Synthesis and Applications of *Bi*-2-naphthol Derivatives

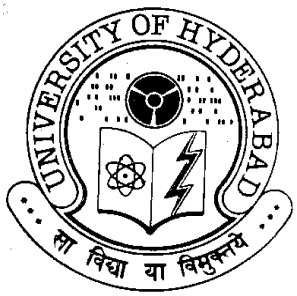
A Thesis

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

VENKANNA BODA



SCHOOL OF CHEMISTRY

UNIVERSITY OF HYDERABAD

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TELANGANA, INDIA

October 2019

Dedicated to My Family

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DECLARATION

I, **Venkanna boda** hereby declare that this thesis entitled "**Synthesis and Applications of *Bi*-2-naphthol Derivatives**" submitted by me under the guidance and supervision of **Professor M. Periasamy** is a bonafide research work which is also free from plagiarism. I also declare that it has not been submitted previously in part or in full to this University or any other University or Institution for the award of any degree or diploma. I hereby agree that my thesis can deposit in Shodganga/INFLIBNET.

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CERTIFICATE

This is to certify that the thesis entitled " **Synthesis and Applications of *Bi*-2-naphthol Derivatives** " submitted by **Mr. Venkanna Boda** bearing registration number **09CHPH01** in partial fulfillment of the requirements for award of Doctor of Philosophy in the School of Chemistry is a bonafide work carried out by him under my supervision and guidance.

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1. Methods of synthesis of piperazine derivatives containing chiral *bi*-2-napthyl moiety; Periasamy. M.;* Venkanna. B.; Nagaraju, M.; Mohan L**.** (DOI): 10.1055/s-0037-1610731; Art ID: SS-2019-z0241-op.

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Ackonwledgements

It gives immense pleasure to express my heartfelt gratitude and profound respect to my supervisor ***Prof. M. Periasamy*** *for his inspiring guidance, constyant encouragement and personal motivation and valuable advice throught the tenure of my work, It is always pleasure for me to be his student and I will be indebted to him for this.*

I extent my heartfelt thanks to Prof. D. Basavaiah, Prof. M. V. Rajasekharan, Prof.M. Durga Prasad and Prof. T. P. Radhakrishan Deans, School of Chemistry, for providing all the necessary facilities to carry out my research work. I am thankful to my doctoral committee members Prof. R. Nagarajan and Prof. R. Balamurugan for their generous support.

I wish to thank my senior colleague Dr. Mallesh Beesu for his help during the initial stages of my research. I extend my sincere thanks to my past Dr. P. Vairaprakash, Dr. Shaik Anwar, Dr. S. Selva Ganesan, Dr. Sakilam Satishkumar, Dr. M. Nagaraju, Dr. N. Sanjeeva Kumar, Dr. Guru Brahmam, Dr. Manasi Dalai, Dr. A. Laxman, and labmates Dr. P. Obula Reddy, Dr. S. Suresh, Dr, M. Shanmuka Raja, Dr. A. Edukondalu, Dr. B. Uday Kumar, Dr. L. Mohan, Dr. E. Ramesh, Dr. M. Ramusagar, Dr. V. Harish, Dr. G. Ananda, Dr. I. Satyanarayana, Mr. Yesu and Mr. Srinivas for creating a pleasant work atmosphere.

I extent my heartfelt thanks extremely helpful, I thank them all. I specially thank School and college teachers Srinivas Madatha, Yakaiah, Laxman, Rajamouli, SimhaChary and Jr. College lecturers Dr. Boddu Ramesh, Venkateswarlu, Das, T.Sreenivasa Chary and seniors Dr. Shyam Perugu, Rajender, Chandu, close friends Rajender Maloth, Srinuvas Daravath, Degree college friends Vankam Bhasker, Pagidi Obulesu, Prabhakar Shinday, Dr. K. Sippy Issac, Dr. Appala naidu, malli babu. Native friends Dr. Mohan Bhukya, Babu bhukya, Prabhakar Birru, Dr. Shiva Prasad Madavi, Dr. Maloth Swamy Naik, Dharamsothu Veranna, Dr. Naveen, Dr. Srenivas, Vamshi, Halvath Ramesh, Dr. Bhukya Shankar, Rajesh ravi and A to Z are to mention. I also thank all my Tamil friends of University of Hyderabad.

All the non-teaching staff of the School has been helpful, I thank them all. Mr. Ramana. Mr. Shetty, Mr. S. Satyanarayana, Mr. V. Bhaskar Rao, Mr. Asia Parwez, Mr. Vijaya Bhaskar, Mr. Abraham, Mr. K. R. V. Prasad, Mahesh Rathod, Mr. Joseph, Mr. Santosh and, Mr. Anand, are a few to mention.

I extent my heartfelt thanks Dr. Sampath Kumar, Dr. MangaThayar Girija and Tara Andhra Vidyalaya Post graduate College, Gagan Mahal-Liberty, for his inspiring teaching and also to my M.Sc.,

classmates Syam Sunder Goud, Naresh Jetty, Shashider Reddy. Marri, M, Vamshi Chinthakindi, Shyam Prasad, Suresh, Sathish (Teacher), Sudhakar, Dr. Ram Thilak, Raju. M, Purushottam, Naveen, Shiva, Sanjeev Kumar, Suhashini, Dr.Sandeep (BARK), Dr.Shanthi Priya, Githa, Maduri, Madavi, Srilekha and all the people college atmosphere made my stay here enjoyable and memorable one.

I extent my heartfelt thanks Dr. Sitharam Naik, Dr. Mallaiah, Dr. Vasudava Reddy, Dr. Ravindar, Dr. Balaswamy, Dr. Shamitha, Dr. Bixapathi, University Arts and Science College, Subhedari, Hanamkonda for his inspiring teaching and also to my B.Sc., Classmates Prabhakar Ganta, Goutham Kokkineni, Banothu Bhadrinadh, Rajababu, Sunil Kumar, Dr. Nagaraju, Srinivas, I specially thank all of my B.Sc., Classmates for their help and thoughtful discussion during my B.Sc., days.

My parents need a special mention of thanks for their stuggle and patience to keep me in education side. I am indebte to my gand father late, Boda Esthari, grand mother Boda Poli, father Mr. Boda Lachiram My mother Boda Laxmi and my wife Lalitha (Sonal). Late, Ramavath Seethya, Mangli. My uncle Hemla, Somla, Bhemla and I always thank to my brother Veranna Boda, Sandeep, Siddu, my sisters Boda Sridevi, Banoth Vijay kumar, Rathan naik, Anusri, Eswar, Vishnu R. Bixapathi, Sandeep, Bittu, Chintu, sindupriya, my cousin brothers Ajmeera Shekar, Boda Surender, Suman, Rajashekar, and friends Banoth Punnaiah, Ravi, Gopi. Above all, I cannot express my thankfulness in mere words, without their grace, I would not have reached to his extent besides others interest, encouragement, for their support, affections and caring throughout my life for his love, care and moral support at all my obstacles.

I wish to extend my sincere thanks to the University authorities for providing all the necessary facility for this work. The X-ray crystallography data were collected in the National Single Crystal X-ray facility funded by DST, New Delhi.

Finally, I would like to thank the HRDG, CSIR-UGC, New Delhi for the financial support during my tenure. Also, financial assistance from the research grant of DST-SERB and DST-IC BOSE National fellowship of Prof. M. Periasamy is gratefully acknowledged.

Venkanna Boda

Contents

Abbreviations

Ac	acetyl
aq.	aqueous
Ar	aryl
Bn	benzyl
Boc	*tert*-butoxycarbonyl
BINOL	1,1'-bi-2-naphthol
bp	boiling point
brs	broad singlet (spectral)
Bu	butyl
^{t}Bu	*ter*-butyl
cat.	catalytic
DABCO	1,4-diazabicyclo[2.2.2]octane
DCM	dichloromethane
dr	diastereomeric ratio
de	diastereomeric excess
EI	electron impact (in mass spectrometry)
eq.	equation
equiv.	equivalent
Et	ethyl
h	hour(s)
HPLC	high-performance liquid chromatography
IR	infrared
J	coupling constant (in NMR spectroscopy)
O^{i}Pr	isopropyloxy
liq.	liquid
Lit.	literature
m	multiplet (spectral)
Me	methyl

MHz	megahertz
mp	melting point
Ms	methanesulfonyl
n-	primary
Nu	nucleophile
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
Py	pyridine
PTSA	*p*-toluenesulfonic acid
q	quartet
rt	room temperature
s	singlet
t-	tertiary
TBAI	tetrabutylammonium iodide
THF	tetrahydrofuran
TMS	tetramethylsilane
Tol	tolyl
Ts	toluenesulfonyl
X	halide
y	yield

Abstract

This thesis entitled "**Synthesis and Applications of *Bi*-2-naphthol Derivatives** comprises of four chapters. The work described is exploratory in nature. The first chapter presents **General Introduction** with **References** on ***Bi*-2-naphthol derivatives.** The second, third and fourth chapters are subdivided into four sections namely **Introduction, Results and Discussion**, **Conclusions** and **Experimental Section** along with **References.**

The first chapter describes a brief review on the synthesis of various 3,3, 4,4, and 6,6-disubstituted 1,1'-*bi*-2-naphthyl derivatives. In the second chapter, synthesis of five and six membered heterocycles containing chiral *bi*-2-naphthyl moiety starting from various 6-oxoacyl and 6,6-dioxodiacyl substituted *bi*-2-naphthyl methyl ether derivatives are described (Chart 1).

Chart 1

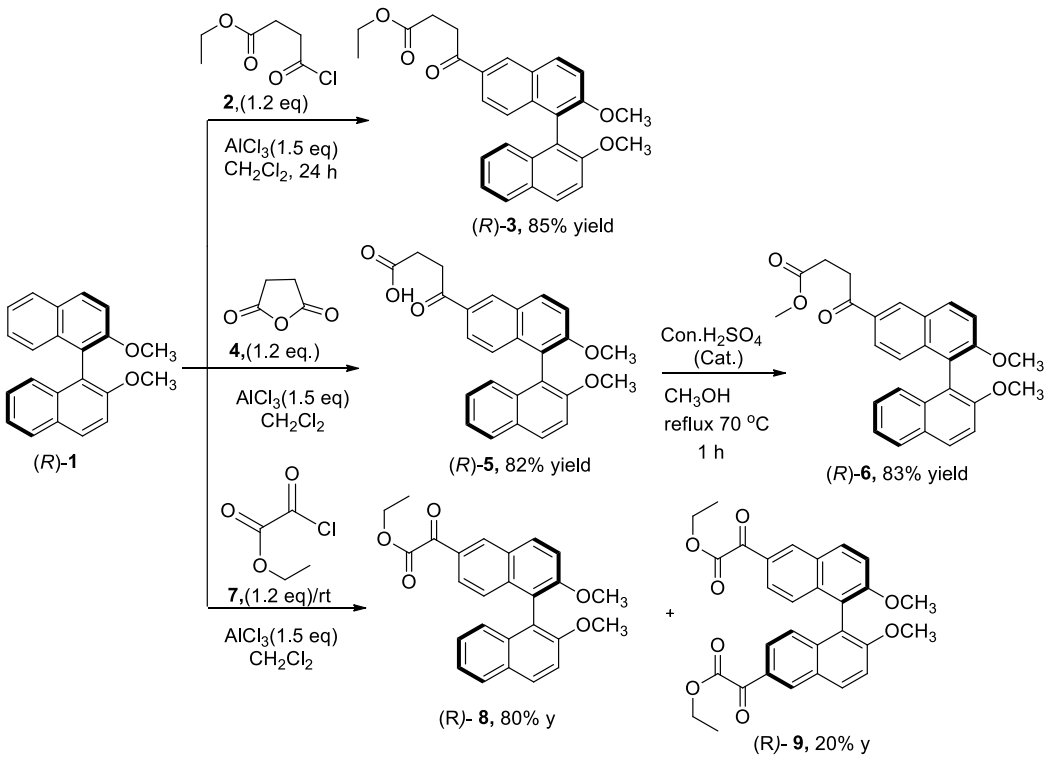


Chart 1: *continued.*

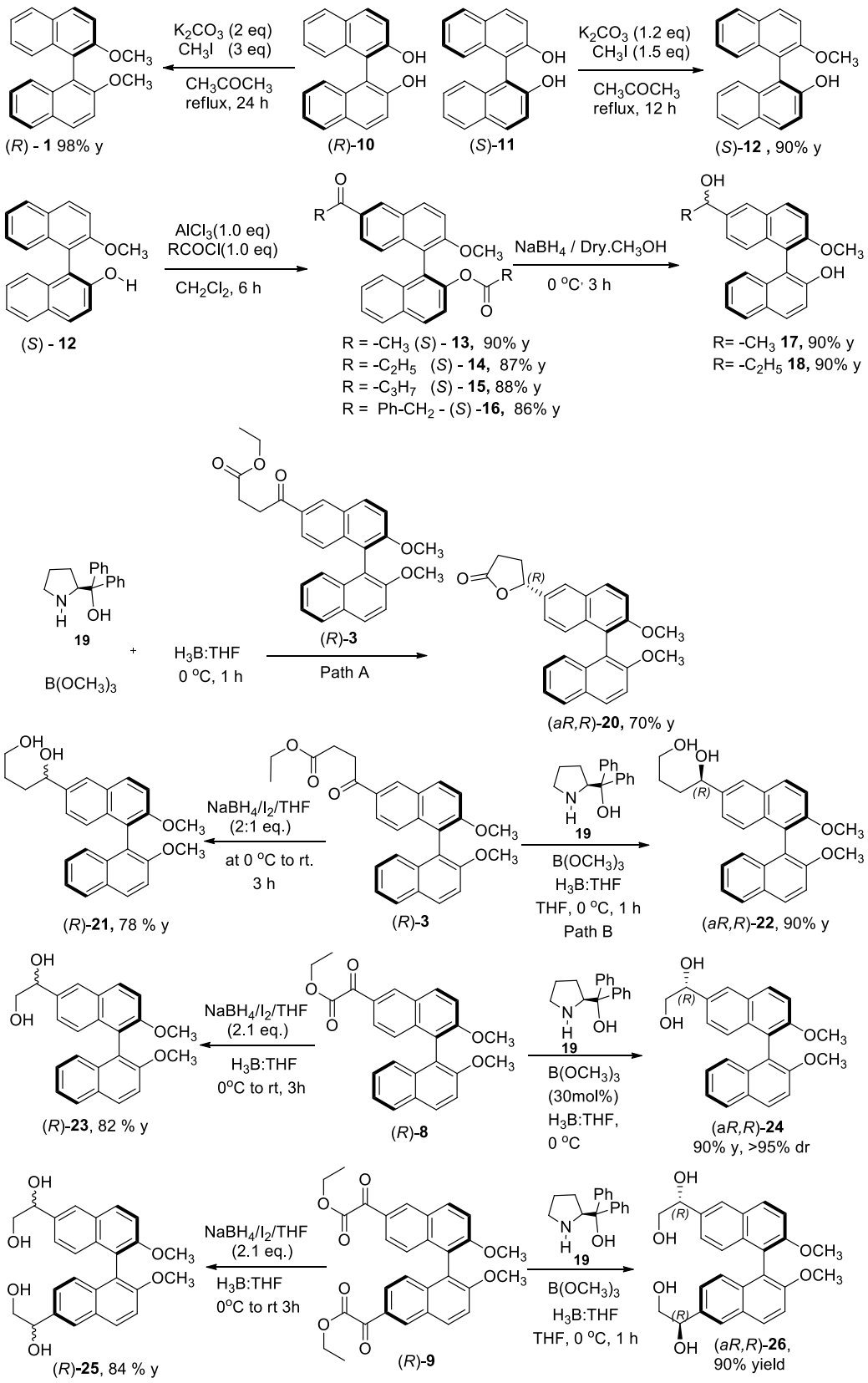
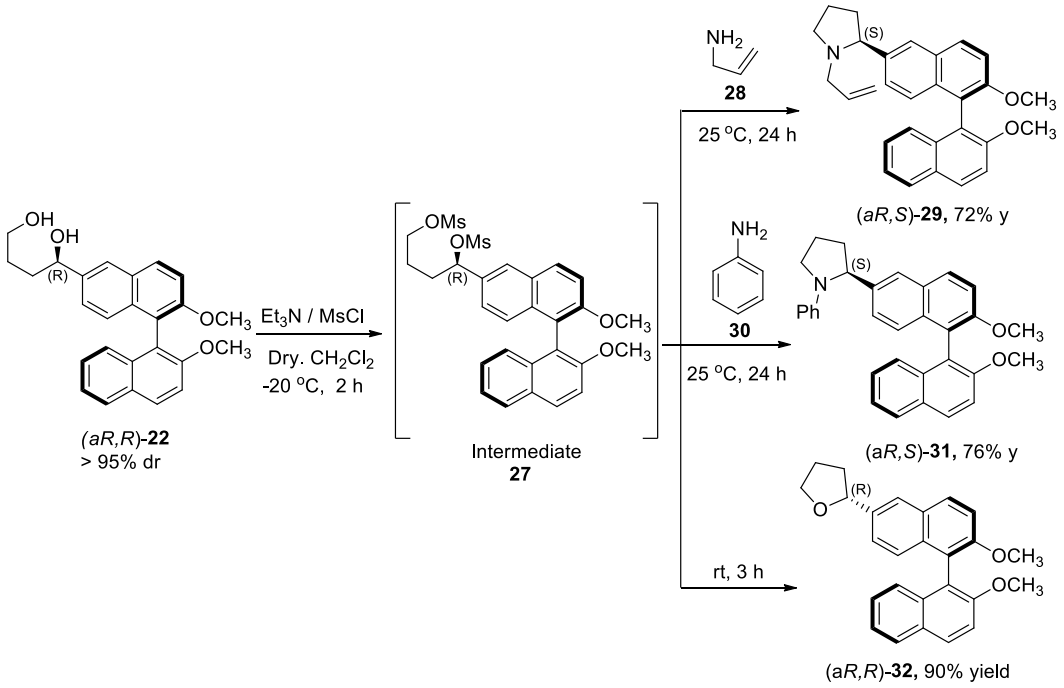


Chart 1: *Continued.*



The results are discussed considering reports on the oxazaborolidine catalyzed asymmetric reductions and mechanisms expected for the observed nucleophilic cyclization reactions.

Next, methods developed for the synthesis of piperazine derivatives containing *bi*-2-naphthyl moiety are described (Chart 2).

Chart 2

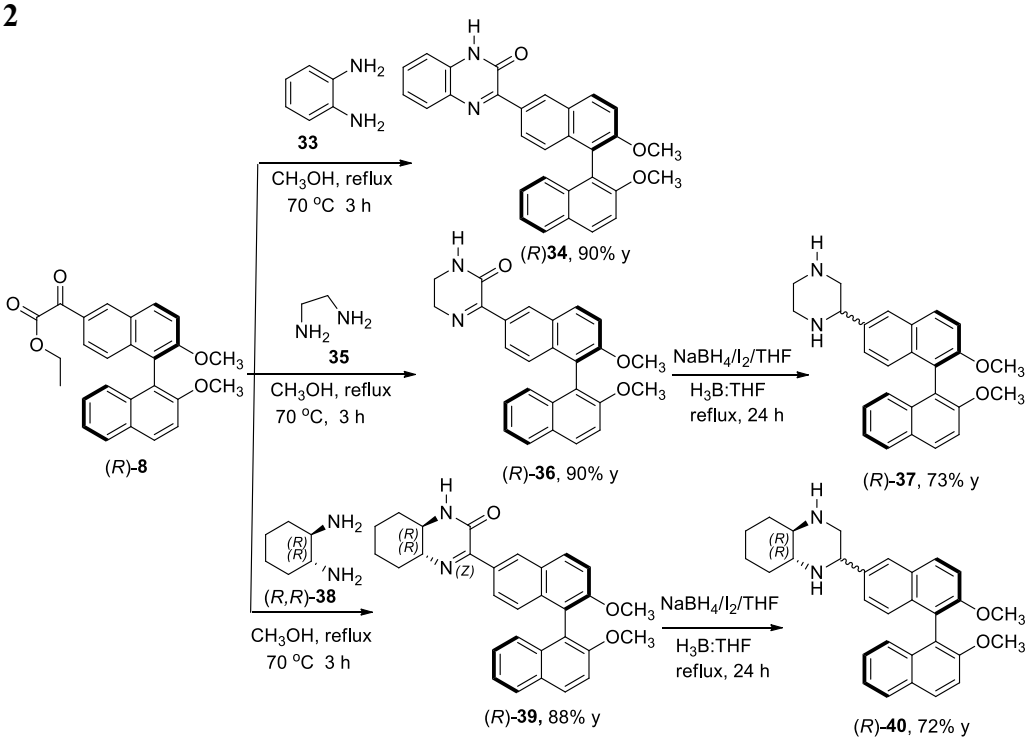
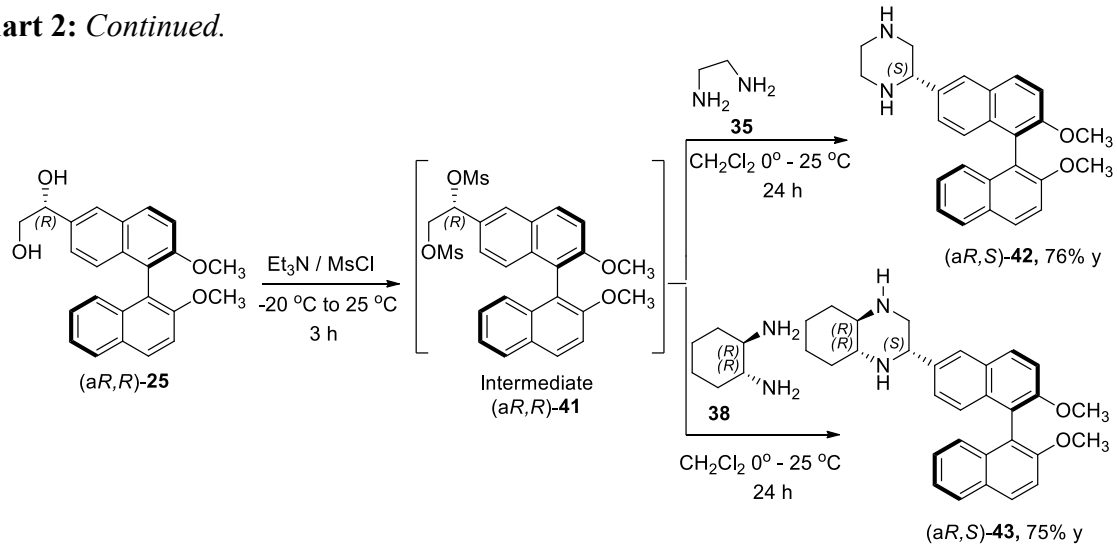


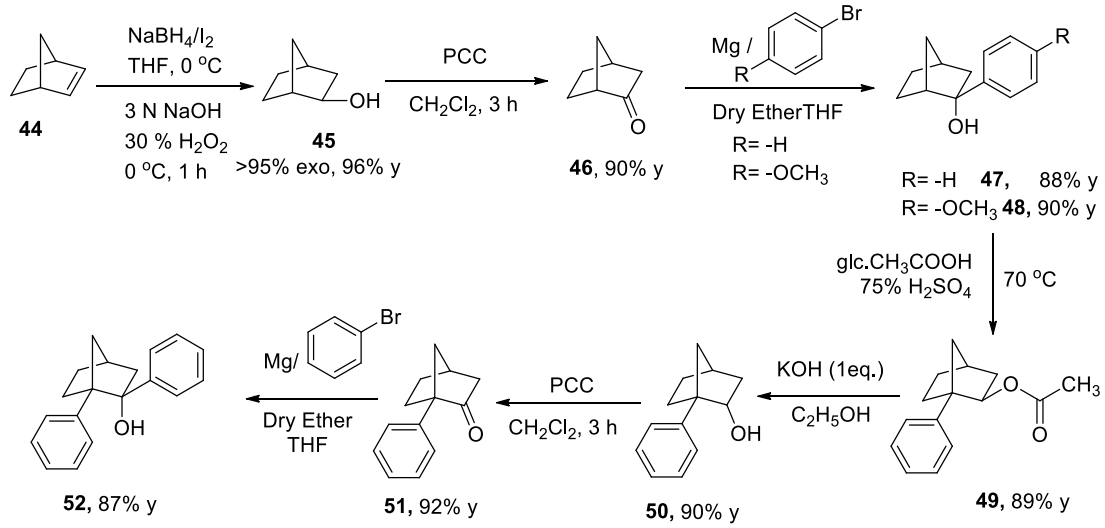
Chart 2: *Continued.*



Again, the results are discussed considering the tentative mechanisms expected for these transformations.

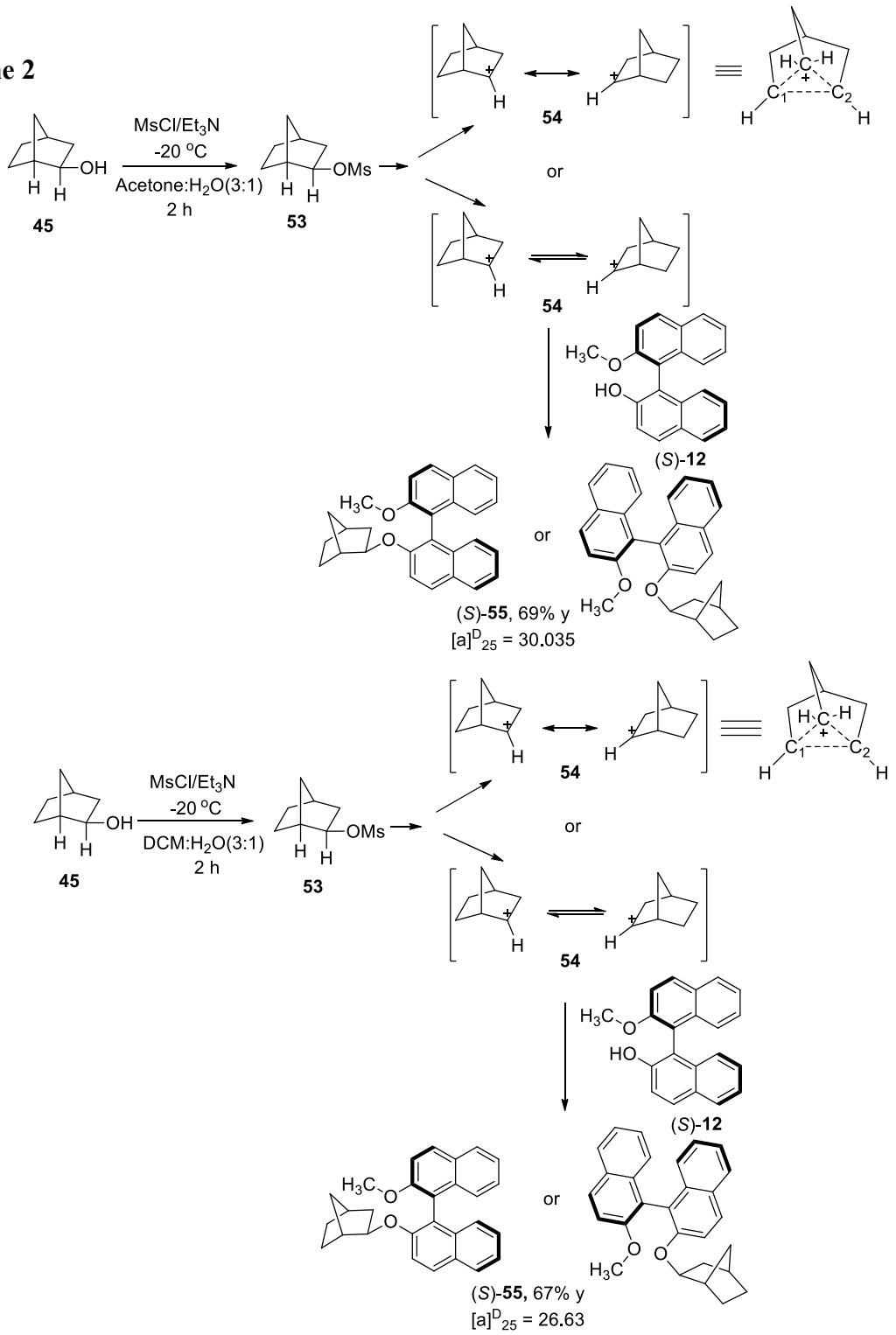
The third chapter deals with studies on the reaction of 2-norbornylcation and 1,2-diphenyl-2-norbornylcation with monomethoxy-*bi*-2-naphthol. The required *exo*-2-norbornanol and 1,2-diphenyl-*endo*-2-norbornanol were prepared following closely related reported procedures (Scheme 1).

Scheme 1



Preliminary investigation on the reaction of secondary 2-norbornylcation with the monomethoxy-*bi*-2-naphthol as nucleophile was carried out using the mesylate derivative prepared *in situ* in acetone-H_2O or DCM-H_2O systems (Scheme 2).

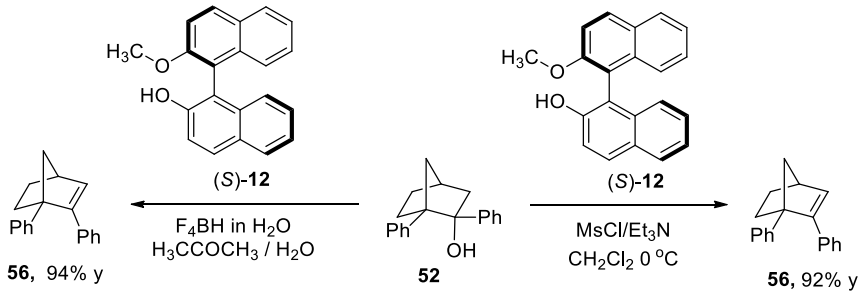
Scheme 2



Interestingly, only one of the expected products was obtained. Unfortunately the configuration of the newly formed stereogenic centre in the product could not be assigned. The mechanism of this transformation is briefly discussed.

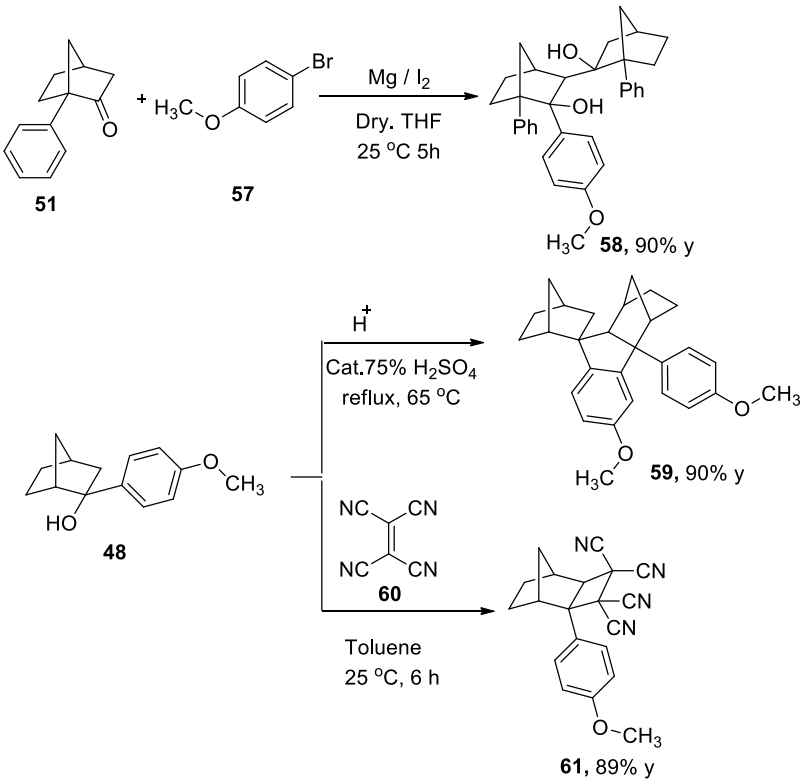
The reaction of monomethoxy-*bi*-2-naphthol with 1,2-diphenyl-2-norbornylcation prepared *in situ* was also studied (Scheme 3). However, only the corresponding elimination product was obtained in this reaction.

Scheme 3



During the investigations on the 2-norbornyl system, we have also uncovered some interesting transformations (Chart 3).

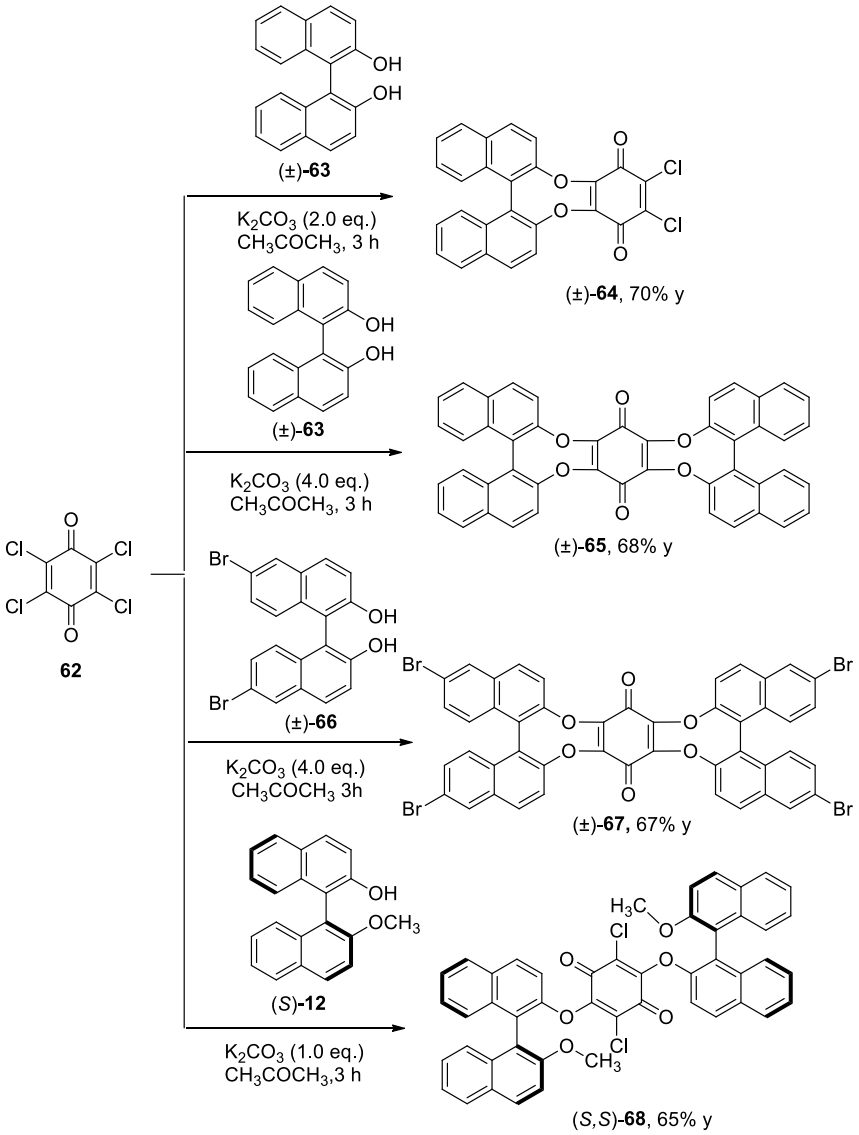
Chart 3



Plausible mechanisms involved in these transformations are discussed.

In chapter 4, studies undertaken on the synthesis of *bi*-2-naphthyoxybenzoquinone derivatives are described (Chart 4).

Chart 4



Electron transfer reactions of these *bi*-2-naphthyloxybenzoquinones with amine donors were investigated by ESR spectral analysis. The results are discussed considering possible reasons for variation in ESR signal strength with time.

Experimental procedures, physical constant and spectral data are described in the experimental sections.

Note: The compound number given in this abstract is different from those given in the chapters.

Chapter 1

General Introduction on Synthesis of Bi-2-naphthol Derivatives

1.1. Introduction

2,2'-Disubstituted derivatives of 1,1'-*bi*-2-naphthyl have been widely used in organic synthesis[1]. The most important compound of this type is 1,1'-binaphthyl-2,2'-diol or 1,1'-*bi*-2–diol BINOL. The chiral atropoisomers **(*R*)-(+)-1** and **(*S*)-(-)-1** are stable at high temperature up to 100 ^{o}C and have useful for numerous asymmetric reactions under various experimental conditions[2].

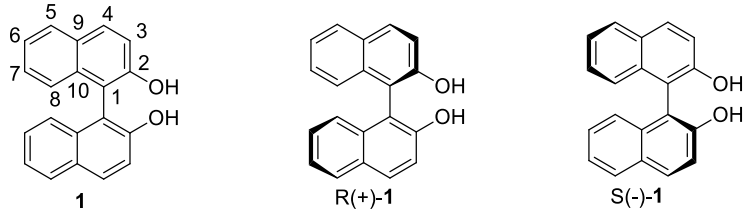


Figure 1

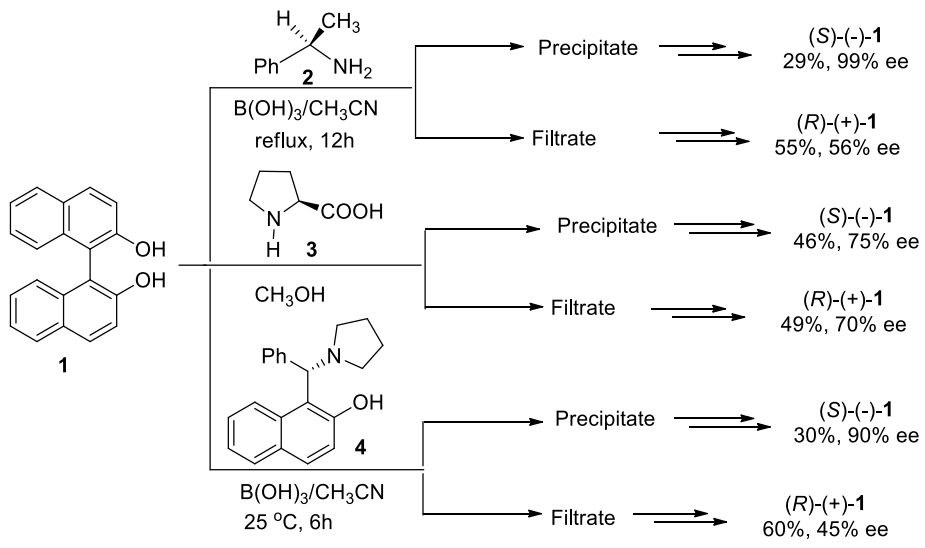
In terms of ligand symmetry, C_2-symmetrical ligands possessing axial chirality have found particularly wide utility in asymmetric catalysis.[3] BINOL **1** is the best known representative of axially chiral molecule.[4] Also, 2,2'-*bi*-2-naphthol (BINOL) and its derivatives have generated particular interest because their versatile backbone can be modified, there by affecting the reaction environment. Substitution of BINOL may affect not only the steric environment around the molecule but also the electronic properties of oxygen atoms. Although BINOL was first synthesized in 1926,[5] its potential as a ligand for metal-mediated catalysis was first recognized in 1979 by Noyori in the reduction of aromatic ketones and aldehydes.[6] BINOL itself, however, does not always give satisfactory results in asymmetric catalysis, and since Noyori's discovery there has been an ongoing interest in application of BINOL ligands. The outcome of a given asymmetric transformation depends on both steric and electronic properties of the chiral ligand. Therefore, strategic placement of substituents within the framework of a given BINOL derivative may lead to improved

catalysis. BINOL **1** is a white solid with a melting point of 208-210 °C and a p*K*a(H_2O) value of 10.28.[7] It is soluble in most organic solvents such as THF, MeCN, DMSO, methanol, dichloromethane, etc. Although resistant toward racemization under neutral conditions, BINOL is known to racemize under basic or acidic conditions.[8] The original synthesis of BINOL, reported by Pummerer *et al*. in 1926, involves facile oxidative coupling of the two 2-naphthol units induced by $FeCl_3$.[5] Since then, a wide range of other coupling methods for the preparation of both enantiomerically pure and racemic BINOL ligands have been developed. Generally, there are two methods available for the preparation of chiral binaphthol ligands: (a) through coupling reactions of substituted naphthol units and (b) through regioselective modification of the bi-2-naphthol scaffold. Both methods have received considerable attention.

1.1 Previous reports on 1,1'-*bi*-2-naphthol from this laboratory

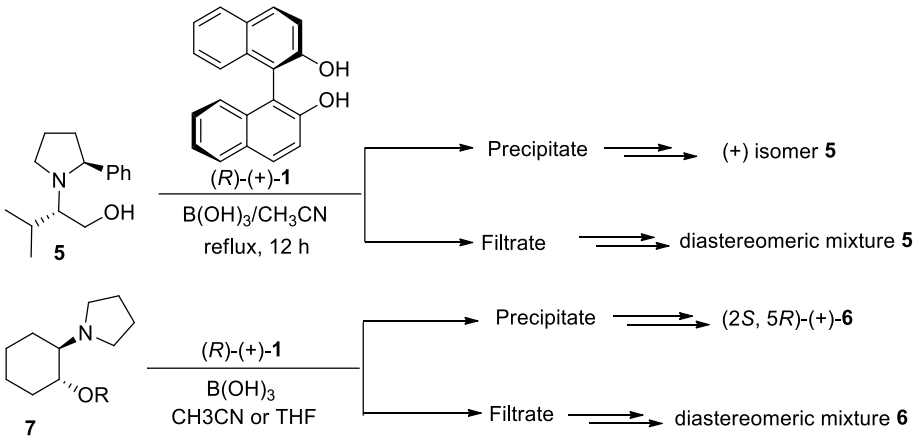
In recent years, methods have been developed in this laboratory to easily access chiral 1,1'-*bi*-2-naphthol in optically pure form. For example, the racemic 1,1'-*bi*-2-naphthol **1** was resolved using boric acid and (*S*)-proline **2** as well as chiral α-methylbenzylamine **3** in this as laboratory.[9] Recently, racemic BINOL was resolved using (*S*)-amino naphthol **4** and boric acid in CH_3CN solvent (Scheme 1).

Scheme 1



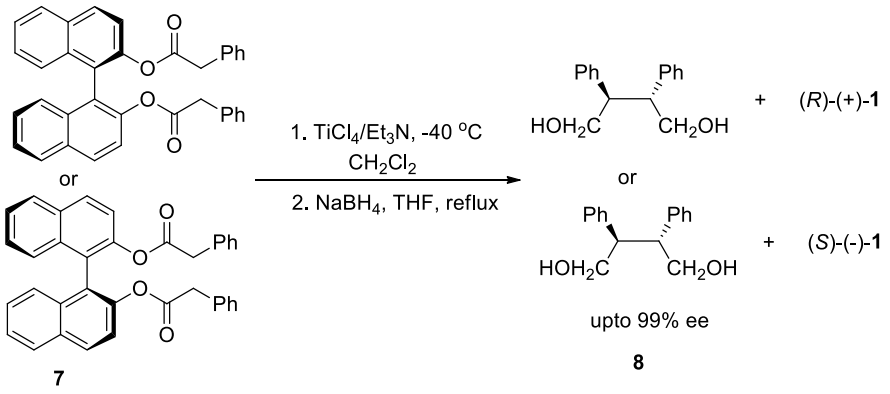
Chiral 1,1'-*bi*-2-naphthol **1** in alliance with boric acid was utilized for the purification of diastereomeric mixture of **5** as well as for the resolution of trans-(±)-2-(pyrrolidinyl)cyclohexanol **6** and its methyl ether derivative (Scheme 2).[10]

Scheme 2



Enantiomerically pure 2,3-diphenyl-1,4-butanediol **8** was synthesized in good yields through intramolecular oxidative coupling of the titanium enolates of phenylacetic acid esters **7** of enantiomerically pure 1,1'-*bi*-2-naphthol followed by the reduction with the $NaBH_4/I_2$ reagent system (Scheme 3)[11].

Scheme 3



Convenient methods were developed for the preparation of chiral 1, 1'-bi-2-naphthol derived amino ether derivatives **9**, **10** and **11** through opening of aziridinium ion intermediate derived from trans (±)-2-(1-pyrrolidinyl)cyclohexanol (Figure 2). [12]

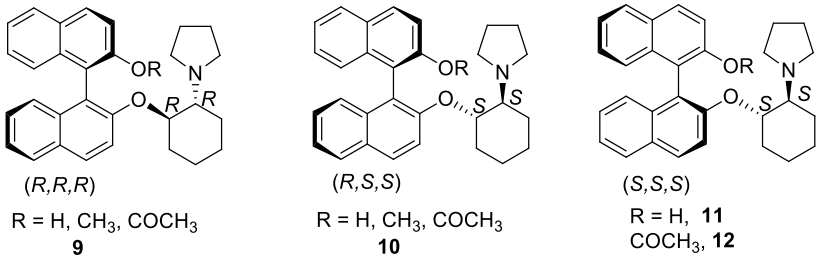


Figure 2 trans (±)-2-(1-pyrrolidinyl)cyclohexanol derivatives

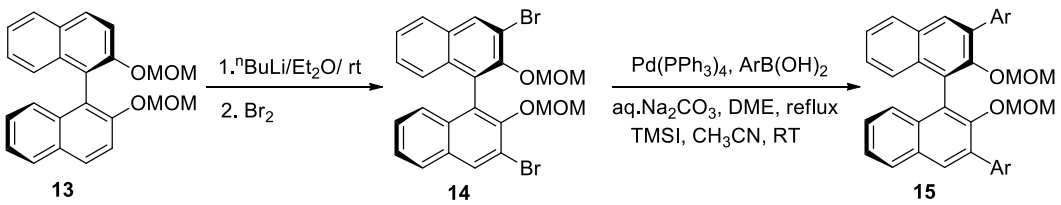
In continuation of these research efforts on the synthesis and applications of chiral *bi*-2-naphthol derivatives, we became interested in the preparation of 6-acyl and 6,6'-diacyl-1,1'-*bi*-2-naphthol derivatives for use in synthesis of heterocyclic desymmetrization of 2-norboronyl cation and for the synthesis of benzoquinonone derivatives containing *bi*-2-naphthyl moiety. Accordingly, it is of interest to briefly review the literature reports on the applications of *bi*-2-naphthyl derivatives.

1.2 Substitution on *Bi*-2-naphthol

1.2.1 3,3'-Substituted BINOL Derivatives

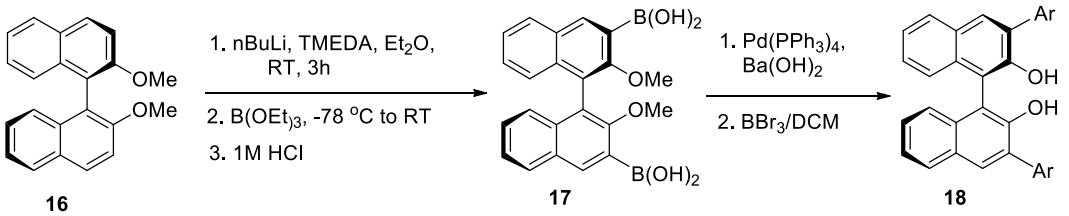
Cram and co-workerswas prepared a series of 3,3'-disubstituted BINOL derivatives.[13,14] Interesting transformation employing with phenyl- or 2-naphthylboronic acids under modified Suzuki cross-coupling conditions, followed by MOM deprotection, gave **14** and **15** in 87% and 85% yields, respectively (Scheme 4).

Scheme 4



Jørgensen et al.[15] reported another synthetic route toward 3,3'-diaryl-BINOLs **15** by the reaction of the 3,3'-diboronic acid of bis(methoxy)-BINOL with commercially available aromatic bromides by a Suzuki cross-coupling reaction (Scheme 5).

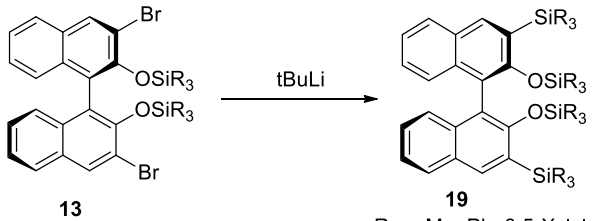
Scheme 5



16 **17** **18**

Yamamoto and co-workers[16] reported a method for sterically hindered chiral 3,3'-bis-(trialkylsilyl)-1,1-*bi*-2-naphthol (*R*)-**19** or (*S*)-**19** was reported by Yamamoto and co-workers, based on a facile 1,3-rearrangement of bis(trialkylsilyl ether) **37** with ^{t}BuLi (Scheme 6).

Scheme 6

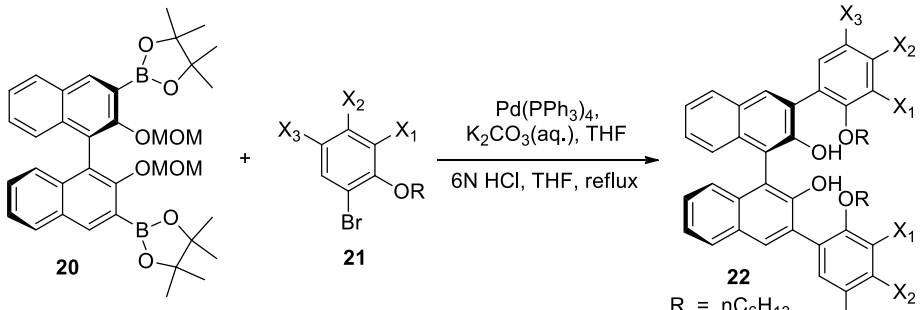


13

19
R = Me, Ph, 3,5-Xylyl
R_3 = $tBuMe_2$, $tBuPh_2$

Pu and co-workers[17] reported a method of synthesis of the chiral bi-naphthyl derivatives (*S*)-**20**, where multiple electron-withdrawing fluorine atoms were introduced to the 3,3'-aryl groups, by the Suzuki coupling of **21** with aryl bromides **22a-e**, followed by acid hydrolysis (Scheme 7).

Scheme 7



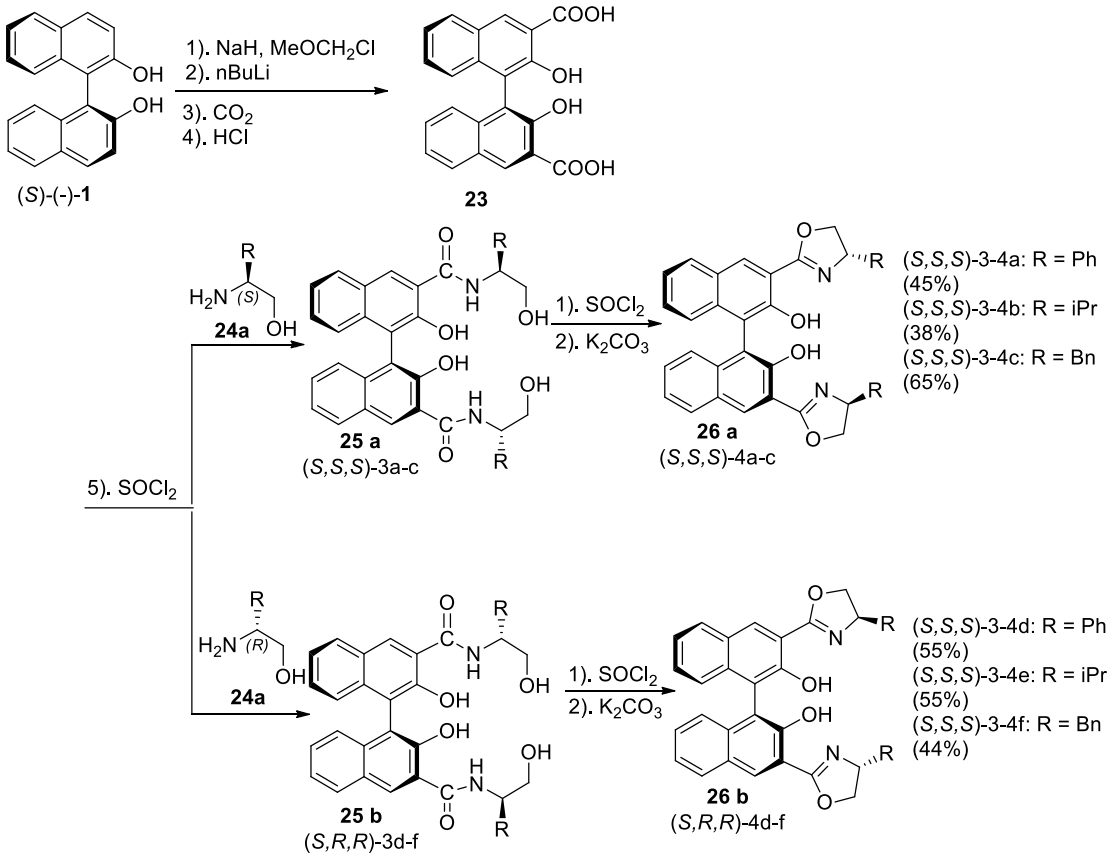
20 **21**

22
R = nC_6H_{13}
X_1 = H, Me, F
X_2 = H, F
X_3 = F

Ohta and co-workers reported a method of synthesis 3,3'-bis(2-oxazolyl)-1,1'-bi-2-naphthol (BINOL-Box) ligands **22** starting from (*S*)-BINOL (Scheme 24).[33] The MOM-protected BINOL was subjected to ortholithiation, followed by carboxylation, to give the corresponding 3,3'-dicarboxylic acid. The acid was then transformed into acid chloride by

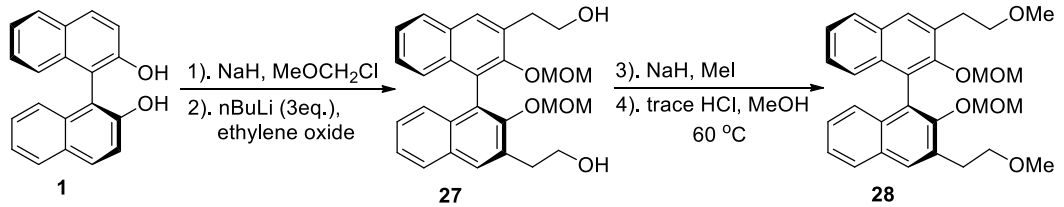
exposing it to thionyl chloride, followed by treatment with chiral amino alcohols, to afford amides **25**. The amides **25** were halogenated with thionyl chloride, and the resulting compounds were cyclized in the presence of potassium carbonate to afford the BINOL-Box in good yields (Scheme 8).

Scheme 8



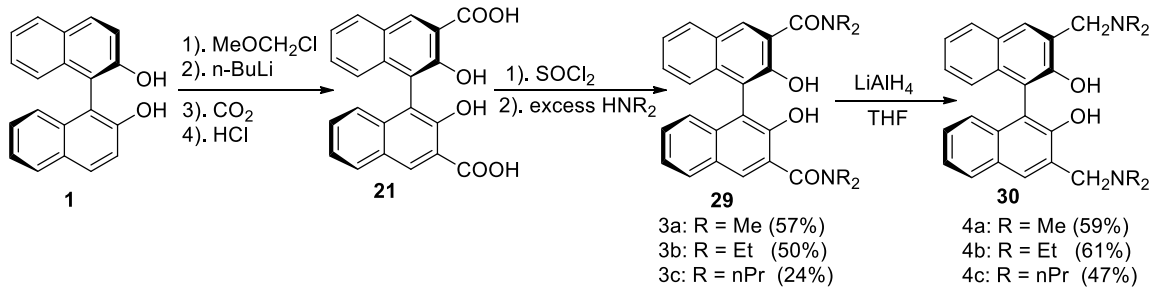
Qian's *et al.*[18] reported a method of synthesis of (*S*)-3,3'-bis(methoxyethyl)-BINOL **28** in an overall yield of 37% from (*S*)-BINOL in four steps (Scheme 9).

Scheme 9



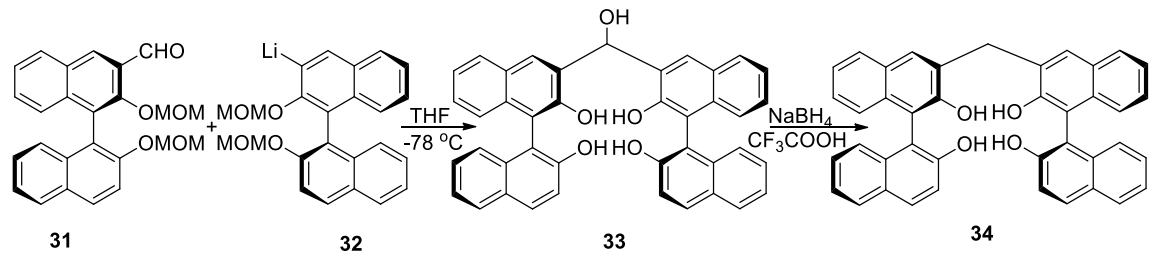
Katsuki and co-workers[19] reported a method of synthesis of a new type of BINOL derivatives, 1,1'-bi-2-naphthol-3,3'-dicarboxamides **29**, and their application as chiral ligands in the asymmetric Simmons-Smith cyclopropanation of (*E*)-allylic alcohols. Ligands **30** were prepared from (*R*)-BINOL in six steps, as outlined in Scheme 12. Reduction of **30** by $LiAlH_4$ gave **29** bearing tertiary aminomethyl groups at the 3,3'-positions (Scheme 10).

Scheme 10



Shibasaki and co-workers[20] reported a novel class of linked BINOL ligands **34** which introduced new possibilities for multifunctional asymmetric catalysis. The syntheses of both carbon-linked BINOLs **31, 32** and oxygen-linked BINOL **34** have been described (Scheme 11).

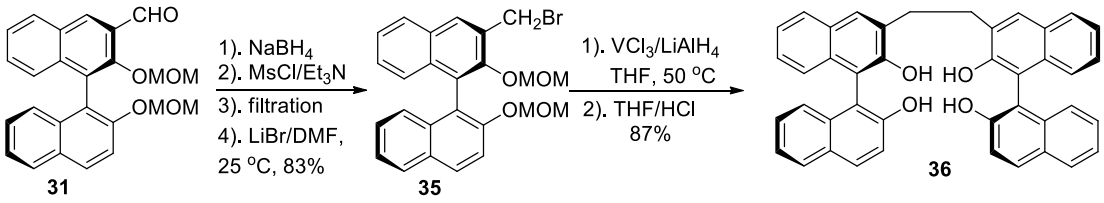
Scheme 11



Shibasaki *et al.*[21] A synthetic approach to (*R*, *R*)-**33** is outlined in Reduction of aldehyde (*R*)-**33** with $NaBH_4$ in MeOH/THF at 0 °C yielded 3-(hydroxymethyl)-BINOL, which after mesylation, filtration of $Et_3N{\cdot}HCl$, and treatment with LiBr in DMF gave the

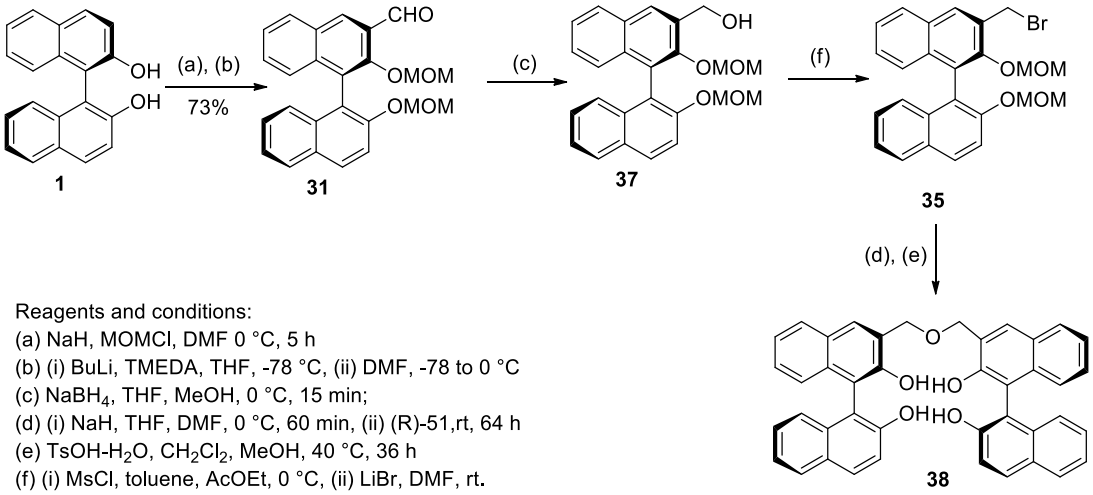
brominated compound in 83% overall yield. Reductive coupling of the latter in THF at 50 °C, followed by deprotection of the MOM group, afforded (*R*, *R*)-**36** in 87% yield (Scheme 12).

Scheme 12



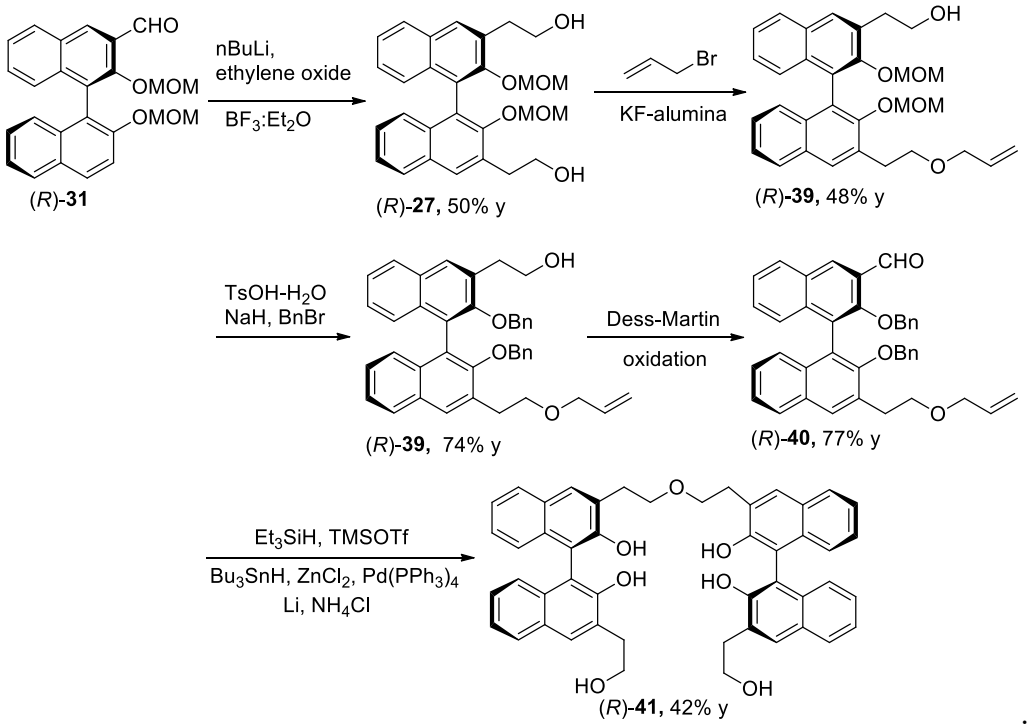
It is presumed that the oxygen atom in the linker coordinates to the metal center, creating complexes with suitable asymmetric environments. The Shibasaki group further prepared the oxygen-linked chiral ligand **38** on the basis of the reports by Cram (Scheme 13).[13]

Scheme 13



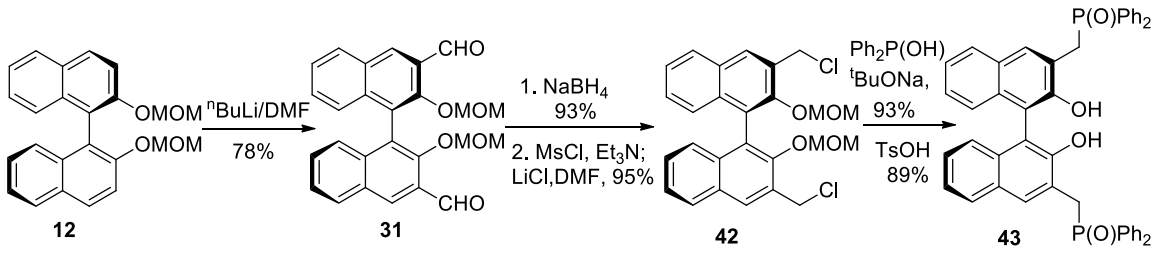
With the goal of developing novel Lewis acid-Brønsted base bifunctional catalysts, Shibasaki and Yoshikawa designed another class of oxygen-linked BINOL, **38,** for the synthesis of ligand **41** starting from MOM-protected (*R*)-BINOL (Scheme 14).

Scheme 14



The phosphine oxide **43** was synthesized in the Shibasaki laboratory starting from the MOM protected BINOL derivative in high overall yield, as outlined in (Scheme 15).

Scheme 15



1.2.2 6,6'-Substituted BINOL Derivatives

The most common precursor to the 6, 6'-disubstituted BINOL ligands described in the literature is the 6,6'-dibromo-1,1'-bi-2-naphthol **44**. This BINOL derivative is prepared via electrophilic aromatic bromination of BINOL (Figure 3).[22]

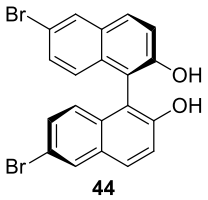
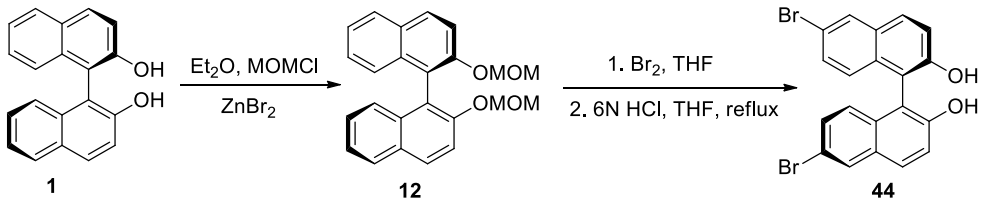


Figure 3 6,6'-dibromo-*bi*-2-naphthol

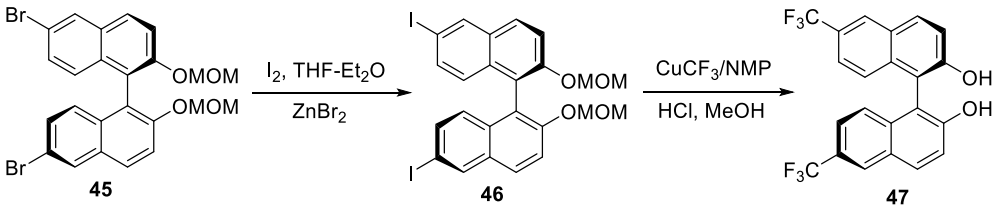
This readily available material has been used as an entry into a wide range of other derivatives. The protection of the hydroxyl groups (via formation of the MOM ether) allows for lithiation of the aryl bromide with ^{n}BuLi, followed by reaction with various electrophiles, resulting in a variety of different 6,6'-disubstituted BINOL ligands (Scheme 16).

Scheme 16



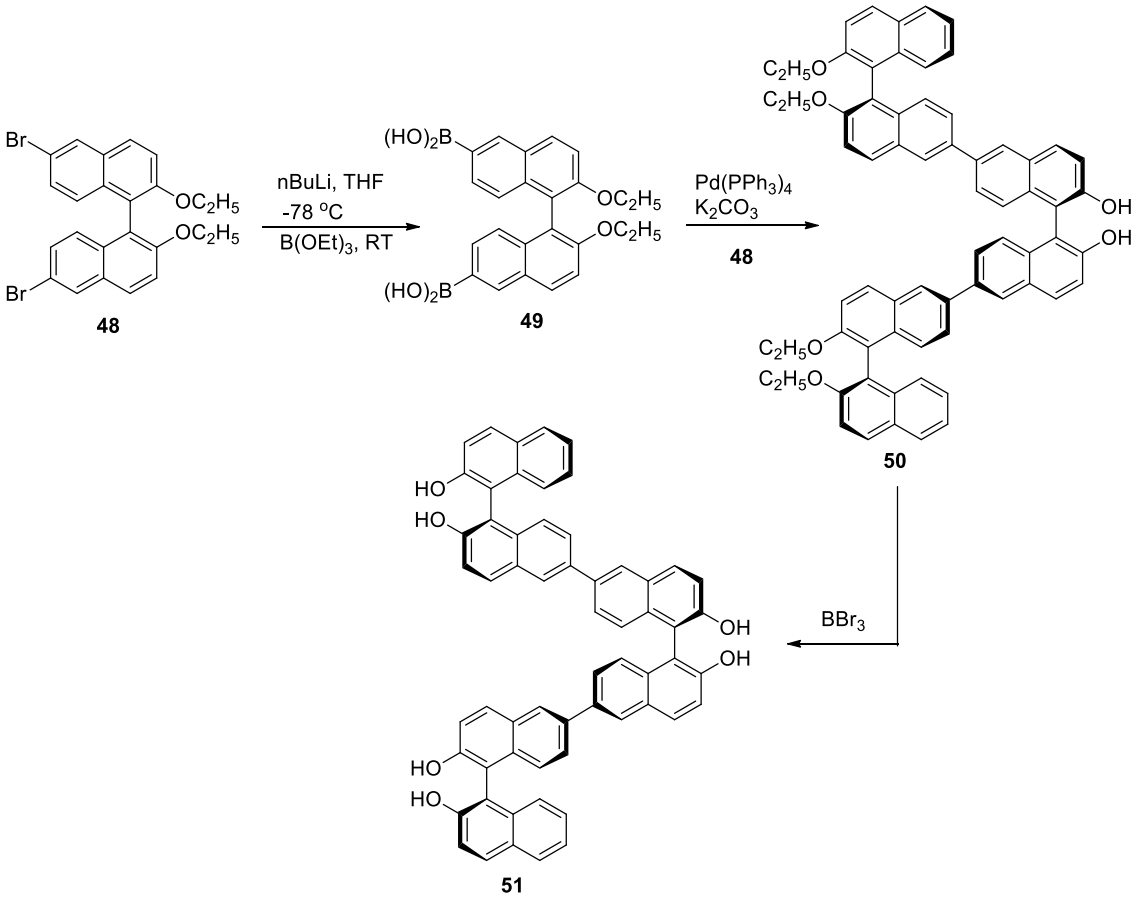
Kobayashi and co-workers[23] reported a method of synthesis of (*R*)-6,6'-bis-(trifluoromethyl)-1,1'-bi-2-naphthol (6,6'-$(CF_3)_2$-BINOL) by converting the bromo substituents at the 6,6'- positions into the iodo groups using I_2, and then to trifluoromethyl groups using $CuCF_3$ in *N*-methylpyrrolidin-2-one (NMP). After deprotection of the MOM groups, 6,6'-$(CF_3)_2$-BINOL **47** was isolated (Scheme 17).

Scheme 17



Lin and co-workers synthesized the oligomeric 6,6'-di(bi-2-naphthyl)-1,1'-*bi*-2-naphthol **48** to **51** (Scheme 18). [24]

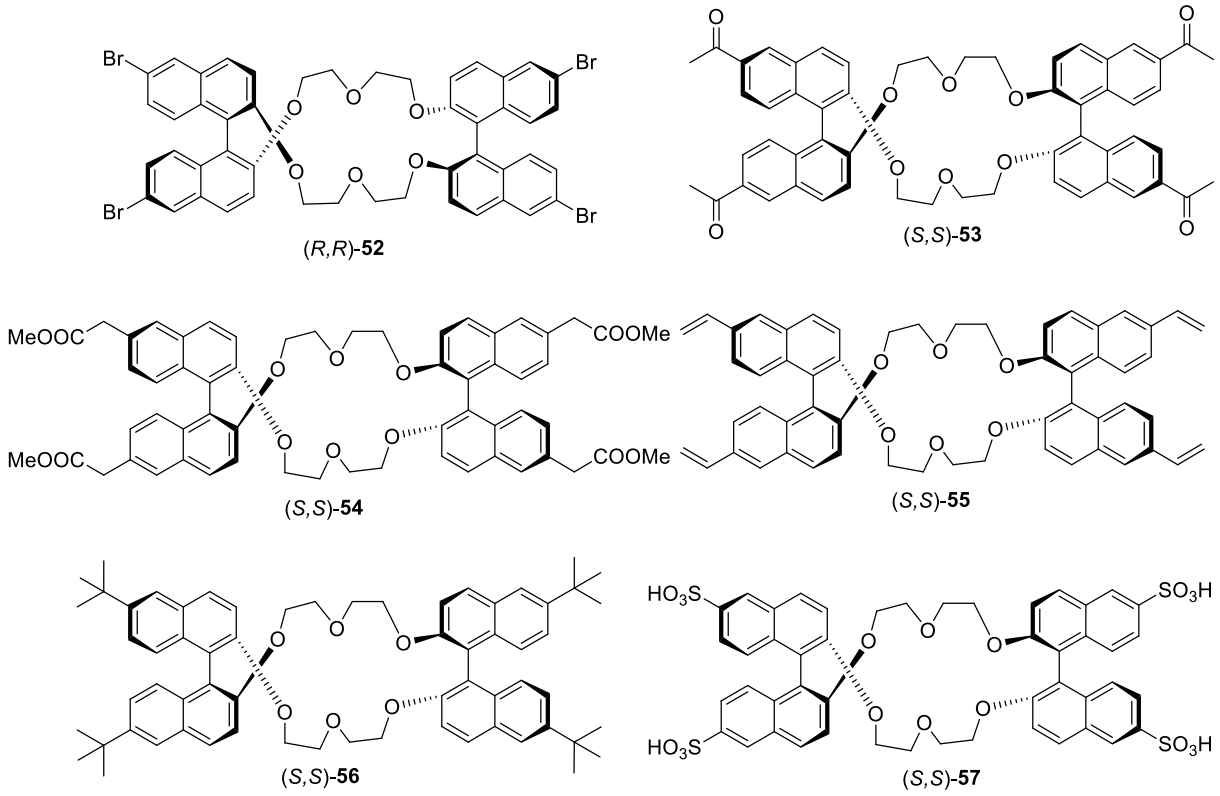
Scheme 18



1.2.3 Chiral *bi*-2-naphthyl macrocycles

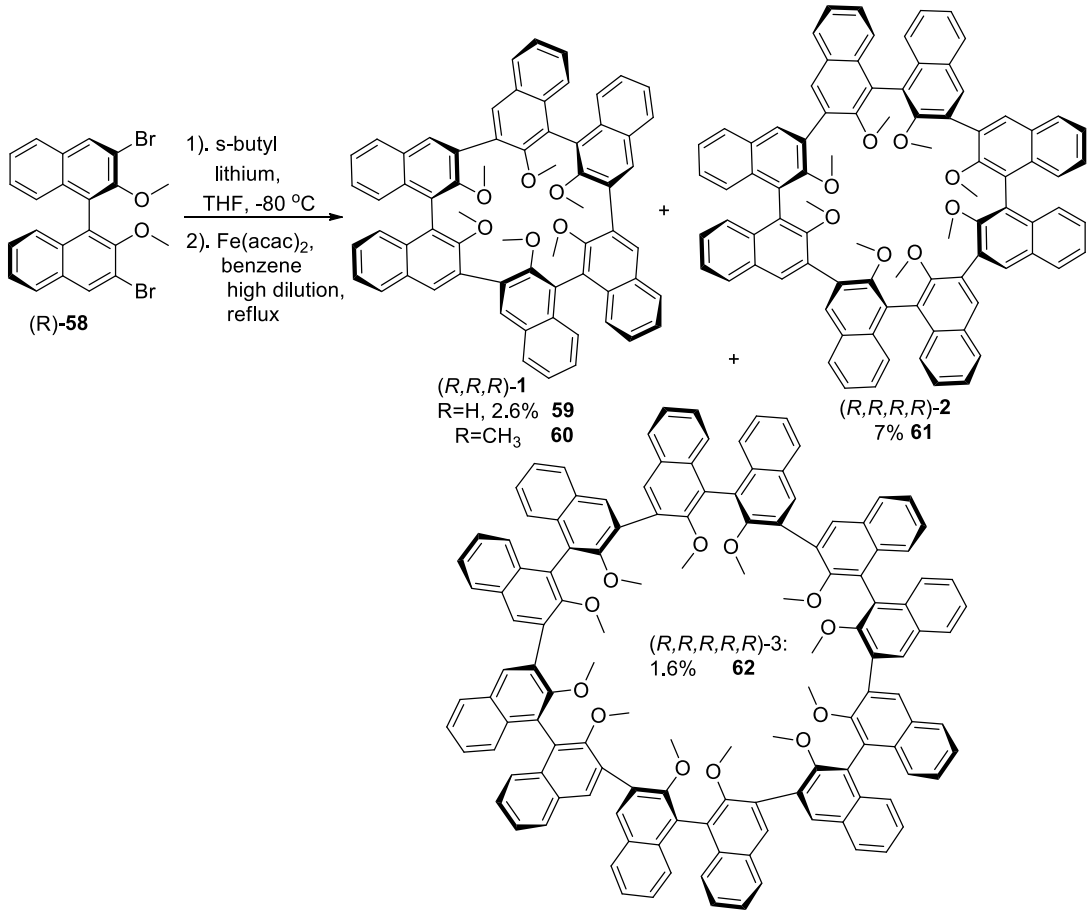
Cram and co-workers[25] reported a method of synthesis of *bis*-binaphthyl macrocycles by either tetrabromination or tetraacylation. The chiral macrocycles **52**-**57** containing different functional groups in the 6,6′-positions were also prepared. Because the 6,6′-positions are some distance away from the crown ether cycle, substituents were introduced in order to adjust the solubility of the -*bi*-naphthyl compounds, or in other cases to further incorporate these compounds into polymers or solid supports without significantly changing the binding properties of the chiral crown ether functions (Scheme 19).

Scheme 19



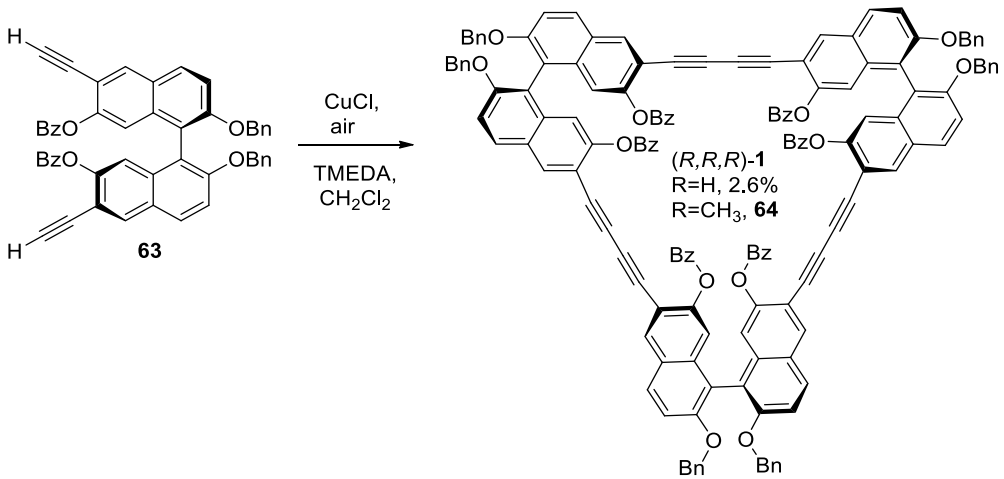
In 1981, Cram and co-workers[26] reported the self-coupling of (*R*)-3,3¢-dibromo-2,2¢-dimethoxy-1,1¢-binaphthyl, (*R*)- **58**, which generated a mixture of chiral macrocycles. In this reaction, (*R*)-**58** was first treated with *sec*-butyllithium at -80 °C in THF, and the resulting solution was then added to a refluxing benzene solution of $Fe(acac)_3$ (acac) acetylacetonate) under very dilute conditions. After completion of the reaction, macrocycles (*R,R,R*)-**59**, (*R,R,R,R*)- **60**, and (*R,R,R,R,R*)-**61** were isolated in 2.6%, 7%, and 1.6% yields, respectively. In (*R,R,R*)-**62**, one of the methyl groups was removed during the isolation. This molecule was converted to (*R,R,R*)-**62** by reaction with potassium hydroxide and $(CH_3)_2SO_4$. These compounds are members of a class called spherands-a family of molecules with completely preorganized ligand systems. They show selective binding with alkaline metal cations as well as ammonium salt (Scheme 20).

Scheme 20



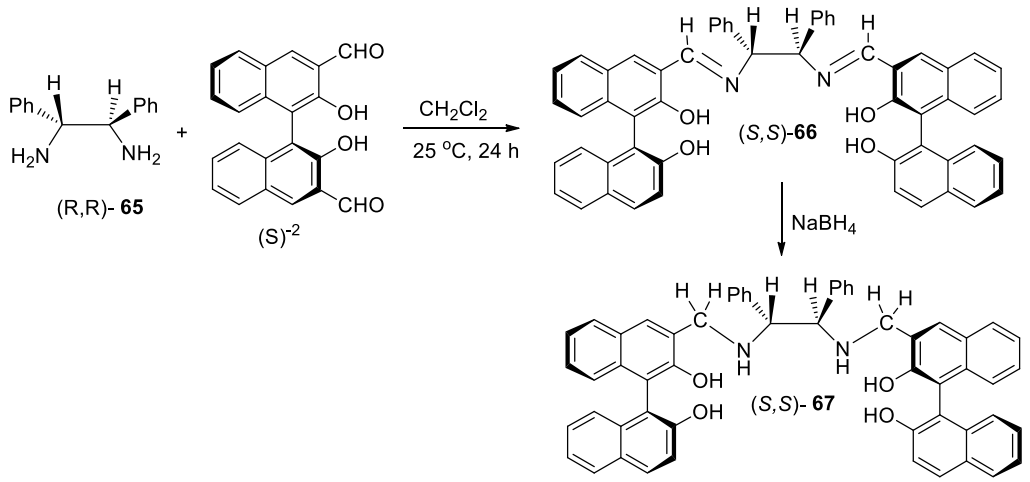
In 1995, Diederich and co-workers reported the self-coupling of a dilute methylene chloride solution of the optically pure binaphthyl alkyne molecule (*R*)-**64** in the presence of CuCl in air (Scheme 21).

Scheme 21



In 1994, Brunner *et al*.[27] found that the reaction of (*R, R*)-**65** with (*S*)-**31** gave a bisbinaphthyl macrocycle (*S,S*)-**66.** However, when (*R*)-**66** was reacted with (*R,R*)-**67**, no macrocycle was produced (Scheme 22).

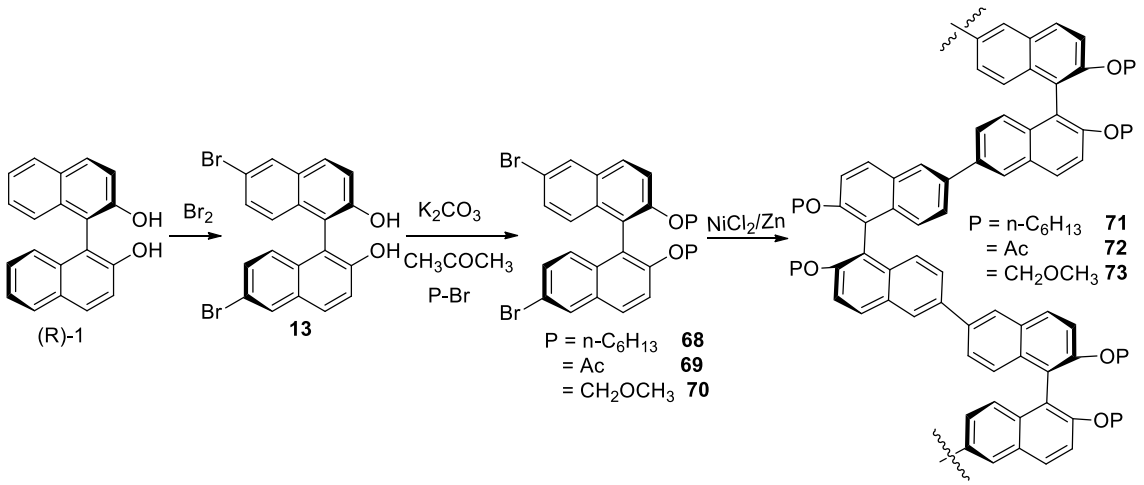
Scheme 22



1.2.4 Bi-2-naphthyl Polymers

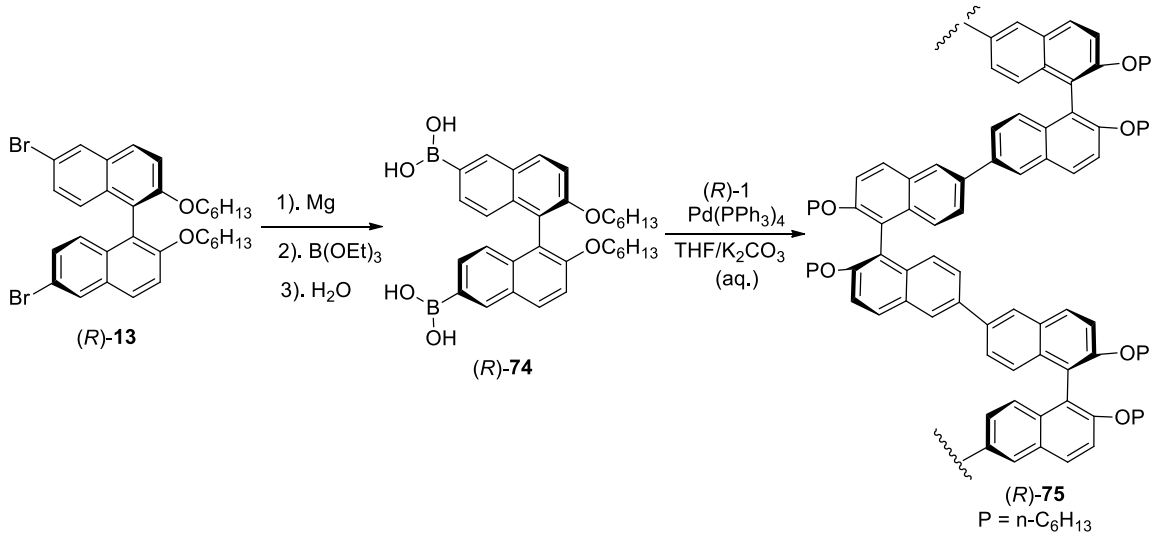
Recently, Pu and co-workersused chiral-*bi*-2-naphthyls to make novel rigid and sterically regular polymer catalysts for asymmetric catalysis (Scheme 23). [28-30]

Scheme 23



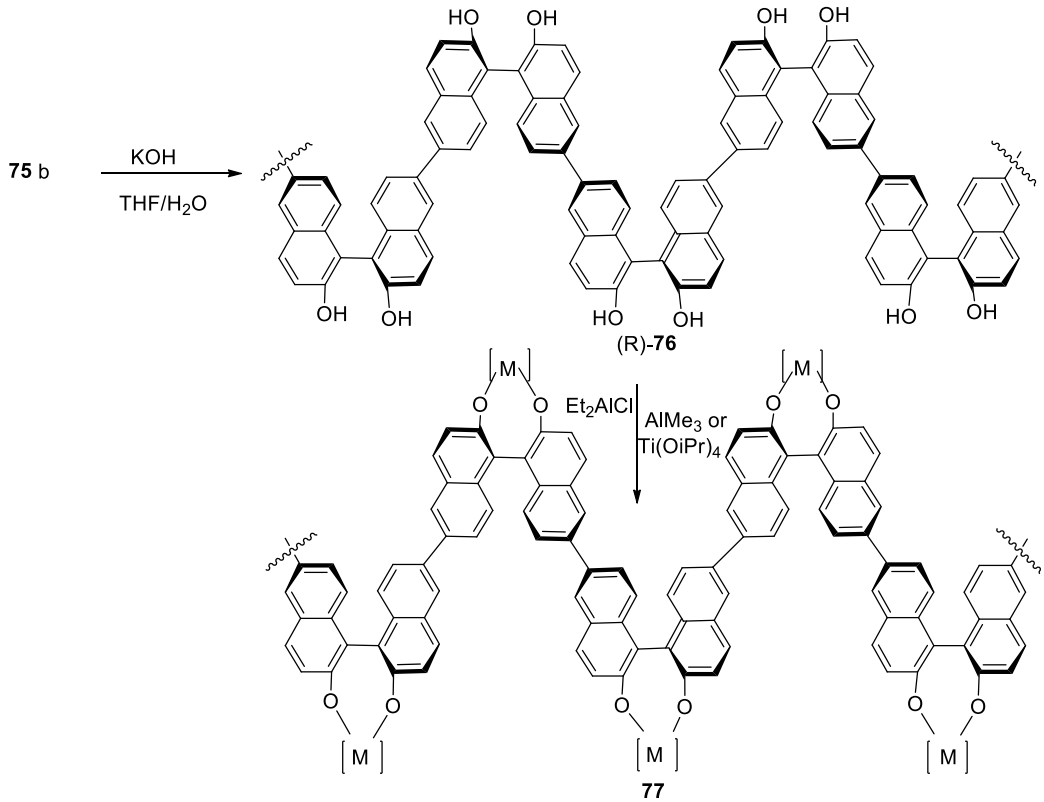
The Suzuki coupling of (*R*)-**13** with (*R*)-**74** in the presence of $Pd(PPh_3)_4$ catalyst was used to prepare (*R*)-**75 (**Scheme 24).

Scheme 24



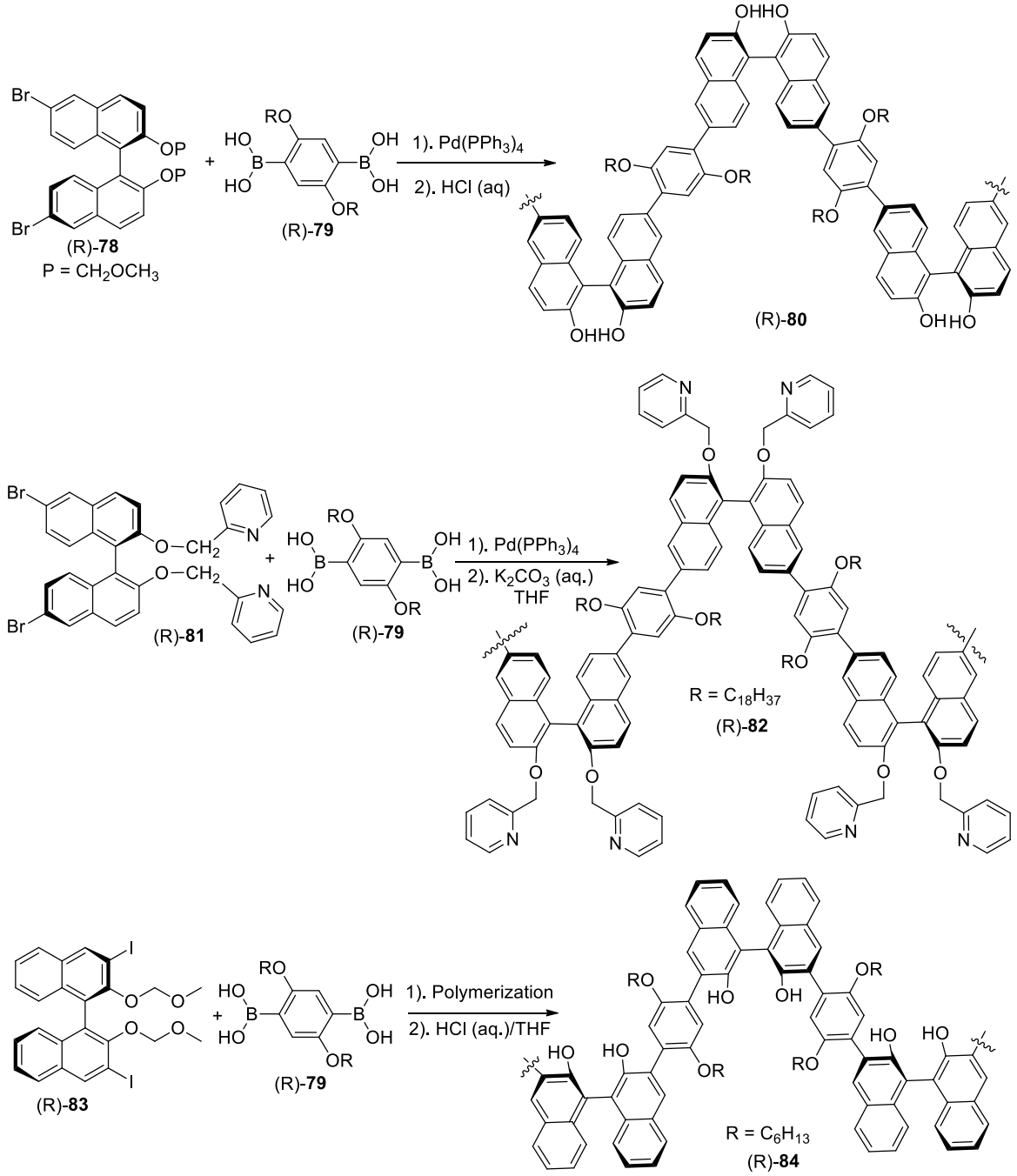
Hydrolysis of poly (BINOL) derivative of *(R)*-**76** in the presence of potassium hydroxide (Scheme 25).

Scheme 25



Another Poly (BINOL) (*R*)-**80** was prepared via the Suzuki coupling of (*R*)-**78** (Chart 1).

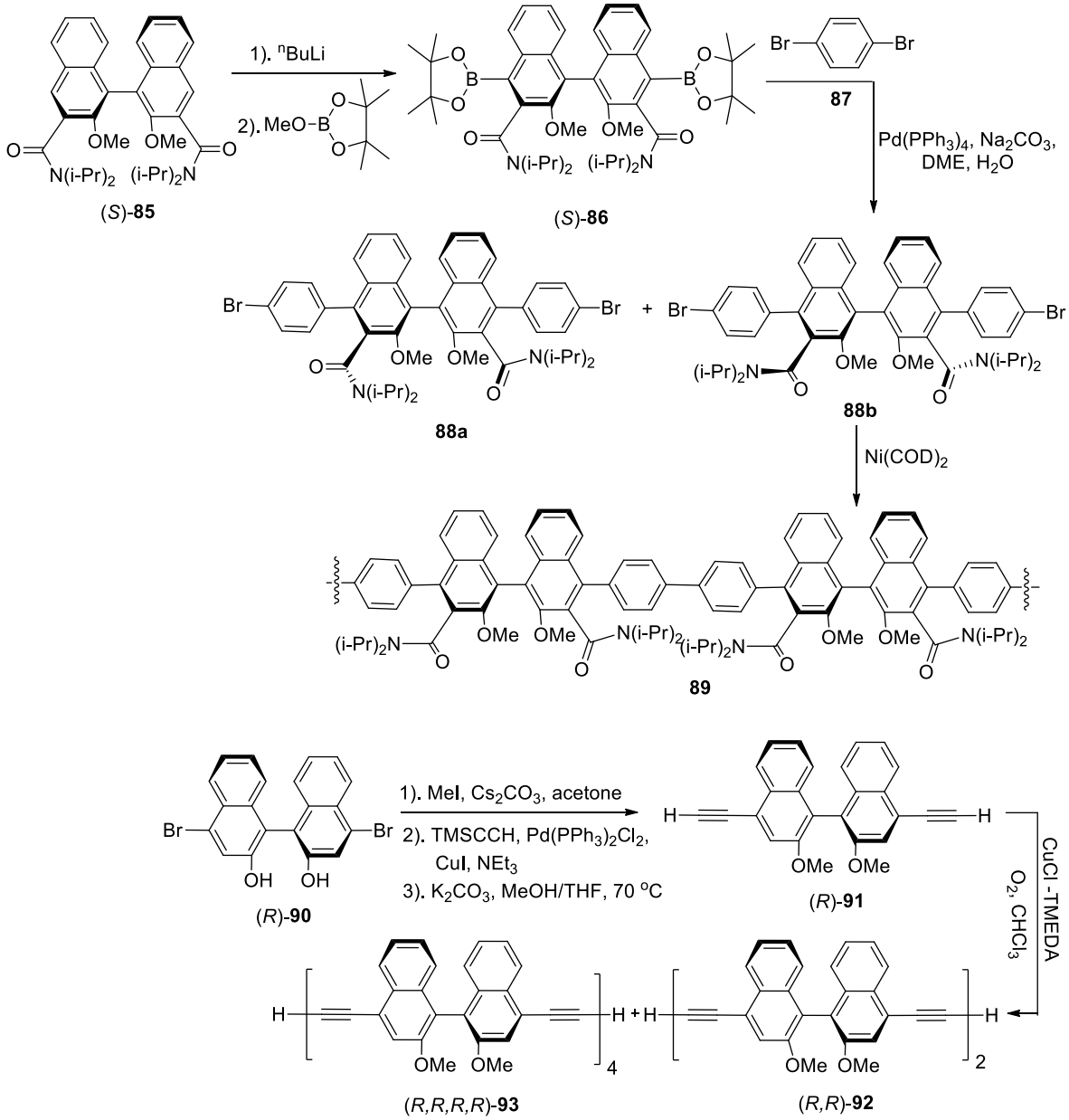
Chart 1



1.3 Polymerization at the 4,4'-Positions

The polymerization of a 1,1-¢-binaphthyl molecule at the 4,4-¢-positions was studied by Tour and Bedworth (Chart 2).

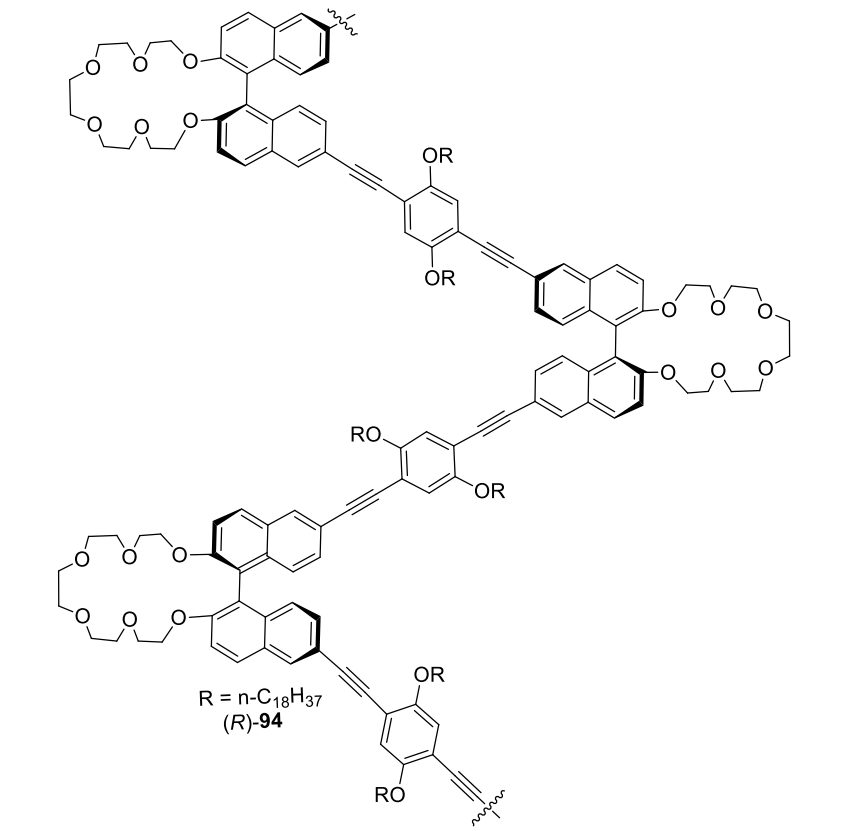
Chart 2

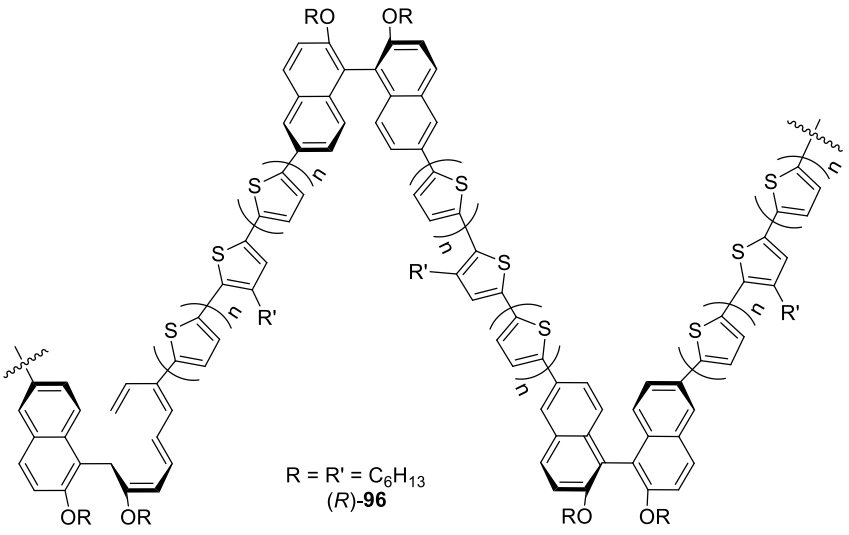


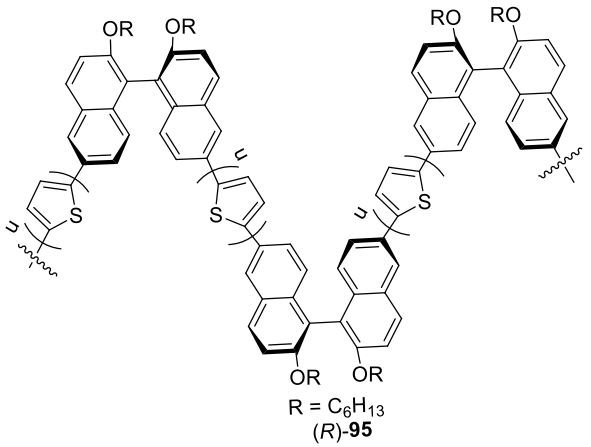
1.4 Polymerization at the 6,6′-Positions

Pu and co-workers reported a series of *bi*-2-naphthyl-based chiral conjugated polymers synthesized by polymerization at the 6,6 ¢-positions of optically active *bi*-2-naphthyl monomers (Chart 3).

Chart 3



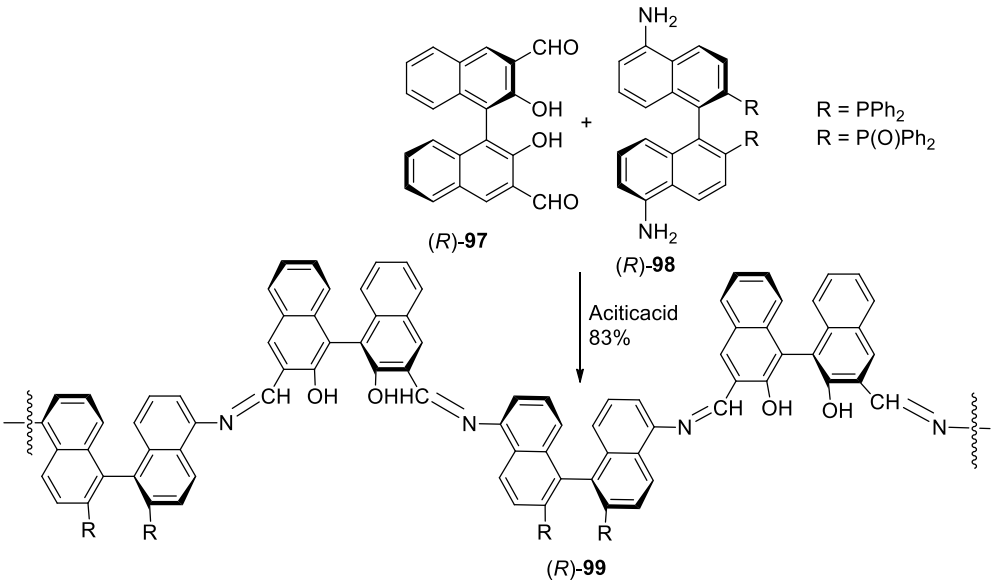




1.5 Modified BINOL ligands in Carbon-Carbon bond forming reactions

Fan and Chan described two soluble bifunctional polymeric ligands (*R*,*R*)-**99 (**Scheme 26**).**

Scheme 26



We have decided to develop methods for the synthesis of *bi*-2-naphthyl derivatives containing pyrrolidine and piperazine heterocyclic moieties. The results are described in the next chapter.

1.2. References

1. Chen, Y.; Yekta, S., Yudin, A. K. *Chem. Rev*.**2003**, *103*, 3155.
2. (a). Meca, L.; Reha, D.; Havlas, Z. *J. Org. Chem.***2003**, *68*, 5677.

   (b) Kyba, E. P.; Gokel G. W.; de Jong F.; Koga, K.,Sousa, L. R., Siegel, M. G.; Kaplan, L.,Sogah, G. D. Y.; Cram, D. J. *J. Org.Chem.***1977**, *42*, 4173.
3. Kagan H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985, *5*, 1.
4. Akimoto, H.; Yamada, S. *Tetrahedron***1971**, *27*, 5999.
5. Pummerer, R,;Prell, E.; Rieche, A. *Chem.Ber.***1926**, *59*, 2159.
6. Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Soc*. **1979,** *101*, 3129.
7. Yudin, A. K.; Martyn, L. P.J.; Pandiyaraju, S.; Zheng, J.;Lough, A.*Org. Lett*. **2000**, *2*, 41.
8. Kyba, E. P.; Gokel, G. W.; Jong F. de; Koga, K.;Sousa, L. R.; Siegel, M. G.; Ka;pan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.
9. (a) Periasamy, M.; Prasad, A. S. B.; J. V. B.; Reddy, Ch. K. *Tetrahedron Asymmetry* **1995**, *6*. 341.

   (b)Venkatraman, L.; Periasamy, M.;*Tetrahedron Asymmetry***1996**, *6*7, 2471.

   (c)Periasamy, M.;VenkatramanL.;Thomas K. R. J. *J. Org.Chem.***1997**, *62*, 4302.

   (d)Periasamy, M.;Venkatraman L.; Kumar, L.; S, S.; Kumar, N. S.; Ramanathan, C. R. *J. Org.Chem.***1999**, *64*, 7643.

   (e)Periasamy, M, Reddy, M. N.; Anwer, S. *Tetrahedron Asymmetry* **2004**, *15*, 1809.

10. (a) Periasamy, M.; Kumar.; S, S.; Rao, V. D.; Ramanathan, C. R. Venkatraman L.; *J. Org.Chem.***2001**, *66*, 3828.

(b) Periasamy, M.; Kumar, N, S.; N. S.,Ramanathan C. R. *Tetrahedron Asymmetry***1999**, *10*, 2307.

11. V. D. Rao.;Periasamy, M. *Tetrahedron Asymmetry***2000**, *11*, 1151.

12. Periasamy, M.; M. Seenivasaperumal, M.; V. D. Rao.; *Tetrahedron Asymmetry***2004**, *15*, 3847.

13. Cram. d. J.; Helgeson, R. C.; Peacock, S. C.; Kalpan, L. J.; Domeier, L. H.; Moreasu, p.; Koga.; K. Mayer, J. M.; Chao, Y.; Siegel, M. D.; Hoffman, D. H.; Soah, G. D. Y. *J. Org.Chem.***1978**, *43*, 1930.

14. Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org.Chem.***1981**, *46*, 393.

15. Simonson, K. B.; Gothelf, K.V.; Jorganson, K. A. *J. Org.Chem.***1998**, *63*, 7536.

16. Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamato, H. *Bull*. *Chem*. **Soc**. Jpn.**1988**, *61*, 2975.

17. Huang, W.; Pu, L. *Tetrahedron*: *Lett.***2000**, *41*, 145.

18. Quin, C.; Zhu, C.; Huang, T. *J*. *Chem*. *Soc*. *Perkin Trans*. *1***1998**, 2131.

19. Kitajima, H.; Aoki, Y.; Ito, K.; Katsuki, T. *Chem.Lett*.**1995**, 1113.

20. Vogl, E. M.; Matsunga, S.; Kanai, M.; Iida, T.; Shibaski, M. *Tetrahedron*: *Lett.***1998**, *39*, 7917.

21. Mutsunga, S.; Das, J.; Roles, J.; Vogl, E. M.; Yamamoto, N.; Iida, T.; Yamaguchi, K.;Shibasaski, M. *J*. *Am*. *Soc*. **2000,** *122*, 2252.

22. Sogah, G. D. J.; Cram, D. J. *J*. *Am*. *Soc*. **1979,** *101*, 3035.

23. Ishitani, H.; Ueno, M.; Kobayashi, S. *J*. *Am*. *Soc*. **2000,** *122*, 8180.

24. Ma, L.; white, P. S.; Lin, W. B. *J. Org.Chem.***2002**, *67*, 7577.

25. (a) Cram , D. J.; Helgenson, R. C.; Peacock, S. C.; Kalpan, L. J.; Domeier, L.A.; moreasu, P.; Koga, K.; Mayer. J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org.Chem.***1978**, *43*, 1930.

(b)Kyba, E. B.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Cram, D. J. *J. Am. Soc.* **1973,** *95*, 2692.

26. Helgeson, R. C.; Mazaleyrat, J.-P.; Cram, D. J.*J. Am. Soc.* **1981,** *103*, 3929.

27. Brunner, H.; Schiessling, H. *Angew. Chem*, *Int. Ed. Engl.* **1994,** *33*, 125.

28. Hu, Q.-S.; Zheng, X.-F.; Pu, L. *J. Org.Chem.***1996**, *61*, 5200.

29. Hu, Q.-S.; Vitharana, D.; Zheng, X.-F.; Wu, Kwan, C. M. S.; Pu, L.*J. Org. Chem.***1996**, *61*, 8370.

30. Vitharna, D.; Hu, Q,-S.; Pu, L. *Polym. Prepr.* **1996**, *37*, 855.

Chapter-2

Synthesis of Chiral Heterocycles Containing *Bi*-2-naphthyl moiety

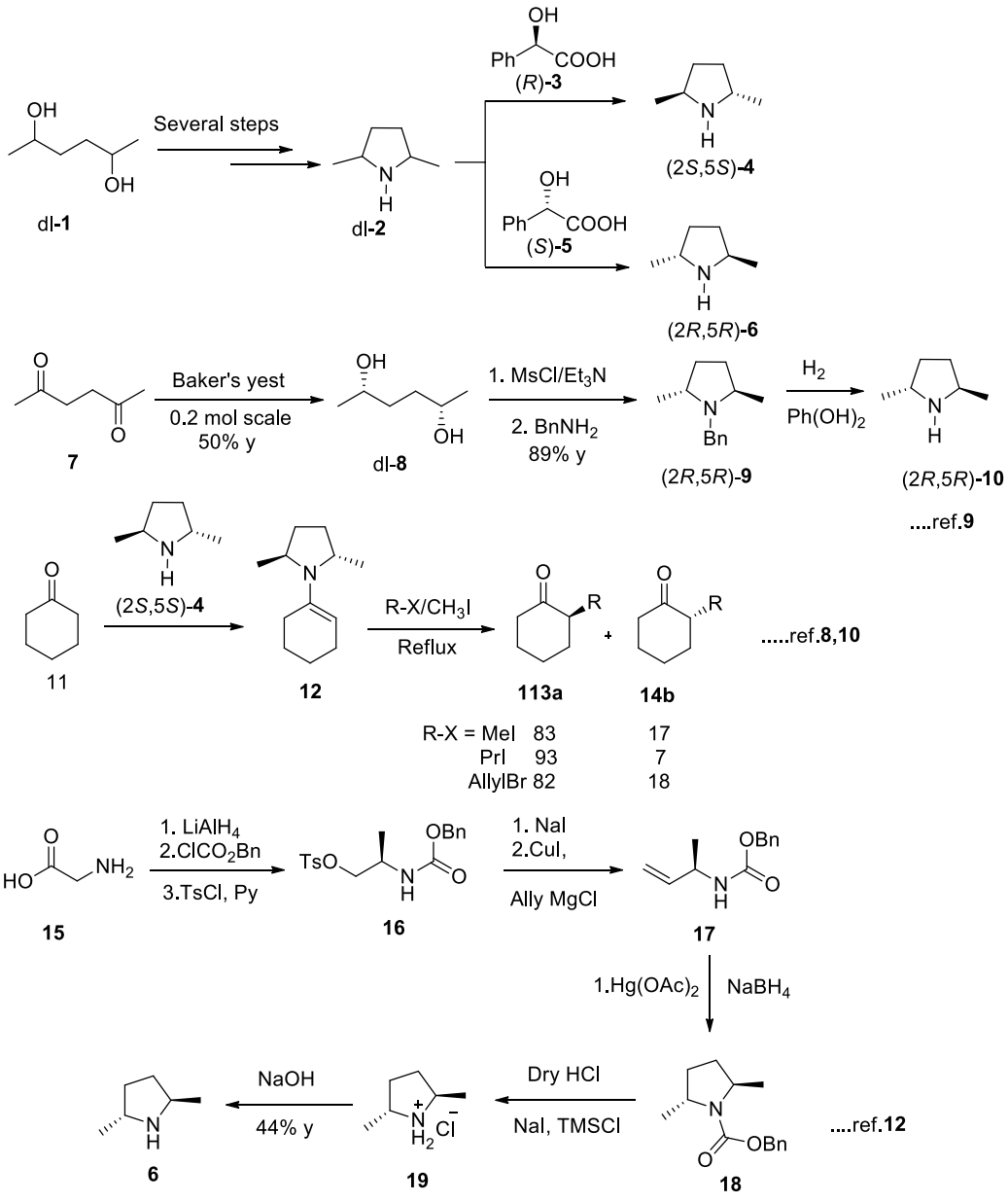
2.1. Introduction

2.1.1 Synthesis of chiral C_2-symmetric nitrogen heterocyclic systems

Chiral C_2-symmetric molecules are widely used as auxiliaries and ligands in asymmetric tranformations.[1] The C_2-symmetric derivatives such as 2,5-disubstituted pyrrolidines,[2] borolanes,[3] thiolanes,[4] and phospholanes[5] have been used extensively in various asymmetric organic transformations including alkylation, radical cyclizations, Michael addition, enantioselective deprotonation, Claisen rearrangements, Diels-Alder reactions, allylic substitutions, reduction of prochiral ketones and in other asymmetric hydrogenation reactions. Chiral C_2-symmetric 3,4-disubstituted pyrrolidines are also useful in dihydroxylations of olefins, asymmetric addition of organometallics to carbonyl compounds and palladium catalysed asymmetric alkylations. Saturated nitrogen heterocycles including pyrrolidines and piperidines occur in a wide of natural products, alkaloids and biologically active compounds[6] there have been numerous reports on the syntheses of substituted pyrrolidines and other heterocycles in theliterature.[7]

The chiral C_2-symmetric 2,5-dimethylpyrrolidine was first introduced in 1977 by Whitesell and co-workers.[8] This amine has been accessed by catalytic reduction of the corresponding *N*-amino derivative followed by resolution by forming the salt using mandelic acid. Later, a convenient route involving asymmetric Baker's yeast reduction of 2,5-hexanedione followed by mesylation, cyclization using benzylamine and debenzylation have been reported to obtain the enantiomerically pure amine (+)-(2*S*,5*S*) derivatives. (Chart 1).[9, 10, 11, 12]

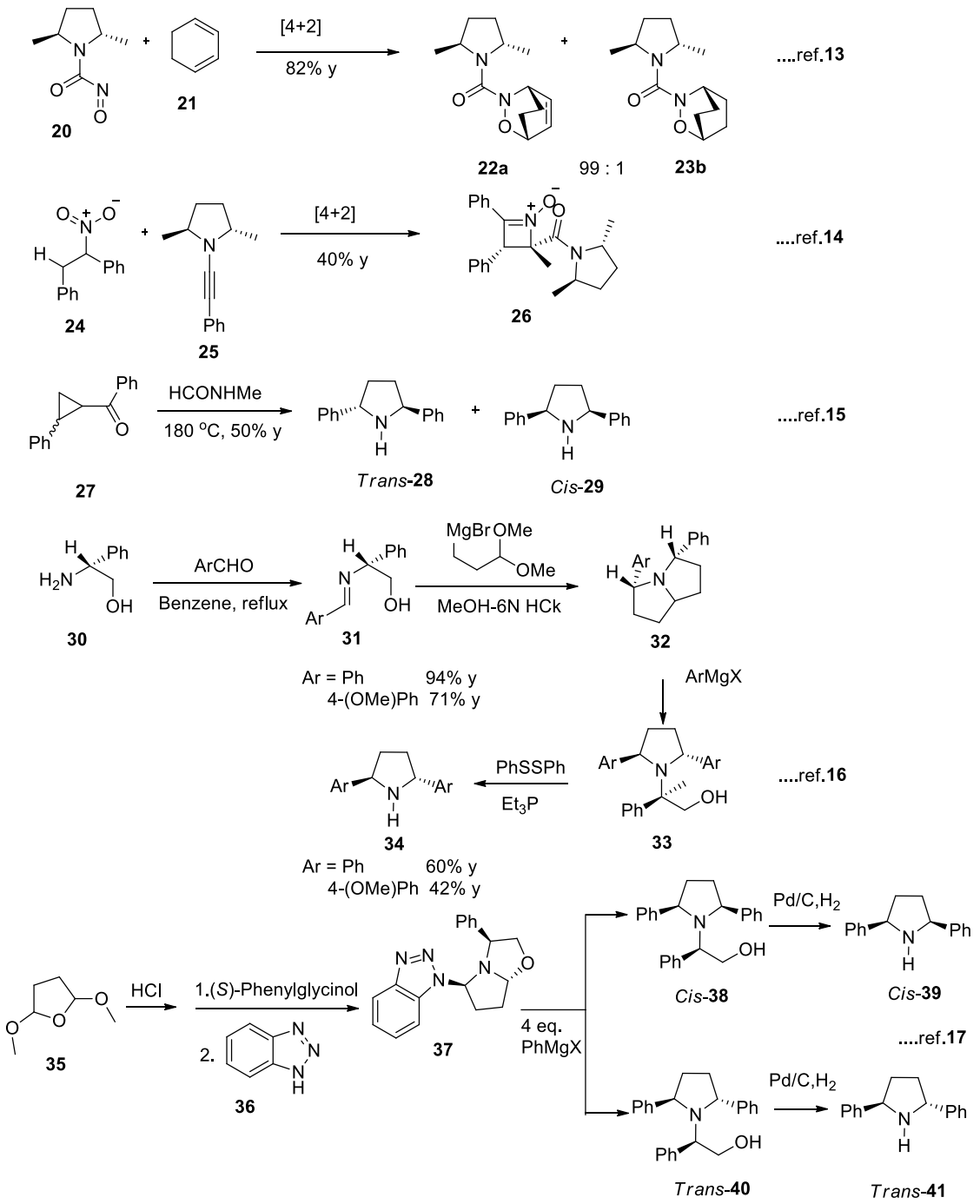
Chart 1



The carbamoyl nitroso dienophile derivative of chiral (-)-*trans*-2,5dimethylpyrrolidine was used in asymmetric Diels-Alder cycloadditions with the diene (Chart 2).[13,14] Also, 2,5-diarylsubstituted pyrrolidine derivatives were prepared by various reactions like ring opening of

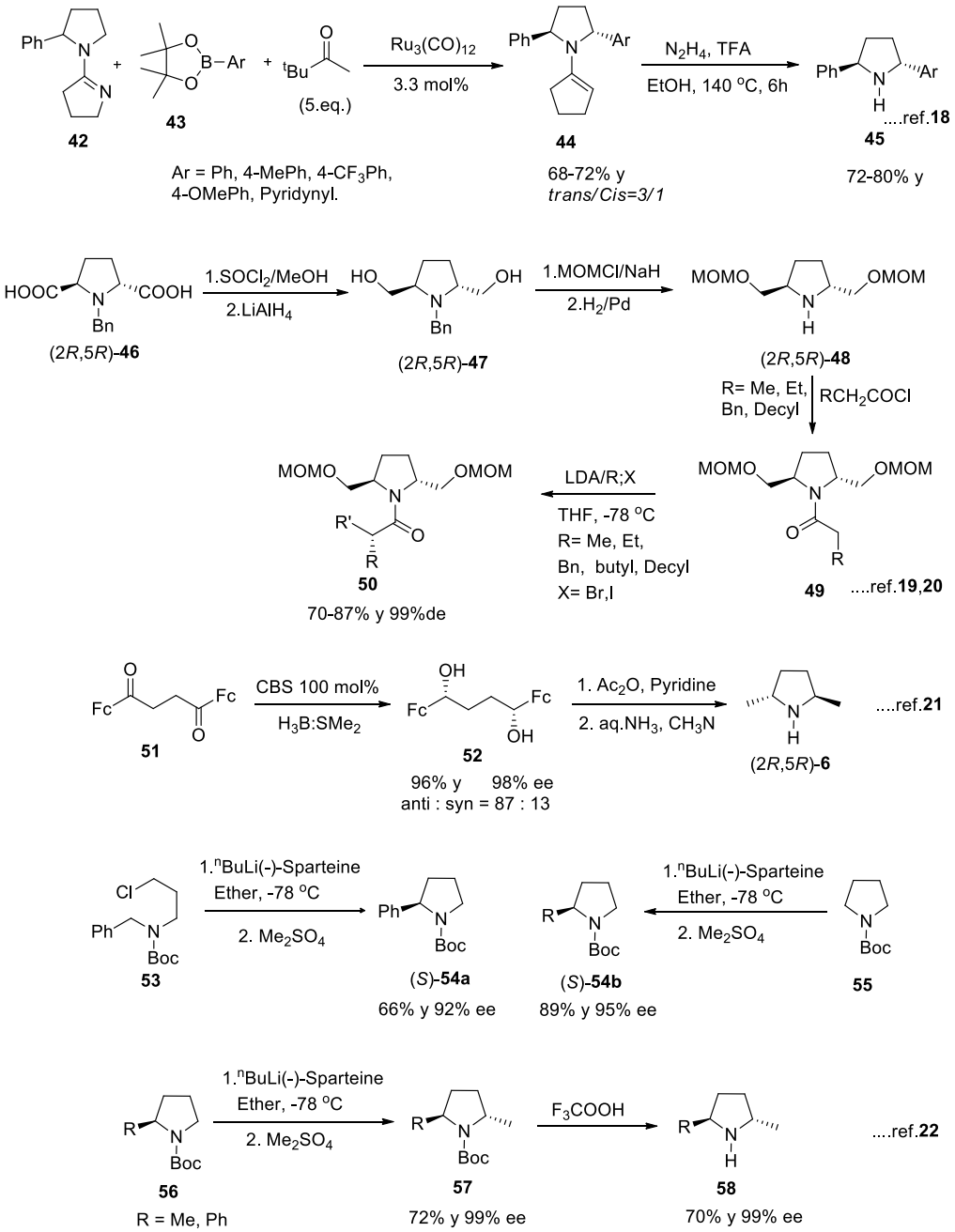
cyclopropane *via* Leuckart reaction,[15] addition of Grignard reagents to chiral imines,[16] and benztriazole substituted pyrrolidine derivatives (Chart 2).[17]

Chart 2



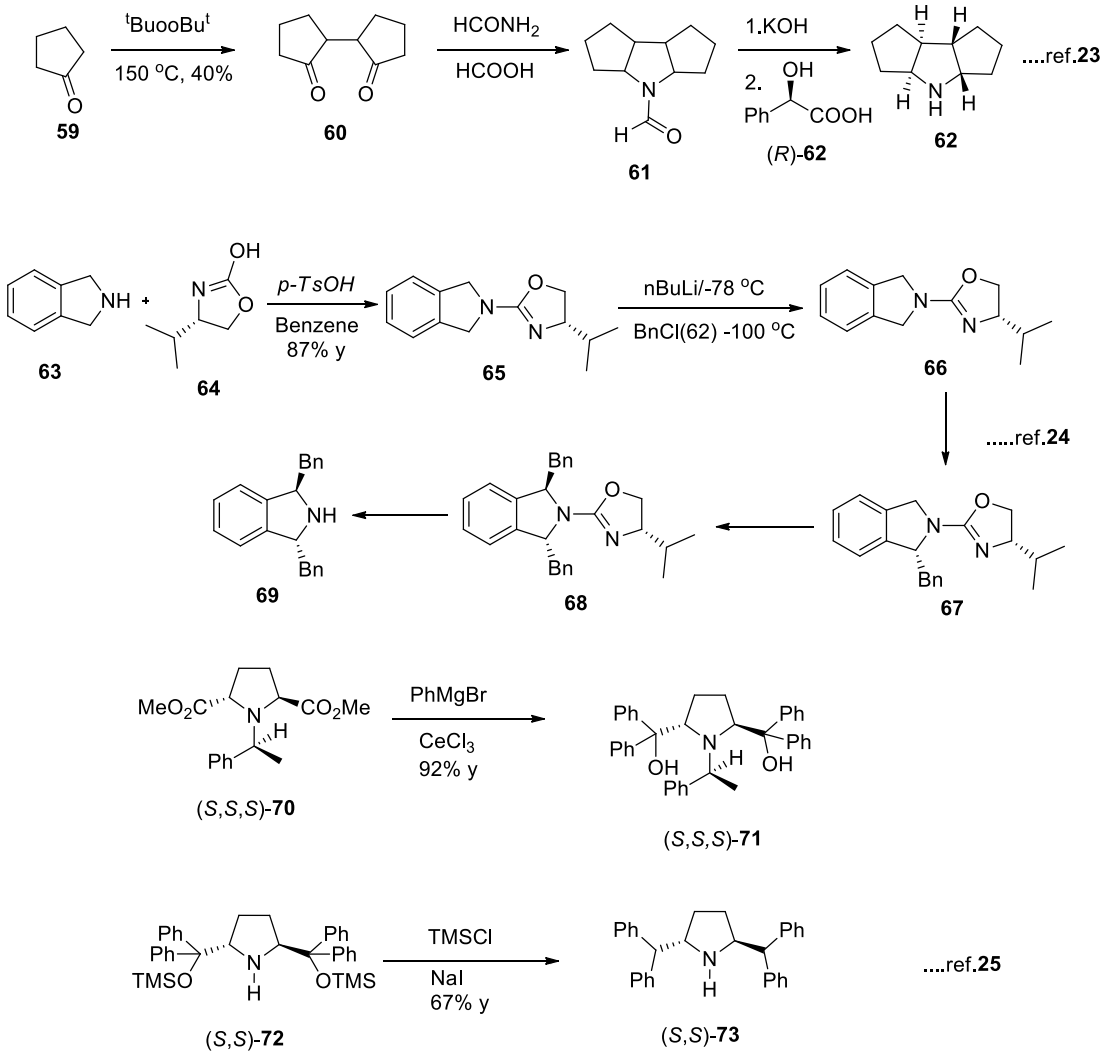
The formation of the mixture of 2,5-diphenylpyrrolidine derivatives by Leuckart reaction using *cis* and *trans*-1-benzoyl-2-phenylcyclopropane *via* opening of the cyclopropane ring with *N*-methylformamide at 180 °C was reported (Chart 3).[18-22]

Chart 3



Synthesis of *trans*-2,5-bis(methoxymethyl)-pyrrolidine was reported from *dl-N* -benzyl-2,5-pyrrolidine dicarboxylic acid which can be readily resolved using D-(-)-threo-(*p*-nitrophenyl)-2-amino-1,3-propanediol. The amine played a prominent role in many asymmetric processes including amide alkylations, acylations, radical additions and Diels-Alder reactions (Chart 4).[23-25]

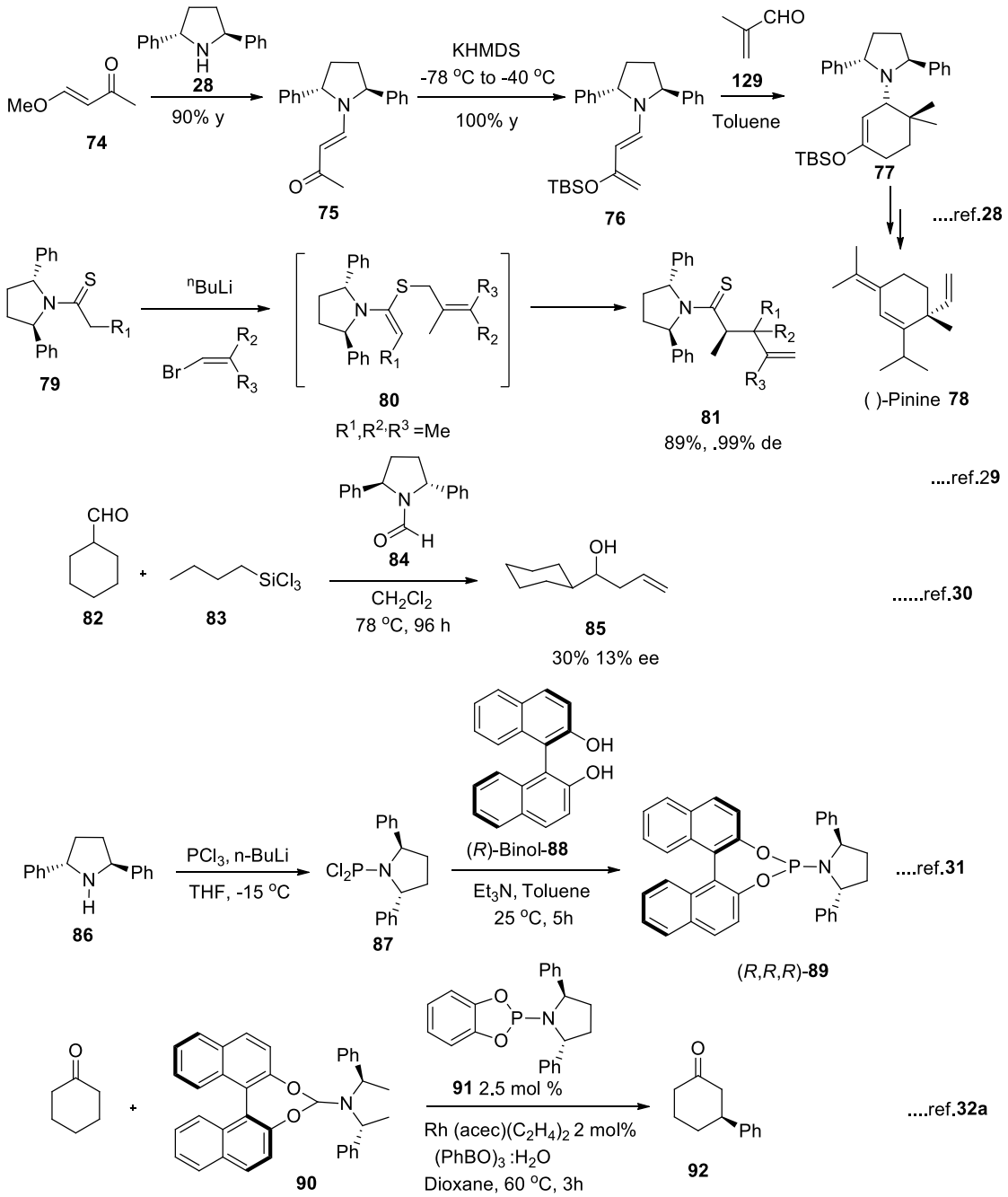
Chart 4



2.1.2 Applications of chiral C_2-symmetric nitrogen heterocyclic systems

The C_2-symmetric chiral amine was prepared from cyclopentanone, followed by resolution using chiral mandelicacid. The utility of this amine has been demonstrated in the synthesis of a 6 membered ring lactone with diastereomeric purity up to 95% de (Chart 5).[26, 28, 32]

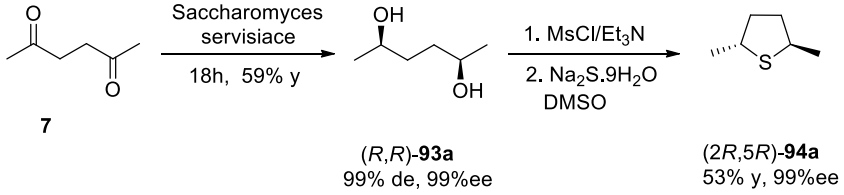
Chart 5



2.1.3 Synthesis of chiral sulfur heterocyclic systems

Chiral ligands containing sulfide moieties are useful in many asymmetric transformations like asymmetric epoxidation, catalytic cyclopropanation of electron deficient alkenes,[33] electrophilic sulfenylation of unsaturated carbon-carbon bonds[34] and aziridination of imines.[35] The chiral sulfides are also useful for the synthesis of chiral alcohols and amines from organo boranes[36] synthesis of carbocycles[37] and functionalized *N*-heterocycles.[38] The chiral C_2-symmetric sulfide (+)-(2*R*,5*R*)-*trans*-2,5-dimethylthiolane was synthesized from (+)-(2*S*,5*S*)-2,5-dimethylhexanediol with 99% de and 99% ee (Scheme 1).[39]

Scheme 1



2.1.4 Applications of chiral sulfur heterocyclic systems

The chiral sulfide (+)-(2*R*,5*R*)-*trans*-2,5-dimethylthiolane was used in stochiometric amounts for one-pot asymmetric synthesis of chiral epoxides from various aldehydes with benzyl bromide and NaOH (Chart 6).[40-42]

Chart 6

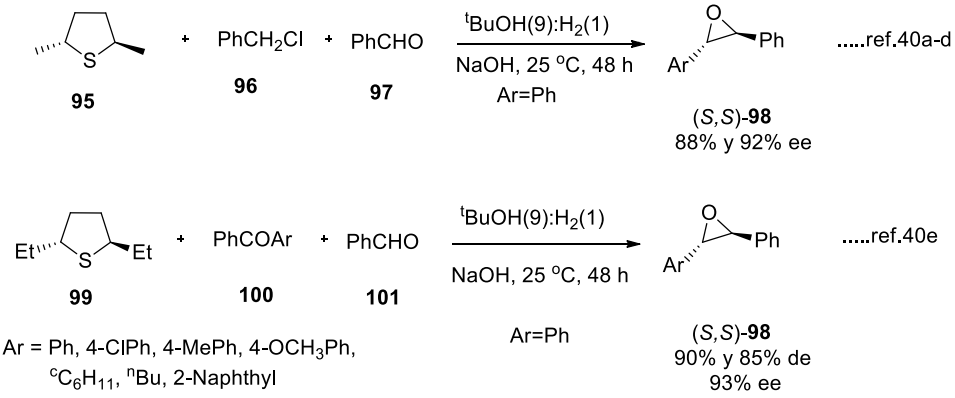
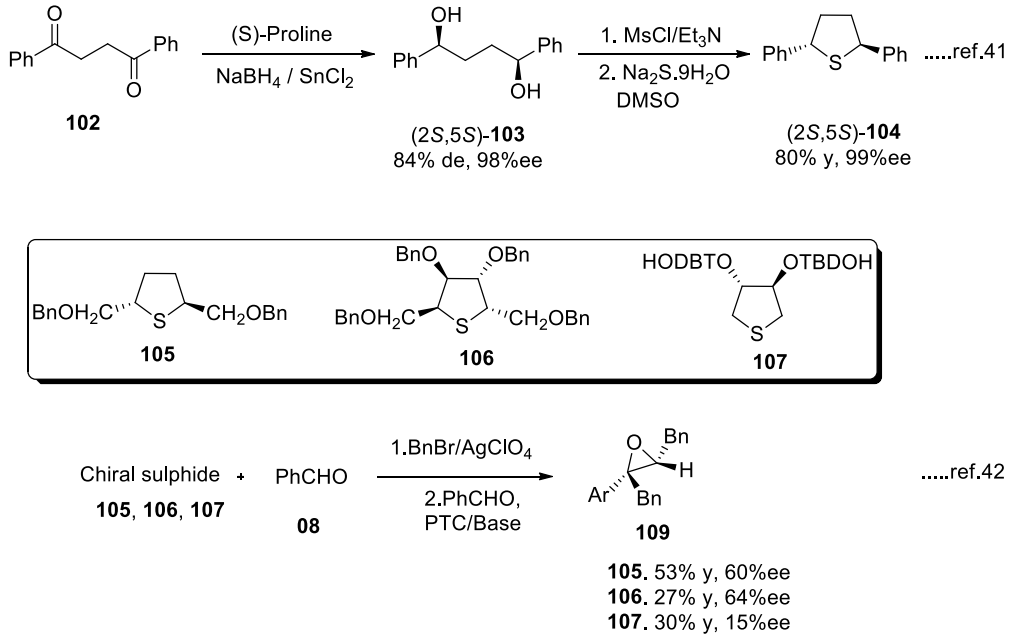


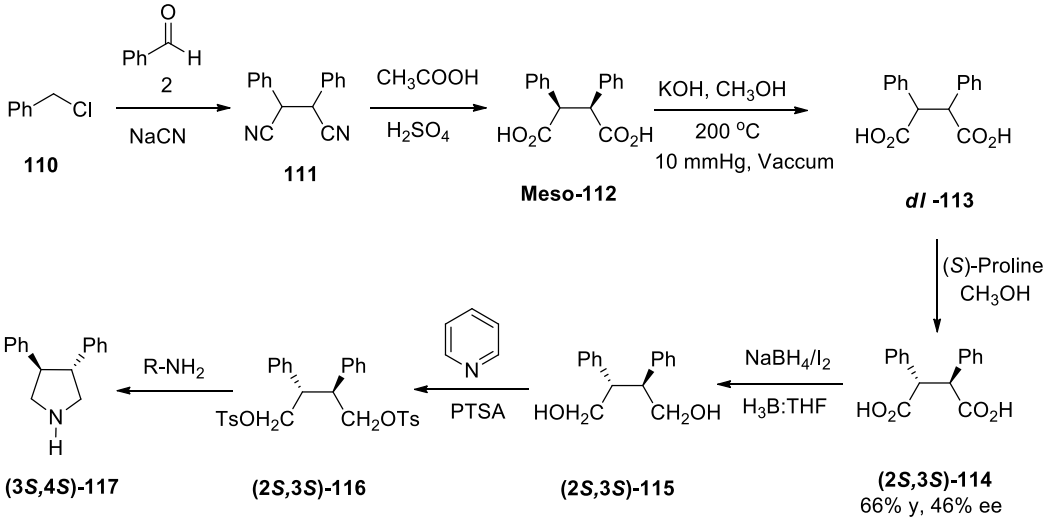
Chart 6 Conti…



2.1.5 Synthesis of chiral 3,4-diphenylpyrrolidine systems

The chiral 3,4-diphenylpyrrolidine system has found extensive applications as a chiral ligand in asymmetric synthesis. Synthesis of the chiral amine was reported starting from 2,3-diphenylsuccinic acid (Scheme 2).[43-46]

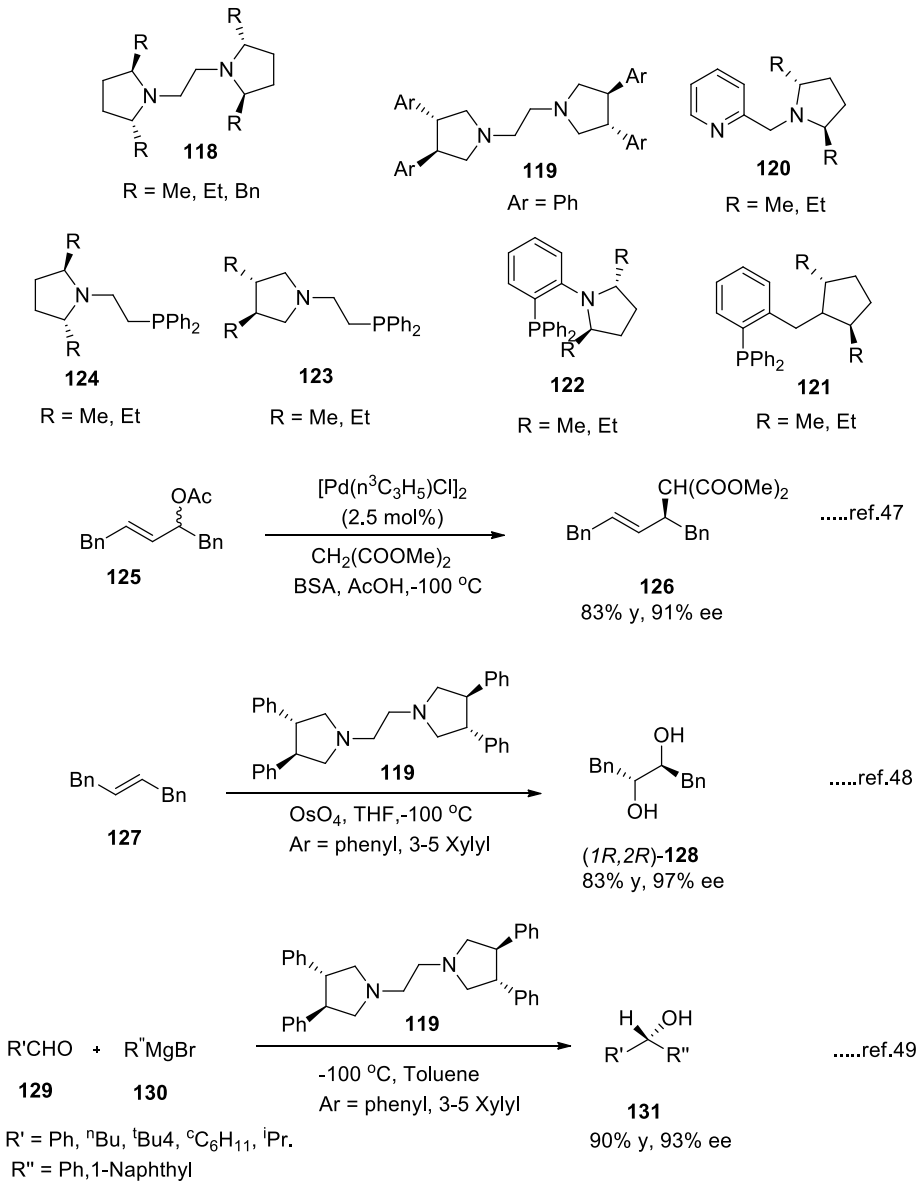
Scheme 2



2.1.6 Applications of chiral 3,4-diphenylpyrrolidine systems

The chiral *C*2-symmetric 2,5- and 3,4-disubstituted pyrrolidine derivatives **118-121** were used in enantioselective palladium-catalyzed alkylations (Chart 7).[47-49]

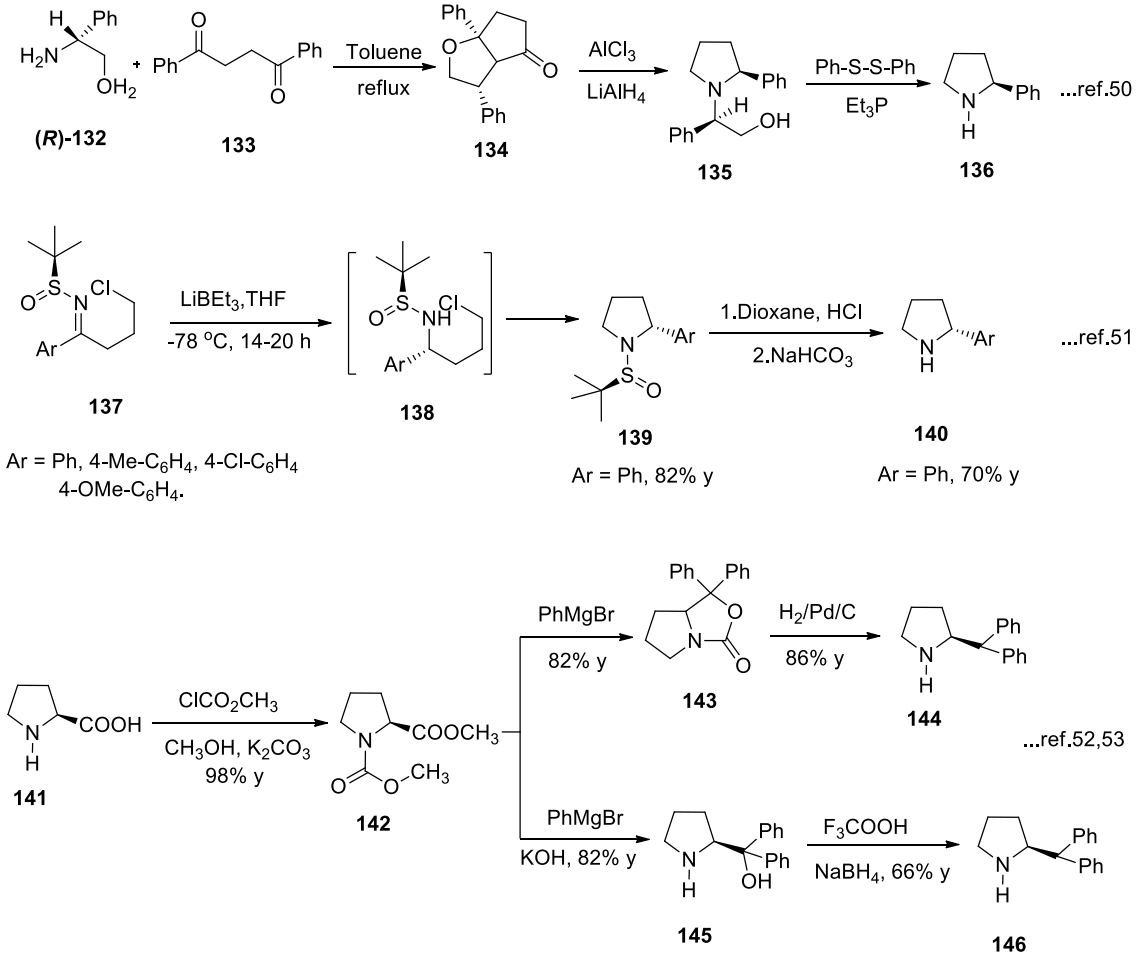
Chart 7



2.1.7 Synthesis and applications of chiral C_1-symmetric nitrogen heterocyclic systems

Asymmetric synthesis of enantiomerically pure 2-substituted pyrrolidines from γ-keto acid and (*R*)-phenylglycinol has been reported.[50-53] The *N*-substituted pyrrolidinone obtained was reduced to the *N*-glycinolpyrrolidine derivative using alane which upon reaction with diphenyl disulfide and triethylphosphine gave the 2-phenylpyrrolidine (Chart 8).

Chart 8



We have undertaken efforts toward developing methods to synthesize chiral heterocycles containing *bi*-2-naphthyl moiety. The results are described in the next section.

2.2. Results and Discussion

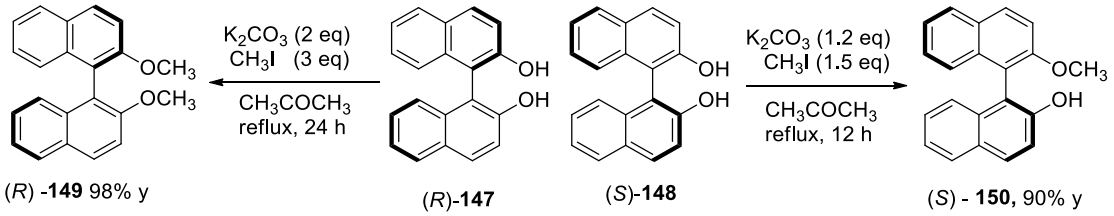
As described in Chapter 1, previously, a simple method for the resolution of racemic bi-2-naphthol[54a] using boric acid and (*R*)-(+)-α-methylbenzylamine as well as (*S*)-proline has been reported from this laboratory.[54b] Racemic BINOL was also resolved with optically active amino naphthol and boric acid in CH_3CN solvent.[54c] Chiral bi-2-naphthol in alliance with boric acid was utilized for the purification of diastereomeric amino alcohol derivatives [54d] as well as for the resolution of trans-(±)-2-(pyrrolidinyl) cyclohexanol and its methyl ether derivative.[55] Intramolecular oxidative coupling of phenyl acetic acid esters of enantiomerically pure bi-2-naphthol was achieved by preparing the corresponding titanium ester enolates with the $TiCl_4/Et_3N$ reagent system.[56] Convenient methods were developed for the preparation of chiral bi-2-naphthol derived amino ethers through opening of aziridinium ion intermediate derived from trans (±)-2-(1-pyrrolidinyl) cyclohexanol.[54] In continuation of these investigations, we became interested in the synthesis of 6,6'-diacyl binaphthyl ether derivatives for further synthetic exploitations.

The 6,6' positions of *bi*-2-naphthol can be selectively functionalized. The most common precursor for the synthesis of the 6,6'-disubstituted BINOL ligands described in the literature is the 6,6'-dibromo *bi*-2-naphthol.[57] However, there is no direct method available to obtain 6,6'-diacyl-*bi*-2-naphthylether derivatives.[58] Initially, we have examined the acylation of *bi*-2-naphthol using various Lewis acids like anhydrous $AlCl_3$, $TiCl_4$ and $ZrCl_4$. For example, we have observed that the reaction of *bi*-2-naphthol with acetyl chloride in the presence of $AlCl_3$ in nitrobenzene at 25°C for 8 h gave the diester derivative in 95% yield (Scheme 1) instead of the desired diketone**.**

2.2.1 Synthesis of *bi*-2-naphthyl ether

We have observed that the 1,1'-*bi*-2-naphthol can be easily converted to mono and di protected 1,1'-*bi*-2-naphthyl methyl ethers (*R*)-**149** and (*S*)-**150** using K_2CO_3 and CH_3I reagent system in acetone solvent depending on the amount of base used (Scheme 3).

Scheme 3



(*R*) -**149** 98% y (*R*)-**147** (*S*)-**148** (*S*) - **150,** 90% y

The structure of the product **150** was confirmed by X-ray structural analysis (Figure 4).

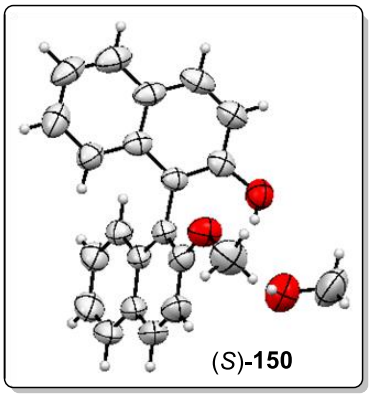
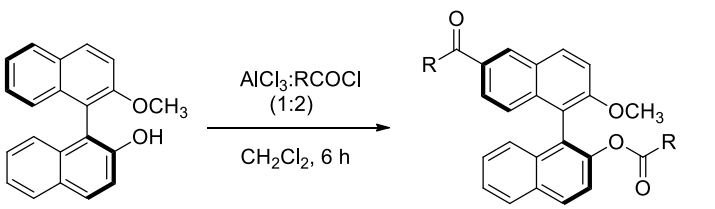


Figure 4. ORTEP representation of the crystal structure **150** (Oak Ridge Thermal Ellipsoids Plot are drawn at 50% probability).

2.2.2 Synthesis of (*S*)-6'acetyl-2'-methoxy-[1,1'-binaphyhalen]-2yl acetate

The monomethoxy-*bi*-2-naphthol (*S*)-**150,** was converted to the 6-acyl and ester derivatives **(*S*)-151** to **(*S*)-154** (Scheme 4).

Scheme 4



(*S*) - **150**

R = -CH_3 (*S*)-**151** 90% y
R = -C_2H_5 (*S*) -**152** 87% y
R = -C_3H_7 (*S*) -**153** 88% y
R = Ph-CH_2 - (*S*)-**154** 86% y

The structure of the product **154** was further confirmed by X-ray structural analysis (Figure 5).

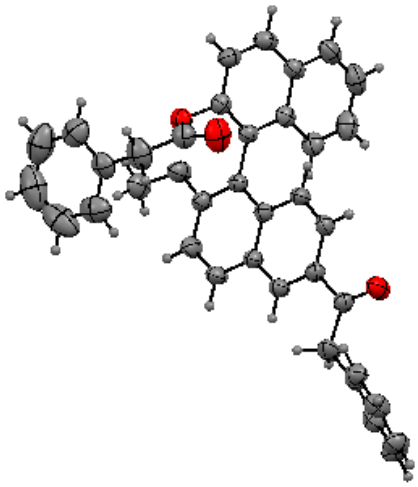
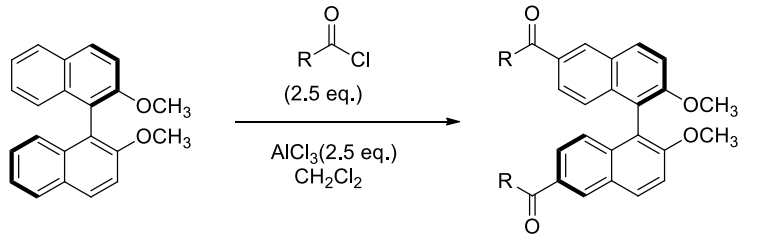


Figure 5. ORTEP representation of the crystal structure (*S*)-**154** (Oak Ridge Thermal Ellipsoids Plot are drawn at (50% probability).

Previously it was reported in this laboratory that FriedalCraft acylation of 2,2'-dimethoxy-1,1'-*bi*-2-naphthalene gave the products (*R*)-**155** to (*R*)-**159** in 60-70% yield (Scheme 5).

Scheme 5

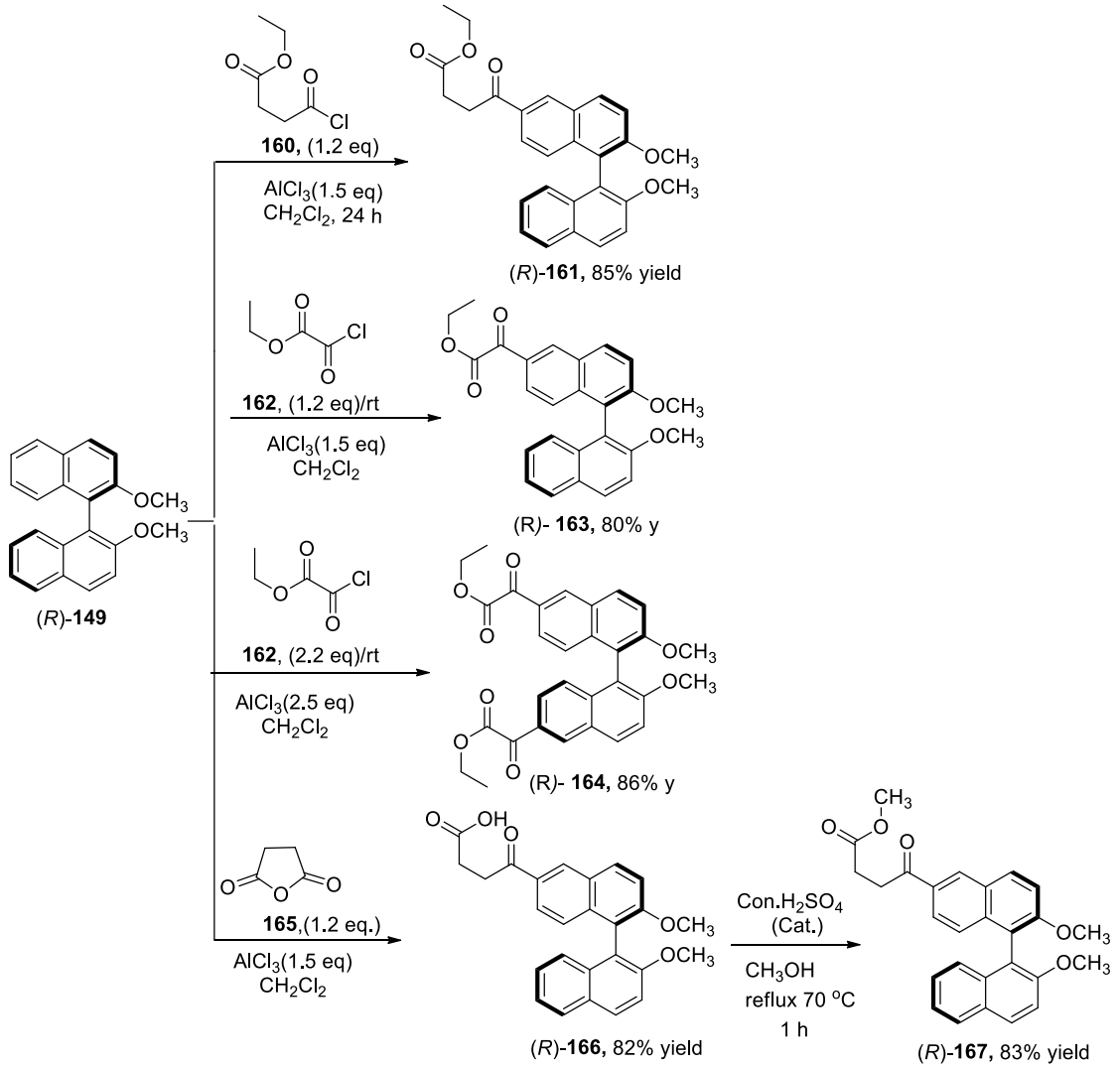


2.2.3 Synthesis of alkyl 4-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4-oxobutanoate

We have then turned our attention towards the reaction of (*R*)-*bi*-2-naphthyldimethyl ether (*R*)-**149** reaction with ethyl-2-chlorooxoacetate and ethyl 4-chloro-4-oxobutanoate in the presence of $AlCl_3$ and gave from (*R*)-**161, (*R*)-163** and **(*R*)-164.** The corresponding product (*R*)-**161** was obtained in 85% yield. Similarly, the reaction using succinic anhydride

resulted in the product (*R*)-**166** in 82% yield which upon reaction with MeOH and conc. H_2SO_4 gave the product (*R*)-**167** in 83% yield (Scheme 6).

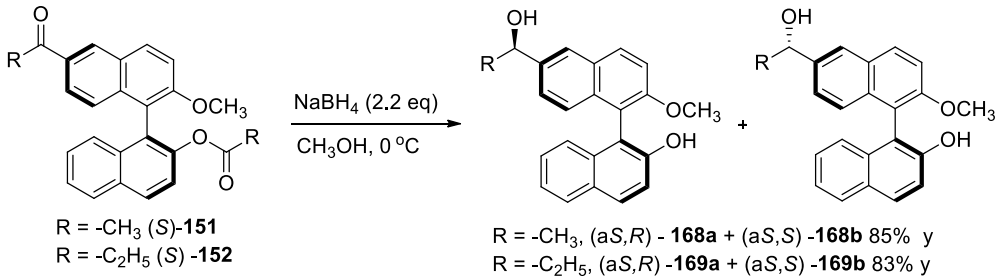
Scheme 6



2.2.4 Synthesis of 6'-(1-hydroxy ethyl)-2'methoxy-[1,1'-binaphthalen]-2-ol

We have observed that reduction of **(*S*)**-6'acetyl-2'-methoxy-[1,1'-binaphyhalen]-2-yl acetate using $NaBH_4$ in methanol solvent gave the products in 83-85% yields respectively in 1:1 ratio without any selectivity (Scheme 7).

Scheme 7



The structure of the product **168a** and **168b** was further confirmed by X-ray analysis (Figure 6)

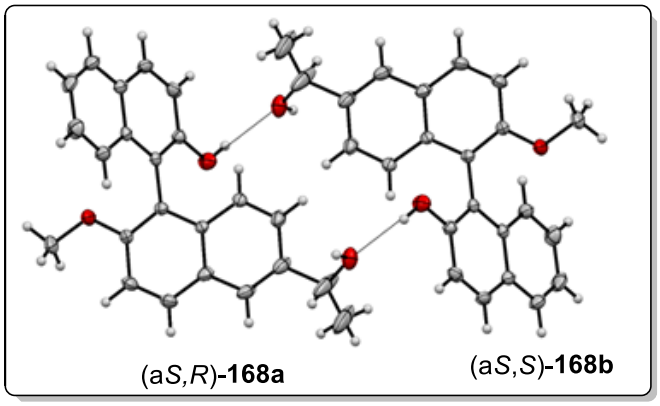
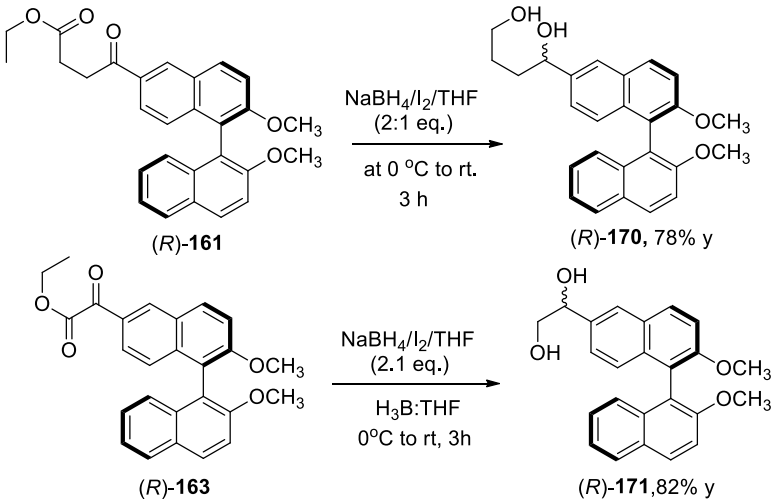


Figure 6. ORTEP representation of the crystal structure **168a** and **168b** (Oak Ridge Thermal Ellipsoids Plot drawn at (50% probability).

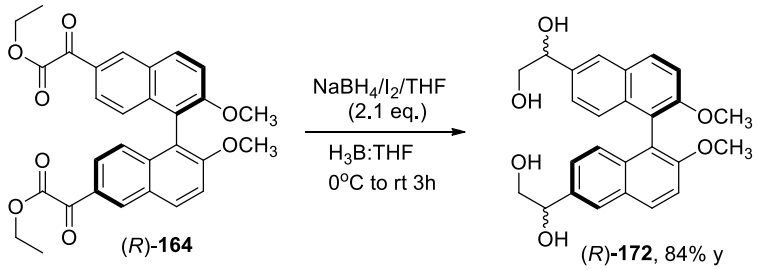
2.2.5 Synthesis for 1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)butane-1,4-diol

The asymmetric induction was also not observed and there was no diastereoselectivity observed in the reduction using I_2/$NaBH_4$ (Scheme 8).

Scheme 8



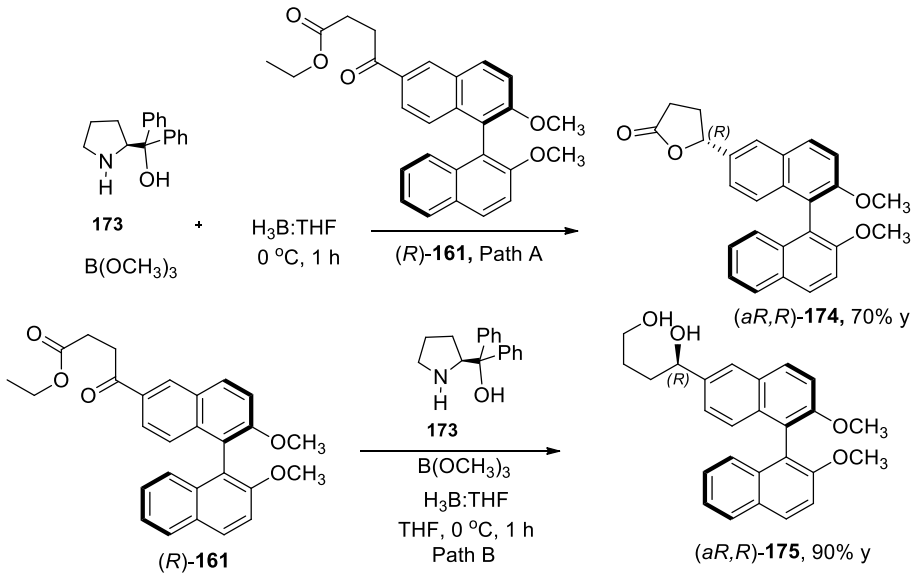
Scheme 8 Cont...



2.2.6 Synthesis of 5-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)dihydrofuran-2(3H)-one

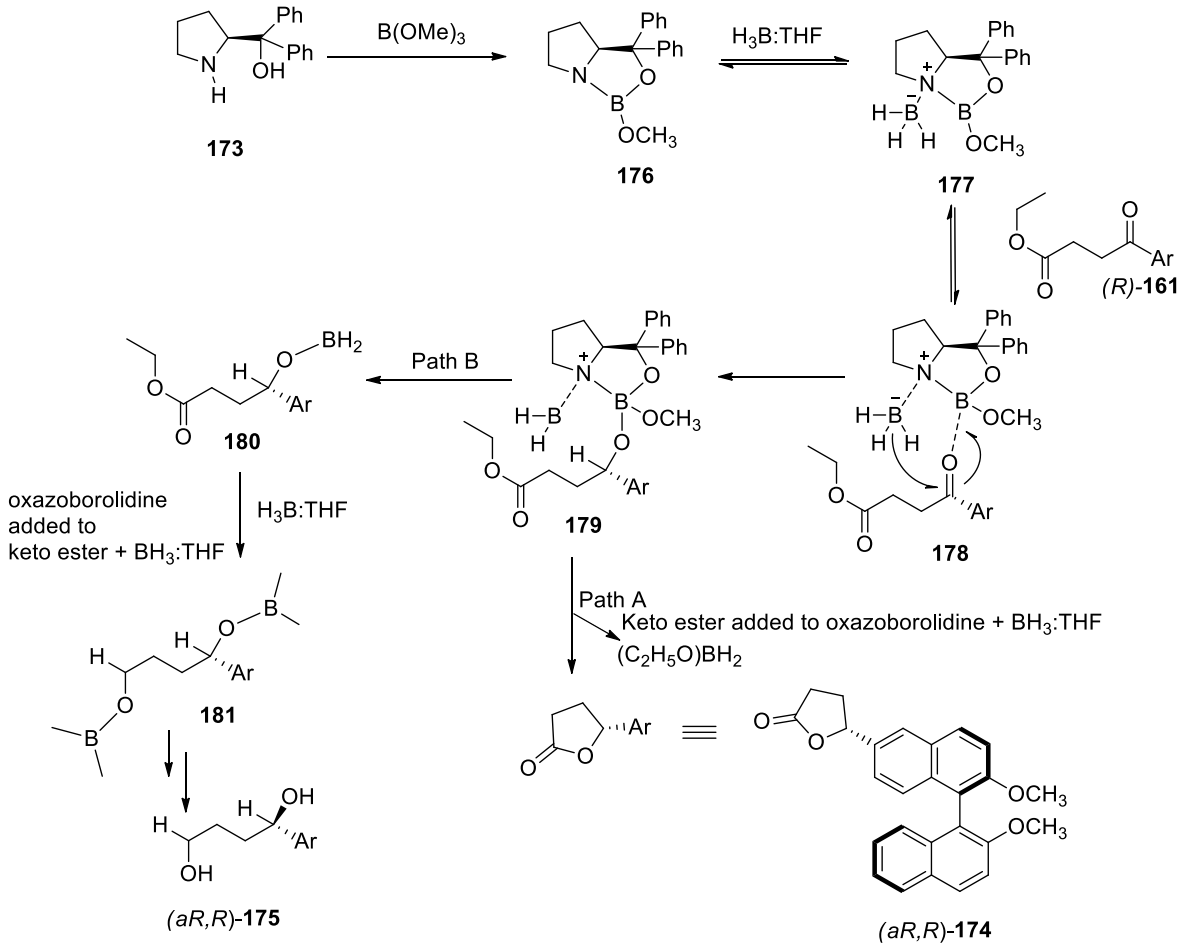
We have then examined the reduction of the product (*R*)-**174** and (*R*)-**175.**[59] We have observed that the chiral α,α-diphenylprolinol *S*-(-)-DPP) reagent **173** in BH_3:THF at 0 ^oC gave the product lactone product (*aR,R*)-**174** or the diol product (*aR,R*)-**175** depending on the procedure followed for the reaction (Scheme 9). Whereas the addition of compound (*R*)-**5** to the α,α-diphenylprolinol *S*-(-)-DPP **173**, $B(OCH_3)_3$, BH_3:THF mixture gave the lactone product 70% yield (Scheme 9, Path A), the addition of the α,α-diphenylprolinol *S*-(-)-DPP **165**, $B(OCH_3)_3$, BH_3:THF mixture to the compound (*aR,R*)-**166** in THF solvent gave the product (*aR,R*)-**167** in 90% yield (Scheme 9, Path B).

Scheme 9



The mechanism outlined in Scheme 10 may be considered to rationalize the formation of the lactone (*aR,R*)-**174** or the 1,4-diol (*aR,R*)-**175** *via* Path A or Path B. When the keto ester derivative **161** is added to the α,α-diphenylprolinol (DPP)-**173**, $B(OCH_3)_3$, BH_3:THF mixture, the keto carbonyl will be reduced faster giving the intermediate in larger quantities leading to the product (*aR,R*)-**174** with concomitant elimination of the $C_2H_5OBH_2$. Whereas, when the keto ester derivative (*aR,R*)-**161** is added to the α,α-diphenylprolinol (DPP)-**173**, $B(OCH_3)_3$, BH_3:THF mixture, the excess of BH_3:THF present may further reduce the ester carbonyl to give the 1,4-diol product (*aR,R*)-**175**.

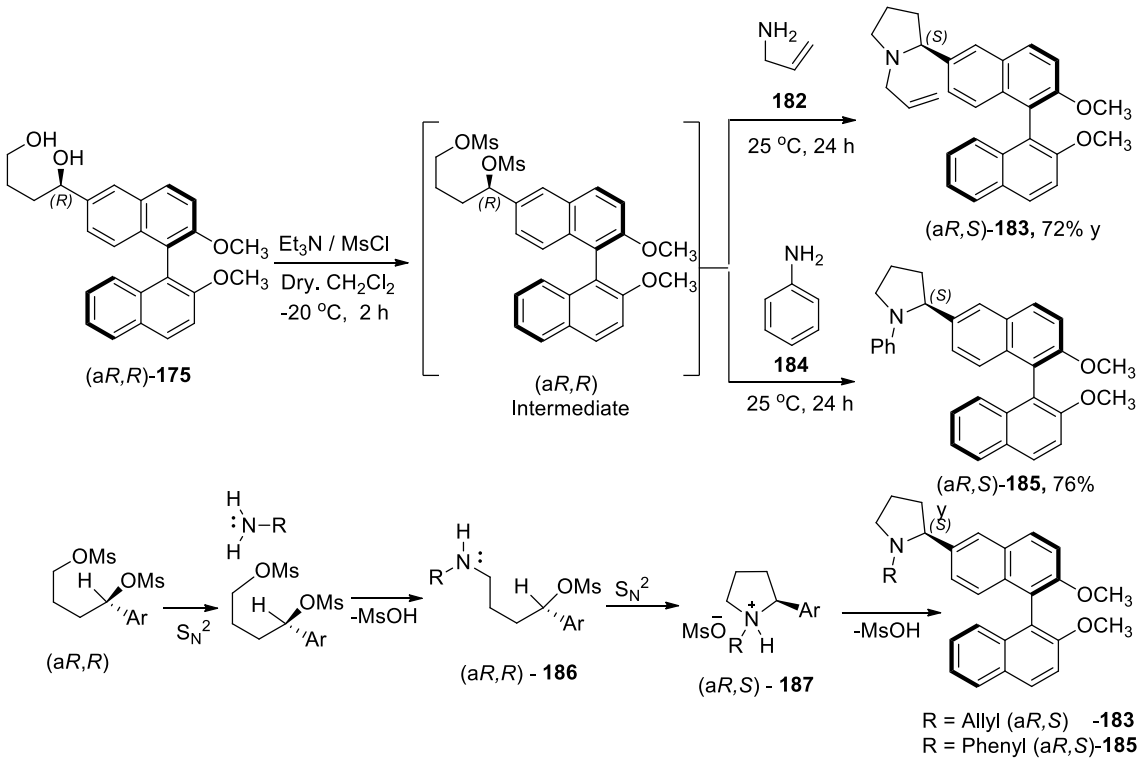
Scheme 10. Plausible mechanism



2.2.7 Methods for synthesis of pyrrolidine and tetrahydrofuran derivatives containing chiral *bi*-2-naphthyl moiety.

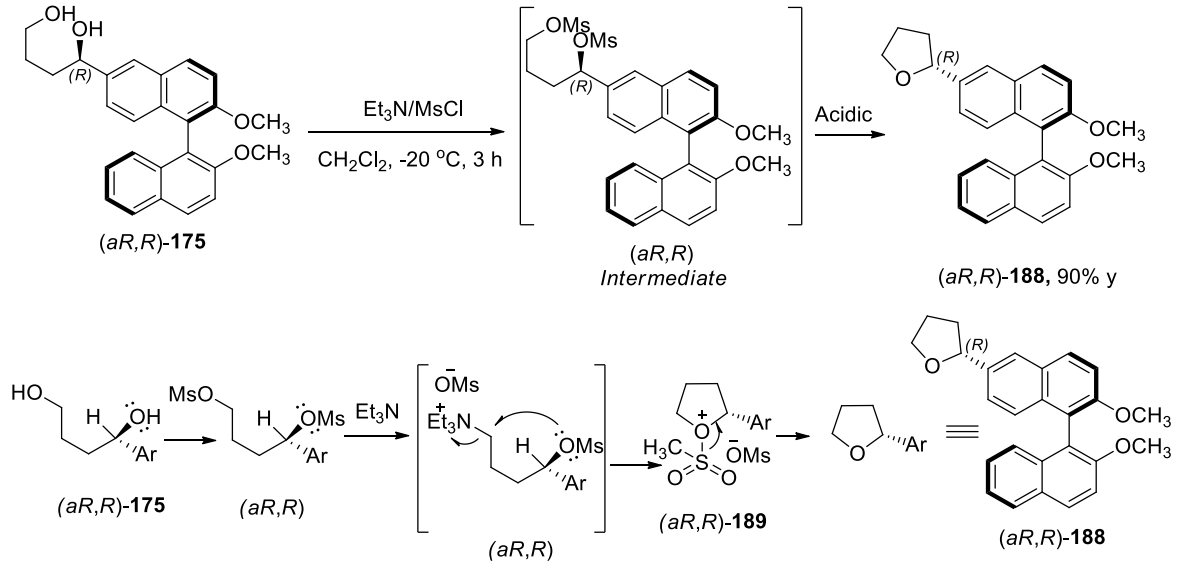
We have next examined the application of the chiral 1,4-diol (*aR,R*)-**175** for the preparation of chiral pyrrolidine derivatives (*aR,S*)-**183** and (*aR,S*)-**185** containing bi-2-naphthyl moiety. Accordingly, allyl amine was added to the dimesylate intermediate (*aR,S*)-**181** generated *in situ* by the reaction with triethylamine and mesyl chloride. In this case, the corresponding *bi*-2-naththyl containing chiral pyrrolidine derivative (*aR,S*)-**183** was obtained in 72% yield (Scheme 11). Similarly, the use of aniline afforded the corresponding *N*-phenyl pyrrolidine derivative (*aR,S*)-**185** in 76% yield under the same conditions (Scheme 11). The configuration at the new pyrrolidine stereogenic centres is expected to be *S* as the initially formed secondary amine intermediate (*aR,S*)-**186** would attack the secondary mesylate in an intramolecular S_N2 type mechanism (Scheme 11).

Scheme 11



Recently, methods were reported for cyclization of 1,4-diols in acidic and basic medium for stereoselective cyclic ethers.[60] We have observed that the dimesylate intermediate prepared in the presence of and Et_3N/MsCl gave the corresponding tetrahydrofuran derivative (*aR,R*)-**186** in 90% yield (Scheme 12). Presumably, the initially formed dimesylate reacts with the triethylamine at the primary mesylate centre to give the product (a*R,R*)-**188** which could then cyclize to give the product (a*R,R*)-**188** *via* the intermediate (a*R,R*)-**189**.

Scheme 12



The newly formed stereogenic center of the tetrahydrofuran derivative (a*R,R*)-**188** was assigned as *R* by single crystal X-ray structure analysis (Figure 7).

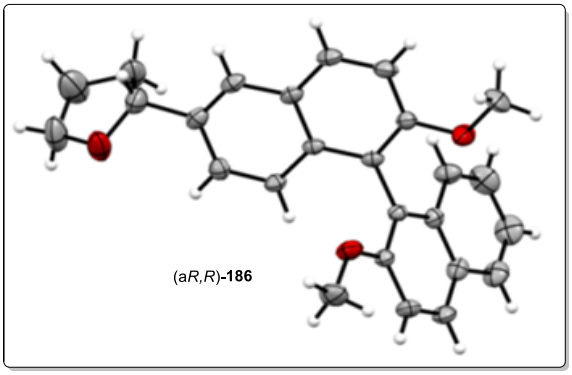
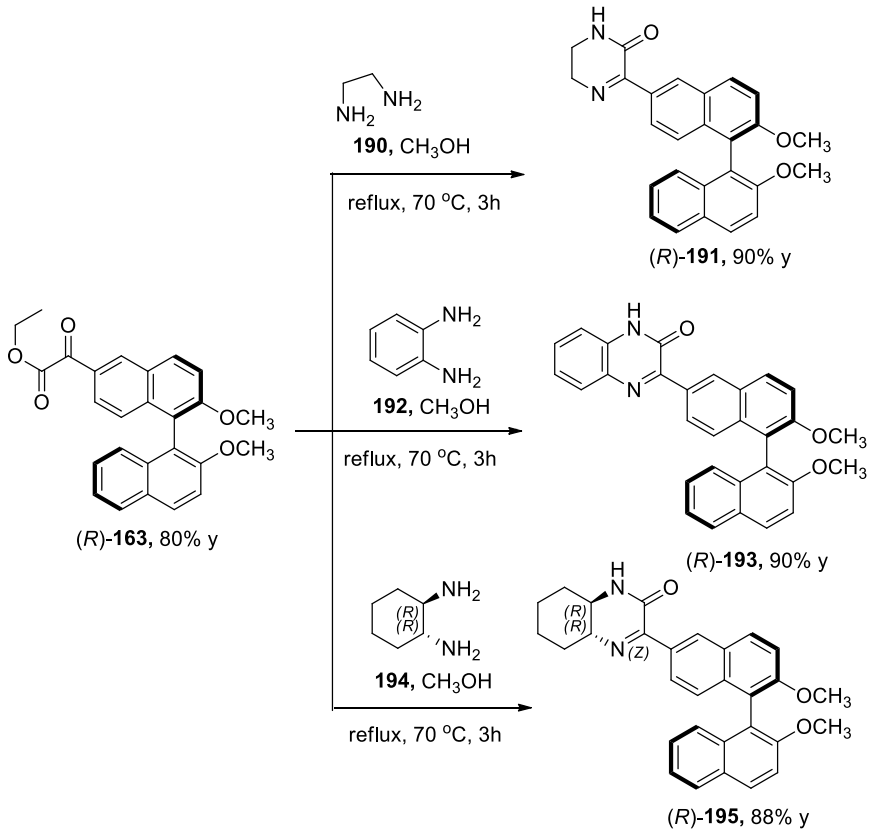


Figure 7 ORTEP representation of the crystal structure (*aR,R*)-**188** (Oak Ridge Thermal Ellipsoids Plot drawn at (with 50% probability).

2.2.8 Methods for synthesis of piperazine derivatives containing chiral *bi*-2-napthyl moiety

We have also described, we report methods for synthesis of piperazine derivatives containing chiral bi-2-napthyl moiety. Initially, the product (*R*)-**163** was prepared in 80% yield by FriedelCraft acylation using *bi*-2-naphthyl derivative (*R*)-**163**, **162** (1.2 eq) and anhydrous $AlCl_3$ (Scheme 13). Subsequent condensation of this keto ester (*R*)-**163** with ethylenediamine **190** in dry CH_3OH gave the product (*R*)-**191** in 90% yield (Scheme 10). We have observed that similar condensation reactions of (*R*)-**163** with 1,2-diaminobenzene (*R*)-**192** and (2*R*,3*R*)-1,2-diaminocyclohexane **194** under reflux conditions furnished cyclic products (*R*)-**193** and (*R*)-**195** in 80% and 90% yields, respectively (Scheme 13).

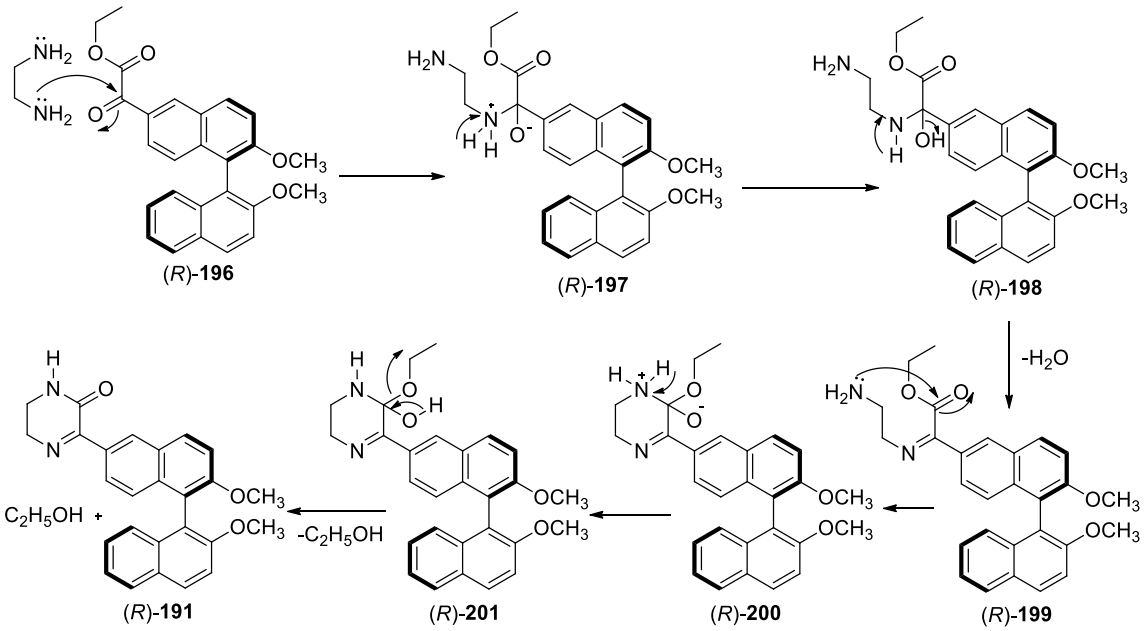
Scheme 13



The mechanism and intermediates shown in Scheme 14 may be considered to rationalize these condensation and cyclization processes. Initial reaction of the more reactive

keto group with the ethylenediamine **190** followed by formation of ketimine and reaction of the amino group with the ester moiety would give the cyclic product (*R*)-**185** (Scheme 14). Similar reactions in the case of the diamines **192** and **194** would give the corresponding condensation products (*R*)-**193** and (*R*)-**195**, respectively.

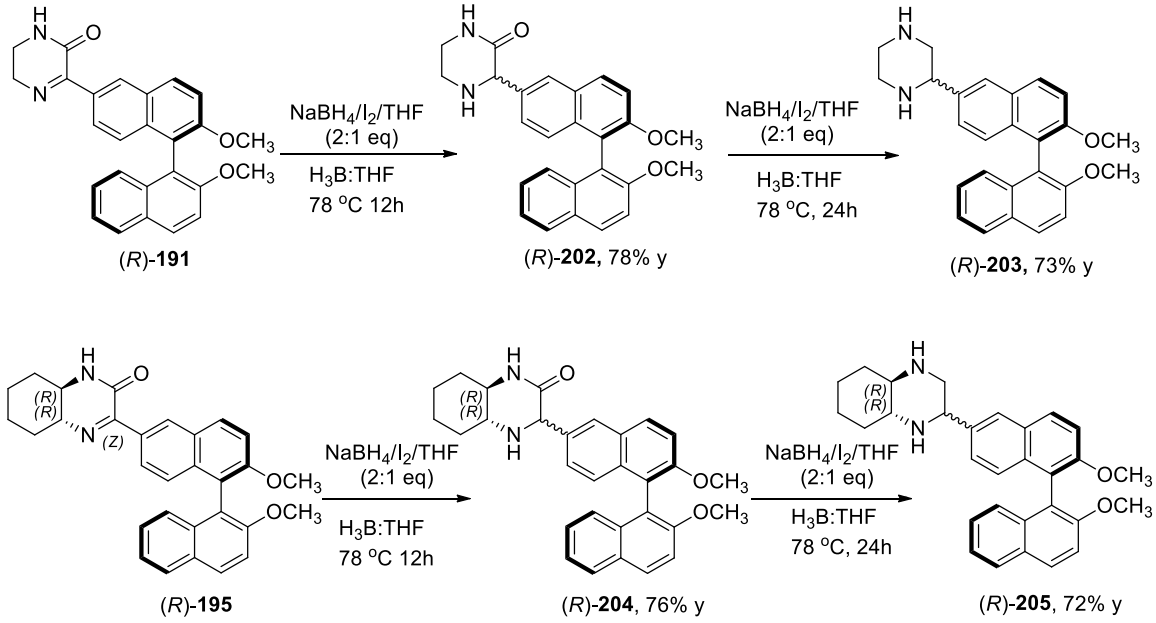
Scheme 14. Plausible mechanism



We have then carried out the reduction of the compound (*R*)-**191** using H_3B:THF prepared *in situ* with the $NaBH_4$ and I_2 reagent combination.[61] We have observed that the reaction at reflux conditions for 12 h gave the product 3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)pyperzin-2-one (*R*)- in 78% yield and further reduction using the $NaBH_4/I_2$ reagent system under reflux conditions for 24 h gave the corresponding piperazine product *R*-**203** in 73% yield (Scheme 15). Unfortunately, the highly sterically hindered (4a*R*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4a,5,6,7,8,8a-hydroquinoxalin-2(1*H*)-one *R*-**193** failed to undergo reduction under the same conditions. However, the (4a*R*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4a,5,6,7,8,8a-hexahydroquinoxalin-2(1*H*)-one (*R*)- gave the corresponding reduction products (4a*R*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)-

octahydroquinoxalin-2(1*H*)-one (*R*)-**203** and (4a*S*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)decahydroquinoxalin (*R*)-**205** in 73% and 72% yields, respectively under the same conditions. Unfortunately, there was no selectivity at the newly formed stereogenic centers in the corresponding piperazine products (*R*)-**203** and (*R*)-**205.** The absence of stereoselectivity in the reduction of piperazenones may be due to remoteness of the atropochiral stereogenic *bi*-2-naphthyl system (Scheme 15).

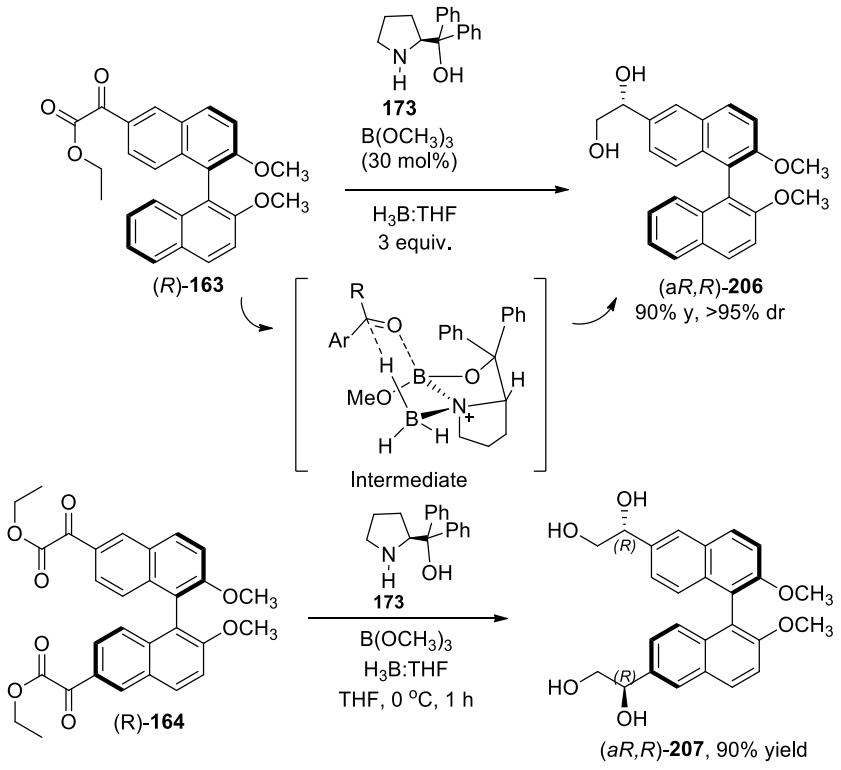
Scheme 15



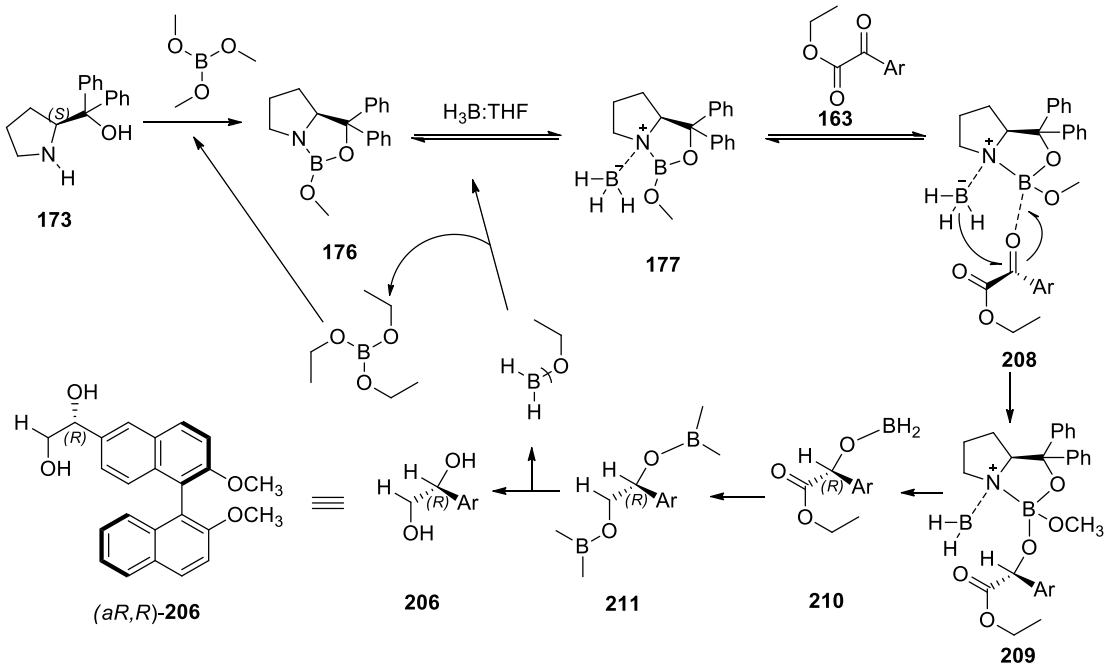
Next, we have turned our attention towards a new protocol involving asymmetric reduction of the carbonyl group in the *bi*-2-naphthyl derivative (*R*)-**163** involving the CBS catalyzed process**.** There have been several reports on the asymmetric reduction of prochiral ketone to corresponding chiral alcohol with 95% ee using (*S*)-DPP and H_3B-Lewis base complexes.[11] In recent years, several borane reagent systems in combination with I_2, benzylchloride and (*S*)-diphenylprolinol (*S*-DPP)-**173** were used in chiral reduction of arylalkyl ketones to obtain the corresponding secondary alcohol with *R* configuration in >95% ee.[12] Also, aryl alkyl ketones containing a chiral biaryl moiety were reduced to the

corresponding secondary alcohols in >95% ee with the S-DPP/$B(OCH_3)_3$-H_3B:THF with *R* configuration at the new stereogenic center.[13a,b] Previously, we have also observed that asymmetric reduction of several 6-acyl derivatives prepared using 2,2'-dimethoxy-1,1'-binaphthalene *(R)*-**149** with the S-DPP/$B(OCH_3)_3$-H_3B:THF reagent combination gave the corresponding alcohols with *R* configuration in >95% ee.[62] Accordingly, we have carried out the asymmetric reduction of the 2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-2-oxoacetate with *S*-DPP (30mol%) and $B(OCH_3)_3$ using H_3B:THF (2 M, 3 equiv.) at 0 ^oC to obtain the corresponding 1,2-diol product (*aR,R*)-**206** in 90% yield, >95% dr. Similarly, *bis*-1,2-diols(*aR,R,R*)-**207** also formed upto 90% yield. In this reaction, alignment of smaller R group with phenyl group in the oxazaborolidine intermediate over the larger bi-2-naphthyl group is expected to result in highly specific transfer of chirality while hydride is transferred to afford the chiral 1,2-diol (*aR,R*)-**206** (Scheme 16).[63]

Scheme 16

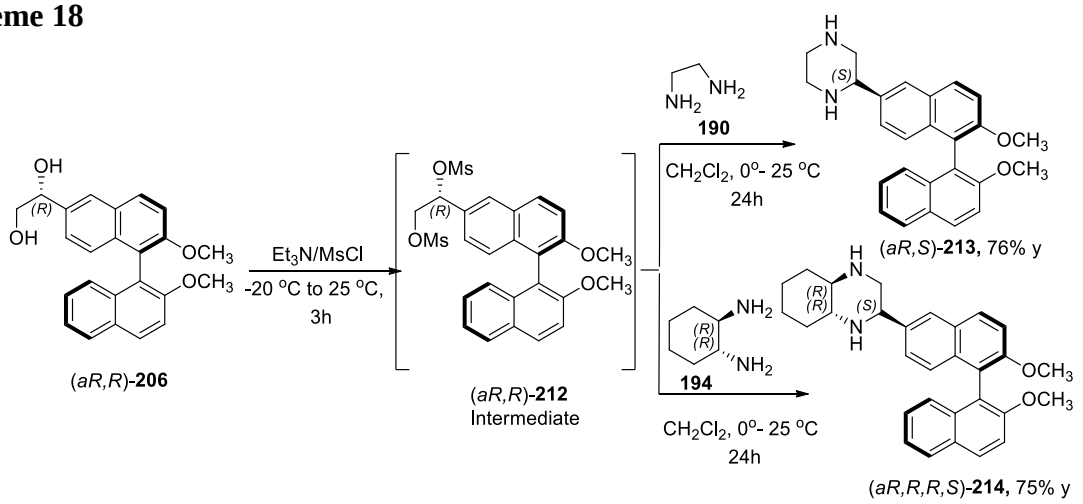


Scheme 17. Plausible mechanism



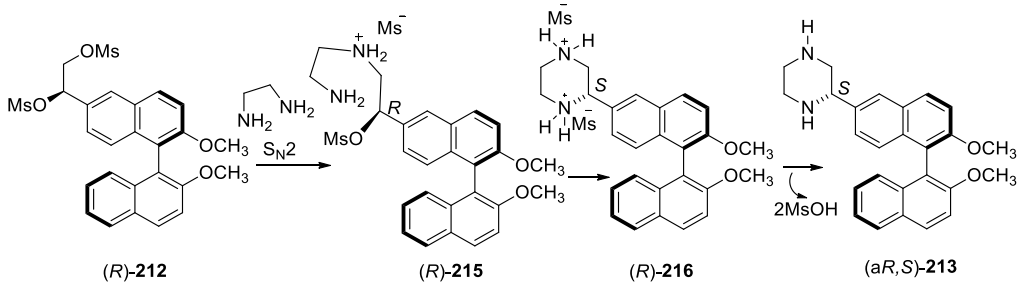
Subsequently, we have carried out the preparation of the dimesylate **208** and its reaction with the diamines **190** and **194** (Scheme 18). Whereas, the **(**2*S*)-2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl) piperazine (a*R*,*S*)-**213** was obtained in 76% yield, the (2*R*,4a*S*,8a*R*)-2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)decahydroquinoxalin (*R*)-**214** was obtained in 75% yield (Scheme 18). In this reaction, the compounds (*R*)-**213** and (*R*)-**214** were obtained in diastereomerically pure forms and other diastereomers were not detected by ^{1}H and ^{13}C NMR spectral data.

Scheme 18



A tentative S_N2 type mechanism may be considered for these transformations as outlined in Scheme 19. Accordingly, the stereochemistry of the new stereogenic centers added in the products **213** and **214** are assigned *S* configuration (Scheme 19).

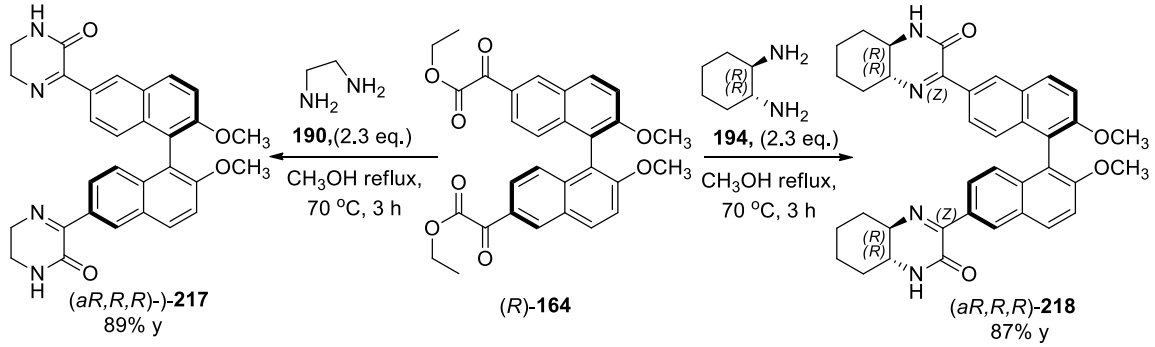
Scheme 19



2.2.9 Synthesis of cyclic–*bis*-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one

The *bis*-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one **217** was readily prepared using amine and dry CH_3OH was added to 2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-2-oxoacetate follow condensation and formed 3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one and gave 90% yield. The subsequent condensation reaction of (*R*)-**164** with same reagent system afford cyclic *bis*-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one in (*R*)-**217** yield 89% and (*aR,R,R*)-**218** with 87 % yields, respectively (Scheme 20).

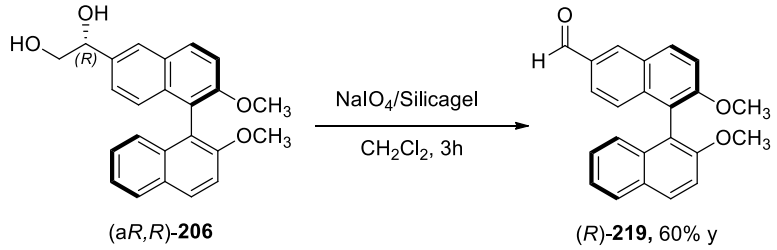
Scheme 20



2.2.10 Reaction of the 1,2 –diol(*aR,R*)-206 with $NaIO_4$

The reaction of 1,2-diol (*aR,R*)-**206** with $NaIO_4$ gave the corresponding aldehyde (*R*)-**219** with 60% yield (Scheme 21).

Scheme 21

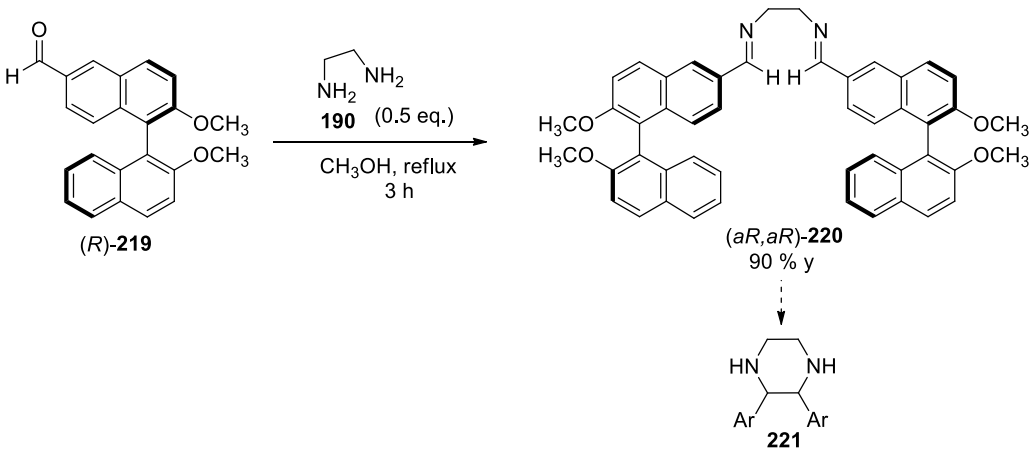


(a*R,R*)-**206** (*R*)-**219,** 60% y

2.2.11 Conversion of the aldehyde derivative (*R*)-219 with ethylenediamine

The aldehyde (*R*)-**219** derivative was readily condensed with diamine **190** to afforded the product in 90% yield (Scheme 22**).**

Scheme 22

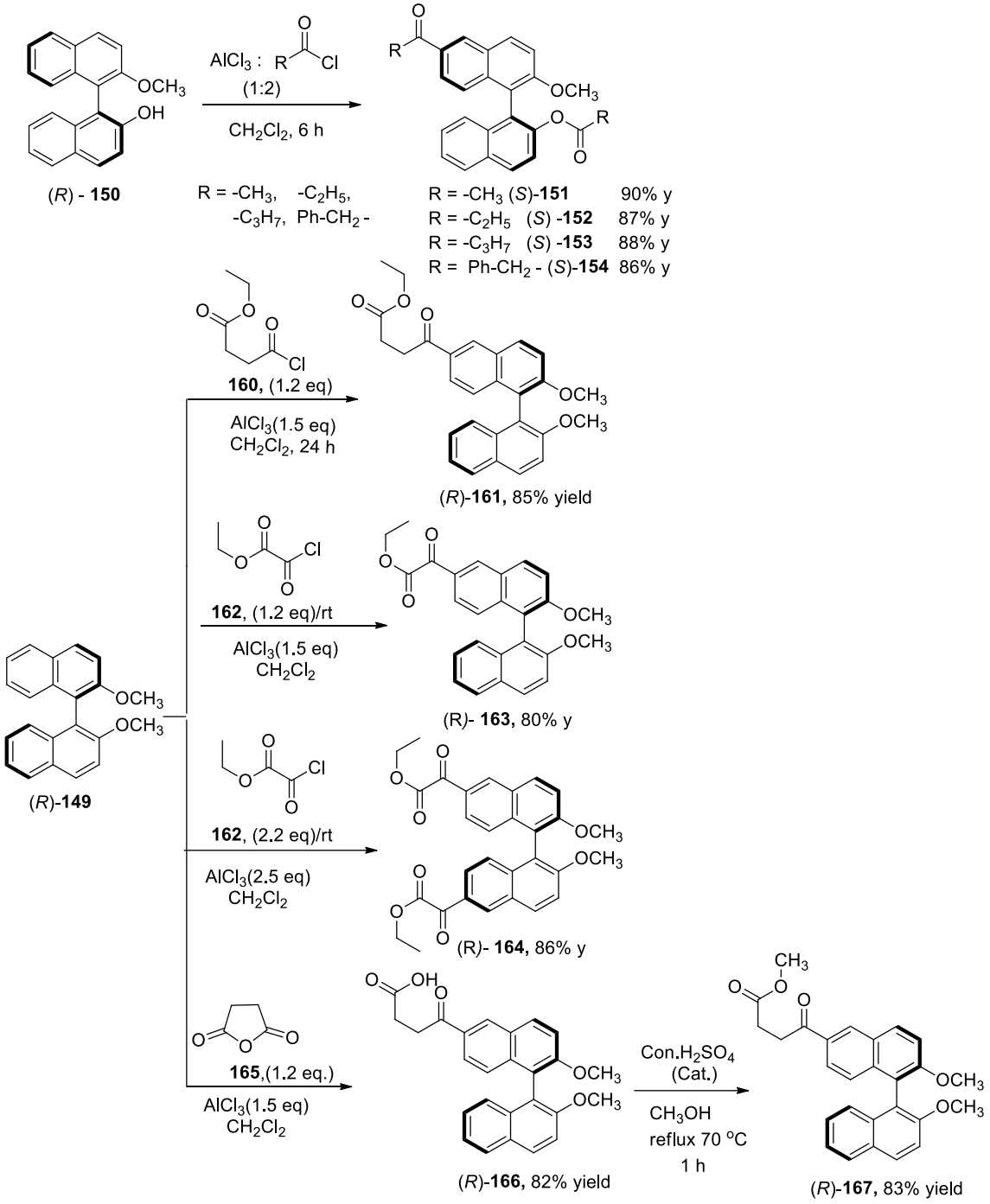


(*R*)-**219** (*aR,aR*)-**220** 90 % y

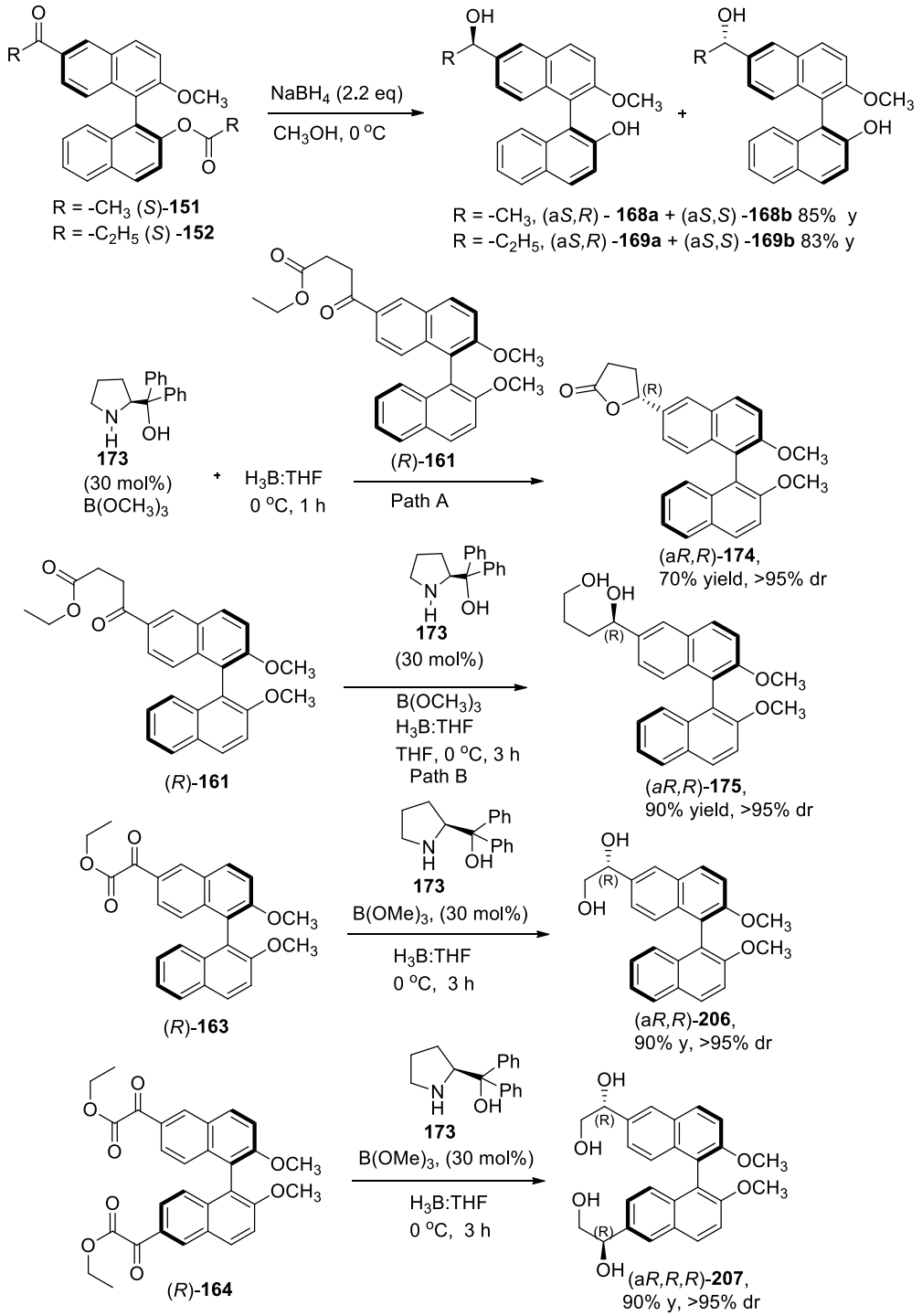
Detailed investigations on intramolecular reductive coupling of the compound (a*R*,a*R*)-**220** may give fruitful results.

2.3. Conclusion

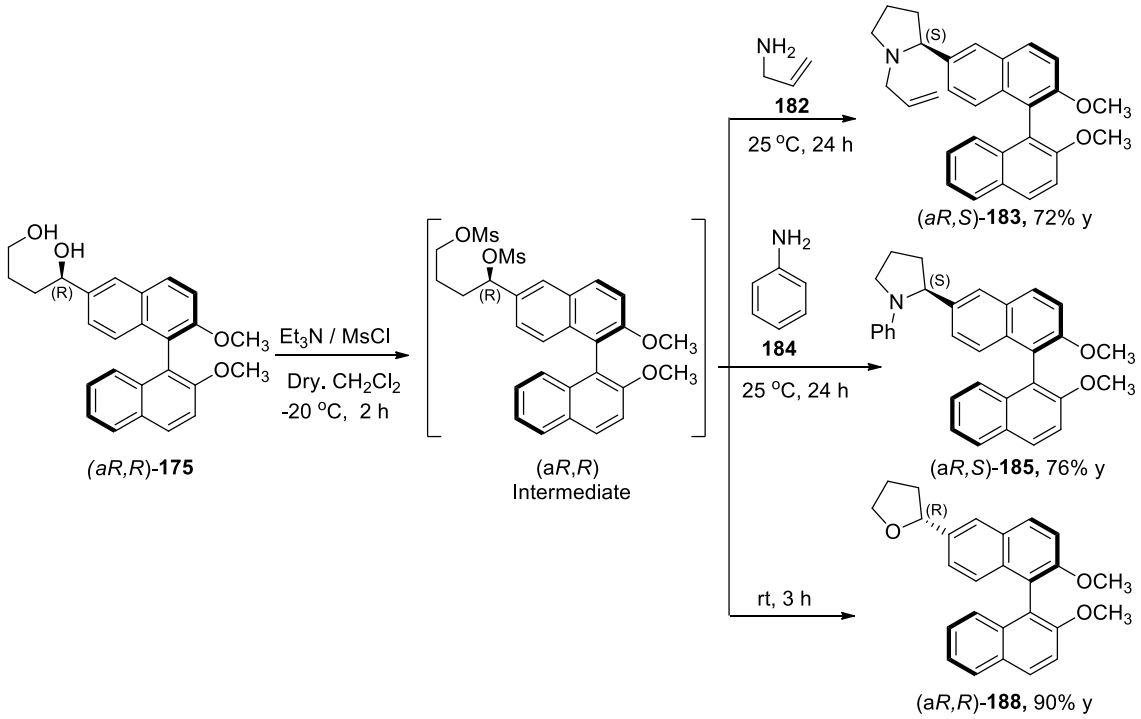
In summary, methods were developed for the synthesis of 6'-acetyl-*bi*-2-naphthylmethoxy acetate using Lewis acids *via* FreidalCraft acylations.



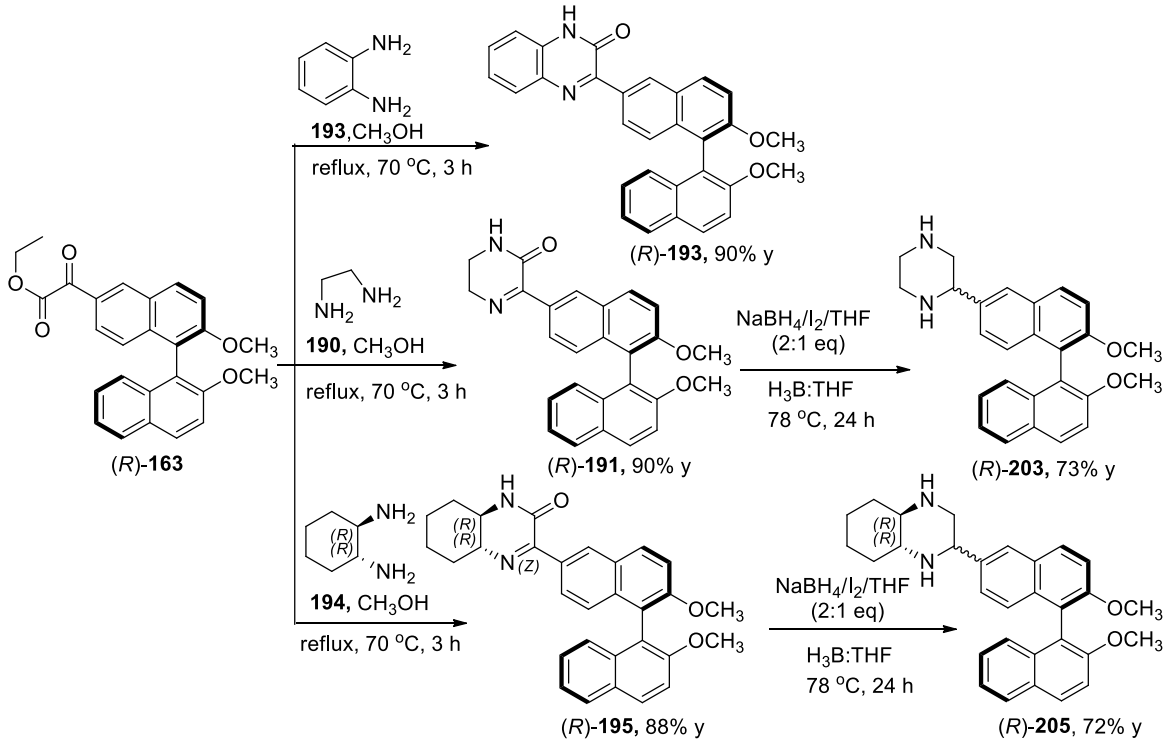
Methods for $NaBH_4$ reduction and asymmetric reduction of carbonyl compounds containing bi-2-naphthyl moiety were developed.

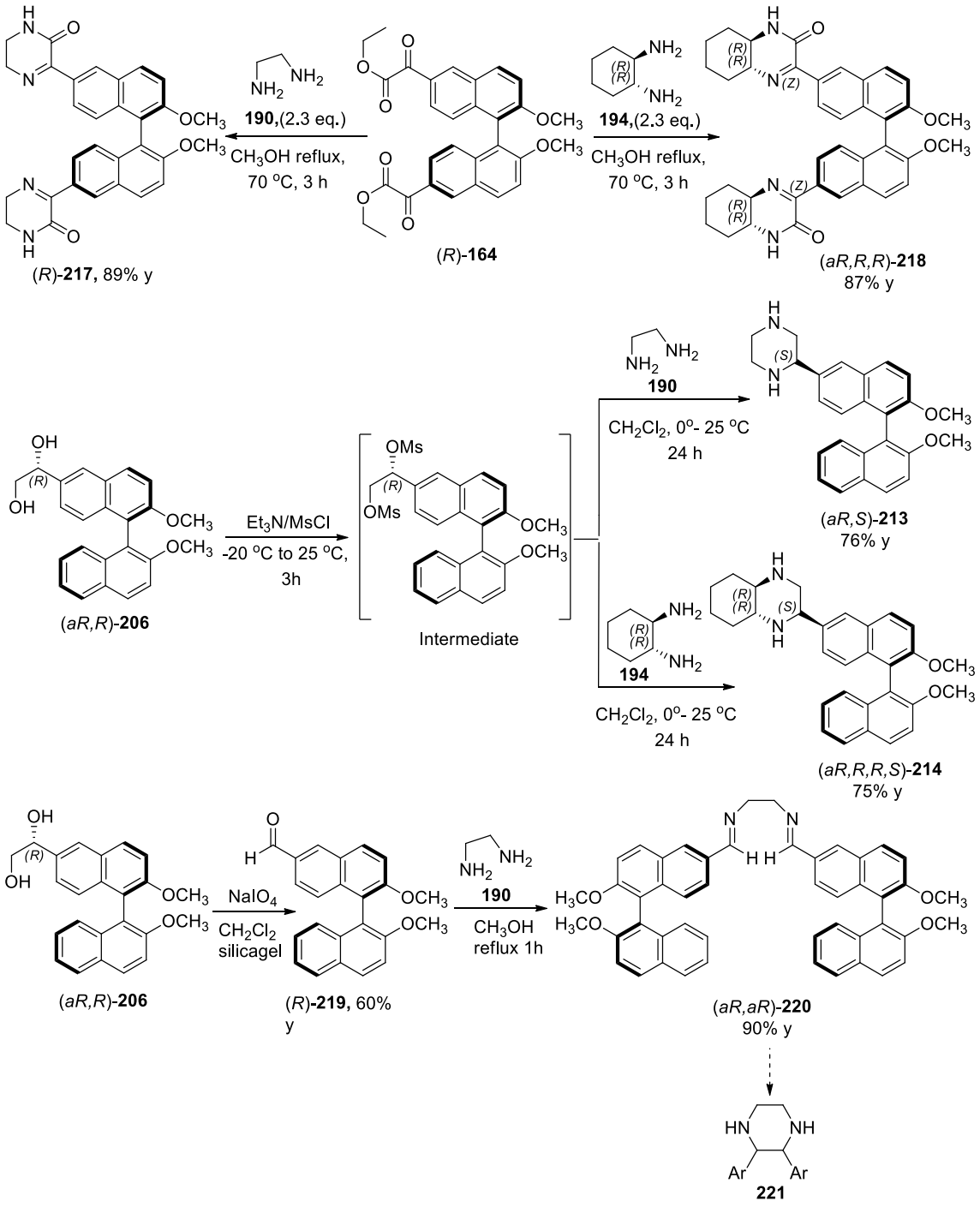


Methods were developed for the preparation of chiral pyrrolidine derivatives (a*R*,*S*)-**183** and (a*R*,*S*)-**184** containing *bi*-2-naphthyl moiety. Also, a method was developed for cyclization of 1,4-diols to prepared cyclic ether (a*R*,*R*)-**188**.



Further efforts were made to synthesize several chiral piperazine derivatives of (a*R*,*S*)-**213** and (*R,R*,a*R,S*)-**214** containing *bi*-2-naphthyl moiety.





These synthetic methods have potential for further exploitation in organic synthesis.

2.4. Experimental Section

General information

Melting points reported in this thesis are uncorrected and were determined using a Super fit capillary point apparatus. IR (KBr) spectra were recorded on JASCO FT-IR Spectrophotometer Model 5300 and the neat IR spectra were recorded on SHIMADZU FT-IR Spectrophotometer Model 8300 with polystyrene as reference. ^{1}H-NMR (400 MHz) and ^{13}CNMR (400 MHz) spectra were recorded on Bruker-Avance-400 spectrometer with chloroform-das solvent and TMS as reference (δ=0 ppm). The chemical shifts are expressed in δ downfield from the signal of internal TMS. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer model-240C and Thermo Finnegan analyzer series Flash EA 1112. Mass spectral analyses were carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Optical rotations were measured in an AUTOPOL-II automatic Polarimeter (readability ± 0.01o). Analytical thin layer chromatographic tests were carried out on glass plates (3x10cm) coated with 250mμ acme's silica gel-G and GF-254 containing 13% calcium sulfate as binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using acme's silica gel (100-200 mesh) or neutral alumina.

All the glassware were pre-dried at 140^{o}C in an air-oven for 4 h, assembled in hot condition and cooled under a stream of dry nitrogen. Unless, otherwise mentioned, all the operations and transfer of reagents were carried out using standard syringe, septum technique recommended for handling air sensitive organometallic compounds. Reagents prepared *in situ* insolvents were transferred using a double-ended stainless steel (Aldrich) needle under a pressure of nitrogen whenever required. In all experiments, a round bottom flask of

appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected by a long tube to the atmosphere.

All dry solvents and reagents (liquids) used were distilled from appropriate drying agents. As a routine practice, all organic extracts were washed with saturated sodium chloride solution (brine) and dried over anhydrous Na_2SO_4 and concentrated on Heidolph-rotary evaporator. All yields reported are of isolated materials judged homogeneous by TLC, IR and NMR spectroscopy. Dichloromethane and chloroform were distilled over CaH_2 and dried over molecular sieves. Methanol and ethanol supplied by Ranbaxy were distilled over CaO_2 before use. Diglyme, toluene, benzene and THF was distilled over sodium-benzophenoneketyl under reduced pressure and freshly distilled before use. Sodium borohydride supplied by E Merck, India. Triethylamine was distilled over CaH_2 and stored over KOH pellets. Methanesulfonyl chloride was supplied by Lobachemie (P) Ltd, India were used after distillation. (*S*)-α,α-diphenylprolinol [(*S*)-DPP] was supplied by Gerchem labs, India, (*S*)-proline supplied by Lancaster Synthesis Ltd., UK were used.

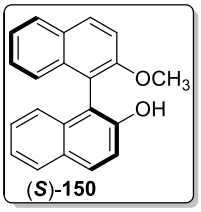
The X-ray diffraction measurements for the compounds were carried out at 298 K on Bruker-Nonius SMART APEX CCD area detector system using graphite monochromated, Mo- Kα (λ = 0.71073 Ao) radiation. Primary unit cell constants were determined with a set of 25 narrow frame scans. Intensity data were collected by the ω scan mode. The data were reduced using SAINT program, without applying absorption correction. The refinement for structure was made by full-matrix least-squares on F^2 (SHELX 97).

2.4.1 Preparation of 2'-(methoxy)-[1,1'-binaphthalene]-2-ol.

A suspension of (+)-(*R*)-1,1¢-*bi*-2-naphthol (4.3 g, 15 mmol) in acetone (50 mL) stirred under N_2 was added K_2CO_3 (2.2 g, 23 mmol) and CH_3I (5 mL, 60 mmol), and the mixture was refluxed at 56 °C for 24 h. The solvent was removed under vacuum and the mixture was diluted with CH_2Cl_2 (30 mL). The organic layer was further washed with H_2O and brine and dried over anhyd Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 90:10) to give (*S*)-**150** as crystalline solid.

2'-(methoxy)-[1,1'-binaphthalene]-2-ol.

Physical State: Solid



(*S*)-150

Color White

Yield 4.0 g (90%)

mp 184-186^{o}C

IR(KBr) 3067, 2934, 2835, 1618, 1589, 1466, 1249, 1089, 895, 810, 746cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):8.0-7.9 (m, 4H), 7.52-.35 (m, 7H), 7.25-7.23 (d, *J* = 8.2 Hz, 1H), 5.2 (s, 1H), 3.8 (s, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):156.1, 151.5, 134.2, 134.0, 131.0, 129.9, 129.5, 129.3, 127.4, 126.6, 125.0, 124.3, 123.4, 117.7, 115.7, 115.2, 113.9, and 56.6 ppm.

MS (EI) *m/z* 300$(M+1)^{+}$

$[\alpha]_D^{25}$ +37.7 (*c* 1.00, $CHCl_3$)

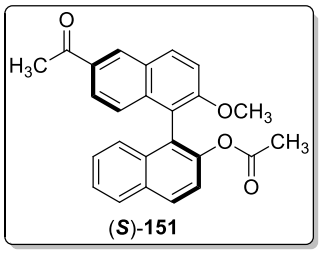
Analytical Data calculated for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37; O, 10.65.

Found C, 83.67; H, 5.21; O, 10.39.

2.4.2 General Procedure for the synthesis of 6-acetyl-*bi*-2-naphthyl acetates using acid chlorides and an.$AlCl_3$.

Anhyd. $AlCl_3$ (2.67 g, 20 mmol) and AcCl (2.0 mL, 20 mmol) were added to CH_2Cl_2 (40 mL) at 25 °C. To this mixture, (*S*)-**150** (3.0 g, 10 mmol) was added, and the mixture was stirred at 25 °C for 3 h. The mixture was poured into ice-cold H_2O and it was shaken with CH_2Cl_2 (30 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic phases were washed with brine (20 mL) and dried (anhyd Na_2SO_4). The solvent was removed and the residue was column chromatographed (silica gel, hexane– EtOAc, 80:20).

6'-acetyl-2'-methoxy-[1,1'-binaphthalene]-2-yl acetate (*S*)-151



(*S*)-**151**

Physical State: Solid

Color Light Yellow

Yield 3.6 g (90%)

mp 194-196 °C

IR (KBr) 3059, 2939, 2841, 1761, 1676, 1616, 1479, 1356, 1194, 810, 760cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.61-8.56 (s, *J* = 2.0 Hz, 1H), 8.16-8.14 (d, *J* = 8.0 Hz, 1H), 8.08-8.05 (d, *J* = 12.0 Hz, 1H), 8.03-8.01 (d, *J* = 8.0 Hz, 1H), 7.97-7.94 (m, 1H), 7.88-7.45 (m, 3H), 7.32-7.22 (m, 2H), 7.19-7.18 (d, *J* = 94.0 Hz, 2H), 3.8 (s, 3H), 2.69 (s, 3H), 1.8 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 197.8, 169.0, 157.1, 146.9, 146.8, 136, 133.4, 133.3, 132.5, 131.5, 130.3, 129.5, 128.3, 127.7, 126.7, 125.8, 124.8, 123.4, 121.9, 117.7, 114.0, 56.5, 26.6, 20.6 ppm.

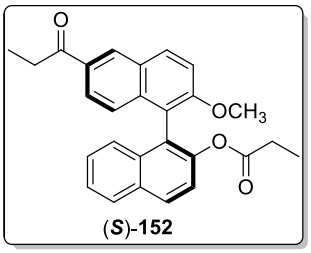
MS (EI) *m/z* 399 $(M+1)^+$

$[\alpha]_D^{25}$ +39.1 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{28}H_{26}O_4$: C, 78.37; H, 5.57; O, 16.06

Found C, 78.25; H, 5.53; O, 16.21

2'methoxy-6'-propionyl-[1,1'-binaphthalen]-2-yl propionate (*S*)-152.



(***S***)-152

Physical State: Solid

Color Light Yellow

Yield 3. 6g (87%)

mp 198-200 ^{o}C

IR (KBr) 2973, 2936, 1748, 1669, 1459, 1350, 1260, 1235, 1051, 912, 805, 756cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$,δ):8.55(s, 1H), 8.15-8.12 (d, *J* = 8.2 Hz, 1H), 8.04-8.01 (d, *J* = 4.8 Hz 1H),7.98-7.96 (d, *J* = 4.2 Hz 1H), 8.82-7.80 (d, *J* = 9.8 Hz 1H),7.51-7.45 (m, 3H), 7.33-7.31 (m, 1H), 7.29-7.19 (m, 1H), 3.81 (s, 3H), 3.13-3.08 (m,2H), 2.10-2.04 (m, 2H), 1.72-1.26 (t, *J* = 8.0 Hz, 3H), 0.69-0.65 (t, *J* = 16.2 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):200, 172.4, 156.9, 146.8, 136, 133.5, 132.2, 131.9, 129.6, 128.2, 127.8, 126.6, 125.8, 124.7, 121.9, 117.8, 113.9, 56.5, 31.7, 27.5, 8.8, 8.4 ppm.

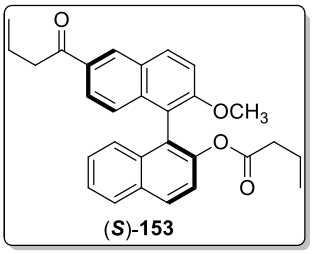
MS (EI) *m/z* 413$(M+1)^{+}$.

$[\alpha]_D^{25}$ +43.8 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{27}H_{24}O_4$: C, 78.62; H, 5.86; O, 15.52

Found C, 78.48; H, 5.66; O, 15.32

6'-butyryl-2'-methoxy -[1,1'-binaphthalen]-2-yl-butyrate (*S*)-153.



(***S***)-153

Physical State: Solid

Color White

Yield 3.88 g (88%):

Mp 198-200 ^{o} C;

IR (KBr): 3381, 3055, 2964, 2870, 1755, 1678, 1614, 1481, 1051, 974, 819, 736cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.6-8.5 (s, 1H), 8.14-8.12 (d, *J* = 8.0 Hz, 1H), 8.04-8.02 (d, *J* = 8.0 Hz, 1H), 7.99-7.97 (d, *J* = 8.0 Hz, 1H), 7.83-7.82 (d, *J* = 8.0 Hz, 1H), 7.82-7.80 (d, *J* = 8.0 Hz, 1H), 7.52-7.4 5 (m, 3H), 7.34-7.32 (t, *J* = 8.0 Hz, 1H), 7.30-7.21 (m, 2H). 3.82 (s, 3H), 3.08-3.04 (t, *J* = 8.0 Hz, 2H), 2.08-2.05 (t, *J* = 8.0 Hz, 2H), 1.87-1.81 (q, *J* = 8.0 Hz, 2H), 1.30-1.15(m, 2H), 1.0-1.04 (t, *J* = 8.0 Hz, 3H), 0.57-0.53 (t, *J* = 8.0 Hz, 3H) ppm.

^{13}C-NMR (100 MHz $CDCl_3$, δ); 200, 171.6, 157, 146.8, 136, 133.5, 132.4, 131.9, 131.8, 129.7, 129.3, 128.2, 127.8, 126.6, 125.8, 125.7, 125.5, 124.8, 124.5, 122, 117, 114, 56.5, 40.5, 35.9, 18.1, 18, 14, 13 ppm.

MS (EI) *m/z*441 $(M+1)^+$.

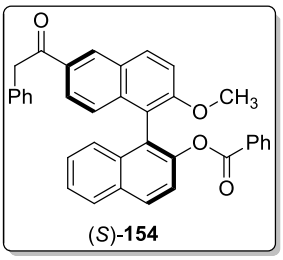
$[\alpha]_D^{25}$ +53.5 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{29}H_{28}O_4$: C, 79.07; H, 6.41; O, 14.53

Found: C, 79.01; H, 6.40; O, 14.12

2'methoxy-6'-(2-phenylacetyl)-[1,1'-binaphthalen]-2-yl 2-phenylacetate (*S*)-154.

Physical State: Solid



(*S*)-**154**

Color Light Yellow

Yield 4.6 g (86%)

mp 182-184^{o}C

IR (KBr) :3030, 2903, 2839, 1746, 1669, 1592, 1479, 1261, 1084, 810, 718, 696cm^{-1}

^{1}H-NMR (400MHz, $CDCl_3$, δ) 8.66-8.64 (t, *J* = 4.2 Hz, 2H), 8.09-8.09 (d, *J* = 14.2 Hz, 2H), 8.05-8.03 (d, *J* = 8.6 Hz, 1H), 8.99-8.97 (d, *J* = 4.6 Hz, 3H), 7.87-7.83 (m, 2H), 7.32-7.30 (m, 4H), 7.49-7.41 (m, 8H), 7.39-7.31 (m, 4H), 7.28-7.20 (m, 2H), 7.18-7.03 (m, 4H), 6.76-6.74 (m, 3H), 4.47(s, 3H),4.47 (s, 3H), 3.72 (s, 2H), 3.69 (s, 3H), 3.4 (s, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):197.3, 169.4, 157.1, 146.8, 136, 134.9, 137.5, 132, 129.5, 128.8, 128.3, 127.7, 126.9, 125.8, 125.1, 124.4, 121.8, 117.4, 114.1, 56.3, 45.5, 41.1ppm.

MS (EI) *m/z* 537$(M+1)^+$.

$[\alpha]_D^{25}$ -48.5 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{37}H_{28}O_4$: C, 82.81; H, 5.26; O, 11.93

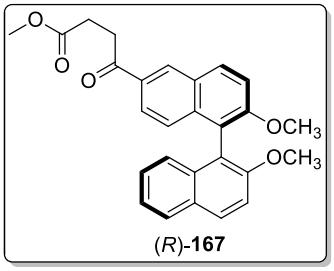
Found C, 82.68; H, 5.21; O, 11.79

2.4.3 Synthesis of (*R*)-methyl 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoate

To a stirred solution of 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoic acid (0.414 g, 1 mmol) in methanol (10 mL) solvent was added catalytic amount of conc. H_2SO_4 (1 drop) and refluxed for 12 h at 65 °C. Methanol was evaporated and the mixture was diluted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (70:30) Hexane/EtOAc mixture to obtain methyl 4-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4-oxobutanoate.

(*R*)-Methyl 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoate (*R*)-167

Physical State: Solid



(*R*)-**167**

Color White

Yield: 0.356 g (83%)

$[\alpha]_D^{25}$ +5.5 (*c* 1.00, $CHCl_3$)

mp 125-127^o C

IR (KBr): 3059, 2930, 285, 1730, 1689, 1616, 1481, 1309, 1251, 804, 746, 468cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.60 (s, 1H), 8.20-8.18 (d, *J* = 6.2 Hz, 1H), 8.15-8.00 (m, 1H), 7.92-7.85 (d, *J* = 8.1 Hz, 1H), 7.79-7.72 (d, *J* = 8.0 Hz, 1H), 7.76-7.48 (d, *J* = 7.8 Hz, 1H), 7.46-7.32 (m, 1H), 7.32-7.23 (m, 1H), 7.23-7.22 (m, 1H), 7.19-7.07 (m, 1H), 3.80-3.77 (m, 6H), 3.75-3.70 (m, 2H), 3.42-3.39 (t, *J* = 6.8 Hz, 2H), 2.86-2.82 (t, *J* = 6.4 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 197.7, 178.9, 155.1, 155.0, 136.6, 134.1, 133.8, 128.1, 126.6, 126.4, 125.8, 125.3, 124.9, 124.2, 123.7, 123.6, 119.6, 118.6, 114.5, 114.2, 114.0, 56.8, 56.7, 56.5, 33.1, 28.2 ppm.

MS (EI) *m/z* 429 $(M+1)^+$.

Analytical Data calculated for $C_{27}H_{24}O_5$: C, 75.68; H, 5.65; O, 18.67:

Found : C, 75.68; H, 5.64; O, 18.65.

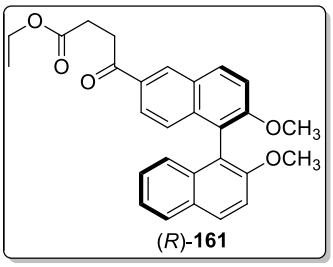
2.4.4 Synthesis of ethyl 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoate

Ethyl 4-chloro-4-oxobutanoate (0.17 mL, 1.2 mmol) and dry anhydrous $AlCl_3$ (0.266g, 2 mmol) added to two necked reaction flask in dry CH_2Cl_2 (5 mL). The (*R*)-2,2'-dimethoxy-1,1'-binaphthalene (0.314 g, 1 mmol) dissolved in dry CH_2Cl_2 (5 mL) was added into the two necked 25 mL round bottom flask. These contents were transferred slowly to the reaction mixture with the help of cannula at room temperature. The reaction mixture was stirred for 24 h at rt and poured into ice cold water. The crude mixture was extracted with CH_2Cl_2 (2X5 mL).The solvent was removed and the residue was chromatographed on a silica gel column using EtOAc mixture to obtain the 4-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4-oxobutanoate.

(*R*)-Ethyl 4-(2, 2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoate(*R*)-161

Physical State: Solid

Color Light Yellow



(*R*)-**161**

Yield 0.359 g (85%);

$[\alpha]_D^{25}$ +3.3 (*c* 0.1, $CHCl_3$);

mp 115-117° C

IR (KBr) 3057, 2932, 2835, 1732, 1686, 1620, 1480, 1250, 1149, 810, 746 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.57 (s, 1H), 8.12-8.10 (d, *J* = 8.8 Hz, 1H), 8.01-7.99 (d, *J* = 8.2 Hz, 1H), 7.89-7.87 (d, *J* = 8.1Hz, 1H), 7.79-7.76 (q, *J* = 6.0 Hz, 1H), 7.53-7.51 (m, 1H), 7.48-7.45 (d, *J* = 12 Hz, 1H), 7.33-7.31 (d, *J* = 6.0 Hz, 1H), 7.26-7.23 (t, *J* = 12.0 Hz,, 1H), 7.17-7.15 (d, *J* = 7.6 Hz, 1H), 7.07-7.05 (d, *J* = 2.8 Hz, 1H), 4.20-4.10 (m, 2H), 3.80 (s, 3H), 3.70 (s, 3H), 3.80-3.7 7 (t, *J* = 6.7 Hz, 2H), 2.814-2.78 (t, *J* = 6.4 Hz, 2H), 1.29-1.25 (t, *J* = 16 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 197.9, 173.1, 157.2, 154.9, 136.5, 133.8, 131.8, 131.4, 130.5, 130.3, 129.8, 129.2, 128.7, 128.4, 128.1, 60.7, 56.7, 56.5, 33.3, 28.4, 14.3 ppm;

MS (EI) *m/z* 443 $(M+1)^+$;

Analytical Data calculated for $C_{28}H_{26}O_5$: C, 76.00; H, 5.92; O, 18.08:

Found : C,76.00; H, 5.91; O, 18.08.

2.4.5 Synthesis of ethyl 2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-2-oxoacetate with ethylchlorooxoacetate with anhydrous $AlCl_3$

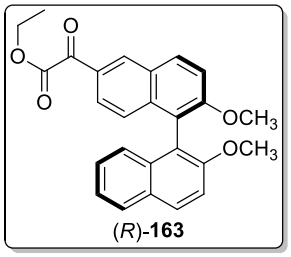
To a mixture of (*R*)-2,2'-dimethoxy-1,1'-binaphthalene (1 mmol) and anhydrous $AlCl_3$ (1.5 mmol), the ethylchlorooxoacetate (1.2 mmol) in dichloromethane (10 mL) was added at

room temperature and stirred for 3h. The reaction mixture was poured into ice-cold H_2O and CH_2Cl_2 (10 mL) was added. The organic layer was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was subjected to column chromatography (silica gel, hexane– EtOAc, 80:20)

Ethyl 2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-2-oxoacetate (*R*)-163

Physical State: Solid

Color Yellow



(*R*)-**163**

Yield 0.332 g (80%)

mp 92-94 ºC

$[\alpha]_D^{25}$ +6.15 (*c* 0.052, $CHCl_3$)

IR(KBr) 3055, 2937, 2839, 1732, 1676, 1614, 1479, 1265, 1045, 910, 808 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.61 (s, 1H), 8.60-8.14 (d, *J* = 4.0 Hz, 1H), 8.12-8.02 (d, *J* = 8.0 Hz, 1H), 8.0-7.90 (d, *J* = 4.0 Hz, 1H), 7.88-7.78 (d, *J* = 94.4 Hz, 1H), 7.78-7.76 (d, *J* = 8.0 Hz, 1H), 7.76-7.76 (d, *J* = 8.3 Hz, 1H), 7.55-7.53 (d, *J* = 8.6 Hz, 1H), 7.48-7.45 (d, *J* = 8.4 Hz, 1H), 7.34-7.23 (m, 2H), 7.06-7.06 (d, *J* = 8.0 Hz, 1H), 4.51-4.41 (q, *J* = 4.0 Hz, 2H), 3.80 (s, 3H), 3.70 (s, 3H), 1.52-1.43 (t, *J* = 8.0 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 186.4, 164.5, 158.3, 155.1, 137.5, 134.3, 133.9, 132.2, 130.1, 129.3, 128.3, 127.9, 127.8, 126.8, 126.4, 124.8, 124.5, 123.8, 119.9, 118.2, 114.7, 113.9, 62.4, 56.4, 56.2, and 14.2 ppm.

MS (EI), *m/z* 415 $(M+1)^+$

Analytical Data calculated for $C_{26}H_{22}O_5$: C, 75.35; H, 5.35; O, 19.30.

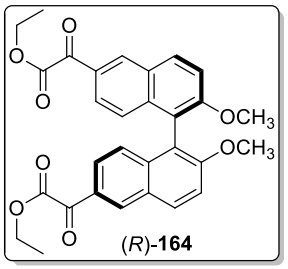
Found : C, 75.25; H, 5.20; O, 19.28.

2.4.6 Synthesis of ethyl 2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-2-oxoacetate

Anhyd $AlCl_3$ (2.66 g, 20 mmol) and ethylchlorooxoacetate (3.0 mL, 20 mmol) were added to CH_2Cl_2 (30 mL) at 25 °C. To this mixture, (*R*)-2,2'-dimethoxy-1,1'-binaphthalene (3.14 g, 10 mmol) was added, and the mixture was stirred at 25 °C for 3 h. The mixture was poured into ice-cold H_2O and it was shaken with CH_2Cl_2 (25 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL) and the combined organic phases were washed with brine (10 mL) and dried (anhyd Na_2SO_4). The solvent was removed and the residue was column chromatographed (silica gel, hexane– EtOAc, 70:30)

2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-2-oxoacetate (*R*)-164

Physical State: Solid



(*R*)-**164**

Color Yellow

Yield 1.79 g (86%)

mp 122-124 °C

$[\alpha]_D^{25}$ +11.7 (*c* 1.0, $CHCl_3$)

IR (KBr) 3055, 2937, 2839, 1732, 1676, 1614, 1479, 1265, 1045, 910,808, 742 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.61(s, 2H), 8.171-8.148(d, *J* = 12.0 Hz, 2H), 7.803-7.99(d, *J* = 16 Hz, 1H), 7.781-7.777(d, *J* = 2.4 Hz, 1H), 7.558-7.533(d, *J* = 2.0 Hz, 2H), 7.144-7.121(d, *J* = 12.0 Hz, 2H), 4.518-4.464(q, *J* = 16.0 Hz, 4H), 3.82(s, 6H), 1.464-1.432(t, *J* = 8.0 Hz, 6H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 186, 164.1, 158, 137, 134.1, 132.4, 127.75, 127.72, 125.7, 124.6, 118.5, 114.4, 62.3, 56.4 ppm.

MS (EI) *m/z* 515 $(M+1)^+$.

Analytical Data calculated for $C_{30}H_{26}O_8$: C, 70.03; H, 5.09; O, 24.88

Found C, 70.02; H, 5.06; O, 24.18

2.4.7 Synthesis of 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoic acid

A mixture of crushed succinic anhydride (0.120 g, 1.2 mmol), 2,2'-dimethoxy-1, 1'-binaphthalene (0.314 g, 1 mmol) and dry CH_2Cl_2 (5 mL) was placed in 10 mL round bottom flask. The contents were stirred for 1 h and dry anhydrous $AlCl_3$ (0.266 g, 2 mmol) was added slowly through a solid additional funnel. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was poured into ice cold water and the crude mixture was extracted with CH_2Cl_2 (2X5 mL). The solvent was removed and the residue was chromatographed on a silica gel column using EtOAc mixture to obtain the 4-(2, 2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4-oxobutanoic acid.

4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoic acid (*R*)-166.

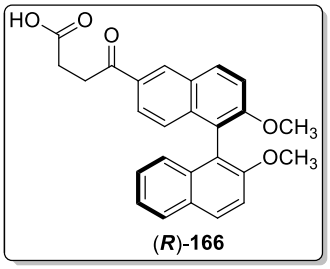
Physical State: Solid

Color White

Yield 0.339 g (82%)

$[\alpha]_D^{25}$ -13.3 (*c* 0.2, $CHCl_3$)

mp 208-210^o C



(*R*)-166

IR (KBr) 3472, 2934, 2843, 1712, 1676, 1614, 1479, 1346, 1249, 1062, 910, 804cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):8.60-8.57 (t, J = 5.2 Hz, 1H), 8.12-8.10 (d, *J* =8.0 Hz, 1H),8.02-7.99 (d, *J* = 8.1 Hz, 1H), 7.93-7.88 (d, *J* = 8.1 Hz, 1H), 7.86-7.80 (d, *J* = 7.8 Hz, 1H), 7.52-7.37 (m, 2H), 7.35-7.32 (t, J = 8.2 Hz, 1H), 7.29-7.20 (m, 3H), 7.19-7.10 (m , 1H), 3.83-3.79 (m, 6H), 3.75-3.38 (q, J = 6.4Hz, 2H), 2.88-2.83 (q, J = 6.2Hz, 2H) ppm.

^{13}C-NMR (400 MHz, $CDCl_3$, δ): 197.7, 178.9, 157.2, 154.9, 136.6, 133.8, 131.6, 131.5, 130.3, 129.8, 129.2, 128.1, 128.0, 126.5, 125.8, 124.9, 124.2, 123.6, 119.6, 118.6, 114.5, 114.0, 56.7, 56.5, 33.1, 28.2 ppm.

MS (EI) *m/z* 415 $(M+1)^+$.

Analytical Data calculated for $C_{26}H_{22}O_5$: C, 75.35; H, 5.35; O, 19.30:

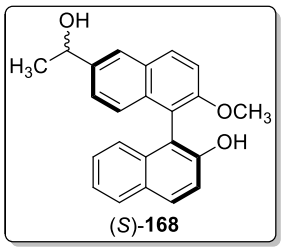
Found : C, 75.35; H, 5.35; O, 19.31.

2.4.8 Reduction of 6'-acetyl-2'-methoxy-[1,1'-binaphthalen]-2-yl acetate using $NaBH_4$ system

To a stirred solution of 6-acyl 1,1'–bi-2-naphthylmethylethers (1.78 g, 5 mmol) dissolved in dry methanol (20 mL) and above suspension was added with help of solid additional funnel $NaBH_4$ (0.29 g, 7.5 mmol) suspension at 0 °C during 1 h. The reaction mixture was further stirred at 25 °C for 3h. The reaction was carefully hydrolyzed with 2N HCl (5 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic extract was washed with brine (25 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified on silica gel (60-120 mesh). The solvent mixture pure ethyl acetate elutes the diastereomeric excessed chiral 6'-(1-hydroxyethyl)-2'-methoxy-[1,1'-bi-2-naphthalen]-ol.

6'-acetyl-2'-methoxy-[1,1'-binaphthalen]-2-yl acetate using $NaBH_4$ system (*S*)-168

Physical State: Solid



(*S*)-**168**

Color White

Yield 1.55 g (90%)

mp 162-164° C

IR (KBr) 3246, 2934, 1618, 1591, 1354, 1267, 1062, 1022, 754, 677cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.07-8.05 (d, *J* = 12.0 Hz, 1H), 7.99-7.94 (d, *J* = 2.0 Hz, 1H), 7.92-7.98(d, *J* = 9.2 Hz, 1H), 7.52-7.49 (d, *J* = 12.0 Hz, 1H), 7.42-

7.40 (d, *J* = 68.0 Hz, 1H), 7.39-7.18 (m, 5H), 7.07-7.05 (d, *J* = 8.0 Hz, 1H), 5.05-5.01 (q, *J* = 2.4 Hz, 1H), 4.97 (ss, 1H), 1.57-1.56 (d, *J* = 4.0 Hz, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm):156, 151.2, 141.4, 133.5, 131, 129.8, 129.2, 128.1, 126.4, 125.4, 124.7, 123.2, 117.4, 115.3, 114, 70.3, 56.7, 25 ppm

MS (EI) *m/z* 345 $(M+1)^+$.

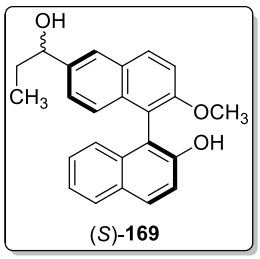
$[\alpha]_D^{25}$ -47.1 (*c* 1.0, $CHCl_3$)

Analytical Data calculated for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85; O, 13.94

Found C, 80.15; H, 5.53; O, 13.71

6'-(1-hydroxypropyl)-2'-methoxy-[1, 1'binaphthalene]-2-ol (*S*)-169

Physical State: Solid



(*S*)-**169**

Color White

Yield 1.6 g (90%)

mp 172-174°C

IR (KBr) 3322, 2961, 2931, 2836, 1594, 1480, 1249, 1090, 1039, 887, 823, 803cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):8.028-8.021 (d, *J* = 14.2 Hz, 1H), 8.01-8.00 (d, *J* = 4.4 Hz, 1H),7.937-7.90 (d, *J* = 8.2 Hz, 1H), 7.88-7.83 (d, *J* = 14.3 Hz, 1H),7.47-7.46 (d, *J* = 4.4 Hz, 1H),7.38-7.36 (d, *J* = 8.2 Hz, 1H),7.35-7.32 (m, 2H), 7.27-7.20 (m, 1H),7.19-7.07 (d, *J* = 8.2 Hz, 1H), 4.68-4.66 (q, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 1.86-1.078 (m, 2H), 0.95-0.92 (m, 3H) ppm .

^{13}C-NMR (100 MHz, $CDCl_3$, δ):155.9, 151.3, 140.2, 133.8, 133.6, 129.8, 129.2, 128.1, 126.4, 125.7, 125.3, 125, 124.9, 124.8, 123.2, 117.6, 115.6, 115, 75.9, 56.7, 31.6, 10.2 ppm.

MS (EI) *m/z* 359$(M+1)^+$.

$[\alpha]_D^{25}$ -65.7 (*c* 1.0, $CHCl_3$)

Analytical Data calculated for $C_{24}H_{20}O_4$: C, 80.42; H, 6.19; O, 13.39

Found C, 80.31; H, 6.12; O, 13.33

2.4.9 Synthesis of (*R*)-5-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-dihydrofuran-2(3H)-one

To a stirred solution (*S*)-(-)-DPP (0.380 g, 1.5 mmol) in THF (3mL) at 25 °C, trimethoxy borate (0.18 mL, 1.5 mmol) was added and stirred for 1 h. To this mixture H_3B:THF (10 mmol, 10 mL, 1 M) was added at 0 °C. The ethyl 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoate (0.442 g, 1 mmol) dissolved in THF (3 mL) and added to the reaction mixture. The reaction mixture was stirred for 1 h at 0 °C to room temperature. The 2 N HCl (1 mL) was added to reaction mixture and the organic layer was separated. The organic extract was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified on silica gel (100-200 mesh) to obtain the product.

5-(2, 2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-dihydrofuran-2(3H)-one (*aR,R*)-174

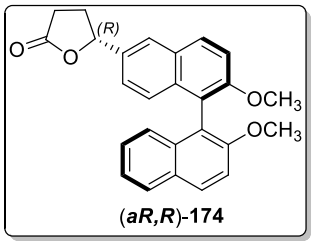
Physical State: Solid

Color White

Yield 0.279 g (70%)

$[\alpha]_D^{25}$ +5.8 (*c* 0.1, $CHCl_3$)

mp 110-114^o C



(*aR,R*)-174

IR (KBr): 3002, 2936, 2832, 1769, 1621, 1589, 1501, 1260, 1068, 915, 816, 756cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.12-7.99 (m, 2H), 7.98-7.84 (m, 2H), 7.50-7.45 (m, 2H), 7.34-7.30 (t, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.15-7.09 (m, 3H), 5.63 (s, 1H), 3.77 (s, 6H), 2.67-2.66 (q, *J* = 6.8 Hz, 2H), 1.57 (s, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 177.3, 155.5, 155.0, 134.2, 133.9, 129.7, 128.7, 128.1, 126.2, 125.7, 124.8, 123.7, 119.5, 114.1, 81.6, 56.7, 33.7, 30.6, 29.0 ppm.

MS (EI) *m/z* 399 $(M+1)^+$.

Analytical Data calculated for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57; O, 16.06:

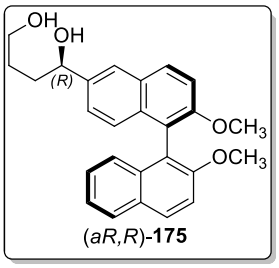
Found : C, 78.25; H, 5.53; O, 16.21.

2.4.10 Synthesis of 1(*R*)-1-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)butane-1,4-diol

To a stirred solution of ethyl 4-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-4-oxobutanoate (0.442 g, 1 mmol) in THF (3 mL), (*S*)-(-)-DPP (0.380 g, 1.5 mmol), trimethoxy borate (0.18 mL, 1.5 mmol) was added at 0 °C. To this mixture, H_3B:THF (1 mmol, 10 mL, 1 M) was added and stirred for 1 h at 0 °C and brought to room temperature. Then 2 N HCl (1 mL) was added and the organic layer was separated. The organic extract was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified on silica gel (100-200 mesh) to obtain the product.

1-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)butane-1,4-diol (*aR,R*)-175

Physical State: Solid



(*aR,R*)-**175**

Color White

Yield 0.362 g (90%)

$[\alpha]_D^{25}$ +28.4 (*c* 0.1, $CHCl_3$)

mp 174-176° C

IR (KBr): 3400, 2934, 2830, 1628, 1598, 1502, 1468, 1260, 1064, 895, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.98-7.93 (m, 2H), 7.88-7.86 (d, *J* = 8.0Hz, 1H), 7.81 (s, 1H), 7.46-7.43 (d, *J* = 8.2Hz, 2H), 7.23-7.19 (d, *J* = 8.0 Hz, 1H), 7.18-7.17 (m, 2H), 7.10-7.08 (d, *J* = 8.5 Hz, 2H), 4.81-4.78 (t, *J* = 2.0 Hz, 1H), 3.72 (s, 6H), 3.66-3.63 (m, *J* = 2.8 Hz, 2H), 2.85-2.30 (bs, 2H), 1.91-1.86 (q, *J* = 1.2 Hz, 2H), 1.70-1.65 (q, *J* = 2.8 Hz, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 154.9, 139.9, 134.0, 133.5, 129.6, 129.3, 129.0, 128.1, 126.4, 125.5, 125.3, 125, 124.9, 124.8, 124.7, 123.6, 119.5, 119.0, 114.3, 114.2, 74.1, 62.4, 56.8, 56.7, 35.9, 29.1 ppm.

MS (EI) *m/z* 403 $(M+1)^+$.

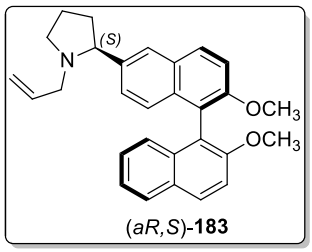
Analytical Data calculated for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51; O, 15.90:

Found : C, 77.59; H, 6.59; O, 15.90.

2.4.11 Procedure for the preparation of (2S)-1-allyl-2-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)pyrrolidine

A solution of (*R*)-1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)butane-1,4-diol (0.402 g, 1 mmol) and triethylamine (0.27 mL, 2 mmol) in dichloromethane (5 mL) were added to contents (methanesulfonyl chloride (0.15 mL, 2 mmol) in dichloromethane (3 mL)) at –20 °C for 2 h. The primary amine (1.1 mmol) was added at 0 °C and stirred for 24 h. The reaction mixture was warmed to 25°C and the residue was dissolved in ether (5 mL), washed with saturated $NaHCO_3$ (5 mL), water (5 mL) and brine (5 mL). The organic extract was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The crude product was purified on silica gel (100-200 mesh) using hexane:ethylacetate (90:10) as eluent to obtain the pure product as colorless gummy liquid.

(2S)-1-allyl-2-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)pyrrolidine (*aR,R*)-183



(*aR,S*)-**183**

Physical State: Gum

Color Dark Brown

Yield 0.304g (72%)

$[\alpha]_D^{25}$ -113.2 (*c* 0.1, $CHCl_3$)

IR (Neat): 3042, 3028, 2918, 2787, 908, 762 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.00-7.95 (m, 2H), 7.93-7.87 (m, 1H), 7.74-7.43 (m, 2H), 7.35-7.30 (m, 2H), 7.26-7.24 (m, 1H), 7.22-7.21 (m, 1H), 7.08-7.05 (m, 2H), 6.32-6.20 (m, 1H), 5.93-5.80 (m, 1H), 5.34-5.30 (m, 1H), 4.44.-4.46 (d, *J* = 6.4 Hz, 1H), 4.34-4.31 (t, *J* = 6.4 Hz, 2H), 3.33-3.76 (m, 6H), 3.20-3.15 (m, 1H), 2.98-2.90 (m, 2H), 2.69-2.76 (m, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 155.2, 154.9, 133.9, 133.7, 133.6, 132.4, 132.0, 129.5, 129.4, 129.2, 128.0, 126.4, 126.2, 125.7, 125.1, 123.8, 123.0, 119.6, 119.3, 114.5, 114.2, 69.2, 68.8, 56.9, 56.8, 46.3, 42.0, 37.5, 32.9 ppm.

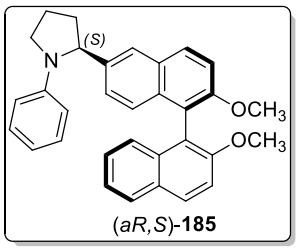
MS (EI) *m/z* 424 $(M+1)^+$.

Analytical Data calculated for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90; N, 3.31; O, 7.55:

Found : C, 82.22; H, 6.90; N, 3.31; O, 7.55.

(2S)-2-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)-1-phenylpyrrolidine (*aR,R*)-185

Physical State: Gum



(*aR,S*)-**185**

Color Dark Brown

Yield 0.348g (76%)

$[\alpha]_D^{25}$ -125.2 (*c* 0.1, $CHCl_3$)

IR (Neat): 3052, 3030, 2958, 2790, 916, 768cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.00-7.90 (d, *J* = 4.4 Hz, 1H), 7.89-7.85 (m, 2H), 7.65-7.63 (d, *J* = 8.0 Hz, 1H), 7.48-7.41 (m, 2H), 7.33-7.31 (m, 1H), 7.21-7.15 (m, 1H), 7.09-7.07 (m, 2H), 6.64-6.62 (m, 3H), 6.57-6.54 (m, 3H), 4.81-4.80 (d, *J* = 4.4 Hz, 1H), 3.80 (s, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.46-3.42 (m, 1H), 2.06-2.0 (m, 1H), 1.98-1.96 (m, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 154.9, 154.7, 147.3, 139.3, 134.0, 133.1, 129.3, 129.1, 128.9, 127.9, 126.2, 125.7, 124.2, 123.4, 119.5, 115.7, 114.3, 114.1, 112.4, 63.0, 57.0, 56.9, 49.1, 35.6, 23.1 ppm.

MS (EI) *m/z* 460 $(M+1)^+$.

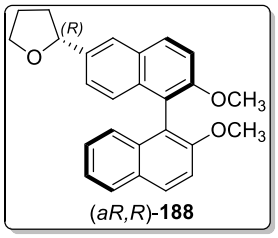
Analytical data calculated for $C_{32}H_{29}NO_2$: C, 83.63; H, 6.36; N, 3.05; O, 6.96:

Found : C, 83.60; H, 6.36; N, 3.05; O, 6.96.

2.4.12 Synthesis of chiral 2(*R*)-2-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)tetrahydrofuran

A solution of chiral 1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)butane-1,4-diol (0.402 g, 1 mmol) and triethylamine (0.27 mL, 2 mmol) in dichloromethane (5 mL) were added to contents(methanesulfonyl chloride (0.15 mL, 2 mmol) in dichloromethane (3 mL) at –20 °C. The mixture was stirred for 1.5 h at –20 °C and quenched with saturated NH_4Cl solution (1 mL). The mixture was warmed to 25°C and stirred for 1.5 h. The solution was diluted with ethyl acetate (10 mL) and washed with saturated sodium bicarbonate (5 mL), water (5 mL) and brine (5 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated. The crude product was purified on silica gel (100-200 mesh) using hexane:ethylacetate (80:20) as eluent to obtain the pure product.

(2*R*)-2-(2,2'-dimethoxy-[1,1'-binaphthalen]-6-yl)tetrahydrofuran (*aR,R*)-188



Physical State: Solid

Color White

Yield 0.345 g (90%)

$[\alpha]_D^{25}$ +5.6 (*c* 0.2, $CHCl_3$);

mp 188-190 ^{o}C;

IR (KBr) 2958, 2830, 1630, 1598, 1507, 1468, 1268, 1084, 910, 808cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ); 8.01-7.98 (m, 2H), 7.91-7.87 (m, 2H), 7.49-7.46 (m, 2H), 7.36-7.33 (t, *J* = 8.2 Hz, 1H), 7.26-7.22 (m, 2H), 7.20-7.12 (m, 2H), 5.0 (t, *J* = 6.8 Hz, 1H), 4.10-4.02 (m, 1H), 3.99-3.97 (m, 2H), 3.86 (s, 6H), 2.38-2.34 (m, 1H), 2.0-1.98 (m, 1H), 1.93-1.87 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 155.0, 154.9, 138.3, 134.0, 133.4, 129.4, 129.2, 129.0, 127.9, 126.3, 125.6, 125.3, 124.7, 124.3, 123.5, 119.7, 119.6, 114.4, 114.2, 80.8, 68.7, 56.9, 34.3, 26.1 ppm.

MS (EI) *m/z* 385 $(M+1)^{+}$.

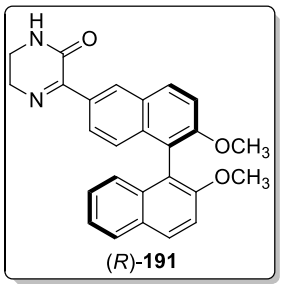
Analytical Data calculated for $C_{26}H_{24}O_3$: C, 81.21; H, 6.29; O, 12.48:

Found : C, 81.21; H, 6.29; O, 12.48.

2.4.13 Synthesis of 3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one condensation with ethylenediamine

To a stirred solution of (*R*)-**163** (1 mmol) in CH_3OH solvent (10 mL) was added ethalenediamine (1 mmol) and the contents were refluxed at 70 ^{o}C for 3 h. It was brought to 25 ^{o}C and filtered in a suction pump. The precipitate was washed thoroughly with saturated NH_4Cl (15 mL), water (2X10 mL) and brine solution (10 mL). The products (*R*)-**5** and (*R*)-**7** were dried under vacuum.

3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one (*R*)-191



(*R*)-**191**

Physical State: Solid

Color Yellow

Yield 0.370 g (90%)

mp 238-240 ^{o}C

IR(KBr) 3270, 3042, 2928, 1682, 1630, 1598, 1460, 1342, 1084, 906, 802 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.61-8.60 (t, *J* = 8.4Hz, 1H), 8.07-8.04 (d, *J* = 8.2Hz, 1H), 7.99-7.97 (d, *J* = 8.1Hz, 2H), 7.87-7.85 (d, *J* =6.8 Hz, 1H), 7.75-7.72 (d, *J* = 8.5Hz, 1H), 7.47-7.44 (m, 2H), 7.43-7.29 (m, 1H), 7.22-7.20 (t, *J* =6.9Hz, 2H), 7.18-7.10 (m, 2H), 7.09-6.23 (m, 2H), 3.97-3.97 (m, 2H), 3.85 (bs, 3H), 3.75 (bs, 3H), 3.54-3.52 (m, 2H) ppm.

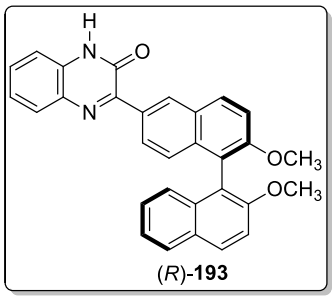
^{13}C-NMR (100 MHz, $CDCl_3$, δ): 161.9, 158, 156.1, 154.9, 135.1, 133.9, 132, 130, 129.4, 127.9, 126, 125, 123.5, 119.5, 114.5, 56.8, 56.6, 48.2, 39.0 ppm.

MS (EI) *m/z* 412 $(M+1)^{+}$.

Analytical Data calculated for $C_{26}H_{22}N_2O_3$: C, 76.08; H, 5.40; N, 6.82; O, 11.69:

Found : C, 76.02; H, 5.28; N, 6.81; O, 11.53.

3-(2,3-dimethoxy-[1,1'-binaphthlen]-6-yl)quinoxalin-2(1*H*)-one (*R*)-193



(*R*)-**193**

Physical State: Solid

Color Dark Brown

Yield 0.412g (90%)

mp 258-260 ^{o}C

IR (KBr) 3272, 3057, 2935, 1680, 1628, 1598, 1467, 1340, 1084, 908, 810 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 12.60-12.52 (bs, 1H), 9.19-9.19 (d, *J* = 816 Hz, 1H), 9.18-9.18 (d, *J* =16 Hz, 1H), 8.70-8.70 (d, *J* = 16.1 Hz, 1H), 8.40-8.24 (t, *J* =

8.0 Hz, 1H), 8.42-8.11 (t, *J* = 12.0Hz, 1H), 7.82-7.80 (t, *J* = 4.0 Hz, 1H), 7.98 (m, 2H), 7.69-7.65 (m, 2H), 7.52-7.50 (t, *J* = 12.0 Hz, 1H), 7.73-7.30 (m, 2H), 7.08-7.00 (m, 1H), 6.39-6.37 (t, *J* = 12.0 Hz, 1H), 4.48-4.67 (m, 1H), 3.99-3.82 (q, *J* = 4.6 Hz, 1H), 3.30 (bs, 6H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 186.9, 164.6, 158.5, 156.4, 155.2, 154, 153, 137, 135.4, 134.4, 132.3, 131.1, 130.5, 129.1, 128.3, 127.2, 124.2, 123.8, 118.5, 117.7, 115.5, 114.7, 56.7 ppm.

MS (EI) *m/z* 459 $(M+1)^+$.

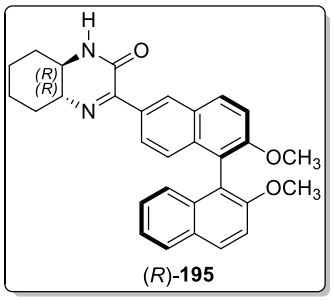
Analytical Data calculated for $C_{30}H_{22}N_2O_3$: C, 78.59; H, 4.84; N, 6.11; O, 10.47

Found : C, 78.47; H, 4.79; N, 6.09; O, 10.20

2.4.14 Synthesis of (4a*R*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4a,5,6,7,8,8a-hexahydroquinoxalin-2(1*H*)-one

To a stirred solution of (*R*)-**163** (1 mmol) and (*R*,*R*)-cyclohexyldiamine-**194** (1 mmol) in dry CH_3OH (10 mL) was added at room temperature and refluxed at 70 ^oC for 3 h. Methanol was removed under rotor evaporator. To the residue saturated NH_4Cl (5 mL) was added. The contents were extracted with EtOAc (2×10 mL) and the combined organic layer was washed with brine solution (10 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography (silica gel, hexane– EtOAc, 20:80).

(4a*R*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-4a,5,6,7,8,8a-hexahydroquinoxalin-2(1*H*)-one (*aR*,*R*,*R*)-195



(*R*)-**195**

Physical State: Gum

Color Dark Brown

Yield 0.400 g (88%)

IR (Neat) 3272, 3057, 2935, 1680, 1598, 1467, 1340, 1268, 1084, 908, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.61-8.60 (d, *J* = 8.2 Hz, 1H), 8.11-8.08 (d, *J* = Hz, 1H), 7.91-7.82-7.82 (m, *J* = 9.1 Hz, 3H), 7.43-7.29 (m, *J* = 9.1 Hz, 4H), 7.25-7.20 (m, *J* = 9.0 Hz, 1H), 7.04-7.02 (d, *J* = 8.0 Hz, 1H), 5.03 (bs, 1H), 3.79 (s, 3H), 3.10-3.09 (d, *J* = 8.8 Hz, 2H), 2.40 (d, *J* = 8.8 Hz, 1H), 1.88-1.77 (m, 2H), 1.74-1.70 (m, 1H), 1.48-1.28 (m, 6H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 160.8, 158.6, 156.9, 151.5, 135.1, 133.8, 129.7, 128.6, 126.7, 124.8, 117, 115, 113.9, 62.7, 60.4, 56.4, 53.9, 31.8, 30.8, 25.1, 23.7 ppm.

MS (EI) *m/z* 465 $(M+1)^+$.

Analytical Data calculated for $C_{30}H_{28}N_2O_3$: C, 77.56; H, 6.08; N, 6.03; O, 10.33,

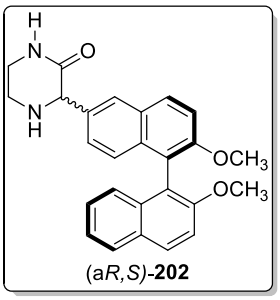
Found : C, 77.47; H, 6.05; N, 6.01; O, 10.21

2.4.15 General procedure for the synthesis of 3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)pyperzin-2-one using $NaBH_4/I_2$ in THF solvent system

Sodiumborohydride (2 mmol) was taken dry THF (10 mL) under inert atmosphere in a two necked septum capped round-bottom flask. Iodine (1 mmol) dissolved in dry THF (5 mL) was taken in liquid additional funnel and was added dropwise slowly at 0 °C during 1 h to prepare the H_3B:THF complex. Then, the compound (***R***)-**191** (1 mmol) dissolved in dry THF was added dropwise slowly. The mixture was stirred at 0 °C for 1 h and brought to rt and refluxed for 12 h. The content was brought to rt and carefully quenched by dropwise addition of 3 N aqueous HCl (2 mL) extracted with ethyl acetate (2X5 mL). The combined organic layer was washed with aqueous $NaHCO_3$ (5 mL), water (5 mL), and brine solution (5

mL) and dried over Na_2SO_4. After removal of the solvent, the product was purified by column chromatography using silica gel, 100–200 mesh, hexane–EtOAc, 20:80.

3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)pyperzin-2-one (*R*)-202


(a*R,S*)-**202**

Physical State: Solid

Color Yellow

Yield 0.320 g (78%)

mp 237-239 ^oC

$[\alpha]_D^{25}$ -72.0 (*c* 0.030, $CHCl_3$)

IR (KBr) 3233, 3049, 2932, 1686, 1620, 1589, 1332, 1261, 1080, 910, 816 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.88-7.84 (m, 1H), 7.83-7.77 (m, 3H), 7.43-7.37 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.20 (m, 1H), 7.18-7.01 (m, 1H), 6.99-6.91 (m, 1H), 4.96-4.63 (m, 2H), 3.78 (s, 3H), 3.7(s, 3H), 2.72 (bs, 1H), 1.63 (bs, 2H) ppm.

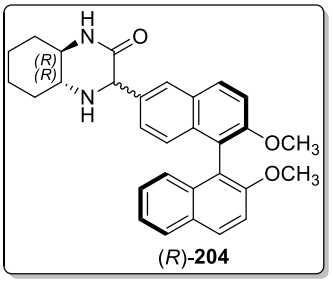
^{13}C-NMR (100 MHz, $CDCl_3$, δ): 167.8, 155.8, 154.9, 133.9, 133.8, 130, 129.9, 129.2, 128.6, 128.1, 126.5, 126.3, 125.9, 125.7, 125, 123.7, 119.3, 119.1, 118.9, 114.8, 114.3, 67.7, 67.5, 57, 56.8, 56.6, 44.7, 44.3, 37.6, 29.7 ppm.

LCMS *m/z* 413 $(M+1)^+$.

Analytical Data calculated for $C_{26}H_{24}N_2O_3$: C, 76.08; H, 5.40; N, 6.82; O, 11.69

Found : C, 76.02; H, 5.39; N, 6.81; O, 11.63.

(4a*R*,8aS)-3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)-octahydroquinoxalin-2(1*H*)-one (*R*)-204


(*R*)-**204**

Physical State: Gum

Color Dark Brown

Yield 0.350 g (76%)

$[\alpha]_D^{25}$ -420.1 (*c* 0.212, $CHCl_3$);

IR(Neat) 3273, 3059, 2937, 2841, 1680, 1593, 1342, 1267,1091, 908, 810 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.92-7.90 (d, *J* =8.6Hz, 2H), 7.87-7.75 (m, 4H), 7.38-7.31 (m, 2H), 7.29-7.23(m, 1H), 7.21-7.20 (m, 9H), 7.19--7.12 (m, 2H), 6.90-6.87 (m, 2H), 4.63 (s, 1H), 4.16-4.123 (m, 3H), 3.95 (s, 3H), 3.7(s, 3H), 2.92 (m, 2H), 2.50 (m, 2H), 1.67-1.6 5(m, 8H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 171, 156, 151.6, 135.1, 133.9, 133.7, 130.6, 129.5, 129.2, 128.3, 128, 127.4, 126.2, 25.5, 124.8, 123, 118, 116.5, 115.3, 114.1, 64.7, 58.4, 58.4, 58, 56.6, 30.8, 30.3, 29.7, 29.3, 24.5 23.7 ppm.

MS (EI) *m/z* 67 $(M+1)^+$

Analytical Data calculated for $C_{30}H_{30}N_2O_3$: C, 77.23; H, 6.48; N, 6.00; O, 10.26.

Found : C, 77.22; H, 6.37; N, 5.57; O, 10.20.

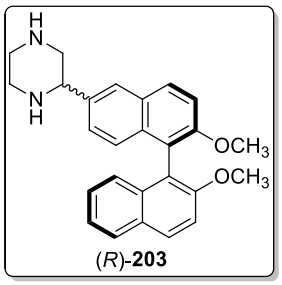
2.4.16 General procedure for the synthesis of 3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)pyperzine using $NaBH_4/I_2$ in THF solvent system

Sodium borohydride (2 mmol) was taken in dry THF (10 mL) under N_2 atmosphere in a two necked septum capped round-bottom flask. Iodine (1 mmol) dissolved in dry THF (5 mL) was taken in liquid additional funnel and was added dropwise slowly at 0 °C during 1 h to prepare the H_3B:THF complex. Then, the compound (***R***)-**202** (1 mmol) dissolved in dry THF was added dropwise slowly. The mixture was stirred at 0 °C for 1 h and brought to rt and refluxed for 24 h. The reaction mixture was brought to rt and carefully quenched by slowly adding with 3 N aqueous HCl (2 mL). The content was extracted with ethyl acetate (2X5 mL). The combined organic layer was washed with aqueous $NaHCO_3$ (5 mL), water (5 mL), and brine solution (5 mL) and dried over Na_2SO_4. After removal of the solvent, the

product was purified by column chromatography using silica gel, 100–200 mesh, hexane–EtOAc, 20:80.

3-(2,2'-dimethoxy-(1,1'-binaphthalyl)-6-yl)pyperzine (*R*)-203

Physical State: Solid



(*R*)-**203**

Color Yellow

Yield 0.290 g (73%)

mp 248-250 ^{o}C

$[\alpha]_D^{25}$ -40.0 (*c* 0.140, $CHCl_3$)

IR (KBr) 3320, 3042, 3010, 2952, 2898, 1590, 1332, 1268, 1042, 889, 802cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.88-7.87 (d, *J* =8.3 Hz, 2H), 7.85-7.84 (d, *J* =8.8Hz, 1H), 7.45-7.43 (m, 2H), 7.33-7.31 (m, 1H), 7.29-7.20 (m, 2H), 7.29-7.07 (m, 2H), 6.90-6.88 (m, 1H), 4.67 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.50-3.40 (m, 1H), 3.33-3.30 (m, 1H), 3.130-3.110 (m, 1H), 3.09-3.00 (m, 1H) ppm.

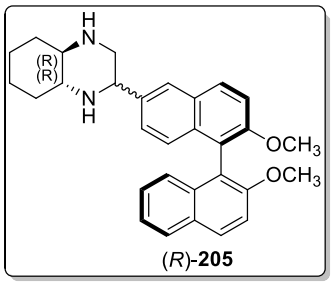
^{13}C-NMR (100 MHz, $CDCl_3$, δ): 155.2, 155, 134.8, 134.1, 133.7, 129.6, 129.5, 129.2, 129.1, 128, 127.8, 127.6, 127.0, 126.9, 126.4, 125.8, 125.3, 123.6, 119.5, 114.3, 114.2, 63.8, 63.6, 56.7, 42.9, 41, 40.8 ppm.

MS (EI) *m/z* 399 $(M+1)^+$.

Analytical Data calculated for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.58; O, 8.03; S, 7.03**:**

Found : C, 78.22; H, 6.51; O, 8.01; S, 7.05.

(4a*S*,8a*R*)-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)decahydroquinoxalin (*aR,R,R*)-205



(*R*)-**205**

Physical State: Gum

Color Dark Brown

Yield 0.320 g (72%)

$[\alpha]_D^{25}$ -782.8 (*c* 0.211, $CHCl_3$)

IR (Neat) 3273, 3059, 2937, 1680, 1593, 1469, 1342, 1267, 1091, 908, 810 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.03-8.01 (m, 1H), 7.99-7.90 (d, *J* = 8.1Hz, 1H), 7.88-7.83 (m, 2H), 7.76-7.75 (d, *J* = 6.8Hz, 1H), 7.47-7.45 (d, *J* =8.2Hz, 1H), 7.38-7.31 (m, 1H), 7.38-7.31 (m, 1H), 7.29-7.21 (m, 1H), 7.19-7.10 (m, 1H), 7.09-7.02 (m, 1H), 3.92 (bs, 1H), 3.78 (s, 4H), 3.52-3.43 (m, 1H), 3.25-3.24 (m, 1H), 2.39-3.33 (m, 2H), 2.16-2.15 (s, 1H), 1.95-1.63 (m, 3H), 1.30-1.25 (m, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 155.0, 151.7, 135.6, 133.7, 129.2, 128.3, 127.1, 125.5, 124.3, 122.0, 118.0, 117.0, 114.0, 113.1, 60.8, 60.6, 58.8, 55.8, 51.7, 48.7, 30.8, 30.49, 24.3, 24.09 ppm.

MS (EI) *m/z* 453 $(M+1)^+$

Analytical Data calculated for $C_{30}H_{32}N_2O_2$: C, 79.61; H, 7.09; N, 6.19; O, 7.07.

Found : C, 79.41; H, 7.09; N, 6.13; O, 7.05.

2.4.17 Synthesis of chiral (*R*)-1-(1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl) ethane-1,2-diol using oxazaborolidine reagent system.

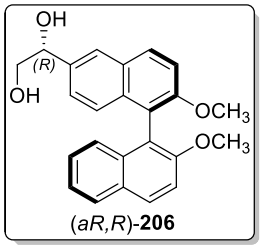
Sodiumborohydride (2 mmol) was taken in dry THF (10 mL) under N_2 atmosphere in a two necked septum capped round-bottom flask. Iodine (1 mmol) dissolved in dry THF (5 mL) was taken in liquid additional funnel and was added drop wise slowly at 0 °C during 1 h to prepare H_3B:THF complex. To this, a solution of (*S*)-DPP **173** (0.3 mmol) [(*S*)-α,α-diphenyl-2-pyrrolidine methanol] and trimethylborate (0.3 mmol) in dry THF (5 mL) was added and the contents were stirred for 20 min. Then, the compound (***R***)-**163** (1 mmol) dissolved in dry THF (5 mL) was added slowly during 1 h at 10 °C and the contents were

further stirred at room temperature for 1 h. It was carefully quenched with 1 N HCl (2 mL) and extracted with diethyl ether (2 × 5 mL). The combined organic extract was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, 100–200 mesh, hexane–EtOAc, 20:80).

1-(1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)ethane-1,2-diol (a*R*,*R*)-206

Physical State: Solid

Color Yellow



Yield 0.330 g(90%);

mp 112-114^{o} C;

$[\alpha]_D^{25}$ +28.4 (*c* 0.100, $CHCl_3$);

IR (KBr) 3402, 2935, 2837, 1622, 1593, 1506, 1462, 1263, 1064, 895, 808 cm^{-1}

^{1}H-NMR (400 MHz, $CHCl_3$, δ): 7.99-7.97 (d, *J* = 8.0 Hz, 1H), 7.89-7.87 (d, *J* = 8.1 Hz, 2H), 7.45-7.49 (d, *J* = 7.8 Hz, 2H), 7.20-7.18 (d, *J* = 8.0 Hz, 2H), 6.97-6.95 (d, *J* = 4.4 Hz, 2H), 4.80-4.77 (t, *J* = 12.0 Hz, 2H), 3.79-3.76 (s, 8H), 2.57 (bs, 1H), 2.09 (bs, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 157.3, 155.1, 154.9, 135.5, 133.9, 133.7, 129.5, 129.2, 128.9, 128, 126.4, 125.6, 125.2, 124.7, 123.6, 119.4, 114.5, 74.6, 67.8, 56.8 ppm.

MS (EI) *m/z* 375 $(M+1)^+$.

Analytical Data calculated for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92; O, 17.09

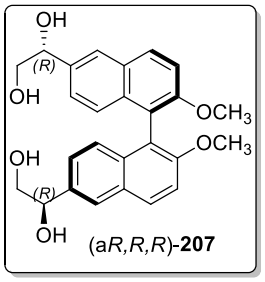
Found : C, 76.02; H, 5.62; O, 16.86.

2.4.18 Synthesis of Chiral *bis*-(1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)ethane-1,2-diol

$NaBH_4$ (1.96 g, 40 mmol) was placed in a 100-mL three-neck round-bottom flask under a N_2 atmosphere in anhyd THF (25 mL). To this I_2 (5.06 g, 20 mmol) in anhyd THF (40 mL) was added under N_2 at 0 °C over 1 h by use of a pressure equalizer. The diborane generated *in situ* was trapped as a BH_3–THF complex. To this reagent, a soln of (*S*)-α,α-diphenyl-2-pyrrolidine methanol [(*S*)- DPP; 6.0 mmol] and trimethylborate (7.5 mmol) in THF (30 mL)] was added and the mixture was stirred for 20 min. Then (***R***)-**164** (4.16 g, 10 mmol) dissolved in THF (30 mL) was added slowly to the reaction mixture with a pressure equalizer over 1 h at 10 °C, and the mixture was further stirred at 25 °C for 1 h. The reaction mixture was brought to 25 °C and carefully quenched with 1 N HCl (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined extracts were washed with brine (30 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, 100–200 mesh, hexane–EtOAc, 20:80).

Chiral *bis*-(1-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)ethane-1,2-diol (*aR,R,R*)-207

Physical State:Solid



(a*R*,*R*,*R*)-**207**

Color Yellow

Yield 3.4 g (90%)

mp 126-128 °C

IR (KBr) 3402, 2935, 2837, 1622, 1593, 1506, 1462, 1263, 1064, 895, 808cm^{-1}

^{1}H-NMR (400 MHz, CD_3OD, δ): 7.99-7.96 (q *J* = 2.4 Hz, 2H), 7.88-7.86 (d, *J* = 2.8 Hz, 2H), 7.48-7.44 (m, 2H), 7.33-7.30 (t, *J* = 2.4 Hz, 1H), 7.27-7.16 (m, 2H), 7.11-

7.0(d, *J* = 2.0 Hz, 2H), 4.92 (bs, 1H), 3.79-3.76 (d, *J* = 12.0 Hz, 6H), 2.5 (bs, 1H), 2.0 (bs, 1H) ppm.

^{13}C-NMR (100 MHz, CD_3OD, δ): 155.1, 154.9, 135.5, 133.9, 133.7, 129.5, 129.2, 128.9, 128, 126.4, 125.6, 125.2, 124.7, 123.6, 119.4, 114.5, 114.1, 74.6, 67.8, 58.8 ppm.

MS (EI) *m/z* 376 $(M+1)^+$.

$[\alpha]_D^{25}$ +5.3 (*c* 1.0, $CHCl_3$)

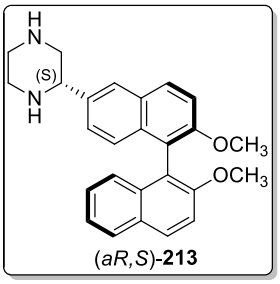
Analytical Data calculated for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92; O, 17.09

Found C, 76.02; H, 5.62; O, 16.86

2.4.19 Synthesis of (2S)-2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)piperazine

To a stirred solution of the compound (*R*)-**206** (1 mmol, 99% ee) and triethylamine (2.2 mmol) in dichloromethane (5 mL), methane-sulfonylchloride (2.2 mmol) was added at -20 °C. The reaction mixture was stirred for 2 h at -20 °C and then quenched with saturated NH_4Cl (2mL). The contents were brought to 25 °C. The organic layer was washed with water (5 mL), saturated $NaHCO_3$ (2mL) and brine solution (5 mL). The organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to approximately 3 mL. This crude dimesylate was added to ethylene diamine (0.5 mL) at 0 °C and stirred at rt for 24 h. The excess amine was removed under reduced pressure. The residue was dissolved in ether (5 mL) and washed successively with saturated $NaHCO_3$ (2 mL), water (5 mL) and brine (5 mL). The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate (95:5) as eluent.

(2S)-2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)piperazine (*R*)-213



(*aR,S*)-**213**

Physical State: Solid

Color Yellow

Yield 0.310 g (76%)

mp 251-253 ^{o}C

$[\alpha]_D^{25}$ -43.4 (*c* 0.140, $CHCl_3$)

IR (KBr) 3320, 3031, 3012, 2952, 2898, 1596, 1328, 1268, 1062, 889, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.88-7.87 (d, *J* = 8.3 Hz, 2H), 7.85-7.84 (d, *J* = 8.8 Hz, 1H), 7.45-7.43 (m, 2H), 7.33-7.31 (m, 1H), 7.29-7.20 (m, 2H), 7.29-7.07 (m, 2H), 6.90-6.88 (m, 1H), 4.67 (s, 1H), 3.75(s, 3H), 3.74 (s, 3H), 3.50-3.40 (m, 1H), 3.33-3.30 (m, 1H), 3.13-3.11 (m, 1H), 3.09-3.0 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 155.2, 155, 134.8, 134.1, 133.7, 129.6, 129.5, 129.2, 129.1, 128, 127.8, 127.6, 127.0, 126.9, 126.4, 125.8, 125.3, 123.6, 119.5, 114.3, 114.2, 63.8, 63.6, 56.7, 42.9, 41, 40.8 ppm.

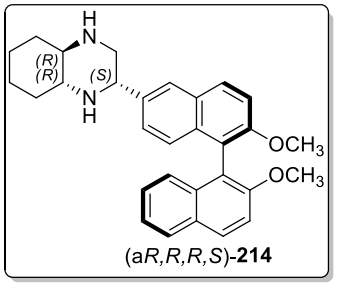
MS (EI) *m/z* 399$(M+1)^+$

Analytical Data calculated for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.58; O, 8.03; S, 7.03

Found : C, 78.20; H, 6.47; O, 8.01; S, 7.05.

(2*R*,4a*R*,8a*R*)-2-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)decahydroquinoxalin

(a*R*,*R*,*R*,*S*)-214



(a*R,R,R,S*)-**214**

Physical State: Gum

Color Dark Brown

Yield: 0.330 g (75%)

$[\alpha]_D^{25}$ -823.05 (*c* 0.210, $CHCl_3$)

IR (Neat) 3273, 3059, 2937, 1680, 1593, 1469, 1342, 1267, 1091, 908, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.03-8.01 (m, 1H), 7.99-7.90 (d, *J* = 8.1Hz, 1H), 7.88-7.83 (m, 2H), 7.76-7.75 (d, *J* = 6.8 Hz, 1H), 7.47-7.45 (d, *J* =8.2 Hz, 1H), 7.38-7.31 (m, 1H), 7.38-7.31 (m, 1H), 7.29-7.21 (m, 1H), 7.19-7.10 (m, 1H), 7.09-7.02 (m, 1H), 3.92 (bs, 1H), 3.78 (s, 4H), 3.52-3.43 (m, 1H), 3.25-3.24 (m, 1H), 2.39-3.33 (m, 2H), 2.16-2.15 (s, 1H), 1.95-1.63 (m, 3H), 1.30-1.25 (m, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$ and CD_3OD, δ): 155.0, 151.7, 135.6, 133.7, 129.2, 128.3, 127.1, 125.0, 124.0, 122.0, 118.0, 117.0, 114.0, 113.1, 60.89, 60.6, 58.8, 55.89, 51.7, 30.8, 30.49, 24.3, 24.0 ppm.

MS (EI) *m/z* 453$(M+1)^+$.

Analytical Data calculated for $C_{30}H_{32}N_2O_2$: C, 79.61; H, 7.09; N, 6.19; O, 7.07

Found : C, 79.37; H, 7.01; N, 6.11; O, 7.05.

2.4.20 Synthesis of *bis*-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one condensation with ethylenediamine.

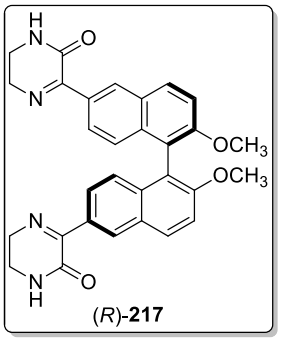
To a stirred solution of (*R*)-**164** (5.15 g, 10 mmol) in CH_3OH solvent (50 mL) were added 1,2-diamine (2.0 mL, 20 mmol) and reflux the reaction mixture under 70 ^{o}C for 3 h. Cool the reaction mixtures and filtered suction pump wash thoroughly with saturated NH_4Cl (25 mL) and wash with water (2X25 mL) and brine (50 mL) solution. Filtered the crude compound (*R*)-**217** under vacuum pump and dried.

***bis*-3-(2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)-5,6-dihydropyperzin-2(1*H*)-one (*R*)-217.**

Physical State: Solid

Color Yellow

Yield 4.5 g (89%)



(*R*)-**217**

mp 238-240 ^{o}C

IR (KBr) 3270, 3042, 2928, 1682, 1630, 1598, 1460, 1342, 1084, 906, 802cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):8.60-8.55 (m, 2H), 8.22-8.06 (m, 1H), 7.10-7.68 (d, *J* = 7.8 Hz, 1H), 7.64-7.62 (d, *J* =8.3 Hz, 1H), 6.78-6.86 (m, 1H), 3.7 (s, 6H), 3.42-3.39 (m, 7H), 2.56 (ss, 2H) ppm

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 161.6, 157.2, 156.1, 134.3, 131.1, 130.9, 130.2, 128.1, 126.2, 124.2, 118.5, 114.7, 56.5, 48.5, 38.5 ppm

MS (EI) *m/z* 507 $(M+1)^{+}$.

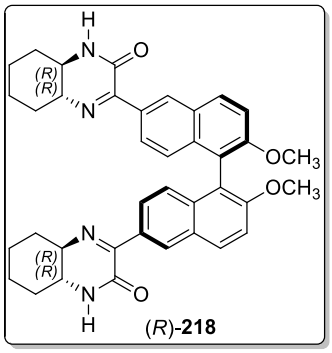
Analytical Data calculated for: $C_{30}H_{26}N_4O_4$: C, 71.13; H, 5.17; N, 11.06; O, 12.63:

Found: C, 71.02; H, 5.13; N, 11.01; O,12.57.

2.4.21 Synthesis of (4a*S*,8a*S*)-3-(2,2'-dimethoxy-6'-((4a*R*,8a*R*)-3-oxo-3,4,4a,5,6,7,8,8a-octahydroquinoxalin-2-yl)-4a,25,6,7,8,8a-hexahydroquinoxalin-2(1*H*)-one (*R*)-215.

To a stirred solution of (*R*)-**164** (2.57 g, 5 mmol) and (*R*,*R*)-cyclohexyldiamine **194** (1.5 mL,10 mmol) in dry CH_3OH (50 mL) was added at room temperature and refluxed at 70 ^{o}C for 3 h. Methanol was removed under rotor evaporator. To the residue saturated NH_4Cl (5 mL) was added. The contents were extracted with EtOAc (2×10 mL) and the combined organic layer was washed with brine solution (10 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography (silica gel, hexane– EtOAc, 30:70).

4a*S*,8a*S*)-3-(2,2'-dimethoxy-6'-((4a*R*,8a*R*)-3-oxo-3,4,4a,5,6,7,8,8a-octahydroquinoxalin-2-yl)-4a,25,6,7,8,8a-hexahydroquinoxalin-2(1*H*)-one (*R*)-218



(*R*)-**218**

Physical State: Gum

Color Dark Brown

Yield 2.67 g (87%)

IR (Neat) 3276, 3058, 2935, 1682, 1628, 1468, 1342, 1269, 1084,906, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.56 (s, 2H), 8.07-8.05 (d, *J* = 9.2 Hz, 2H), 7.77-7.6 (d, *J* = 9.1 Hz, 1H), 7.75-7.74 (d, *J* = 9.1 Hz, 2H), 7.09-7.04 (t *J* = 9.0 Hz, H), 3.7 (s, 6H), 3.27-3.16 (m, 4H), 2.46-2.44 (d, *J* = 9.1 Hz, 2H), 2.07-2.01 (d, *J* = 8.8 Hz, 2H), 1.98-1.91 (d, *J* = 8.8 Hz, 2H), 1.89-1.81 (d, *J* = 8.8 Hz, 2H), 1.78-1.46 (m, 6H), 1.37-1.26 (m, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 161.2, 158.6, 156, 135, 130.8, 130.18, 130.14, 128.4, 125.8, 125.2, 119.1, 113.9, 63, 56.6, 54, 31.9, 30.9, 25.2, 23.7 ppm.

MS (EI) *m/z* 615 $(M+1)^+$.

$[\alpha]_D^{25}$ +56.6 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{38}H_{38}N_4O_4$: C, 74.24; H, 6.23; N, 9.11; O, 10.41

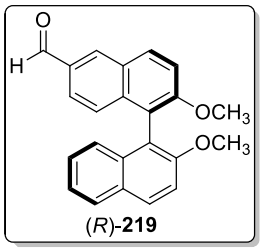
Found C, 74.12; H, 6.20; N, 9.01; O, 10.35

2.4.22 Procedure for the preparation of 2,2'-dimethoxy-(1,1'-binaphthalen)-6-carbaldehyde (*R*)-219.

To a suspension of (*R*)-**206** (1.9 g, 5 mmol) in dry CH_2Cl_2 (30 mL) were added of $NaIO_4$ (Sodium metaperiodate 5 mmol) and silica gel. To this reaction mixture stirred at 25 ^{o}C for 6 h. filtered the crude with filter paper and extracted with DCM and brine (25 mL)

dried over anhydrous Na_2SO_4. The crude product was purified on column chromatography (silica gel, hexane– EtOAc, 20:80).

2,2'-dimethoxy-(1,1'-binaphthalen)-6-carbaldehyde (*R*)-219



(*R*)-**219**

Physical State: Solid

Color Light Yellow

Yield 1.1 g (65%)

mp 236-238 ^{o}C

IR (KBr) 3055, 2937, 2839, 1685, 1620, 1591, 1344, 1267, 1064, 887, 810 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 10.10 (s, 1H), 8.16-8.14(d, *J* = 9.2 Hz, 1H), 8.02-8.00 (d, *J* = 8.1 Hz, 1H), 7.90-7.88 (d, *J* = 8.2 Hz, 1H), 7.70-6.80 (m, 1H), 7.56-7.54 (d, *J* = 6.0 Hz, 1H), 7.49-7.46 (d, *J* = 8.2 Hz, 1H), 7.34-7.32 (t, *J* = 8.8 Hz, 1H), 7.26-7.20 (m, 2H), 7.08-7.06 (d, *J*= 8.6 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 192.1, 157.7, 154.9, 137.4, 135.1, 133.7, 132.2, 131.4, 129.9, 128.1, 126.6, 124.3, 123.7, 120, 118.5, 114.5, 113.9, 56.7, 56.5 ppm.

MS (EI) *m/z* 344 $(M+1)^{+}$.

$[\alpha]_D^{25}$ +133.4 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30; O, 14.02

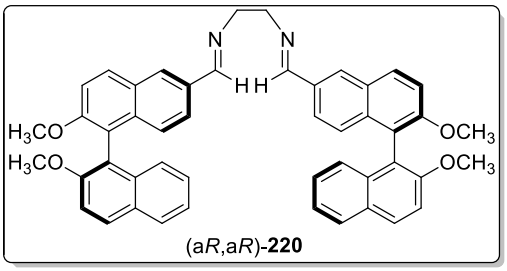
Found C, 80.29; H, 5.12; O, 14.01

2.4.23 Procedure for the preparation of (*N*^{1}1*E*, *N*^{2}*E*)-*N*^{1}, *N*^{2}-bis((2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)methylene-1,2-diamine (*R*)-220

To a Suspension of (*R*)-**219** (1.72 g, 5 mmol) taken in CH_3OH (20 mL) were added ethylenediamine (0.3 mL, 3mmol). The content stirred at 70 ^{o}C for 3h. The reaction mixture

brought to rt. The desired product separate out as crystal of (a*R*,a*R*)-**220** remove the excess amount of methanol.

-*bis*((2,2'-dimethoxy-(1,1'-binaphthalen)-6-yl)methylene-1,2-diamine (*R*)-220



(a*R*,a*R*)-**220**

Physical State: Solid

Color White

Yield 3.2 g (90%)

mp 67-69 ^{o}C

IR (KBr) 3423, 3055, 2934, 2841, 1622, 1591, 1464, 1334, 1265, 1066, 804cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.51 (s, 1H), 8.40 (s, 1H), 8.15 (s, 1H), 8.14-7.98 (m, 3H), 7.88-7.86 (d, *J* = 8.0 Hz, 2H), 7.71-7.65 (m, 2H), 7.49-7.45 (m, 1H), 7.34-7.30 (t, *J* = 8.0 Hz, 2H), 7.23-7.15 (m, 2H), 7.13-7.07 (m, 3H), 3.98 (s, 1H), 3.78-3.70 (m, 11H), 3.05-3.02 (t, *J* = 8.0 Hz, 2H), 2.74 (s, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 162.8, 162.4, 156.1, 156, 154.9, 135.4, 133.9, 131.6, 130.2, 129.6, 128.6, 126.4, 125.9, 124.3, 123.6, 119.7, 114.3, 64.7, 61.8, 56.8, 56.6, 44.9, 42.7 ppm.

MS (EI) *m/z* 709 $(M+1)^{+}$.

$[\alpha]_D^{25}$ +142.7 (*c* 1.00, $CHCl_3$)

Analytical Data calculated for $C_{48}H_{40}N_2O_4$: C, 81.33; H, 5.69; N, 3.95; O, 9.03

Found C, 80.29; H, 5.03; N, 3.52; O, 8.16

2.5. References

1. (a) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581. (b) Hargittai, I.; Hargittai, M. *Symmetry hrough the eyesofa chemist*; VCH publishers; NewYork **1987**.

2. (a) Shi, M.; Satoh, Y.; Masaki, Y. *J. Chem. Soc. Perkin.Trans1.***1998**, 2547. (b) Shi, M.; Satoh,Y.; Makihara,T.; Masaki, Y. *Tetrahedron: Asymmetry.* **1995**, *6,* 2109.

3. Masamune, S.; Kim,B.-M.; Petersen, J. -S.; Sato, T.; Veenstra, S. -J. *J. Am. Chem. Soc.* **1985**, *107*, 4549.

4. (a) Aggarwal, V. K.; Winn, C. L. *Acc. Chem. Res.* **2004**, *8*, 611. (b) Blot, V.; Briere, J.-F.; Davoust, M.; Miniere, S.; Reboul, V.; Metzner, P. *Phosphorous, Sulfur, and Silicon* **2005**, *180*, 1171.

5. (a) Burk, M.J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9*, 2653. (b) Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518. (c) Li, C .-Y.; Sun, X. -L.; Jing, Q.; Tang, Y. *Chem. Commn.*, **2006**, 2980.

   (d).Li,C.-Y.;Zhu,B.-H.;Ye,L.-W.;Jing,Q.;Sun,X.-L.;Tang,Y.;Shen,Q.*Tetrahedron* **2007**, *63*, 8046.

6. (a) Graham, M. A.; Wadsworth, A. H.; Hornton-Pelt, M.; Rayner, C. M. C*hem. Commun.* **2001**, 966. (b) Adamo, M. F. A.; Aggarwal, V. K.; Sage, M. A. *Synth.Commun.* **1999**, *29,* 1747. (c) Davis, F. A.; Song, M.; Augustine, A. *J. Org. Chem*. **2006**, *71*, 2779.

7. Pichon, M.; Figadere, B. *Tetrahedron: Asymmetry;* **1996**, *7,* 927.

8. (a) Whitesell, J. K.; Felman, S. W. *J. Org. Chem*. **1977**, *42*, 1663. (b) Whitesell, J. K.; Felman, S. W. *J. Org. Chem*. **1980**, *45*, 755.

9. Short, R. P.; Kennedy, R.M.; Masamune, S. *J. Org. Chem*.**1989**, *54*, 1755.

10. Whitesell, J. K. *Acc. Chem. Res.* **1985**, *18*, 280.

11. Harding, K.E.; Burks, S. R. *J. Org. Chem*. **1981**, *46*, 3920.

12. Schlessinger, R. H.; Iwanowicz, E. J. *Tetrahedron Lett.* **1987**, *28,* 2083.

13. Defoin, A.; Brouillard-Poichet, A.; Streith, J. *Helv. Chim. Acta* **1991**, *74,* 103.

14. Elburg, P.A.; Honig, G. W. N.; Reinhoudt, D.N. *TetrahedronLett.* **1987**, *28,* 6397.

15. Breuer, E.; Melumad, D. *J. Org. Chem.* **1972**, *37*, 3949.

16. Higashiyama, K.; Inoue, H.; Takahashi, H. *Tetrahedron* **1994**, *50*, 1083.

17. Katrizky, A.R.; Cui, X.L.; Yang, B.; Steel, P. J. *TetrahedronLett.* **1998**, *39*, 1697.

18. Pastine, S.J.; Gribkov, D.V.; Sames, D. *J. Am. Chem. Soc.* **2006**, *128*, 14220.

19. Kawanami, Y.; Ito, Y.; Kitagawa, T.; Taniguchi, Y.; Katsuki, T.; Yamaguchi,M. *TetrahedronLett* .**1984**, *25*, 857.

20. Tokioka, K.; Masuda, S.; Fujii, T.; Hata, Y.; Yamamato, Y. *Tetrahedron:Asymmetry* **1997**, *8,* 101.

21. Knochel, P.; Schwink, L. *Tetrahedron Lett.* **1997,** *38*, 3711.

22. (a) Beak, P.; Kerrick, S. T.; Wu, S.; Chu, J. *J. Am. Chem .Soc.* **1994**, *116*, 3231. (b) Wu, S.; Lee, S.; Beak, P. *J. Am. Chem. Soc.* **1996**, *118*, 715.

23. Whitesell, J. K.; Minton, M.A.; Chen, K. -M. *J. Org. Chem.* **1988**, *53*, 5383.

24. Gawly, R.E.; Chemburkar, S. R.; Smith ,A. L.; Anklekar, T. V. *J. Org. Chem.* **1988**, *53*, 5381.

25. Aggarwal, V. K.; Sandrinelli, F.; Charmant, J. P. H. *Tetrahedron:Asymmetry* **2002**, *13,* 87.

26. Takasu, K.; Misawa, K.; Ihara, M. *Tetrahedron Lett.* **2001**, *42*, 3489.

27. (a)Halland, N.; Hazell, R. G.; Jorgensen, K. A. *J. Org. Chem.* **2002**, *67*, 8331. (b) Melchiorre, P.; Jorgensen, K. A. *J. Org. Chem.* **2003**, *68*, 4151. (c) Halland, N.; Braunton, A.; Bachmann, S.; Marigo, M.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 4790. (d) Bertelsen, S.; Halland, N.; Bachmann, S.; Marigo, M.; B raunton, A.; Jorgensen, K.A.*Chem.Commun.* **2005**, 4821. (e) Marigo, M.; Bachmann, S.; Halland, N.; Braunton, A.; Jorgensen, K. A. *Angew. Chem. Int. Ed.* **2004**, *43*, 5507.

28. (a) Kozmin, S. A.; Rawal, V. H. *J. Am. Chem. Soc.* **1997**, *119*, 7165. (b). Kozmin, S. A.; Rawal, V. H. *J. Am. Chem. Soc.* **1999**, *121*, 9562.

29. He,S.;Kozmin,S.A.;Rawal,V.H.*J.Am.Chem.Soc.***2000**,*122*,190.

30. Iseki, K.; Mizuno,S.; Kuroki, Y.; Kobayashi,Y. *Tetrahedron* **1999**, *55*, 977.

31. Choi, Y. H.; Choi, J. Y.; Yang, H.Y.; Kim, Y. H.*Tetrahedron:Asymmetry* **2002**, *13*, 801.

32. (a) Duursma, A.; Hoen, R.; Schuppan, J.; Hulst, R.; Minnaard, A.J.; Feringa, B. L. *Org. Lett.* **2003**, *5*, 3111. b) Hoen, R.; Berg, M. V. D.; Bernsmann,H.; Minnaard, A. J.; De Vries, J. G.; Feringa, B. L. *Org.Lett.* **2004**, *6*, 1433.

33. (a) Aggarwal, V. K.; Smith, H. W.; Jones, R. V. H.; Fieldhouse, R. *Chem.Commun.* **1997**, 1785. (b) Aggarwal, V. K.; Smith, H. W.; Hynd, G.; Jones, R. V. H.; Fieldhouse, R.; Spey, S.E. *J. Chem. Soc. Perkin. Trans. 1.* **2000**, 3267.

34. Archer, N. J.; Rayner, C.M.; Bell, D.; Miller. D. *Synlett* **1994**, 617.

35. Kokotos, C. G.; Aggarwal, V. K. *Org. Lett.* **2007**, *9*, 2099.

36. (a) Aggarwal, V. K.; Fang, G. Y.; Schmidt, A. T. *J. Am. Chem. Soc.* **2005**, *127*, 1642. (b) Robiette, R.; Fang, G. Y.; Harvey, J. N.; Aggarwal, V. K. *Chem. Commun.***2006**, 741. (c)

Fang, G. Y. ; Wallner, O. A.; Blasio, N.D.; Ginesta, X.; Harvey, J. N.; Aggarwal, V.K. *J. Am .Chem. Soc* .**2007**, *129*, 14632.

37. Nakajima, M.; Tomioka, K.; Koga, K. *Tetrahedron* **1993**, *49*, 9735.

38. (a) Kise, N.; Tokioka, K.; Aoyama,Y. *J. Org. Chem*. **1995**, *60*, 1100. (b) Kise, N.; Kumada, K.; Terao, Y.; Veda, N. *Tetrahedron* **1998**, *54*, 2697. (c) Ramanathan, C. R.; Periasamy, M. *Tetrahedron:Asymmetry* **1998**, *9*, 2651.

39. (a) Wren, H.; Still, C. J. *J. Chem. Soc.* **1915**, *107*, 444. (b) *idem.*, *ibid* .**1915**, *107*, 1449.

40. Berova, N. D.; Kurtev, B. J. *Tetrahedron* **1969**, *25*, 2301.

41. Li, X.; Zhao, G.; Cao, W.-G. *Chin. J. Chem.* **2006**, *24*, 1402.

42. Breau, L.; Ogilvie, W. W.; Durst, T. *Tetrahedron Lett*. **1990**, *31*, 35.

43. Edstrom, E.D.; Livinghouse, T. *J. Am. Chem. Soc.* **1986**,*108*,1334.

44. Aggarwal, V. K.; Vasse, J. L. *Org. Lett*. **2003**, *5*, 3987.

45. Otten,S.; Frohlich,R.; Haufe, G. *Tetrahedron:Asymmetry* **1998**, *9,* 189.

46. (a) Julienne, K.; Metzner, P. *J. Org. Chem*. **1998**, *63*, 4532. (b) Julienne, K.; Metzner, P.; Henryon,V. *J. Chem. Soc. Perkin Trans.1* **1999**, 731. (c) Zanardi, J.; Lamazure, D.; Miniere, S.; Reboul,V.; Metzner, P. *J. Org. Chem*. **2002**, *67*, 9083. (d) Davoust, M.; Briere,J.-F.; Jaffres, P.-A.; Metzner, P. *J. Org.Chem*. **2005**, *70*, 4166. (e) Zanardi, J.; Leriverend, C.; Aubert, D.; Julienne, K.; Metzner, P. *J. Org. Chem*. **2001**, *66*, 5620.

47. (a) Kubota, H.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1993**, *34*, 8135. (b) Sweet, J. A.; Cavallari, J. M.; Price, W. A.; Ziller, J. W.; McGrath, D. V. *Tetrahedron: Asymmetry.* **1997**,*8*,207. (c) Kubota, H.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 6689. (d) Cahill, J.P.;

Cunneen, D.; Guiry, P.J. *Tetrahedron:Asymmetry* **1999**, *10*, 4157. (e) Sweet, J. A.; Cavallari, J. M.; Price, W. A.; Ziller, J. W.; McGrath, D. V. *Tetrahedron:Asymmetry.***1997**, *8*, 201. (f) Chen, H.; Sweet, J. A.; Lam, K.-C.Rheingold,A.L.;McGrath,D.V.*Tetrahedron:Asymmetry* **2009**, *20*, 1672.

48. (a) Tomioka, K.; Nakajima,M.; Koga, K. *TetrahedronLett.* **1990,** *31*, 1741. (b) Nakajima, M.; Tomioka, K.; Iitaka, Y.; Koga, K. *Tetrahedron* **1993**, *49*, 10793.
49. (a) Nakajima, M.; Tomioka, K.; Koga, K. *Tetrahedron* **1993**, *49*, 9751. (b) Tomioka, K.; Nakajima, M.; Koga, K. *Chem. Lett.* **1987**, 65.
50. (a) Meyers, A.I.; Burgess, L.E. *J. Org. Chem.* **1991**, *56*, 2294. (b) Burgess, L.E.; Meyers, A.I. *J. Org. Chem.* **1992**, *57*, 1656.
51. Leemans, E.; Mangelinckxz, S.; Kimpe, N.D. *Chem. Commn.* **2010**, *46*, 3122.
52. Bailey, D. J.; O'Hagan, D.; Tavasli, M. *Tetrahedron: Asymmetry* **1997**, *8,* 149.
53. Anwar, S.; Periasamy,M. Ph.D.Thesis, University of Hyderabad.
54. (a) Periasamy, M.; Prasad, A. S. B.; Kanth, J. V. B.; Reddy, Ch. K. *Tetrahedron: Asymmetry* **1995**, *6,* 341. (b) Periasamy, M.; Venkataraman, L.; Thomas, K. R. J. *J. Org. Chem.* **1997**, *62,* 4302. (c) Periasamy, M.; Venkataraman, L.; Sivakumar, S.; Sampathkumar, N.; Ramanathan, C. R. *J. Org. Chem.* **1999**, *64,* 7643. (d) Periasamy, M.; Reddy, M. N.; Anwar, S. *Tetrahedron: Asymmetry* **2004**, *15,* 1809.
55. Ramanathan, C. R.; Periasamy, M. *Tetrahedron: Asymmetry* **1998**, *9,* 2651.
56. Rao, V. D.; Periasamy, M. *Tetrahedron Asymmetry* **2000**, *11*, 1151.
57. Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org.Chem.***1981**, *46*, 393.

58. Periasamy, M.; M. Seenivasaperumal, M.; Rao, V. D.; *Tetrahedron Asymmetry* **2004**, *15*, 3847.

59. Rao, V. D.; M. Periasamy, *Synthesis* **2000**, *5*, 703.

60. (a) Asai, S.; Kato, M.; Monguchi, Y.; Sajiki, H.; Sawama, Y. *Chem. Commun.* **2017**, *53*, 4787-4790. (b) Bunrit, A.; Dahlstrand, C.; Olsson, S. K.; Srifa, P.; Huang, G.; Orthaber, A.; Sjo¨berg, P. J. R.; Biswas, S.; Himo. F.; Samec, J. S. M. *J. Am. Chem. Soc.,* **2015**, *137*, 4646–4649. (c) Arico, F.; Tundo, P.; Maranzana, A.; Tonachini, G. *ChemSusChem,* **2012**, *5,* 1578–1586.

61. (a) Narayana, C.; Periasamy, M. *J. Organomet. Chem.* **1987**, *323*, 145. (b) Kanth, J. V. B.; Periasamy, M. *J. Org. Chem.* **1991**, 56, 5964. (c) Prasad, A. S. B.; Kanth, J. V. B.; Periasamy, M. *Tetrahedron*, **1992**, 48, 462. (d) Periasamy, M.; Muthukumaragopal, G. P.; Sanjeevakumar, N. *Tetrahedron Lett.* **2007**, *48*, 6966.

62. Nagaraju, M. Ph.D., Thesis, University of Hyderabad, **2012**.

63. (a) Detogu, G.; Fabbri,D.; de Candia.; Patti, S. *Tetrahydron: Asymmetry* **2002**, 13, 891. (b) Delogu, G.; Dettori, M.A.; Patti, A pedotti, S.; A.; Casalone, G. *Tetrahydron: Asymmetry* **2003**, 14, 2467.

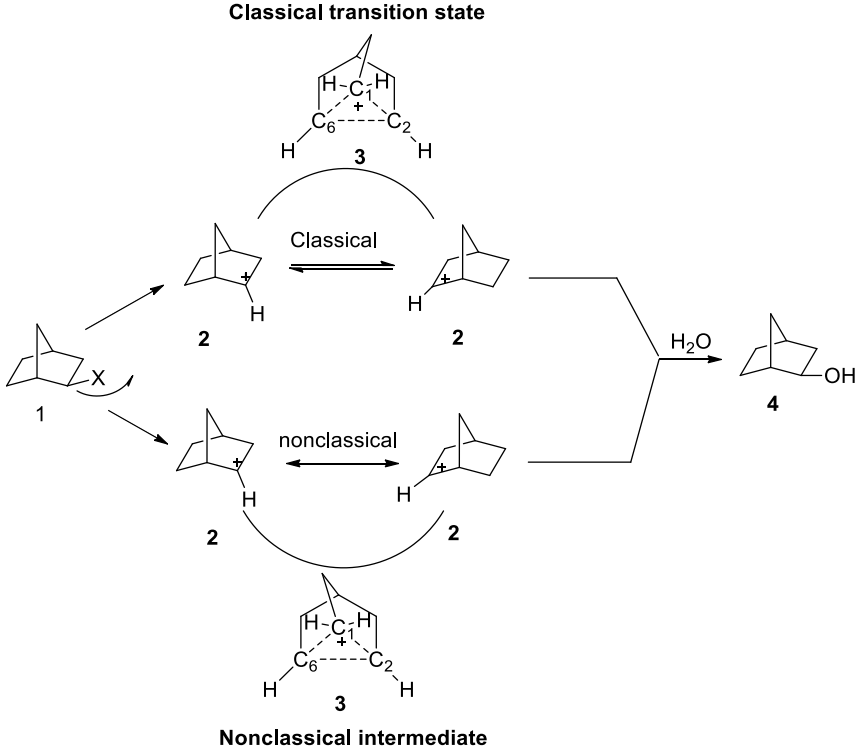
Chapter 3

Reaction of 2-Norbornylcation with Monomethoxy *Bi*-2-naphthol and Synthetic Transformations using the 2-Norbornyl system

3.1. Introduction

The S_N1 reaction of the 2-norboronyl system was studied by several physical organic chemists over the years.[1a,b,c] In the unsymmetrical classical ion formation, the nonclassical structure would be transition state for the degenerate equilibrium of the cation but the resonance between the classical ions would lead to the nonclassical bridged ion intermediate (Scheme 1).[2]

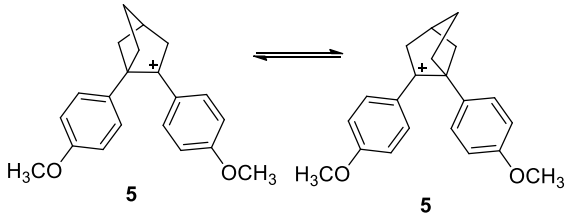
Scheme 1



Over the years, many leading chemists contributed to studies on the nonclassical – classical ion problem. There is a general acceptance that both in usual S_N1 reactions in polar solvents and under stable ion conditions in super acid medium (SbF_5-FSO_3H), the results indicate that tertiary carbocations are best represented by the unsymmetrical classical carbocation and the secondary cation may have nonclassical structure[1].

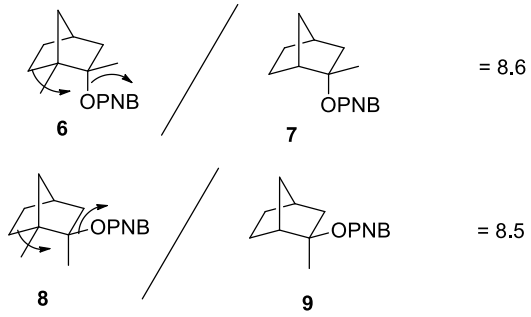
For example, evidences, especially ^{1}H-NMR spectral data, support the existence of the 1,2dianisyl -2-norbornylcation as a rapidly equilibrating pair (Scheme 2). [3]

Scheme 2



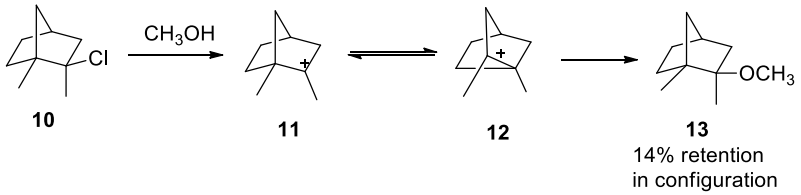
Comparison of the rates of solvolysis of *exo* and *endo*-2-methyl and 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates was expected to provide evidence for anchimeric assistance and symmetrical nonclassical resonance but there was no difference and hence the data were not in accordance with anchimeric assiatance and symmetrical nonclassicalions formation (Scheme 3).[4]

Scheme 3



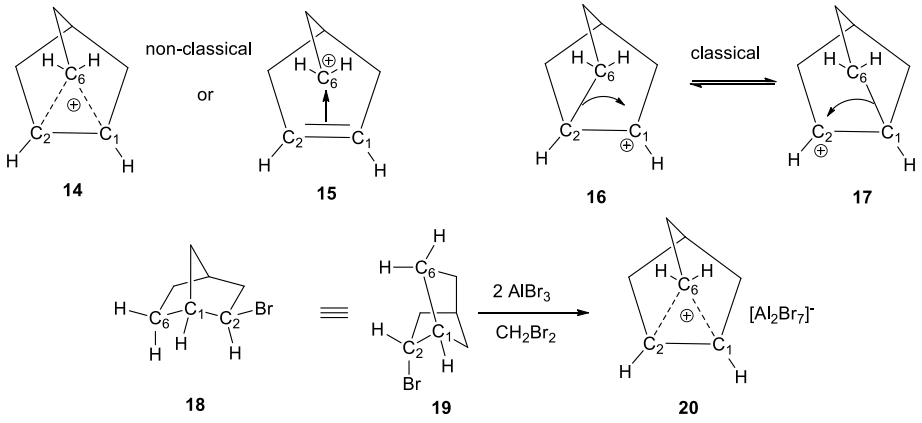
Also, it was reported that the optically active 1,2-dimethyl-exo-norboronylchloride gave up to 14% retention in methanol indicating the capture of the initially formed unsymmetrical cation before complete equilibration (Scheme 4).[5]

Scheme 4



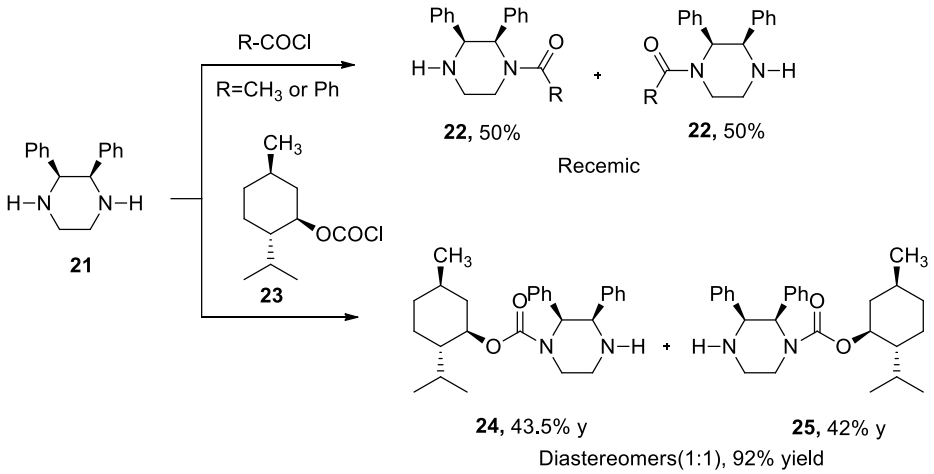
However, more recently, X-ray crystallographic structure analysis of crystals at 40° Kelvin indicated that the data correlated with the bridged nonclassical structure of the norbornyl cation for the $[Al2Br_7]^-$ salt (Scheme 5).[6]

Scheme 5



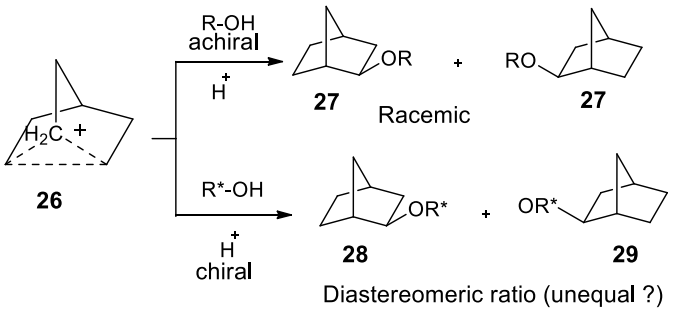
Previously, desymmetrization of symmetric meso 2,3 –diphenyl piperazine was carried out in this laboratory (Scheme 6).[7]

Scheme 6



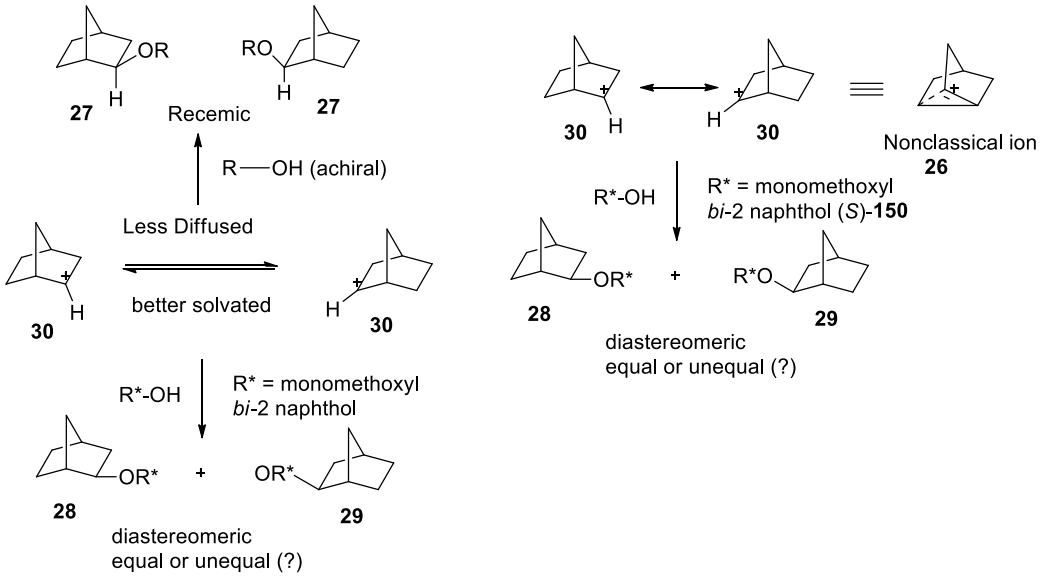
Accordingly, we have decided to carry out such desymmetrization of studies of the symmetrical 2-norbornyl cation using nucliophilic reagents (Scheme 7)

Scheme 7



The less diffused equilibrating unsymmetrical classical 2-norbornyl cations are expected to be solvated by nucliophilic solvents to more extent compared to the diffused unsymmetrical ion (Scheme 8).

Scheme 8



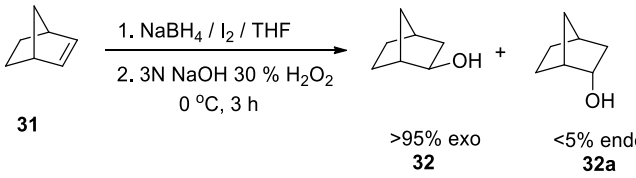
We have examined these possibilities using the chiral monomethoxy-*bi*-2-naphthol (**2**) in the reaction with the 2-norbornylcation. We have also uncovered interesting synthetic transformations of some substituted 2-norbornyl derivatives. These results are described in the next section.

3.2. Results and Discussion

3.2.1 Reaction of 2-norbornyl cation with monomethoxy-*bi*-2-naphthol

The *exo*-2-norbornanol was prepared from commercially available norbornene by hydroboration, using the $NaBH_4/I_2$ system followed by H_2O_2/OH^- oxidation. The desired product **32** was isolated in upto 98% yield as racemic mixture [95:5 (exo:endo)] (Scheme 9).

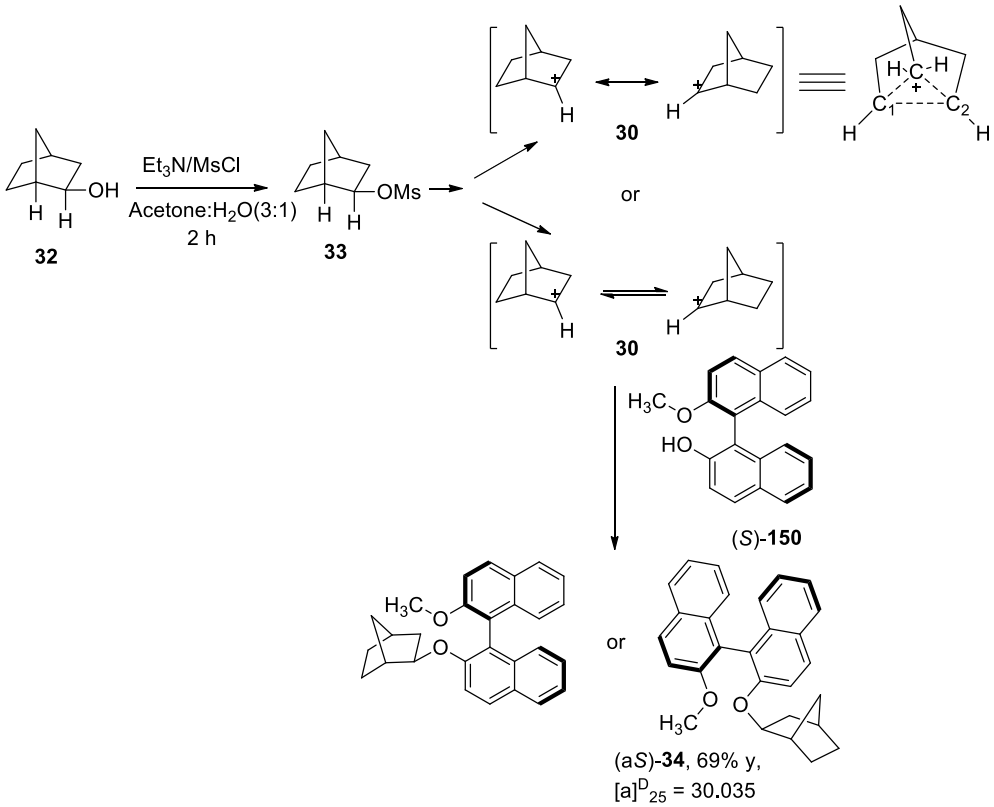
Scheme 9



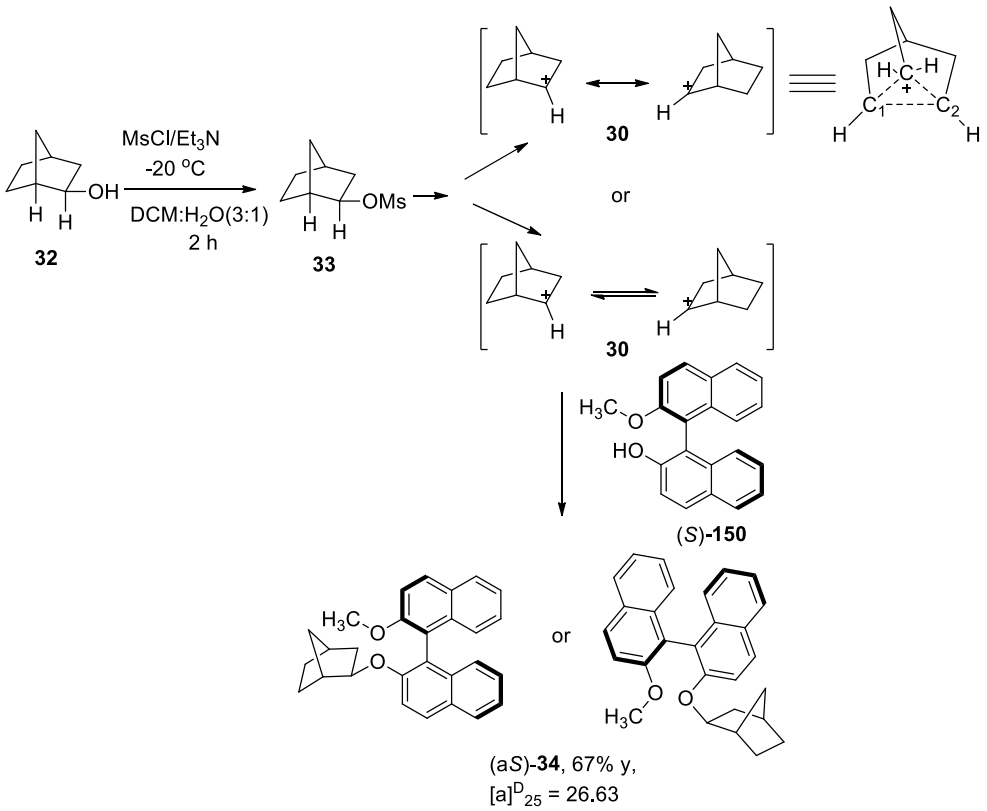
3.2.2 Reaction of *exo*-2-norbornanol 25 with (*S*)-2'methoxy[1,1'-binaphthalen]-2-ol under different conditions

We have carried out the reaction of 2-norbornyl alcohol under different conditions. The corresponding 2-norbornyl-*bi*-2-naphthyloxy products (*S*)-**34** were isolated in 69-72% yield (Scheme 10).

Scheme 10



Scheme 10. Continues…..



Surprisingly, the ^{13}C-NMR spectra gave only 8 lines in the aliphatic region indicating only one of the two expected isomeric products are formed.

Since nucliophilic reaction is expected be faster with the less diffused unsymmetrical classical ion compared to the more diffused nonclassical ion and hence the reactive classical ion is expected to selectively react with the monomethoxy-*bi*-2-naphthol through a low energy transition state with subsequent convertion of the other isomer of the cation to the more reactive cation as there is degenarete equilibrium between the two ions (Scheme 10). However, similar selectivity can be expected if the reaction of the symmetrical nonclassical ion is highly reactive.

Unfortunately, our efforts to obtain crystals suitable for single X-ray structure analysis were not successful, Hence, the configuration of the newly formed stereocentre could not be

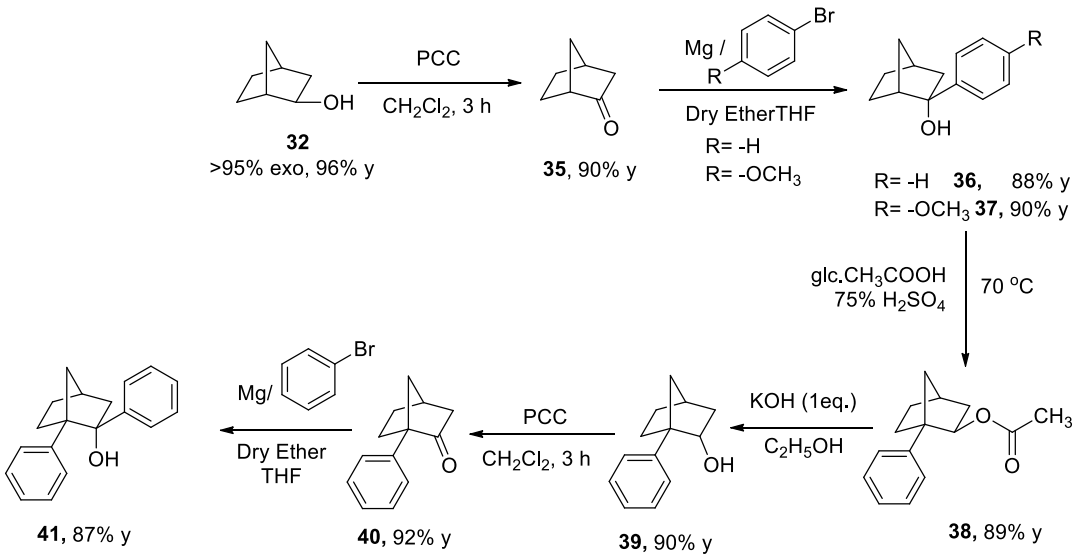
assigned. Further systematic studies using several other chiral nucleophiles may lead to more fruitful results as the selectivities are expected to vary depending on the structure of the chiral nucleophiles.

We have next turned our attention towards preparation of 1,2-diphenyl-*endo*-2-norbornyl derivatives for investigating the reaction monomethyl-*bi*-2-naphthol.

3.2.3 Preparation of 1,2-diphenyl-*endo*-2-norbornanol

The 1,2-diphenyl-*endo*-2-norbornanol **41** was prepared starting from 2-norborneol **32** following closely related reported procedures (Scheme 11)[10]. The 2-norbornanol **32** was converted to 2-norbornanone **35** by PCC oxidation which after Grognard reaction followed by Wagner-Meervin rearrangement and hydrolysis gave the 1-phenyl-2-norbornanone **40.** Grignard reaction of the compound **40** gave the desired endo 1,2-diphenyl-2-norbornanol **41**.

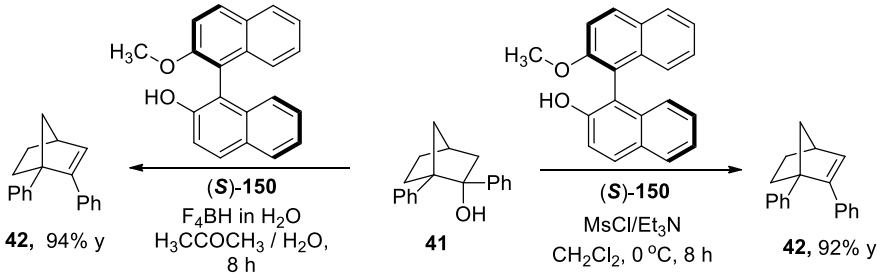
Scheme 11



3.2.4. Reaction of aq.HBF_4 or MsCl in Et_3N in DCM: H_2O or Acetone: H_2O

We have then carried out the reaction 1,2 diphenyl-*exo*-2-norbornanol with HBF_4 in the presence of monomethoxy-*bi*-2-naphthol. Unfortunately, only the olefinic product **42** was obtained. Also, attempted preparation of the mesylate intermediate *in situ* for reaction with monomethyl-*bi*-2-naphthol also gave only the elimination product **42**. Therefore, we did not pursue further studies on this topic (Scheme 12).

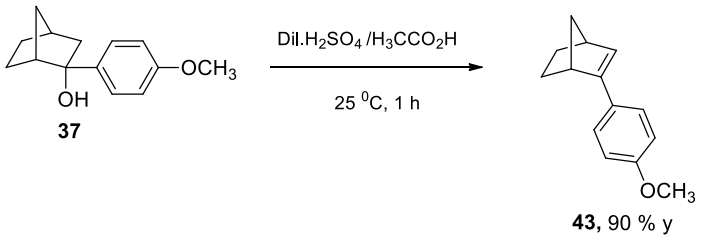
Scheme 12



3.2.5 Reaction of 4-methoxy phenyl-*endo*-2-norbornanol 37

We have observed that the acid catalyzed reaction of *endo*-4-methoxy-2-norbornanol **37** gave the product (1*R*,4*S*)-2-(4-methoxyphenyl)bicycle[2.2.1]hept-2-ene in up to 90% yield (Scheme 13).

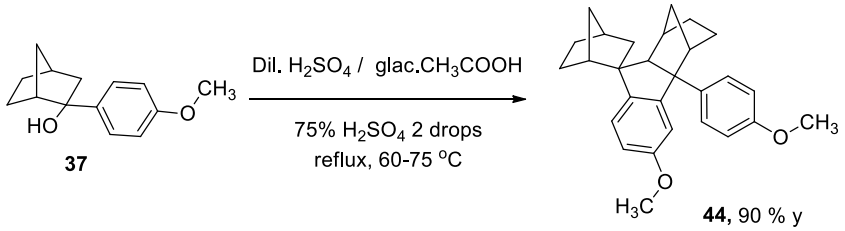
Scheme 13



3.2.6 Reaction of *endo* 2-anisyl norbornyl alcohol under acidic condition

The reaction of 2-(4-methoxyphenyl)-2-norbornanol in glacial aceticacid with 2 drops of 75% H_2SO_4 at 60-75 ºC gave the product **44** in 90% yield. (Scheme 14).

Scheme 14



The structure of the product **44** was further confirmed by X-ray structural analysis (Figure 2).

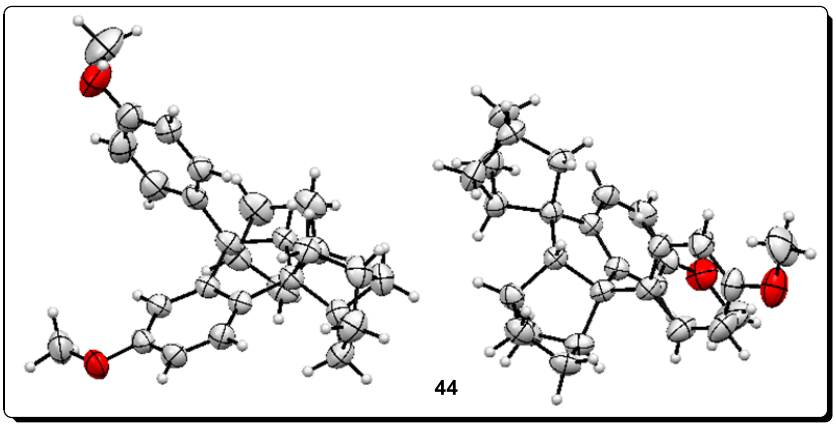
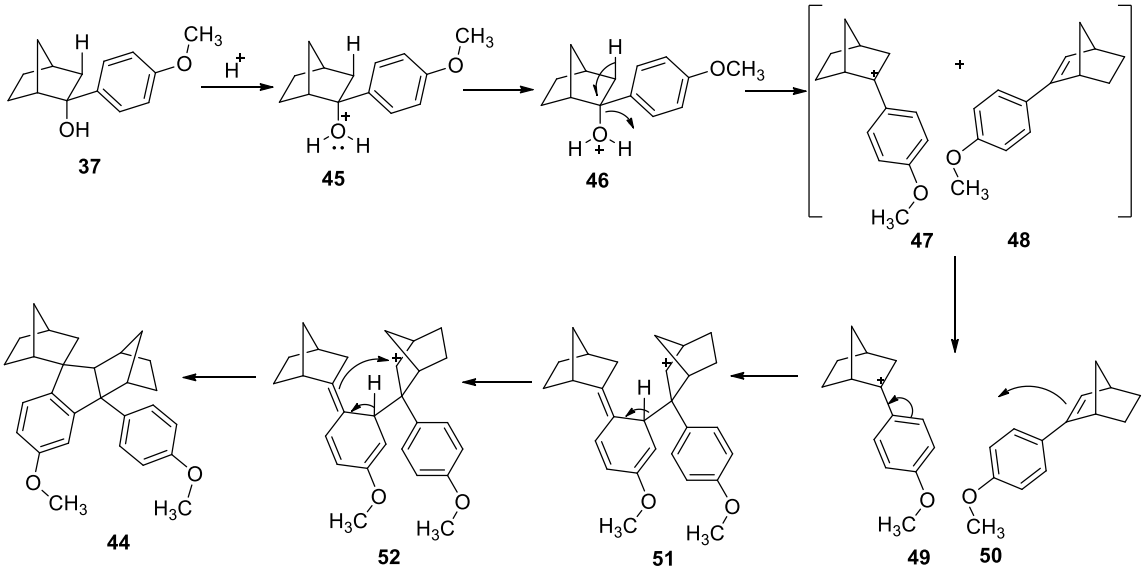


Figure 2. ORTEP representation of the crystal structure **44** (Oak Ridge Thermal Ellipsoids Plot are drawn at 50% probability).

The mechanism outlined in Scheme 15 may be considered to rationalize the product formation. The 2-anisyl-*endo*-2-norbornanol dehydrate in the presence of any acid to gave the electron deficient corbans in the resonance structure of the olefin. The electron rich 2-anisyl -2-norbornene would react with 2-anisyl 2-norbornyl cation to give the spiro compound **44.**

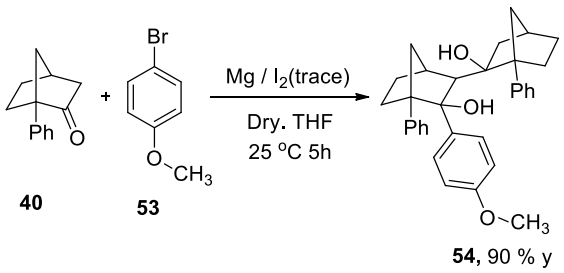
Scheme 15. Plausible mechanism



3.2.7 Reaction of 1-phenyl-2-norbornanone and 4-bromoanisole with in Mg

Also, we have observed that the Grignard reaction of 4-bromoanisole gave the product **54** is upto 90% yield (Scheme 16).

Scheme 16



The structure of the product **54** was further confirmed by X-ray structural analysis (Figure 3)

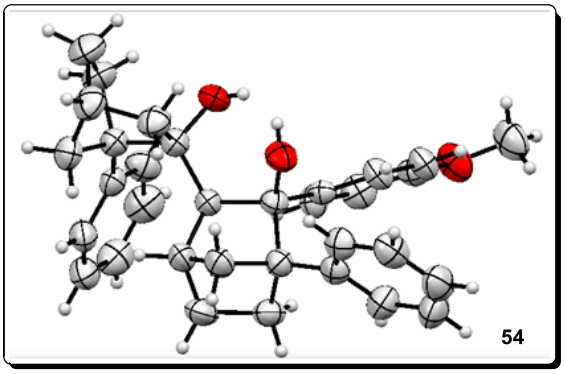
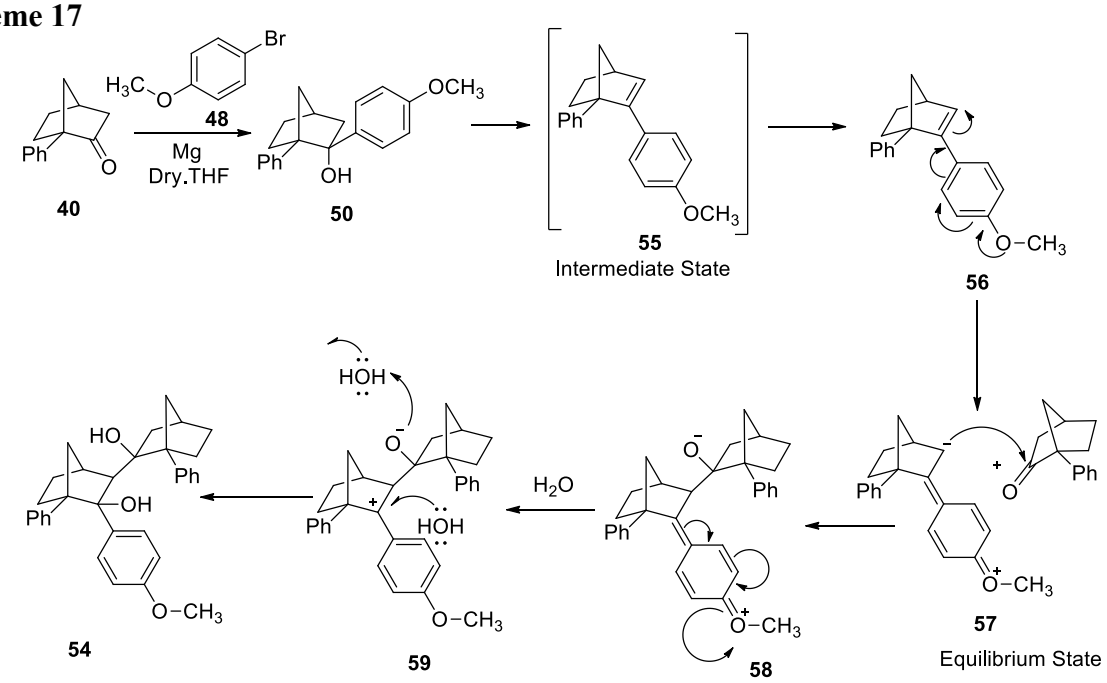


Figure 3. ORTEP representation of the crystal structure **54** (Oak Ridge Thermal Ellipsoids Plot are drawn at 50% probability).

The mechanism outlined in scheme 17 may be considered to rationalize the product formation. The 4-bromoanisole would react with 1-phenyl-2-norbornone to give 1-phenyl 2-anisyl-1,2-norbornanol **50** which after dehydration would react with the 1-phenyl-2-norbornanol to give zwitter ions **58** and **59** leading to the diol product **54** after reaction with water (Scheme 17).

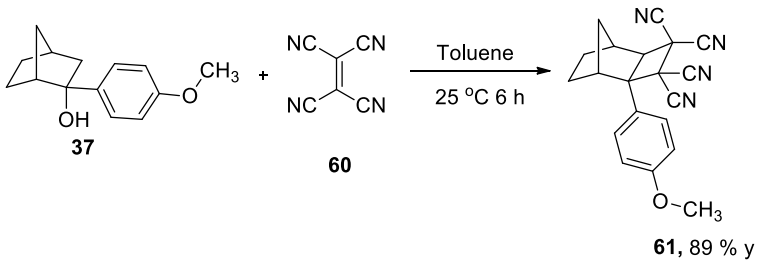
Scheme 17



3.2.8 Reaction of *endo*-2-anisyl norbornanol with tetracyano ethylene

We have observed that the reaction of 2-(4-methoxyphenyl)-*endo*-2-norbornanol and tetracyanoethylene to give the corresponding tricyclic product **61** in 89% yield (Scheme 18).

Scheme 18



The structure of the product **61** was further confirmed by X-ray structural analysis (Figure 4).

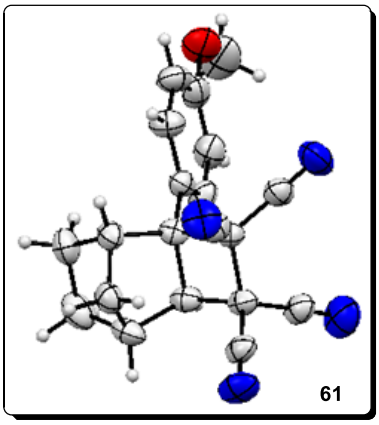
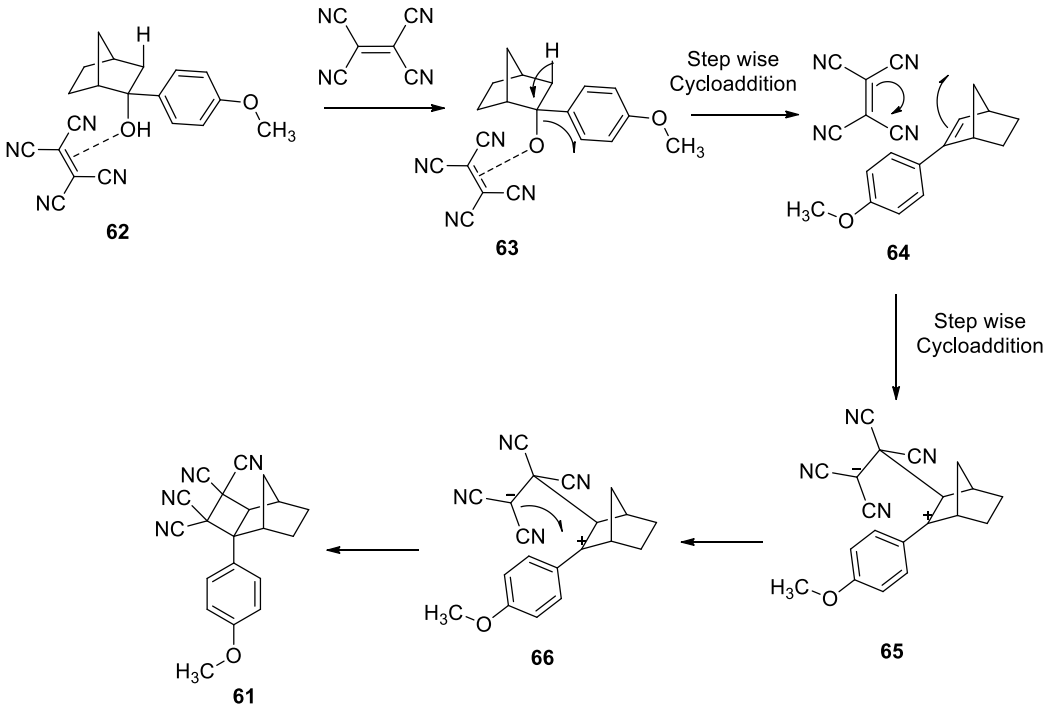


Figure 4. ORTEP representation of the crystal structure **61** (Oak Ridge Thermal Ellipsoids Plot are drawn at 50% probability).

The mechanism outlined in Scheme 19 may be considered to rationalize the product formation. The *endo*-2-anisyl norbornanol would eliminate the water molecule upon interaction

with teracyanoethylene which would then undergo stepwise addition to give the corresponding product **61** (Scheme 19).

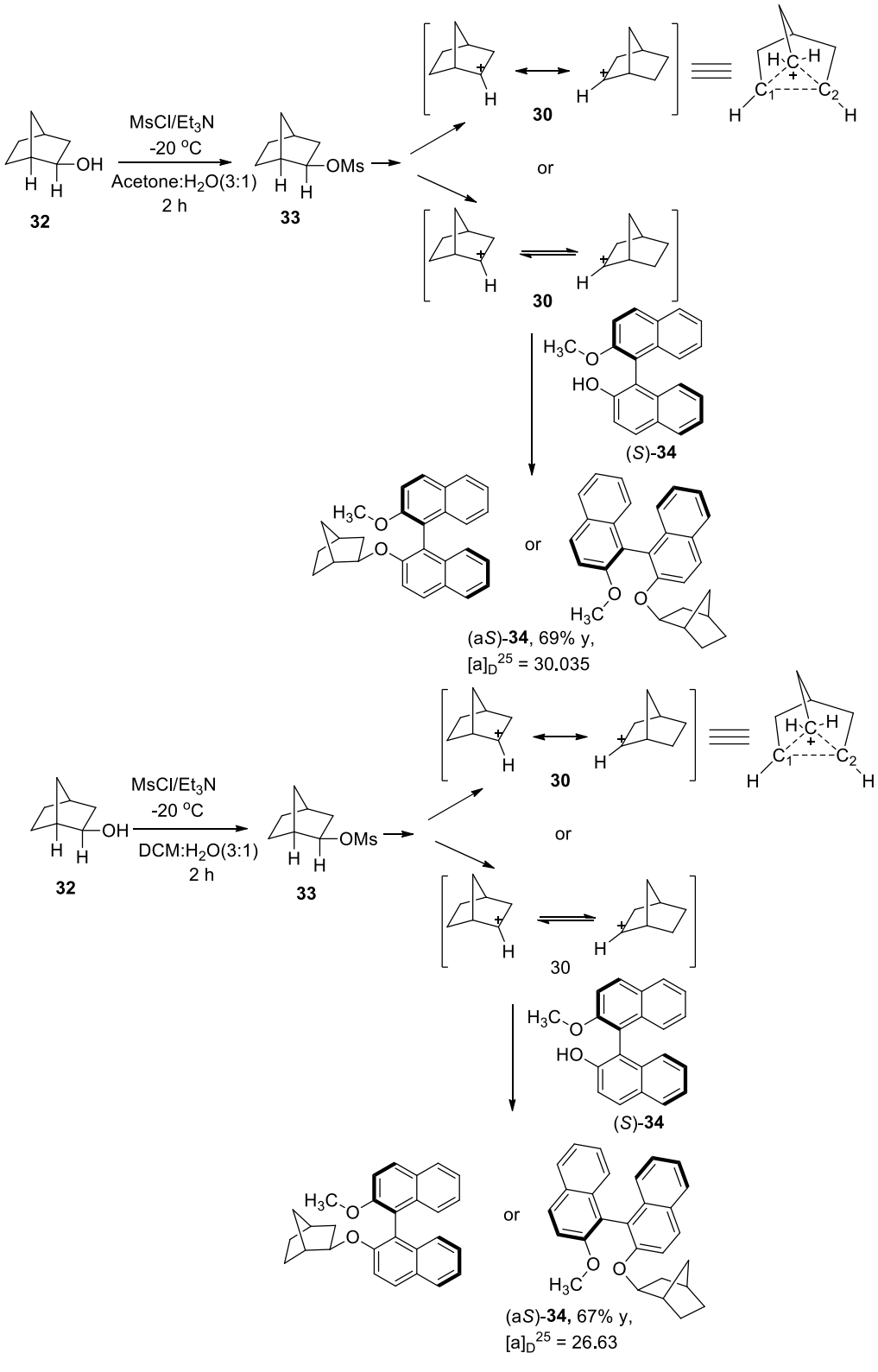
Scheme 19

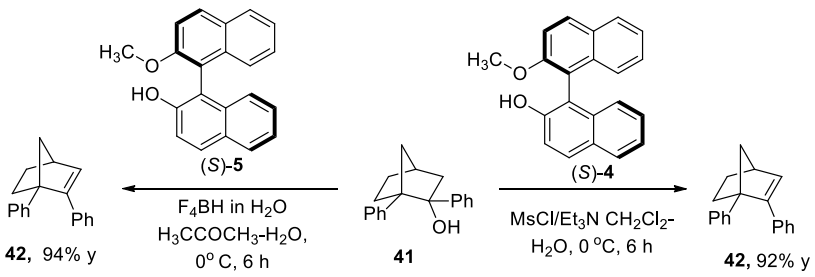


Systematic further investigations on these transformations are required to assess the scope of these reactions for applications in organic synthesis.

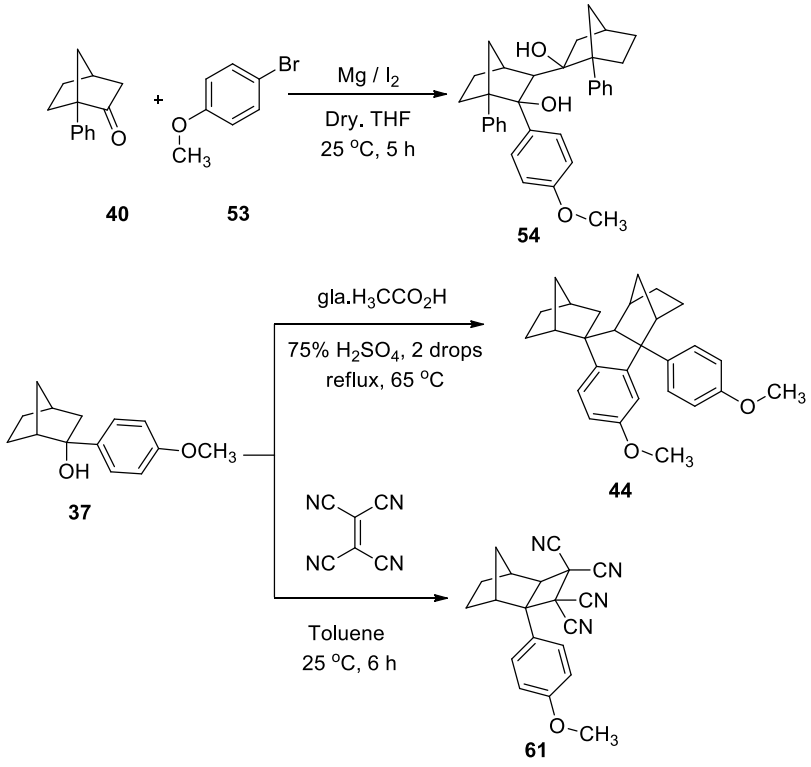
3.3 Conclusion

Preliminary investigations were carried out on the reaction of 2-norbornanol with optically active monomethyl-*bi*-2-naphthol (*S*)-**34** and 1,2-diphenyl-*endo*-2-narboenanol **42.**





We have also uncovered some interesting transformations in the reaction of certain 2-norbornyl systems up to 90% yield.



Systematic further studies on these reactions will be helpful for generalization of the results.

3.4 Experimental Section

General information

Melting points reported in this thesis are uncorrected and were determined using a Super fit capillary point apparatus. IR (KBr) spectra were recorded on JASCO FT-IR Spectrophotometer Model 5300 and the neat IR spectra were recorded on SHIMADZU FT-IR Spectrophotometer Model 8300 with polystyrene as reference. ^{1}H-NMR (400 MHz) and ^{13}CNMR (400 MHz) spectra were recorded on Bruker-Avance-400 spectrometer with chloroform-das solvent and TMS as reference (δ = 0 ppm). The chemical shifts are expressed in δ downfield from the signal of internal TMS. Mass spectral analyses were carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Optical rotations were measured in an AUTOPOL-II automatic polarimeter (readability ± 0.01o). Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250 mμ acme's silica gel-G and GF 254 containing 13% calcium sulfate as binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using acme's silica gel (100-200 mesh) or neutral alumina.

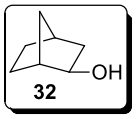
The X-ray diffraction measurements for the compounds were carried out at 298 K on Bruker-Nonius SMART APEX CCD area detector system using graphite monochromated, Mo-Kα (λ = 0.71073 A^{o}) radiation. Primary unit cell constants were determined with a set of 25 narrow frame scans. Intensity data were collected by the ω scan mode. The data were reduced using SAINT program, without applying absorption correction. The refinement for structure was made by full-matrix least-squares on F^2 (SHELX 97).

3.4.1 Preparation of *exo*-2-norboranol

$NaBH_4$ (1.0 g, 28 mmol) was taken in dry THF and I_2 (3.54 gr, 14 mmol, 30 mL dry THF) was added slowly at 0ºC for 1h. A solution of norbornene (2.35 gr, 25 mmol) in dry THF was added to reaction mixture through a cannula at 0 ºC and the mixture was stirred for 3 h. 3 N NaOH (17 mL) and 30% H_2O_2 (17 mL) were added slowly at 0 ºC and stirred at rt for 2h. The content was extracted with diethyl ether (2X25 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the product was obtained in 95% yield.

(1*R*,2*R*,4*S*)-bicyclo[2.2.1]heptan-2-ol

Physical State: Solid



32

Color White

Yield 2.6 g (95%)

IR (KBr) 3432, 3058, 3028, 2868, 1508, 1446, 1309, 1145, 1018, 762, 701 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):3.71-3.70 (d, *J* = 5.6 Hz, 1H), 2.21 (s, 1H), 2.57-2.14 (d, *J* = 6.0 Hz, 1H), 2.10 (s, 1H), 1.63-1.60 (m, 1H), 1.58-1.58 (d, *J* = 2.0 Hz, 1H), 1.55-1.27 (m, 2H), 1.24-1.24 (d, *J* = 2.0 Hz, 1H), 1.0-0.9 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):74.7, 44.1, 42.2, 35.4, 34.3, 28.1, 24.4 ppm.

MS (EI) *m/z* 112 $(M+1)^+$.

Analytical Data calculated for $C_7H_{12}O$: C, 74.95; H, 10.78; O, 14.26.

Found C, 74.60; H, 10.68; O, 13.20.

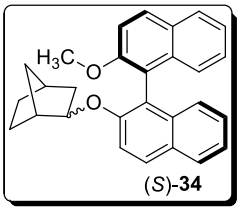
3.4.2 Reaction of *exo*-2-narbornanol with monomethyl–*bi*-2-naphthol in acetone:H_2O system

Methanesulfonylchloride (0.4 mL, 5.3 mmol), *exo*-2-norbornanol (0.56 g, 5 mmol) and triethylamine (0.87 mL, 6.2 mmol) were taken in acetone-water (7:3 mL). The reaction mixture was stirred for 2h at -20 °C. A solution of 1,1'-*bi*-2-naphthylmethylether (1.5 g, 5 mmol, in dry Et_3N (0.8 mL, 6 mmol) was taken in acetone- water (7:3 mL) at 0 °C, and stirred for 1h at rt and added to the reaction mixture through a cannula at 0 °C, stirred for 3h from 0 °C to rt. Saturated NH_4Cl (5 mL) was added and the contenst were extracted with DCM (30 mL). The combined organic layer was dried over Na_2SO_4, the solvent was removed and the residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc.

(*S*)-2-((1*R*,2*R*,4*S*)-bicyclo[2.2.1]heptan-2-yloxy)-2'-methoxy-1,1'-binaphthalene

Physical State: Solid

Color White



(*S*)-**34**

Yield 1.36 g (69%)

mp 58-60 °C

$[\alpha]_D^{25}$ 26.63 (*c* 0.3, $CHCl_3$)

IR (KBr) 3057, 2955, 2872, 1627, 1600, 1512, 1271, 1084, 810, 745cm^{-1}

^{1}H-NMR (400MHz, $CDCl_3$, δ): 8.10-8.04 (d, *J* = 9.0 Hz, 1H), 7.93-7.91 (m, 3H), 7.88-7.86 (d, *J* = 8.6 Hz, 1H), 7.49-7.47 (d, *J* = 8.1 Hz, 2H), 7.38-7.30 (m, 2H), 7.29-7.21 (m, 2H), 7.08-7.06 (d, *J* = 7.9 Hz, 1H), 5.1 (ss, 1H), 3.81 (d, 3H), 3.74-3.73 (q, *J* = 6.9 Hz, 1H), 2.69-2.62 (t, *J* = 5.6 Hz, 1H), 2.13-2.12 (t, *J* = 6.1Hz, 1H), 2.07-

2.05 (d, *J* = 4.8 Hz, 1H), 166-1.65 (m, 1H), 1.58-1.58 (m, 3H) 1.45-1.41 (m,1H), 1.29-1.27 (m, 1H), 1.03-1.00 (m, 2H), 1.01-1.00 (m, 1H) ppm.

^{13}C-NMR (100MHz, $CDCl_3$, δ): 156, 151.7, 134.2, 134.1, 130.7, 129.8, 129.4, 129.2, 128.2, 127.2, 126.5, 125.1, 124.9, 124.1, 123.2, 118, 116.5, 115.3, 114, 74.8, 56.6, 44.1, 42.1, 35.5, 34.5, 28.3, 24.5 ppm.

MS (EI) *m/z* 395$(M+1)^+$

Analytical Data calculated for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64; O, 8.11.

Found C, 85.22; H, 6.60; O, 8.09.

3.4.3 Reaction of *exo*-2-narbornanol with monomethyl–*bi*-2-naphthol in DCM:H_2O system

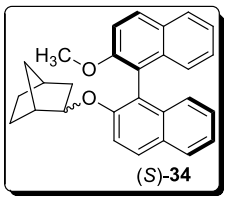
Methanesulfonylchloride (0.4 mL, 5.3 mmol), *exo*-2-norbornanol (0.56 g, 5 mmol) and triethylamine (0.87 mL, 6.2 mmol) were added in dichloromethae-water (7:3 mL). The reaction mixture was stirred for 2 h at -20 °C. The monomethyl–*bi*-2-naphthol (1.5 g, 5 mmol) and dry Et_3N (0.8 mL, 6 mmol) were taken in DCM-H_2O (7:3 mL) at 0 ºC and added through a cannula at 0 ºC and stirred for 3h from 0 °C to rt. The contents were quenched with saturated NH_4Cl solution (5 mL), diluted with ethyl acetate (30 mL) and the organic layer was washed with saturated sodium bicarbonate (10 mL), water (20 mL), brine (20 mL) dried over Na_2SO_4. The solvent was removed and the residue was transferred on a silica gel column using (90:10) hexane/EtOAc.

(*S*)-2-((1*R*,2*R*,4*S*)-bicyclo[2.2.1]heptan-2-yloxy)-2'-methoxy-1,1'-binaphthalene

Physical State: Solid

Color White

Yield 1.32 g (67%)



(*S*)-**34**

mp 58-60 ^{o}C

$[\alpha]_D^{25}$ 30.35 (*c* 0.3, $CHCl_3$)

IR (KBr) 3061, 2934, 2835, 1620, 1592, 1480, 1249, 1089, 895, 810, 746 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.11-8.05 (d, *J* = 8.6 Hz, 1H), 7.92-7.91 (m, 3H), 7.87-7.86 (d, *J* = 8.5 Hz, 1H), 7.49-7.48 (d, *J* = 8.2 Hz, 2H), 7.39-7.31 (m, 2H), 7.29-7.21 (m, 2H), 7.08-7.06 (d, *J* = 7.6 Hz, 1H), 5.1 (ss, 1H), 3.81 (d, 3H), 3.74-3.73 (q, *J* = 7.6 Hz, 1H), 2.69-2.62 (t, *J* = 5.6 Hz, 1H), 2.13-2.12 (t, *J* = 6.8 Hz, 1H), 2.06-2.05 (d, *J* = 4.8 Hz, 1H), 1.67-1.65 (m, 1H), 1.59-1.58 (m, 3H) 1.46-1.41 (m,1H), 1.29-1.27 (m, 1H), 1.03-1.02 (m, 2H), 1.01-1.00 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 156, 151.9, 134.4, 134.1, 130.7, 129.8, 129.4, 129.2, 128.2, 127.2, 126.5, 125.1, 124.9, 124.1, 123.2, 118, 116.5, 115.3, 114, 74.9, 56.6, 44.1, 42.1, 35.6, 34.6, 28.4, 27.2, 24.6 ppm.

MS (EI) *m/z* 395$(M+1)^+$

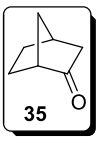
Analytical Data calculated for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64; O, 8.11.

Found C, 85.21; H, 6.62; O, 8.02.

3.4.4 PCC oxidation of *exo*-2-narbornanol

2-Norbornanol (2.24 g, 20 mmol) and pyridyniumchlorochromate (PCC 5.0 g, 23 mmol) were dissolved in dry CH_2Cl_2. The reaction mixture was stirred at rt for 3h. The reaction mixture was filtered by a celite to obtain the product.

Physical State: Liquid



35

Color Colorless

Yield 2.0 g (90%)

IR (KBr) 3032, 2950, 1746, 1520, 1293, 1171, 932, 810, 560 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):2.62-2.61 (d, *J* = 4.4 Hz, 1H), 2.54-2.53 (d, *J*= 4.4 Hz, 1H), 2.02-1.97 (dd, *J* = 12 Hz, 1H), 1.79-1.77 (d, *J* = 8.8 Hz, 1H), 1.75-1.66 (m, 3H), 1.51-1.50 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):218, 53.4, 49.8, 45.1, 37.6, 35.2, 27.1, 24.1 ppm.

MS (EI) *m/z*110 $(M+1)^+$.

Analytical Data calculated for $C_7H_{10}O_1$: C, 76.33; H, 9.15; O, 14.52.

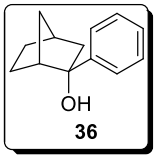
Found C, 75.9; H, 8.62; O, 13.87.

3.4.5 Grignard reaction of 2-narbornanone

Magnesium turnings (0.43 g, 18 mmol) and trace amount of I_2 were stirred at room temperature for 30 min. Then dry THF (10 mL) and bromobenzene (1.8 mL, 18 mmol) were added. The reaction mixture was stirred at rt 1h. The solution of 2-norbornanone (1.65 g, 15 mmol, in dry THF) was added through a cannula and stirred at rt for 6 h. The saturated NH_4Cl (5 mL) was added and the organic layer was extracted with ether (25 mL). The combined organic layers were washed with brine solution (30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc to obtain the product.

(1*R*,2*S*,4*S*)-2-phenylbicyclo[2.2.1]hepan-2-ol

Physical State: Gummy Liquid



36

Color Colorless

Yield 2.5 g (88%)

IR (KBr) (cm^{-1}):3400, 3057, 3026, 2871, 1501, 1446, 1309, 1145, 1019, 761, 701.

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.54-7.52 (q, *J* = 8.0 Hz, 2H), 7.37-7.35 (t, *J* = 8.2 Hz, 2H), 7.34-7.23 (m, 1H), 2.61 (s, 1H), 2.33-2.29 (m, 2H), 2.23-2.17 (m,1H), 1.83 (s, 1H), 1.67-1.63 (m, 1H), 1.6-1.53 (m, 4H), 1.51-1.34 (m,1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):149.3, 128.2, 126.7, 126.0, 80.6, 47.2, 46.7, 38.9, 37.7, 29.2, 22.2, 22.4 ppm.

MS (EI) *m/z* 189$(M+1)^+$.

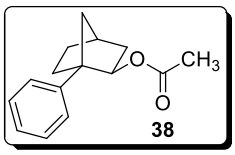
Analytical Data calculated for $C_{13}H_{16}O$: C, 82.94; H, 8.57; O, 8.50.

3.4.6 Wagner-Meervin Rearrangement reaction of 2-phenyl-*endo*-2-nornonanol.

2-Phenyl-*endo*-2-norbornanol (1.10 g, 10 mmol) in glacial acetic acid (5 mL) and one drop of 70 % H_2SO_4 were added and stirred at 75 ºC for 3h. Then saturated $NaHCO_3$ (10 mL) added and stirred at rt for 1 h. The organic phase was extracted with CH_2Cl_2 (2X25 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (95:05) hexane/EtOAc to obtain the product.

(1*S*,2*S*,4*S*)-1-methylbicycle[2.2.1]heptanes-2-yl acetate

Physical State: Liquid



38

Color Colorless

Yield 2.0 g (89 %)

IR (KBr) 2957, 2872, 1736, 1495, 1369, 1243, 1035, 756, 701 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.29-7.27 (d, *J* = 8.1 Hz, 3H), 7.25 (s, 1H), 7.19-7.18 (m, 1H), 2.61 (s, 1H), 5.01-4.99 (t, *J* = 11.7 Hz, 1H), 2.33-2.29 (m, 2H), 2.23-2.17 (m,1H), 1.83 (s, 1H), 1.67-1.63 (m, 1H), 1.6-1.53 (m, 4H), 1.51-1.34 (m,1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):169.6, 141.8, 127.9, 127.4, 126.1, 78.4, 55, 40.9, 38.7, 35.5, 32.28, 30.1, 20.7 ppm.

MS (EI) *m/z* 232 $(M+1)^+$.

Analytical Data calculated for $C_{14}H_{18}O_2$: C, 78.23; H, 7.88; O, 13.89.

Found : C, 78.06; H, 7.69; O, 12.96.

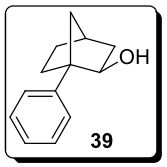
3.4.7 Hydrolysis reaction of 1-phenyl-*exo*-2-norbornyl acetate.

1-Phenyl *exo*-2-norbornylacetate (1.85 g, 8 mmol) and KOH (0.56 g, 10 mmol) were added to ethanol and the reaction mixture stirred at 60 ºC for 3 h. Excess ethanol was removed and the crude product was extracted with CH_2Cl_2. The combined organic phases washed with brine solution (30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc to obtain the pure product.

(1*S*,2*S*,4*S*)-1-phenylbicyclo[2.2.1]heptane-2-ol

Physical State: Solid

Color White



39

Yield 1.35 g (90%)

mp 91-93 ºC

IR (KBr) 3531, 3420, 3026, 2957, 1601, 1494, 1336, 1287, 1046, 761, 619, 531cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.37-7.30 (m, 3H), 7.27-7.23 (s, 2H), 3.83-3.81 (t, *J* = 12.0 Hz, 1H), 2.34 (s, 1H), 2.06-2.03 (d, *J* = 12.0 Hz, 1H), 1.88-1.87 (m, 1H), 1.85-1.82 (m, 2H), 1.83-1.68 (m, 1H), 1.65-1.64 (t, *J* = 4.0 Hz, 1H), 1.63-1.30 (m,1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):142.3, 128.4, 127.7, 126.4, 77.5, 56.5, 41.37, 37.0, 35.4, 32.2, 30.3 ppm.

MS (EI) *m/z* 189 $(M+1)^+$.

Analytical Data calculated for $C_{13}H_{16}O$: C, 82.94; H, 8.57; O, 8.50.

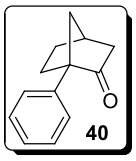
Found C, 82.64; H, 8.25; O, 7.98.

3.4.8 PCC Oxidation reaction of 1-phenyl-*exo*-2-norbornanol

1-Phenyl-*exo*-2-norbornanol (0.94 g, 5 mmol) and pyridyniumchlorochromate (1.34 g, 6.25 mmol) were dissolved in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 3h. The content was filtered by a celite and the CH_2Cl_2 was evaporated to obtain the product.

(1*S*,4*S*)-1-phenylbicyclo[2.2.1]heptane-2-one

Physical State: Solid



40

Color White

Yield 0.86 g (92 %)

IR (KBr) 3032, 2950, 2868, 1746, 1520, 1298, 1170, 932, 810, 560 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.39-7.35 (t, *J* = 68.0 Hz, 2H), 7.31-7.27 (m, 1H), 2.75 (s, 1H), 2.37-2.36 (d, *J*= 4.6 Hz, 1H), 2.36-2.32 (d, *J* =4.0 Hz, 1H), 2.23-2.21 (d, *J* = 8.0 Hz, 1H), 2.13-1.99 (m, 1H), 1.69-1.64 (m, 1H) ppm..

^{13}C-NMR (100MHz, $CDCl_3$, δ): 215.2, 138.4, 128.2, 127.7, 126.9, 61.7, 45.9, 42.2, 33.9, 31.2, 28.9 ppm.

MS (EI) *m/z* 187 $(M+1)^+$

Analytical Data calculated for $C_{13}H_{14}O$: C, 83.83; H, 7.58; O, 8.59.

Found C, 82.90; H, 7.16; O, 8.31.

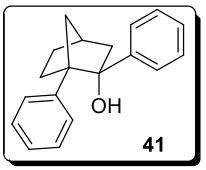
3.4.9 Grignard reaction of 1-phenyl-2-narbornanone

Magnesium turnings (0.086 g, 3.6 mmol) and trace amount of I_2 were taken in dry THF and stirred at room temperature for 30 min. Bromobenzene (0.36 mL, 3.6 mmol) in dry THF was added and stirred at rt 1h. A solution of 1-phenyl-2-norbornanone (0.56 g, 3 mmol) was added through a cannula and stirred at rt for 6h. Saturated NH_4Cl (3 mL) was added and the organic layer was extracted with ether (25 mL). The combined organic layers were washed with brine solution (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc to obtain the product.

(1*S*,2*R*,4*S*)-1,2-diphenyl bicyclo[2.2.1]heptane-2-ol

Physical State: Solid

Color White



41

Yield 0.7 g (87%)

mp 66-68 ºC

IR (KBr) 3560, 3084, 3052, 2953, 2871, 1600, 1494, 1446, 1057, 761, 695, 569 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.43-7.41 (t, *J* = 8.1 Hz, 1H), 7.39-7.35 (t, *J* = 7.9 Hz, 2H), 7.33-7.31 (t, *J* = 6.7 Hz, 3H), 7.28- 7.24 (m, 1H), 6.97- 6.84 (m, 2H), 6.41-6.39 (d, *J* = 6.9 Hz, 1H), 2.77-2.75 (d, *J* = 4.8 Hz, 1H), 2.37- 2.35 (m, 1H), 2.27- 2.26 (m, 1H), 2.24- 2.22 (m, 1H), 2.21- 2.16 (m, 1H), 2.09- 2.05 (m, 1H), 2.04- 2.0 (m, 1H), 1.68- 1.66 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):146.7, 142.7, 127.7, 127.4, 127.3, 127.2, 126.9, 126.4, 125.9, 83.1, 60.8, 47.8, 40.9, 36.0 31.7, 29.9 ppm.

MS (EI) *m/z* 265 $(M+1)^+$

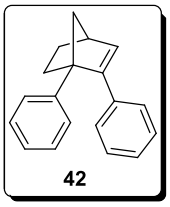
Analytical Data calculated for $C_{19}H_{20}O$: C, 86.32; H, 7.63; O, 6.05.

Found C, 86.28; H, 7.27; O, 6.01.

3.4.10 Reaction of 1,2-diphenyl-*endo*-2-norbornanol with monomethyl-*bi*-2-naphthol in DCM-H_2O solvent system.

Methanesulfonyl chloride (0.2 mL, 2.3 mmol), 1,2-diphenyl-*exo*-2-norbornanol (0.53 g, 2 mmol) and triethylamine (0.3 mL, 2.3 mmol) was taken in acetone-water (7:3 mL), stirred for 2 h at -20 °C. Monomethyl-*bi*-2-naphthol (0.6 g, 2 mmol) and dry Et_3N (0.3 mL, 2.3 mmol) was taken in acetone- water (7:3 mL) at 0 °C, and stirred for 1h at rt and then added mixture through a cannula at 0 °C, stirred for 3h, from 0 °C to rt. Saturated NH_4Cl (3 mL) was added and the organic layer extracted with ethyl acetate (15 mL), dried over Na_2SO_4 and the solvent was removed. The residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc to obtain the product.

(1*S*,4*S*)-1,2-dihenylbicyclo[2.2.1]hept-2-ene


42

Physical State Liquid

Color Colorless

Yield 0.45 g (92%)

IR (KBr) 3064, 3060, 3018, 2950, 2855, 1602, 1498, 1057, 762, 682, 565 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.46-7.37 (t, *J* = 2.0 Hz, 2H), 7.35-2.28 (t, *J* = 2.0 Hz, 2H), 7.28-7.24 (t, *J* = 38.0 Hz, 1H), 7.18-7.08 (m, 3H), 7.07-7.06 (d, *J* = 4.0 Hz, 1H), 6.4 (s,1H), 3.14 (s, 1H), 2.49-2.43 (m, 1H), 2.20-2.15 (t, *J* = 4.0 Hz, 1H), 2.09-2.07 (d, *J* = 80.0 Hz, 1H), 1.82-1.77 (m, 1H), 1.61-1.6 (d, *J* = 8.2 Hz, 1H), 1.38-1.34 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):149.9, 143.2, 136.5, 133.6, 128.3, 128.1, 127.2, 126.2, 126.2, 126.1, 60.1, 56.9, 42.3, 29.2, 28.09 ppm.

MS (EI) *m/z* 247 $(M+1)^+$

3.4.11. Reaction of 1,2-diphenyl-*endo*-2-norbornanol in tetrafluoroboricacid with monomethyl-*bi*-2-naphthol in H_3CCOCH_3-H_2O solvent system.

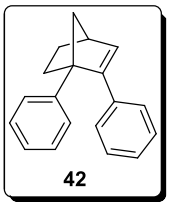
1,2-Diphenyl-*exo*-2-norbornanol (0.53 g, 2 mmol) and tetrafluoroboric acid (2 drops) were taken in H_3CCOCH_3-H_2O (7 mL:3 mL) and stirred for 2 h at 0 °C and added. Monomethyl-*bi*-2-naphthol (0.6 g, 2 mmol) was taken H_3CCOCH_3-H_2O (7 mL:3 mL)) and added through a cannula. The reaction mixture was stirred at 0 °C for 6h. Saturated NH_4Cl (2 mL) and the organic layer was extracted with ethyl acetate (20 mL), dried over Na_2SO_4 and the solvent was removed. The residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc.

(1*S*,4*S*)-1,2-dihenylbicyclo[2.2.1]hept-2-ene

Physical State: Liquid

Color Colorless

Yield 0.46 g (94%)

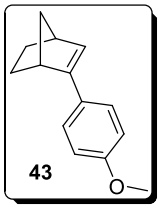


42

2.4.12 Reaction of 2-(4-methoxy phenyl)-*endo*-2-narbornanol

2-(4-Methoxyphenyl)-2-Norbornanol (1.1 g, 5 mmol) in glacial acetic acid (5 mL), one drop of 70 % H_2SO_4 was added and the reaction mixture was stirred at 25 ^oC for 3h. Saturated $NaHCO_3$ (10 mL) added and stirred at rt for 1h. The organic layer was extracted with CH_2Cl_2 (2X25 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on silica gel column using (95:05) hexane/EtOAc.

(1*R*,4*S*)-2-(4-methoxyphenyl)-bicyclo[2.2.1]hept-2-ene



Physical State: Liquid

Color Brown

Yield 0.9 g (90%)

IR (KBr) 3046, 2969, 2871, 2838, 1605, 1506, 1463, 1243, 1183, 1041, 805 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.40-7.38 (d, *J* = 8.0 Hz, 2H), 6.89-6.88 (d, *J* = 4.2 Hz, 2H), 6.19 (s, 1H), 3.84 (s, 3H), 3.78 (s, 1H), 3.0 (s, 1H), 1.82-1.78 (m, 2H), 1.59-1.54 (m, 2H), 1.28-1.26 (m, 1H), 1.22-1.15 (m, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):158.6, 147.2, 128.6, 127.4, 126.1, 113.9, 55.3, 47.9, 43.4, 43.27, 24.9 ppm.

MS (EI) *m/z* 201$(M+1)^+$.

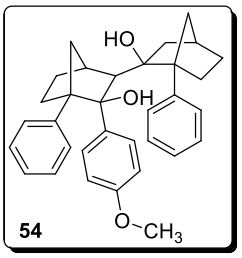
Analytical Data calculated for $C_{14}H_{16}O$: C, 83.96; H, 8.05; O, 7.99.

Found C, 83.91; H, 7.97; O, 7.91.

3.4.13 Reaction of 1-phenyl 2-norbornanone with 4-methoxyphenylbromobenzene.

Magnesium turnings (0.086 g, 3.6 mmol) and trace amount of I_2 were stirred at room temperature for 30 min in dry THF (10 mL). 4-bromoanisole (0.38 mL, 3.6 mmol) in dry THF (10 mL) was added stirred at rt 1h. A solution of 1-phenyl-2-norbornanone (0.56 g, 3 mmol) in dry THF (5 mL) was added through a cannula and stirred at rt for 6h. Saturated NH_4Cl (5 mL) was added, and extracted with ether (25 mL). The combined organic layers were washed with brine solution (30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc to obtain the product.

(1*R*,1*S*,2*R*,*3'S*,4'*S*)-3-(4-methoxyphenyl)-1,4-diphenyl-[2,2-bi(bicycle[2,2,1]heptane)]-2,3-diol.



Physical State: Solid

Color Colorless

Yield 0.3 g (90%)

mp 128-130 °C

IR (KBr) 3555, 2947, 2868, 1510, 1452, 1258, 1070, 1002, 815, 755 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):8.09-8.06 (m, 1H), 7.95-7.89 (m, 3H), 7.59-7.58 (m, 2H), 7.51-7.49 (m, 1H), 7.43-7.41 (m, 2H), 7.39-7.38 (m, 2H), 7.37-7.36 (m, 1H), 7.35-7.34 (m, 1H), 7.33-7.32 (m, 1H), 7.30-7.28 (m, 1H), 7.26-7.22 (m, 1H), 7.11-7.09 (m, 5H), 3.82 (ss, 3H), 4.79-4.72 (bs, 1H), 2.39-2.35 (m, 1H), 2.26.53-2.25 (m, 1H), 1.96-1.95 (m, 2H), 1.94-1.90 (m, 2H), 1.68-1.67 (m, 1H), 1.37-1.36 (m, 3H), 1.34-1.33 (m, 2H), 1.29-1.27 (m, 6H), 1.00-0.86 (m, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):156, 151.3, 146.1, 134, 133.8, 131, 129.8, 129.1, 128.1, 127.9, 127.3, 126.8, 126.7, 124.9, 124.2, 123.2, 117.5, 115.5, 114.3, 114.3, 113.8, 83.6, 57.7, 56.7, 53.5, 50.4, 46.8, 45.6, 43.6, 43.3, 43, 31.2, 29.9, 27, 26.5, 21.7, 21.6, 21.6, 19.8, 19.1, 9.8, 9.3, 8.4 ppm

MS (EI) *m/z* 480$(M+1)^{+}$.

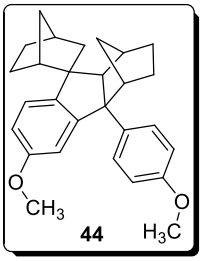
Analytical Data calculated for $C_{33}H_{36}O_3$: C, 82.46; H, 7.55; O, 9.99.

Found C, 82.38; H, 7.45; O, 9.66.

3.4.14 Reaction of 4-methoxyphenyl-*endo*-2-norbornanol.

4-Methoxyphenyl *exo*-2-norbornanol (0.65 g, 3 mmol) was taken in glacial acetic acid (5 mL) and a drop of 70% H_2SO_4 was added and heated at 60º-75ºC for 3h. Saturated $NaHCO_3$ was added and stirred for 1h. The combined organic layers were extracted with DCM (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (90:10) hexane/EtOAc to obtain the product.

(1*R*,1'*R*,2'*S*,4*S*,4a*R*,4'*S*,9a*R*)-6-methoxy-4a-(4-methoxyphenyl)-1,2,3,4,4a,9a-hexahydrospiro[1,4-methanoflourene-9,2'-bicyclo[2.2.1]heptane]



44

Physical State: Solid

Color White

Yield 0.54 g (90%)

mp 146-148 ºC

IR (KBr) 3046, 2969, 2871, 2838, 1605, 1506, 1463, 1243, 1183, 1041, 805cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.26-7.24 (d, *J* = 8.0 Hz, 2H), 7.08-70 (d, *J* = 8.0 Hz, 1H), 6.84-6.82 (d, *J* = 8.0 Hz, 2H), 6.68-6.52 (dd, *J* = 2.4 Hz, 1H), 6.50-6.51 (d, *J* = 4.4 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.92 (s, 1H), 2.92 (s, 1H), 2.75 (s, 1H), 2.74 (s, 1H), 2.56-2.55 (d, *J* = 2.4 Hz, 1H), 2.48 (s, 1H), 2.25 (s, 1H), 1.78-170 (m, 2H), 1.69-1.53 (m, 7H), 1.52-1.50 (d, *J* = 6.8 Hz, 1H), 1.42-1.38 (d, *J* = 6.4 Hz, 1H), 1.27-1.25 (d, *J* = 6.8 Hz, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):158.5, 157.2, 152.4, 140.7, 139.8, 128.8, 125.7, 113.5, 112.1, 108.4, 70.4, 65.3, 53.6, 55.4, 55.1, 45.4, 44.8, 42.1, 38.9, 37.9, 35.5, 29.8, 28.9, 25.7, 24.7 ppm.

MS (EI) *m/z* 401 $(M+1)^+$.

Analytical Data calculated for $C_{28}H_{32}O_2$: C, 83.96; H, 8.05; O, 7.99.

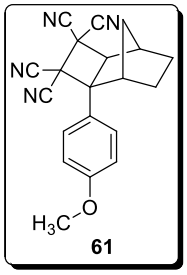
Found C, 83.16; H, 7.89; O, 7.46.

3.4.15 Reaction of 2-(4-methoxy phenyl)-*endo*-2-norbornanol with tetracyanoethylene

4-Methoxyphenyl-*exo*-2-norbornanol (0.66 g, 3 mmol) and tetracyanoethylene (0.38 g, 3 mmol) were taken in toluene at rt and stirred for 6h. The reaction mixture was chromatographed on a silica gel column using (80:20) hexane/EtOAc to obtain the product.

(1*R*,2*S*,6*S*)-2-(4-methoxyphenyl)tricyclo[4.2.1.$0^{2,5}$]nonane-3,3,4,4-tetracarbonitrile.

Physical State: Solid



61

Color Yellow

Yield 0.88 g (89%)

mp 174-176 ºC

IR (KBr) 3046, 2969, 2871, 2838, 1605, 1506, 1463, 1243, 1183, 1041, 805cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ):7.54-7.35 (d, *J* = 8.0 Hz, 1H), 7.16-7.15 (d, *J* = 16.0 Hz, 1H), 7.0-6.86 (m, 2H), 3.86 (m, 3H), 3.56 (s, 1H), 2.99 (s, 1H), 2.70 (s, 2H), 2.19-1.99 (t, *J* = 8.0 Hz, 1H), 1.90-1.75 (m, 1H), 1.58-1.54 (m, 1H), 1.0-0.9 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ):160.4, 128.3, 127.8, 127.5, 116.3, 113.9, 111.4, 109.7, 109.2, 108.7, 62.0, 54.4, 52.6, 44.5, 43.3, 38.2, 36.2, 35.4, 25.7, 25.0 ppm.

MS (EI) *m/z* 329$(M+1)^+$.

Analytical Data calculated for $C_{20}H_{16}N_4O$: C, 73.15; H, 4.96; N, 17.06; O, 4.87.

Found C, 73.02; H, 4.66; N, 17.01; O, 4.57.

3.5 References

1. a) Brown, H. C., Acc. Chem. Res.**1983**, *16*, 432-440.

   b) For a detailed discussion of the 2-norbornyl problem, see: Brown H. C. "The Nonclassical Ion Problem" with comments by Schleyer, P.v. R.; Plenum Press; New York, **1977**.

   c) Brown, H. C., Berneis, H.L.J.; *J. Am. Chem. Soc*. **1953**, *75*, 10.

   d) Eliel, E.L. In "Steric Effects in Organic Chemistry"; Newman, M.S., Ed.; Wiley; New York, 1956; Chapter 2.

2. Winstein, S.; Trifan, D.S. *J. Am. Chem. Soc*. **1952**, *74*, 1147, 1154.

3. Scheyer, P. v. R.; Kleinfelter, D.C.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 479

4. Brown H.C.; Ravindranathan, M.; Rao, C. G.; Chloupek, F. J.; Rai, M. H. *J. Org. Chem.* **1980**, 43, 3667.

5. (a) Goering, H.L.; Humski, K. J. Am. *Chem*. *Soc*. **1968**, *90*, 6213.

6. F. Scholz, D. Himmel, F.W. Heinemann, P.v.R. Schleyer, K. Mayer, I. Krossing, *Science*, **2013**, 341.

7. Periasamy, M, Edukondalu, A., and Ramesh, E, *Chemistry Selec*t, **2017**, *2*, 1-7.

Chapter 4

Synthesis of *Bi*-2-naphthyloxybenzoquinone Derivatives for Applications in Electron Transfer Reactions.

4.1. Introduction

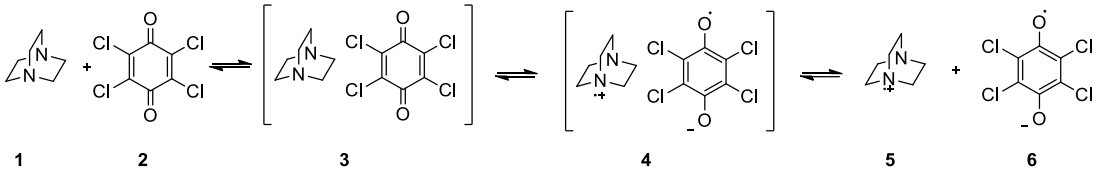
4.1.1 Reactions of amines with *p*-Chloranil.

Several organic donors with acceptors form charge transfer complexes. In some cases, charge transfer leads to formation of anion radicals and cation radicals. Kochi *et. al*[1] reviewed such electron-transfer reactions of organic electron donors and acceptors in 2008. They proposed a model based on the van der Waals radii of electron donors and acceptor.[2] The molecular interactions in outer-sphere processes are viewed as between donor and acceptor separated beyond their van der Waals radii.

Whereas in inner-sphere complexes the distance between donor and acceptor is likely to be less than their van der Waals radii and hence in these complexes the donor/acceptor are packed closely with enhanced interactions.[3] Therefore, sterically hindered donor/acceptor complexes are expected to form outer-sphere complexes, while less sterically hindered donor and acceptor complexes would prefer to form inner-sphere complexes.[4]

Formation of stable radical cation of 1,4-diazabicyclo[2.2.2] octane (DABCO) **1** was reported in 1965.[5] It is stable due to the through-space interaction of nitrogen orbitals.[6] In 1977, the charge transfer (CT) complex **4** was reported in the reaction of DABCO with *p*-chloranil **2**.[7] Also, the CT complex was considered to be in equilibrium with the electron transfer (ET) complex and diradicals radical cation (**5**)-anion (**6**) pair (Scheme 1). The esr signals were found to be stronger in more polar solvent such as THF compared to benzene (Scheme 1).

Scheme 1

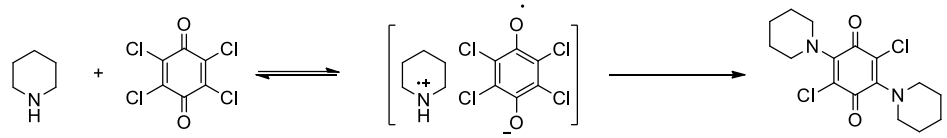


1 2 3 4 5 6

The electron transfer complex **4** exhibited one line ESR spectrum. In this case, the hyperfine coupling was not observed. Presumably, the paramagnetic species **4** is still in a complexed form. In 1957, the line broadening of ESR spectra of naphthalenide ion was observed when excess naphthalene was added.[8] The reported rate constants for electron transfer between naphthalene negative ion and naphthalene are in the range 10^7-10^9 liter mole^{-1}sec.$^{-1}$ Such line broadening was also reported in the case of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) radical anion with DDQ with fast exchange rate constant 2.5 x 10^9 M^{-1} S^{-1} and activation energy of 1.6 kcal mol^{-1} at 23 °C.[1]

Previously, it was observed in this laboratory that the reaction of *p*-Chloranil **2** with secondary amine **7** in DCM or PC solvent gives an ESR signal. The intensity of signal decreases with time and disappears in 24h with formation of the aminoquinone **9** product (Scheme 2).[9]

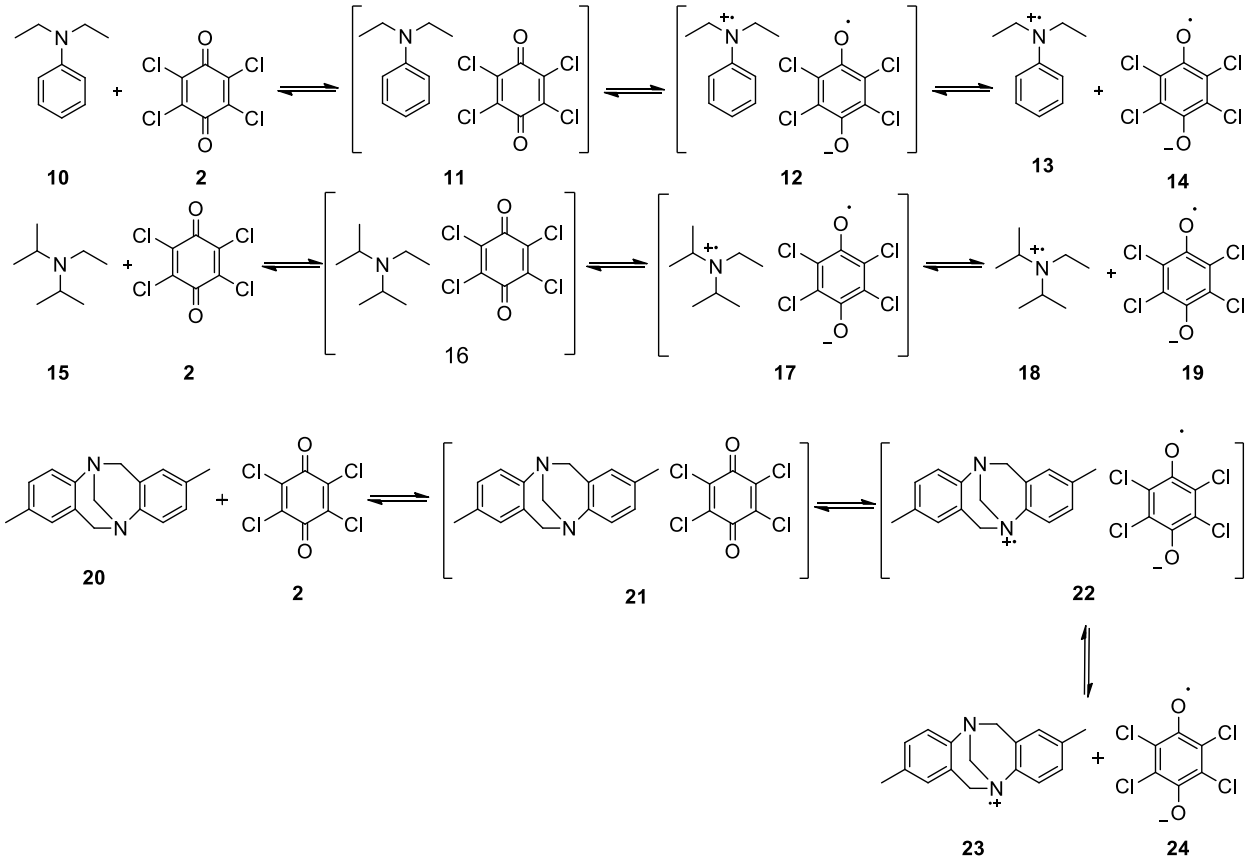
Scheme 2



7 2 8 9

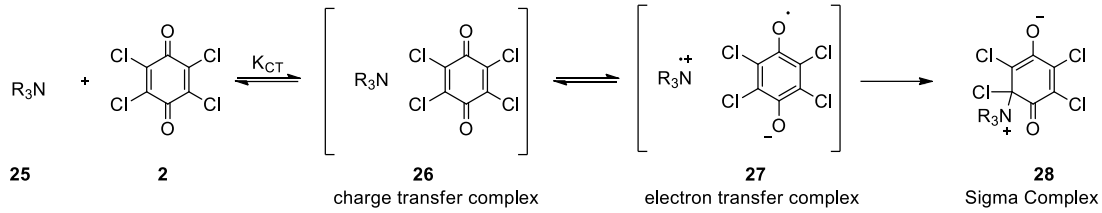
It was also observed that the tertiary amines **10**, **15** and **20** form charge transfer complexes with *p*-Chloranil in PC solvent. The reaction of amine **15** with *p*-Chloranil gave very strong ESR signal and the intensity of ESR signal decreased with time (Chart 1).[9-10]

Chart 1



The nature of the complex, paramagnetic species and the reason for the reduction of ESR signal intensity with time are not clearly understood. One possibility is slow formation of a diamagnetic 1,4 addition product **28** (Scheme 4) as the reactivity of the tertiary amines and secondary amines are expected to be similar. However, could not isolate any such product with tertiary amine. Presumably, the charge transfer complex formed may decompose to give the starting amine and *p*-chloranil upon work up (Scheme 3).

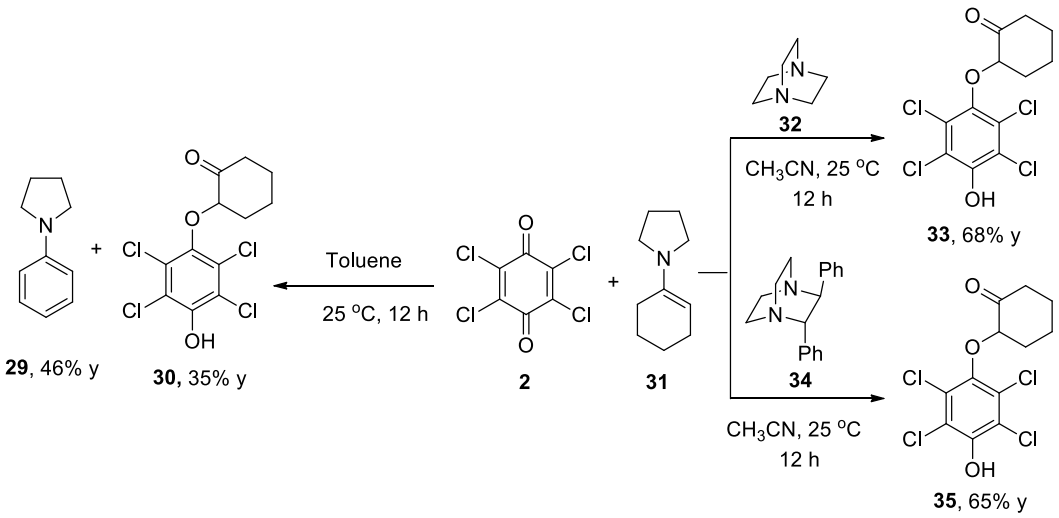
Scheme 3



Unfortunately, such complexes could not be crystallized under the present reaction conditions. Although, the nature of the electron transfer complexes is not clearly understood, such complexes are readily accessible as illustrated here.

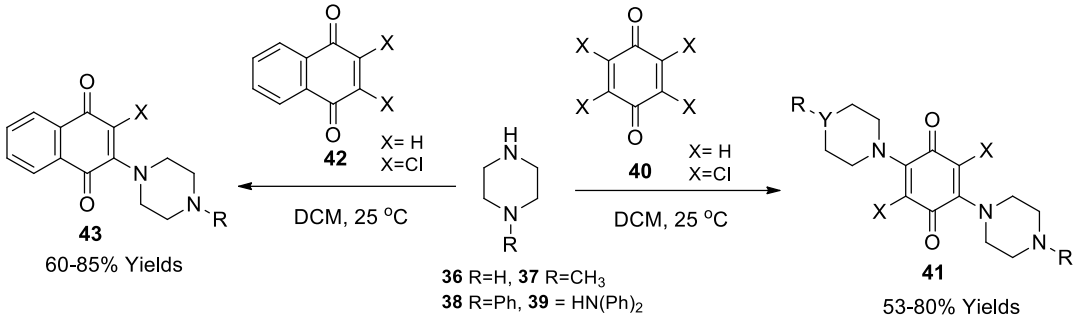
It was reported in this laboratory that the enamine **31** reacts with Chloranil **2** and DABCO derivatives **33** at room temperature to give the compound **33** and **35** in 65-68% yields. It was also observed that the enamine becomes aromatized to *N*-phenylpyrrolidine **29** in 46% yield besides the formation of compound **30** in 35% yield in toluene at 25 °C (Scheme 4).

Scheme 4



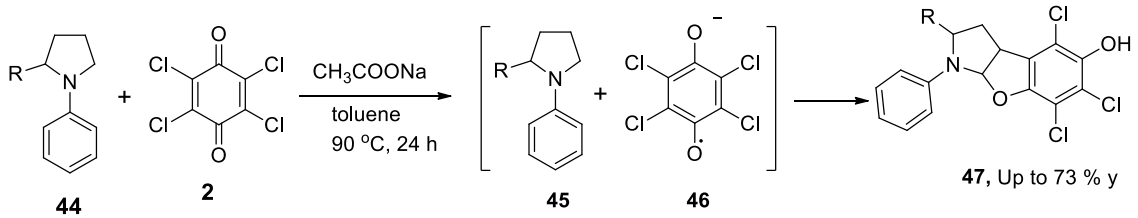
It was also found that the N-substituted piperazine derivatives **42** reacts with 1,4-naphthaquinone **43** in DCM solvent to give paramagnetic species via single electron transfer mechanism. In this case, the corresponding 1,4-substitution products were obtained (Scheme 5).

Scheme 5



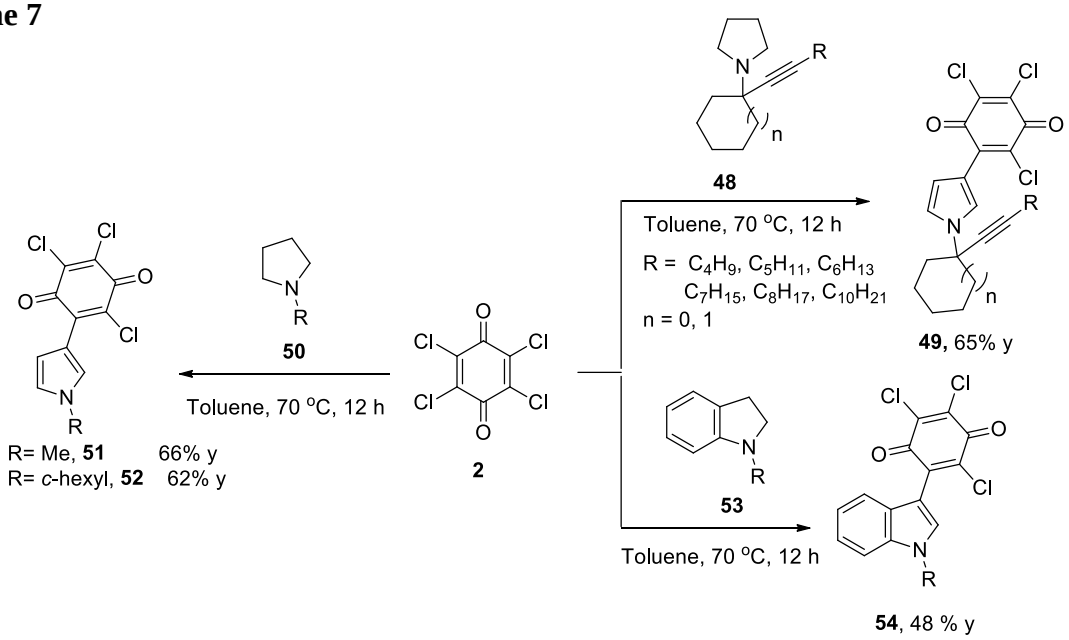
The cyclic products of **47** are formed in the reaction of *N*-arylpyrrolidine and *p*-Chloranil in toluene solvent at 90 °C (Scheme 6)

Scheme 6



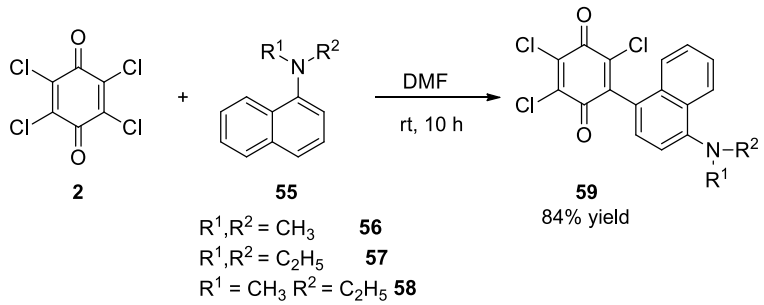
Very recently, it was observed that the reaction of propargylamine derivatives **48** with *p*-Chloranil gave the corresponding substituted pyrroles **49** through dehydrogenation of enamines (scheme 7).[11]

Scheme 7



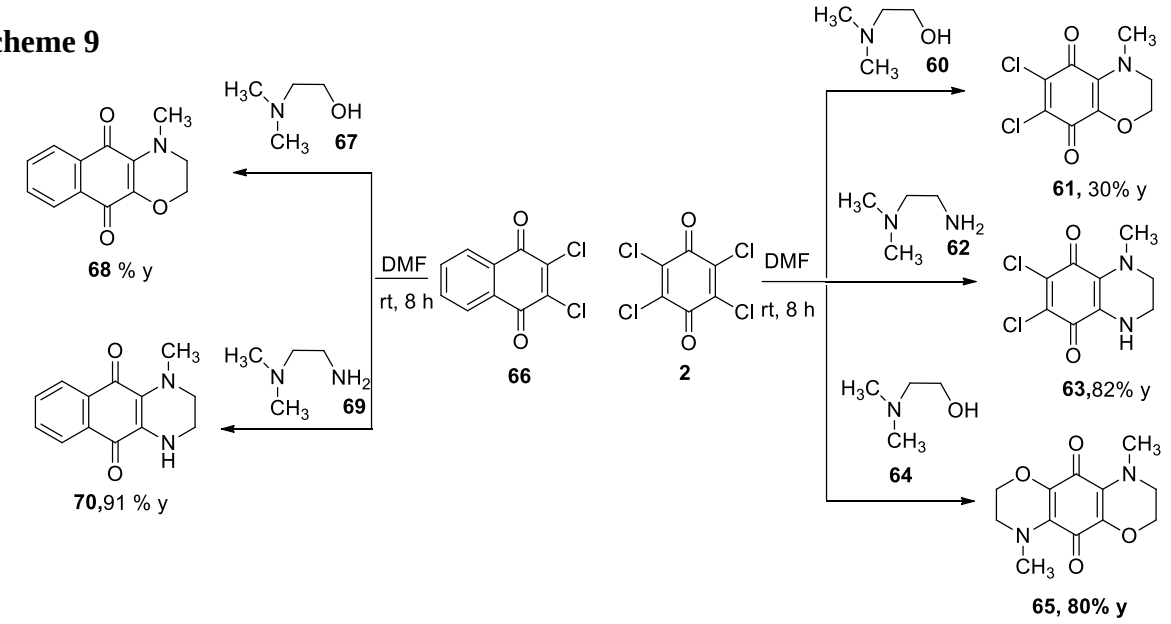
Systematic studies on the reaction of tertiary aryl amines, acyclic tertiary amino alcohols, cyclic tertiary amino alcohols and cyclic secondary amino alcohols with *p*-Chloranil were also carried out in this laboratory. The reactions gave paramagnetic intermediates but the esr signal strength decreased with time, indicating that the initially formed paramagnetic intermediates participate in further reactions. Accordingly, we have developed several new synthetic methodswere developed in this laboratory based on these electron transfer reactions. For example, a method for the synthesis of monosubstituted *N,N'*- dialkyl-1-naphthylaminoquinone derivatives by the reactions of different *N,N*-dialkylnapthalene **59** derivatives with *p*-chloranil was developed (Scheme 8)

Scheme 8



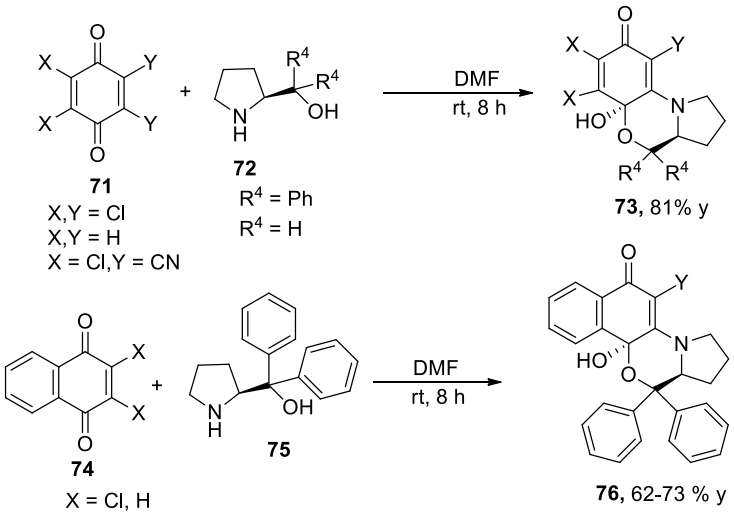
Further, a method for the synthesis of fused aminoquinone derivatives by the reaction of *p*-Chloranil with *N,N*-dimethylaminoethanol was developed.(Scheme 9)

Scheme 9



Also, a new method for the synthesis of chiral tricyclic products using quinone derivatives and different cyclic secondary amino alcohols was developed (Scheme 10)

Scheme 10



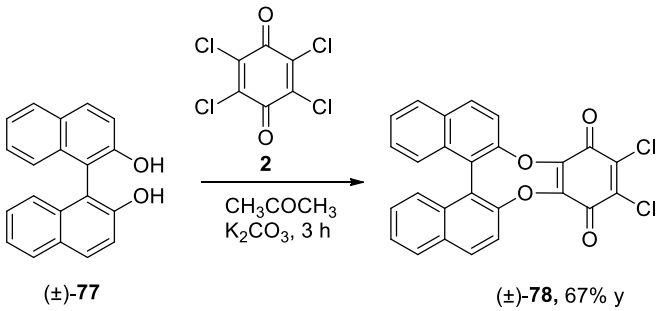
We have decided to explore the preparation of new quinone derivatives by the reaction of *bi*-2-naphthol derivatives with *p*-Chloranil for use in electron transfer reaction. The results are discussed in the next section.

4.2. Results and Discussion

4.2.1 Reaction of *bi*-2-naphthol with *p*-Chloranil

We have observed that the reaction of *bi*-2-naphthol with *p*-Chloranil gives the corresponding *bi*-2-naphthyloxy substituted benzoquinone (±)-**78** is 67% yield (Scheme 11).

Scheme 11



The structure of the product (±)-**78** was further confirmed by X-ray structural analysis.

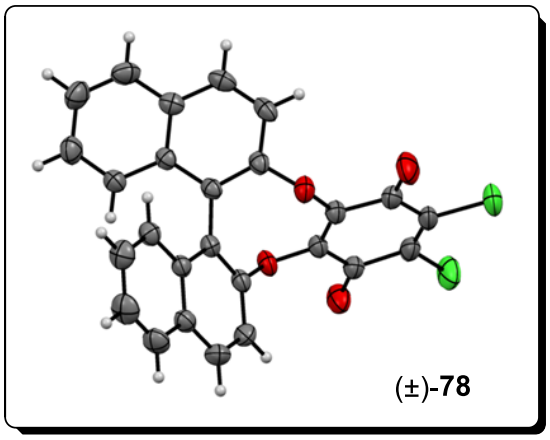
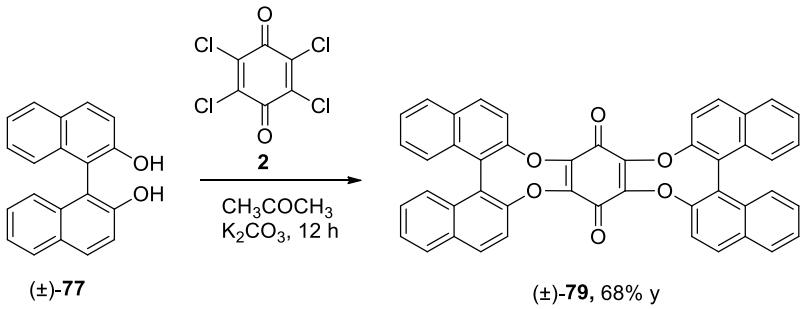


Figure 1. ORTEP representation of the crystal structure (±)-**78** (Oak Ridge Thermal Ellipsoids Plot are drawn at 50% probability).

When the reaction of *bi*-2-naphthol with *p*-chloranil was carried out in the 2:1 ratio, the *bis*-bi-2-naphthyloxybenzoquinone (±)-**79** was obtained in 68% yield (Scheme 12).

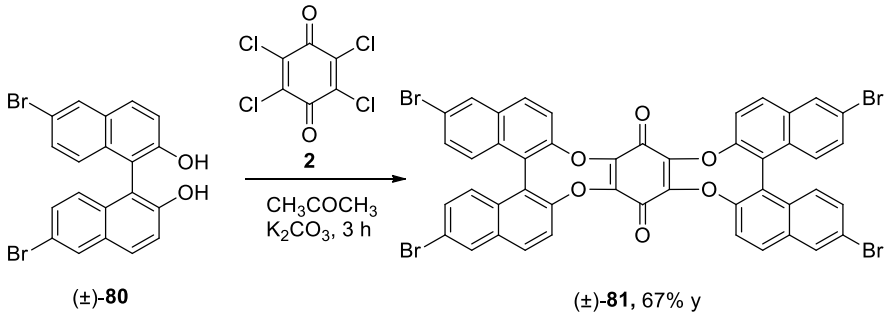
Scheme 12



(±)-**77** (±)-**79,** 68% y

Similarly, the use of (±) 6,6'-dibromo-*bi*-2-naphthol with place of (±) *bi*-2-naphthol gave the corresponding *bis*-6,6'-dibromo-*bi*-2-naphthylhyloxybenzoquinone **(±)-81** in 67% yield (Scheme 13).

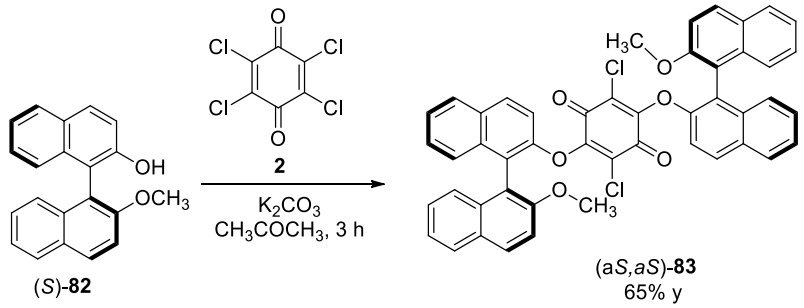
Scheme 13



(±)-**80** (±)-**81,** 67% y

We have also observed that the chiral(*S*)-monomethoxy-*bi*-2-naphthol (*S*)-**82** gave the product (a*S*,a*S*)-**83** in 65% yield (Scheme 14).

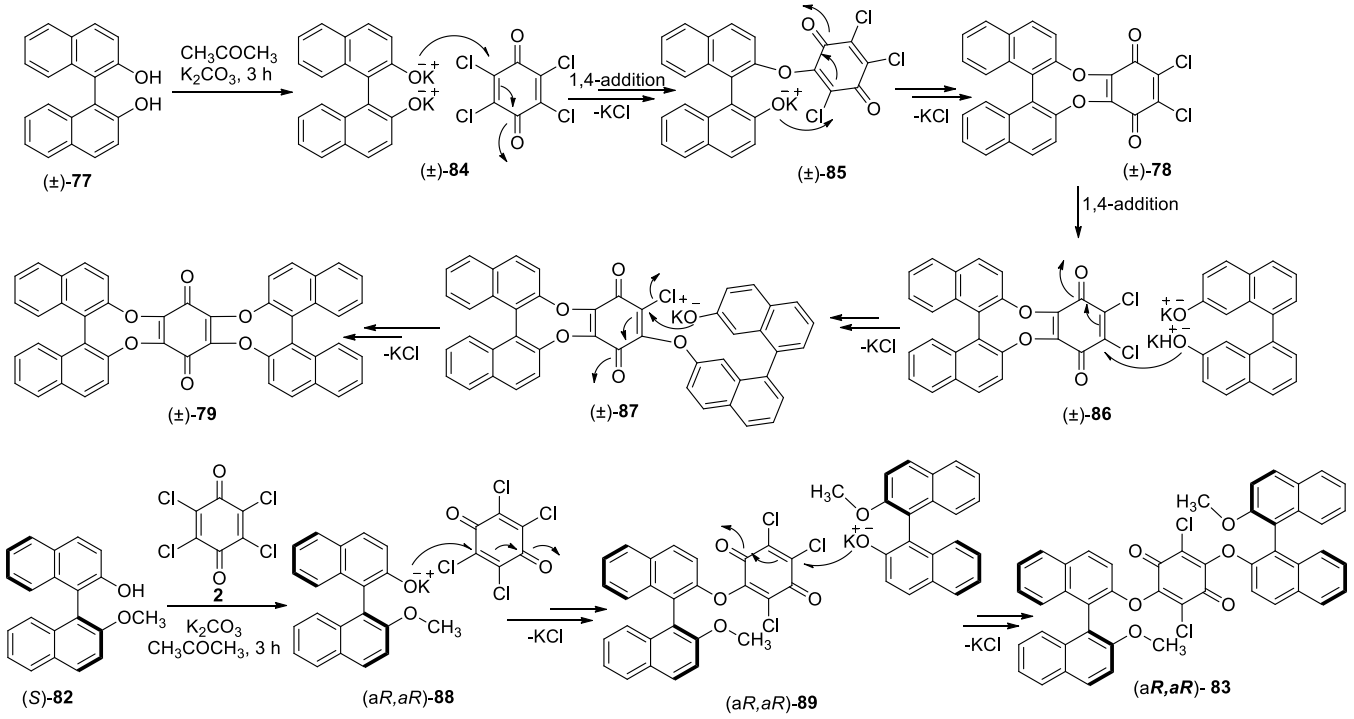
Scheme 14



(*S*)-**82** (a*S*,*aS*)-**83** 65% y

The reaction mechanisms outlined in chart may be considered to rationalize these transformations (Chart 2).

Chart 2. Plausible mechanism

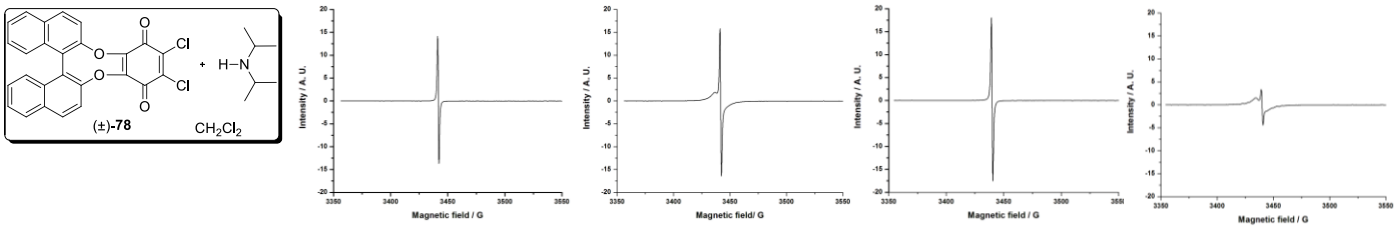


We have then carried out the electron transfer reactions of these *bis*-bi-2-naphthyloxybenzoquinone derivatives using amines.

4.2.2 Electron transfer reactions of *bi*-2-naphthyloxybenzoquinone with amines

We have undertaken ESR spectral studies using diisopropylamine, DABCO or diisopropylethylamine to investigate the electron acceptor nature of the *bi*-2-naphththyloxybenzoquinone derivatives. The ESR spectra obtained for the reaction mixture of *bi*-2-naphthyloxydichlorobenzoquinone **78** with diisopropylamine is presented in Figure 1. Initially there is increase in intensity followed by decrease with time. Presumably, the reaction is slow but after sometime signal strength decreases due to formation of corresponding charge transfer complex.

Figure 2 ESR spectra of dichloro-*bi*-2-naphthyloxybenzoquinone (±)-**78** with DIA in DCM[a]

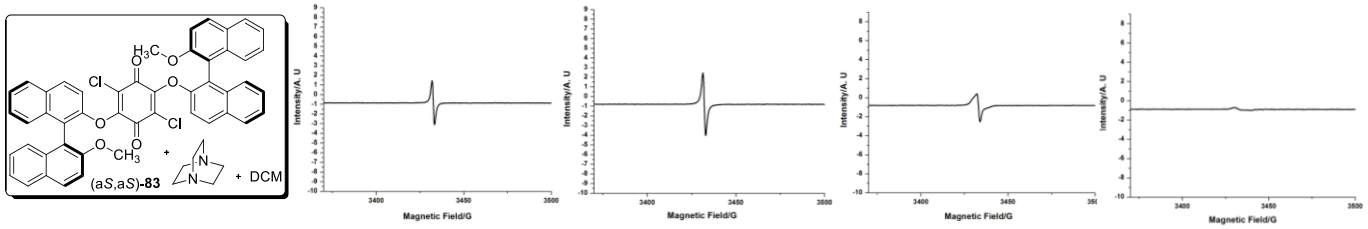


1 h 6 h 12 h 24 h

[a]Experiment in the ESR tube by mixing dichloro-*bi*-2-naphthyloxybenzoquinone (±)-**78** (0.02 mmol) with DIA (0.02 mmol) in DCM solvent.

The ESR spectrum for the reaction of the dichloro-*bi*-2-naphthyloxydichlorobezoquinone (±)-**78** with DABCO is presented in Figure 3. In this case the signal strength is somewhat low indicating the sterically hindered nature of the benzoquinone derivatives.

Figure 3 ESR spectra of *bis*-dichloro-*bi*-2-naphthylmethoxybenzoquinone (a*S*,a*S*)-**83** with DABCO in DCM[a]

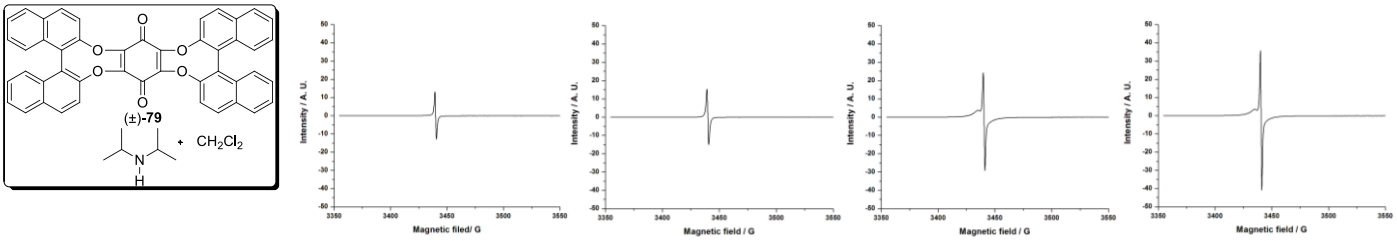


1 h 6 h 12 h 24 h

[a]Experiment in the ESR tube by mixing *bis*-dichloro-*bi*-2-naphthylmethoxybenzoquinone (a*S*,a*S*)-**83** (0.02 mmol) with DABCO (0.02 mmol) in DCM solvent.

The ESR spectra obtained for the reaction of the of *bis*-*bi*-2-naphthyloxybezoquinone in DCM and PC are presented in Figure **4** and **5**. Whereas the signal strength slowly increases in DCM solvent (Figure 4), in the more polar PC solvent the initial stronger ESR initial signal becomes less intense presumbly with the formation of the corresponding charge transfer complex (Figure 5).

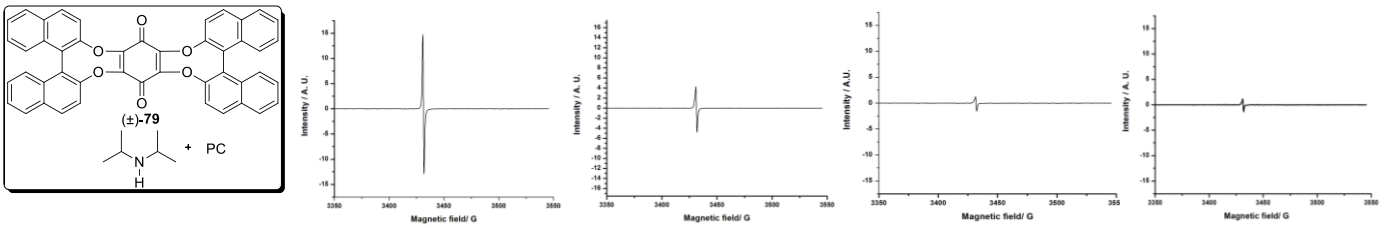
Figure 4 ESR spectra of *bis-bi*-2-naphthyloxybezoquinone **(±)-79** with DIA in DCM[a]



1 h 6 h 12 h 24 h

[a]Experiment in the ESR tube by mixing *bis-bi*-2-naphthyloxybezoquinone **(±)-79** (0.02 mmol) with DIA (0.02 mmol) in DCM solvent (0.02 mmol).

Figure 5 ESR spectra of *bis-bi*-2-naphthyloxybezoquinone **(±)-79** with DIA in DCM.

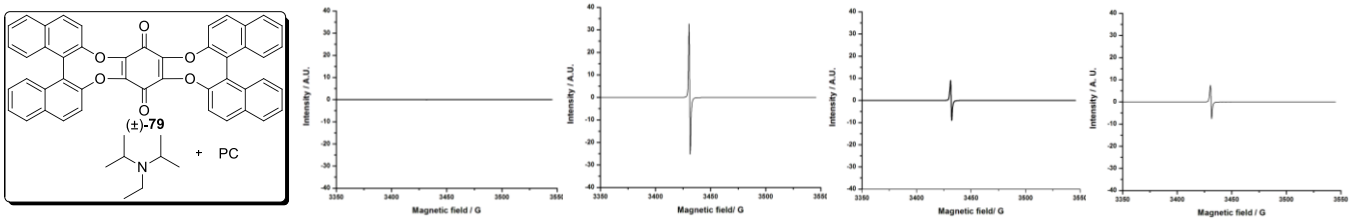


1h 5h 12h 24 h

[a]Experiment in the ESR tube by mixing *bis-bi*-2-naphthyloxybezoquinone (±)-**79** (0.02 mmol) with DIA (0.02mmol) in DCM solvent.

In the case of sterically hindered diisopropylethylamine, the reaction is very slow but even here the ESR signal strength decreased with time.

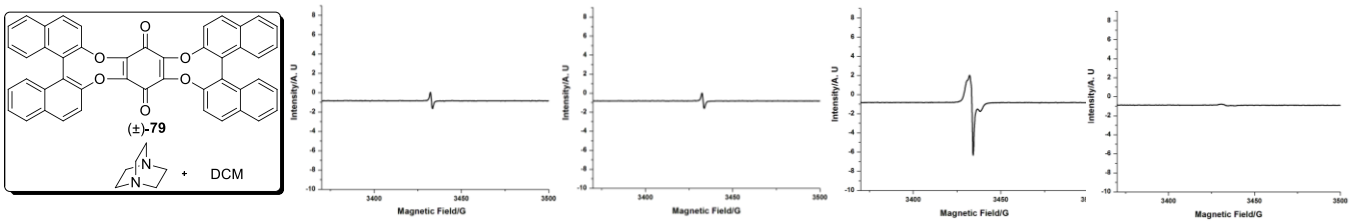
Figure 6 ESR spectra of *bis-bi*-2-naphthyloxybezoquinone **(±)-79** in propelenecarbonate (PC)[a]



1 h 5 h 12 h 24 h

[a]Experiment in the ESR tube by mixing *bis-bi*-2-naphthyloxybezoquinone **(±)-79** (0.02 mmol) with ethyl diisopropyaamine(0.02 mmol) in PC solvent.

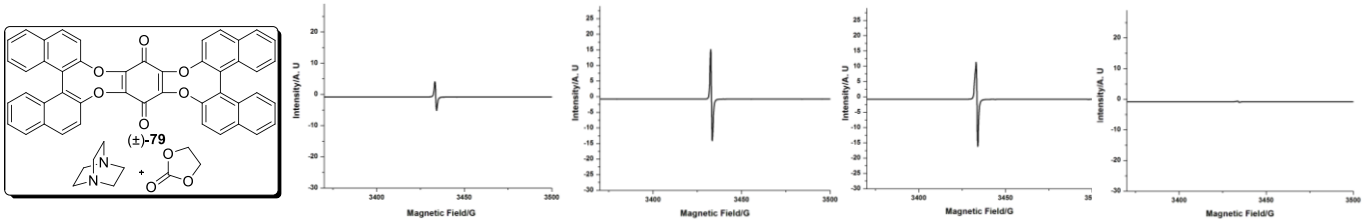
Figure 7 ESR spectra of *bis*-*bi*-2-naphthyloxybezoquinone (±)-**79** with DABCO in DCM[a]



1 h 2 h 5 h 24 h

[a]Experiment in the ESR tube by *bis*-*bi*-2-naphthyloxybezoquinone **(±)-79** (0.02 mmol) with dabco(0.02 mmol) in DCM solvent.

Figure 8 ESR spectra of *bis*-*bi*-2-naphthyloxybezoquinone **(±)-79** in DABCO in PC[a]



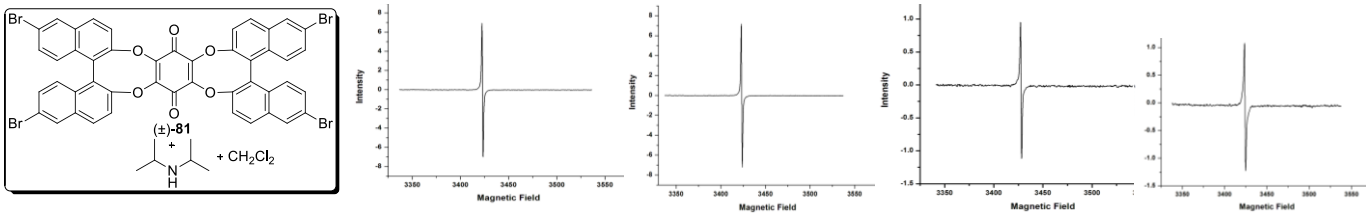
1h 6 h 12 h 24 h

[a]Experiment in in the ESR tube by mixing *bis*-*bi*-2-naphthyloxybezoquinone **(±)-79** (0.02 mmol) with (0.02 mmol) in propelene carbonate (PC) solvent.

The ESR spectra obtained for the reaction of *bis*-*bi*-2-naphthyloxybenzoquinone with DABCO are presented in Figure **7** an **8.** Whereas weak signals are obtained in CH_2Cl_2 solvent which decreases with time, stronger signals are observed in PC solvent which also decreases with time presumably due to formation of charge transfer complexes.

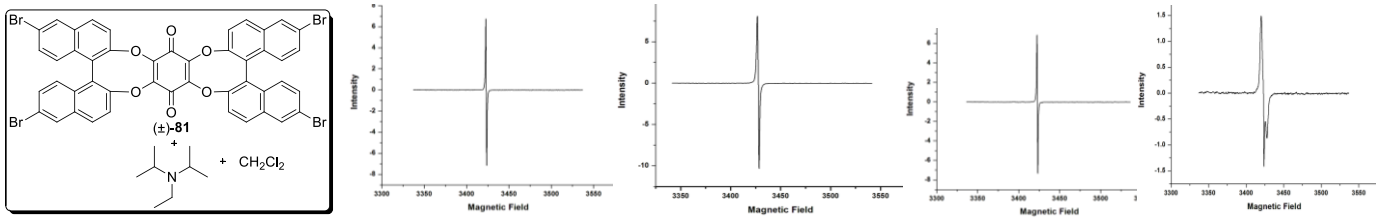
We have also carried out studies using *bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone derivative **(±)-81** as acceptor with diisopropylamine or diisopropylethylamine as presented in Figure **8** and **9**. Interestingly, the observed weak ESR signals get stronger with in 24h time as expected for highly hindered but more electron deficient nature of their *bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone derivatives.

Figure 8 ESR spectra of *bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone **(±)-81** of DIA in DCM[a]



[a]Experiment in the ESR tube by of *bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone **(±)-81** (0.02 mmol) with DIPEA (0.02 mmol) in DCM solvent.

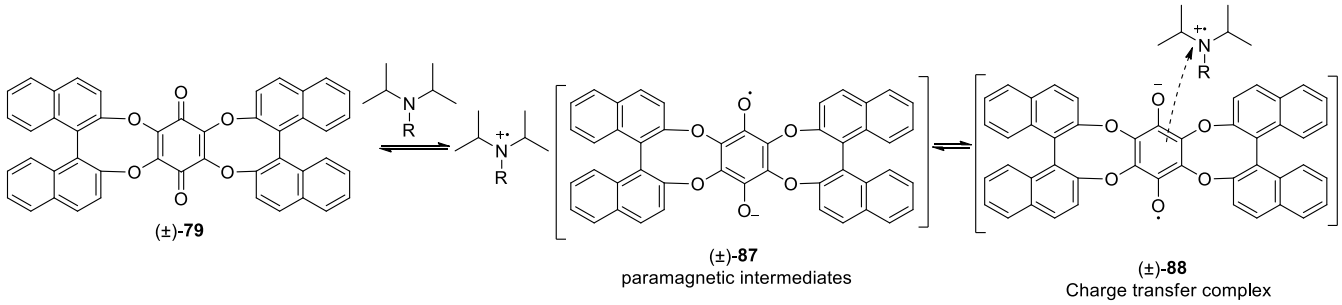
Figure 9 ESR spectra of *bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone **(±)-81** with DIPEA in DCM[a]



[a]Experiment in the ESR tube by of *bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone **(±)-81** (0.02 mmol) with DIPEA (0.02 mmol) in DCM solvent.

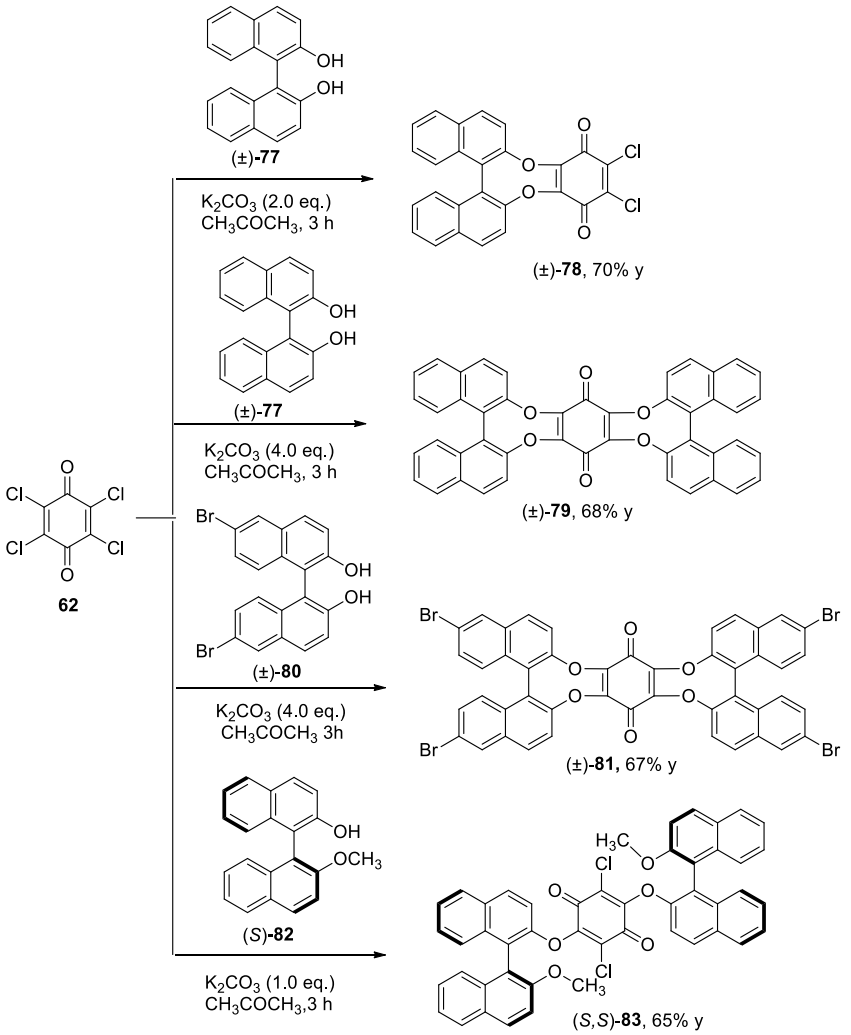
The results are in accordance with slow formation of radical ions in electron exchange reactions followed by formation of donor-acceptor charge transfer complete in equilibrium with the corresponding radical ions (Scheme 15).

Scheme 15



4.3 Conclusion

We have prepared *bi*-2-naphthyloxybenzoquinone derivatives by the reaction of *p*-Chloranil with (±)-*bi*-2-naphthol derivatives.



We have also carried out the electron transfer reactions of these of *bi*-2-naphthyloxybenzoquinone derivatives with amine donors and monitored the intermediates formed by ESR spectral analysis. The results have potential for further applications in the construction of organic electrochemical cells.

4.4. Experimental Section

General information

Melting points reported in this thesis are uncorrected and were determined using a Super fit capillary point apparatus. IR (KBr) spectra were recorded on JASCO FT-IR Spectrophotometer Model 5300 and the neat IR spectra were recorded on SHIMADZU FT-IR Spectrophotometer Model 8300 with polystyrene as reference. ^{1}H-NMR (400 MHz) and ^{13}CNMR (400 MHz) spectra were recorded on Bruker-Avance-400 spectrometer with chloroform-das solvent and TMS as reference (δ = 0 ppm). The chemical shifts are expressed in δ downfield from the signal of internal TMS. Mass spectral analyses were carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Optical rotations were measured in an AUTOPOL-II automatic polarimeter (readability ± 0.01o). Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250 mμ acme's silica gel-G and GF 254 containing 13% calcium sulfate as binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using acme's silica gel (100-200 mesh) or neutral alumina.

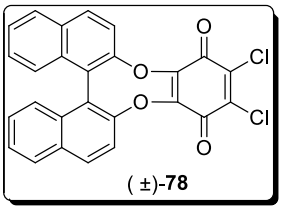
The X-ray diffraction measurements for the compounds were carried out at 298 K on Bruker-Nonius SMART APEX CCD area detector system using graphite monochromated, Mo- Kα (λ = 0.71073 A^{o}) radiation. Primary unit cell constants were determined with a set of 25 narrow frame scans. Intensity data were collected by the ω scan mode. The data were reduced using SAINT program, without applying absorption correction. The refinement for structure was made by full-matrix least-squares on F^2 (SHELX 97).

4.4.1 Reaction of *p*-Chloranil (1.0 eq.) trapping with (±)-*bi*-2-naphthol (1.0 eq.)

p-Chloranil (1.26 g, 5 mmol,) was taken in acetone (30 mL) and stirred for 30 min at rt. To this K_2CO_3 (1.32 g, 10 mmol,) was added and stirred for 1h. (±)-*Bi*-2-naphthol (1.43 g, 5 mmoL,) was added and the contents were stirred for 12h at rt. Acetone was removed and the residue was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (95:10) hexane/EtOAc.

Dichloro-*bi*-2-naphthyloxybenzoquinone

Physical State: Crystalline.



(±)-**78**

Color Red

Yield 4.41gr. (92%)

mp 258-260 °C

IR (KBr) 3057, 2934, 2837, 1668, 1620, 1589, 1249, 1093, 1062, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.06-8.04 (d, *J* = 6.8 Hz, 2H), 7.98-7.97 (d, *J* = 8.2 Hz, 2H), 7.58-7.55 (t, *J* = 6.2 Hz, 2H), 7.54- 7.36 (m, 5H), 7.29-7.28 (m, 1H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 173.9, 149.3, 144.2, 139, 132.1, 132, 128.4, 127.3, 126.6, 126.3, 124.5, 120.2 ppm.

MS (EI) 460 *m/z*$(M+1)^+$.

Analytical Data calculated for $C_{26}H_{12}Cl_2O_4$: C, 67.99; H, 2.63; Cl, 15.44; O, 13.93.

Found C, 67.91; H, 2.48; Cl, 15.16; O, 13.65.

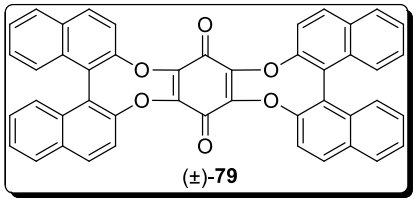
4.4.2 Reaction of *p*-Chloranil (1.0 eq.) trapping with (±)-bi-2-naphthol (2.0 eq.)

p-Chloranil (0.5 g, 2 mmol) was taken in acetone (20 mL) and stirred for 30 min at rt. To this K_2CO_3 (0.53 g, 4 mmol) was added and stirred for 1h. (±)-*bi*-2-naphthol (0.57 g, 2 mmoL) was added and the contents were stirred for 12 h at rt. Acetone was removed and the

residue was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with brine solution (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (95:10) hexane/EtOAc to obtain the product.

***Bis-bi*-2-naphthyloxybenzoquinone**

Physical State: Crystalline



(±)-**79**

Color Dark Brown

Yield 5.20 gr. (80%)

mp 270-272 °C

IR (KBr) 057, 2934, 2837, 1668, 1620, 1589, 1249, 1062, 810cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.03-8.00 (m, 2H), 7.99-7.94 (m, 3H), 7.69-7.87 (m, 1H), 7.58-7.51 (m, 1H), 7.49-7.40 (m, 8H), 7.39-7.35 (m, 2H), 7.31-7.15 (m, 2H) ppm.

^{13}C-NMR (400 MHz, $CDCl_3$, δ): 178.2, 152.8, 149.5, 142.2, 133.5, 132.1, 131.6, 130.8, 129.3, 128.4, 127.3, 127, 126.5, 125.7, 124.9, 124.3, 123.9, 121, 117.9 ppm.

MS (EI) 673*m/z* $(M+1)^+$

Analytical Data calculated for $C_{46}H_{24}O_6$: C, 82.13; H, 3.60; O, 14.27.

Found C, 82.01; H, 3.53; O, 14.14.

4.4.3 Reaction of *p*-Chloranil (1.0 eq.) trapping with 6,6'-dibromo(±)-*bi*-2-naphthol (2.0 eq.)

p-Chloranil (0.5 g, 2 mmol) was taken in acetone (30 mL) and stirred for 30 min at rt. To this K_2CO_3 (0.53 g, 4 mmol) was added and stirred for 1h. 6,6'-Dibromo(±)-*bi*-2-naphthol (0.88 g, 2 mmol) was added contents were stirred for 12 h at rt. Acetone was removed and the residue was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with brine

solution (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using (95:10) hexane/EtOAc to obtain the product.

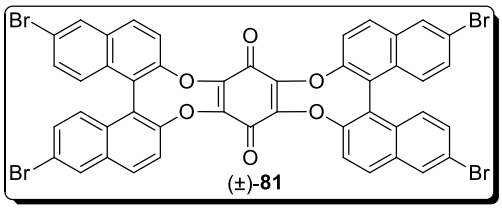
***Bis*-tetrabromo-*bi*-2-naphthyloxybenzoquinone**

Physical State: Solid

Color Yellow

Yield 3.2 gr. (80%)

mp 239-241°C



IR (KBr) 057, 2934, 2837, 1668, 1620, 1589, 1249, 1062, 810cm^{-1}

^{1}H-NMR MHz, $CDCl_3$, δ): 8.44-8.42 (d, *J* = 8.2 Hz, 2H), 8.21-8.19 (d, *J* = 8.6 Hz, 2H), 7.63-7.61 (m, 2H), 7.50-7.49 (d, *J* = 8.6 Hz, 2H), 7.24-7.22 (d, *J* = 7.9 Hz, 2H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 177.3, 150, 142.1, 133.3, 131.5, 131.1, 130.9, 130.3, 128.3, 124.3, 123.1, 120.1ppm.

MS (EI) 987*m/z* $(M+1)^+$

Analytical Data calculated for $C_{46}H_{20}Br_4O_6$: C, 55.91; H, 2.04; Br, 32.34, O, 14.27.

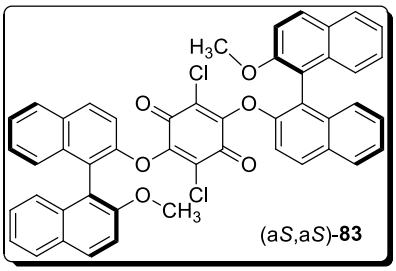
Found C, 55.67; H, 2.02; Br, 32.27, O, 14.07.

4.4.4 Reaction of *p*-Chloranil (1.0 eq) with (*S*)-monomethoxy-*bi*-2-naphthol (2.0 eq)

p-Chloranil (0.5 g, 2 mmol,) was taken in acetone (30 mL) and stirred for 30 min at rt. To this K_2CO_3 (0.53 g 4 mmol) was added and stirred for 1h. (*S*)-Monomethoxy-*bi*-2-naphthol (0.6 g, 2 mmol) was added and the contents were stirred for 12h. Acetone was removed and the residue was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with brine solution (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and

the residue was chromatographed on a silica gel column using (95:10) hexane/EtOAc to obtain the product.

(*S*,*S*)-*bis*-dicloro-*bi*-2-naphthylmethoxybenzoquinone



Physical State: Solid

Color Dark Brown

Yield 6.95 gr. (90%)

mp 265-267 °C

IR (KBr) 3057, 2934, 2837, 1668, 1620, 1589, 1249, 1062, 810 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.06-8.04 (d, *J* = 8.0 Hz, 1H), 8.00-7.98 (d, *J* = 8.2 Hz, 1H), 7.96-7.90 (d, *J* = 8.1 Hz, 1H), 7.88-7.77 (d, *J* = 8.3 Hz, 1H), 7.67-7.65 (d, *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 1H), 7.33-7.30 (m, 3H), 7.29-7.28 (m, 1H), 7.22-7.20 (m, 1H), 6.91-6.89 (d, *J* = 8.5 Hz, 1H) 3.8 (ss, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$, δ): 170.8, 169.8, 169.5, 155.7, 153, 140.8, 139, 138, 133, 131, 129, 128.5, 127.9, 126.2, 125.8, 124.8, 124.9, 123.9, 120.7, 116, 114, 113, 112, 56.9, 56.1ppm.

MS (EI) 774 *m/z* $(M+1)^{+}$

Analytical Data calculated for $C_{48}H_{30}Cl_2O_6$: C, 74.52; H, 3.91; Cl, 9.17; O, 12.41.

Found C, 74.25; H, 3.67; Cl, 9.06; O, 12.21.

4.5. References

1 Rosokha, S. V.; Kochi, J. K. *Acc. Chem. Res.* **2008**, *41*, 641.

2 (a) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119,* 9393. (b) Bondi, A. *J. Phys. Chem*. **1964**, *68*, 441.

3 (a) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc*. **1980**, *102*, 2928. (b) Kochi, J. K. *Pure Appl. Chem.* **1990**, *52*, 571. (c) Kochi, J. K. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1227. (d) Sun, D. L.; Rosokha, S. V.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc*. **2003**, *125*, 15950.

4 (a) Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc*. **2007**, *129*, 3683. (b) Sun, D.; Rosokha, S. V.; Kochi, J. K. *J. Phys. Chem. B*. **2007**, *111*, 6655.

5 Mckinney, T. M.; Geske, D. H. *J. Am. Chem. Soc*. **1965**, *87*, 3013.

6 (a) Nelsen, S. F.; Ippoliti, j. T. *J. Am. Chem. Soc*. **1986**, *108*, 4879. (b) Zwier, J. M.; Brouwer, A. M.; Keszthelyi, T.; Balakrishnan, G.; Offersgaard, J. F.; Wilbrandt, R.; Barbosa, F.; Buser, U.; Amaudrut, J.; Gescheidt, G.; Nelsen, F. S.; Little, C. D. *J. Am. Chem. Soc*. **2002**, *124*, 159. (c) Zheng, Z. R.; Evans, D. H.; Nelsen, S. F. *J. Org. Chem.* **2000**, *65*, 1793.

7 Sersen, F.; Koscal, S; Banacky, P.; Krasnec, L. *Collection Czechoslov. Chem. Commun*. **1977**, *42*, 2173.

8 Ward, R. L.; Weissman, S. I. *J. Am. Chem. Soc*, **1957**, *79*, 2086.

9 Periasamy, M.; Shanmugaraja, M.; Ramusagar, M. *unpublished results*.

10. Suresh, S. Ph.D., Thesis **2016**, School of Chemistry, University of Hyderabad

11 Edukondalu A, ; Ph.D., Thesis, **2017**, University of Hyderabad.

12 Ramusagar, M,; Ph.D., Thesis, **2018**, University of Hyderabad.

13 Anand Kumar Gunda,; Ph.D., Thesis, **2018**, University of Hyderabad.

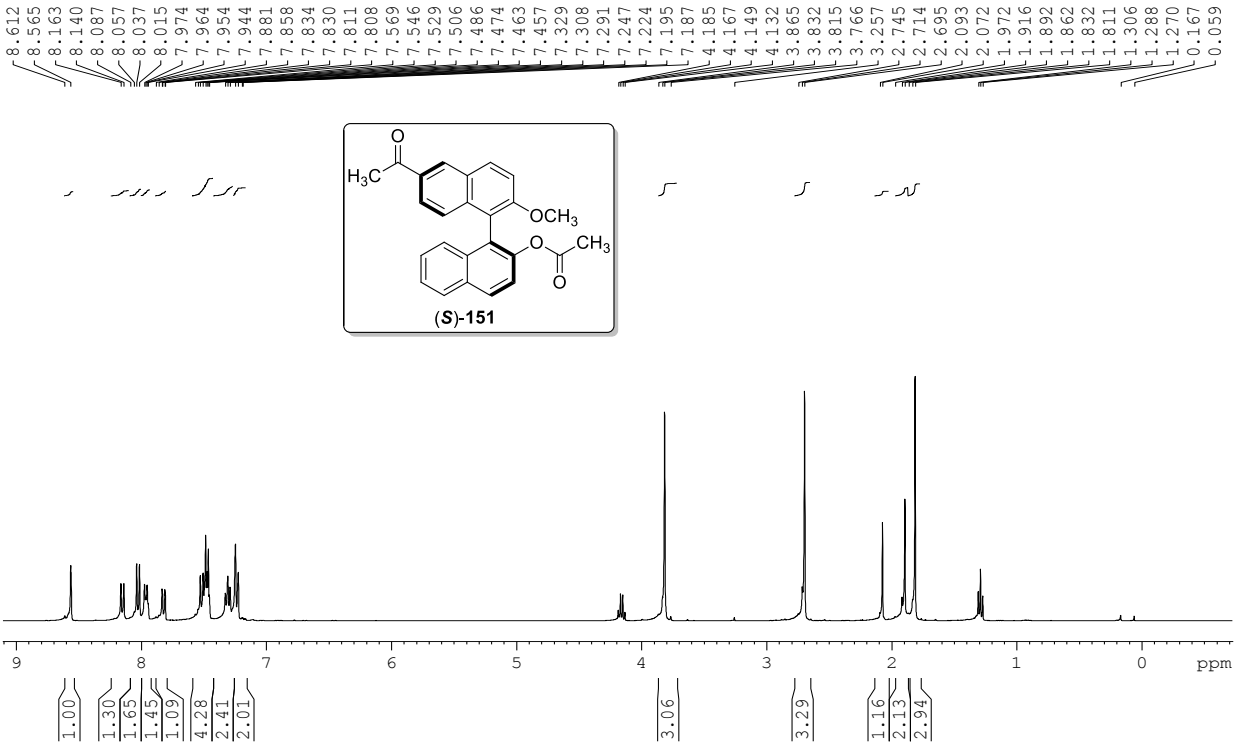
14 Udaykumar Bantu,;Ph.D., Thesis, **2018**, University of Hyderabad.

15 Egala Ramesh,; Ph.D., Thesis, **2018**, University of Hyderabad.

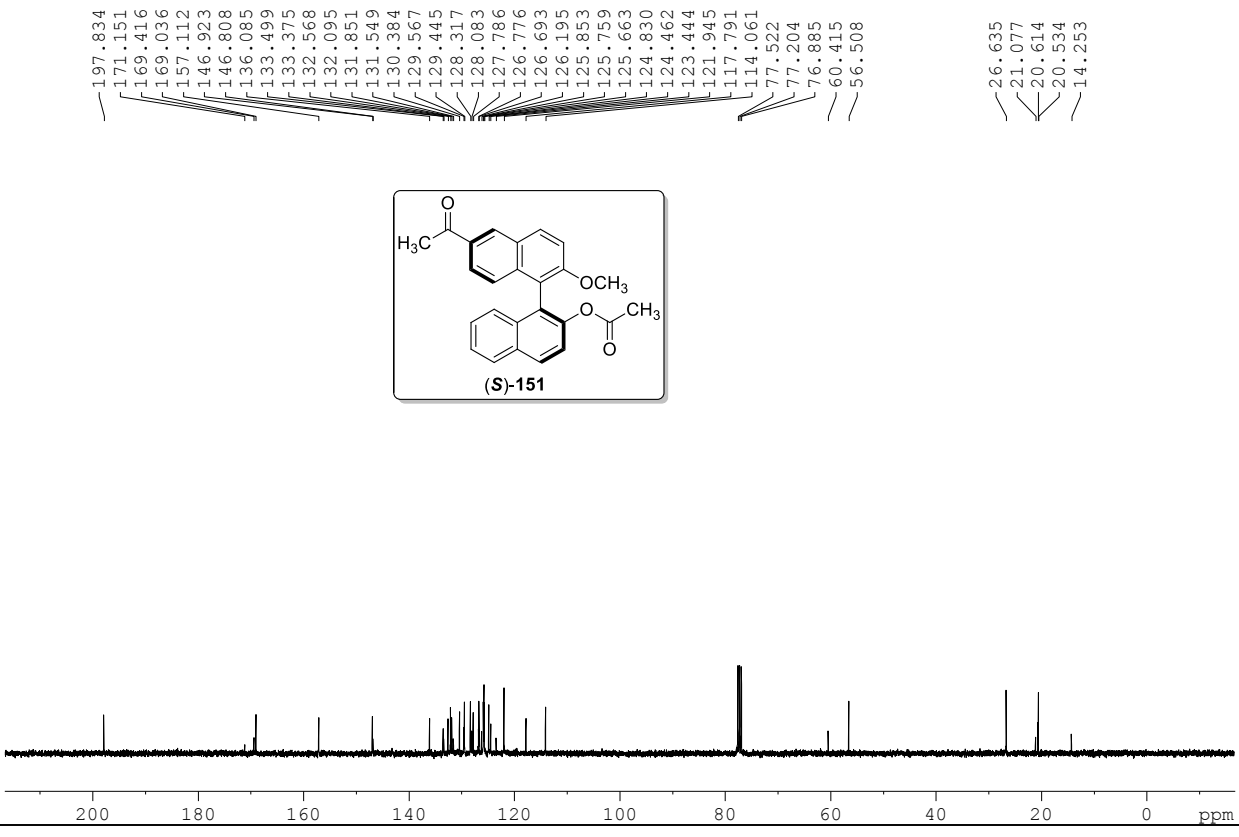
Appendix-I

Representative Spectra

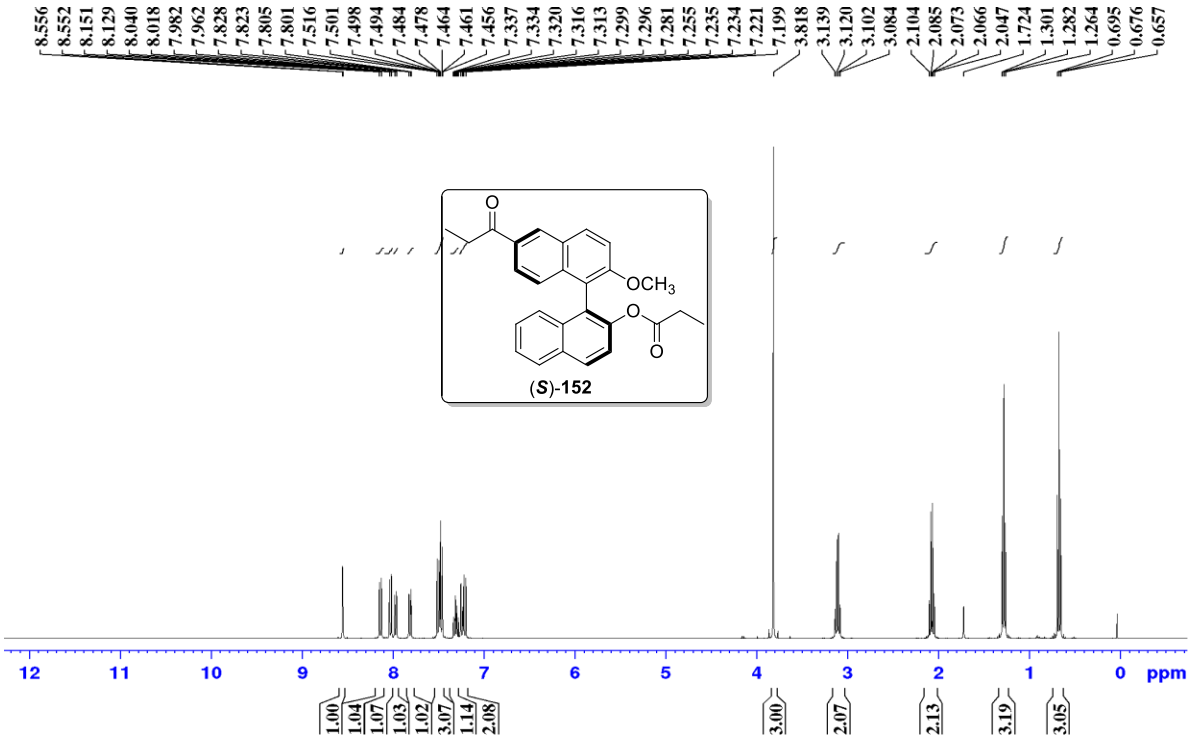
Spectrum No. 1 (Chapter 2, Section 2.2.2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



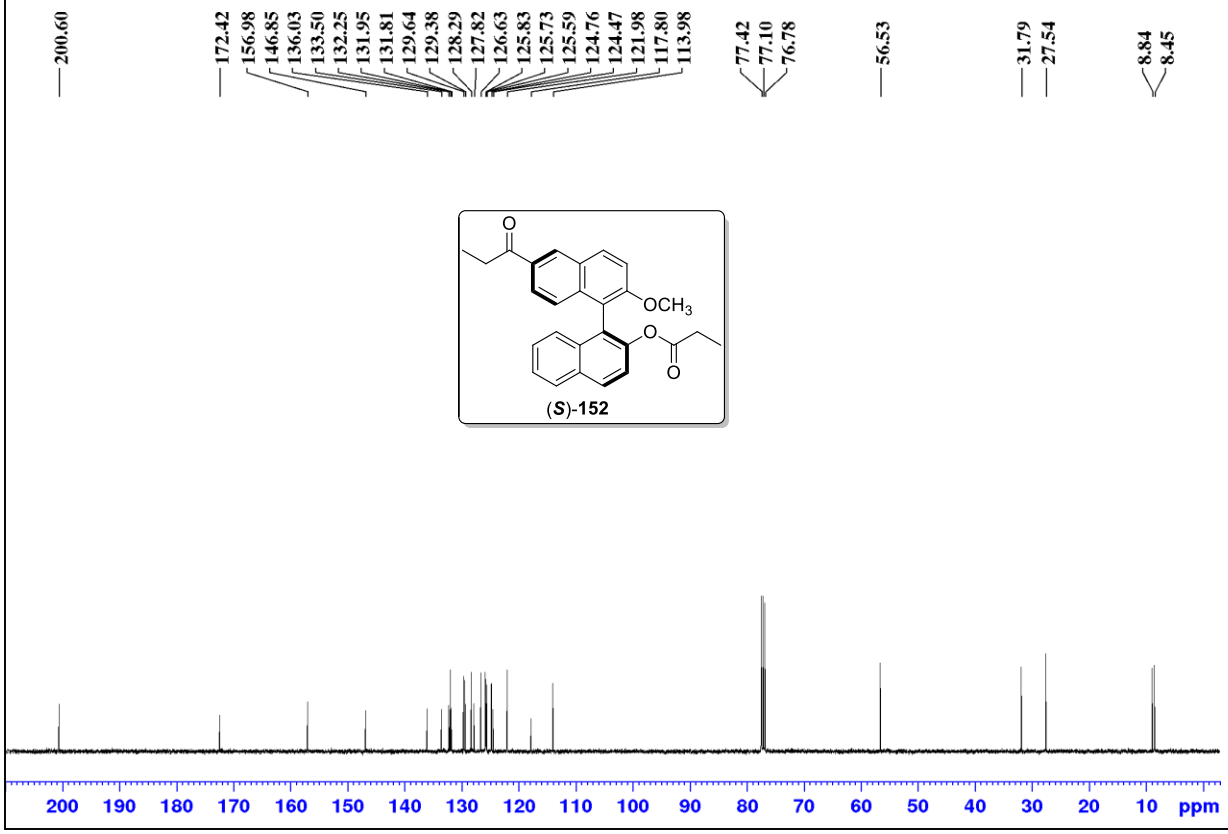
Spectrum No. 2 (Chapter 2, Section 2.2.2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



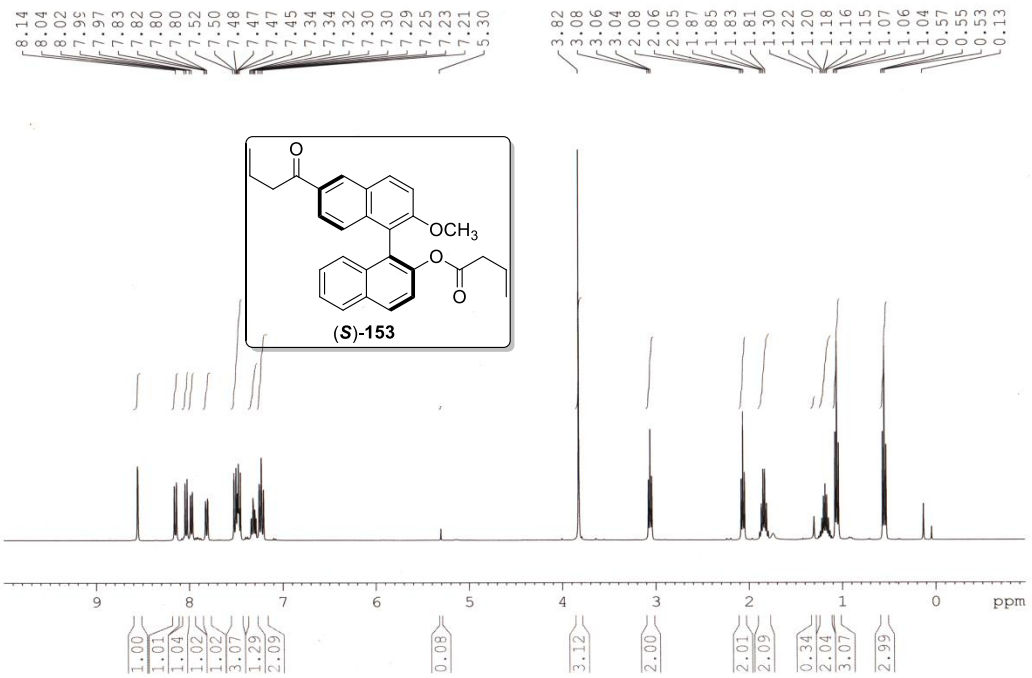
Spectrum No. 3 (Chapter 2, Section 2.2.2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



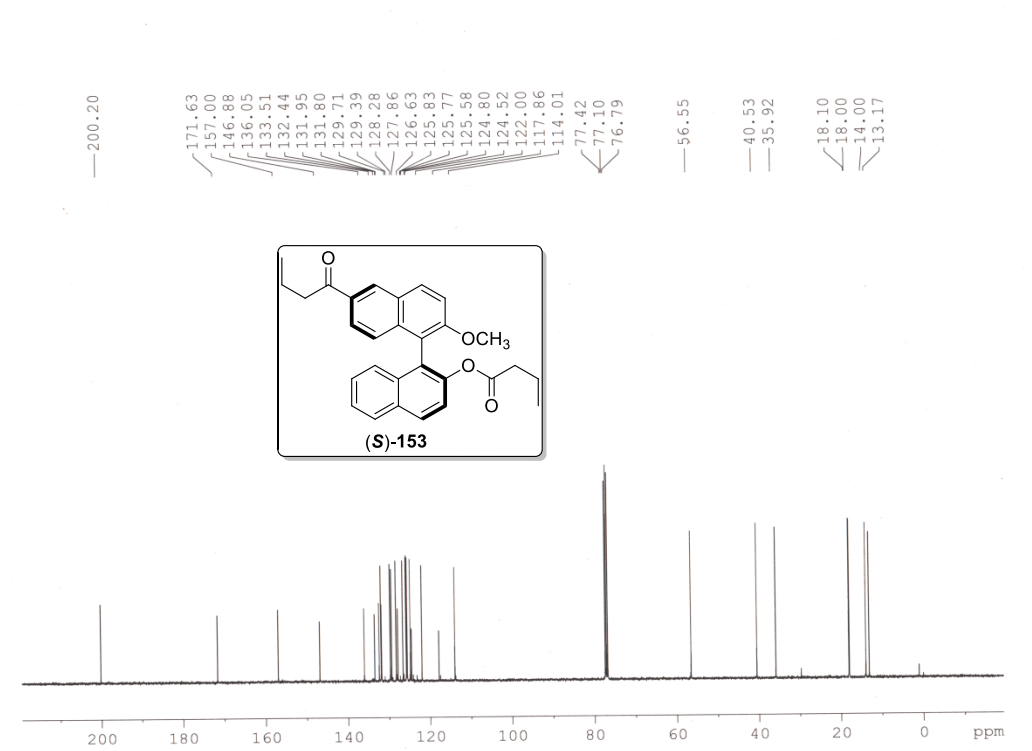
Spectrum No. 4 (Chapter 2, Section 2.2.2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



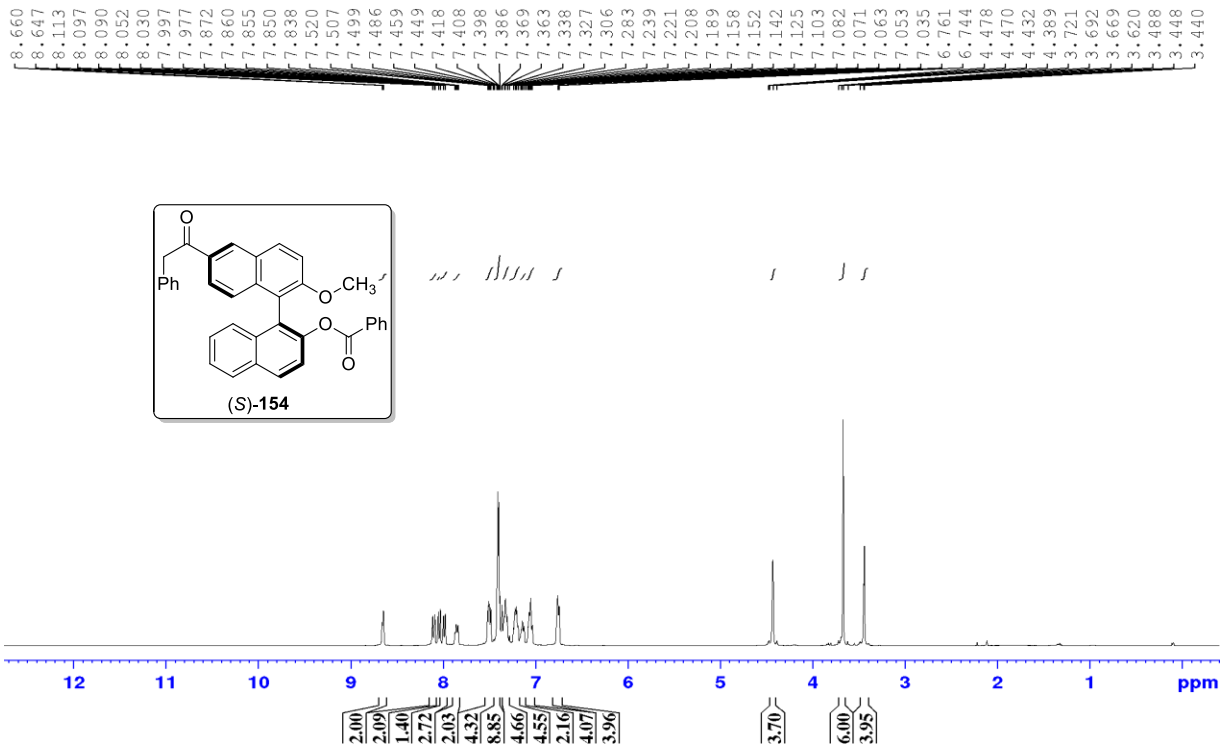
Spectrum No. 5 (Chapter 2, Section 2.2.2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



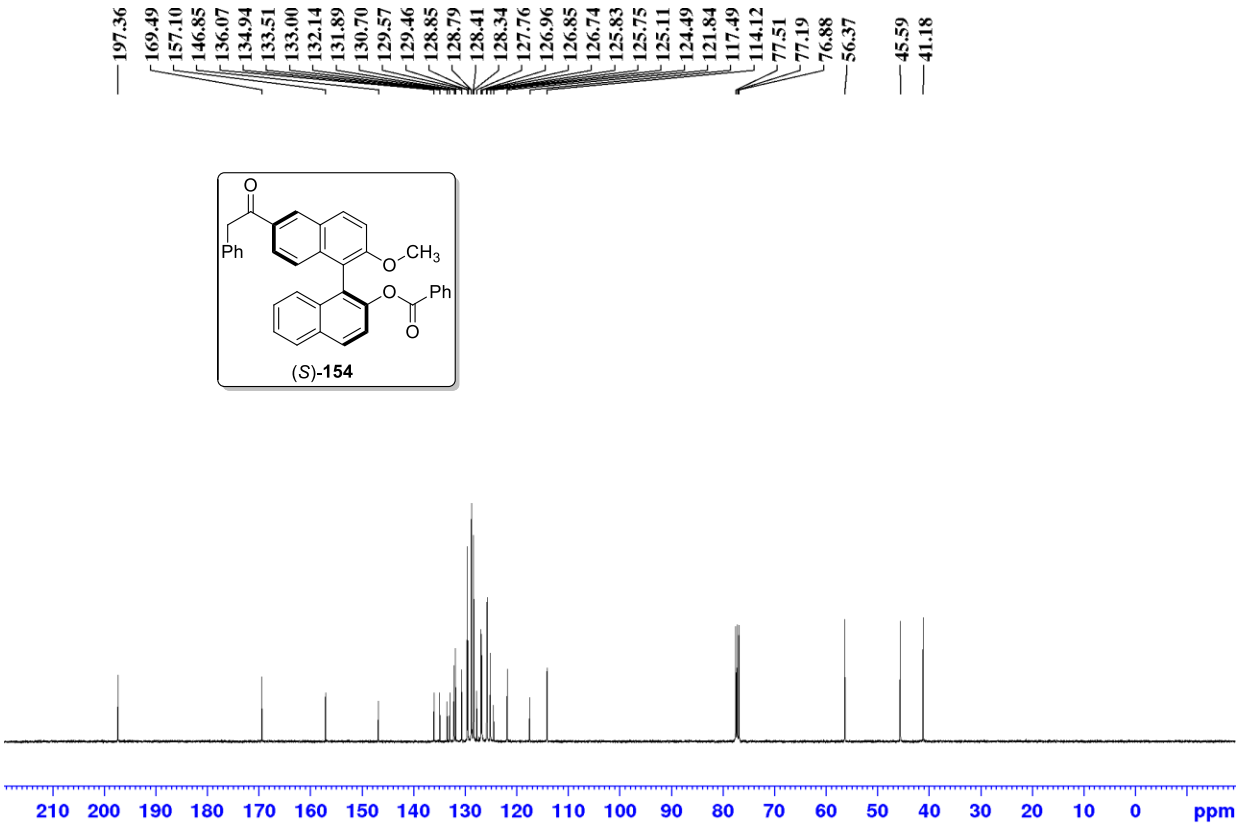
Spectrum No. 6 (Chapter 2, Section 2.2.2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



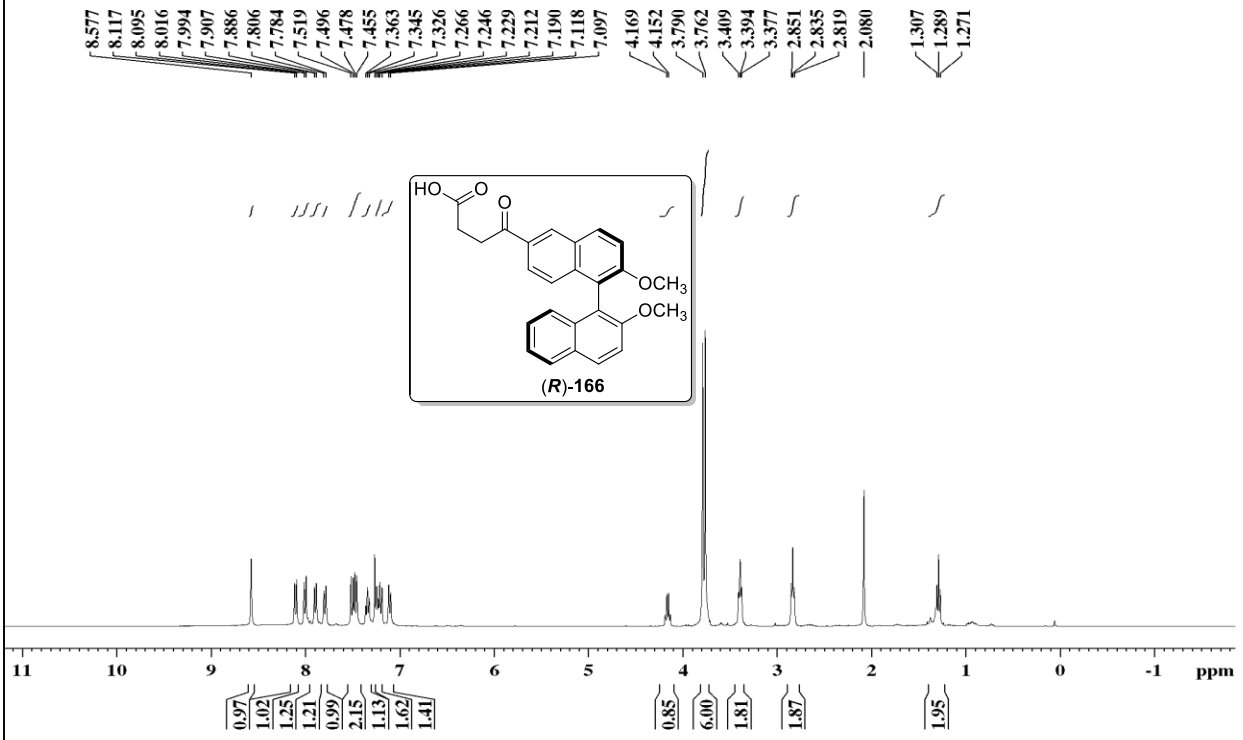
Spectrum No. 7 (Chapter 2, Section 2.2.2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



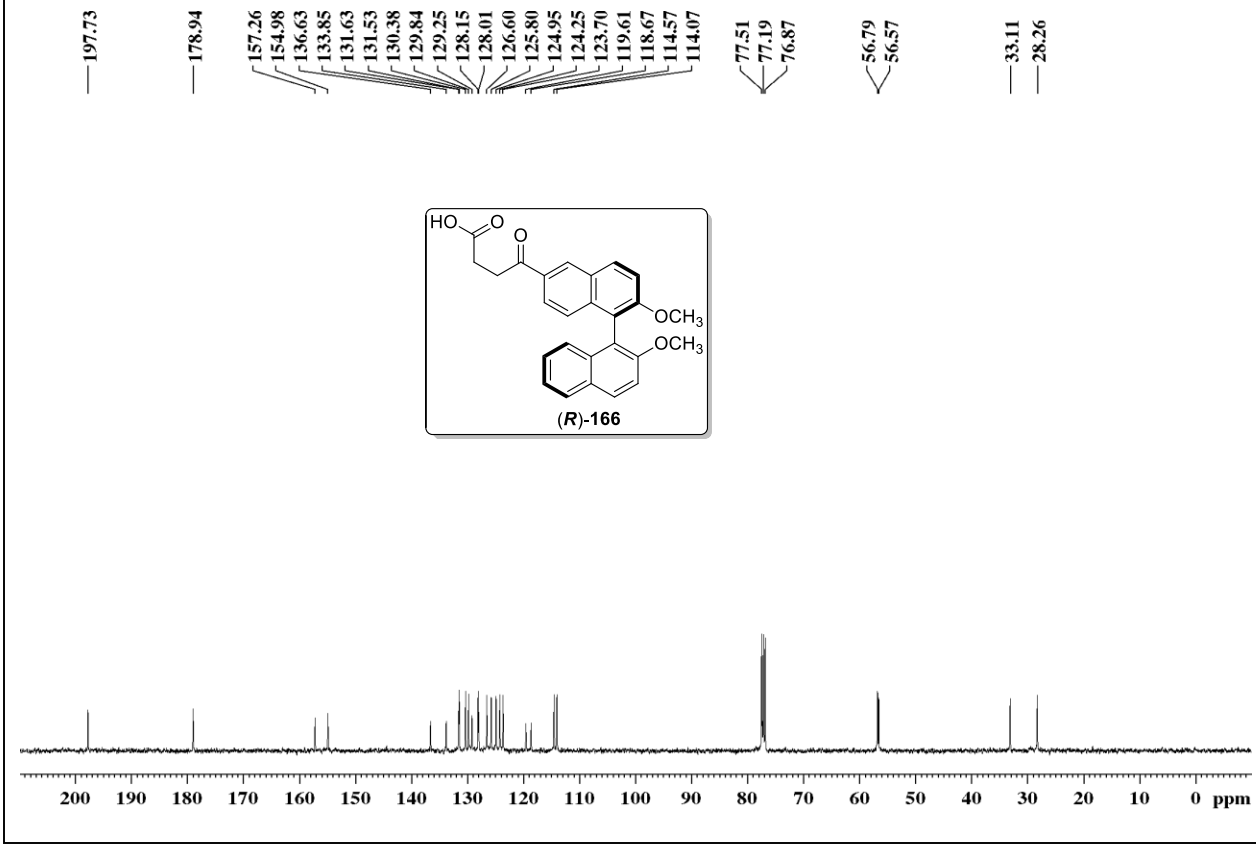
Spectrum No. 8 (Chapter 2, Section 2.2.2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



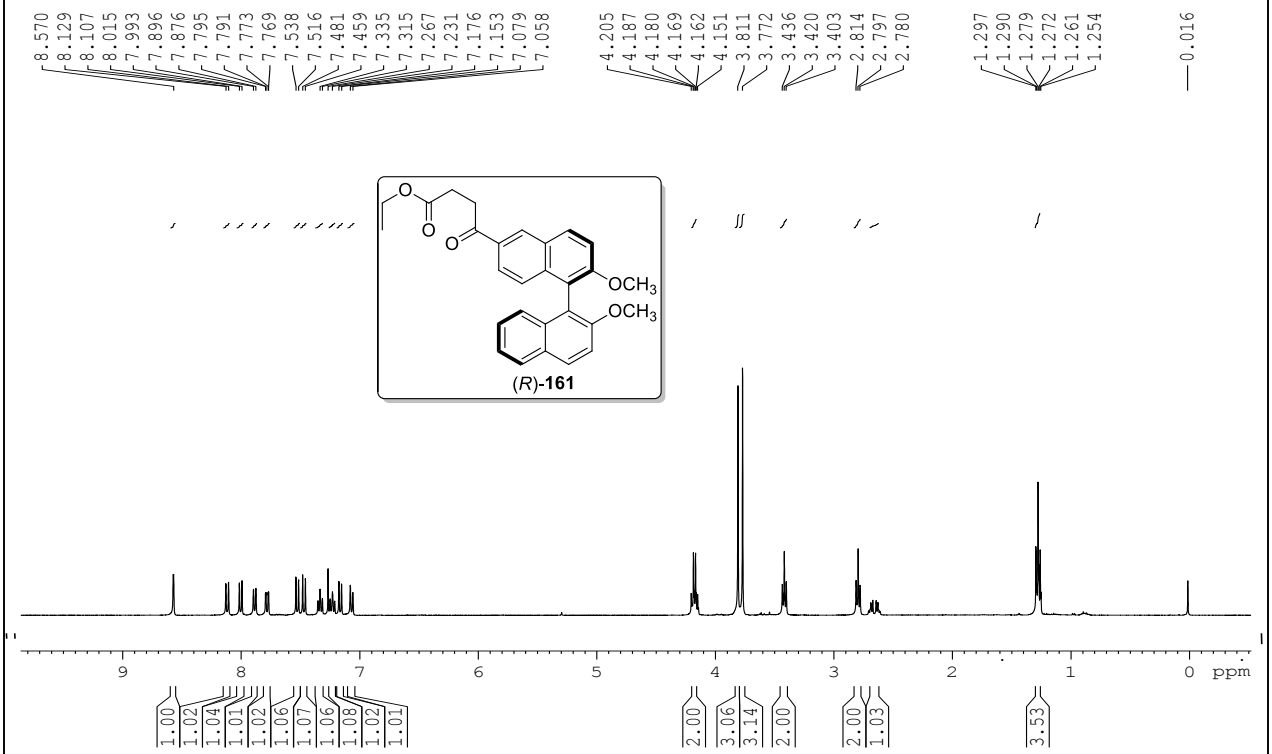
Spectrum No. 9 (Chapter 2, Section 2.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



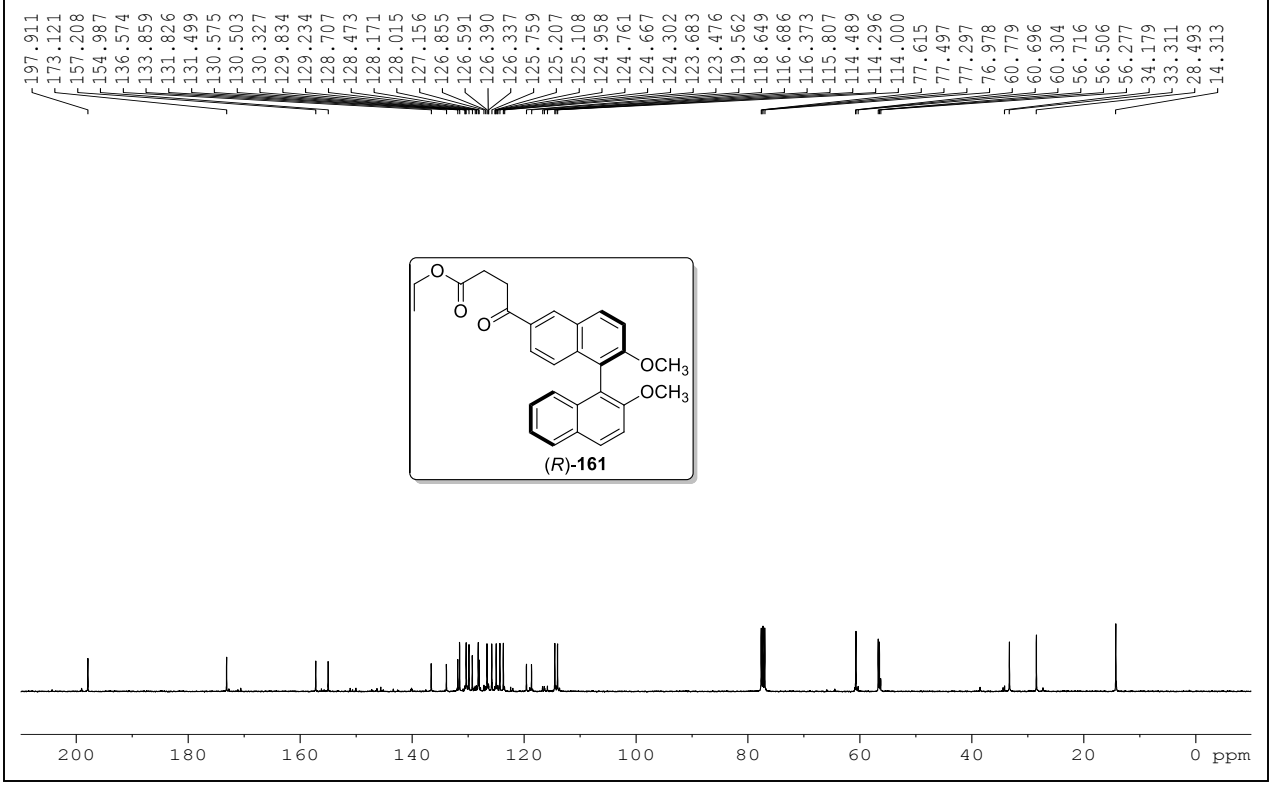
Spectrum No. 10 (Chapter 2, Section 2.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



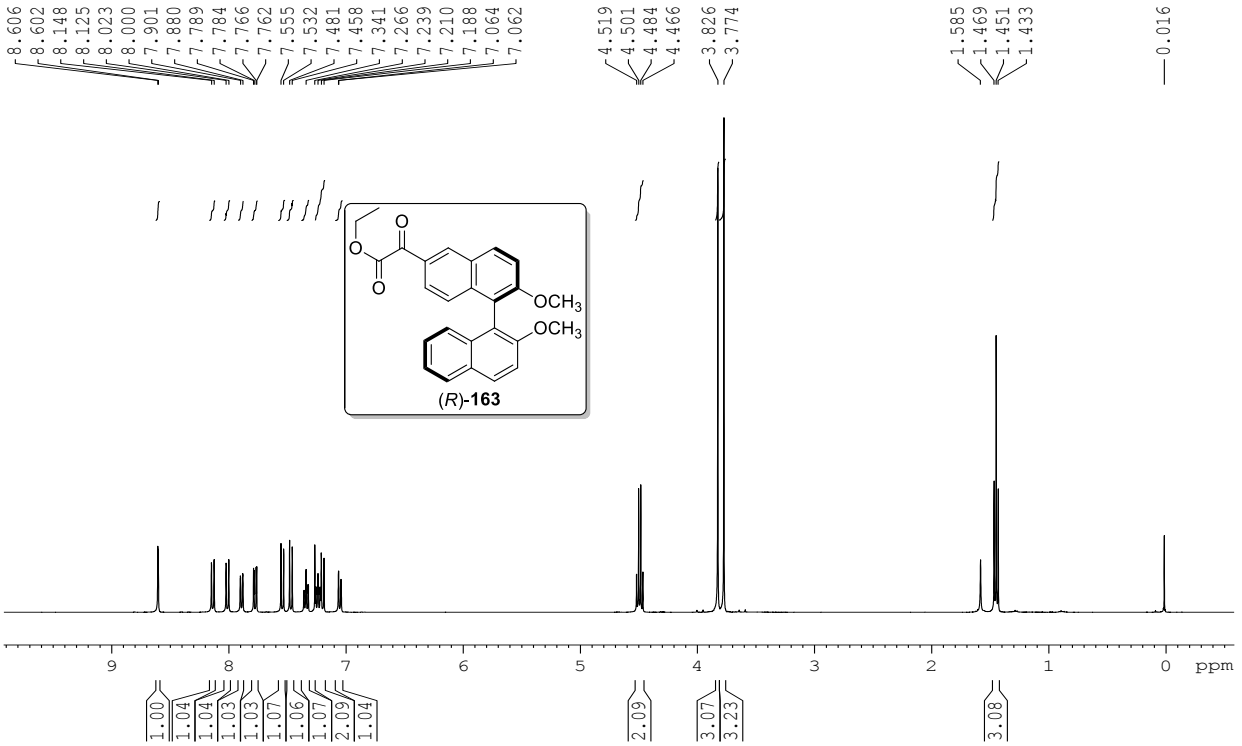
Spectrum No. 11 (Chapter 2, Section 2.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



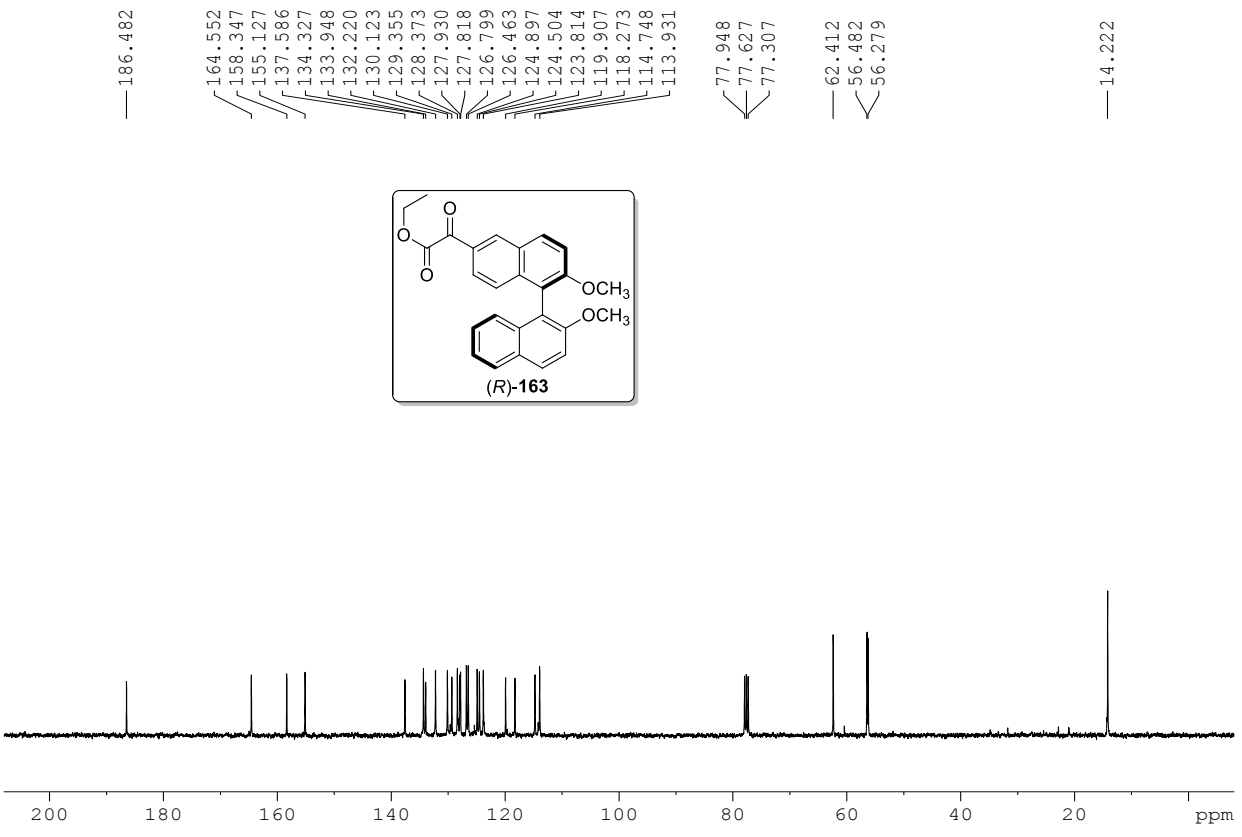
Spectrum No. 12 (Chapter 2, Section 2.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



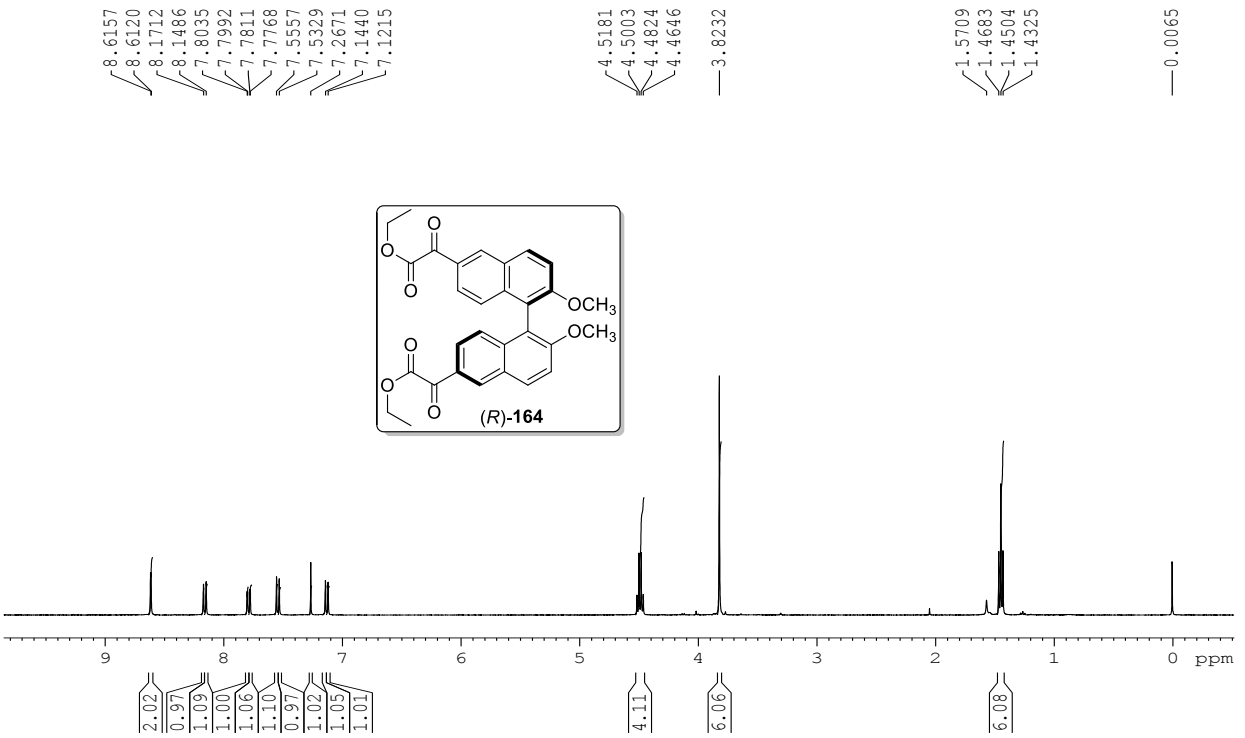
Spectrum No. 13 (Chapter 2, Section 2.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



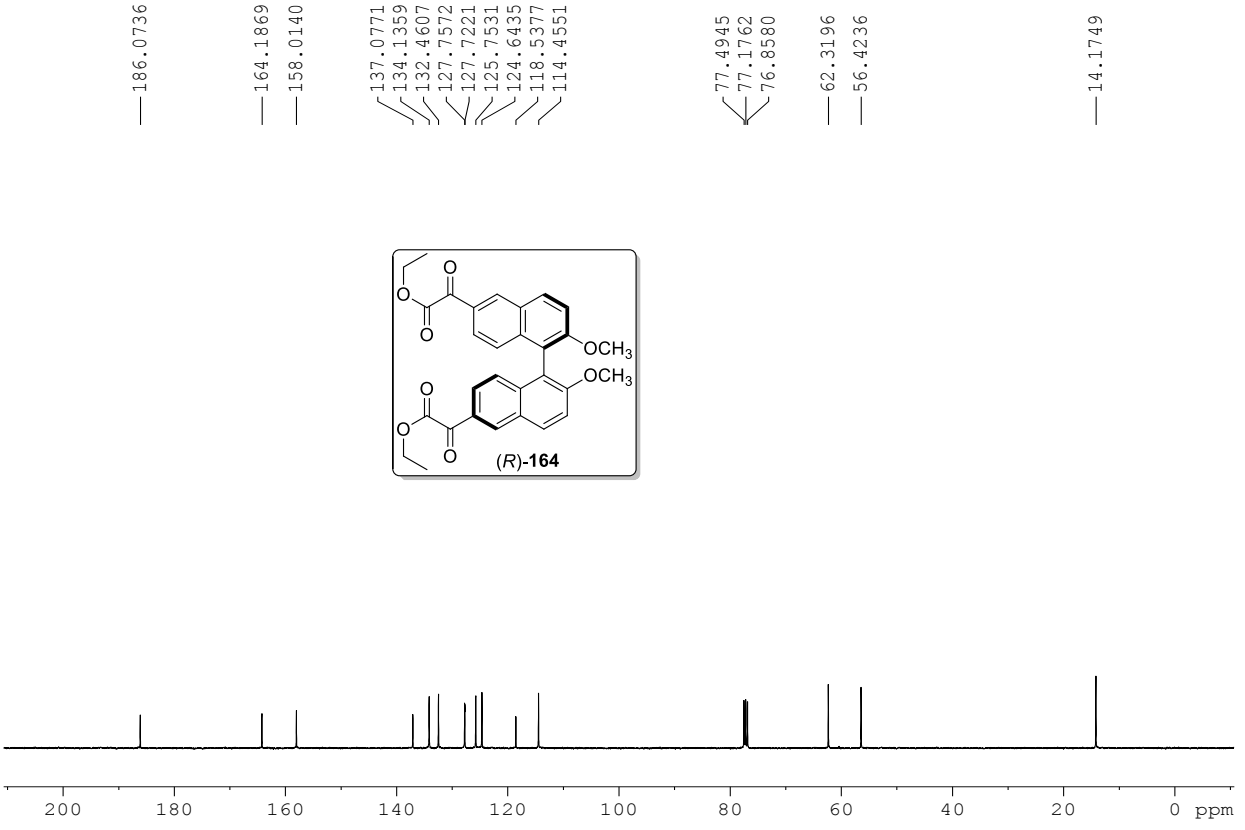
Spectrum No. 14 (Chapter 2, Section 2.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



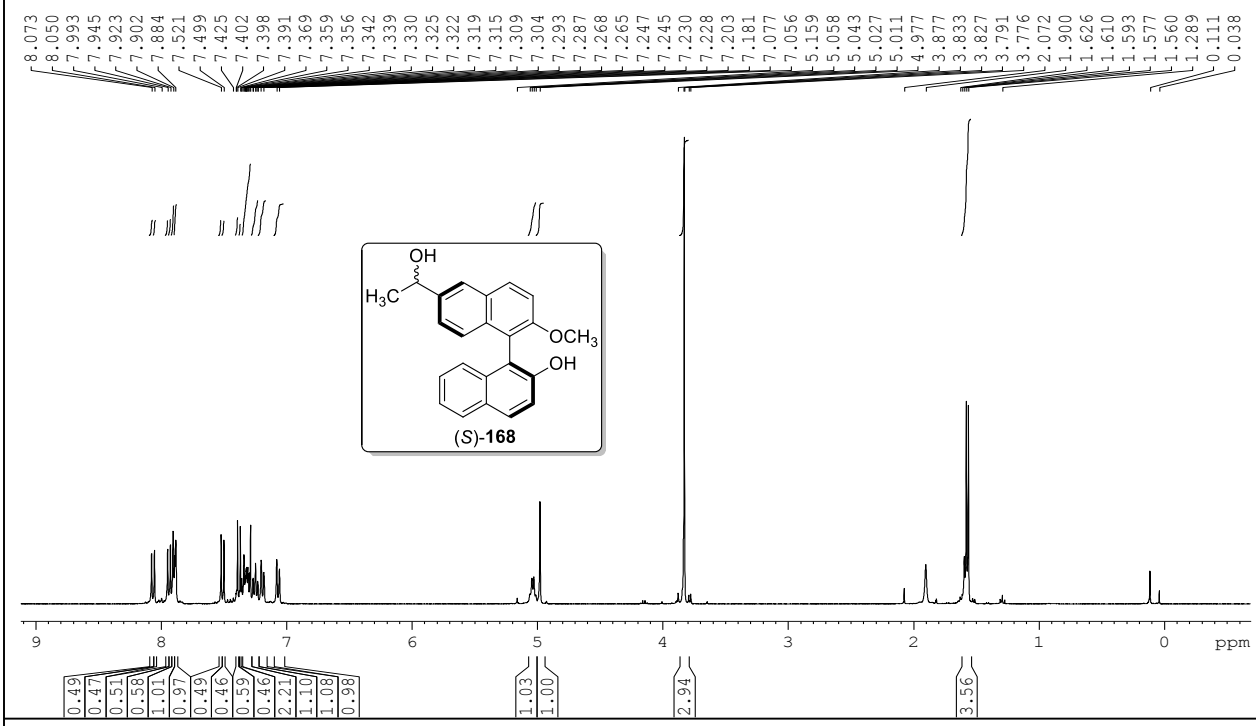
Spectrum No. 15 (Chapter 2, Section 2.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



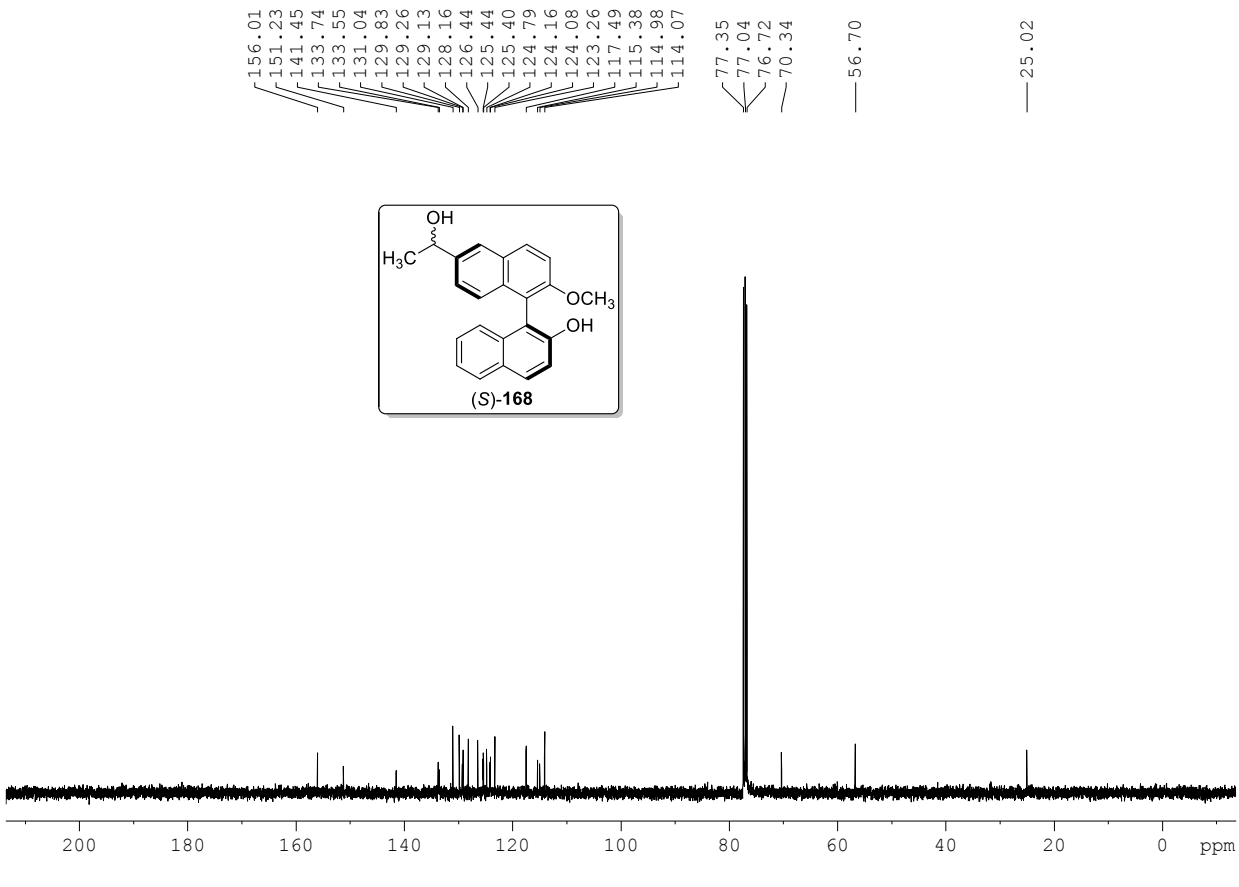
Spectrum No. 16 (Chapter 2, Section 2.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



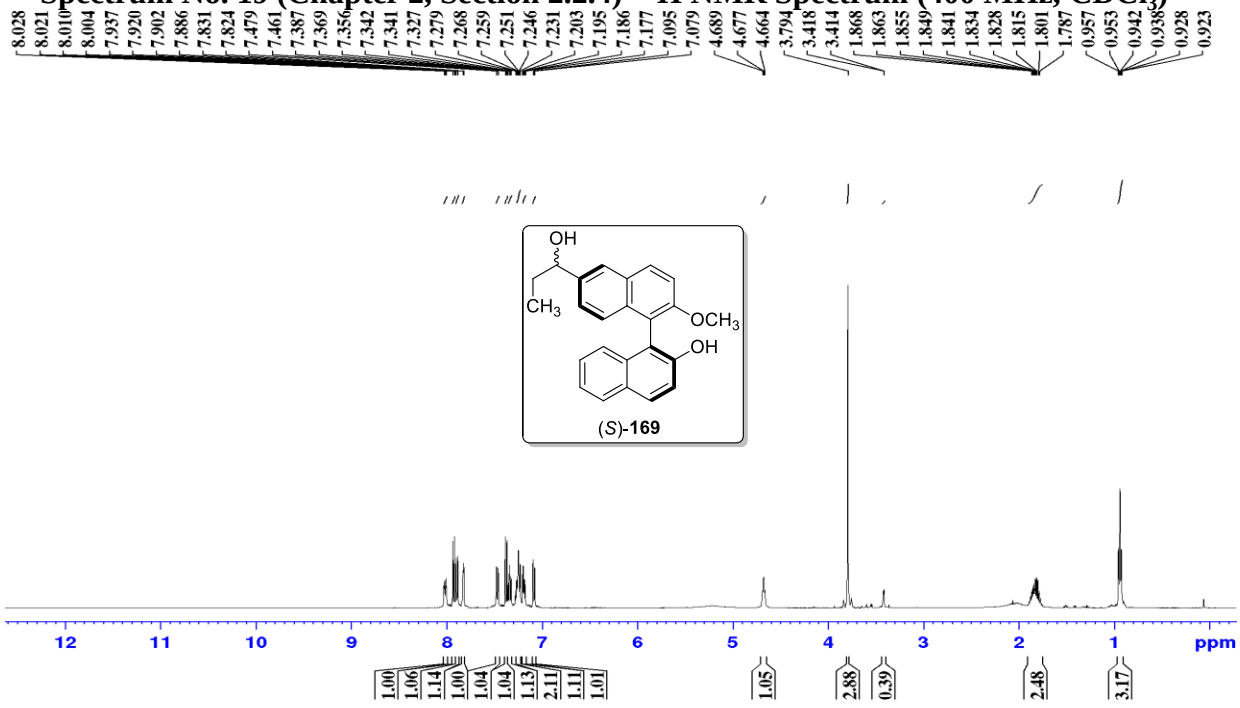
Spectrum No. 17 (Chapter 2, Section 2.2.4) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



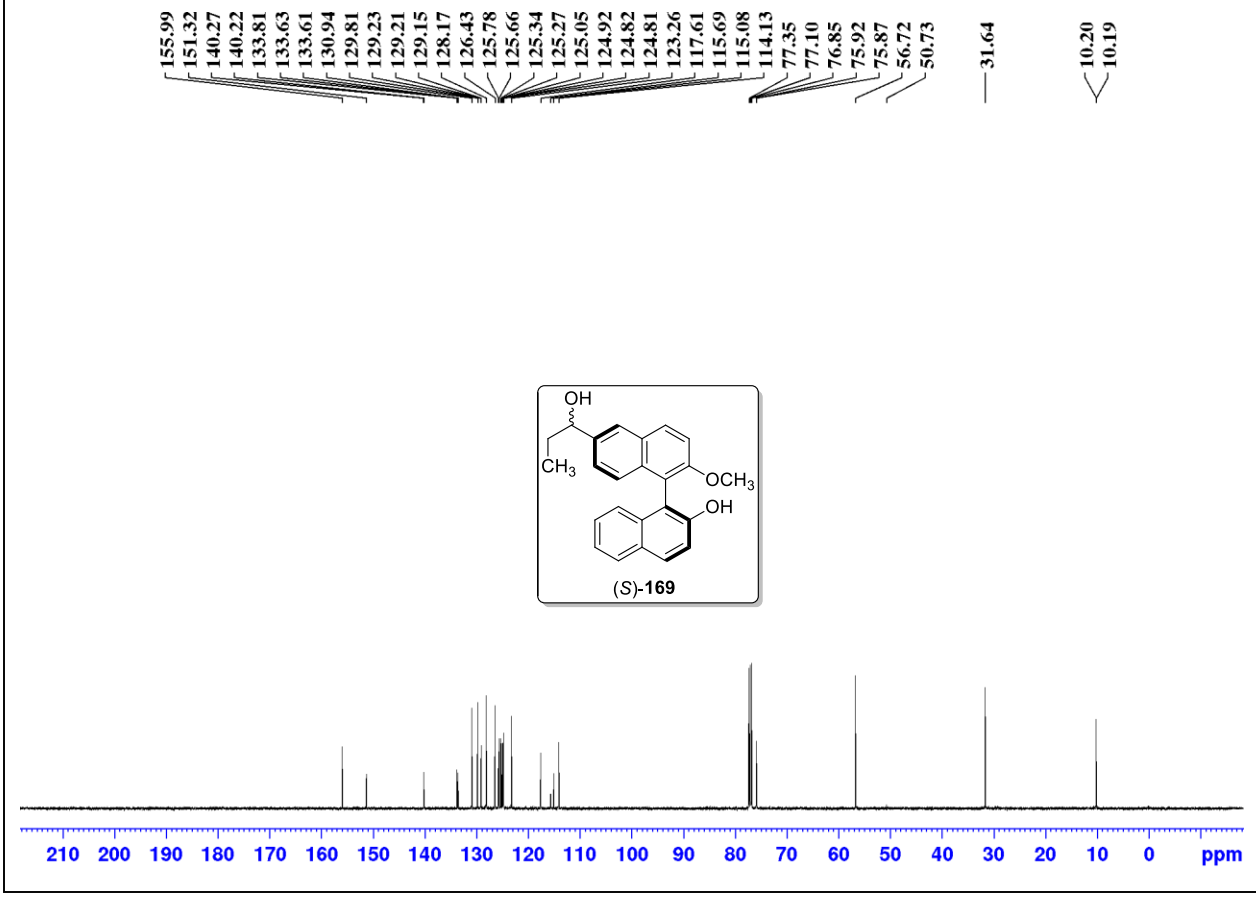
Spectrum No. 18 (Chapter 2, Section 2.2.4) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



Spectrum No. 19 (Chapter 2, Section 2.2.4) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)

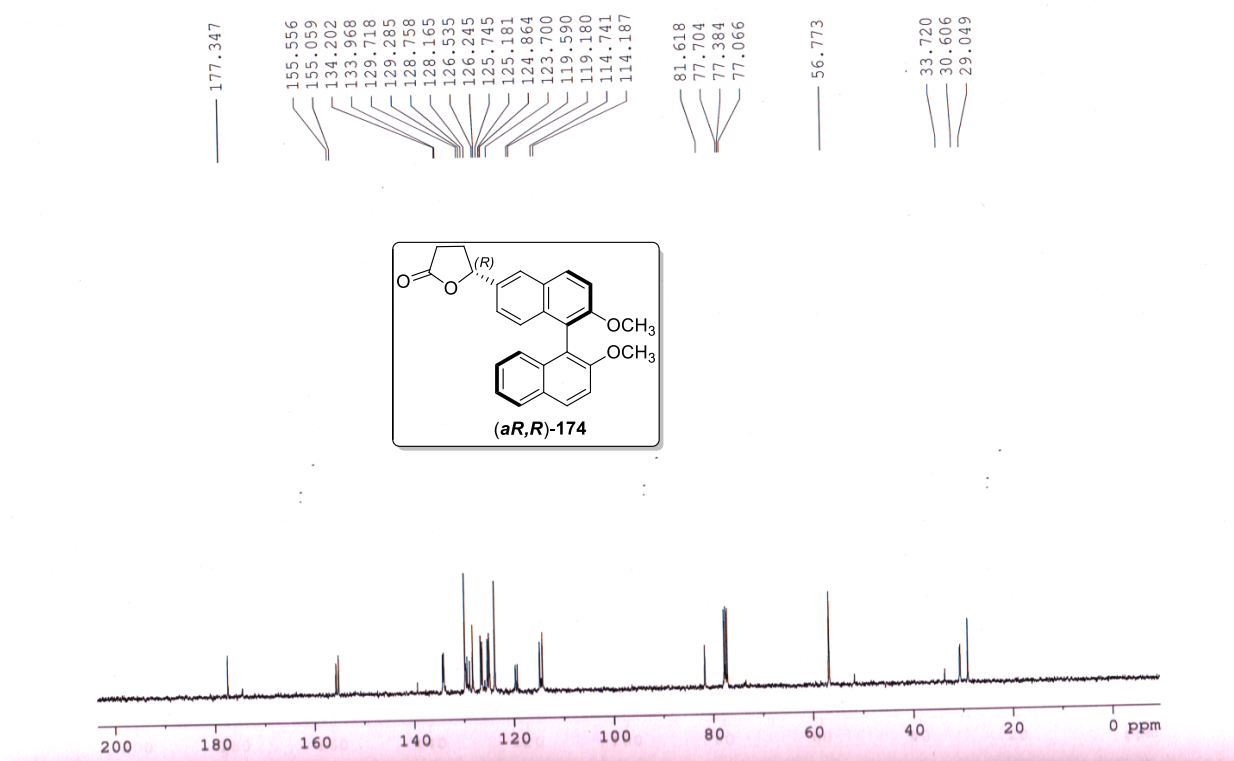


Spectrum No. 20 (Chapter 2, Section 2.2.4) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)

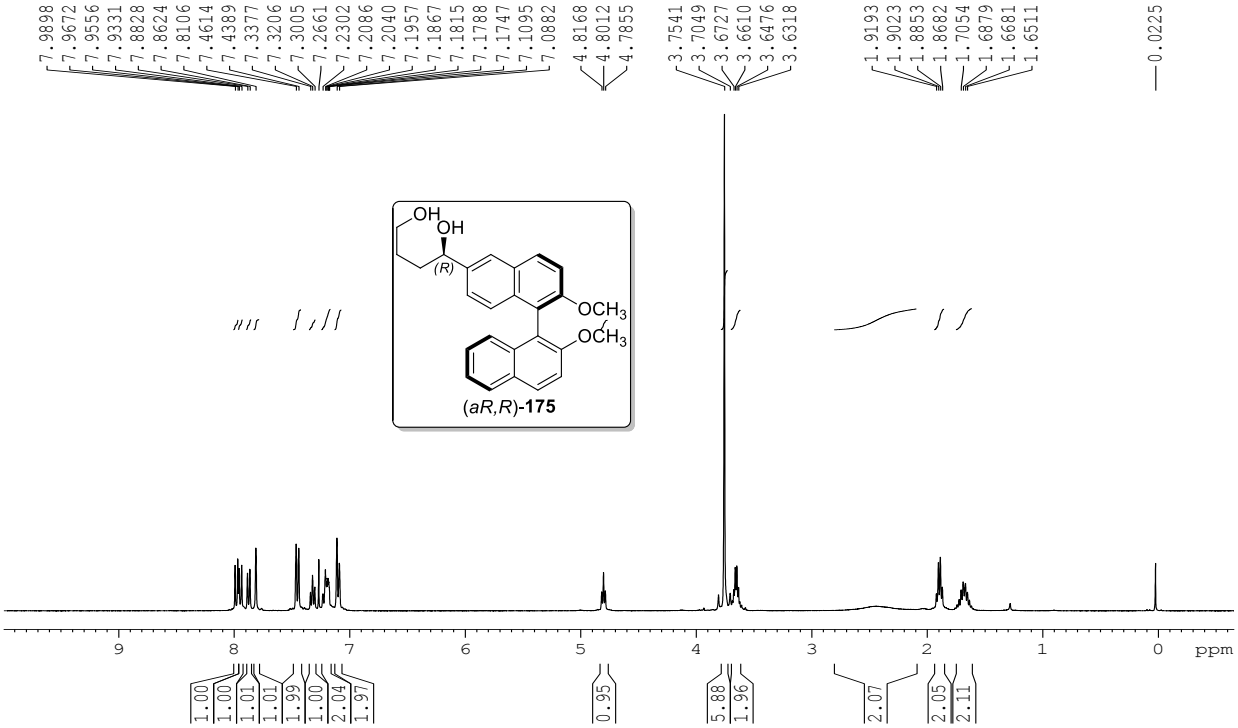


Spectrum No. 21 (Chapter 2, Section 2.2.6) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)

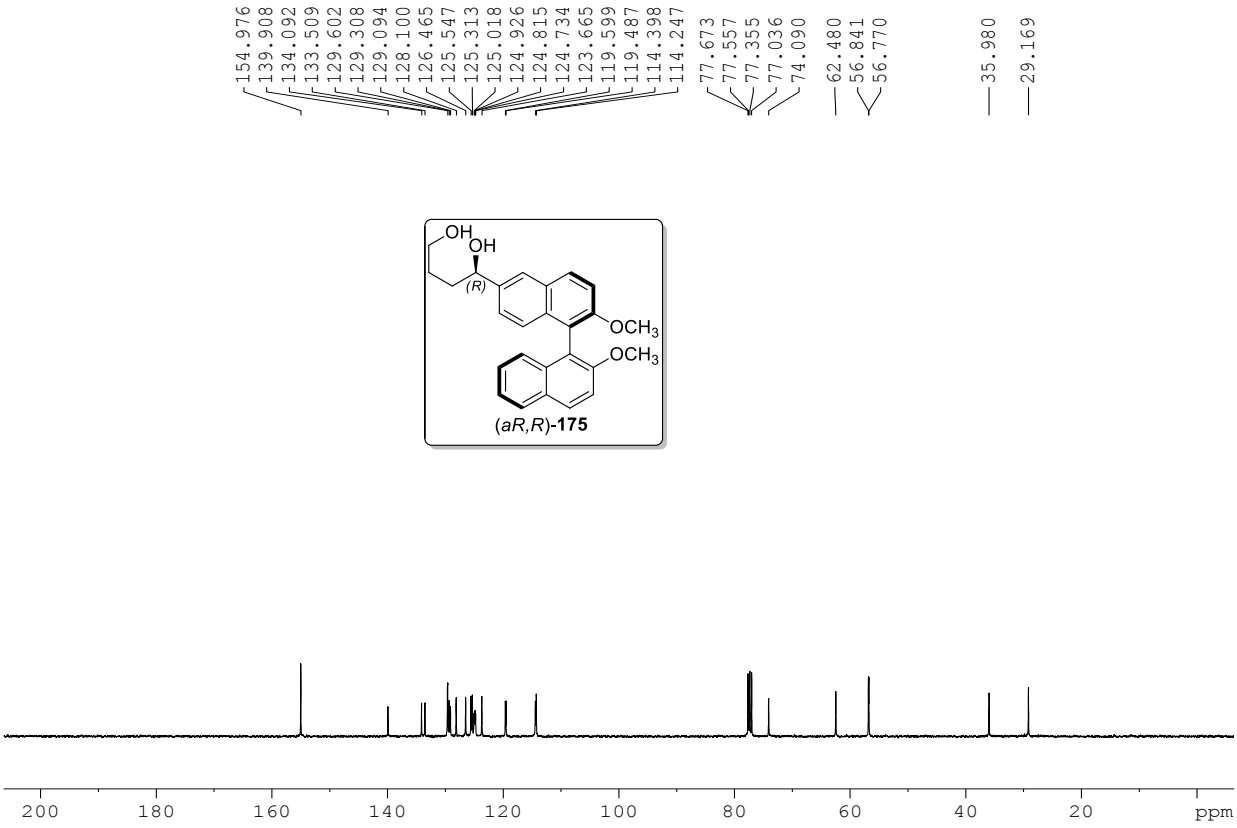
Spectrum No. 22 (Chapter 2, Section 2.2.6) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



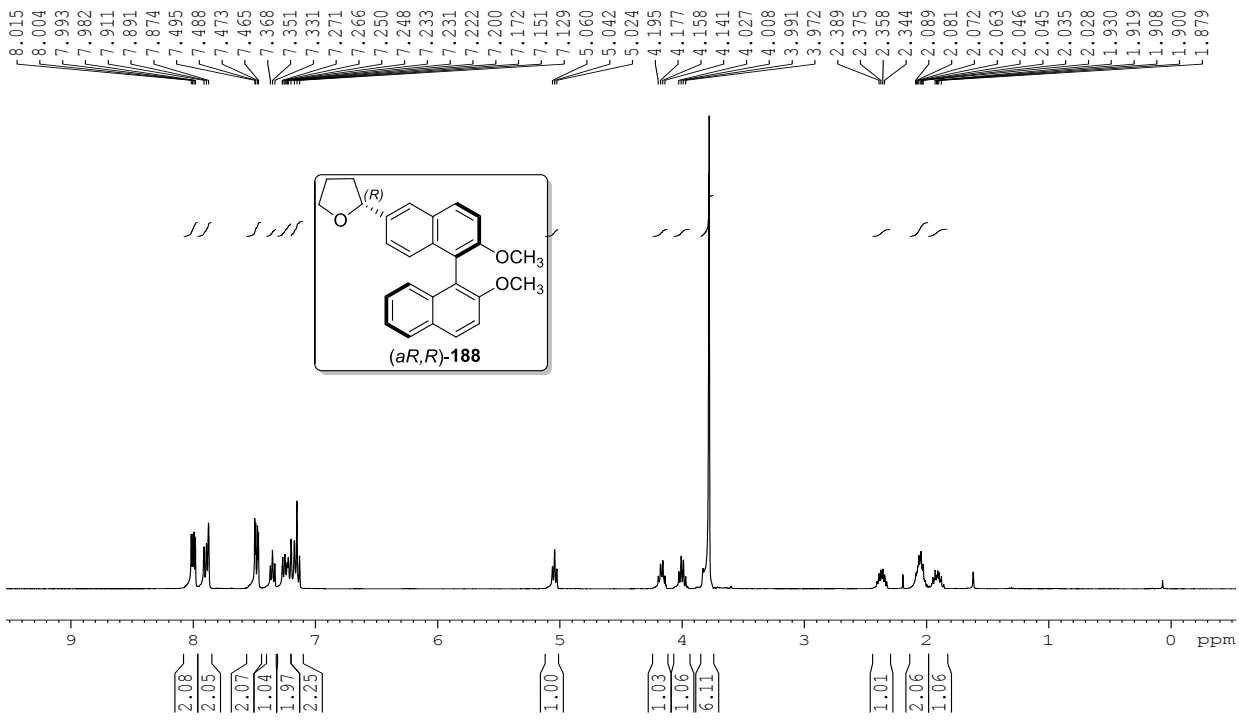
Spectrum No. 23 (Chapter 2, Section 2.2.6) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



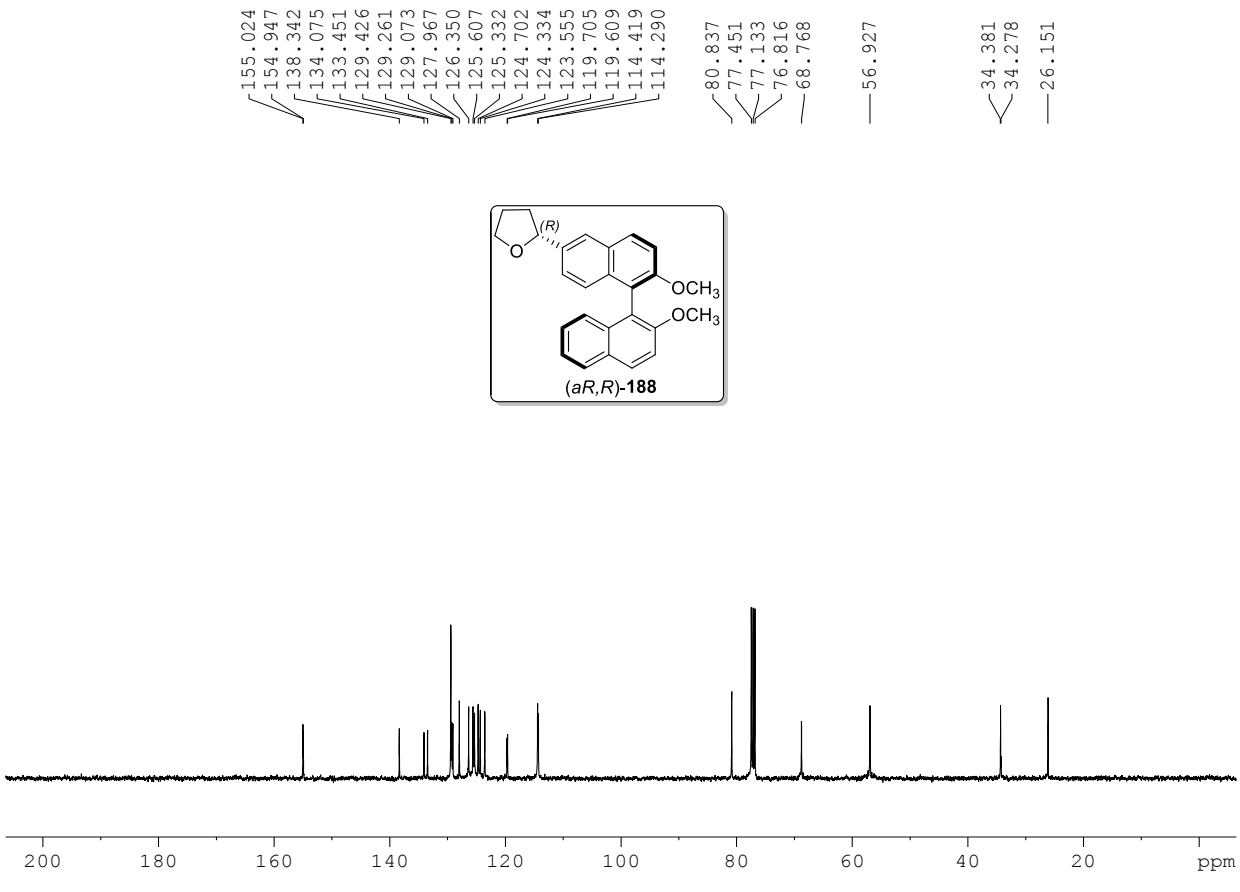
Spectrum No. 24 (Chapter 2, Section 2.2.6) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



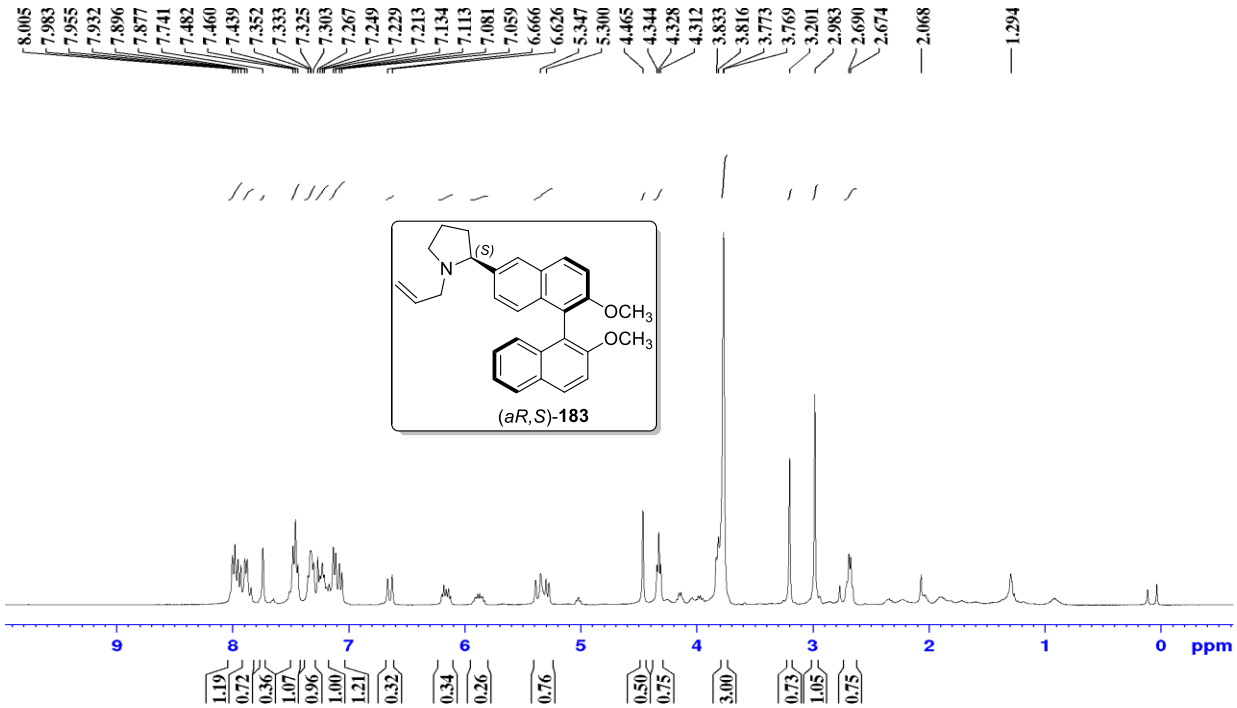
Spectrum No. 25 (Chapter 2, Section 2.2.7) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



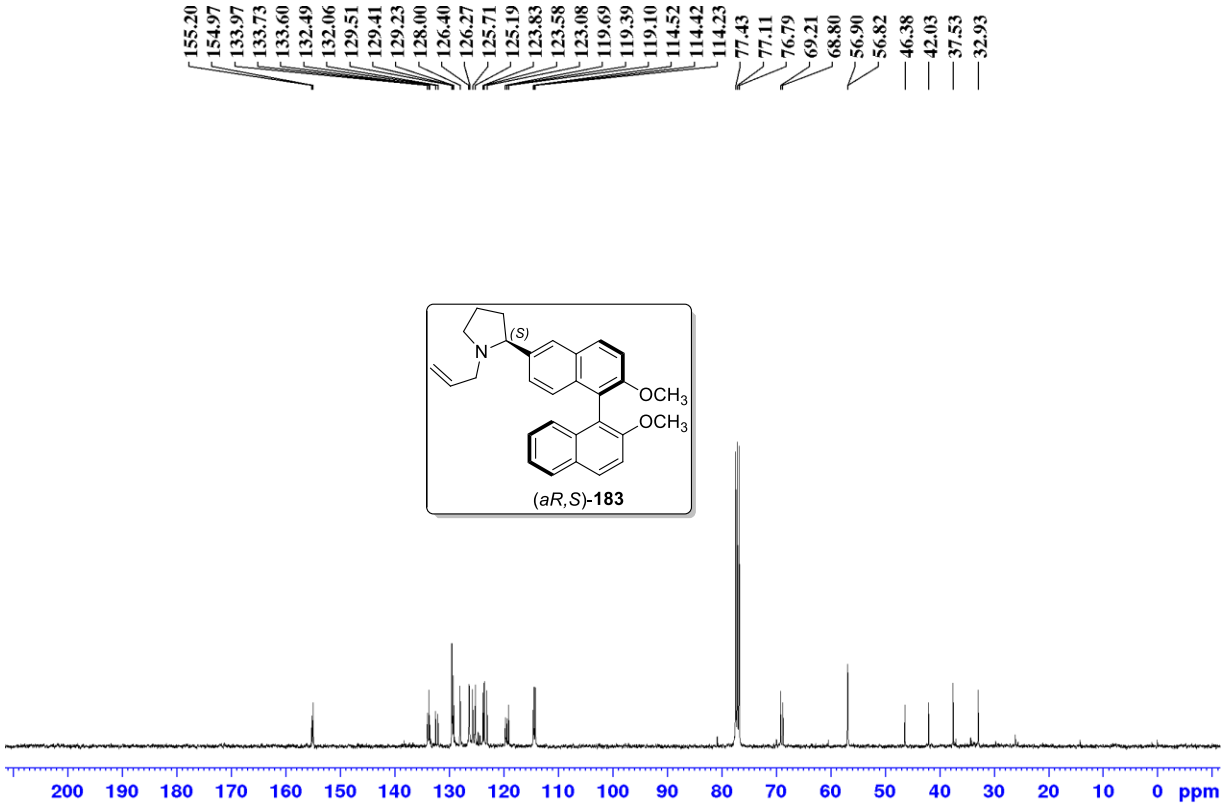
Spectrum No. 26 (Chapter 2, Section 2.2.7) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



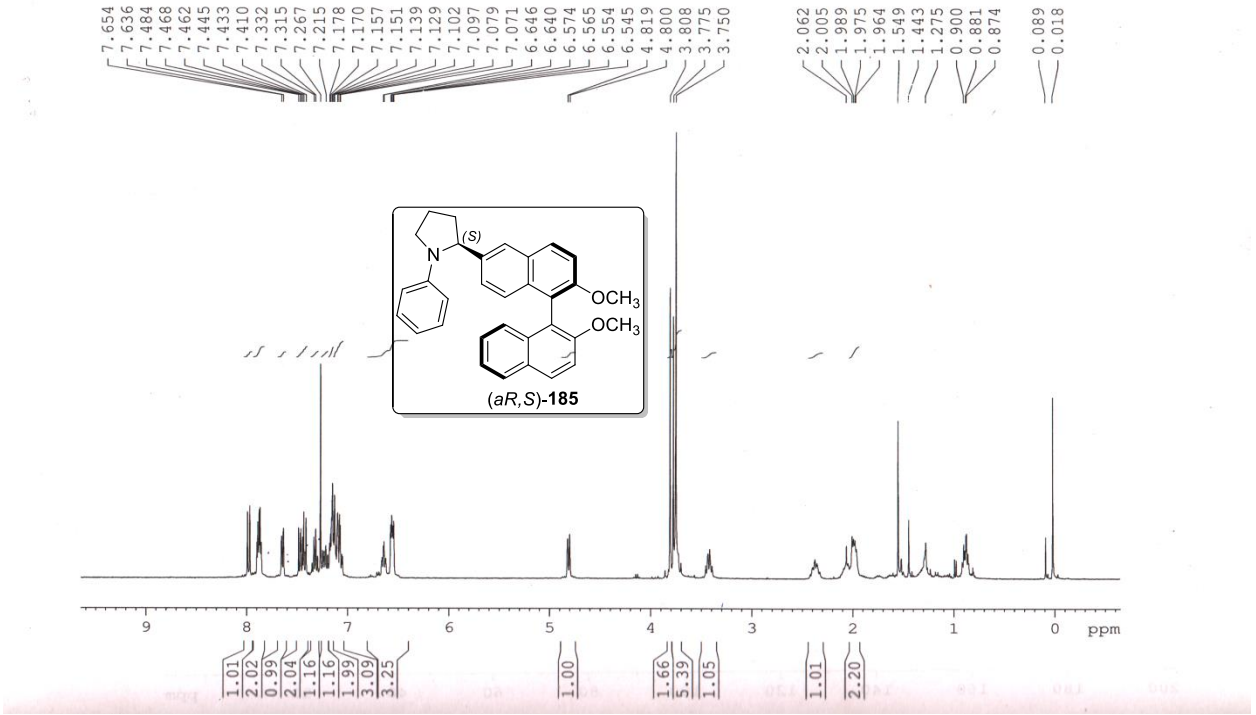
Spectrum No. 27 (Chapter 2, Section 2.2.7) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



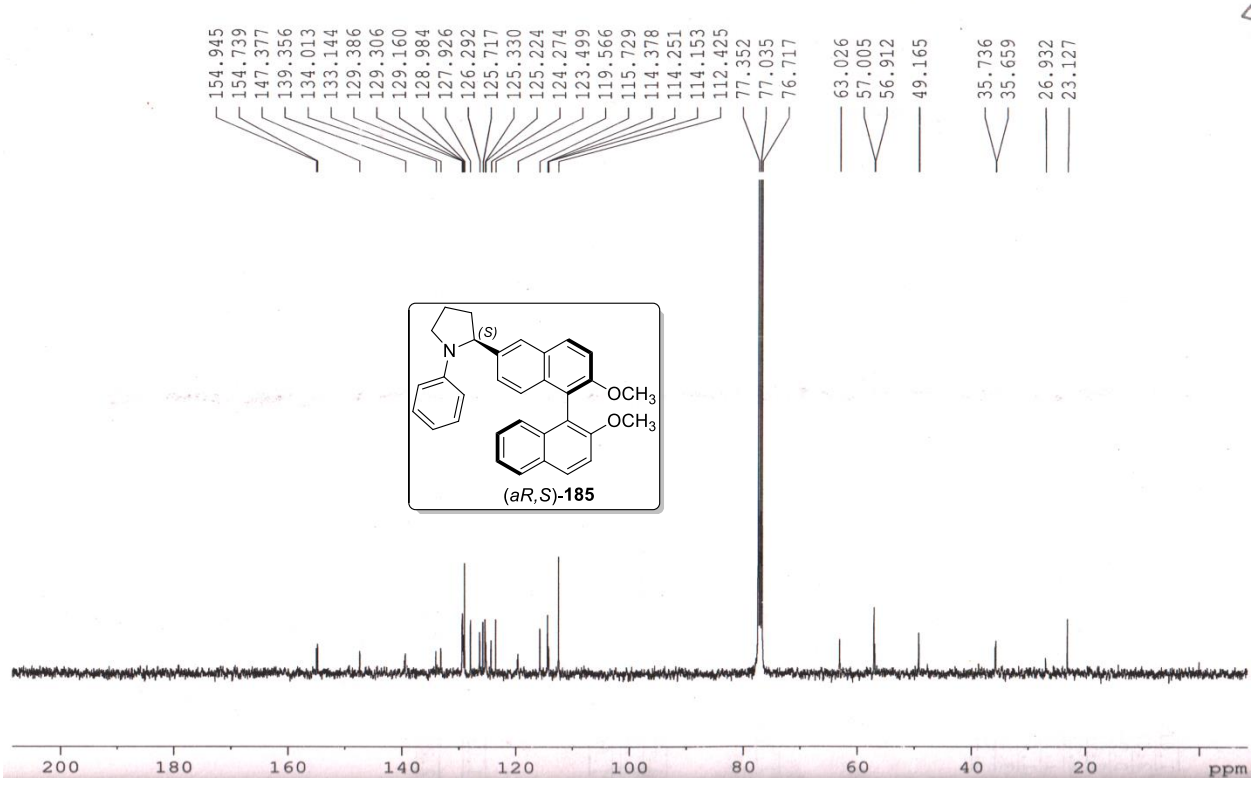
Spectrum No. 28 (Chapter 2, Section 2.2.7) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



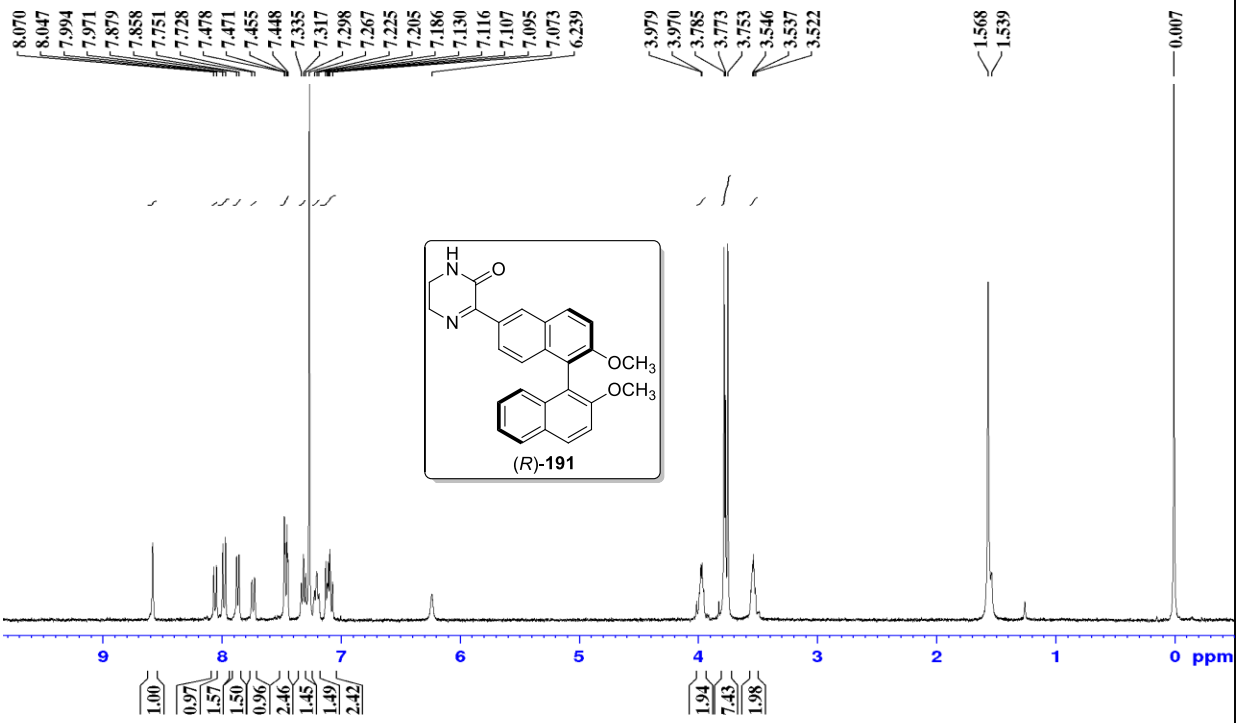
Spectrum No. 29 (Chapter 2, Section 2.2.7) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



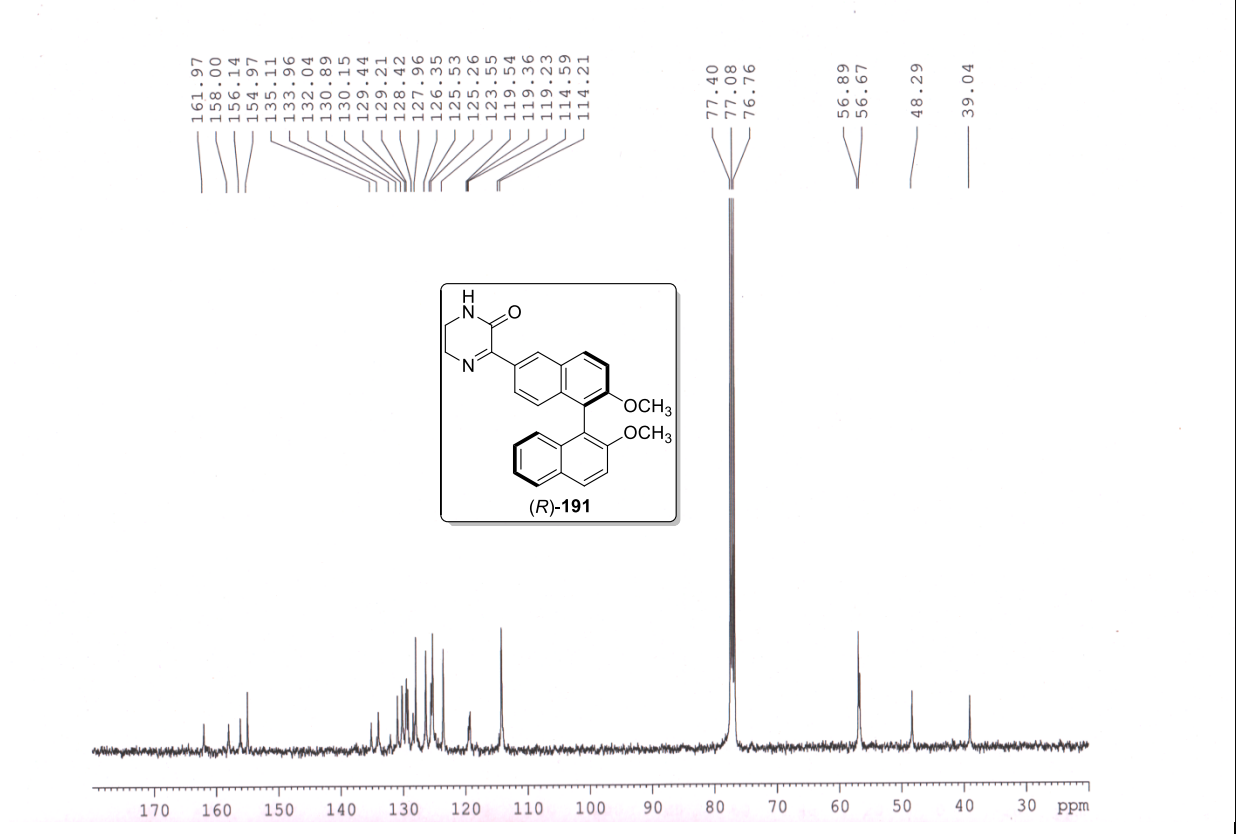
Spectrum No. 30 (Chapter 2, Section 2.2.7) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



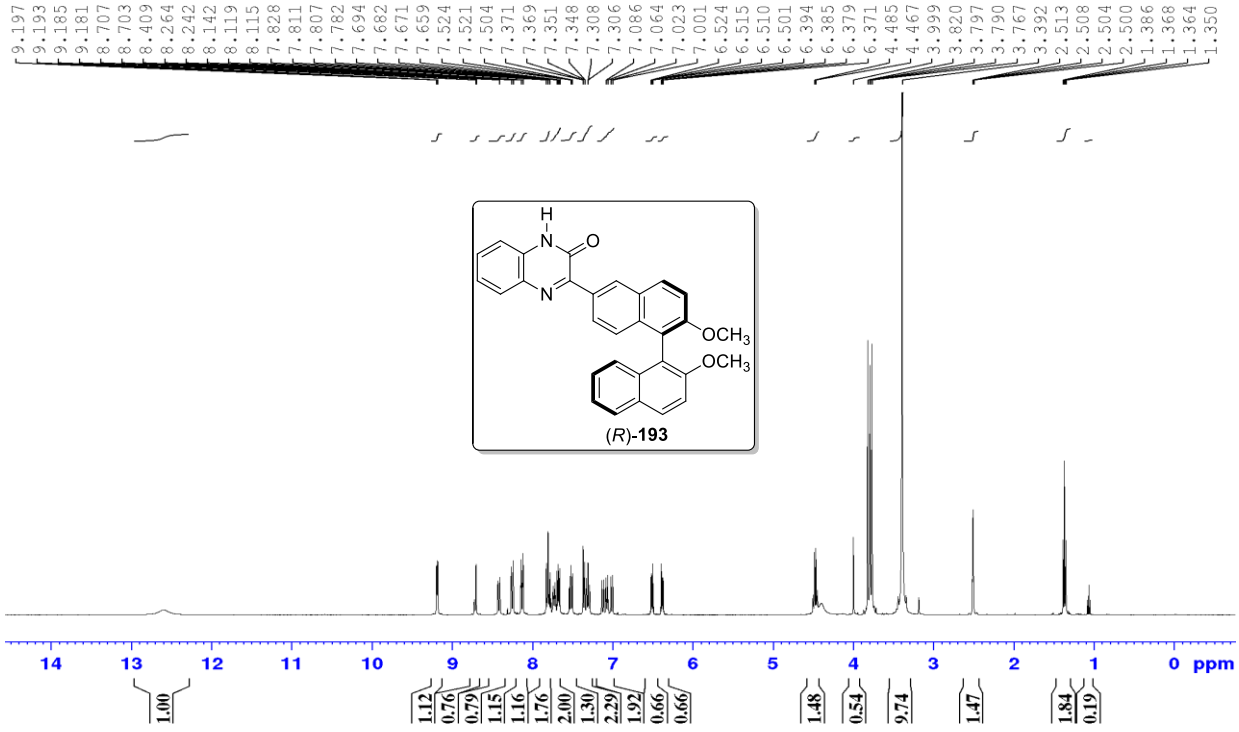
Spectrum No. 31 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



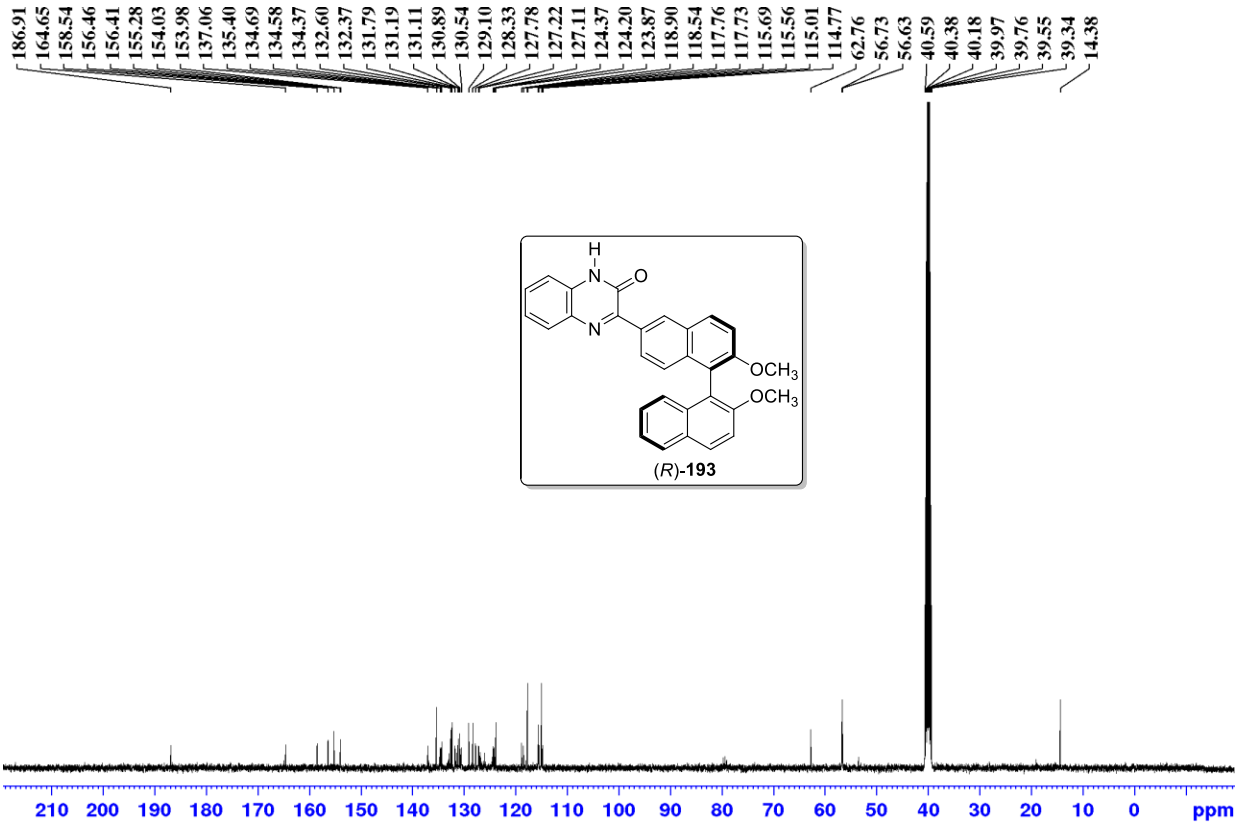
Spectrum No. 32 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



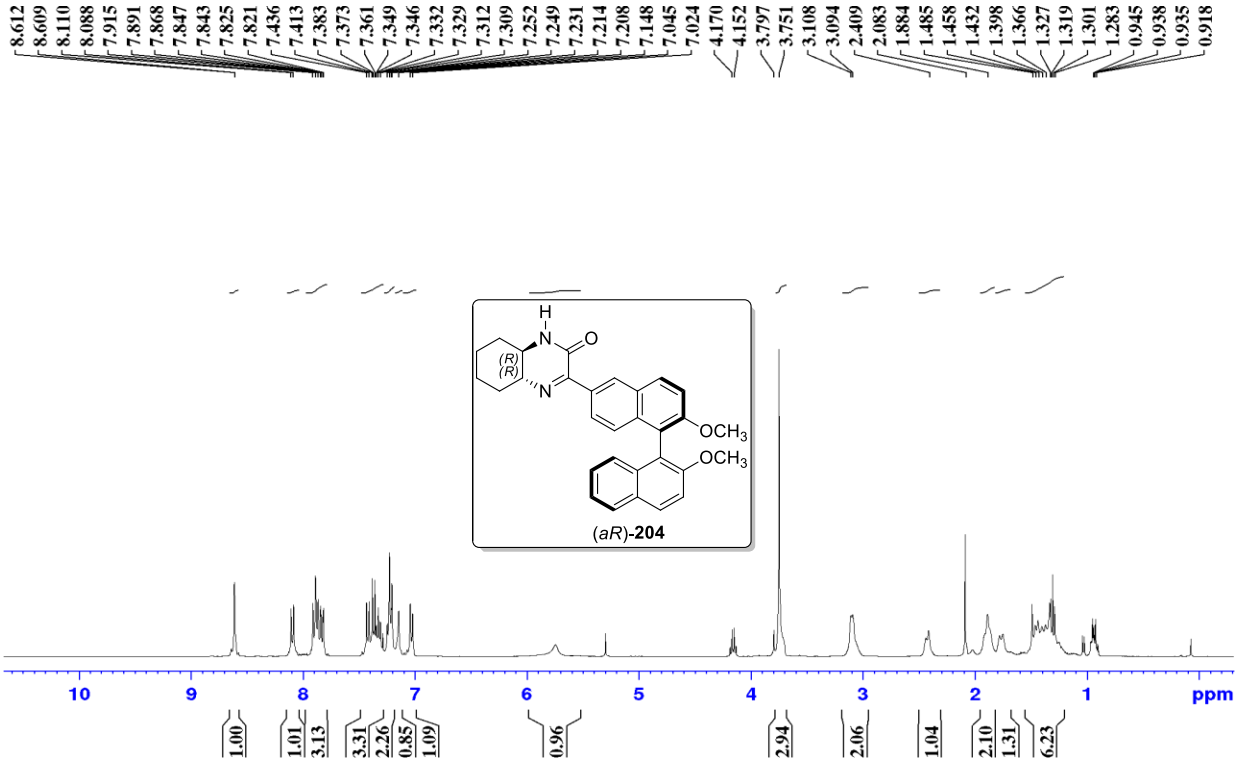
Spectrum No. 33 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



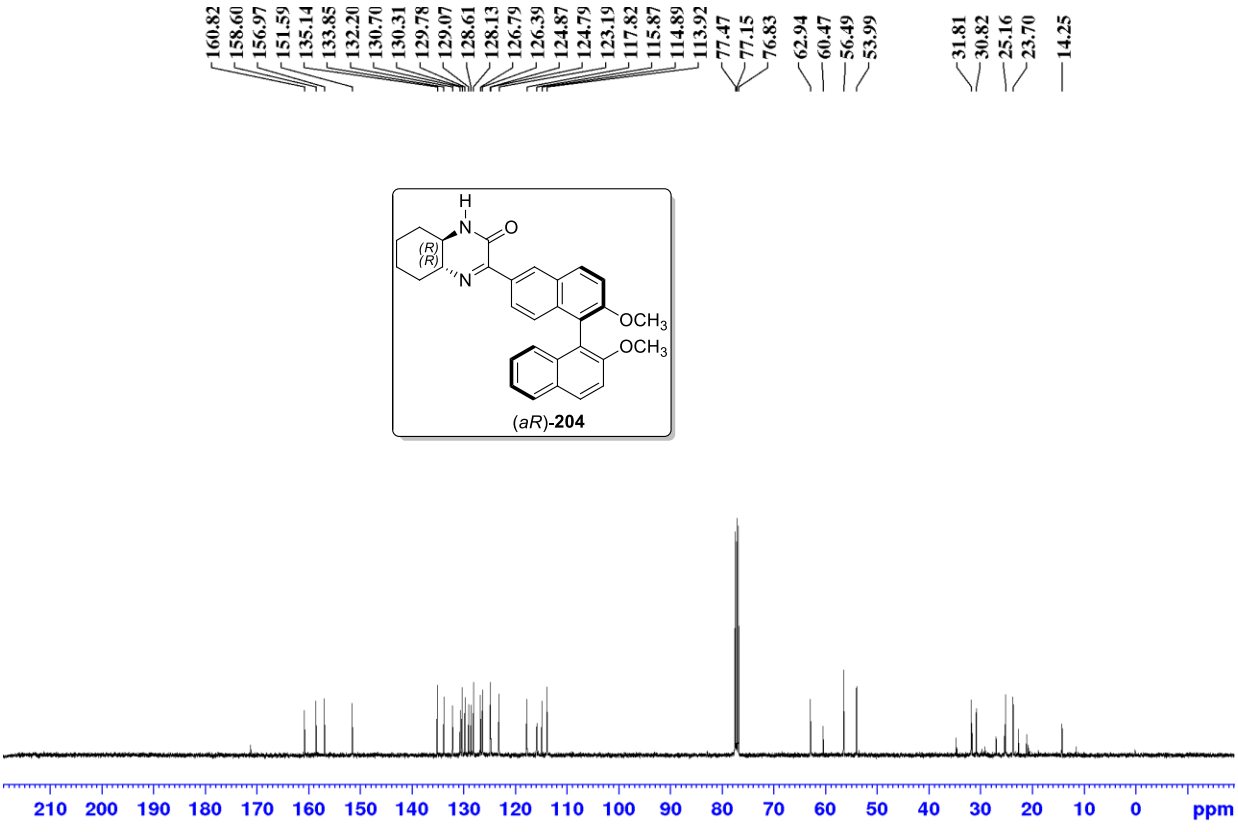
Spectrum No. 34 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



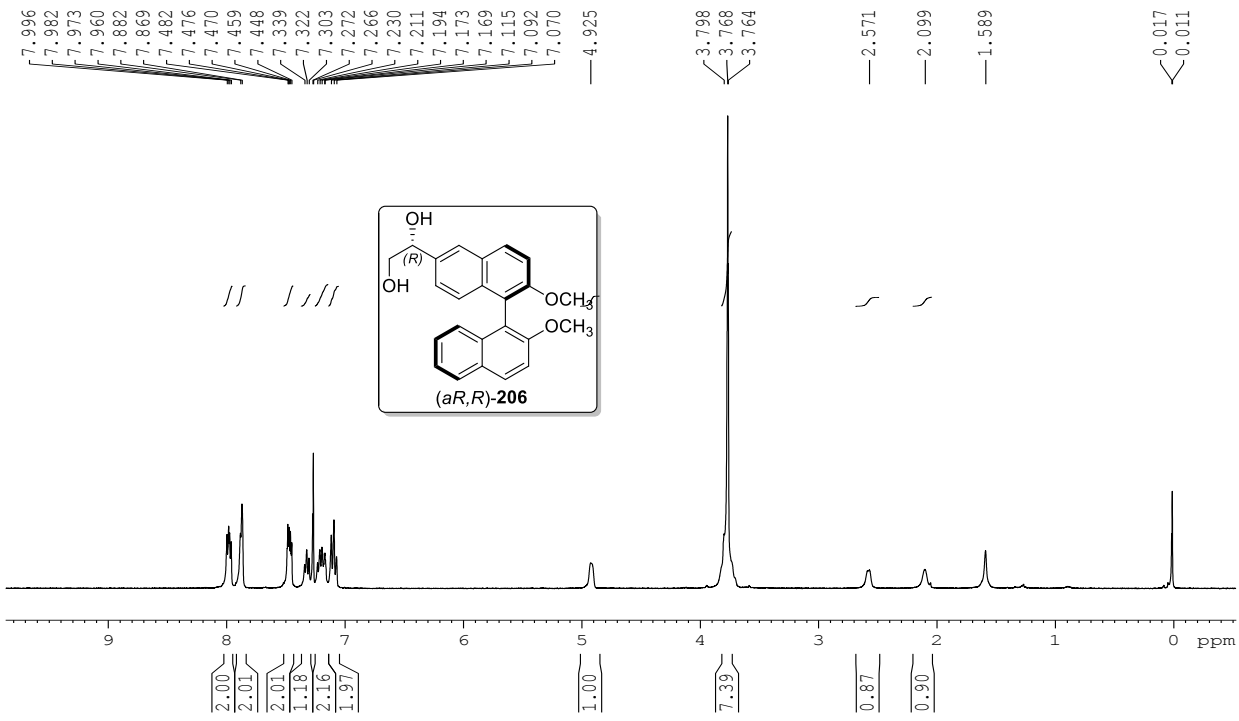
Spectrum No. 35 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



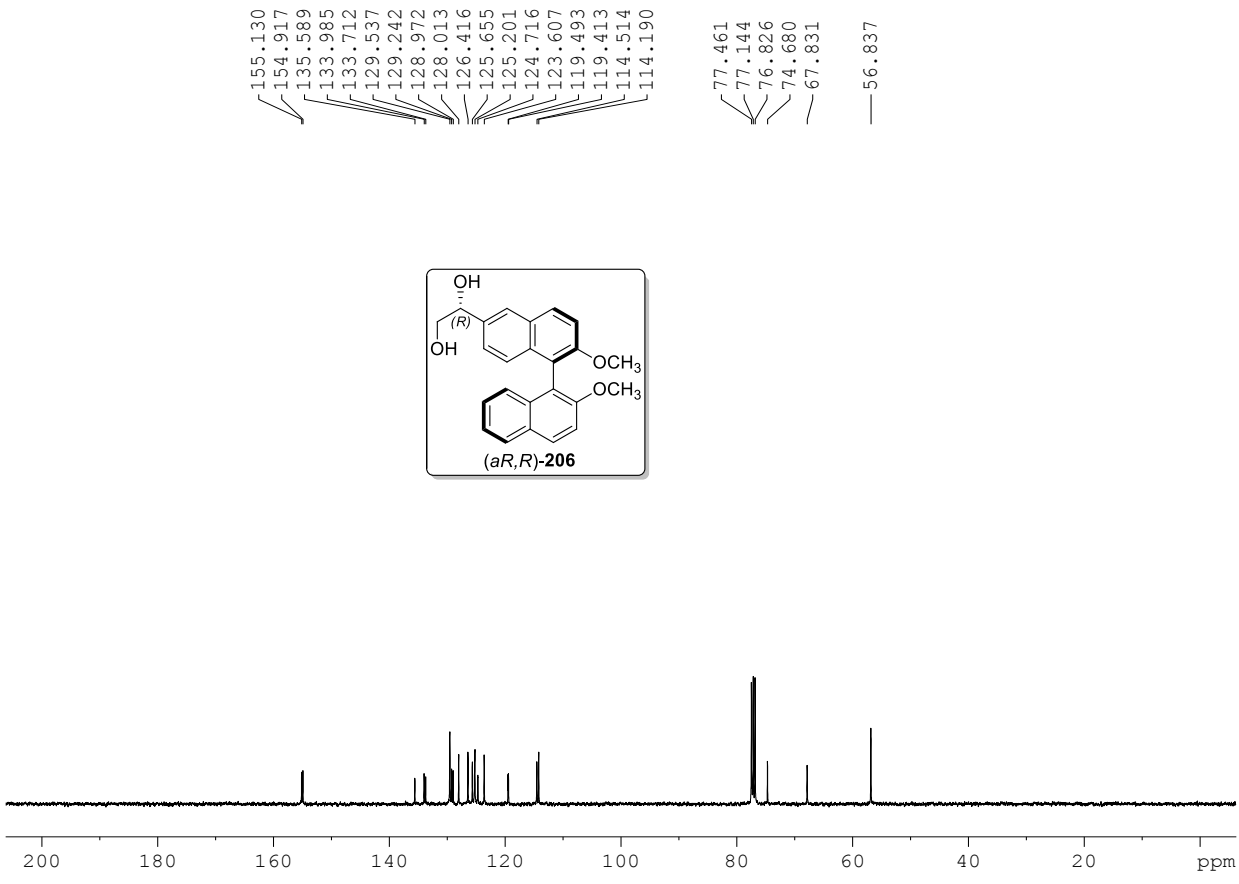
Spectrum No. 36 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



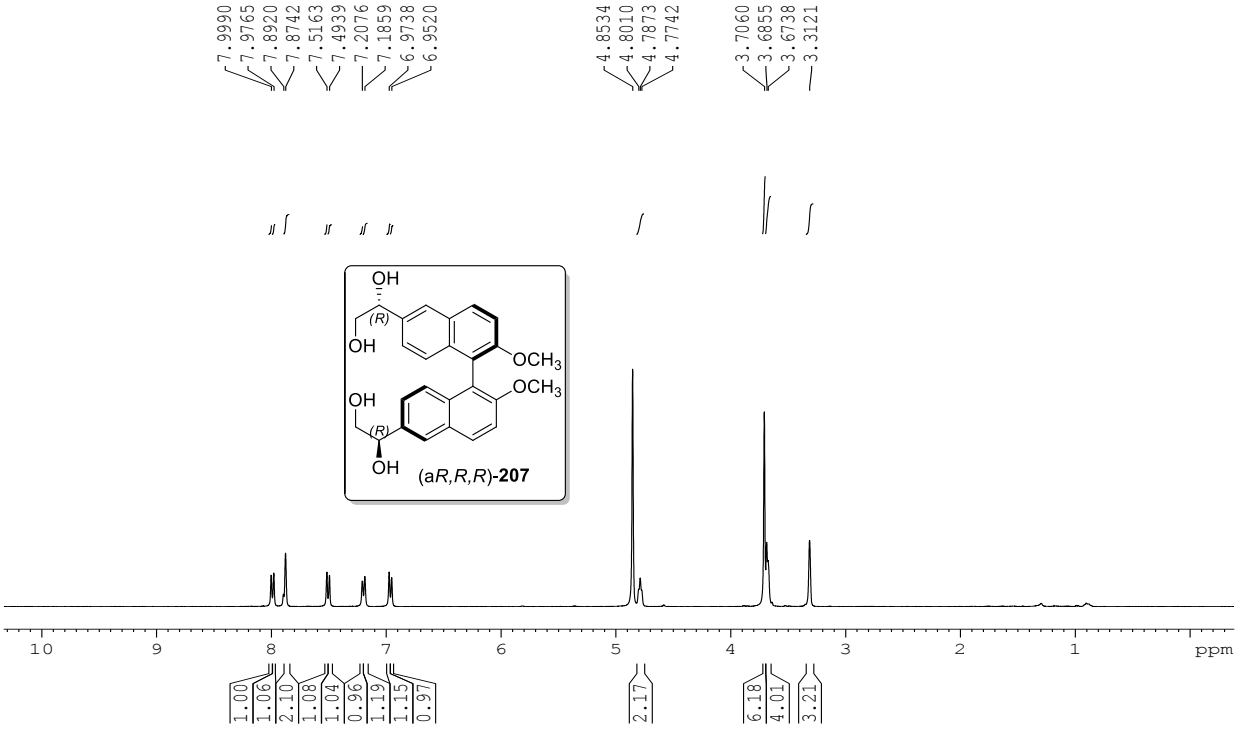
Spectrum No. 37 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



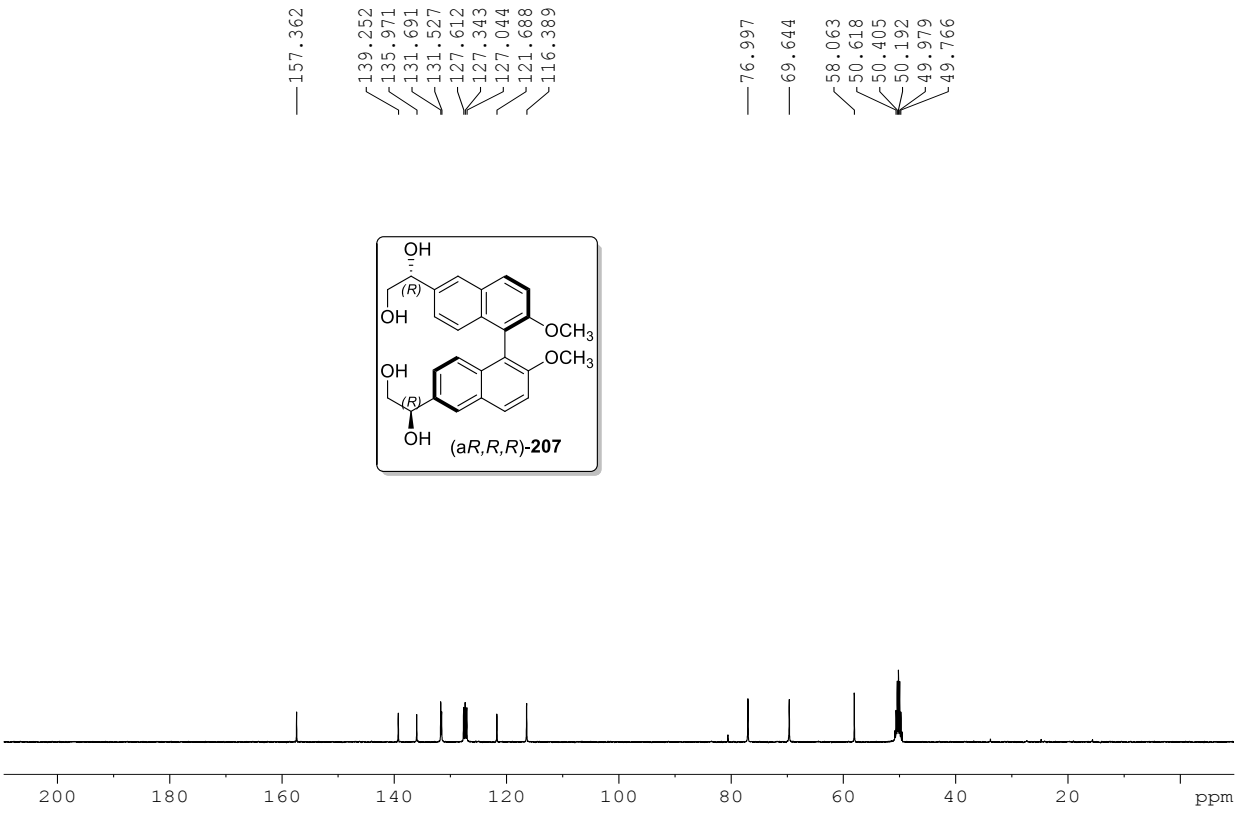
Spectrum No. 38 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



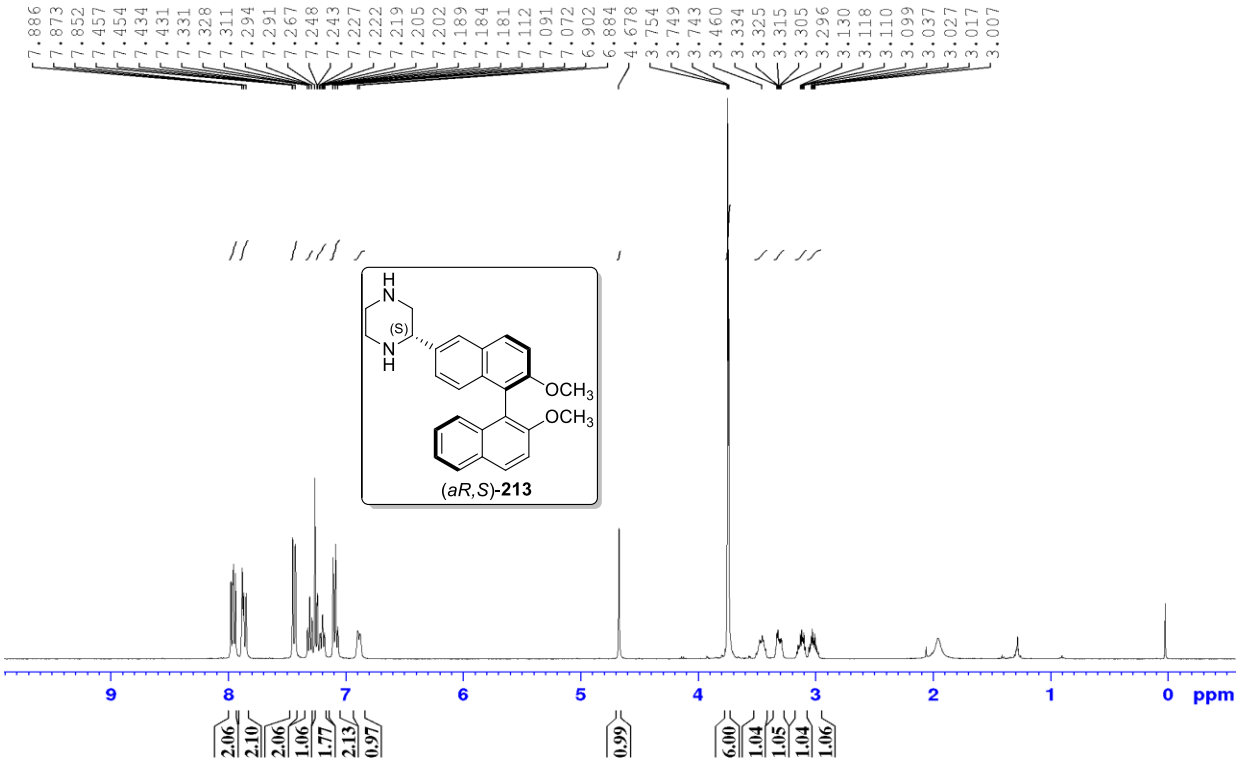
Spectrum No. 39 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



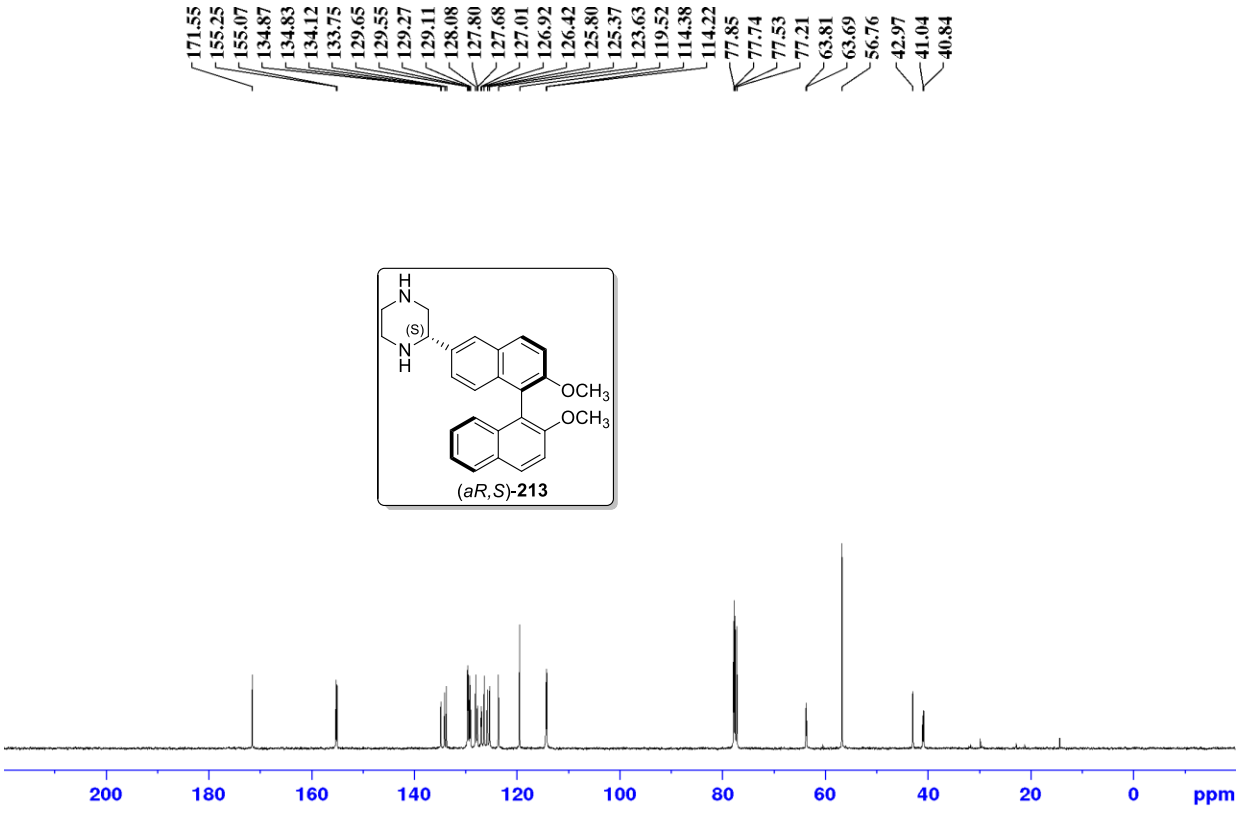
Spectrum No. 40 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



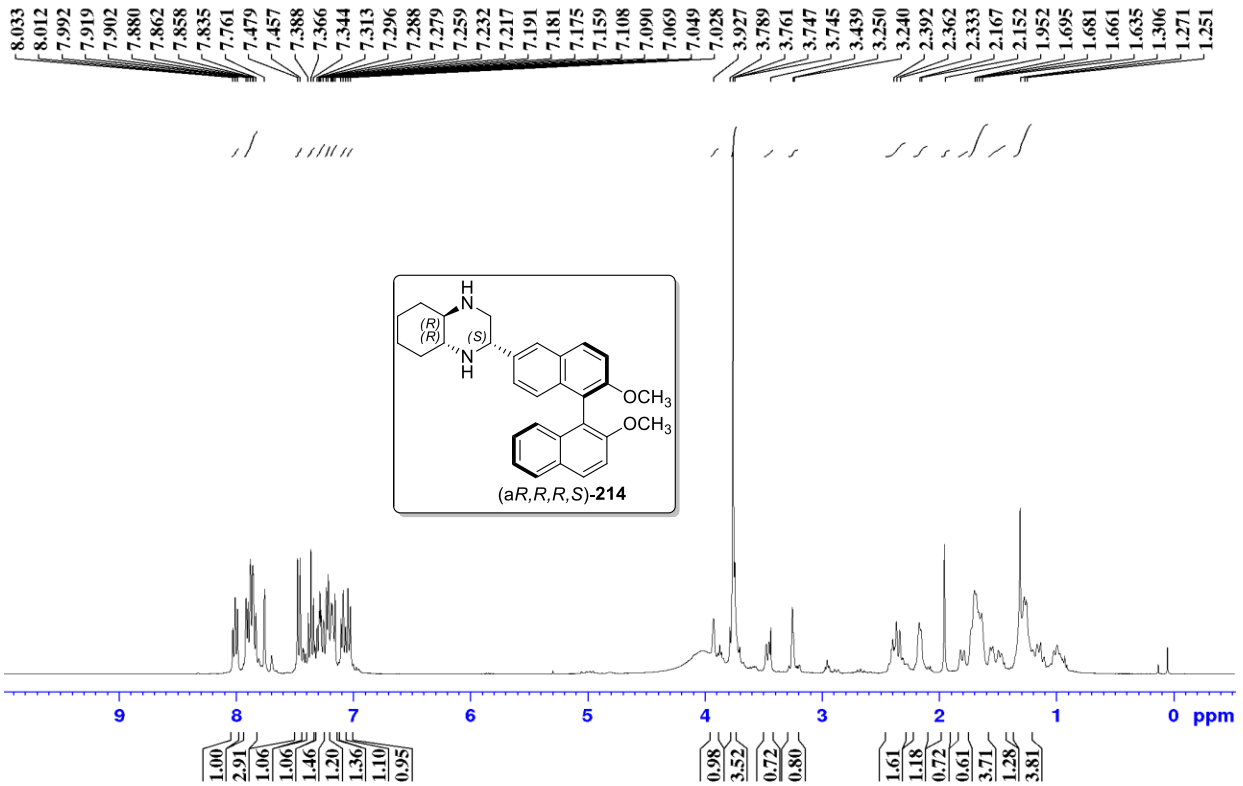
Spectrum No. 41 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 Hz, $CDCl_3$)



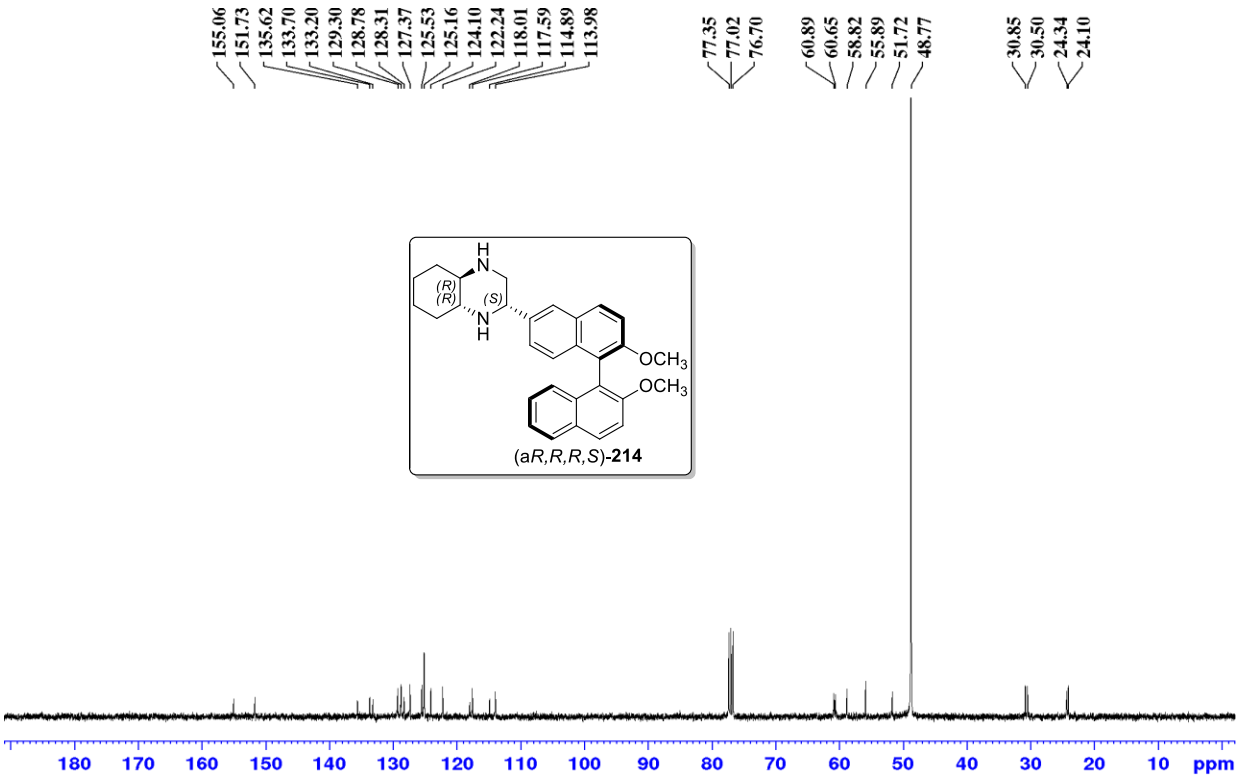
Spectrum No. 42 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



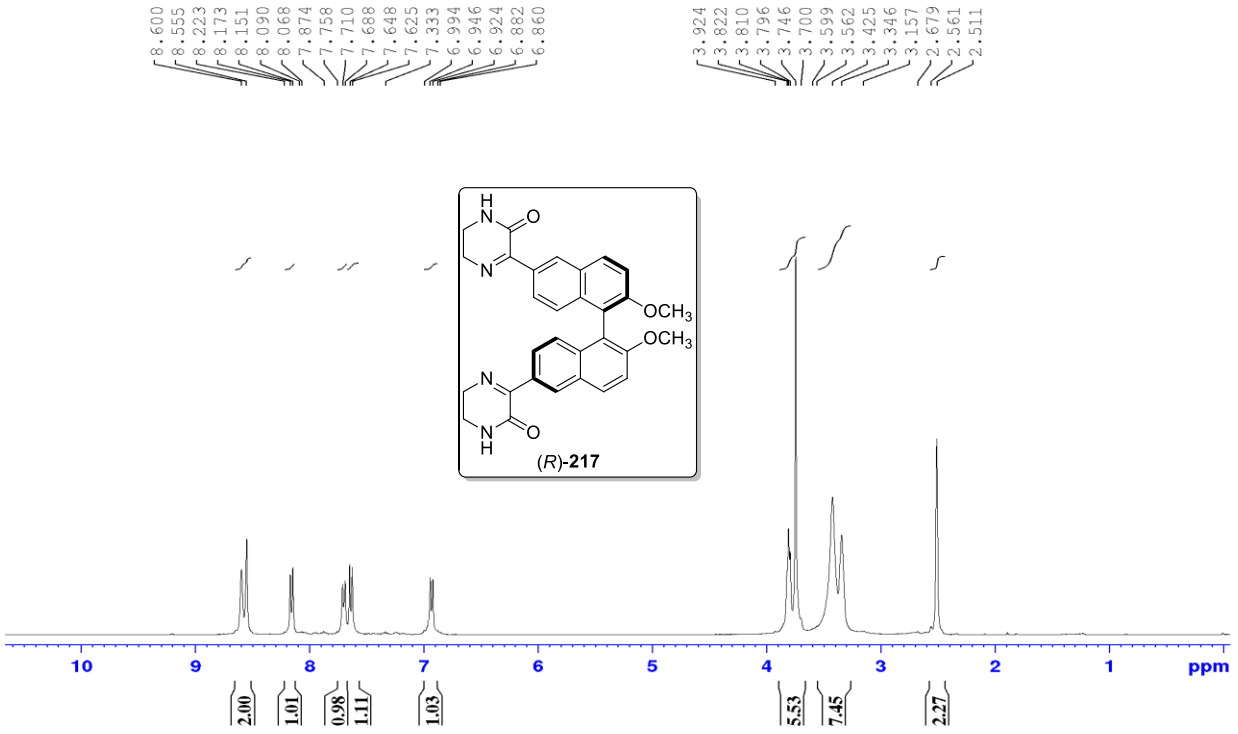
Spectrum No. 43 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



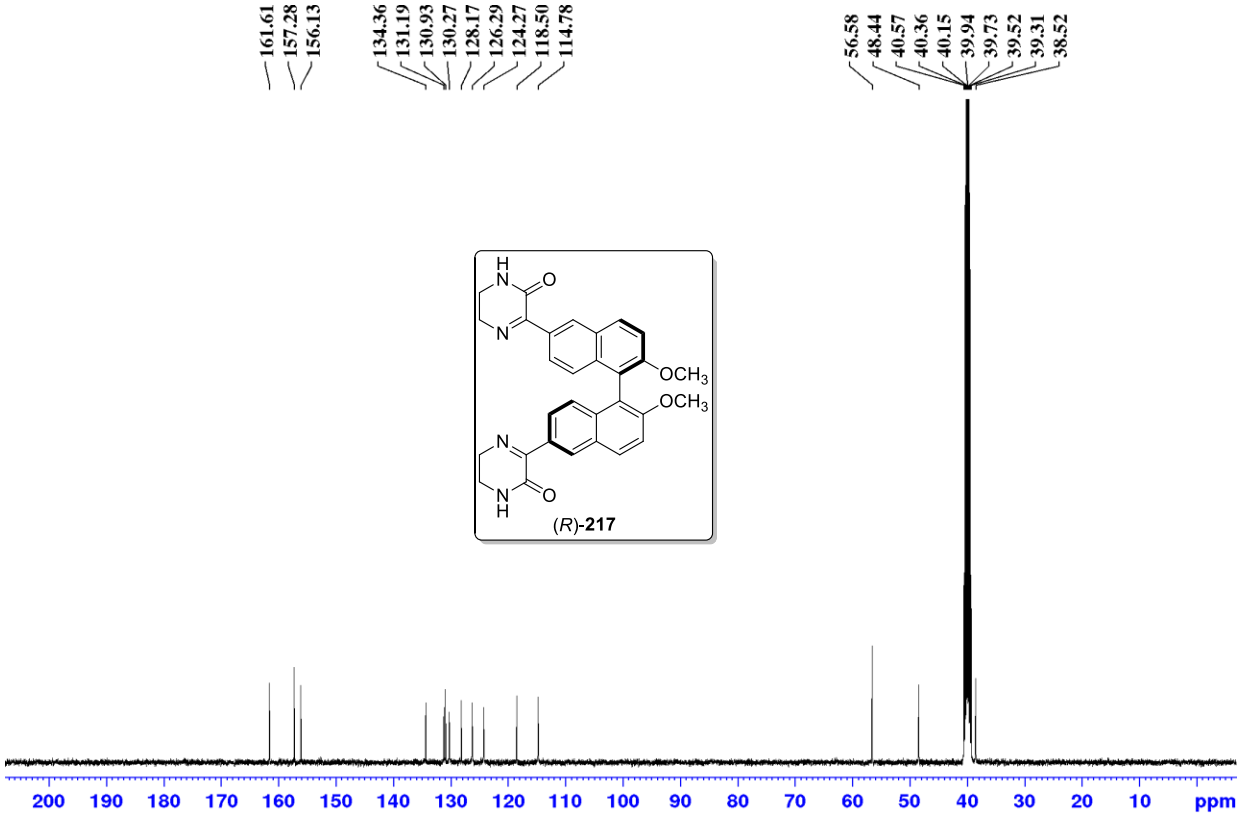
Spectrum No. 44 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



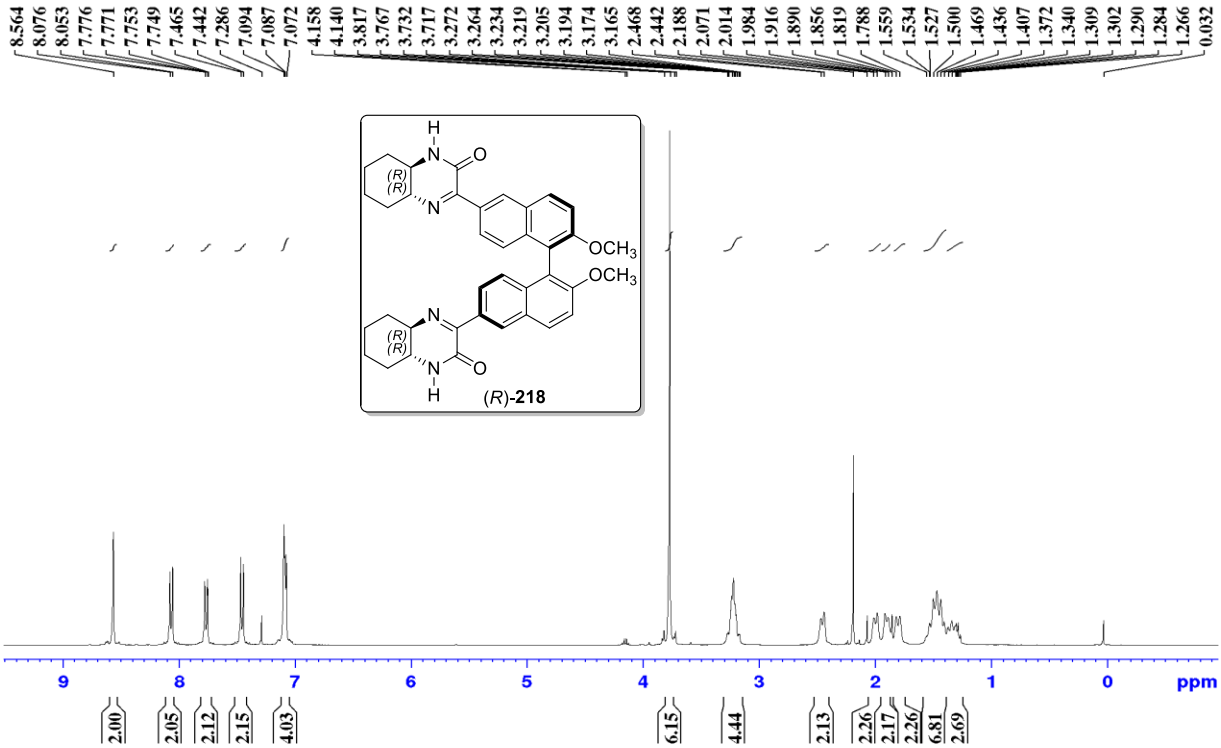
Spectrum No. 45 (Chapter 2, Section 2.2.9) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



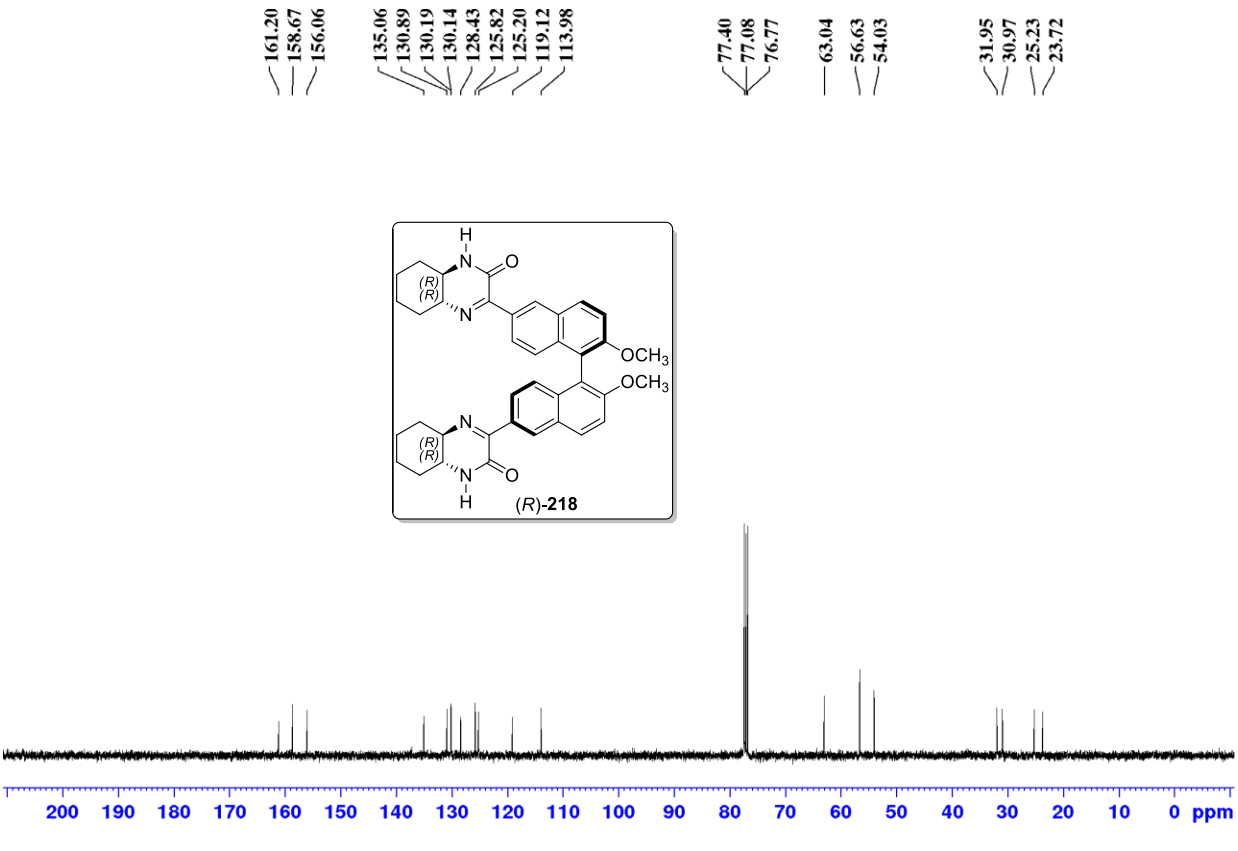
Spectrum No. 46 (Chapter 2, Section 2.2.9) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



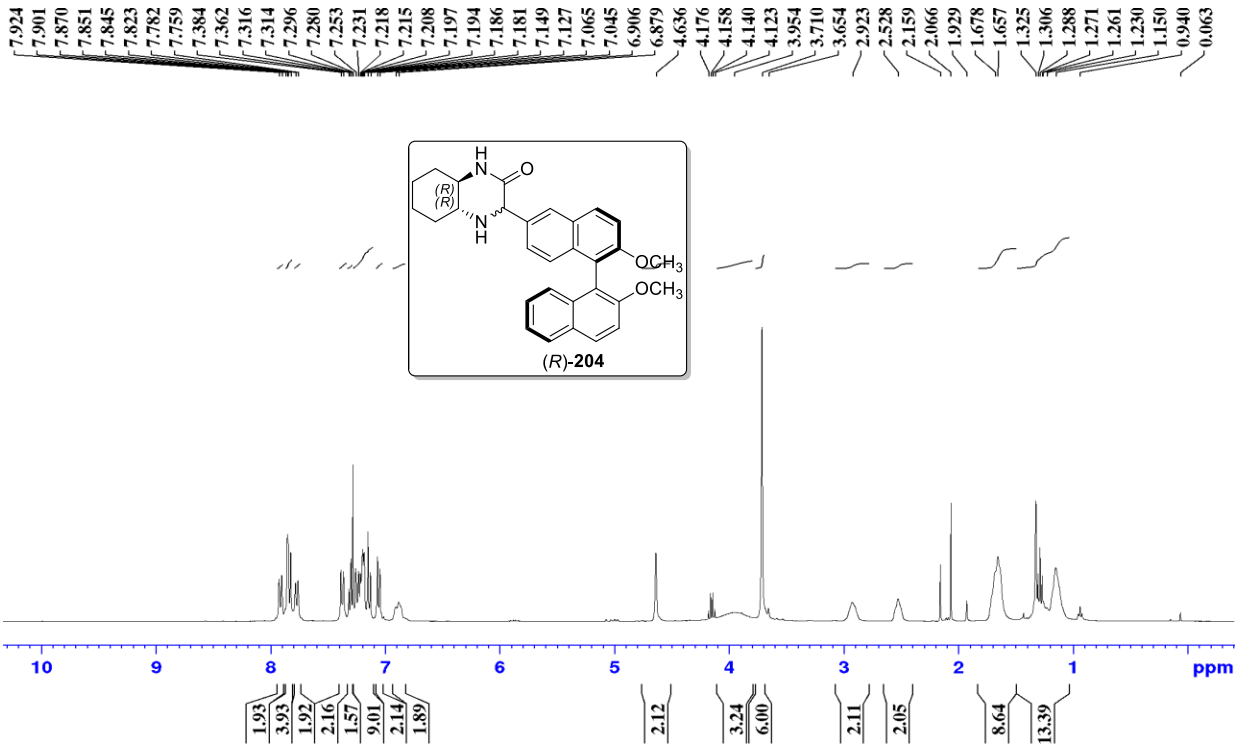
Spectrum No. 47 (Chapter 2, Section 2.2.9) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



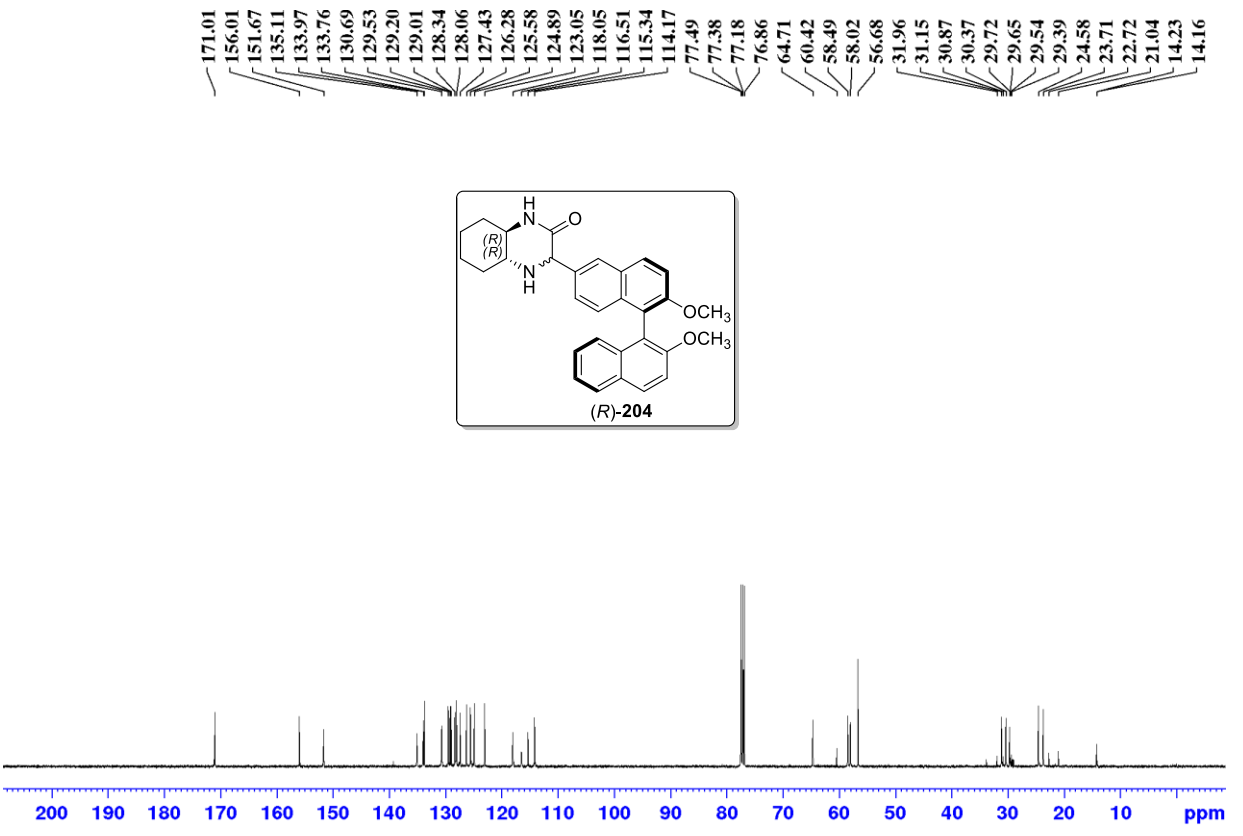
Spectrum No. 48 (Chapter 2, Section 2.2.9) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



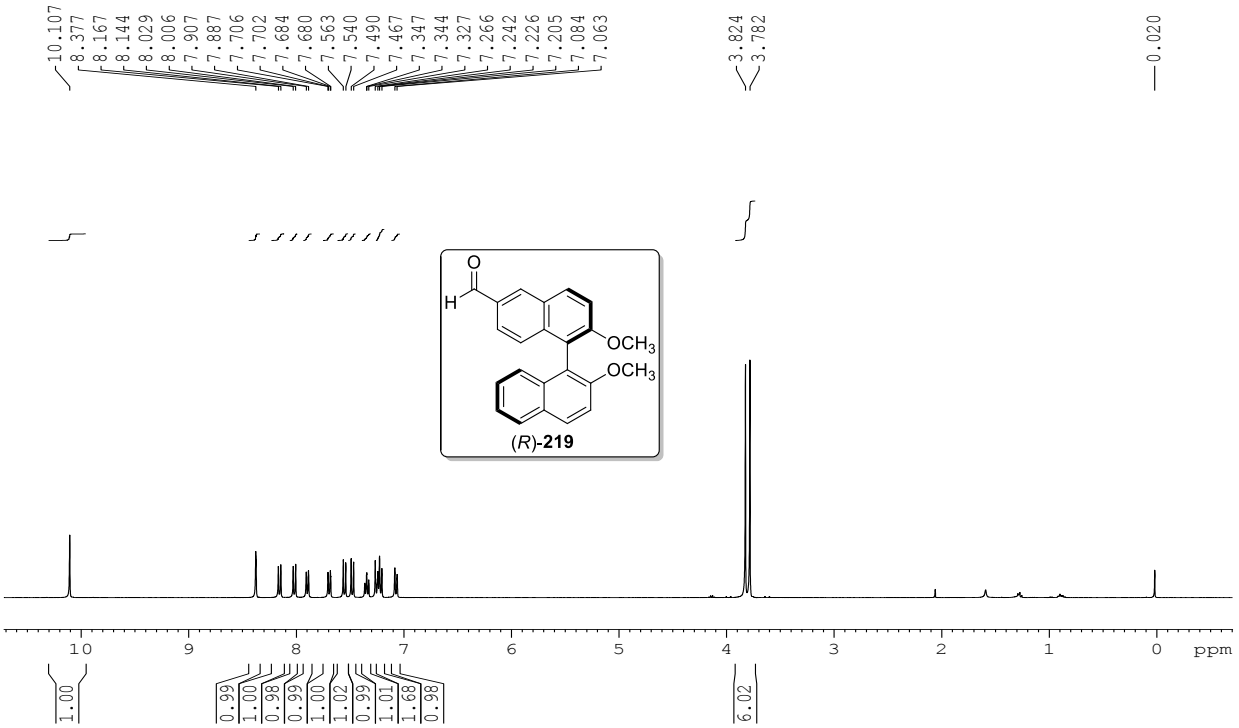
Spectrum No. 49 (Chapter 2, Section 2.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



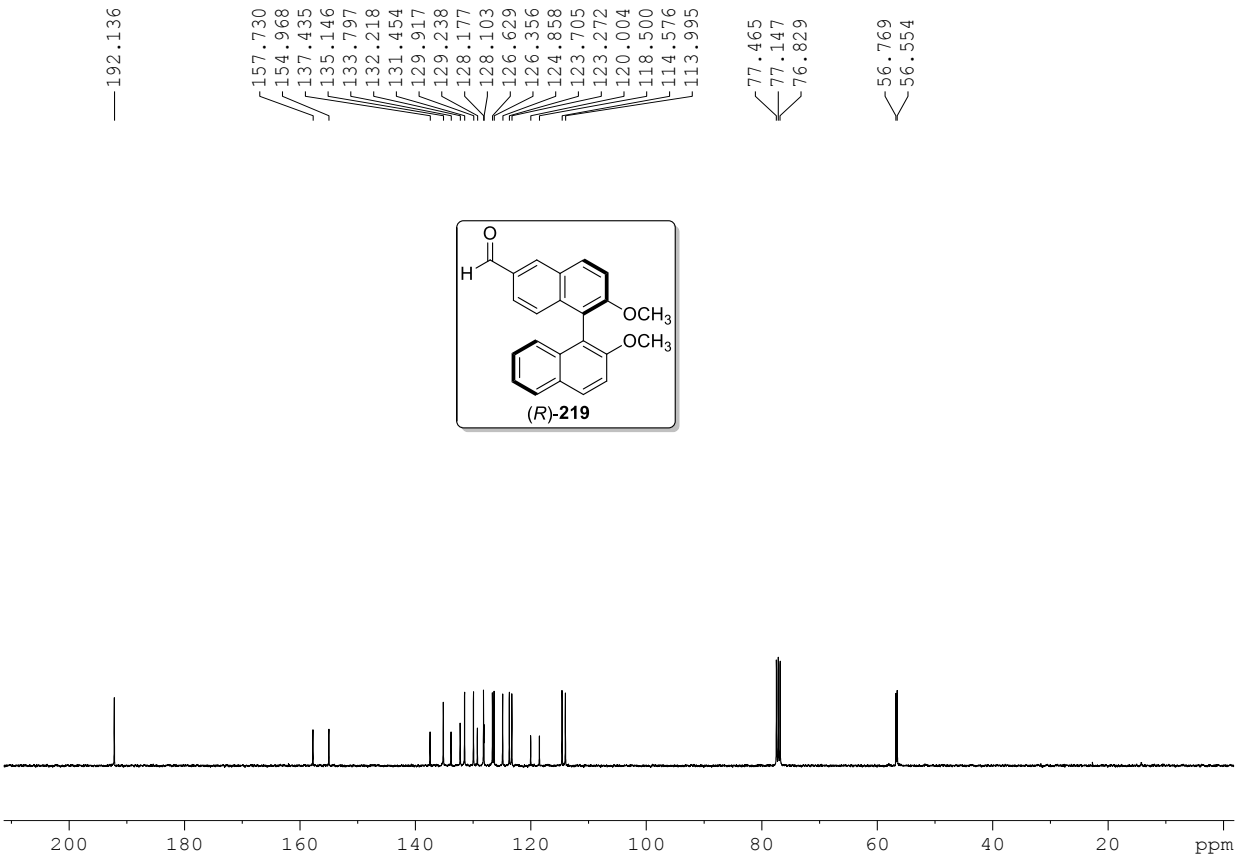
Spectrum No. 50 (Chapter 2, Section 2.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



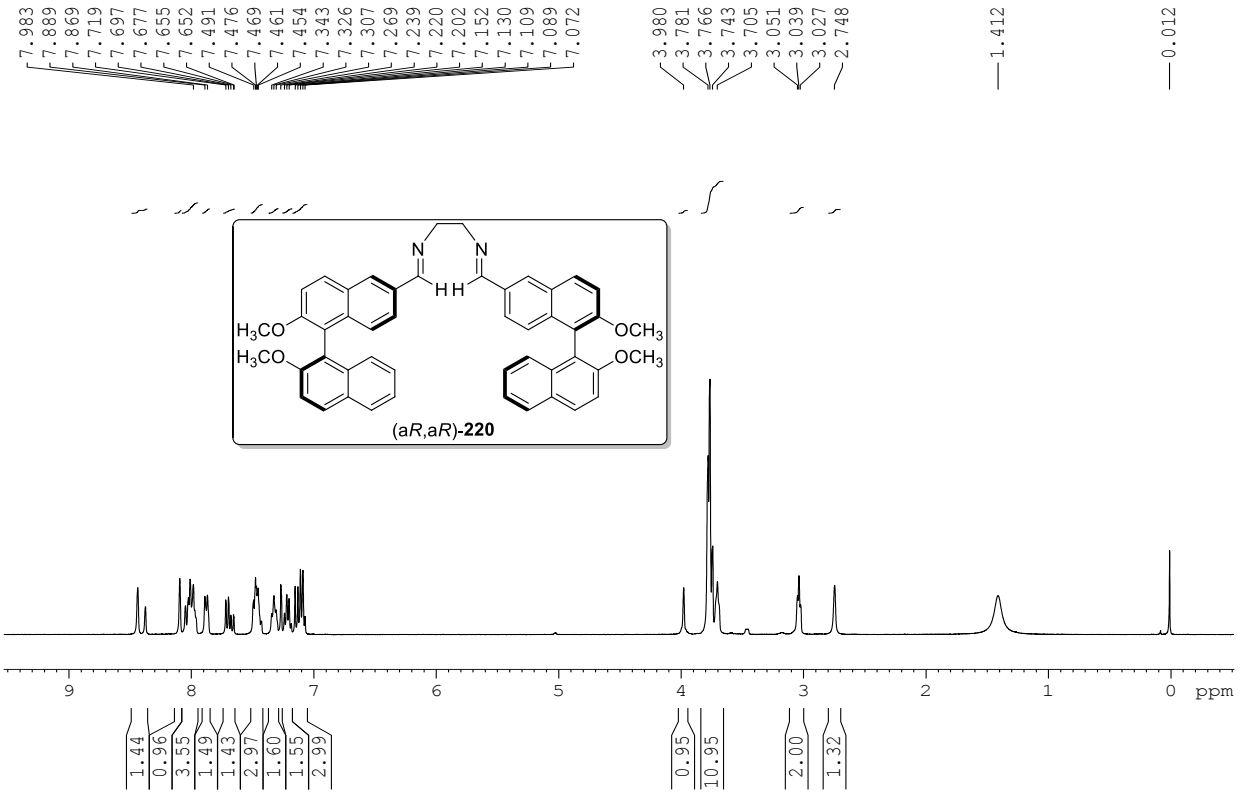
Spectrum No. 51 (Chapter 2, Section 2.2.10) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



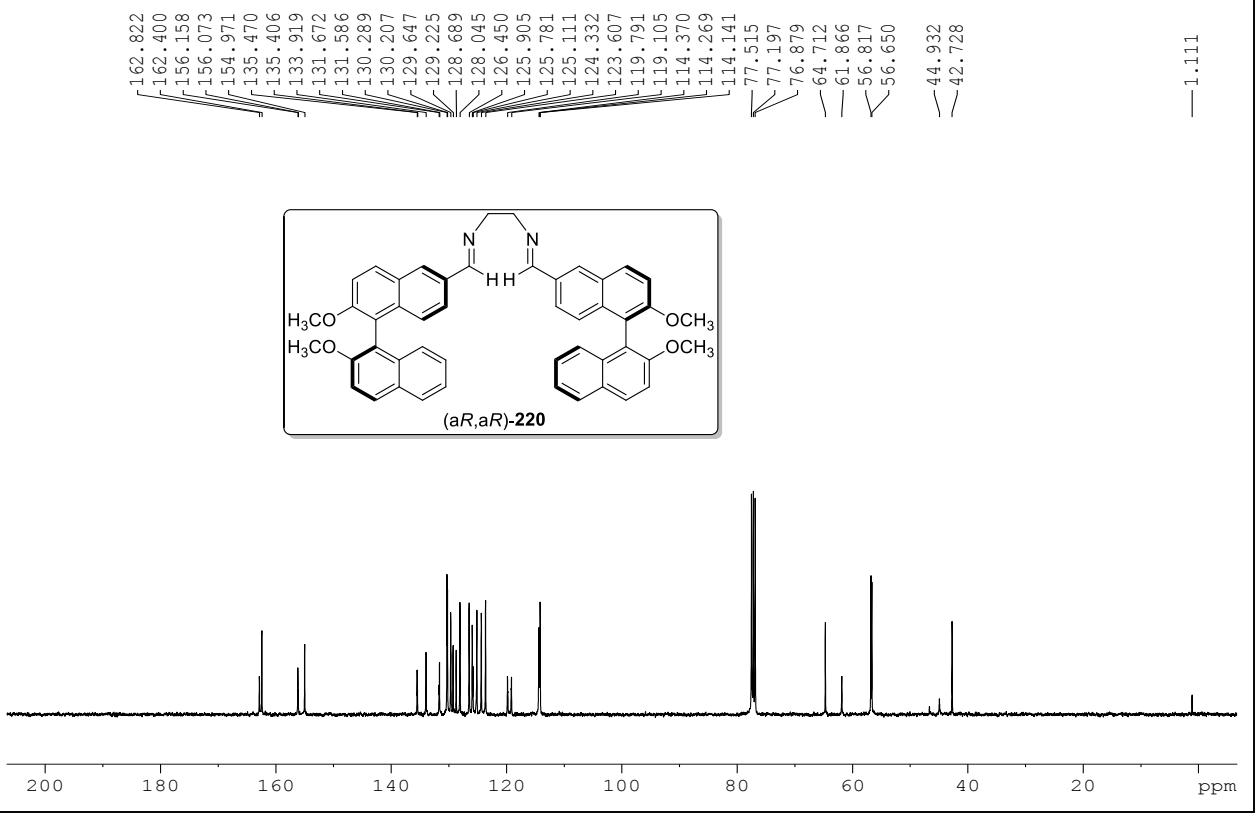
Spectrum No. 52 (Chapter 2, Section 2.2.10) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



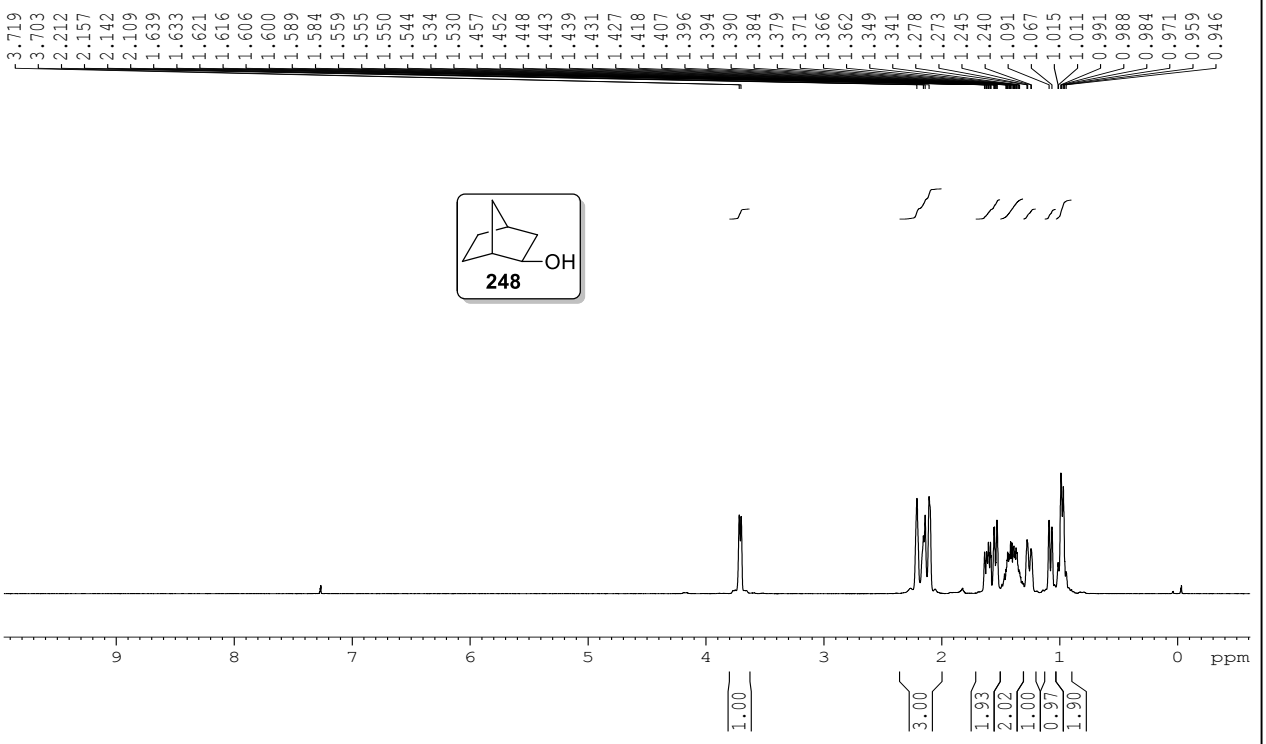
Spectrum No. 53 (Chapter 2, Section 2.2.11) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



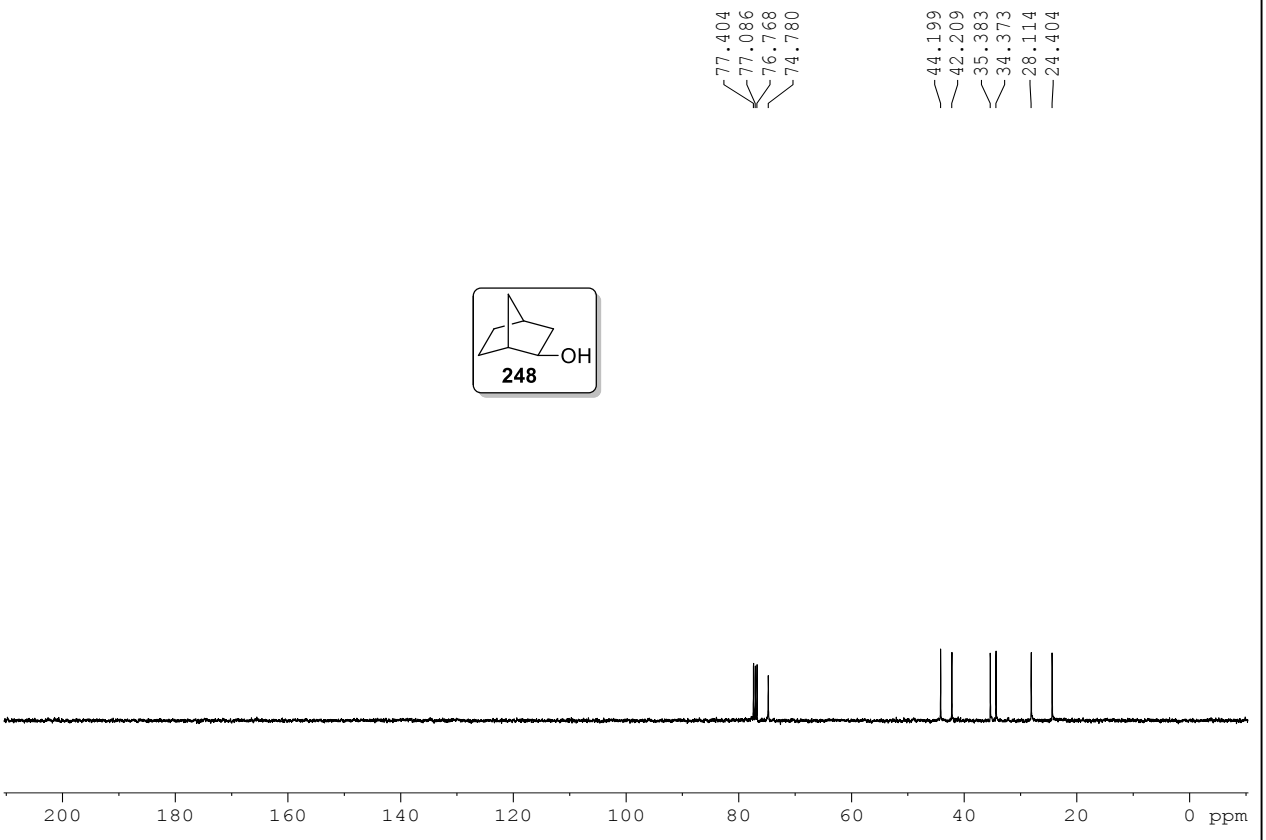
Spectrum No. 54 (Chapter 2, Section 2.2.11) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



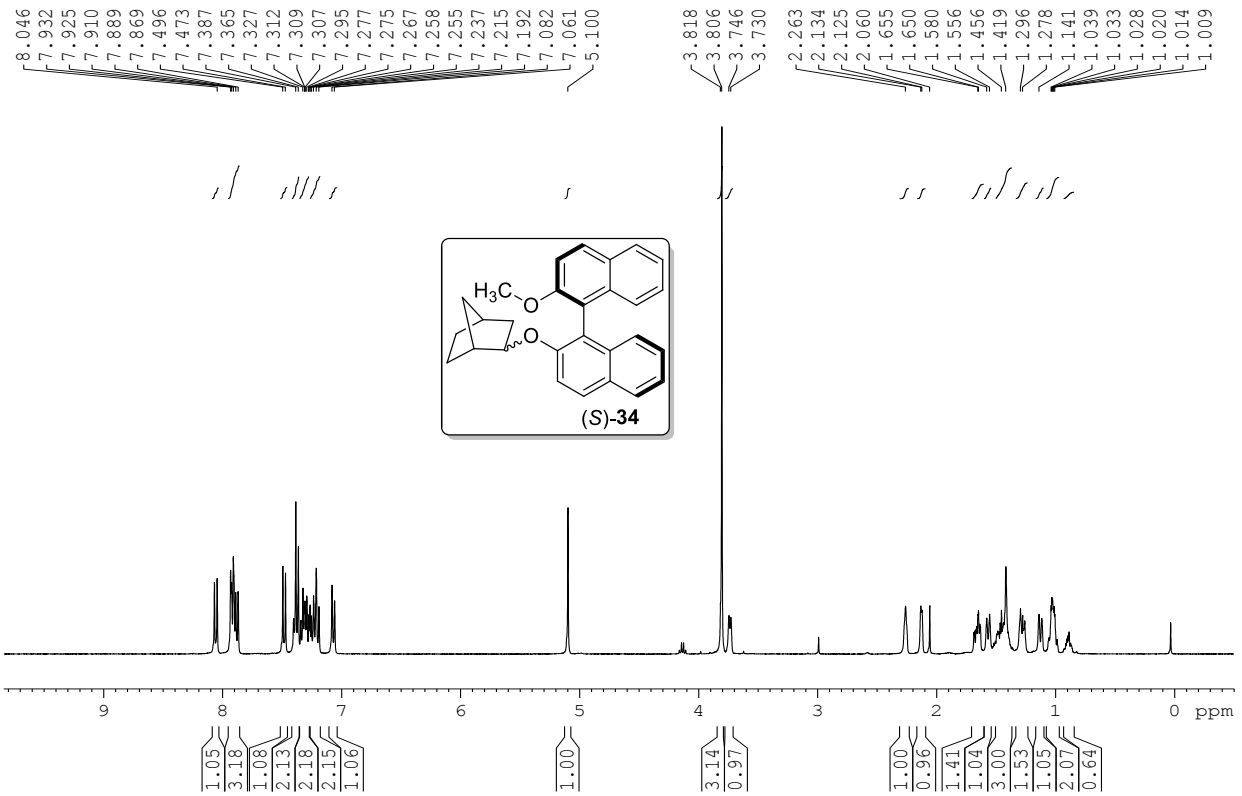
Spectrum No. 55 (Chapter 3, Section 3.2.1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



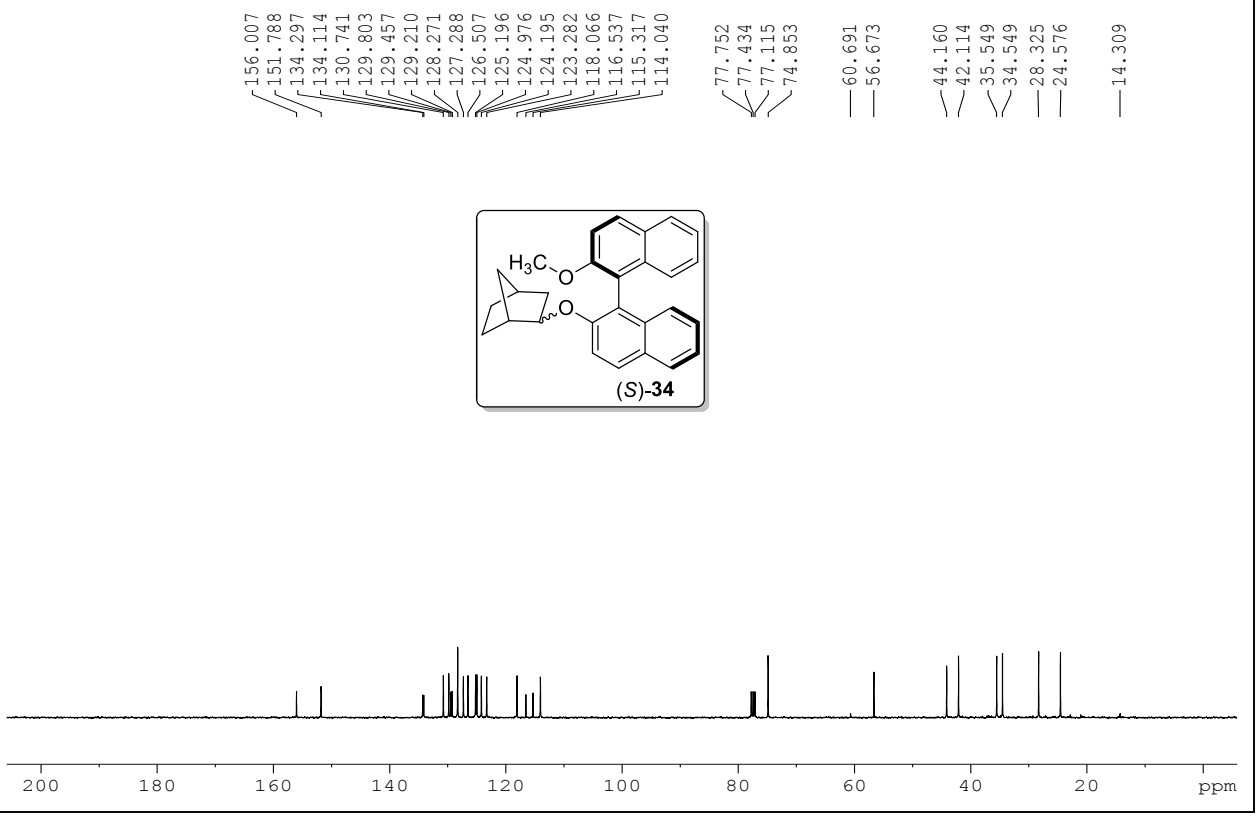
Spectrum No. 56 (Chapter 3, Section 3.2.1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



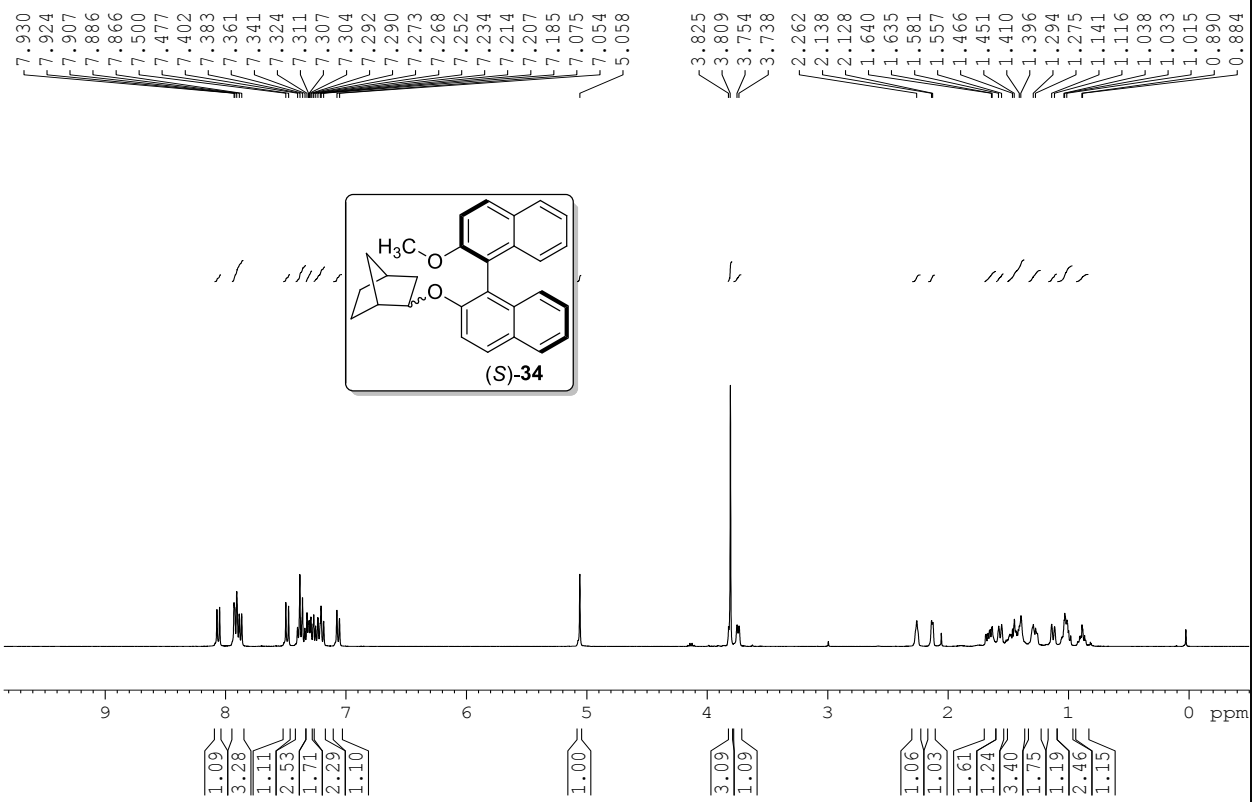
Spectrum No. 57 (Chapter 3, Section 3.2.2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



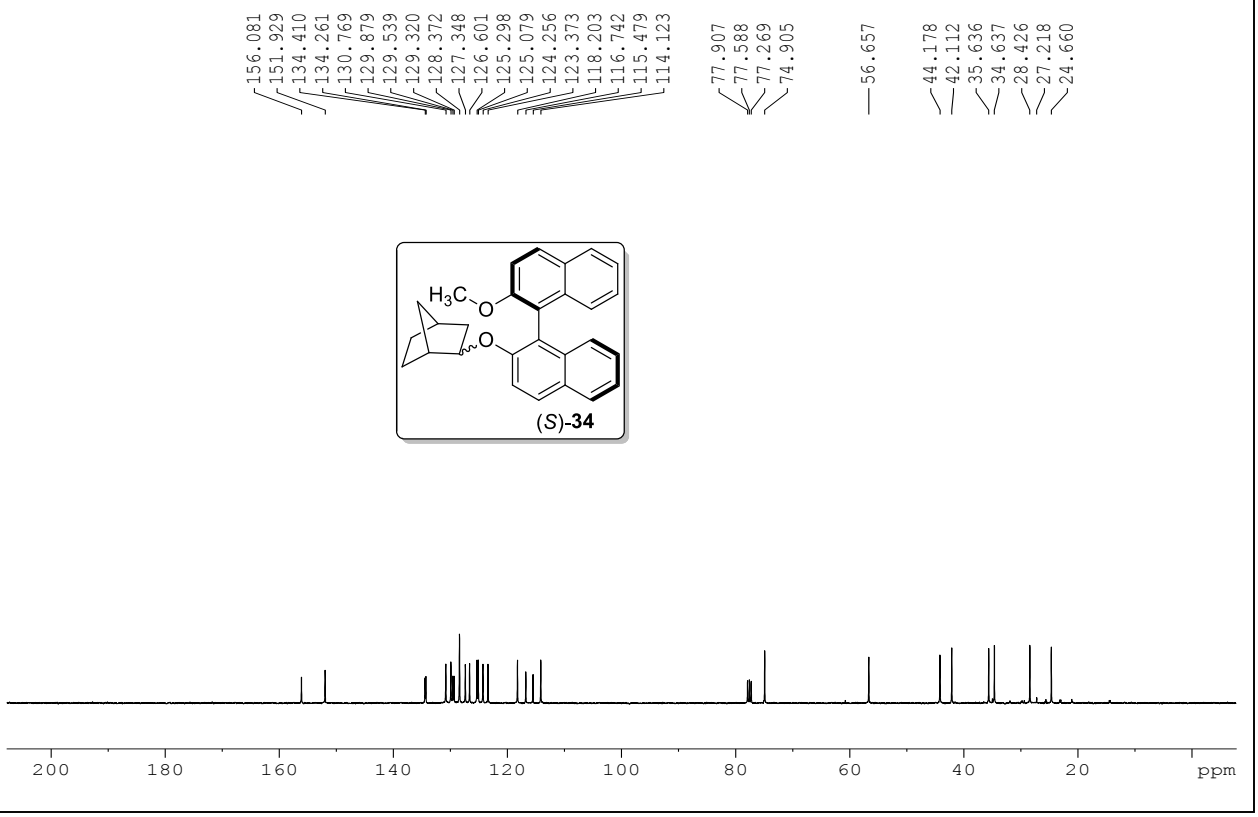
Spectrum No. 58 (Chapter 3, Section 3.2.2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



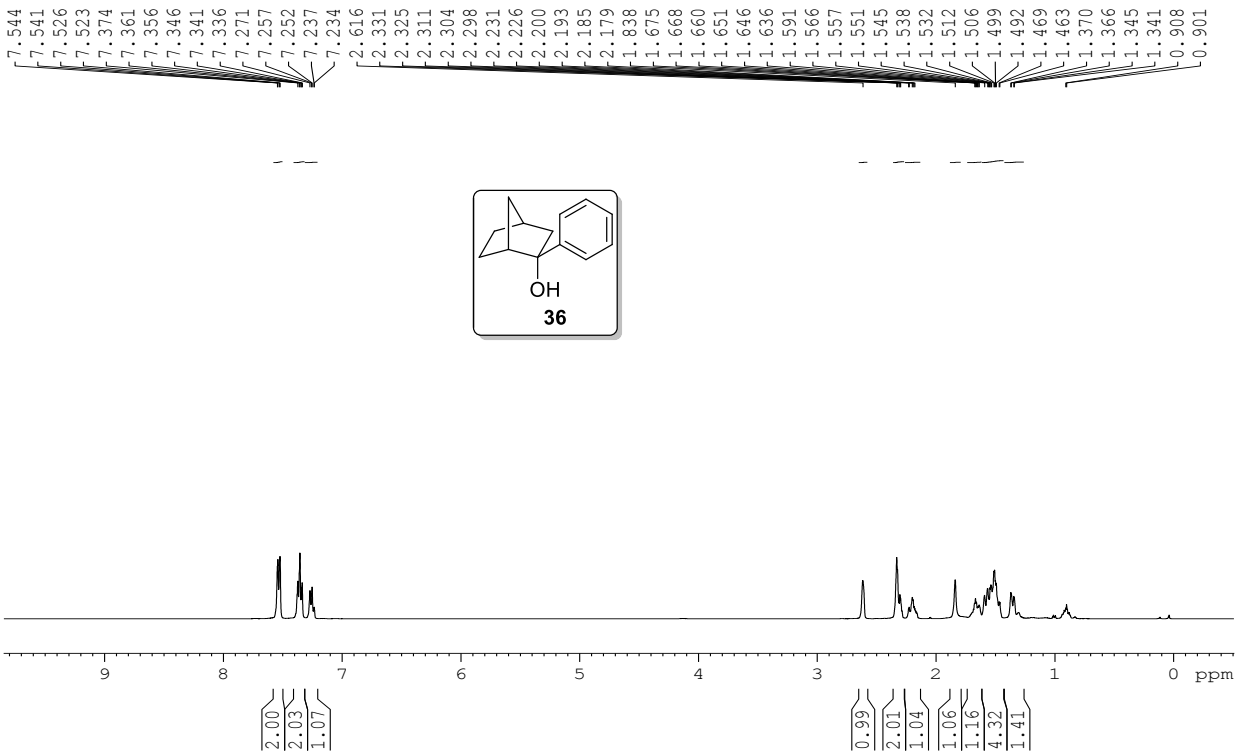
Spectrum No. 59 (Chapter 3, Section 3.2.2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



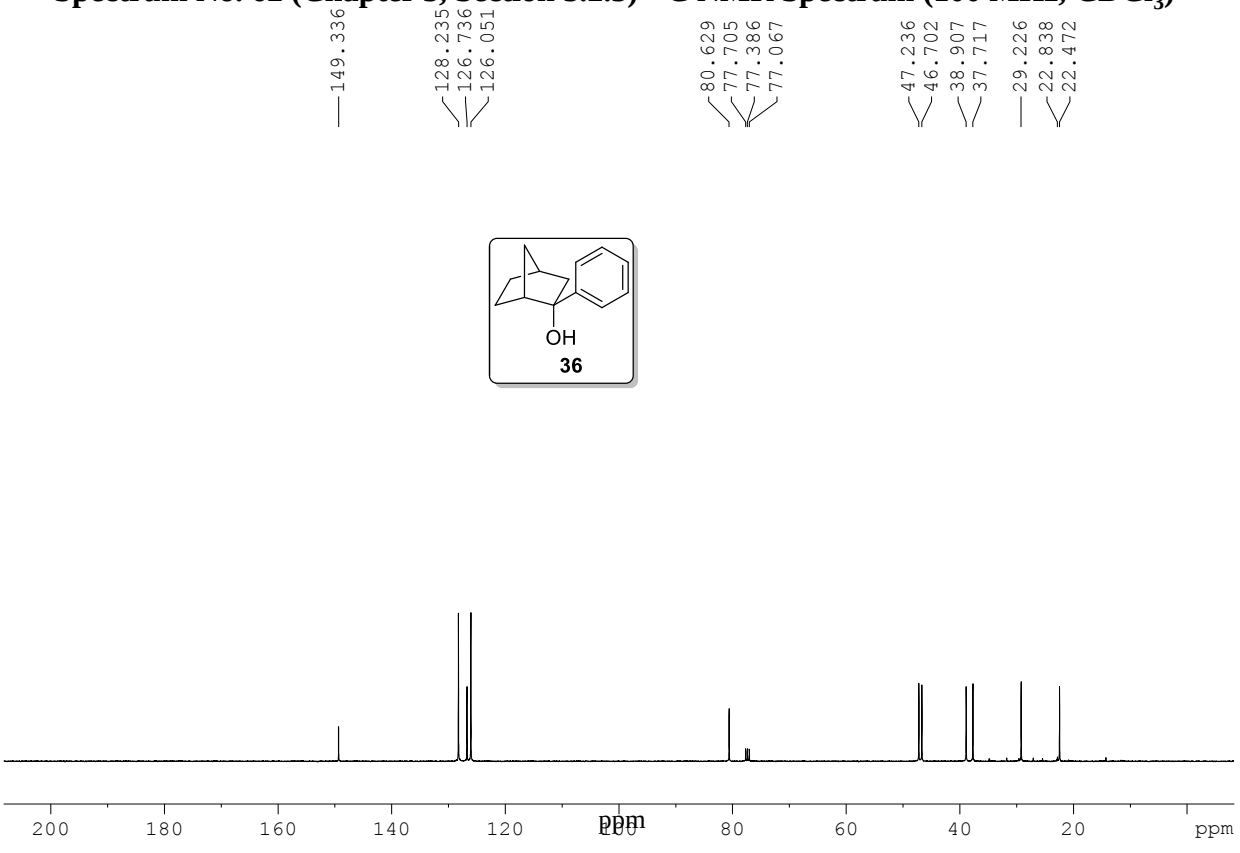
Spectrum No. 60 (Chapter 3, Section 3.2.2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



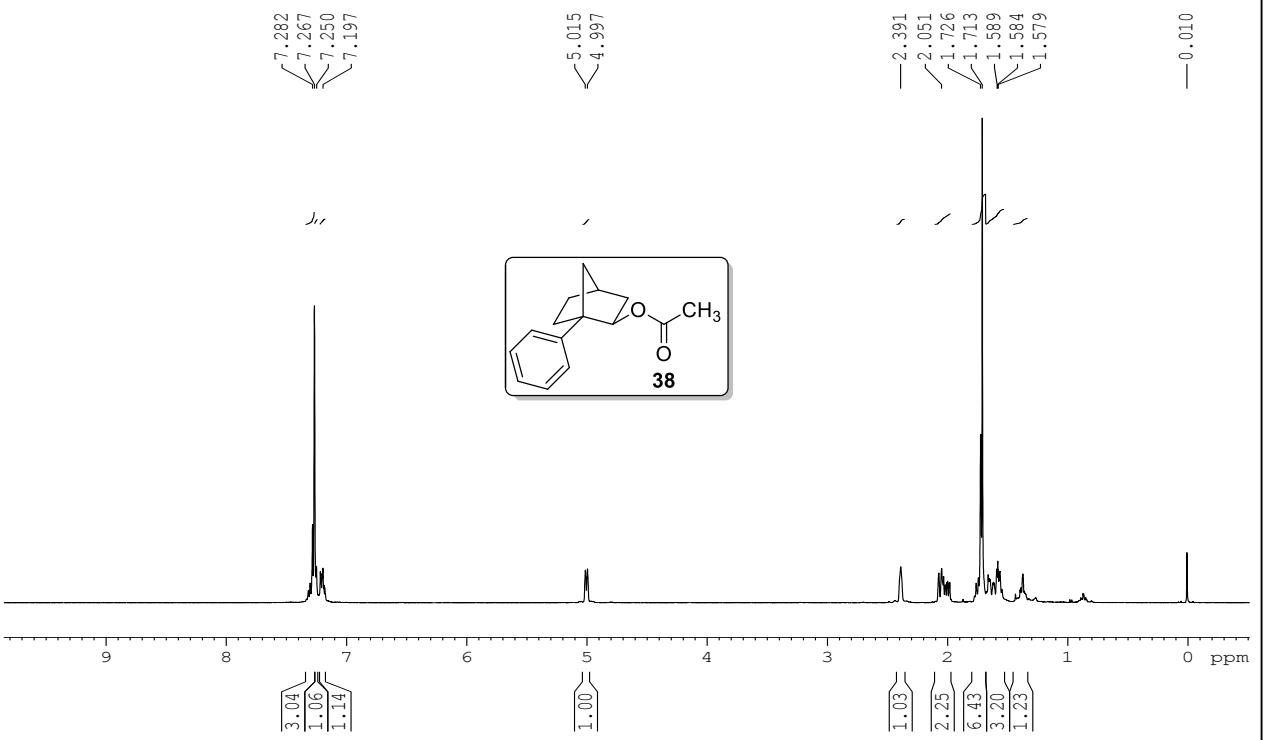
Spectrum No. 61 (Chapter 3, Section 3.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



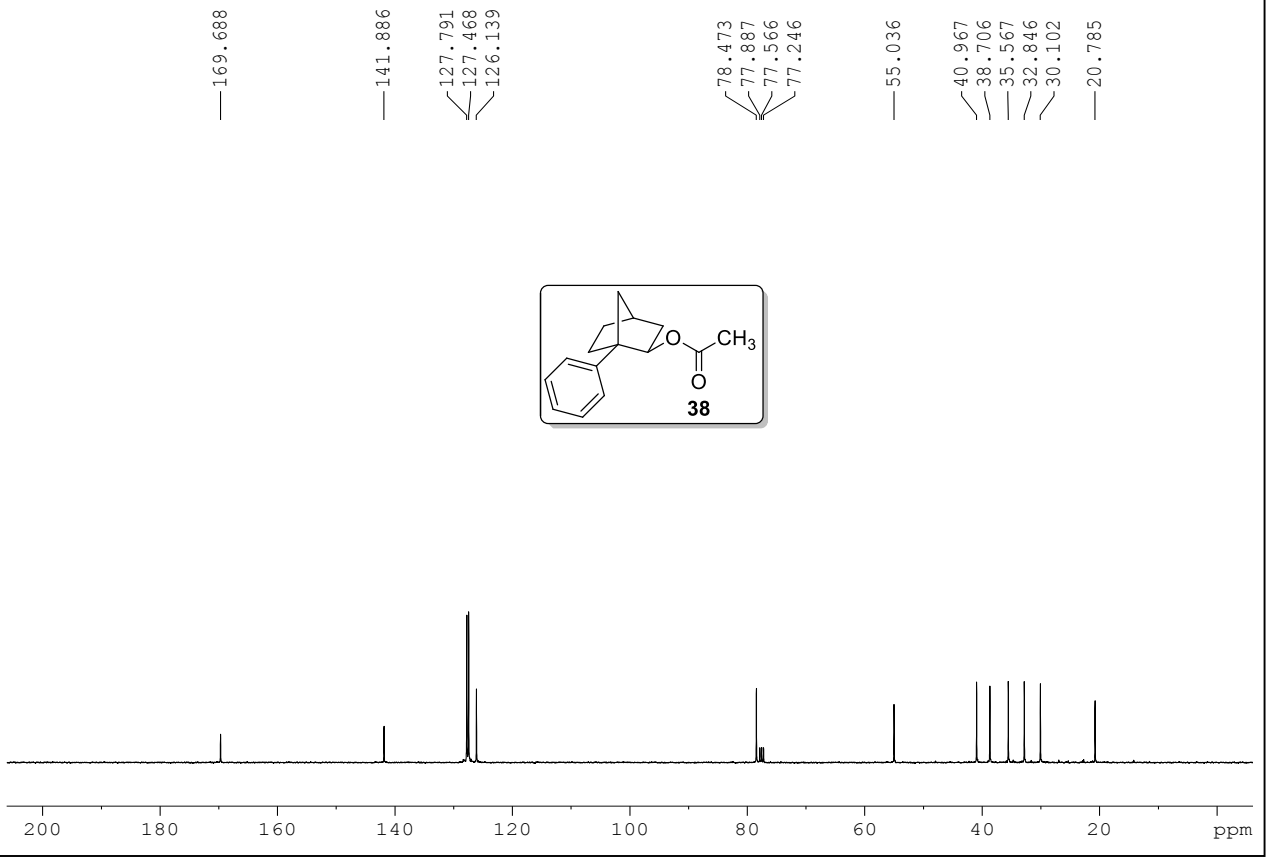
Spectrum No. 62 (Chapter 3, Section 3.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



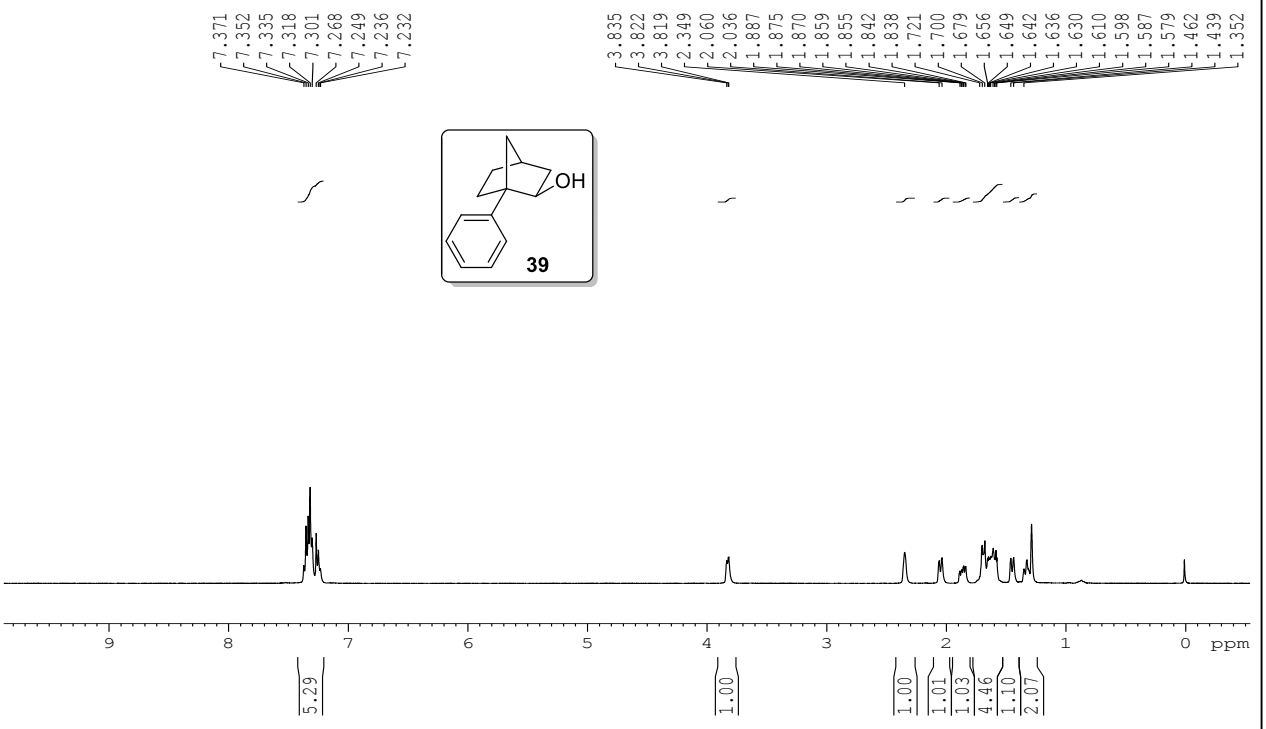
Spectrum No. 63 (Chapter 3, Section 3.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



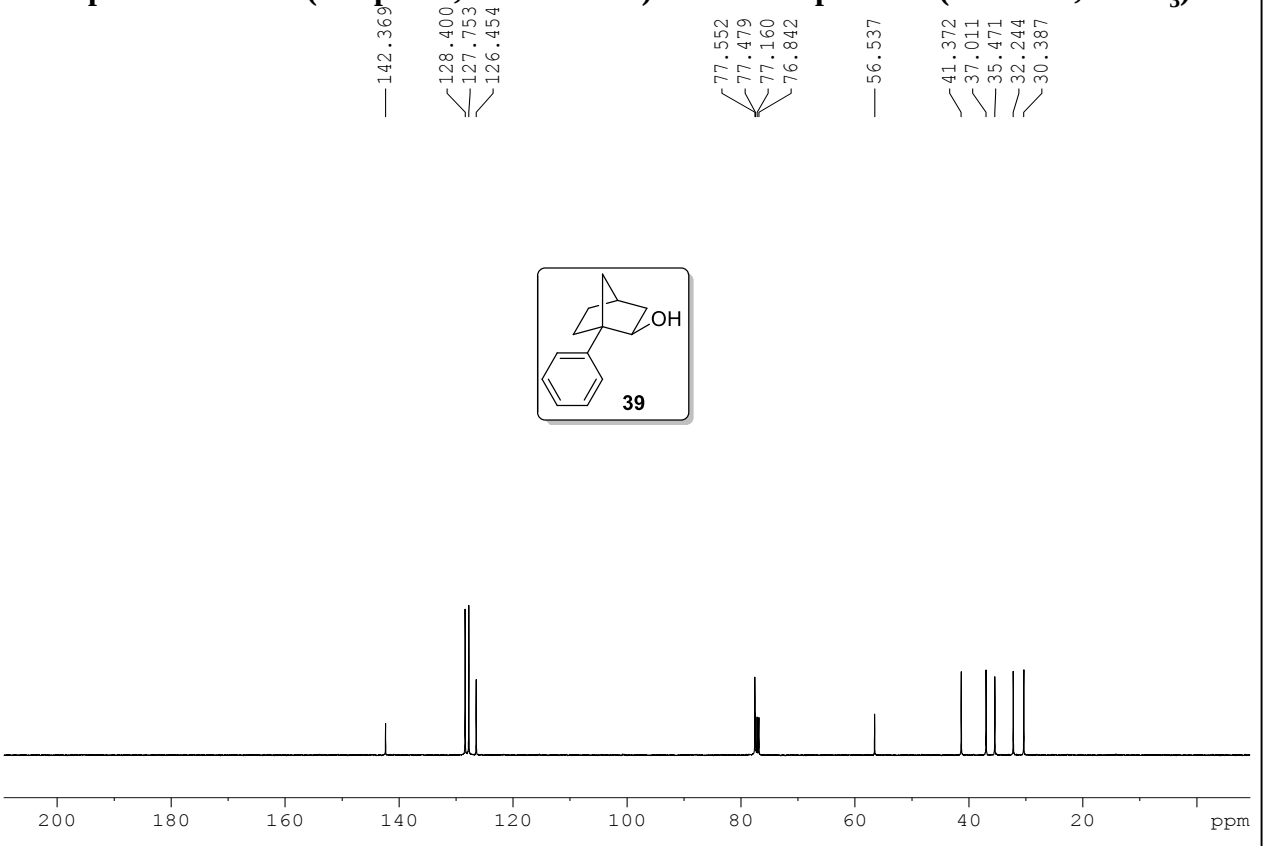
Spectrum No. 64 (Chapter 3, Section 3.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



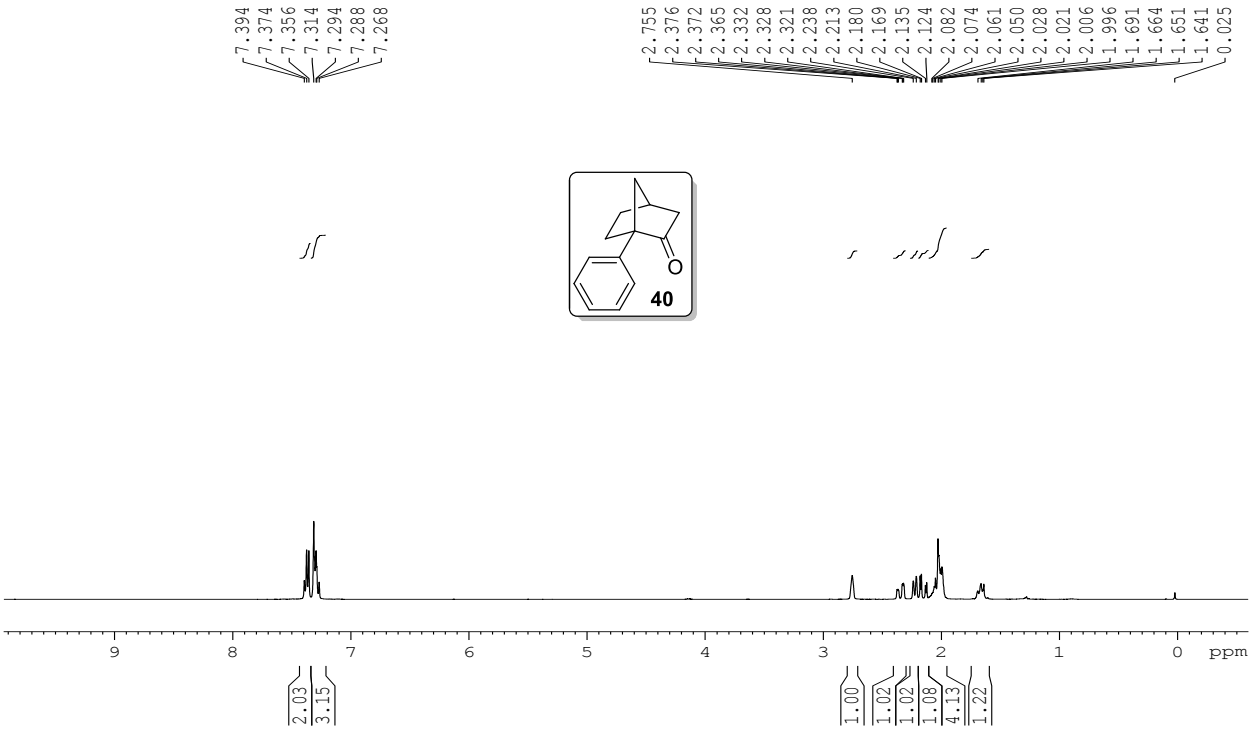
Spectrum No. 65 (Chapter 3, Section 3.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



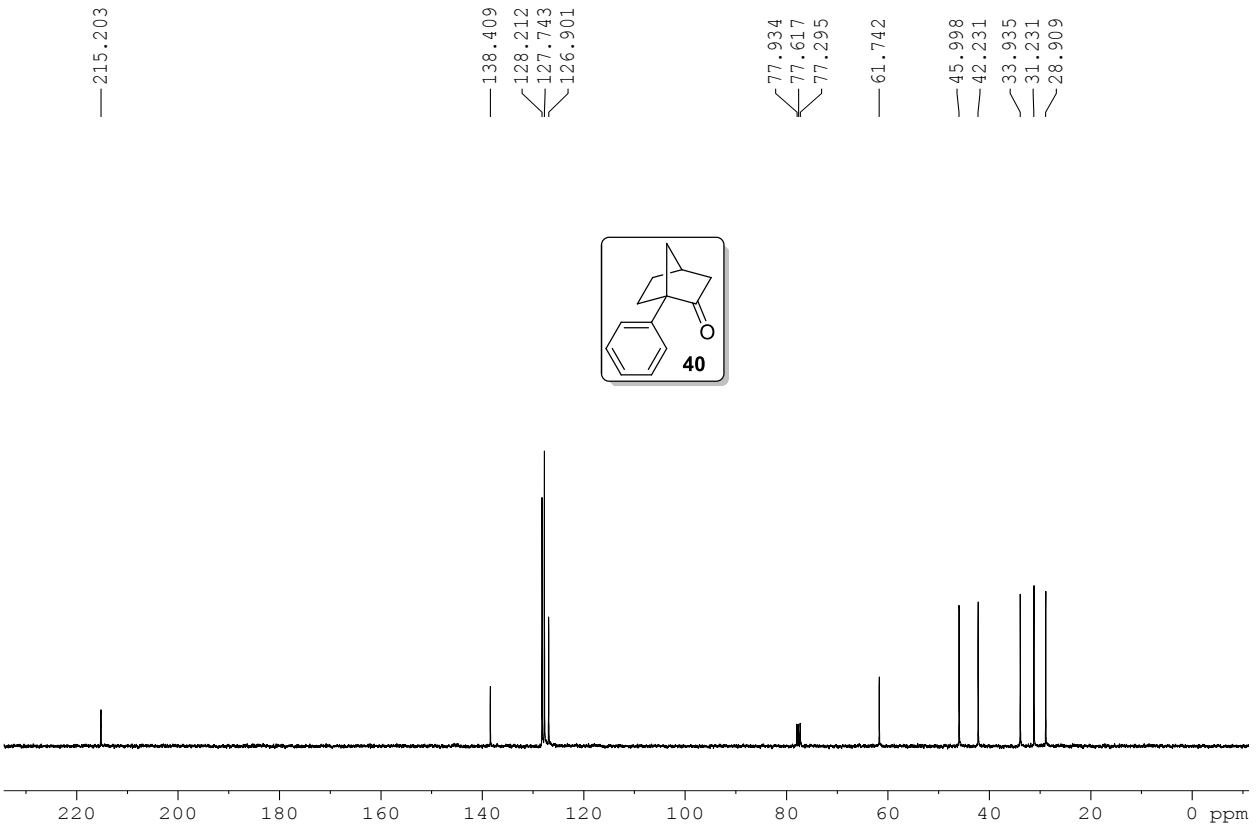
Spectrum No. 66 (Chapter 3, Section 3.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



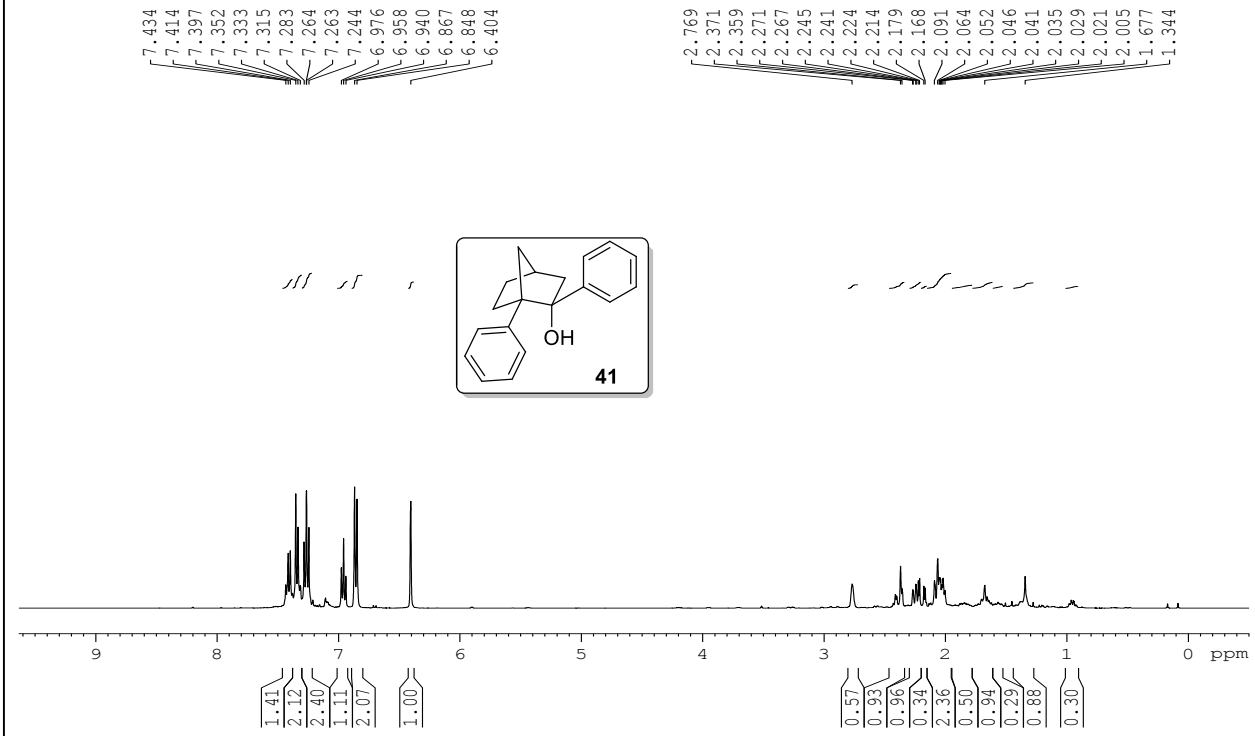
Spectrum No. 67 (Chapter 3, Section 3.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



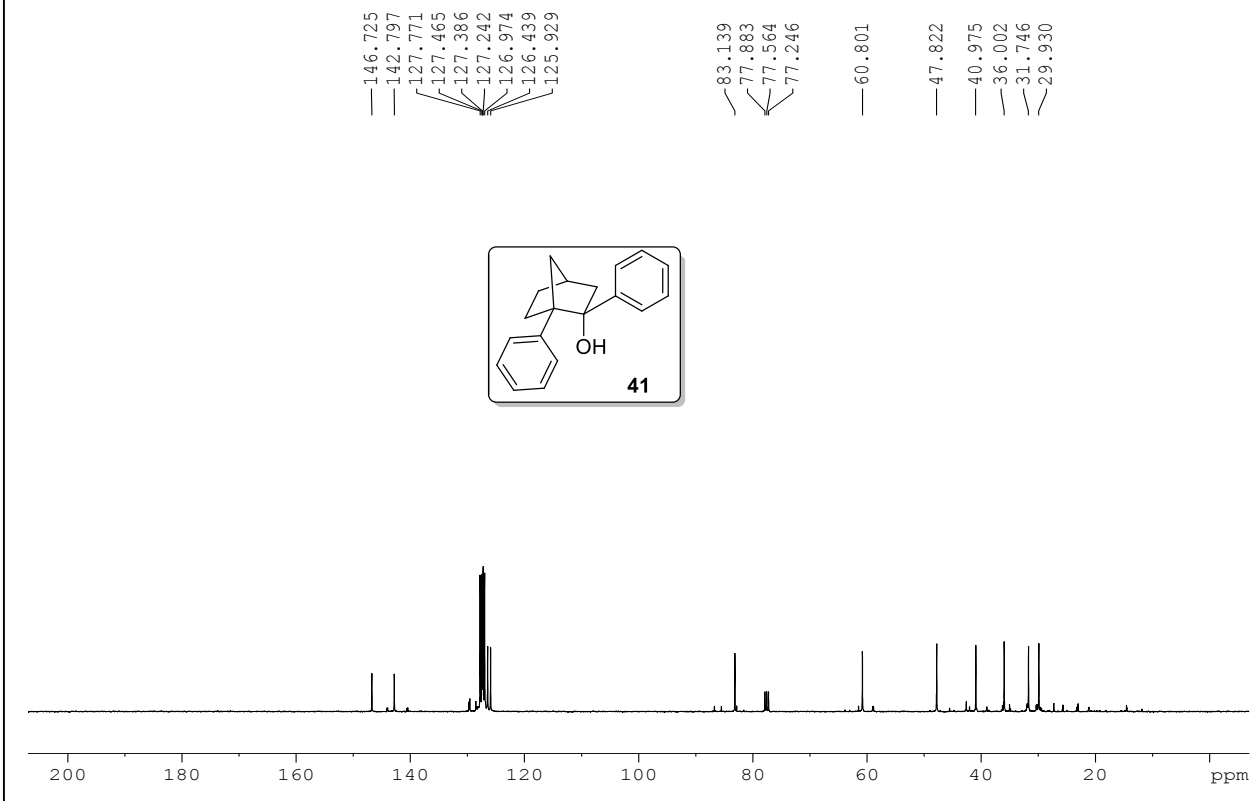
Spectrum No. 68 (Chapter 3, Section 3.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



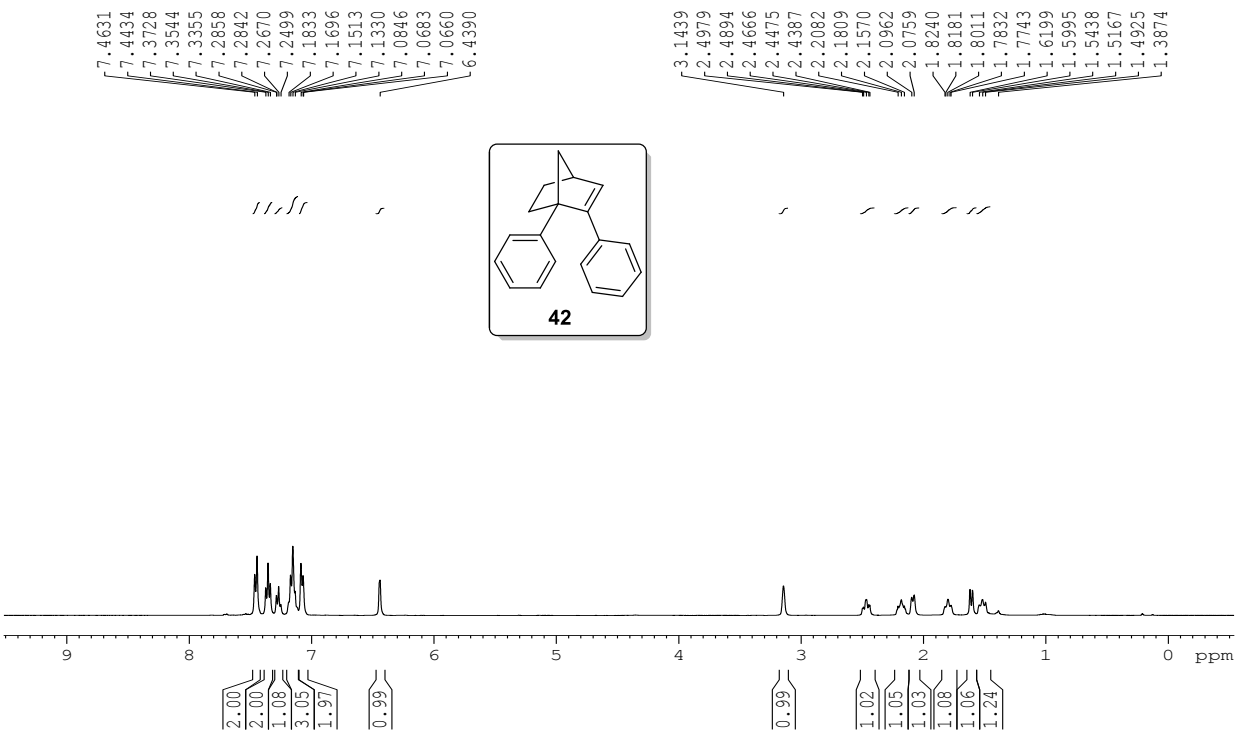
Spectrum No. 69 (Chapter 3, Section 3.2.3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



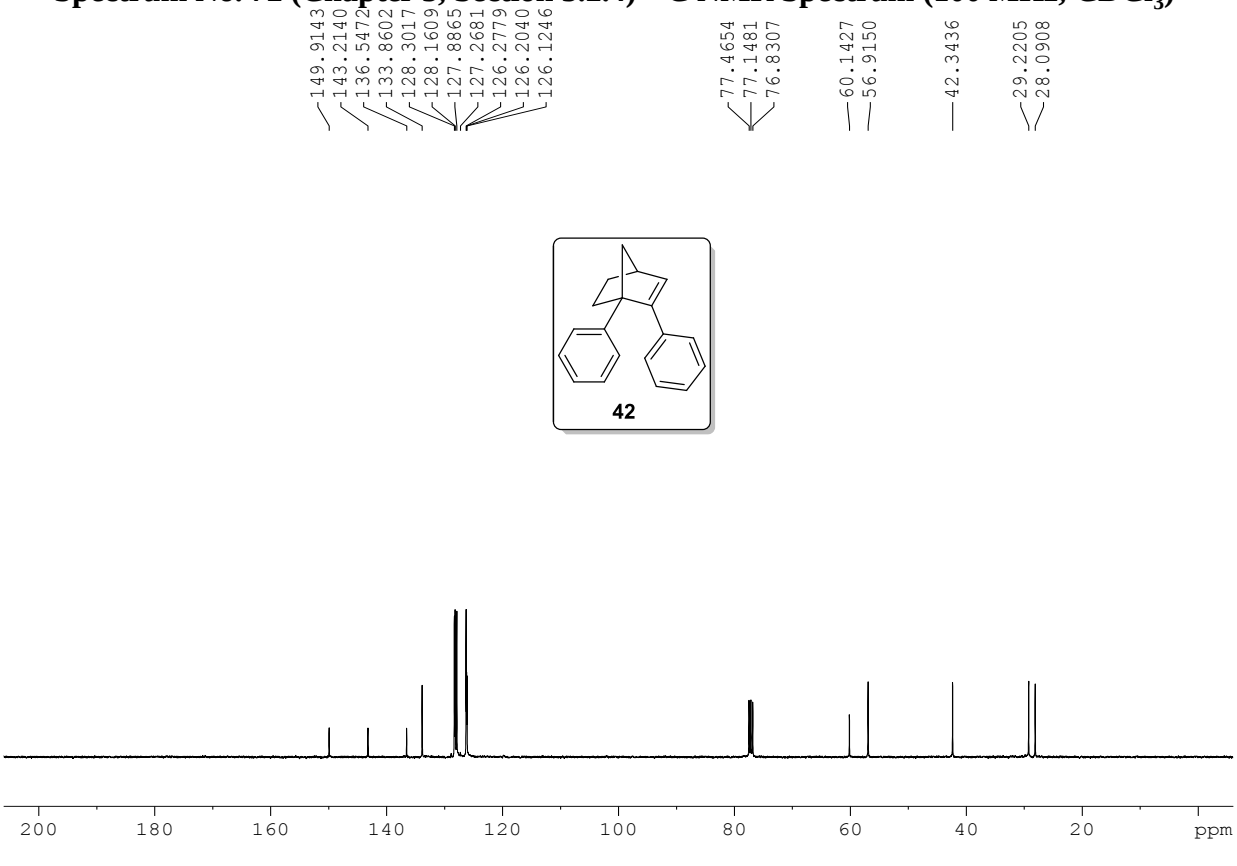
Spectrum No. 70 (Chapter 2, Section 3.2.3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



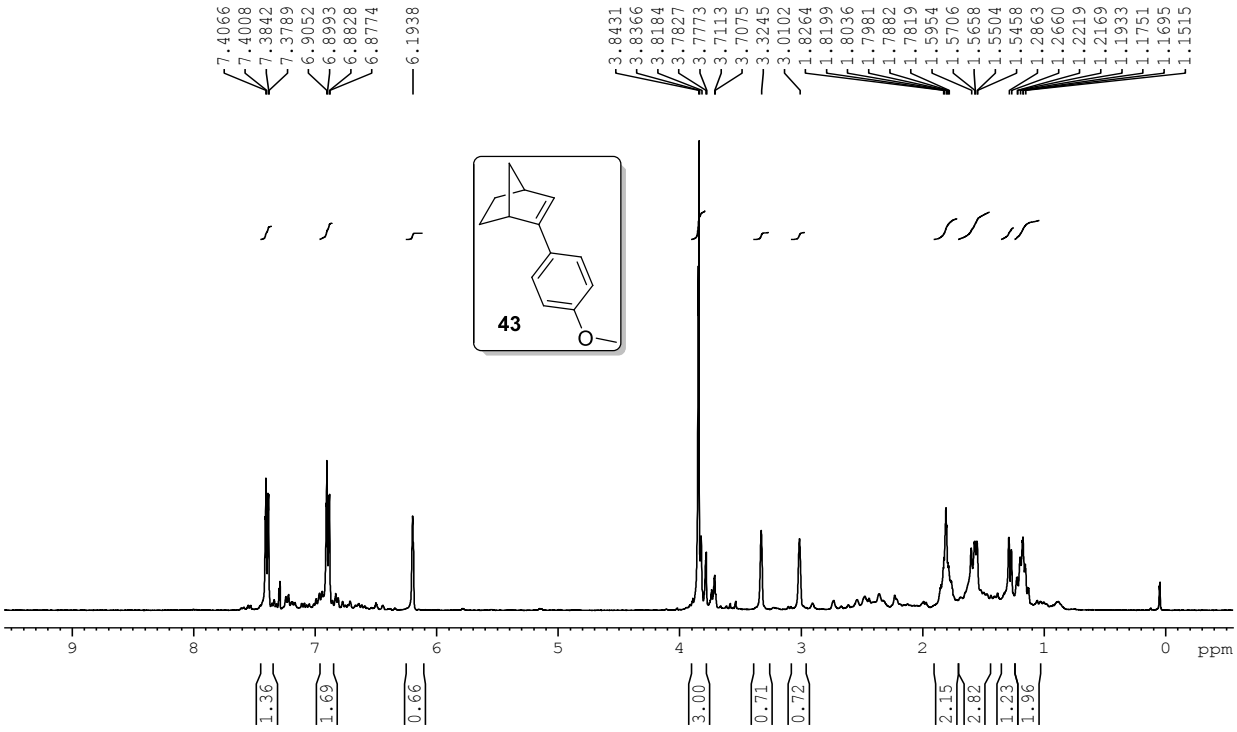
Spectrum No. 71 (Chapter 3, Section 3.2.4) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



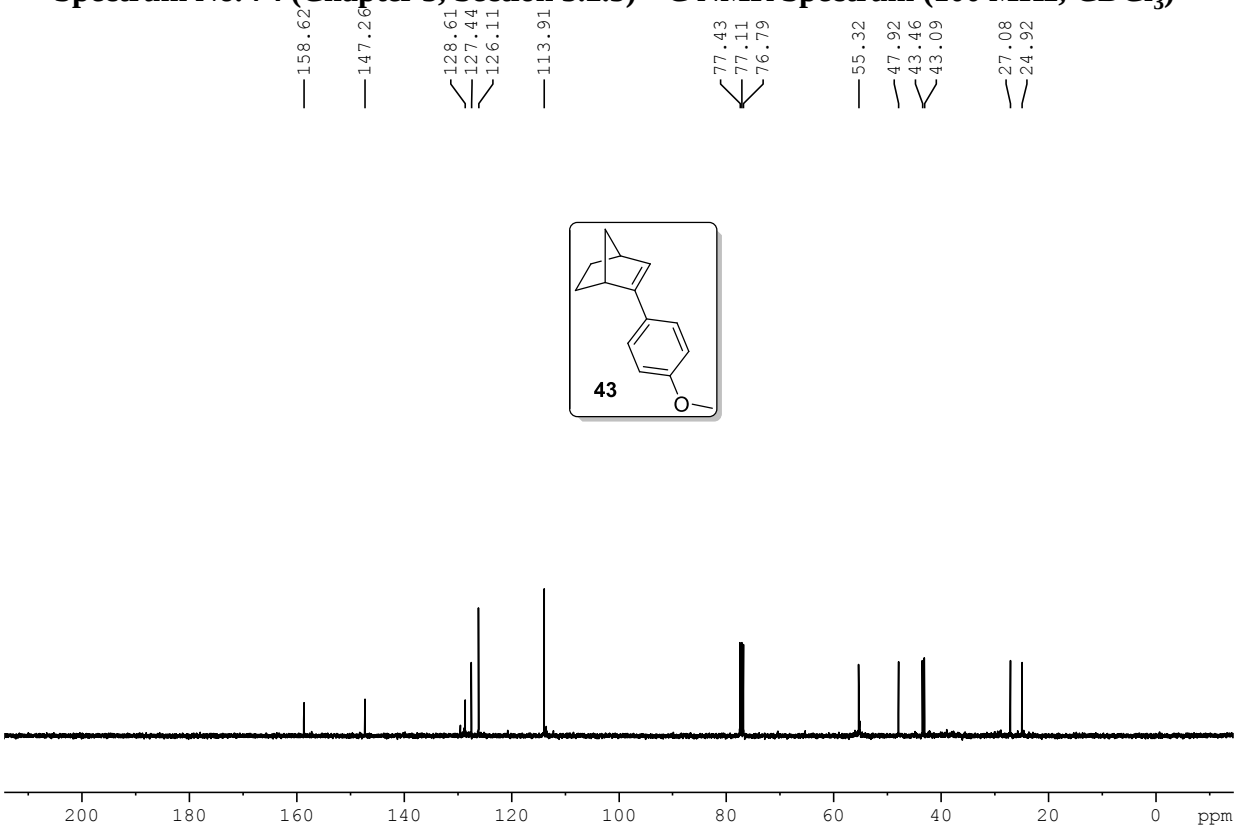
Spectrum No. 72 (Chapter 3, Section 3.2.4) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



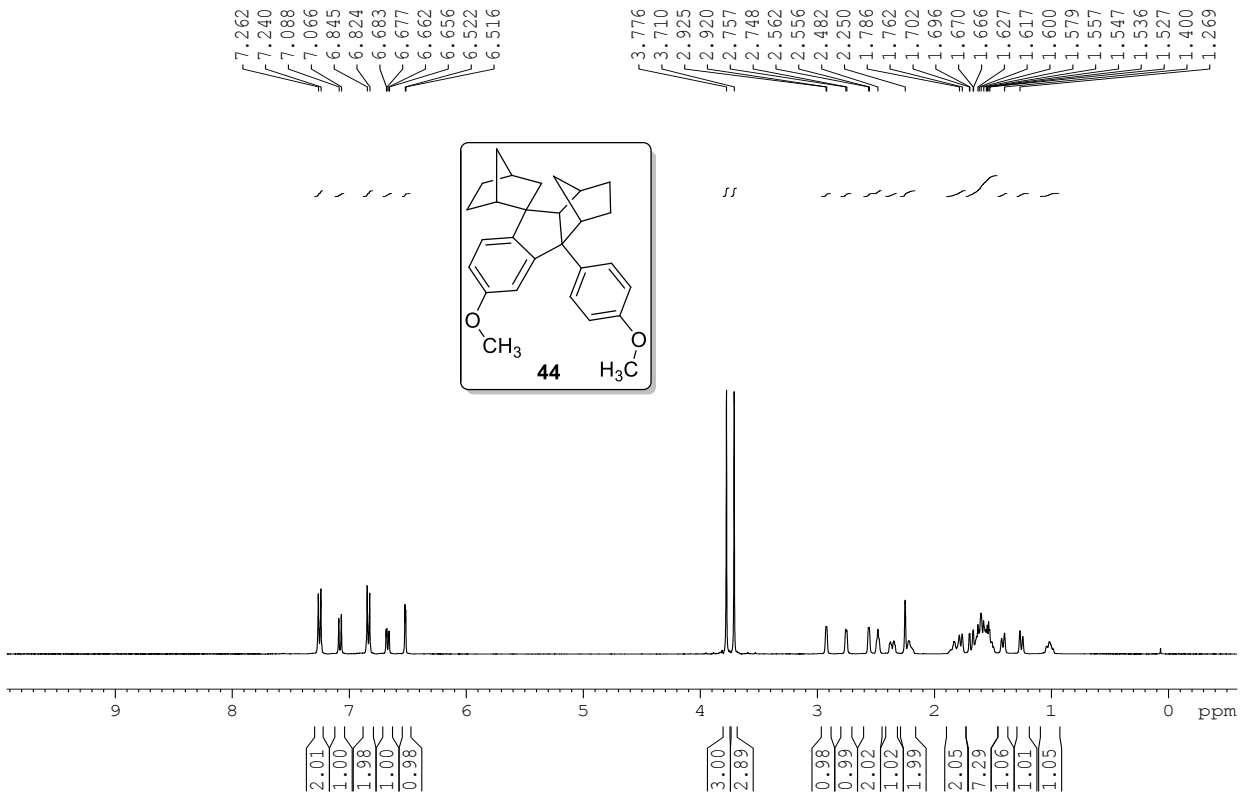
Spectrum No. 73 (Chapter 3, Section 3.2.5) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



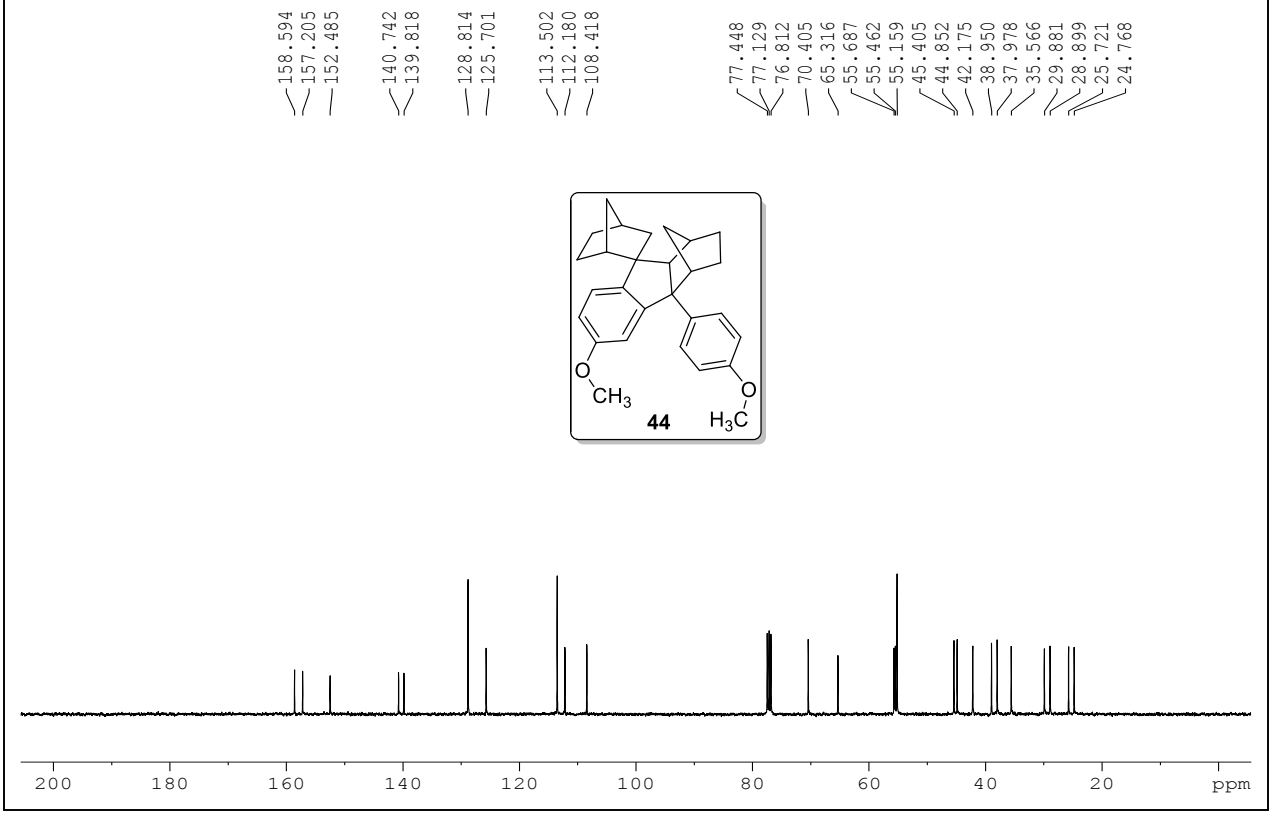
Spectrum No. 74 (Chapter 3, Section 3.2.5) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



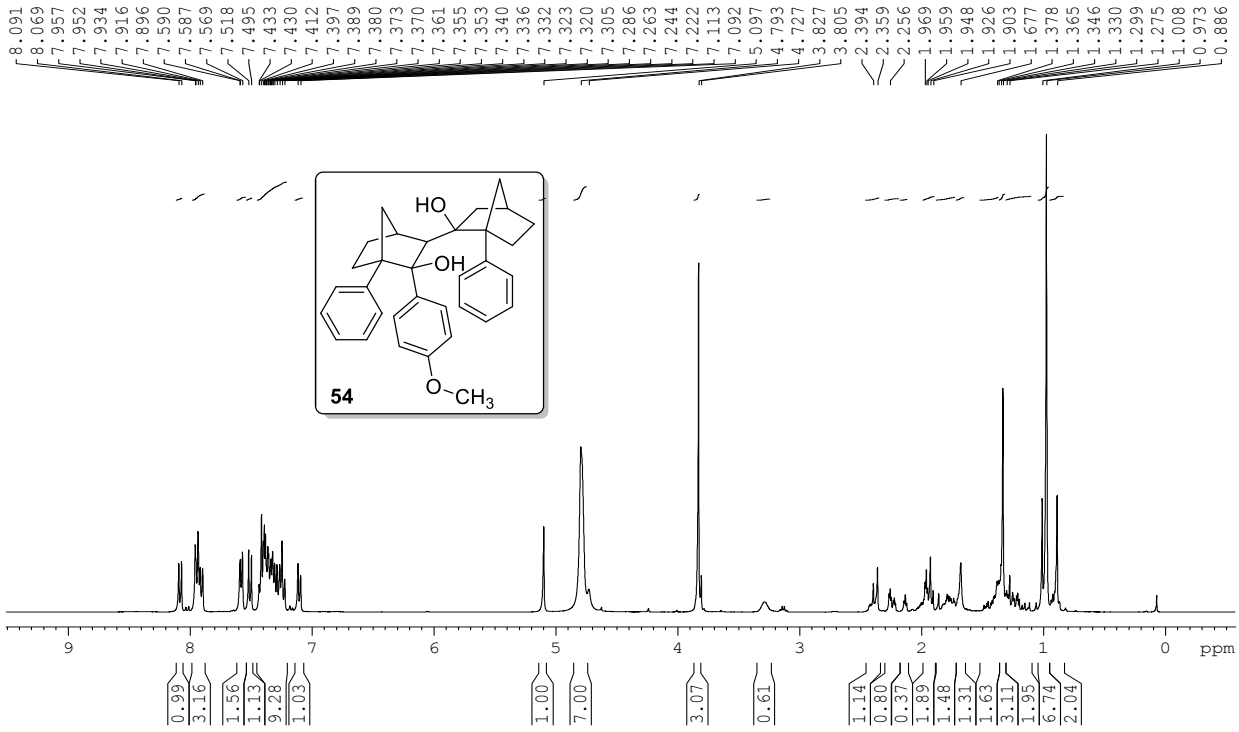
Spectrum No. 75 (Chapter 3, Section 3.2.6) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



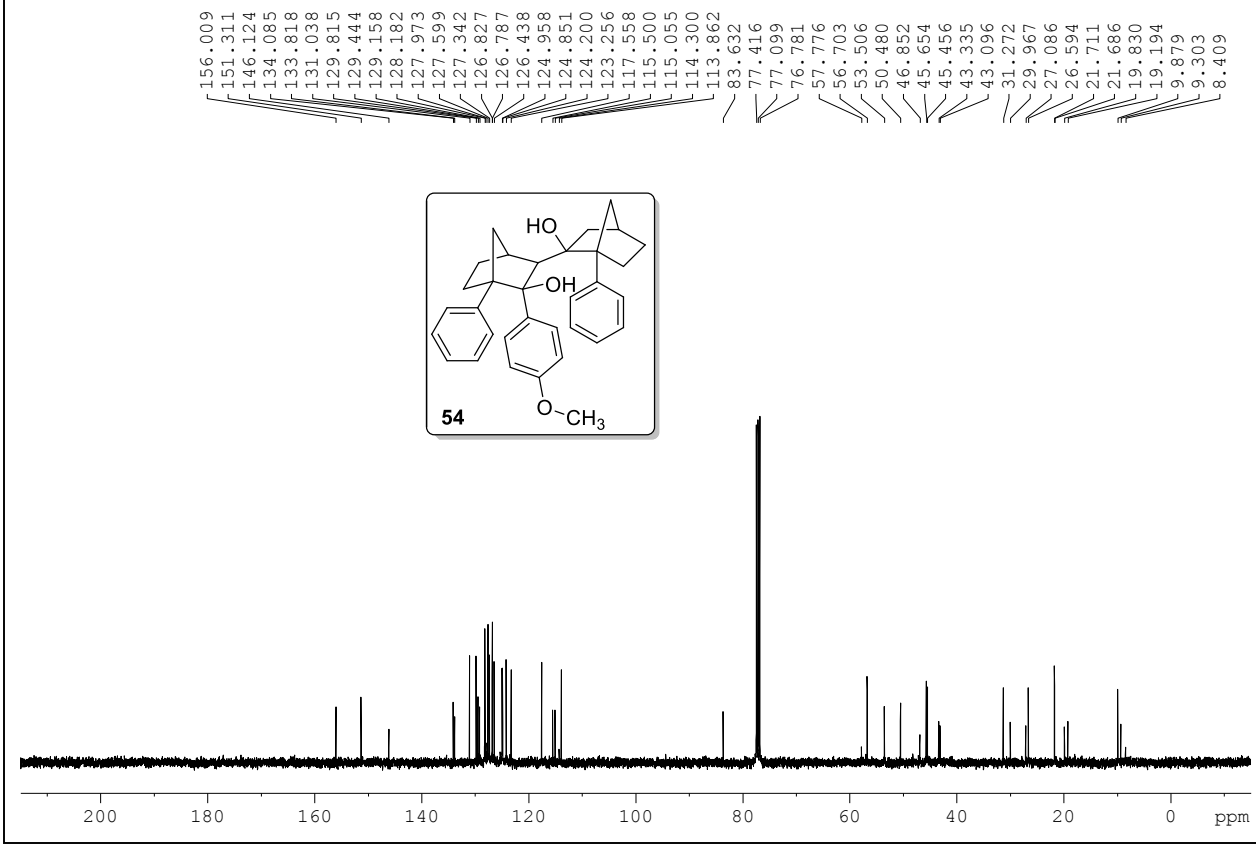
Spectrum No. 76 (Chapter 3, Section 3.2.6) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



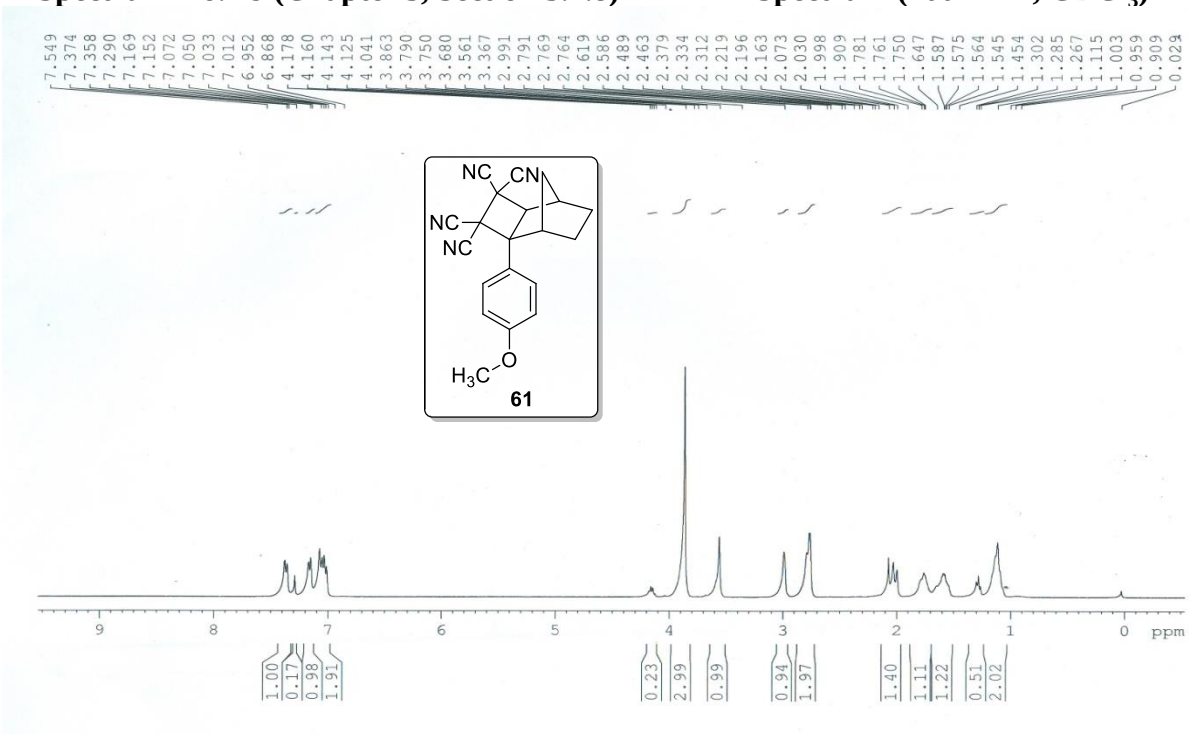
Spectrum No. 77 (Chapter 3, Section 3.2.7) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



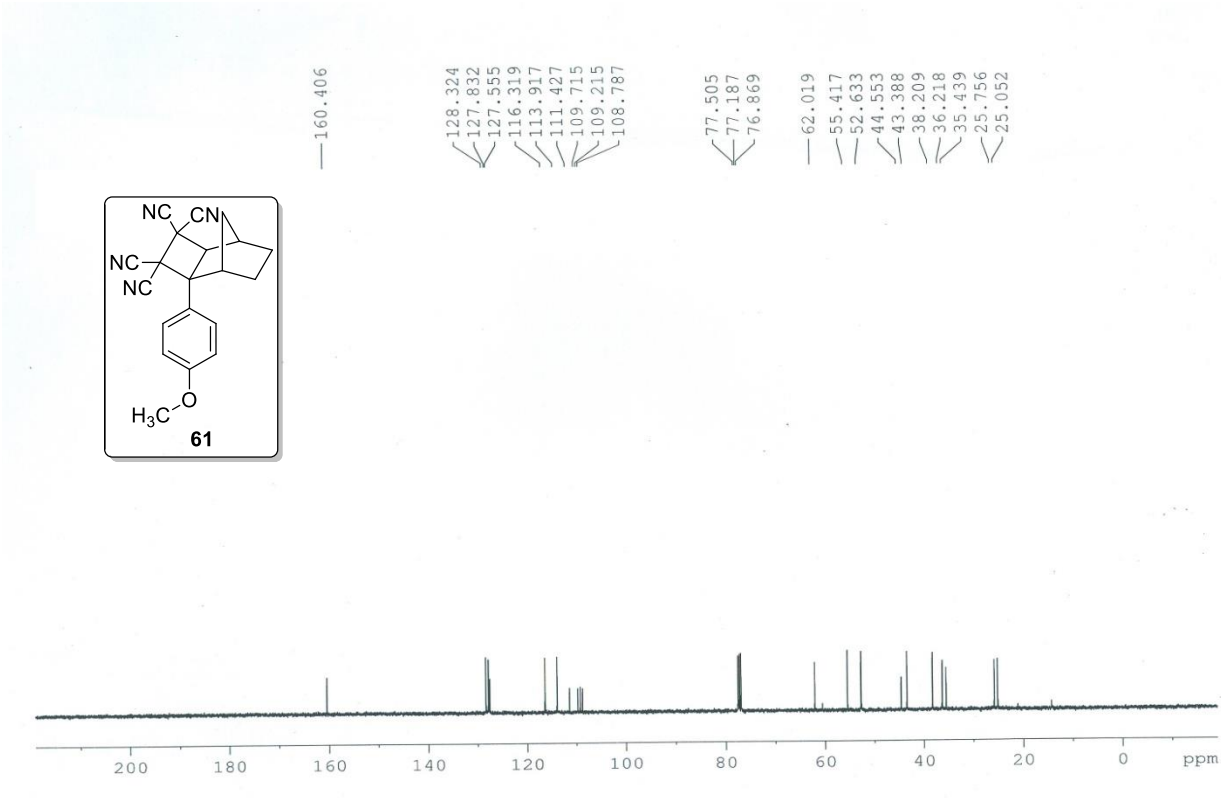
Spectrum No. 78 (Chapter 3, Section 3.2.7) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



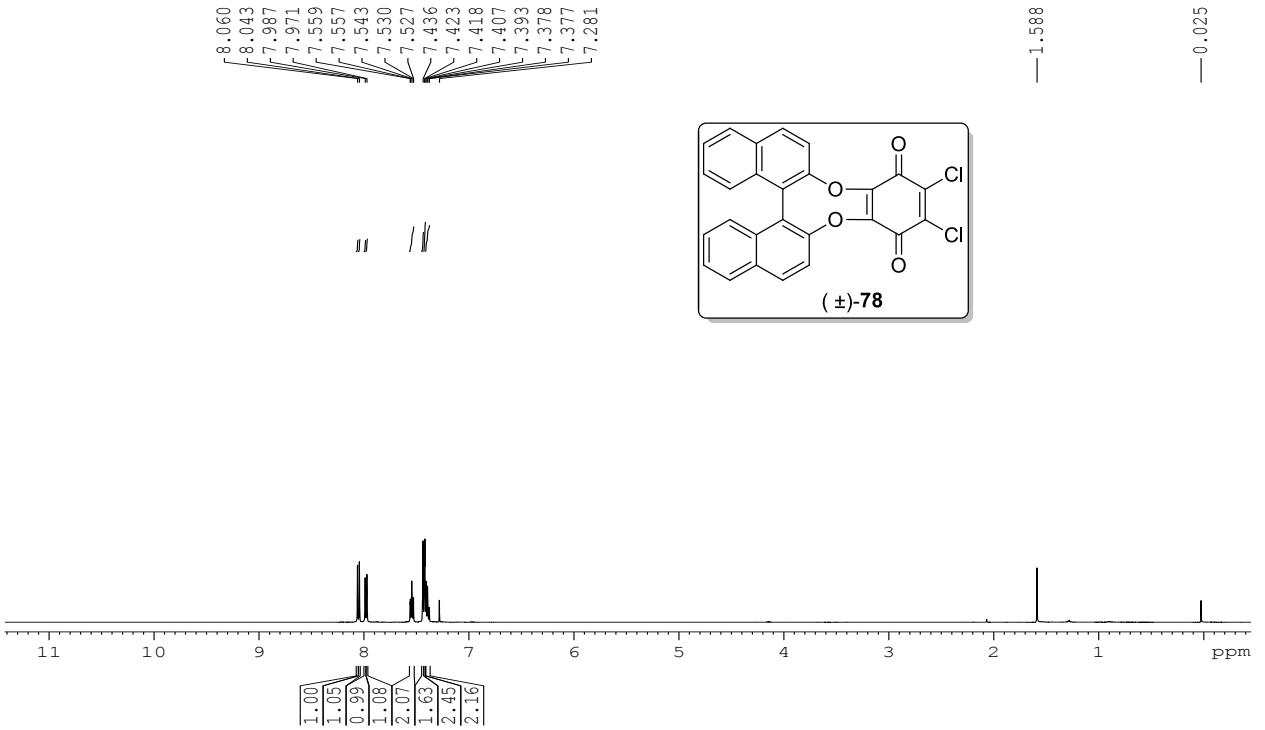
Spectrum No. 79 (Chapter 3, Section 3.2.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



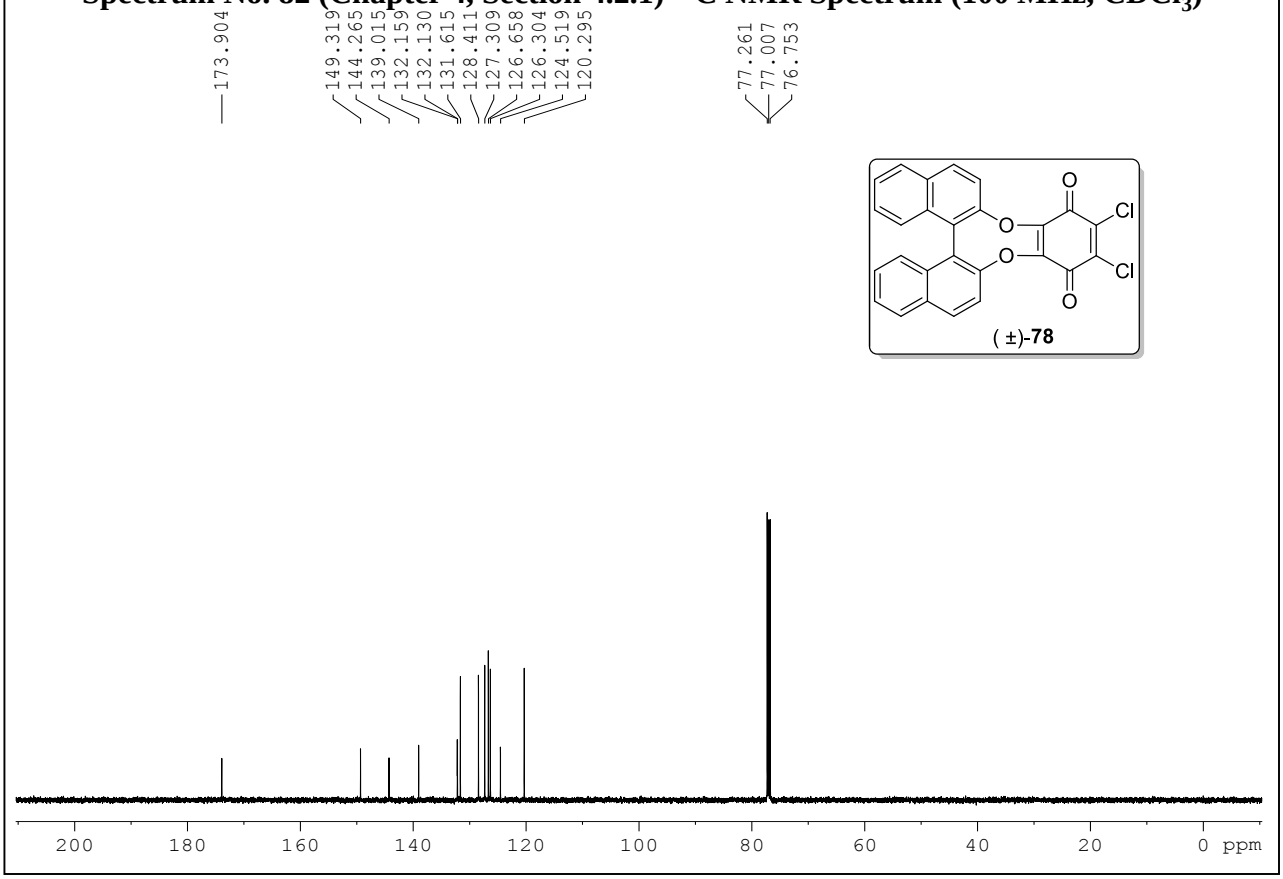
Spectrum No. 80 (Chapter 3, Section 3.2.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



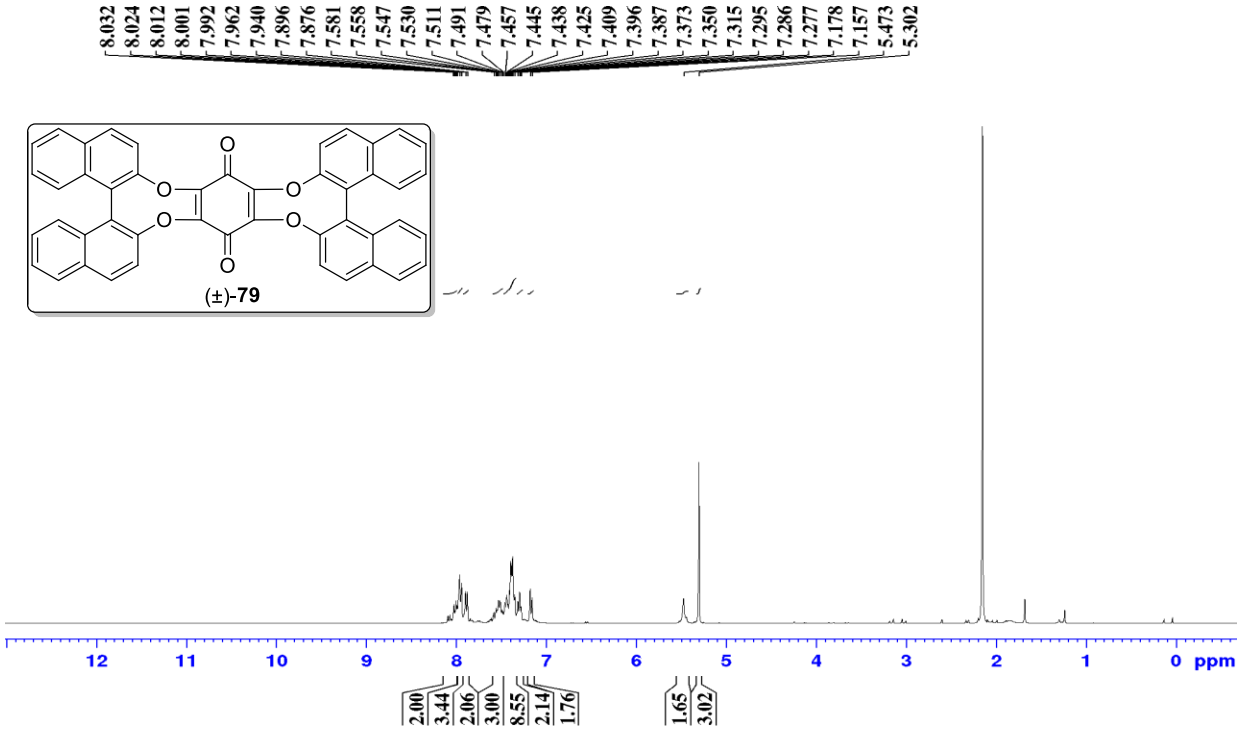
Spectrum No. 81 (Chapter 4, Section 4.2.1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



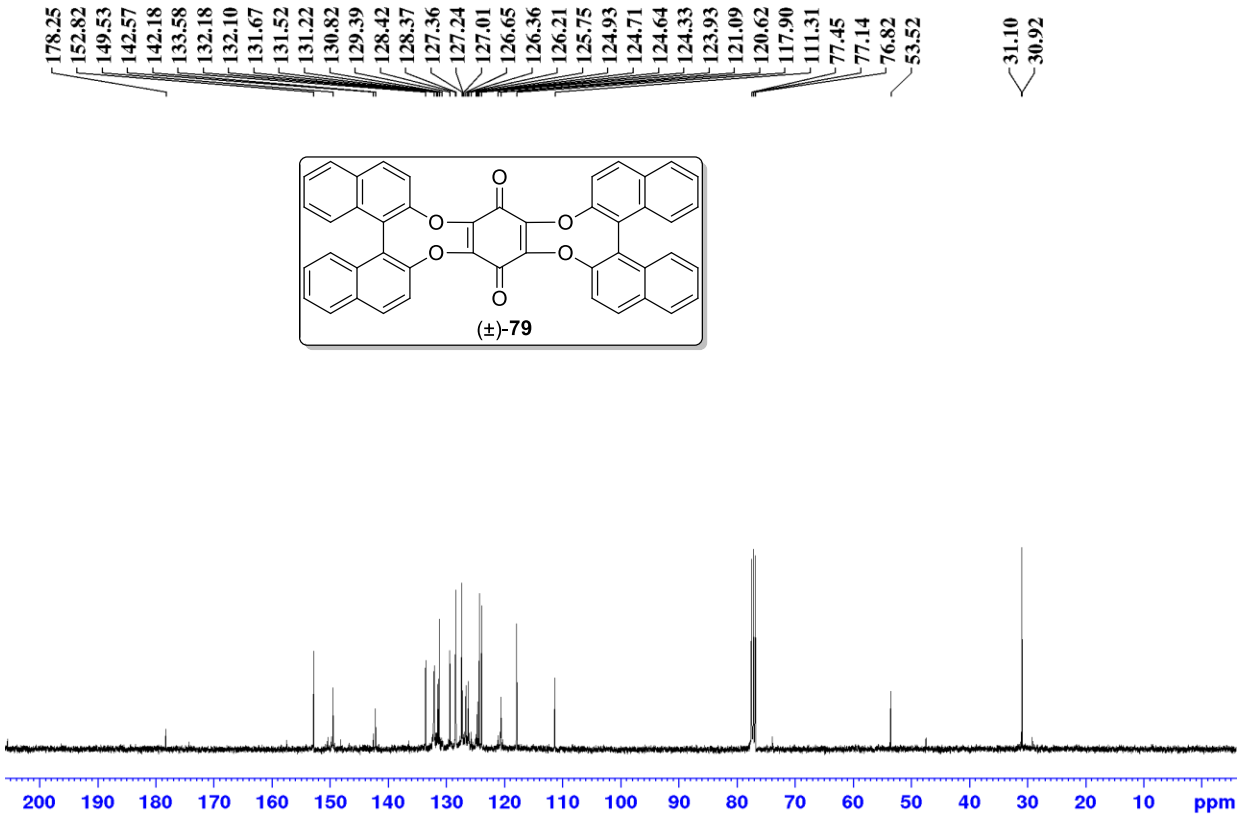
Spectrum No. 82 (Chapter 4, Section 4.2.1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



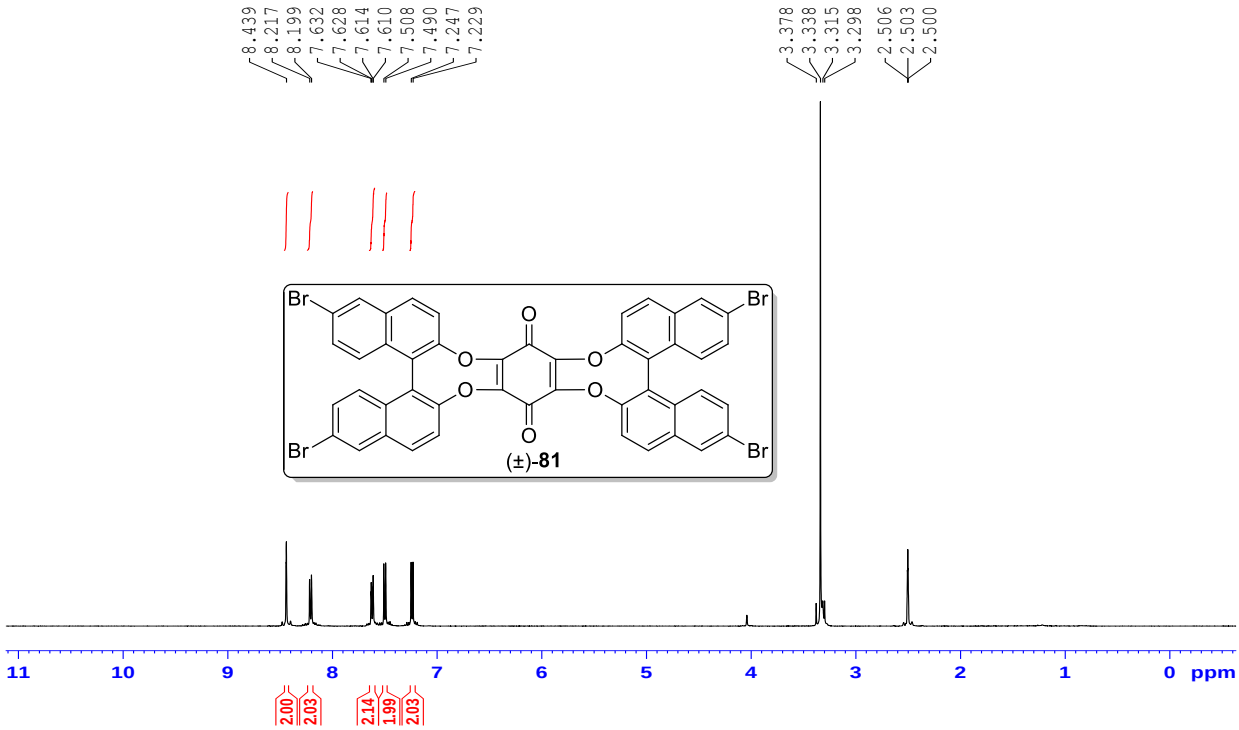
Spectrum No. 83 (Chapter 4, Section 4.2.1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



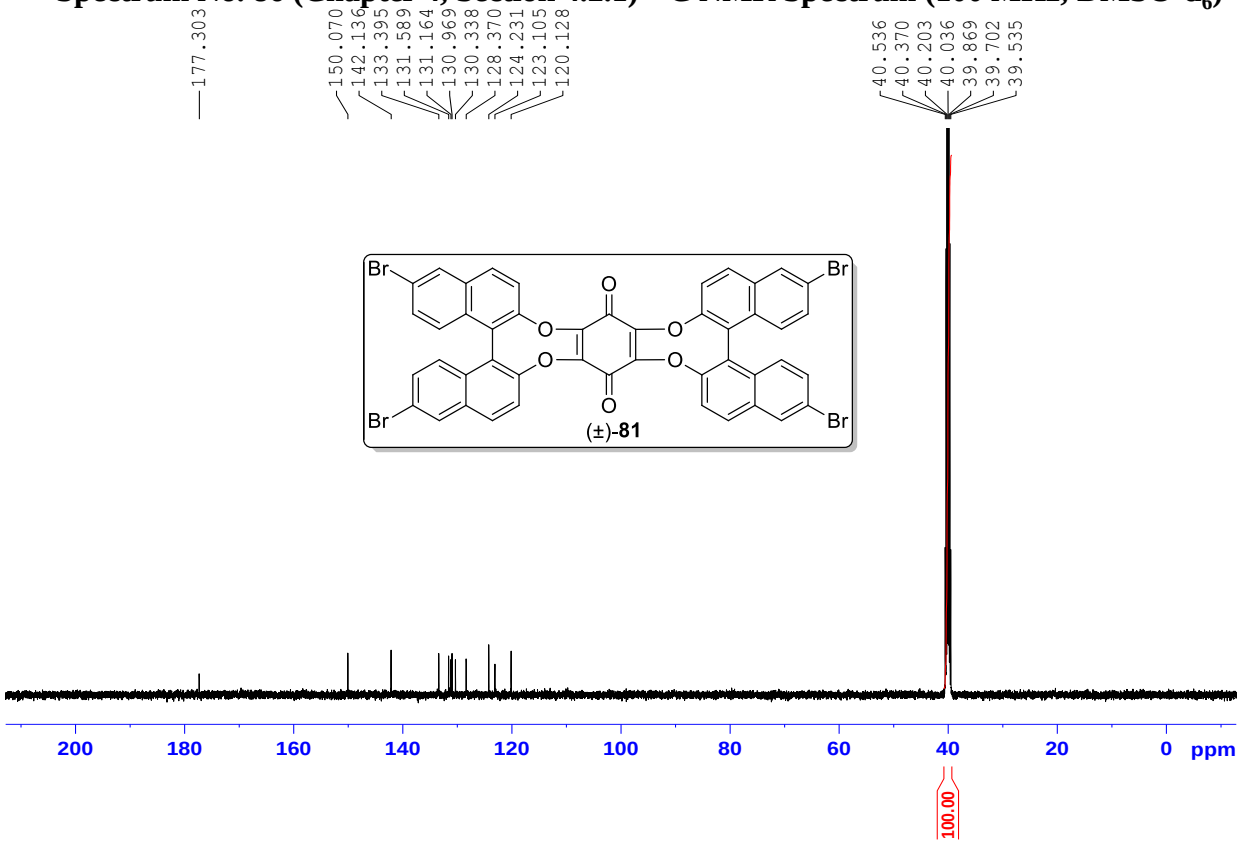
Spectrum No. 84 (Chapter 4, Section 4.2.1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



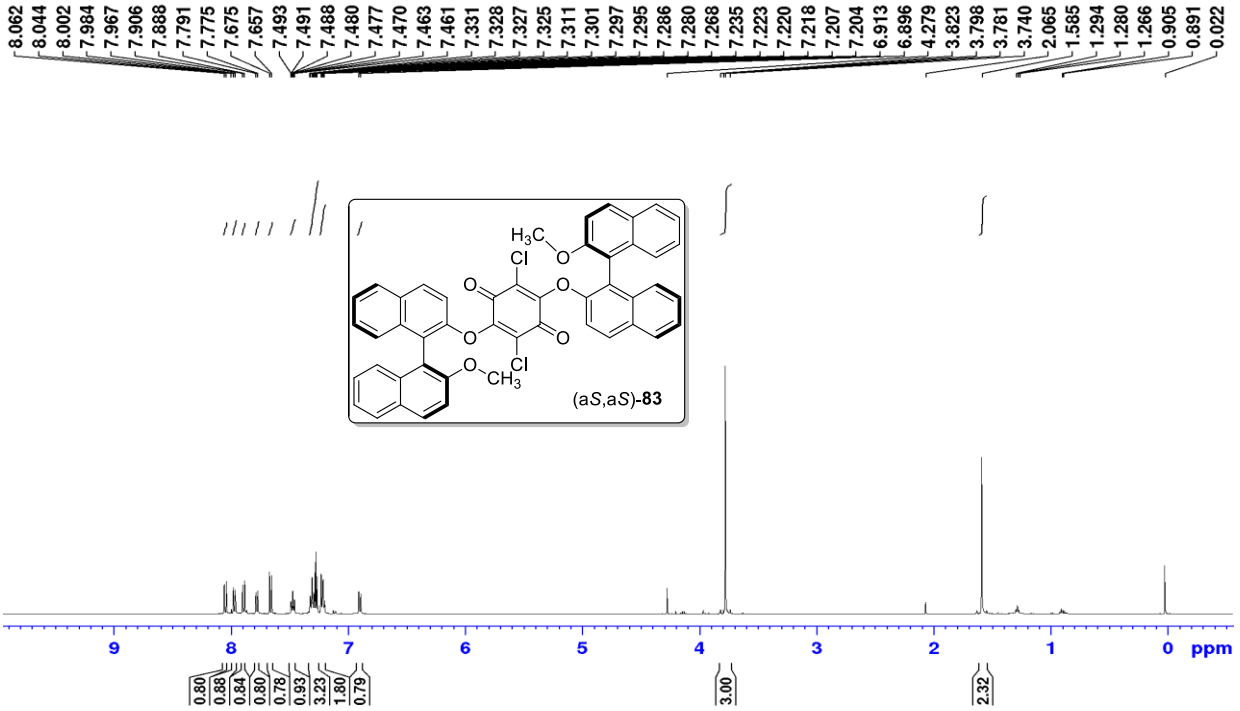
Spectrum No. 85 (Chapter 4, Section 4.2.1) ^{1}H NMR Spectrum (400 MHz, DMSO-d_6)



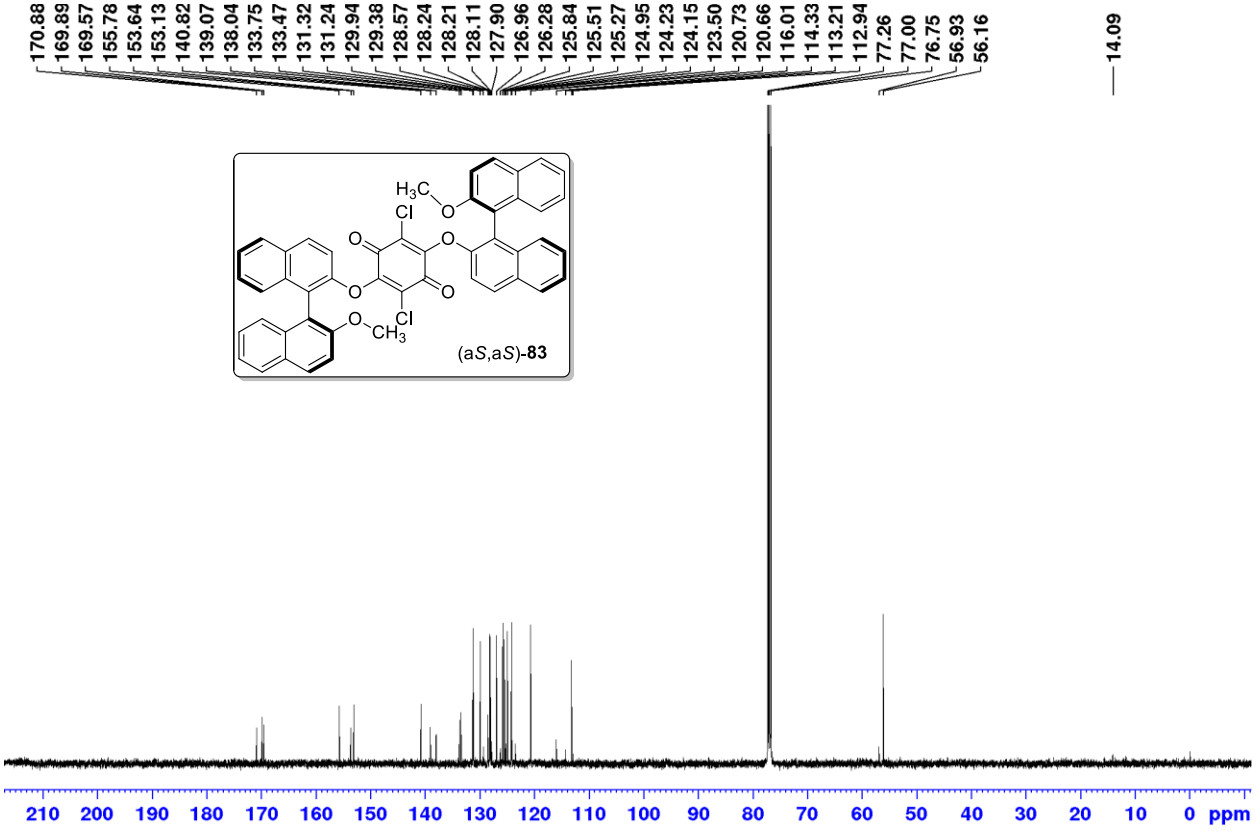
Spectrum No. 86 (Chapter 4, Section 4.2.1) ^{13}C NMR Spectrum (100 MHz, DMSO-d_6)



Spectrum No. 87 (Chapter 4, Section 4.2.1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



Spectrum No. 88 (Chapter 4, Section 4.2.1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



Appendix-II

(X-ray Crystallographic Data)

Table 1. Crystal data and structure refinement for compound 150

Identification code	Compound 150	
Empirical formula	$C_{21}H_{16}O_2$	
Formula weight	332.38	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.0683(6) Å	α=90°.
	b = 11.3169(6) Å	β=90°.
	c = 19.2408(12) Å	γ=90°.
Volume	1756.84(19) $Å^3$	
Z	4	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.661 mm^{-1}	
F(000)	704	
Crystal size	0.22 x 0.20 x 0.18 mm^3	
Theta range for data collection	4.53 to 72.04°.	
Index ranges	-9<=h<=9, -9<=k<=13, -23<=l<=22	
Reflections collected	6967	
Independent reflections	3257 [R(int) = 0.0323]	
Completeness to theta = 72.04°	98.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3257 / 0 / 231	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1234	
R indices (all data)	R1 = 0.0907, wR2 = 0.1508	
Absolute structure parameter	0.2(4)	
Extinction coefficient	0.0041(6)	
Largest diff. peak and hole	0.134 and -0.139 e.$Å^-$	

Table 2. Crystal data and structure refinement for compound 154

Identification code	Compound 154	
Empirical formula	$C_{37}H_{28}O_4$	
Formula weight	536.59	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 11.3404(4) Å	α= 90°.
	b = 12.0073(4) Å	β= 90°.
	c = 20.2833(6) Å	γ = 90°.
Volume	2761.93(16) $Å^3$	
Z	4	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	1128	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.971 to 25.000°.	
Index ranges	-13<=h<=13, -12<=k<=14, -24<=l<=24	
Reflections collected	14053	
Independent reflections	4650 [R(int) = 0.0339]	
Completeness to theta = 25.000°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4650 / 0 / 371	
Goodness-of-fit on F^2	0.914	
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1226	
R indices (all data)	R1 = 0.0611, wR2 = 0.1377	
Absolute structure parameter	-0.6(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.127 and -0.182 e.$Å^-$	

Table 3. Crystal data and structure refinement for 168

Identification code	Compound 168	
Empirical formula	$C_{28}H_{26}O_4$	
Formula weight	1377.56	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 29.1471(14) Å	α=90°.
	b = 8.0774(4) Å	β=104.854(2)°.
	c = 15.3326(6) Å	γ=90°.
Volume	3489.2(3) $Å^3$	
Z	2	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	1456	
Crystal size	0.360 x 0.240 x 0.120 mm^3	
Theta range for data collection	2.235 to 26.413°.	
Index ranges	-36<=h<=36, -10<=k<=10, -19<=l<=19	
Reflections collected	67955	
Independent reflections	14272 [R(int) = 0.0784]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14272 / 1 / 938	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.1041, wR2 = 0.2789	
R indices (all data)	R1 = 0.1441, wR2 = 0.3090	
Absolute structure parameter	-0.3(6)	
Extinction coefficient	0.030(4)	
Largest diff. peak and hole	0.611 and -0.468 e.$Å^{-3}$	

Table 4. Crystal data and structure refinement for (*aR,R*)188

Identification code	Compound 186	
Empirical formula	$C_{26}H_{24}O_3$	
Formula weight	384.45	
Temperature	299(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P 31	
Unit cell dimensions	a = 9.7393(11) Å	α= 90°.
	b = 9.7393(11) Å	β= 90°.
	c = 18.745(3) Å	γ = 120°.
Volume	1539.9(4) $Å^3$	
Z	3	
Density (calculated)	1.244 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	612	
Crystal size	0.62 x 0.42 x 0.38 mm^3	
Theta range for data collection	2.415 to 26.365°.	
Index ranges	-12<=h<=12, -12<=k<=12, -23<=l<=23	
Reflections collected	18138	
Independent reflections	3935 [R(int) = 0.1507]	
Completeness to theta = 25.242°	94.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3935 / 1 / 262	
Goodness-of-fit on F^2	0.974	
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1741	
R indices (all data)	R1 = 0.1304, wR2 = 0.1994	
Absolute structure parameter	-0.2(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.229 and -0.261 $e.Å^{-3}$	

Table 6. Crystal data and structure refinement for 44

Identification code	Compound 44	
Empirical formula	$C_{28}H_{32}O_2$	
Formula weight	801.07	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.4700(19) Å	□= 87.60(3)°.
	b = 11.900(2) Å	□= 83.30(3)°.
	c = 19.300(4) Å	□ = 88.90(3)°.
Volume	2158.0(8) $Å^3$	
Z	2	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	864	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.71 to 26.14°.	
Index ranges	-11<=h<=11, -14<=k<=14, -23<=l<=23	
Reflections collected	22694	
Independent reflections	8534 [R(int) = 0.0242]	
Completeness to theta = 26.14°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8534 / 0 / 575	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1235	
R indices (all data)	R1 = 0.0607, wR2 = 0.1325	
Largest diff. peak and hole	0.200 and -0.237 $e.Å^{-3}$	

Table.7 Crystal data and structure refinement for Compound 54

Identification code	Compound 54
Empirical formula	$C_{33}H_{36}O_3$
Formula weight	29.02
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 26.875(5) Å □= 90°.
	b = 9.7855(18) Å □= 114.311(6)°.
	c = 21.521(4) Å □ = 90°.
Volume	5157.8(17) $Å^3$
Z	152
Density (calculated)	1.420 Mg/m^3
Absorption coefficient	0.132 mm^{-1}
F(000)	2280
Crystal size	0.22 x 0.20 x 0.18 mm^3
Theta range for data collection	2.241 to 27.541°.
Index ranges	-34<=h<=34, -12<=k<=12, -28<=l<=27
Reflections collected	23032
Independent reflections	5504 [R(int) = 0.0651]
Completeness to theta = 25.242°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5504 / 6 / 325
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0656, wR2 = 0.1522
R indices (all data)	R1 = 0.1218, wR2 = 0.1777
Extinction coefficient	n/a
Largest diff. peak and hole	0.636 and -0.235 $e.Å^{-3}$

Table.8 Crystal data and structure refinement for Compound 61

Identification code	Compound 61
Empirical formula	$C_{20}H_{16}N_4O$
Formula weight	328.37
Temperature	299(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I -4
Unit cell dimensions	a = 20.9495(16) Å □= 90°.
	b = 20.9495(16) Å □= 90°.
	c = 8.3286(6) Å □ = 90°.
Volume	3655.3(6) $Å^3$
Z	8
Density (calculated)	1.193 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	1376
Crystal size	0.22 x 0.20 x 0.18 mm^3
Theta range for data collection	2.632 to 27.480°.
Index ranges	-26<=h<=27, -27<=k<=26, -10<=l<=10
Reflections collected	13662
Independent reflections	4058 [R(int) = 0.0441]
Completeness to theta = 25.242°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4058 / 0 / 231
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0786, wR2 = 0.2299
R indices (all data)	R1 = 0.1116, wR2 = 0.2530
Absolute structure parameter	-1.1(8)
Extinction coefficient	0.010(4)
Largest diff. peak and hole	1.069 and -0.342 $e.Å^{-3}$

Table 9.Crystal data and structure refinement for (±)-78

Identification code	Compound (±)-78	
Empirical formula	$C_{26}H_{12}Cl_2O_4$	
Formula weight	64.47	
Temperature	301(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6064(6) Å	α= 99.452(4)°.
	b = 10.7317(9) Å	β= 94.449(4)°.
	c = 11.1038(9) Å	γ = 97.444(4)°.
Volume	997.98(14) $Å^3$	
Z	16	
Density (calculated)	1.716 Mg/m^3	
Absorption coefficient	1.159 mm^{-1}	
F(000)	512	
Crystal size	?x ?x ? mm^3	
Theta range for data collection	2.399 to 25.177°.	
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=13	
Reflections collected	24438	
Independent reflections	3567 [R(int) = 0.0488]	
Completeness to theta = 25.178°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3567 / 0 / 289	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.1202	
R indices (all data)	R1 = 0.0531, wR2 = 0.1362	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.202 and -0.280 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **150** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	2835(3)	3673(2)	2080(1)	73(1)
O(2)	-576(3)	3415(2)	2941(1)	77(1)
C(3)	2533(4)	5232(3)	3801(1)	53(1)
C(4)	2667(4)	3166(2)	3304(2)	50(1)
C(5)	4029(4)	1318(3)	3649(2)	63(1)
C(6)	4176(4)	5163(3)	4049(2)	59(1)
C(7)	2980(6)	1630(3)	5013(2)	82(1)
C(8)	-726(5)	5463(3)	3337(2)	75(1)
C(9)	3193(4)	2949(3)	2627(2)	57(1)
C(10)	127(5)	4389(3)	3248(2)	62(1)
C(11)	4149(4)	1972(3)	2458(2)	67(1)
C(12)	3076(4)	2327(3)	3830(2)	54(1)
C(13)	1735(5)	4263(3)	3462(1)	51(1)
C(14)	36(6)	6389(3)	3645(2)	73(1)
C(15)	2482(6)	7269(3)	4227(2)	77(1)
C(16)	2557(5)	2466(3)	4525(2)	64(1)
C(17)	4901(5)	6089(3)	4380(2)	70(1)
C(18)	1668(5)	6313(3)	3890(2)	62(1)
C(19)	4408(6)	502(3)	4169(3)	84(1)
C(20)	4050(6)	7149(3)	4467(2)	80(1)
C(21)	4549(5)	1179(3)	2949(2)	71(1)
C(22)	3917(5)	637(3)	4831(2)	84(1)
C(23)	-2186(5)	3518(4)	2634(2)	102(1)
O(3)	783(5)	5616(3)	1782(2)	123(1)
C(2)	775(7)	5482(5)	1082(2)	128(2)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for compound **154** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(001)	4366(2)	4514(2)	4055(1)	48(1)
O(002)	5224(2)	6666(2)	4820(1)	54(1)
O(003)	10820(3)	3951(2)	2405(1)	60(1)
O(004)	5243(3)	3498(3)	3276(1)	80(1)
C(005)	11519(3)	5576(3)	1435(1)	41(1)
C(006)	7478(3)	5324(3)	3823(2)	38(1)
C(007)	9301(3)	5026(3)	2883(2)	39(1)
C(008)	6071(3)	6545(3)	4345(2)	41(1)
C(009)	7868(3)	6221(3)	3426(2)	39(1)
C(00A)	10280(3)	4824(3)	2409(2)	41(1)
C(00B)	6125(3)	4546(3)	4700(1)	38(1)
C(00C)	6566(3)	5495(3)	4295(1)	38(1)
C(00D)	8778(3)	6050(3)	2961(2)	41(1)
C(00E)	6769(3)	4143(3)	5257(2)	40(1)
C(00F)	5075(3)	4045(3)	4552(2)	40(1)
C(00G)	6324(3)	3217(3)	5617(2)	43(1)
C(00H)	4632(3)	3132(3)	4898(2)	46(1)
C(00I)	4550(3)	4197(3)	3426(2)	53(1)
C(00J)	8896(3)	4122(3)	3271(2)	42(1)
C(00K)	11368(3)	4831(3)	923(2)	50(1)
C(00L)	6452(3)	7428(3)	3951(2)	48(1)
C(00M)	5254(3)	2721(3)	5415(2)	49(1)
C(00N)	8016(3)	4259(3)	3722(2)	42(1)
C(00O)	7815(3)	4652(3)	5474(2)	51(1)
C(00P)	7333(3)	7272(3)	3504(2)	46(1)
C(00Q)	12190(4)	4762(3)	423(2)	55(1)
C(00R)	12510(3)	6243(3)	1432(2)	53(1)
C(00S)	3208(4)	5873(4)	3172(2)	57(1)

C(00T)	13332(4)	6169(3)	931(2)	62(1)
C(00U)	4557(4)	7663(3)	4832(2)	61(1)
C(00V)	6937(4)	2854(3)	6181(2)	57(1)
C(00W)	10591(4)	5771(3)	1949(2)	56(1)
C(00X)	13168(4)	5429(3)	429(2)	61(1)
C(00Y)	7940(4)	3381(4)	6389(2)	65(1)
C(00Z)	8372(4)	4281(4)	6029(2)	63(1)
C(010)	2190(4)	5868(5)	3542(2)	73(1)
C(011)	3653(5)	6894(5)	2981(2)	78(1)
C(012)	3772(5)	4806(4)	2956(2)	77(1)
C(013)	3088(7)	7859(5)	3140(3)	107(2)
C(014)	2094(7)	7847(7)	3494(3)	113(3)
C(015)	1631(5)	6856(7)	3705(3)	105(2)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Compound **168** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(23)	9325(3)	1225(12)	1630(5)	38(2)
C(78)	3137(3)	6880(12)	2877(6)	38(2)
O(1)	4062(2)	3767(10)	3733(4)	54(2)
O(12)	11573(2)	2728(11)	6507(4)	58(2)
O(4)	4276(2)	1254(9)	2658(5)	58(2)
O(6)	6559(2)	2816(12)	37(4)	66(2)
O(2)	3439(2)	7341(10)	4963(4)	54(2)
O(5)	5957(2)	6357(9)	1291(5)	58(2)
O(11)	10941(3)	6380(11)	4689(5)	71(2)
O(8)	8423(2)	7238(12)	-1529(4)	68(2)
C(19)	10523(3)	3090(14)	3527(6)	44(2)
C(70)	3645(3)	4509(11)	3251(5)	36(2)
O(7)	9055(2)	3606(10)	278(5)	63(2)
C(81)	3858(3)	7751(14)	4783(5)	46(2)

C(11)	11072(3)	2899(14)	5072(5)	45(2)
C(79)	3567(3)	6173(9)	3376(5)	28(2)
C(35)	8857(3)	7662(11)	-936(5)	33(2)
C(91)	5719(2)	8888(10)	2335(5)	30(2)
C(73)	2786(3)	5968(11)	2307(6)	34(2)
C(57)	6050(3)	3027(11)	1005(5)	33(2)
C(15)	10302(3)	1549(15)	4682(6)	54(3)
C(54)	6943(4)	1510(14)	2063(7)	49(2)
C(62)	5618(3)	2618(13)	1199(5)	40(2)
C(74)	2359(3)	6655(14)	1830(7)	50(2)
C(20)	10643(3)	2614(14)	4430(5)	45(2)
C(8)	11965(4)	1660(18)	4847(6)	62(3)
C(10)	11455(3)	4008(13)	4823(6)	48(2)
C(27)	7760(3)	5669(12)	495(6)	42(2)
C(89)	4380(2)	7577(10)	3809(5)	28(2)
C(80)	3940(3)	7237(11)	4027(6)	35(2)
C(9)	11875(3)	3323(15)	4737(6)	44(2)
C(49)	7140(3)	5942(15)	2772(6)	50(2)
C(56)	6428(3)	4008(13)	1616(6)	42(2)
C(84)	4724(3)	8643(12)	4405(6)	42(2)
C(87)	4923(3)	7392(13)	2837(5)	42(2)
C(43)	9363(2)	7447(10)	562(5)	29(2)
C(33)	8564(3)	5960(11)	190(5)	33(2)
C(3)	12131(3)	6056(17)	4353(6)	59(3)
C(32)	8118(3)	6656(11)	256(6)	36(2)
C(1)	11364(3)	5694(13)	4652(6)	45(2)
C(63)	5508(3)	3178(13)	2007(5)	42(2)
C(48)	6720(3)	6675(16)	2340(6)	61(3)
C(88)	4505(3)	7018(13)	3039(5)	42(2)
C(83)	4612(3)	9165(14)	5175(7)	56(3)
C(41)	9897(3)	7229(14)	2087(6)	49(2)
C(66)	4841(3)	1301(17)	804(7)	63(3)

C(82)	4189(3)	8809(14)	5374(6)	49(2)
C(76)	2650(3)	9355(12)	2430(7)	53(3)
C(75)	2291(3)	8437(12)	1872(6)	46(2)
C(72)	2884(3)	4260(11)	2188(6)	39(2)
C(6)	12738(4)	2091(17)	4533(7)	64(3)
C(4)	12221(3)	4361(15)	4522(6)	50(3)
C(17)	9766(4)	1749(17)	3188(7)	65(3)
C(61)	5278(3)	1684(13)	583(5)	45(2)
C(50)	7227(4)	4219(14)	2710(6)	52(3)
C(44)	8339(3)	7758(16)	-2420(5)	56(3)
C(36)	9197(3)	8602(14)	-1176(6)	52(3)
C(16)	9864(4)	1128(19)	4053(6)	69(3)
C(5A)	12665(3)	3639(15)	4459(7)	50(2)
C(71)	3295(3)	3569(9)	2682(5)	35(2)
C(28)	7349(3)	6341(18)	569(7)	62(3)
C(46)	10690(3)	8809(11)	3363(5)	37(2)
C(18)	10107(3)	2757(16)	2957(7)	57(3)
C(65)	4745(3)	1720(20)	1567(7)	76(4)
C(37)	9597(3)	8973(13)	-601(6)	48(2)
C(34)	8921(3)	7013(10)	-62(6)	33(2)
C(2)	11696(4)	6790(20)	4401(7)	79(4)
C(24)	8632(3)	4289(12)	361(6)	44(2)
C(60)	5374(4)	1035(15)	-209(6)	58(3)
C(30)	7627(4)	9097(14)	268(8)	61(3)
C(25)	8282(3)	3350(10)	582(6)	40(2)
C(14)	10401(4)	853(15)	5538(7)	62(3)
C(26)	7885(4)	3989(12)	653(7)	52(2)
C(58)	6133(3)	2405(11)	188(5)	38(2)
C(13)	10824(4)	1264(15)	6183(7)	58(3)
C(77)	3051(3)	8624(12)	2938(7)	44(2)
C(64)	5084(4)	2740(20)	2165(7)	75(4)
C(47)	6374(3)	5635(13)	1748(6)	43(2)

C(31)	8032(3)	8408(11)	172(7)	43(2)
C(12)	11170(3)	2380(16)	5924(6)	60(3)
C(67)	6661(3)	2305(16)	-763(6)	59(3)
C(59)	5792(3)	1443(14)	-407(6)	52(2)
C(86)	5258(3)	8345(18)	3428(6)	59(3)
C(38)	9707(3)	8440(12)	309(6)	40(2)
C(42)	9483(3)	6772(11)	1476(6)	41(2)
C(7)	12391(4)	1021(19)	4738(8)	70(4)
O(3)	6126(4)	8190(30)	3844(9)	196(9)
C(55)	6868(3)	3208(11)	2099(5)	32(2)
C(40)	10232(3)	8168(19)	1828(6)	67(4)
C(52)	7715(4)	1910(20)	3109(9)	83(5)
C(53)	7366(4)	854(17)	2529(8)	71(3)
C(51)	7643(4)	3334(19)	3209(7)	58(3)
C(85)	5153(3)	9006(17)	4206(6)	57(3)
C(39)	10126(3)	8817(14)	953(7)	54(3)
O(9)	11099(3)	8060(30)	2276(8)	158(6)
C(45)	10723(3)	8410(30)	2488(7)	126(8)
C(29)	7266(4)	8119(17)	433(8)	65(3)
C(21)	11690(4)	2060(20)	7434(7)	91(5)
C(68)	4257(4)	1460(40)	1724(7)	139(10)
C(90)	5723(4)	8830(30)	3204(8)	108(6)
C(22)	9316(4)	1180(30)	2526(9)	97(5)
O(10)	8930(6)	650(40)	2748(12)	289(17)
C(02W)	3880(4)	1220(40)	1138(9)	198(15)
C(92)	3328(4)	7950(20)	5769(7)	85(5)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for

compound **(*aR,R*)-188**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
O(1)	11610(6)	9748(6)	5928(2)	61(1)
O(2)	7596(6)	6457(6)	6766(2)	56(1)
O(3)	2883(7)	2877(9)	3838(3)	89(2)
C(10)	8046(7)	6627(7)	5070(3)	37(1)
C(15)	11227(8)	5396(8)	6595(3)	47(2)
C(20)	10930(8)	6206(7)	6043(3)	39(1)
C(5)	7777(8)	7502(7)	4541(3)	43(2)
C(2)	10349(7)	9027(7)	5456(3)	41(2)
C(1)	9363(7)	7428(7)	5542(3)	37(1)
C(11)	9694(7)	6552(7)	6112(3)	35(1)
C(12)	8759(7)	6074(7)	6723(3)	39(1)
C(9)	6984(7)	4962(7)	5105(3)	40(1)
C(13)	9069(9)	5280(8)	7273(3)	52(2)
C(7)	5459(8)	5110(8)	4119(3)	50(2)
C(4)	8858(8)	9134(8)	4472(3)	49(2)
C(6)	6452(8)	6703(9)	4085(3)	46(2)
C(14)	10266(9)	4940(8)	7215(4)	53(2)
C(23)	4161(10)	4302(11)	3565(4)	71(2)
C(21)	12487(11)	11434(9)	5943(5)	79(3)
C(3)	10116(9)	9889(8)	4914(3)	53(2)
C(16)	12510(10)	5084(10)	6524(5)	66(2)
C(8)	5747(8)	4234(9)	4641(3)	48(2)
C(22)	6585(10)	5995(12)	7369(4)	75(3)
C(17)	13432(11)	5543(11)	5932(5)	74(2)
C(19)	11899(9)	6631(9)	5426(4)	55(2)
C(26)	2187(11)	1798(16)	3260(5)	99(3)
C(18)	13113(11)	6294(11)	5377(5)	76(3)
C(25)	3242(15)	2374(17)	2652(6)	124(5)

C(24)	4697(13)	3763(15)	2904(4)	98(4)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **44** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
O(2)	2262(1)	-609(1)	961(1)	63(1)
C(29)	1928(1)	3593(1)	7403(1)	39(1)
O(3)	2230(1)	1627(1)	9205(1)	69(1)
C(31)	1629(1)	4275(1)	6757(1)	38(1)
C(32)	711(1)	3167(1)	7776(1)	39(1)
C(33)	-28(1)	4177(1)	6766(1)	38(1)
C(34)	-629(1)	3570(1)	7477(1)	39(1)
C(35)	-1490(1)	4302(1)	8002(1)	41(1)
C(36)	749(2)	2503(1)	8381(1)	46(1)
C(14)	3782(2)	506(1)	2449(1)	41(1)
C(15)	2579(2)	952(1)	2813(1)	41(1)
C(6)	5125(2)	774(1)	2764(1)	44(1)
C(37)	2431(2)	3924(1)	6049(1)	45(1)
C(38)	3210(2)	3418(1)	7682(1)	49(1)
C(39)	-588(2)	3439(1)	6226(1)	48(1)
C(17)	3743(2)	-28(1)	1828(1)	46(1)
C(40)	3262(2)	2767(1)	8281(1)	53(1)
C(23)	2039(2)	958(1)	4167(1)	49(1)
C(20)	1314(2)	936(1)	2510(1)	49(1)
C(41)	2044(2)	2289(1)	8623(1)	50(1)
C(42)	-1480(2)	2590(1)	7233(1)	48(1)
C(16)	2866(2)	1467(1)	3483(1)	42(1)
C(18)	2462(2)	-86(1)	1561(1)	47(1)
C(8)	6014(2)	1530(1)	2235(1)	48(1)
C(5)	4527(2)	1318(1)	3470(1)	43(1)
C(43)	4049(2)	3886(1)	6043(1)	53(1)

C(19)	1257(2)	414(1)	1897(1)	52(1)
C(44)	-558(2)	2269(1)	6573(1)	55(1)
C(28)	2362(2)	2723(1)	3532(1)	51(1)
C(13)	5734(2)	2668(1)	2167(1)	53(1)
O(4)	-3930(2)	6210(1)	9462(1)	84(1)
O(1)	8327(2)	3519(2)	686(1)	97(1)
C(7)	5916(2)	-290(1)	3021(1)	57(1)
C(46)	-2807(2)	3071(1)	6937(1)	55(1)
C(47)	3011(2)	5733(1)	6067(1)	56(1)
C(12)	6468(2)	3362(2)	1662(1)	61(1)
C(48)	2269(2)	5000(2)	5601(1)	57(1)
C(49)	2117(2)	5521(1)	6767(1)	48(1)
C(4)	5074(2)	497(1)	4019(1)	52(1)
C(50)	-1224(2)	5421(1)	8047(1)	52(1)
C(24)	433(2)	950(2)	4138(1)	58(1)
C(51)	-2192(2)	3651(2)	6245(1)	58(1)
C(52)	4442(2)	5123(2)	6093(1)	62(1)
C(53)	-2560(2)	3855(2)	8482(1)	60(1)
C(54)	-3077(2)	5628(2)	8975(1)	59(1)
C(27)	1406(2)	2768(2)	4222(1)	61(1)
C(9)	7062(2)	1096(2)	1754(1)	64(1)
C(2)	6693(2)	634(2)	3981(1)	65(1)
C(3)	4981(2)	-631(1)	3686(1)	60(1)
C(55)	-2006(2)	6090(2)	8522(1)	62(1)
C(25)	6(2)	2195(2)	4155(1)	66(1)
C(26)	2139(2)	1900(2)	4668(1)	61(1)
C(11)	7525(2)	2914(2)	1204(1)	66(1)
C(1)	7276(2)	62(2)	3309(1)	70(1)
C(56)	-3340(2)	4505(2)	8958(1)	70(1)
C(57)	993(2)	1283(2)	9631(1)	91(1)
C(10)	7806(2)	1776(2)	1249(1)	74(1)
C(21)	3468(2)	-1009(2)	549(1)	77(1)

C(58)	-3802(3)	7396(2)	9435(1)	101(1)
C(22)	8131(3)	4706(2)	660(1)	114(1)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **54** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
O(001)	4391(1)	5123(2)	7097(1)	54(1)
O(002)	4302(1)	7929(2)	7339(1)	60(1)
O(003)	4151(1)	7785(2)	4334(1)	69(1)
C(004)	3923(1)	6090(2)	5980(1)	39(1)
C(005)	3859(1)	5469(2)	6591(1)	41(1)
C(006)	3548(1)	6370(2)	6923(1)	42(1)
C(007)	3082(1)	8898(2)	7178(1)	45(1)
C(008)	3516(1)	4102(2)	6421(1)	44(1)
C(009)	4316(1)	5573(3)	5785(1)	47(1)
C(00A)	3782(1)	2931(2)	6216(1)	46(1)
C(00B)	2928(1)	4442(3)	5903(1)	53(1)
C(00C)	3586(1)	8358(3)	7751(1)	46(1)
C(00D)	3148(1)	5324(3)	7018(1)	52(1)
C(00E)	3432(1)	3940(3)	7081(1)	53(1)
C(00F)	2562(1)	8483(3)	7088(1)	55(1)
C(00G)	3609(1)	7161(3)	5587(1)	51(1)
C(00H)	3916(1)	7242(3)	7539(1)	46(1)
C(00I)	4097(1)	7172(3)	4875(1)	50(1)
C(00J)	4406(1)	6098(3)	5245(1)	53(1)
C(00K)	3119(1)	9806(3)	6703(2)	60(1)
C(00L)	3997(1)	9491(3)	8149(2)	62(1)
C(00M)	3693(1)	7685(3)	5045(1)	56(1)
C(00N)	4201(1)	2168(3)	6696(1)	53(1)
C(00O)	2667(1)	5178(3)	6327(2)	63(1)

C(00P)	3617(1)	2562(3)	5541(1)	59(1)
C(00Q)	4228(1)	6493(3)	8222(1)	59(1)
C(00R)	3521(1)	7661(3)	8355(1)	57(1)
C(00S)	2103(1)	8937(3)	6538(2)	63(1)
C(00T)	4439(1)	1092(3)	6502(2)	64(1)
C(00U)	4122(1)	7345(3)	8749(1)	64(1)
C(00V)	2150(1)	9817(3)	6070(2)	69(1)
C(00W)	2657(1)	10248(3)	6157(2)	71(1)
C(00X)	4574(1)	7308(4)	4161(2)	79(1)
C(00Y)	4267(1)	755(3)	5830(2)	71(1)
C(00Z)	3855(1)	1484(3)	5349(2)	72(1)
C(010)	4388(1)	8750(3)	8807(2)	75(1)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **61** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
O(1)	4086(2)	8976(2)	3197(7)	77(2)
N(3)	3295(3)	6689(3)	11106(6)	70(2)
C(4)	3598(2)	7353(2)	5798(5)	38(1)
C(16)	4057(2)	5993(2)	7627(7)	42(1)
C(19)	3548(3)	6675(3)	9899(7)	47(1)
C(13)	2684(2)	6717(2)	7125(7)	44(1)
C(18)	4720(3)	5957(2)	7102(7)	50(1)
C(15)	3866(2)	6679(2)	8322(6)	37(1)
N(1)	3832(3)	4986(2)	9360(8)	68(2)
C(20)	4396(3)	7135(3)	8420(7)	48(1)
C(8)	3407(2)	6782(2)	6792(5)	37(1)
N(4)	4795(3)	7496(3)	8500(9)	78(2)
N(2)	5224(3)	5906(3)	6620(9)	82(2)
C(5)	3952(2)	7300(3)	4394(7)	47(1)

C(9)	3582(2)	6100(2)	6184(6)	42(1)
C(17)	3931(2)	5438(3)	8647(8)	50(1)
C(6)	4124(3)	7824(3)	3504(7)	55(1)
C(3)	3406(3)	7968(2)	6263(7)	51(1)
C(12)	2362(3)	6684(3)	5470(8)	56(1)
C(14)	2607(3)	6020(3)	7658(7)	48(1)
C(10)	2950(3)	5742(3)	6186(7)	51(1)
C(11)	2546(3)	6030(3)	4826(8)	65(2)
C(1)	3942(3)	8425(3)	4008(8)	52(1)
C(2)	3576(3)	8494(3)	5388(8)	56(1)
C(7)	4422(4)	8928(4)	1734(14)	103(3)
O(2)	4058(4)	10011(4)	7690(12)	133(3)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (±)-**78** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
Cl(01)	554(1)	-1999(1)	4517(1)	60(1)
Cl(02)	-307(1)	-1713(1)	7298(1)	66(1)
O(003)	3991(2)	2122(1)	8388(1)	37(1)
O(004)	4580(2)	2015(1)	5843(1)	40(1)
O(005)	1810(2)	321(1)	8873(1)	55(1)
O(006)	3007(2)	40(2)	4235(1)	62(1)
C(007)	8002(2)	3714(2)	8126(2)	32(1)
C(008)	5179(2)	5374(2)	7441(2)	31(1)
C(009)	6325(2)	3402(2)	7958(2)	31(1)
C(00A)	5301(2)	4038(2)	7189(2)	31(1)
C(00B)	5648(2)	2405(2)	8461(2)	33(1)
C(00C)	4393(2)	3311(2)	6193(2)	34(1)
C(00D)	4171(2)	5884(2)	6629(2)	35(1)
C(00E)	8832(2)	4695(2)	7622(2)	37(1)

C(00F)	3527(2)	1160(2)	6258(2)	35(1)
C(00G)	3261(2)	1215(2)	7439(2)	33(1)
C(00H)	8889(2)	3002(2)	8822(2)	37(1)
C(00I)	6036(2)	6219(2)	8453(2)	37(1)
C(00J)	2044(2)	290(2)	7813(2)	37(1)
C(00K)	3338(2)	3791(2)	5424(2)	39(1)
C(00L)	3238(2)	5060(2)	5646(2)	41(1)
C(00M)	2712(2)	117(2)	5287(2)	39(1)
C(00N)	6515(2)	1695(2)	9142(2)	41(1)
C(00O)	1472(2)	-814(2)	5661(2)	40(1)
C(00P)	10551(2)	3318(2)	8995(2)	48(1)
C(00Q)	1125(2)	-708(2)	6819(2)	41(1)
C(00R)	4174(3)	7219(2)	6819(2)	48(1)
C(00S)	6013(3)	7504(2)	8598(2)	48(1)
C(00T)	8112(3)	1987(2)	9312(2)	45(1)
C(00U)	10436(2)	4974(2)	7817(2)	47(1)
C(00V)	11301(2)	4283(2)	8515(2)	54(1)
C(00W)	5082(3)	8008(2)	7752(2)	55(1)

List of Publications

1. Periasamy, M.;Venkanna. B.; Nagaraju, M.; Mohan, L.; Methods of synthesis of piperazine derivatives containing chiral *bi*-2-napthyl moiety, ***Synthesis***, 0000, 2019, (DOI): 10.1055/s-0037-1610731; Art ID: SS-2019-z0241-op.

2. Periasamy, M.; Venkanna, B.; Mohan, L.; Methods for synthesis of chiral alcohols and their conversion to heterocycles containing *bi*-2-naphthyl moiety (***Communicated.***)

3. Periasamy, M.; Ramesh, E.; Venkanna, B.; Ramusagar, M.; Shanmugaraja, M.; Methods for synthesis of amino, aminoalkoxy, aryloxy, *bi*-2-naphthyloxy and bis-*bi*-2-naphthyloxybennzoquinone derivatives (***To be communicated.*)**

4. Periasamy, M.; Venkanna, B.; Trapping of *exo*-2-norbornylcation with chiral nucleophiles: Implication on the unsymmetrical vs symmetrical norbornylcation.
   (***To be communicated.*)**

Synthesis and Applications of Bi-2-naphthol derivatives

by Venkanna Boda

Submission date: 16-Oct-2019 04:10PM (UTC+0530)
Submission ID: 1193941752
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Word count: 7747
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Synthesis and Applications of Bi-2-naphthol derivatives

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