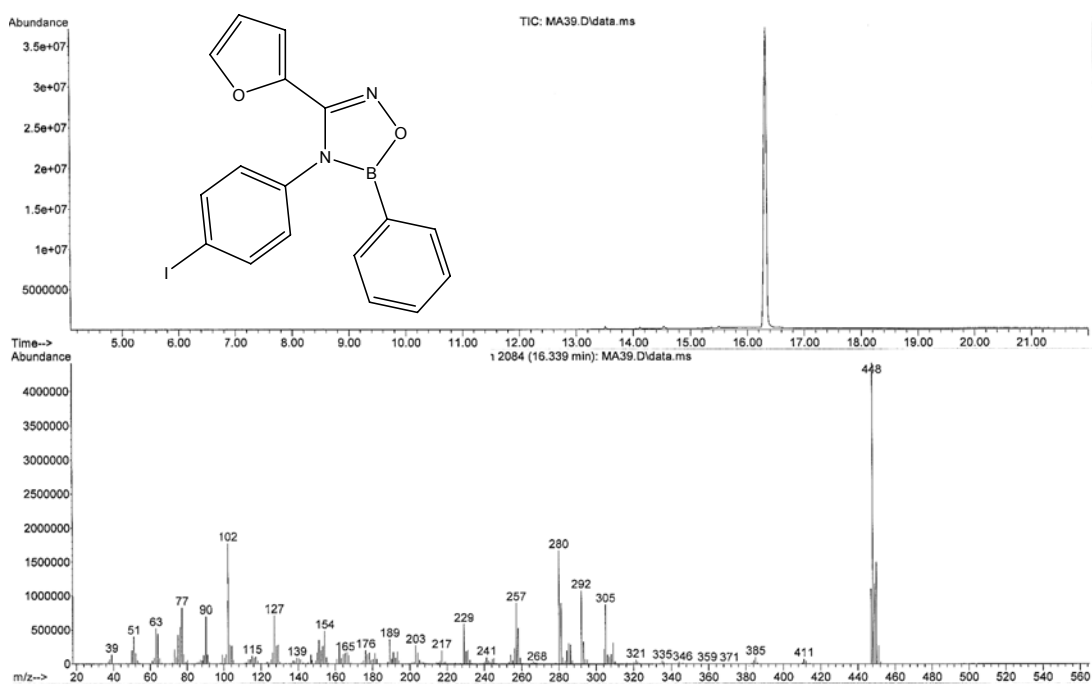


Figure 89D: The mass spectrum of **18t**

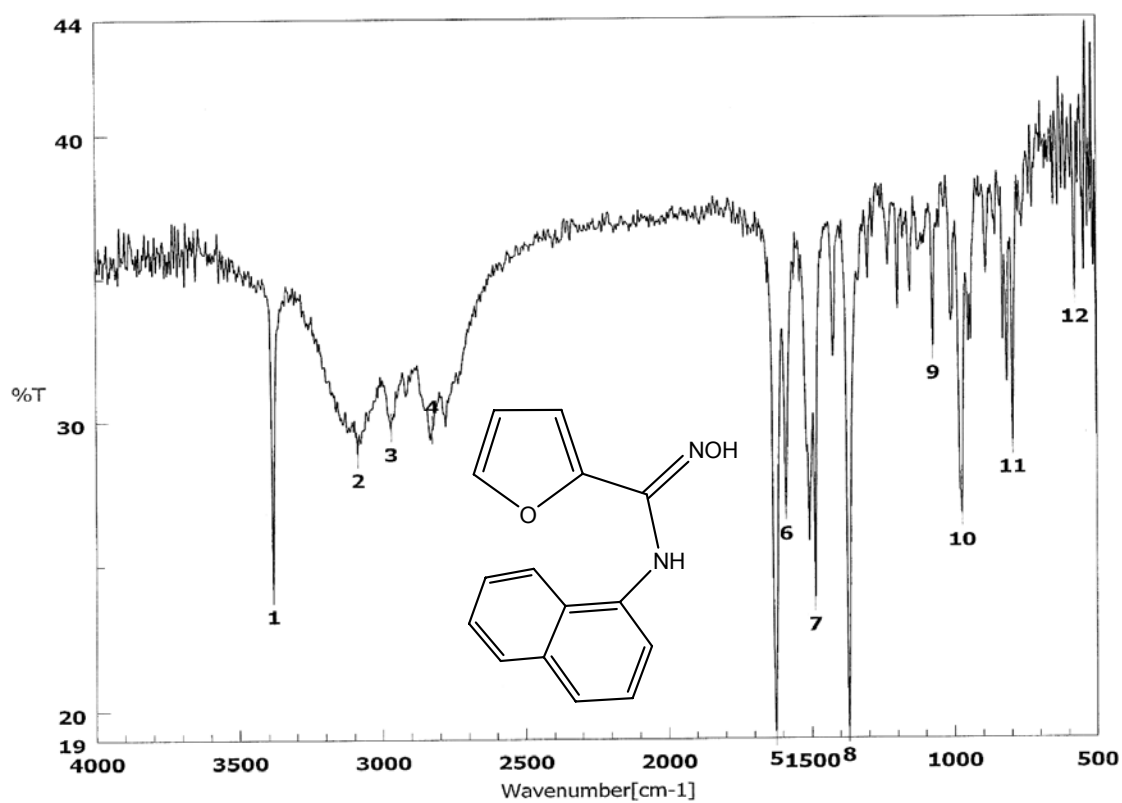


Figure 90: The IR spectrum of **12u**

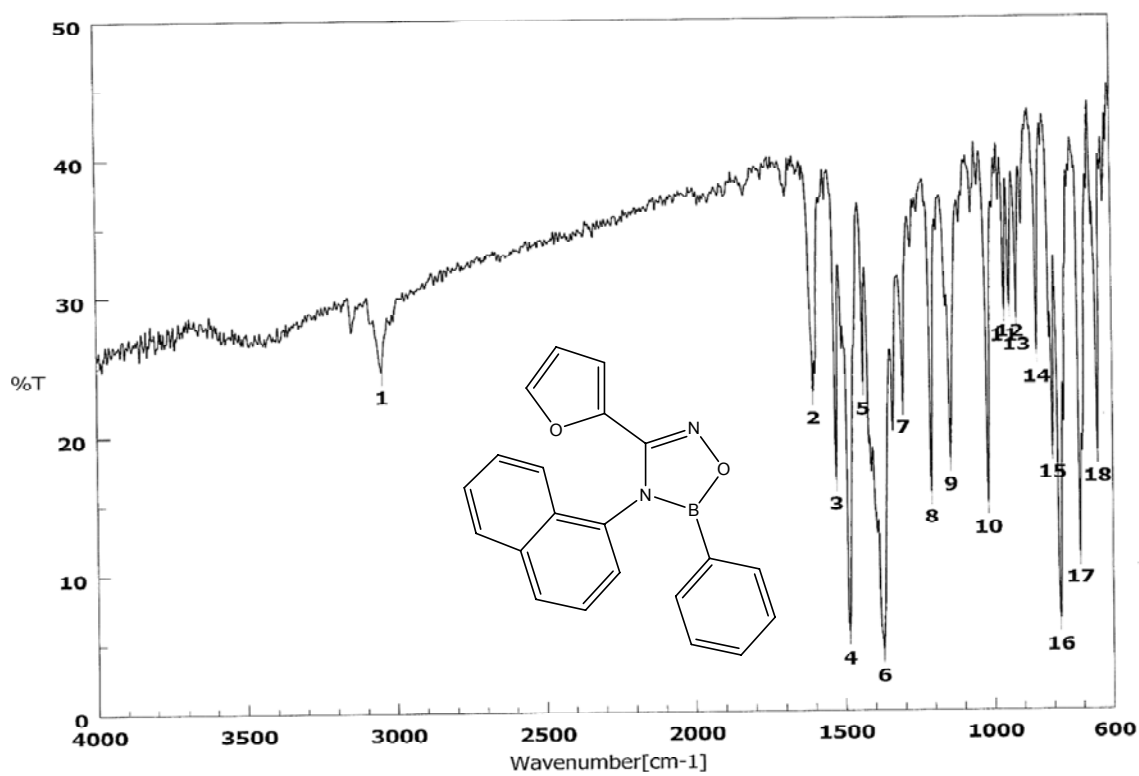


Figure 91A: The IR spectrum of **18u**

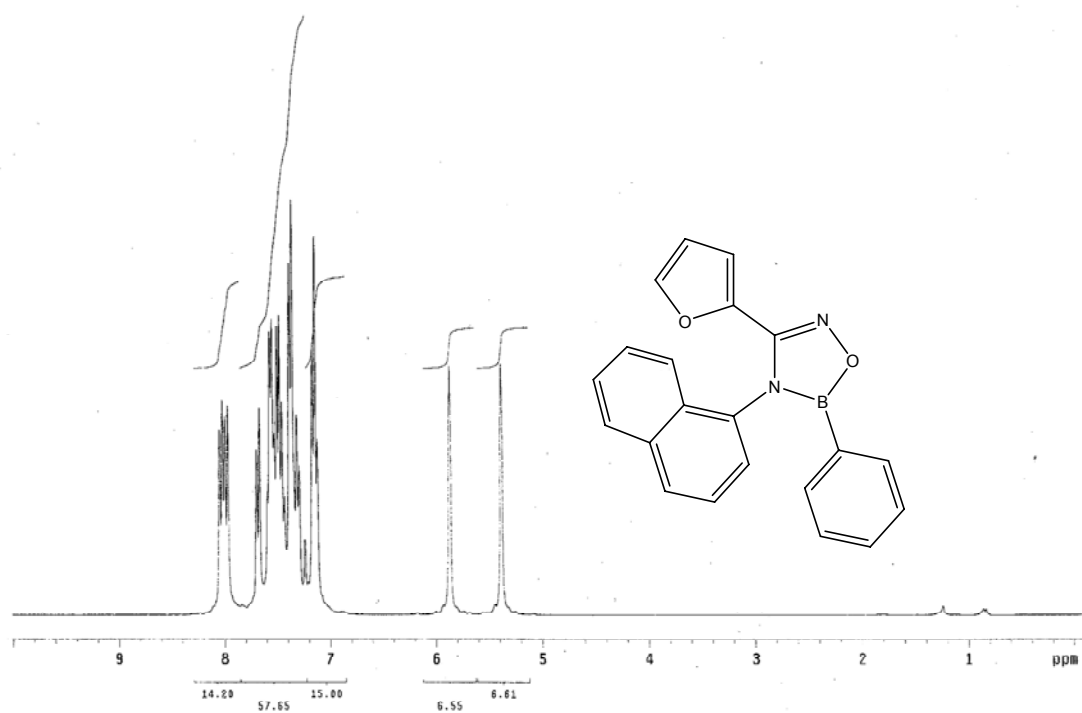


Figure 91B: The ¹H-NMR spectrum of **18u**

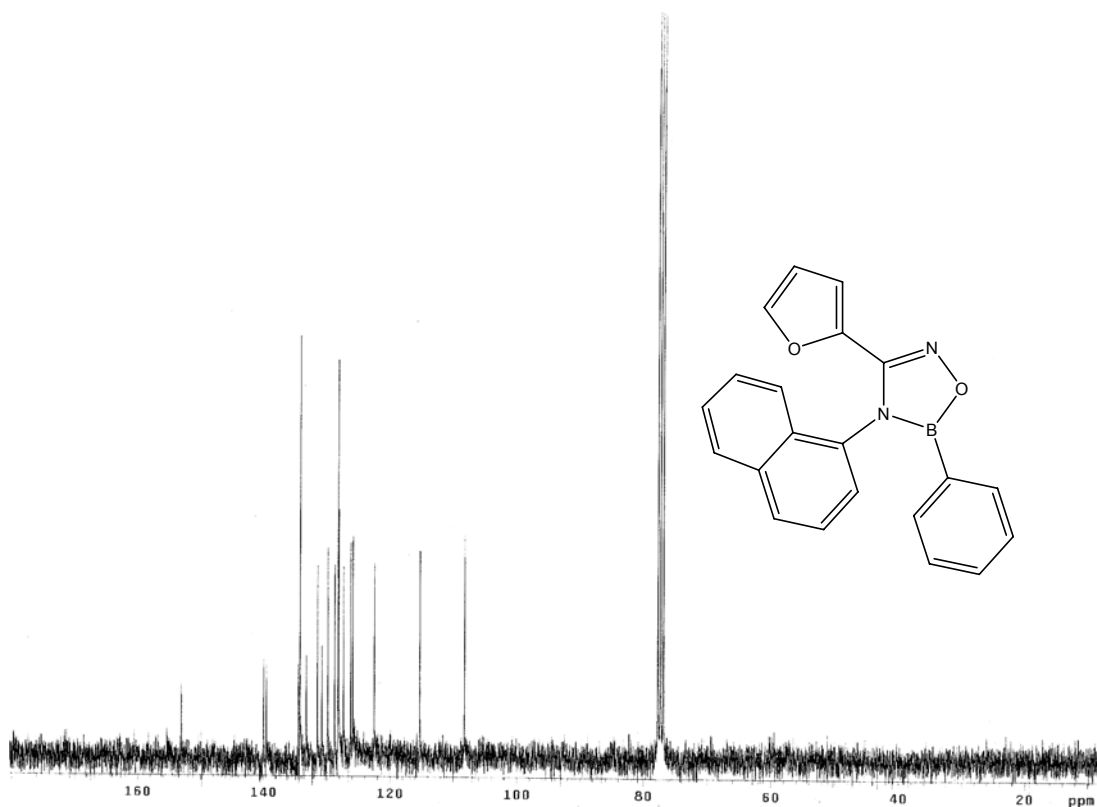


Figure 91C: The ^{13}C -NMR spectrum of **18u**

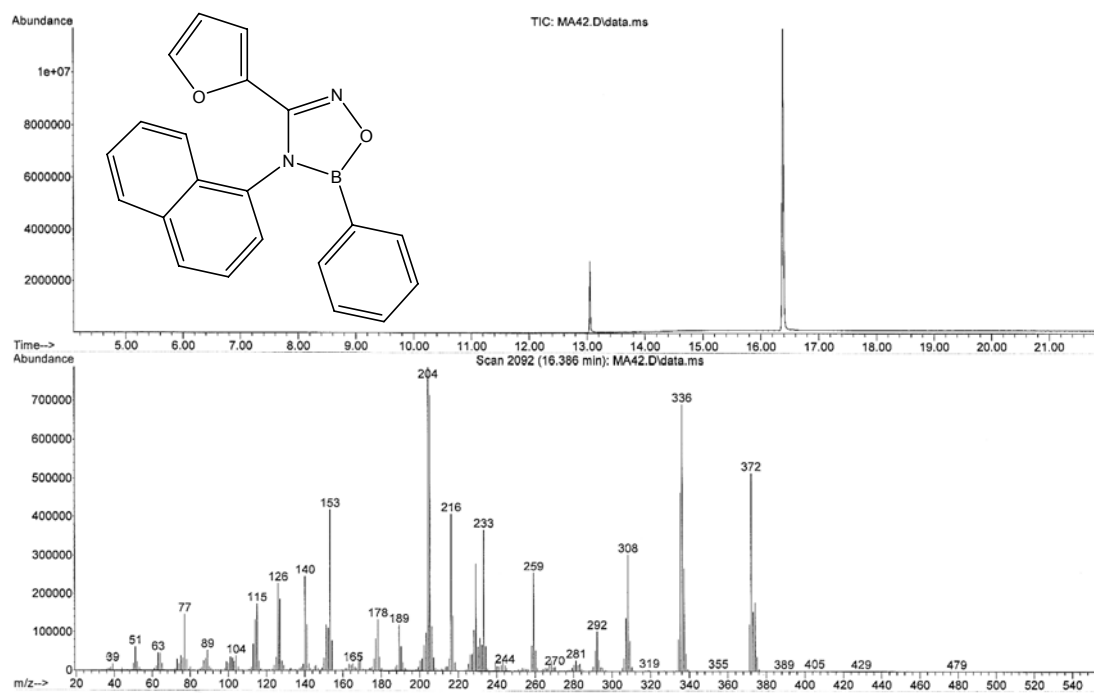


Figure 91D: The mass spectrum of **18u**

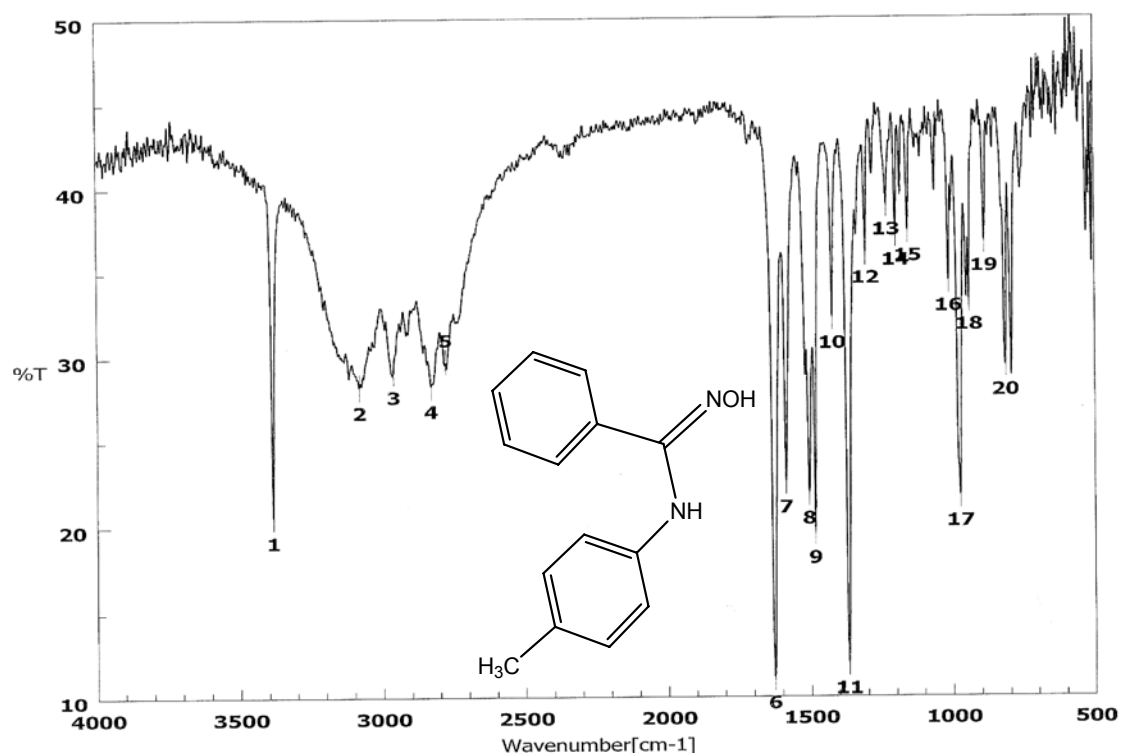


Figure 92: The IR spectrum of **13p**

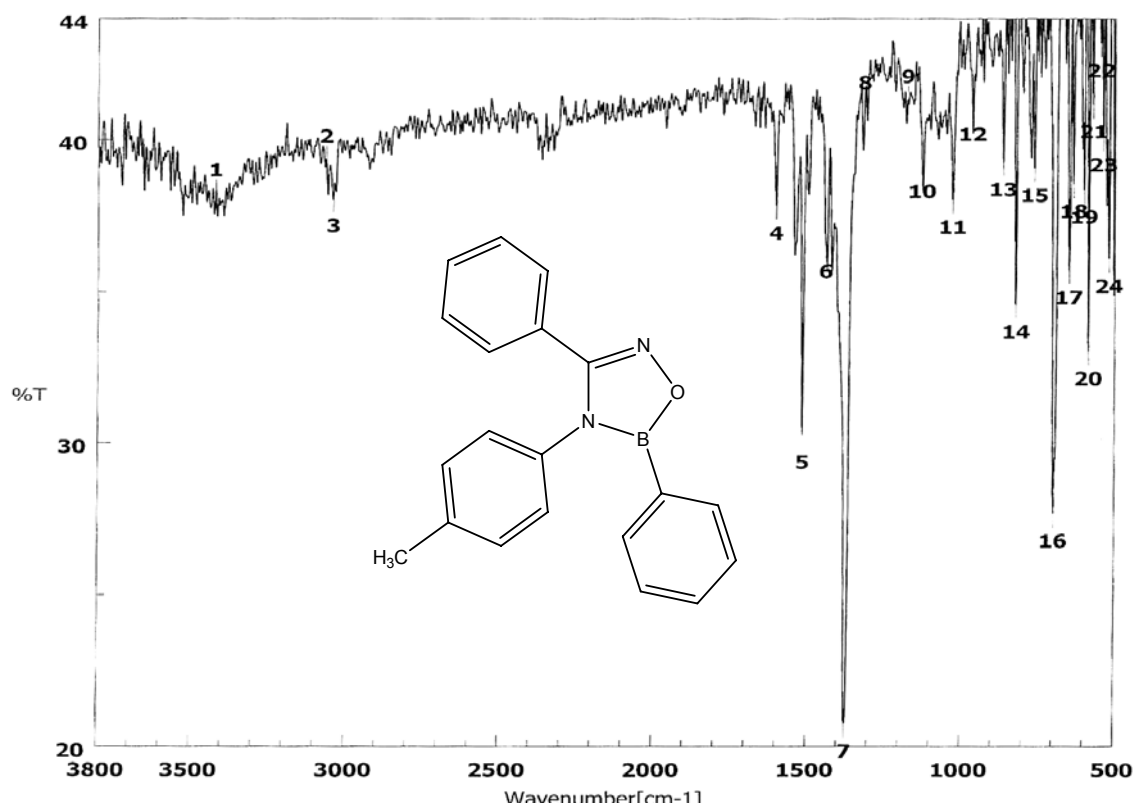


Figure 93A: The IR spectrum of **19p**

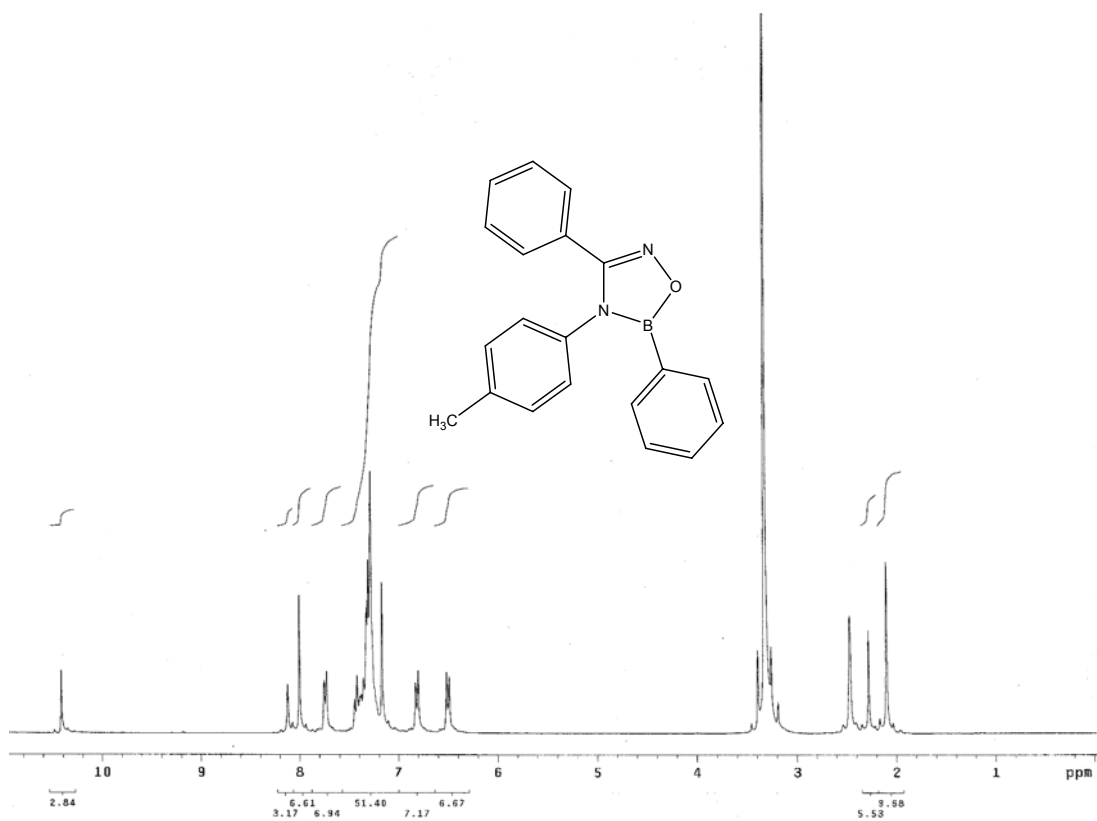


Figure 93B: The ¹H-NMR spectrum of **19p**

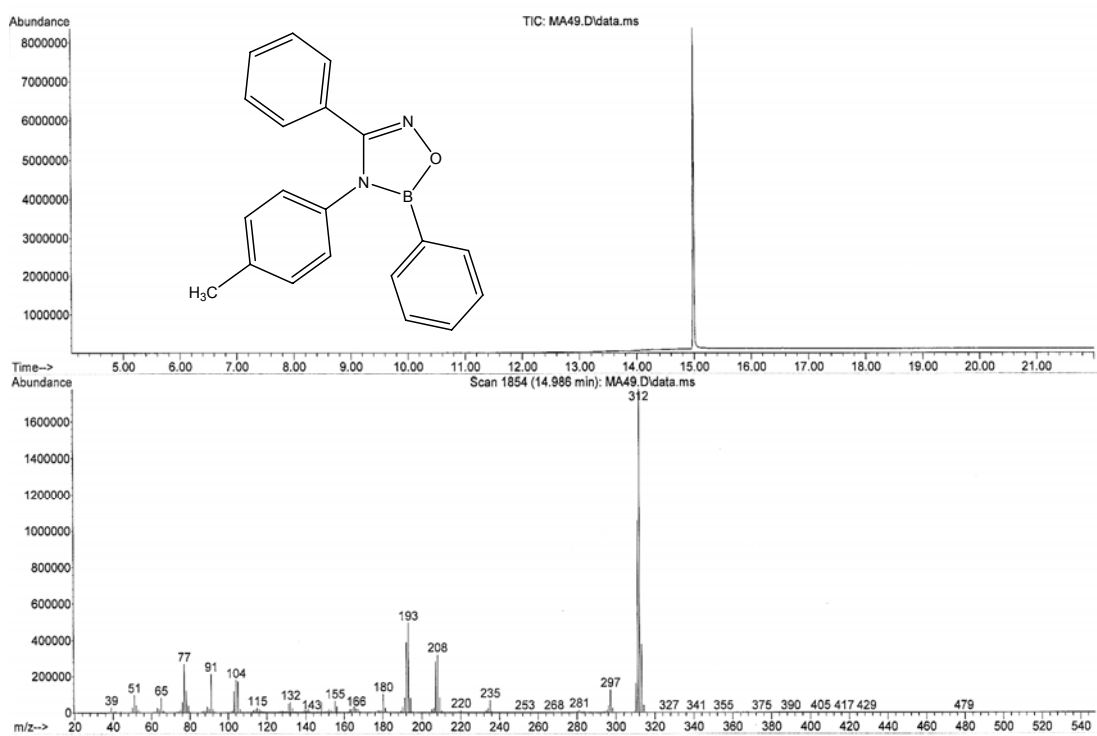


Figure 93C: The mass spectrum of **19p**

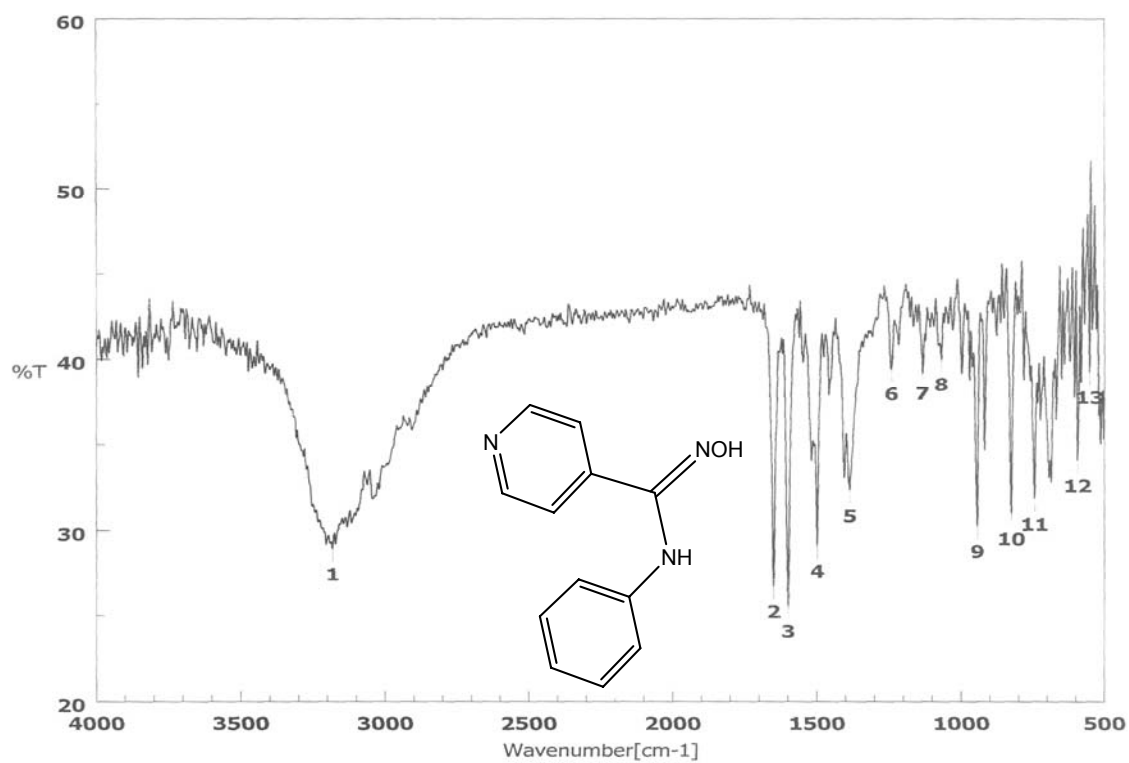


Figure 94: The IR spectrum of **14o**

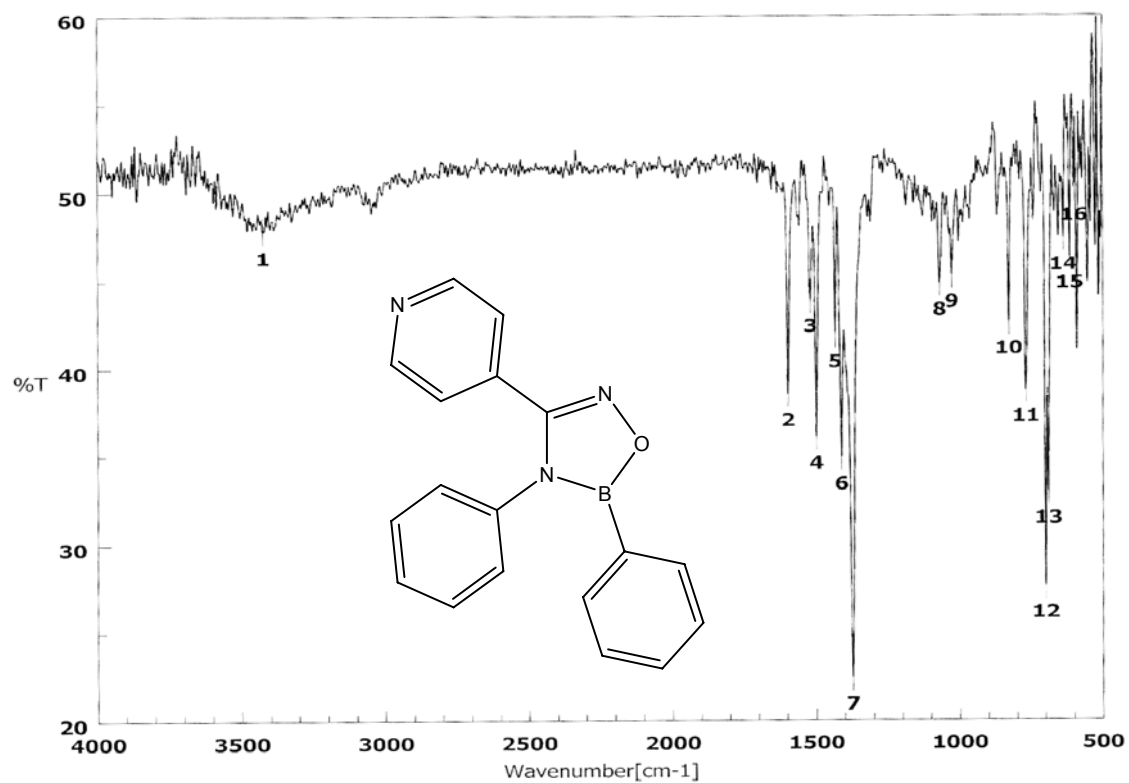


Figure 95A: The IR spectrum of **20o**

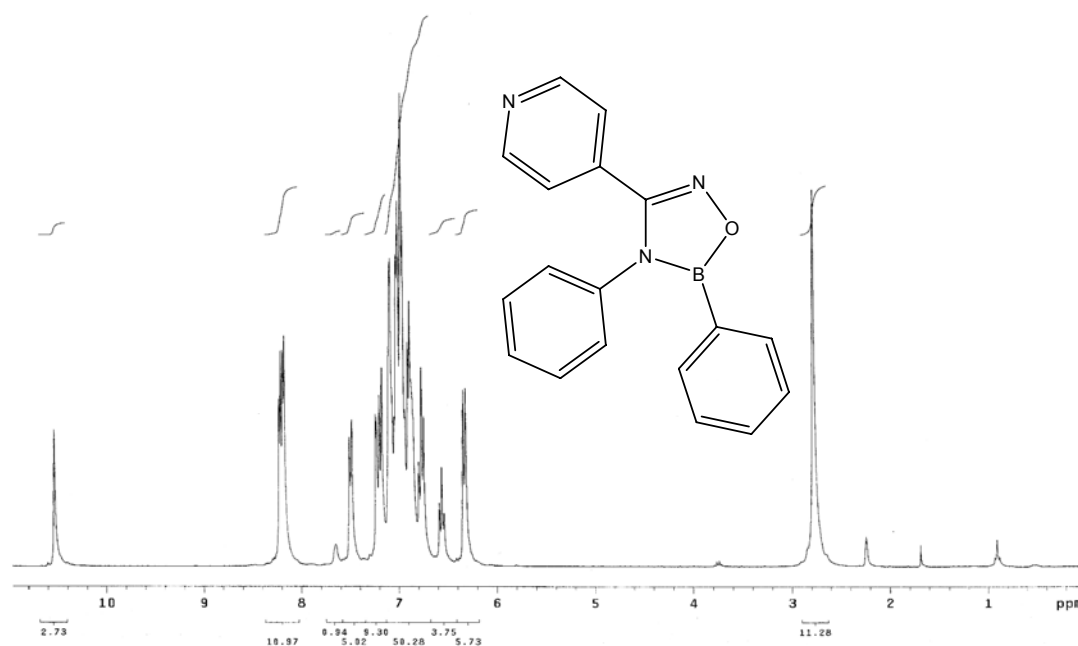


Figure 95B: The ¹H-NMR spectrum of **20o**

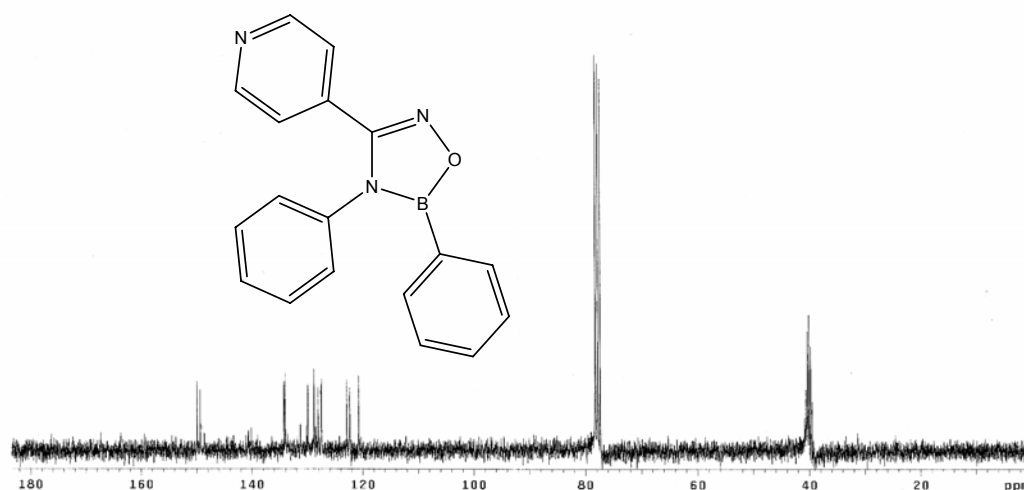


Figure 95C: The ¹³C-NMR spectrum of **20o**

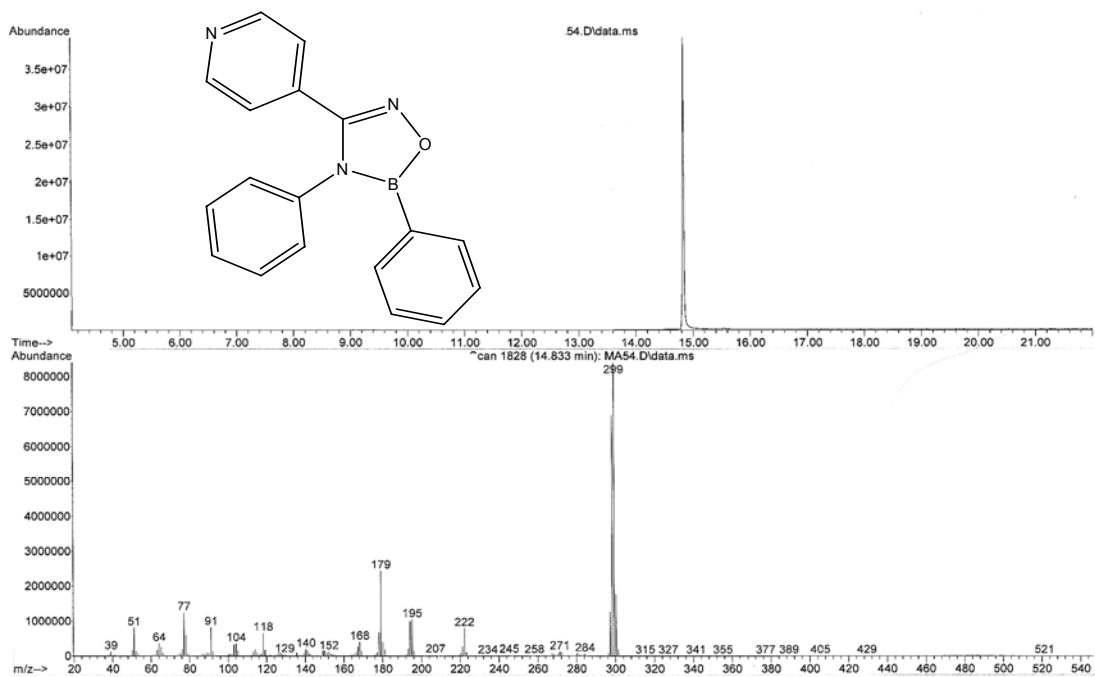


Figure 95D: The mass spectrum of **20o**

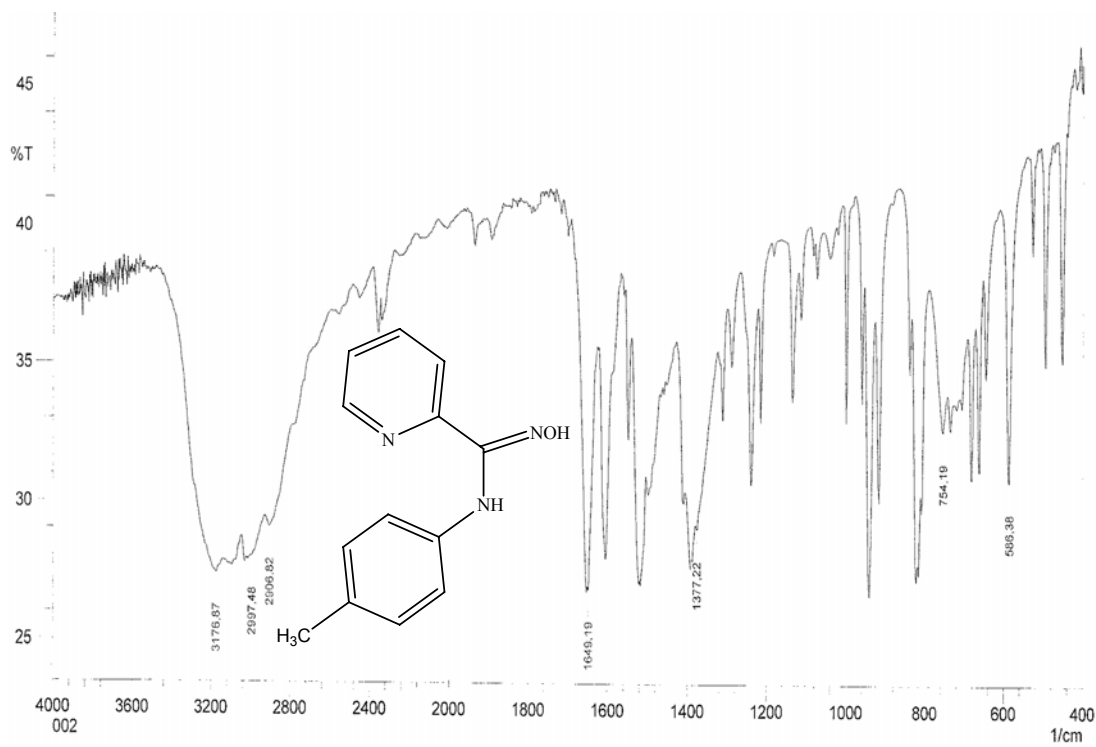


Figure 96: The IR spectrum of **14p**

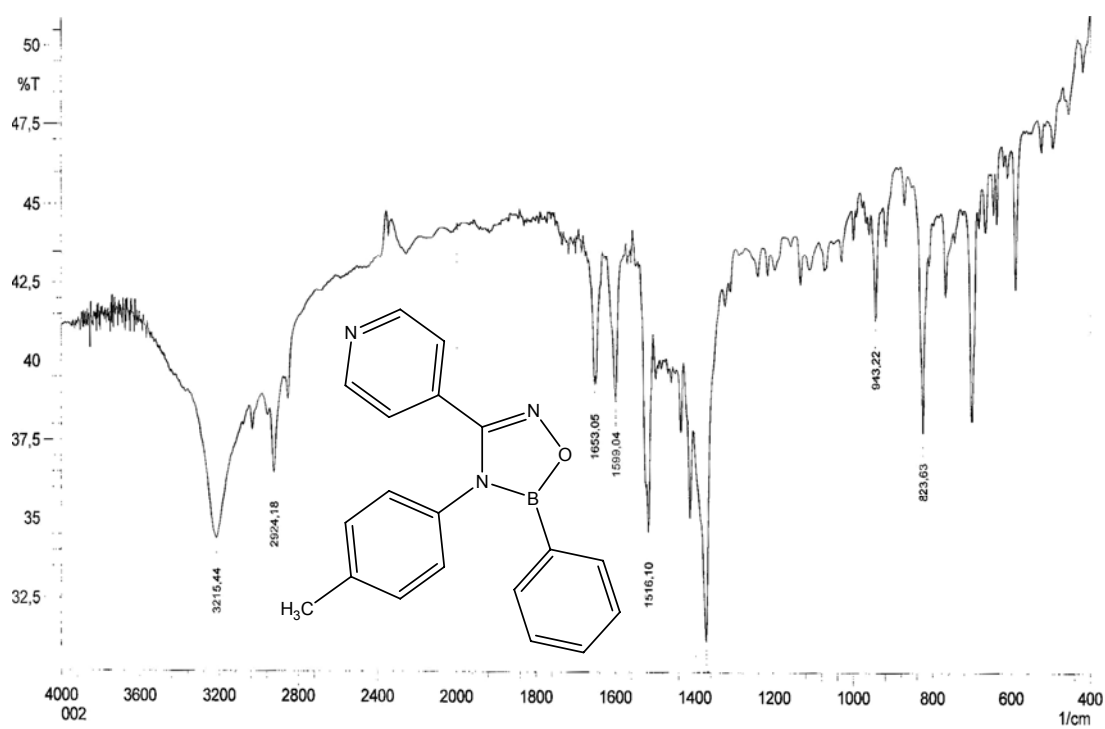


Figure 97A: The IR spectrum of **20p**

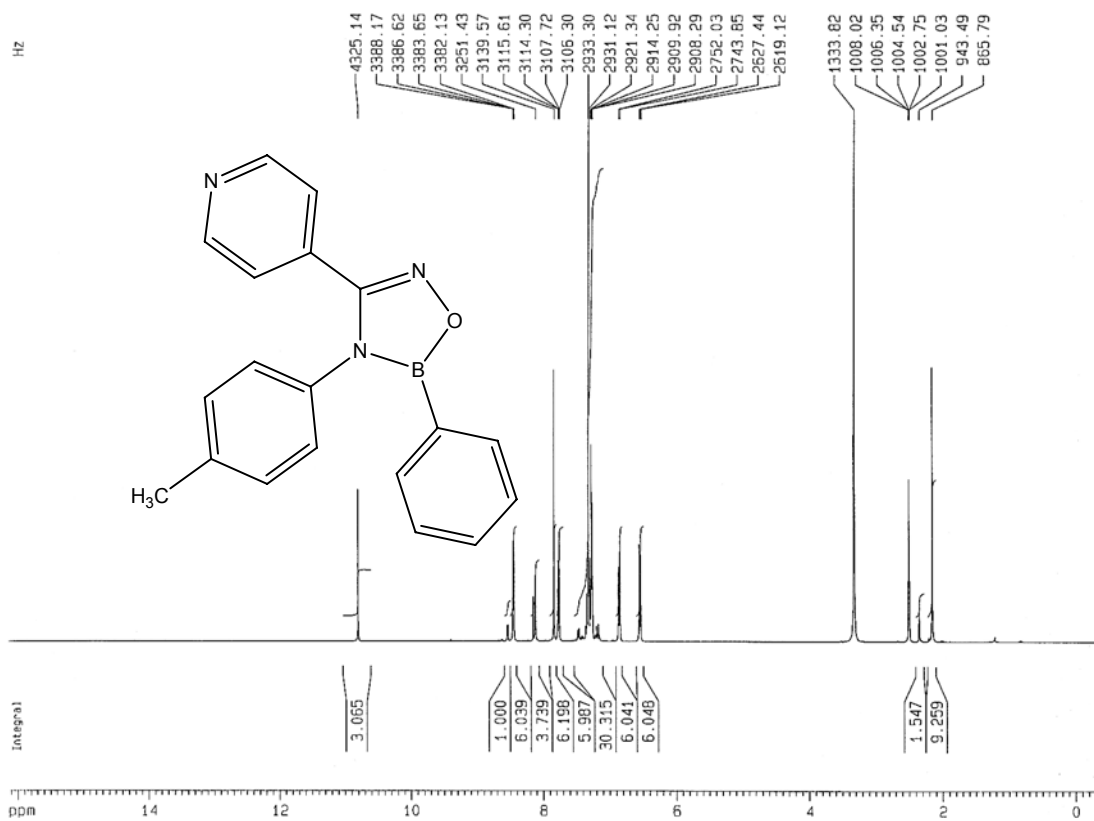


Figure 97B: The ¹H-NMR spectrum of **20p**

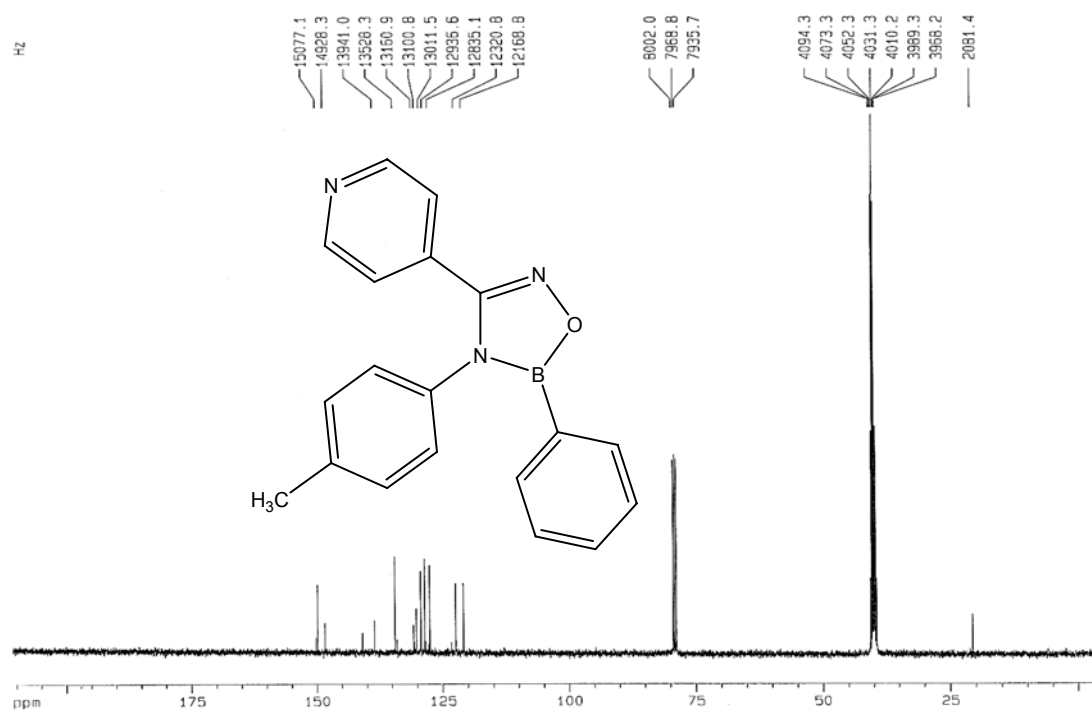


Figure 97C: The ¹³C-NMR spectrum of **20p**

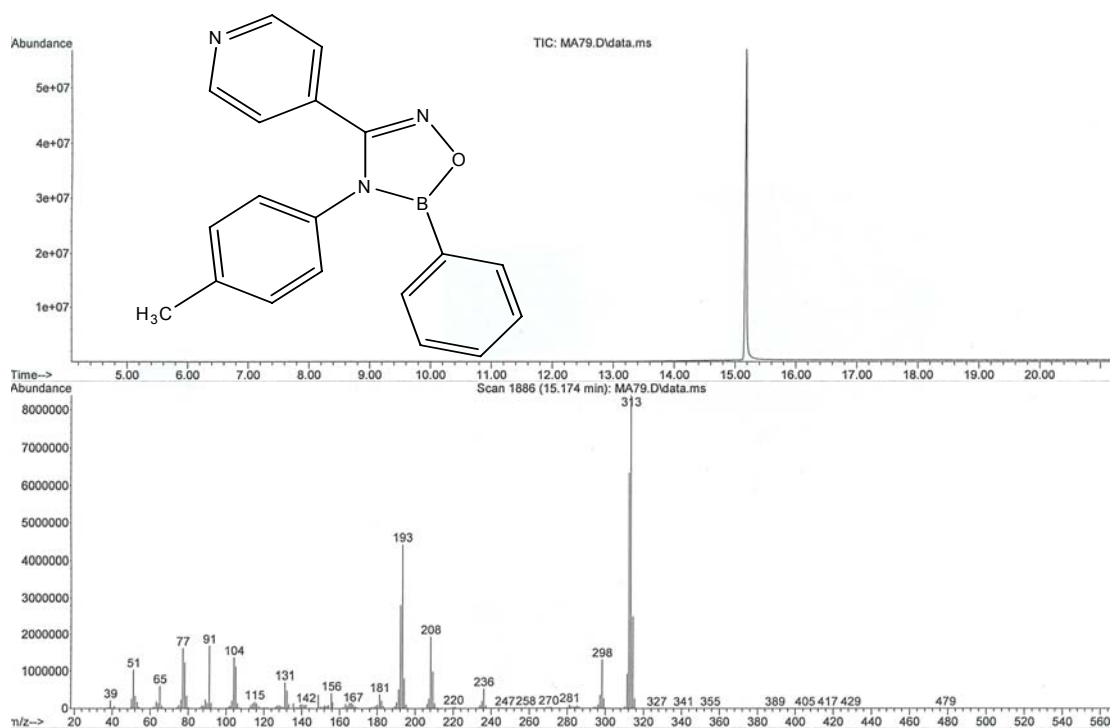


Figure 97D: The mass spectrum of **20p**

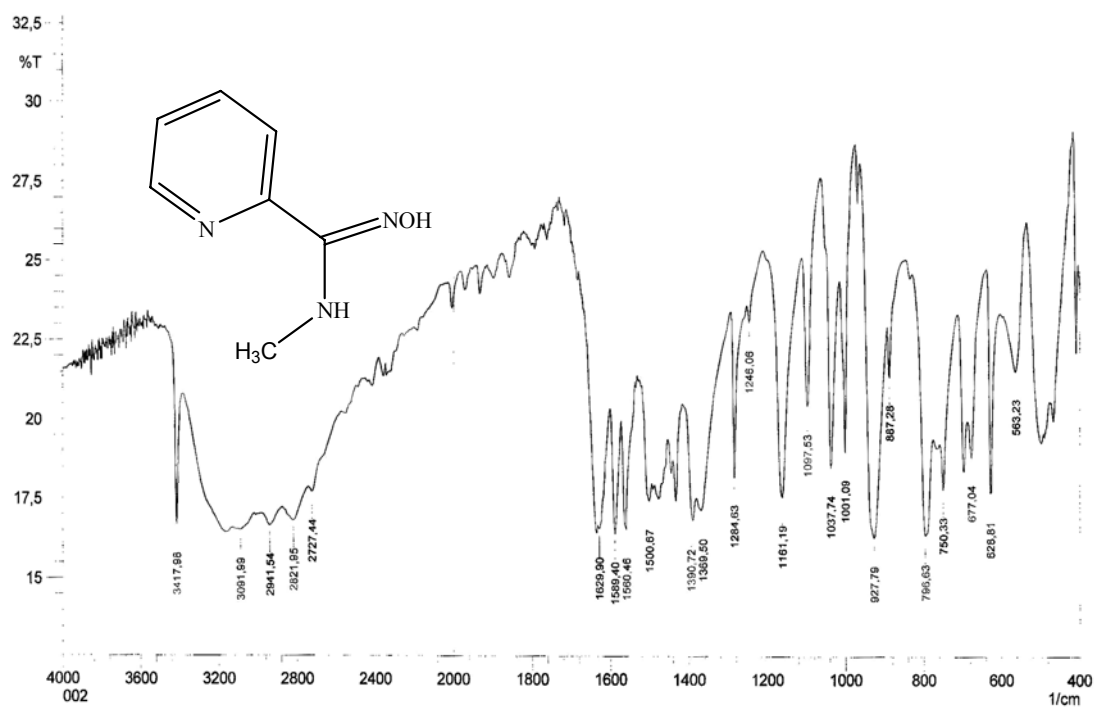


Figure 98: The IR spectrum of **15v**

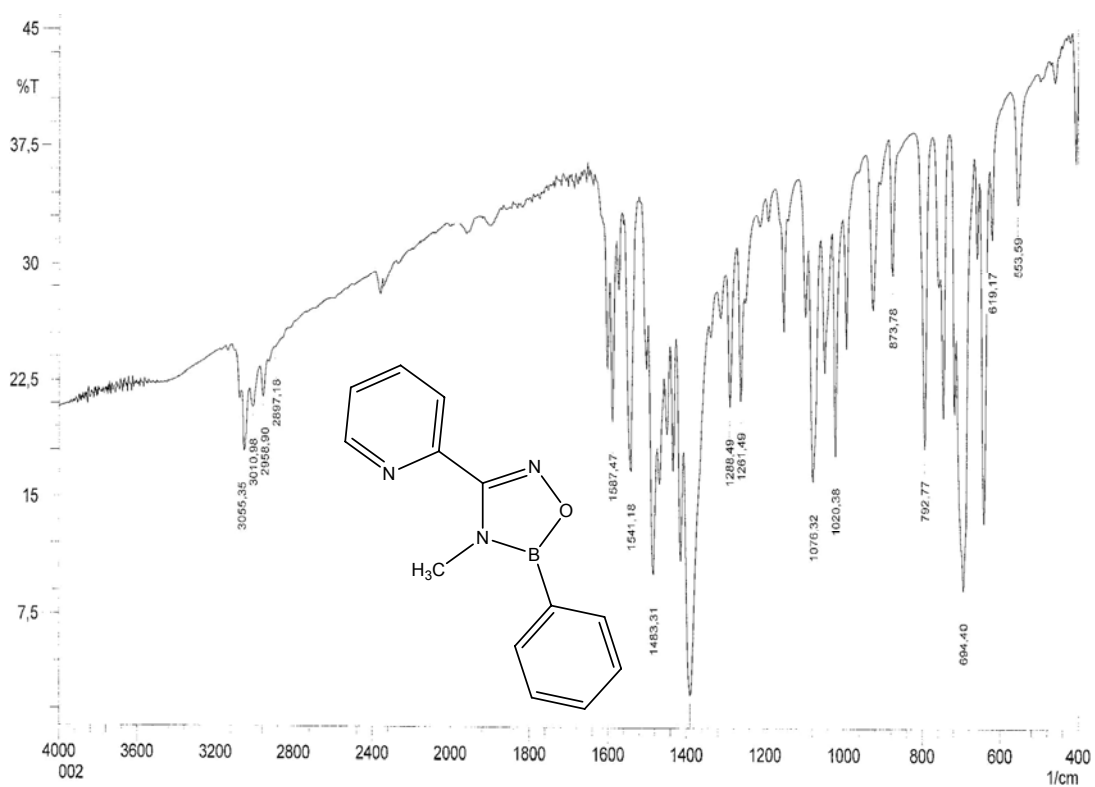


Figure 99A: The IR spectrum of **21v**

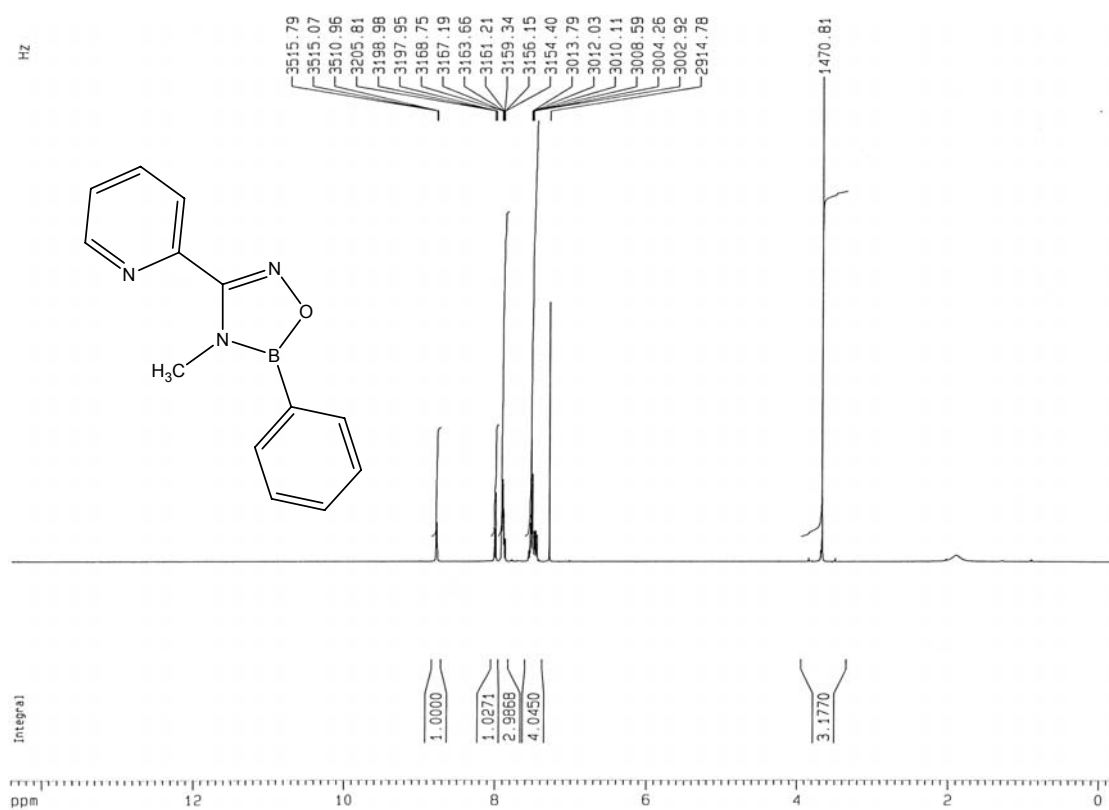


Figure 99B: The ¹H-NMR spectrum of **21v**

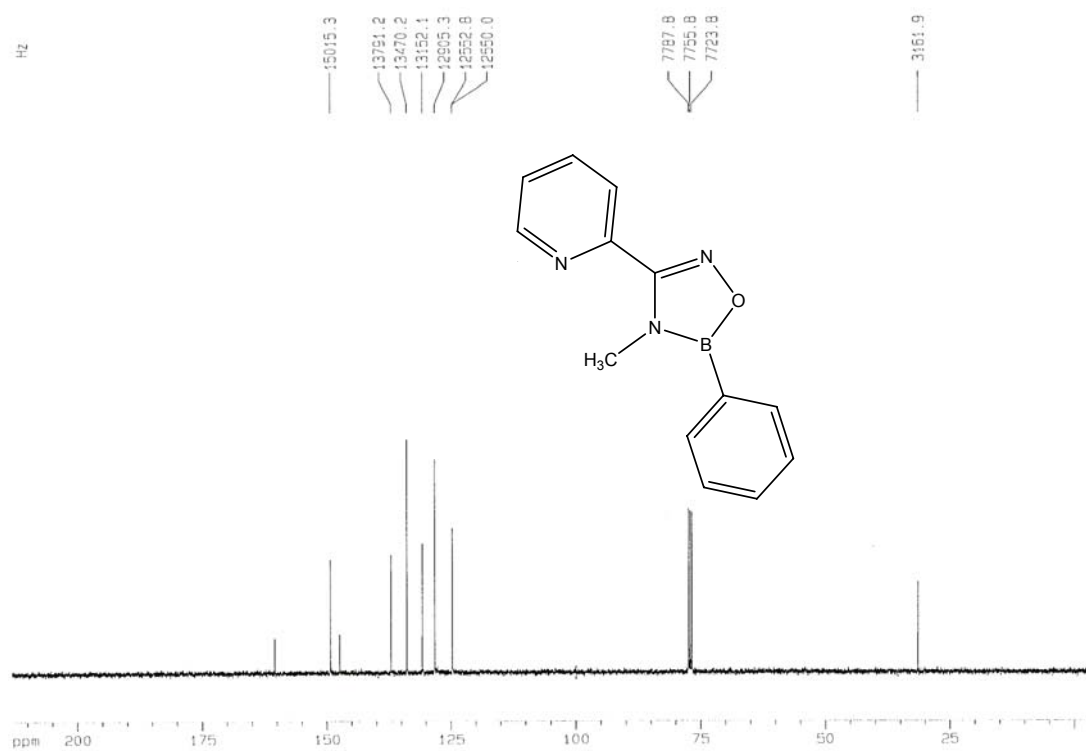


Figure 99C: The ¹³C-NMR spectrum of **21v**

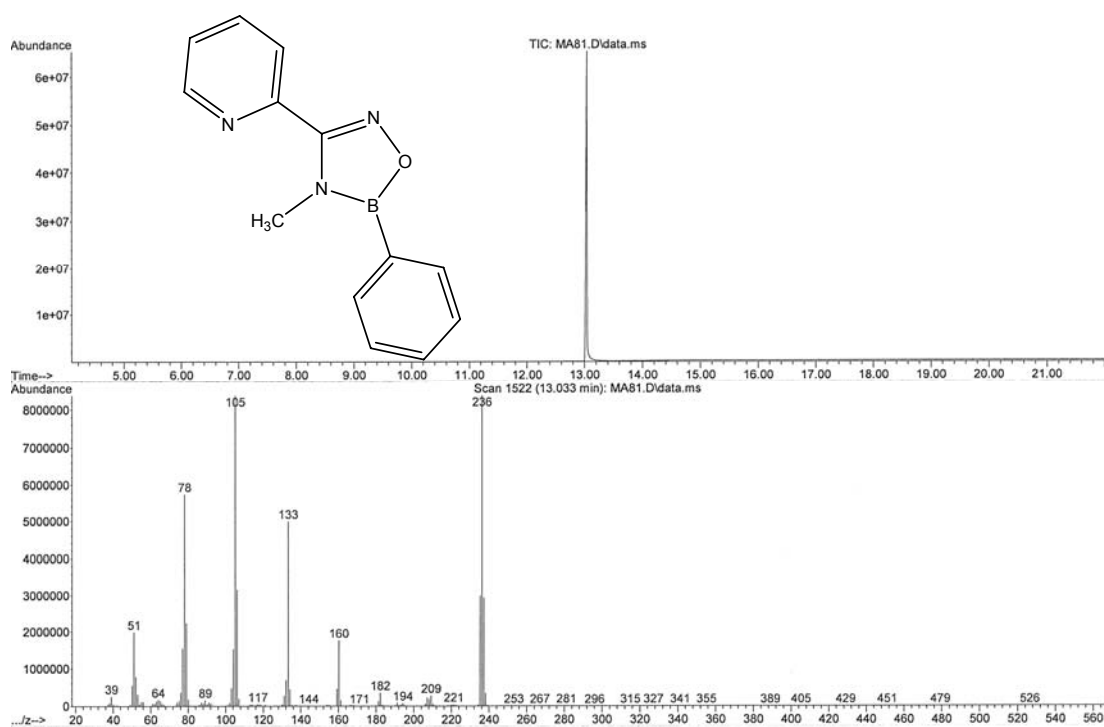


Figure 99D: The mass spectrum of **21v**

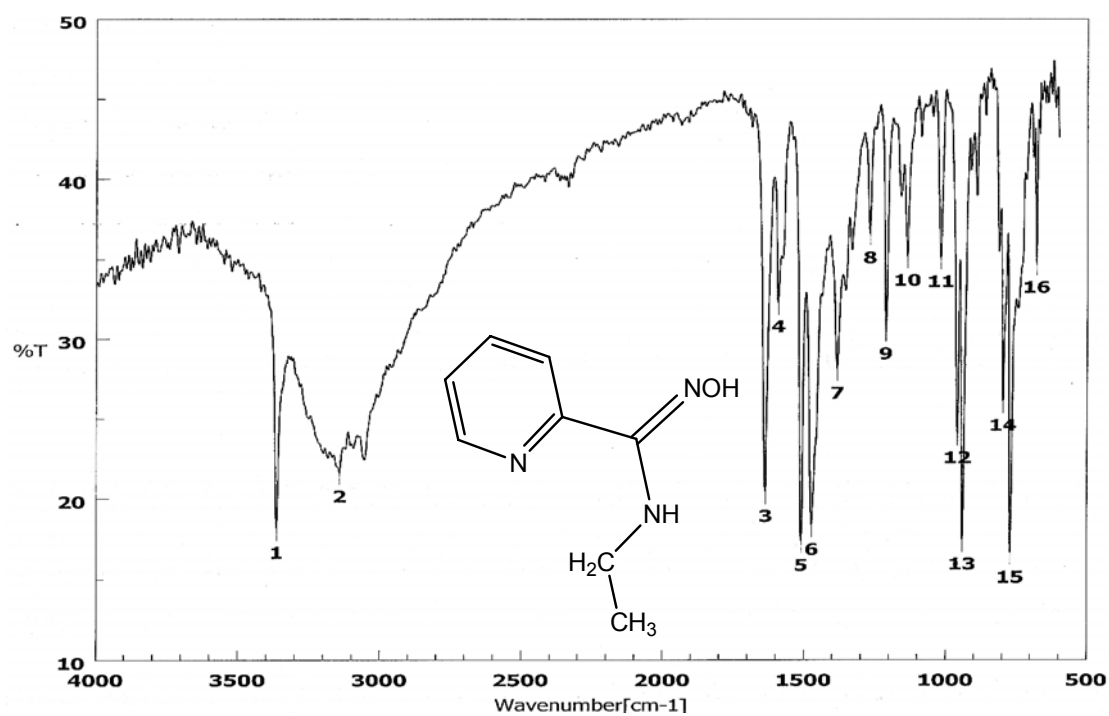


Figure 100: The IR spectrum of **15w**

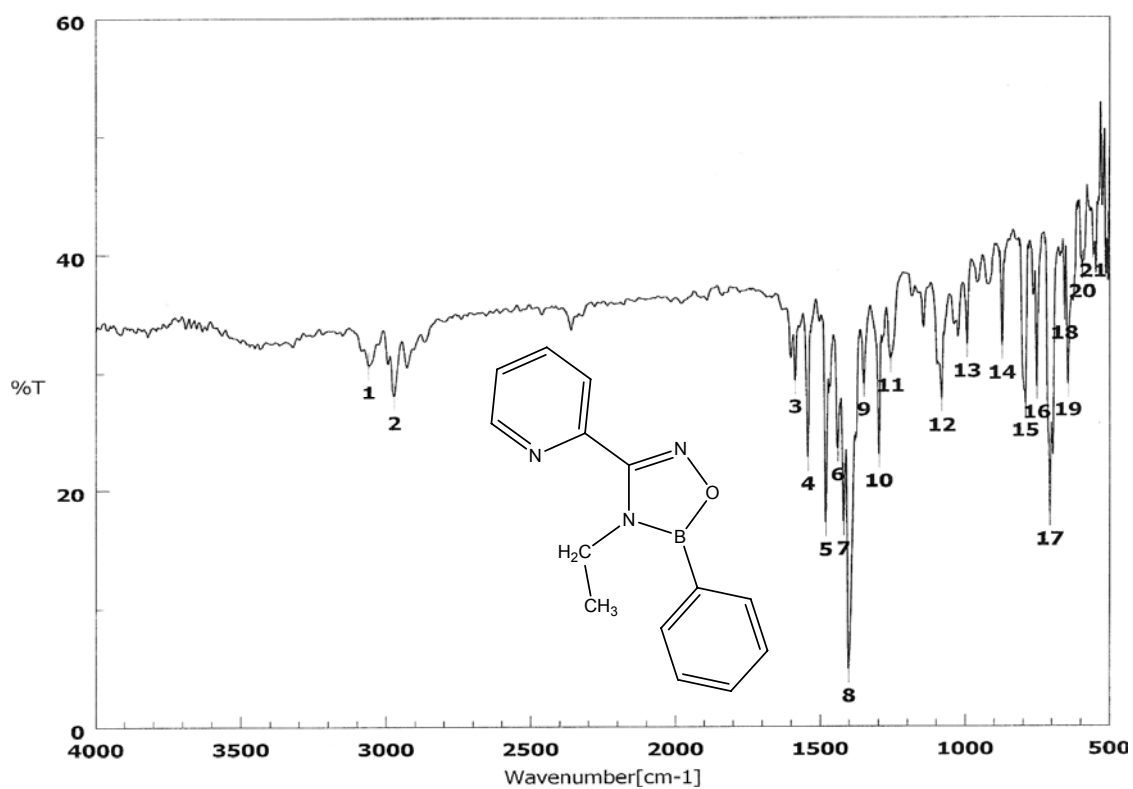


Figure 101A: The IR spectrum of 21w

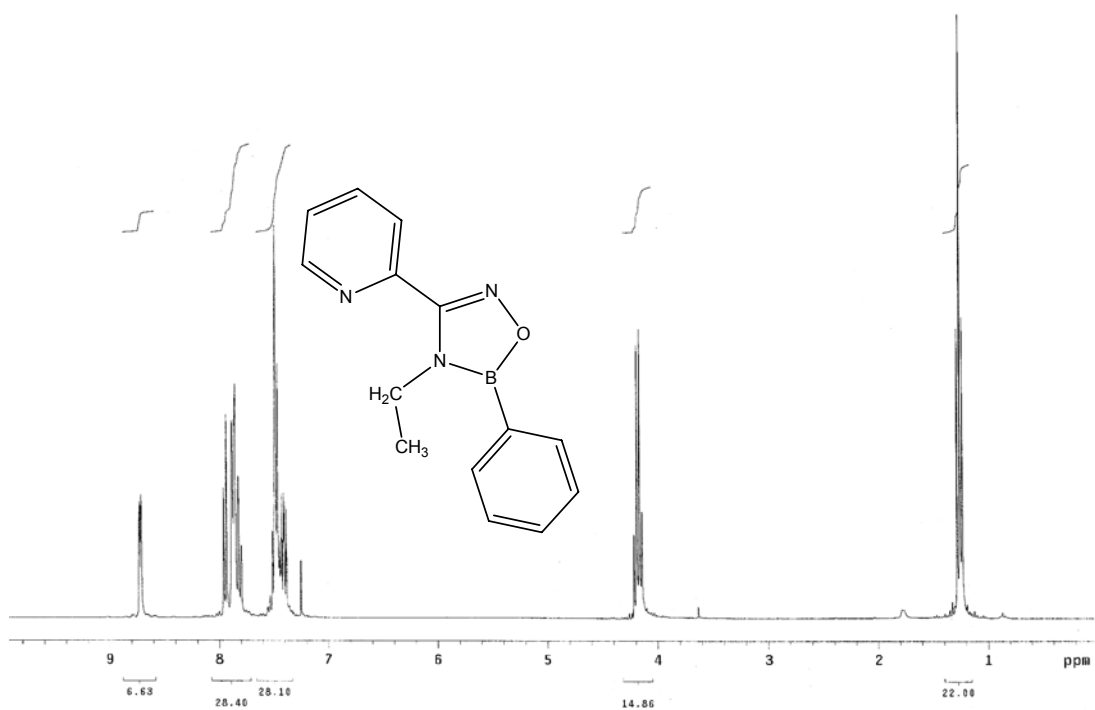


Figure 101B: The ¹H-NMR spectrum of 21w

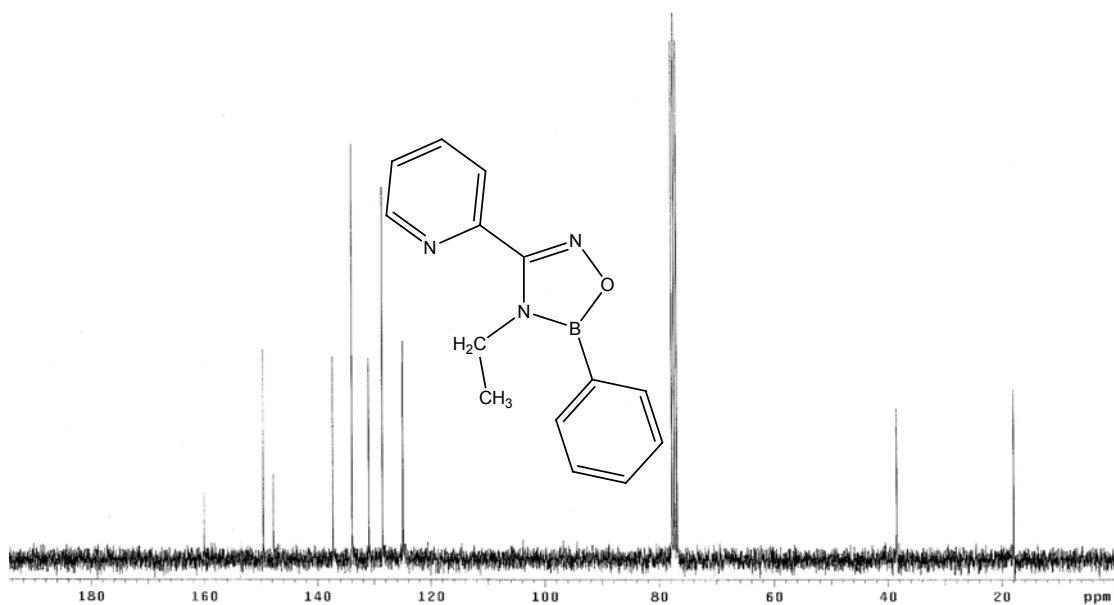


Figure 101C: The ^{13}C -NMR spectrum of **21w**

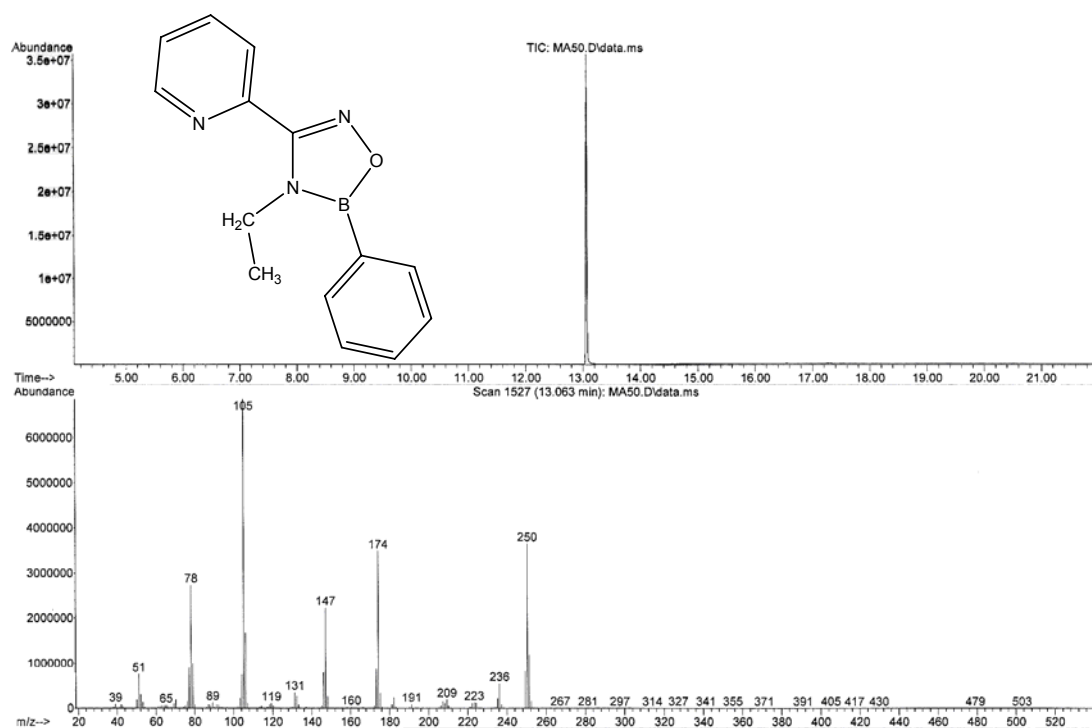


Figure 101D: The mass spectrum of **21w**

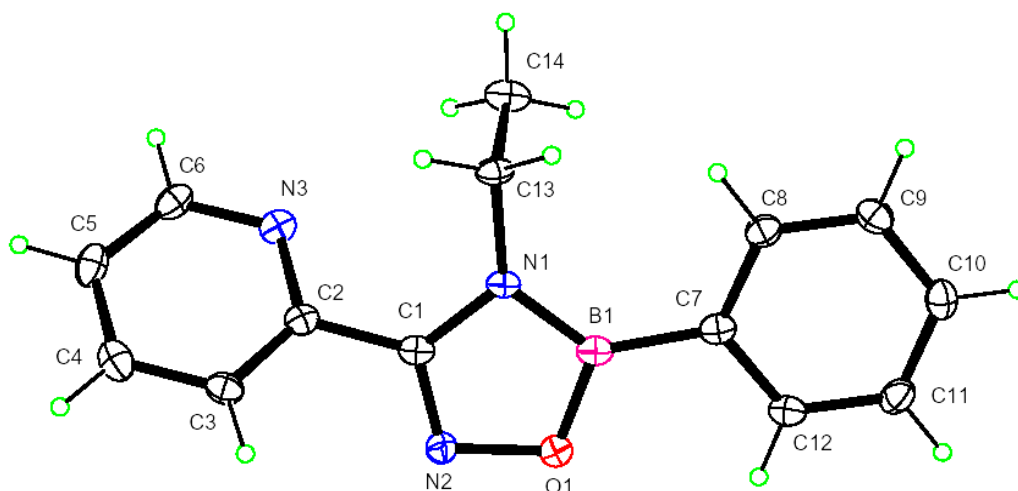


Figure 101E: The X-Ray pattern of **21w**

Crystal data

$C_{14}H_{14}BN_3O$

$M_r = 251.09$

Orthorhombic

Pbca

$a = 11.600 (2) \text{ \AA}$

$b = 10.1778 (17) \text{ \AA}$

$c = 21.602 (4) \text{ \AA}$

$V = 2550.4 (8) \text{ \AA}^3$

$Z = 8$

$D_x = 1.308 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3295 reflections

$\theta = 2.5\text{--}27.8^\circ$

$\mu = 0.084 \text{ mm}^{-1}$

$T = 90 \text{ K}$

Lath fragment

Colorless

$0.30 \times 0.07 \times 0.03 \text{ mm}$

Crystal source: local laboratory

Data collection

KappaCCD (with Oxford Cryostream)	$I > 2\sigma(I)$
diffractometer	$R_{\text{int}} = 0.052$
ω scans with κ offsets	$\theta_{\text{max}} = 27.8^\circ$
Absorption correction: none	$h = -15 \rightarrow 15$
23865 measured reflections	$k = -13 \rightarrow 13$
3022 independent reflections	$l = -28 \rightarrow 28$
2142 reflections with	intensity decay: $<2\%$

Table 5: Crystal data and refinement of **21w**

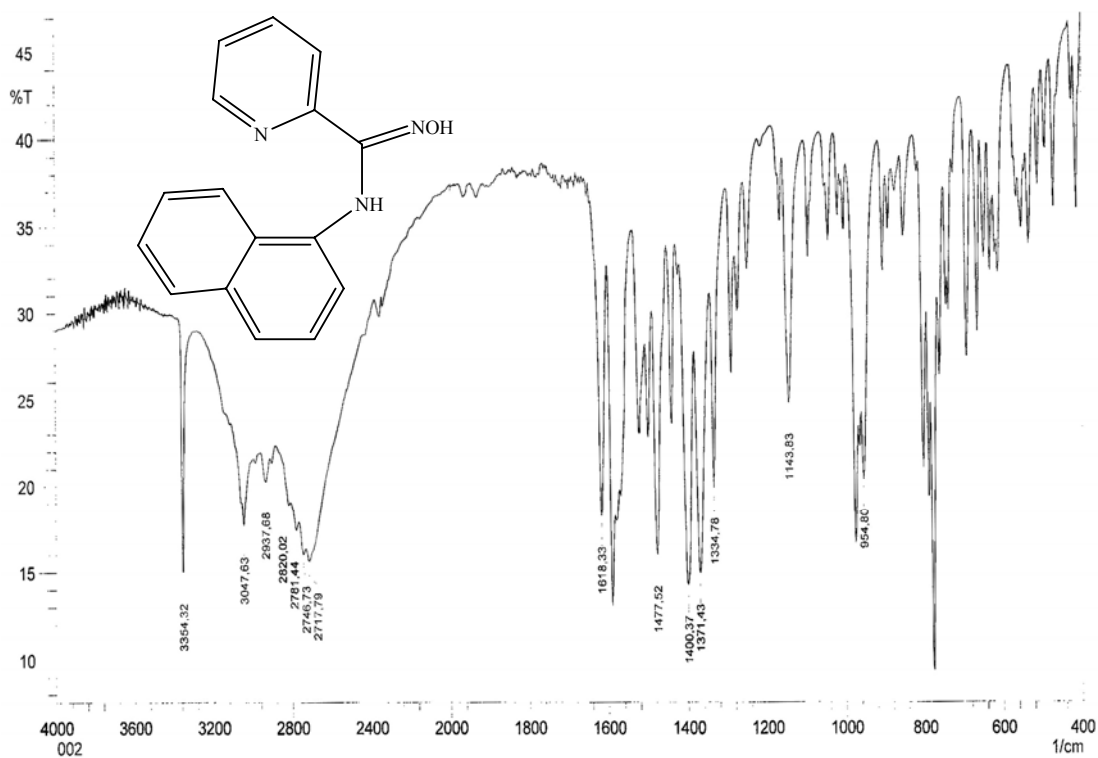


Figure 102: The IR spectrum of **15u**

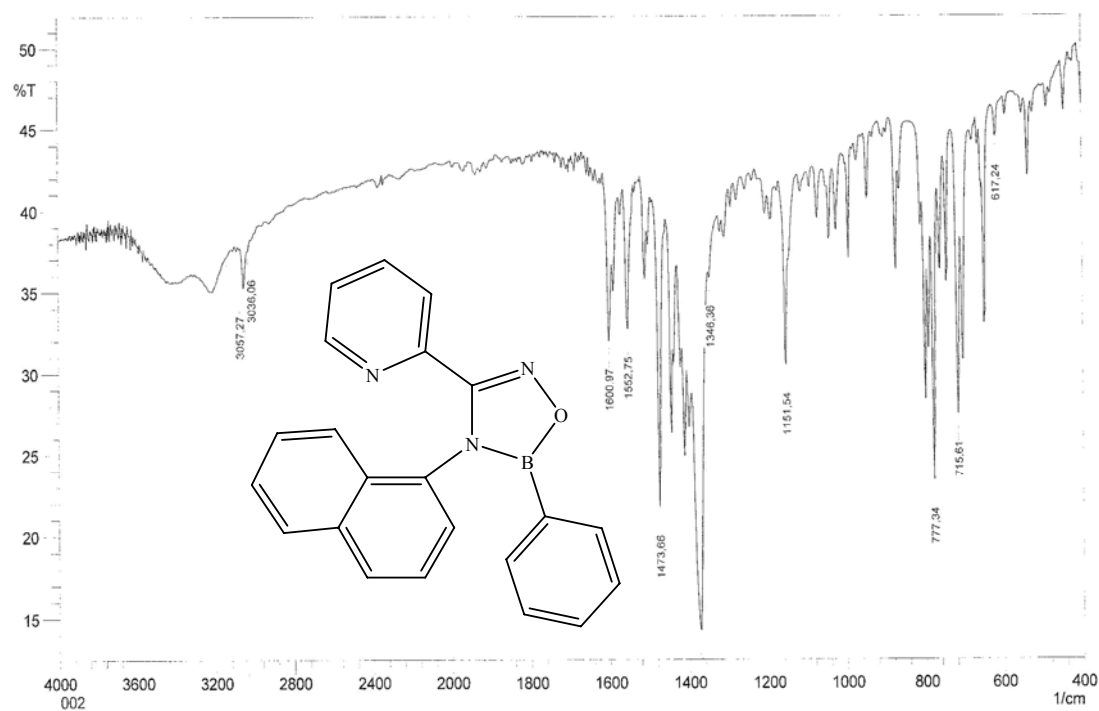


Figure 103A: The IR spectrum of **21u**

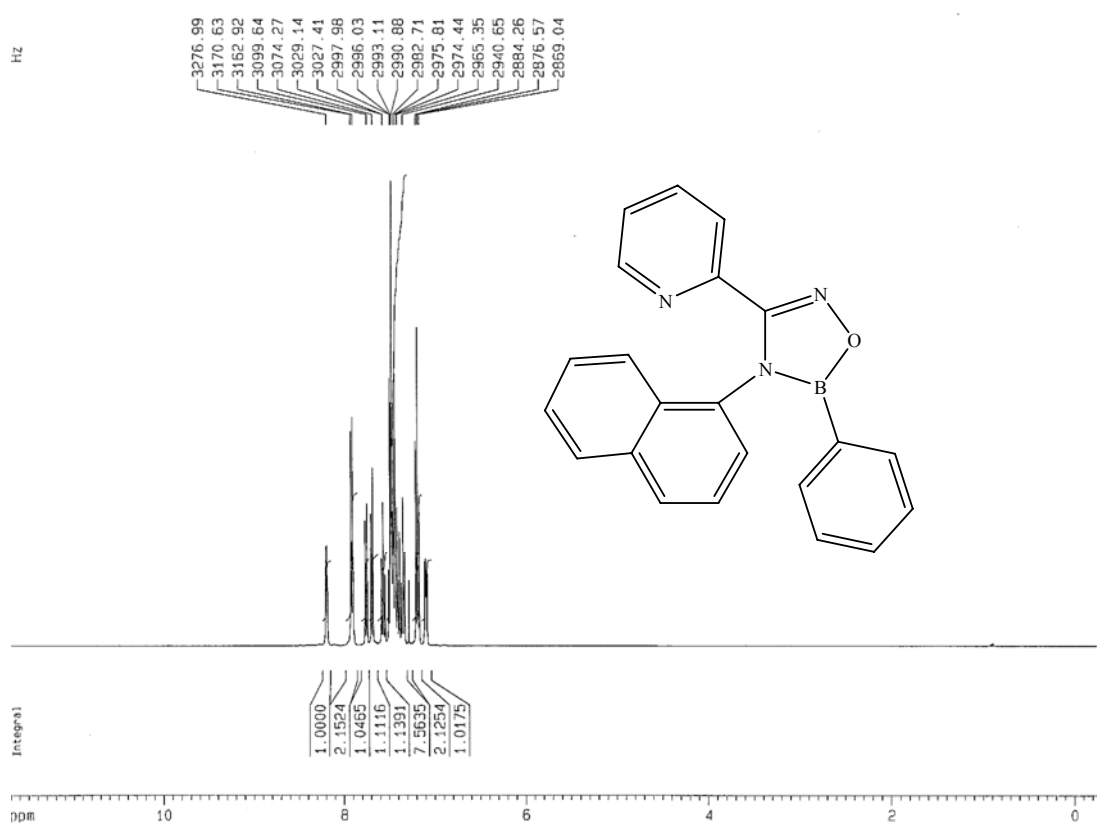


Figure 103B: The ¹H-NMR spectrum of **21u**

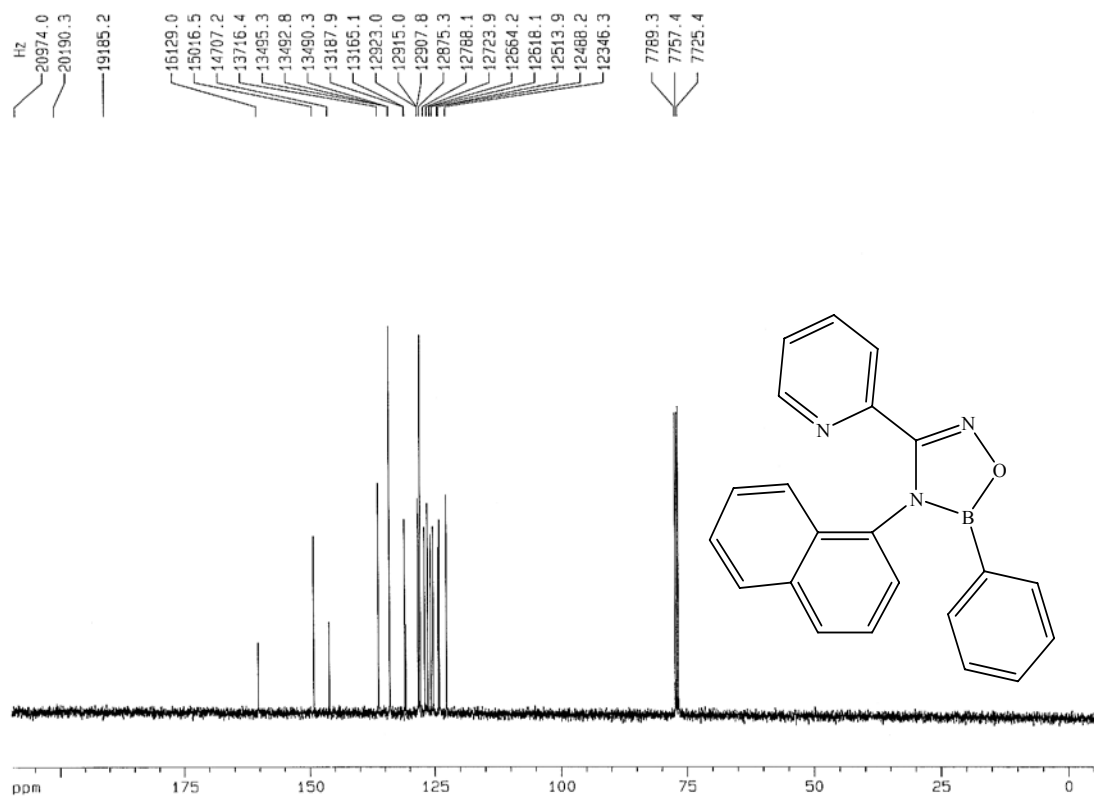


Figure 103C: The ¹³C-NMR spectrum of **21u**

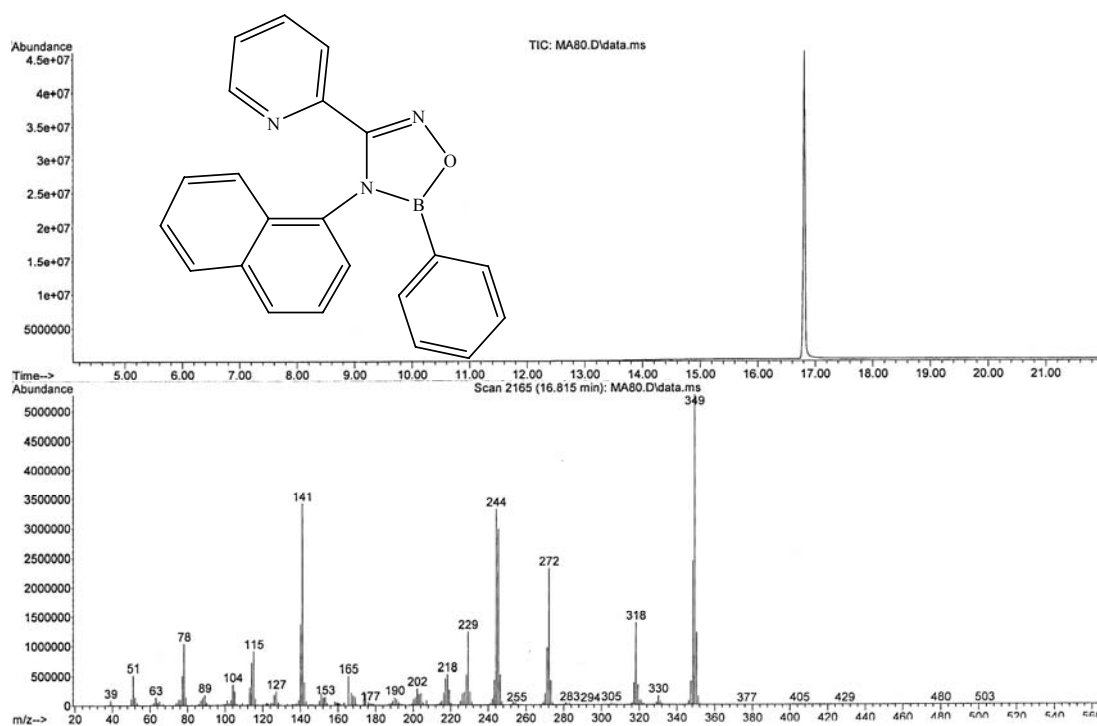


Figure 103D: The mass spectrum of **21u**