Chapter 2

Synthesis and Applications of Oxazolines

Part I: Synthesis of Oxazolines

Part II: Application in Mizoroki-Heck Reaction

Oxazolines are established as efficient and widely accepted ligands for various organic transformations due to their easy accessibility and better binding ability with metals which has been summarised in Chapter 1. In accordance with the chapter 1, we have synthesized some oxazoline molecules and screened them for palladium catalyzed Mizoroki-Heck reaction which will be discussed in this chapter.

The carbon-carbon bond forming reactions are very important in building organic molecules. A large number of such type of reactions have been developed. Among all these reactions, transition metal catalysed reactions like Mizoroki-Heck reaction, Suzuki coupling, Sonogashira coupling and Michael reaction etc. are most versatile.

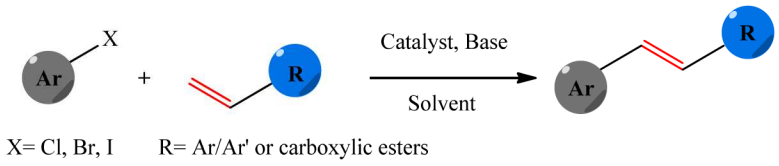
In this chapter we will be focusing on palladium catalyzed Mizoroki-Heck reaction.

Introduction

Mizoroki-Heck Reaction:

Transition metal catalyzed attachment of vinyl moiety to aryl halides, mostly using palladium based catalysts, is known as "Mizoroki-Heck reaction." It is an extremely useful and extensively studied method of the formation of carbon-carbon bond. In this reaction *trans* olefins are predominantly formed as major product.

In late 1960s, Heck and Mizoroki independently discovered arylation and alkenylation of olefins, originally by Heck[1a] or Mizoroki-Heck[1b] reaction. This reaction was further developed by Heck described in a number of fundamental papers into a general method of organic chemistry. The reaction was catalysed by Pd in the presence of base **[Scheme 1]**.



Scheme 1: General Scheme for Mizoroki-Heck reaction

The catalyst in the standard Heck reaction is a Pd(0) species stabilized by suitable ligands. The reaction mechanism includes four steps **[Figure 1]**:

1) A σ-aryl-Pd (II) complex is formed *via* oxidative addition.
2) Either one of the ligands or halide anion dissociates from the complex, leaving behind a vacant coordination site that is occupied by the olefin substrate. Insertion of the olefin at the aryl-Pd bond takes place subsequently.
3) An intramolecular β-hydride elimination occurs, which gives the coupling product.
4) PdL_2 catalyst is regenerated after the removal of HX from the complex mediated by the base.

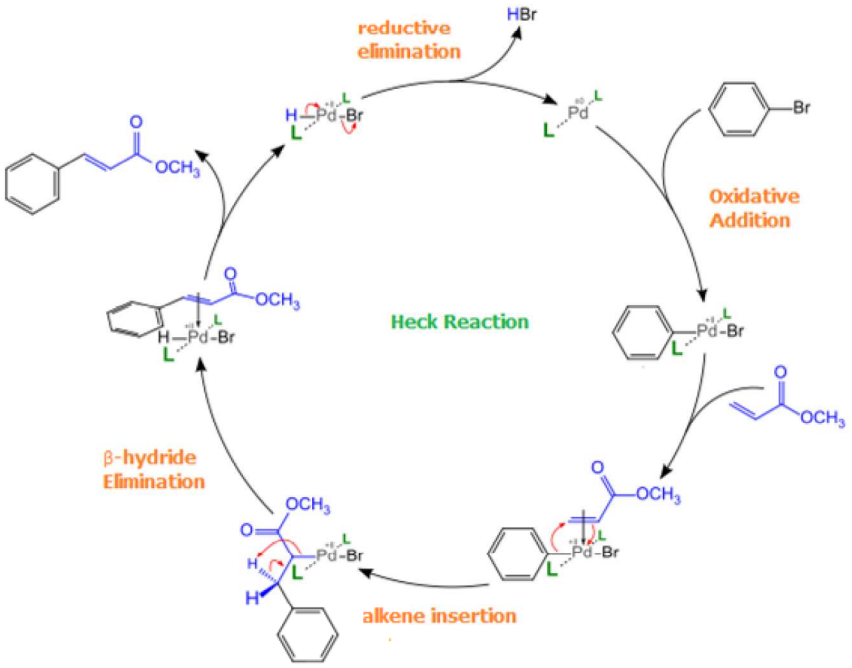


Figure 1: Mechanism for the Mizoroki-Heck reaction

Most of the examples of Heck reaction are usually carried out in presence of phosphine ligands such as 1,3-bis(diphenylphosphino)propane (*dppp*), 1,2-bis(diphenylphosphino)ethane (*dppe*) or tripheylphosphine and its derivatives *etc.* under inert atmosphere.[2]

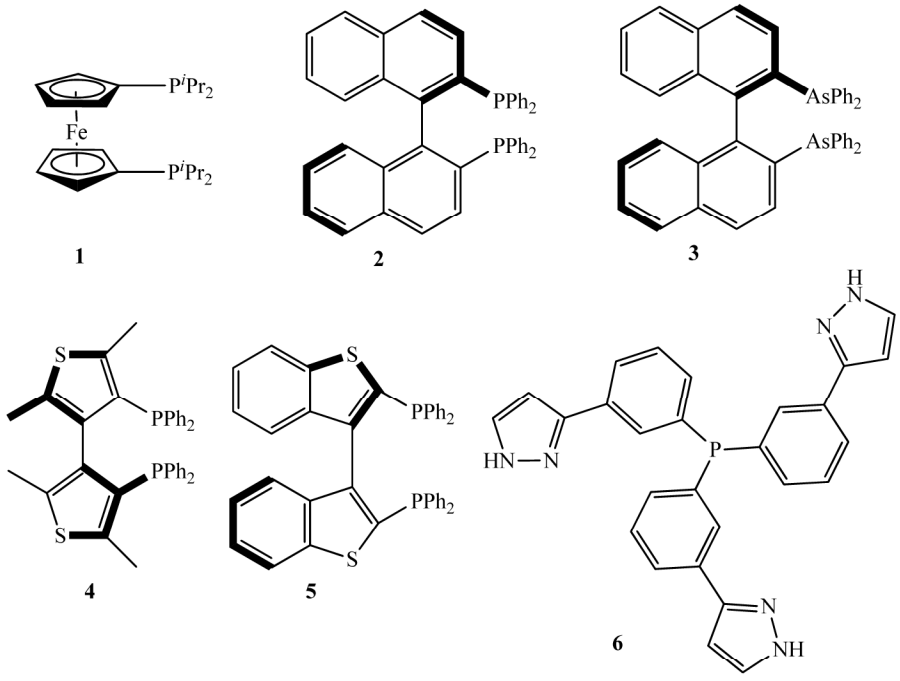


Figure 2: Phosphine ligands used for Mizoroki-Heck reaction

Boyes and co-workers have reported the use of palladium(II)chloride complexes of (diisopropylphosphino)ferrocene **1** as efficient catalyst for Heck reaction of aryl iodide and acrylates to afford cinnamate derivatives with good results.[3] Palladium complexes of Ligands **2** to **5** have been used successfully for the intramolecular asymmetric Heck reaction by Guiry.[4] Some heterocyclic based phosphine ligands were also developed for this reaction, an example of pyrazolyl substituted triphenylphosphine ligand **6** has been developed by Thiel *et al* for the palladium catalyzed Heck reaction with excellent results.[5]

Number of palladacyles in which Pd is attached to any carbon atom of the ligand with a σ bond has resulted as a new class of catalyst for Mizoroki-Heck reaction.[6] This discovery was made by Hermann and Beller *et al* who introduced $Pd_2(P(o\text{-}Tol)_3)_2(\mu\text{-}OAc)_2$ **7** as efficient homogeneous catalyst **[Figure 3]**.[7]

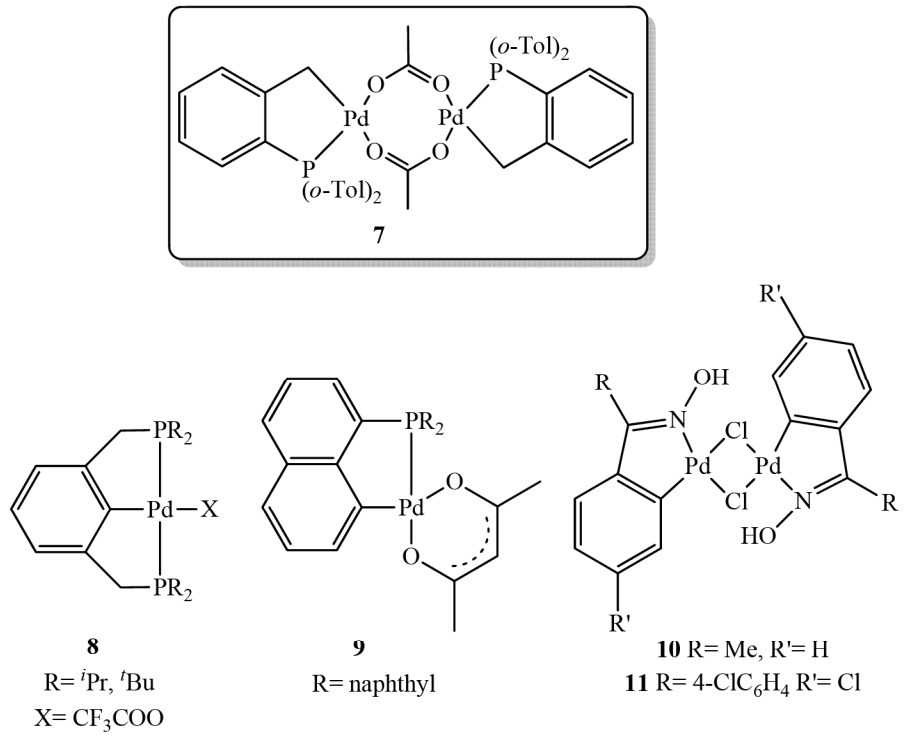
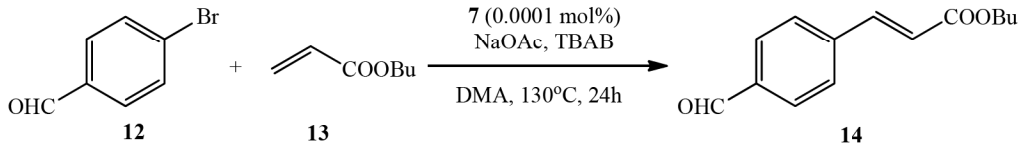


Figure 3: Structures of the palladacycles

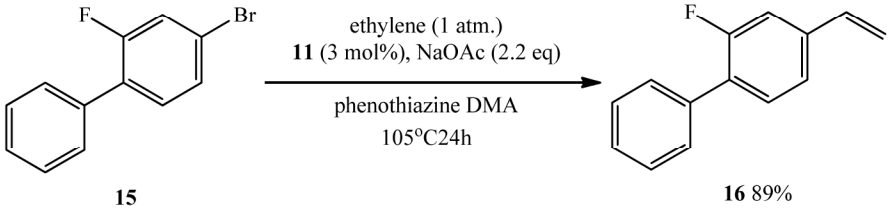
Using **7** for Heck reaction of aryl bromides with olefins with very low catalyst loading gave excellent results having high TON (Turn Over Number) in the range of 10^6. In case of 4-bromobenzaldehyde **12** and butyl acrylate **13** using **7** (0.0001 mol%) as the catalyst, NaOAc as base and *N*,*N*-dimethylacetamide (DMA) as solvent at 135 ^oC for 24 h gave olefin **14** with 100% conversion and high TON in the range of 10^6 as well as Turn Over Frequency (TOF) of 42000 h^{-1} **[Scheme 2]**.



Scheme 2: Use of Hermann's phosphine palladacycle **7** for Heck reaction

Milstein introduced efficient catalysis with complex **8**[8] and Shaw introduced complex **9**[9] as the catalyst system for reactive aryl halides in the Heck reaction.

Smith *et al* have reported reaction of aryl bromides **15** in the presence of catalytic amounts of a palladacycle **10** and **11** which were derived from acetophenone oxime and potassium acetate with ethylene under pressure (1 atm) to give the corresponding vinylarene **16** in excellent yield **[Scheme 3]**.[10]



Scheme 3: Application of phosphine palladacycle **11** in Heck reaction

Although the phosphine ligands are efficient and versatile for such reactions, they have disadvantages because they are expensive, toxic and unrecoverable. In large-scale applications on industrial and semi-industrial scale, the phosphines may pose serious economic burden. Recently, some phosphine free Mizoroki-Heck reactions to overcome some of these shortcomings have been reported.[11-13] Mostly, nitrogen based ligands and carbene complexes have been studied as a secondary option **[Figure 4]** and **[Figure 5].**

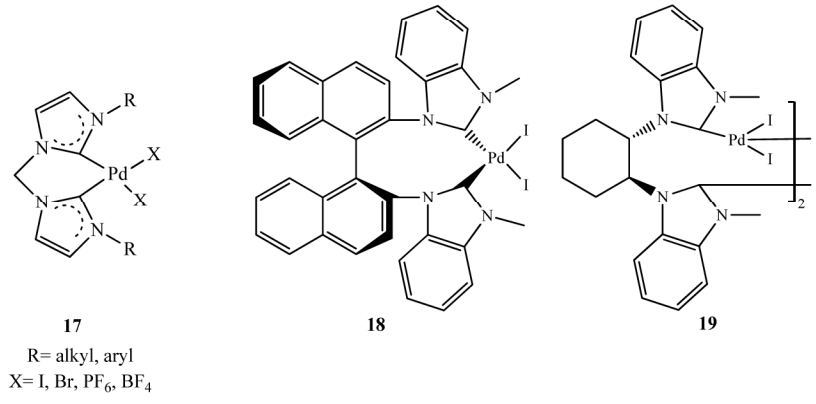


Figure 4: Phosphine free Palladacycle catalyst systems for Mizoroki-Heck reaction

A new principle for designing catalysts for Pd-catalyzed reactions have been proposed by Hermann *et al*.[14] Stable heterocyclic carbenes, derived from imidazole and 1,2,4-triazole, turned out to be excellent ligands forming a wide range of complexes.[15-17] Carbene ligands are

strong σ-donors which lack any appreciable ability for π-acceptor back bonding, and in this respect these ligands resemble donor phosphines, though with somewhat lower steric bulk. Hermann has also contributed to the development NHC-Pd complexes such as **17** for Mizoroki-Heck reaction to construct number of substituted olifins.[7] In 2005, Shi and co-workers have reported two new class of NHC-Pd(II) complexes for Heck reaction providing good results. They have reported benzimidazolium binaphthyl based NHC-Pd(II) complex **18** and dimeric bidentated NHC–Pd(II) complex **19** derived from *trans*-cyclohexane-1,2-diamine for Heck reaction.[18]

As another option certain number of nitrogen based catalyst system has also been documented in Literature which proved to be as effective as conventional reported palladium complexes **[Figure 5]**.

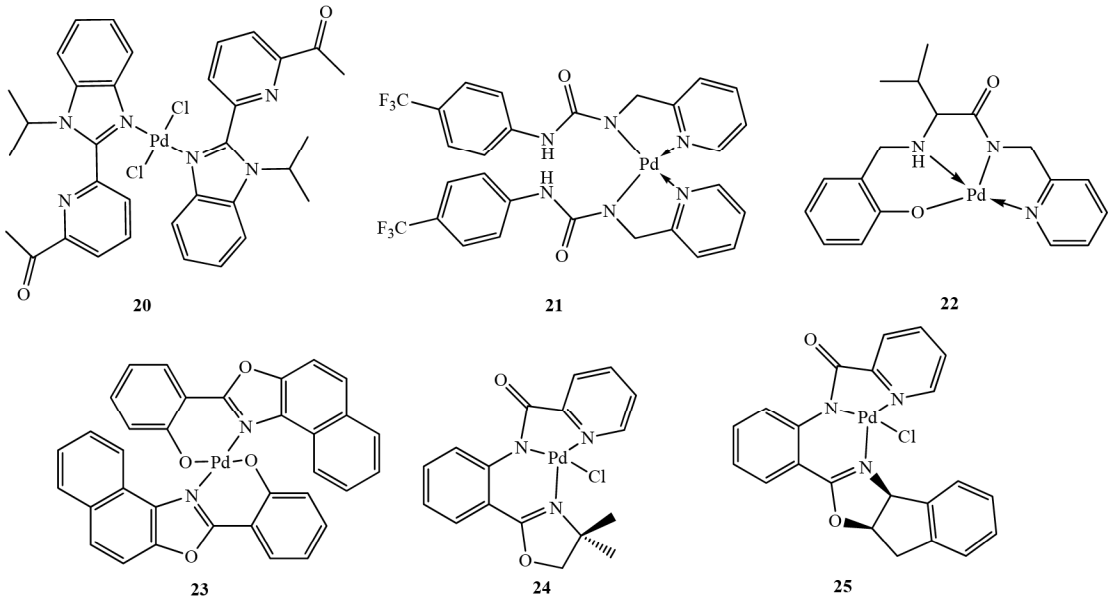
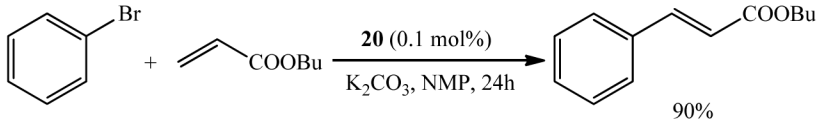


Figure 5: Nitrogen based catalyst system for Mizoroki-Heck reaction

Pd(II)-pyridylbenzoimidazole catalyst system **20** was used by Xi and co-workers for Heck reaction of bromobenzene with butylacrylate to exhibit good conversion **[Scheme 4]**.[19]



Scheme 4: Application of catalyst **20** in Mizoroki-Heck reaction

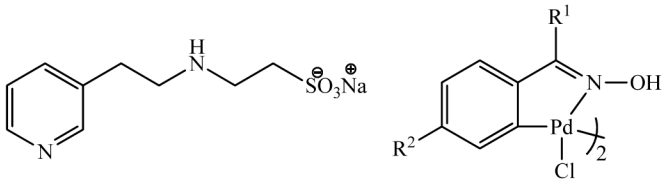
The synthesis and structure of palladium(II) complexes bearing uridato/pyridyl ligands **21** as an anionic *N*-donor coordination sites are reported by Srinivas *et al*. The complexes have been shown to be highly active catalysts for the Heck reaction of aryl bromides and moderate activity for the activation of aryl chlorides under phosphine-free conditions.[20]

N,N',N'',O-Tetrafunctional Pd(II) complex **22** prepared from the easily available amino acid were shown to be highly efficient catalysts for the Heck reaction of deactivated aryl bromides and iodides with high turnover numbers up to 10^4 under phosphine-free conditions by the same group.[21] Few 1,3-oxazole **23**[22a] and oxazoline[22b] **24** and **25** based ligands have also been used for the complexation with palladium salts to generate efficient catalyst system to be used for Mizoroki-Heck reaction [see **Figure 5**].

Many of the phosphine-less ligands and the corresponding active catalysts are difficult to prepare and are not readily available. Hence, there is a further need to find an effective combination of readily available *N,N*-ligands/palladium catalyst for this important reaction. Considering the wide application of nitrogen based ligands for the Mizoroki-Heck reaction we have also made an effort to contribute by synthesizing some *N,N*-oxazoline ligands for the purpose to screen them in palladium catalyzed Mizoroki-Heck reaction which will be discussed in this chapter. The oxazolines have certain advantages over conventional reported ligands, they are easy to synthesize as well as their purification and handling is simple, not only that, they are stable in basic medium even at high temperature which made them useful in many organic transformations.[23-25]

Heck reaction is generally performed in high boiling solvents such as toluene, DMA, DMF, NMP etc. Hence, much attention has been paid to develop milder and operationally simple procedures for Heck reaction in recent years. The non classical conditions e.g. ultrasounds, microwaves, alternative solvent system or combinations of these can be used to perform the Heck reaction in a greener way or in an environment friendly way. This problem could be fully or partially solved by using one of the most highly polar solvents, water as a reaction medium. The use of aqueous solvent contribute to the development of environmentally and technologically safe processes because it is termed as "perfect green solvent" and it is an attractive option of "Green Synthesis". According to the mechanistic aspect, it must have an accelerating influence on the Heck reaction as it promotes the migratory insertion to follow the cationic mechanism.

There are number of reports available where such reactions were carried out with few additives like quaternary ammonium salts as surfactants or cyclodextrrins etc.[26-28]



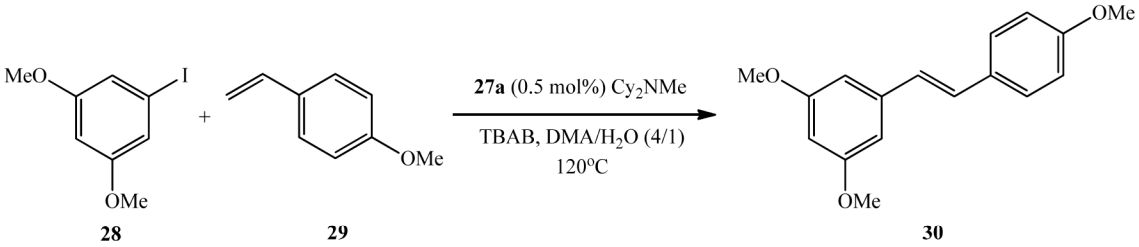
26 **27**

a; R^1= Me, R^2= OH

b; R^1= 4-ClC_6H_4, R^2= Cl

Figure 6: Catalysts used in aqueous Heck reactions

Thore has reported the use of sodium 2-(2-pyridin-3-ylethylamino)sulfonate **26** as an efficient ligand and base for Pd-catalyzed Heck reaction of arylhalides and acrylates in aqueous media to give cinnamate derivatives with excellent yield in shorter time.[29] Such green processes can also be useful for the development of structural analogues of biologically active molecules like resveratrol. Najera *et al* have used oxime based palladacycle **27** for synthesis of methylated resveratrol **30** and its analogues by performing Heck reaction in aqueous media **[Scheme 5]**.[30]



Scheme 6: Synthesis of methylated resveratrol **30** using aqueous Heck methodology

Most of the examples of Mizoroki-Heck reaction are usually carried out in the presence of phosphine ligands under inert atmosphere.

Hence we have developed the greener methodology by using water as solvent system and screened our oxazoline ligands for the Mizoroki-Heck reaction which will also be discussed in this chapter.

Result and Discussion:

Part I: Synthesis of Oxazolines:

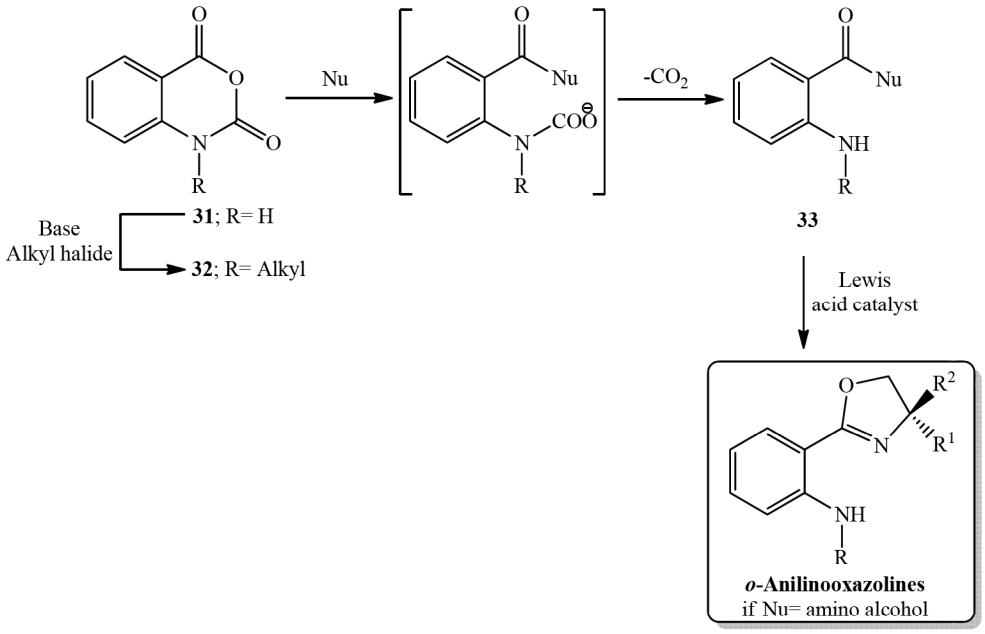
Oxazolines are established as efficient and widely accepted ligands due to their easy accessibility and better binding ability which has been summarised in Chapter 1. In accordance with the previous chapter, we have synthesized number of oxazoline derivatives,

1. *o*-Anilino oxazoline derivatives from isatoic anhydride; *N*-alkylsubstituted amino oxazolines from *N*-alkylated isatoic anhydride**.**
2. *N,O*-mono(oxazolines) i.e. *o*-Phenolato oxazolines from *o*-cyanophenol
3. Bis(oxazolines) from 1,2-dicyanobenzene.

For the practical application, these synthesized oxazoline molecules were screened as ligands in palladium catalyzed Mizoroki-Heck reaction as well as in its aqueous version as an option of "Green Chemistry" which will be discussed in Part II of this chapter.

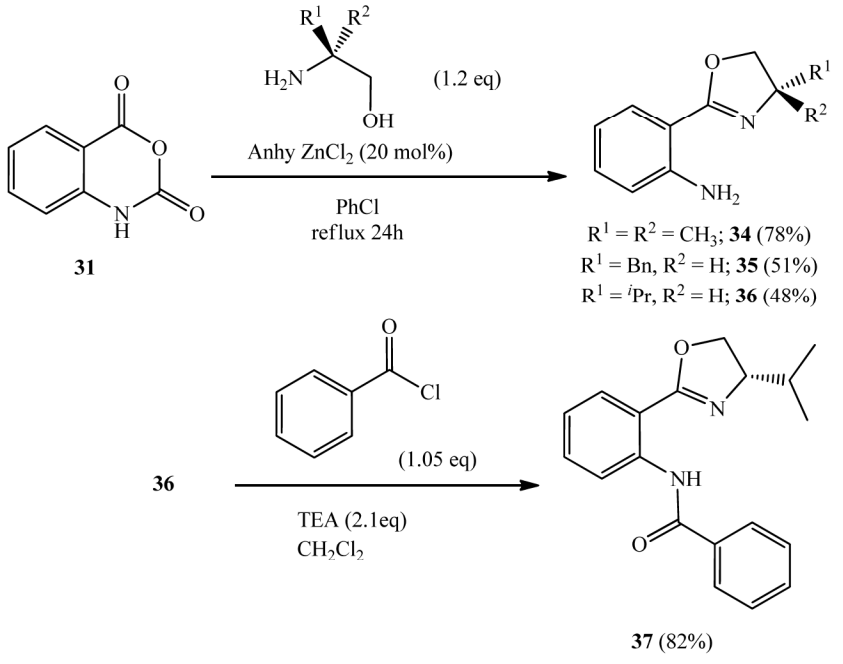
Synthesis of amino oxazolines:

We have chosen o-anilino oxazoline skeleton, which has two nitrogens, one from oxazoline ring and the other one from amino group, to offer a chelating moiety, for our study. Another reason for the choice of this system is due to the simple preparation of such ligands as well as ease of their purification. These compounds are also quite stable in air and at high temperature in basic medium. The precursors for the synthesis of aminooxazoline ligands are readily available. The class of amino oxazoline ligands can be prepared from isatoic anhydride **31**. Isatoic anhydride is an internally protected and activated form of 2-aminobenzoic acid. The C-4 carbonyl of the heterocyclic ring is highly susceptible to an attack by a variety of nucleophiles to give **33** along with carbon dioxide as the only by-product. The amide nitrogen of **31** (R= H) can be readily alkylated by deprotonation with suitable base followed by reaction with an alkyl halide to give an *N*-substituted isatoic anhydride **32**. If commercially available 2-amino alcohol is used as a nucleophile, oxazoline moiety can be obtained after *in situ* cyclization using Lewis acid catalyst **[Scheme 7]**.



Scheme 7: General scheme for the synthesis of aminooxazolines from isatoic anhydride **(31)** and its derivatives **(32)**

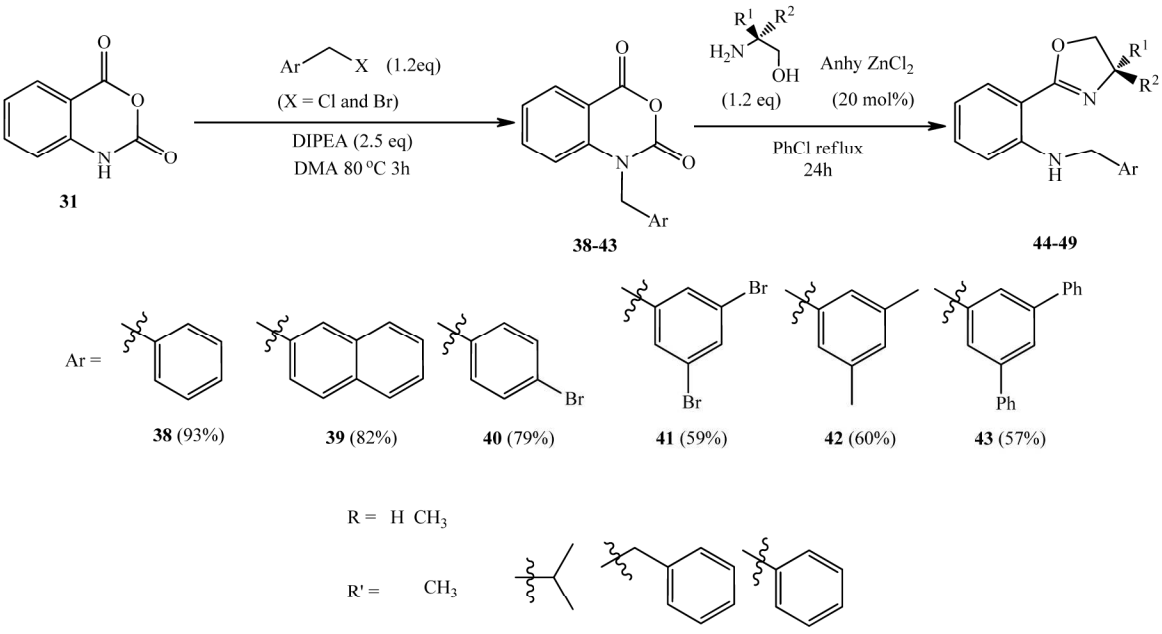
We have synthesized a number of amino oxazoline derivatives from isatoic anhydride **31** and appropriate 2-amino alcohols from standard method using catalytic amount of anhydrous zinc chloride (which was prepared from melting zinc chloride at high temperature under vacuum under the nitrogen blanket). The reaction was run in dry chlorobenzene under reflux condition for 24 h to afford a product with good conversion **[Scheme 8]**. Isolation of the products was carried out by column chromatography on neutral aluminium oxide because of large difference in Rf value of substrate and the final product.



Scheme 8: Synthesis of monooxazolines **34-37**

Reaction of isatoic anhydride **31** with 2-amino-2-methyl-propane-1-ol (1.2 eq) in presence of anhydrous zinc chloride (20 mol%) in dry chlorobenzene at reflux temperature for 24 h, after work up and purification by column chromatography on neutral aluminium oxide afforded corresponding achiral amino oxazoline **34** with 78% yield as white crystalline solid which was then characterised by spectral analysis. This methodology was also applied for the synthesis of chiral amino oxazoline derivatives **35** and **36** from the isatoic anhydride **31** and L-phenylalaninol and L-valinol to afford product in 51% and 48% yields respectively which were also characterised by usual spectral techniques. To check the effect of benzoyl substituted amino group on complexation with metal, oxazoline **36** was converted to its benzoyl derivative by treatment with 1.05 equivalent of benzoyl choride in presence of triethylamine as base, yielded corresponding product **37** in 82% isolated yield.

Similarly, to study the effect of substitution at amino group, various alkyl substituted amino oxazoline derivatives have been synthesized using the same described method but prior to that isatoic anhydride **31** was alkylated with variety of benzylhalides using *N,N*-diisopropyl ethylamine as base and *N,N*-dimethylacetamide as solvent at 80 ^{o}C for 3h to afford *N*-alkyl derivatives **38-43** in good yields which were then converted to *N*-substituted amino oxazolines **44-49** using appropriate achiral as well as chiral 2-aminoalcohols **[Scheme 9]**. The N-alkylated isatoic anhydride derivatives **38**-**43** were purified by single crystallization in ethanol and used for the preparation of amino oxazoline derivatives **44-49**.



Scheme 9: Synthesis of *N*-alkylated isatoic anhydride derivatives **38-43** and aminooxazolines **44-49**

The list of achiral as well as chiral *N*-substituted amino oxazolines is shown in **Figure 7** and **Figure 8**.

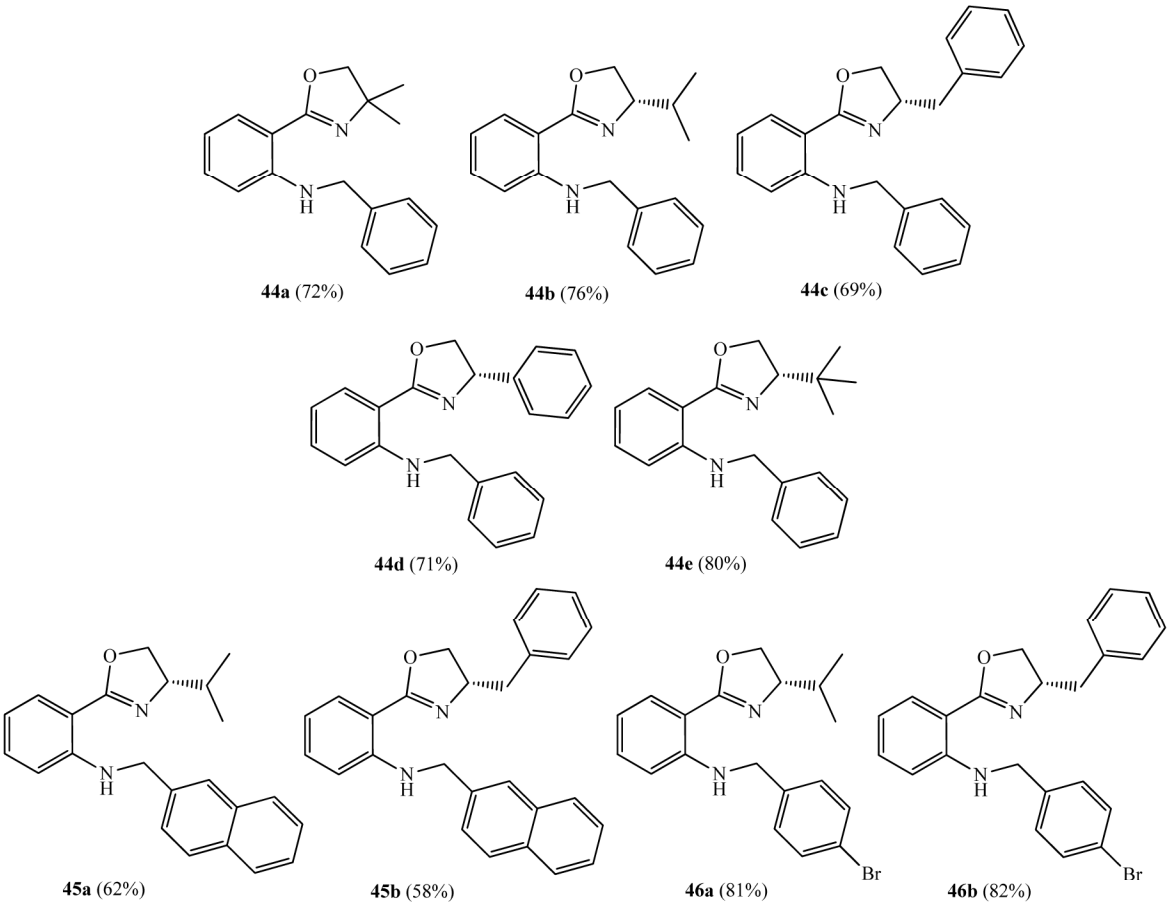


Figure 7: List of *N*-substituted aminooxazolines **44-46**

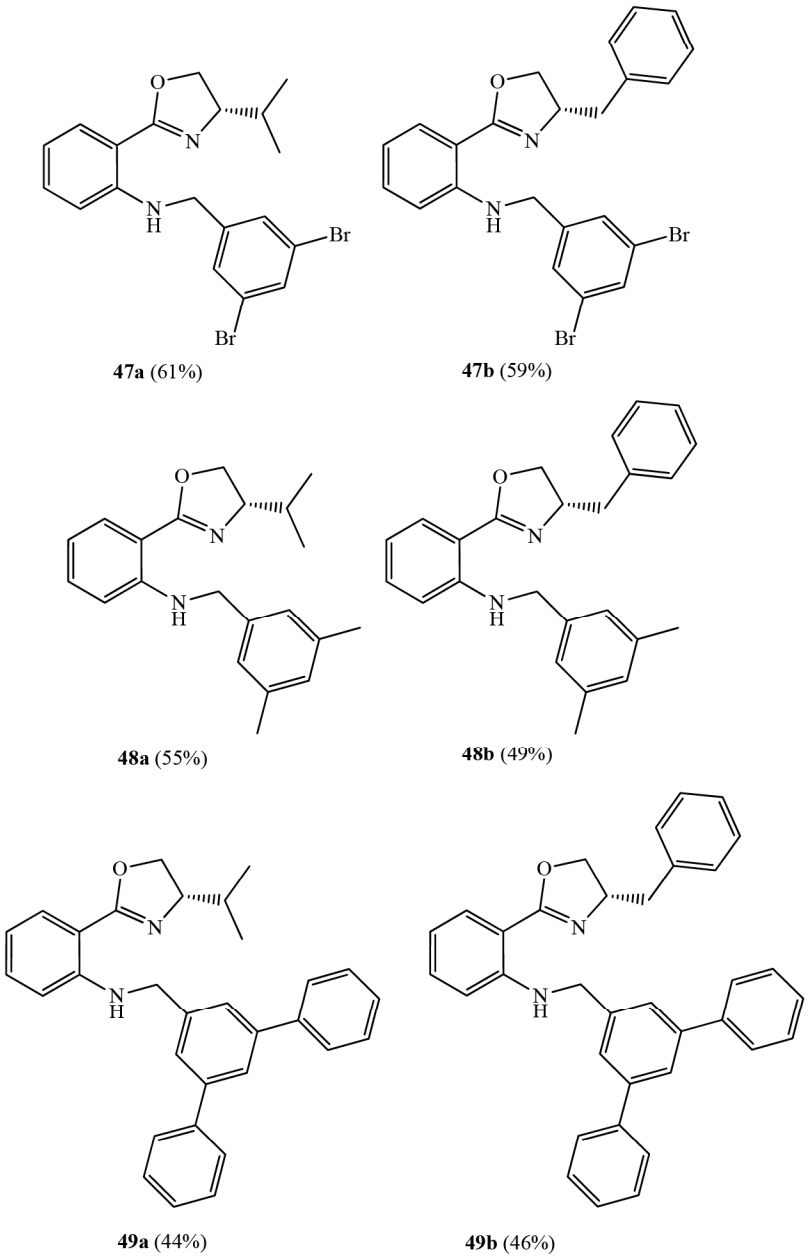
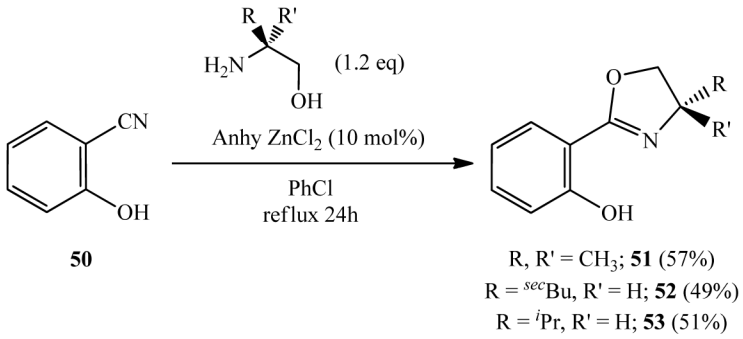


Figure 7: List of *N*-substituted aminooxazolines **47-49**

These derivatives were isolated, purified by column chromatography on neutral aluminium oxide with mixture of ethyl acetate and petroleum ether as eluent and the final products were characterized by usual spectral techniques.

Synthesis of *N,O*-mono(oxazolines):

The *N,O*-mono(oxazolines), also an important class of ligands, were synthesized from o-cyanophenol **50** and appropriate aminoalcohols using catalytic amount of zinc chloride to afford corresponding oxazoline derivatives in good yields **[Scheme 10]** which were isolated, purified and characterised using usual spectral techniques.

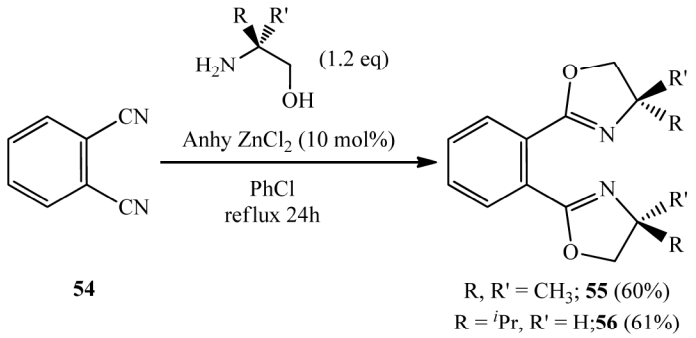


Scheme 10: Synthesis of *N,O*-mono(oxazoline) derivatives **51-53**

This set of ligands was tried for dihydroxylation of *trans*-stilbene using standard method but unfortunately it could not catalyze the reaction to form a product. However, the ligand **51** gave good result for Pd-catalyzed Mizoroki-Heck reaction and the results will be presented in next section.

Synthesis of *N,N*-Bis(oxazoline) derivatives:

Bis(oxazoline) derivatives **55** and **56** were synthesized from 1,2-dicyanobenzene **54** and appropriate amino alcohol using earlier described method of using catalytic amount of zinc choride **[Scheme 11]**.

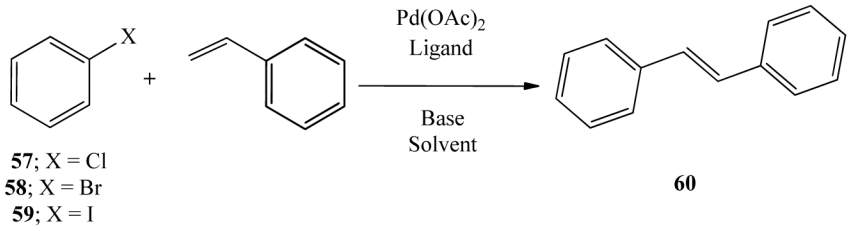


Scheme 11: Synthesis of bis(oxazoline) derivatives **55** and **56**

Amongst all these oxazolines the achiral ones have been screened for Mizoroki-Heck reaction as described in the next part of this chapter.

Part II: Application of oxazolinyl ligands in Mizoroki-Heck reaction

To demonstrate the practical application of the oxazolinyl ligands **34**, **44a**, **51** and **55**, we have screened these molecules in palladium catalyzed Mizoroki-Heck reaction of aryl halides and styrene as well as acrylates to generate variety of olefins.



Scheme 12: General scheme for Mizoroki-Heck reaction

In order to compare these oxazolinyl ligands for the Heck reaction commercially available 1,10-phenanthroline **61** and 1,3-bis(diphenylphosphino)propane, *dppp*, **62** were also considered.

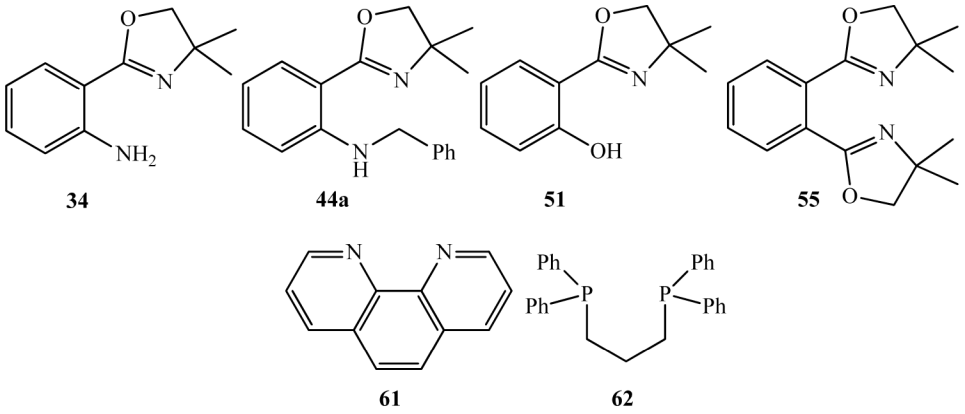


Figure 9: List of ligands screened for the Mizoroki-Heck reaction

The ligands **34**, **44a**, **51**, **55, 61** and **62** were then systematically screened in the standard Heck reaction of aryl halides **57-59** and styrene for the search of best condition, **[Scheme 12]** and the results are summarized in **Table-1**.

Table-1: Search for suitable conditions for Heck reaction with oxazolinyl ligands

No	Aryl halide (mol eq.)	Styrene mol eq.	Ligand (mol %)	$Pd(OAc)_2$ (mol %)	Solvent	Base (2 eq.)	Additive (0.25 eq.)	Temp. (^oC)	Time (h)	Isolated yield (%) of **60**	TON	
1	PhCl (1.0)	1.5	**34** (5.0)	2.0	DMF	NaOAc	--	120	48	--	--	
2	PhBr (1.0)	1.5	**34** (5.0)	2.0	DMA	NaOAc	--	140	24	64	32	
3	PhI (1.0)	1.5	**34** (5.0)	2.0	DMA	NaOAc	--	140	24	84	43	
4	PhI (1.0)	1.5	**34** (1.25)	0.5	DMA	K_2CO_3	--	140	24	85	170	
5	PhBr(1.0)	1.5	**34** (0.25)	0.1	DMA	K_2CO_3	--	140	24	19	190	
6	PhI (1.0)	1.5	**34** (0.25)	0.1	DMA	K_2CO_3	--	140	40	94	940	Solvent Study
7	PhI (1.0)	1.5	**34** (0.25)	0.1	TOLUENE	K_2CO_3	--	110	40	--	--	
8	PhI (1.0)	1.5	**34** (0.25)	0.1	DMF	K_2CO_3	--	140	40	88	880	
9	PhI (1.0)	1.5	**34** (0.25)	0.1	ACN	K_2CO_3	--	80	40	3	--	
10	PhI (1.0)	1.5	**34** (0.25)	0.1	NMP	K_2CO_3	--	140	40	86	860	
11	PhI (1.0)	1.5	**34** (0.25)	0.1	DMA	NaOAc	--	140	40	66	660	Base study
12	PhI (1.0)	1.5	**34** (0.25)	0.1	DMA	KO^{t}Bu	--	140	40	24	240	
13	PhI (1.0)	1.5	**34** (0.25)	0.1	DMA	TEA	--	140	40	92	920	

No	Aryl halide (mol eq.)	Styrene mol eq.	Ligand (mol %)	$Pd(OAc)_2$ (mol %)	Solvent	Base (2 eq.)	Additive (0.25 eq.)	Temp. (oC)	Time (h)	Isolated yield (%) of 60	TON	
14	PhI (1.0)	1.5	**34**(0.125)	0.1	NMP	K_2CO_3	--	140	40	90	900	
15	PhI (1.0)	1.5	**34**(0.025)	0.01	DMA	K_2CO_3	--	140	40	50	5000	
16	PhBr(1.0)	1.5	**34** (0.25)	0.1	DMA	K_2CO_3	--	140	40	27	270	Additive Study
17	PhBr(1.0)	1.5	**34** (0.25)	0.1	DMA	K_2CO_3	TBAB	140	40	87	870	
18	PhBr(1.0)	1.5	**34** (0.25)	0.1	DMA	K_2CO_3	18-Crown-6	140	40	85	850	
19	PhCl(1.0)	1.5	**34**(0.25)	0.1	DMA	K_2CO_3	TBAB	140	40	--	--	
20	PhI(1.0)	1.5	**34**(0.025)	0.01	DMA	K_2CO_3	TBAB	140	40	93	9300	
21	PhI (1.0)	1.5	**44a**(0.25)	0.1	DMA	K_2CO_3	--	140	40	95	950	
22	PhI (1.0)	1.5	**51** (0.25)	0.1	DMA	K_2CO_3	--	140	40	4	--	
23	PhI (1.0)	1.5	**55** (0.25)	0.1	DMA	K_2CO_3	--	140	40	92	920	
24	PhI (1.0)	1.5	**61** (0.25)	0.1	DMA	K_2CO_3	--	140	40	28	284	
25	PhI (1.0)	1.5	**62** (0.25) (dppp)	0.1	DMA	K_2CO_3	--	140	40	92	920	

Initially a combination of slight higher amount of Pd (2 mol %) and ligand **34** (5 mol %) was used to see the efficiency and as expected iodobenzene **59** and styrene gave the desired *trans*-stilbene **60** in very good yield [Entry-3, Table 1] but with rather poor turn over number (TON). Reactivity of aryl halides was also compared, chloro derivative **57** did not work to produce desired product **60** even though the higher amount of Pd was used, on the other side bromo **58** and iodo **59** derivative gave *trans*-stilbene **60** as exclusive product in 64% and 84% respectively under identical condition [Entry 1-3, Table 1]. Further reactions with lower amount of catalyst/ligand were encouraging and reasonably low concentrations (0.10/0.25 mol %) gave good isolated yield of stilbene **60** with high TON [Entry-6, Table-1]. Further reactions indicated K_2CO_3 to be a suitable base and *N*,*N*-dimethylacetamide (DMA), dimethylformamide (DMF) or *N*-Methylpyrrolidone (NMP) to be good solvent for this conversion [Entries-6 to13, Table-1].

Altering the ratio of ligand and $Pd(OAc)_2$ did not affect the outcome significantly (entry-14) while lower concentrations of catalyst dropped the yield considerably, although TON was higher [Entry-15, Table-1]. Additives like tetrabutylammonium bromide (TBAB)[14] or 18-crown-6 show remarkable acceleration in case of bromobenzene **58** [Entry-16 to 18, Table-1] or for iodobenzene with low concentration of catalyst [Entry-20, Table-1]. Further study revealed that the amino ligands **34** and **44a** were effective but the phenol analogue **51** showed poor reactivity [Entry-6 & 21 to 23, Table-1]. Interestingly, reasonably good result was observed when a bisoxazoline **55** is used as ligand for the reaction [Entry-23, Table-1]. At the same time commercial *N*,*N*-ligand 1,10-phenanthroline **61** was less effective but the *dppp* **62** gave nearly similar results under our experimental conditions [Entry 24 & 25, Table-1]. At this stage it is established that the amino oxazolinyl ligands **34** and **44a** and the bis-oxazoline **55** works as well as *dppp* in this conversion.

The role of ligand in this reaction was proved by performing two sets of reaction of bromobenzene **58** with styrene under our standard condition for 24 h and 40 h, one in presence of the ligand and the other in absence of ligand. The former gave 19 % of stilbene **60** in 24 h while resulted with 27 % of the product in 40 h experiment, on the other hand reaction in absence of ligand provided 6% in 24 h and 9% in 40 h. The results are presented in graphical manner as below [Figure 10].

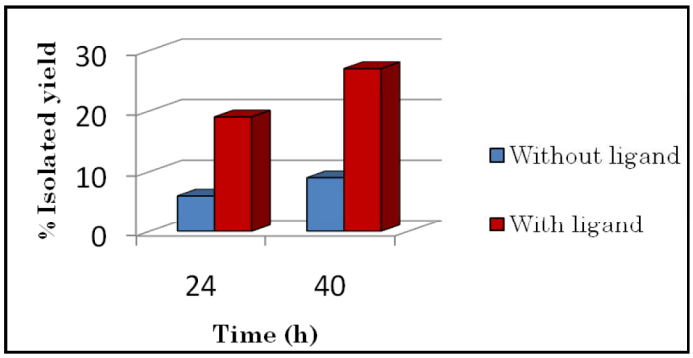
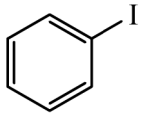
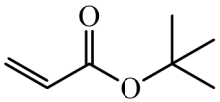
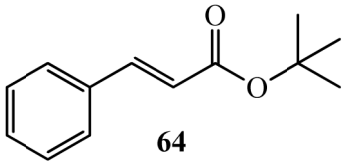
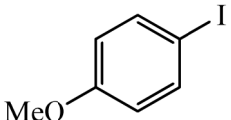
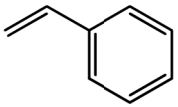
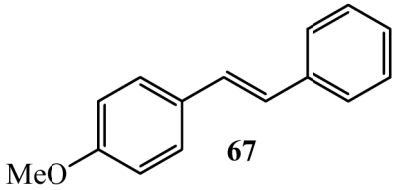
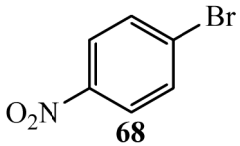
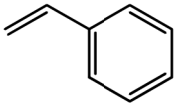
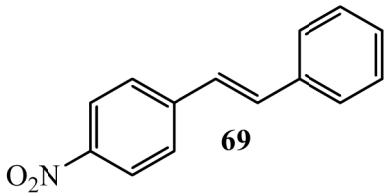
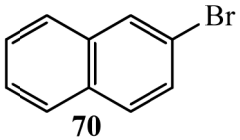
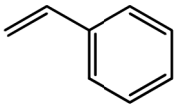
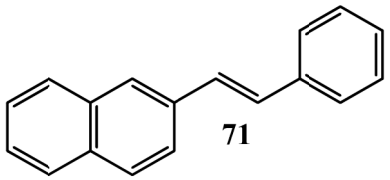


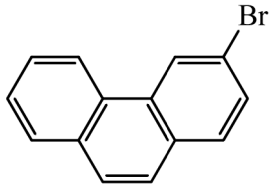
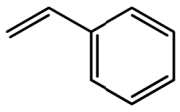
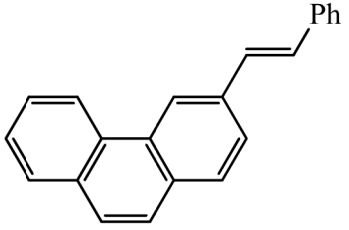
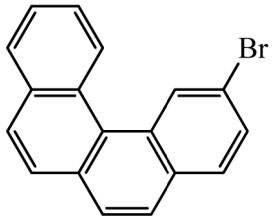
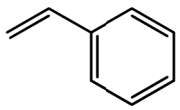
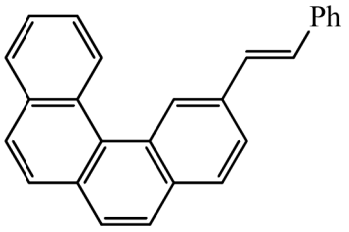
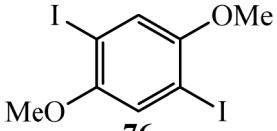
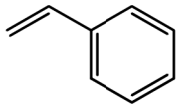
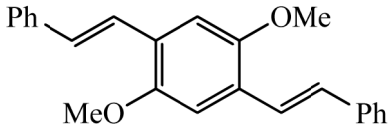
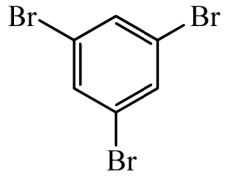
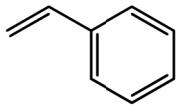
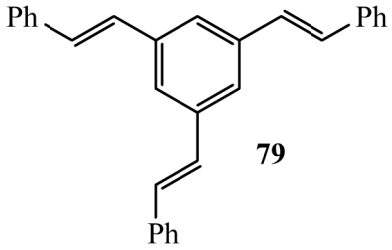
Figure 10: Graphical presentation for the role of ligand in Mizoroki-Heck reaction

The well established catalytic cycle of the Heck reaction starts with reduction of Pd(II) to Pd(0), often referred as pre-activation, followed by oxidative addition of arylhalide, insertion of olefin and finally reductive elimination.[31,32] In case of phosphine free reaction conditions it is possible that the initial reduction of palladium during pre-activation is assisted by nucleophilic amines of the ligands rather from alkene.

Having established the standard reaction parameters we have applied this system for several Heck reactions to produce variety of olefins and the results are tabulated in **Table 2**, which were obtained after careful chromatography and characterized by ^{1}H-NMR analysis.

Table 2: Examples of Mizoroki-Heck reaction

No.	Arylhalides	Olefin (eq)	$Pd(OAc)_2$ (mol%)	Ligand (mol%)	Additive	Product	Yield (%)
1	 **59**	 **63** (1.5 eq)	0.5	1.25	--	 **64**	80
2	 **65**	 **66** (1.5 eq)	0.5	1.25	--	 **67**	79
3	 **68**	 **66** (1.5 eq)	0.5	1.25	TBAB (25)	 **69**	82
4	 **70**	 **66** (1.5 eq)	0.5	1.25	TBAB (25)	 **71**	88

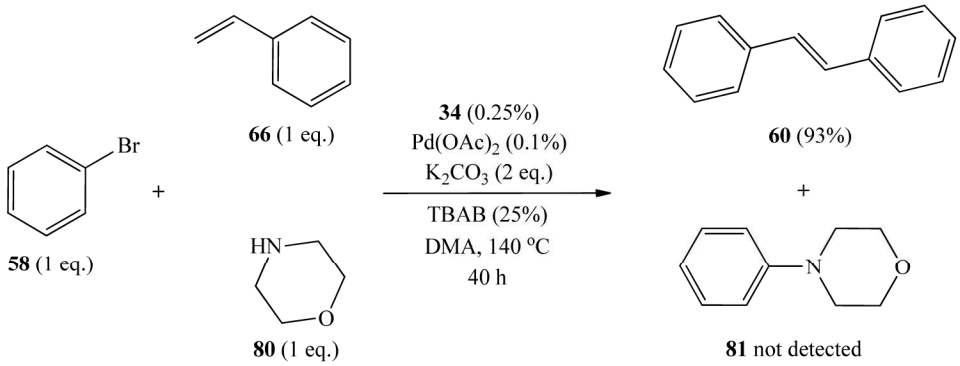
5	 **72**	 **66** (1.5 eq)	1.0	2.5	TBAB (25)	 **73**	95
6	 **74**	 **66** (1.5 eq)	2.0	4.5	TBAB (25)	 **75**	95
7	 **76**	 **66** (3.0 eq)	1.0	2.5	--	 **77**	78
8	 **78**	 **66** (6.0 eq)	1.5	3.0	TBAB (25)	 **79**	62

Reaction Condition: DMA (10-15mL), 140 °C, 40 h, N_2 atmosphere

Reaction of iodobenzene **59** and *tert*-butyl acrylate **63** was smoothly conducted to prepare the corresponding ester of cinnamic acid **64** in good yield [Entry1, Table 2]. Similarly, substituted stilbenes **67** and **69** were prepared from the corresponding halides **65** and **68** respectively, styrene **66** and ligand **34** with good conversions [Entry 2 and 3, Table 2].

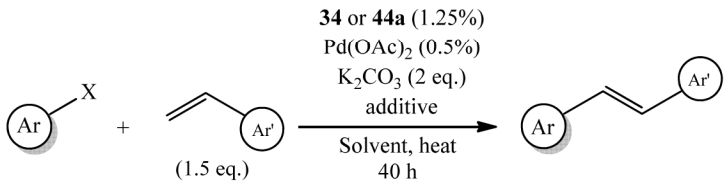
The photocyclization of substituted styrene is a standard method of preparation of the derivatives of phenanthrenes.[33] This is also a widely employed method for the synthesis of polycyclic aromatic compounds.[34] Considering this, we have prepared a series of such derivatives of stilbenes (**71**, **73**, **75** & **79**) from the corresponding bromo compounds (**70**, **72**, **74** & **78** respectively) in very good yields [Entry 4-6 & 8, Table-2].

This catalytic system was further investigated for the condensation of aryl halides and amines according to the reported protocol of Hartwig or Buchwald.[35] Recently its variant using Cu catalyst with nitrogen containing ligands has also been reported.[36] However, under our experimental conditions [$Pd(OAc)_2$/Ligand-**34**] the amination product was not detected significantly. A controlled experiment of reaction of bromobenzene **58** with equal molar mixture of styrene **66** and morpholine **80** was conducted with the present catalytic system. Careful analysis of the reaction indicated the formation of stilbene **60** as a single product in 93% yield. The absence of *N*-phenyl morpholine **81**, the amination product indicate that the reaction works well for the Heck reaction selectively even in the presence of active nucleophilic species, such as alkyl amines **[Scheme 13]**.



Scheme 13: Controlled experiment for catalyst system selectivity towards Mizoroki-Heck reaction

Driven by environmental concerns, we have also developed reaction conditions for this phosphine free oxazolinyl ligand mediated Pd catalyzed Mizoroki-Heck reaction in water as part of solvent system **[Scheme 14]**. Initially the reaction was carried out in aqueous mixture of DMA in different proportions in order to solubilise the substrates. It is well known that the presence of surfactants can help to dissolve water insoluble molecules in aqueous systems *via* their stabilisation in micellar system. We investigated the use of cetyltrimethylammonium bromide (CTAB) at concentrations higher than CMC for our catalytic Heck reaction in pure water. This reduces the use of DMA as co-solvent in the reaction and can be consider as contribution to the "Green Chemistry".



Scheme 14: Examples for aqueous version of Mizoroki-Heck reaction

Conditions were optimised for the use of amino oxazoline ligands **34** and **44a** in aqueous medium for the Heck reaction [Table 3].

Table 3: Condition optimization for aqueous Mizoroki-Heck reaction

No.	Aryl Halide 1 eq	$Pd(OAc)_2$ (mol %)	Ligand **9** (mol %)	Solvent (DMA:water)	Yield[a] % [TON]	Additive
1	Iodobenzene	1	2.5	1:2	98 [98]	--
2	Iodobenzene	0.1	0.25	1:2	86 [863]	--
3	Iodobenzene	0.1 ($PdCl_2$)	0.25	1:2	98 [977]	--
4	Iodobenzene	0.5	1.25	1:2	87 [174]	CTAB (0.1 eq)
5	Bromobenzene	0.5	1.25	1:2	34 [68]	--
6	Bromobenzene	0.5	1.25	1:2	54 [108]	CTAB (0.1 eq)
7	Bromobenzene	0.5	1.25	1:2	66 [132]	TBAB (0.1 eq)
8	Iodobenzene	0.5	1.25	0:1	86 [172]	CTAB (0.1 eq)
9	Iodobenzene	0.5	1.25	0:1	52 [104]	--

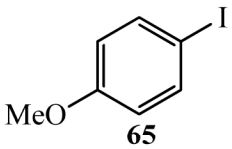
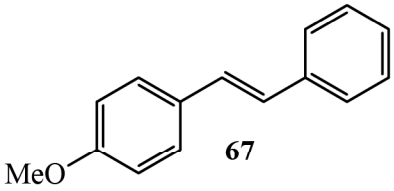
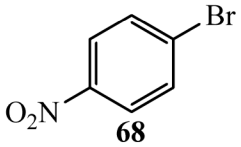
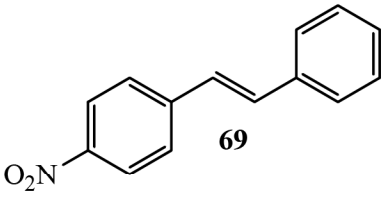
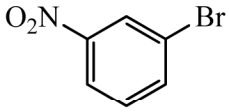
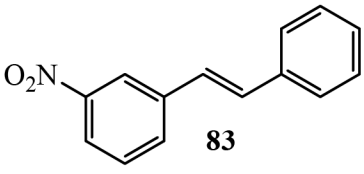
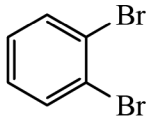
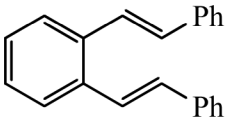
Reaction Condition: All reactions with styrene (1.5 eq.), K_2CO_3 (2 eq.). Entry 1 to 8 carried out at 120°C; entry 9 and 10 carried out at 100°C [a]Isolated.

Initially, higher amount of $Pd(OAc)_2$ was used to study the efficiency of the catalyst system in aqueous medium, in this reaction of iodobenzene **59** with styrene **66** gave 98% of the product **60** where reaction was conducted in the mixture of DMA:water (1:2) heated at 120 °C for 40 h [Entry

1, Table-3]. It was clearly seen that this catalyst system worked well in aqueous DMA but the amount of palladium salt used was the question of concern. This was solved by lowering the amount of palladium salt for the reaction which gave slightly lower yield [Entry 2 & 4]. As it was known to use surfactants for the aqueous version of Heck reaction, we have also used catalytic amount of CTAB which improved the yield of the product up to certain extent. But whenever bromobenzene is used for the reaction in which water is added as part of solvent system then compared to CTAB the use of TBAB becomes more effective whereas CTAB was found to show excellent results where only water is used as solvent system [Entry 8 & 9].

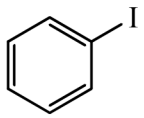
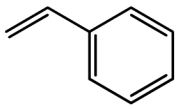
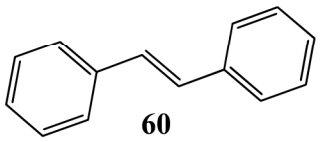
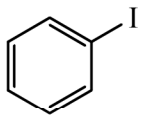
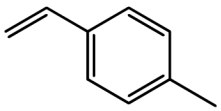
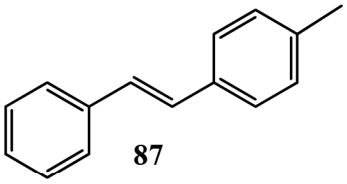
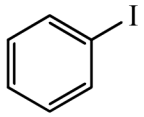
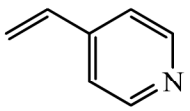
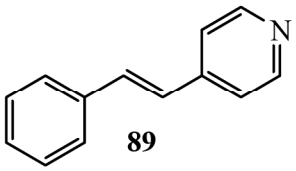
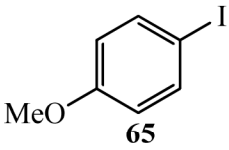
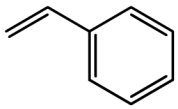
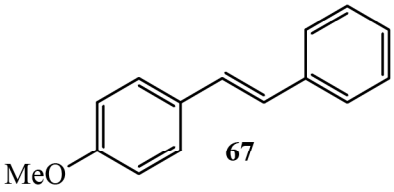
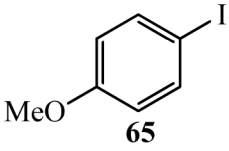
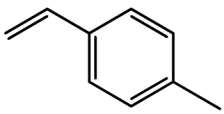
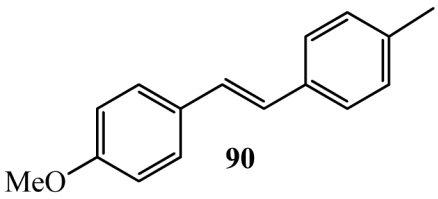
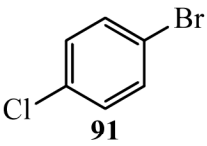
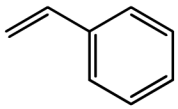
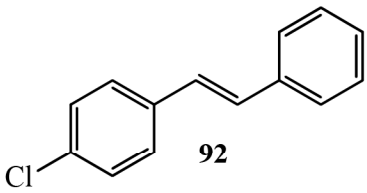
To demonstrate the generality for the catalyst system in DMA-water and aqueous Heck reaction, numbers of stilbene derivatives have been prepared from corresponding arylhalides and styrenes which are summarised in **Table-4** and **Table-5**.

Table 4: Synthesis of stilbene derivatives using DMA-water system

No	Aryl halide	Product	Yield/%[a] [TON][b]
1	 **65**	 **67**	89 [179]
2	 **68**	 **69**	64 [127]
3	 **82**	 **83**	90 [180]
4	 **84**	 **85**	58 [58]

Reaction Condition: Entry 1-3 with styrene (1.5 eq.), K_2CO_3 (2 eq.), $Pd(OAc)_2$ (0.5%), **34** (1.25 %) and entry 4 with styrene (3.0 eq.), K_2CO_3 (4 eq.), $Pd(OAc)_2$ (1.0 %), **34** (2.5 %). All reactions with DMA-Water (1:2), 120 ^{o}C, for 40 h, TBAB (10 % for entry 1-3 and 20% for entry 4), [a]Isolated, [b]TON= Turn Over Number = moles of product formed/moles of catalyst used.

Table 5: Examples for Mizoroki-Heck reaction in Water-CTAB system

No	Aryl halide	Olefin	Product	Yield/%[a] [TON][b]
1	 **59**	 **66** (1.5 eq)	 **60**	87 [174]
2	 **59**	 **86** (1.5 eq)	 **87**	88 [176]
3	 **59**	 **88** (1.2 eq)	 **89**	94 [186]
4	 **65**	 **66** (1.5 eq)	 **67**	82 [172]
5	 **65**	 **86** (1.5 eq)	 **90**	95 [190]
6	 **91**	 **66** (1.5 eq)	 **92**	71 [141]

All reactions with ligand $Pd(OAc)_2$ (0.5 %), **34** (1.25%), K_2CO_3 (2.0 eq.) CTAB (10 mol%) at 100 °C for 40 h. [a]Isolated, [b]TON= Turn Over Number = moles of product formed/moles of catalyst used.

Generally the disadvantage of homogeneous system is its inability to reuse the catalyst, usually this is overcome for the Mizoroki-Heck by using heterogeneous palladium catalysts.[37] Alternatively, this deficiency may be addressed if the catalyst can be recovered and reused for the next set of reaction. Since the product of the standard Heck reaction is stilbene which can be extracted in non polar solvent such as petroleum ether, the catalyst/ligand may remain in aqueous

portion and may be recycled. Accordingly a separate set of experiment was run, the product stilbene extracted and aqueous system used as such for the second cycle. The yields of 1st and 2nd cycle were comparable (88 and 84 %), however there was a drop in the third cycle (60 %) probably due to slight solubility of CTAB in petroleum ether. In order to check this, half of the original quantity of CTAB was added in the 4th cycle and run the experiment. The yield was enhanced substantially for this experiment (73 %) [*see* **Figure-11**].

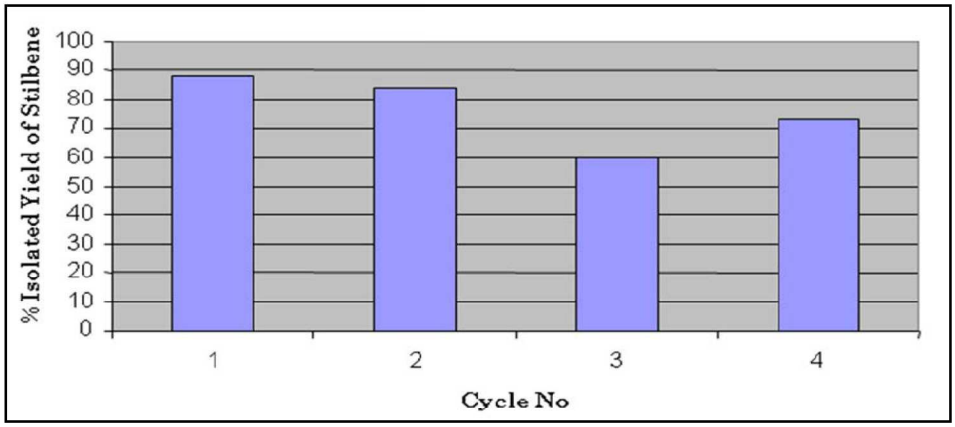


Figure 11: Recycle study of the catalyst system for Mizoroki-Heck reaction

Thus, we have demonstrated that the present phosphine free catalyst system not only works well in water-CTAB or water-DMA solvent but it can be recovered and reused effectively for subsequent reactions.

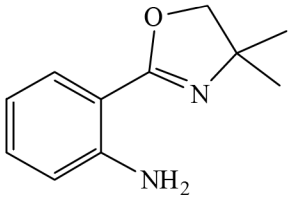
Experimental Section

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens Limited etc. DMA was distilled and stored 24h over molecular sieves (4 Å). Toluene was distilled and stored 24 h over molecule sieves (4 Å) prior to use. Thin Layer Chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. All the compounds were purified by column chromatography using SRL make silica gel (60-120 mesh) unless mentioned otherwise. ^{1}H-NMR Spectra were recorded on Bruker Avance 200 or 400 and INOVA-500 Spectrometers and were run in $CDCl_3$ unless otherwise stated. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. IR spectra were recorded on a Perkin-Elmer FTIR RXI spectrometer as KBr pallets. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

Part I – Synthesis of Oxazolinyl Ligands

Synthetic Procedures:

2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)aniline (34):



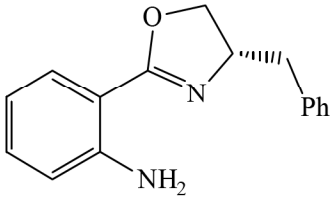
In a 100-mL two-neck flask, anhydrous zinc chloride (0.080 g, 0.62 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), isatoic anhydride **31** (0.50 g, 3.06 mmol) and 2-Amino-2-methylpropan-1-ol (0.32 g, 3.67 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25-30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed under vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford **34** (0.455 g; 78 %) as white solid.

M.P. 103 - 106 ^{o}C (Lit..[38] 104 - 106 ^{o}C).

IR (KBr): 3445, 3284, 3032, 2962, 1632, 1381, 1331, 1186, 754 cm.$^{-1}$

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.67 – 7.70 (dd, *J* = 1.6 & 8.0 Hz, 1H), 7.17 – 7.21 (m, 1H), 6.63 – 6.69 (m, 2H), 5.81 (s, 2H), 4.00 (s, 2H), 1.37 (s, 6H).

(S)-2-(4-Benzyl-4,5-dihydrooxazol-2-yl)aniline (35):



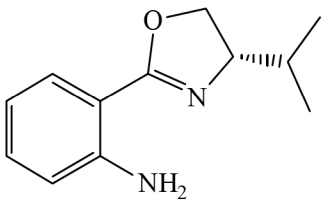
In a 100 mL two-necked flask, anhydrous zinc chloride (0.08 g, 0.31 mmol, 10 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (0.50 g, 3.06 mmol) and L-Phenylalaninol (0.55 g, 3.67 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford **35** (0.39 g, 51%) as off white solid.

M.P. 62 - 64 ^oC. (Lit..[39] 64 – 65 ^oC); $[\alpha]_D^{30}$ = +43.0 (*c* 0.51, $CHCl_3$). [Lit..[39] $[\alpha]_D$= +43.3 (*c* 0.51, CH_2Cl_2)].

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.69 (dd, *J* = 1.2 & 8 Hz, 1H), 7.36 – 7.22 (m, 6H), 6.74 – 6.67 (m, 2H), 6.13 (bs, 2H), 4.67 – 4.60 (m, 1H), 4.33 – 4.28 (t, *J* = 8.4 Hz, 1H), 4.08 – 4.04 (t, J = 8.4 Hz, 1H), 3.19 – 3.14 (dd, *J* = 6.4 & 13.6 Hz, 1H), 2.82 – 2.77 (dd, *J* = 8.0 & 13.6 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.09, 148.63, 138.37, 132.12, 129.62, 129.26, 128.54, 126.47, 116.05, 115.70, 109.00, 70.24, 68.13, 42.31.

(S) 2-(4-Isoprolyl-4,5-dihydrooxazol-2-yl)aniline (36):



To the 100 mL two-necked flask, anhydrous zinc chloride (0.08 g, 0.62 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (0.50 g, 3.06

mmol) and L-valinol (0.38 g, 3.67 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford **36** (0.30 g, 48%) as off white solid.

M.P. 65 - 64 ^{o}C. (Lit..[40] 64 – 65 ^{o}C); $[\alpha]_D^{30}$ = -1.4 (*c* 0.80, $CHCl_3$). [Lit..[38] $[\alpha]_D$= -1.35 (*c* 0.85, $CHCl_3$).]

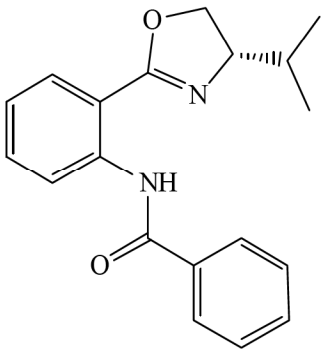
IR (KBr): 3381, 3275, 3066, 2945, 1668, 1629, 1591, 1450, 1170, 1082, 1041, 754 cm.$^{-1}$

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.68 (dd, *J* = 1.6 & 7.6 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.73 – 6.65 (m, 2H), 4.36 – 4.32 (q, *J* = 8.0 Hz, 1H), 4.14 – 4.10 (m, 1H), 4.04 – 4.00 (t, *J* = 8.0 Hz, 1H), 1.83 – 1.78 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.51, 148.59, 131.90, 129.56, 115.98, 115.63, 109.17, 72.91, 68.75, 33.22, 19.00, 18.62.

MS (EI): *m/z* (%) 203.80 (57), 160.79 (100), 132.80 (76), 118.44 (11), 105.81 (14), 92.10 (5).

(S)-N-(2-(4-Isopropyl-4,5-dihydrooxazol-2-yl)phenyl)benzamide (37):



To the solution of **36** (0.10 g, 0.49 mmol) in dichloromethane (10 mL), triethylamine (0.10 g, 1.03 mmol) was added at 0 ^{o}C and stir it for 30 min. Then benzoyl chloride (0.07 g, 0.51 mmol) was added at the same temperature. Stir this reaction mixture overnight at room temperature. Reaction was checked by TLC. After completion, reaction mixture was washed with water (2 x 10 mL). Organic later was dried on sodium sulfate and evaporated on rotary evaporator. Crude product was then purified by column chromatography on silica gel (60 – 120 mesh) using ethylacetate and petroleum ether as eluents. The pure product **37** (0.124 g, 82%) was isolated as white solid.

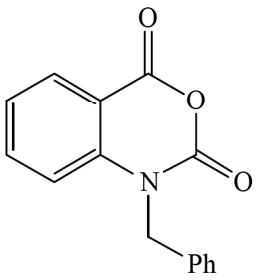
M.P. 88 – 90 °C; $[\alpha]_D^{28}$ = +82.8 (*c* 1.00, $CHCl_3$). [Lit.[41] $[\alpha]_D$= +83 (*c* 1.00, $CHCl_3$)].

IR (KBr): 3176, 3041, 2957, 2888, 2864, 1823, 1669, 1635, 1496, 1445, 1187, 1161, 1102, 1049, 977, 883, 802, 757, 703 $cm.^{-1}$

^{1}H-NMR (400 MHz, $CDCl_3$): δ 13.11 (s, 1H), 8.99 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.47 (m, 4H), 7.15 – 7.12 (t, *J* = 7.6 Hz, 1H), 4.46 – 4.42 (t, *J* = 8.4 Hz, 1H), 4.28 – 4.22 (m, 1H), 4.12 – 4.08 (t, *J* = 8 Hz, 1H), 1.86 (d, *J* = 5.6 Hz, 1H), 1.04 (d, *J* = 6 Hz, 3H), 0.99 (d, *J* = 6 Hz, 3H).

MS (EI): *m/z* (%) 307.99 (100), 264.70 (49), 230.88 (39), 145.76 (20), 104.48 (53), 76.84 (35).

1-Benzyl-1H-benzo[d][1,3]oxazine-2,4-dione **(38):**



Add *N,N*-diisopropylethylamine (1.98 g, 15.33 mmol) to the solution of 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (1.00 g, 6.13 mmol) in *N,N*-dimethylacetamide (10 mL) at 0 °C and stir the reaction mixture for 30 min. To this solution Benzyl bromide (1.26 g, 7.36 mmol) was added and heated for 3h at 80 °C. After the completion of reaction cool the reaction mixture to room temperature and pour into ice cold water, solid separated which was filtered, washed with cold water and recrystallized from ethanol to afford **38** (1.44 g, 93%) as colourless crystals.

Melting Point: 142 - 144 °C. (Lit.[42] 137 - 140 °C)

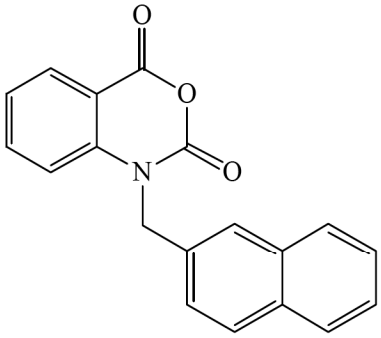
IR (KBr): 3079, 2971, 1778, 1717, 1605, 1492, 1475, 1454, 1379, 1364, 1321, 1312, 1265, 1243, 1191, 1160, 1083, 1052, 1030, 792, 759, 743, 707, 682 $cm.^{-1}$

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.19 – 8.17 (dd, *J* = 1.6 & 8 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.40-7.27 (m, 6H), 7.15 – 7.13 (d, *J* = 8.4 Hz, 1H), 5.33 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.37, 148.50, 141.40, 137.24, 134.38, 130.87, 129.17, 128.16, 126.60, 124.20, 114.75, 111.83, 48.53.

MS (EI): *m/z* (%) 253 (78), 208 (23), 180 (100), 91 (56), 76 (19).

1-(Naphthalen-2-ylmethyl)-1H-benzo[d][1,3]oxazine-2,4-dione (39):



To the solution of 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (1.00 g, 6.13 mmol) in *N,N*-dimethylacetamide (10 mL) was added *N,N*-diisopropylethylamine (1.98 g, 15.33 mmol) at 0 ^{o}C and stir the reaction mixture for 30 min. To the same flask 2-(bromomethyl)naphthalene (1.62 g, 7.36 mmol) was added slowly and heated for 3h at 80 ^{o}C. After the completion of reaction cool the reaction mixture to room temperature and pour into ice cold water, solid separated which was filtered, washed with cold water and recrystallized from ethanol to afford **39** (1.52 g, 82%) as tan colour crystals.

Melting Point: 206 ^{o}C

IR (KBr): 3059, 2953, 1787, 1706, 1606, 1478, 1381, 1338, 1269, 1200, 1166, 1138, 1067, 1035, 954, 860, 811, 755 cm.$^{-1}$

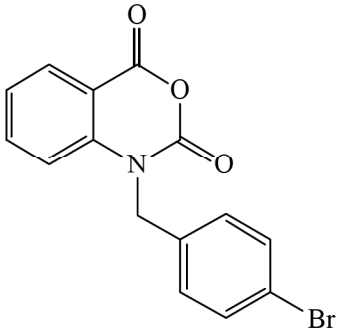
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.21 – 8.19 (dd, *J* = 1.6 & 8 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.74 (s, 1H), 7.64 – 7.60 (m, 1H), 7.53 – 7.49 (m, 2H), 7. 46 – 7.44 (dd, *J* = 1.6 & 8.4 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.18 (d, *J* = 8.8Hz, 1H), 5.49 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.41, 148.61, 141.38, 137.28, 133.28, 131.81, 130.88, 129.26, 128.16, 127.80, 127.76, 126.71, 126.43, 125.48, 124.25, 114.83, 111.85, 48.79.

MS (EI): *m/z* (%) 302.92 (100), 258.80 (48), 229.91 (60), 201.73 (6), 140.91 (51), 114.8 (9), 77.02 (1).

Anal. Calcd. for $C_{19}H_{13}NO_3$ C, 75.24; H, 4.32; N, 4.62 Found C, 74.92; H, 4.80; N, 4.70 %.

1-(4-Bromobenzyl)-1H-benzo[d][1,3]oxazine-2,4-dione (40):



Add *N,N*-diisopropylethylamine (1.98 g, 15.33 mmol) to the solution of 1*H*-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (1.00 g, 6.13 mmol) in *N,N*-dimethylacetamide (10 mL) at 0 °C and stir the reaction mixture for 30 min. To this solution 4-bromobenzyl bromide (1.84 g, 7.36 mmol) was added and heated for 3h at 80 °C. After the completion of reaction cool the reaction mixture to room temperature and pour into ice cold water, solid separated which was filtered, washed with cold water and recrystallized from ethanol to afford **40** (1.61 g, 79%) as white crystals.

Melting Point: 192 °C

IR (KBr): 3063, 2976, 1785, 1707, 1592, 1477, 1168, 1064, 1013, 837, 750 $cm.^{-1}$

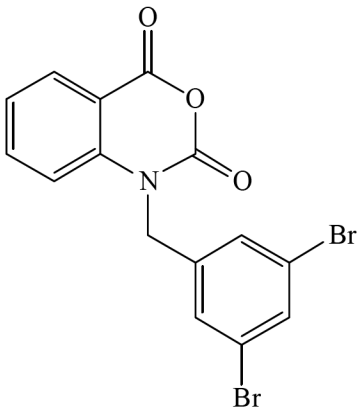
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.18 (dd, *J* = 1.6 & 8 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.52 – 7.49 (m, 2H), 7.33 – 7.29 (m, 1H), 7.22 – 7.20 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.27 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.13, 148.43, 141.13, 137.30, 133.44, 132.34, 131.06, 128.38, 124.38, 122.16, 114.47, 111.86, 47.99.

MS (EI): *m/z* (%) 332.68 (100), 330.57 (98), 289.08 (15), 286.48 (27), 260.05 (26), 257.66 (42), 170.73 (42), 168.70 (41), 90.11 (6), 75.44 (7).

Anal. Calcd. for $C_{15}H_{10}BrNO_3$ C, 54.24; H, 3.03; N, 4.22 Found C, 54.12; H, 3.22; N, 4.25 %.

1-(3,5-Dibromobenzyl)-1H-benzo[d][1,3]oxazine-2,4-dione (41):



To the solution of 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (1.00 g, 6.13 mmol) in *N,N*-dimethylacetamide (10 mL) was added *N,N*-diisopropylethylamine (1.98 g, 15.33 mmol) at 0 °C and stir the reaction mixture for 30 min. To this solution 1,3-dibromo-5-(bromomethyl)benzene (2.42 g, 7.36 mmol) dissolved in *N,N*-dimethylacetamide (5 mL) was added dropwise and heated for 3h at 80 °C. After the completion of reaction cool the reaction mixture to room temperature and pour into ice cold water, solid separated which was filtered, washed with cold water and recrystallized from ethanol to afford **41** (1.49 g, 59%) as

white crystals.

Melting Point: 212 - 214 ºC.

IR (KBr): 3073, 1795, 1669, 1480, 1376, 1028, 751, 677, 531 cm.$^{-1}$

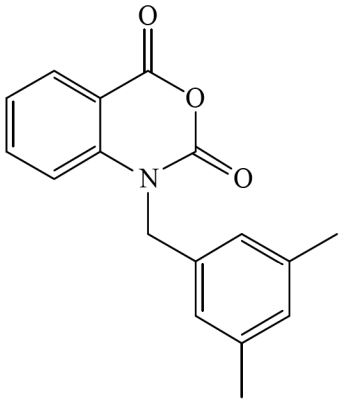
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.21 (dd, *J* = 1.6 & 8.4 Hz, 1H), 7.46 – 7.70 (m, 1H), 7.64 – 7.63 (t, *J* = 2.0 & 3.6 Hz, 1H), 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.26 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.93, 148.38, 140.86, 138.42, 137.55, 134.09, 131.23, 128.40, 124.66, 123.82, 114.22, 111.86, 47.47.

MS (EI): *m/z* (%) 412.82 (26), 410.83 (51), 408.81 (28), 339.87 (27), 338.87 (37), 337.86 (50), 259.94 (93), 257.94 (91), 179.04 (42), 178.03 (35), 132.01 (29), 104.00 (26), 89.03 (100), 77.02 (67).

Anal. Calcd. for $C_{15}H_9Br_2NO_3$ C, 43.83; H, 2.21; N, 3.41 Found C, 43.82; H, 3.03; N, 4.26%.

1-(3,5-Dimethylbenzyl)-1H-benzo[d][1,3]oxazine-2,4-dione (42):



Add *N,N*-diisopropylethylamine (1.98 g, 15.33 mmol) to the solution of 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (1.00 g, 6.13 mmol) in *N,N*-dimethylacetamide (10 mL) at 0 ^{o}C and stir the reaction mixture for 30 min. To this solution 1-(bromomethyl)-3,5-dimethylbenzene (1.46 g, 7.36 mmol) was added and heated for 3h at 80 ^{o}C. After the completion of reaction cool the reaction mixture to room temperature and pour into ice cold water, solid separated which was filtered, washed with cold water and recrystallized from ethanol to afford **42** (1.03 g, 60%) as off white solid.

Melting Point: 200 - 202 ºC.

IR (KBr): 2993, 2960, 1782, 1724, 1604, 1452, 1259, 1039, 756 cm.$^{-1}$

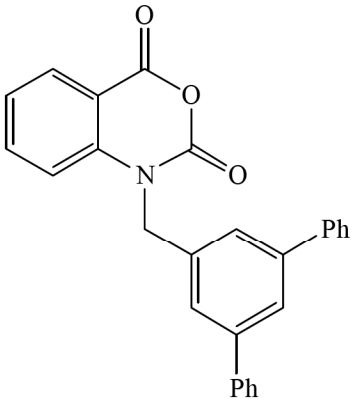
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.64 (t, *J* = 7.6 Hz, 1H), 7.30 –

7.26 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.98 – 6.91 (m, 3H), 5.24 (s, 2H), 2.30 (s, 6H).

MS (EI): *m/z* (%) 282.24 (19), 281.28 (100), 280.66 (84), 237.09 (31), 236.16 (19), 208.19 (33), 193.44 (53), 118.90 (51), 90.90 (5), 76.70 (4).

Anal. Calcd. for $C_{17}H_{15}NO_3$ C, 72.58; H, 5.37; N, 4.98 Found C, 72.13; H, 5.01; N, 5.36%.

1-(3,5-Diphenyllbenzyl)-1H-benzo[d][1,3]oxazine-2,4-dione (43):



Add *N,N*-diisopropylethylamine (1.98 g, 15.33 mmol) to the solution of 1H-benzo[d][1,3]oxazine-2,4-dione or isatoic anhydride **31** (1.00 g, 6.13mmol) in *N,N*-dimethylacetamide (10 mL) at 0 ^{o}C and stir the reaction mixture for 30 min. To this solution 5'-(bromomethyl)-1,1':3',1''-terphenyl (2.38 g, 7.36 mmol) dissolved in *N,N*-dimethylacetamide (5 mL) was added dropwise and heated for 3h at 80 ^{o}C. After the completion of reaction cool the reaction mixture to room temperature and pour into ice cold water, solid separated which was filtered, washed with cold water and recrystallized from ethanol to afford **43** (1.45 g, 57%) as off white solid.

Melting Point: 198 - 200 ^{o}C.

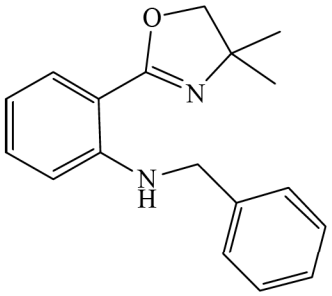
IR (KBr): 3059, 3035, 1782, 1727, 1605, 1494, 1318, 1032, 753, 698 cm.$^{-1}$

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.21 – 8.19 (dd, *J* = 1.2 & 7.6 Hz, 1H), 7.76 – 7.75 (t, *J* = 1.6 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.62 – 7.59 (m, 4H), 7.50 – 7.45 (m, 6H) 7.42 – 7.38 (2H), 7.38 – 7.30 (m, 1H), 7.21 (d, *J* = 8.8 Hz, 1H).

MS (EI): *m/z* (%) 406.54 (10), 405.72 (100), 361.47 (8), 332.82 (15), 331.72 (15), 256.14 (21), 242.92 (27).

Anal. Calcd. for $C_{27}H_{19}NO_3$ C, 79.98; H, 4.72; N, 3.45 Found C, 79.45; H, 4.01; N, 3.64%.

N-Benzyl-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline (44a):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.05 g, 0.39 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-benzyl-1H-benzo[d][1,3]oxazine-2,4-dione **38** (0.50 g, 1.97 mmol) and 2-Amino-2-methyl-propane-1-ol (0.21 g, 2.37 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **44a** (0.43 g, 72%) as white crystals.

M.P. 80 ^{O}C (Lit.[18] 80 ^{o}C)

IR (KBr): υ 3262, 2963, 1918, 1811, 1628, 1384, 1089, 925, 840, 766 cm.$^{-1}$

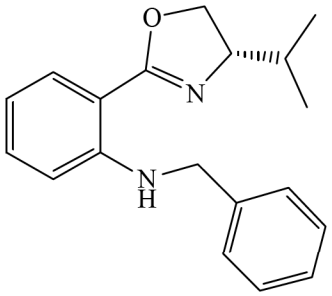
^{1}H-NMR (CDCl$_3$, 400 MHz): δ 1.36 (s, 6 H), 4.01 (s, 2 H), 4.51 (s, 2 H), 6.59 - 6.62 (t, *J* = 14.2 Hz & 5.88 Hz, 2 H), 7.19 - 7.25 (m, 2H), 7.37 - 7.30 (m, 4 H), 7.74 - 7.76 (d, *J* = 7.4 Hz, 1 H), 8.96 (bs, 1H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ 162.33, 148.89, 139.55, 132.28, 129.68, 128.50, 126.81, 114.63, 110.80, 108.93, 76.74, 67.83, 46.87, 28.73.

MS (EI): *m/z* (%) 280.42 (59), 278.99 (100), 222.73 (18), 193.70 (17), 104.64 (15), 90.92 (9), 76.80 (3).

Anal. Calcd. for C$_{18}$H$_{20}$N$_2$O C, 77.11; H, 7.18; N, 9.99. Found C, 77.12; H, 7.36; N, 10.02%.

N-Benzyl-2-(4–isopropyl-4,5-dihydrooxazol-2-yl)aniline (44b):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.05 g, 0.39 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-benzyl-1*H*-benzo[d][1,3]oxazine-2,4-dione **38** (0.50 g, 1.97 mmol) and L-valinol (0.24 g, 2.37 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **44b** (0.44 g, 76%) as colourless crystals.

M.P. 74 - 76 ^{o}C; $[\alpha]_D^{35}$ = -18.67 (*c* 0.41, $CHCl_3$)

IR (KBr): υ 3235, 3067, 3030, 2963, 2894, 2869, 1637, 1581, 1518, 1457, 1358, 1332, 1287, 1271, 1166, 1144, 1079, 1049, 747 cm.$^{-1}$

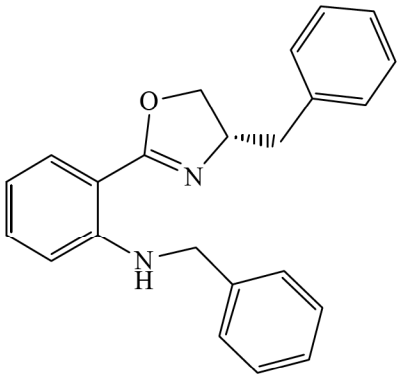
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.07 (bs, 1H), 7.77 (d, *J* = 8 Hz, 1H), 7.43 – 7.26 (m, 6H), 6.69 – 6.63 (m, 2H), 4.52 (s, 2H), 4.37 – 4.33 (t, *J* = 8.8 Hz, 1H), 4.14 – 4.08 (q, *J* = 8.0 Hz, 1H), 4.04 – 4.00 (t, *J* = 8Hz, 1H), 1.81 – 1.73 (m, 1H), 0.98 (d, *J* = 6.8Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.80, 148.95, 139.31, 132.36, 129.80, 128.56, 127.15, 126.97, 114.58, 110.66, 108.76, 72.88, 68.77, 47.11, 33.32, 18.85, 18.78.

MS (EI): *m/z* (%) 294.48 (50), 293.05 (94), 207.69 (100), 194.23 (26), 90.85 (30), 76.71 (9).

Anal. Calcd. for $C_{19}H_{22}N_2O$ C, 77.52; H, 7.53; N, 9.52 Found C, 77.08; H, 7.21; N, 9.62%.

N-Benzyl-2-(4–benzyl-4,5-dihydrooxazol-2-yl)aniline (44c):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.05 g, 0.39 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-benzyl-1H-benzo[d][1,3]oxazine-2,4-dione **38** (0.50 g, 1.97 mmol) and L-phenylalaninol (0.36 g, 2.37 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **44c** (0.47 g, 69%) as white crystals.

M.P. 80 - 82 ^{o}C; $[\alpha]_D^{35}$ = +20.33 (*c* 1.00, $CHCl_3$).

IR (KBr): υ 3258, 3061, 3027, 2896, 2851, 1631, 1588, 1525, 1451, 1363, 1330, 1273, 1234, 1164, 1142, 1071, 1050, 971, 749, 697 cm.$^{-1}$

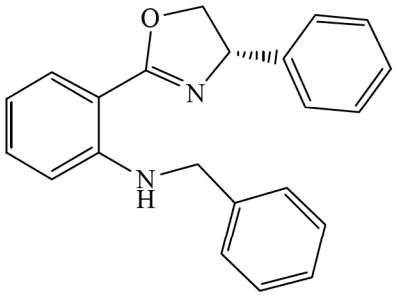
^{1}H-NMR (400 MHz, CDCl3): δ 9.01 (bs, 1H), 7.77 (d, *J* = 8 Hz, 1H), 7.41 – 7.23 (m, 11H), 6.66 – 6.63 (m, 2H), 4.63 – 4.58 (m, 1H), 4.54 (s, 2H), 4.34 – 4.30 (t, *J* = 8.4 Hz, 1H), 4.09 – 4.05 (t, J = 8.0 Hz, 1H), 3.14 – 3.09 (dd, *J* = 6.4 & 13.6 Hz, 1H), 2.84 – 2.78 (dd, *J* = 7.6 & 13.6 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.34, 149.02, 139.45, 138.32, 132.54, 129.90, 129.29, 128.61, 128.49, 126.96, 126.93, 126.45, 114.66, 110.84, 108.63, 70.12, 68.10, 46.92, 42.31.

MS (EI): *m/z* (%) 342.50 (57), 341.05 (100), 250.85 (67), 207.76 (85), 194.15 (23), 193.07 (24), 90.82 (6).

Anal. Calcd. for $C_{23}H_{22}N_2O$ C, 80.67; H, 6.48; N, 8.18 Found C, 80.36; H, 6.24; N, 8.61%.

N-Benzyl-2-(4–phenyl--4,5-dihydrooxazol-2-yl)aniline (44d):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.05 g, 0.39 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-benzyl-1H-benzo[d][1,3]oxazine-2,4-dione **38** (0.50 g, 1.97 mmol) and L-phenylglycinol (0.32 g, 2.37 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **44d** (0.46 g, 71%) as white crystals.

M.P. 116 - 118 ^{o}C; $[\alpha]_D^{35}$ = +137.76 (*c* 0.40, $CHCl_3$).

IR (KBr): υ 3248, 3062, 3026, 2966, 1632, 1584, 1521, 1493, 1269, 1168, 103, 897, 749, 730, 696 cm.$^{-1}$

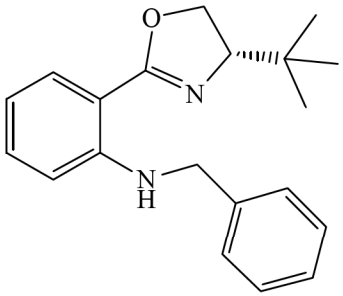
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.13 – 9.10 (t, *J* = 5.6 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.42 – 7.25 (m, 11H), 6.71 – 6.67 (m, 2H), 5.53 – 5.48 (dd, *J* = 8.4 & 10 Hz, 1H), 4.76 – 4.71 (dd, *J* = 8.4 & 9.6 Hz, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 4.2 – 4.15 (t, *J* = 8.4 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.33, 149.21, 142.79, 139.43, 132.75, 130.10, 128.72, 128.55, 127.54, 126.89, 126.92, 114.72, 111.01, 108.44, 72.92, 70.14, 46.88.

MS (EI): *m/z* (%) 328.41 (87), 327.05 (100), 223.24 (24), 208.24 (30), 179.03 (38), 146.76 (55), 105.03 (49), 90.88 (54), 76.61 (27).

Anal. Calcd. for $C_{22}H_{20}N_2O$ C, 80.46; H, 6.14; N, 8.53 Found C, 80.21; H, 5.79; N, 8.71%.

N-Benzyl-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)aniline (44e):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.05 g, 0.39 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-benzyl-1H-benzo[d][1,3]oxazine-2,4-dione **38** (0.50 g, 1.97 mmol) and L-*tert*-leucinol (0.28 g, 2.37 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **44e** (0.49 g, 80%) as white crystals.

M.P. 96 - 98 ^{o}C; $[\alpha]_D^{30}$ = -20.67 (*c* 0.80, $CHCl_3$).

IR (KBr): υ 3255, 3063, 3031, 2968, 2954, 2887, 1632, 1578, 1574, 1515, 1497, 1470, 1452, 1361, 1328, 1287, 1263, 1240, 1167, 1143, 1091, 1076, 1050, 1028, 975, 906, 749, 700, 670 cm.$^{-1}$

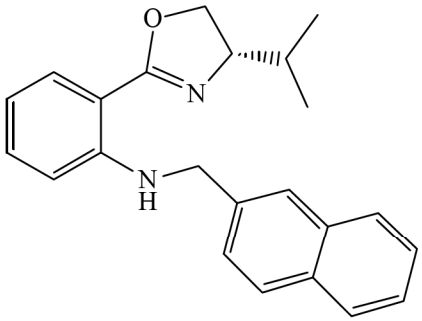
^{1}H-NMR (400 MHz, CDCl3): δ 9.08 (bs, 1H), 7.77 – 7.75 (dd, *J* = 0.8 & 7.6 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.27 (q, *J* = 4.8 & 7.6 Hz, 2H), 6.70 – 6.63 (m, 2H), 4.51 (d, *J* = 4.8 Hz, 2H), 4.30 – 4.23 (m, 1H), 4.15 – 4.07 (m, 2H), 0.91 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.74, 148.98, 139.25, 132.34, 129.78, 128.57, 127.27, 127.01, 114.53, 110.59, 108.72, 76.27, 66.80, 47.18, 33.86, 25.86.

MS (EI): *m/z* (%) 307.83 (100), 250.79 (63), 207.77 (57), 194.14 (21), 90.85 (10).

Anal. Calcd. for $C_{22}H_{20}N_2O$ C, 77.89; H, 7.84; N, 9.08 Found C, 77.24; H, 7.43; N, 9.94%.

2-(4-Isopropyl-4,5-dihydrooxazol-2-yl)-N-(naphthalen-2-ylmethyl)aniline (45a):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.09 g, 0.66 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(naphthalen-2-ylmethyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **39** (1.00 g, 3.30 mmol) and L-valinol (0.41 g, 3.96 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **45a** (0.70 g, 62%) as white crystals.

M.P. 128 - 130 ^{o}C; $[\alpha]_D^{30}$ = -24.30 (*c* 0.80, $CHCl_3$).

IR (KBr): υ 3250, 3053, 2959, 2927, 2898, 2871, 1631, 1586, 1523, 1463, 1362, 1318, 1273, 1236, 1163, 1144, 1087, 1049, 967, 904, 853, 816, 748, 686 cm.$^{-1}$

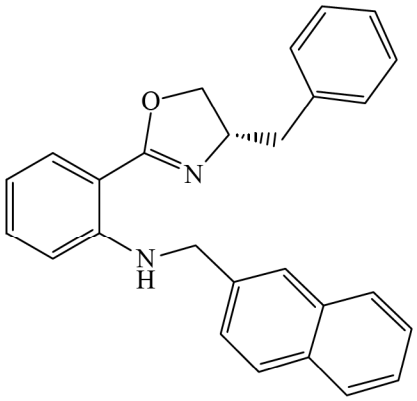
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.17 – 9.14 (t, *J* = 4.8 Hz, 1H), 7.83 – 7.78 (m, 4H), 7.76 – 7.74 (dd, *J* = 1.6 & 8.0 Hz, 1H), 7.51 – 7.49 (dd, *J* = 1.6 & 8.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.25 – 7.20 (m, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.64 – 6.60 (m, 1H), 4.69 – 4.60 (m, 2H), 4.35 – 4.28 (m, 1H), 4.13 – 4.09 (m, 1H), 4.03 – 3.99 (t, *J* = 7.6 Hz, 1H), 1.80 – 1.72 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.83, 148.99, 136.87, 133.51, 132.67, 132.37, 129.80, 128.28, 127.77, 127.68, 126.03, 125.54, 125.52, 125.41, 114.67, 110.79, 108.85, 72.87, 68.72, 47.31, 33.30, 18.91, 18.72.

MS (EI): *m/z* (%) 345.20 (60), 344.19 (100), 302.37 (39), 233.31 (23), 144.01 (15), 91.90 (10).

Anal. Calcd. for $C_{23}H_{24}N_2O$ C, 80.20; H, 7.02; N, 8.13 Found C, 79.94; H, 6.87; N, 8.47 %.

2-(4-Benzyl-4,5-dihydrooxazol-2-yl)-N-(naphthalen-2-ylmethyl)aniline (45b):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.09 g, 0.66 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(naphthalen-2-ylmethyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **39** (1.00 g, 3.30 mmol) and L-phenylalaninol (0.60 g, 3.96 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **45b** (0.75 g, 58%) as white crystals.

M.P. 124 ^{o}C; $[\alpha]_D^{35}$ = +10.10 (*c* 0.70, $CHCl_3$).

IR (KBr): υ 3255, 3056, 3024, 2885, 2851, 1627, 1580, 1516, 1452, 1363, 1328, 1281, 1240, 1166, 1080, 1034, 983, 905, 867, 819, 750 cm.$^{-1}$

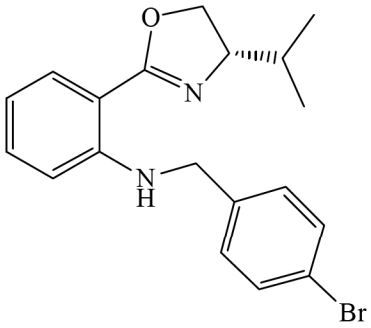
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.11 (bs, 1H), 7.88 – 7.78 (m, 5H), 7.54 – 7.49 (m, 3H), 7.28 – 7.18 (m, 6H), 6.71 – 6.65 (m, 2H), 4.70 – 4.64 (m, 3H), 4.34 – 4.31 (t, *J* = 8.4 Hz, 1H), 4.10 – 4.06 (t, *J* = 7.6 Hz, 1H), 3.15 – 3.10 (dd, *J* = 6.4 & 13.6 Hz, 1H), 2.85 – 2.79 (dd, *J* = 7.6 & 13.6 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.45, 149.05, 138.22, 136.90, 133.54, 132.71, 132.62, 129.93, 129.25, 128.44, 128.34, 127.81, 127.71, 126.43, 126.09, 125.59, 125.41, 114.80, 110.98, 108.62, 70.19, 67.97, 47.23, 42.26.

MS (EI): *m/z* (%) 392.48 (100), 301.18 (43), 258.19 (83), 244.22 (31), 140.94 (56), 90.84 (16), 76.81 (7).

Anal. Calcd. for $C_{27}H_{24}N_2O$ C, 82.62; H, 6.16; N, 7.14 Found C, 82.43; H, 6.01; N, 7.42 %.

N-(4-Bromobenzyl)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline (46a):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.08 g, 0.60 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(4-bromobenzyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **40** (1.00 g, 3.01 mmol) and L-valinol (0.37 g, 3.61 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **46a** (0.91 g, 81%) as colourless crystals.

M.P. 100 - 102 ^{o}C; $[\alpha]_D^{35}$ = -6.72 (*c* 0.70, $CHCl_3$).

IR (KBr): υ 3243, 2958, 2864, 1632, 1488, 1455, 1239, 1308, 805, 748 cm.$^{-1}$

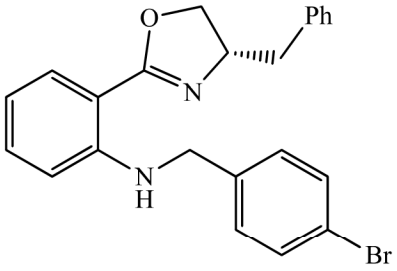
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.08 (bs, 1H), 7.78 – 7.59 (dd, *J* = 1.6 & 7.6 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.29 – 7.24 (m, 3H), 6.67 – 6.63 (m, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.46 (d, *J* = 4.4 Hz, 2H), 4.37 – 4.33 (q, *J* = 8.0 Hz, 1H), 4.15 – 4.11 (m, 1H), 4.05 – 4.01 (t, *J* = 7.6 Hz, 1H), 1.82 – 1.74 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.84, 148.71, 138.45, 132.47, 132.41, 131.62, 129.89, 128.82, 120.67, 114.91, 110.66, 108.90, 72.79, 68.77, 46.51, 33.27, 18.89, 18.70.

MS (EI): *m/z* (%) 373.62 (100), 371.82 (30), 331.18 (11), 328 (17), 287.10 (21), 285.54 (44), 272.05 (11), 270.83 (6).

Anal. Calcd. for $C_{19}H_{21}BrN_2O$ C, 61.13; H, 5.67; N, 7.50 Found C, 60.67; H, 5.31; N, 7.99 %.

2-(4-Benzyl-4,5-dihydrooxazol-2-yl)-N-(4-bromobenzyl)aniline (46b):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.08 g, 0.60 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(4-bromobenzyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **40** (1.00 g, 3.01 mmol) and L-valinol (0.37 g, 3.61 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **46b** (1.03 g, 82%) as colourless crystals.

M.P. 104 - 106 ^{o}C; $[\alpha]_D^{35}$ = +8.78 (*c* 0.60, $CHCl_3$).

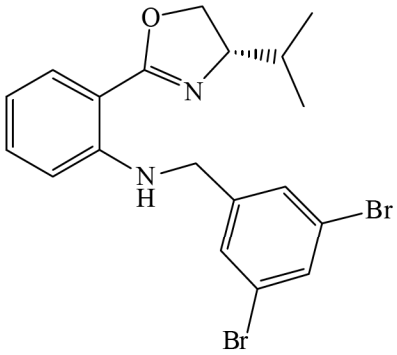
^{1}H-NMR (400 MHz, CDCl3): δ 9.01 – 9.98 (t, *J* = 5.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.24 (m, 8H), 6.67 – 6.63 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 4.63 – 4.59 (m, 1H), 4.51 – 4.41 (m, 2H), 4.35 – 4.31 (t, *J* = 8.4 Hz, 1H), 4.09 – 4.05 (t, *J* = 7.2 Hz, 1H), 3.11 – 3.06 (dd, *J* = 6.8 & 13.6 Hz, 1H), 2.84 – 2.79 (dd, *J* = 7.6 & 13.6, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.31, 148.73, 138.48, 138.27, 132.54, 131.66, 129.94, 129.24, 128.68, 128.47, 126.48, 120.63, 114.94, 110.75, 108.77, 70.19, 68.07, 46.37, 42.33.

MS (EI): *m/z* (%) 421.77 (88), 419.49 (100), 330.76 (74), 328.63 (67), 288.14 (47), 287.10 (30), 285.49 (78), 271.56 (45), 192.83 (24), 170.73 (23), 168.75 (22), 91 (33), 77 (17).

Anal. Calcd. for $C_{19}H_{21}BrN_2O$ C, 65.57; H, 5.02; N, 6.65 Found C, 65.01; H, 4.62; N, 6.98 %.

N-(3,5-Dibromobenzyl)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline (47a):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.06 g, 0.49 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(3,5-dibromobenzyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **41** (1.00 g, 2.43 mmol) and L-valinol (0.30 g, 2.92 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **47a** (0.67 g, 61%) as colourless crystals.

M.P. 118 - 120 ^{o}C; $[\alpha]_D^{35}$ = -17.15 (*c* 0.50, $CHCl_3$).

IR (KBr): υ 3216, 3085, 2959, 2899, 2864, 1637, 1586, 1520, 1463, 1357, 1328, 1080, 1049, 964, 849, 744, 682, 632, 588, 537 cm.$^{-1}$

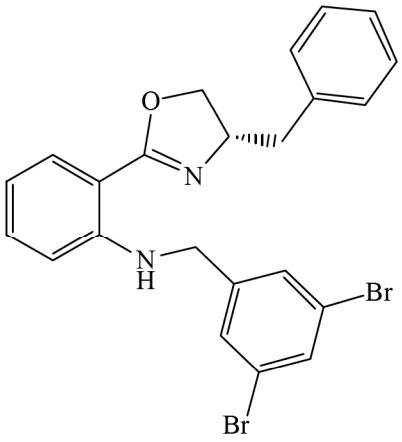
^{1}H-NMR (400 MHz, CDCl3): δ 9.15 (bs, 1H), 7.79 – 7.77 (dd, *J* = 1.6 & 8.0 Hz, 1H), 7.58 – 7.57 (m, 1H), 7.48 – 7.47 (m, 2H), 7.29 – 7.25 (m, 1H), 6.71 – 6.67 (m, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.51 – 4.41 (q, *J* = 15.6 Hz, 2H), 4.39 – 4.34 (m, 1H), 4.17 – 4.11 (m, 1H), 4.07 – 4.03 (t, *J* = 8.0 Hz, 1H), 1.84 – 1.77 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.82, 148.44, 143.83, 132.70, 132.48, 129.94, 128.78, 123.19, 115.32, 110.59, 109.16, 76.74, 72.77, 68.78, 46.25, 18.97, 18.69.

MS (EI): *m/z* (%) 453.70 (74), 452.37 (48), 451.81 (31), 450.95 (100), 449.22 (91), 410.12 (17), 409.03 (28), 408.10 (31), 406.35 (33), 368.18 (26), 367.12 (30), 365.54 (99), 363.46 (53), 146.51 (39), 104.51 (36), 76.75 (18).

Anal. Calcd. for $C_{19}H_{20}Br_2N_2O$ C, 50.47; H, 4.46; N, 6.20 Found C, 50.05; H, 3.98; N, 6.45 %.

2-(4-Benzyl-4,5-dihydrooxazol-2-yl)-N-(3,5-dibromobenzyl)aniline (47b):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.06 g, 0.49 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(3,5-dibromobenzyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **41** (1.00 g, 2.43 mmol) and L-phenylalaninol (0.44 g, 2.92 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **47b** (0.72 g, 59%) as colourless crystals.

M.P. 112 - 114 ^{o}C; $[\alpha]_D^{35}$ = +4.36 (*c* 0.71, $CHCl_3$).

IR (KBr): υ 3210, 3067, 3027, 2844, 1636, 1553, 1526, 1468, 1365, 1238, 1028, 847, 750, 693, 571, 541 cm.$^{-1}$

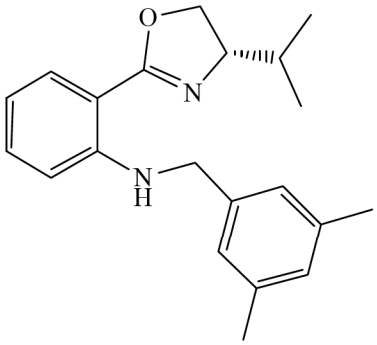
^{1}H-NMR (400 MHz, CDCl3): δ 9.01 (bs, 1H), 7.79 – 7.77 (dd, *J* = 1.6 & 7.6 Hz, 1H), 7.59 – 7.58 (t, *J* = 1.6 Hz, 1H), 7.48 – 7.47 (m, 2H), 7.34 – 7.24 (6H), 6.71 – 6.66 (m, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.68 – 4.64 (m, 1H), 4.46 (d, *J* = 4.8 Hz, 2H), 4.36 – 4.32 (t, *J* = 8.4 Hz, 1H), 4.11 – 4.08 (q, *J* = 7.2 Hz, 1H), 3.17 – 3.12 (dd, *J* = 6.4 & 13.6 Hz, 1H), 2.87 – 2.82 (dd, *J* = 7.6 & 13.6 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.93, 149.51, 139.83, 138.72, 138.50, 132.95, 130.21, 129.68, 129.02, 128.88, 126.95, 125.12, 114.93, 111.21, 108.92, 70.40, 68.62, 47.43, 43.10.

MS (EI): *m/z* (%) 501.64 (57), 500.05 (70), 499.07 (50), 497.99 (52), 410.59 (66), 409.00 (71), 407.71 (100), 405.98 (51), 367.75 (31), 363.81 (19), 362.63 (26), 351.91 (30), 350.67 (25), 349.59 (16), 248.46 (12), 90.87 (8).

Anal. Calcd. for $C_{23}H_{20}Br_2N_2O$ C, 55.22; H, 4.03; N, 5.60 Found C, 54.88; H, 3.71; N, 5.93 %.

N-(3,5-Dimethylbenzyl)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline (48a):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.09 g, 0.71 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(3,5-dimethylbenzyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **42** (1.00 g, 3.55 mmol) and L-valinol (0.44 g, 4.27 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **48a** (0.63 g, 55%) as colourless crystals.

M.P. 102 - 104 ^{o}C; $[\alpha]_D^{35}$ = -36.91 (*c* 0.60, $CHCl_3$).

IR (KBr): υ 3230, 2892, 1639, 1519, 1455, 1356, 1332, 1271, 1236, 1160, 1075, 1045, 967, 739, 682, 719, 682 cm.$^{-1}$

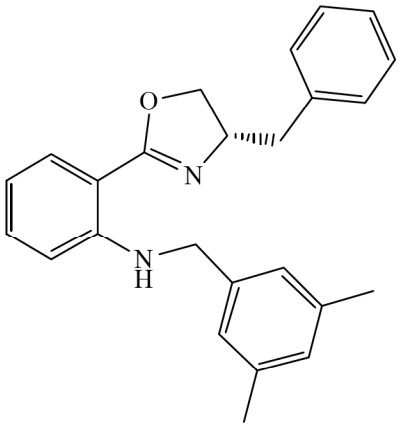
^{1}H-NMR (400 MHz, CDCl3): δ 8.99 (bs, 1H), 7.78 – 7.76 (dd, *J* = 1.6 & 7.6 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.05 (s, 2H), 6.935 (s, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.67 – 6.63 (m, 1H), 4.45 – 4.39 (m, 2H), 4.37 – 4.33 (m, 1H), 4.14 – 4.08 (m, 1H), 4.04 – 4.00 (t, *J* = 8.0 Hz, 1H), 2.33 (s, 6H), 1.81 – 1.73 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.81, 149.08, 139.19, 132.39, 129.76, 128.65, 125.01, 114.46, 110.63, 108.70, 72.92, 68.81, 47.21, 33.37, 21.34, 18.86, 18.83.

MS (EI): *m/z* (%) 322.51 (51), 321.05 (89.91), 278.84 (21), 235.83 (100), 146.75 (15), 105.03 (9), 90.82 (9), 76.71 (7).

Anal. Calcd. for $C_{21}H_{26}N_2O$ C, 78.22; H, 8.13; N, 8.69 Found C, 77.87; H, 7.78; N, 8.81 %.

2-(4-Benzyl-4,5-dihydrooxazol-2-yl)-N-(3,5-dimethylbenzyl)aniline (48b):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.09 g, 0.71 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-(3,5-dimethylbenzyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **42** (1.00 g, 3.55 mmol) and L-phenylalaninol (0.64 g, 4.27 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **48b** (0.65 g, 49%) as colourless liquid.

$[\alpha]_D^{35} = +18.44$ (*c* 1.01, $CHCl_3$)

IR (KBr): υ 3257, 3026, 1633, 1234, 1061, 841, 748 $cm.^{-1}$

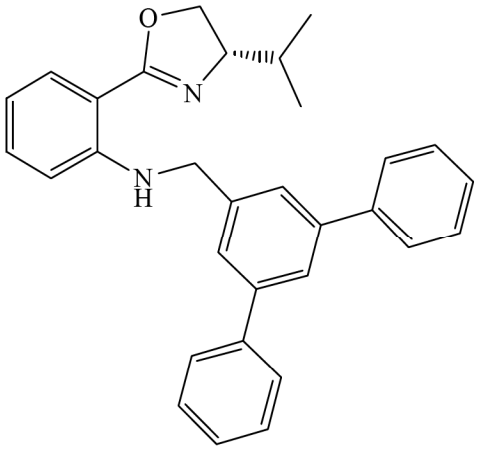
^{1}H-NMR (400 MHz, CDCl3): δ 8.97 – 8.94 (t, *J* = 5.2 Hz, 1H), 7.77 – 7.75 (dd, *J* = 1.6 & 7.6 Hz, 1H), 7.31 – 7.21 (m, 7H), 7.03 (s, 2H), 6.93 (s, 1H), 6.67 – 6.61 (m, 2H), 4.67 – 4.59 (m, 1H), 4.50 – 4.42 (m, 2H), 4.33 – 4.29 (t, *J* = 8.4 Hz, 1H), 4.08 – 4.04 (q, *J* = 7.2 Hz, 1H), 3.16 – 3.11 (dd, *J* = 6.4 & 13.6 Hz, 1H), 2.83 – 2.78 (dd, *J* = 8 & 13.6 Hz, 1H), 2.33 (s, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.36, 149.18, 139.45, 138.32, 138.10, 132.55, 129.83, 129.28, 128.62, 128.48, 126.45, 124.78, 114.53, 110.86, 108.55, 70.07, 68.12, 47.00, 42.27, 21.42.

MS (EI): *m/z* (%) 370.64 (61), 369.05 (100), 178.98 (86), 236.44 (79), 221.02 (27), 118.82 (32), 90.94 (42), 76.75 (12).

Anal. Calcd. for $C_{25}H_{26}N_2O$ C, 81.05; H, 7.07; N, 7.56 Found C, 80.67; H, 6.72; N, 7.91 %

N-([1,1':3',1''-Terphenyl]-5'-ylmethyl)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline (49a):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.06 g, 0.49 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-([1,1':3',1''-terphenyl]-5'-ylmethyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **43** (1.00 g, 2.47 mmol) and L-valinol (0.31 g, 2.96 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **49a** (0.48 g, 44%) as colourless crystals.

M.P. 126 ^{o}C; $[\alpha]_D^{35}$ = -37.35 (*c* 0.51, $CHCl_3$).

IR (KBr): υ 3217, 3064, 2945, 1633, 1525, 1246, 1047, 765, 758, 698 cm.$^{-1}$

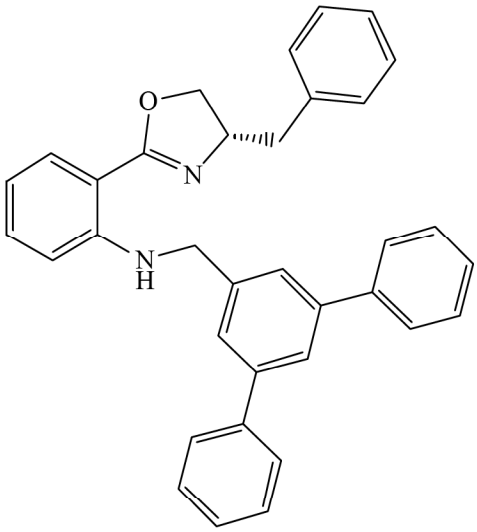
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.18 – 9.15 (t, *J* = 4.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.67 – 7.63 (t, *J* = 7.6 Hz, 6H), 7.49 – 7.45 (t, *J* = 7.6 Hz, 4H), 7.41 – 7.37 (m, 2H), 7.32 – 7.28 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.68 – 6.65 (t, *J* = 7.6 Hz, 1H), 4.68 – 4.58 (m, 2H), 4.36 – 4.31 (m, 1H), 4.13 – 4.07 (m, 1H), 4.03 – 3.99 (t, *J* = 8.4 Hz, 1H), 1.77 – 1.68 (m, 1H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.80, 148.98, 142.10, 141.12, 140.51, 132.43, 129.83, 128.77, 127.44, 127.33, 125.07, 124.96, 114.74, 110.70, 108.98, 72.80, 68.67, 47.37, 33.21, 18.76, 18.59.

MS (EI): *m/z* (%) 446.14 (100), 444.53 (50), 360.33 (57), 358.73 (34), 347.45 (10), 346.63 (14), 104.82 (12), 90.90 (10), 76.80 (13).

Anal. Calcd. for $C_{31}H_{30}N_2O$ C, 83.37; H, 6.77; N, 6.27 Found C, 82.93; H, 6.51; N, 6.42 %.

N-([1,1':3',1''Tterphenyl]-5'-ylmethyl)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)aniline (49b):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.06 g, 0.49 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-([1,1':3',1''-terphenyl]-5'-ylmethyl)-1*H*-benzo[d][1,3]oxazine-2,4-dione **43** (1.00 g, 2.47 mmol) and L-phenylalaninol (0.45 g, 2.96 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **49b** (0.56 g, 46%) as colourless liquid.

$[\alpha]_D^{36} = +19.53$ (*c* 0.50, $CHCl_3$)

IR (KBr): υ 3236, 3028, 2895, 1632, 1238, 1165, 1030, 972, 758, 698 $cm.^{-1}$

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.14 (bs, 1H), 7.80 – 7.75 (m, 2H), 7.71 – 7.64 (m, 6H), 7.50 – 7.46 (m, 4H), 7.41 – 7.37 (m, 2H), 7.32 – 7.19 (m, 6H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.68 – 6.65 (t, *J* = 7.6 Hz, 1H), 4.67 – 4.60 (m, 3H), 4.34 – 4.30 (t, *J* = 8.4 Hz, 1H), 4.09 – 4.05 (t, *J* = 8.0 Hz, 1H), 3.14 – 3.09 (dd, *J* = 6.0 & 13.6 Hz, 1H), 2.81 – 2.76 (dd, *J* = 8.0 & 13.6 Hz, 1H).

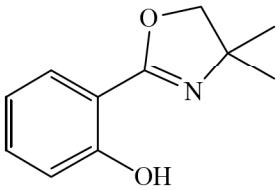
^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.38, 149.11, 142.12, 141.16, 140.69, 138.24, 132.60, 129.92, 129.22, 128.81, 128.45, 127.47, 127.34, 126.43, 124.94, 124.82, 114.84, 110.93, 108.79, 70.10, 68.13, 47.23, 42.27.

MS (EI): *m/z* (%) 494.74 (41), 493.66 (49), 492.53 (53), 403.43 (17), 402.33 (37), 360.11 (100),

358.73 (38), 346.82 (23), 344.91 (19), 243.14 (22), 241.11 (14), 116.90 (9), 90.84 (9).

Anal. Calcd. for $C_{35}H_{30}N_2O$ C, 84.99; H, 6.11; N, 5.66 Found C, 84.61; H, 5.88; N, 5.81 %.

2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenol (51):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.11 g, 0.84 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 2-cyanophenol **50** (0.50 g, 4.20 mmol) and 2-amino-2-methyl-propane-1-ol (0.45 g, 5.04 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **51** (0.45 g, 57%) as white crystals.

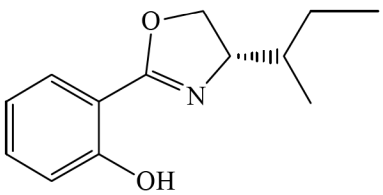
M.P. 57 - 8 ^{o}C (Lit..[43] 58 – 60 ^{o}C)

IR (KBr): 2972, 1948, 1895, 1633, 1493, 1259, 1184, 1063, 959, 875, 758 cm.$^{-1}$

^{1}H-NMR ($CDCl_3$, 400 MHz): δ12.15 (bs, 1H), 7.64 – 7.61 (dd, *J* = 1.7 & 7.8 Hz, 1 H), 7.38 – 7.33 (m, 1H), 7.02 - 6.99 (dd, *J* = 0.9 & 8.3 Hz, 1 H), 6.88 – 6.84 (td, *J* = 1.1 & 7.8 Hz, 1 H), 4.09 (s, 2 H), 1.39 (s, 6 H).

MS (EI): *m/z* (%) 192.13 (13), 191.17 (93), 190.42 (100), 176.27 (33), 175.49 (53), 160.22 (4), 148.19 (24), 120.18 (40), 119.10 (70), 91.09 (12).

2-((S)-4-((R)-sec-Butyl)-4,5-dihydrooxazol-2-yl)phenol (52):

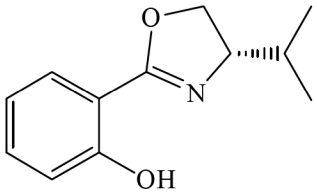


In a 100 mL two-necked flask, anhydrous zinc chloride (0.11 g, 0.84 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry

chlorobenzene (10 mL), 2-cyanophenol **50** (0.50 g, 4.20 mmol) and L-*iso*-leucinol (0.59 g, 5.04 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **52** (0.45 g, 49%) as yellowish liquid.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ12.35 (bs, 1H), 7.64 – 7.62 (dd, *J* = 1.7 & 7.8 Hz, 1 H), 7.38 – 7.34 (m, 1H), 7.01 - 6.99 (dd, *J* = 0.9 & 9.3 Hz, 1 H), 6.88 – 6.84 (m, 1H), 4.33 – 4.39 (m, 1H), 4.26 – 4.20 (m, 1H), 4.13 – 4.09 (t, *J* = 8.1Hz, 1H), 1.68 – 1.58 (m, 2H), 1.28 – 1.20 (m, 2H), 0.97 – 0.93 (m, 3H), 0.89 (d, *J* = 6.7 Hz, 3H).

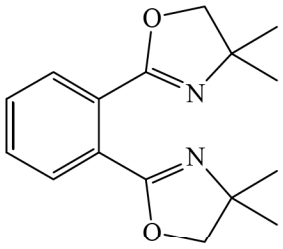
2-(4-Isopropyl-4,5-dihydrooxazol-2-yl)phenol (53):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.11 g, 0.84 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 2-cyanophenol **50** (0.50 g, 4.20 mmol) and L-valinol (0.52 g, 5.04 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **53** (0.44 g, 51%) as yellowish liquid.[40]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ12.35 (bs, 1H), 7.64 – 7.62 (dd, *J* = 1.7 & 7.8 Hz, 1 H), 7.38 – 7.34 (m, 1H), 7.01 - 6.99 (dd, *J* = 0.9 & 8.4 Hz, 1 H), 6.88 – 6.84 (m, 1H), 4.33 – 4.39 (m, 1H), 4.16 – 4.09 (m, 1H), 1.83 – 1.73 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H).

1,2-bis(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)benzene (55):



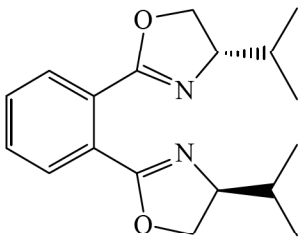
In a 100 mL two-necked flask, anhydrous zinc chloride (0.10 g, 0.78 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1,2-dicyanobenzene **54** (0.50 g, 3.90 mmol) and 2-amino-2-methyl-propane-1-ol (0.41 g, 4.68 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **55** (0.65 g, 60%) as yellowish liquid.[44]

IR (KBr): 3068, 2968, 1651, 1599, 1493, 1383, 1249, 1189, 1080, 989, 921, 864, 776, 689 $cm.^{-1}$

^{1}H-NMR ($CDCl_3$, 400 Hz): δ 7.76 - 7.74 (m, 2H), 7.48 - 7.45 (m, 2H), 4.07 (s, 2H),1.39 (s, 12H).

MS (EI): *m/z* (%) 272.20 (20), 258.86 (31), 201.81 (100), 174.80 (23), 160.19 (11), 148.14 (8), 130.09 (9).

1,2-bis((S)-4-Isopropyl-4,5-dihydrooxazol-2-yl)benzene (56):



In a 100 mL two-necked flask, anhydrous zinc chloride (0.10 g, 0.78 mmol, 20 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1,2-dicyanobenzene **54** (0.50 g, 3.90 mmol) and L-valinol (0.48 g, 4.68 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 x 20 mL) and the aqueous phase was extracted again with dichloromethane (2 x 20 mL). The combined organic phase was dried with anhydrous sodium sulphate and the solvent was removed in a vacuum. The resulting oil was

purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford pure product **56** (0.70 g, 61%) as sticky colourless liquid.[44]

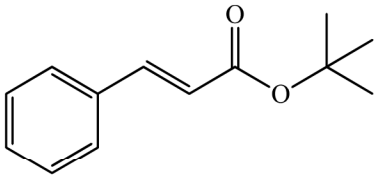
^{1}H-NMR ($CDCl_3$, 400 Hz): δ 7.76 - 7.74 (m, 2H), 7.48 - 7.45 (m, 2H), 4.38 – 4.34 (m, 2H), 4.10 – 4.05 (m, 4H), 1.89 – 1.87 (m, 2H), 1.04 (d, *J* = 6.7 Hz, 6H), 0.96 (d, *J* = 6.7 Hz, 6H).

IR (KBr): 3051, 2967, 1643, 1574, 1352, 1165, 1058, 978, 859, 767 cm.$^{-1}$

Part II – Application of oxazolines in Mizoroki-Heck reaction

Synthetic Procedures:

tert-Butyl cinnamate (64):



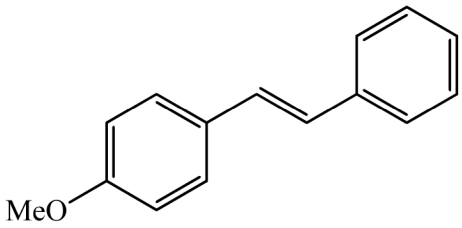
In a typical procedure a catalyst solution was separately prepared in an oven dry, N_2 flushed two neck r.b. flask. A solution of palladium acetate (0.0013 g, 0.0061 mmol, 0.5 mol %) and ligand **34** (0.0029 g, 0.015 mmol, 1.25 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of iodobenzene **59** (0.25 g, 1.22 mmol), dry K_2CO_3 (0.34 g, 2.45 mmol) in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^oC and *tert*-butylacerylate **63** (0.23 g, 1.83 mmol) was slowly added. After the addition temperature was increased (100 ^oC) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 $\pm$ 5 ^oC for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure *tert*-butyl cinnamate **64** (0.20 g, 80 %) as colourless liquid.[45]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 16.04 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.37 – 7.35 (m, 3H), 6.37 (d, *J* = 16.04 Hz, 1H), 1.53 (s, 9H).

IR (neat): 2978, 1711, 1635, 1578, 1496, 1475, 1450, 1392, 1367, 1328, 1257, 1207, 1150 cm.$^{-1}$

(E)-1-Methoxy-4-styrylbenzene (67):



Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0055 mmol, 0.5 mol %) and ligand **34** (0.0026 g, 0.0137 mmol, 1.25 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 4-iodoanisole **65** (0.250 g, 1.10 mmol), dry K_2CO_3 (0.297 g, 2.20 mmol) in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^oC and styrene **66** (0.172 g, 1.65 mmol) was slowly added. After the addition temperature was increased (100 ^oC) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 $\pm$ 5 ^oC for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **67** (0.178 g, 79 %) as white solid.

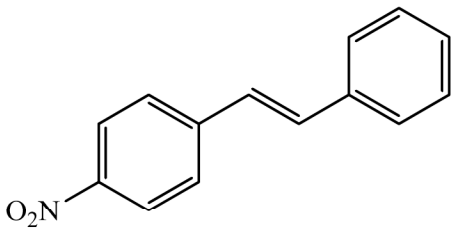
M.P. 134 - 135 ^oC (Lit..[46] 135 - 136 ^oC).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.50 - 7.44 (m, 4 H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, *J* = 16.31 Hz, 1H), 6.97 (d, *J* = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

IR (KBr): 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 $cm.^{-1}$

MS (EI): *(m/z)* 210 (M^+, 100), 179 (14), 167 (27), 105 (7), 76(3).

(E)-1-Nitro-4-styrylbenzene (69):



Priorly, in an oven dry flask catalyst solution of palladium acetate (0.0014 g, 0.0062 mmol, 0.5 mol %) and ligand **34** (0.0029 g, 0.015 mmol, 1.25 mol %) was prepared in dry *N*,*N*-dimethylacetamide

(5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 4-bromonitrobenzene **68** (0.25 g, 1.23 mmol), dry K_2CO_3 (0.34 g, 2.47 mmol), TBAB (0.099 g, 0.31 mmol, 25 mol%) in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^oC and styrene **66** (0.19 g, 1.85 mmol) was slowly added. After the addition temperature was increased (100 ^oC) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 $\pm$ 5 ^oC for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **69** (0.23 g, 82 %) as yellow crystals.

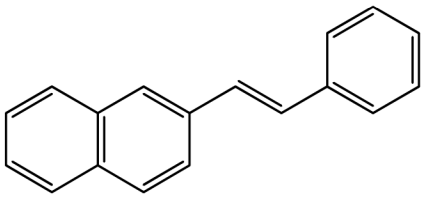
M.P. 159-60 ^oC (Lit.[47] 157 ^oC).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, *J* = 9.2 Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, *J* = 16.3 Hz, 1H), 7.14 (d, *J* = 16.3 Hz, 1H), ,

IR (KBr) 2922, 1590, 1340, 1107, 970, 694 $cm.^{-1}$

MS (EI): *(m/z)* 225 (M^+, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

(E)-2-Styrylnaphthalene (71):



In a typical procedure a catalyst solution was separately prepared in an oven dry, N_2 flushed two neck r.b. flask. A solution of palladium acetate (0.0013 g, 0.0060 mmol, 0.5 mol %) and ligand **34** (0.0028 g, 0.0151 mmol, 1.25 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 2-bromonaphthalene **70** (0.25 g, 1.20 mmol), dry K_2CO_3 (0.34 g, 2.41 mmol) and TBAB (0.097 g, 0.30 mmol, 25 mol%)in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^oC and styrene **66** (0.19 g, 1.80 mmol) was slowly added. After the addition temperature was increased (100 ^oC) and previously prepared palladium catalyst solution was added

drop wise and the reaction mixture heated to 140 ± 5 °C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **71** (0.244 g, 88 %) as white solid.

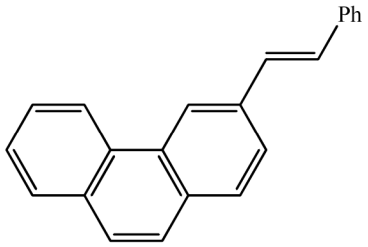
M.P. 146 – 7 °C (Lit.[48] 147 – 149 °C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.85 – 7.77 (m, 4H), 7.75 – 7.73 (dd, *J* = 1.3 & 8.6 Hz, 1H), 7.57 – 7.55 (dd, *J* = 1.3 & 8.6 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 7.30 – 7.24 (m, 3H).

IR (KBr): 3077, 3045, 1595, 1510, 1496, 1448, 1350, 1074, 957, 794, 775 $cm.^{-1}$

MS (EI): *(m/z)* 230 (M^+, 100), 215 (21), 115 (15), 107 (9.1).

(E)-3-Styrylphenanthrene (73):



In a typical procedure a catalyst solution was separately prepared in an oven dry, N_2 flushed two neck r.b. flask. A solution of palladium acetate (0.0022 g, 0.0097 mmol, 1.0 mol %) and ligand **34** (0.0046 g, 0.024 mmol, 2.5 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 3-bromophenanthrene **72** (0.25 g, 0.97 mmol), dry K_2CO_3 (0.27 g, 1.94 mmol) and TBAB (0.078 g, 0.24 mmol, 25 mol%)in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 °C and styrene **66** (0.15 g, 1.46 mmol) was slowly added. After the addition temperature was increased (100 °C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 ± 5 °C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **73** (0.26 g, 95 %) as white solid.

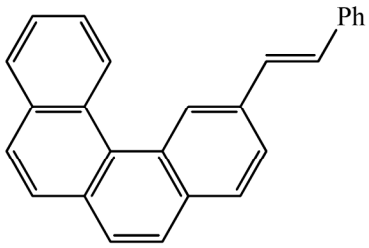
M.P. 152 – 154 ^{o}C (Lit.[49] 154 ^{o}C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 4.4 Hz, 1H), 8.76 (s, 1H), 7.93 – 7.85 (m, 3H), 7.75 – 7.68 (m, 3H), 7.65 – 7.62 (m, 3H), 7.45 – 7.40 (m, 3H), 7.36 – 7.30 (m, 2H).

IR (KBr): 3023, 1595, 1487, 1109, 1034, 940, 771, 738 cm.$^{-1}$

MS (EI) (m/z): 281 (M^{+1}, 22.6), 280 (M^{+}, 100), 263 (8.7), 140 (19).

(E)-2-Styrylbenzo[c]phenanthrene (75):



In a typical procedure a catalyst solution was separately prepared in an oven dry, N_2 flushed two neck r.b. flask. A solution of palladium acetate (0.0036 g, 0.016 mmol, 2.0 mol %) and ligand **34** (0.0069 g, 0.036 mmol, 4.5 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

In another two neck round bottom flask a mixture of 2-bromobenzo[c]phenanthrene **74** (0.25 g, 0.81 mmol), dry K_2CO_3 (0.23 g, 1.63 mmol) and TBAB (0.064 g,0.20 mmol, 25 mol%)in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^{o}C and styrene **66** (0.13 g, 1.22 mmol) was slowly added. After the addition temperature was increased (100 ^{o}C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 $\pm$ 5 ^{o}C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **75** (0.255 g, 95 %) as white solid.

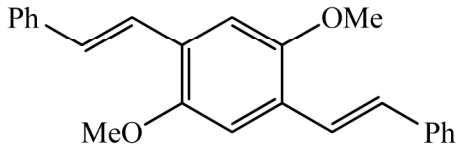
M.P. 142 ^{o}C (Lit.[50] 140 ^{o}C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 9.19 (d, *J* = 3.6 Hz, 1H), 9.18 (s, 1H), 8.07 – 8.04 (m, 2H), 7.94 – 7.89 (m, 3H), 7.86 – 7.81 (m, 2H), 7.78 – 7.43 (m, 1H), 7.69 – 7.63 (m, 3H), 7.45 - 7.41 (m, 3H), 7.35 - 7.28 (m, 3H).

IR (KBr): 3017, 1600, 1499, 1072, 1043, 982, 902, 782, 744 $cm.^{-1}$

MS (EI): *(m/z)* 331 (M^{+1}, 28), 330 (M^{+}, 100), 226 (12.3), 164 (23.6).

((1E,1'E)-(2,5-Dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene (77):



In a typical procedure a catalyst solution was separately prepared in an oven dry, N_2 flushed two neck r.b. flask. A solution of palladium acetate (0.0014 g, 0.0064 mmol, 1.0 mol %) and ligand **34** (0.0030 g, 0.016 mmol, 2.5 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

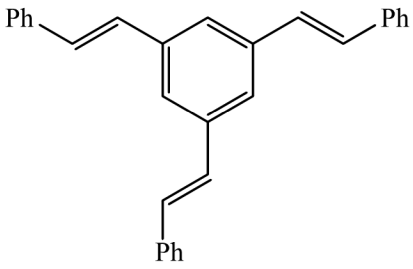
In another two neck round bottom flask a mixture of 1,4-diiodo-2,5-dimethoxybenzene **76** (0.25 g, 0.81 mmol), dry K_2CO_3 (0.23 g, 1.63 mmol) in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^{o}C and styrene **66** (0.20 g, 1.92 mmol) was slowly added. After the addition temperature was increased (100 ^{o}C) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 $\pm$ 5 ^{o}C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with water (2 x 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **77** (0.171 g, 78 %) as light yellow crystals.

M.P. 184 - 186 ^{o}C (Lit.[51] 177 - 178 ^{o}C)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.85 – 7.77 (m, 4H), 7.75 – 7.73 (dd, *J* = 1.3 & 8.6 Hz, 2H), 7.57 – 7.55 (dd, *J* = 1.3 & 8.6 Hz, 4H), 7.49 – 7.42 (m, 4H), 7.40 – 7.34 (m, 4H), 7.12 (d, *J* = 16 Hz, 4H), 3.93 (s, 6H).

MS (EI): *(m/z)* 343 (M^{+1}, 25), 342 (M^{+}, 100), 171 (11), 105 (35).

1,3,5-tri((E)-Styryl)benzene (79):



In a typical procedure a catalyst solution was separately prepared in an oven dry, N_2 flushed two neck r.b. flask. A solution of palladium acetate (0.0014 g, 0.0064 mmol, 1.0 mol %) and ligand **34** (0.0030 g, 0.016 mmol, 2.5 mol %) was prepared in dry *N*,*N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

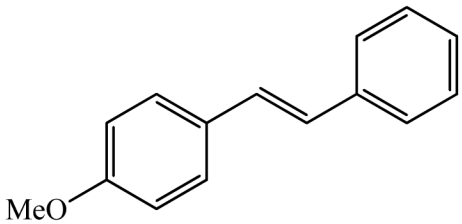
In another two neck round bottom flask a mixture of 1,3,5-tribromobenzene **78** (0.25 g, 0.79 mmol), dry K_2CO_3 (0.22 g, 1.58 mmol) TBAB (0.064 g, 0.20 mmol, 25 mol%)in dry *N*,*N*-dimethylacetamide (5 mL) was taken and repeatedly degassed by purging with N_2 gas. The solution was heated to 60 ^oC and styrene **66** (0.49 g, 4.76 mmol) was slowly added. After the addition temperature was increased (100 ^oC) and previously prepared palladium catalyst solution was added drop wise and the reaction mixture heated to 140 $\pm$ 5 ^oC for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 × 30 mL). The organic layer was washed with water (2 X 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure **79** (0.189 g, 62 %) as white solid.

M.P. 200 ^oC (Lit.[52] 202 ^oC).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.57 – 7.55 (m, 9H), 7.40 – 7.36 (m, 6H), 7.30 – 7.26 (m, 3H), 7.21 (d, *J* = 16.32 Hz, 3H), 7.15 (d, *J* = 16.32 Hz, 3H).

IR (KBr): 3025, 1595, 1494, 1263, 1073, 956, 883, 750 cm.$^{-1}$

(E)-1-Methoxy-4-styrylbenzene (67):



Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol%) and **34** (0.0025 g, 0.0133 mmol, 1.25 mol%) was prepared in DMA:Water (1:2, 5 mL). The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask 4-iodoanisole (**65**) (0.250 g, 1.06. mmol), K_2CO_3 (0.29 g, 2.13 mmol), TBAB (0.034 g, 0.106 mmol) were mixed in DMA:Water (1:2, 5 mL). Then the solution was heated up to 60 ^oC and styrene (0.17 g, 1.60 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 120 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **67** (0.200 g, 89%) as white solid.

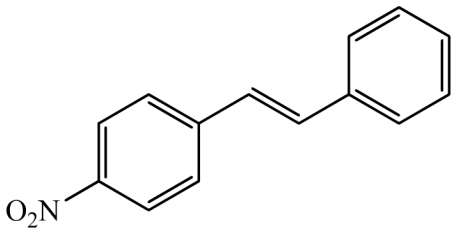
M.P. 134 - 135 ^oC (Lit..[46] 135 - 136 ^oC).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.50 - 7.44 (m, 4 H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, *J* = 16.31 Hz, 1H), 6.97 (d, *J* = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

IR (KBr): 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 $cm.^{-1}$

MS (EI): *(m/z)* 210 (M^+, 100), 179 (14), 167 (27), 105 (7), 76(3).

(E)-1-Nitro-4-styrylbenzene (69):



Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0062 mmol, 0.5 mol %) and **34** (0.0029 g, 0.0154 mmol, 1.25 mol%) was prepared in DMA:Water (1:2, 5 mL). The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask 4-bromonitrobenzene **68** (0.25 g, 1.23 mmol), dry K_2CO_3 (0.34 g, 2.47 mmol), TBAB (0.039 g, 0.123 mmol, 10 mol%) were mixed in DMA:Water (1:2, 5 mL). Then the solution was heated up to 60 ^oC and styrene (0.193 g, 1.85 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 120 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **69** (0.179 g, 64%) as yellow solid.

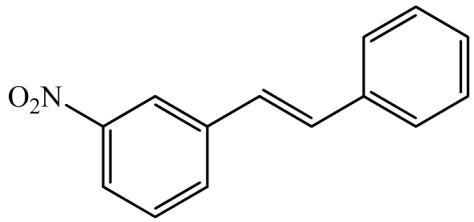
M.P. 159 - 160 ^oC (Lit.[47] 157 ^oC).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, *J* = 9.2 Hz, 1H), 7.90 - 7.60 (m, 2H), 7.60 - 7.58 (m, 2H), 7.42 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 (d, *J* = 16.3 Hz, 1H), 7.14 (d, *J* = 16.3 Hz, 1H).

IR (KBr) 2922, 1590, 1340, 1107, 970, 694 $cm.^{-1}$

MS (EI): *(m/z)* 225 (M^+, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

(E)-1-Nitro-3-styrylbenzene (83):



Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0062 mmol, 0.5 mol %) and **34** (0.0029 g, 0.0154 mmol, 1.25 mol%) was prepared in DMA:Water (1:2, 5 mL). The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask 3-bromonitrobenzene **82** (0.25 g, 1.23 mmol), dry K_2CO_3 (0.34 g, 2.47 mmol), TBAB (0.039 g, 0.123 mmol, 10 mol%) were mixed in DMA:Water (1:2, 5 mL). Then the solution was heated up to 60 ^oC and styrene (0.193 g, 1.85 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 120 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **83** (0.250 g, 90%) as light yellow solid.

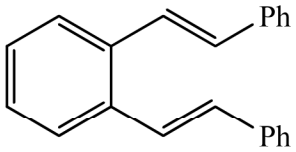
M.P. 108-110 ^{o}C (Lit.[53] 111-112 ^{o}C)

^{1}H-NMR (DMSO, 400 MHz): δ 8.44 (s, 1H), 8.12 – 8.07 (m, 2H), 7.70 – 7.66 (m, 3H), 7.53 – 7.40 (m, 4H), 7.34 – 7.31 (m, 1H).

IR (KBr): 2925, 1588, 1355, 1117, 980, 714 cm.$^{-1}$

MS (EI): *(m/z)* 225 (M^{+}, 60), 178 (100), 152 (23), 76(12).

1,2-Di((E)-styryl)benzene (85):



Catalyst Solution: A solution of palladium acetate (0.0023 g, 0.0105 mmol, 1.0 mol %) and **34** (0.0049 g, 0.026 mmol, 2.5 mol%) was prepared in DMA:Water (1:2, 5 mL). The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask 1,2-dibromobenzene **84** (0.25 g, 1.05 mmol), dry K_2CO_3 (0.59 g, 4.23 mmol), TBAB (0.067 g, 0.21 mmol, 20 mol%) were mixed in DMA:Water (1:2, 5 mL). Then the solution was heated up to 60 ^{o}C and styrene (0.163 g, 1.57 mmol) was added. After 15 mins temperature was raised to 90 ^{o}C and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 120 ^{o}C for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **85** (0.173 g, 58%) as light yellow solid.

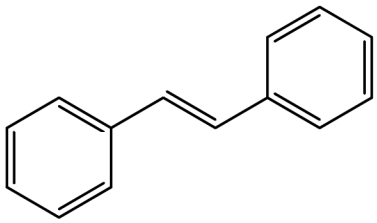
M.P. 115 ^{o}C (Lit.[54] 111-112 ^{o}C)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.60 – 7.58 (m, 2H), 7.54 – 7.51 (m, 4H), 7.46 (d, J = 16.4 Hz, 2H), 7.38 – 7.34 (m, 4H), 7.30 – 7.24 (m, 4H), 7.00 (d, J = 16.4 Hz, 2H).

IR (KBr): 3086, 3053, 3019, 1600, 1491, 1213, 1158, 1071, 956, 758, 691 cm.$^{-1}$

MS (EI): *(m/z)* 223 (M^{+1}, 8.9), 282 (M^{+}, 38), 191 (100), 178(5.6), 91 (12.3).

(E)-1,2-Diphenylethene or trans-Stilbene (60):



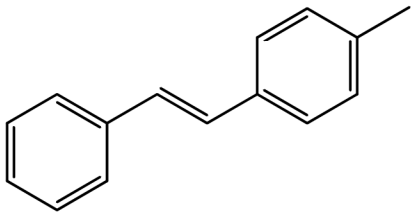
Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.006 mmol, 0.5 mol%) and **34** (0.0029 g, 0.0153 mmol, 1.25mol%) was prepared in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask Iodobenzene (**59**) (0.25 g, 1.2 mmol), K_2CO_3 (0.338 g, 2.45 mmol), CTAB (0.045 g, 0.123 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 ^oC and styrene **66** (0.19 g, 1.838 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **60** (0.192 g, 87%) as white crystals.

M.P. 120 - 122 ^oC (Lit.[55] 121 - 123 ^oC).

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 4H), 7.42 – 7.38 (m, 4H), 7.32 – 7.28 (m, 2H), 7.16 (s, 2H).

(E)-1-Methyl-4-styrylbenzene (87):



Initially, in a round bottom flask catalyst solution was prepared by mixing palladium acetate (0.0014 g, 0.006 mmol, 0.5 mol%) and **34** (0.0029 g, 0.0153 mmol, 1.25 mol%) was prepared in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask iodobenzene **59** (0.250 g, 1.2 mmol), K_2CO_3 (0.338 g, 2.45 mmol), CTAB (0.045 g, 0.123 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 ^oC and 4-methylstyrene **86** (0.21 g, 1.838 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **87** (0.209 g, 88%) as white crystals.

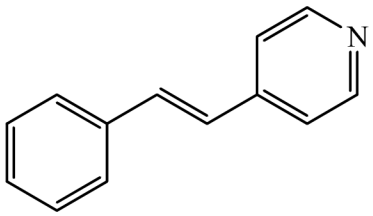
M.P. 112 - 114 ^oC (Lit.[56] 114 - 116 ^oC)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.54 – 7.52 (m, 2H), 7.44 (d, *J* = 8 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.29 – 7.25 (m, 1H), 7.20 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 16.2 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H), 2.38 (S, 3H).

IR (KBr): 2925, 1588, 1355, 1117, 980, 714 $cm.^{-1}$

MS (EI): *(m/z)* 195 (M^+, 93.5), 179 (100), 89 (11), 76 (5.3).

(E)-4-Styrylpyridine (89):



Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.006 mmol, 0.5 mol%) and **34** (0.0029 g, 0.0153 mmol, 1.25mol%) was prepared in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask iodobenzene **59** (0.250 g, 1.23 mmol), K_2CO_3 (0.338 g, 2.46 mmol), CTAB (0.045 g, 0.123 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 ^oC and 4-vinylpyridine **88** (0.154 g, 1.47 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **89** (0.208 g, 94%) as off white solid.

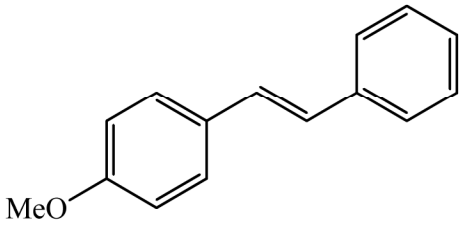
M.P. 126 - 128 ^{o}C (Lit.[57] 129 ^{o}C)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.60 – 8.58 (dd, *J* = 1.6 & 4.8 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.57 – 7.55 (m, 2H), 7.32 (d, *J* = 16.2 Hz, 1H), 7.04 (d, *J* = 16.2 Hz, 1H).

IR (KBr): 3022, 1590, 1564, 1485, 1309, 1187, 1022, 962, 800, 752 cm.$^{-1}$

MS (EI): *(m/z)* 180 (M^{-1}, 100), 181 (M^{+}, 80.57), 97 (29), 71 (21)

(E)-1-Methoxy-4-styrylbenzene (67):



Catalyst Solution: A solution of palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol%) and **34** (0.0025 g, 0.0132 mmol, 1.25 mol%) was prepared in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask 4-iodoanisole (**65**) (0.250 g, 1.06. mmol), K_2CO_3 (0.29 g, 2.13 mmol), CTAB (0.039 g, 0.106 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 ^{o}C and styrene **66** (0.166 g, 1.60 mmol) was added. After 15 mins temperature was raised to 90 ^{o}C and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^{o}C for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 X 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **67** (0.184 g, 82%) as off white solid.

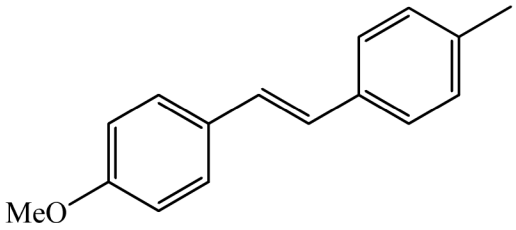
M.P. 134 - 135 ^{o}C (Lit..[47] 135 - 136 ^{o}C).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.50 - 7.44 (m, 4 H), 7.36 - 7.32 (m, 2H), 7.25 - 7.23 (m, 1H), 7.07 (d, *J* = 16.31 Hz, 1H), 6.97 (d, *J* = 16.31 Hz, 1H), 6.91 - 6.89 (m, 2H), 3.83 (s, 3H).

IR (KBr): 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm.$^{-1}$

MS (EI): *(m/z)* 210 (M^{+}, 100), 179 (14), 167 (27), 105 (7), 76(3).

(E)-1-Methoxy-4-(4-methylstyryl)benzene (90):



Initially, in a oven dry round bottom flask catalyst solution was prepared by mixing palladium acetate (0.0012 g, 0.0053 mmol, 0.5 mol%) and **34** (0.0025 g, 0.0132 mmol, 1.25 mol%) in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

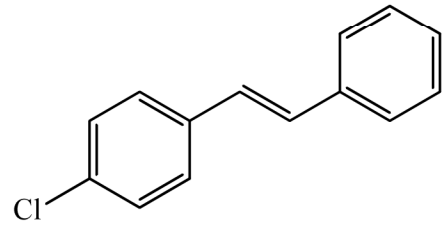
In another two neck round bottom flask 4-iodoanisole **65** (0.250 g, 1.06. mmol), K_2CO_3 (0.295 g, 2.13 mmol), CTAB (0.039 g, 0.106 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 ^oC and 4-methylstyrene **86** (0.190 g, 1.60 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **90** (0.228 g, 95%) as off white solid.

M.P.160 ^oC (Lit.[56]160-162 ^oC)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45 – 7.42 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 16.2 Hz), 6. 94 (d, *J* = 16.2 Hz, 1H), 6.90 - 6.88 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H).

IR (KBr): 3014, 2913, 2840, 1605, 1510, 1250, 1172, 1037, 967, 825 $cm.^{-1}$

(E)-1-Chloro-4-styrylbenzene (92):



Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0065 mmol, 0.5 mol%) and **34** (0.0031 g, 0.0162 mmol, 1.25mol%) was prepared in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask 4-bromochlorobenzene **91** (0.250 g, 1.30 mmol), K_2CO_3 (0.36 g, 2.61 mmol), CTAB (0.047 g, 0.129 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 ^oC and styrene **66** (0.203 g, 1.96 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^oC for 40 hrs. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 x 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent to afford **92** (0.200 g, 71%) as white crystals.

M.P. 130 ^oC (Lit.[56] 129-130 ^oC)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.54 – 7.52 (m, 2H), 7.47 – 7.45 (m, 2H), 7.41 – 7.30 (m, 5H), 7.11 (d, *J* = 16.2 Hz, 1H), 7.06 (d, *J* = 16.2 Hz, 1H).

IR (KBr): 2925, 1588, 1355, 1117, 980, 714 $cm.^{-1}$

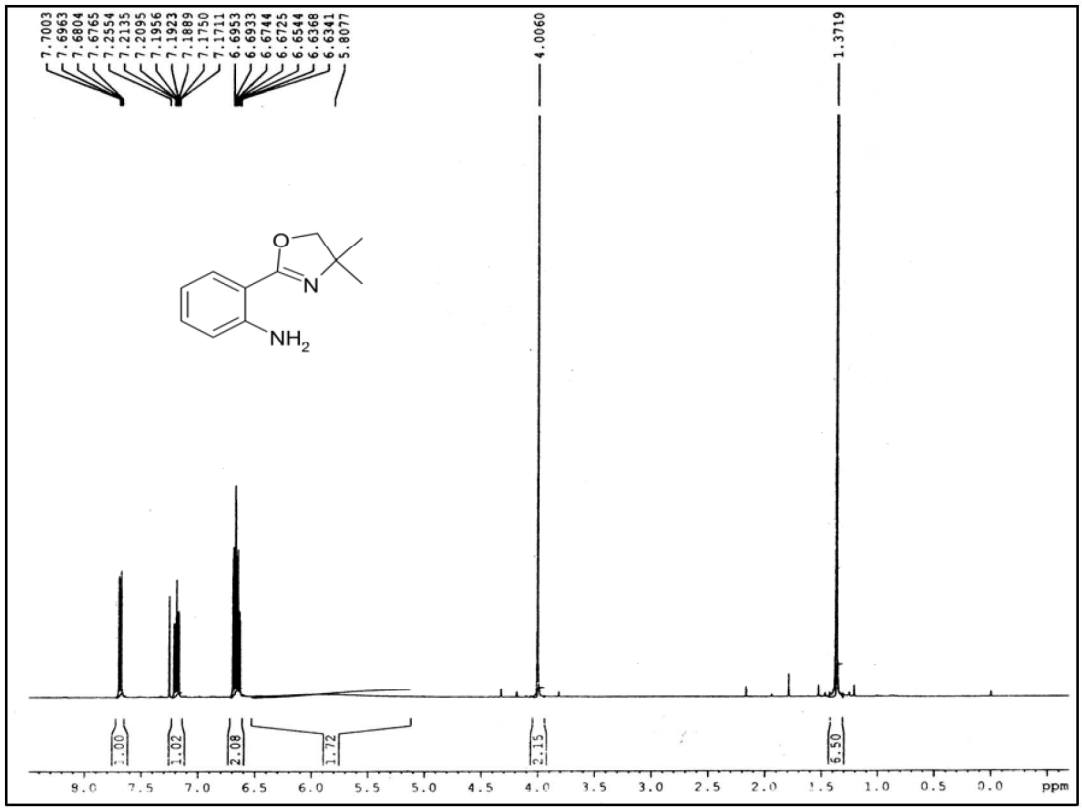
MS (EI): *(m/z)* 214 (M^+, 80), 179 (100), 89 (33), 76 (20).

Recycle experiment:

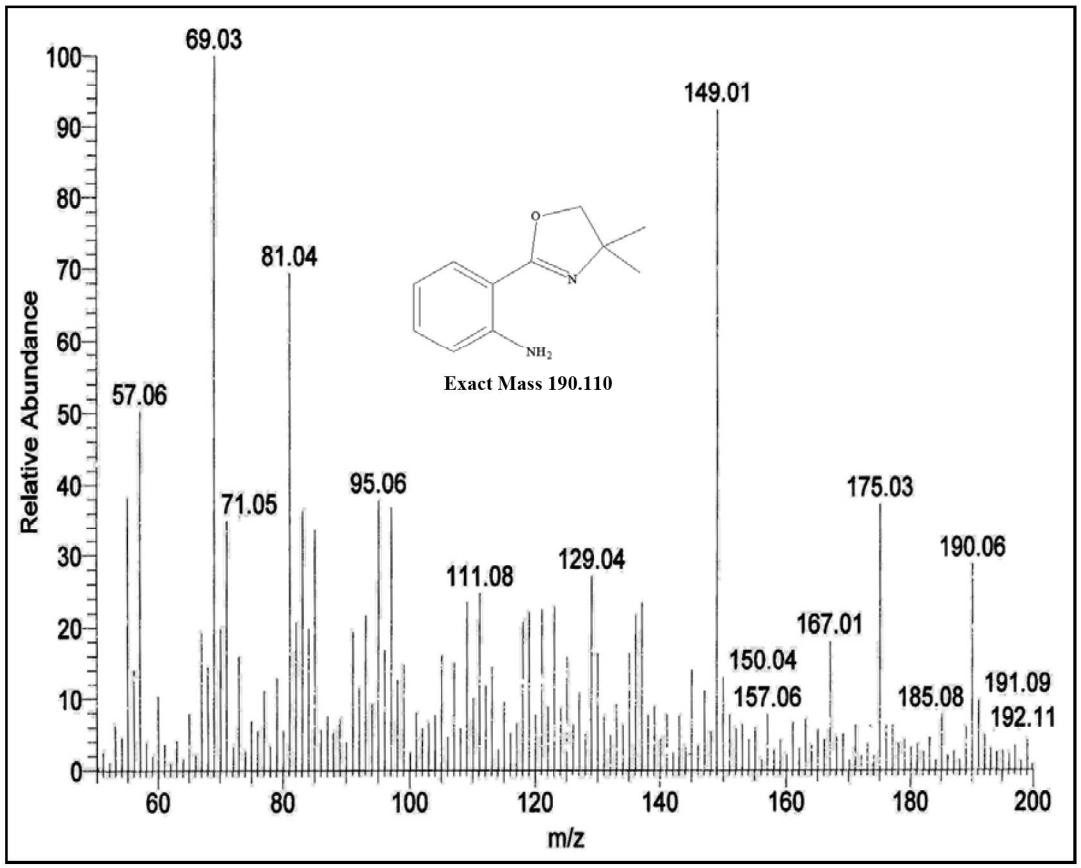
Catalyst Solution: A solution of palladium acetate (0.0014 g, 0.0613 mmol, 0.5 mol%) and **34** (0.0029 g, 0.0153 mmol, 1.25 mol%) was prepared in water (5mL). The mixture was sonicated in ultrasonic water bath for 5 min.

In another two neck round bottom flask iodobenzene **59** (0.250 g, 1.2 mmol), K_2CO_3 (0.338 g, 2.45 mmol), CTAB (0.044 g, 0.123 mmol) in water (5mL) were mixed. Then the solution was heated up to 60 ^oC and styrene **66** (0.19 g, 1.84 mmol) was added. After 15 mins temperature was raised to 90 ^oC and to this mixture the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 ^oC for 40 hrs. The cooled mixture was poured in water (10 mL), extracted with petroleum ether (40 mL) for 7 to 8 times (till complete removal of product from aqueous layer, as indicated by TLC). The combined organic layer was washed with water and dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent. Aqueous layer was collected in another round bottom flask quantitatively which contain catalyst solution. To this solution all the other starting materials for next cycle were added and the reaction was conducted. The same procedure was employed for the recycle study.

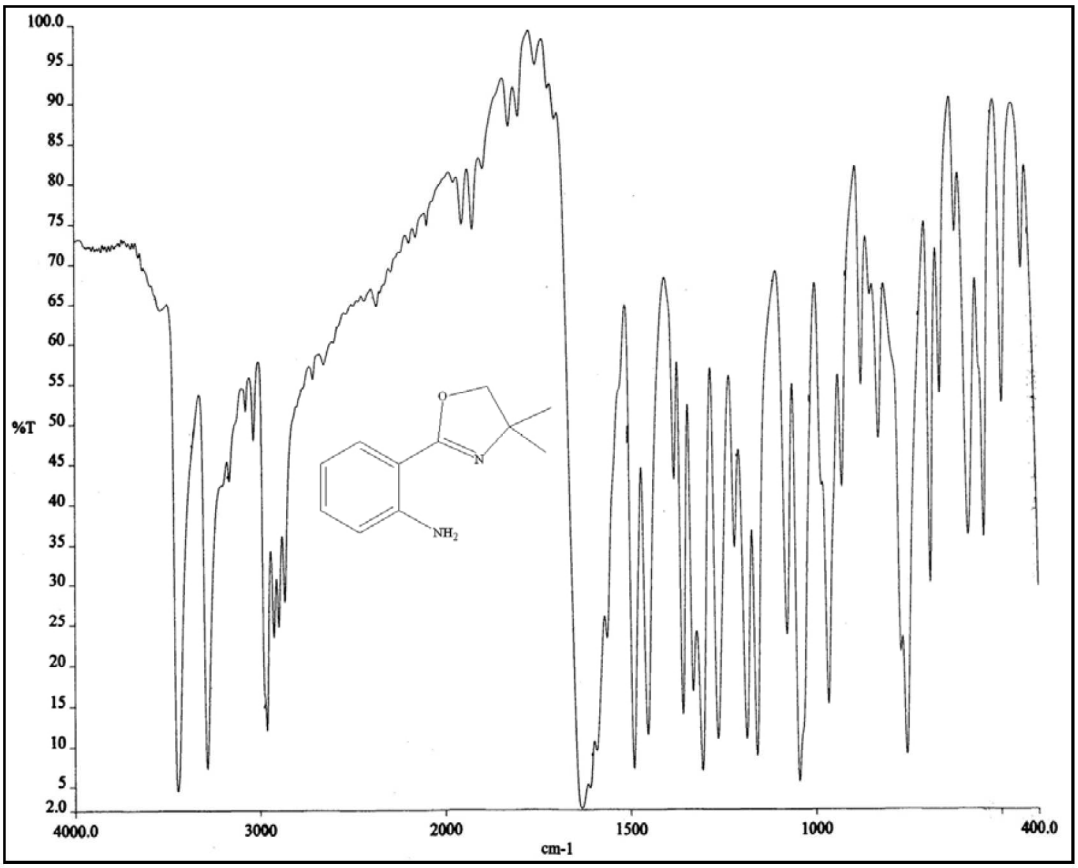
Spectral Data for Part-I: Synthesis of Oxazolinyl Ligands



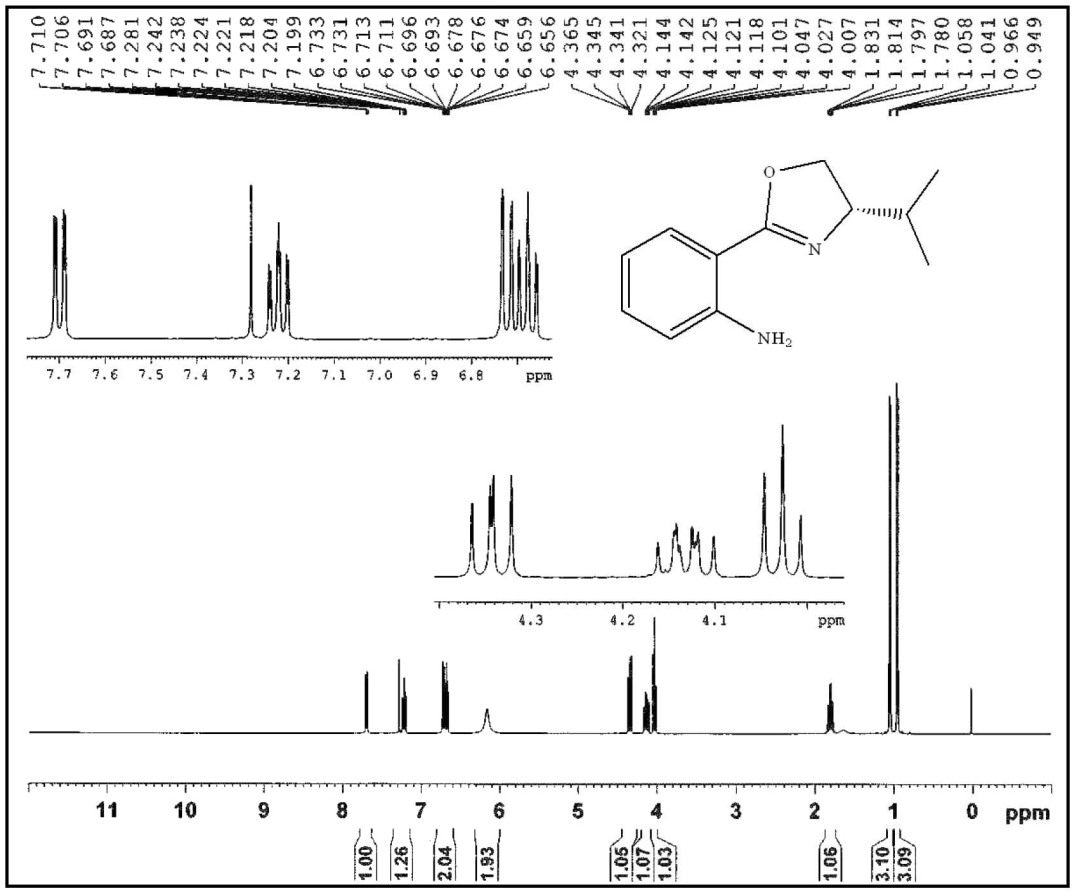
^{1}H-NMR spectra of compound 34 (400MHz, $CDCl_3$)



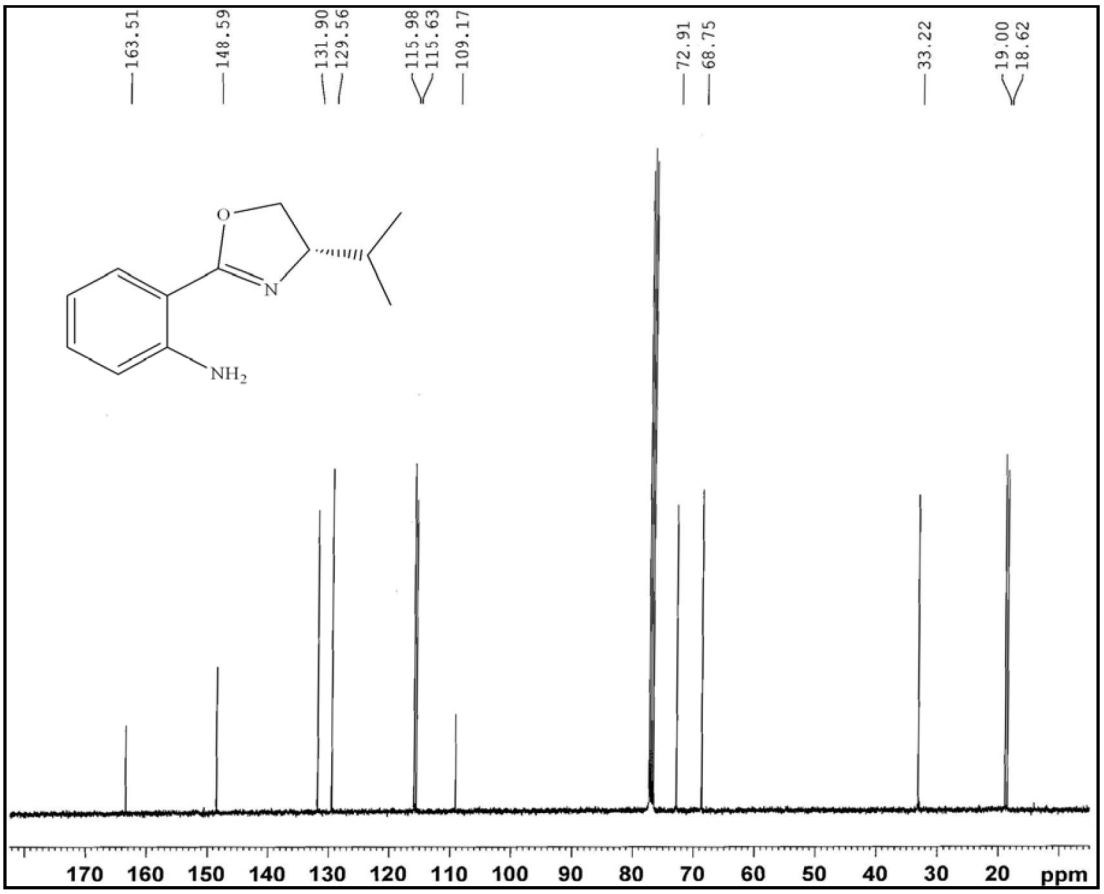
EI-Mass Spectra of Compound 34



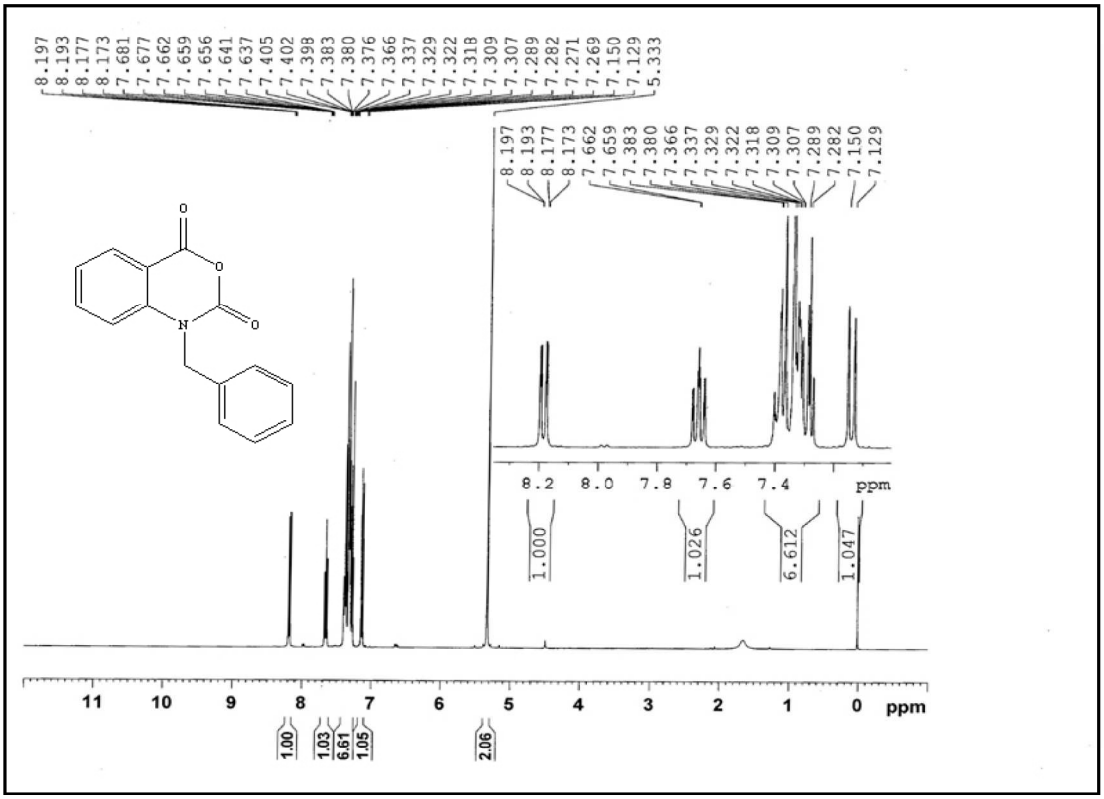
IR Spectra of Compound 34



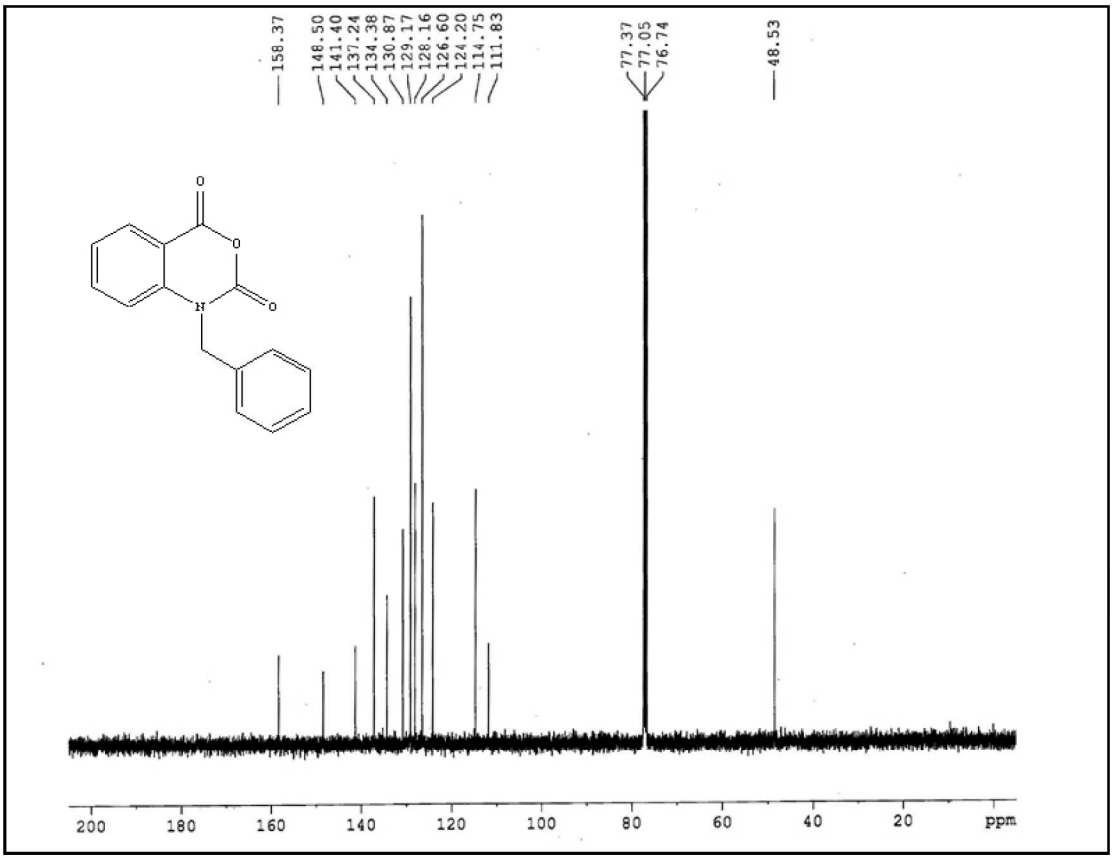
^{1}H-NMR spectra of compound 36 (400MHz, $CDCl_3$)



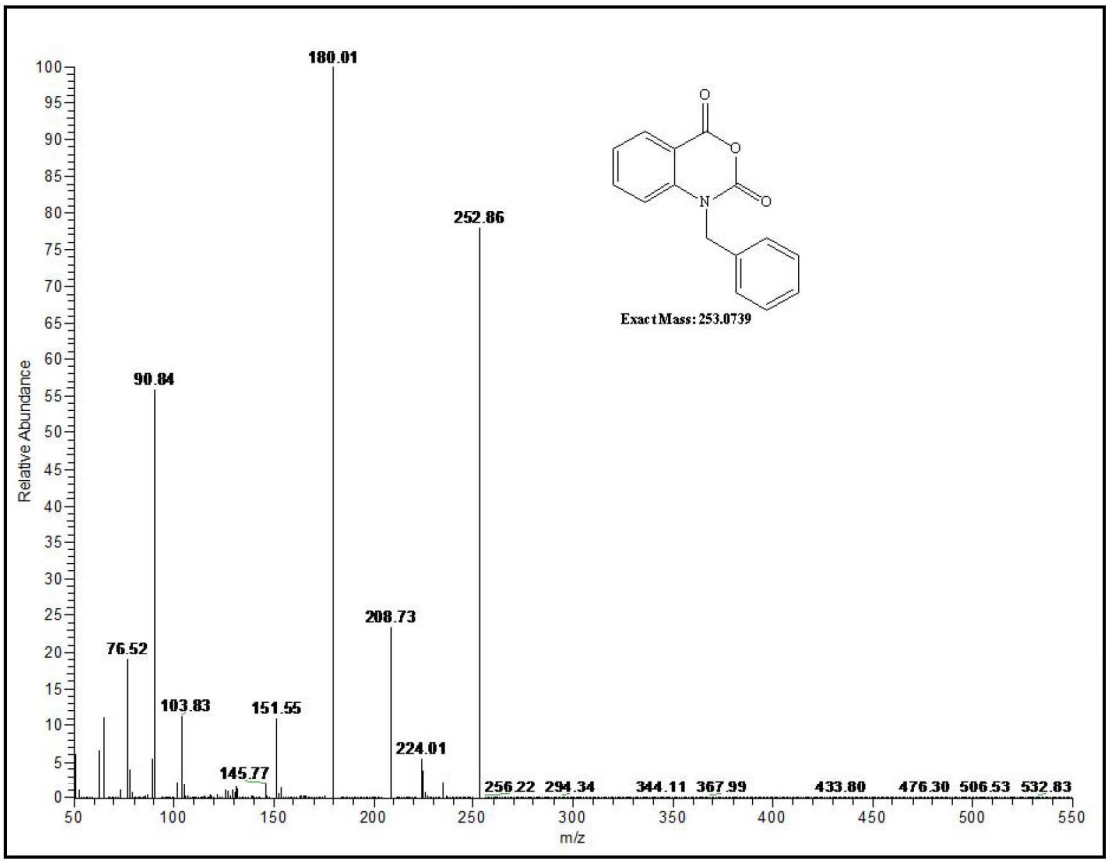
^{13}C-NMR of the compound 36 (100 MHz, $CDCl_3$)



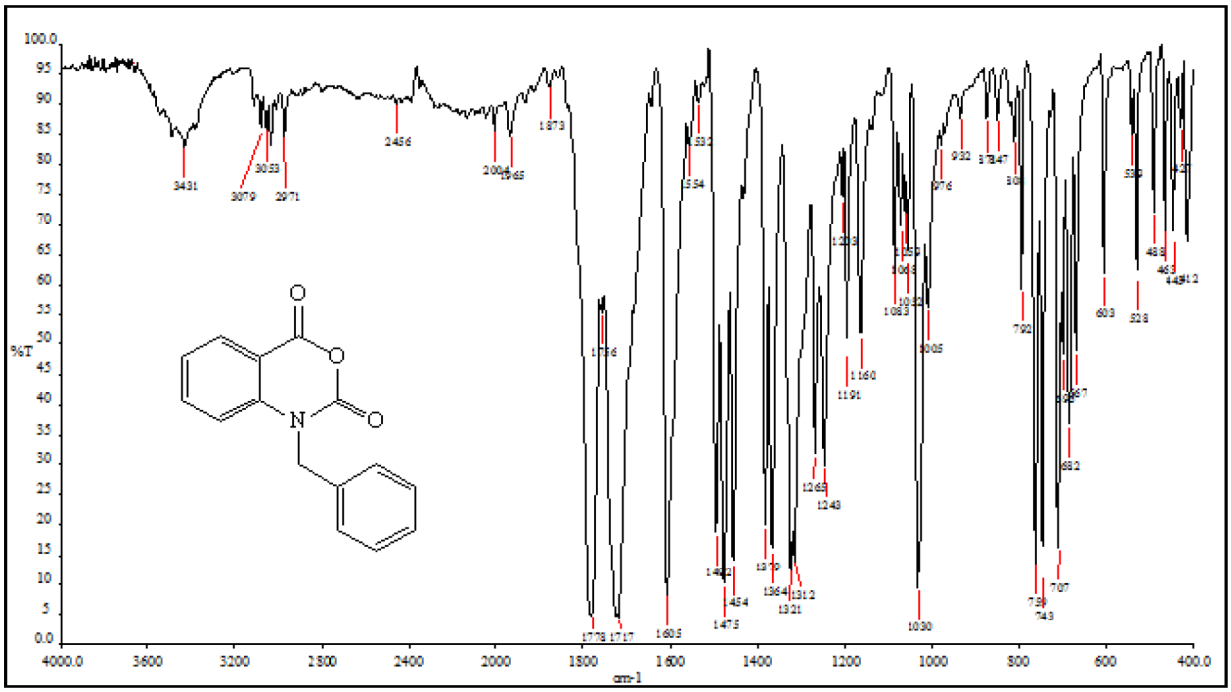
^{1}H-NMR spectra of compound 38 (400MHz, $CDCl_3$)



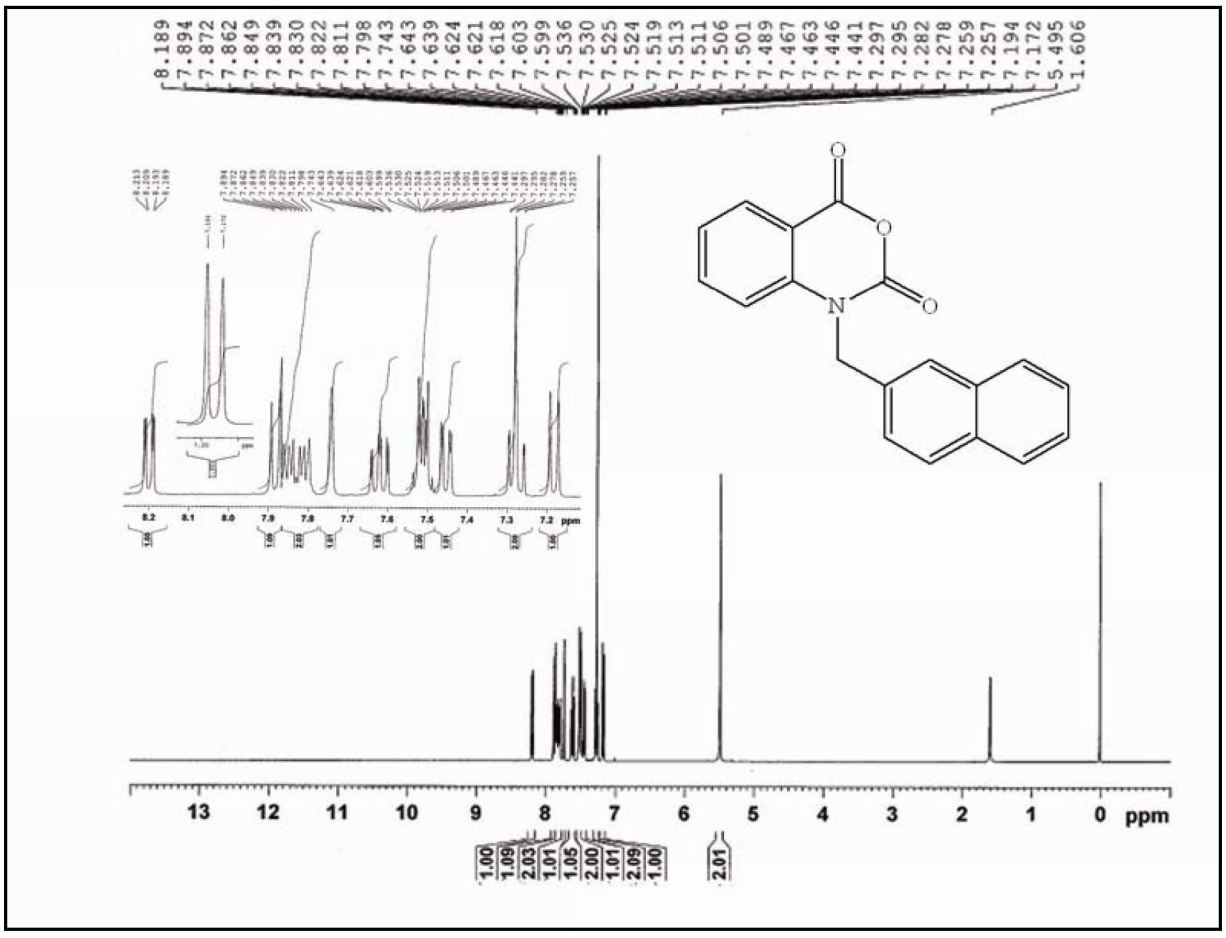
^{13}C-NMR of the compound 38 (100 MHz, $CDCl_3$)



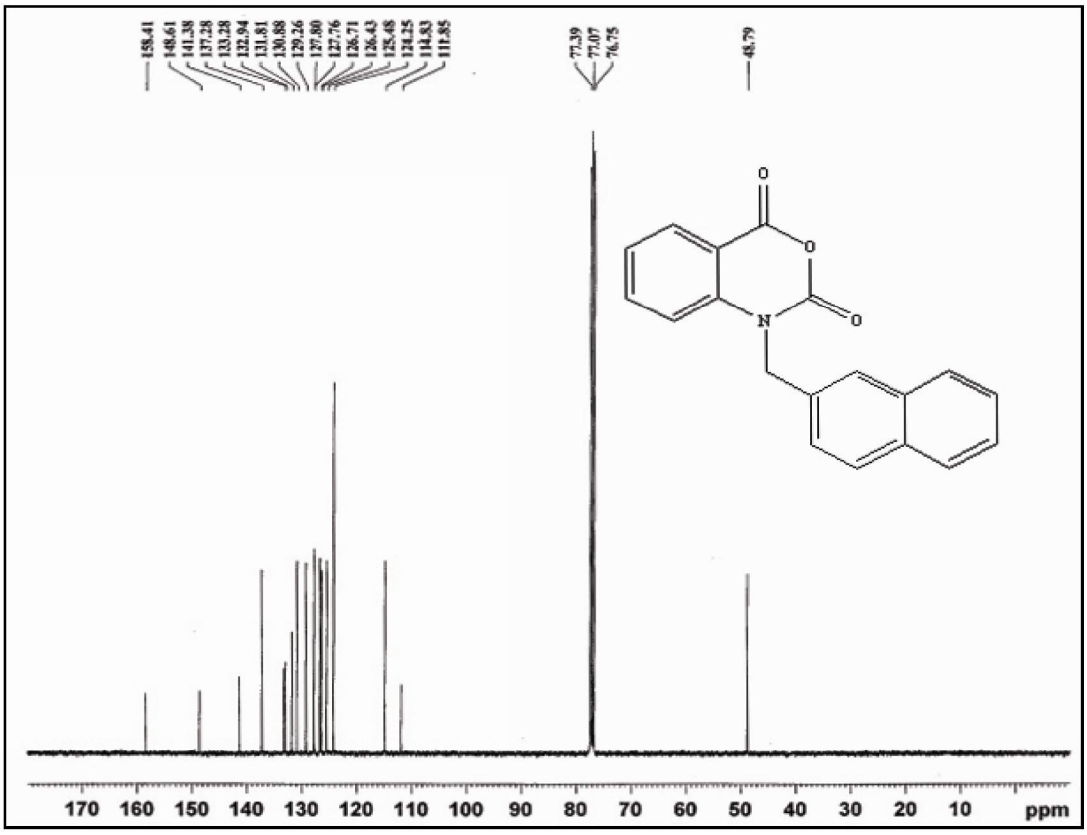
EI-MS spectra of Compound 38



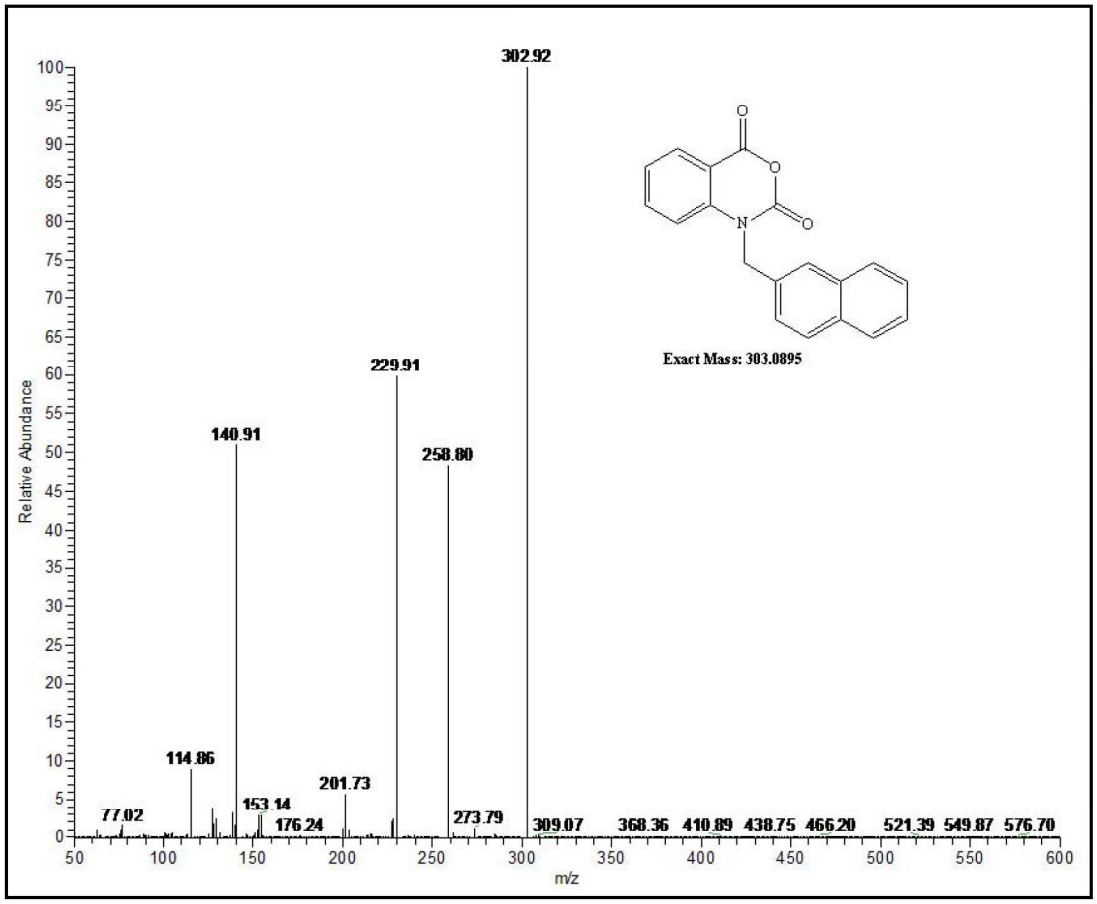
IR-spectra of Compound 38



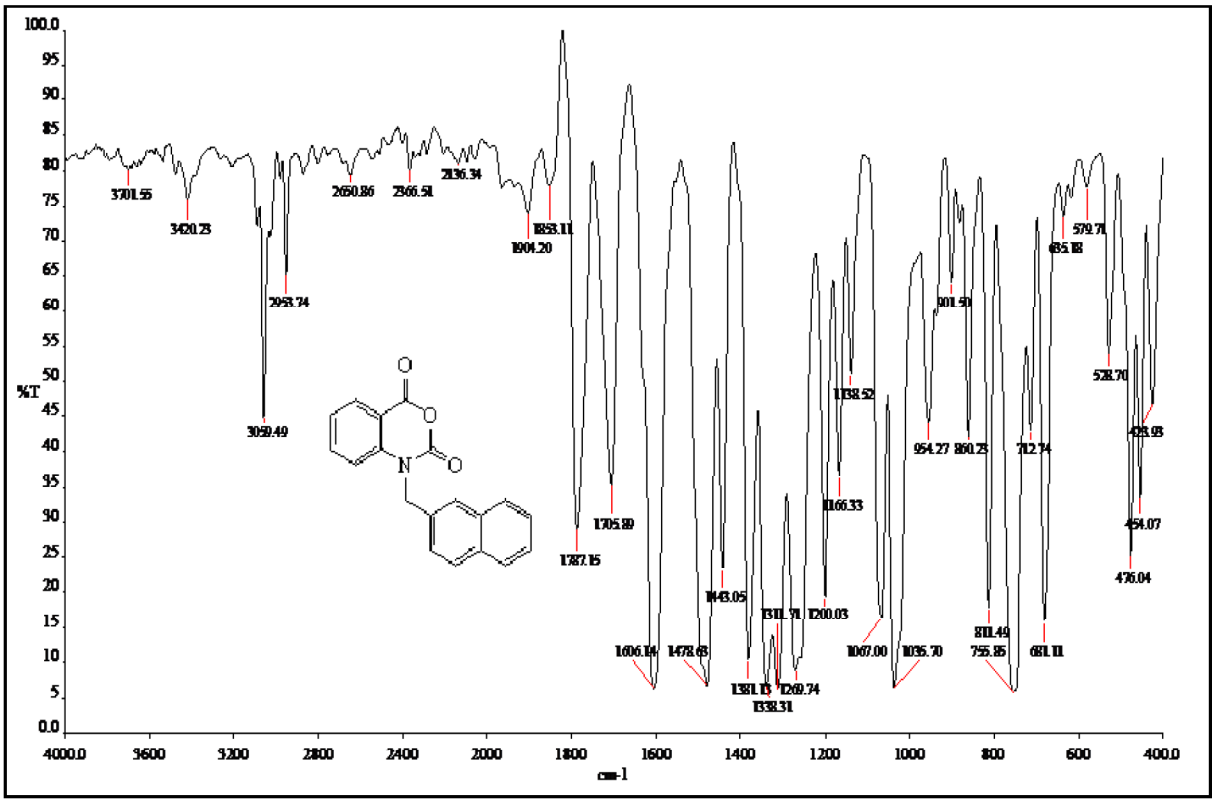
^{1}H-NMR spectra of compound 39 (400MHz, $CDCl_3$)



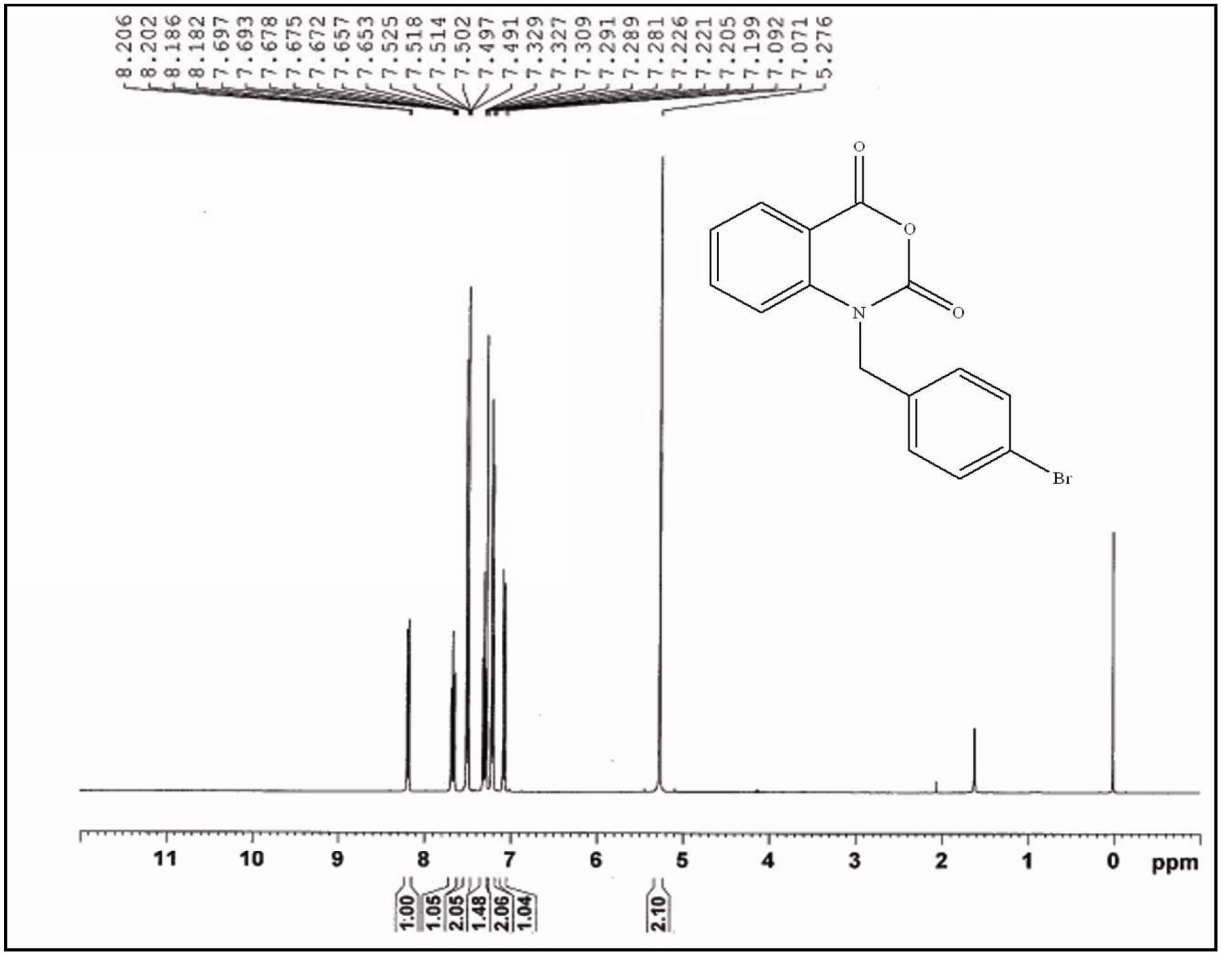
^{13}C-NMR of the compound 39 (100 MHz, $CDCl_3$)



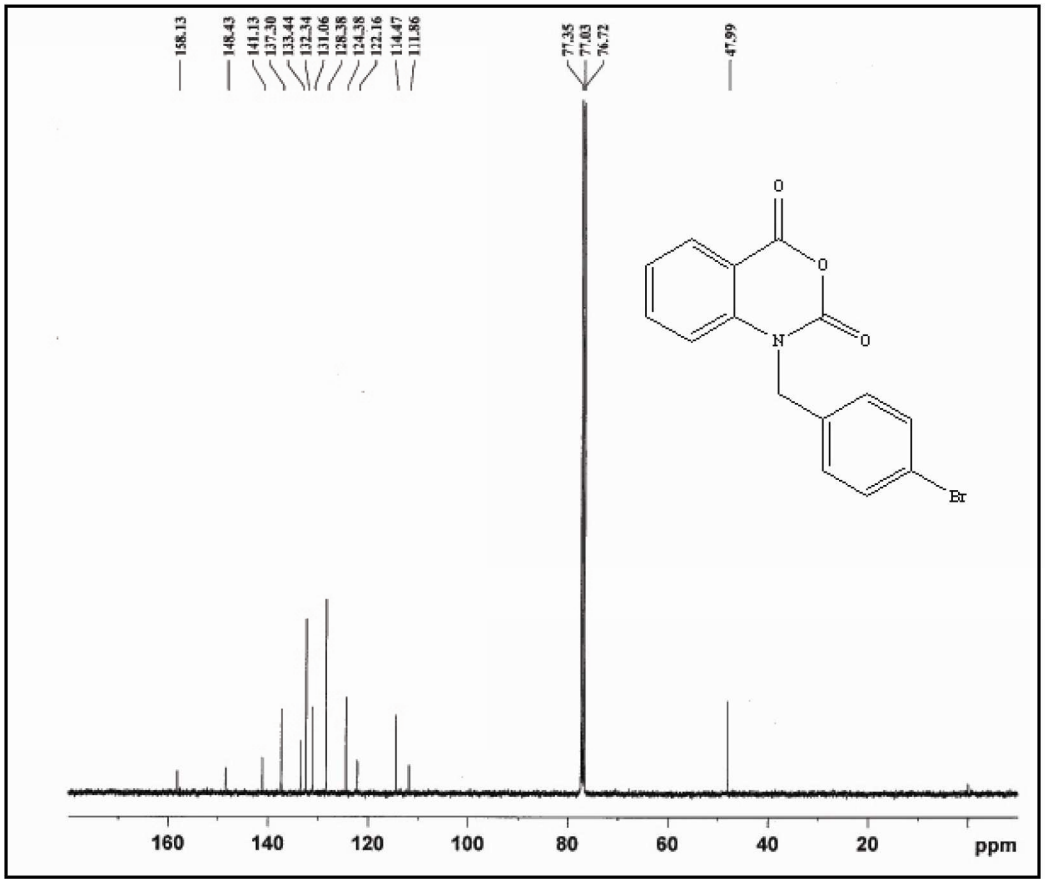
EI-Mass Spectra of Compound 39



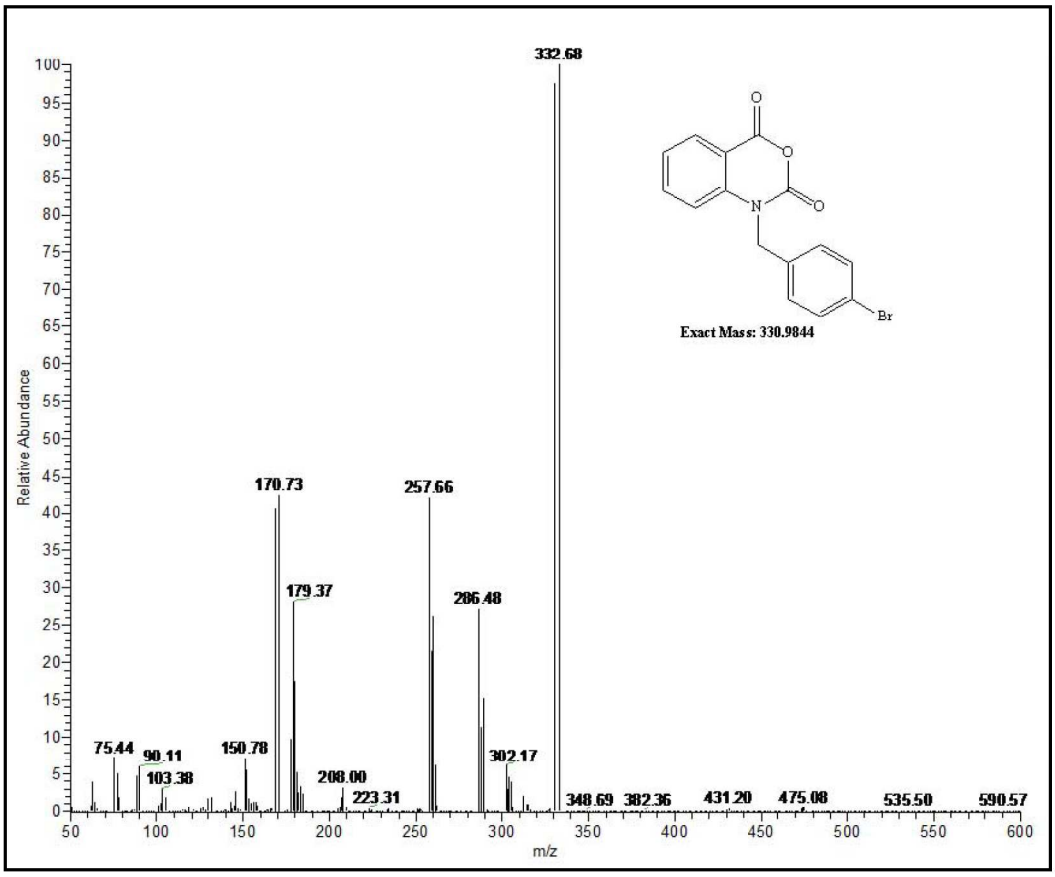
IR-spectra of Compound 39



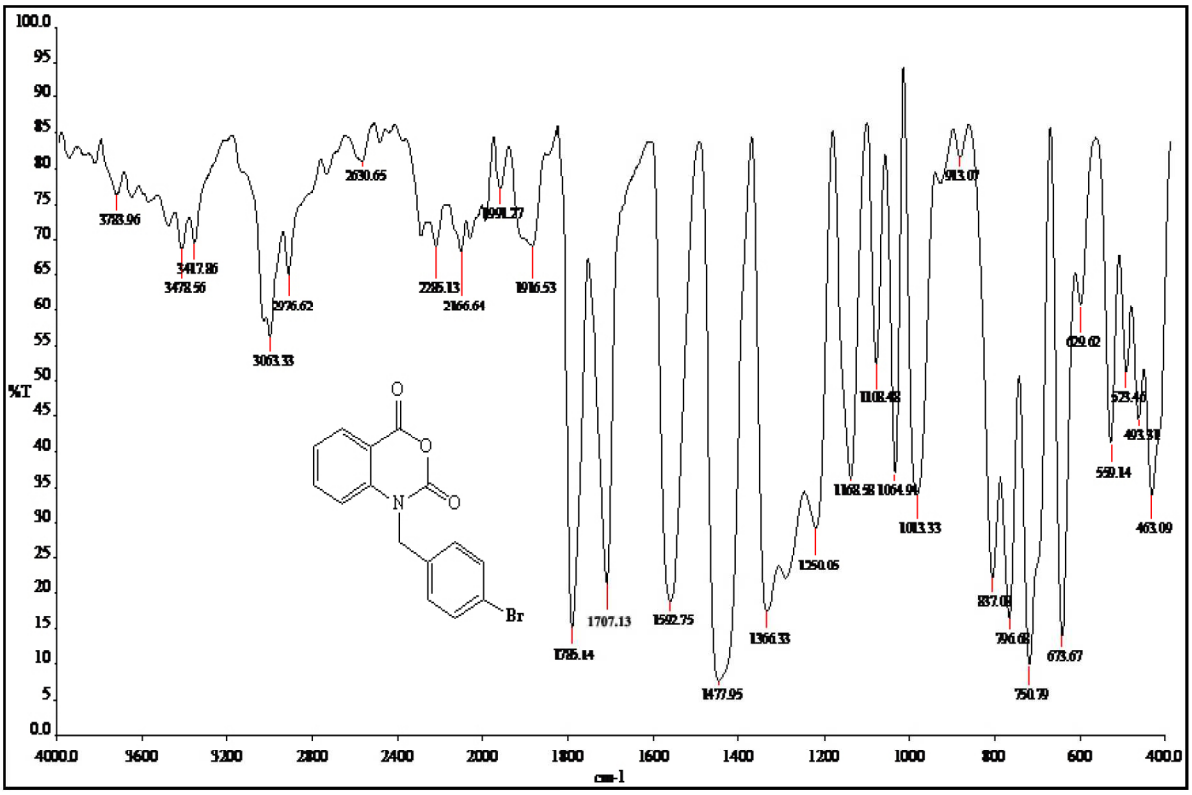
^{1}H-NMR spectra of compound 40 (400MHz, $CDCl_3$)



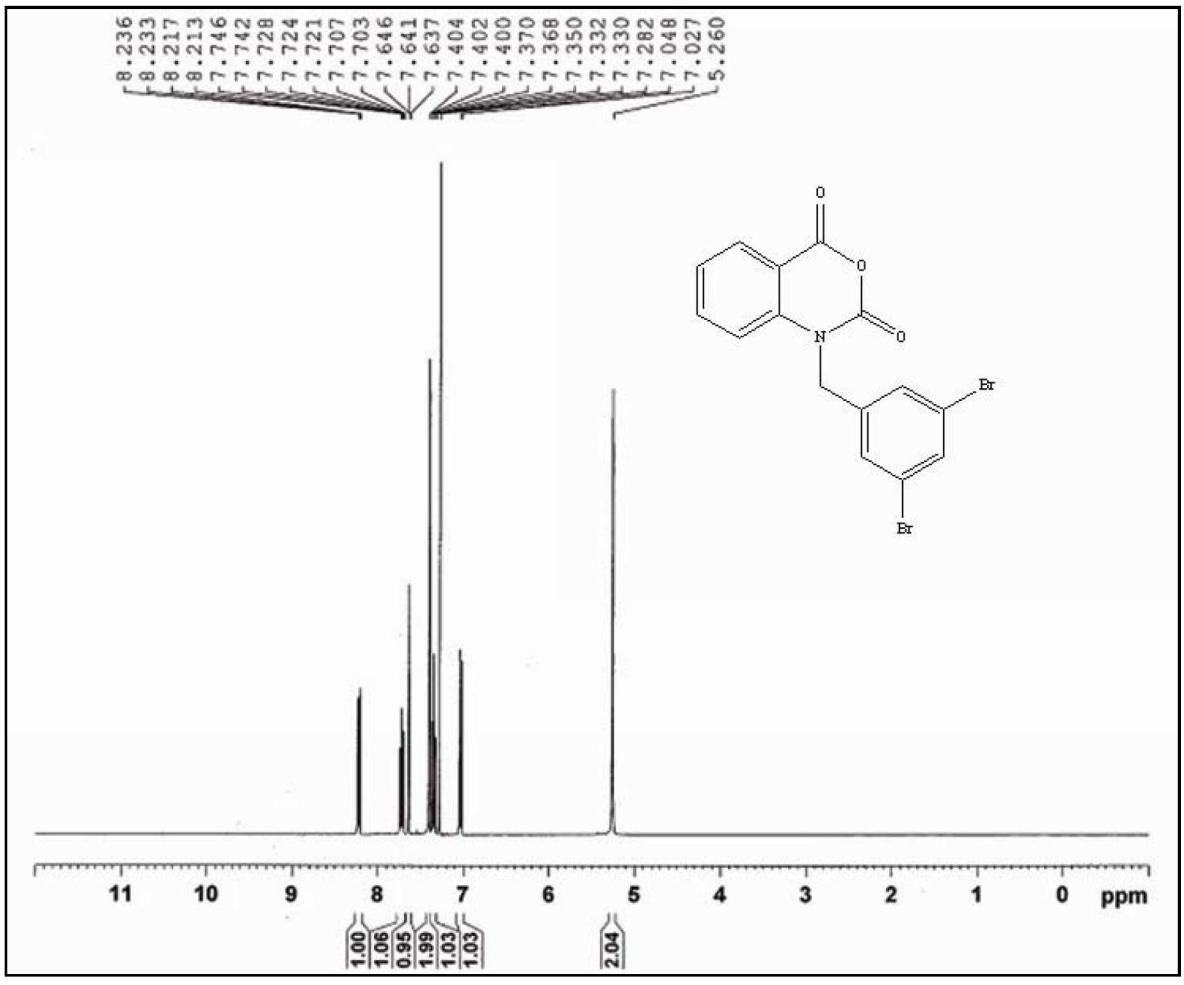
^{13}C-NMR of the compound 40 (100 MHz, $CDCl_3$)



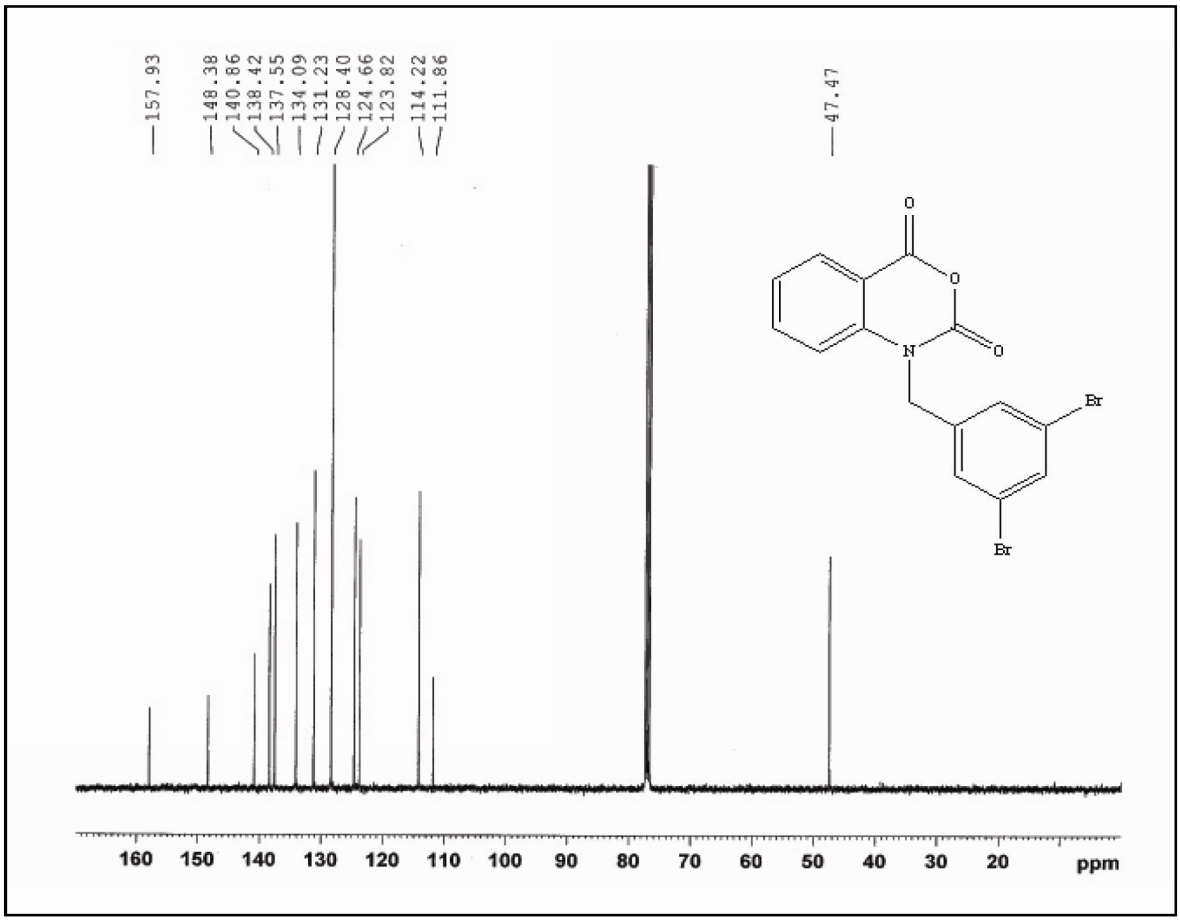
EI-Mass Spectra of Compound 40



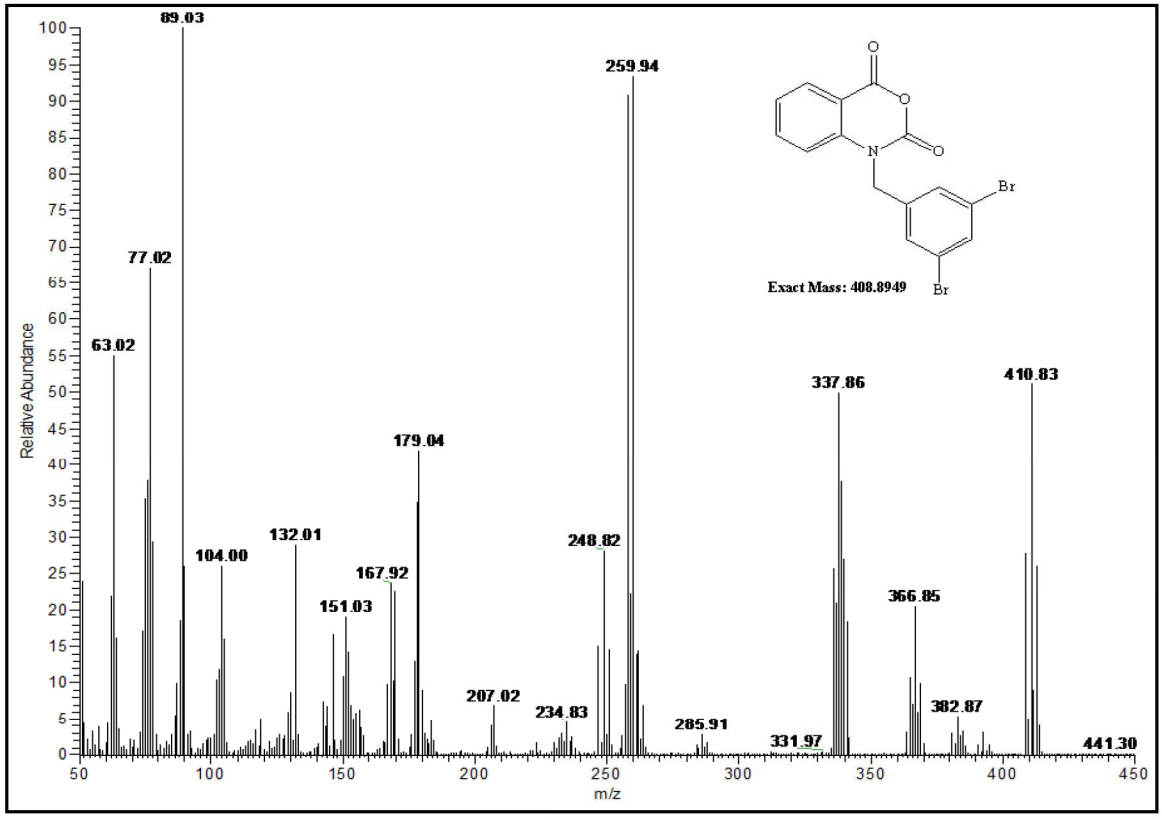
IR-spectra of Compound 40



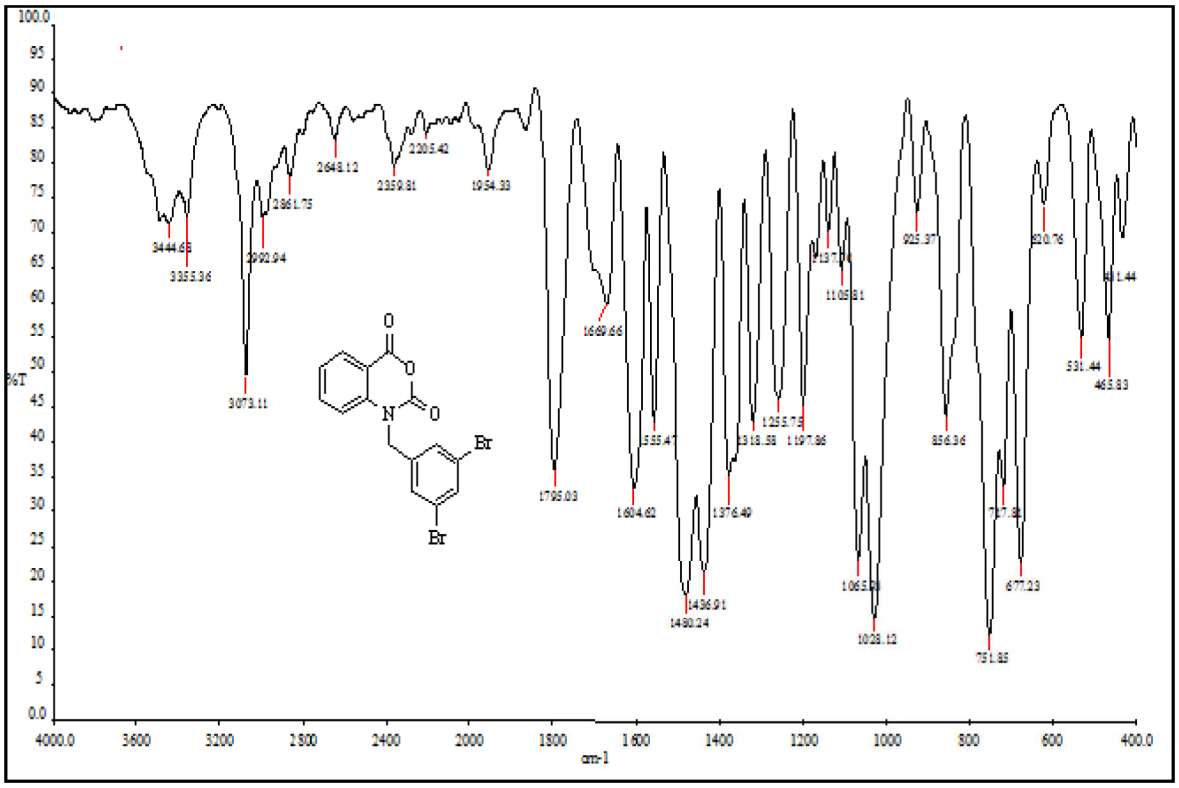
^{1}H-NMR spectra of compound 41 (400MHz, $CDCl_3$)



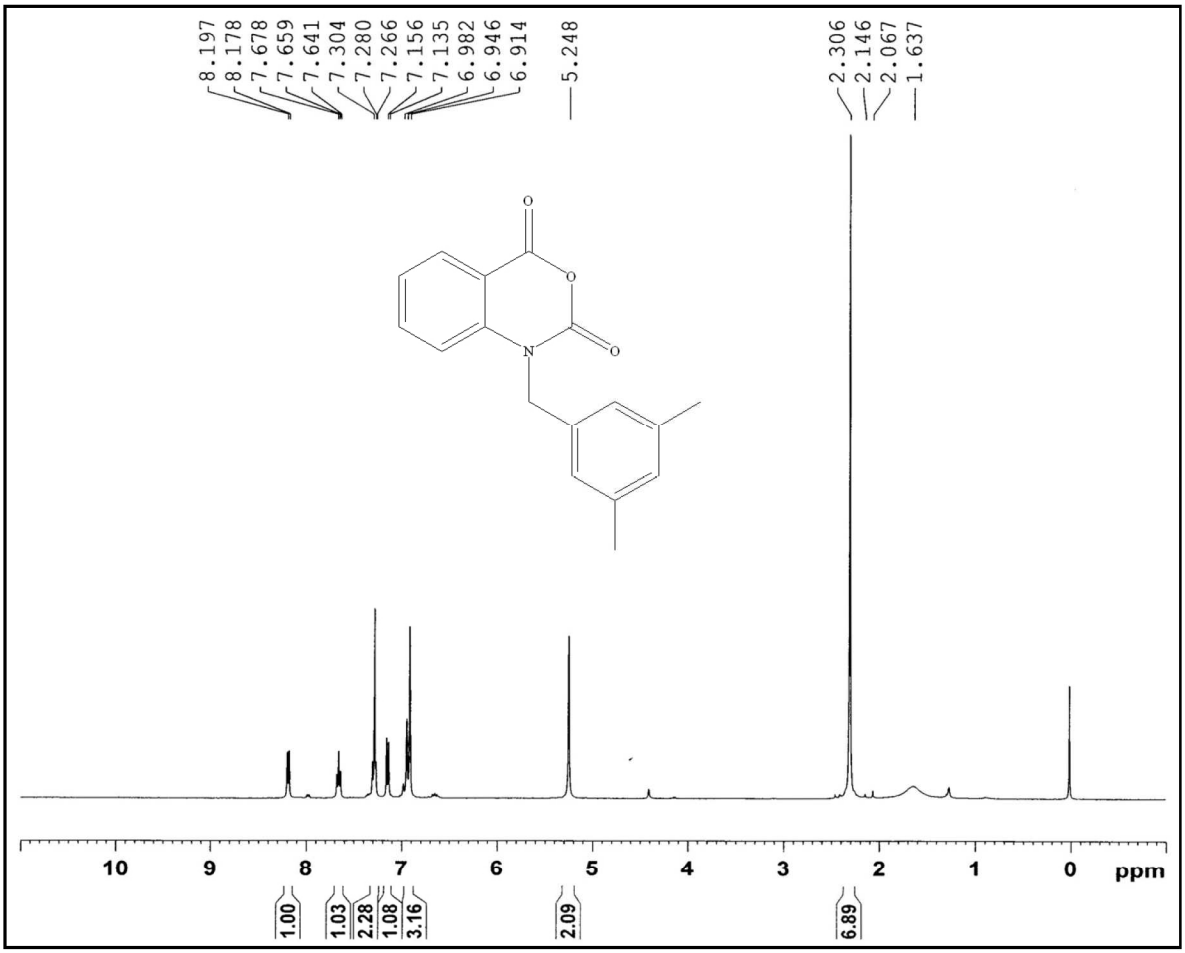
^{13}C-NMR of the compound 41(100 MHz, $CDCl_3$)



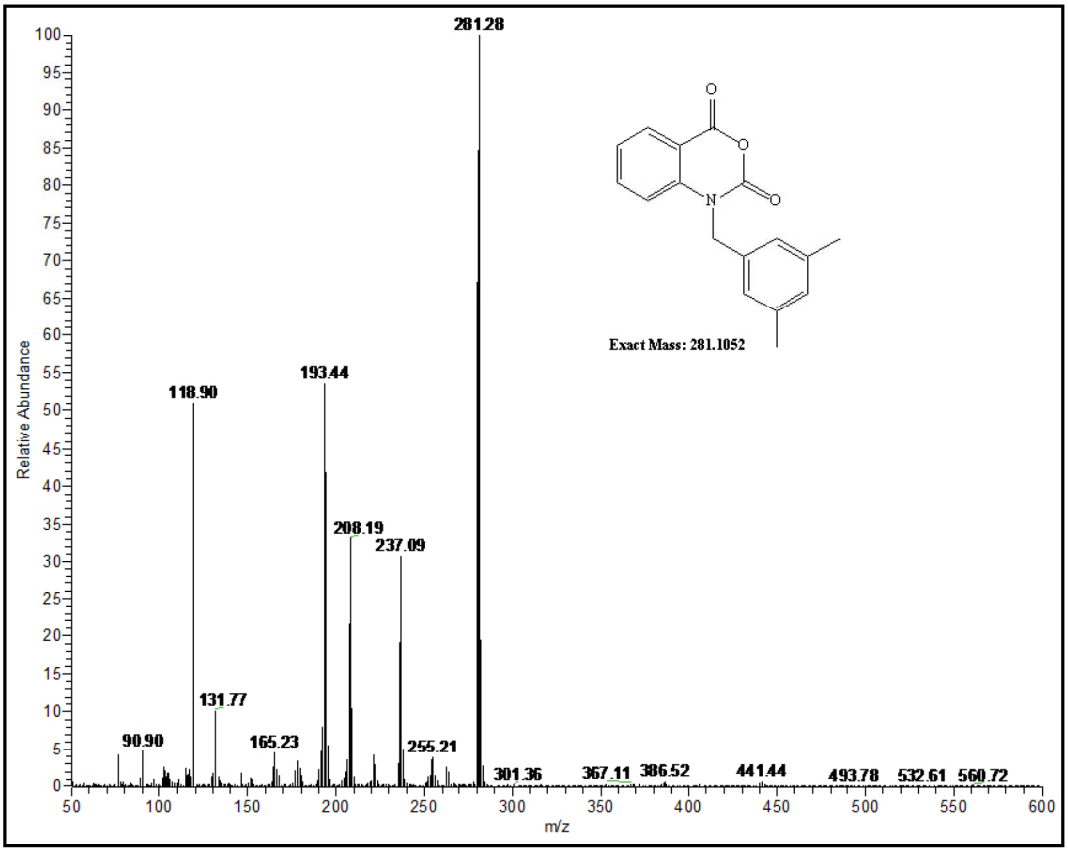
EI-Mass Spectra of Compound 41



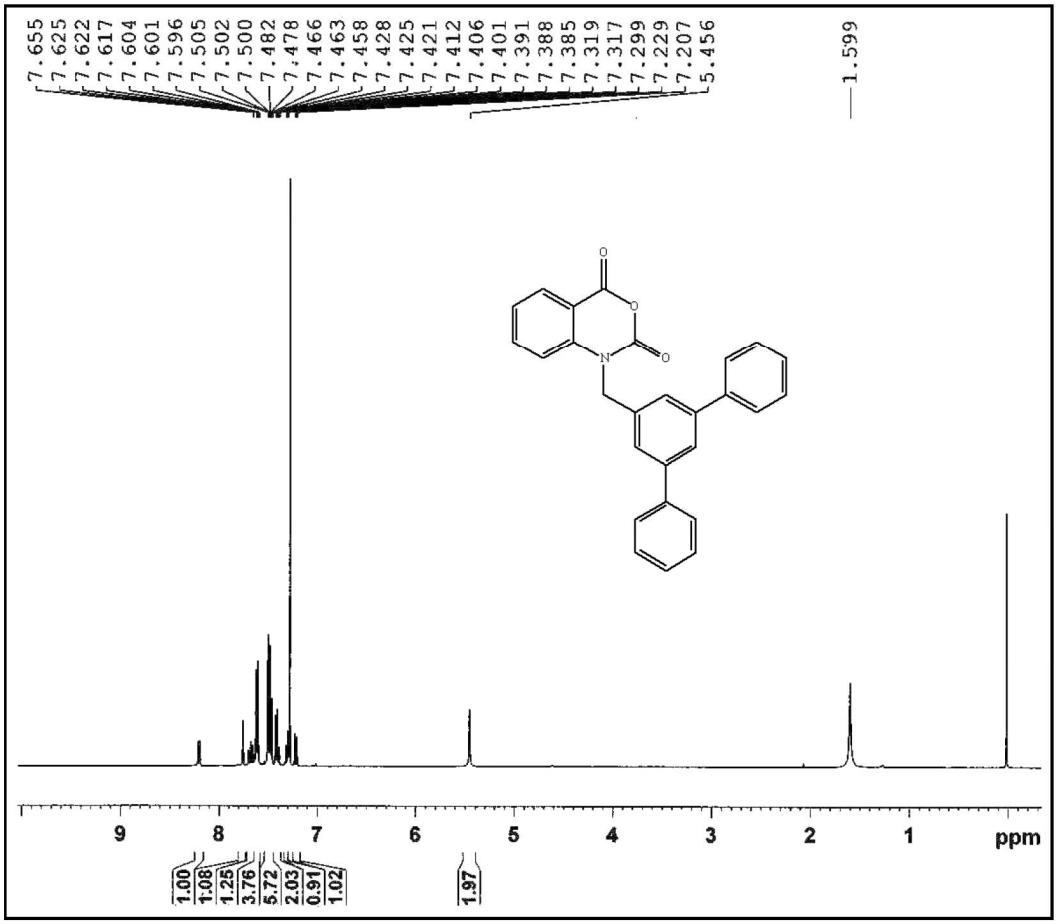
IR Spectra of Compound 41



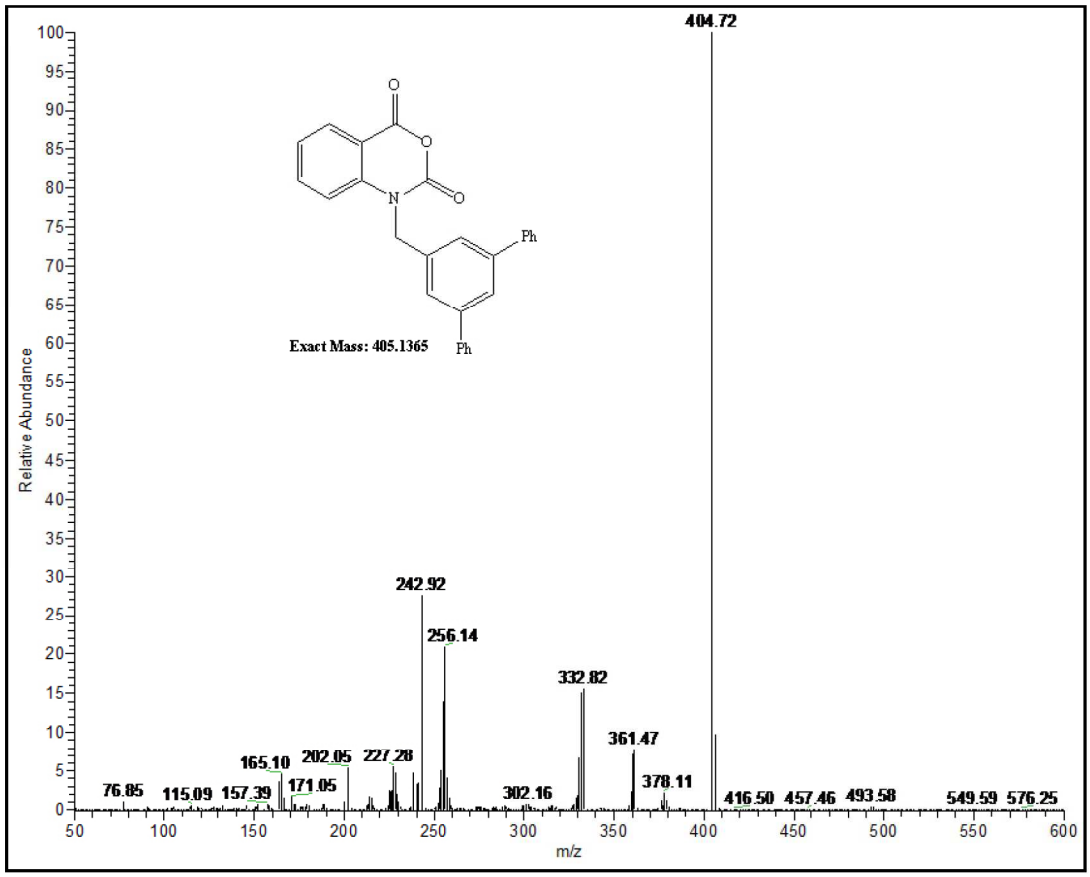
^{1}H-NMR spectra of compound 42 (400MHz, $CDCl_3$)



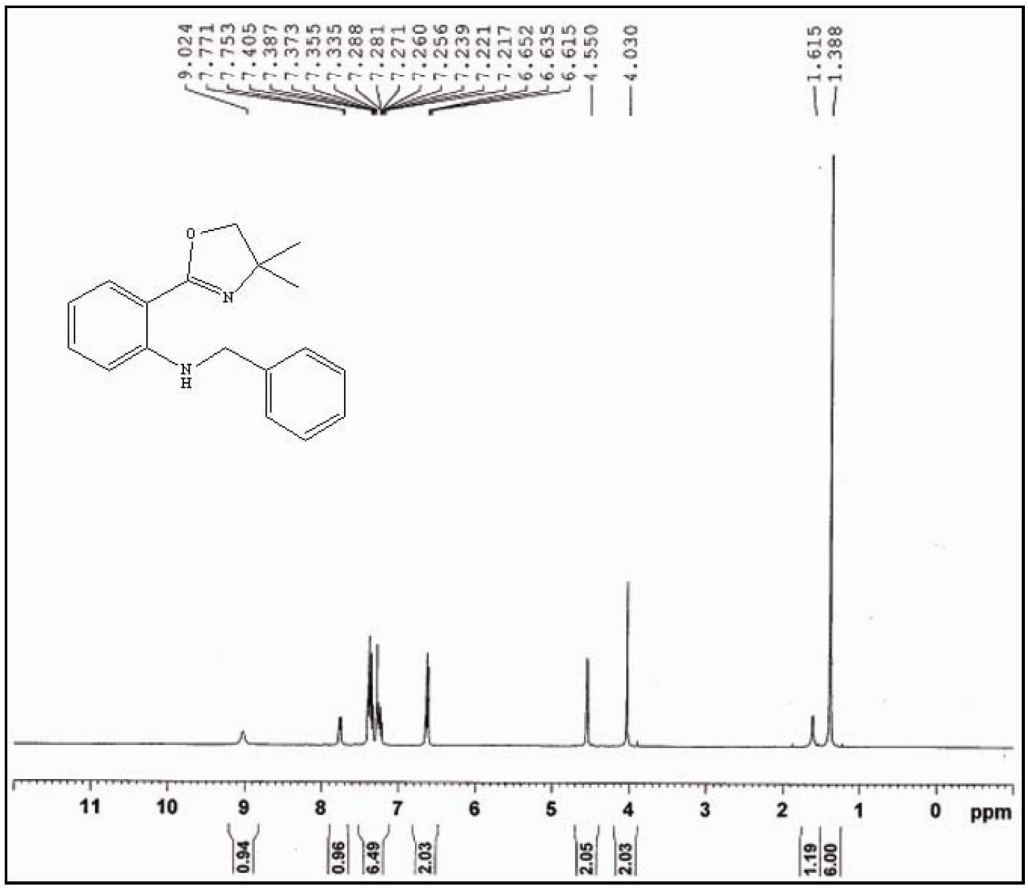
EI-Mass Spectra of Compound 42



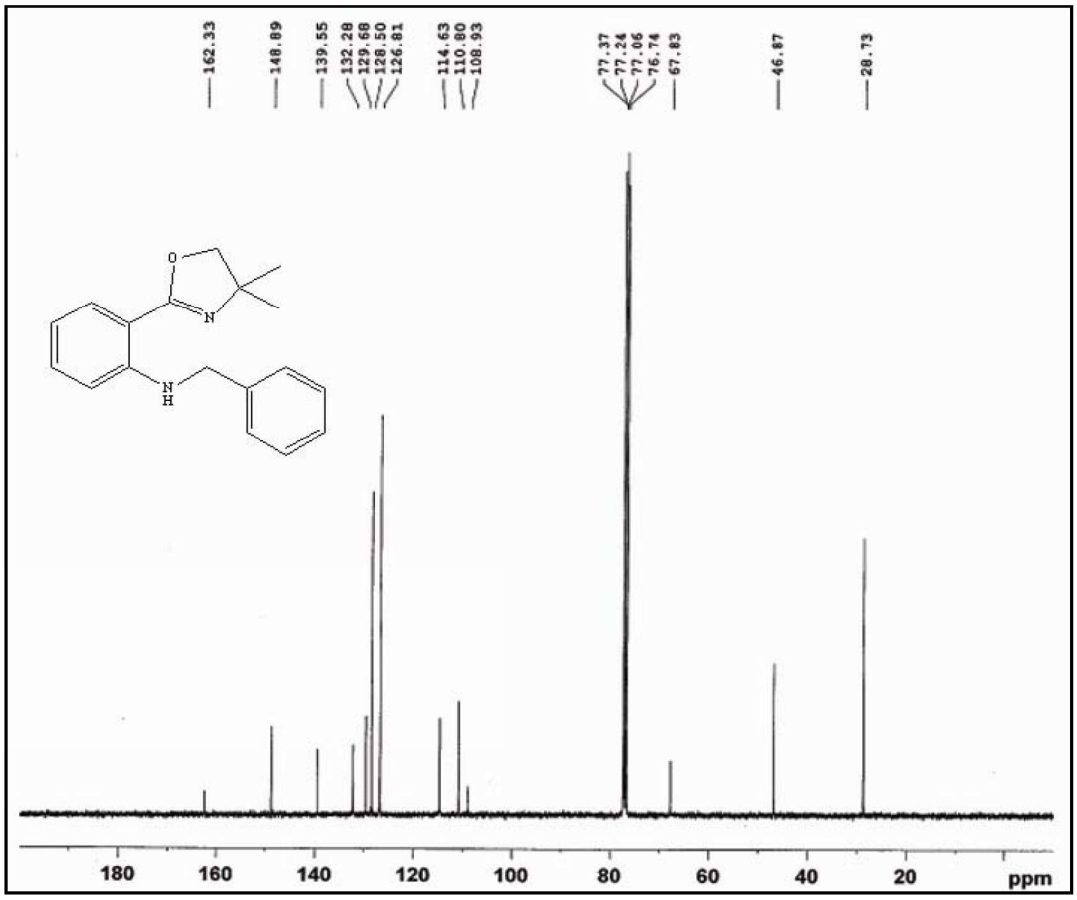
^{1}H-NMR spectra of compound 43 (400MHz, $CDCl_3$)



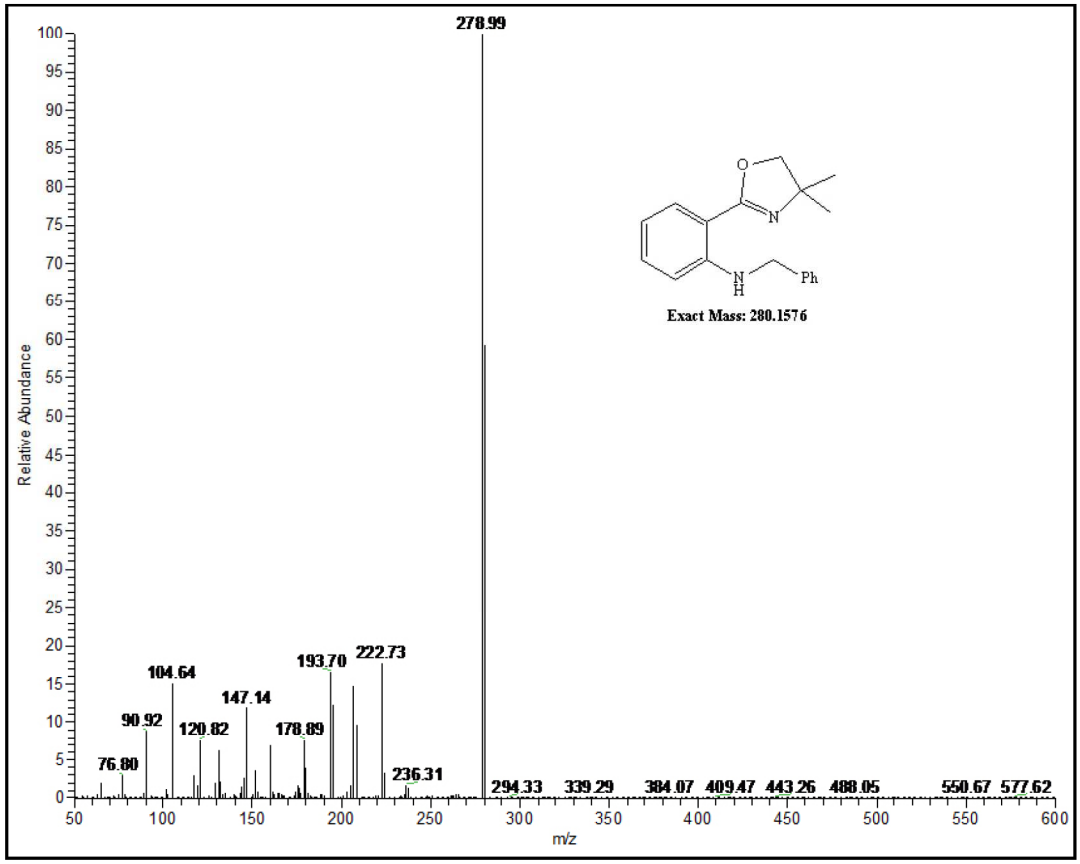
EI-Mass Spectra of Compound 43



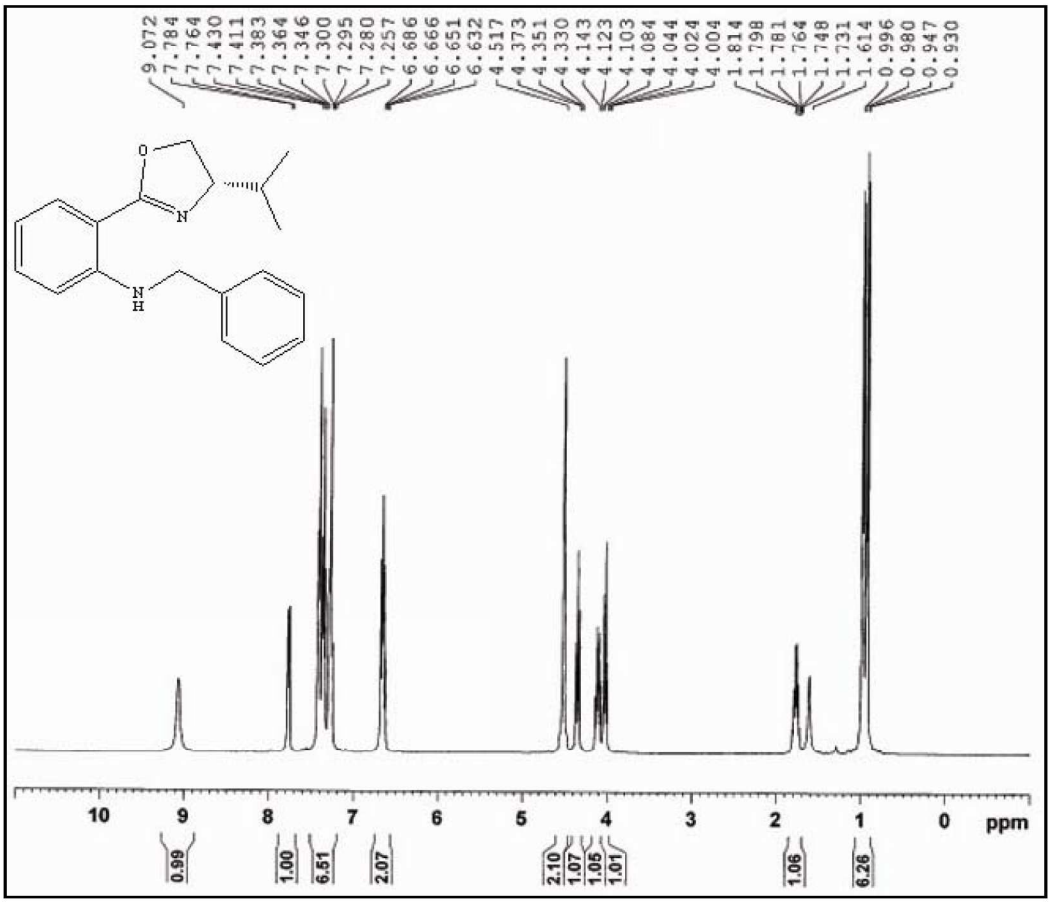
^{1}H-NMR spectra of compound 44a (400MHz, $CDCl_3$)



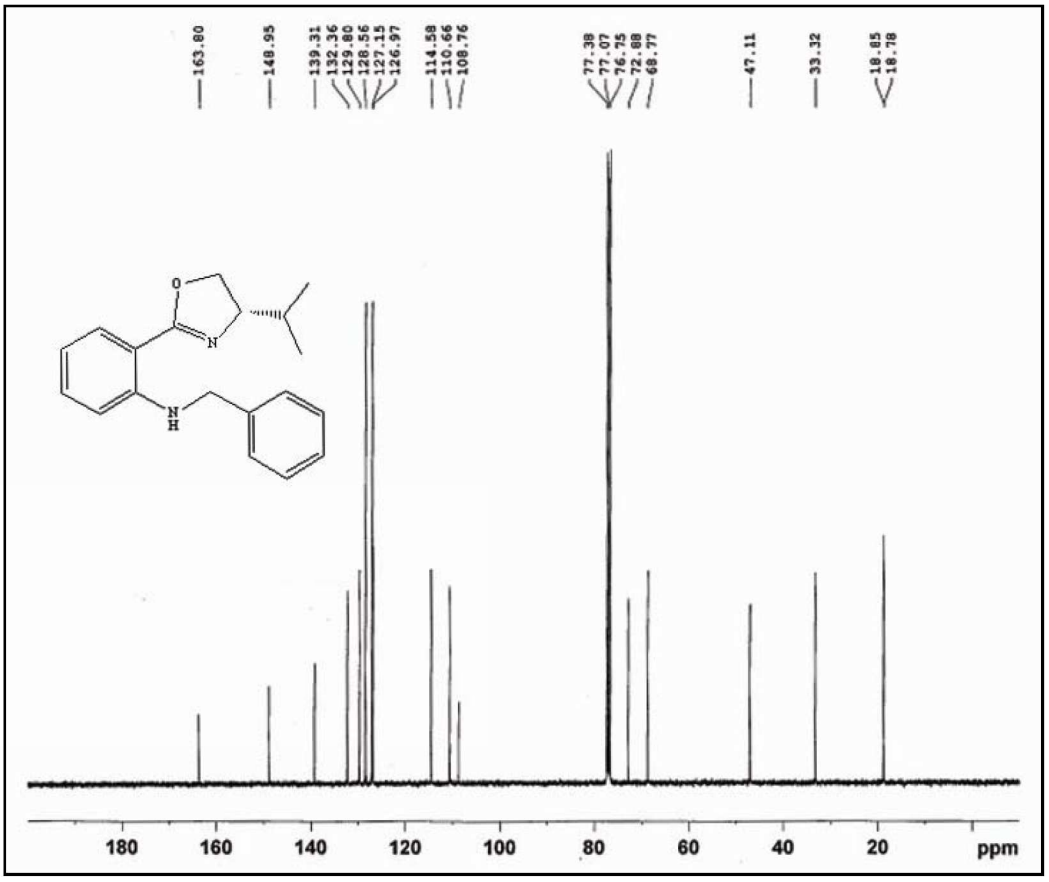
^{13}C-NMR of the compound 44a (100 MHz, $CDCl_3$)



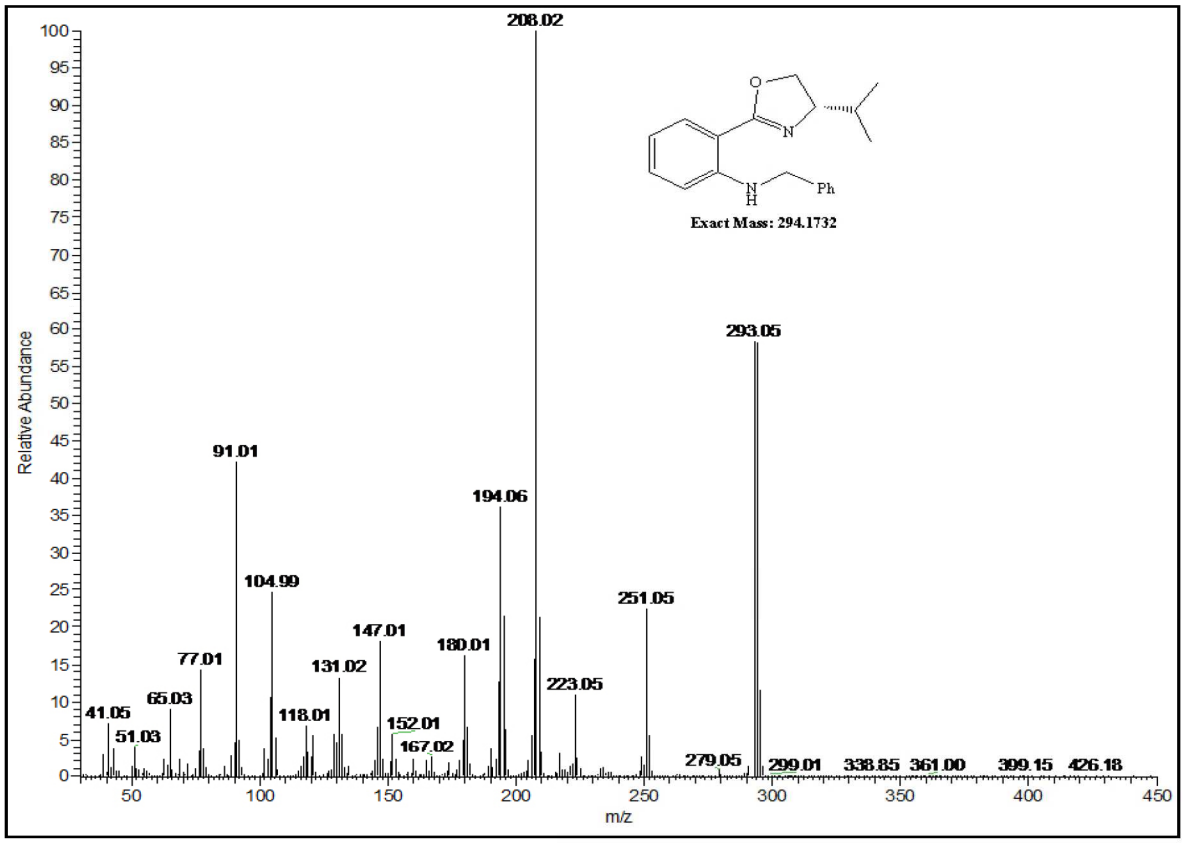
EI-Mass Spectra of Compound 44a



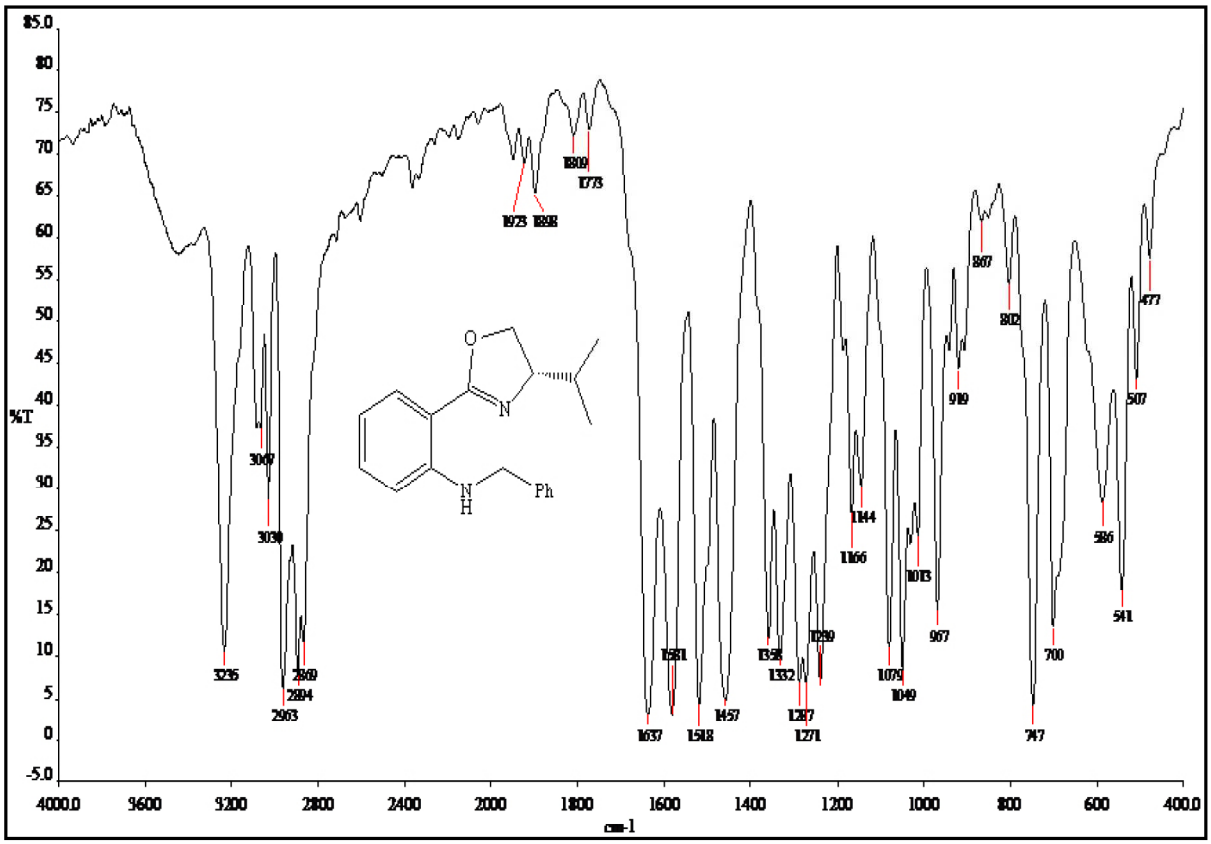
^{1}H-NMR spectra of compound 44b (400MHz, $CDCl_3$)



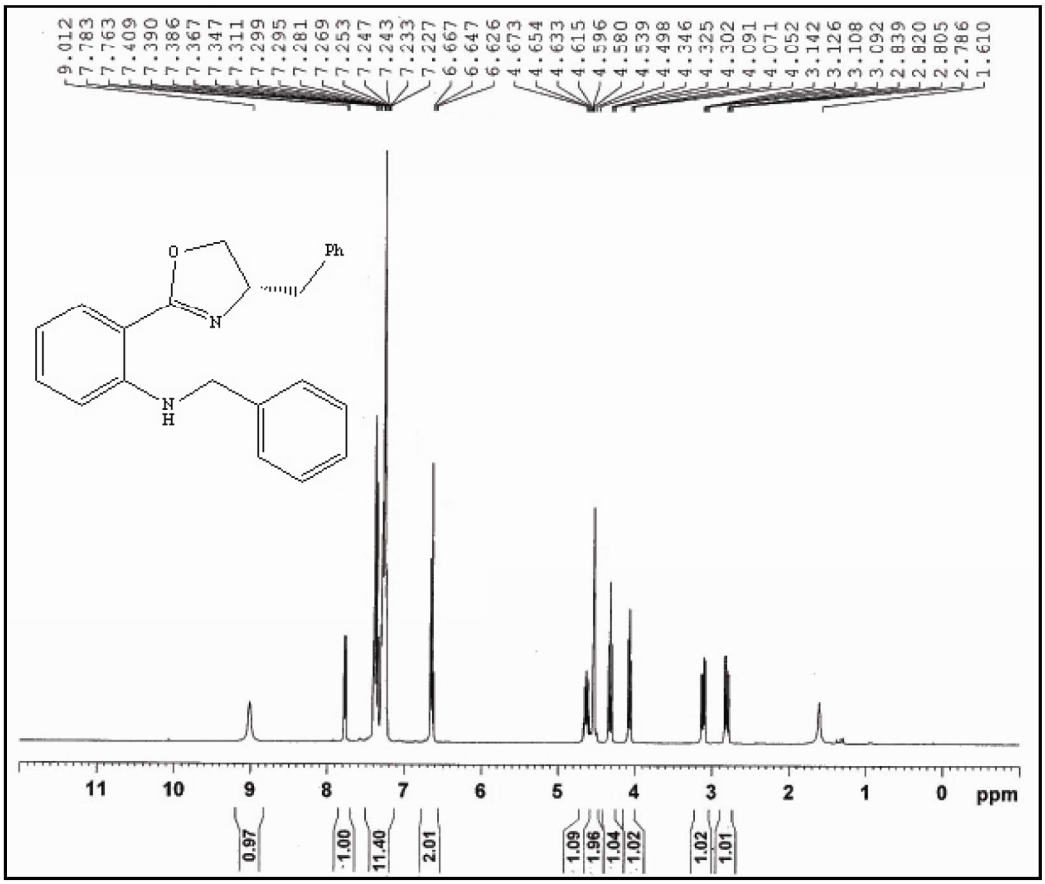
^{13}C-NMR of the compound 44b (100 MHz, $CDCl_3$)



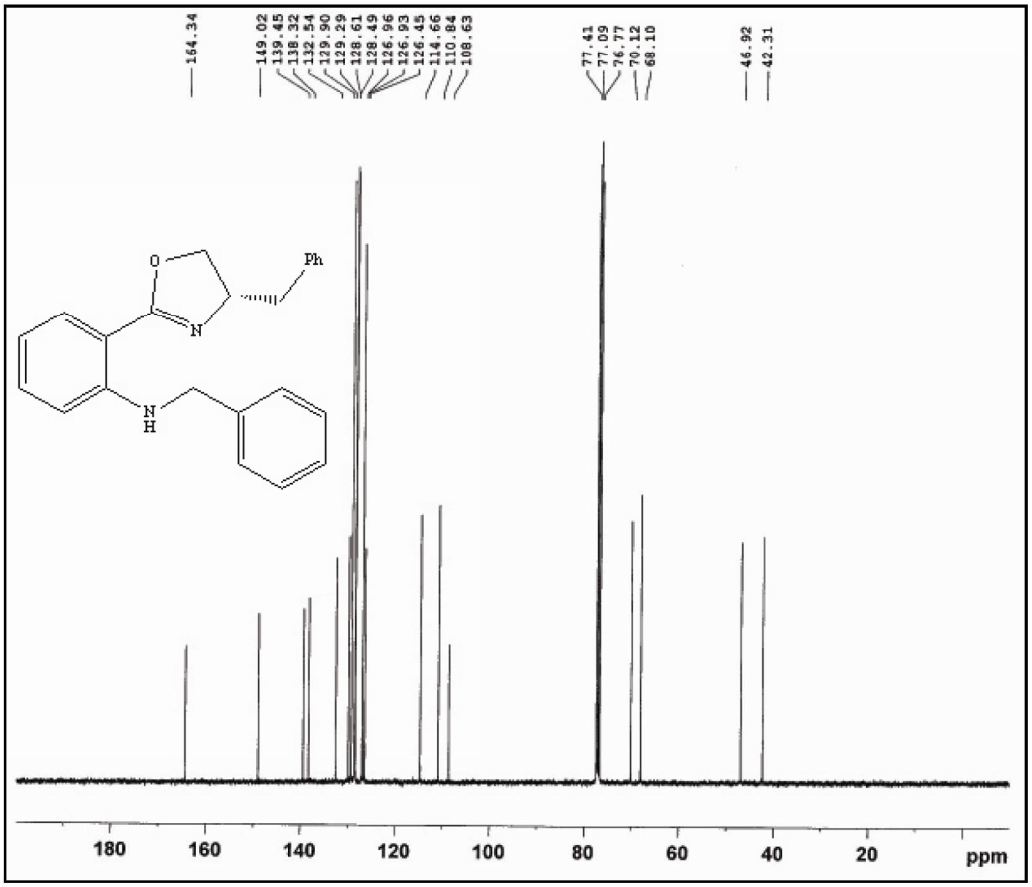
EI-Mass Spectra of Compound 44b



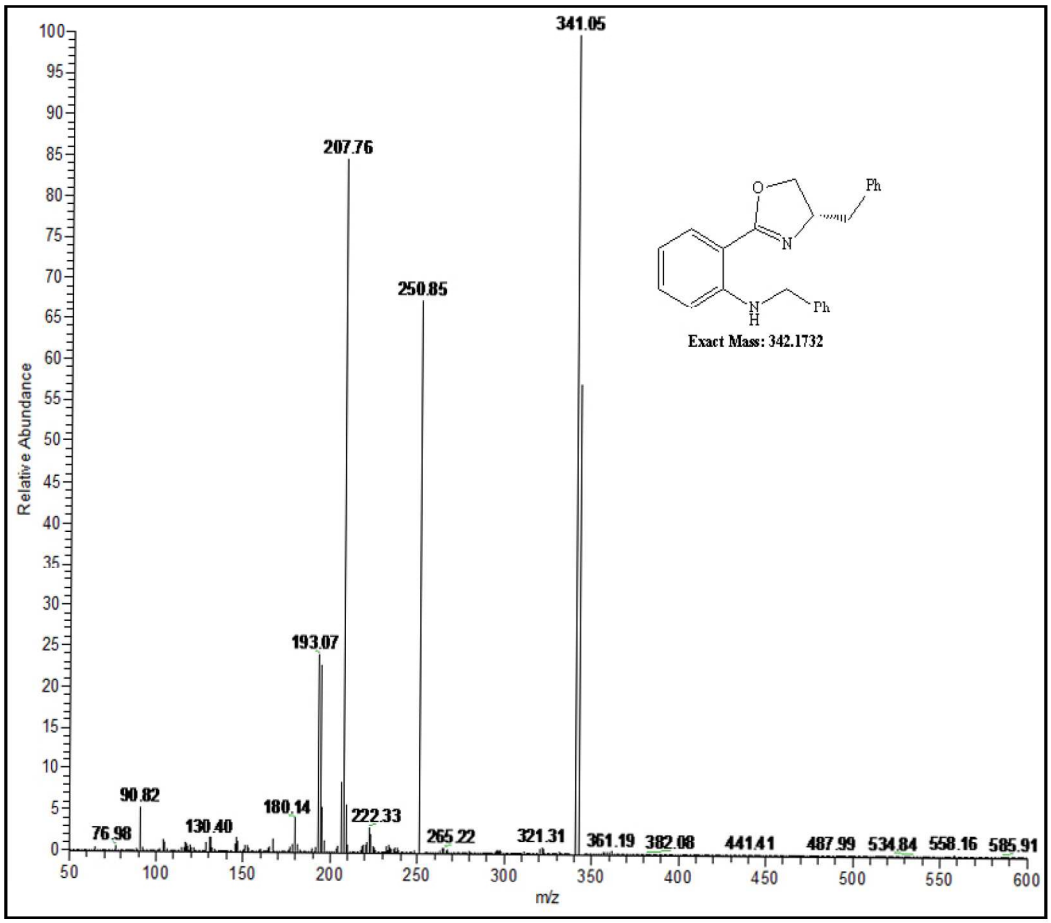
IR Spectra of Compound 44b



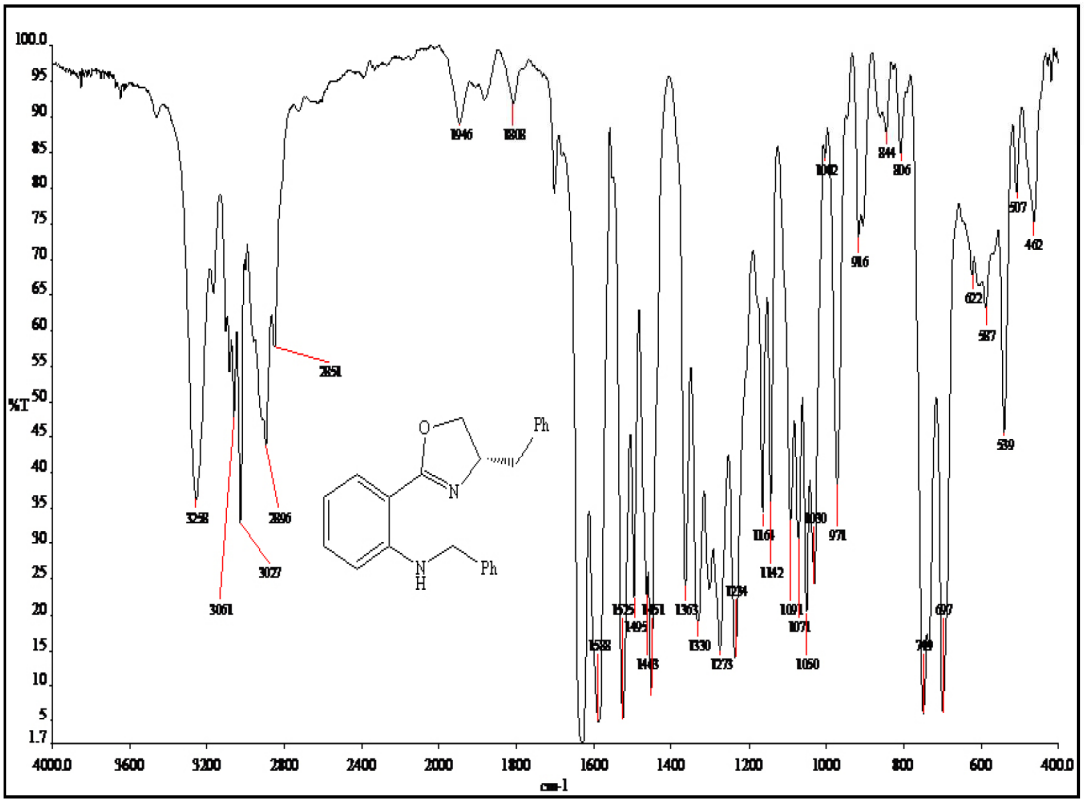
^{1}H-NMR spectra of compound 44c (400MHz, $CDCl_3$)



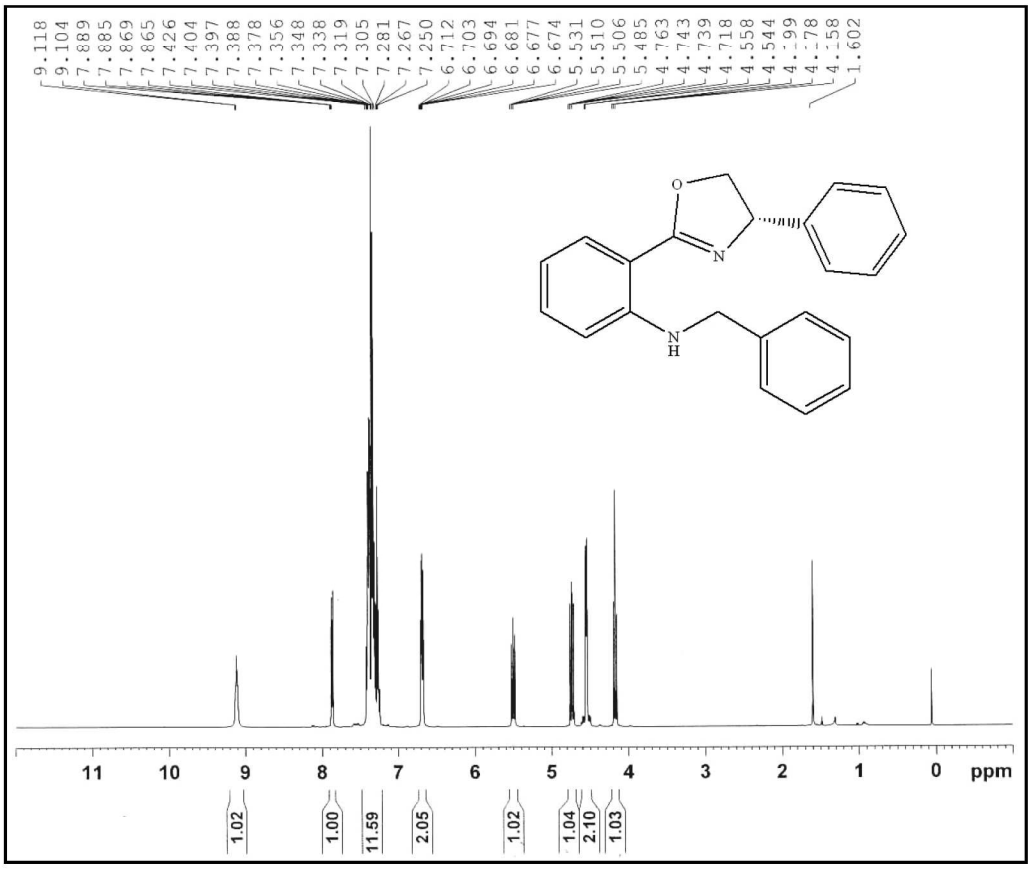
^{13}C-NMR of the compound 44c (100 MHz, $CDCl_3$)



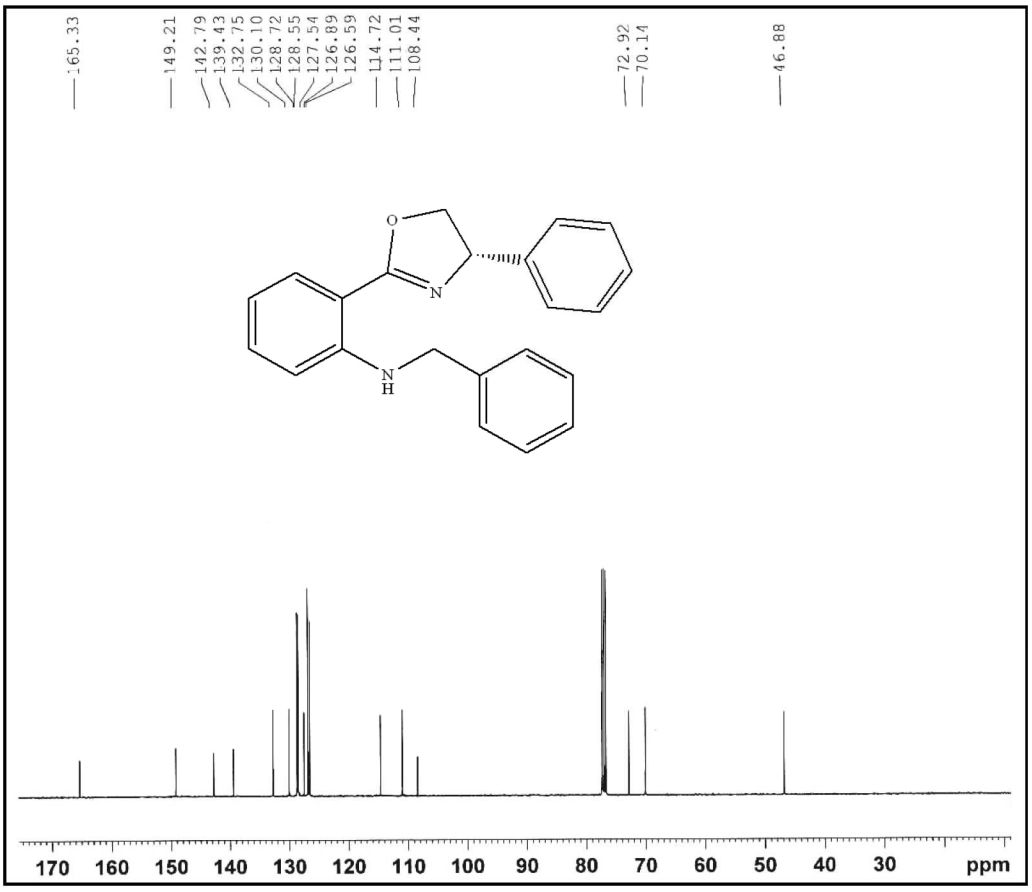
EI-Mass Spectra of Compound 44c



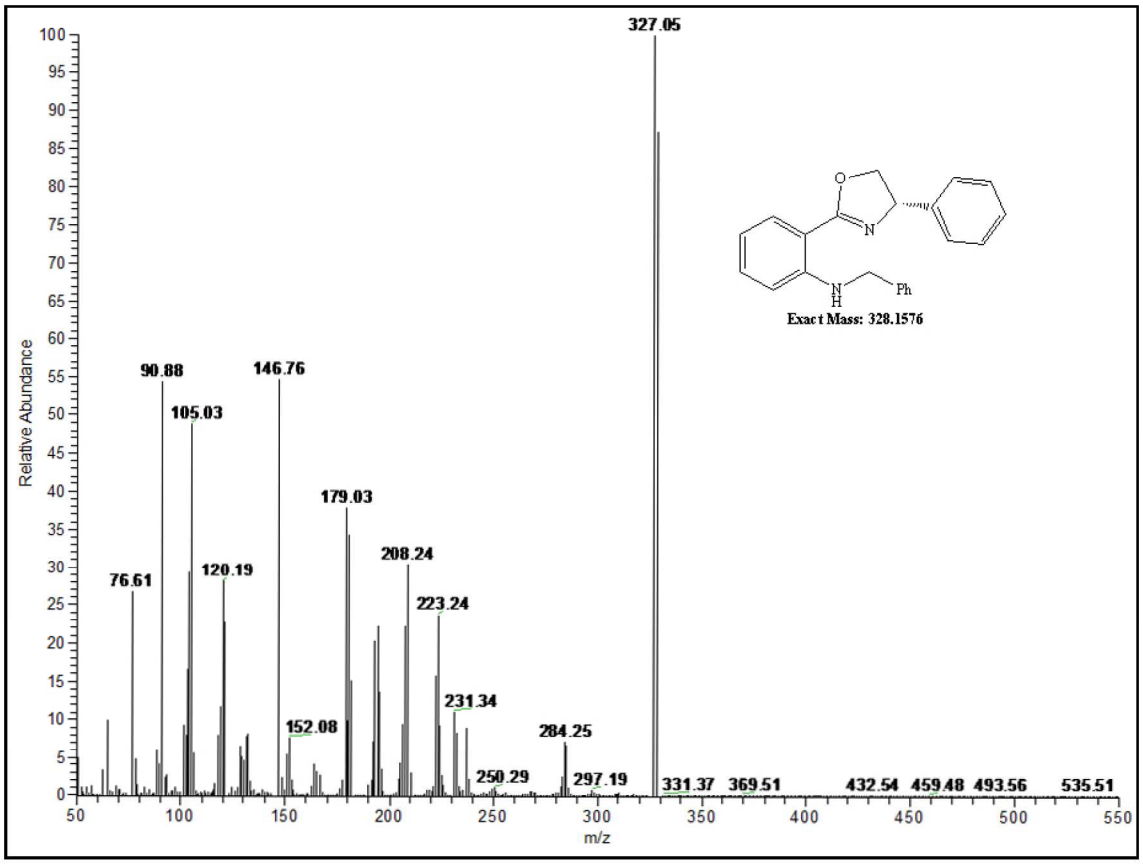
IR Spectra of Compound 44c



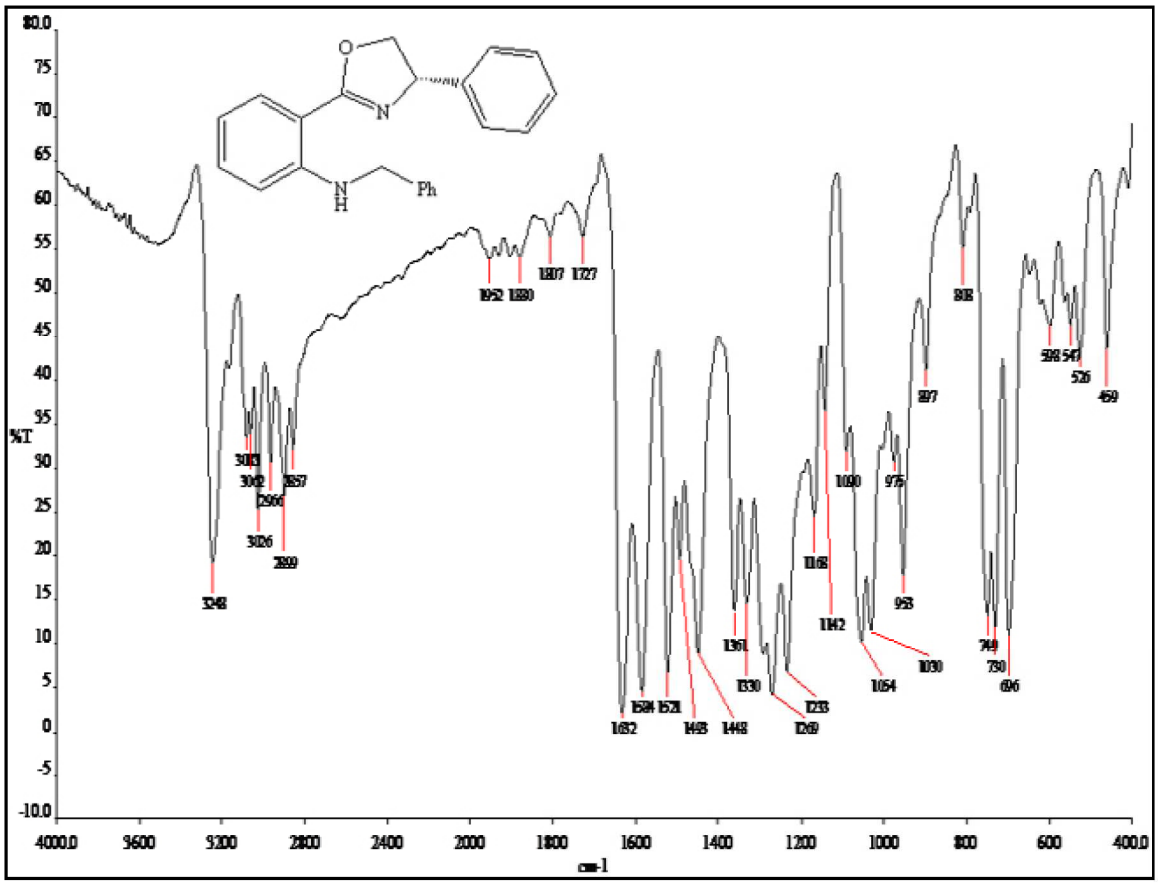
^{1}H-NMR spectra of compound 44d (400MHz, $CDCl_3$)



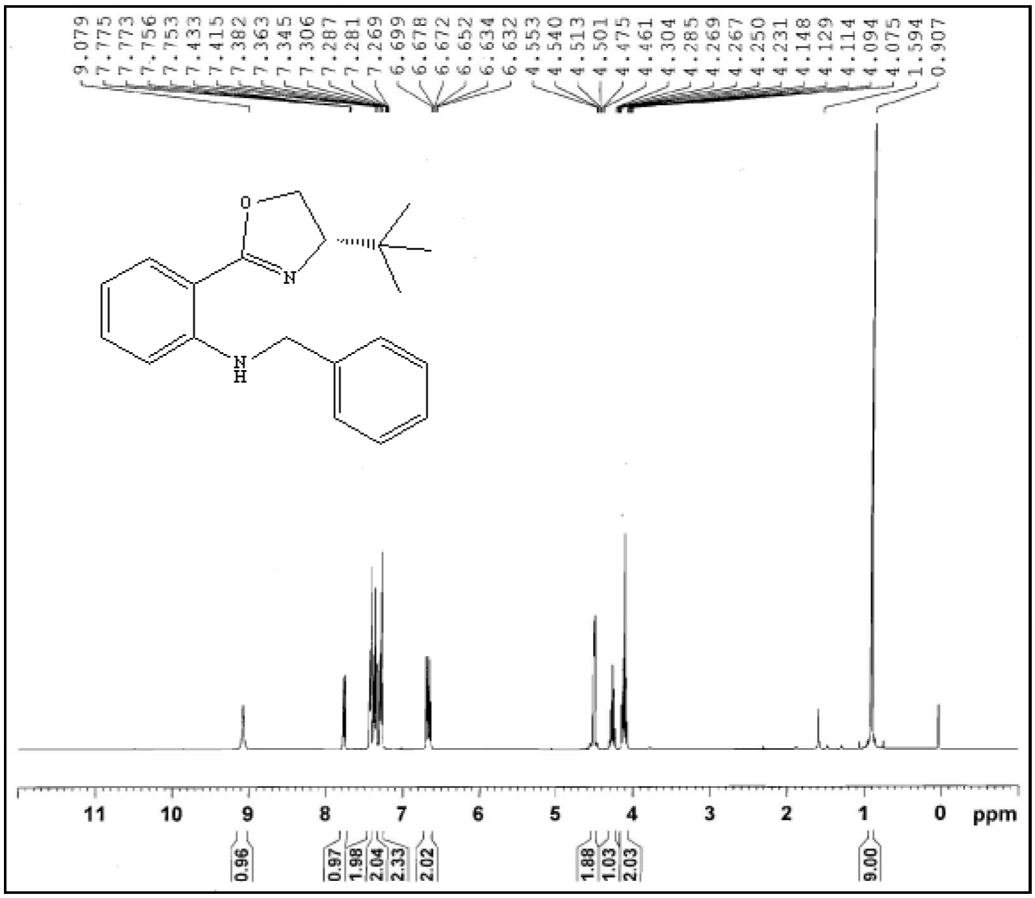
^{13}C-NMR of the compound 44d (100 MHz, $CDCl_3$)



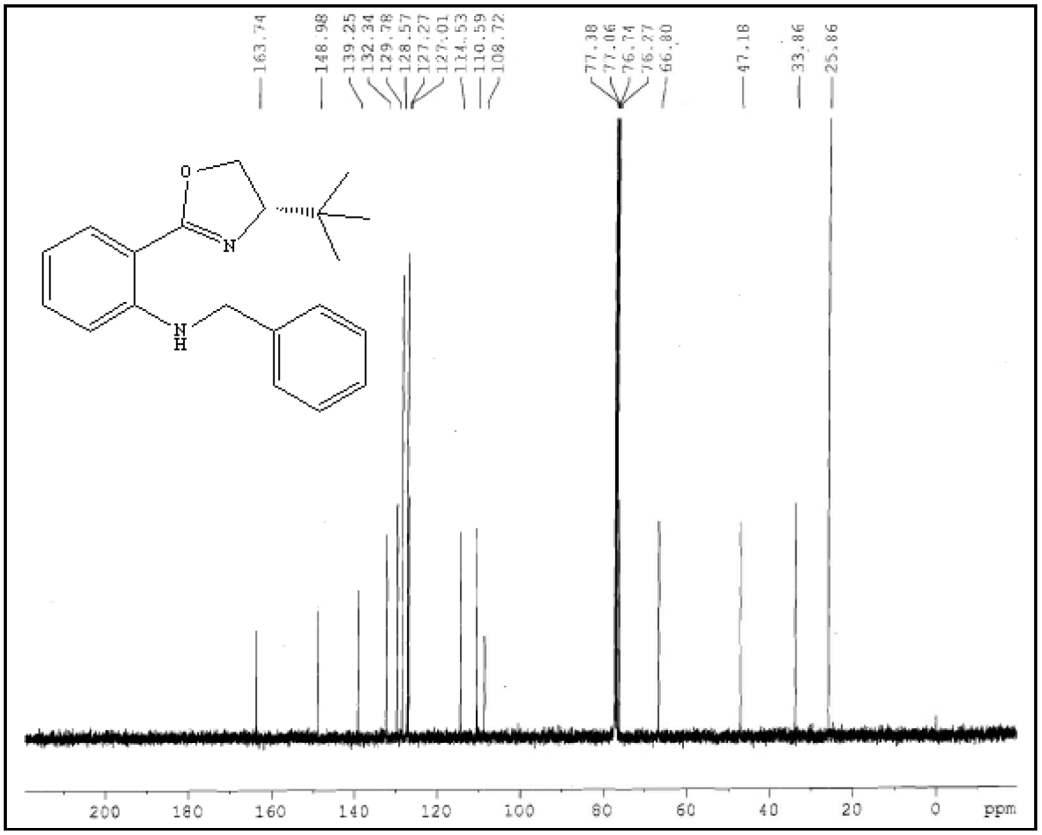
EI-Mass Spectra of Compound 44d



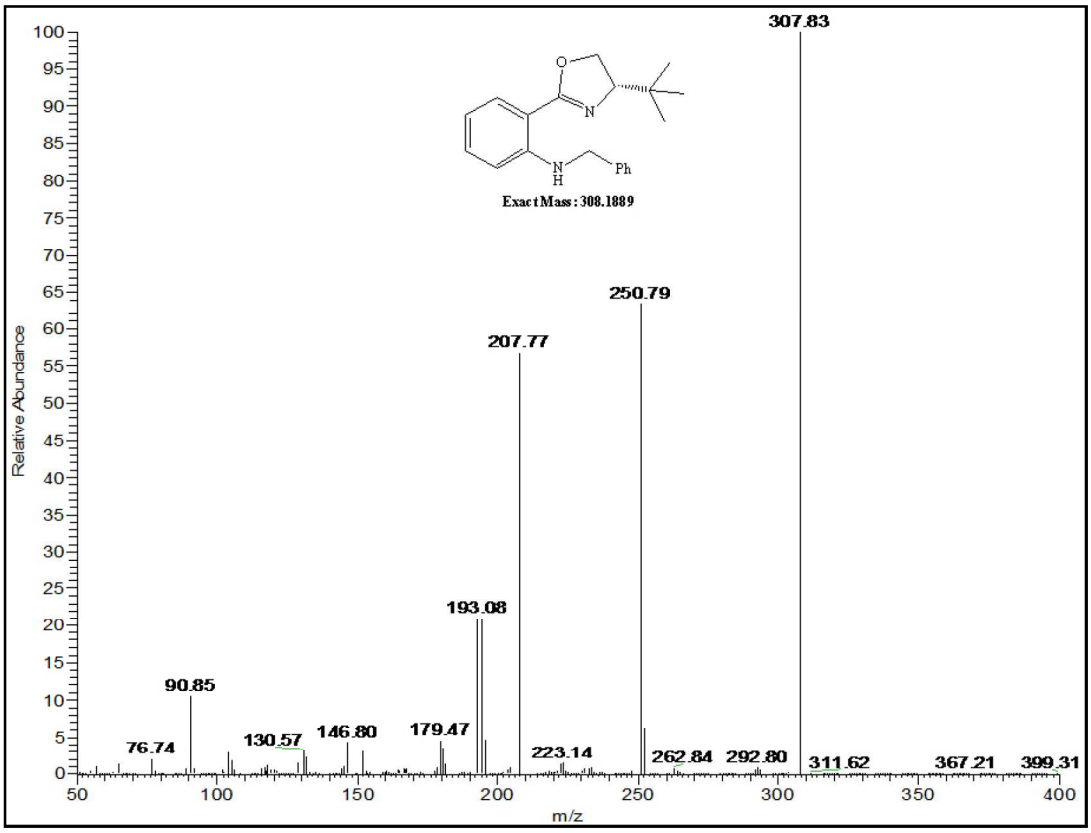
IR Spectra of Compound 44d



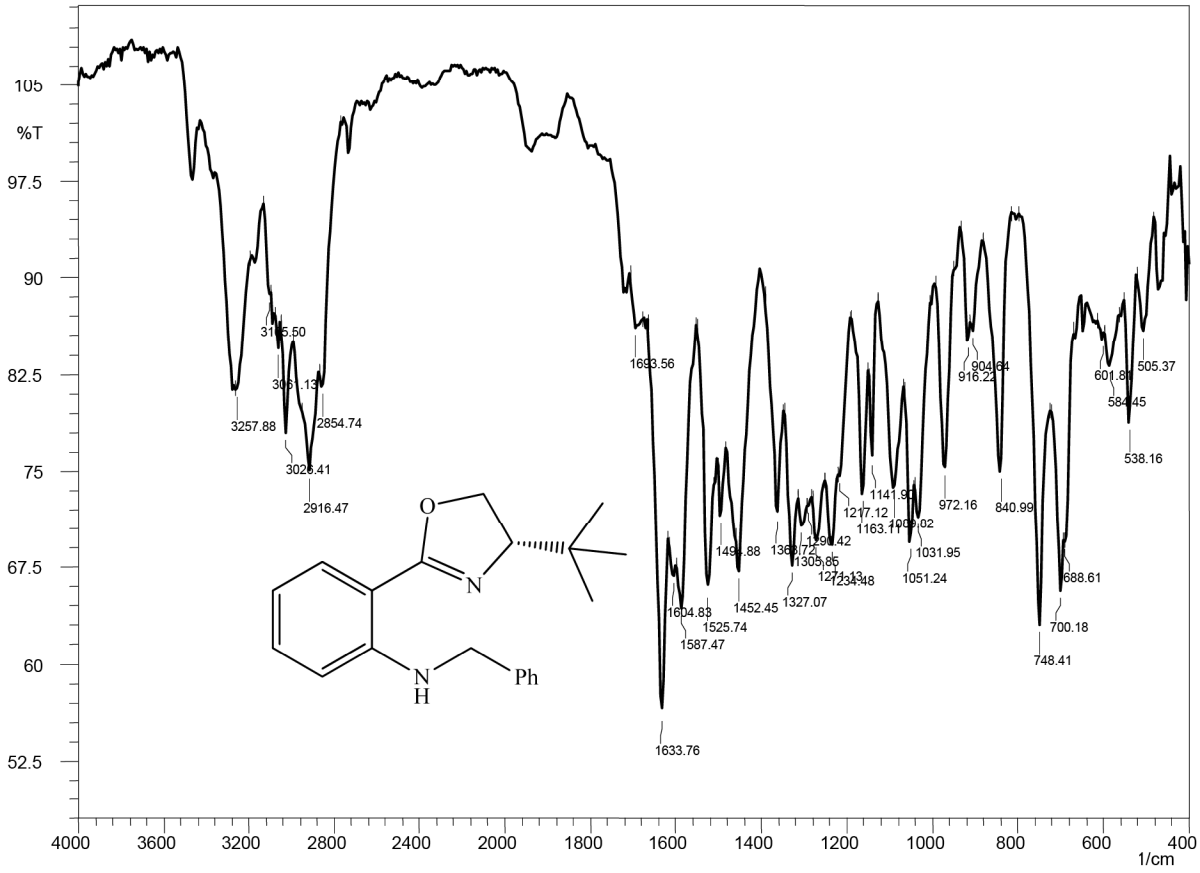
^{1}H-NMR spectra of compound 44e (400MHz, $CDCl_3$)



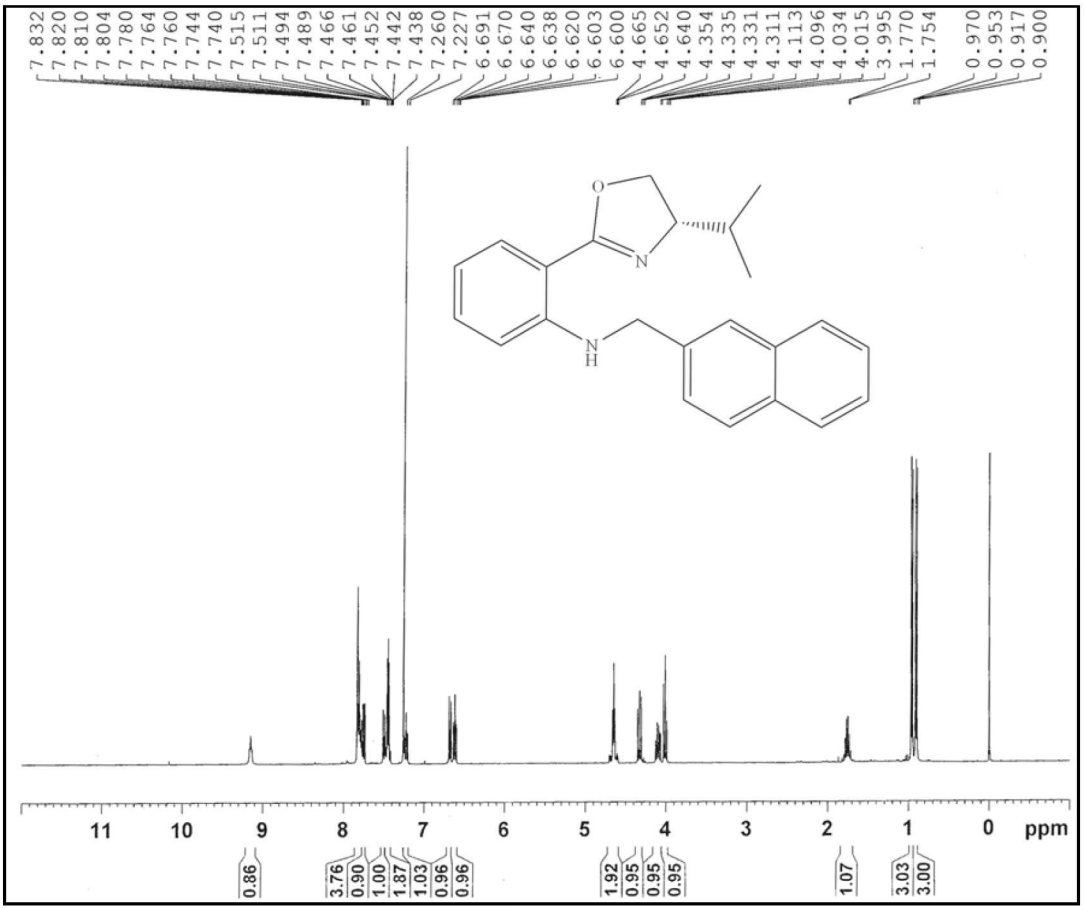
^{13}C-NMR of the compound 44e (100 MHz, $CDCl_3$)



EI-Mass Spectra of Compound 44e

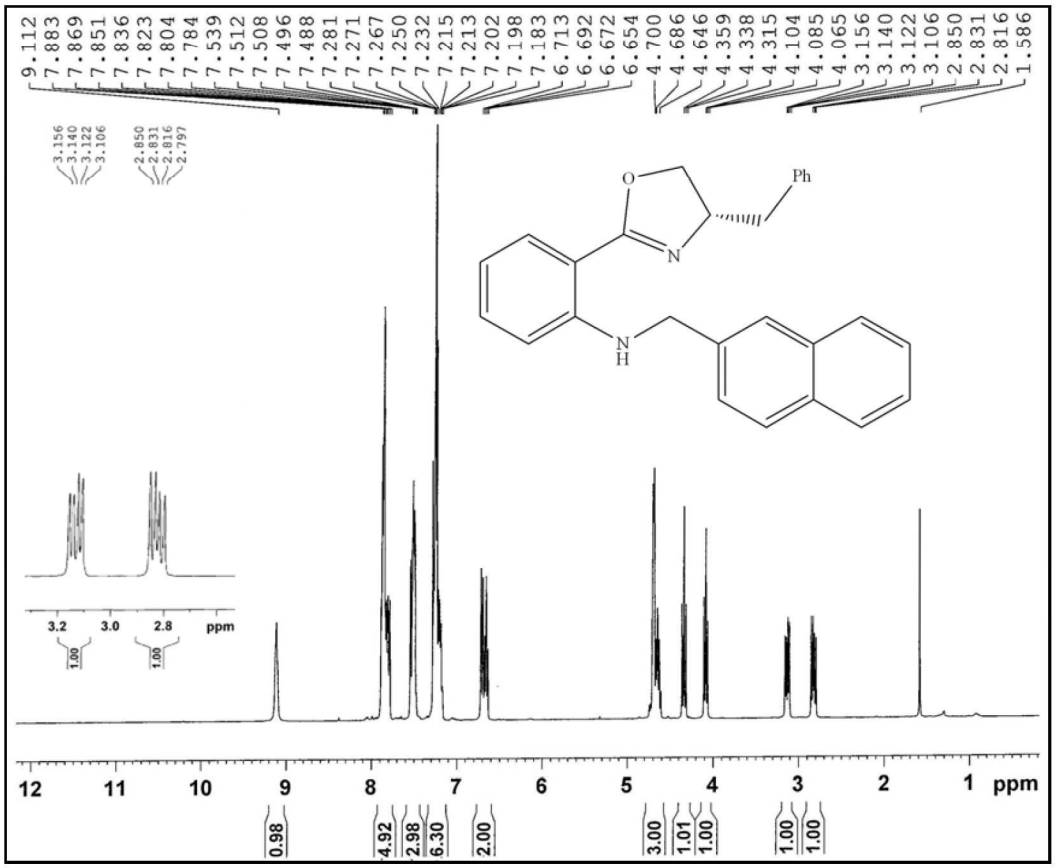


IR Spectra of Compound 44e

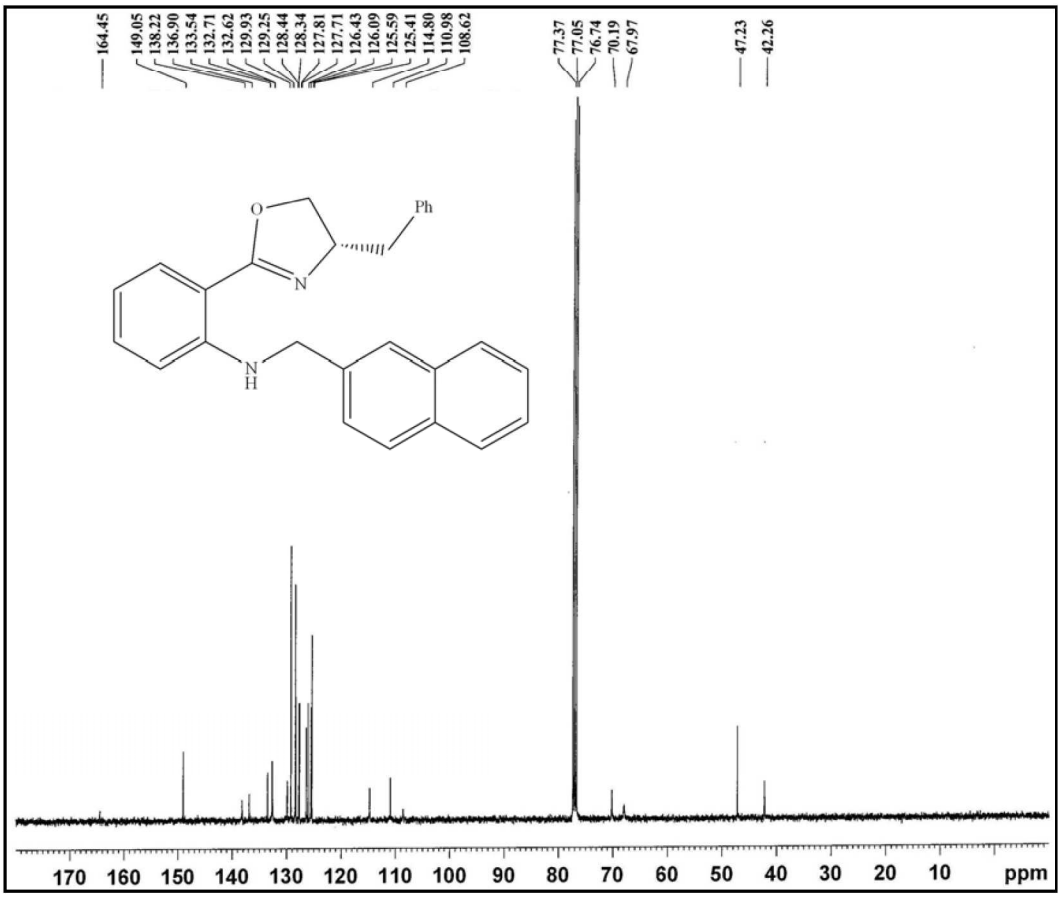


^{1}H-NMR spectra of compound 45a (400MHz, $CDCl_3$)

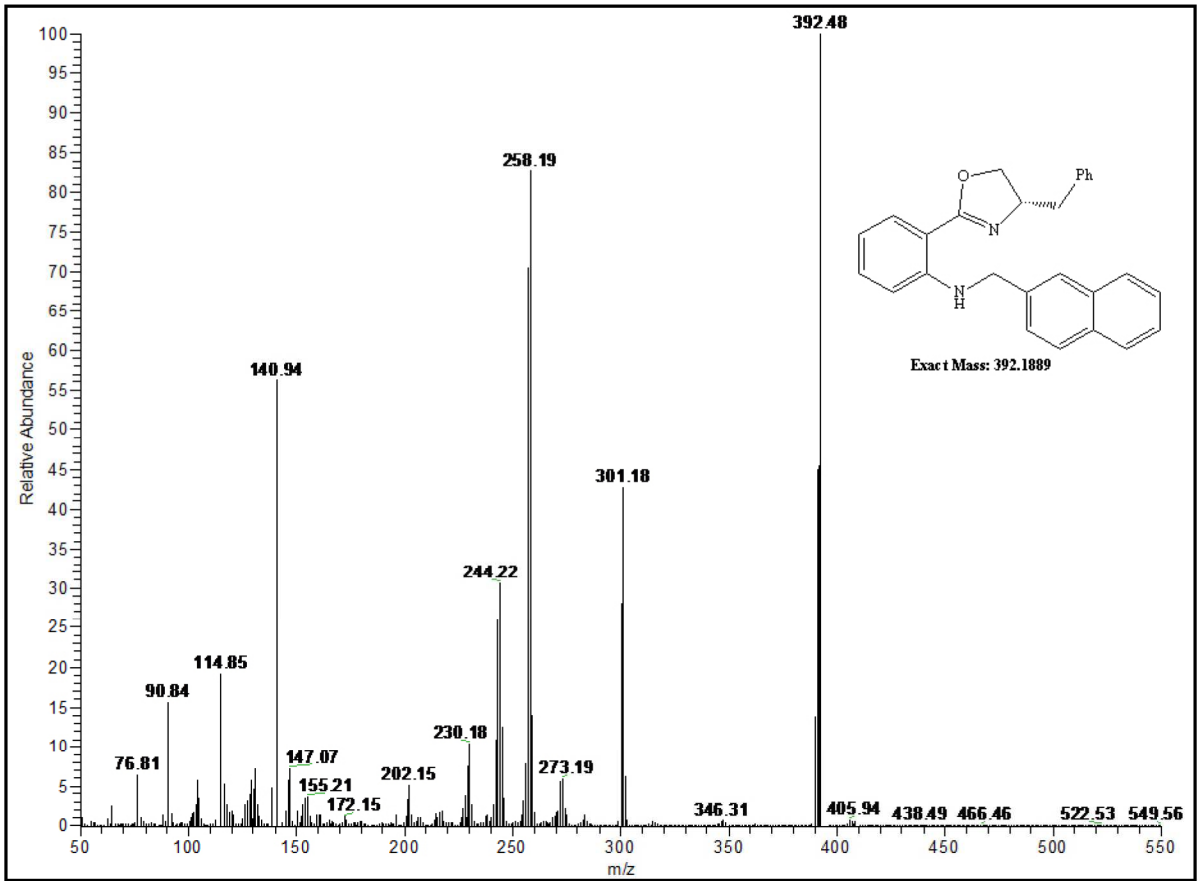
^{13}C-NMR of the compound 45a (100 MHz, $CDCl_3$)



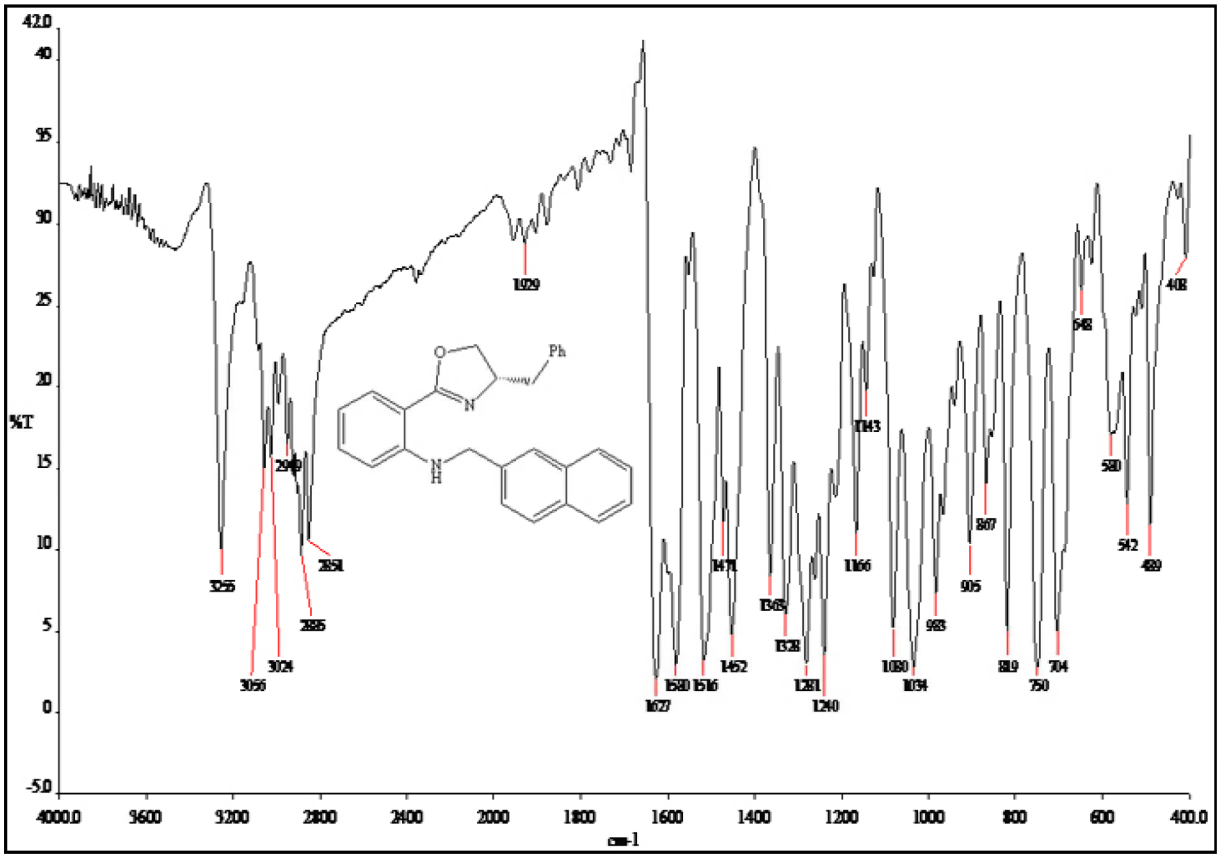
^{1}H-NMR spectra of compound 45b (400MHz, $CDCl_3$)



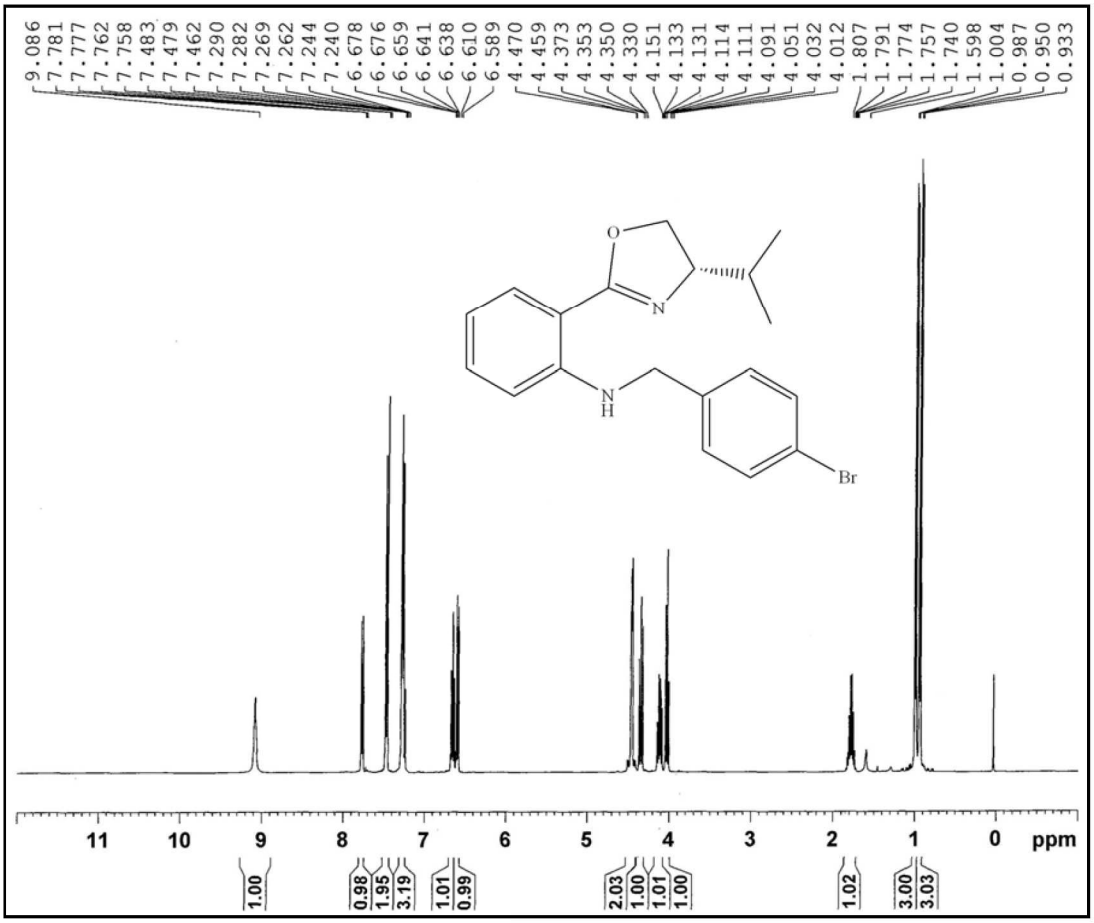
^{13}C-NMR of the compound 45b (100 MHz, $CDCl_3$)



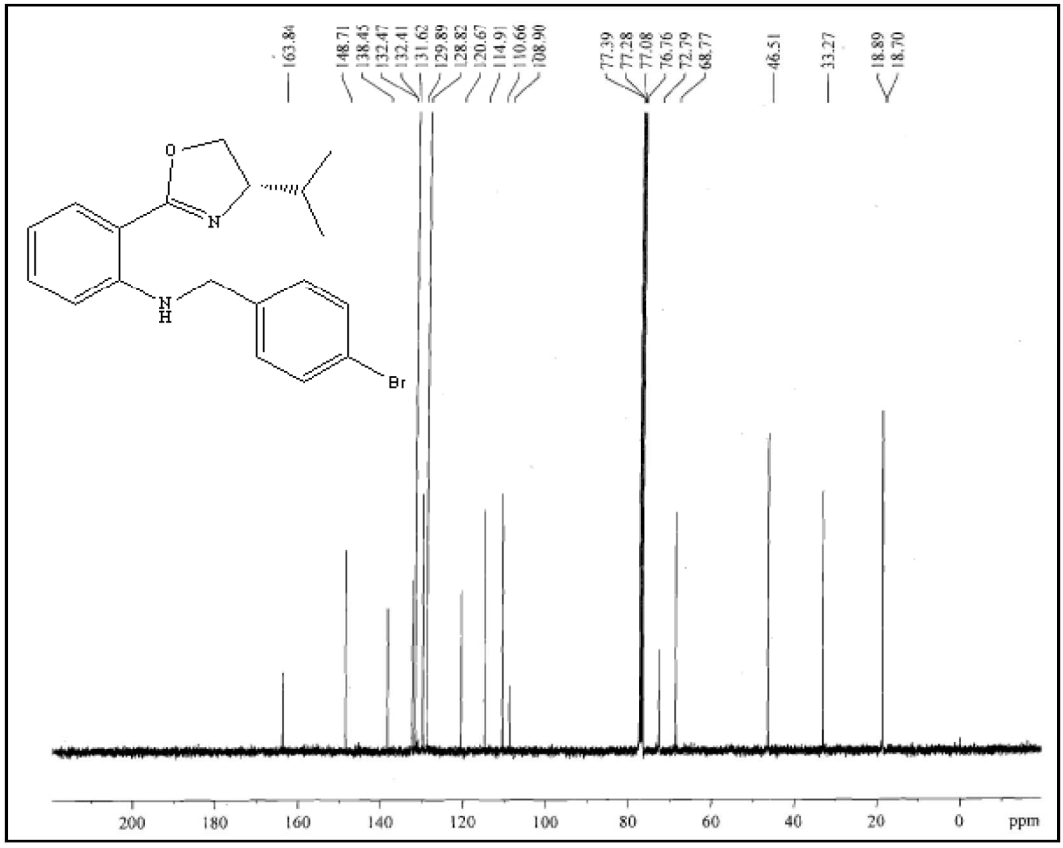
EI-Mass Spectra of Compound 45b



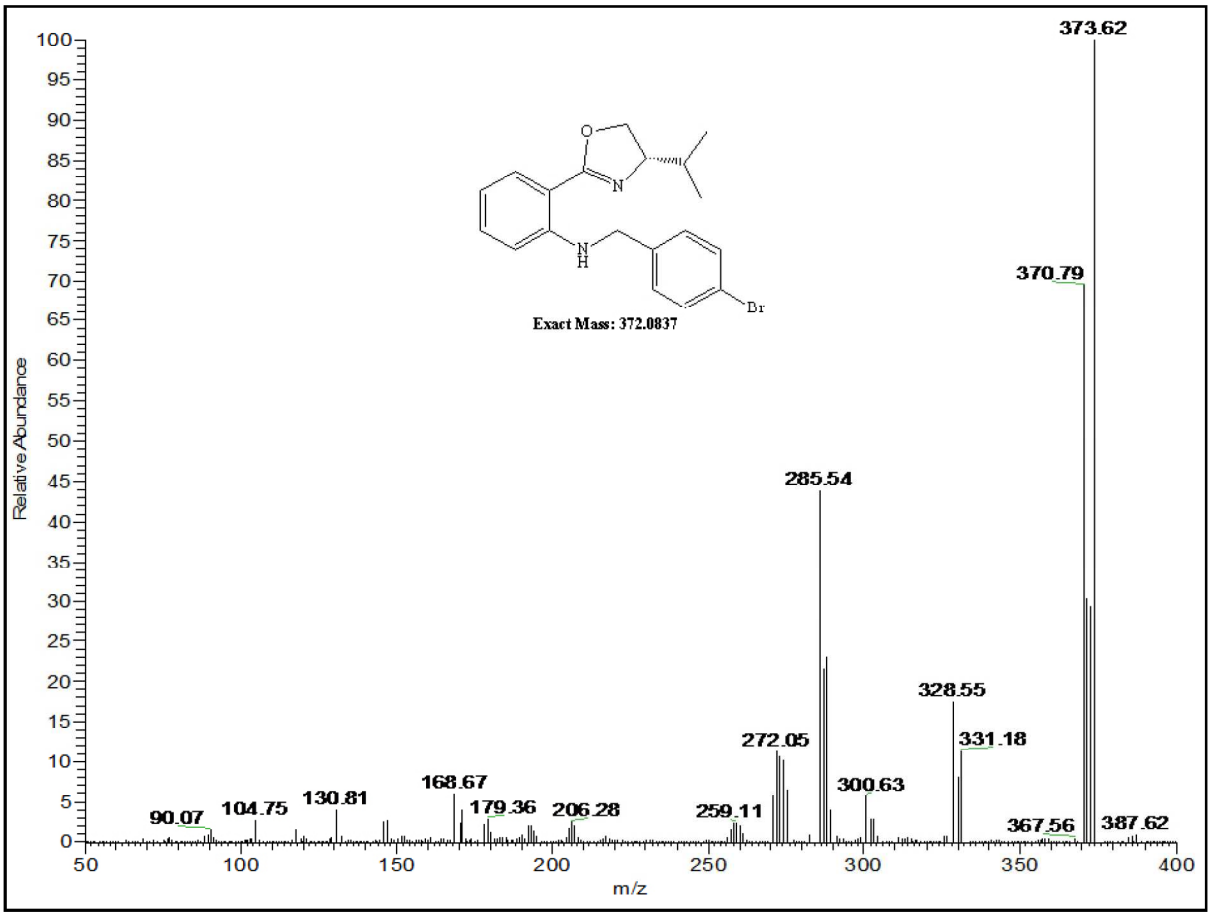
IR Spectra of Compound 45b



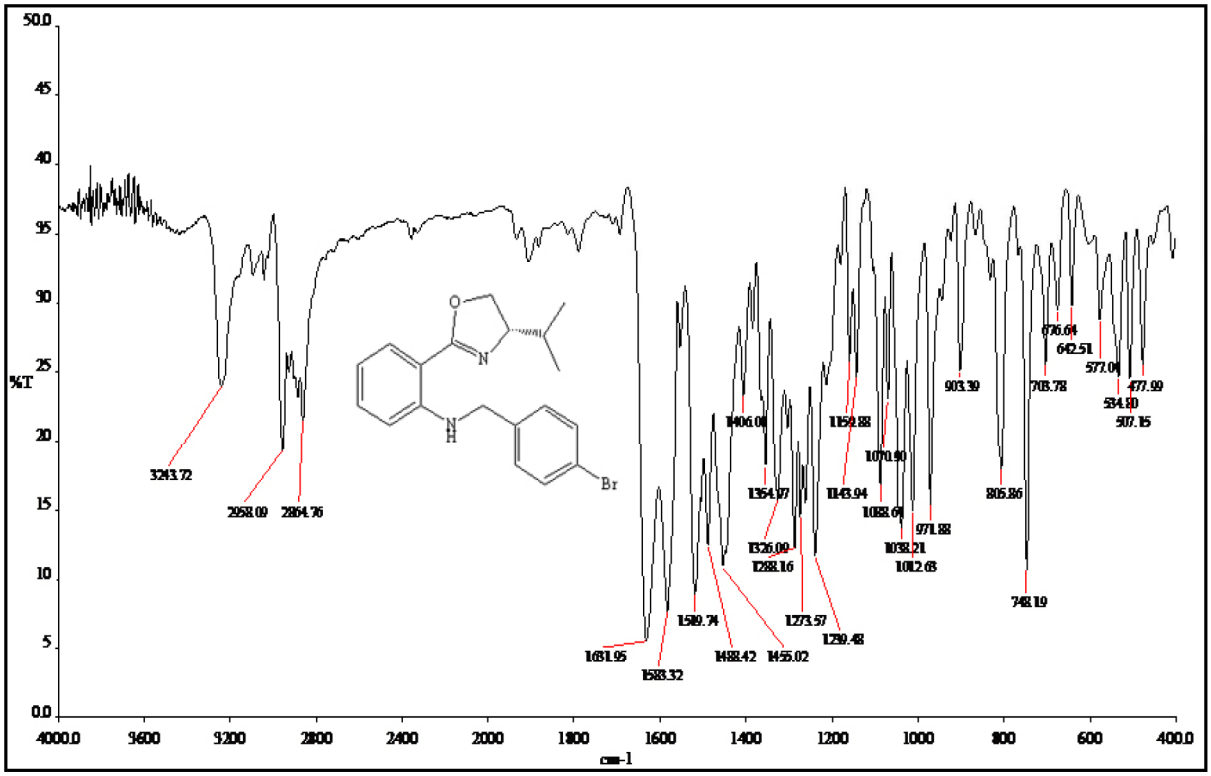
^{1}H-NMR spectra of compound 46a (400MHz, $CDCl_3$)



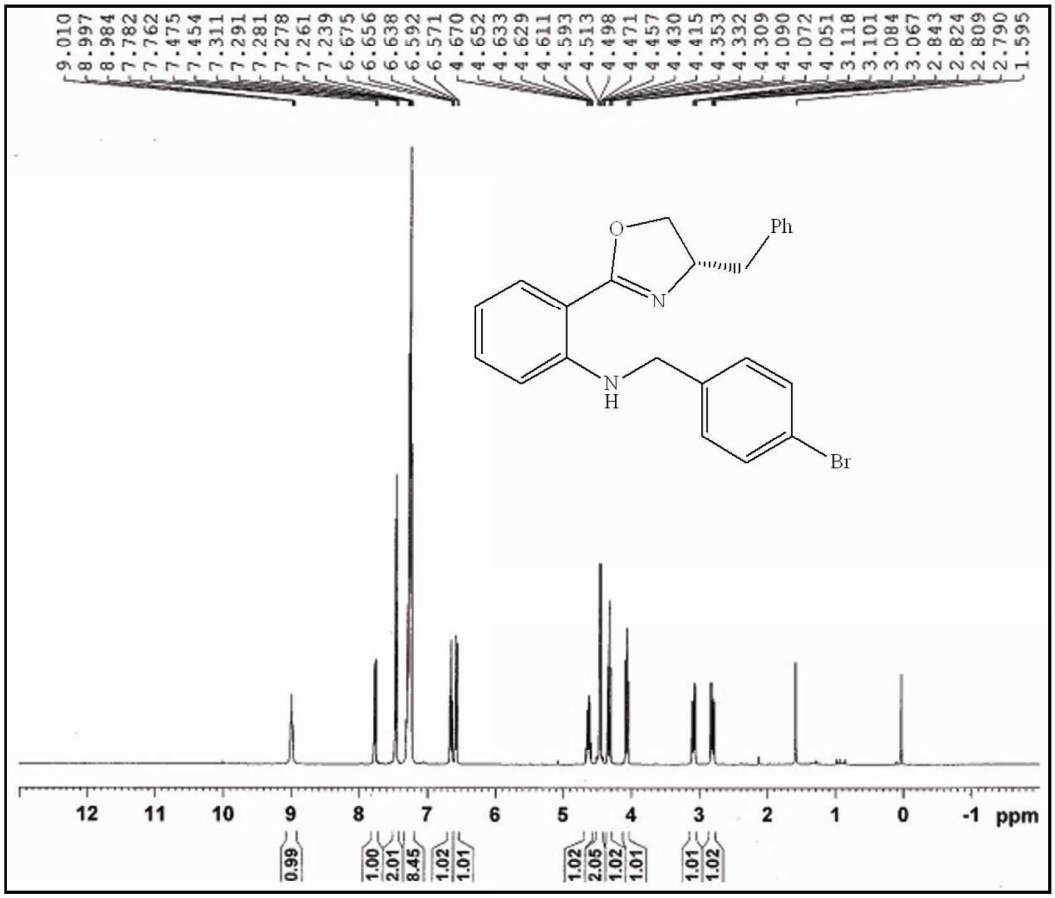
^{13}C-NMR of the compound 46a (100 MHz, $CDCl_3$)



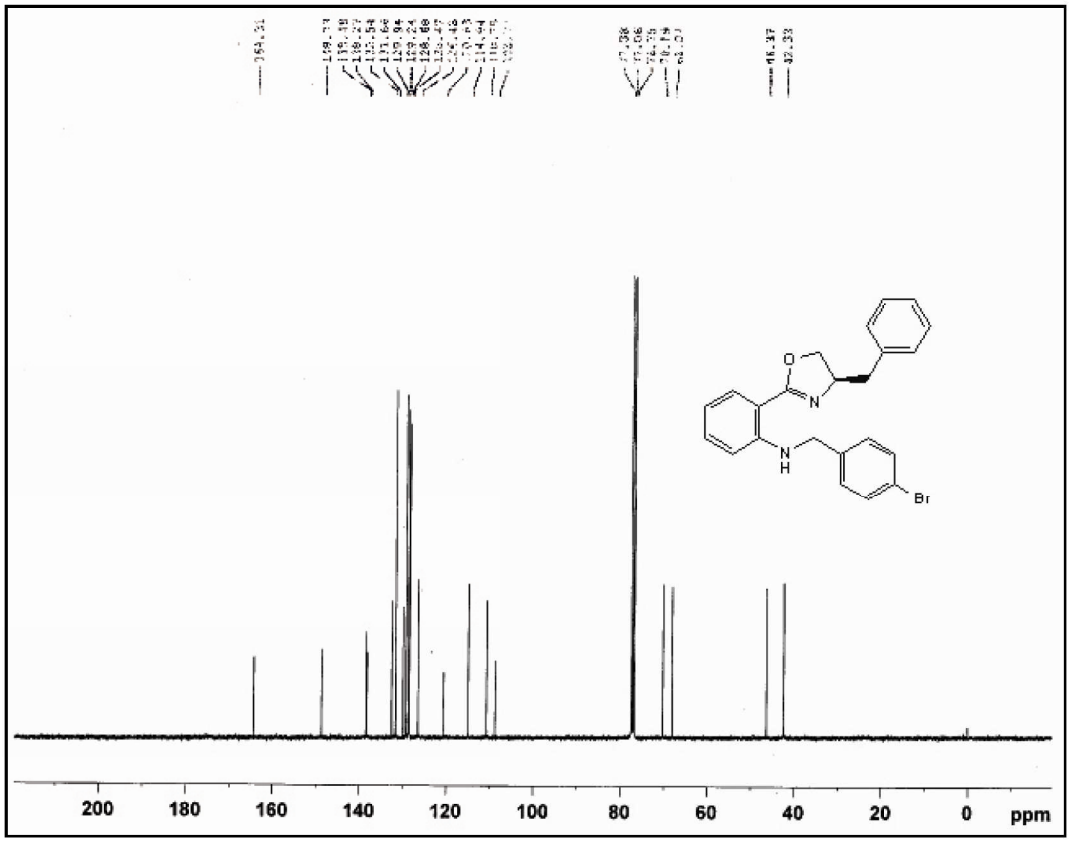
EI-Mass Spectra of Compound 46a



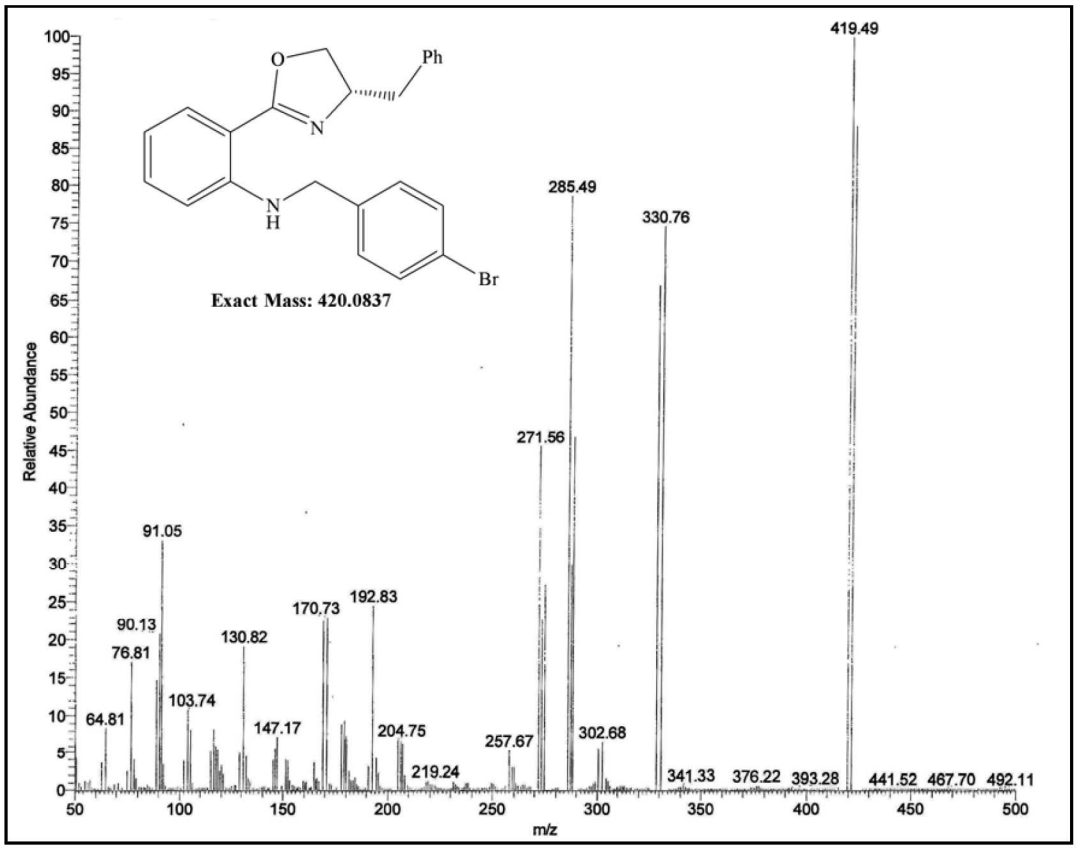
IR Spectra of Compound 46a



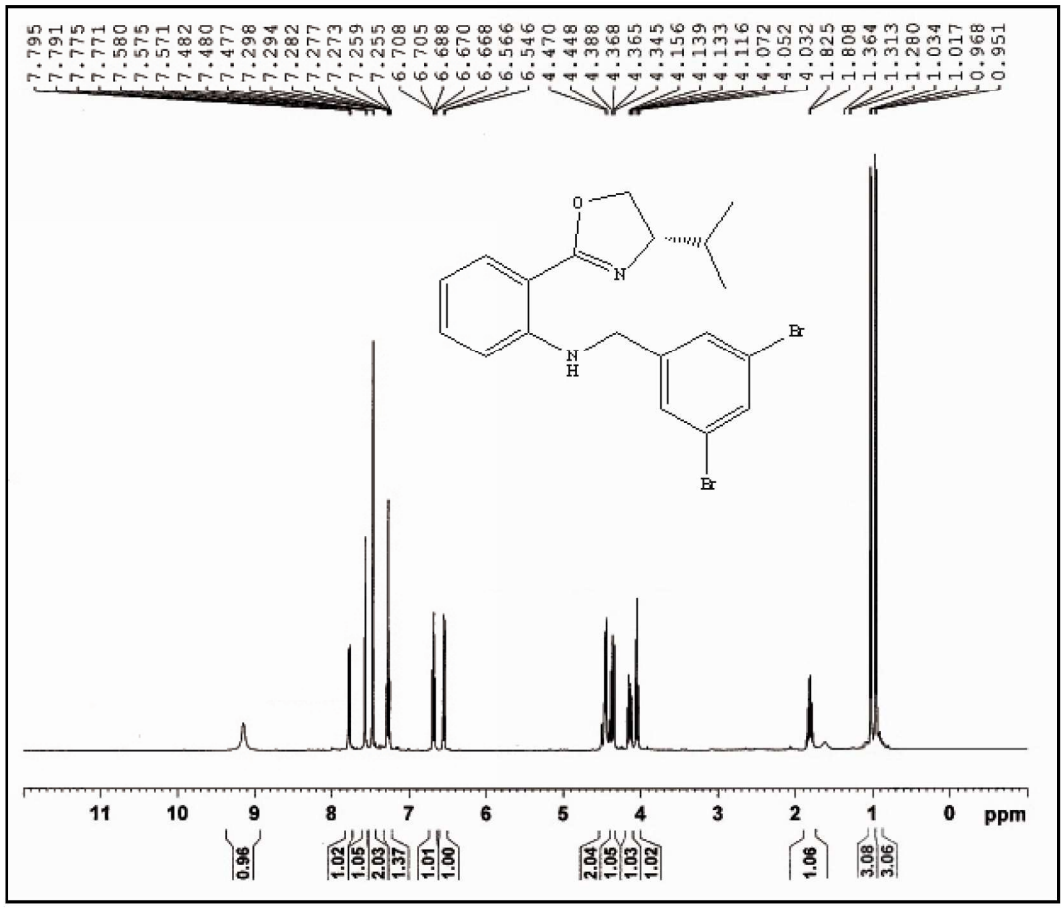
[1]H-NMR spectra of compound 46b (400MHz, $CDCl_3$)



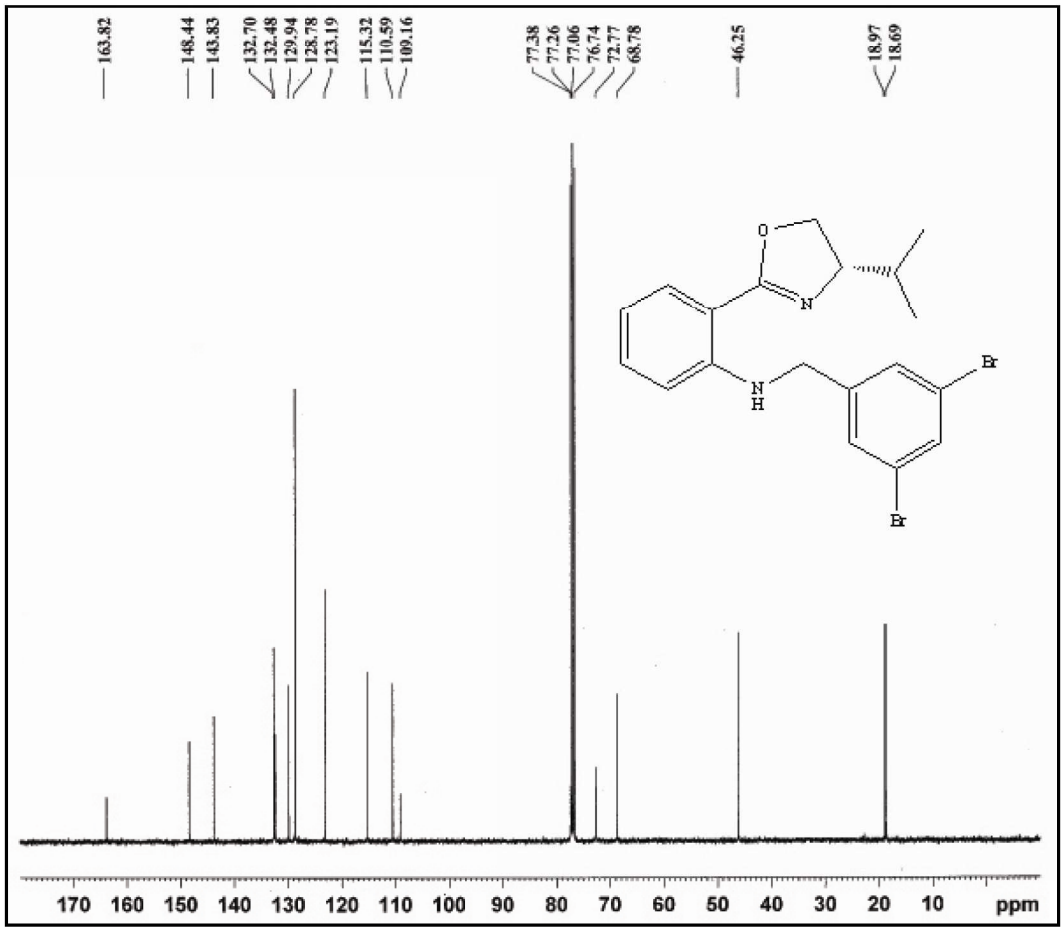
[13]C-NMR of the compound 46b (100 MHz, $CDCl_3$)



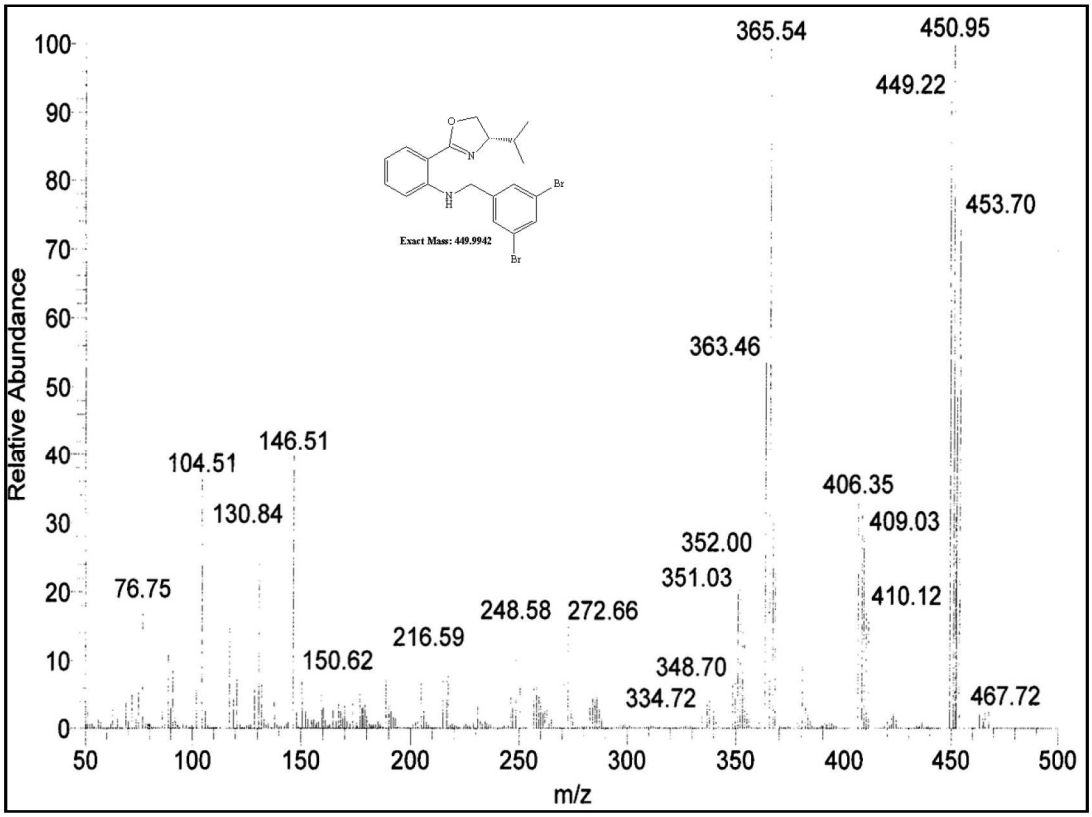
EI-Mass Spectra of Compound 46b



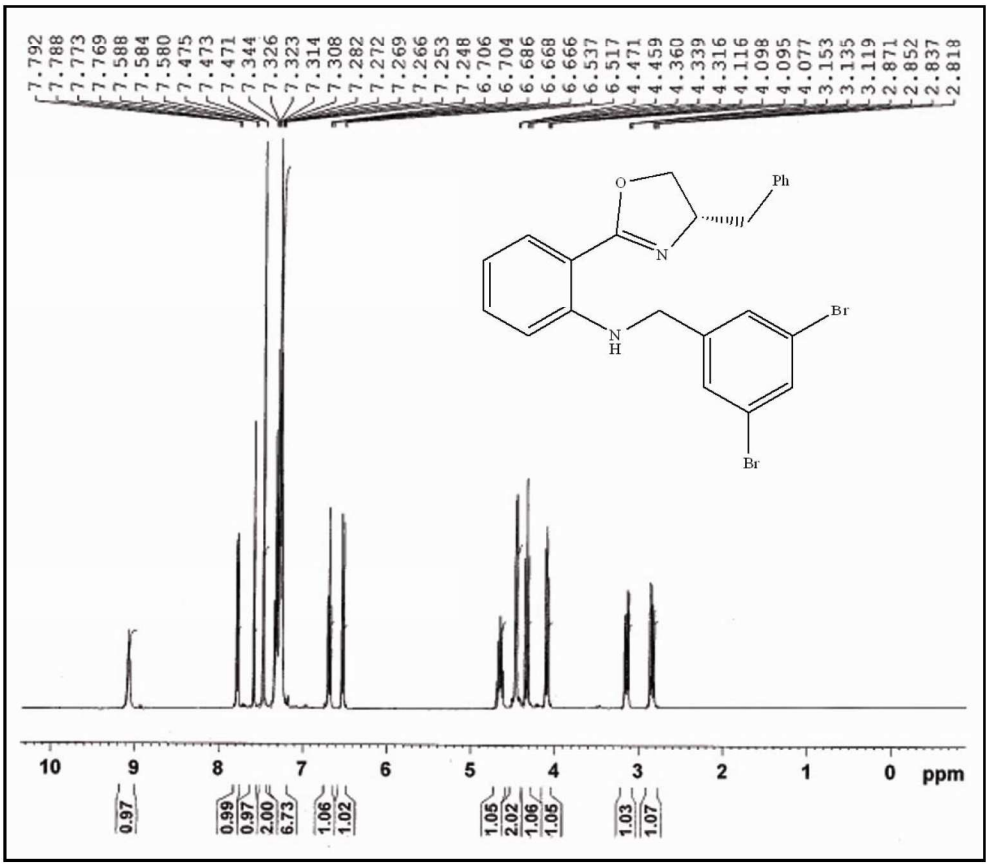
^{1}H-NMR spectra of compound 47a (400MHz, $CDCl_3$)



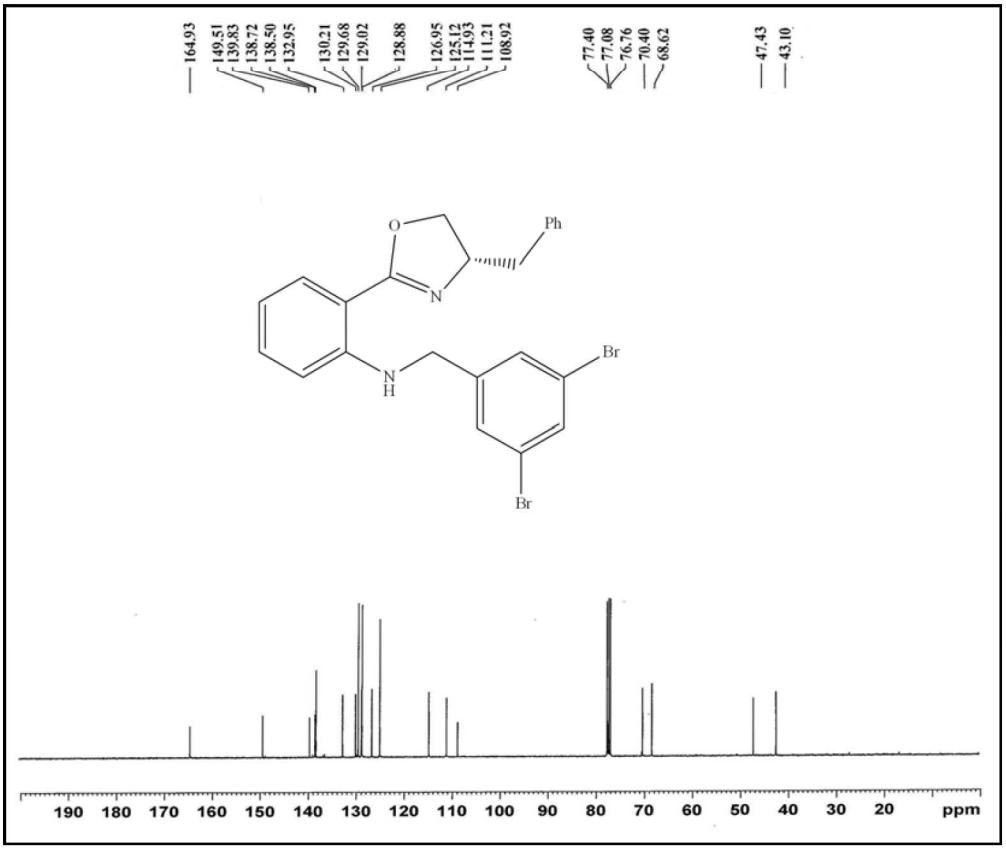
^{13}C-NMR of the compound 47a (100 MHz, $CDCl_3$)



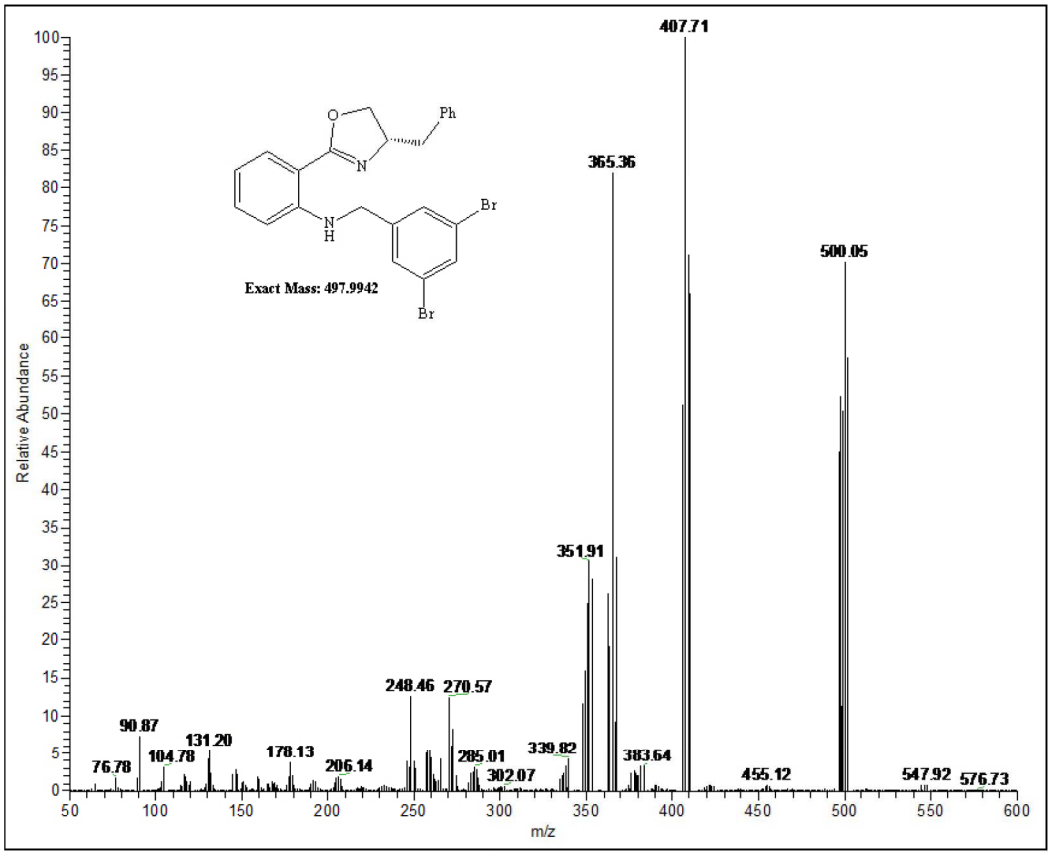
EI-Mass Spectra of Compound 47a



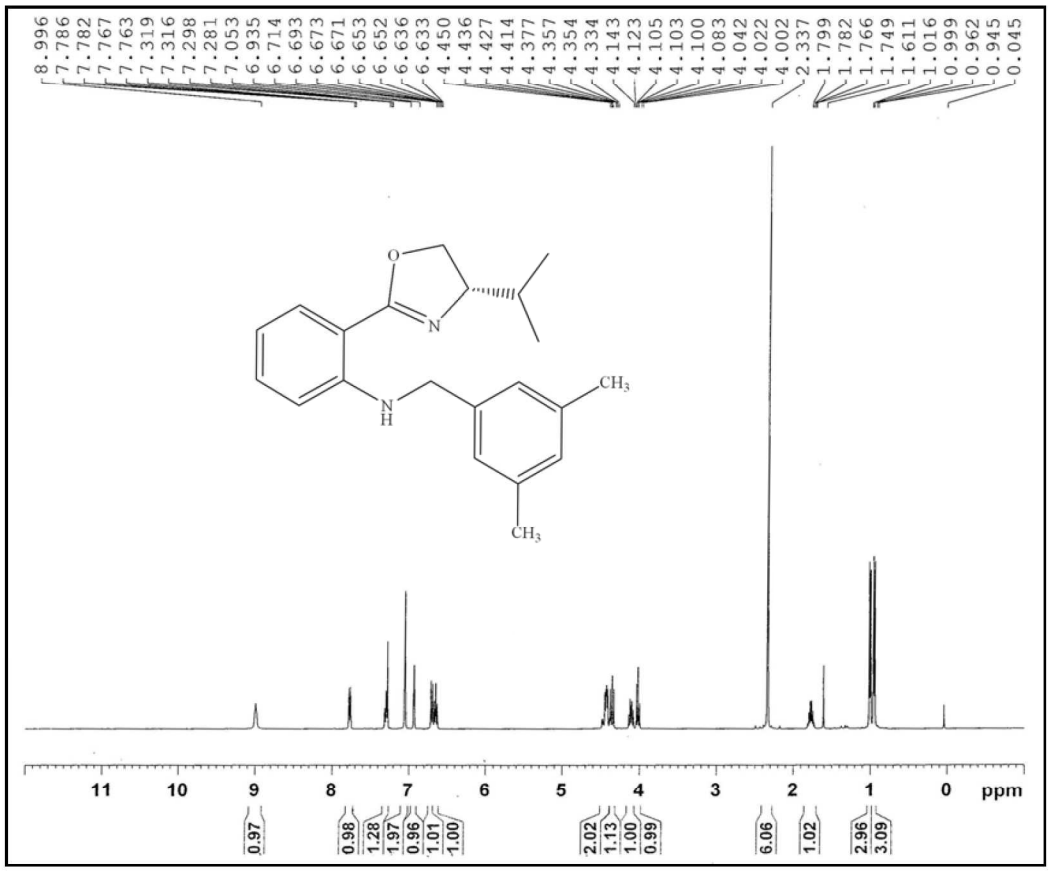
^{1}H-NMR spectra of compound 47b (400MHz, $CDCl_3$)



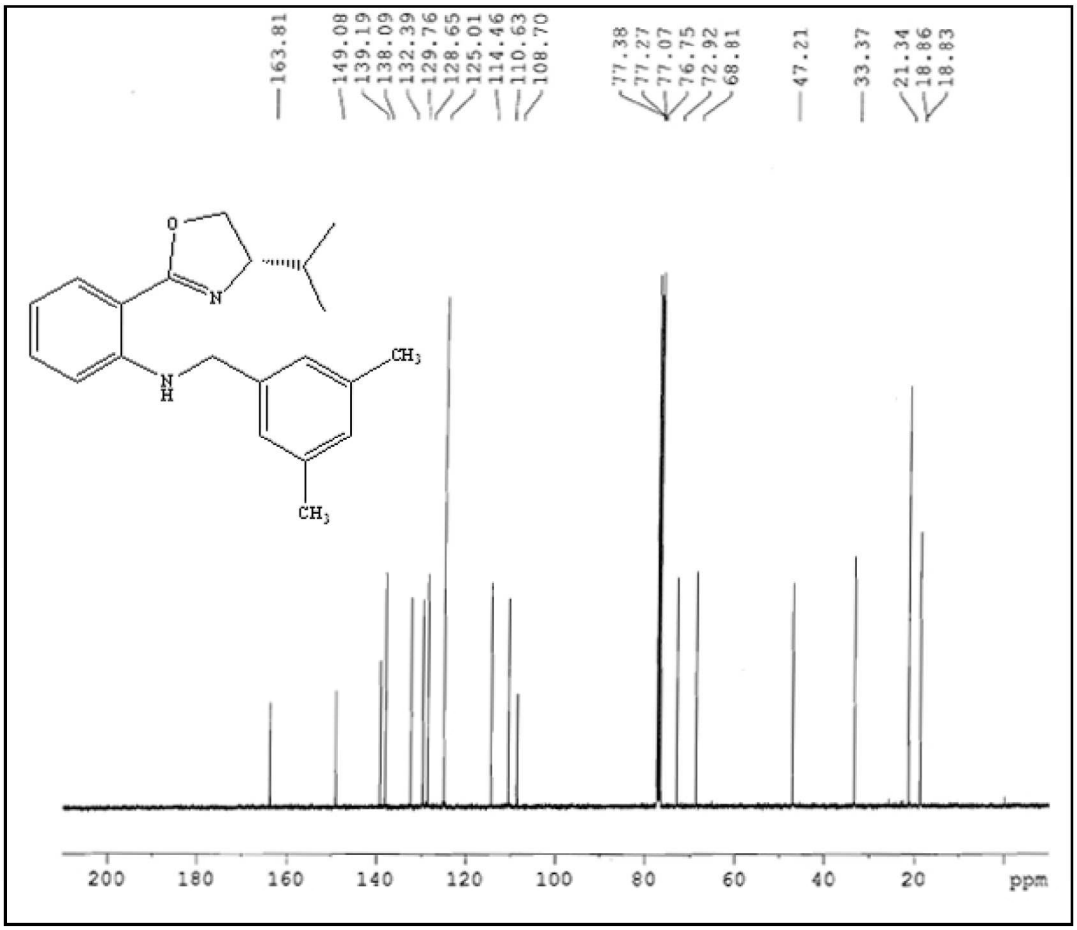
^{13}C-NMR of the compound 47b (100 MHz, $CDCl_3$)



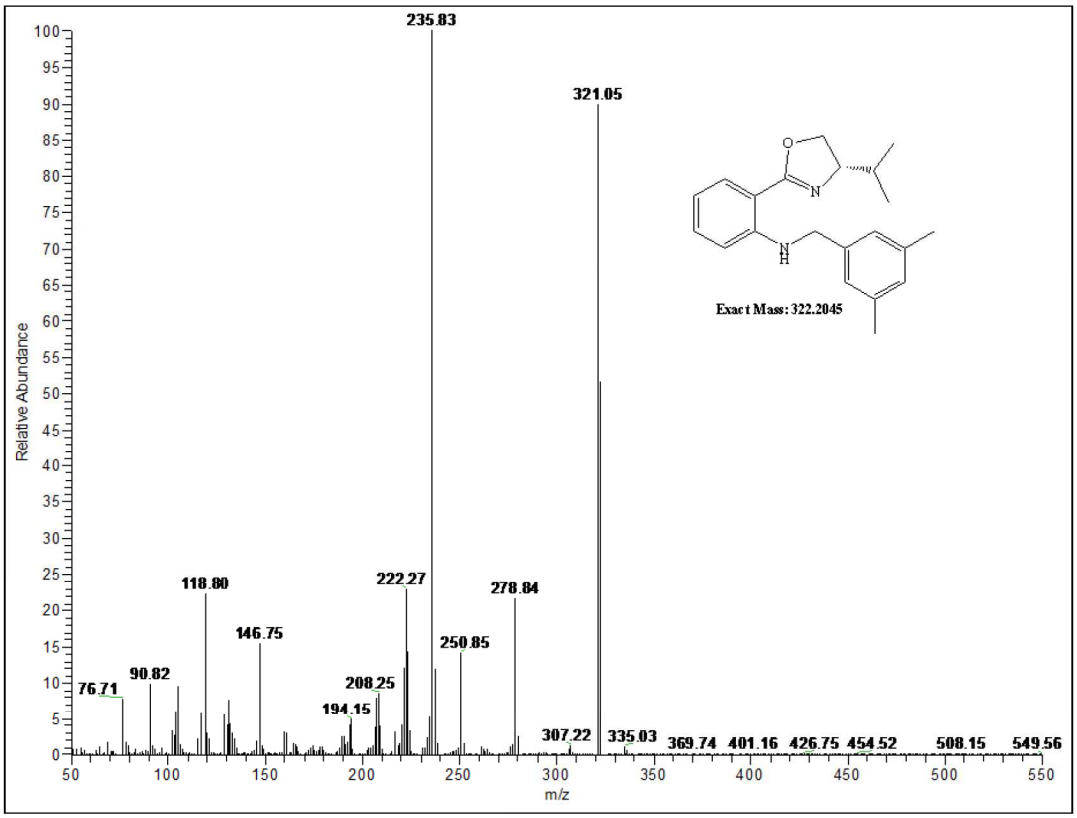
EI-Mass Spectra of Compound 47b



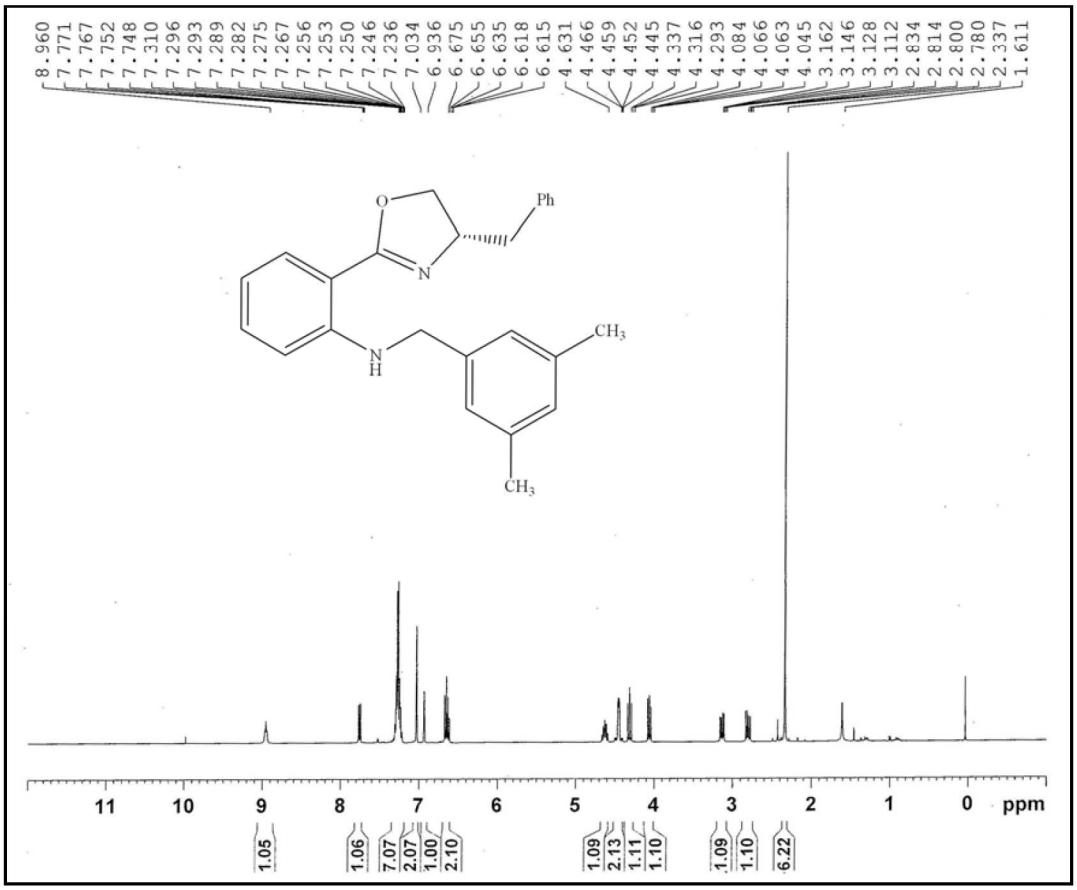
^{1}H-NMR spectra of compound 48a (400MHz, $CDCl_3$)



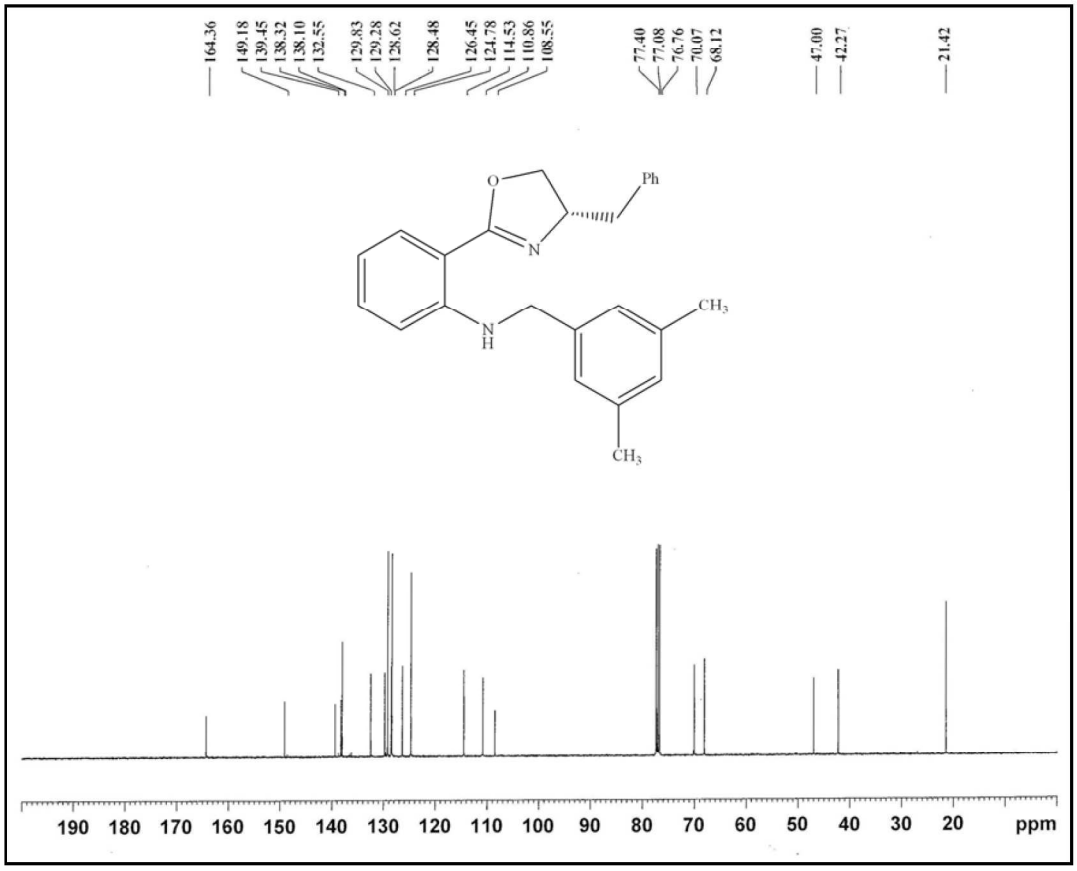
^{13}C-NMR of the compound 48a (100 MHz, $CDCl_3$)



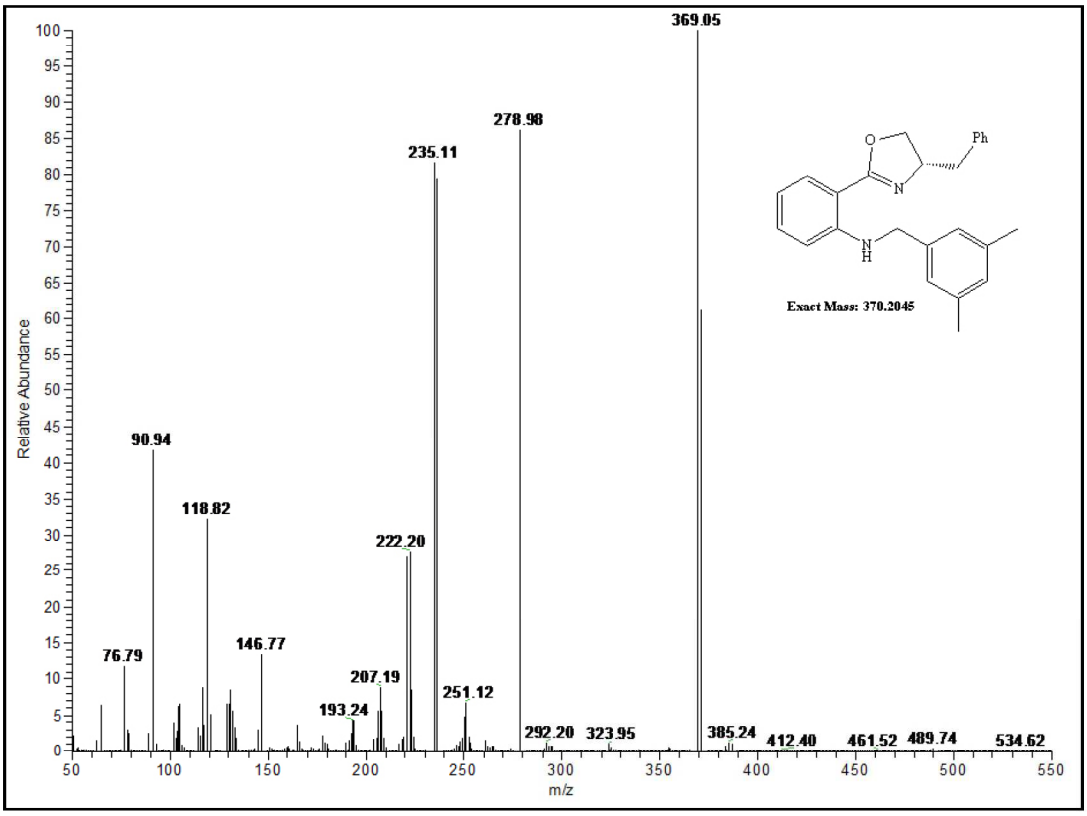
EI-Mass Spectra of Compound 48a



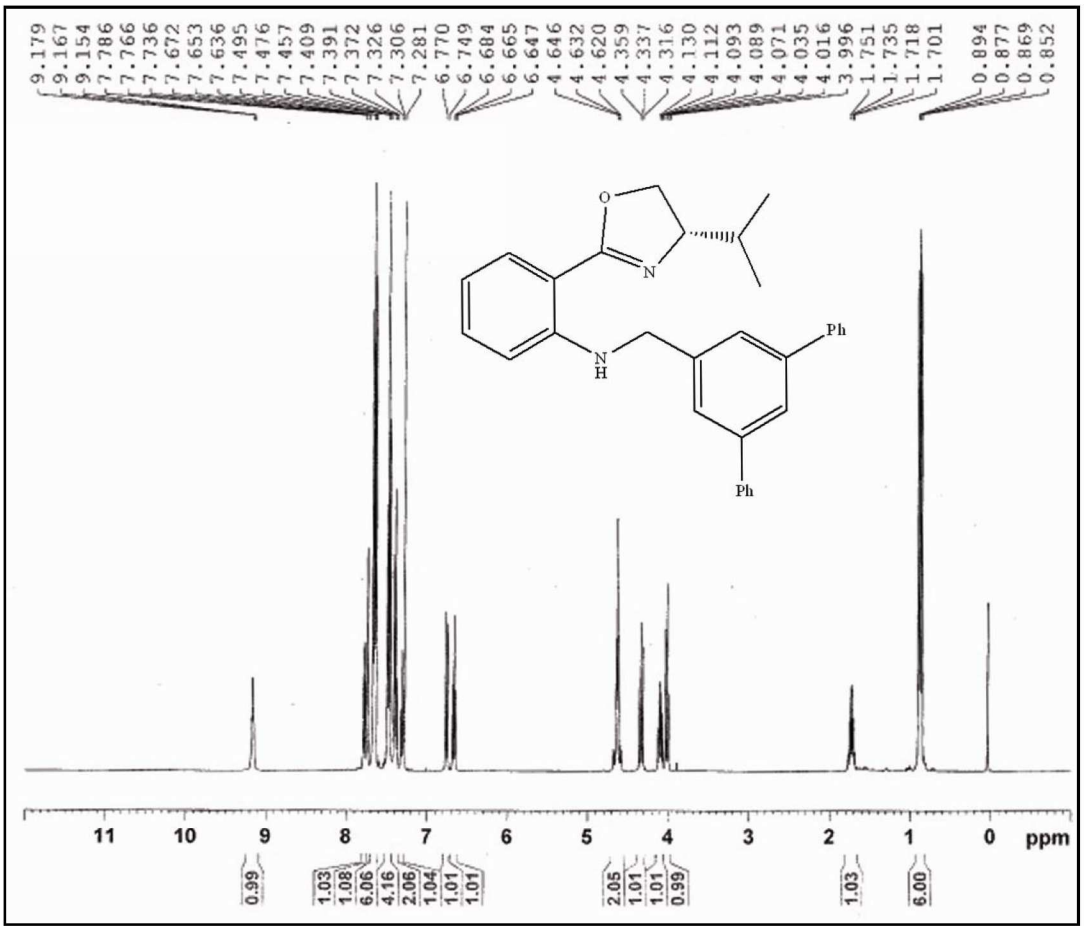
[1]H-NMR spectra of compound 48b (400MHz, $CDCl_3$)



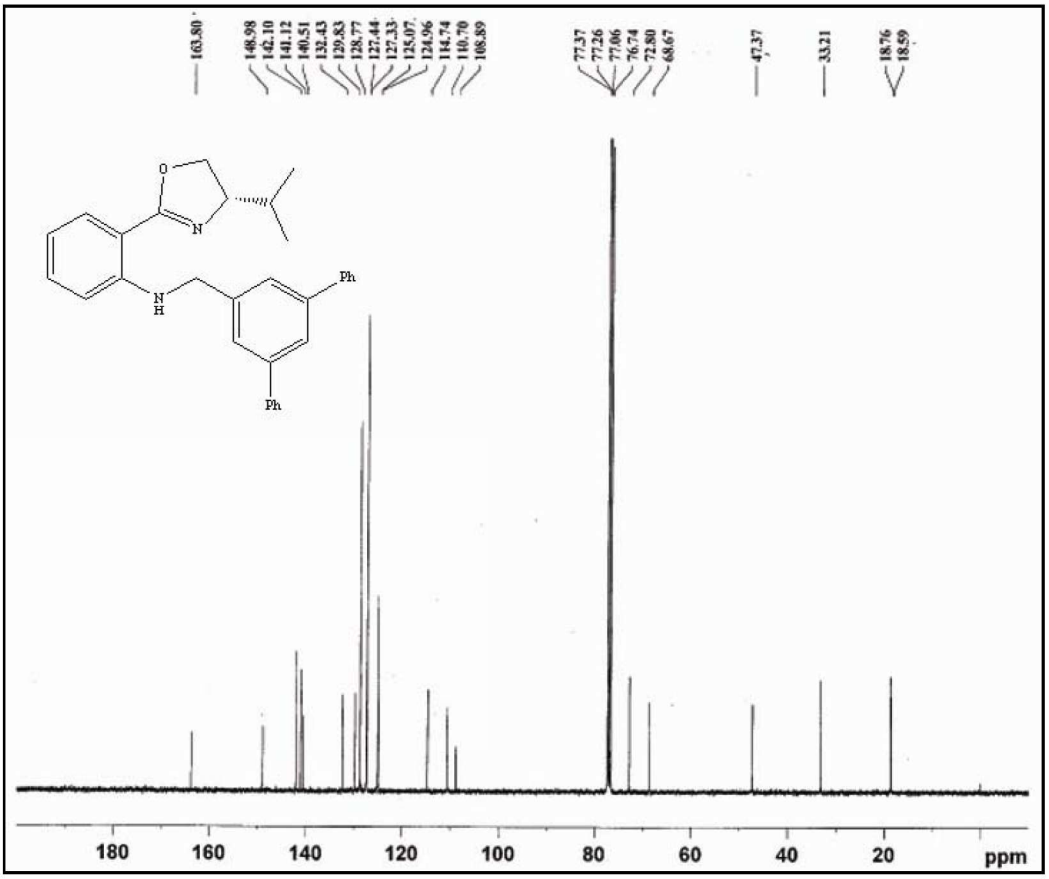
[13]C-NMR of the compound 48b (100 MHz, $CDCl_3$)



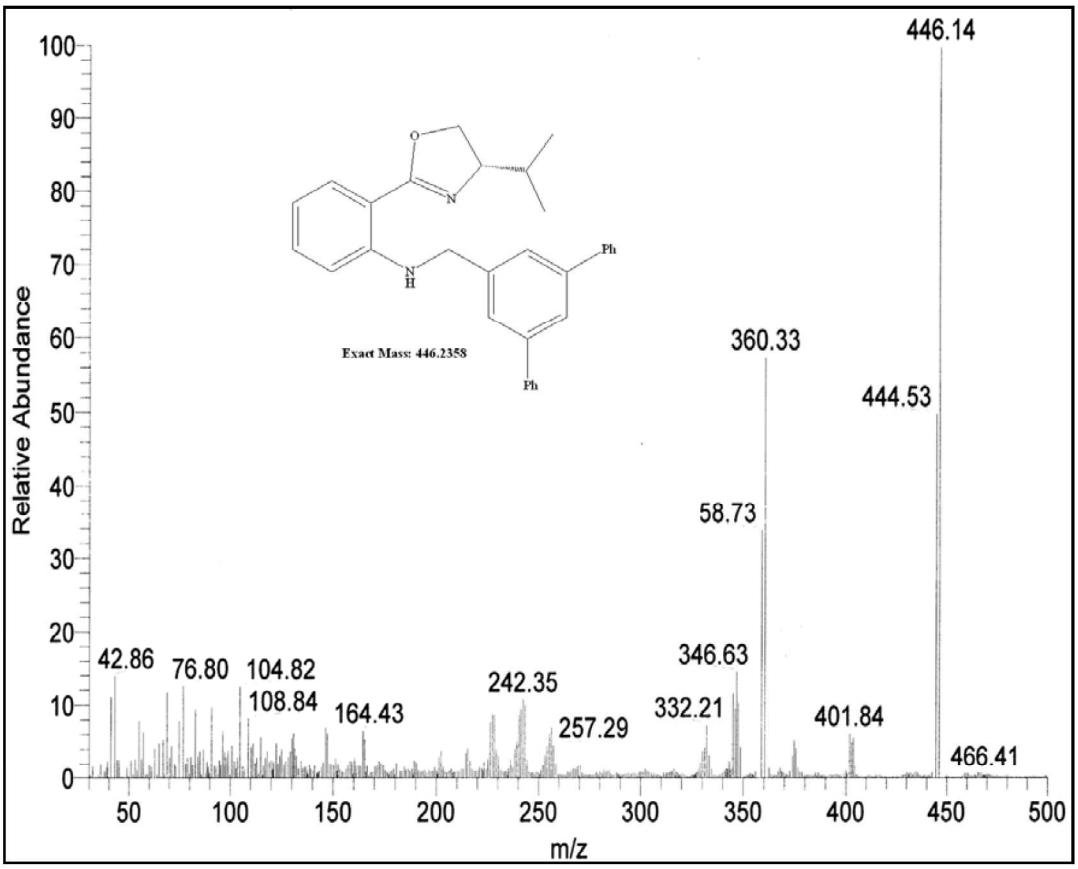
EI-Mass Spectra of Compound 48b



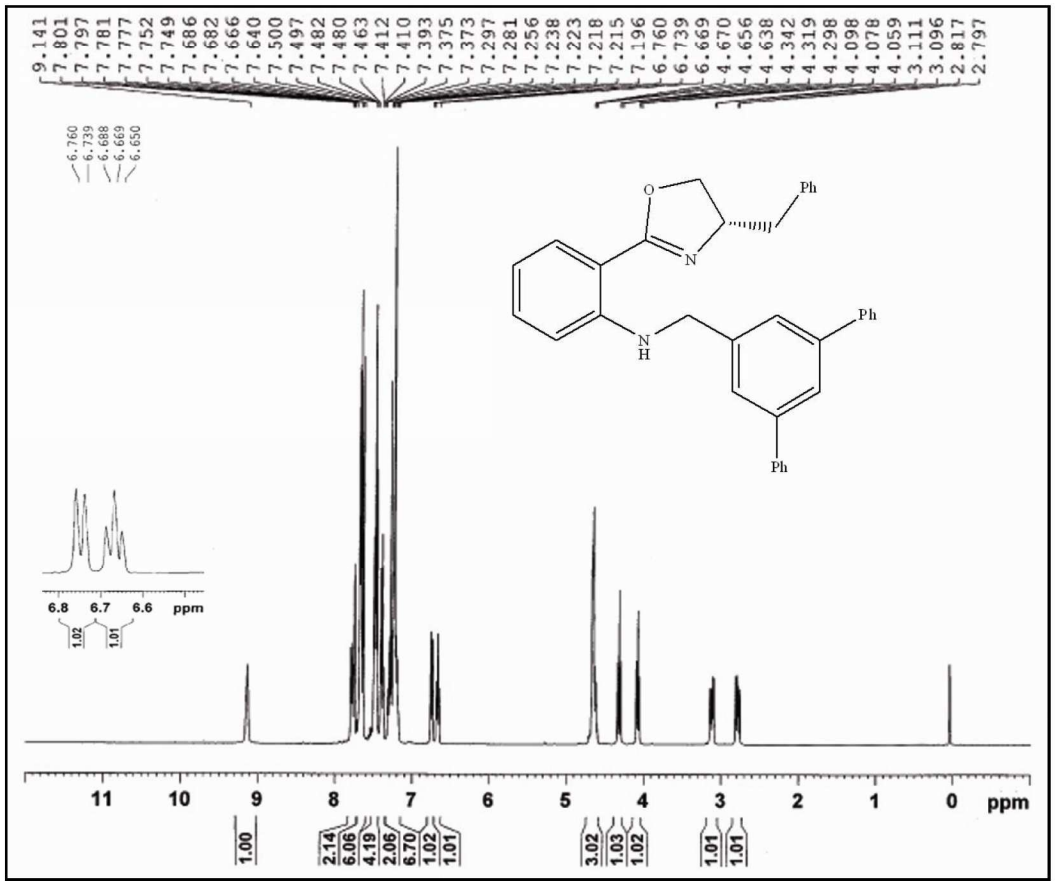
^{1}H-NMR spectra of compound 49a (400MHz, $CDCl_3$)



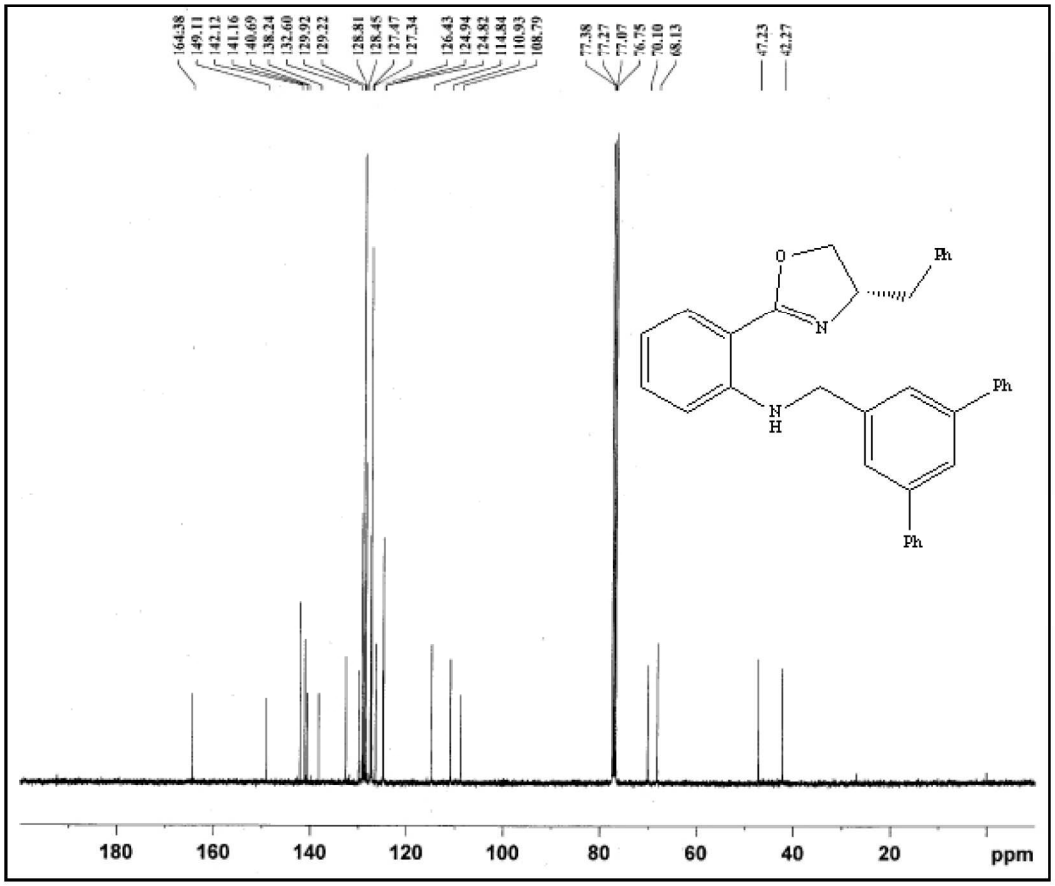
^{13}C-NMR of the compound 49a (100 MHz, $CDCl_3$)



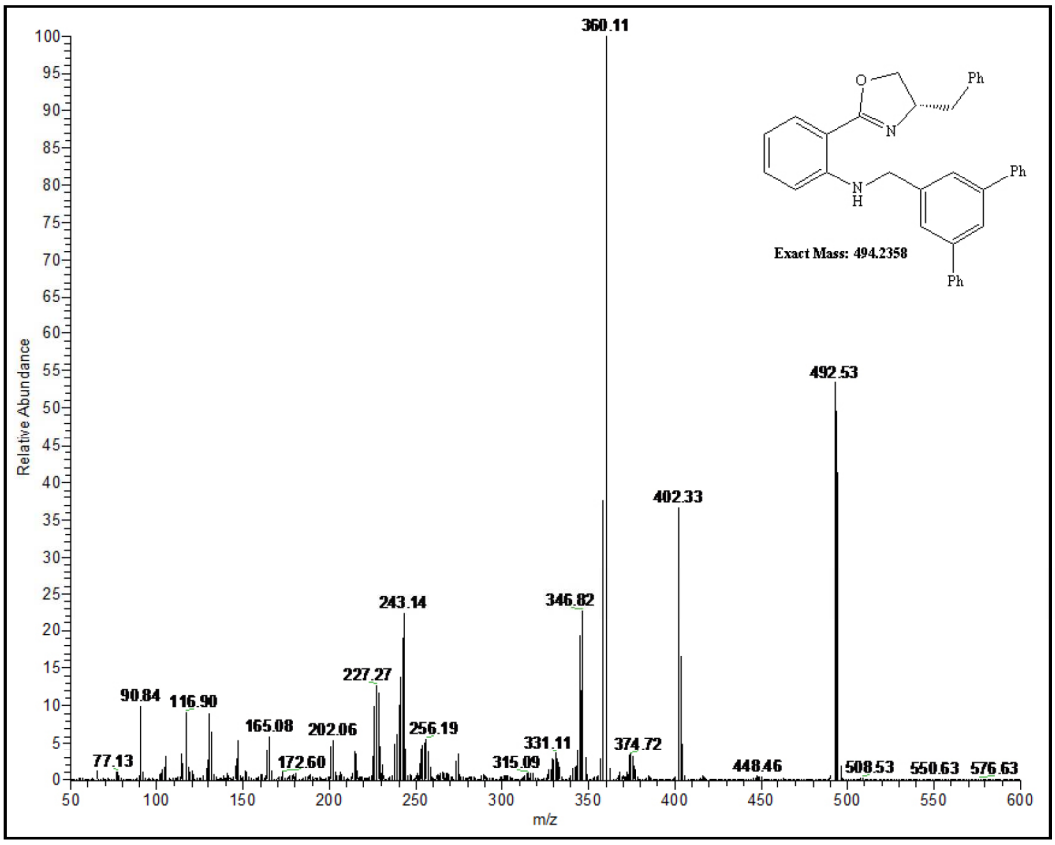
EI-Mass Spectra of Compound 49a



^{1}H-NMR spectra of compound 49b (400MHz, $CDCl_3$)

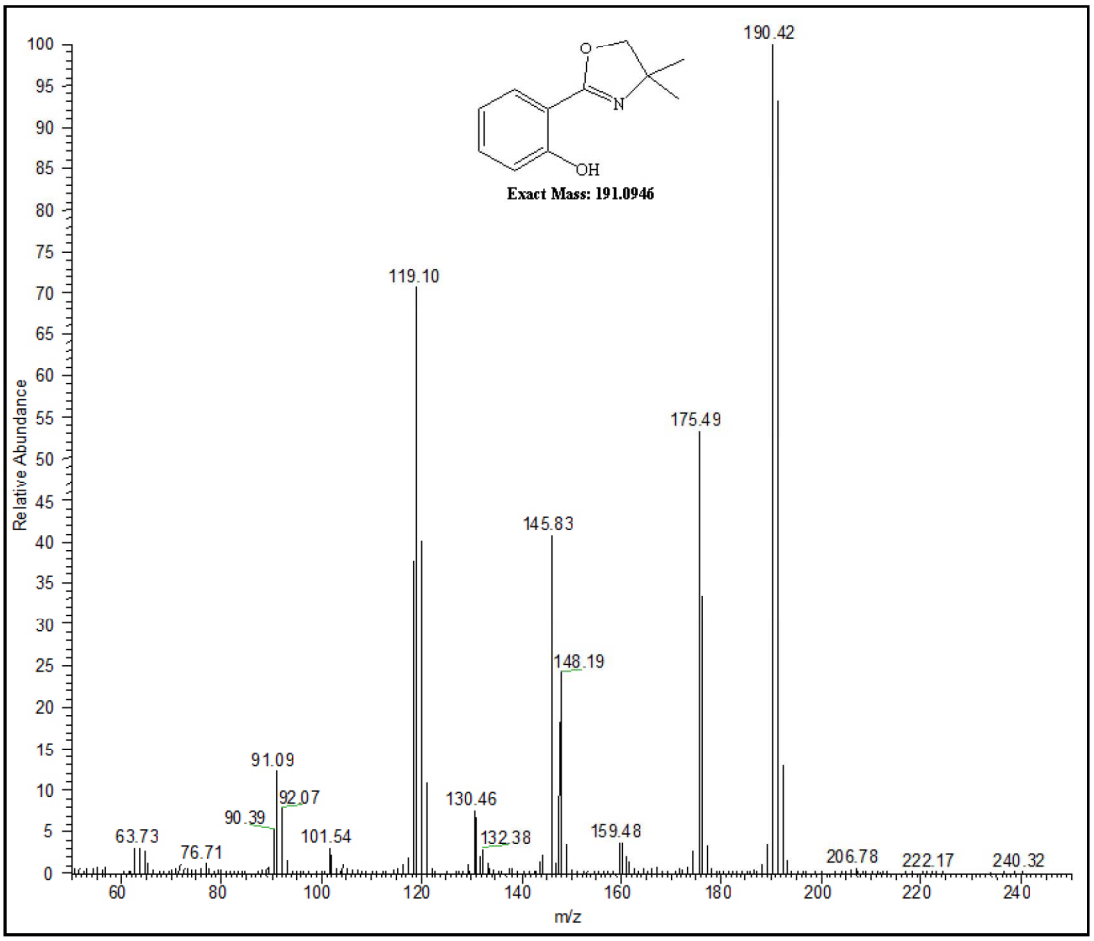


^{13}C-NMR of the compound 49b (100 MHz, $CDCl_3$)

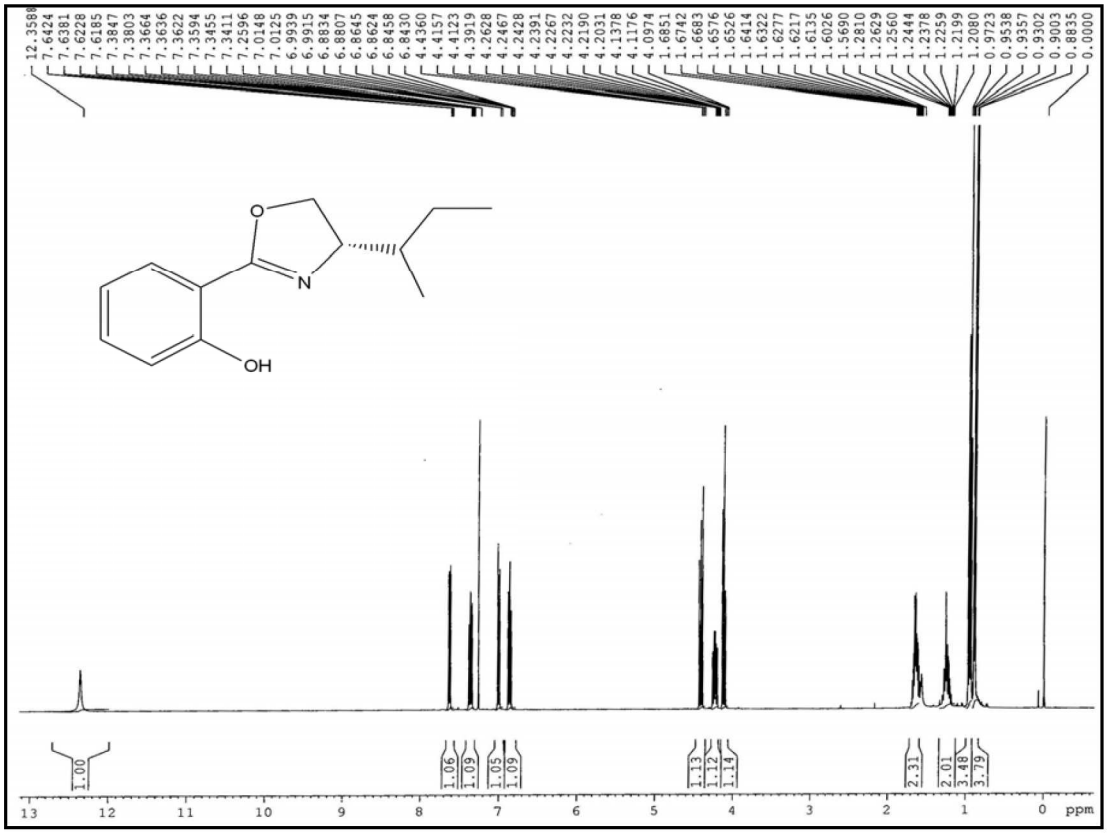


EI-Mass Spectra of Compound 49b

^{1}H-NMR spectra of compound 51 (400MHz, $CDCl_3$)

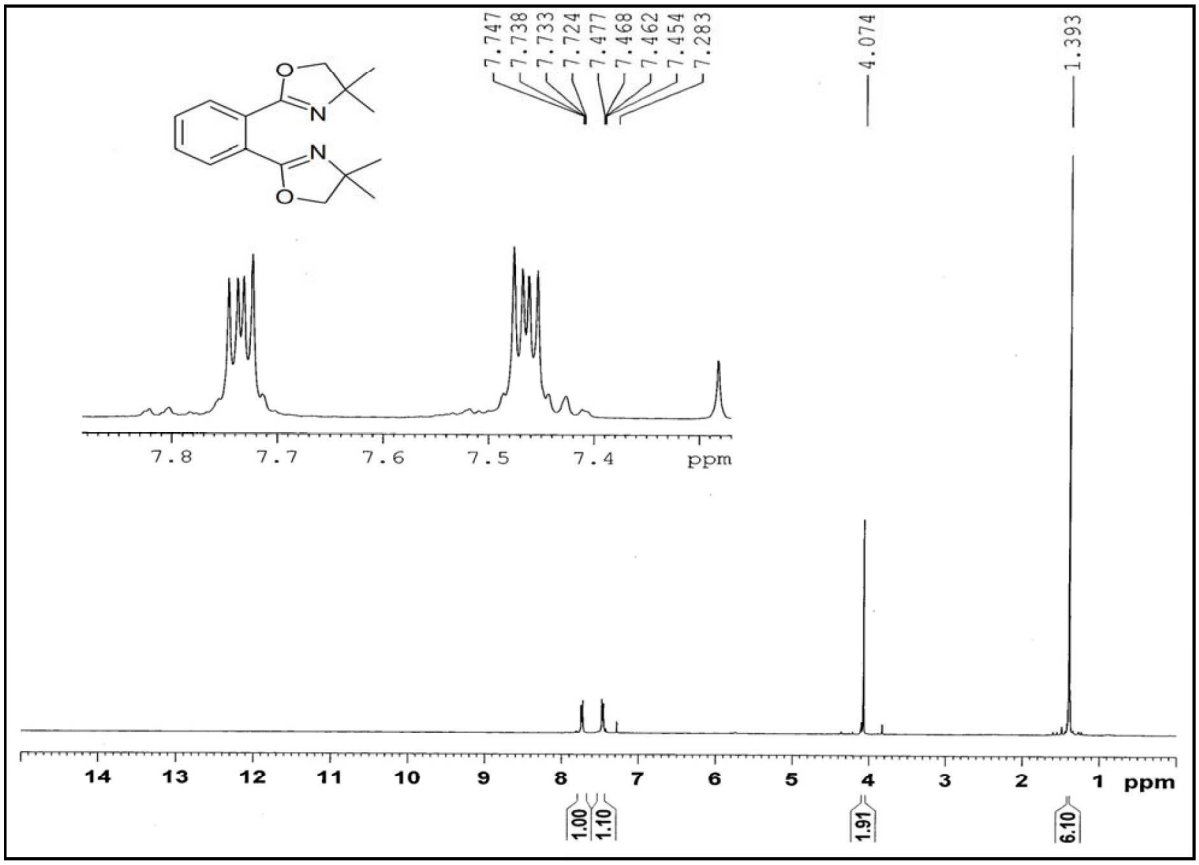


EI-Mass Spectra of Compound 51

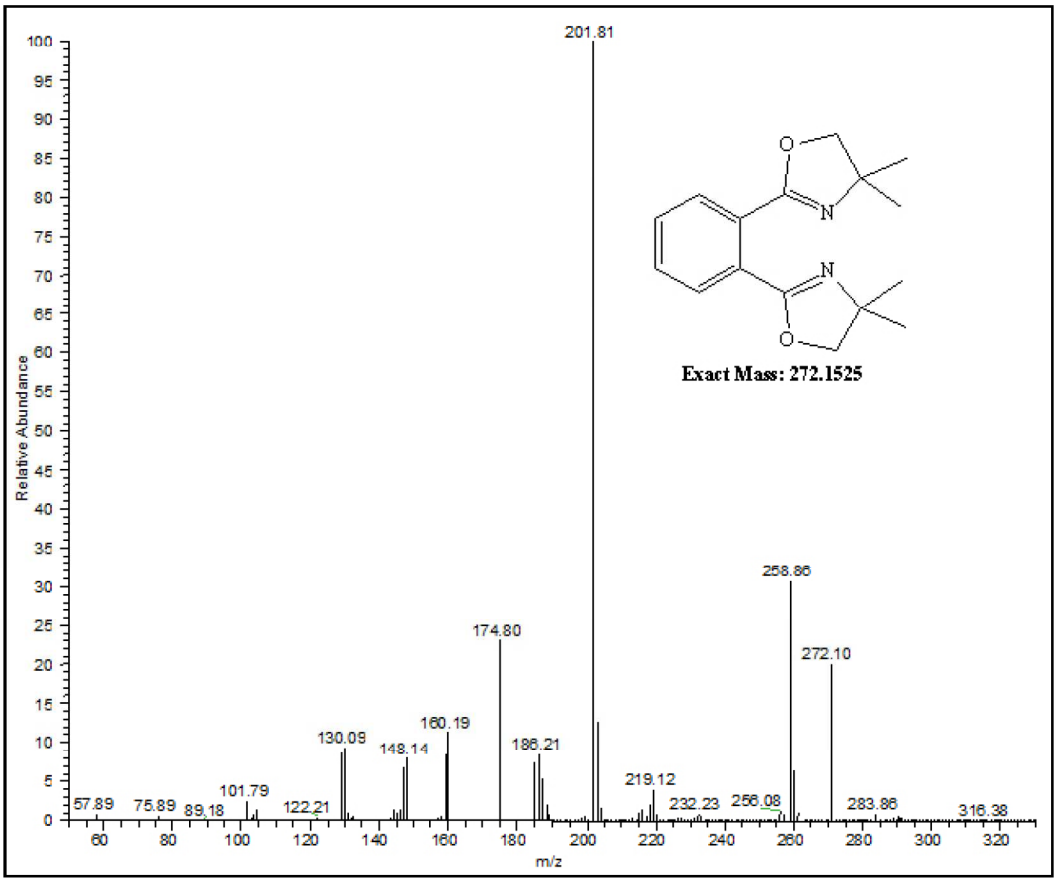


^{1}H-NMR spectra of compound 52 (400MHz, $CDCl_3$)

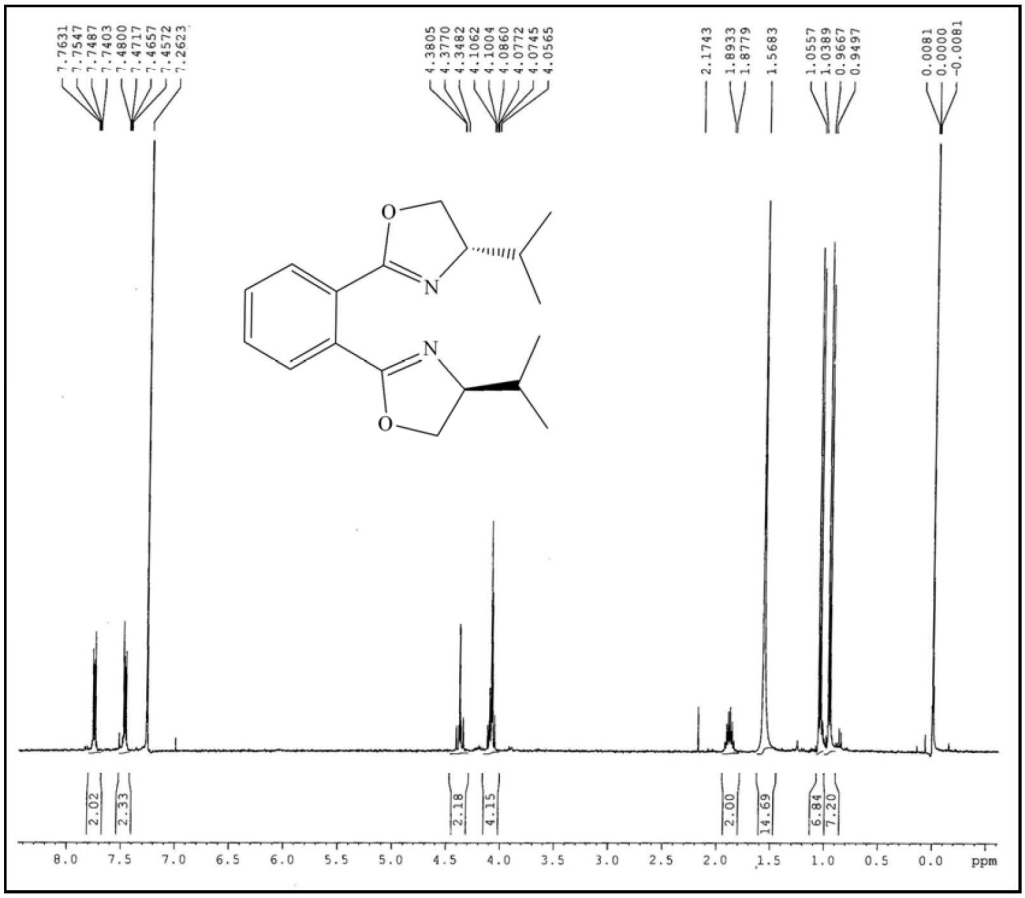
^{1}H-NMR spectra of compound 53 (400MHz, $CDCl_3$)



^{1}H-NMR spectra of compound 55 (400MHz, $CDCl_3$)



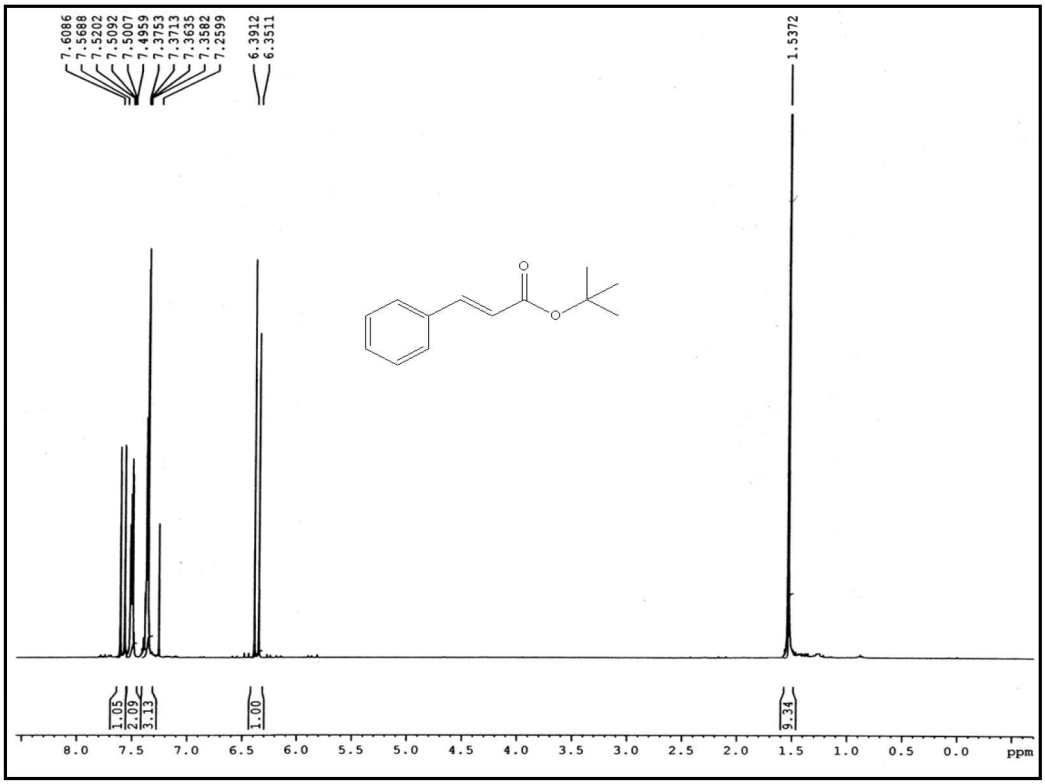
EI-Mass Spectra of Compound 55



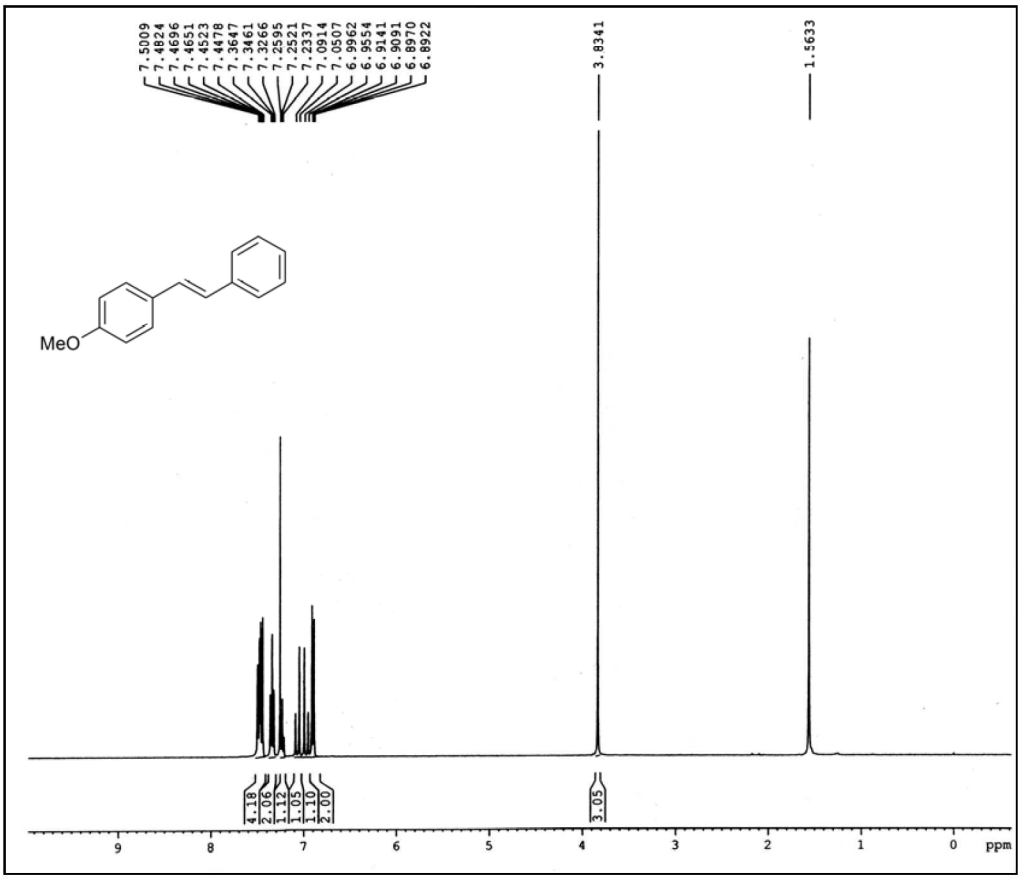
^{1}H-NMR spectra of compound 56 (400MHz, $CDCl_3$)

Specral Data for Part-II: Application of Oxazolinyl Ligands in Mizoroki-Heck Reaction

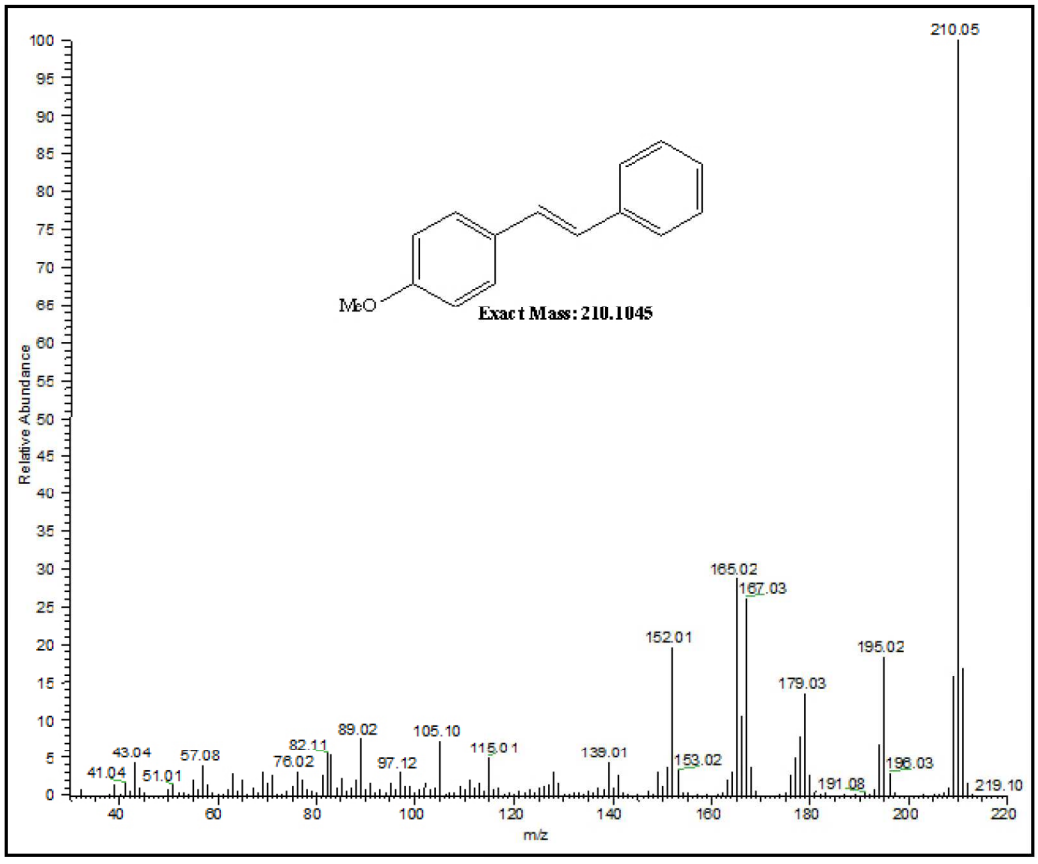
^{1}H-NMR of compound 60 (400 MHz, $CDCl_3$)



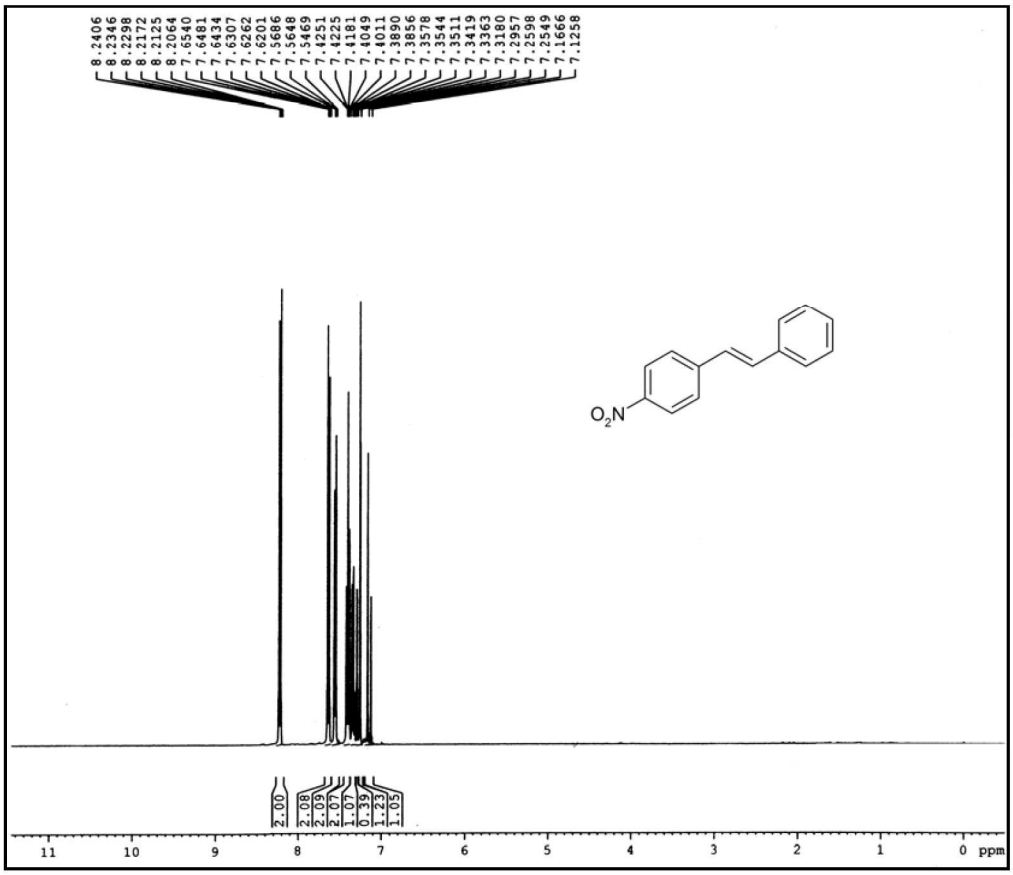
^{1}H-NMR of compound 64 (400 MHz, $CDCl_3$)



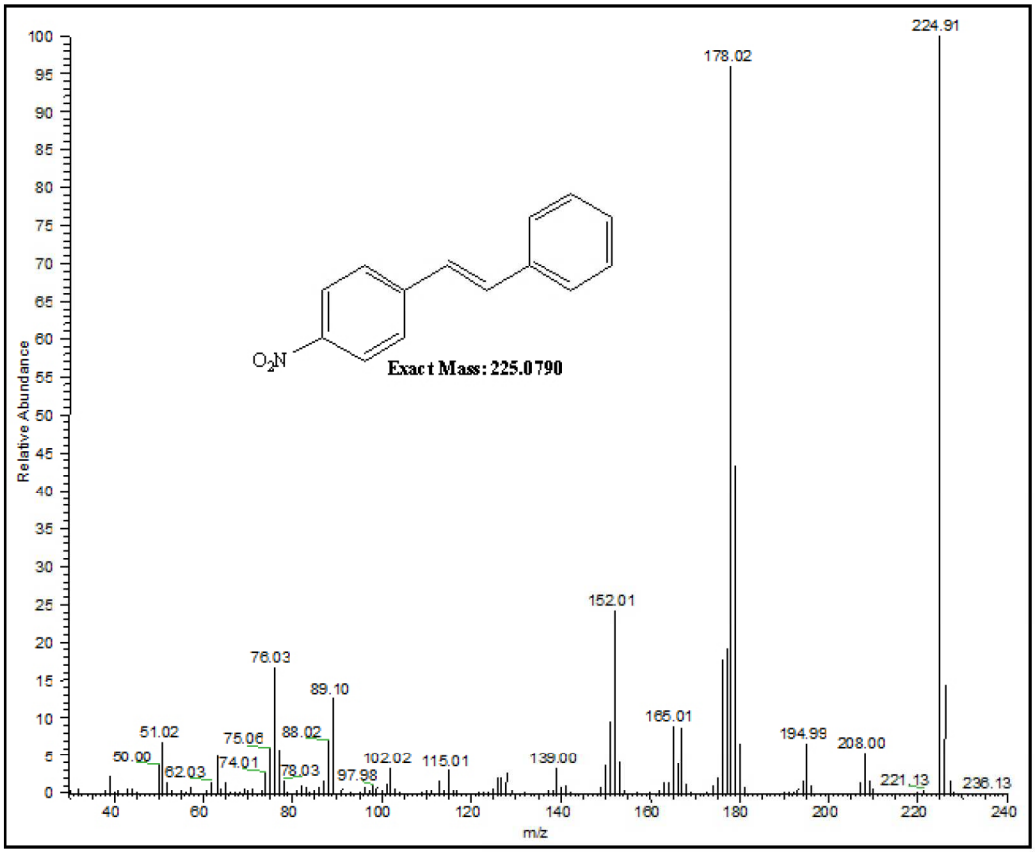
^{1}H-NMR of Compound 67 (400 MHz, $CDCl_3$)



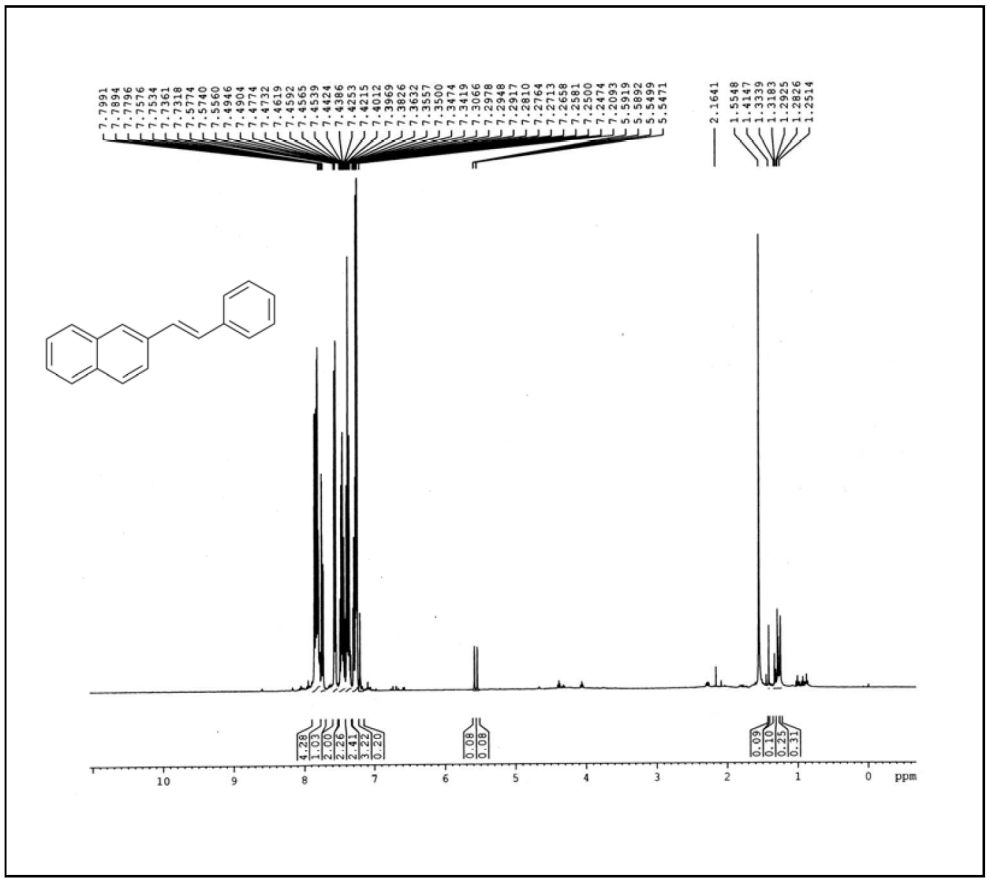
EI-Mass Spectra of Compound 67



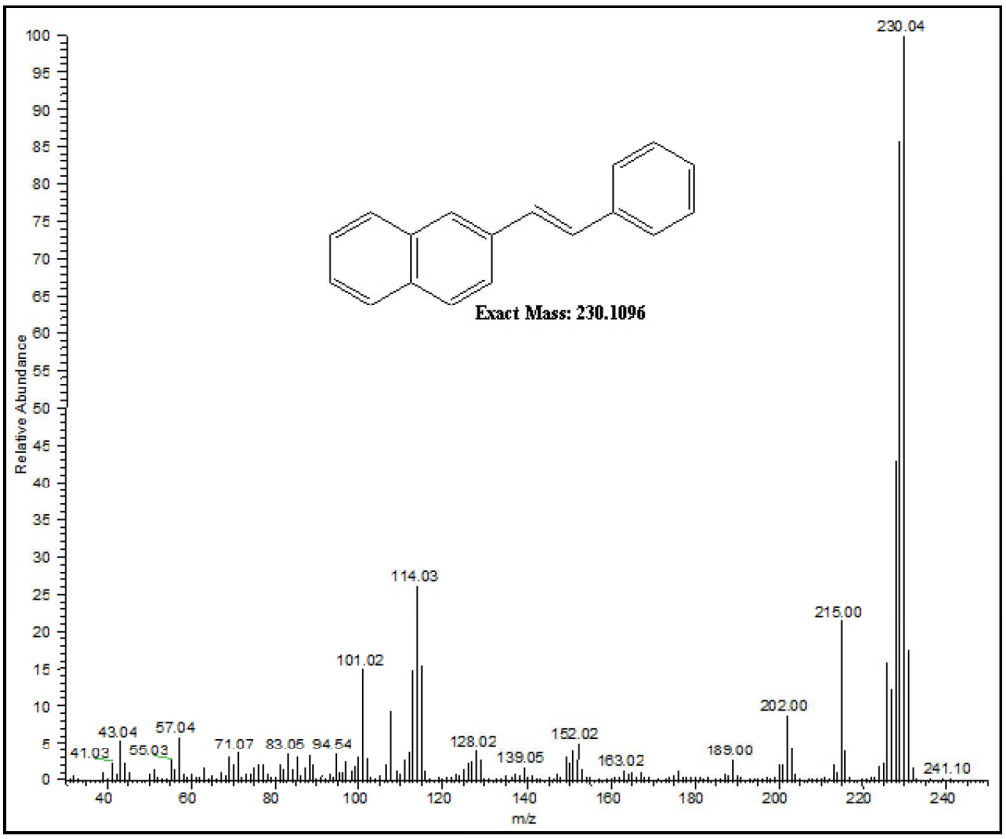
^{1}H-NMR of Compound 69 (400 MHz, $CDCl_3$)



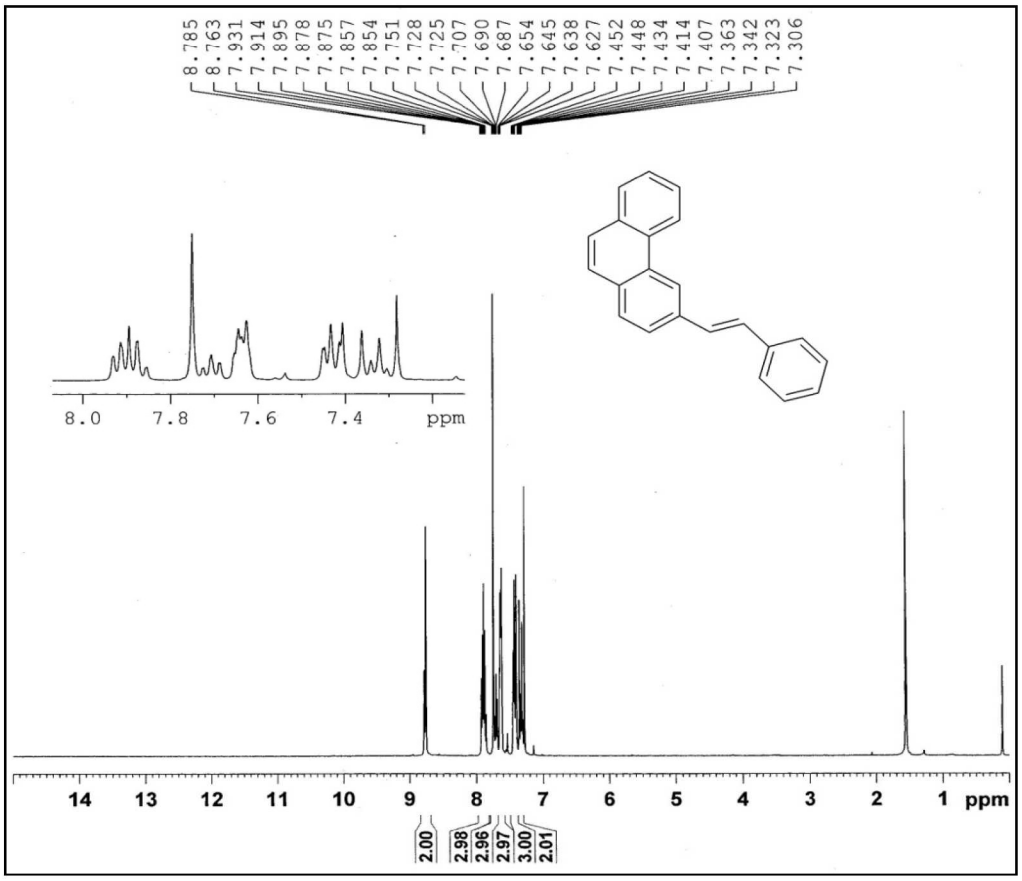
EI-Mass Spectra of Compound 69



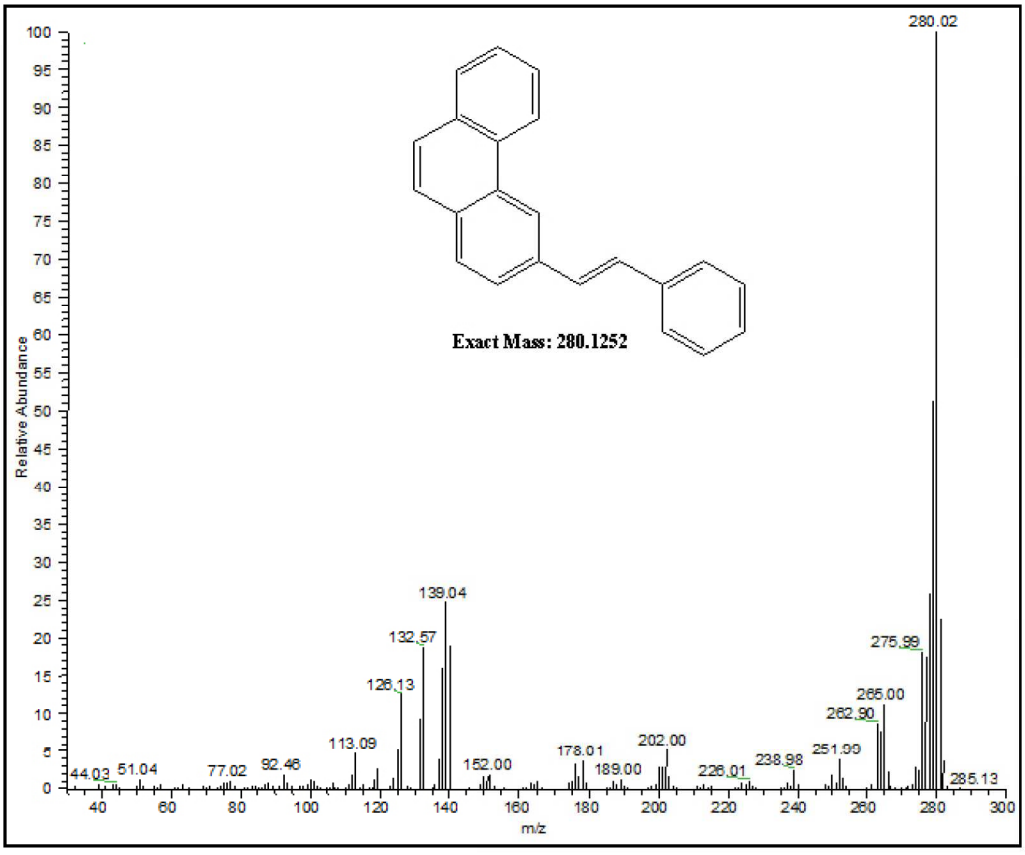
^{1}H-NMR of Compound 71 (400 MHz, $CDCl_3$)



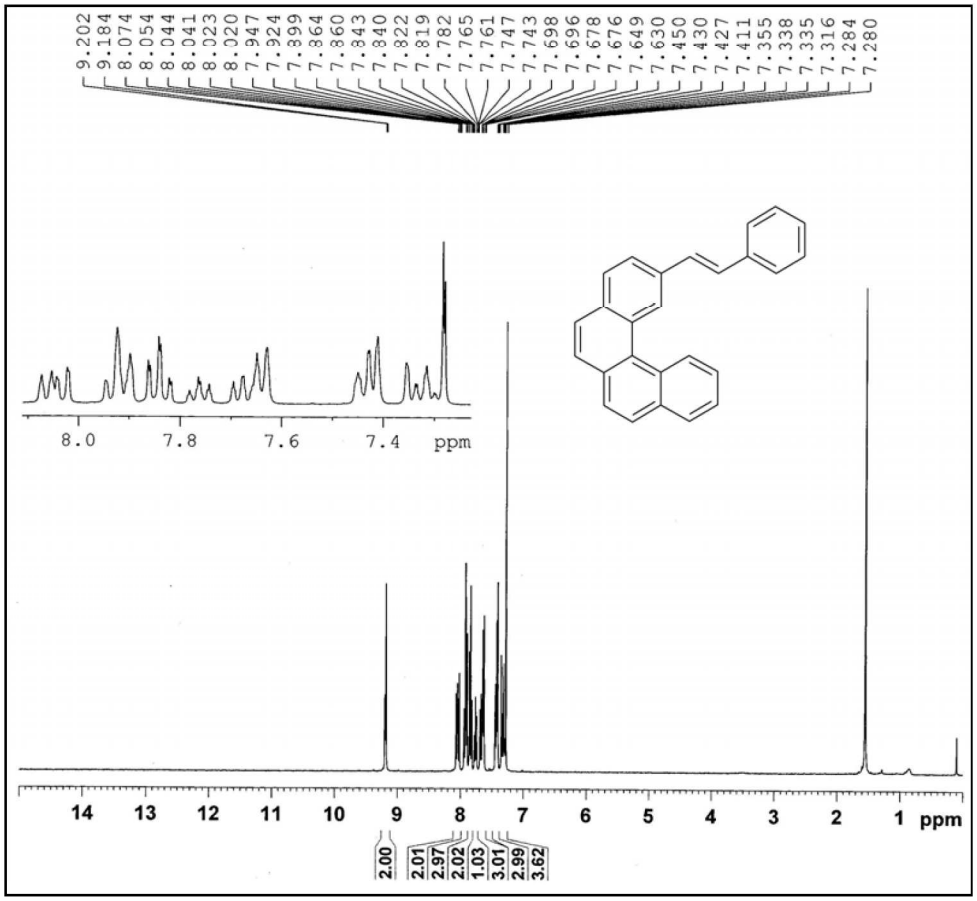
EI-Mass Spectra of Compound 71



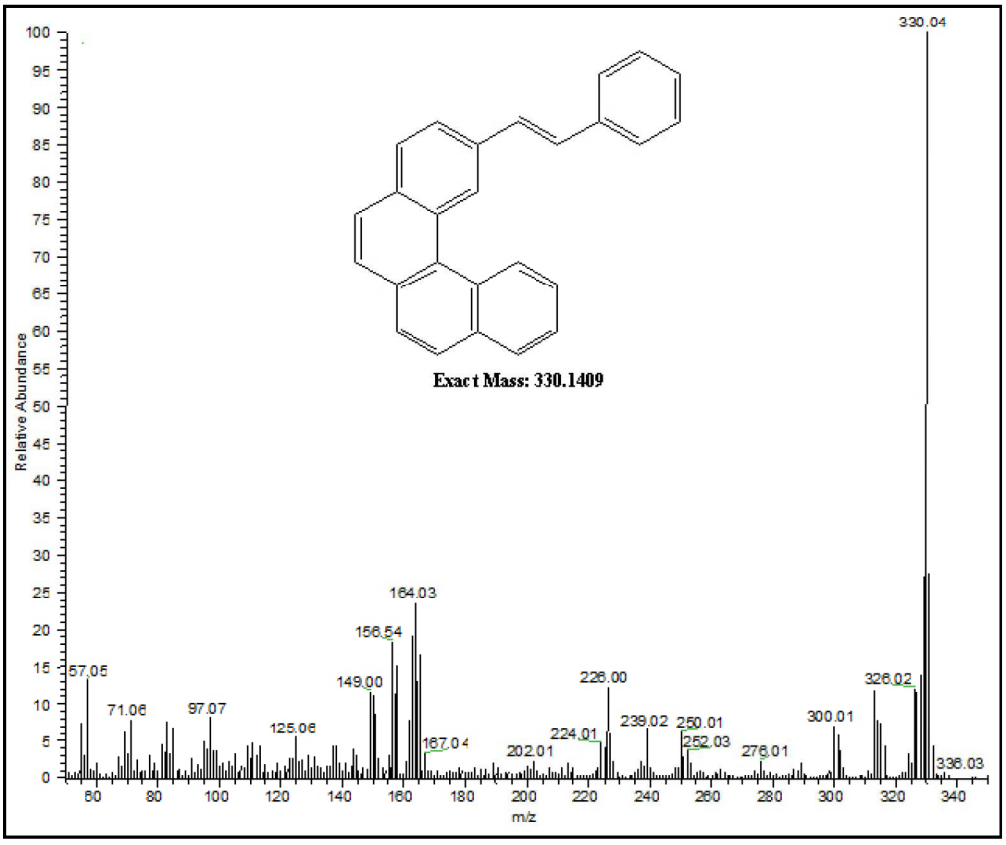
^{1}H-NMR of Compound 73 (400 MHz, $CDCl_3$)



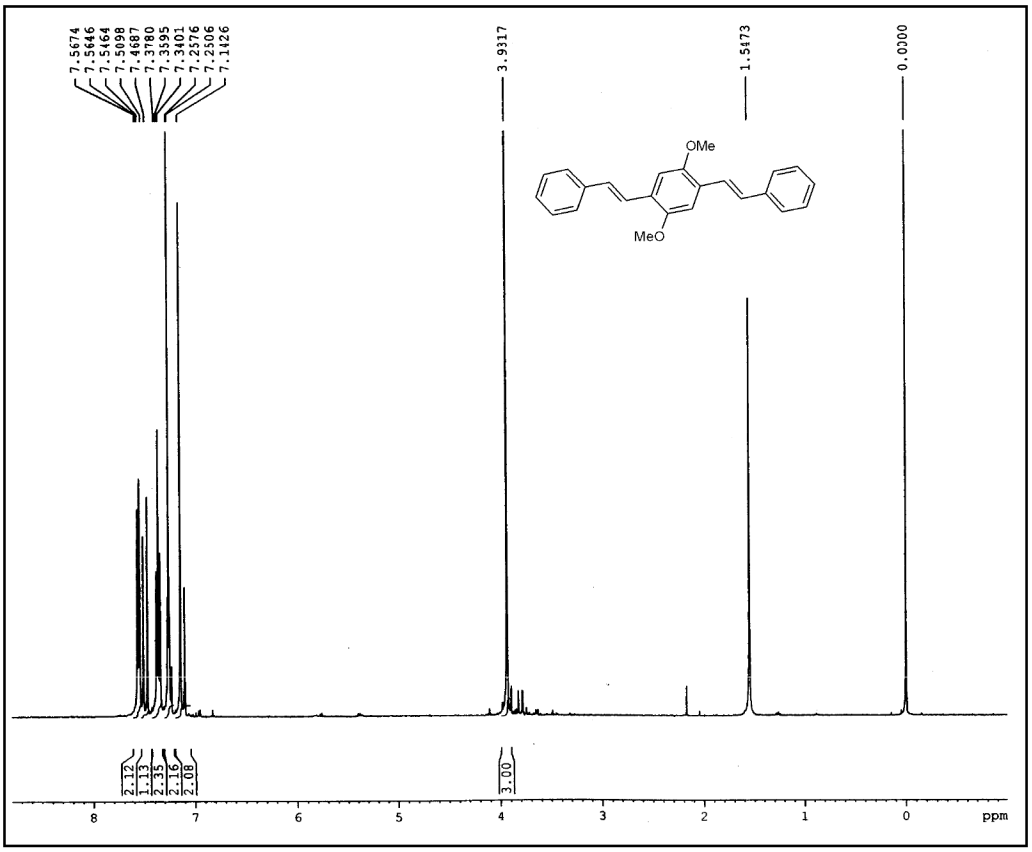
EI-Mass Spectra of Compound 73



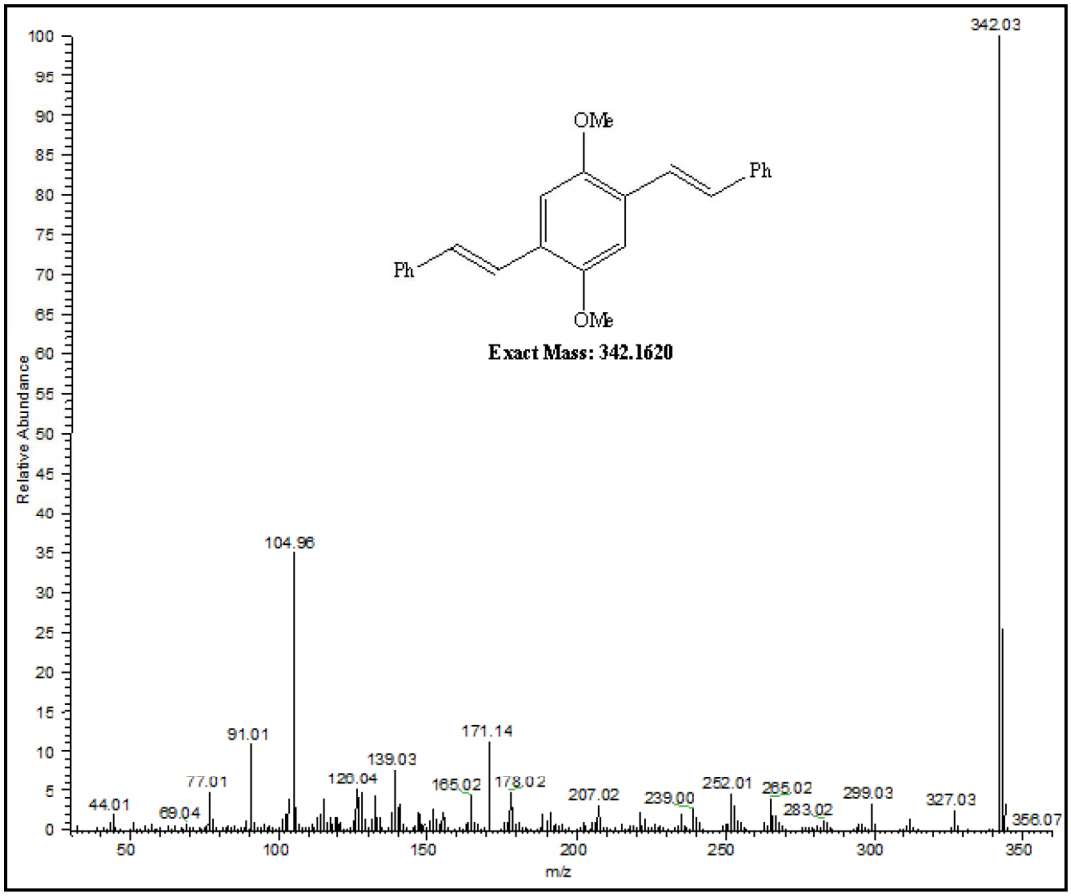
^{1}H-NMR of Compound 75 (400 MHz, $CDCl_3$)



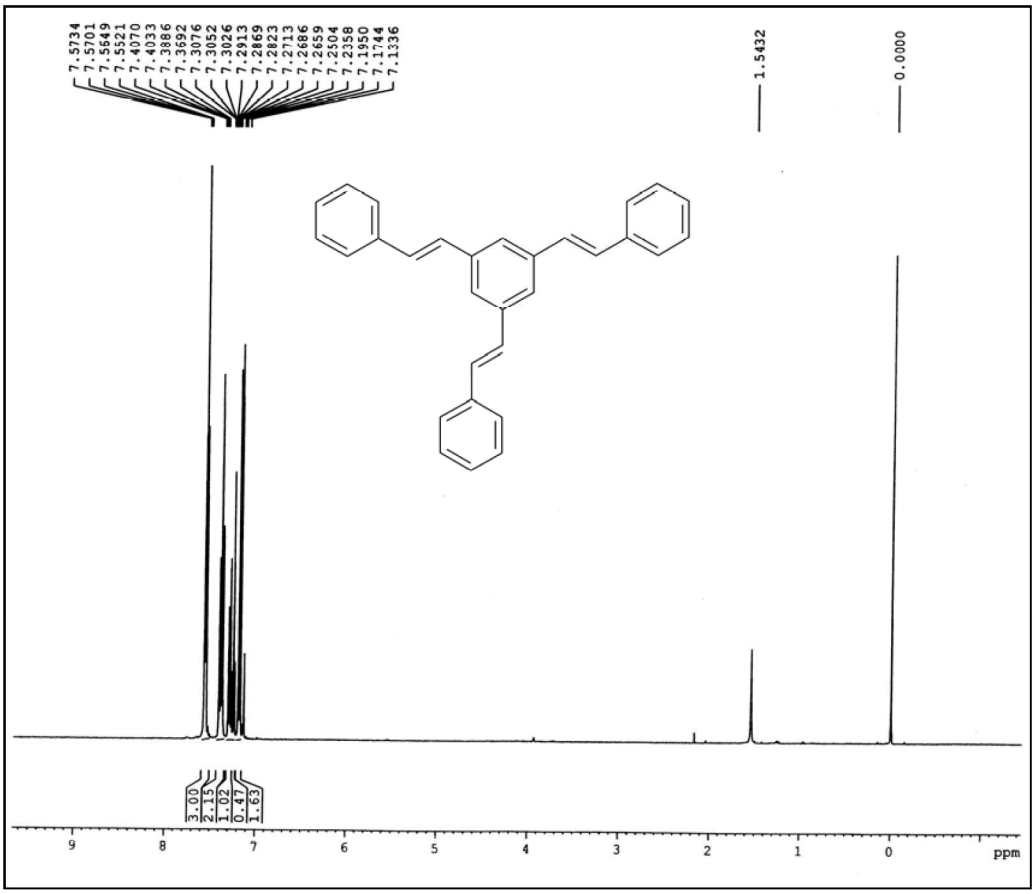
EI-Mass Spectra of Compound 75



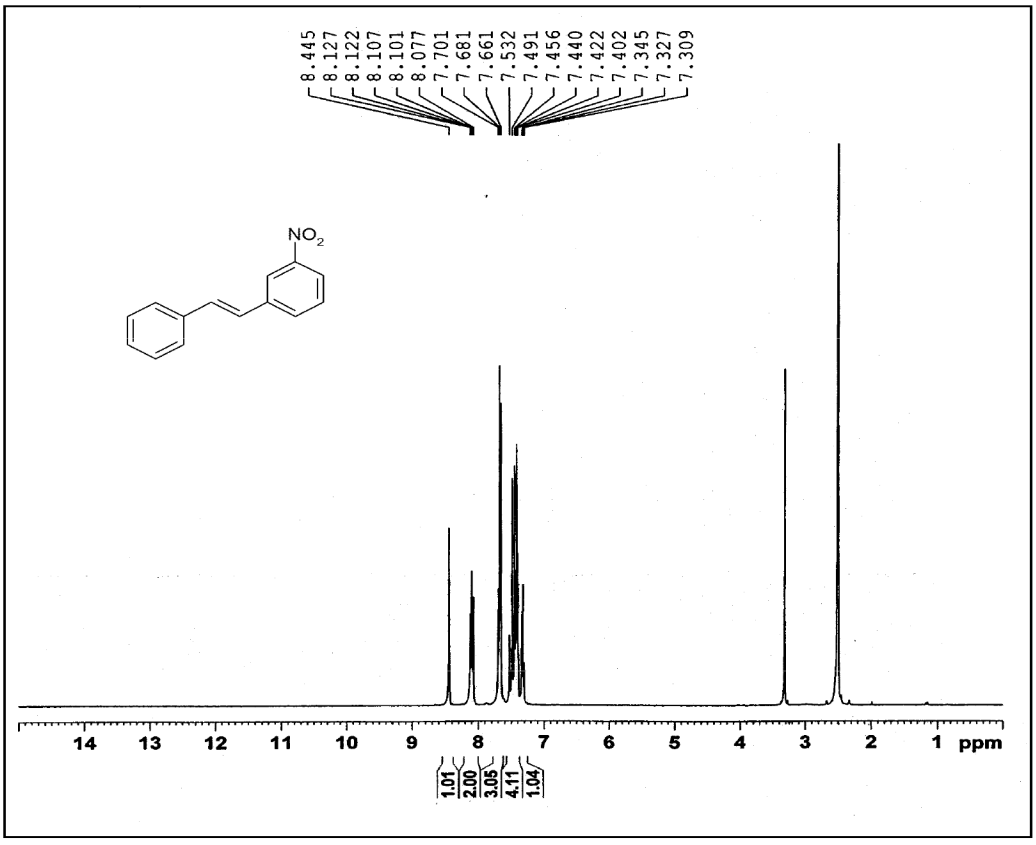
^{1}H-NMR of Compound 77 (400 MHz, $CDCl_3$)



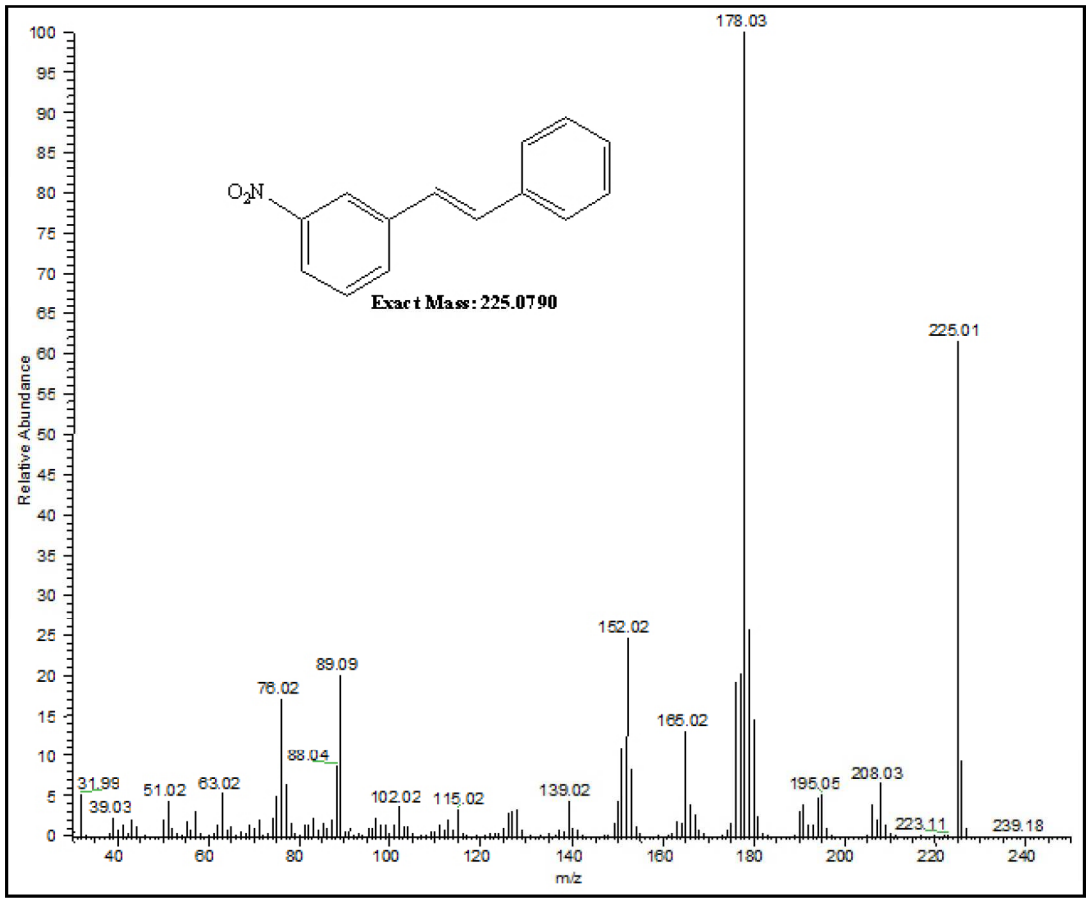
EI-Mass Spectra of Compound 77



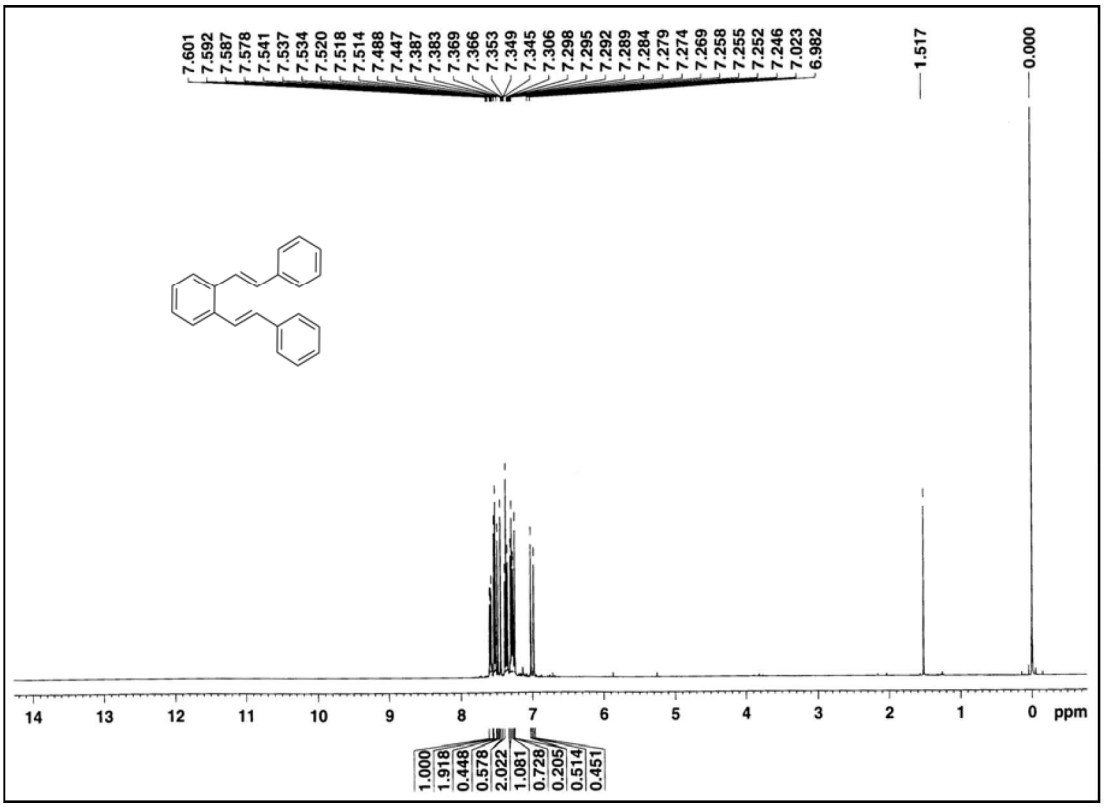
^{1}H-NMR of Compound 79 (400 MHz, $CDCl_3$)



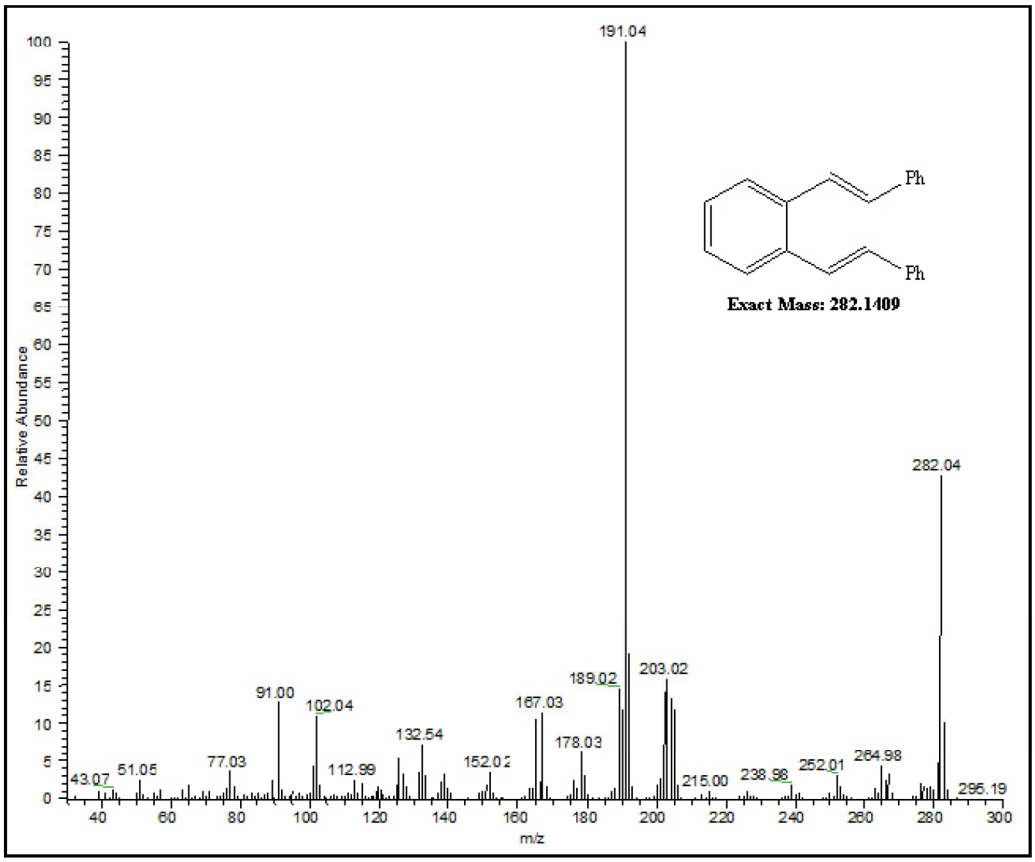
^{1}H-NMR of Compound 83 (400 MHz, DMSO)



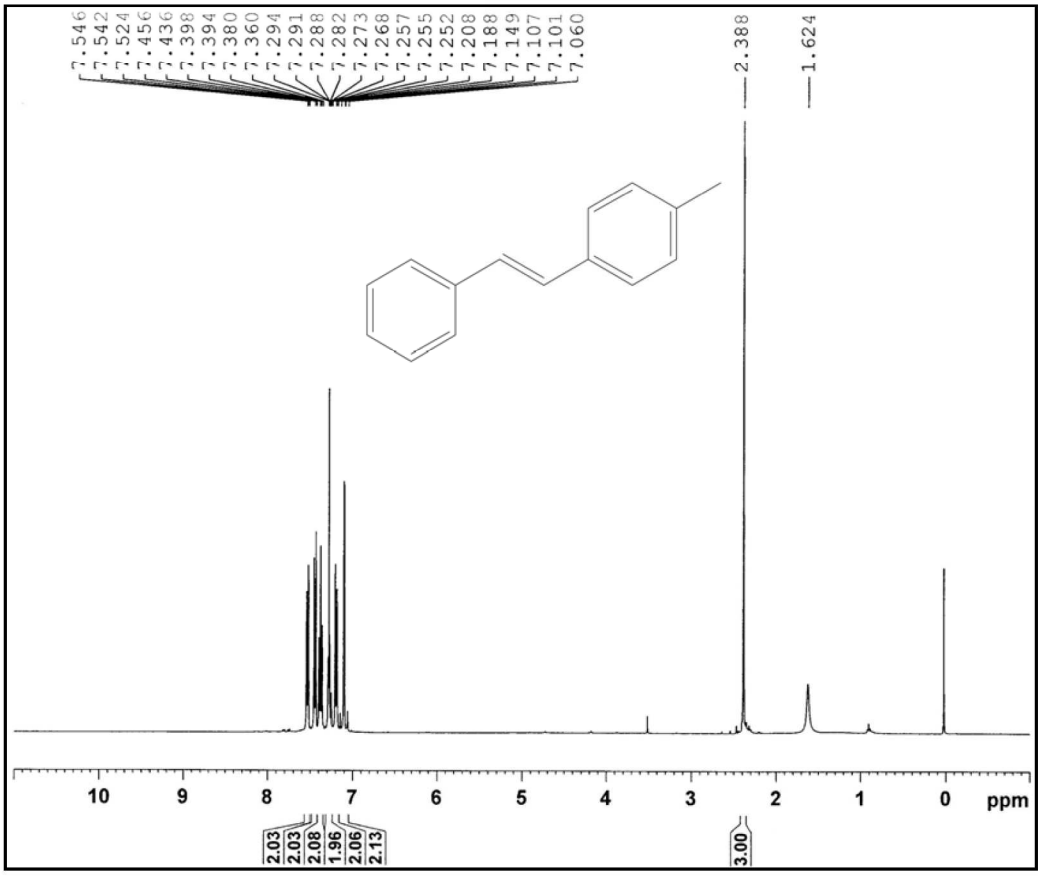
EI-Mass Spectra of Compound 83



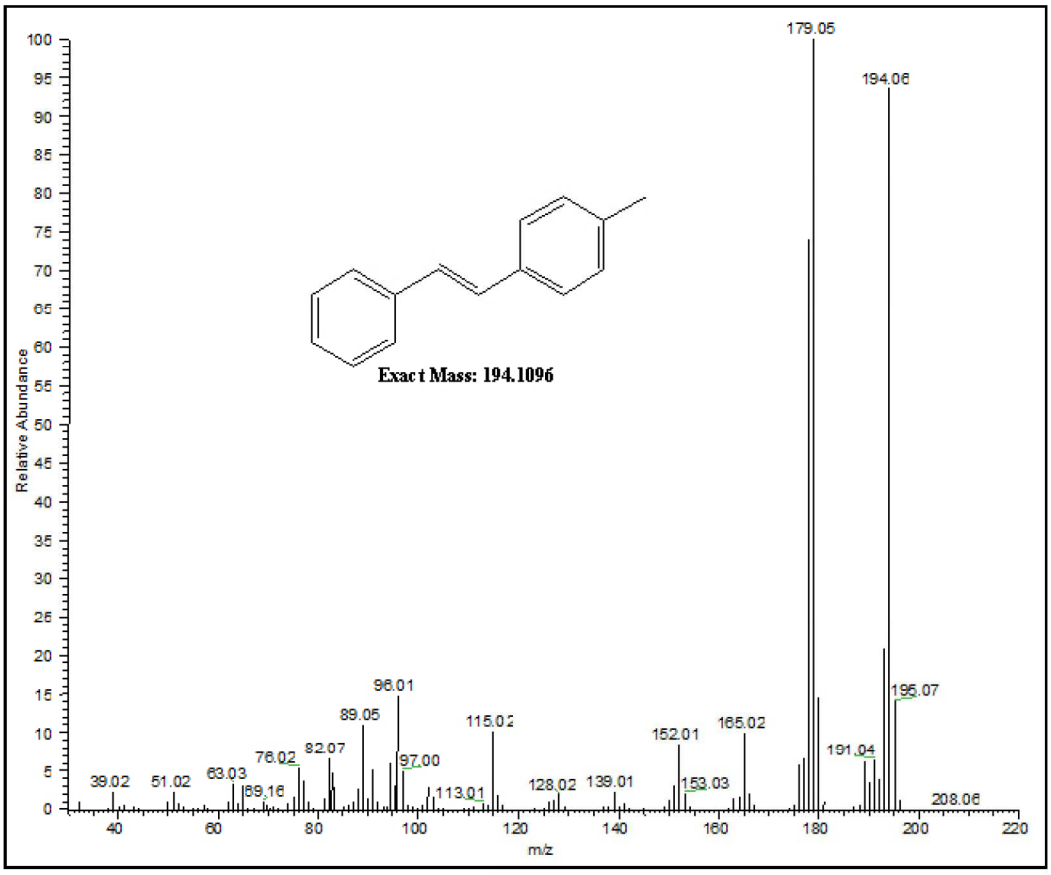
^{1}H-NMR of Compound 85 (400 MHz, $CDCl_3$)



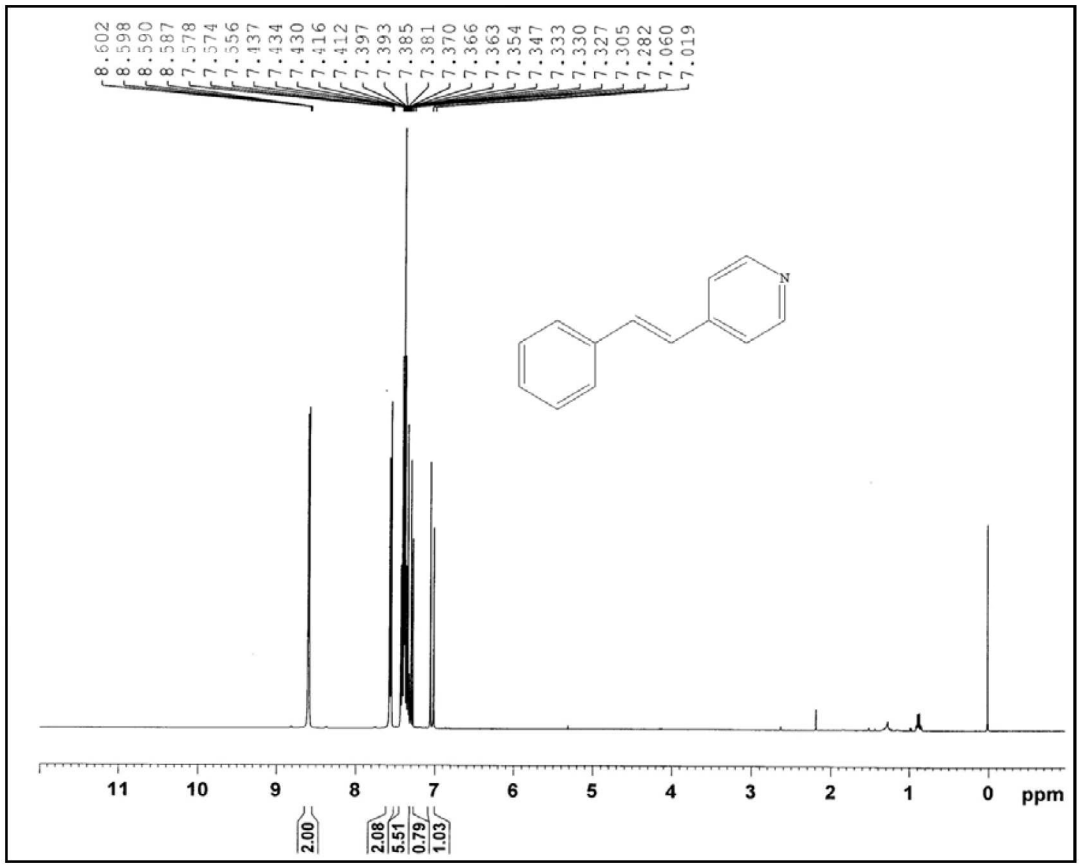
EI-Mass Spectra of Compound 85



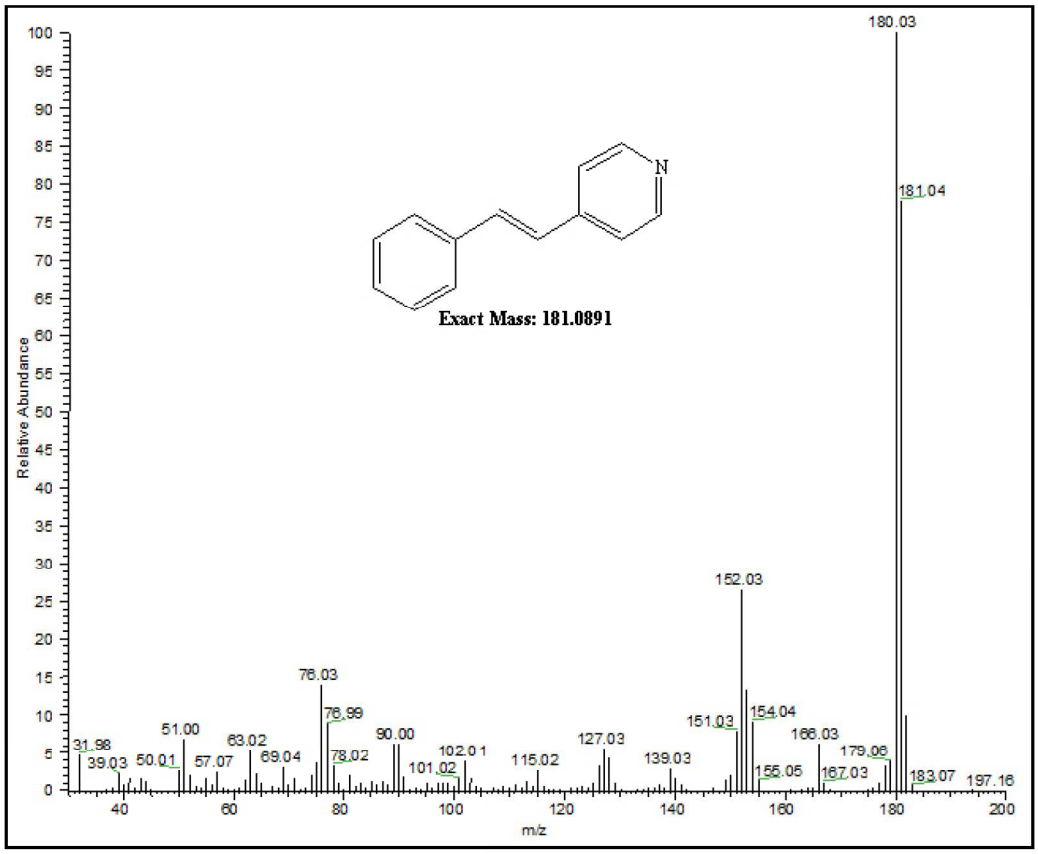
^{1}H-NMR of Compound 87 (400 MHz, $CDCl_3$)



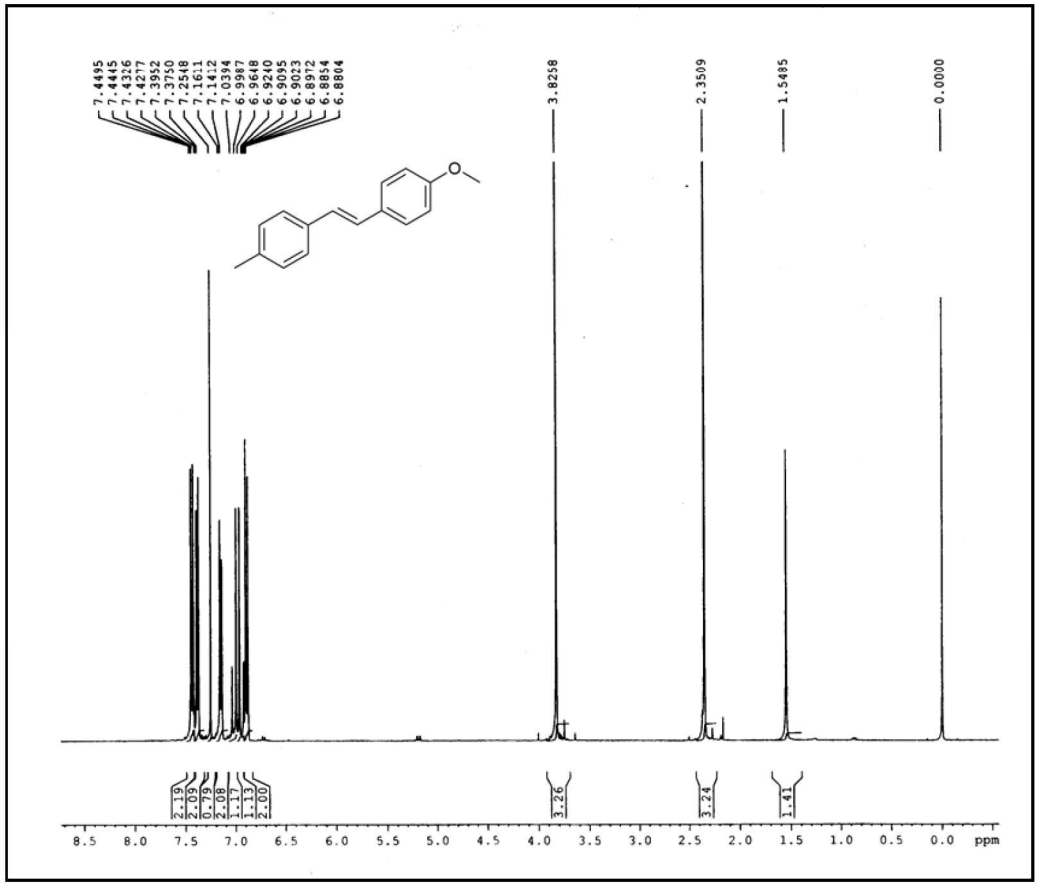
EI-Mass Spectra of Compound 87



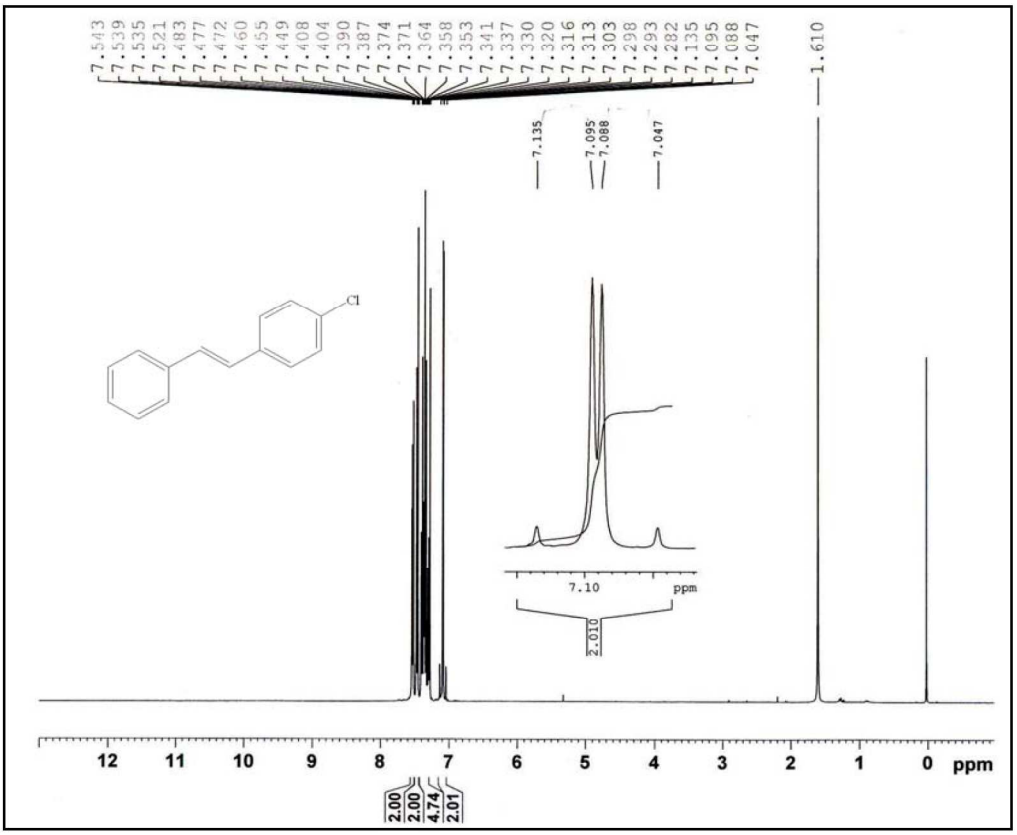
^{1}H-NMR of Compound 89 (400 MHz, $CDCl_3$)



EI-Mass Spectra of Compound 89



^{1}H-NMR of Compound 90 (400 MHz, $CDCl_3$)



^{1}H-NMR of Compound 92 (400 MHz, $CDCl_3$)

Conclusion

- We have synthesized and characterized new achiral as well as chiral oxazolines by IR, Mass, ^{1}H & ^{13}C-NMR and elemental analysis.
- The preparation of such ligands is simple, efficient as well as purification is straightforward and the ligands are stable in air and even at high temperature under basic condition.
- We have successfully used oxazolines as ligands for Mizoroki-Heck reaction and its aqueous version for the synthesis of substituted stilbenes to contribute for the development of "Green Chemistry".
- Our phosphine free catalyst system not only works well with aqueous version of Mizoroki – Heck reaction but it can be recovered and reused effectively for subsequent reactions.

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