# “Synthesis, Characterization and Applications of Novel Helical Molecules”

*A Thesis Submitted to*
*The Maharaja Sayajirao University of Baroda*
*for the Award of the Degree of*
*Doctor of Philosophy in Chemistry*

*By*

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# CERTIFICATE

This is to certify that the work presented in the thesis entitled **"Synthesis, Characterization and Applications of Novel Helical Molecules"** submitted by **Mr. Harish Ramesh Talele** for the award of the degree of **Doctor of Philosophy in Chemistry** is the authentic and original research work carried out by him under my guidance and supervision in the Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara – 390 002 India.

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# DECLARATION

I hereby declare that all the information in the thesis entitled **Synthesis, Characterization and Applications of Novel Helical Molecules** has been obtained and presented in accordance with the academic rules and ethical conduct. To the best of my knowledge no part of this thesis has been submitted for any Degree or Diploma to this University or any other University or Institute. Any errors in fact or interpretation in the thesis are purely the fault of the researcher.

03-11-2012

**Harish Ramesh Talele**

***DEDICATED***

***TO***

***MY LATE PARENTS WHO INSTILLED IN ME***
***THE QUALITIES THAT DEFINE ME TODAY***

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**Harish Ramesh Talele**

# Contents

# List of Abbreviations and Symbols

| | |
|---|---|
| CCDC | Cambridge Crystallographic Data Centre |
| CD | Circular dichroism |
| cm | Centimeter |
| CPL | Circularly polarized luminescence |
| DDQ | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinon |
| DMF | N,N-Dimethylformamide |
| dppp | 1,3-Bis(diphenylphosphino)propane |
| *ee* | enantiomeric excess |
| EI-Mass | Electron Impact Ionization Mass Spectrometry |
| ESI-Mass | Electrospray Ionization Mass Spectrometry |
| $FSO_3H\cdot SbF_5$ | Magic acid (1:1 mol mixture of fluorosulfonic acid ($HSO_3F$) and antimony pentafluoride ($SbF_5$)) |
| FTIR | Fourier transform infrared spectroscopy |
| HMPA | Hexamethylphosphoramide |
| HOF | Hypofluorous acid |
| HRMS | High-resolution mass spectrometry |
| LAH/$LiAlH_4$ | Lithium aluminium hydride |
| LiHMDS | Lithium bis(trimethylsilyl)amide |
| M.p. | Melting point |
| MALDI-TOF-MS | Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry |
| min | Minute |
| NBS | N-Bromosuccinimide |
| *n*-BuLi | *n*-Butyllithium |
| *n*-$Bu_4NF$ | Tetrabutylammonium fluoride |
| NMO | N-Methylmorpholine-N-oxide |
| NMR | Nuclear magnetic resonance |
| ORD | Optical rotatory dispersion |
| $PPh_3$ | Triphenylphosphine/ triphenylphosphane |
| RT | Room temperature |
| THF | Tetrahydrofuran |

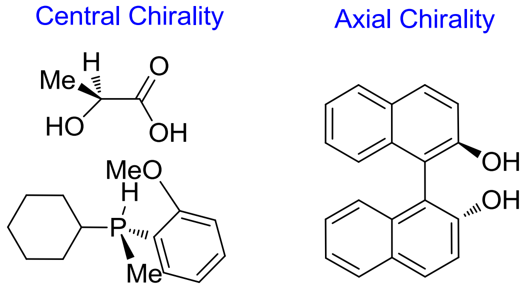
| | |
|---|---|
| TLC | Thin layer chromatography |
| TON | Turnover number |
| TfOH | Trifluoromethane sulphonic acid |
| TsOH | *p*-Toluenesulfonic acid or tosylic acid |
| UV | Ultraviolet–visible spectroscopy |
| VAZO | 1,1′-Azobis(cyclohexanecarbonitrile) |
| VT-NMR | Variable temperature nuclear magnetic resonance |
| ORTEP | Oak Ridge thermal ellipsoid plot |
| CHN | Elemental analyzer |
| m/z | Mass-to-charge ratio |
| XRD | X-Ray diffraction |
| mmol | Millimoles |
| mL | Milliliters |
| w/v | Mass concentration/ Weight to volume ratio |
| $C$ | Concentration |
| α | Alpha |
| β | Beta |
| δ | Delta |
| ° | Degree |
| ppm | parts per million |
| mHz | Mega hertz |
| $\theta$ | Theta |
| Å | Angstrom |
| nm | Nanometer |
| °C | Degree Celsius |
| K | Kelvin |
| mg | Milligrams |
| g | Grams |

# Chapter - 1

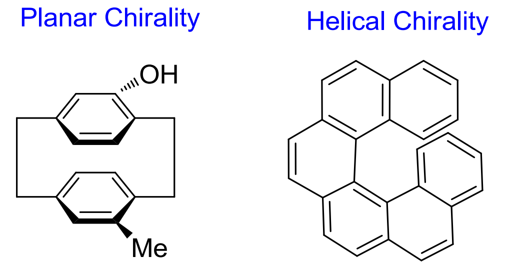
# Introduction

Chemistry of chiral compounds is an important branch of organic chemistry because of the significance of these kinds of molecules in various areas directly or indirectly affecting the life of a modern man. Many molecules having applications as pharmaceuticals, agrochemicals, flavors and fragrances, artificial sweeteners, materials, sensors etc. are chiral in nature. The chirality is result of the arrangement of atoms and groups in different space resulting in the stereochemically different arrangements in molecules.

There are mainly four types of chiral molecules: 1) molecules with $sp^3$ chiral centre, 2) molecules with chiral axis, 3) molecules with planar chirality and 4) molecules with helical chirality, as shown in [**Figure-1**]. The present work deals with molecules of the last type.


Central Chirality

Axial Chirality


Planar Chirality

Helical Chirality

**Figure 1:** Types of Chirality

The helix (the shape) is a three dimension structure which is discernible in the natural world over a range of scales and context. For example tornado (whirlwind) and snail shells both display helical structure. While in context of chemistry, the conspicuous macromolecular structure of the DNA and many proteins are based upon the helical tertiary structure. These type of structures exhibit distortions from planarity and show the chirality.

Helicenes[1] are polycyclic aromatic compounds with nonplanar screw-shaped skeletons formed by *ortho*-fused benzene or other aromatic rings with helical chirality. The first helicenes **1** and **2** were synthesized in 1903.[2] During the next few decades, little was discovered about the chemistry of helicenes, except for the synthesis of some other derivatives **3-7**.[3] However, after Newman and co-workers reported[4] the synthesis and resolution of hexahelicene **8** in the 1950s, the study of the chemistry of helicenes really took off. Some of the prominent members of such helical molecules are represented in [**Figure-2**].

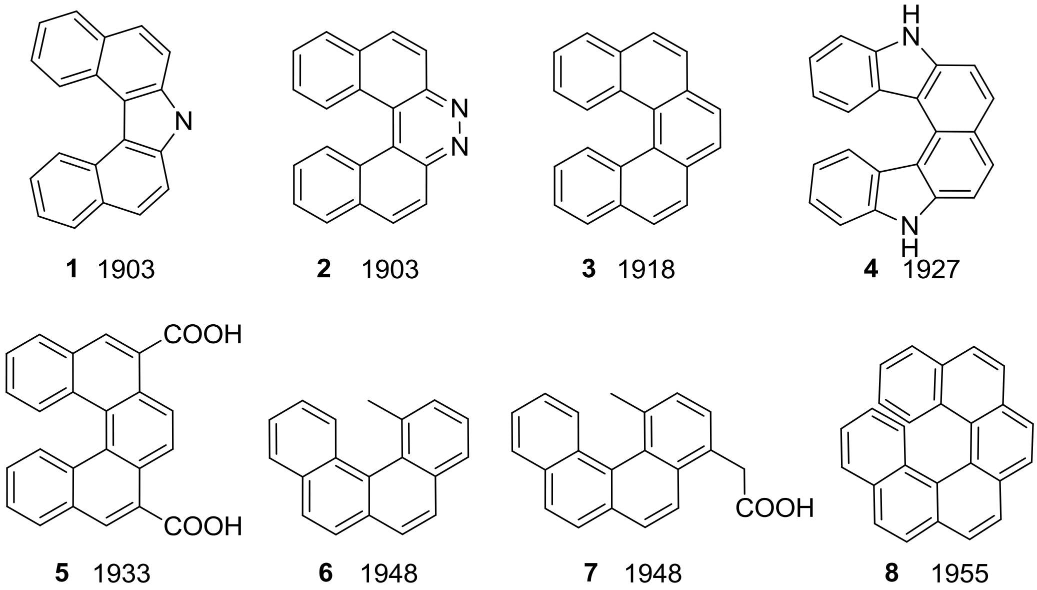


**Figure 2:** Some Helicene prepared before 1960

During the next 30 years, Wynberg,[1a,5] Martin,[1b,6] Laarhoven,[1f,7] and Katz[8] carried out pioneering studies on the synthesis, spectral properties, and structural aspects of the helicenes. Helicenes; carbo helicenes (I) and hetero helicenes (II) [**Figure-3**], which present fascinating left and right handed chiral helical structures (*M* and *P* configuration respectively) [**Figure-3**], have been intensively studied for their excellent self assembling, non linear optical properties, as well as in asymmetric synthesis, molecular recognition, synthesis of sensors and in polymer fields.

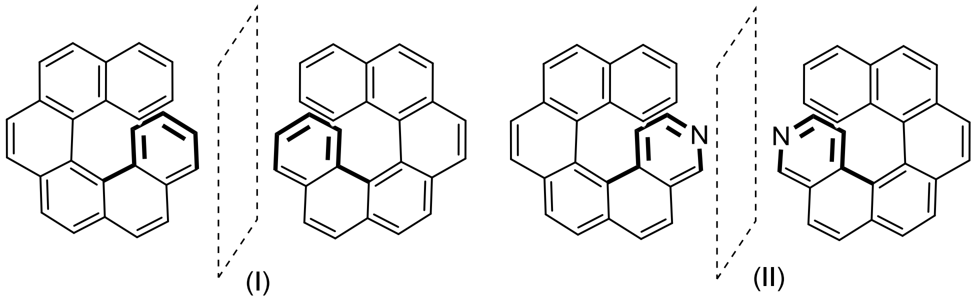
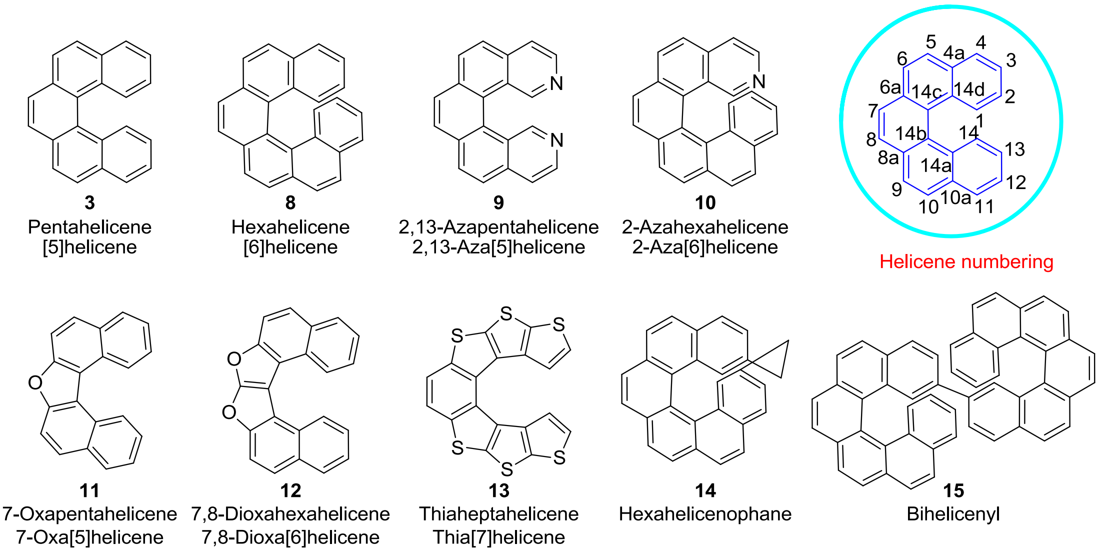


**Figure 3:** Types of Helicene (I) Carbohelicene and (II) Heterohelicene

In order to simplify the IUPAC nomenclature, Newman and Lednicer first introduced the name hexahelicene for phenanthro[3,4-*c*]phenanthrene in 1956.4(b) Adding a Greek prefix or using a number *n* in brackets [*n*] to the helicene name was also adopted: thus, pentahelicene becomes [5]helicene.1b,d,4b The prefix or number indicate the number of aromatic rings in the helical backbone. Carbohelicenes are composed exclusively of benzene rings in the backbone, while heterohelicenes contain at least one heteroatom in the screw skeleton.1b When the heteroaromatic rings are thiophenes, pyridines or pyrroles, furans they are named as thia[*n*]helicenes **13**, aza[*n*]helicenes **9**, **10**, and oxa[*n*]helicenes **11**, **12**, respectively or [*n*]helicenes for simplicity and clarity.



**3**
Pentahelicene
[5]helicene

**8**
Hexahelicene
[6]helicene

**9**
2,13-Azapentahelicene
2,13-Aza[5]helicene

**10**
2-Azahexahelicene
2-Aza[6]helicene

**11**
7-Oxapentahelicene
7-Oxa[5]helicene

**12**
7,8-Dioxahexahelicene
7,8-Dioxa[6]helicene

**13**
Thiaheptahelicene
Thia[7]helicene

**14**
Hexahelicenophane

**15**
Bihelicenyl

**Figure 4:** Nomenclature and Numbering of Helicene

The other type of the helicenes, double helicenes, are composed of two fused screw structures which may be of different type.1b,h Bihelicenyls **15** involve two distinct helicene moieties connected by a single bond,1b,h and helicenes in which two terminal rings are linked by an alkyl chain, like **14** a clamped helicene are called helicenophanes.1h

## General Properties of Helicenes

The defining property of a helicene is its helical structure. Because of the steric hindrance of the terminal rings, helicenes can wind in opposite directions and have a $C_2$-symmetric axis, which is perpendicular to the helical axis shown in [**Figure-5 (a)**]. This renders them chiral even though they have no asymmetric carbons or other chiral centers.

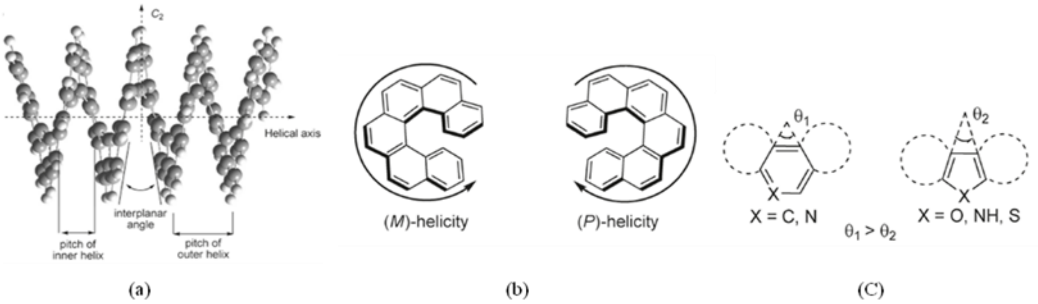


**Figure 5:** (a) ball and stick model of [25]helicene, (b) Schematic representation of helicity, and (c) Comparision of the in-plane turn (θ) of different rings.

There is a general relationship between the absolute configuration and the chirality proposed by Cahn, Ingold and Prelog in 1966 on the basis of helicity rule, a left-handed helix is designated by "minus" and denoted by *M,* whereas right handed helix is designated "plus" and denoted by *P* [**Figure-5(b)**].[9] There is a general relationship according to the ORD and CD spectroscopy between the absolute configuration and Chirality: (*P*)-helicenes are dextrorotatory, while (*M*)-helicenes are levorotatory.[5d,10] As the number of fused rings increases, the helical spirals up along the helical axis to form a cylindrical structural with a constant pitch in both the inner and the outer helixes.[1h]

Another interesting feature is that the helicenes composed of six membered aromatic rings takes nearly six rings to cover a complete 360° rotation of a screw,[10c] while four thiophene and three benzene units are required for thiahelicenes[11] because of the smaller in-plane turn (θ) that the thiophene units contribute to the helical structure[5c] [**Figure-5(c)**]. As five membered rings are incorporated in the skeleton, more rings are required for one complete 360° rotation in the molecule.

The non-planar structure is formed or the molecule is twisted due to the steric interaction between the terminal rings. The interplanar angles (or the dihedral angles) of the two terminal rings depend on the lengths of the helicenes and the substituents present. For example, the interplanar angles of carbohelicenes increases as the helicenes are elongated from [4]helicene **16** (26.7°) to [6]helicene **8** (58.5°) but decrease with further elongation for [7]helicene **19**. Moreover, if the terminal rings are linked by a short alkyl chain such as in **20**, the angle also tends to be reduced.[12]

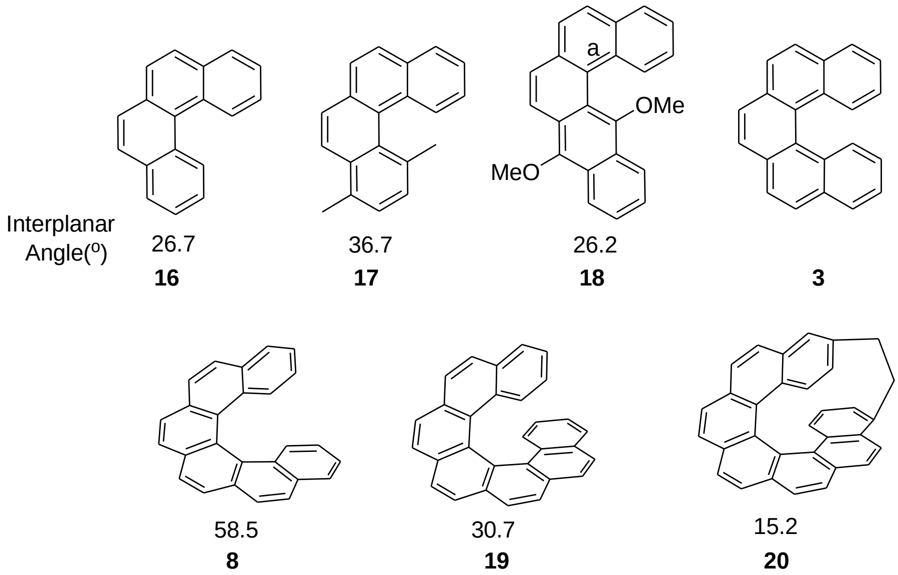


**Figure 6:** Comparison of the dihedral angle of helicenes from [4]helicenes to higher number of different helicenes

According to the interplanar angles, a comparison of **16**[13] with **17**[13] and **18**[14] suggests that the extent of steric hindrance is Me > MeO > H [**Figure-6**]. In addition, overlap of the rings as well as the van der Waals interactions between nearby groups have been demonstrated by observing, shielding and deshielding effects in the $^1$H NMR spectra of these helicenes.[1b,f]

As a result of torsional strain, the bond lengths in the skeleton are different, with different C-C bonds having features of a single bond or a double bond. In comparison with the bond length of benzene (1.393 Å),[15] the average bond length of the C-C bonds in the inner helix is lengthened to about 1.430 Å, while the average length of the ones on the periphery is shortened to about 1.360 Å.[1f,g] The bond a in **18** even elongated to 1.480 Å.[14] Surprisingly, numerous studies on the crystallographic structures of helicenes [4a,10c-10e,11,12-14,16,17] have always shown that there is a lack of $C_2$ symmetry, not only because of the bond lengths but also because of the torsional angles between the inner carbon atoms, although the atoms on the same ring are approximately coplanar.[1f] This phenomena is still not well understood.[17c]

Helicenes, like other polycyclic aromatic compounds, are good *π*-donors and can form charge-transfer complexes with many *π*-acceptors.[4a,18] These have been employed for the optical resolution of helicenes with chiral *π*-acceptor reagents through an enthalpy-driven process. In addition, the π-π interactions play an important role in determining many properties[19] and the self-assembly behavior[20] of helicenes in either the solution or in the solid state. Some other interactions in crystals, such as hydrogen bonding,[21] CH-*π* interactions,[17t,v] S-S interactions,[17x] and H-H interactions,[22] have also been reported. For some helicenes, recrystallization spontaneously affords homochiral conglomerates[23] or enantio enriched crystals,[5g,6b] which is indicative of a strong interaction between the homochiral helicenes and allows optical resolution by crystal picking. Moreover, some unusual behaviour of helicenes have been observed in confined environments such as micelles[18h, 24] and vesicles.[25] In aqueous SDS micelles, 2-hydroxymethyl[5]thiaheterohelicene formed a 1:2 charge-transfer complex with TAPA. After sonication, a 1:1 complex with a reverse Cotton effect was observed.[18h] If the thiaheterohelicene was incorporated in chiral (L)-DMPC vesicles, the equilibrium of the transformation between (*P*)- and (*M*)-enantiomers was affected and an enantiomeric excess of *M* was observed according to the CD spectra.[25b]

Some helicenes display high 'proton sponge' basicity by forming linear $N\cdots H\cdots N$ hydrogen bonds, which releases the steric strain [**Figure-7**].[26]

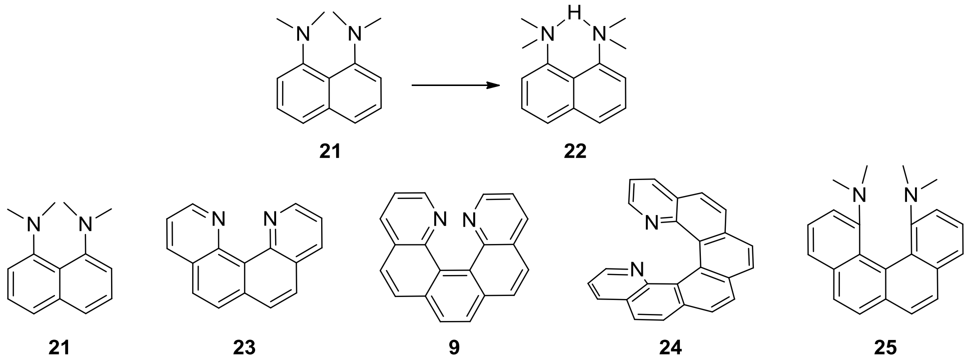


**Figure 7:** Helical 'Proton Sponges'

On the basis of transprotonation experiments,[27] **23** (pKa ~ 12.8) shows a stronger basicity than **21** (pKa ≈ 12.1) while the basicity of **9** is 2 orders of magnitude smaller than that of **23**. However, **24** with a similar basicity to pyridine, did not show 'proton sponge' properties as the two nitrogen atoms were not able to form a strong linear hydrogen bond.[28] In the case of **25**, the steric strain was not released significantly after protonation and its basicity is also negligible.[29]

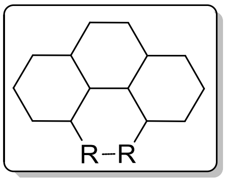
The solubility of helicenes is much higher than that of similar planar polycyclic aromatic system, although some helicenes still suffer from low solubility.[17j] Fortunately the solubility can be improved by introducing appropriate substituents such as alkyloxy and alkyl groups which have hitherto been found to be the most effective.[30]

## Synthetic Methodologies for the Helicenes, Hetrohelicens and Helicene like molecule

The synthetic routes towards helicene and helicene like molecules are lengthy, tedious and difficult. Methodologies for synthesis of helicenes are given below from highly strained small helicenes like phenanthrenes with helical shape to the higher member of helicenes/helical molecules.

### 1) Synthesis of the helical phenanthrenes and its different synthetic methodologies.

Basically carbo helicenes can be viewed as extended phenanthrenes, with additions of aromatic rings ortho to its terminal rings. Hence understanding synthesis of phenanthrenes is important for the study of higher helicenes.



The concept of helical or nonplanar or twisted phenanthrenes was first introduced by Newman in 1940.[31] Newman made three assumptions about the twisted methyl substituted phenanthrene at 4 and 5 positions: (1) the methyl groups lie bent away from each other but in the same plane as the aromatic rings; (2) the aromatic rings are distorted in some way; (3) the methyl groups are bent out of the plane of the aromatic rings. Of these the latter seems more likely from the theoretical study by Lassettre and Harris,[31] should this indeed be the case, optical activity would be possible, for 4,5-dimethylphenanthrene (and similar compounds where certain groups must be forced out of the plane of the aromatic rings) which can be represented in two non-superimposable forms which are mirror images [**Figure-8**].[32]

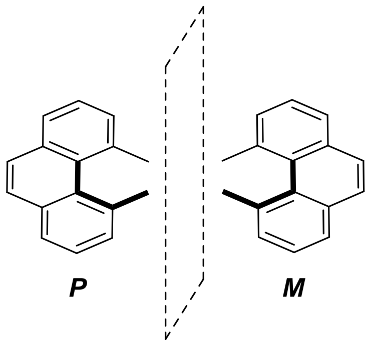
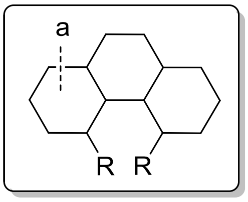
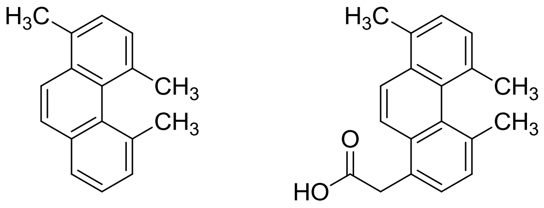


**Figure 8:** The two isomers of helical/twisted phenanthrene due to steric interaction of methyl groups

## *Approach 1a: 1) Synthesis of 1,4,5-trimethylphenanthrene 26 and 4,5,8-trimethyl-1-phenanthrylacetic acid 27:*



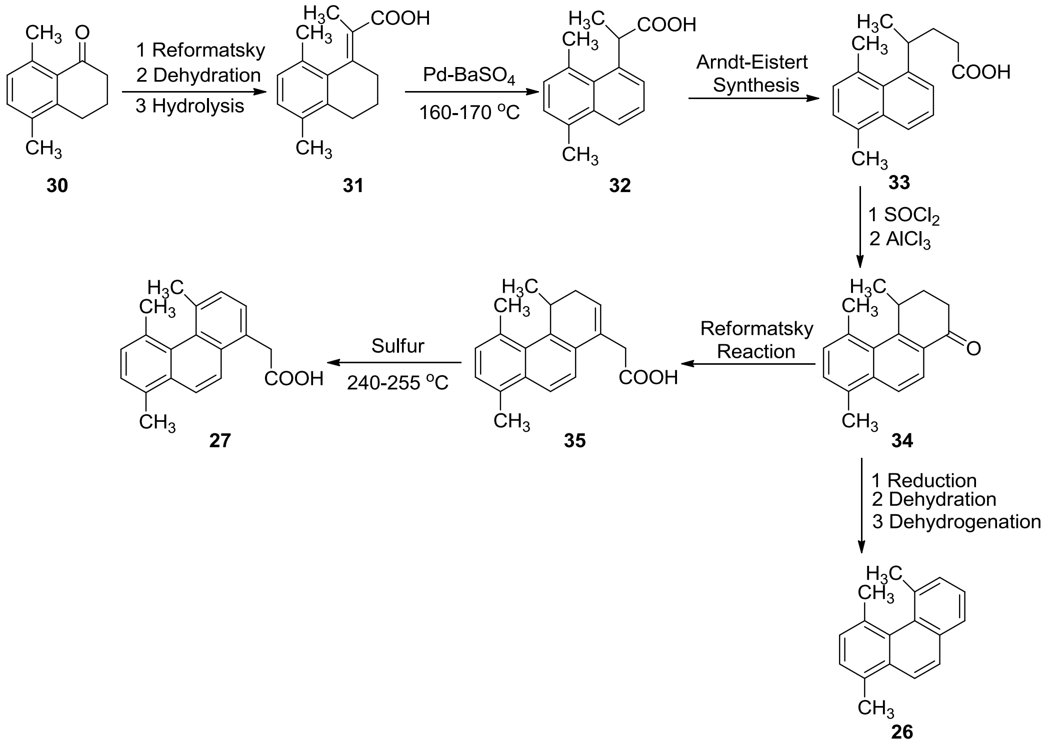
Keeping the concept in mind, Newmann et al. synthesized phenanthrenes with methyl groups attached at 4- and 5- positions to give the twist to the molecule. In this effort 1,4,5-trimethylphenanthrene **26** and 4,5,8-trimethyl-1-phenanthrylacetic acid **27**, were synthesized and resolved.



**26** **27**

**Figure 9:** 1,4,5-trimethylphenanthrene **26** and 4,5,8-trimethyl-1-phenanthrylacetic acid **27**

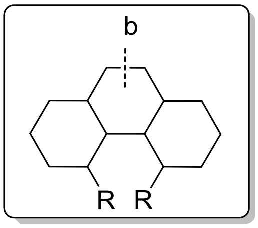
The compound **27** was resolved by Newman separating its salt with Brucine by fractional crystallization, as the best sample had optical rotation $[\alpha]_D^{26}$ 2.4 $\pm$ 0.5 (0.054 in 2 mL ethyl acetate) and established the optical activity due to the new type of steric hindrance.[33]



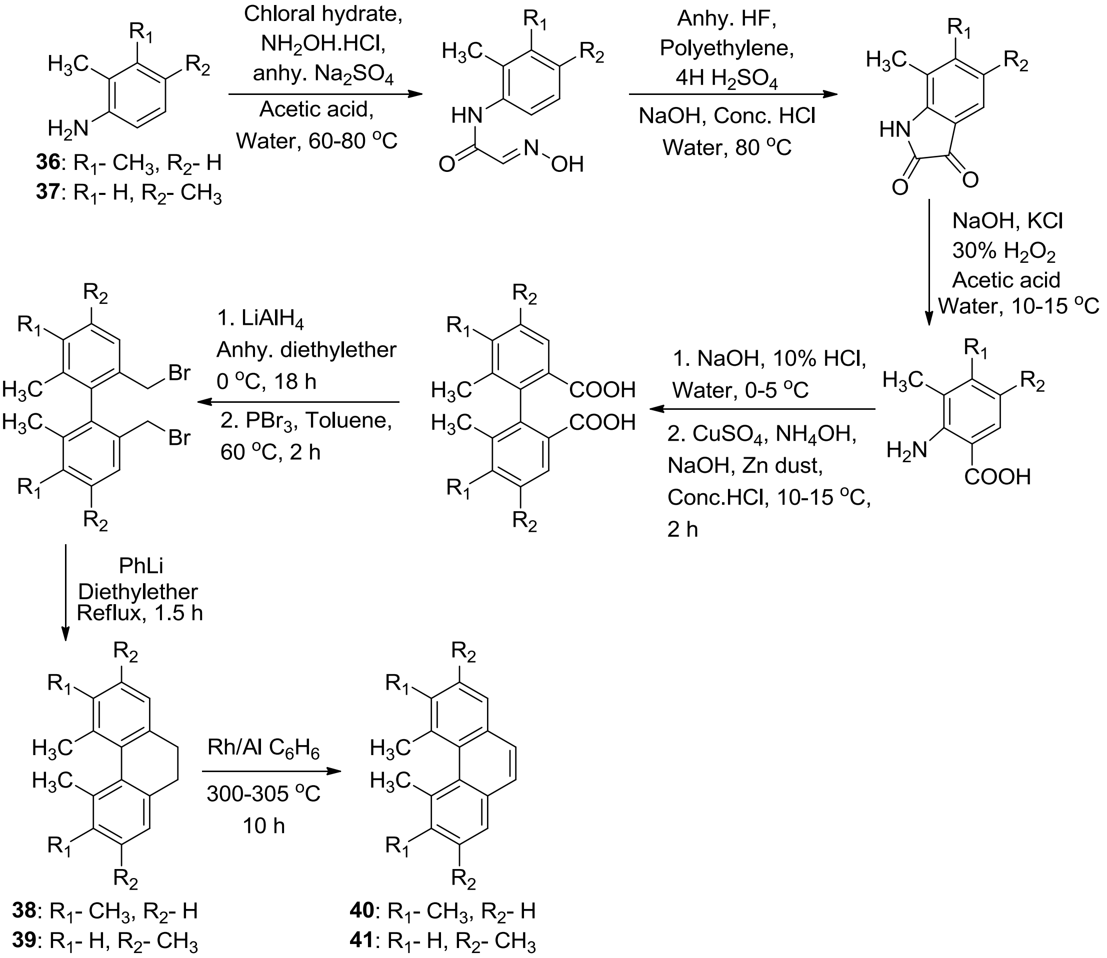
**Scheme 1:** Synthesis of 1,4,5-trimethylphenanthrene **26** and 4,5,8-trimethyl-1-phenanthrylacetic acid **27**

The final racemic acid was prepared by an eleven step synthesis sequence, starting from 5,8-dimethyl-l-keto-1,2,3,4-tetrahydronaphthalene **30**. A Reformatsky reaction with ethyl α-bromopropionate, followed by dehydration, dehydrogenation and hydrolysis afforded *α*-(5,8-dimethyl-l-naphthyl)-propionic acid **31**. By two successive Arndt-Eistert reactions this was converted into γ-(5,8-dimethyl-l-naphthy1)valeric acid **33**, which on ring closure yielded 4,5,8-trimethyl-1-keto-1,2,3,4-tetrahydrophenanthrene **34**. Another Reformatsky reaction, followed by dehydration, dehydrogenation and hydrolysis resulted in the formation of the desired acid **27**.

### *Approach 1b: 1) Synthesis of 3,4,5,6-tetramethylphenanthrene 40 and 2,4,5,7-tetramethylphenanthrene 41:*



In 1965 Newman and co-workers synthesized high-purity samples of 3,4,5,6- and 2,4,5,7 tetramethylphenanthrenes, studied their properties such as heats of combustion and vapor pressure measurements and established the buttressing effect of the methyl groups in the 3- and 6-positions on the 4- and 5-methyl groups as 3.6 ± 1 kcal./mole/$CH_3$ group. The buttressing effect of the fused rings in 1',9-dimethyl-1,2-benzanthracene is 3.0 ± 1kcal./mole.[34]

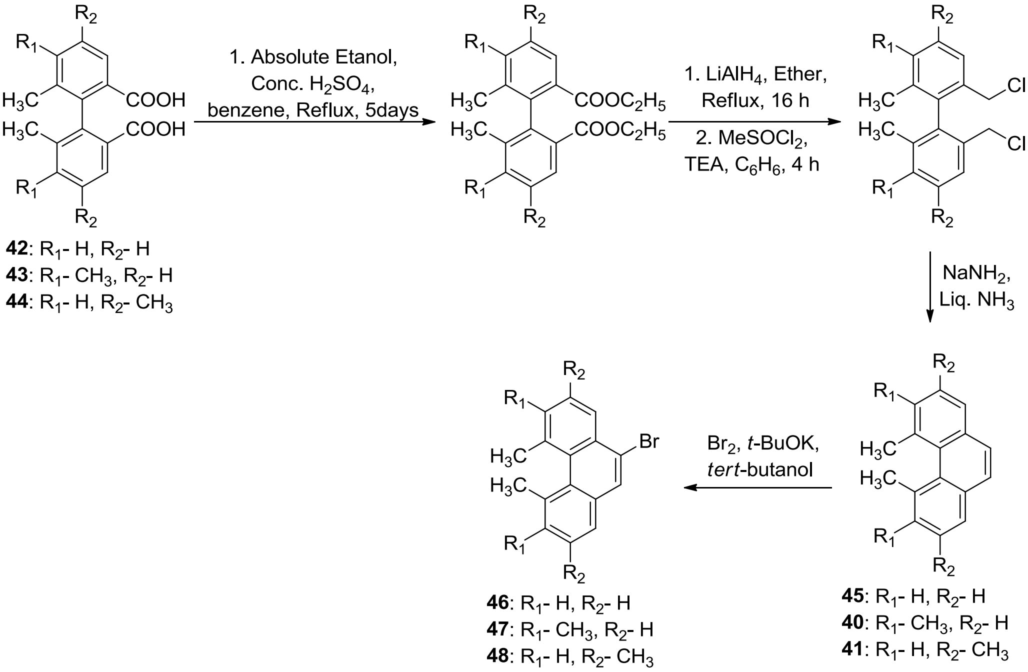


**Scheme 2:** Synthesis of 3,4,5,6-tetramethylphenanthrene **40** and 2,4,5,7-tetramethylphenanthrene **41**

The substituted phenanthrenes were synthesized from the corresponding 2,3-dimethylaniline **36** and 2,4-dimethylaniline **37** and studied the stability by strain energy, wherein one derivative has a strain energy of 12.1° 1.5 kcal./mole for the 4,5 methyl group interaction. This must be considered as a lower limit, since phenanthrene itself is non-planar owing to interference between the 4,5-hydrogens, the magnitude of this effect is however not known. By comparison, the data for compounds **40** and **41**, which contain the same 4,5-methyl group interaction, but with -$CH_3$ buttressing groups in the 3,6-positions instead of H atoms, show a difference in the stabilities of 7.2 ±1.4 kcal./mole. These $CH_3$ groups are causing 7.2 kcal/mole more distortion than the H atoms in the 3,6- positions and thus exerting a buttressing effect, decreasing the stability of **41**.[35]

### *Approach 1b: 2) Synthesis of 9-bromo-4,5-dimethylphenanthrene 46, 9-bromo-3,4,5,6-tetramethylphenanthrene 47 and 9-bromo2,4,5,7-tetramethylphenanthrene 48:*

Newman and Lilje in 1979, synthesized bromo derivatives of hindered phenanthrenes at 9-positions from corresponding 2,2'-diphenic acid (**42**, **43**, **44**)[35] converted to its ethyl ester which on reduction with $LiAlH_4$ formed the corresponding diol. The diol was converted to the chloromethyl derivative, which was converted to sterically hindered phenanthrenes **45**, **40** and **41** using sodium amide in liquor ammonia.



**Scheme 3:** Synthesis of 9-bromo derivatives of 4,5-dimethylphenanthrene **43**, 3,4,5,6-tetramethylphenanthrene **44** and 2,4,5,7-tetramethylphenanthrene **45**

These phenanthrenes are converted to their 9-bromo derivatives by using bromine in carbon tetrachloride to obtain the 9,10-dibromophenanthrene as a product following bromination. This dibromo derivative of phenanthrene was converted to 9-bromophenanthrene derivative using potassium *tert*-butoxide.

These molecules were examined by Armstrong and Ammon.[36] The molecular structures and conformational stabilities of 4,5-dimethylphenanthrene **45** and 3,4,5,6-tetramethylphenanthrene **40** have been examined by X-ray crystallography, the temperature dependence of the kinetics of the pseudorotation process, and force-field calculations of the molecular geometries of the ground-state and transition-state structures.

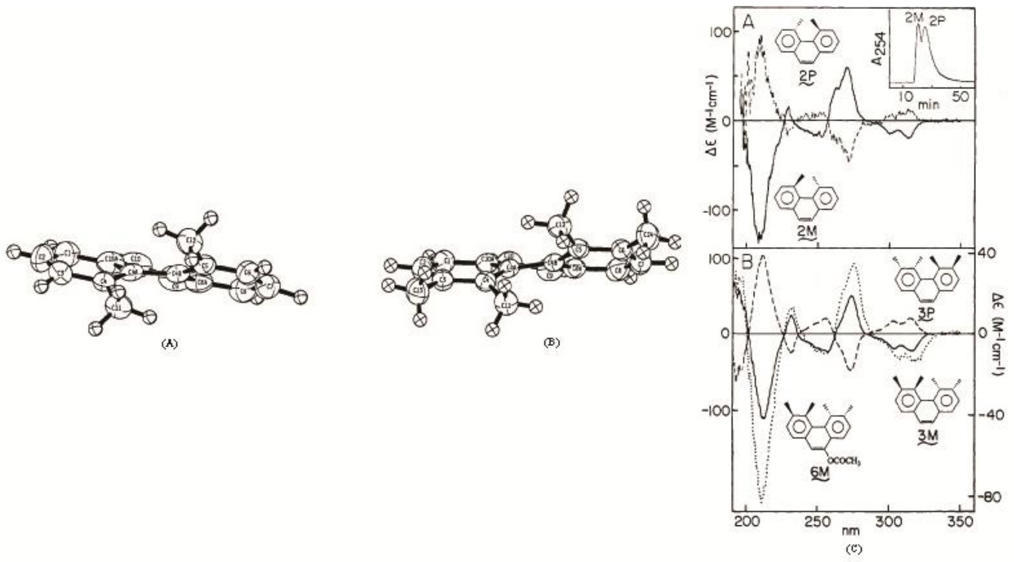
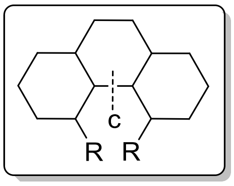


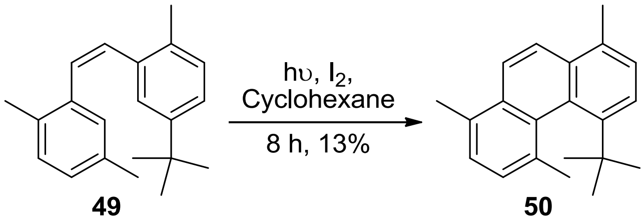
**Figure 10:** (a) ORTEP drawing of the compounds **45 (A)** and **45 (B)** showing the twirl in the molecules Fig. **(C)** Shows the CD spectra of (A) **45*M*** (-), **45*P*** (····) and (B) **40*M*** (-), **40*P*** (····)[36]

Crystal structures of **45** and **40** show the aromatic systems to have the expected helical twist imposed by the methyl groups at the 4- and 5-positions. The angle between the mean planes of the outer rings in **45** of 27.9° is increased to 29.2° in **40** due to the buttressing effect of the methyl groups at the 3- and 6-positions. Force-field calculations with the MMP2 program have given good reproductions of the ground-state structures of **45** and **40** and provide heat-of-formation data in reasonable agreement with previously determined experimental values. The strain energy of **45** with respect to phenanthrene is calculated to be 10.5 kcal/mol with the methyl groups at the 3- and 6-positions of **40** contributing a buttressing effect of 2.2 kcal/mol, a data which corroborates with the experimental values.

The conformational enantiomers of **45** and **40** can be separated by chromatography on (+)-poly(triphenylmethy1methacrylate) coated silica, the former compound being separable only at cryogenic temperatures (-70 to -80 °C) **.** Absolute configurations of the antipodes are deduced by circular dichroism (CD) spectroscopy. Molecular mechanics calculations provide reasonable transition-state structures for **45** and **38** which have activation barriers (17.4 and 23.1 kcal/mol) in good agreement with the experimental measurements. The experimental (or calculated) buttressing effect of the additional methyl groups in **40** in the ground state and in the barrier to pseudorotation are used to estimate a difference in the strain energies of **45** and **40** in the transition state of 8-10 kcal/mol. The structural manifestation of the added methyl groups in the transition state for **40** appears in part as an increase in the in-plane pivoting of the outer rings away from methyl-methyl interaction.

### *Approach 1c: 1) Synthesis of 4-tert-butyl-1,5,8-trimethylphenanthrene 50:*

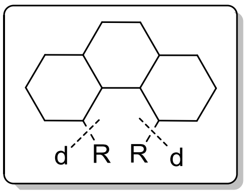




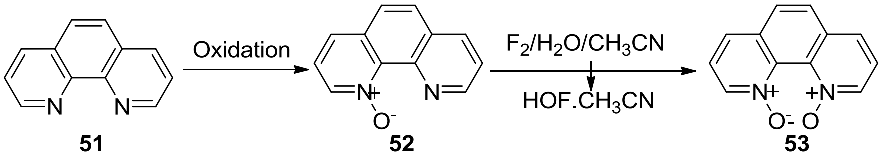
**Scheme 4:** Synthesis of 4-*tert*-butyl-1,5,8-trimethylphenanthrene

In 1996 Vogtle and co-workers, synthesized the highly strained helical 4-*tert*-butyl-1,5,8-trimethylphenanthrene by photochemically induced dehydrocyclization.[37] The helical deformation of the aromatic carbon skeleton was observed by the X-ray structure, was found to be 36.6° which was the largest value found for a twisted phenanthrene hydrocarbon. A systematic quantum chemical investigation of strained 4,5-substituted phenanthrene derivatives was conducted. The geometrical parameters describing the strain in these helical molecules were compared with X-ray data from the literature and were found to be generally in good agreement.[31,36,38] Substantial deviations between theory and experiment for the helical deformation angles are observed while in the case of the chlorine substituted molecules the difference is about 5° which indicates the importance of crystal packing effects. A prediction of the structure of the unknown 4,5-di-*tert*-butylphenanthrene, that could be detected by GC-MS, but has not been isolated. The total strain energies of 4,5-di-*tert*-butylphenanthrene and 4-*tert*-butyl-1,5,8-trimethylphenanthrene **50** were calculated to be 49.6 and 34.0 kcal mol$^{-1}$, respectively, and were distributed to non-bonded and aromatic ring deformation contributions.

### **Approach 1d: 1)** ***Synthesis 1,10-Phenanthroline-N,N'-dioxide 53:***



A novel approach was introduced by Rozen in the synthesis of novel helical shaped molecule, 1,10-phenanthroline-N,N-dioxide **53**.[39]



**Scheme 5:** Synthesis of 9,10-phenanthroline-N,N-dioxide

In this approach the synthesis of 1,10-phenanthroline-N,N-dioxide **53** was achieved by oxidation of phenanthroline with HOF-$CH_3CN$. This reagent was generated in situ with $F_2$ in water/acetonitrile. The progress of the reaction is monitored by reacting aliquots with an acidic aqueous solution of potassium iodide and then estimating the liberated iodine with thiosulfate. Typical concentrations of the oxidizing reagent were around 0.3-0.4 M. This reagent was treated with 1,10-phenanthroline **51** in chloroform and after basic workup a product 1,10-phenanthroline-N,N'-dioxide **53** was obtained.

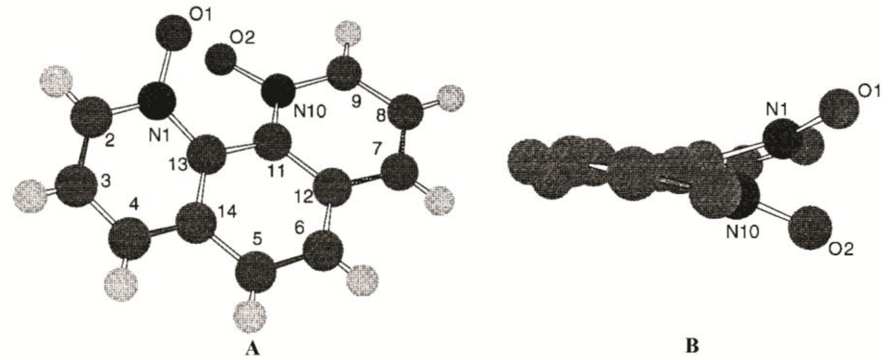
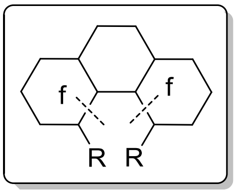


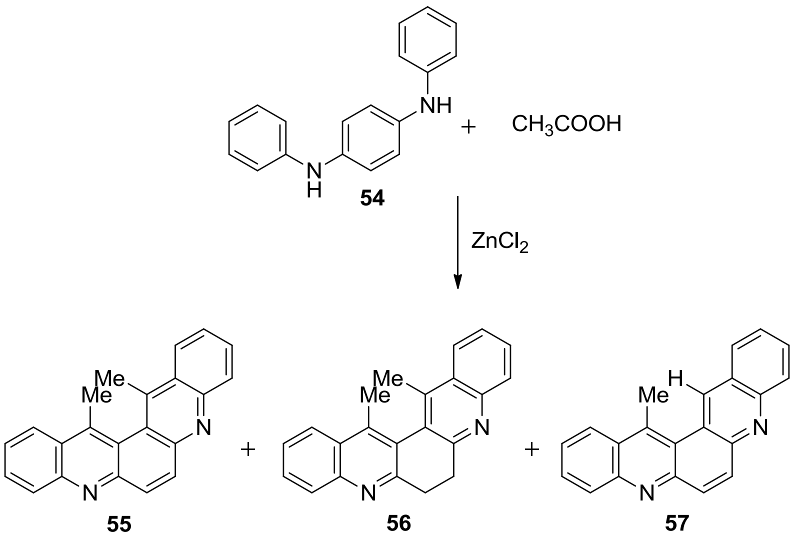
**Figure 11:** Structure of 1,10-phenanthroline-N,N-**53** dioxide in the solid state. A) View from above; B) side view without hydrogen atoms

The stuctural study found that the N,N'-dioxide crystallizes in the chiral space group P21/c (Z = 8), with two independent molecules in the asymmetric unit. The crstal structure [**Figure-11**] shows that the two oxygen atoms force the whole phenanthroline skeleton away from planarity. Thus while the least squares deviation from plane for 1,10- phenanthroline **51** is only 0.025., the deviation for N,N'-dioxide **53** is 0.52. The torsion angle of O1-N1-C13-C11 was found to be -14.3(2)°, while that of O2-N10-C11-C13 was -14.1(2)°. The torsion angle of N1-C13-C11-N10 for 1,10-phenanthroline **57** is less than -0.58°, for the monoxide **52** it is -0.98°, but for the dioxide **53** the value increases to -31.7(2)°. These parameters are responsible for the helical character of the whole molecule [**Figure-11 (A), (b)**]. The individual aromatic rings are also somewhat distorted.

### **Approach 1f: 1)** ***Synthesis of Optically active aromatics possessing helical chirality: one-pot synthesis of 13,14-dimethyldibenzo[b,j][4,7]phenanthroline 55 and its dihydro form as a novel chiral building block:***



Tanaka and co-workers reported[40] a one-pot synthesis and optical resolution, crystal structure of a heteroaromatic helically chiral 13,14-dimethyldibenzo-[*b*,*j*][4,7]phenanthroline **55** and its dihydroform **56**.



**Scheme 6:** Syntheis of 13,14-dimethyldibenzo[*b*, *j* ][4,7]phenanthroline **55** and its derivatives

The synthesis of these compounds 13,14-dimethyldibenzo[*b*,*j*][4,7] phenanthroline **55** and its dihydroform **56**. While the condensation of N,N-diphenyl-*p*-phenylenediamine **54** with acetic acid in the presence of $ZnCl_2$ as Lewis acid gave a resinous material, Soxhlet extraction of the material and purification over column chromatography gave a mixture of three components, the major one was 13,14-dimethyl[*b*,*j*][4,7]-phenanthroline **55**.

In the NMR spectrum the two methyl groups of both the structure were found at δ 2.82 and δ 2.56 ppm and must be quivalent, suggesting the symmetrical structure. The theoretical study of these molecules indicate that the aromatic rings in both the compounds **55**, **56**, (while **57** is a planar molecule) were twisted due to the proximity of the two methyl groups giving rise to the left- and right- handed helix forms, a pair of enantiomers (*M*- and *P*- form).

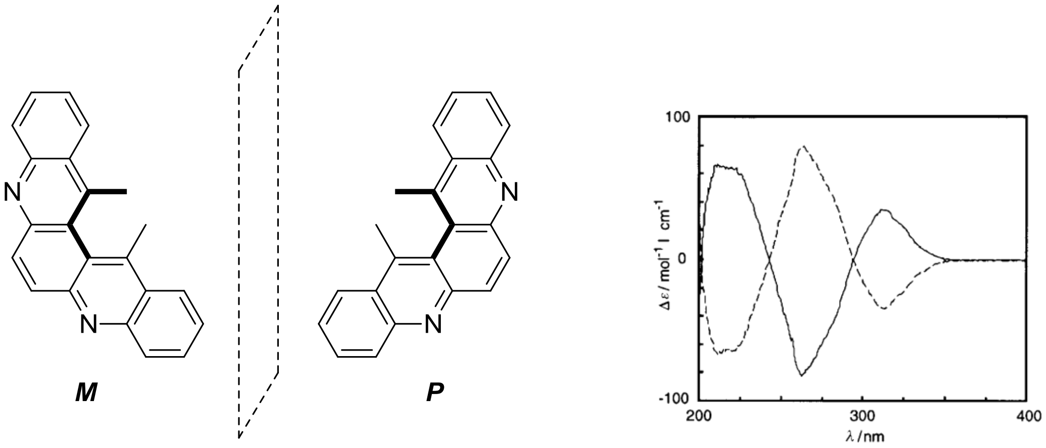
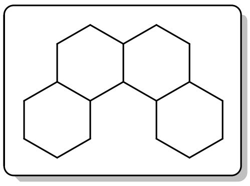


**Figure 12:** The helical isomers of the compound 13,14-dimethyldibenzo[*b,j*]-[4,7]phenanthroline and the CD spectrum of compound **55**

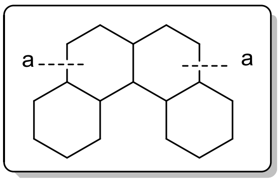
On addition of the shift reagent *R*-(-)-1,1'-binaphthyl-2,2'-diyl to **55** the H-NMR splitting of the methyl signals were observed due to the formation of the acid base complex between diastereomers of (*M*) and (*P*) isomers and the reagent. The chiral HPLC analysis also shows two peaks in these molecules **55** and **56**. However **55** underwent easy racemisation while the compound **56** was quite stable.

The compound **56** was also synthesized by the reduction of **71** by using $LiAlH_4$ in diethyl ether and the isomers were separated by the preparative chiral HPLC. The separated enantiomers split up and show opposite curves to each other in the CD spectrum [**Figure-12**].

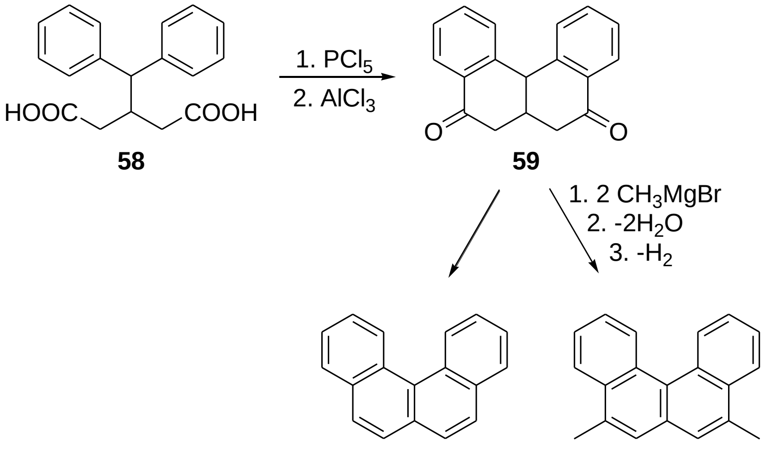
2) **Synthesis of the helical benzo[*c*]phenanthrenes/[4]helicenes and its different synthetic methodologies.**



***Approach 2a: 1) Synthesis of benzo[c]phenanthrene 16 and 5,8-dimethylbenzo[c]-phenanthrene 60:***



Cook and co-workers,[41] have reported the carcinogenic activity of the above molecules in 1935 but there was no method for their synthesis till 1938. Newman and co-workers introduced the general method for the synthesis of substituted benzo[*c*]phenanthrene/[4]Helicene as shown in above [**Scheme-7**].[42]



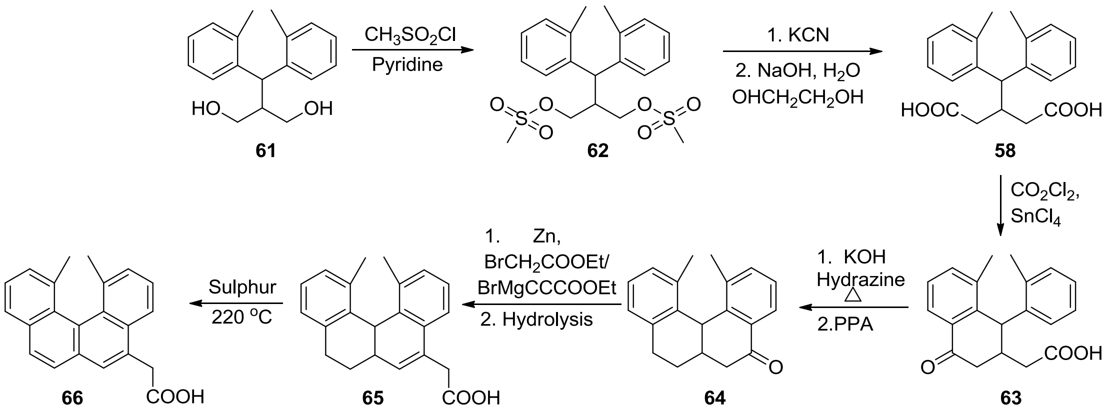
**Scheme 7:** Synthesis of benzo[*c*]phenanthrene **16** and 5,8-dimethylbenzo[*c*]phenanthrene **60**

In this synthesis the β-benzohydryl glutaric acid **58** was cyclised with phosphorous pentachloride and aluminium chloride in tetrachloroethane to give compound 2,9-diketo-1,2,9,10,11,12-hexahydro-3,4-benzphenanthrene **59**. This diketo derivative was converted to benzo[*c*]phenanthrene **16** by standard steps.

Similarly 2,9-diketo-1,2,9,10,11,12-hexahydro-3,4-benzphenanthrene **59** treated with two equivent of methylmagnesium bromide followed by dehydration and dehydrogenation with sulphur gave 2,9-dimethyl-3,4-benzphenanthrene **60**.

### Approach 2a: 2) *Synthesis and resolution of 1,12-Dimethylbenzo[c]phenanthrene-5-acetic Acid 66:*

Newman and co-workers, synthesized[4c] the compound 1,12-dimethylbenzo[*c*]phenanthrene-5-acetic acid **66** by routine methodology (above approach) with some modifications with good yield on a large scale. The compound **66** was resolved by preparing its salt with *l*-(-)-cinchonidine and its fractional crystallization. The sample of **66** with specific optical rotation $[\alpha]_D^{23} - 332^{\circ}$ (*c* 1.20 in acetone) was isolated. By using the similar process with the *d*-(+)-cinchonidine other enantiomer was obtained with specific optical rotation of $[\alpha]_D^{23} - 347^{\circ}$ (*c* 0.29 in acetone).

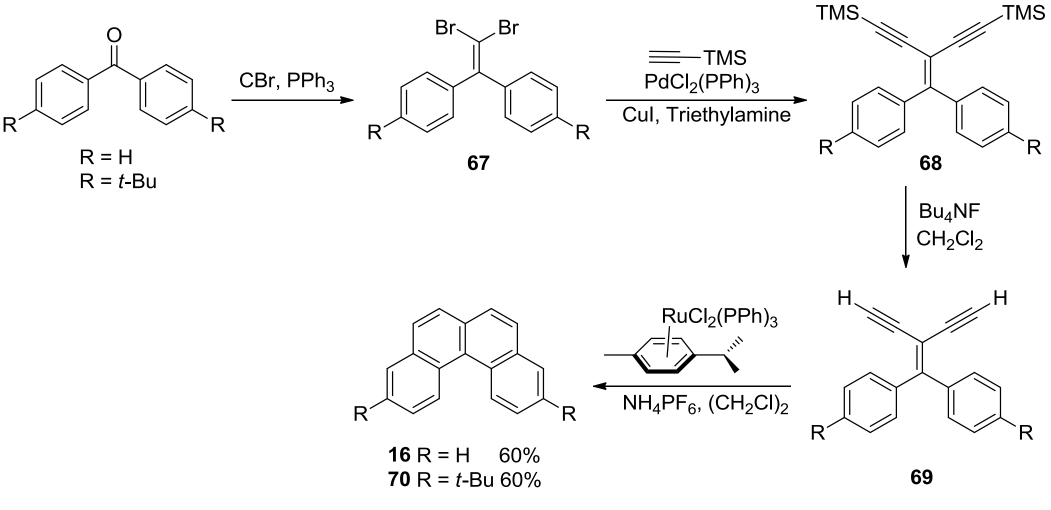


**Scheme 8:** Synthesis of 1,12-Dimethylbenzo[c]phenanthrene-5-acetic Acid **89**

On the resolution, both pure enantiomers of **66** were studied for their thermal stability It was concluded that this compound was thermally stable upto 250 °C. When the temperature was raised above 250 °C, the compound racemized and the optical rotation was found to be zero.

### *Approach 2a: 3) Synthesis of Benzo[c]phenanthrene 16 and substituted Benzo[c]-phenanthrene 70:*

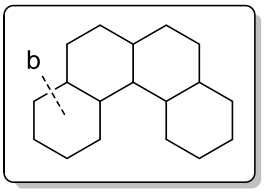
Scott and co-workers introduced[44] the synthesis of polycyclic aromatic hydrocarbons by the transition metal catalyzed double ring closure of 1,1-diaryl-2,2-diethynylethylene **69** from the naphthalene ring system embedded in a larger polycyclic network. The diynes required for this procedure are synthesized from diaryl ketones by Corey-Fuchs olefination, the benzophenone derivatives were converted to 1,1-dibromo-2,2-diphenylethene **67** by phosphorous tribromide and triphenyl phosphine.



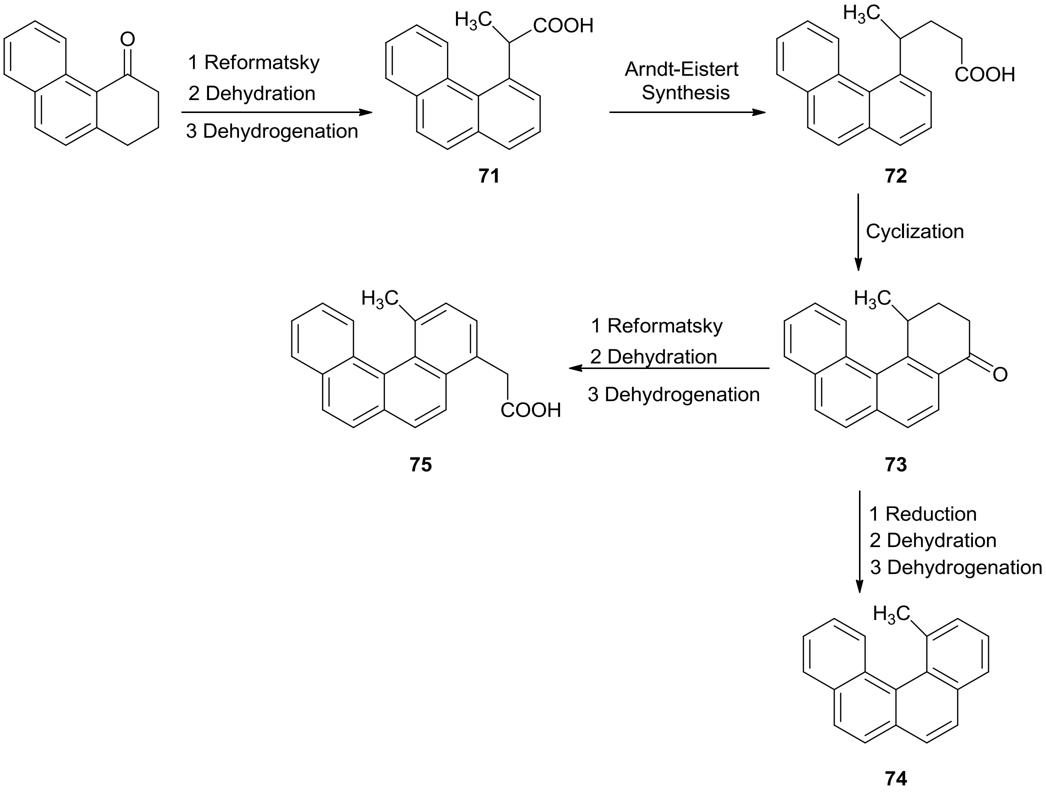
**Scheme 9:** Synthesis of benzo[c]phenanthrene **16** and its derivatives **70** by transition metal catalyzed double ring closer reaction

The resulting 1,1-dibromoalkene was then transformed to the corresponding 1,1-diphenyl-2,2-*bis*(trimethylsilylethynyl)ethene **68** by Sonogashira coupling using trimethylsilyl acetylene. The 1,1-diphenyl-2,2-bis(trimethylsilylethylene)ethene **68** was deprotected using tetrabutyl ammonium fluoride in dichloromethane to give 1,1-diethynyl-2,2-diphenylethene **69**. The diethynyl derivative **69** was cyclized with $RuCl_2(PPh_3)(\eta^6$–*para*–cymene) and ammonium hexafluorophosphate to obtain benzo[*c*]phenanthrene **16** and substituted benzo[*c*]phenanthrene **70**.

### Approach 2b: 1) *Synthesis of 1-Methylbenzo[c]phenanthrene 74 and 4-(1-Methylbenzo[c]phenanthryl)-acetic acid 75:*



The first synthesis of sterically crowded benzo[*c*]phenanthrene/[4]Helicene was reported by Newman et al. in 1948,[3d] the mixture of unsaturated esters resulting from the Reformatsky reaction of corresponding ketone and ethyl α-bromopropionate was dehydrogenated over palladized charcoal to yield the acid **71**.



**Scheme 10:** Synthesis of Methylbenzo[c]phenanthrene **74** and 4-(1-Methylbenzo-[c]phenanthryl)-1-acetic acid **75**

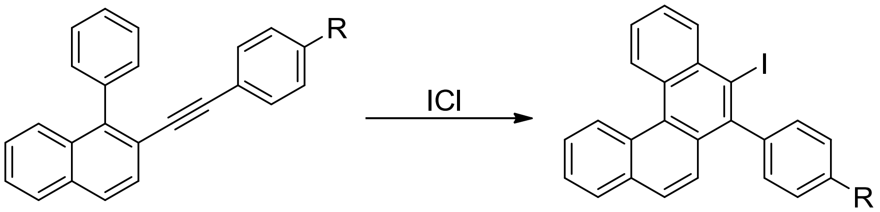
By two successive Arndt-Eistert reactions the acid was converted into γ-4-phenanthrylvaleric acid **72**, which on ring closure using thionyl chloride, pyridine and then stannic chloride yielded 4-keto-1-methyl-l,2,3,4-tetrahydrobenzo-[*c*]phenanthrene **73**. A Reformatsky reaction using ethyl bromoacetate, followed by dehydration, dehydrogenation and hydrolysis resulted in the formation of the desired acid 4-(1-methylbenzo[*c*]phenanthryl)acetic acid **75**.

Another simpler molecule 1-methylbenzo[*c*]phenanthrene **74** was similarly synthesized from 4-keto-1-methyl-l,2,3,4-tetrahydrobenzo[*c*]phenanthrene **73** by reduction, dehydration and dehydrogenation steps.

The compound 4-(1-methylbenzo[*c*]phenanthryl)-acetic acid **75** was resolved by via its diastereomeric ester with chiral alcohol *l*-menthol. The diastereomers were separated by recrystallization. After hydrolysis of ester the chiral 4-(1-methylbenzo[*c*] phenanthryl)acetic acid was obtained. The chiral properties of this molecule were further studied by comparing the optical rotation of the compound.

**Approach 2b: 2)** ***Synthesis of 6-methoxy-5-phenylbenzo[c]phenanthrene and 6-iodo-5-phenylbenzo[c]phenanthrene by electrophic cyclization reaction:***

Larock and co-worker reported an efficient synthesis of [4]helicenes/benzo[*c*]phenanthrenes in moderate to excellent yields by electrophilic cyclization under the mild reaction condition [**Scheme-11**].[44] The precursors, 2-(1-alkynyl)biaryls, were prepared by Sonogashira coupling reaction between terminal alkynes and the corresponding 2-iodobiaryl **76**, **77**.



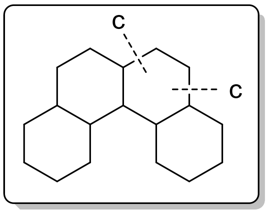
**76** R = OMe
**77** R = H

**78** R = OMe 97%
**79** R = H 48%

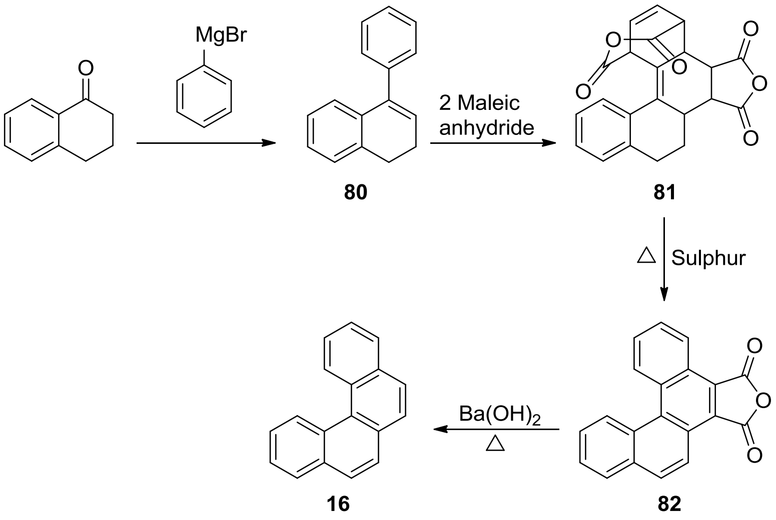
**Scheme 11:** Synthesis of 6-methoxy-5-phenylbenzo[*c*]phenanthrene **78** and 6-iodo-5-phenylbenzo[*c*]phenanthrene **79**

The alkylnated biaryl treated with the electrophile ICl, underwent cyclization through a cationic intermediate to give the products. The higher yield of the methoxy substituted benzo[*c*]phenanthrene **78** compare with the non-substituted was attributed to the electron donating character of the methoxy group and the stability to the intermediate. The products were converted to more complex compounds by subsequent palladium catalysed reactions.

**Approach 2c: 1)** ***Synthesis of benzo[c]phenanthrene 16 by Diels-Alder reaction:***



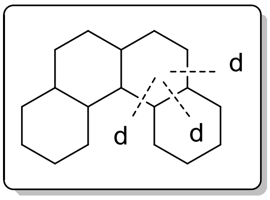
On the conclusion of the successful synthesis of benzo[*c*]phenanthrene and substituted benzo[*c*]phenanthrene Newman and co-workers developed[45] another synthetic path involving a key step of Diels-Alder reaction. The synthesis begins with the reaction of tetralone or substituted tetralones [**Scheme-12**], with corresponding phenyl magnesium bromide followed by dehydration to a 1-phenyl-3,4-dihydronaphthalene **80** or corresponding aryl dihydro-naphthalenes.



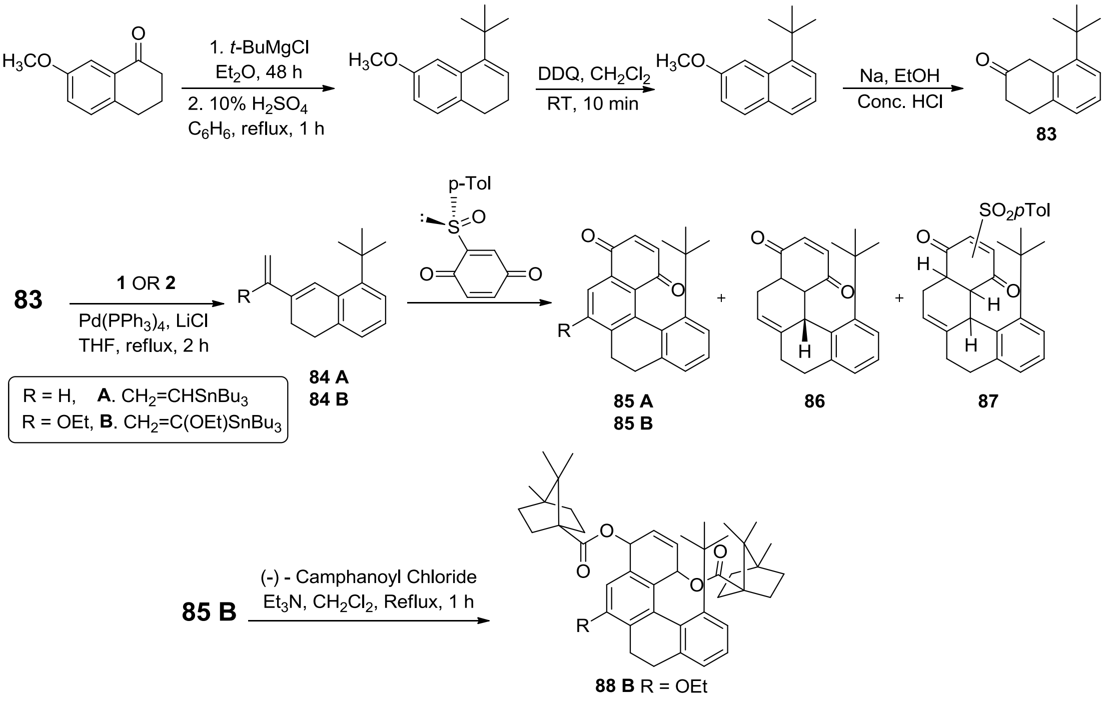
**Scheme 12:** Synthesis of substituted benzo[c]phenanthrene **16** by Diels-Alder reaction

Double Diels-Alder reaction of aryldihydronaphthtalene with maleic anhydride gave aromatic type dianhydrides **81**, the reaction of this dianhydride with sulphur at ~ 280 °C aromatized the ring and completely converted to monoanhydride **82**. The treatment of intermediate product monoanhydride with bariumhydroxide and copper bronze gave the product benzo[*c*]phenanthrene/[4]helicene **16**.

### Approach 2d: 1) *Synthesis of 12-tert-butyl substituted 7,8-dihydrobenzo[c] phenanthrene-1,4-quinones 85, 86, 87and 88:*



In 2001 Carreño and Urbano introduced the first enantioselective synthesis of 12-*tert*-butyl substituted 7,8-dihydrobenzo[*c*]phenanthrene-1,4-quinone having helical chirality.[46] This was achieved with good chemical and optical yield through a domino Diels–Alder reaction–sulfoxide elimination–oxidation process starting from enantiopure (*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone and 5-*tert*-butyl substituted 3-vinyl-1,2-dihydronaphthalenes as dienes.



**Mixture of diastereomers with helicity (*P*) and (*M*)**

**Scheme 13:** Synthesis of [4]helicenebisquinones and and it's diastereomeric camphanoyl derivatives

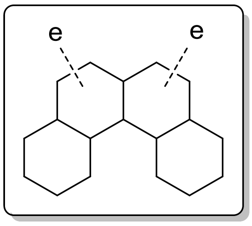
The 5-*tert*-butyl substituted 3-vinyl-1,2-dihydronaphthalenes as dienes were synthesized by addition of *tert*-butyl magnesium chloride to 7-methoxy-1-tetralone and product obtained was subjected to acid catalysed dehydration followed by aromatization using DDQ. The Birch reduction and hydrolysis of resulting ether gave 8-*tert*-butyl-2-tetralone **83**.

The intermediate product 8-*tert*-butyl-2-tetralone was converted to corresponding enol triflate and by Stille coupling with corresponding *tert*-

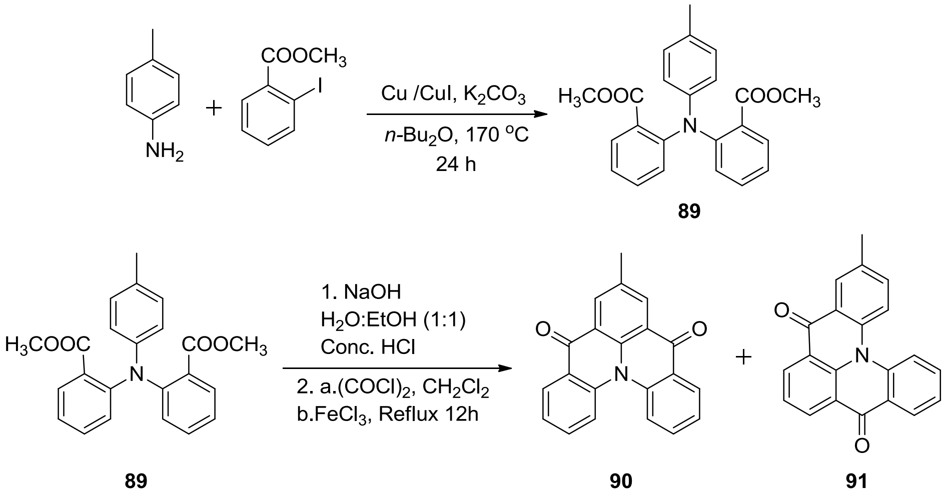
butylvinylstannane and 1-ethoxyvinyltributylstannane to 5-*tert*-butyl-3-vinyl-1,2-dihydronaphthalene and 5-*tert*-butyl-3-(1-ethoxyvinyl)-1,2-dihydronaphthalene **84A/84B**. Both these vinyl naphthalenes were converted to [4]helicene by domino Diels-Alder approach using (*SS*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone as dienophile to form the corresponding [4]helicenes. The mixture of these [4]Helicenes **85(A & B)**, **86** and **87** ratio of (15, 25, 60) were separated by flash column chromatography, the compounds were having enantiomeric enrichment upto 72 % ee.

The racemic **85B** and enantiomerically pure **85B** were converted to its diastereomeric form with the helical chirality (*P*) and (*M*) **88** by using making its ester with (-)-camphanoyl chloride and its optical purity and absolute configuration was established.

### Approach 2e: 1) *Synthesis of 7-Methyl-13b-aza-naphtho[3,2,1-de]anthracene-5,9-dione 90 and 3-Methyl-13b-aza-naphtho[3,2,1-de]anthracene-5,9-dione 91:*



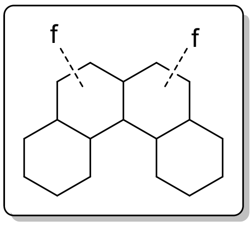
In 2003 Venkataraman and co-workers[17u] have used the framework of triarylamines for the construction of the helicenes with a bridge head nitrogen atom. They established the three step synthesis to construct helicenes bearing a bridgehead nitrogen atom in the molecule in moderate yield. As shown in [**Scheme-14**] the triarylamine prepared by copper catalysed Ullmann coupling was converted to corresponding diester **89**.



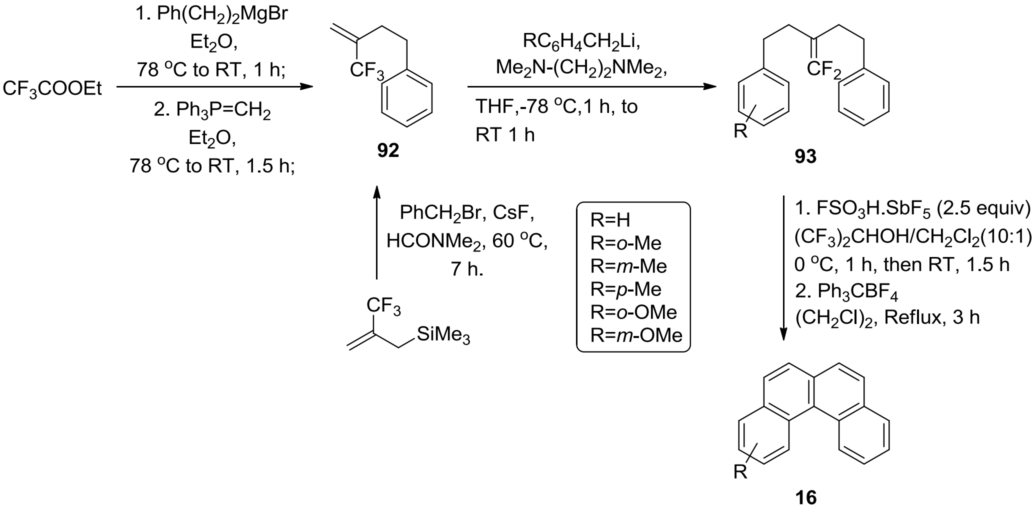
**Scheme 14:** Synthesis of [4]helicenes by Friedel-Crafts type reaction

The diester was hydrolysed to diacid, its subsequent treatment with oxalyl chloride gave diacid chloride, which on further Friedel-Craft reaction in the presence of $FeCl_3$ afforded the mixture of symmetrical and unsymmetical [4]helicene named as 7-methyl-13b-aza-naphtho[3,2,1-*de*]anthracene-5,9-dione **90** and 3-methyl-13b-aza-naphtho[3,2,1-*de*]anthracene-5,9-dione **91** which were inseperable by column chromatography.

### Approach 2f: 1) *Synthesis of Benzo[c]phenanthrene 16 and its derivatives:*



Ichikawa and co-worker introduced another Friedel-Crafts cyclization type approach for the synthesis of helicenes.[47] In this synthesis the Friedel-Crafts cyclization occurred *via* an α,α-diflurocarbocation. The starting material used was 1,1-difluoro-1-alkenes **93** bearing two aryl groups, each of which was linked to the vinylic carbon atom by a two-methylene-unit tether.

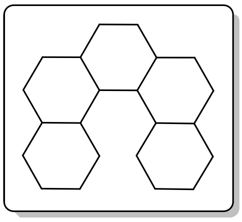


**Scheme 15:** Synthesis of substituted benzo[c]phenanthrene by Friedel-Crafts cyclization

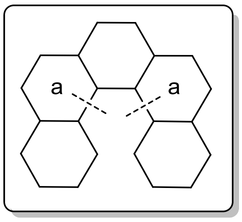
The symmetrical 1,1-difluroalkenes were synthesized by readily available 2,2,2-trifluoroethyl 4-methylbenzenesulfonate **92** ($CF_3CH_2OTs$) and trialkyl boranes prepared by the hydroboration of vinyl arenes. Other 1,1 difluoroalkenes **93**, including nonsymmetrical 1,1-difluoroalkenes, were prepared by $S_N2$ reaction of aryl methyl anions with the trifluoromethyl substituted vinyl compound, which was obtained readily from ethyl trifluoroacetate by a Grignard reaction followed by a Wittig reaction.

The trifluoromethylsubstituted vinyl compound has been synthesized by another methodology using benzyl bromide and (trifluoromethyl)allylsilane in presence of cesium fluoride in good yield. The aryl substituted 1,1-difluoroalkenes were cyclised by domino Friedel-Crafts type cyclization using $FSO_3H.SbF_5$ in 1,1,1,3,3,3-hexafluoropropan-2-ol to form the cyclised product 5,6,7,8-tetrahydrobenzo[*c*]phenanthrene and dehydrogenation using the triphenylmethylium tetrafluoroborate giving benzo[*c*]phenanthrene **16** in good yield. This method was well established and a number of derivatives of benzo[*c*]phenanthrene were synthesized by the authors.

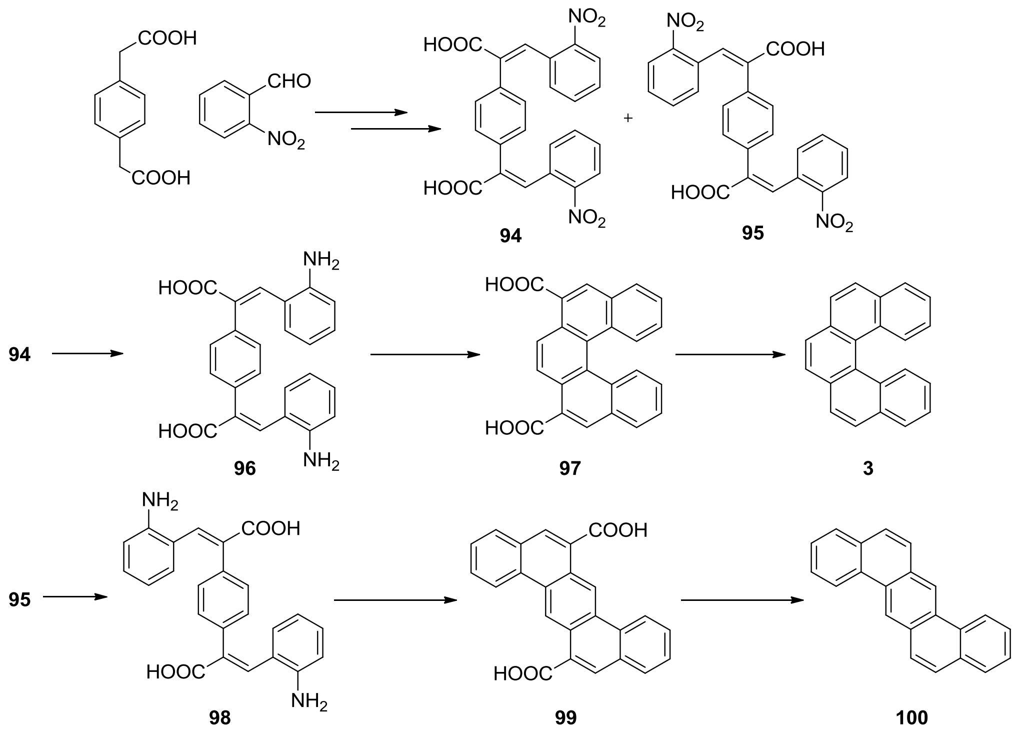
3) **Synthesis of [5]Helicene/pentahelicene and its different synthetic methodologies.**



**Approach 3a: 1) *Synthesis of [5]helicene 3 and 1,2,5,6-dibenzanthracene 100:***



The synthesis of [5]helicene/dibenzo[*c*,*g*]phenanthrene was first introduced by Pschorr involving a series of reactions.[3e] A sequence of a series of reactions from the 2,2'-(1,4-phenylene)diacetic acid and *ortho*-nitrobenzaldehyde lead to the formation of the *cis* and *trans* mixture of 2,2'-(1,4-phenylene)bis(3-(2-nitrophenyl)acrylic acid) **94** and **95**. The dinitro derivative were reduced to diamino **96**, **98** and after the cyclisation of the *cis*-diamino **96** derivative formed dibenzo[*c*,*g*]phenanthrene-2,5-dicarboxylic acid **97** and after the decarboxylation formed the [5]helicene **3**.

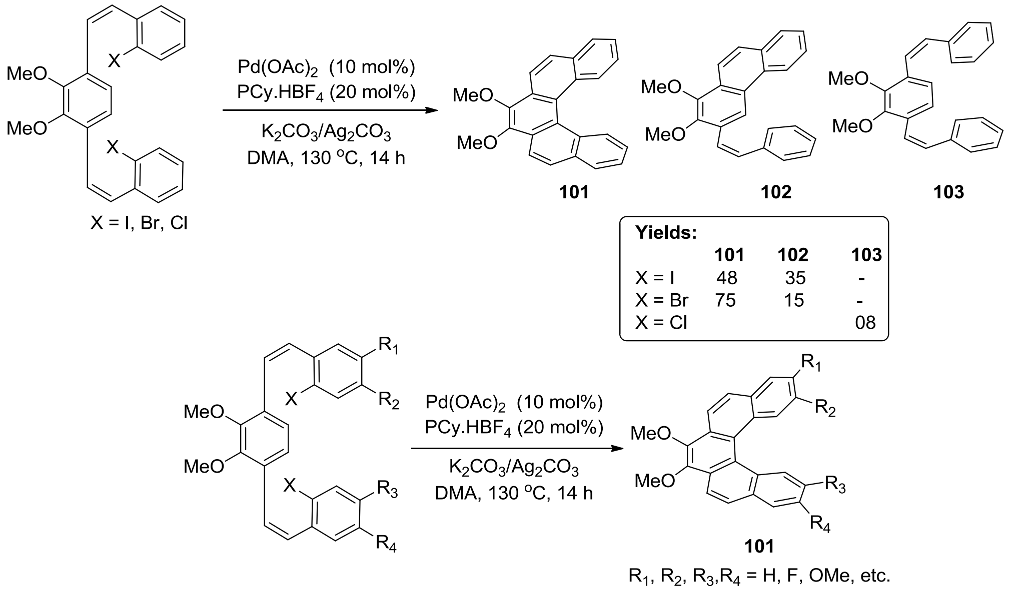


**Scheme 16:** The first synthesis of [5]helicene **3**

Similarly the *trans*-diamino derivative **98** was also converted to 1,2,5,6-dibenzanthracene **100** by Pschorr series of reactions.

### Approach 3a: 2) *Synthesis of 7,8-dimethoxy[5]helicene 101 and its derivatives by palladium catalysed C-H arylation:*

The next approach involved palladium mediated key step of cyclization of appropriate aryl halide.



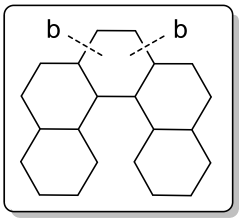
Yields:

| | 101 | 102 | 103 |
|---|---|---|---|
| X = I | 48 | 35 | - |
| X = Br | 75 | 15 | - |
| X = Cl | | | 08 |

**Scheme 17:** Synthesis of 7,8-dimethoxy[5]helicene **101** by palladium catalysed C-H arylation approach

Kamikawa and co-worker have reported[48] the synthesis of [5]helicene involving initially synthesis of distyryl derivative by conducting Wittig reaction on 2,3-dimethoxy-1,4-dicarbaldehyde. The olefin on palladium catalyzed C-H arylation using PCy·$HBF_4$ as a ligand afforded [5]helicene **101** and its derivatives in moderate to good yield. This approach has a good tolerance for the presence of electron-withdrawing substituents at the 3- and 12-positions, while the two methoxy groups were required to direct the cyclisation reaction to afford the helical framework. The effect of halogens was also studied and presence of bromine is a tolerable for this reaction. Absence of the two methoxy groups in the bis-styryl starting matrial; lead to the formation of a complex mixture. Using this methodology the authors have synthesized phenanthrenes as well as [6]helicenes.

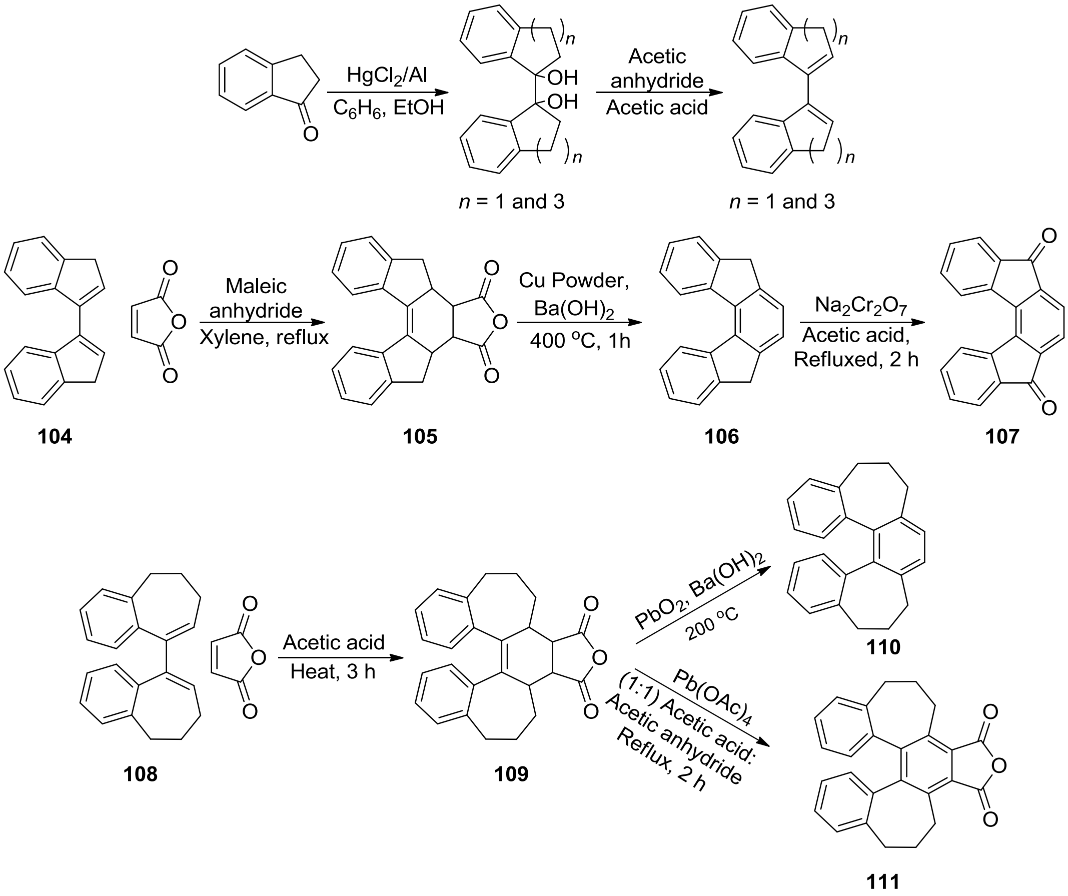
**Approach 3b: 1)** ***Synthesis of 5,5a,6,7,7a,8-Hexahydroindino[2,1-c]fluorine-6,7-dicarboxylic anhydride 105, 5,8-Dihydroindino[2,1,c]fluorine 106, 5,8-Dihydro-5,8-dioxoindeno[2,1,c]fluorine 107, 5,6,7,7a,8,9,9a,10,11,12-Decahydrodi-(benzocyclo-hepta)[6,5-a:5',6'-c]benzene-8,9-dicarboxylic anhydride 109, 5,6,7,10,11,12-Hexahydrodi(benzocyclohepta)-[6,5-a,5',6'-c]benzene 110 and5,6,7,10,11,12-Hexahydrodi-(benzocyclohepta)[6,5-a:5'6'-c]benzene-8,9-dicarboxylic anhydride 111:***



Ginsburg and Altman introduced another methodology for the synthesis of [5]helicene like molecules by Diels-Alder reaction [**Scheme-18**].[49] The synthesis involves indane-1-one and benzocyclohepten-1-one as starting material. These were converted to 1'1'-bi-indanyl-1,l'-diol and 2,3:2',3'-dibenzobi(cyclopent-3-enyl)-1,1'-diol, respectively.[50] The dehydration of diol with a mixture of acetic anhydride and acetic acid gave a crystalline diene product **104**.

The diene **104** and maleic anhydride in xylene were heated under reflux to form the product 5,5a,6,7,7a,8-hexahydroindino[2,1-*c*]fluorine-6,7-dicarboxylic anhydride **105**. The compound on decarboxylation and dehydrogenated with copper powder and barium hydroxide at high temperature gave the product 5,8-dihydroindino[2,1,*c*]fluorine **106**, which was structurally similar to

[5]helicene/pentahelicene, on oxidation with sodium dichromate in acetic acid gave 5,8-dihydro-5,8-dioxoindeno[2,1,*c*]fluorine **107**.



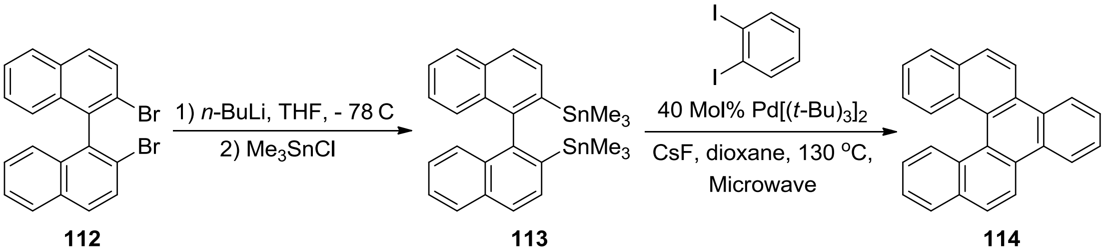
**Scheme 18:** Synthesis of [5]helicene like molecules and its derivatives

Subsequentely, the compound 2,3:2’,3’-dibenzobi(cyclopent-3-enyl)-1,1’-diol was converted to its diene using a mixture of acetic acid and acetic anhydride. The diene **108** and maleic anhydride was heated and inially formed intermediate was treated with acetic acid and acetic anhydride to give the final product 5,6,7,7a,8,9,9a,10,11,12-decahydrodi(benzocyclohepta)[6,5-*a*:5’,6’-*c*]benzene-8,9-dicarboxylic anhydride **109**. This was further treated for decarboxylation and dehydrogenation with lead oxide and barium hydroxide to form 5,6,7,10,11,12-hexahydrodi(benzocyclohepta)[6,5-a,5’,6’-*c*]benzene as a [5]helicene like molecule **110**.

The compound 5,6,7,10,11,12-hexahydrodi(benzocyclohepta)[6,5-a:5’6’-*c*]benzene-8,9-dicarboxylic anhydride **111** was synthesized from 5,6,7,7a,8,9,9a,10,11,12-decahydrodi(benzocyclohepta)[6,5-*a*:5’,6’-*c*]benzene-8,9-dicarboxylic anhydride treated with lead tetra acetate in a mixture of acetic anhydride and acetic acid under reflux condition.

### Approach 3b: 2) *Synthesis of benzo[5]helicene 150:*

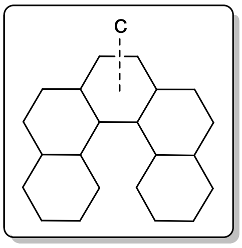
Another elegant approach involvs palladium catalyzed double coupling of organo tin reagent with suitable aryl iodide. Scott and co-workers have synthesized benzo[5]helicene **114** for its pyrrolytic thermal dehydrogenation to form the benzo[*ghi*]perylene like structure.[51] For this study a large amount of the benzo[5]helicene is required, therefore they developed methodology for the synthesis of benzo[5]helicene, involves 1,2'-dibromo-1,1'-binaphthalene **112** as a starting material.



**Scheme 19:** Synthesis of benzo[5]helicene by double Stille coupling reaction

The starting material was converted to 2,2'-bis(trimethylstannyl)-1,1'-binaphthyl **113** by using the *n*-butyl lithium and trimethylstannyl chloride at -78 °C in tetrahydrofuran. The double Stille coupling on this intermediate of the stannyl derivative with *o*-diiodobenzene using palladium catalyst, cesium fluoride in dioxane in microwave to form the benzo[5]helicene **114**. The benzo[5]helicene was used for the synthesis of perylene derivative under thermal vacuum pyrrolysis condition.

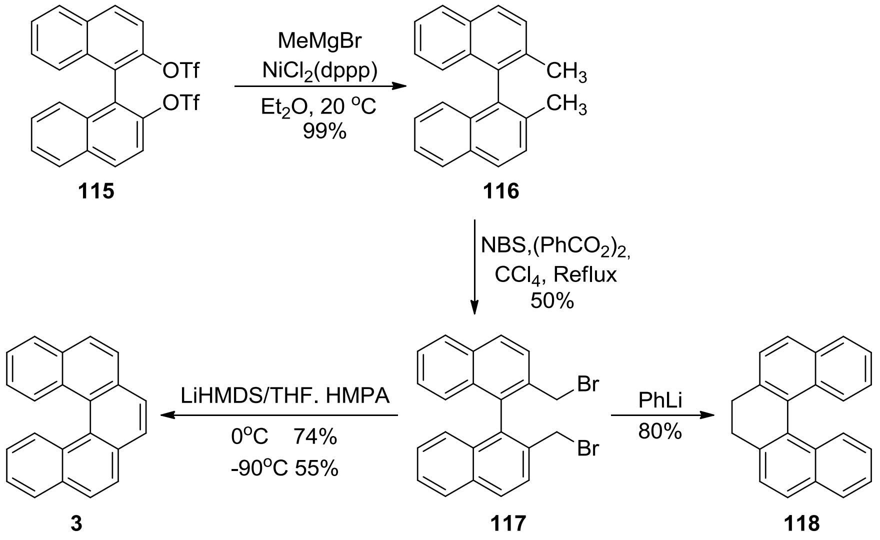
### Approach 3c: 1) *Synthesis of [5]helicene 3 by metal induced McMurry coupling reaction and carbenoid coupling reactions:*



Gingras and Dubois have reported the synthesis of [5]helicene **3** by using metal catalysed reaction involving carbon-carbon double bond formation for the construction of benzene ring for the synthesis of carbohelicenes.[52] Gingras reported in 1998 the carbenoid coupling for the synthesis of [5]helicene from the BINOL, the BINOL was converted to its triflates using the triflic anhydride [**Scheme-21**].

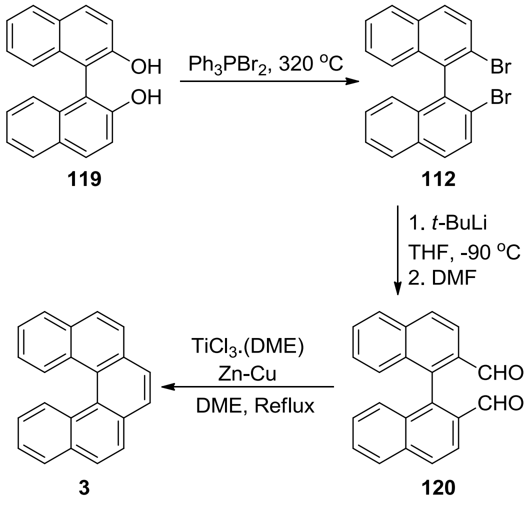
The triflate derivative **115** of binaphthalene was converted to 2,2’-dimethyl-1,1’-binaphthlene **116** by Snieckus method[53] using methylmagnesium bromide in the presence of catalytic $NiCl_2$(dppp) in excellent yield. Under the radical bromination with N-bromosuccinimide the bromosubstituted binaphtyls **117** is obtained. The carbenoid coupling was done by Jones methodology[54] using LiHMDS at -90 °C to get the product [5]helicene **3** in moderate yield. The carbenoid coupling was also used for the synthesis of 7,8-tetrahydro[5]helicene **118** using the phenyllithium and the enantio-enriched binaphthyltriflate derivative given the enantiomerically enriched 7,8-tetrahydro[5]helicene **118** in 55% *ee* product.

## Carbenoid Coupling Reaction:



**Scheme 20:** Synthesis of [5]helicene **3** and 7,8-tetrahydro[5]helicene **118** by carbenoid coupling reaction

## McMurry Coupling Reaction:

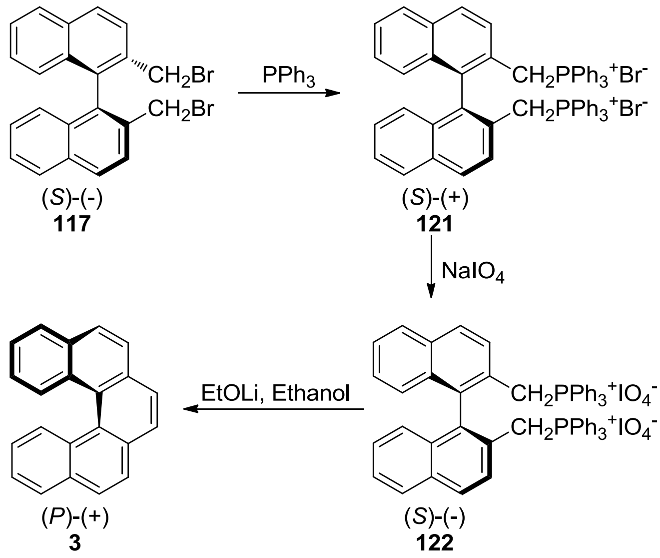


**Scheme 21:** Synthesis of [5]helicene **3** by McMurry coupling reaction

The authors have also synthesized the [5]helicene by using the McMurry coupling reaction [**Scheme-21**]. The synthesis started with the BINOL **119**, converted it to 2,2’-dibomo-1,1’-binaphthalene **112** using the $Ph_3PBr_2$. The dibromoderivative converted to dicarbaldehyde using *n*-Buli and DMF. The intramolecular dialdehyde McMurry coupling of 2,2’-dicarbaldehyde-1,1’-binaphthalene **120** was done under the most reproducible condition with $TiCl_3 \cdot (DME)_{1.5}$ and Zn-Cu condition in refluxing DME.

## Approach 3: 3) *Synthesis of enantiomerically pure [5]helicene 3:*

In 1972, Both and Bestmann reported synthesis of the enantiometrically pure [5]helicene **3** by lithium induced reaction.[10f,g]

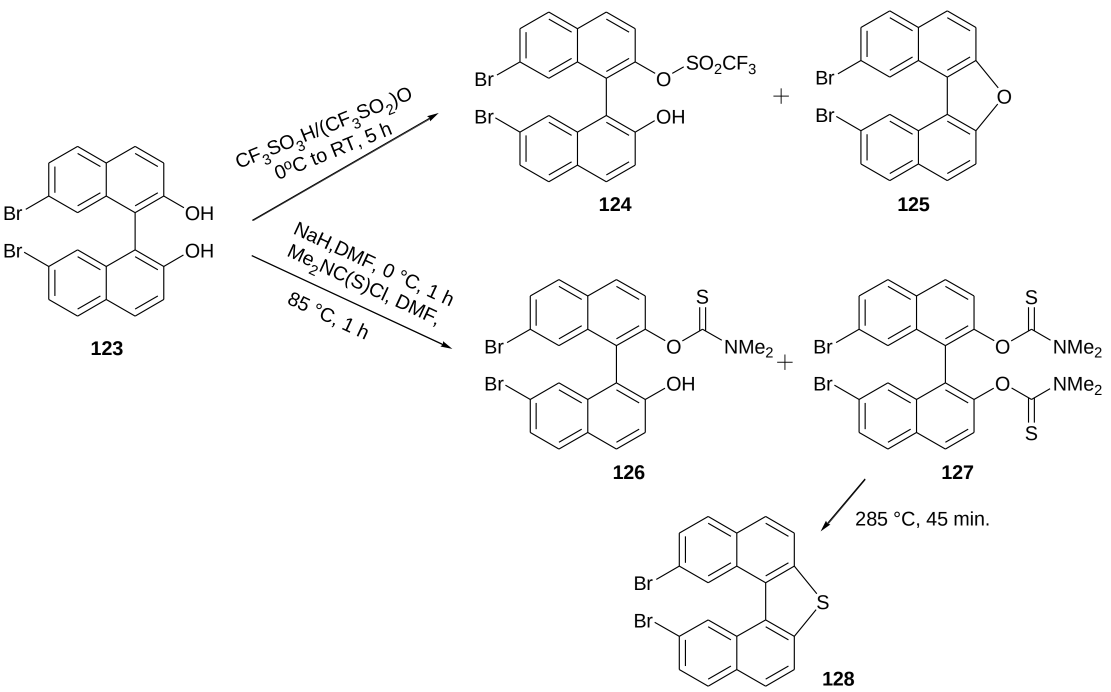


**Scheme 22:** Synthesis of enantiomerically pure [5]helicene

The reaction started with the enantiomerically pure binaphthyl derivative (*S*)-(-)-2,2’-bis(bromomethyl)-1,1’-binaphthyl **117**, which was converted to its (+)-bisphosphine salt **121**. The phosphine salt on reaction with sodium periodate formed the (*S*)-(+)-bisphosphino periodate **122** and its further reaction with lithium ethoxide at -5 °C to 0 °C formed the (+)-[5]helicene **3**, with an absolute configuration of (*P*).

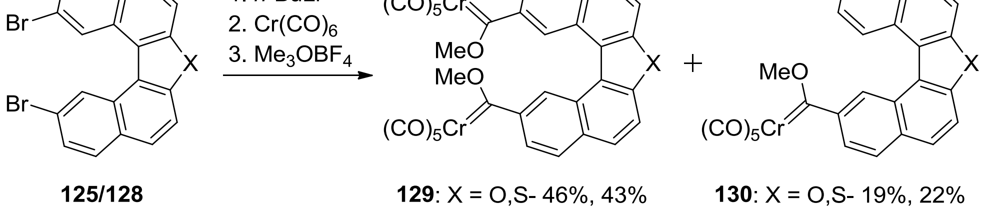
## Approach 3c: 4) *Synthesis of 2,11-dibromo-oxa[5]helicene 125, 2,11-dibomo thia[5]-helicene 128, oxa[7]helicenebisquinone and thia[7]helicenebisquinone 133:*

Dotz and co-workers further synthesized structurally similar oxa[5]helicene and thia[5]helicene using the precursors 7,7’-dibromo-2,2’-dihydroxy-1,1’-binaphthyl **123**.[55]



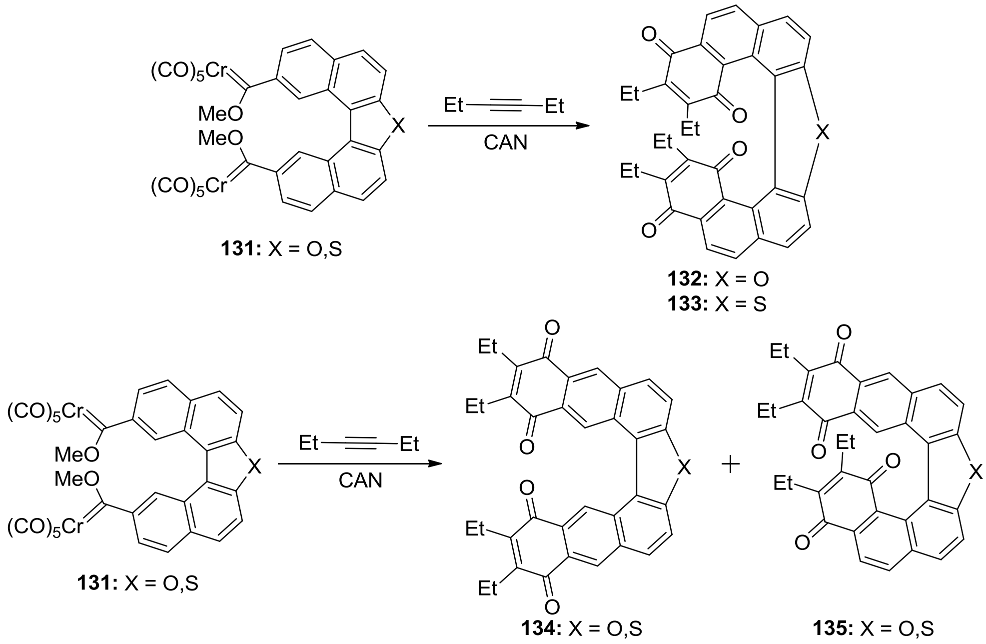
**Scheme 23:** Synthesis of oxa- and thia-[5]helicenes **166** and **169**

A different type of helical molecule, oxa[5]helicene **125**, was synthesized using the trifluoromethanesulfonic acid and trifluoromethane sulphonic anhydride in benzene to form the desired product **125** as well as an uncyclized 2-trifluoromethanesulfonyloxy-7,7’-dibromo-2’-hydroxy-1,1’-binaphthalene **124**. The similar sulphur analogues of thia[5]helicene, were synthesized using NaH and *N*,*N*-dimethylthiocarbamoyl chloride. Two intermediates 7,7’-dibromo-2-(*N*,*N*-dimethyl-thiocarbamoyloxy)-2’-hydroxy-1,1’-binaphthyl **126** and 7,7’-dibromo-2,2’-bis(*N*,*N*-dimethylthiocarbamoyloxy)-1,1’-binaphthyl **127** were synthesized. Out of which **127** was converted by straightforward Newman–Kwart rearrangement to the product 2,11-dibromo-thia[5]helicene **128**.



**Scheme 23-A:** Synthesis of oxa- and thia-helicenes bisquinones **172**, **173** and **174** from chromium carbene complexes

The dibromo-oxa and thia[5]helicene **125** and **128** were then converted to their chromium carbene complex to form the 2,12-(dinaphtho[2,1-*b*:1’,2’-*d*]furandiyl)bis (methoxycarbene) bis-[(pentacarbonyl)chromium] and 2,12-(dinaphtho[2,1-*b*:1',2'-*d*]thiophenediyl) bis-(methoxycarbene)bis[(pentacarbonyl)chromium] **131**.

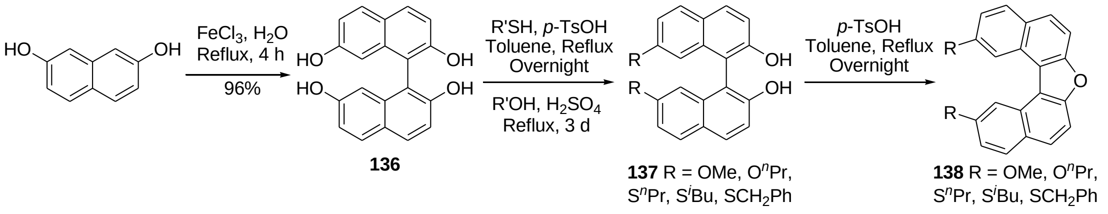


**Scheme 24:** Synthesis of oxa- and thia-helicenes bisquinones **172**, **173** and **174** from chromium carbene complexes

These were precursors for the helicenebis-quinones **132**, **133** and **134** [**Scheme-23-A**]. The chromium carbenes was treated with different alkynes in dichloromethane and addition of ceric ammonium nitrate to form the oxa and thia helical bisquinones [**Scheme 24**].[55]

## Approach 3c: 5) *Synthesis of 2,12-disubstituted-7-oxa[5]helicene 138:*

Thongpunchang and co-workers have reported an efficient and scalable sequence to synthesize 2,12-disubstituted-7-oxa[5]helicene from cheap commercially available materials.[56] As shown in [**Scheme-25**] 7,7'-dihydroxy-2,2'-binaphthol **136** was obtained form 2,7-dihydroxynaphthalene by oxidative coupling with $FeCl_3$ in a excellent yield.

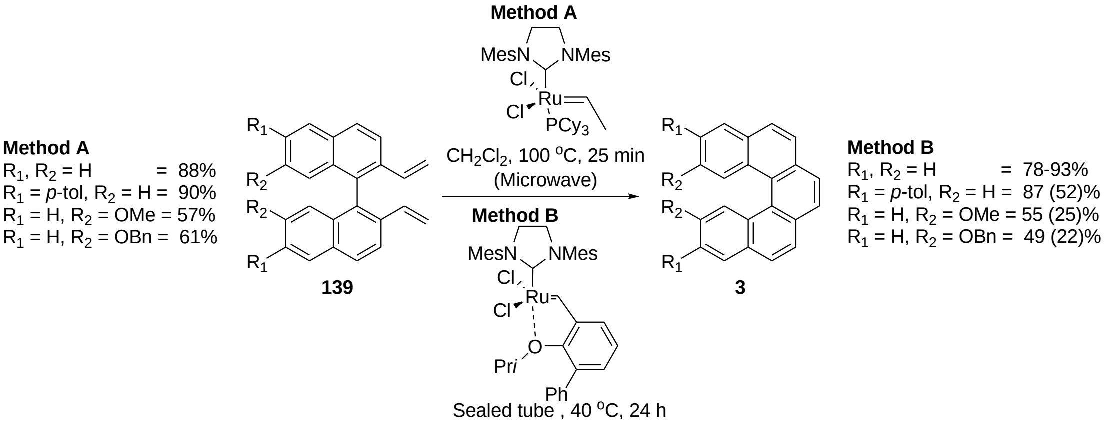


**Scheme 25:** Synthesis of 2,12-disubstituted-7-oxa[5]helicenes

After substitution using different nucleophiles and subsequent ring closure using *p*-toluene sulphonic acid in toluene at reflux condition afforded 2,12-disubstituted-7-oxa[5]helicene **138** in a good yields.

### Approach 3c: 6) *Synthesis of [5]helicenes 3 and its derivatives by using ring closing olefin metathesis:*

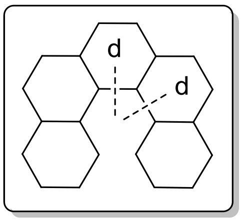
In 2006, Collins and co-workers reported the synthesis of helicenes and its derivatives in good yields by the ring closing olefin metathesis methodology. They developed two different methodologies, Method A and Method B for the synthesis of helicenes and its derivatives.[57]



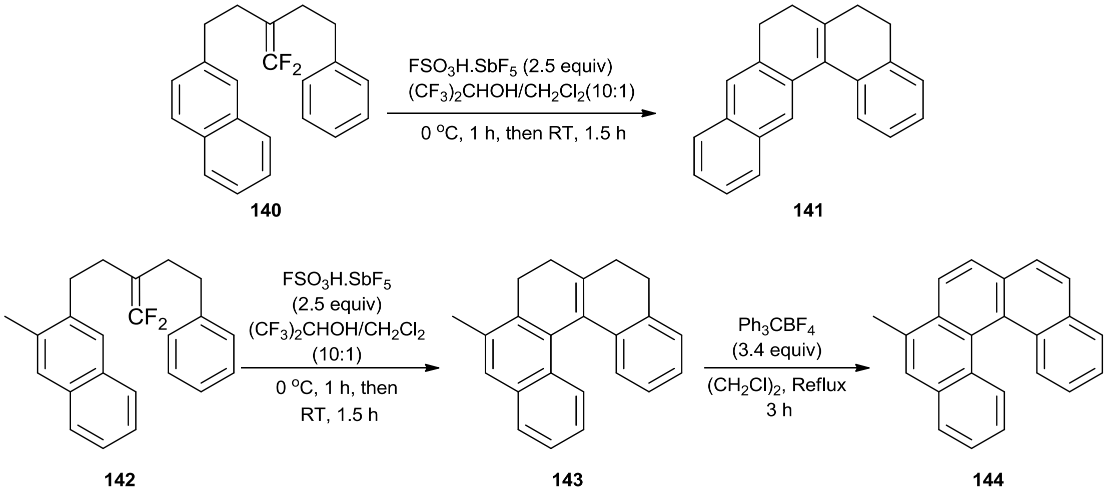
**Scheme 26:** Synthesis of [5]helicene and it's derivatives using ring closing olefin metathesis

The method A is efficient but requires high temperature (100 °C) in microwave which can result in pyrolysis. The method B occurs under milder condition at 40 °C but requires the longer reaction time. The synthesis started with the precursor 2,2'binaphthol and its derivatives, it being converted to the divinyl precursor **139**, followed by its ring closing olefin metathesis to give the product [5]helicene **3** and its derivatives. Using this methodology the authors have also synthesized [6]helicene and [7]helicene in a good yields.

### Approach 3d: 1) *Synthesis of 6-methyl[5]Helicene 144:*



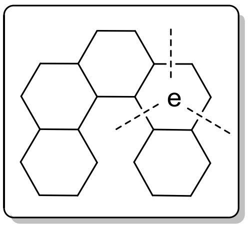
The similar methodology like benzo[*c*]phenanthrene was used by Ichikawa and co-worker for the synthesis of [5]helicene.[58] The same authors had previously observed that naphthyl-substituted difluoroalkenes **140** underwent the Friedel–Crafts-type cyclization regioselectively at the C1-position of the ring because of electronic effects,[64] the domino cyclization and dehydrogenation of the naphthalene derivative would lead to the corresponding [5]helicene. However, it underwent cyclization exclusively at the 3-position of the naphthalene ring to give 5,6,7,8-tetrahydronaphtho[1,2-*a*]anthracene **141** in good yield [**Scheme-27**].



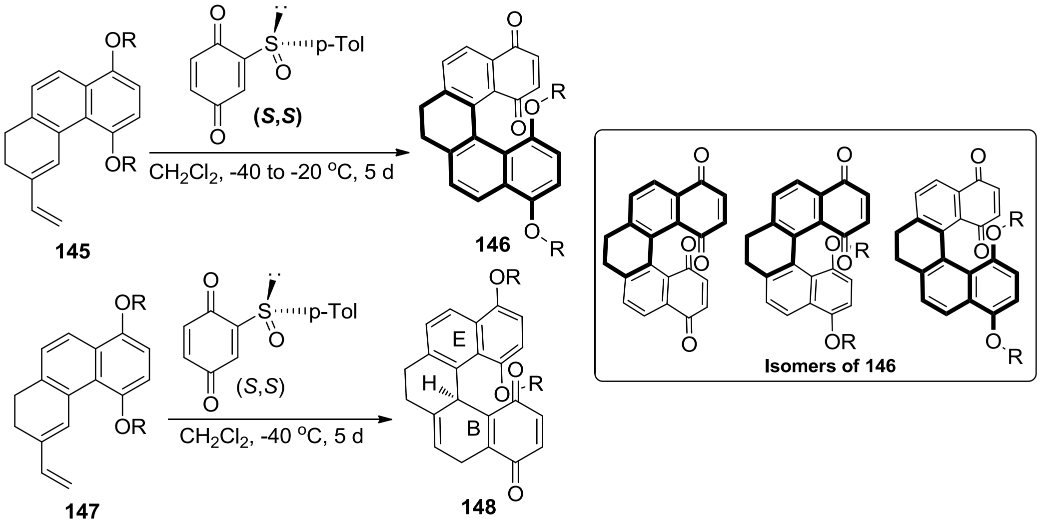
**Scheme 27:** Synthesis of 6-methyl[5]helicene **144** by Friedel-Craft type cyclization reaction

Thus, the regiochemistry of the reaction was controlled by steric effects rather than by electronic effects in the construction of sterically hindered polycyclic systems. Therefore a methyl group was strategically placed at C3 position to prevent cyclization at unwanted location of the naphthalene ring. Upon the treatment of ($FSO_3H{\bullet}SbF_5$), the compound 2-[4,4-difluoro-3-(2-phenylethyl)but-3-en-1-yl]-3-methylnaphthalene **142** furnished 2-methyl-3,4,5,6-tetrahydrodibenzo[*c*,*g*] phenanthrene **143** as the desired compound. The dehydrogenation using the triphenylmethylium tetrafluoroborate in 1,2-dichloroethane at reflux temperature provided the 6-methyl[5]helicene **144**.

### Approach 3e: 1) *Synthesis of (P) and (M)-dihydro[5]helicenequinones:*



Carreno and Urbano have synthesized the (*P*) and (*M*)-dihydro[5]helicenequinones by the domino asymmetric Diels-Alder/spontaneous sulphoxide elimination process between a vinyl dihydrophenanthrene **145** and **147** as diene and enantiopure (*S,S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone.[59]

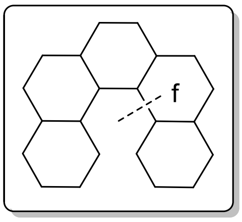


**Scheme 28:** Synthesis of [5]helicene-quinones by asymmetric Diels-Alder approach

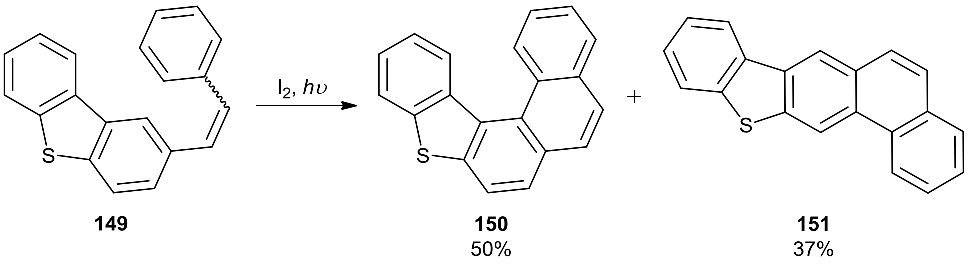
The domino asymmetric Diels–Alder reaction/spontaneous sulfoxide elimination process between a vinyl dihydrophenanthrene as diene and enantiopure (*SS*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone gave access to a tetrahydroaromatic pentacyclic derivative possessing central chirality which led, in a divergent way, to helically chiral (*P*) or (*M*) enantiomers of dihydro[5]helicenequinones **146** and **148** in good to excellent chemical and optical yields simply by selecting the appropriate oxidant reagent which makes the final aromatization.

### Approach 3f: 1) *Synthesis of thiohetero[5]helicene 150 and its linear derivative by photocyclodehydrogenation methodolody:*

Castle and co-workers synthesized the hetero thia[5]helicene **151** by a photocyclization method.[60] They have followed the photocyclodehydrogenation pathway to synthesize derivative of thia[5]helicene from the corresponding stilbene derivative. The disconnection is shown as ‘f’ in the following figure.



When the thiophene ring was replaced with a benzene ring, the selectivity was much better.

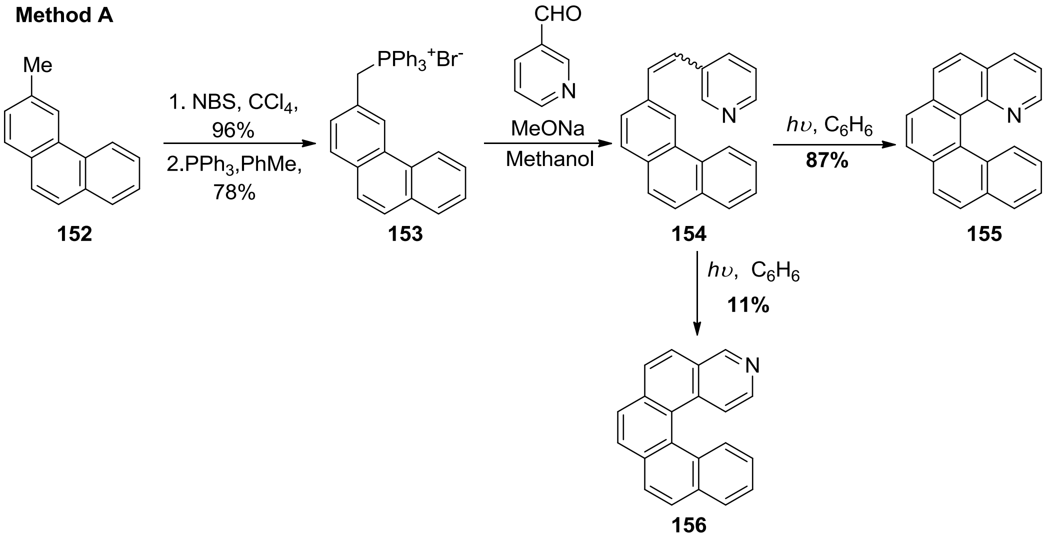


**Scheme 29:** Synthesis of thia[5]helicene **151**

The synthesis of thiohetero[5]helicene using the corresponding olefin **149**, catalytic amount of iodine in a benzene and irradiated with mercury vapour lamp to obtained the angular product thia[5]helicene **150** and linear derivative **151**.

### Approach 3f: 2) ***Synthesis of 1-aza[5]helicene 193 and 3-aza[5]helicene 194 by photocyclodehydrogenation methodology:***

In 2005, Caronna and co-workers have reported the aza[5]helicene[17ac] and its theroretical[61] study for the photocyclodehydrogenation of styryl derivative **154** containing the heteroatom and the favourable site for the cyclization in the molecules. For the synthesis of 1- and 3-aza[5]helicenes **155** and **156** two reports were mentioned.

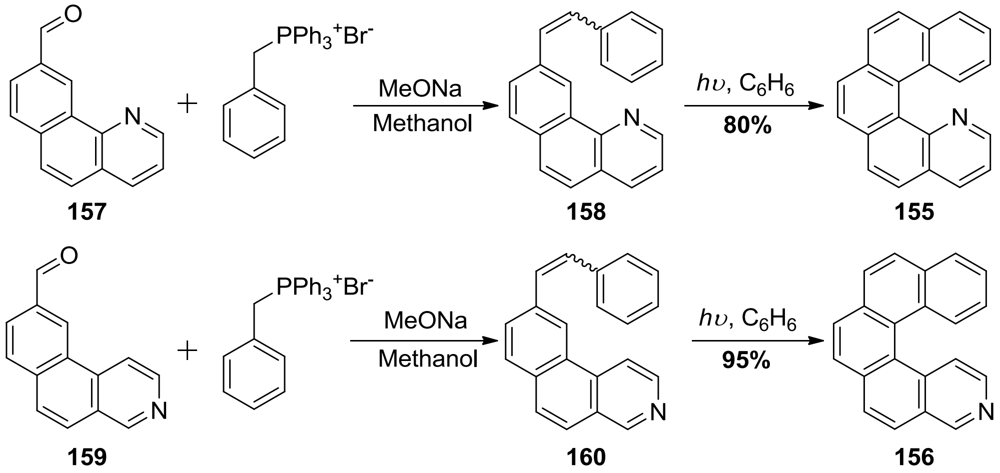


**Scheme 30:** Synthesis of aza[5]helicene **193** and **194** by Mallory's Phototcyclization Method

The method A [**Scheme-30**] starts involves building of an ethylene derivative with a phenanthrene on one side and a 3-pyridine on the other. Its photochemical ring closure gave a mixture of two products such as 1-aza[5]helicene **155** and 3-aza[5]helicene **156** in 87% and 11% (in ratio 9:1) respectively.

The second synthetic approach [**Scheme-31**] may be considered longer, because it was necessary to synthesize a starting phenanthridine. However, this route was found to be more selective for both the aza[5]helicenes. The benzo[*h*]quinoline-9-carbaldehyde **157** on Wittig reaction with benzylbromide phosphonium salt converted to 9-styryl-benzo[*h*]quinoline **158** and photocyclodehydrogenation in open air using benzene as a solvent to obtain the compound 1-aza[5]helicene **155** in good yield.

**Method B**

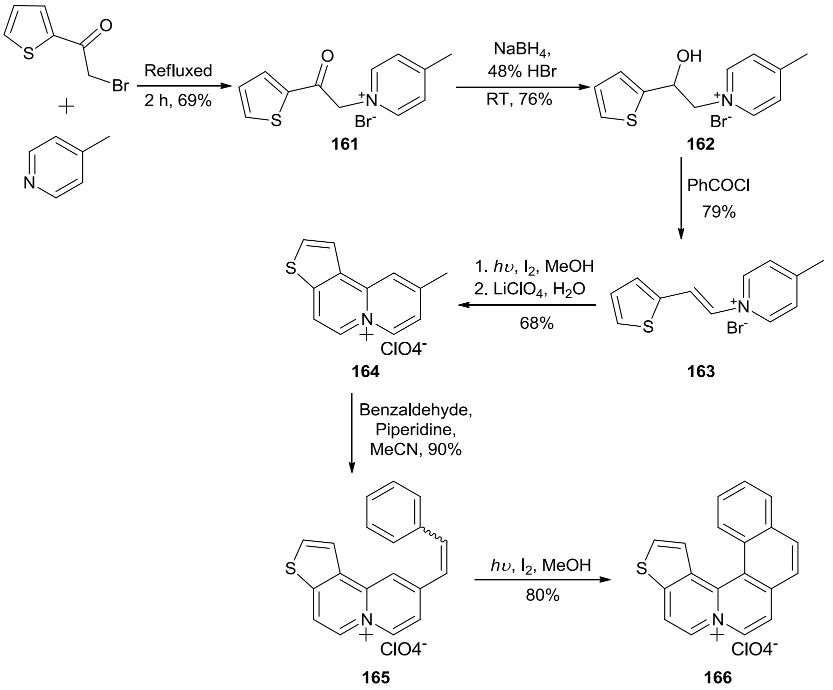


**Scheme 31:** Synthesis of aza[5]helicene by Mallory's Phototcyclization Method

Subsequently 3-aza[5]helicene **156** was synthesized using a starting material benzo[*f*]isoquinoline-9-carbaldehyde **159** which on Wittig reaction with benzylbromide phosphonium salt using sodium methoxide to obtain 9-styrylbenzo[*f*]isoquinoline **160**. The 9-styrylbenzo[*f*]isoquinoline was cyclized by photocyclodehydrogenation in open air in benzene as a solvent to obtain the product 3-aza[5]helicene **156** in excellent yield.

### Approach 3f: 3) *Synthesis of Azonia[5]helicenes containing terminal thiophene ring such as 5a-azonia-3-thia[5]helicene perchlorate 166:*

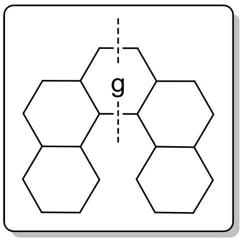
Arai and co-workers reported a new type of stilbene precursor for the synthesis of helicenes bearing bridgehead quaternary nitrogen atom at the periphery of the helical structure.[62] On reduction and elimination, the quaternary ammonium salt was transformed into a stilbene-type structure **163**, which underwent photoinduced ring closure in the presence of iodine using methanol as solvent to give compound 9-methylthieno[3,2-*a*]quinolizinium perchorate **164**. The reaction with benzaldehyde and piperidine in acetonitrile under reflux form (*E*)-9-styrylthieno[3,2-*a*]quinolizinium perchlorate **165**.



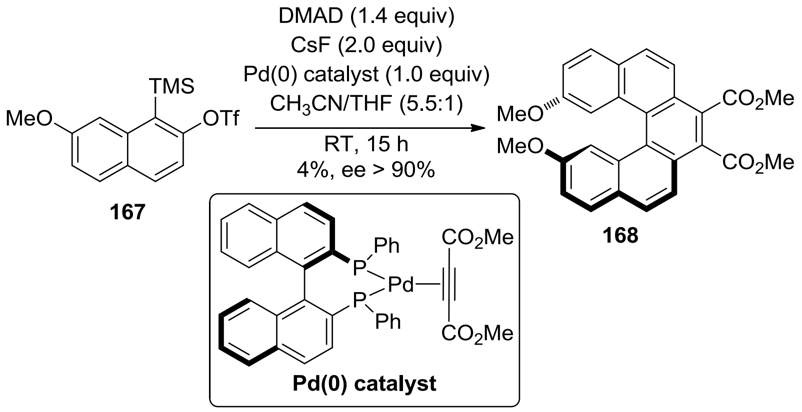
**Scheme 32:** Synthesis of azonia[5]helicene **166** by Mallory's photocyclization methodology

The styryl compound **165** on photocyclization using catalytic amount of iodine in methanol irradiated by HPMV lamp gave the cyclised product 5*a*-azonia-3-thia[5]helicene perchlorate **166**. Using this methodology several other similar other thia-helicenes are also synthesized.

## Approach 3g: 1) *Synthesis of enantio-enriched [5]helicene as 9,12-dimethoxy-3,4-dibenzo[c,g]phenanthrenedicarboxylate 168:*



In 2006, Perez, Guitian and co-workers reported asymmetric [2 + 2 + 2] cycloaddition involving arynes for the preparation of helicenes [**Scheme-33**].[16] The key reaction for this approach involve coupling of an aryl unit by metal catalyzed reaction on silylated aromatic system in combination of cycloaddition with electron deficient alkyne reagent such as dimethyl acetylene dicarboxylate.

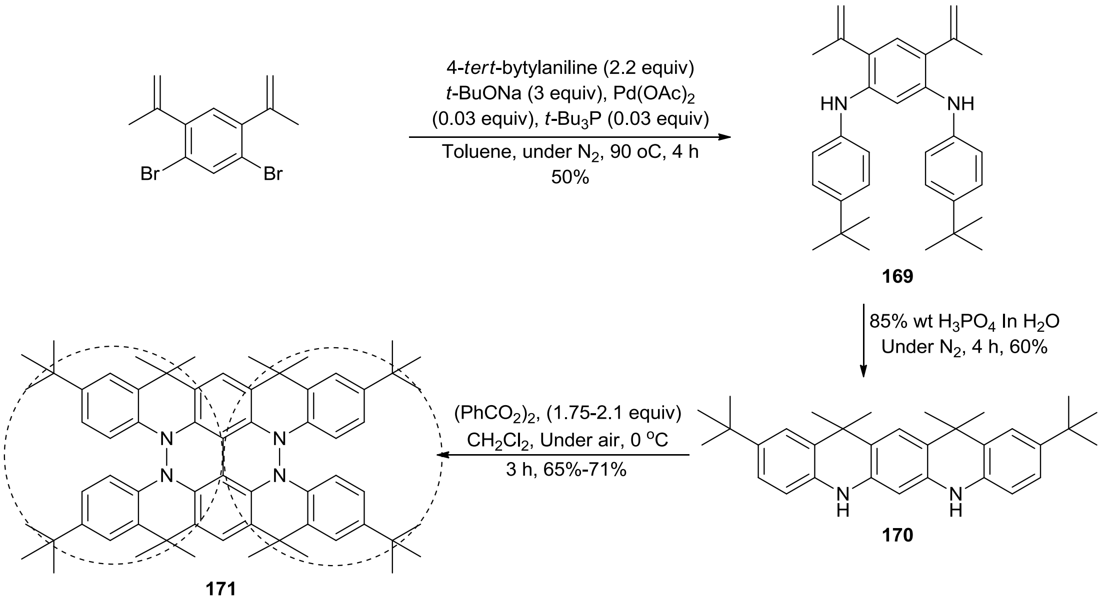


**Scheme 33:** Asymmetric synthesis of [5]helicene by [2 + 2 + 2] cycloaddition approach

However in this complex reaction several isomers were obtained, at the same time the enantiomeric excesses of helicenes varied upto 90% with different yields under different reaction conditions. Besides the addition reactions of arynes and alkynes, biaryls were also important precursors to enantioenriched helicene **168**.

### Approach 3g: 2) *Synthesis of Double [5]Helicene via a Sequence of Three Oxidative CC- and NN-Homocouplings:*

Rajca and co-workers have synthesized the double aza[5]helicenes by the oxidative coupling of C-C and N-N homocouplig reaction.[63]



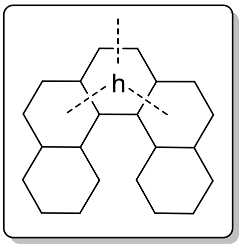
**Scheme 34:** Synthesis of double [5]helicene

The Buchwald and Hartwig coupling[64] of 4,6-diisopropenyl-1,3-dibromobenzene and 4-*tert*-butylaniline in presence of catalyst system of palladium acetate, tris-tert-butylphosphine and sodium butoxide gave the corresponding 4,6-diisopropenyl-*N*,*N'*-di(4-*t*-butylphenyl)-1,3-benzenediamine **169**. The diamine 4,6-

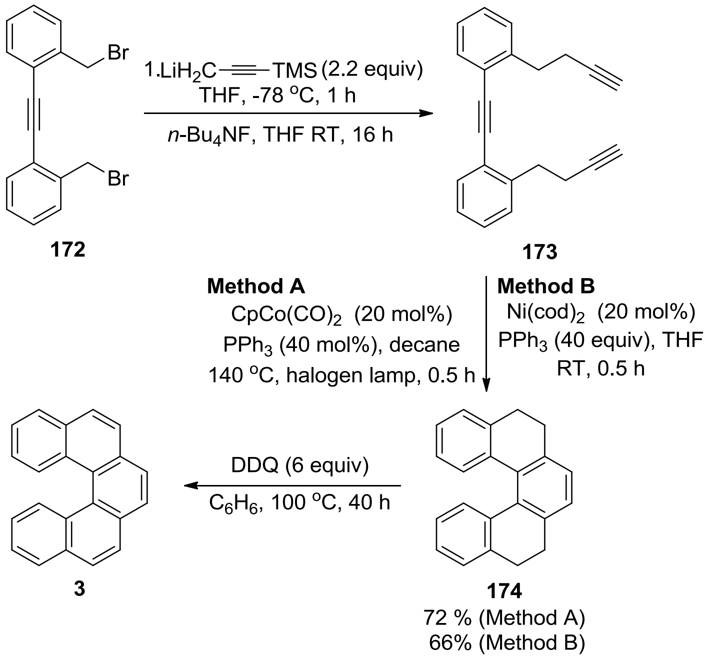
diisopropenyl-*N*,*N'*-di(4-*t*-butylphenyl)-1,3-benzenediamine **169** on reaction with $H_3PO_4$ efficiently gave the cyclized diamine **170**.

The diamine on reaction with benzoylperoxide in dichloromethane formed the final product dihydrazine as a double [5]helicene **171**. The thermal stability as well as isomerisation of these types of compounds was further studied.

### Approach 3h: 1) *Synthesis of [5]helicenes 3 by the metal catalysed [2 + 2 + 2] cyclizations:*

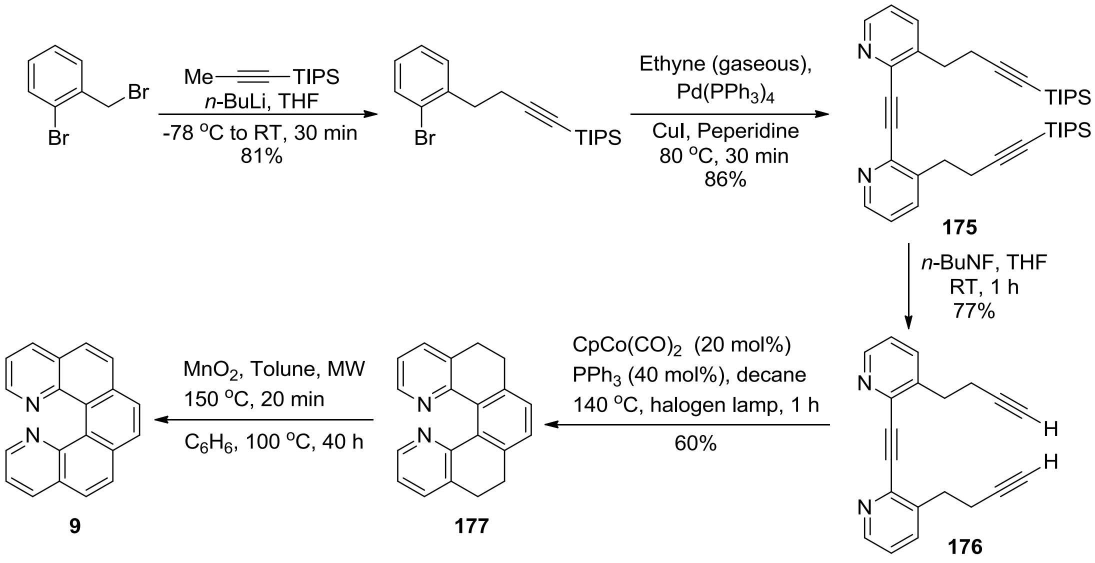


A group of researchers from Czech Republic have synthesized the [5]helicene by [2 + 2 + 2] cycloisomerization by metal catalysed methodology using Co(I) and Ni(I) catalysis [**Scheme-35**].[65,66]



**Scheme 35:** Synthesis of [5]helicene **3** by [2 + 2 + 2] cycloisomerization

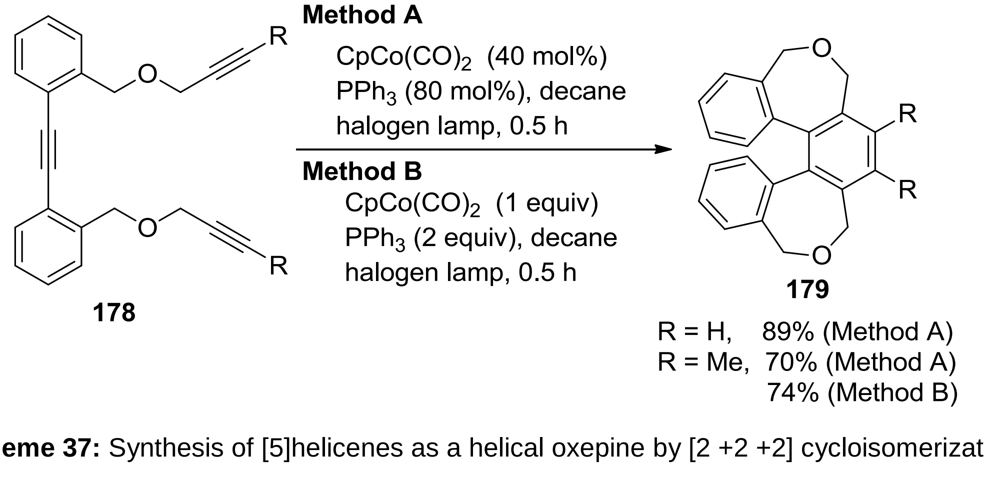
The synthesis of tetrahydro[5]helicene begins with the dibromide **172**, the displacement of bromine with $LiCH_2C{\equiv}CTMS$ (generated *in situ* by $CH_3C{\equiv}CTMS$ and *n*-butyllitium) proceeded smoothly to build up a triyne framework, with partially desilated terminal alkyne units. The reaction mixture was quickly treated with an excess of *n*-BuNF this procedure gave an unprotected triyne **173**. The reaction of triyne with the catalyst $CpCo(CO)_2$, $PPh_3$, in decane at 140 °C and irradiation of the reaction mixture under halogen lamp gave tetrahydro[5]helicene **174**.



**Scheme 36:** Synthesis of 1,14-diaza[5]helicene **9** by [2 + 2 + 2] cycloisomerization

Using similar methodology the authors have also synthesized a 1,14-diaza[5]helicene [**Scheme-36**]. Furthermore, $Ni(cod)_2$- based catalytic system is found more active, allowing the cyclotrimerization at ambient temperature to obtain tetrahydro[5]helicene **174**. Finally treatement with DDQ in benzene at 100 °C gave the product [5]helicene **3**. Using this methodology the authors also synthesized tetrahydro[6]helicene and tetrahydro[7]helicene.

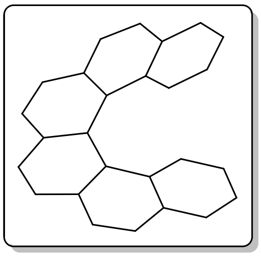
### **Approach 3h: 2) *Synthesis of pentacyclic helicene 179 as 1,3,6,8-tetrahydrobenzo[c]-benzo-[5',6']oxepino[3',4':5,6]benzo[e]oxepin / 4,5-dimethyl-1,3,6,8-tetrahydro-benzo[c]-benzo[5',6']-oxepino[3',4':5,6]benzo[e]oxepin by the metal catalysed [2+2+2] cyclizations:***



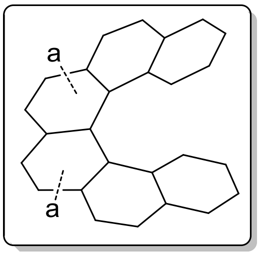
**Scheme 37:** Synthesis of [5]helicenes as a helical oxepine by [2 +2 +2] cycloisomerization

A novel strategy for the [2 + 2 + 2] cycloisomerization by Co/Ni catalyst for the synthesis of helicenes was proposed by Stray, Stara and co-workers. In 1998 Stary and group first proposed the methodology for the preparation of helicene like molecule **179**.[65,66] Upon treatment with catalytic amount of $CpCo(CO)_2/PPh_3$ as well as stoichiometric amount in *n*-decane and simultaneous irradiation at 140 °C, triynes with terminal or methylsubstituted acetylenes moieties afforded cleanly the product such as helicenes or helicene like molecules such as 1,3,6,8-tetrahydrobenzo[*c*]benzo[5',6']oxepino- [3',4':5,6]benzo[*e*]oxepin and 4,5-dimethyl-1,3,6,8-tetrahydrobenzo[*c*]benzo[5',6']-oxepino[3',4':5,6]benzo[*e*]oxepin **179** [**Scheme-37**]. After the success of methodology further synthesis of [6] and [7]helicene or [7]helicene like molecules was explored by this methodology.[67]

4) **Synthesis of [6]Helicene/hexahelicene and its different synthetic methodologies.**

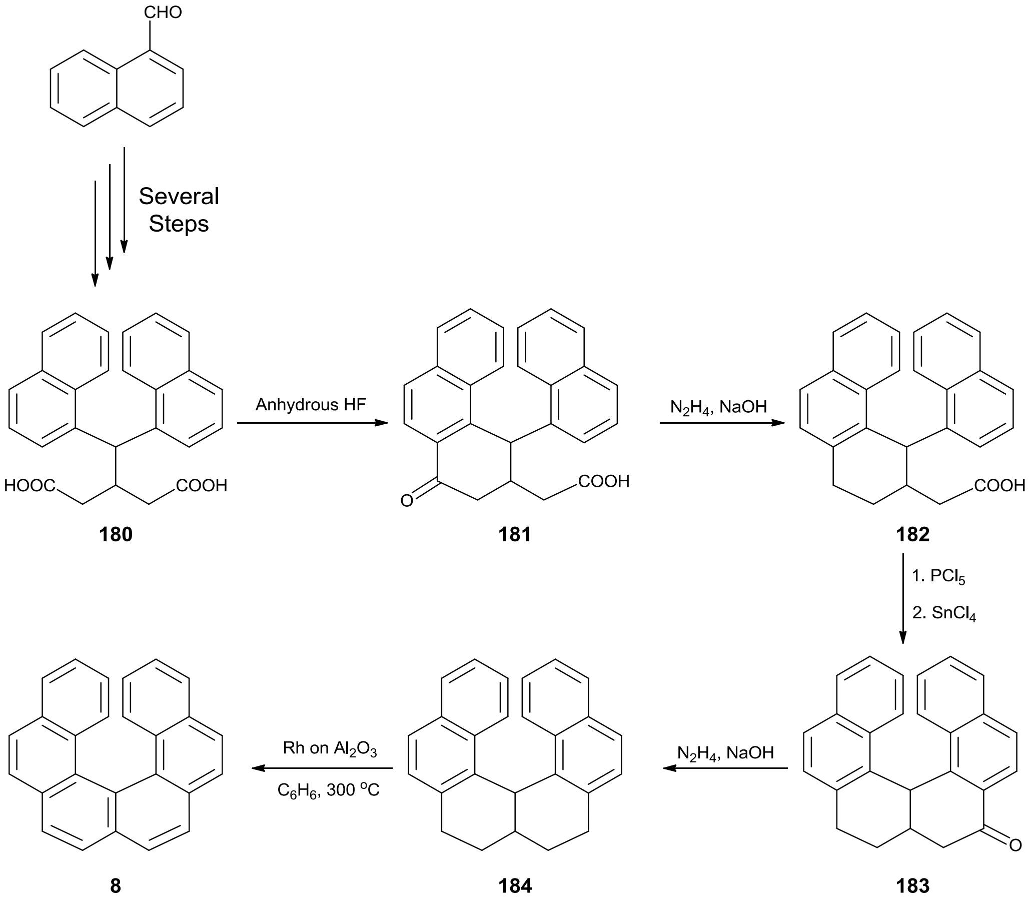


**Different approaches for the synthsis of [6]helicene**



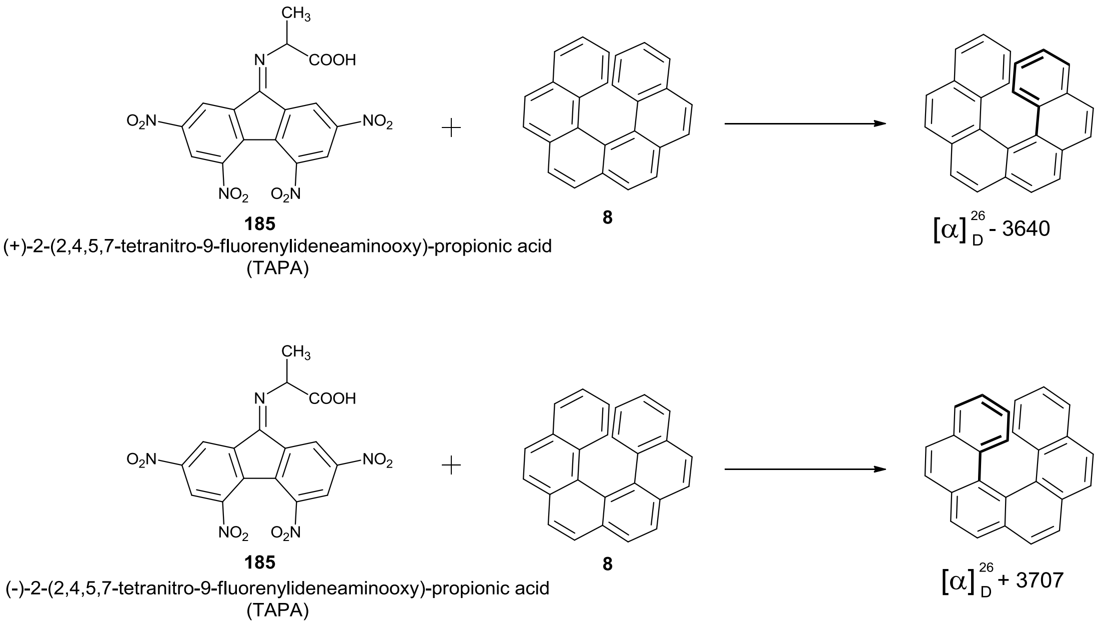
**Approach 4a. 1)** ***Synthesis of [6]Helicene OR Hexahelicene 8:***

The classical synthesis of hexahelicene,[4a,c] introduce by Newman in 1956, begins with 1-naphthaldehyde and its reaction with diethyl malonate and piperidine in refluxing benzene to form diethyl 1-naphthylmethylenemalonate. The addition of 1-naphtylmagnesium bromide to diethyl-1-naphtylmethylenemalonate formed diethyl-1-dinaphtylmalonate, the product was reduced to the corresponding diol by $LiAlH_4$ reduction. After mesitylation of the diol with mesityl chloride and pyridine the corresponding mesityl derivative was directely converted to the dicyno/dinitrile derivative. The dinitrile converted directly to the diacid by hydrolysis with NaOH in ethylene glycol to obtain 3-[di-(1-naphthyl)methyl]glutaric acid **180**. The diglutaric acid was cyclised by Friedel-Craft acylation using anhydrous hydrogen fluoride to form the product 1,2,3,4-tetrahydro-4-(l-naphthyl)-l-oxo-3-phenanthreneacetic acid **181**.



**Scheme 38:** The first synthesis of [6]helicene **8**

The keto group was reduced by Huang-Minlon procedure (hydrazine and sodium hydroxide) to obtain 1,2,3,4-tetrahydro-4-(1-naphthyl)-3-phenanthreneacetic acid **182**. The monoacid product 1,2,3,4-tetrahydro-4-(1-naphthyl)-3-phenanthreneacetic acid was cyclised by using phosphorous pentachloride and subsequent Friedel-Crafts acylation to form the cyclised keto product 7,8,8a,9,10,16c-hexahydro-7-oxo[6]helicene **183** which on reduction with hydrazine and sodium hydroxide formed completely cyclised product. The cyclised product 7,8,8a,16c-tetrahydro[6]helicene **184** was aromatized on treatment with Rh/alumina at high temperature to form completely aromatized polycyclic hydrocarbon (PAH) as hexahelicene or [6]helicene **8**.

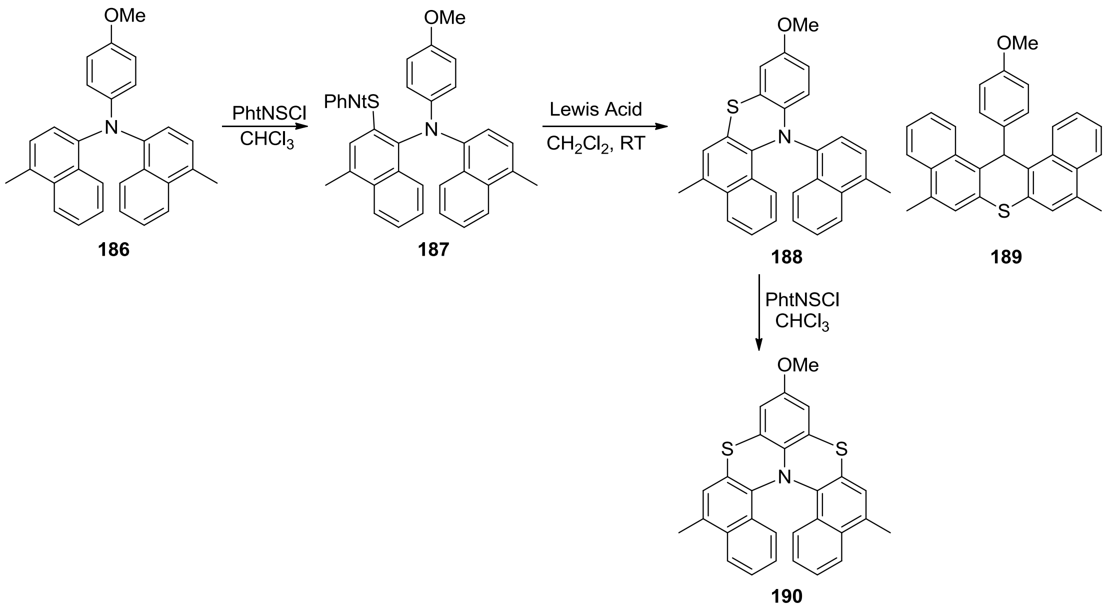


**Scheme 39:** Resolution of [6]helicene **8** using TAPA **185**

The resolution of the isomers of Hexahelicene[4a] using the chiral resolving agent, 2-(2,4,5,7-tetranitro -9-fluorenylideneaminooxy)-propionic acid (TAPA) **185** was achived. The solution of hexahelicene **8** and (-)-TAPA **185** was refluxed in benzene and after cooling ethanol was added to the solution to give yellow coloured plates. The yellow plates after several recrystallisation gave enantiomerically pure product (-)-hexahelicene, and the corresponding second enentiomer (+)-hexahelicene obtained from the (+)-TAPA and racemic hexahelicene. Thus the synthesis of chirally pure [6]helicene **8** by Newman still remains one of the landmarks in the synthesis of chiral helicenes, even after over half a century.

### Scheme 4a: 2) *Synthesis of thia-bridged Triarylamine heterohelicenes/ [6]helicene:*

Menichetti and co-workers introduced the synthesis of thia-bridged aza hetero[6]helicene **190**.[68] In this synthesis the monosulfenylation of amine with phthalimidesulfenyl chloride formed by the chemoselective and regioselective sulfenamide product. The monosulfenamide product was cyclised with an excess of $BF_3$•$Et_2O$ to the expected –thiazine products such as 9-methoxy-5-methyl-12-(4-methylnaphthalen-1-yl)-12*H*-benzo[*a*]phenothiazine **188** and 14-(4-methoxyphenyl)-5,9-dimethyl-14*H*-dibenzo[*a,j*]phenothiazine **189** in a (10:1) ratio respectively.

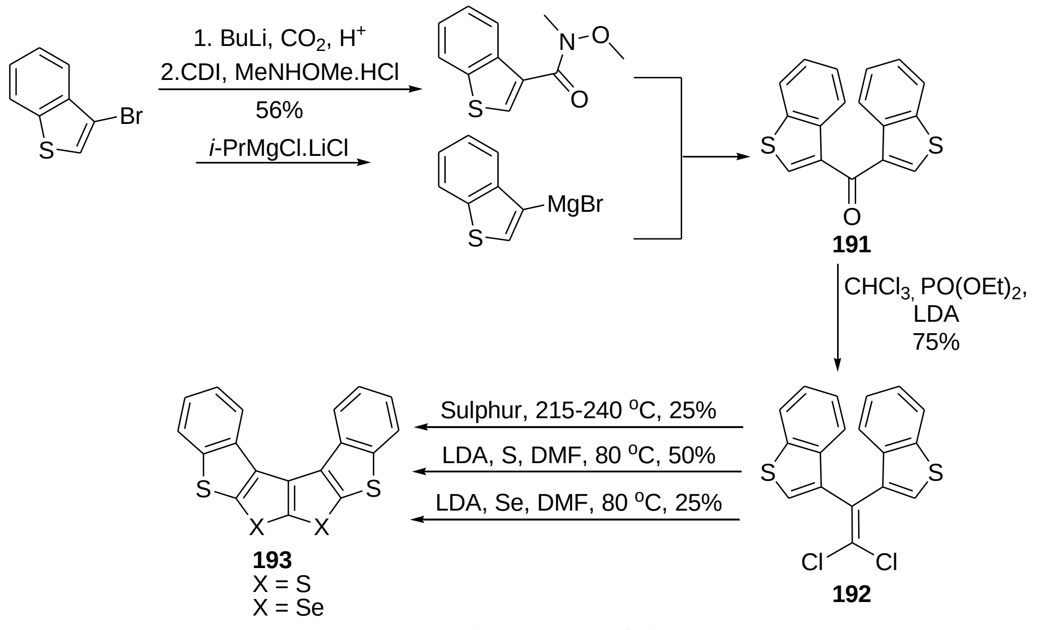


**Scheme 40:** Synthesis of aza-thia[6]helicene **190**

The major isomer 9-methoxy-5-methyl-12-(4-methylnaphthalen-1-yl)-12*H*-benzo[*a*]phenothiazine **188** reacts with phthalimidesulfenyl chloride under the above-described conditions, and thereby undergoes sulfenylation followed by a spontaneous intramolecular proton-mediated cyclization, to afford hetero[6]helicene **190** [**Scheme-40**].

### Approach 4a: 3) *Synthesis of Tetrathia[6]helicene 193:*

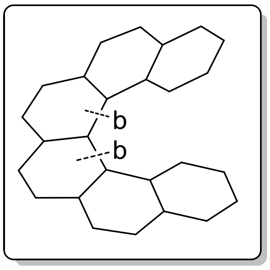
Recently, Nenajdenko and co-workers have reported two new strategies for the synthesis of thiaheterohelicenes.[69]



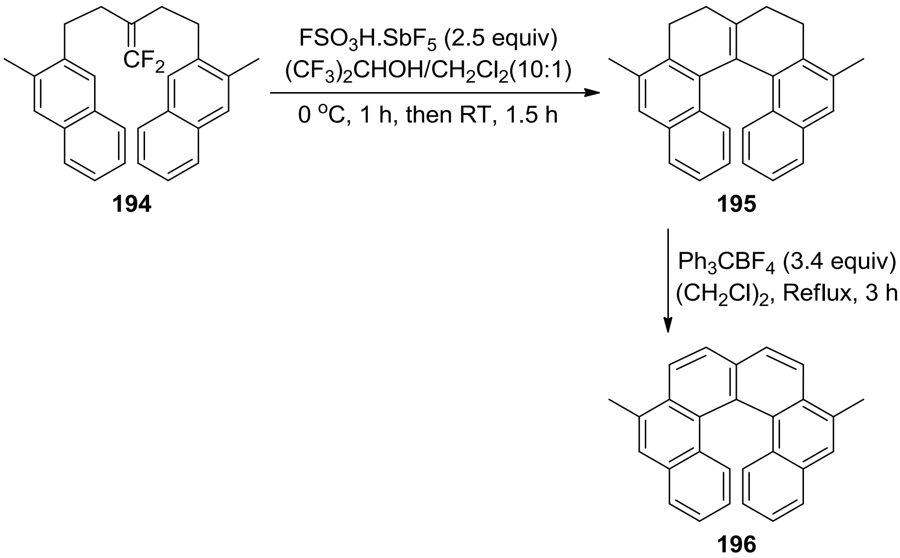
**Scheme 41:** Synthesis of tetrathia[6]helicenes **193**

Reaction of the bromothiophene with LDA and sulfur followed by treatment with $CH_2Br_2$ afforded thioether. After formylation with carbamate, 10*H*-bisthienodithiocin-10-one was obtained. Subsequent cyclization took place by deprotonation followed by reaction with $BF_3 \cdot Et_2O$ [**Scheme-41**]. In other strategy, ketone, synthesized by reaction between the carboxamide and the Grignard reagent, was converted into dichloroethene **192** by a phosphorus ylide. Heterohelicenes **193** were then obtained under different condition.

**Approach 4b: 1)** ***Synthesis of 6,11-Dimethylhexahelicene 196:***



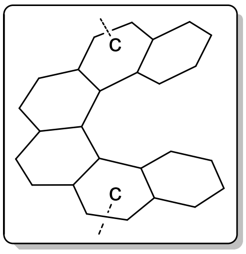
Ichikawa and co-worker introduced another Friedel-Crafts cyclization reaction based approach for the synthesis of helicenes in 2008.[47] In this synthesis the Friedel-Crafts cyclization occurred *via* a α,α-diflurocarbocation, for which the starting material 1,1-difluoro-1-alkenes as 1,1-difluoro-4-(3-methyl-2-naphthyl)-2-[2-(3-methyl-2-naphthyl)ethyl]but-1-ene **194** was synthesized from 2,2,2-trifluoroethyl 4-methylbenzenesulfonate and 2-methyl-3-vinylnaphthalene using sodium methoxide, *n*-butyllithium, tris[2-(3-methyl-2-naphthyl)ethyl]borane [borane–THF complex] and bromine at -78 °C.



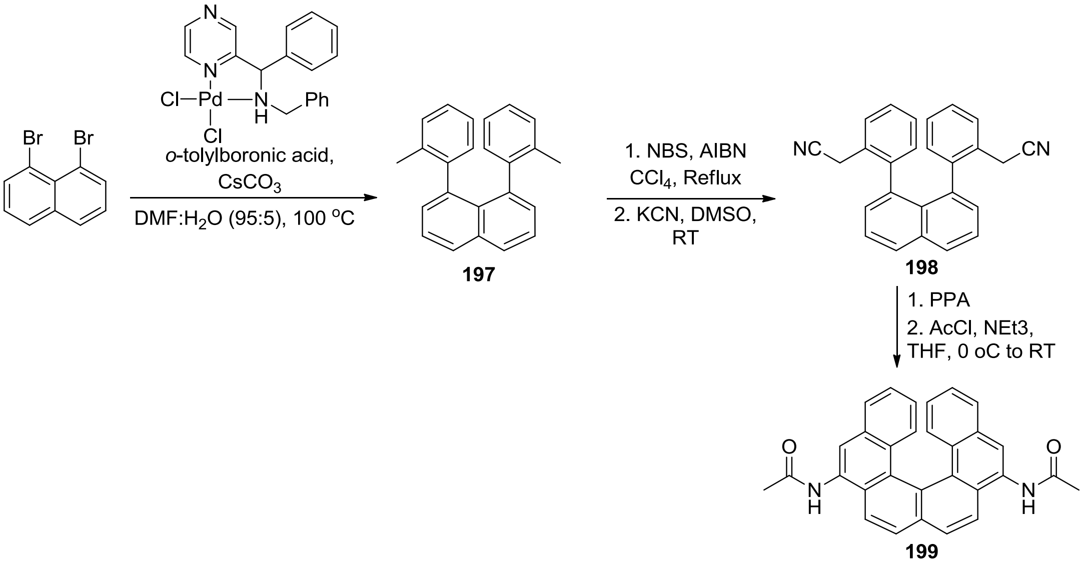
**Scheme 42:** Synthesis of 6,11-dimethyl[6]helicene **196**

The domino Friedel-Crafts type cyclization of 1,1-difluoro-4-(3-methyl-2-naphthyl)-2-[2-(3-methyl-2-naphthyl)ethyl]but-1-ene **194** using $FSO_3H{\bullet}SbF_5$ in 1,1,1,3,3,3-hexafluoropropan-2-ol to form the cyclised product 6,11-dimethyl-7,8,9,10-tetrahydrohexahelicene **195** and its dehydrogenation proceeded efficiently, gave 6,11-dimethyl[6]helicene **196** in good yield.

**Approach 4c: 1)** ***Synthesis of 6,11-diacetamido [6]Helicene 199:***



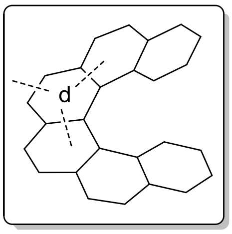
Recently, Gaucher and co-workers reported the synthesis of 6,11-diamino-[6]helicene **199**,[70] starting from the 1,8-dibromonaphthalene *via* Suzuki-Miyaura coupling with *o*-tolylboronic acid giving intermediate product 1,8-di(*o*-tolyl)naphthalene **197**. After the side chain bromination of 1,8-di(*o*-tolyl)naphthalene using N-bromosuccinimide and AIBN, the brominated product was converted to 1,8-di(2-cyanomethylphenyl)naphthalene **198** using potassium cyanide at room temperature.



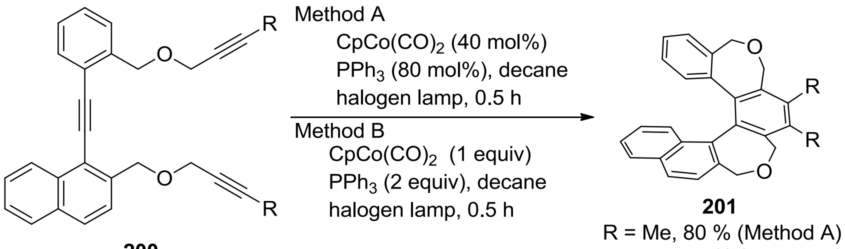
**Scheme 43:** Synthesis of 6,11-diamino-[6]helicene **251**

The dinitrile was cyclized with polyphosphoric acid to form 6,11-diamino-[6]Helicene which was converted *in situ* to 6,11-diacetamido-[6]-helicene **199** using acetyl chloride and triethylamine in tetrahydrofuran. Subsequently the authors also synthesized 3,14-dimethoxy-6,11-diacetamido[6]helicene by same strategy.

**Approach 4d: 1) *Synthesis of [6]helicene such as 4,5-Dimethyl-1,3,6,8 tetrahydrobenzo-[c]naphtho[1'',2'':5',6']oxepino[3',4':5,6]benzo[e]oxepin 201 by the metal catalysed [2 + 2 + 2] cyclizations:***



On successful synthesis of [5]helicene, Stary, Stara and group extended the strategy to [6]helicene and similar molecule 4,5-dimethyl-1,3,6,8 tetrahydrobenzo[*c*]naphtho[1'',2'':5',6']oxepino[3',4':5,6]benzo[*e*]oxepin[65a,66] by the novel strategy for the [2 + 2 + 2] cycloisomerization using Co/Ni catalyst.



**200**

**201**

**Scheme 44:** Synthesis of [6]helicene as a helical oxepine **201**

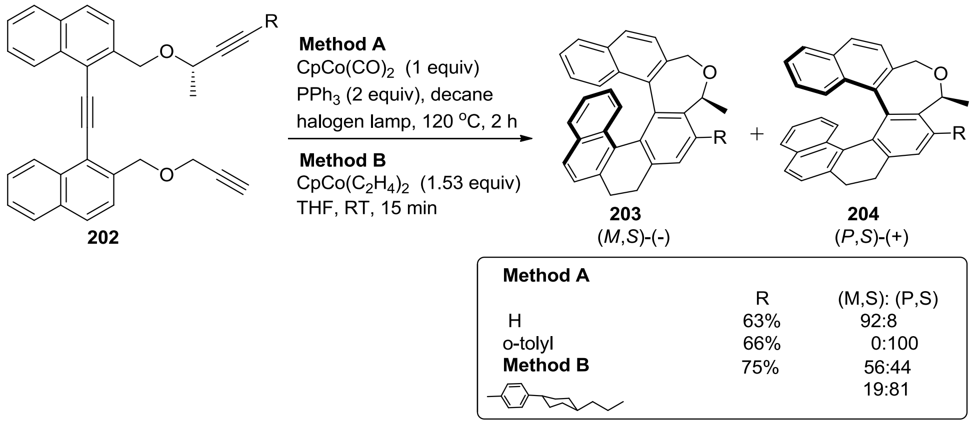
Treatment of the triene, with terminal or methylsubstituted acetylenes moieties, with catalyst system $CpCo(CO)_2/PPh_3$ and simultaneous irradiation at 140 °C, afforded the product such as [6]helicene **201** or its derivatives [**Scheme-44**].

## *Asymmetric synthesis of Helicenes or Helicene like molecules:*

Since the helical molecules posses unique chirality due to its helical shape many applications are envisaged for these isomers if available in chirally pure form. Hence asymmetric synthesis of helical compounds is a critical area, many methods are reported in this direction.

*Synthesis of (M,1S)-(-)-1-Methyl-1,3,16,17-tetrahydrobenzo[5,6]phenanthro-[3,4-c]naphtho[1,2-e]oxepine **203** and (P,1S)-1-Methyl-1,3,16,17-tetrahydrobenzo[5,6]-phenanthro-[3,4-c]-naphtho[1,2-e]oxepine **204** by cycloisomerisation methodology:*

Stary, Stara and coworkers reported an eligant helicity-controlled strategy for the asymmetric synthesis of [7]helicene-like molecules **203** and **204**.[71] As shown in [**Scheme-45**], an asymmetric $sp^3$ carbon is present in the triyne **202**.



| **Method A** | R | (M,S): (P,S) |
|---|---|---|
| H | 63% | 92:8 |
| o-tolyl | 66% | 0:100 |
| **Method B** | 75% | 56:44 |
| | | 19:81 |

**Scheme 45:** Synthesis of diastereomeric [7]helicene as helical oxepine **203** and **204** by [2 + 2 + 2] cycloisomerization methodology

During cyclization under catalysis of CpCo(CO)$_2$/PPh$_3$, the stereogenic chirality was transferred to helical chirality. Interestingly, the functional group R had a marked impact on the diastereoselectivity: when R = H, (*M*, *S*)- was the major isomer (with a diasteromeric ratio of 92:8), while the diastereoselectivity was reversed and became higher for R = o-tolyl. For CpCo(C$_2$H$_4$)$_2$-mediated cycloisomerization at room temperature with considerable loss of diastereoselectivity. However, the diastereoselectivity could be enhanced by raising the temperature, indicating that a thermodynamic-controlled process was involved.

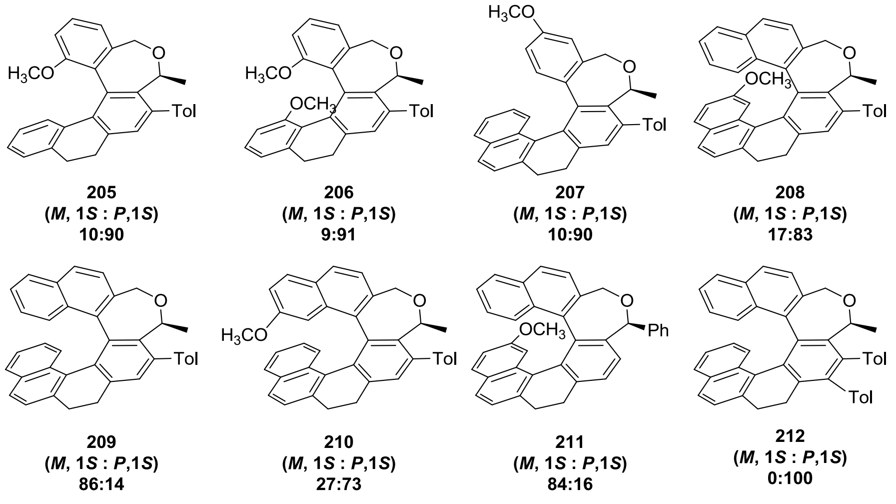
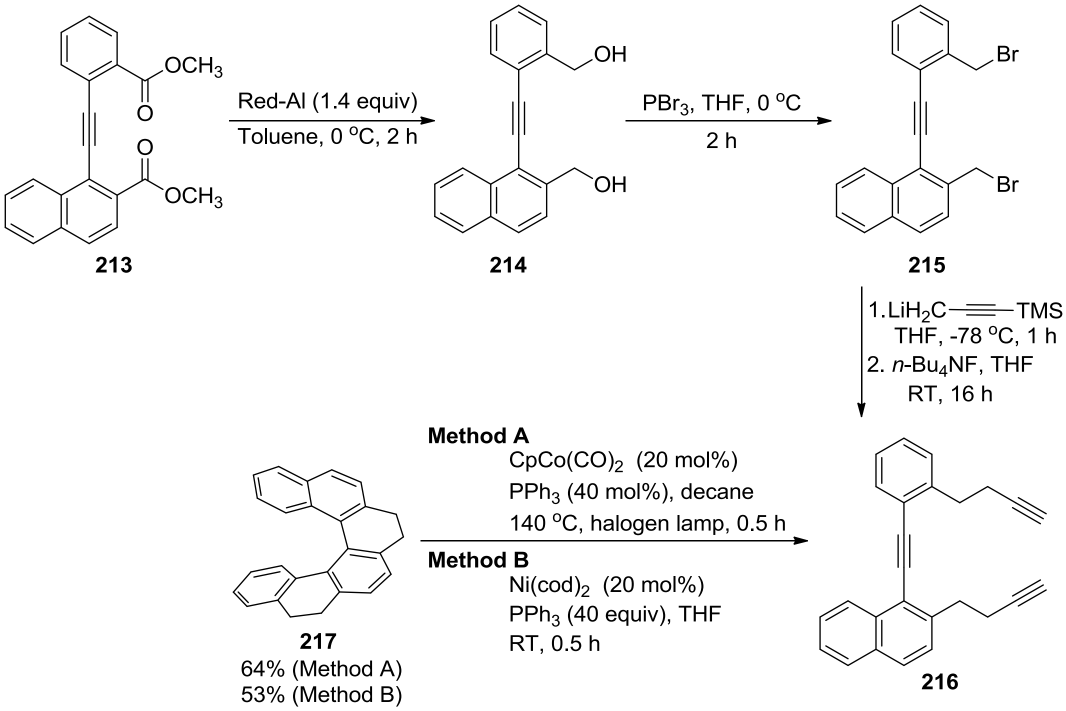


**Figure 13:** Different diastereomeric Helical oxepine synthesized by [2 + 2 + 2] cycloisomerization methodology

### Approach 4d: 2) *Synthesis of tetrahydro[6]helicenes 217 by the metal catalysed [2 + 2 + 2]cycloisomerization:*

Stara, Stary and co-workers have synthesized the [5]helicene by the [2 + 2 +2] cyclotrimerization by metal catalysed methodology using Co(I) and Ni(I) catalysis.[65b] Using a similar methodology tetrahydro[6]helicene was synthesized from the corresponding diester. The diester reduction was carried out with Red-Al® to diol and the diol was converted to dibromide using phosphorous dibromide. Displacement of bromine with $LiCH_2C\equiv CTMS$ (generated *in situ* by $CH_3C\equiv CTMS$ and *n*-butyllitium) proceeded smoothly to build up a triyne framework. The reaction mixture was quickly treated with an excess of *n*-$Bu_4NF$ to obtain the unprotected triyne **216**.

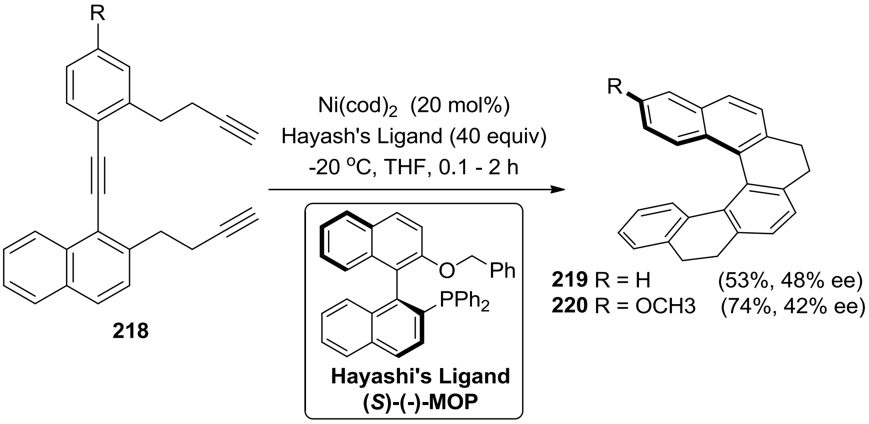


**Scheme 46:** Synthesis of tetrahydro[6]helicene **217** by [2 + 2 + 2] cycloisomerization methodology

The reaction of triyne with the catalyst $CpCo(CO)_2$ and irradiate the reaction mixture using halogen lamp obtained the tetrahydro[6]helicene **217** in good yield. The second method with the $Ni(cod)_2$- and the chiral phosphine ligand *S*-(-)-MOP in tetrahydrofuran at room temperature was found effective for the chiral induction in the synthesis of chiral tetrahydro[6]helicene with 43% *ee*.

### Approach 4d: 3) *Asymmetric synthesis of tetrahydro[6]helicenes by the metal catalysed [2 + 2 + 2]cycloisomerization:*

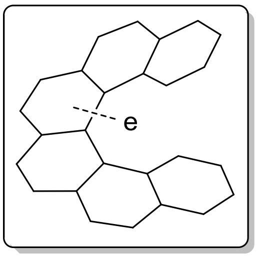
Stary, Stara and co-workers first disclosed[65a,e,71a] the asymmetric synthesis of tetrahydrohelicene using a Ni(0) catalyst with Hayashi's ligand[72] [**Scheme-47**]. The routine cycloisomerization by metal and chiral ligand found that the helicity of (+)-tetrahydro[6]helicene **219** and **220** was successfully controlled by asymmetric [2 + 2 + 2] cycloisomerization.



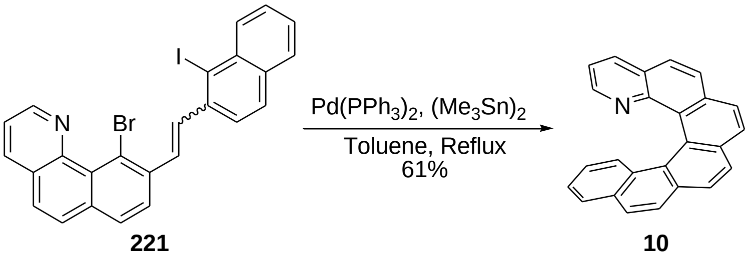
**Scheme 47:** Synthesis of enantioenriched tetrahydro[6]helicenes **219** and **220** by [2 + 2 + 2] cycloisomerization methodology

This one-step, efficient route made the enantioenriched precursors of the helicenes easily accessible in moderate yields and good selectivity of 42-48% ee.

### Approach 4e: 1) *Synthesis of 1-aza[6]helicene 10 its derivatives and converted it to N-oxides:*

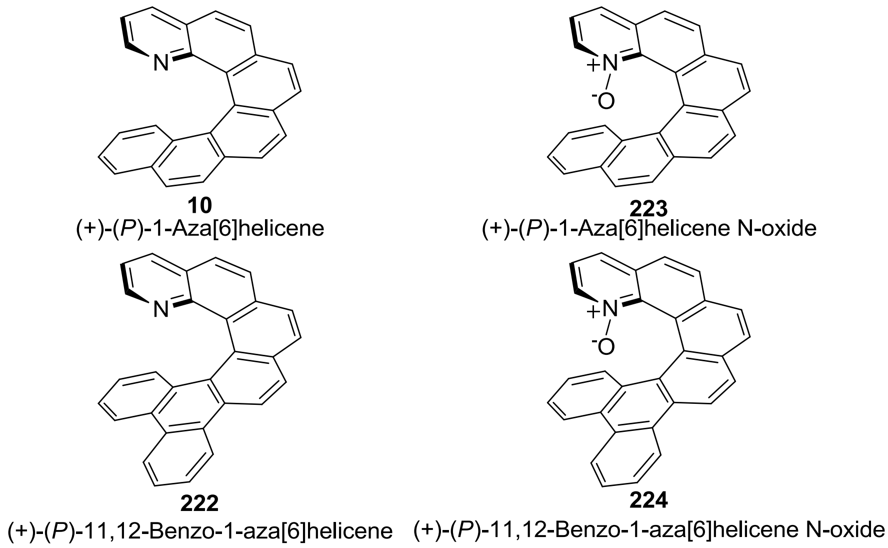


Takenaka and co-workers reported[73] the formation of 1-aza[6]helicene **10** and its derivatives by innovative metal mediated intramolecular coupling reaction. The starting material 221 with two aryl halides was synthesized in a highly *Z*-selective Wittig olefination and was subjected to palladium catalysed Stille-Kelly coupling reaction[74] for the cyclization.



**Scheme 48:** Synthesis of 1-aza[6]helicene **10** by Stille-Kelly coupling

Similarly the synthesis of azahelicene was also based on the *Z*-selective Wittig reaction beween (2-bromo-4-methylbenzyl)triphenylphosphonium bromide and 2-bromo-3-pyridinecarboxaldehyde.


**10**
(+)-(*P*)-1-Aza[6]helicene

**223**
(+)-(*P*)-1-Aza[6]helicene N-oxide

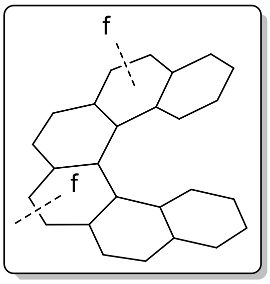
**222**
(+)-(*P*)-11,12-Benzo-1-aza[6]helicene

**224**
(+)-(*P*)-11,12-Benzo-1-aza[6]helicene N-oxide

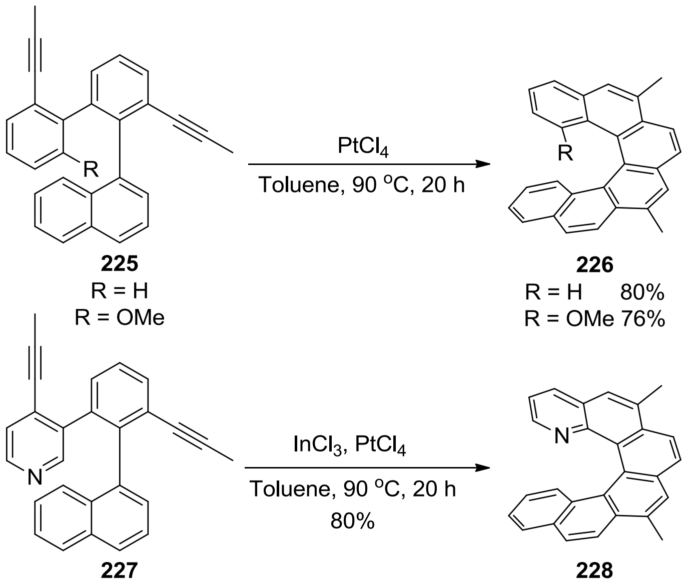
**Figure 14:** Azahelicenes and its helical N-oxide derivatives

The product (*Z*)-2-bromo-3-(2-bromo-4-methylstyryl)pyridine **221**, was then subjected to the Stille-Kelly coupling conditions. Further side chain bromination and Nef reaction gave benzoquinoline carbaldehyde. A second set of *Z*-selective Wittig olefination of ((1-iodonaphthalen-2-yl)methyl)triphenylphosphonium bromide and carbaldehyde in DMF gave the desired helicene precursor. The Stille-Kelly coupling reaction[74] on this afforded the final product 1-aza[6]helicene **10**. The 1-aza[6]helicene **10** and its derivative **222** were separated in their optically pure form by using preparative chiral HPLC. And the optically active helicene were converted to (+)-(*P*)-1-aza[6]helicene *N*-oxide **223** and its derivative **224** by using suitable per acid. These chiral helical *N*-oxides were screened as ligand in desymmetrization of *meso* epoxides.

**Approach 4f: 1)** ***Synthesis of 6,10-dimethylhexahelicene, 1-methoxy-6,10-dimethylhexahelicene 226 and 1-aza-6,10-dimethylhexahelicene 228 by double cycloisomerization of triyene:***



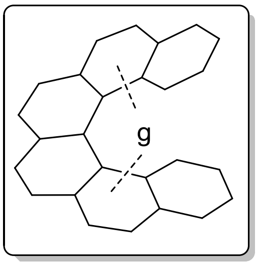
In 2009, Storch and co-workers introduced the strategy for the synthesis of hexahelicene in good yields by double [2 + 2 + 2] cycloisomerization of biphenylyl-naphthtalenes.[75]



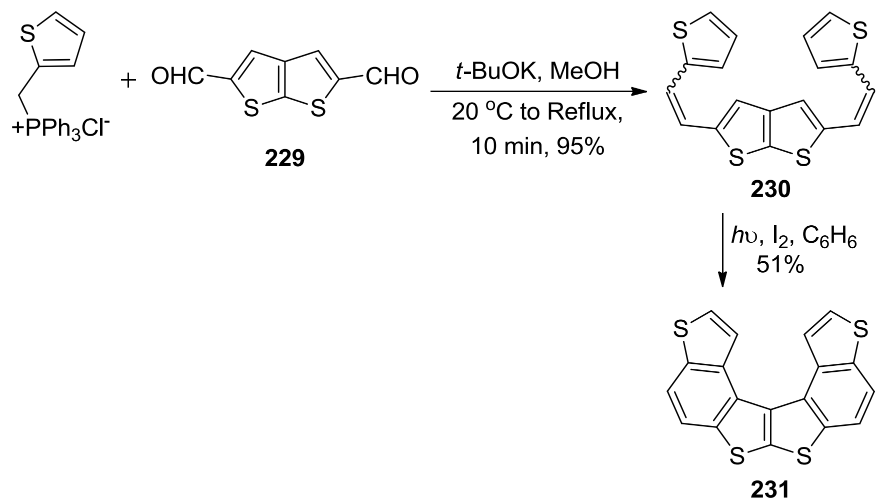
**Scheme 50:** Synthesis of [6]helicene and aza[6]helicene by [2 + 2 + 2] by cycloisomerization

The corresponding building blocks **225** and **227** were easily prepared by the Sonagashira and Suzuki reactions starting from 1-bromo-2-iodobenzene and 2-bromo-1-iodo-3-methoxybenzene and converted into the corresponding boronic acids. The palladium catalysed Suzuki reaction of the corresponding boronic acids with 2-(naphthalen-1-yl)-3-(propyn-1-yl)phenyl trifluoromethane-sulfonate to obtain 3,6′-di(propyn-1-yl)biphenyl-2-yl)naphthalene and 1-(2′-methoxy-3,6′-di(propyn-1-yl)biphenyl-2-yl)naphthalene **225**. The double cycloisomerisation of the corresponding binaphthalene using catalytic amount of platinum chloride in toluene at reflux to obtain the desired products 6,10-dimethyl[6]helicene and 1-methoxy-6,10-dimethyl[6]helicene **226** in 80% and 76% yields respectively. Subsequently, in 2010 the same group also synthesized 1-aza-6,10-dimethyl[6]helicene **228** from the corresponding starting material 5-(2-(propyn-1-yl)-6-(4-(propyn-1-yl)pyridin-3-yl)phenyl)-isoquinoline **227**. The useful methodology was further developed using other catalysts such as $PtCl_2$ and $InCl_2$ for this reaction.

### **Approach 4g: 1)** ***Synthesis of Dithieno[3,2-e:3',2'-e'][l]benzothieno[2,3-b][l]benzothiophene/ 3,6,7,10-tetrathio[6]helicene 231 by photocyclodehydrogenation methodology:***



Wynberg and co-workers reported the double photocyclization methodology for the construction of thiahelicenes.[5c,i] The Wittig olefination of thieno[2,3-*b*]thiophene-2,5-dicarboxaldehyde and the Wittig salt 2-triphenyl- phosphoniomethyl-thiophene bromide in the presence of potassium *tert*-butoxide in methanol a precursor 2,5-di[*β*-(2-thienyl)vinyl]thieno[2,3-*b*]thiophene **230** of helicene was obtained.

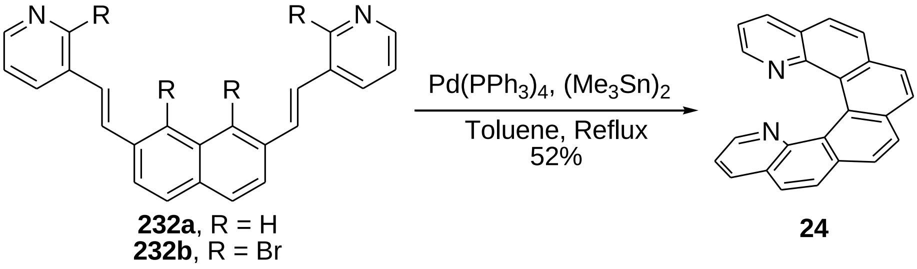


**Scheme 51:** Synthesis of 3,6,7,10-tetrathio[6]helicene **231**

The photocyclisation of the 2,5-di[*β*-(2-thienyl)vinyl]thieno[2,3-*b*]thiophene **230** in presence of catalytic amount of iodine gave the product 3,6,7,10-tetrathio[6]helicene **231**.

**Approach 4g: 2)** ***Synthesis of 1,16-diaza[6]helicene:***

Staab and co-workers reported the synthesis of 1,16-diaza[6]helicene by using the double Stille-Kelly coupling.[28] The synthesis was initially studied with photocyclodehydrogenation of **232a**, however the product 24 was obtained in poor yield (1.7%).

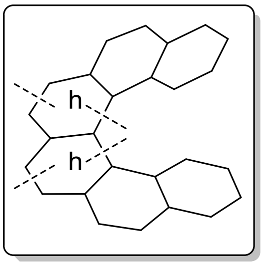


**Scheme 52:** Synthesis of 1,16-diaza[6]helicene by double Stille-Kelly coupling

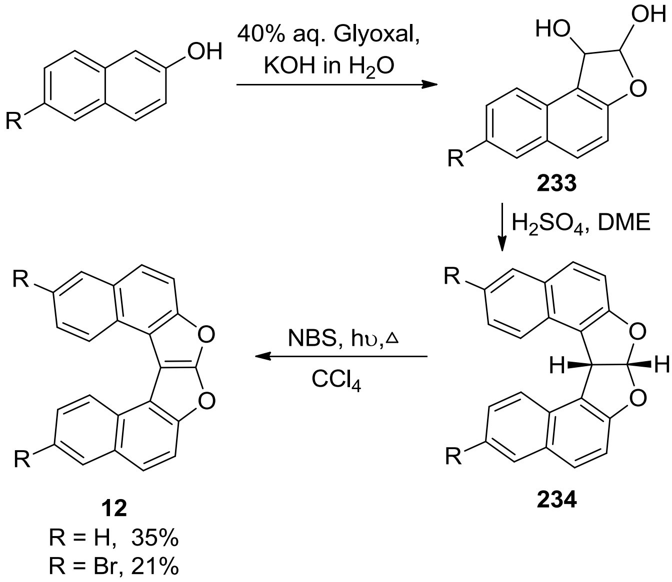
Thereafter the authors synthesized the desired compound by intramolecular cyclization of 1,8-dibromo-2,7-bis[2-(2-bromo-3-pyridyl)vinyl]naphthalene **232b** obtained from the Wittig olefination reaction of 2-bromo-3-carbaldehyde with 1,8-

dibromo-2,7-bis(triphenylphosphoniomethyl)naphthalene dibromide. The 1,8-dibromo-2,7-bis[2-(2-bromo-3-pyridyl)vinyl]naphthalene **232b** was converted to 1,16-diaza[6]helicene **24** by its reaction in presence of tetrakis(triphenylphosphine)-palladium and hexamethyldistanane [**Scheme-52**]. The structural aspects and proton sponge properties of this molecule were investigated and found that the molecule does not show the latter even in the highly acidic condition due to the sterically crowded helical structure of the compound.

### Approach 4h: 1) *Synthesis of 7,8-dioxa[6]helicene 12 OR Naphtho[2,1-b]naphtha-[1',2':4,5]furo[3,2-d]furan and its bromo derivative:*



Bechgaard and co-workers have synthesized 7,8-dioxa[6]helicene **12** by dehydrogenation of *cis*-7a,14c-dihydro-7,8-dioxa[6]helicenes **234** in the presence of NBS under illumination of sunlight.[18i] The total sequence is presented below.

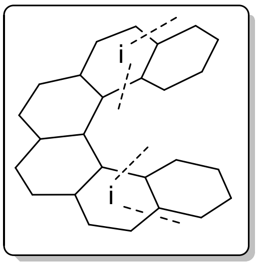


**Scheme 53:** Synthesis of 7,8-dioxa[6]helicene **12** and it's bromo derivative

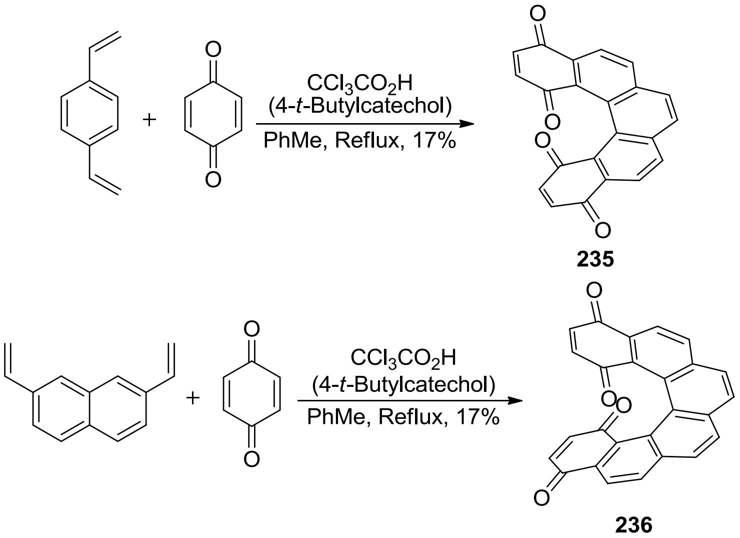
The suitably substituted naphthol was converted to 1,2-dihydronaphtho[2,3-*b*]furan-1,2-diol **233** using glyoxal in basic condition to obtain the mixture of naphthol and the product. Which was dissolved in DME and was converted to *cis*-7a,14c-dihydro-7,8-dioxa[6]helicenes **234** on acidification. After the treatment with NBS and irradiated with UV light to get the 7,8-dioxa-[6]helicene **12**. Subsequently

3,12dibromo-7,8-dioxa[6]helicene(3,12-dibromo-naphtho[2,1-*b*]naphtho[1,,2,:4,5]-furo[3,2,*d*]furan) was synthesized from the 6-bromo-2-napthtol. The geometry and steric factors of these compounds were studied by its single crystal X-ray diffraction analysis.

### Approach 4i: 1) *Synthesis of [5]helicenebisquinone 235 and [6]helicenebisquinone 236:*



In 1990, Katz and Liu had reported the first synthesis of [5]helicenebisquinone in multi gram quantity and reported its resolution by the enzymatic hydrolysis to access the optically active quinine.[30,76]



**Scheme 54:** Synthesis of [5], [6]helicenebisquinones by Diels-Alder approach

The 1,4-divinylbenzene, benzoquone (12 eq.), with a crystal of trichloroacetic acid and 4-*t*-butylcatechol in toluene was refluxed to obtain the [5]helicenebenzoquinone **235 [Scheme-54]**. The [5]helicenebenzoquinone was acetylated with acetic anhydride and then hydrolysed using pancreas extract and 40% sodium taurocholate (an emulsifier) in water-ether system to obtain an optically active [5]helicenebenzoquinone **237** and **238** with very high specific optical rotation values.

Similar methodology was also employed for the synthesis of [6]helicene from the 2,7-divinyl naphthalene and benzoquinone.[30] Also a number of higher members of carbohelicenes and heterohelicene were synthesized using the same method. Another method was developed for the synthesis of helicenes, in which a basic alumina is used in place of trichloroacetic acid with dramatic increase in the efficiency.

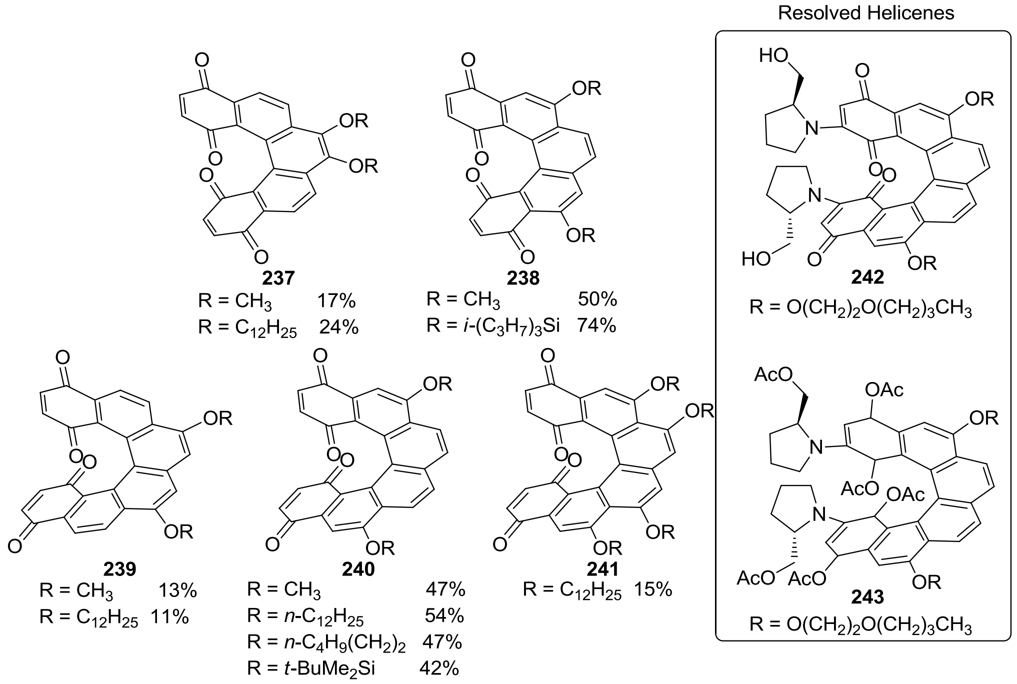
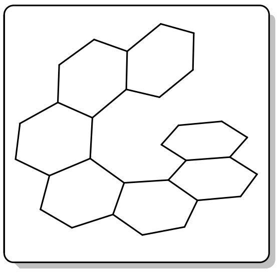


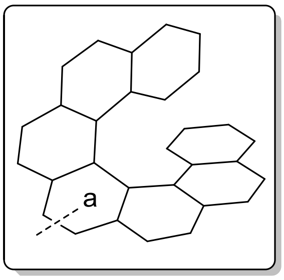
**Figure 15:** Various [5], [6]helicenebisquinones and its diastereomers

As catalyst, alumina is more efficient than trichloroacetic acid for the synthesis of helicenebenzoquinones. The isomers of [6]helicenequinone were resolved by the action with (*S*)-(-)-prolinol in presence of copper acetate monohydrate in the mixture of chloform:methanol to obtain the diastereomers **242** and **243**. These were further purified by column chromatography and after oxidation final enantionmerically pure [6]helicenebisquinone is obtained.

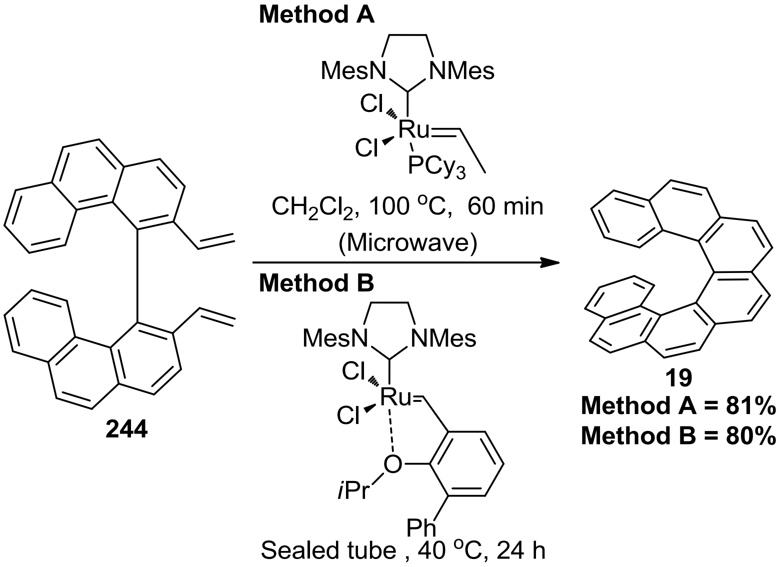
### *5) Synthesis of [7]Helicene and its different synthetic methodologies.*



### Approach 5a: 1) *Synthesis of [7]helicenes 19 by using ring closing olefin metathesis:*



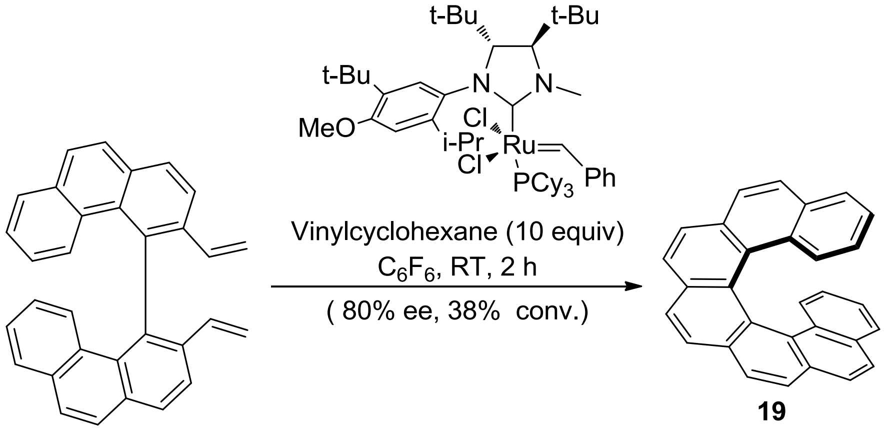
In 2006, Collins and co-workers reported the synthesis of helicenes and its derivatives in good yields by the ring closing olefin metathesis methodology.[57] The authors developed two different methodologies, Method A and Method B for the synthesis of helicenes and its derivatives. Using these methodologies synthesis of [7]helicene **19** was achieved in good yields.



**Scheme 55:** Synthesis of [7]helicene by ring closing metathesis

The method A is very fast as it requires a short time and higher temperature in microwave to obtain [7]helicene in a good yield (80%). The method B occurs under milder condition but requires longer time, quite similar to the process discussed in Scheme-26.

Similalry the authors have synthesized the enantiomerically enriched [7]helicene **19** using ring closing olefin methodology with chiral catalysts for the methathesis reaction.[77]



**244**

**19**

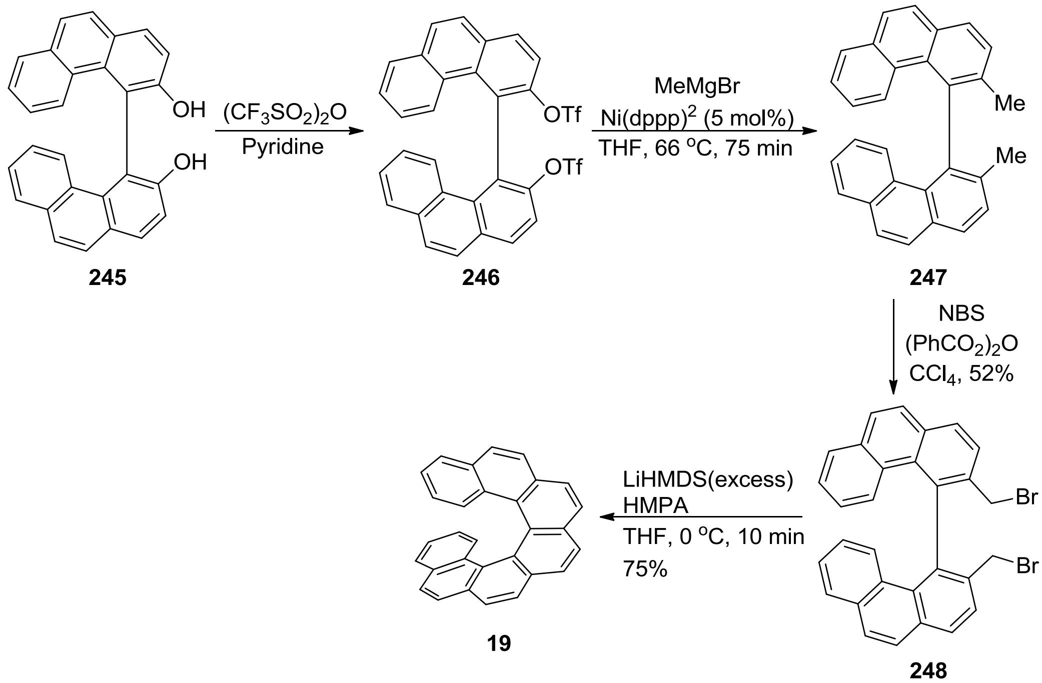
M-(-)-[7]helicene

**Scheme 56:** Synthesis of enantioenriched [7]helicene by ring closing metathesis

## Approach 5a: 2) *Synthesis of [7]helicene by metal induced carbenoid coupling reaction and McMurry coupling reaction:*

### Carbenoid Coupling Reaction:

In 1998, Gingras and Dubois have reported the synthesis of [5]helicene involving metal catalysed reaction of carbon-carbon double formation for the construction of benzene ring for the synthesis of carbohelicenes.[52b] Using similar methodology more derivatives of [7]helicenes **19** have been synthesized. The sequence of synthsis was started with 3,3'-dihydroxy-4,4'diphenanthryl **245** obtained from 3-phenanthrol, *via* the oxidative Cu-coupling under oxygen free condition.



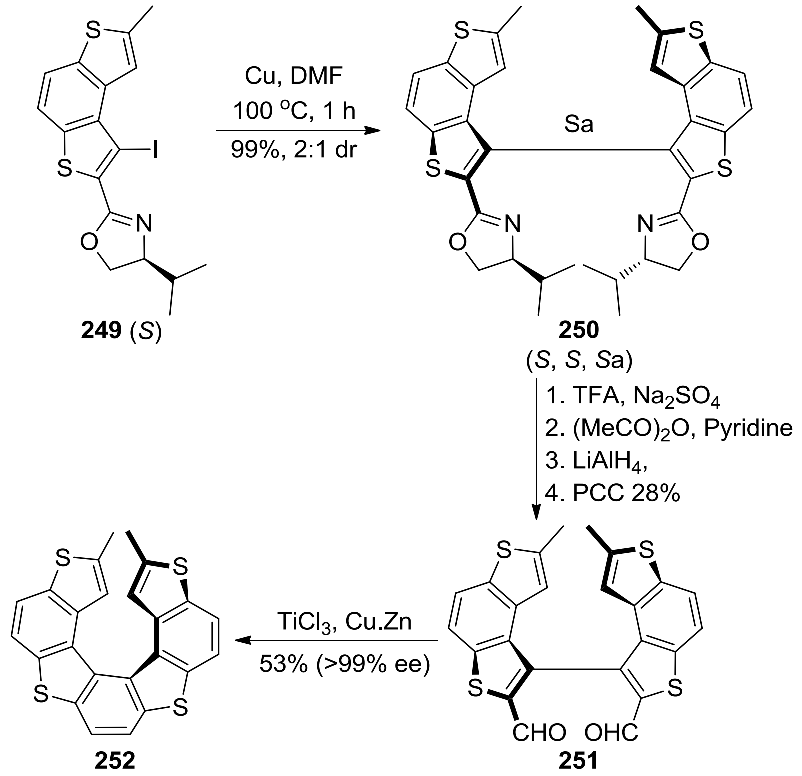
**245** **246** **247** **248** **19**

**Scheme 57:** Synthesis of [7]helicene **19** by carbenoid coupling reaction

The 3,3’-dihydroxy-4,4’phenanthryl **245** was converted to its triflates **246** using triflic anhydride, which was then converted to 3,3’-dimethyl-4,4’-biphenanthrene **247** involving $NiCl_2$(dppp) catalyzed coupling with methyl-magnesiumbromide. The side chain bromination on this gave the desired bis-bromomethyl moiety, suitable the carbenoid coupling with LiHMDS/THF/HMPA towards [7]helicene **19**.

### Approach 5a: 3) *Synthesis of enantiomerically pure tetrathia[7]helicene such as 2,13-Dimethyldithieno[3,2-c:3’,2’-c’]benzo[1,2-b:4,3-b’]bis[1]benzothiophene 252 using McMurry coupling reaction:*

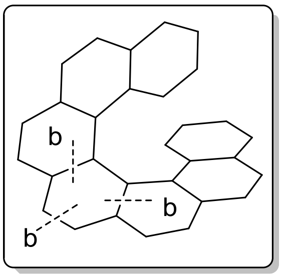
Tanaka et al. synthesized tetrathiahetero[7]helicene[78] in near perfect selectivity of 99% *ee via* a strategy based on asymmetric Ullmann coupling reaction. The suitable aryl halide with chiral auxiliary, (*S*)-1-iodo-2-(4-isopropyloxazolin-2-yl)-7-methylbenzo[1,2-*b*:4,3-*b*’]dithiophene **249** on coupling reaction gave the product 2,2’-bis(4-(*S*)-isopropyloxazol-2-yl)-7,7’dimethyl-1,1’-bi[benzo[1,2-*b*:4,3-*b*’]dithiophene] **250** in excellent yield and with high selectivity.



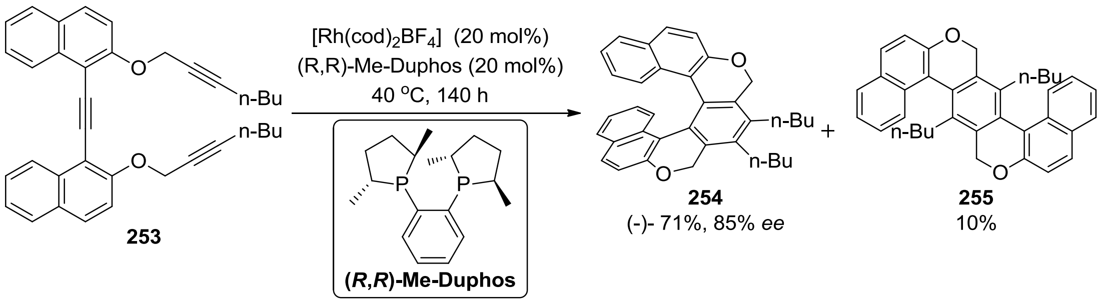
**Scheme 58:** Asymmetric synthesis of tetrthiahetero[7]helicene by McMurry coupling reaction

It was converted into dialdehyde such as 2,2’-diformyl-7,7’-dimethyl-1,1’-bi[benzo[1,2-*b*:4,3-*b*’]dithiophene] **251** and its subsequent intramolecular McMurry coupling was done. By this mode the central chirality was successfully transformed into helical chirality *via* axial chirality and gave the optically pure tetrathiahetero[7]helicene **252** [**Scheme-58**]. The oxazoline substituents play a key role not only in the enantioselectivity but also in providing an atropisomeric biaryl compound with stable $C_2$ symmetry, which subsequently is converted into dialdehyde for further coupling reaction.

### Approach 5b: 1) *Synthesis of [7]helicenes and long helicenes by the metal catalysed [2 + 2 + 2] cyclosoimerization:*

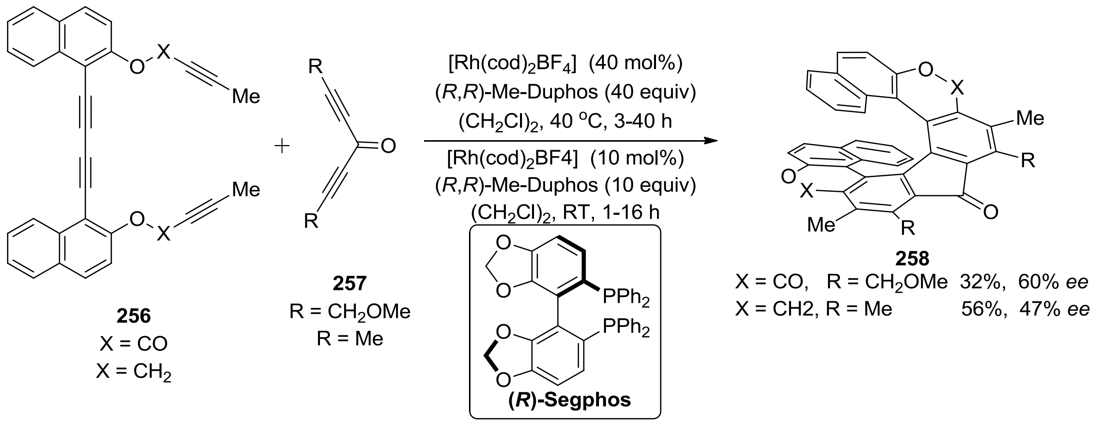


Tanaka and co-workers introduced a new method for the synthesis of helicenes in a one step reaction using chiral bidentate phosphine ligands with [Rh(cod)$_2$]BF$_4$ to synthesize [5]-, [7]-, and [9]helicene-like molecules.[79] In the cyclization of triynes, (*R*,*R*)-Me-Duphos and (S)-xyl-Segphos were examined.

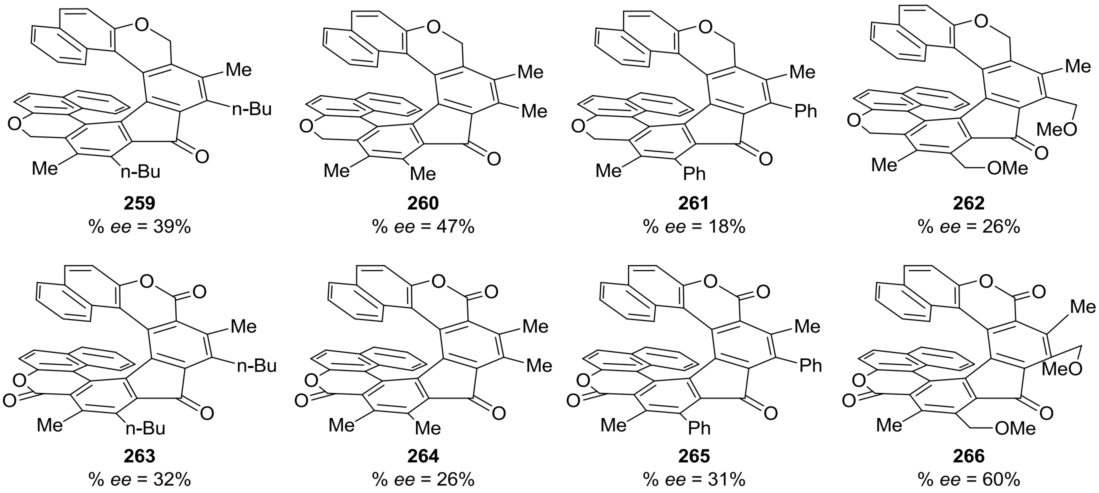


**Scheme 59:** Synthesis of enantioenriched [7]helicene by [2 + 2 + 2] cycloisomerization method

Triyne **253** gave the best result with a Rh(I)/(*R*,*R*)-Me-Duphos catalyst, forming (-)-[7]helicene **254** in 71% yield and 85% ee. Interestingly, in addition to the [2 + 2 + 2] [7]helicene product, the [2 + 1 + 2 + 1] the linear product **255** was also found in small amount as a result of a –C–C– triple bond cleavage process in the intermediate step due to the steric interaction [**Scheme-59**]. This method, producing enantioenriched helicene-like molecules in up to 60% ee, is highly efficient in terms of building five rings in one step.



**Scheme 60:** Synthesis of enantioenriched [9]helicene **258** by [2 + 2 + 2] cycloisomerization method

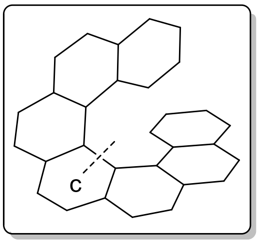


**259** % *ee* = 39%
**260** % *ee* = 47%
**261** % *ee* = 18%
**262** % *ee* = 26%
**263** % *ee* = 32%
**264** % *ee* = 26%
**265** % *ee* = 31%
**266** % *ee* = 60%

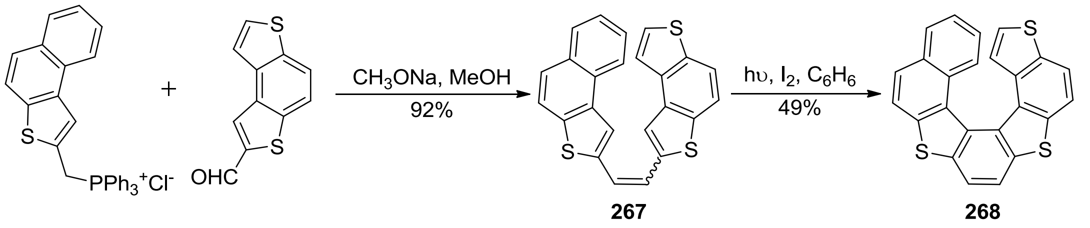
**Figure 16:** Derivatives of [9]helicenes synthesized by [2 + 2 + 2] cycloisomerization

Similarly using this methodology several other helicenes **259-266** were syntththesized [**Figure-16**].

### Approach 5c: 1) *Synthesis of Benzo[e]thieno[3,2-e']benzo[l,2-b,4,3-b']bis[l] benzothiophene/ 3,6,9-trithio[7]helicene 268 by photocyclodehydrogenation methodology:*

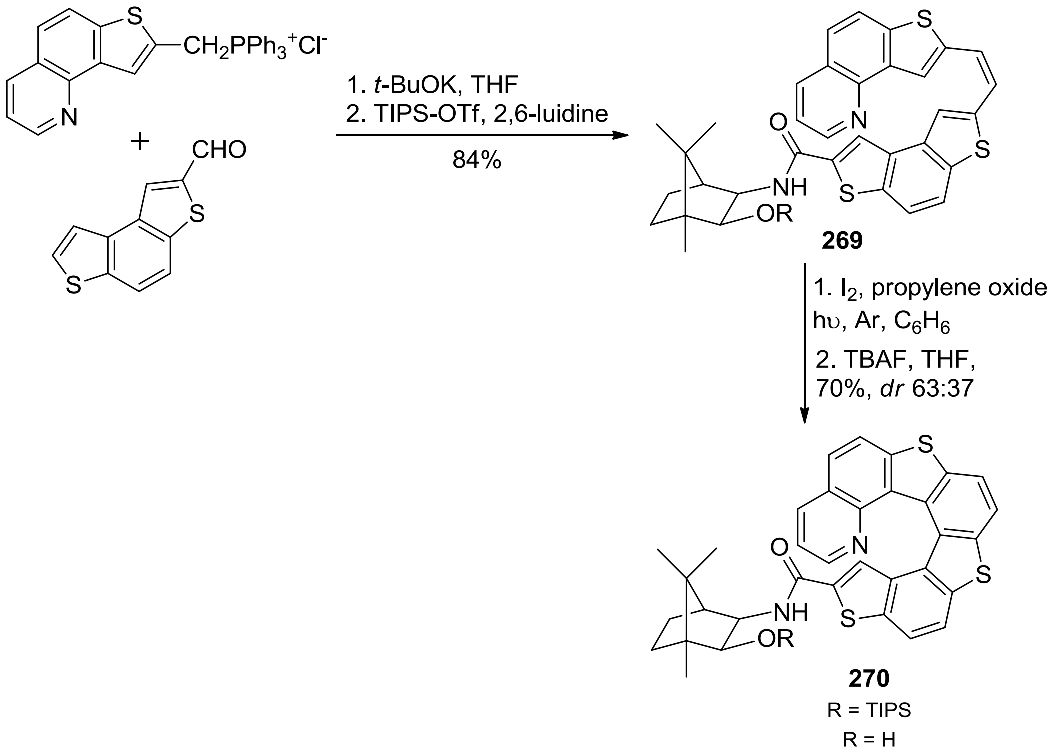


Wynberg and co-workers have synthesized[5b,c,i] the trithio[7]helicene by photocyclization methodology. The Wittig olefination reaction of benzo [l,2-b: 4,3-b'] dithiophene-2-carboxaldehyde and 2-triphenylphosphoniomethylnaphtho[2,1-b] thiophene chloride gave 2-[β-(2-naphtho[2,1-b] thienyl)vinyl] benzo[l,2-b:4,3-b'] dithiophene **267** as a precursor for the helicene **268**.



**Scheme 61:** Synthesis of trithia[7]helicene **268** by Mallory photocyclization reaction

After the photocyclization using catalytic amount of iodine in benzene and irradiated in high pressure mercury vapour lamp gave the product benzo[e]thieno[3,2-e']benzo[l,2-b,4,3-b']bis[l] benzothiophene/ 3,6,9-trithio[7]helicene **268**. Following similar methodology the authors have synthesized a number of sulphur containing helicenes. The resolution of these helicenes by means of crystal picking technique was investigated.

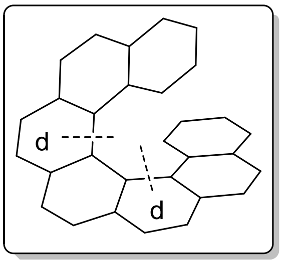


**Scheme 62:** Synthesis of diastereomeric azathia[7]helicene **326** by Katz's photocyclization methodology

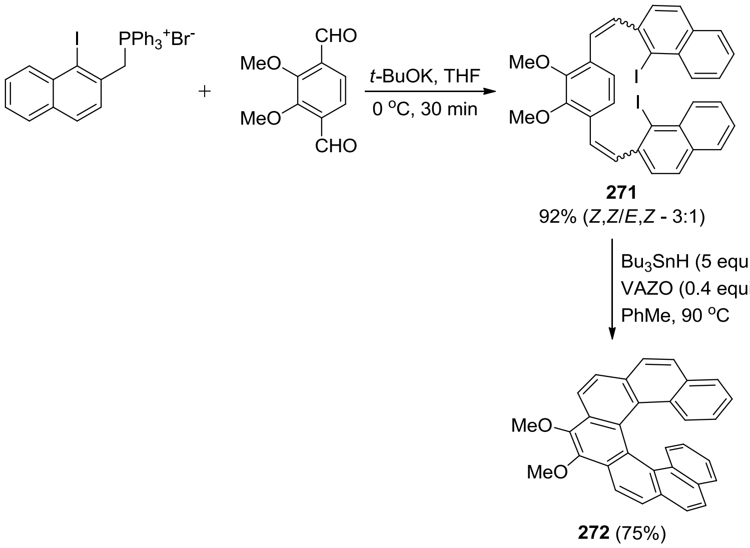
Similar photocyclodehydrogenation methodology was attempted by Osuga and co-workers[80] for one of the early asymmetric synthesis of helicenes. The authors utilized 3-amino-2-hydroxybornene as the chiral auxiliary to control the diastereoselectivity in the synthesis of *N*-[(1*R*,2*S*,3*R*,4*S*)-2-(triisopropylsilyloxy)-

1,7,7-trimethylbicyclo[2,2,1]heptan-3-yl][1]benzothieno[5',4':2,3][1]benzothieno-[4',5':4,5]thieno[3,2-*f*]quinoline-2-carboxamide **270** in the photocyclization process. Although the yield was good, the diastereomeric ratio was low, which suggests that only one chiral auxiliary may not be sufficient and that a better result might be achieved if the carboxamide unit was situated at the most sterically hindered position.

### Approach 5d: 1) *Synthesis of 9,10-dimethoxy[7]helicenes 272 by the aryl radical addition reaction:*



In 2006, Harrowven and co-workers introduced,[17n] an intramolecular aryl radical addition reaction for the synthesis of helicenes with reasonable yields. The Wittig reaction of phosphonium salt of substituted 1-iodonaphthalene treated with 2,3-dimethoxy-1,4-carbaldehyde using potassium *tert*-butyloxide obtained the mixture of *cis-trans* isomers of substituted bis styryl derivatives **271** in good yield.



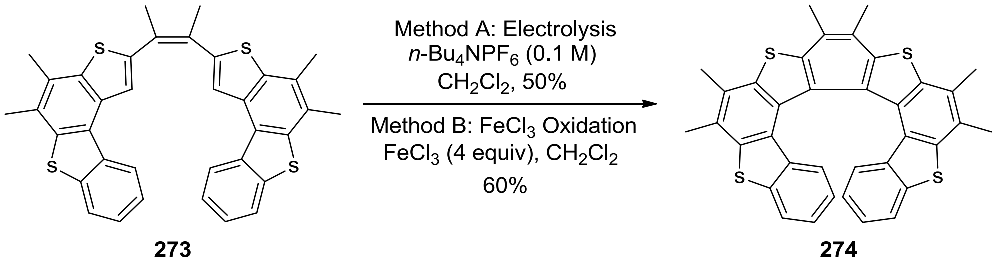
**Scheme 63:** Synthesis of 9,10-dimethoxy[7]helicene **272** by intramolecular aryl radical addition

Treatment of **271** with excess of tributyltin hydride and 0.4 equivalent of VAZO as radical initiator gave 9,10-dimethoxy[7]helicene **272** in good yield.

## Synthetic approaches for the higher member of Helicenes

### Approach 1) *Synthesis of Tetrathio[9]helicene 274:*

In 1996, Larsen and Bechaard reported the synthesis of tetrathia[9]helicene **274** by cyclization of stilbene type precursors using electrolysis and $FeCl_3$ oxidation reaction.[81] The electrolysis dissolved the stilbene derivative **273** in dichoromethane containing $nBu_4NPF_6$ (0.1 M) in a two component cell equipped with a platinum basket counter electrode, after the completion of reaction the product tetrathio[9]helicene **274** was obtained.

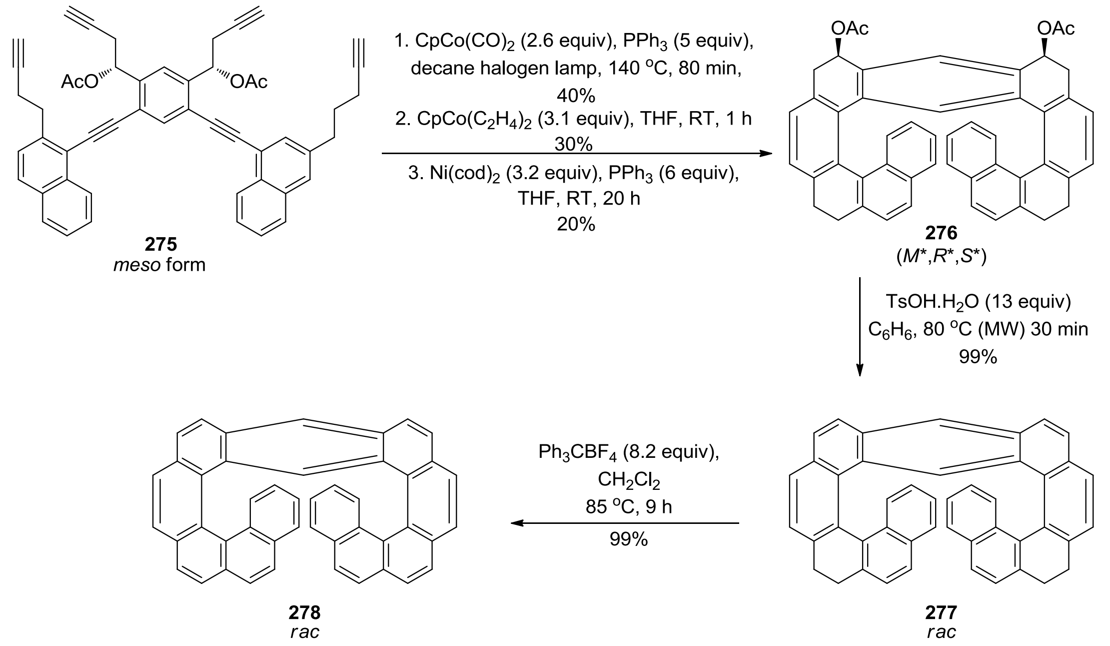


**Scheme 64:** Synthesis of tetrathio[9]helicene **274**

Another method involving $FeCl_3$ oxidation step for the stilbene cyclization was also invstigated. In this reaction the ethylene was treated with four equivlent of $FeCl_3$ in dichloromethane to obtain the tetrathio[9]helicene **274**.

### Approach 2) *Synthesis of higher helicene such as anthra[11]helicene 278:*

Recently Strara and Strary synthesized anthra[11]helicene by metal catalyzed [2 + 2 +2] cycloisomerization of tryne.[66] In this synthesis the diastereomerically pure trine **275** was converted to anthra[11]helicene **278** by cycloisomerization methodology in a moderate yield. The *meso* hexyne (*R*,*S*)-**275** was cyclized to the anthra[11]helicene derivative (*M**,*R**,*S**)-**276** in a moderate yield employing $CpCo(CO)_2$ with $PPh_3$ and the helical chirality assigned by the $^1H$ and ROESY $^1H$ NMR spectrum. The use of catalyst $CpCo(C_2H_4)_2$ or $Ni(cod)_2$ with $PPh_3$ at room temperature also resulted in the formation of the desired product but in lower yields. The aromatization of (*M**,*R**,*S**)-**276** was a straightforward operation.

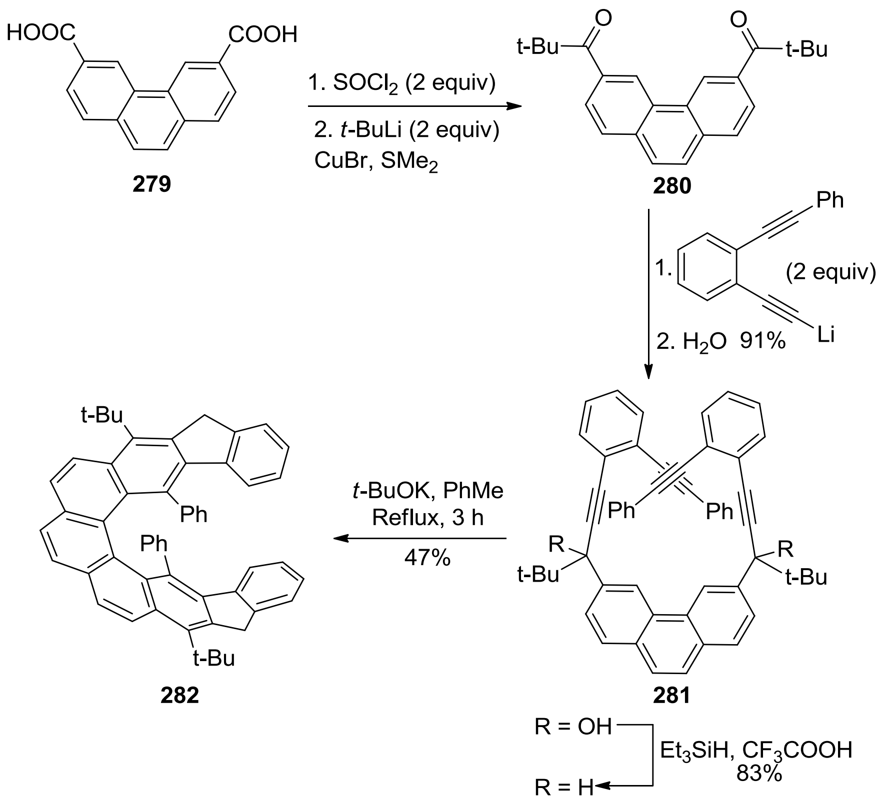


**Scheme 65:** Synthesis of anthra[11]helicene **278** by [2 + 2 + 2]cycloisomerization

Acid-assisted elimination of acetoxy groups followed by dehydrogenation with trityl tetrafluoroborate completed the synthesis of *rac*-anthra[11]helicene **278** [**Scheme-65**].

### Approach 3) *Synthesis of Diindinofused 1,14-diphenyl[5]helicene 282:*

Another radical induced double-cyclization approach for the synthesis of helicenes was reported by Wang and co-workers in 2007.[17w,82] The reaction of phenanthrene 3,6-dicarboxylic acid **279** with thionyl chloride followed by the treatment with *tert*-butyl copper (prepared from *tert*-butyl lithium and CuBr.SMe$_2$) gave the 3,6-dipivalophenanthrene **280**. After the reaction with 2 equivalent of lithium acetylide furnished the benzannulated enediynyl alcohol as a mixture of two diastereomers. Treatment of this diastereomers mixture with triethylsilane in the presence of trifluoroacetic acid at room temperature for 10 min produced the benzannulated enediyne **281** also as a mixture of the two diastereomers in same ratio. The mixture of the diasteriomeric product was treated with *tert*-butoxide in refluxing toluene to obtain the diindeno-fused 1,14-diphenyl[5]helicene **282**.

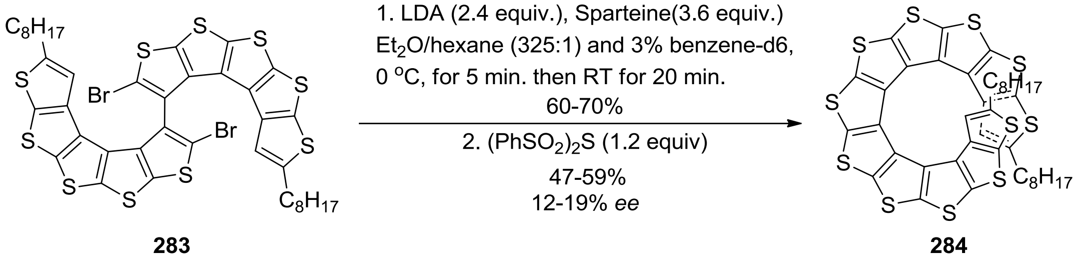


**Scheme 66:** Synthesis of diindinofused 1,14-diphenyl[5]helicene **282**

Using this methodology other helical compounds, such as diindeno-fused 1,12-diphenylbenzo[*c*]phenanthrene and diindeno-fused-4,5-diphenyl-phenanthrene have been synthesized.

### *Approach 4) Synthesis of Carbon-Sulfur[11]helicene 284:*

The higher sulphur containing heterohelicene was synthesized by Rajca in 2005[17y,17z] using the decathiophene **283**, which on treatment with LDA (2.4 equiv) gives dilithiated intermediate in the presence of (-)-sparteine, dilithiated salt is formed in good yield, however no asymmetric induction was detected at this stage.



**Scheme 67:** Synthesis of Carbon-Sulphur[11]helicene **284**

Addition of bis(phenylsulfonyl)sulfide ($(PhSO_2)_2S$) to lithiated (-)- sparteine gives enantioenriched carbon-sulphur[11]helicene (-)-**284** in a moderate yields [**Scheme-67**].

# Applications of Helical Molecules

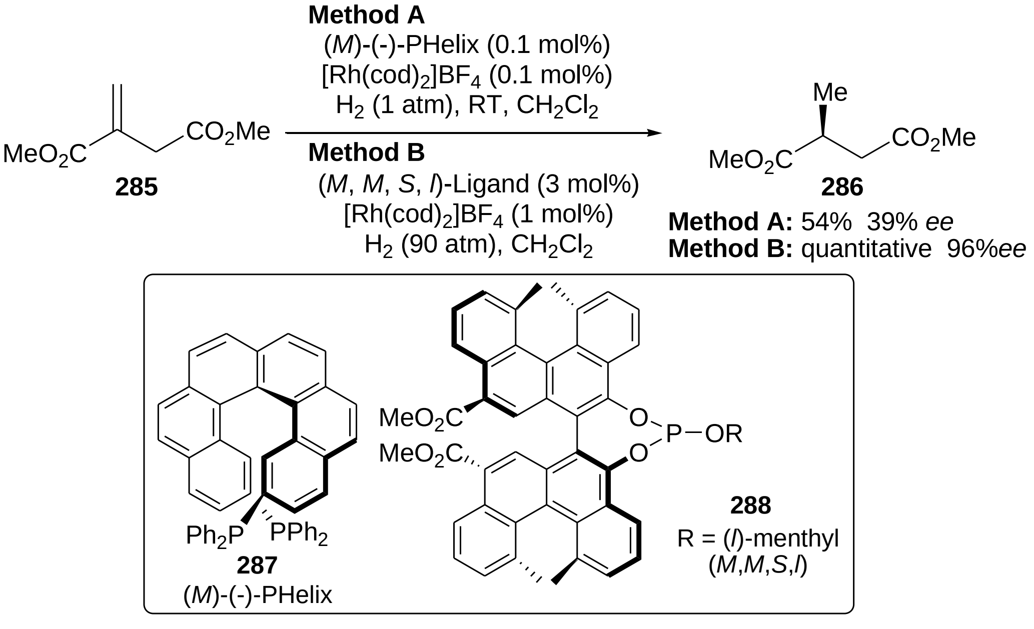
The research in the area of helical molecules has not only synthesized a large number of helical molecules for the scientific community of search their applications. This section deals with a short account of different applications of helical compounds.

## 1) Asymmetric Catalysis:

### • Rhodium Catalysed Asymmetric Reduction:

The first asymmetric catalyst was used by Bredig in 1912 for the synthesis of mandelonitrile in 10% *ee* by utilizing quinine as a catalyst.[83] After that initial work the area of asymmetric catalysts has developed to a mammoth extent and a huge number of different types of chiral ligands are produced. In this series many different kinds of chiral ligands and catalyst were developed but the helically shaped chiral molecules OR helicene as ligand/catalyst was not taken up until 1997.

Reetz and co-workers reported the first catalyst based on a helical chiral ligand.[84] The catalyst was synthesized *in situ* by the stoichiometric reaction of (*M*)-PHelix **287** and $Rh^+•(cod)_2BF_4^-$ and it was used for the enantioselective hydrogenation of the itaconate **285** to afford the diester (*S*)-methyl succinate **286** in 54% yield and 39% *ee*. The rhodium catalysed hydrogenation was also studied by Yamaguchi and Nakano in 2003.[85] Other bihelicenol phosphite ligand (*M,M,S,l*)-**288** was studied, interestingly a match/mismatch phenomenon was found responsible for the selectivity, and the ligand bearing both (*M*)-helical and (*S*)-axial Chirality gave the best result (quantitative yield and 96% ee).

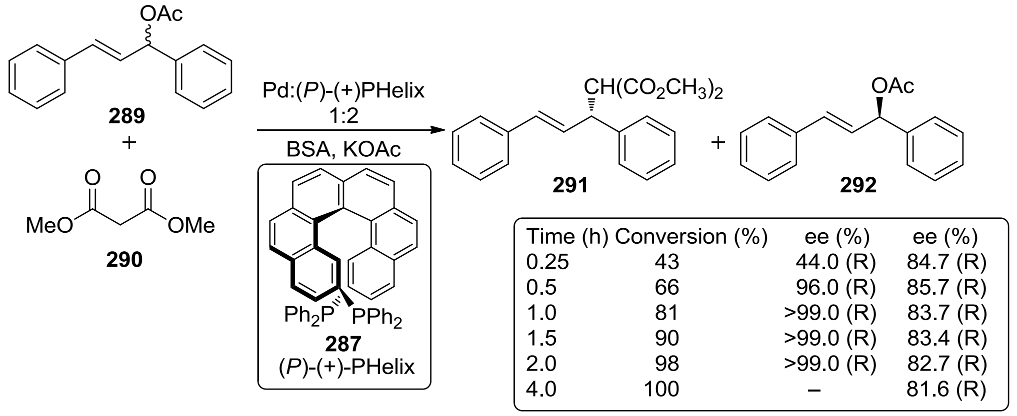


**Scheme 68:** Rhodium catalysed asymmetric hydrogenation using helical phosphine ligands

The reaction was also studied with bihelicenol (*M,M,S,d*)-phosphate ligand and produced the product (*S*)-methyl succinate **286** in quatitative yield and 85% *ee*.

## • Palladium Catalysed Allylic Substitution:

Reetz and co-workers also investigated the kinetic resolution[86] of *rac*-1,3-diphenylpropenyl acetate **289** by Pd-catalysed allylic substitution using (*P*)-(+)-PHelix **287** as a ligand. In this case the PHelix behaved only as a chiral monodentate ligand because of the long distance between the two phosphorous atoms.



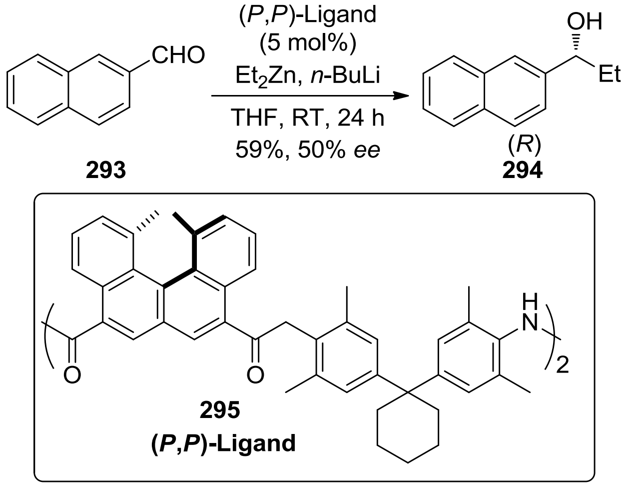
| Time (h) | Conversion (%) | ee (%) | ee (%) |
|---|---|---|---|
| 0.25 | 43 | 44.0 (R) | 84.7 (R) |
| 0.5 | 66 | 96.0 (R) | 85.7 (R) |
| 1.0 | 81 | >99.0 (R) | 83.7 (R) |
| 1.5 | 90 | >99.0 (R) | 83.4 (R) |
| 2.0 | 98 | >99.0 (R) | 82.7 (R) |
| 4.0 | 100 | – | 81.6 (R) |

**Scheme 69:** Palladium catalyzed allylic substitution using helical phosphine ligand

The conditions were optimised till the authors found that the Pd-PHelix ratio of 1:4 gave excellent selectivity for the kinetic resolution, with high conversion and nearly perfect selectivity (99% *ee*).

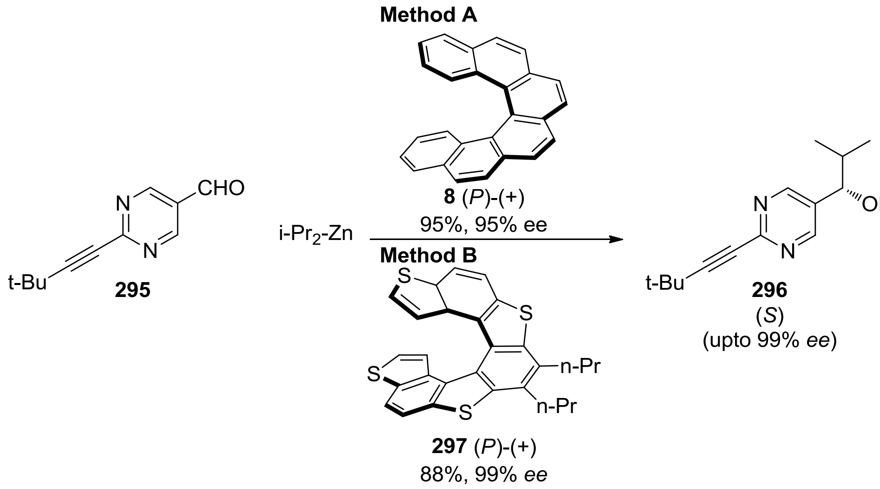
## • Zinc Catalysed Asymmetric Addition Raction:

In 1998, Yamaguchi and co-workers[87] reported the use of optically pure macrocyclic amide (*P*,*P*)- **295** containing two [4]helicene moieties for the catalytic asymmetric addition of diethylzinc to aromatic aldehydes [**Scheme-70**].



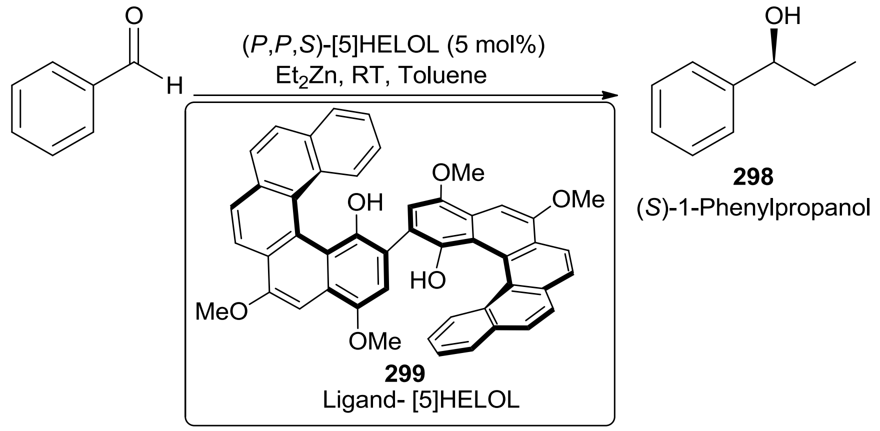
**Scheme 70:** Helical macrocyclic amide ligand **295** in the diethyl zinc addition reaction

In 2001 Soai and co-workers have used the enantiomerically pure samples of pentahelicene and hexahelicene as the asymmetric trigger for the autocatalysis reaction between diisopropylzinc and pyrimidyl aldehyde **295** [**Scheme-71**].[88a] Similarly, chiral tetrathia[7]helicene **297** was also used to induce the autocatalytic reaction.[88b]



**Scheme 71:** Helicenes **8** and thiahelicenes **297** as autocatalysts in *iso*-propylzinc addition

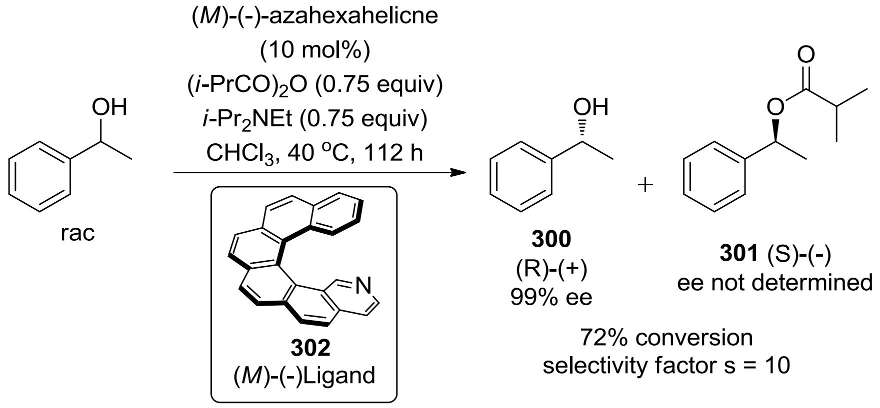
In these reactions, all (*P*)-helicenes induced formation of the (*S*)-alcohol in high *ee* through either Method A or Method B (Reactions were carried out in toluene at 0 °C. Method A: Aldehyde and *i*-Pr$_2$Zn were added in two portions. Method B: Aldehyde and *i*-Pr$_2$Zn were added in three portions and the *ee* value was determined by chiral HPLC analysis). They have also used (*M*)-helicenes for this transformation and obtained excellent results similar to (*P*)-helicenes. Interestingly, even if helicenes with very low *ee* were used, for example, (*P*)-hexahelicene **8** in nearly 0.13% *ee* and (*P*)-tetrathia[7]helicene **297** in 2% ee, the reactions still gave products with 56% and 83% *ee*, respectively.



**Scheme 72:** [5]HELOL as a ligand in asymmetric diethyl zinc addition

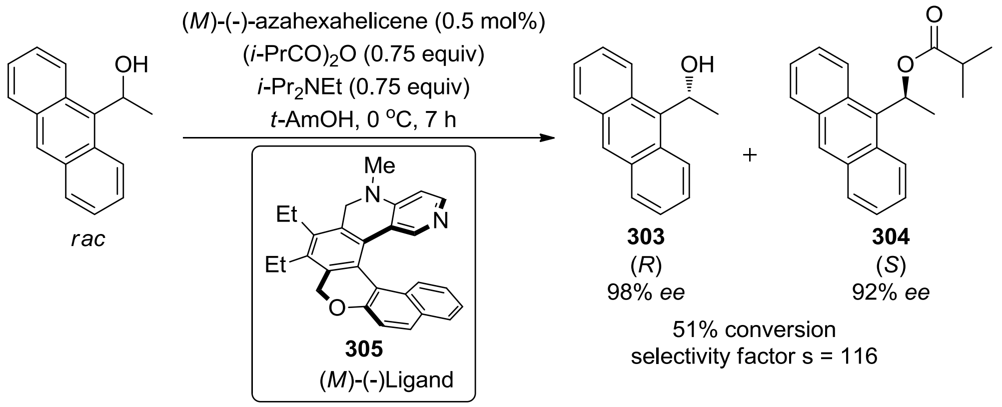
In 2009, Katz and co-workers[89] have used (*P*,*P*,*S*)-[5]HELOL **358** as a helical ligand in the catalytic asymmetric addition of diethylzinc to benzaldehyde, which afforded (*S*)-1-phenylpropanol as a product in 81% *ee* [**Scheme-72**]. The reaction was suggested to involve intermediate, in which the zinc atom is bound to [5]HELOL **299** and coordinated to the benzaldehyde. Consequently, the *Re* face of the aldehyde is blocked by the bottom part of the helicene, which forces the $Et_2Zn$ to enter the groove from the other side.

- **Catalytic Acyl Trasfer reaction:**



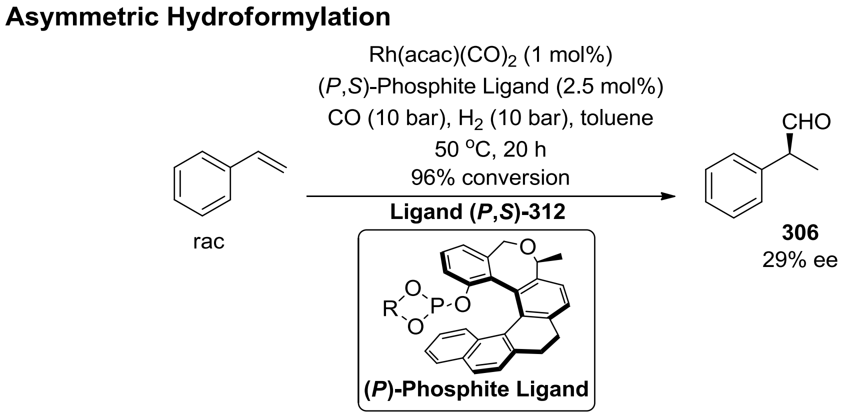
**Scheme 73**: Asymmetric acyl transfer by enantiopure 2-aza[6]helicene **302** as a ligand

Stary, Stara and co-workers utilized (*P*)-1-aza- and (*M*)-2- aza[6]helicene **302** as organocatalysts in the asymmetric acyl transfer reaction of *rac*-1-phenylethanol [**Scheme-73**].[90] They found that (*P*)-1-aza[6]helicene **10** had low activity (<5% conversion), which might be a result of the limited accessibility because the N atom is at the most sterically hindered position. However, (*M*)-(-)-2-aza[6]helicene **302**, with high proton affinity and a pKa (in $H_2O$) of 5.28, showed good catalytic efficiency, affording (*R*)-phenylethanol **300** in 99% *ee* with up to 72% conversion when the reaction was carried out using ($i$-PrCO)$_2$O as the anhydride and $i$-Pr$_2$NEt as the base.



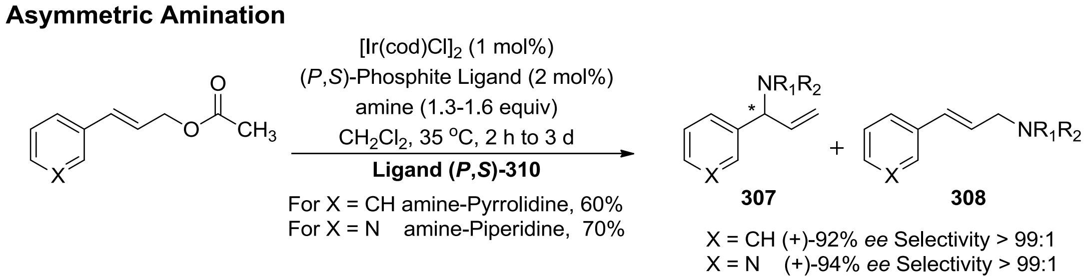
**Scheme 74**: Asymmetric acyl transfer by enantiopure aza[6]helicene **304** as a ligand

Recently Carbery and co-workers have re-examined the kinetic resolution of the secondary alcohols.[91] They designed a helicenoidal DMAP analogue **305** bearing a dialkylaminopyridine unit and the helical scaffold as a Lewis base catalyst, which afforded (*R*)-1-(9-anthranyl)-ethanol **303** in 98% *ee* and its acyl product (*S*)- **304** in 92% *ee* (51% conversion). This organocatalyst showed high level of selectivity (selectivity factor s up to 116) and excellent reactivity (exceptionally low catalyst loading of 0.05%) in the reaction.



**Scheme 75**: Helical Phosphite ligands in asymmetric Rh catalyzed hydroformylation

Stary, Stara and co-workers subsequently studied four helicene based phosphate ligand [**Figure-17**] as ligands in asymmetric Rh catalyzed hydroformylation and Ir- catalyzed allylic amination.[92]



**Scheme 76**: Helical Phosphite ligands in asymmetric Ir- catalyzed allylic amination

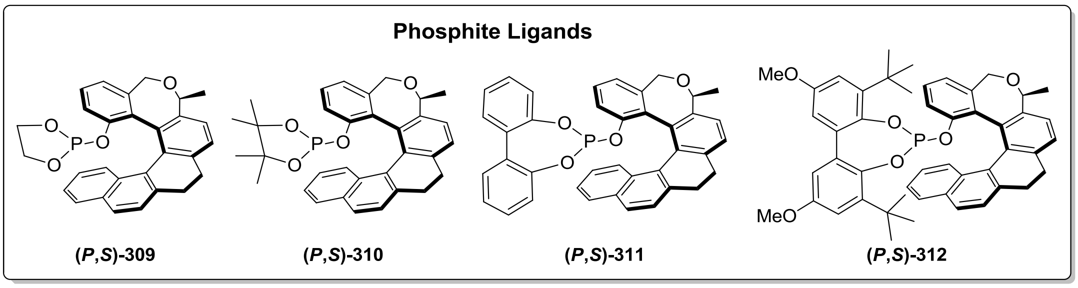
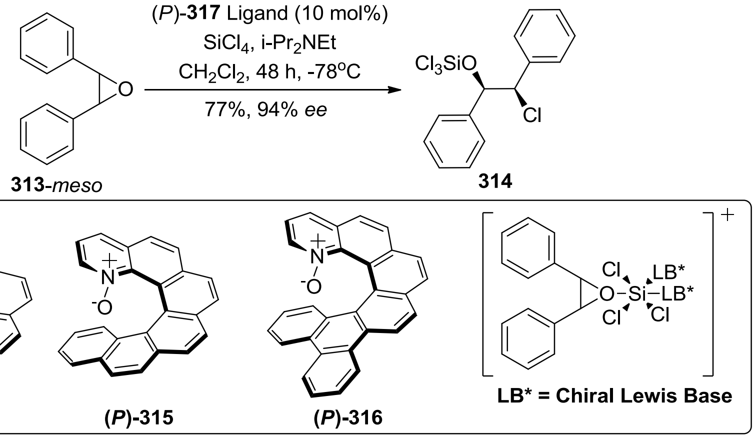


**Figure 17:** Phosphite ligands for the organic transformations

The Rh-catalysed hydroformylation proceeded with excellent regioselectivity (up to 99:1) and but enantioselectivity (up to 32% *ee*) was observed.

Hydroformylation of the styrene gave (*S*)-2-phenylpropanal **306** in 29% *ee* (96% conversion) with a regioselectivity of 93:7 in the presence of Ru(acac)$(CO)_2$ and (*P*,*S*)-**312** as a ligand [**Scheme-75**]. The same catalyst was scanned for Ir-mediated asymmetric amination with excellent regioselectivity [**Scheme-76**]. The best result was found with the $[Ir(cod)Cl]_2$ and (*P*,*S*)-**310** as a ligand in the amination of cinnamyl methyl carbonate and (pyridinyl)allyl carbonate, which afforded *branched* and *linear* products > 99:1 regioselectivity in 92% *ee* and 94% *ee*, respectively.

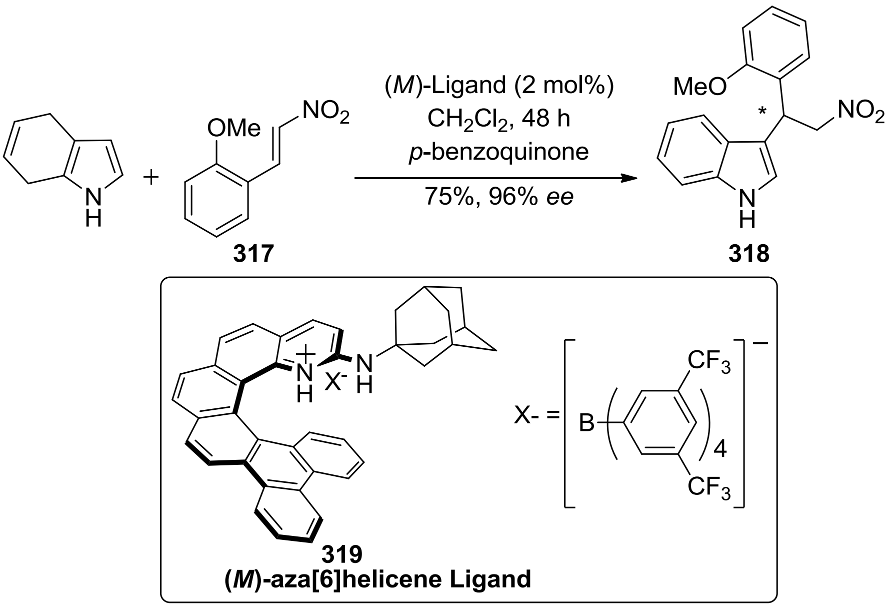
Recently, Takenaka and co-workers have reported two novel series of asymmetric catalysts based on the unique properties of 1-azahelicene.[73b] Initially, the authors synthesized the helical chiral pyridine N-oxides **223**, **315** and **316** by oxidation of the corresponding 1-azahelicene in the presence of *m*-CPBA and found that the N-oxides could perform Lewis base catalysed enantioselective ring opening of the *meso*-epoxide.



**Scheme 77**: Asymmetric ring opening of *meso* epoxide by helical N-oxide ligands

The reaction is thought to involve a cationic species that enables the chloride anion to add from the less hindered side and gave in up to 94% *ee* [**Scheme-77**].

Furthermore, modification of the helical pyridine N-oxides can increase both the substrate scope and the enantioselectivity. More recently,[73c] another new kind of helicene bearing a 2-aminopyridinium terminal **319** ring was synthesized and shown to be an efficient dual-hydrogen-bond donor catalyst for the addition reaction of dihydroindole to nitroalkene at low temperature to obtain the product **318**; the reaction proceeds with high enantioselectivity [**Scheme-78**].



**Scheme 78**: Helically chiral 2-aminopyridium ion as a hydrogen donar in asymmetric addition reaction

## 2) Applications of Helical Molecules in Molecular Machines:

### Molecular Rachet:

Field of Molecular machines is growing rapidly and it is considered as the future area of significant research. Kelly and co-workers designed and synthesized a novel ratchet **320** by employing a triptycene as a toothed wheel and a [4]helicene as the pawl and the spring.[93]

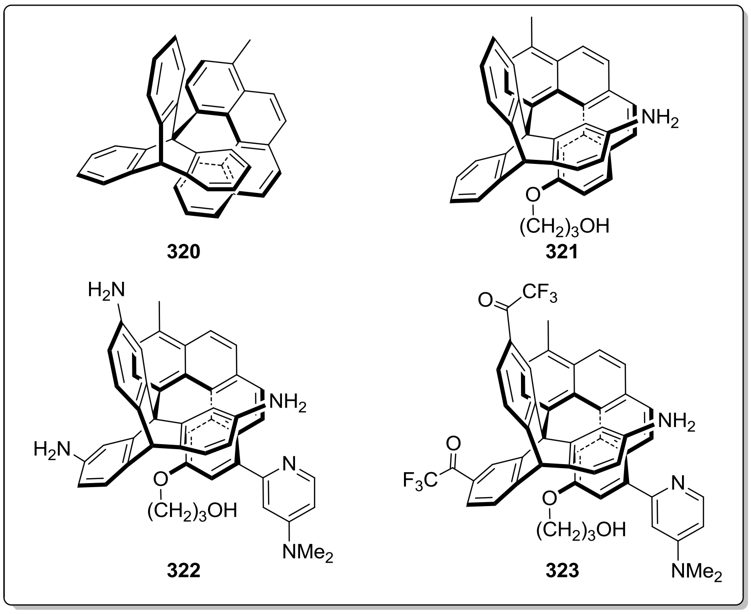
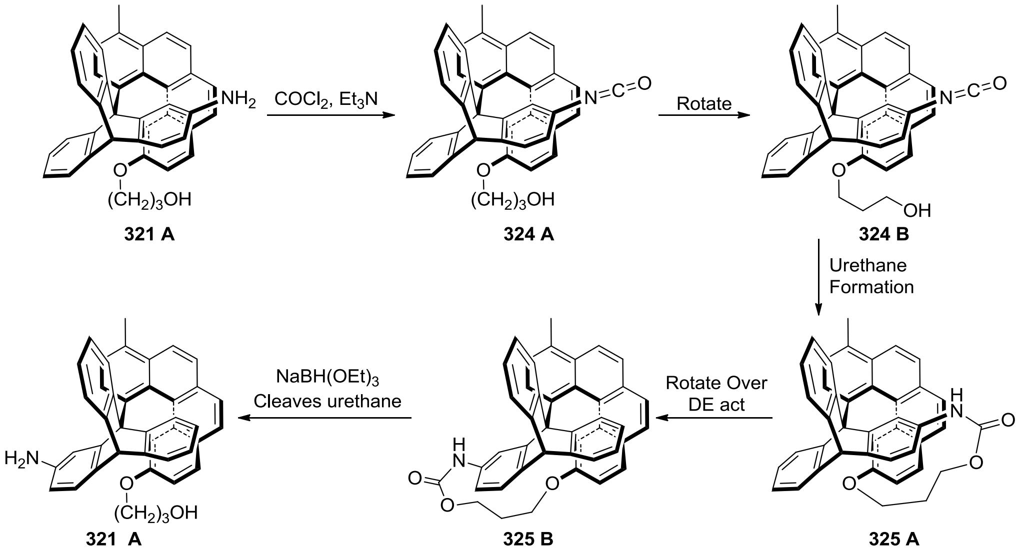


**Figure 18:** Rational design of molecular ratchets

Slow rotation of the triptycene was observed based on the peak broadening in $^1$H NMR spectra recorded at high temperature (160 °C), while spin polarization transfer NMR results indicated a bidirectional rotation to the same extent.



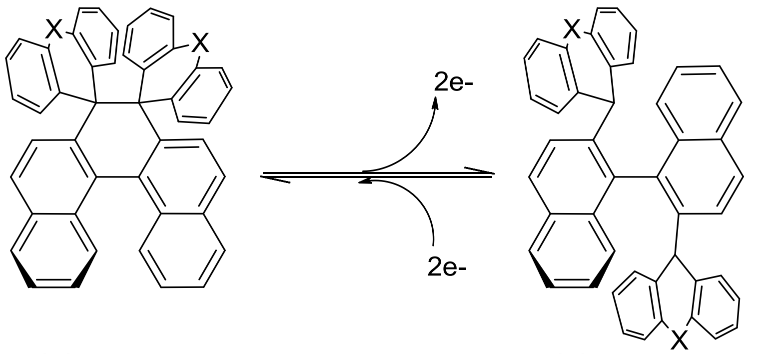
**Scheme 79:** Synthesis and the success rotation of the molecular ratchet

To realize this objective, a significant improvement was made by introducing a tether on the helicene unit of **321** while using carbonyl dichloride (phosgene) as a chemical energy provider, like ATP in biological activities, enabled successful rotation by 120 $^{o}$ in one direction around the single bond between the two units. Carbamoyl chloride was formed by adding carbonyl dichloride to **321**, which was readily converted into the isocyanate **324** in the presence of triethylamine.

This activation of the ratchet is the basis of the unidirectional rotation, not only by fostering the clockwise rotation to form urethane by the reaction of isocyanate and a hydroxyl group (otherwise the two groups are too far away to react) but also by lowering the activation energy ($\Delta E_{act}$) of the rotation (clockwise rotation from A to B) by raising the energy of the rotamer **325**; this also results in the counter clockwise route (from B to A) requiring a higher $\Delta E_{act}$. The rotation is the rate determining step (the half-life was nearly 3 h), and **325** (B) was obtained by urethane cleavage. Thus, the unidirectional, chemically powered rotation was realized.

### 3) Chiroptical swithes:

In 2001, Suzuki and co-workers constructed the first example of redox switches with dramatic chiroptical response based on dihydro[5]helicene and induced by electron transfer.[94] Because the redox pairs were stable and no racemization occurred at room temperature, optically active (*P*)-**326** and (*S*)-**327** were utilized to examine the electrochemical response.

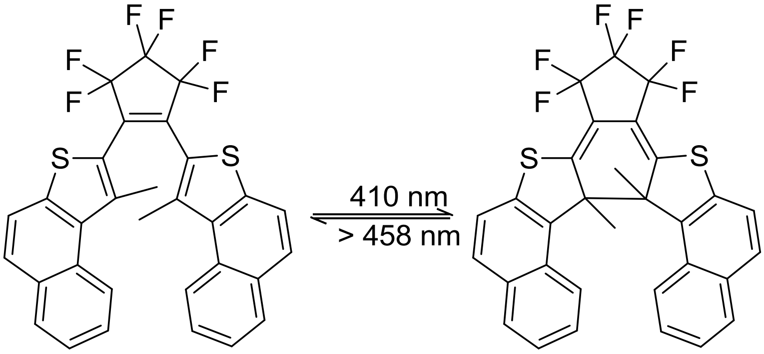


**(*P*)-326** X = O, S

**(*S*)-327** X = O, S

**Figure 19**: Electron transfer in chiroptical switches

Photochromism phenomena had been studied for a long time because of its potential applications in devices such as switches and optical memories. Branda and co-workers described the reversible formation of a dimethyl[7]helicene in which irradiation of the open form **328** [yellow] in dichloromethane at 410 nm afforded a structure **329** consisting of the closed form [orange] and the open form in a ratio of 74:36. In the reverse process, irradiation of **329** by light with λ > 458 nm regenerated **328** through a rapid ring-opening process [**Figure-20**].[95a]



**328**
[Yellow]

**329**
[Orange]

**Figure 20:** Photochromism for the dimethyl[7]helicene **329**

Later, Branda's group reported chiral discrimination phenomena in such photochromic thiahelicenes.[105b] Comparing **330** with **328**, the key difference is the remote chiral moiety, which introduces steric hindrance, making (*M*)-**331** a major product of photolysis of **330** at 400 nm, (*M*)-**331** can be photobleached by irradiation with light of λ > 434 nm. Even though photolysis of **330** gave just 40% conversion to (*M*)-**331**, this system is still a good candidate for a chiroptical photoswitches not only because of the thermal stability but also by its large difference in the optical rotation ($\Delta[\alpha] = 8698^{o}$).

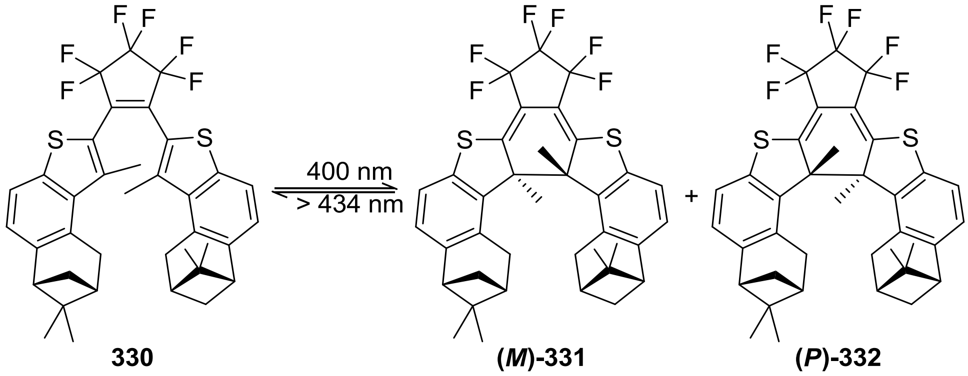
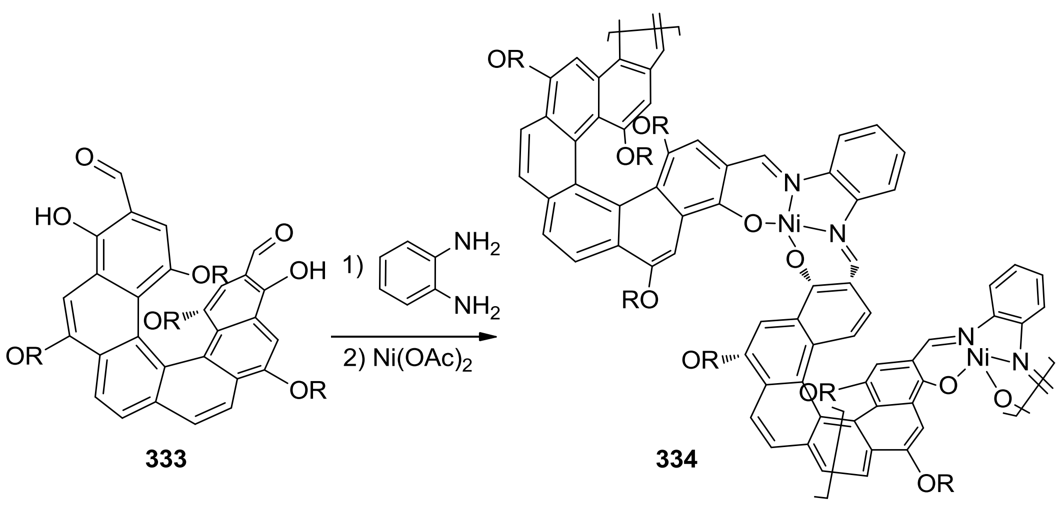


**Figure 21:** Phtotochromic thiahelicenes

### 4) Helical conjugated Ladder Polymers:

Design and synthesis of novel polymeric compounds is important aspect of material chemistry. Several polymers possessing helical isomers were also prepared and studied by different groups. Katz and co-workers described the first synthesis of two novel ladder polymers bearing heptahelicene connected by nickel salophen units in which the square planar geometry made the π-conjugation extend from the helicenes to the whole polymer.[96] To synthesize the salophen ligands using 1,2-phenylenediamine, the formyl groups were properly situated at the 3,14-positions of **333**. As a result, different types of polymers were obtained by virtue of the strong coordination between ligands and metal centers. The polymer **334** has two winding directions with the nickel-salophen units having a right handed helix and the helicene units having the opposite helicity. Polymer **334** with number-average molecular weights of ~ 7000, had good solubility in number of organic solvents. Moreover, their CD spectra were generally similar to those of the helicene precursors, with only a slight bathochromic shift.

Besides this example several other polymer attached helical molecules or polymeric helical compounds were reported in the literature. These have some of the unique properties such as chiroptical property.



**Scheme 80:** Synthesis of chiral helical ladder polymer

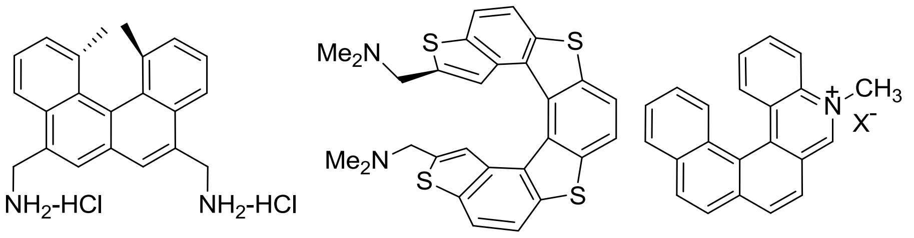
Some other polymers with helical units containing chiral as well as non chiral are synthesized and studied for their special properties.[97]

5) **Biological Applications of Helical molecules:**

Besides applications in material science there are recent reports of study of the biological action of helical molecules. This is expected because there are many biological systems possessing helical shape or twist and hence there may be a scope to find out matching interactions with the two helical entities.

In 2002, Yamaguchi and co-workers first presented evidence of the chiral recognition between the helicenediamine **335** and B-DNA. [**Figure-22**].[98] The apparent changes in the UV and CD spectra caused by adding calf thymus DNA to the solutions of (*P*)- and (*M*)-**335** suggested that DNA-helicene complexes were formed. According to isothermal titration calorimetry, the binding constant of (*P*)-helicene was slightly larger than that of its enantiomer, whereas the chiral recognition whereby (*P*)-**335** favors right-handed helicity was probably driven by entropy. That (*P*)-helicene **336** can bind Z-DNA selectively and convert B-DNA into Z-DNA was first reported by Sugiyama and co-workers.[99] However, although (*M*)-**336** exhibited selective binding with Z-DNA, the binding constant of the (*P*)-enantiomer was five times greater. Interestingly, when the amino groups were replaced by hydroxyl groups, the structural selectivity vanished, indicating that the protonated amino substituents were important in binding Z-DNA.

Recently, Latterini and co-workers reported counterion effects in the binding between helicenes and DNA using the same organic azahelicenium moiety **337** with different anions ($I^-$, $NO_3^-$, and $CF_3CO_2^-$).[100] The counterions affected the interaction greatly with $CF_3CO_2^-$ and $NO_3^-$ ions had the highest number of binding sites. This suggests a mixed mechanism involving intercalation and external binding with different anions of **337** favoring formation of intercalation complexes according to CD and AFM studies.



(*P*)-**335** (*P*)-**336** **337**

**Figure 22**: Examples of helical molecules examined for biological applications

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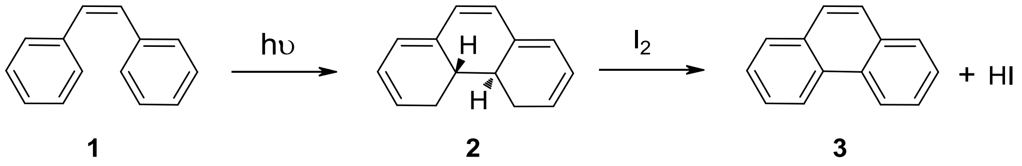
# Chapter-2

# Improved Methodology for the Synthesis of Helicenes and their Derivatives

## Introduction:

The oxidative photocyclizations of stilbenes was discovered earlier during studies of the photochemical isomerisation of stilbenes,[1] but the reaction was not established as a synthetic tool for many years. Its true utility was recognized by Mallory when he discovered the use of iodine as efficient catalyst for this reaction.[2,3] Mallory and co-workers first reported this reaction with stilbene in the presence of molecular oxygen in cyclohexane under the irradiation to form phenanthrene.[4] The reaction was extensively reviewed by Mallory as a part of *Organic Reactions* series.[5] Other reviews[6-10] discuss various aspects and applications of this important reaction. This section will focus on the reaction as a useful tool in synthesis, covering developments reported since 1984. More information is also covered in other reviews and articles on the photocyclodehydrogenation of stilbenes/helicenes.[11]

The basic chemical reaction in the photoirradiation of the stilbene takes place in two steps. The first involves the isomerisation of *trans* stilbene to *cis* sitilbene **1** by ultraviolet light, which further undergoes isomerisation to give the *trans*-4a,4b-dihydrophenanthrene **2** as an intermediate. This intermediate then looses hydrogen in presence of oxidative reagent to form the phenanthrene **3** [**Scheme-1**].

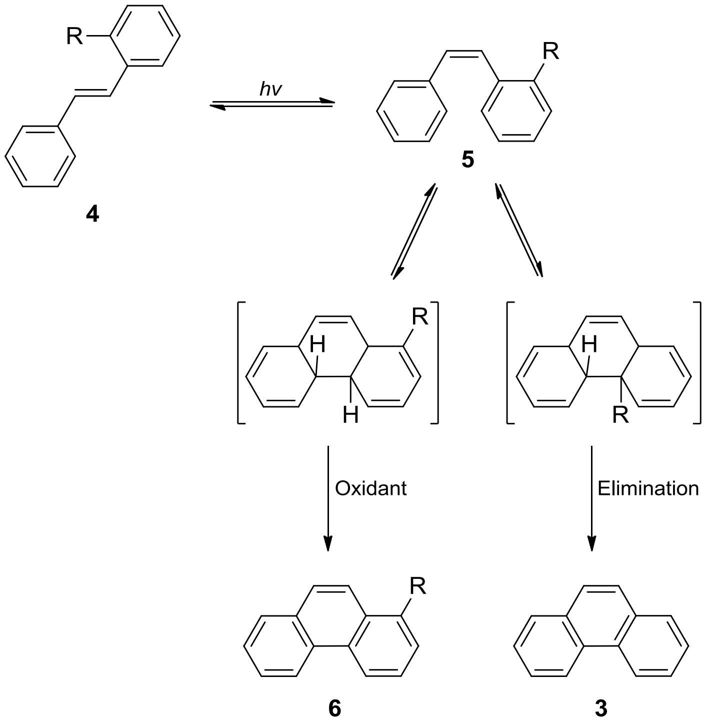


**Scheme 1:** Synthesis of phenanthrene by photocyclodehydrogenation

The reagents routinely used for this oxidative step or as hydrogen acceptors for the photocyclodehydrogenation of stilbenes include, oxygen,[4,12] iodine,[2,3] amines and other bases like $K_2CO_3$, DBU, $Et_3N$, $CaCO_3$,[13,14,15] tetracyanoethylene, the Nafion membrane micro-reactor or stilbazole salts.[16] The stages of photocyclization of stilbenes and their derivatives collectively take place to furnish the final cyclised product, the derivative of phenanthrene, usually in good to excellent conversions and hence this approach remains most efficient.

**Oxidative Photocyclization and Its Mechanism:**

The reaction pathway for the Mallory photo induced cyclization reaction involving the isomerisation of the double bond has been extensively studied.[8-11] From the synthetic point of view the *cis/trans*-isomerization of stilbene occurs rapidly under the reaction condition in such a way that both *cis*- and *trans*-stilbenes give the same product. Thus, the stilbene isomers can be used as stoichiometric mixtures in the photocyclization, although only the *cis*- isomer **5** is capable of further cyclization. The intermediate dihydrophenanthrene formed is unstable and will, unless trapped, relaxes back to the stilbene **4**. There are also examples of hydrogen-shifts at this stage under nonoxidative conditions.[5] The dihydrophenanthrene can be trapped by oxidation to form a phenanthrene, or by elimination given a suitable substituent in the *ortho*-position on one of the aromatic rings [**Scheme-2**].



**Scheme 2:** Reaction pathway for the photodehydrocyclization of stilbenes

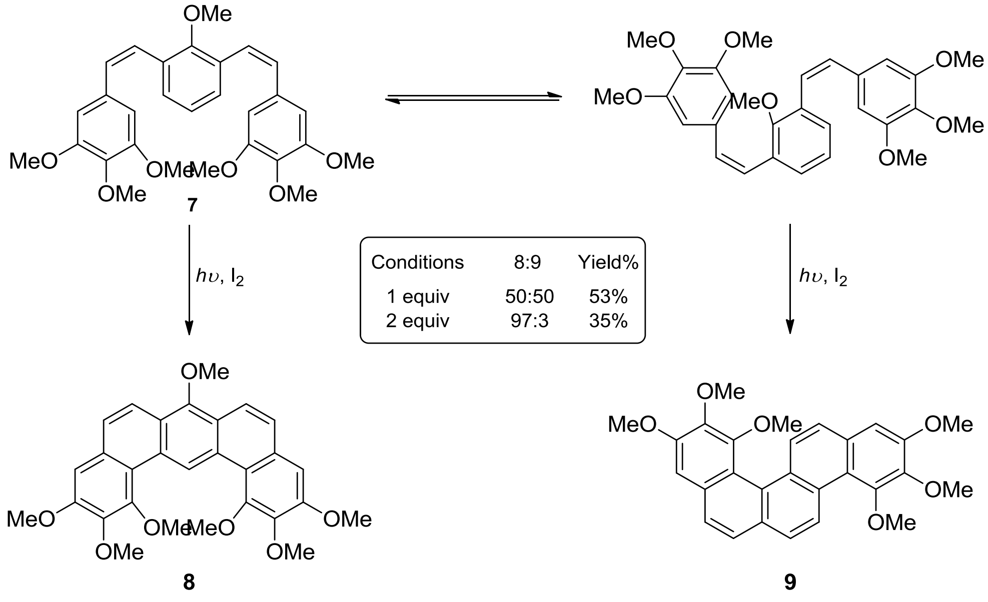
The third mode involves the formation of a dimer by [2+2] cycloaddition reaction in the more concentrated reaction mixture.[5,8,17] Mallory concluded that the oxidative trapping occurs much faster when traces of iodine were used together with

$O_2$,[2] but higher concentration of iodine does not affect the rate of reaction. This aspect of the role of iodine was further explained where the iodine was photochemically cleaved into radicals that react in a chain of reactions.

$$\begin{array}{lllll}
\text{Initiation:} & I_2 + h\upsilon & \longrightarrow & I^{\bullet} + I^{\bullet} \\
\text{Propagation:} & PH_2 + I^{\bullet} & \longrightarrow & PH^{\bullet} + IH \\
 & PH + I_2 & \longrightarrow & P + HI + I^{\bullet} \\
\hline
 & PH_2 + I_2 & \longrightarrow & P + 2\,HI
\end{array}$$

**Scheme 3:** Mechanism for the oxidative photodehydrocyclization of stilbenes

The hydrogen iodide is then oxidized back to iodine by oxygen. The reaction was compatible with fluoro, chloro, bromo, methoxy, methyl, trifluoromethyl, phenyl and carboxyl, but not so with nitro, acetyl or dimethylamino substituents. However, presence of iodine as a substituent could not withstand and got detached during the reaction. Dilute solutions tend to favour intramolecular reactions. Concentrations were usually 0.01 mole/Litre of stilbene.[3] Higher concentrations lead to more [2+2] cycloaddition between two stilbenes. The concentration of iodine can influence both product yields and product selectivity. This was nicely demonstrated in the following example of poly methoxylated stilbene derivative. One equivalent of iodine per cyclization can prevent elimination of methanol[17] [**Scheme-4**].



| Conditions | 8:9 | Yield% |
|---|---|---|
| 1 equiv | 50:50 | 53% |
| 2 equiv | 97:3 | 35% |

**Scheme 4:** Stoichiometric amount of iodine can prevent elimination cyclization

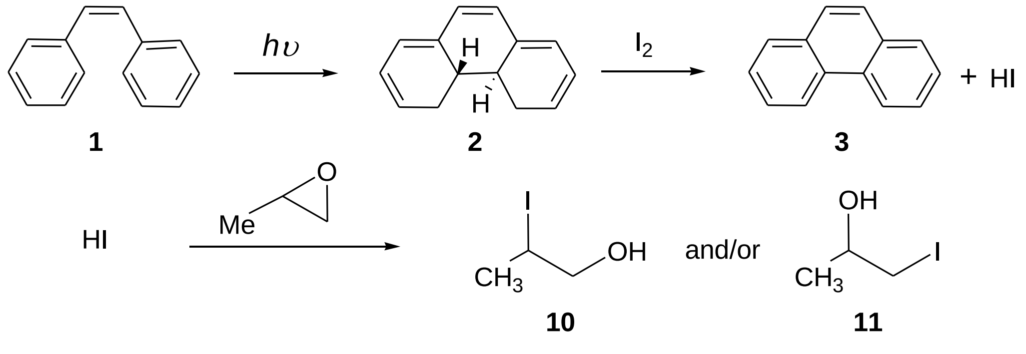
Use of the increased amount of iodine concentration has some drawbacks; such as it leads to the formation of more amount of hydrogen iodide that can saturate the starting stilbene and also contribute to the other side reactions. Therefore, Katz and co-workers developed an improved methodology for the photocyclodehydrogenation of stilbenes.[18]

**Katz Methodology for the photocyclodehydrogenation of stilbenes:[17]**

Katz and co-workers[18] also developed another impressive strategy using excess propylene oxide plus a stoichiometric amount of iodine in an inert atmosphere, which not only enhances the yields greatly compared with the traditional conditions for the photocyclization of stilbenes but also prevent photoreduction or photooxidative side reactions of the double bonds. This strategy has become the standard procedure for the photocyclization of stilbenoid precursors.

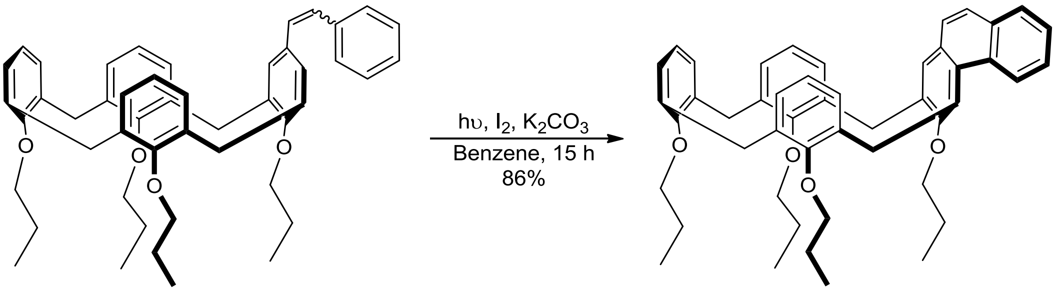
The increased amounts of iodine result in better yields in some systems, the increased concentration of hydrogen iodide causes side-reactions that limit the efficacy. Katz's group officially introduced new conditions in 1991[18] to solve this problem by scavenging the biproduct hydrogen iodide with methyloxirane (propylene oxide) and to prevent the side-reactions.[19,20]

As the byproduct iodide could not be reoxidized by oxygen, a stoichiometric quantity of iodine was needed and the reaction could then be performed under an inert atmosphere preventing side reactions caused by oxygen. The combination of hydrogen iodide and light can reduce the double bond in stilbene.[18] It was initially observed that the catalytic amount of iodine gave purer products and higher yields for many systems. It is not oxygen itself that is the destructive agent, but rather substances formed by the action of oxygen during the photocyclization that contribute to the poorer yields and lower efficiancy.



**Scheme 5:** Stoichiometric amount of iodine as an oxidant and propylene oxide as a scavenger of hydroiodic acid is used for the photocyclization

In 2002, Dyker and co-workers had used potassium carbonate as a HI scavenger in the photocyclodehydrogenation to prevent the cleavage of the long chain alkyloxy chains in the synthesis of calix[4]arenes **13**.[15]



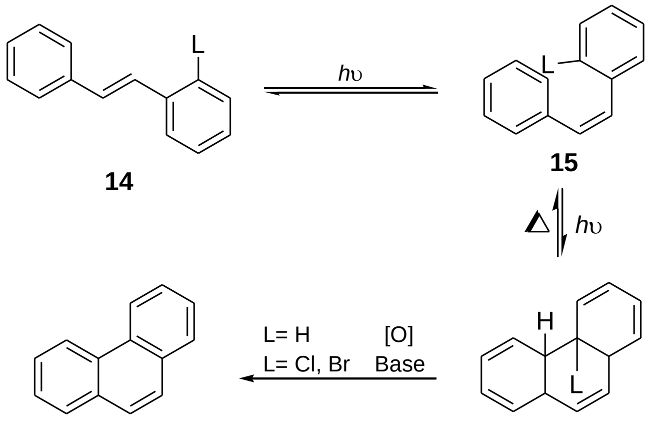
**12** **13**

**Scheme 6:** Potassium carbonate as scavenger of hydroiodic acid

## Elimination Photocyclizations:

### *A) Base-induced elimination photocyclization of 1,2-diaryl-1-tosylethenes:*[14a,b]

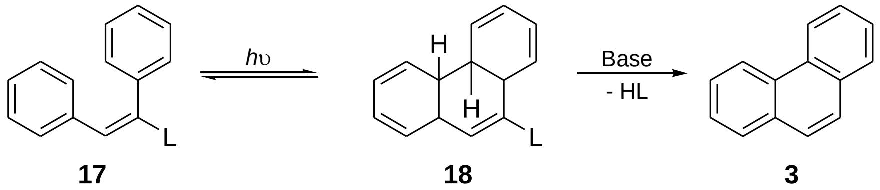
Recently Tojo and co-workers introduced another approach for the photocyclization of stilbenes [**Scheme-7**], this reaction consists of the irradiation, in presence of a base, a stilbene containing appropriately placed good leaving group, normally a chlorine or bromine at the *ortho* position of one of the phenyl rings.[21a,b]



**Scheme 7:** Synthesis of phenanthrene by base induced elimination phtocyclization

In this case, the unsubstituted phenanthrene **3** was produced by the base induced elimination of HL from the intermediate substituted dihydrophenathrene **16**.

Extending this concept Tojo and co-workers developed another methodology, by introducing a leaving group introduced on the alkene bond. The photocyclization in the presence of base formed the phenanthrene by removal of HL from the substituted stilbenes. A good leaving group, tosylate was placed at the double bond position.[14a,b]



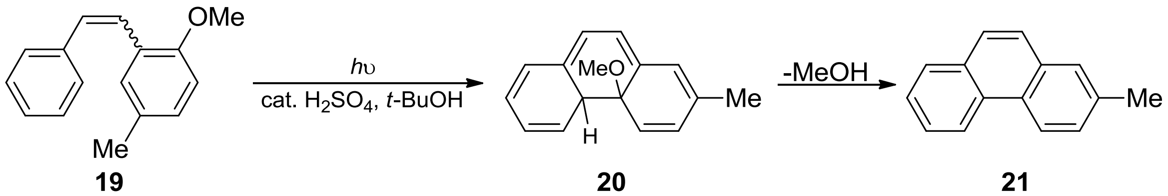
| Bases | Solvent | %Yield |
|---|---|---|
| DBU | | |
| (4 equiv) | Tetrahydrofuran | 95% |
| (4 equiv) | Methanol | 90% |
| $Et_3N$ | | |
| (40 equiv) | Dichloromethane | 75% |
| (40 equiv) | Benzene | 53% |
| (40 equiv) | Methanol | 30% |
| $CaCO_3$ | | |
| (10 equiv) | Tetrahydrofuran | 62% |
| (3equiv) | Methanol | 58% |

**Scheme 8:** Synthesis of phenanthrene by elimination phtocyclization

The three different types of bases were used such as DBU, $Et_3N$ and $CaCO_3$ and tetrahydrofuran/benzene as solvent, out of these bases DBU was found more effective for the reaction with good yield. The cyclization conditions were applied to other tosylstilbenes and stilbenoids leading to excellent yields of the corresponding phenanthrenes **3** and phenanthrenoids [**Scheme-8**].

### *B) Acid-Induced Elimination Photocyclization of Methoxy substituted stilbenes:*[22]

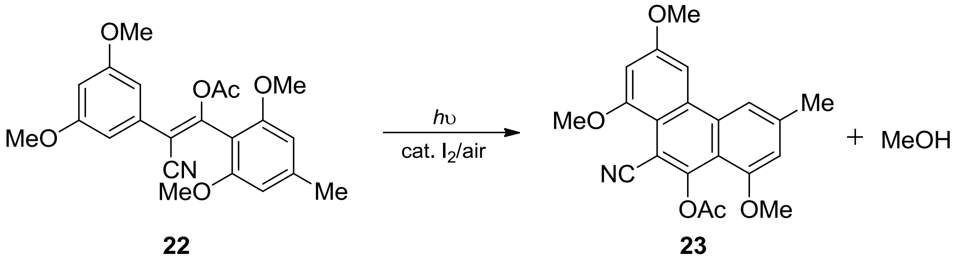
In 1989, Mallory and co-workers employed the use of catalytic amount of sulphuric acid to assist the elimination of methoxy group in the form of methanol during photocyclization. Presence of acid helps to control the selectivity and improvement of the elimination process of the methanol.[22]



**Scheme 9:** Synthesis of 2-methylphenanthrene by acid induced photocyclization

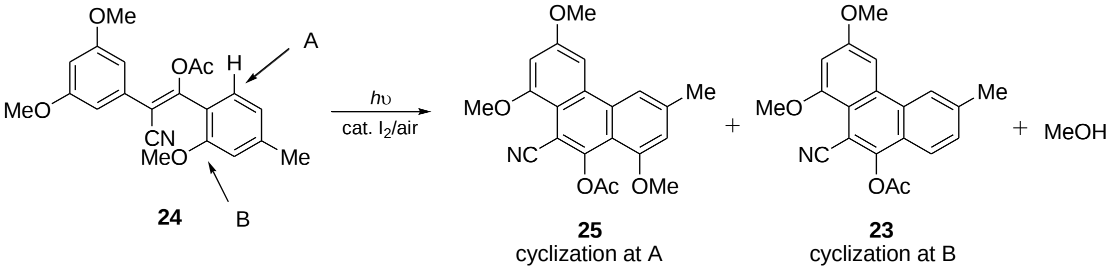
### *C) Elimination Photocyclization of Methoxy substituted stilbenes by catalytic amount of Iodine:*

The $I_2/O_2$ condition occasionally produces significant amount of by-products due to the elimination of *ortho*-methoxy- groups on the stilbenes.[23] Finne and co-workers used this elimination approach for the selective synthesis of phenanthrene by attaching the methoxy group at the *ortho* position of stilbene [**Scheme 10**].[24]



**Scheme 10:** Elimination of either *ortho*-methoxy group gave the same product

If the stilbene has only one *ortho*-methoxy group then there are two possible products after the phocyclization of *ortho*-unsubstituted stilbenes, and the photocyclization will remain selective [**Scheme 11**].

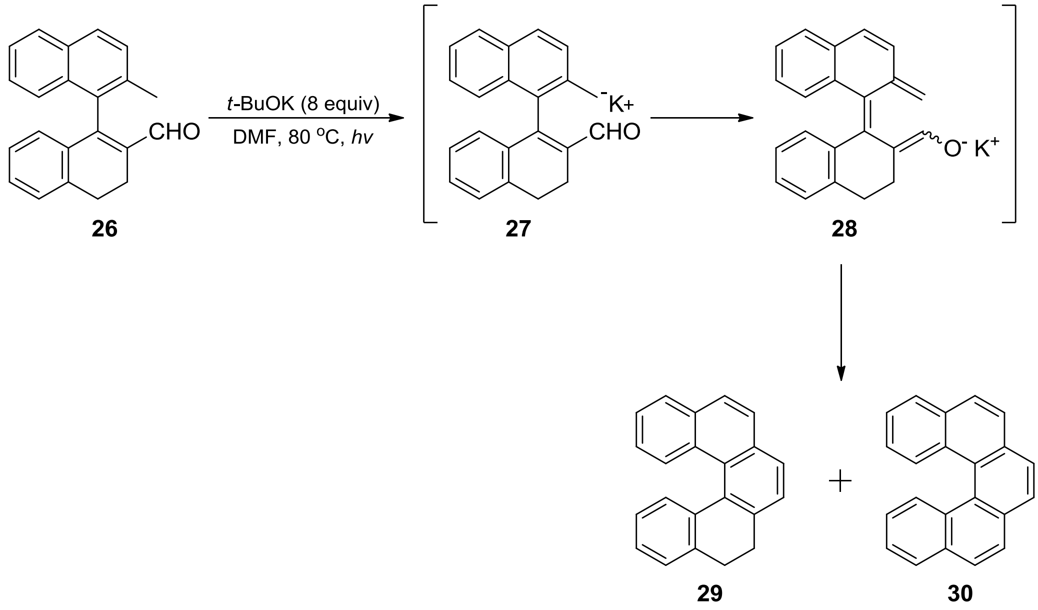


**Scheme 11:** Elimination of either *ortho*-methoxy group or the proton at *ortho*-position gave two different products

*Synthesis of [5]helicene or Pentahelicene by photocyclization through isomerisation by using t-BuOK as a base.*[25,26]

In 2004, de Koning and co-workers described different types of photocyclization methodologies for the preparation of [5]helicene using *t*-BuOk as a base to obtain the product in good yield.[25,26] The synthesis of [5]helicene started with the α-tetralone and treatment with phosphorous tribromide, dimethylformamide in dichloromethane to obtain 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde. The Suzuki coupling of the brominated product with 2-methyl-1-naphthylboronic acid to give 1-(2-methyl-1-naphthyl)-3,4-dihydronaphthalene-2-carbaldehyde as product **26**.

After cyclization with potassium *tert*-butoxide in *N*,*N*-dimethylformamide at 80 °C and irradiation of the reaction mixture for a short time with high pressure mercury lamp to obtain the final product [5]helicene/pentahelicene **30**.



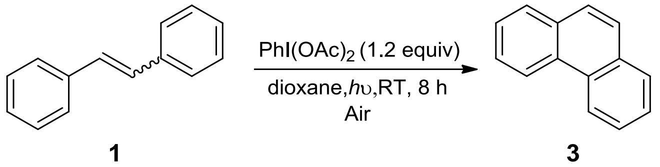
**Scheme 12:** Synthesis of [5]helicene and 5,6-dihydro[5]helicene

The mechanism proposed for the reaction, involves abstraction of a proton of the methyl group by *t*-BuOK to form **27**, followed by its transformation to enolate **28**, which undergoes photocyclization through isomerisation [**Scheme-12**].

*Diacetoxy-iodobenzene is used as oxidant for the photocyclodehydrogenation of the stilbenes:*[27]

Recently, Shi and co-workers reported the photocyclization using the diacetoxy iodobenzene as an oxidant. The method has two approaches reported such as isolation of stilbene and photocyclization of the isolated stilbene and second one is *semi-one-pot* photocyclization of the stilbene using diacetoxy-iodobenzene in dioxane solvent.[27]

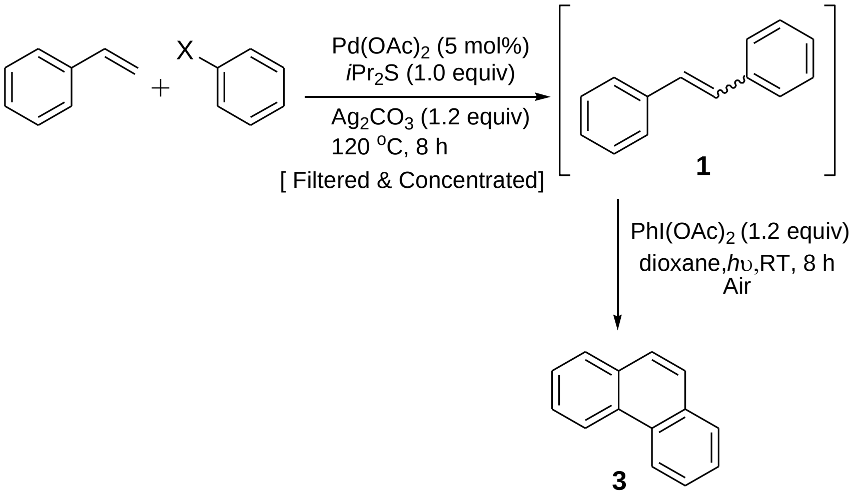
It was observed that the reaction rate was reduced when any radical scavenger is present in the photocyclization indicating towards poosibility of reaction taking pkace involving a radical process [**Scheme-13**].



| Additive 91 equiv) | GC Yield (%) |
|---|---|
| None | 87 |
| TEMPO | 61 |
| AIBN | 38 |

**Scheme 13:** Photocyclization of stilbene using $PhI(OAc)_2$ as oxidant

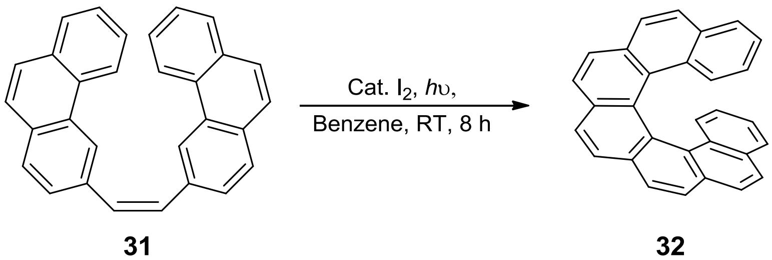
Similarly another method for the synthesis of stilbene involves Mizoroki-Heck reaction and phtocyclization by a *semi-one-pot* sequence. The initially formed stilbene by coupling reaction was subjected to photocyclization reaction without workup of the crude reaction mixture in dioxane irradiated with 500W HPMV lamp to obtain the phenanthrenes **3**. This elegant methodology was found more feasible with the electron deficient substituent than the electron rich substituents [**Scheme-14**].



**Scheme 14:** Photocyclization of stilbene using $PhI(OAc)_2$ as oxidant by *semi-one-pot* approach

## First synthesis of Helicene by Mallory photocyclization approach

Using the basic photocyclization methodologies Martin and co-workers reported the first synthesis of heptahelicene/[7]helicene in 1967.[28] The synthesis of helicene achieved by adopting the Mallory's methodology with a 1,2-di(phenanthrene-3-yl)ethene **31** and catalytic amount of iodine in benzene under the irradiation with HPMV lamp to obtain [7]helicene **32** [**Scheme-15**].



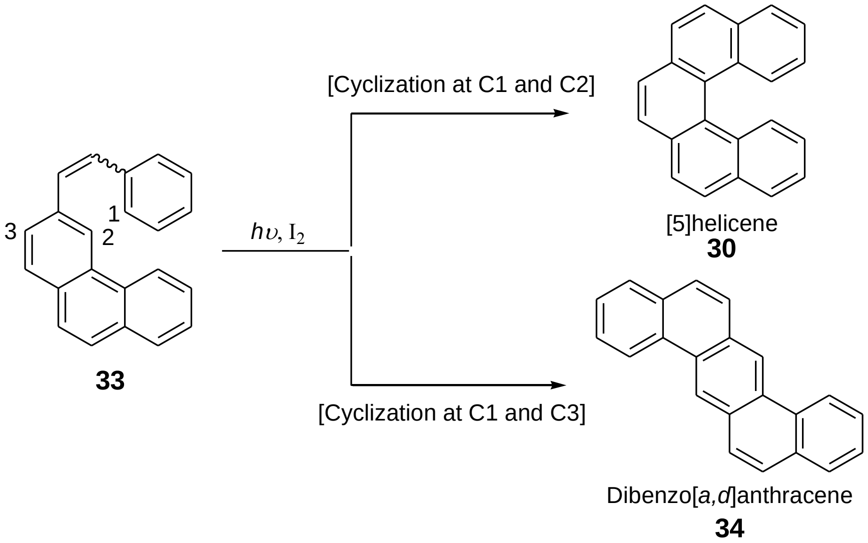
**31** **32**

**Scheme 15:** The first synthesis of [7]helicene **32** by phocyclization methodology

Since this landmark synthesis the photocyclization process has become one of the most important methods for the preparation of many helicene homologous and derivatives, The main advantage is an easy access to the precursors by Wittig olefination or the Mizoroki-Heck coupling reactions. Combination of easy access and subsequent feasible cyclization has led to many synthesis of helicenes.[29]

Importantly two aspects of the process need to be considered while attempting to extend this methodology for higher helicenes:

(I) Photocyclization can take place at either the 2- or the 3- position of the precursor **33**, for example, resulting in isomers which are sometimes difficult to separate [**Scheme-16**].[29]

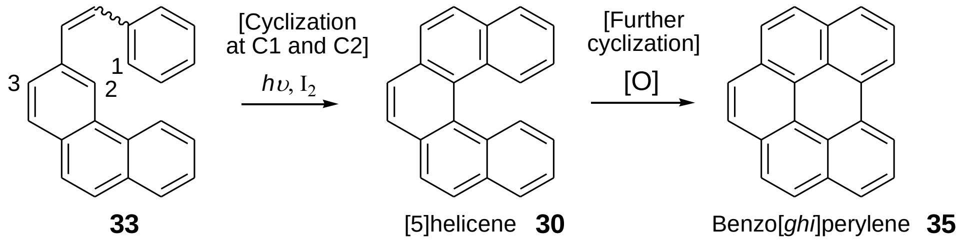


**Scheme 16:** Two ways of the photosynthesis of helicene precursors

The selectivity of the reaction sites during the photocyclization have been studied by the HMO theory. For the appropriate atoms, *r* and *s*, in excited state cyclization, Scholtz, Muhlstadt and Dietz proposed the free valance (*F*r*) and the localization energy (*L*r,s*) methods as means of analysis.[29f]

Laarhoven and co-workers[29g] demonstrated that (a) photodehydrocyclizations do not occur unless $\Sigma F^* > 1.0$, and (b) other products may be formed if $\Delta\Sigma < 0.1$ for different cyclization processes. In the absence of HMO calculations, a simple empirical rule to predict the major product is that the preferred route of isomer is the one that forms the largest number of the benzene rings in the structure.[29h] Experimental studies with highly dilute solutions (to avoid intermolecular dimerisation), resemble the systems studied theoretically, have been reported by Mattay and co-workers.[29e]

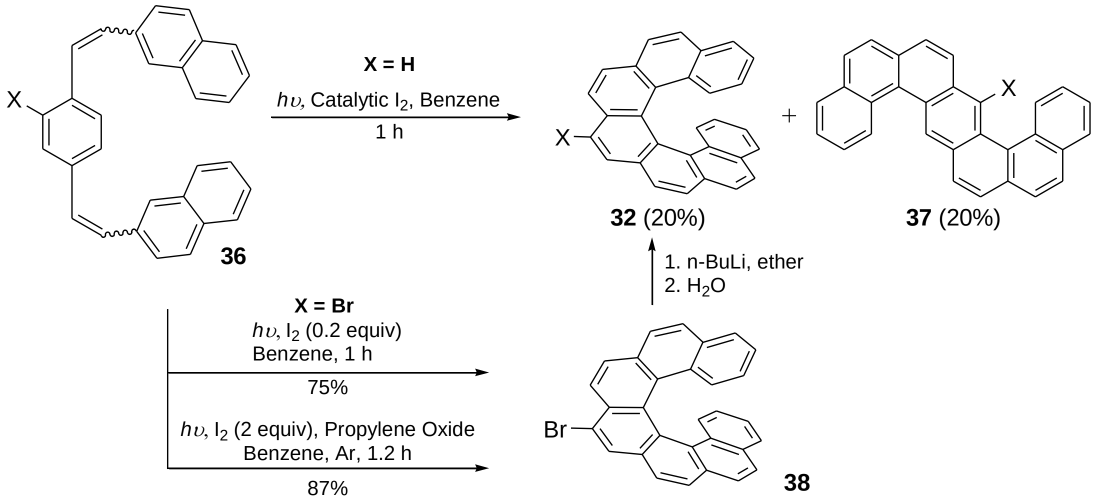
(II) The HI produced by the cyclization reaction might cause reduction of the double bond.[29] In some cases, further cyclization of the newly formed helicene has been found to occur.[5,29,30]



**Scheme 17:** Further photocyclization occurs during the synthesis of [5]helicene

## Bromine is used as directing group in photocyclization of stilbenes:

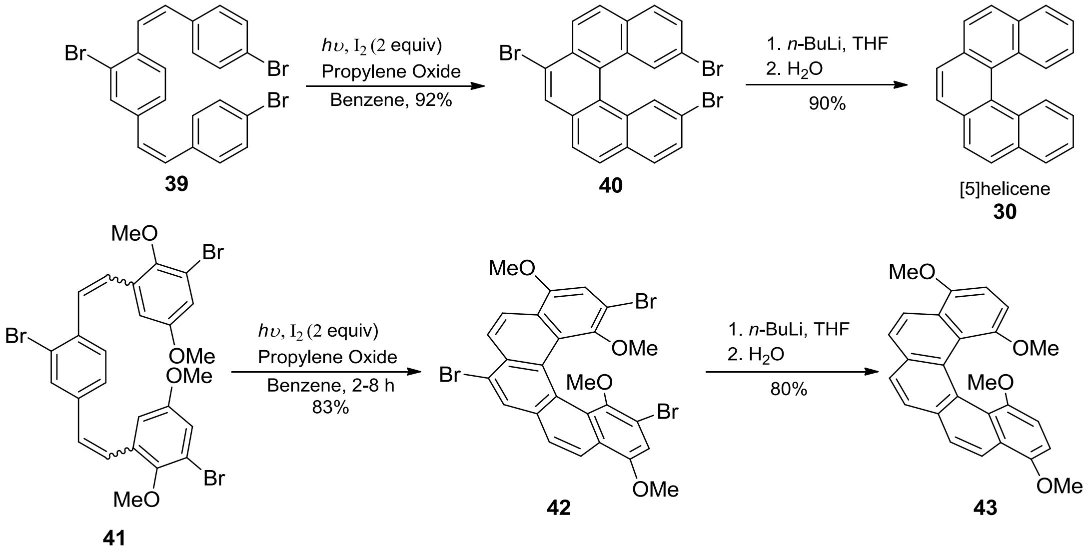
In the above discussion (I), the two way cyclization is possible due to the steric interaction and in order to control the regioselectivity, Katz and co-workers developed an efficient bromine-directed phototcyclization method[31] in which the helicene can be produced in good yield by selectively directing the cyclization [**Scheme-18**]. In this scheme due to the bromine the *ortho*-position of benzene ring was protected and the helicene was exclusively formed while the angular product **37** was not synthesized during the phocyclization. In a way the bromine was present as a protecting group at the neighbouring carbon. Subsequently this bromine could be exchanged after photocyclization using the n-BuLi and a hydrogen source.



**Scheme 18:** Bromine directed synthesis of [7]helicene

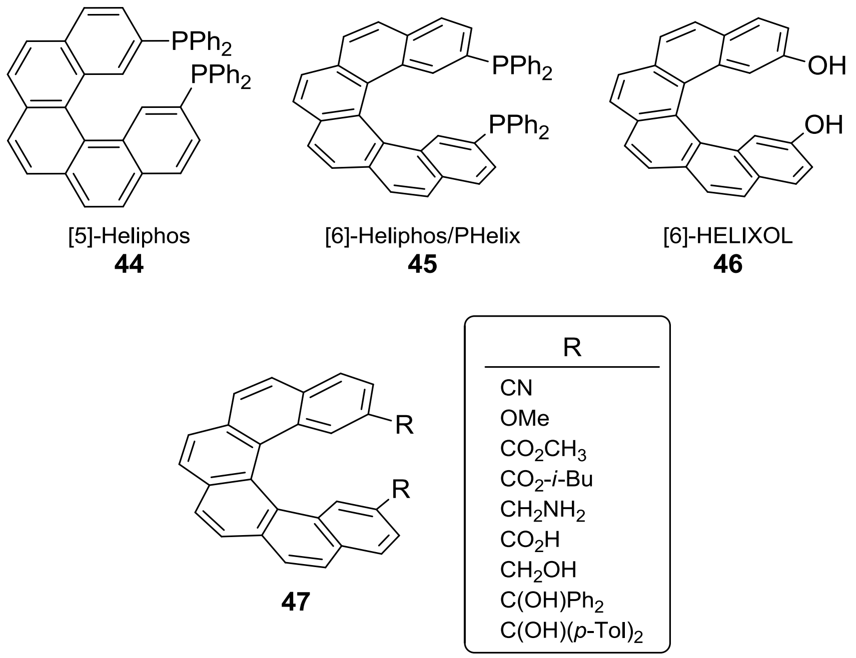
The use of bromine substituent on benzene ring to direct photocyclizations away from its *ortho*- position was a significant observation. Using this information

Katz and co-workers have synthesized [5]helicene using bromine as a proctecting group of *ortho* position [**Scheme-19**]. Also this principle prevents [5]helicenes from further cyclization towards perylene. Interestingly the presence of bromine also prevented elimination of methoxy group during photocyclizing as in case of **41**. This approach makes it possible to achieve the photosynthesis of [5]helicene **30** and its tetramethoxy-derivative **43**.



**Scheme 19:** Bromine directed synthesis of [5]helicene and tetramethoxy[5]helicene

Out of these methodologies the Katz's method is the most popular way for the synthesis of helicene. Using this methodology several important helical compounds were synthesized such as, helical phosphane ligands-heliphos used in asymmetric catalysis, prepared independently by Brunner's group.[32] In 1997 Reetz's group also synthesized the Heliphos/PHelix **44**, **45** by photocyclization methodology, the ligands successfully used in the rhodium catalysed asymmetric hydrogenation.[33] Further in 2001, Reetz and Sostmann introduced the another important helical ligand [6]HELIXOL **46**.[34] Similarly other helicene derivatives have also been synthesized by Katz's photocyclization methodology[35] using propylene oxide as HI scavenger, [**Figure-1**].



[5]-Heliphos
**44**

[6]-Heliphos/PHelix
**45**

[6]-HELIXOL
**46**

**47**

R
CN
OMe
$CO_2CH_3$
$CO_2$-*i*-Bu
$CH_2NH_2$
$CO_2H$
$CH_2OH$
$C(OH)Ph_2$
$C(OH)(p\text{-Tol})_2$

**Figure 1:** Some disubstituted helicenes by Katz's photocyclization methodology

## Synthesis of heterohelicenes by photocyclization methodologies in the presence and absence of scavenger:

Similar to the synthesis of carbohelicenes, photoinduced synthetic routes based on several modified stilbene-type precursors [**Figure-2**] have been widely used for the synthesis of heterohelicenes. However, there are some differences between the two cases because the heteroatoms on the aryl moieties can have an effect on the reactions.[36]

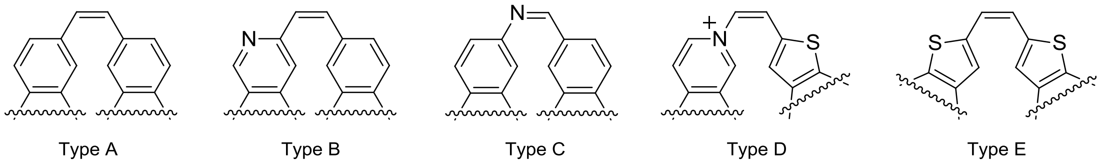


**Figure 2:** Different types of stilbene precursors for photocyclization

For example, in type B, the nitrogen atom can direct the ring closure to occur at the carbon site of the pyridine ring [**Schemes-21**, **22** and **27**] or can become involved in the photocyclization to give a quaternary ammonium cation in the helicene backbone [(**Schemes-25, 29**), (**Figure-3**)]. For types D and E, the low reactivity of the S atom similarly acts as a block, leading to unidirectional ring closure at the *β*-C atom of thiophenes [**Schemes-30, 31**].

The first heterohelicenes/sulphur containing heterohelicene were synthesized by Wijnberg in 1968 using photocyclization methodology.

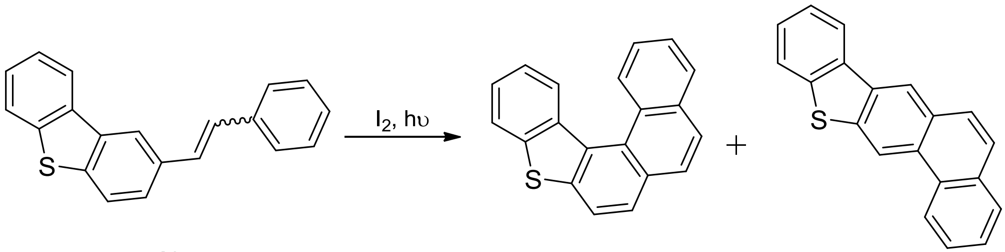
The methodologies based on these observations are presented here.

1) **Type A stilbenes precursor in the synthesis of Heterohelicenes:**

In these reactions, no heteroatom is present in the stilbene portion expected to undergo cyclization, but the molecule possesses hetero-ring in the precursor, which can influence the cyclization process.

A) Synthesis of thiahetero[5]helicene:

Castle and co-workers have synthesized thiahetero[5]helicene **49** by a photocyclization method.[37] Unlike in the preparation of carbo[5]helicene, where the yield of the linear product **50** was negligible,[38,39] reaction of **48** gave two isomers **49** (angular) and **50** (linear) in 50% and 37% yields, respectively [**Scheme-20**].



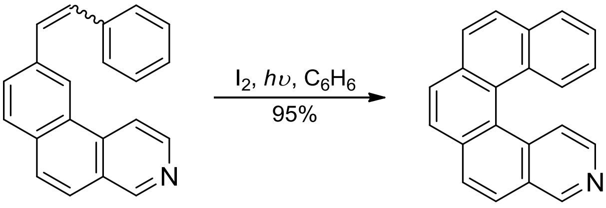
**48** **49** (50%) **50** (37%)

**Scheme 20:** Synthesis of thiahetero[5]helicene by photocyclization

This low regioselectivity might result from the smaller energy gap of the reaction (8.6 kcal/ mol; compared to the energy gap for photocyclization of the corresponding carbohelicene is 17.4 kcal/mol).[40] But in this synthesis there was also possibility of the further cyclization of the [5]helicene **49** to perylene type product.

B) Synthesis of 1-aza[5]helicene and 3-aza[5]helicene**:**

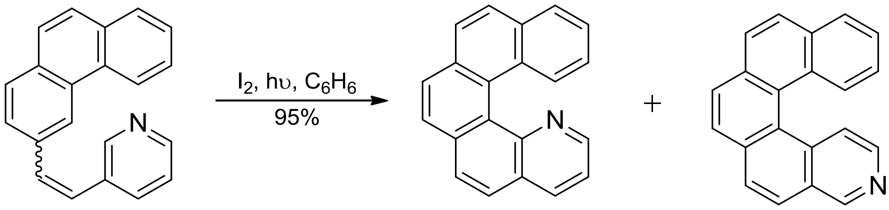
In 2006 Caronna and co-workers reported the synthesis of 3-aza[5]helicene **52** by photocyclization methodology.[40] When the thiophene ring (as in **48**) was replaced by a benzene ring, the selectivity was much better [**Scheme-21**].



**51** **52**

**Scheme 21:** Synthesis of 3-aza[5]helicene by photocyclization

In this reaction the 9-styrylbenzo[*f*]isoquinoline **51** and catalytic amount of iodine in benzene was irradiated in presence of HPMV lamp to give 3-aza[5]helicene **52** in 95% yield. If the reaction was done by different route starting from 3-(2-phenanthren-3-ylvinyl)pyridine **53** as a precursor, then the 3-azahelicene was formed as a minor product and 1-aza[5]helicene **54** was a major product due to the regioselectivity of the nitrogen [**Scheme-22**].



**53**

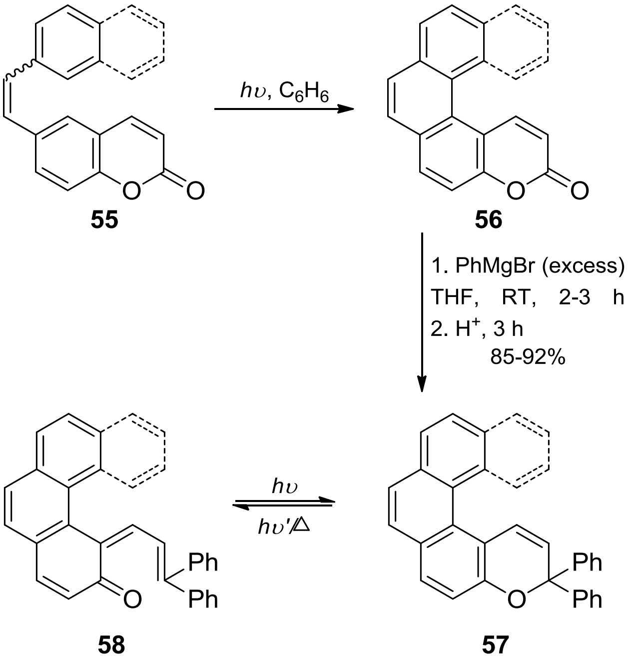
**54** (87%)
Major

**52** (11%)
Minor

**Scheme 22:** Synthesis of azahetero[5]helicene by photocyclization.

C) Synthesis of pyranone annulated [4] and [5]helicenes:

Moorthy and co-workers have recently synthesized the pyranone annulated helicenes by the photocyclodehydrogenation of coumarin stilbenes **55**.[41] The styryl derivative of coumarin was cyclised by passing oxygen through the solution of benzene irradiated in presence of HPMVL. After the completion of the reaction the corresponding pyranone annulated [4]/[5]helicenes **56** was obtained.



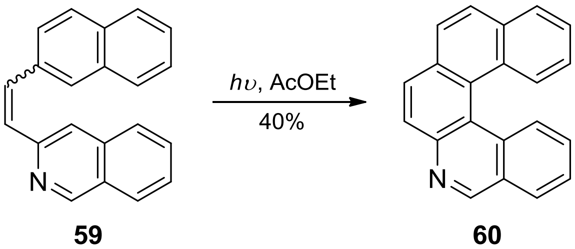
**Scheme 23:** Synthesis of pyranone annulated helicenes by photocyclization

The pyranone was converted to chromene by using excess of Grignard reagent PhMgBr followed by dehydration led to diphenylpyrans (chromones) **57-58**. The authors have further studied the helicity dependence fluorocence properties of the pyranones and chromones.

2) **Type B stilbenes precursor in the synthesis of Heterohelicenes:**

A) Synthesis of 6-aza[5]helicene:

Caronna and co-workers have reported[42] the synthesis of 6-aza[5]helicene **60** by using the 2-(3-isoquinolyl)-1-(2-naphthyl)ethane **59** as a precursor containing the nitrogen at the directing position of the aryl moiety. After the photocyclization in ethyl acetate in open air to form the 6-aza[5]helicene **60** in 40% of yield [**Scheme-24**].

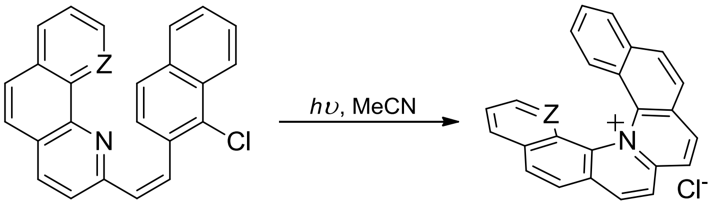


**59** **60**

**Scheme 24:** Synthesis of 6-aza[5]helicene by photocyclization

B) Synthesis of azoniahelicene:

Arai and co-workers developed a novel route to synthesize azoniahelicenes bearing quinolizium systems in moderate yield by photocyclization methodology. The azoniahelicene are expected to have bioactivity.[43]



**61** Z = CH, N

**62** Z = (CH-40%)
(N-32%)

**Scheme 25:** Synthesis of azonia[6]helicene by photocyclization

A solution of (*E*)-2-[2-(1-chloro-2-naphthyl)vinyl]benzo[*h*]quinoline and (*E*)-2-[2-(1-chloro-2-naphthyl)vinyl]-1,10-phenanthroline **61** in acetonitrile was irradiated through an aqueous nickel sulphate filter with 300W HPMV lamp and the reaction monitored by UV spectroscopy. After the suitable workup the yellow solids such as

12c-azonia[6]helicene perchlorate and 12-aza-12c-azonia[6]helicene perchlorate **62** were obtained [**Scheme-25**].

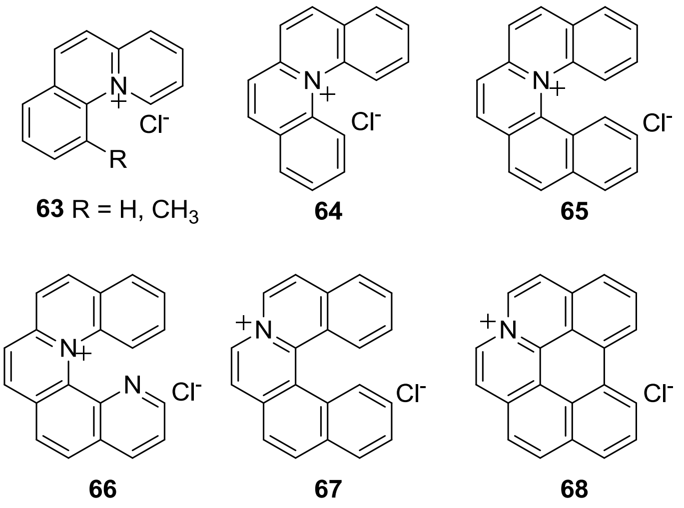
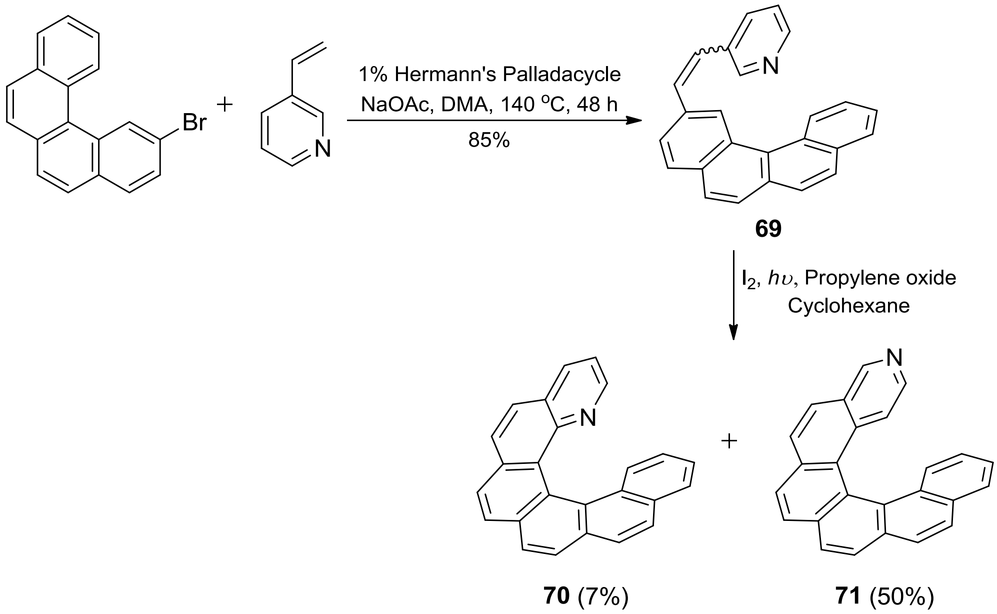


**Figure 3:** Derivatives of azoniahelicenes synthesized by photocyclization methodology

Using this methodology the authors have synthesized derivatives of azonia helicenes such as phenanthrenes, benzo[*c*]phenanthrene and [5]helicenes [**Figure-3**].[43]

C) Synthesis of 3-aza[6]helicene and 1-aza[6]helicene:

Recently, Hassine and co-workers utilized *β*-styrylpyridine as one aryl moiety to give two helicene isomers **70** and **71** after Mizoroki-Heck coupling and the Katz's methodology for the photocyclization [**Scheme-36**].[44]



**Scheme 26:** Synthesis of 1-aza[6]helicene and 3-aza[6]helicene

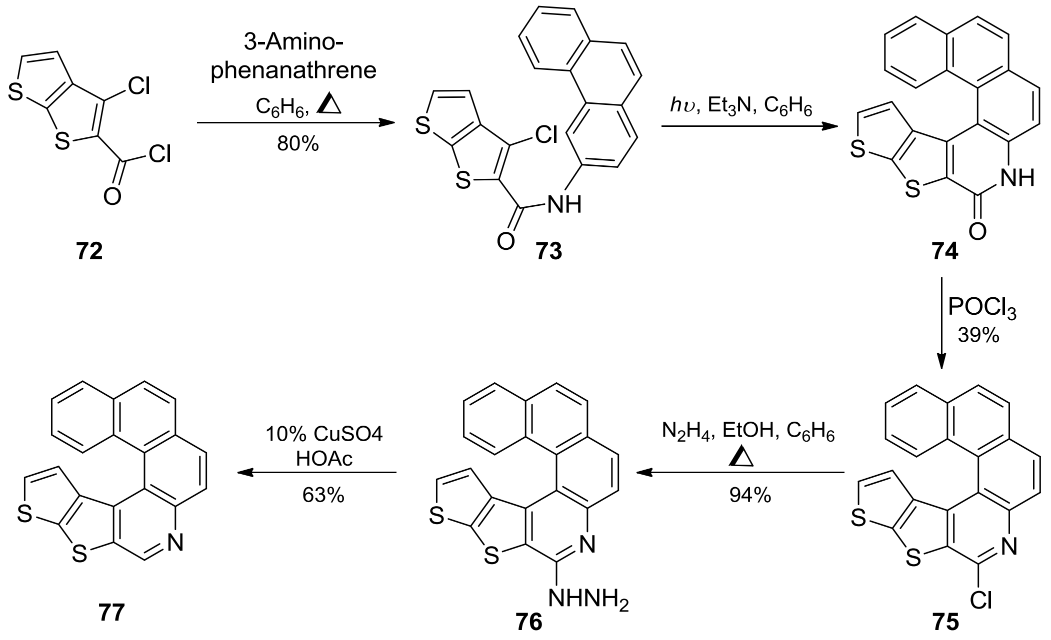
These three reactions clearly show that the nitrogen atom in the type **B** precursors can play different roles as a blocking group, as a participant in the cyclization, or as a regulator to control the regioselectivity.

3) **Type C stilbenes precursor in the synthesis of Heterohelicenes:**

The type **C** stilbenes have been less commonly utilized for the synthesis of heterohelicenes by photocyclization methodology. Only two successful syntheses of stilbenoid precursors by isomerization of amides have been described in the literature.

A) Synthesis of thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]quinoline **77**:

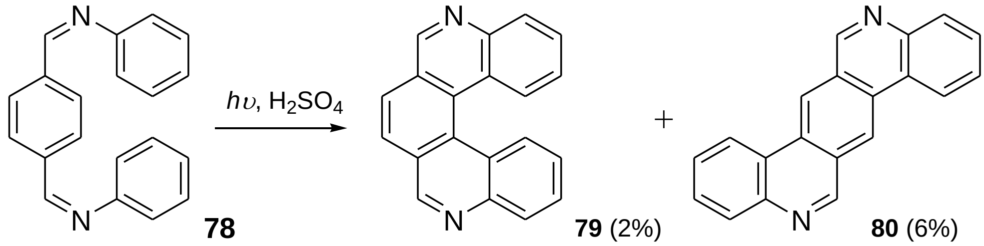
In 1997, Castle and co-workers synthesized[45] thieno[3',2':4,5]thieno[2,3-*c*]naphtha- [1,2-*f*]quinoline **77** as a heterohelicene by photocyclization as the key step in this synthesis. The compound 3-chloro-*N*-(3-phenantryl)thieno[2,3-b]thiophene-2-carboxamode **73** on irradiation by HPMV lamp in presence of triethylamine in benzene to obtain the key product thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]quinoline-6(5*H*)-one **74**, which was converted to heterohelicene **77** with several steps [**Scheme-27**].



**Scheme 27:** Synthesis of thieno[3',2':4,5]thieno[2,3-*c*]naphtho[1,2-*f*]quinoline

B) Synthesis of 5,10-diaza[5]helicene **79** and quinolino[4,3,*j*]phenanthridine **80**:

Caronna and co-workers performed the ring closure of the Schiff base **78** under acidic conditions using strong acid $H_2SO_4$ and irradiated in HPMV lamp to find that the yield of 5,10diaza[5]helicene **79** and quinolino[4,3,j]phenanthridine **80** was low [**Scheme-28**].[46]

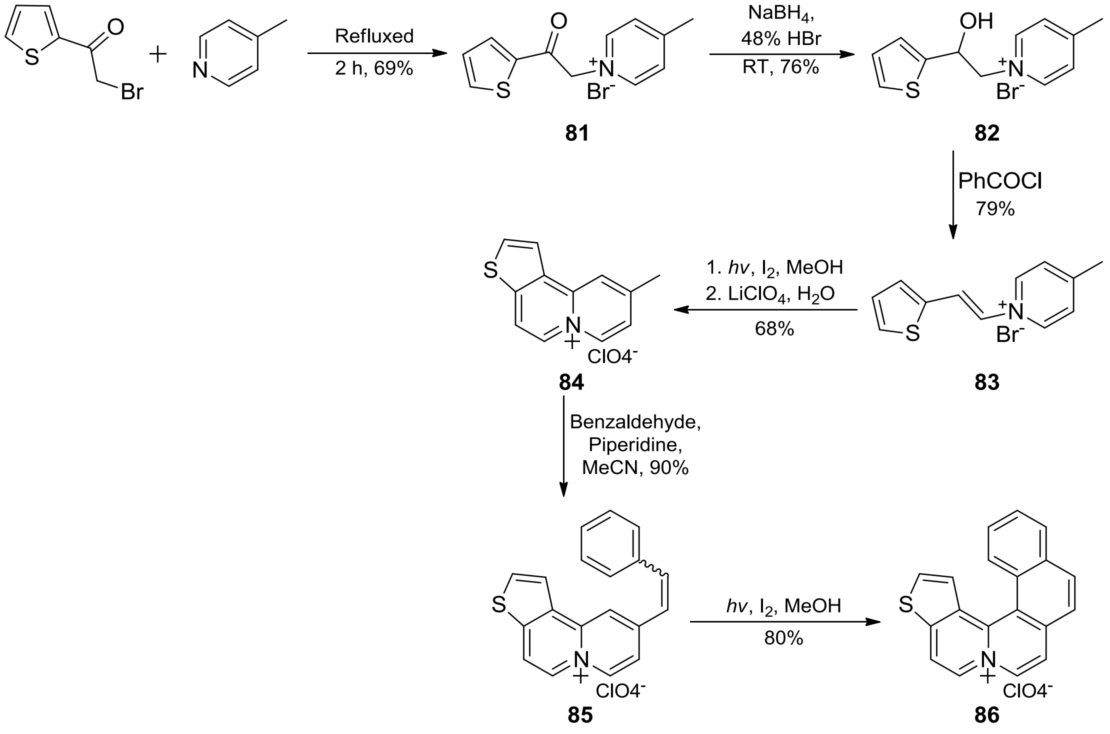


**Scheme 28:** Synthesis of 5,10-diaza[5]helicene and quinolino[4,3,*j*]phenanthridine

4) **Type D stilbenes precursor in the synthesis of Heterohelicenes:**

A) <u>Synthesis of azonia[5]helicenes containing terminal thiophene ring such as 5a-azonia-3-thia[5]helicene perchlorate:</u>

Arai and co-workers reported the new type of stilbene-like precursor for the synthesis of helicenes bearing bridgehead quaternary nitrogen atoms at the periphery of the helical structure [**Scheme-29**].[47]



**Scheme 29:** Synthesis of 5a-azonia-3-thia[5]helicene perchlorate by photocyclization method

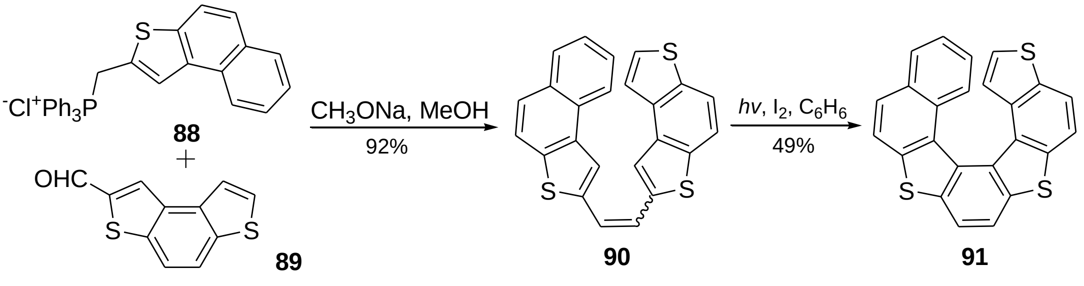
After reduction and elimination, the quaternary ammonium salt was transformed into a stilbene-type structure, which underwent photoinduced ring closure in the presence of iodine in methanol as solvent to give compound 9-methylthieno[3,2-*a*]quinolizinium perchorate **84**. Its reaction with benzaldehyde and piperidine in acetonitrile under reflux condition furnished (*E*)-9-styrythieno[3,2-*a*]quinolizinium perchorate **85**. The styryl compound on photocyclization using catalytic amount of iodine in methanol irradiated by 450 W HPMV lamp gave the product 5a-azonia-3-thia[5]helicene perchlorate **86**, using this methodology the synthesis of 5a-azonia-1-thia[5]helicene perchlorate is also achieved.

5) **Type E stilbenes precursor in the synthesis of Heterohelicenes:**

Pioneering work on the synthesis of thiaheterohelicenes *via* mono [**Scheme-30**] or double [**Scheme-31**] photocyclization was carried out by Wynberg and co-workers,[48] in which the precursors were prepared by Wittig olefination in moderate to good yields. Since then, a wide variety of thiaheterohelicenes have been prepared by this simple and easy approach.[49,50,51]

### A) *Synthesis of Benzo[e]thieno[3,2-e']benzo[l,2-b,4,3-b']bis[l] benzothiophene/ 3,6,9-trithia[7]helicene by photocyclodehydrogenation methodology:*

In 1970, Wynberg and co-workers have synthesized the trithio[7]helicene by photocyclization methodology [**Scheme-30**].[48] The Wittig olefination reaction of benzo[l,2-*b*: 4,3-*b*']dithiophene-2-carboxaldehyde **89** and 2-triphenyl-phosphoniomethylnaphtho[2,1-*b*] thiophene chloride **88** using sodium methoxide in methanol, to obtain 2-[*β*-(2-naphtho[2,1-*b*]thienyl)vinyl]benzo[l,2-*b*:4,3-*b*'] dithiophene **90** as a precursor for the helicene.

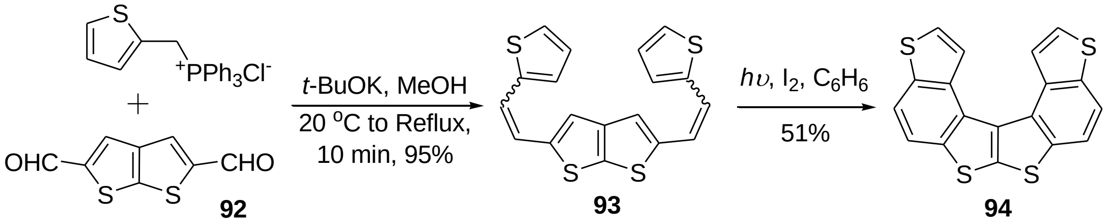


**Scheme 30:** Synthesis of 3,6,9-trithia[7]helicene **91**

The photocyclization of **90** using catalytic amount of iodine in benzene and irradiated in HPMV lamp gave the product benzo[*e*]thieno[3,2-*e*']benzo[l,2-*b*,4,3-*b*']bis[l]benzothiophene/ 3,6,9-trithio[7]helicene **91**. Using similar methodology the authors have synthesized a number of sulphur containing heterohelicenes/thiahelicenes. Its isomers were also resolved by crystal picking method and the changes of the optical rotation with respect to the wavelength were studied on Zeiss polarimeter.

B) *Synthesis of dithieno[3,2-e:3',2'-e'][l]benzothieno[2,3-b][l]benzothiophene/ 3,6,7,10-tetrathio[7]helicene by photocyclodehydrogenation methodology:*

Wynberg and co-workers further explored simultaneous double photocyclization methodology for the construction of thiahelicenes [**Scheme-31**].[48]



**Scheme 31:** Synthesis of 3,6,7,10-tetrathia[6]helicene **94**

The Wittig olefination of thieno[2,3-*b*]thiophene-2,5-dicarboxaldehyde **92** and the ylide from 2-triphenyl phosphoniomethylthiophene bromide gave 2,5-di[*β*-(2-thienyI)vinyl]thieno[2,3-*b*]thiophene **93** as a precursor of helicene. The photocyclisation of **93** in presence of catalytic amount of iodine in benzene gave the product dithieno[3,2-e:3',2'-e'][l]benzothieno[2,3-b][l]benzothiophene/ 3,6,7,10-tetrathio[7]helicene **94**.

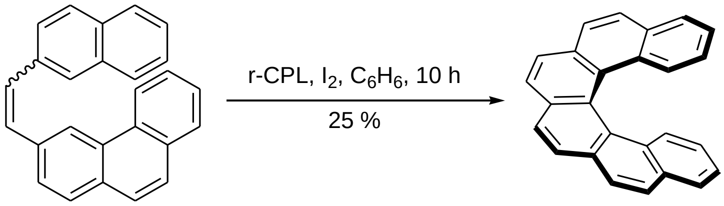
## Asymmetric synthesis of helicenes by photocyclization methododlogy

A) *CPL-Induced Asymmetric Photocyclization:*

The role of the circularly polarised light (CPL) to synthesize optically pure materials was recognized early by Kagan, Kelvin and others. The initial work with CPL involved asymmetric synthesis of helicenes.[52] Three mechanisms for such chirality transfer were proposed: (i) asymmetric photodestruction,[53] in which the enantiomerically enriched helicenes were produced by preferential destruction of the other enantiomer induced by CPL; (ii) partial photoresolution,[54] such that when the racemic dihydrohelicene was initially formed by cyclization, one enantiomer might have a stronger absorption and selectively revert to the starting olefin, thus making the subsequent oxidation slower and leading to optical activity; and (iii) asymmetric synthesis,[55] based on unequal amounts of different conformations of precursors under certain CPL conditions, resulting in enantioenriched products.[52d]

### Synthesis of hexahelicene/[6]helicene by photocyclization using CPL:

Kagan, Buchardt and co-workers synthesized the optically pure or enantioenriched [6]helicenes **96** by using the photochemical methodology.[52] The reaction used the *r*-circularly polarised light (*r*-CPL) by mercury super-high-pressure arc lamp. After focalization with a quartz lens**,** the 290-370 nm band was isolated, using a nickel chloride-cobalt chloride solution[56] as a filter, and then linearly polarized light was obtained with a PL 40 filter (Polacoat, Inc.). Finally circular polarization was achieved by traversing the light beam through an isotrope silica plate, which was made birefractive by compression.



**95**

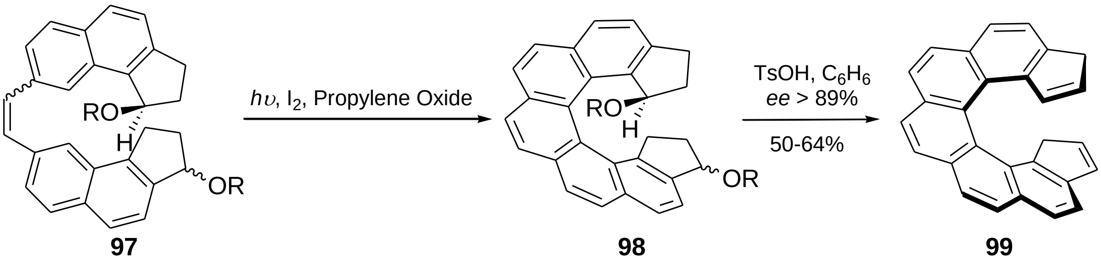
(*M*)-[6]helicene **96**

**Scheme 32:** Asymmetric synthesis of (*M*)-[6]helicene

All irradiations were carried out with a circularly polarized light at 313 nm. And then the *r*-CPL was passed through the olefinic solution for 10 h to obtain the optically active (*M*)-[6]helicene **96**. After the success of this asymmetric synthesis the method was applied for the substituted olefins on phenyl ring and studied their effect.

### B) *Chemically-induced asymmetric photocyclization using Katz method for the synthesis of helicenes:*

Katz and Sudhakar introduced[57] an asymmetric synthesis of helicene by placing a large *tert*-butyl-dimethylsiloxy group at the C(1) position on one terminal ring of **97** which directed the cyclization by keeping the bulky silyloxy substituent outside to lower the activation energy.



**97**
(R = TBDMS)

**98**

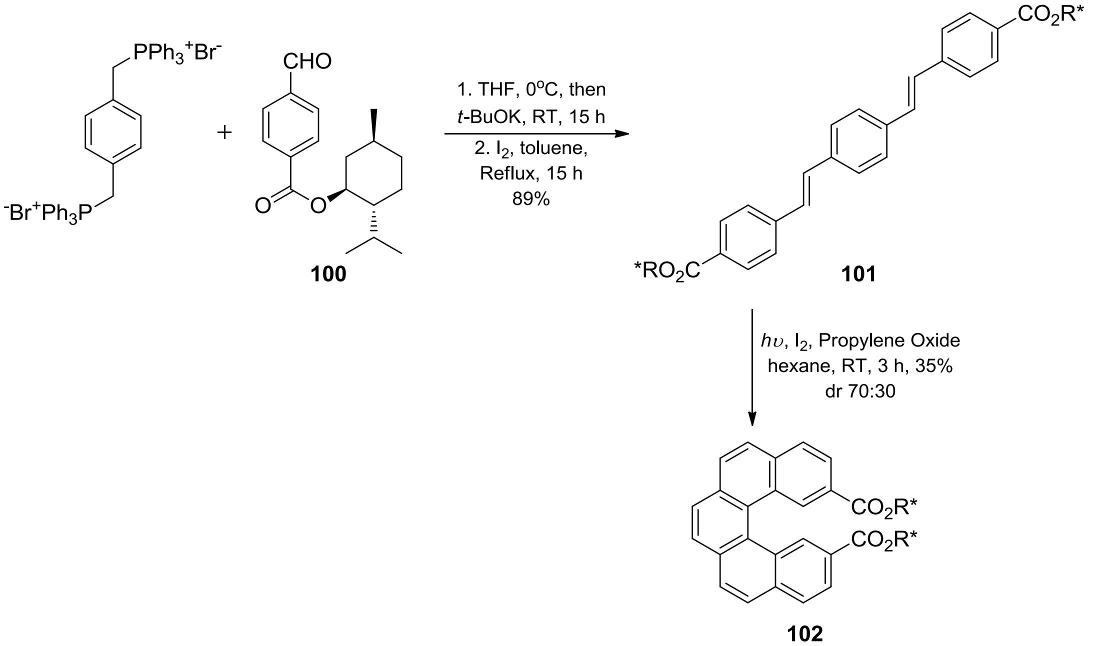
**99**

**Scheme 33:** Asymmetric synthesis of [7]helicene by the photocyclization method

When the stilbene was coiled into a helical structure, (*M*)-helicene **98** bearing two cyclopentadiene moieties was obtained with good yield and enantioselectivity. This can be easily converted to **99** by acid catalyzed eliminations.

*Chemically-induced asymmetric photocyclization using Katz method for the synthesis of distereomeric helicenes:*

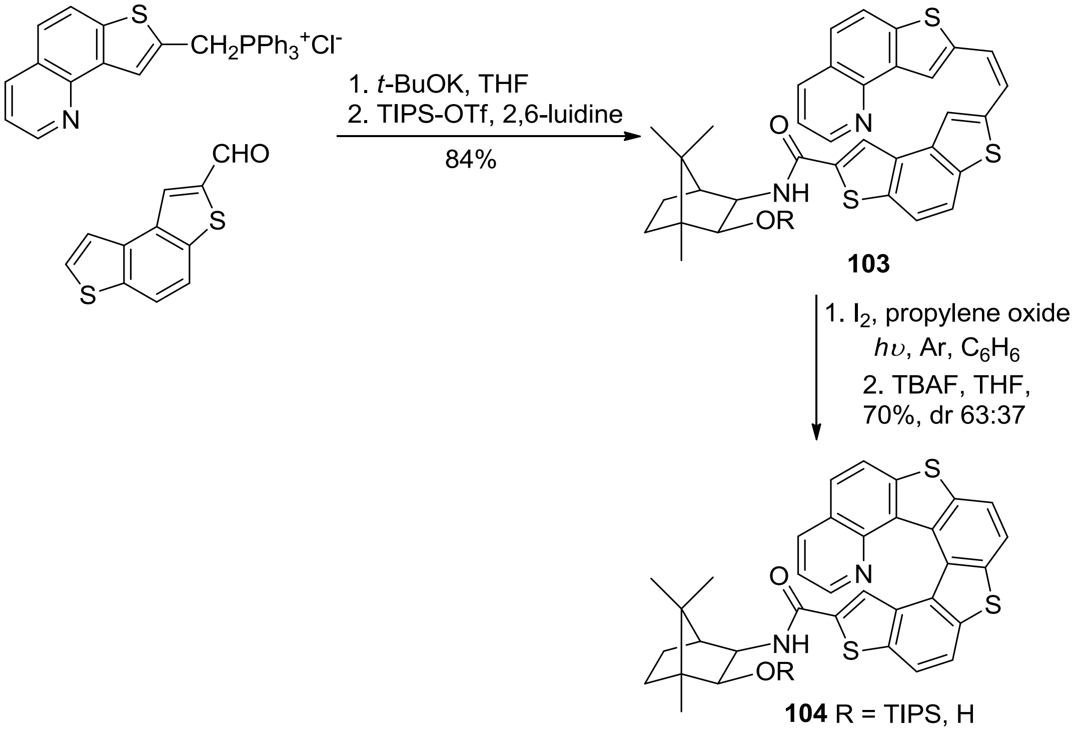
Recently, Carbery and co-workers have reported[58] the asymmetric photosynthesis of helicenes using the Katz photocyclization methodology [**Scheme-34**]. The diastereoselective synthesis of helicenes from the olefins **101** containing two chiral (-)-menthyl groups was achieved. The chiral auxiliary of menthol was able to direct the cyclization during the photosynthesis. In this reaction the authors have used propylene oxide as a scavenger of HI. The menthyl substituted chiral carboxaldehyde **100** and the corresponding Wittig salt was employed for preparation of the olefin **101** as a *cis-trans* mixture. The photocyclization of this olefin **101** converted it to the corresponding diastereomeric helicenes **102**.



**Scheme 34:** Synthesis of diastereomeric [5]helicene

*Chemically-Induced asymmetric photocyclization using Katz method for the synthesis of distereomeric helicenes:*

Using Katz photocyclodehydrogenation methodology Osuga and co-workers[59] utilized 3-amino-2-hydroxyborane as a chiral auxiliary to control the diastereoselectivity for the synthesis of *N*-[(1*R*,2*S*,3*R*,4*S*)-2-(triisopropylsilyloxy)-1,7,7-trimethylbicyclo[2,2,1]heptan-3-yl][1]benzothieno[5',4':2,3][1]benzothieno-[4',5':4,5]thieno[3,2-*f*]-quinoline-2-carboxamide **104** in the photocyclization process. Accordingly, chiral styrene derivative **103** using camphor based auxiliary was built and subjected to Katz method for photocyclization [**Scheme-35**].



**Scheme 35:** Synthesis of diastereomeric heterohelicene

Although the yield was good, the diastereomeric ratio was low, which suggests that only one chiral auxiliary is not sufficient and that a better result might be achieved if the carboxamide unit was at the most sterically hindered position.

# Results and Discussion

In the previous section many methods for the photocyclodehydrogenation were discussed, out of all these the method developed by Katz and co-workers is widely followed for cyclization.

In the classical iodine mediated photocyclodehydrogenation, propylene oxide is used as a scavenger to neutralize the co-product hydrogen iodide.[18] This reagent is expensive and has a low boiling point. In a typical photo reaction even under careful cooling, the reaction mixture warms up which causes the loss of propylene oxide. Thus the disadvantage of using propylene oxide is its low boiling point and high cost. Generally the reaction medium gets slightly warm on irradiation and the low boiling propylene oxide (b.p. 34 °C) escapes from the reaction vessel even if proper cooling is done. Our group has explored the possibility of using THF as an alternative for this purpose.[60] The boiling point of tetrahydrofuran, THF, is relatively high (65-67 °C) and it is less likely to escape during the reaction. The THF is relatively cheap and routinely available in any research laboratory. Tetrahydrofuran is cyclic ether, can get protonated and undergo a ring opening reaction when brought in contact with HI. Hence, with this concept we have explored its use as alternative scavenger of HI in this key photocyclization reaction.

However, the five member cyclic ether of THF is more stable and hence will be less reactive towards the acid catalyzed ring opening with HI. The comparison between the reactivity was investigated by performing an experiment to determine the kinetic parameters. For this study a sample of propylene oxide or tetrahydrofuran was treated with fix and known quantity of HI and the pH of the system was monitored by a digital pH meter. The pH goes on increasing as the HI gets consumed with respect to the time and the graph was plotted to determine the progress [**Figure-4**]. The values of pH are presented in **Table 1** for propylene oxide and for THF. As can be clearly seen both the cyclic ethers do open with HI as the pH is gradually increasing indicating its consumption. It is also apparant from the figure that consumption of HI in case of THF is slower than for propylene oxide, the observation is consistent with the expected higher reactivity of epoxide due to the internal strain. We can conclude by this simple experiment that although THF is slow in reacting with HI, it does open and hence may be used as a scavenger of HI. The low reactivity of THF may be compensated by using it in larger amount.

**Table 1:** Observed pH of reaction of propylene oxide and tetrahydrofuran.

| Time<br>min | HI & propylene oxide<br>pH | HI & tetrahydrofuran<br>pH |
|---|---|---|
| 5 | 2.00 | 1.75 |
| 15 | 2.32 | 1.86 |
| 25 | 2.46 | 1.96 |
| 35 | 2.66 | 2.04 |
| 45 | 2.78 | 2.10 |
| 55 | 2.82 | 2.17 |
| 65 | 2.88 | 2.20 |
| 75 | 2.96 | 2.23 |

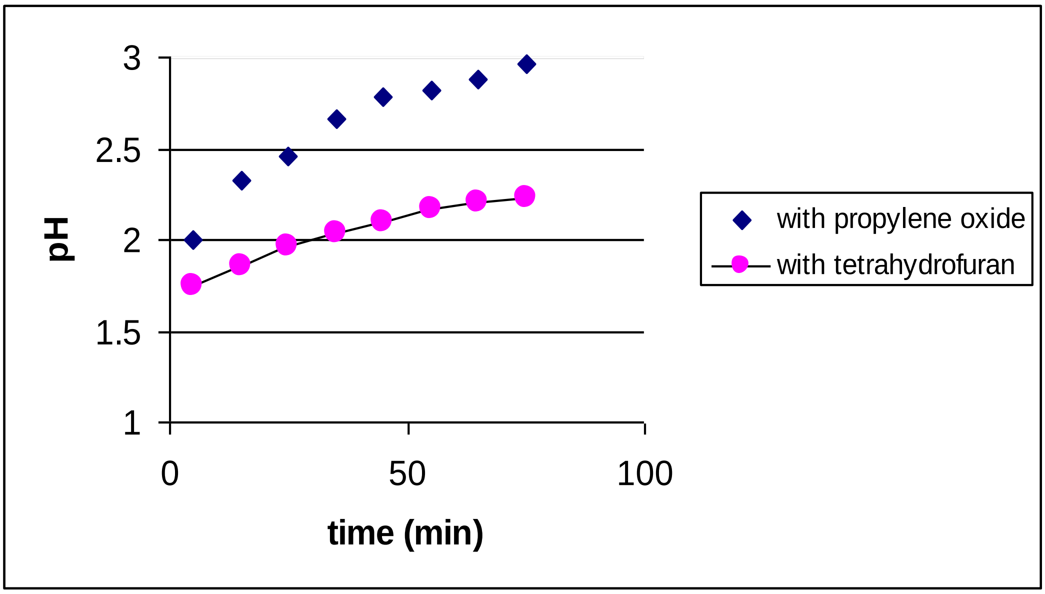
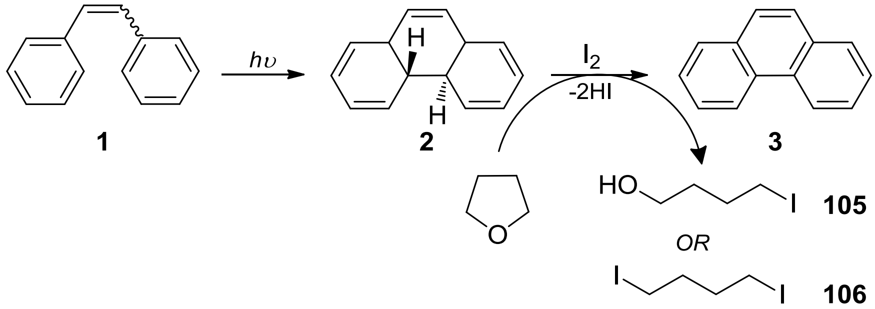


**Figure 4**: Comparison of propylene oxide and tetrahydrofuran as scavenger of HI

The ability of tetrahydrofuran to react with HI is also reported in the literature.[61] The acid promoted opening of tetrahydrofuran when exposed to *in situ* generated HI should give 4-iodobutan-1-ol or 1,4-iodobutane **105, 106**.

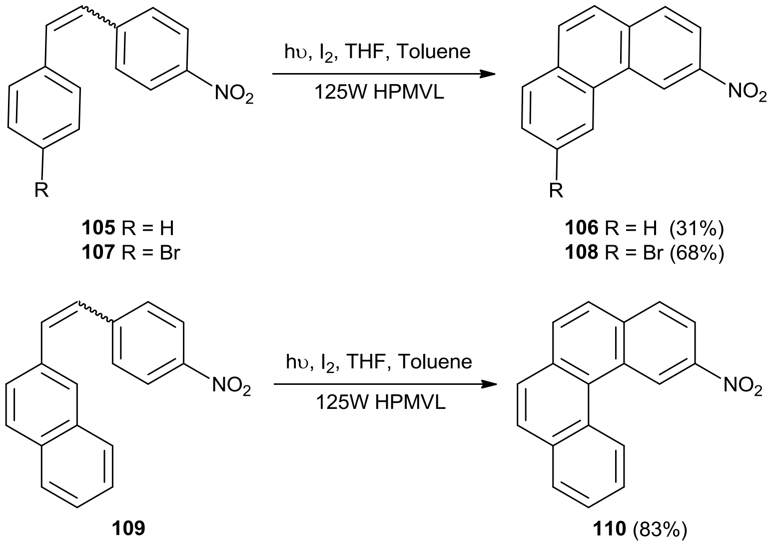
To test this concept a sample of *E*-stilbene was exposed to light from a 125-W high pressure mercury vapor lamp (HPMVL) in a routine immersion well photoreactor with iodine (1.1 equiv), tetrahydrofuran (20 equiv) in toluene for 7 h [**Scheme-36**]. The product formed was separated and identified as phenanthrene (TLC, Mp, and $^1$H-NMR). The isolated yield of **3** was excellent and comparable to the reportedly obtained with oxygen and or with propylene oxide.[2,18]



**Scheme 36:** Synthesis of phenanthrene by using Tetrahydrofuran as a HI scavenger

To the best of our knowledge THF has not been used as HI scavenger in such cases, although occasionally used as a solvent. However, there is a literature reference[62] of the combined use of excess of THF and propylene oxide, where HI should preferentially react with more strained epoxide ring than the former. This means that the THF is actually used only as a solvent and may not work as scavenger of HI in this reported example.[62]

There is a possibility of the oxygen from air to act as oxidant in place of $I_2$ as known from the literature. To test this hypothesis, another experiment was run with carefully degassing the reaction mixture by applying low vacuum, or bubbling $N_2$ gas, and sonication and subjected to photoirradiation. However, the similar result was obtained confirming that $I_2$-THF is the actual reagent for the second step of aromatization. A separate experiment with $I_2$ toluene but without THF was very sluggish, establishing the role of THF to drive the reaction. Encouraged by this result a number of stilbene derivatives were synthesized by Wittig reaction[32,35e] and subjected to the photocyclization under the present, modified conditions, [**Table-2**]. A series of mono- and di-substituted phenanthrenes were obtained after careful chromatography and showed satisfactory $^1$H-NMR analysis. It is noteworthy to have succeeded in photocyclization of nitro-substituted stilbene to the corresponding phenanthrene, which was known to be difficult.[6,63] We found that the presently developed methodology could also tolerate the nitro group, demonstrated by the synthesis of the nitro substituted phenanthrenes **106**, **108** or benzo[*c*]phenanthrene **110** in good isolated yield.



**Scheme 37:** Synthesis of nitro-substituted angularly fused arenes

The results summarised in Table 2 indicate the tolerability of different functional groups for the present conditions and the good to high yield support the possibility to apply this method for practical applications. The photocyclization is extended for the construction of higher members of angularly fused aromatic ring systems, such as [n]helicenes, from the corresponding stilbene derivatives. The present methodology was further explored for the synthesis of benzo[*c*]phenanthrene as well as substituted benzo[*c*]phenanthrenes [**Table-3**].

**Table 2:** Photocyclization of stilbenes with $I_2$-THF:

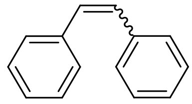
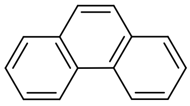
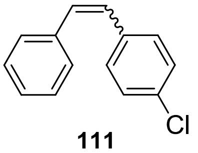
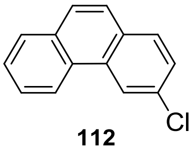
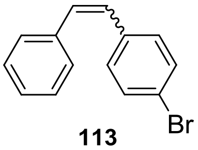
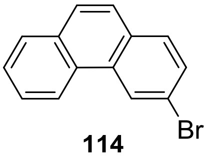
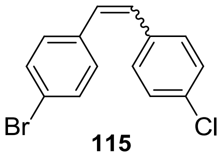
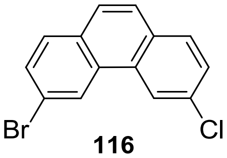
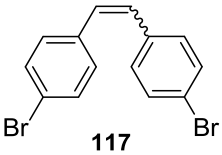
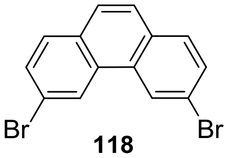
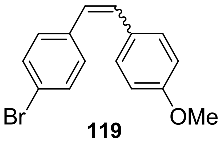
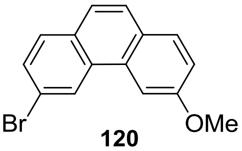
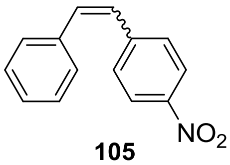
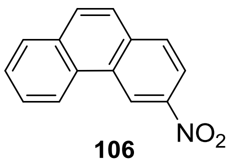
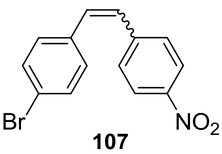
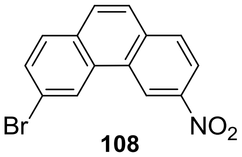
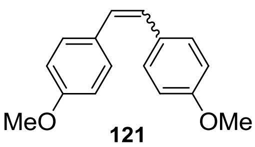
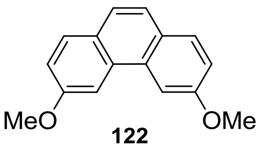
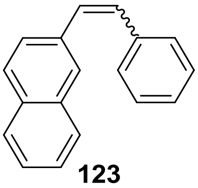
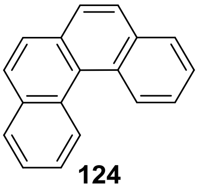
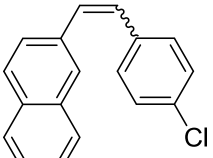
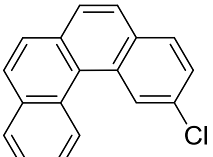
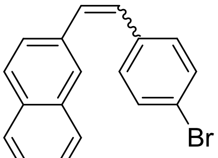
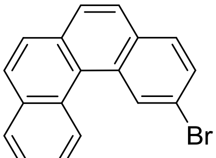
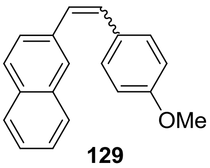
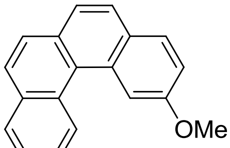
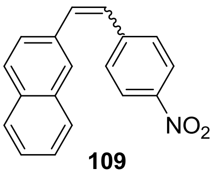
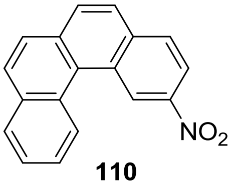
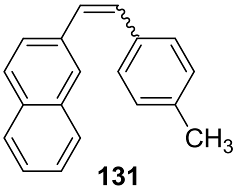
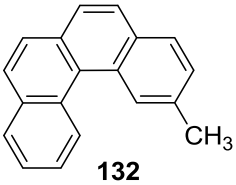
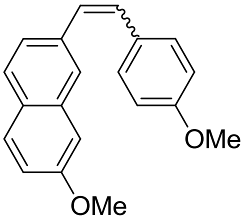
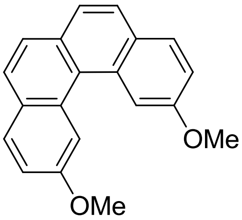
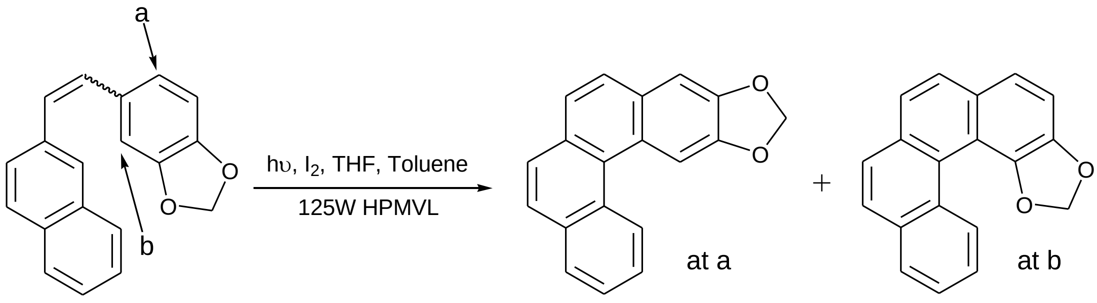
| Entry | Stilbenes | Phenanthrenes | Time/h with 125 W HPMVL | Isolated Yields% [Reported Yield %][ref] | Mp/ °C (Lit.)[ref] |
|---|---|---|---|---|---|
| 1 |  **1** |  **3** | 7 | 98<br>[73][63] | 100-101<br>(98-100)[63] |
| 2 |  **111** |  **112** | 7 | 78<br>[76][63] | 79-81<br>(79-80)[63] |
| 3 |  **113** |  **114** | 20 | 84<br>[76][63] | 80-82<br>(81-83)[63] |
| 4 |  **115** |  **116** | 9 | 83 | 186-188 |
| 5 |  **117** |  **118** | 16 | 97<br>[77][64] | 194<br>(194)[64] |
| 6 |  **119** |  **120** | 40 | 47 | 100-102 |
| 8 |  **105** |  **106** | 36 | 31 | 175-177<br>(175-177)[65] |
| 7 |  **107** |  **108** | 29 | 68 | 234-235 |
| 9 |  **121** |  **122** | 36 | 65 | 104-106<br>(104-105)[66] |

**Table 3:** Photocyclization of *β*-styrylnaphthalenes with $I_2$-THF

| Entry | Stilbenes | benzo[*c*]phenanthrene | Time/h with 125 W HPMVL | Isolated Yields% [Reported Yield %] | Mp/ °C (Lit.) |
|---|---|---|---|---|---|
| 1 |  **123** |  **124** | 13 | 84 | 68-69<br>(67-68)[67] |
| 2 |  **125** |  **126** | 16 | 67 | 62-64[67] |
| 3 |  **127** |  **128** | 20 | 96<br>[78][44] | 87-88<br>(87-88)[44] |
| 4 |  **129** |  **130** | 22 | 75 | 78-80<br>(78-79)[68] |
| 5 |  **109** |  **110** | 23 | 83 | 150-152 |
| 6 |  **131** |  **132** | 20 | 96 | 79-81<br>(79-80)[67] |
| 7 |  **133** |  **134** | 36 | 97 | 138-140 |

The results indicate the usefulness of the present method with efficient synthesis of substituted phenanthrenes and benzo[*c*]phenanthrenes.

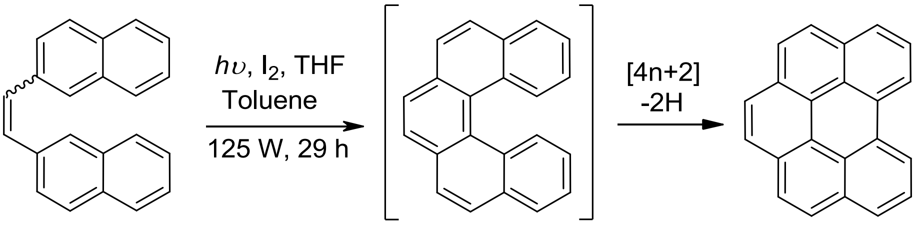
The methodology was further extended for the synthesis for cyclization of another derivative 5-(2-(naphthalen-2-yl)vinyl)benzo[*d*][1,3]dioxole[69] **135**. The cyclization reaction can take place at two sites, "a" or "b" [**Scheme-38**], leading to the formation of **136** and **137** respectively. The cyclization in the present condition resulted in the formation of linear product **136,** established by its $^1$H-NMR. Probably the desired cyclization at "b" site is difficult due to steric constraints.



**135** **136** **137**

**Scheme 38:** Synthesis of benzo[5,6]phenanthro[2,3-*d*][1,3]dioxole

On achieving the synthesis of [4]helicenes or benzo[*c*]phenanthrenes the present method was screened for cyclization of 1,2-bis(2-naphthyl)ethylene **138** with an aim to prepare [5]helicene **30**. However, the initially formed [5]helicene **30** was not isolated but underwent further [4n+2] cyclization to form benzo[*ghi*]perylene **35** in good yield [**Scheme-39**]. The structure of the **35** was confirmed by $^1$H-NMR and by comparing its melting point.[29e,38a,70]

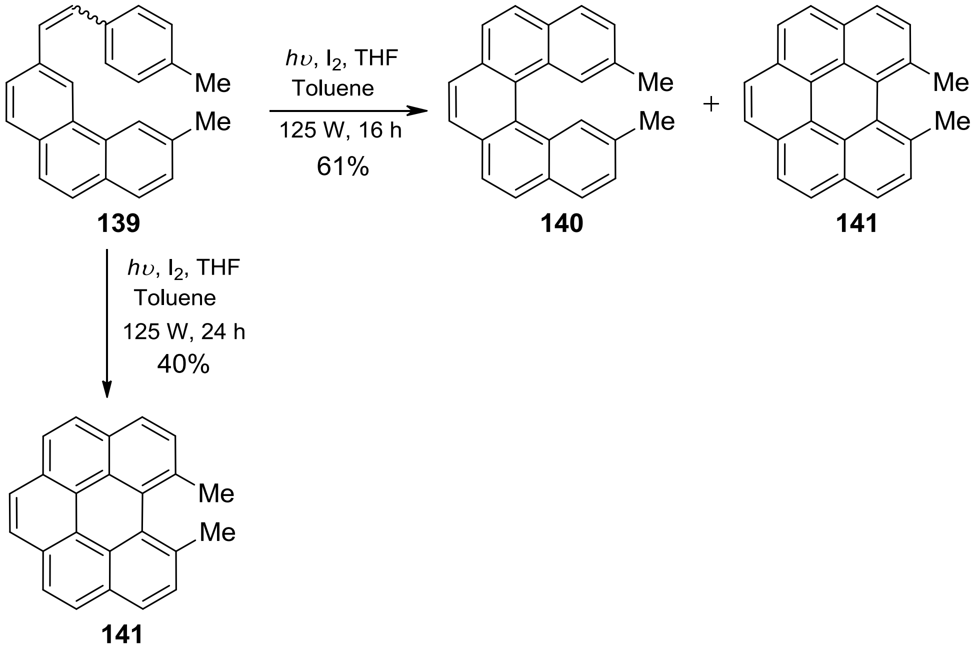


**138** **30** **35** (43%)

**Scheme 39:** Synthesis of benzo[*ghi*]perylene

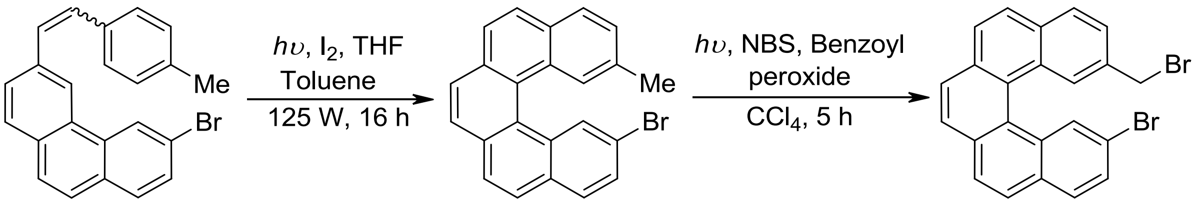
Selective synthesis [5]helicene was not favourable due to further cyclization. Introducing a suitable bulky group such as methyl at appropriate position of stilbene derivative may prevent the undesired second photocyclization step due to steric interaction. Accordingly the stilbene derivative **139** was synthesized and subjected to the photolysis under $I_2$-THF condition and the products obtained were identified as 2,13-dimethyl[5]helicene **140** and 7,8-dimethylbenzo[*ghi*]perylene **141** in the ratio 69:31. However prolonged irradiation (~ 24 h) under the same condition gave **141** as the main product [**Scheme-40**].

In the $^1$H-NMR spectrum of the 7,8-dimethyl[*ghi*]perylene **141** the methyl protons appeared at the δ 2.78, and the $^1$H-NMR spectrum of the mixture of 2,13-dimethyl[5]helicene **140** and 7,8-dimthylbenzo[*ghi*]perylene **141** the methyl signal were seen at δ 2.37 and δ 2.78 ppm respectively. On prolonged irradiation only **141** was detected.



**Scheme 40:** Attempted synthesis of 2,13-dimethyl[5]helicene

Effect of bromine substituents on benzene rings of stilbenes to direct the photocyclization away from their *ortho* positions is already discussed in the earlier section. Based by these observations Katz and co-workers have synthesized [5]helicene using bromine as a protecting group of *ortho*-position.[31] To avoid further [4n+2] photocyclization in the synthesis of [5]helicene and to check the feasibility of our method with this concept we have synthesized 2-bromo-13-methyl[5]helicene[71] **143** using $I_2$-THF methodology.

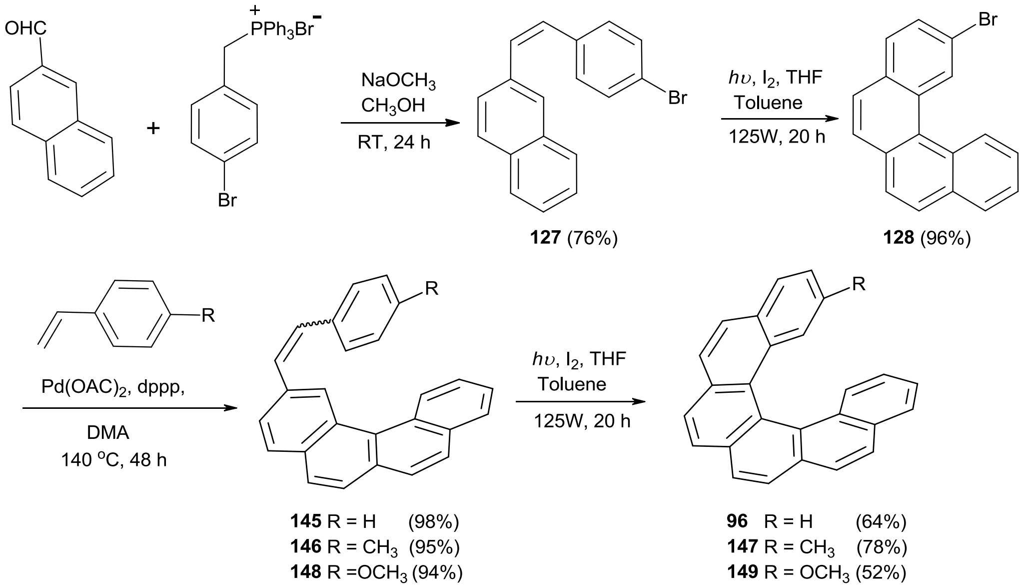


**142** **143** (61%) **144** (39%)

**Scheme 41:** Synthesis of 2-bromo-13-methyl[5]helicene **143** by $I_2$-THF Method and 2-bromo-13-(bromomethyl)-[5]helicene **144**

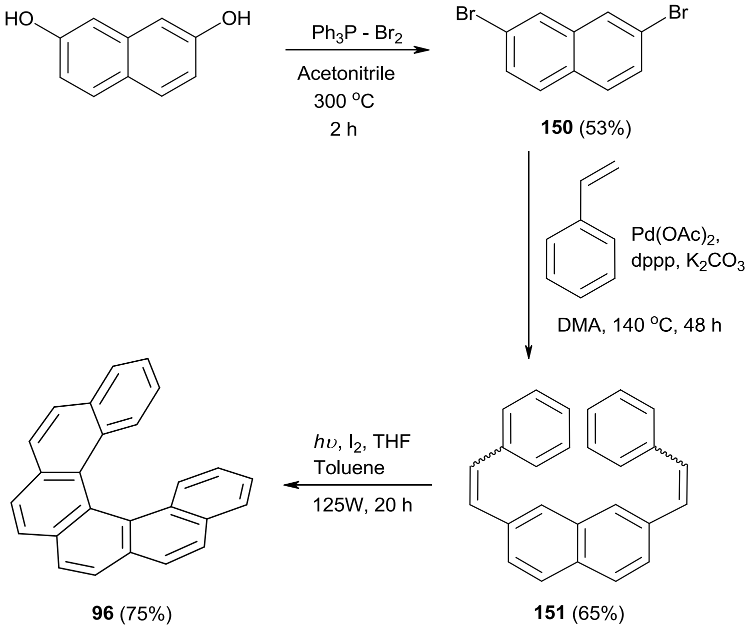
On achieving the synthesis of 2-bromo-13-methyl[5]helicene **143**, it was converted to the 2-bromo-13-(bromomethyl)-[5]helicene **144** by the side chain bromination with *N*-bomosuccinimide, benzoyl peroxide under the irradiation of tungsten lamp [**Scheme-41**]. The $^1$H-NMR of the compound **144** shows the protons of -$CH_2$ group are separated in the spectrum due to the effect of the helical shape of the molecule. There is a possibility that these protons are out of the plane of the molecule. In the spectrum one proton is observed at δ 4.59 as doublet ($J$ = 10 Hz) and second one is obtained at 4.49 also as a doublet ($J$ = 10 Hz) in the $^1$H-NMR spectrum.

The modified method was further extended for the synthesis of higher helicenes. Based on the previous results, some derivatives of [6]helicene have been synthesized as shown in **Scheme-42**. Readily accessible 2-naphthaldehyde was converted into 2-(4- bromostyryl)naphthalene **127** by reaction with the Wittig salt (4-bromobenzyl)triphenyl phosphonium bromide under standard conditions. The photodehydrocyclization of **127** in toluene with iodine-THF gave 2-bromobenzo[*c*]phenanthrene **128** in high yield. Reaction of **128** with styrene, 4-methylstyrene and 4-methoxystyrene using well-known Pd•dppp catalyzed Heck reaction[72] resulted into 2-styrylbenzo[*c*]phenanthrene **145**,[73] 3-(4-methylstyryl)benzo[*c*]phenanthrene **146**[74] and 3-(4-methoxystyryl)benzo[*c*]-phenanthrene **148**[75] respectively in excellent yield. Further photoirradiation of **145**, **146** and **148** under the present reaction condition furnished [6]helicene **96**,[29g] 2-methyl[6]helicene **147**[76] and 2-methoxy[6]helicene **149**[77] respectively in good to excellent yield.



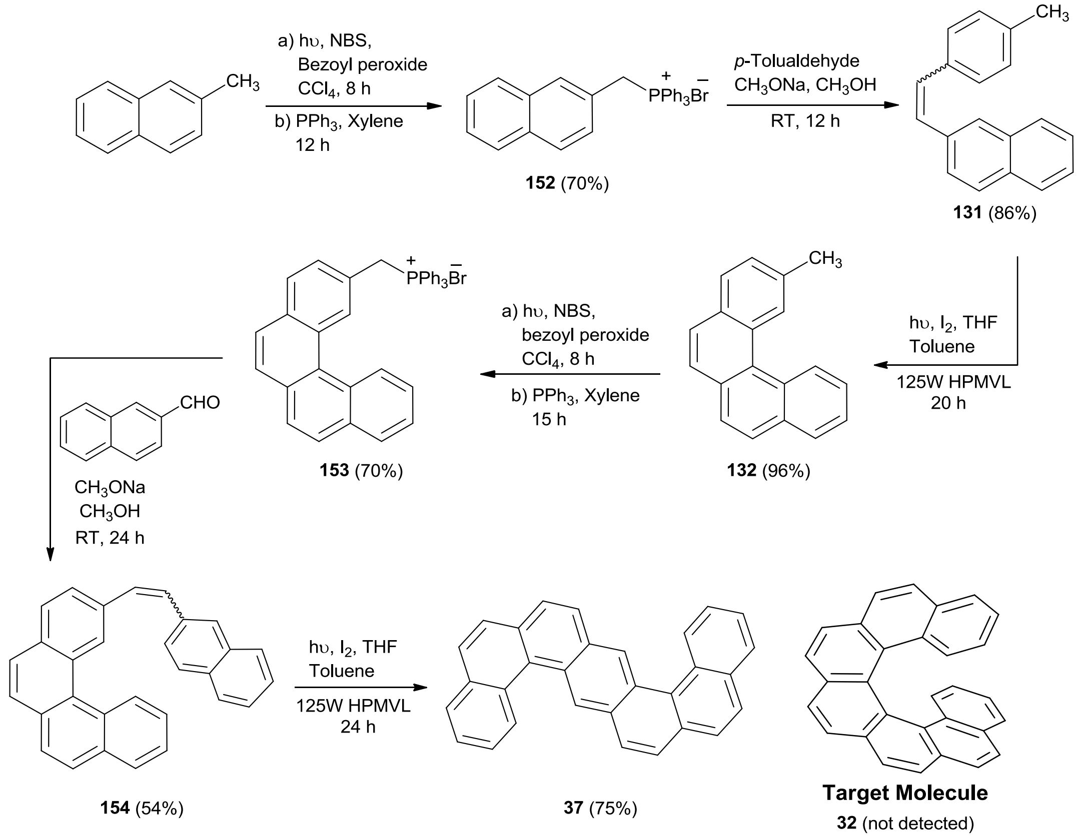
**Scheme 42:** Synthesis of [6]helicene and its derivatives by $I_2$-THF Methodology

Alternatively the synthesis of [6]helicene **96** was achieved by a double photocyclization process utilizing the $I_2$-THF methodology. For the cascade photodehydrocyclization the substrate 2,7-bis-styrylnaphthalene was synthesized by Mizoroki-Heck reaction. This new route is presented in **Scheme-43**, where initially 2,7- dihydroxynaphthalene was converted into the corresponding 2,7-dibromonaphthalene **150**, which was reacted with styrene under Mizoroki-Heck conditions with Pd•dppp to afford 2,7-bis-styrylnaphthalene **151**.[78] This was then subjected to the photodehydrocyclization to afford [6]helicene **96** in a single step.



**Scheme 43:** Synthesis of [6]helicene by double photocyclization using $I_2$-THF method

The method is further applied for the syntheses of [7]helicene and the synthetic route is outlined in **Scheme-44**. The readily available 2-methylnaphthalene was converted to its Wittig salt **152** *via* benzylic bromination with NBS, and its reaction with triphenylphosphine. The ylide was generated from salt **152**, which on Wittig reaction with 4-tolualdehyde gave 2-(4-methylstyryl)naphthalene **131** in good yield, mostly as the *E* isomer, which upon photoirradiation ($I_2$-THF) resulted into formation of 2-methylbenzo[*c*]phenanthrene **132**. Similarly **132** was converted to the new Wittig salt **153**,[79] *via* its bromomethyl derivative. Standard Wittig reaction of **153** with 2-naphthaldehyde gave 2-(2-vinylnaphthyl)benzo[*c*]phenanthrene **154**[80] in 54% of yield, predominantly in the *E* form. However, the photodehydrocyclization of **154** led to an unexpected result. The ring closure was directed to the less crowded site yielding the linear derivative, dinaphtho[1,2-*a*:2',1'-*h*]anthracene **37** instead of the expected [7]helicene **32**. The structure of compound **37** was established by comparison of spectroscopic data and its melting point.[80]



**Scheme 44:** Unexpected synthesis of dinaphtho[1,2-*a*:2',1'-*h*]anthracene by $I_2$-THF method

Two possible routes of the cyclization are shown in the **Figure-5** leading to photocyclization of 2-(2-vinylnaphthyl)benzo[*c*]phenanthrene **154**. Cyclization by route “a” (**Site a**) is feasible only due to the steric interaction within the molecule. The targeted molecule [7]helicene **32** was not formed as the route “b” was not followed due to steric crowding. The presence of bulky naphthalene ring may have prevented cyclization of **154** at the required angular location.

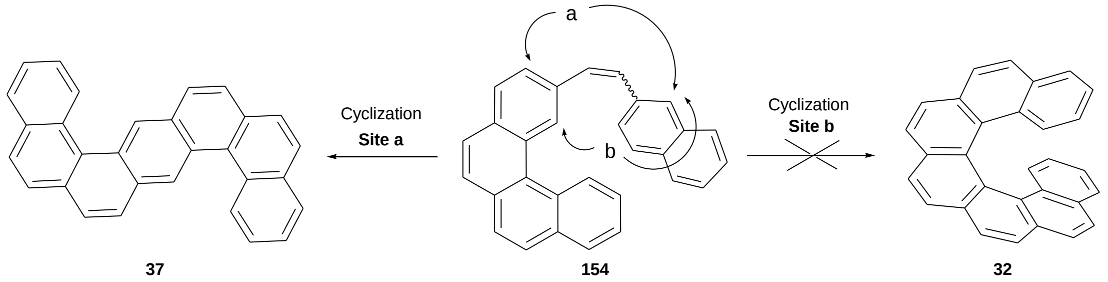
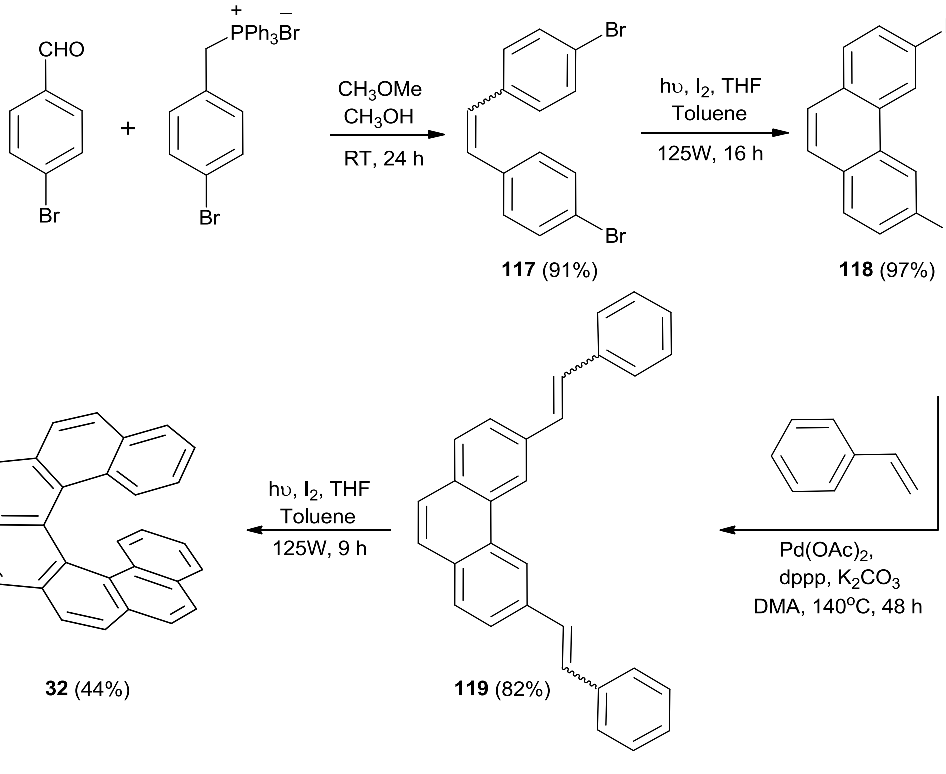


**Figure 5:** Routes for photocyclization of 2-(2-vinylnaphthyl)benzo[*c*]phenanthrene **154**

In a modified route the double photocyclization on 3,6-(bis-styryl)phenanthrene **155** was attempted where the bulk of naphthalene ring in **154** was replaced by phenyl ring [**Scheme-45**].



**Scheme 45:** Synthesis of [7]helicene using double photocyclization by $I_2$-THF methodology

Accordingly the required 3,6-(bis-styryl)phenanthrene **155** was synthesized by combination of Witting reaction, photocyclization and Heck reaction. Reaction of 3,6-dibromophenanthrene with styrene gives the 3,6-distyrylphenanthrene, where the entire sequence begins with 4-bromobenzaldehyde. Photocyclization of **155** under the improved conditions of $I_2$-THF gave the desired [7]helicene **32** although in moderate yield.[28,71]

The $^1$H-NMR spectra of [7]helicene **32** and dinaphtho[1,2-*a*:2',1'-*h*]anthracene **37** were compared and the structures of the isomers clearly established [**Figure-5**]. The assignments of the observed peaks are made as per the expected values of the chemical shifts.

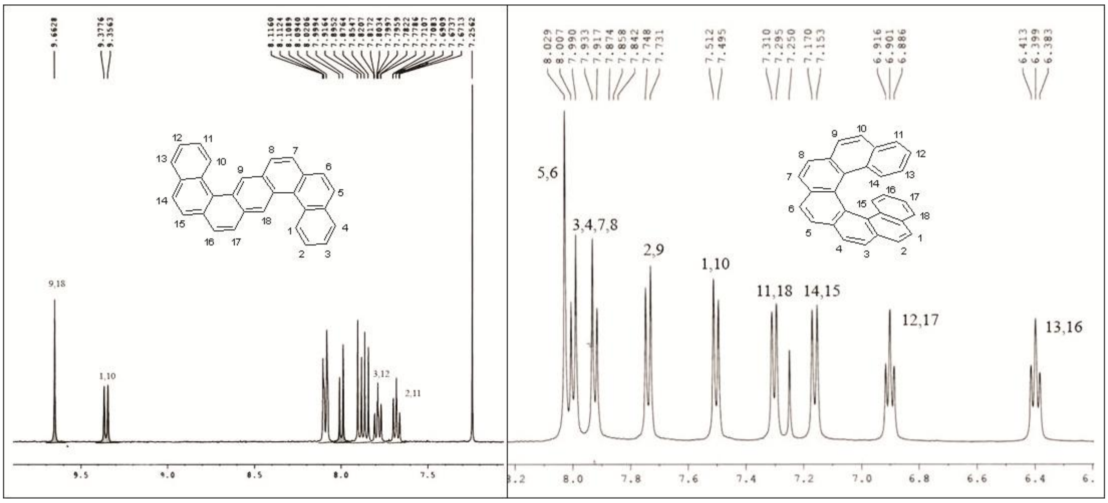


**Figure 5:** $^1$HNMR Spectrum of [7]helicene **32** and dinaphtho[1,2-*a*:2',1'-*h*]anthracene **37**

In the above figure the internal proton of dinaphtho[1,2-*a*:2',1'-*h*]anthracene **37** are the symmetrical protons H9, H18 which show singlet and H1, H10 show doublet at the downfield, similar type of pattern was also found in benzo[*c*]phenanthrene. At the same time the symmetrical protons H5,H6 of [7]helicene **32** shows doublet at downfield and the different pattern of the internal symmetrical proton H13, H16 show a triplet at up field region due to the shielding effect due to the ring current.[28]

This type of effect was also found in the all aromatic helical molecules from phenanthrene **3** up to the [7]helicene **32** as the size of the helicene increases, the shielding effect increases due to the ring current [**Figure-6**]. The shielding effect was observed very strongly in the [7]helicene **32** on the internal proton, and due to this effect the internal proton of the [7]helicene was observed at up field at δ 7.16 (d, $J$ = 8.50 Hz) as compared to the down field internal proton of the phenanthrene at δ 9.14 (d, $J$ = 8.00 Hz).

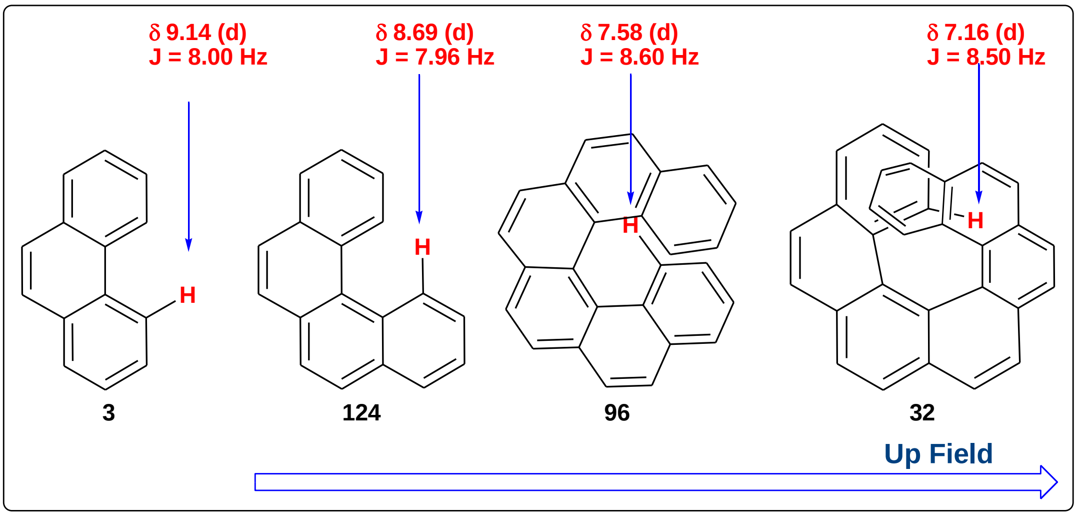
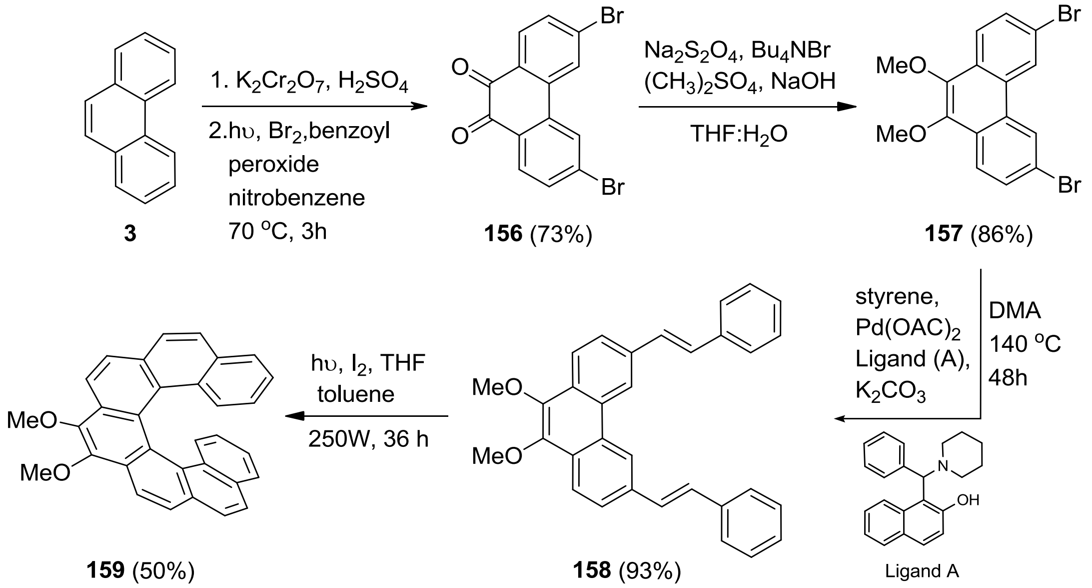


**Figure 6:** Shielding Effect of the Internal Proton in Benzologous Compounds

The photocyclization method was further extended for the synthesis of substituted [7]helicene. In this connection it was required to develop a process for the synthesis of 9,10-dialkoxy[7]helicenes. Some of the molecules of 9,10-dialkyloxy[7]helicene may be useful in material chemistry with applications in liquid crystals or in optical materials. With this aim commercial sample of phenanthrene **3** was converted to 9,10-phenanthraquinone[81a] by oxidation, and then to 3,6-dibromo-9,10-phenanthraquinone[81b] **156** by bromination. The required 3,6-dibromo-9,10-dimethoxyphenanthrene **157**[82] was prepared by reduction of **156** with $Na_2S_2O_4$ followed by its *in situ* *O*-methylation using dimethyl sulfate. The desired double $Pd(OAc)_2$ catalyzed Heck reaction of **157** with styrene to give 3,6-(bis-styryl)-9,10-dimethoxyphenanthrene **158** proved to be difficult with dppp as ligand. However, the Mizoroki-Heck coupling reaction was successful with an aminophenol (**Ligand A**, 1-(α-aminobenzyl)-2-naphthol) which has been used in our laboratory.[83] Subsequent photocyclization with $I_2$-THF of **158** gave 9,10-dimethoxy[7]helicene[84] **159** in moderate yield [**Scheme-46**].



**Scheme 46:** Synthesis of 9,10-dimethoxy[7]helicene **159**

The structure of helical molecules should have a framework suitable for the two helical isomers to exist at ambient conditions without isomerisation. This aspect was studied by their HPLC analysis on suitable chiral solid phase HPLC columns. The isomers were studied by the HPLC analysis of [6]helicene **96** and 2-methyl[6]helicene **147** performed on chiral phase column (Chiralcel-OD-H, isopropanol: n-hexane- 5:95 system) and the two helical isomers were clearly visible and separable, see [**Figure-7**].

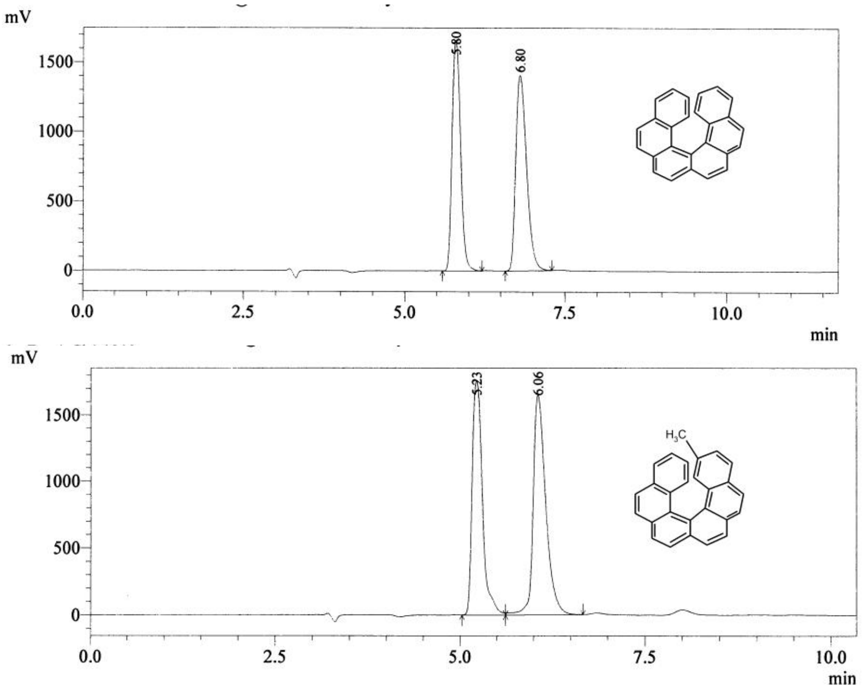
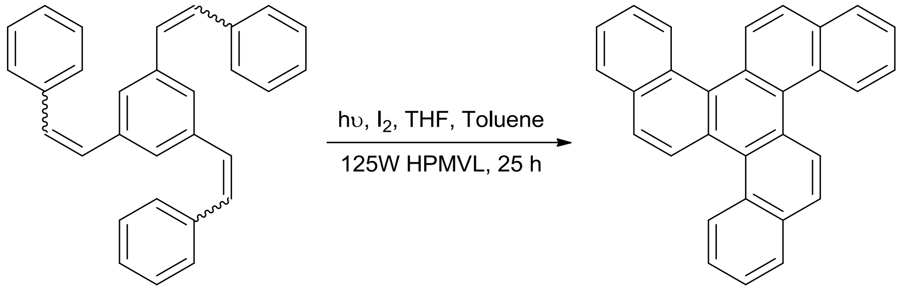


**Figure 7:** HPLC spectrum indicating two different isomers of [6]helicene **96** and 2-methyl[6]helicene **147**

Encouraged by the successful mono and double photocyclization methodologies the modified method of $I_2$-THF was applied for the triple photocyclization. For this purpose we have investigated this methodology for the photocyclization of 1,3,5-tristyrylbenzene **160**. In this experiment the solution of 1,3,5-tristyrylbenzene **161**, iodine (3.3 eq.) and tetrahydrofuran (60 eq.) in toluene was irradiated using 125W HPMV lamp for 25 h and benzo[*c*]naphtho[2,1-*p*]chrysene **161** was obtained as a product [**Scheme-47**].

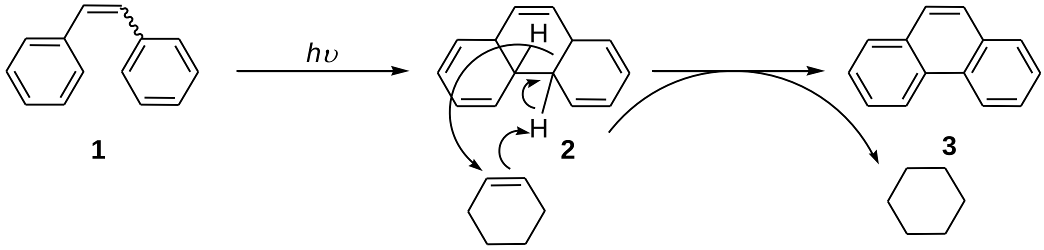


**160** **161** (33%)

**Scheme 47:** Synthesis of benzo[*c*]naphtho[2,1-*p*]chrysene **161** by triphotocyclization using $I_2$-THF

The standard method of photocyclization of stilbene involves the use of iodine, either in catalytic quantity or in stoichiometric amount. Both the conditions lead to the formation of HI, which needs to be neutralized to avoid interference and damage of the products. But if one does not use iodine, no HI will be formed as side product nor there will be any need for its neutralization. Cyclohexene can be used to abstract hydrogen from the reaction system as it has a tendency to get saturated.

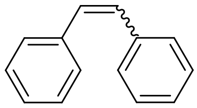
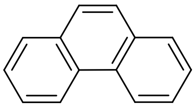
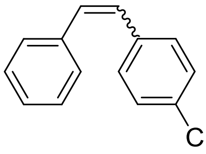
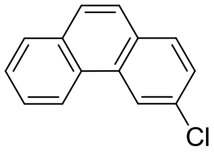
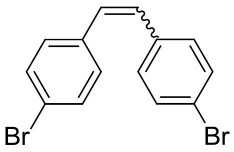
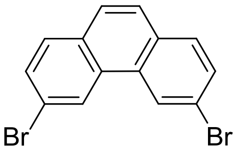
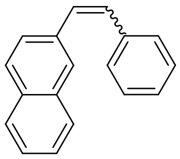
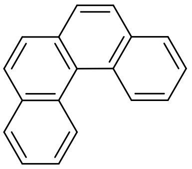
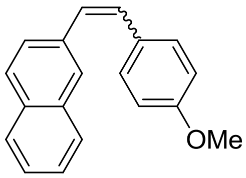
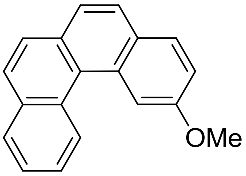
The first step of the photocyclization of stilbene is the formation of **3** and our present modification deals with the second step, i.e., aromatization toward **3**. In this part of the conversion we have envisaged the use of cyclohexene to abstract the hydrogen as shown in [**Scheme-48**]. In this works, since the iodine is not used there is no possibility of the generation of HI and one need not use any scavenger, neither propylene oxide nor THF. To test this concept a sample of stilbene was exposed to photolysis in the presence of excess of cyclohexene (20 equiv) in toluene.



**Scheme 48:** Synthesis of phenanthrene using cyclohexene

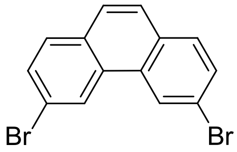
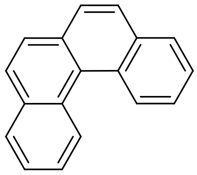
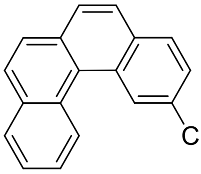
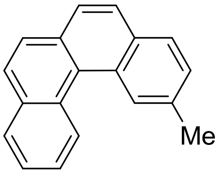
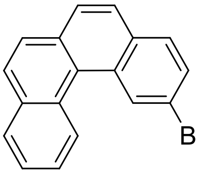
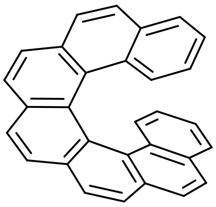
A careful isolation of the product indicated the formation of phenanthrene in good yield and this method is extended to more examples, [**Table 4**]. This method is an acid free photocyclization methodology, after the cyclization the aromatization occurs with the abstraction of hydrogen (probably as proton) by cyclohexene, followed by abstraction of another hydrogen (probably as hydride) to give the aromatized product phenanthrene as well as the side product cyclohexane.

**Table 4:** Photocyclization of Stilbene and β-Styrylnaphthalenes in the Presence of Cyclohexene

| Entry | Stilbenes | Phenanthrenes | Time/h with 125 W HPMVL | Isolated Yield/% |
|---|---|---|---|---|
| 1 |  |  | 16 | 86 |
| 2 |  |  | 23 | 63 |
| 3 |  |  | 20 | 54 |
| 4 |  |  | 17 | 36 |
| 5 |  |  | 18 | 35 |

In order to establish the current method the results of the photocyclization of stilbenes and its derivatives with $I_2$-THF methodology were compared with the reported Katz methodology using the propylene oxide as a scavenger of HI. We found that the new deleloped method is comparable with standard methodology for photocyclization with $I_2$-THF [**Table-5**].

**Table 5:** Comparison of photodehydrocyclization of styryl derivatives in presence of tetrahydrofuran and propylene oxide

| Entry | Compounds | % Yield with $I_2$-THF | % Yield with $I_2$-Propylene oxide | Ref. |
|---|---|---|---|---|
| 1 |  | 97 | Not mentioned | 35a |
| 2 |  | 84 | 60-95 | 67 |
| 3 |  | 67 | 70 | 67 |
| 4 |  | 96 | 57 | 67 |
| 5 |  | 96 | 80 | 44 |
| 6 |  | 44 | 90 | 64a |

Thus in this section two modifications of photocyclization methodologies are developed and many examples are scanned for their applications in building polyaromatic hydrocarbons such as phenanthrenes and helicenes.

# Experimental Section

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens Limited etc. Tetrahydrofuran was refluxed over sodium benzophenone-ketyl and freshly distilled prior to its use. Toluene was distilled and stored 24 h over molecule sieves (4 Å) prior to use. Thin Layer Chromatography was performed on Merck 60 $F_{254}$ Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. Photo reactions were performed in immersion well photo reactor with water jacket for cooling with 125 or 250 W high pressure mercury vapor lamp (HPMVL) from GE electrical.

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. Kinetic experiments were run on ELICO LI127 pH meter.

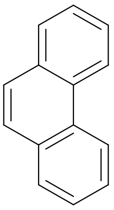
*Comparison of propylene oxide and tetrahydrofuran as scavenger of HI:*

For the comparison of the rate of the opening of propylene oxide and tetrahydrofuran by HI, it was synthesized by heating NaI (5.0 g, 0.033 mol) and $H_3PO_4$ (3.7 mL, 0.05 mol, 1.5 eq.) in a round bottom flask. The vapours were carefully condensed in a dry round bottom flask. From the distilled sample HI (0.505 g) was taken and diluted to 25 mL in measuring flask. For the comparison study two sets were made, one for propylene oxide and another for tetrahydrofuran. From this diluted solution (5 mL, 0.103 g of HI, 0.8 mmol) was used for each set. In one flask propylene oxide (0.094 g, 0.11 mL, 1.6 mmol, 2 equiv) and distilled water was taken to make the volume of system to exactly 15 mL. Similarly, for the second set, tetrahydrofuran (0.116 g, 0.13 mL, 1.6 mmol, 2 eq.) was mixed with distilled water to make the volume of system to 15 mL.

Both the sets were stirred at the same speed continuously while the pH was measured using glass electrode attached to the pH meter. Reading of pH was recorded at the interval of 10 min after the mixing of two liquids, HI solution with propylene oxide or tetrahydrofuran solution in the said two sets. Readings for the comparison are presented in [**Table-1, Page no. 26**] and graph was plotted (pH *vs* time in min.) as shown in [**Figure-4, Page No. 26**].

## *Synthetic procedures:*

### *Phenanthrene (3):*



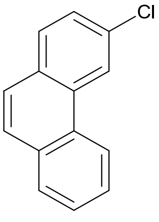
A solution of stilbene **1** (0.10 g, 0.55 mmol), iodine (0.154 g, 0.61 mmol, 1.1 eq), THF (0.88 g, 0.99 mL, 12.2 mmol) in toluene (0.425 L) was irradiated using 125W HMPV lamp for 7 h. After the reaction was over (tlc) the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product, phenanthrene **3**, was isolated as colourless solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.097 g, 98%), **M.p**. 100-101 °C (Lit. 98-100 °C).[63]

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.69 (d, *J* = 7.96 Hz, 2H), 7.89 (ddd, *J* = 0.96 Hz, 1.44 Hz & 7.64 Hz, 2H), 7.74 (s, 2H), 7.66 (ddd, *J* = 1.48 Hz, 7.0 Hz & 8.4 Hz, 2H), 7.60 (ddd, *J* = 1.32 Hz, 8.0 Hz & 9.0 Hz, 1H).

**IR (KBr):** 3432, 3050, 2926, 1600, 1524, 1497, 1452, 1426, 1299, 1241, 1139, 948, 869, 817, 731, 712 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 178 (92), 177 (90), 176 (24), 175 (21), 149 (27), 137 (21), 136 (18), 97 (27), 83 (32), 81 (89), 71 (37), 69 (100), 68 (86), 57 (39).

### *3-Chlorophenanthrene (112):*



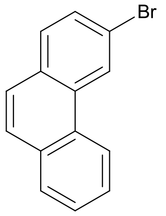
A solution of 4-chlorostilbene **111** (0.10 g, 0.46 mmol), iodine (0.13 g, 0.51 mmol, 1.1 eq), THF (0.67 g, 0.76 mL, 9.31 mmol) in toluene (0.425 L) was irradiated using 125W HMPV lamp for 7 h. After the reaction was over (tlc) the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was isolated 3-chlorophenanthrene **112** as colourless solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.078 g, 78%), **M.p**. 79-81 °C (Lit. 79-80 °C).[63]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.65 (d, *J* = 1.84 Hz, 1H), 8.60 (d, *J* = 8.04 Hz, 1H), 7.89 (dd, *J* = 1.28 Hz & 7.60 Hz, 1H), 7.82 (d, *J* = 8.48 Hz, 1H), 7.74 (d, *J* = 8.88 Hz, 1Hz), 7.70 (d, *J* = 8.48 Hz, 1H), 7.69-7.61 (m, 2H), 7.55 (dd, *J* = 1.96 Hz, 8.44 Hz, 1H).

**IR (KBr):** 3434, 3049, 2925, 2854, 1893, 1654, 1591, 1544, 1512, 1495, 1443, 1419, 1396, 1342, 1231, 1097, 1084, 1037, 1014, 947, 867, 852, 833, 745, 704, 617 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 214 (27) [M+2], 213 (43) [M+1], 212 (100), 211 (75), 177 (17), 176 (54), 175 (23), 150 (15), 149 (15), 96 (16), 81 (19), 71 (19), 57 (28).

***3-Bromophenanthrene (114):***



A solution of 4-bromostilbene **113** (0.100 g, 0.39 mmol), iodine (0.11 g, 0.42 mmol, 1.1 eq), THF (0.56 g, 0.62 mL, 9.31 mmol) in toluene (0.425 L) was irradiated using 125W HMPV lamp for 20 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product 3-bromophenanthrene **114** was isolated as a colourless solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.084 g, 84%), **M.p**. 80-82 °C (Lit. 83-84 °C).[63]

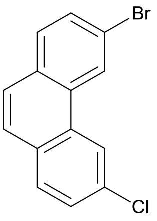
**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.80 (d, *J* = 1.6 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 1.2 Hz & 9.2 Hz, 1H), 7.74-7.72 (m, 2H), 7.74-7.59 (m, 4H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** 132.20 (Cq), 131.76 (Cq), 130.55 (Cq), 130.09 (CH), 129.73 (CH), 129.21 (Cq), 128.66 (CH), 127.43 (CH), 127.24 (CH), 126.94 (CH), 126.29 (CH), 125.57 (CH), 122.71 (CH), 120.86 (CH).

**IR (KBr):** 3036, 2901, 1576, 1426, 1236, 1180, 1063, 870, 831, 786, 699, 632, 545 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 259 (08) [M+2], 258 (08) [M+1], 256 (16), 176 (08), 149 (11), 136 (10), 122 (12), 109 (13), 94 (25), 81 (59), 79 (09), 71 (12), 69 (100).

***3-Bromo-6-chlorophenanthrene (116):***



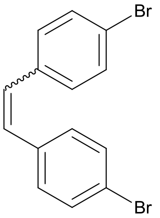
A solution of 4-bromo-4'-chlorostilbene **115** (0.100 g, 0.34 mmol), iodine (0.095 g, 0.37 mmol, 1.1 eq), THF (0.49 g, 0.55 mL, 6.80 mmol) in toluene (0.425 L) was irradiated using 125W HMPV lamp for 9 h. After the reaction was over the excess of iodine was removed by washing with aqueous solution $Na_2S_2O_3$, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was isolated 3-bromo-6-chlorophenanthrene **116** as white solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.082 g, 83%), **M.p**. 186-188 °C (Lit. 188-192 °C).

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.71 (d, *J* = 1.64 Hz, 1H), 8.54 (d, *J* = 1.96 Hz, 1H), 7.83 (d, *J* = 8.48 Hz, 1H), 7.76 (d, *J* = 8.48 Hz, 1H), 7.73-7.68 (m, 3H), 7.58 (dd, *J* = 2.08, 8.52 Hz, 1H).

**IR (KBr):** 3429, 3051, 2923, 2853, 1903, 1664, 1588, 1497, 1429, 1409, 1381, 1342, 1152, 1109, 1088, 1074, 948, 869, 836, 771, 740, 635, 622, 587 cm.$^{-1}$

**MS (EI):** *m/z*, (%) 294 [m+4] (38), 293 [M+3] (49), 292 [M+2] (98), 291 [M+1] (99), 290 [M] (100), 289 (80), 211 (08), 209 (13), 177 (10), 176 (81), 175 (52), 174 (39), 149 (11), 87 (57), 75 (06).

***4,4'-Dibromostilbene (117):***



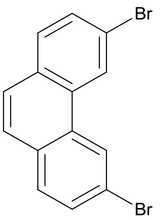
A solution of Na (0.068 g, 2.97 mmol) in anhydrous methanol (5 mL) was added dropwise to a suspension of the 4-(bromobenzyl)triphenyl-phosphonium bromide (1.523 g, 2.97 mmol) and *p*-bromobenzaldehyde (0.5 g, 2.7 mmol) in anhydrous methanol (10 mL) under $N_2$ at room temperature. The solution colour changed to yellow. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* product of the 4,4'-dibromostilbene **117** as white solid (0.708 g, 78%), **M.p**. 210-212 °C (Lit. 215-216 °C).[36]

**$^1$HNMR (400 MHz, CDCl$_3$):** δ 7.48 (d, *J* = 8.55 Hz, 4H), 7.37 (d, *J* = 8.55 Hz, 4H), 7.02 (s, 2H).

**IR (KBr):** 3049, 1901, 1721, 1584, 1494, 1405, 1379, 1230, 1151, 1104, 1070, 1018, 837, 769, 695, 607, 575, 517 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 340 (23), 339 (8), 338 (47), 336(27), 179 (16), 178 (100), 177 (16), 176 (21), 152 (10), 151 (10), 89 (48), 88 (33).

### *3,6-Dibromophenanthrene (118):*



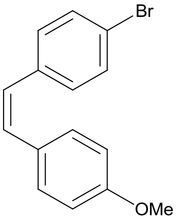
A solution of 4,4'-dibromostilbene **117** (0.250 g, 0.74 mmol), iodine (0.206 g, 0.81 mmol, 1.1 eq.), tetrahydrofuran (1.067 g, 1.2 mL, 14.8 mmol, 20 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 16 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product 3,6-dibromophenanthrene **118** was obtained after column chromatography as white solid (0.241 g, 97%), **M.p**. 194 °C (Lit.- 194 °C).[64]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.76 (d, *J* = 1.56 Hz, 2H), 7.82 (d, *J* = 8.48 Hz, 2H), 7.75-7.71 (m, with overlapping d, *J* = 8.48 Hz, 4 H),

**IR (KBr):** 3467, 3049, 2918, 1583, 1494, 1405, 1379, 1151, 1069, 1017, 948, 837, 769, 732, 606, 517 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 338 (30), 336 (61), 334 (33), 177 (17), 176 (100), 175 (20), 174 (17), 168 (18), 167 (38), 150 (26), 149 (99), 88 (63), 87 (25), 71 (26).

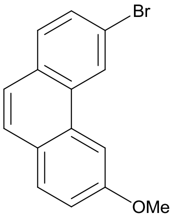
### *4-bromo-4'-methoxystilbene (119):*



A solution of Na (0.185 g, 8.08 mmol) in anhydrous methanol (5 mL) was added drop wise to a suspension of the 4-(bromobenzyl)triphenyl-phosphonium bromide (4.14 g, 8.08 mmol) and *p*-anisaldehyde (1.0 g, 7.34 mmol) in anhydrous methanol (20 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford the title stilbene 4-bromo-4'-methoxystilbene **119** as white solid mostly in *trans* form. (2.076 g, 97%), **M.p**. 201-202 °C (*trans* product).

**$^1$H-NMR (400 MHz, CDCl$_3$):** (*trans* product) δ 7.45 (m, 4H), 7.35 (td, *J* = 1.84, 8.48 Hz, 2H), 6.90 (td, *J* = 2.04, 8.76 Hz, 2H), 6.89 (d, *J* = 16.32 Hz, 1H), 3.83 (s, 3H).

***3-Bromo-6-methoxyphenanthrene (120):***



A solution of 4-bromo-4'-methoxystilbene (0.500 g, 1.73 mmol), iodine (0.483 g, 1.9 mmol), THF (12.46 g, 14 mL, 173 mmol) in toluene (1.2 L) was irradiated with 250W HMPV lamp for 36 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was isolated 3-bromo-6-methoxyphenanthrene **120** as white solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.335 g, 67 %), **M.p**. 100-102 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.71 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.74-7.65 (m, 3H), 7.55 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H).

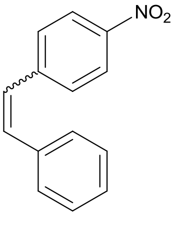
**Anal. Calcd. for $C_{15}H_{11}BrO$:** C 62.74, H 3.86. Found: C 62.28, H 4.08.

**IR (KBr):** 3011, 2962, 2931, 1615, 1590, 1510, 1460, 1444, 1255, 1220,1073, 1028, 866, 843, 777, 592, 553, 537 cm$^{-1}$.

**MS (EI): *m/z*, (%)** 289 (16), 288 (92), 287 (19), 286 (100), 273 (24), 271 (24), 245 (38), 243 (42), 208 (10), 207 (32), 176 (07), 164 (16), 163 (23), 96 (07), 86 (15), 84 (25).

***E-4-Nitrostilbene (105):***

Mizoroki-Heck Reaction:



Preparation of Catalyst Solution:

A solution of palladium acetate (0.011 g, 0.005 mmol, 0.1 mol%) and 1-(α-1-piperidylbenzyl)-2-naphthol (ligand A) (0.0018 g, 0.0059 mmol, 1.2 eq. of $Pd(OAc)_2$) was prepared in N,N-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous solution was obtained. This catalyst solution was degassed several times prior to use.

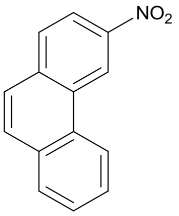
A two neck r.b. flask was charged with *p*-bromonitrobenzene (1.0 g, 4.95 mmol), dry potassium carbonate (1.71 g, 12.37 mmol, 2.5 eq.), TBAB (0.319 g, 0.99 mmol, 20 mol%) and N,N-dimethylacetamide (15 mL). The solution was repeatedly degassed and purged with $N_2$. To this styrene (0.773 g, 7.42 mmol, 1.5 eq.) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (100:00 to 95:5) as eluent to afford 4-nitrostilbene **105** as pale yellow solid (0.623, 77%), **M.p**. 156 °C (Lit. 154–157 °C).[24]

**$^1$H-NMR (400 MHz,CDCl$_3$):** δ 8.22 (td, *J* = 2.4, 9.32 Hz, 2H), 7.64 (td, *J* = 2.36, 9.32 Hz, 2H), 7.57-7.55 (m, 2H), 7.42-7.38 (m, 2H), 7.36-7.34 (m, 1H), 7.28 (d, *J* = 16.32 Hz, 1H), 7.15 (d, *J* = 16.32 Hz, 1H).

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

**MS (EI):** ***m/z*, (%)** 226 (15), 225 (100), 208 (06), 195 (06), 180 (07), 179 (43), 178 (99), 177 (19), 152 (25), 151 (10), 89 (13), 76 (06).

### *3-Nitrophenanthrene (106):*



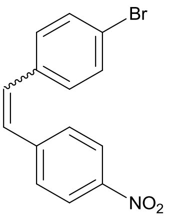
A solution of 4-nitrostilbene **105** (0.250 g, 1.11 mmol), iodine (0.309 g, 1.22 mmol, 1.1 eq), THF (1.6 g, 1.8 mL, 22.2 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 36 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was isolated 3-nitrophenanthrene **106** as yellow solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.077 g, 31%), **M.p**. 175-177 °C (Lit. 175-177 °C).[65]

**$^1$H-NMR (500 MHz, $CDCl_3$):** δ 9.63 (d, *J* = 2.5 Hz, 1H), 8.77 (d, *J* = 8.5 Hz, 1H), 8.40 (dd, *J* = 2.0, 9.0 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H ), 7.98 (m, 2H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.79 (ddd, *J* = 1.5, 7.0, 8.5 Hz, 1H), 7.74 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H).

**IR (KBr):** 3433, 2925, 1720, 1610, 1535, 1503, 1336, 1232, 1199, 1107, 1035, 892, 844, 804,735cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 224 (16), 223 (100), 193 (27), 177 (62), 176 (72), 167 (21), 165 (43), 151 (51), 150 (28), 149 (81), 88 (25), 81 (34), 57 (49).

***trans-1-Bromo-4-(4-nitrostyryl)benzene (107):***



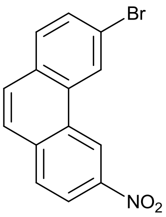
A solution of Na (0.083 g, 3.63 mmol) in anhydrous methanol (5 mL) was added drop wise to a suspension of the 4-bromobenzylphosphonium-bromide salt (1.685 g, 3.63 mmol) and *p*-nitrobenzaldehyde (0.500 g, 3.63 mmol) in anhydrous methanol (10 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitates of product. The aqueous solution along with the precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-bromo-4-(4-nitrostyryl)benzene **107** as yellow solid (0.915 g, 91%), **M.p**. 198-201 °C (lit. 201-203 °C).[25b]

**$^1$H-NMR (400 MHz,$CDCl_3$):** δ 8.23 (ddd, *J* = 1.88, 2.32, 8.88 Hz, 2H), 7.63 (ddd, *J* = 1.84, 2.32, 9.32 Hz, 2H), 7.53 (ddd, *J* = 1.84, 2.28, 8.88 Hz, 2H), 7.42 (ddd, *J* = 1.9, 2.2, 9.0 Hz, 2H), 7.20 (d, *J* = 16.36 Hz, 1H), 7.13 (d, *J* = 16.36 Hz, 1H ).

**IR (KBr):** 3436, 1632, 1589, 1505, 1333, 1178, 1103, 1069, 1004, 968, 842, 811, 747 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 306 (04), 305 (14), 304 (04), 303 (14), 279 (09), 178 (29), 177 (11), 167 (39), 166 (10), 150 (15), 149 (100), 113 (11), 76 (13), 71 (19).

***3-Bromo-6-nitrophenanthrene (108):***



A solution of *trans*-1-bromo-4-(4-nitrostyryl)benzene **107** (0.250 g, 0.822 mmol), iodine (0.229 g, 9.04 mmol, 1.1 eq), THF (1.305 g, 1.47 mL, 18.1 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 29 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained after column chromatography using petroleum ether: ethyl acetate (100:00 to 98:2) as eluent to obtained 3-bromo-6-nitrophenanthrene **108** as pale yellow solid (0.169 g, 68%), **M.p**. 243-235 °C (Lit. 234-235 °C).[17]

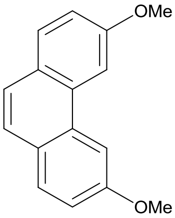
**$^1$H-NMR (400 MHz,CDCl$_3$):** δ 9.52 (d, *J* = 2.4 Hz, 1H), 8.89 (d, *J* = 2.2 Hz, 1H), 8.43 (dd, *J* = 2.2, 8.8 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.83-7.81 (m, 2H).

**Anal. Calcd. for $C_{14}H_8BrNO_2$:** C 55.65, H 2.66, N 4.63. Found: C 54.93, H 2.71, N 4.60.

**IR (KBr):** 3082, 2925, 1621, 1591, 1530,1497, 1437, 1342, 1075, 1028, 845, 736, 588, 509 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 304 (3), 303 (10), 302 (4), 301 (12), 176 (21), 175 (8), 149 (15), 137 (17), 136 (17), 121 (18), 109 (17), 95 (27), 69 (100).

***3,6-Dimethoxyphenanthrene (122):***

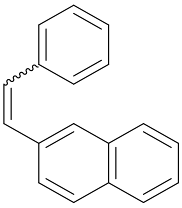


A solution of 4-4'-dimethoxystilbene **121** (0.30 g, 1.25 mmol), iodine (0.348 g, 1.75 mmol), THF (1.80 g, 2.03 mL, 25.0 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 36 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was isolated 3,6-dimethoxyphenanthrene **122** as white solid by column chromatography over silica gel, further crystallized from light petroleum ether (0.194 g, 65 %), **M.p**. 104-106 °C.[66]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.96 (d, *J* = 2.44 Hz, 2H), 7.80 (d, *J* = 8.72 Hz, 2H), 7.56 (s, 2H), 7.25 (dd, *J* = 2.52 Hz & 8.8 Hz, 2H).

**IR (KBr):** 3098, 3054, 2994, 2936, 1606, 1565, 1511, 1465, 1449, 1412, 1369, 1346, 1290, 1217, 1177, 1092, 1036, 962, 940, 848, 827, 809, 676, 569 cm.$^{-1}$

***1-phenyl-2-(2-naphtyl)ethylene (123):***



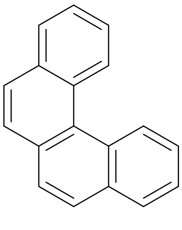
A solution of Na (0.119 g, 5.18 mmol) in anhydrous methanol (10 mL) was added dropwise to a suspension of the [(2-naphthyl)methyl]-triphenylphosphonium bromide salt (2.50 g, 5.18 mmol) and benzaldehyde (0.50 g, 4.71 mmol) in anhydrous methanol (20 mL) under $N_2$ at room temperature. The solution colour changed to yellow. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with the precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-phenyl-2-(2-naphtyl)ethylene **123** as white solid and *cis* isomer as oil (Total yield: 1.01 g, 94%). For *trans* isomer – **M.p**. 144-146 °C (Lit. 146 °C).[67]

For *cis* isomer:

**$^1$H-NMR (200 MHz, CDCl$_3$):** δ 7.85-7.17 (m, 12H), 6.77 (d, *J* = 12.0 Hz, 1H), 6.67 (d, *J* = 12.0 Hz, 1H).

**IR (KBr):** 3436, 3079, 3053, 3021, 2924, 1949, 1654, 1636, 1627, 1595, 1575, 1505, 1493, 1447, 1434, 1275, 964, 903, 821, 737, 691 cm.$^{-1}$

***Benzo[c]phenanthrene (124):***



A solution of 1-phenyl-2-(2-naphtyl)ethylene **123** (0.250 g, 1.10 mmol), iodine (0.306 g, 1.21 mmol), THF (1.58 g, 1.78 mL, 21.92 mmol, 20 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 13 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained benzo[*c*]phenanthrene **124** as colourless solid after column chromatography using petroleum ether as eluent (0.208 g, 84%), **M.p**.68-69 °C (Lit. 67-68 °C).[67]

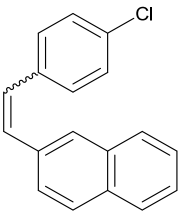
**$^1$H-NMR (200 MHz, CDCl$_3$):** δ 9.14 (d, *J* = 8.0 Hz, 2H), 8.03 (dd, *J* = 2.0 Hz & 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.73-7.58 (m, 4H).

**Anal. Calcd. for $C_{14}H_{12}$:** C 94.70, H 5.30. Found: C 95.30, H 5.41.

**IR (KBr):** 3432, 3042, 3007, 2926, 2361, 2343, 1618, 1599, 1542, 1494, 1458, 1418, 1227, 1129, 866, 832, 744, 667, 614, 576 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 230 (02), 229 (19), 228 (100), 227 (48), 226 (43), 224 (09), 113 (17), 112 (06).

### *1-(p- Chlorophenyl)-2-(2-naphtyl)ethylene (125):*



A solution of Na (0.090 g, 0.39 mmol) in anhydrous methanol (5 mL) was added dropwise to a suspension of the [(2-naphthyl)methyl]-triphenylphosphonium bromide salt (1.89 g, 0.39 mmol) and *p*-chlorobenzaldehyde (0.50 g, 0.35 mmol) in anhydrous methanol (5 mL) under $N_2$ at room temperature. The solution colour changed to yellow. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with the precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-(*p*-chlorophenyl)-2-(2-naphtyl)ethylene **125** as white solid and *cis* isomer as low melting solid (Combined yield: 0.836 g, 89%), *trans* isomer- **M.p**. 183-184 °C.

For *cis* isomer:

**$^1$H-NMR (200 MHz, CDCl$_3$):** δ 7.80-7.18 (m, 11H), 6.78 (d, *J* = 12.0 Hz, 1H), 6.60 (d, *J* = 12.0 Hz, 1H).

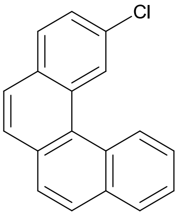
**IR (KBr):** 3423, 3048, 3001, 2925, 2853, 2365, 1904, 1702, 1627, 1593, 1484, 1362, 1273, 1144, 1082, 1013, 967, 950, 900, 867, 822, 800, 731, 662, 642 cm.$^{-1}$

For *trans* isomer:

**$^1$H-NMR (200 MHz, CDCl$_3$):** δ 7.85-7.79 (m, 4H), 7.72 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.51-7.42 (m, 5H), 7.36-7.30 (m, 1H), 7.22-7.18 (m, 2H).

**IR (KBr):** 3433, 3054, 3014, 2924, 2853, 2362, 2341, 1624, 1588, 1488, 1464, 1403, 1097, 967, 855, 821, 743, 639 cm.$^{-1}$

### *2-Chlorobenzo[c]phenanthrene (126):*



A solution of 1-(*p*-chlorophenyl)-2-(2-naphtyl)ethylene **125** (0.150 g, 0.58 mmol), iodine (0.161 g, 0.63 mmol), THF (0.830 g, 0.934 mL, 11.52 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 16 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained 2-chlorobenzo[*c*]phenanthrene as white solid after column chromatography using petroleum ether as eluent (0.100 g, 67%), **M.p**. 62-64 °C (Lit. 61.4-61.8 °C).[67]

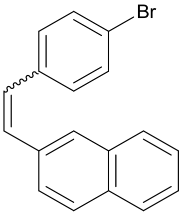
**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 9.12 (d, *J* = 1.32 Hz, 1H), 9.05 (d, *J* = 8.52 Hz, 1H), 8.03 (dd, *J* = 0.84, 7.76 Hz, 1H), 7.95 (d, *J* = 8.52 Hz, 1H), 7.92 (d, *J* = 8.52 Hz, 1H), 7.88-7.80 (m, 3H), 7.73 (ddd, *J* = 1.4, 7.0, 8.36 Hz, 1H), 7.65 (ddd, *J* = 0.92, 7.84, 1H), 7.57 (dd, *J* = 1.96, 8.56 Hz, 1H).

**Anal. Calcd. for $C_{18}H_{11}Cl$:** C 82.28, H 4.22. Found: C 81.52, H 4.27.

**IR (KBr):** 3046, 2924, 1596, 1487, 1440, 1419, 1092, 1039, 838, 779, 747 cm.$^{-1}$

**MS (EI): m/z, (%)** 265 (06), 264 (32), 263 (20), 262 (100), 228 (10), 227 (57), 226 (84), 225 (21), 224 (23), 113 (72), 112 (33).

### *1-(p-Bromophenyl)-2-(2-naphtyl)ethylene (127):*



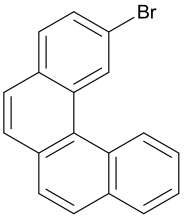
A solution of Na (0.169 g, 7.37 moles) in anhydrous methanol (10 mL) was added drop wise to a suspension of naphthaldehyde (1.0 g, 6.7 mmol) and 4-bromobenzylphosphoniumbromide salt (3.777 g, 7.37 mmol) in anhydrous methanol (20 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-(*p*-bromophenyl)-2-(2-naphtyl)ethylene **127** as white solid (1.575 g, 76%), **M.p**. 192 °C. (Lit. 188.5-189 °C).[44]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.85-7.80 (m, 4H), 7.72 (dd, *J* = 1.68, 8.64 Hz, 1H), 7.51-7.41 (m, 6H), 7.26 (d, *J* = 16.32 Hz, 1H), 7.15 (d, *J* = 16.32 Hz, 1H).

**IR (KBr):** 3049, 2362, 1583, 1483, 1396, 1072, 965, 853, 820, 741 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 311 (13), 310 (61), 309 (15), 230 (15), 229 (89), 228 (100), 226 (33), 202 (15), 152 (06), 128 (07), 114 (57), 101 (26).

***2-Bromobenzo[c]phenanthrene (128):***



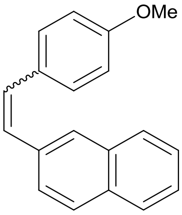
A solution of 1-(*p*-bromophenyl)-2-(2-naphtyl)ethylene **127** (1.0 g, 3.2 mmol), iodine (0.903 g, 3.6 mmol, 1.1 eq), THF (4.67 g, 64 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 30 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained 2-bromobenzo[*c*]phenanthrene **128** as white solid after column chromatography using petroleum ether (0.953 g, 96%), **M.p**. 87-88 °C (Lit. 87-88 °C).[44]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 9.48 (s, 1H), 9.05-9.03 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H).

**IR (KBr):** 3044, 1600, 1588, 1485, 1440, 1109, 1082, 1039, 839, 781, 746, 599, 570, 529 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 308 (50), 307 (12), 306 (51), 227 (44), 226 (76), 225 (19), 224 (22), 149 (39), 114 (27), 113 (100), 112 (51), 111 (23), 97 (17).

### *1-(p-Methoxyphenyl)-2-(2-naphtyl)ethylene (129):*



A solution of Na (1.00 g, 0.73 mmol) in anhydrous methanol (5 mL) was added dropwise to a suspension of the [(2-naphthyl)methyl]triphenyl-phosphonium bromide salt (3.95 g, 0.81 mmol) and *p*-anisaldehyde (0.186 g, 0.81 mmol) in anhydrous methanol (10 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with the precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-(*p*-methoxyphenyl)-2-(2-naphtyl)ethylene **129** as white solid (1.701 g, 89%), *trans* isomer- **M.p**. 172-174 °C.

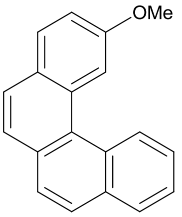
For *cis* isomer:

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.76-7.68 (m, 3H), 7.64 (d, *J* = 8.52 Hz, 1H), 7.43-7.38 (m, 2H), 7.37 (d, *J* = 9.76 Hz, 1H), 7.22-7.18 (m, 2H), 6.74-6.71 (m, 2H), 6.66 (d, *J* = 12.16 Hz, 1H), 6.60 (d, *J* = 12.16 Hz, 1H), 3.74 (s, 3H).

For *trans* isomer:

**$^1$H-NMR (400 MHz, DMSO-d$^6$):** δ 7.83-7.76 (m, 5H), 7.52-7.45 (m, 4H), 7.21 (d, *J* = 15.96 Hz, 1H), 7.14 (d, *J* = 15.36 Hz, 1H), 6.93 (s, 2H), 3.83 (s, 3H).

### *2-Methoxybenzo[c]phenanthrene (130):*



A solution of 1-(*p*-methoxyphenyl)-2-(2-naphtyl)ethylene **129** (0.250 g, 0.961 mmol), iodine (0.268 g, 1.057 mmol), THF (1.386 g, 1.552 mL, 19.23 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 22 h. After the reaction was over the excess of iodine was removed by washing the solution with aqueous $Na_2S_2O_3$, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained 2-methoxybenzo[*c*]phenanthrene as white solid after column chromatography using petroleum ether: ethyl acetate (100:00 to 98:2) as eluent (0.186 g, 75%), **M.p**.78-80 °C (Lit. 78-79 °C).[68]

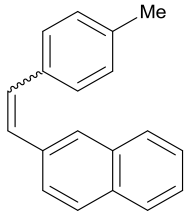
**$^1$HNMR (400 MHz, $CDCl_3$):** δ 9.19 (d, *J* = 8.5 Hz, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 8.01 (dd, *J* = 1.4 Hz & 7.8 Hz,1H), 7.93 (d, *J* = 7.96 Hz, 1H), 7.88-7.79 (m, 3H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.66 (m, 1H), 7.61 (ddd, *J* = 1.32 Hz, 7.16 Hz &7.96 Hz, 1H), 7.29 (dd, *J* = 2.5 Hz & 8.8 Hz, 1H), 4.02 (s, 3H).

**Anal. Calcd. for $C_{19}H_{14}O$:** C 88.34, H 5.46. Found: C 87.80, H 5.54.

**IR (KBr):** 3046, 3001, 2951, 2925, 1608, 1505, 1449, 1239, 1219, 1102, 1045, 881, 836, 792, 749 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 259 (08) [M+1], 258 (100), 243 (17), 242 (24), 225 (12), 215 (19), 214 (20), 213 (18), 212 (14), 189 (08), 188 (08), 94 (10), 81 (08), 69 (11), 83 (20), 71 (20).

***1-(p- Methylphenyl)-2-(2-naphtyl)ethylene (131):***

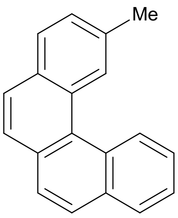


A solution of Na (0.429 g, 18.65 mmol) in anhydrous methanol (20 mL) was added drop wise to a suspension of the (2-naphthylmethyl)-phosphonium bromide (9.106 g, 18.65 mmol) salt and *p*-tolualdehyde (2.038 g, 2 mL, 16.96 mmol) in anhydrous methanol (30 mL) under $N_2$ at room temperature. The solution colour changed to pale yellow. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-(*p*-methylphenyl)-2-(2-naphthyl)ethylene **131** as white solid. (3.552 g, 86%), **M.p**. 183-184 °C (Lit. 181-183 °C).[67]

**IR (KBr):** 3016, 2913, 2361, 1907, 1591, 1508, 1411, 1363, 1274, 1112, 965, 901, 853, 821, 740 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 245 (21), 244 (100), 243 (23), 230 (18), 229 (85), 228 (60), 167 (28), 148 (69), 129 (16), 122 (15), 121 (22), 114 (22), 113 (23), 101 (15), 83 (20), 71 (20).

### *2-Methylbenzo[c]phenanthrene (132):*



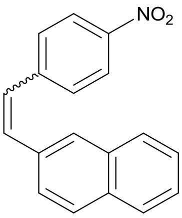
A solution of 1-(*p*-methylphenyl)-2-(2-naphtyl)ethylene **131** (0.250 g, 1.02 mmol), iodine (0.286 g, 1.12 mmol, 1.1 eq.), THF (1.477 g, 1.66 mL, 20.49 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 24 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product 2-methylbenzo[*c*]phenanthrene as white solid was obtained after column chromatography using petroleum ether as eluent (0.180 g, 73%). **M.p**. 79-81 °C (Lit. 79-80 °C).[67]

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 9.14 (d, *J* = 8.44 Hz, 1H), 8.94 (d, *J* = 0.64 Hz, 1H), 8.01 (dd, *J* = 1.4 Hz & 7.96 Hz, 1H), 7.91 (d, *J* = 8.12 Hz, 1H), 7.86 (t, *J* = 8.28 Hz, 2H), 8.80 (d, *J* = 8.52 Hz, 1H), 7.75 (d, *J* = 8.48 Hz, 1H), 7.68 (ddd, *J* = 1.52, 6.84, 8.4 Hz, 1H), 7.61 (ddd, *J* = 1.16, 7.0, 8.0 Hz, 1H), 7.45 (dd, *J* = 1.32, 8.08 Hz, 1H), 2.65 (s, 3H).

**IR (KBr):** 3047, 3010, 2919, 1598, 1518, 1493, 1417, 838, 785, 754, 669 $cm.^{-1}$

**MS (EI):** ***m/z*, (%)** 243 (22), 242 (100), 241 (17), 227 (29), 226 (31), 167 (8), 149 (27), 121 (12), 120 (15), 119 (31), 113 (25), 106 (10), 81 (8).

### *1-(p-Nitrophenyl)-2-(2-naphtyl)ethylene (109):*



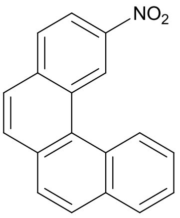
A solution of Na (0.250 g, 1.65 mmol) in anhydrous methanol (5 mL) was added drop wise to a suspension of the [(2-naphthyl)methyl]triphenylphosphonium bromide salt (0.958 g, 1.98 mmol) and *p*-nitrobenzaldehyde (0.250 g, 1.65 mmol) in anhydrous methanol (5 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with the precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-(*p*-nitrophenyl)-2-(2-naphtyl)ethylene **109** as yellow solid (0.411 g, 90%), **M.p**. 169-171 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.23 (d, *J* = 8.72 Hz, 2H), 7.89 (d, *J* = 16.4 Hz, 1H), 7.84-7.82 (m, 3H), 7.75 (dd, *J* = 1.24, 8.6 Hz, 1H), 7.66 (d, *J* = 8.36 Hz, 2H), 7.53-7.47 (m, 2H), 7.42 (d, *J* = 16.3 Hz, 1H), 7.24 (d, *J* = 16.3 Hz, 1H).

**IR (KBr):** 3431, 2922, 1625, 1589, 1509, 1335, 1179, 1105, 965, 861, 831, 745, 688 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 276 (20), 275 (100), 229 (33), 228 (85), 227 (33), 226 (36), 202 (24), 114 (26), 113 (29), 101 (21), 83 (12), 81 (11).

***2-Nitrobenzo[c]phenanthrene (110):***



A solution of 1-(*p*-nitrophenyl)-2-(2-naphtyl)ethylene **109** (0.250 g, 0.909 mmol), iodine (0.253 g, 1.0 mmol, 1.1 eq), THF (1.310 g, 1.47 mL, 18.18 mmol, 20 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 23 h. After the reaction was over the excess of iodine was removed by washing with aqueous Na$_2$S$_2$O$_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained 2-nitrobenzo[*c*]phenanthrene **110** as yellow solid after column chromatography using petroleum ether: ethylactate (100:00 to 98:2) as eluent (0.165 g, 83%), **M.p**.150-152 °C (Lit. 150-152 °C).[17]

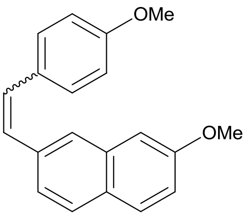
**$^1$H-NMR (400 MHz,CDCl$_3$):** δ 10.0 (d, *J* = 2.0 Hz, 1H), 8.96 (d, *J* = 8.5 Hz, 1H), 8.37 (dd, *J* = 2.2, 8.8 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 8.05 (dd, *J* = 2.4, 8.7 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.81-7.77 (m, 1H), 7.72-7.68 (m, 1H).

**Anal. Calcd. for $C_{18}H_{11}NO_2$:** C 79.10, H 4.05, N 5.12. Found: C 78.68, H 4.16, N 5.02.

**IR (KBr):** 3052, 3006, 2924, 1601, 1530, 1510,1378, 1334, 845, 828, 800, 759, 736 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 275 (11), 274 (60), 273 (95), 264 (25), 257 (13), 227 (18), 226 (53), 225 (13), 219 (82), 131 (37), 100 (19).

***2-Methoxy-7-(4-methoxystyryl)naphthalene (133):***



Mizoroki-Heck Reaction:

Preparation of Catalyst Solution:

A solution of palladium acetate (0.038 g, 0.0168 mmol, 1 mol%) and 1,3-bis(diphenylphasphino)propane (0.139 g, 0.0038 mmol, 2 eq. of $Pd(OAc)_2$ was prepared in N,N-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous solution was obtained. This catalyst solution was degassed several times prior to use.

A two neck r.b. flask was charged with 2-bromo-7-methoxynaphthalene (0.40 g, 1.69 mmol), dry potassium carbonate (0.466 g, 3.37 mmol), TBAB (0.108 g, 0.337 mmol, 20 mol%) and N,N-dimethylacetamide (10-15 mL). The solution was repeatedly degassed and purged with $N_2$. To this 4-vinylanisole (0.271 g, 2.02 mmol) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (100:00 to 70:30) as eluent to afford 2-methoxy-7-(4-methoxystyryl)naphthalene **133** as a white solid (0.409, 83%), **M.p**. 236-237 °C.

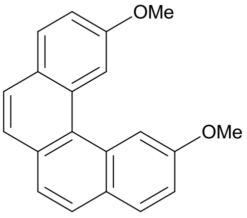
**$^1$H-NMR (400 MHz,$CDCl_3$):** δ 7.73-7.72 (m, 2H), 7.70 (d, *J* = 8.84 Hz, 1H), 7.58 (dd, *J* = 1.64, 8.64 Hz, 1H), 7.50 (td, *J* = 1.88, 8.72 Hz, 2H), 7.19 (d, *J* = 16.32 Hz, 1H), 7.11 (m, 2H), 7.10 (d, *J* = 16.56 Hz, 1H), 6.92 (td, *J* = 1.96, 8.76 Hz, 2H), 3.93 (s, 3H), 3.85 (s, 3H).

**Anal. Calcd. for $C_{20}H_{18}O_2$:** C 82.73, H 6.25. Found: C 82.63, H 6.41.

**IR (KBr):** 2958, 2895, 2837, 1637, 1622, 1597, 1507, 1252, 1178, 1066, 1028, 962, 898, 861, 837, 814, 764, 696, 630 cm.$^{-1}$

**MS (EI): *m/z*, (%)** 291 (21), 290.7 (50), 290.1 (35), 275 (09), 274 (12), 259 (14), 258 (14), 247 (08), 244 (08), 243 (08), 232 (10), 231 (12), 216 (10), 215 (26), 214 (19), 203 (11), 202 (16), 201 (15).

***2,11-Dimethoxybenzo[c]phenanthrene (134):***



A solution of 2-methoxy-7-(4-methoxystyryl)naphthalene **133** (0.250 g, 0.86 mmol), iodine (0.240 g, 0.95 mmol), THF (1.242 g, 1.4 mL, 17.22 mmol) in toluene (1.2 L) was irradiated using 250W HMPV lamp for 36 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained 2,11-dimethoxybenzo[*c*]phenanthrene **134** as colourless solid after column chromatography using petroleum ether: ethyl acetate (100:00 to 95:5) as eluent (0.241 g, 97%), **M.p**.138-140 °C.

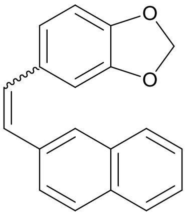
**$^1$HNMR (400 MHz, $CDCl_3$):** δ 8.63 (d, *J* = 2.36 Hz, 2H), 7.93 (d, *J* = 8.76 Hz, 2H), 7.82 (d, *J* = 8.44 Hz, 2H), 7.68 (d, *J* = 8.52 Hz, 2H), 7.28 (dd, *J* = 2.44, 8.8 Hz, 2H), 4.02 (s, 6H).

**Anal. Calcd. for $C_{20}H_{16}O_2$:** C 83.31, H 5.59. Found: C 83.91, H 5.42.

**IR (KBr):** 3187, 2994, 2898, 2828, 1673, 1606, 1560, 1506, 1462, 1354, 1293, 1243, 1217, 1175, 1117, 1075, 840, 735, 688, 627 cm.$^{-1}$

**MS (EI): m/z, (%)** 289 (18), 288 (37), 287 (100), 258 (17), 257 (10), 241 (17), 212 (34), 202 (13), 201 (14), 200 (14), 144 (09).

***5-(2-(naphthalen-2-yl)vinyl)benzo[d][1,3]dioxole (135):***



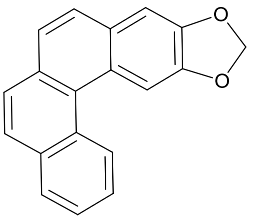
A solution of Na (0.084 g, 3.66 moles) in anhydrous methanol (5 mL) was added drop wise to a suspension of piperanal (0.50 g, 3.33 mmol) and [(2-naphthyl)methyl]triphenylphosphonium bromide salt **152** (1.79 g, 3.66 mmol) in anhydrous methanol (20 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 5-(2-(naphthalen-2-yl)vinyl)benzo[*d*][1,3]dioxole **135** as white solid (0.839 g, 91%), **M.p**.159-160 °C. (Lit. 155-156 °C).[69]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.82-7.79 (m, 4H), 7.70 (dd, *J* = 1.6, 8.64 Hz, 1H), 7.45 (m, 2H), 7.15 (d, *J* = 16.24 Hz, 1H), 7.13-7.11 (m, 1H), 7.09 (d, *J* = 16.32 Hz, 1H), 6.98 (dd, *J* = 1.72, 8.08 Hz, 1H), 6.82 (d, *J* = 8.08 Hz), 5.98 (s, 2H).

**IR (KBr):** 3050, 2901, 2798, 1601, 1502, 1441, 1389, 1350, 1283, 1270, 1241, 1217, 1182, 1086, 1048, 964, 926, 868, 817, 739, 645 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 275 (30), 274.6 (46), 274 (100), 273 (77), 272 (24), 244 (09), 243 (17), 242 (14), 216 (21), 215 (47), 214.9 (60), 214 (33), 213 (23), 212 (16), 189 (12), 188 (10), 108 (23), 107 (10), 94 (10).

***Benzo[c]phenanthreno[2,3-d]-1,3-dioxole (136):***



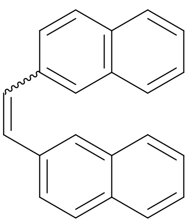
A solution of 5-(2-(naphthalen-2-yl)vinyl)benzo[*d*][1,3]-dioxole **135** (0.20 g, 0.73 mmol), iodine (0.203 g, 0.80 mmol), THF (1.053 g, 14.59 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 22 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained benzo[*c*]phenanthreno[2,3-d]-1,3-dioxole **136** as colourless solid after column chromatography using petroleum ether: ethyl acetate (100:00 to 95:5)as a eluent. (0.73 g, 37%), **M.p**.154-155 °C.

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 9.03 (d, *J* = 8.48 Hz, 1H), 8.52 (s, 1H), 7.98 (dd, *J* = 1.52, 7.76 Hz, 1H), 7.82-7.69 (four overlapping d, 4H), 7.66-7.58 (two overlapping m, 2H), 7.33 (s, 1H), 6.13 (s, 2H).

**IR (KBr):** 3429, 3049, 2905, 1632, 1602, 1494, 1463, 1361, 1200, 1172, 1119, 1071, 1036, 945, 931, 857, 833, 796, 761 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 273 (08), 272 (100), 214 (10), 213 (24), 212 (17), 211 (07), 107 (08), 106 (14).

### *1,2-Bis(2-naphthyl)ethylene (138):*

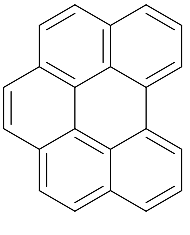


A solution of Na (0.81 g, 3.52 mmol) in anhydrous methanol (5 mL) was added drop wise to a suspension of the [(2-naphthyl)methyl]triphenyl-phosphonium bromide salt (1.72 g, 3.52 mmol) and 2-naphthaldehyde (0.500 g, 3.2 mmol) in anhydrous methanol (15 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1,2-bis-(2-naphthyl)ethylene **138** as white solid (0.540 g, 60%), **M.p**. 251-252 °C (Lit. 257-258 °C).[70]

**IR (KBr):** 3049, 2361, 1621, 1504, 1439, 1362, 960, 896, 862, 818, 747 $cm.^{-1}$

**MS (EI): *m/z*, (%)** 281 (23), 280 (100), 279 (72), 278 (33), 265 (17), 152 (14), 140 (34), 139 (43), 126 (20), 97 (23).

### *Benzo[ghi]perylene (35):*



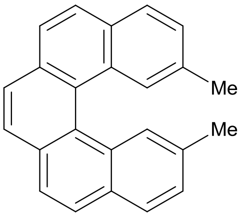
A solution of 1,2-bis(2-naphthyl)ethylene **138** (0.250 g, 0.89 mmol), iodine (0.249 g, 0.98 mmol, 1.1 eq), THF (1.29 g (1.45 mL), 1.78 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 30 h. After the reaction was complete the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained benzo[*ghi*]perylene **35** as pale yellow solid after column chromatography using petroleum ether as eluent (0.106 g, 43%), **M.p**. 265-270 °C (Lit. 270 °C).[70]

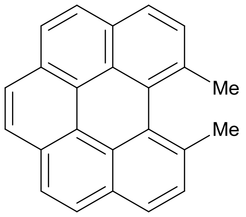
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 9.00 (dd, *J* = 0.8, 7.8 Hz, 2H), 8.34 (s, 2H), 8.19 (dd, *J* = 0.8, 7.7 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H).

**IR (KBr):** 3044, 2925, 1612, 1595, 1510, 1445, 844, 811, 767, 753 $cm.^{-1}$

**MS (EI): m/z, (%)** 278 (3), 277 (25), 276 (100), 275 (14), 274 (23), 138 (58), 137 (44), 136 (19), 125 (8), 124 (7).

***2,13-dimethyl[5]helicene (140) and 7,8-dimethylbenzo[ghi]perylene (141):***



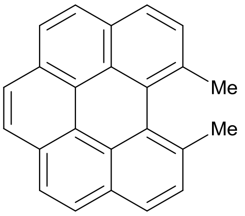


A solution of 3-methyl-6-(4-methylstyryl) phenanthrene **139** (0.250 g, 0.81 mmol), iodine (0.226 g, 0.89 mmol, 1.1 eq), THF (2.35 g, 2.83 mL, 40.53 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 16 h. After the reaction was complete the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The product was obtained mixture of 2,13-dimethyl[5]helicene **140** and 7,8-dimethylbenzo[*ghi*]perylene **141** as yellow solid after column chromatography using petroleum ether as eluent (0.150 g, 61%).

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.43 (s, 2H), 8.38 (s, 0.6H), 8.19 (d, *J* = 7.2 Hz, 2H), 7.93-7.83 (m, 8.8H), 7.40 (dd, *J* = 0.80, 8.0 Hz, 2H), 2.78 (s, 1.86H (-$CH_3$) for 7,8-dimethylbenzo[*ghi*]perylene), 2.37 (s, 6H (-$CH_3$) for 2,13-dimethyl[5]helicene).

[Ratio of the 2,13-dimethyl[5]helicene and 7,8-dimethylbenzo[*ghi*]perylene by $^1$HNMR is 69:31 respectively.]

***7,8-dimethylbenzo[ghi]perylene (141):***

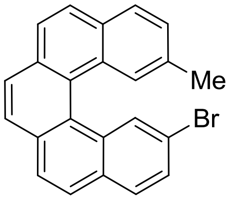


A solution of 3-methyl-6-(4-methylstyryl) phenanthrene **139** (0.250 g, 0.81 mmol), iodine (0.226 g, 0.89 mmol, 1.1 eq), THF (2.35 g, 2.83 mL, 40.53 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 24 h. After the reaction was complete the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The product was obtained mixture of 7,8-dimethylbenzo[*ghi*]-perylene **141** as yellow solid after column chromatography using petroleum ether as eluent (0.098 g, 40%).

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.37 (s, 2H), 8.20-8.18 (m, 6H), 7.89 (d, *J* = 8.0 Hz, 2H), 2.78 (s, 6H).

**MS (EI): m/z, (%)** 305 (26), 304 (100), 289 (50), 288 (41), 287 (24), 150 (10), 143 (18), 122 (07), 77 (06).

### *2-bromo-13-methyl[5]helicene (143):*



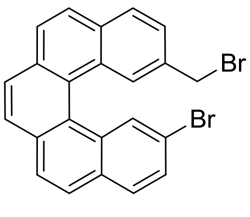
A solution of 3-bromo-6-(4-methylstyryl)phenanthrene **142** (0.100 g, 0.27 mmol), iodine (0.075 g, 0.29 mmol, 1.1 eq), THF (0.96 g, 1.09 mL, 13.39 mmol) in toluene (500 L) was irradiated using 125W tungstan lamp for 16 h. After the reaction was complete the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The product was obtained mixture of 2-bromo-13-methyl[5]helicene **143** as pale yellow solid after column chromatography using petroleum ether as eluent (0.061 g, 61%).

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.79 (s, 1H), 8.37 (s, 1H), 7.93-7.80 (m, 8H), 7.63 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 2.44 (s, 3H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 134.50 (Cq), 132.61 (Cq), 132.60 (Cq), 131.92 (Cq), 131.40 (CH), 131.0 (Cq), 130.84 (Cq), 130.28 (Cq), 129.40 (CH), 129.26 (CH), 128.53 (CH), 128.30 (CH), 128.03 (CH), 127.90 (CH), 127.65 (CH), 127.02 (2 X CH), 126.82 (CH), 126.43 (Cq), 126.02 (Cq), 125.45 (CH), 118.31 (Cq), 21.78 ($\underline{C}H_3$).

**MS (EI): m/z, (%)** 374 (22), 373 (96), 372 (65), 371 (100), 370 (45), 320 (21), 293 (23), 292 (83), 291 (31), 277 (05)

### *2-bromo-13-(bromomethyl)-[5]helicene (144):*

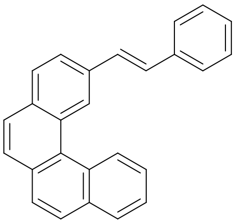


A solution of 2-methyl[5]helicene **143** (0.032 g, 0.08 mmol), N-bromosuccinimide (0.017 g, 0.095 mmol) and benzoyl peroxide (0.002 g, 0.008 mmol) in carbon teterachloride (10 mL) was irradiated in 200W tungsten lamp and stirred for 5 h. At the end of this time the reaction mixture was cooled and the succinimide produced was removed by filtration. The filtrate was washed with sodium thiosulphate solution, water and dried over sodium sulfate, the solvent was removed on rotary evaporator to obtain the crude product purified by column chromatography on silica gel using ethyl acetate: petroleum ether (2:98) as eluent to obtained product as white solid. (0.015 g, 39%).

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.69 (d, *J* = 1.6 Hz, 1H), 8.57 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.95-7.87 (m, 6H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.61 (dd, *J* = 2.0, 8.4 Hz, 1H), 4.58 (d, *J* = 10.0 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H).

**MS (EI): m/z, (%)** 453 (15), 452 (16), 451 (33), 450 (22), 449 (18), 447 (09), 400 (05), 398 (05), 373 (12), 372 (35), 371 (100), 370 (36), 369 (91), 292 (07), 291 (13), 289 (05), 61 (12).

***1-Phenyl-2-(2-benzo[c]phenanthrenyl)ethylene (145):***



Preparation of Catalyst Solution: A solution of palladium acetate (0.0015 g, 0.0065 mmol, 1 mol%) and 1,3-bis(diphenylphospino)propane (0.004 g, 0.0097 mmol, 1.5eq. of Pd(OAc)$_2$) was prepared in N,N-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous solution was obtained. This solution was degassed several times prior to use.

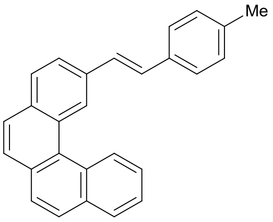
In another r.b. flask mixture of 2-bromobenzo[*c*]phenanthrene **128** (0.2 g, 0.65 mmol), dry potassium carbonate (0.180 g, 1.3 mmol, 2 eq.), TBAB (0.104 g, 0.13 mmol, 20 mol%) was prepared in dry N,N-dimethylacetamide (15 mL) and degassed. This was heated to 60 °C and charged with styrene (0.102 g, 0.97 mmol, 1.5 eq.) and the mixture was heated up to 100 °C. When the temperature reached to 100 °C, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel to get pure product 1-phenyl-2-(2-benzo[*c*]phenanthrenyl)ethylene **145** as a white solid (0.204 g, 95%), **M.p**. 140-142 °C (Lit. 140 °C).[30,73]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 9.19 (d, *J* = 7.2 Hz, 1H), 9.18 (s, 1H), 8.07-8.04 (m, 2H), 7.94-7.89 (m, 2H), 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):** 3018, 2364, 1601, 1497, 1445, 957, 832, 783, 745, 687 cm.$^{-1}$

**MS (EI): m/z, (%)** 331(26), 330 (100), 329 (29), 328 (15), 313 (10), 226 (8), 165 (30), 164 (22), 163 (21), 157 (25), 156 (18), 151 (8).

### *1-(p-methylphenyl)-2-(2-benzo[c]phenanthrenyl)ethylene (146):*



Preparation of catalyst solution:

A solution of palladium acetate (0.0036 g, 0.016 mmol, 1 mol%) and 1,3-bis(diphenylphospino)propane (0.02 g, 0.024 mmol, 1.5 eq. of $Pd(OAc)_2$) was prepared in N,N-dimethylacetamide (5 mL), and purged with dry nitrogen. The mixture was stirred at room temperature until homogeneous solution was obtained. This solution was degassed several times prior to use.

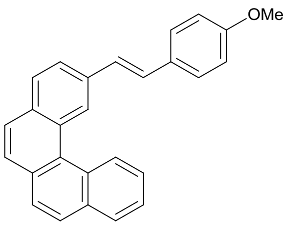
In another r.b. flask 2-bromobenzo[*c*]phenanthrene **128** (0.5 g, 1.62 mmol), dry potassium carbonate (0.45 g, 3.25 mmol, 2 eq.), TBAB (0.105 g, 0.32 mmol, 20 mol%) and N,N-dimethylacetamide (10-15 mL) were taken and repeatedly degassed and purged with $N_2$. This mixture was heated to 60 °C and 4-methylstyrene (0.288 g, 0.32 mL, 2.44 mmol, 1.5 eq.) was added and the mixture was further heated to 100 °C. When the temperature reached to 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel to afford 1-(*p*-methylphenyl)-2-(2-benzo[*c*]phenanthrenyl)ethylene **146** as a white solid using petroleum ether as eluent (0.554 g, 99%), **M.p**. 115-116 °C (Lit. 118-119 °C).[31,74]

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 9.15 (d, *J* = 8.56 Hz, 1H), 9.12 (s, 1H), 8.02 (dd, *J* = 1.32, 8.0 Hz, 1H), 7.97 (d, *J* = 8.36 Hz, 1H), 7.90-7.84 (m, 3H), 7.80 (d, *J* = 8.56 Hz, 1H), 7.77 (d, *J* = 8.48 Hz, 2H), 7.72 (ddd, *J* = 1.48, 6.96, 8.48 Hz, 1H), 7.63 (ddd, *J* = 1.08, 7.0, 8.0 Hz, 1H), 7.49 (d, *J* = 8.04 Hz, 2H), 7.34 (d, *J* = 16.36 Hz, 1H), 7.26 (d, *J* = 16.36 Hz, 1H), 7.20 (d, *J* = 7.88 Hz, 1H), 2.37 (s, 3H).

**IR (KBr):** 3023, 2915, 1598, 1508, 1414, 1230, 1181, 961, 838, 802, 747, 671, 610 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 345(29), 344 (100), 329 (15), 328 (19), 226 (07), 165 (22), 164 (34), 156 (13).

***1-(p-methoxyphenyl)-2-(2-benzo[c]phenanthrenyl)ethylene (148)***[75]***:***



Preparation of catalyst solution:

A solution of palladium acetate (0.0044 g, 0.019 mmol, 1 mol%) and 1,3-bis(diphenylphospino)propane (0.016 g, 0.039 mmol, 2.0 eq. of $Pd(OAc)_2$) was prepared in N,N-dimethylacetamide (5 mL), and purged with dry nitrogen. The mixture was stirred at room temperature until homogeneous solution was obtained. This solution was degassed several times prior to use.

In another r.b. flask 2-bromobenzo[*c*]phenanthrene **128** (0.60 g, 1.95 mmol), dry potassium carbonate (0.540 g, 3.91 mmol, 2 eq.), TBAB (0.126 g, 0.39 mmol, 20 mol%) and *N*,*N*-dimethylacetamide (20 mL) were taken and repeatedly degassed and purged with $N_2$. This mixture was heated to 60 °C and 4-methoxystyrene (0.314 g, 0.31 mL, 2.34 mmol, 1.2 eq.) was added and the mixture was further heated to 100 °C. When the temperature reached to 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (100:00 to 98:2) to afford 1-(*p*-methoxyphenyl)-2-(2-benzo[*c*]phenanthrenyl)ethylene **148** white solid (0.665 g, 94%), **M.p**. 166-168 °C

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 9.15 (d, *J* = 8.4 Hz, 1H), 9.09 (s, 1H), 8.02 (dd, *J* = 0.8, 8.00 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.84 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.72 (ddd, *J* = 1.6, 7.2, 8.4 Hz, 1H), 7.63 (td, *J* = 0.8, 7.6 Hz, 1H), 7.52 (td, *J* = 2.8, 4.8, 9.6 Hz, 2H), 7.24 (m, 2H), 6.92 (td, *J* = 2.8, 4.8, 10 Hz, 2H), 3.83 (s, 3H).

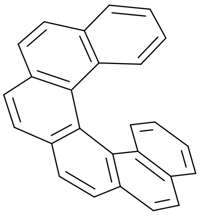
**$^{13}$C-NMR (100.6 MHz, $CDCl_3$):** δ 159.40 (Cq), 135.54 (Cq), 133.54 (Cq), 132.84 (Cq), 131.36 (Cq), 130.68 (Cq), 130.39 (Cq), 130.39 (Cq), 130.20 (CH), 128.92 (CH), 128.72 (CH), 128.64 (CH), 127.86 (2 X CH), 127.55 (CH), 127.33 (Cq), 127.19 (CH), 127.17 (CH), 126.93 (CH), 126.75 (CH), 126.69 (CH), 126.24 (CH), 125.89 (CH), 123.13 (CH), 114.22 (2 X CH), 55.38 ($-O\underline{C}H_3$).

**Anal. Calcd. for $C_{27}H_{20}O$:** C 89.97, H 5.59. Found: C 89.63, H 5.48.

**IR (KBr):** 3031, 2967, 2843, 1733, 1595, 1507, 1437, 1363, 1297, 1247, 1176, 1025, 961, 869, 839, 812, 740, 672 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 361 (98), 360 (22), 359 (100), 325 (15), 317 910), 316 (15), 315 919), 314 (12), 313 (16), 302 909), 301 (10), 300 (12), 180 (18), 172 912), 164 (10), 162 (17), 158 (20), 156 (24), 150 (13), 143 (08).

***[6]Helicene (96):***



A solution of 1-phenyl-2-(2-benzo[*c*]phenanthrenyl)ethylene **145** (0.130 g, 0.39 mmol), iodine (0.109 g, 0.43 mmol, 1.1 eq), THF (0.567 g, 7.87 mmol, 20 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 24 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product [6]helicene **96** was obtained after column chromatography using petroleum ether: ethyl acetate (100:00 to 98:2) as yellow solid, which was further crystallized in light petroleum ether (0.083 g, 64%). **M.p**. 231-232 °C. (Lit. 231 °C).[31]

*Same compound was also synthesized by double photocyclization of **18** (scheme-6).*

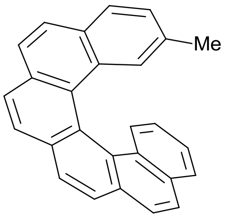
A solution of 2,7-distyrylnaphthalene **151** (0.110 g, 0.38 mmol), iodine (0.214 g, 0.84 mmol 2.2 eq.), tetrahydrofuran (1.1 g, 1.23 mL, 15.2 mmol, 40 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 22 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product [6]helicene **96** was obtained after column chromatography after column chromatography using ethyl acetate: petroleum ether (2:98) as yellow solid (0.081 g, 75%) (for further purification crystallized from petroleum ether). **M.p**. 231-232 °C (Lit. 231°C).[31]

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.01-7.96 (m, 4H), 7.95-7.90 (m, 4H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.21 (dd, *J* = 7.2, 7.7 Hz, 2H), 6.67 (m, 2H).

**IR (KBr):** 3042, 1601, 1500, 1468, 1434, 844, 828, 799, 753 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 329 (26), 328 (100), 301 (43), 300 (69), 163 (49), 162 (60), 161 (27), 156 (50), 150 (48), 149 (45), 111 (32), 97 (49), 85 (61), 83 (61).

***2-Methyl[6]helicene (147):***



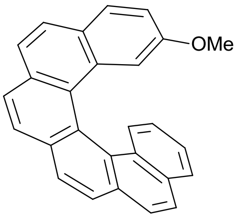
A solution of 1-(*p*-methylphenyl-2-(2-benzo[*c*]phenanthrenyl)- ethylene **146** (0.250 g, 0.75 mmol), iodine (0.135 g, 0.80 mmol, 1.1 eq), THF (1.08 g, 15 mmol, 20 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 24 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product 2-methyl[6]helicene **147** was obtained after column chromatography as pale yellow solid, recrystallized from mixture of ethyl acetate-petroleum ether (0.193 g, 78%), **M.p**. 194-196 °C (Lit. 194-198 °C).[32]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.02-7.92 (m, 6H), 7.88-7.82 (m, 2H), 7.80 (dd, *J* = 0.8 Hz & 8.04 Hz, 1H), 7.70 (d, *J* = 8.08,Hz, 1H), 7.59 (d, *J* = 8.48, Hz, 1H), 7.36 (s, 1H), 7.22 (dd, *J* = 0.88, 7.88 Hz, 1H), 7.04 (dd, *J* = 1.32, 8.08 Hz, 1H), 6.67 (ddd, *J* = 1.32, 6.92, 8.36 Hz, 1H), 1.75 (s, 3H).

**IR (KBr):** 3045, 2911, 1603, 1504, 1475, 1438, 1144, 1036, 951, 848, 833, 794, 747, 733, 618 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 343 (30), 342 (100), 327 (49), 326 (35), 300 (45), 171 (14), 163 (60), 162 (62), 150 (28).

***2-Methoxy[6]helicene (149):***[77]



A solution of 1-(*p*-methoxyphenyl-2-(2-benzo[*c*] phenanthrenyl)ethylene **148** (0.350 g, 0.97 mmol), iodine (0.271 g, 1.06 mmol, 1.1 eq), THF (3.50 g, 3.94 mL, 48.5 mmol, 50 eq.) in toluene (1.2 L) was irradiated using 250W HMPV lamp for 24 h. After the reaction was over the excess of iodine was removed by washing the solution with aqueous $Na_2S_2O_3$, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product 2-methoxy[6]helicene **149** was obtained after column chromatography as pale yellow solid, recrystallized from petroleum ether: ethyl acetate (100:00 to 98:2) (0.180 g, 52%), **M.p**. 210-211 °C.

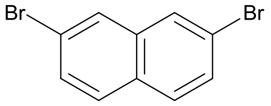
**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.04-7.95 (m, 5H), 7.91-7.83 (m, 4H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.29-7.26 (m, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 2.4 Hz & 8.8 Hz, 1H), 6.75 (ddd, *J* = 1.2 Hz, 7.2 Hz & 8.4 Hz, 1H), 2.89 (s, 3H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** 157.09 (Cq), 133.07 (Cq), 131.84 (Cq), 131.61 (Cq), 131.23 (Cq), 131.04 (Cq), 130.23 (Cq), 129.05(CH), 127.66 (Cq), 127.59 (CH), 127.54 (CH), 127.52 (CH), 127.47 (CH), 127.35 (Cq), 127.29 (CH), 127.08 (CH), 127.00 (CH), 126.89 (CH), 126.84 (Cq), 126.59 CH), 125.98 (CH), 124.89 (CH), 124.16 (Cq), 123.89 (CH), 177.54 (CH), 107.65 (CH), 54.24 (-OCH$_3$).

**Anal. Calcd. for C$_{27}$H$_{18}$O:** C 90.47, H 5.06. Found: C 89.22, H 5.42.

**MS (EI):** ***m/z*, (%)** 359 (24), 358 9100), 357 (79), 327 (51), 326 (71), 325 (24), 324 (22), 323 (21), 313 (30), 312 (29), 311 (13), 300 (37), 299 (25), 163 (22), 162 (14), 156 (16), 155 (13), 150 (18).

### ***2,7-Dibromonaphthalene (150):***



A 250 mL round bottom flask was charged with triphenylphosphine (14.41g, 54.9 mmol, 2.2 eq.) and dry acetonitrile (20 mL). The suspension was cooled to 0 °C and to this mixture dry bromine (8.77 g, 2.8 mL, 54.93 mmol, 2.2 eq.) was added dropwise in such a way that temperature was maintained below 5 °C. The heavy white precipitates were formed. To this mixture 2,7-dihydroxynaphthalene in acetonitrile (40 mL) was added in one portion. The precipitates become even thicker and stirring was maintained. The mixture was heated to 70-80 °C at which point precipitates dissolved and reaction continued for 1.5 h. The flask was fitted with air cooled distillation assembly and acetonitrile was distilled at atmospheric pressure. The temperature was then gradually increased up to 250 °C. Evolution of HBr appeared to begin with strong heating (~190 °C). This evolved HBr was trapped by saturated NaOH solution. The temperature was maintained around 280-300 °C for 2 h and dark oil was obtained which was allowed to cool to 100 °C at which point 50 mL of absolute ethanol was added and stored at 4 °C for overnight. The product was extracted with petroleum ether, and separated by column chromatography (SiO$_2$, Petroleum ether) to afford 2,7-dibromonaphthalene as a colorless solid (3.76 g, 53%), which was recrystallized from ethanol for further purification. **M.p**. 138-140 °C (Lit. 140-141 °C).[78a]

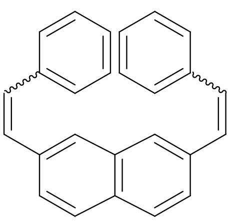
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.90 (d, *J* = 1.6 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.55 (dd, *J* = 1.6, 8.8 Hz, 2H).

**$^{13}$C-NMR (100.61 MHz, $CDCl_3$):** δ 135.4 (Cq), 130.21 (Cq), 129.75 (CH), 129.51 (CH), 129.00 (CH), 121.04 (Cq).

**IR (KBr):** 3052, 1606, 1567, 1482, 1344, 1178, 933, 903, 867, 836, 636, 592, 538, 473 cm.$^{-1}$

**MS (EI):** ***m/z* (%)** 288 (42), 286 (100), 284 (46), 207 (21), 205 (23), 144 (09), 143 (18), 142 (09), 126 (84), 125 (10), 103 (08), 74 (11), 63 (38).

***2,7-Distyrylnaphthalene (151):***



Preparation of Catalyst Solution :

A solution of palladium acetate (0.0078 g, 3.5 mmol, 2 mol%) and 1,3-bis(diphenylphospino)propane (0.0112 g, 1.5 eq. of $Pd(OAc)_2$) was prepared in N,N-dimethylacetamide (5 mL) under the nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous solution was obtained. This solution was degassed several times prior to use.

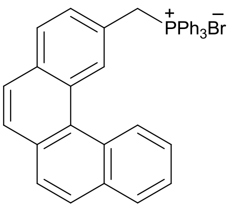
The 2,7-dibromonaphthalene **150** (0.500 g, 1.74 mmol), dry potassium carbonate (0.967 g, 6.96 mmol, 4 eq.), TBAB (0.112 g, 0.34 mmol, 20 mol%) and N,N-dimethylacetamide (10-15 mL) were taken in two neck r.b. flask and repeatedly degassed and purged with $N_2$. To this styrene (0.546 g, 5.24 mmol, 3 eq.) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached to 100 °C, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase, washed with water, brine and dried over sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel to afford 2,7-distyrylnaphthalene **151** as white solid (0.377 g, 65%), **M.p**. 262-264 °C (Lit. 260-262 °C).[78b]

**$^1$H-NMR (400 MHz, d$^6$-DMSO):** δ 7.98-7.92 (m, 12H contains 1 olefin H), 7.83-7.79 (m, 2H, for olefin *J* = 17.6 Hz), 7.62-7.60 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.28 (m, 2H).

**IR (KBr):** 3053, 3022, 1619, 1492, 1445, 966, 913, 836, 747, 691 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 333 (27) 332 (100), 254 (7), 253 (26), 229 (11), 228 (20), 226 (09), 166 (12), 164 (9), 158 (26), 151 (13).

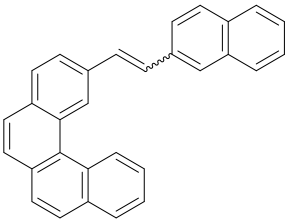
***2-Benzo[c]phenanthrylmethyltriphenylphosphonium bromide (153):***



A solution of 2-methylbenzo[*c*]phenanthrene **131** (0.250 g, 1.03 mmol), N-bromosuccinimide (0.184 g, 1.03 mmol) and benzoyl peroxide (0.025 g, 0.1 mmol) in carbon teterachloride (10 mL) was heated to reflux and stirred for 8 h. At the end of this time the reaction mixture was cooled and the succinimide produced was removed by filtration. The filtrate was washed with sodium thiosulphate solution, water and dried over sodium sulfate, the solvent was removed on rotary evaporator.

The crude product (0.330 g) and triphenylphosphine (0.295 g, 1.12 mmol) was dissolved in xylene and refluxed with stirring for 8 h. The precipitates formed were collected, washed with petroleum ether and dried in vacuum to afford white solid, (0.61 g, 98%), **M.p**. 298-302 °C. (Lit. 308 °C).[79]

***1-(β-Naphthyl)-2-(2-benzo[c]pheantryl)ethylene (154):***



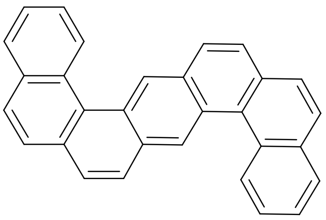
A solution of Na (0.081 g, 35.21 mmol) in anhydrous methanol (5 mL) was added drop wise to a suspension of the 2-benzo[*c*]phenanthrylmethyltriphenylphosponium bromide **153** (1.632 g, 35.21 mmol) and 2-naphthaldehyde (0.50, 32 mmol) in anhydrous methanol (20 mL) under $N_2$ at room temperature. After completion of the addition, the resulting solution was stirred for 24 h at room temperature, when no starting material was seen on tlc. After the completion of the reaction, the mixture was poured on cold water to separate the precipitate. The aqueous solution along with precipitates was extracted with ethyl acetate and solvent layer was washed with water, brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure and crude product was purified on silica gel column to afford mostly *trans* form of the 1-(*β*-naphthyl)-2-(2-benzo[*c*]pheantryl)ethylene **154** as white solid (0.660 g, 54%), **M.p.** 198-200 °C (Lit. 200-201 °C).[22,80]

**$^1$H-NMR (500 MHz, CDCl$_3$):** δ 9.19 (d, *J* = 8.5 Hz, 1H), 9.18 (s, 1H), 8.06-8.02 (m, 2H), 7.85-7.81 (m, 10H), 7.78-7.75 (m, 1H), 7.68-7.65 (m, 1H), 7.55-7.45 (m, 4H, 2-aromatic & 2-olefinic protons, *J* = 16.5 Hz for olefinic H).

**IR (KBr):** 3046, 2364, 1919, 1595, 1500, 1426,1237, 959,895, 820, 811, 744, 621 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 381 (31), 380 (100), 379 (36), 378 (16), 363 (11), 226 (7), 190 (37), 189 (38), 188 (27), 182 (26), 176 (6).

***Dinaphtho[1,2-a:2',1'-h]anthracene (37):***



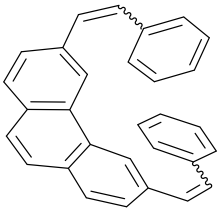
A solution of 1-(β-naphthyl)-2-(2-benzo[*c*]-phenanthryl)-ethylene **154** (0.125 g, 0.35 mmol), iodine (0.098 g, 0.38 mmol, 1.1 eq), THF (0.506 g, 0.569 mL, 7.02 mmol) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 24 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was obtained after column chromatography using petroleum ether as eluent to afford yellow Solid (0.093 g, 75%). **M.p**. 230-231 °C (Lit. 230-231 °C).[80]

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 9.66 (s, 2H), 9.37 (d, *J* = 8.52, 2H), 8.12-8.09 (m, 4H), 8.01 (d, *J* = 8.48 Hz, 2H), 7.89 (dd, *J* = 8.48, 8.68 Hz, 4H), 7.80 (ddd, *J* = 1.4, 1.48, 6.92 Hz, 2H), 7.69 (ddd, *J* = 0.96, 1.0, 7.92 Hz, 2H).

**IR (KBr):** 3047, 1596, 1501, 1419, 1387, 1223, 902, 841, 797, 753 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 379 (30), 378 (91), 376 (22), 256 (16), 189 (48), 188 (44), 187 (48), 129 (34), 111 (49), 98 (58), 97 (81), 85 (90), 83 (100), 82 (49), 71 (98).

***3,6-Distyrylphenanthrene (155):***



Preparation of catalyst solution:

A solution of palladium acetate (0.0033 g, 0.015 mmol, 2 mol%) and 1,3-bis(diphenylphospino)propane (0.012 g, 2 eq. of Pd(OAc)$_2$) was prepared in N,N-dimethylacetamide (5 mL), under nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous solution was obtained. This solution was degassed several times prior to use.

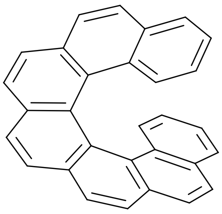
In another r.b. flask 3,6-dibromophenanthrene **118** (0.250 g, 0.74 mmol), dry potassium carbonate (0.412 g, 2.97 mmol, 4 eq.), TBAB (0.048 g, 0.014 mmol, 20 mol%) and N,N-dimethylacetamide (10 mL) were taken and repeatedly degassed and purged with $N_2$. To this styrene (0.235 g, 2.23 mmol, 3 eq.) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was concentrated and the crude product was purified by column chromatography on silica gel to obtained 3,6-distyrylphenanthrene **155** as white solid[71] (0.233 g, 82 %), **M.p**.198-200 °C.

**$^1$H-NMR (500 MHz, $CDCl_3$):** δ 8.76 (s, 2H), 7.89-7.85 (m, 4H), 7.70 (s, 2H), 7.30 (d, $J$ = 7.5 Hz, 2H), 7.64 (d, $J$ = 7.0 Hz, 4H), 7.45-7.40 (m, 6H), 7.34 (d, $J$ = 16.5 Hz, 2H).

**IR (KBr):** 3022, 1802, 1601, 1494, 1446, 1154, 958, 886, 840, 788, 750, 688 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 384 (4), 383 (32), 382 (100), 303 (13), 302 (9), 289 (8), 278 (8), 277 (6), 276 (10), 191 (19), 183 (10), 182 (17), 151 (13).

***[7]Helicene (32):***



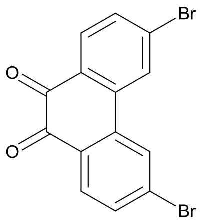
A solution of 3,6-distyrylphenanthrene **155** (0.150 g, 0.39 mmol), iodine (0.219 g, 8.64 mmol, 2.2 eq.), tetrahydrofuran (1.32 g, 1.27 mL, 15.71 mmol, 40 eq.) in toluene (1.2 L) was irradiated using 125W HMPV lamp for 12 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product [7]helicene **32** as yellow solid was obtained after column chromatography (0.066 g, 44%), **M.p**. 254-256 °C (Lit. 254-255 °C.).[28,71]

**$^1$H-NMR (500 MHz, $CDCl_3$):** δ 8.03 (s, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* =7.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 2H), 6.40 (t, *J* = 7.0 Hz, 2H).

**IR (KBr):** 2925, 2364, 1610, 1049, 839, 608 cm.$^{-1}$

**MS (EI) : *m/z,* (%)** 378 (31), 377 (12), 351 (10), 350 (8), 256 (18), 187 (26), 129 (31), 111 (46), 98 (59), 97 (76), 83 (96), 71 (100).

***3,6 -Dibromo-9,10-phenanthraquinone (156):***



To a suspension of phenanthrene **3** (3.0 g, 17 mmol) in dilute $H_2SO_4$ (30 mL, conc. $H_2SO_4$ & 60 mL $H_2O$), $K_2Cr_2O_7$ (18 g) was added at 90-95 °C (water bath) in small lots (0.5-1 g) until a vigorous reaction sets in. The external heating was removed and temperature of mixture was kept approximately 110-115 °C. The temperature of reaction mixture was not allowed to fall below 85 °C (hot water bath can be used if necessary). Finally the mixture was heated on boiling water bath for 30 min, cooled, water (200 mL) was added and the crude product was filtered, washed with water, purified by suspending in rectified spirit (30 mL) and stirred with saturated sodium bisulphate solution (30 mL). The mixture was stirred for 10 min, diluted with water (175 mL), Filtered. The filtrate was treated with saturated sodium carbonate solution. The precipitated 9,10-phenanthraquinone was filtered, washed with water, crystallized from glacial acetic acid, to obtained orange solid. (4.046 g, 57.7%), **Mp**. 207-209 °C (Lit. 208.5-210 °C).[81a] **IR (KBr):** 3067, 2964, 1675, 1593, 1478, 1451, 1229, 972, 893, 766, 716 cm.$^{-1}$

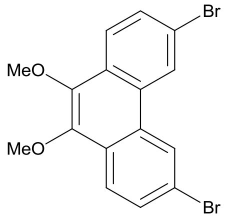
A mixture of 9,10-phenantrquinone (0.5 g, 2.4 mmol), dry nitrobenzene (3.0 mL) and dry bromine (1.35 mL, 26.4 mmol, dried over conc. $H_2SO_4$) and benzoyl peroxide (0.029 g, 0.12 mmol) was exposed to tungsten lamp. Within about 10 min, evolution of gas bubbles could be seen. The temperature of the reaction was kept at 75 °C. After about 1 hr, the evolution of gas became imperceptible and cluster of needles gradually separated. The crude product 3,6-dibromo-9,10-phenanthraquinone **156** was filtered, dried and recrystallized from absolute ethanol to obtain the orange needles (0.50 g, 72.5%). **M.p**. 258-260 °C (Lit. 259-276 °C).[81b]

**$^1$H-NMR (200 MHz, $CDCl_3$):** δ 8.11 (s, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H),

**IR (KBr):** 3101, 3034, 2921, 2852, 1677, 1583, 1545, 1470, 1225, 967, 903, 828, 701 cm.$^{-1}$

**MS (EI): m/z, (%)** 368 (8), 366 (14), 339 (28), 337 (55), 335 (30), 230 (21), 228 (22), 150 (100), 149 (24), 129 (20), 115 (23), 83 (26), 81 (18), 75 (56), 74 (25),71 (24).

***3,6-Dibromo-9,10-dimethoxyphenanthrene (157):***



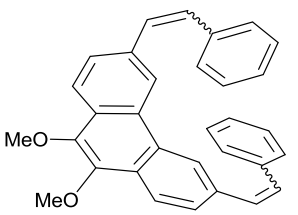
A mixture of 3,6-dibromo-9,10-phenanthraquinone **156** (2.5 g, 6.83 mmol), tetrabutylbutyl ammonium bromide (0.704 g, 2.186 mmol), sodium dithionite (3.567 g, 20.49 mmol), THF (30 mL) and $H_2O$ (30 mL) in round bottom flask was stirred for 30 min, then dimethyl sulfate (3.36 mL, 35.52 mmol) was added, followed by aqueous NaOH (3.56 g in 20 mL water). The mixture was stirred for 15 min, while after 3 min, 5-6 g of ice added to keep mixture at ambient temperature. The aqueous layer was separated and extracted with ethyl acetate, the combined organic layer was washed with water, dilute ammonia, brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate: petroleum ether (2:98) as eluent to obtained 3,6-dibromo-9,10-dimethoxyphenanthrene **157** as white solid (2.35 g, 82 %), **M.p**. 134-136 °C.[82]

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.57 (d, *J* = 1.44 Hz, 2H), 8.01 (d, *J* = 8.72 Hz, 2H), 7.64 (dd, *J* = 1.44, 8.72 Hz, 2H), 3.99 (s, 6H).

**IR (KBr):** 3438, 2932, 2837, 2366, 2340, 1906, 1720, 1614, 1587, 1482, 1458, 1422, 1394, 1345, 1311, 1229, 1202, 1121, 1091, 1064, 1023, 985, 861, 820, 707, 601 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 398 (43), 396 (91), 394 (53), 382 (35), 380 (75), 378 (43), 352 (33), 337 (24), 273 (56), 271 (57), 165 (42), 163 (22), 150 (100), 148 (95), 81 (28).

***3,6-Distyryl-9,10-dimethoxyphenanthrene (158):***



Preparation of Catalyst Solution:

A solution of palladium acetate (0.0028 g, 0.0126 mmol, 1 mol %) and 1-(α-1-Piperidylbenzyl)-2-naphthol (Ligand A) (0.0048 g, 0.01515 mmol, 1.2 eq. of $Pd(OAc)_2$) was prepared in N,N-dimethylacetamide (5 mL), under nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous solution was obtained. This solution was degassed several times prior to use.

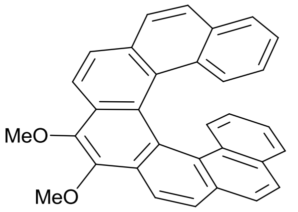
In another r.b. flask 3,6-dibromo-9,10-dimethoxynaphthalene **157** (0.500 g, 1.26 mmol), dry potassium carbonate (0.873 g, 6.31 mmol, 5 eq.), TBAB (0.163 g, 0.51 mmol, 20 mol%) and N,N-dimethylacetamide (10-15 mL) were taken in and repeatedly degassed and purged with $N_2$. To this styrene (0.526 g, 0.58 mL, 5.05 mmol, 3 eq.) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 °C for 48 h. After the completion of reaction, the mixture was poured in 6N HCl and extracted with dichloromethane. The combined organic phase was washed with water, brine and dried over sodium sulfate. The solvent was concentrated and the crude product 3,6-distyryl-9,10-dimethoxyphenanthrene **158** was isolated as white solid by column chromatography on silica gel and petroleum ether as eluent (0.52 g, 93%), **M.p**. 116-120 °C,

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.72 (d, *J* = 1.2 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 1.6, 8.8 Hz, 2H), 7.63-7.62 (m, 4H), 7.44-7.28 (m, 10 H, overlapping the *trans* coupling proton signals d, *J* = 16.4 Hz), 4.11 (s, 6H).

**IR (KBr):** 3438, 3024, 2931, 2835, 1602, 1503, 1446, 1419, 1364, 1327, 1243, 1202, 1121, 1062, 986, 954, 816, 751 cm.$^{-1}$

**MS (EI): *m/z*, (%)** 443 (33), 442 (100), 428 (13), 427 (41), 399 (23), 221 (53), 213 (10), 192 (10), 191 (14), 184 (15), 183 (13), 182 (18), 177 (23), 176 (34), 175 (12), 169 (32), 163 (11).

***9,10-dimethoxy-[7]helicene (159):***



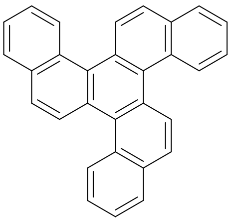
A solution of 3,6-distyryl-9,10-dimethoxyphenanthrene **158** (0.450 g, 1.02 mmol), iodine (0.568 g, 2.24 mmol, 2.2 eq.), tetrahydrofuran (7.34 g, 8.25 mL, 10.18 mmol, 100 eq.) in toluene (1.2 L) was irradiated using 250W HMPV lamp for 36 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product 9,10-dimethoxy-[7]helicene **159** was obtained as orange-yellow crystals after column chromatography (0.225 g, 50%), **M.p**. 270-272 °C, (Lit. > 250 °C.).[84]

**$^1$H-NMR (500 MHz, $CDCl_3$):** δ 8.38 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.29 (dd, *J* = 1.0, 8.5 Hz, 2H), 6.90 (ddd, *J* = 1.5, 8.0, 8.5 Hz, 2H), 6.39 (ddd, *J* = 1.5, 7.0, 8.5 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.25 (s, 6H).

**IR (KBr):** 3435, 3045, 2977, 2941, 2362, 1600, 1571, 1519, 1469, 1418, 1375, 1277, 1096, 1048, 987, 828, 749 cm.$^{-1}$

**MS (EI):** ***m/z*, (%)** 439 (21), 438 (63), 423 (28), 395 (28), 380 (24), 350 (25), 203 (22), 195 (30), 181 (36), 180 (34), 175 (100), 174 (40), 168 (24), 111 (22), 97 (33), 85 (43), 84 (22), 83 (43), 71 (43).

***Benzo[c]naphtho[2,1-p]chrysene (161):***



A solution of 1,3,5-tristyrylbenzene **160** (0.090 g, 0.23 mmol), iodine (0.196 g, 0.77 mmol, 3.3 eq.), tetrahydrofuran (1.014 g, 1.14 mL, 14.05 mmol, 60 eq.) in toluene (425 L) was irradiated using 125W HMPV lamp for 25 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product benzo[*c*]naphtho[2,1-*p*]chrysene **161** was obtained as pale yellow solid after column chromatography (0.030 g, 33%), **M.p**. 230-231 °C, (Lit. 233-234 °C.).[85]

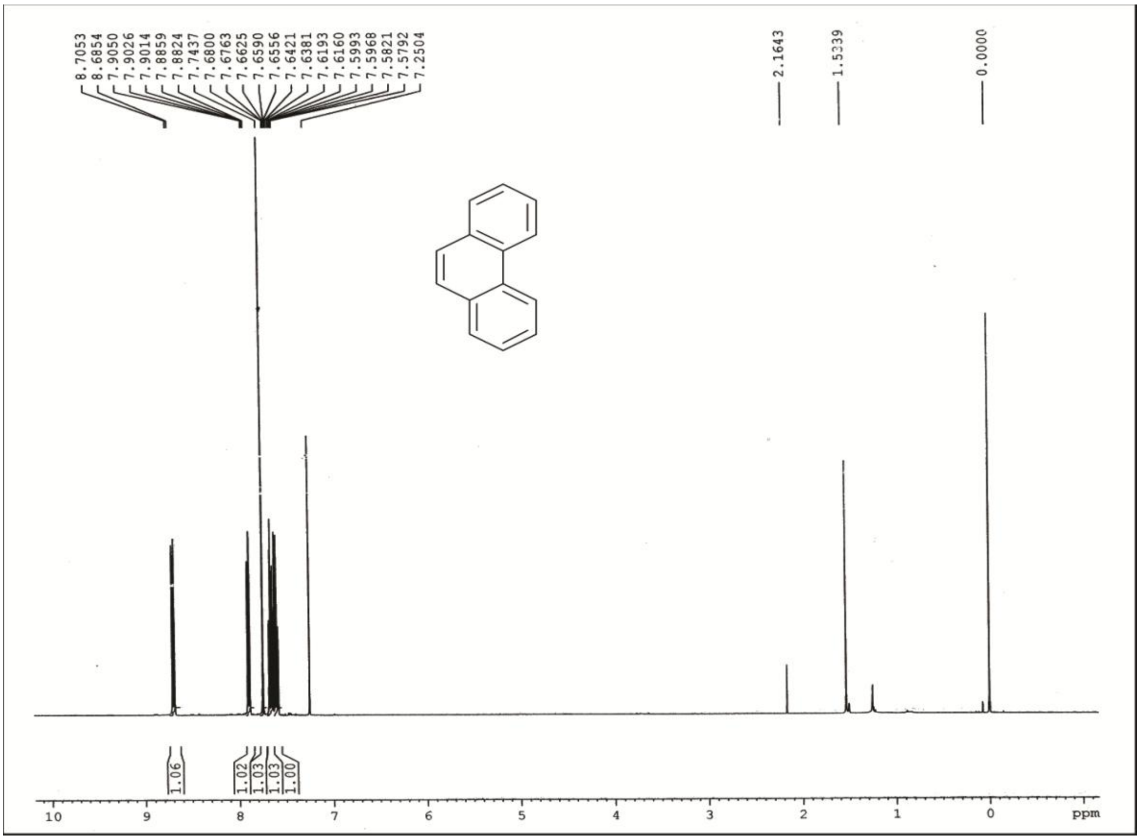
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.97-8.93 (m, 6H), 8.08-8.06 (broad m, 3H), 7.97 (d, *J* = 9.08 Hz, 3H), 7.68-7.67 (broad m, 6H).

**IR (KBr):** 3434, 3045, 3014, 2924, 1656, 1637, 1588, 1564, 1491, 1097, 1072, 1008, 971, 948, 827, 715 cm.$^{-1}$

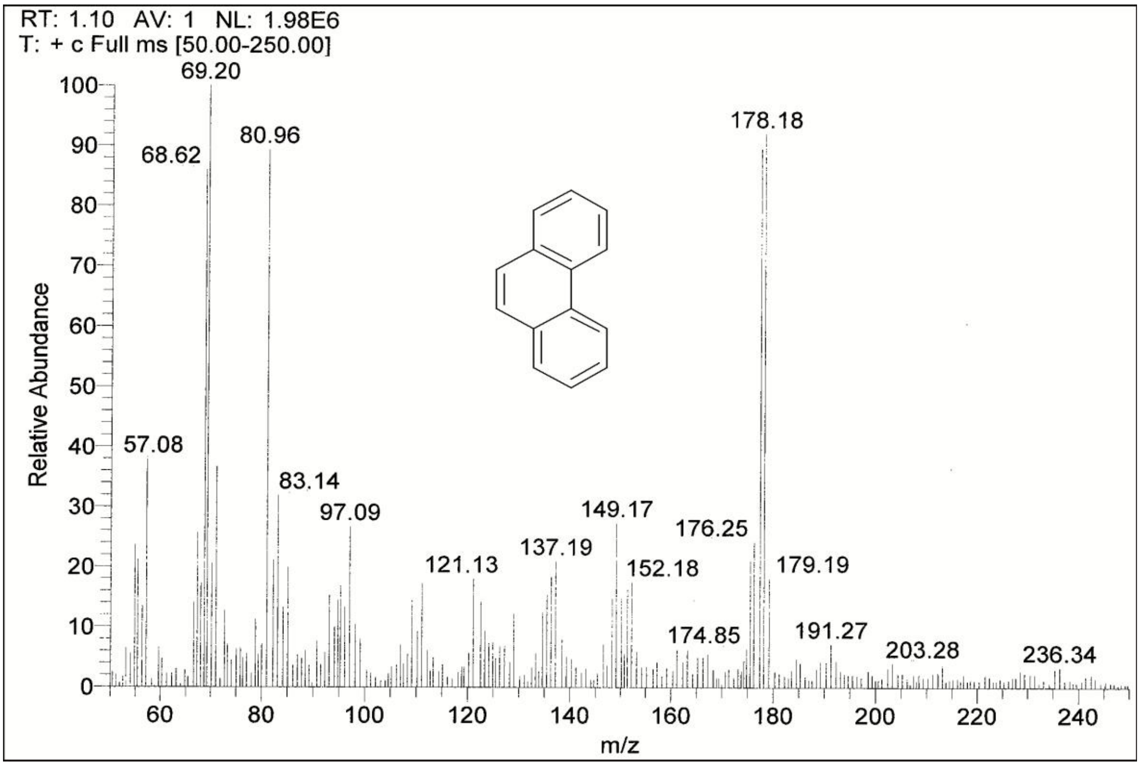
**MS (EI):** ***m/z*, (%)** 379 (21), 378 (100), 377 (90), 376.7 (32), 376 (39), 375 (27), 374 (25), 373 (21), 188 (20), 187 (28), 186 (13), 185 (10), 180 (09).

# Spectral Data

## Spectral data of phenanthrene (3)

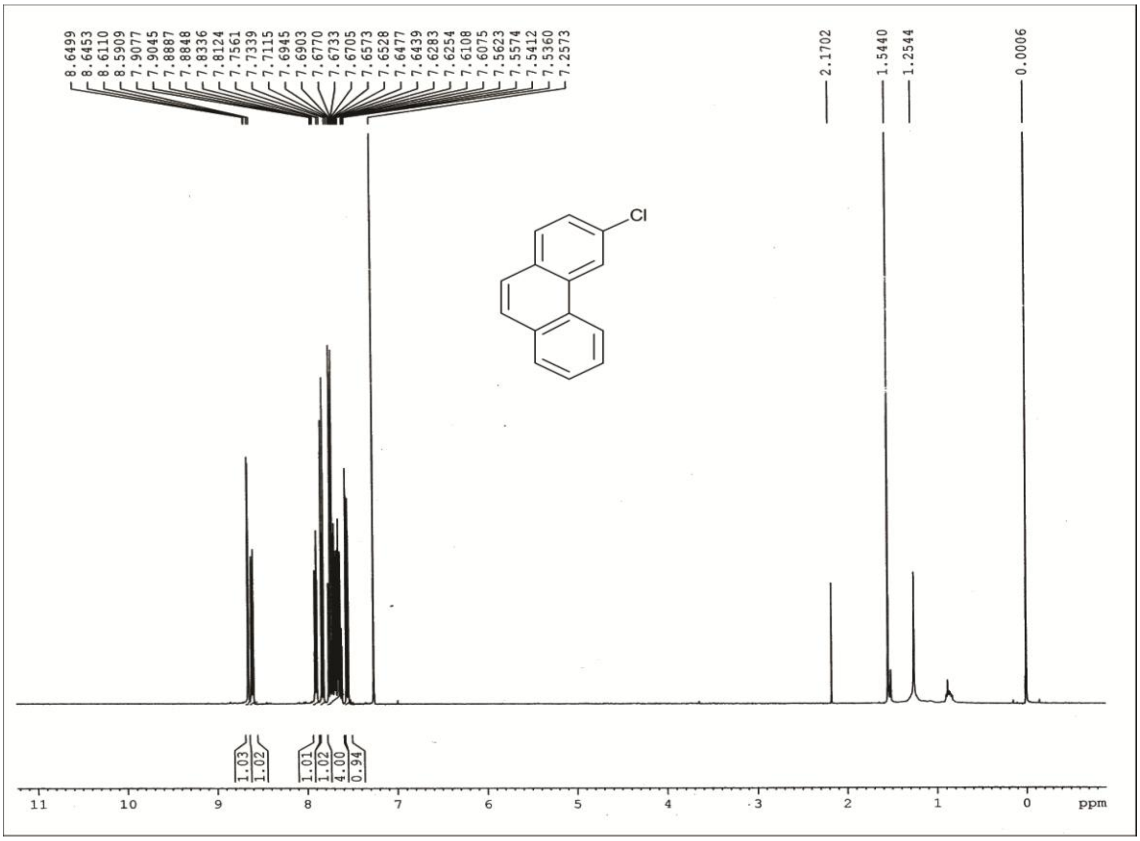


**$^1$H-NMR spectrum of phenanthrene (3) in $CDCl_3$ at 400 MHz**

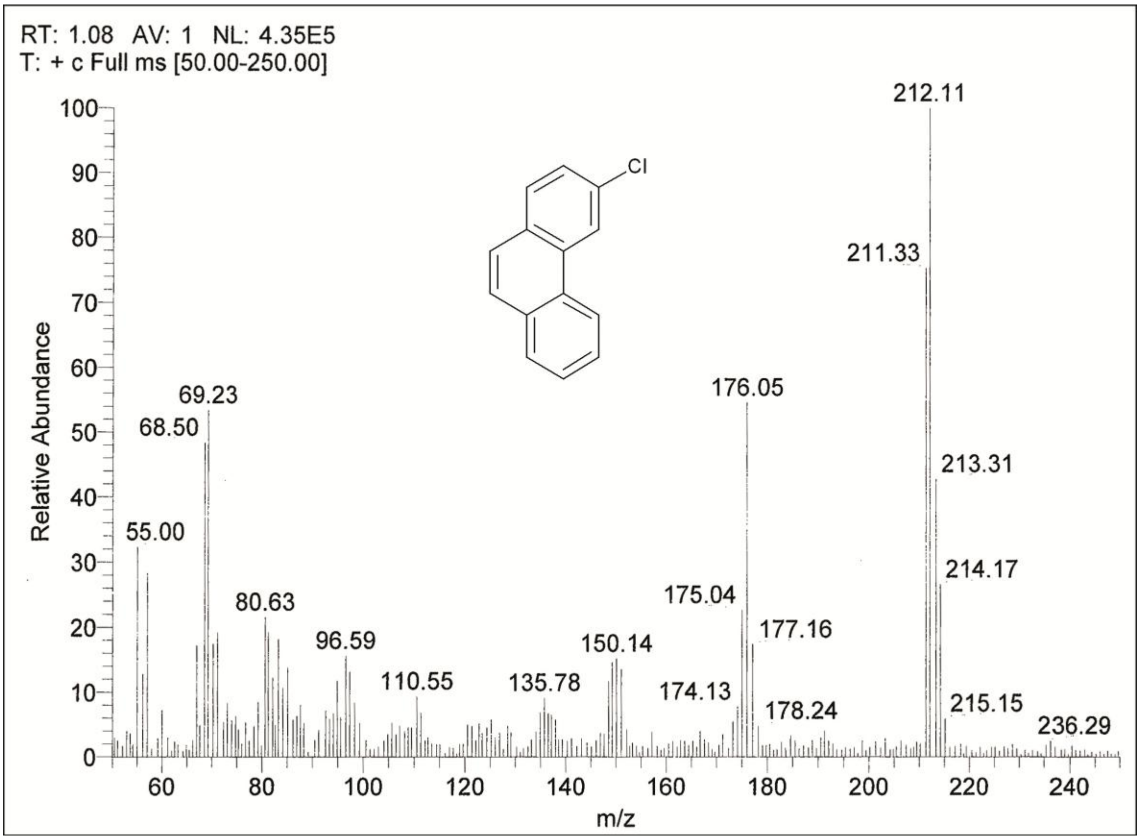


**EI-Mass spectrum of phenanthrene (3)**

## Spectral data of 3-chlorophenanthrene (112)

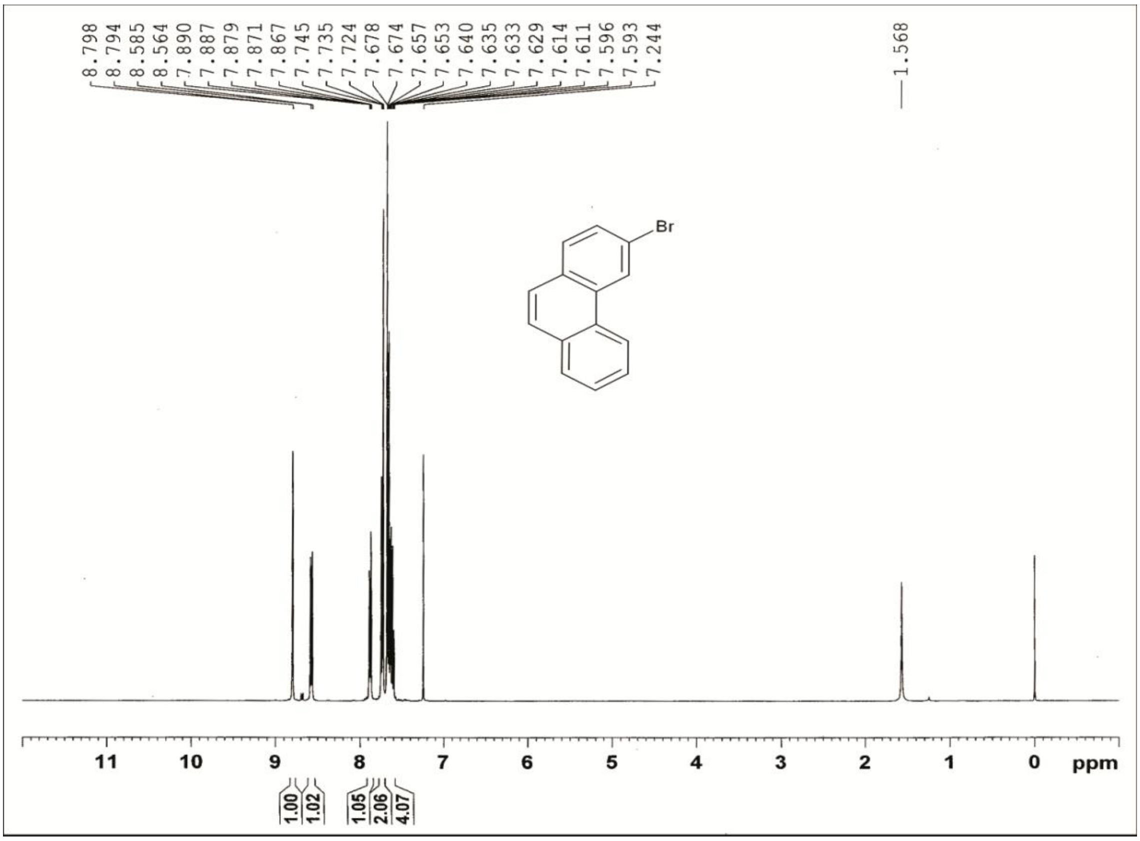


**$^1$H-NMR spectrum of 3-chlorophenanthrene (3) in $CDCl_3$ on 400 MHz**

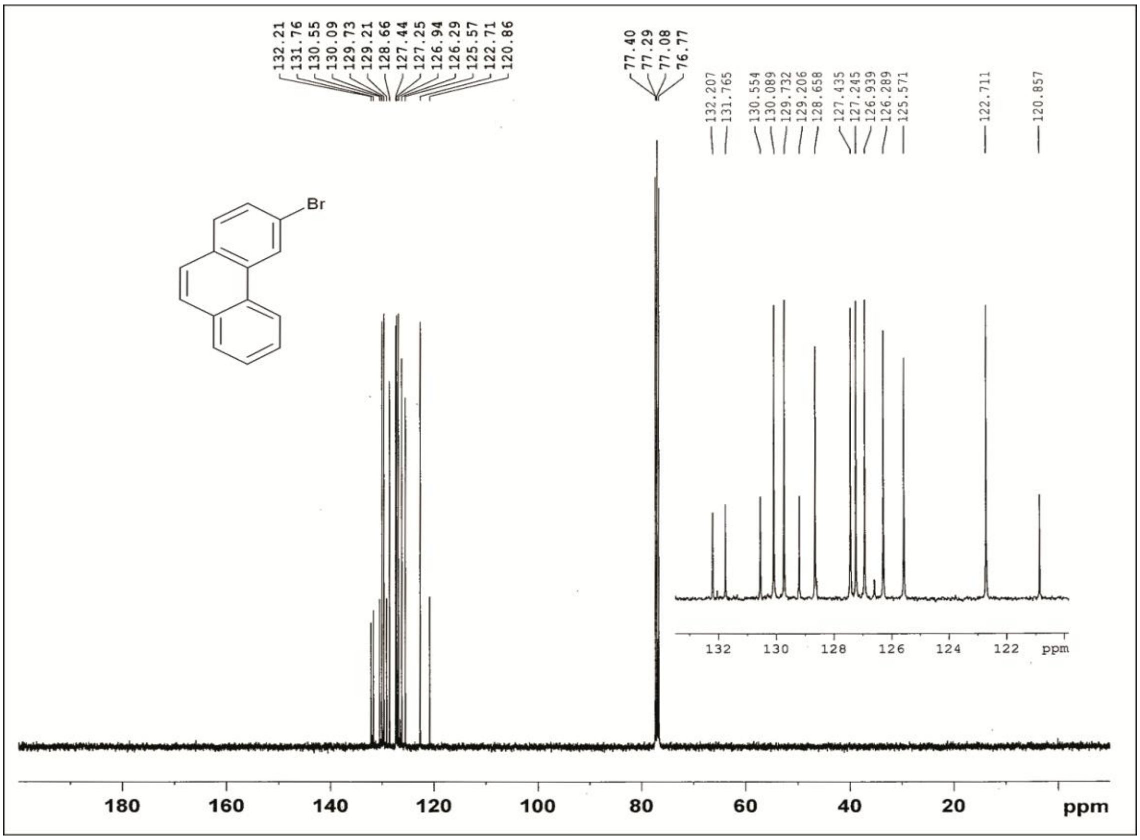


**EI-Mass spectrum of 3-chlorophenanthrene (3)**

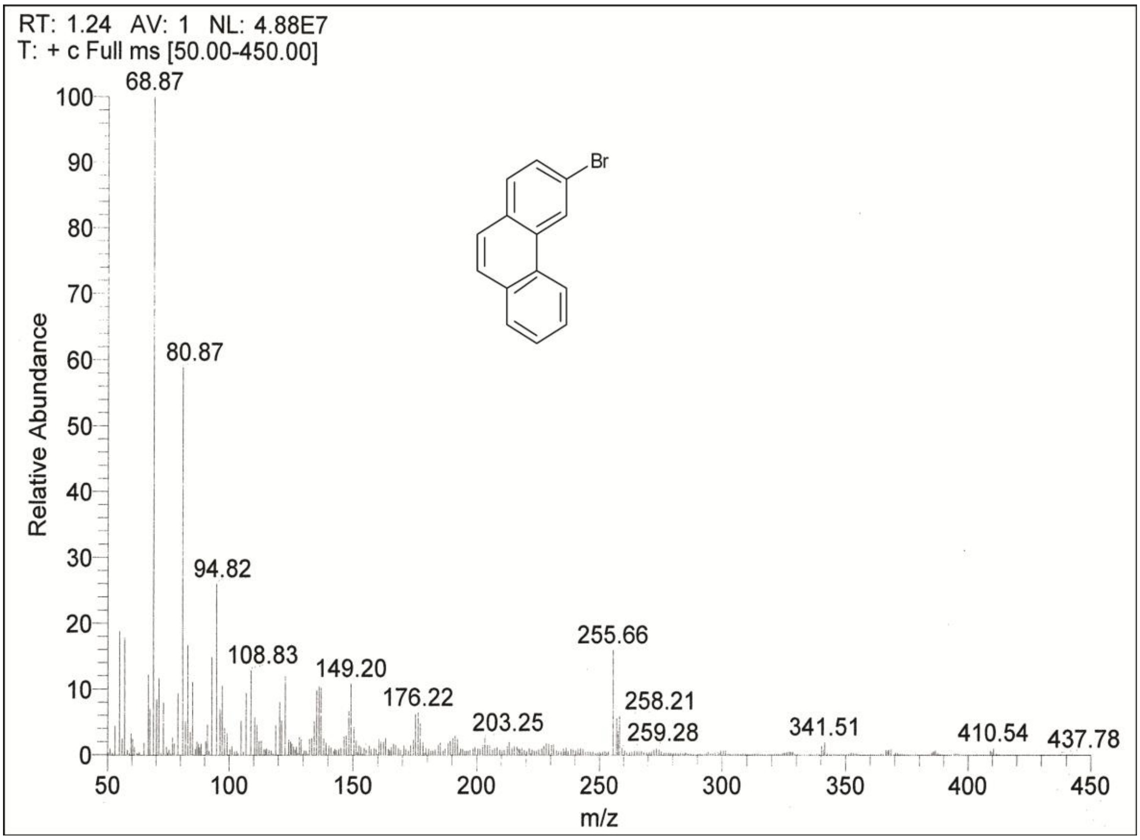
## Spectral data of 3-bromophenanthrene (114)



**$^1$H-NMR spectrum of 3-bromophenanthrene (114) in CDCl$_3$ on 400 MHz**

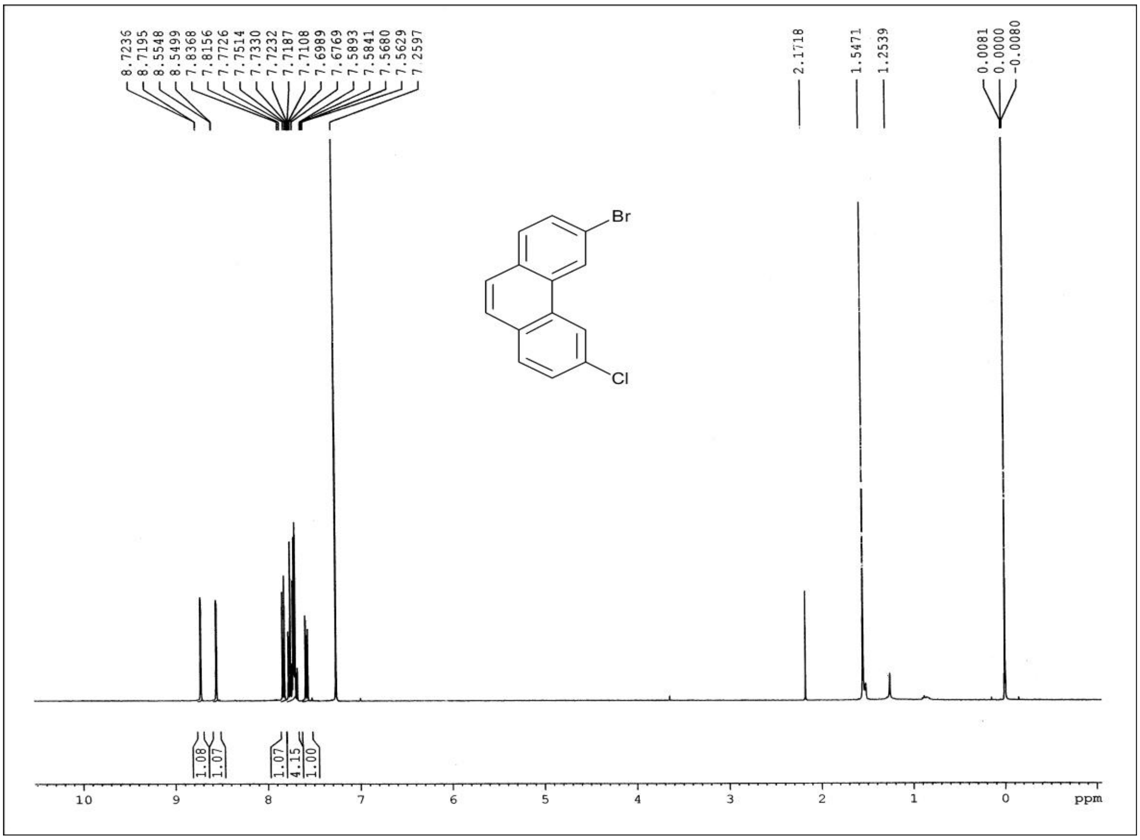


**$^{13}$C-NMR spectrum of 3-bromophenanthrene (114) in CDCl$_3$ on 100.6 MHz**

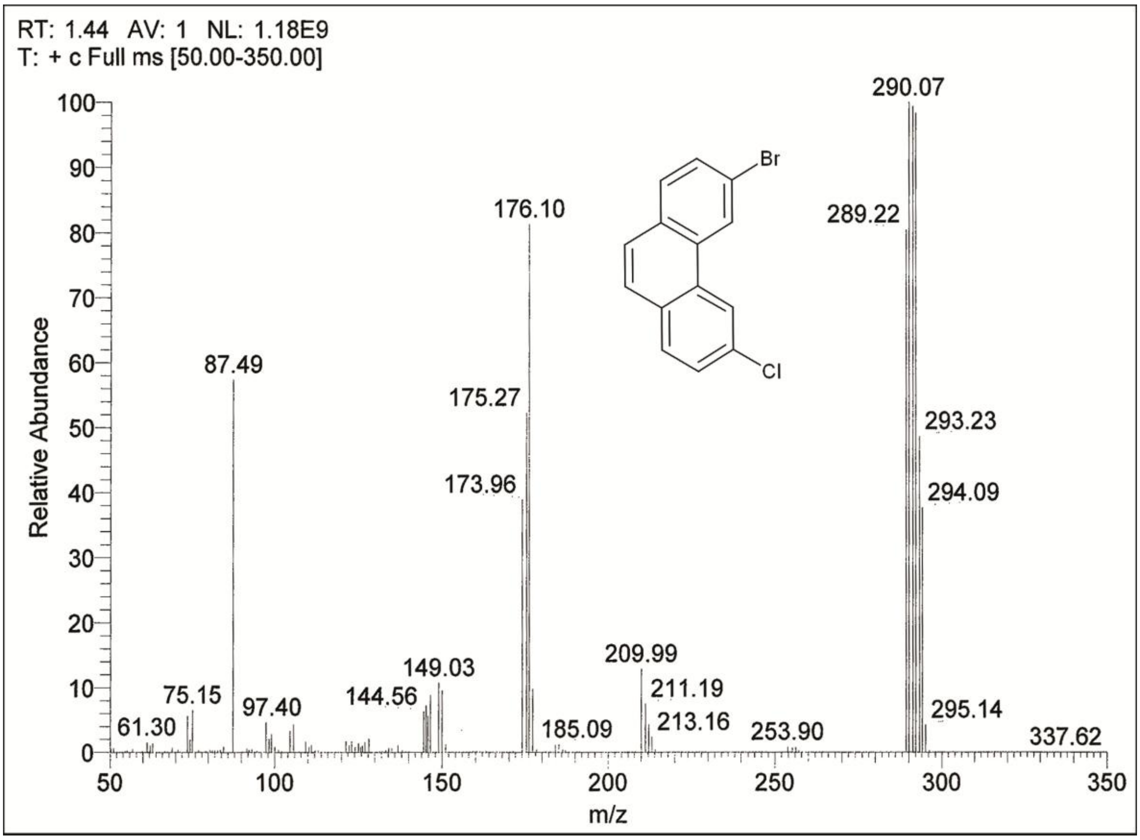


**EI-Mass spectrum of 3-bromophenanthrene (114)**

## Spectral data of 3-bromo-6-chlorophenanthrene (116)



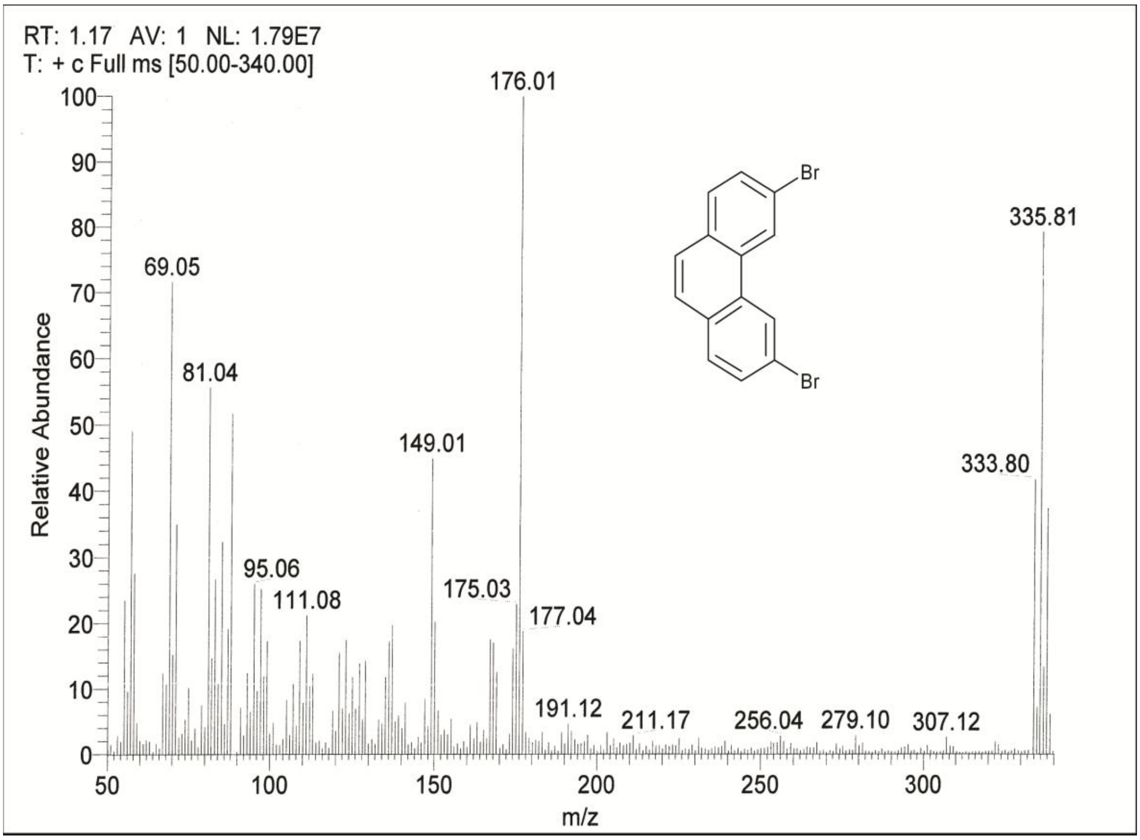
$^1$H-NMR spectrum of 3-bromo-6-chlorophenanthrene (116) in $CDCl_3$ on 400 MHz



**EI-Mass spectrum of 3-bromo-6-chlorophenanthrene (116)**

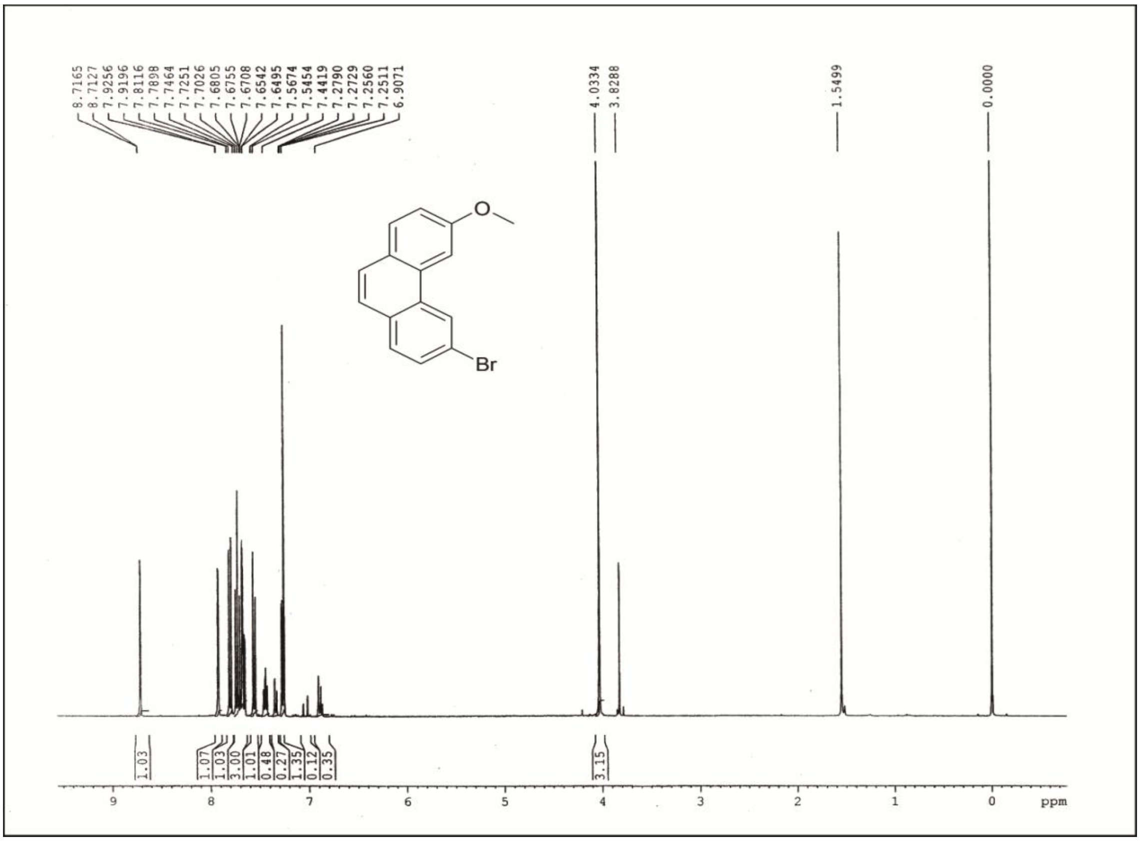
## Spectral data of 3,6-dibromophenanthrene (118)

**$^1$H-NMR spectrum of 3,6-dibromophenanthrene (118) in $CDCl_3$ on 400 MHz**

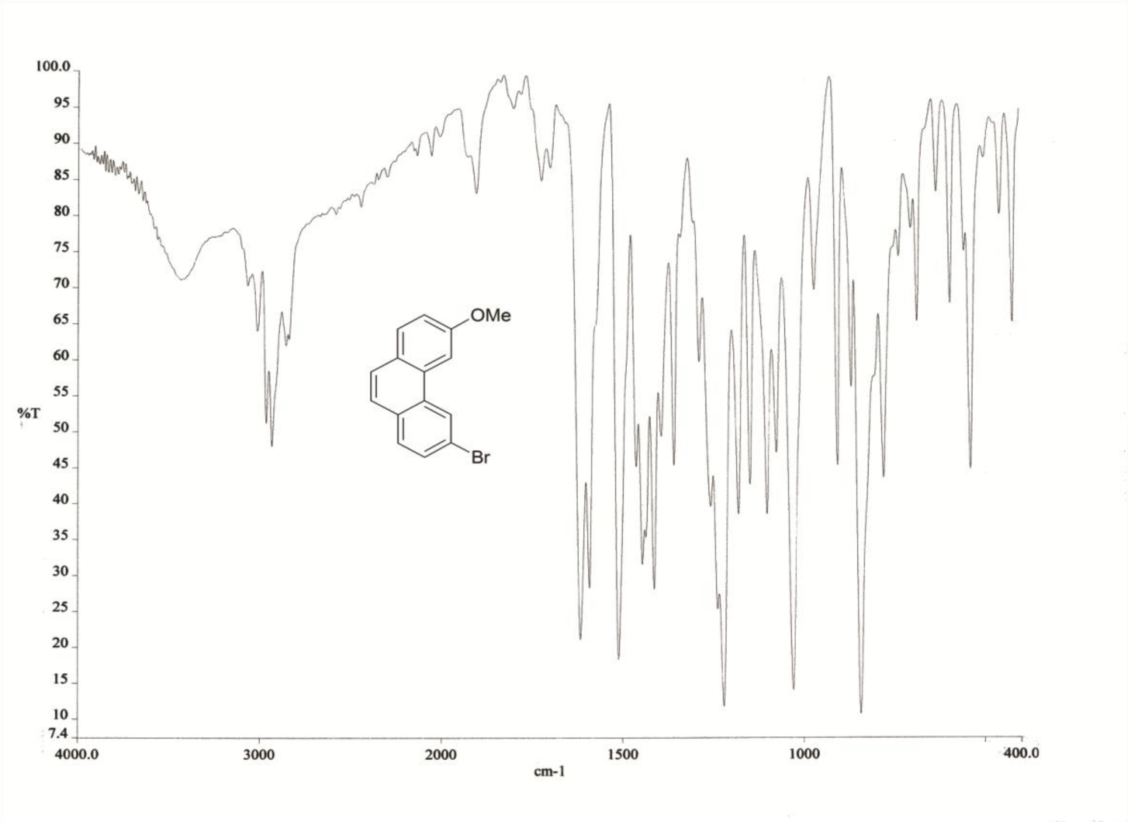


**EI-Mass spectrum of 3,6-dibromophenanthrene (118)**

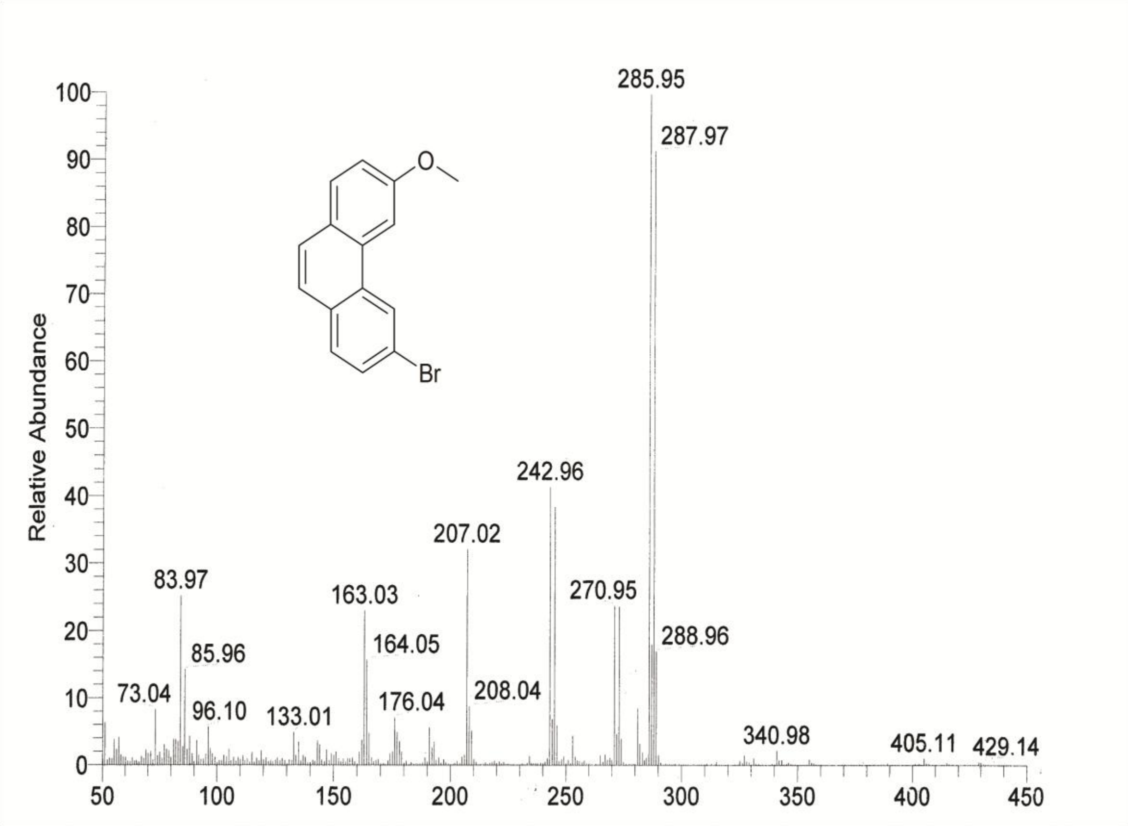
## Spectral data of 3-bromo-6-methoxyphenanthrene (120)



**$^1$H-NMR spectrum of 3-bromo-6-methoxyphenanthrene (120) in $CDCl_3$ on 400 MHz**

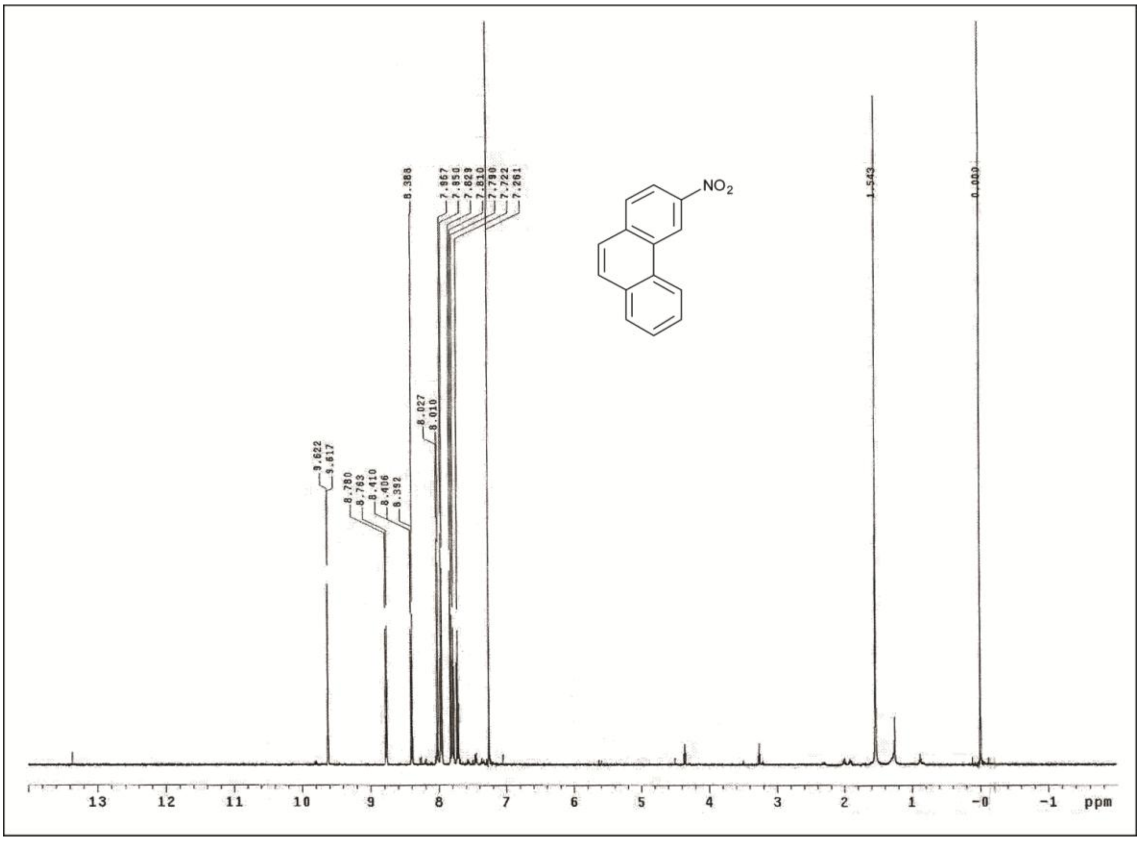


**IR spectrum of 3-bromo-6-methoxyphenanthrene (120)**

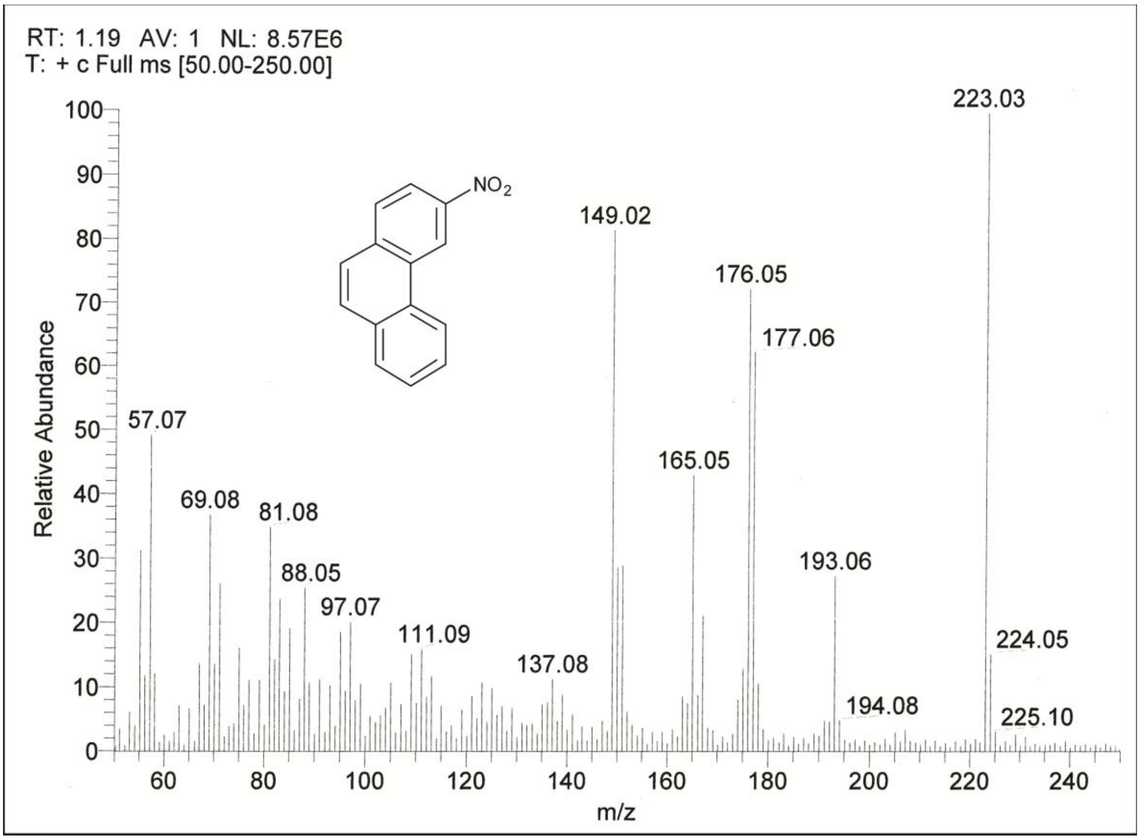


**EI-Mass spectrum of 3-bromo-6-methoxyphenanthrene (120)**

## Spectral data of 3-nitrophenanthrene (106)

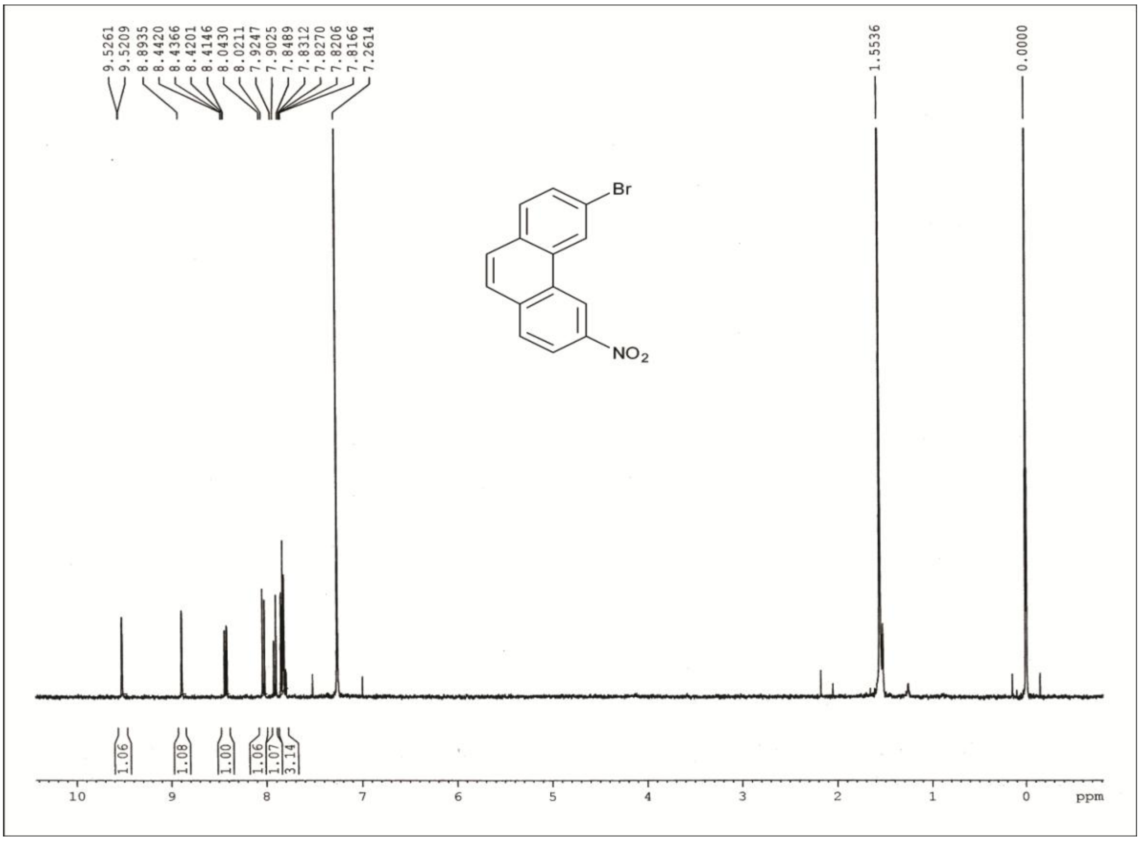


**$^1$H-NMR spectrum of 3-nitrophenanthrene (106) in $CDCl_3$ on 500 MHz**

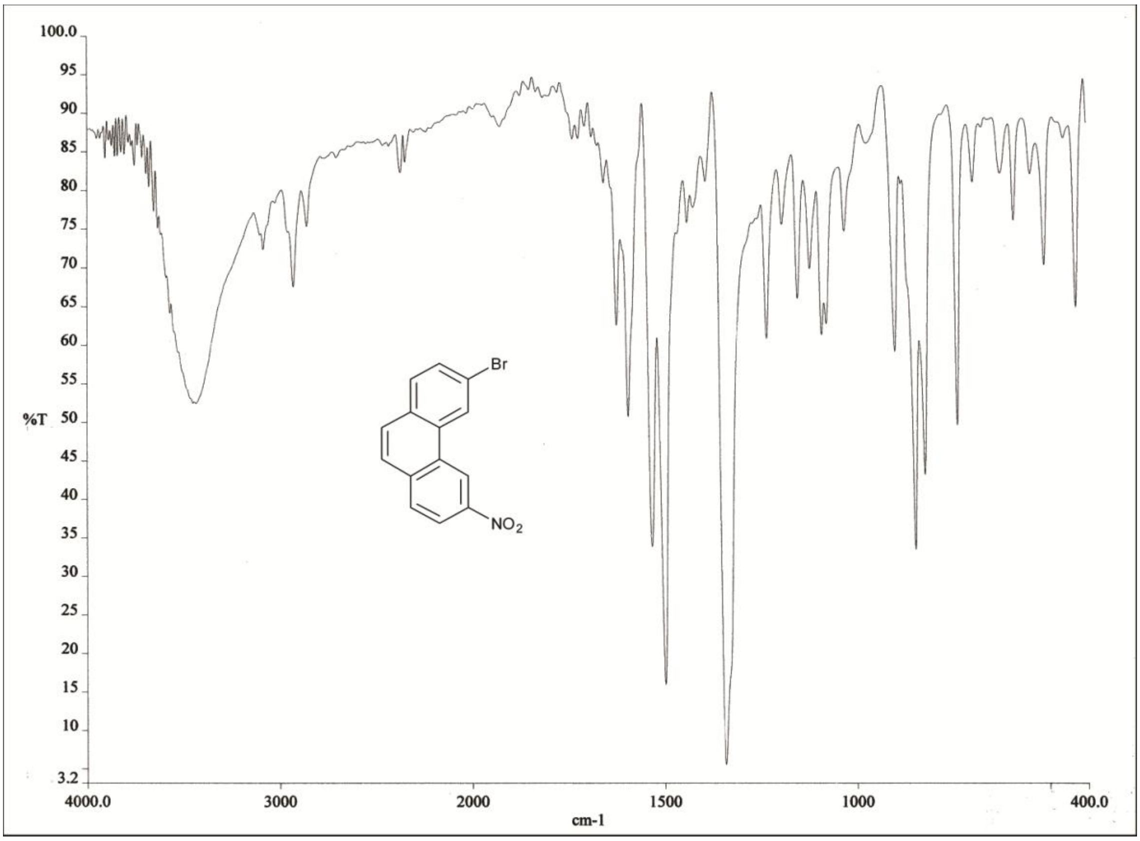


**EI-Mass spectrum of 3-nitrophenanthrene (106)**

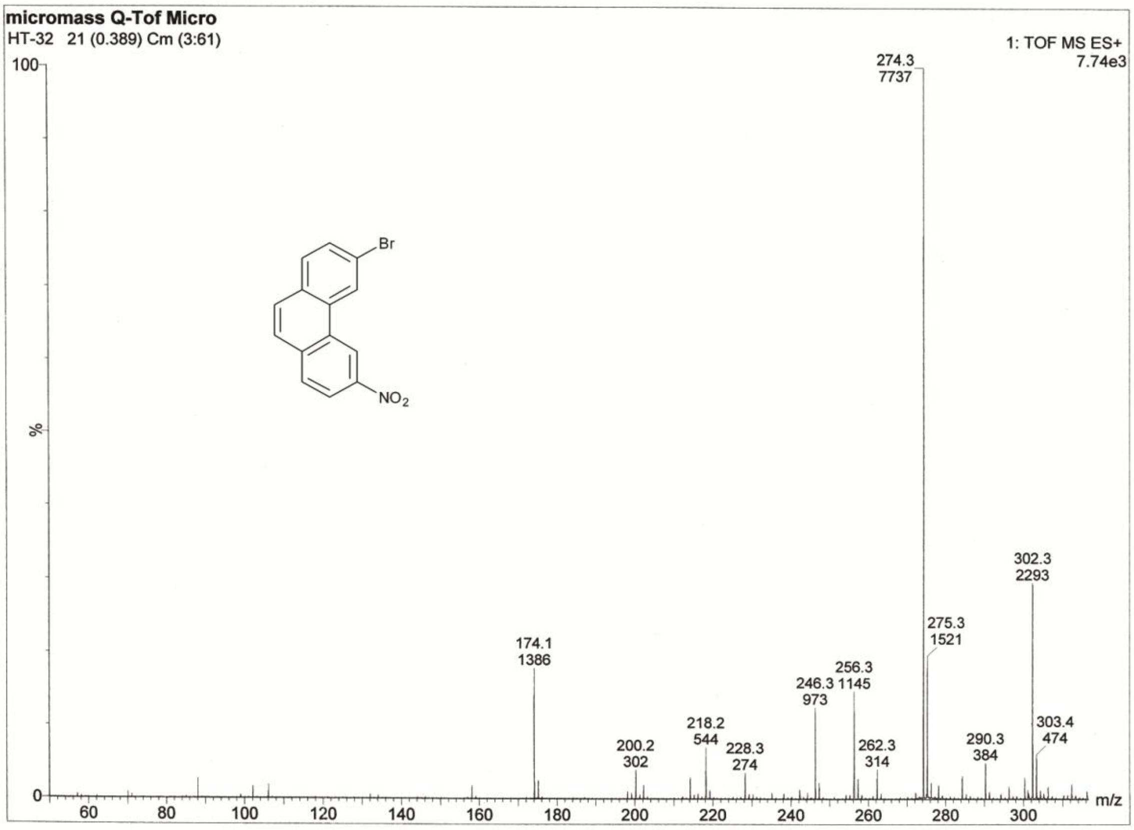
## Spectral data of 3-bromo-6-nitrophenanthrene (108)



**$^1$H-NMR spectrum of 3-bromo-6-nitrophenanthrene (108) in $CDCl_3$ on 400 MHz**



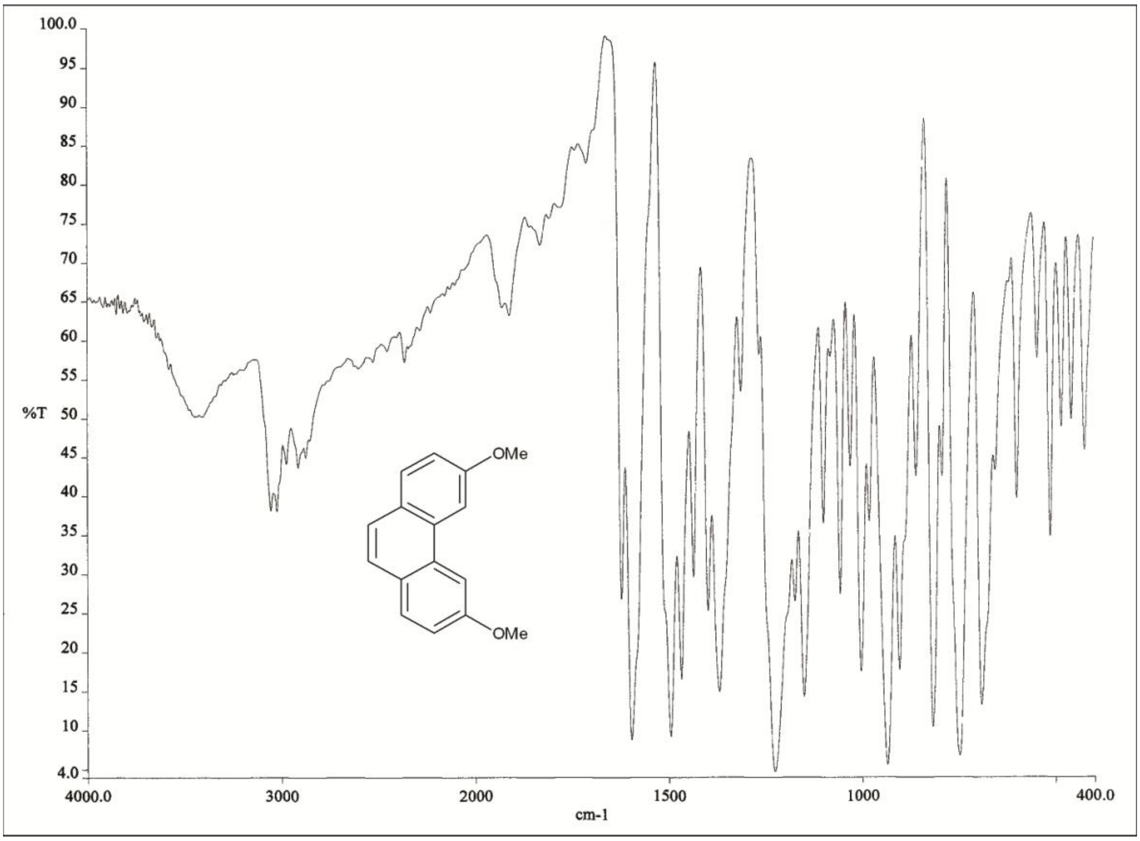
**IR spectrum of 3-bromo-6-nitrophenanthrene (108)**



ESI-Mass spectrum of 3-bromo-6-nitrophenanthrene (108)

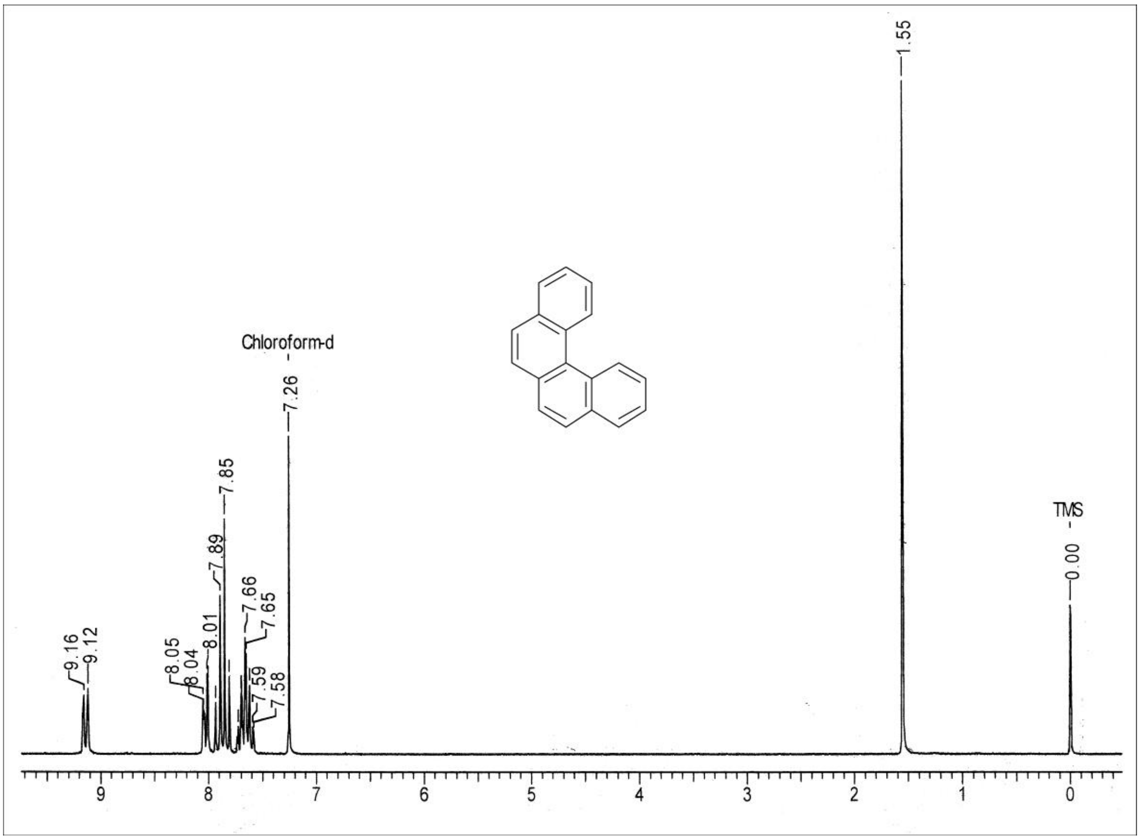
## Spectral data of 3,6-dimethoxyphenanthrene (122)

$^1$H-NMR spectrum of 3,6-dimethoxyphenanthrene (122) in $CDCl_3$ on 400 MHz

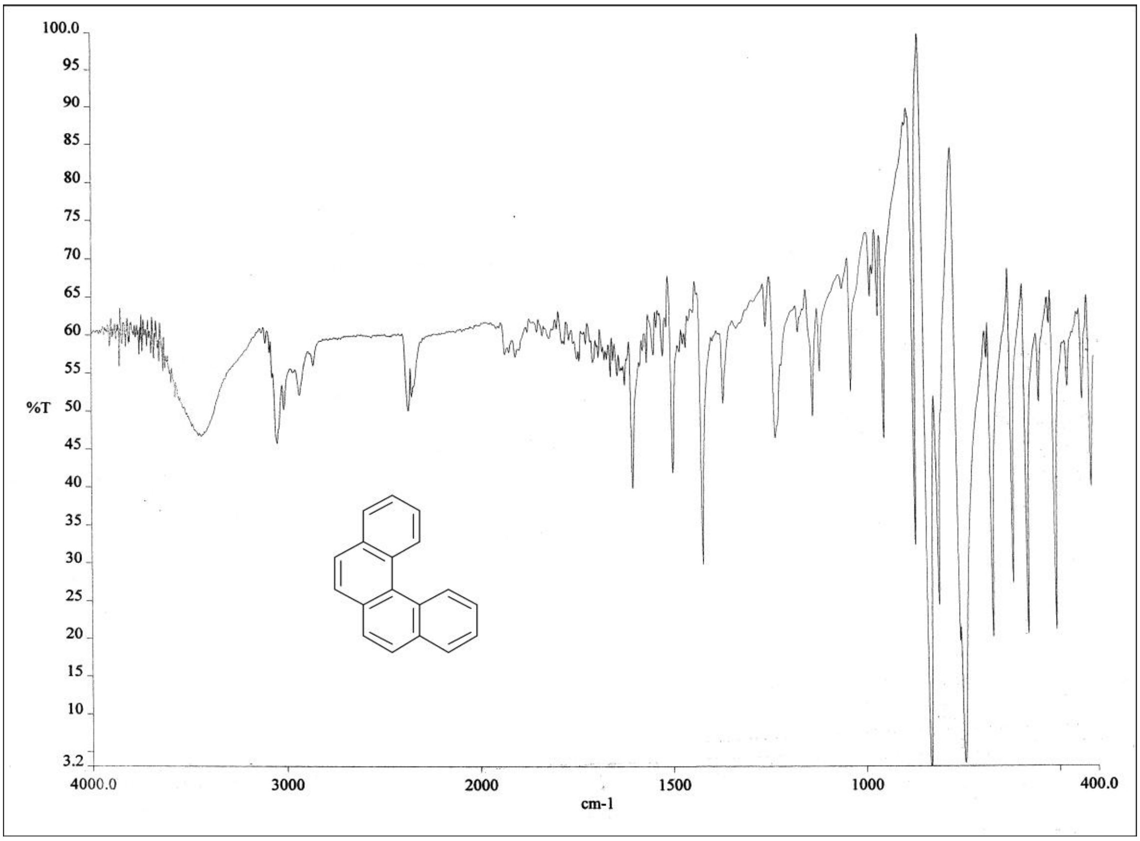


**IR spectrum of 3,6-dimethoxyphenanthrene (122)**

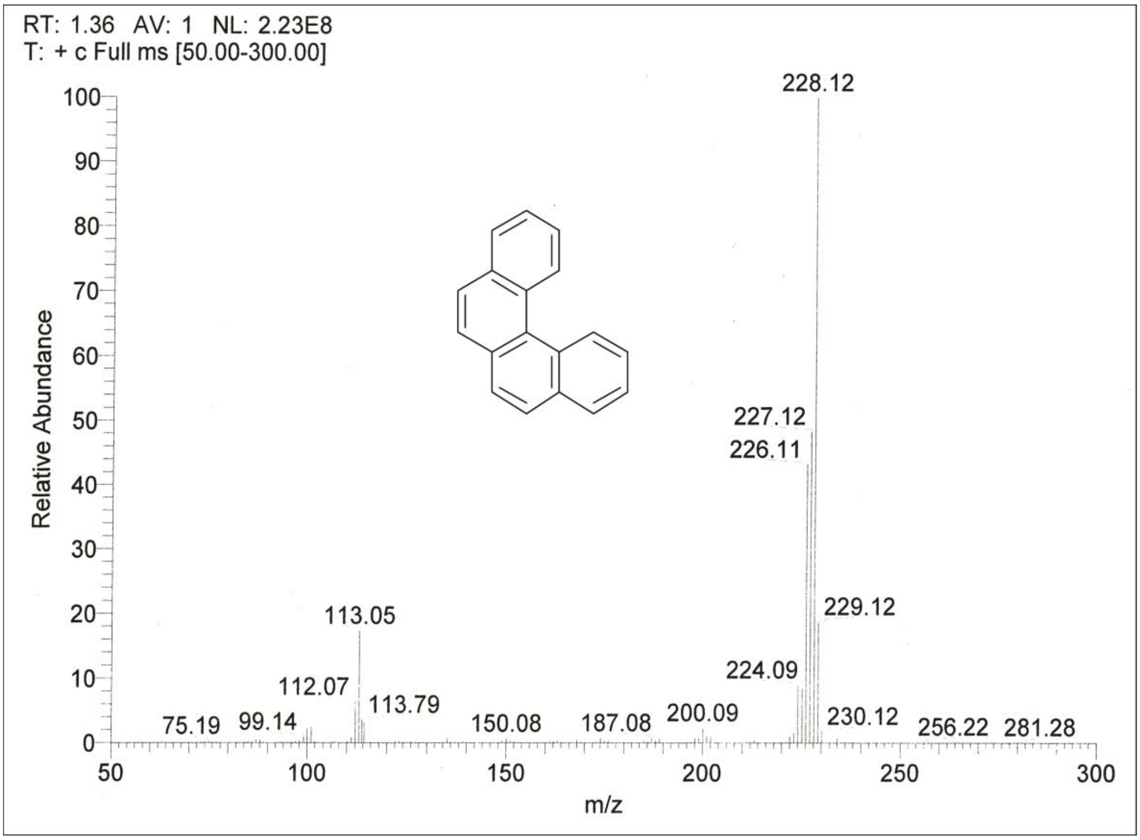
## Spectral data of benzo[*c*]phenanthrene (124)



**$^1$H-NMR spectrum of benzo[*c*]phenanthrene (124) in $CDCl_3$ on 200 MHz**

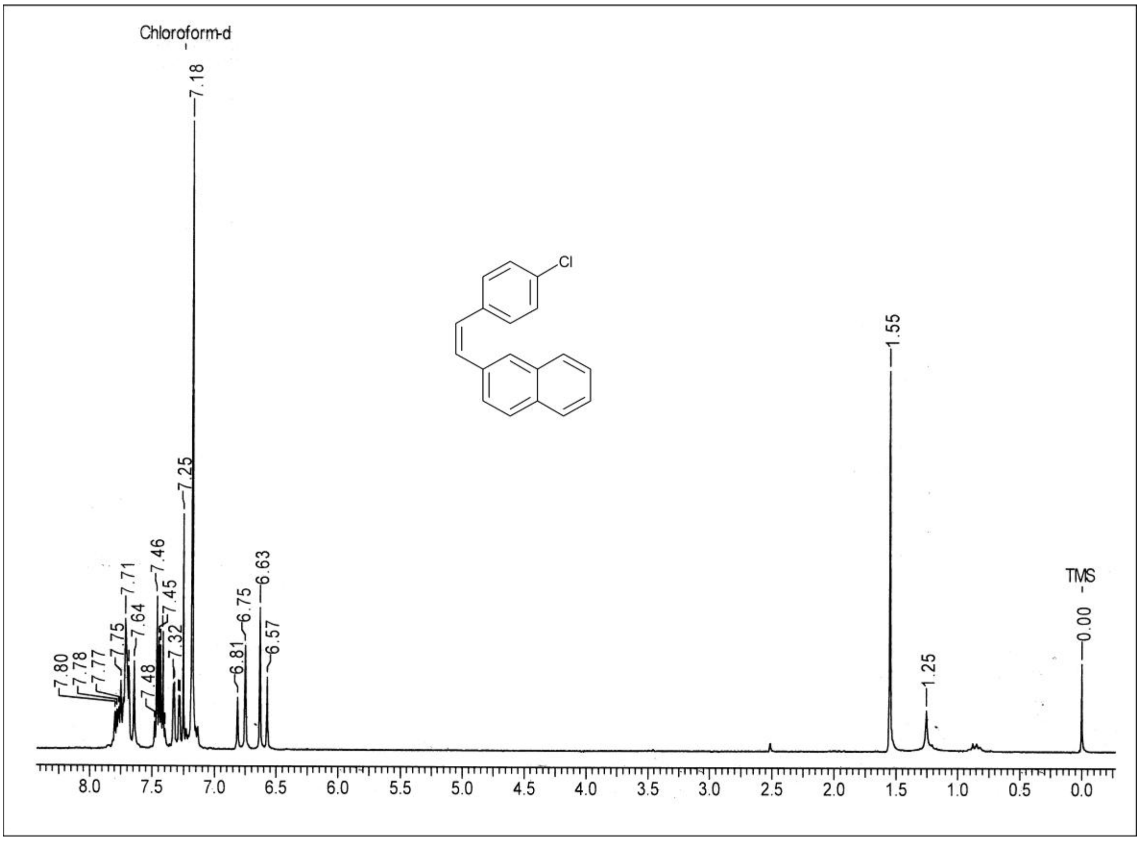


**IR spectrum of benzo[*c*]phenanthrene (124)**

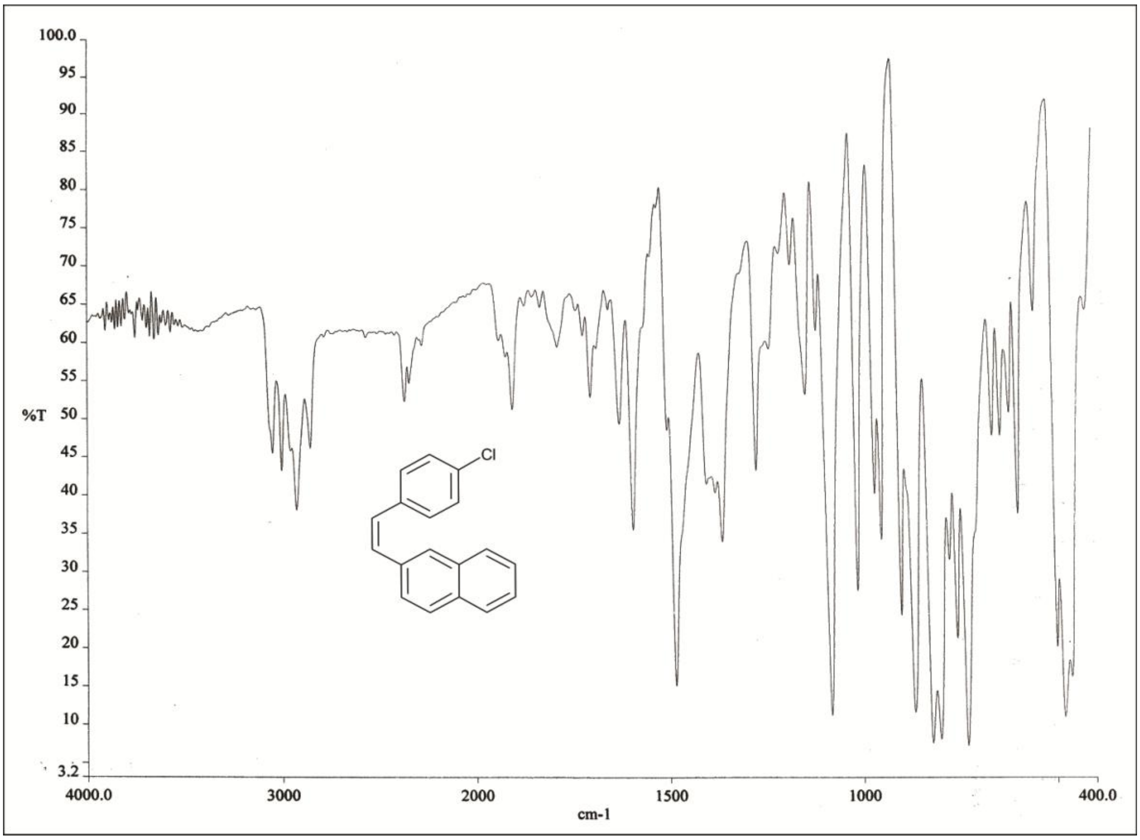


**EI-Mass spectrum of benzo[*c*]phenanthrene (124)**

## Spectral data of (*Z*)-2-(4-chlorophenyl)ethenylnaphthalene(125)

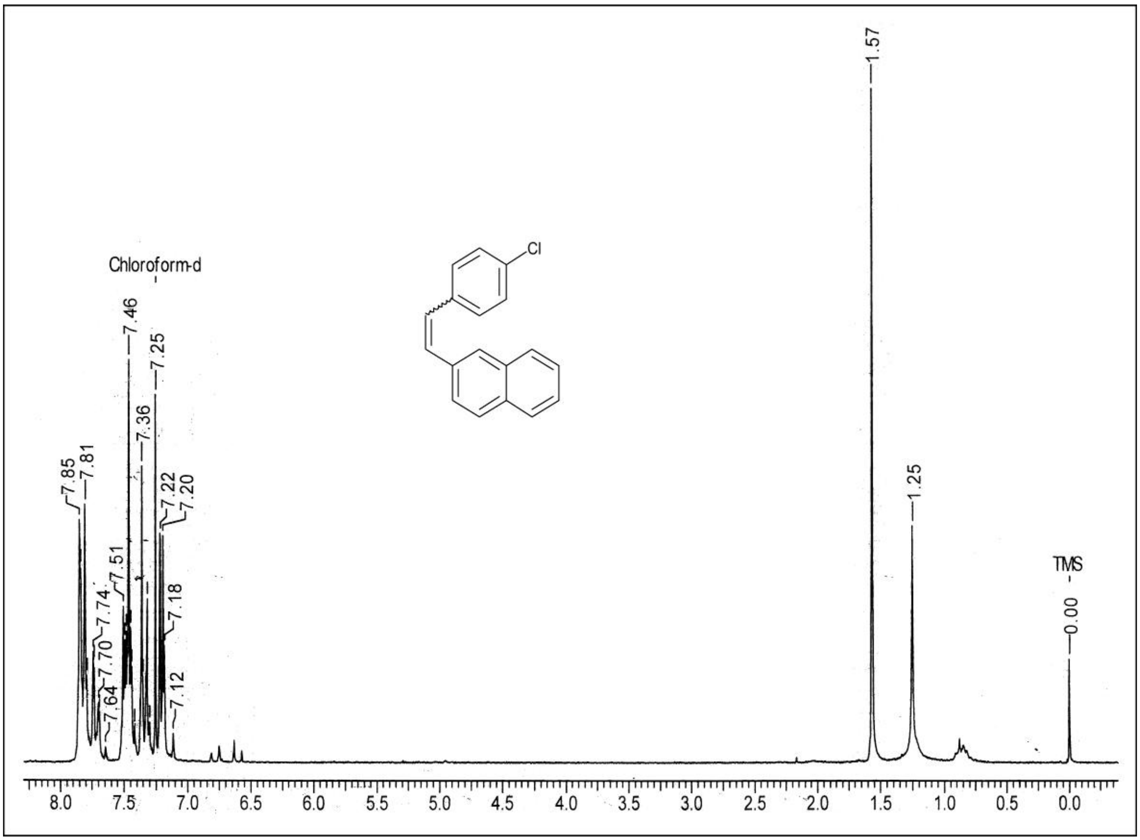


**$^1$H-NMR spectrum of (*Z*)-2-(4-chlorophenyl)ethenylnaphthalene(125) in $CDCl_3$ on 200 MHz**

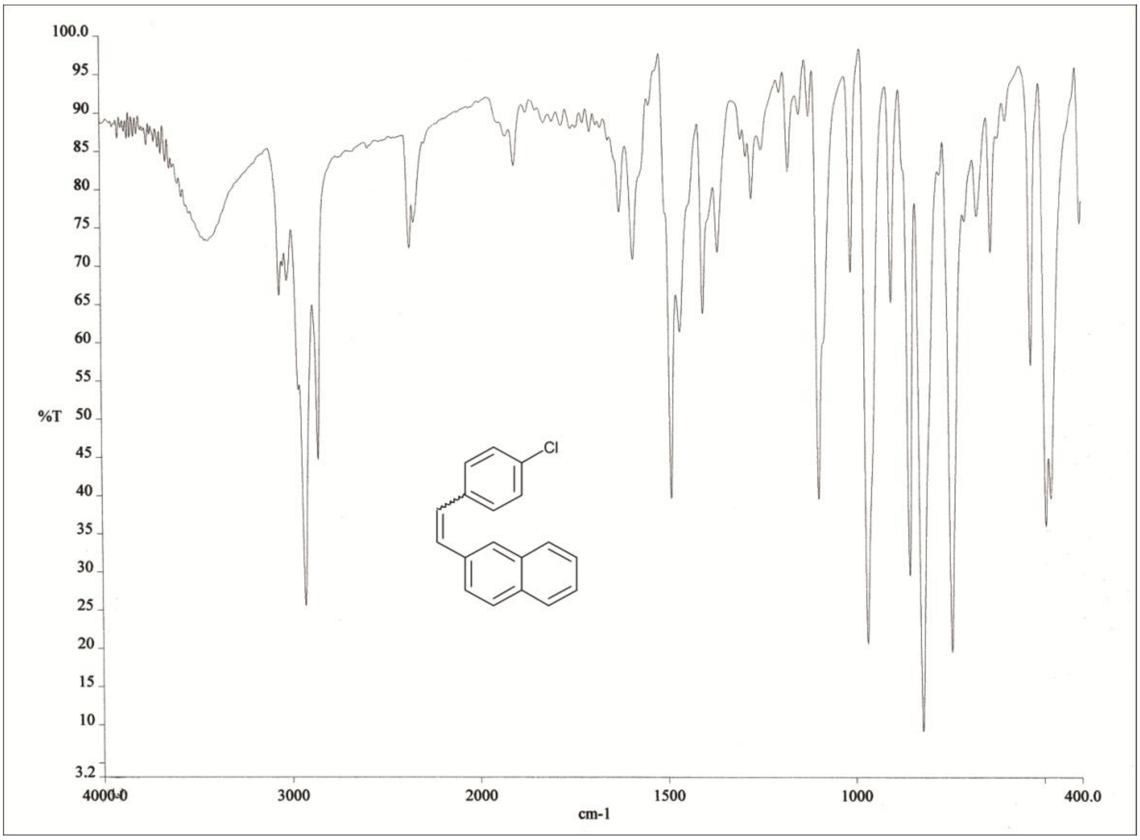


**IR spectrum of (*Z*)-2-(4-chlorophenyl)ethenylnaphthalene(125)**

## Spectral data of (*E*)-2-(4-chlorophenyl)ethenylnaphthalene(125)

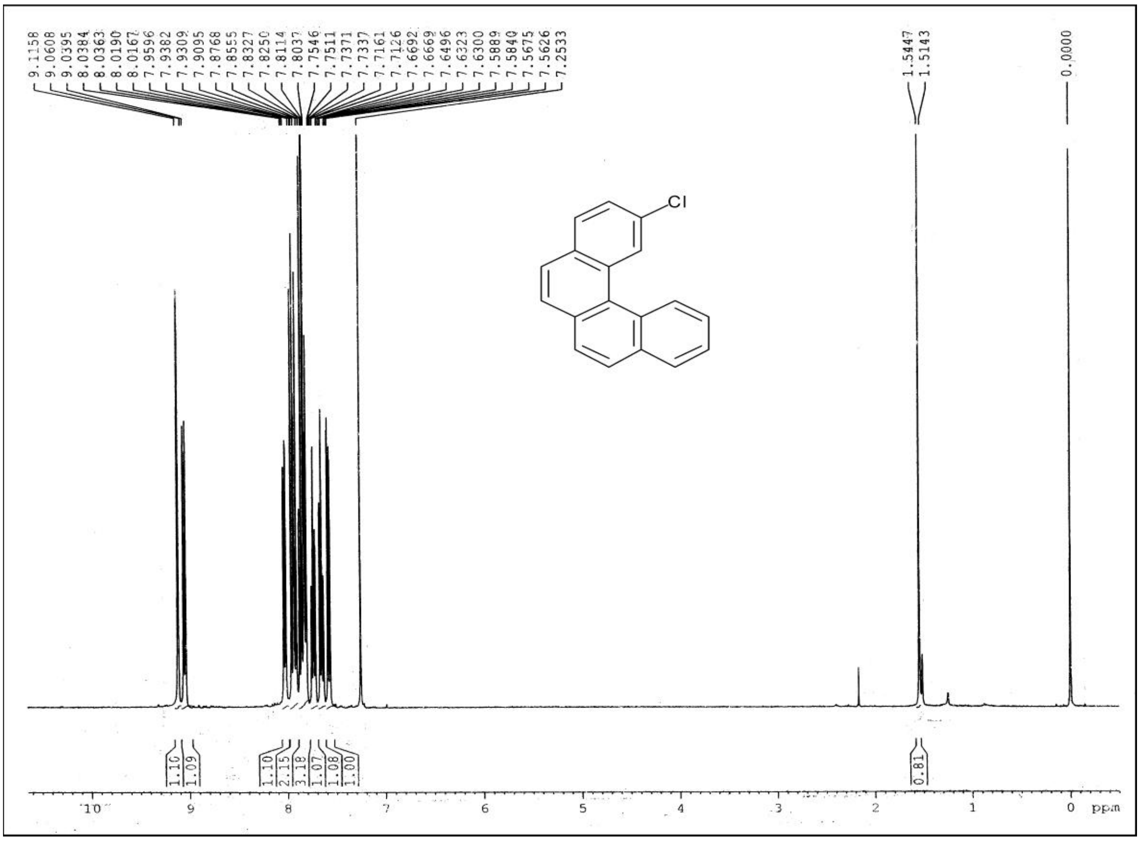


**$^1$H-NMR spectrum of (*E*)-2-(4-chlorophenyl)ethenylnaphthalene(125) in CDCl$_3$ on 200 MHz**

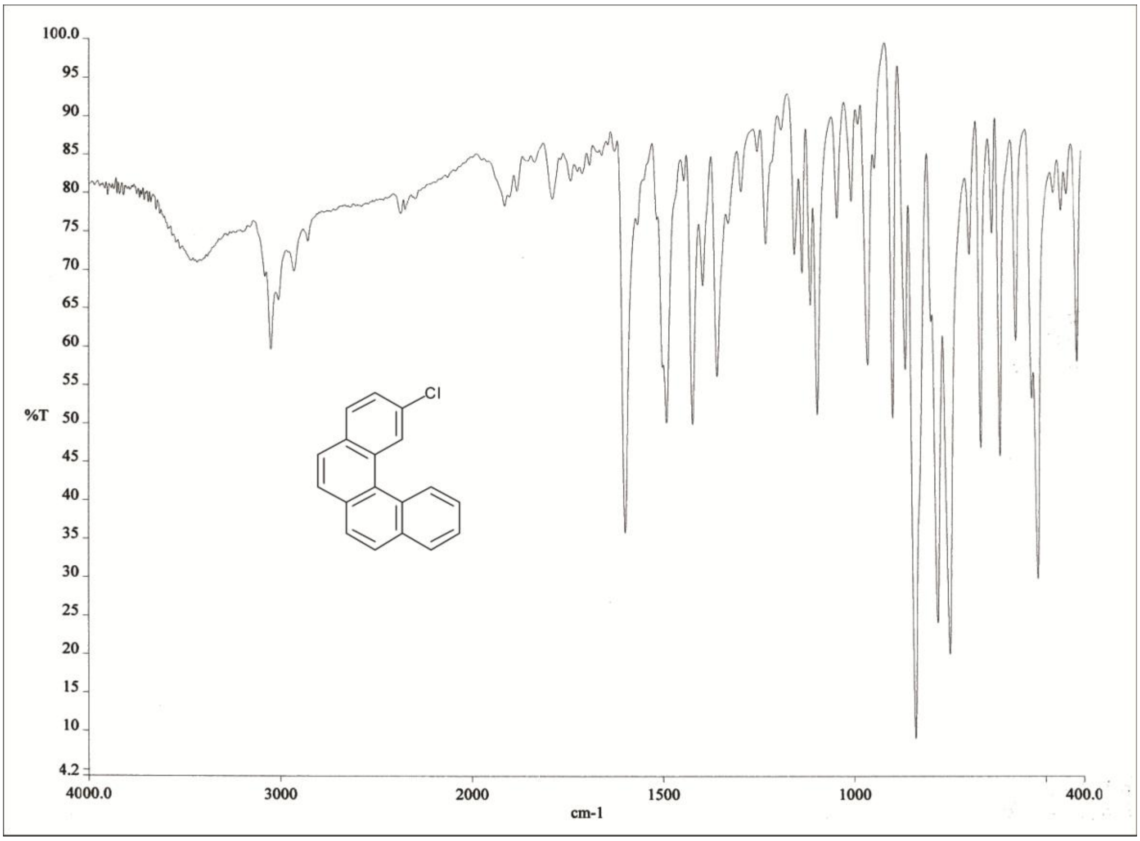


**IR spectrum of (*E*)-2-(4-chlorophenyl)ethenylnaphthalene(125)**

## Spectral data of 2-chlorobenzo[*c*]phenanthrene (126)

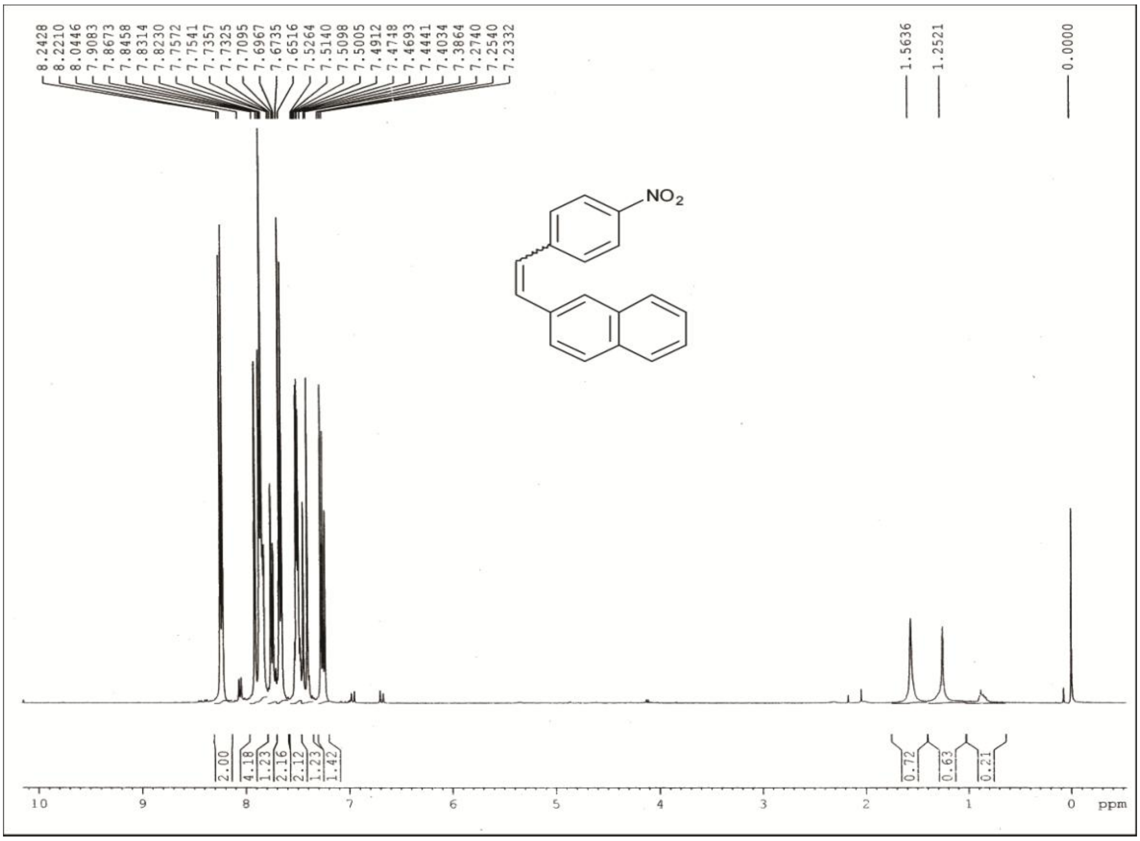


$^1$H-NMR spectrum of 2-chlorobenzo[*c*]phenanthrene (126) in $CDCl_3$ on 400 MHz

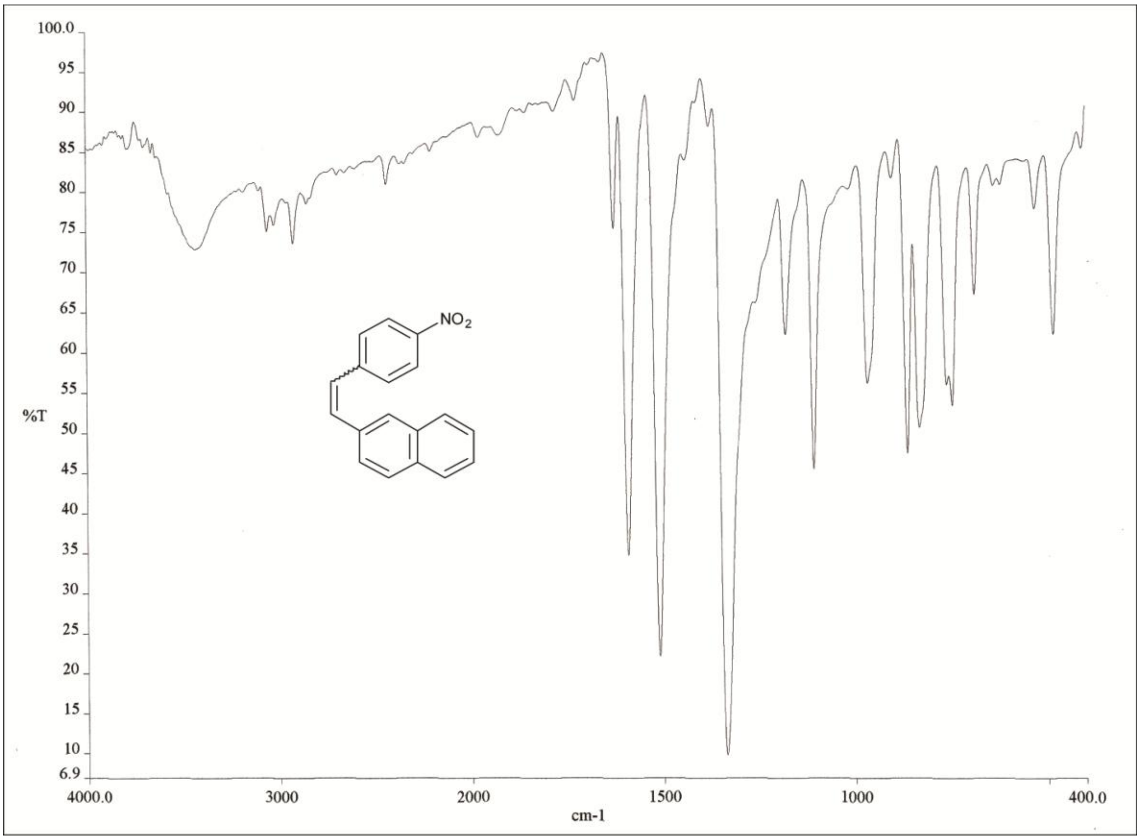


IR spectrum of 2-chlorobenzo[*c*]phenanthrene (126)

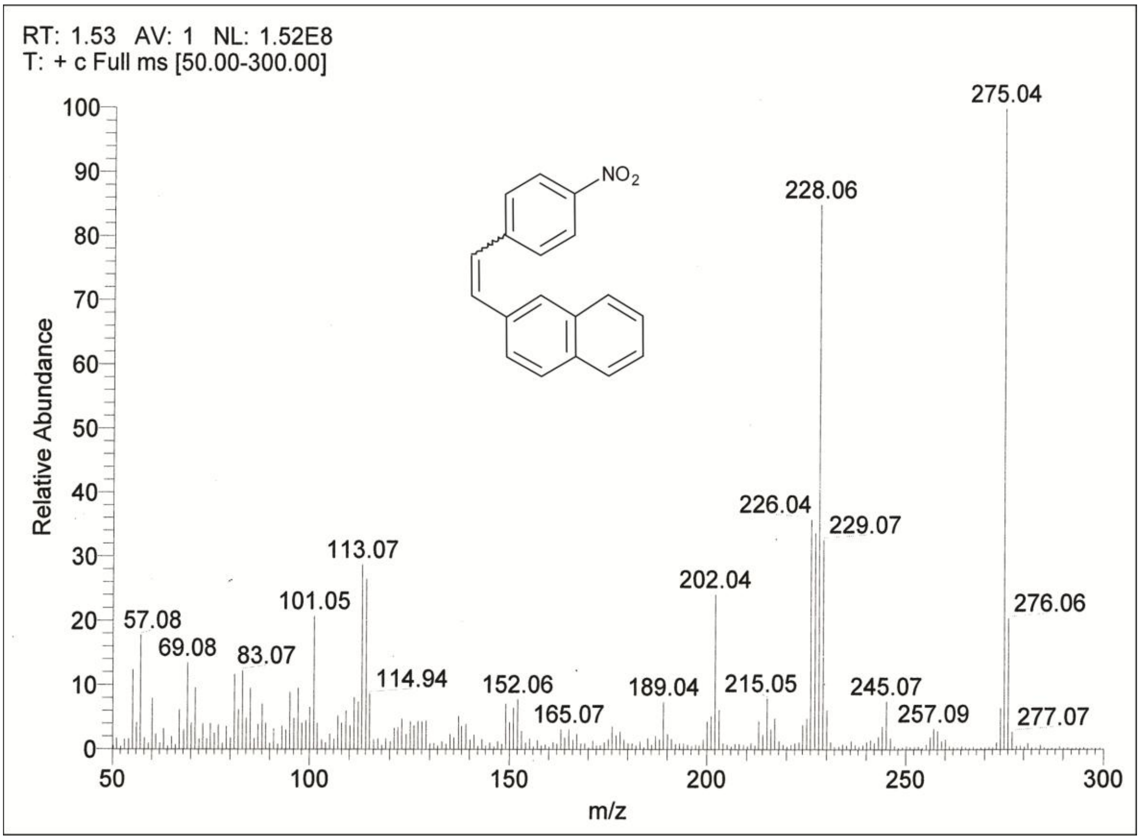
## Spectral data of 2-(4-nitrophenyl)ethenylnaphthalene(109)



**$^1$H-NMR spectrum of 1-(*p*-nitrophenyl)-2-(2-naphtyl)ethylene (109) in $CDCl_3$ on 400 MHz**

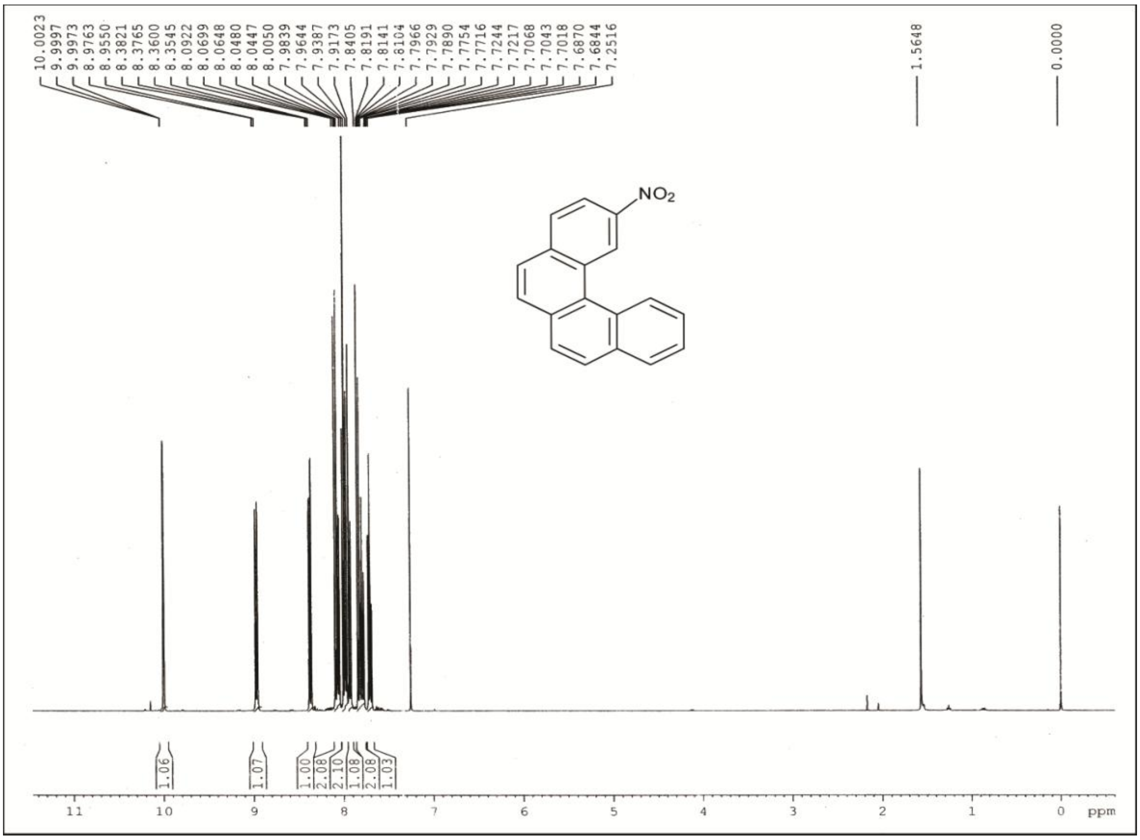


**IR spectrum of 1-(*p*-nitrophenyl)-2-(2-naphtyl)ethylene (109)**

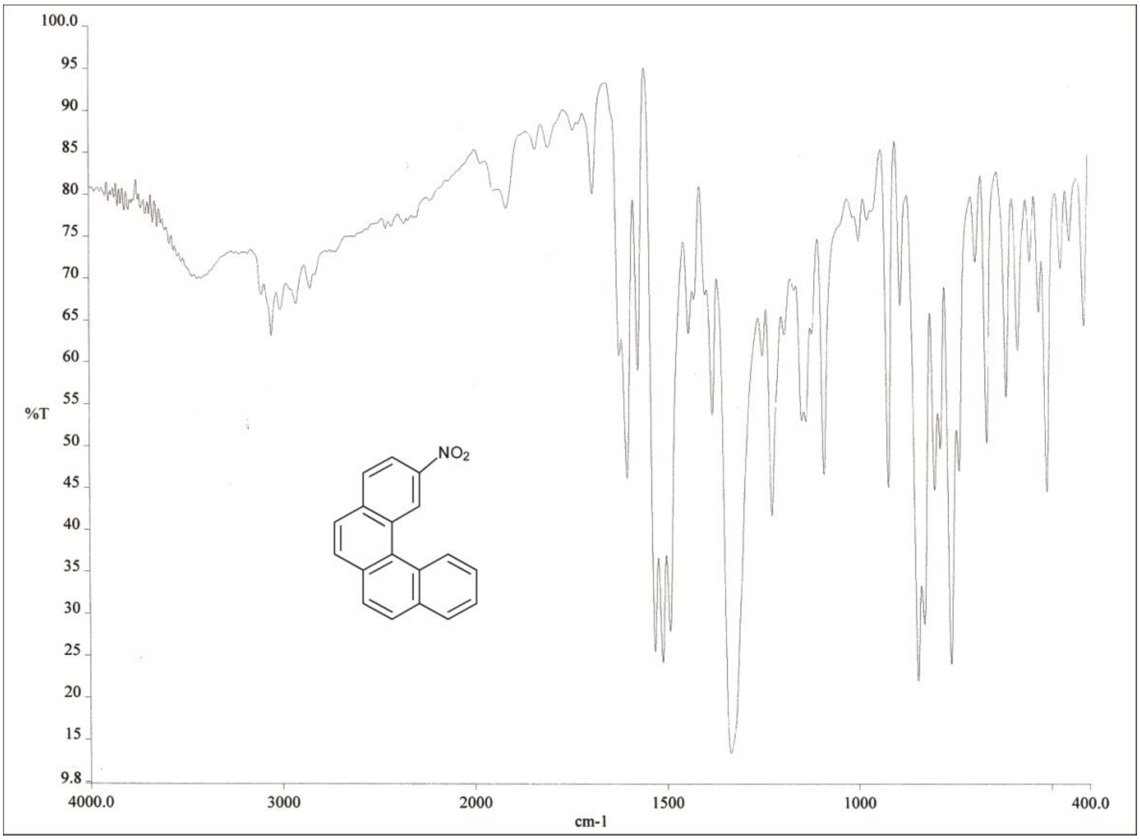


**EI-Mass spectrum of 1-(*p*-Nitrophenyl)-2-(2-naphtyl)ethylene (109)**

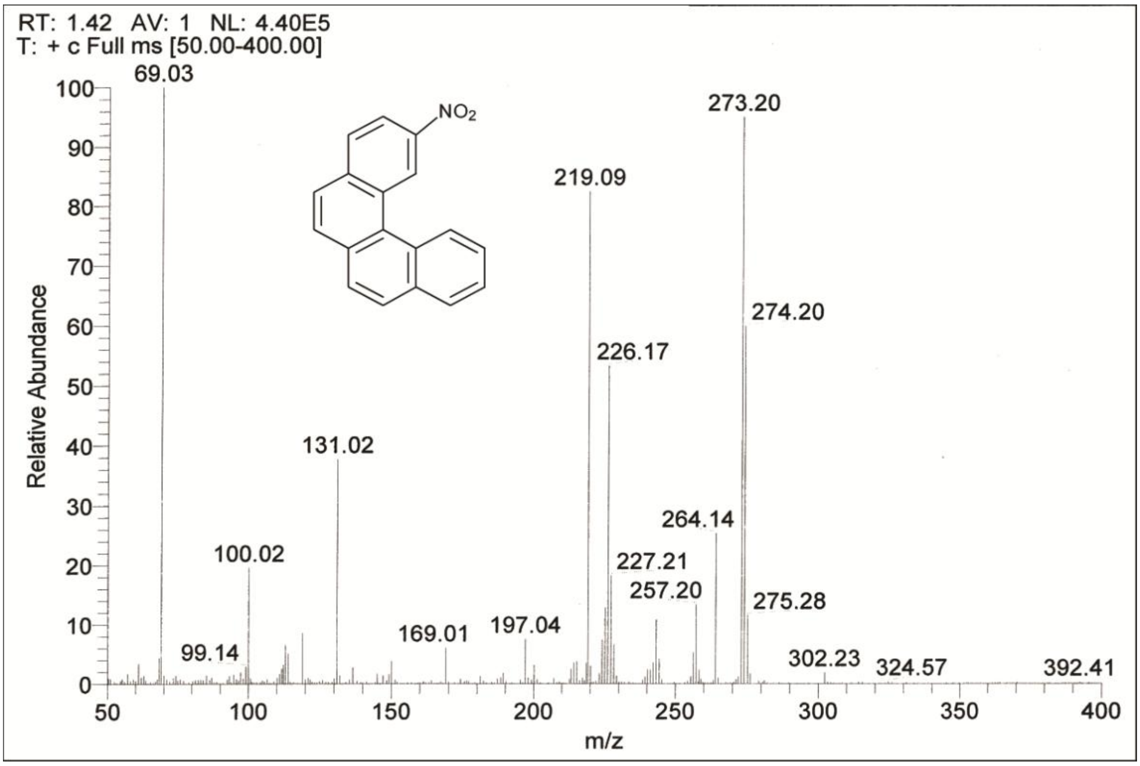
## Spectral data of 2-nitrobenzo[*c*]phenanthrene (110)



**$^1$H-NMR spectrum of 2-nitrobenzo[*c*]phenanthrene (110) in $CDCl_3$ on 400 MHz**

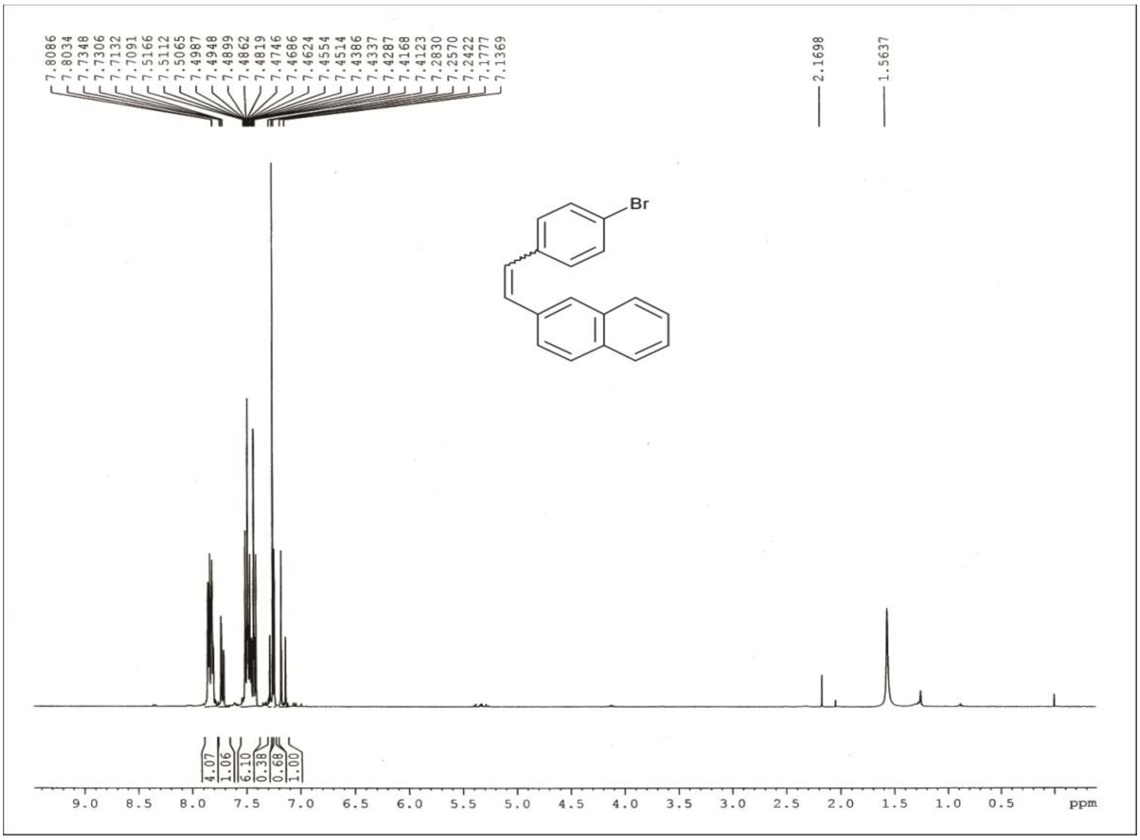


**IR spectrum of 2-nitrobenzo[*c*]phenanthrene (110)**

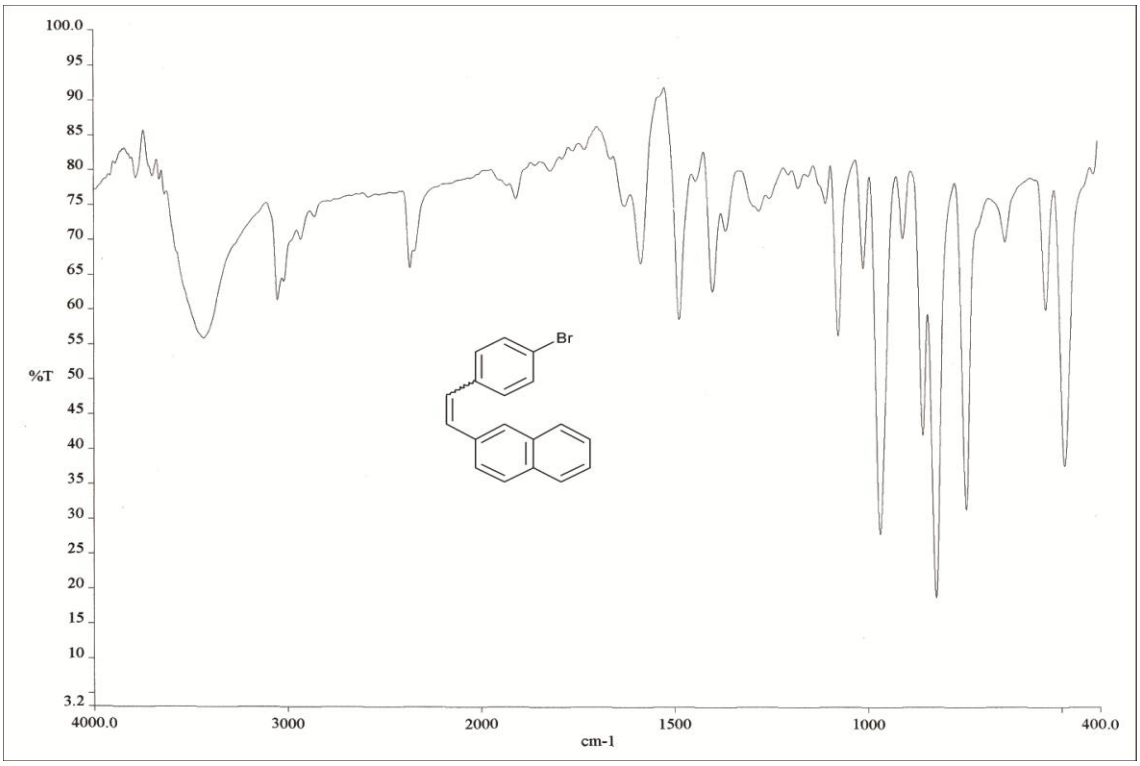


**EI-Mass spectrum of 2-nitrobenzo[*c*]phenanthrene (110)**

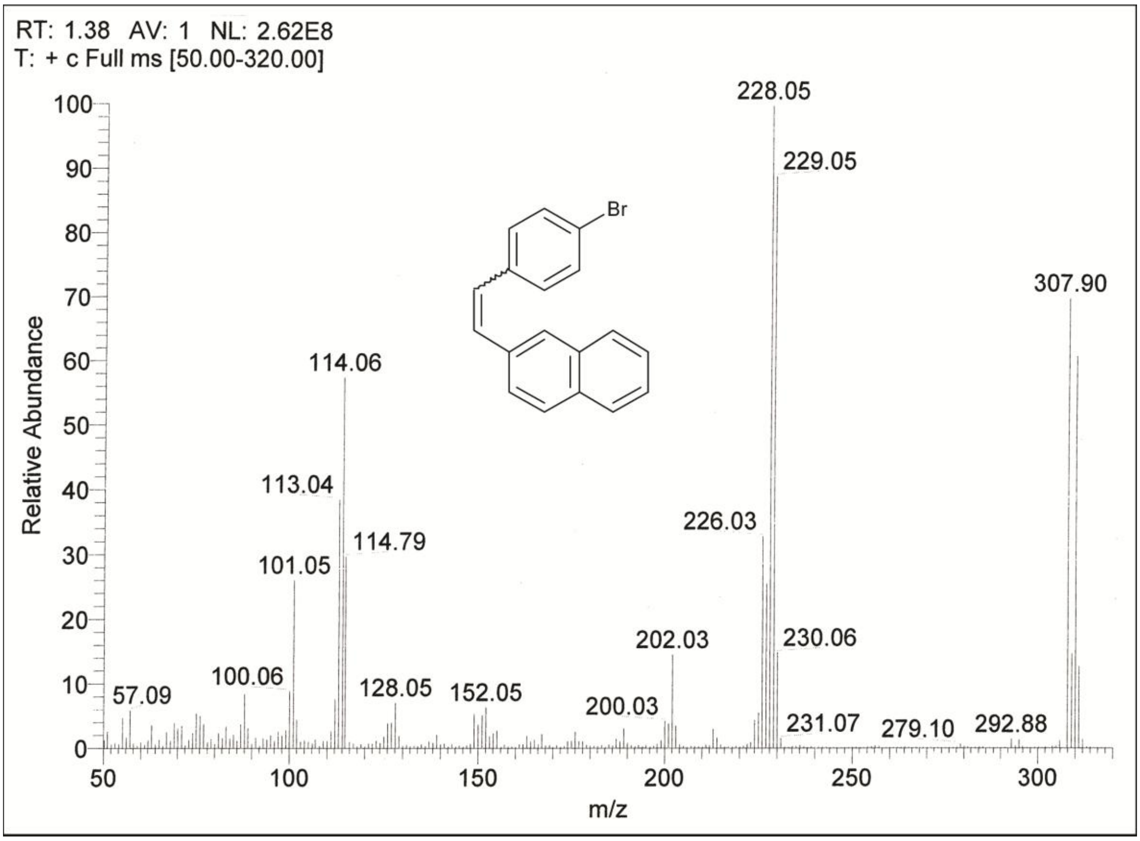
## Spectral data of 1-(*p*-bromophenyl)-2-(2-naphtyl)ethylene (127):



$^1$H-NMR spectrum of 1-(*p*-bromophenyl)-2-(2-naphtyl)ethylene (127) in $CDCl_3$ on 400 MHz

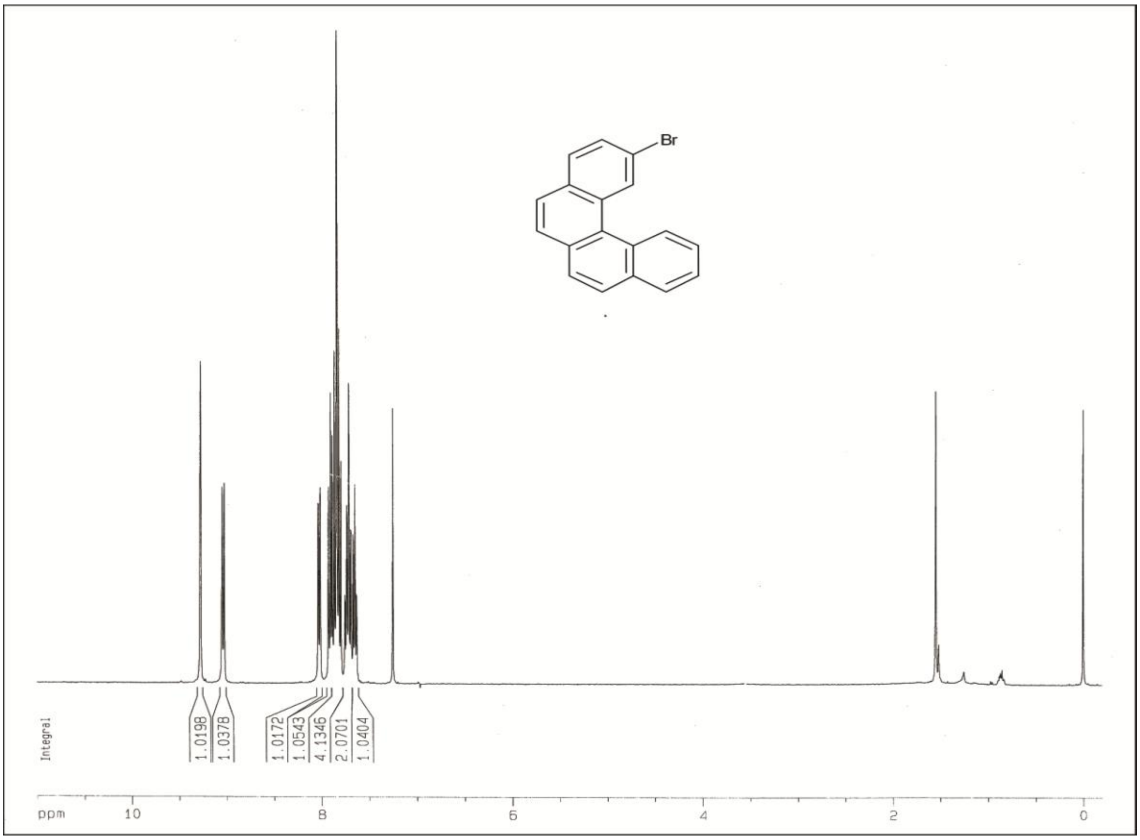


IR spectrum of 1-(*p*-bromophenyl)-2-(2-naphtyl)ethylene (127)

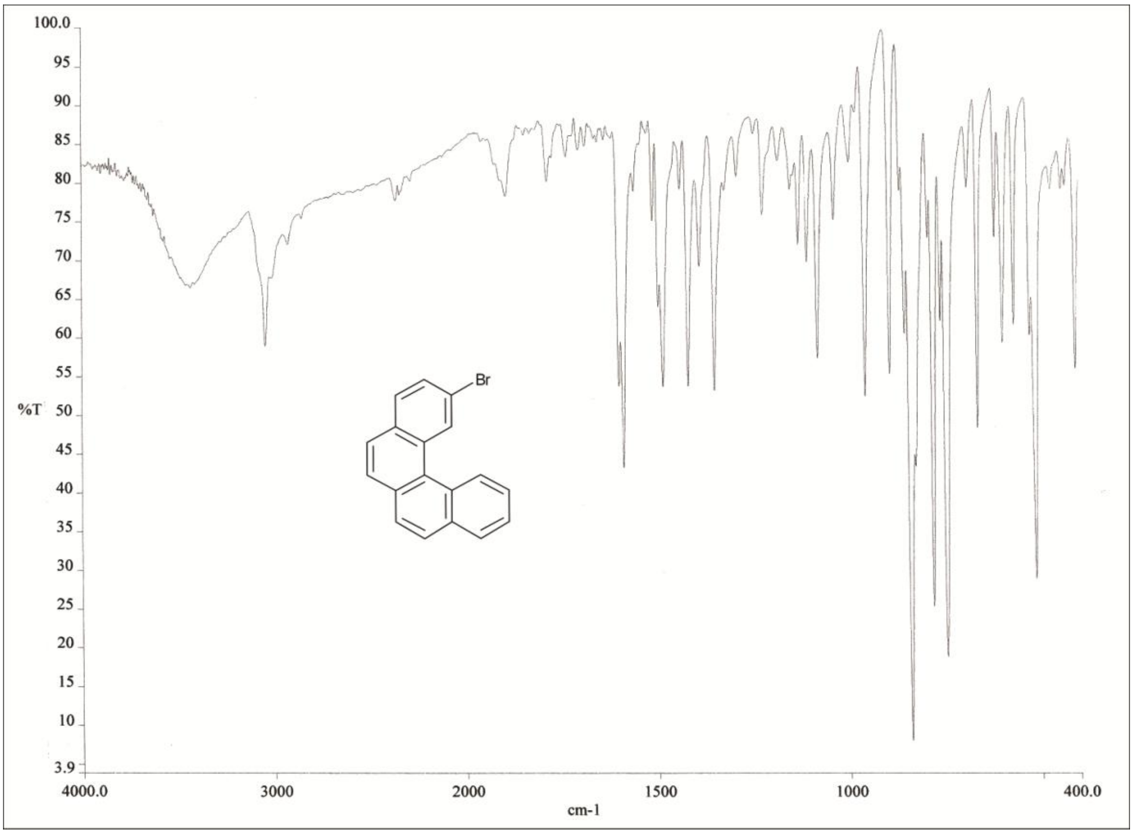


**EI-Mass spectrum of 1-(*p*-bromophenyl)-2-(2-naphtyl)ethylene (127)**

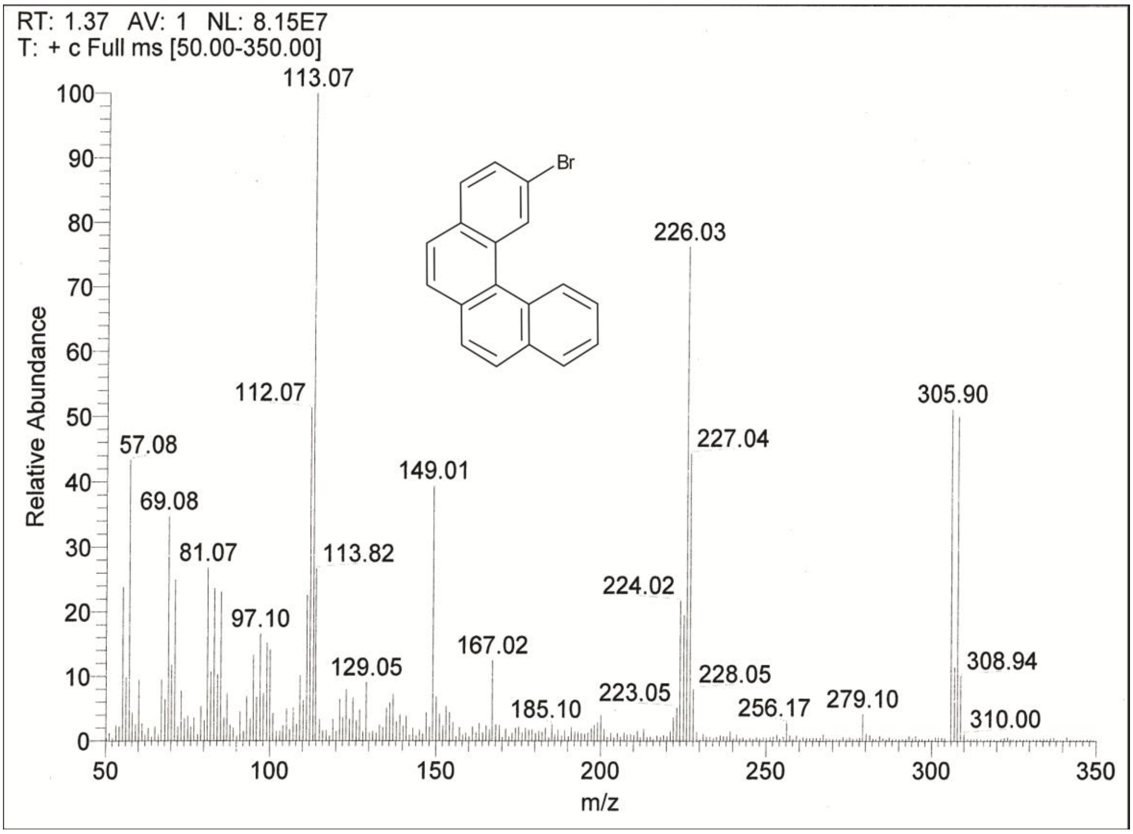
## Spectral data of 2-bromobenzo[*c*]phenanthrene (128)



$^1$**H-NMR spectrum of 2-bromobenzo[*c*]phenanthrene (128) in CDCl$_3$ on 400 MHz**

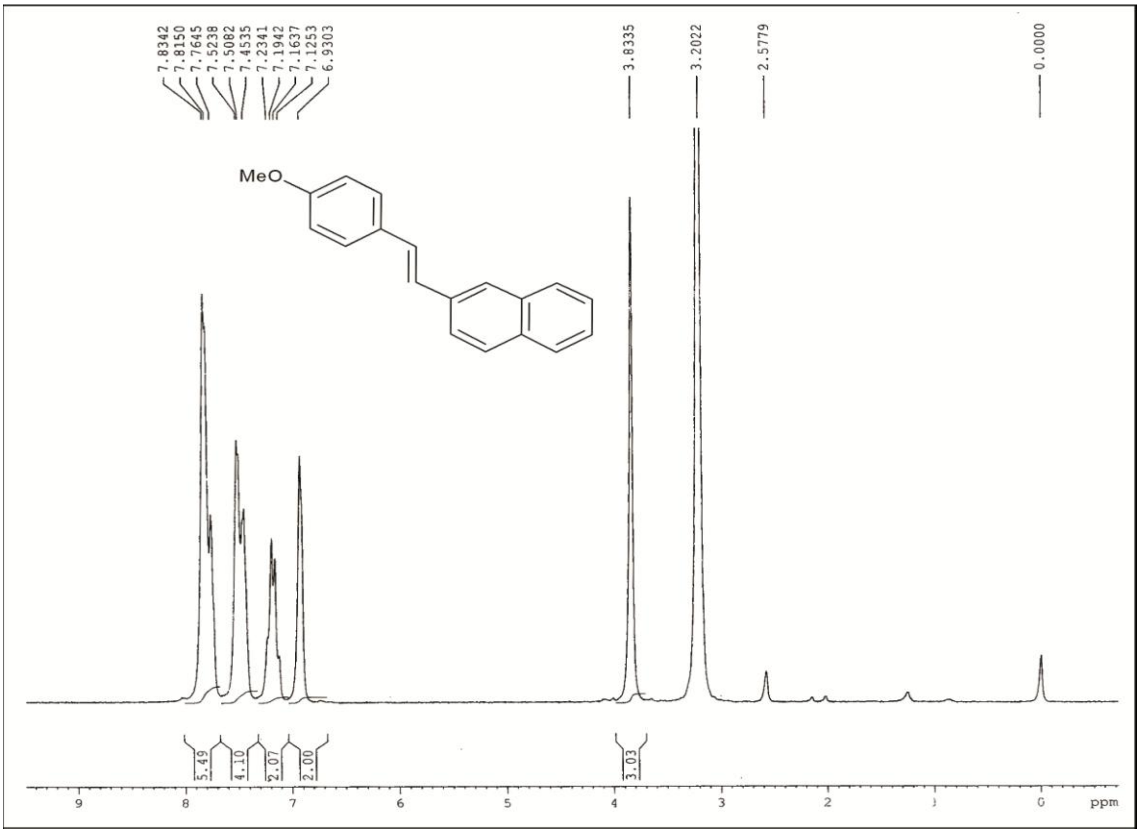


**IR spectrum of 2-bromobenzo[*c*]phenanthrene (120)**



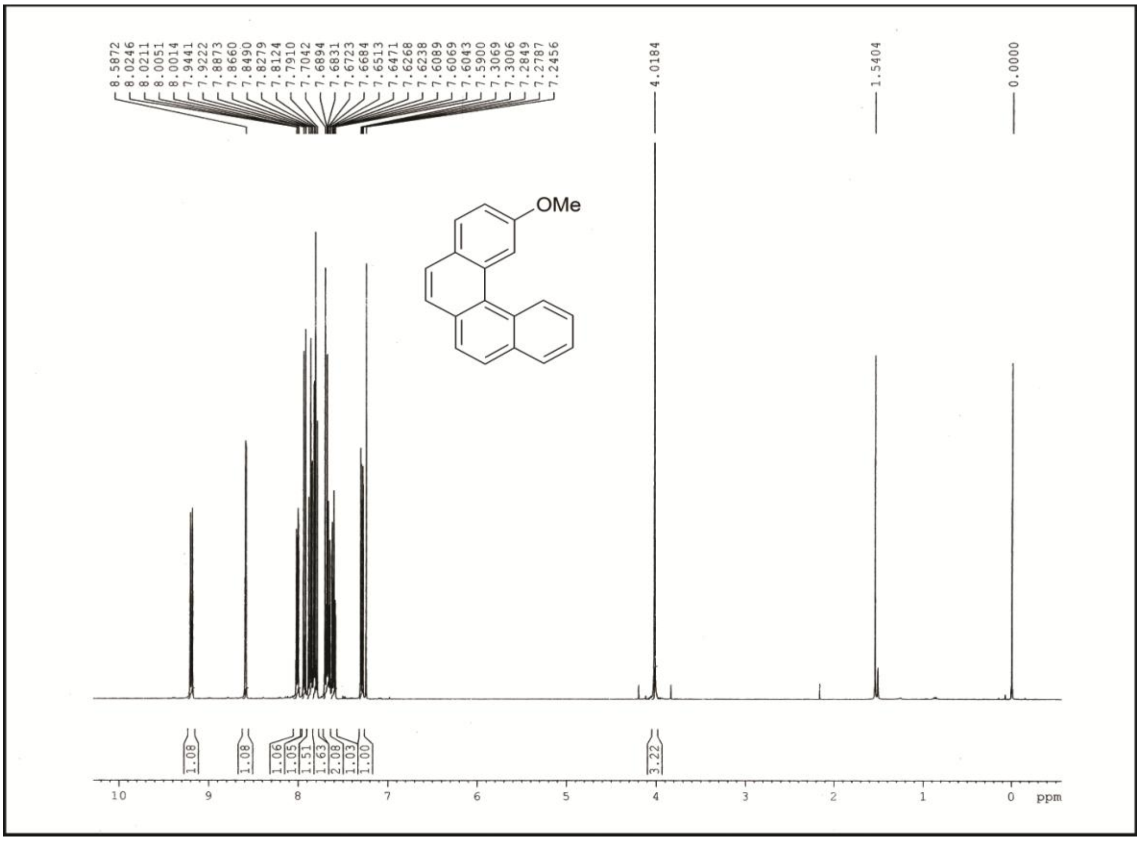
**EI-Mass spectrum of 2-bromobenzo[*c*]phenanthrene (120)**

## Spectral Data of (*E*)-2-(4-methoxystyryl)naphthalene (129)

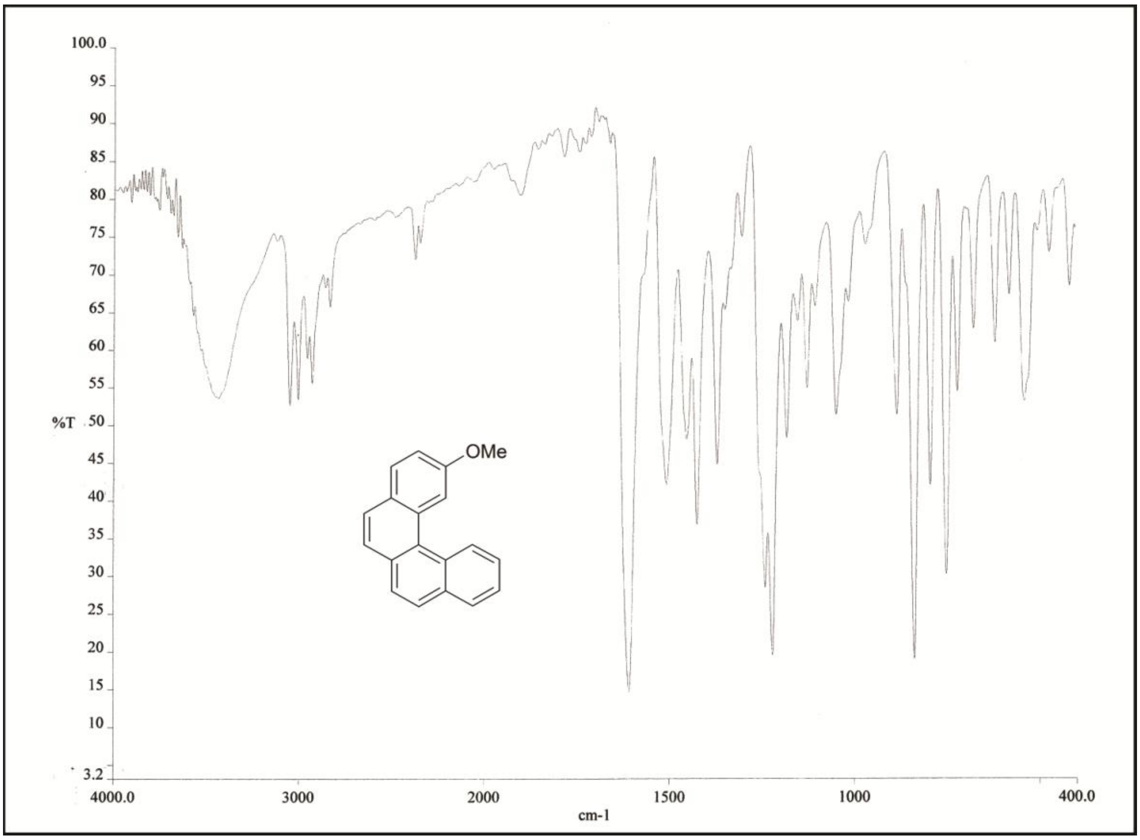


$^1$H-NMR spectrum of (*E*)-2-(4-methoxystyryl)naphthalene (129) in DMSO-$d^6$ on 400 MHz

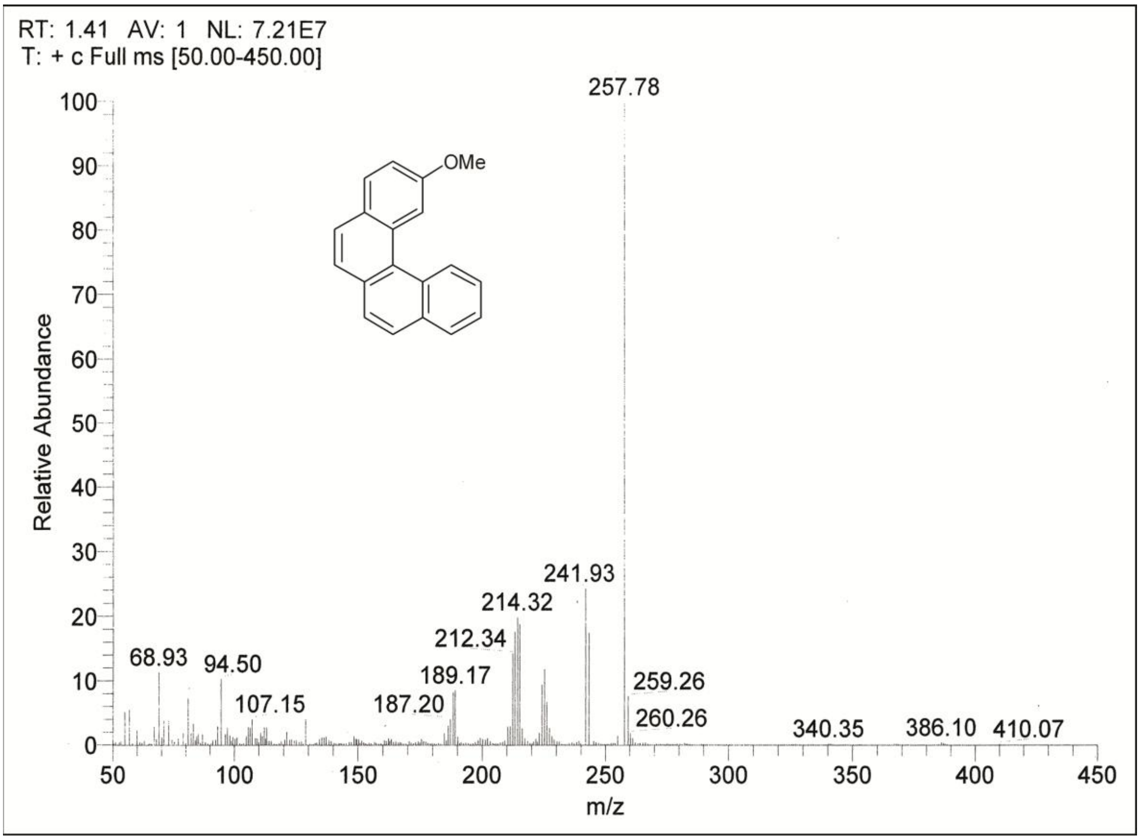
## Spectral data of 2-methoxybenzo[*c*]phenanthrene (130)



$^1$H-NMR spectrum of 2-methoxybenzo[*c*]phenanthrene (130) in $CDCl_3$ on 400 MHz

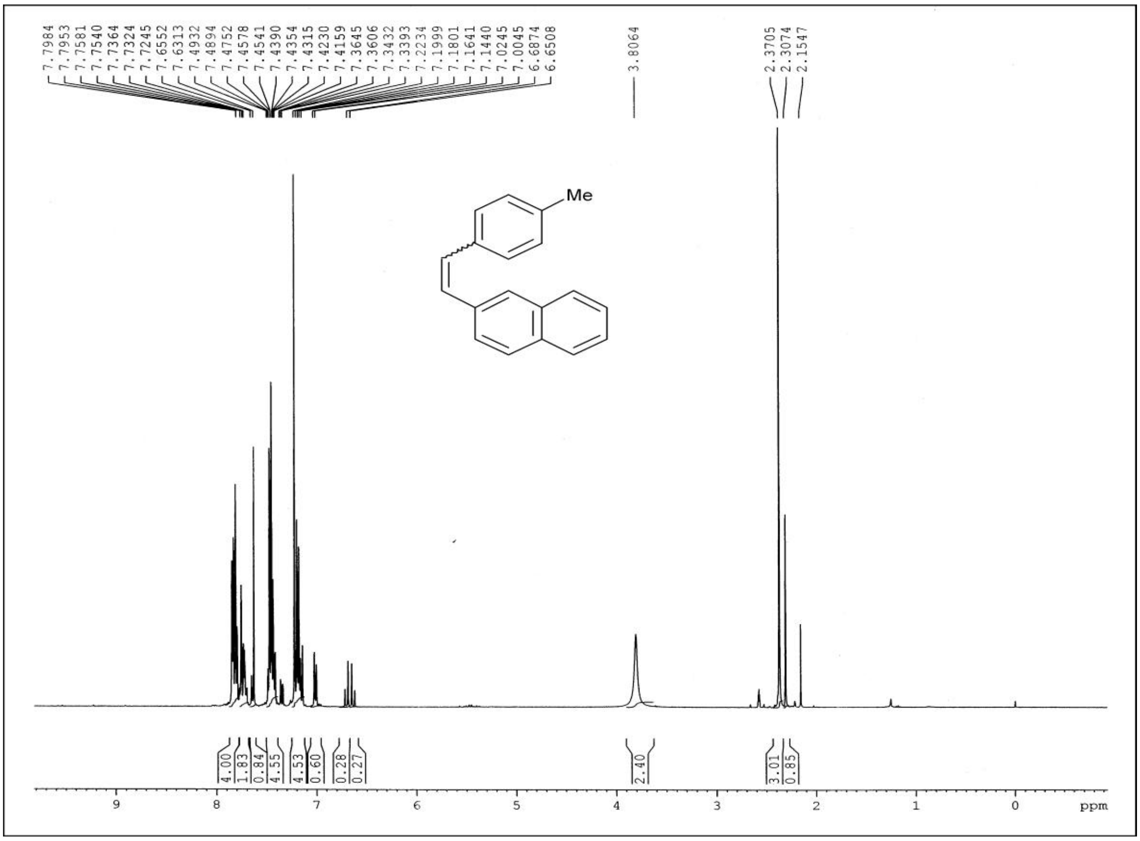


**IR spectrum of 2-methoxybenzo[*c*]phenanthrene (130)**

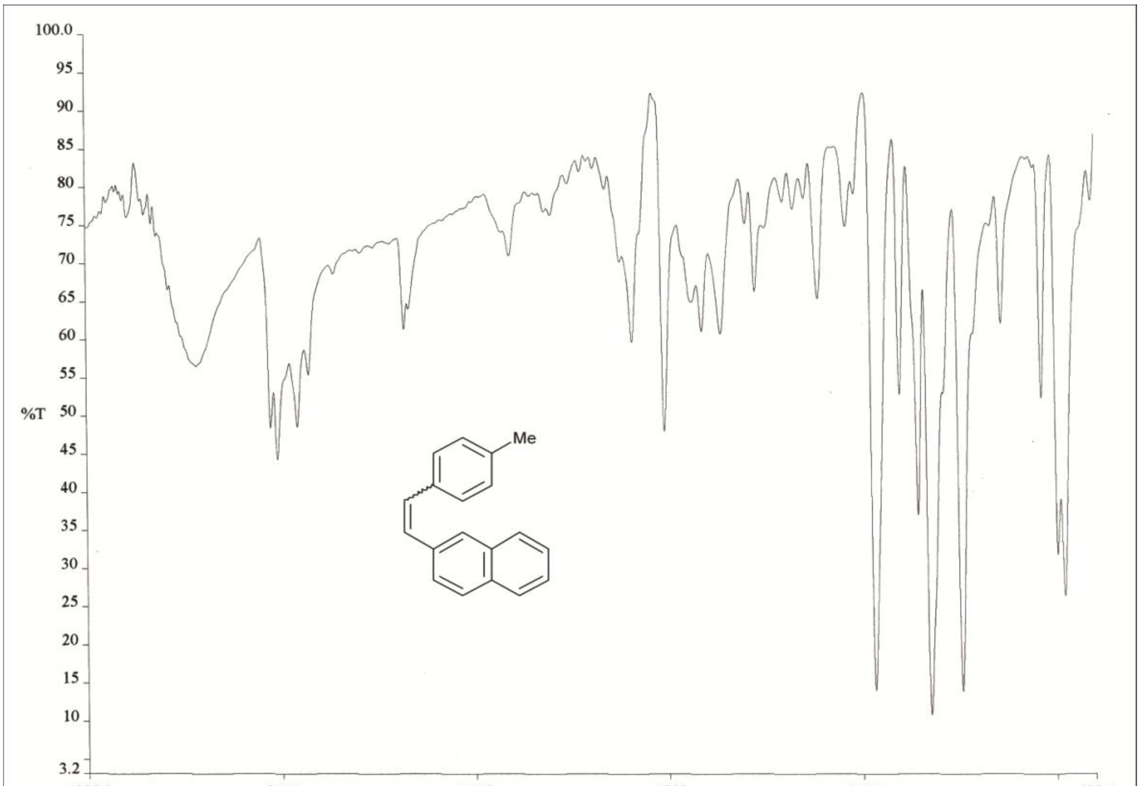


**EI-Mass spectrum of 2-methoxybenzo[*c*]phenanthrene (130)**

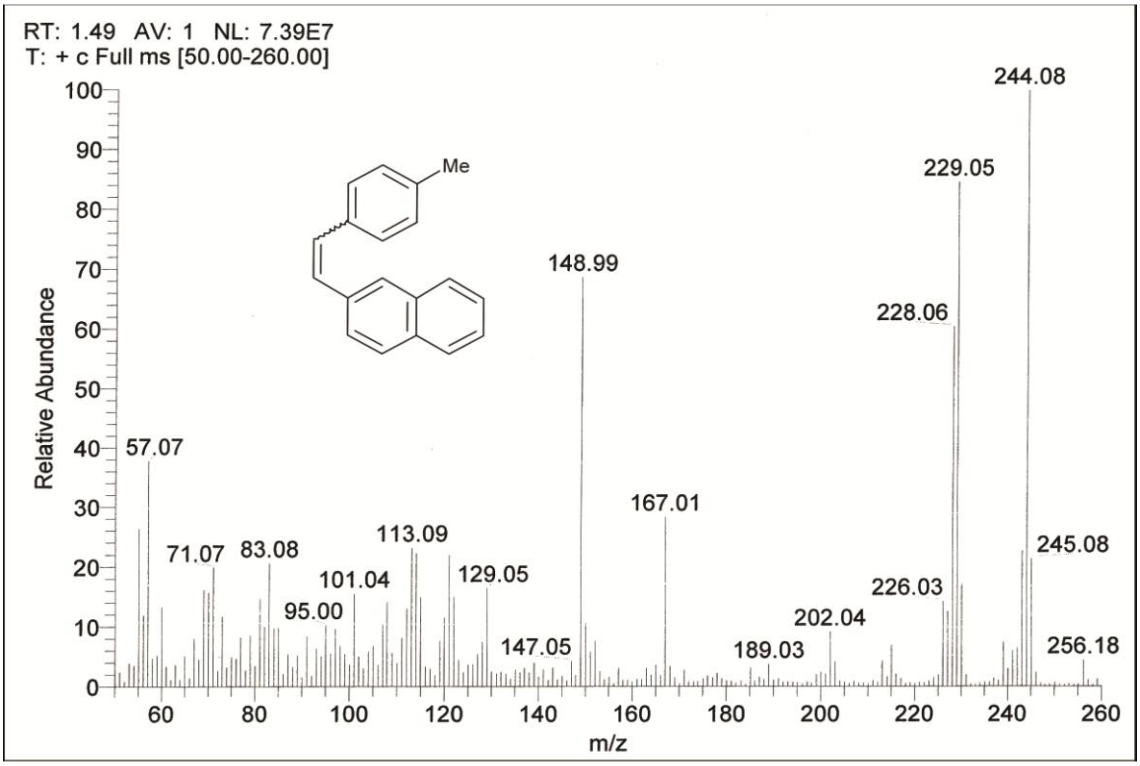
## Spectral data of 2-[2-(4-methylphenyl)ethenyl]naphthalene (131)



**$^1$H-NMR spectrum of 2-[2-(4-methylphenyl)ethenyl]naphthalene (131) in $CDCl_3$ on 400 MHz**

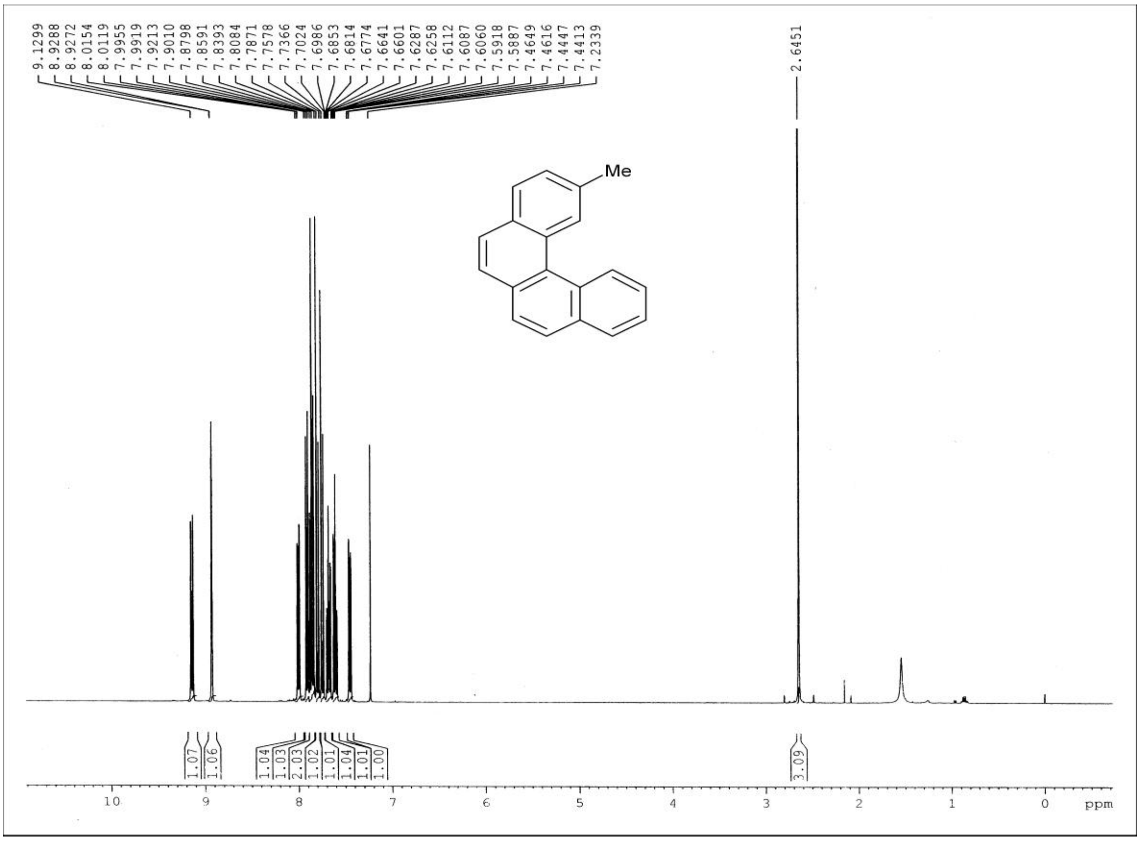


**IR spectrum of 2-[2-(4-methylphenyl)ethenyl]naphthalene (131)**

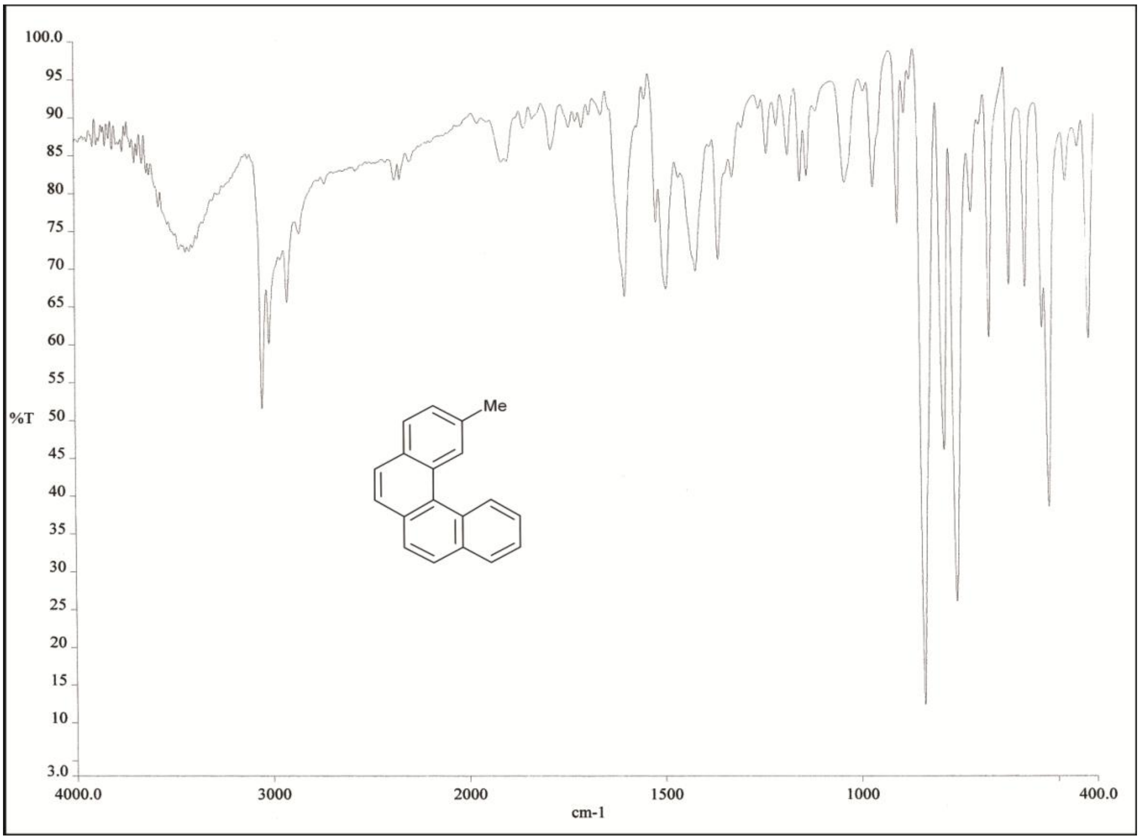


**ESI-MS spectrum of 2-[2-(4-methylphenyl)ethenyl]naphthalene (131)**

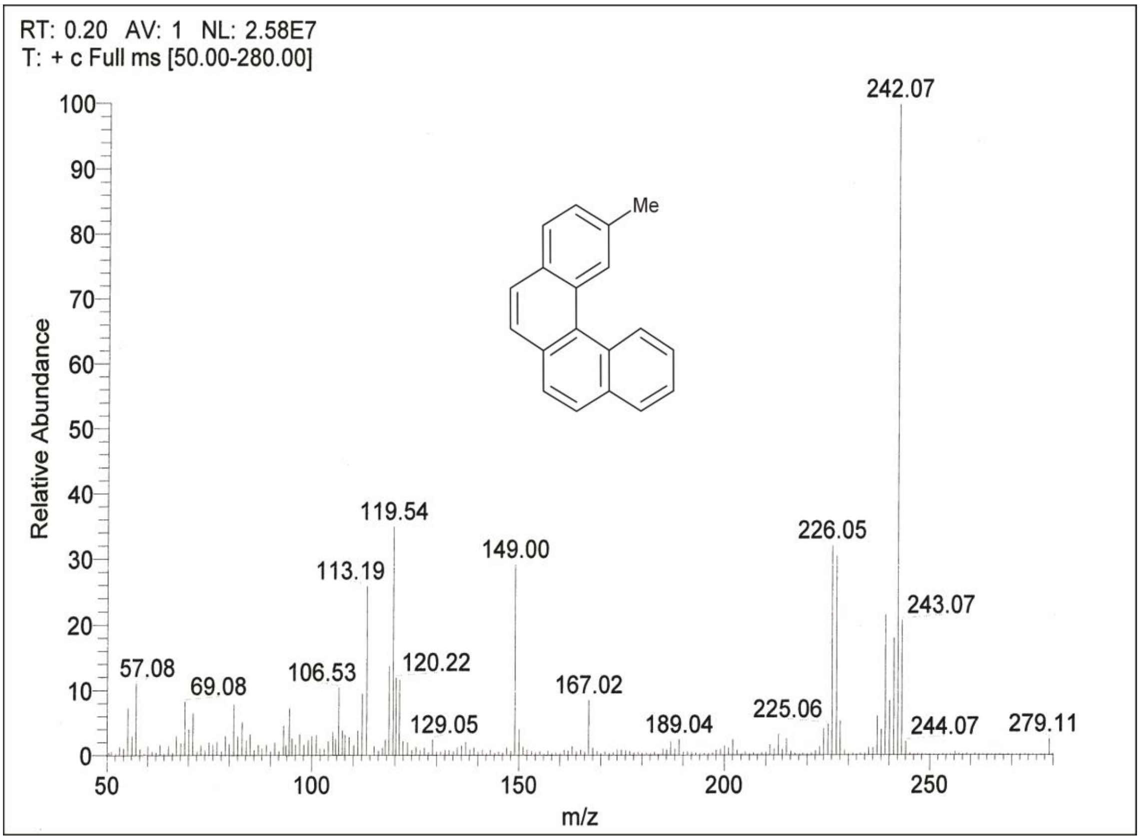
## Spectral data of 2-methylbenzo[*c*]phenanthrene (132)



**$^1$H-NMR spectrum of 2-methylbenzo[*c*]phenanthrene (132) in $CDCl_3$ on 400 MHz**

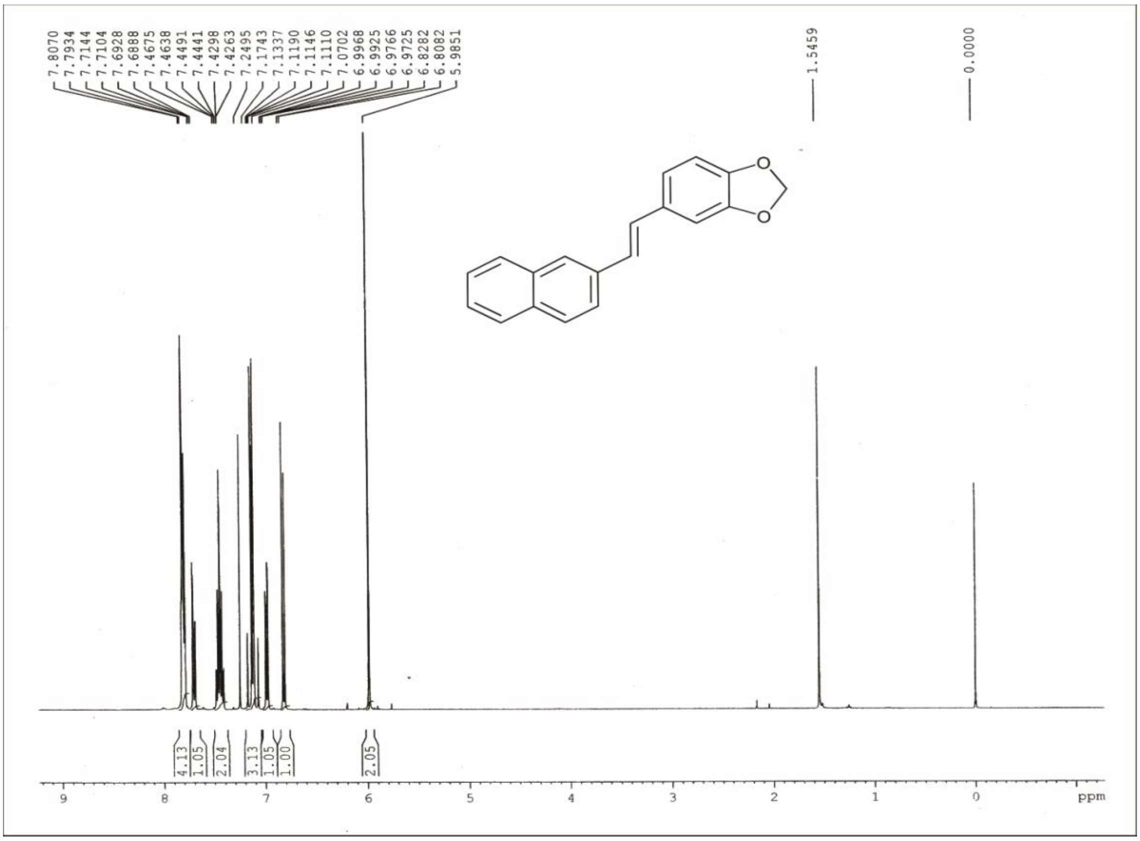


**IR spectrum of 2-methylbenzo[*c*]phenanthrene (132)**

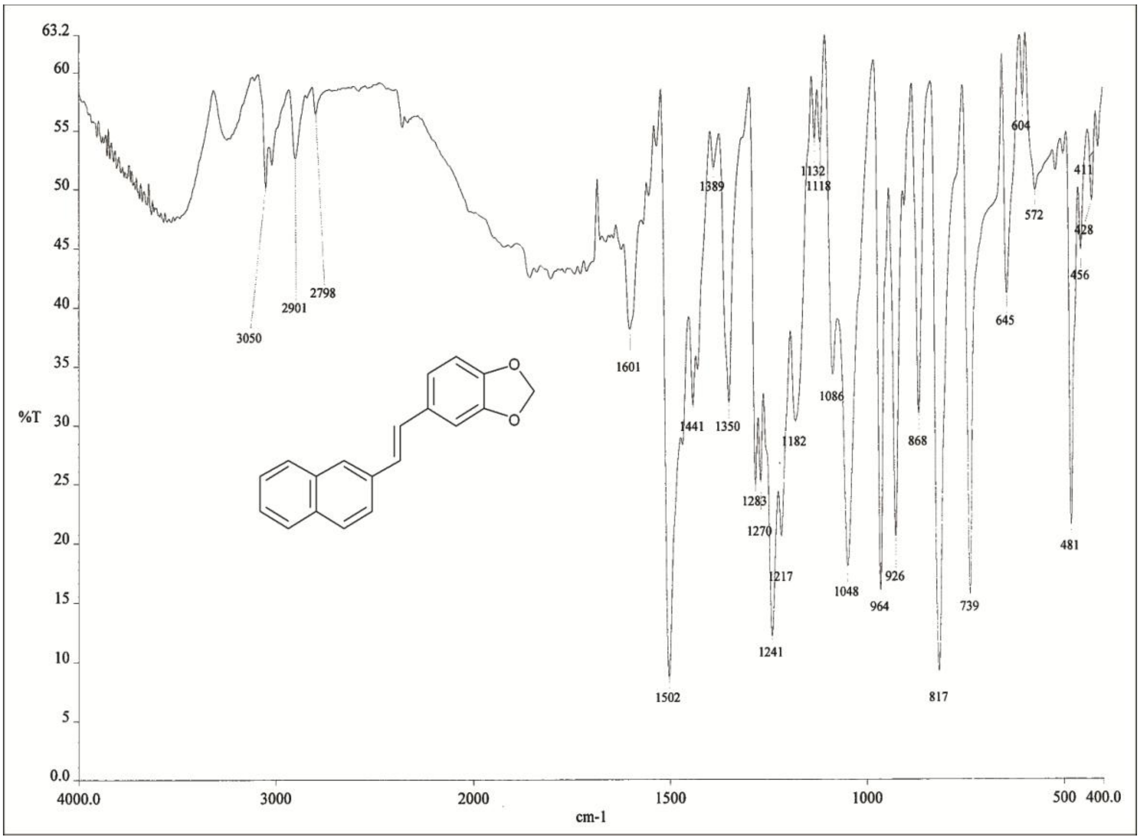


**EI-Mass spectrum of 2-methylbenzo[*c*]phenanthrene (132)**

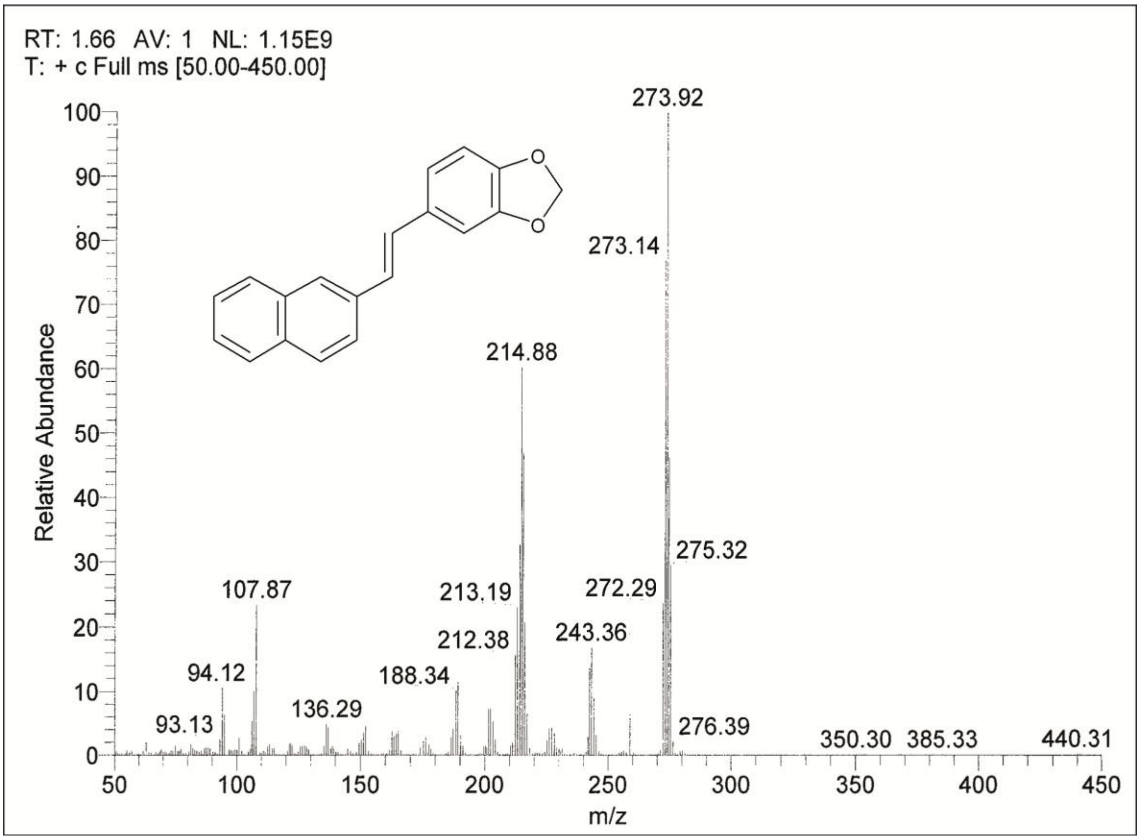
## Spectral data of (*E*)-5-(2(naphthalene-2-yl)vinyl)benzo[*d*][1,3]dioxole (135)



**$^1$H-NMR spectrum of (*E*)-5-(2(naphthalene-2-yl)vinyl)benzo[*d*][1,3]dioxole (135) in $CDCl_3$ on 400 MHz**

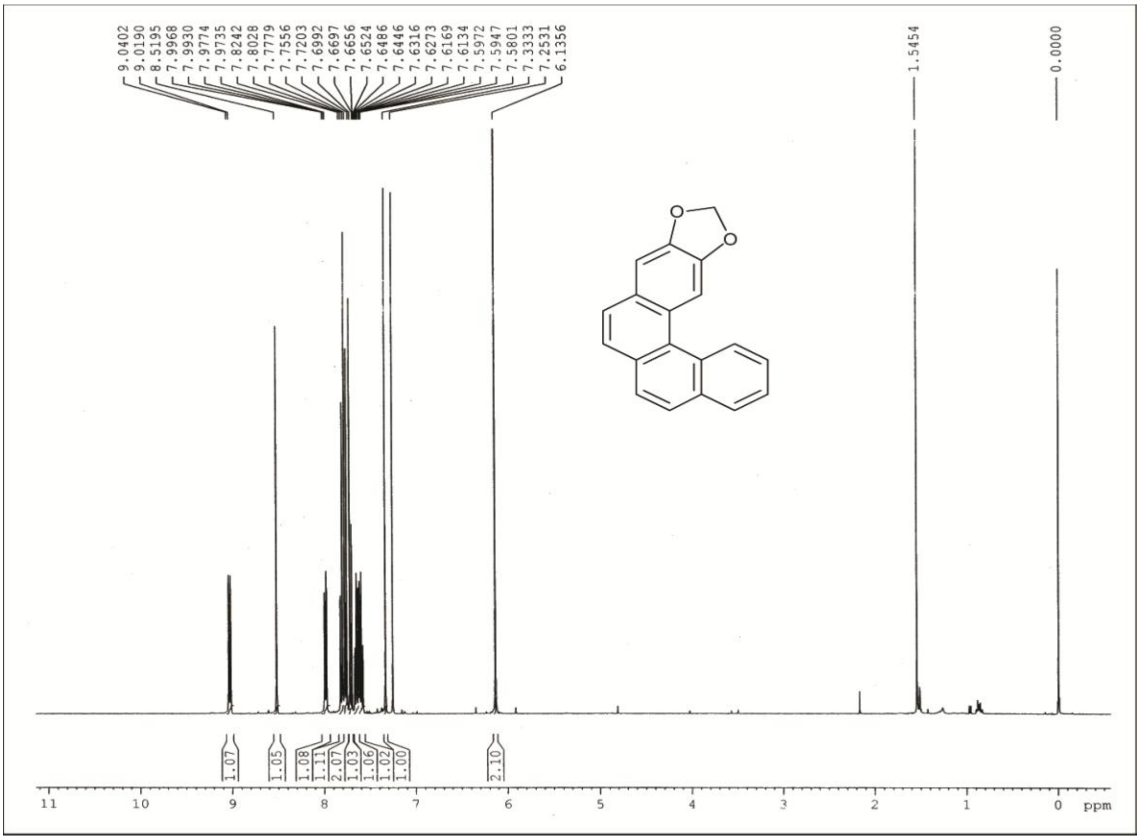


**IR Spectrum of (*E*)-5-(2(naphthalene-2-yl)vinyl)benzo[*d*][1,3]dioxole (135)**

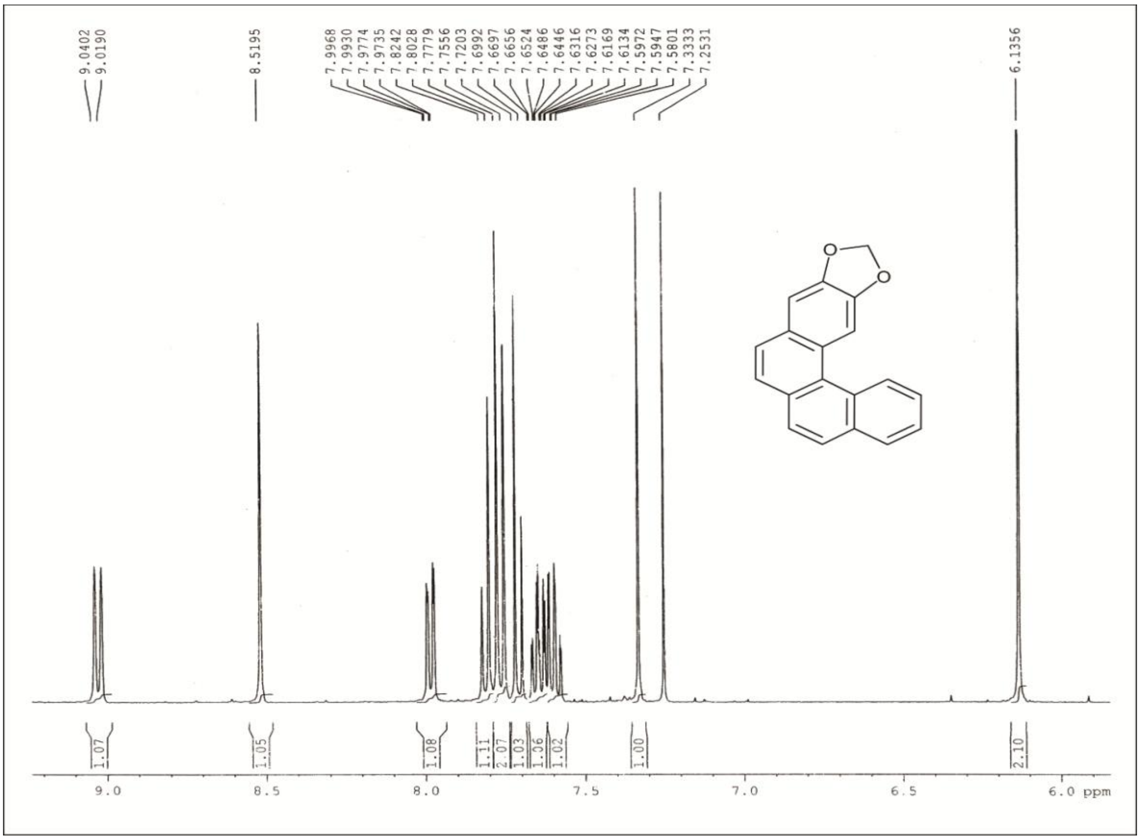


**EI-Mass Spectrum of (*E*)-5-(2(naphthalene-2-yl)vinyl)benzo[*d*][1,3]dioxole (135)**

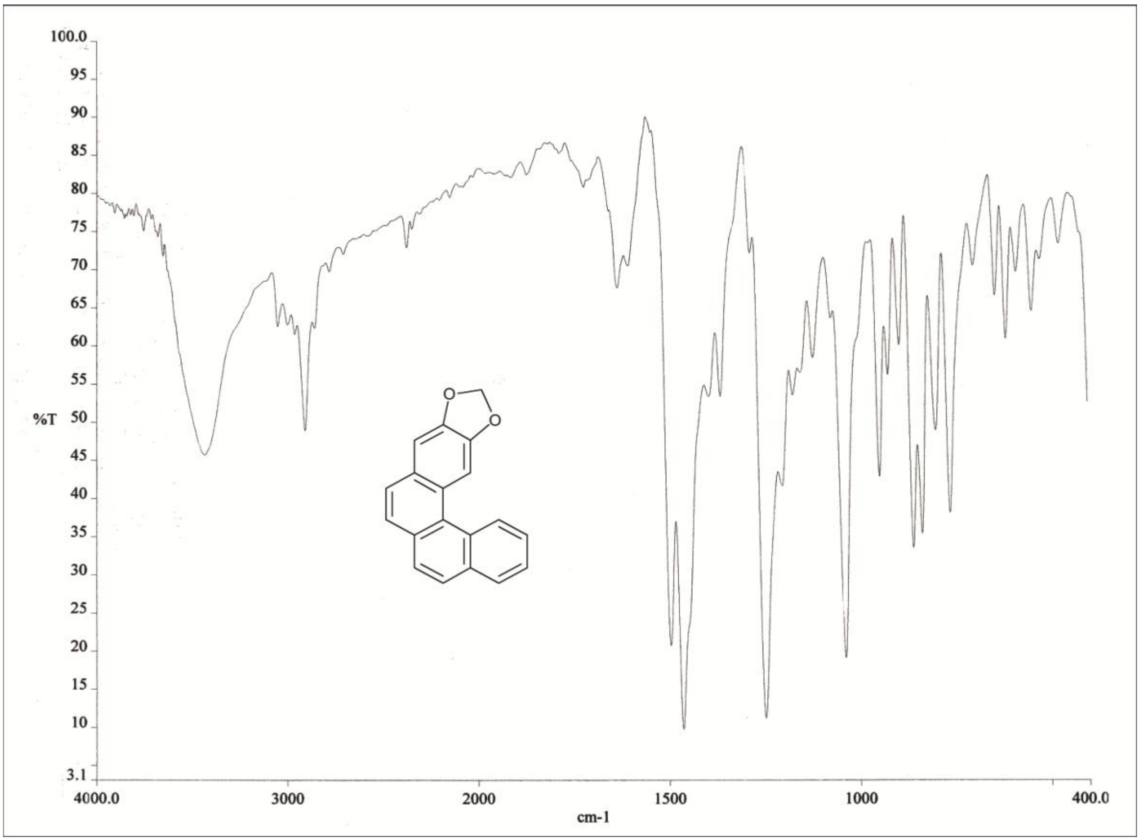
## Spectral data of benzo[*c*]phenanthreno[2,3-*d*]-1,3-dioxole (136)



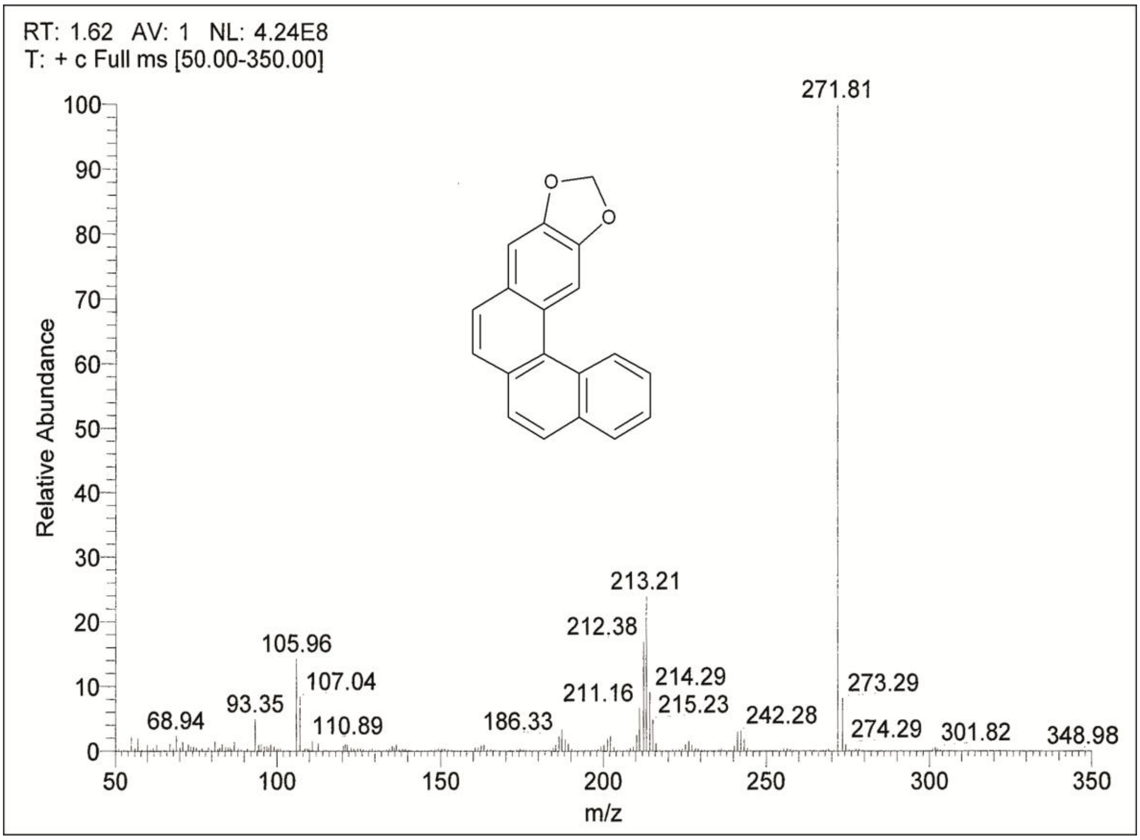
**$^1$H-NMR spectrum of benzo[*c*]phenanthreno[2,3-*d*]-1,3-dioxole (136) in $CDCl_3$ on 400 MHz**



**$^1$H-NMR of enlarge spectrum of benzo[*c*]phenanthreno[2,3-*d*]-1,3-dioxole (136) in $CDCl_3$ on 400 MHz**

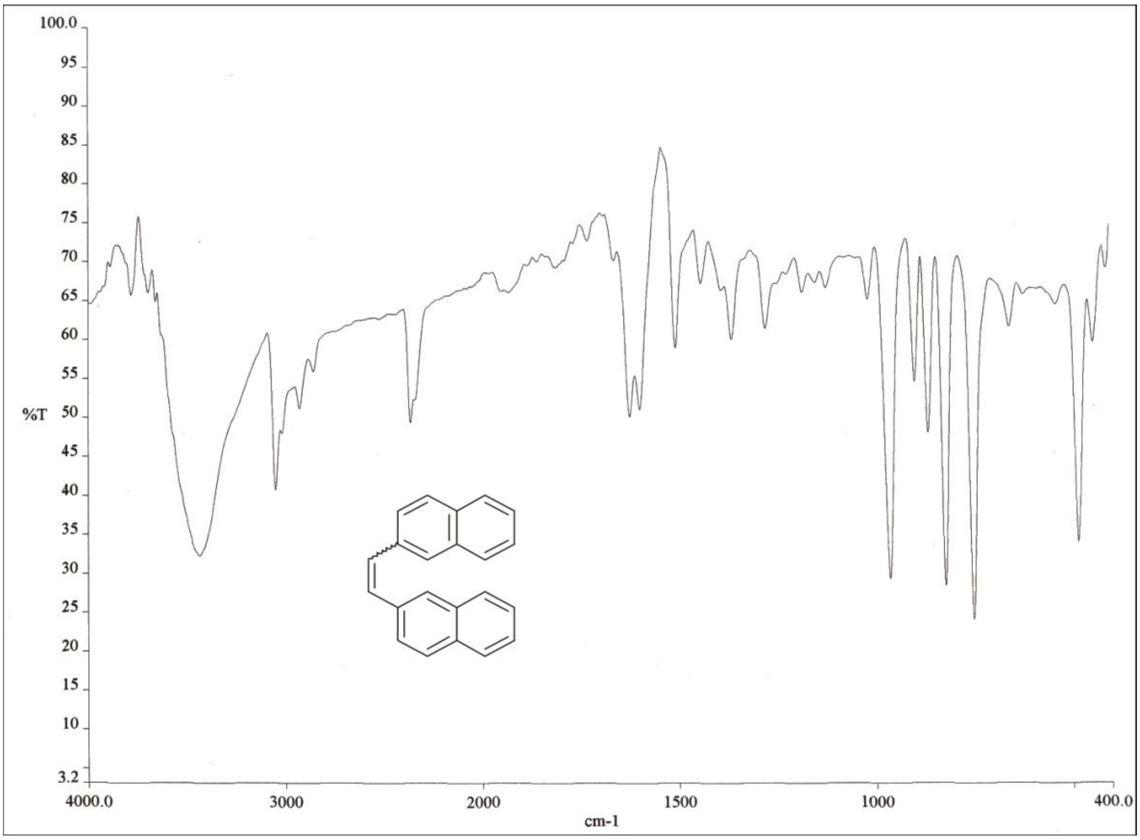


**IR spectrum of benzo[*c*]phenanthreno[2,3-*d*]-1,3-dioxole (136)**

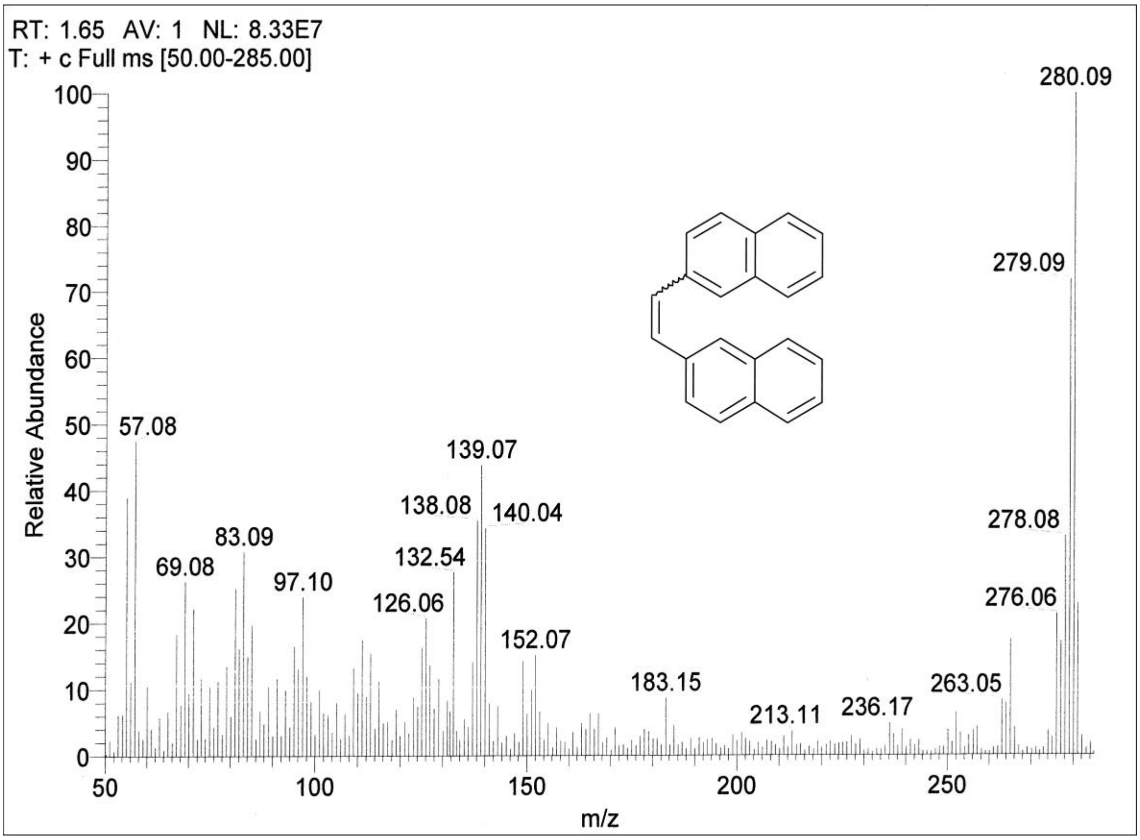


**EI- Mass spectrum of benzo[*c*]phenanthreno[2,3-*d*]-1,3-dioxole (136)**

## Spectral data of 1,2-bis(2-naphthyl)ethylene (138)

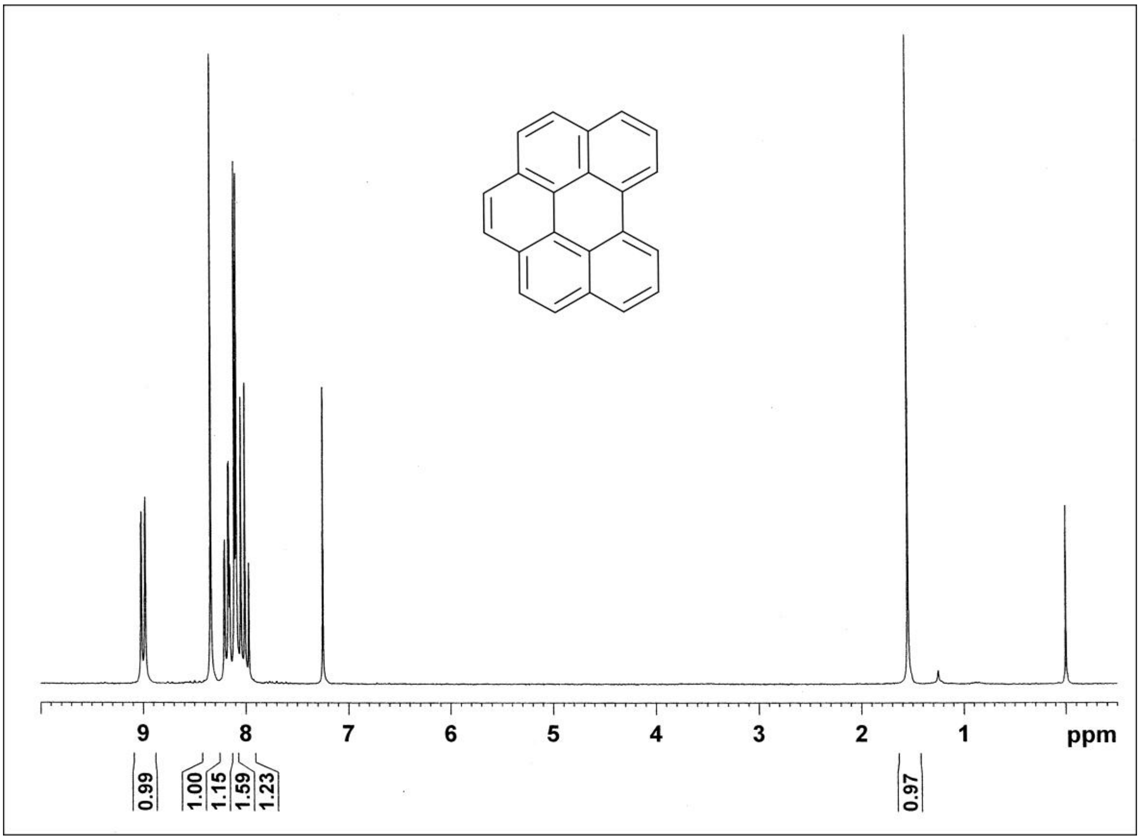


**IR spectrum of 1,2-bis(2-naphthyl)ethylene (138)**

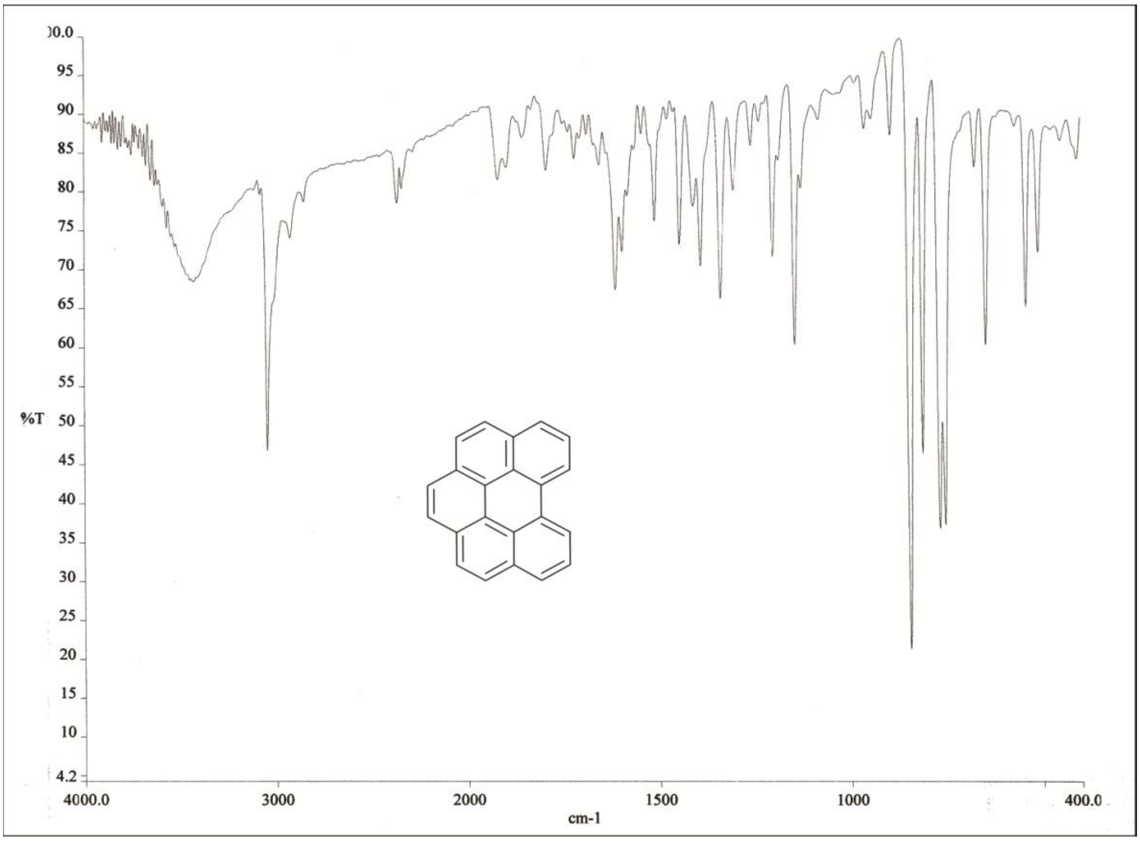


**EI-Mass spectrum of 1,2-Bis(2-naphthyl)ethylene (138)**

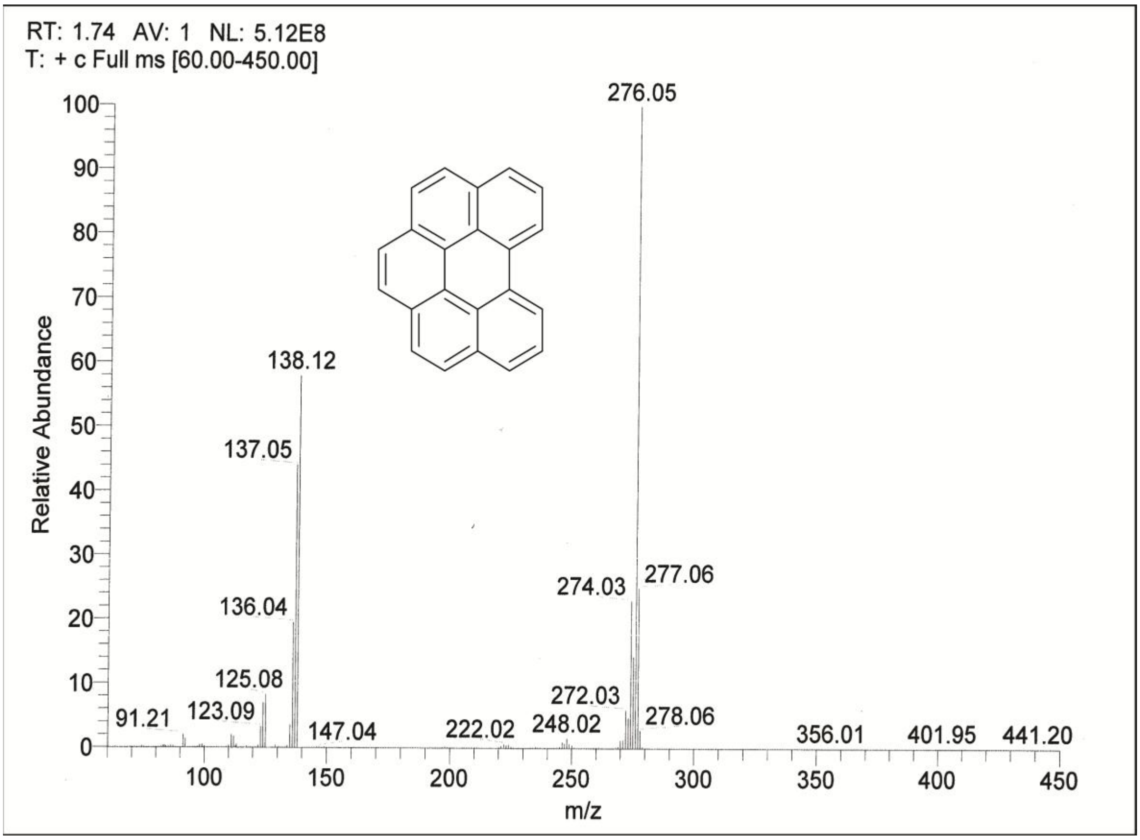
## Spectral data of benzo[*ghi*]perylene (35)



**$^1$H-NMR spectrum of benzo[*ghi*]perylene (35) in CDCl$_3$ on 400 MHz**

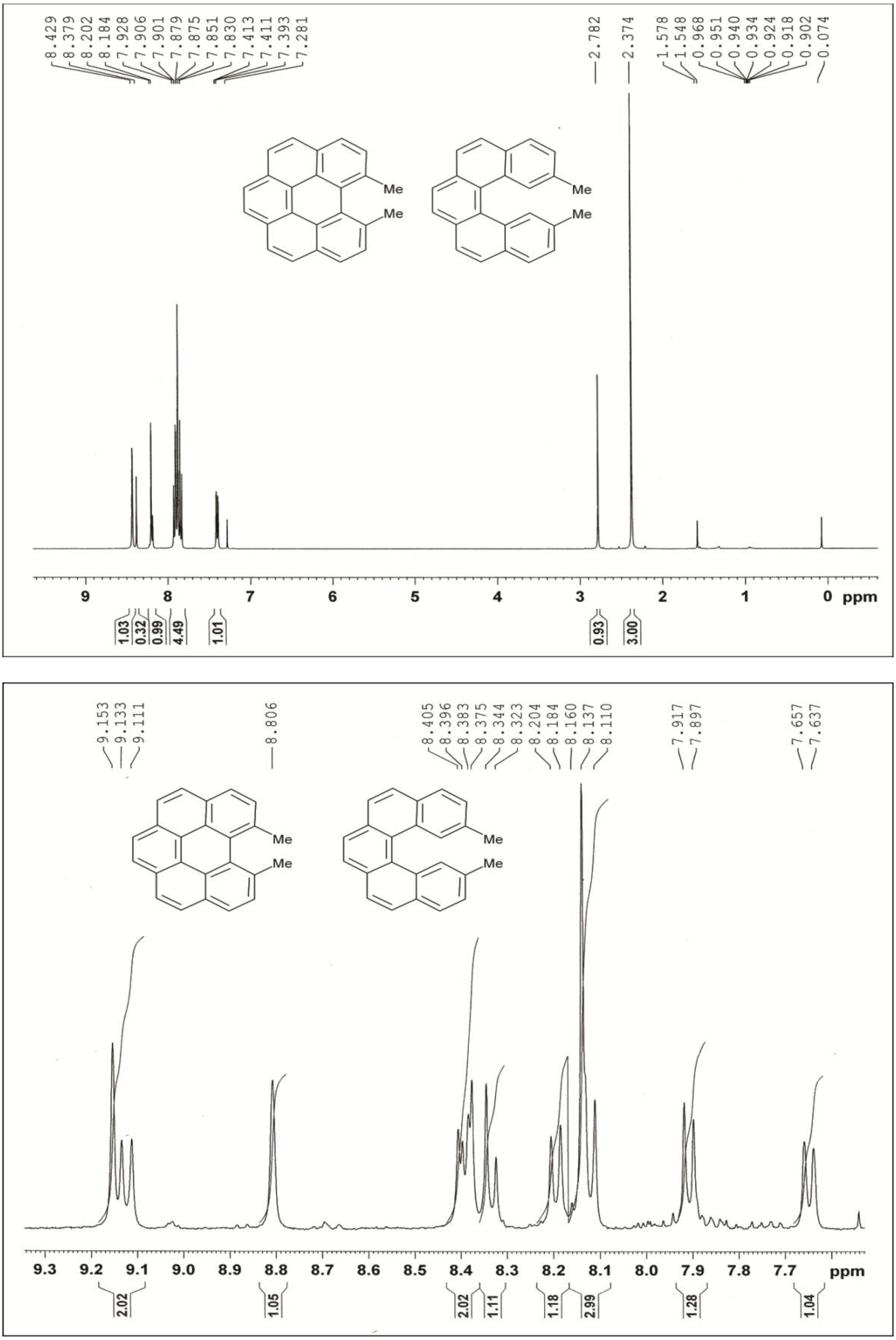


**IR spectrum of benzo[*ghi*]perylene (35)**

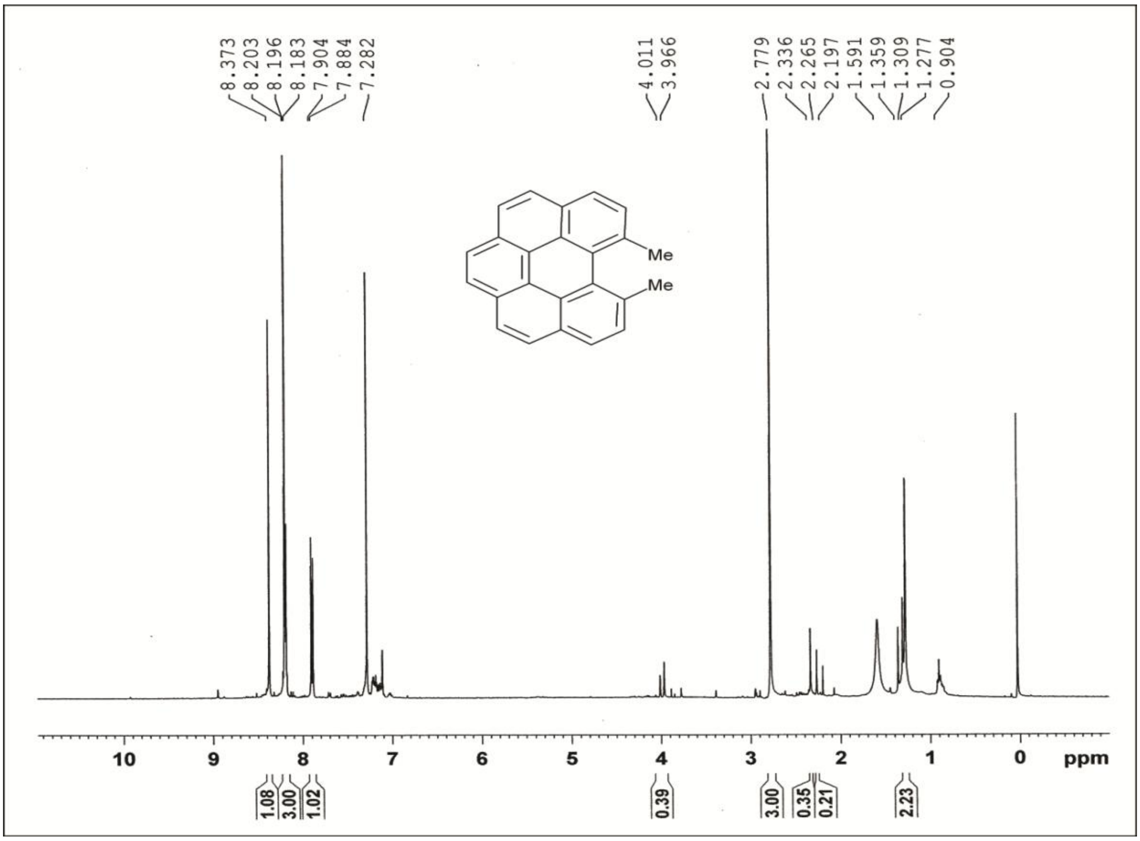


**EI-Mass spectrum of benzo[*ghi*]perylene (35)**

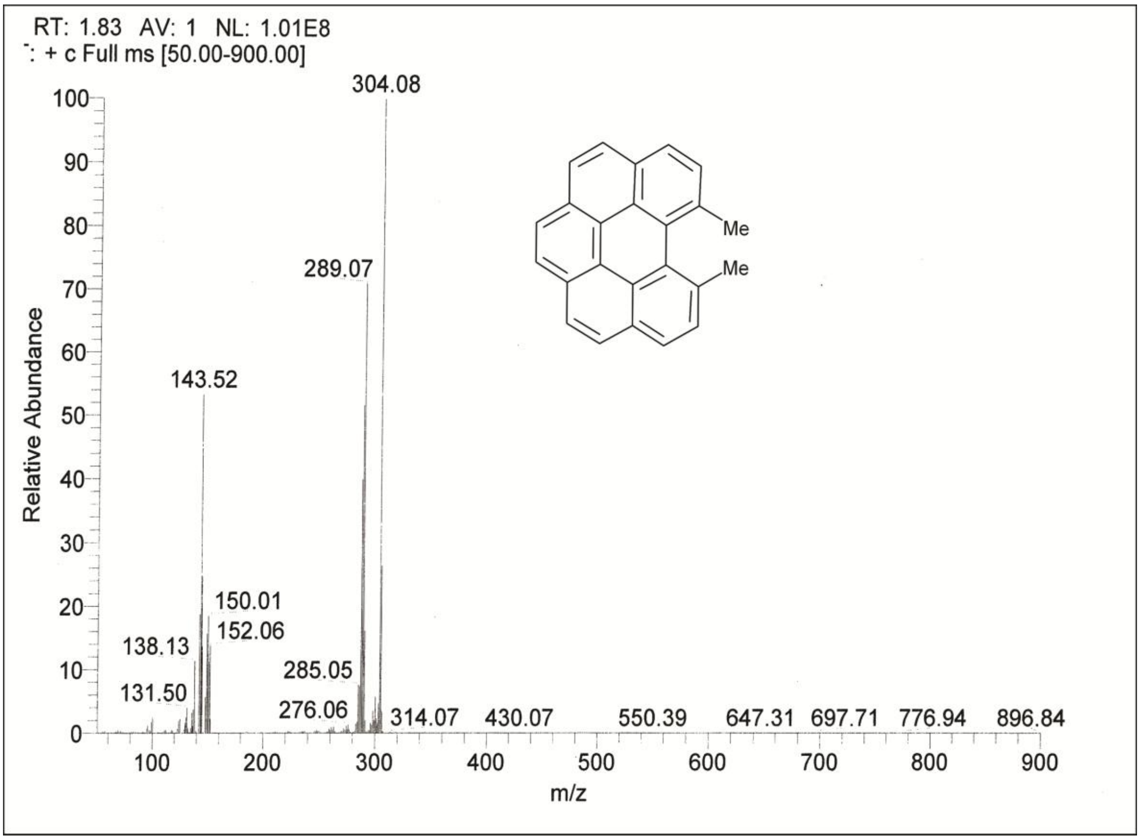
## Spectral data of 2,13-dimethyl[5]helicene (140) and 7,8-dimethylbenzo[*ghi*]perylene (141)



**$^1$H-NMR with enlarge spectrum of 2,13-dimethyl[5]helicene (140) and 7,8-dimethylbenzo[*ghi*]perylene (141)**

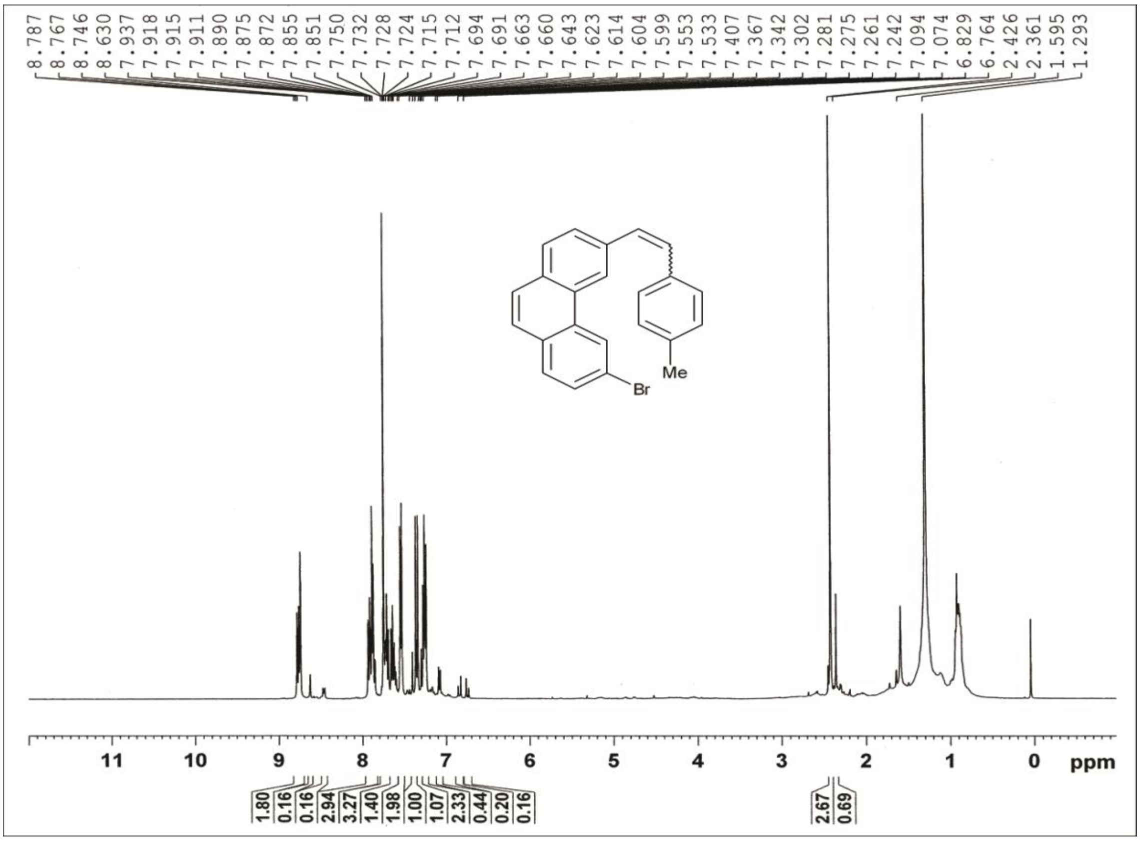


**$^1$H-NMR spectrum of 7,8-dimethylbenzo[*ghi*]perylene(141) in $CDCl_3$ on 400 MHz**

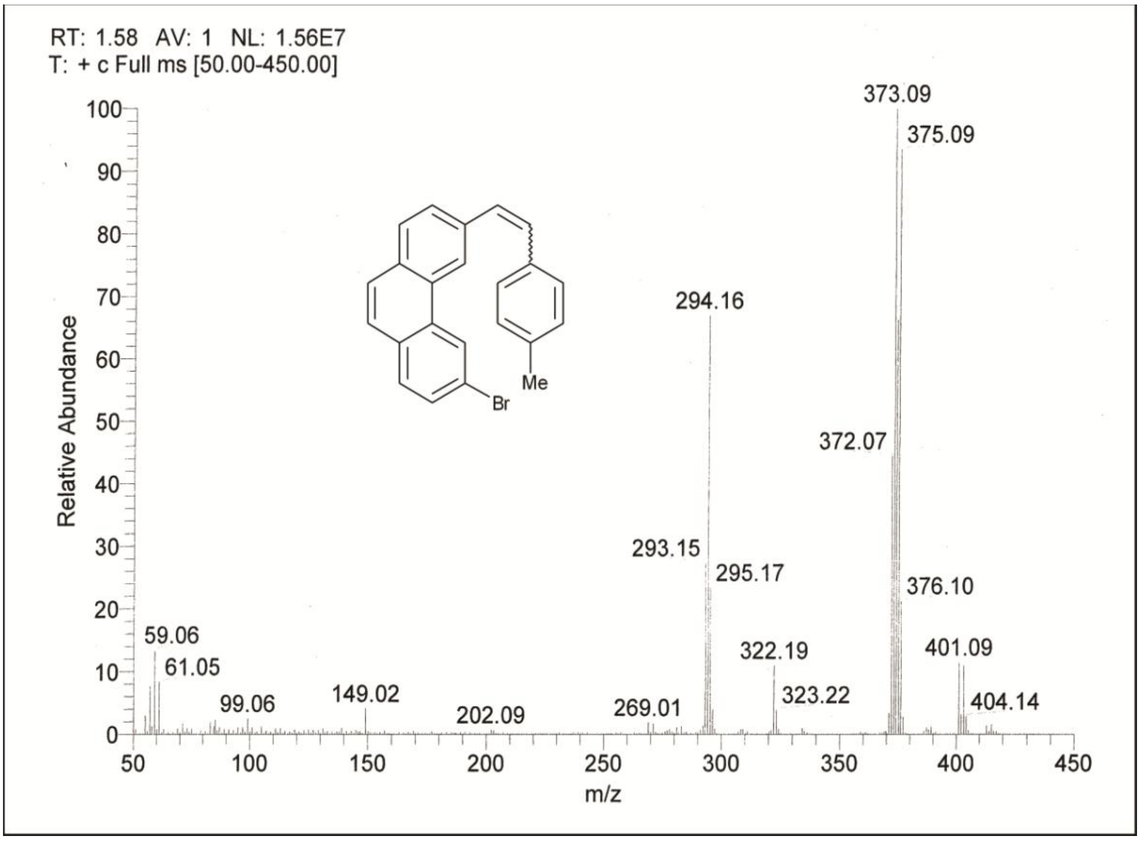


**EI-Mass spectrum of 7,8-dimethylbenzo[*ghi*]perylene(141)**

## Spectral data of 3-bromo-6-(4-methylstyryl)phenanthrene (142)

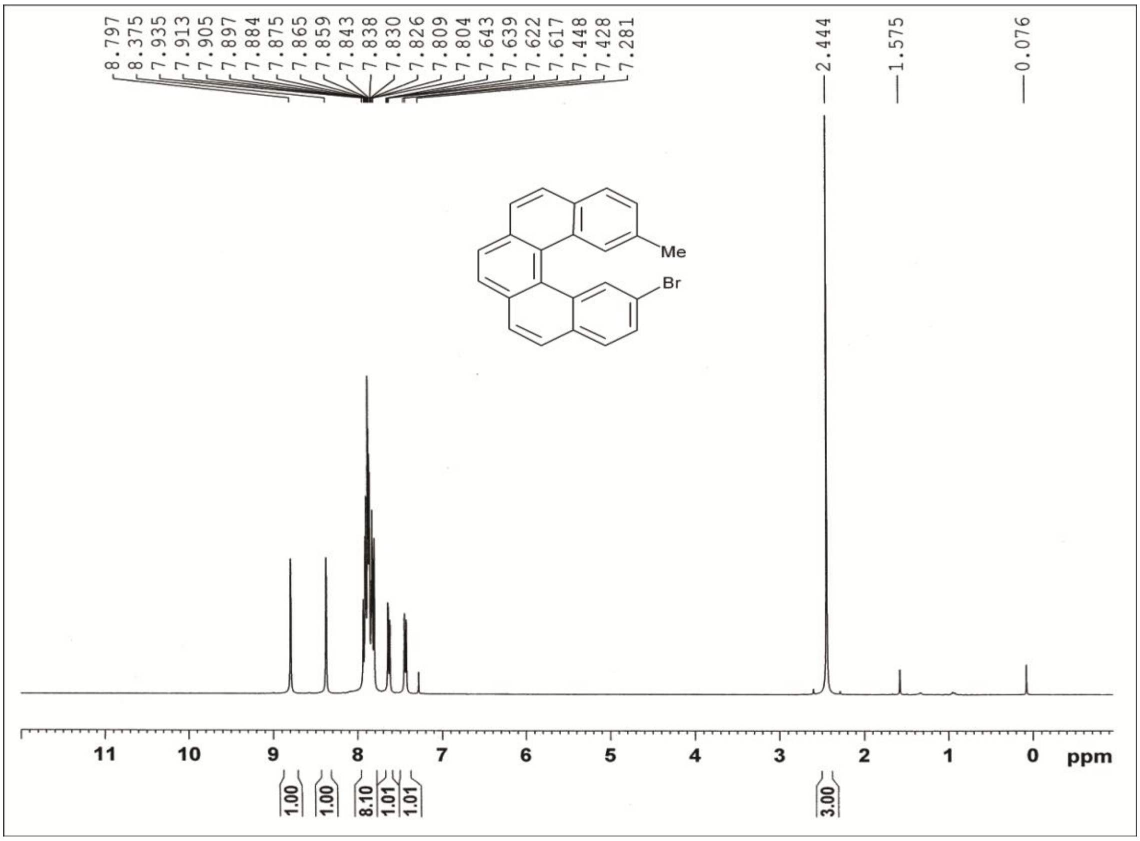


**$^1$H-NMR spectrum of 3-bromo-6-(4-methylstyryl)phenanthrene (142) in $CDCl_3$ on 400 MHz**

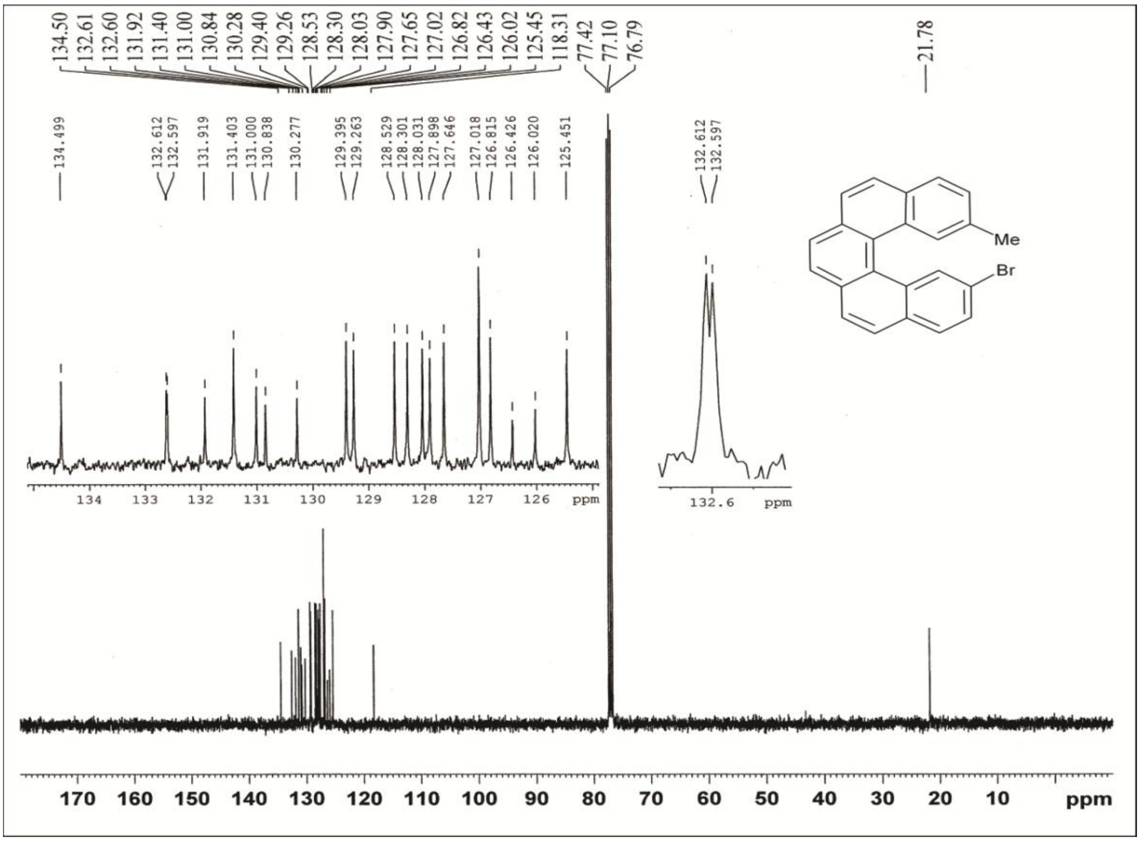


**EI-Mass spectrum of 3-bromo-6-(4-methylstyryl)phenanthrene (142)**

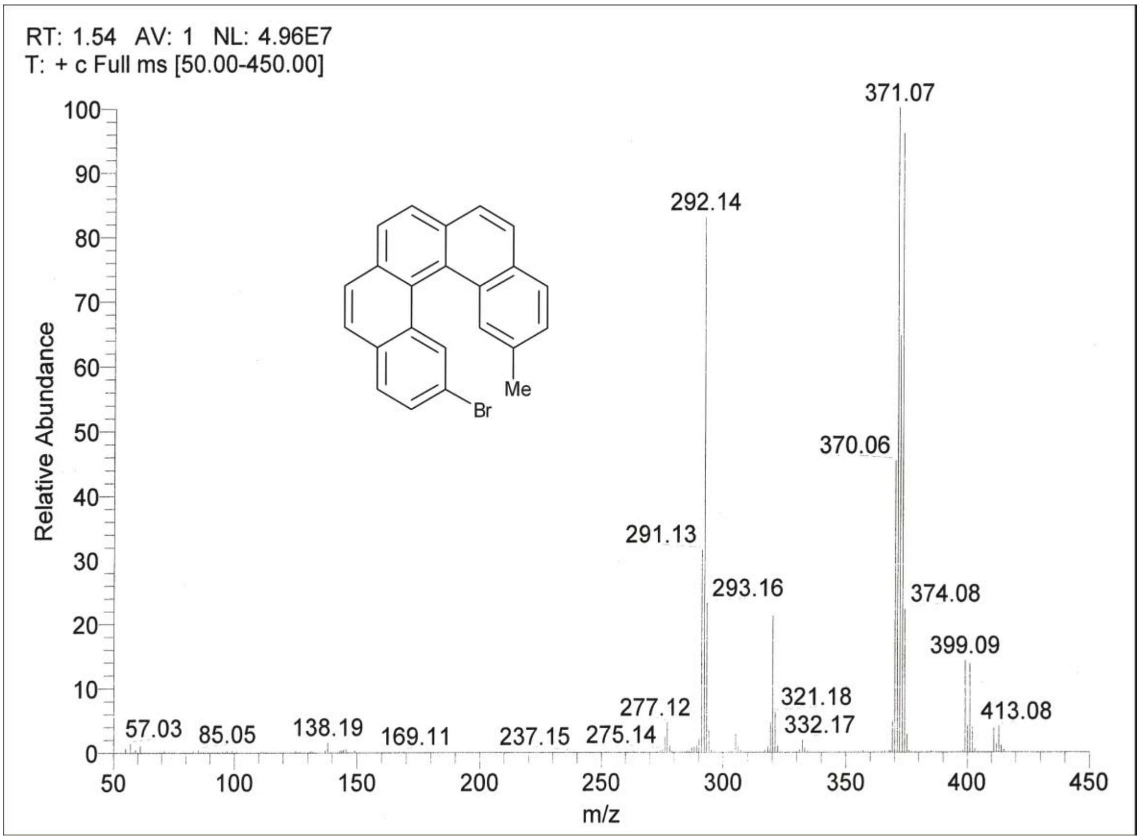
## Spectral data of 2-bromo-13-methyl[5]helicene (143)



**$^1$H-NMR spectrum of 2-bromo-13-methyl[5]helicene (143) in $CDCl_3$ on 400 MHz**

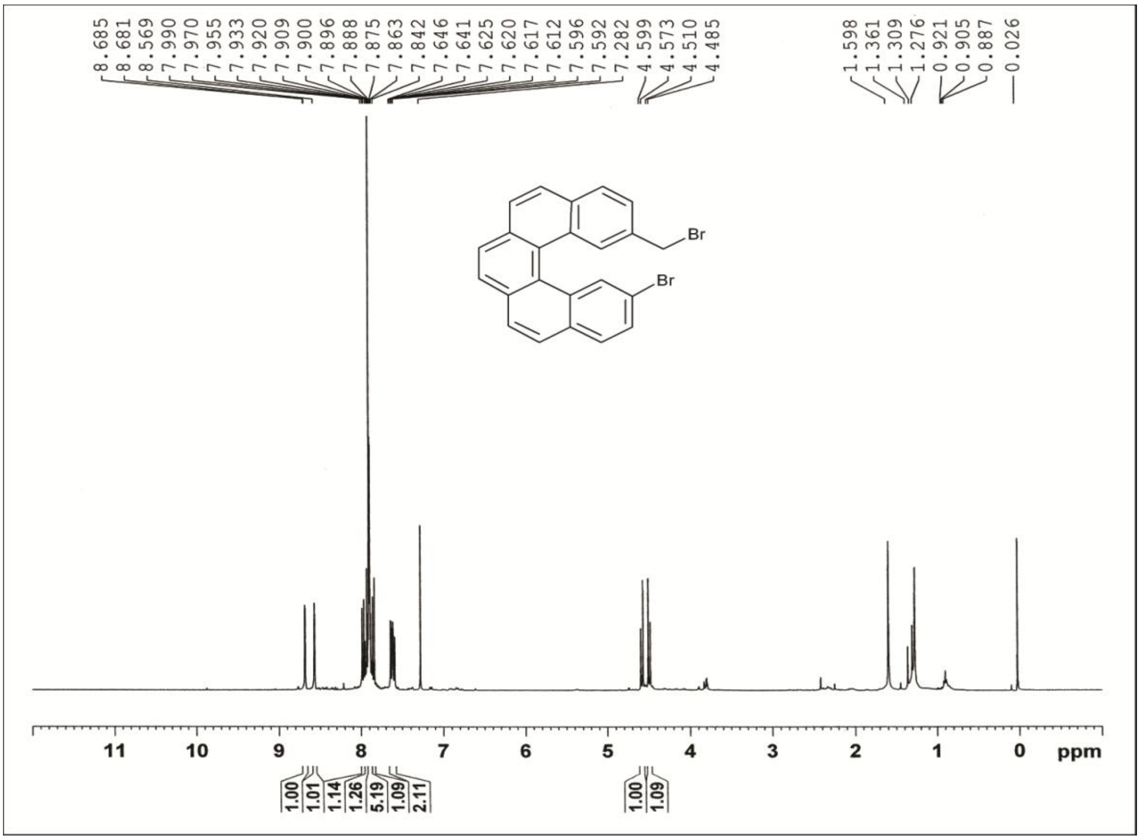


**$^{13}$C-NMR spectrum of 2-bromo-13-methyl[5]helicene (143) in $CDCl_3$ on 100.6 MHz**

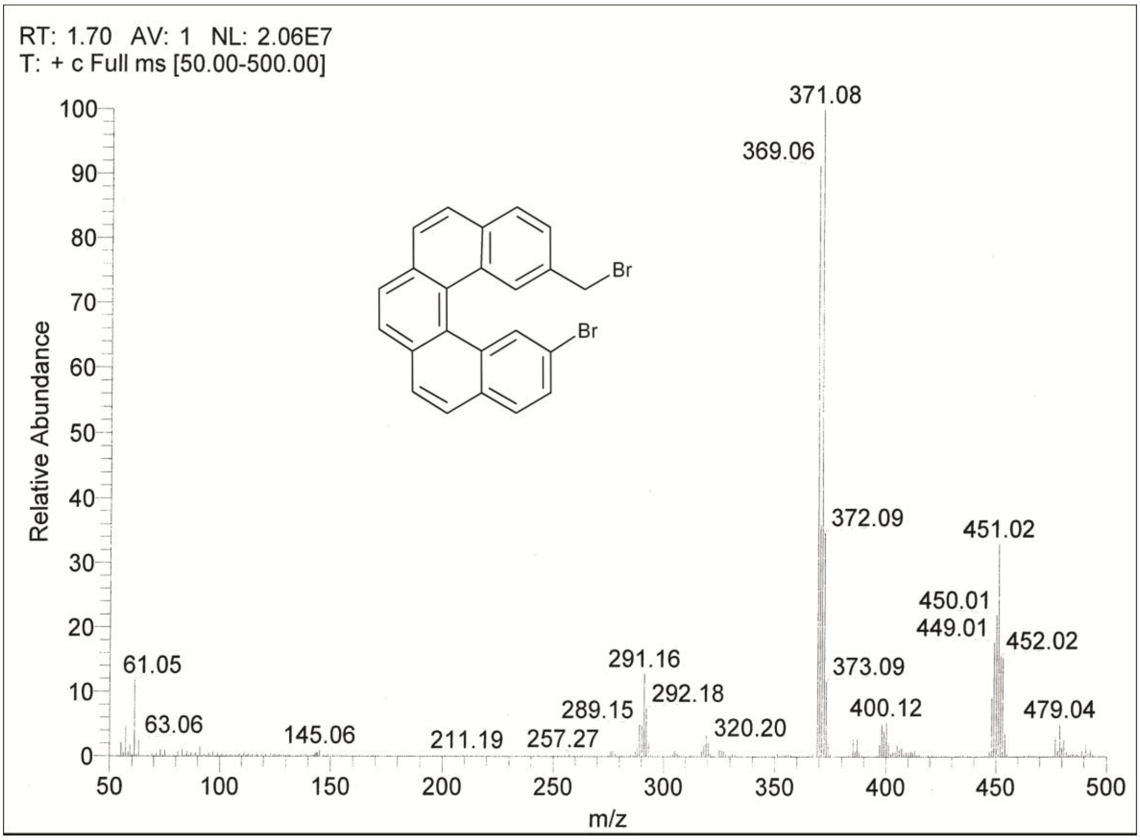


**EI-Mass spectrum of 2-bromo-13-methyl[5]helicene (143)**

## Spectral data of 2-bromo-13-(bromomethyl)[5]helicene (144)

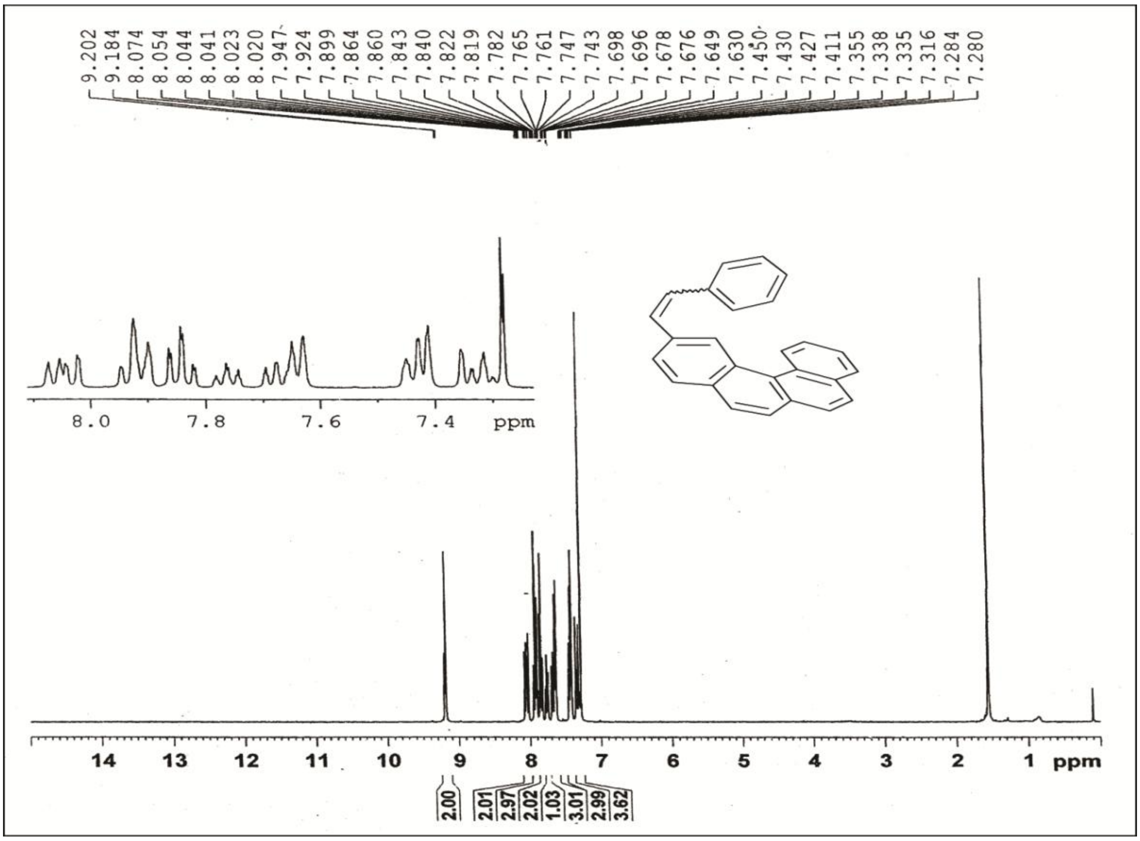


**$^1$H-NMR spectrum of 2-bromo-13-(bromomethyl)[5]helicene in $CDCl_3$ on 400 MHz**

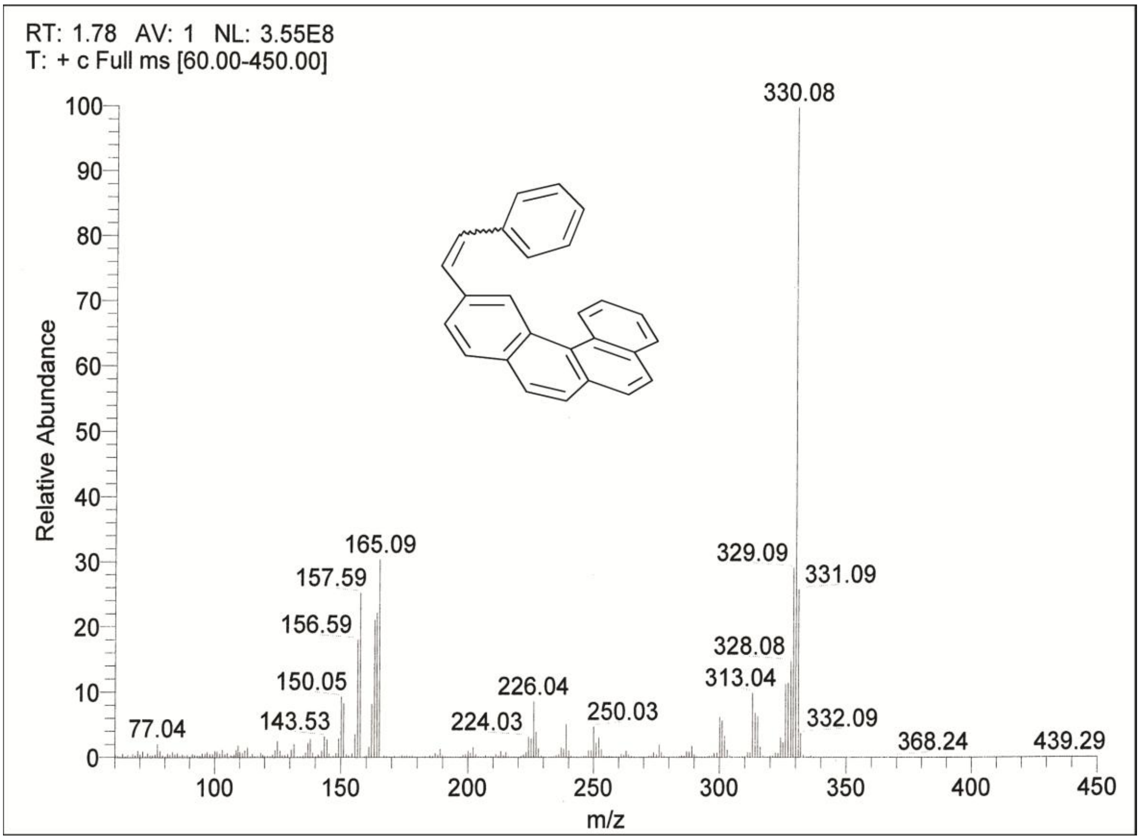


**EI-Mass spectrum of 2-bromo-13-(bromomethyl)[5]helicene (144)**

**Spectral data of 2-styrylbenzo[*c*]phenanthrene (145)**

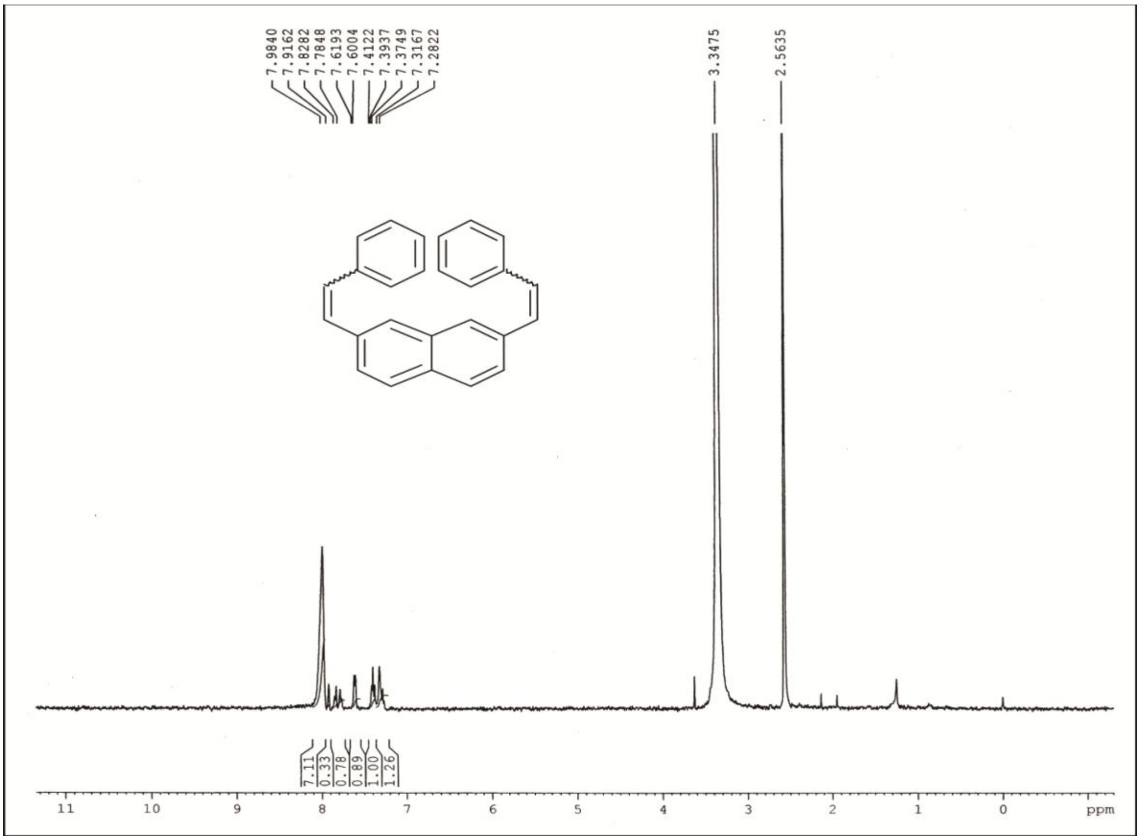


**$^1$H-NMR of 2-styrylbenzo[*c*]phenanthrene (145) in $CDCl_3$ on 400 MHz**

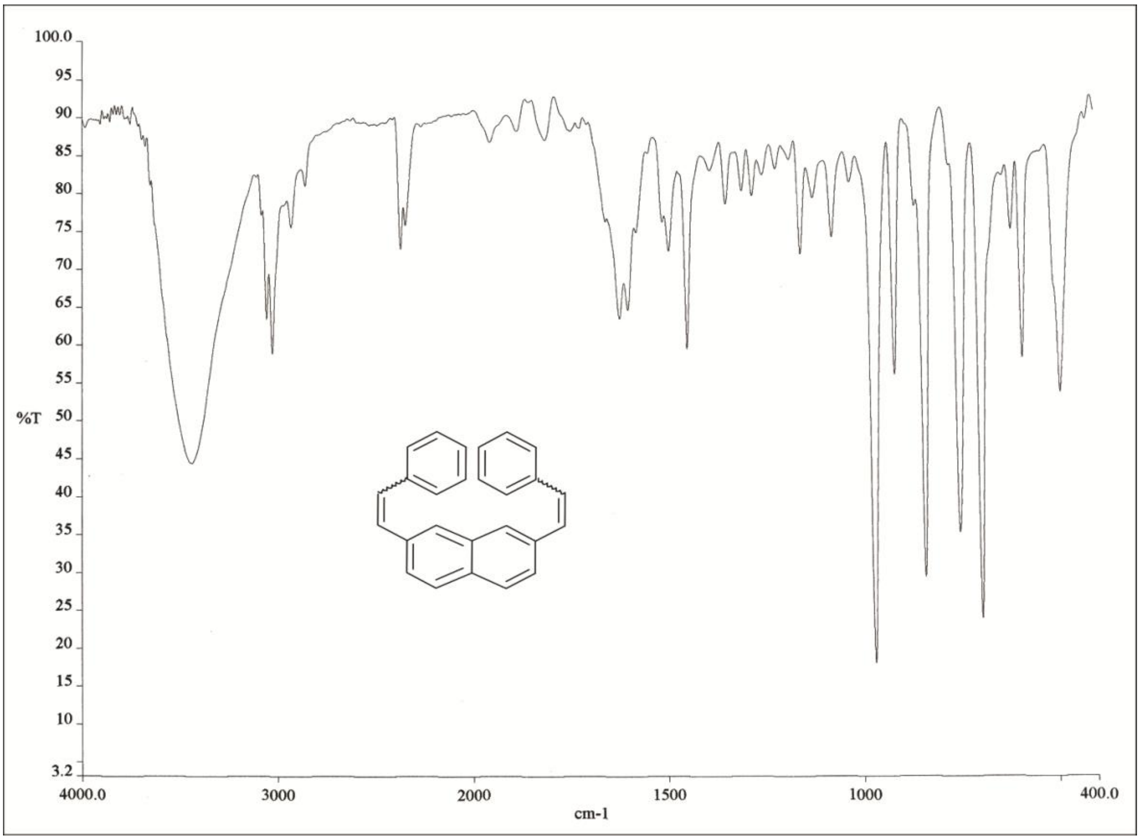


**EI-Mass spectrum of 2-styrylbenzo[*c*]phenanthrene (145)**

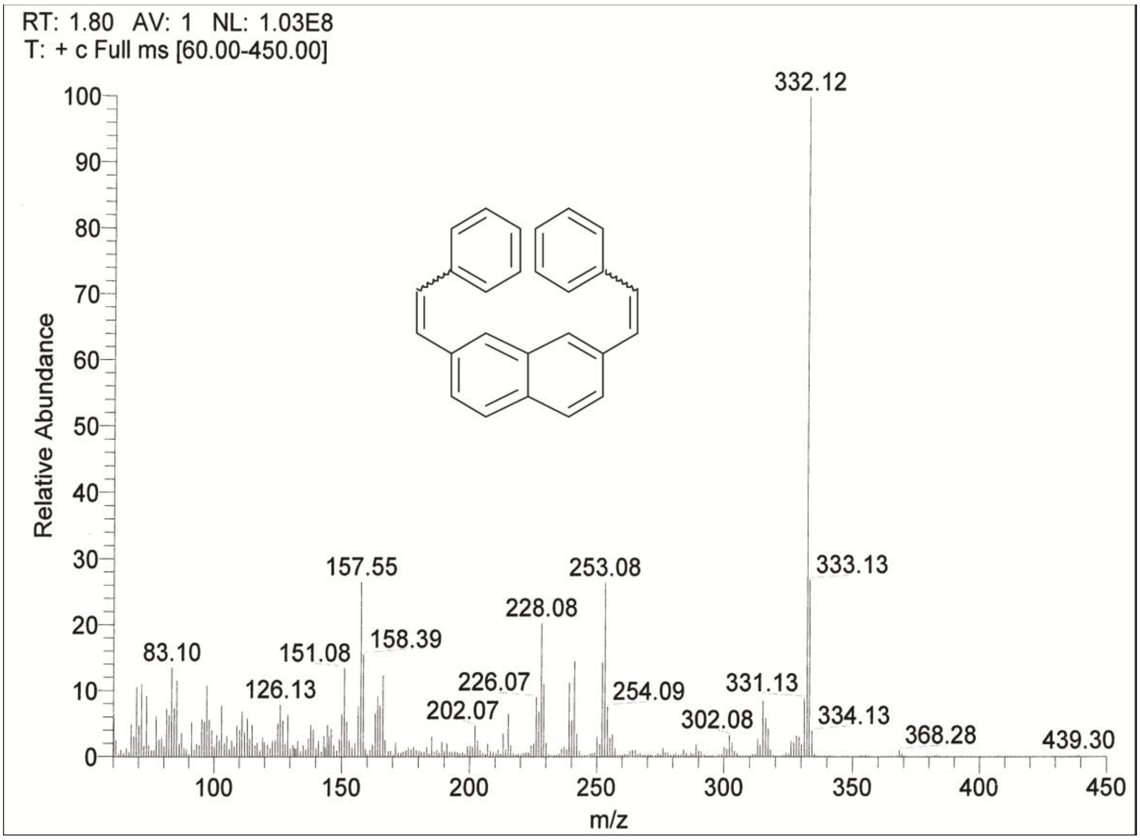
## Spectral data of 2,7-distyrylnaphthalene (151)



**$^1$H-NMR spectrum of 2,7-distyrylnaphthalene (151) in DMSO-*d*$^6$ on 400 MHz**

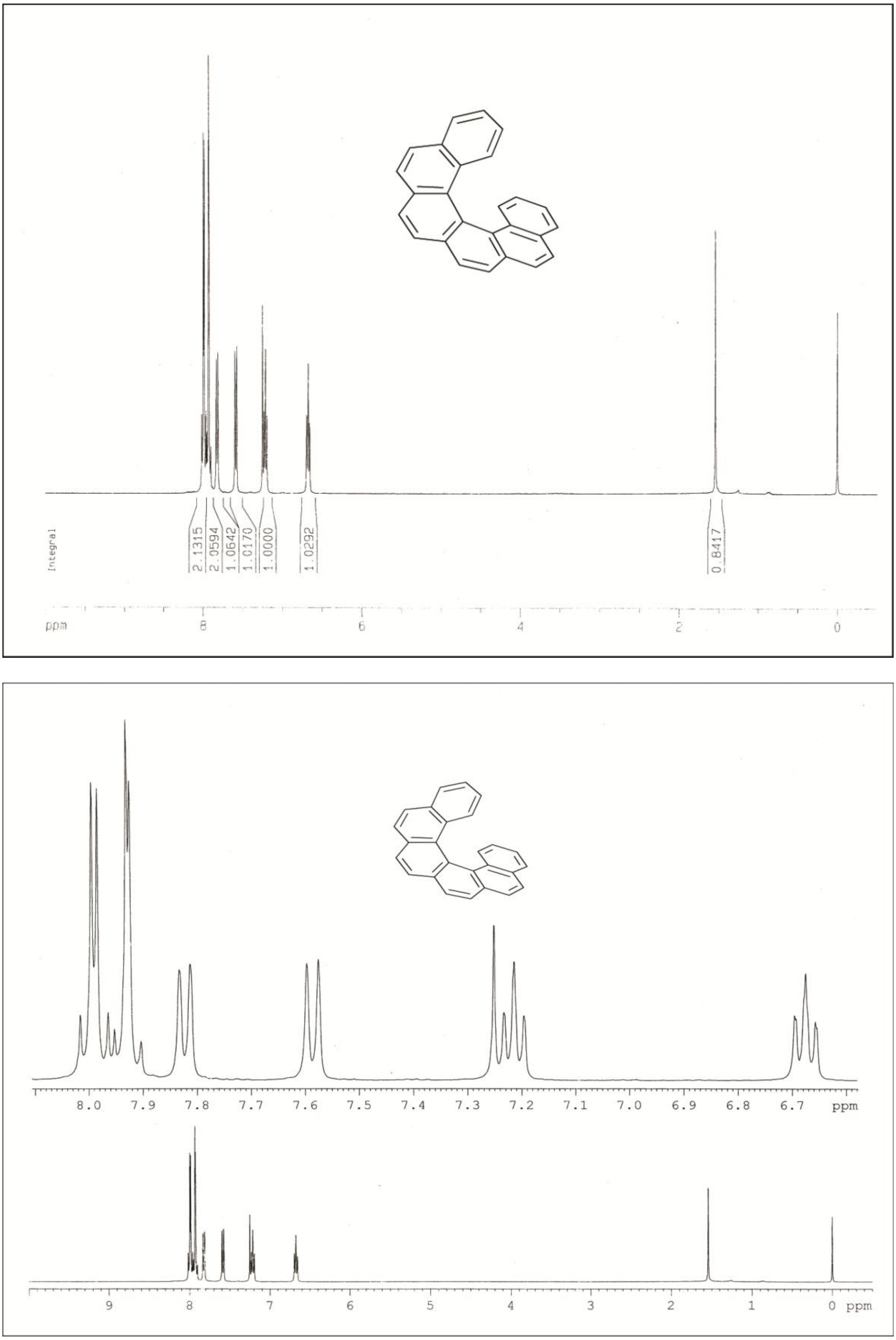


**IR spectrum of 2,7-distyrylnaphthalene (151)**

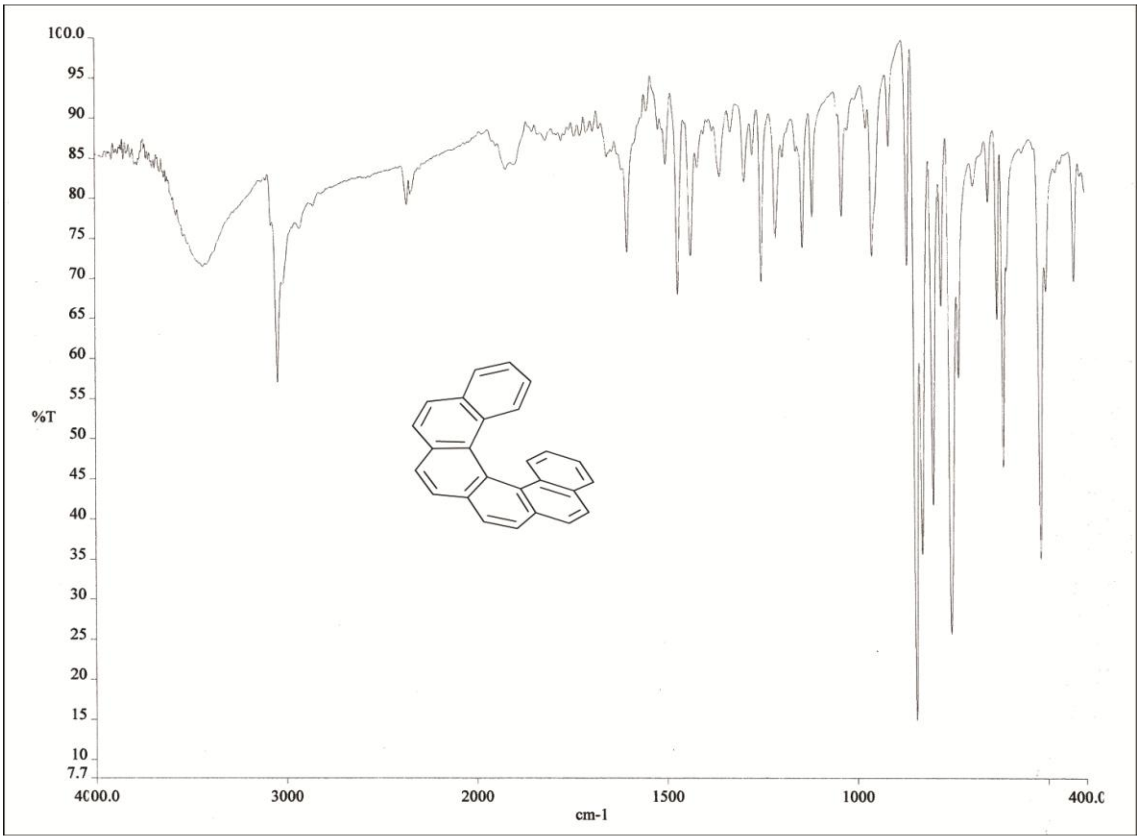


**EI-Mass spectrum of 2,7-distyrylnaphthalene (151)**

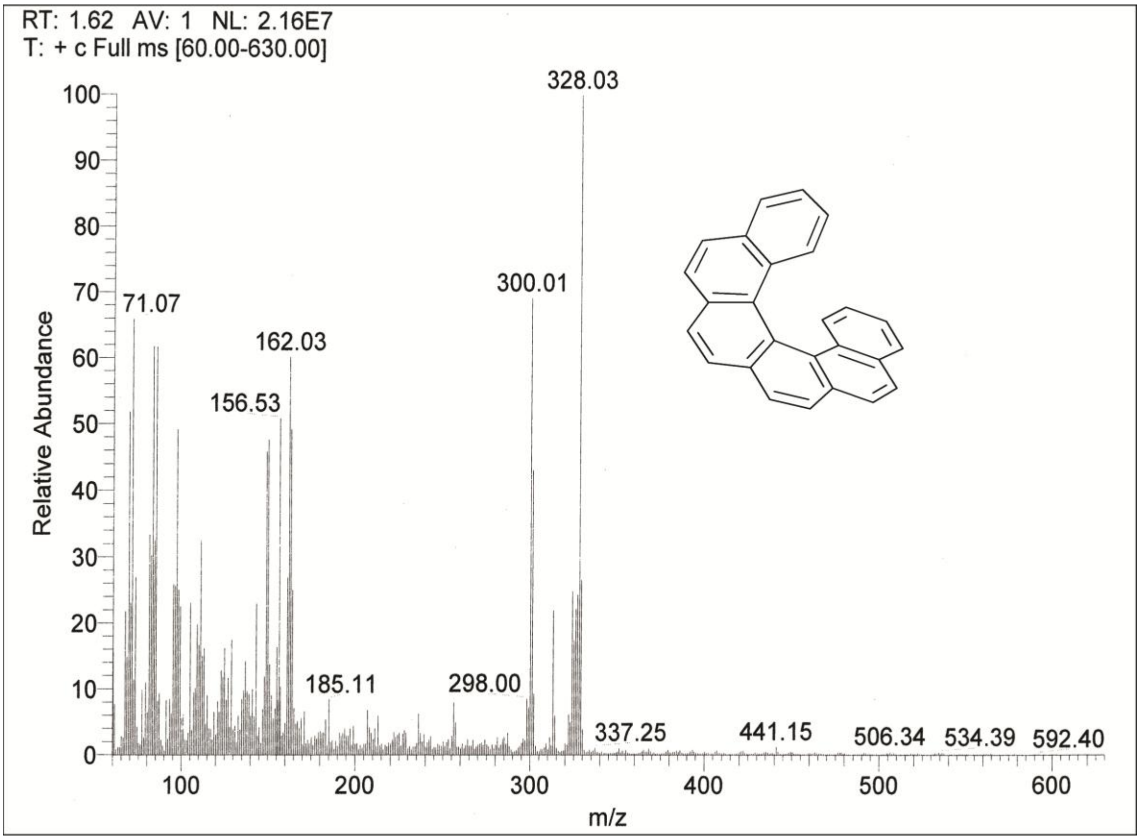
## Spectral data of [6]helicene (96)



**$^1$H-NMR with enlarge spectrum of [6]helicene (96) in $CDCl_3$ on 400 MHz**

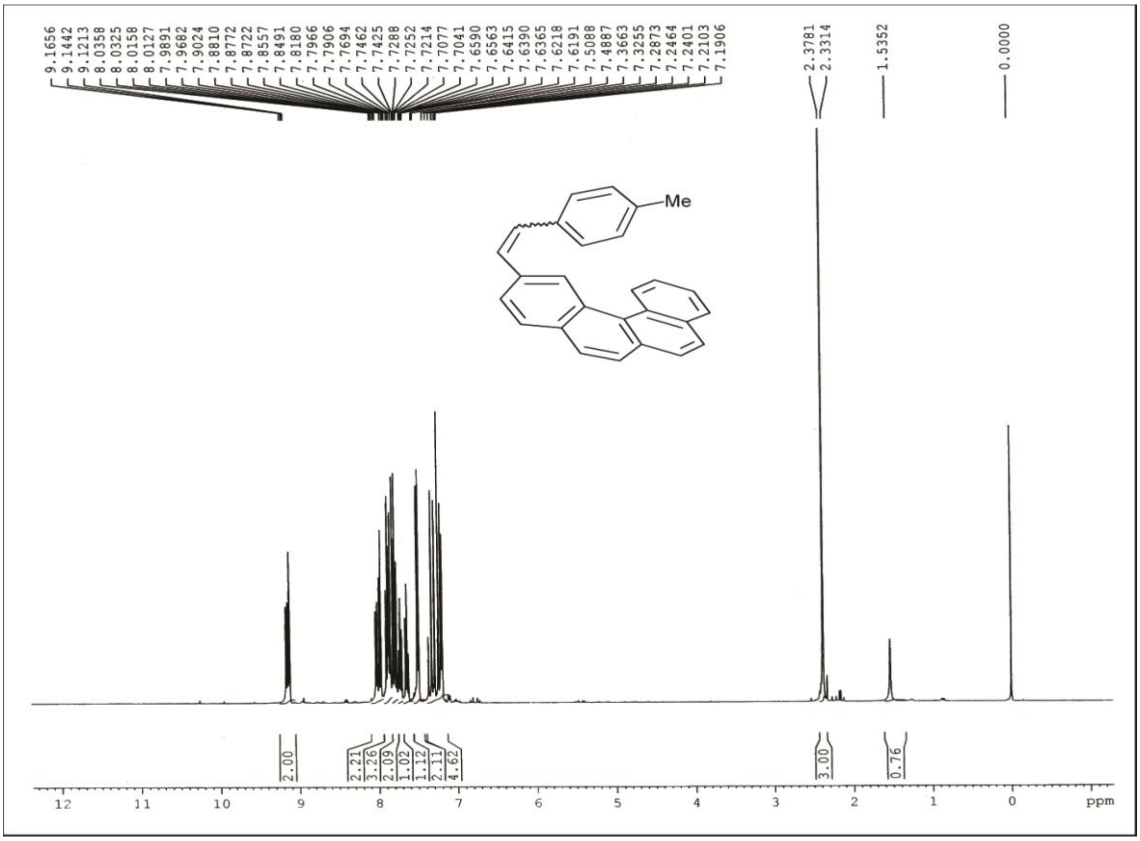


IR spectrum of [6]helicene (96)

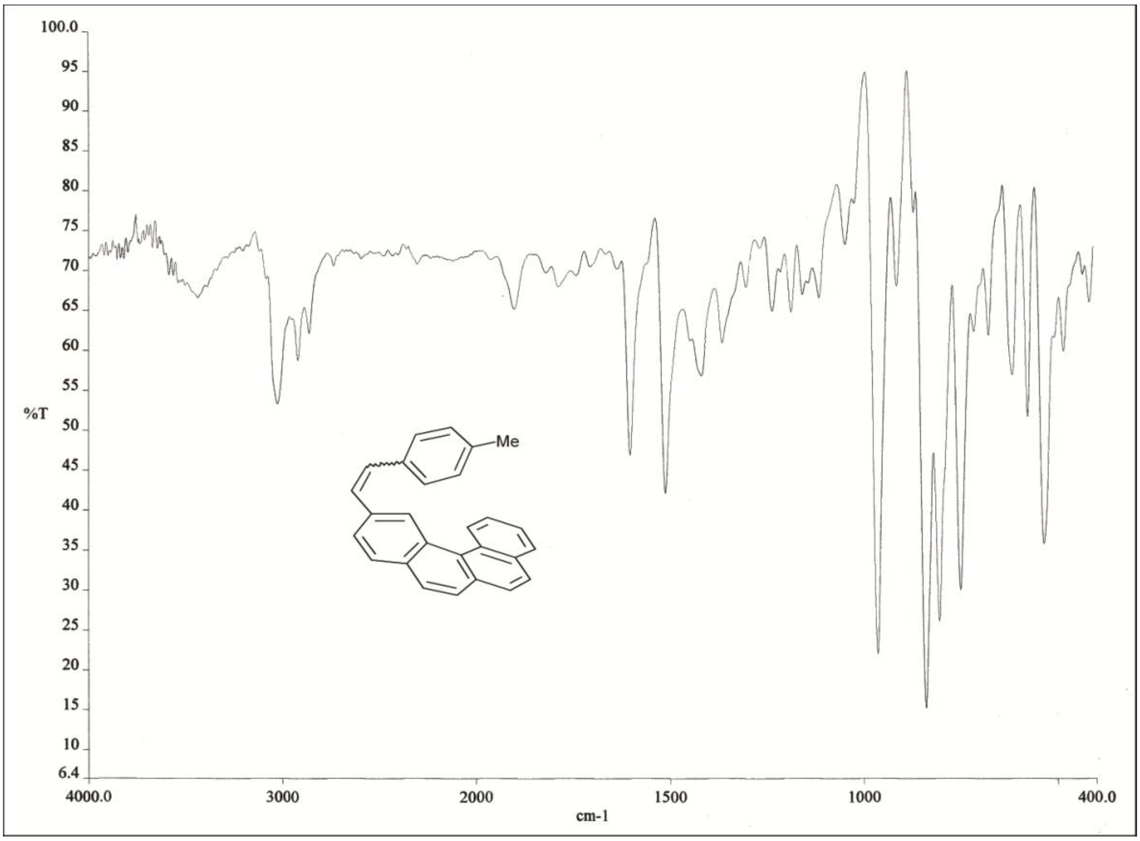


EI- Mass spectrum of [6]helicene (96)

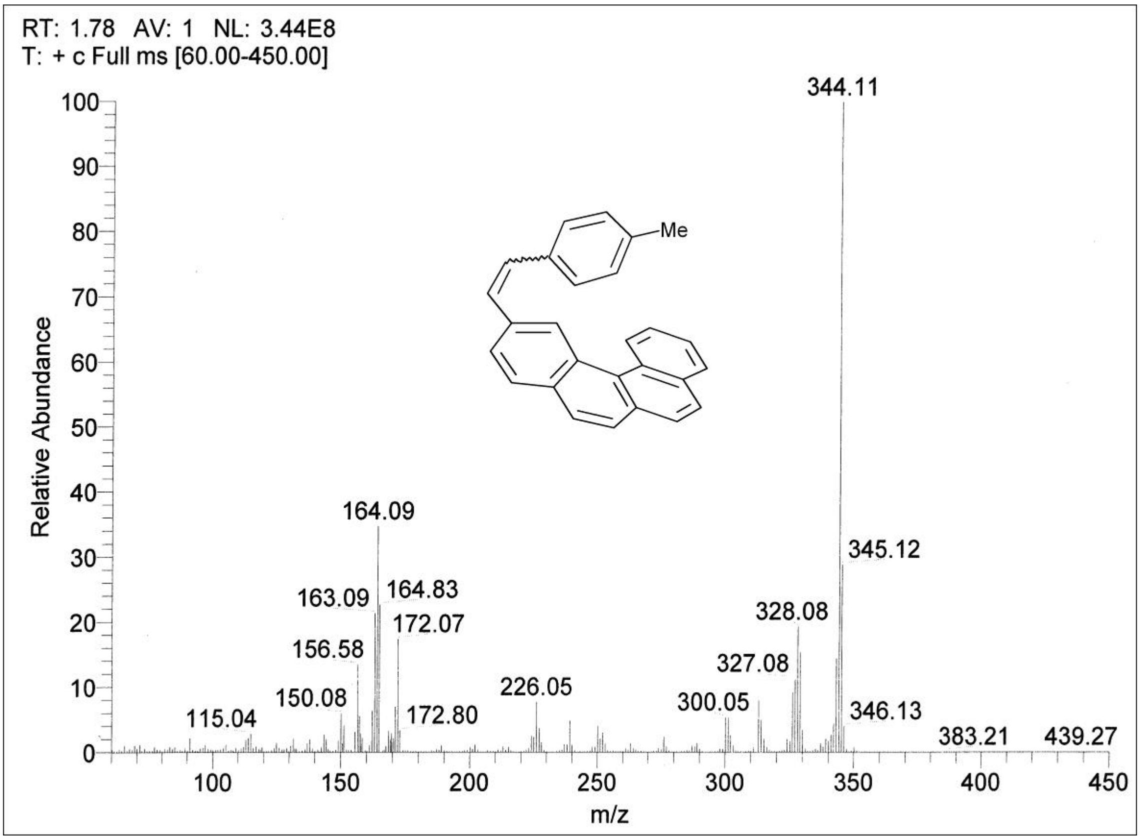
## Spectral data of 2-[2-(4-methylphenyl)ethenyl]benzo[*c*]phenanthrene (146)



**$^1$H-NMR spectrum of 2-[2-(4-methylphenyl)ethenyl]benzo[*c*]phenanthrene (146) in $CDCl_3$ on 400 MHz**

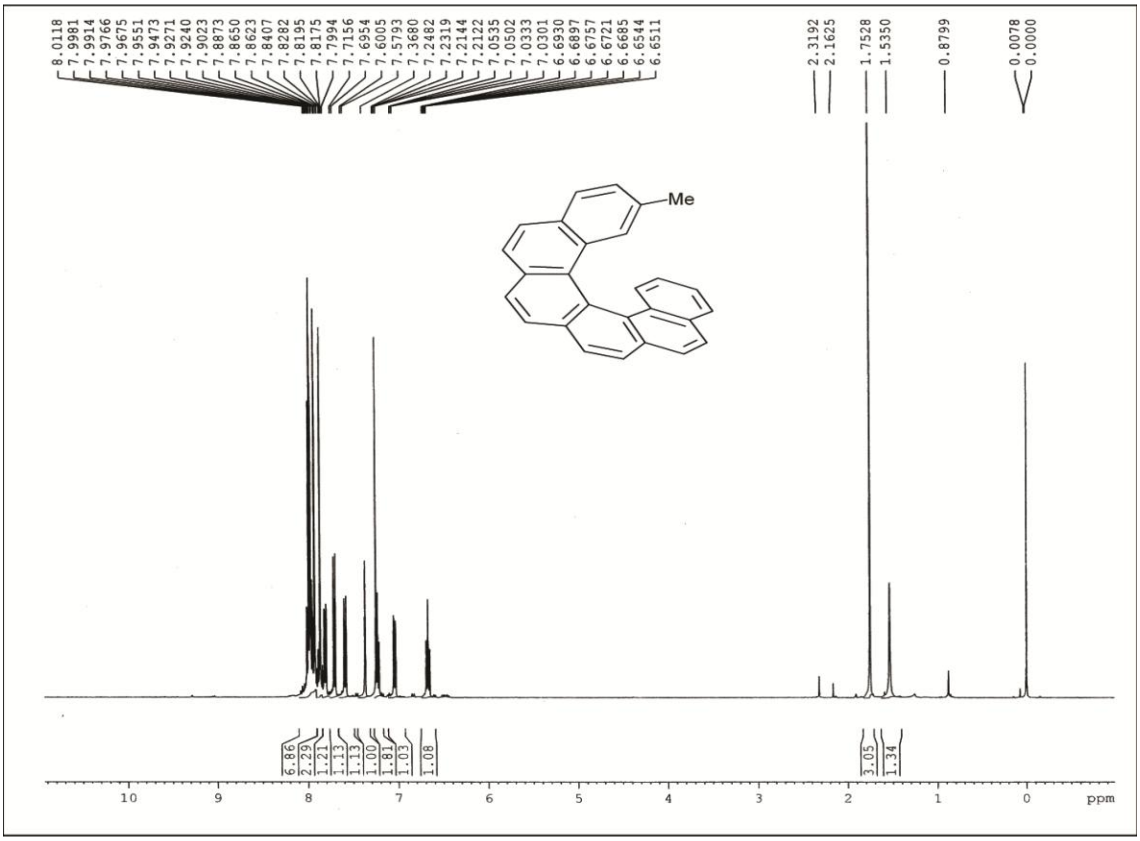


**IR spectrum of 2-[2-(4-methylphenyl)ethenyl]benzo[*c*]phenanthrene (146)**

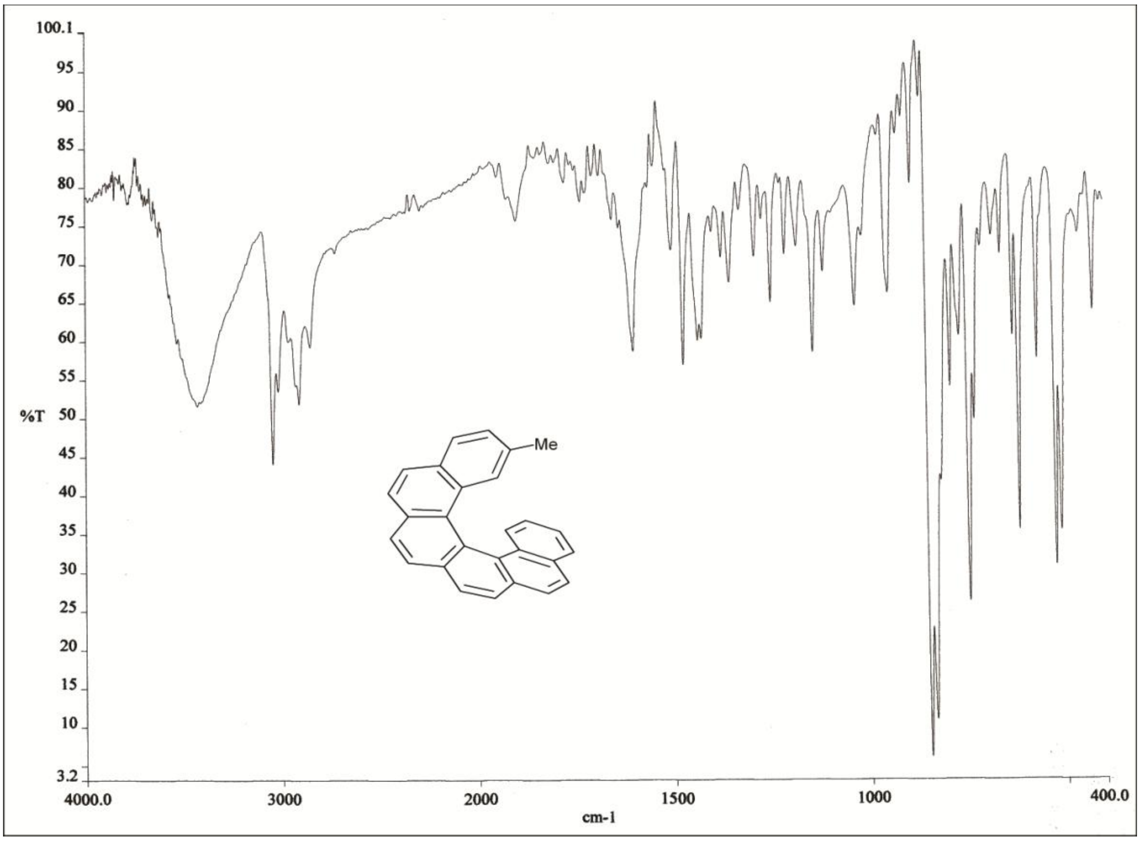


**EI-Mass spectrum of 2-[2-(4-methylphenyl)ethenyl]benzo[*c*]phenanthrene (146)**

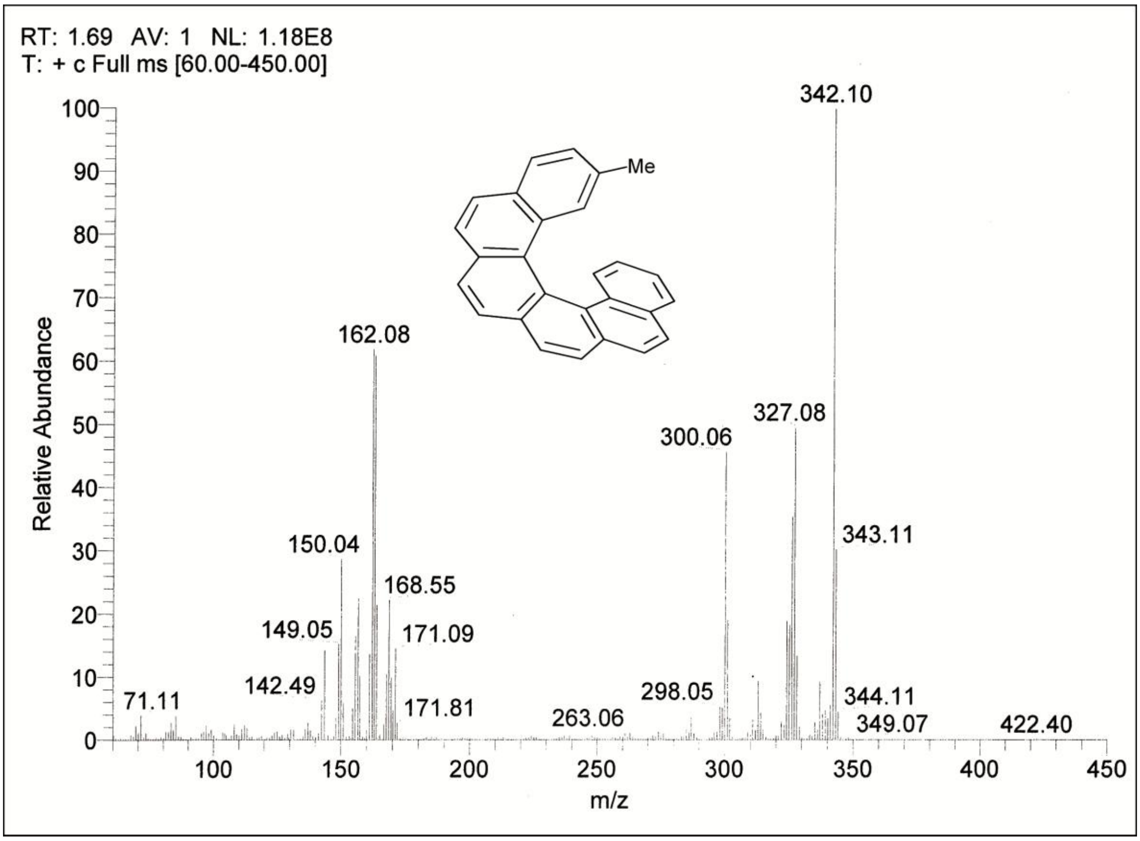
## Spectral data of 2-methyl[6]helicene (147)



**$^1$H-NMR spectrum of 2-methyl[6]helicene (147) in $CDCl_3$ on 400 MHz**

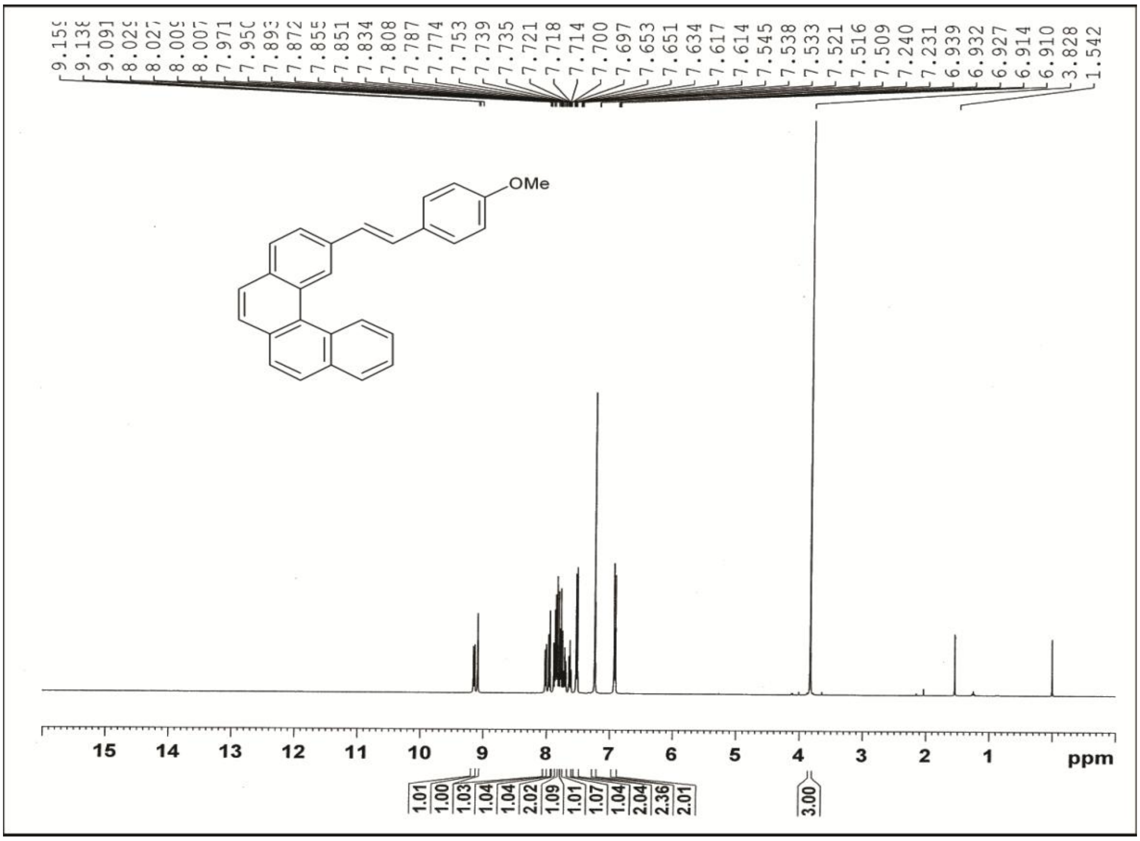


**IR spectrum of 2-methyl[6]helicene (147)**

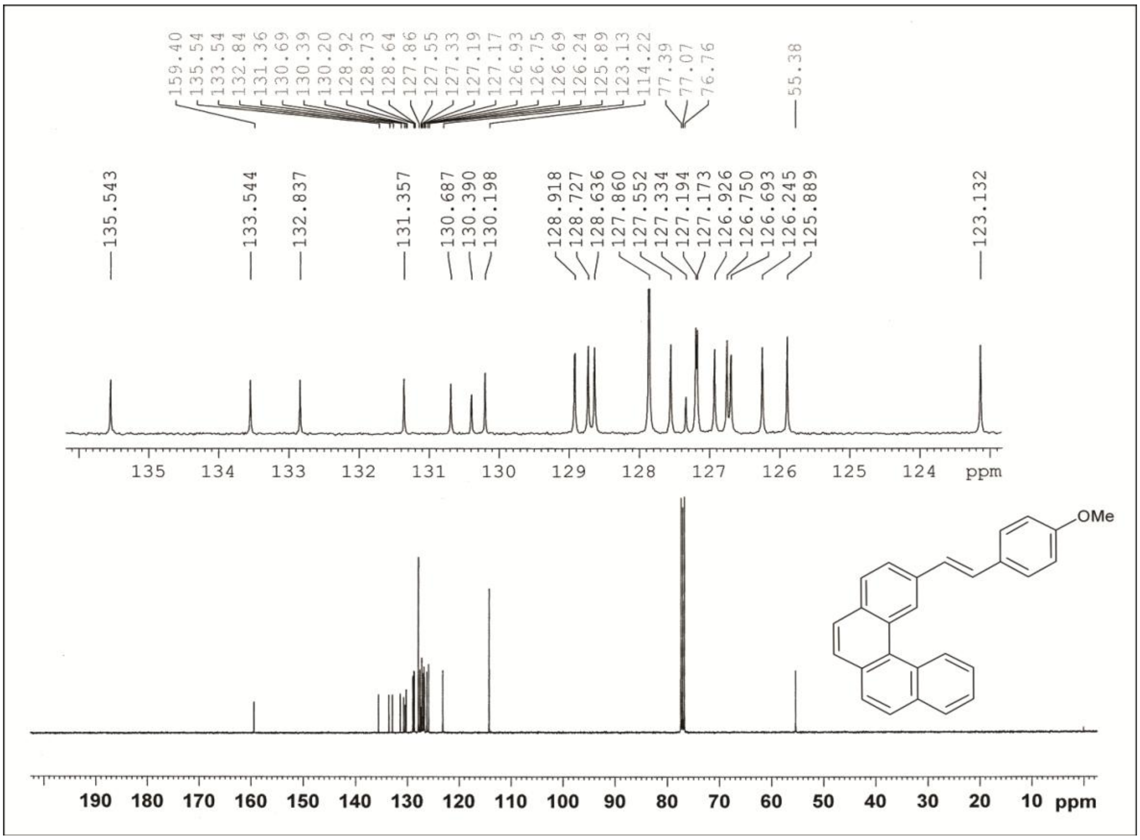


**EI-Mass spectrum of 2-methyl[6]helicene (147)**

## Spectral data of 2-[2-(4-methoxyphenyl)ethenyl]benzo[*c*]phenanthrene (148)

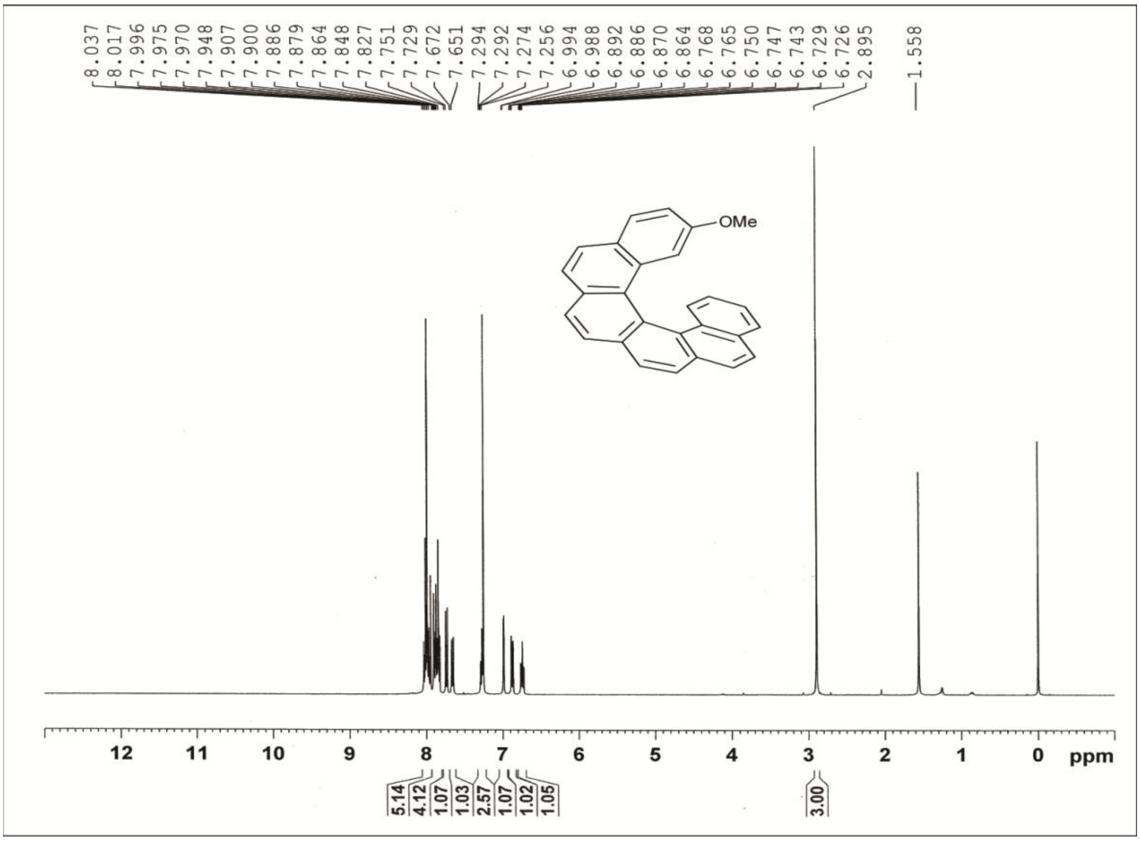


**$^{1}$H-NMR spectrum of 2-[2-(4-methoxyphenyl)ethenyl]benzo[*c*]phenanthrene (148) in $CDCl_3$ on 400 MHz**

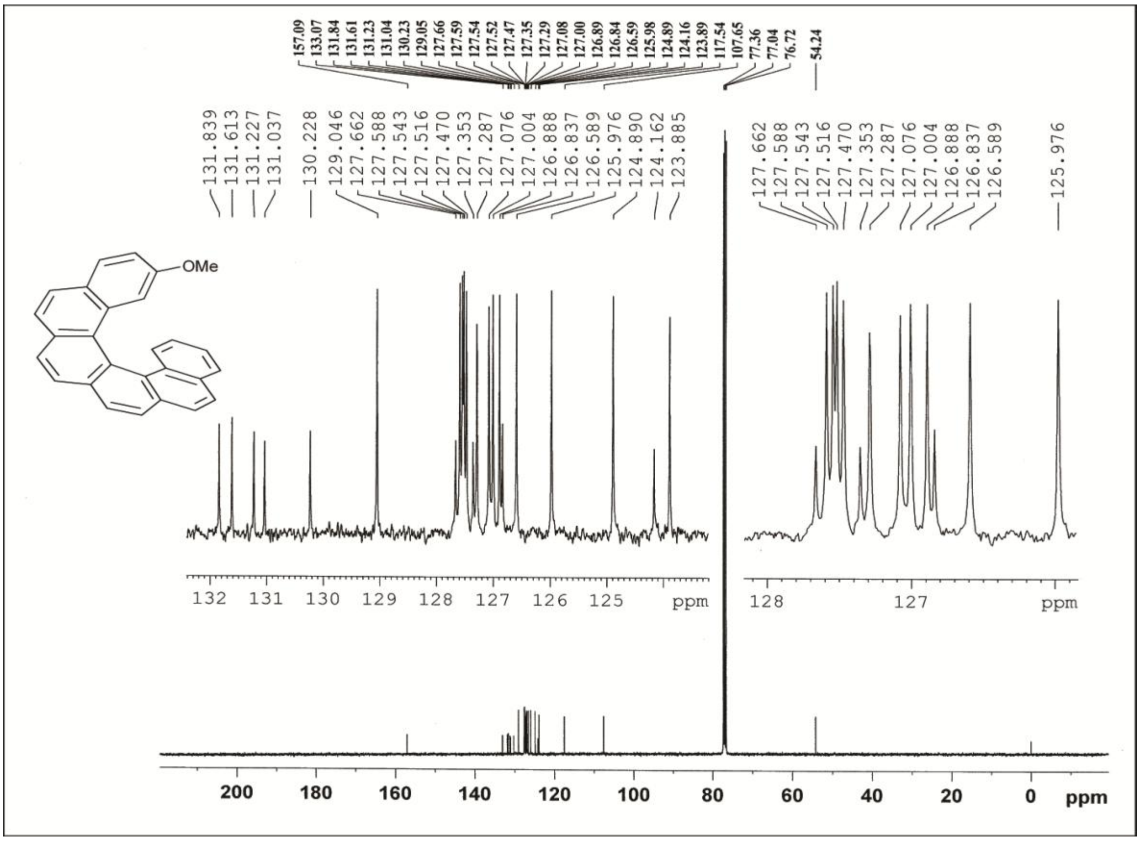


**$^{13}$C-NMR spectrum of 2-[2-(4-methoxyphenyl)ethenyl]benzo[*c*]phenanthrene (148) in $CDCl_3$ on 100.6 MHz**

## Spectral data of 2-methoxy[6]helicene (149)

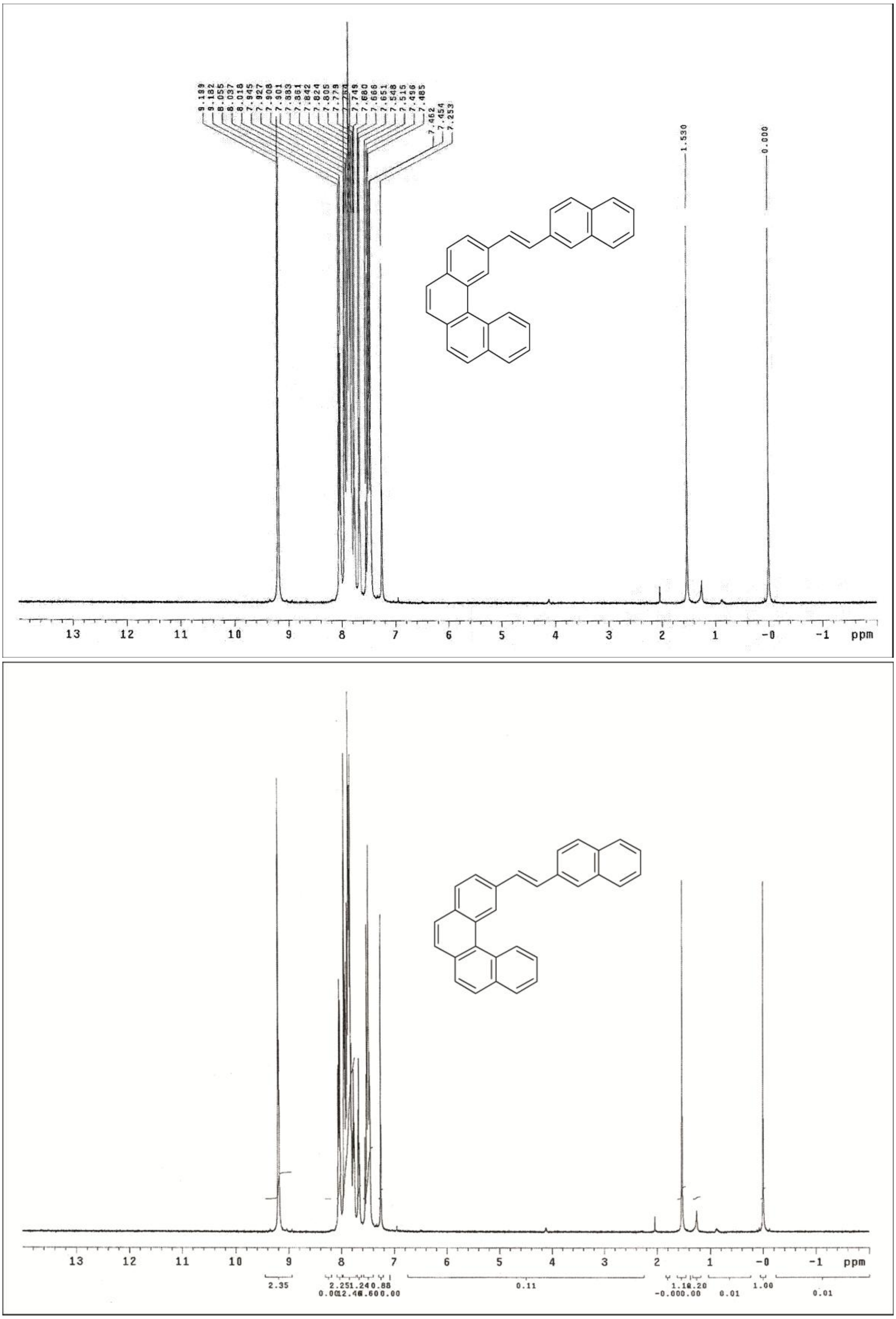


**$^1$H-NMR spectrum of 2-methoxy[6]helicene (149) in $CDCl_3$ on 400 MHz**

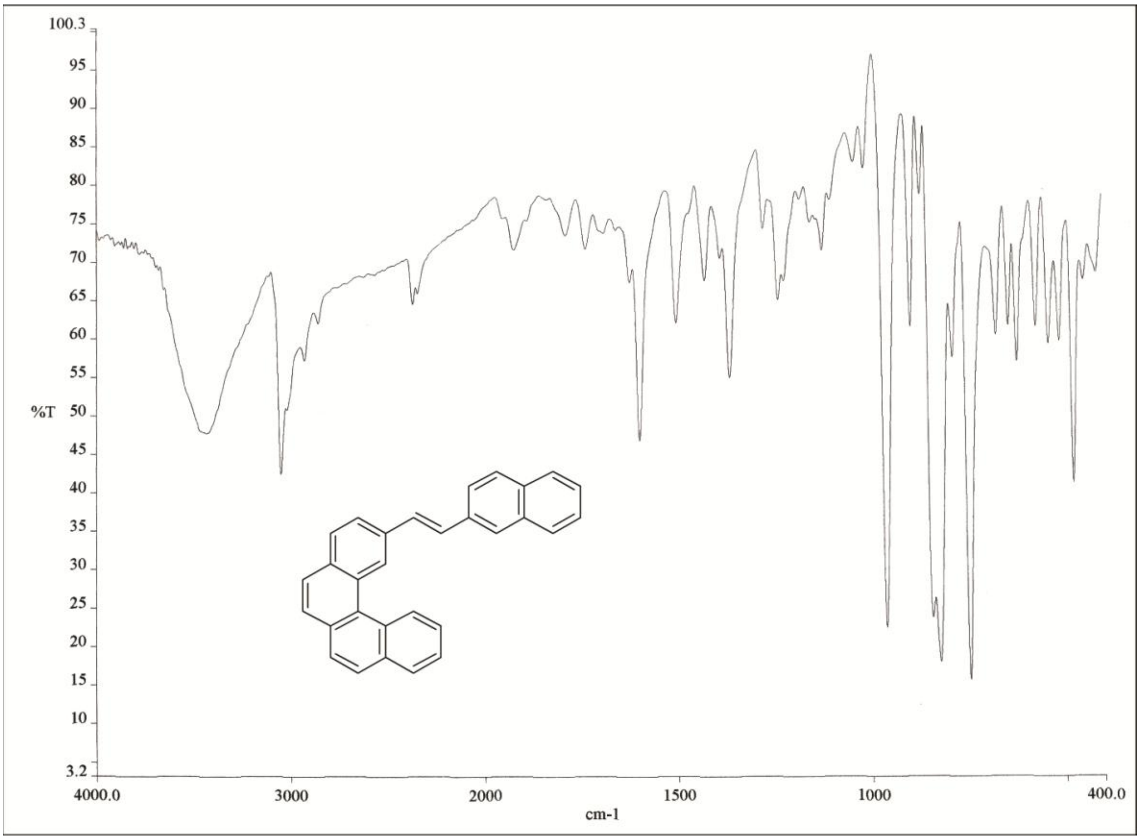


**$^{13}$C-NMR spectrum of 2-methoxy[6]helicene (149) in $CDCl_3$ on 100.6 MHz**

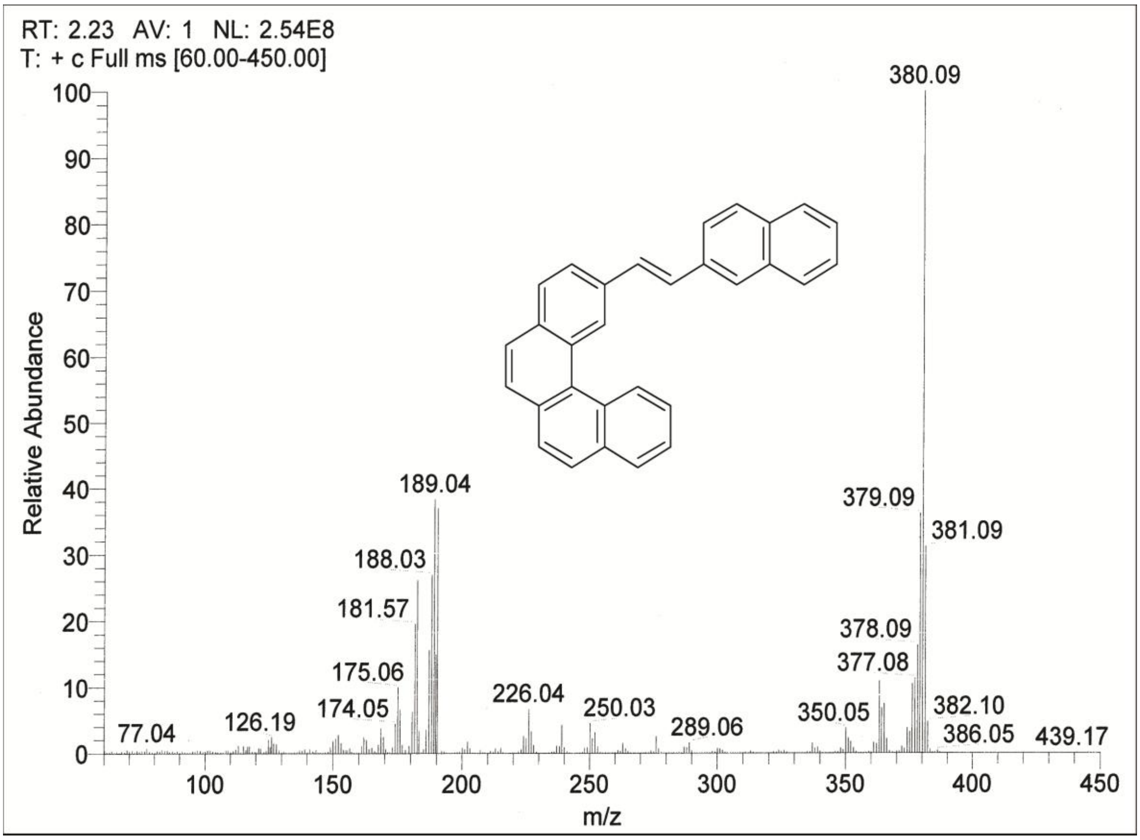
## Spectral data of 2-[2-(naphthyl)ethenyl]benzo[*c*]phenanthrene (154)



**$^{1}$H-NMR with enlarge spectrum of 2-[2-(naphthyl)ethenyl]benzo[*c*]phenanthrene (154) in $CDCl_3$ on 400 MHz**

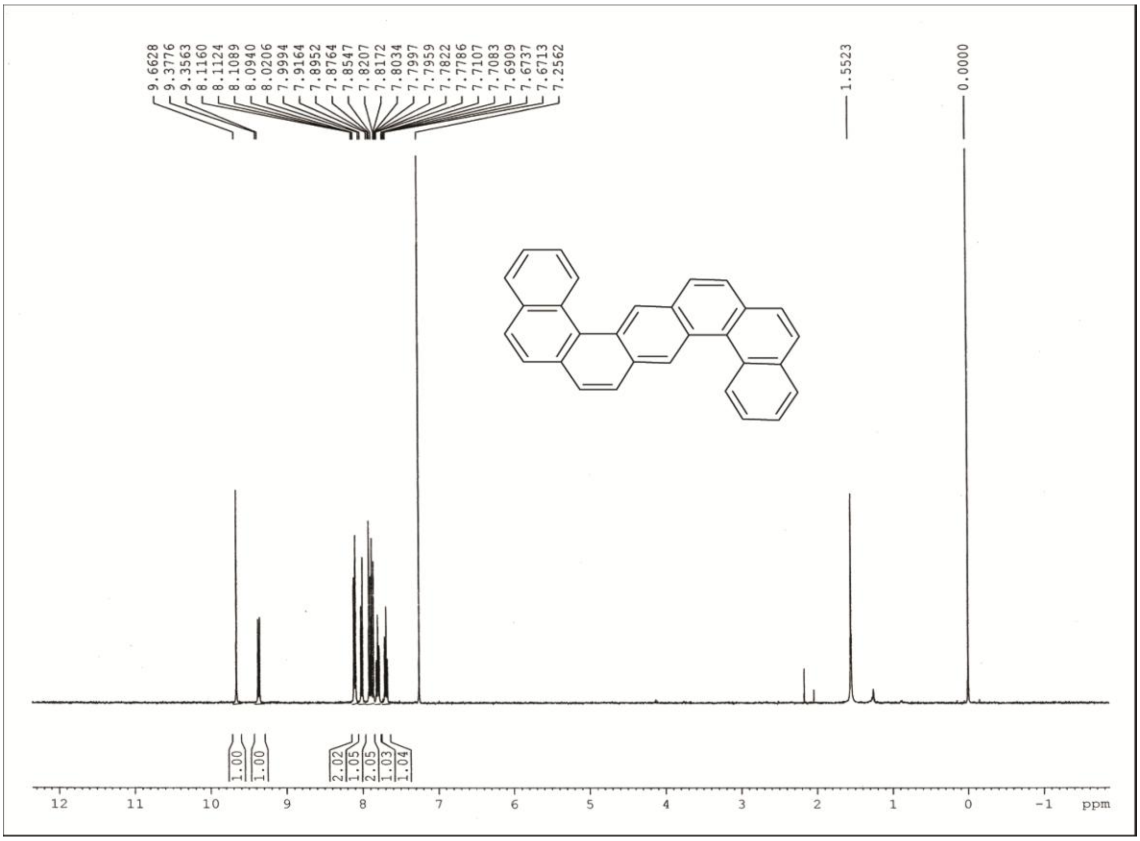


**IR spectrum of 2-[2-(naphthyl)ethenyl]benzo[*c*]phenanthrene (154)**

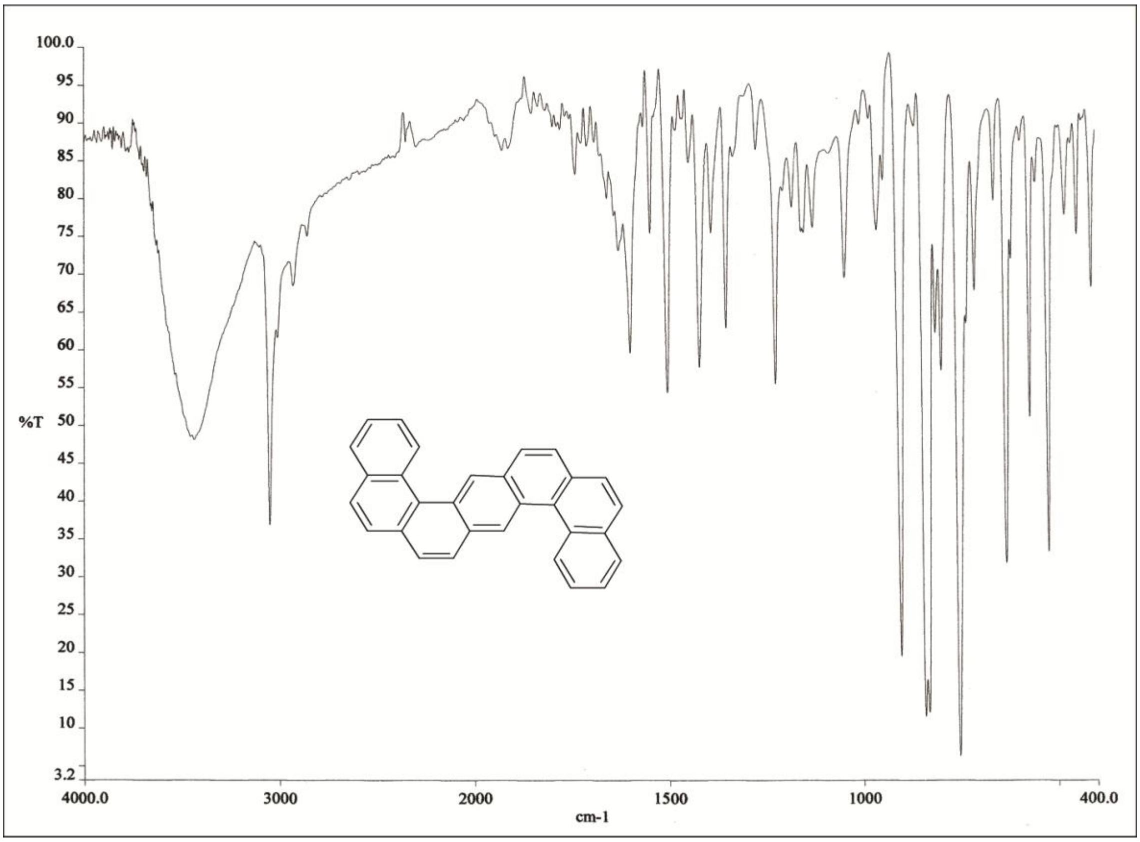


**EI-Mass spectrum of 2-[2-(naphthyl)ethenyl]benzo[*c*]phenanthrene (154)**

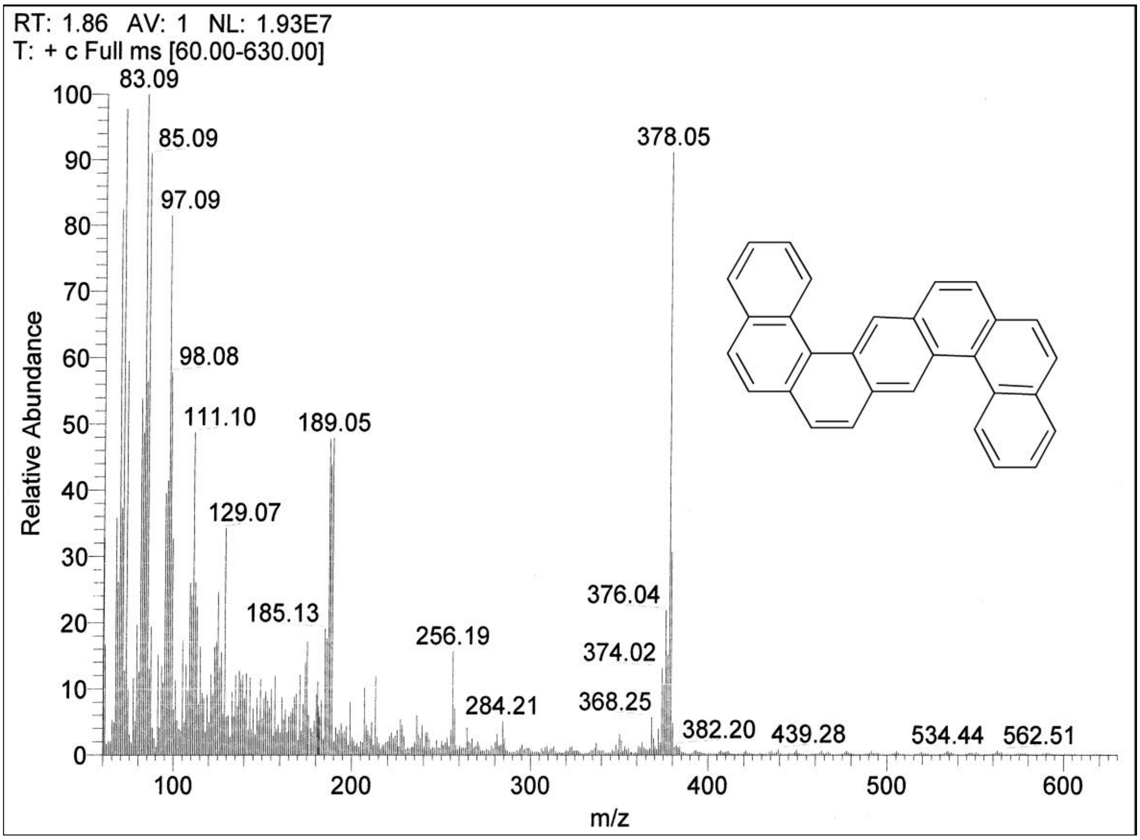
## Spectral data of dinaphtho[1,2-*a*:2’,1’-*h*]anthracene (37)



$^1$H-NMR spectrum of dinaphtho[1,2-*a*:2’,1’-*h*]anthracene (37) in $CDCl_3$ on 400 MHz

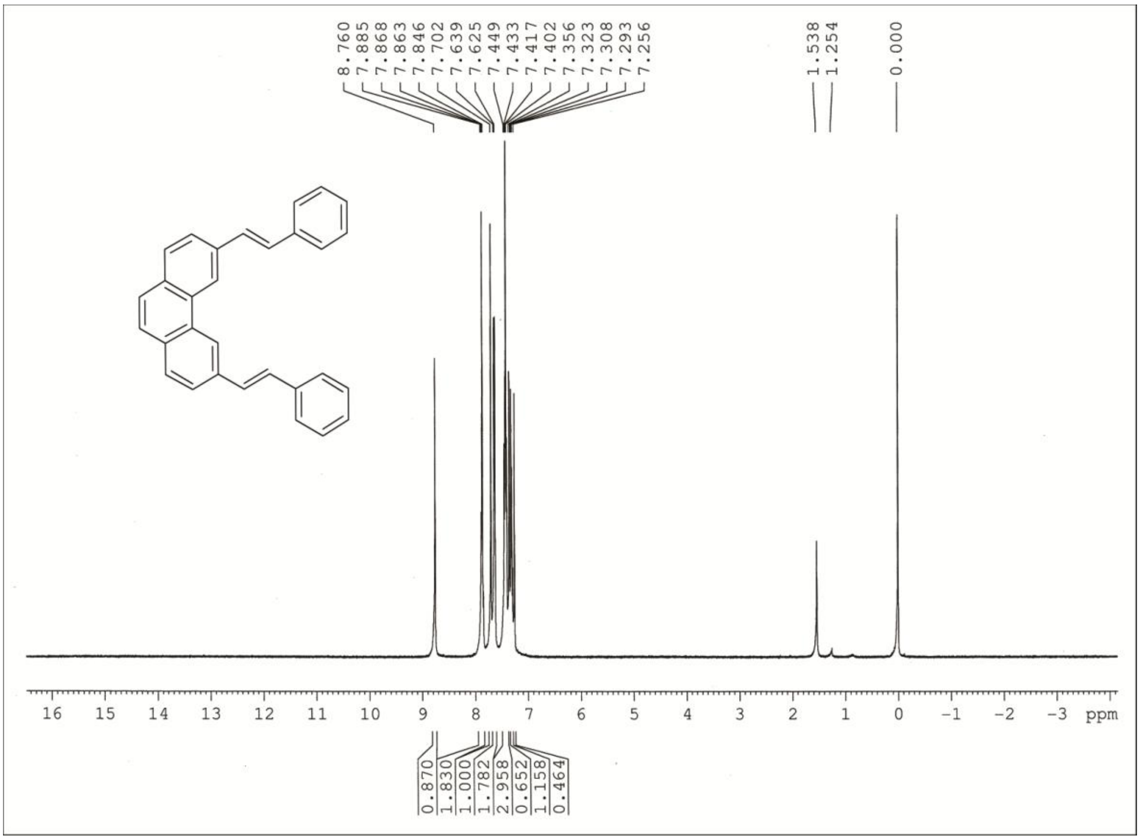


IR spectrum of dinaphtho[1,2-*a*:2’,1’-*h*]anthracene (37)

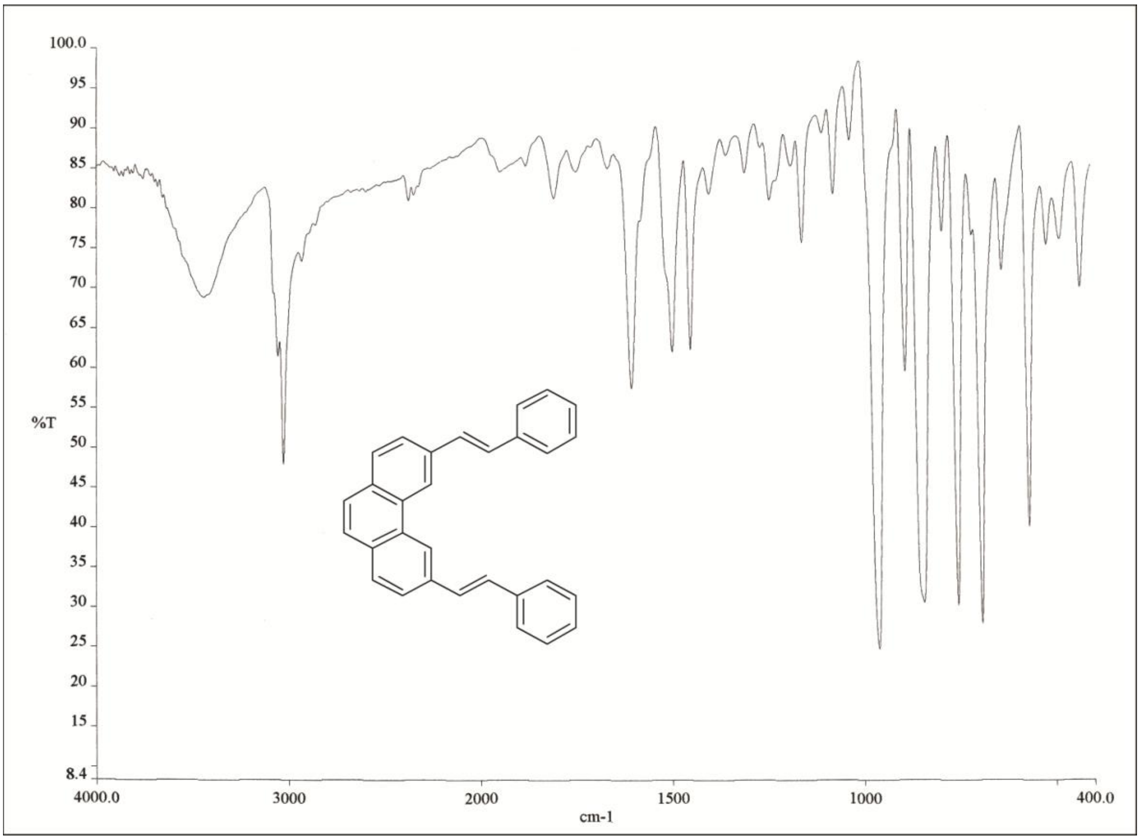


**EI-Mass spectrum of dinaphtho[1,2-*a*:2',1'-*h*]anthracene (37)**

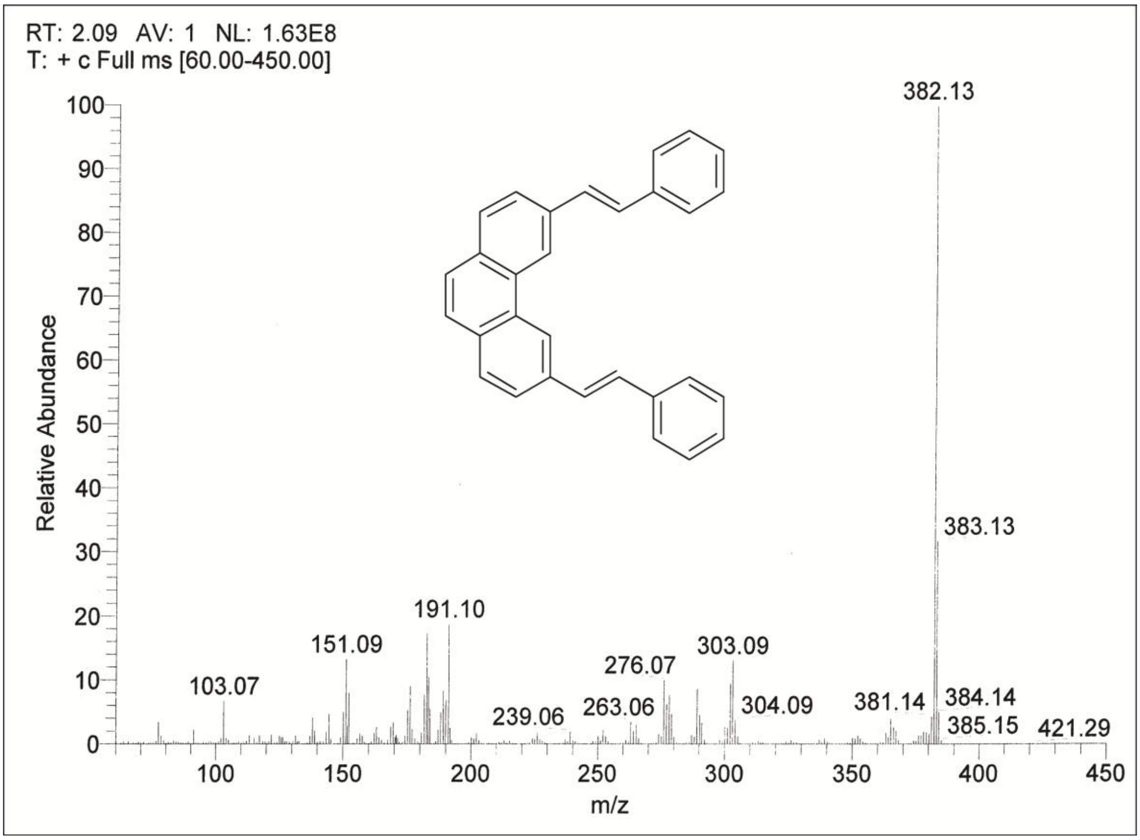
## Spectral data of 3,6-distyrylphenanthrene (155)



**$^1$H-NMR spectrum of 3,6-distyrylphenanthrene (155) in $CDCl_3$ on 400 MHz**

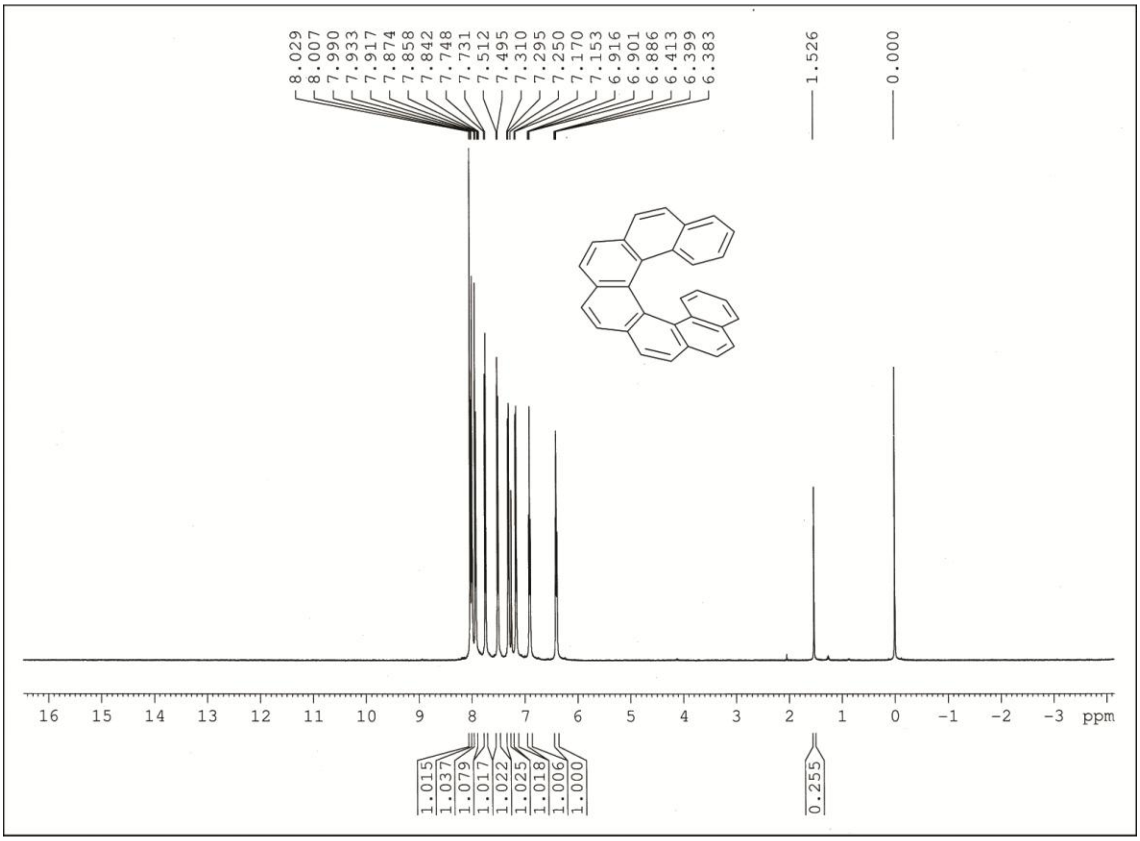


**IR spectrum of 3,6-distyrylphenanthrene (155)**

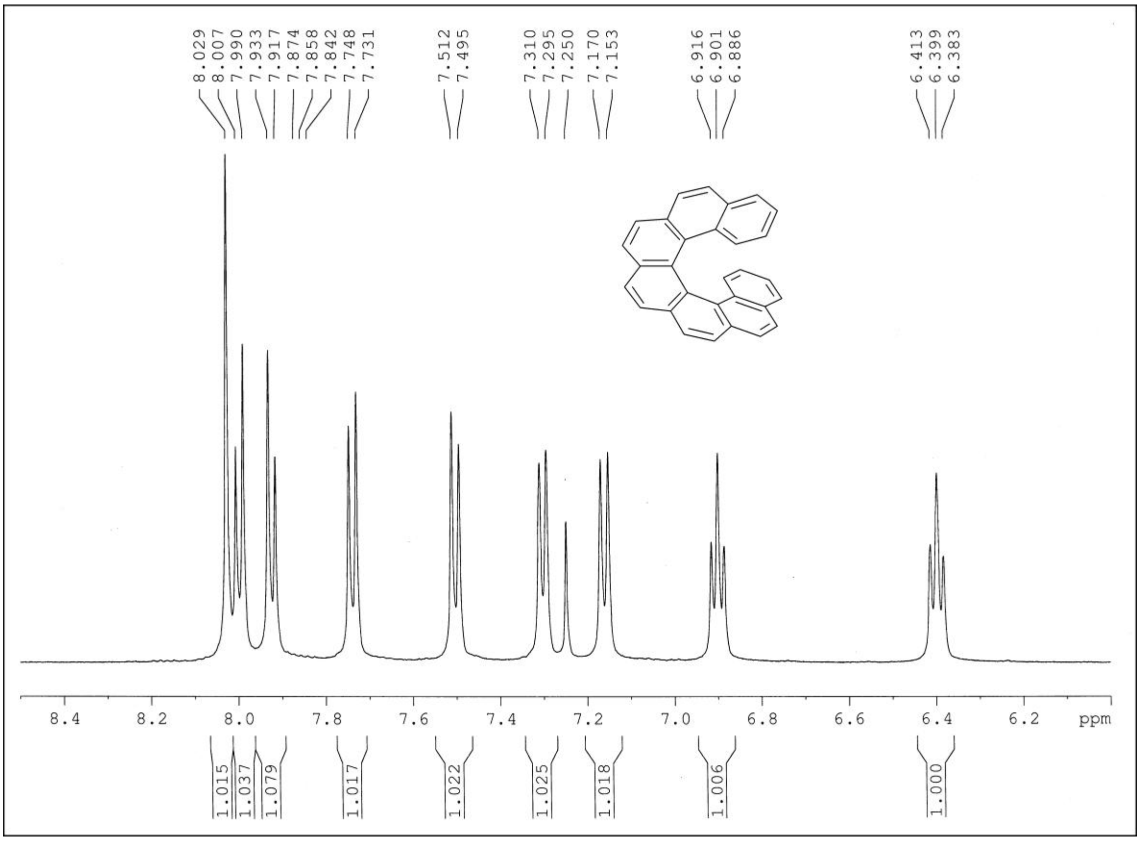


**EI-Mass Spectrum of 3,6-distyrylphenanthrene (155)**

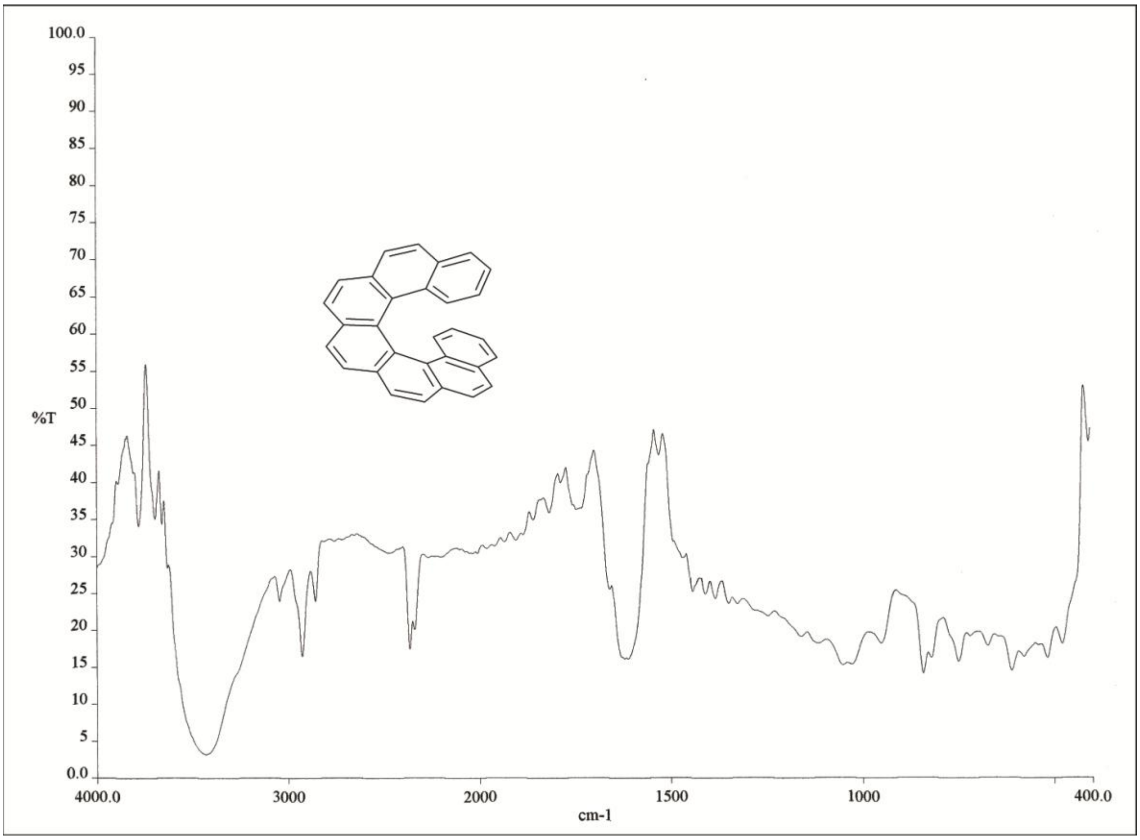
## Spectral data of [7]helicene (32)



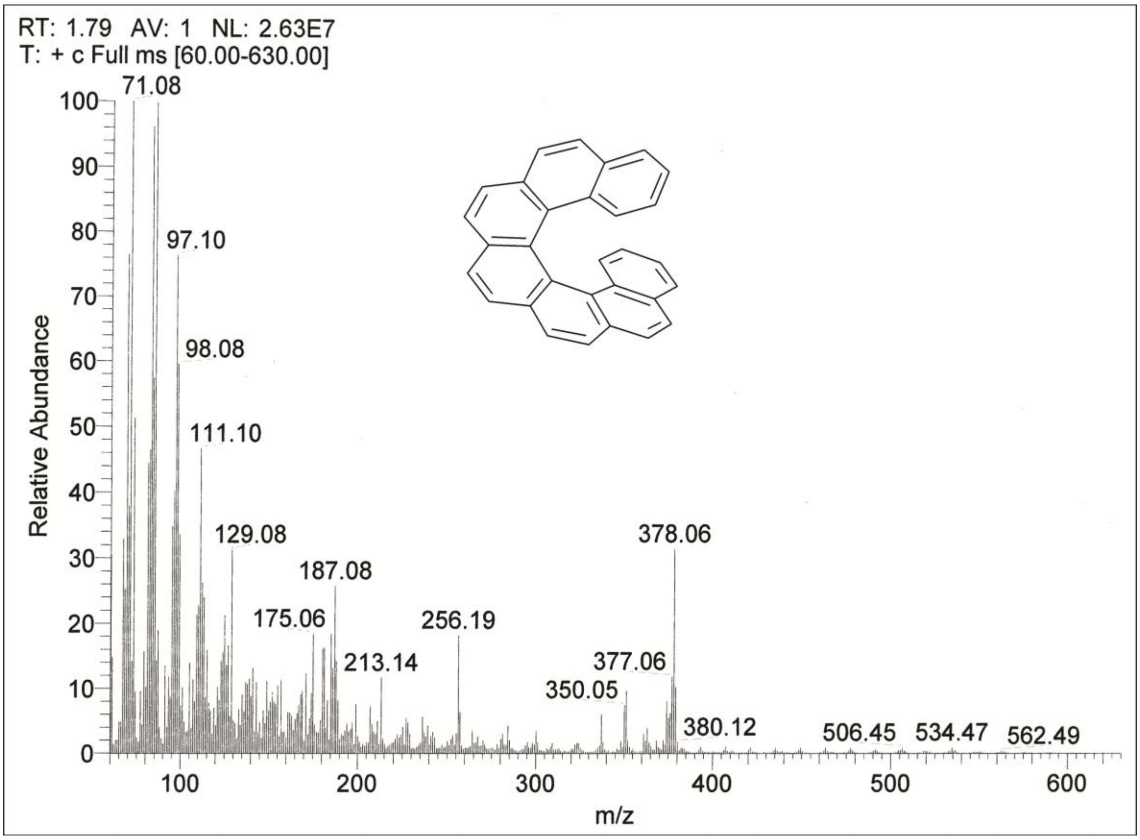
**$^1$H-NMR spectrum of [7]helicene (32) in $CDCl_3$ on 400 MHz**



**$^1$H-NMR enlarge spectrum of [7]helicene (32) in $CDCl_3$ on 400 MHz**

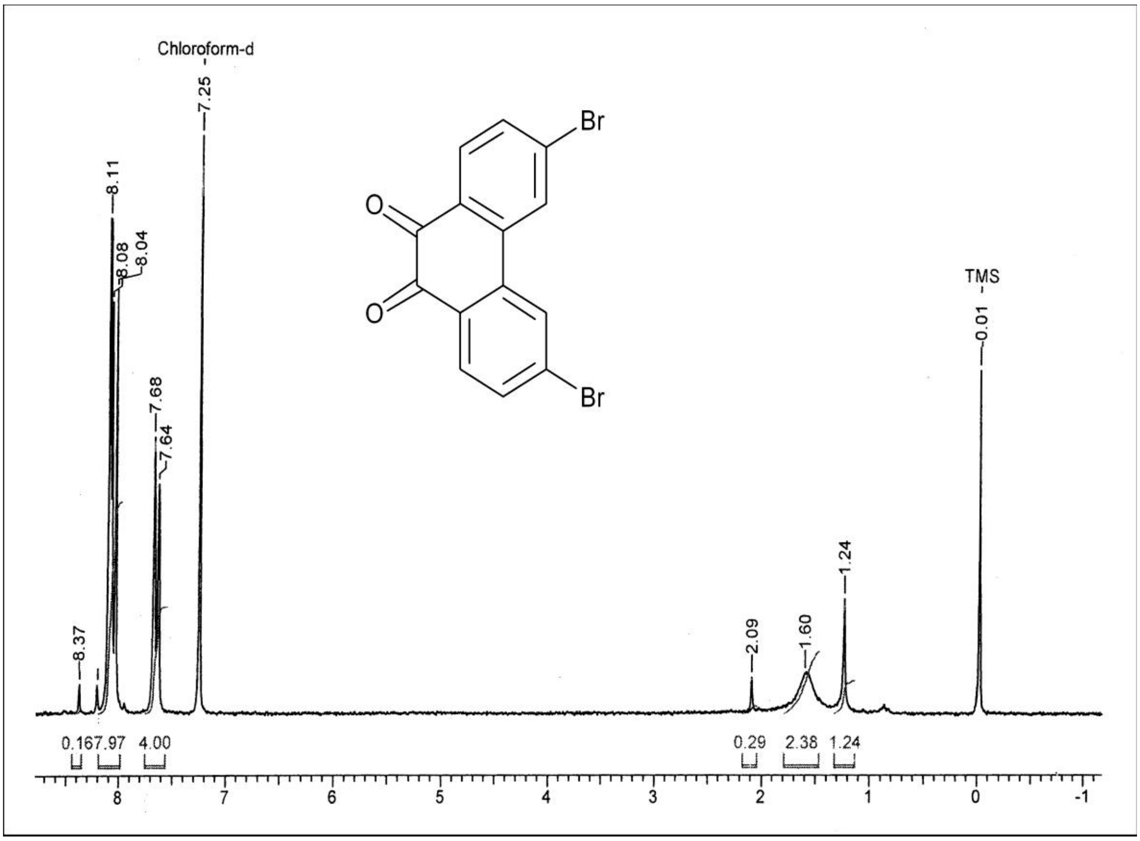


**IR spectrum of [7]helicene (32)**

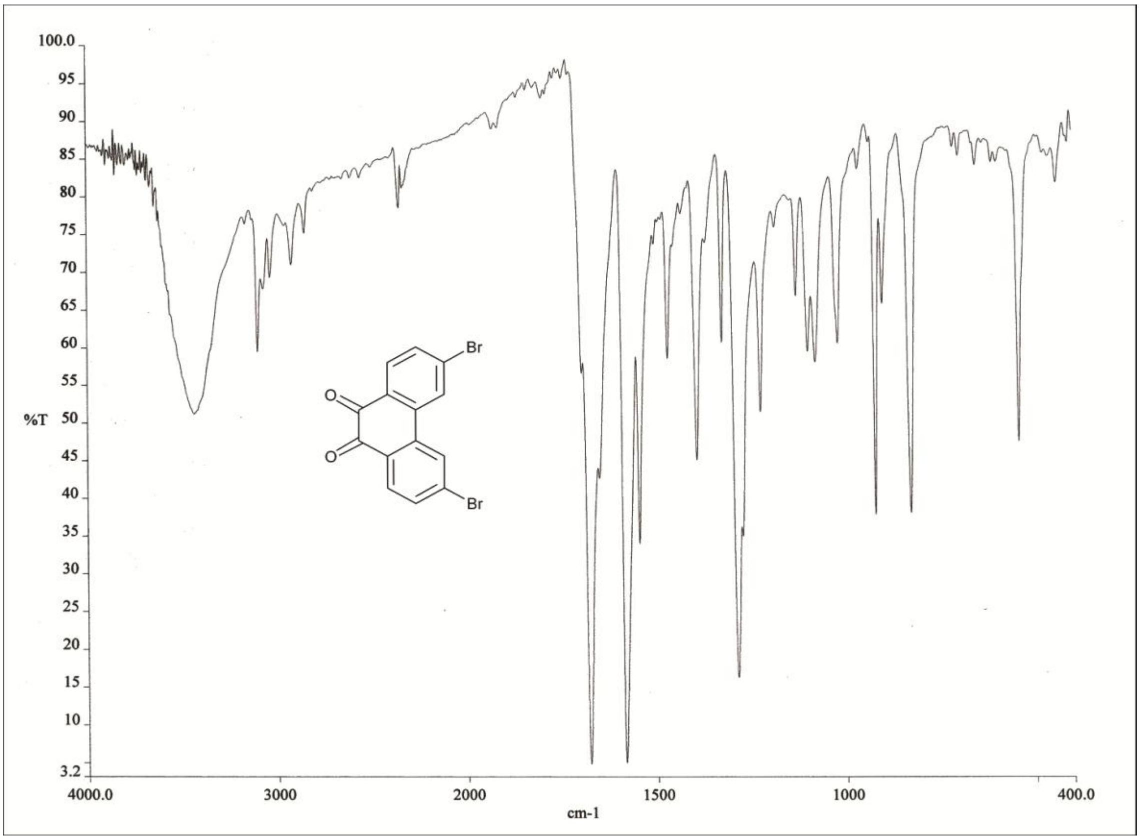


**EI-Mass spectrum of [7]helicene (32)**

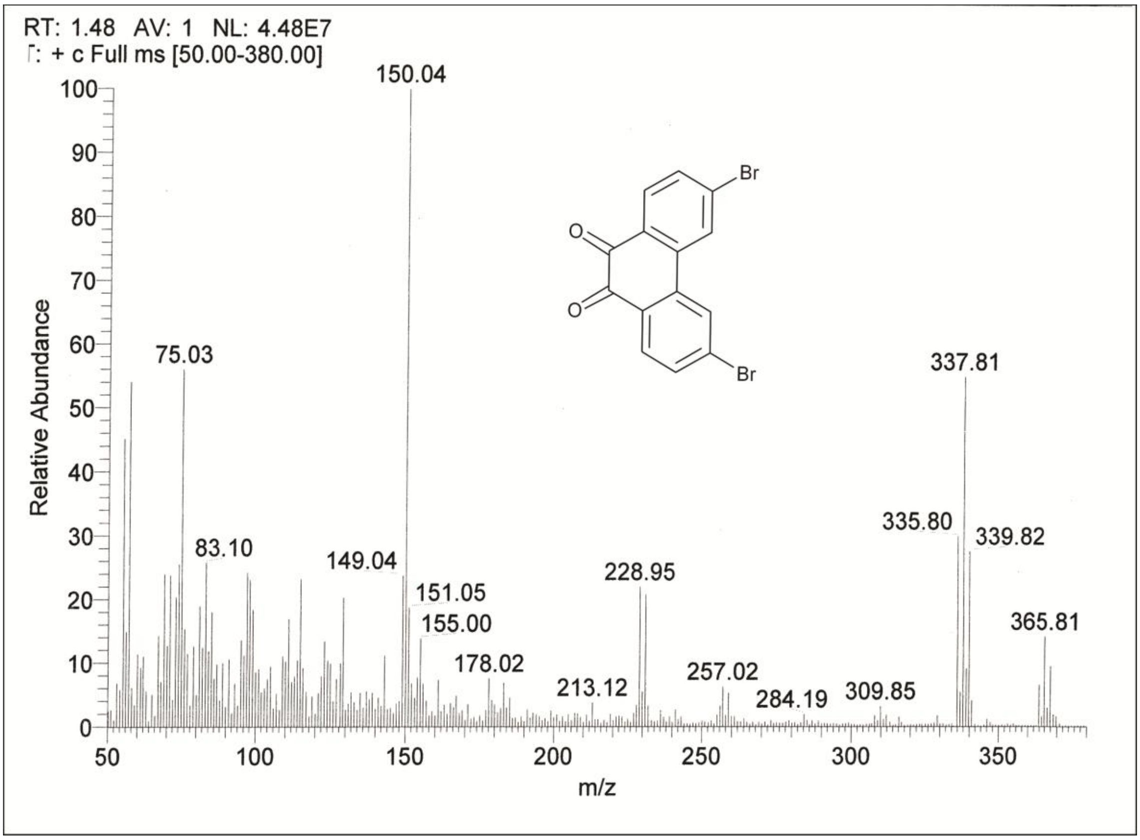
## Spectral data of 3,6-dibromo-9,10-phenanthraquinone (156)



$^1$H-NMR of 3,6-dibromo-9,10-phenanthraquinone (156) in CDCl$_3$ on 200 MHz

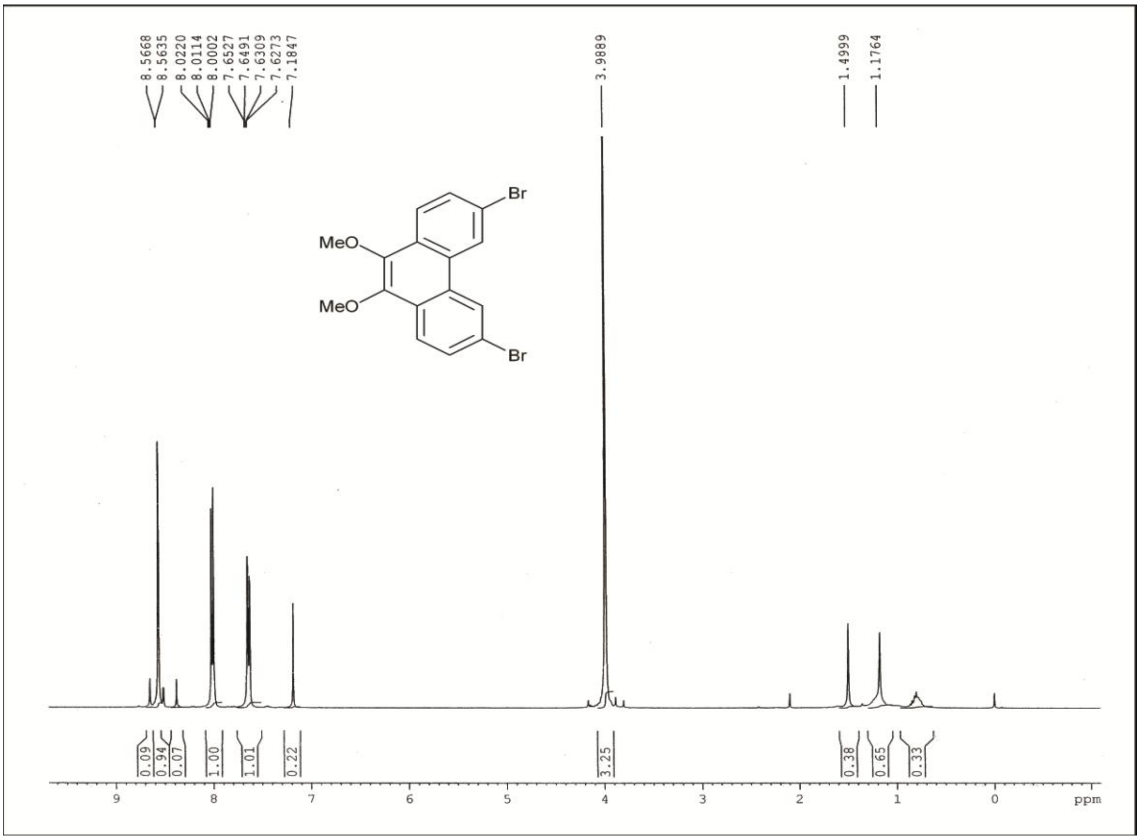


IR spectrum of 3,6-dibromo-9,10-phenanthraquinone (156)

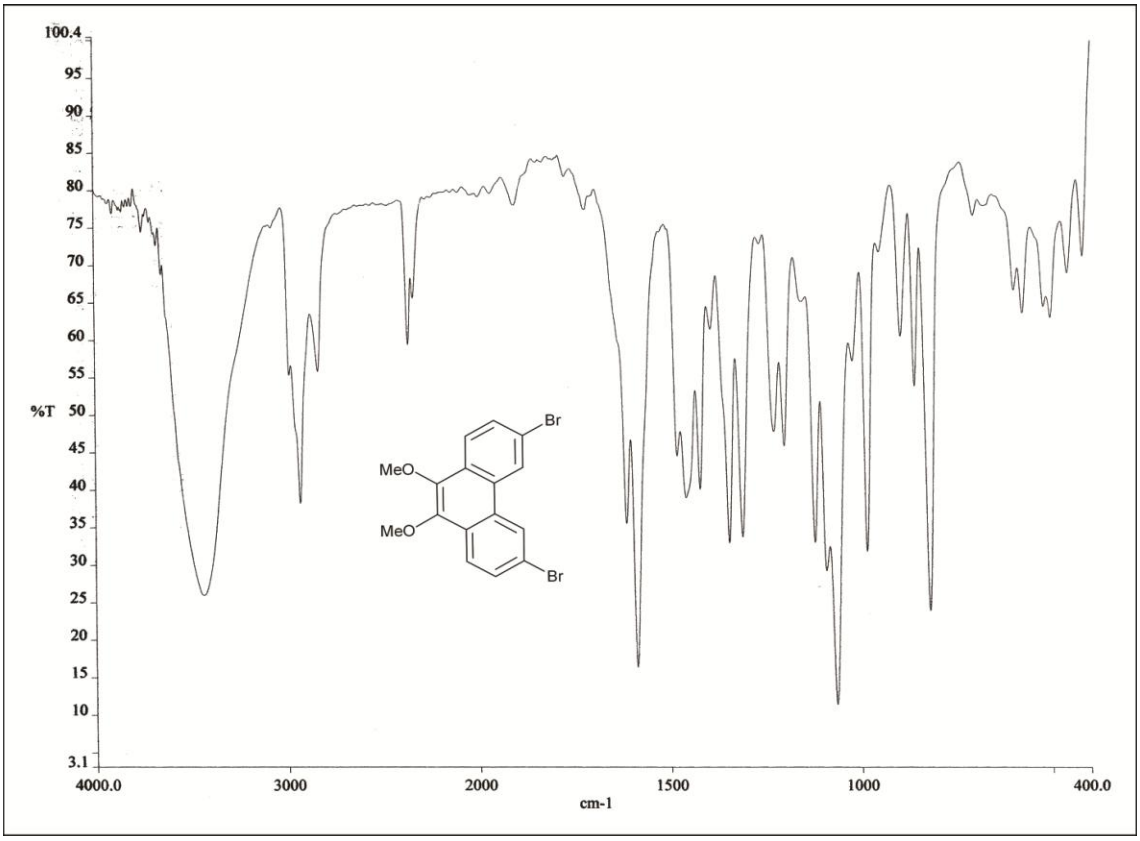


**EI-Mass spectrum of 3,6-dibromo-9,10-phenanthraquinone (156)**

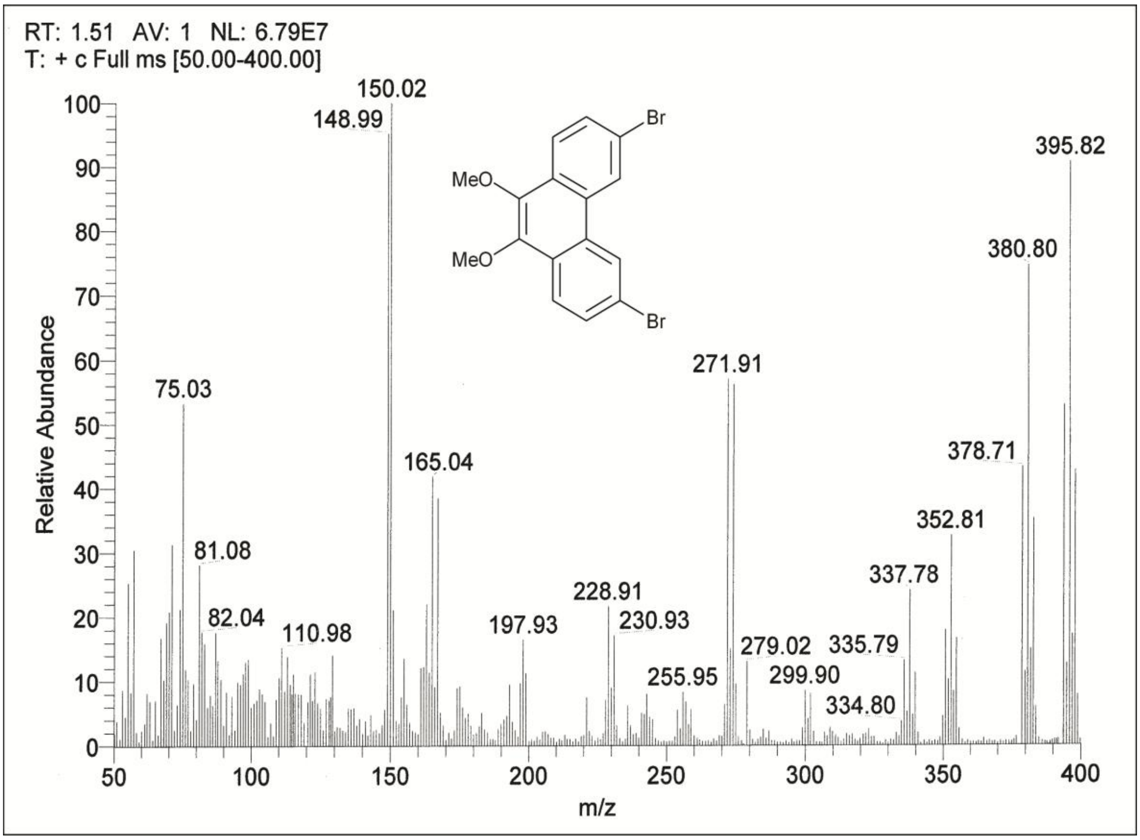
## Spectral data of 3,6-dibromo-9,10-dimethoxyphenanthrene (157)



**$^1$H-NMR of 3,6-dibromo-9,10-dimethoxyphenanthrene (157) in $CDCl_3$ on 400 MHz**

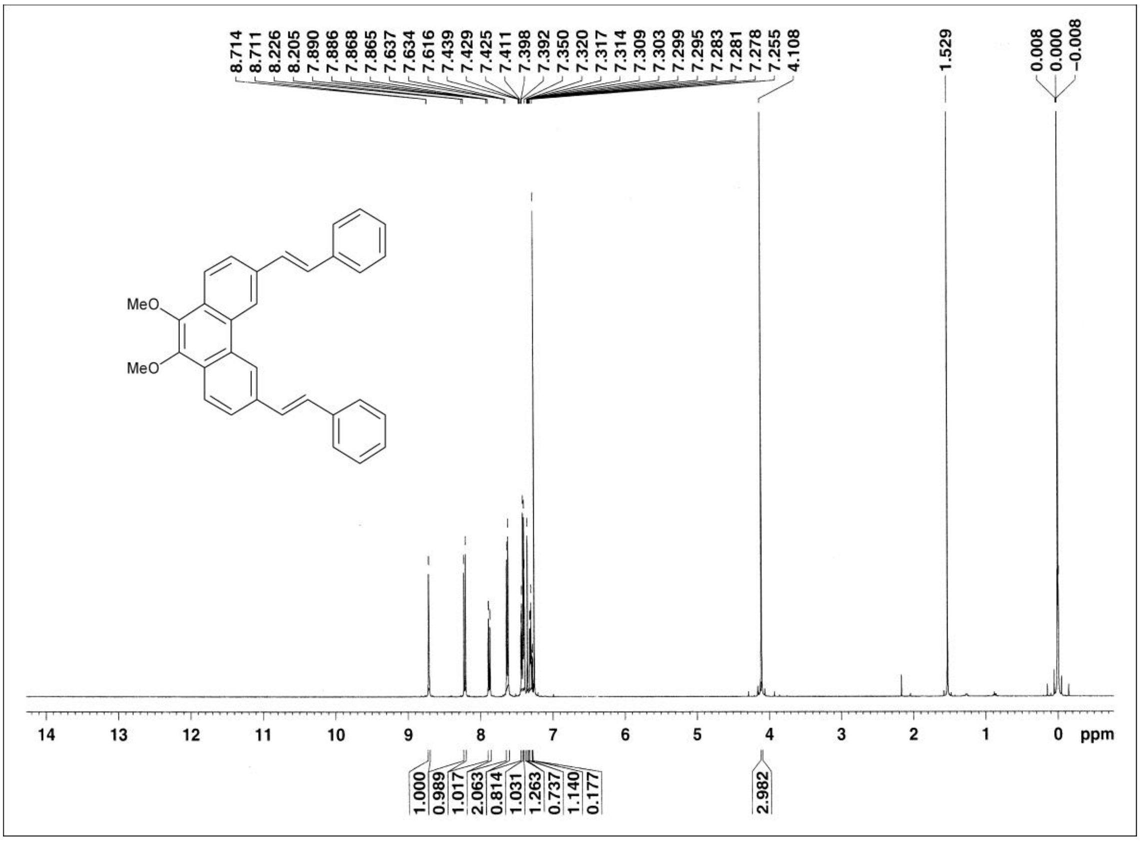


**IR spectrum of 3,6-dibromo-9,10-dimethoxyphenanthrene (157)**

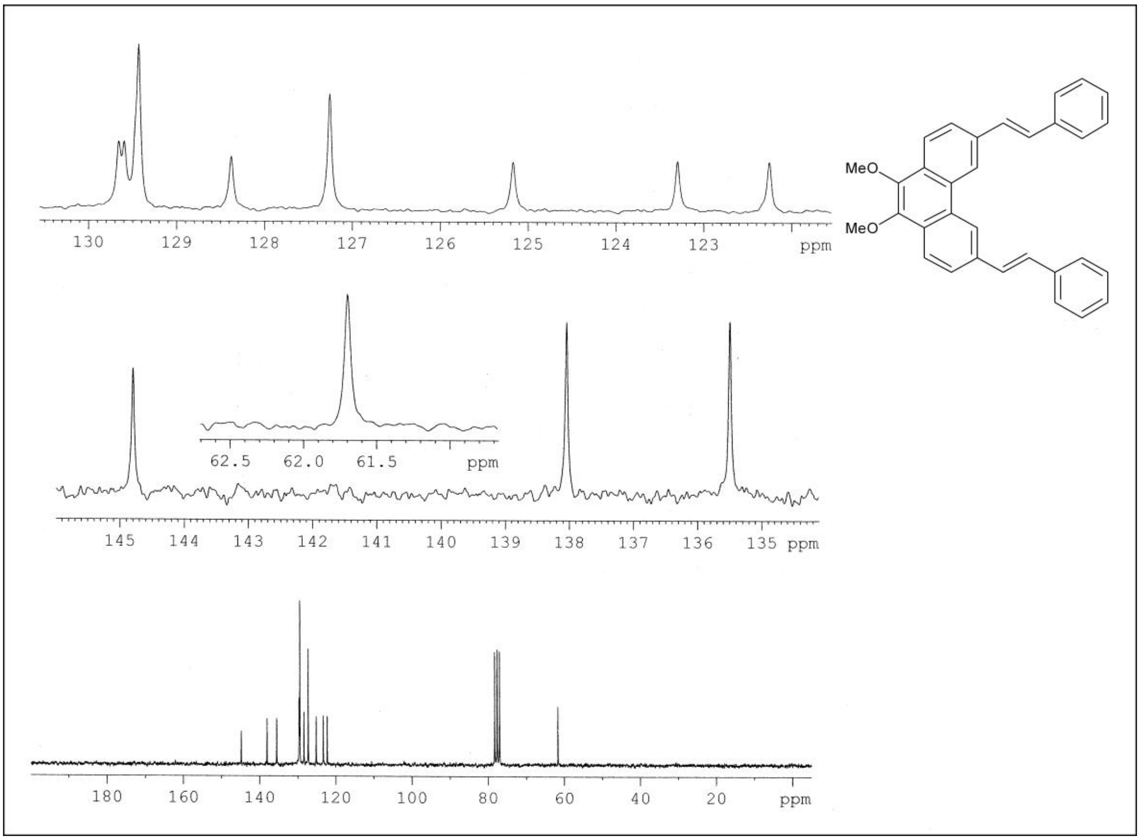


**EI-Mass spectrum of 3,6-dibromo-9,10-dimethoxyphenanthrene (157)**

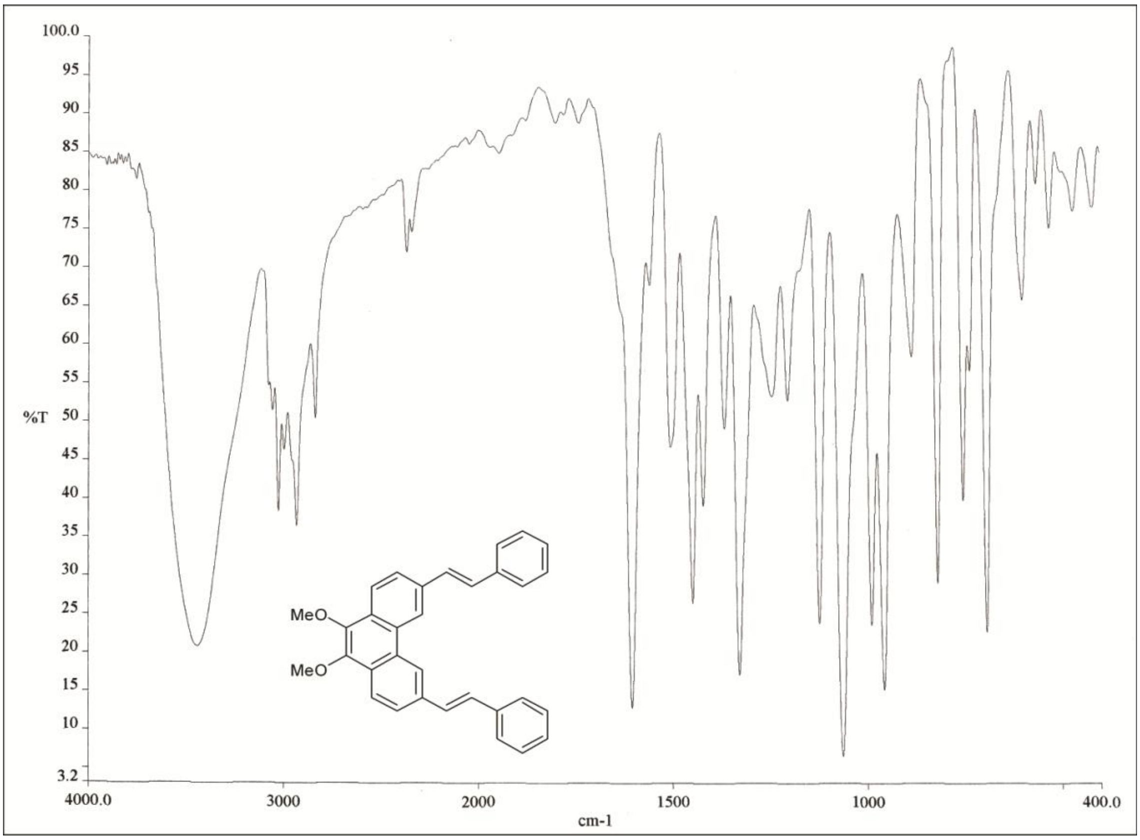
## Spectral data of 9,10-dimethoxy-3,6-distyrylphenanthrene (158)



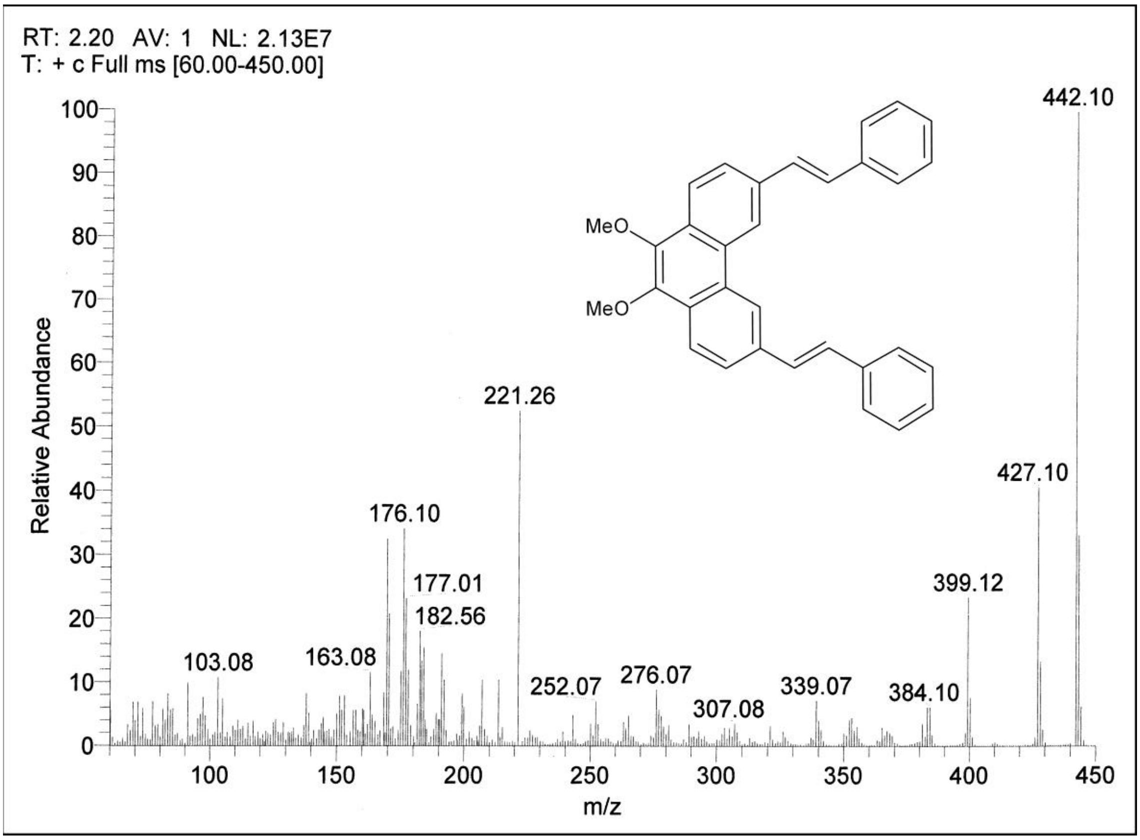
**$^1$H-NMR of 9,10-dimethoxy-3,6-distyrylphenanthrene (158) in CDCl$_3$ on 400 MHz**



**$^{13}$C-NMR spectrum of 9,10-dimethoxy-3,6-distyrylphenanthrene (158) in CDCl$_3$ on 100.6 MHz**

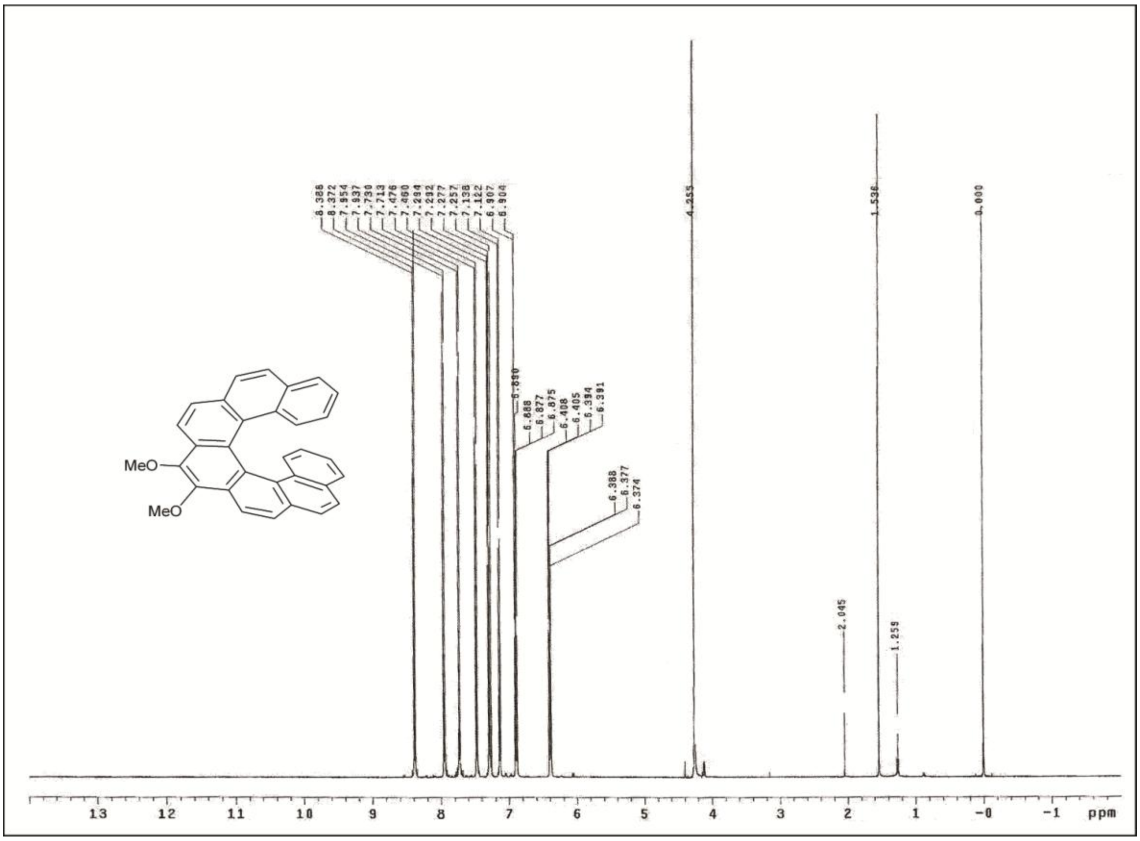


**IR spectrum of 9,10-dimethoxy-3,6-distyrylphenanthrene (158)**

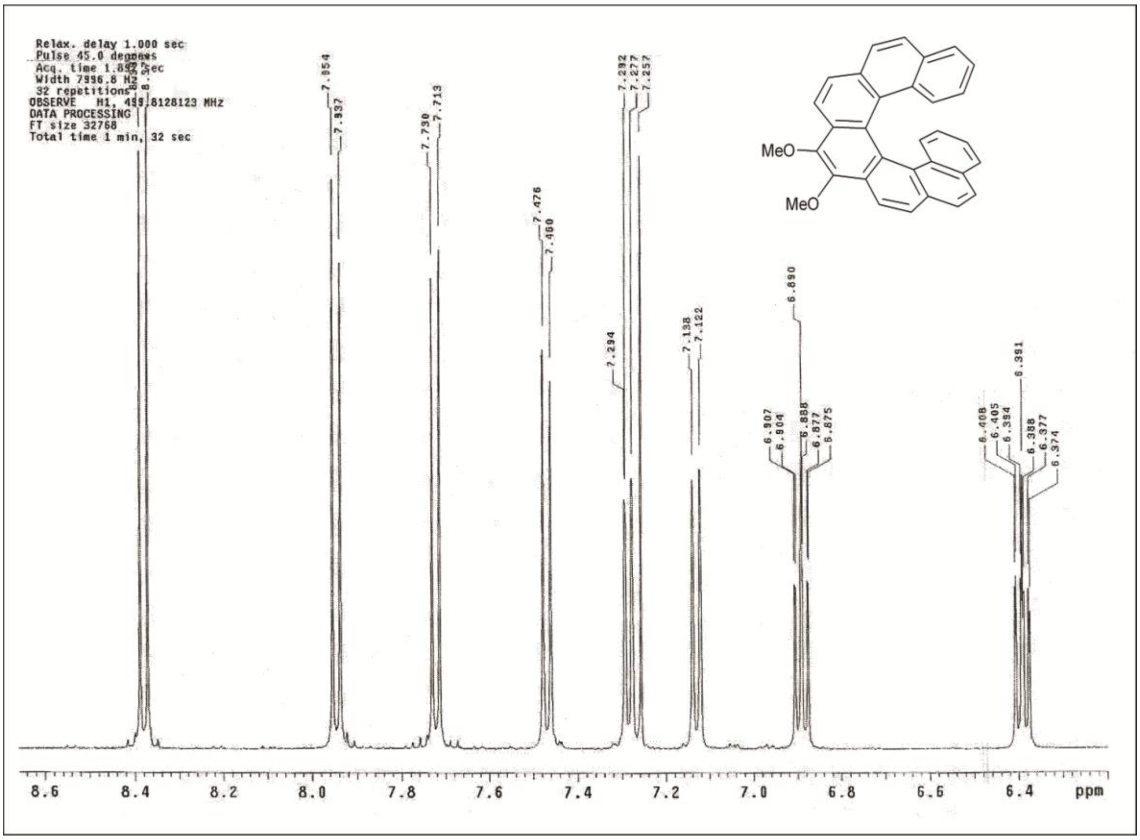


**EI-Mass spectrum of 9,10-Dimethoxy-3,6-distyrylphenanthrene (158)**

## Spectral data of 9,10-dimethoxy[7]helicene (159)



**$^1$H-NMR spectrum of 9,10-dimethoxy[7]helicene (159) in $CDCl_3$ on 400 MHz**



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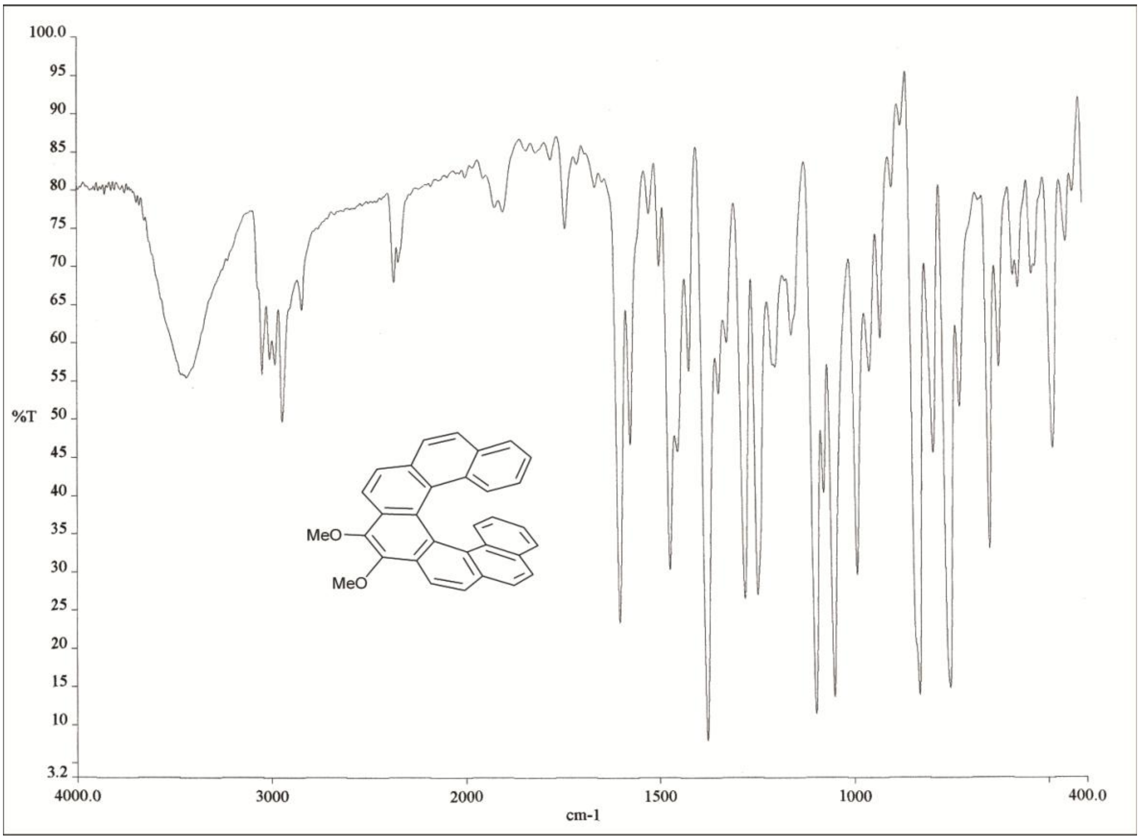
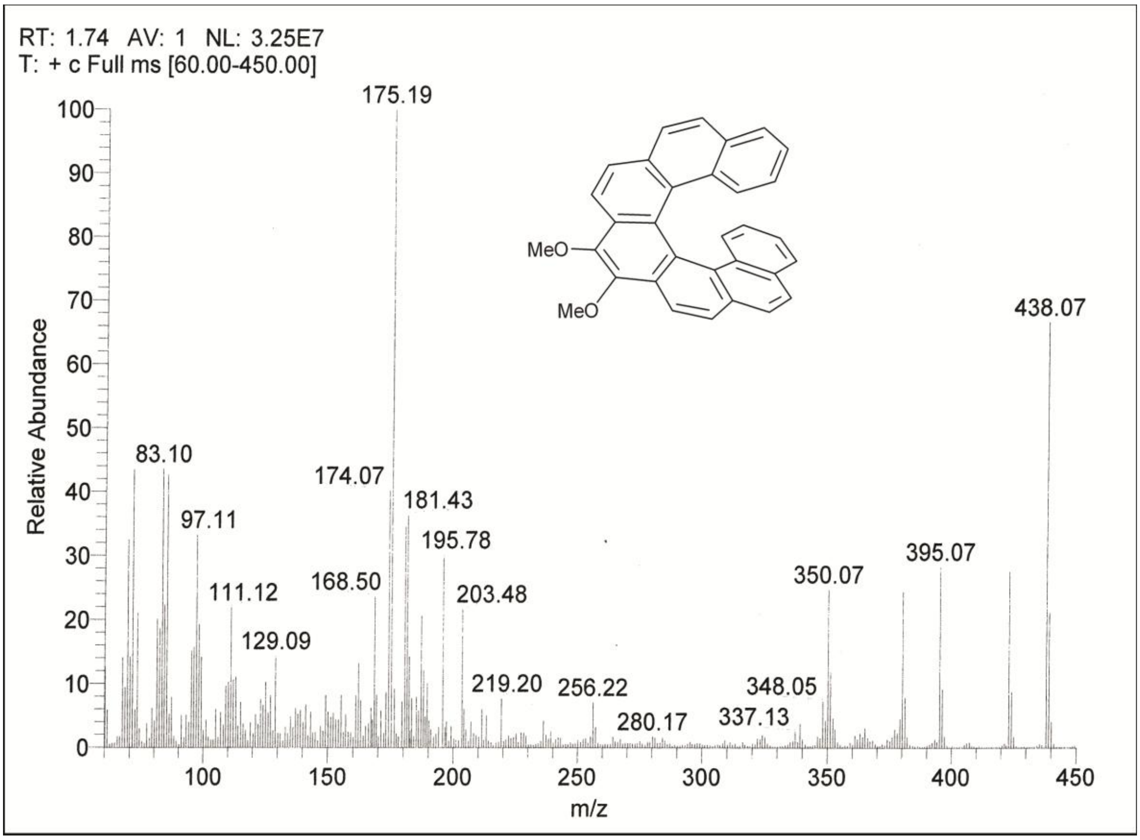
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.8 Hz
32 repetitions
OBSERVE   H1, 499.8128123 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 32 sec
```

**$^1$H-NMR enlarge spectrum of 9,10-dimethoxy[7]helicene (159) in $CDCl_3$ on 400 MHz**

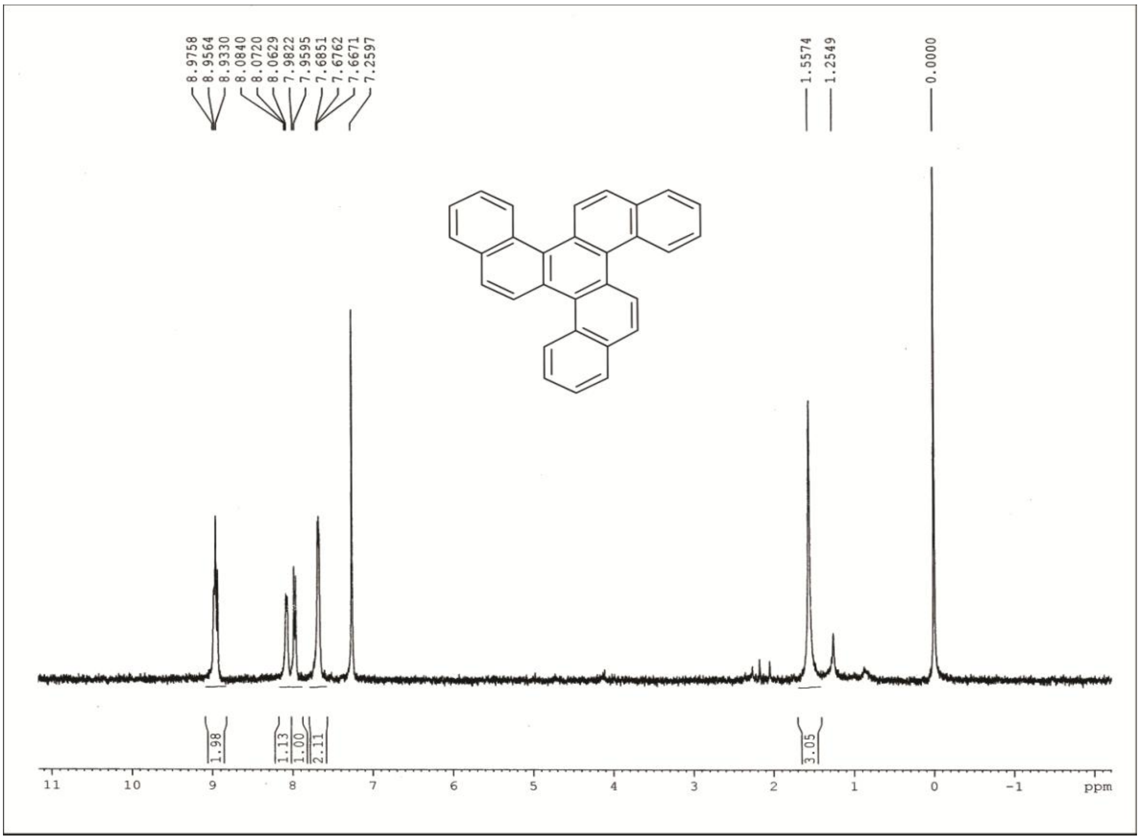


**IR spectrum of 9,10-dimethoxy[7]helicene (159)**

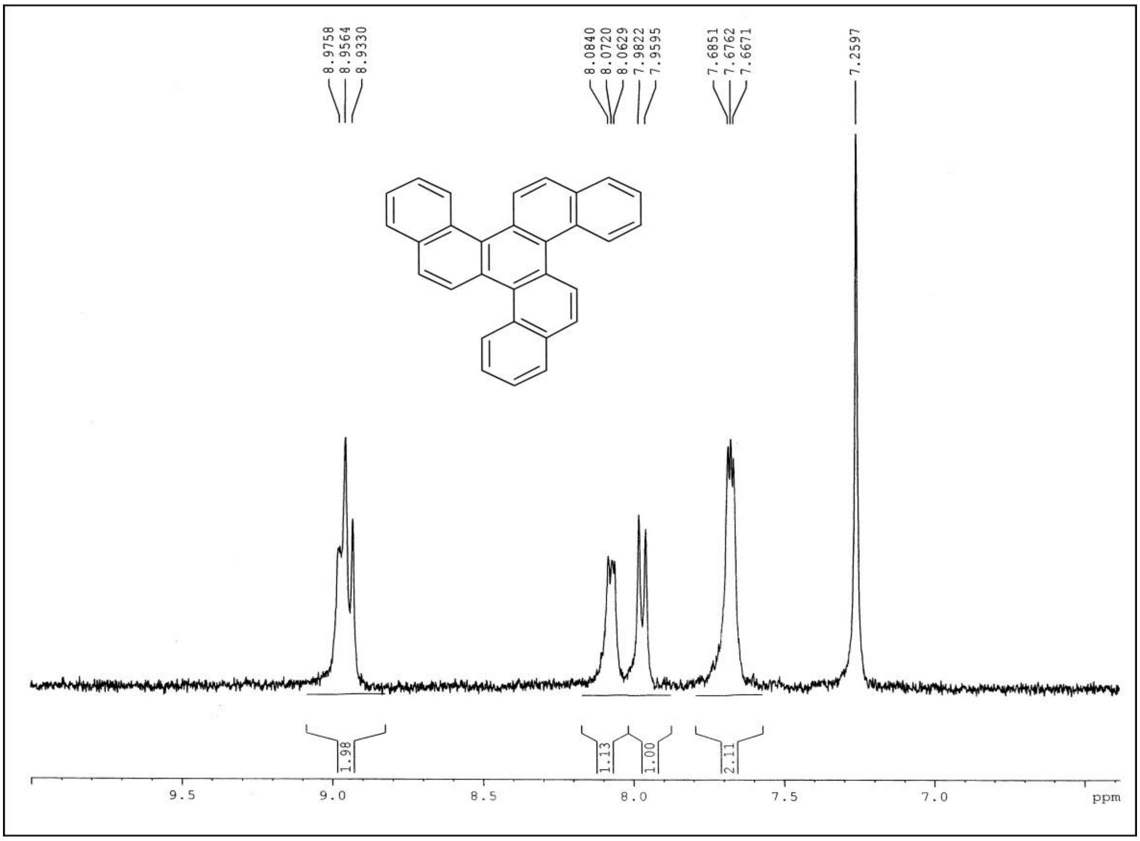


**EI-Mass spectrum of 9,10-dimethoxy[7]helicene (159)**

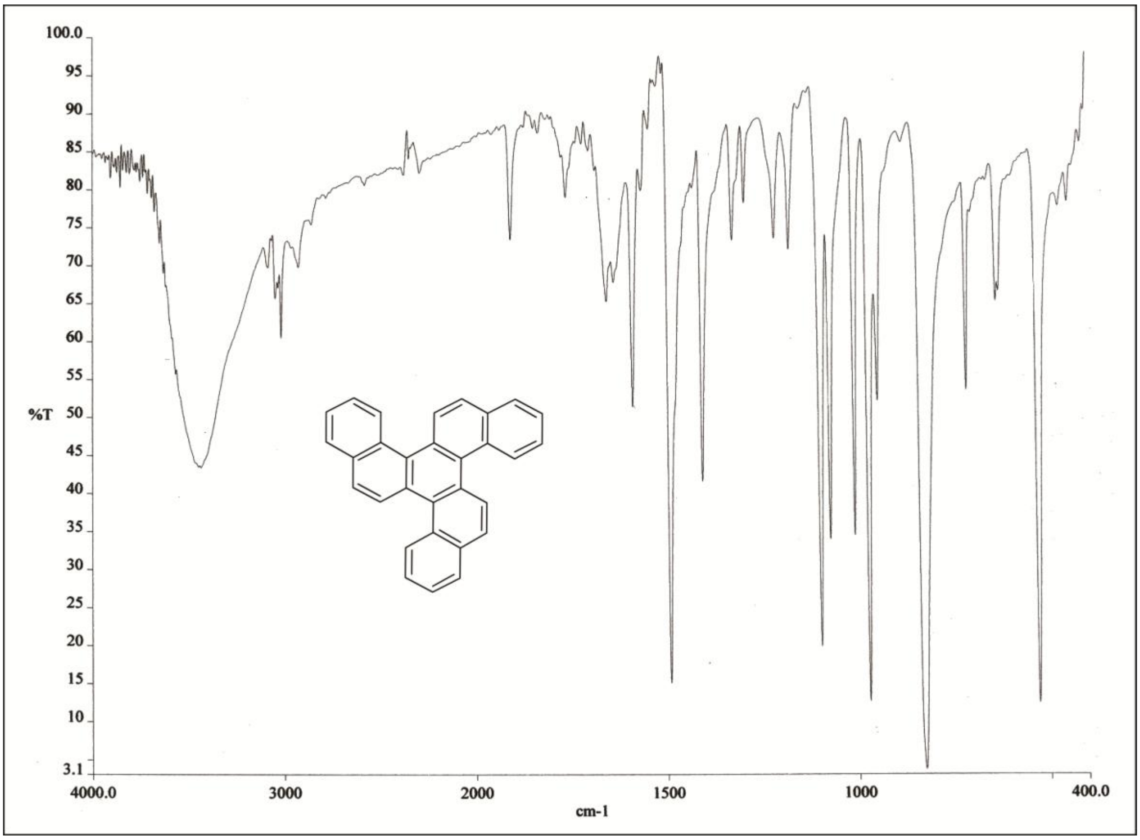
## Spectral data of benzo[*c*]naphtho[2,1-*p*]chrysene (161):



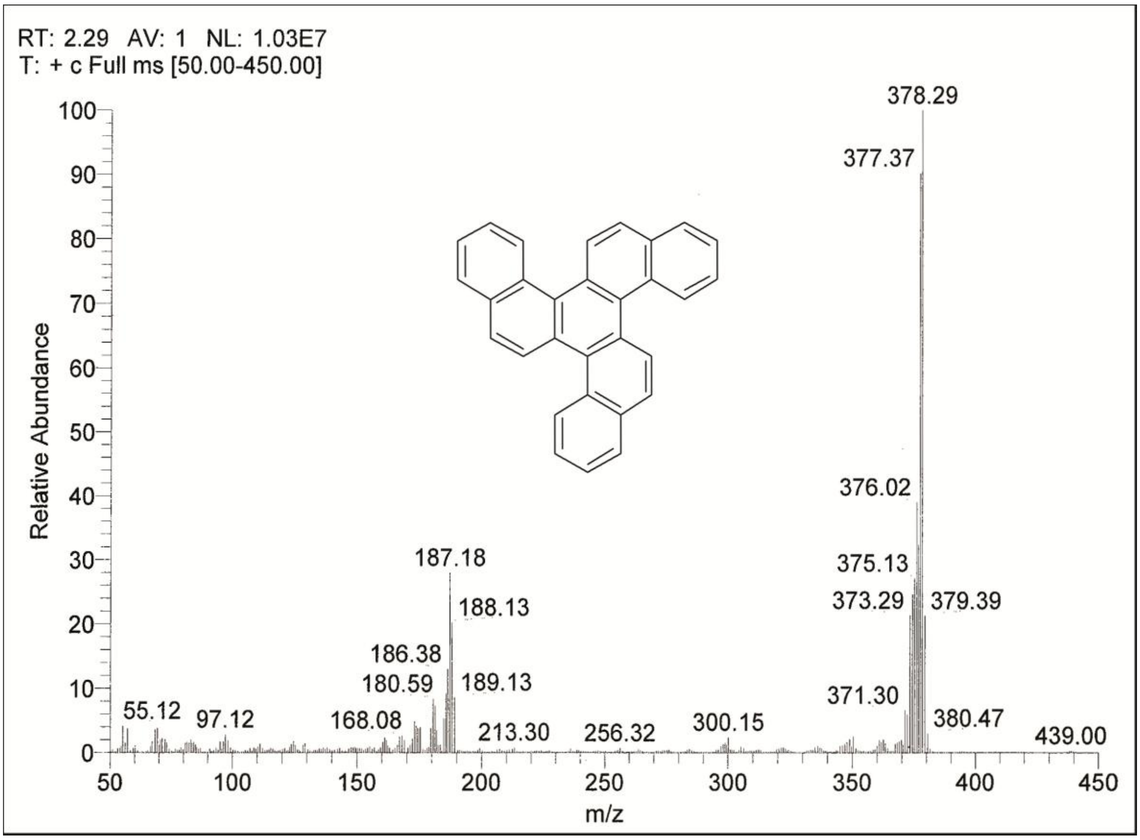
**1H-NMR spectrum of benzo[*c*]naphtho[2,1-*p*]chrysene (161) in $CDCl_3$ on 400 MHz**



**1H-NMR enlarge spectrum of benzo[*c*]naphtho[2,1-*p*]chrysene (161) in $CDCl_3$ on 400 MHz**



**IR spectrum of benzo[*c*]naphtho[2,1-*p*]chrysene (161)**



**EI-Mass spectrum of benzo[*c*]naphtho[2,1-*p*]chrysene (161)**

# Conclusion

In the present work we have developed two simple and efficient methods for photocyclization of substituted stilbenes to phenanthrenes and benzo[*c*]phenanthrenes using readily available and cheap reagents. The commonly used scavenger of hydroiodic acid propylene oxide was replaced by tetrahydrofuran. The advantages of using THF include high boiling point and ready availability. This eliminates the need of extra care to prevent evaporation during photolysis. In the second method we report the use of cyclohexene to assist the second step of the cyclization sequence. The low cost and easy availability of the reagents are the main advantages of these methods.

In this study we have extended the present method of using $I_2$-THF for photodehydrocyclization of stilbenes and substituted stilbenes to make phenanthrenes and higher helicenes. We also present the comparison of the reaction with $I_2$-THF with the conventional use of $I_2$-propylene oxide for the cyclization reactions. In most of the cases use of this readily available reagent is comparable in efficacy for the said photoconversion and we hope this method can offer an alternative, if not a substitute for construction of phenanthrenes, helicenes and polyaromatic hydrocarbons.

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# Chapter-3

## Part 1

## Synthesis and Study of Novel Helical Oxazines

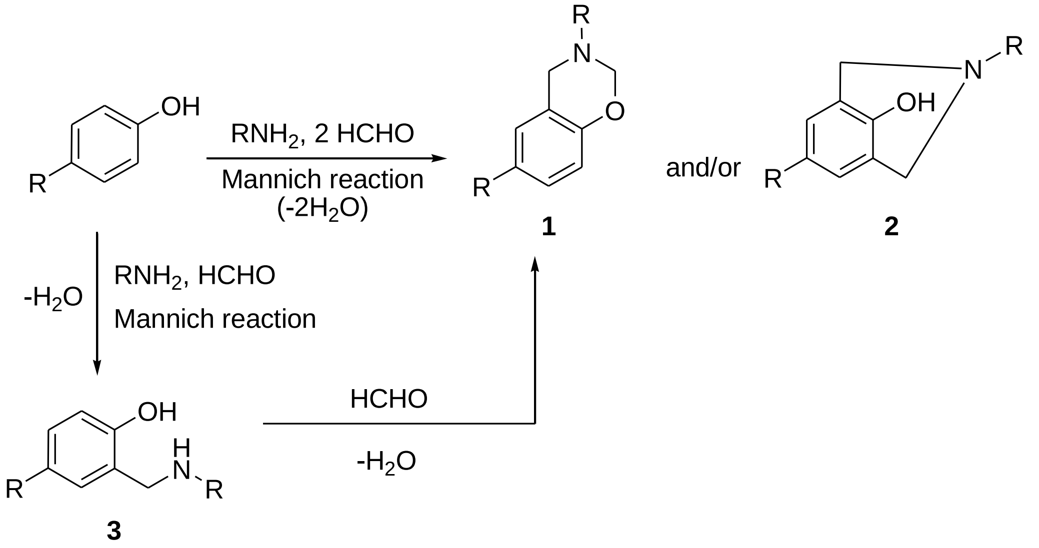
### Introduction:

Search for new chiral molecules with different shape, size and functional group is an extremely crucial aspect of modern organic chemistry. This is particularly vital in the field of molecular recognition, supramolecular and medicinal chemistry, asymmetric synthesis and enantioselective catalysis, material chemistry etc. Amongst this class of compounds helically chiral molecules find a unique place due to some special chiroptical properties. Since the pioneering work on helicene by Newman in 1956,[1] the area has presented a number of new helical molecules with a wide range of applications.[2-5]

Primarily the helically shaped molecules are of two types: carbo-helicenes and helicenes with hetero atoms, or heterohelicenes.[6,7] The heterohelicenes possessing a 1,3-oxazine unit in the framework are not reported in the literature, with an exception of one system,[7d] although this heterocyclic moiety is present in few biologically active molecules.[8] In this chapter we present synthesis, characterization and determination of absolute configuration of three types of novel helical 1,3-oxazines.

Heterocyclic moieties are the important entities to study several other aspects including their biological behaviour. We are also interested to synthesize some helical molecules with heteroatoms situated at the bite of the helical unit.

The reaction of phenols with formaldehyde and secondary amines gives the dialkylaminomethyl substituents in positions *ortho* or *para* to the hydroxyl group.[9] The first aromatic oxazines were prepared by Holly and Cope, when they synthesized 1,3-oxazines using the phenols or naphthols, formaldehyde and primary amines in the ratio of 1:2:1 to form the new heterocyclic ring containing the nitrogen and oxygen atoms at the C1and C3 position of the heterocyclic ring [**Scheme-1**].[10]



**Scheme 1**: Synthesis of 1,3-oxazines

The reaction of *p*-substituted phenols with formaldehyde and primary amines in a molar ratio of 1:2:1, respectively. This procedure led to the formation in good yield of 3,4-dihydro-3,6-disubstituted-1,3-2H-benzoxazines **1**. In an alternate method, equimolar quantities of the *p*-substituted phenol, formaldehyde, and primary amine (1:1:1) react to give *O*-alkylaminomethyl-*O*-substituted phenol **3** as an intermediate. Conversion of **3** to **1** took place readily on treatment with formaldehyde in the presence of a basic catalyst. In some cases the *N*-methylamines are capable of attacking *p*-substituted phenols at the free *ortho* positions[9] to form the possible alternate structure **2**.

Using this concept Burke and Urbanski have synthesized a number of 1,3-oxazines and have scaned these molecules for different medicinal applications[8,11] [**Figure-1**].

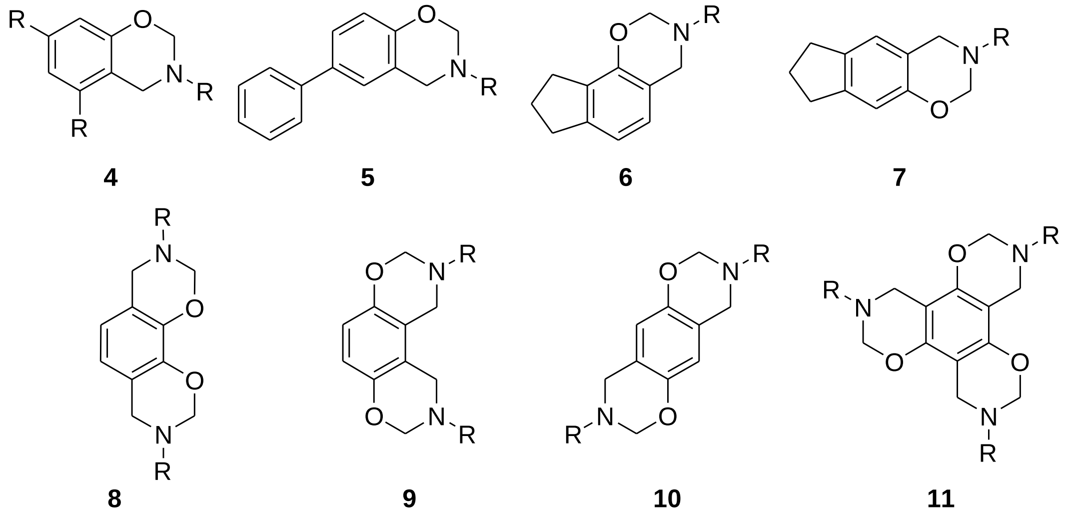
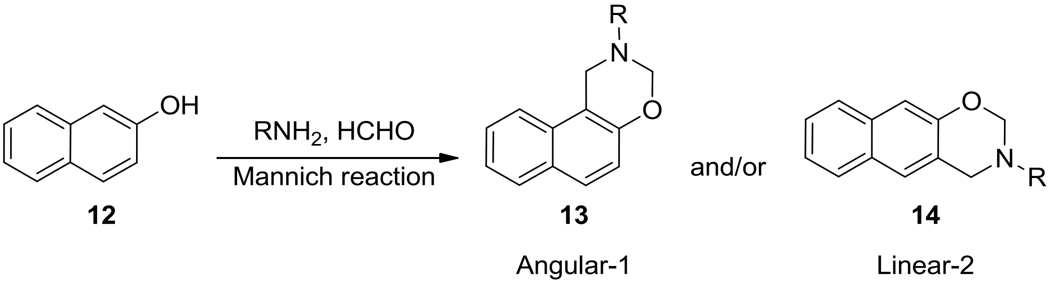


**Figure 1:** Different mono-, bis- and tris- [1,3]oxazines

Similarly, by this method the first naphthoxazine synthesized by Burke,[12] by the aromatic Mannich reaction of β-naphthol with an aldehyde and amine. When two equivalent of aldehyde such as formaldehyde was used the new heterocyclic moiety 'oxazine' was formed, which had a six member ring with O and N fused with naphthalene. There were two possible sites of 2-hydroxy naphthalene, C-1 and C-3, to react with intermediate imine to form angular-**1** or linear-**2** [**Scheme-2**].



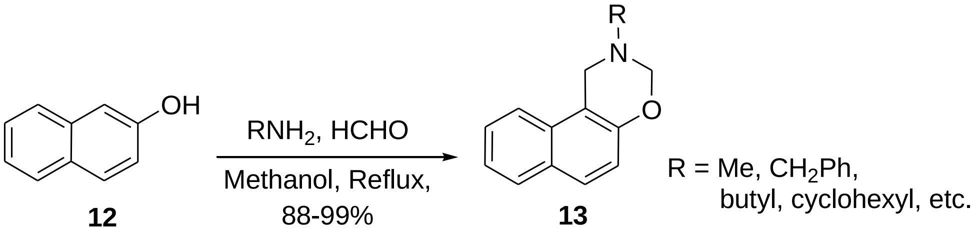
**Scheme 2:** Synthesis of Linear and Angular 1,3-oxazines from β-naphthol

## Synthesis of Mono-Oxazines with Naphthols:

Many methods are available in the literature for the synthesis of 1,3-oxazines from phenols by the aromatic Mannich reaction. A large number of racemic and chiral 1,3-oxazines were synthesized from phenols and their wide range of applications were studied. These include uses as chromophoric materials,[13] polymers,[14] in medicinal chemistry[8,15] etc. while derivatives from different substituted aminophenols/aminonaphthols[16] are known.

### Synthesis of 2,3-dihydro-2-alkyl-1*H*-naphth[1,2,*e*]-*m*-oxazine:

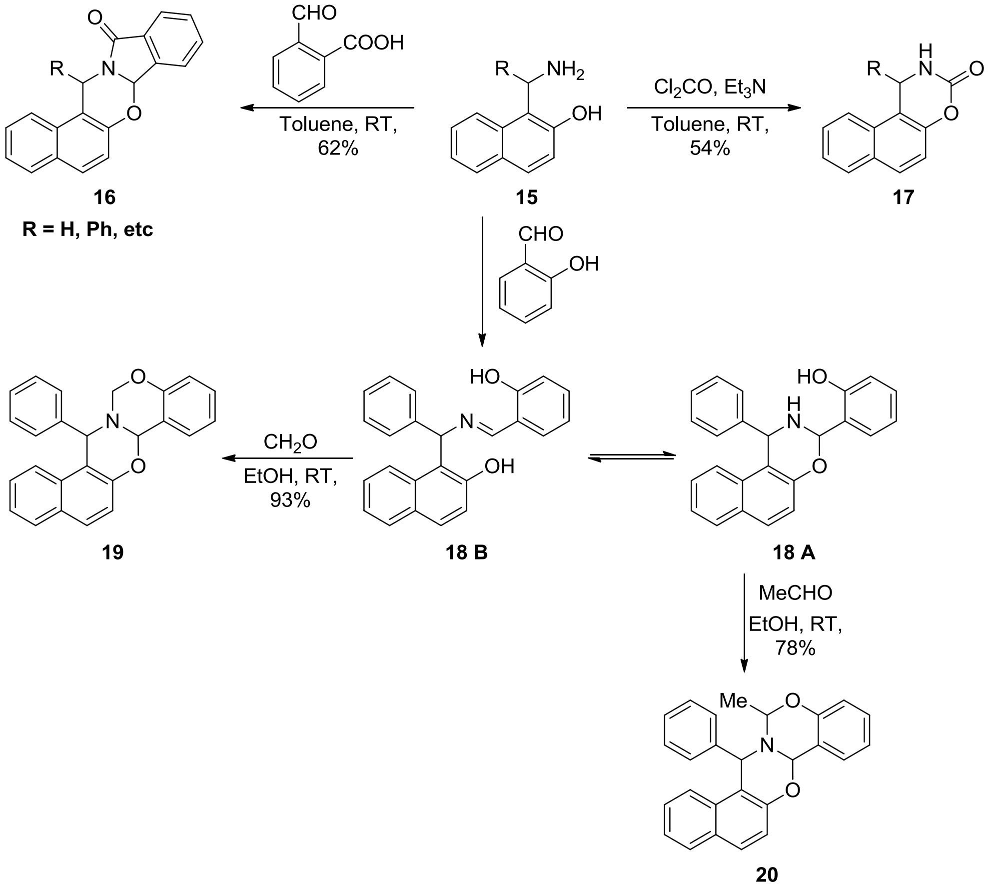
In 1952 Burke and co-workers first synthesized[12] [1,3]-napthoxazine from β-naphthol, formaldehyde and primary amine taken in the ratio (1:2:1) in refluxing methanol to obtain the product naphthoxazines in good to excellent yields [**Scheme-3**]. After the synthesis of these oxazines intermediates, further derivatives were also prepared.



**Scheme 3:** Synthesis of naphth[1,2,*e*]-*m*-oxazines

## Synthesis of mono 1,3-oxazines from Betti base:

Reaction of β-naphthol with an aldehyde and ammonia gives 1-(α-aminobenzyl)-2-naphthol, known as Betti base **15**. The ring closure of the Betti base with formaldehyde was extensively studied by Fulop and co-workers.[17]



**Scheme 4:** Synthesis of various 1,3-oxazines from Betti Base

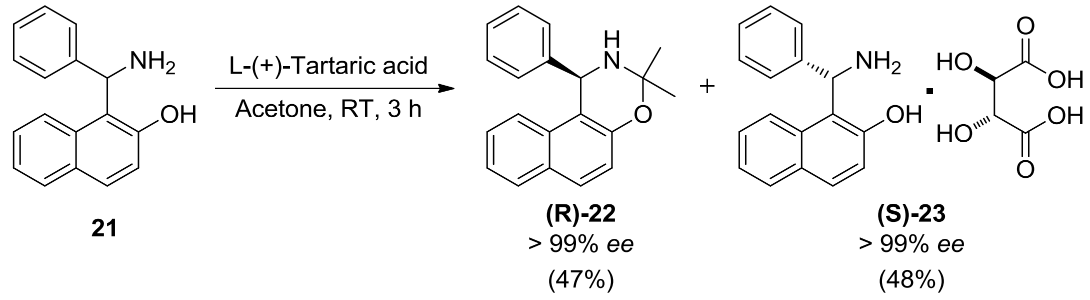
Insertion of one carbon segment by the action of **15** with formaldehyde results in naphthalene-condensed 1,3-oxazines with unique characteristics.[18,19] If the oxo compound used in this reaction contain another functional group capable of reacting with the amino group of initially formed naphthoxazine, the tautomeric equilibrium can be shifted completely toward the ring-closed form by participation of the second ring, resulting in nitrogen-bridged heterocycles. The reactions of aminonaphthols **15** with 2-carboxybenz-aldehyde under mild conditions at room temperature gave the corresponding isoindole-condensed naphthoxazines **16**.

When aminonaphthols **15** were treated with phosgene in the presence of $Et_3N$, the corresponding naphthalene condensed 1,3-oxazin-2-ones **17** was formed[17]

[**Scheme-4**]. The further ring closure of **15** with salicyladehyde was not feasible if the R was hydrogen, but if R was phenyl this reaction proceeds to form **19** and **20** in excellent yields due to the tautomeric equilibrium towards the predominant cyclic *cis* form.[19,20]

### Synthesis of chiral mono 1,3-oxazines by using *rac*-Betti Base and chiral auxiliary:

In 2005 Hu and co-workers[21] obtained a chiral 1,3-oxazine from a racemic sample of Betti base **21** using chiral L-(+)-tartaric acid. Sample of **21** was treated with chiral acid (0.75 eq.) in acetone to obtain the precipitate of optically pure salt (*S*)-**23** as solid.

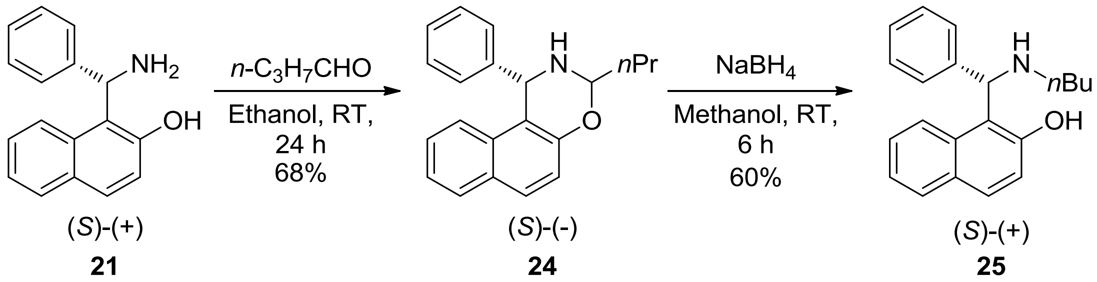


**Scheme 5:** Synthesis of (+)-3,3-Dimethyl-1-phenyl-2,3-dihydro-1H-naphtho[1,2-*e*][1,3]oxazine

The mother liquid was treated with aqueous $Na_2CO_3$ and extracted with dichloromethane, which was concentrated to obtain the crude product (*R*)-(+)-3,3-dimethyl-1-phenyl-2,3-dihydro-1H-naphtho[1,2-*e*][1,3]oxazine **22** and after recrystallization obtained the enantiomer of product **22** in optically pure form.

### Synthesis of chiral Mono 1,3-oxazines by using chiral Betti Base:

The chiral Betti base was also used for the synthesis of optically pure 1,3-oxazines.



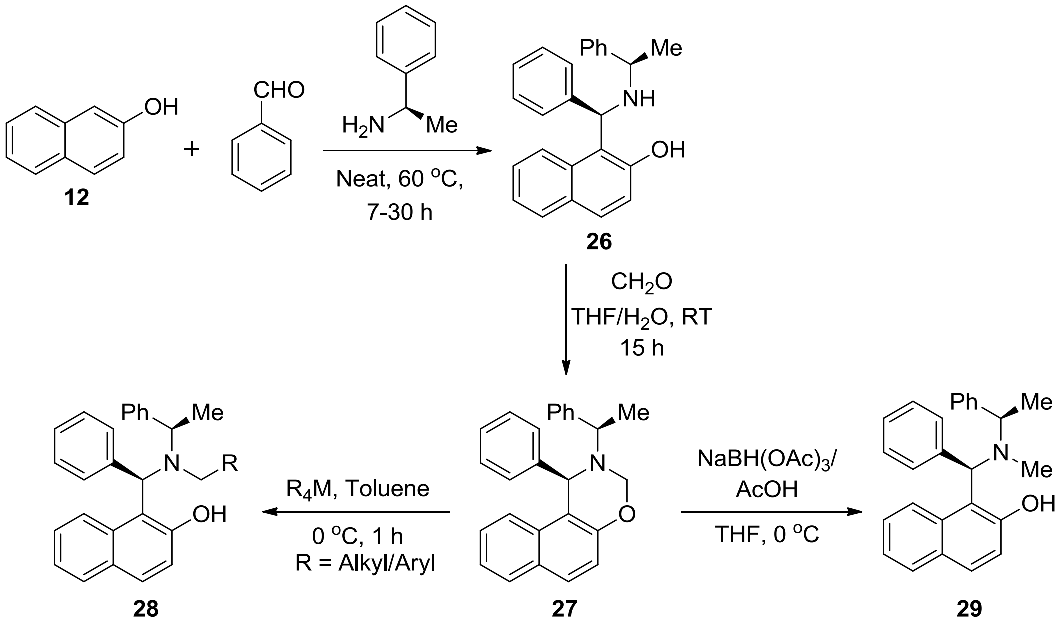
**Scheme 6:** Synthesis of 1-Phenyl-3-*n*-propyl-2,3-dihydro-1H-naphth[l,2-*e*][1,3]oxazine and 1-( α-*N*-butylaminobenzyl)-2-naphthol

Naso and co-workers synthesized[16a] chiral 1,3-oxazines using (*S*)-(+)-Betti base **21** and *n*-propanal in ethanol to obtain the product (*S*)-(-)-1-phenyl-3-*n*-propyl-2,3-dihydro-1H-naphth[l,2-*e*][1,3]oxazine **24** in a good yield.

The chiral isomer of oxazine (*S*)-**24** was further converted to 1-(α-*N*-butylaminobenzyl)-2-naphthol by its reduction with sodium borohydride at ambient conditions in good yield. The compound **25** was used for further applications in asymmetric synthesis.

### Synthesis of chiral Mono 1,3-oxazines by using chiral primary amine:[16c,22]

Palmeri and co-workers[16c,22] have synthesized novel chiral 1,3-oxazines **26** from β-naphthol, benzaldehyde and (*R*)-(+)-1-phenylethylamine, practically as a single diastereoisomer, by a solvent free synthesis process in excellent yield and selectivity (99:1 d.r.). The chiral aminonaphthol **26** was treated with aqueous solution of formaldehyde in tetrahydrofuran at room temperature to afford chiral oxazine (1*R*)-1-phenyl-2-[(1'*R*)-1'-phenylethyl]-2,3-dihydro-1H-naphtho[1,2-*e*][1,3]oxazine **27** in excellent yield.



**Scheme 7:** Synthesis of (1*R*)-1-Phenyl-2-[(1'*R*)-1'-phenylethyl]-2,3-dihydro-1Hnaphtho[1,2-*e*][1,3]oxazine and its aminonaphthols

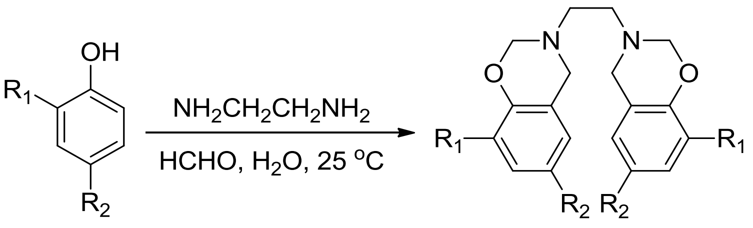
On achieving the synthesis of this chiral oxazine the authors transformed it into different chiral aminonaphthols. The opening of the *N-O* cyclic acetal with organometallic reagents allow the introduction of a variety of *N*-substituents on the aminonaphthols. The compound **27** was treated with different Grignard reagents, the addition of the alkyl/aryl group at the *N-O* cyclic acetal carbon atom to obtain the (*R*,*R*)-aminonaphthols **28**.

A different method is also used to open the *N-O* cyclic acetal ring, the chiral oxazine **27** was treated with sodium borohydride and acetic acid in tetrahydrofuran at 0 °C to afford the compound 1-[(1*R*)-phenyl{methyl[(1'*R*)-1'-phenylethyl]-amino}methyl]-2-naphthol **29** in good yield.

## Synthesis of Bis-Oxazines:

### Synthesis of 1,2-bis(2H-benzo[e]-1,3-oxazin-3(4H)-yl)ethanes:

Nath and co-workers have synthesized a series of bis-1,3-oxazines with various phenols in water.[23]



**30** **31**

$R_1R_2$ = H, Cl

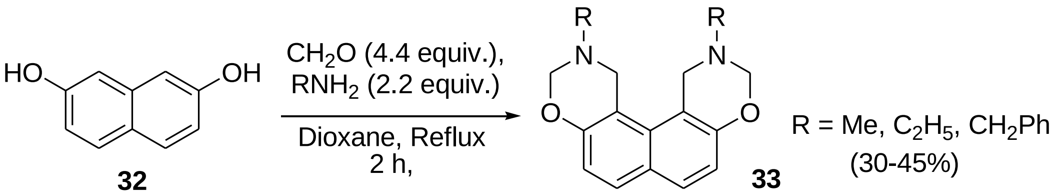
(70-87%)

**Scheme 8:** Synthesis of 1,2-bis(2H-benzo[e]-1,3-oxazin-3(4H)-yl)ethanes

The reaction of phenols with the solution of ethylenediamine and formaldehyde in water for 30 min at 25 °C afforded the differently substituted compounds 1,2-bis(2H-benzo[e]-1,3-oxazin-3(4H)-yl)ethanes **31** in excellent yield. These compounds were screened for the biological activity and were found to have significant *in vitro* antimicrobial effect.[8d]

### Synthesis of dihydro-1,3-bisoxazine derivatives:

In 1959 Urbanski and co-workers had synthesized dihydro-1,3-bisoxazines with primary amines and formaldehyde to study their biological properties[8b,c,d] [**Scheme-9**].



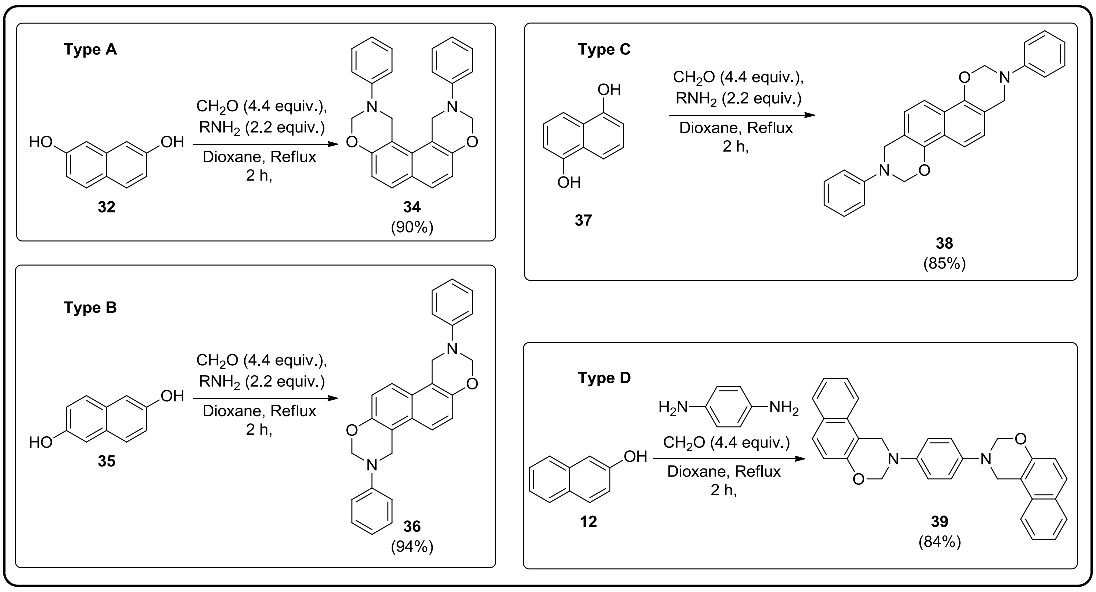
**32** **33**

**Scheme 9:** Synthesis of dihydro-1,3-bisoxazines derivatives

The series of 1,3-bisoxazines were screened for the biological activity, particularly were found to posses antitumor and antibacterial activities.

**Synthesis of dihydro-1,3-bisoxazine derivatives**:[14]

Interest in these molecules was renewed in 1996, when Ishida and co-workers screened them for synthesis of polyfunctional polymers.[14] A series of hydroxyl naphthalenes were converted to these derivatives and studied [**Scheme 10**].

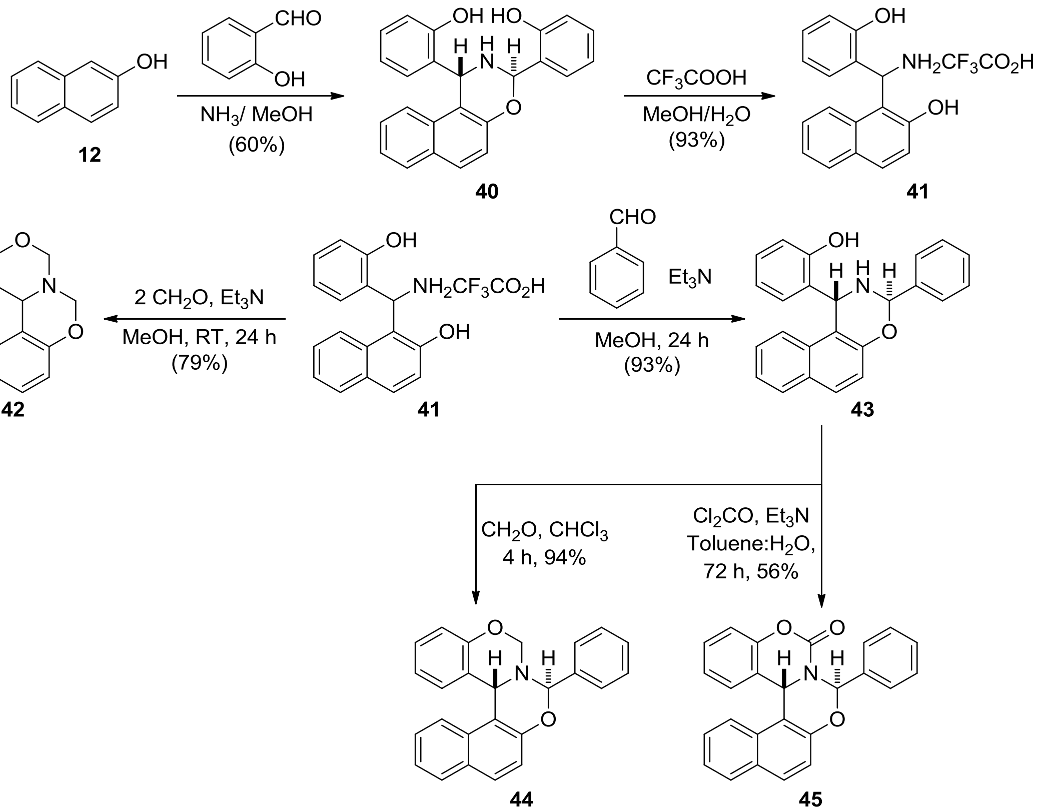


**Scheme 10:** Synthesis of Dihydro-1,3-bisoxazines derivatives

A series of bis-naphthoxazines were synthesized from different binaphthols, formaldehyde and primary amines include 2,11-diphenyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene **34** [**Type-A**], 3,9-diphenyl-2,3,4,8,9,10-hexahydro-naphtho[1,2-*e*:5,6-*e*']bis([1,3]oxazine) **36** [**Type-B**], 2,8-dophenyl-1,2,3,7,8,9-hexahydronaphtho[2,1-*e*:6,5-*e*']bis([1,3oxazine) **38** [**Type-C**] and 1,4-bis(1*H*-naphtho[1,2-e][1,3]oxazine-2(3*H*)-yl)benzene **39** [**Type-D**]. The authors found all the compounds were obtained in a excellent yields and their thermal studies showed the compound **38** [**Type-C**] could be successfully cured and give void-free resin[14i] probably due to its linear structure.

### Synthesis of naphth[1’,2’:5,6]-[1,3]oxazino[3,4-c][1,3]benzoxazine 42, (8R*,15bS*)-8-phenylnaphth[1,,2,:5,6][1,3]oxazino[3,4-c][1,3]benzoxazine 44 and (8R*,15bS*)-8-phenylnaphth[1’,2’:5,6][1,3]oxazino[3,4-c][1,3]benzoxazin-10-one 45:

Fulop and Kleinpeter have synthesized fused bisoxazines with each other and with its derivatives from the Betti Base. The structures of these oxazines were similar to the structure of the [5]helicene. The structural and conformational analysis of these molecules was studied by molecular modelling experiments [**Scheme-11**].[24]



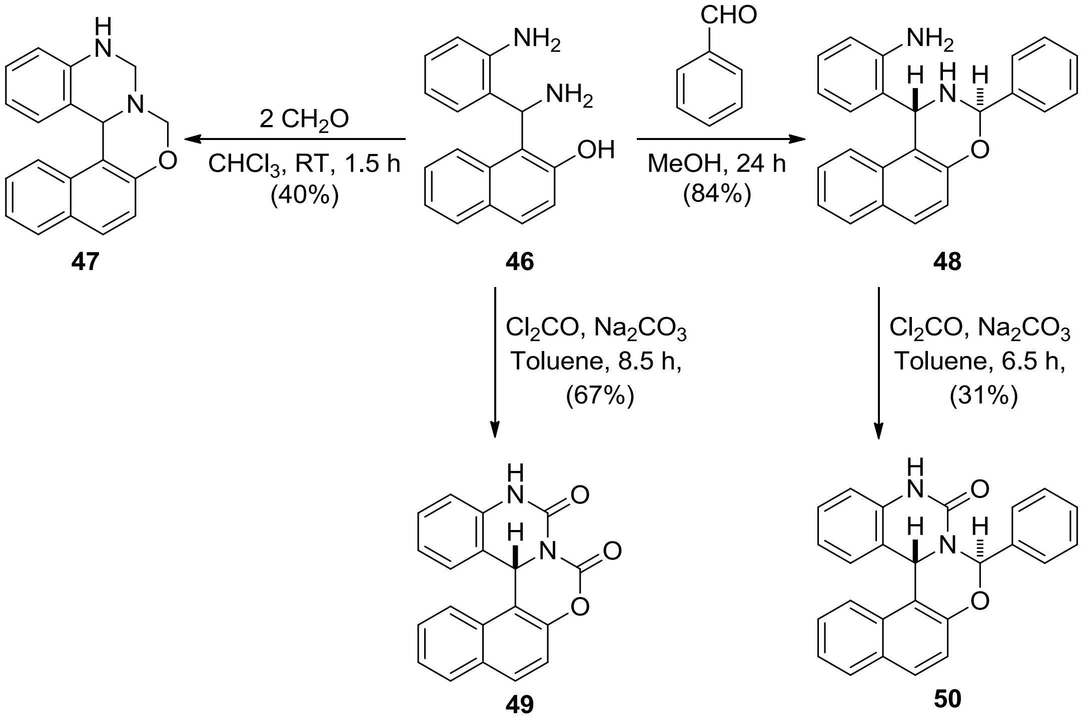
**Scheme 11:** Synthesis of [1,3]-oxazine containing [5]helicene like molecules **44** and **45**

The compound 1,3-di(2-hydroxyphenyl)-2,3-dihydro-1*H*-naphth-[1,2-*c*][1,3]-oxazine **40** was synthesized from β-naphthol, salicylaldehyde and methanolic ammonia solution to in excellent yield. The oxazine **40** was treated with trifluoroacetic acid to obtain 1-α-amino-(2-hydroxyphenyl)methyl-2-naphthol trifluoroacetate **41** as a salt of trifluoroacetic acid.

The compound 1-α-amino(2-hydroxyphenyl)methyl-2-naphthol•trifluoro-acetate **41** was treated with the triethylamine and excess of formaldehyde in methanol to form the [5]helicene like structure of the product naphth[1’,2’:5,6][1,3]-

oxazino[3,4-*c*][1,3]-benzoxazine **42** in good yield. The compound **41** was also treated with the equimolar amount of the triethyl amine and salicylaldehyde in methanol at room temperature for 24 h to give a mono [1,3]-oxazine product such as 1-(2-hydroxyphenyl)-3-phenyl-2,3-dihydro-1H-naphth[1,2-*c*][1,3]oxazine **43** which was converted to (8R*,15bS*)-8-phenylnaphth-[1',2':5,6][1,3]-oxazino[3,4-*c*][1,3]-benzoxazine by using a solution formaldehyde in methanol in an excellent yield.

The compound 1-(2-hydroxyphenyl)-3-phenyl-2,3-dihydro-1*H*-naphth[1,2-*c*][1,3]-oxazine **43** was treated with phosgene to obtain the product (8R*,15bS*)-8-phenylnaphth[1',2':5,6][1,3]oxazino[3,4-*c*][1,3]benzoxazin-10-one **45**. Subsequently, the authors have used *ortho*-nitrobenzaldehyde in place of salicylaldehyde and protected amines instead of ammonia solution to obtain the intermediate compound 1-[amino-(2-aminophenyl)methyl]-2-naphthol **46** [**Scheme-12**].[25]



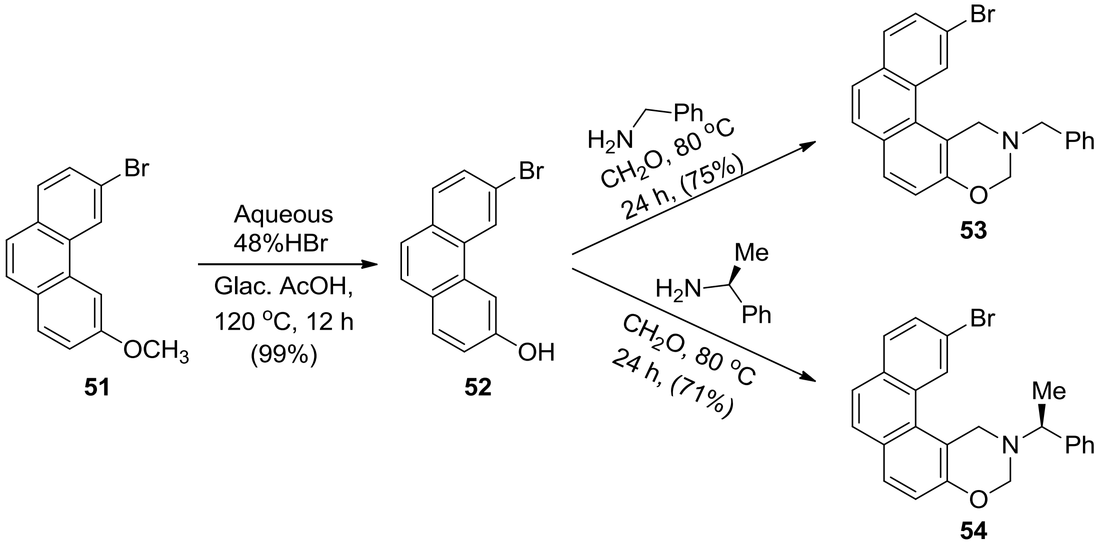
**Scheme 12:** Synthesis of [1,3]-oxazine containing [5]helicene like molecule **47** and its keto-derivatives **49** and **50**

The intermediate compound 1-(amino-(2-aminophenyl)methyl)-2-naphthol **46** was treated with excess of formaldehyde in chloroform at ambient conditions to obtain the [5]helicene like compound 10,11-dihydro-8*H*,15b*H*-naphth[1,2-*e*][1,3]oxazino[3,4-*c*]quinazoline **47** in a moderate yield. The authors also converted **47** to 2-(phenyl)-4-(2-hydroxynaphthalen-1-yl)-1,2,3,4-tetra-hydroquinazolines **48** using one equivalent of benzaldehyde in methanol at room temperature in excellent yield. After the synthesis of 2-(phenyl)-4-(2-hydroxynaphthalen-1-yl)-1,2,3,4-tetrahydroquinazolines **48** this compound was treated with phosgene in presence of a base at room temperature to obtain (8*R**,15b*S**)-phenyl-10,11-dihydro-8*H*,15b*H*-naphth[1,2-*e*][1,3]oxazino[3,4-*c*]quinazolin-10-one **50**. The compound **47** was separately treated with phosgene to afford 10,11-dihydro-8*H*,15b*H*-naphth[1,2-*e*][1,3]oxazino[3,4-*c*]quinazolin-8,10-dione **49** in good yield. All these compounds **48**, **49** and **80** were studied by the aid of molecule modelling from the point of view of theoretical aspects.

# Result and Discussion

The oxazines are useful class of compounds and the element of chirality can be easily introduced in its framework. In the present work we intend to introduce an additional element of chirality by giving a helical shape to the oxazine containing molecules.

The design of helically shaped 1,3-oxazine is based on the construction of the heterocyclic ring on the *ortho* fused aromatic ring system. Initially phenanthrene was chosen for this purpose and the 1,3-oxazine was synthesized from its hydroxyl derivative **52** [**Scheme-13**]. Two derivatives **53** and **54** were synthesized from benzyl amine and (*S*)-α-methylbenzyl amine respectively. The molecules prepared were fully characterized by usual spectral and analytical techniques.



**Scheme 13:** Synthesis of 11-bromo-2-methyl-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene **53** and 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene **54**

In this scheme two types of 1,3-oxazines were synthesized, the starting material 3-bromo-6-hydroxyphenanthrene **52** was obtained from the previously prepared 3-bromo-6-methoxyphenanthrene **51** by improved photocyclization methodology, discussed earlier.[26,27] The sample of 3-bromo-6-methoxyphenanthrene **51** was treated with the aqueous HBr solution in glacial acetic acid to obtain the product 3-bromo-6-hydroxyphenanthrene[28] **52** in excellent yield.

The phenol **52** was then converted to 1,3-oxazine **53** (11-bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene) with benzyl amine and formaldehyde in moderate yield. The compound **53** was fully characterized by the standard analytical techniques. The $^1$H-NMR spectrum shows the three singlet signals for the oxazine -$CH_2$ protons such as Ph-C$\underline{H}_2$-N- protons at δ 3.80, Ar-C$\underline{H}_2$-N at δ 4.86 and the N-C$\underline{H}_2$-O at δ 4.99. The characteristic internal aromatic proton of the phenanthrene *ortho* to -Br was observed as a downfield singlet at δ 8.43.

The presence of bromine atom helped its crystal quality and the single crystal X-ray diffraction analysis indicated a small bite angle $\theta$ (~12°) between the planes of the two terminal rings of the phenanthrene system in **53** [**Figure-2**]. However, the chiral phase HPLC analysis using Diacel OD-H column showed only one peak. This did not conclusively confirm the presence of helical isomers on **53** in solution at ambient conditions [**Figure-3**].

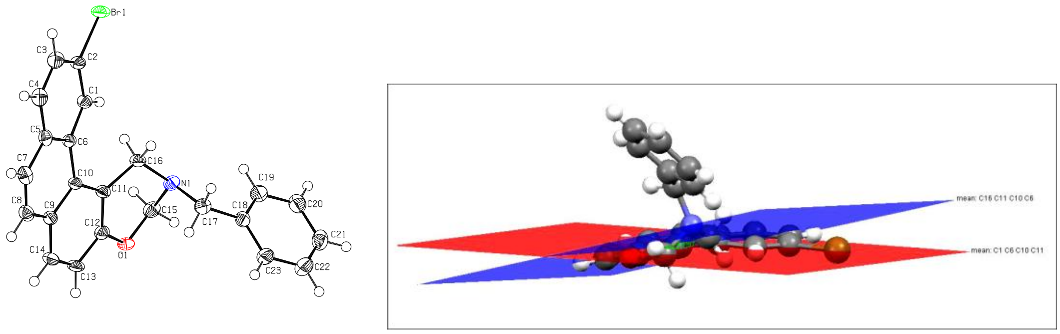


**Figure 2:** ORTEP diagram of the compound 11-bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene **53** with atom numbering scheme (50% probability factor for the thermal ellipsoids) and calculate the angles between two planes

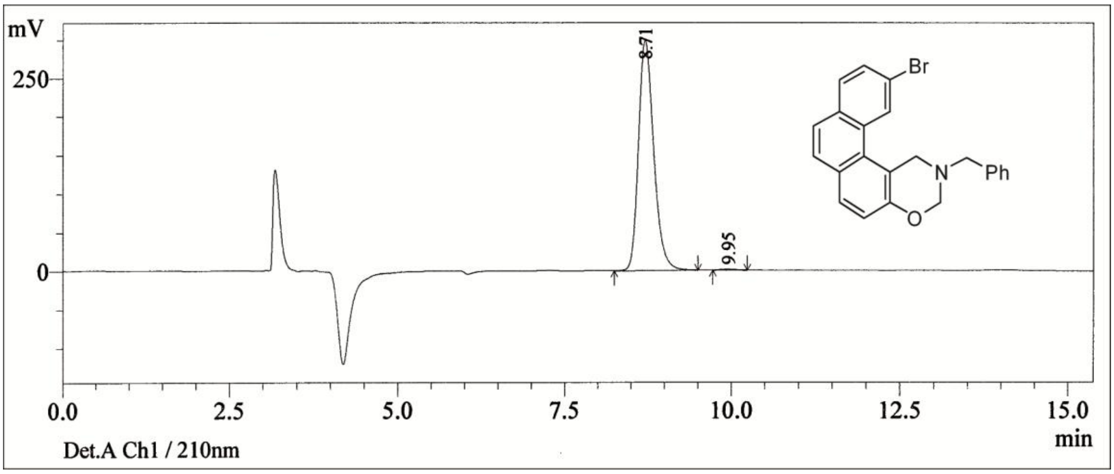


**Figure 3:** Chiral HPLC graph of 11-bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene **53**

The variable temperature $^1$H-NMR was also done for this compound **53** to study its helical stability. However it was seen that at low temperature the protons of the oxazine ring get merged with each other but do not separate [**Figure-4**].

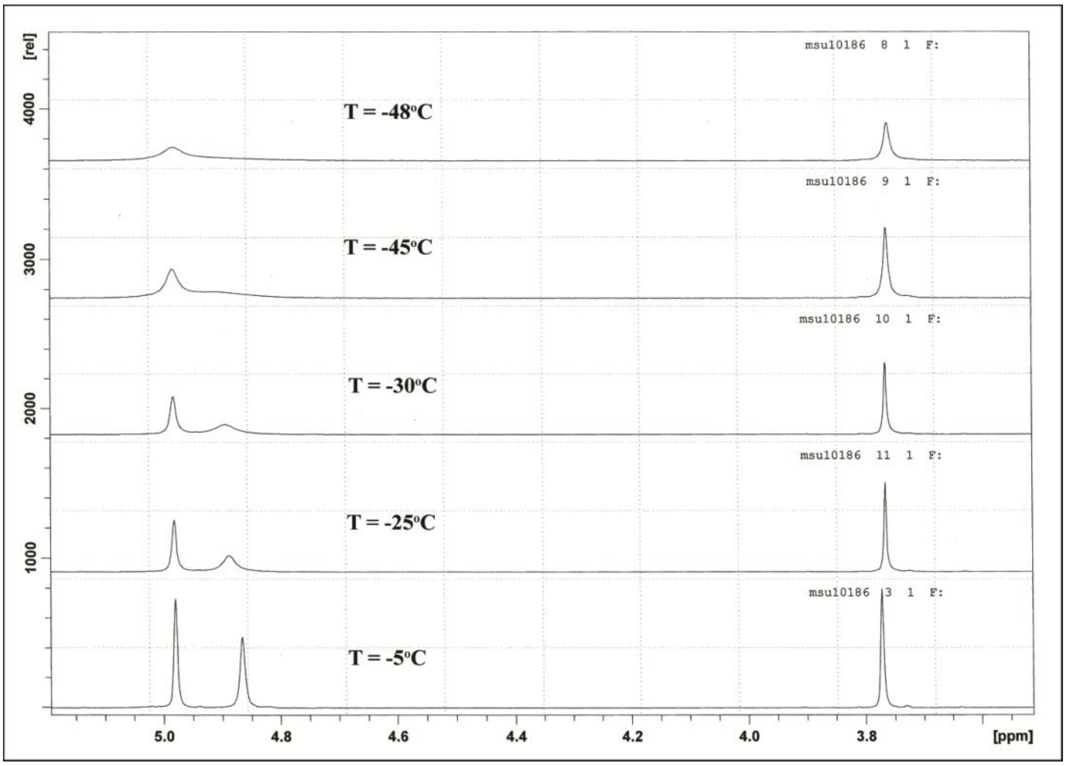


**Figure 4:** Cryogenic Variable temperature $^1$H-NMR of 11-bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene **53**

The EI-mass spectrum of the molecule **53** showing the *m/z* 405 $[M+2]^{\cdot+}$, *m/z* 404 $[M+1]^{\cdot+}$ and 403 $[M]^{\cdot+}$ peaks and the further stable fragmentations of continuous cleavage of $[Ph\text{-}CH_2]^{\cdot+}$ at *m/z* 312, $[\text{-}Br]^{\cdot+}$ at *m/z* 233, $[\text{-}N\text{-}CH_2]^{\cdot+}$ at *m/z* 205 and $[\text{-}O\text{-}CH_2]^{\cdot+}$ at *m/z* at 175. The base peak observed at *m/z* 204 for $[\text{phenanthryl-}O\text{-}CH_2]^{\cdot+}$ stable fragment of the compound **53**.

The IR spectrum of the compound **53** showing the peak at 2850 cm$^{-1}$for Ar-H stretching, peak at 1621-1587 cm$^{-1}$ for aromatic -C=C- stretching, peak at 1135 cm$^{-1}$ for -C-N- stretching of tertiary amine, peak at 1247-1207 cm$^{-1}$ for -C-O- stretching.

Another derivative of similar oxazine was synthesized by using a chiral amine instead of benzyl amine, we chose (*S*)-α-methylbenzyl amine, and formaldehyde. Thus the synthesis of 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene **54** was achieved under the similar conditions.

The NMR analysis of **54** was slightly different due to the presence of the chiral center in the molecule. The $^1$H-NMR of this compound showed four *dd* of each proton of the oxazine ring of the two protons of -CH$_2$ groups. Two doublets were seen at δ 5.14 (*J* = 10.0 Hz, 1H), and 4.91 (*J* = 10.0 Hz, 1H) attributing to the methylene protons of -N-C$\underline{H}_2$-O- linkage.

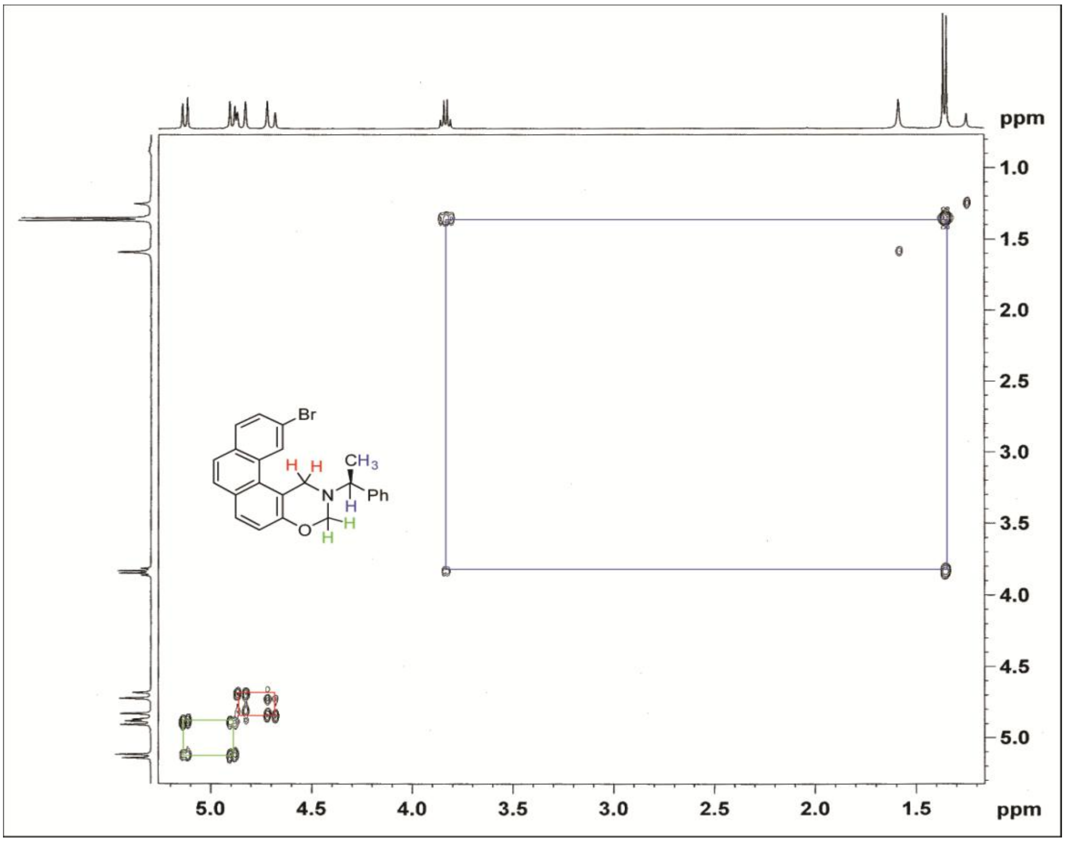


**Figure 5:** $^1$H-$^1$H COSYGPSW correlation spectrum of the **54**

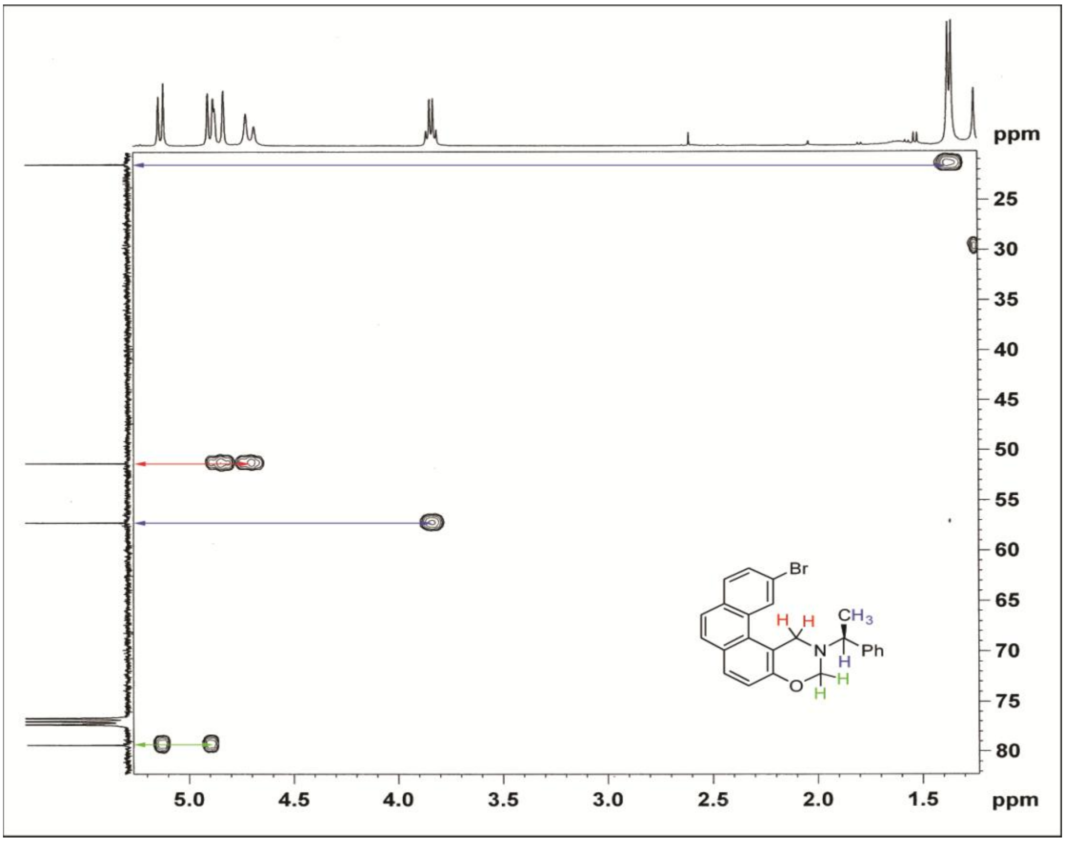


**Figure 6:** $^1$H-$^{13}$C HSQCGP correlation spectrum of the **54**

Same molecule was also characterized by the HSQCGP ($^1$H-$^{13}$C Correlation) and COSYGPSW ($^1$H-$^1$H Correlation) to find out the correlation of these protons with the carbons. The doublets observed at δ 4.88 ($J$ = 16.0 Hz, 1H) and δ 4.77 ($J$ = 15.6 Hz, 1H) for the -$CH_2$ of Ar-C$\underline{H}_2$-N- protons while its correlation is shown here [**Figure-5** and **6**].

The stability of the conformation of compound 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene **54** was studied by the variable temperature $^1$H-NMR analysis, we found that the diastereomeric oxazine -C$\underline{H}_2$ protons did not merge with each other even at higher temperature (up to 50 °C) [**Figure-7**]. Introduction of the element of chirality by selecting the chiral amine affected the conformational change in the [1,3]-oxazine ring in the compound 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene.

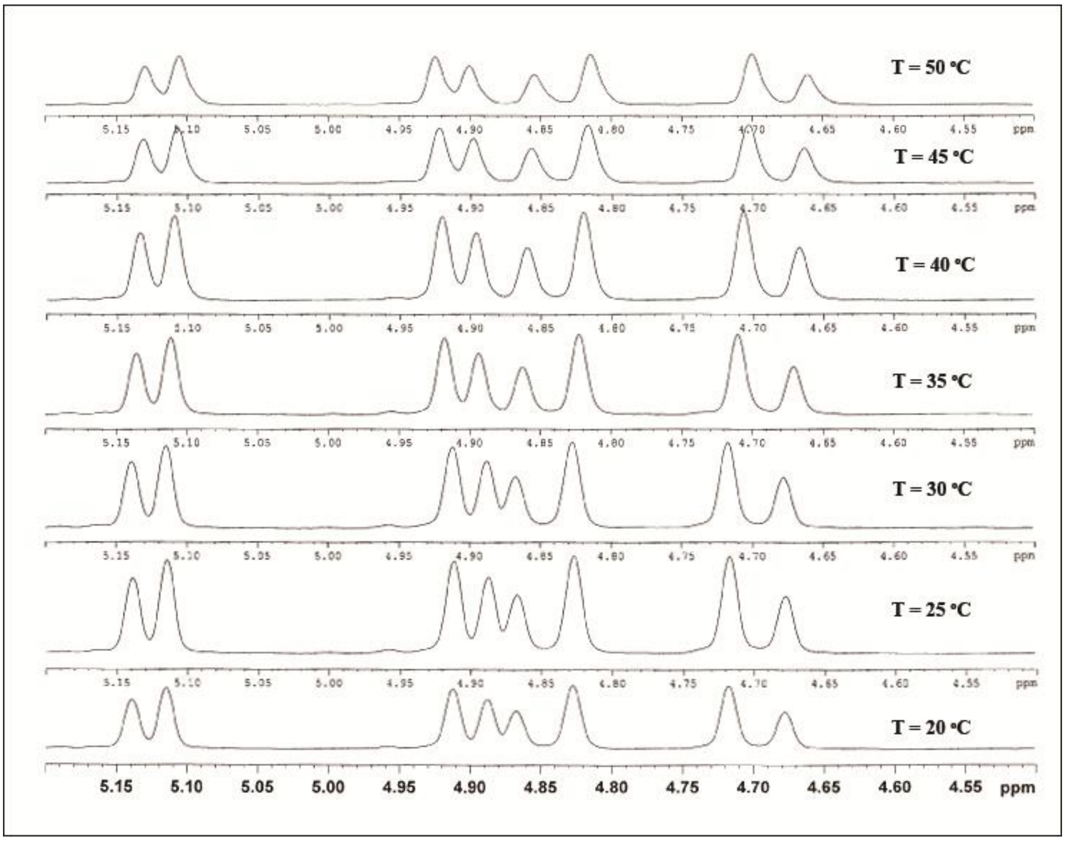
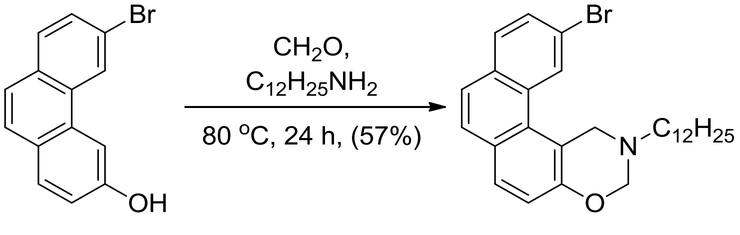


**Figure 7:** Variable temperature$^1$H-NMR of compound **54** for the stability study

During the course of the present work another oxazine with a long chain attached to its nitrogen such as dodecylamine was synthesized. Hence, the compound 11-bromo-2-dodecyl-2,3-dihydro-1*H*-phenanthro[4,3-*e*][1,3]oxazine **55** was prepared and characterised with the usual spectroscopic techniques [**Scheme-14**]. However this compound also did not show the required helical twist while the $^1$H-NMR signal of both hydrogen atoms of Ar-C$H_2$-N showed a single singlet.

The EI-mass spectrum of the molecule **54** showing the *m/z* 419 $[M+2]^{\cdot+}$, *m/z* 418 $[M+1]^{\cdot+}$ and 407 $[M]^{\cdot+}$ peaks and the further stable fragmentations of continuous cleavage of $[-CH_3]^{\cdot+}$ at *m/z* 402, $[-Ph-CH]^{\cdot+}$ at *m/z* 313, $[-N-CH_2]^{\cdot+}$ at *m/z* 285 and $[-O-CH_2]^{\cdot+}$ at *m/z* at 175. The base peak observed at *m/z* 204 for the $[\text{phenanthryl-O-}CH_2]^{\cdot+}$ stable fragment of the compound **54** supported the structure.

The IR spectrum of the compound **54** showed the peaks at 3051, 2857 cm$^{-1}$for -C-H stretching, peak at 1599-1503-1430 cm$^{-1}$ for aromatic -C=C- stretching, peak at 1125 cm$^{-1}$ for -C-N- stretching of tertiary amine, peak at 1212 cm$^{-1}$ for -C-O- and 1125 cm$^{-1}$ for -C-O-C- stretching.

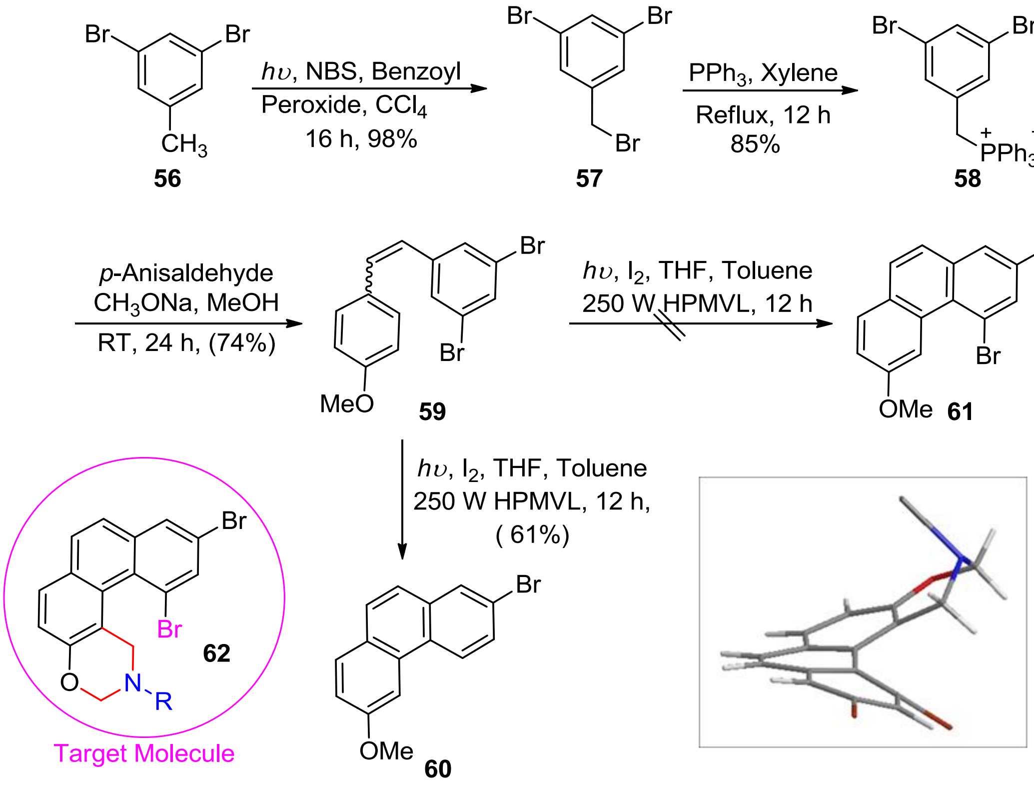


**52** **55**

**Scheme 14:** Synthesis of 11-bromo-2-dodecyl-2,3-dihydro-1*H*-phenanthro[4,3-e][1,3]oxazine

In this strategy we failed to synthesize any helically shaped phenanthrene fused oxazines stable at the ambient temperature. In order to achieve this objective we need to increase bulk at the inner portion of the phenanthrene ring to create the helical twist. With this aim another molecule **62** was designed where the inside bromine may provide the requisite bulk and give a twist in the compound. Attempts were made to prepare this compound as shown in the **scheme 15**. The starting material for the synthesis of **62** will be 2,4-dibromo-6-hydroxypenanthrene. This phenanthrene derivative shows the bite angle of 38.5° on the basis of basic energy minimization using MMP2 programme [**Scheme-15**].

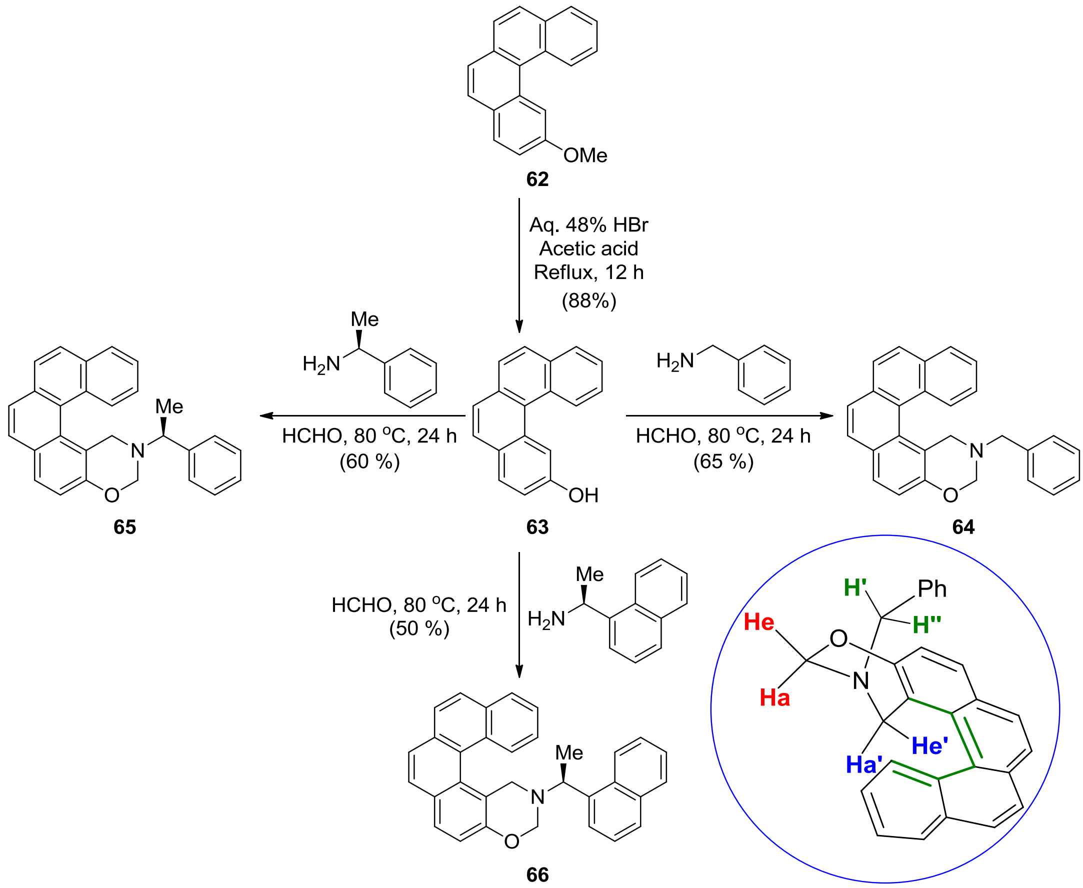
The synthesis of 2,4-dibormo-6-methoxyphenanthrene **61** was planned to start from the 3,5-dibromotolunene **56**, which was converted to 3,5-dibromobenzylbromide **57** by benzylic bromination with NBS in good yield. The compound **57** was then converted to its Wittig salt 3,5-dibromobenzyltriphenylphosphonium bromide **58**, which was used for Wittig reaction with *p*-anisaldehyde to obtain 1,3-dibromo-5-(4-methoxystyryl)benzene **59** in a good yield.



**Scheme 15:** Attempted synthesis of 2,4-dibromo-6-methoxyphenanthrene **61**

The styryl derivative **59** was cyclized with our improved methodology to obtain a white solid crystalline compound. However its $^1$H-NMR and the mass spectral analysis clearly indicated the loss of one of the bromine atoms. Such observation of a loss of a halogen in photolysis is reported in the literature.[29] The $^1$H-NMR analysis confirmed the loss of the internal bromine at 4-position during photocyclization. Hence the target compound **62** could not be synthesized.

In order to achieve a stable helical structure perhaps it is required to add one more aromatic *ortho* fused ring in the above system [**Scheme-16**]. This synthesis will require 2-hydroxybenzo[*c*]phenanthrene **63** as the phenol to build the desired 1,3-oxazine system. In the present study this phenol was efficiently synthesized from the 2-methoxybenzo[*c*]-phenanthrene **62** by cleavage of alkyloxy group using the aqueous HBr in glacial acetic acid. The required 2-hydroxybenzo[*c*]phenanthrene **63** was synthesized and then converted to the corresponding [1,3]-oxazine derivatives by the Mannich reaction with primary amine and formaldehyde. Three different amines, one benzyl amine and two chiral α-methylbenzyl amines were selected to prepare three derivatives of oxazine attached to benzo[*c*]phenanthrene.



**Scheme 16**: Synthesis of three derivatives of 1,3-oxazine anchored to benzo[*c*]phenanthrene

The reaction of 2-hydroxybenzo[*c*]phenanthrene **63** with benzyl amine and excess of formaldehyde under the standard condition gave 2-benzyl-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **64** in good yield. The structure of the compound **64** was further studied by the spectroscopic techniques to determine the shape of the molecule [**Scheme-16**].

The $^1$H-NMR spectrum of this molecule **64** indicated that the -C$\underline{H}_2$- protons of the [1,3]-oxazine ring and the -C$\underline{H}_2$Ph groups appeared as doublets and or as doublet of doublet. The tentative assignment of the protons of **64** is given in Fig. 8. The $^1$H-NMR spectrum of **64** showed the internal protons of the -CH$_2$- group He' and Ha' having a significant difference in the position of ~ 2.1 ppm. Usually the equatorial proton were found at the deshielding zone as compare to geminal axial proton but in this molecule these protons appear at the shielding zone (δ 2.95-2.90). This could be because the proton He' is positioned in the ring current and is highly shielded. Another dd was observed due to further, long range 'W' type 1,4 coupling with the coupling constant $J$ = 1.84 & 16.64 Hz. Other proton on the same carbon atom was observed at the δ 5.03-4.99 ppm as a doublet having the coupling constant *J* = 16.64 Hz [**Figure-8**].

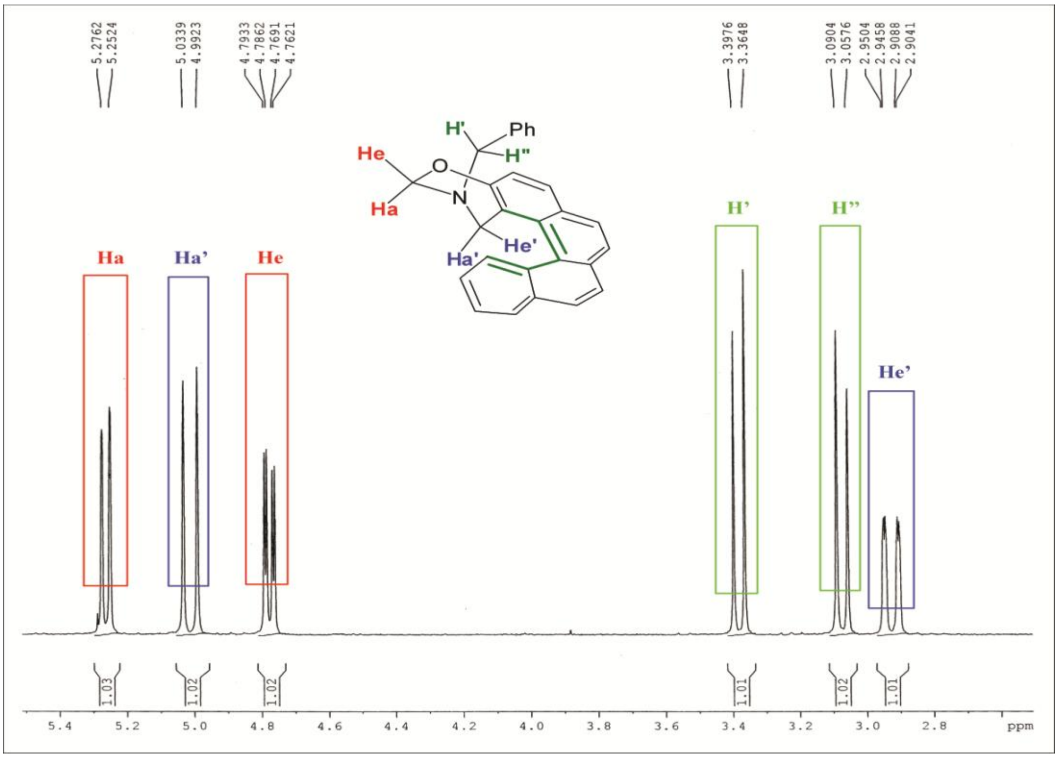


**Figure 8:** Enlarge $^1$H-NMR spectrum of aliphatic region of 2-benzyl-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **64**

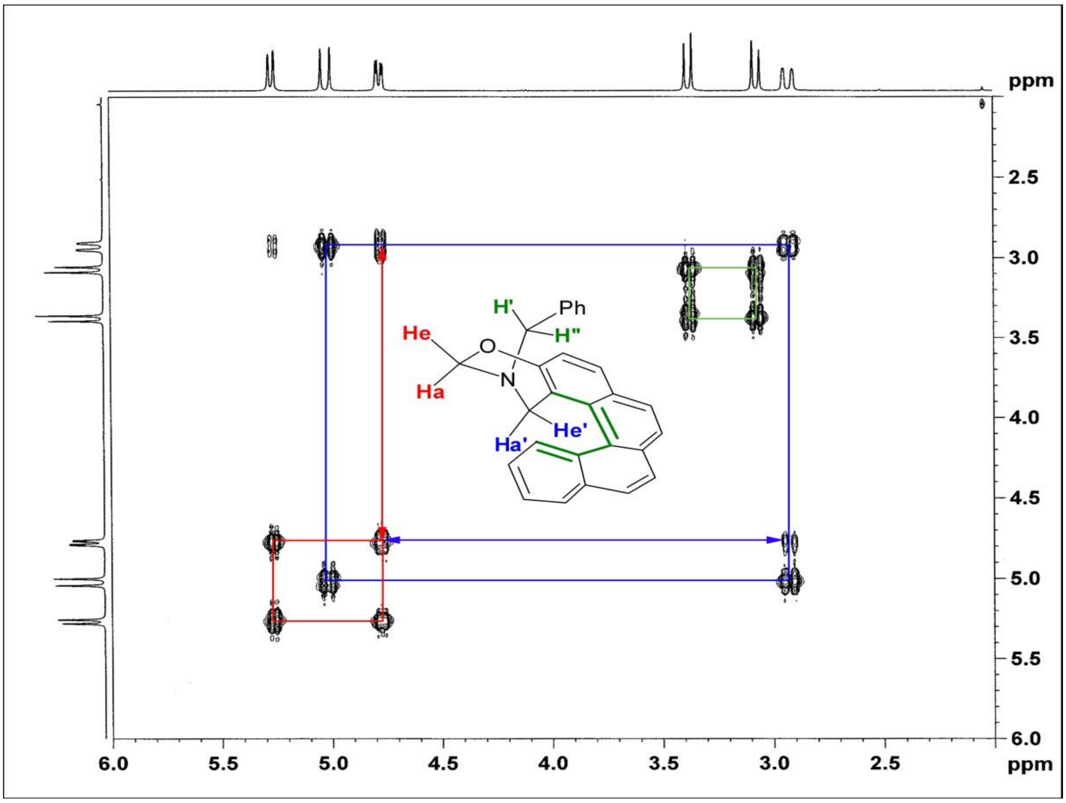


**Figure 9:** $^1$H-$^1$H COSYGPSW correlation spectrum of 2-benzyl-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **64**

The benzylic protons Ph-C$\underline{H}_2$-N- were observed as two separate doublets at δ 3.37 and 3.07 with the coupling constant of 13.12 Hz for the protons H' and H'' respectively (in Fig. 9). At the same time the protons of -N-C$\underline{H}_2$-O- were observed as d at δ 5.27 for Ha having the coupling constant of 9.52 Hz for Ha and another d at δ 4.77 for He having the coupling constant 2.84 and 9.68 Hz due to long range coupling or 'W' shape coupling with the proton He' and observed at the up-field, there is possibility that the proton will be shielded in the ring current of the aromatic ring. The 2D NMR techniques such as $^1$H-$^1$H COSY and $^1$H-$^{13}$C HSQCGP were also applied to further establish the correlation of the all the -C$\underline{H}_2$ protons of the oxazine ring system [**Figure-9** and **10**].

The EI-mass spectrum of the molecule **64** showing the *m/z* 376 $[M+1]^{\cdot+}$ and 375 $[M]^{\cdot+}$ peaks and the further stable fragmentations of cleavage of $[Ph-CH_2-N-CH_2]^{\cdot+}$ and the corresponding fragments observed at *m/z* 119 and *m/z* 236 respectively.

In the IR spectrum of the molecule **64** as peak observed at 3028 cm$^{-1}$ for Ar-H stretching, 2843 cm$^{-1}$ for -C-H stretching, 1591-1486 cm$^{-1}$ for aromatic -C=C- stretching and 1126 cm$^{-1}$-C-O stretching vibrations.

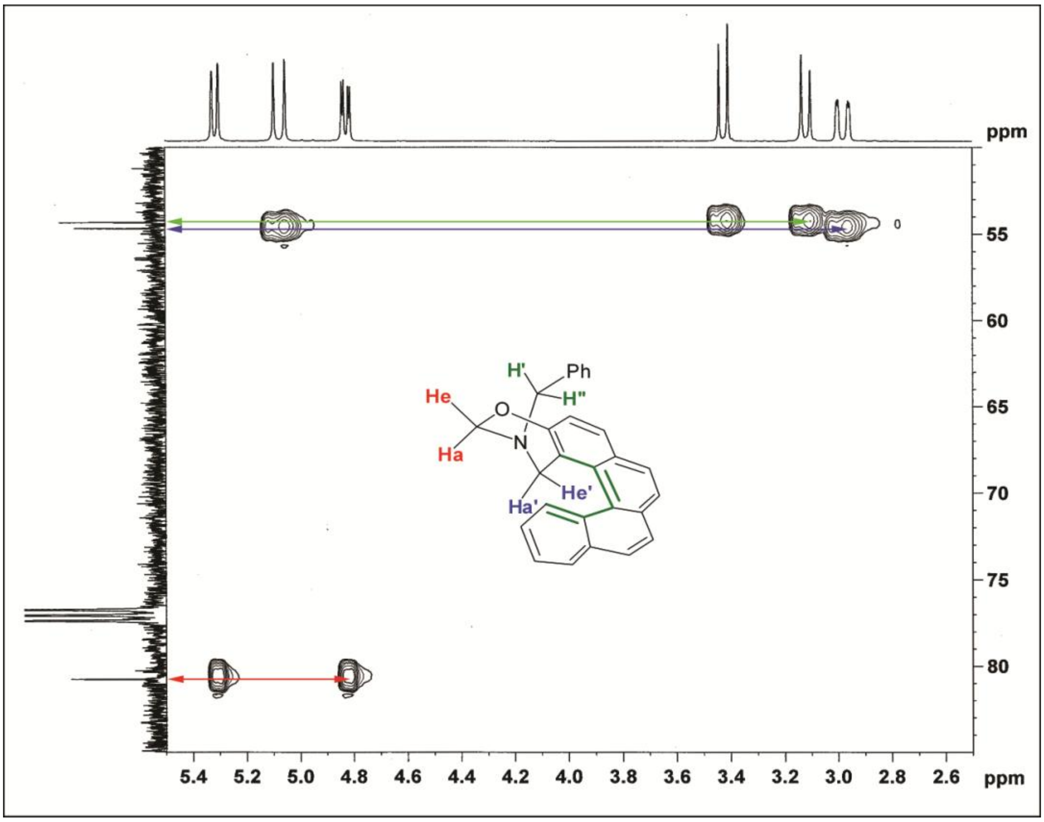


**Figure 10:** $^1$H-$^{13}$C HSQCGP correlation spectrum of 2-benzyl-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-e][1,3]oxazine **64**

Having established the structure of **64** by spectral analysis it was necessary to determine the exact shape of the helical form and its bite angle. It was possible for us to grow good quality crystal of this compound and its structure was determined by single crystal X-ray diffraction analysis. The ORTEP diagram and the intersection of the two phases passing through the terminal aromatic rings is presented in **Figure 11**.

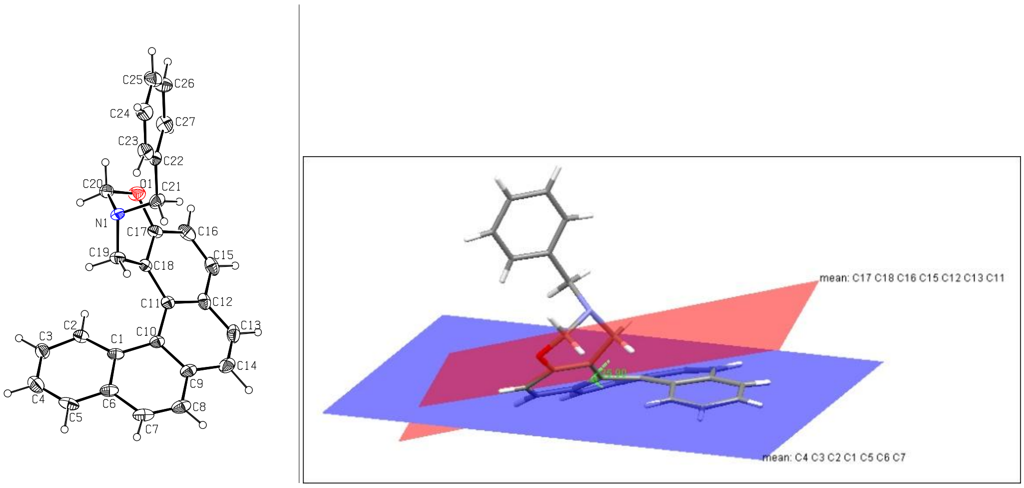


**Figure 11:** ORTEP diagram of the compound with atom numbering scheme (50% probability factor for the thermal ellipsoids) and the calculated planes for the crystal of **64**

The helical shape of this compound is clearly visible and the healthy bite angle of about ~ $36^{o}$ is seen between the last two rings, or over C1-C10-C11-C18 (planes C17-C18-C16-C15-C12-C13-C11 and C4-C3-C2-C1-C5-C6-C7) part of the molecule [**Figure-11**].

The two isomers obtained were stable and can be isolated on chiral phase HPLC column (Chiralcel OD-H). The HPLC chart is reproduced in **Figure-12**, where the isomers have ample separation. However our analysis of **64** on different chiral phase HPLC column as well as under different solvent systems never resulted in the separation of two isomers to the base line. This probably is due to the possible presence of dynamic equilibrium between the two helical isomers of **64** in the solution state at ambient condition of the analysis.

From the above results we can conclude that a synthesis of helical [1,3]-oxazine with separable diastereomeric isomers is achieved. However for the practical applications separation of their helical isomers is crucial. To felicitate the separation of oxazine isomers, it was planned to prepare diastereomeric oxazine with a hope of feasible separation of these isomers because of the presence of additional chiral element.

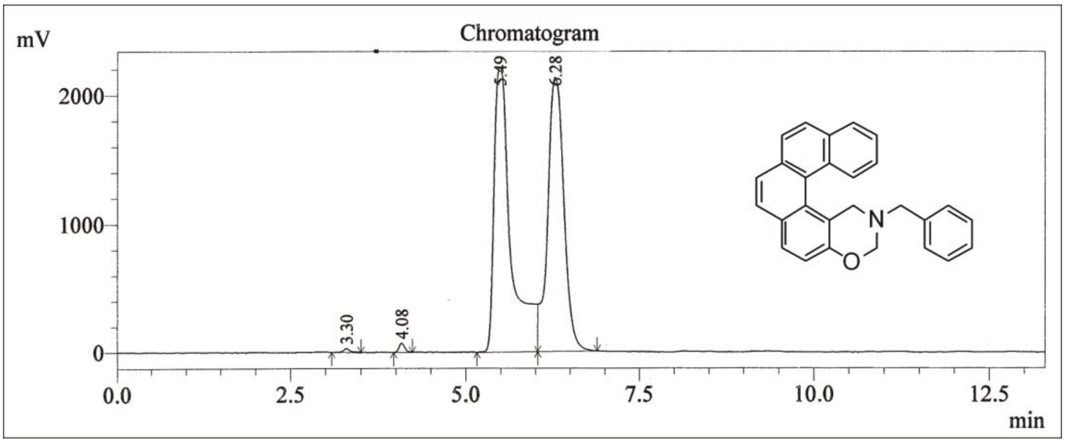


**Figure 12:** Chiral HPLC chromatogram of 2-benzyl-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **64**

With this aim similar strategy of synthesis of oxazine attached to benzo[*c*]phenanthrene was followed with phenol **63** and two different chiral amines, shown in **Scheme 16**.

The reaction of 2-hydroxybenzo[*c*]phenanthrene **63** with (*S*)-α-methylbenzylamine and excess of formaldehyde under similar reaction condition gave the compound (*S*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **65** in a good yield. Interestingly the compound **65** did show two close spot on tlc, however, our attempts to separate those two spots, presumable of the two diastereomers, by careful column chromatography were not successful. The $^1$H-NMR analysis shows presence of the mixture of the diasteromers in the ratio of 57:43.

Since the separation of diastereomers of **65** was not successful the other analogous compound **66** was also prepared in reasonable yield from phenol **63** and (*S*)-(-)-1-(1-naphthtyl)ethylamine/formaldehyde. However, isomers of (*S*)-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **66** also showed almost equal properties in tlc and were not separable on column chromatography. The $^1$H-NMR analysis of **66** showed the mixture of the diasteromers in the ratio of 60:40, with only a marginal improvement of the diastereomers compared to **65**. The diastereomeric ration of this compound was also established by HPLC analysis using chiral column [**Figure-13**].

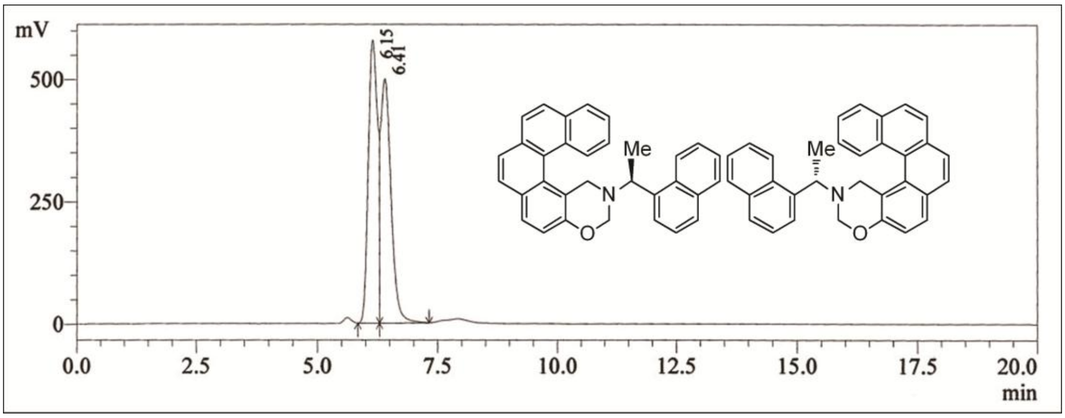
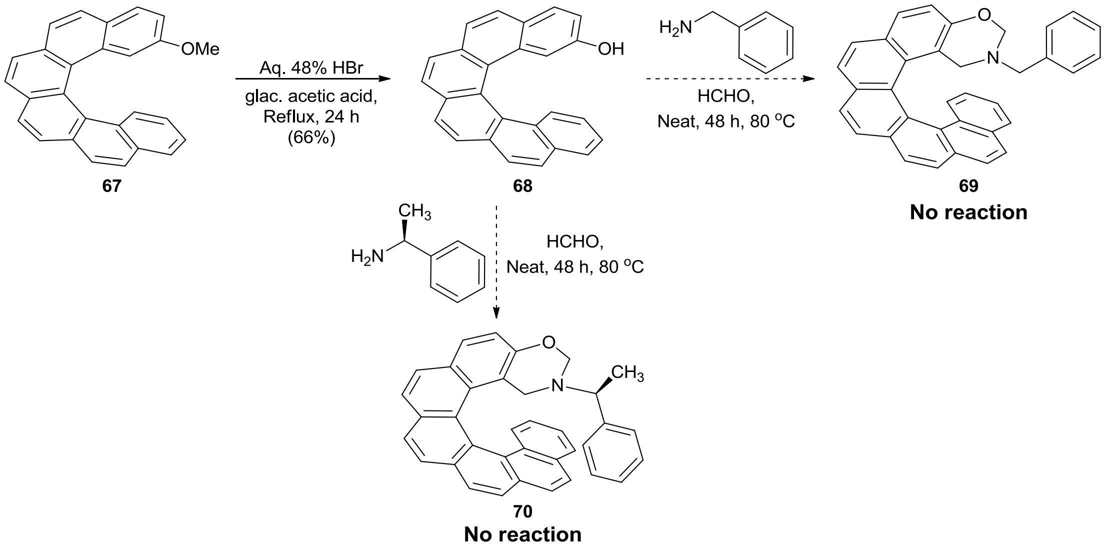


**Figure 13:** Chiral HPLC chromatogram of diastereomeric mixture of (*S*)-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-*e*][1,3]oxazine **66**

Since the isomers of **65** and **66** were not separable the design of the molecules needed alteration. It was felt to add an extra aromatic ring on the *ortho* fused ring system to build the required bulk. With this aim it was planned to prepare oxazine system with six ortho fused aromatic ring system and for this purpose the starting phenol selected was 2-hydroxy[6]helicene **68**. This phenol **68** was synthesized from the previously prepared 2-methoxy[6]helicene **67**.

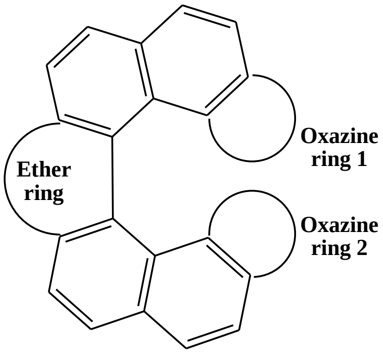
The methoxy group of 2-methoxy[6]helicene **67** was cleaved with concentrated HBr in glacial acetic acid, under reflux condition and the product 2-hydroxy[6]helicene **68** was quickly purified over silica gel column chromatography [**Scheme-17**].



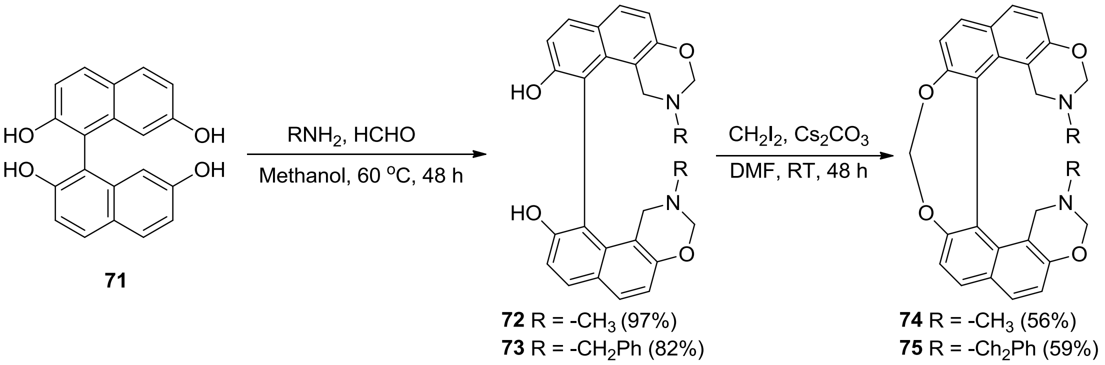
**Scheme 17:** Attempted synthesis of helical mono-oxazine[7]helicene

However, the reaction of 2-hydroxy[6]helicene **68** with two primary amines such as benzylamine and chiral (*S*)-α-methylbenzyl amine under similar condition did not furnish expected products, **69** and **70** respectively.

With the understanding of the structural requirements of the synthesized mono-oxazines another class of similar systems were designed. In this class two oxazine rings were placed at the two ends of the helical framework. The helical framework was based on the binaphthalene system fused on a central ether ring, schematically represented below.



The synthesis of such rings will begin from a binaphthalene unit with appropriate substituents to enable us to build the required hetero cyclic rings. Accordingly, the 7,7’-dihydroxy-2,2’-binaphthol **71**[30] was converted to the required atropisomeric intermediates **72** and **73** [**Scheme-18**].



**Scheme 18:** Synthesis of 2,2'-dimethyl-2,2',3,3'-tetrahydro-1H,1'H-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol **74** and helical bis-oxazine **75**

The reaction of 7,7’-dihydroxy-2,2’-binaphthol **71** with the excess of formaldehyde and methylamine in methanol gave the compound 2,2'-dimethyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol **72** in an excellent yield. The compound **72** was then transformed to the methylene bridged helicene-like compound **74** by using diiodomethane and suitable base in good yield,[31] both these compound were fully characterized by usual spectral and analytical techniques.

The $^1$H-NMR analysis of compound **72** showed a singlet at δ 5.06 for the two hydroxyl protons, a doublet at δ 4.74 (*J* = 9.2 2H) and another doublet at δ 4.61 (*J* = 9.2 Hz, 2H) for the 4H of the two hydrogens of each methylene of –N-C$\underline{H}_2$-O. At the same time the hydrogens of the –C$\underline{H}_2$ group of Ar-CH$_2$-N- of the oxazine ring appear as doublet at δ 3.63 (*J* = 16.8 Hz, 2H) and another doublet at δ 3.19 (*J* = 16.8 Hz, 2H). There was no doublet of doublet observed of the long range (1,4)-“W” type coupling in this molecule.

The EI-mass spectrum of the molecule **72** showing the *m/z* 429 $[M+1]^{\cdot+}$ and 428 $[M]^{\cdot+}$ peaks and the further continuous stable fragmentations of cleavage of $[-CH_3]^{\cdot+}$ at *m/z* 398, $[(-CH_3-N)_2]^{\cdot+}$ at *m/z* 370, and the base peak observed at *m/z* 58.

In the IR spectrum of compound **72** the peak observed at 3464 cm$^{-1}$ for -OH group, 1613-1519 cm$^{-1}$ for aromatic -C=C- stretching, peat at 1345 cm$^{-1}$ for -N-CH$_3$ and 1302 cm$^{-1}$ -C-O stretching vibrations.

The $^1$H-NMR spectra of the helicene-like molecule **74** shows a singlet at δ 5.64 ppm for two equivalent hydrogens of the methyl bridge –C$\underline{H}_2$ of –O-C$\underline{H}_2$-O. The doublet at δ 4.53 with a coupling constant of 9.2 Hz for 2H and double of doublet similar to the compound **64** observed at δ 4.51-4.48 ppm having the coupling constant of 2.4 and 9.6 Hz for 2H of the -C$\underline{H}_2$ group of -N-C$\underline{H}_2$-O. The internal -C$\underline{H}_2$ group proton of Ar-C$\underline{H}_2$-N- observed at the two doublets at δ 2.66 and 2.39 each doublet having a coupling constant *J* = 16.4 Hz for 2H.

The EI-mass spectrum of the molecule **73** showing the molecular ion peak at 580 $[M]^{\cdot+}$ and the further stable fragmentations of cleavage of $[Ph-CH_2-N]^{\cdot+}$ at *m/z* 370, $[2 X (-CH_2-O)_2]^{\cdot+}$ at *m/z* 326, and the base peak observed at *m/z* 91.

The IR spectrum of compound **73** the peak observed at 3511 cm$^{-1}$ for -OH group, 1611 cm$^{-1}$ for aromatic -C=C- stretching, peak at 1343 cm$^{-1}$ for aromatic -C-O- stretching, 1138 cm$^{-1}$ -O-C- stretching for ether linkage and 1078 for -N-C- stretching vibrations.

The chiral HPLC analysis on the chiral Lux Amylose-2 column shows the two peaks at R$_t$- 8.39 min and R$_t$- 11.33 min. The analysis shows that there are two helical isomers present and the separation up to the baseline shows the stability of the isomers at ambient temperature [**Figure-14**]. The helical like isomers of **74** are not in dynamic equilibrium as in earlier cases.

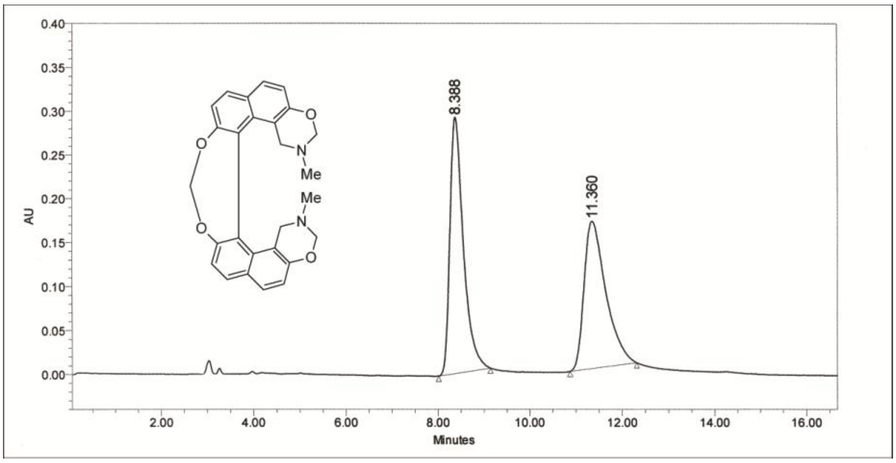


**Figure 14:** Chiral HPLC chromatogram of helical bis-oxazine **74**

Subsequently the compound 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol **73** was also synthesized by using benzylamine in place of methylamine and product was obtained in good yield. The compound **73** was transformed to the methylene bridged helical bis-oxazine compound **75** according to the earlier method.

The $^1$H-NMR analysis of compound **73** showed a singlet at δ 4.95 for the two hydroxyl protons. The -C$\underline{H}_2$ protons of -N-C$\underline{H}_2$-O observed as a doublet at δ 4.62 (*J* = 9.6 Hz for 2H) and another doublet at δ 4.48 (*J* = 9.2 Hz for 2H). The broad singlet at δ 3.53 was for benzylic protons and the two protons of -C$\underline{H}_2$ group of Ar-CH$_2$-N- showed two doublets at δ 3.46 and 3.20 (*J* = 16.8 Hz) for the of the oxazine ring.

The EI-mass spectrum of the molecule **74** showing the molecular ion peak at 440 $[M]^{\cdot+}$ and the base peak observed at *m/z* 439. The molecule was also analysed by MALDI-TOF-MS and showed the mass *m/z* 441.1183 ($[M+H]^{\cdot+}$).

The IR spectrum of compound **74** showed the peak at 3070 cm$^{-1}$ for aromatic -C-H stretching, 2951, 2890 cm$^{-1}$ for -C-H stretching, 1610 cm$^{-1}$ for aromatic -C=C- stretching, peak at 1362 cm$^{-1}$for –C-N- for -N-CH$_3$, peak at 1236 cm$^{-1}$ for aromatic -C-O- stretching, 1127 cm$^{-1}$ -O-C- stretching for ether linkage and 1050 for -N-C- stretching for *tert*-amine group vibrations.

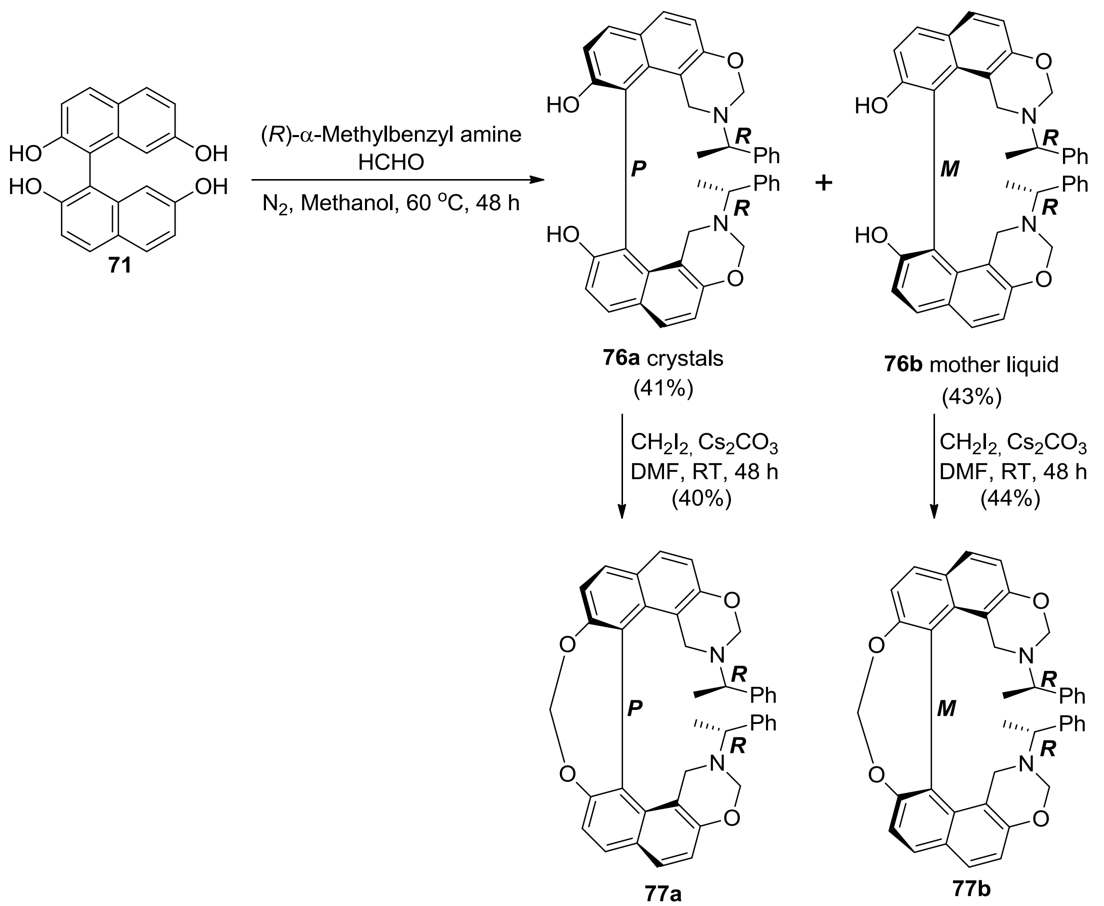
The $^1$H-NMR of helical bis-oxazine **75** showed a singlet at δ 5.59 for methylene bridge of -O-C$\underline{H}_2$-O. The doublet at δ 4.59 (*J* = 9.6 Hz, 2H) and a doublet of doublet similar to the compound **74** observed at δ 4.50 (*J* = 2.0 and 9.2 Hz, 2H) for the protons of the -C$\underline{H}_2$ group of -N-C$\underline{H}_2$-O. The benzylic –C$\underline{H}_2$ protons observed as two doublets at δ 3.37 and 3.24 having the coupling constant 12.8 Hz for 4H. The internal -C$\underline{H}_2$ group proton of Ar-C$\underline{H}_2$-N- observed as two doublets at δ 2.71 and 2.53 with coupling constant of 16.4 Hz for 4H.

The EI-mass spectrum of the molecule **75** showing the molecular ion peak at *m/z* 592 $[M]^{\cdot+}$ and the observed stable fragment of $[2 \text{ X } (PhCH_2N_2)]^{\cdot+}$ ion peak at *m/z* 382 and the base peak observed at *m/z* 91.

In the IR spectrum of compound **75** a peak observed at 3026 cm$^{-1}$ for aromatic -C-H stretching, 2990 cm$^{-1}$ for -C-H stretching, 1610 cm$^{-1}$ for aromatic -C=C- stretching, peak at 1363 cm$^{-1}$for -C-O- for aromatic, peak at 1236 cm$^{-1}$ for aromatic -C-O- stretching, 1127 cm$^{-1}$ -O-C- stretching for ether linkage.

Although these helicene like oxazines, **74** and **75**, were found to have stable helical shape and existed as two isomers at ambient conditions, their physical separation by column chromatography was not possible since they are enantiomeric in nature having only one chiral element present in them. For easy separation it would be necessary to introduce a second chiral element making them diastereomeric in nature and expecting them to show separate physical properties such as their solubility and chromatographic separations.

A racemic sample of 7,7’-dihydroxy-2,2’-binaphthol **71** was subjected to similar reaction of synthesis of bis-oxazine with chiral amines [**Scheme-19**]. The resulting molecule should be diastereomeric in nature due to the presence of two chiral elements, an axial chirality for the binaphthyl system and another from chiral amine. In this attempt the Mannich reaction of 7,7’-dihydroxy-2,2’-binaphthol **71** with (*R*)-(+)-α-methylbenzylamine and formaldehyde in methanol furnished a white solid. The analysis of this solid established it to be one of the single diastereomers of the expected compound, **76**. The mother liquid contained the second isomer, analysed by tlc at this stage. The purified solid material was carefully analyzed and its structure established as (*S*)-2,2'-bis((*R*)-1-phenylethyl)-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol **76a**.



**Scheme 19:** Synthesis of pure diastereomers of Helical Bis-oxaines **77a** and **77b**

The mother liquid and washings of the solid material were combined and concentrated to the obtained a brown solid, this crude product was then purified by column chromatography over silica gel to obtained the pale yellow solid, which was later established as (*R*)-2,2'-bis((*R*)-1-phenylethyl)-2,2',3,3'-tetrahydro-1H,1'H-[10,10'-binaphtho[1,2-e][1,3]- oxazine]-9,9'-diol **76b**. Both these compounds were fully characterized by the usual analytical techniques such as $^{1}$H and $^{13}$C-NMR, DEPT-90 and 135, $^{1}$H-$^{1}$H COSYGPSW and X-ray single crystal analysis for structural conformation and determination of the stereochemistry [**Figure-15** and **16**].

The good quality crystal of this solid, precipitated sample was obtained from the saturated solution of compound **76a** in acetonitrile as colourless needles. The pure crystal was analysed by single crystal X-ray diffraction analysis.

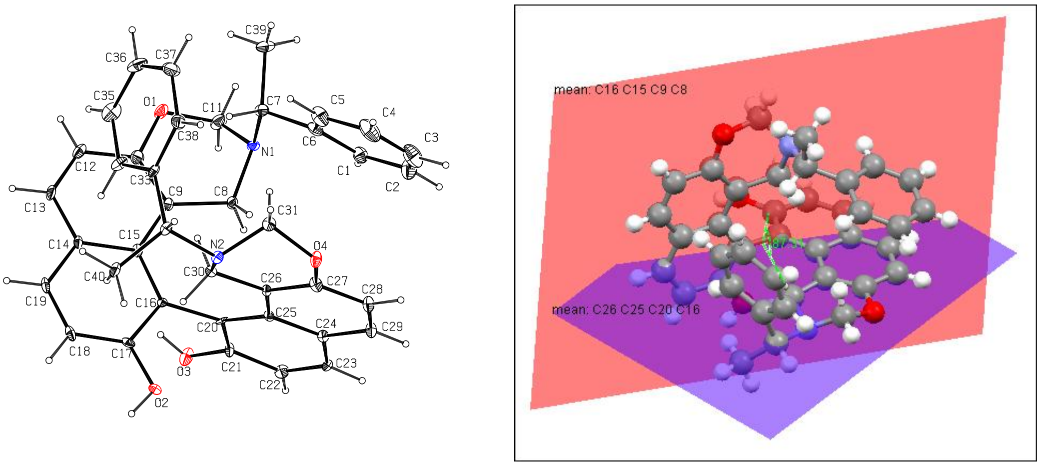


**Figure-15:** ORTEP diagram of the compound with atom numbering scheme (50% probability factor for the thermal ellipsoids) and the angle between the planes

In the X-ray diffraction analysis the angle between the planes passing through the two planes from the axis of the molecules was established. The planes C16-C15-C9-C8 and C26-C25-C20-C16 passed from the axis of the molecules and measured angle between the planes was found to be ~ 87° and the stereochemistry of the axis clearly show the *S*-configuration by considering the known chirality in the molecule from the chiral (*R*)-(+)-phenylethylamine.

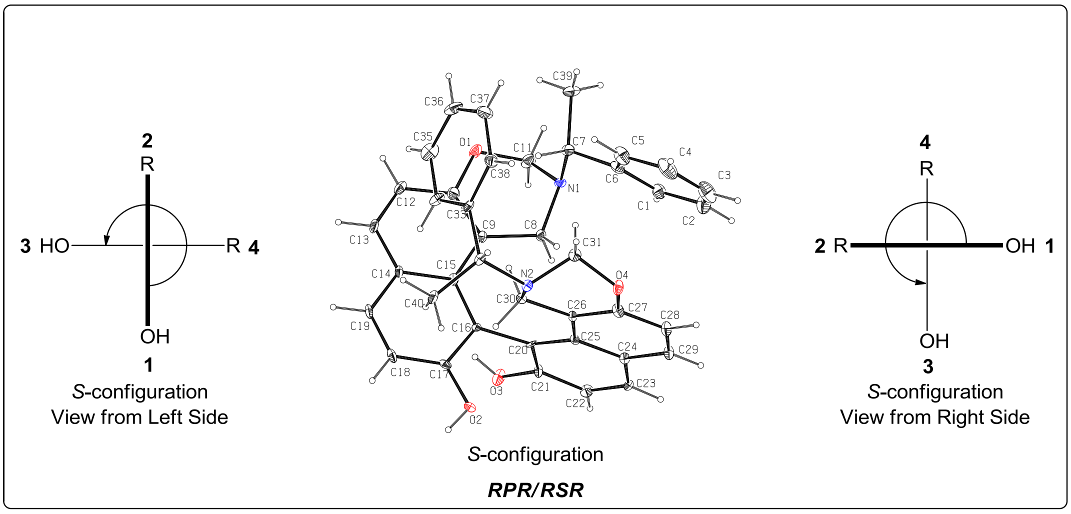


**Figure 16:** Configuration of the compound **76a** from the single crystal structure

From the crystal it was clear that the compound **76a** having the configuration *RPR* (or *RSR*), in this configuration '*P*' stands for the right handed helical chirality in the molecule.[32] The optical rotation of the pure compound **76a** (solid) was $[\alpha]_D^{28} = +$ 204 ($c$ = 0.5 in CHCl$_3$) and the optical rotation of the crude sample of **76b** (left in solution) was $[\alpha]_D^{28} = -$ 271 ($c$ = 0.5 in CHCl$_3$). From the opposite sign of the specific rotation we may conclude that the compound **76b** will be having the opposite configuration at the axis (*RMR* or *RRR)*.

The $^1$H-NMR analysis of compound **76a** shows a singlet at $\delta$ 5.02 for the two hydroxyl protons, a doublet at $\delta$ 4.60 ($J$ = 9.2 Hz, 2H) and another doublet at $\delta$ 4.45 ppm ($J$ = 9.2 Hz, 2H) for the protons of the two -CH$_2$ group of –N-C$\underline{\text{H}}_2$-O. The quartet signal for the –C$\underline{\text{H}}$ group appeared at $\delta$ 3.64-3.59 for the –Ph-C$\underline{\text{H}}$-CH$_3$. The two doublets were seen at $\delta$ 3.51 and $\delta$ 3.11 ($J$ = 16.8 Hz, 4H) for the Ar-C$\underline{\text{H}}_2$-N. There was no doublet of doublet observed similar to the compound **68** and **69** of the long range (1,4)-“W” shape coupling in this molecule.

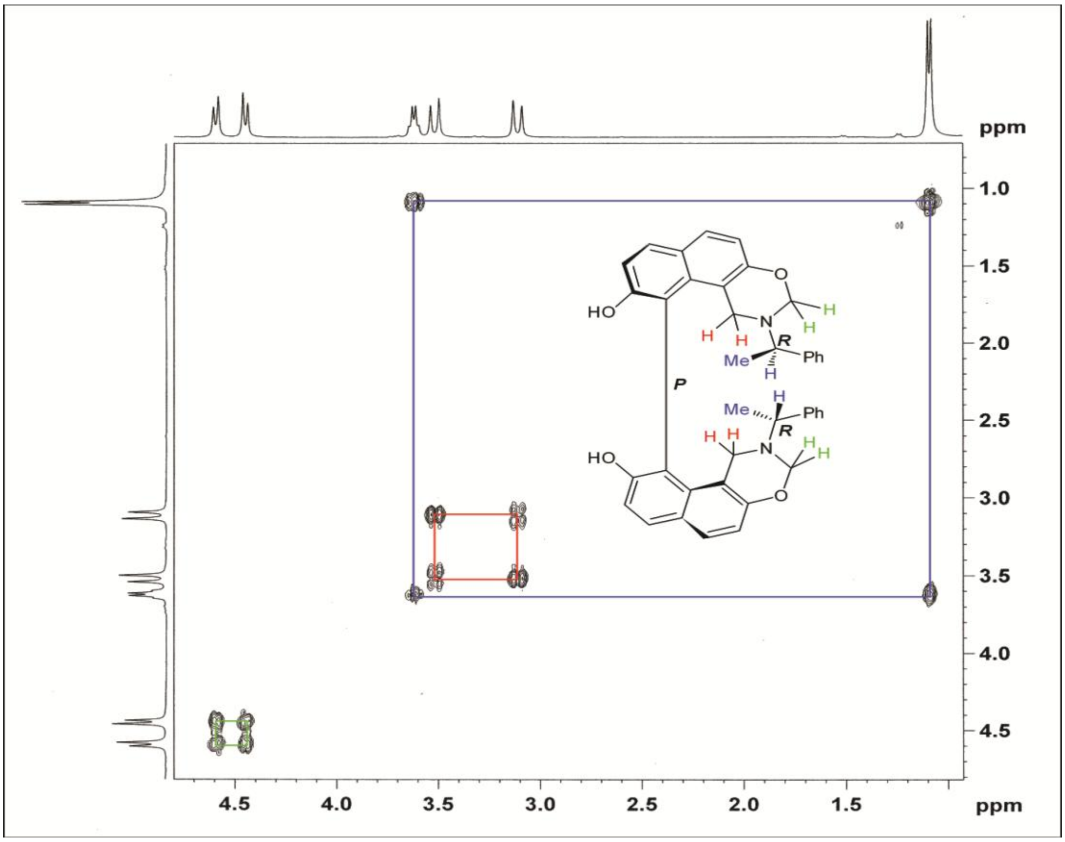


**Figure 17:** $^1$H-$^1$H COSY spectrum of the compounds **76a**

The NMR analysis for the compound **76b** shows a similar pattern but the positions of signals were slightly shifted in the spectrum. The main difference was seen in the number of protons. The internal proton of the oxazine ring such as Ar-C$\underline{\text{H}}_2$-N in **76b** were seen slightly up-field as compare to the internal protons of the oxazines of **76a**. A doublet was observed at $\delta$ 3.33 ($J$ = 17.2 Hz) for the compound **76a** for 4 H and the correlation of these protons was established by the 1H-1H COSYGPSW 2D-NMR analysis [**Figure-17** and **18**].

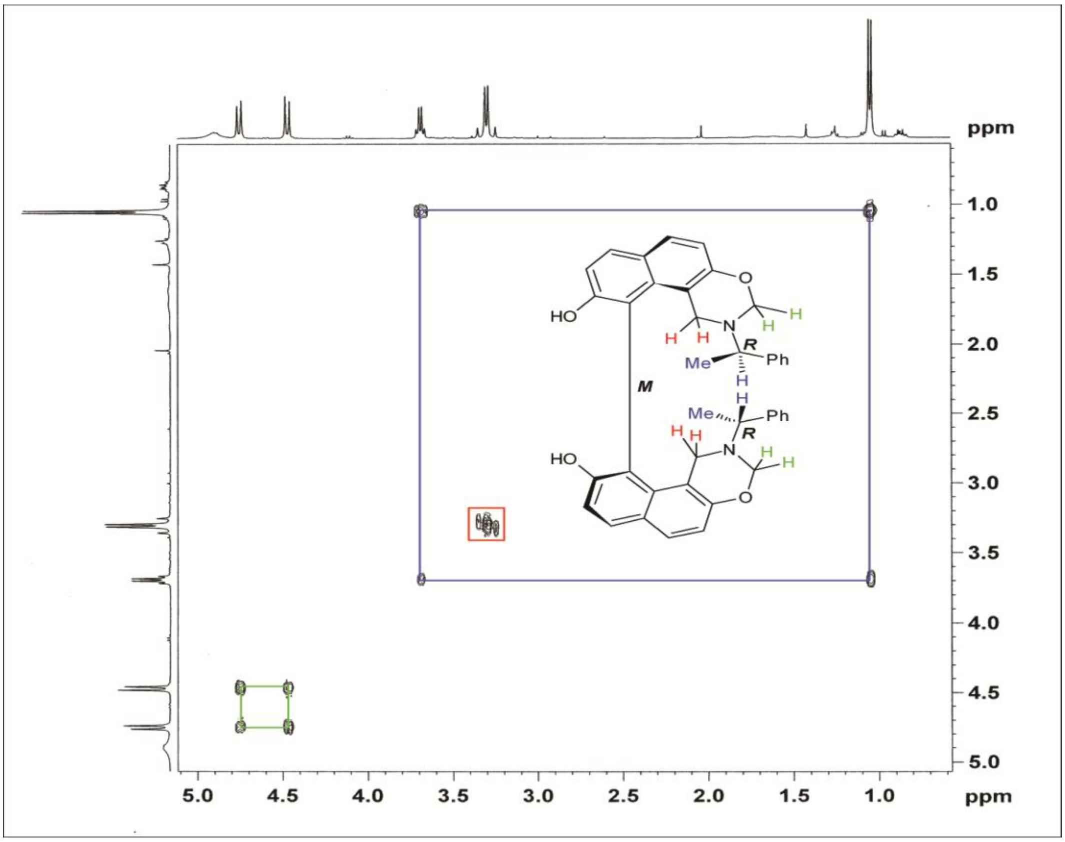


**Figure 18:** $^1H$-$^1H$ COSY spectrum of the compounds **76b**

The square marked in Figures **17** and **18** indicates the correlation of the diagonally crossed proton to each other. The internal -C$\underline{H}_2$ Protons of bis-oxazines were in the different pattern in the compound **76a** and **76b** but they are on the same diagonal and crossed each other diagonally.

The ESI-mass spectrum of the molecule **76a** and **76b** showing the similar molecular ion peak at *m/z* 610 $[M+1]^{\cdot+}$, *m/z* 609 $[M]^{\cdot+}$ but the different base peaks at *m/z* 609 and *m/z* 293 respectively.

The IR spectrum of compound **76a** showed peaks at 3509 $cm^{-1}$ for -OH group, 3058 aromatic -C-H stretching, 2976, 2884 $cm^{-1}$ for -C-H stretching, 1611 $cm^{-1}$ for aromatic -C=C- stretching, peak at 1388 $cm^{-1}$for -C-O- for aromatic, 1140 $cm^{-1}$ -O-C- stretching for ether linkage and peak at 1067 $cm^{-1}$ for -C-N- stretching frequency for *tert*-amine .

In the IR spectrum of compound **76b** the peak observed at 3496 $cm^{-1}$ for -OH group, 3060 aromatic -C-H stretching, 2926, 2889 $cm^{-1}$ for -C-H stretching, 1611 $cm^{-1}$ for aromatic -C=C- stretching, peak at 1367-1342 $cm^{-1}$for -C-O- for aromatic, and peak at 1063 $cm^{-1}$ for -C-N- stretching frequency for *tert*-amine.

The ether unit was introduced by the reaction of **76a** and **76b** with diiodomethane and suitable base at room temperature to get the two compounds of bis-oxazines **77a** (*RPR* or *RSR*) and **77b** (*RMR* or *RRR*) in a moderate yields respectively.

The $^1$H-NMR spectra of the helicene like bis-oxazine **77a** (*RPR* or *RSR*) shows a doublet at δ 4.47 (*J* = 9.6 Hz) for the oxazine protons and a doublet of doublet at δ 4.30 (*J* = 9.6 and 2.4 Hz) for the $-C\underline{H}_2$ protons of the $-N-C\underline{H}_2-O$. The internal protons of the bis-oxazine appear as a doublet of doublet at δ 2.94 (*J* = 16.8 and 1.6 Hz) and a doublet at δ 2.70 (*J* = 16.4 Hz) respectively for the $-C\underline{H}_2$ of the $Ar-C\underline{H}_2-N$.

The opposite splitting pattern was observed for the bis-oxazine (*RMR* or *RRR*) **77b**, the oxazine protons shows doublet of doublet of doublet at δ 4.89 (*J* = 9.6 and 2.4 Hz) and a doublet at δ 4.59 (*J* = 9.6 Hz) respectively for $-C\underline{H}_2$ protons of the $N-C\underline{H}_2-O$. The internal proton showed double at δ 2.53 (*J* = 16.8 Hz) and doublet of doublet at δ 2.48 (*J* = 1.2 and 16.4 Hz) respectively for $-C\underline{H}_2$ group of $Ar-C\underline{H}_2-N$.

The MALDI-TOF-MS spectrum of the molecule **77a** and **77b** showed the molecular ion peak at *m/z* 621.1390 ($[M+H]^+$) and *m/z* 621.0923. The HRMS analysis of the compounds **79a** shows the molecular ion peak at $C_{41}H_{37}N_2O_2$ ($[M+H]^+$): 621.2753, found: 621.2729.

The IR spectrum of compound **77a** showed a peak at 3059 $cm^{-1}$ aromatic -C-H stretching, 2969, 2894 $cm^{-1}$ for -C-H stretching, 1611 $cm^{-1}$ for aromatic -C=C- stretching, peak at 1371 $cm^{-1}$ for $-CH_3$ group, peak at 1325 $cm^{-1}$for -C-O- for aromatic, 1126 $cm^{-1}$ -O-C- stretching for ether linkage and peak at 1061 $cm^{-1}$ for -C-N- stretching frequency for *tert*-amine.

The IR spectrum of compound **77b** the peak observed at 2970 $cm^{-1}$ aromatic –C-H stretching, 2924, 2853 $cm^{-1}$ for -C-H stretching, 1612 $cm^{-1}$ for aromatic -C=C- stretching, peak at 1243 $cm^{-1}$for -C-O- for aromatic, and peak at 1067 $cm^{-1}$ for -C-N- stretching frequency for *tert*-amine .

Further decoupling experiment were performed by irradiating the doublet of doublet to find out the correlation between the protons for the compound **77a** [**Figure-19**]. When the proton signal at δ 4.29 was irradiated it shows the decrease in the intensity of the double at δ 4.47 and the doublet of doublet at δ 2.94 was converted to the doublet, this shows the correlation of these protons in spectrum **A**. In the spectrum **B** the proton signal at $\delta$ 2.94 was irradiated and which results in a decrease in the intensity of the doublet at $\delta$ 2.70 and the pattern of doublet of doublet at $\delta$ 4.29 changed to a doublet only. The spectrum **C** indicates that the proton signal at $\delta$ 2.70 was irradiated. As a consequence of this irradiation the proton shows decrease in the intensity of the doublet and broadening of the peak for the singlet at $\delta$ 2.94. This clearly shows the correlation of the internal proton of the –C$\underline{H}_2$ of Ar-C$\underline{H}_2$-N.

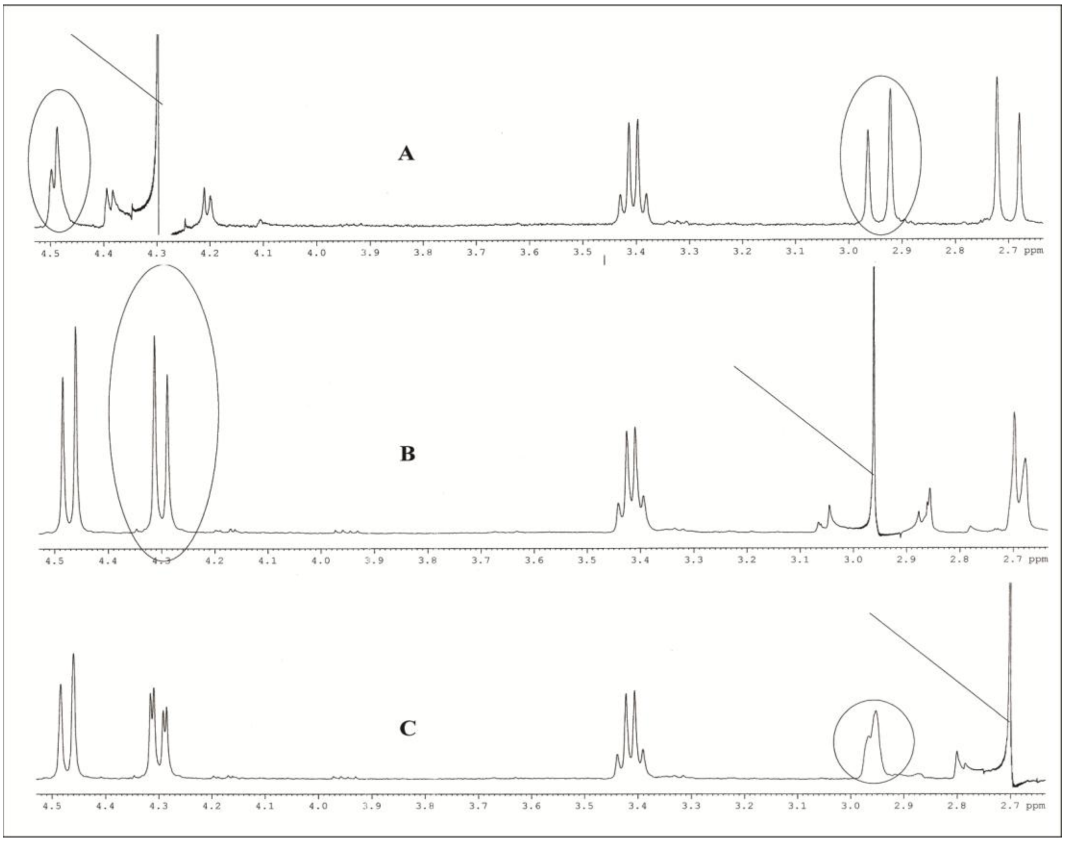
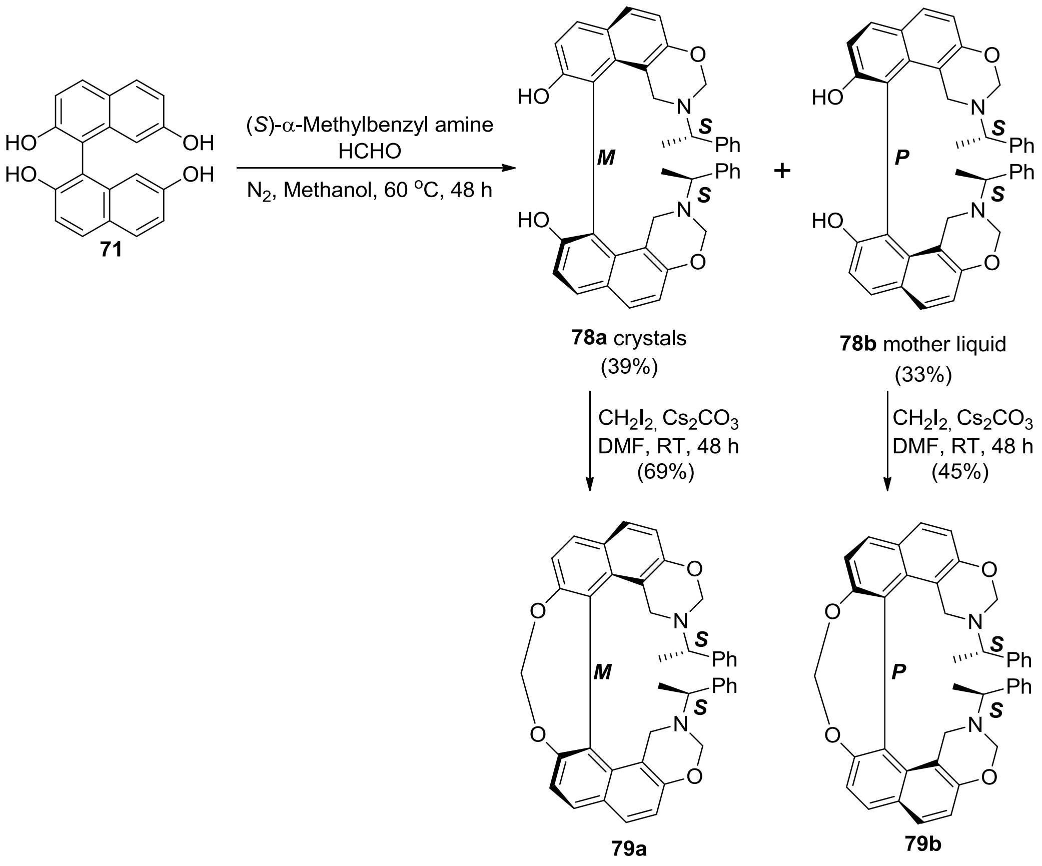


**Figure 19:** The proton decoupling experiment of helical bis-oxazine **77a**

In order to establish the relationship of the two chiral elements another set of similar compounds was prepared from **71** and the other isomer of the same amine. The other set of isomers (*R*)-2,2'-bis((*S*)-1-phenylethyl)-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol **78a** and (*S*)-2,2'-bis((*S*)-1-phenylethyl)-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol **78b** were prepared by the Mannich reaction of 7,7'-dihydroxy-2,2'-binaphthol **71** with the (*S*)-(-)-$\alpha$-methylbenzylamine and formaldehyde in methanol. Similar to the previous case the precipitated solid was washed with the methanol to obtain the white solid of **78a**. The mother liquid and the washings are combined and concentrated to the obtained the crude brown coloured solid, which was purified by column chromatography on silica gel to obtain pale yellow solid **78b** [**Scheme-20**].



**Scheme 20:** Synthesis of pure diastereomers of helical Bis-oxaines **79a** and **79b**

The compounds **78a-76a** and **78b-76b** had the identical $^{1}$H &$^{13}$C-NMR, IR and Mass but has the opposite optical rotation and opposite nature of Circular Dichroism spectra (CD Spectrum) of the similar concentrations and in the same solvent.

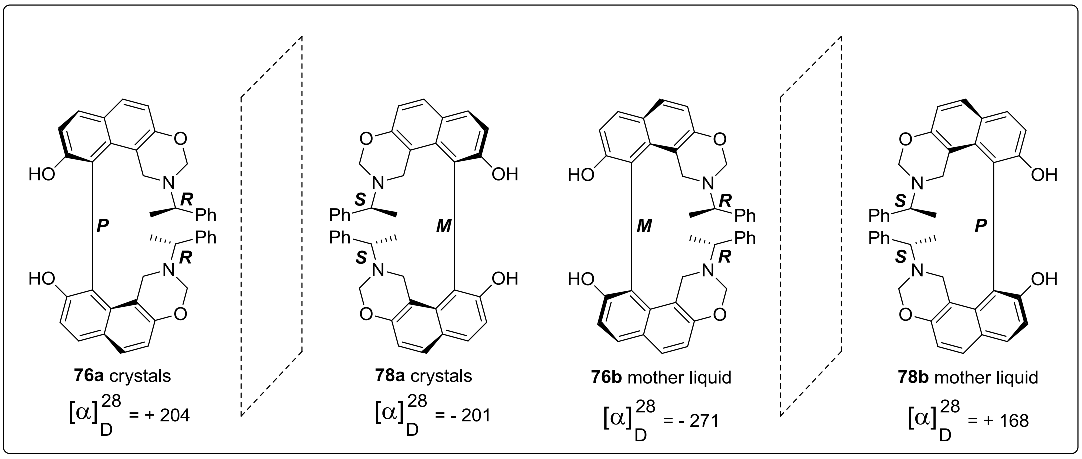


**Figure 20:** Optical rotations and enantiomer pairs of the compounds **76a-78a** and **76b-78b**

The optical rotations of the all these compounds was taken in chloroform of the concentration of 0.5% w/v of solution. The pure enantiomer **76a** and **78a** have opposite sign of optical rotation with the similar specific rotation. However, the sample of **78b** was slightly impure and hence had a small difference in its specific rotation value compared to **76b**. [**Figure-20**]. The CD spectrum of these compounds was run in chloroform, acetonitrile as well as in tetrahydrofuran. The different solvents were used other than chloroform since it has a strong absorbance in the UV range and may interfere in the analysis.

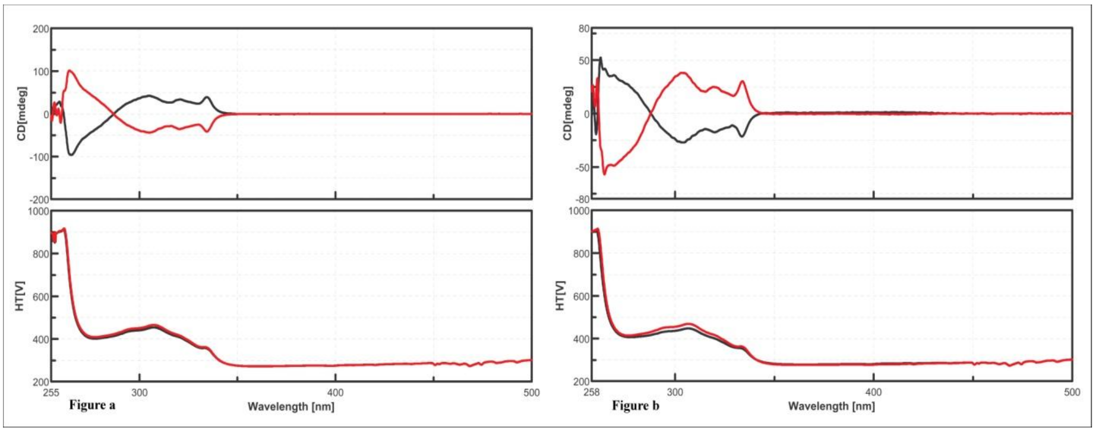


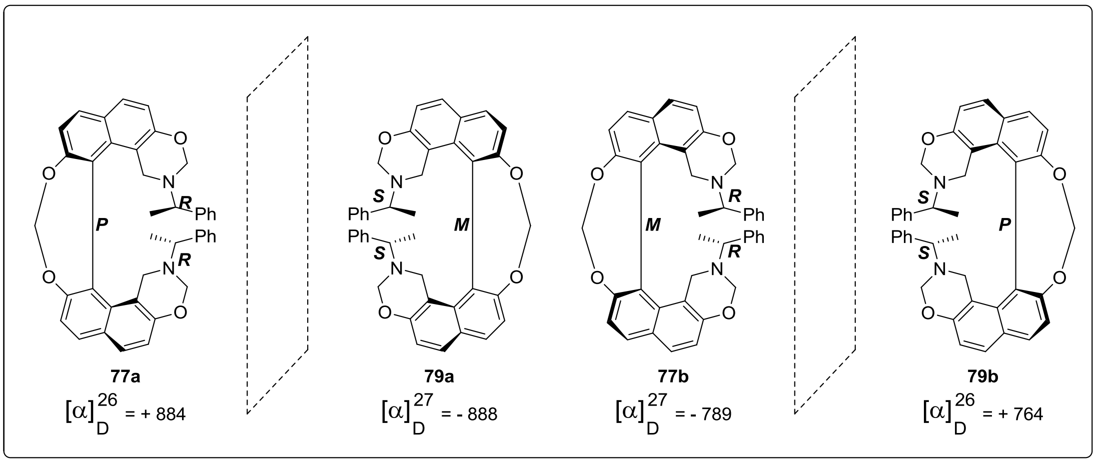
**Figure 21:** (a) Circular dichroism spectra of resolved helical bis-oxazines: (red line) **76a** and (black line) **78a** (*c* 1 x $10^{-7}$ M in acetonitrile, 25 °C) (b) Circular dichroism spectra of resolved helical oxazines: (red line) **76b**, (black line) **78b**, (*c* 1 x $10^{-7}$ M in acetonitrile, 25 °C)

The oxazines **76a-78a** and **76b-78b** show typical UV and CD spectral features [**Figure-15**].[32,33] Signals in the CD spectrum at 336.2 (-39.6), 322.5 (-34.3), 305.9 (-42.5), 265.7 (+102.6) for **76a** and 335.7 (+41.8), 320.9 (+36.2), 301.8 (+44.8), 265.8 (-94.6) for **78a** shows the enantiomer pair. The signals at 265.7 (+102.6), 305.9 (-42.5) and 265.8 (-94.6), 301.8 (+44.8) were attributed to the (*P*)/(*S*)-**76a** and (*M*)/(*R*)-**78a** configuration respectively.

Similarly the CD spectrum shows the signals at 335.6 (-22.8), 322.4 (-12.8), 305.2 (-29.9), 260.1(+54.5) for **76b** and 335.4 (+30.0), 320.1 (+25.3), 305.5 (+41.1), 264.1 (-59.9) **78b** shows the enantiomer pair. And signals at 305.2 (-29.9), 260.1(+54.5) and 264.1 (-59.9), 305.5 (+41.1) were attributed to the (*M*)/(*R*)-**76b** and (*P*)/(*S*)-**78b** configuration respectively.

The helicene like compounds bis-oxazines **79a** and **79b** were synthesized from the compounds **78a** and **78b** by using the diiodomethane and $Cs_2CO_3$ in DMF at room temperature to obtain the products in a moderate yield. The $^1$H & $^{13}$C-NMR, IR of both these compounds **77a-79a** and **77b-79b** were identical but the optical rotation values and the CD spectrum are opposite to each other in the similar solvents at same concentrations [**Figure-22**].

The MALDI-TOF-MS spectrum of the compounds **79a** and **79b** shows the molecular ion peak at *m/z* 621.1062 ([M+H]$^+$) and *m/z* 621.1373. The HRMS analysis of the compounds **79a** showed the molecular ion peak of $C_{41}H_{37}N_2O_2$ ([M+H]$^+$): at 621.2753, while the calculated one would be 621.2781.



**77a** $[\alpha]_D^{26}$ = + 884

**79a** $[\alpha]_D^{27}$ = - 888

**77b** $[\alpha]_D^{27}$ = - 789

**79b** $[\alpha]_D^{26}$ = + 764

**Figure 22:** Optical rotations and enantiomer pairs of the compounds **77a-79a** and **73b-79b**

The optical rotations of the all these compounds was recorded in chloroform at the concentration of about 0.5% w/v of solution. The pure enantiomer **77a-79a** had the opposite sign of optical rotation with the same rotation value. The compound **77b** and **79b** showed a small difference in the value of observed rotation due to the presence of small impurity of the starting material **79b**. The CD spectrum of these compounds was run in chloroform and acetonitrile.

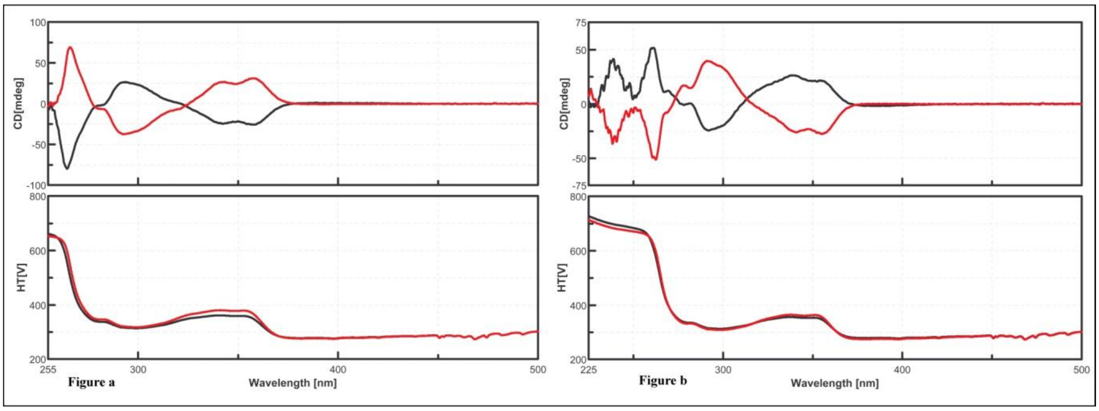
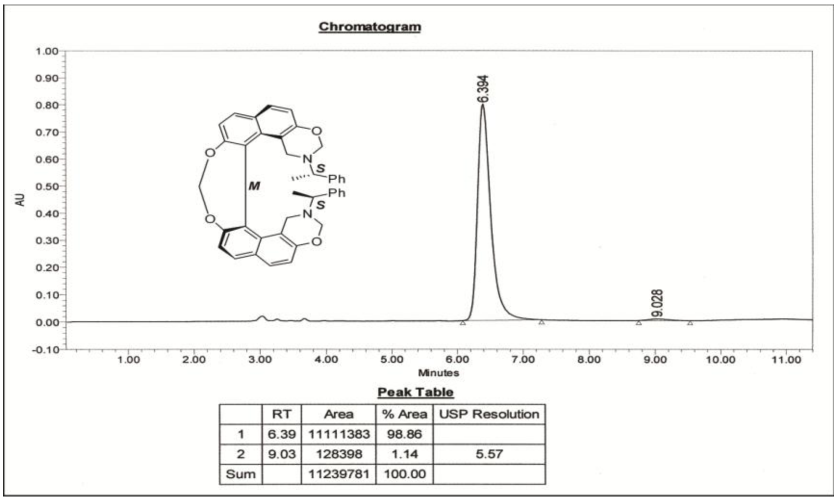


**Figure 23:** (a) Circular dichroism spectra of resolved helical bis-oxazines: (red line) **77a** and (black line) **79a** (*c* 1 x 10$^{-7}$ M in acetonitrile, 25 °C) (b) Circular dichroism spectra of resolved helical oxazines: (red line) **77b**, (black line) **79b**, (*c* 1 x 10$^{-7}$ M in acetonitrile, 25 °C)

The helical bis-oxazines **77a** & **79a** and **77b** & **79b** showed a typical UV and CD spectral features [**Figure-23**].[32,33] Signals for the CD spectrum at 357.8 (+32.5), 344.4 (+24.9), 292.6 (-35.4), 269.9 (+70.8) for **77a** and 358.0 (-26.8), 344.5 (-25.2), 295.2 (+27.1), 266.1 (-80) for **79a** showed the enantiomer pair. The signals at 292.6 (-35.4), 269.9 (+70.8) and 295.2 (+27.1), 266.1 (-80) were attributed to the (*P*)-**77a** and (*M*)-**79a** configuration respectively.

The CD spectrum of the isomers **77b** and **79b** were different than the **77a** and **79a,** it shows a strong absorbance signal at ~ 240 nm and the overall signals at 356.2 (+22.0), 342.0 (+26.2), 290.1 (-25.0), 260.2 (+52.1), 239.8 (+38.5) for **77b** and 356.6 (-28.4), 343.2 (-26.1), 289.8 (+36.8), 261.8 (-51.9), 238.8 (-38.3) for **79b** confirming that they are a perfect enantiomer pair. And signals at 290.1 (-25.0), 260.2 (+52.1) and 289.8 (+36.8), 261.8 (-51.9) were attributed to the (*M*)-**77b** and (*P*)-**79b** configuration respectively.

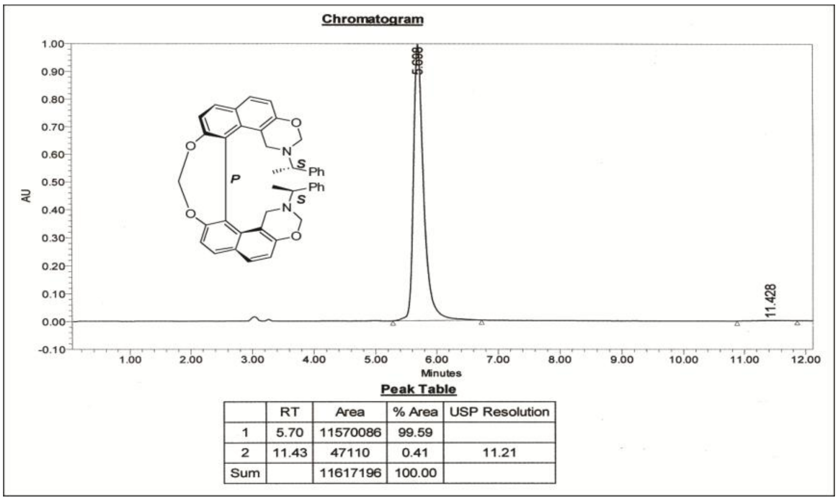
The enantiomerically pure helicene like bis-oxazines **79a** and **79b** were synthesized and the chiral purity of each compound was checked by HPLC analysis on the chiral Lux Amylose 2 column [**Figure-24 and 25**].



Peak Table

| | RT | Area | % Area | USP Resolution |
|---|---|---|---|---|
| 1 | 6.39 | 11111383 | 98.86 | |
| 2 | 9.03 | 128398 | 1.14 | 5.57 |
| Sum | | 11239781 | 100.00 | |

**Figure 24:** Chiral HPLC chromatogram of the helical Bis-oxazines **79a**



Peak Table

| | RT | Area | % Area | USP Resolution |
|---|---|---|---|---|
| 1 | 5.70 | 11570086 | 99.59 | |
| 2 | 11.43 | 47110 | 0.41 | 11.21 |
| Sum | | 11617196 | 100.00 | |

**Figure 25:** Chiral HPLC chromatogram of the helical Bis-oxazines **79b**

The HPLC analyses on chiral columns clearly show the enantiomeric purity of the compound to be over 99%, confirming the purity determined by NMR analysis and optical rotation.

After the establishment of the chiral purity of the helicene like bi-oxazines it was found that the step involving the methylene bridge formation retains the stereochemistry of the axis in (*RSR*)-**76a**, (*RRR*)-**76b**, (*SRS*)-**78a** and (*SSS*)-**78b**. The absolute configuration of the methylene bridged compounds **77a**, **77b**, **79a** and **79b** was accepted to be *RPR*, *RMR*, *SMS* and *SPS* respectively.

Helical molecules generally show large specific optical rotation and molecular optical rotations. Our observations of the high specific optical rotation and the molecular optical rotations were also in accordance with this phenomena [**Table-1**].

**Table 1:** Specific optical rotations and molecular optical rotations of the helical bis-oxazines

| Sr. No. | Compound | Specific Optical Rotation ($[\alpha]_D$) | Molecular Optical Rotation ($[\Phi]_D$) |
|---|---|---|---|
| 1 | **77a** | + 884 | + 5487 |
| 2 | **77b** | - 789 | - 4894 |
| 3 | **79a** | - 888 | - 5508 |
| 4 | **79b** | + 764 | + 4738 |

From the present study it was observed that there is a huge difference in the specific optical rotation of the atropisomeric bis-oxazines and in the methylene bridged helicene like bis-oxazines. This enhancement of the degree of optical rotation when the atropisomeric open structure is converted to a rigid form of helicene like structure by introducing the bridge is in accordance with the recent observation.[31]

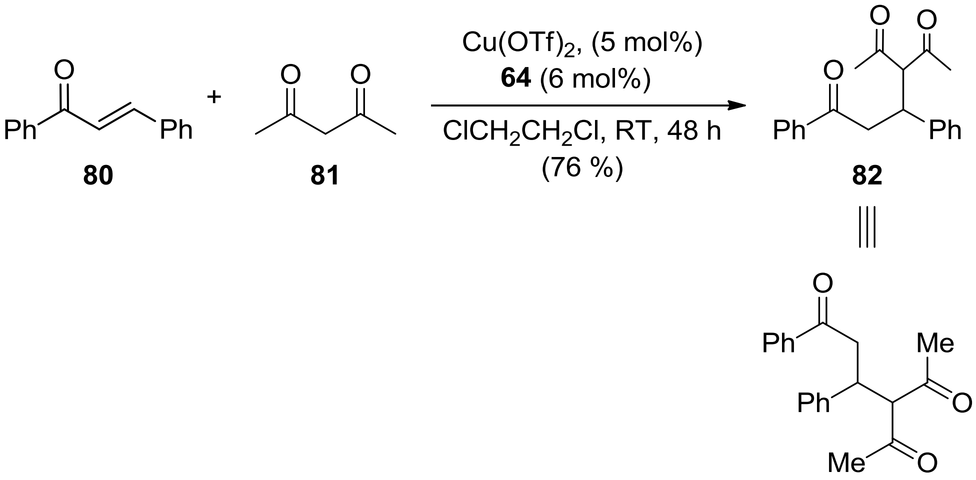
The cyclized form with the methylene bridge also provides stability to the helical shape. This was confirmed when a solution of compound **77a** was refluxed in toluene for over 12 h without any visible isomerisation. After the heating its sample was checked with $^1$H-NMR analysis and compared with the original values. The $^1$H-NMR was identical with the $^1$H-NMR of the pure compound **77a**. This experiment eliminates the possibility of conversion of **77a** to **77b** due to the axial instability at high temperature.

# Preliminary study of the applications of helicene like mono- or bis-oxazines

Oxazines are the nitrogen and oxygen containing heterocyclic compounds and due to these heteroatoms it can bind with some metal ions and catalyze chemical transformations. To test this concept in the present study we have run a couple of important catalytic reactions. If the reactions are catalyzed effectively with oxazine ligands, then the chiral oxazines may be screened for asymmetric catalytic reactions.

## 1] Copper catalysed Michael Reaction:

The first reaction investigated was the Michael reaction of α,β-unsaturated ketones, an important process extensively used in synthetic organic chemistry.[34] The catalytic Michael reaction of chalcones involves the formation of new Carbon-Carbon bond[35] by using acetylacetone, $Cu(OTf)_2$ and our mono-oxazine 2-benzyl-2,3-dihydro-1H-benzo[5,6]- phenanthro[4,3-*e*][1,3]oxazine **64** as ligand in dichloromethane at ambientconditions to obtain 4-acetyl-1,3-diphenylhexane-1,5-dione in excellent yield.

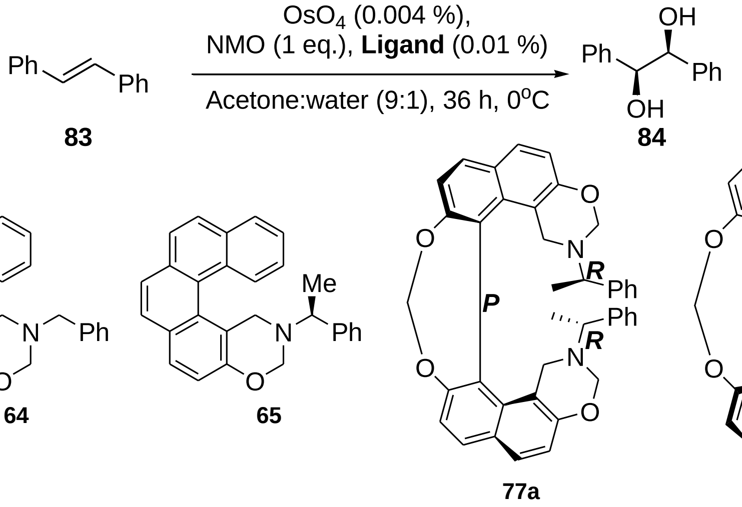


**Scheme 21:** Michael reaction of chalcone using **64**•$Cu(OTf)_2$ as a catalyst system

## 2] Osmium catalysed dihydroxylation of alkenes:

Osmium tetroxide catalyzes *cis*-dihydroxylation of alkenes by hydrogen peroxide or other oxidants in the presence of water is a widely used proces.[36] It is well established that the reaction proceeds by complexation of $Os^{VIII}O_4$ with alkenes $R_2C{=}CR_2$ to afford cyclic "esters" $R_4C_2O_2Os^{VI}O_2$, which undergo hydrolysis to give the vicinal diol and release a reduced osmium oxide ($Os^{VI}$).

Lewis bases such as tertiary amines and pyridines increase the reaction rate. This "ligand-acceleration" arises *via* the formation of adduct OsO4•L, which adds more rapidly to the alkene. If the amine is chiral, then the dihydroxylation can proceeds with enantioselectivity. One such application is commonly named as Sharpless asymmetric dihydroxylation[36] where alkaloids of quinine family are used as ligands. The catalyst $OsO_4$ is often used in catalytic amounts due to its toxicity and high cost. The osmium catalyst can be regenerated by *in situ* oxidation, with reagents such as $H_2O_2$, *N*-methylmorpholine-*N*-oxide (NMO), $K_3FeCN_6$ etc.[37] Since the Lewis bases such as tertiary amines induce the activity of $OsO_4$, in the present study the oxazolines were scanned for the dihydroxylation of alkenes. In this standard, preliminary reaction *trans*-stilbene was subjected to the dihydroxylation reaction[38] in presence of catalytic quantity of osmium tetraoxide, NMO and oxazine ligands. In the present preliminary work **64**, **65**, **77a** and **77b** were scanned as ligands.



**Scheme 22:** Dihydroxylation of stilbene using *rac*- and chiral oxazines

The reaction was scanned with the *rac*-**64**, **65** and with chiral **77a** and **77b** used as ligand, it was found that the reaction did proceeded with good conversion and with very high turn-over number (TON) as mentioned below [**Table-2**].

**Table 2:** Helical oxazine ligands scanned for the dihydroxylation of alkenes

| Sr. No. | Ligand | Yields (%) | SOR ($[\alpha]_D$) | % ee | Turnover Number (TON) |
|---|---|---|---|---|---|
| 1 | **64** | 55% | - | - | 1,37,989 |
| 2 | **65** | 83% | - | - | 2,06,983 |
| 3 | **79a** | 76% | + 2 | 1% | 1,89,314 |
| 4 | **79b** | 72% | + 4.30 | 2% | 1,80,900 |

However, during the preliminary study it was observed that although the reaction proceeds well, there was almost no asymmetric induction observed in these reactions.

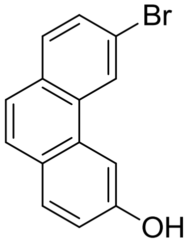
# Experimental Section

## Part 1

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc. All solvents used were stored on activated molecular sieves (4 Å). All commercial products were used without further purification. Tetrahydrofuran was refluxed and freshly distilled on sodium benzophenone-ketyl. Toluene was distilled and stored 24 h over molecule sieves (4 Å) prior to use. Thin Layer Chromatography (tlc) was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. Photo reactions were performed in immersion well photo reactor with water jacket for cooling with 125 W or 250 W high pressure mercury vapour lamp made by General Electric (CEMA Electric Lighting Products India Pvt. Ltd). All the compounds were purified by column chromatography using SRL silica gel (60-120 mesh). All reactions were carried out under an inert atmosphere (nitrogen) unless other conditions are specified. $^{1}$H and $^{13}$C NMR spectra were recorded on a 400 MHz or Bruker Avance 400 Spectrometer (100 MHz for $^{13}$C respectively), 500 MHz Bruker Avance 500 Spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), quartet of triplets (qt), septet (sept) and multiplet (m). 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. CD spectra were measured on a Jasco J-815 CD spectropolarimeter at 25 °C. The specific optical rotation (SOR) measured on the Polarimeter Jasco P-2000. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected. For the HPLC analysis chiral Lux 5μ Amylose 2 column or chiral Diacel OD-H column was used on Waters 996 photodiode Array Detector and Waters 2690 Separation Module HPLC system.

## Experimental Procedures

### *3-Bromo-6-hydroxyphenanhrene (52):*

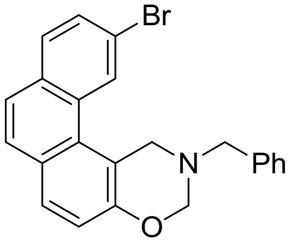


A solution of 3-bromo-6-methoxyphenanthrene (0.350 g, 1.22 mmol) and 48% aqueous hydrobromic acid (0.147 g, 0.308 mL, 1.83 mmol) in glacial acetic acid (10 mL) was refluxed for 24 h or till the starting material was consumed (tlc). After completion of the reaction, the mixture was poured on ice-water (50 mL), and extracted with ethyl acetate (3 X 25 mL). The solvent layer was washed with saturated sodium bicarbonate solution, water, brine, dried over sodium sulfate and the organic layer was concentrated under reduced pressure to obtain a brown coloured mass, which was purified by column chromatography over silica gel with petroleum ether: ethyl acetate (100:00 to 85:15) as eluent to afford a white solid. (0.326 g, 98%), **M.p.** 178-180 ºC (Recrystallized from ethylacetate: petroleum ether).

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.59 (d, *J* = 1.56 Hz, 1H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.44 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 1.84, 8.56 Hz, 1H), 7.47 (d, *J* = 8.84 Hz, 1H), 7.12 (dd, *J* = 2.48, 8.64 Hz, 1H), 5.16 (s, 1H for -OH).

**MS (EI):** ***m/z*, (%)** 275 (14.7), 274 (98), 273 (18), 272 (100), 194 (8), 192 (7), 166 (11), 165 (68), 164 (29), 163 (41), 137 (29), 136 (23), 97(12), 96 (15), 83 (18), 82 (28).

### *11-Bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza-benzo[c]phenanthrene (53):*



A solution of benzylamine (0.047 g, 0.048 mL, 0.44 mmol) and 37% formaldehyde solution (0.065 mL, 0.024 g, 0.81 mmol) was stirred for 30 min at room temperature under $N_2$ atmosphere. Then 3-bromo-6-hydroxyphenanhrene **52** (0.100 g, 0.37 mmol) was added and the reaction mixture was stirred for 24 h at 80 ºC. After the completion of reaction the crude product was purified by column chromatography on silica gel using petroleum ether:ethylacetate (100:00 to 90:10) as eluent to afford white solid (0.112 g, 75%). **M.p.** 164-165 ºC.

**$^1$H-NMR (400 MHz, $CDCl_3$)**: δ 8.43 (s, 1H), 7.80-7.76 (m, 2H), 7.70-7.68 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.37-7.28 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 1H), 4.99 (s, 2H), 4.86 (s, 2H), 3.79 (s, 2H).

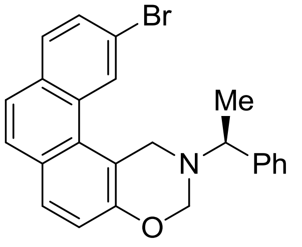
**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: δ 153.34 (Cq), 137.57 (Cq), 132.46 (Cq), 131.62 (Cq), 130.13 (CH), 130.05 (CH), 129.86 (Cq), 129.16 (CH), 129.11 (2 x CH), 128.53 (2 x CH), 128.40 (Cq), 128.23 (CH), 127.55 (CH), 124.26 (CH), 119.10 (Cq), 118.47 (CH), 115.53 (Cq), 79.80 (O$\underline{C}$H$_2$N), 54.93 (ArCH$_2$N), 54.13 (NCH$_2$Ar).

**MS (EI)**: *m/z*, (%) 405 (16), 403 (16), 206 (19), 205 (100), 199 (09), 178 (26), 176 (41), 151 (11), 129 (25), 97 (14), 95 (09), 91 (28), 85 (10), 83 (13), 73 (13), 71 (13), 70 (08).

**Anal. Calcd. for C$_{23}$H$_{18}$BrNO**: C 68.33, H 4.49; N 3.46. Found: C 68.30, H 4.45, N 3.68.

**IR (KBr)**: 2850, 1621, 1600, 1587, 1505, 1454, 1435, 1367, 1341, 1247, 1207, 1188, 1135, 1094, 1083, 1026, 998, 941, 882, 869, 846, 785, 744, 731, 699, 686, 666, 607, 565, 547 cm.$^{-1}$

***11-Bromo-2-((S)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza benzo[c]phenanthrene (54):***



A solution of *S*-(-)-phenylethylamine (0.053 g, 0.055 mL, 0.44 mmol) and 37% formaldehyde solution (0.026 g, 0.071 mL, 0.88 mmol) was stirred for 30 min at room temperature under N$_2$ atmosphere. Then 3-bromo-6-hydroxyphenanhrene **52** (0.100 g, 0.37 mmol) was added and the reaction mixture was stirred for 24 h at 80 ºC. After the completion of reaction the crude product was purified by column chromatography on silica gel using petroleum ether:ethylacetate (100:00 to 90:10) as eluent to afford white solid (0.109 g, 71%). **M.p.** 148-150 ºC (Recrystallized from Petroleum ether); $[\alpha]_D^{30}$ = - 11.17 (*c* = 0.1 in CHCl$_3$).

**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 8.37 (d, *J* = 0.8 Hz, 1H), 7.74 (t, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.31-7.22 (m, 5H), 7.18 (d, *J* = 8.8 Hz, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 3.85 (q, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: δ 153.98 (Cq), 143.61 (Cq), 132.41 (Cq), 131.54 (Cq), 130.02 (CH), 129.98 (Cq), 129.71 (Cq), 129.05 (CH), 128.94 (CH), 128.51 (2 X CH), 128.21 (CH), 128.18 (CH), 127.38 (CH), 127.31 (2 X CH), 124.10 (CH), 118.96

(CH), 118.31 (Cq), 115.84 (Cq), 79.40 (O<u>C</u>$H_2$N), 57.23 (PhMe<u>C</u>HN), 51.31(Ar<u>C</u>$H_2$N), 21.43 (<u>C</u>$H_3$).

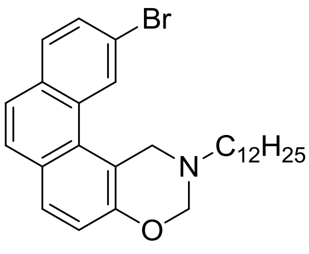
**MALDI-TOF-MS**: *m/z* = 418.9932 ($[M+H]^+$).

**MS (EI)**: *m/z*, (%) 419 (41), 418 (38), 416 (77), 401 (9), 314 (17), 313 (15), 311 (28), 286 (10), 285 (12), 284 (25), 232 (12), 206 (22), 205 (50), 204 (100), 177 (28), 176 (82), 151 (9), 149 (15), 105 (48), 88 (9).

**Anal. Calcd. for $C_{24}H_{20}BrNO$**: C 68.91, H 4.82; N 3.35. Found: C 69.25, H 4.27, N 3.19.

**IR (KBr)**: 3051, 3022, 2970, 2857, 1599, 1585, 1503, 1430, 1388, 1368, 1342, 1282, 1246, 1212, 1125, 1100, 1071, 982, 932, 843, 744, 697, 608, 545 $cm.^{-1}$

***11-bromo-2-dodecyl-2,3-dihydro-1H-phenanthro[4,3-e][1,3]oxazine (55):***

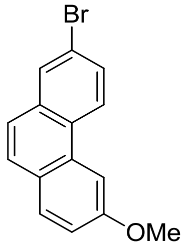


A solution of dodecylamine (0.075 g, 0.093 mL, 0.40 mmol) and 37% formaldehyde solution (0.024 g, 0.066 mL, 0.81 mmol) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 3-bromo-6-hydroxyphenanhrene **52** (0.100 g, 0.37 mmol) was added and the reaction mixture was stirred for 24 h at 80 ºC. After the completion of reaction the crude product was purified by column chromatography on silica gel using gradient petroleum ether:ethylacetate (100:00 to 90:10) as eluent to afford off white solid (0.101 g, 57%). **M.p.** 84-86 ºC.

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 8.45 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, *J* = 1.6, 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 5.08 (s, 2H), 4.77 (s, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.54 (t, *J* = 6.8 Hz, 2H), 1.24 (broad s, 18H), 0.89 (t, *J* = 6.4 Hz, 3H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 153.49 (Cq), 132.45 (Cq), 130.11 (2 X CH), 129.98 (Cq), 129.10 (CH), 128.92 (CH), 128.25 (CH), 128.22 (Cq), 124.09 (2 X CH), 119.04 (Cq), 118.38 (Cq), 115.83 (Cq), 80.85 (N-<u>C</u>$H_2$-O), 53.81 (Ar-<u>C</u>$H_2$-N), 50.73 (-N-<u>C</u>$H_2$), 31.92, 29.63, 29.59, 29.48, 29.36, 28.16, 27.21, 22.71, 14.15 (-<u>C</u>$H_3$).

***2-Bromo-6-methoxyphenanthrene (60):***

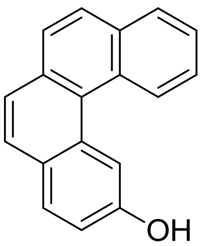


A solution of 1,3-dibromo-5-(4-methoxystyryl)benzene (0.300 g, 0.81 mmol), iodine (0.227 g, 0.89 mmol), THF (5.87 g, 6.61 mL, 81.5 mmol) in toluene (1.2 L) was irradiated using 250W HMPV lamp for 12 h. After the reaction was over the excess of iodine was removed by washing with aqueous $Na_2S_2O_3$ solution, followed by distilled water. The organic layer was concentrated at reduced pressure. The pure product was isolated as white solid by column chromatography over silica gel, further crystallized from petroleum ether (0.181 g, 61 %), **M.p**. 91-92 ºC.

**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 8.42 (d, *J* = 9.2 Hz, 1H), 8.00 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 2.4 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.67 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.25 (dd, *J* = 2.4, 8.8 Hz, 1H), 4.00 (s, 3H).

**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: δ 158.74 (Cq), 133.84 (Cq), 131.26 (Cq), 130.69 (CH), 130.16 (CH), 129.15 (CH), 128.37 (Cq), 127.85 (CH), 126.60 (Cq), 124.51 (CH), 123.37 (CH), 120.60 (Cq), 117.13 (CH), 103.74 (CH), 55.52 ($\underline{C}H_3$).

***2-Hydroxybenzo[c]phenanthrene (63):***

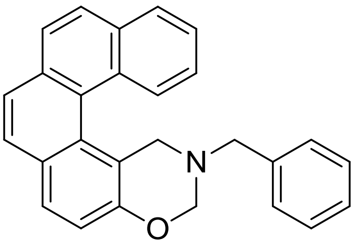


A solution of 2-methoxybenzo[*c*]phenanthrene (1.00 g, 3.9 mmol) and 48% aqueous hydrobromic acid (0.47 g, 0.98 mL, 5.84 mmol) in glacial acetic acid (25 mL) was refluxed for 24 h or till starting material was consumed (tlc). After completion of the reaction, it was poured on ice-water (50 mL) and extracted with ethyl acetate (2 X 50 mL). The solvent layer was washed with saturated sodium bicarbonate solution, water, brine, dried over sodium sulfate and concentrated under reduced pressure to obtain a brown coloured residue. The crude product was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (100:00 to 95:5) as eluent to afford a white solid. (0.83 g, 88%) **M.p.** 114-116 ºC (Recrystallized from cyclohexane) (Lit.[49] 115-116 ºC).

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 9.10 (d, *J* = 8.56 Hz, 1H), 8.54 (d, *J* = 2.32 Hz, 1H), 7.98 (dd, *J* = 1.56, 7.72 Hz, 1H), 7.88 (dd, *J* = 8.52, 8.68 Hz, 2H), 7.78 (dd, *J* = 8.48, 8.56 Hz, 2H), 7.67 (d, *J* = 8.48 Hz, 1H), 7.65-7.56 (m, 2H), 7.20 (dd, *J* = 2.44, 8.68 Hz, 1H), 5.28 (s, 1H, -OH group).

**IR (KBr):** 3229, 3042, 1604, 1524, 1496, 1415, 1360, 1308, 1204, 1179, 830, 744 cm$^{-1}$

***9-Benzyl-9,10-dihydro-8H-7-oxa-9-aza-dibenzo[c,g]phenanthrene (64):***



A solution of benzylamine (0.158 g, 0.161 mL, 1.47 mmol) and 37% formaldehyde solution (0.220 mL, 0.81 g, 2.7 mmol) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2-hydroxybenzo[*c*]phenanthrene (0.300 g, 1.23 mmol) was added and the reaction mixture was stirred for 24 h at 80 ºC. After the completion of reaction the crude product was purified by column chromatography using neutral aluminium oxide and petroleum ether as eluent to afford white solid. (0.298 g, 65%). **M.p**. 149-151 ºC.

**$^1$H-NMR (400 MHz, CDCl$_3$)**: δ 8.08 (ddd, *J* = 0.82, 3.20, 7.40 Hz, 1H), 7.99 (ddd, *J* = 0.96, 2.80, 9.44 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.87 (dd, *J* = 2.00, 8.40 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.57 (td, *J* = 3.60, 7.2, 10.0 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.17-7.16 (m, *J* = 3H), 7.02-7.00 (m, 2H), 5.30 (d, *J* = 9.2 Hz, 1H), 5.06 (d, *J* = 16.4 Hz, 1H), 4.82 (dd, *J* = 2.8, 9.6 Hz, 1H), 3.42 (d, *J* = 12.8 Hz, 1H), 3.11 (d, *J* = 12.8 Hz, 1H), 2.97 (dd, *J* = 1.6, 16.4 Hz, 1H).

**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: δ 152.91 (Cq), 137.59 (Cq), 132.45 (Cq), 131.95 (Cq), 130.44 (Cq), 129.96 (Cq), 128.96 (2 X CH), 128.88 (Cq), 128.80 (CH), 128.59 (CH), 128.23 (2 X CH), 127.86 (CH), 127.51 (CH), 127.46 (CH), 127.22 (CH), 126.14 (CH), 125.81 (Cq), 125.23 (CH), 125.20 (CH), 123.69 (CH), 117.99 (CH), 114.82 (Cq), 80.70 (O$\underline{C}H_2$N), 54.70 (ArCH$_2$N), 54.33 (NCH$_2$Ph).

**MALDI-TOF-MS**: *m/z* = 376.6220 ([M+H]$^+$).

**MS (EI)**: *m/z*, (%) 376 (66), 375 (24), 257 (08), 256 (47), 255 (100), 254 (12), 239 (33), 227 (32), 226 (47), 225 (09), 120 (04), 119 (11), 113 (25), 112 (10), 91 (52).

**Anal. Calcd. for $C_{27}H_{21}BrNO$**: C 86.37, H 5.63; N 3.73. Found: C 85.61, H 5.53, N 3.67.

**IR (KBr)**: 3028, 3001, 2923, 2843, 1591, 1515, 1486, 1445, 1361, 1272, 1244, 1216, 1203, 1172, 1126, 1078, 1059, 1045, 1003, 932, 911, 878, 835, 787, 747, 731, 702 cm.$^{-1}$

**HPLC Analysis:**

**Method A:**

Observed two peaks of seperated enantiomers at 1) $R_t$ = 6.95 min and 2) $R_t$ = 9.01 min.

Solvent System: *n*-Hexane: *Iso*-propanol (95:05), Flow rate: 1 mL/min.

Detector: UV-Vis. Column: Chiralpak Diacel-OD H.

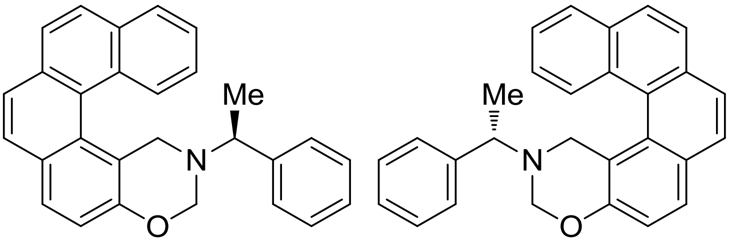
**Method B:**

Observed two peaks of seperated enantiomers at 1) $R_t$ = 5.49 min and 2) $R_t$ = 6.28 min.

Solvent System: *n*-Hexane: *Iso*-propanol (85:15), Flow rate: 1 mL/min.

Chiral Column: Lux Amylose 2

***Mixture of P/M-(S)-2-(1-phenylethyl)-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-e][1,3]-oxazine (65):***



A solution of *S*-(-)-α-methylbenzyl amine (0.15 g, 1.6 mL, 1.22 mmol) and 37% formaldehyde solution (0.061 g, 0.17 mL, 2.04 mmol) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2-hydroxybenzo[*c*]phenanthrene (0.25 g, 1.02 mmol) was added and the reaction mixture was stirred for 24 h at 80 ºC. After the completion of reaction the crude product was purified by column chromatography using neutral aluminium oxide and petroleum ether as eluent to afford white solid (0.24 g, 60%). **M.p.** 64-78 ºC (Acetonitrile), $[\alpha]_D^{30}$ = - 147.6 (*c* = 0.1 in $CHCl_3$).

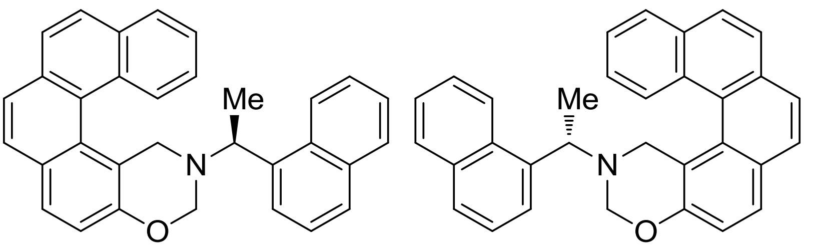
**$^1$H-NMR (400 MHz, $CDCl_3$)**: δ [Aromatic protons from the mixture of both diastereomers : 8.07-7.13 (m, 27H, Aromatic 1 and 2 diastereomer), 6.85 (t, *J* = 7.24, 7.36 Hz, 1H), 6.76 (t, *J* = 7.36, 7.64 Hz, 1H), 6.44 (d, *J* = 7.36 Hz, 1H)], 5.35 (d, *J* = 9.8 Hz, 1H, 2 diastereomer), 5.24 (dd, *J* = 2.92, 9.88 Hz, 1H, 2 diastereomer), 5.19 (d, *J* = 9.68 Hz, 1H, 1 diastereomer), 4.90 (d, *J* = 16.84 Hz, 1H,1 isomer), 4.61 (dd, *J* = 3.00, 9.64 Hz, 1H, 2 diastereomer), 3.35 (dd, *J* = 1.72, 16.72 Hz, 1H 1 diastereomer), 3.26 (q, *J* = 6.6 Hz, 1H, 1 diastereomer), 3.15 (q, *J* = 6.6 Hz, 1H, 2 diastereomer), 2.62 (dd, *J* = 1.8, 16.5 Hz, 1H, 2 diastereomer), 1.22 (dd, *J* = 6.6, 3H, -$CH_3$ for 2 diastereomer), 0.58 (dd, *J* = 6.6 Hz, 3H, -$CH_3$ for 1 diastereomer).

$^{13}$C-NMR is not included since it is a unseparable diastereomer mixture and the spectra is extremely complex.

**IR (KBr)**: 3042, 2969, 2925, 1590, 1516, 1488, 1436, 1346, 1273, 1243, 1217, 1125, 1041, 966, 928, 907, 868, 836, 803, 737, 699, 647 cm.$^{-1}$

**MS (EI)**: *m/z*, (%) 389 (100), 257 (07), 256 (40), 255 (25), 254 (50), 253 (40), 238 (61), 227 (27), 226 (23), 225 (56), 224 (13), 104 (25).

***Mixture of P/M-(S)-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1H-benzo[5,6]phenanthro-[4,3-e][1,3]oxazine (66):***



A solution of *S* (-)-α-(1-naphthyl)ethylamine (0.16 g, 0.15 mL, 0.90 mmol) and 37% formaldehyde solution (0.2 mL, 0.07 g, 0.24 mmol) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2-hydroxybenzo[*c*]phenanthrene (0.20 g, 0.82 mmol) was added and the reaction mixture was stirred for 24 h at 80 ºC. After the completion of reaction the crude product was purified by column chromatography using neutral aluminium oxide and petroleum ether:ethyl acetate (100:00 to 98:2) as eluent to afford white solid (0.18 g, 50 %). **M.p.** 192-196 ºC. $[\alpha]_D^{30}$ = - 653 (*c* = 0.1 in $CHCl_3$).

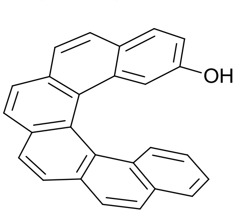
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ [Aromatic protons mixture of both the diastereomers- 8.11 (dd, *J* = 1.8, 7.6 Hz, 1.15H), 8.03-7.91 (m, 4.82 H), 7.89-7.86 (m, 2.36H), 7.81-7.76 (m, 2.37H), 7.70-7.66 (m, 2.64H), 7.62-7.52 (m, 3.98H), 7.45-7.33(m, 5.92H), 7.30-7.26 (m, 1.18H), 7.25-7.16 (m, 0.79H), 7.1-7.02 (m, 1.29H), 6.91-6.86 (m, 0.67H)], 5.42 (dd, *J* = 1.28, 9.96 Hz, 0.67H, 2-diastereomer), 5.32 (dd, *J* = 3.0, 10.0 Hz, 0.67H, 2-diastereomer), 5.25 (d, *J* = 9.8 Hz, 0.99 H, 1-diastereomer), 5.00 (d, *J* = 16.84 Hz, 0.99 H, 1-diastereomer), 4.73 (d, *J* = 16.72 Hz, 1H, 2-diastereomer), 4.62 (dd, *J* = 2.88, 9.84 Hz, 1H, 1-diastereomer), 4.06 (q, 1.68H, 1 & 2-diastereomer), 3.49 (dd, *J* = 1.84, 16.88 Hz, 0.99H, 1-diastereomer), 2.65 (dd, *J* =

1.8, 16.7 Hz, 0.67H, 2-diastereomer), 1.34 (d, *J* = 6.64 Hz, 2.06H, –$CH_3$ for 2-diastereomer), 0.72 (d, *J* = 6.68 Hz, 3.02H, -$CH_3$ for 1-diastereomer).

**IR (KBr):** 3041, 2967, 2898, 1590, 1512, 1486, 1458, 1367, 1312, 1244, 1218, 1154, 1124, 1086, 1051, 968, 926, 900, 840, 802, 778, 742, 685 $cm^{-1}$.

**MS (EI)**: *m/z*, (%) 439 (09), 257 (08), 256 (45), 255 (100), 254 (20), 240 (08), 239 (39), 227 (32), 226 (54), 225 (14), 224 (12), 156 (11), 154 (13), 153 920), 152 (10), 128 (09), 115 (08), 113 (18), 112 (09).

***2-hydroxy[6]helicene (68):***



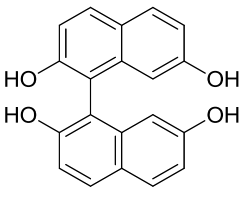
A solution of 2-methoxy[6]helicene (0.110 g, 0.31 mmol) and 48% w/v aqueous hydrobromic acid (0.030 g, 0.062 mL, 0.36 mmol) in glacial acetic acid (5 mL) was refluxed for 24 h or till starting material was consumed. After completion of the reaction, the mixture was poured on ice-water 20 mL, and extracted with ethyl acetate. The solvent layer was washed with saturated sodium bicarbonate solution, water, brine, dried over sodium sulfate and concentrated under reduced pressure obtained a brown solid. Purification of compound by column chromatography on silica gel using gradient petroleum ether: ethyl acetate (100:00 to 80:20) as eluent to afford a white solid. (0.070 g, 66%)

**M.p**. 226-230 ºC.

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 1H), 7.94 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.83 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.64 (dd, *J* = 0.4, 8.0 Hz, 1H), 6.76 (ddd, *J* = 1.6, 6.8, 8.4 Hz, 1H), 4.30 (s, 1H, -OH group).

**MS (EI)**: *m/z*, (%) 345 (09), 344 (100), 327 (13), 326 (12), 325 (12), 324 (11), 300 (36), 299 (15), 298 (05), 162 (06), 149 (06).

***7,7'-dihydroxy-2,2'-binaphthol (71):***

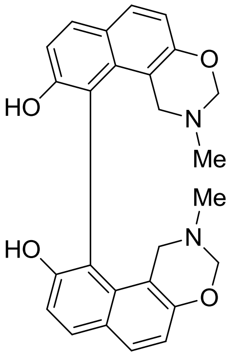


A solution of $FeCl_3 \cdot 6H_2O$ (24.290 g, 89.8 mmol) in water (200 mL) was added drop wise for 1 h at 100 ºC to the solution of 2,7-dihydroxynaphthalene (12.00 g, 74.90 mmol) in 500 mL of water. After the addition the reaction mixture was refluxed for 24 h and then cooled to room temperature and extracted with ethyl acetate (2 x 500 mL) the solvent was dried over sodium sulphate and concentrated under reduced pressure to obtain the crude black mass. Purification of compound by column chromatography on silica gel using gradient petroleum ether: ethyl acetate (100:00 to 80:20) as eluent to obtained an off white solid (10.10 g, 85%).

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 9.2 Hz, 2H), 6.99 (dd, *J* = 2.4, 8.8 Hz, 2H), 6.45 (d, *J* = 2.4 Hz, 2H), 5.11 (s, 2H for -OH group).

**MS (EI):** *m/z*, (%) 319 (22), 318 (100), 301 (09), 300 (38), 289 (07), 281 (06), 273 (11), 271 (09), 226 (06), 215 (08), 213 (11), 202 (07), 189 (06), 160 (07), 150 (10), 131 (09), 113 (16), 106 (12).

***2,2'-Dimethyl-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'-diol (72):***



A solution of 37% w/v formaldehyde solution (0.45 g, 1.22 mL, 15.0 mmol) and methylamine solution (0.215 g, 0.536 mL, 40% w/v, 6.91 mmol) in methanol was stirred for 30 min under nitrogen atmosphere, to this solution 7,7'-dihydroxy-2,2'-binaphthol **71** (1.00 g, 3.14 mmol) was added in one portion. Then the solution was stirred for 48 h at 60 ºC. The white precipitate separated out which were filtered, the solid was washed with methanol (3 X 10 mL) dried under vacuum. Yield = 0.775 g (57.75%).

The mother liquid and washings are combined together and concentrated to obtain brown solid. The crude product was purified by column chromatography on silica gel using gradient petroleum ether:ethyl acetate (100:0 to 50:50) as eluent to obtain a white solid dried in vacuum. Yield = 0.525 g (39%).

**Total Yield =** 1.3 g, (96.75%); **M.p.** 209-210 ºC.

**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.06 (s, 2H, -OH), 4.74 (d, *J* = 9.2 Hz, 2H), 4.60 (d, *J* = 9.2 Hz, 2H), 3.63 (d, *J* = 16.8 Hz, 2H), 3.20 (d, *J* = 16.8 Hz, 2H), 2.82 (s, 6H).

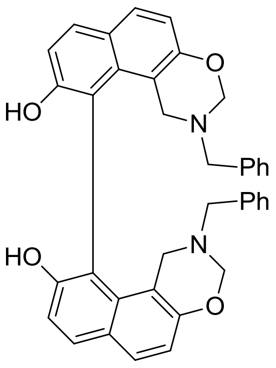
**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: δ 153.97 (Cq), 153.60 (Cq), 133.16 (CH), 132.92 (Cq), 129.80 (CH), 125.82 (Cq), 117.03 (CH), 114.33 (CH), 111.88 (Cq), 111.32 (Cq), 82.36 (O$\underline{C}$H$_2$N), 50.85 (Ar$\underline{C}$H$_2$N), 39.25 (N$\underline{C}$H$_3$).

**MS (EI)**: *m/z*, (%) 429 (15), 428 (53), 427 (13), 398 (11), 385 (13), 384 (13), 370 (13), 369 (17), 368 (31), 325 (22), 324 (13), 314 (14), 313 (34), 297 (24), 295 (14), 271 (14), 239 (27), 226 (21), 213 (19), 58 (100), 57 (34).

**Anal. Calcd. for $C_{26}H_{24}N_2O_4$**: C 72.88, H 5.64; N 6.54. Found: C 72.78, H 5.40, N 6.64.

**IR (KBr)**: 3464, 2891, 1613, 1519, 1455, 1345, 1302, 1250, 1087, 1021, 938, 878, 861, 815, 756, 700, 598 cm.$^{-1}$

***2,2'-dibenzyl-2,2',3,3'-tetrahydro-1H,1'H-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol (73):***



A solution of formaldehyde solution (1.04 g, 37% w/v, 2.814 mL, 34.68 mmol) and benzylamine (1.70 g, 1.74 mL, 15.89 mmol) in methanol was stirred for 30 min under nitrogen atmosphere, to this solution 7,7’-dihydroxy-2,2’-binaphthol **71** (2.30 g, 72.24 mmol) was added in one portion. Then the solution was stirred for 48 h at 60 ºC. After the completion of the reaction the mixture was concentrated and the crude product was purified by column chromatography on silica gel using gradient petroleum ether:ethyl acetate (100:0 to 60:40) as eluent to obtain a white solid which was dried in vacuum. Yield = 3.450 g (82%).

**Mp**. 190-192 ºC

**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.16 (m, 6H), 6.95 (m, 6H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 2H), 4.62 (d, *J* = 9.6 Hz, 2H), 4.48 (d, *J* = 9.2 Hz, 2H), 3.55 (m, 4H), 3.47 (d, *J* = 16.8 Hz, 2H), 3.20 (d, *J* = 16.8 Hz, 2H).

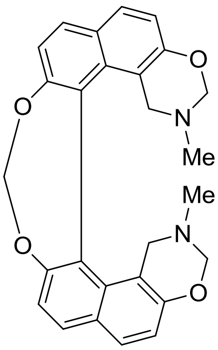
**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: δ 153.91 (Cq), 153.81 (Cq), 137.45 (Cq), 132.95 (CH), 132.73 (Cq), 129.49 (CH), 128.32 (2 X CH), 128.25 (2 X CH), 127.01 (CH), 125.50 (Cq), 117.20 (CH), 114.11 (CH), 111.84 (Cq), 111.74 (Cq), 80.73 ($O\underline{C}H_2N$), 55.34 ($Ar\underline{C}H_2N$), 48.56 ($N\underline{C}H_2Ph$).

**MS (EI)**: *m/z*, (%) 579 (21), 550 (06), 488 (11), 460 (12), 444 (08), 369 (28), 324 (36), 313 (48), 312 (52), 311 (62), 296 (24), 238 (48), 194 (78), 134 (32), 118 (94), 92 (12), 91 (100), 89 (08).

**Anal. Calcd. for $C_{38}H_{32}N_2O_4$**: C 78.60, H 5.55; N 4.82. Found: C 78.22, H 5.19, N 4.77.

**IR (KBr):** 3511, 2882, 1611, 1514, 1449, 1343, 1138, 1078, 1024, 932, 833, 734, 705, 608 cm.$^{-1}$

***Synthesis of compound Helical [1,3]-Bis-oxazine (74):***



A solution of pure 2,2'-dimethyl-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'-diol (1.0 g, 2.33 mmol) in dry DMF (15 mL) was added $CH_2I_2$ (0.94 g, 0.43 mL, 3.49 mmol) and the mixture was stirred for 48 h at room temperature. After the completion of the reaction (monitored by tlc) the reaction mixture was poured in ice cold water. The aqueous was extracted with chloroform (3 X 100 mL) combine the extract and washed with water (2 X 100 mL) and the organic layer was dried over $Na_2SO_4$ and evaporated to obtain brown viscous oil. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether:ethyl acetate (100:00 to 70:30) as eluent to get a white solid.

Yield = (0.57 g, 56 %) **M.p**. 178-179 ºC;

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.64 (s, 2H), 4.53 (d, *J* = 9.2 Hz, 2H), 4.50 (dd, *J* = 2.4, 9.6 Hz, 2H), 2.66 (d, *J* = 16.4 Hz, 2H), 2.39 (d, *J* = 16.4 Hz, 2H), 2.06 (s, 6H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 152.65 (Cq), 151.03 (Cq), 133.92 (Cq), 131.17 (CH), 129.52 (CH), 127.89 (Cq), 126.23 (Cq), 118.05 (CH), 117.20 (CH), 111.84 (Cq), 102.17 ($O\underline{C}H_2O$), 82.77 ($O\underline{C}H_2N$), 51.30 ($Ar\underline{C}H_2N$), 38.59 ($\underline{C}H_3$).

**MALDI-TOF-MS**: *m/z* = 441.1183 ($[M+H]^+$).

**MS (EI)**: *m/z*, (%) 440 (32), 439 (100), 410 (10), 396 (12), 382 (22), 381 (18), 380 (11), 354 (11), 353 (11), 352 (15), 323 (29), 312 (17), 311 (11), 295 (14), 239 (15), 238 (12), 69 (10).

**Anal. Calcd. for $C_{27}H_{24}N_2O_4$**: C 73.62, H 5.49, N 6.35. Found: C 73.28, H 5.74, N 6.35.

**IR (KBr)**: 3070, 2951, 2890, 1610, 1509, 1450, 1362, 1321, 1296, 1236, 1195, 1162, 1127, 1083, 1050, 1000, 922, 839, 795, 721 cm.$^{-1}$

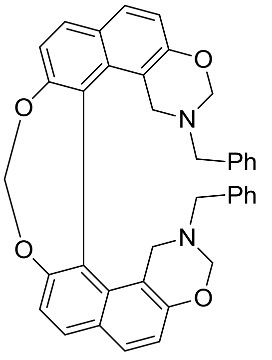
**HPLC analysis:**

Observed two peaks of seperate enantiomers at 1) $R_t$ – 8.38 min and 2) $R_t$ – 11.36 min.

Solvent System: *n*-Hexane: *Iso*-propanol (85:15), Flow rate: 1 mL/min.

Chiral Column: Lux Amylose 2

***Synthesis of compound Helical [1,3]-Bis-oxazine (74):***



A solution of pure 2,2'-bis-(1-phenyl-ethyl) 2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'-diol (0.550 g, 0.95 mmol) and $Cs_2CO_3$ (1.543 g, 4.74 mmol) in dry DMF (10 mL) and $CH_2I_2$ (0.380 g, 0.114 mL, 1.42 mmol) was added and the mixture was stirred 48 h at room temperature. After the completion of the reaction (monitored by tlc) the reaction mixture was poured in ice cold water. The aqueous layer was extracted with chloroform (3 X 100 mL) combine the extract and washed with water (2 X 100 mL) and the organic layer was dried over $Na_2SO_4$ and evaporated to obtained crude solid. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether/ethyl acetate as eluent (100:00 to 80:20) giving a white solid.

Yield = (330 g, 59%), **M.p.** 222 ºC;

**$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 9.2 Hz, 2H), 7.23-7.20 (m, 6H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.99-6.97 (m, 4H), 6.96 (d, *J* = 9.2 Hz, 2H), 4.57 (d, *J* = 9.6 Hz, 2H), 4.50 (dd, *J* = 2.0, 9.2 Hz, 2H), 3.37 (d, *J* = 12.8 Hz, 2H), 3.23 (d, *J* = 12.8 Hz, 2H), 2.71 (d, *J* = 16.4 Hz, 2H), 2.53 (d, *J* = 16.4 Hz, 2H).

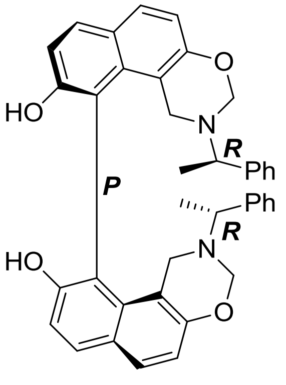
**$^{13}$C NMR ($CDCl_3$, 100.6 MHz):** δ 152.85 (Cq), 150.84 (Cq), 137.45 (Cq), 133.74 (Cq), 130.90 (CH), 129.56 (CH), 129.04 (2 X CH), 128.23 (2 X CH), 127.79 (Cq), 127.11 (CH), 126.27 (Cq), 117.98 (CH), 117.13 (CH), 112.03 (Cq), 102.04 (O-$\underline{C}H_2$-O), 80.34 (N$\underline{C}H_2$O), 54.44 (Ar$\underline{C}H_2$N), 49.41 (N$\underline{C}H_2$Ph).

**MS (EI)**: *m/z*, (%) 592 (08), 536 (09), 439 (14), 382 (25), 298 (31), 256 (27), 255 (28), 236 (31), 182 (36), 127 (26), 119 (29), 111 (35), 97 (42), 95 (37), 91 (100), 85 (28), 84 (32), 83 (75), 81 (48), 71 (47).

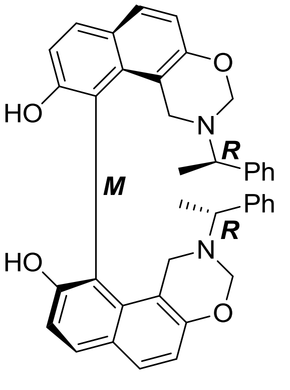
**Anal. Calcd. for $C_{39}H_{32}N_2O_4$**: C 79.03, H 5.44, N 4.73. Found: C 78.64, H 5.30, N 4.65.

**IR (KBr):** 3026, 2990, 2929, 2885, 2858, 1610, 1509, 1453, 1363, 1323, 1244, 1199, 1155, 1132, 1068, 1036, 1009, 925, 839, 786., 745, 696 cm.$^{-1}$

***(P)/(S)-2,2'-Bis-((R)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi-[naphtha-[1,2-e][1,3]oxazinyl]-9,9'-diol (76a) and (M)/(R)-2,2'-bis-((R)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'-diol (76b):***



**76a** crystals



**76b** mother liquid

A solution of formaldehyde (0.45 g, 37% w/v, 1.22 mL, 6.91 mmol) and *R*-(-)-phenylethyl amine (0.837 g, 0.879 mL, 6.91 mmol) in methanol was stirred for 30 min under nitrogen atmosphere. To this solution 7,7'-dihydroxy-2,2'-binaphthol (1.00 g, 3.14 mmol) was added in one portion. The solution was stirred for 48 h at 60 ºC. The white precipitates were filtered and washed with methanol (3 X 10 mL), the solid was dried under vacuum.

**(*76a*) Yield** = 0.707 g (37%), **M.p.** 219-220 ºC; $[\alpha]_D^{28}$ = + 204 (*c* = 0.5 in $CHCl_3$).

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.09-7.08 (m, 6H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.93-6.91 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.02 (s, 2H), 4.59 (d, *J* = 9.6 Hz, 2H), 4.45 (d, *J* = 9.2 Hz, 2H), 3.62 (q, *J* = 6.4 Hz, 2H), 3.52 (d, *J* = 16.8 Hz, 2H), 3.12 (d, *J* = 16.8 Hz, 2H), 1.09 (d, *J* = 6.4 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 154.57 (Cq), 153.80 (Cq), 143.40 (Cq), 133.00 (CH), 132.50 (Cq), 129.24 (2 X CH), 128.26 (CH), 126.96 (CH), 126.64 (2 X CH), 125.51 (Cq), 117.34 (CH), 113.88 (CH), 112.52 (Cq), 111.80 (Cq), 79.13 ($O\underline{C}H_2N$), 58.14 ($PhMe\underline{C}HN$), 46.91 ($Ar\underline{C}H_2N$), 21.00 ($\underline{C}H_3$).

**MS (ESI)**: *m/z*, (%) 609.30 ($[M]^+$) (100.00), 610.28 ($[M+1]^+$) (42.81), 611.33 ($[M+2]^+$) (9.18).

**Anal. Calcd. for $C_{40}H_{36}N_2O_4$**: C 78.92, H 5.96; N 4.60. Found: C 78.85, H 5.70, N 4.45.

**IR (KBr)**: 3509, 3058, 3023, 2976, 2884, 1611, 1515, 1452, 1388, 1367, 1140, 1067, 1029, 937, 898, 835, 782, 759, 703, 611 cm.$^{-1}$

The mother liquor and earlier washings were combined and concentrated to obtain brown solid. The crude product was purified by column chromatography on silica gel using gradient petroleum ether: ethyl acetate 100:0 to 80:20 as eluent to obtain a pale yellow solid dried in vacuum (1.016 g, 53%). By $^1$H-NMR analyses it was found to be a mixture of diastereomers (85:15). The mixture was dissolved in methanol (5 mL) and white solid crystallised after ~15 h.

**(*76a*) Yield** = 0.080 g (4.18%), **M.p.**199-200 ºC. The $^1$H-NMR was found to be in agreement with the above product. The mother liquor was concentrated under reduced pressure to obtain the white solid, dried under vacuum.

**(*76b*)Yield** = 0.828 g (43.3%), **M.p.**139-141 ºC (Crude Product); $[\alpha]_D^{28}$ = – 271 (*c* = 0.5 in $CHCl_3$).

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.25-7.21 (m, 3H), 7.01-6.99 (m, 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.89 (s, 2H for OH), 4.75 (d, *J* = 10.0 Hz, 2H), 4.47 (d, *J* = 9.6 Hz, 2H), 3.70 (q, *J* = 6.8 Hz, 2H), 3.33 (d, *J* = 17.2 Hz, 2H), 3.27 (d, *J* = 17.2 Hz, 2H), 1.05 (d, *J* = 6.4 Hz, 6H).

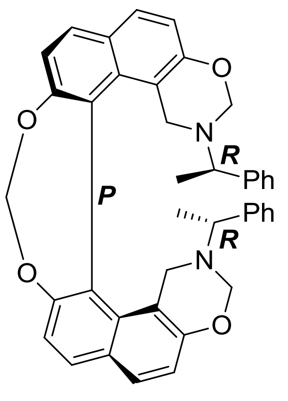
**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 154.59 (Cq), 153.70 (Cq), 143.74 (Cq), 132.98 (Cq), 132.84 (CH), 129.43 (CH), 128.41 (2 X CH), 127.15 (2 X CH), 127.06 (Cq), 125.47 (Cq), 117.02 (CH), 114.14 (CH), 112.61 (Cq), 111.80 (Cq), 78.83 ($O\underline{C}H_2N$), 57.88 ($PhMe\underline{C}HN$), 46.78 ($Ar\underline{C}H_2N$), 21.14 ($\underline{C}H_3$).

**MS (ESI)**: *m/z*, (%) 609.30 ($[M]^+$) (20.12), 610.30 ($[M+1]^+$) (8.75).

**Anal. Calcd. for $C_{40}H_{36}N_2O_4$**: C 78.92, H 5.96; N 4.60. Found: C 78.39, H 5.96, N 4.21.

**IR (KBr)**: 3496, 3060, 3025, 2971, 2926, 2889, 1611, 1516, 1453, 1367, 1342, 1303, 1244, 1224, 1138, 1063, 933, 834, 816, 754, 700 cm.$^{-1}$

***Synthesis of compound Chiral Helical [1,3]-Bis-oxazine (77a):***



**77a**

A solution of pure 2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'-diol **76a** (0.50 g, 0.82 mmol) in dry DMF (10 mL) with $Cs_2CO_3$ (1.39 g, 4.10 mmol) and $CH_2I_2$ (0.33 g, 0.10 mL, 1.23 mmol) was stirred for 48 h at room temperature. The completion of the reaction was monitored by TLC and the reaction mixture was poured in ice cold water. The aqueous portion was extracted with chloroform (3 X 100 mL), combine extract was washed with water (2 X 100 mL) and was dried over $Na_2SO_4$ and evaporated to obtain brown viscous oil. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether: ethyl acetate (100:00 to 80:20) as eluent giving a white solid.

**Yield** = (0.204 g, 40%), **M.p.** 191-192 ºC; $[\alpha]_D^{26}$ = + 884 (*c* = 0.5 in $CHCl_3$).

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.24-7.15 (m, 6H), 7.09-7.06 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.63 (s, 2H), 4.47 (d, *J* = 9.6 Hz, 2H), 4.29 (dd, *J* = 2.4, 9.6 Hz, 2H), 3.40 (q, *J* = 6.4 Hz, 2H), 2.94 (dd, *J* = 1.6, 16.8 Hz, 2H), 2.70 (d, *J* = 16.4 Hz, 2H), 0.87 (d, *J* = 6.4 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 153.37 (Cq), 150.87 (Cq), 143.42 (Cq), 133.58 (Cq), 131.07 (CH), 129.57 (CH), 128.31 (2 X CH), 127.82 (Cq), 127.45 (CH), 127.19 (2 X CH), 126.38 (Cq), 118.05 (CH), 116.93 (CH), 112.03 (Cq), 102.24 ($O\underline{C}H_2O$), 79.93 ($O\underline{C}H_2N$), 56.23 ($PhMe\underline{C}HN$), 46.56 ($Ar\underline{C}H_2N$), 20.92 ($\underline{C}H_3$).

**HMRS (EI)**: Exact mass calculated for $C_{41}H_{37}N_2O_2$ ($[M+H]^+$): 621.2753, found: 621.2729.

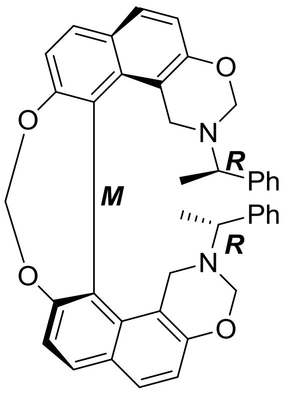
**MALDI-TOF-MS**: *m/z* = 621.1390 ($[M+H]^+$)

**MS (EI)**: *m/z*, (%) 621 (07), 620 (09), 515 (12), 514 (11), 513 (08), 342 (12), 341 (15), 340 (10), 312 (08), 311 (14), 295 (08), 294 (06), 106 (07), 105 (100), 103 (08), 102 (09), 91 (15), 79 (23), 77 (21).

**Anal. Calcd. for $C_{41}H_{36}N_2O_4$**: C 79.33, H 5.85; N 4.51. Found: C 79.35., H 5.54, N 4.75.

**IR (KBr)**: 3058, 3022, 2969, 2893, 1610, 1510, 1453, 1367, 1325, 1239, 1206, 1127, 1059, 1027, 922, 924, 837, 776, 701 cm.$^{-1}$

***Synthesis of compound Helical [1,3]-Bis-oxazine (77b):***



**77b**

A solution of pure 2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3] oxazinyl]-9,9'-diol **76b** (0.60 g, 0.98 mmol) in dry DMF (15 mL) with $Cs_2CO_3$ (1.605 g, 4.93 mmol) and $CH_2I_2$ (0.40 g, 0.12 mL, 1.48 mmol) was stirred for 48 h at room temperature. After the completion of the reaction (tlc) the reaction mixture was poured in ice cold water. The aqueous portion was extracted with chloroform (3 X 100 mL), combine extract was washed with water (2 X 100 mL) and dried over $Na_2SO_4$ and evaporated to obtain brown viscous oil. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether: ethyl acetate (100:00 to 80:20) as eluent giving a white solid.

**Yield** = (0.27 g, 44 %); **M.p.** 198-200 ºC; $[\alpha]_D^{27} = -789$ ($c = 0.5$ in $CHCl_3$).

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.21-7.12 (m, 6H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 1.6, 8.0 Hz, 4H), 5.39 (s, 2H), 4.90 (dd, *J* = 2.4, 9.6 Hz, 2H), 4.58 (d, *J* = 9.6 Hz, 2H), 3.31 (q, *J* = 6.8 Hz, 2H), 2.53 (d, *J* = 16.4 Hz, 2H), 2.38 (dd, *J* = 1.2, 16.8 Hz, 2H), 1.14 (d, *J* = 6.8 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 153.29 (Cq), 150.37 (Cq), 143.72 (Cq), 133.55 (Cq), 130.29 (CH), 129.12 (CH), 128.23 (2 X CH), 127.51 (Cq), 126.82 (2 X CH), 126.79 (CH), 126.18 (Cq), 117.63 (CH), 116.89 (CH), 112.80 (Cq), 101.62 ($O\underline{C}H_2O$), 78.67 ($O\underline{C}H_2N$), 56.86 ($MePh\underline{C}HN$), 47.89 ($Ar\underline{C}H_2N$), 20.45 ($\underline{C}H_3$).

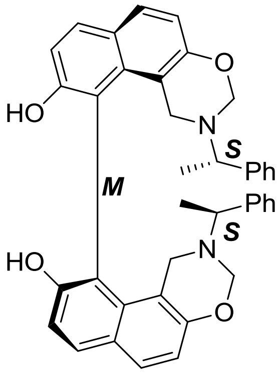
**MALDI-TOF-MS**: *m/z* = 621.0923 ([M+H]$^+$).

**MS (EI)**: *m/z*, (%) 621 (08), 620 (09), 516 (08), 515 (08), 514 (10), 342(08), 341 (10), 340 (08), 256 (10), 133 (12), 111 916), 105 (100), 103 (12), 97 (15), 83 (39), 79 (27), 77 (17).

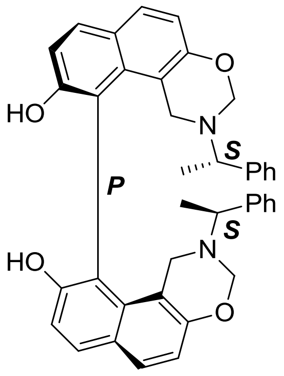
**Anal. Calcd. for $C_{41}H_{36}N_2O_4$**: C 79.33, H 5.85; N 4.51. Found: C 79.25, H 5.44, N 4.69.

**IR (KBr)**: 3024, 3001, 2976, 2928, 2814, 2768, 1612, 1511, 1450, 1408, 1356, 1325, 1279, 1244, 1164, 1139, 1068, 1026, 982, 839, 816, 792, 766, 701 cm.$^{-1}$

***(M)/(R)-2,2'-Bis-((S)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi-[naphtho[1,2-e][1,3]oxazinyl]-9,9'diol(78a) and (P)/(S)- 2,2'-Bis-((S)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'diol (78b):***



**78a** crystals



**78b** mother liquid

A solution of formaldehyde (0.45 g, 37% w/v, 1.22 mL, 6.91 mmol) and *S*-(-)-phenylethylamine (0.837 g, 0.879 mL, 6.91 mmol) in methanol was stirred under nitrogen atmosphere (30 mins), to this solution 7,7'-dihydroxy-2,2'-binaphthol **71** (1.00 g, 3.14 mmol) was added in one portion. The solution was stirred for additional 48 h at 60 ºC. The white precipitate was separated out, filtered, washed with methanol (3 X 10 mL) and dried under vacuum.

***(78a)*** **Yield** = 0.690 g (36%), **M.p.** 220-221 ºC; $[\alpha]_D^{28} = -201$ ($c = 0.5$ in $CHCl_3$).

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.09-6.84 (m, 14H), 5.04 (s, 2H, -OH), 4.59 (d, *J* = 8.8 Hz, 2H), 4.45 (d, *J* = 9.2 Hz, 2H), 3.62 (broad d, *J* = 6.0 Hz, 2H), 3.52 (d, 16.4 Hz, 2H), 3.12 (d, *J* = 16.8 Hz, 2H), 1.09 (d, *J* = 5.6 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 154.60 (Cq), 153.84 (Cq), 143.43 (Cq), 133.03 (CH), 132.54 (Cq), 129.28 (CH), 128.29 (2 X CH), 127.00 (CH), 126.68 (2 X CH), 125.55 (Cq), 117.37 (CH), 113.92 (CH), 112.56 (Cq), 111.85 (Cq), 79.17 ($O\underline{C}H_2N$), 58.17($PhMe\underline{C}HN$), 46.95($Ar\underline{C}H_2N$), 21.04 ($\underline{C}H_3$).

**MS (ESI)**: *m/z*, (%) 609.32 ($[M]^+$) (100.00), 610.30 ($[M+1]^+$) (43.50), 611.33 ($[M+2]^+$) (9.6).

**Anal. Calcd. for $C_{40}H_{36}N_2O_4$**: C 78.92, H 5.96; N 4.60. Found: C 78.45, H 6.23, N 4.62.

**IR (KBr)**: 3511, 3057, 3023, 2974, 2885, 1613, 1577, 1530, 1490, 1451, 1367, 1341, 1267, 1239, 1224, 1189, 1067, 1028, 959, 939, 899, 834, 814, 782, 760, 704 cm.$^{-1}$

The mother liquor and the earlier washings were combined and concentrated to obtain brown solid. The crude product was purified by column chromatography on silica gel using gradient petroleum ether:ethyl acetate (100:0 to 80:20) as eluent to obtain a pale yellow solid. Yield = 0.922 g (48%). The $^1$H-NMR analysis indicated presence of a mixture of diastereomers (85:15). The mixture was dissolved in methanol (5 mL) and kept overnight to obtain a white solid.

***(78a)*** Yield = 0.065 g (3.39%), **M.p.** 219-220 ºC. The $^1$H NMR was in accordance with the above sample of crystallized product **78a**.

The mother liquor was concentrated under reduced pressure to obtain a white solid, which was dried under vacuum.

***(78b)*** **Yield** = 0.630 g (33%), **M.p.** 128-130 ºC (Crude Product); $[\alpha]_D^{28}$ = + 168 (*c* = 0.5, $CHCl_3$).

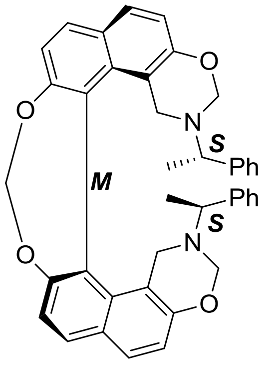
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.25-7.20 (m, 6H), 7.03-6.99 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.88 (bs, 2H for –OH), 4.76 (d, *J* = 9.6 Hz, 2H), 4.48 (d, *J* = 9.6 Hz, 2H), 3.69 (q, *J* = 6.8 Hz, 2H), 3.36-3.25 (two doublets are merged *J* = 17.2 Hz and 16.8 Hz, 4H), 1.06 (d, *J* = 6.8 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100.6 MHz)**: δ 154.56 (Cq), 153.67 (Cq), 143.71 (Cq), 132.96 (Cq), 132.78 (CH), 129.39 (CH), 128.38 (2 x CH), 127.11 (CH), 127.02 (2 x Cq), 125.44 (Cq), 116.98 (CH), 114.11 (CH), 112.59 (Cq), 111.80 (Cq), 78.80 ($O\underline{C}H_2N$), 57.86 ($PhMe\underline{C}HN$), 47.76 ($Ar\underline{C}H_2N$), 21.10 ($CH_3$).

**MS (ESI)**: *m/z*, (%) 609.31 ($[M]^+$) (10.53), 610.31 ($[M+1]^+$) (4.51).

**IR (KBr)**: 3467, 1611, 1516, 1451, 1342, 1241, 1225, 1138, 931, 830, 702 cm.$^{-1}$

### ***Synthesis of compound Helical Chiral [1,3]-Bis-oxazine (79a):***



**79a**

A solution of pure 2,2'-bis-((S)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl]-9,9'-diol (0.50 g, 0.82 mmol) in dry DMF (10 mL) was added $Cs_2CO_3$ (1.34 g, 0.41 mmol) and $CH_2I_2$ (0.33 g, 0.1 mL, 0.12 mmol) and the stirred for 48 h at room temperature. On the completion of the reaction (tlc) the mixture was poured on ice cold water. The aqueous layer was extracted with chloroform (3 X 100 mL), combine extract was washed with water (2 X 100 mL) and was dried over $Na_2SO_4$ and evaporated to obtain brown viscous oil. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether:ethyl acetate (100:0 to 80:20) as eluent giving a white solid (0.353 g, 69 %). **M.p.** 189-191 ºC; $[\alpha]_D^{26}$ = – 888 ($c$ = 0.5 in $CHCl_3$)

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.24-7.16 (m, 6H), 7.10-7.07 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.63 (s, 2H), 4.47 (d, *J* = 9.2 Hz, 2H), 4.39 (dd, *J* = 2.8, 9.6 Hz, 2H), 3.41 (q, *J* = 6.4 Hz, 2H), 2.94 (dd, *J* = 1.6, 16.8 Hz, 2 H), 2.70 (d, *J* = 16.4 Hz, 2H), 0.88 (d, *J* = 6.4 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100 MHz)**: δ 153.38 (Cq), 150.89 (Cq), 143.42 (Cq), 133.59 (Cq), 131.07 (CH), 129.58 (CH), 128.31 (2 X CH), 127.83 (Cq), 127.46 (2 X CH), 127.19 (CH), 126.38 (Cq), 118.06 (CH), 116.94 (CH), 112.05 (Cq), 102.24 ($O\underline{C}H_2O$), 79.94 ($O\underline{C}H_2N$), 56.25 ($PhMe\underline{C}HN$), 46.57 ($Ar\underline{C}H_2N$), 20.92 ($\underline{C}H_3$).

**HMRS (EI)**: Exact mass calculated for $C_{41}H_{37}N_2O_2$ ($[M+H]^+$): 621.2753, found: 621.2781.

**MALDI-TOF-MS**: *m/z* = 621.1062 ($[M+H]^+$).

**MS (EI)**: *m/z*, (%) 621 (08), 620 (09), 516 (11), 515 (13), 514 (08), 342 915), 341 (20), 312 (13), 311 (14), 310 (07), 295 (11), 294 (08), 134 (16), 133 (11), 105 (100), 103 (08), 102 (08), 91 (16), 79 (17), 77 (19).

**Anal. Calcd. for $C_{41}H_{36}N_2O_4$**: C 79.33, H 5.85; N 4.51. Found: C 79.35, H 5.54, N 4.75.

**IR (KBr)**: 3059, 3023, 2969, 2924, 2894, 2853, 1611, 1510, 1452, 1371, 1325, 1241, 1209, 1157, 1126, 1061, 1026, 997, 925, 836, 776, 702 cm.$^{-1}$

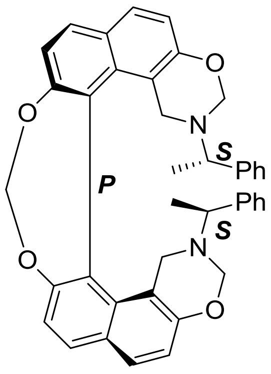
**HPLC analysis:**

Observed 2 peaks of seperated enantiomers at 1) $R_t$ – 6.39min (98.86%) and 2) $R_t$ – 9.02 min (1.14).

Solvent System: n-Hexane: *Iso*-propanol (85:15), Flow rate: 1 mL/min.

Chiral Column: Lux Amylose 2.

***Synthesis of compound Helical-[1,3]-Bis-oxazine (79b):***



**79b**

A solution of pure 2,2'-bis-((*S*)-1-phenyl-ethyl)-2,3,2',3' tetrahydro-1H,1'H-[10,10']bi[naphtho[1,2-e][1,3]oxazinyl] -9,9'-diol **78b** (0.45 g, 0.74 mmol) in dry DMF (10 mL) was added $Cs_2CO_3$ (1.21 g, 3.69 mmol) and $CH_2I_2$ (0.29 g, 0.09 mL, 1.09 mmol) and the mixture was stirred for 48 h at room temperature. On the completion of the reaction (tlc) the mixture was poured on ice cold water. The aqueous was extracted with chloroform (3 X 100 mL) combine the extract and washed with water (2 X 100 mL) and the organic layer was dried over $Na_2SO_4$ and evaporated to obtain brown viscous oil. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether:ethyl acetate (100:0 to 80:20) as eluent giving a white solid.

**Yield** = (0.208 g, 45 %), **M.p.** 201-203 ºC; $[\alpha]_D^{27}$ = + 764 (*c* = 0.5 in $CHCl_3$)

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.60 (d, *J* = 9.2 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.20-7.12 (m, 6H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.78 (dd, *J* = 1.2, 8.0 Hz, 4H), 5.39 (s, 2H), 4.90 (dd, *J* = 2.4, 9.6 Hz, 2H), 4.58 (d, *J* = 9.6 Hz, 2H), 3.32 (q, *J* = 6.8 Hz, 2H), 2.53 (d, *J* = 16.4 Hz, 2H), 2.39 (dd, *J* = 0.8, 16.4 Hz), 1.14 (d, *J* = 6.8 Hz, 6H).

**$^{13}$C NMR ($CDCl_3$, 100 MHz)**: δ 153.28 (Cq),150.36 (Cq), 143.72 (Cq), 133.54 (Cq), 130.28 (CH) 129.12 (CH), 128.22 (2 X CH), 127.50 (Cq), 126.81 (2 X CH), 126.78 (CH), 126.18 (Cq), 117.63 (CH), 116.89 (CH), 112.80 (Cq), 101.61 ($O\underline{C}H_2O$), 78.66 ($O\underline{C}H_2N$), 56.85 ($MePh\underline{C}HN$), 47.89 ($Ar\underline{C}H_2N$), 20.45 ($\underline{C}H_3$).

**MALDI-TOF-MS**: *m/z* = 621.1373 ($[M+H]^+$).

**MS (EI)**: *m/z*, (%) 621 (09), 620 (09), 619 (10), 516 (26), 515 (30), 514 (14), 342 (12), 341 (23), 340 (25), 312 (11), 311 (14), 295 (06), 294 (07), 106 (07), 105 (100), 103 (08), 102 (08), 91 (12), 79 (13), 77 (18).

**IR (KBr)**: 2970, 2924, 2853, 2815, 2769, 1612, 1511, 1454, 1325, 1278, 1243, 1165, 1139, 1067, 1026, 983, 839, 716, 794, 766, 701 cm.$^{-1}$

**HPLC analysis:**

Observed two peaks of seperated enantiomers at 1) $R_t$ – 5.70min (99.59%) and 2) $R_t$ – 11.43min (0.41%).

Solvent System: n-Hexane: *Iso*-propanol (85:15), Flow rate: 1 mL/min.

Chiral Column: Lux Amylose 2.

## UV-Vis and CD Spectra

UV and CD spectra were recorded on Perkin Elmer Lambda-35 and Jasco J-815 spectrophotometer respectively, at room temperature and by using a 1 or 0.2 cm path length quartz cell. Spectra were recorded in the 220–500 nm wavelength range. The CD spectra with a 1 nm band width, 0.1 nm band pitch and 20 nm/min scanning speed in chloroform.

| Compound | CD Data [ λ(nm)(εΔε[M-1cm-1])] |
|---|---|
| **76a** | 339.2 (+18.0), 334.3 (-17.2), 273.2 (+77.7), 269.9 (-25.9), 265.6 (-7.8). |
| **76b** | 338.5 (-6.7), 332.4 (+7.4), 312.8 (-6.6), 303.6 (+1.0), 274.3 (-37.4), 265.5 (-25.2) |
| **78a** | 339.2 (-17.9), 334.3 (+17.3), 273.2 (-77.5), 270.0 (+25.9), 265.6 (+7.7). |
| **78b** | 338.4 (+6.6), 332.4 (-7.4), 312.8 (+6.5), 304.0 (-1.1), 274.5 (+37.5). |
| **77a** | 360.1 (+44.3), 350.5 (+28.4), 343.4 (+34.4), 294.5 (-67.4), 273.0 (+61.0). |
| **77b** | 357.5 (-41.8), 345.9 (-29.0), 342.1 (-35.6), 301.3 (+77.9), 293.7 (+85.9), 269.1 (-18.6). |
| **79a** | 359.9 (-44.3), 350.6 (-28.5), 343.4 (-34.4), 294.9 (+67.4), 273.2 (-59.8). |
| **79b** | 357.5 (+40.5), 345.8 (+29.1), 342.2 (36.6), 340.3 (+42.2), 301.4 (-45.6), 293.9 (-46.7), 266.1 (+23.4). |

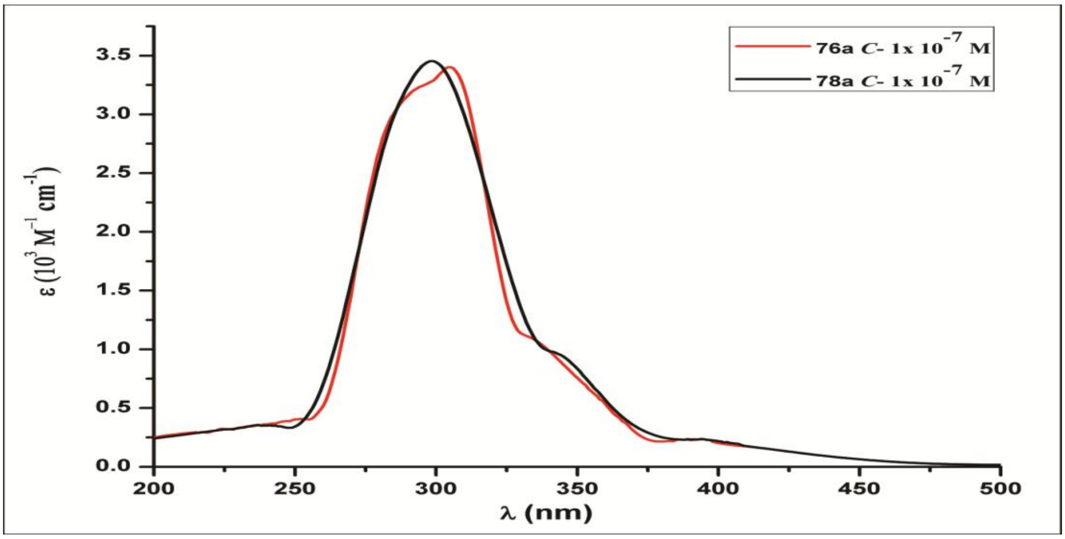
In this experiment we found that the chloroform has, the absorbance in the range of UV region, hence the circular dichroism experiments were run in tetrahydrofuran and acetonitrile. The excellent results were obtained in acetonitrile.

The CD spectra were also recorded in acetonitrile and in THF in some cases. The data for the spectra are provided here.

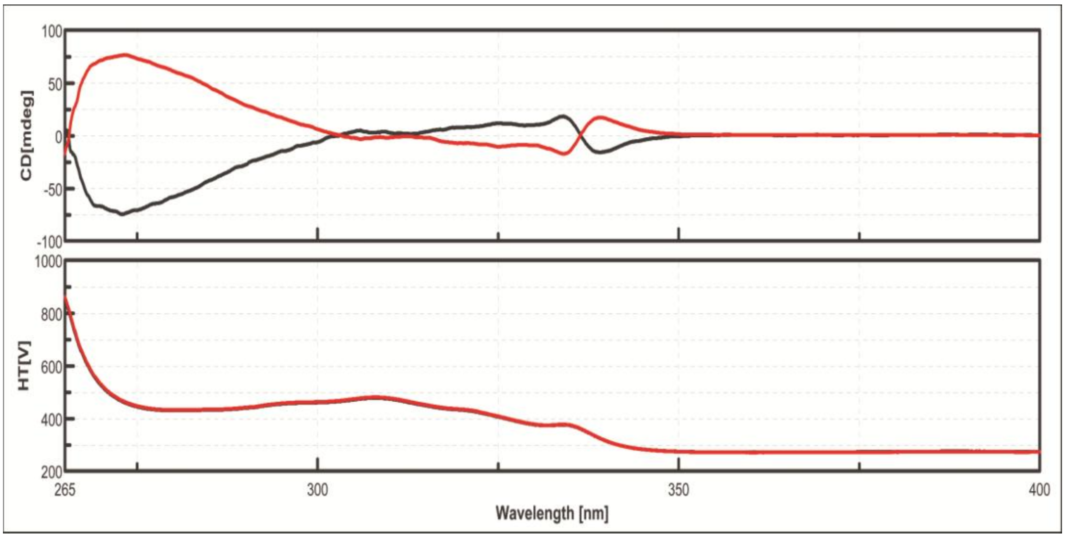
| Compound | CD Data [ λ(nm)(εΔε[M-1cm-1])] |
|---|---|
| **76a** | 336.2 (-39.6), 322.5 (-34.3), 305.9 (-42.5), 265.7 (+102.6). |
| **76b** | 335.6 (-22.8), 322.4 (-12.8), 305.2 (-29.9), 260.1(+54.5). |
| **76a*** | 336.1 (-54.0), 321.8 (-48.2), 310.5 (-55.5), 269.0 (+98.1). |
| **78a** | 335.7 (+41.8), 320.9 (+36.2), 301.8 (+44.8), 265.8 (-94.6). |
| **78a*** | 336.4 (+50.2), 322.4 (+46.8), 308.1 (52.8), 270.2 (-102.4). |
| **78b** | 335.4 (+30.0), 320.1 (+25.3), 305.5 (+41.1), 264.1 (-59.9). |
| **77a** | 357.8 (+32.5), 344.4 (+24.9), 292.6 (-35.4), 269.9(+70.8). |
| **77b** | 356.2 (+22.0), 342.0 (+26.2), 290.1 (-25.0), 260.2 (+52.1), 239.8 (+38.5). |
| **79a** | 358.0 (-26.8), 344.5 (-25.2), 295.2 (+27.1), 266.1 (-80). |
| **79b** | 356.6 (-28.4), 343.2 (-26.1), 289.8 (+36.8), 261.8 (-51.9), 238.8 (-38.3). |

(* Solvent for analysis - Tatrahydrofuran)

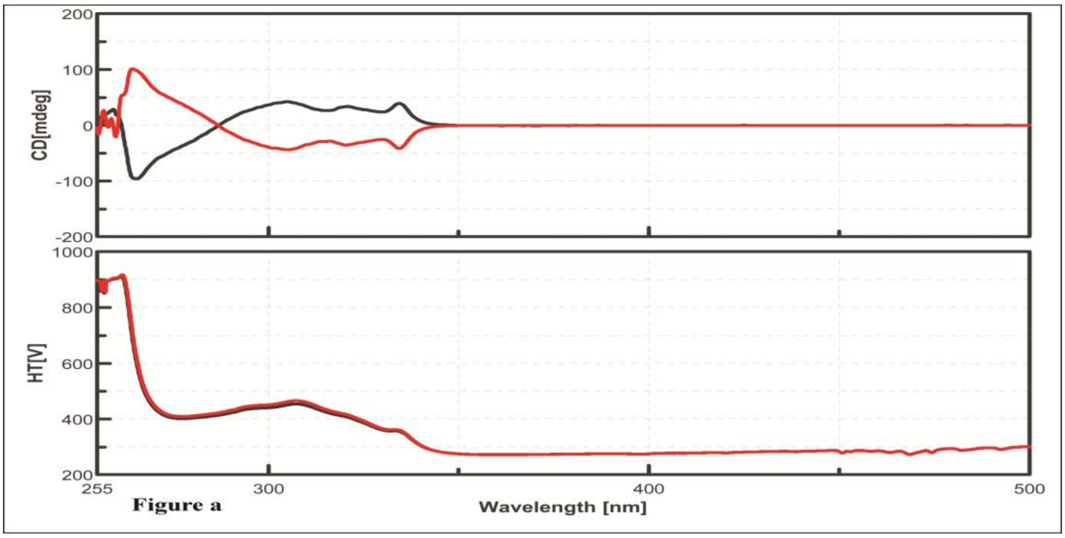
**UV spectra of Helical Oxazines:** (red line) **76a** and (black line) 7**8a** (1x$10^{-7}$ M in $CHCl_3$, 25 ºC).



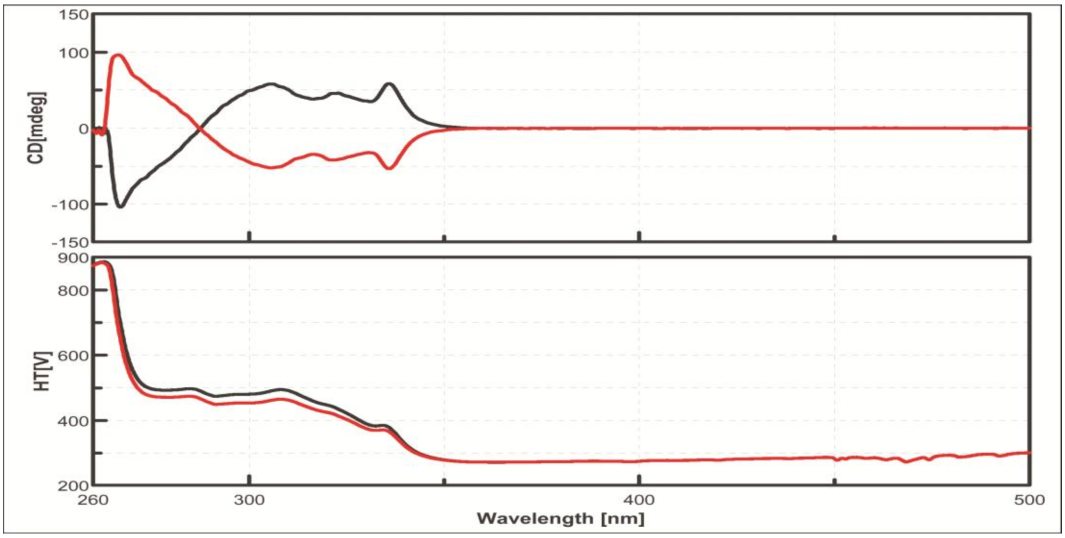
**Circular dichroism spectra of resolved Helical Oxazines:** (black line) **76a** and (red line) 7**8a** (1x$10^{-7}$ M in $CHCl_3$, 25 ºC).



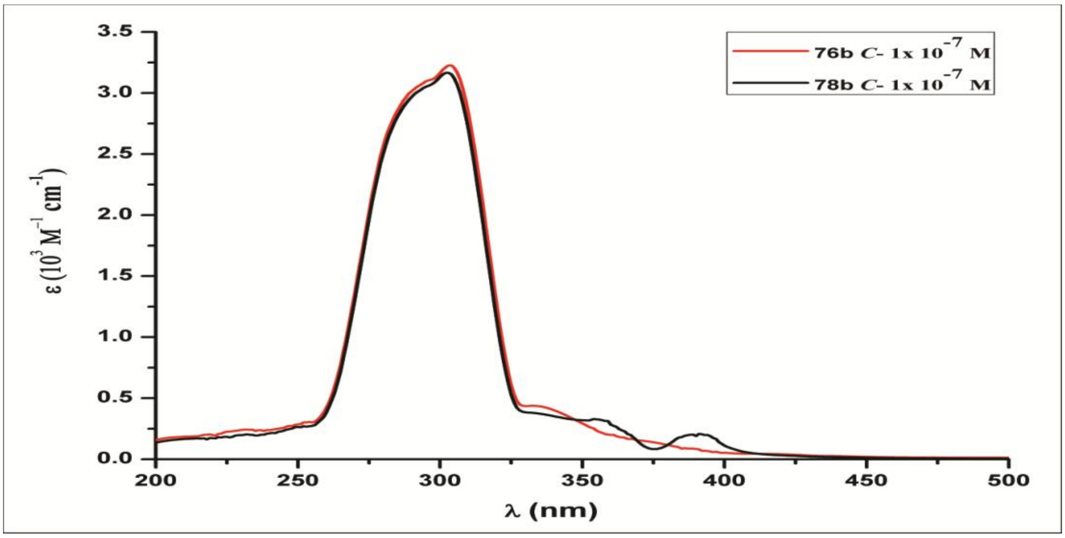
**Circular dichroism spectra of resolved Helical Bis-Oxazines:** (red line) **76a** and (black line) **78a** (*c* 1 x $10^{-7}$ M in Acetonitrile, 25 ºC)



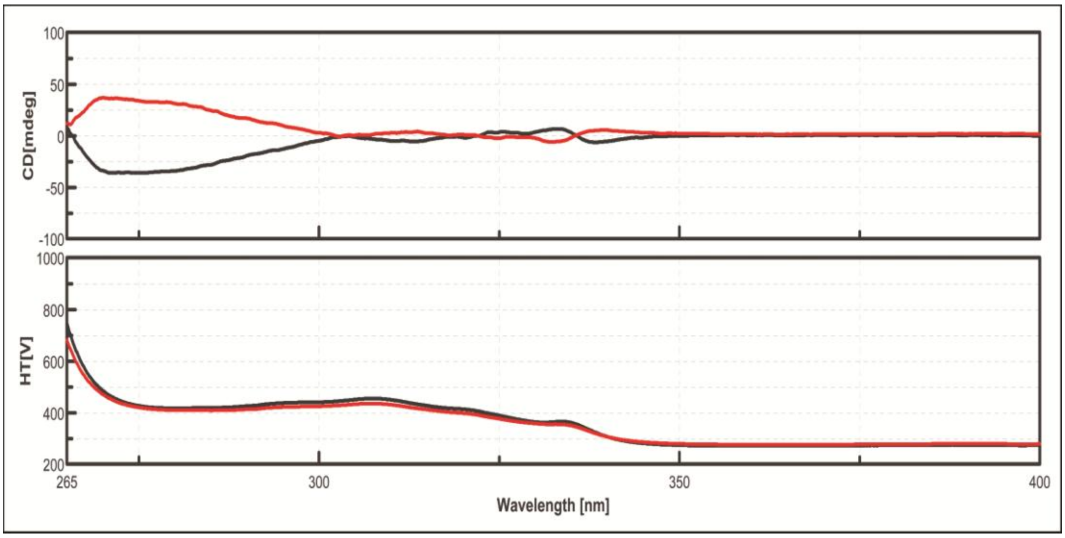
**Circular dichroism spectra of resolved Helical Bis-Oxazines:** (red line) **76a** and (black line) **78a** (*c* $1 \times 10^{-7}$ M in Tetrahydrofuran, 25 ºC)



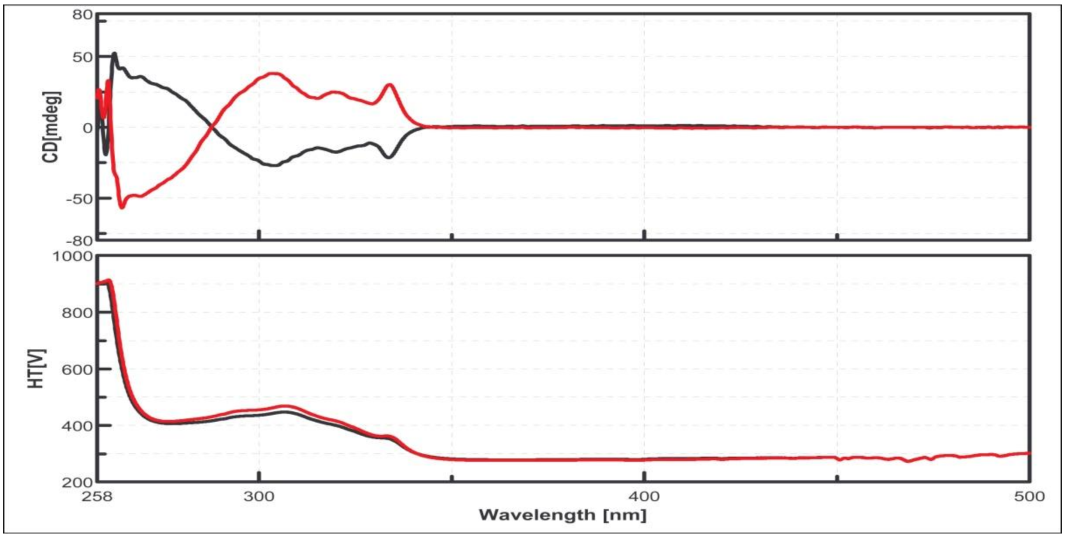
**UV spectra of Helical Oxazines:** (red line) **76b** and (black line) 7**8b** ($1 \times 10^{-7}$ M in $CHCl_3$, 25 ºC).



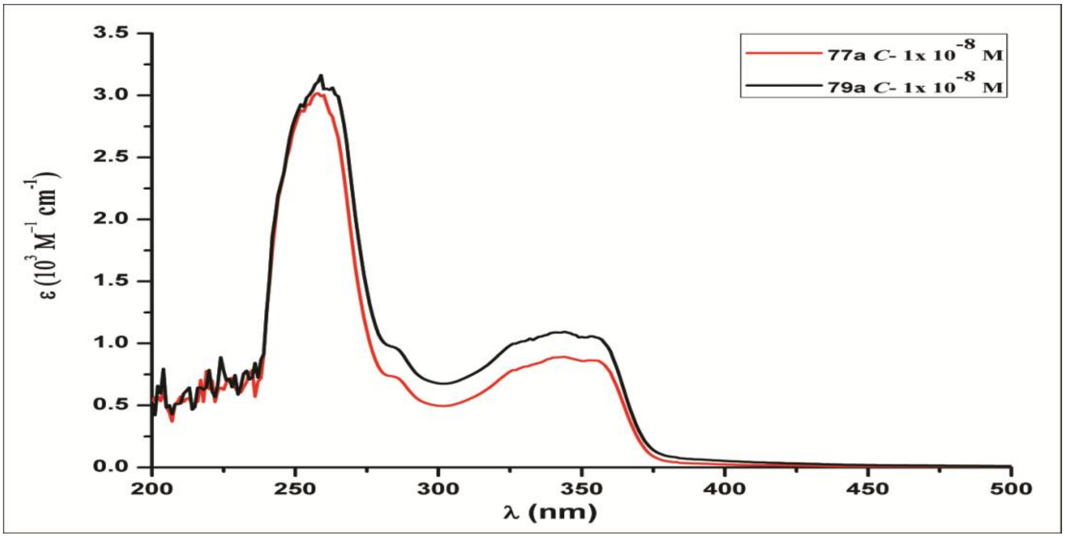
**Circular dichroism spectra of resolved Helical Oxazines:** (black line) **76b** (red line) **78b**, ($1 \times 10^{-7}$ M in $CHCl_3$, 25 ºC).



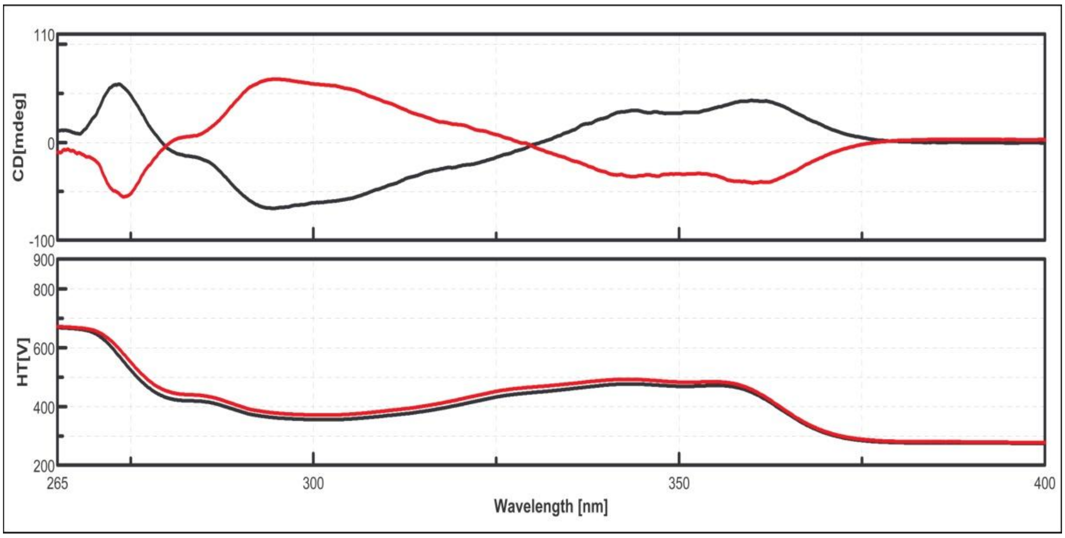
**Circular dichroism spectra of resolved Helical Oxazines:** (red line) **76b**, (black line) **78b**, (*c* 1 x $10^{-7}$ M in Acetonitrile, 25 °C).



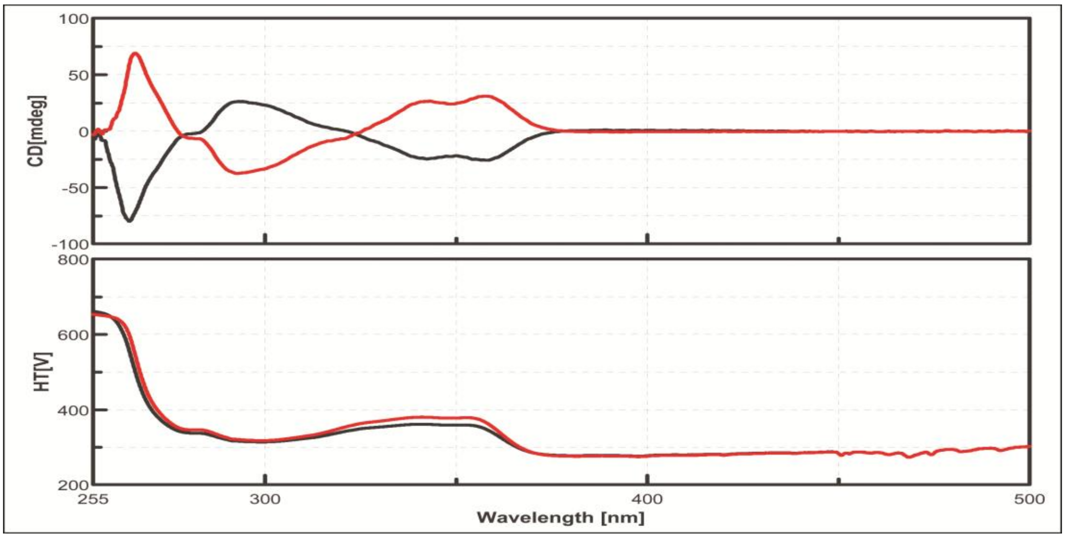
**UV spectra of resolved Helical Oxazines:** (red line) **77a** and (black line) **79a**, (1x$10^{-8}$ M in $CHCl_3$, 25 ºC).



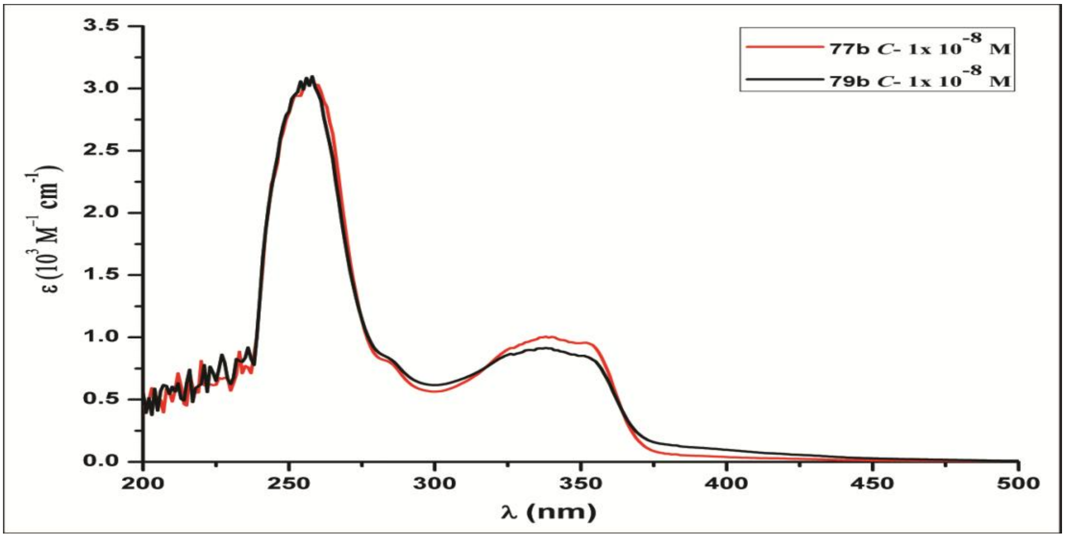
**Circular dichroism spectra of resolved Helical Oxazines:** (red line) **77a** and (black line) **79a**, (1x$10^{-7}$ M in $CHCl_3$, 25 ºC).



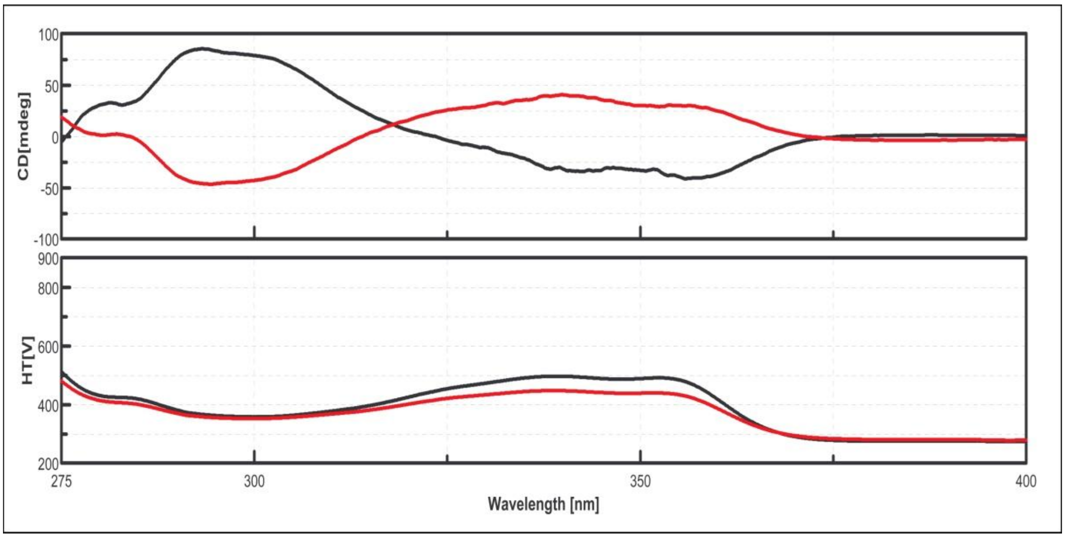
**Circular dichroism spectra of resolved Helical Bis-Oxazines:** (red line) **77a** and (black line) **79a** (*c* 1 x $10^{-7}$ M in Acetonitrile, 25 ºC)



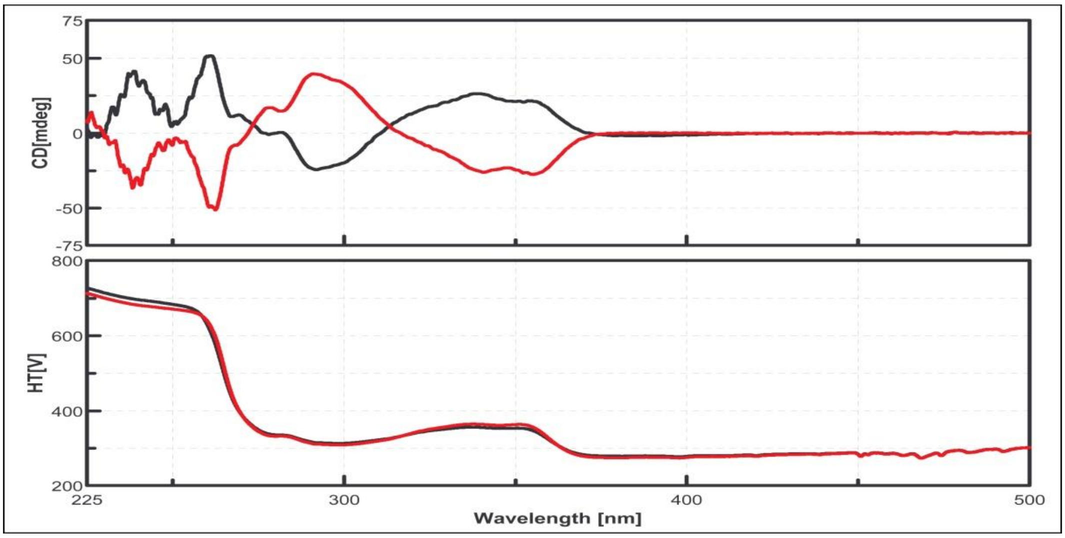
**UV spectra of resolved Helical Oxazines:** (red line) **77b** and (black line) **79b** (*c* = 1x$10^{-8}$ M in $CHCl_3$, 25 ºC).



**Circular dichroism spectra of resolved Helical Oxazines:** (red line) **77b** and (black line) **79b** (*c* = 1x$10^{-7}$ M in $CHCl_3$, 25 ºC).



**Circular dichroism spectra of resolved Helical Oxazines:** (red line) **77b**, (black line) **79b**, ($c$ 1 x $10^{-7}$ M in Acetonitrile, 25 ºC)



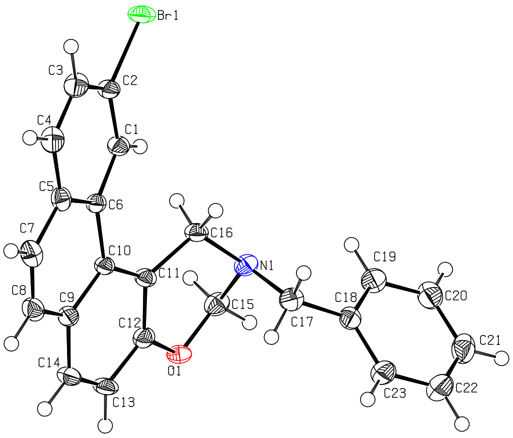
# X-ray Crystal Data

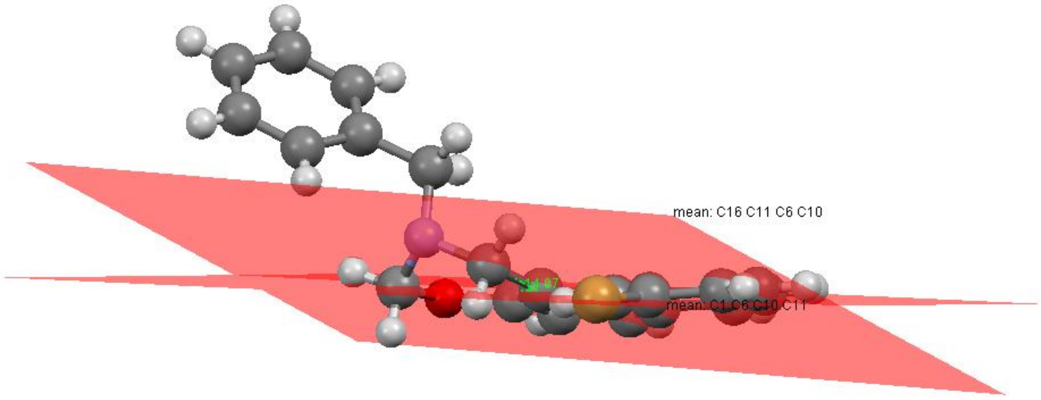
The details of the X-ray structure were deposited at the Cambridge Crystallographic Data Centre Crystal Data for **Compound 53 (CCDC-880821)**, **Compound 64 (CCDC-880822)** and **Compound 76a (CCDC-880823)** and the details can be obtained via: www.ccdc.cam.ac.uk/data_request/cif.

***Crystal data of compound 11-bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza benzo[c]phenanthrene (53):***

| **Details** | **Compound 53**<br>**CCDC-880821** |
|---|---|
| Empirical formula | $C_{23}H_{18}BrNO$ |
| Formula weight | 404.29 |
| Temperature | 110(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P21/c |
| Unit cell dimensions | a = 15.141(2) Å<br>b = 5.8073(9) Å<br>c = 20.844(3) Å<br>α = 90°<br>β = 103.408(2)°<br>γ = 90° |
| Volume | 1782.9(5) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.506 $Mg/m^3$ |
| Absorption coefficient (μ) | 2.317 $mm^{-1}$ |
| F(000) | 824 |
| Crystal Size | 0.43x0.21x0.12 mm |
| θ range for data collection | 2.69-28.05° |
| Reflections collected | 8362 |
| Independent reflections | 3373 [R(int) = 0.0269] |
| Max. And Min. Transmission | 0.7684 and 0.4357 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3373/0/ 235 |
| Goodness-of-fit on $F^2$ | 1.069 |
| Final R indices [I>2sigma(I)] | R1 = 0.0394<br>wR2 = 0.1044 |
| R indices (all data) | R1 = 0.0502<br>wR2 = 0.1163 |
| Largest difference peak and hole | 1.041 and – 0.563 e/ $Å^3$ |

ORTEP diagram of the compound 11-bromo-2-methyl-2,3-dihydro-1H-4-oxa-2-aza benzo[*c*]phenanthrene **53** with atom numbering scheme (50% probability factor for the thermal ellipsoids).





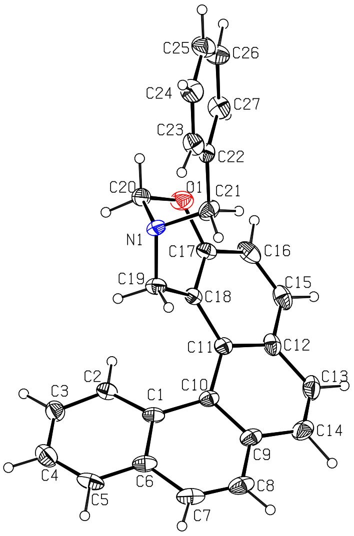
The planes passing through the molecule from the carbons C-16C-11C-6C-10 and C1-C6-C10-C11 showing the twist and the angle between the two planes are 14.97°.

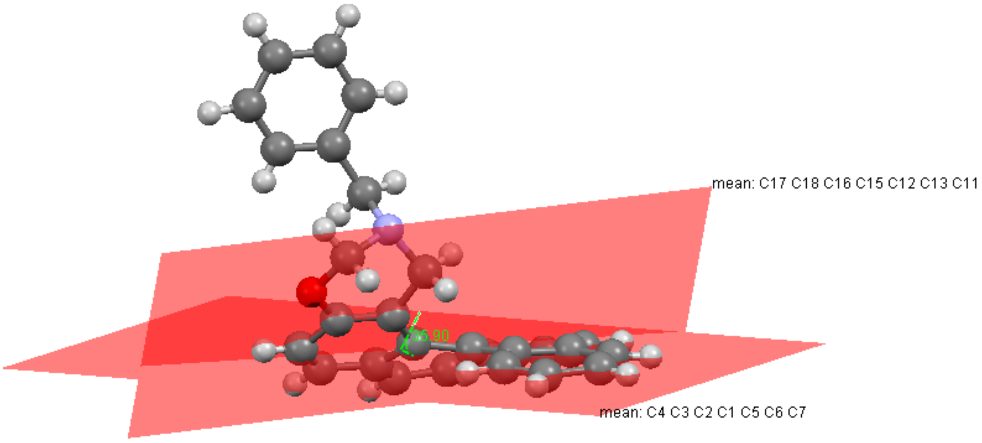
### *Crystal data For Compound*

### *2-benzyl-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-e][1,3]oxazine (64):*

| **Details** | **Compound 64**<br>**CCDC-880822** |
|---|---|
| Empirical formula | $C_{40}H_{36}N_2O_4$ |
| Formula weight | 375.45 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P21/c |
| Unit cell dimensions | a = 12.3621(14) Å<br>b = 6.0846(7) Å<br>c = 25.548(3) Å<br>α = 90°<br>β = 96.044(2) °<br>γ= 90° |
| Volume | 1911.0(7) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.305 $Mg/m^3$ |
| Absorption coefficient (μ) | 0.079 $mm^{-1}$ |
| F(000) | 792 |
| Crystal Size | 0.54x0.29x0.08 mm |
| θ range for data collection | 1.60-25.00º |
| Reflections collected | 9089 |
| Independent reflections | 3359 [R(int) = 0.0482] |
| Max. And Min. Transmission | 0.9937 and 0.9588 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3359/0/ 346 |
| Goodness-of-fit on $F^2$ | 1.299 |
| Final R indices [I>2sigma(I)] | R1 = 0.1058<br>wR2 = 0.1861 |
| R indices (all data) | R1 = 0.1323<br>wR2 = 0.1970 |
| Largest difference peak and hole | 0.223 and – 0.259 e/ $Å^3$ |

ORTEP diagram of the compound 2-benzyl-2,3-dihydro-1H-benzo[5,6]phenanthro[4,3-e][1,3]oxazine **64** with atom numbering scheme (50% probability factor for the thermal ellipsoids ).



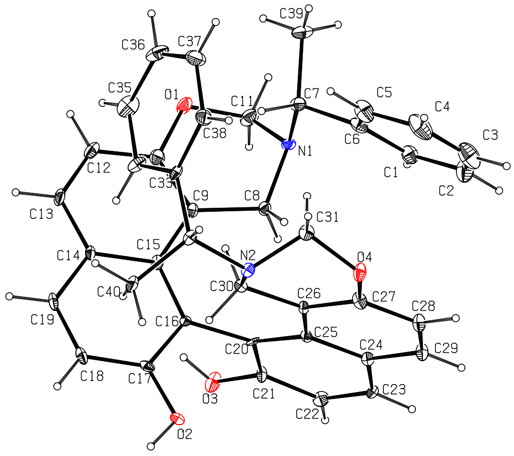


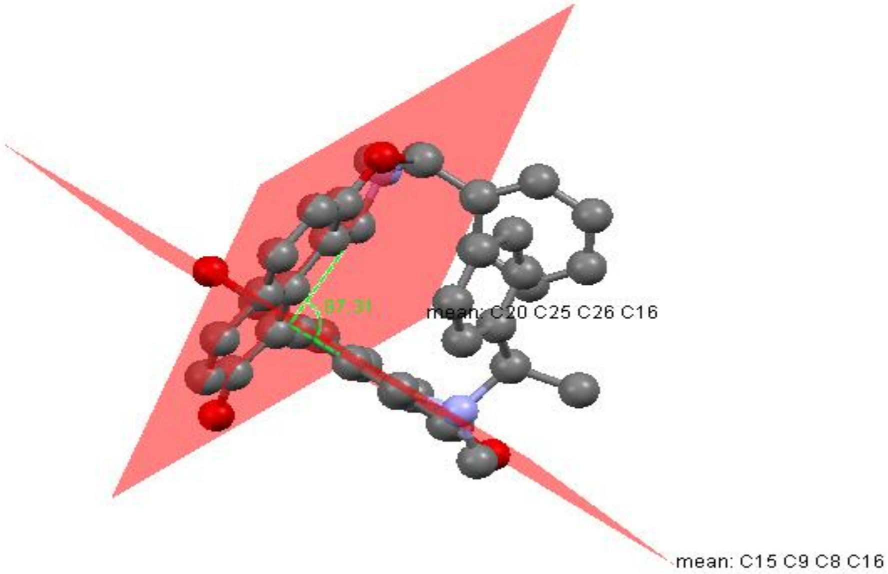
The planes passing through the molecule from the carbons C4-C3-C2-C1-C5-C6-C7 and C17-C18-C16-C15-C12-C13-C11 showing the twist more than the compound **53** and the angle between the two planes are 35.90°.

### *Crystal data For Compound (S)-2,2'-bis((R)-1-phenylethyl)-2,2',3,3'-tetrahydro-1H,1'H-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol (76a):*

| **Details** | **Compound 76a**<br>**CCDC-880823** |
|---|---|
| Empirical formula | $C_{40}H_{36}N_2O_4$ |
| Formula weight | 608.71 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | P212121 |
| Unit cell dimensions | a = 9.705(4) Å<br>b = 10930(4) Å<br>c = 30.350(12) Å<br>α = 90°<br>β = 90°<br>γ = 90° |
| Volume | 3219(2) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.256 $Mg/m^3$ |
| Absorption coefficient (μ) | 0.081 $mm^{-1}$ |
| F(000) | 1288 |
| Crystal Size | 0.23x0.18x0.12 mm |
| θ range for data collection | 1.98-24.00° |
| Reflections collected | 14972 |
| Independent reflections | 5035[R(int) = 0.0728] |
| Max. And Min. Transmission | 0.9903 and 0.9816 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5035/0/419 |
| Goodness-of-fit on $F^2$ | 1.253 |
| Final R indices [I>2sigma(I)] | R1 = 0.1004<br>wR2 = 0.1794 |
| R indices (all data) | R1 = 0.1208<br>wR2 = 0.1867 |
| Largest difference peak and hole | 0.249 and – 0.228 e/ $Å^3$ |

ORTEP diagram of the compound (*S*)-2,2'-bis((*R*)-1-phenylethyl)-2,2',3,3'-tetrahydro-1H,1'H-[10,10'-binaphtho[1,2-e][1,3]oxazine]-9,9'-diol with atom numbering scheme ( 50% probability factor for the thermal ellipsoids).

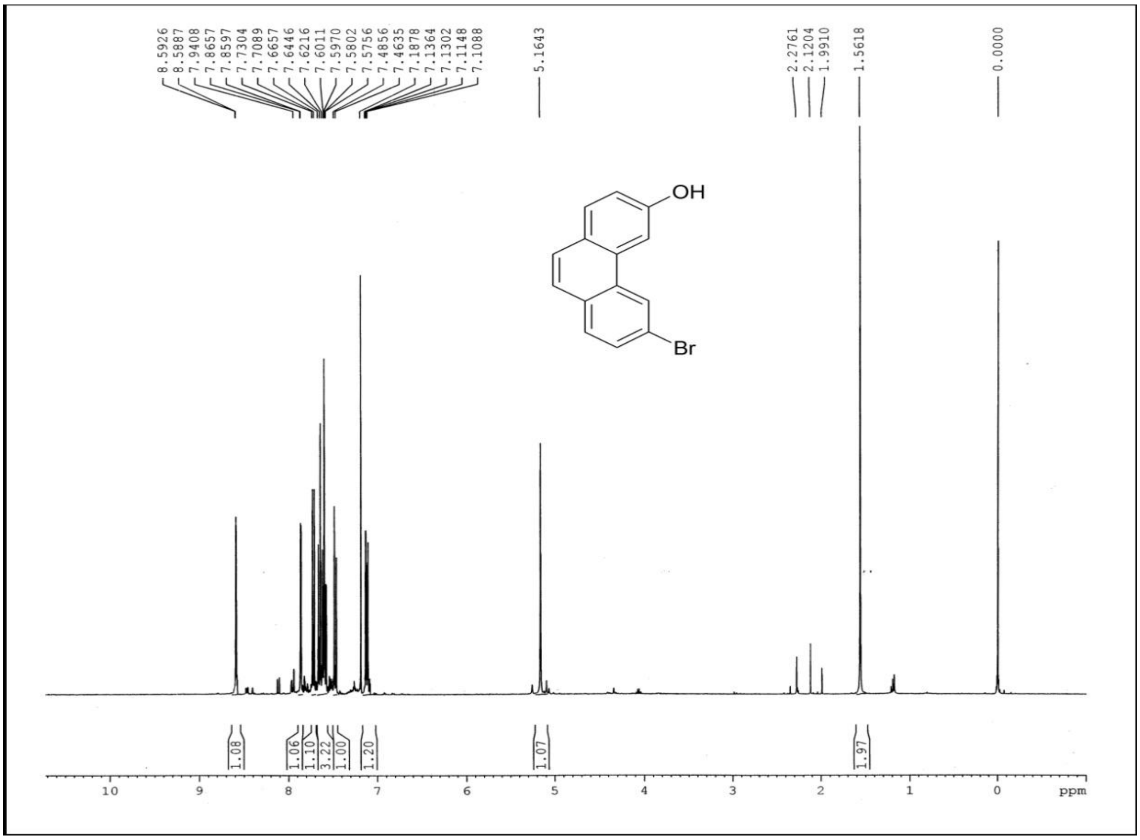




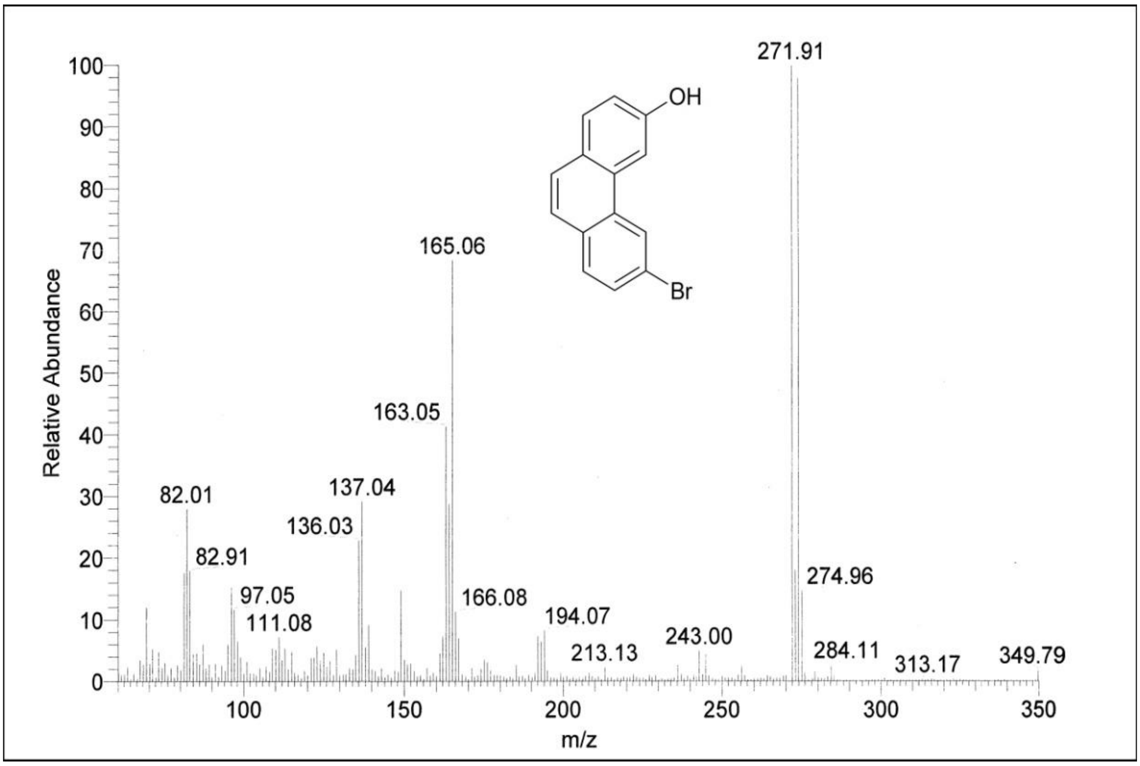
The planes passing through the molecule from the carbons C15-C9-C8-C16 and C20-C25-C26-C16 showing the twist and the angle between the two planes are 87.31°.

# Spectral Data

## Spectral data of 3-bromo-6-hydroxyphenanthrene (52)

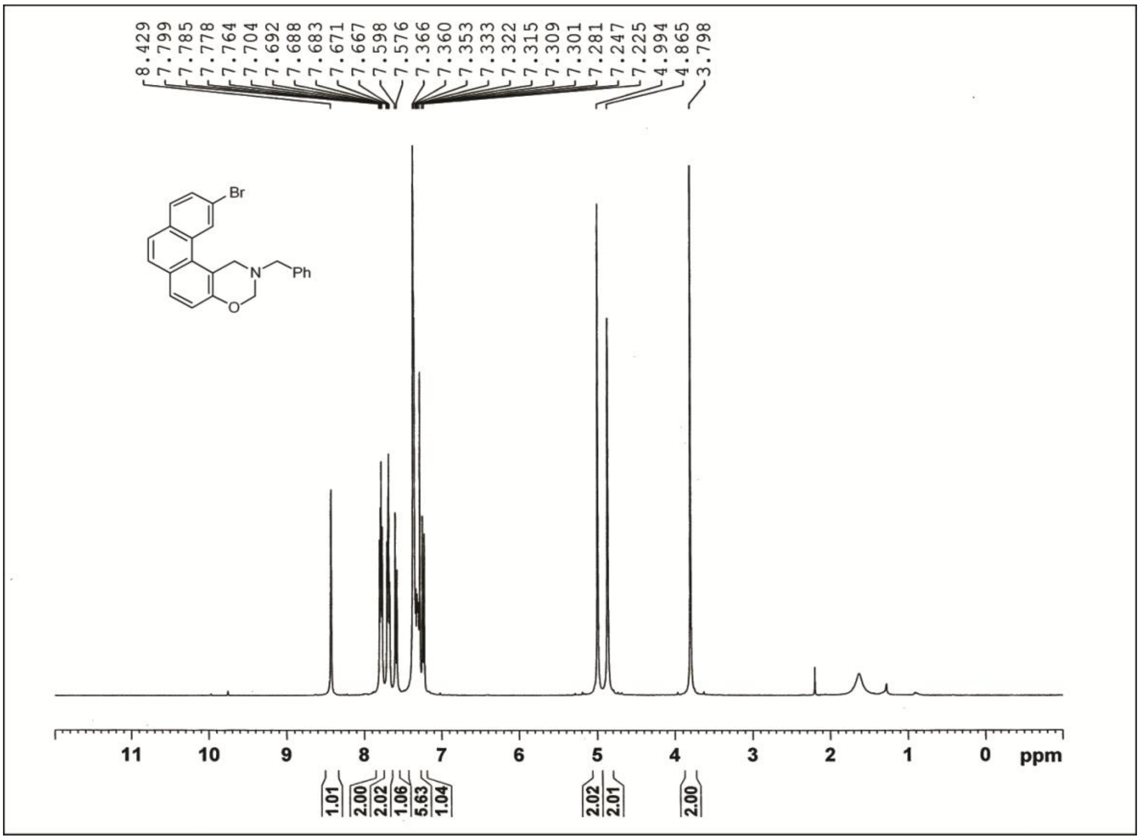


**$^1$H-NMR spectrum of 3-bromo-6-hydroxyphenanthrene (52) in $CDCl_3$ on 400 MHz**

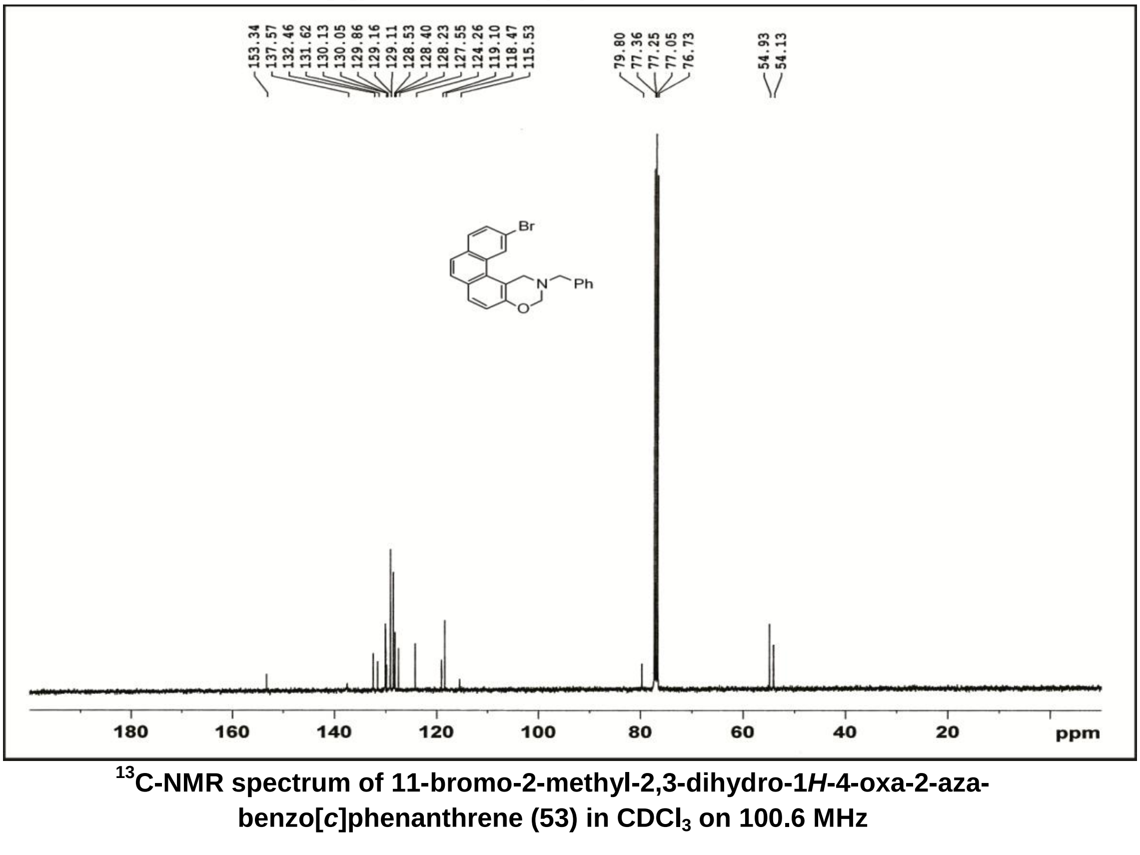


**EI-Mass spectrum of 3-bromo-6-hydroxyphenanthrene (52)**

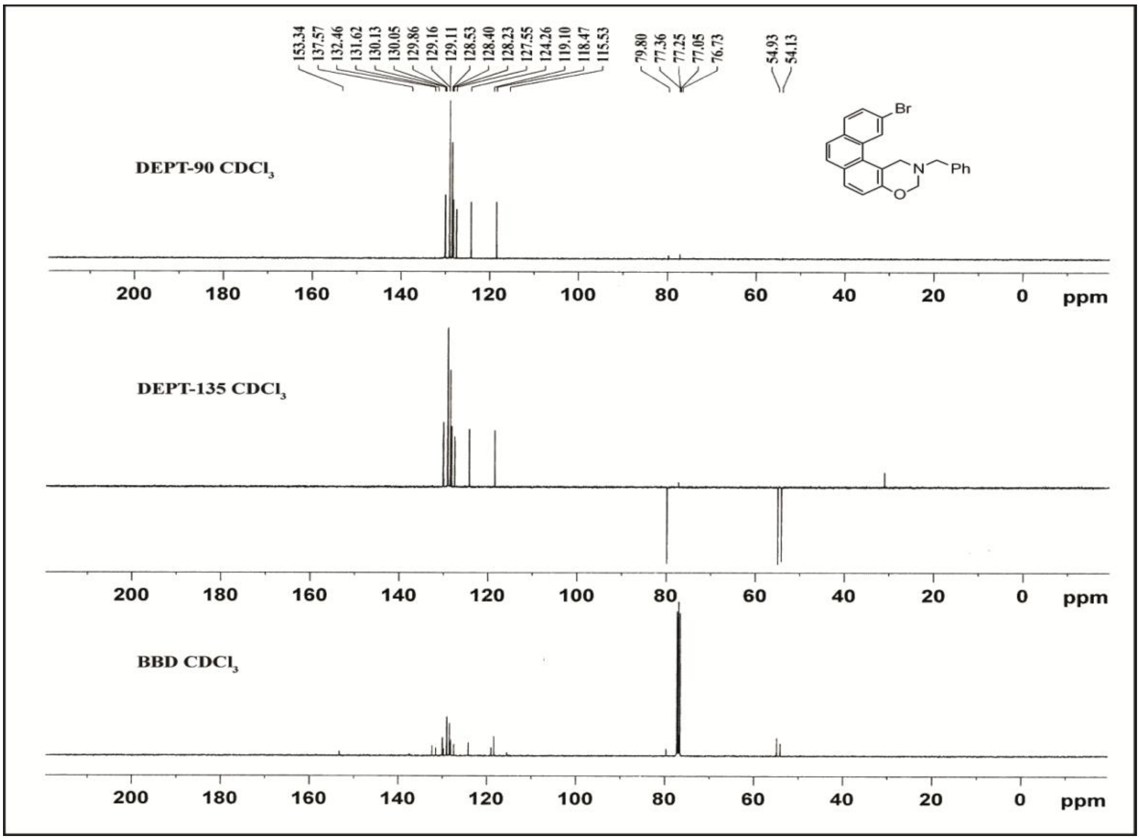
## Spectral data of 11-bromo-2-methyl-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene (53)



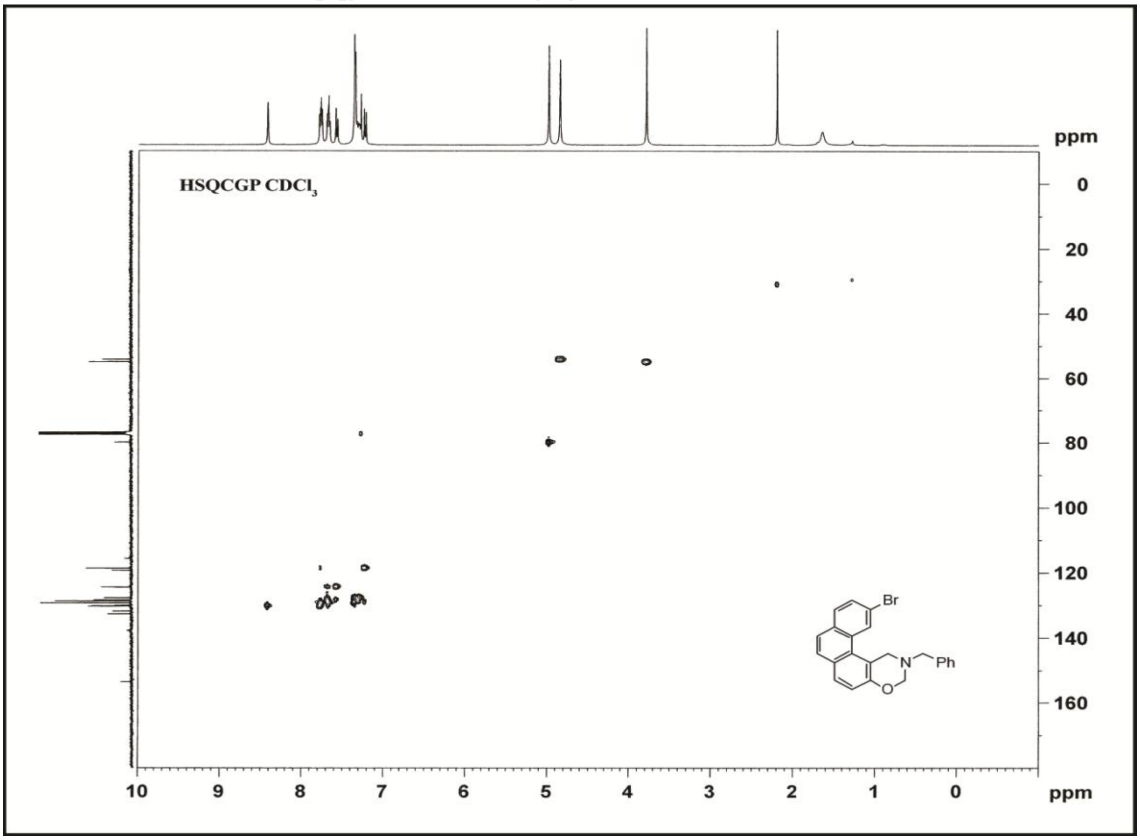
**$^1$H-NMR spectrum of 11-bromo-2-methyl-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene (53) in $CDCl_3$ on 400 MHz**



**$^{13}$C-NMR spectrum of 11-bromo-2-methyl-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene (53) in $CDCl_3$ on 100.6 MHz**

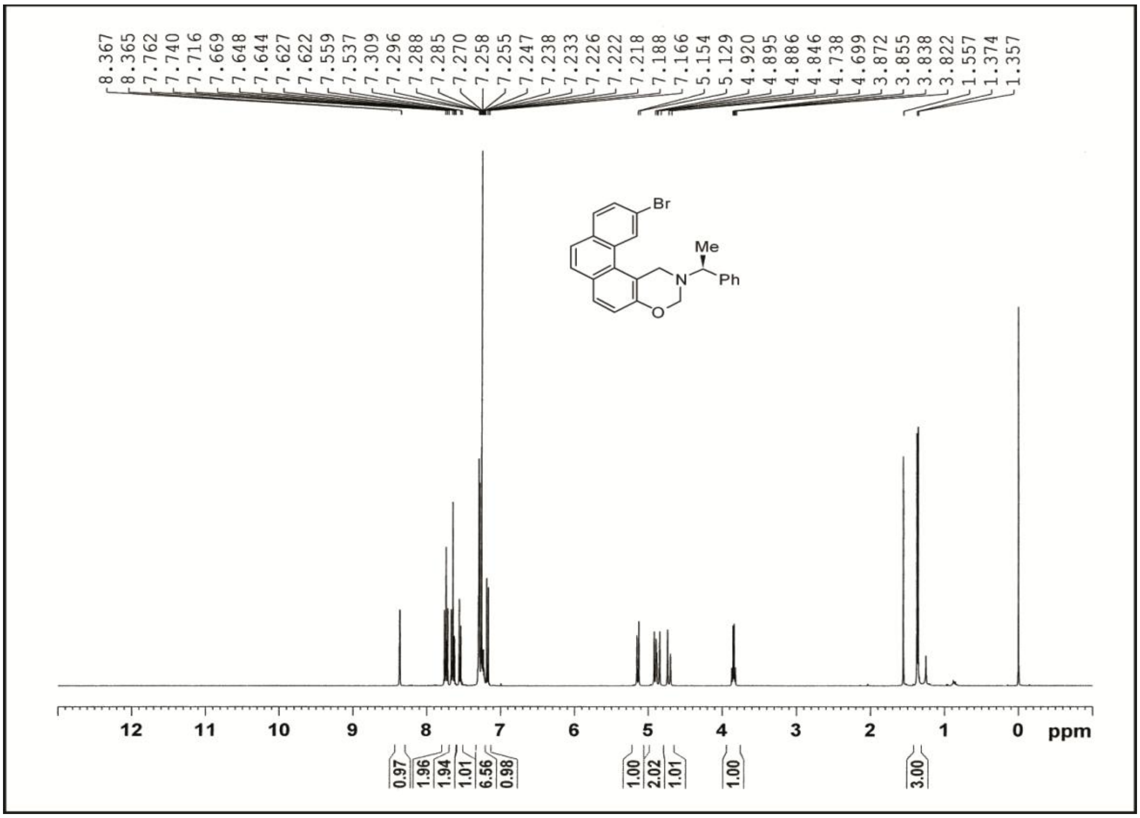


$^{13}$C-NMR BBD and DEPT spectrum of 11-bromo-2-methyl-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene (53) in $CDCl_3$ on 100.6 MHz

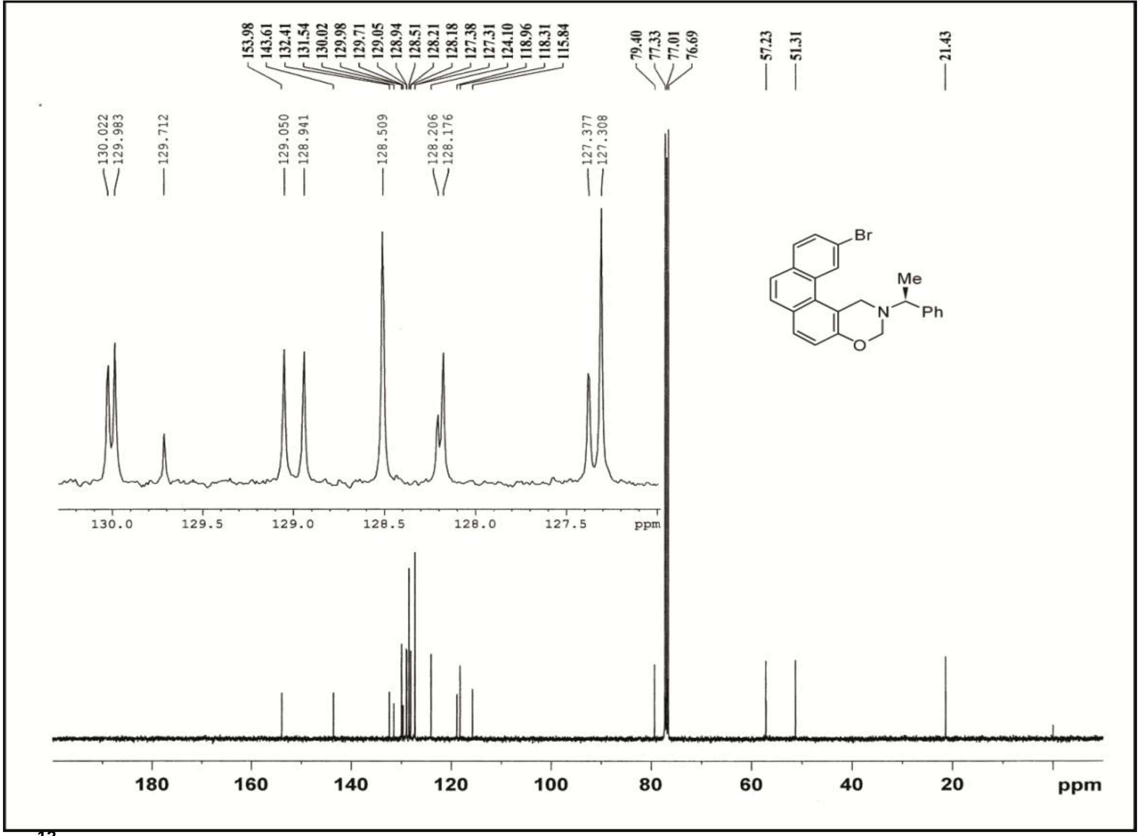


$^{1}$H-$^{13}$C Correlation HSQCGP spectrum of 11-bromo-2-methyl-2,3-dihydro-1*H*-4-oxa-2-aza-benzo[*c*]phenanthrene (53) in $CDCl_3$ on 400 MHz

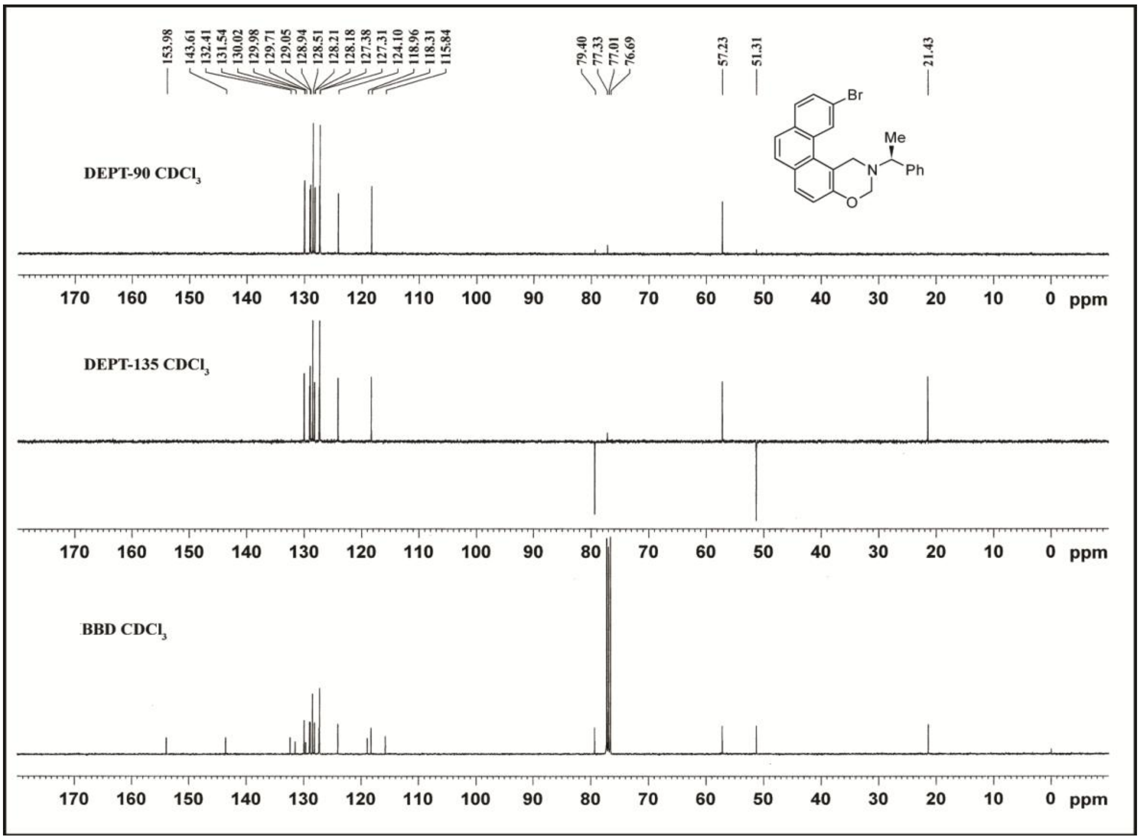
## Spectral data of 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54)



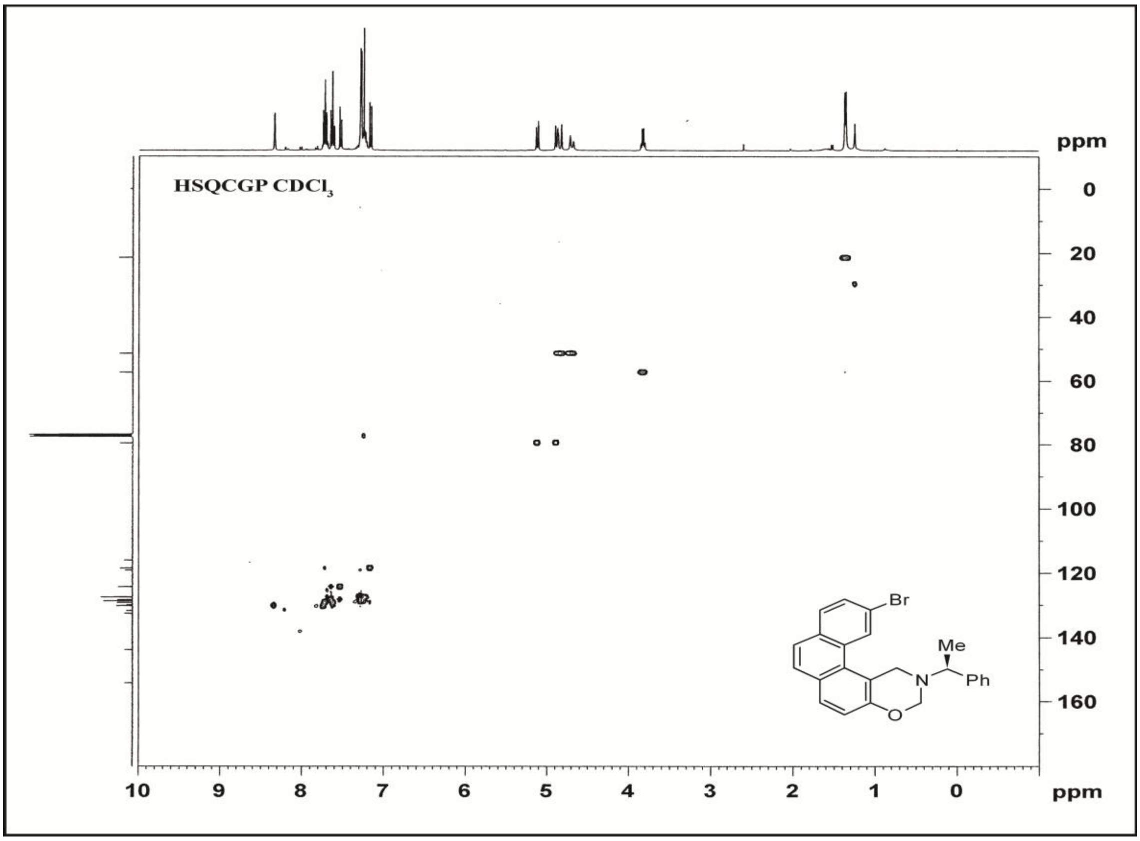
**$^1$H-NMR spectrum of 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54) in CDCl$_3$ on 400 MHz**



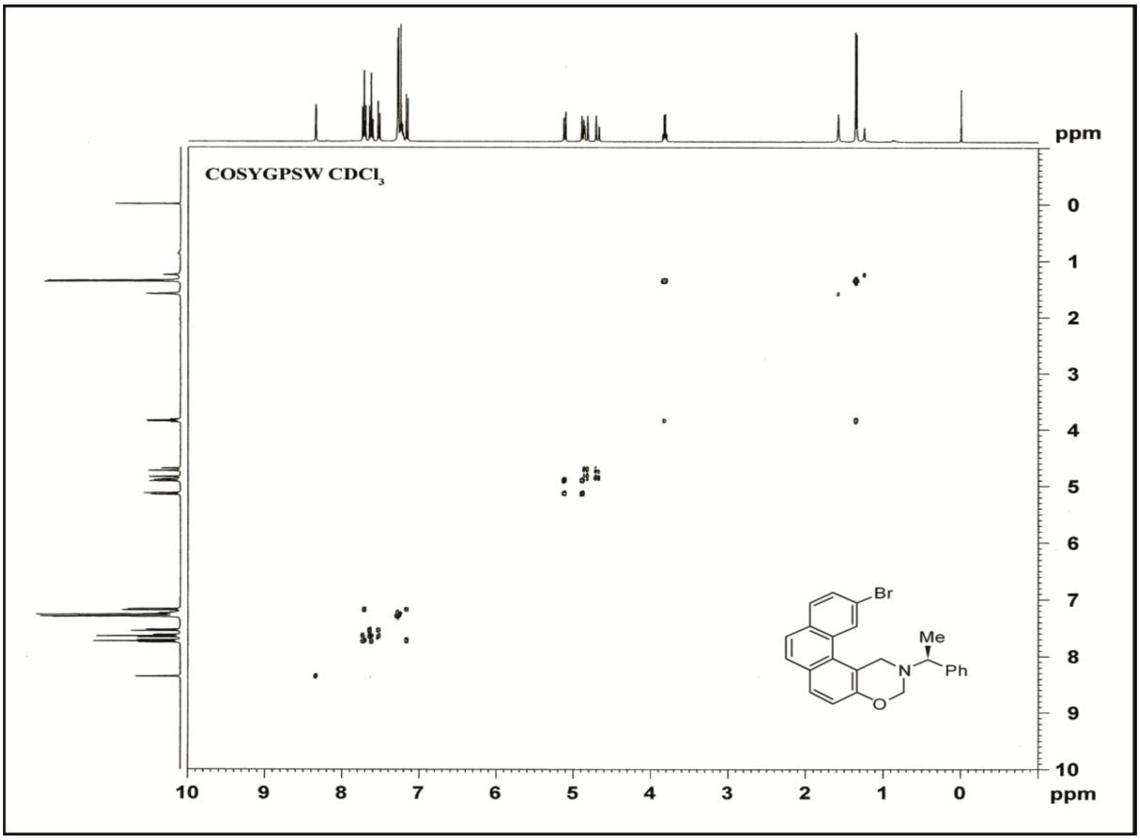
**$^{13}$C-NMR spectrum of 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54) in CDCl$_3$ on 100.6 MHz**



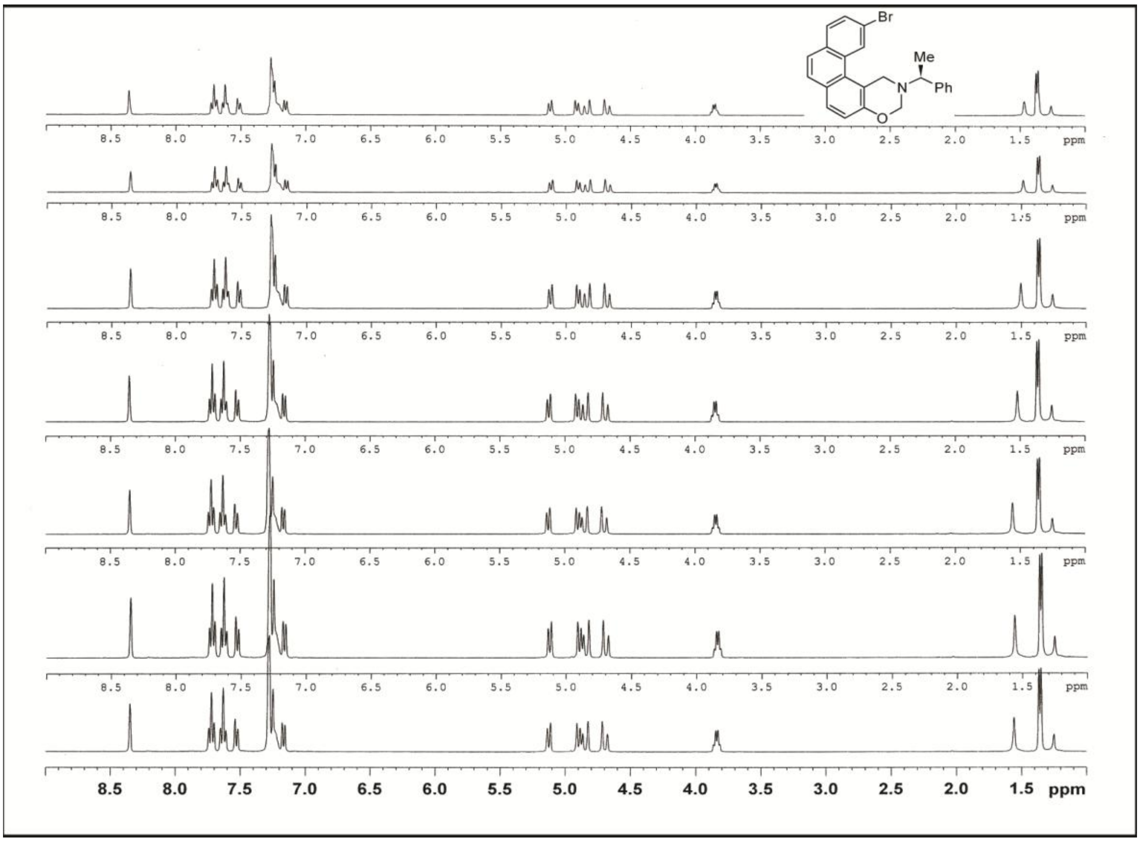
**$^{13}$C-NMR BBD and DEPT spectrum of 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54) in $CDCl_3$ on 100.6 MHz**



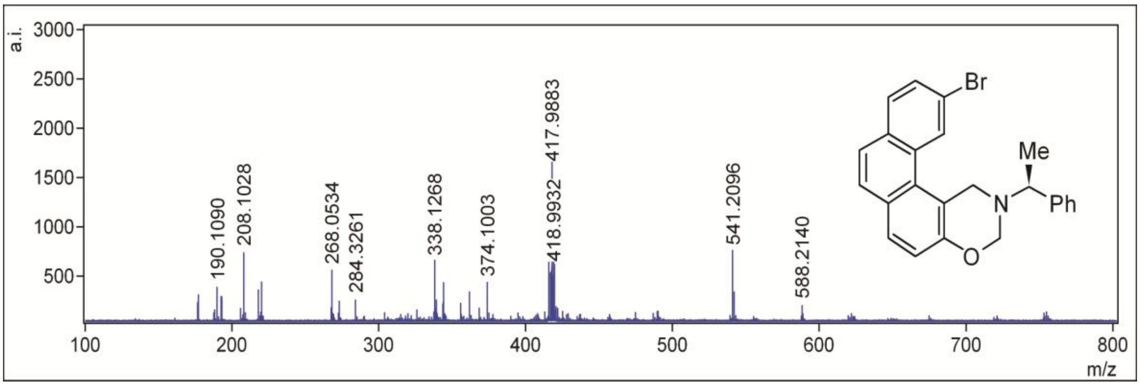
**$^{1}$H-$^{13}$C Correlation HSQCGP spectrum of 11-bromo-2-((*S*)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54) in $CDCl_3$ on 400 MHz**



**$^1$H-$^1$H Correlation COSYGPSW spectrum of 11-bromo-2-((S)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54) in CDCl$_3$ on 400 MHz**

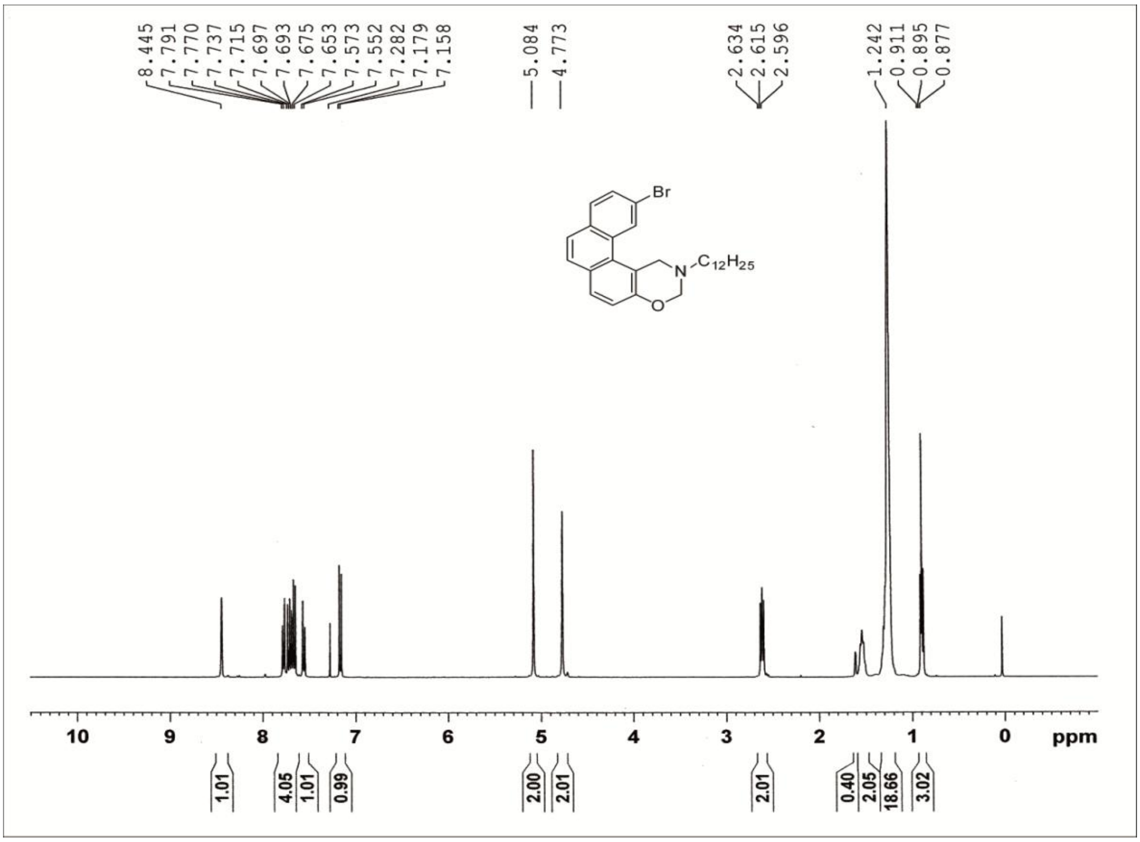


**Variable temperature $^1$H-NMR spectrum of 11-bromo-2-((S)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54) in CDCl$_3$ on 400 MHz**

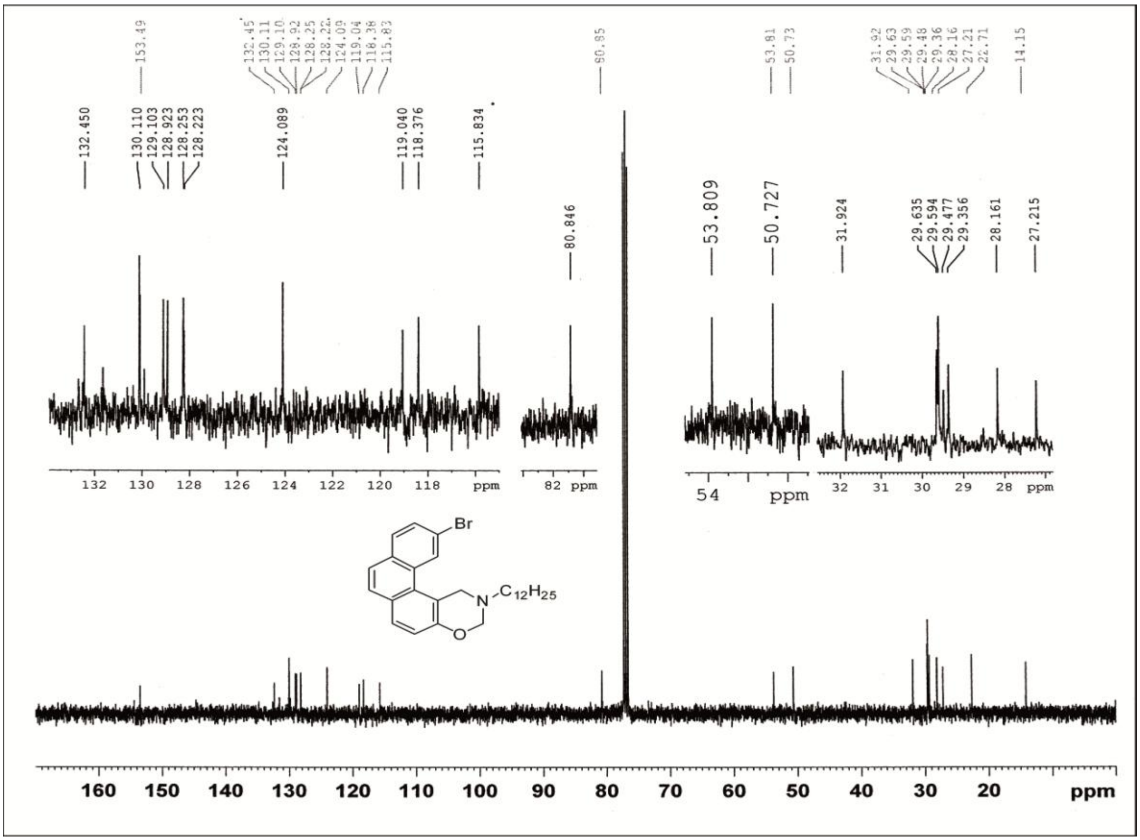


**MALDI-TOF-MS spectrum of 11-bromo-2-((S)-1-phenyl-ethyl)-2,3-dihydro-1H-4-oxa-2-aza-benzo[*c*]phenanthrene (54)**

## Spectral data of 11-bromo-2-dodecyl-2,3-dihydro-1*H*-phenanthro[4,3-*e*][1,3]oxazine (55)

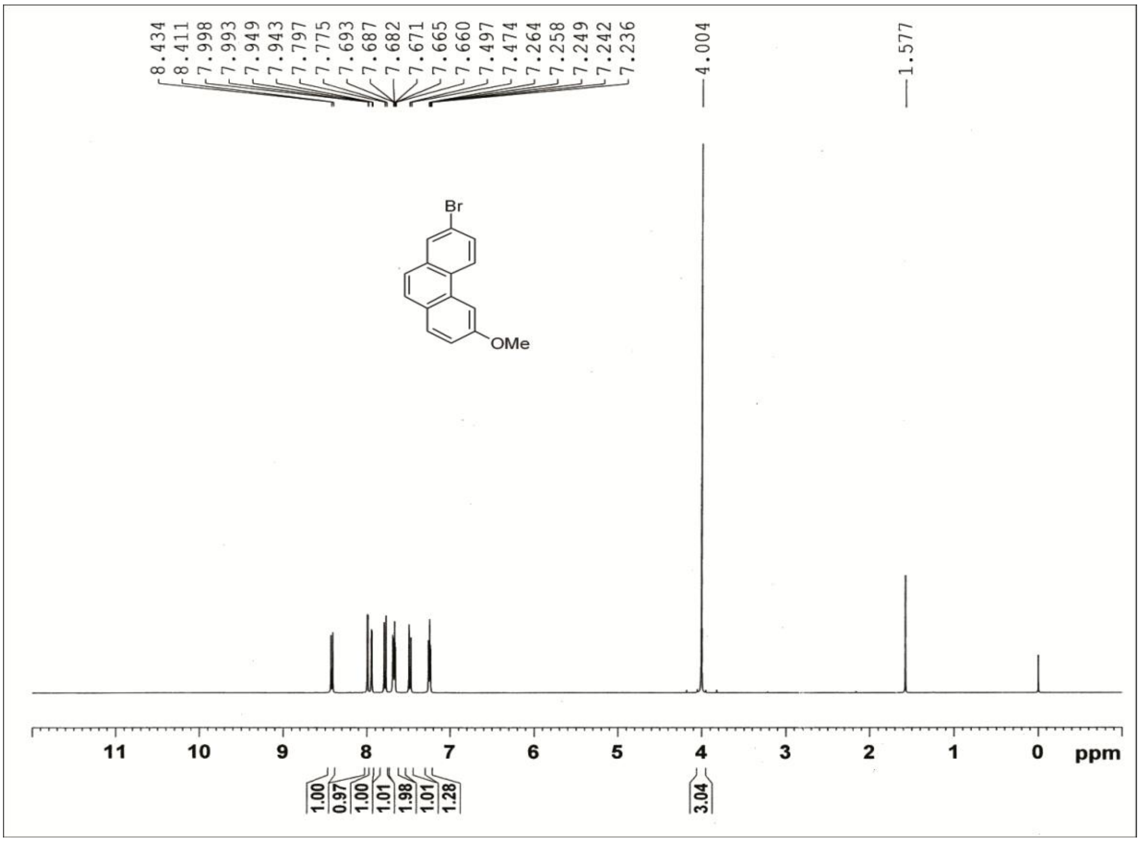


**$^1$H-NMR spectrum of 11-bromo-2-dodecyl-2,3-dihydro-1*H*-phenanthro[4,3-*e*][1,3]oxazine (55) in $CDCl_3$ on 400 MHz**

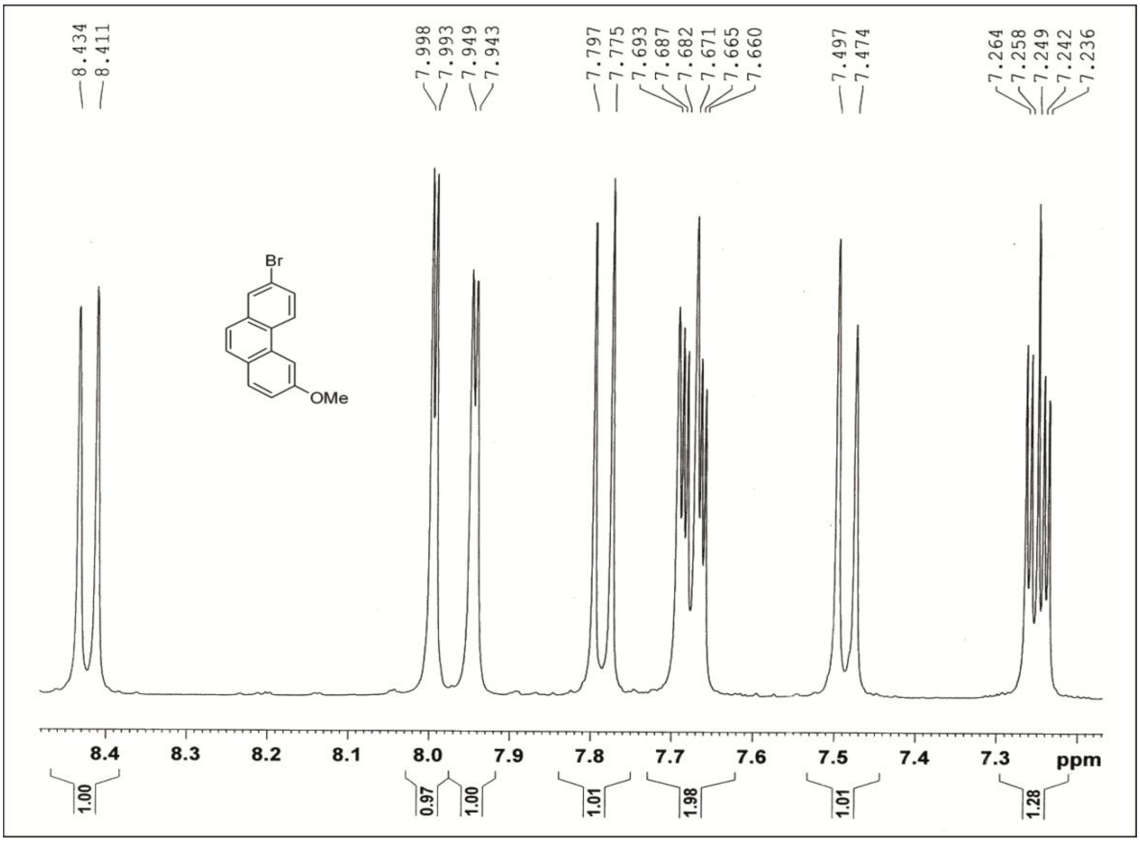


**$^1$H-NMR spectrum of 11-bromo-2-dodecyl-2,3-dihydro-1*H*-phenanthro[4,3-*e*][1,3]oxazine (55) in CDCl$_3$ on 400 MHz**

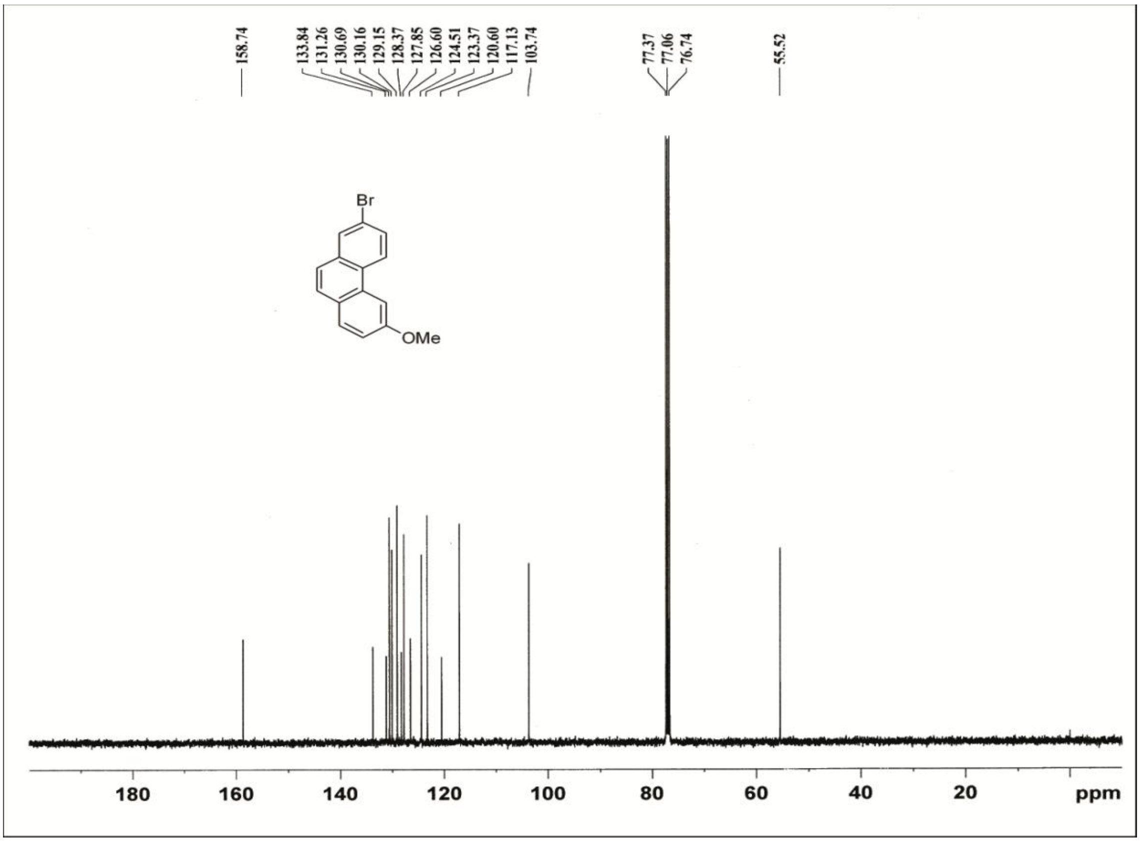
## Spectral data of 2-bromo-6-methoxyphenanthrene (60)



**$^1$H-NMR spectrum of 2-bromo-6-methoxyphenanthrene (60) in CDCl$_3$ on 400 MHz**

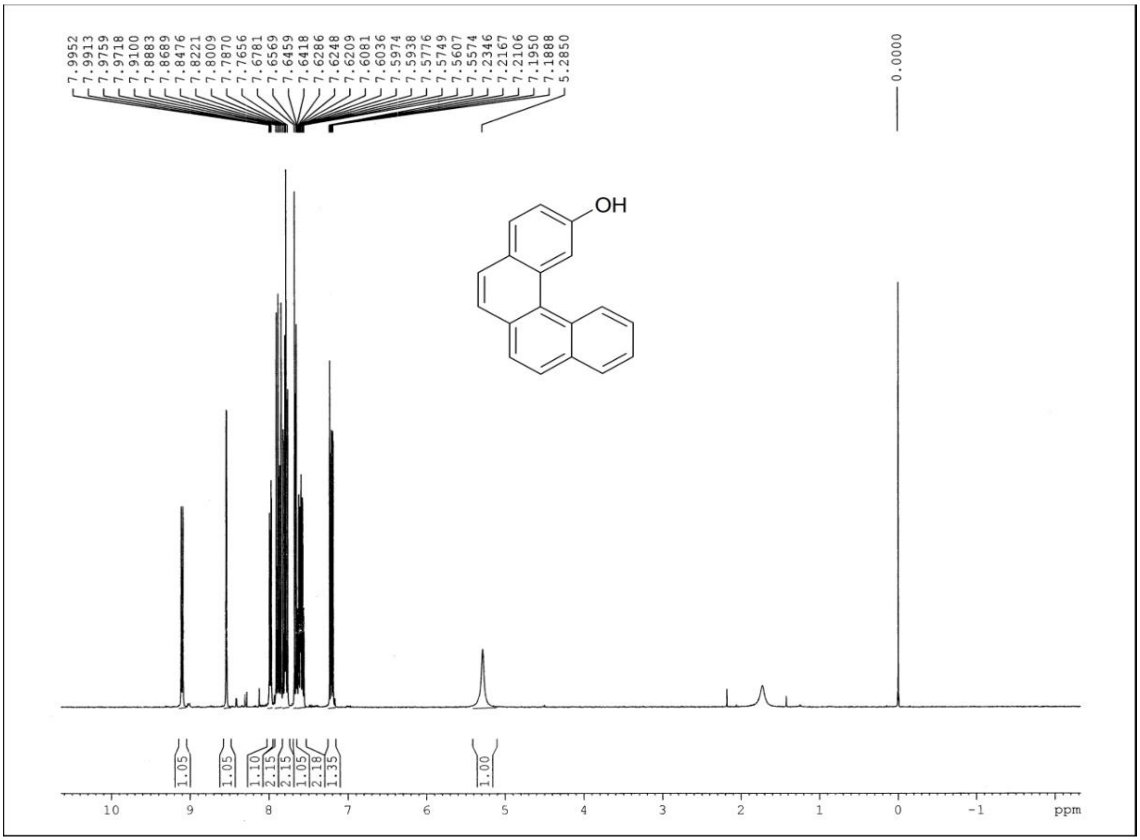


**$^{1}$H-NMR enlarge spectrum of 2-bromo-6-methoxyphenanthrene (60) in CDCl$_3$ on 400 MHz**

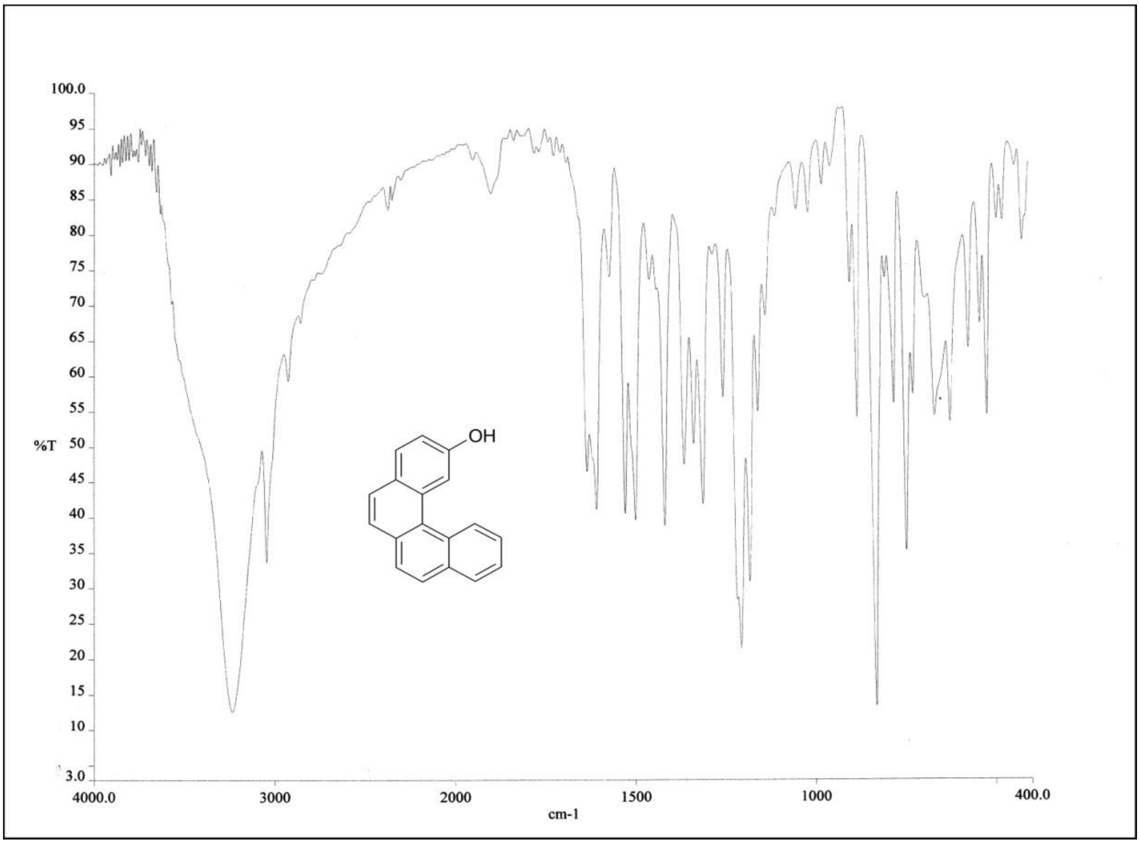


**$^{13}$C-NMR spectrum of 2-bromo-6-methoxyphenanthrene (60) in CDCl$_3$ on 100.6 MHz**

## Spectral data of 2-hydroxybenzo[*c*]phenanthrene (63)

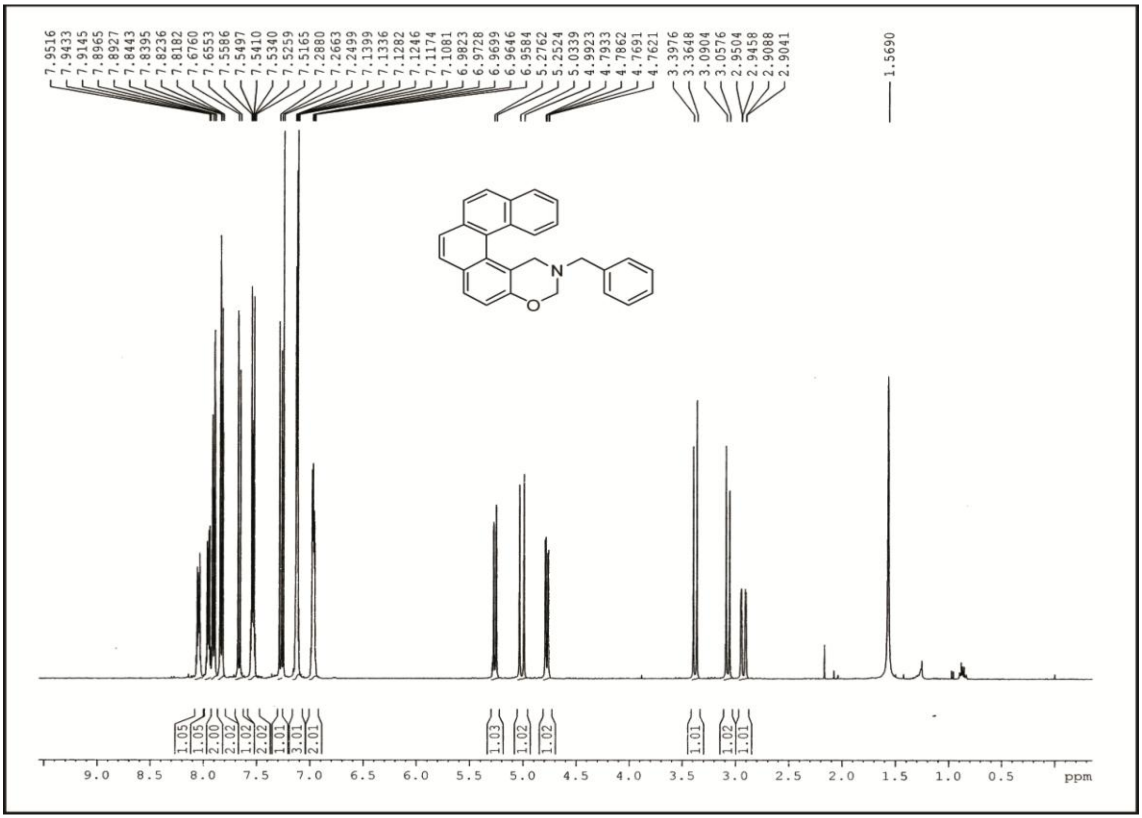


$^1$H-NMR spectrum of 2-hydroxybenzo[*c*]phenanthrene (63) in $CDCl_3$ on 400 MHz

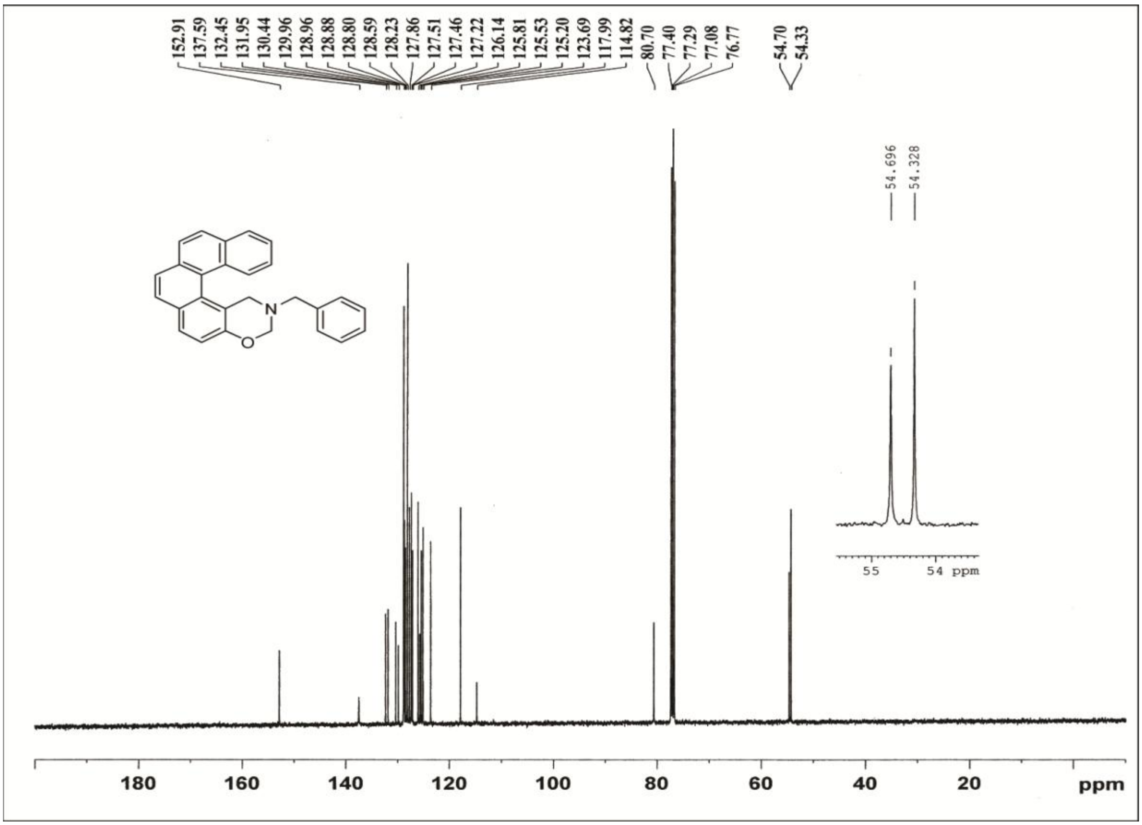


IR spectrum of 2-hydroxybenzo[*c*]phenanthrene (63)

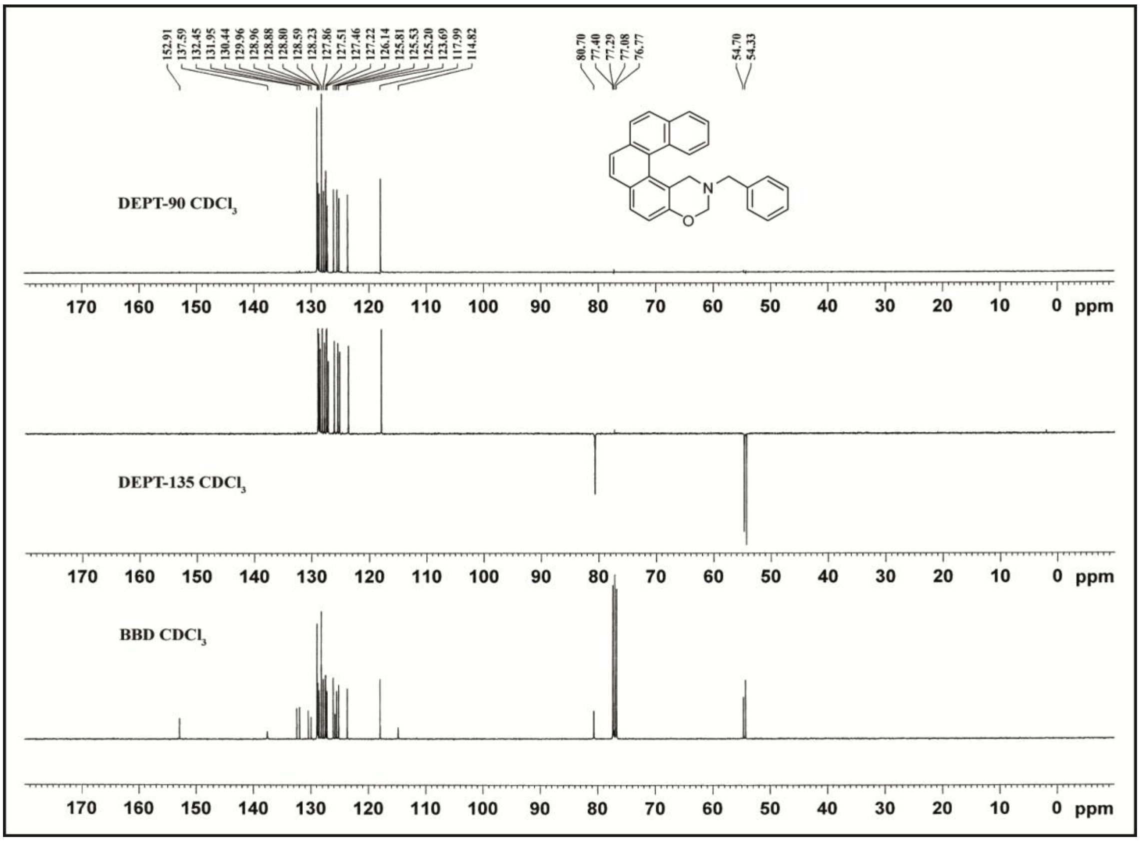
**Spectral data of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64) in CDCl$_3$ on 400 MHz**



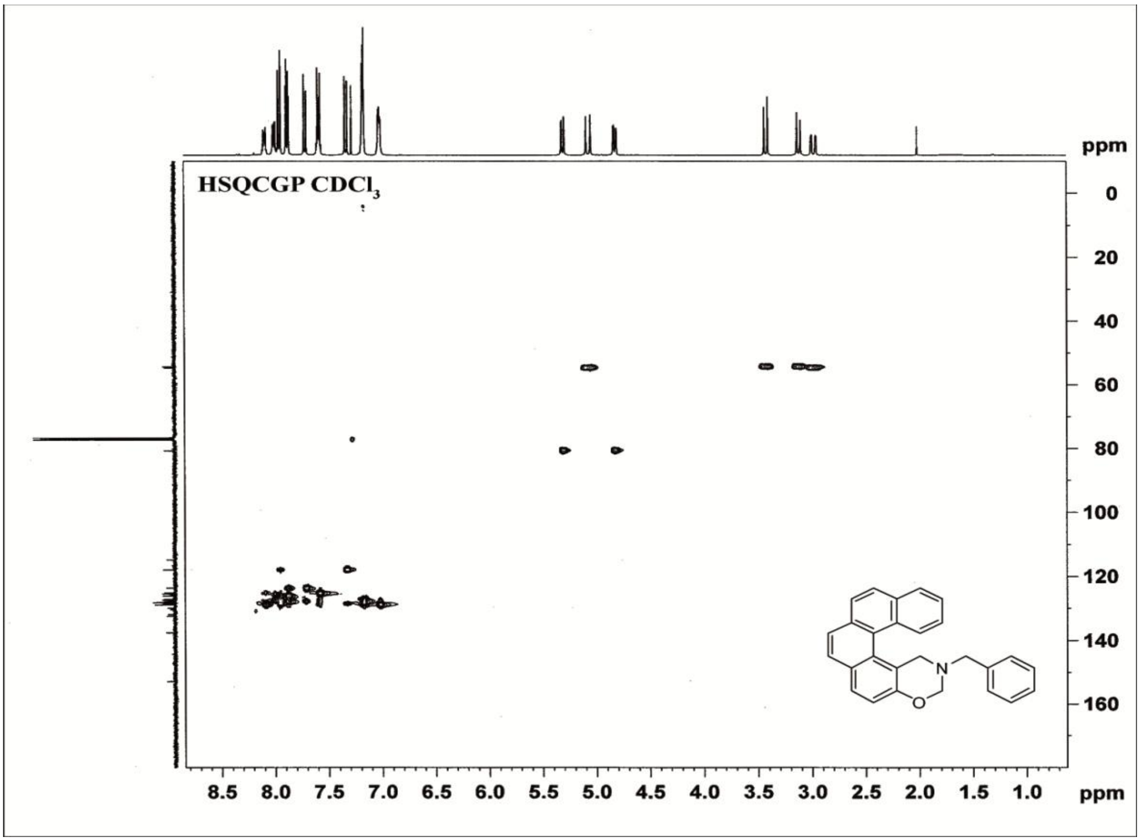
$^1$H-NMR spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64) in CDCl$_3$ on 400 MHz



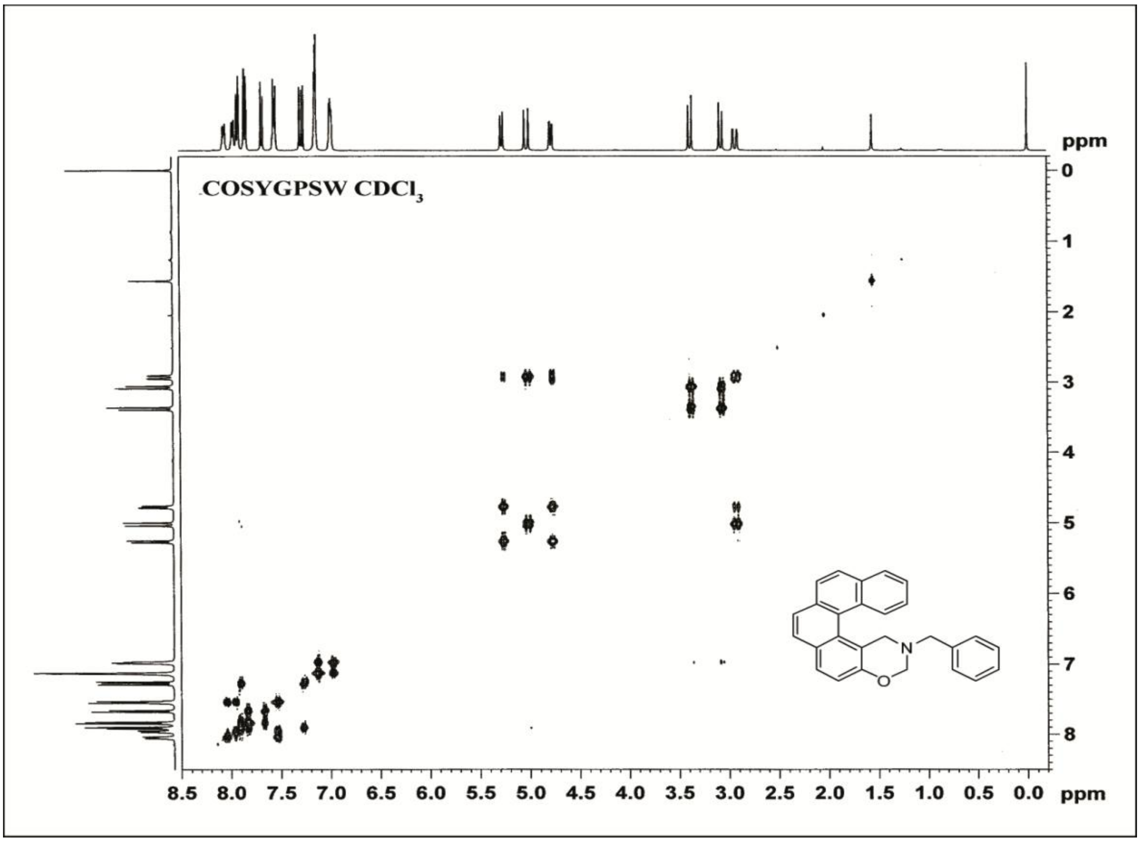
$^{13}$C-NMR spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64) in CDCl$_3$ on 100.6 MHz



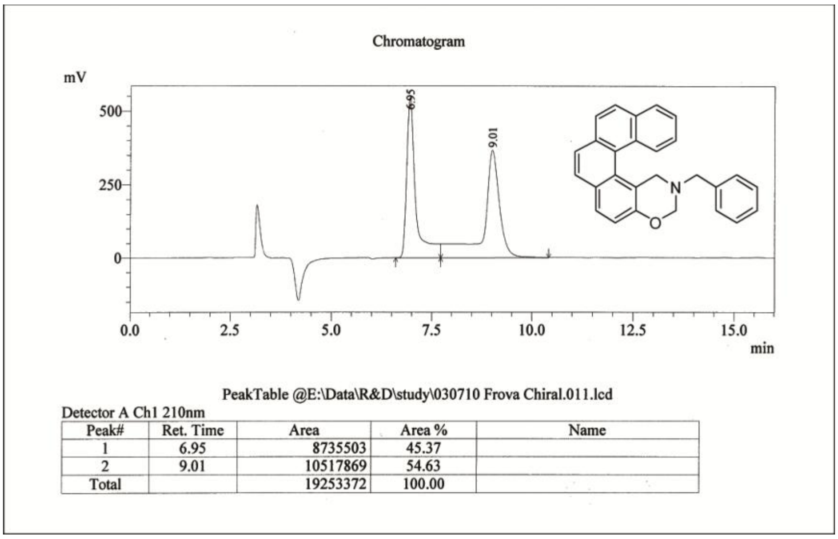
**$^{13}$C-NMR BBD and DEPT spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64) in CDCl$_3$ on 100.6 MHz**



**$^1$H-$^{13}$C Correlation HSQCGP spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64) in CDCl$_3$ on 400 MHz**



**$^1$H-$^1$H Correlation COSYGPSW spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64) in CDCl$_3$ on 400 MHz**



Chromatogram

PeakTable @E:\Data\R&D\study\030710 Frova Chiral.011.lcd

Detector A Ch1 210nm

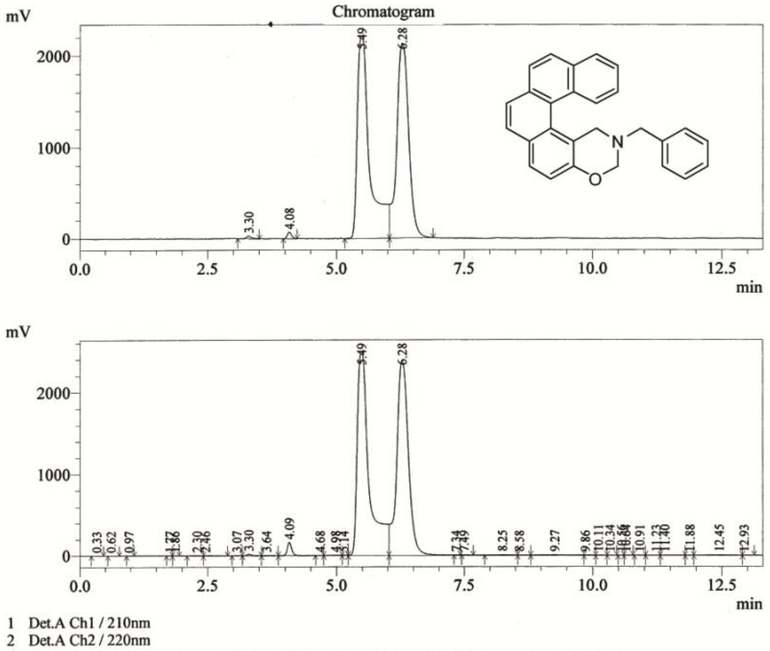
| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6.95 | 8735503 | 45.37 | |
| 2 | 9.01 | 10517869 | 54.63 | |
| Total | | 19253372 | 100.00 | |

## Method A:

Observed two peaks of seperated enantiomers at 1) R$_t$ - 6.95 min and 2) R$_t$ – 9.01 min.

Solvent System: *n*-Hexane: *Iso*-propanol (95:05), Flow rate: 1ml/min.

Detector: UV-Vis. Column: Chiralpak Diacel-OD H.



PeakTable @E:\Data\R&D\Frova\Chiral\030710 Frova Chiral.003.lcd

Detector A Ch1 210nm

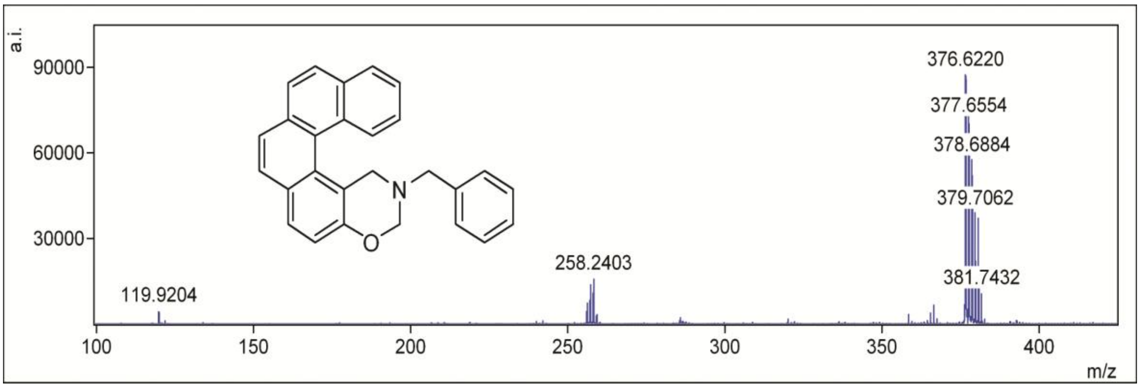
| Peak# | Ret. Time | Area | Area % | Relative Retention Time | Name |
|---|---|---|---|---|---|
| 1 | 3.30 | 176223 | 0.24 | 0.23 | Unknown impurity |
| 2 | 4.08 | 386121 | 0.53 | 0.28 | |
| 3 | 5.49 | 37333557 | 51.29 | 0.38 | |
| 4 | 6.28 | 34886982 | 47.93 | 0.43 | |
| Total | | 72782882 | 100.00 | | |

## Method B:

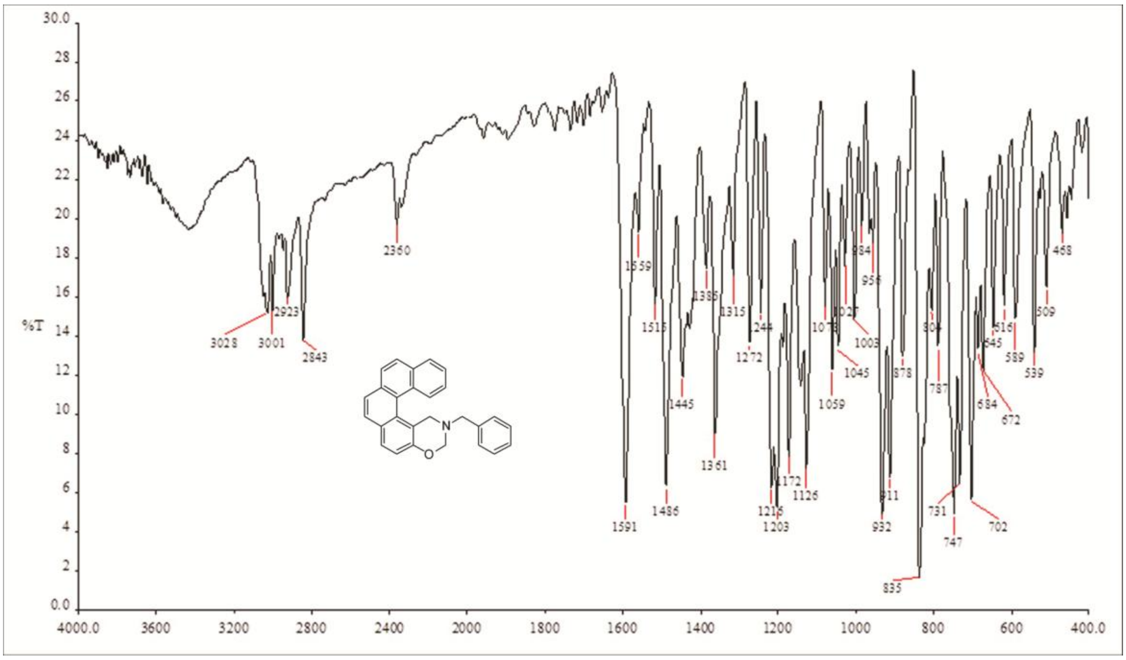
Observed two peaks of seperated enantiomers at 1) $R_t$ – 5.49 min and 2) $R_t$ – 6.28 min.

Solvent System: *n*-Hexane: *Iso*-propanol (85:15), Flow rate: 1ml/min.

Chiral Column: Lux Amylose 2

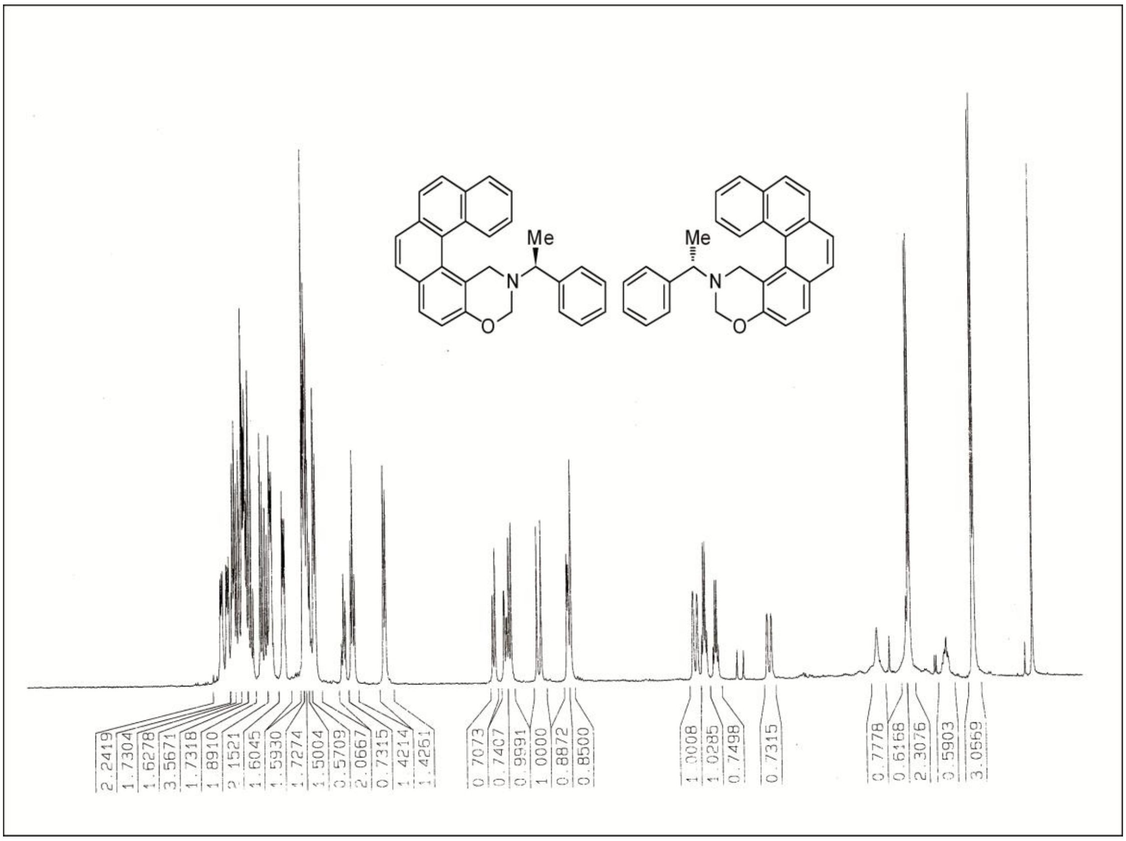


**MALDI-TOF-MS spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64)**

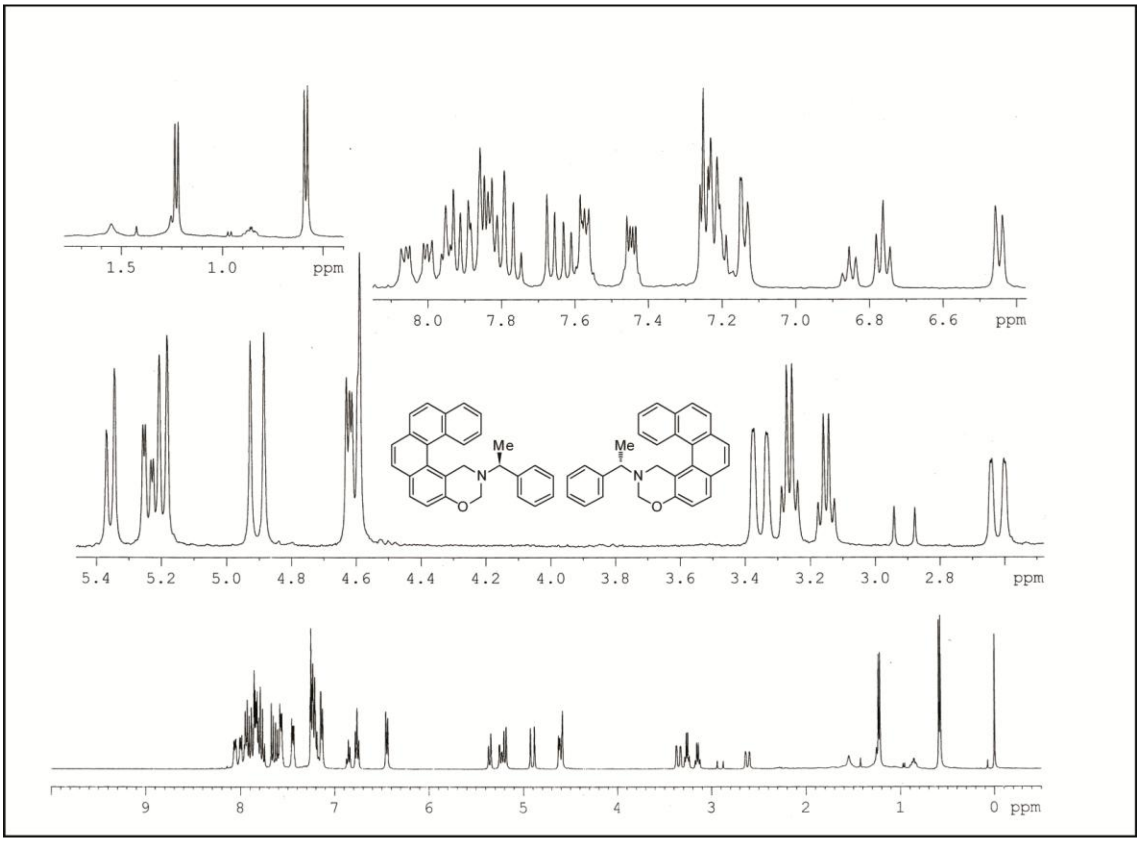


**IR spectrum of 9-benzyl-9,10-dihydro-8*H*-7-oxa-9-aza-dibenzo[*c*,*g*]phenanthrene (64)**

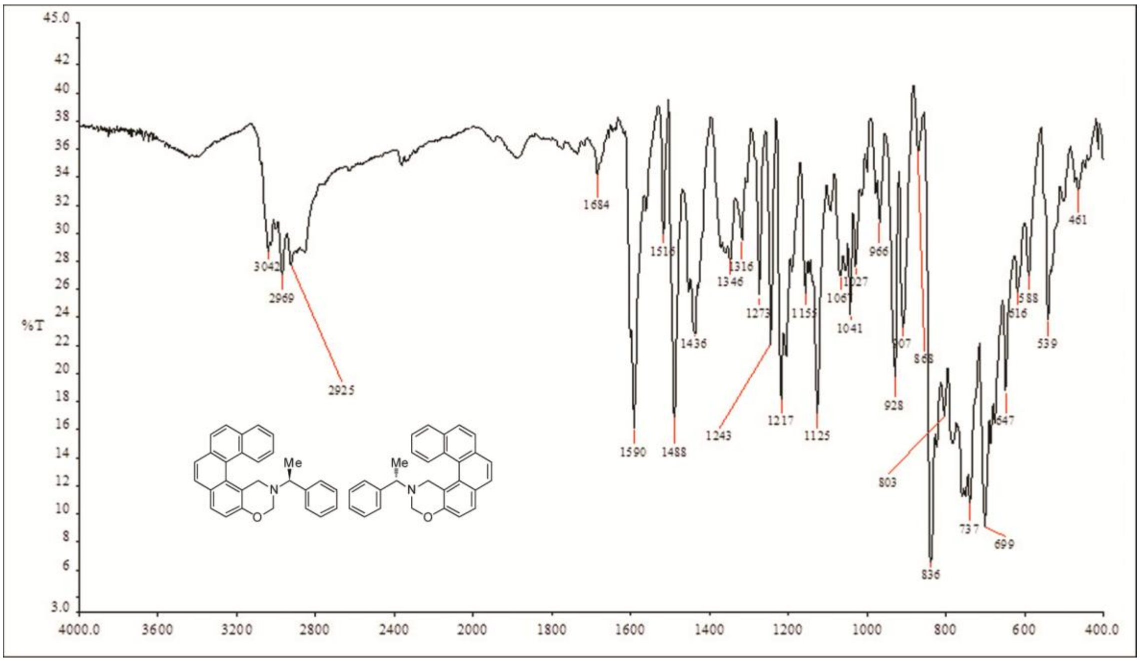
## Spectral Data of *P*-*M*-(*S*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-*e*][1,3]-oxazine (65)



**$^1$H-NMR spectrum of *P*-*M*-(*S*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-e][1,3]-oxazine (65) in CDCl$_3$ on 400 MHz**

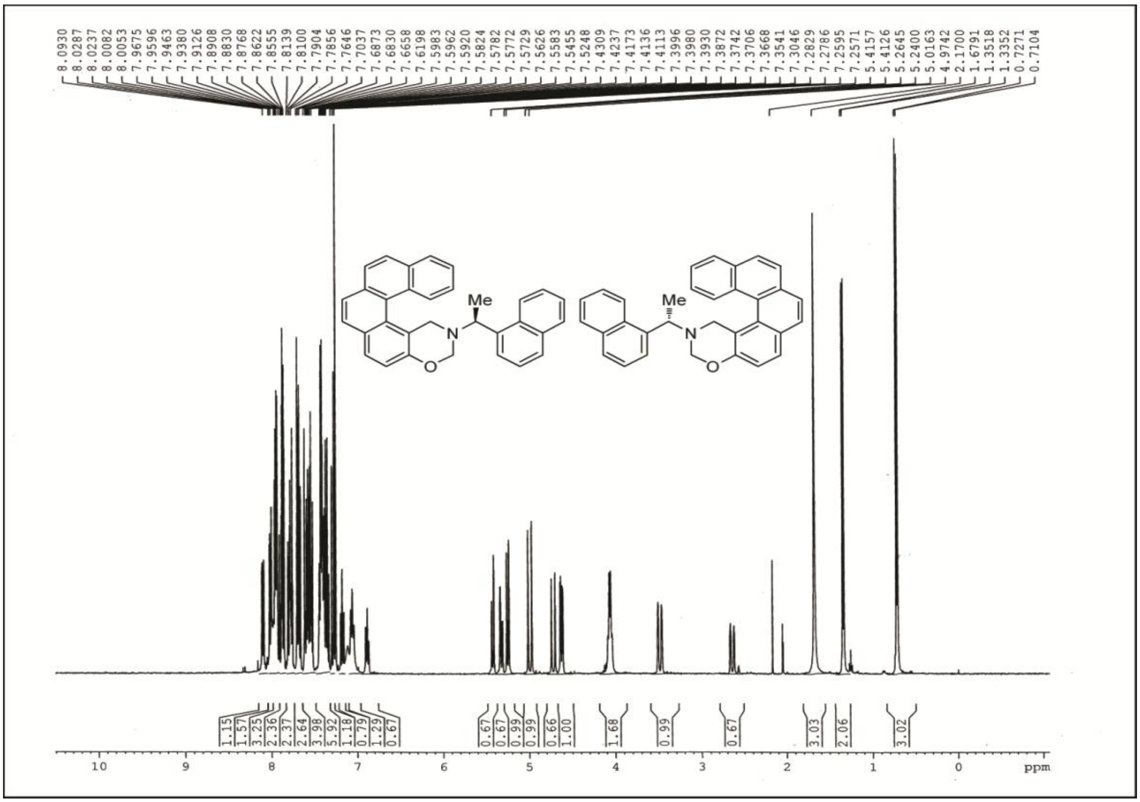


**$^1$H-NMR enlarge spectrum of *P*-*M*-(*S*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-e][1,3]-oxazine (65) in $CDCl_3$ on 400 MHz**

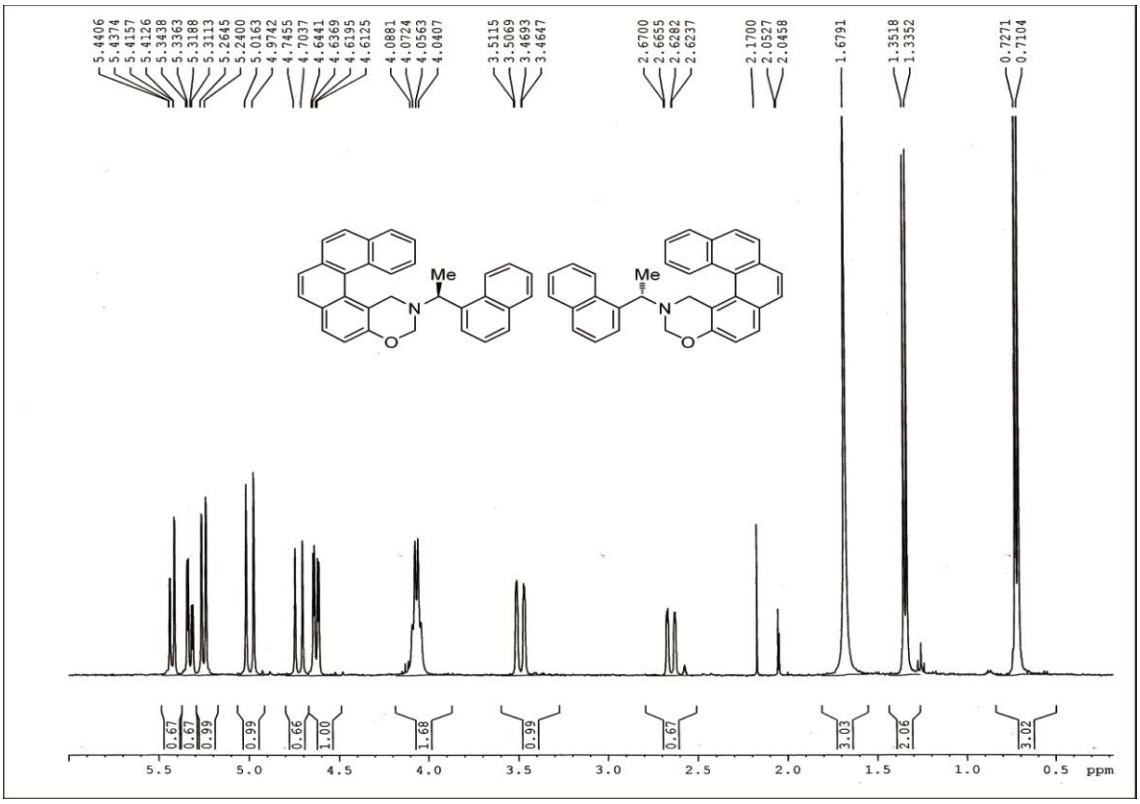


**IR spectrum of *P*-*M*-(*S*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro[4,3-*e*][1,3]-oxazine (65)**

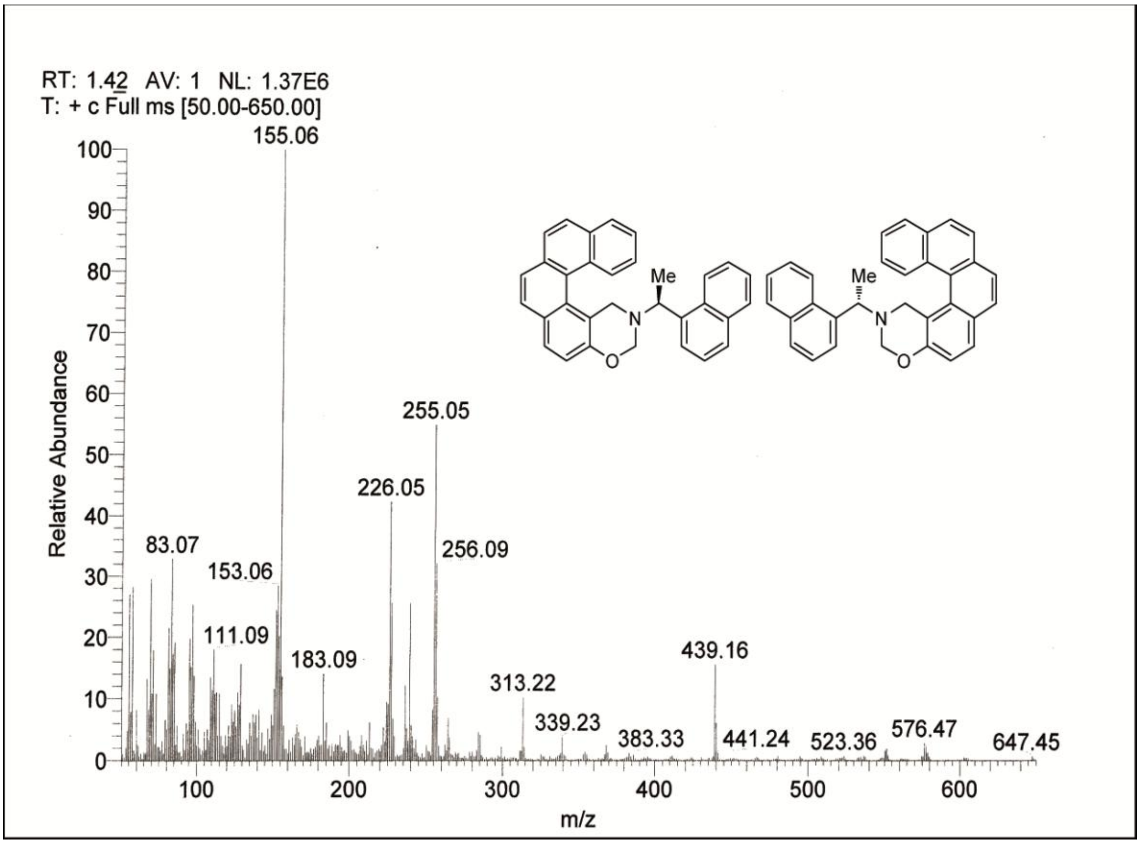
## *Spectral Data of P-M-(S)*-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro-[4,3-*e*][1,3]oxazine (66)



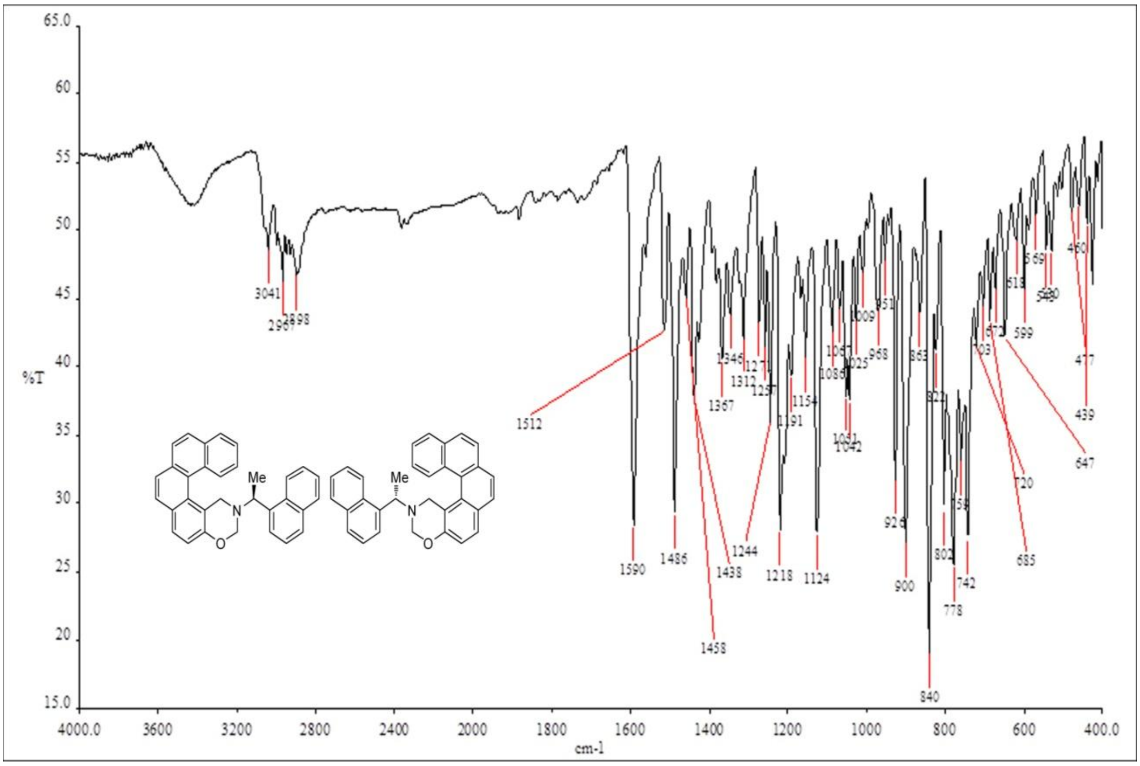
$^1$H-NMR spectrum of *P-M-(S)*-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro-[4,3-*e*][1,3]oxazine (66) in $CDCl_3$ on 400 MHz



$^1$H-NMR enlarge spectrum of *P-M-(S)*-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro-[4,3-*e*][1,3]oxazine (66) in $CDCl_3$ on 400 MHz

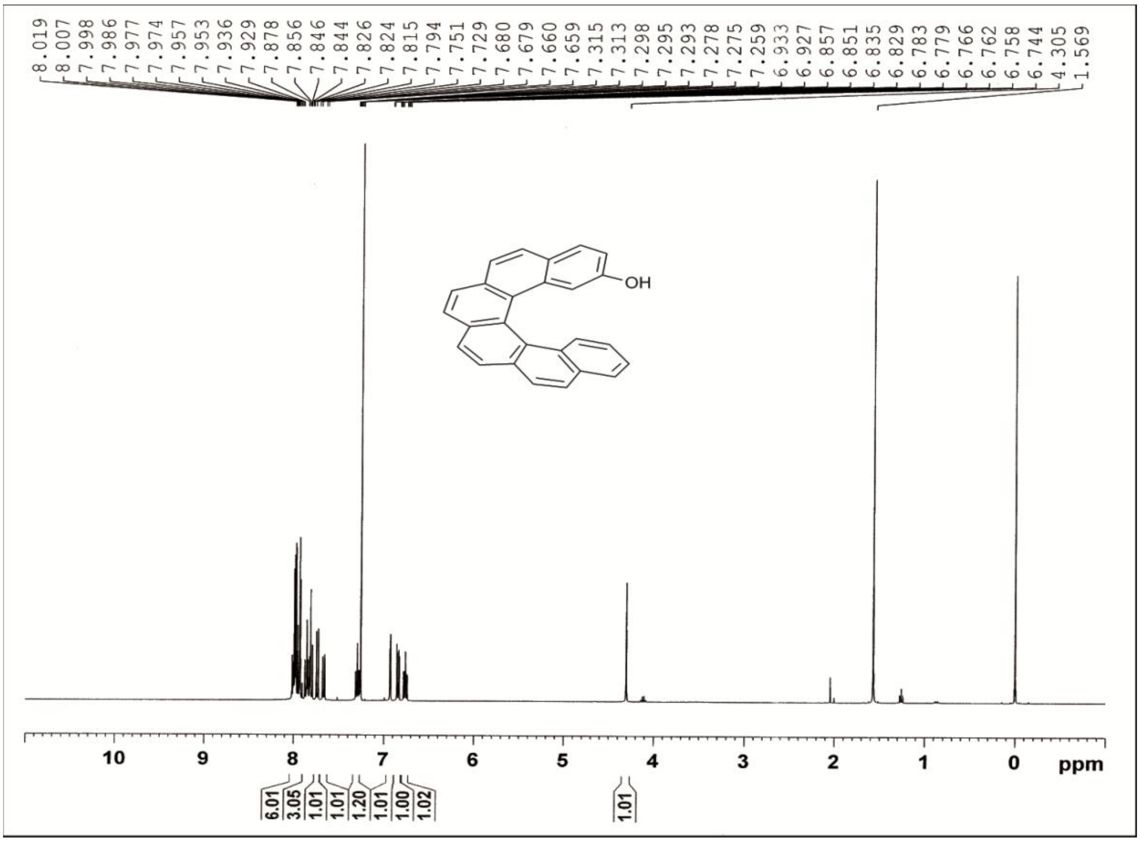


**EI-Mass spectrum of *P*-*M*-(*S*)-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]phenanthro-[4,3-*e*][1,3]oxazine (66)**

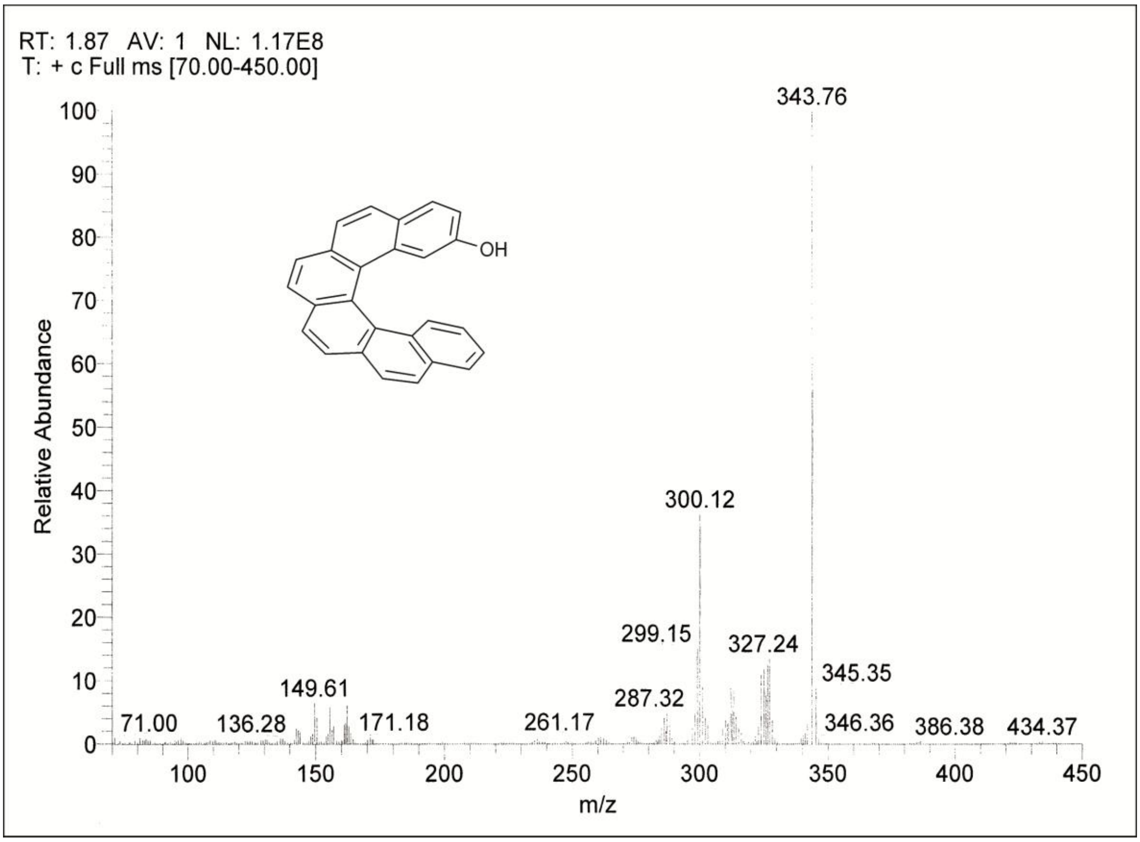


**IR spectrum of *P*-*M*-(*S*)-2-(1-(naphthalen-1-yl)ethyl)-2,3-dihydro-1*H*-benzo[5,6]-phenanthro-[4,3-*e*][1,3]oxazine (66)**

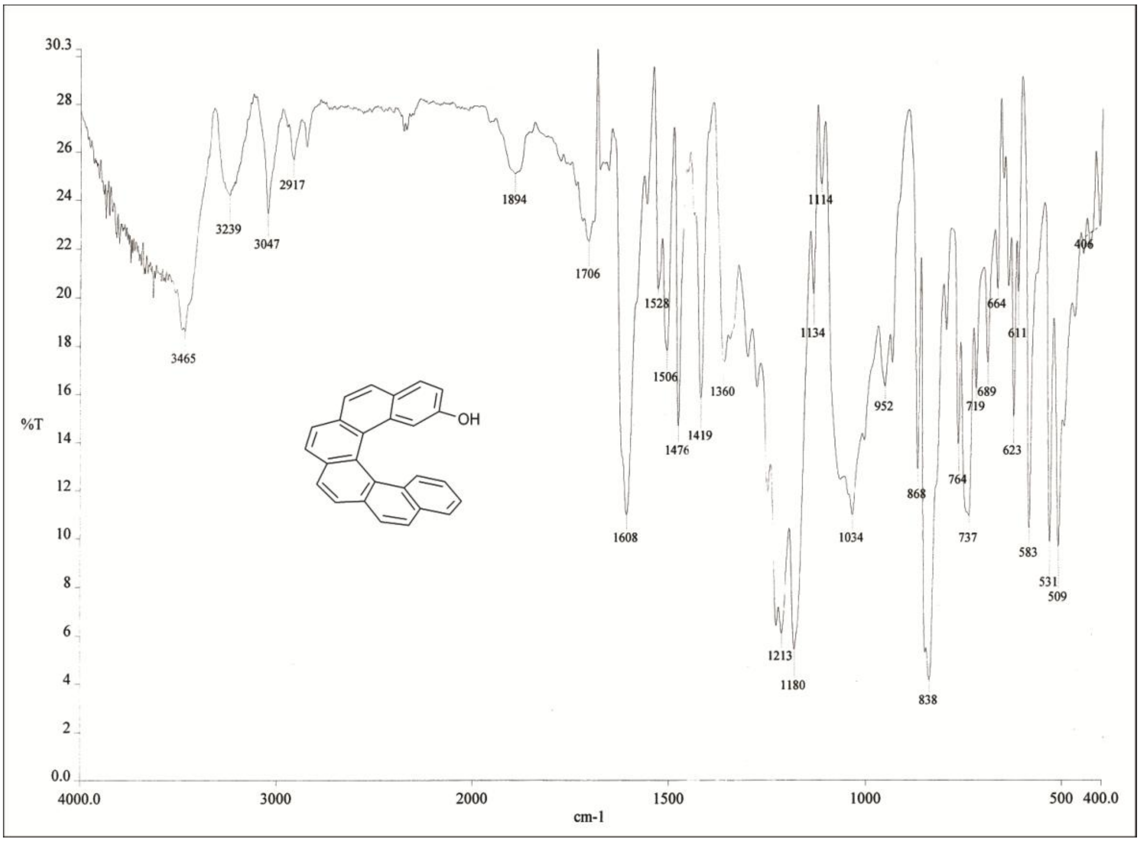
## Spectral Data of 2-hydroxy[6]helicene (68)



**$^1$H-NMR spectrum of 2-hydroxy[6]helicene (68) in $CDCl_3$ on 400 MHz**

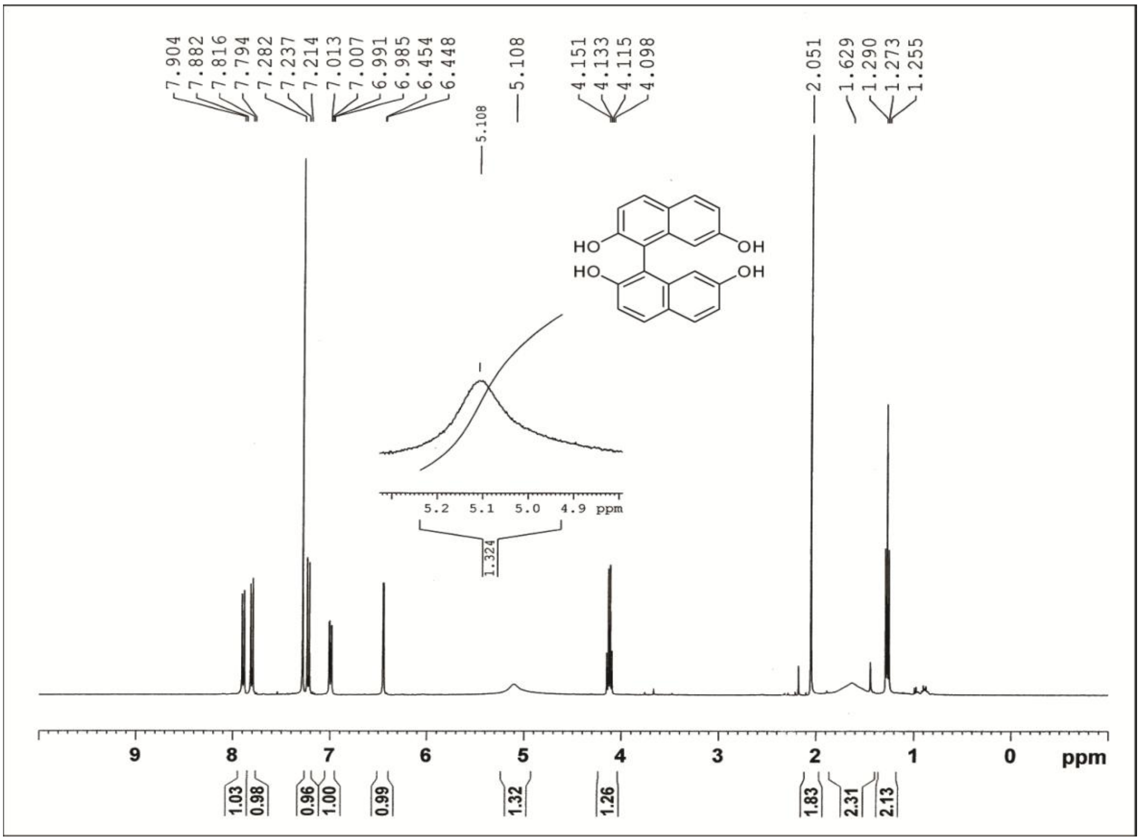


**EI-Mass spectrum of 2-hydroxy[6]helicene (68)**

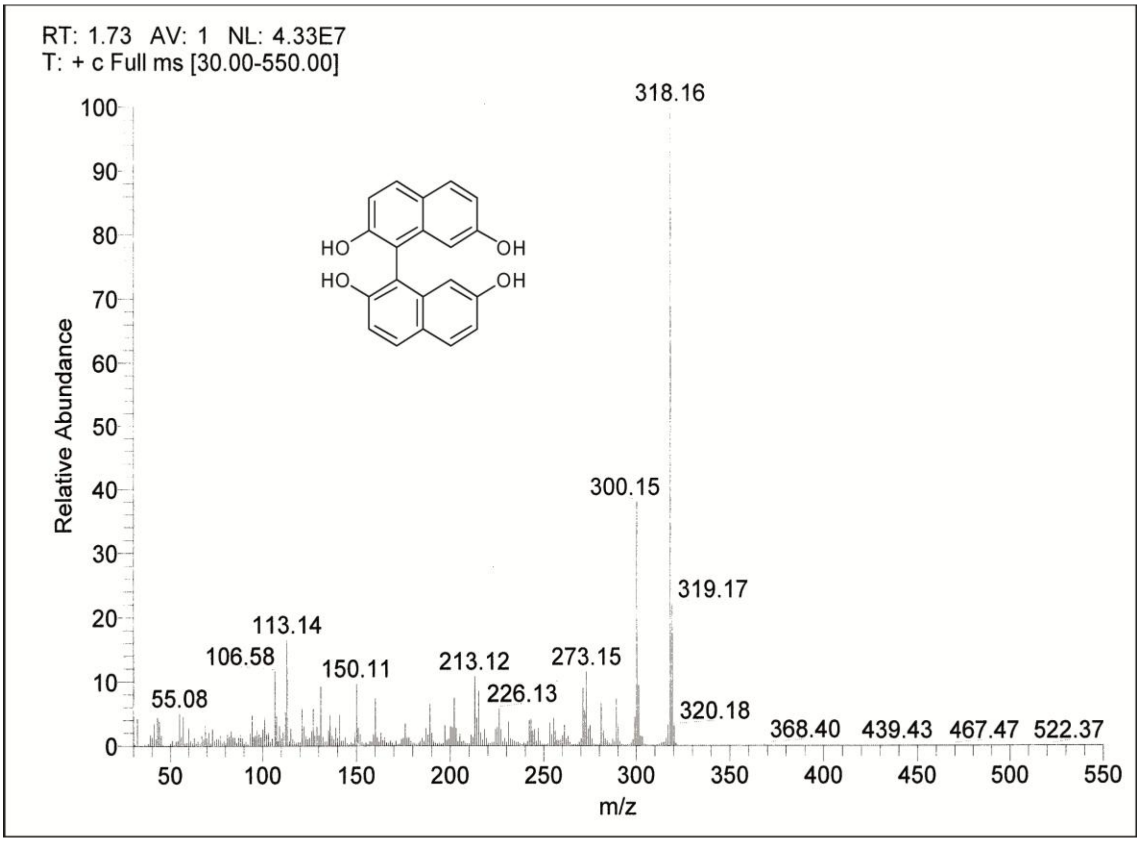


**EI-Mass spectrum of 2-hydroxy[6]helicene (68)**

## Spectral data of 7,7’-dihydroxy-2,2’-binaphthol (71)

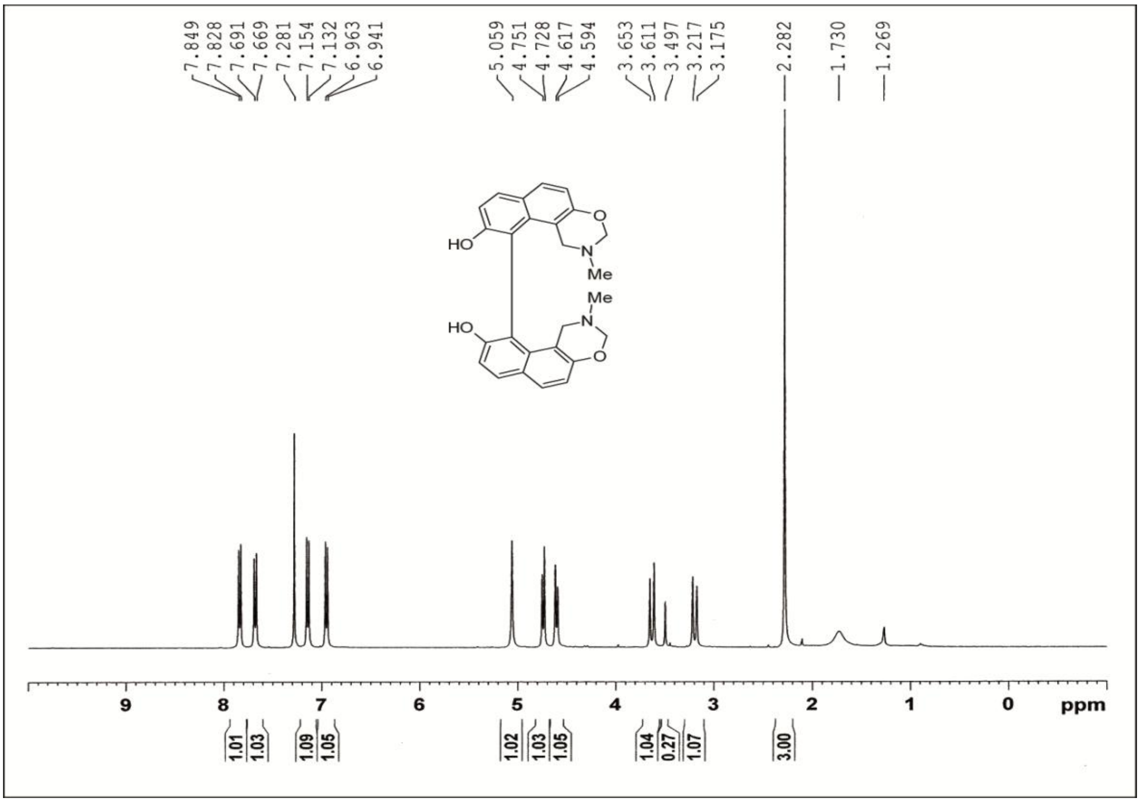


**$^1$H-NMR enlarge spectrum of 7,7’-dihydroxy-2,2’-binaphthol (71) in $CDCl_3$ on 400 MHz**

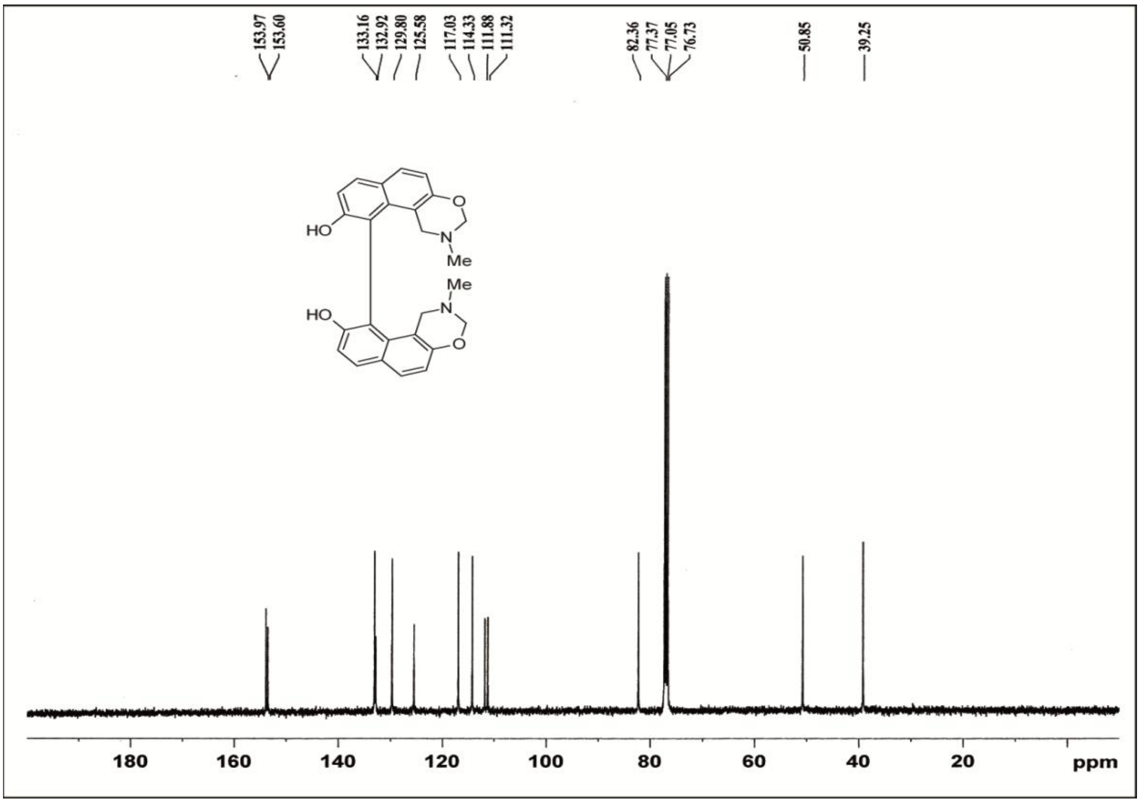


**EI-Mass spectrum of 7,7’-dihydroxy-2,2’-binaphthol (71)**

## Spectral data of 2,2'-dimethyl-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho-[1,2-*e*][1,3]oxazinyl]-9,9'-diol (72)

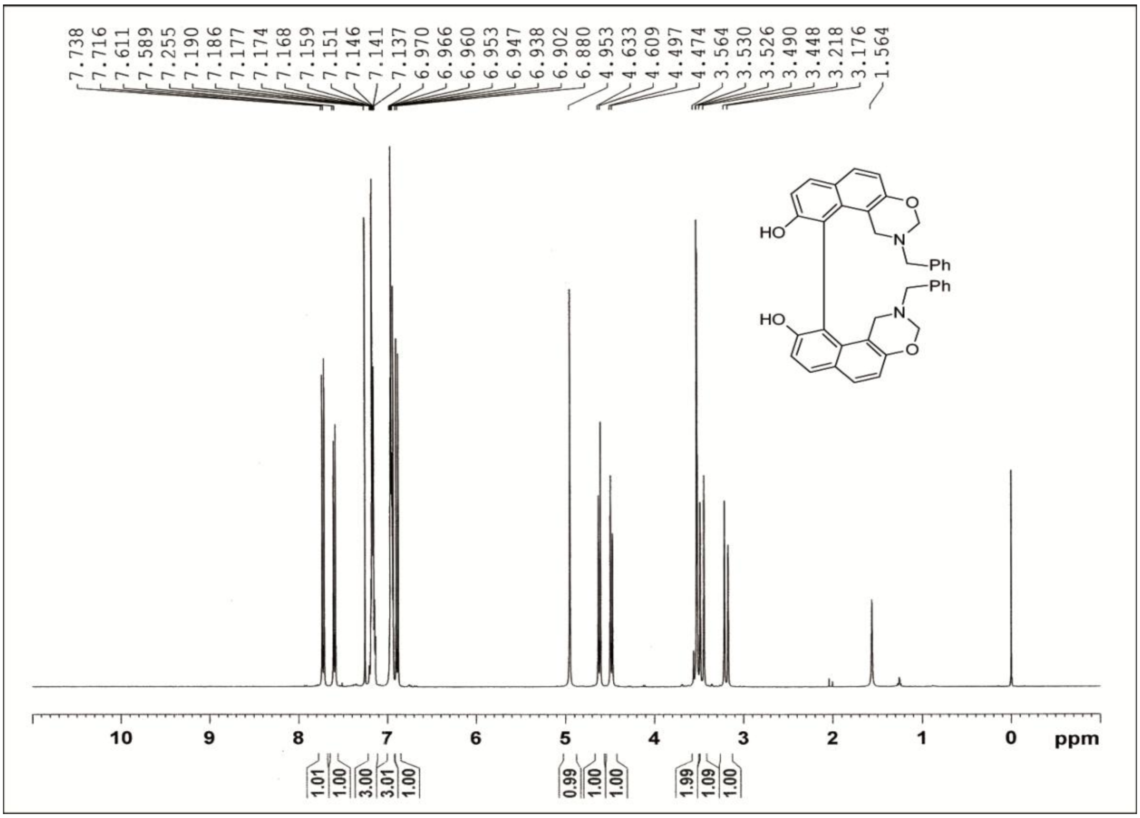


**$^1$H-NMR spectrum of 2,2'-Dimethyl-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (72) in $CDCl_3$ on 400 MHz**

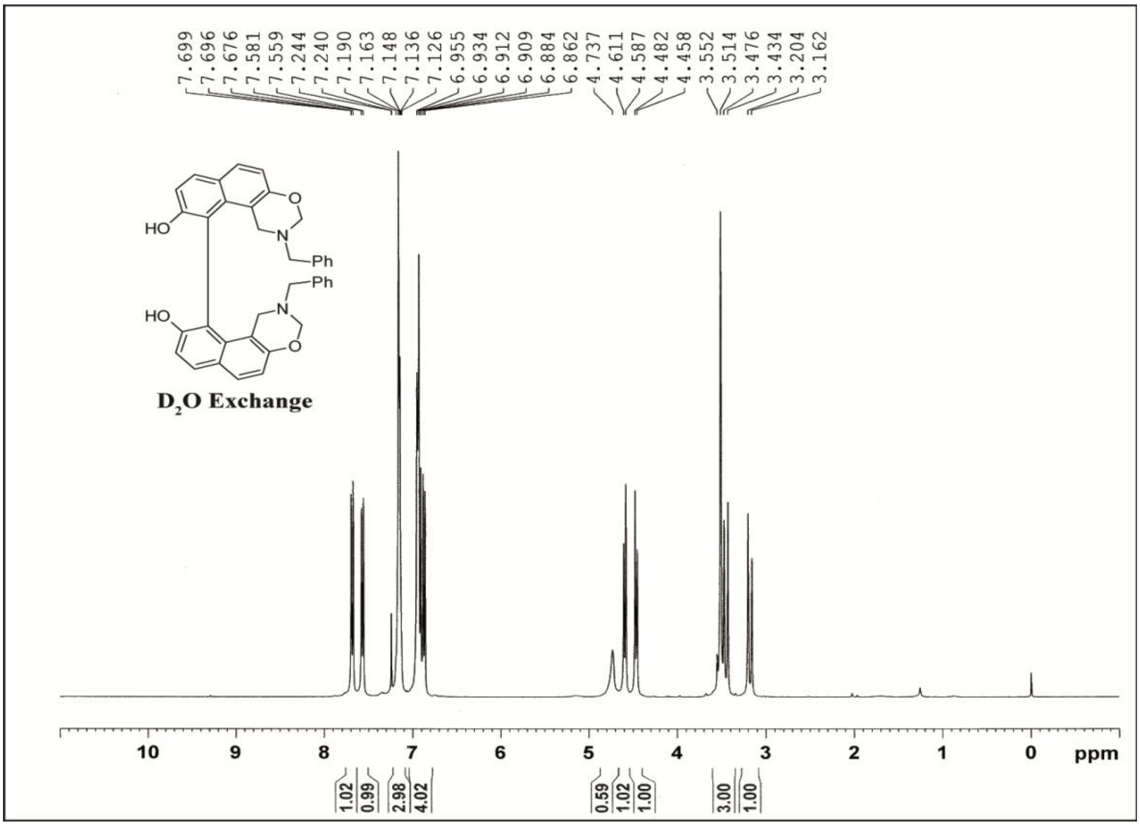


$^{13}$C-NMR spectrum of 2,2'-Dimethyl-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (72) in $CDCl_3$ on 100.6 MHz

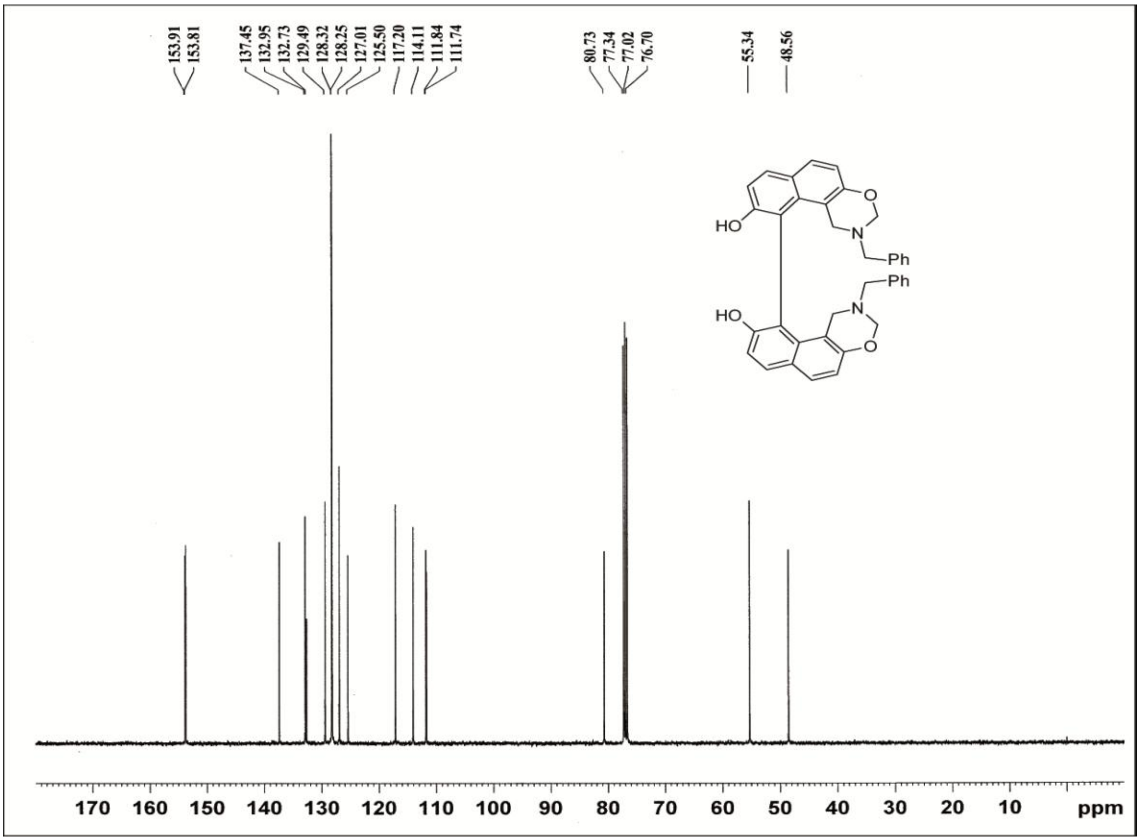
## Spectral data of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol (73):



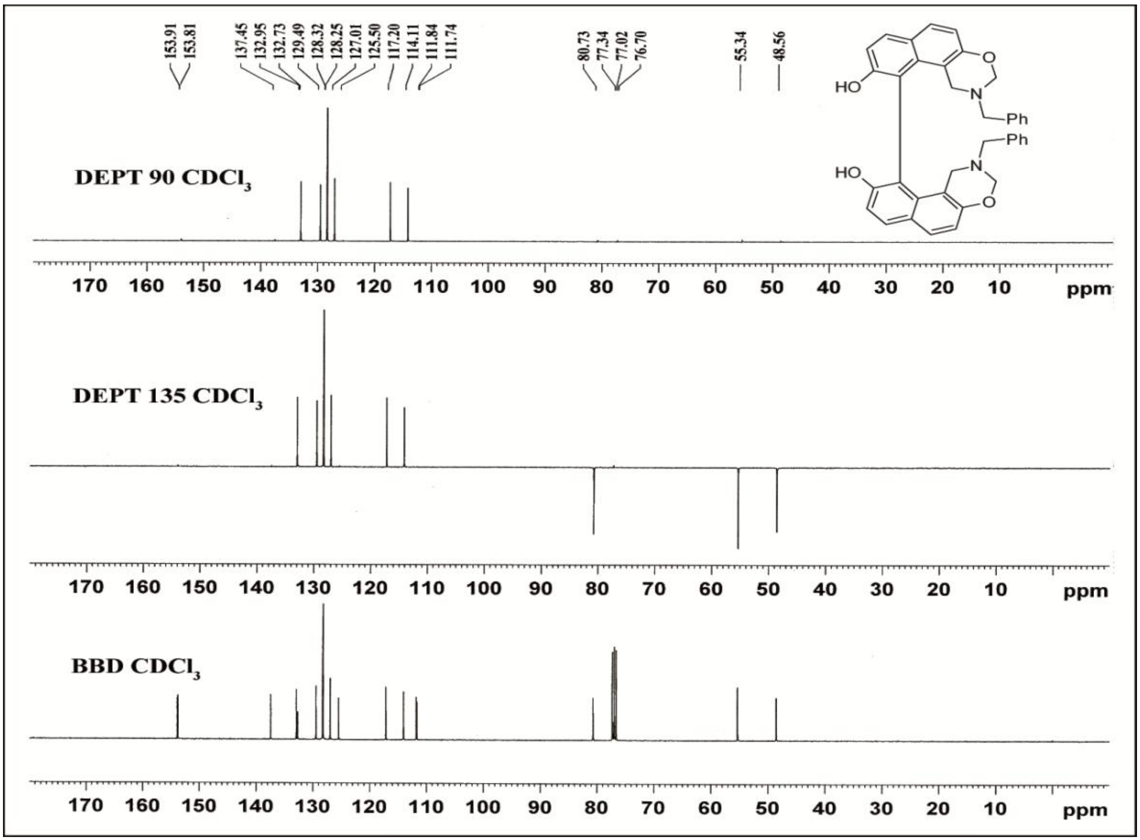
$^{1}$HNMR spectrum of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol (73) in $CDCl_3$ on 400 MHz



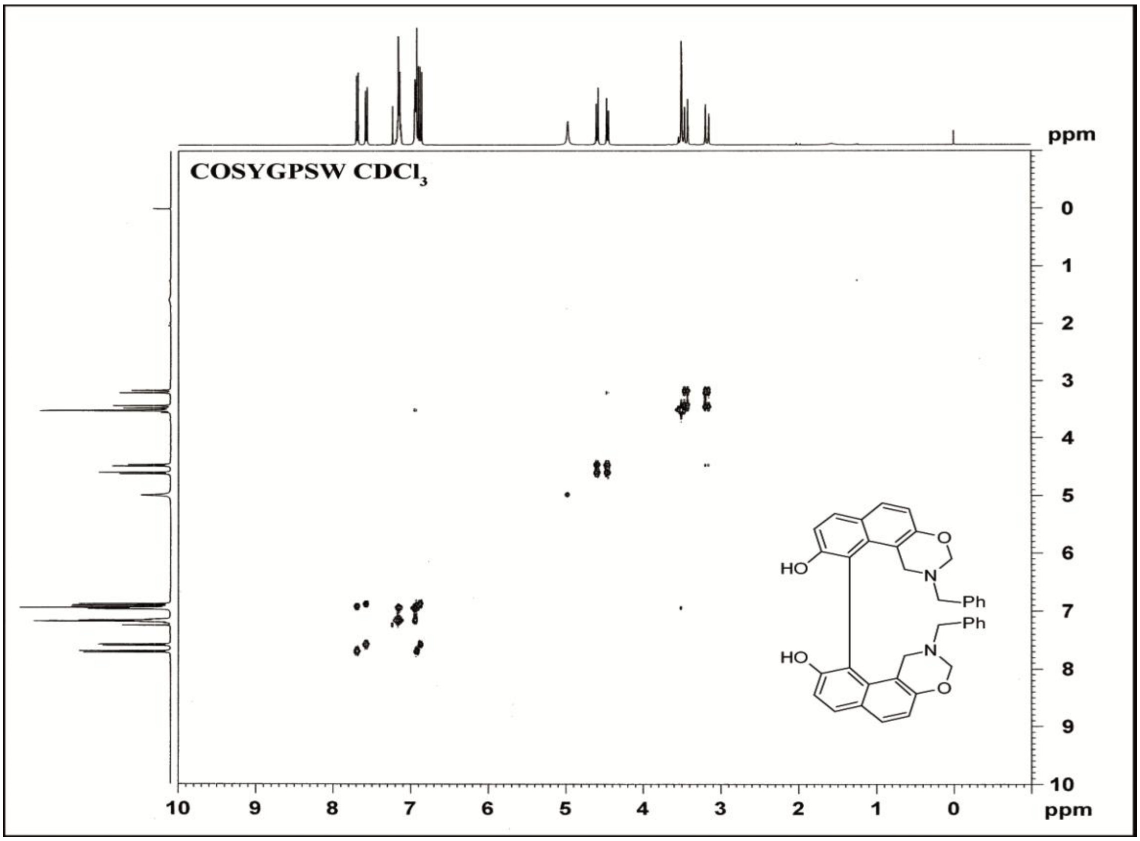
**$^1$HNMR ($D_2O$ exchange) spectrum of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol (73) in $CDCl_3$ on 400 MHz**



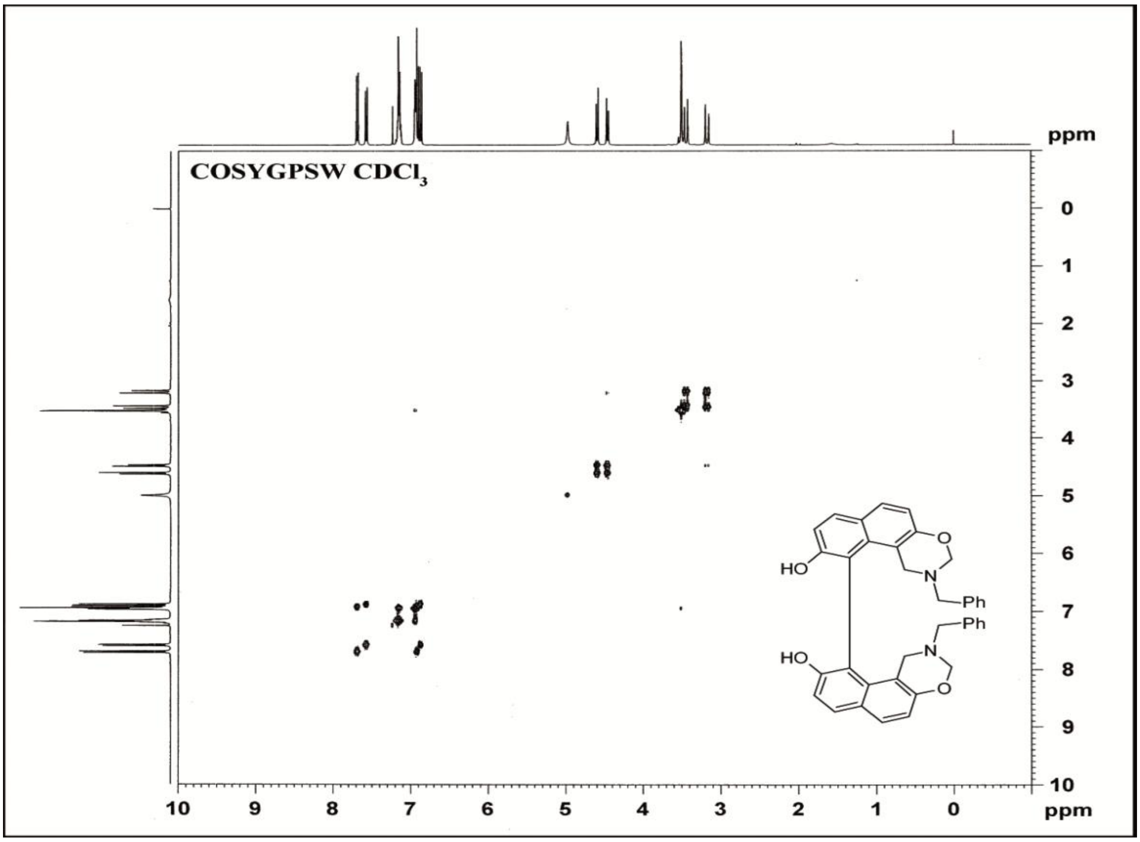
**$^{13}$C-NMR spectrum of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*]-[1,3]oxazine]-9,9'-diol (73) in $CDCl_3$ on 100.6 MHz**



$^{13}$C-NMR BBD, DEPT 90 & 135 spectrum of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol (73) in CDCl$_3$ on 100.6 MHz

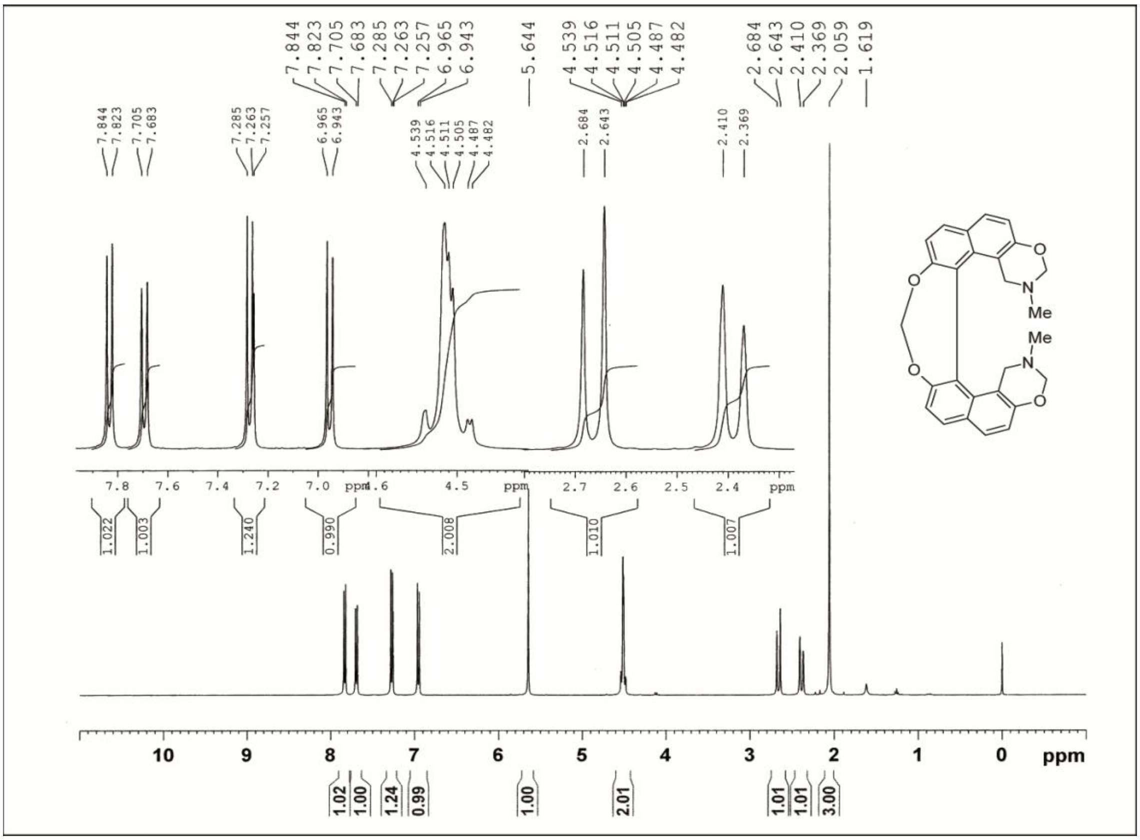


$^1$H-$^1$H correlation COSYGPSW spectrum of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol (73) in CDCl$_3$ on 400 MHz

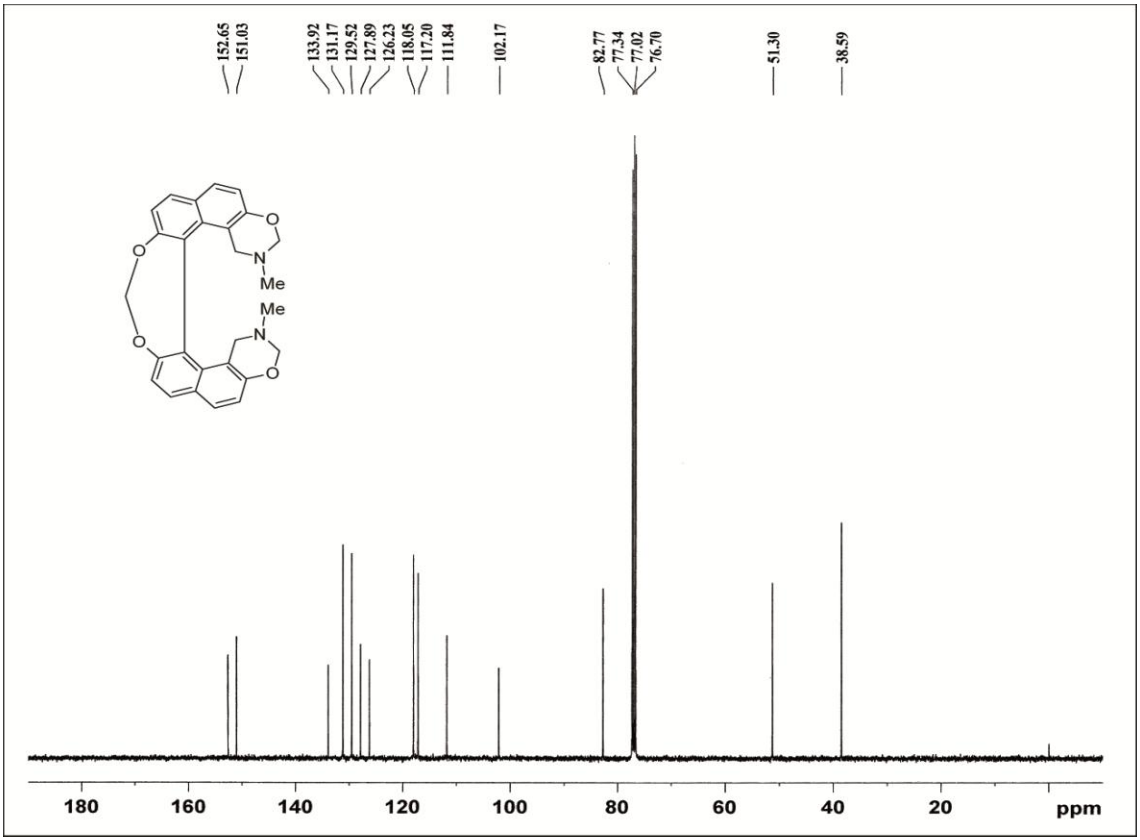


$^1$H-$^1$H COSYGPSW spectrum of 2,2'-dibenzyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[10,10'-binaphtho[1,2-*e*][1,3]oxazine]-9,9'-diol (73)

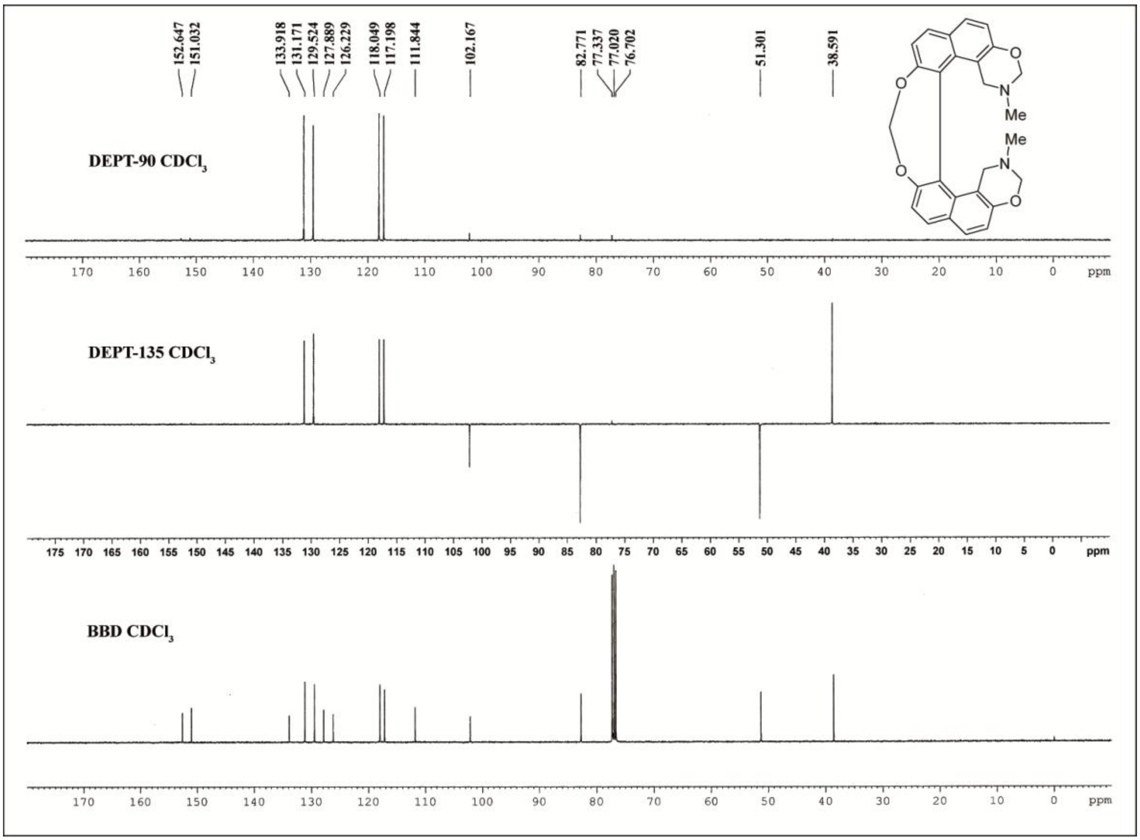
## Spectral data of Helical Bis-[1,3]oxazine (74)



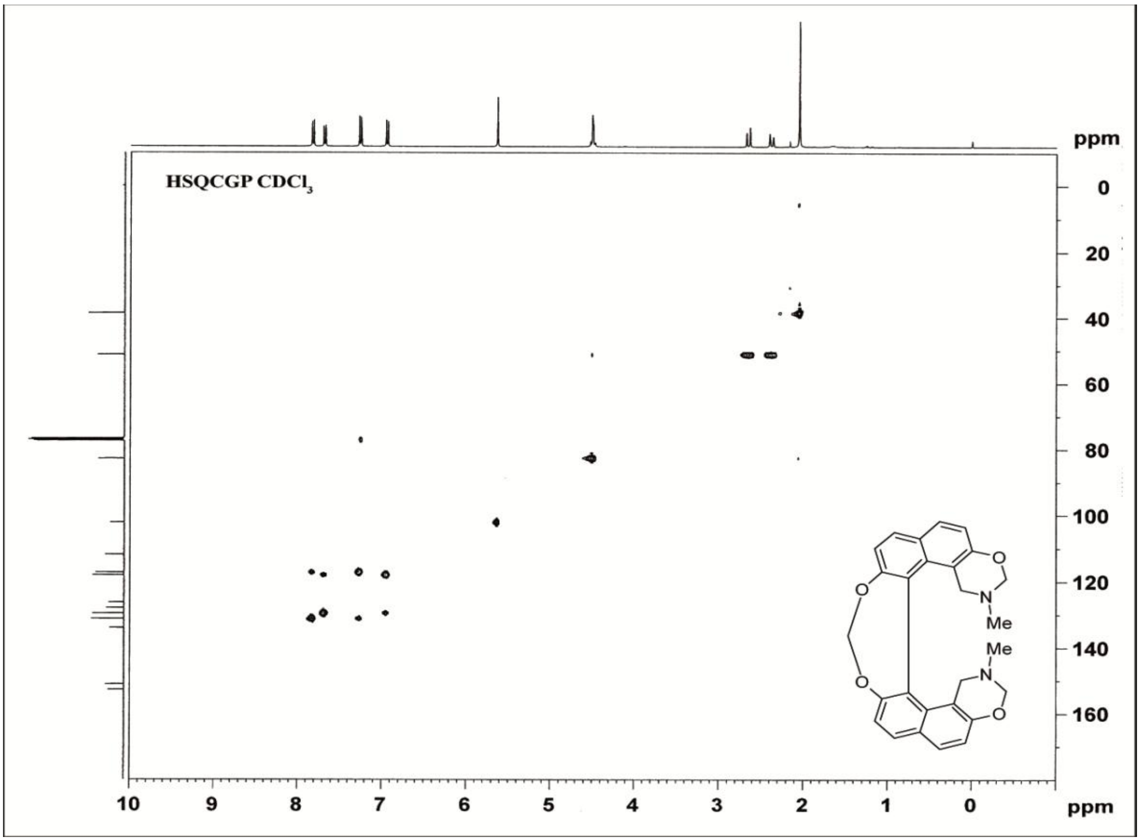
$^1$H-NMR spectrum of Helical Bis-[1,3]oxazine (74) in CDCl$_3$ on 400 MHz



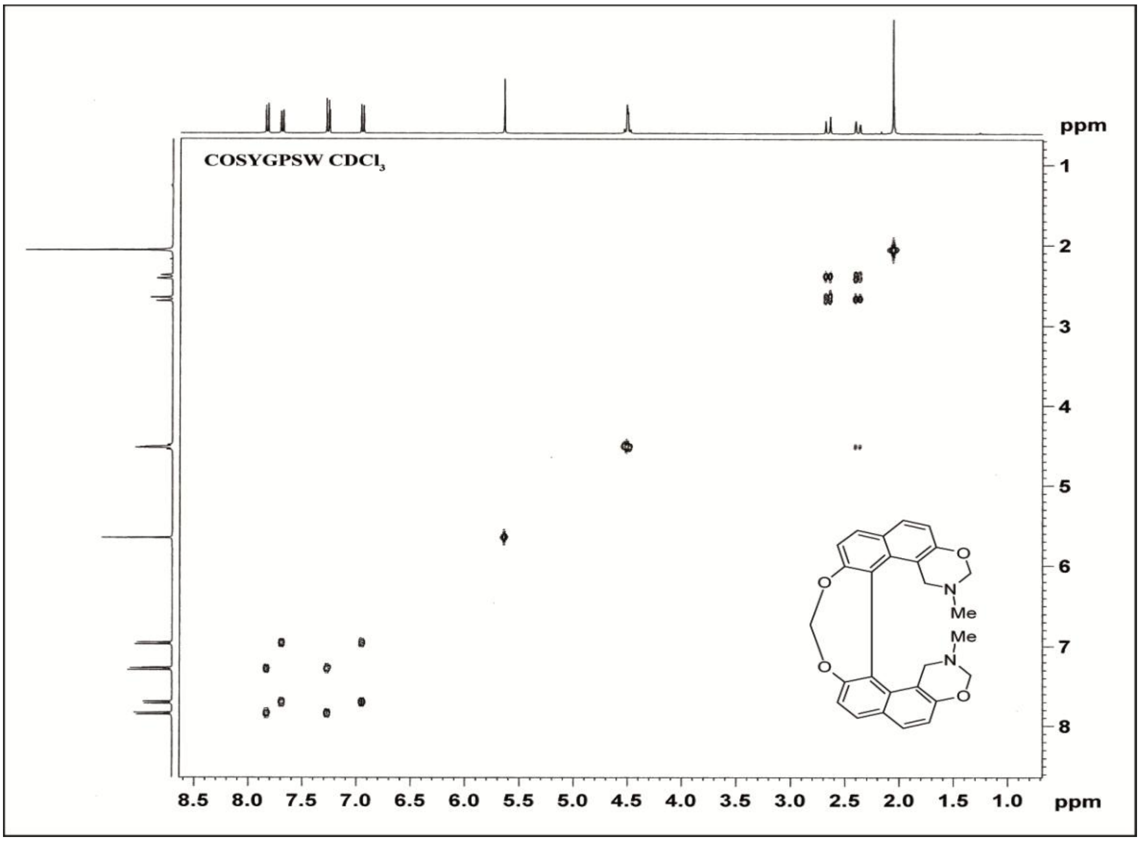
$^{13}$C-NMR spectrum of Helical Bis-[1,3]oxazine (74) in $CDCl_3$ on 100.6 MHz



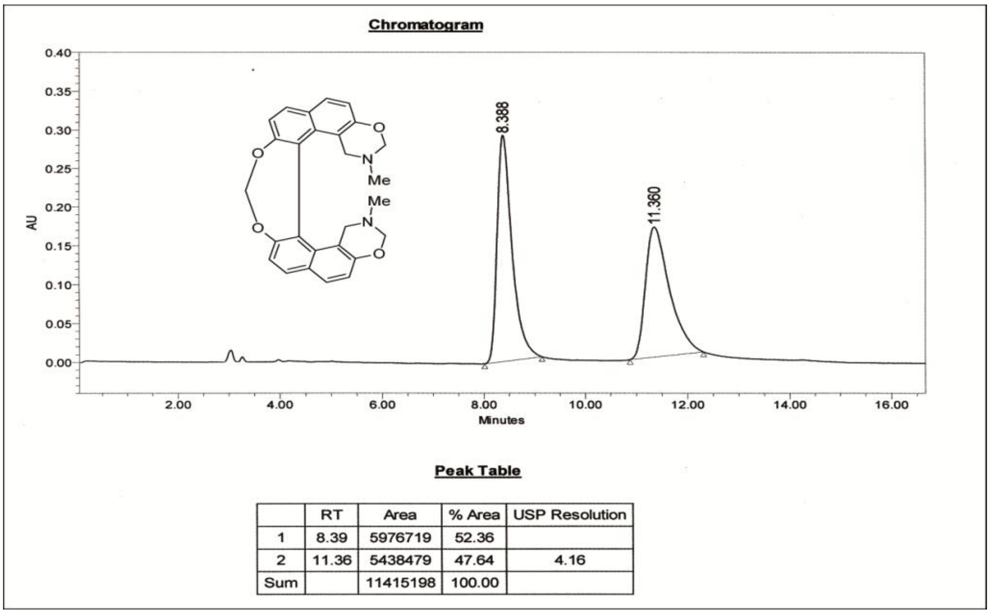
$^{13}$C-NMR BBD, DEPT 90 & 135 spectrum of Helical Bis-[1,3]oxazine (74) in $CDCl_3$ on 100.6 MHz



$^1$H-$^{13}$C correlation HSQCGP spectrum of Helical Bis-[1,3]oxazine (74) in CDCl$_3$ on 400 MHz



$^1$H-$^1$H correlation COSYGPSW spectrum of Helical Bis-[1,3]-oxazine (74) in CDCl$_3$ on 400 MHz



Peak Table

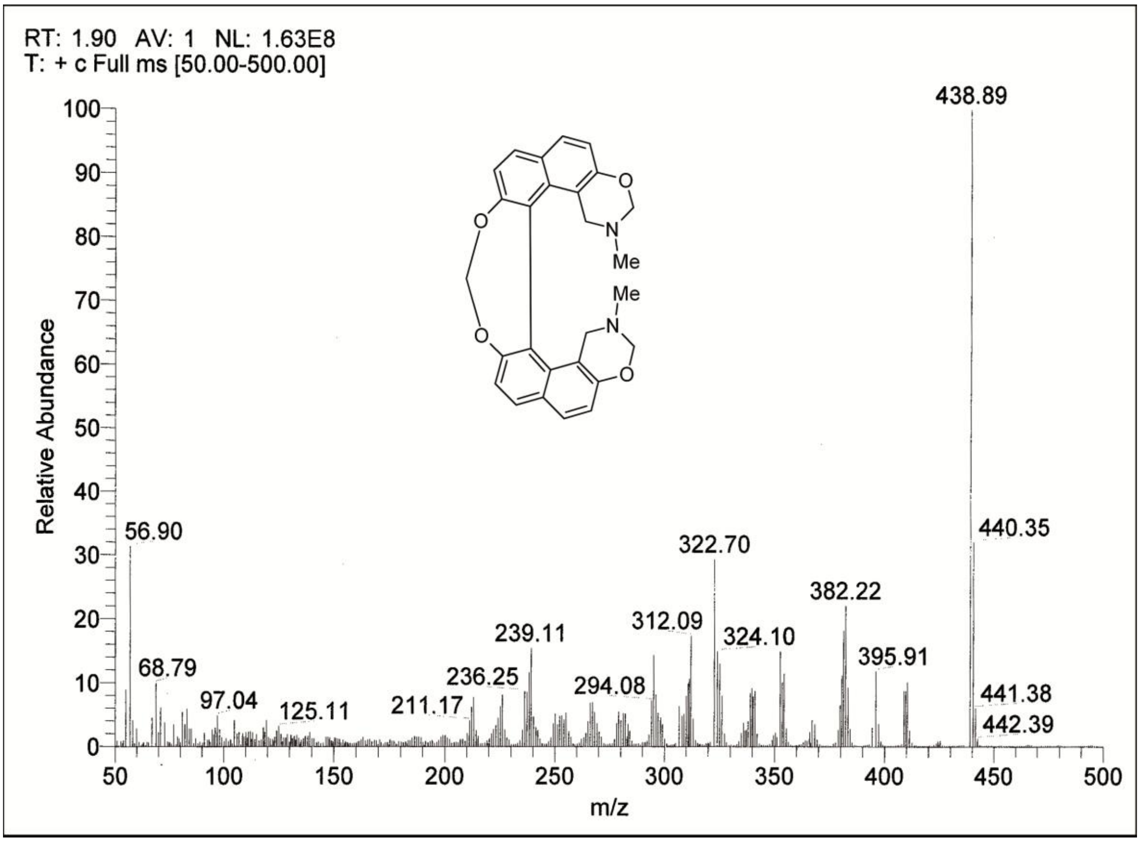
|  | RT | Area | % Area | USP Resolution |
|---|---|---|---|---|
| 1 | 8.39 | 5976719 | 52.36 |  |
| 2 | 11.36 | 5438479 | 47.64 | 4.16 |
| Sum |  | 11415198 | 100.00 |  |

**HPLC analysis:**

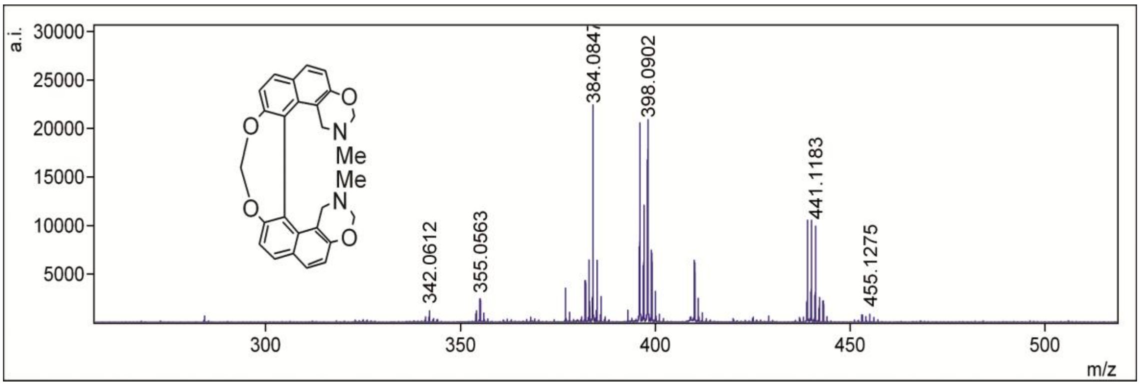
Observed two peaks of seperated enantiomers at 1) $R_t$ – 8.38 min and 2) $R_t$ – 11.36 min.

Solvent System: *n*-Hexane: *Iso*-propanol (85:15), Flow rate: 1mL/min.

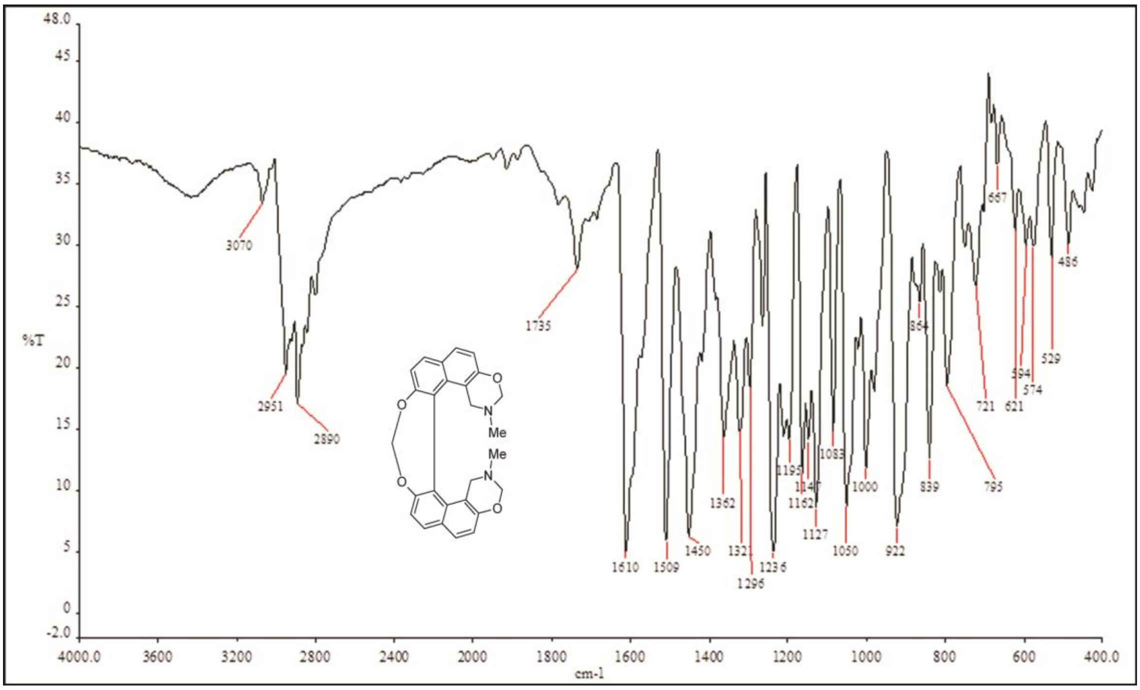
Chiral Column: Lux Amylose 2



**EI-Mass spectrum of Helical Bis-[1,3]oxazine (74)**

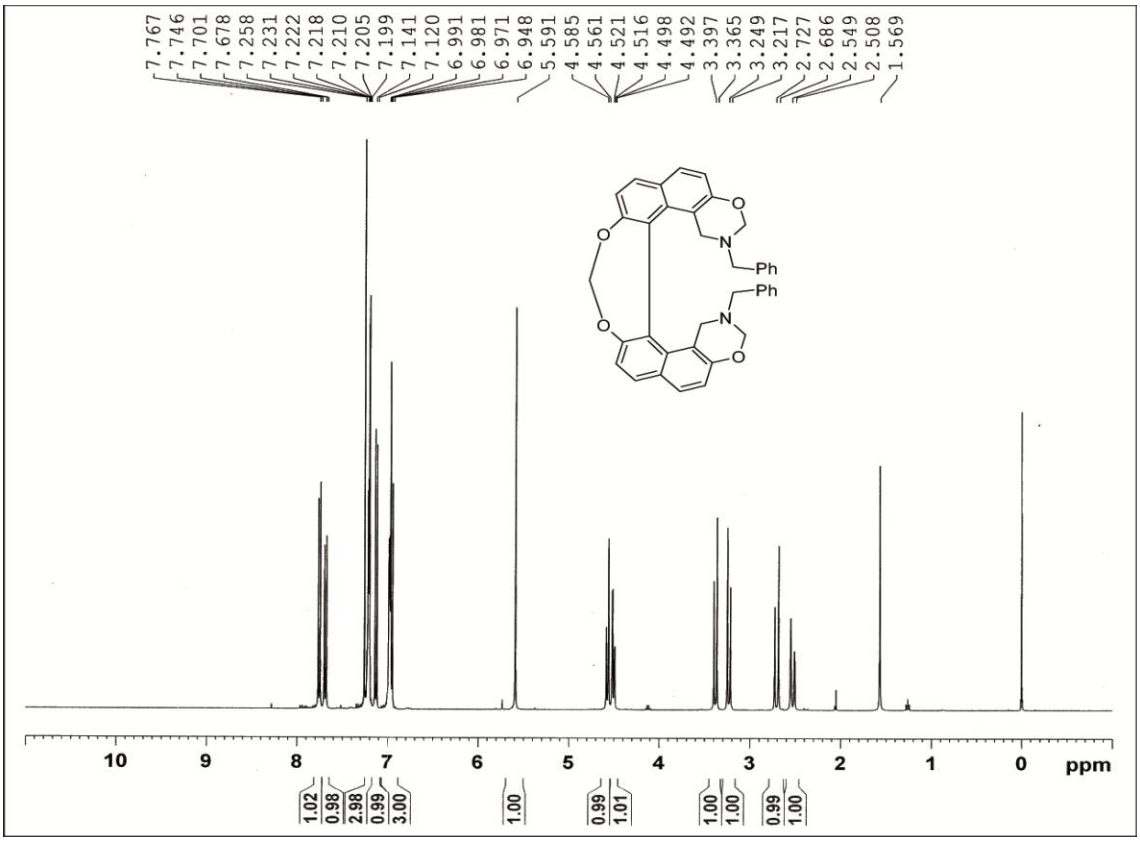


**MALDI-TOF-MS spectrum of Helical Bis-[1,3]oxazine (74)**

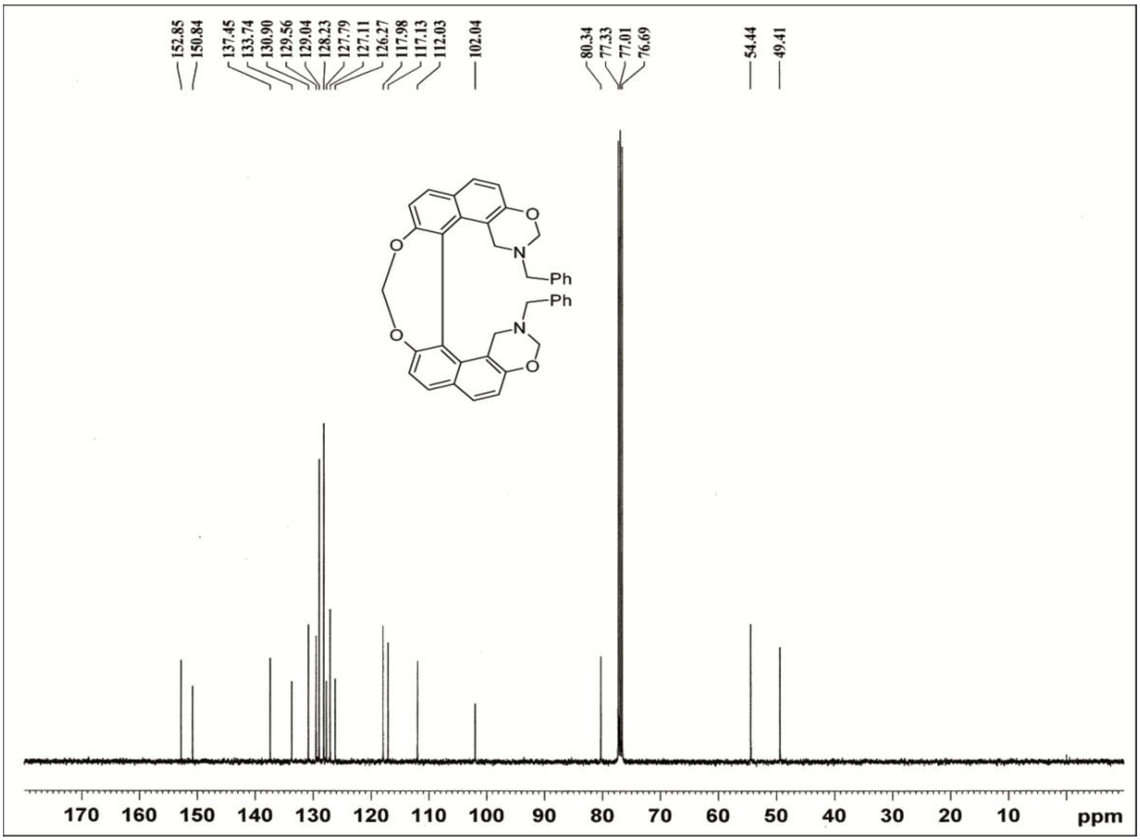


**IR spectrum of Helical Bis-[1,3]oxazine (74)**

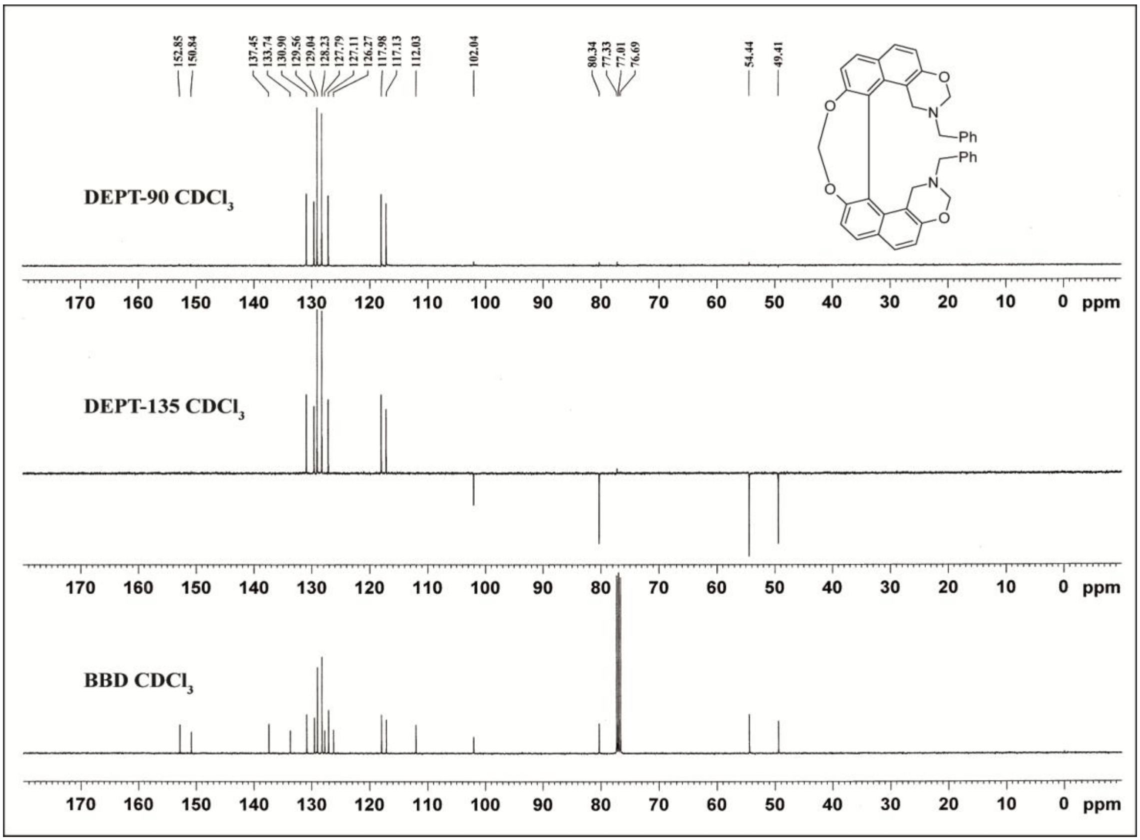
## Spectral data of Helical Bis-[1,3]oxazine (75)



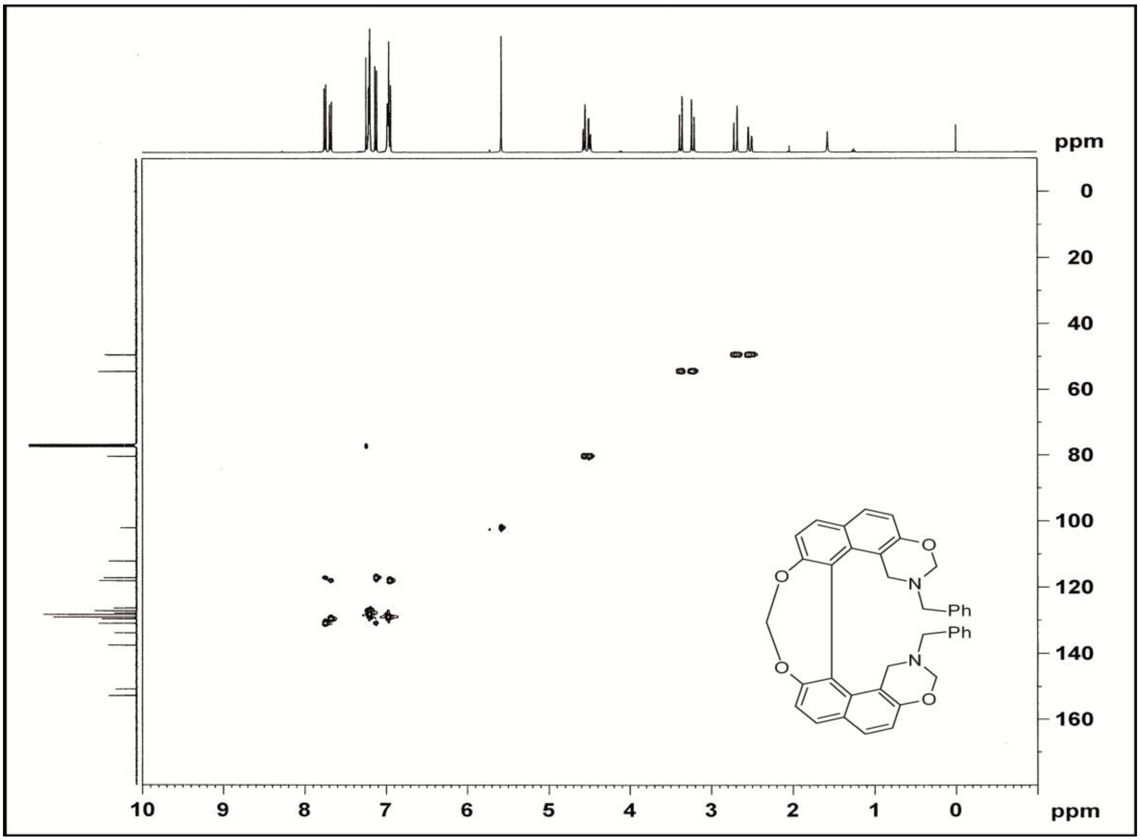
**$^1$H-NMR spectrum of Helical Bis-[1,3]oxazine (75) in $CDCl_3$ on 400 MHz**



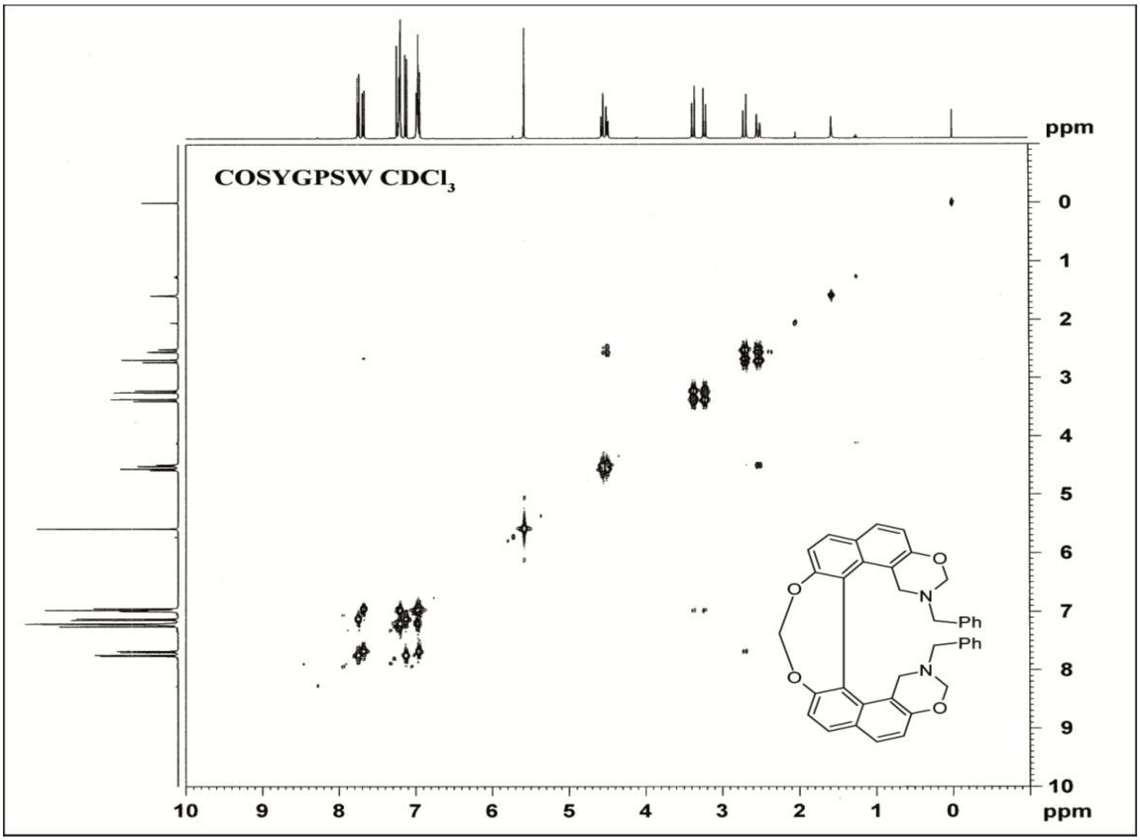
**$^{13}$C-NMR spectrum of Helical Bis-[1,3]oxazine (75) in $CDCl_3$ on 100.6 MHz**



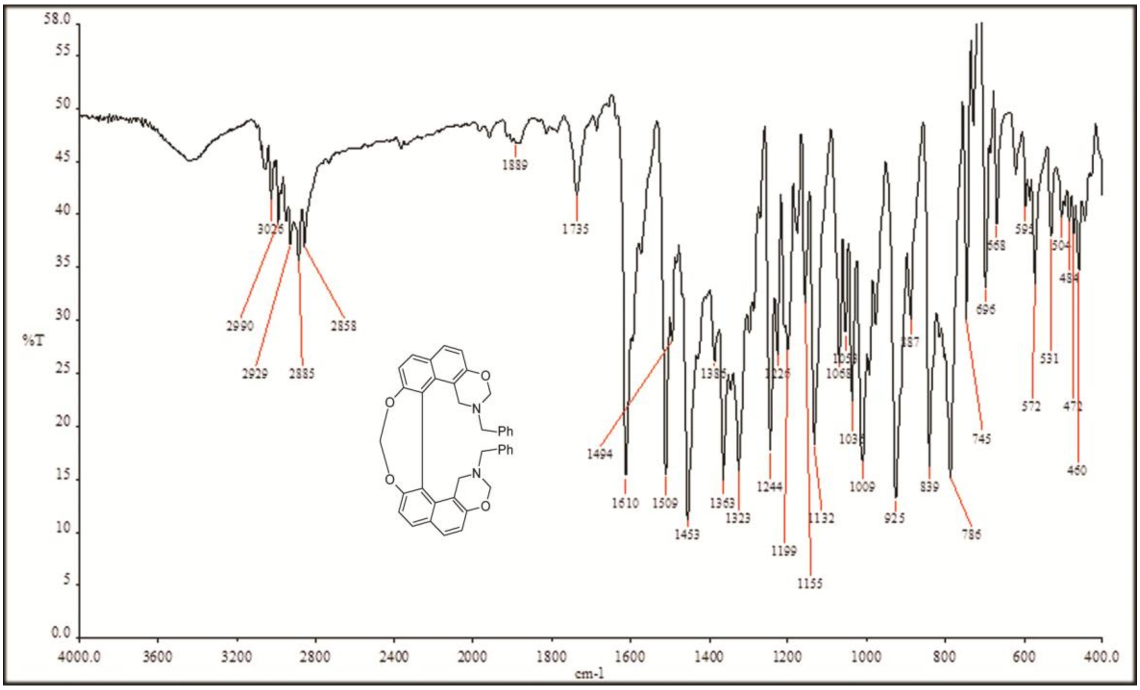
**$^{13}$C-NMR BBD, DEPT-90 & 135 spectrum of Helical Bis-[1,3]oxazine (75) in $CDCl_3$ on 100.6 MHz**



**$^{1}$H-$^{13}$C correlation HSQCGP spectrum of Helical Bis-[1,3]oxazine (75) in $CDCl_3$ on 400 MHz**

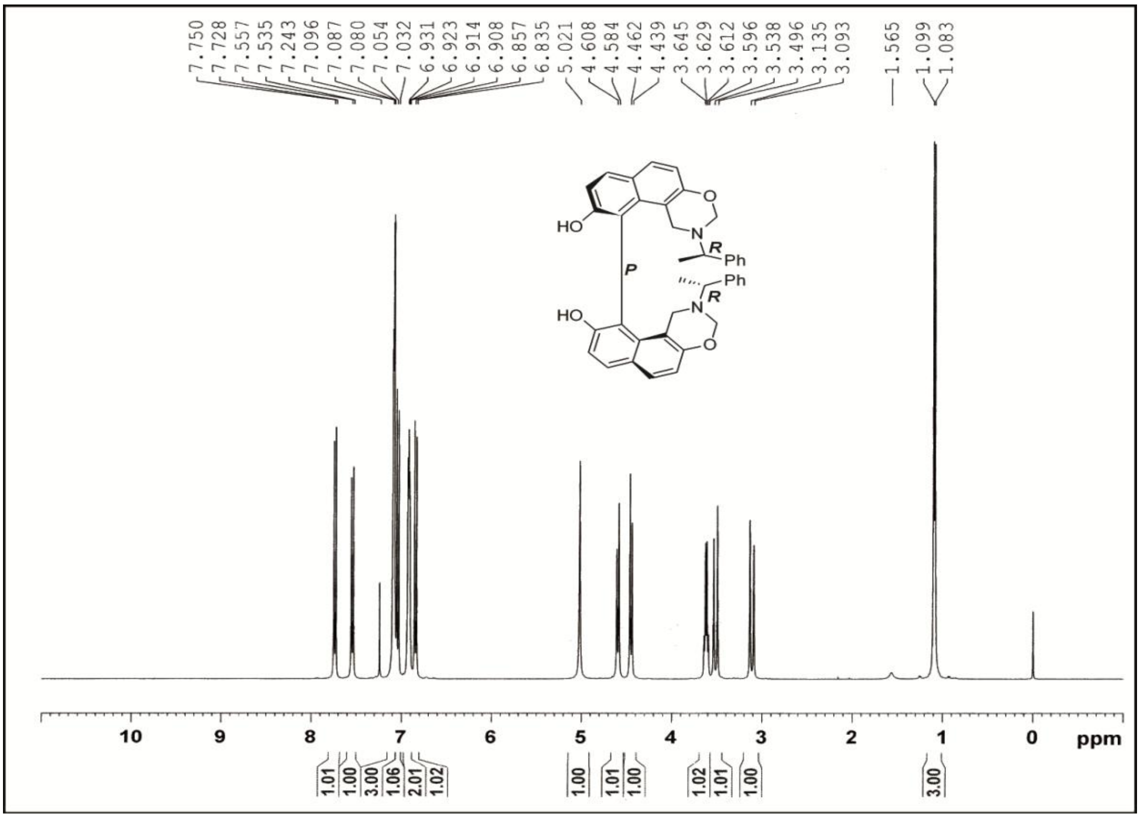


**$^1$H-$^1$H correlation COSYGPSW spectrum of Helical Bis-[1,3]oxazine (75) in CDCl$_3$ on 400 MHz**

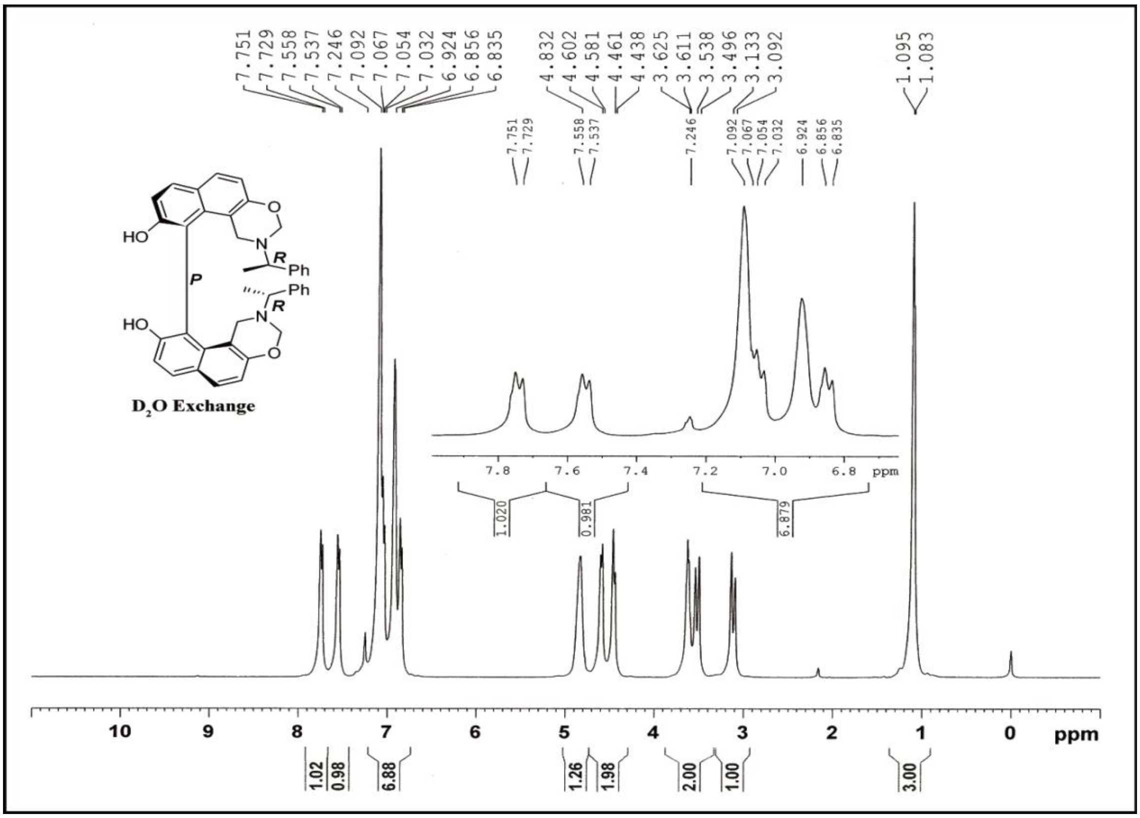


**IR Spectrum of Helical Bis-[1,3]oxazine (75)**

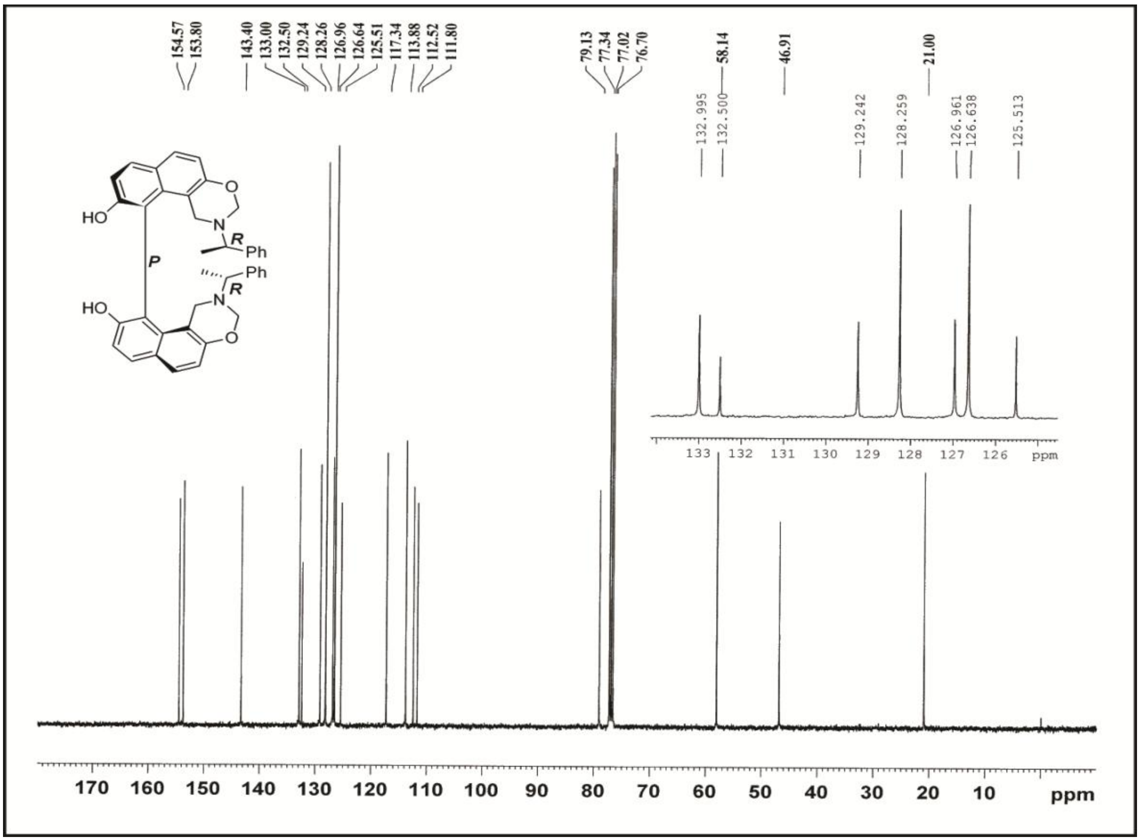
## Spectral data of (*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a)



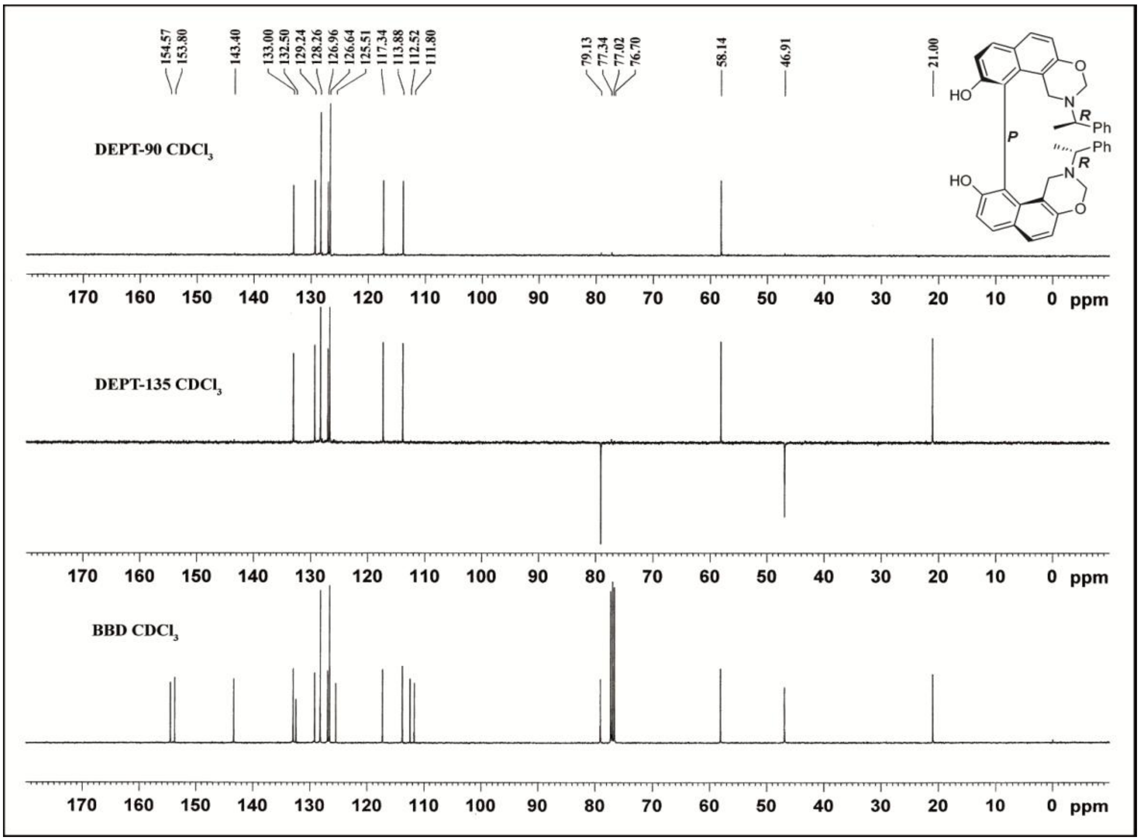
$^1$H-NMR of (*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a) in $CDCl_3$ on 400 MHz



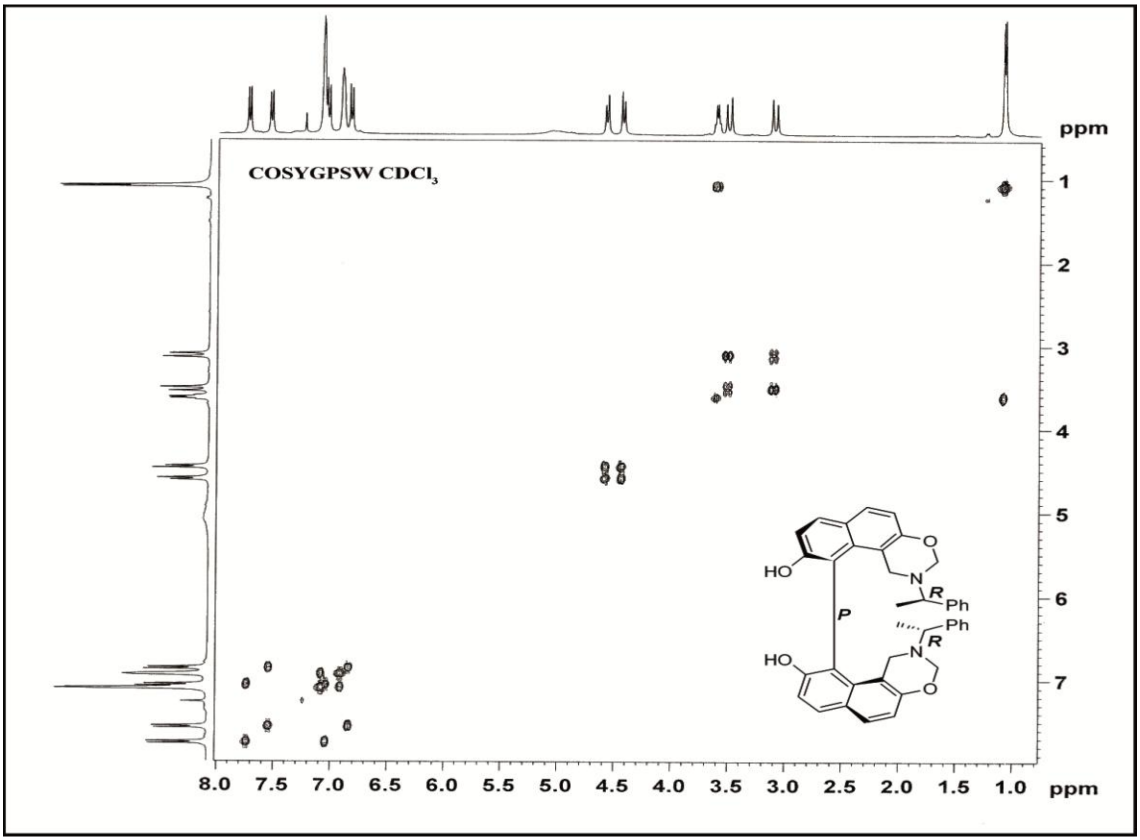
$^1$H-NMR ($D_2O$ Exchange) of (*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a) in $CDCl_3$ on 400 MHz



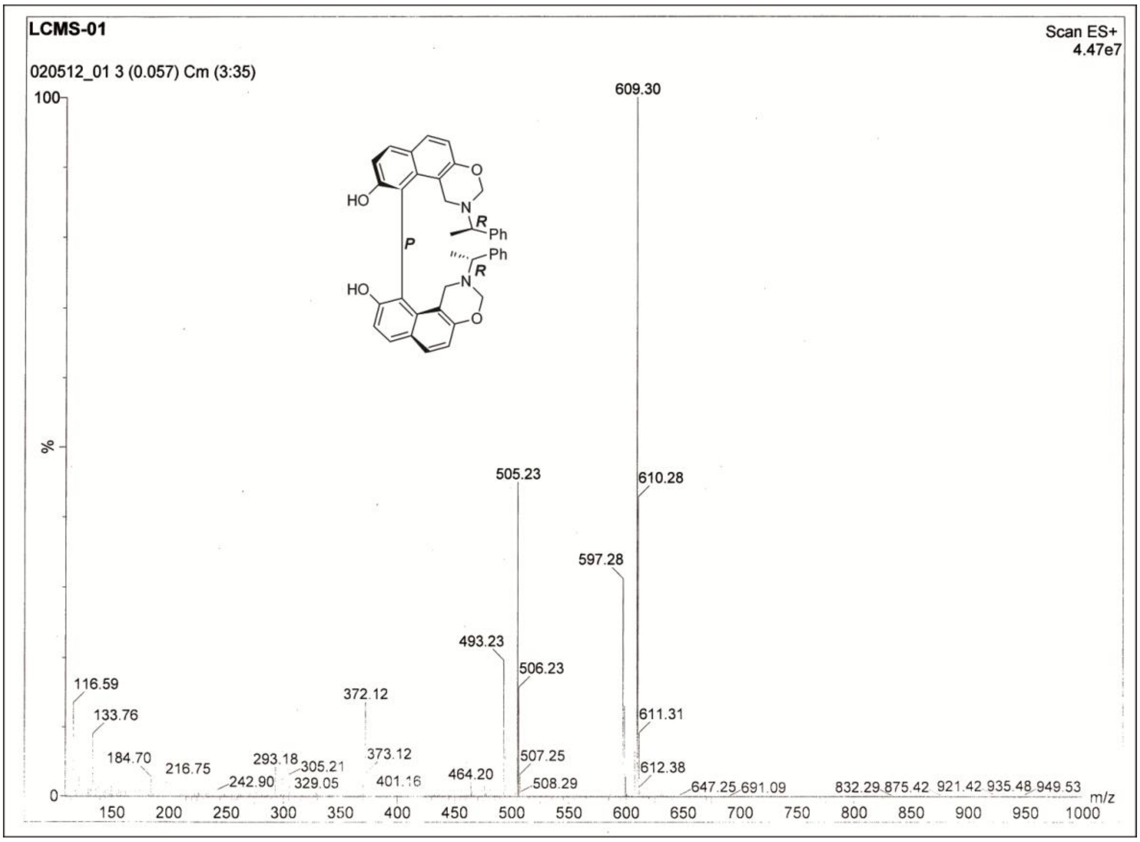
**$^{13}$C-NMR of (*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a) in CDCl$_3$ on 100.6 MHz**



**$^{13}$C-NMR BBD, DEPT-135 of (*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a) in CDCl$_3$ on 100.6 MHz**

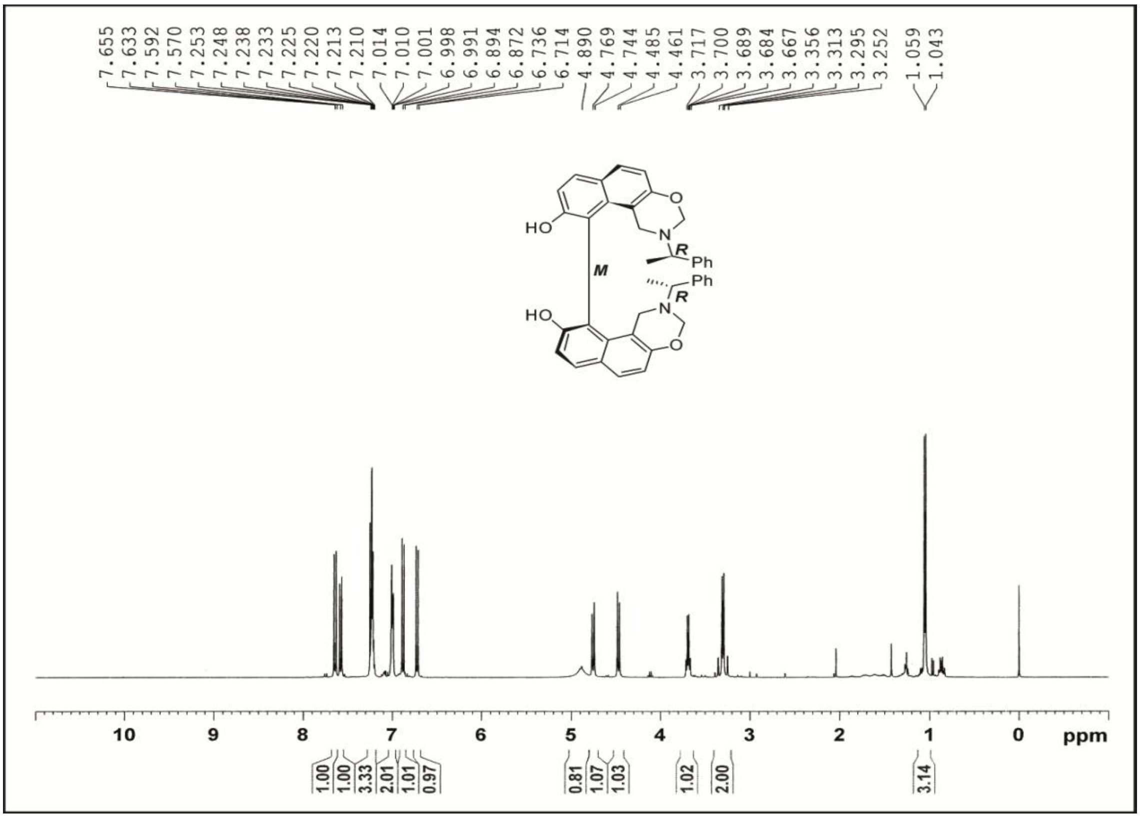


$^1$H-$^1$H correlation COSYGPSW spectrum of **(*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a) in CDCl$_3$ on 400 MHz**

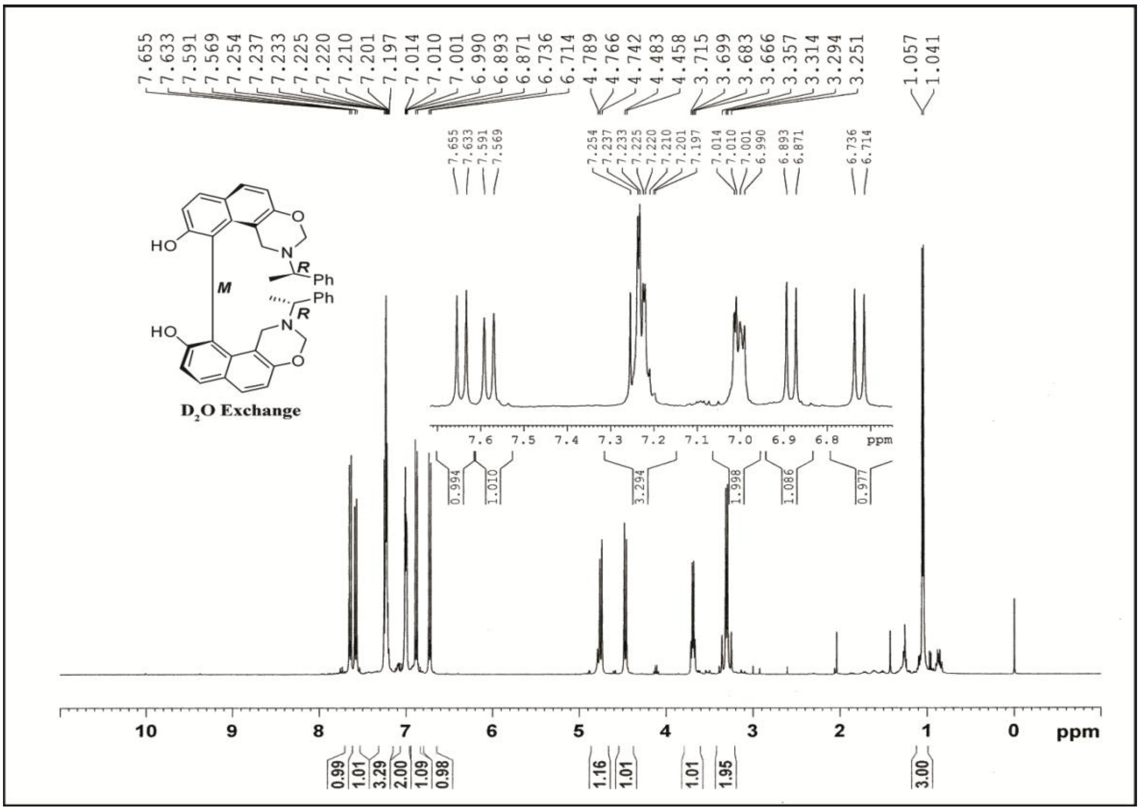


**ESI-Mass of (*P*)/(*S*)-2,2'-Bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76a)**

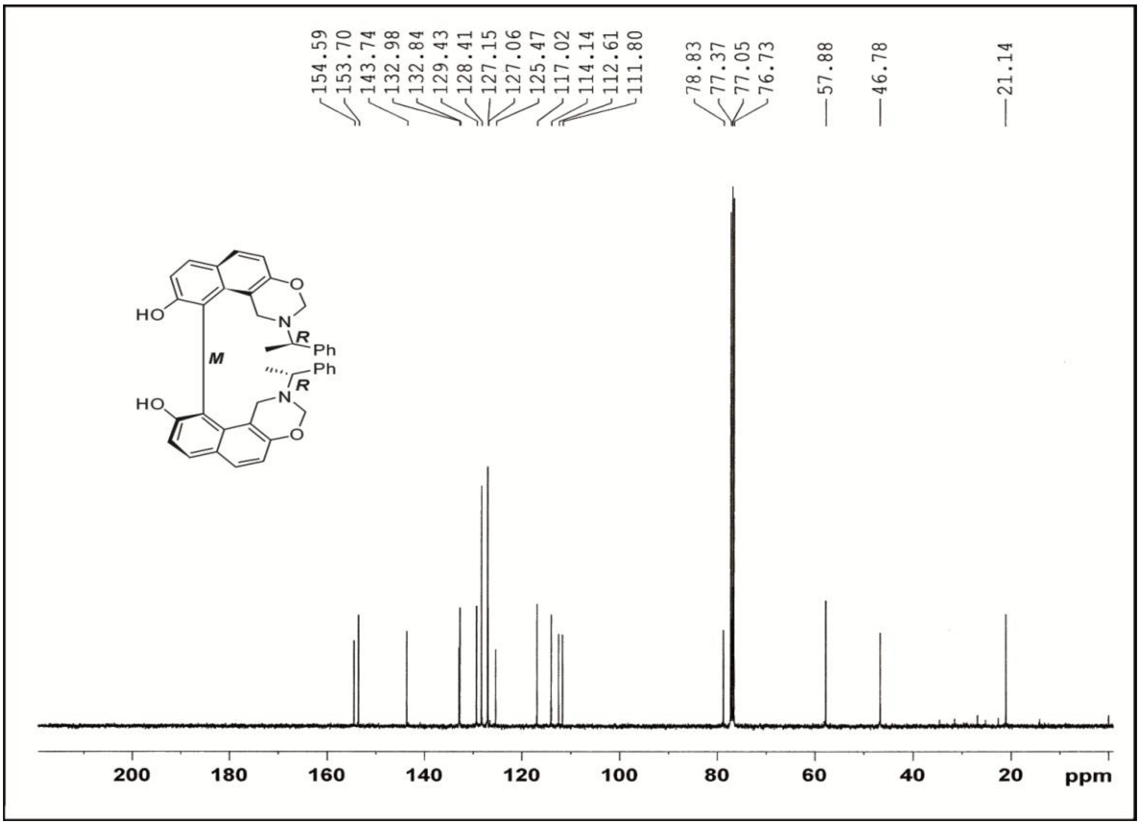
## Spectral data of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b)



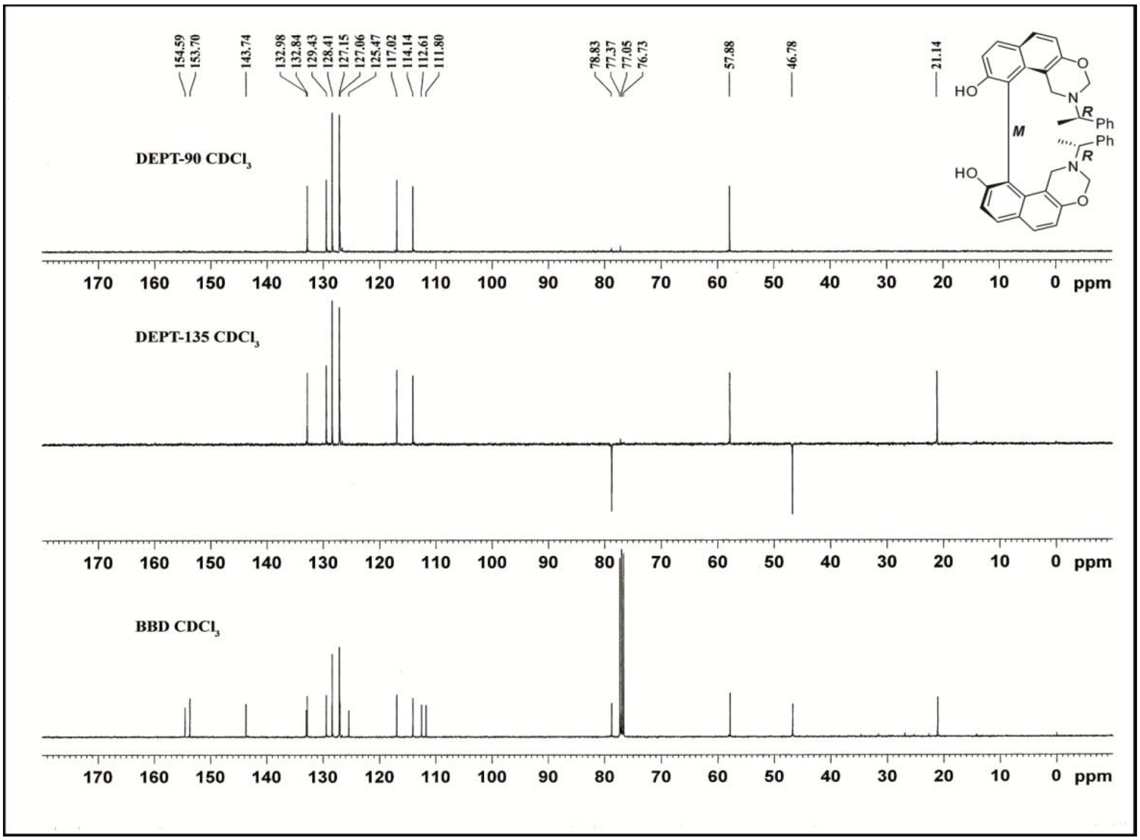
$^1$H-NMR spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b) in $CDCl_3$ on 400 MHz



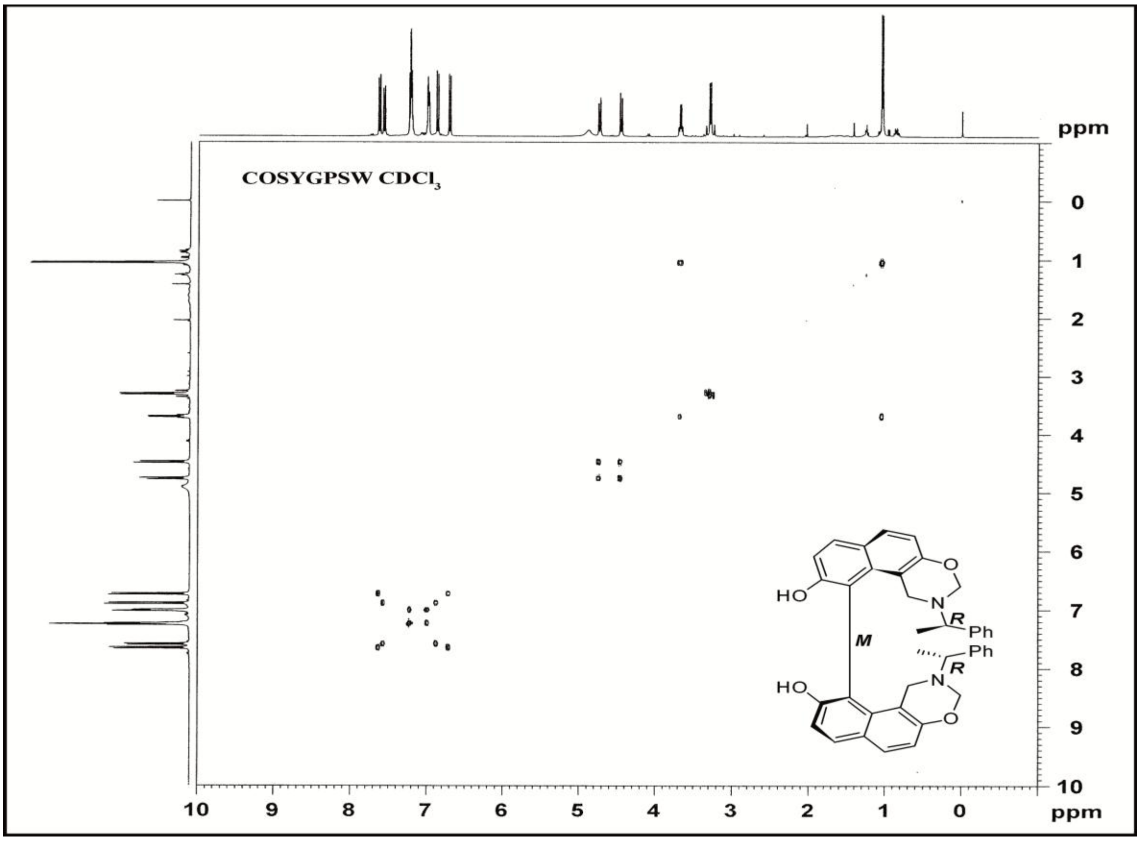
$^1$H-NMR ($D_2O$ Exchange) spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b) in $CDCl_3$ on 400 MHz



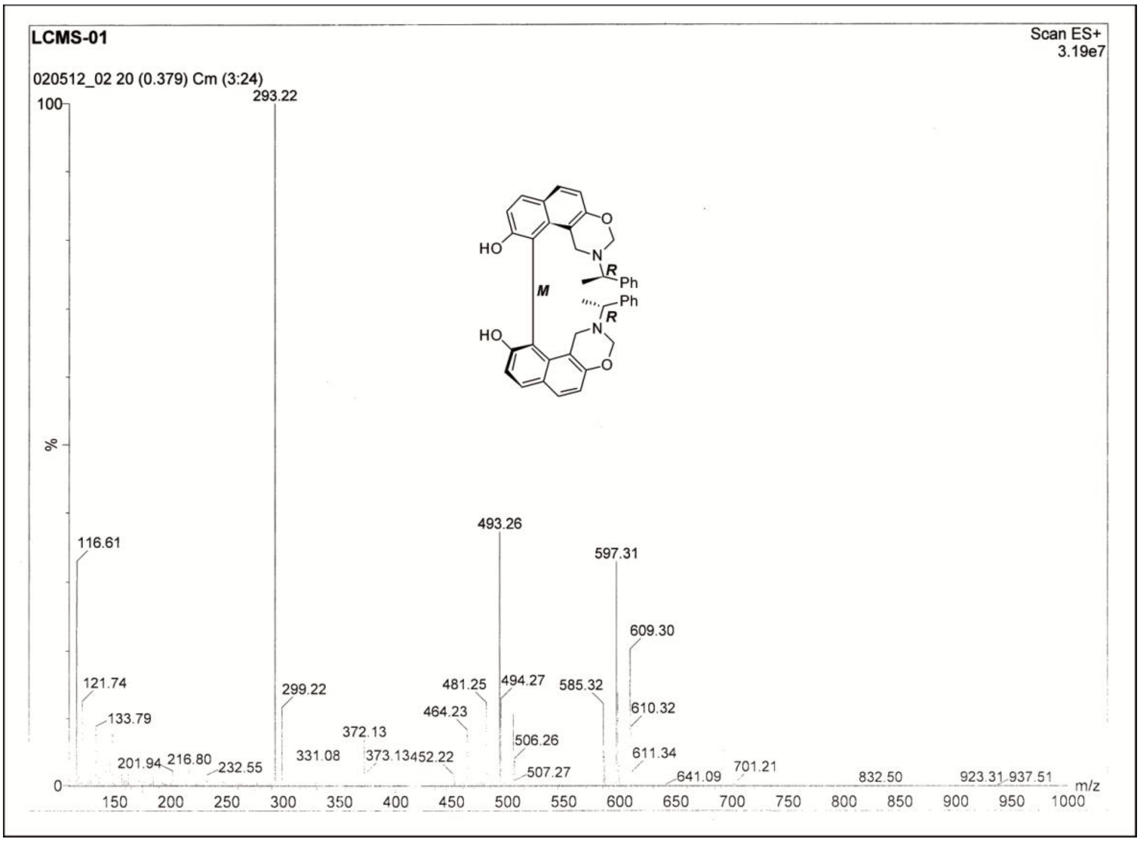
$^{13}$C-NMR spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b) in $CDCl_3$ on 100.6 MHz



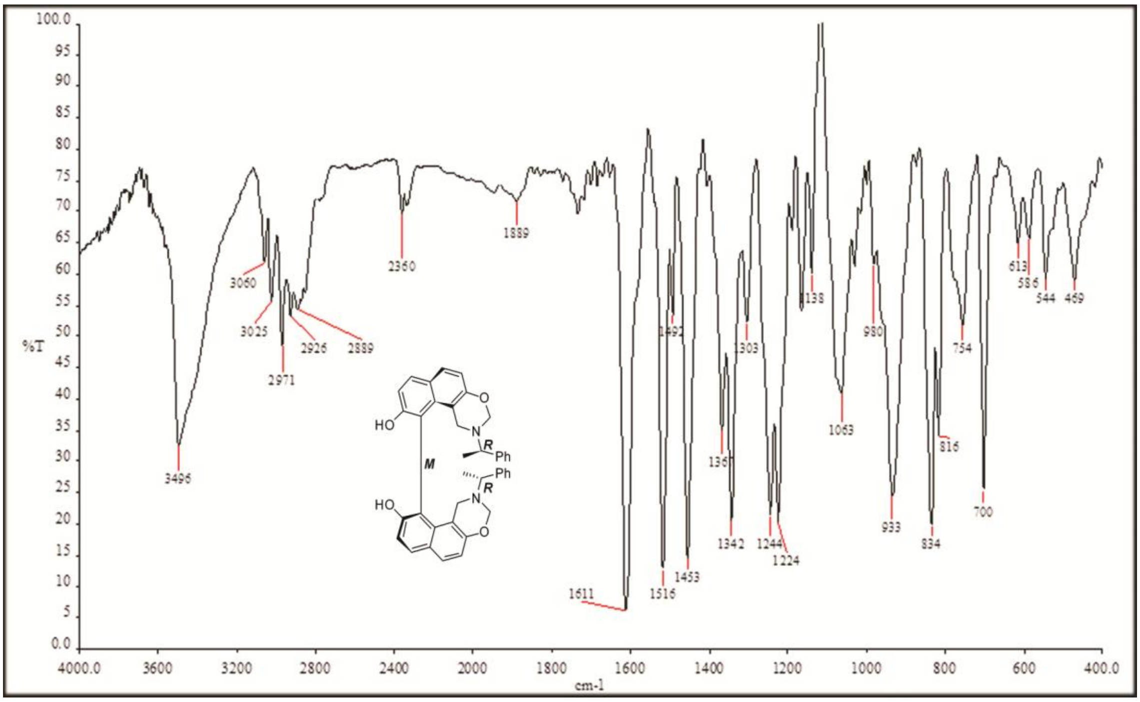
$^{13}$C-NMR BBD, DEPT-90 & 135 spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b) in $CDCl_3$ on 100.6 MHz



**H-H Correlation COSYGPSW spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b) in CDCl$_3$ on 400 MHz**

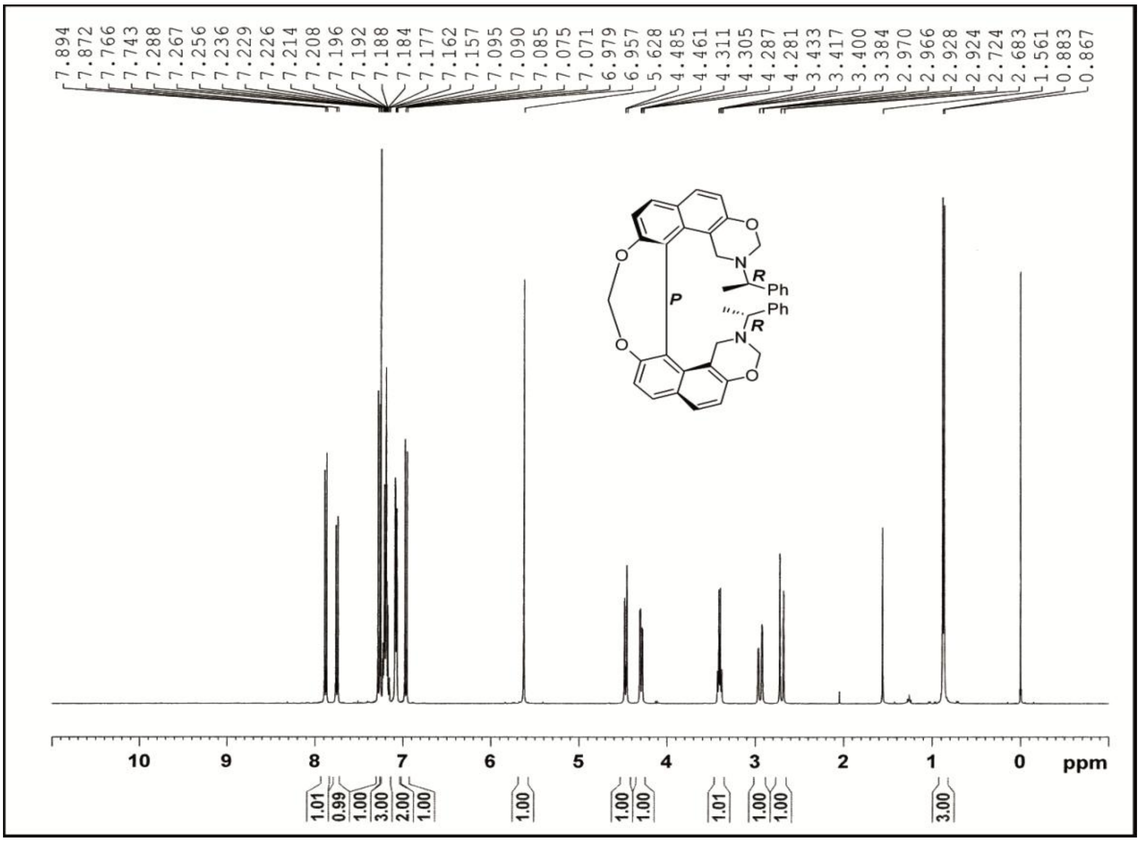


**ESI-Mass spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b)**

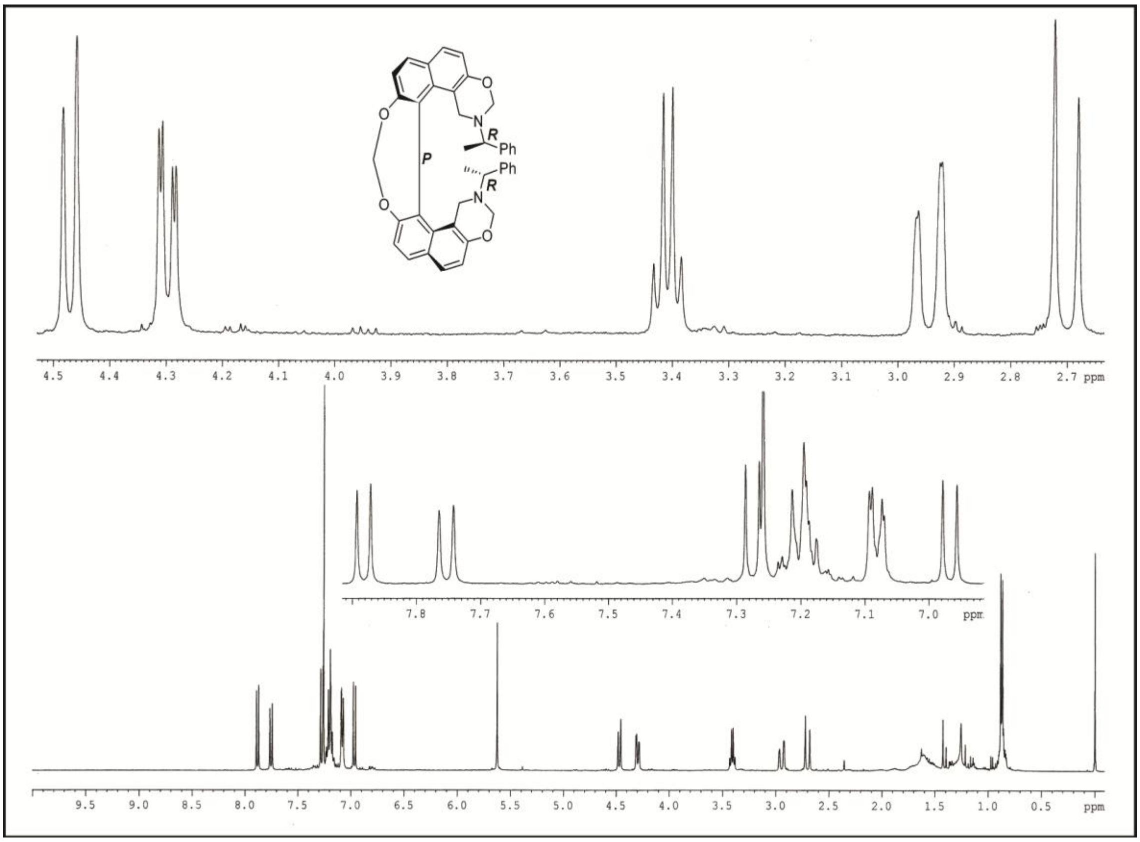


**IR spectrum of (*M*)/(*R*)-2,2'-bis-((*R*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'-diol (76b)**

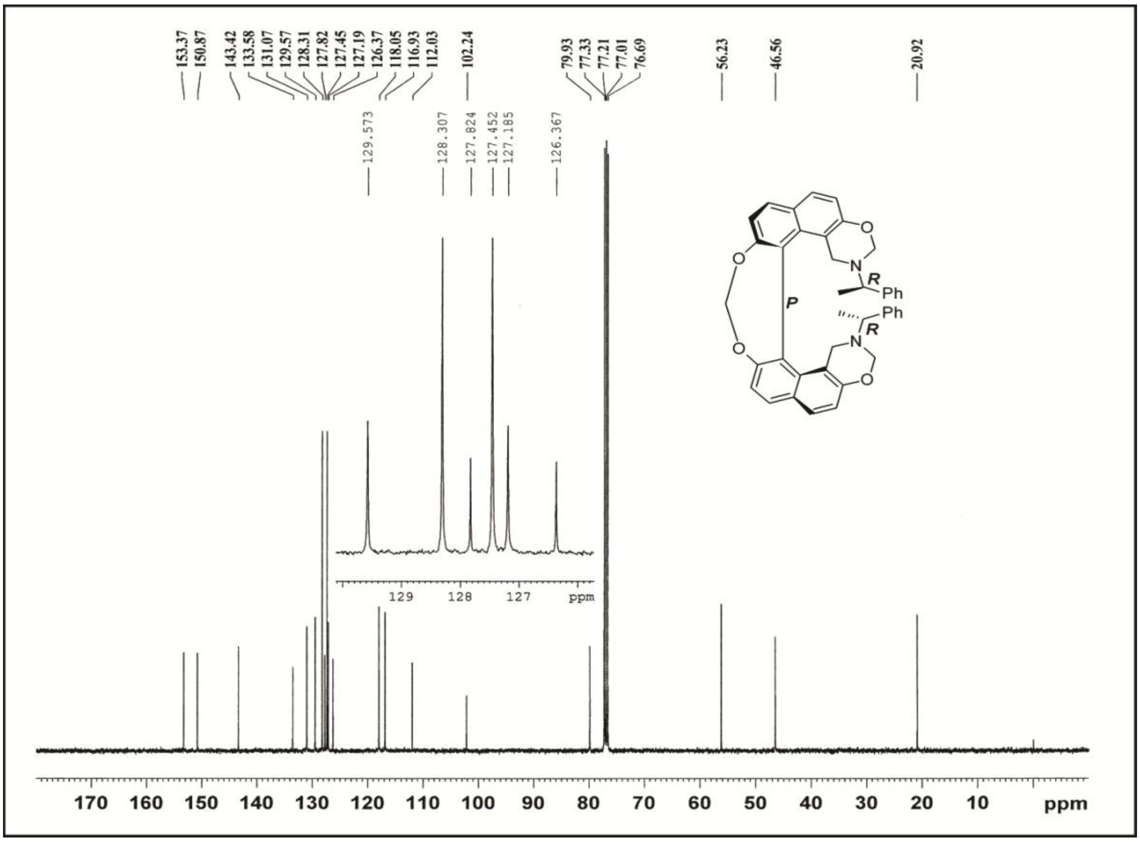
## Spectral data of Chiral Helical Bis-[1,3]oxazine (77a)



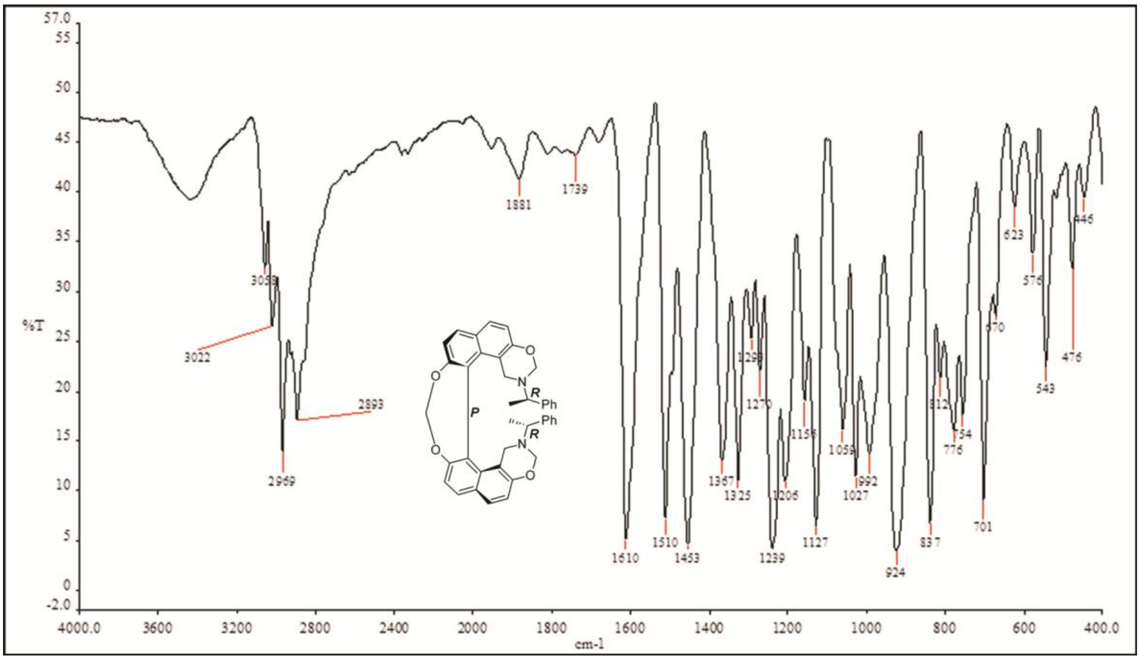
**$^1$H-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (77a) in $CDCl_3$ on 400 MHz**



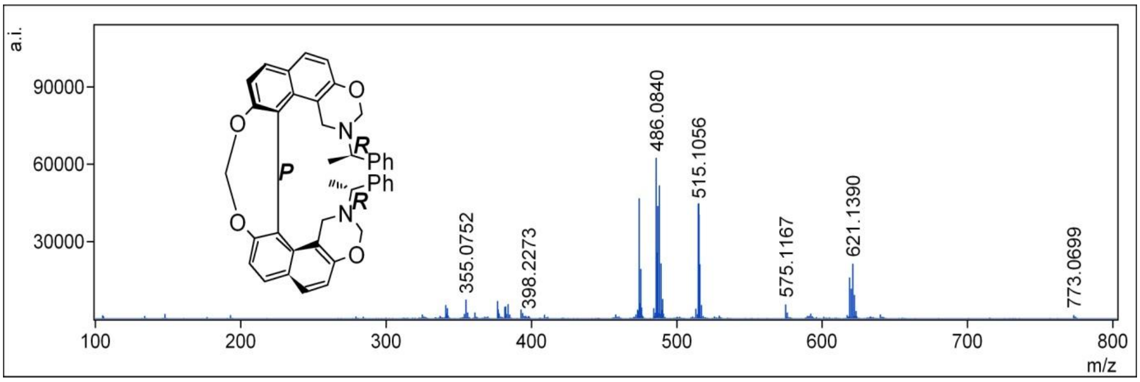
Thermal stability $^1$H-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (77$^a$ in CDCl$_3$ on 400 MHz



$^{13}$C-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (77a) in CDCl$_3$ on 100.6 MHz

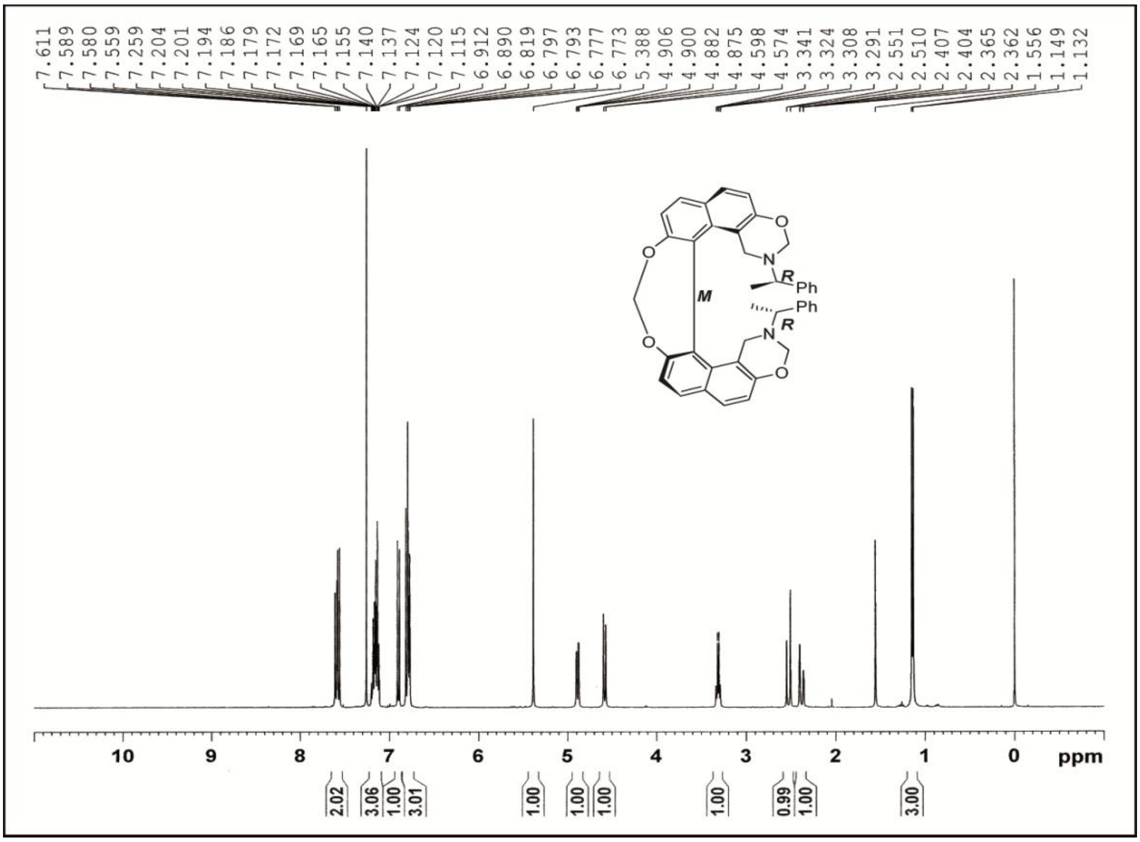


IR spectrum of Chiral Helical Bis-[1,3]oxazine (77a)

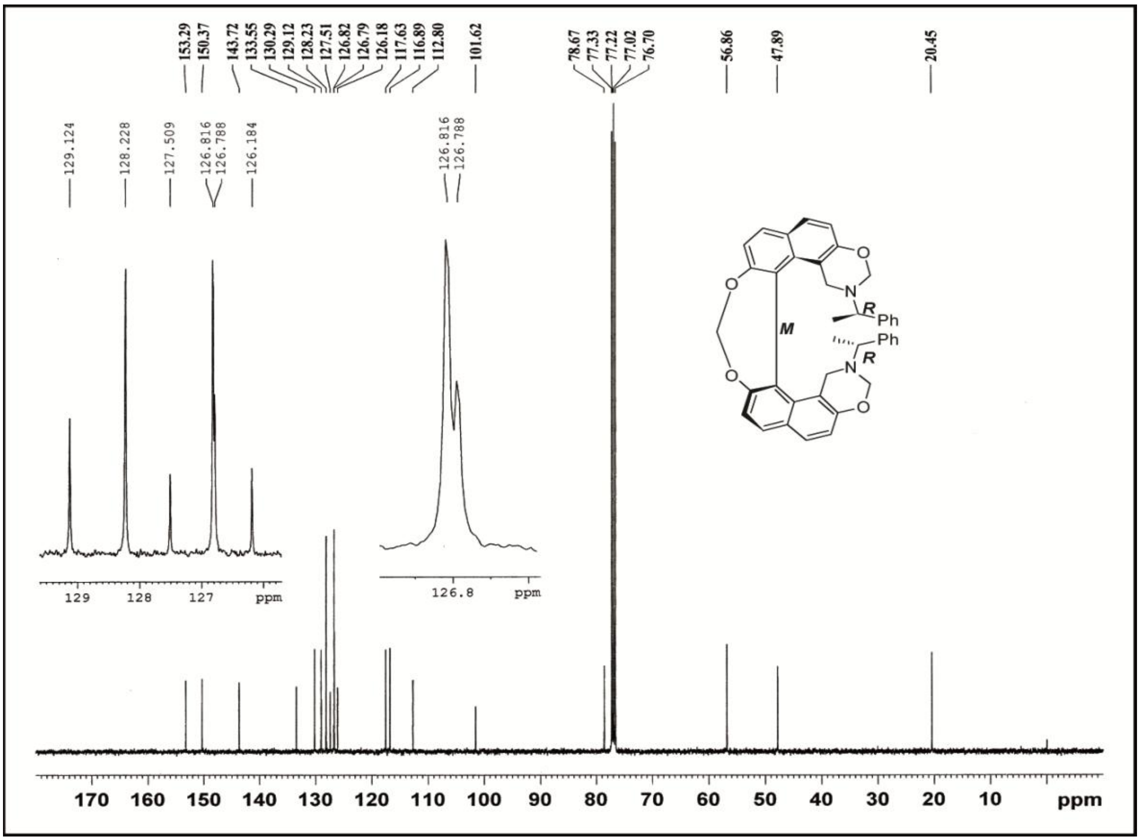


MALDI-TOF-MS spectrum of Chiral Helical Bis-[1,3]oxazine (77a)

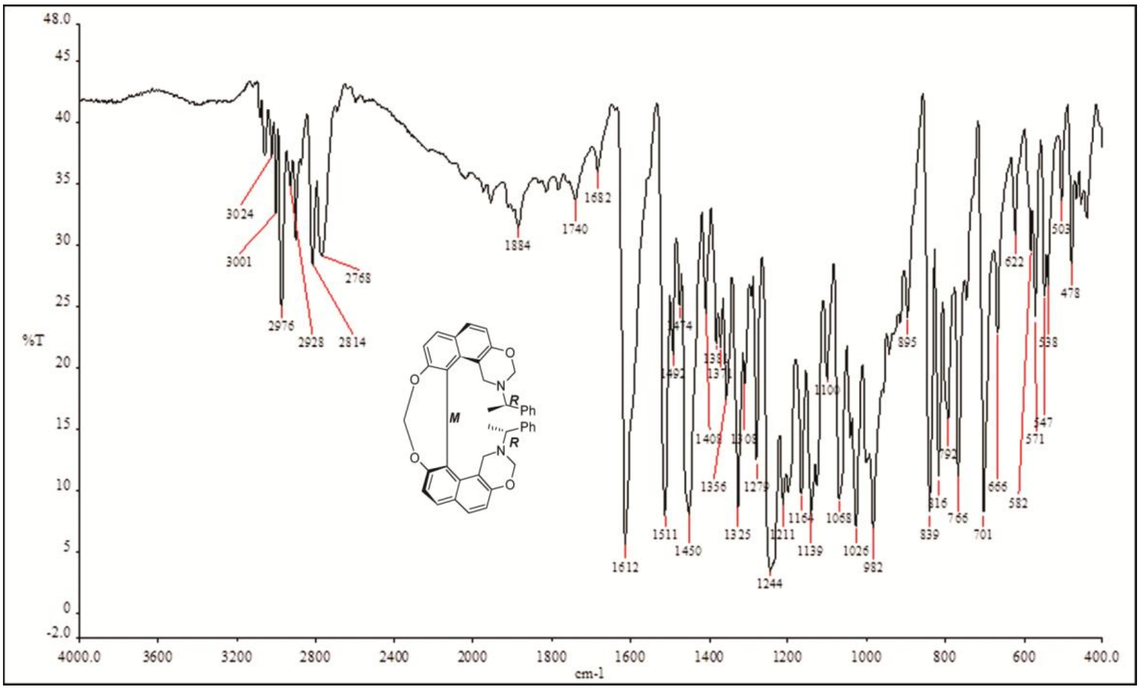
## Spectral Data of Chiral Helical Bis-[1,3]oxazine (77b)



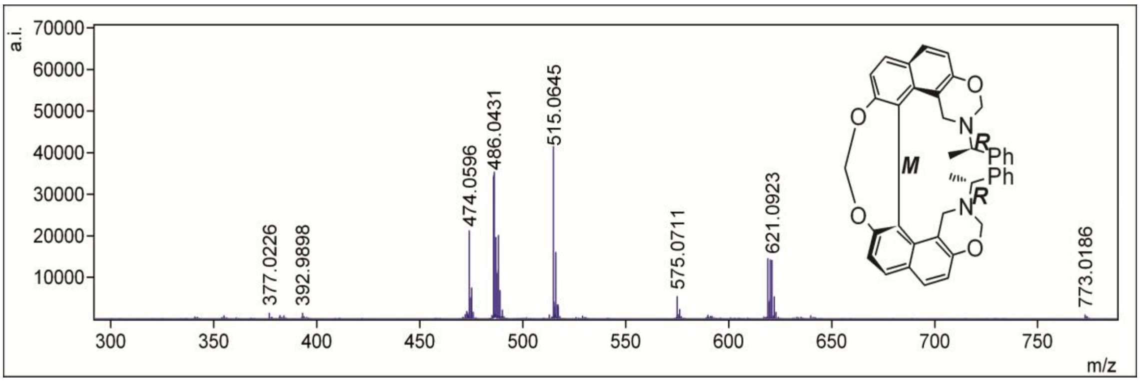
$^1$H-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (77b) in $CDCl_3$ on 400 MHz



$^{13}$C-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (77b) in $CDCl_3$ on 100.6 MHz

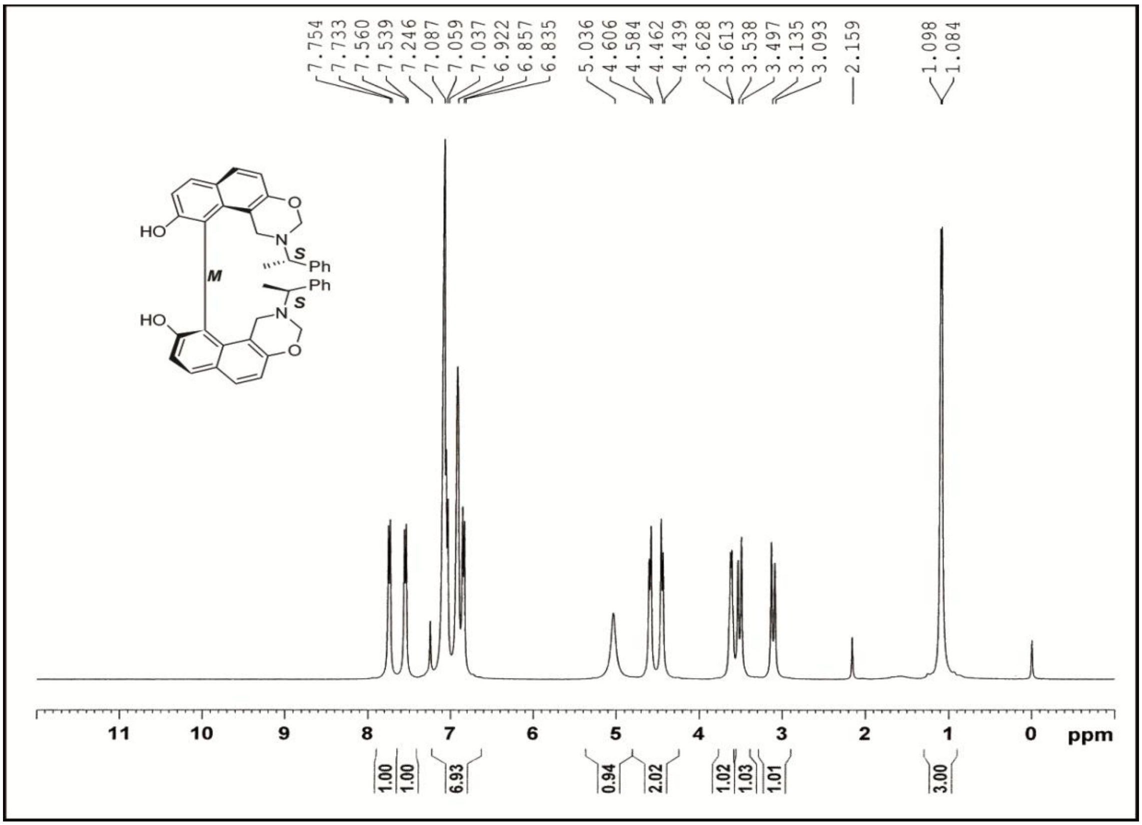


IR spectrum of Chiral Helical Bis-[1,3]oxazine (77b)

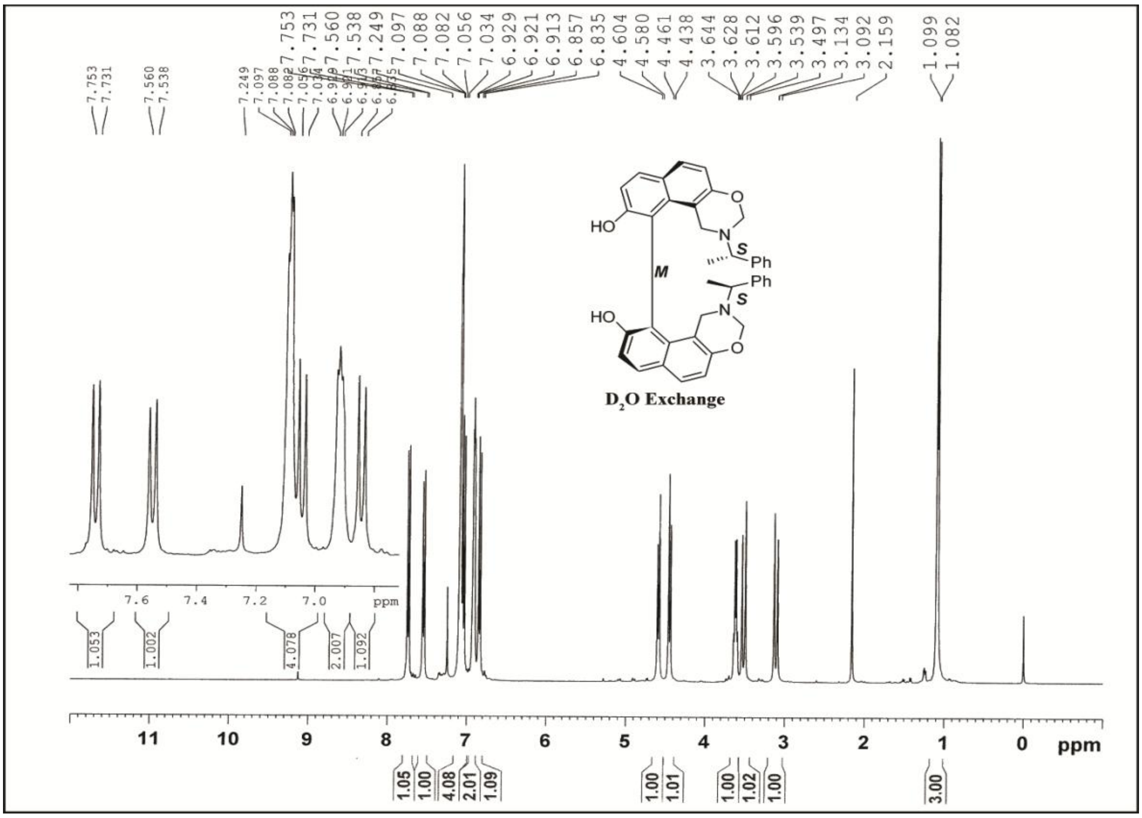


MALDI-TOF-MS spectrum of Chiral Helical Bis-[1,3]oxazine (77b)

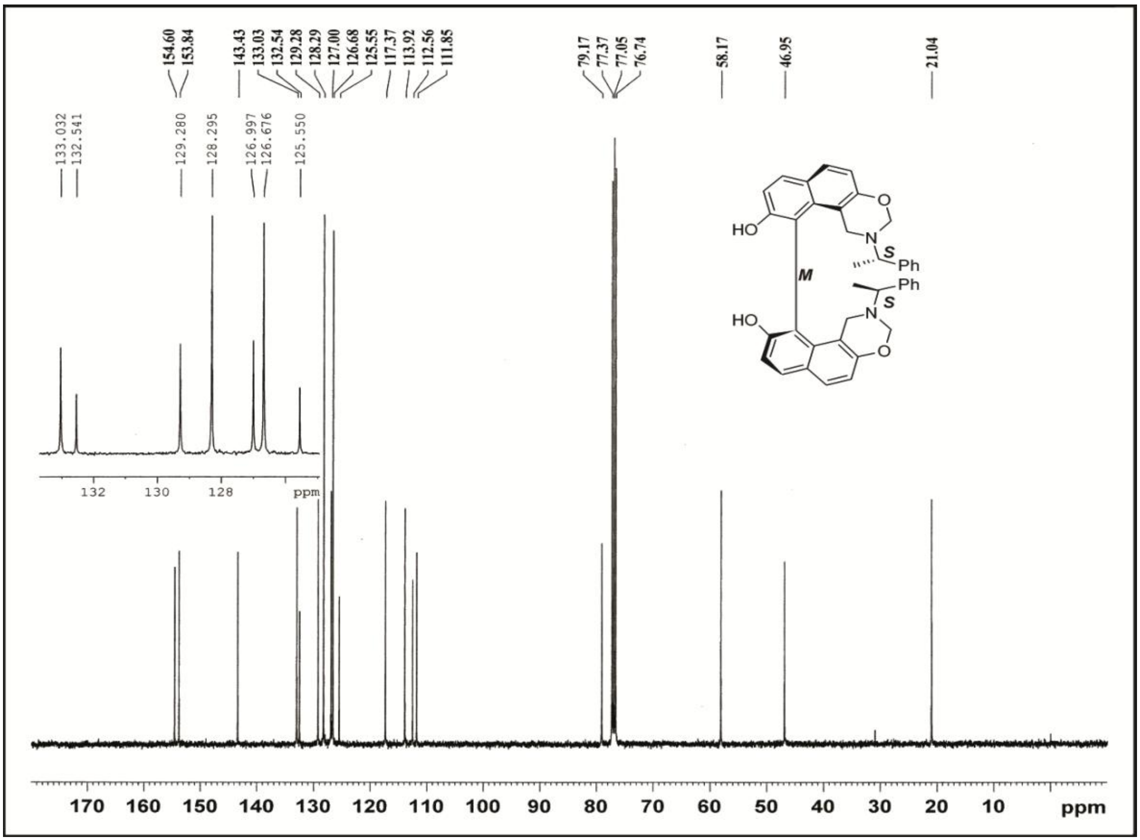
## Spectral data of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a)



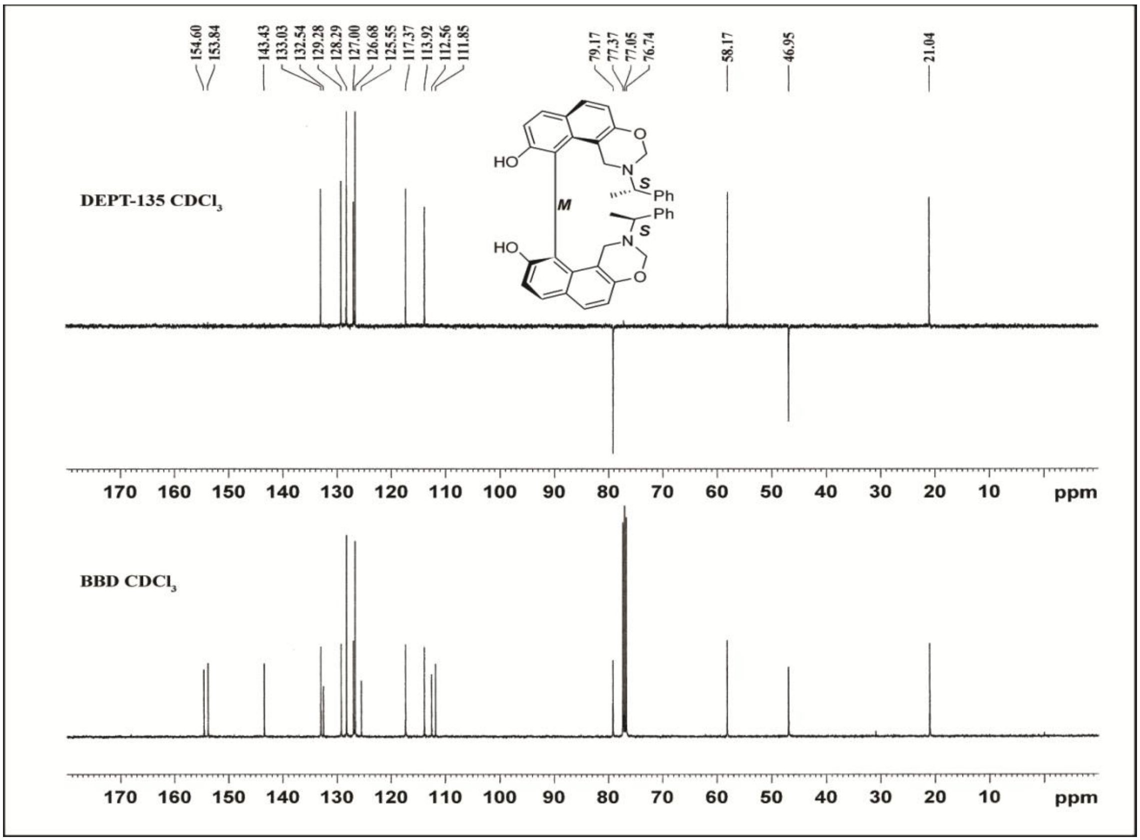
$^1$H-NMR spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a) in $CDCl_3$ on 400 MHz



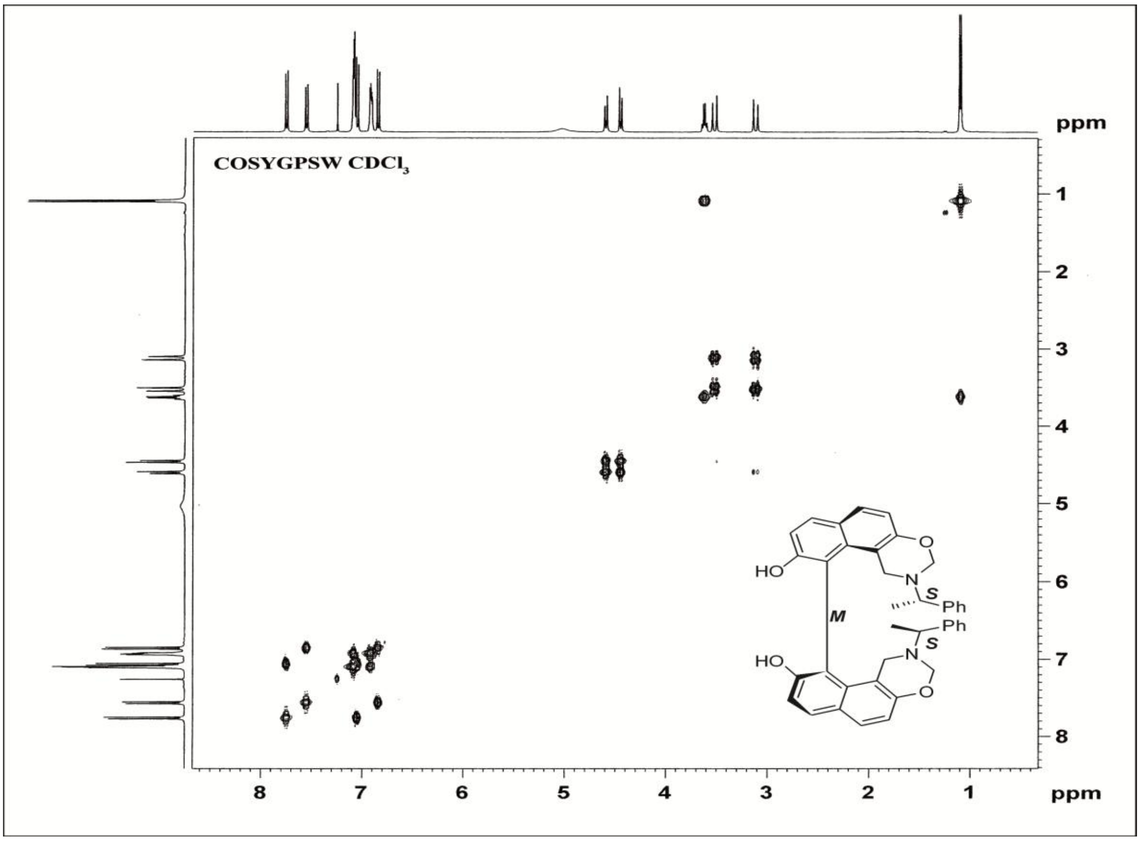
$^1$H-NMR ($D_2O$ exchange) spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a) in $CDCl_3$ on 400 MHz



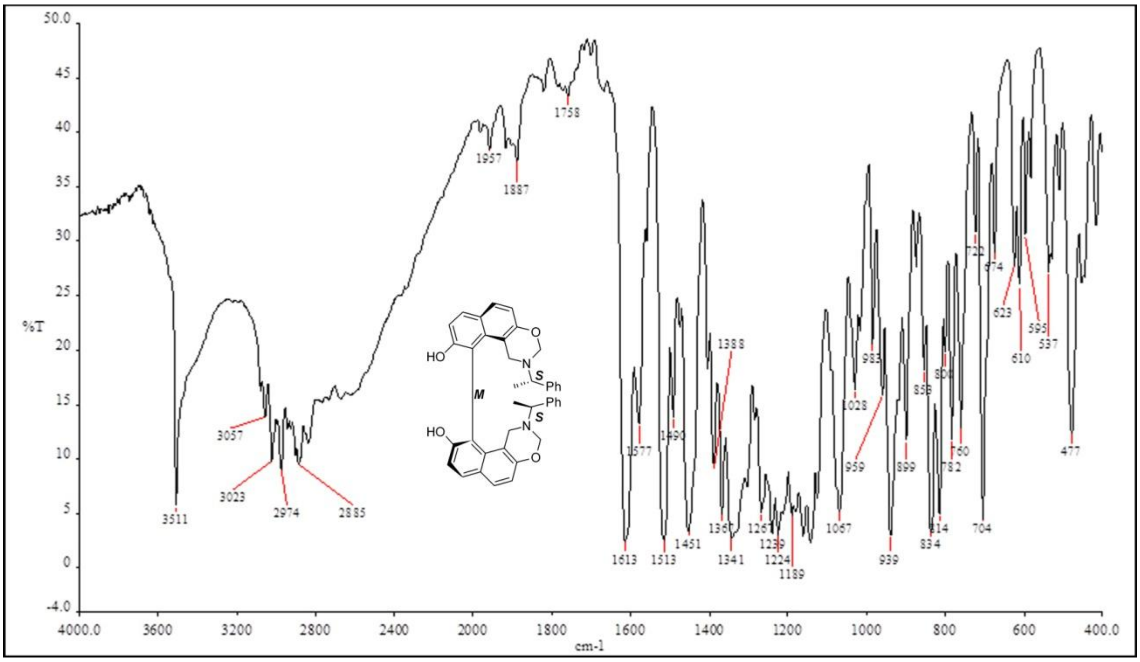
**$^{13}$C-NMR spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a) in $CDCl_3$ on 100.6 MHz**



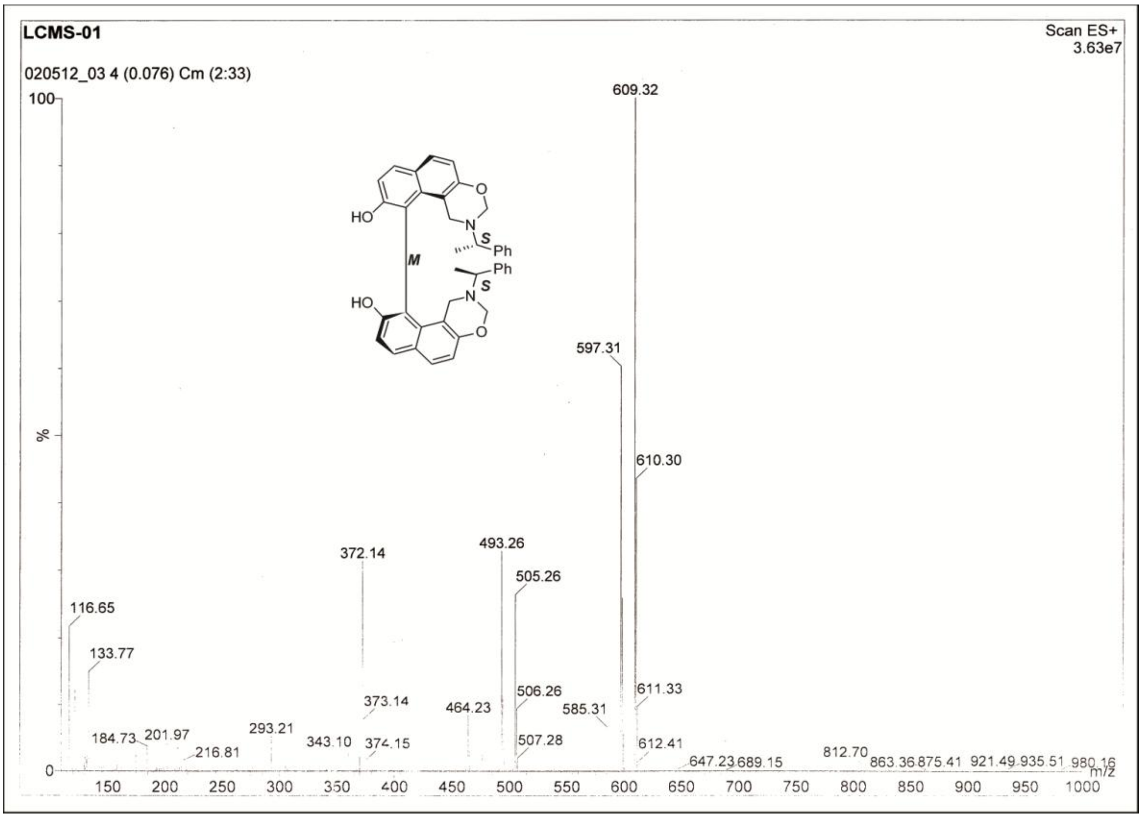
**$^{13}$C-NMR BBD & DEPT-135 spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a) in $CDCl_3$ on 100.6 MHz**



$^1$H-$^1$H correlation COSYGPSW spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a) in CDCl$_3$ on 400 MHz

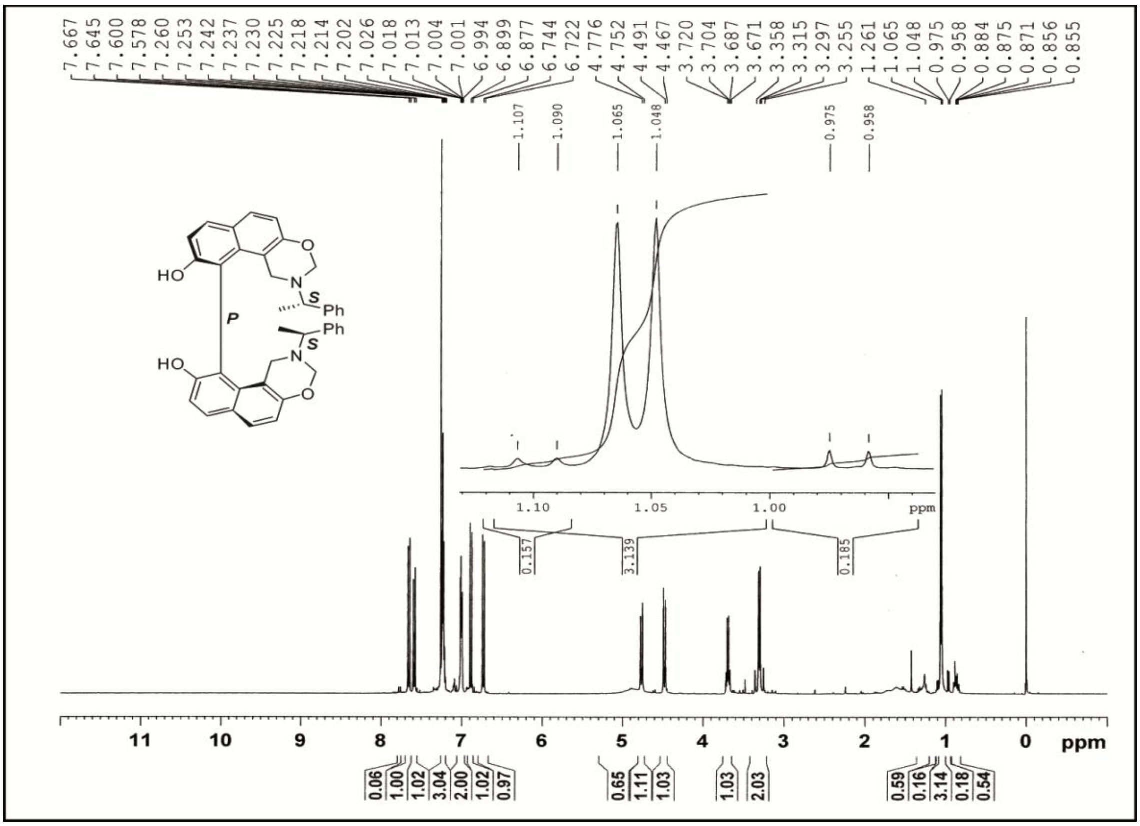


IR spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a)

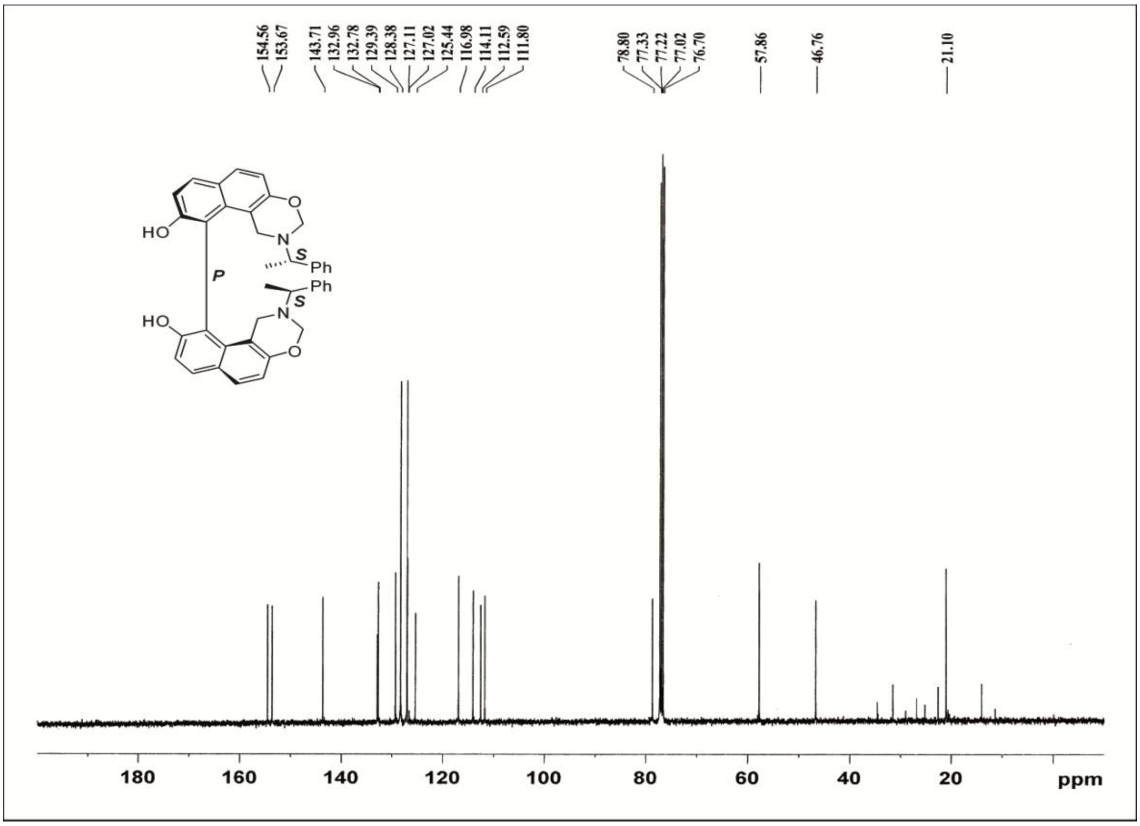


**ESI-Mass spectrum of (*M*)/(*R*)-2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78a)**

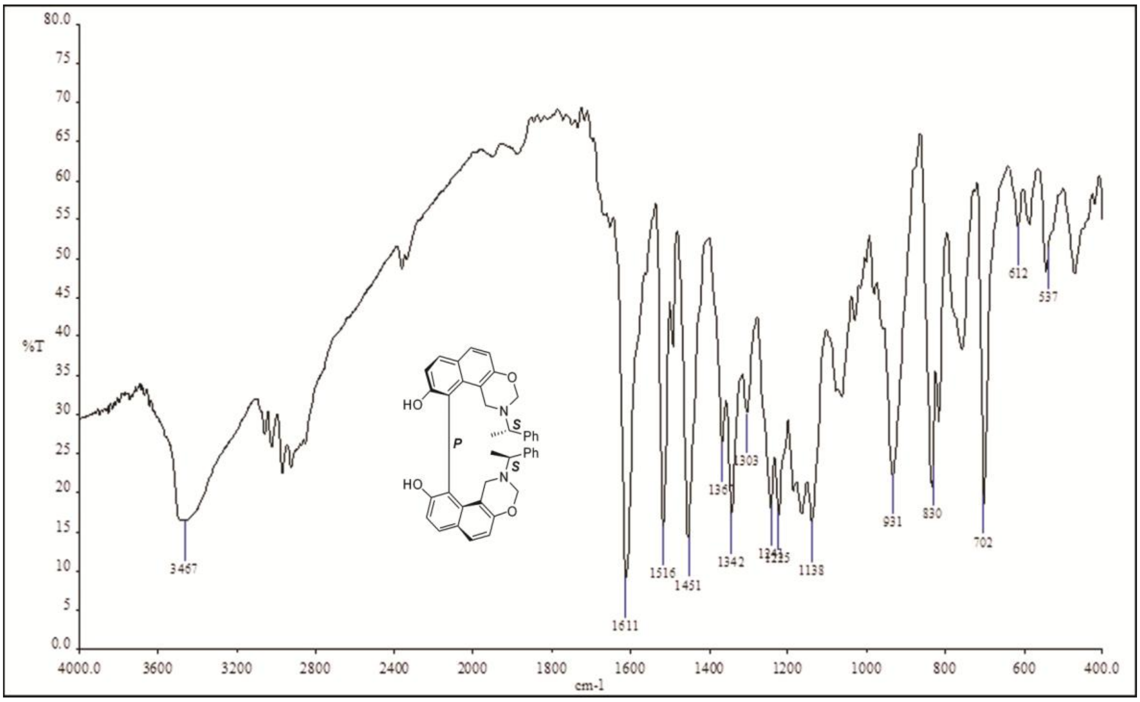
### Spectral data of (*P*)/(*S*)- 2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78b)



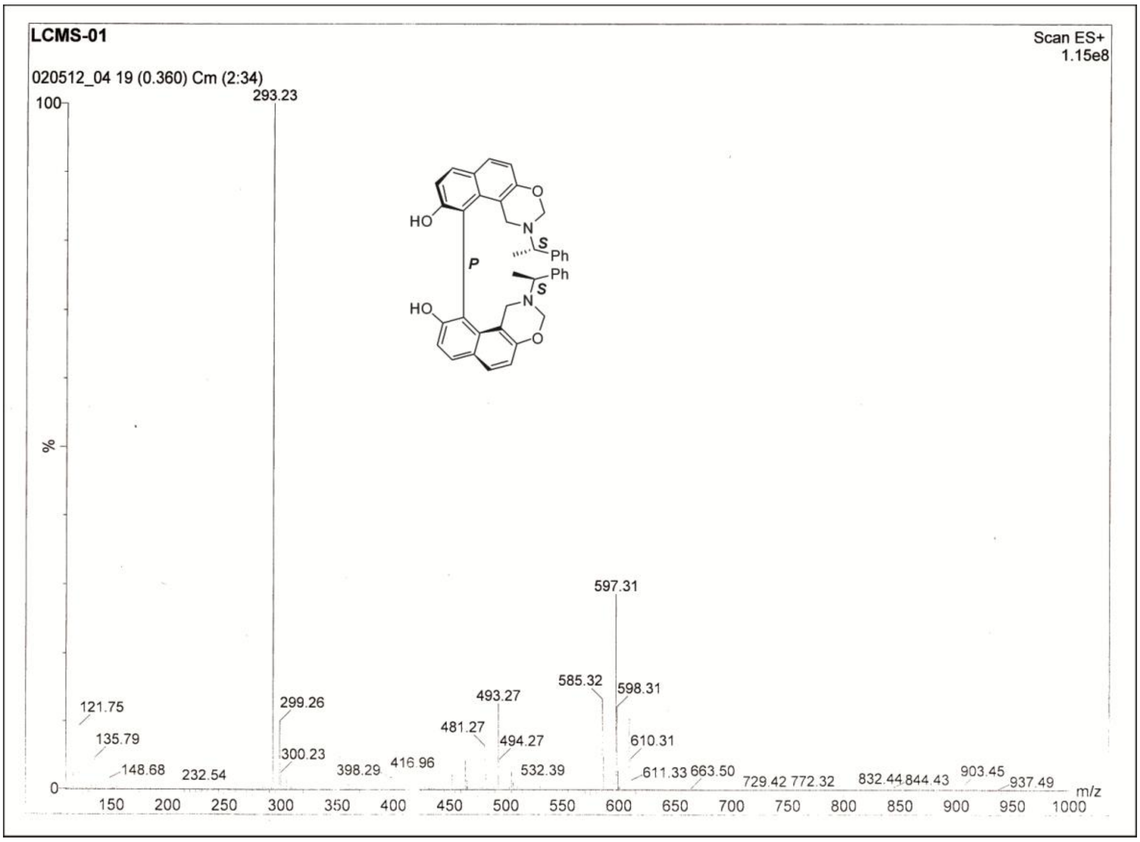
**$^1$H-NMR spectrum of (*P*)/(*S*)- 2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78b) in CDCl$_3$ on 400 MHz**



$^{13}$C-NMR spectrum of (*P*)/(*S*)- 2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78b) in CDCl$_3$ on 100.6 MHz

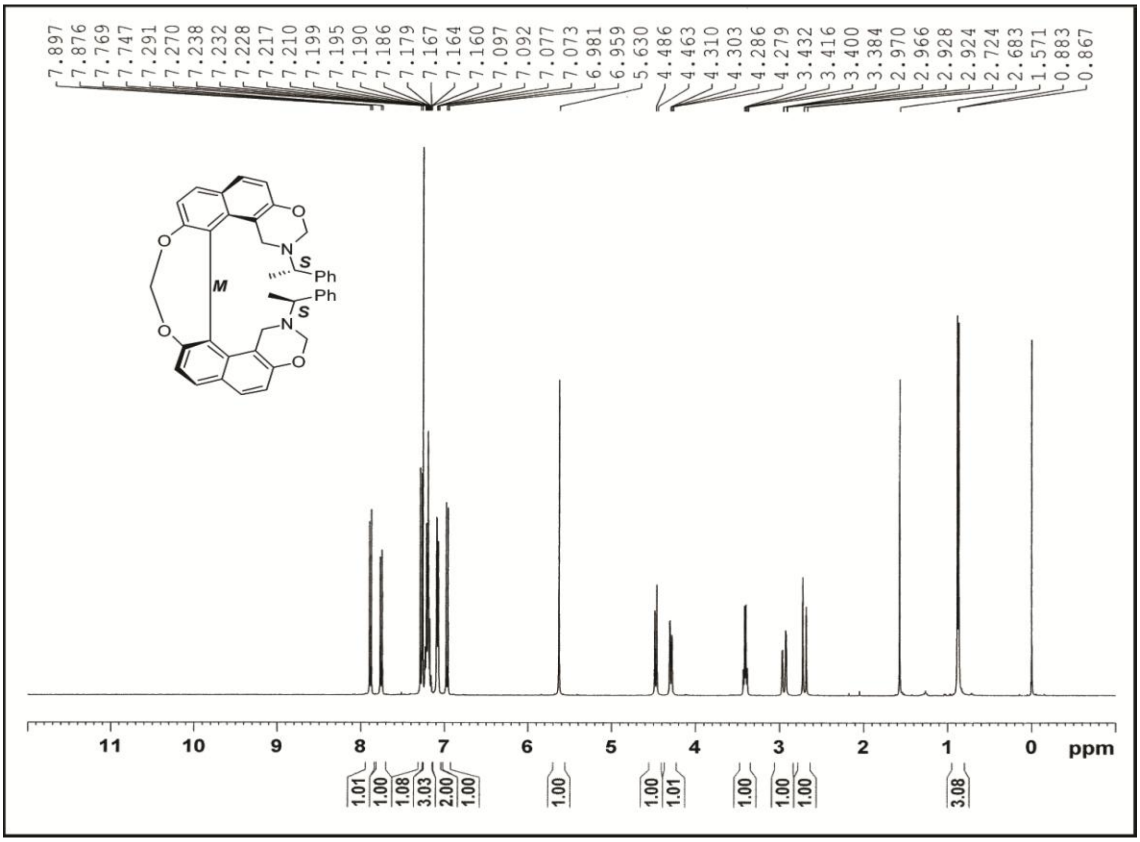


IR spectrum of (*P*)/(*S*)- 2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H* [10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78b)

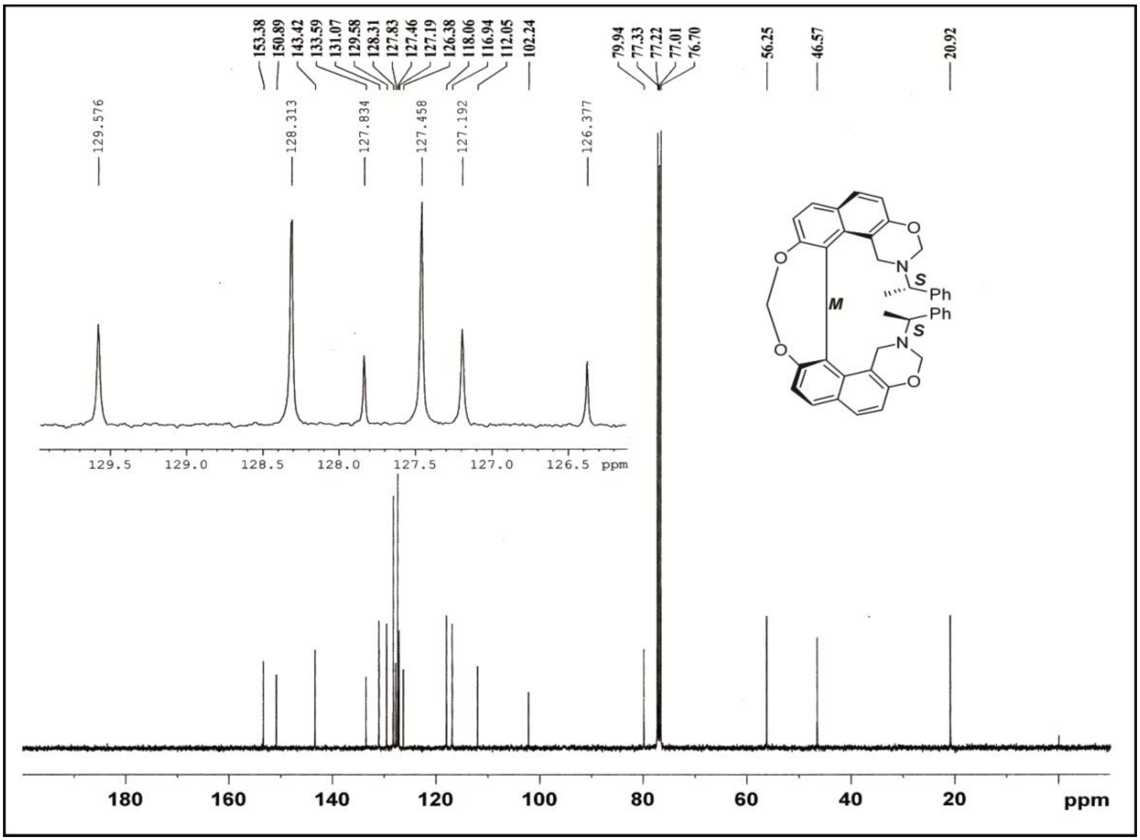


**ESI-Mass spectrum of (*P*)/(*S*)- 2,2'-Bis-((*S*)-1-phenyl-ethyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[10,10']bi[naphtho[1,2-*e*][1,3]oxazinyl]-9,9'diol (78b)**

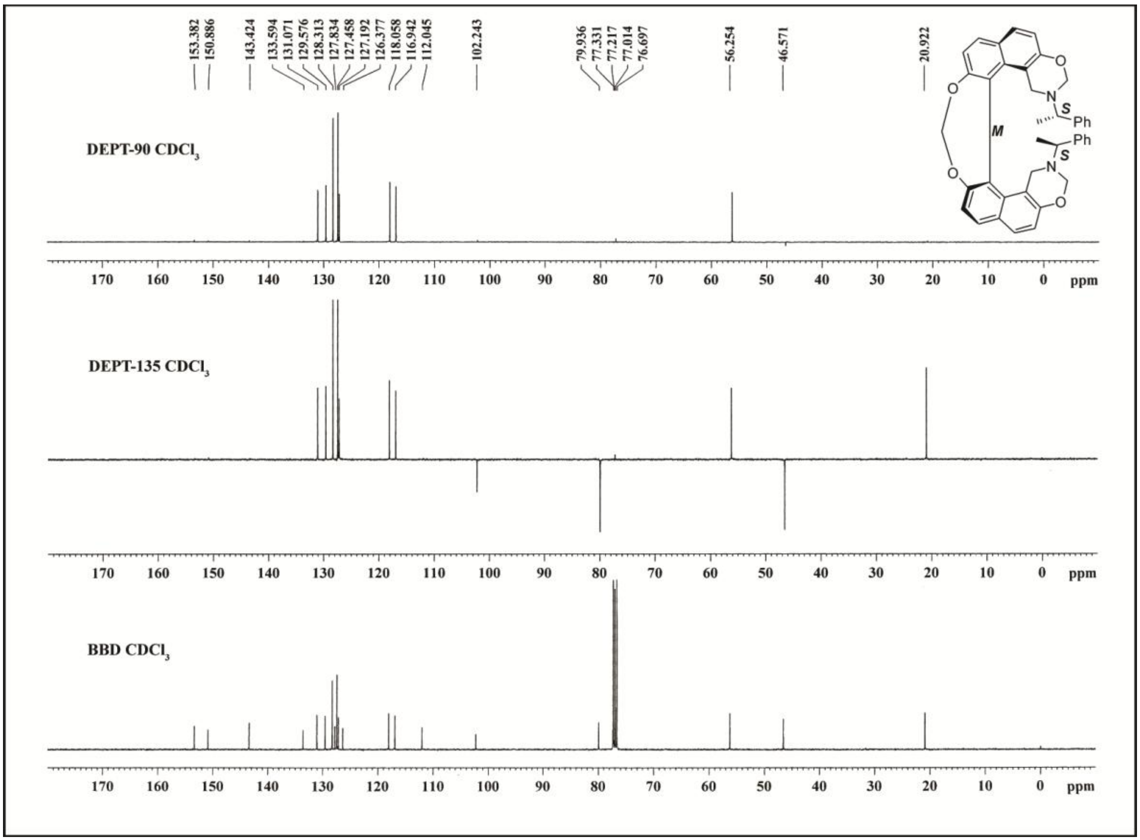
## Spectral data of Helical Chiral Bis-[1,3]oxazine (79a)



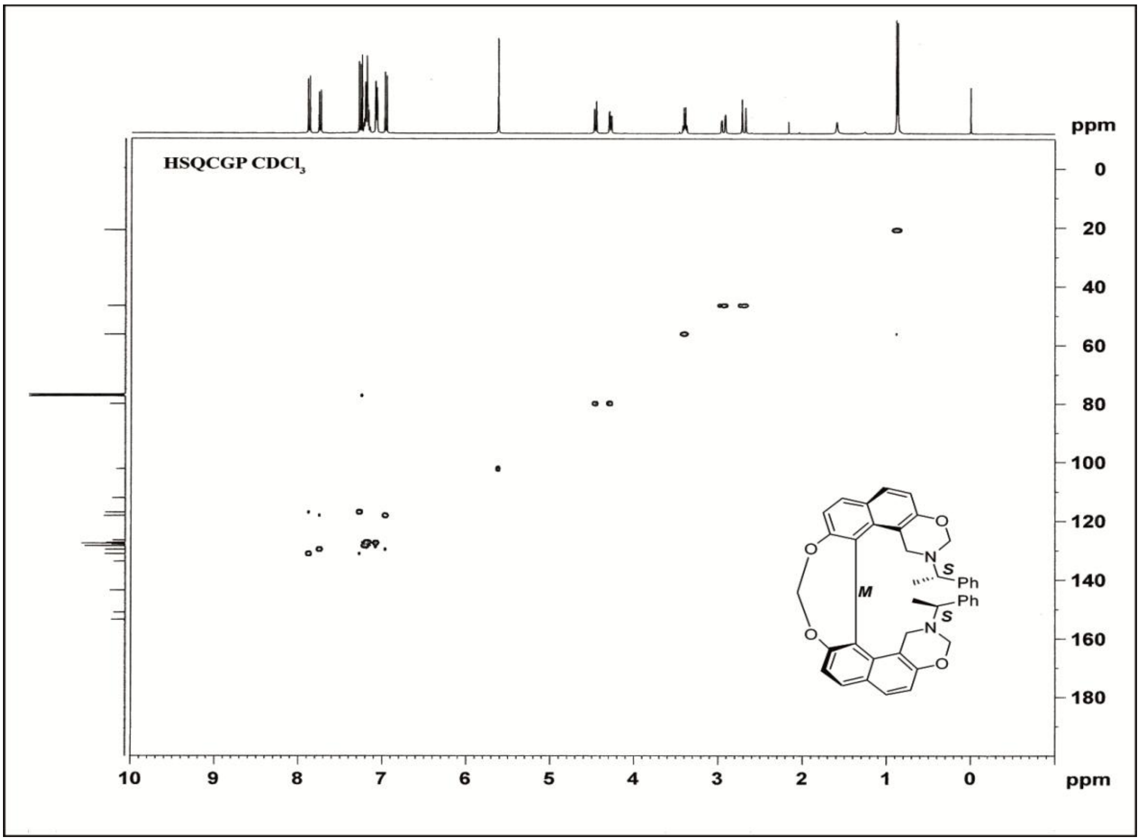
**$^1$H-NMR spectrum of Helical Chiral Bis-[1,3]oxazine (79a) in $CDCl_3$ on 400 MHz**



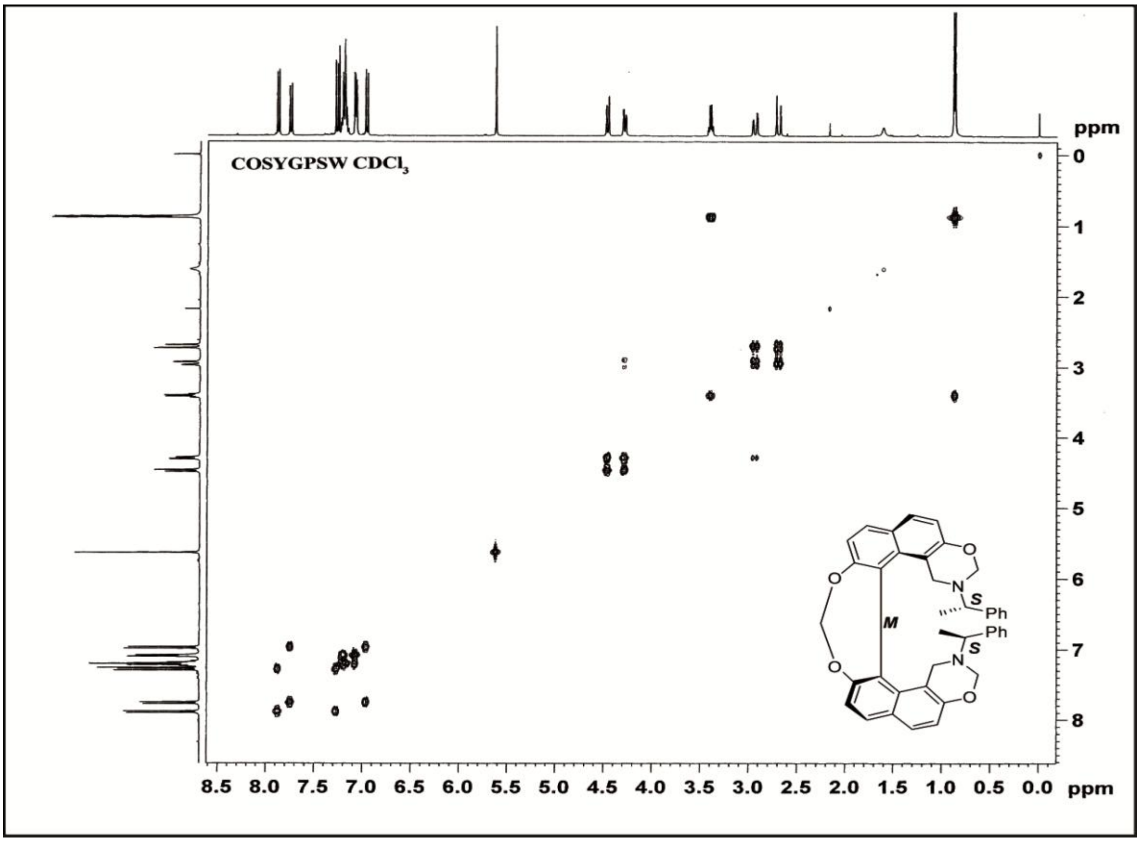
$^{13}$**C-NMR spectrum of Helical Chiral Bis-[1,3]oxazine (79a) in CDCl$_3$ on 100.6 MHz**



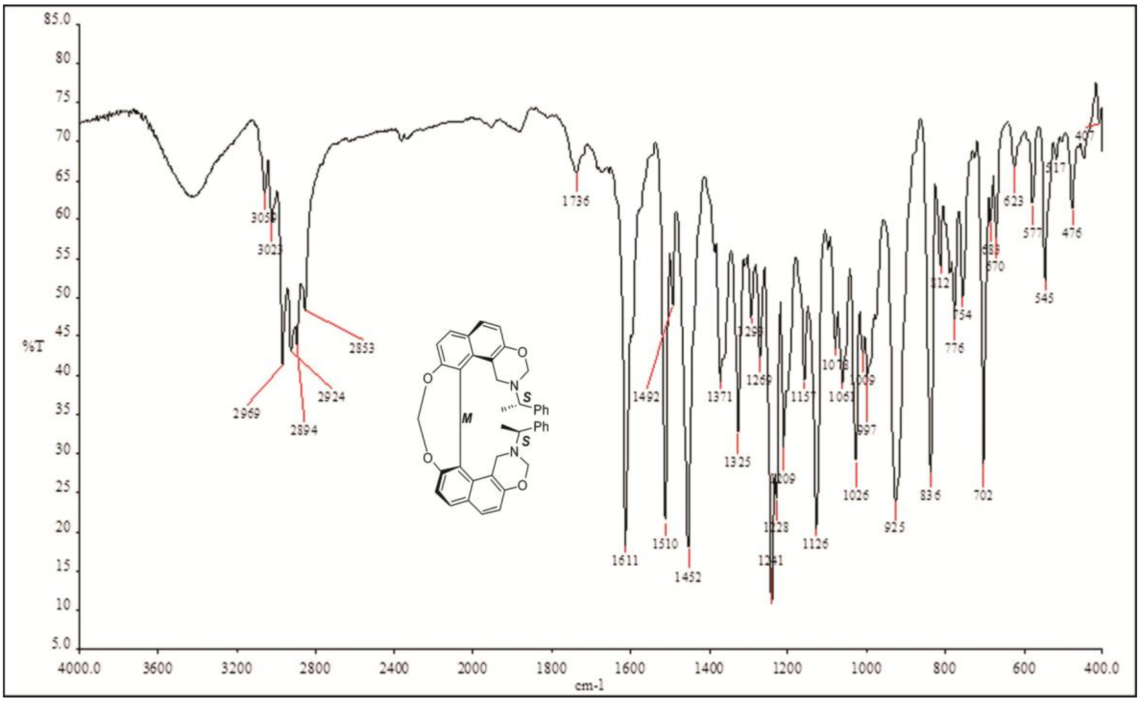
$^{13}$**C-NMR BBD, DEPT-90 & 135 spectrum of Helical Chiral Bis-[1,3]oxazine (79a) in CDCl$_3$ on 100.6 MHz**



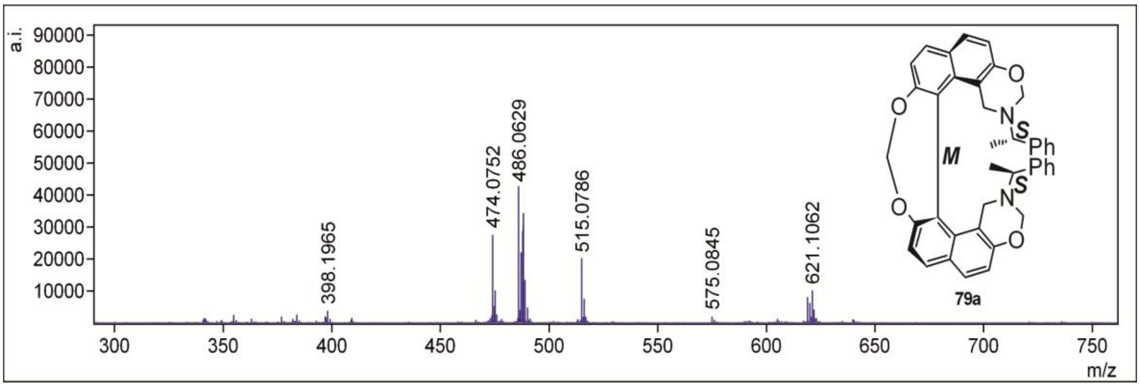
**$^1$H-$^{13}$C correlation HSQCGP spectrum of Helical Chiral Bis-[1,3]oxazine (79a) in $CDCl_3$ on 400 MHz**



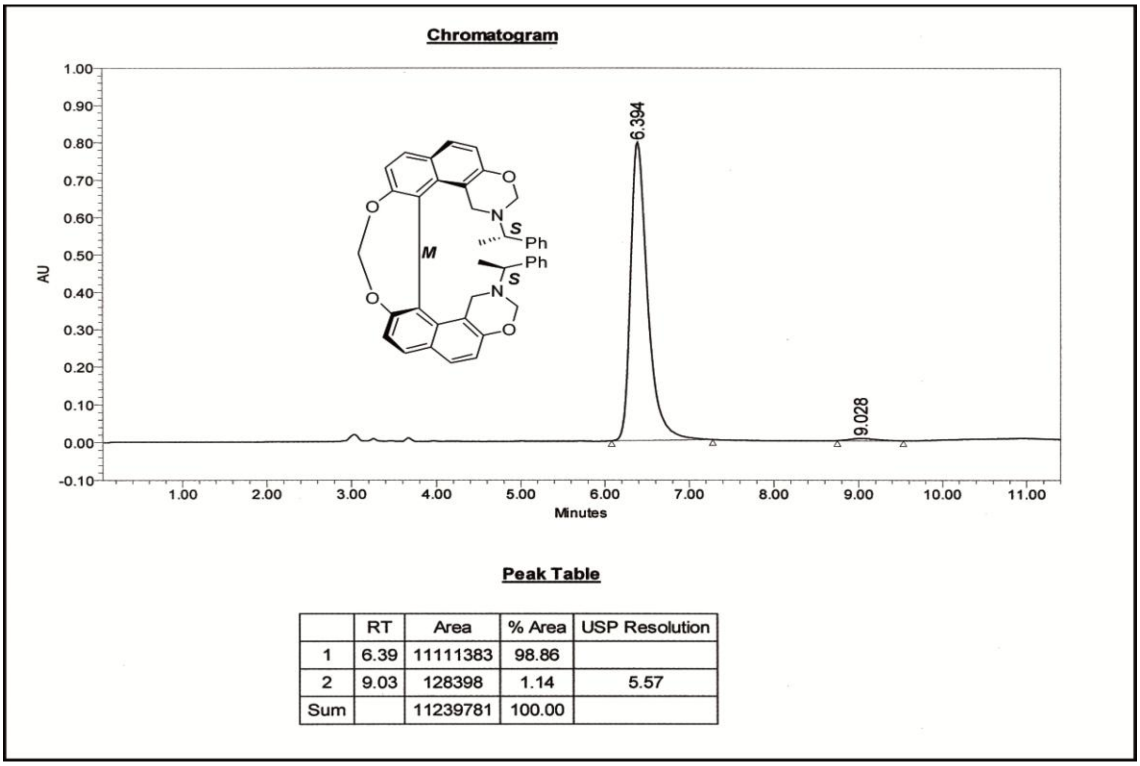
**$^1$H-$^1$H correlation HSQCGP spectrum of Helical Chiral Bis-[1,3]oxazine (79a) in $CDCl_3$ on 400 MHz**



IR spectrum of Helical Chiral Bis-[1,3]oxazine (79a)



MALDI-TOF-MS spectrum of Helical Chiral Bis-[1,3]oxazine (79a)



Peak Table

|  | RT | Area | % Area | USP Resolution |
|---|---|---|---|---|
| 1 | 6.39 | 11111383 | 98.86 |  |
| 2 | 9.03 | 128398 | 1.14 | 5.57 |
| Sum |  | 11239781 | 100.00 |  |

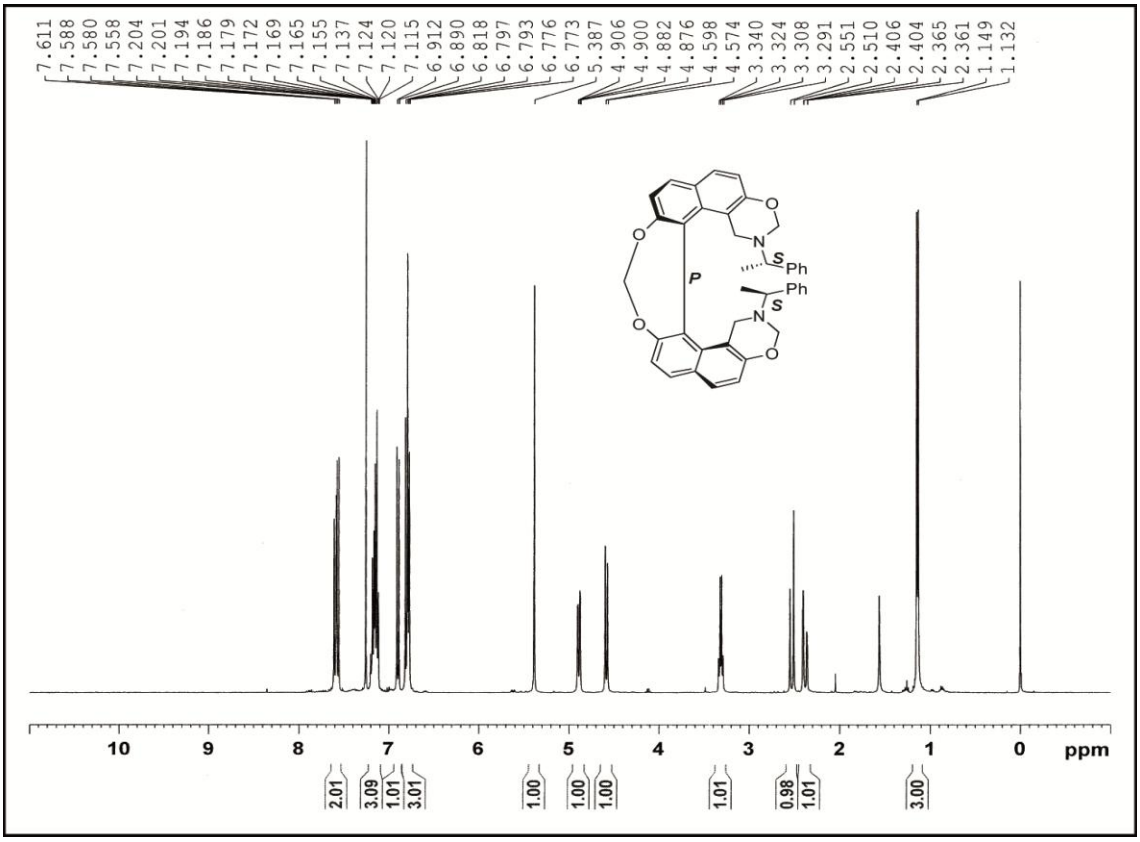
**HPLC analysis:**

Observed two peaks of seperated enantiomers at 1) $R_t$ – 6.39min (98.86%) and 2) $R_t$ – 9.02 min (1.14%).

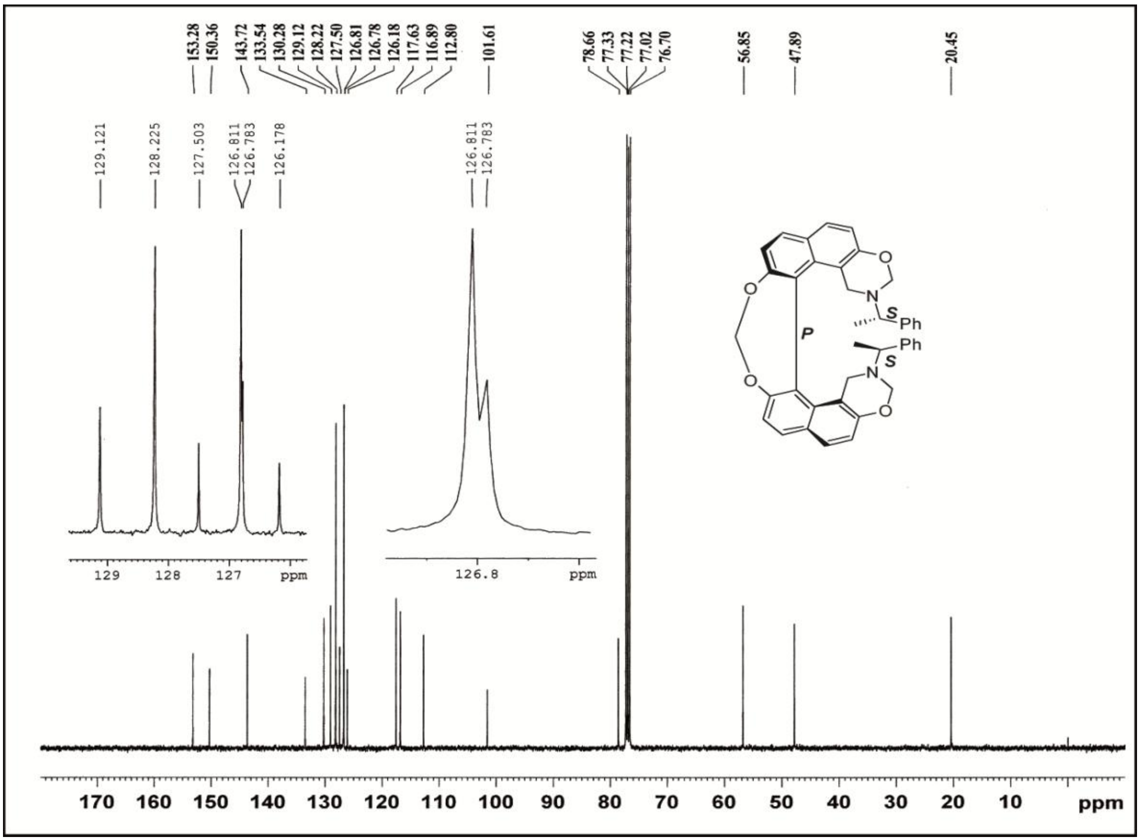
Solvent System: *n*-Hexane: *Iso*-propanol (85:15), Flow rate: 1ml/min.

Chiral Column: Lux Amylose 2

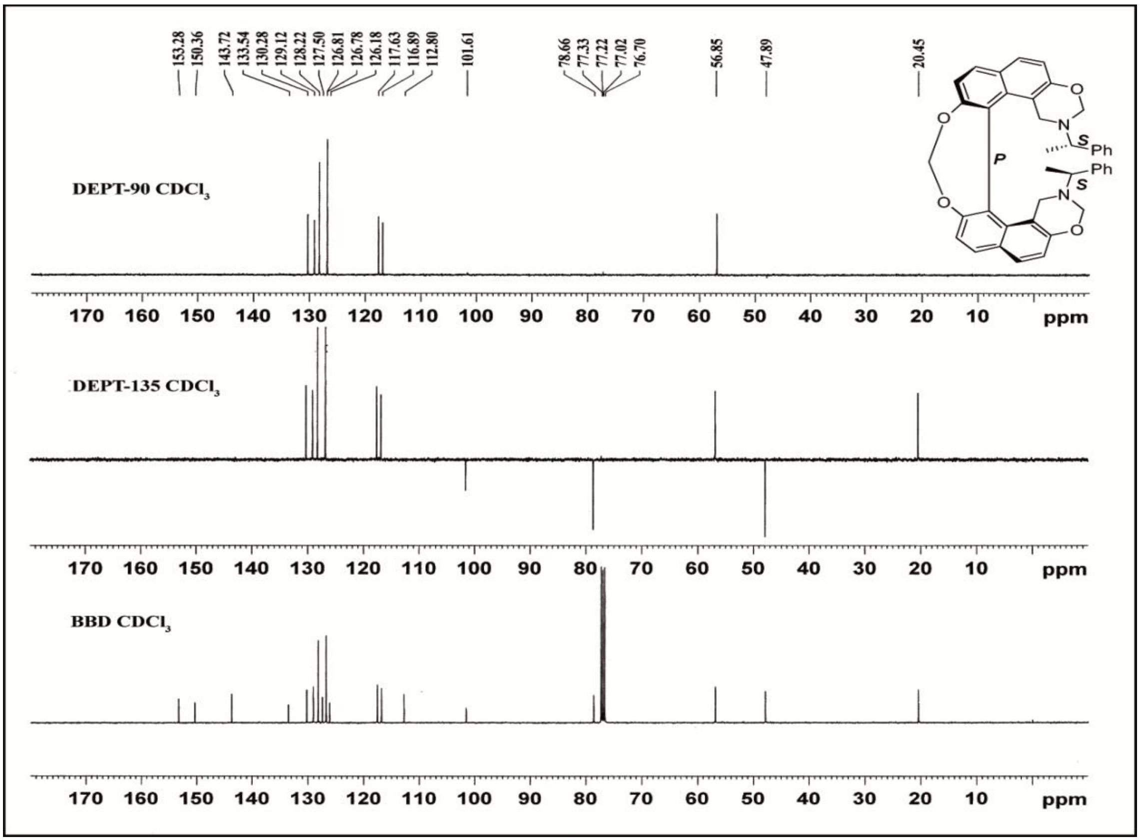
## Spectral data of Chiral Helical Bis-[1,3]oxazine (79b)



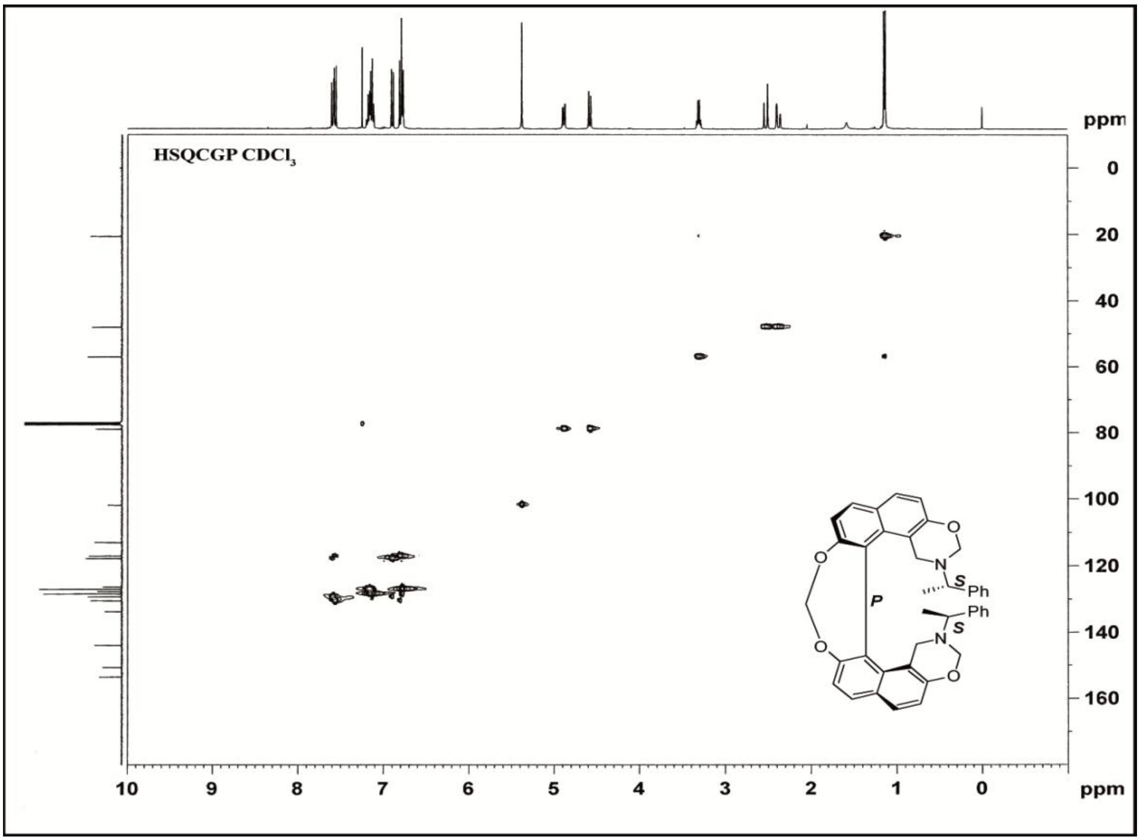
**$^1$H-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (79b) in $CDCl_3$ on 400 MHz**



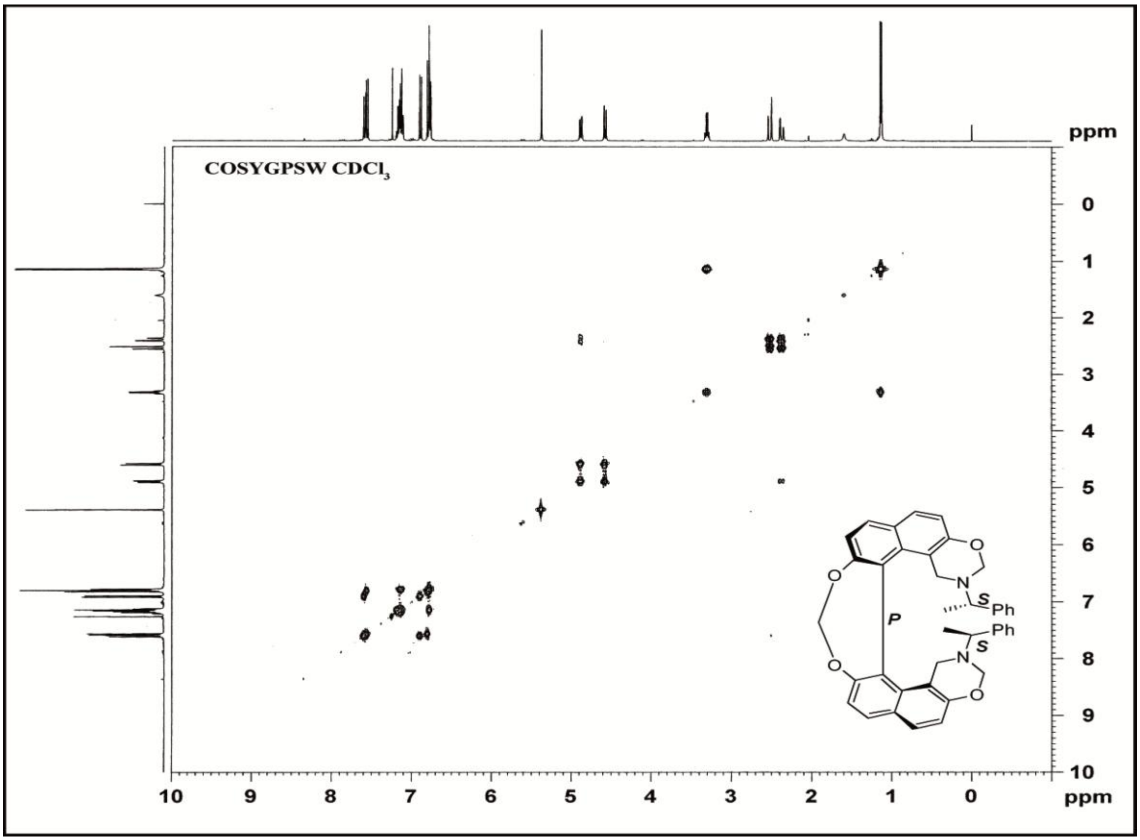
**$^{13}$C-NMR spectrum of Chiral Helical Bis-[1,3]oxazine (79b) in $CDCl_3$ on 100.6 MHz**



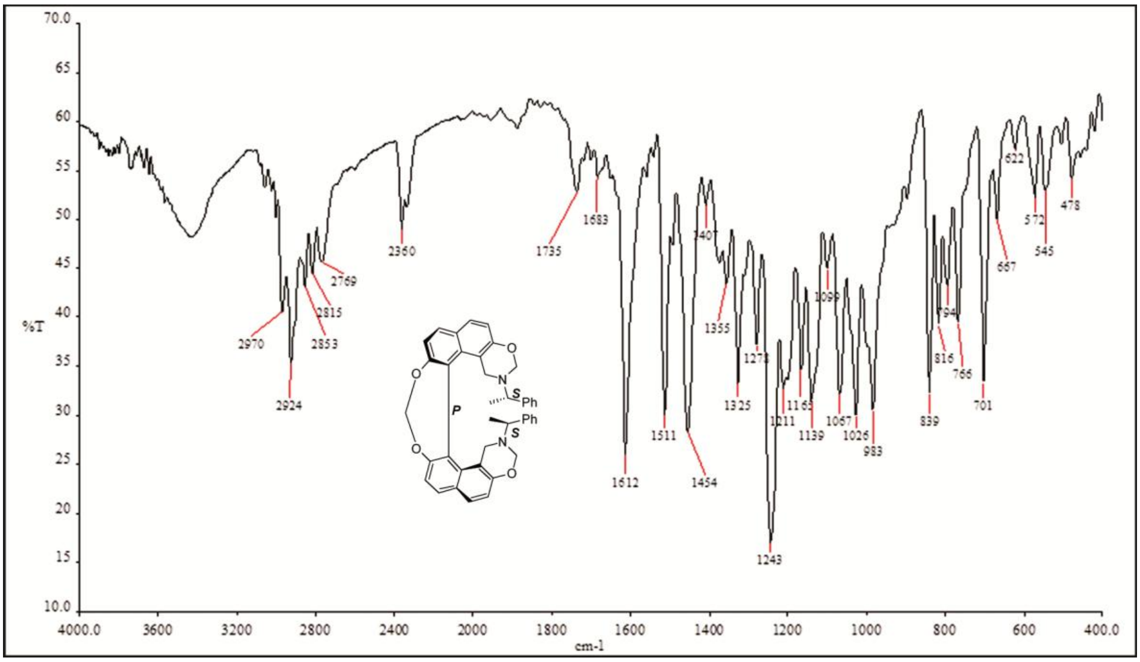
**$^{13}$C-NMR BBD, DEPT-90 & 135 spectrum of Chiral Helical Bis-[1,3]oxazine (79b) in $CDCl_3$ on 100.6 MHz**



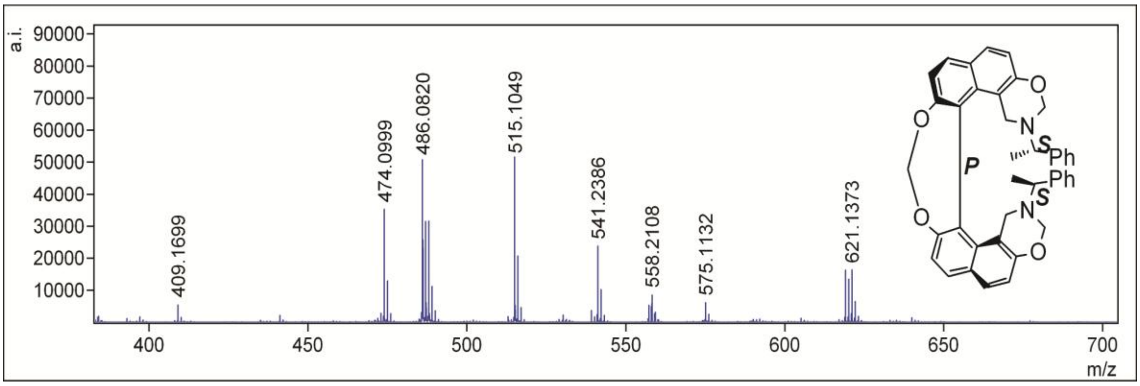
**$^{1}$H-$^{13}$C correlation HSQCGP spectrum of Chiral Helical Bis-[1,3]oxazine (79b) in $CDCl_3$ on 400 MHz**



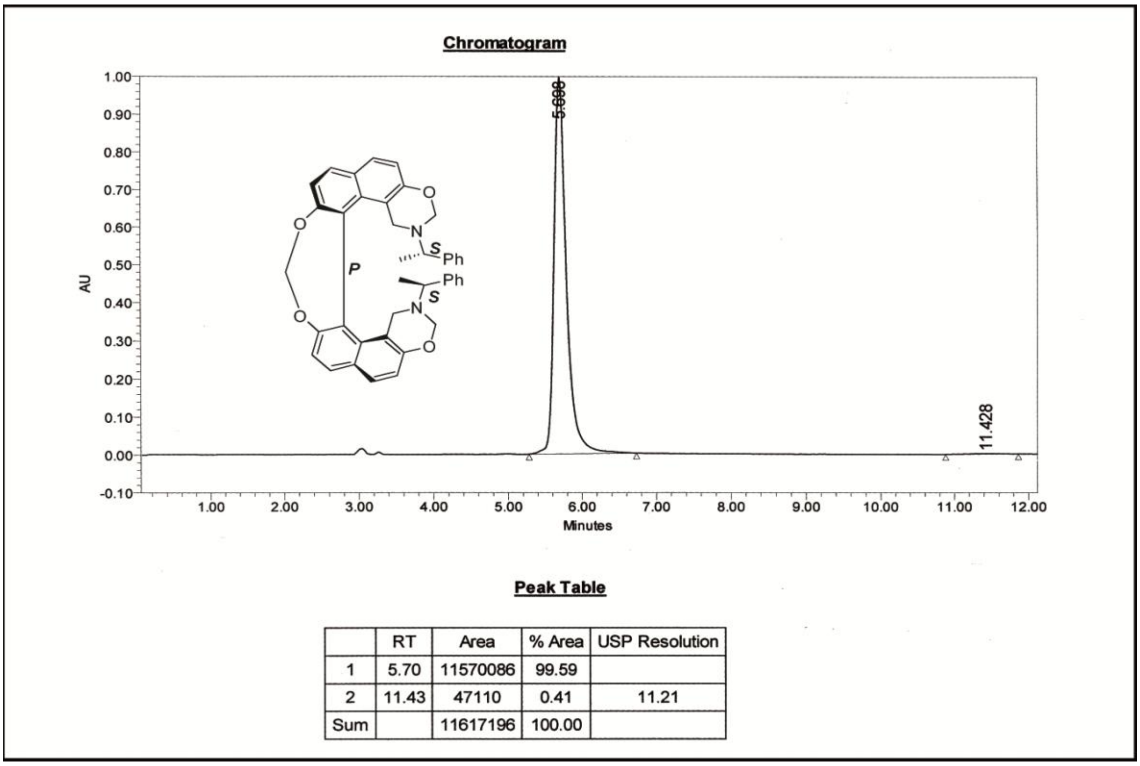
$^1$H-$^1$H correlation COSYGPSW spectrum of Chiral Helical Bis-[1,3]oxazine (79b) in CDCl$_3$ on 400 MHz



IR spectrum of spectrum of Chiral Helical Bis-[1,3]oxazine (79b) in CDCl$_3$



**MALDI-TOF-MS spectrum of Helical Chiral Bis-[1,3]oxazine (79b)**



Peak Table

|  | RT | Area | % Area | USP Resolution |
|---|---|---|---|---|
| 1 | 5.70 | 11570086 | 99.59 |  |
| 2 | 11.43 | 47110 | 0.41 | 11.21 |
| Sum |  | 11617196 | 100.00 |  |

**HPLC analysis:**

Observed two peaks of seperated enantiomers at 1) $R_t$ – 5.70 min (99.59%) and 2) $R_t$ – 11.43 min (0.41%).

Solvent System: *n*-Hexane: *Iso*-propanol (85:15), Flow rate: 1ml/min.

Chiral Column: Lux Amylose 2

# Chapter-3

## Part 2

# Synthesis of chiral bis-oxazines: A preliminary assessment of helical conformational framework

## Introduction:

The “Helical” shape has a distinct place in nature and has inspired man to adopt it for the construction of objects of functional utility and aesthetic value. This shape is the basis for design of architectural and artistic objects. The chemists have synthesized molecules which acquire a helical shape, either as supramolecular assemblies or as a single molecular unit. The inherent, internal helical shape is a result of distortion caused by crowding in the structure, benzo[*c*]phenanthrene or [4]helicene **85** is an example of such phenomena. Construction of such distorted aromatic molecules is a topic of continuous developments.[39]

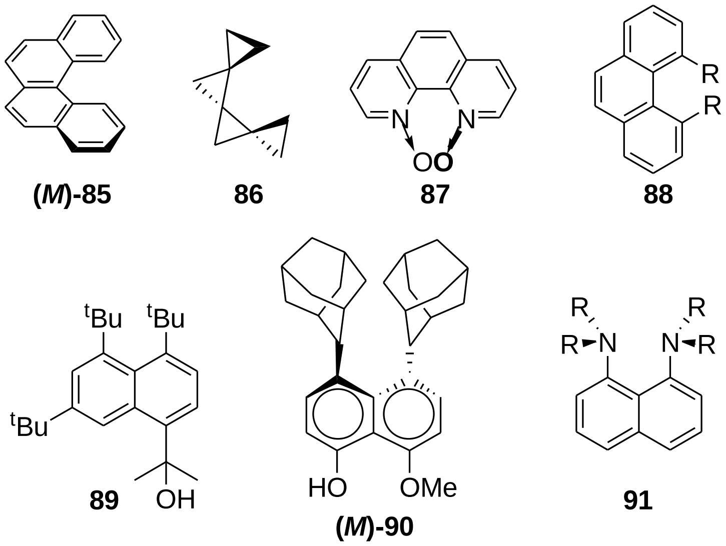


**Figure 26**: Examples of small helical molecules, besides [4]helicene

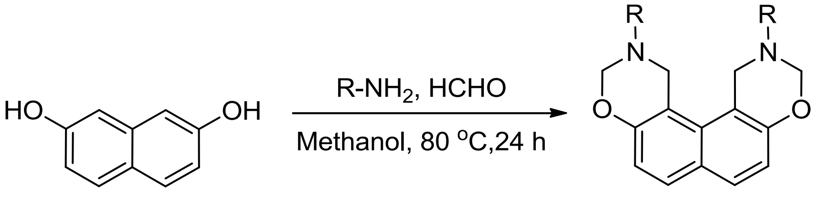
The synthesis and separation of π-helical isomers of [6]helicene by Newman[1] has triggered a significant growth in this area.[2] The other type is σ-helicenes and [4]triangulane **86**, one of the smallest molecules to show such helical shape.[40] Another small molecule capable of showing helical form is 1,10-phenanthroline-*N*,*N*-dioxide **87**, which was synthesized by oxidation of 1,10-phenanthroline with HOF.[41] 4,5-Dialkyl phenanthrene **88** is likely to show similar helical shape due to the twisting of two terminal rings arising from internal strain.[42] Naphthalene derivatives with substitutions at $C_1$ and $C_8$ positions show peculiar *peri* interactions.[43] Such 1,8-disubstituted naphthalene moieties having chiral distorted forms, such as 1,8-di(*tert*-butyl)naphthalene derivative **89** is known to racemize at ambient conditions due to low enantiomerization barrier.[44] Recently an adamantyl derivative of similar compound **90** is reported where this barrier is quite large and the isomers are stable at room temperature. The single enantiomer of **90** is separated and its absolute configuration is established.[45] Several other examples of distorted structures of 1,8-naphthalene derivatives are also known.[46] Another group of such compounds is 1,8-diamino naphthalene **91**, also known as proton sponge.[47]

The derivatives of naphthalene with substitutions at 1,8 positions show twisted, distorted structure giving rise to helical isomers due to *peri* interaction. Such compounds, referred as [2]helicenes, with sufficiently high barrier of interconversion at ambient conditions can be resolved.[45]

## Result and Discussion

In the present work our efforts were also focused towards synthesis of naphthalene units with heterocyclic rings attached on $C_1$-$C_2$ and $C_7$-$C_8$ bonds. The molecules are studied to ascertain the presence of isomers caused by the conformational twist on the system.

The reaction of phenols with formaldehyde and primary amine gives the oxazines, this concept was extended towards 2,7-dihydroxynaphthalene **93** as the phenol. For the purpose **93** was treated with primary amine and excess of formaldehyde. A series of primary amines were chosen for this experiment and a numbers of bis-oxazine derivatives were synthesized [**Scheme-23**].



**93**

**94** R = Me (20%)
**95** R = $CH_2Ph$ (54%)
**96** R = Ph (22%)
**97** R = *tert*-Butyl (59%)

**Scheme 23:** Synthesis of bis-oxazines

The reaction of 2,7-dihydroxynaphthalene **93** with primary amines including methylamine, benzylamine, aniline and *tert*-butylamine and excess of formaldehyde in methanol at reflux condition, gave corresponding products 1,3-bisoxazines-2,11-dimethyl-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e'*]bis-([1,3]-oxazine) **94**, 2,11-dibenzyl-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e'*]bis([1,3]oxazine) **95**, 2,11-diphenyl-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e'*]bis([1,3]-oxazine) **96** and 2,11-di-*tert*-butyl-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e'*]bis([1,3]oxazine) **97,** respectively. All these bis-oxazines were purified and characterized by usual spectral and analytical techniques. The $^1$H-NMR showed a symmetrical pattern and the two methylene protons appeared as two sharp singlets. The inside hydrogens of Ar-C$\underline{H}_2$-N appear at the high field region while the ones flanked by two electronegative atoms, N-C$\underline{H}_2$-O, appeared at downfield region. This clearly establishes absence of helical form in solution at ambient conditions for all the cases of **94** to **97**, as that would have made the two hydrogens unequal. This can also be due to rapid flipping of the two conformations of the flexible oxazine rings, if at all helical forms are created.

This concept was examined by performing $^1$H-NMR analysis at low temperature [**Figure**- **27**].

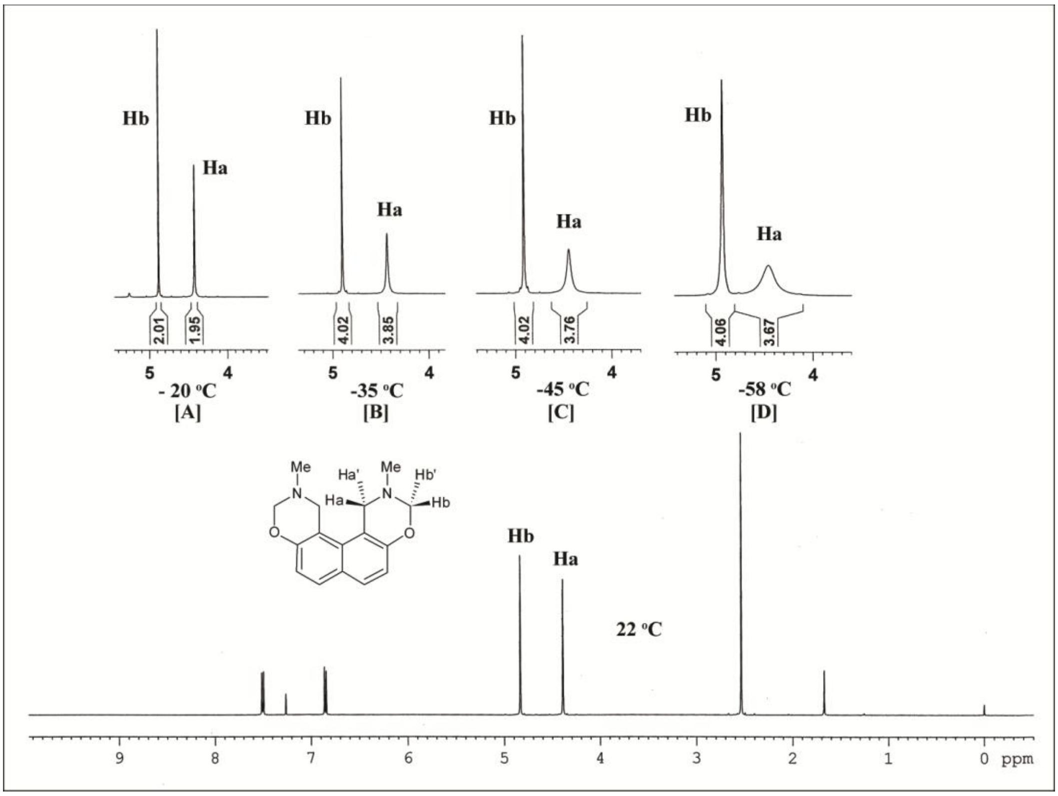
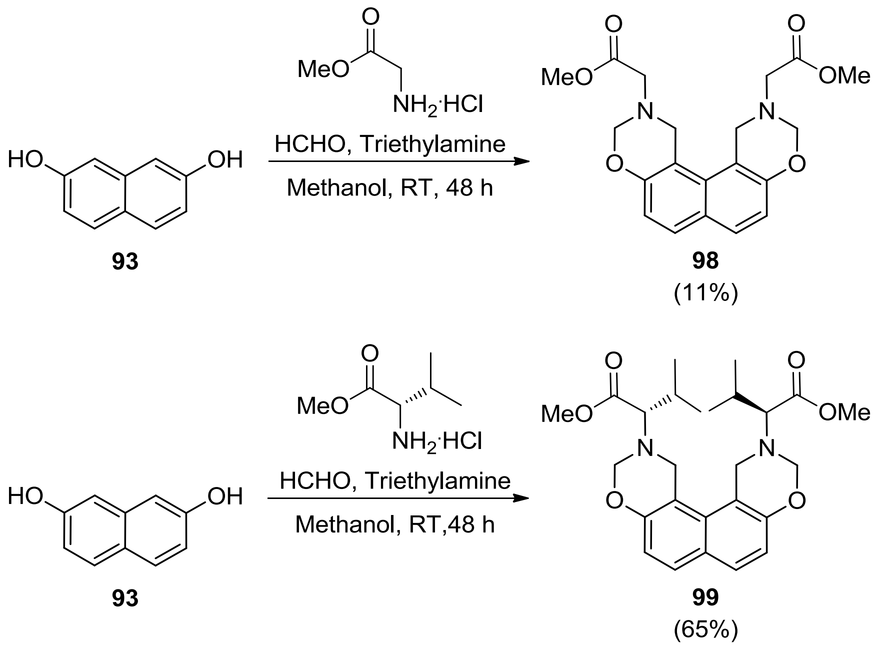


**Figure 27:** Variable Temperature $^1$H-NMR of compound **94**. **[A]** = - 20°C; **[B]** = - 35 °C; **[C]** = - 45 °C; **[D]** = - 58 °C. The down field signal is for Hb & Hb', remains unchanged at low temperature, while the inside Ha and Ha' appear at the up field and show broadening of the signal

The peripheral protons remained unchanged as sharp singlet when the $^1$H-NMR was run at – 58 °C, while the inside hydrogens appeared as a broad signal. Even though the inside protons did not show two signals at this condition, there appears to have a tendency of this conformation to gain slight rigidity. The low temperature $^1$H-NMR study does not indicate the presence of helical form but definitely hints towards the possibility of acquiring a rigid conformational deviation or slow rate of isomerization.

The variable temperature analysis for all the **94** – **97** derivatives were almost similar, although it was expected that bulkier *N*-substitutions such as *tert*-Butyl group may offer necessary steric mass for the formation of the required twist.

To continue our attempt to build the required helical framework on the naphthalene unit we also examined introduction of an additional chiral element by selecting a chiral primary amine for the aromatic aza-Michael reaction. One of the options considered for this synthesis would be amino acid based amino compounds, since such compounds are readily available. In this synthesis the chiral amines selected were glycine methyl ester and L-valine methyl ester [**Scheme-24**].



**Scheme 24:** Synthesis of chiral bis-oxazines **98** and **99** from the chiral amino esters

The synthesis of these two bis-oxazines, dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)diacetate **98** and (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methyl-butanoate) **99** was achieved by using the glycine methyl ester•hydrochloride and L-valine methyl ester•hydrochloride, while triethyl amine was added to neutralize the hydrochloride salt, the crude products were purified by column chromatography over silica gel.

The reaction with glycine methyl ester gave the product **98**, the structure of the compound **98** was established by usual mass spectral and by $^{1}$H- and $^{13}$C-NMR analysis. The $^{1}$H-NMR of **98** shows the similar pattern for inside hydrogens of Ar-C$\underline{H}_2$-N appeared at the high field region while the ones flanked by two electronegative atoms, -N-C$\underline{H}_2$-O, appeared at downfield region. However, the $^{1}$H-NMR of the bis-oxazine (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) **99** shows a different pattern. The outside oxazine protons for methylene of -N-C$\underline{H}_2$-O were observed as a doublet at δ 5.00 (*J* = 10.0 Hz, 2H) and a doublet of doublet at δ 4.94 (*J* = 9.6 & 1.6 Hz, 2H). The internal protons of the oxazines methylene of Ar-C$\underline{H}_2$-N also show two doublets at δ 4.64 and 4.37 (*J* = 15.6 Hz, 4H).

The correlation of the methylene protons of this bis-oxazine **99** was also established by the $^{1}$H-$^{13}$C correlation 2D NMR experiment HSQCGP as shown below [**Figure-28**].

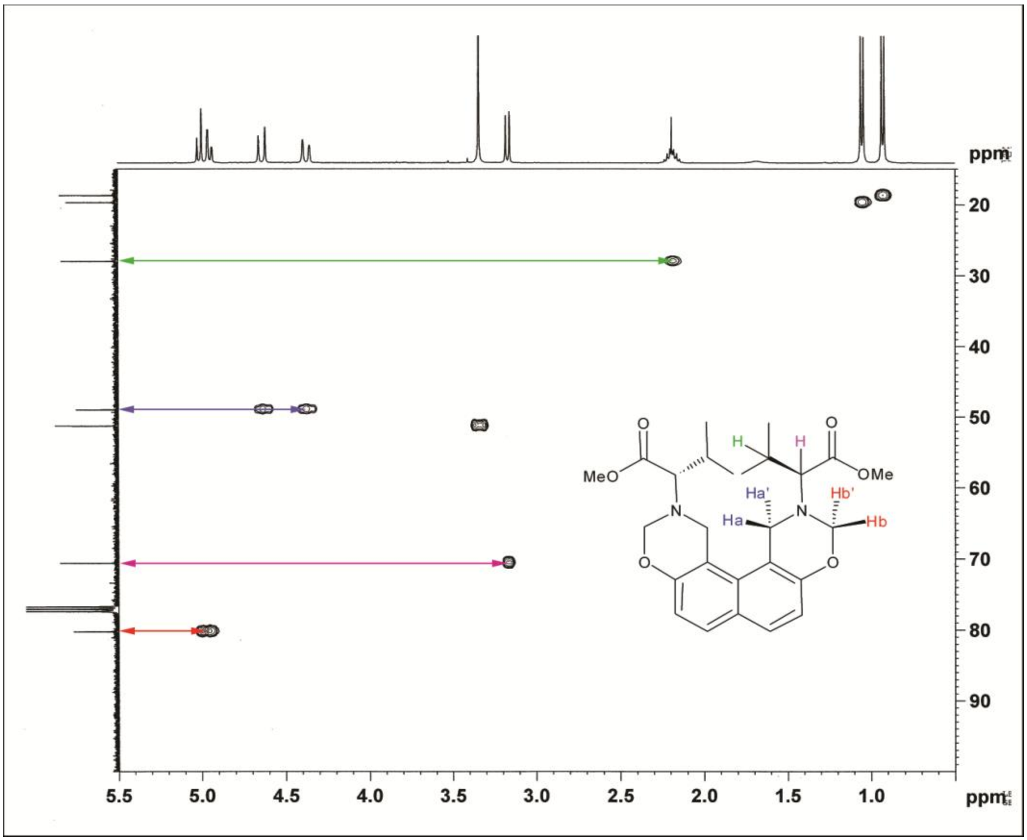


**Figure 28:** $^{1}$H-$^{13}$C Correlation (HSQCGP) spectrum of the bis-oxazine **99**

In the $^{1}$H-$^{13}$C correlation spectrum the carbon at δ 80.25 correlates with the protons at δ 5.00 and 4.95 of the oxazine outer -N-C$\underline{H}_2$-O while the carbon at d 49.0 correlates with the internal protons Ar-C$\underline{H}_2$-N of the bis-oxazines at δ 4.64 and 4.37. The carbons at δ 70.61 and 28.01 were correlated with the protons at δ 3.18 and a multiplate at δ 2.23-2.14 respectively.

The H-NMR pattern of **99** clearly indicates that the hydrogens on methylene bridge are not equal as in case of the bis-oxazines built with achiral amines. This may be due to the combination of two aspects, the presence of a chiral centre making them diastereotopic and other one could be the twisted shape of the molecule, the second aspect is crucial for the present goal.

In the IR spectrum of the molecule **99** as peak observed at 2976 cm$^{-1}$ for Ar-H stretching, peak at 1732 cm$^{-1}$ for -C=O stretching for -COOCH$_3$, 1610 cm$^{-1}$ for aromatic -C=C- stretching and peak at 1371 cm$^{-1}$ aromatic -C-O stretching and 1045 cm$^{-1}$for -C-N stretching vibrations for *tert*-amines.

The twist in the framework was also found by the single crystal X-ray diffraction analysis. The angle between the two planes C19-C15-C14-C8 and C7-C8-C14-C15 on **99** bisect each other at an angle of about ~11.5° due to the twisted conformation of the two oxazine rings [**Figure-29**].

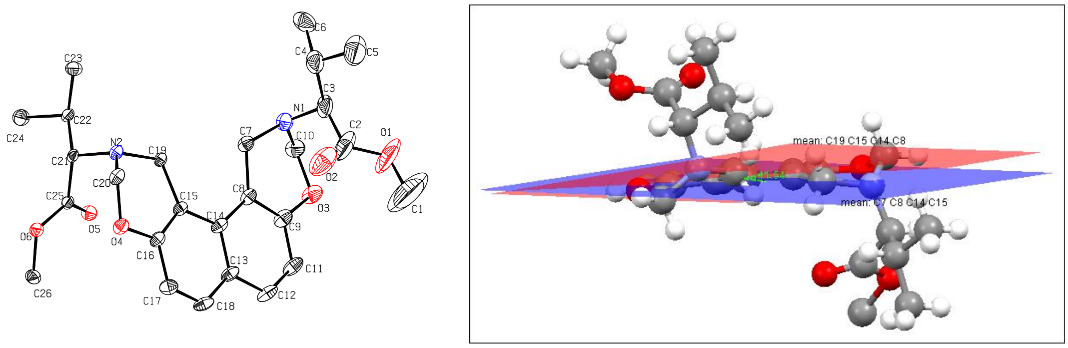


**Figure 29:** ORTEP diagram of **99** with atom numbering scheme (30% probability factor for the thermal ellipsoids. Hydrogen atoms are omitted for clarity) and measurement of the angle of the planes passing through the oxazine rings

Further investigation to check the conformational stability of this molecule was done by running $^{1}$H-NMR spectra of **99** at high temperature. In this study one of the outside hydrogens which showed a doublet of doublet at δ 4.94 ($J$ = 9.6, 1.6 Hz) at 22 $^{o}$C temperature slowly merged to a doublet at + 40 $^{\circ}$C, while all the germinal proton doublets appear closer or shifted towards each other and perhaps with the possibility to be merged at even high temperature [**Figure-30**].

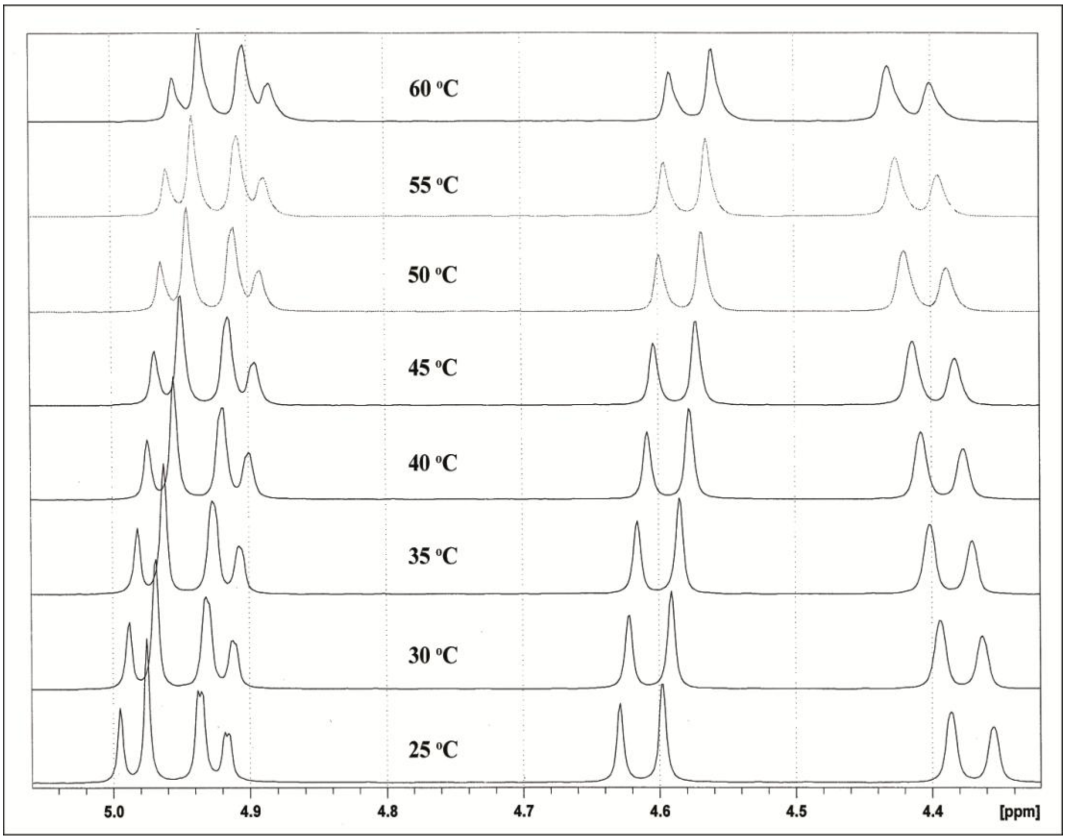
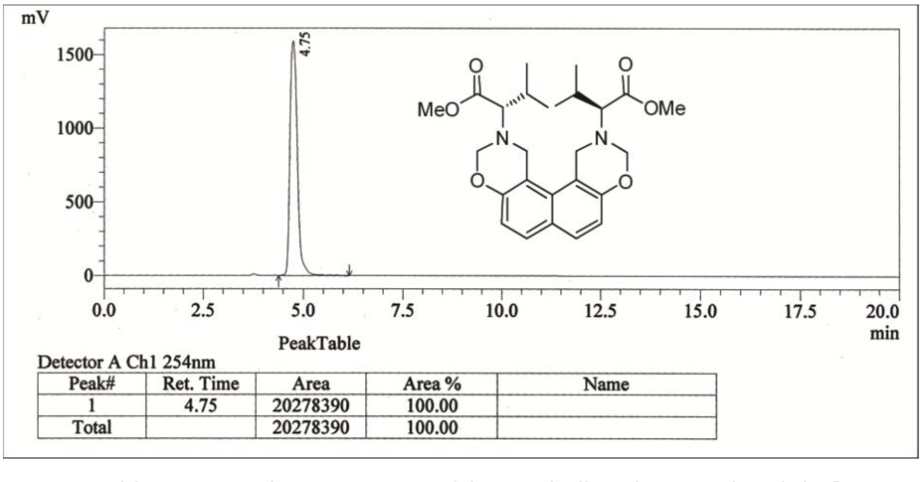


**Figure 30:** VT-NMR of bis-oxazine (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) **99**

The HPLC analysis of this compound on chiral stationary phase column showed single peak, probably indicating the absence of two isomers in solution at ambient conditions [**Figure-31**].



PeakTable

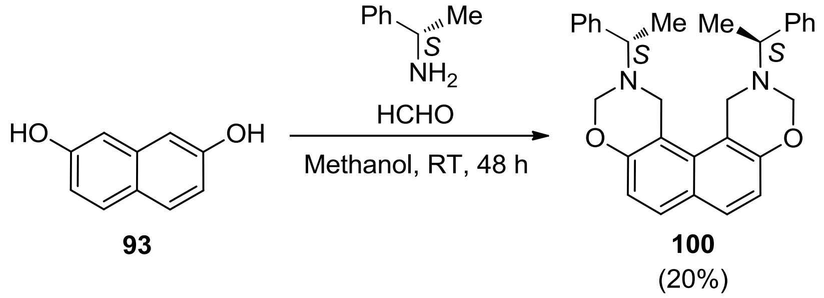
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 4.75 | 20278390 | 100.00 | |
| Total | | 20278390 | 100.00 | |

**Figure 31:** Chiral HPLC chromatogram of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) **99**

Another chiral amine was utilized to study the similar aspect of attempting to construct helicene like twist in the conformation of the two oxazine rings mounted on naphthalene.

The reaction of the (*S*)-α-methylbenzyl amine and excess of formaldehyde with 2,7-dihydroxynaphthalene **93** gave another chiral bis-oxazine 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **100** [**Scheme-25**].



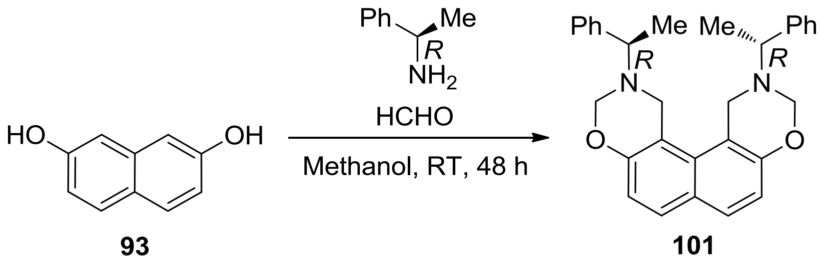
**Scheme 25:** Synthesis of bis-oxazine 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **100**

The $^1$H-NMR spectrum of this bis-oxazine **100** shows a similar pattern for the hydrogens of the oxazine ring like other compounds. The inside hydrogens of Ar-C$\underline{H}_2$-N in **100** appeared as two signals, one doublet at δ 4.18 (*J* = 16.4 Hz, 1H) and another doublet at δ 4.05 (*J* = 16.4 Hz, 1H). However, it was interesting to observe different pattern for the outside hydrogens, O-C$\underline{H}_2$-N. These hydrogens show one doublet at δ 4.83 (*J* = 10.0 Hz, 1H) and another doublet of doublet δ 5.08 (*J* = 10.0 & 1.2 Hz, 1H). This could be attributed to the diastereotopic nature of the hydrogens and probably due to the twisting of the conformational framework of the oxazine.

The EI-mass spectrum of the molecule **100** showed the *m/z* 450 [M]$^{\cdot+}$ and further signals due to fragmentations of [2 X (-NCH-CH$_3$Ph)]$^{\cdot+}$ at *m/z* 212, the base peak at *m/z* 105 for the [Ph-CH-CH$_3$].$^{\cdot+}$

The IR spectrum of **100** showed a peak at 3024 cm$^{-1}$ for Ar-H stretching, peak at 2990 cm$^{-1}$for -C-H stretching, peak at 1611 cm$^{-1}$ for aromatic -C=C- stretching, peak at 1386 cm$^{-1}$ aromatic -C-O stretching, and 1065 cm$^{-1}$for -C-N stretching vibrations for *tert*-amines.

Similarly the other isomer of the bis-oxazine were synthesized by using (*R*)-α-methylbenzyl amine and excess of formaldehyde from 2,7-dihydroxynaphthalene. The other enantiomer will be 11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **101** [**Scheme-26**].



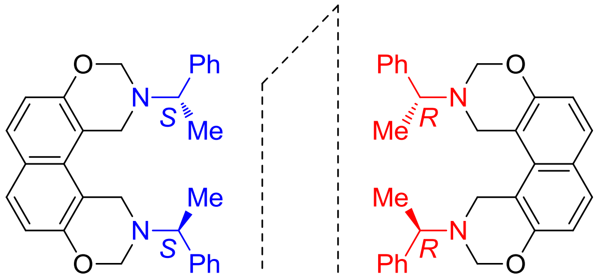
**93**

**101**
(25%)

**Scheme 26:** Synthesis of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **101**

The above synthesised compound **101** was characterized by the usual spectroscopic technique and found similar properties with the compound **100**.

The specific rotation of the compounds **100** and **101** was recorded and as expected were found to be of opposite sign, with some deviation in the degree of rotation, probably can be attributed to some impurity in the sample or an error in weighing the sample. [**Figure-33**].



**100**

$[\alpha]_D^{34} = +175$

**101**

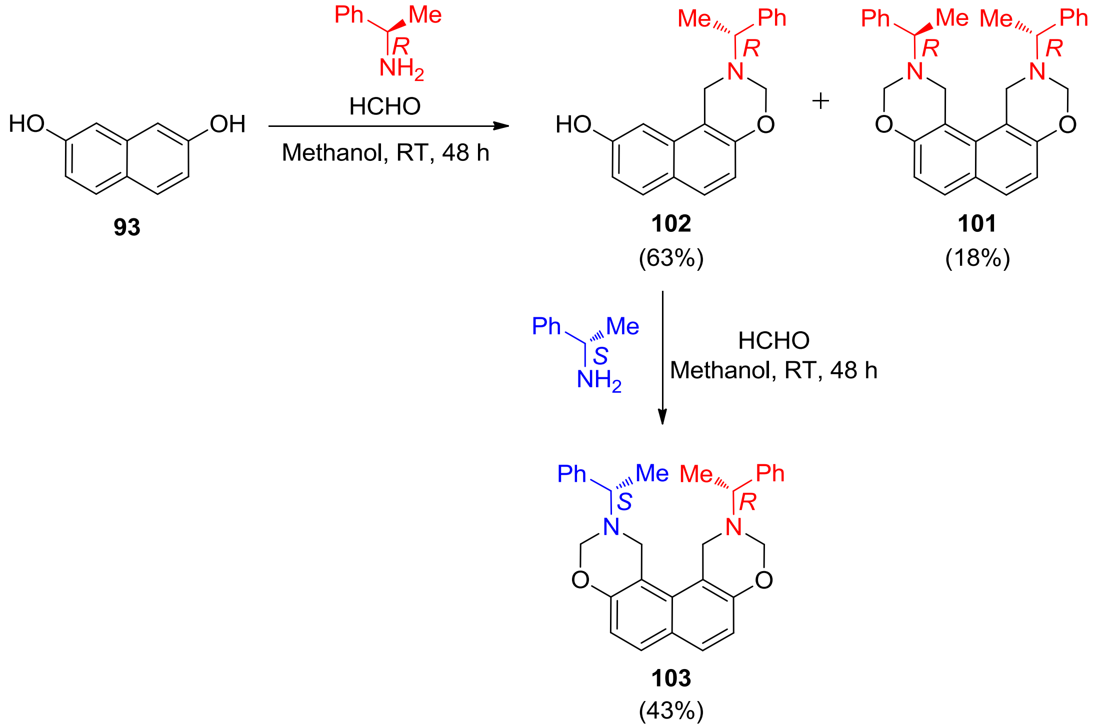
$[\alpha]_D^{34} = -189$

**Figure 32:** Relation of the isomer of the bis-oxazines **100** and **101**

The third possible isomer of **100** and **101** will be a *meso* isomer. The *meso* isomer **104** was prepared in stepwise manner from **93**, *via* mono-oxazine **103** by utilizing both chiral forms of the same amine. The $^1$H-NMR spectra of both isomers of **100** and **101** were identical, while that of **103** was slightly different. The splitting pattern in **100** and **103** is almost similar, but very small deviation in the chemical shift was detected.

The *meso* isomer of bis-oxazine 2-((*R*)-1-phenylethyl)-11-((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **103** was prepared from the 2,7-dihydroxynaphthalene **93** as outlined in [**Scheme-27**].

The reaction of 2,7-dihydroxynaphthalene with one equivalent of (*R*)-α-methylbenzyl amine and excess of formaldehyde at room temperature gave mono-oxazine (R)-2-(1-phenylethyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazin-9-ol **102** as the major product, along with small quantity of bis-oxazine **101.** The mono-oxazine **102** was separated and subsequently converted to the *meso* bis-oxazine 2-((*R*)-1-phenylethyl)-11-((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **103** by using (*S*)-α-methylbenzyl amine and formaldehyde. The bis-oxazine **103** was purified and characterized by usual analytical techniques.



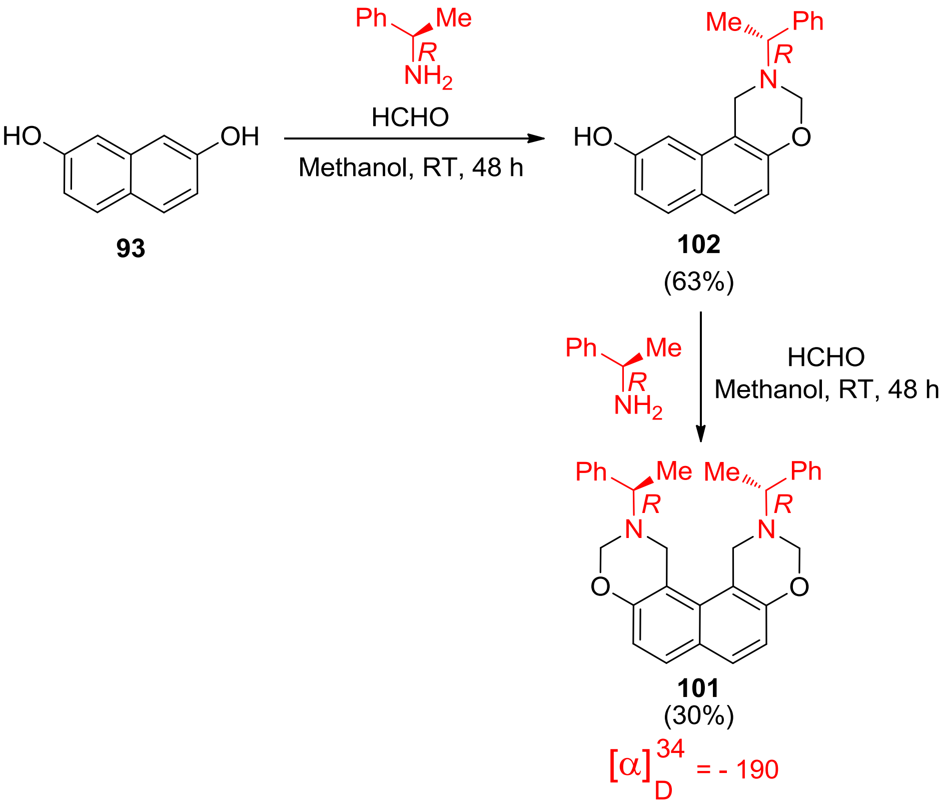
**Scheme 27:** Synthesis of *meso* bis-oxazine 2-((*R*)-1-phenylethyl)-11-((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **103**

The EI-mass spectrum of the molecule **102** showing the peaks at *m/z* 306 $[M+1]^{\cdot+}$ and *m/z* 305 $[M]^{\cdot+}$ and further stable fragmentation due to the cleavage of $[PhCHCH_3]^{\cdot+}$ at *m/z* 200. The base peak observed at *m/z* 105 for the $[Ph\text{-}CH\text{-}CH_3]^{\cdot+}$ stable fragment of the compound **102**.

The IR spectrum of the molecule **102** showed peaks at 3391 $cm^{-1}$ for -OH group, at 3029 $cm^{-1}$ for Ar-H stretching, at 2973 $cm^{-1}$for -C-H stretching, at 1626 $cm^{-1}$ for aromatic -C=C- stretching and at 1217 $cm^{-1}$ aromatic -C-O stretching and peak at 1134 $cm^{-1}$ for -C-O- for -C-O-C- ether linkage vibrations.

The optical rotation of *meso* isomer is expected to be zero, if no other chiral unit is present. The observed optical rotation of **103** was - 44°, hence it may indicate the presence of third chiral element.

During the time of publication of this work a referee had expressed the possibility of the isomerisation of the chiral centre of one of the oxazines. In order to check this possibility bis-oxazine **101** was synthesized by stepwise manner from the **102**, but again using the same isomer of amine in second step, (*R*)-α-methylbenzyl amine and formaldehyde. The $^1$H-NMR of this compound synthesized by stepwise matches exactly with the $^1$H-NMR of **101** synthesized in a single step and the optical rotation of this compound was almost same [**Scheme-28**].

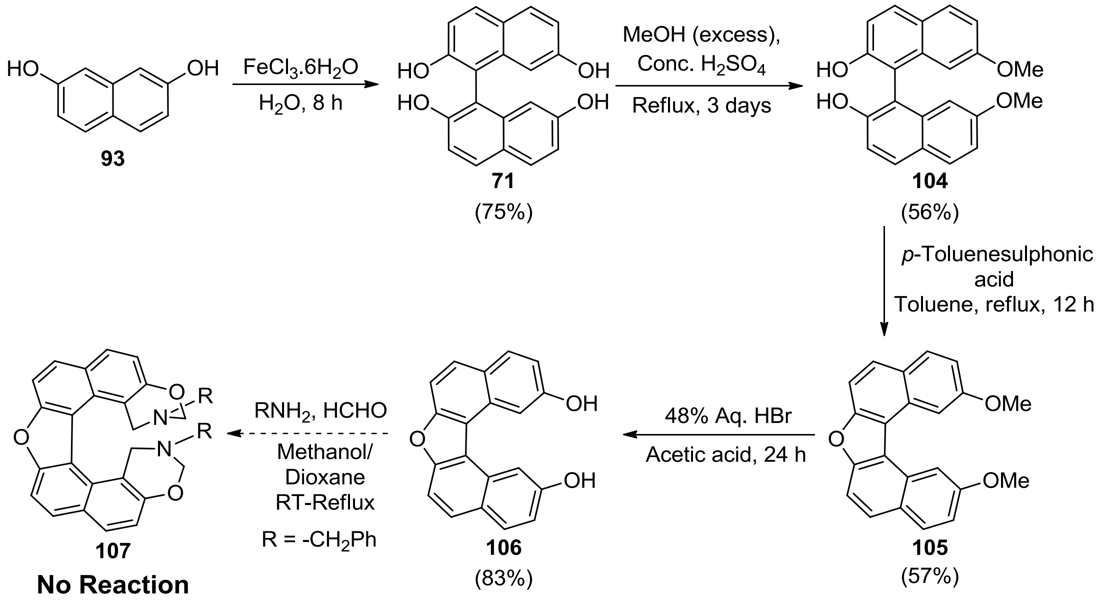


**Scheme 28:** Stepwise synthesis of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine) **101**

The additional chiral element in **103** could be the helical twist created by the two half chair conformations of 1,3-oxazines pointing towards the opposite directions. If this hypothesis is considered then we may have created an asymmetric synthesis of the helical chiral unit in this molecule. The X-ray crystal analysis of **99** indicates the configuration of the projected helical system to be *P* if the direction of the two half chair conformations of oxazine rings were to be considered, in reference to the known configuration of the *L*-valine ester.

On achieving the synthesis of these bis-oxazines with 2,7-dihydroxynaphthalene it was designed to construct its analogue having two such systems. The proposed molecule and its attempted synthesis is outlined in **Scheme-29**. The final target molecule, a bis-oxazines may be described as dinaphtho[2,1-b:1',2'-d]furan-2,12-diol/2,12-dihydroxy-7-oxa[5]helicene **106** [**Scheme-29**].

The synthesis of this material began by few known steps from 2,7-dihydroxynaphthalene **93**. This diol was converted to the 7,7’-dihydroxy-2,2’-binaphthol **71** by the known procedure.[30] Initially the tetra phenol **71** was converted to **106** *via* few steps of synthetic manipulations. The less crowded two hydroxyl groups of **71** were converted to the methyl ether **104**, selectively using acid catalyzed conditions. Cyclization of the two free hydroxyl groups, for the synthesis of **105**, was attempted with the *p*-toluene sulphonic acid, H-β and H-Y Zeolite in toluene and dichloromethane at high temperature the reaction not occurred. However, synthesis of 2,12-dimethoxy-7-oxa[5]helicene **105** was achieved by reported methodology.[48] The 7,7’-dihydroxy-2,2’-binaphthol **71** was converted to 7,7’-dimethoxy-2,2’-binaphthol **104** using the concentrated sulphuric acid in methanol to obtain the product in good yield.



**Scheme 29:** Attempted synthesis of bis-oxazine[7]helicene **108**

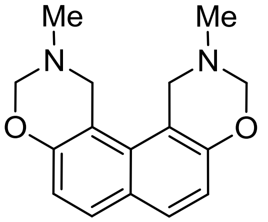
Further diol **104** was cyclised to the ether using the *p*-toluene sulphonic acid in hot toluene to give the 2,12-dimethoxy-7-oxa[5]helicene **105** in good yield. The reaction of 2,12-dimethoxy-7-oxa[5]helicene with the excess of aqueous 48% HBr in glacial acetic acid under reflux gave 2,12-dihydroxy-7-oxa-[5]helicene **106**.

The reaction of **106** with benzylamine and excess of formaldehyde did not proceed at room temperature or at reflux temperature. An attempt to carry out this reaction in dioxane at refluxed temperature furnished a bluish-green solid material, which was not soluble in organic solvents perhaps indicating its polymeric nature. Hence the synthesis of **107** is currently abandoned.

## Experimental Section

## Part 2

***2,11-Dimethyl-2,3,11,12-tetrahydro-1H,10H,-4,9-dioxa-2,11-diaza-benzo[c]-phenanthrene (94):***



An aqueous methylamine solution (0.484 g, 1.211 mL, 40% w/v, 15.6 mmol) and formaldehyde solution (1.125 g, 3.75 mL, 37% w/v, 37.46 mmol) was stirred for 30 min at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (1.0 g, 6.24 mmol) was added and the reaction mixture was stirred for 24 h at 80 °C. After the completion of reaction absolute ethanol was added to precipitate out the crude product, which was filtered and recrystallized from ethylacetate: petroleum ether afford white solid (0.340 g, 20%). **Mp.** 180-182 $^{o}$C. (Lit.$^{8d}$ M.p. 171-173 °C).

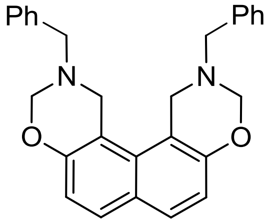
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, $J$ = 8.8 Hz, 2H), 6.85 (d, $J$ = 8.8 Hz, 2H), 4.84 (s, 4H), 4.39 (s, 4H), 2.54 (s, 6H).

**IR (KBr):** 3058, 2986, 2952, 2886, 1605, 1510, 1468, 1445, 1417, 1390, 1358, 1304, 1239, 1193, 1158, 1117, 1055, 1026, 998, 973, 917, 864, 824, 768, 753, 681 cm.$^{-1}$

**MS (EI)**: *m/z*, (%) 271 (11), 270 (64), 228 (08), 227 (48), 226 (09), 213 (14), 212 (99), 198 (07), 186 (12), 185 (17), 184 (100), 156 (27), 155 (14), 129 (06), 128 (40), 127 (15), 126 (06), 101 (06).

**Anal. Calcd. for $C_{16}H_{18}N_2O_2$**: C 71.09, H 6.71, N 10.36. Found: C 71.11, H 6.36, N 10.38.

***2,11-Dibenzyl-2,3,11,12-tetrahydro-1H,10H,-4,9-dioxa-2,11-diaza-benzo[c]phenanthrene (95):***



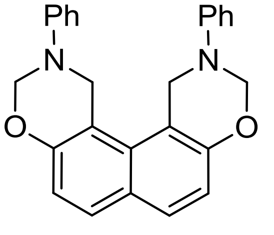
A solution of benzylamine (1.672 g, 1.70 mL, 15.6 mmol) and formaldehyde (1.125 g, 3.75 mL, 37% w/v, 37.46 mmol) was stirred for 30 min at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (1.0 g, 6.24 mmol) was added and the reaction mixture was stirred for 24 h at 80 °C. After the completion of reaction absolute ethanol was added to precipitate out the crude product, which was filtered and recrystallized from ethylacetate: petroleum ether afford white solid (1.425 g, 54%). **M.p.** 123-124 °C. (Lit.$^{8d}$ 123-124 °C).

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.46 (d, $J$ = 8.8 Hz, 2H), 7.27-7.17 (m, 10H), 6.81 (d, $J$ = 8.76 Hz, 2H), 4.78 (s, 4H), 4.24 (s, 4H), 3.73 (s, 4H).

**IR (KBr):** 3415, 3062, 3030, 2995, 2947, 2892, 2859, 1945, 1882, 1776, 1609, 1516, 1495, 1443, 1387, 1350, 1301, 1266, 1223, 1187, 1136, 1090, 1079, 1014, 985, 934, 872, 833, 777, 734, 696 cm$^{-1}$.

**Anal. Calcd. for $C_{28}H_{26}N_2O_2$**: C 79.59, H 6.20, N 6.63. Found: C 79.58, H 6.00, N 6.13.

### *2,11-Diphenyl-2,3,11,12-tetrahydro-1H,10H,-4,9-dioxa-2,11-diaza-benzo[c]phenanthrene (96):*



A solution of aniline (1.862 g, 1.82 mL, 20.0 mmol) and formaldehyde (1.802 g, 4.870 mL, 37% w/v, 60.0 mmol) was stirred for 30 min at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (1.6 g, 10.0 mmol) was added and the reaction mixture was stirred for 24 h at 80 °C. After the completion of reaction absolute ethanol was added to precipitate out the crude product, which was filtered and recrystallized from ethylacetate:petroleum ether afford white solid (0.831 g, 22%). **M.p.** 164-165 °C. (Lit.[14f] 138 °C).

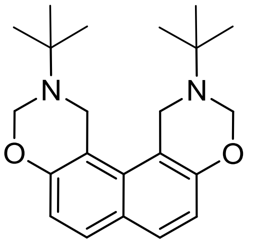
**$^1$H-NMR (500 MHz, $CDCl_3$):** δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.25-7.22 (m, 4H), 7.08-7.07 (m, 4H), 6.95-6.92 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.43 (s, 4H), 5.14 (s, 4H).

**IR (KBr):** 3433, 3011, 2900, 1924, 1607, 1494, 1447, 1363, 1222, 1165, 1111, 1029, 994, 940, 832, 786, 757, 693 cm.$^{-1}$

**MS (EI)**: *m/z*, (%) 395 (05), 394 (08), 290 (06), 289 (27), 288 (10), 274 (17), 186 (12), 185 (09), 184 (42), 156 (08), 155 (05), 128 (18), 127 (07), 106 (29), 105 (100), 104 (57), 102 (06), 178 (06), 77 (32).

**Anal. Calcd. for $C_{28}H_{26}N_2O_2$**: C 79.16, H 5.62, N 7.10. Found: C 78.88, H 5.59, N 6.98.

### *2,11-Di-tert-butyl-2,3,11,12-tetrahydro-1H,10H-4,9-dioxa-2,11-diaza-benzo[c]phenanthrene (97):*



A solution of *tert*-butyamine (1.142 g, 1.64 mL, 15.6 mmol) and formaldehyde solution (0.844 g, 2.280 mL, 37% w/v, 28.0 mmol) was stirred for 30 min at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (1.0 g, 6.24 mmol) was added and the reaction mixture was stirred for 24 h at 80 °C. After the completion of reaction absolute ethanol was added to precipitate out the crude product, which was filtered and recrystallized from ethylacetate: petroleum ether afford white solid (1.30 g, 59%). **M.p.** 160 $^o$C.

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.07 (s, 4H), 4.61 (s, 4H), 1.20 (s, 18H).

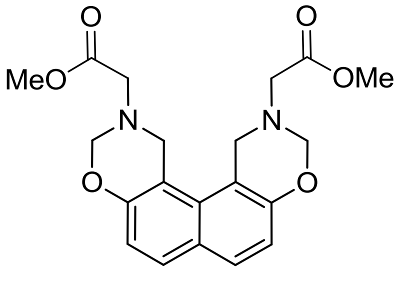
**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 154.25 (2 x Cq), 132.46 (Cq), 129.11 (2 x CH), 125.50 (Cq), 116.23 (2 x CH), 115.40 (2 x Cq), 77.65 (NC$\underline{H}_2$O), 54.23 [-NC$\underline{H}$-(CH$_3$)$_3$], 46.97 (C$\underline{H}_2$), 28.32 (C$\underline{H}_3$)$_3$.

**IR (KBr):** 3439, 3030, 3023, 2963, 2883, 2870, 2359, 1894, 1878, 1760, 1607, 1547, 1515, 1468, 1441, 1381, 1361, 1308, 1259, 1232, 1218, 1205, 1133, 1103, 1029, 1006, 923, 907, 827, 771 cm.$^{-1}$

**MS (EI)**: *m/z*, (%) 355 (05) ([M+1]$^+$), 354 (08), 270 (04), 269 (18), 254 (06), 213 (18), 212 (24), 198 (16), 186 (09), 185 (61), 184 (100), 182 (03), 157 (05), 156 (08), 155 (05), 128 (15), 127 (07), 86 (09), 70 (16), 57 (19).

**Anal. Calcd. for $C_{22}H_{30}N_2O_2$**: C 74.54, H 8.53, N 7.90. Found: C 74.35, H 8.62, N 7.60.

***Dimethyl 2,2'-(naphtho[1,2-e:8,7-e']bis([1,3]oxazine)-2,11(1H,3H,10H,12H)-diyl)diacetate (98):***

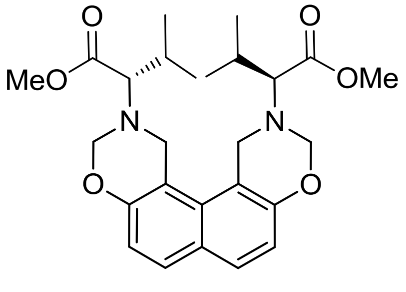


A solution of glycinemethylester hydrochloride (0.862 g, 6.87 mmol), formaldehyde solution (0.450 g, 1.22 mL, 37% w/v, 14.98 mmol) and triethylamine (0.758 g, 1.044 mL, 7.49 mmol) in methanol (10 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (0.500 g, 3.12 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After the completion of the reaction, the solvent was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether:ethylacetate (100:00 to 50:50) as gradient for the elution of the compound (0.123 g, 11%).

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.52 (d, $J$ = 8.8 Hz, 2H), 6.87 (d, $J$ = 8.8 Hz, 2H), 4.95 (s, 4H), 4.52 (s, 4H), 3.75 (s, 6H), 3.53 (s, 4H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 171.03 (2 x Cq), 152.85 (2 x Cq), 133.63 (Cq), 129.70 (2 x -C$\underline{H}$), 125.74 (Cq), 116.23 (2 x -C$\underline{H}$), 111.55 (2 x Cq), 81.54 (2 x -C$\underline{H}_2$), 52.48 (-C$\underline{H}_2$), 52.26 (C$\underline{H}_2$), 52.10 (C$\underline{H}_2$).

### *(2S,2'S)-dimethyl 2,2'-(naphtho[1,2-e:8,7-e']bis([1,3]oxazine)-2,11(1H,3H,10H,12H)-diyl)bis-(3-methylbutanoate) (99):*



A solution of L-valinemethylester hydrochloride (1.152 g, 6.86 mmol), formaldehyde solution (0.450 g, 1.22 mL, 37% w/v, 14.98 mmol) and triethylamine (0.79 g, 1.044 mL, 7.49 mmol) in methanol (10 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (0.500 g, 3.12 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After the completion of reaction, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether:ethylacetate (100:00 to 80:20) as gradient for the elution of the compound (0.955 g, 65%); $[\alpha]_D^{34}$ = +231 (*c* 0.1 in $CHCl_3$). **M.p.** 121-122 °C.

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.00 (d, *J* = 10.00 Hz, 2H), 4.94 (dd, *J* = 1.6, 9.6 Hz, 2H), 4.64 (d, *J* = 15.6 Hz, 2H), 4.37 (broad d, *J* = 15.6 Hz, 2H), 3.34 (s, 6H), 3.17 (d, *J* = 9.2 Hz, 2H), 2.23-2.16 (m, 2H), 1.05 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.8 Hz, 6H).

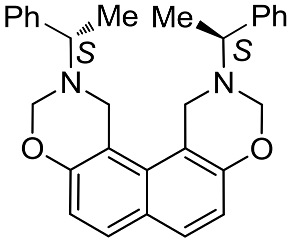
**$^{13}$C-NMR (100.6 MHz, $CDCl_3$):** δ 172.97 (2 x Cq), 153.38 (2 x Cq), 132.81(Cq), 129.23 (2 x -CH), 125.48 (Cq), 116.19 (2 x -CH), 113.52 (2 x Cq), 80.25 (2 x $-\underline{C}H_2$), 70.61 (2 x -$\underline{C}$H), 51.30 (2 x $-COO\underline{C}H_3$), 49.00 (2 x $-\underline{C}H_2$), 28.01 (2 x -$\underline{C}$H), 19.72 (2 x $-\underline{C}H_3$), 18.75 (2 x $-\underline{C}H_3$).

**IR (KBr)**: 2962, 2930, 2874, 1740, 1674, 1610, 1516, 1441, 1370, 1286, 1237, 1193, 1122, 1043, 1027, 938, 9831, 759, 685 cm.$^{-1}$

**MS (EI)**: *m/z*, (%) 470 (06), 354 (12), 311 (19), 268 (37), 213 (16), 212 (100), 198 (33), 197 (09), 185 (13), 184 (46), 156 (15), 155 (10), 144 (25), 128 (28), 127 (09),116 (10), 100 (17), 84 (55).

**Anal. Calcd. for $C_{30}H_{30}N_2O_2$**: C 66.36, H 7.28, N 5.95. Found: C 66.48, H 6.79, N 5.68.

### *2,11-bis((S)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7-e']bis([1,3]oxazine) (100):*



A solution of (*S*)-α-methylbenzylamine (0.416 g, 3.43 mmol) and formaldehyde solution (0.608 mL, 37% w/v, 7.48 mmol) in methanol (10 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (0.250 g, 1.56 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After completion of the reaction, it was concentrated under the reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether:ethylacetate (100:00 to 80:20) as gradient for the elution of the compound (0.141 g, 20%); $[\alpha]_D^{34}$ = +174.5 (*c* 0.1 in $CHCl_3$). **M.p.** 190-191°C (decomposed).

**IR (KBr)**: 3443, 3024, 2977, 2887, 2844, 1883, 1611, 1517, 1491, 1461, 1450, 1440, 1386, 1359, 1320, 1235, 1198, 1165, 1129, 1065, 1016, 941, 836, 778, 753, 701 cm.$^{-1}$

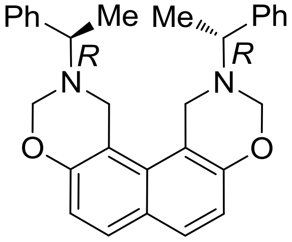
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.34-7.23 (m, 10H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.08 (dd, *J* = 1.2, 10.0 Hz, 2H), 4.83 (d, *J* = 10.0, 2H), 4.18 (d, *J* = 16.4 Hz, 2H), 4.05 (d, *J* = 16.4 Hz, 2H), 3.85 (q, *J* = 6.4 Hz, 2H), 1.41 (d, *J* = 6.8 Hz, 6H).

**$^{13}$C-NMR (100.6 MHz, $CDCl_3$):** δ 153.71 (2 x Cq), 144.23 (2 x Cq), 133.49 (Cq), 129.33 (2 x CH), 128.56 (4 x CH), 127.33 (2 x CH), 127.27 (4 x CH), 125.63 (Cq), 115.91 (2 x CH), 112.53 (2 x Cq), 78.61 (2 x -$\underline{C}H_2$), 56.99 (2 x -$\underline{C}H_2$), 49.77 (2 x –CH), 21.32 (2 x –$\underline{C}H_3$).

**MS (EI)**: *m/z*, (%) 450 (07), 317 (20), 316 (04), 213 (20), 212 (33), 198 (07), 185 (22), 184 (33), 134 (05), 128 (09), 127 (05), 106 (08), 105 (100), 103 (10), 91 (07), 79 (13), 77 (13).

**Anal. Calcd. for $C_{30}H_{30}N_2O_2$**: C 79.97, H 6.71, N 6.22. Found: C 80.09, H 6.54, N 5.78.

### *2,11-bis((R)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7-e']bis([1,3]-oxazine) (101):*



A solution of (*R*)-α-methylbenzylamine (0.833 g, 6.86 mmol) and formaldehyde solution (1.09 mL, 37% w/v, 14.98 mmol) in methanol (10 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (0.500 g, 3.12 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After the completion of the reaction, the mixture was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether:ethylacetate (100:00 to 80:20) as gradient for the elution of the compound.

**Yield** = 0.349 g (25%); $[\alpha]_D^{34}$ = -189 ($c$ 0.11 in $CHCl_3$).

**M.p.** 188-190 °C (decomposed).

**IR (KBr):** 3440, 3055, 3024, 2977, 2886, 2844, 1952, 1883, 1760, 1610, 1517, 1491, 1451, 1440, 1386, 1367, 1359, 1320, 1305, 1235, 1198, 1165, 1128, 1117, 1065, 980, 940, 836, 770, 703 $cm.^{-1}$

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.30-7.19 (m, 10H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.05 (d, *J* = 10.0 Hz, 2H), 4.80 (d, *J* = 10.0 Hz, 2H), 4.14 (d, *J* = 16.0 Hz, 2H), 4.01 (d, *J* = 16.4 Hz, 2H), 3.83 (q, *J* = 6.8 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 6H).

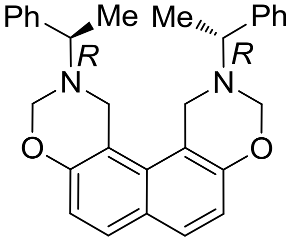
**$^{13}$C-NMR (100.6 MHz, $CDCl_3$):** δ 153.69 (2 x Cq), 144.19 (2 x Cq), 133.46 (Cq), 129.33 (2 x $\underline{C}$H), 128.55 (4 x $\underline{C}$H), 127.33 (2 x $\underline{C}$H), 127.26 (4 x $\underline{C}$H), 125.63 (Cq), 115.90 (2 x $\underline{C}$H), 112.50 (2 x Cq), 78.60 (2 x $\underline{C}H_2$), 57.00 (2 x $\underline{C}H_2$), 49.75 (2 x -$\underline{C}$H), 21.29 (2 x $\underline{C}H_3$).

**MS (EI)**: *m/z*, (%) 450 (05), 318 (04), 317 (18), 316 (04), 213 (19), 212 (31), 198 (08), 185 (24), 184 (35), 134 (05), 128 (10), 127 (05), 106 (08), 105 (100), 103 (11), 91 (07), 79 (12), 77 (13).

**Anal. Calcd. for $C_{30}H_{30}N_2O_2$:** C 79.97, H 6.71, N 6.22. Found: C 79.81, H 6.77, N 5.94.

### *Stepwise Synthesis of (101):*

### *2,11-bis((R)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7-e']bis([1,3]-oxazine)[101]:*



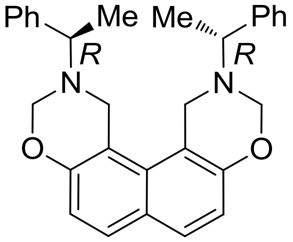
A solution of (*R*)-α-methylbenzylamine (0.096 g, 0.79 mmol) and formaldehyde solution (0.128 mL, 37% w/v, 1.58 mmol) in methanol (10 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then compound **102** [(*R*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol] (0.200 g, 0.659 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After the completion of reaction concentrated the reaction mixture under reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether: ethylacetate (100:00 to 80:20) as gradient for the elution of the compound. Compound **101** eluted with (petroleum ether:ethylacetate 4:1). **Yield** = 0.036 g (30%); $[\alpha]_D^{34}$ = -190 ($c$ 0.1 in $CHCl_3$).

**M.p**. 189-190 °C (decomposed).

### *2,11-bis((R)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7-e']bis([1,3]-oxazine) (101), (R)-2-(1-phenylethyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazin-9-ol (102) and 2-((R)-1-phenylethyl)-11-((S)-1-phenylethyl)-1,2,3,10,11,12-hexahydro-naphtho[1,2-e:8,7 e']bis([1,3]oxazine) (103):*

A solution of (*R*)-α-methylbenzylamine (0.726 g, 5.99 mmol) and formaldehyde solution (0.972 mL, 37% w/v, 11.98 mmol) in methanol (15 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then 2,7-dihydroxynaphthalene (0.800 g, 4.94 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After the completion of reaction concentrated the reaction mixture under reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether:ethylacetate (100:00 to 70:30) as gradient for the elution of the compounds.

### *2,11-bis((R)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7-e']bis([1,3]oxazine) (101):*

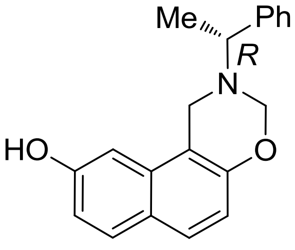


Eluted with (4:1, petroleum ether:ethylacetate).

**Yield** = 0.268 g (18%);

**M.p.** 188-190 °C (decomposed).

### *(R)-2-(1-phenylethyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazin-9-ol [102]:*



Eluted with (7:3, petroleum ether:ethylacetate).

**Yield** = 0.957 g (63%);

**M.p.** 118-119 °C (decomposed).

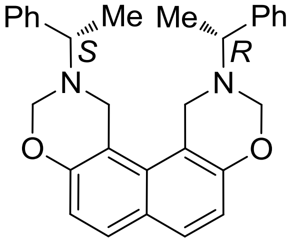
**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.68 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.39-7.28 (m, 5H), 6.95 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.93 (d, *J* = 9.2 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 5.18 (dd, *J* = 1.2, 10.4 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 4.31 (d, *J* = 16.8 Hz, 1H), 4.05 (m, 2H), 1.53 (d, *J* = 6.4 Hz, 3H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 154.35 (Cq), 153.13 (Cq), 144.48 (Cq), 133.25 (Cq), 130.54 (CH), 128.62 (2 x CH), 127.77 (CH), 127.39 (2 x CH), 127.36 (CH), 124.17 (CH), 115.98 (CH), 114.95 (CH), 110.68 (Cq), 103.81 (-CH), 79.83 (-$\underline{C}H_2$), 58.25 (-$\underline{C}H_2$), 46.19(-$\underline{C}H$), 21.52 (-$\underline{C}H_3$).

**IR (KBr):** 3440, 3055, 3024, 2977, 2886, 2844, 1952, 1883, 1760, 1610, 1517, 1491, 1451, 1440, 1386, 1367, 1359, 1320, 1305, 1235, 1198, 1165, 1128, 1117, 1065, 980, 940, 836, 770, 703 cm.$^{-1}$

**Anal. Calcd. for $C_{30}H_{30}N_2O_2$**: C 78.66, H 6.27, N 4.59. Found: C 77.93, H 6.42, N 4.42.

### Synthesis of *2-((R)-1-phenylethyl)-11-((S)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho-[1,2-e:8,7 e']bis([1,3]oxazine) (103):*



A solution of (*S*)-α-methylbenzylamine (0.238 g, 1.96 mmol) and formaldehyde solution (0.318 mL, 37% w/v, 3.93 mmol) in methanol (10 mL) was stirred for 30 min. at room temperature under $N_2$ atmosphere. Then Compound [(R)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol] **102** (0.500 g, 1.64 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After the completion of the reaction it was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel and petroleum ether:ethylacetate (100:00 to 80:20) as gradient for the elution of the compound (0.305 g, 41%); $[\alpha]_D^{34}$ = -44 (*c* 0.1 in $CHCl_3$).

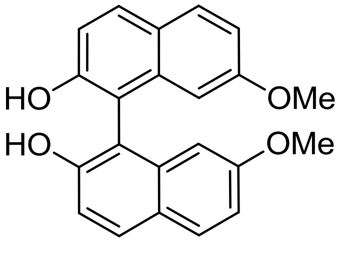
**M.p**. 188-190 °C (decomposed).

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.35-7.19 (m, 10H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.05 (dd, *J* =1.6, 10.4 Hz, 2H), 4.80 (d, *J* = 10.0 Hz, 2H), 4.14 (d, *J* = 16.4 Hz, 2H), 4.01 (d, *J* = 16.0 Hz, 2H), 3.82 (q, *J* = 6.4 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 6H).

**IR (KBr):** 3436, 2977, 2886, 2844, 1883, 1611, 1516, 1491, 1461, 1450, 1440, 1371, 1359, 1235, 1198, 1165, 1129, 1065, 1016, 991, 980, 941, 931, 836, 779, 770, 753, 702 cm.$^{-1}$

**Anal. Calcd. for $C_{30}H_{30}N_2O_2$**: C 79.97, H 6.71, N 6.22. Found: C 79.77, H 6.44, N 5.84.

### *7,7'-Dimethoxy-2,2'-binaphthol (104):*



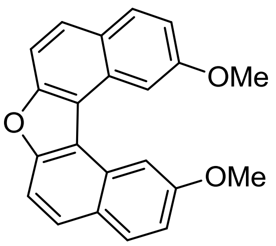
To a solution of 7,7'-dihydroxy-2,2'-binaphthol **71** (1.00 g, 3.14 mmol) in MeOH (15 mL) was added concentrated $H_2SO_4$ (0.308 g, 0.167 mL, 3.14 mmol). The reaction mixture was allowed to gently reflux for 3 days. After quenching with saturated potassium carbonate solution, the crude product was extracted with ethyl acetate. Column chromatography on silica gel using petroleum ether:ethyl acetate 100:00 to 4:1 as gradient for elution followed by crystallization from ethyl acetate:petroleum ether provided 7,7'-dimethoxy-2,2'-binaphthol **104** as white crystals (0.610 g, 56%).

**M.p**. 148-149 °C (Lit.[48] 144-146 °C)

**$^{1}$H-NMR (400 MHz, CDCl$_3$):** δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.06 (dd, *J* =2.8, 9.2 Hz, 2H), 6.50 (d, *J* = 2.4 Hz, 2H), 5.09 (s, 2H for –OH), 3.60 (s, 6H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 159.08 (Cq), 153.33 (Cq), 134.70 (Cq), 131.14 (CH), 130.02 (CH), 124.77 (Cq), 116.04 (CH), 115.11 (CH), 110.05 (Cq), 103.10 (CH), 55.16 (-O$\underline{C}$H$_3$).

***2,12-dimethoxy-7-oxa-[5]-helicene (105):***



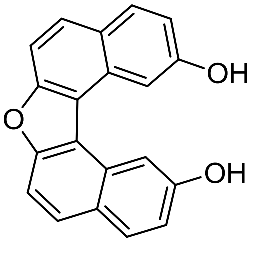
A solution of 7,7'-dimethoxy-2,2'-binaphthol **104** (0.13 g, 0.37 mmol) in toluene (20 mL) was refluxed in the presence of *p*-TsOH (80 mg, 0.37 mmol) for 24 h. After quenching with saturated potassium carbonate solution, the crude product was extracted with ethyl acetate. Column chromatography purification on silica gel using petroleum ether:ethylacetate (100:00 to 80:20) as gradient for elution followed by crystallization from ethylacetate:petroleum ether to obtain 2,12-dimethoxy-7-oxa-[5]- helicene **105** (0.070 g, 57% yield) as a white powder.

**M.p**. 178-179 °C (Lit.[48] 160-165 °C)

**$^{1}$H-NMR (400 MHz, CDCl$_3$):** δ 8.48 (d, *J* = 2.4 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.24 (dd, *J* = 2.4, 9.2 Hz, 2H).

**$^{13}$C-NMR (400 MHz, CDCl$_3$):** δ 157.94 (Cq), 154.79 (Cq), 130.23 (CH), 129.80 (Cq), 127.79 (CH), 126.29 (Cq), 118.64 (Cq), 114.97 (CH), 110.24 (CH), 107.22 (CH), 55.72 (-O$\underline{C}$H$_3$).

***2,12-Dihydroxy-7-oxa-[5]-helicene (105):***



A solution of 2,12-dimethoxy-7-oxa-[5]- helicene **105** (0.330 g, 1.0 mmol) and aqueous solution of HBr (0.244 g, 0.508 mL, 48% w/v, 3.0 mmol) in glacial acetic acid (20 mL) was refluxed for 24 h. After quenching with saturated potassium carbonate solution, the crude product was extracted with ethyl acetate. Column chromatography purification on silica gel using petroleum ether:ethylacetate (100:00 to 70:30) as gradient for elution followed by crystallization from ethylacetate to obtain 2,12-dihydroxy-7-oxa-[5]- helicene **106** (0.250 g, 83% yield) as a white powder.

**$^1$H-NMR (400 MHz, $CDCl_3$ + drop of DMSO-*d*$^6$):** δ 9.43 (s, 2H for -OH), 8.57 (d, *J* = 7.6 Hz, 2H), 7.96-7.84 (m, 4H), 7.67-7.61 (m, 2H), 7.21-7.17 (m, 1H).

**$^{13}$C-NMR (100.6 MHz, $CDCl_3$ + drop of DMSO-*d*$^6$):** δ 155.66 (Cq), 154.45 (Cq), 131.18 (CH), 129.83 (Cq), 128.00 (CH), 125.66 (Cq), 118.22 (Cq), 116.21(CH), 109.52 (CH), 109.35 (CH).

**MS (EI)**: *m/z*, (%) 301 (10), 300 (100), 271 (06), 213 (09), 149 (03)120 (03), 113 (10), 111 (03), 109 (03), 106 (04), 83 (04).

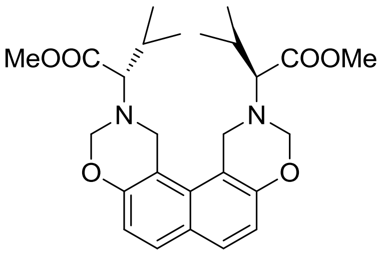
# X-ray Crystal Data

The details of the X-ray structure are deposited at the Cambridge Crystallographic Data Centre Crystal Data for **Compound 99 (*CCDC-882285*)** and the details can be obtained via: www.ccdc.cam.ac.uk/data_request/cif.

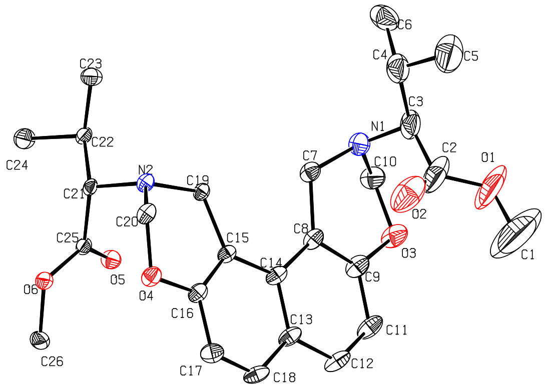
***Crystal Data for Compound 11 (CCDC-882285)***

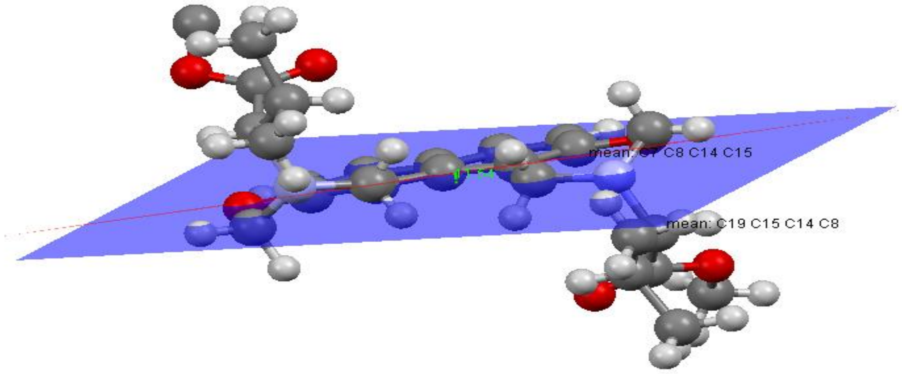
| **Details** | **Compound 99** |
|---|---|
| Empirical formula | $C_{26}H_{31}N_2O_6$ |
| Formula weight | 467.53 |
| Temperature | 110(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Tetragonal |
| Space group | P43 |
| Unit cell dimensions | a = 17.0527(7) Å<br>b = 17.0527(7) Å<br>c = 8.4671(7) Å<br>$\alpha = 90°$<br>$\beta = 90°$<br>$\gamma = 90°$ |
| Volume | 2462.2(2) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.261 $Mg/m^3$ |
| Absorption coefficient ($\mu$) | 0.090 $mm^{-1}$ |
| F(000) | 996 |
| Crystal Size | 0.43x0.37x0.29 mm |
| $\theta$ range for data collection | 1.69-28.28° |
| Reflections collected | 14632 |
| Independent reflections | 5685 [R(int) = 0.0294] |
| Max. and Min. transmission | 0.9744 and 0.9624 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5685 / 1 / 409 |
| Goodness-of-fit on $F^2$ | 1.081 |
| Final R indices [I>2sigma(I)] | R1 = 0.0669<br>wR2 = 0.1597 |
| R indices (all data) | R1 = 0.0751<br>wR2 = 0.1650 |
| Largest difference peak and hole | 0.624 and - 0.217 e/ $Å^3$ |

**Structure of the compound 99**.



ORTEP Diagram of compound **99** with the atomic numbering scheme. Ellipsoids are drawn at the 30% probability level for non-H atoms, and the H atoms are omitted for clarity.

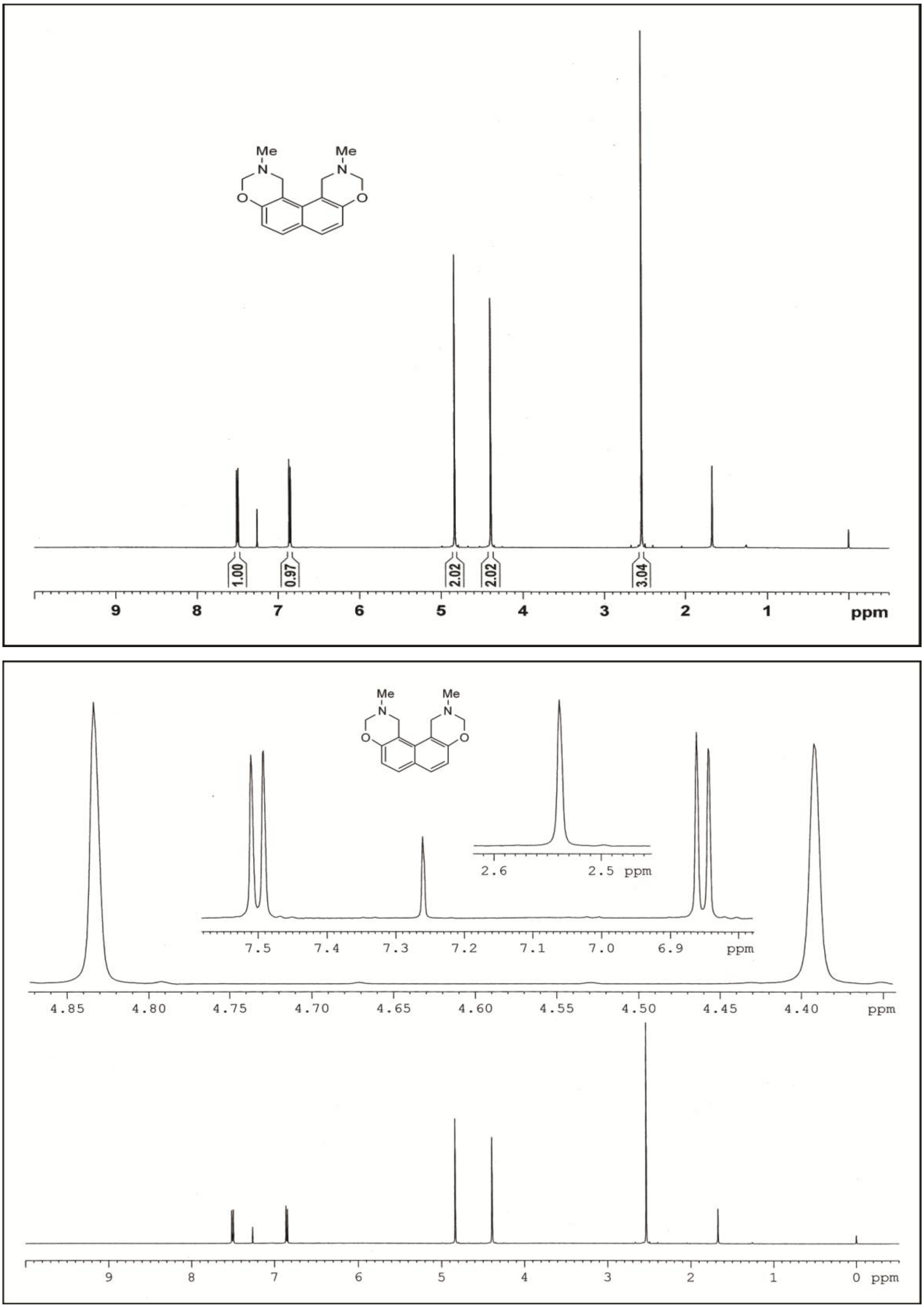




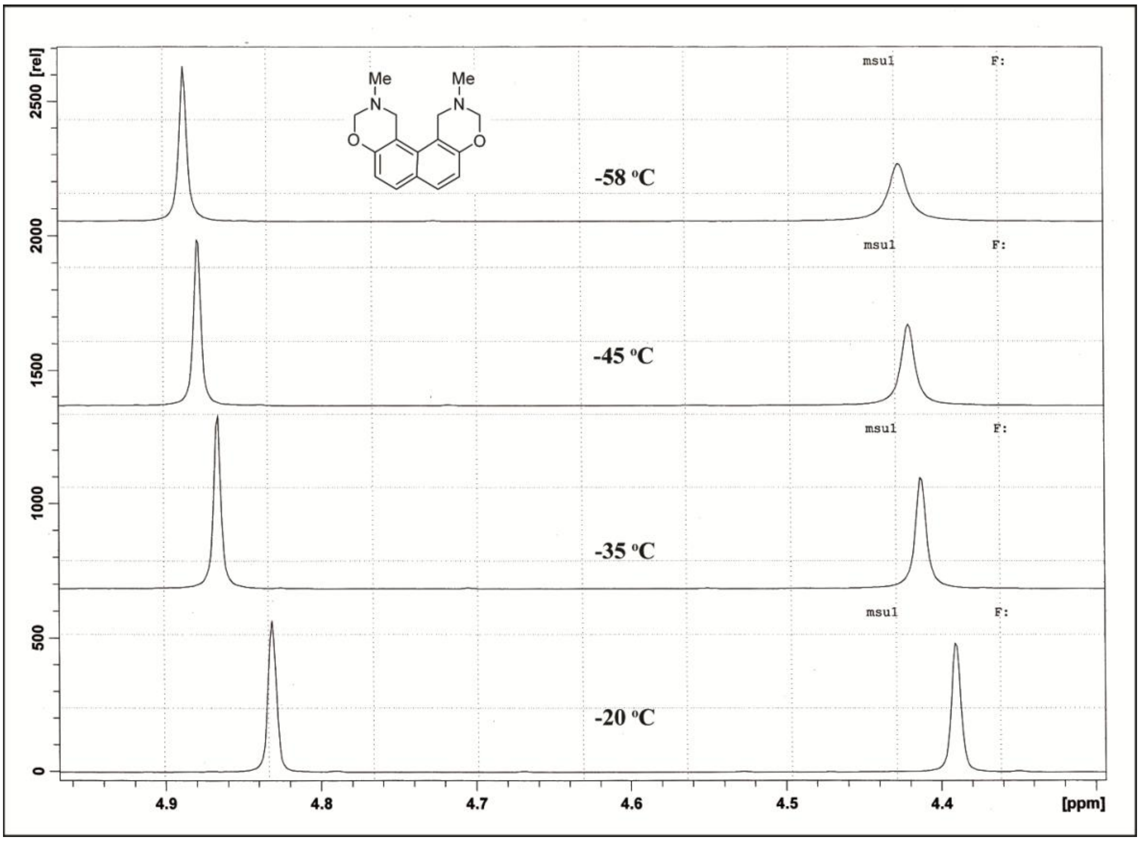
The measurement of the plane showing the twist in the conformations of oxazines, angle between the planes passing through the C7-C8-C14-C15 and C19-C15-C14-C8 is near about 11.54°.

# Spectral Data

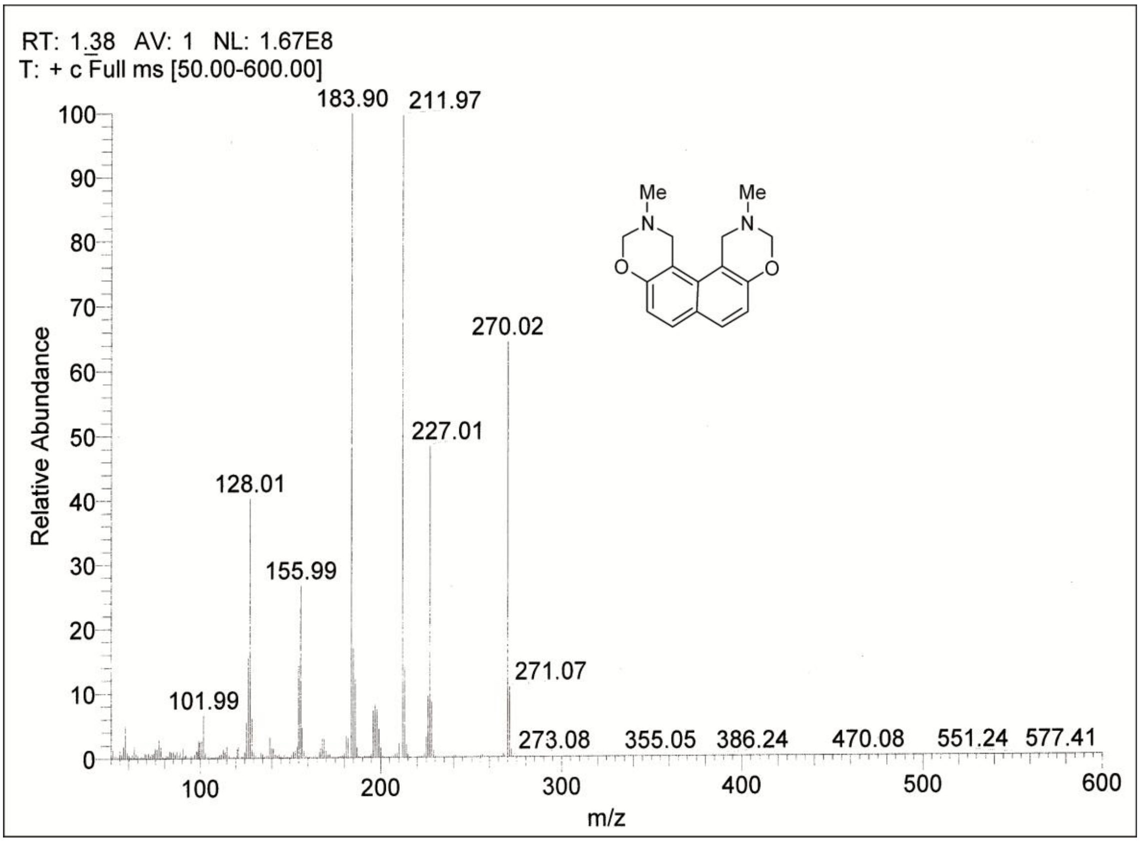
## Spectral data of 2,11-dimethyl-2,3,11,12-tetrahydro-1H,10H,-4,9-dioxa-2,11-diaza-benzo[c]phenanthrene (94)



**$^1$H-NMR spectrum of 2,11-Dimethyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (94) in $CDCl_3$ on 400 MHz**

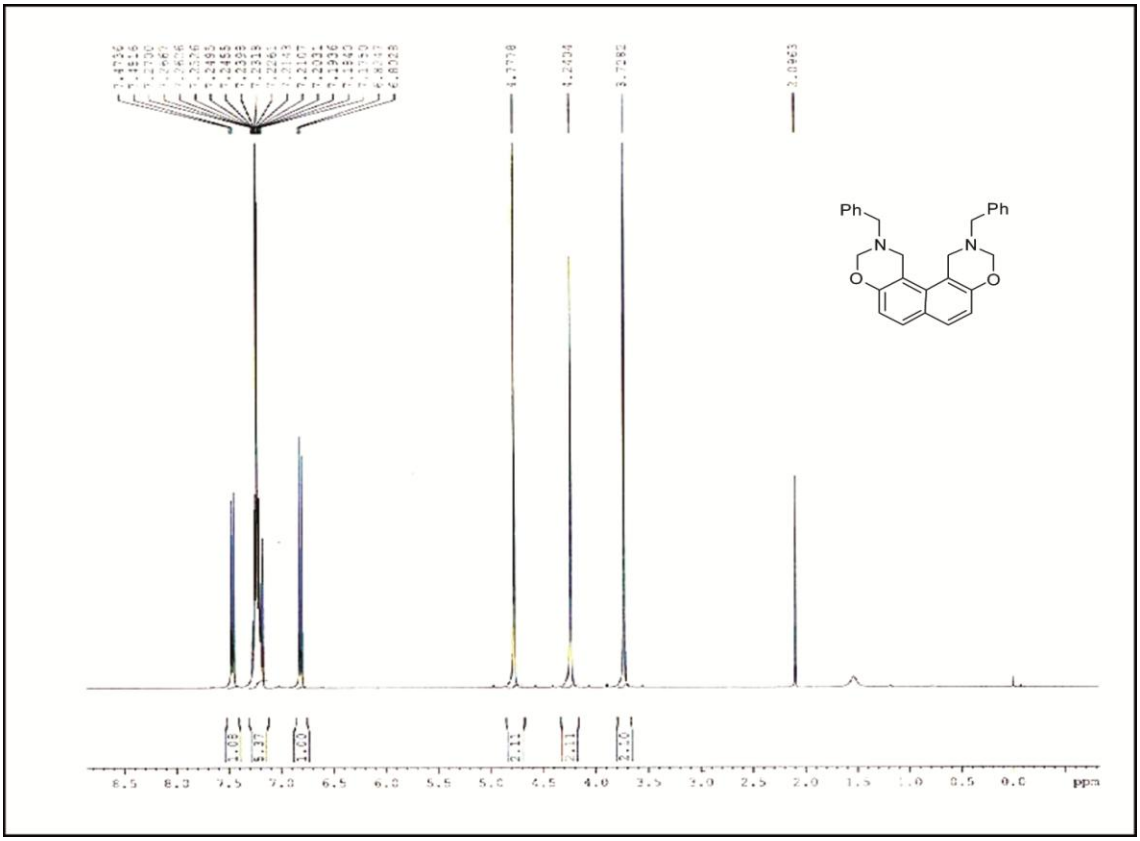


**Variable temperature $^1$H-NMR spectrum of 2,11-Dimethyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (94) in $CDCl_3$ on 400 MHz**

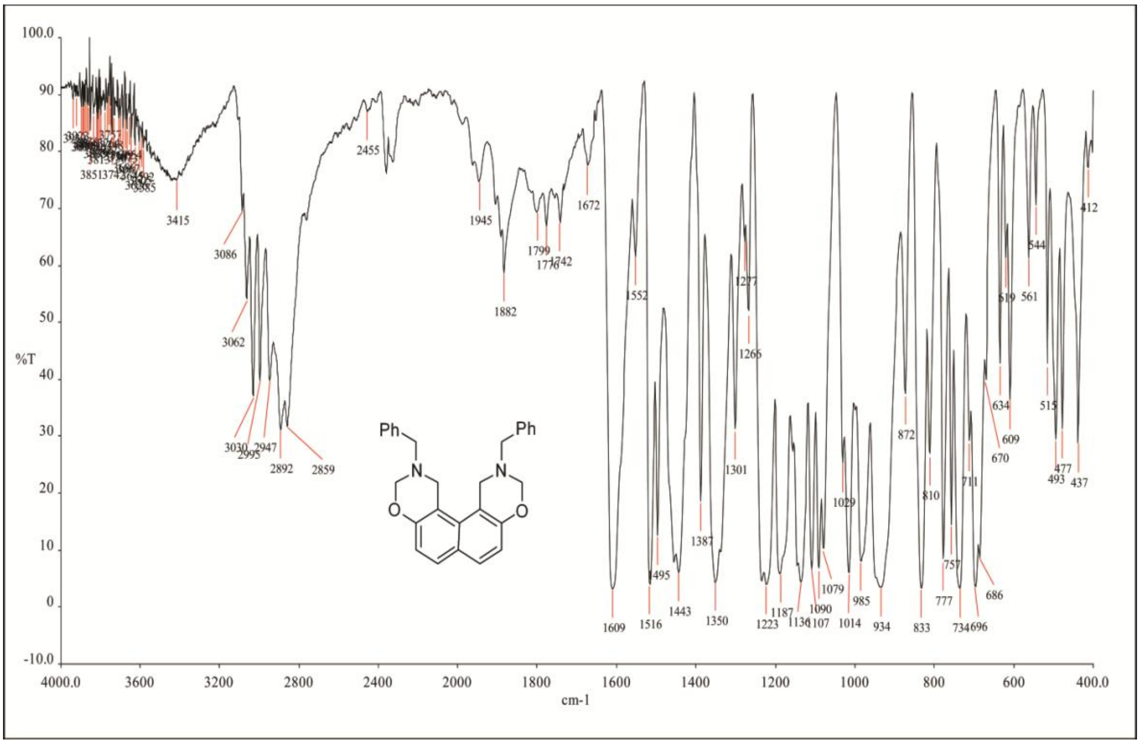


**EI-Mass spectrum of 2,11-Dimethyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (94)**

## Spectral data of 2,11-dibenzyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (95)

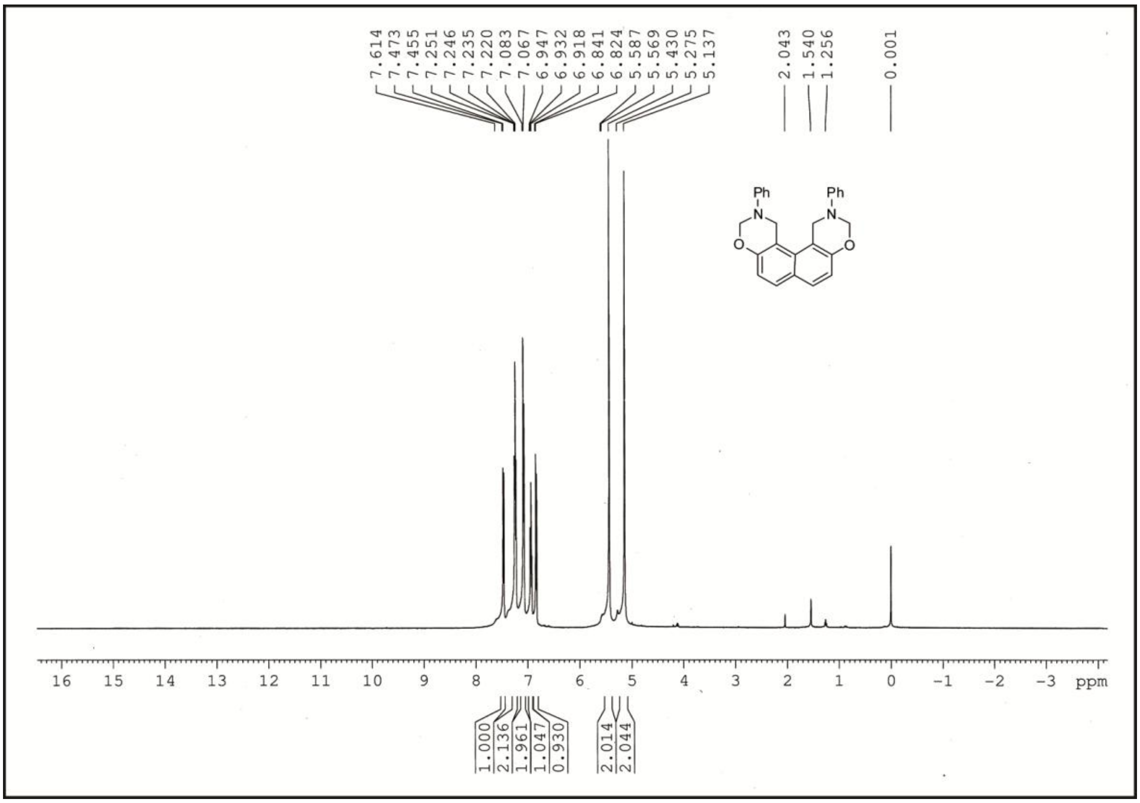


**$^1$H-NMR spectrum of 2,11-dibenzyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (95) in $CDCl_3$ on 400 MHz**

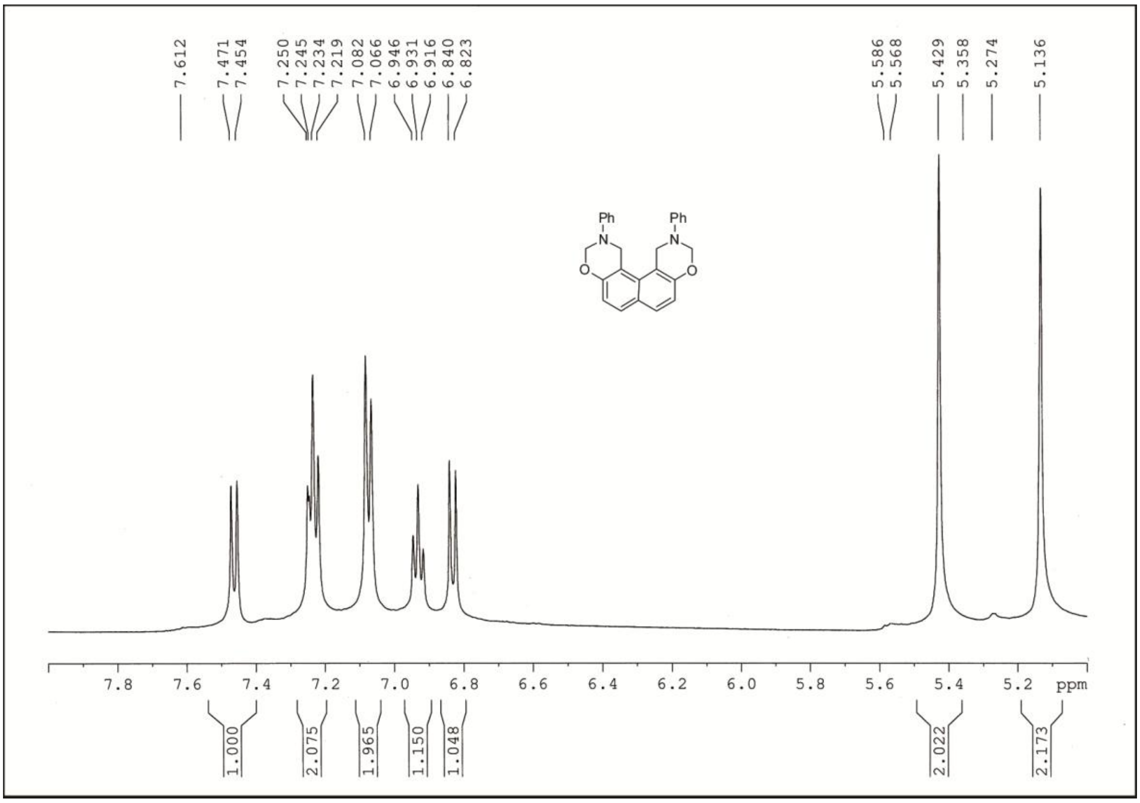


**IR spectrum of 2,11-dibenzyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (95)**

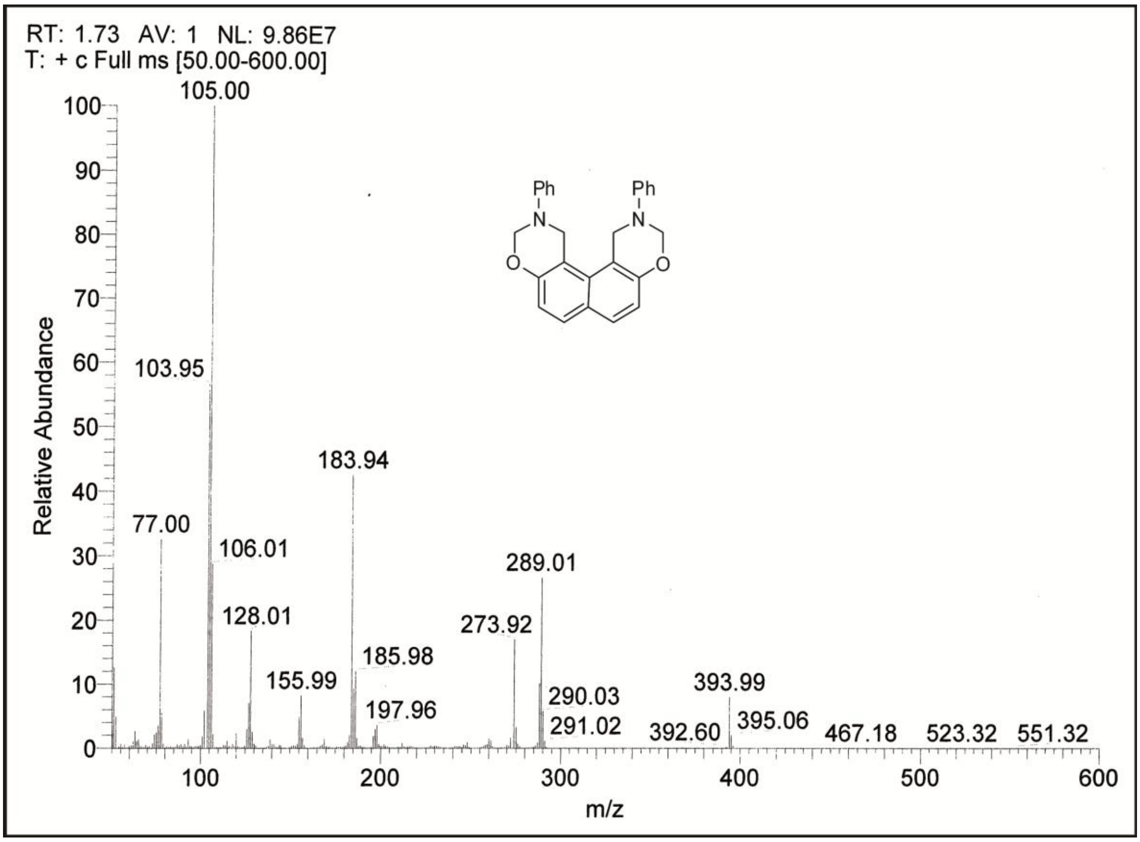
## Spectral data of 2,11-diphenyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (96)



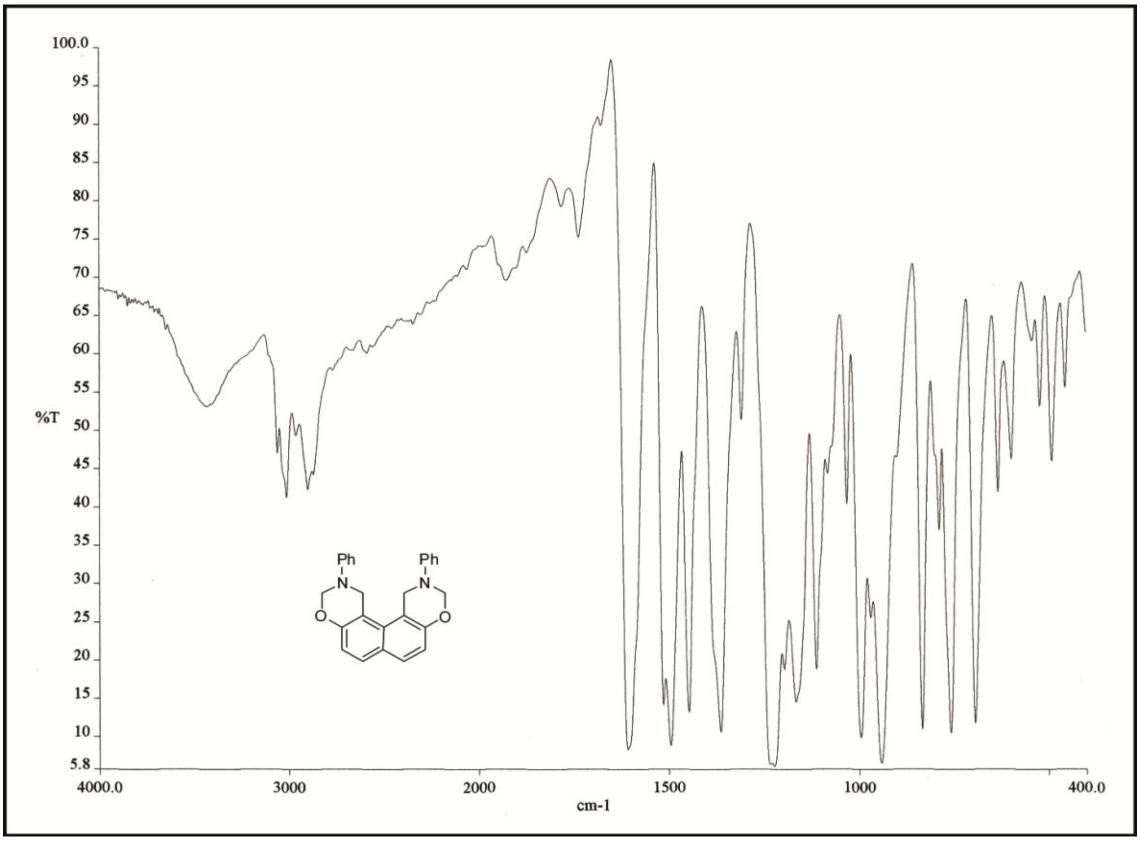
**$^{1}$H-NMR spectrum of 2,11-diphenyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (96) in CDCl$_3$ in 400 MHz**



**$^{1}$H-NMR enlarge spectrum of 2,11-diphenyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (96) in CDCl$_3$ in 400 MHz**

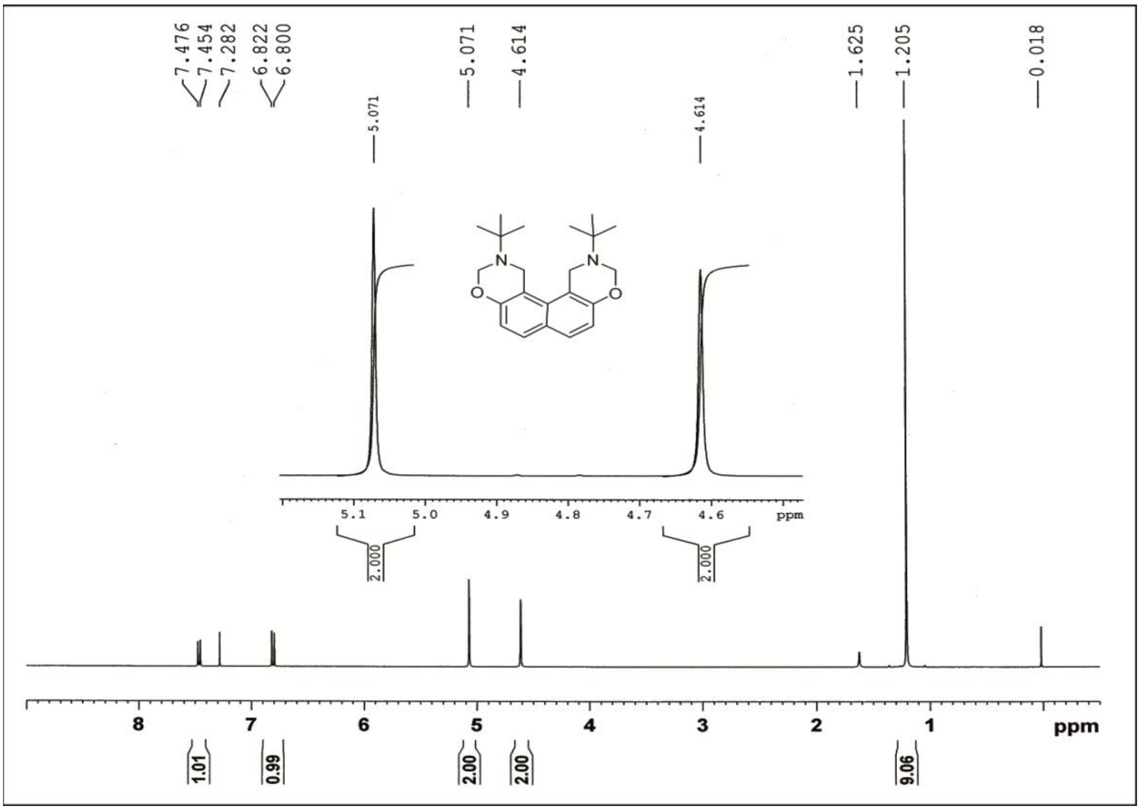


**EI-Mass spectrum of 2,11-diphenyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (96)**

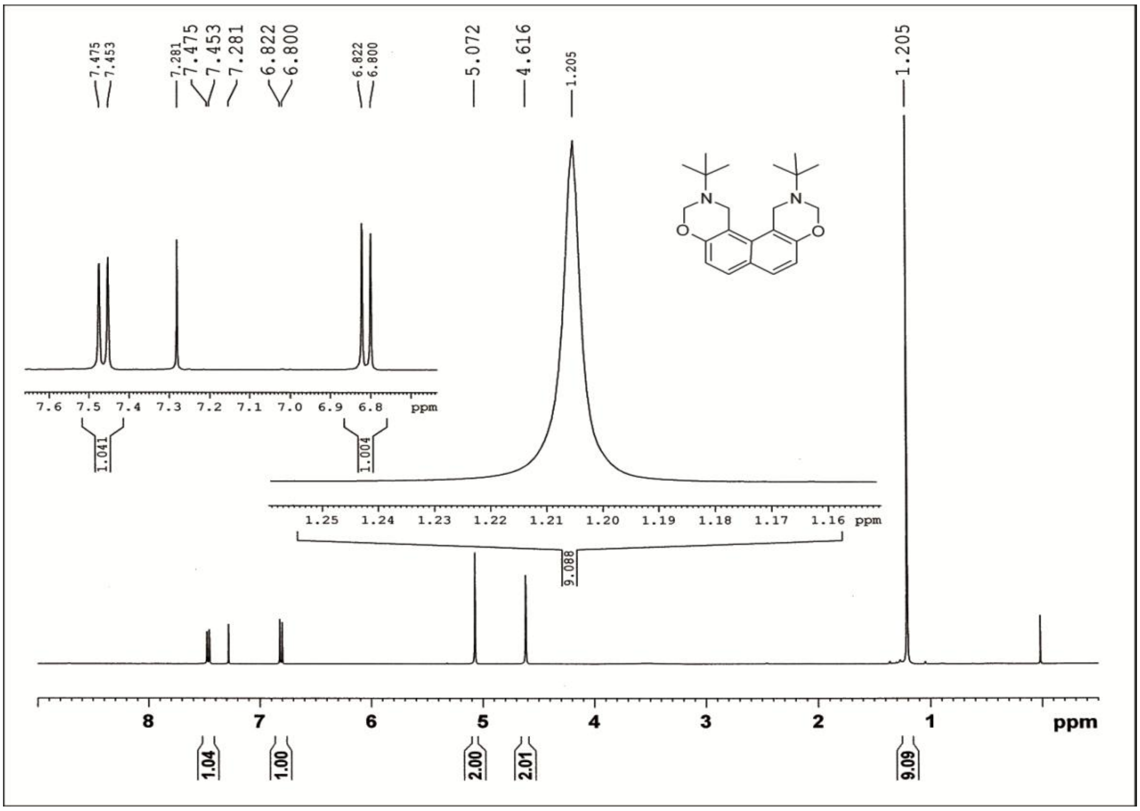


**IR spectrum of 2,11-diphenyl-2,3,11,12-tetrahydro-1*H*,10*H*,-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (96)**

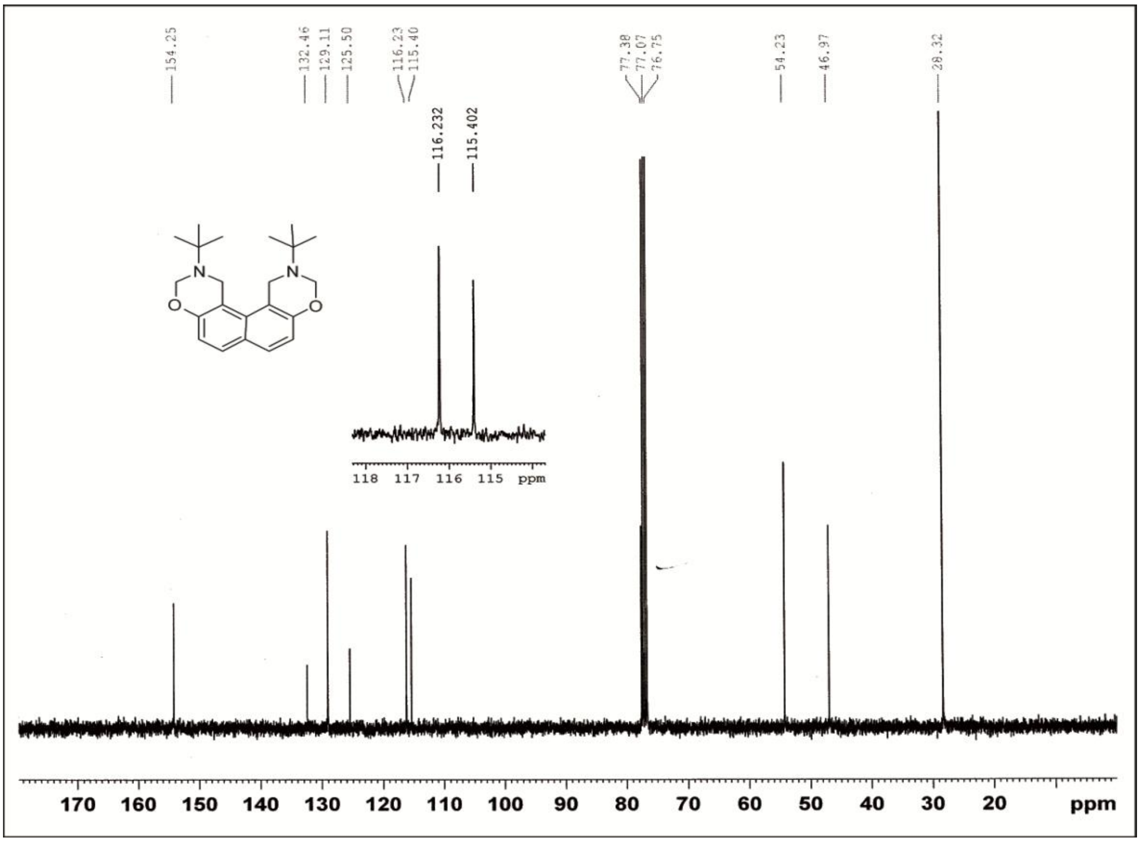
## Spectral data of 2,11-di-*tert*-butyl-2,3,11,12-tetrahydro-1*H*,10*H*-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (97)



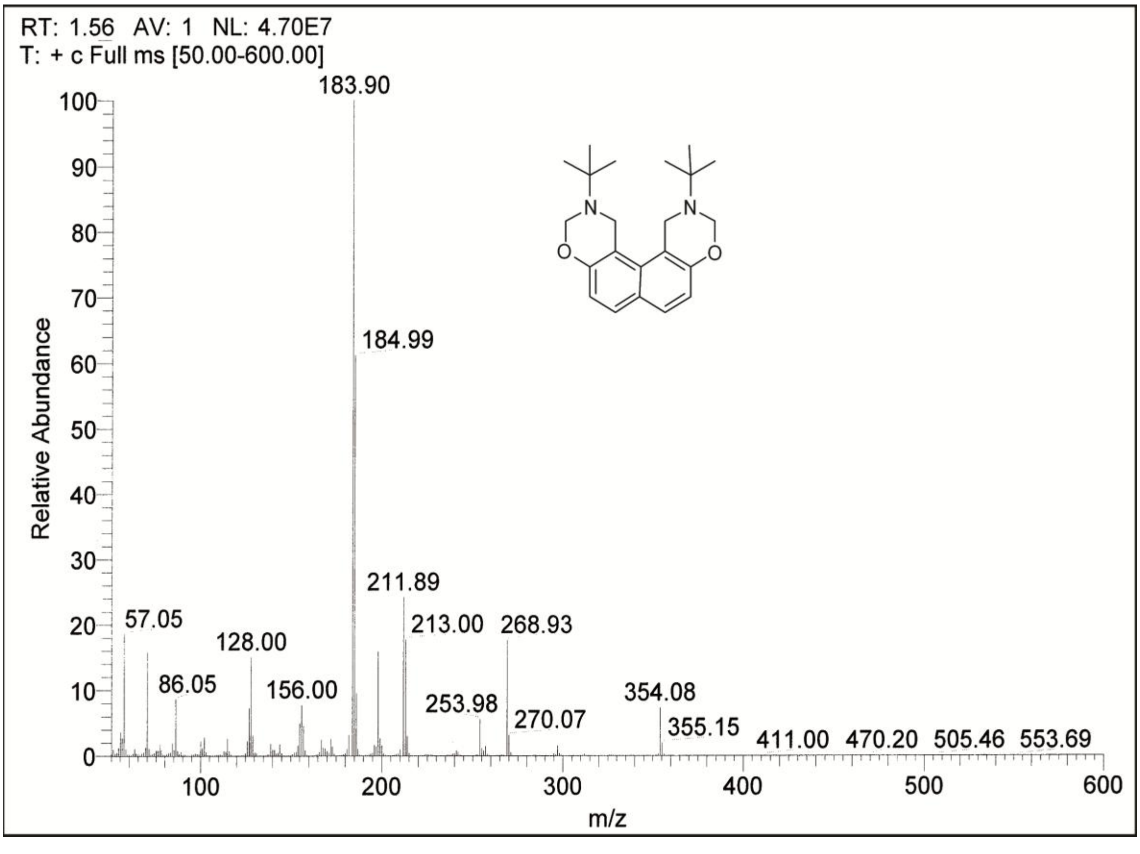
**$^1$H-NMR spectrum of 2,11-di-*tert*-butyl-2,3,11,12-tetrahydro-1*H*,10*H*-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (97) in $CDCl_3$ on 400 MHz**



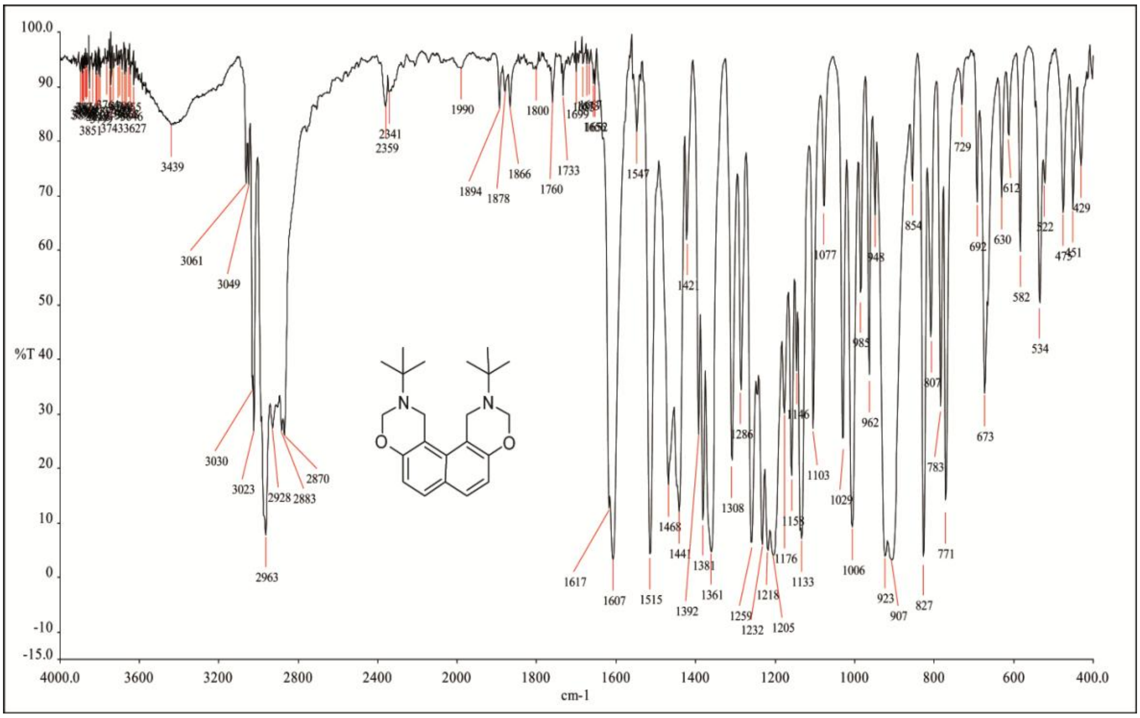
**$^1$H-NMR spectrum of 2,11-di-tert-butyl-2,3,11,12-tetrahydro-1*H*,10*H*-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (97) in $CDCl_3$ on 400 MHz**



**$^{13}$C-NMR spectrum of 2,11-di-*tert*-butyl-2,3,11,12-tetrahydro-1*H*,10*H*-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (97) in $CDCl_3$ on 100.6 MHz**

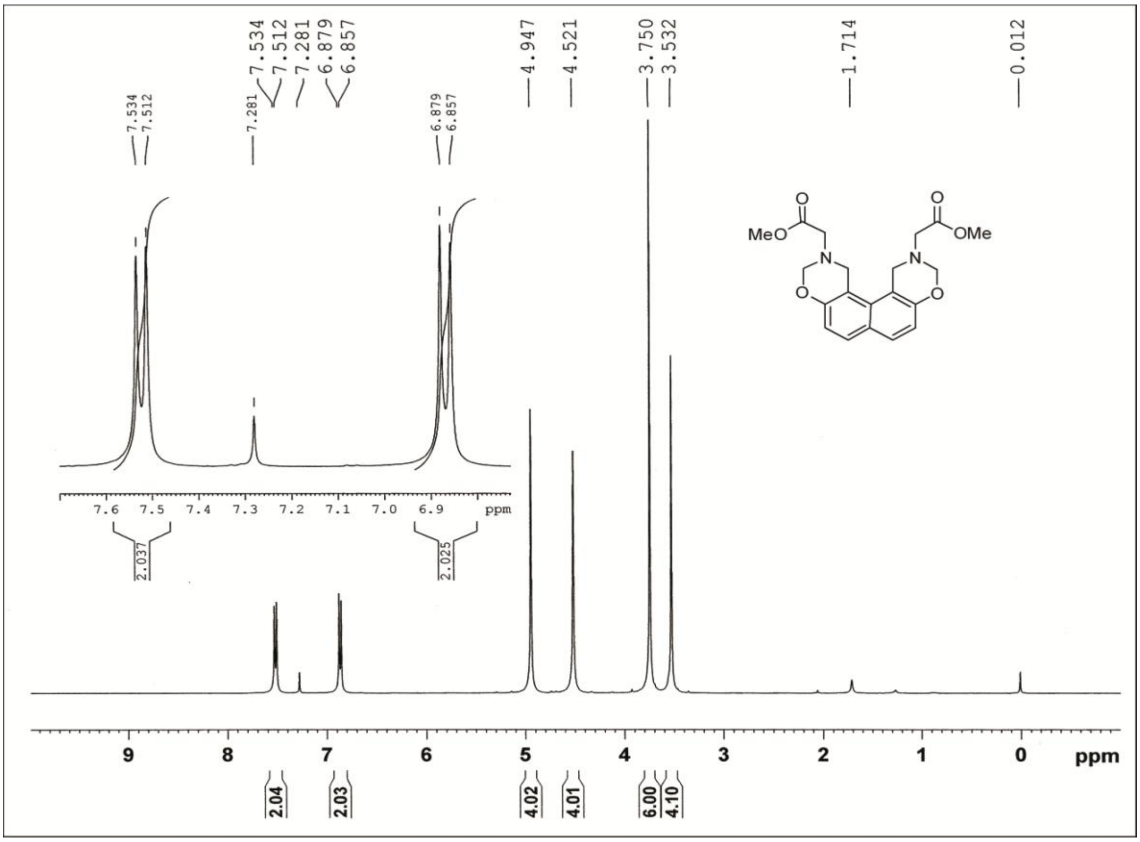


**EI-Mass spectrum of 2,11-di-*tert*-butyl-2,3,11,12-tetrahydro-1*H*,10*H*-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (97)**

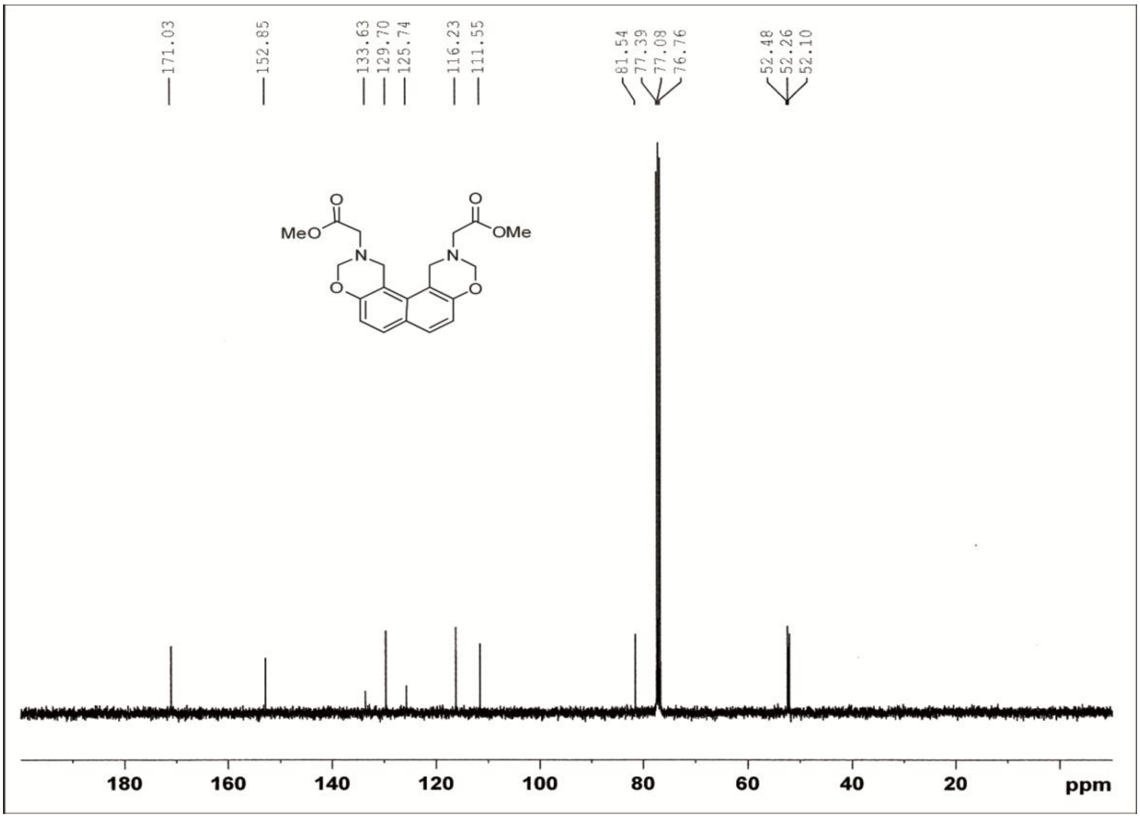


**IR spectrum of 2,11-di-*tert*-butyl-2,3,11,12-tetrahydro-1*H*,10*H*-4,9-dioxa-2,11-diaza-benzo[*c*]phenanthrene (97)**

## Spectral data of dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)diacetate (98)

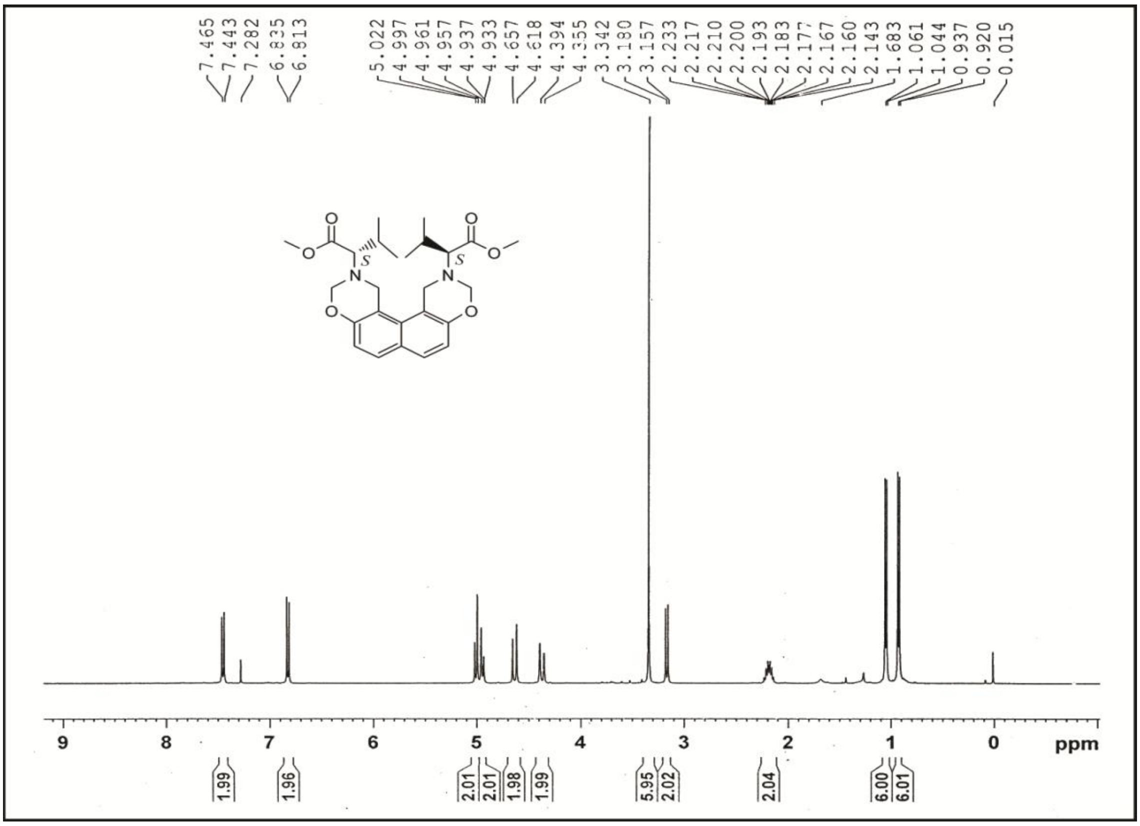


**$^1$H-NMR spectrum of dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)diacetate (98) in $CDCl_3$ on 400 MHz**

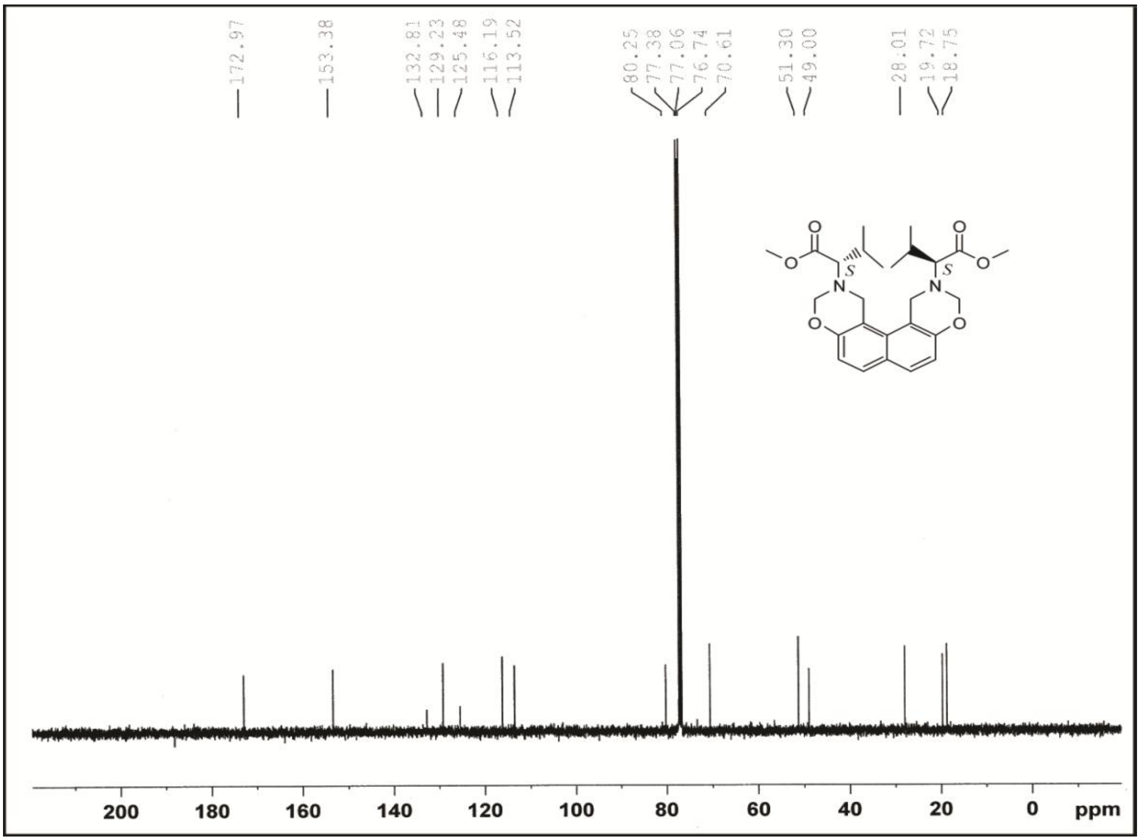


**$^{13}$C-NMR spectrum of dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)diacetate (98) in CDCl$_3$ on 100.6 MHz**

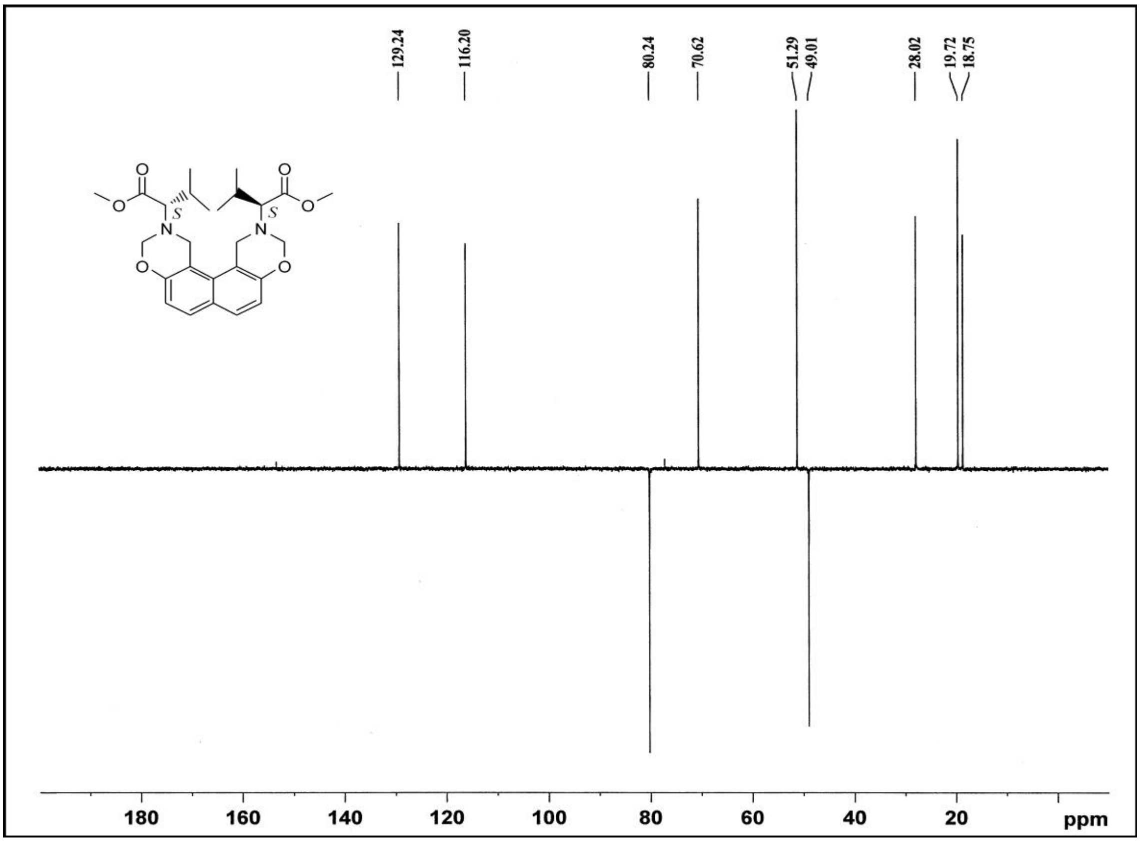
### Spectral data of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) (99)



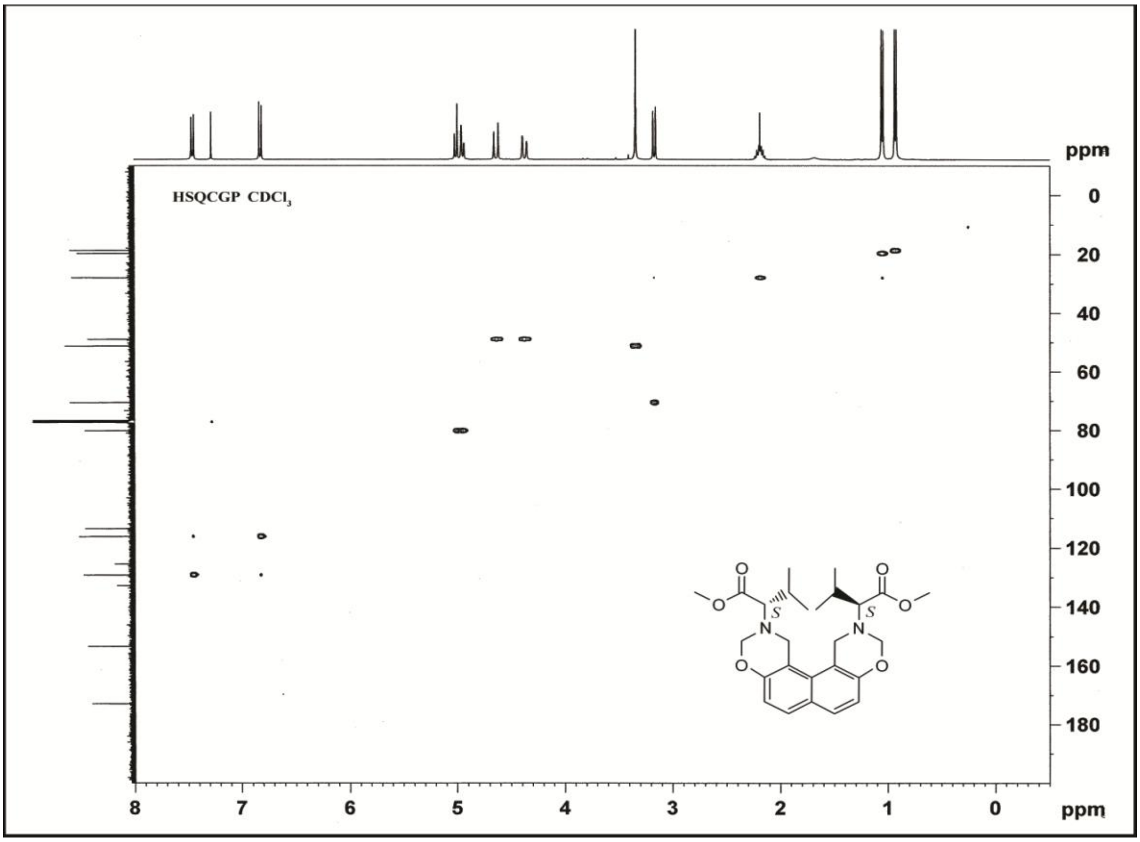
**$^{1}$H-NMR spectrum of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) (99) in CDCl$_3$ on 400 MHz**



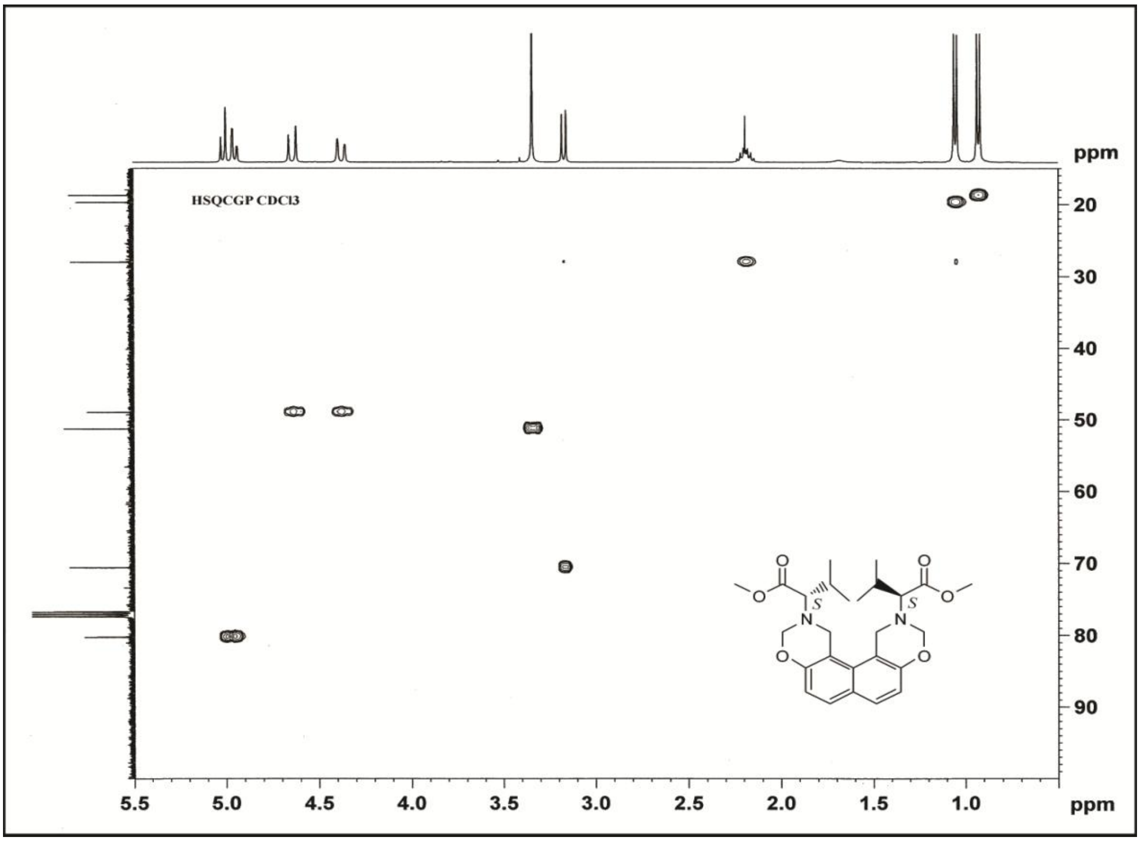
$^{13}$C-NMR spectrum of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) (99) in $CDCl_3$ on 100.6 MHz



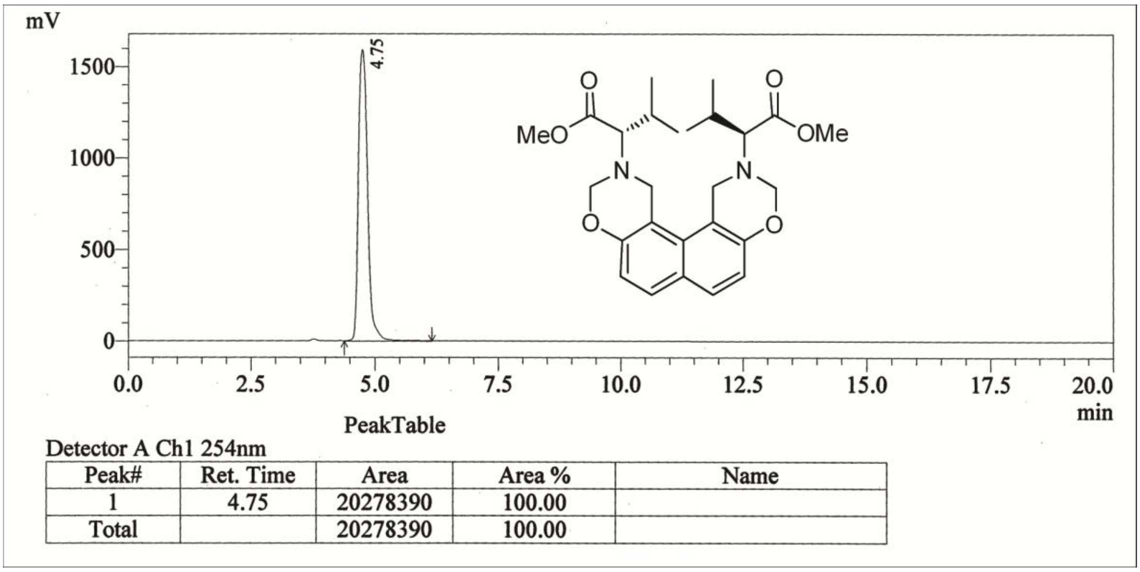
$^{13}$C-NMR DEPT-135 spectrum of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) (99) in $CDCl_3$ on 100.6 MHz



**$^1$H-$^{13}$C correlation spectrum of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) (99) in $CDCl_3$ on 400 MHz**



**$^1$H-$^{13}$C correlation enlarge spectrum of (2*S*,2'*S*)-dimethyl 2,2'-(naphtho[1,2-*e*:8,7-*e*']bis-([1,3]oxazine)-2,11(1*H*,3*H*,10*H*,12*H*)-diyl)bis(3-methylbutanoate) (99) in $CDCl_3$ on 400 MHz**



Detector A Ch1 254nm

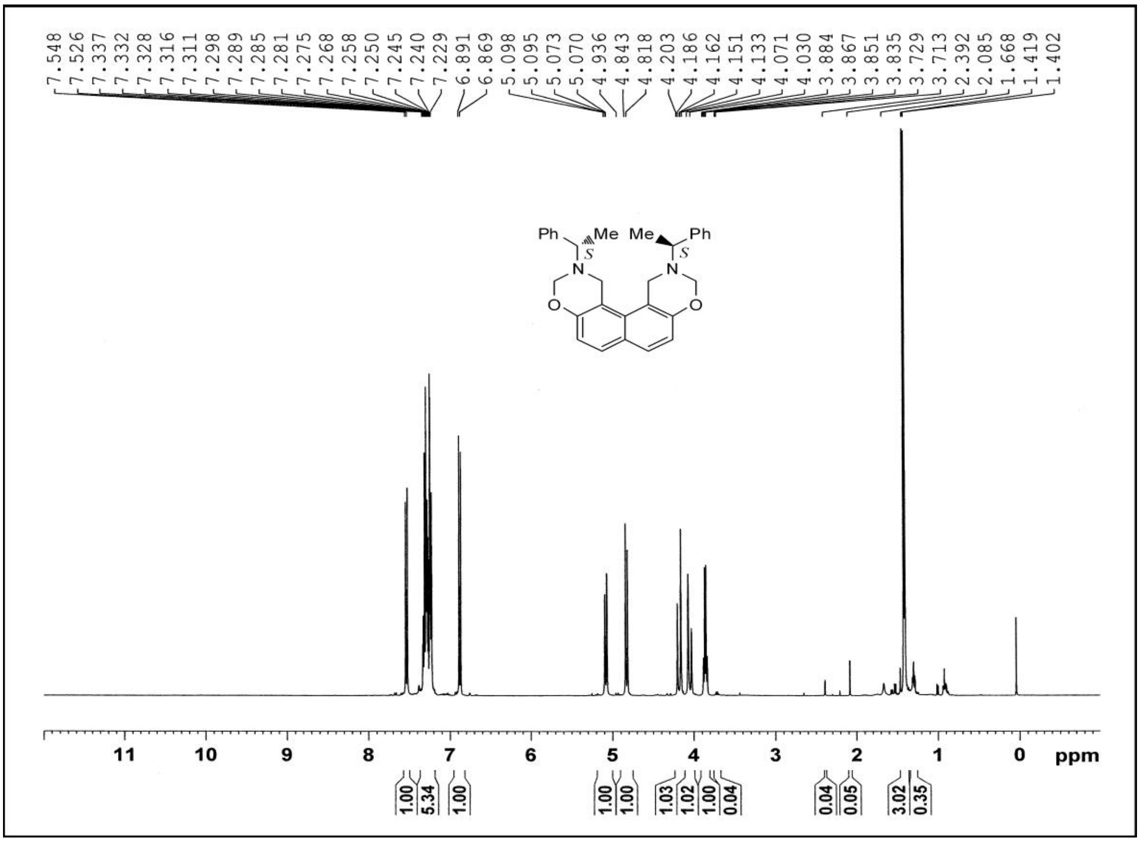
| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 4.75 | 20278390 | 100.00 | |
| Total | | 20278390 | 100.00 | |

**Method For HPLC Analysis**

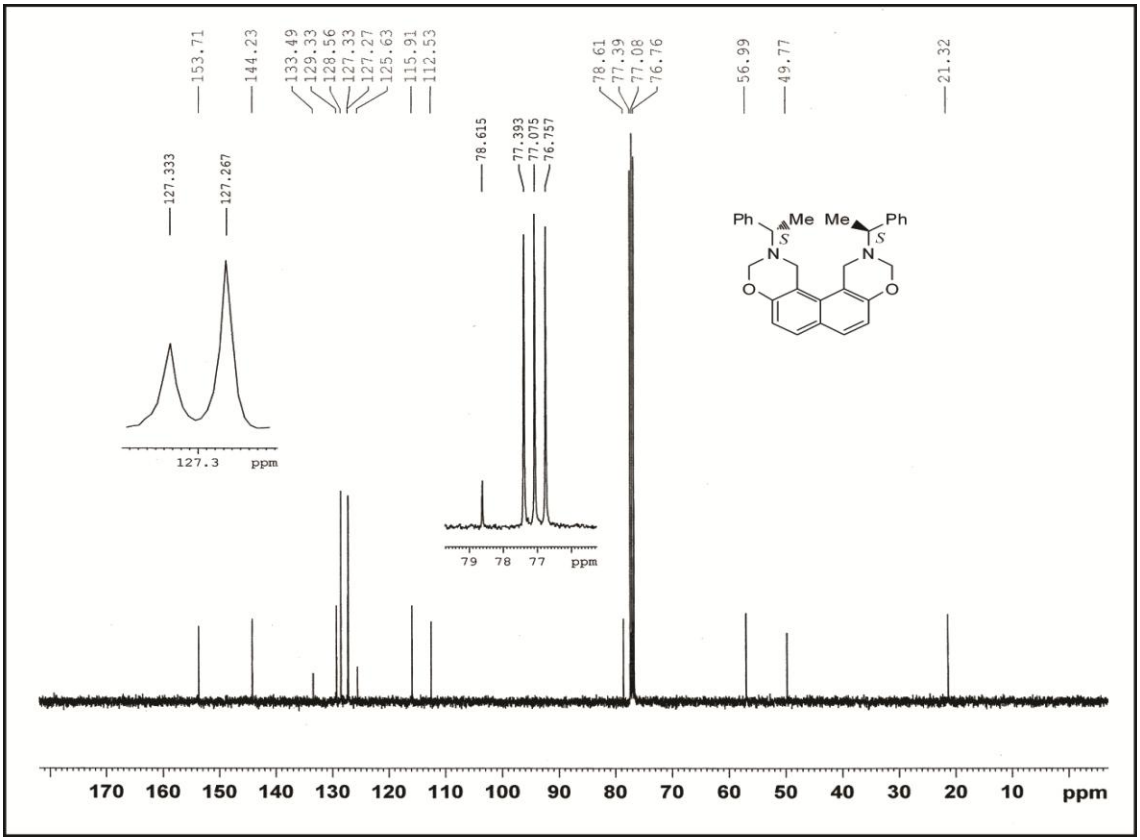
Solvent System: *n*-Hexane: *Iso*-propanol (60:40), Flow rate: 1 mL/min, Injection vol.: 10 μL, Detector: UV-Vis (λ max – 254 nm), Oven Temperature: 27 °C

Chiral Column: Diacel OD-H

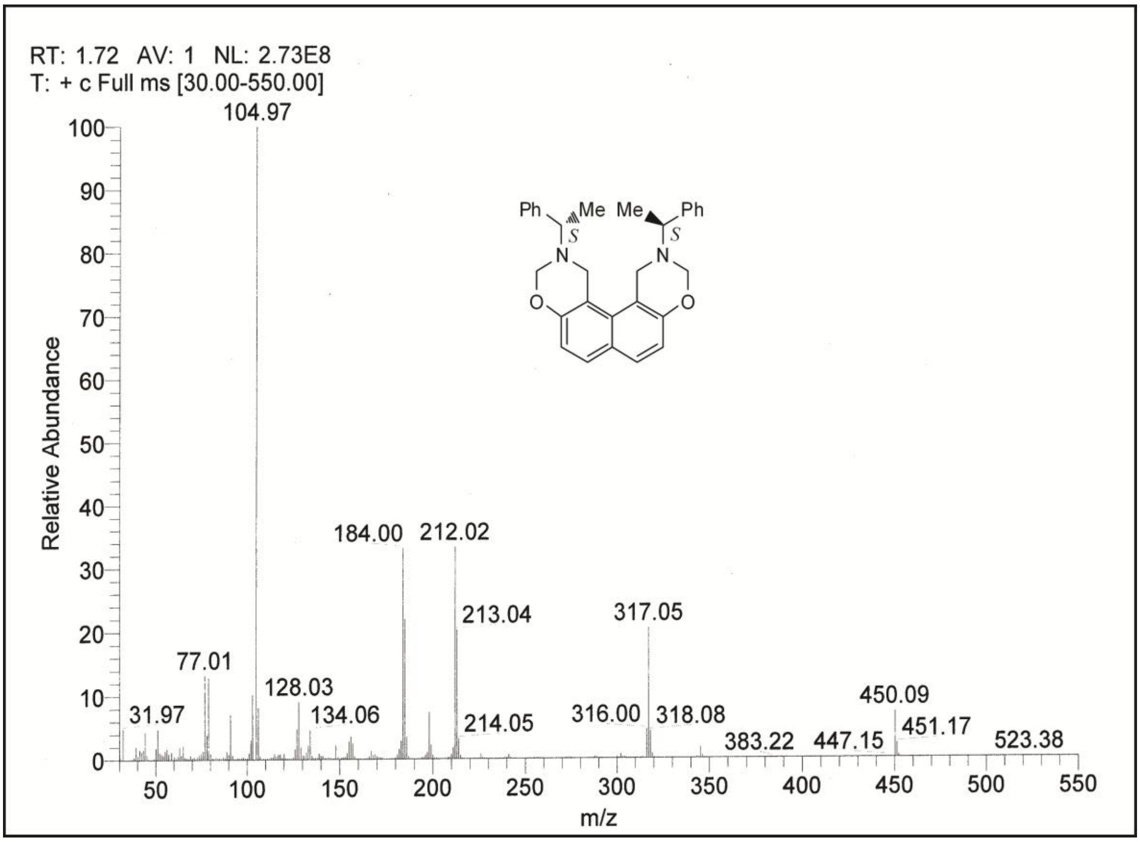
## Spectral data of 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (100)



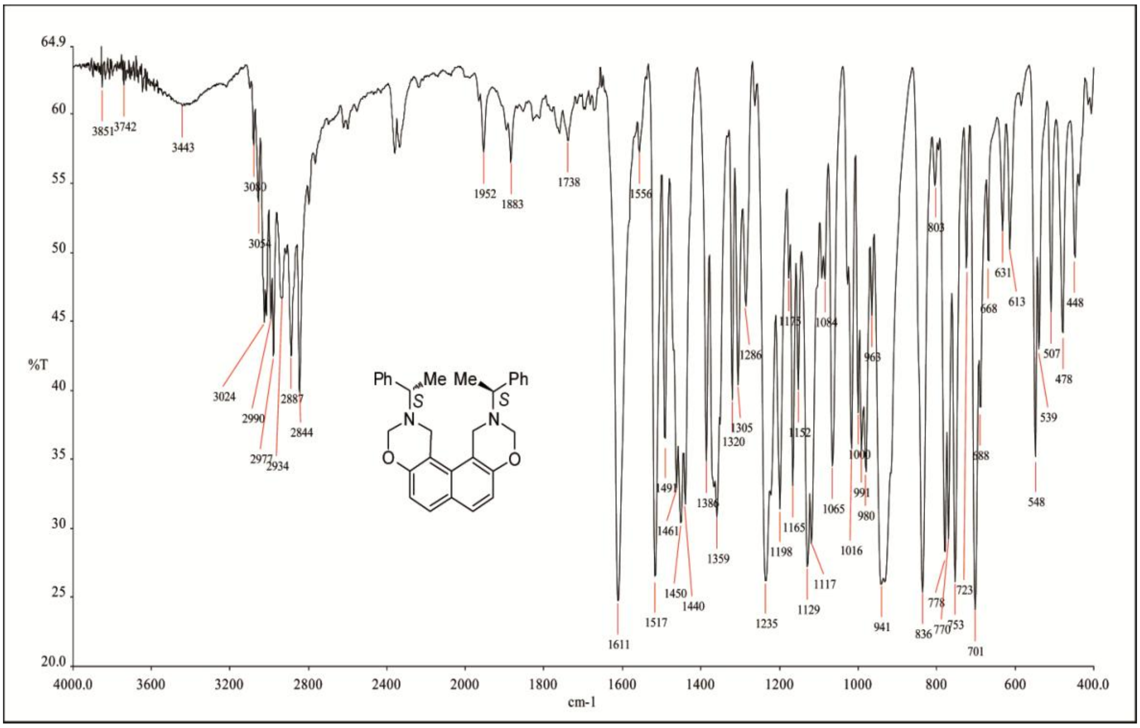
$^1$**H-NMR spectrum of 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (100) in CDCl$_3$ on 400 MHz**



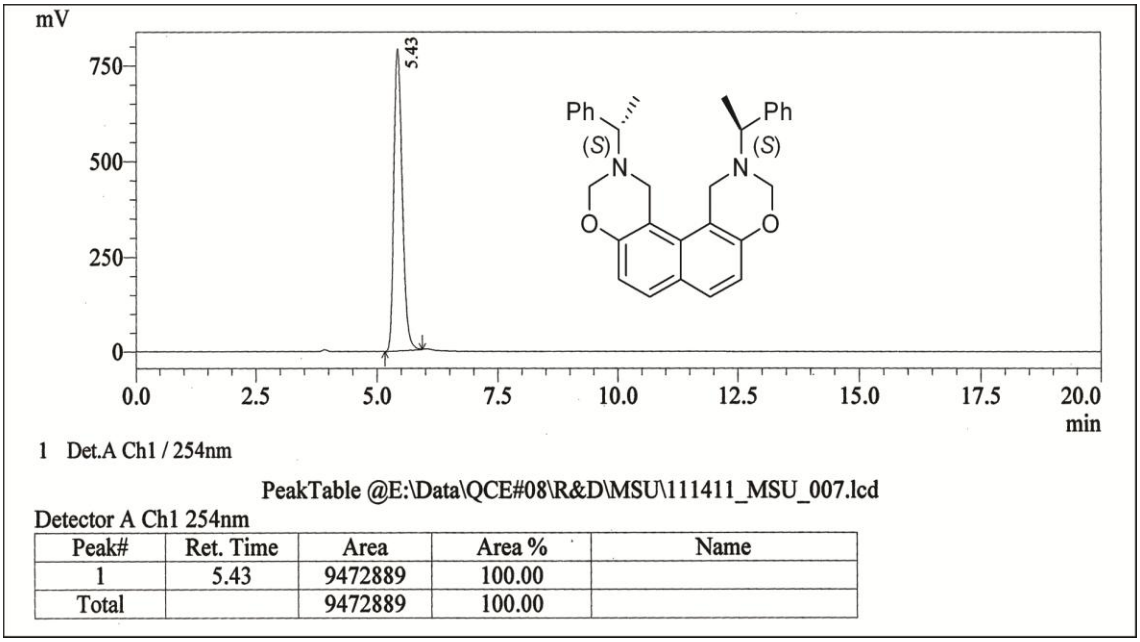
$^{13}$C-NMR spectrum of 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (100) in $CDCl_3$ on 100.6 MHz



EI-Mass spectum of 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (100)



**IR spectum of 2,11-bis((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (100)**



PeakTable @E:\Data\QCE#08\R&D\MSU\111411_MSU_007.lcd

Detector A Ch1 254nm

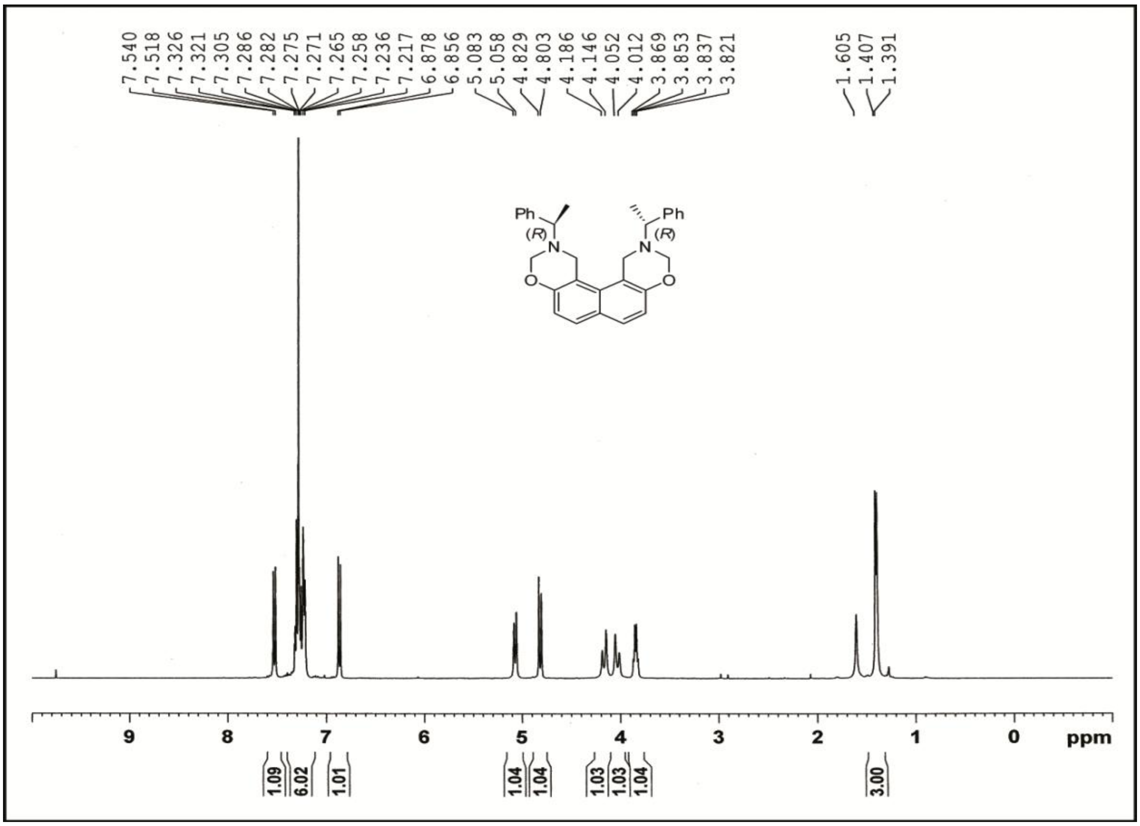
| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 5.43 | 9472889 | 100.00 | |
| Total | | 9472889 | 100.00 | |

**Method For HPLC Analysis**

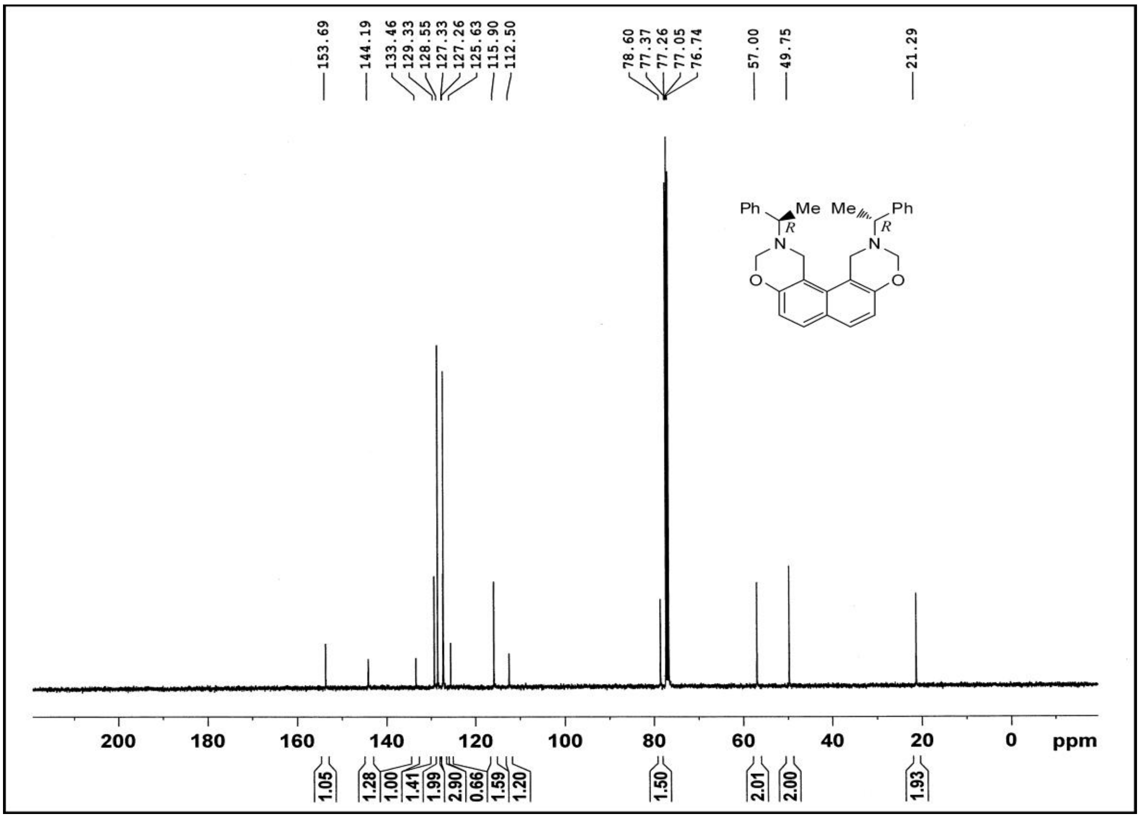
Solvent System: *n*-Hexane: *Iso*-propanol (60:40), Flow rate: 1 mL/min., Injection vol.: 10 μL, Detector: UV-Vis (λ max – 254 nm), Oven Temperature: 27 °C

Chiral Column: Diacel OD-H

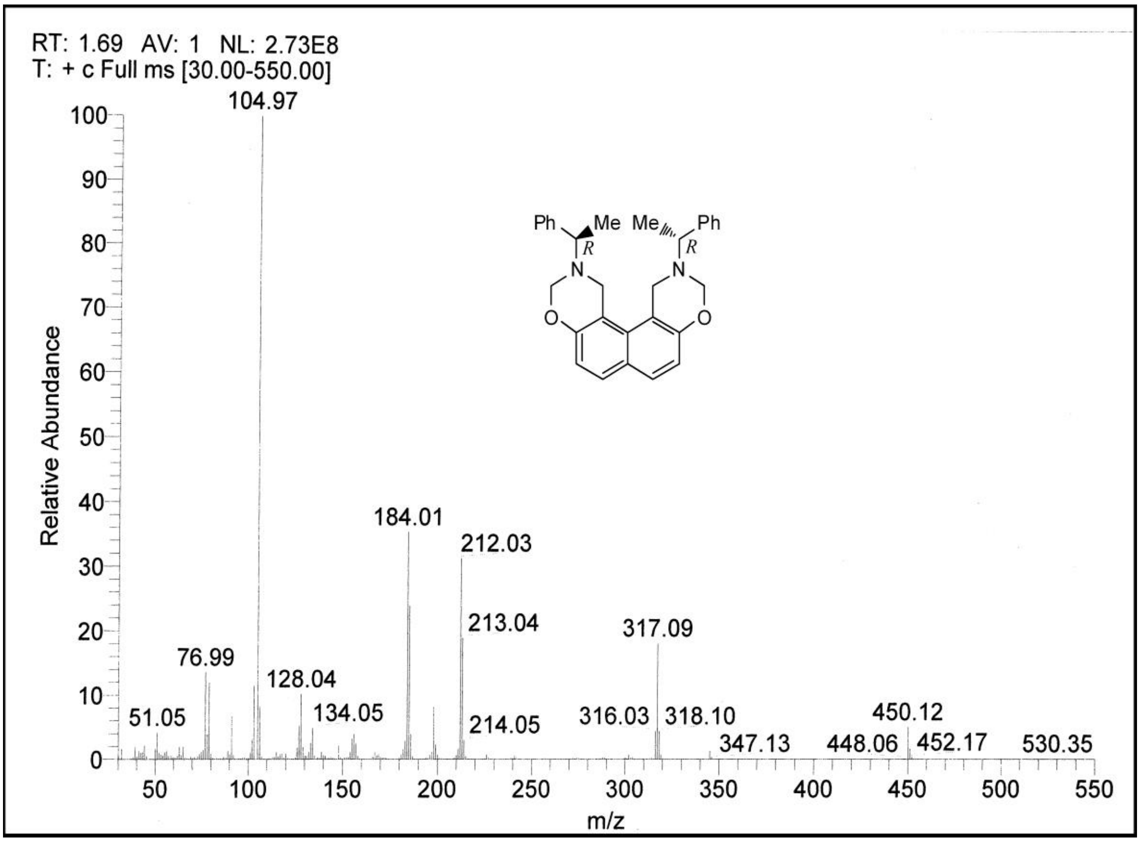
## Spectral data of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (101)



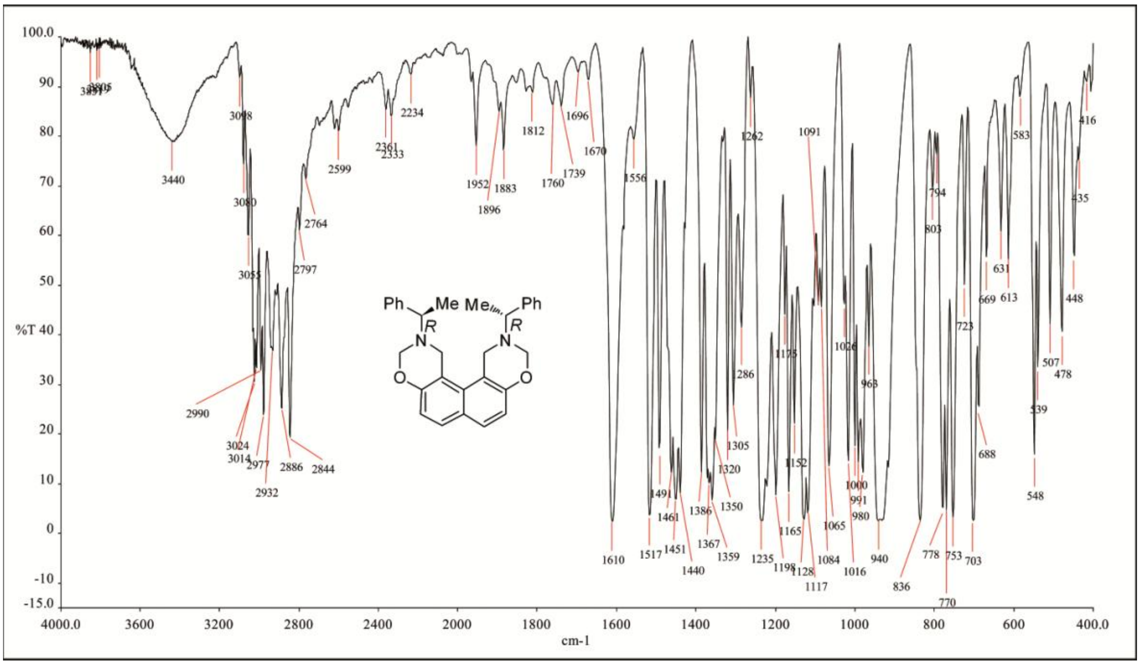
$^1$H-NMR spectrum of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (101) in $CDCl_3$ on 400 MHz



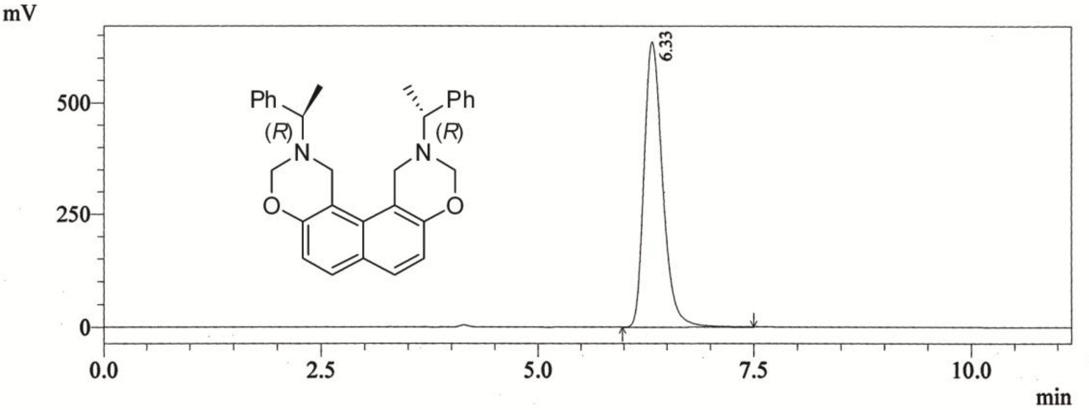
$^{13}$C-NMR spectrum of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (101) in $CDCl_3$ on 100.6 MHz



**EI-Mass spectrum of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (101)**



**IR spectrum of 2,11-bis((*R*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-*e*:8,7-*e*']bis([1,3]oxazine (101)**



1 Det.A Ch1 / 254nm

PeakTable @E:\Data\QCE#08\R&D\MSU\111411_MSU_008.lcd

Detector A Ch1 254nm

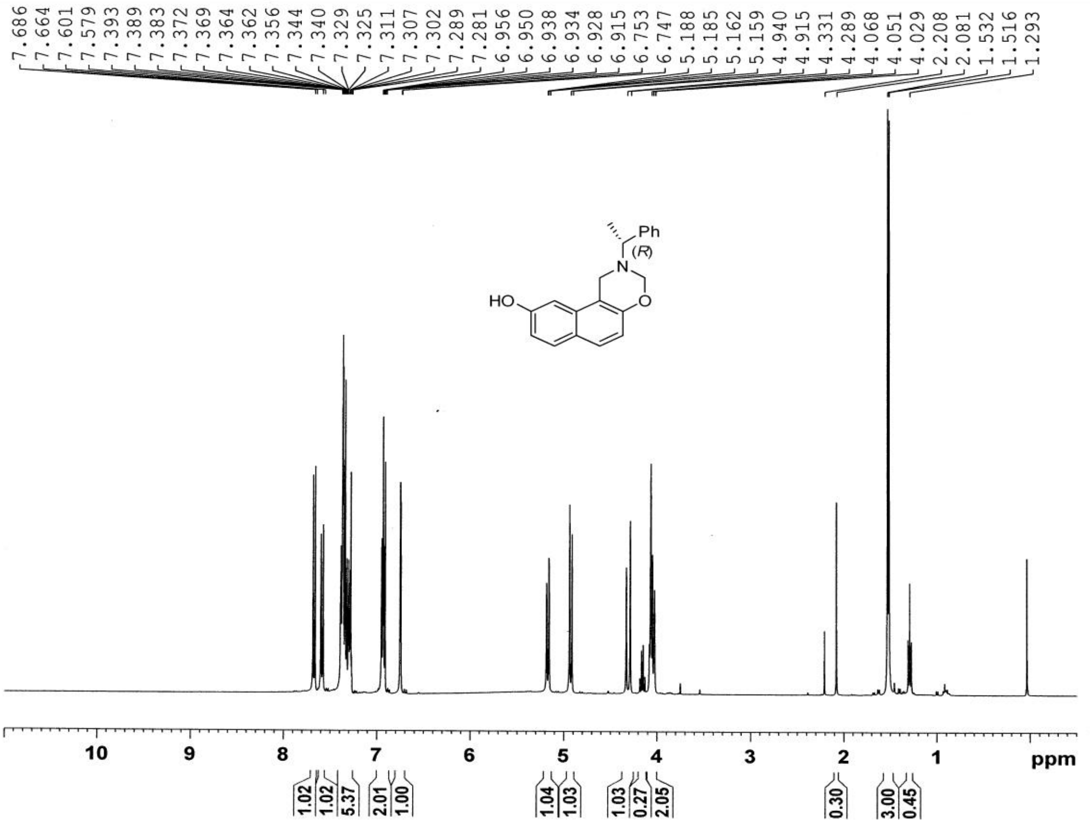
| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6.33 | 9448540 | 100.00 | |
| Total | | 9448540 | 100.00 | |

**Method For HPLC Analysis**

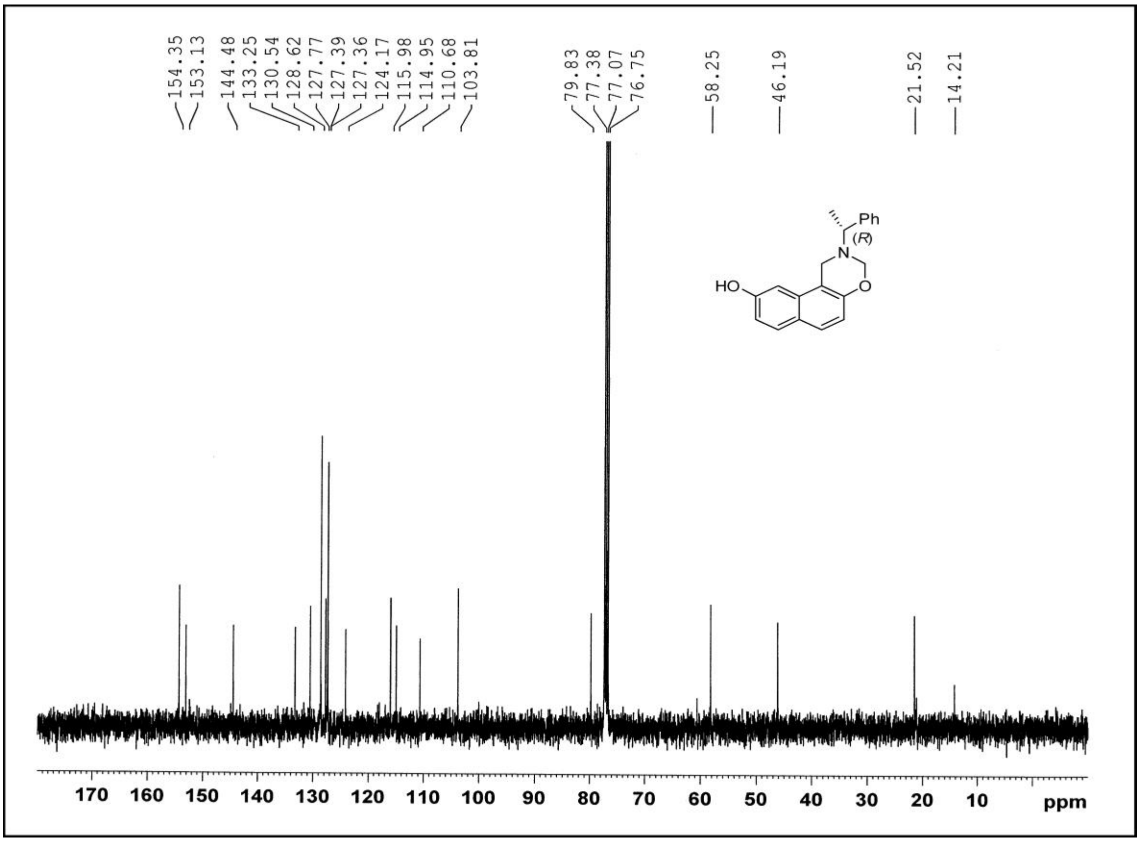
Solvent System: *n*-Hexane: *Iso*-propanol (60:40), Flow rate: 1 mL/min., Injection vol.: 10 µL, Detector: UV-Vis (λ max – 254 nm), Oven Temperature: 27 °C

Chiral Column: Diacel OD-H

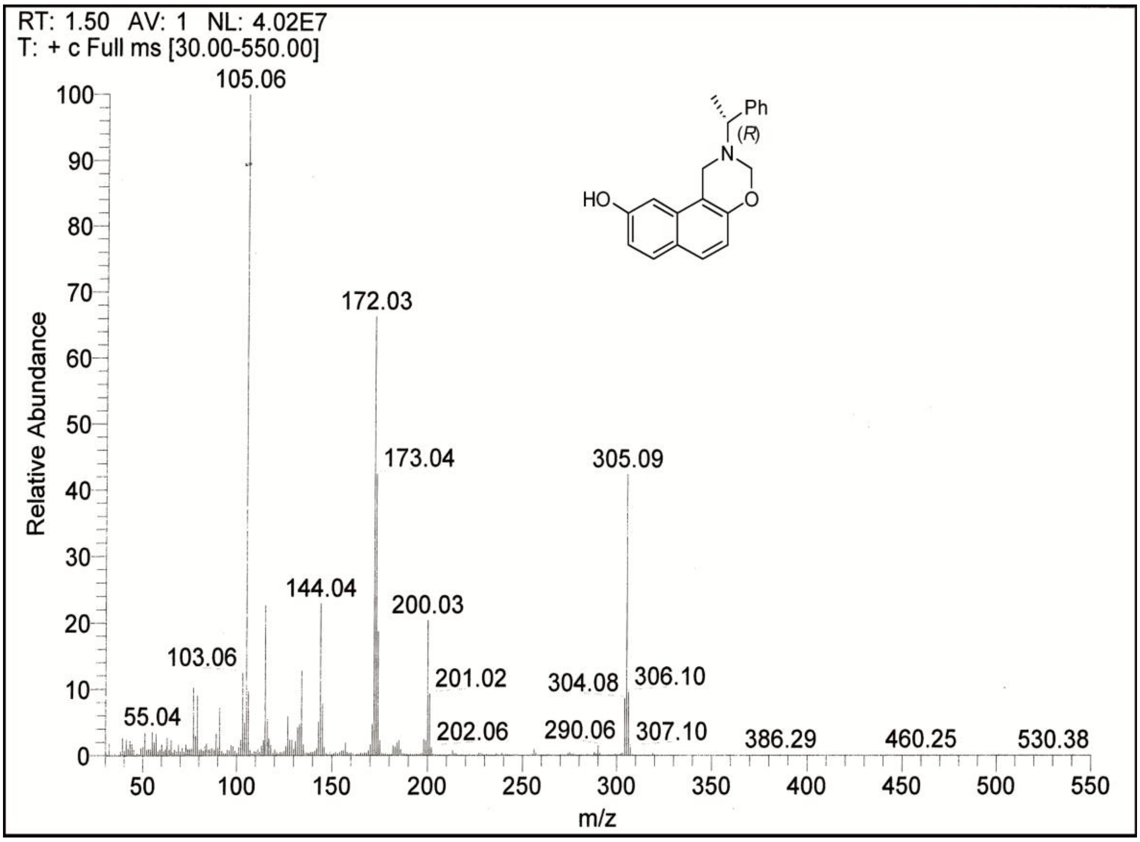
## Spectral data of (*R*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol (102)



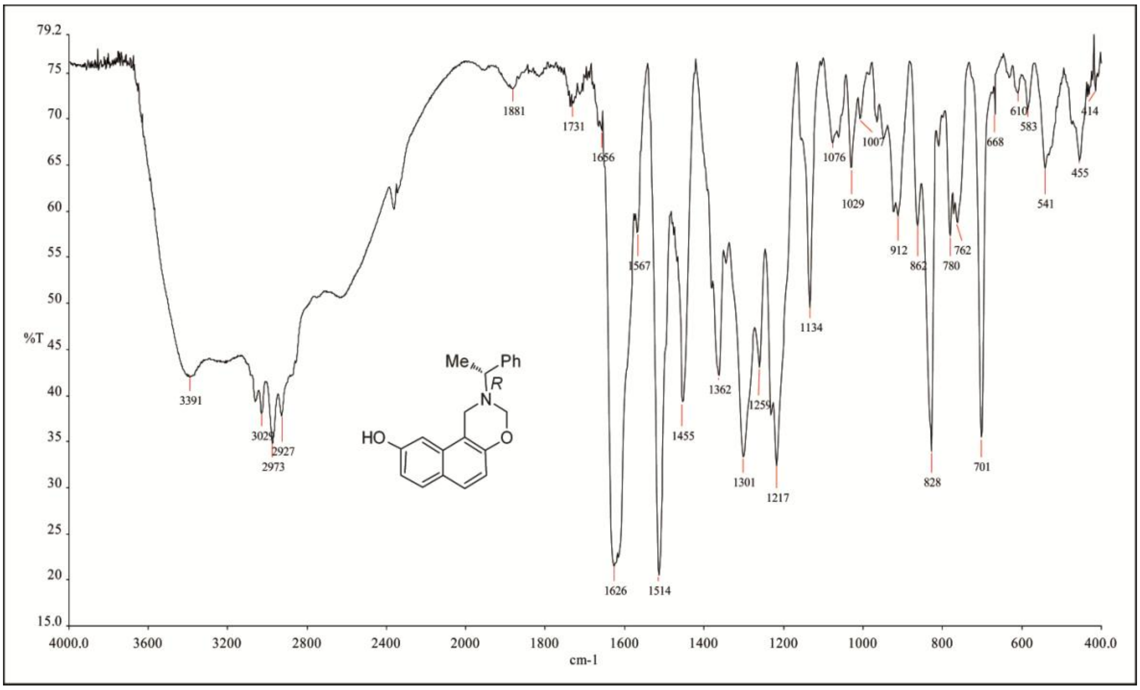
**$^1$H-NMR spectrum of (*R*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol (102) in $CDCl_3$ on 400 MHz**



**$^{13}$C-NMR spectrum of (*R*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol (102) in $CDCl_3$ on 400 MHz**

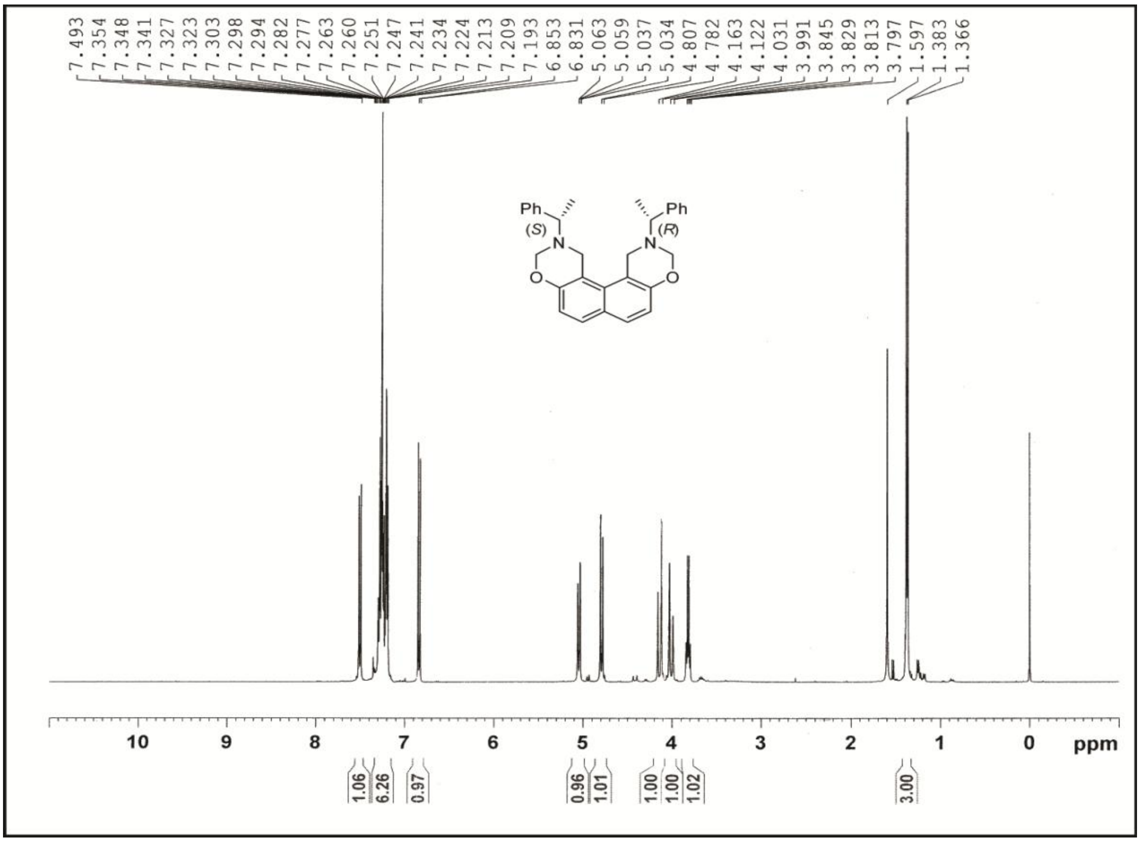


**EI-Mass spectrum of (*R*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol (102)**

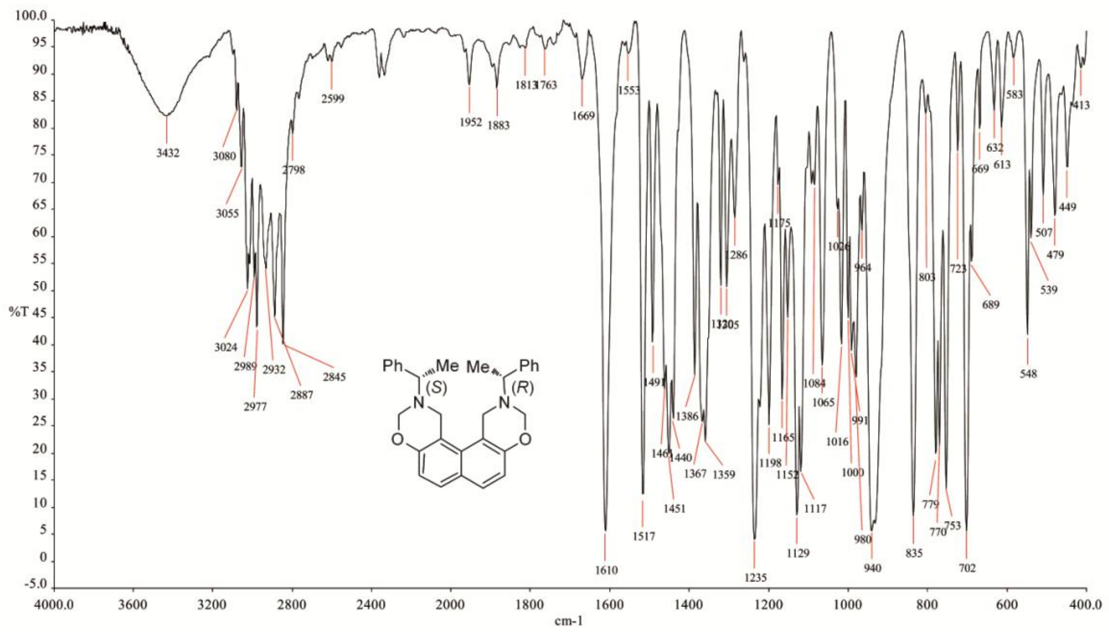


**IR spectrum of (*R*)-2-(1-phenylethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazin-9-ol (102)**

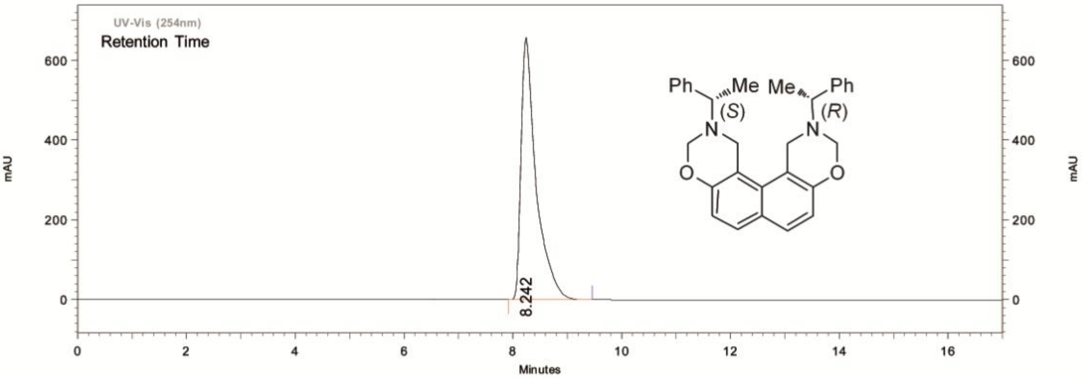
## Spectral data of 2-((*R*)-1-phenylethyl)-11-((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7 e']bis([1,3]oxazine) (103)



**$^1$H-NMR spectrum of 2-((*R*)-1-phenylethyl)-11-((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7 e']bis([1,3]oxazine) (103) in $CDCl_3$ on 400 MHz**



**IR spectrum of 2-((*R*)-1-phenylethyl)-11-((*S*)-1-phenylethyl)-1,2,3,10,11,12-hexahydronaphtho[1,2-e:8,7 e']bis([1,3]oxazine) (103)**



UV-Vis (254nm)

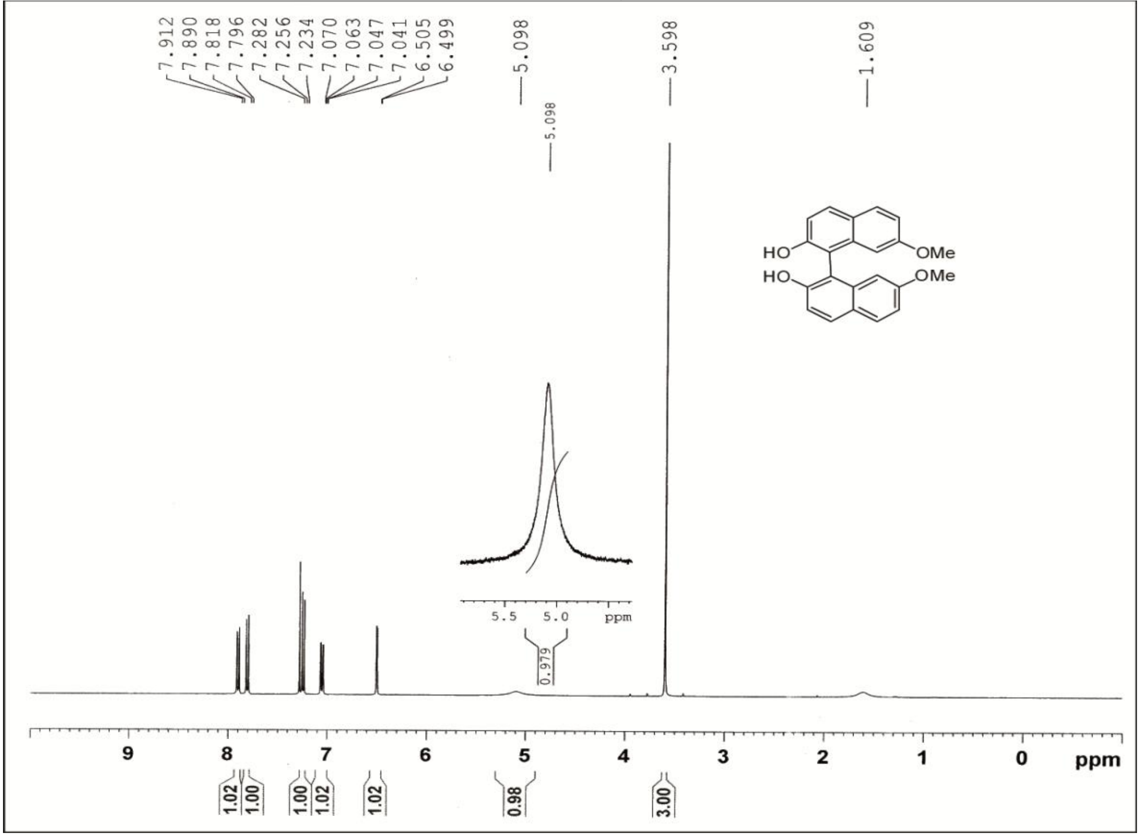
| Name | Retention Time | Area | Theoretical plates | Resolution | Area Percent |
|---|---|---|---|---|---|
| | 8.242 | 12587054 | 0.00 | 0.00 | 100.00 |
| Totals | | 12587054 | | | 100.00 |

**Method For HPLC Analysis**

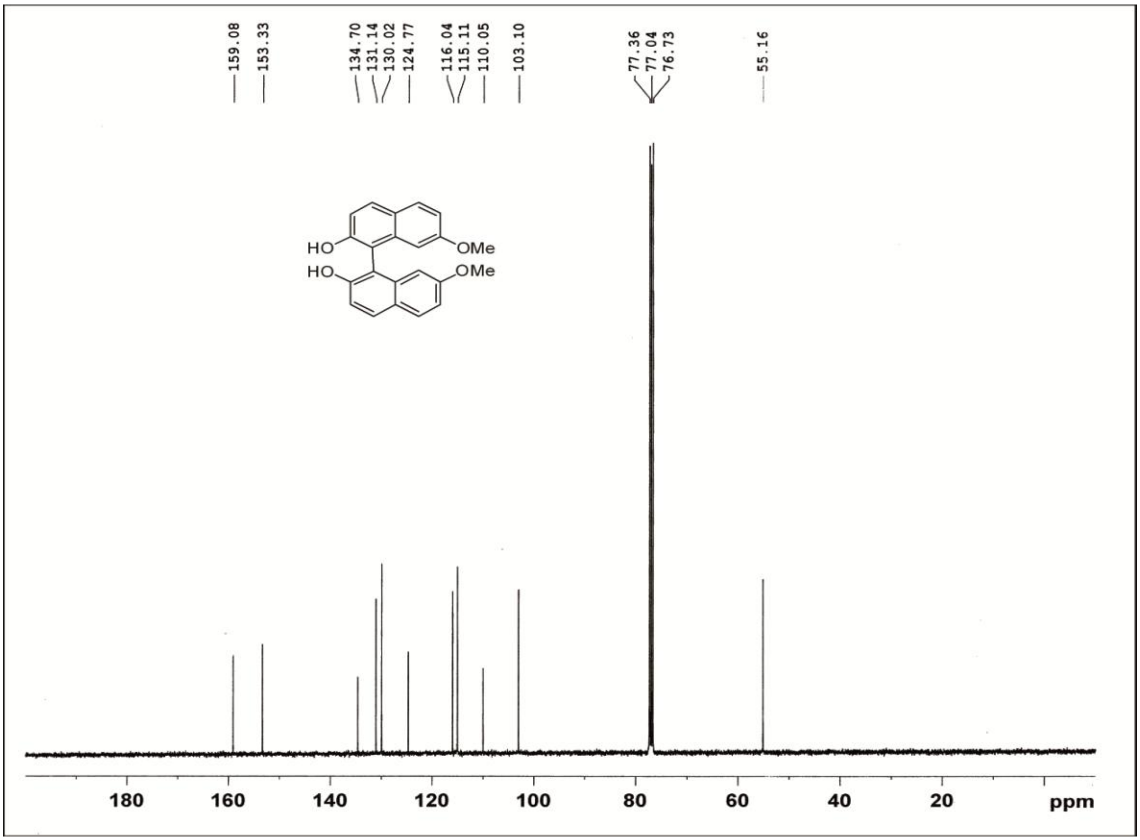
Solvent System: *n*-Hexane: *Iso*-propanol (94:1), Flow rate: 1 mL/min, Injection vol.: 20 μL, Detector: UV-Vis (λ max – 254 nm), Oven Temperature: 27 °C

Chiral Column: Diacel AD-H (Instrument - Shimadzu CLASS-VP V 6.14)

## Spectral data of 7,7’-dimethoxy-2,2’-binaphthol (104)

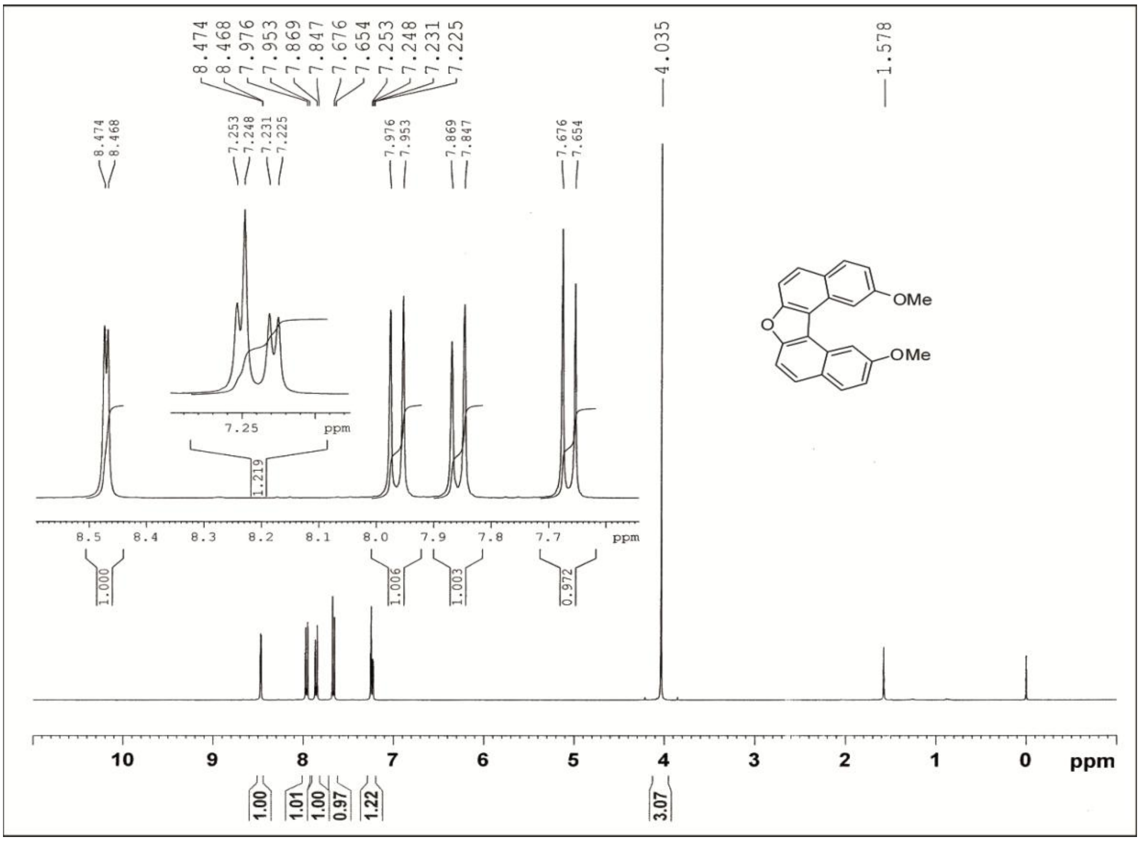


**$^1$H-NMR spectrum of 7,7’-dimethoxy-2,2’-binaphthol (104) in $CDCl_3$ on 400 MHz**

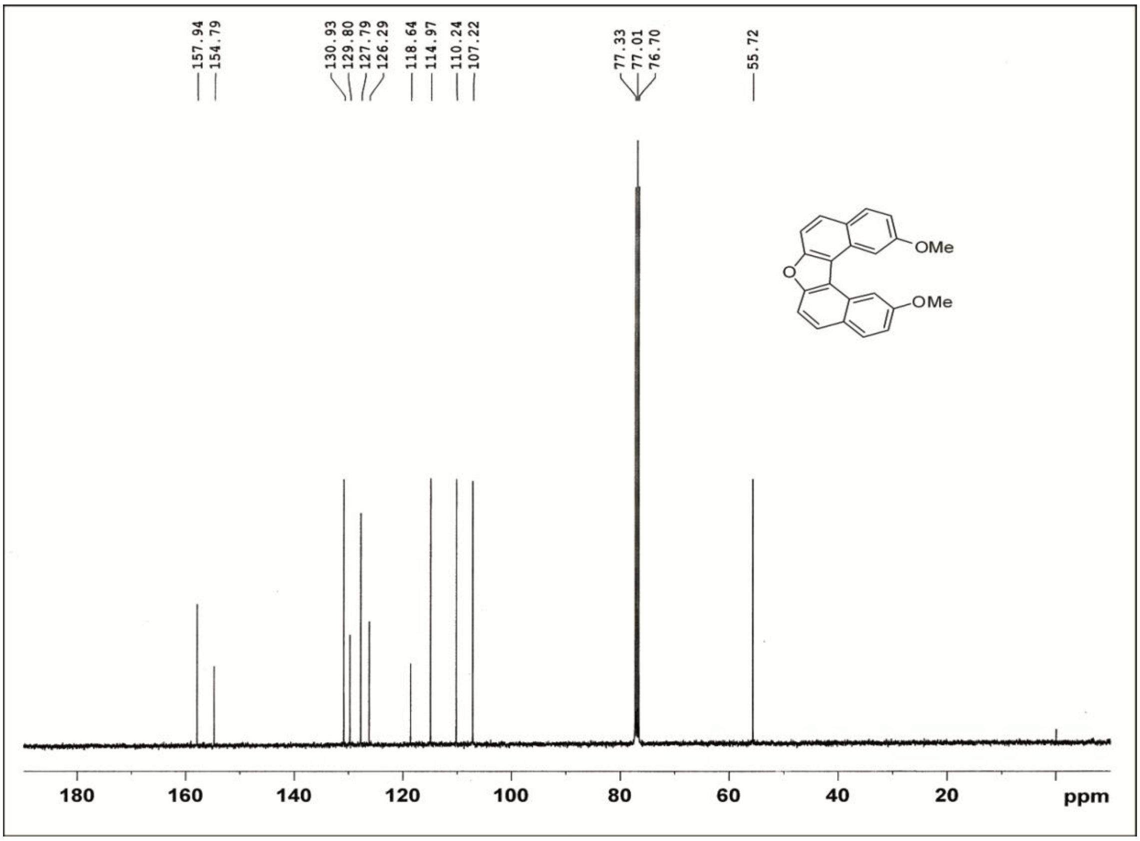


**$^{13}$C-NMR spectrum of 7,7’-dimethoxy-2,2’-binaphthol (104) in $CDCl_3$ on 100.6 MHz**

## Spectral data of 2,12-dimethoxy-7-oxa[5]helicene (105)

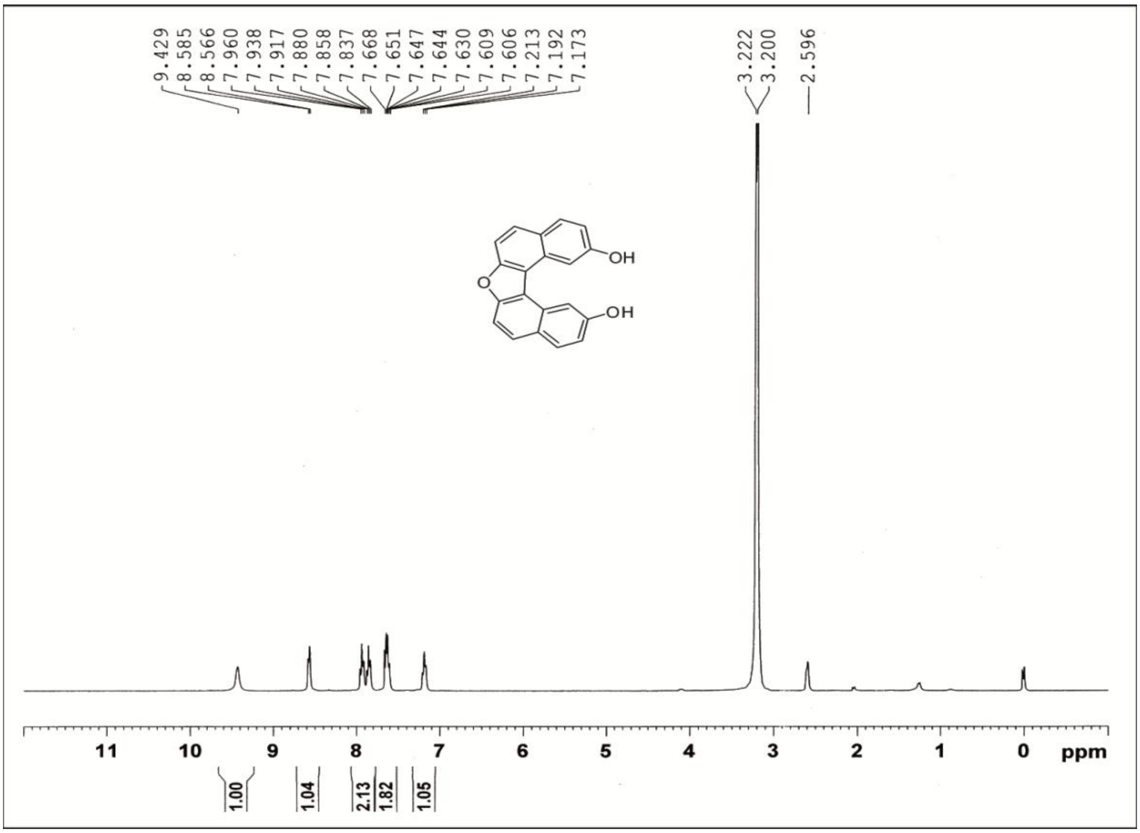


**$^1$H-NMR spectrum of 2,12-dimethoxy-7-oxa[5]helicene (105) in $CDCl_3$on 400 MHz**

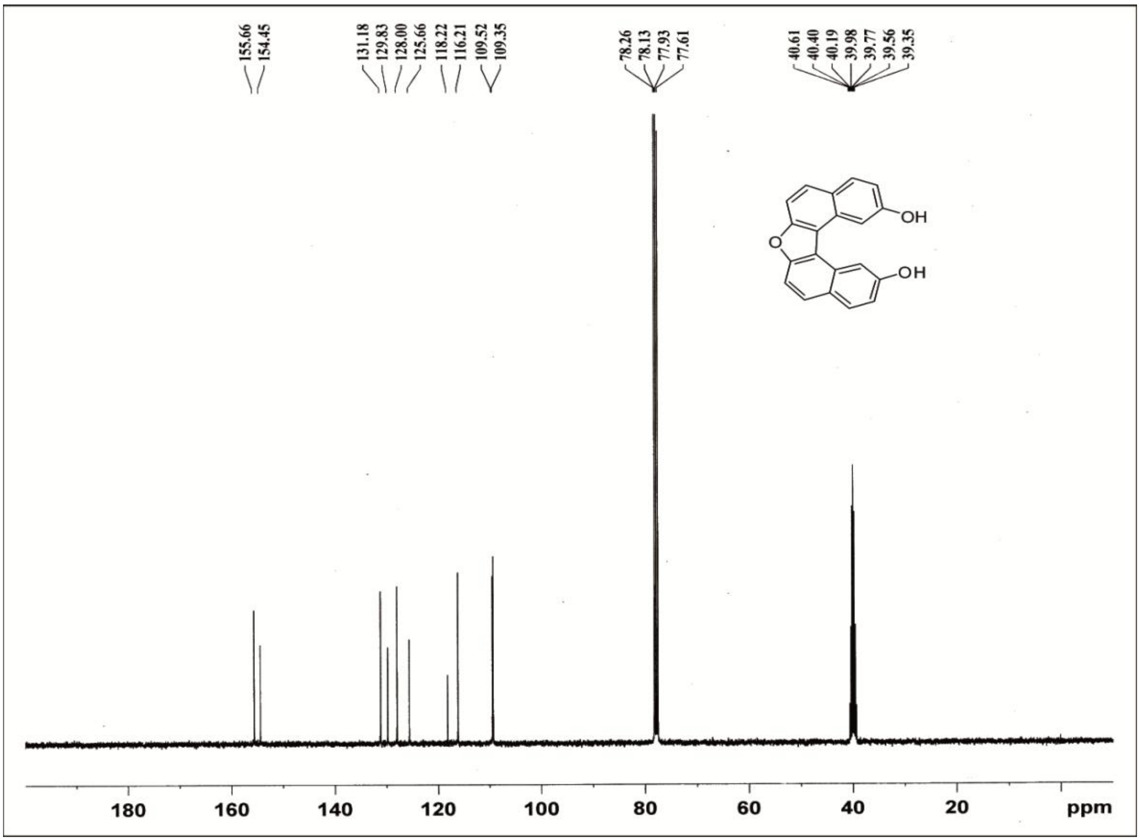


**$^{13}$C-NMR spectrum of 2,12-dimethoxy-7-oxa[5]helicene (105) in $CDCl_3$on 100.6 MHz**

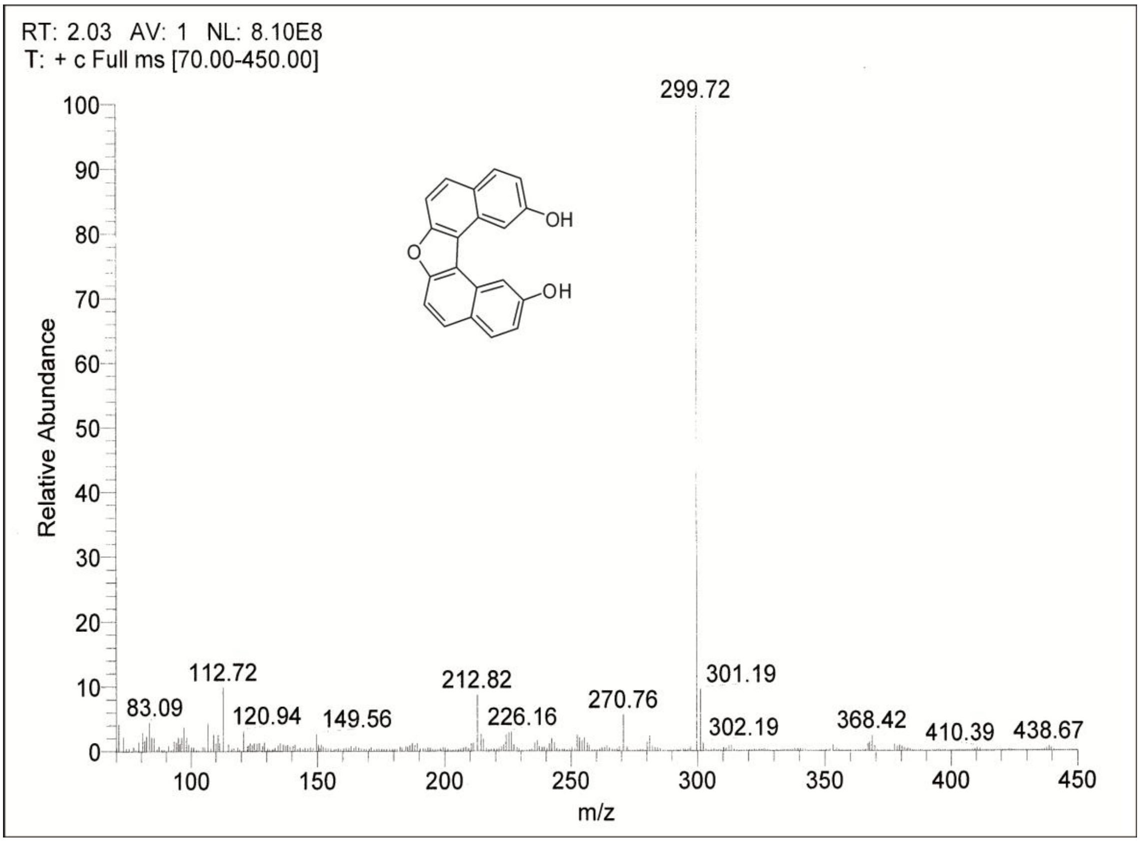
## Spectral data of 2,12-dihydroxy-7-oxa-[5]helicene (106)



$^1$H-NMR spectrum of 2,12-dihydroxy-7-oxa-[5]helicene (106) in $CDCl_3$ + drop of DMSO-*d6* on 400 MHz



$^{13}$C-NMR spectrum of 2,12-dihydroxy-7-oxa-[5]helicene (106) in $CDCl_3$ + drop of DMSO-*d6* on 400 MHz



**EI-Mass spectrum of 2,12-dihydroxy-7-oxa-[5]helicene (106)**

# Conclusion

In this chapter we report the synthesis of a number of heterocyclic helical molecules containing [1,3]-oxazine ring. The helical shape oxazines synthesized cover [1,3]-oxazine[4]helicene, [1,3]-oxazine[5]helicene and attempted synthesis of [1,3]-oxazine[7]helicene. However, we faced difficulties to prepare higher members of helical oxazine. Efforts were made to separate the diastereomers of the [1,3]-oxazine[5]helicene by introducing chirality on the oxazine ring built with the chiral amine. These isomers could not be separated due to low racemisation barrier established by HPLC analysis.

Another set of helical bis-[1,3]-oxazines possessing seven ring system was synthesized through axially chiral, diastereomeric intermediate. These diastereomers were separated by crystallization due to the solubility difference in the isomers. The optically pure atropisomers were cyclized by making methylene bridged ether linkage to adopt the final helical shape. The pair of opposite enantiomers of the helicene like oxazines was synthesized by choosing two antipodes of the corresponding chiral amine. Presence of opposite chirality was confirmed by circular dichroism (CD) study. The helicene like oxazines were found to be the thermally stable up to reflux toluene temperature.

In the second part we have presented the synthesis of naphthalene attached bis-[1,3]oxazines which are likely to show helical twist due to 1,8-*peri* interaction. The twist in the framework of such system due to the conformational considerations was supported by the single crystal X-ray diffraction analysis and spectral study.

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# Chapter 4

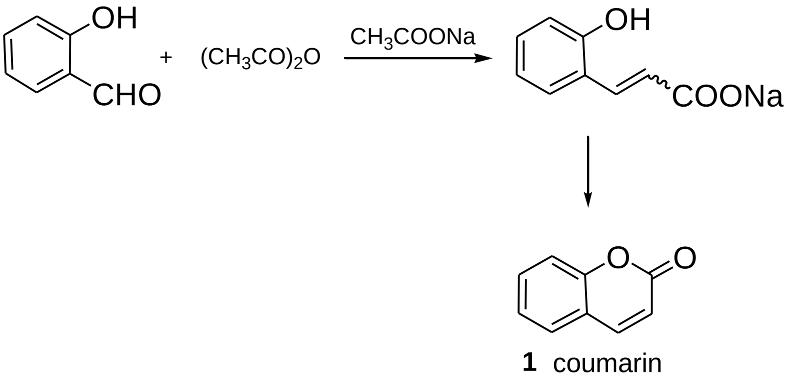
# Efforts Towards the Synthesis of Helical Coumarins

Coumarins, which consists of a lactone attached to an aromatic ring, have been investigated and synthesized since 1800's because of their pharmacological properties[1]and other uses.[2]

There are many synthetic routes developed to obtain this compound by by different methodologies such as Pechmann,[3a] Perkin,[3b] Knoevenagel[3c] and Reformastsky[3d] reactions.

***Perkin reaction:***[3b]

Perkin first synthesized coumarin from salicylaldehyde by heating it with acetic anhydride and anhydrous sodium acetate.

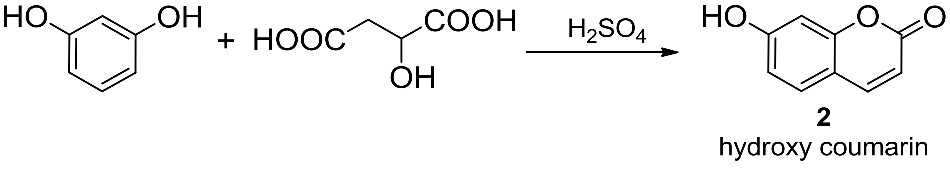


**Scheme 1:** Synthesis of coumarin **1** by Perkin reaction

This method has some limitations, mainly the appropriate starting material *o*-hydroxyaldehydes is rather difficult to obtain. This method gives coumarins without any substitution in the pyrone ring while the isolated chemical yields are often low.

***Pechmann reaction:***[3a]

Pechmann found that a coumarin derivative is formed when a mixture of a phenol and malic acid is heated in the presence of concentrated sulfuric acid.



**Scheme 2:** Synthesis of hydroxyl coumarin **2** by Pechmann condensation reaction

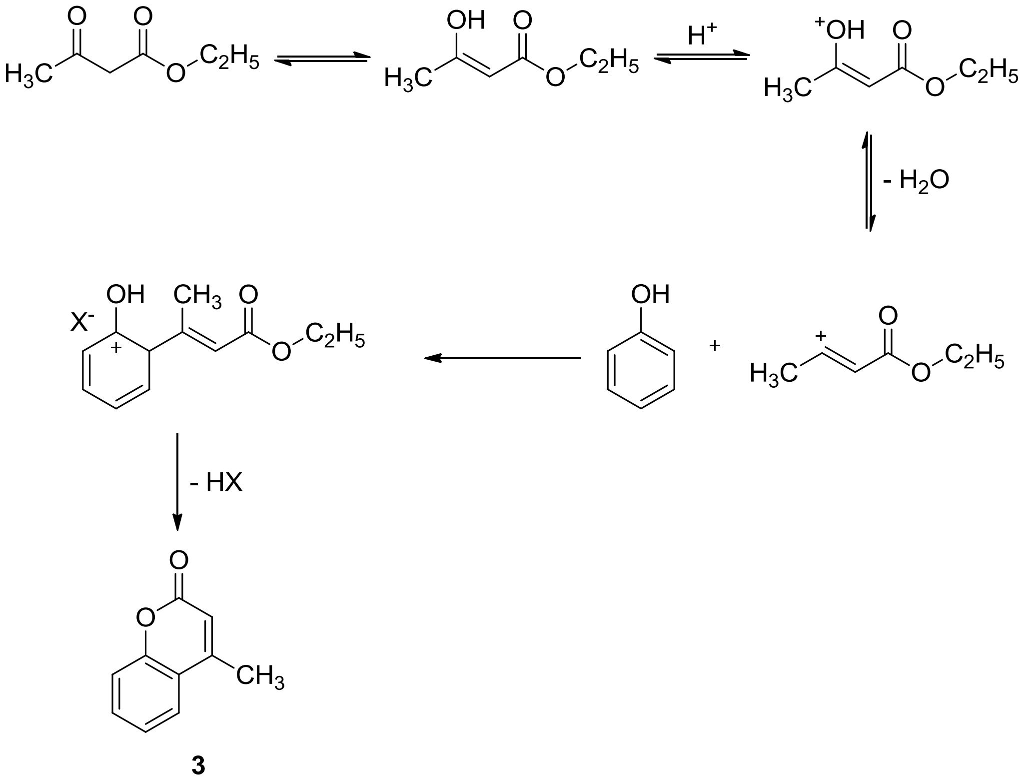
Pechmann–Duisberg reaction which is an important and established option for the synthesis of benzocoumarins.[3a,4] The Pechmann reaction is based on the condensation of a substituted phenol with a β-keto ester in acidic conditions.

Three factors that affect the product distribution of the reaction are:

1) Structure of the β-keto ester

2) Structure of phenol

3) Condensing agent



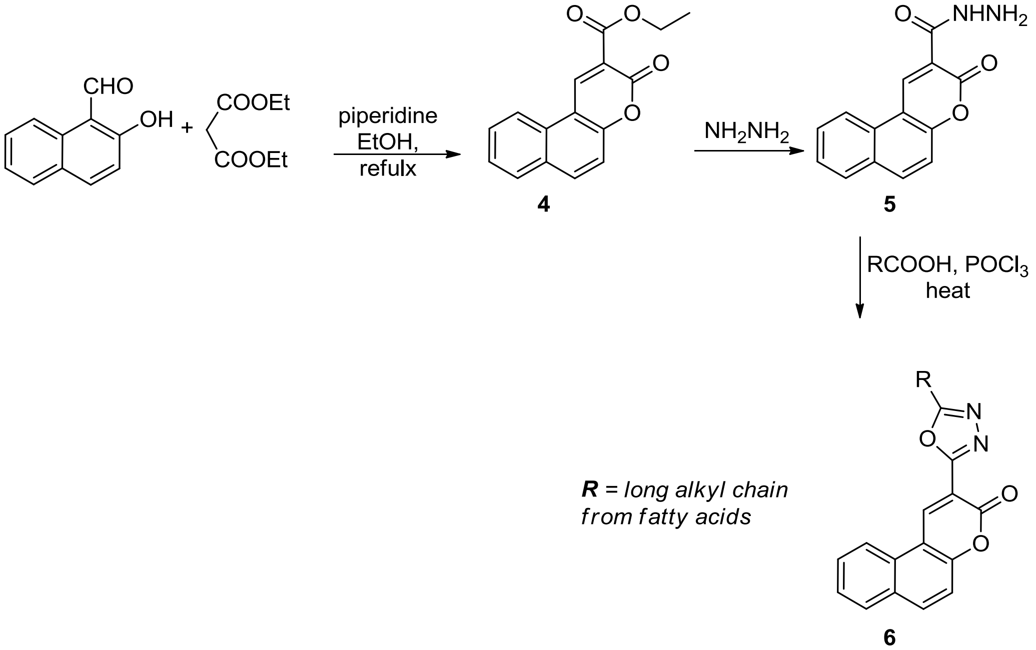
**Scheme 3:** Mechanism of the Pechmann condensation reaction[5]

Recently new methods have been developed instead of the classical ones by taking environmental conditions in to the consideration, using ionic liquids, clays and microwave irradiation.[6]

Coumarins played vital role in electro photographic and electroluminescent devices and laser dyes. Several 3-substituted 7-hydroxycoumarins rank among the most efficient photostable laser dyes emitting in blue-green region of the visible spectrum. The lasing range covered by coumarin dyes is appreciably extended when the C-3 substituent is a heterocyclic moiety.[7]

### *Synthesis of benzocoumarins as a biological and fluorescent active material 6:*

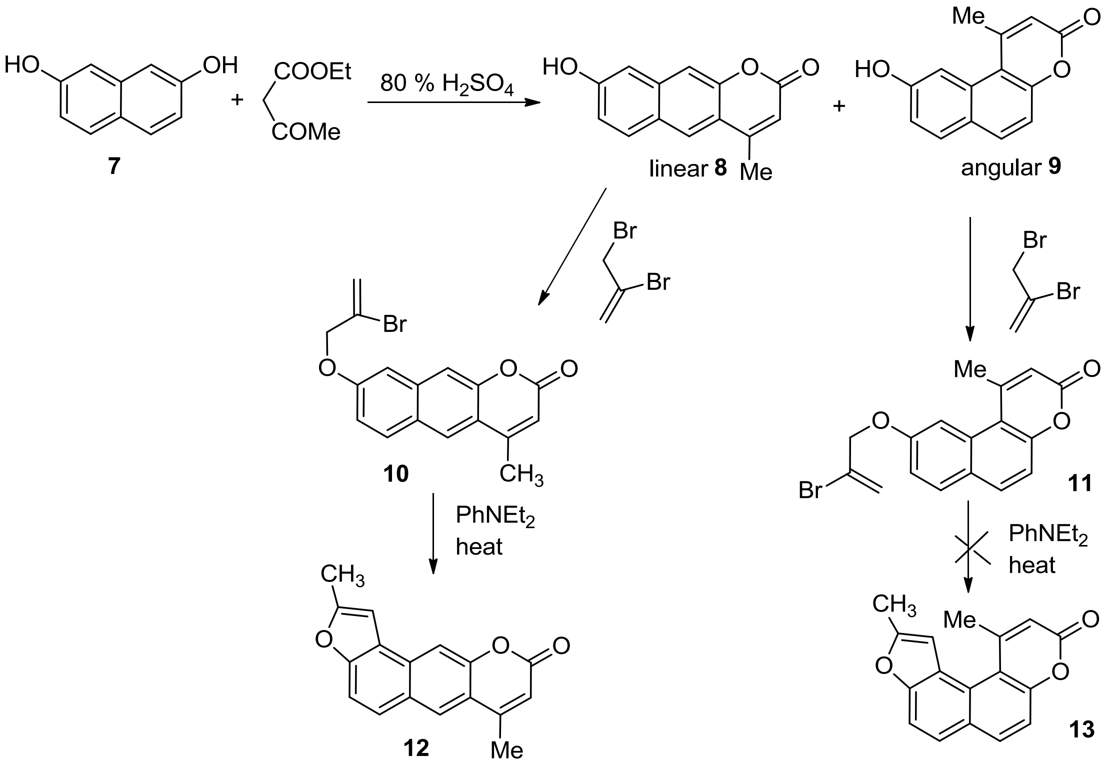
Recently Takadate *et al.*, have studied fluorescence properties of coumarins and benzocoumarins.[8] Authors have observed that benzocoumarins and their derivatives with different heterocycles at position C-3 are strongly fluorescent. Benzocoumarins coupled with oxadiazolyl ring system are in general comparatively easy to prepare and numerous derivatives have been designed and prepared for potential use as fluorescent active materials for biological applications. The fatty acids are introduced to increase the solubility of synthesized compounds for further applications. The classical synthesis of benzocoumarins involves condensation of aromatic hydroxy aldehyde with an active methylene compound to obtain the coumarin **4**. The ester **4** was transformed to the corresponding amide with hydrazine to obtain the compound **5**. Which was converted to an oxadiazole derivative **6** using fatty acid in presence of $POCl_3$. The reaction is facile and is most widely used synthetic method for the preparation of both benzocoumarins and their derivatives.



**Scheme 4:** Synthesis of fluroscent coumarins **6**

### *Synthesis of 4-methyl-8-hydroxynaphtho[2,3-b]pyran-2-one 8 and 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone 9:*

The Pechmann Condensation[9] of napthalene-2,7-diol with ethyl acetoacetate in 80% $H_2SO_4$ at cold reaction conditions afforded the regioisomers namely, linear **8** and angular **9** in the ratio of 3:2.



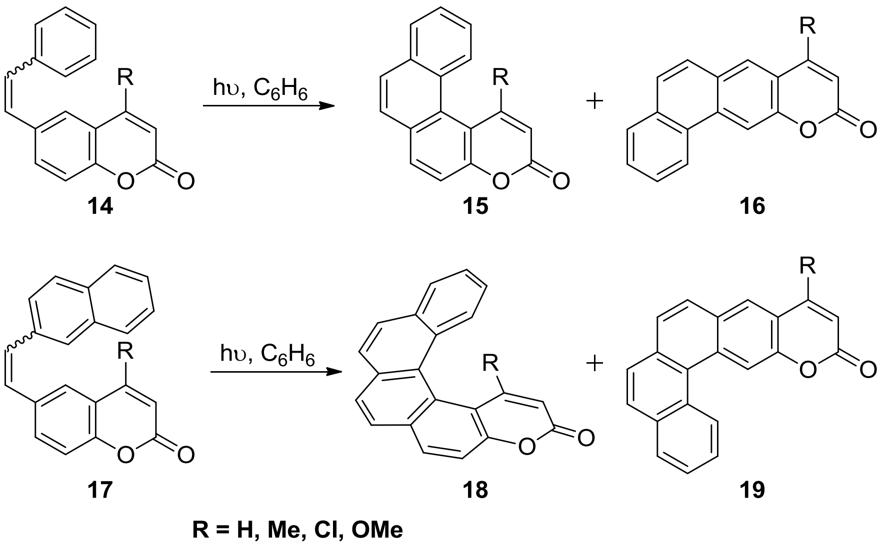
**Scheme 5:** Synthesis of *4-methyl-8-hydroxynaphtho[2,3-b]pyran-2-one* ***8*** *and 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone* ***9*** and its derivative **12**

Hydroxynapthopyrone **8** and **9** readily reacted with 2,3-dibromopropene to give 4-methyl-8-(2'-bromoallyloxy)-naphtho[2,3-b]pyran-2-one **10** and 1-methyl-9-(2'-bromoallyloxy)-naphtho[2,1-b]pyran-3-one **11**, latter was refluxed in N,N-diethylaniline to yield 2H-4,9-dimethylfuro[2,3:7,8]naphtha[2,3-b]pyran-2-one **12** and the same reaction with the angular product gave a complex mixture of the products without desired furonapthopyrone **13**.

The lactone containing helicene type coumarins were synthesized by different groups for the access of the axially chiral compounds such as ligands[10] as well as some of the natural products[11] and the fluorescent materials.[12]

### *Synthesis of [4]helicene 15 and [5]helicenes 18 type coumarin derivatives:*

Moorthy and co-workers have recently synthesized the pyranone annulated helicenes by the photocyclodehydrogenation of styryl derivatives of coumarins **14** and **17**.[12] The styryl derivative of coumarin was cyclised by passing oxygen through the solution of benzene irradiated with HPMV lamp. The cyclization reaction furnished an angular helical coumarins **15** and **18** and linear products **16** and **19.**



**Scheme 6:** Synthesis of helical coumarins **15** and **18** by photocyclization

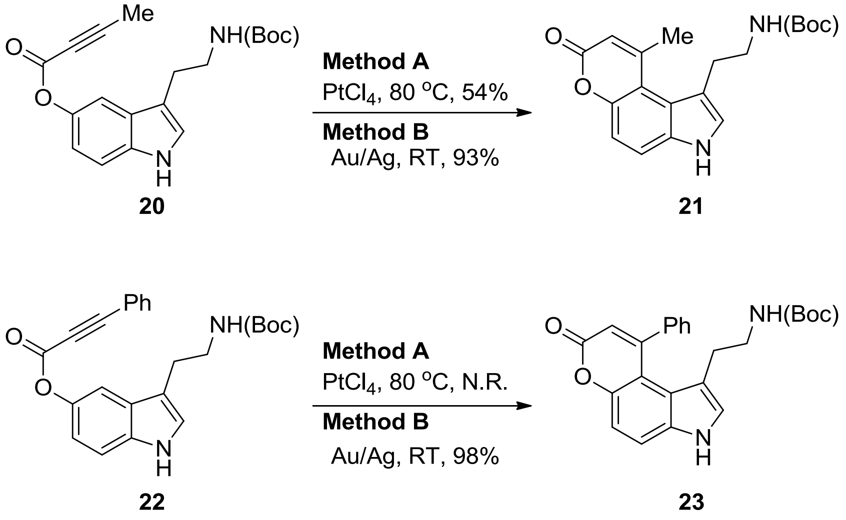
The authors have further studied the helicity dependence fluorocence properties of the pyranones and chromones form the synthesized coumarins, as discussed in chapter-1.

### *Synthesis of helical shape coumarins such as tert-butyl-9-methyl-pyrano[3,2-e]indol- 7(3H)-one-1-ethylcarbamate 21 and tert-Butyl 9-Phenylpyrano[3,2-e]indol-7(3H)-one 1-Ethylcarbamate 23:*

During the preparation of this thesis, Sames and Vadola have published their novel approaches for C-H bond functionalization for the synthesis of complex organic compounds. However, many C−H functionalization reactions suffer from poor compatibility with Lewis basic functional groups, especially amines, which are often essential for biological activity.

In this study a systematic examination of the substrate scope of catalytic hydroarylation in the context of complex amino coumarin synthesis is presented. The more active gold catalyst demonstrated excellent functional group tolerance, and the ability to catalyze the formation of strained, helical products.

In this synthesis the authors have developed two different conditions for the synthesis of helical coumarins containing serotonin analog **21** and **23**. The reaction of N-Boc-seretonin analog with the 2-butynoic acid and phenyl-2-propynoic acid gives the precursors of helical coumarins **20** and **22** respectively.



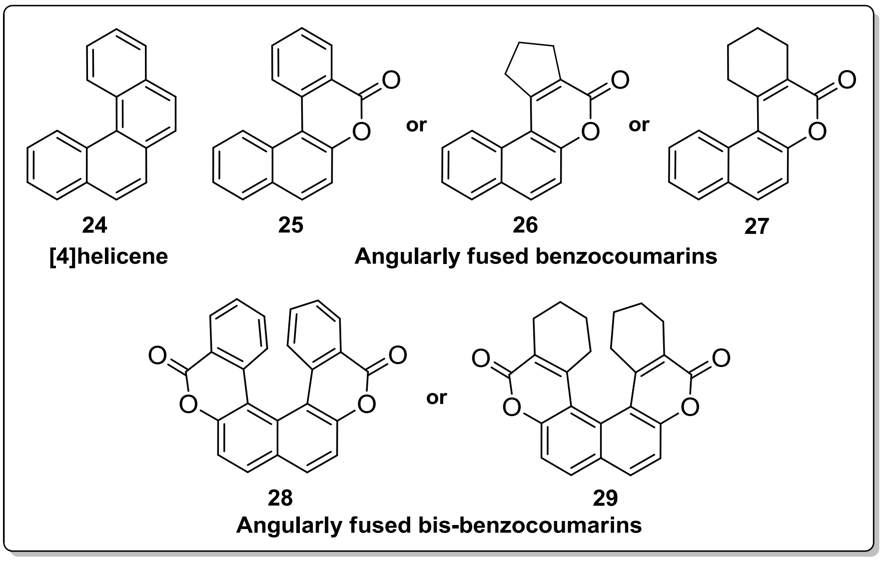
**Scheme 7:** Synthesis of Helical shape coumarins **21** and **23**

Further reaction of this precursor with $PtCl_4$ under mild conditions gave a single product **21**, However, the present condition was not suitable for the synthesis of helical coumarin **23**.

The reaction of **20** and **22** with $Ag(PPh_3)Cl$ and $AgSbF_6$ in dichloroethane:dioxane gives the helical coumarin **21** and **23** in excellent yields, the linear product or sterically less hindered coumarins are not formed in this reaction. The helical shape of the molecule is evident from the single crystal X-ray analysis with a dihydral angle in the molecule of about 19.4 °.

# Results and Discussion

In the previous section we have discussed the many methods for the synthesis of coumarins. In the present work we also have designed coumarin structures which will be capable of exhibiting the structural twist and showing the helical isomers. With this aim synthesis of a list of coumarins with a possibility of existing helical shape is attempted.

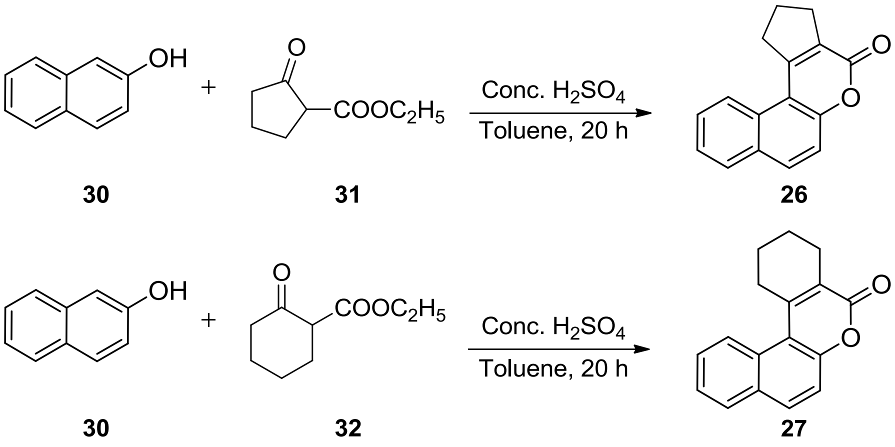


**24** [4]helicene **25** **26** **27** Angularly fused benzocoumarins

**28** **29** Angularly fused bis-benzocoumarins

**Figure 1:** Proposed helical shape coumarins

In the direction of the synthesis of helical coumarins the following molecules, 3,4-cyclopenten[5,6]benzocoumarin **26** and 3,4-cyclohexano[5,6]benzocoumarin **27** by the reported procedure[14] have been synthesized from β-naphthol as the starting phenol and cyclic β-ketoesters **31** and **32**.



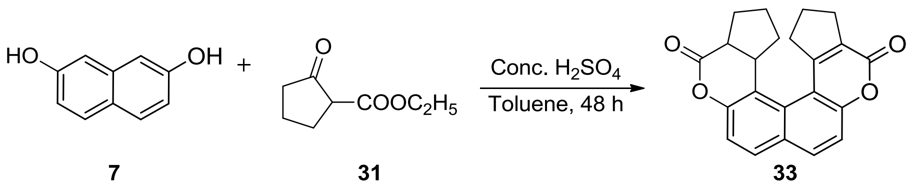
**30** **31** **26**

**30** **32** **27**

**Scheme 8:** Synthesis of 3,4-cyclopenten[5,6]benzocoumarin **26** and 3,4-cyclohexano[5,6]benzocoumarin **27**

An active phenol β-naphthol **30** was treated with the ethylcyclopentanone-2-carboxylate **31** and ethylcyclohexanone-2-carboxylate **32** in presence of concentrated sulphuric acid in toluene at room temperature to obtain the products 3,4-cyclopenten[5,6]benzocoumarin **26** and 3,4-cyclohexano[5,6]benzocoumarin **27** respectively in a good yields. The synthesized compounds were characterized by the usual analytical methods such as $^1$H-NMR, $^{13}$C-NMR and Mass analysis. It was expected that the $^1$H-NMR spectrum of both these coumarins **26** and **27** would give typical signals due to presence of a twist in the molecule. However such was not observed. Further study on chiral HPLC columns were undertaken to establish presence of two helical isomers if present in ambient condition in solution state. The HPLC analysis was performed on chiral phase Diacel OD-H column but, the analysis showing the presence of a single peak. We may hence conclude that the helical isomers of **26** even if present are not stable and may exist in rapid equilibrium at ambient conditions in solution state.

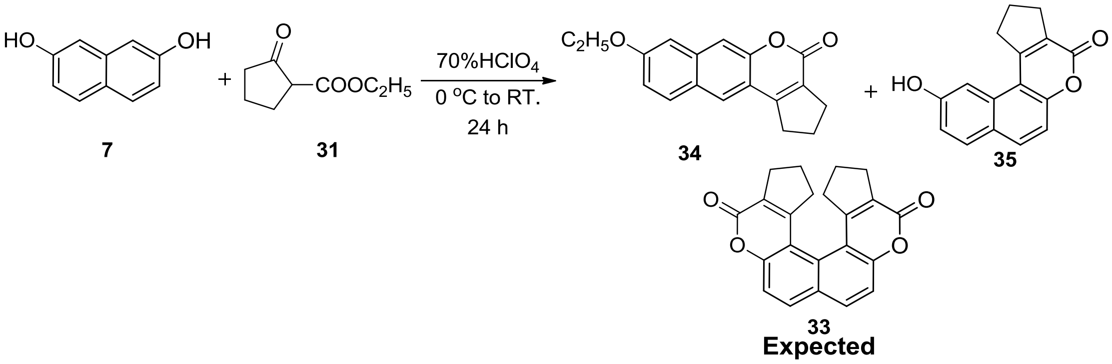
In order to achieve stable and resolvable helical isomers further modifications of the design indicated the need to build steric bulk on the inside of the proposed helical unit. With this aim structure of a bis-coumarin **33** was envisaged. The molecule **33** could be easily synthesized from similar reaction done on 2,7-dihydroxynaphthalene. Reaction of 2,7-dihydroxynaphthalene with **31** under acid catalyzed condition was investigated, **Scheme-9**.



**Scheme 9:** Attempted synthesis of helical bis-coumarin **33**

In this reaction the 2,7-dihydroxynaphthalene treated with ethylcyclopentanone-2-carboxylate **31** and concentrated sulphuric acid in toluene for 48 h at room temperature to obtain a complex reaction mixture. Several attempts to isolated the required bis-coumarin **33** were not successful. Attempts to conduct the condensation reaction under different conditions did not result in formation or isolation of the desired target bis-coumarin **33**.

In this present study the reaction was attempted with 70% perchloric acid as a catalyst for the synthesis of bis-coumarin from 2,7-dihydroxynaphthalene **7** and ethylcyclopentanone-2-carboxylate **31** in the neat reaction condition to obtained a crude product. Which after purification gave a pure compound 8-ethoxy-2,3-dihydrobenzo[*g*]cyclopenta[*c*]chromen-4(1*H*)-one **34**, its structure was established with $^1$H-$^{13}$C-NMR and mass analysis. There may be is possibility of small amount of the presence of mixture of **33** and **35**.



**Scheme 10:** Attempted synthesis of helical bis-coumarin **33**

Since out attempts did not succeed, another strategy of introducing the bulk at appropriate position was investigated. By introducing a suitable moiety (R) at the 8-position may create substantial *peri* interaction and may result in the helical form in the naphthalene unit, similar to 1,8-disubstituted systems [**Figure-2**].

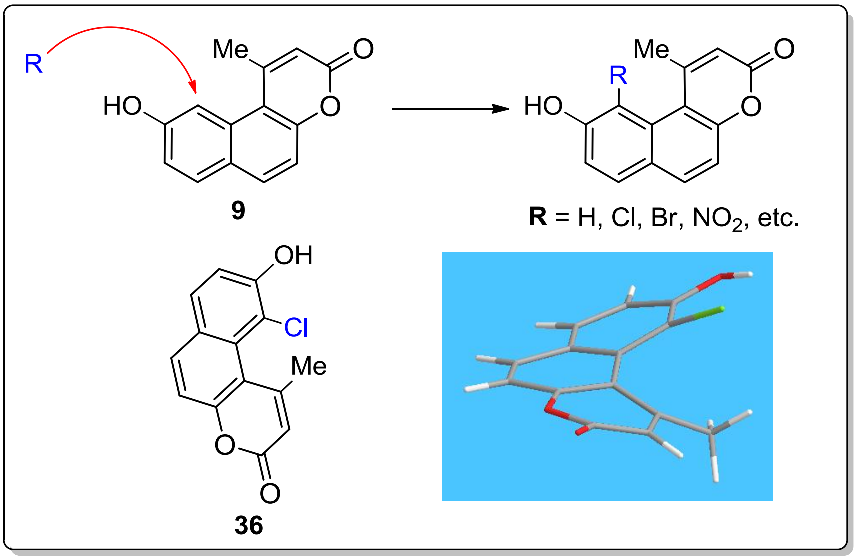
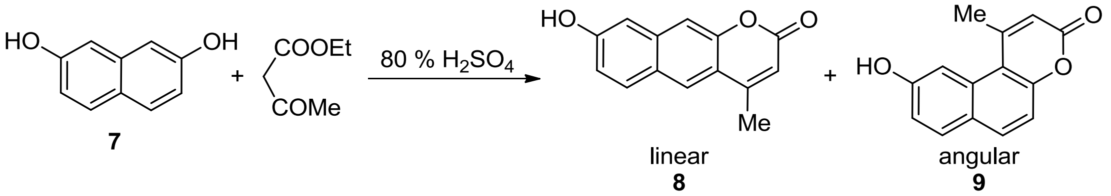


**Figure 2:** Helical shape coumarin **36** showing twirl on MMP2 calculation figure

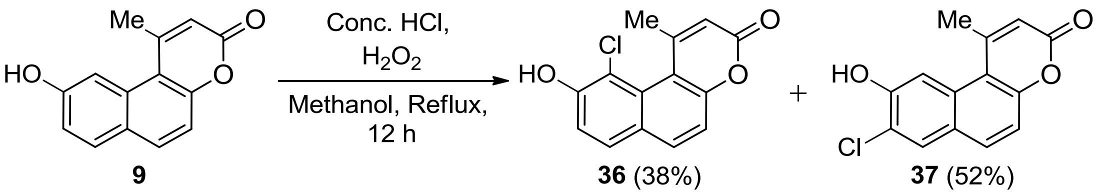
Attempts were made in this direction to synthesize the required angular coumarin **9** from 2,7-dihydroxynaphthalene and ethylacetoacetate by Pechman reaction. Presence of hydroxyl group can help to direct the introduction of a bulky group at the C8 position of naphthalene framework. The said Pechman reaction gave two products due condensation at linear and angular position. Accordingly synthesis of 4-methyl-8-hydroxynaphtho[2,3-b]pyran-2-one **8** and 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** was achieved by this methodology.[9]



**Scheme 9:** Synthesis of 4-methyl-8-hydroxynaphtho[2,3-b]pyran-2-one **8** and 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9**

Structures of coumarins **8** and **9** will have a possibility to introduce an electrophile at the C-10 position, which will be inside the helical shape. Because of the introduction of the different substituent at the C-10 position of the angularly fused coumarin **9** the required steric interaction will be achieved. The basic theoretical minimize energy MMP2 calculations of this compound with the different substituent at C-10 position helps to predict the presence of a twirl in the molecule shown in **Figure-2**.

The first attempt to introduce a substituent at C-10 position was done by chlorination of the compound 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** [**Scheme-10**].[15] Reaction of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** with concentrated HCl and hydrogen peroxide in methanol under reaction for 12 h generated the product 8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **37** and 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **36** in good yields. The electrophilic chlorination occurs via *in situ* generation of HOCl.



**Scheme 10:** Synthesis of 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **36**

The compounds 36 and 37 were characterized by the usual spectral analysis and an interesting pattern was found in the $^1$H-NMR spectrum of the compound 10-

chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **36**. The methyl protons resonated as a doublet at δ 1.77 with a coupling constant *J* = 1.6 Hz in this spectrum. However, for the linear compound **35** and the starting material **9** it showed a singlet at δ 2.49 and δ 2.88 respectively [**Figure-3**].

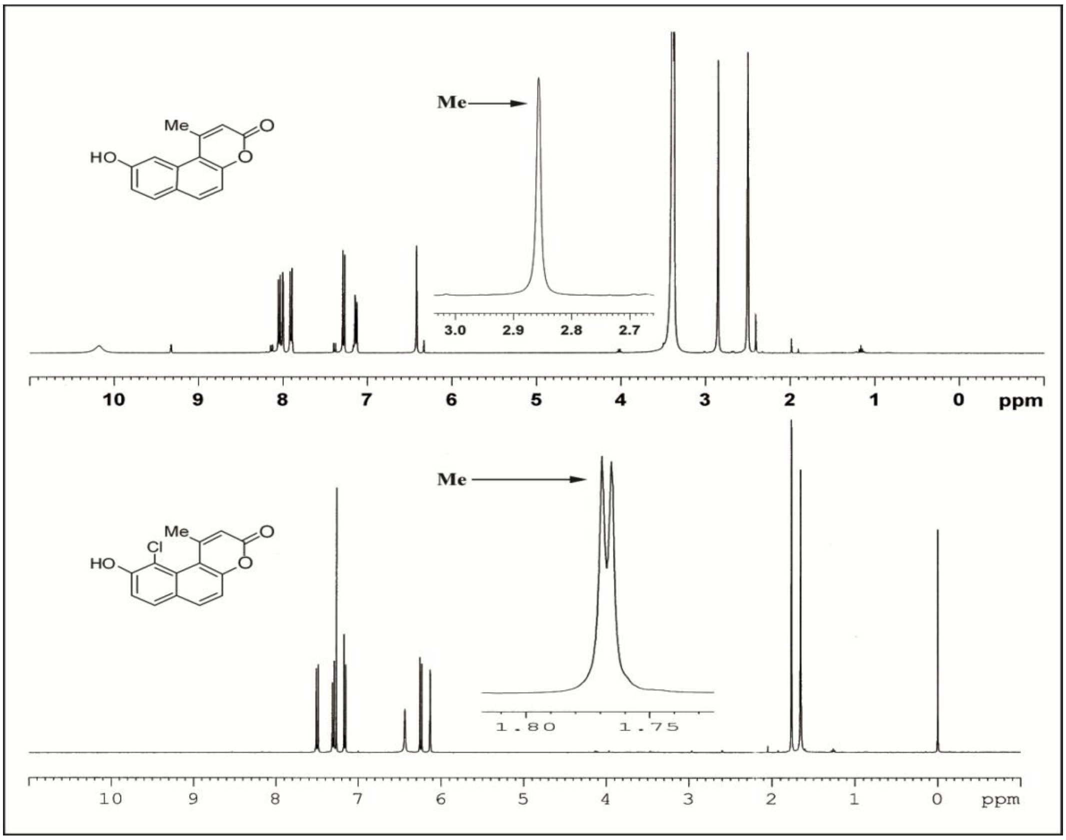
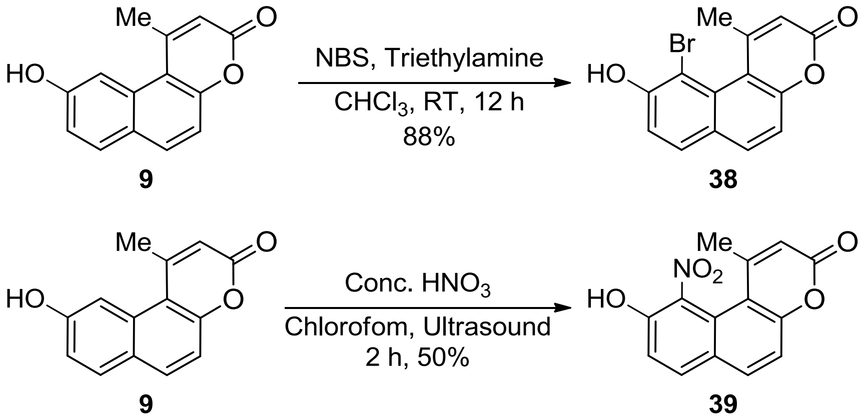


**Figure 3:** Comparision of the Methyl protons in H-NMR spectrum of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **36**

The $^{1}$H-NMR spectrum of coumarins **9** and **36** showing the difference between the methyl protons as well as the olefinic –CH proton indicating structural difference. The olefinic proton of the compound **36** is showing the quartet at δ 6.14 with the coupling constant of 1.6 Hz, while the olefinic proton of the compound **9** showing the typical singlet at δ 6.21. We presume that the difference between the proton signals is due to the helical shape or the twirl adopted by the compound **36** after the introduction of the chorine atom at the hindered position at C-10. However, our attempts to analyze **36** on chiral phase HPLC system of the compound did not result in good separation. We have examined two chiral HPLC columns, Diacel OD-H and Lux Amylose-2 for this analysis.

Similarly, on preparation of compound 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **36** its bromo-analogue was synthesized by adopting different standard brominating reagents.

To introduced the substituent at C-10 position several reagents for bromination[16] were investigated. Reaction of **9** with N-bromosuccinimide and triethylamine in chloroform at room temperature for 12 h gave the brominated product 10-bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **37** in good yield.



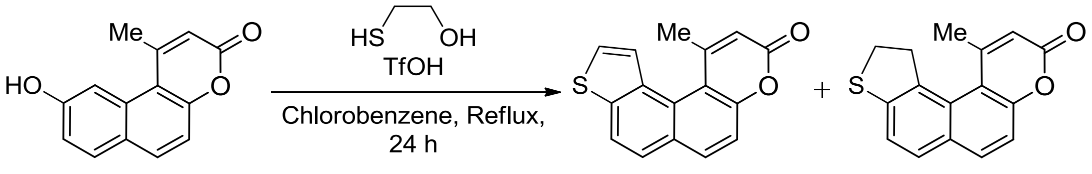
**Scheme 11:** Synthesis of 10-bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **38** and 10-bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **39**

The nitro substituted derivative of the coumarin 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9**, was also synthesized. For this reaction of the coumarin **9**, was conducted with concentrated nitric acid in chloroform kept under ultrasound for 2 h at room temperature. This gave the desired 10-nitro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **39**, both the compounds **37** and **38** were characterized by the usual analytical techniques.

However, the NMR and HPLC analysis of both these molecules were not conclusive in establishing the helical shape in them.

In continuation of our efforts to synthesize helical molecule our next attempts included attaching five member heterocyclic ring at the C-9 and C-10 position of the system. By attaching such a ring it was imagined that the corresponding chloro, bromo and nitro derivatives may show requisite helical twist to the framework. In this effort a reported efficient use of trifluoromethanesulfonic acid (TfOH) mediated oxygen–sulfur replacement reaction[17,18] was investigated. This reaction converts an aromatic phenol to a five member sulfur containing heterocyclic ring.

In this reaction a mixture of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9**, 2-mercaptoethanol and trifluoromethane sulphonic acid was refluxed in chlorobenzene and after the basic workup two compounds 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40** and 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2H)-one **41** were isolated. The compounds **40** and **41** were characterized by usual analytical techniques.



**Scheme 12:** Synthesis of 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40** and 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one **41**

The $^1$H-NMR of these compounds **40** and **41** showed the similar characteristic doublet signal for the methyl protons similar to the compound **36**. The $^1$H-NMR spectrum of the compounds **40** and **41** show the long range coupling of the methyl protons with the olefinic protons only a difference in this case was that the olefinic protons show a doublet instead of the quartet observed for **36**. The correlation of this methyl proton and the olefinic proton was studied by the 2-D $^1$H-$^1$H COSYGPSW NMR spectral analysis [**Figure-4** and **5**].

The $^1$H-$^1$H correlation COSYGPSW spectrum of the compound 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40** shows a relation between the methyl proton at δ 2.51 ($J$ = 0.8 Hz) and the olefinic proton at δ 6.40 ($J$ = 1.2 Hz) by making the cross square on the diagonal of the spectrum [**Figure-4**].

The correlation of this long range coupling might be possible due to the twirl or the helical shape in the compound 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40.**

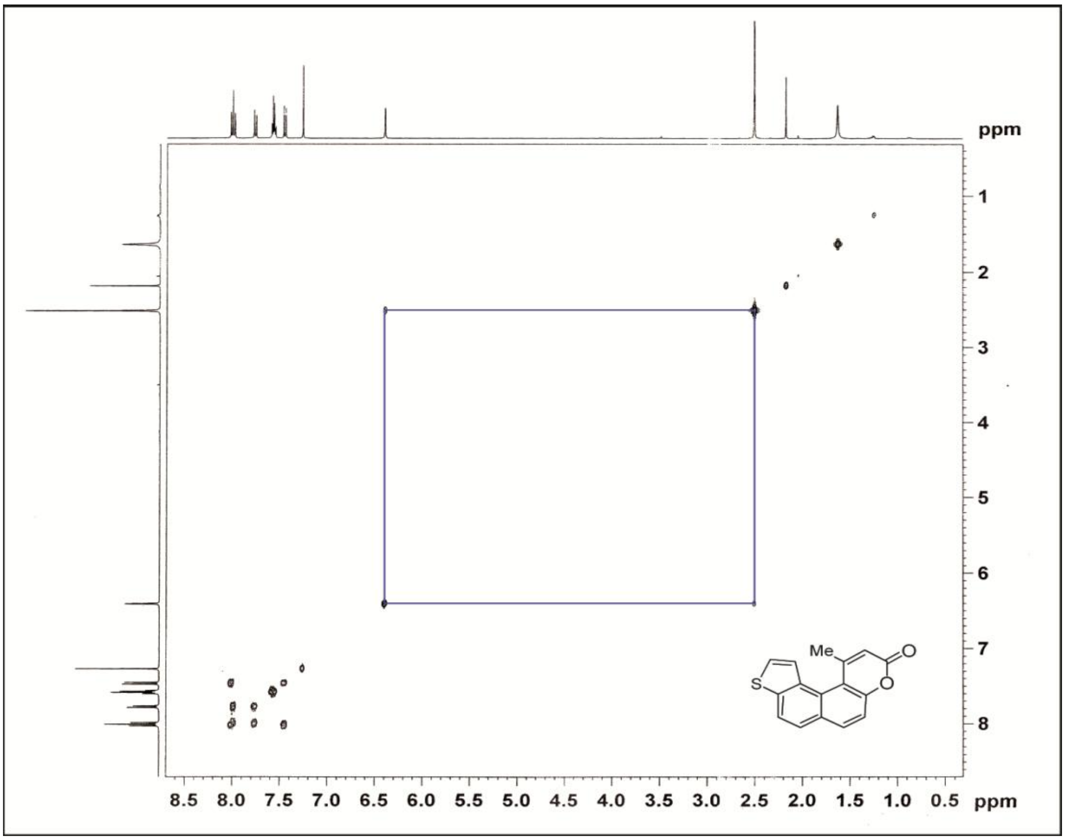
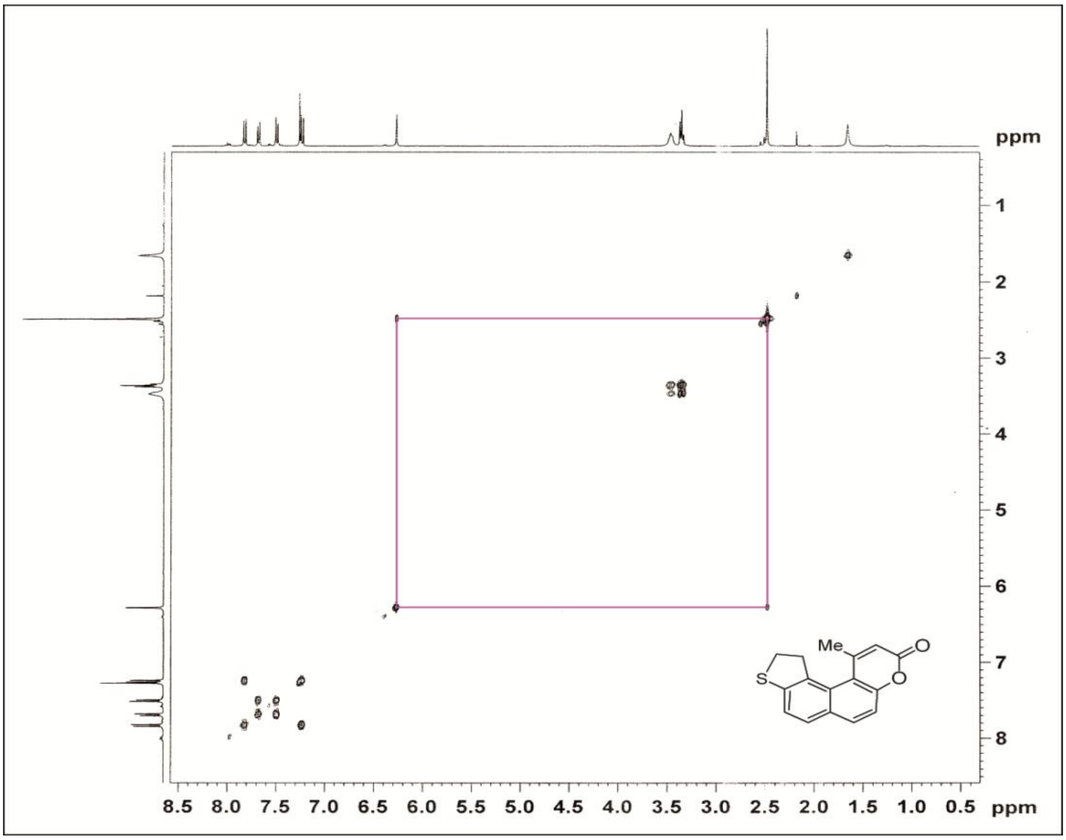


**Figure 4:** $^1H$-$^1H$ correlation COSYGPSW spectrum of 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40**



**Scheme 12:** $^1H$-$^1H$ correlation COSYGPSW spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2H)-one **41**

The $^1$H-$^1$H correlation COSYGPSW spectrum of the compound 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2H)-one **41** showing the similar correlation like compound 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40,** between the methyl proton at δ 2.48 ($J$ = 1.2 Hz) and the olefinic proton at δ 6.27 ($J$ = 0.8 Hz) by making the cross square on the diagonal of the spectrum [**Figure-5**].

The correlation of this long range coupling might be possible due to the twirl or the helical shape in the compound 11-methyl-1H-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one **41.**

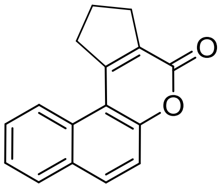
From all these correlations there is possibility of the helical shape or twirl in the compound **40** and **41**.

# Experimental Section

Reagents were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc. All solvents that were used were stored on oven dried molecular sieves (4Å). All commercial products were used without further purification. 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 silica gel (60-120 mesh). All reactions were carried out under an inert atmosphere (nitrogen) unless other conditions are specified. $^1$H and $^{13}$C NMR spectra are recorded on a 400 MHz Bruker Avance 400 Spectrometer (100 MHz for $^{13}$C respectively) spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Signal multiplicity is denoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), quartet of triplets (qt), septet (sept) and multiplet (m). 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. For the HPLC analysis chiral Lux 5μ Amylose 2 column and chiral Diacel OD-H column used on Waters 996 photodiode Array Detector and Waters 2690 Separation Module HPLC system.

## Experimental Procedures:

### *3,4-Cyclopenteno[5,6]benzocoumarin (26):*



To a well stirred solution of 2-napthol (0.720 g, 4.49 mmol) and ethyl cyclopentenone-2-carboxylate (1.30 mL, 8.99 mmol) in toluene, conc. $H_2SO_4$ (1 mL) was added drop wise by using dropping funnel. The stirring was continued for about 48 h under dry condition. Completion of reaction was checked by TLC The reaction mixture was then neutralized with saturated $NaHCO_3$ solution and extracted with toluene .Organic layer was washed with water, dried over sodium sulphate and concentrated. The product was purified by column chromatography using petroleum ether and ethyl acetate as an eluent. The solid was recrystalised in petroleum ether and ethyl acetate mixture and obtained as colourless solid crystals (0.160 g, 16%).

**M.p.:** 198 °C

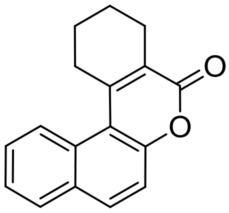
**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.60 (t, *J* = 6.8, 8.4 Hz, 1H), 7.53 (t, *J* = 7.2, 7.6, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 3.55 (s, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.20 - 2.27 (m, 2H).

**$^{13}$C-NMR (100.6 MHz, $CDCl_3$):** δ 159.9 (-C=O), 155.6 (Cq), 154.0 (Cq), 132.1 (CH), 130.8 (Cq), 129.7 (Cq), 128.6 (CH), 127.6 (CH), 125.4 (CH), 124.3 (CH), 117.4 (CH), 113.7 (Cq), 37.9 ($-CH_2$), 29.7 ($-CH_2$), 22.9 ($-CH_2$).

**Mass (EI):** ***m/z*, (%)** 237 (17) $[M+1]^{\cdot+}$, 236 (100) $[M]^{\cdot+}$, 235 (74), 219 (22), 207 (24), 181 (16).

**IR (KBr)**: 2908, 2840, 1732, 1687, 1605, 1552, 1466, 1197, 1119, 1063, 998, 867, 802 cm.$^{-1}$

### *3,4-Cyclohexenon[5,6]benzocoumarin (27):*



A 150 mL round bottom flask was charged with β-naphthol (0.500 mg, 3.1 mmol) in toluene (10 mL) and stirred for few minutes. To this solution ethyl cyclohexanone-2-carboxylate (0.99 mL, 6.20 mmol) was added, followed by drop wise addition of 1 ml concentrated $H_2SO_4$. The reaction mixture was heated at 100 °C for 48 h and monitored by TLC in ethyl acetate-petroleum ether (10:90) system. The reaction mixture was poured into water and treated with $NaHCO_3$

till solution became neutral. Extraction was done with toluene, organic layer was washed with water, dried and concentrated. Products obtained in this reaction were separated using silica gel column chromatography, using petroleum ether and ethyl acetate as the solvent. The solid product was recrysalised in mixture of ethyl acetate and petroleum ether.

Weight of the colorless crystals: 0.30 g (32.5%)

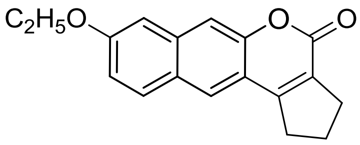
**M.p.** 191-192° C

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.92-7.88 (m, 2H), 7.60 (ddd, *J* = 1.2, 6.8, 8.4 Hz, 1H), 7.53 (td, *J* = 0.8, 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz,1H), 3.30 (t, *J* =6.0 Hz, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 1.93-1.83 (m, 4H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 161.4 (-C=O), 151.9 (Cq), 150.05 (Cq), 132.11 (CH), 131.59 (Cq), 129.68 (Cq), 129.60 (CH), 127.03 (CH), 125.85 (CH), 125.09 (CH), 123.72 (Cq), 117.57 (CH), 115.52 (Cq), 32.81 (-CH$_2$), 25.02 (-CH$_2$), 22.68 (-CH$_2$), 21.23 (-CH$_2$).

**Mass (EI):** ***m/z*, (%)** 251 (19) $[M+1]^{\cdot+}$, 250 (100) $[M]^{\cdot+}$, 249 (20), 235 (54), 222 (17), 221 (16), 194 (50), 165 (38).

***8-Ethoxy-2,3-dihydrobenzo[g]cyclopenta[c]chromen-4(1H)-one (34):***



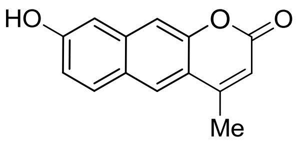
In a solution of 2,7-dihydroxynaphthalene (0.50 g, 3.12 mmol) in perchloric acid (10 mL, 70 %) was added ethylcyclopentanone-2-carboxylate (2.44 g, 2.31 mL, 15.6 mmol) at 0 °C over 15 min with a vigorous stirring. After the addition the reaction mixture was stirred for additional 24 h at room temperature, ice-water (100 mL) was added and continued the stirring (1 h) the brown coloured solid separated out filter and dried the solid as a crude product. The crude product was purified by the column chromatography using silica gel (petroleum ether:ethylacetate, 100:00 to 50:50) as a gradient for the elution to obtain white pure solid 8-ethoxy-2,3-dihydrobenzo- [*g*]cyclopenta[*c*]chromen-4(1*H*)-one **34** (0.262 g, 30%) and slightly impure mixture (0.219 g, 25%).

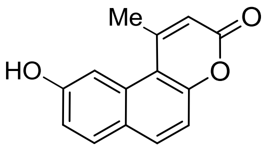
**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.82 (s, 1H), 7.80-7.78 (d, *J* = 8.8 Hz, 1H), 7.61 (s, 1H), 7.15-7.12 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.11-7.10 (d, *J* = 2.4 Hz, 1H), 4.21-4.15 (q, *J*= 7.2 Hz, 2H), 3.19-3.15 (m, 2H), 2.98-2.95 (m, 2H), 2.29-2.22 (m, 2H), 1.52-1.49 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** δ 160.48 (-CO), 158.52 (-Cq), 155.91 (-Cq), 151.69 (-Cq), 135.99 (-Cq), 129.84 (-CH), 127.38 (Cq), 125.58 (Cq), 124.34 (-CH), 119.61 (-CH), 119.74 (-Cq), 111.39 (-CH), 105.46 (-CH), 63.68 (-OCH$_2$), 32.12 (-CH$_2$), 30.82 (-CH$_2$), 22.49 (-CH$_3$), 14.75 (-CH$_3$).

**MS (EI):** ***m/z*, (%)** 281 (15) [M+1]$^{\cdot+}$, 280 (100) [M]$^{\cdot+}$, 279 (79), 252 (33), 251 (38), 224 (49), 223 (89), 196 (13), 195 (22), 194 (15), 165 (28), 164 (13), 152 (18), 151 (12), 98 (15), 84 (13), 70 (21), 69 (12), 56 (31), 54 (19).

### *4-Methyl-8-hydroxynaphtho[2,3-b]pyran-2-one (8) and 1-Methyl-9-hydroxy-naphtho[2,1-b]pyranone (9):*





To a mixture of of 2,7-dihydroxynaphthalene (8.0 g, 50.0 mmol) and ethylacetoacetate (16 mL, 156 mmol) was added 80% H$_2$SO$_4$ (60 mL) drop wise at 0 °C. The mixture was stirred for 24 h at room temperature and after the addition of ice/water (200 mL) obtained a solid, which was filtered, washed with water and dried to give a mixture of 4-methyl-8-hydroxynaphtho[2,3-b]pyran-2-one **8** and 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9**. The filter cake was dissolved in aqueous NaOH (10%) and the insoluble material was filtered. To the filtrate was treated with conc. HCl until pH changed to 1 to 2. The solid was collected by filtration, washed with water, dried and recrystallized from acetic acid to give 4-methyl-8-hydroxynaphtho[2,3-b]pyran-2-one **8** (4.83 g, 43%). The filtrate was left overnight to obtain crystals of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** (3.15 g, 28%).

4-Methyl-8-hydroxynaphtho[2,3-b]pyran-2-one **8:**

**M.p.** 275-276 °C, (Lit.$^4$ 274 °C).

1-Methyl-9-hydroxy-naphtho[2,1-b]pyranone **9:**

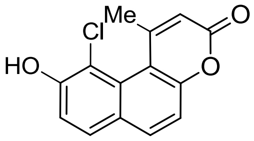
**M.p.** 281-283 °C, (Lit.$^4$ 284 °C).

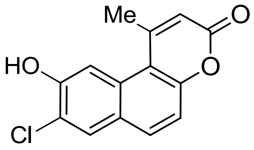
**$^1$H-NMR (400 MHz, DMSO-*d*$^6$):** δ 10.18 (s, 1H for -OH group), 8.05 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.13 (dd, *J* = 2.0, 8.8 Hz, 1H), 6.42 (s, 1H), 2.86 (s, 3H).

**MS (EI):** ***m/z*, (%)** 226 (69), 198 (36), 197 (41), 115 (25), 98 (24), 97 (24), 85 (38), 84 (32), 83 (37), 81 (23), 74 (18), 73 (30), 71 (40), 70 (19), 69 (45), 67(18), 60(36), 57 (100), 56 (27), 55 (76).

**IR (KBr):** 3200, 2364, 2078, 1687, 1614, 1474, 1243, 1130, 931 cm.$^{-1}$

### *10-Chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (36) and 8-Chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (37):*





A solution of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** (0.100 g, 0.44 mmol), conc. HCl (0.11 mL, 0.88 mmol) and 30% w/v aqueous hydrogen peroxide (0.050 mL, 0.44 mmol) in methanol (5 mL) and reflux the reaction mixture for 12 h. After the completion of the reaction, water (10 mL) was added and extracted with ethylacetate (2 X 50 mL), the organic layer was washed with water, dried over sodium sulphate and concentrated at reduced pressure to obtain the crude solid. The purification of the compound by column chromatography over silica gel using petroleum ether:ethylacetate (100:00 to 60:40) as gradient for the elution to obtain the compound 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **36** (0.041 g, 36%) and 8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **37** (0.060 g, 52%); the compound **37** was eluted first from the column.

### *8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (36):*

**$^1$H-NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, $J$ = 10.0 Hz, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.17 (d, $J$ = 8.4 Hz, 1H), 6.44 (s, 1H for -OH group), 6.25 (d, $J$ = 10 Hz, 1H), 6.135 (q, $J$ = 1.6 Hz, 1H, olefinic H), 1.767 (d, $J$ = 1.6 Hz, 3H).

The $D_2O$ exchange shows the disappearance of the singlet at δ 6.44 ppm for -OH group.

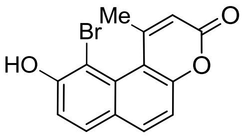
**MS (EI): *m/z*, (%)** 262 (18) $[M+2]^+$, 261 (10) $[M+1]^+$, 260 (59) $[M+]^+$, 234 (10), 233 (07), 232 (28), 231 (12), 225 (29), 198 (15), 197 (100), 169 (10), 168 (14), 167 (08), 141 (11), 140 (10), 139 (30), 115 (10), 84 (08), 69 (11).

### *8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (37):*

**$^1$H-NMR (400 MHz, DMSO-$d^6$):** δ 11.06 (s, 1H, -OH group), 8.02-7.90 (m, 2 H), 7.34 (m, 2H), 6.34 (s, 1H), 2.48 (broad peak, 3H for $–CH_3$ merged with solvent peak prove by 1H-13-C HSQCGP NMR analysis).

**$^{13}$C-NMR (100.6 MHz, DMSO-$d^6$):** δ 159.70 (-CO), 155.44 (Cq), 155.21 (Cq), 155.13 (Cq), 133.65 (-CH), 129.88 (Cq), 129.57 (-CH), 126.92 (Cq), 117.86 (-CH), 114.45 (-CH), 114.27 (Cq), 113.73(Cq), 112.34 (-CH), 23.63 ($-CH_3$).

***10-Bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (38):***



A solution of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** (0.050 g, 0.22 mmol), N-bromosuccinimide (0.039 g, 0.22 mmol) and triethylamine (0.090 mL, 0.66 mmol) in chloroform (5 mL) was stirred at room temperature for 12 h. After the completion of the reaction, the mixture was poured in water and extracted with chloroform (2 X 25 mL), the organic layer washed with the water, dried over sodium sulphate and concentrated at reduced pressure to obtain the crude solid. The purification of the compound by column chromatography over silica gel using petroleum ether:ethylacetate (100:00 to 90:10) gradient for the elution to obtain the compound 10-bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **38** (0.059 g, 88%).

**$^1$H-NMR (400 MHz, CDCl$_3$):** δ 7.84 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 6.21 (s, 1H), 2.59 (s, 3H).

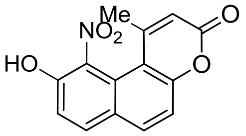
**Chiral HPLC analysis:**

Observed one peak at 1) $R_t$ – 5.67 min

Solvent System: *n*-Hexane: *Iso*-propanol (60:40), Flow rate: 1 mL/min.

Detector: UV-Vis. Column: Chiralpak Diacel-OD H.

***10-Nitro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (39):***

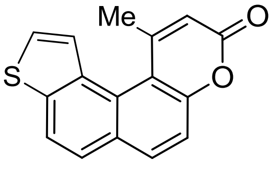


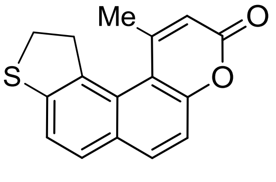
A solution of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** (0.150 g, 0.66 mmol) and nitric acid (0.063 g, 0.045 mL, 0.99 mmol) in chloroform (5 mL) was kept in ultrasound sonicator at room temperature for 2 h. After completion of the reaction, it was poured on ice-cold water and extracted with ethylacetate (2 X 50 mL), the organic layer was washed with water, dried over sodium sulphate and concentrated at reduced pressure to obtain the crude yellow solid. The purification of the compound by column chromatography over silica gel using petroleum ether:ethylacetate (100:00 to 80:20) gradient for the elution obtained the compound 10-nitro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **39** (0.090 g, 50%).

**$^1$H-NMR (400 MHz, CDCl$_3$):** 11.2 (s, 1H for –OH group), 8.02 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.29 (s, 1H), 2.28 (s, 3H).

**$^{13}$C NMR (100.6 MHz, CDCl$_3$)**: 159.57 (-CO), 157.27 (-Cq), 155.91 (-Cq), 153.00 (-Cq), 138.56 (-CH), 131.96 (-CH), 130.82 (-Cq), 126.16 (-Cq), 123.33 (-Cq), 118.81 (-CH), 117.39 (-CH), 115.55 (-Cq), 114.50 (-CH), 20.43 (-CH$_3$).

### *11-methyl-9H-thieno[2',3':5,6]benzo[1,2-f]chromen-9-one 40 and 11-methyl-1H-thieno[2',3':5,6]benzo[1,2-f]chromen-9(2H)-one 41:*





A solution of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone **9** (0.300 g, 1.42 mmol), 2-mercaptoethanol (0.600 mL, 8.56 mmol) and trifluoromethane sulphonic acid (0.315 mL, 3.56 mmol) in chlorobenzene was refluxed for 24 h. After completion of the reaction the mass was poured on ice/water, extracted with ethyl acetate (2 X 50 mL), the organic layer was washed with NaOH solution (10 %), water, dried over sodium sulphate and concentrated under reduced pressure to obtain the crude pale yellow solid. Purification of the compound by column chromatography over silica gel using petroleum ether:ethylacetate (100:00 to 80:20) gradient for the elution to obtain the compound 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40** and 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2H)-one **41**. The compound 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one **40** (0.046 g, 12%) was eluted first from the column followed by **41** (0.032 g, 9%).

### *11-methyl-9H-thieno[2',3':5,6]benzo[1,2-f]chromen-9-one 40:*

**$^{1}$H-NMR (400 MHz, CDCl$_3$):** 8.03-7.98 (m, 2H), 7.77 (d, $J$ = 8.8 Hz, 1H), 7.59 (d, $J$ = 5.6 Hz, 1H), 7.56 (d, $J$ = 5.6 Hz, 1H), 7.45 (d, $J$ = 8.4 Hz, 1H), 6.40 (d, $J$ = 1.2 Hz, 1H), 2.51 (d, $J$ = 0.8 Hz, 3H).

**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: 160.55 (-CO), 154.39 (-Cq), 153.51 (-Cq), 140.29 (-Cq), 134.21 (-Cq), 132.98 (-CH), 128.99 (-Cq), 127.23 (-CH), 125.88 (-Cq), 124.93 (-CH), 124.91 (-CH), 121.22 (-CH), 115.91 (-CH), 115.48 (-Cq), 114.92 (-CH), 22.98 (-CH$_3$).

**MS (EI):** ***m/z*, (%)** 267 (19) M+2, 266 (100) M, 265 (95), 248 (15), 238 (22), 236 (72), 255 (37), 224 (62), 223 (28), 209 (26), 207 (72), 194 (31), 164 (14), 162 (23), 148 (14), 96 (14), 88 (11), 76 (13), 74 (18).

**Chiral HPLC analysis:**

Observed one peak at 1) $R_t$ – 20.15 min

Solvent System: *n*-Hexane: *Iso*-propanol (90:10), Flow rate: 1 mL/min.

Detector: UV-Vis. Column: Lux Amylose-2.

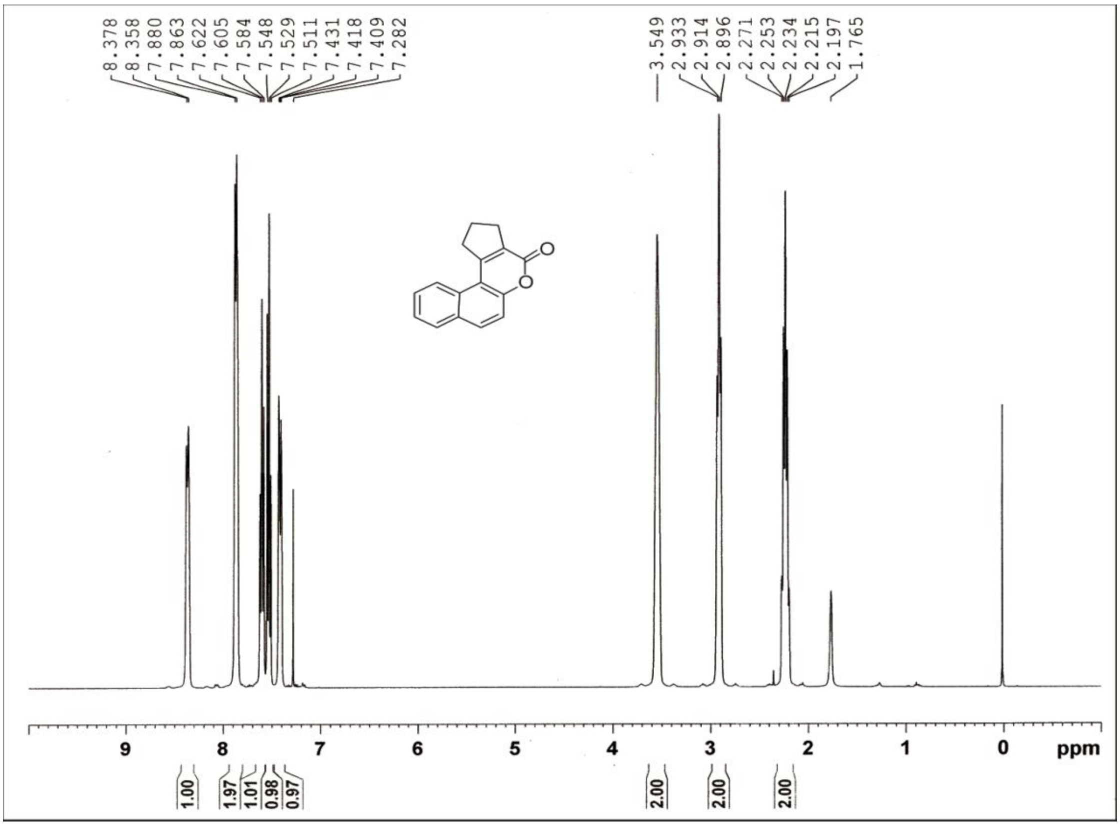
***11-methyl-1H-thieno[2',3':5,6]benzo[1,2-f]chromen-9(2H)-one 41:***

**$^1$H-NMR (400 MHz, CDCl$_3$):** 7.83 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 6.28 (d, *J* = 0.8 Hz, 1H), 3.47-3.45 (m, 2H), 3.37-3.34 (m, 2H), 2.48 (d, *J* = 1.2 Hz, 3H).

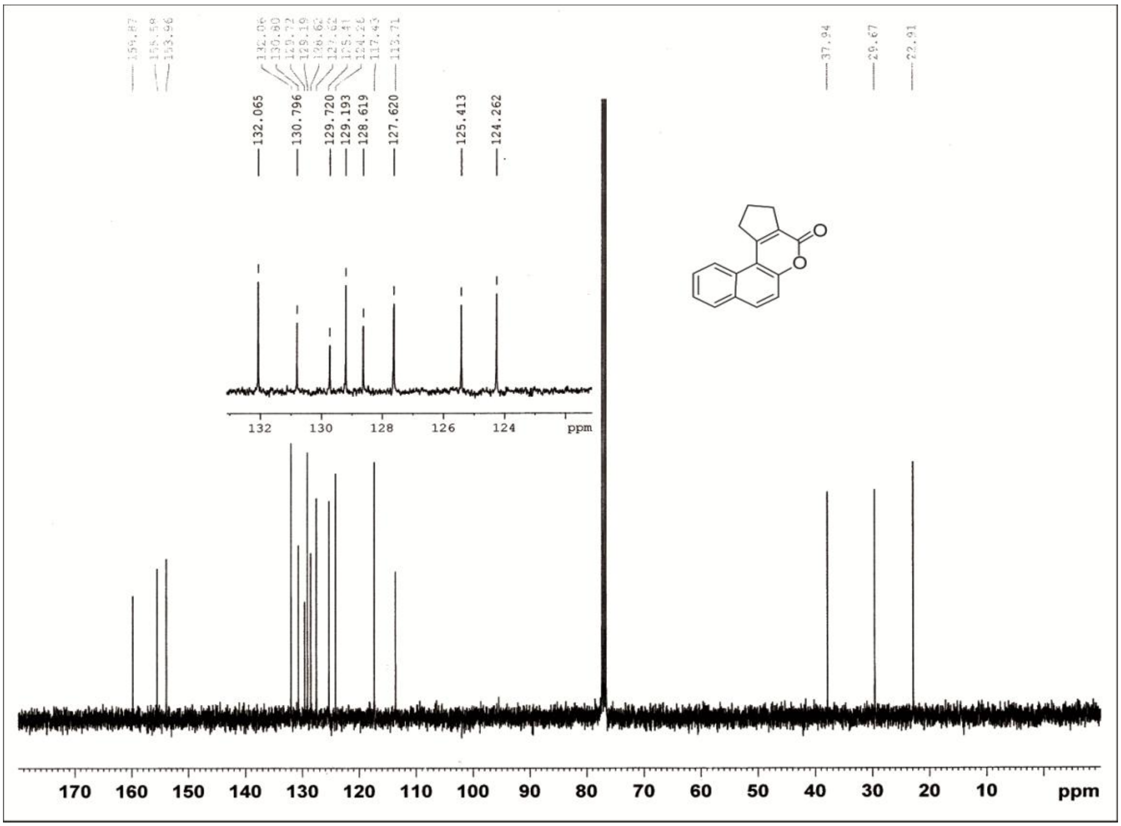
**$^{13}$C NMR (CDCl$_3$, 100.6 MHz)**: 160.53 (-CO), 155.26 (-Cq), 153.40 (-Cq), 143.89 (-Cq), 133.83 (-Cq), 133.63 (-CH), 129.42 (-Cq), 128.56 (-CH), 127.84 (-Cq), 121.95 (-CH), 115.23 (-CH), 115.06 (Cq), 113.34 (-CH), 39.75 (-CH$_2$), 34.89 (-CH$_2$), 22.79 (-CH$_3$).

# Spectral Data

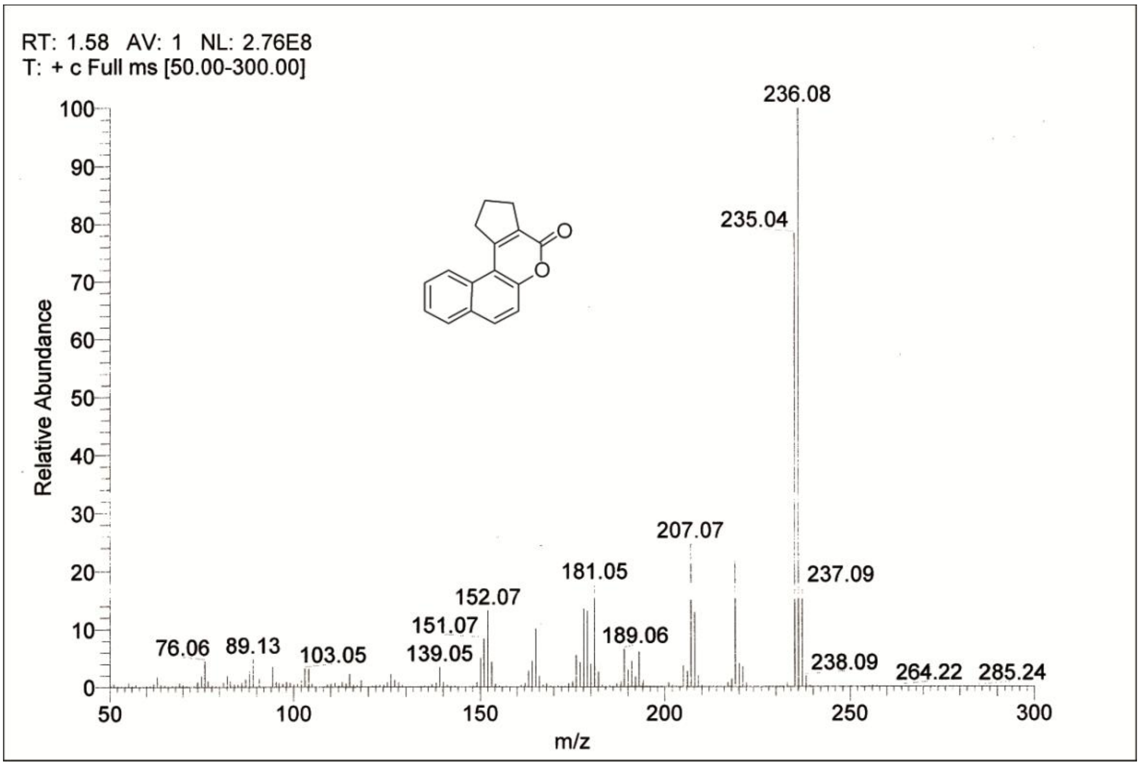
## Spectral data of 3,4-cyclopenteno[5,6]benzocoumarin (26)



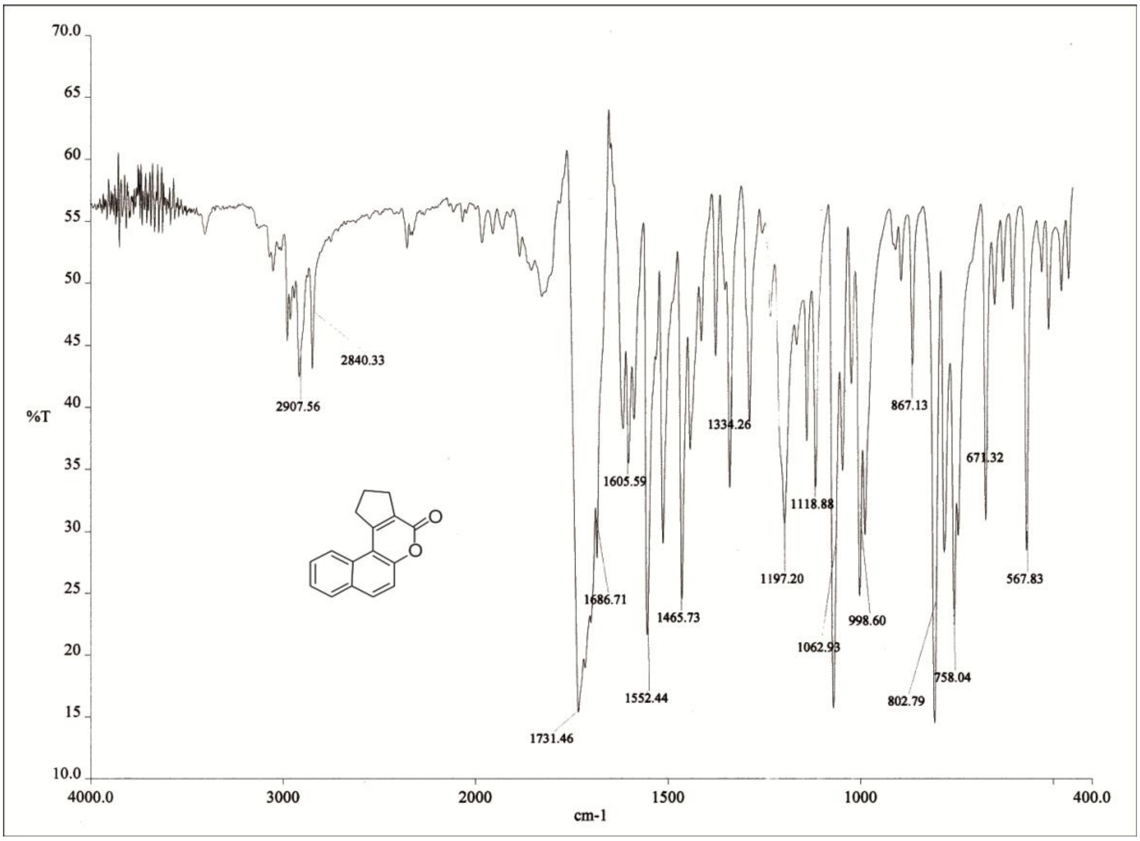
**$^{1}$H-NMR spectrum of 3,4-cyclopenteno[5,6]benzocoumarin (26) in $CDCl_3$ on 400 MHz**



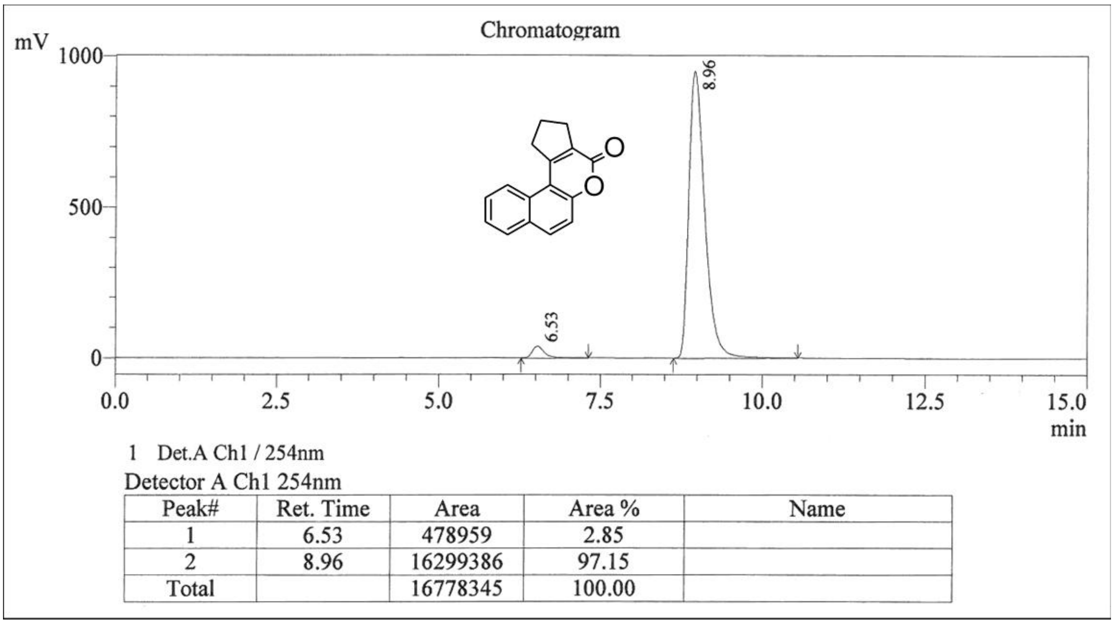
**$^{13}$C-NMR spectrum of 3,4-cyclopenteno[5,6]benzocoumarin (26) in $CDCl_3$ on 100.6 MHz**



EI-Mass spectrum of 3,4-cyclopenteno[5,6]benzocoumarin (26)



IR spectrum of 3,4-cyclopenteno[5,6]benzocoumarin (26)



1 Det.A Ch1 / 254nm

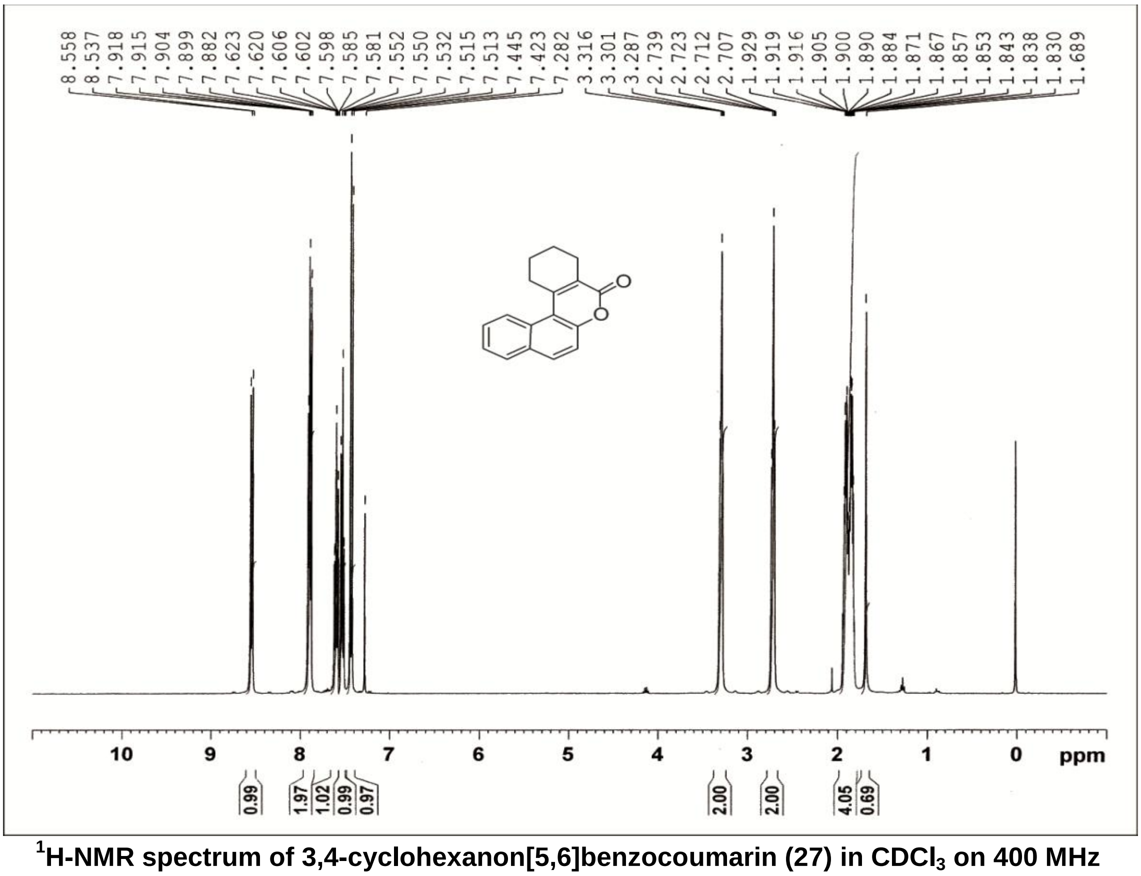
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6.53 | 478959 | 2.85 | |
| 2 | 8.96 | 16299386 | 97.15 | |
| Total | | 16778345 | 100.00 | |

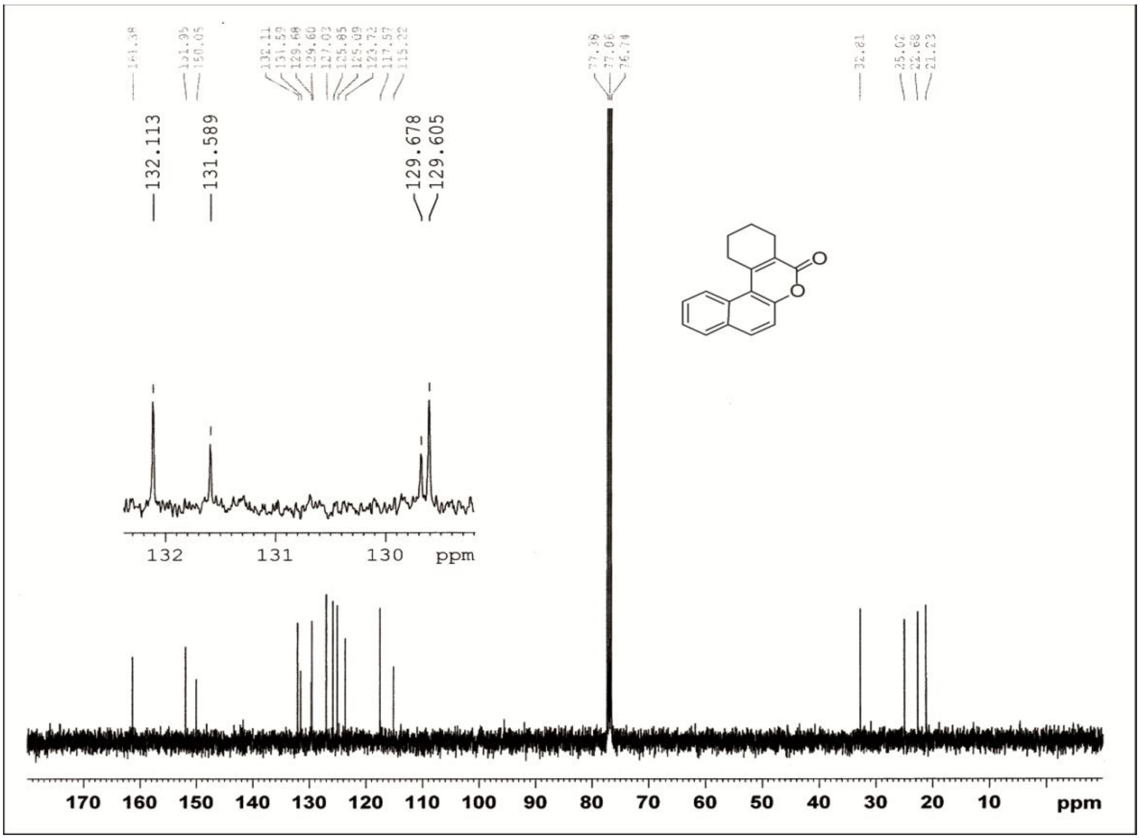
## Chiral HPLC analysis:

Observed one peak at 1) $R_t$ – 8.96 min
Solvent System: *n*-Hexane: *Iso*-propanol (60:40), Flow rate: 1 mL/min.
Detector: UV-Vis. Column: Chiralpak Diacel-OD H.

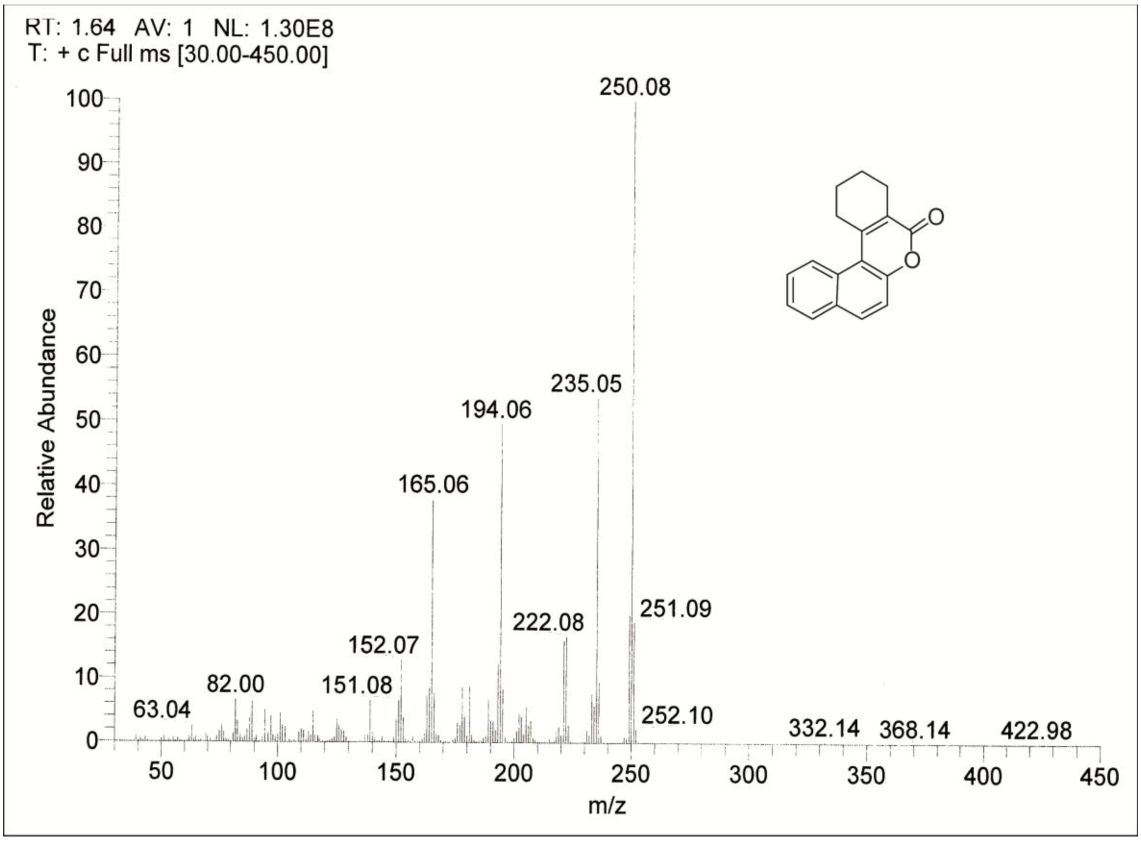
### Spectral Data of 3,4-cyclohexenon[5,6]benzocoumarin (25)



**$^1$H-NMR spectrum of 3,4-cyclohexanon[5,6]benzocoumarin (27) in $CDCl_3$ on 400 MHz**

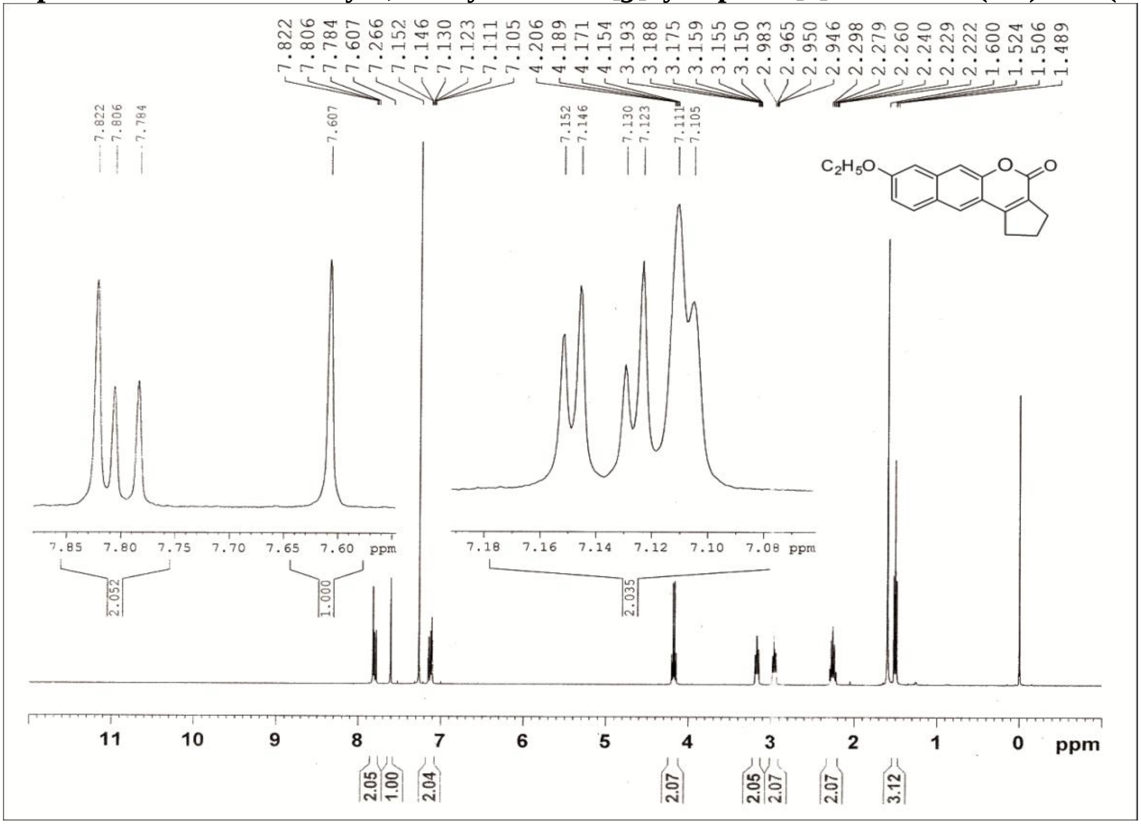


$^{13}$C-NMR spectrum of 3,4-cyclohexanon[5,6]benzocoumarin (27) in CDCl$_3$ on 100.6 MHz

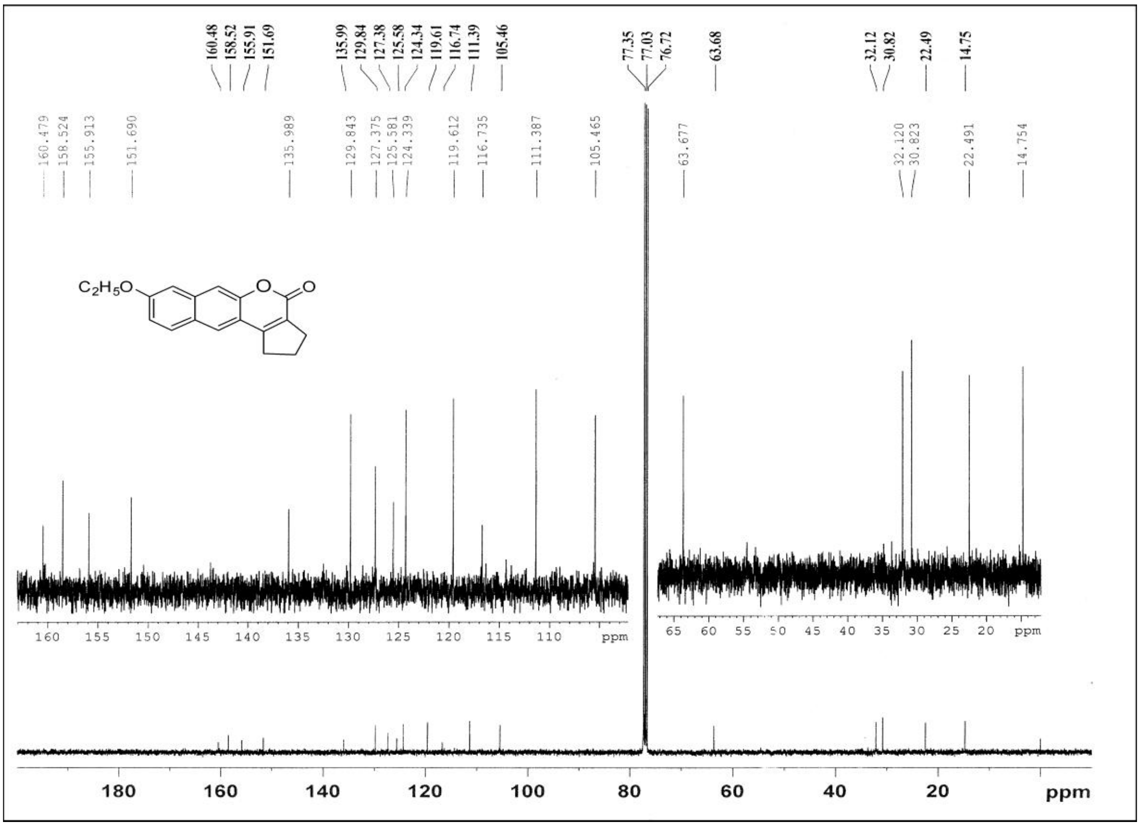


**EI-Mass spectrum of 3,4-cyclohexanon[5,6]benzocoumarin (27)**

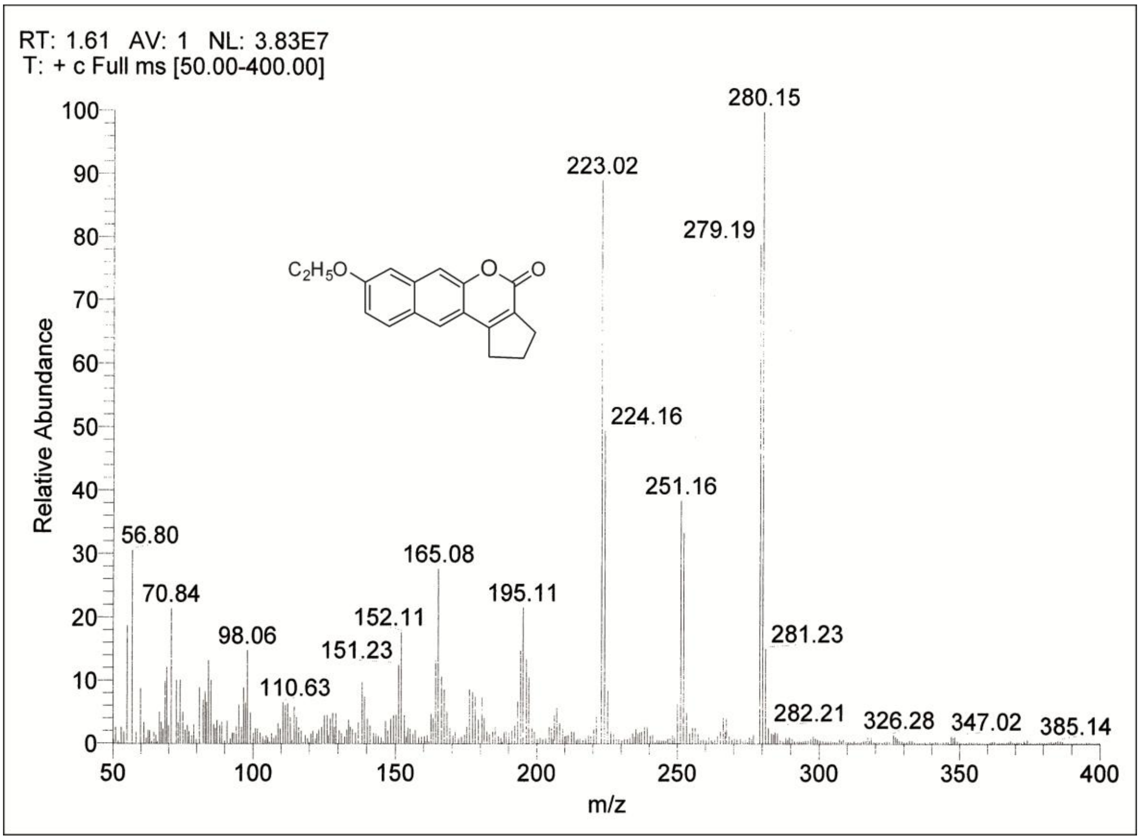
## Spectral data of 8-ethoxy-2,3-dihydrobenzo[*g*]cyclopenta[*c*]chromen-4(1*H*)-one (34)



$^1$H-NMR spectrum of 8-ethoxy-2,3-dihydrobenzo[*g*]cyclopenta[*c*]chromen-4(1*H*)-one (34) in $CDCl_3$ on 400 MHz

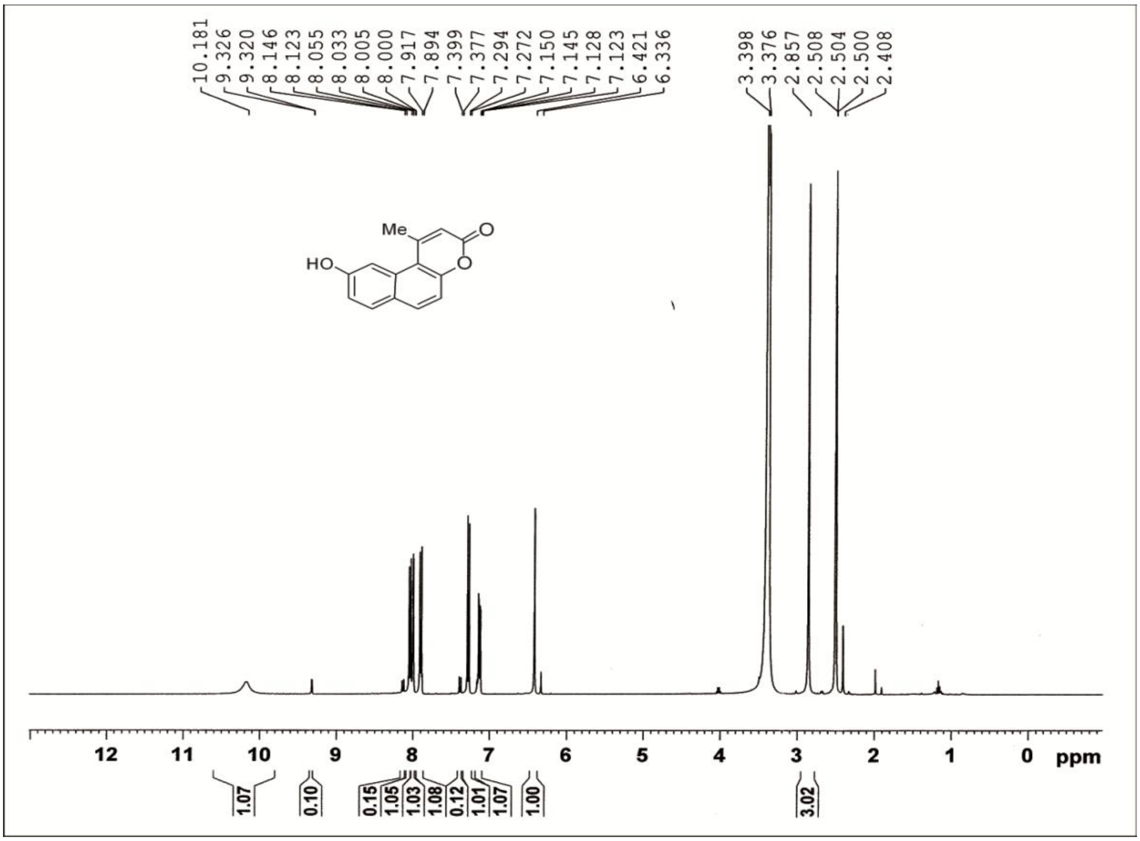


$^{13}$C-NMR spectrum of 8-ethoxy-2,3-dihydrobenzo[*g*]cyclopenta[*c*]chromen-4(1*H*)-one (34) in $CDCl_3$ on 100.6 MHz

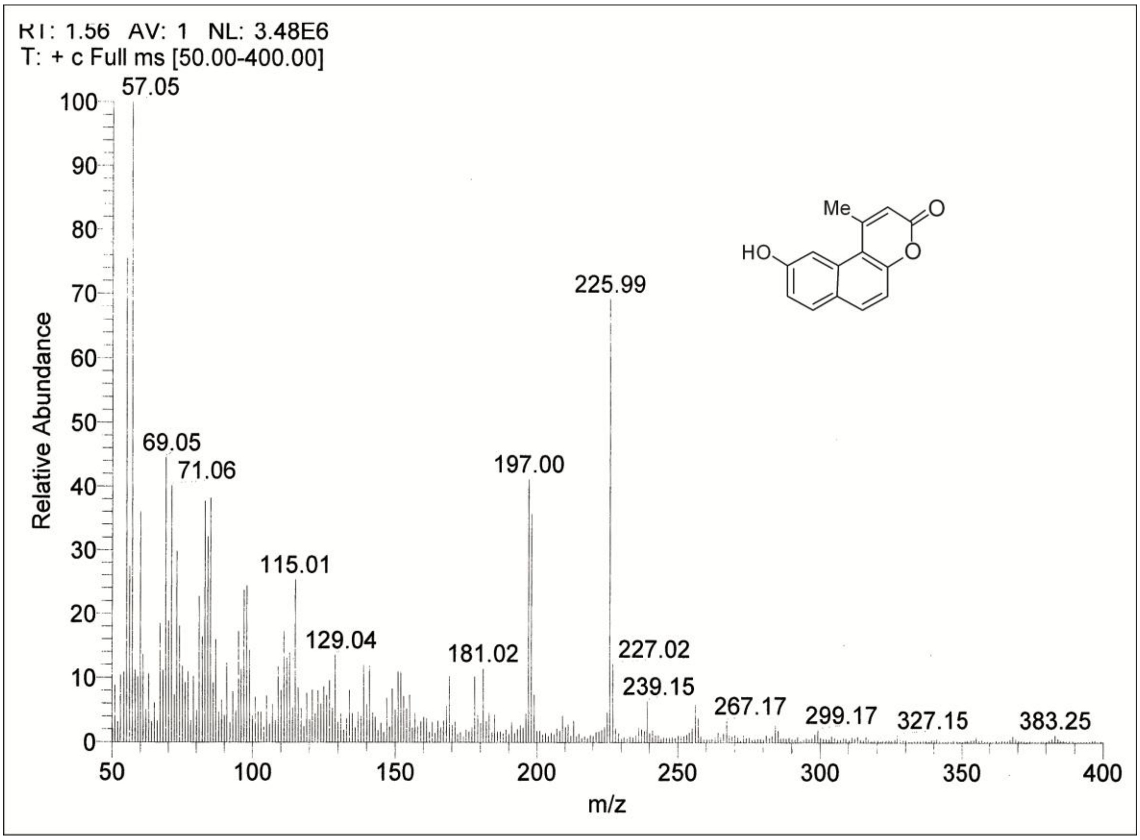


**EI-Mass spectrum of 8-ethoxy-2,3-dihydrobenzo[*g*]cyclopenta[*c*]chromen-4(1*H*)-one (34)**

## Spectral data of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (9)

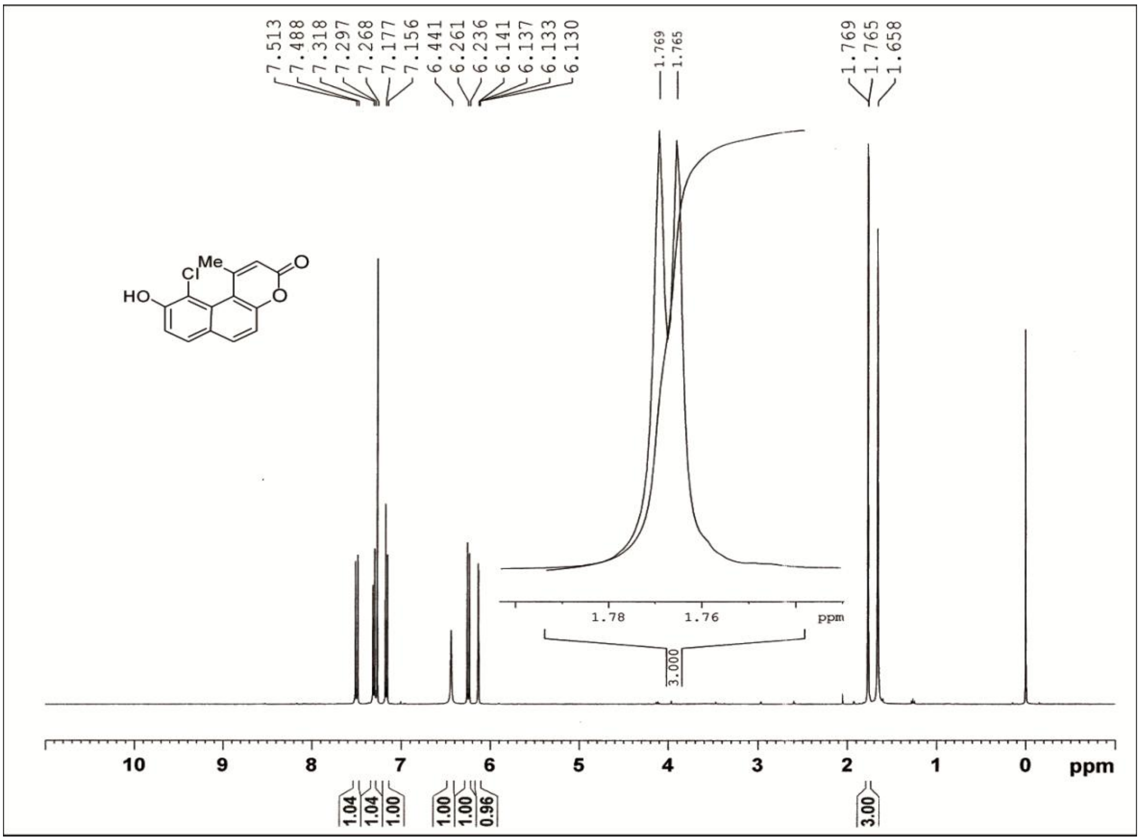


**$^1$H-NMR spectrum of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (9) in $CDCl_3$ on 400 MHz**

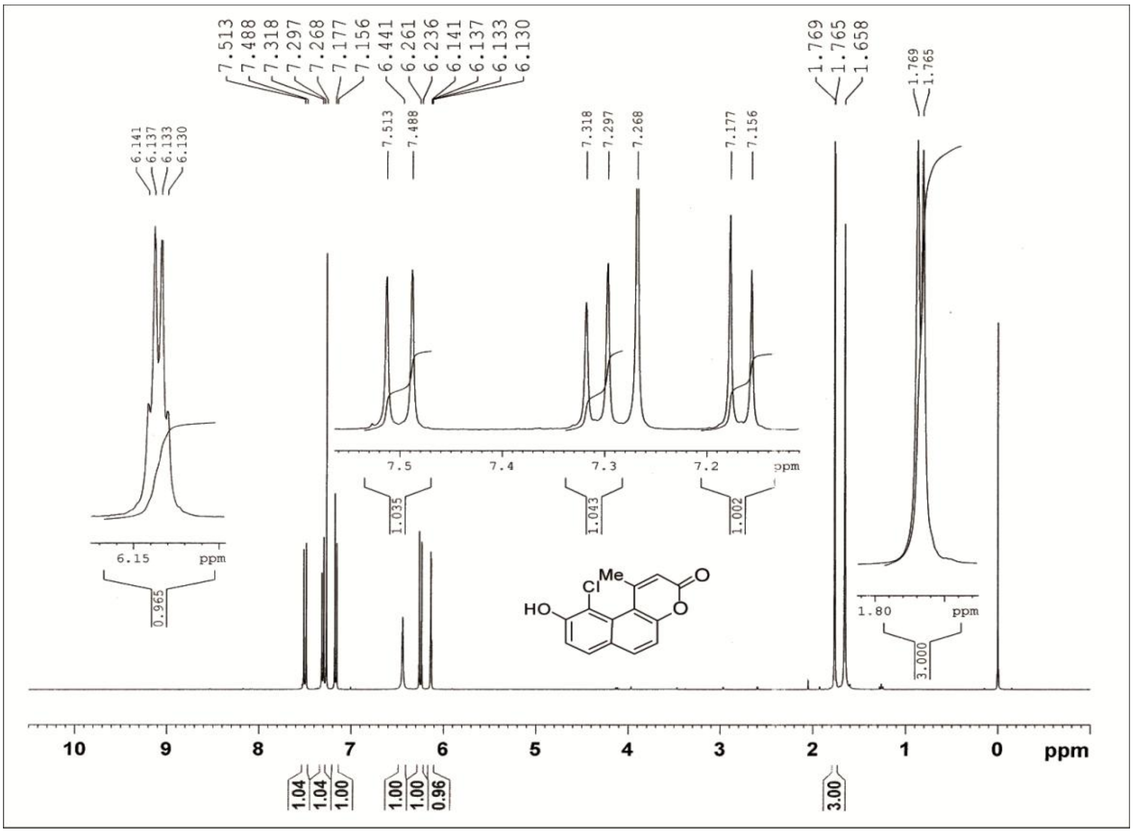


**EI-Mass spectrum of 1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (9)**

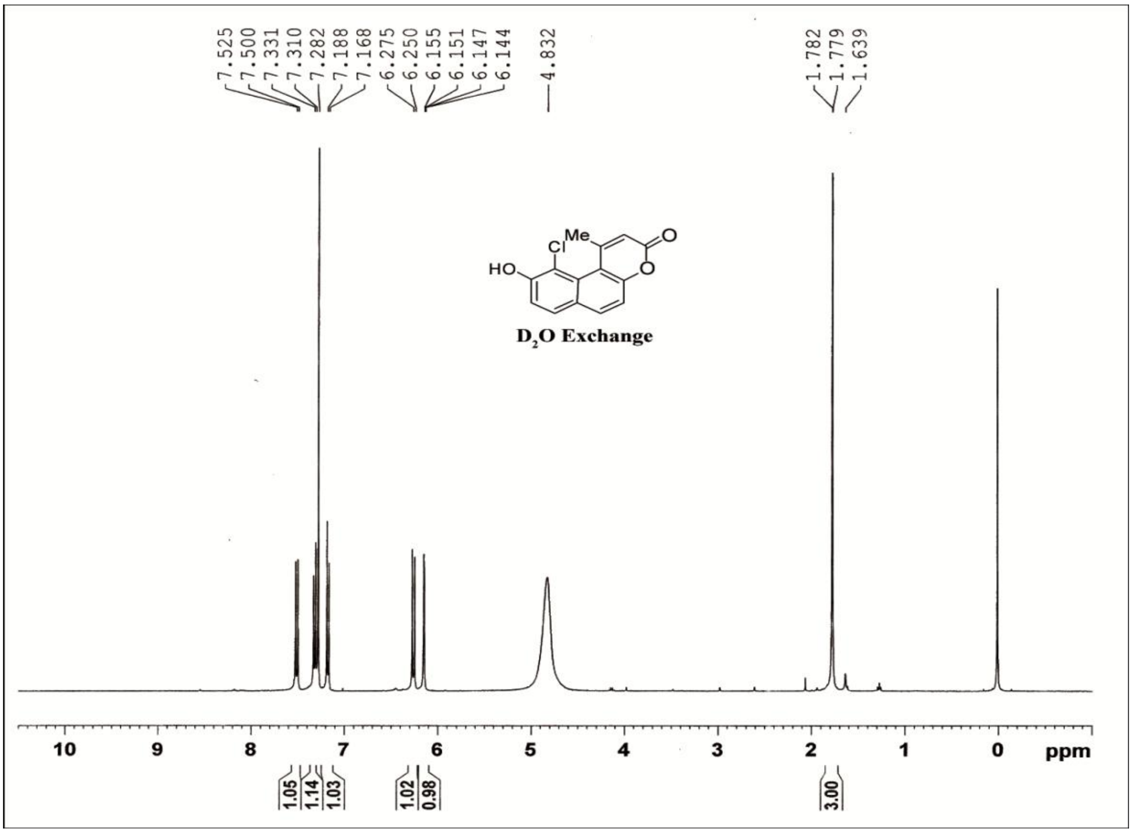
## Spectral data of 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (36)



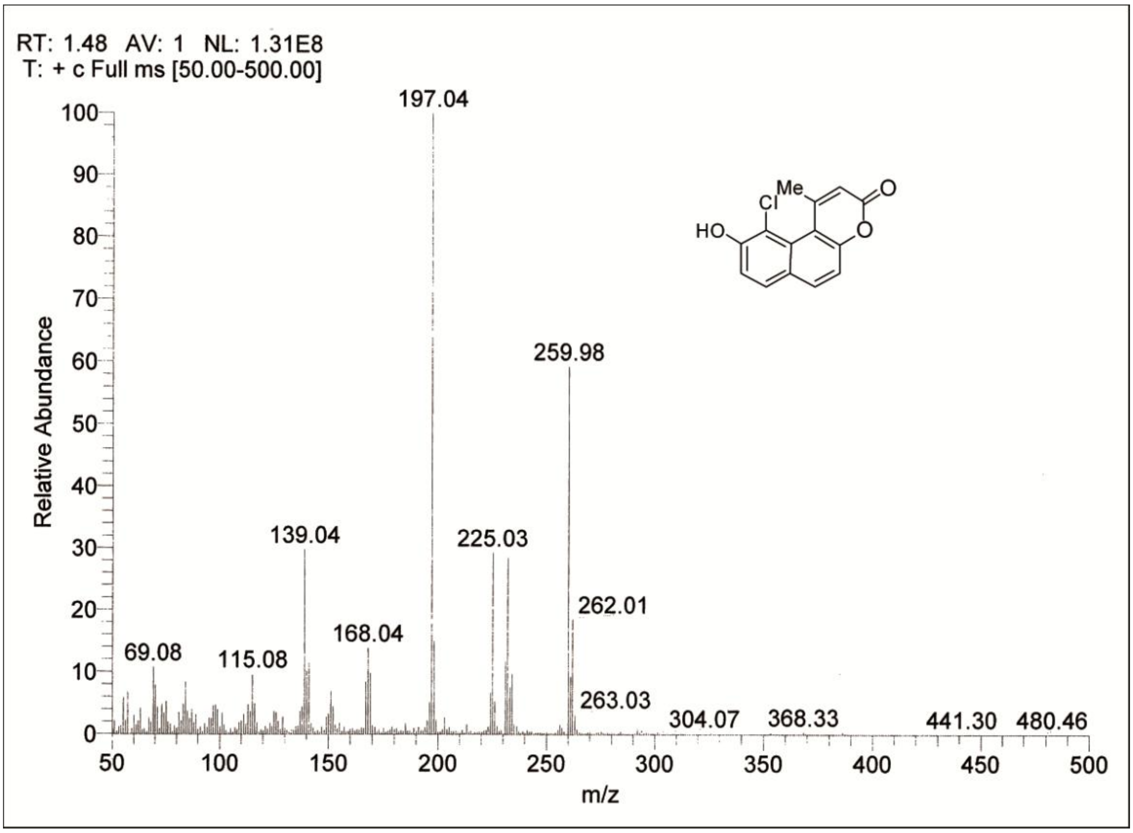
**$^1$H-NMR spectrum of 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (36) in $CDCl_3$ on 400 MHz**



$^1$**H-NMR enlarge spectrum of 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (36) in $CDCl_3$ on 400 MHz**

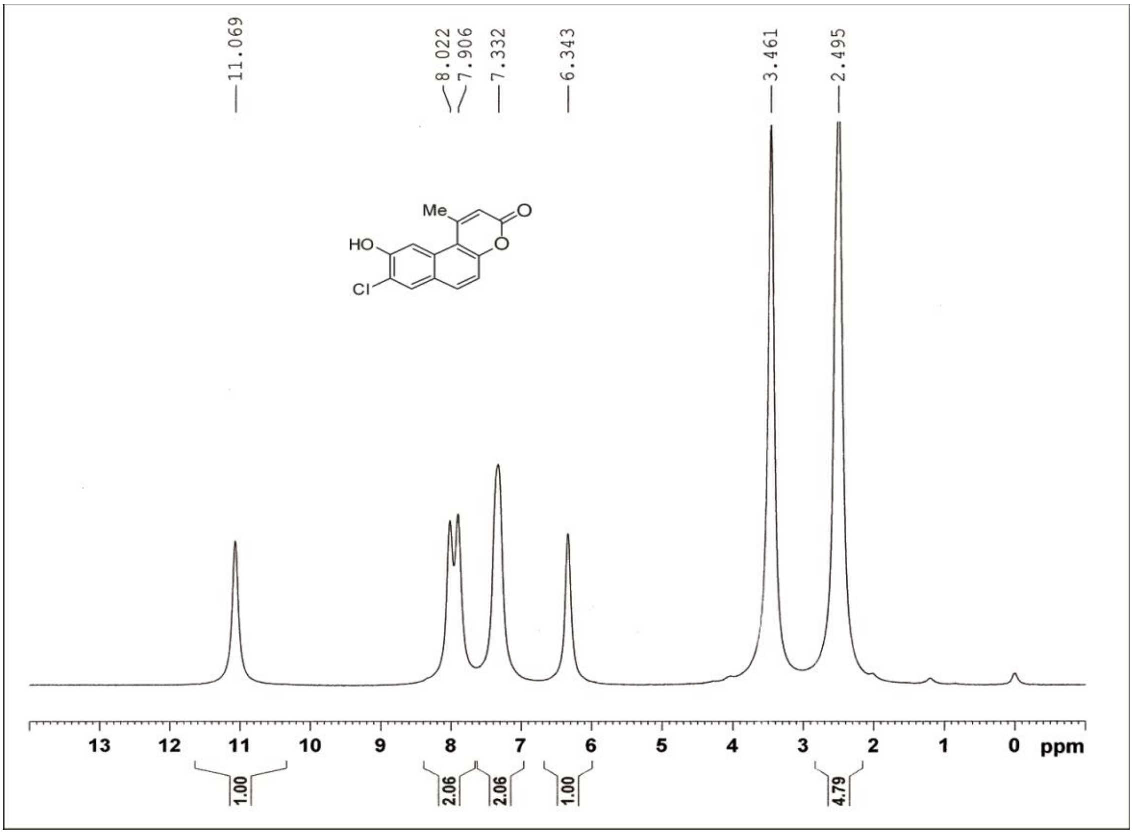


$^1$**H-NMR spectrum $D_2O$ exchange spectrum of 10-chloro-1-methyl-9-hydroxy-naphtho-[2,1-b]pyranone (36) in $CDCl_3$ on 400 MHz**

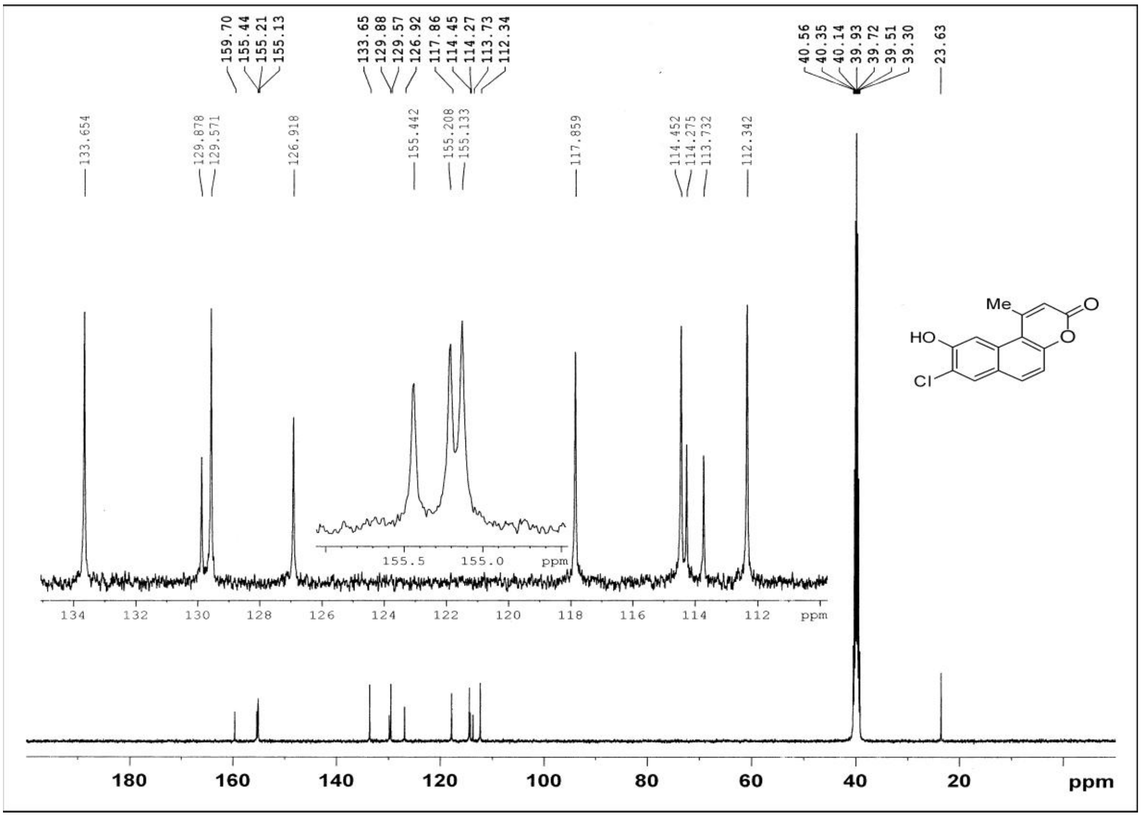


**EI-Mass spectrum of 10-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (36)**

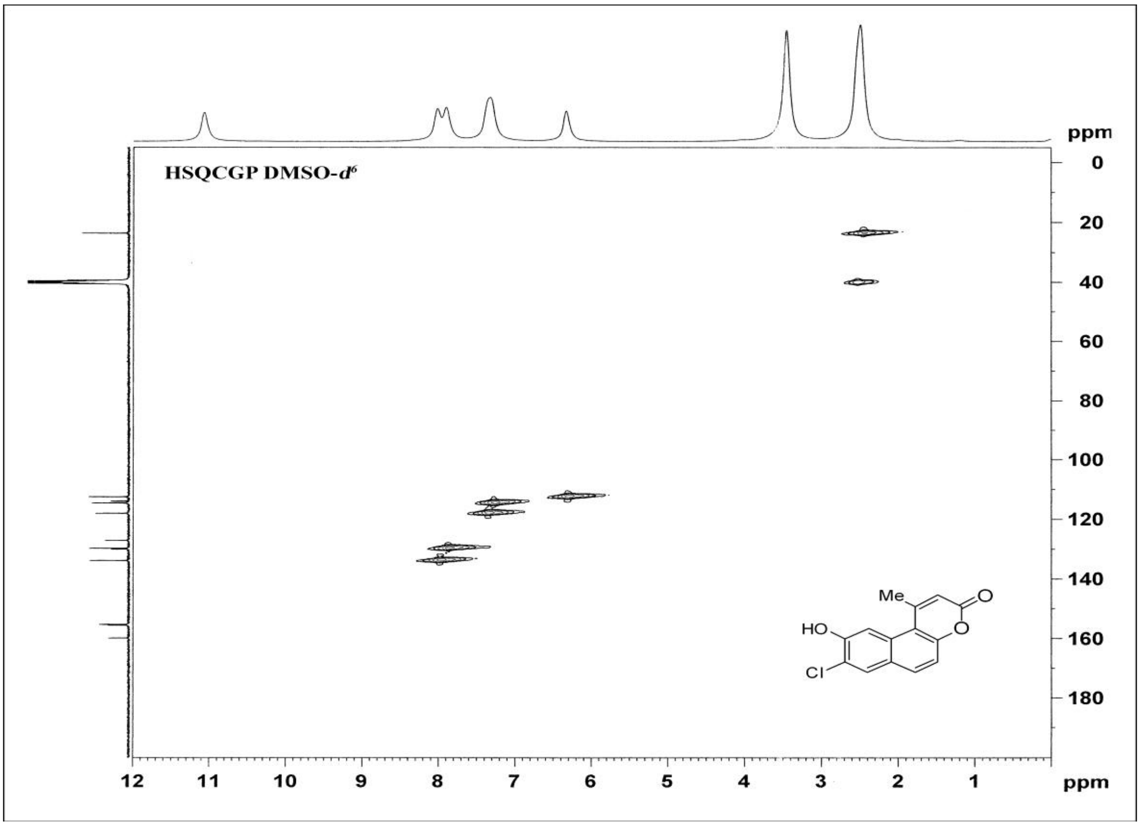
## Spectral data of 8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (37)



$^1$H-NMR spectrum of 8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (37) in DMSO-*d*$^6$ on 400 MHz

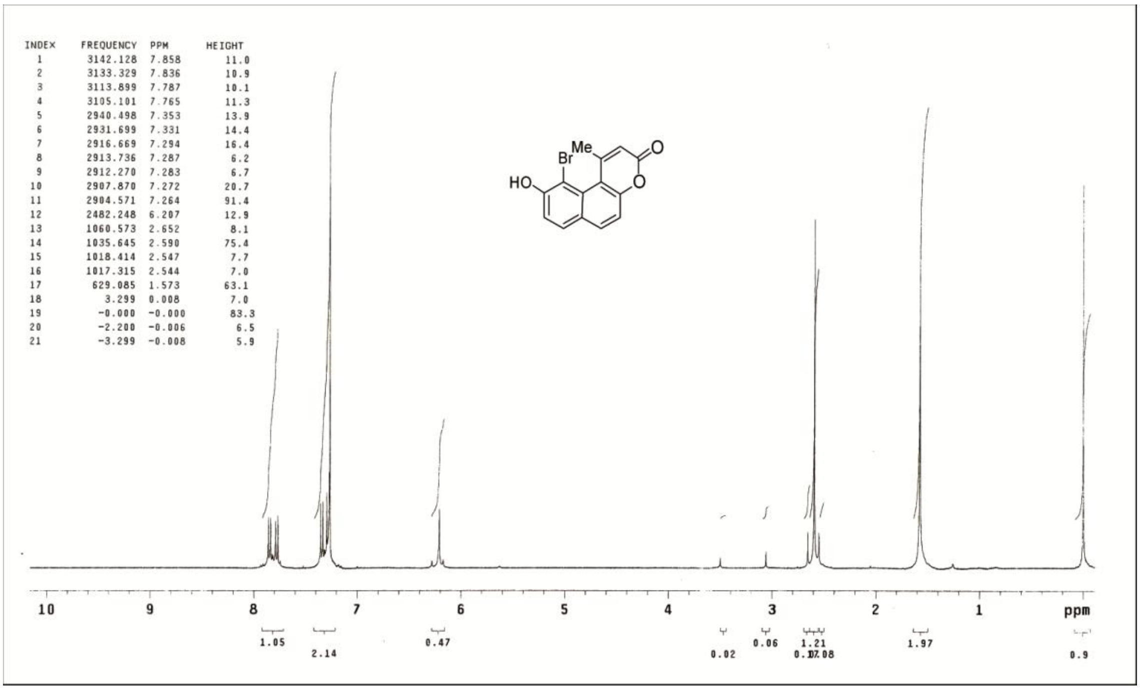


$^{13}$**C-NMR spectrum of 8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (37) in DMSO-*d*$^{6}$ on 100.6 MHz**



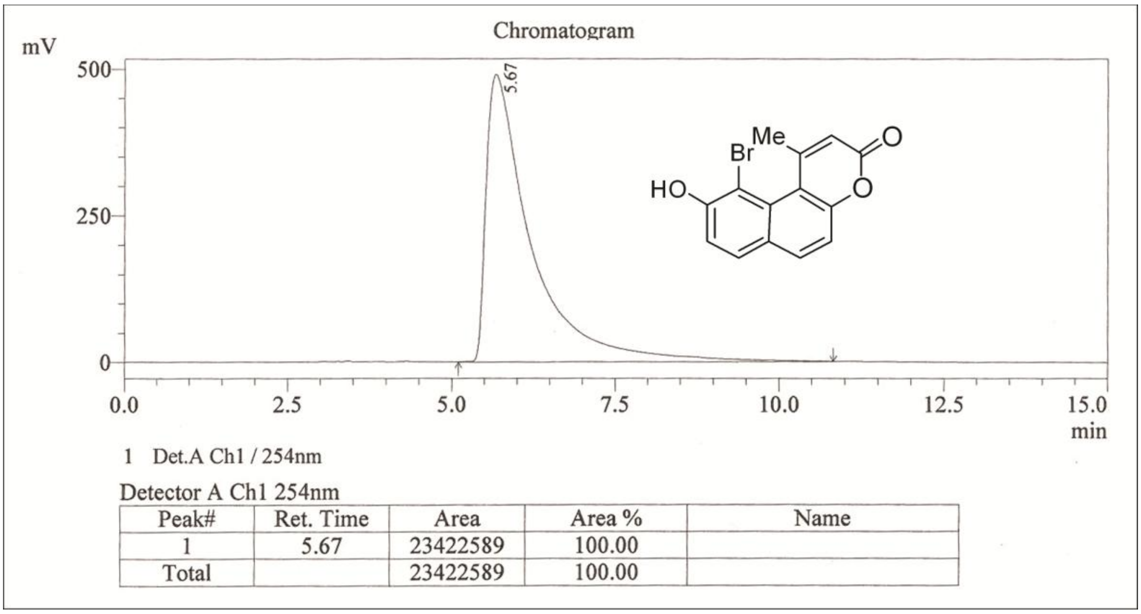
$^{1}$**H-**$^{13}$**C correlation HSQCGP NMR spectrum of 8-chloro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (37) in DMSO-*d*$^{6}$ on 400 MHz**

## Spectral data of 10-bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (38)



| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 3142.128 | 7.858 | 11.0 |
| 2 | 3133.329 | 7.836 | 10.9 |
| 3 | 3113.899 | 7.787 | 10.1 |
| 4 | 3105.101 | 7.765 | 11.3 |
| 5 | 2940.498 | 7.353 | 13.9 |
| 6 | 2931.699 | 7.331 | 14.4 |
| 7 | 2916.669 | 7.294 | 16.4 |
| 8 | 2913.736 | 7.287 | 6.2 |
| 9 | 2912.270 | 7.283 | 6.7 |
| 10 | 2907.870 | 7.272 | 20.7 |
| 11 | 2904.571 | 7.264 | 91.4 |
| 12 | 2482.248 | 6.207 | 12.9 |
| 13 | 1060.573 | 2.652 | 8.1 |
| 14 | 1035.645 | 2.590 | 75.4 |
| 15 | 1018.414 | 2.547 | 7.7 |
| 16 | 1017.315 | 2.544 | 7.0 |
| 17 | 629.085 | 1.573 | 63.1 |
| 18 | 3.299 | 0.008 | 7.0 |
| 19 | -0.000 | -0.000 | 83.3 |
| 20 | -2.200 | -0.006 | 6.5 |
| 21 | -3.299 | -0.008 | 5.9 |

**$^1$H-NMR spectrum of 10-bromo-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (38) in $CDCl_3$ on 400 MHz**



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 5.67 | 23422589 | 100.00 | |
| Total | | 23422589 | 100.00 | |

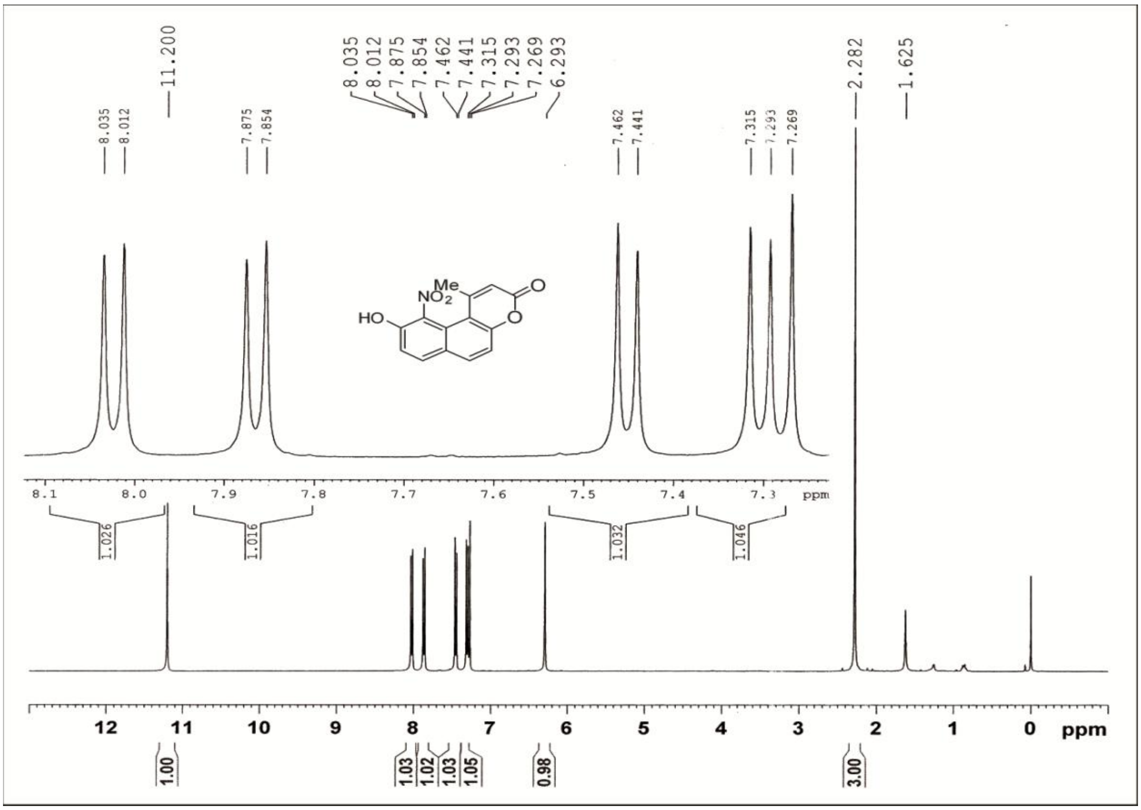
**Chiral HPLC analysis:**

Found 1 peak at 1) $R_t$ – 5.67 min

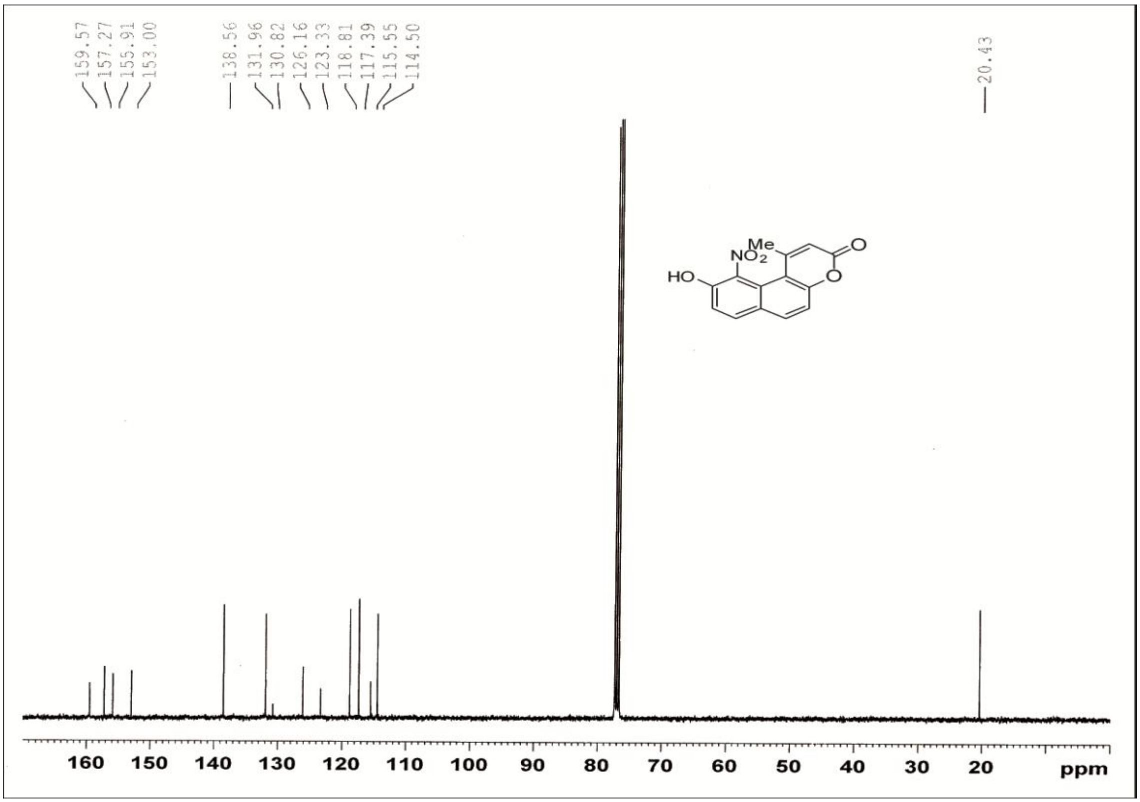
Solvent System: *n*-Hexane: *Iso*-propanol (60:40), Flow rate: 1ml/min.

Detector: UV-Vis. Column: Chiralpak Diacel-OD H.

## Spectral data of 10-nitro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (39)

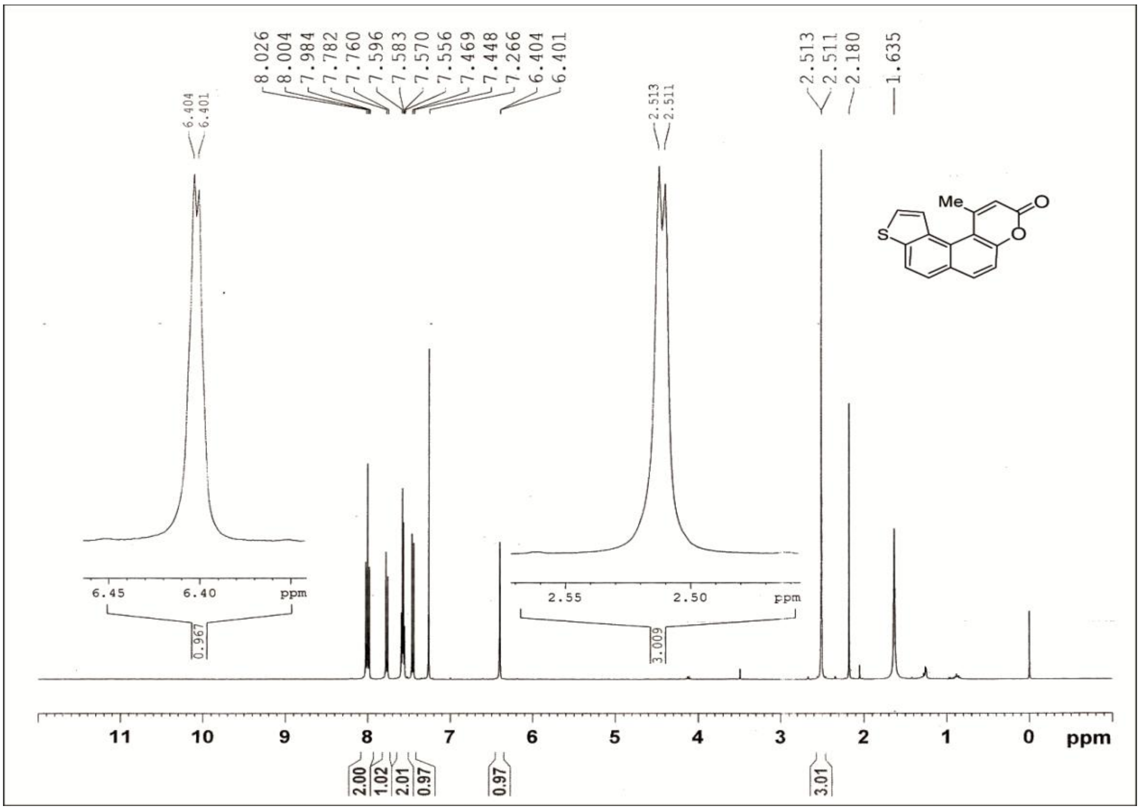


**$^{1}$H-NMR spectrum of 10-nitro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (39) in $CDCl_3$ on 400 MHz**

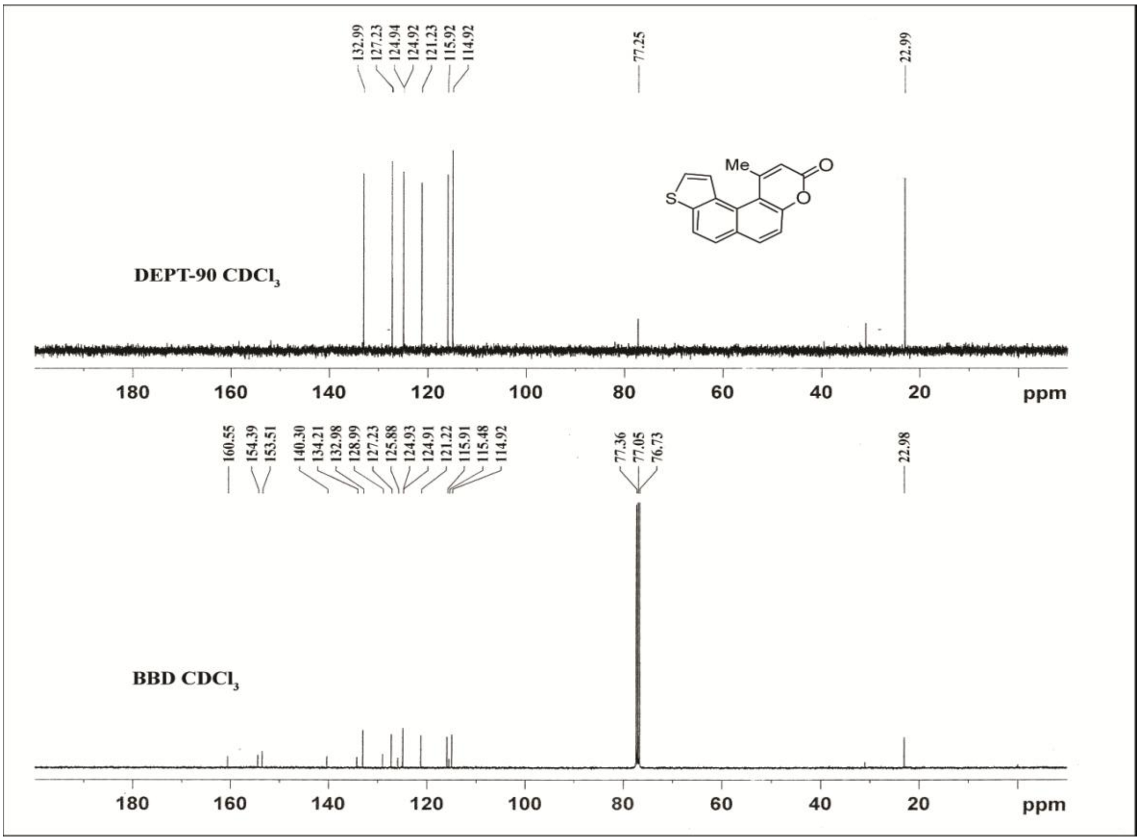


**$^{13}$C-NMR spectrum of 10-nitro-1-methyl-9-hydroxy-naphtho[2,1-b]pyranone (39) in $CDCl_3$ on 400 MHz**

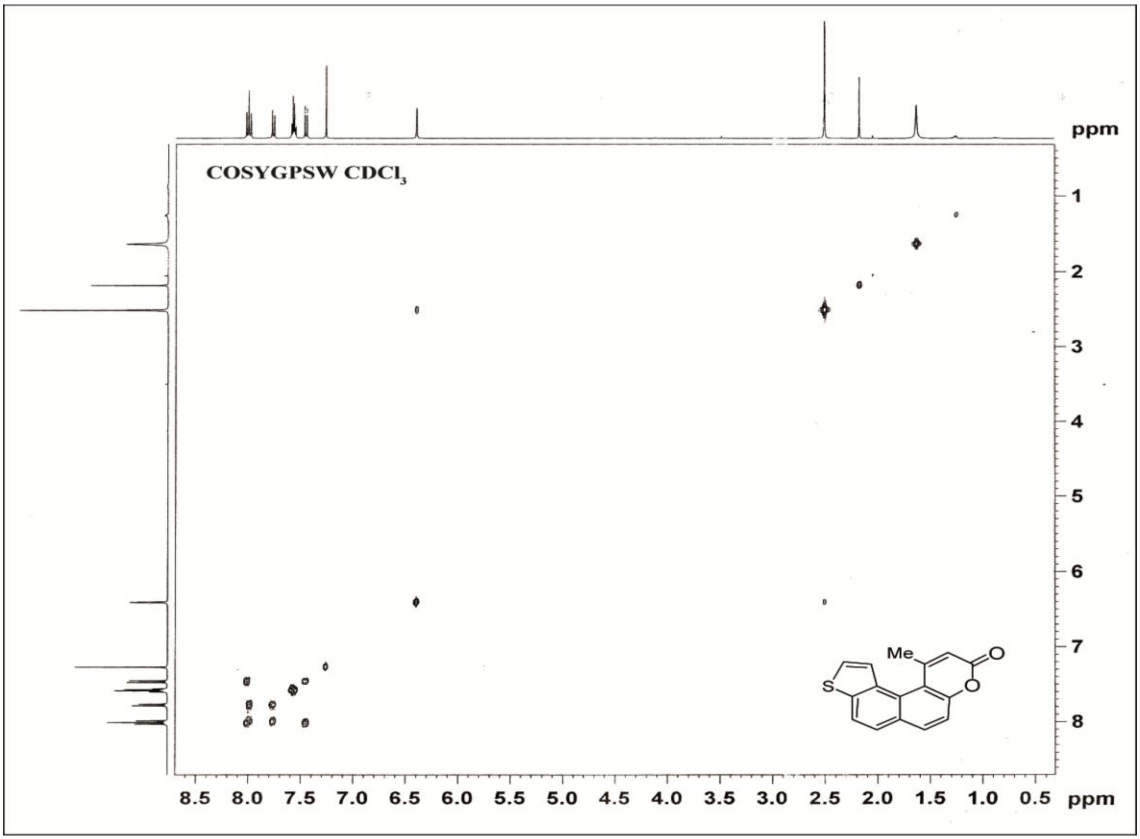
## Spectral data of 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9-one (40)



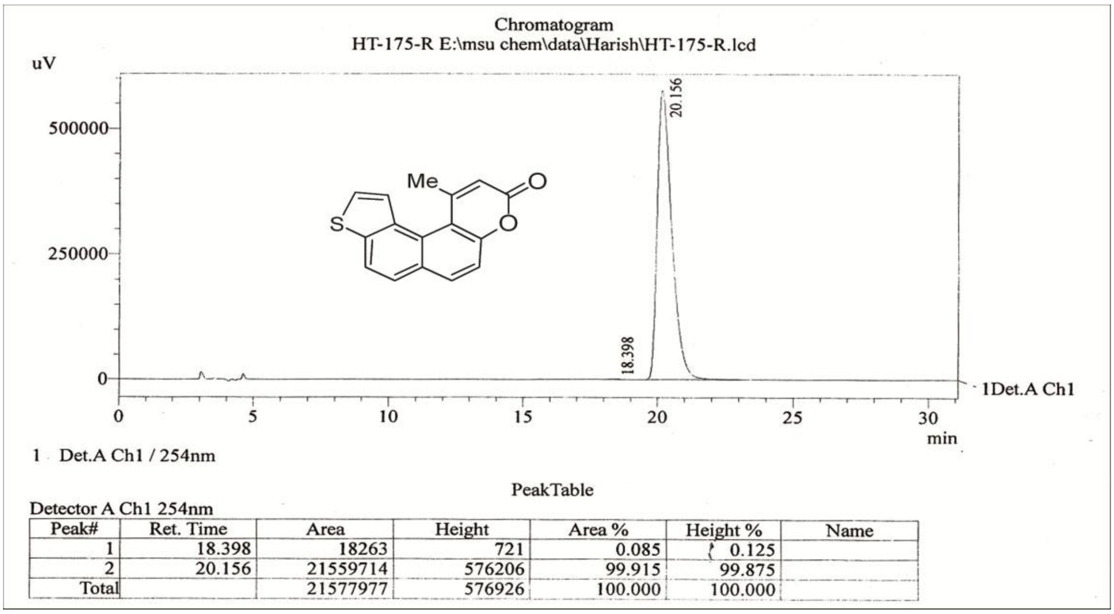
$^1$H-NMR spectrum of 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen 9-one (40) in CDCl$_3$ on 400 MHz



$^{13}$C-NMR BBD and DEPT-90 spectrum of 11-methyl-9*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen 9-one (40) in CDCl$_3$ on 100.6 MHz



**$^1$H-$^{13}$H-NMR correlation COSYGPSW spectrum of 11-methyl-9*H* thieno[2',3':5,6]benzo[1,2-*f*]chromen 9-one (40) in CDCl$_3$ on 400 MHz**



Chromatogram

HT-175-R E:\msu chem\data\Harish\HT-175-R.lcd

1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % | Name |
|---|---|---|---|---|---|---|
| 1 | 18.398 | 18263 | 721 | 0.085 | 0.125 | |
| 2 | 20.156 | 21559714 | 576206 | 99.915 | 99.875 | |
| Total | | 21577977 | 576926 | 100.000 | 100.000 | |

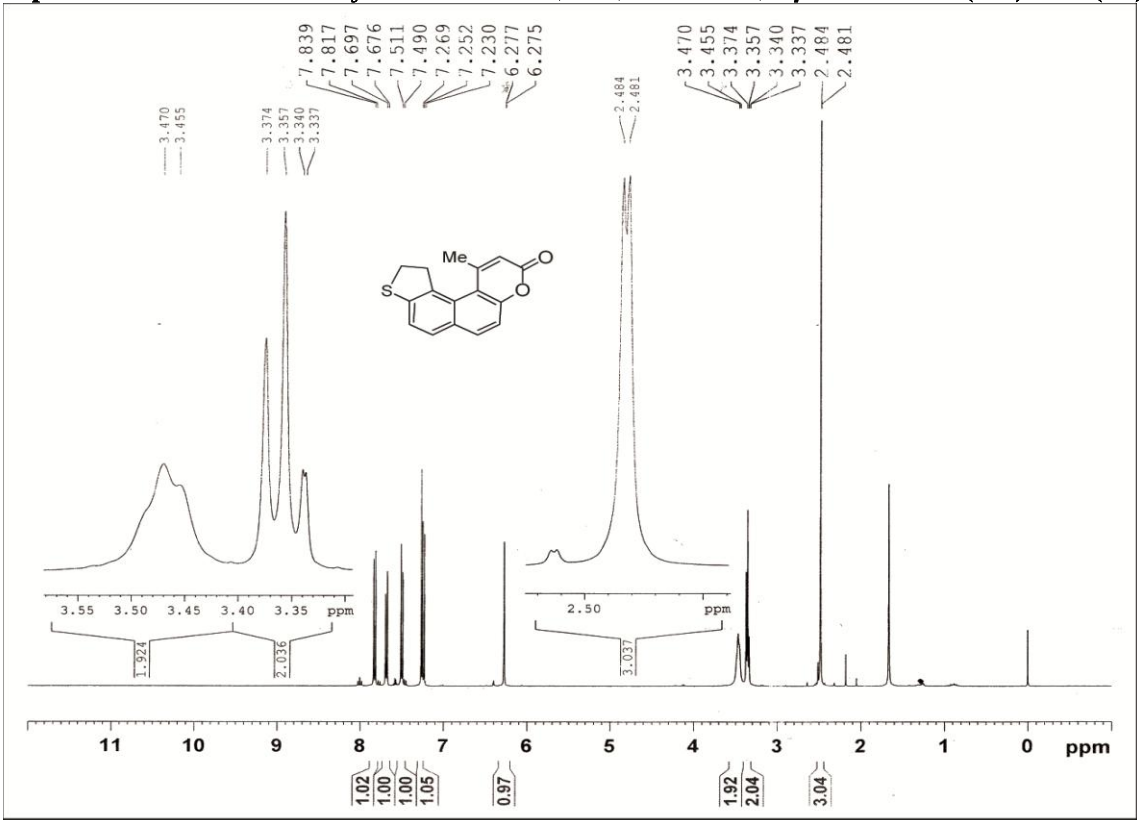
**Chiral HPLC analysis:**

Observed one peak at 1) R$_t$ – 20.15 min

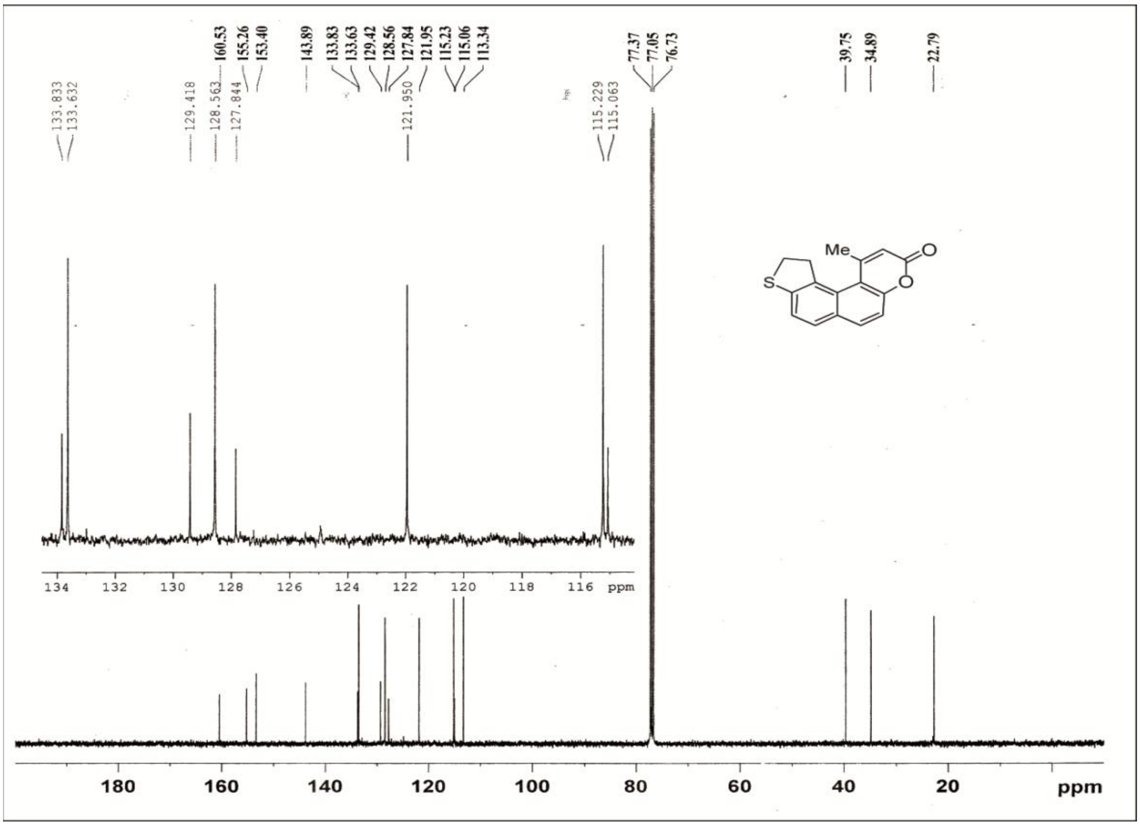
Solvent System: *n*-Hexane: *Iso*-propanol (90:10), Flow rate: 1 mL/min.

Detector: UV-Vis. Column: Lux Amylose-2.

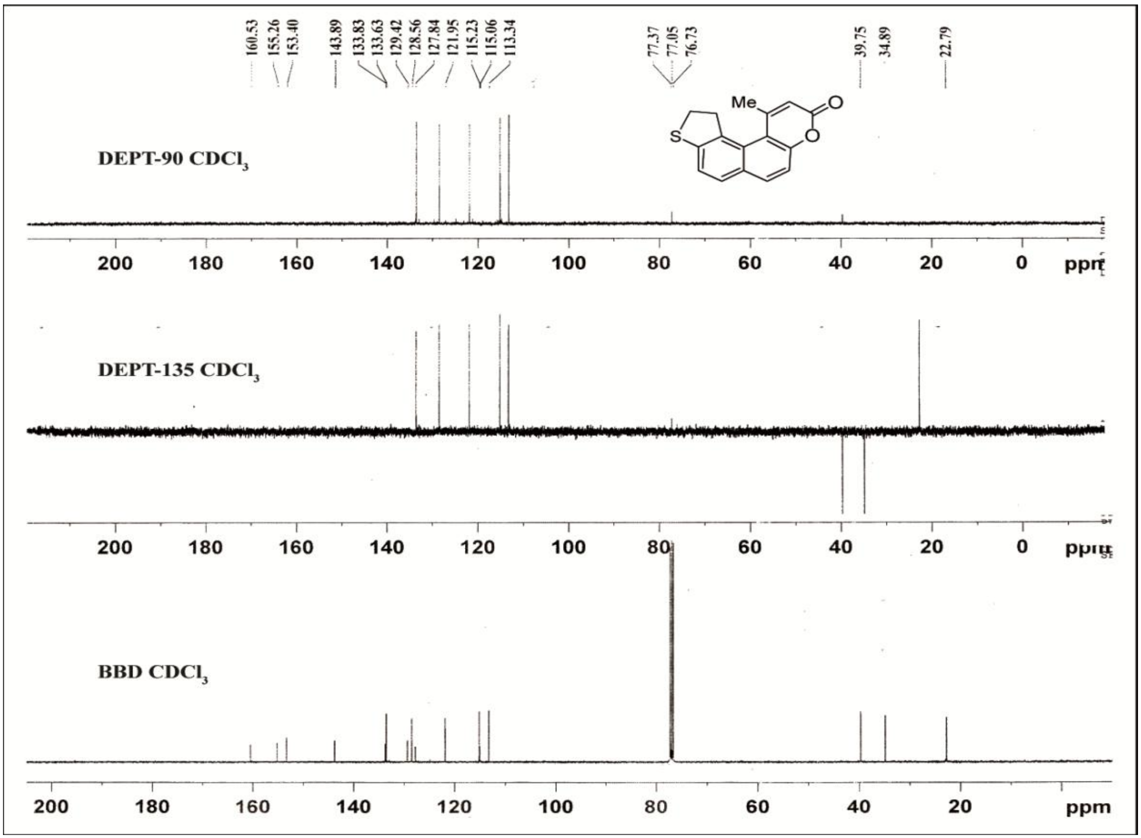
## Spectral data of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41)



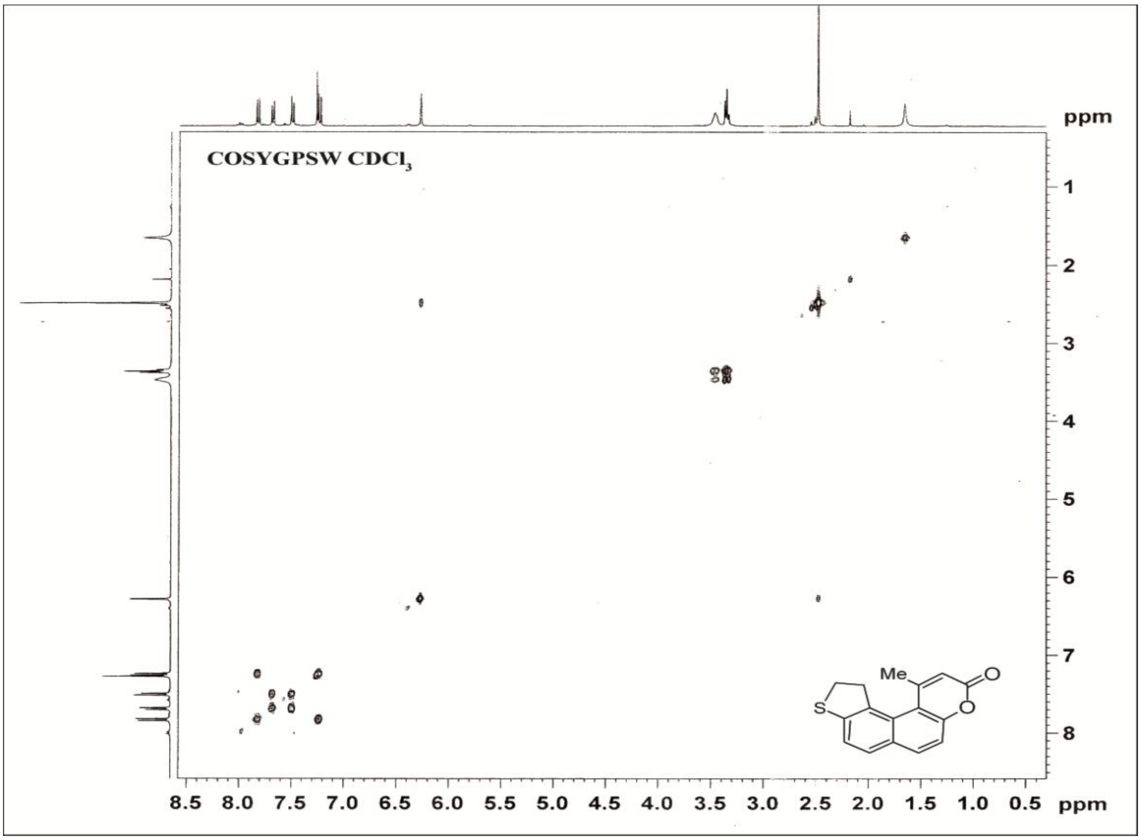
$^1$H-NMR spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41) in $CDCl_3$ on 400 MHz



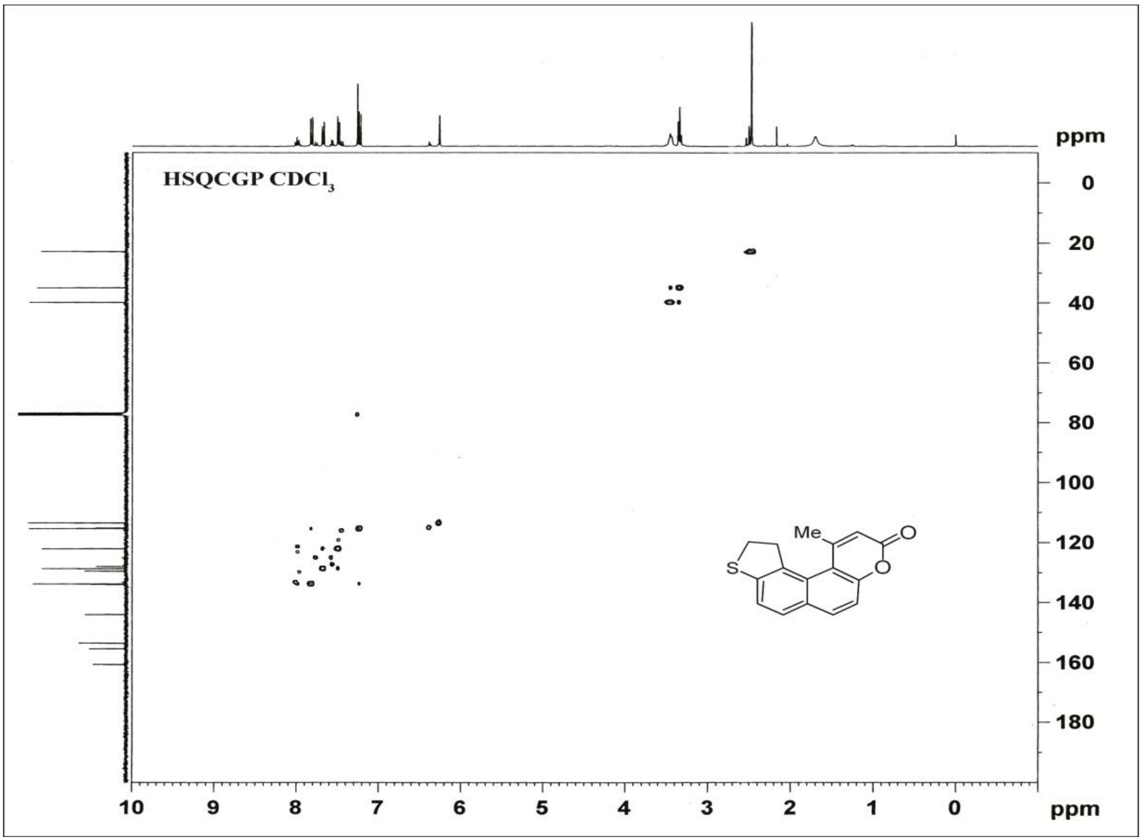
$^{13}$C-NMR spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41) in $CDCl_3$ on 100.6 MHz



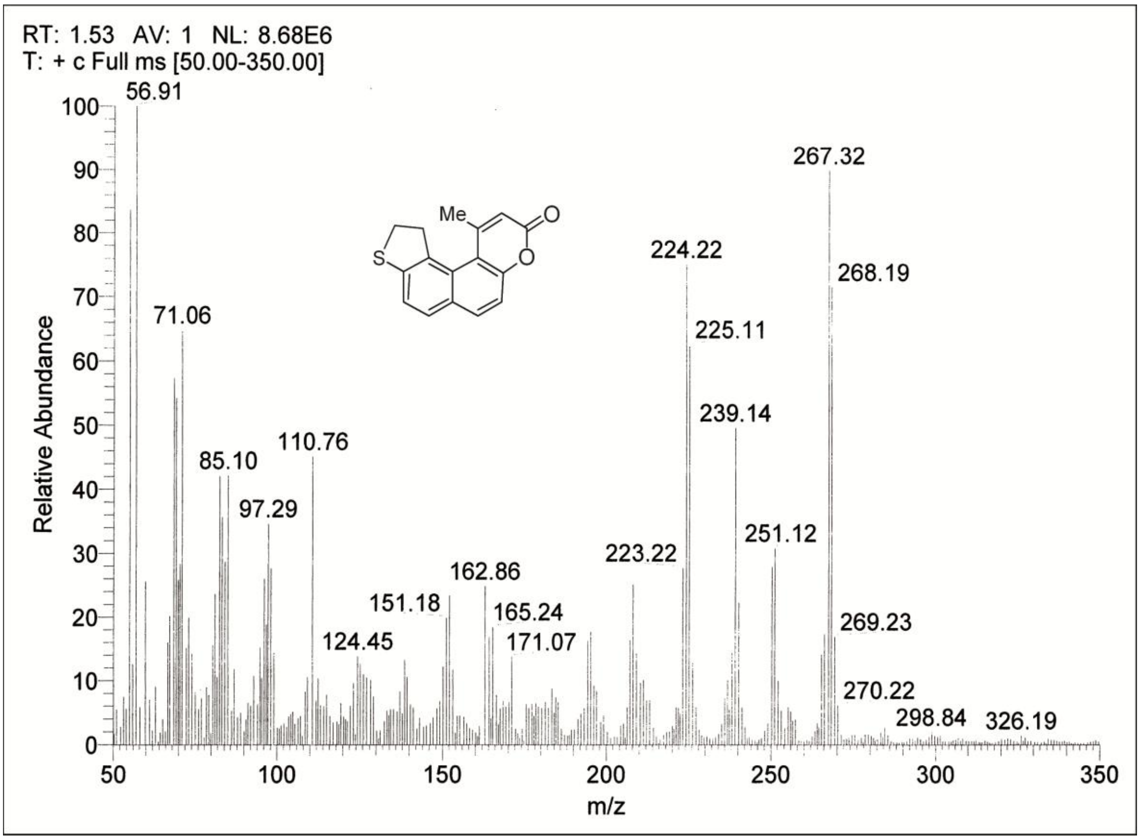
$^{13}$C-NMR BBD, DEPT-90 & 135 spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41) in CDCl$_3$ on 100.6 MHz



$^1$H-$^1$H correlation COSYGPSW NMR spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41) in CDCl$_3$ on 400 MHz



$^1$H-$^{13}$C correlation HSQCGP NMR spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41) in $CDCl_3$ on 400 MHz



EI-Mass spectrum of 11-methyl-1*H*-thieno[2',3':5,6]benzo[1,2-*f*]chromen-9(2*H*)-one (41)

# Conclusion

In this part of the work a number of attempts were made to synthesize helical shape coumarin molecules utilizing simple chemical approaches. A couple of such heterocyclic compounds with cyclohexyl and cyclopentyl rings attached to the parent benzocoumarins were synthesized and characterized by usual spectroscopic techniques. We are also attempt to synthesize the bis-helical coumarins by using the penta- and haxa-cyclic keto ester but we are not succeded.

The introduction of the substituents at the sterically hindered position of the coumarins shows the interesting change in the H-NMR pattern and it might be due to the helical shape or a twist in the molecule. More study will be required before coming to more affirmative conclusion on the existence of helical shape of these molecules.

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