Sterically Rigid Bi-dentate *N*-(Aryl)imino-Acenapthenone (Ar-BIAO) Ligands in Zinc Coordination Sphere- Syntheses and Structures

A Project Report

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By

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Declaration

I hereby declare that the matter embodied in this report is a result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. Tarun K. Panda**.

In keeping with general practice of reporting scientific observations, due acknowledgment has been made wherever the work described is based on the findings of other investigators.

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Approval Sheet

This thesis entitled **“Sterically Rigid Bi-dentate N-(Aryl)imino-Acenapthenone (Ar-BIAO) Ligands in Zinc Coordination Sphere- Syntheses and structures”** by Supriya Rej is approved for the degree of Master of Science from IIT Hyderabad.

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Co-Adviser

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Chairman

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Dedicated

To

My Beloved Parents

Contents

Abstract

My thesis work describes the synthesis of six different 1-alkyl-*N*-(arylimino)acenaphthylen-1-ol compounds **1a, 1b, 2a, 2b, 3a** and **3c** as the racemic products by varying steric demand on the imino nitrogen atom of *N*-(aryl)imino-acenapthenone (Ar-BIAO) ligand. The synthesized imino-alcohols are characterized by FT-IR, ^{1}H, ^{13}C{^{1}H} NMR spectroscopy. The soild state structures of compounds **1a, 1b, 2a** and **3a** are established by single crystal X-ray diffraction analysis. In the molecular structure compounds **1a** and **3a** crystallize only *R*-isomers in their respective asymmetric unit, whereas compound **1b** has *S*-isomer only in its asymmetric unit. However compound **2a** crystallizes in both *R*- and *S*-isomers in its asymmetric unit. In addition with this work one new chiral ligand, *N*-(1-phenylethylamine)imino-acenaphthenone (**4**) was synthesized by the reaction of acenaphthenequinone and (*R*)-1-phenylethylamine in 1:1 ratio. Compound **4** was characterized by FT-IR and ^{1}H NMR spectroscopy.

In the latter part of my thesis, synthesis of four zinc complexes of molecular formulae $[ZnI_2$(2,6-dimethylphenyl-BIAO)$]_2$ (**6**), $[ZnBr_2$(2,6-dimethylphenyl-BIAO)$]_2$ (**7**), $[ZnBr_2$(mes-BIAO)$]_2$ (**8**) and $[ZnBr_2$(dipp-BIAO)$]$ (**9**) of rigid unsymmetrical iminoacenaphthenone ligands, (2,6-dimethylphenyl-BIAO) (**2**), (mesityl-BIAO) (**3**) and (diisopropylphenyl-BIAO) (**1**) are discussed. The zinc complexes **7, 8** and **9** are prepared by the reaction of $ZnBr_2$ and neutral (2,6-dimethylphenyl-BIAO) (**2**), (mesityl-BIAO) (**3**) and (diisopropylphenyl-BIAO) (**1**) ligand respectively. However complex **6** is achieved by the reaction of ZnI_2 and neutral ligand (2,6-dimethylphenyl-BIAO) (**2**) in dichloromethane at ambient temperature. All the zinc (II) complexes are characterized by FT-IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The solid state structure of the complexes **6, 7, 8** and **9** are confirmed by single crystal X-ray diffraction analysis. The molecular structures of complexes **6, 7** and **8** reveal dimeric nature and subsequently the center atom zinc is penta-coordinated to have distorted trigonal bipyramidal geometry around it. In the complex **9**, it is in monomeric form zinc ion is tetra coordinated to adopt distorted tetrahedral geometry around zinc center.

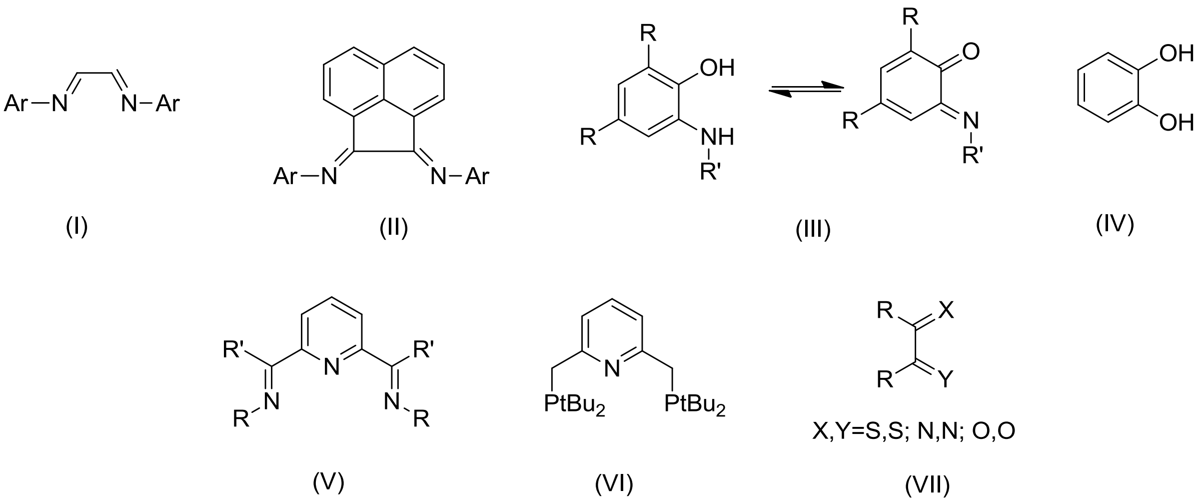
1. Introduction

In the past few years, there were numerous efforts to develop efficient phosphine-based catalysts for the cross-coupling of an aryl halide with an aryl boronic acid to form different biaryl compounds. [1-5] The different kind of [NO]- based ligands have exhibited good activity for the Suzukie Miyaura cross-coupling that is often attributed to their σ-donating ability which allows for the formation of a strong metal-imine bond that helps to prevent catalyst decomposition. [6] Moreover, the other attractive features are that these type of phosphine-free ligands are easily accessible synthetically and that they have rather flexible like or rigid like structure. All these properties allow for the steric and electronic effects to be tuned to a large extent, giving the possibility of screening these compounds for their catalytic properties. For example, salicylaldimine palladium complexes show fine catalytic activities. [7, 8]

The different ligands can binds with different metal centre and accordingly can change the size and co-ordination number of the metal centre and thereby can reduce the activity of the bear metal. [9, 10] As a result, we can tune the catalytic activity. For an example, Raney Ni having very active metal surface reduces compounds with multiple bonds, aromatics and carbonyl-containing compounds, reductive alkylation of amines and the amination of alcohols and additionally will reduce heteroatom-heteroatom bonds, such as hydrazines, nitro groups and nitrosamines. The olefin polymerisation was more commercialized in the last century globally by the use of different transition metals complexes with variety of ligand systems which are both electronically as well as sterically changes the path way for the formation of different molecular weight polymers. Among all these different type of ligands, rigid sterically bulky bidentate α-diimine based ligand system introduce to a new class of catalyst which were already proved to be a very much useful as far as the polymer chemistry is concerned. [11, 12]

Redox active moieties are used as a ligand is called redox active ligand. Redox active ligands supplement the electrons/ holes transferred from the metal, which can facilitate reactions that required multi electron transfers. Organometallic complexes containing redox active ligands have been studied for many years, but their use in catalysis reaction is not so much popular. The use of redox active-ligands for the processing of the small molecules are widely spread in enzymology, especially for O_2 processing, and synthetic models containing redox active ligands have been made. Some of redox active ligands are given bellow in the

Fig. 1. The co-ordination modes of redox active ligands are flexible and many types of co-ordination of ligand to metal are possible like neutral, mono-anionic, di-anionic modes. Apart from this, π mode co-ordination is also well known for redox active ligand. [13]



(I) (II) (III) (IV)

(V) (VI) (VII)

Fig. 1.

The complexes of redox active ligands with alkali metals, alkaline earth metals [14] and transition metals are well known and complexes of some of lanthanides with redox active ligands are also known [15] but it is not so much explored till now. Some of research group has already done with the complexes of redox active ligands and various types of transition metals. Complexes of transition metals and redox active ligand are also known because of this type of complexes may have some application like- i) redox active ligand- lanthanide complexes may act as active catalyst to oxidise H_2 to H^+ & electron i.e. generating of fuel. ii) Complexes of redox active ligand with lanthanide can also act as a catalyst in oxidative addition or reductive elimination reaction. iii) Redox active ligand can increase the oxidation number of metal as a result complex can act as a good Lewis acid, hence it can be a good catalyst. It is reported in literature that the redox active ligand complexes with various group 2 metals are generally prepared through two pathways, the salt metathesis reaction via any other alkali metal complexes or direct metallation. [16] Redox active ligands are co-ordinated to metal ion in a di-anionic mode or mono-anionic mode, depending on the reaction conditions and nature of the metal. Similarly transition metals are also can react and bind with redox active ligand. One group already prepared the ytterbium complex with redox active ligand by direct metallation method.

2. Aim of the Project

The sterically rigid bi-dentate [NO] based ligands were introduced by many group, *N*-(aryl)imino-acenaphthenone (Ar-BIAO) ligand is one of them, which has keto- and imine both groups in such a fashion that it can bind with metal as a bi-dentate ligand. Bi-dentate [NO] based ligand has two types of binding site, one is imine nitrogen and other one is the oxygen of the carbonyl group. [17] Now we are interested in designing a different kind of rigid bi-dentate [NO] based ligand system. We aimed at changing the electronic effect of the ligand by replacing the carbonyl O- donor site with alcohol O- donor site as well as changing the steric demand by different N- substituent. By changing that donor site we want to tune the electronic properties of O- site and the formed complex with different metals also can show different types of catalytic activity because of different donating ability of ligand in complex. With the continuation we are also focussing to synthesize the chiral Ar-BIAO ligand where the chirality is in the N-substituted carbon, which does not affect the N-, O- co-ordination with metals.

Our group has already reported rigid bi-dentate [NO] based ligand system [17] and the complexes of $ZnCl_2$ with the [NO] based Ar-BIAO ligand, which can have catalytic activity. Now we are aiming for the complexes of ZnI_2 and $ZnBr_2$ with different N- substituted rigid Ar-BIAO ligands. The resultant complexes has iodine or bromine in the 3rd and 4th co-ordination site of Zinc (II) and as iodine and bromine are bulkier and good leaving group than chlorine atom so the resultant complexes can be more reactive and can show better catalytic activity in polymerisation reactions or different types of organic reactions like the reduction of carbonyl group. [18]

3. Scope of work

Already there are many report of complexes with metal and α-diimine ligands moiety, among all α-diimine ligands, DAB and BIAN ligand systems are very much well known. All these ligands and there complexes with various transition metals and alkaline earth metals are already reported by different group. Recently our group reported the modified ligand framework from di-imine type ligand to a rigid chiral [NO] bi-dentate system.[19] Hence, we focused to explore more about the mixed donor atoms to be nitrogen and oxygen based ligands shown in Scheme 2 viz. compound 1-methyl-[*N*-(2,6-diisopropylphenyl)imino]-acenaphthylen-1-ol (**1a**), 1-ethyl-[*N*-(2,6-diisopropylphenyl)imino]-acenaphthylen-1-ol (**1b**), 1-methyl-[*N*-(2,6-dimethylphenyl)imino]-acenaphthylen-1-ol (**2a**), 1-ethyl-[*N*-(2,6-dimethylphenyl)imino]-acenaphthylen-1-ol (**2b**), 1-methyl-*N*-(mesityl)imino-acenaphthylen-1-ol (**3a**) and 1-ethyl-*N*-(2,6-mesityl)imino-acenaphthylen-1-ol (**3b**). Now the Ar-BIAO ligand has two types of active reaction centres for Grignard reaction, however Grignard reagent reacts exclusively on to carbonyl moiety only because of higher electronegativity of oxygen atom than nitrogen and shows more affinity towards RMgX. So, Grignard reaction takes place with carbonyl carbon centre preferably compared to imine group. In this class of ligands system, two different donor atoms, stronger donating ability of nitrogen atom of imine moiety and weaker donating capacity of the oxygen atom of the alcohol, are available for co-ordination with metal which vary the accumulated electron density over metal ion thereby can influence the catalytic activity towards polymerisation reaction. Beside the Ar-BIAO-ol ligand the other type chiral ligand is *N*-(1-phenylethylamine)imino-acenaphthenone (**4**) where the chirality is not in co-ordination sphere, chirality is on the nitrogen substituent. Like other Ar-BIAO ligands this chiral Ar-BIAO ligand also can form complexes with transition metals, which complexes can also be catalytically active.

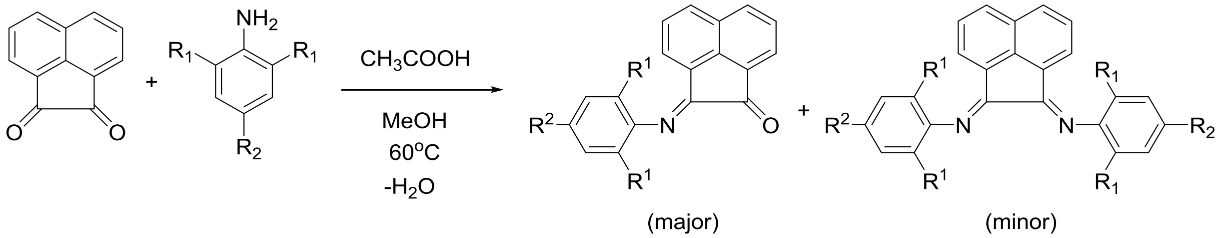
The rigid bi-dentate nitrogen based di-imine ligand bis(*N*-arylimino)acenaphthene (Ar-BIAN), which was first introduced by *van Asselt* and *Elsevier* in the early 1992 in transition metal chemistry[13] and subsequently used in various catalytic process has been attracted by number of researchers as an auxiliary ligand[14-16]. The electronic nature depends on the donor atom of this class of ligands as electronegativity factor guides the capable donation of electron as well as acceptance ability in the metal centre. As a result it is mutual involvement of both for a complex formation. On the other hand, the steric demand in the ligand is partially reduced for the coordination of the metal centre. Hence complex formation by this ligand backbone depends on both electronic as well as steric factors present in the ligand. In present study, we are considering the rigid unsymmetrical imine, carbonyl mixed ligand *N*-(aryl)imino -acenaphthenone (Ar-BIAO) as a ligand, which can be obtained by the single condensation of aryl amine to one of the carbonyl group of the acenaphthenequinone. [17] On reacting ligand **1**, **2** and **3** with $ZnBr_2$, we obtained [$ZnBr_2$(dipp-BIAO)] (**9**), [$ZnBr_2$(2,6-dimethylphenyl-BIAO)]$_2$ (**7**) and [$ZnBr_2$(mes-BIAO)] (**8**) respectively and by reacting ligand **2** with ZnI_2, we obtained [ZnI_2(2,6-dimethylphenyl-BIAO)]$_2$ (**6**).

In these class of ligand system, two different donor atoms, stronger donating ability of nitrogen atom and weaker donating capacity of oxygen atom, are available for coordination with zinc (II) which can vary the accumulated electron density over zinc ion thereby can influence the catalytic activity towards polymerization activity of the metal complexes.

4. Results and Discussions

4.1 Synthesis of *N*-(aryl)imino-acenaphthenone (Ar-BIAO) Ligands:

The ligands **1**, **2** and **3** (Ar-BIAO) were successfully synthesized as a major product according to the literature methods [17] by the following Scheme 1 and bis(*N*-aryl)acenaphthenequinonediimine (Ar-BIAN) formed as a by-product. All compounds **1**, **2** and **3** were confirmed by FT-IR, ^{1}H, ^{13}C{^{1}H} NMR spectroscopy and single crystal X-ray diffraction analyses.

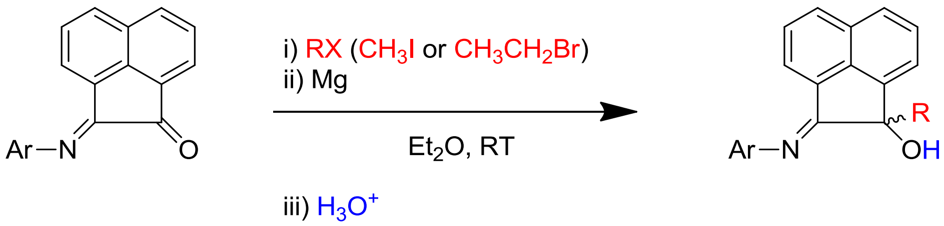


R^2 = H, R^1 = Diisopropyl (**1**)
R^2 = H, R^1 = Me (**2**)
R^2 = R^1 = Me (**3**)

Scheme 1. Synthesis of (Ar-BIAO)

4.2 Synthesis of 1-alkyl-*N*-(arylimino)acenaphthylen-1-ol (Ar-BIAO-ol) ligands:

Compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** has been synthesized by Grignard reaction with Ar-BIAO ligand **1**, **2** and **3**. The Grignard reagent was prepared by the reaction of Mg and alkyl halide (respectively for **1a**, **2a** and **3a** methyl iodide and for **1b**, **2b** and **3b** ethyl bromide) in dry diethyl ether solvent by maintaining inert atmosphere. The solution of compound **1**, **2** and **3** in diethyl ether was combined with respective Grignard reagent (scheme 2). Finally after work up with Na_2SO_4 solution Ar-BIAO-ol ligand was isolated by removal of the organic layer. Yields of the various Ar-BIAO-ol compounds were up to 82%. The white crude product of compound **1a**, **1b**, **2a** and **3a** were crystalized from dichloromethane. All Ar-BIAO-ol compounds were characterized by FT-IR, ^1H and ^{13}C NMR spectroscopy. The melting point of all Ar-BIAO-ol compounds were within the region 120-130^{o}C. Among all six Ar-BIAO-ol the solid state structure of **1a, 1b, 2a, 3a** were established by single crystal X-ray diffraction analysis.



Ar = 2,6-$iPr_2C_6H_3$ (**1**)
= 2,6-$Me_2C_6H_3$ (**2**)
= 2,4,6-$Me_3C_6H_2$ (**3**)

Compound	Ar	R	Yield
1a	2,6-$iPr_2C_6H_3$	Me	79%
1b	2,6-$iPr_2C_6H_3$	Et	74%
2a	2,6-$Me_2C_6H_3$	Me	71%
2b	2,6-$Me_2C_6H_3$	Et	79%
3a	2,4,6-$Me_3C_6H_2$	Me	82%
3b	2,4,6-$Me_3C_6H_2$	Et	71%

Scheme 2. Synthesis of six imine-alcohol compound (**1a**, **1b**, **2a**, **2b**, **3a** & **3b**)

In FT-IR spectra of compound **1a** a strong absorption at 1660 cm^{-1} for the C=N bond stretching which is comparable with **1b** (1658 cm^{-1}), **2a** (1661 cm^{-1}), **2b** (1659 cm^{-1}), **3a** (1660 cm^{-1}) and **3b** (1660 cm^{-1}) can be observed. The broad absorption at 3306, 3309, 3344, 3307, 3244 and 3308 cm^{-1} respectively for compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** can be assigned for O-H bond stretching. Absorption bands at 2961, 2962, 2966, 2966, 2961 and 2966 cm^{-1} respectively for compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** can be assigned for aromatic C-H bond stretching are indicating the presence of aromatic moiety. In the ^1H NMR spectrum of compound **1a** and **1b** similar type four doublet signals at δ = 1.18 ppm, 1.08 ppm, 0.95 ppm and 0.75 ppm for **1a** and δ = 1.19, 1.05, 0.99 and 0.78 ppm for **1b** in 1:1:1:1 ratio are obtained, which can be assigned as the methyl protons attached to isopropyl groups on the aromatic ring. The singlet signal obtained at δ = 1.86 ppm for the methyl proton attached with the quaternary carbon atom for **1a** but for compound **1b** triplet peak at δ = 0.80 ppm is describing the methyl group attached with methylene carbon. For compound **1b** quartet peak at δ = 2.24 ppm can be assigned for methylene group attached with quaternary carbon.

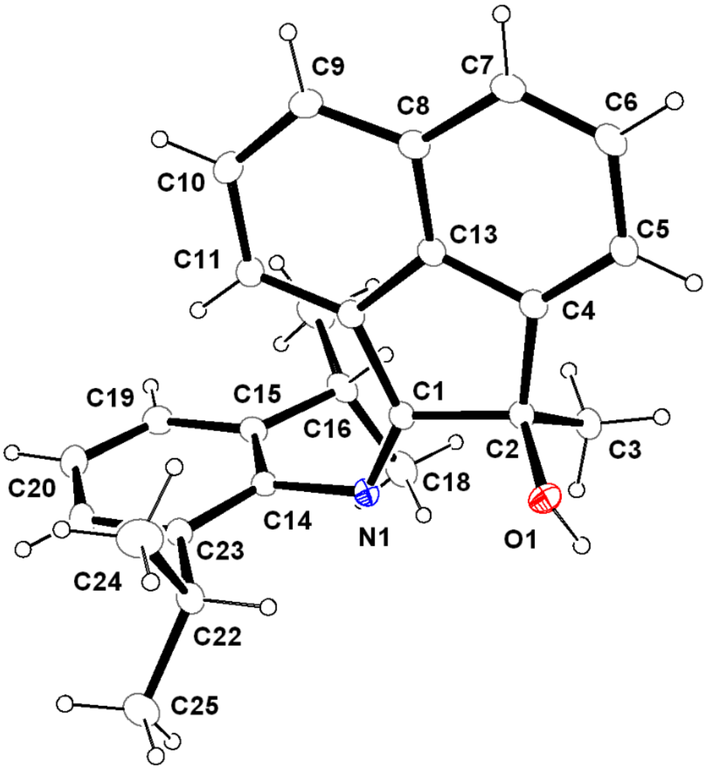


Fig. 2. Solid-state structure of **1a** (*R*-isomer) showing the atom labelling scheme. Selected bond lengths in [Å]: O(1)-C(2) 1.4257(15), N(1)-C(1) 1.2742(16)**,** N(1)-C(14) 1.4345(15), C(1)-C(12) 1.4837(17), C(1)-C(2) 1.5611(16), C(2)-C(4) 1.5158(18), C(2)-C(3) 1.5196(18); Selected bond angles in [^{o}]: C(1)-N(1)-C(14) 118.08(10), N(1)-C(1)-C(12) 131.17(11), N(1)-C(1)-C(2) 120.17(11), C(12)-C(1)-C(2) 108.63(10), O(1)-C(2)-C(4) 108.97(10), O(1)-C(2)-C(3) 112.85(10), C(4)-C(2)-C(3) 111.96(10), O(1)-C(2)-C(1) 110.87(10), C(4)-C(2)-C(1) 102.15(10), C(3)-C(2)-C(1) 109.53(10), C(5)-C(4)-C(2) 131.41(12), C(13)-C(4)-C(2) 109.51(11).

Two septet signals at δ = 2.91 ppm and 2.74 ppm corresponds to the resonance of the CH proton present in the isopropyl groups similarly for compound **1b** two septet peaks obtained at δ = 2.97 and 2.69 ppm can be assigned for the CH proton present in the isopropyl groups. In compound **2a** sharp peaks at δ = 2.12 and 2.00 ppm are due to the resonance of two groups of three methyl protons located at 2,6 position of N-substituted aromatic group similarly for compound **2b** mentioned peaks are obtained at δ = 2.09 and 1.88 ppm. Three methyl protons attached with quaternary carbon for compound **2a** is appear at 1.93 as a sharp singlet. In compound **2b** triplet and quartet peaks at 0.76 and 2.27 ppm respectively can be assigned for three protons of methyl group and two protons of methylene group attached with quaternary carbon. Two sharp singlet peaks at 2.37 and 1.93 ppm in compound **3a** can be assigned for three protons of methyl group at *p*-position of the mesityl group and six protons of two o-position's methyl group of the mesityl group respectively. Three methyl protons attached with quaternary carbon in compound **3a** are appear at 2.08 ppm as a sharp singlet. In compound **3b** two groups of singlet peaks at δ = 2.14 and 1.93 ppm can be assigned for methyl group protons located at 2,6 position of the mesityl group. Sharp triplet peaks at 0.82 ppm described as the three protons of ethyl group attached with methylene carbon in compound **3b**. In compound **3b** methylene group attached with quaternary carbon and methyl group at *p*-position of the mesityl group are merged at 2.35 ppm. In compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** broad peaks at δ = 3.25, 3.12, 3.45, 3.36, 3.51 and 3.35 ppm respectively are obtained for alcohol group proton resonance. The resonance of the protons attached to the acenapthene moiety and the phenyl ring are in the expected regions for all compounds **1a**, **1b**, **2a**, **2b**, **3a** and **3b**. In the $^{13}C\{^1H\}$ NMR spectrum of compound **1a**, **2a**, **3a** and **3b** the imine carbon are deshielded compare to compound **1**, **2**, **3** and appears at δ = 174.6, 175.5, 174.9 and 181.0 ppm, and the phenyl carbon attached to nitrogen atom at δ = 146.3, 147.3, 145.3 and 141.3 ppm are observed respectively. Peaks at δ = 78.8, 82.0, 78.8, 82.2, 78.7 and 82.0 ppm can be assigned for the carbon atom attached with alcohol group for compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** respectively. For compound **1b** and **2b** absent of imine carbon peaks is described by less relaxation period. Peaks for all aromatic carbons in compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** are comparable with compound **1**, **2** and **3**.

Though all Ar-BIAO-ol compounds were forming in racemic mixture still it was crystallising in dichloromethane any of one isomer (*R*-isomer or *S*-isomer). From solid state structure it was observed that compound **1a** and **3a** were having only *R*-isomer as an asymmetric unit in their unit cell, whereas compound **1b** were having only *S*-isomer as an asymmetric unit in its unit cell. Compound **1a** & **1b** both crystallizes in the triclinic space group *P*-1 having two molecules in the unit cell. Compound **3a** also crystallizes in the triclinic space group *P*-1 but having four molecules in the unit cell.

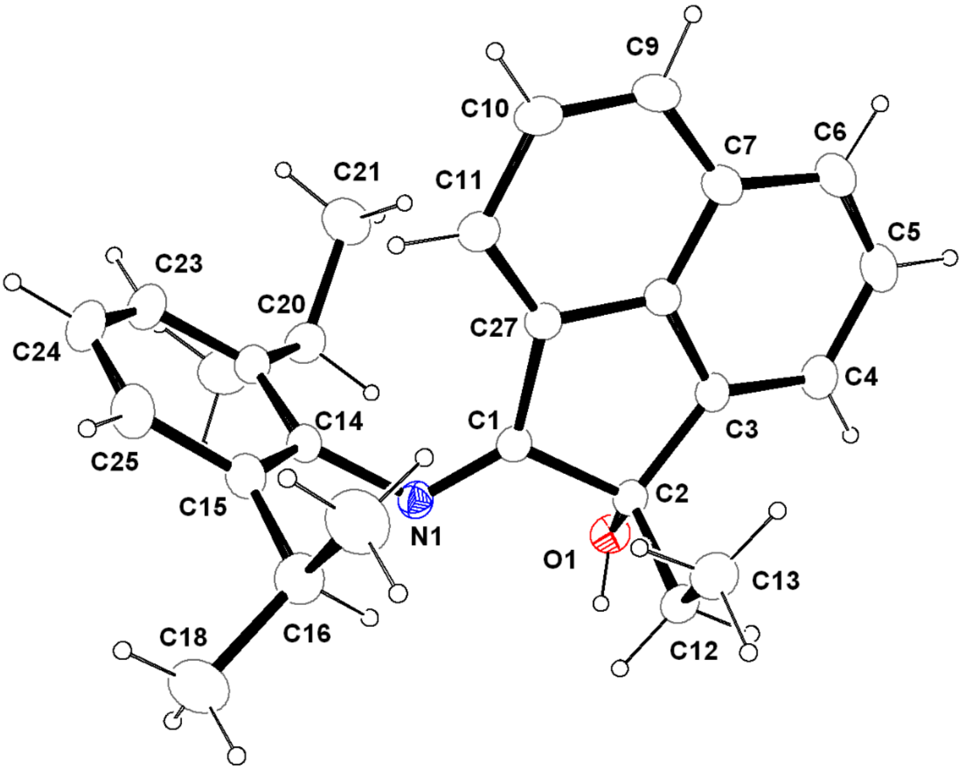


Fig. 3. Solid-state structure of **1b** (*S*-isomer) showing the atom labelling scheme. Selected bond lengths in [Å]: O(1)-C(2) 1.414(2), N(1)-C(1) 1.268(2), N(1)-C(14) 1.432(2), C(1)-C(27) 1.489(2), C(1)-C(2) 1.559(2), C(2)-C(3) 1.511(3), C(2)-C(12) 1.534(2); Selected bond angles in [°]: C(2)-O(1)-H(3) 109.5, C(1)-N(1)-C(14) 119.36(15), N(1)-C(1)-C(27) 131.70(16), N(1)-C(1)-C(2) 119.97(15), C(27)-C(1)-C(2) 108.21(14), O(1)-C(2)-C(3) 110.19(15), O(1)-C(2)-C(12) 110.40(14), C(3)-C(2)-C(12) 112.02(14), O(1)-C(2)-C(1) 111.24(13), C(3)-C(2)-C(1) 101.67(14), C(12)-C(2)-C(1) 111.07(14), C(4)-C(3)-C(8) 119.08(19).

The molecular structures of compound **1a** (*R*-isomer), **1b** (S-isomer) and **3a** (*R*-isomer) are shown in the Fig.2, Fig. 3 and Fig. 4 respectively. In the compound **1a**, the C-O bond length of 1.4257(15) Å is within the range of typical C-O single bond, the C-N bond length of 1.2742(16) Å is also in the range of imines bond length which is comparable with Ar-BIAO (**1**) compound and C1-C2 bond length is 1.5611(16) Å and shows C-C single bond.

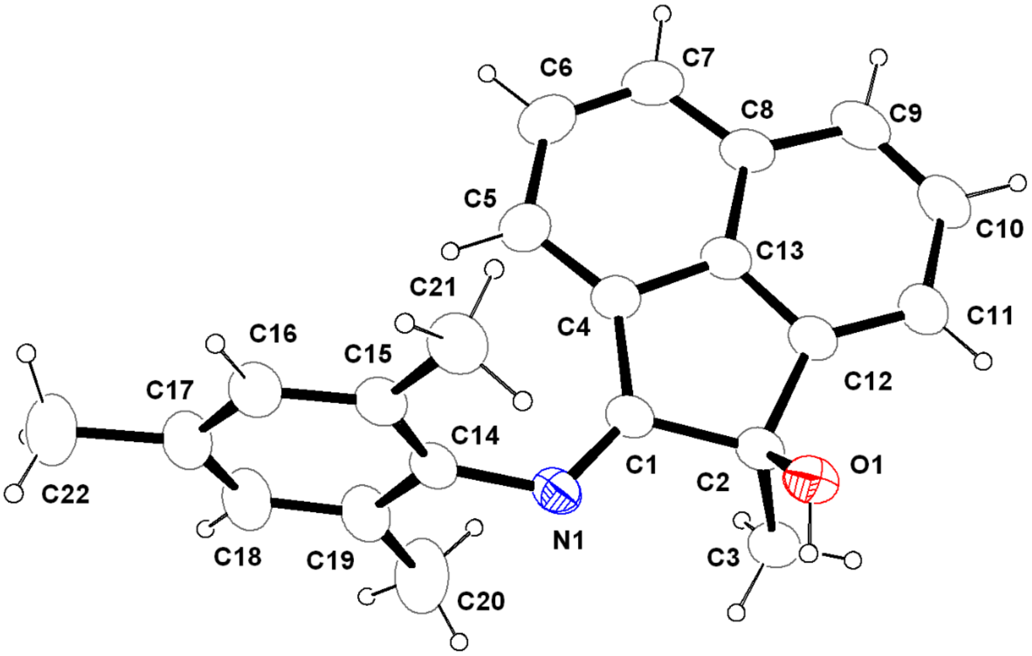


Fig. 4. Solid-state structure of **3a** (*R*-isomer) showing the atom labelling scheme. Selected bond lengths in [Å]: O(1)-C(2) 1.419(2), N(1)-C(1) 1.270(2), N(1)-C(14) 1.427(2), C(13)-C(12) 1.398(3), C(4)-C(1) 1.481(3), C(1)-C(2) 1.547(3), C(12)-C(2) 1.511(3), C(2)-C(3) 1.533(2); Selected bond angles in [^{o}]: C(2)-O(1)-H(1) 109.5, C(1)-N(1)-C(14) 122.31(17), N(1)-C(1)-C(4) 131.86(19), N(1)-C(1)-C(2) 119.52(17), C(4)-C(1)-C(2) 108.62(15), C(11)-C(12)-C(2) 131.55(19), C(13)-C(12)-C(2) 109.00(16), O(1)-C(2)-C(12) 108.96(15), O(1)-C(2)-C(3) 111.73(16), C(12)-C(2)-C(3) 111.97(16), O(1)-C(2)-C(1) 111.32(15), C(12)-C(2)-C(1) 102.48(15), C(3)-C(2)-C(1) 110.03(16).

In the similar compounds (3,5-xylyl-BIAO), (4-Cl-BIAO), and (2,6-xylyl-BIAO) reported by Jones and co-workers, similar N–C bond lengths [1.2763(14), 1.2742(15), and 1.2777(9) Å, respectively] are observed.[20,21] Similarly for the compound **1b** and **3a,** the C-O bond length of 1.414(2) and 1.419(2) Å respectively are also in the range of typical C-O single bond, the C-N bond length of 1.268(2) and 1.270(2) Å respectively are also in the range of imines(C=N) bond length.

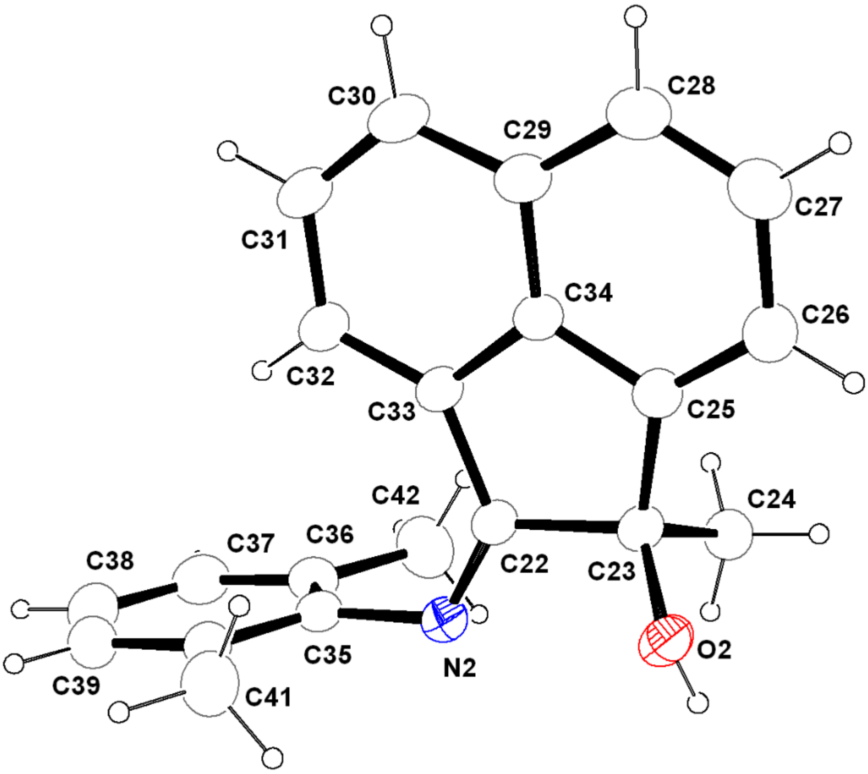


Fig. 5. Solid-state structure of **2a** (*R*-isomer) showing the atom labelling scheme. Selected bond lengths in [Å]: O(2)-C(23) 1.419(2), N(2)-C(22) 1.275(2), N(2)-C(35) 1.431(2), C(23)-C(25) 1.514(2), C(23)-C(24) 1.527(3), C(23)-C(22) 1.550(2); Selected bond angles in [^{o}]: C(23)-O(2)-H(2) 109.5, C(22)-N(2)-C(35) 120.80(15), O(2)-C(23)-C(25) 110.59(15), O(2)-C(23)-C(24) 111.04(14), C(25)-C(23)-C(24) 111.19(16), O(2)-C(23)-C(22) 111.74(14), C(25)-C(23)-C(22) 102.28(14), C(24)-C(23)-C(22) 109.71(15), C(36)-C(35)-N(2) 117.52(17), C(40)-C(35)-N(2) 120.54(18), N(2)-C(22)-C(33) 130.86(16), N(2)-C(22)-C(23) 120.71(15).

Comparably for the compound **2a** the crystallographic structural parameters are entirely different. Compound **2a** crystallizes in the monoclinic space group $P2_{1/c}$ having eight molecules in the unit cell. Solid state structure stated that compound **2a** having both *R*-isomer and *S*-isomer as asymmetric unit in its unit cell. The molecular structure of compound **2a** is shown in Fig. 5 and Fig. 6 respectively for *R*-isomer and *S*-isomer. The structural parameters of Ar-BIAO-ol compounds **1a**, **1b**, **2a** and **3a** are given in Table 1.

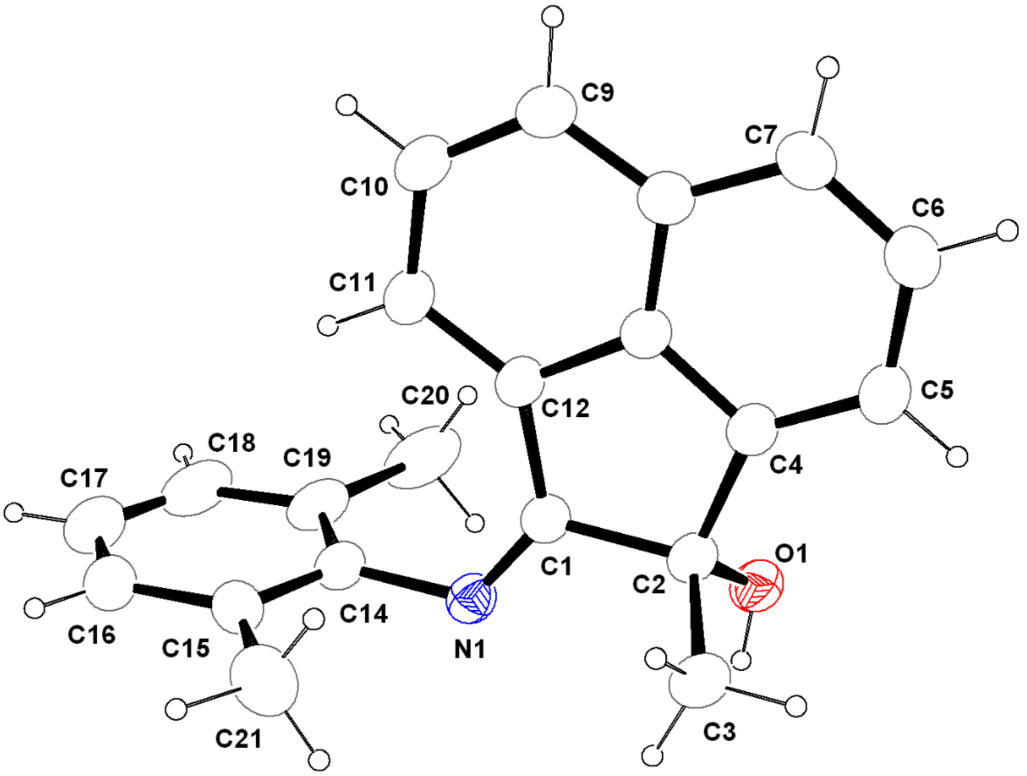


Fig. 6. Solid-state structure of **2a** (*S*-isomer) showing the atom labelling scheme. Selected bond lengths in [Å]: O(1)-C(2) 1.422(2), O(1)-H(1) 0.8200, N(1)-C(1) 1.275(2), N(1)-C(14) 1.431(2), C(13)-C(8) 1.402(3), C(2)-C(4) 1.510(3), C(2)-C(3) 1.521(3), C(2)-C(1) 1.543(3), C(1)-C(12) 1.479(3); Selected bond angles in [^{o}]: C(2)-O(1)-H(1) 109.5, C(1)-N(1)-C(14) 121.11(16), O(1)-C(2)-C(4) 109.96(16), O(1)-C(2)-C(3) 111.30(17), C(4)-C(2)-C(3) 111.71(18), O(1)-C(2)-C(1) 111.36(16), C(4)-C(2)-C(1) 102.71(15), C(3)-C(2)-C(1) 109.51(16), C(5)-C(4)-C(2) 132.41(19), C(13)-C(4)-C(2) 108.88(16).

UV-visible absorption spectra of **1, 2** and **3** (Fig. 7) were measured in dichloromethane at room temperature and displayed a nearly comparable absorption pattern at 230, 303 nm. UV-visible absorption spectra of those Ar-BIAO compounds were attributed to the π→π* transition and n→π* transition respectively. Similarly UV-visible absorption spectra of compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** (Fig. 8) were also measured in dichloromethane at room temperature and displayed a similar kind of absorption pattern at 230 and 273 nm (Table 3). Compare to Ar-BIAO compounds for Ar-BIAO-ol compounds wavelength for n→π* transition are obtained at lower value as expected carbonyl group reduced to alcohol group. Energy gap between non-bonding and π* orbitals are more for Ar-BIAO-ol compounds because of stabilisation of non-bonding orbital. As a result for compound Ar-BIAO-ol wave length of n→π* transition is obtained at lower value than Ar-BIAO compound.

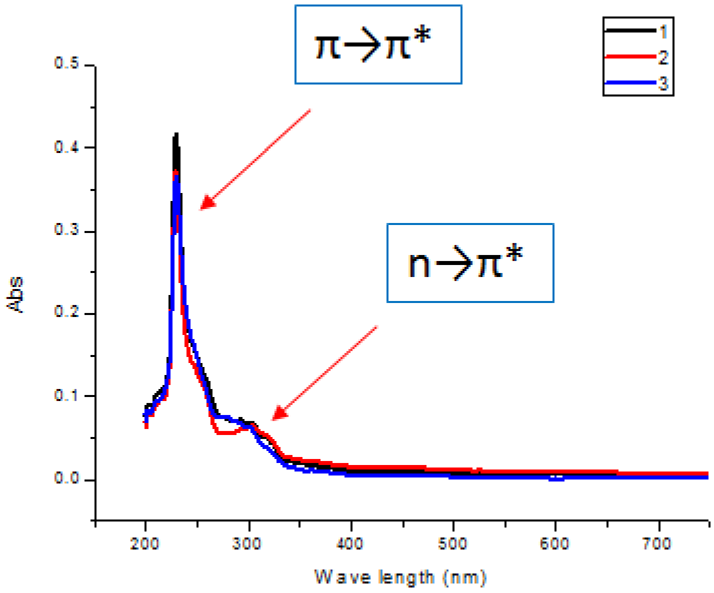


Fig. 7. The UV-vis absorption spectra of compound **1-3** in DCM at RT (3.2068 × 10^{-6} M).

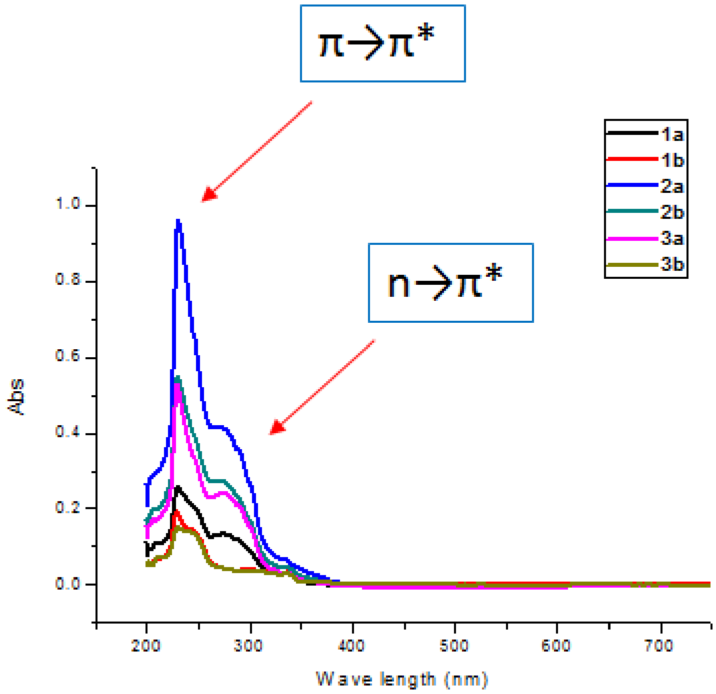
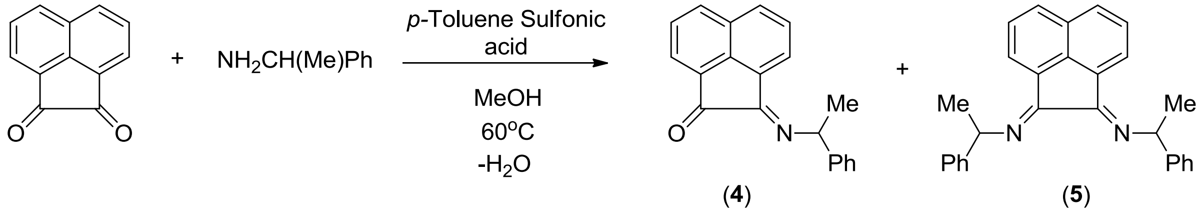


Fig. 8. The UV-vis absorption spectra of compound **1a**, **1b**, **2a**, **2b**, **3a** and **3b** in DCM at RT (3.2068 × 10^{-6} M).

4.3 Synthesis of chiral [*N*-(aryl)imino] acenaphthenone Ar-BIAO ligand:

Previously our group has already reported bulkier rigid bi-dentate ligand Ar-BIAO with different aromatic substitution and we have also synthesized the chiral 1-alkyl-*N*-(arylimino)acenaphthylen-1-ol (Ar-BIAO-ol) ligand where the chirality is on the co-ordination site means in the alcohol attached carbon, so because of lack of planarity it can show different kind of co-ordination, Now, we have synthesized chiral Ar-BIAO ligand (scheme 3) where the chirality is in the remote position not near to co-ordination centre, which is not disturbing the planarity of the molecule. So this chiral Ar-BIAO can have some special features which is increasing its importance in co-ordination chemistry.



Scheme 3. Synthesis of chiral Ar-BIAO ligand (**4**).

To a methanol dissolved solution of acenaphthenequinone, solution of (R)-1-phenylethylamine and catalytic amount *p*-toluene-sulfonic acid in methanol were added and stirred in reflux condition at 60˚C temperature. After 10 h, the solvent was removed by a rotary evaporator and as a major product single condensed compound **4** was obtained some amount of minor double condensed compound **5** (scheme 3). The crude product was purified by column chromatography (hexane and ethyl acetate in 98:2, silica gel) to afford a red solid.

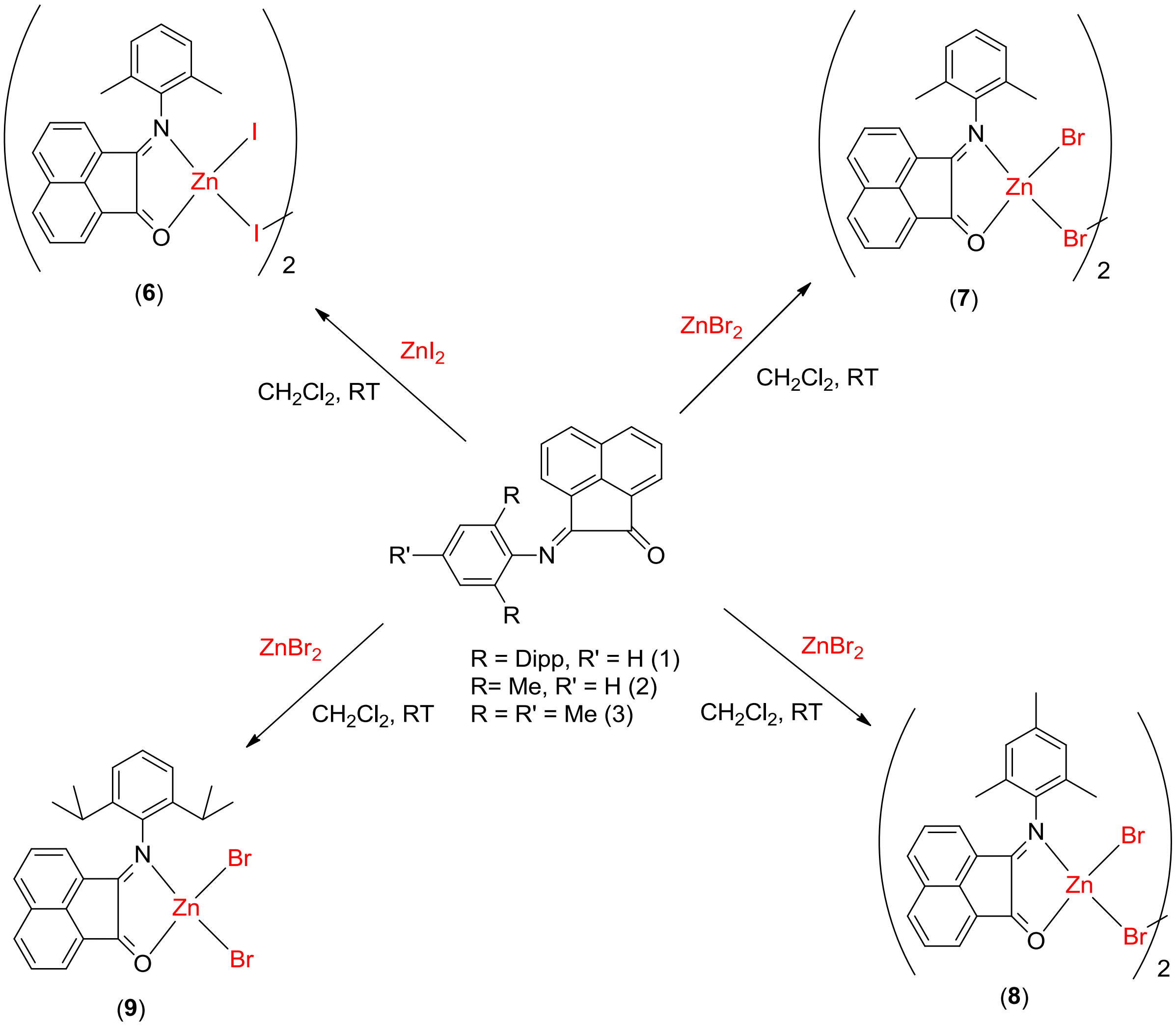
In FT-IR spectra of the compound **4** show strong bands at 1718 cm^{-1} for carbonyl C=O bond stretching and 1660 cm^{-1} can be assigned for C=N bond stretching of the iminoacenapthenone moiety. In ^1H NMR spectrum compound **4** measured in $CDCl_3$, revels one set of doublet protons around 1.92ppm which can be assigned for CH_3 group of the chiral position and doublet observed for benzylic proton, whereas around 6.48 ppm quartet is coming for benzylic proton and splitting is for three protons in methyl group. Others all aromatic peaks are coming in the range of 7.10-8.49 ppm which is indicating the presence of chiral Ar-BIAO compound (**4)**. Compound **4** dissolved in polar solvent like dichloromethane, ethyl acetate and sparingly soluble in non-polar solvent like pet ether.

4.4 Zinc (II) complexes with *N*-(aryl)imino-acenaphthenone (Ar-BIAO) ligands:

Transition metal catalysts modified by *N*-(aryl)imino -acenaphthenone (Ar-BIAO) ligands are one of most successful examples of practical catalysis. Clearly, most of the applied metals (e.g., Pd, Rh, Ru, Ir) displayed difficulties by their low abundance, high price or toxicity. But zinc complexes are less toxic, has high abundance and low price. On the basis of that, research groups are now focussing on different zinc complex for catalytic activity in organic transformations. Stephan Enthaler has already reported the reduction of alkyl and aryl carbonyl by using zinc complex as a catalyst. Besides the reduction of carbonyl, zinc complex also catalysed hydrosilylation reaction and exhibits polymerisation reaction. Complex **6**, **7, 8** and **9** are potentially active for polymerization of ethylene and further catalytic studies are in progress.

Anhydrous zinc (II) iodide was added to a dichloromethane dissolved solution of ligand **2**. The reaction mixture was stirred for overnight at room temperature. Under inert atmosphere the reaction solution was filtered and then washed the yellow crude product with petroleum ether. The compound $[ZnI_2(2,6\text{-dimethylphenyl-BIAO})]_2$ (**6**) was recrystallized from dichloromethane (Scheme 4). Yellowish orange X-ray quality crystals were obtained after 3 days.

In FT-IR spectra of the compound **6** show strong bands at 1687 cm^{-1} for C=O bond stretching, which is slightly deviated from ligand carbonyl C=O bond stretching and 1645 cm^{-1} for C=N bond stretching of the iminoacenapthenone moiety. ^1H NMR spectrum of the compound **6** in $CDCl_3$ shows singlet peak at 2.36 ppm which can be assigned for six methyl protons at *o*-position of the phenyl group this is slightly high field shifted compare to free ligand **2**. The resonances of the protons of acenaphthene back bone and aryl ring are in the expected region in between 6.86-8.51 ppm and in well agreement with the free ligand **2** but all the chemical shift values are shifted to high field region. In $^{13}C\{^1H\}$ NMR spectrum of the compound **6,** carbonyl carbon is mostly de-shielded and appear at $\delta = 189.7$ ppm. The imine carbon is at 161.7 ppm and the phenyl carbon attached to nitrogen atom at 147.1 ppm which is slightly shifted to the high field region because of co-ordination with zinc (II).



Scheme 4. Synthesis of zinc (II) complexes of **6**, **7**, **8** and **9.**

The solid state structure of the complex **6** was established by single crystal X-ray diffraction analysis. The structural parameters of the compound **6** are given in Table 2. The titled compound **6** crystallize in the triclinic space group *P*-1 having only one independent molecule in its asymmetric unit. The molecular structure of complex **6** is shown in Fig. 9. The compound **6** was forming in dichloromethane solvent as a dimer. The zinc (II) complex **6** is an iodo-bridged dimeric complex which contains two iodine bridges joining two asymmetric ligated zinc units. Hence, the complex is centro-symmetric due to presence of an inversion centre in the centre of Zn1-I1^{i}-Zn1^{i}-I1 four membered bridged metallacycle. There are two more metallacycles viz. Zn1-N1-C9-C10-O1 and Zn1^{i}-N1^{i}-C9^{i}-C10^{i}-O1^{i} in each zinc units are ligated through the lone pair of neutral imine nitrogen and the lone pair of neutral carbonyl oxygen atoms.

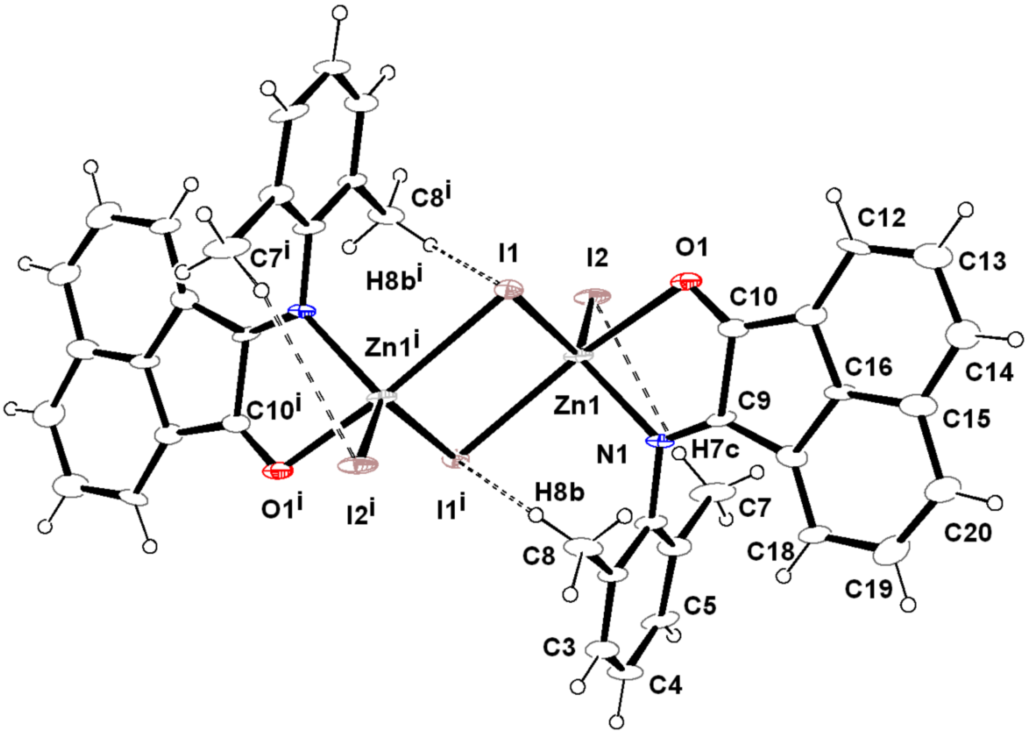


Fig. 9. Solid-state structure of compound **6** showing the atom labelling scheme. Selected bond lengths in [Å]: I(1)-Zn(1) 2.6529(13), I(1)-Zn(1)^{i}1 2.8263(15), I(2)-Zn(1) 2.5377(13), Zn(1)-N(1) 2.104(8), Zn(1)-O(1) 2.392(8), Zn(1)-I(1)^{i}1 2.8263(15), O(1)-C(10) 1.222(14), N(1)-C(9) 1.259(13), N(1)-C(1) 1.452(11), C(9)-C(10) 1.554(13); Selected bond angles in [^{o}]: Zn(1)-I(1)-Zn(1)^{i}1 87.89(4), N(1)-Zn(1)-O(1) 76.0(3), N(1)-Zn(1)-I(2) 118.0(2), O(1)-Zn(1)-I(2) 91.63(19), N(1)-Zn(1)-I(1) 111.4(2), O(1)-Zn(1)-I(1) 80.23(18), I(2)-Zn(1)-I(1) 126.07(5), N(1)-Zn(1)-I(1)^{i}1 95.6(2), O(1)-Zn(1)-I(1)^{i}1 165.42(19), I(2)-Zn(1)-I(1)^{i}1 102.89(5), I(1)-Zn(1)-I(1)^{i}1 92.11(4), C(10)-O(1)-Zn(1) 106.7(6), C(9)-N(1)-C(1) 119.0(8), C(9)-N(1)-Zn(1) 117.2(6), C(1)-N(1)-Zn(1) 123.8(6).

Here the notable change that we see in respect to the general coordination number of zinc (II) is from 4 to 5 [12, 13] as a result of which, the geometry of zinc complex **6** will be best described as a distorted square pyramidal geometry or distorted trigonal pyramidal geometry instead of distorted tetrahedral geometry. In the compound **6** penta co-ordinated zinc (II) centre surrounded by I1, I1^i, N1, O1 and I2. O(1)-Zn(1)-I(1)^{i}1 bond angle is 165.42(19) degree which is closed to 180 degree, is strongly supporting that zinc centre is in distorted trigonal bi-pyramidal geometry where I2 and I1^i are in axial position whereas I1, N1 and O1 are in equatorial position. The Zn(1)-N(1) bond distance is 2.104(8) Å which is comparable with the reported one as 2.106(5) Å and 2.069(4) Å respectively in the complex [ZnCL$_2$(Mes-BIAO)]$_2$ [22, 23] and the complex [EtZn{N(^{t}-Bu)CH$_2$C(NEt)O}]$_2$ [14] . But the Zn(1)-O(1) bond distance is 2.392(8) Å which is bit smaller than the reported one as 2.410(4) Å in the complex [ZnCL$_2$(mes-BIAO)]$_2$ [24] because of the presence of iodine instead of chlorine atom electronic effect also is changing and causing more strong bond of Zn with carbonyl oxygen atom. The three different Zn-Br bond distances are observed viz. I(1)-Zn(1) 2.6529(13) Å, I(1)^i-Zn(1) 2.8263(15) Å, I(2)-Zn(1) 2.5377(13) Å suggesting three different linkages with the zinc(II). One of the Iodine (I1) atom is simultaneously bounded covalently and in bridging mode which is slightly more than the normal I(2)-Zn(1) covalently bonded distance while with the other one i.e. I1^i is still much higher than the normal one as it satisfies purely the fifth coordination of zinc(II). Same kind of situation arises in second zinc (Zn1^i) atom. There is no bonding interaction between two zinc (II) atoms in the complex **6**. The C-O and C-N bond distance are respectively 1.222(14) Å and 1.259(13) Å, which are similar and unperturbed compare to that of the respective ligand. C(9)-C(10) bond distance is 1.554(13) Å, which is telling that the bond is a C-C single bond, so this Ar-BIAO ligand is not behaving like redox active DAB or BIAN ligand. [5-7] The acenaphthene plane and the plan containing N, O and Zn atoms are almost coplanar.

Anhydrous zinc (II) bromide was added to a dichloromethane dissolved solution of ligand **2**, **3** and **1** respectively then the reaction mixture was stirred for overnight at room temperature, under inert atmosphere the reaction solution was filtered and then washed the yellow crude product with petroleum ether, finally compound [ZnBr$_2$(2,6-dimethylphenyl-BIAO)]$_2$ (**7**), [ZnBr$_2$(mes-BIAO)]$_2$ (**8**) and [ZnBr$_2$(dipp-BIAO)] (**9**) were obtained. Complex **7**, **8** and **9** were recrystallized from dichloromethane (Scheme 4). Yellowish orange X-ray quality crystals were obtained after 3 days. In FT-IR spectra of the compound **7**, **8** and **9** show strong bands at 1726, 1729 and 1726 cm^{-1} respectively can be assigned for C=O bond stretching and 1650, 1648 and 1649 cm^{-1} for the C=N bond stretching of the iminoacenapthenone moiety. ^{1}H NMR spectrum of the compound **7** in CDCl$_3$ shows singlet peak at 2.29 ppm which can be assigned for six methyl protons at *o*-position of the phenyl group this is slightly high field shifted compare to free ligand **2**. The resonances of the protons of acenaphthene back bone and aryl ring are in the expected region in between 6.86-8.48 ppm and in well agreement with the free ligand **2** but all the chemical shift values are shifted to high field region. Compound **8** shows two singlet peaks at 2.34 and 2.25 ppm which can be assigned for six methyl protons at *o*-position of the phenyl group this is slightly high field shifted compare to free ligand **3**. Peak at 2.40 ppm is assigned for the three methyl proton of the mesityl group at *p*-position. The resonances of the protons of acenaphthene back bone and aryl ring are in the expected region in between 6.90-8.47 ppm like complex **7** and in well agreement with the free ligand **3** but all the chemical shift values are shifted to high field region compare to ligand **3**. For compound **9**, two doublet peaks at 0.74 and 1.22 ppm in 1:1 ratio which can be assigned as the methyl protons attached to the isopropyl groups on the aromatic ring and this is slightly high field shifted compare to free ligand **1**. The septet at δ = 3.01 ppm which is also slightly down field shifted compare to that of *N*-(2,6-diisopropylphenyl)imino-acenaphthenone (2.8 ppm), ligand **1** corresponds to the resonance of the CH proton present in the isopropyl group. The resonances of the protons of acenaphthene back bone and aryl ring for compound **9** also are in the expected region in between 6.66-8.42 ppm and in well agreement with the free ligand **1** but all the chemical shift values are shifted to high field region compare to ligand **1**. In $^{13}C\{^{1}H\}$ NMR spectrum of the compound **7,** carbonyl carbon is mostly de-shielded and appear at δ = 190.7 ppm. The imine carbon is at 162.7 ppm and the phenyl carbon attached to nitrogen atom at 147.8 ppm which is slightly shifted to the high field region because of co-ordination with zinc (II). Notably all the proton and carbon peaks are comparable with the compound **6**, which already discussed in above and little bit shifting in compound **7** than in compound **6** is because of co-ordination of ligand **2** with $ZnBr_2$ instead of ZnI_2. For the compound **8,** carbonyl carbon is mostly de-shielded and appear at δ = 189.7 ppm and the imine carbon is at 164.3 ppm which is slightly shifted to the high field region because of co-ordination with zinc (II). For compound **9** also carbonyl carbon is mostly de-shielded among all carbon peaks and appear at δ = 189.8 ppm. Like complex **6**, **7** and **8** the imine carbon is at 162.3 ppm. In complex **9** the phenyl carbon attached to nitrogen atom at 146.9 ppm which is slightly shifted to the high field region because of co-ordination with zinc (II).

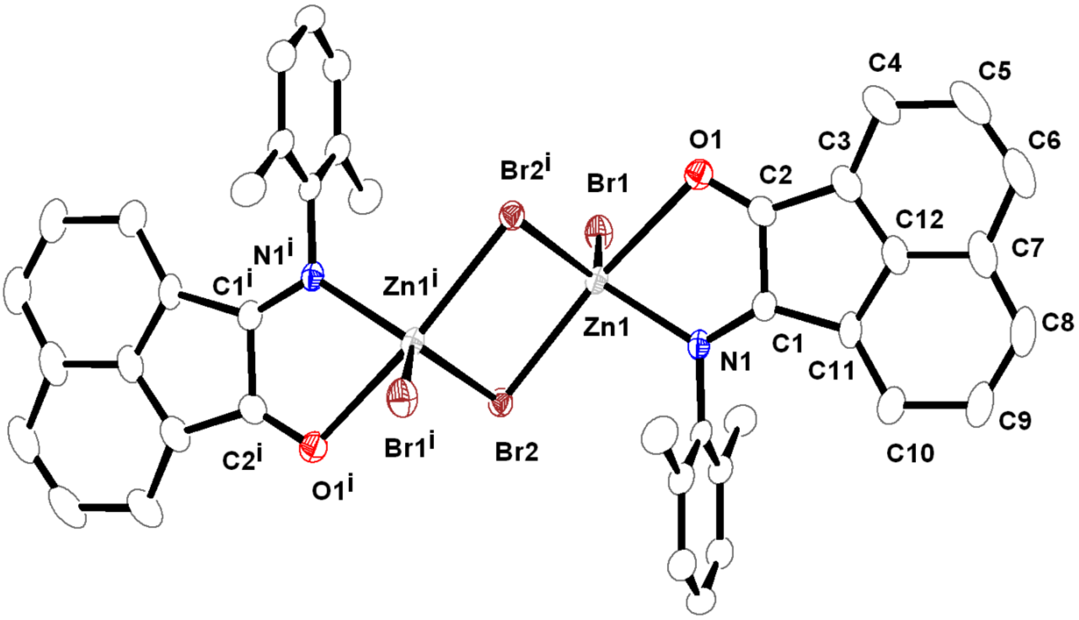


Fig. 10. Solid-state structure of compound **7** showing the atom labelling scheme. Selected bond lengths in [Å]: Br(1)-Zn(1) 2.3266(6), Br(2)-Zn(1)^{i}1 2.4243(6), Br(2)-Zn(1) 2.5980(7), Zn(1)-N(1) 2.073(3), Zn(1)-Br(2)^{i}1 2.4243(6), Zn(1)-O(1) 2.483(3), O(1)-C(2) 1.223(5), N(1)-C(1) 1.274(5), N(1)-C(13) 1.455(5), C(1)-C(11) 1.464(5), C(1)-C(2) 1.536(5); Selected bond angles in [^{o}]: Zn(1)^{i}1-Br(2)-Zn(1) 88.50(2), N(1)-Zn(1)-Br(1) 116.29(9), N(1)-Zn(1)-Br(2)^{i}1 117.64(9), Br(1)-Zn(1)-Br(2)^{i}1 121.54(2), N(1)-Zn(1)-O(1) 74.91(11), Br(1)-Zn(1)-O(1) 89.52(7), Br(2)^{i}1-Zn(1)-O(1) 84.01(7), N(1)-Zn(1)-Br(2) 96.30(9), Br(1)-Zn(1)-Br(2) 103.50(2), Br(2)^{i}1-Zn(1)-Br(2) 91.50(2), O(1)-Zn(1)-Br(2) 166.65(7), C(2)-O(1)-Zn(1) 105.8(3), C(1)-N(1)-C(13) 118.8(3), C(1)-N(1)-Zn(1) 118.6(3), C(13)-N(1)-Zn(1) 122.4(2) N(1)-C(1)-C(11) 134.2(4), N(1)-C(1)-C(2) 119.0(3), C(11)-C(1)-C(2) 106.9(3), O(1)-C(2)-C(3) 132.7(4), O(1)-C(2)-C(1) 121.4(4).

The solid state structure of the complex **7** and **8** were established by single crystal X-ray diffraction analysis. The structural parameters of the compound **7** and **8** are given in Table 2. The titled compound **7** and **8** both crystallize in the triclinic space group *P-1* having only one independent molecule in its asymmetric unit. The molecular structure of complex **7** and **8** are shown in Fig. 10 and Fig. 11 respectively. The compound **7** and **8** both are dimer. Both the zinc (II) complexes **7** and **8** are bromo-bridged μ$_2$-dimeric complex which contains two bromine atoms bridges joining two asymmetric ligated zinc units. The complex **7** is centro-symmetric due to presence of an inversion centre in the centre of Zn1-Br2^{i}-Zn1^{i}-Br2 four membered bridged metallacycle. There are two more metallacycles viz. Zn1-N1-C1-C2-O1 and Zn1^{i}-N1^{i}-C1^{i}-C2^{i}-O1^{i} in each zinc units are ligated through the lone pair of neutral imine nitrogen and the lone pair of neutral carbonyl oxygen atoms.

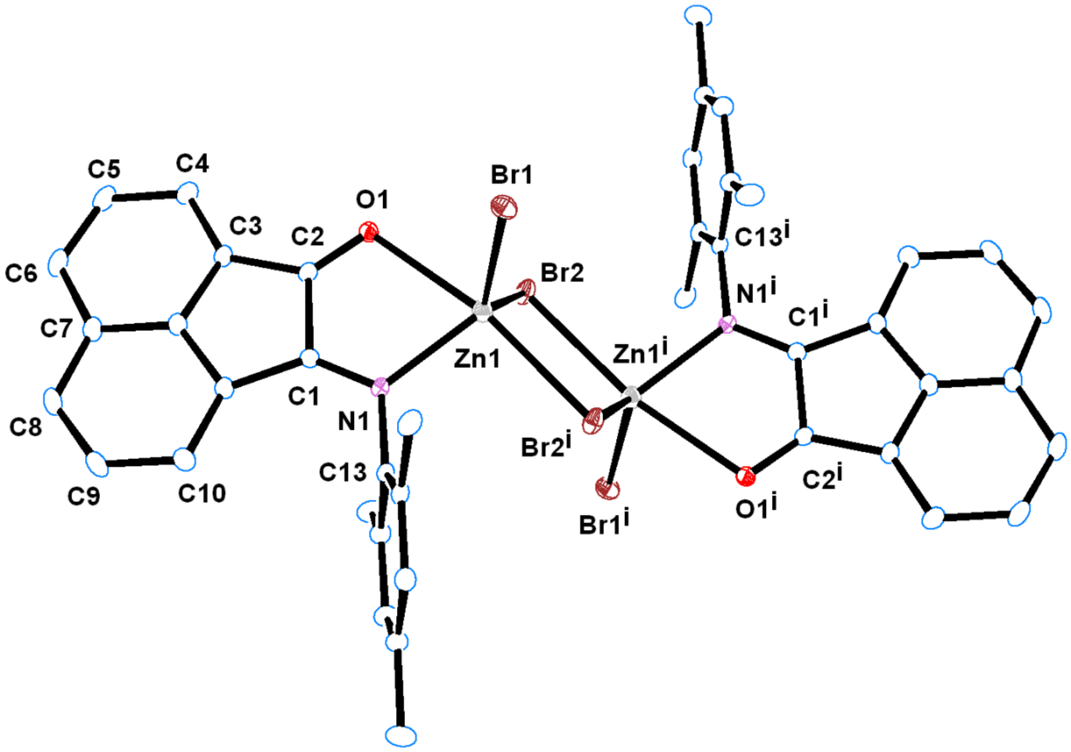


Fig. 11. Solid-state structure of **8** showing the atom labelling scheme. Selected bond lengths in [Å]: Br(2)-Zn(1) 2.4512(7), Br(2)-Zn(1)^{i}1 2.5639(7), Br(1)-Zn(1) 2.3435(7), Zn(1)-N(1) 2.104(4), Zn(1)-O(1) 2.414(3), Zn(1)-Br(2)^{i}1 2.5639(7), O(1)-C(2) 1.212(6), N(1)-C(1) 1.286(6), N(1)-C(13) 1.442(5), C(1)-C(11) 1.466(6), C(1)-C(2) 1.535(6), C(2)-C(3) 1.466(6); Selected bond angles in [^{o}]: Zn(1)-Br(2)-Zn(1)^{i}1 89.08(2), N(1)-Zn(1)-Br(1) 114.62(10), N(1)-Zn(1)-O(1) 75.58(12), Br(1)-Zn(1)-O(1) 87.64(8), N(1)-Zn(1)-Br(2) 117.29(10), Br(1)-Zn(1)-Br(2) 122.18(3), O(1)-Zn(1)-Br(2) 82.14(8), N(1)-Zn(1)-Br(2)^{i}1 96.74(10), Br(1)-Zn(1)-Br(2)^{i}1 106.71(3), O(1)-Zn(1)-Br(2)^{i}1 165.60(8), Br(2)-Zn(1)-Br(2)^{i}1 90.92(2), C(2)-O(1)-Zn(1) 107.3(3), C(1)-N(1)-C(13) 118.9(4), C(1)-N(1)-Zn(1) 117.3(3), C(13)-N(1)-Zn(1) 123.7(3), N(1)-C(1)-C(2) 117.6(4), O(1)-C(2)-C(3) 131.4(4), O(1)-C(2)-C(1) 122.1(4), C(3)-C(2)-C(1) 106.5(4).

Similarly complex **8** also is centro-symmetric due to presence of an inversion centre in the centre of Zn1-Br2^{i}-Zn1^{i}-Br2 four membered bridged metallacycle. There are two more metallacycles viz. Zn1-N1-C1-C2-O1 and Zn1^{i}-N1^{i}-C1^{i}-C2^{i}-O1^{i} in each zinc units are ligated through the lone pair of neutral imine nitrogen and the lone pair of neutral carbonyl oxygen atoms.

Here the notable change that we see in respect to the general coordination number of zinc (II) is from 4 to 5 [12, 13] as a result of which, the geometry of zinc complex **7** and **8** will be best described as a distorted square pyramidal geometry or distorted trigonal pyramidal geometry instead of distorted tetrahedral geometry. In the compound **7** and **8** penta co-ordinated zinc (II) centre surrounded by Br2, Br2^{i}, N1, O1, Br1 and Br2, Br2^{i}, N1, O1, Br1 respectively. In compound **7** O(1)-Zn(1)-Br(2) bond angle is 166.65(7)° which is closed to 180°, is strongly supporting that zinc centre is in distorted trigonal bi-pyramidal geometry where Br2 and O1 are in axial position whereas Br1, N1 and Br2^{i} are in equatorial position. Similarly in the compound **8** O(1)-Zn(1)-Br(2)^{i} bond angle is 165.60(8)° which is also closed to 180°, is also supporting that zinc centre is in distorted trigonal bi-pyramidal geometry where Br2 and O1 are in axial position whereas Br1, N1 and Br2^{i} are in equatorial position. In compound **7** and **8** the Zn(1)-N(1) bond distances are 2.073(3) and 2.104(4)Å which are comparable with the reported one as 2.106(5)Å and 2.069(4)Å respectively in the complex [ZnCL$_2$(Mes-BIAO)]$_2$ [22, 23] and the complex [EtZn{N(^{t}-Bu)CH$_2$C(NEt)O}]$_2$, [14] similar with the Zn(1)-O(1) bond distance in the compound **7** and **8** are 2.483(3) Å and 2.414(3) Å respectively, which are comparable with the reported one as 2.410(4) Å in the complex [ZnCL$_2$(Mes-BIAO)]$_2$ [24] but slightly higher than the reported one as 2.123(4) Å in complex (EtZn[N(^{t}-Bu)CH$_2$C(NEt)O])$_2$. In compound **7** three different Zn-Br bond distances are observed viz. Br(1)-Zn(1) 2.3266(6) Å, Br(2)-Zn(1) 2.5980(7) Å, Zn(1)-Br(2)^{i}1 2.4243(6) Å suggesting three different linkages with the zinc(II). One of the bromine (Br2^{i}) atom is simultaneously bounded covalently and in bridging mode which is slightly more than the normal Br1-Zn1 covalently bonded distance while with the other one i.e. Br2 is still much higher than the normal one as it satisfies purely the fifth coordination of zinc (II). Similarly in compound **8** also three different Zn-Br bond distances are observed viz. Br(2)-Zn(1) 2.4512(7)Å, Br(1)-Zn(1) 2.3435(7) Å, Zn(1)-Br(2)^{i}1 2.5639(7) Å suggesting three different linkages with the zinc(II). One of the Bromine (Br2) atom is simultaneously bounded covalently and in bridging mode which is slightly more than the normal Br1-Zn1 covalently bonded distance while with the other one i.e. Br2^{i} is still much higher than the normal one as it satisfies purely the fifth coordination of zinc (II)

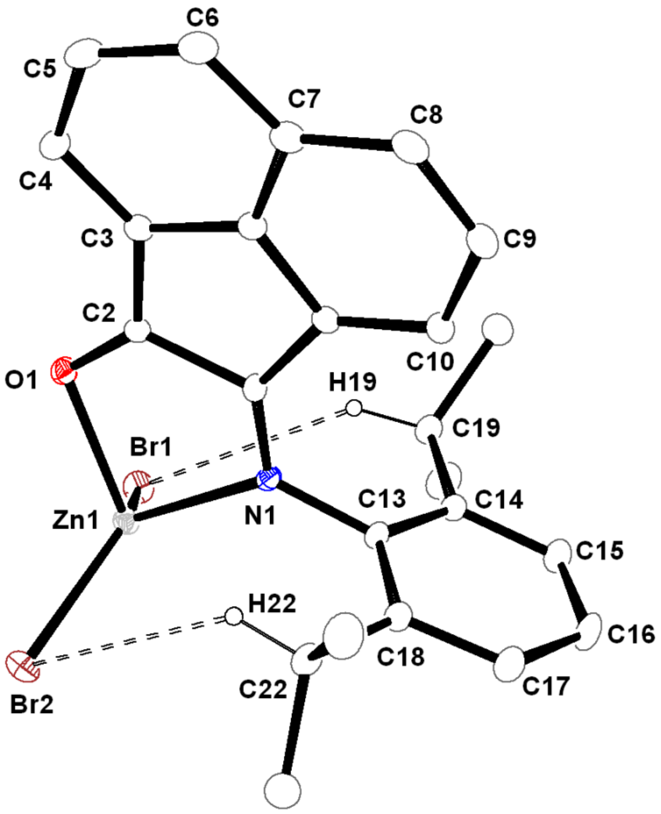


Fig. 22. Solid-state structure of compound **9** showing the atom labelling scheme. Selected bond lengths in [Å]: Zn(1)-N(1) 2.086(2), Zn(1)-O(1) 2.162(2), Zn(1)-Br(1) 2.3181(6), Zn(1)-Br(2) 2.3280(6), O(1)-C(2) 1.227(4), N(1)-C(1) 1.278(4), N(1)-C(13) 1.460(4), C(1)-C(11) 1.460(4), C(1)-C(2) 1.539(4), C(2)-C(3) 1.463(4); Selected bond angles in [^{o}]: N(1)-Zn(1)-O(1) 81.03(9), N(1)-Zn(1)-Br(1) 114.77(7), O(1)-Zn(1)-Br(1) 107.52(6), N(1)-Zn(1)-Br(2) 113.13(7), O(1)-Zn(1)-Br(2) 104.90(6), Br(1)-Zn(1)-Br(2) 125.08(2), C(2)-O(1)-Zn(1) 109.00(19), C(1)-N(1)-C(13) 118.1(3), C(1)-N(1)-Zn(1) 111.5(2), C(13)-N(1)-Zn(1) 130.30(19), N(1)-C(1)-C(11) 135.3(3), N(1)-C(1)-C(2) 117.4(3), O(1)-C(2)-C(3) 132.4(3), O(1)-C(2)-C(1) 121.0(3), C(3)-C(2)-C(1) 106.5(3).

Same kind of situation arises in second zinc (Zn1^i) atom for both compound **7** and **8**. There is no bonding interaction between two zinc (II) atoms in the complex **7** and **8**. The C=O bond distance in compound **7** and **8** are 1.223(5) Å and 1.212(6) Å respectively and the C=N bond distances are 1.274(5) and 1.286(6) Å respectively, which are similar and unperturbed compare to that of the respective ligand. C(1)-C(2) bond distance are 1.536(5) Å and 1.535(6) Å for compound **7** and **8**, which indicates that the bond is a C-C single bond. The acenaphthene plane and the plan containing N, O and Zn atoms are almost coplanar for both complexes **7** and **8**.

The solid state structure of the complex **9** was established by single crystal X-ray diffraction analysis. The structural parameters of the compound **9** are given in Table 2. The titled compound **9** crystallize in the monoclinic space group $P2_{1/c}$ having eight molecules in its asymmetric unit. The molecular structure of complex **9** is shown in Fig. 22. The compound **9** was forming in dichloromethane solvent as a monomer.

General coordination number of zinc (II) is from 4 to 5 [12, 13] as a result of which, the geometry of zinc complex **9** will be best described as a distorted tetrahedral geometry instead of distorted square pyramidal or trigonal bi-pyramidal geometry. In the compound **9** tetra co-ordinated zinc (II) centre surrounded by Br2, N1, O1 and Br1. The bond angle of N(1)-Zn(1)-O(1) is 81.03(9), which is unlike with tetrahedral geometry and this deviation of bond angle is because of N- and O- donor sites are rigidly bind with acenaphthene moiety. The Zn(1)-N(1) bond distance is 2.086(2) Å which is comparable with the reported one as 2.106(5) Å and 2.069(4) Å respectively in the complex $[ZnCL_2(mes\text{-}BIAO)]_2$ [22, 23] and the complex $[EtZn\{N(^t\text{-}Bu)CH_2C(NEt)O\}]_2$, [14] the Zn(1)-O(1) bond distance is 2.162(2) Å which is comparable with the reported one as 2.123(4) Å in the complex $[EtZn\{N(^t\text{-}Bu)CH_2C(NEt)O\}]_2$ [24] but slightly lower than the reported one as 2.410(4) Å in complex $[ZnCl_2(mes\text{-}BIAO)]_2$ because of monomer form. The C-O and C-N bond distance are respectively 1.227(4) Å and 1.278(4) Å, which are similar and unperturbed compare to that of the respective ligand. C(1)-C(2) bond distance is 1.539(4) Å, which is telling that the bond is a C-C single bond. The acenaphthene plane and the plan containing N, O and Zn atoms are almost coplanar.

5. Conclusion

In conclusion, we successfully reproduced the ligand *N*-(2,6-diisopropylphenyl)imino-acenaphthenone (**1**), *N*-(2,6-dimethylphenyl)imino-acenaphthenone (**2**) and *N*-(2,4,6-trimethylphenyl)imino-acenaphthenone (**3**) by the reported procedures. Using these ligands **1**, **2** and **3**, we successfully synthesized the all six Ar-BIAO-ol ligands i.e. **1a, 1b, 2a, 2b, 3a** and **3b**. As already we have discussed our main aim is to develop sterically hindered rigid bi-dentate ligand and study of complex with transition metals with this type of ligand, so parallel with all that six Ar-BIAO-ol ligands here we have also synthesized one example of chiral Ar-BIAO ligand *N*-(1-phenylethylamine)imino-acenaphthenone (**4**), where the chirality located at *N*-substituent and characterized by spectroscopic technique like FT-IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. As in here the chirality is outside of the co-ordination sphere, the chiral ligand **4** can show different type of co-ordination with various transition metals.

In addition, we have successfully synthesized the dimeric penta coordinated zinc complexes (**6**), (**7**) and (**8**) viz. [ZnI_2(2,6-dimethylphenyl-BIAO)]$_2$, [$ZnBr_2$(2,6-dimethylphenyl-BIAO)]$_2$ and [$ZnBr_2$(Mes-BIAO)]$_2$ respectively from the ligand **2** and **3** and the monomeric tetra coordinated zinc complex (**9**) viz. [$ZnBr_2$(Dipp-BIAO)] from ligand **1** and which were characterized by FT-IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and the solid state structure was determined by X-ray diffraction analyses. These complexes are potentially active for ring opening polymerization of ε-caprolactone in near future.

6. Experimental section

General:

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out in an argon atmosphere using the standard Schlenk technique or argon-filled glove box. Dichloromethane, diethylether and petroleum ether were dried with P_2O_5 followed by distillation and kept under molecular sieves prior to use. ^{1}H NMR (400 MHz) and ^{13}C{H} NMR (100 MHz) spectra were recorded with a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. HRMS was measured with an Agilent Technology Q-TOF instrument. Elemental analyses were performed with a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. $ZnBr_2$ and ZnI_2 were purchased from Sigma Aldrich and used as such.

1) Preparation of compounds ***1a, 2a*** *and* ***3a****:*

An ether solution of methyl magnesium iodide was prepared from Mg turnings, catalytic amount of I_2 and methyl iodide in 10 mL of dry ether as per standard procedures. After formation of Grignard reagent, an ether solution of ligand **1**, **2** and **3** was added drop wise via a syringe at ambient temperature to get compound **1a**, **2a** and **3a** respectively. Violet colour reaction mixture was stirred for 3h at ambient temperature. Reaction mixture was quenched by saturated NH_4Cl solution and extracted with ether (3x10 mL). Combined organic layers were dried over Na_2SO_4 solvent was removed by a rotary evaporator. For all the compound **1a**, **2a** and **3a** the white crude product was crystallized from dichloromethane. **1a:** Yield: 165 mg, 79%. M.P. 126°C. FT-IR (selected frequency): ν = 3306 (broad peak, O-H), 2961, 2925, 2867, 1660 (C=N), 1597, 1433, 1193, 1012, 781,729 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81(d, 1H, ArH), 7.75 (d, 1H, ArH), 7.66 (d, 1H, ArH), 7.60 (t, 1H, ArH), 7.25 (t, 1H, ArH), 7.18 (m, 3H, ArH), 6.45 (d, 1H, ArH), 3.25 (broad s, 1H, OH), 2.91 (sept, 1H, $CH(CH_3)_2$), 2.74 (sept, 1H, $CH(CH_3)_2$), 1.86 (s, 3H, CH_3), 1.18 (d, 3H, $CH(CH_3)_2$), 1.08 (d, 3H, $CH(CH_3)_2$), 0.95 (d, 3H, $CH(CH_3)_2$), 0.75 (d, 3H, $CH(CH_3)_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 174.6 (C=N), 146.3, 142.9, 138.7, 136.5, 135.9, 131.1, 129.6, 129.1, 128.6, 128.1, 125.1, 124.3, 123.78, 123.72, 123.4, 119.7, 78.8 (C-OH), 28.4, 28.0, 27.6, 23.48, 23.45, 23.1 ppm; HRMS (+APCI) m/z calculated for $C_{25}H_{27}NO$ $(M+H)^+$: 358.2165; found: 358.2170.

2a: Yield: 150 mg, 71%. M.P. 128°C. FT-IR (selected frequency): ν = 3344 (broad peak, O-H), 2966, 2919, 2852, 1661 (C=N), 1592, 1434, 1196, 1010, 779, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, 1H, ArH), 7.82 (d, 1H, ArH), 7.69 (m, 2H, ArH), 7.34 (t, 1H, ArH), 7.11 (m, 3H, ArH), 6.58 (d, 1H, ArH), 3.45 (broad s, 1H, OH), 2.12 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.93 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 175.5 (C=N), 147.3, 142.8, 138.5, 131.0, 129.5, 129.3, 128.6, 128.3, 126.2, 125.8, 125.0, 124.0, 123.0, 119.7, 78.8 (C-OH), 27.59 (CH_3), 17.6 (CH_3), 17.5 (CH_3) ppm. HRMS (+APCI) m/z calculated for $C_{21}H_{19}NO$ $(M+H)^+$: 302.1539; found: 302.1544.

3a: Yield: 260 mg, 82%. M.P. 129°C. FT-IR (selected frequency): ν = 3246 (broad peak, O-H), 2961, 2922, 2853, 1660 (C=N), 1598, 1431, 1194, 1013, 781, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, 1H, ArH), 7.82 (d, 1H, ArH), 7.68 (m, 2H, ArH), 7.35 (t, 1H, ArH), 6.95 (d, 2H, ArH), 6.65 (d, 1H, ArH), 3.51 (broad s, 1H, OH), 2.37 (s, 3H, p-CH_3), 2.08 (s, 3H, CH_3), 1.93 (d, 6H, *o*-CH_3 and *p*-CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 174.9 (C=N), 145.3, 143.0, 138.4, 133.0, 131.0, 129.6, 129.2, 129.1, 129.0, 128.5, 128.3, 125.7, 125.2, 124.9, 122.9, 119.6, 78.7 (C-OH), 27.6, 22.3, 20.9, 17.5. HRMS (+APCI) m/z calculated for $C_{22}H_{21}NO$ $(M+H)^+$: 316.1696; found: 316.1700.

*2) Preparation of compound **1b, 2b** and **3b**:*

An ether solution of ethyl magnesium bromide was prepared from Mg turnings, catalytic amount of I_2 and ethyl bromide in 10 mL of dry ether as per standard procedures. After formation of Grignard reagent, an ether solution of ligand **1**, **2** and **3** was added drop wise via a syringe at ambient temperature to get compound **1b**, **2b** and **3b** respectively. Violet colour reaction mixture was stirred for 3h at ambient temperature. Reaction mixture was quenched by saturated NH_4Cl solution and extracted with ether (3x10 mL). Combined organic layers were dried over Na_2SO_4 solvent was removed by a rotary evaporator. For all the compound **1b**, **2b** and **3b** the white crude product was crystallized from dichloromethane.

1b: Yield: 162mg, 74%. M.P. 122°C. FT-IR (selected frequency): ν = 3309 (broad peak, O-H), 2962, 2927, 2868, 1658 (C=N), 1560, 1434, 1187, 1011, 783, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, 2H, ArH), 7.61 (m, 2H, ArH), 7.18 (m, 4H, ArH), 6.44 (d, 1H, ArH), 3.12 (broad s, 1H, OH), 2.97 (sept, 1H, $CH(CH_3)_2$), 2.69 (sept, 1H, $CH(CH_3)_2$), 2.24 (m, 2H, CH_2CH_3), 1.19 (d, 3H, $CH(CH_3)_2$), 1.05 (d, 3H, $CH(CH_3)_2$), 0.99 (d, 3H, $CH(CH_3)_2$), 0.80 (t, 3H, CH_2CH_3), 0.78 (d, 3H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$,100 MHz): δ = 141.0, 139.5, 131.0, 128.4, 127.8, 125.0, 123.7, 123.3, 123.2, 120.2, 82.0 (C-OH), 33.93

($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 27.8 (CH_2CH_3), 23.7 ($CH(CH_3)_2$), 23.3 ($CH(CH_3)_2$), 23.1 ($CH(CH_3)_2$), 22.85 ($CH(CH_3)_2$), 8.3 (CH_2CH_3) ppm. HRMS (+APCI) m/z calculated for $C_{26}H_{29}NO$ $(M+H)^+$: 372.2322; found: 372.2328.

2b: Yield: 174 mg, 79%. M. P. 121°C. FT-IR (selected frequency): ν = 3307 (broad peak, O-H), 2966, 2917, 2878, 1659 (C=N), 1592, 1434, 1187, 1011, 782, 765 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, 1H, ArH), 7.75 (d, 1H, ArH), 7.61 (t, 2H, ArH), 7.26 (t, 1H, ArH), 7.04 (m, 3H, ArH), 6.52 (d, 1H, ArH), 3.36 (broad s, 1H, OH), 2.27 (q, 2H, CH_2CH_3), 2.09 (s, 3H, o-CH_3), 1.88 (s, 3H, o-CH_3), 0.76 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$,100 MHz): δ = 141.1, 139.5, 131.0, 130.2, 129.7, 128.8, 128.7, 128.4, 126.5, 125.9, 125.2, 124.2, 122.8, 120.4, 82.2(C-OH), 34.1 (CH_2CH_3), 18.1 (CH_3), 17.7 (CH_3), 8.6 (CH_2CH_3) ppm. HRMS (+APCI) m/z calculated for $C_{22}H_{21}NO$ $(M+H)^+$: 316.1696; found: 316.1701.

3b: Yield: 235 mg, 71%. M.P. 122°C. FT-IR (selected frequency): ν = 3308 (broad peak, O-H), 2966, 2916, 2855, 1660 (C=N), 1601, 1434, 1187, 1010, 782, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, 2H, ArH), 7.68 (s, 2H, ArH), 7.35 (t, 1H, ArH), 6.95 (d, 2H, ArH), 6.65 (d, 1H, ArH), 3.35 (broad s, 1H, OH), 2.35 (s, 5H, p-CH_3 & CH_2CH_3), 2.14 (s, 3H, o-CH_3), 1.91 (s, 3H, o-CH_3), 0.82 (t, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 181.0 (C=N), 141.1, 139.5, 131.1, 129.3, 129.0, 128.5, 128.2, 125.0, 122.7, 120.2, 82.0 (C-OH), 34.0 (CH_2CH_3), 20.9 (Ar-CH_3), 17.9 (Ar-CH_3), 17.5 (Ar-CH_3), 8.5 (CH_2CH_3) ppm. HRMS (+APCI) m/z calculated for $C_{23}H_{23}NO$ $(M+H)^+$: 330.1852; found: 330.1860.

3) Synthesis of N-(1-phenylethylamine)imino-acenaphthenone (4):

Acenaphthenequinone (500 mg, 2.74 mmol) was taken in a round bottom flask at 60°C in methanol (60 mL). (*R*)-1-phenylethylamine (332 mg, 2.74 mmol) and catalytic amount *p*-toluene-sulfonic acid (50mg) in methanol (100 mL) were added drop-wise to the acenaphthene-quinone solution for 2 h. After 10 h stirring, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (hexane, silica gel) to afford a red solid. Yield: 71%. FT-IR (selected frequency): ν = 3059, 2968, 2926, 1718 (C=O), 1660 (C=N), 1586, 1451, 1340, 1240, 780, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (dd, 2H, ArH), 8.09 (t, 2H, ArH), 7.64 (t, 2H, ArH), 7.43 (m, 2H, ArH), 7.24 (m, 2H, ArH), 7.15 (m, 1H, ArH), 6.48 (q, 1H, $HC(CH_3)Ph$), 1.92 (d, 3H, CH_3) ppm.

4) Synthesis of [ZnI_2(2,6-dimethylphenyl-BIAO)]$_2$ (6):

In a dry degassed Schlenk tube, ligand **2** (200 mg, 0.70mmol) was taken and about 10 mL of CH_2Cl_2 was added and to this mixture anhydrous ZnI_2 (225mg, 0.70mmol) was added under inert atmosphere. The reaction mixture was stirred for another 12 h, the reaction mixture was filtered using cannula filtration. Deep reddish-orange filtrate was evaporated under *vacuo* to result a concentrated clear solution which was subjected for re-crystallisation at -40^0C. Single crystals of light orange colour were obtained after recrystallization from dichloromethane. Yield: 84%. FT-IR (selected frequency): ν = 3053, 2918, 2850, 1687 (C=O), 1645 (C=N), 1584, 1420, 1288, 1221, 833, 775 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (q, 2H, ArH), 8.28 (d, 1H, ArH), 8.05 (t, 1H, ArH), 7.65 (t, 1H, ArH), 7.29 (m, 3H, ArH), 6.87 (d, 1H, ArH), 2.36 (s, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 189.77 (C=O), 161.75 (C=N), 147.1, 140.9, 135.0, 132.1, 130.0, 128.8, 128.4, 127.4, 127.3, 127.0, 126.8, 126.5, 126.3, 125.4, 124.6, 122.6, 19.7 ppm. Dimeric penta-coordinated complex was characterized by single crystal X-ray diffraction analysis.

*5) Synthesis of [$ZnBr_2$(2,6-dimethylphenyl-BIAO)]$_2$ (***7***):*

In a dry degassed Schlenk tube, ligand **2** (200 mg, 0.70mmol) was taken and about 10 ml of CH_2Cl_2 was added and to this mixture anhydrous $ZnBr_2$ (158.0mg, 0.70mmol) was added under inert atmosphere. The reaction mixture was stirred for 12 h, and the reaction mixture was filtered using cannula filtration. Deep reddish-orange filtrate was evaporated under *vacuo* to result a concentrated clear solution which was subjected to crystallization at -40^0C. Single crystals of light orange colour were obtained after recrystallization from dichloromethane. Dimeric tetra-coordinated complex was characterized by X-ray crystallography. Yield: 76%. FT-IR (selected frequency): ν = 3065, 2919, 2851, 1726 (C=O), 1650 (C=N), 1587, 1434, 1280, 1221, 777, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.47 (t, 2H, ArH), 8.27 (d, 1H, Ar-H), 8.05 (dd, 1H, ArH), 7.65 (dd, 1H, ArH), 7.30 (m, 3H, ArH), 6.86 (d, 1H, ArH), 2.29 (s, 6H, Ar-Me) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 190.71 (C=O), 162.79 (C=N), 147.8, 142.2, 135.8, 133.0, 132.6, 130.9, 129.7, 129.5, 129.3, 128.4, 128.1, 128.0, 127.8, 127.5, 127.0, 126.6, 125.6, 123.7, 18.9 ppm.

6) Synthesis of [$ZnBr_2$(Mes-BIAO)]$_2$ (8):

In a dry degassed Schlenk tube, ligand **3** (200 mg, 0.67mmol) was taken and about 10 ml of CH_2Cl_2 was added and to this mixture anhydrous $ZnBr_2$ (150mg, 0.67mmol) was added under inert atmosphere. The reaction mixture was stirred for 12 h, and the reaction mixture was filtered using cannula filtration. Deep reddish-orange filtrate was evaporated under vacuo to result a concentrated clear solution which was subjected to crystallisation at -40^{0}C. Single crystals of light orange colour were obtained after recrystallization from dichloromethane. Yield: 80%. FT-IR (selected frequency): ν = 2920, 2851, 1729 (C=O), 1648 (C=N), 1587, 1435, 1290, 1224, 779, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (q, 2H, ArH), 8.28 (d, 1H, ArH), 8.16 (d, 2H, ArH), 8.03 (q, 1H, ArH), 7.66 (q, 1H, ArH), 7.60 (q, 1H, ArH), 7.06 (s, 5H, ArH), 6.96 (d, 1H, ArH), 6.91 (d, 2H, ArH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 190.1 (C=O), 164.32 (C=N), 140.2, 138.1, 137.3, 136.0, 133.1, 132.4, 130.9, 130.0, 129.7, 129.6, 129.3, 128.3, 127.1, 126.4, 125.8, 125.7, 125.6, 21.0, 18.9 ppm.

5) Synthesis of [$ZnBr_2$(Dipp-BIAO)] (9):

In a dry degassed Schlenk tube, **1** (200 mg, 0.59mmol) was taken and about 10 ml of CH_2Cl_2 was added on to it. To this solution mixture, anhydrous $ZnBr_2$ (132 mg, 0.59mmol) was added. The orange reaction mixture was stirred for 12 hours at ambient temperature. Deep orange-yellow colour filtrate was obtained after filtration of the reaction mixture using cannula filtration method. The CH_2Cl_2 was evaporated under *vacuo* resulting in a concentrated clear solution which was subjected to crystallization at -40^{0}C. After second time crystallization single crystals of light orange colour were obtained. Yield: 78%. FT-IR (selected frequency): ν = 3063, 2963, 2927, 1726 (C=O), 1649 (C=N), 1586, 1434, 1274, 778, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (t, 2H, ArH), 8.21 (d, 1H, ArH), 7.98 (t, 1H, ArH), 7.55 (q, 1H, ArH), 7.41 (t, 1H, ArH), 7.32 (d, 2H, ArH), 6.68 (d, 1H, ArH), 3.01 (sept, 2H, $CH(CH_3)$), 1.22 (d, 6H, $CH(CH_3)$), 0.75 (d, 6H, $CH(CH_3)$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$,100 MHz): δ = 189.82 (C=O), 162.36 (C=N), 146.9, 138.4, 138.2, 135.1, 132.1, 129.9, 128.8, 128.0, 127.8, 126.2, 125.7, 125.4, 124.1, 122.6, 27.9, 23.9, 23.7 ppm.

7. X-Ray Crystallography:

Single crystals of compound **1a, 1b, 2a, 3a, 4**, **5**, **6** and **7** were grown from a solution of CH_2Cl_2 in outside atmosphere at a temperature of 0°C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer 256 of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made with an Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-Kα (1.54184 Å) or Mo-Kα (0.71073 Å) radiation. Crystal data and structure refinement parameters are summarized in the Table 1. The structures were solved by direct methods (SIR92) [17] and refined on F^2 by full-matrix least squares methods; using SHELXL-97. [18]

Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = [\mathrm{Max}(Fo^2,0) + 2Fc^2] / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{½}$, respectively. The ORTEP-3 program was used to draw the molecule.

Table 1. Crystallographic details of compound **1a, 1b, 2a** and **3a**.[a)].

Compound	**1a**	**1b**	**2a**	**3a**
Identification code	exp_936	exp_1494	exp_3225	exp_3123
Empirical formula	$C_{25}H_{27}NO$	$C_{27}H_{31}Cl_2NO$ (**1b**.DCM)	$C_{21}H_{19}NO$	$C_{22}H_{21}NO$
Formula weight	357.48	456.43	301.37	315.40
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
space group	*P-1*	*P-1*	*P* $2_{1/c}$	*P-1*
a [Å]	8.6868(10)	10.7614(7)	21.1517(16)	8.1845(6)
b [Å]	8.9781(12)	11.2065(10)	11.0520(7)	13.2124(11)
c [Å]	14.0518(19)	12.0353(13)	15.6075(12)	17.9902(18)
α [^{o}]	92.717(11)	110.492(9)	90	102.434(8)
β [^{o}]	105.543(11)	103.284(7)	111.338(9)	102.180(7)
γ [^{o}]	107.993(11)	101.698(7)	90	93.473(6)
Volume, [Å^3]	994.0(2)	1257.74(19)	3398.4(4)	1845.5(3)
Z	2	2	8	4
Calculated density (mg/3a)	1.194	1.205	1.178	1.135
Temperature, K	293(2)	293(2)	293(2)	293(2)
Wavelength	1.54184 Å	1.54184	1.54184	1.54184
Absorption coefficient	0.552	2.450	0.560	0.535
θ range for data collection[^{o}]	3.30 to 70.81	4.15 to 70.88	4.49 to 70.78	3.79 to 70.91
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Reflections collected	6855	8670	13435	11705
Reflections Unique	3729 [R(int) = 0.0234]	4717 [R(int) = 0.0222]	6383 [R(int) = 0.0277]	6639 [R(int) = 0.0292]

Completeness to θ	97.3%	97.2%	97.5%	93.4%
Data / restraints / parameters	3729 / 0 / 250	4717 / 0 / 286	6383 / 0 / 424	6639 / 0 / 444
R indices (R_1; wR_2)	0.0473; 0.1200	0.0662; 0.1791	0.0723; 0.1609	0.0791; 0.1991
GOOF	1.044	1.043	1.017	1.107

a) Programs used: SHELXS-97 and SHELXL-97.

Table 2. Crystallographic structure refinement parameters of compound **4, 5**, **6** and **7.** [a)]

Compound	[ZnI_2(2,6-dimethylphenyl-BIAO)]$_2$ (**6**)	[$ZnBr_2$(2,6-dimethylphenyl-BIAO)]$_2$-(**7**)	[$ZnBr_2$(Mes-BIAO)]$_2$ (**8**)	[$ZnBr_2$(Dipp-BIAO)] (**9**)
Identification code	exp_2886	exp_3346	exp_3347	exp_3359
Empirical formula	C42 H34 Cl4 I4 N2 O2 Zn2 (**6**.2DCM)	C44 H40 Br4 Cl8 N2 O2 Zn2 (**7**.4DCM)	C46 H42 Br4 Cl8 N2 O2 Zn2 (**8**.4DCM)	C25 H25 Br2 Cl2 N O Zn (**9**.DCM)
Formula weight	1378.85	1362.76	1388.80	651.55
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
space group	*P* -1	*P*-1	*P*-1	*P* $2_{1/c}$
a, [Å]	9.9975(7)	10.0011(7)	10.6008(5)	10.9846(2)
b[Å]	10.5491(7)	11.6551(8)	11.0655(6)	22.4432(6)
c[Å]	11.4155(8)	11.6837(10)	11.8075(6)	21.2265(3)
Alpha[°]	95.125(5)	105.093(6)	103.848(4)	90
Beta[°]	105.503(6)	102.068(6)	101.399(4)	92.4480(10)
Gamma[°]	90.461(5)	96.284(5)	93.204(4)	90
Volume, [$Å^3$]	1154.85(14)	1266.34(16)	1310.50(12)	5228.18(18)
Z	1	1	1	8
Calculated density (mg/3a)	1.983	1.787	1.760	1.656
Temperature, K	150(2)	150(2)	150(2)	150(2)
Wavelength	1.54184	1.54184	0.71073	1.54184

Absorption coefficient	24.686	9.053	4.411	6.903
θ range for data collection[°]	4.04 to 70.81	3.99 to 70.78	1.82 to 25.76	3.94 to 70.67
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Reflections collected	7606	8946	8982	22231
Reflections Unique	4315 [R(int) = 0.0565]	4777 [R(int) = 0.0339]	4913 [R(int) = 0.0300]	9874 [R(int) = 0.0333]
Completeness to θ	97.2%	98.0%	97.7%	98.3%
Data / restraints / parameters	4315 / 0 / 255	4777 / 0 / 281	4913 / 0 / 292	9874 / 0 / 585
R indices (R_1; wR_2)	R1 = 0.0858; wR2 = 0.2262	R1 = 0.0503; wR2 = 0.1246	R1 = 0.0542; wR2 = 0.1407	R1 = 0.0481; wR2 = 0.0862
GOOF	1.078	1.040	0.956	1.020

a) Programs used: SHELXS-97 and SHELXL-97.

Table 3. Comparison of wavelength, absorbance and molar absorptivity between $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transition in the compounds **1a**, **1b**, **2a**, **2b**, **3a** and **3b**.

Compound	Electron jump	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$
1a	Wavelength of maximum absorption (nm)	274	230
	Absorbance	0.134	0.225
	Molar absorptivity (M^{-1} cm^{-1})	4.178 x 10^4	7.01 x 10^4
1b	Wavelength of maximum absorption (nm)	274	229
	Absorbance	0.043	0.194
	Molar absorptivity (M^{-1} cm^{-1})	1.34 x 10^4	6.05 x 10^4
2a	Wavelength of maximum absorption (nm)	273	230
	Absorbance	0.414	0.960
	Molar absorptivity (M^{-1} cm^{-1})	12.91 x 10^4	29.94 x 10^4
2b	Wavelength of	273	230

	maximum absorption (nm)		
	Absorbance	0.273	0.548
	Molar absorptivity (M^{-1} cm^{-1})	8.51 x 10^4	17.09 x 10^4
3a	Wavelength of maximum absorption (nm)	274	229
	Absorbance	0.241	0.527
	Molar absorptivity (M^{-1} cm^{-1})	7.5 x 10^4	16.43 x 10^4
3b	Wavelength of maximum absorption (nm)	273	230
	Absorbance	0.043	0.151
	Molar absorptivity (M^{-1} cm^{-1})	1.34 x 10^4	4.71 x 10^4

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Appendix

Supporting Information

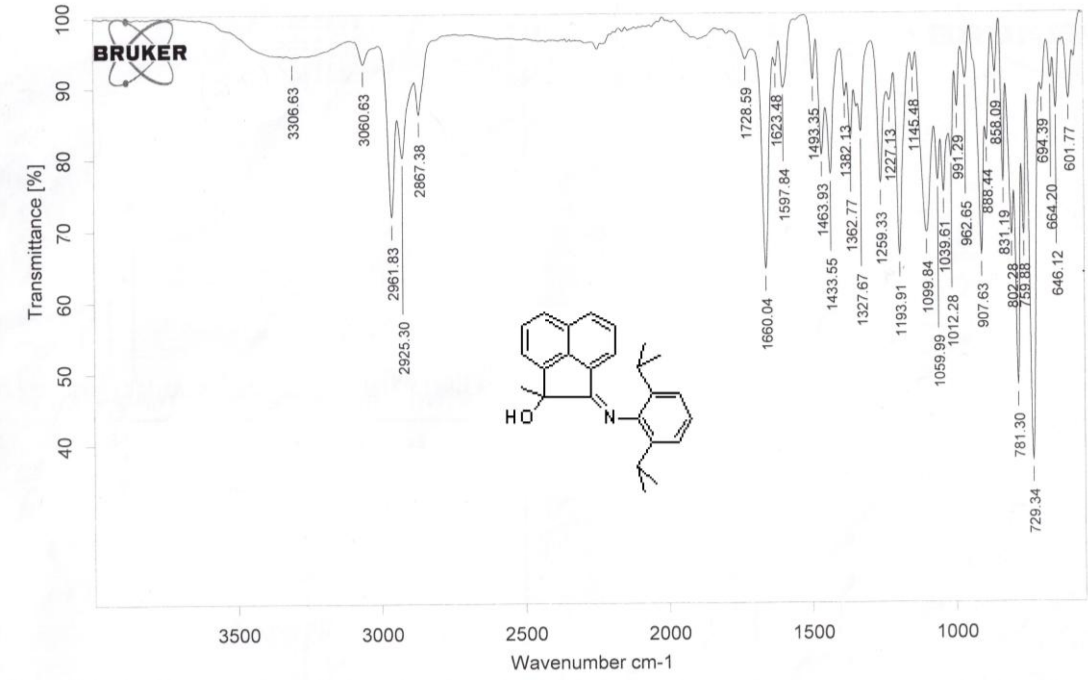

Fig. S1: FT-IR spectra of Compound **1a**

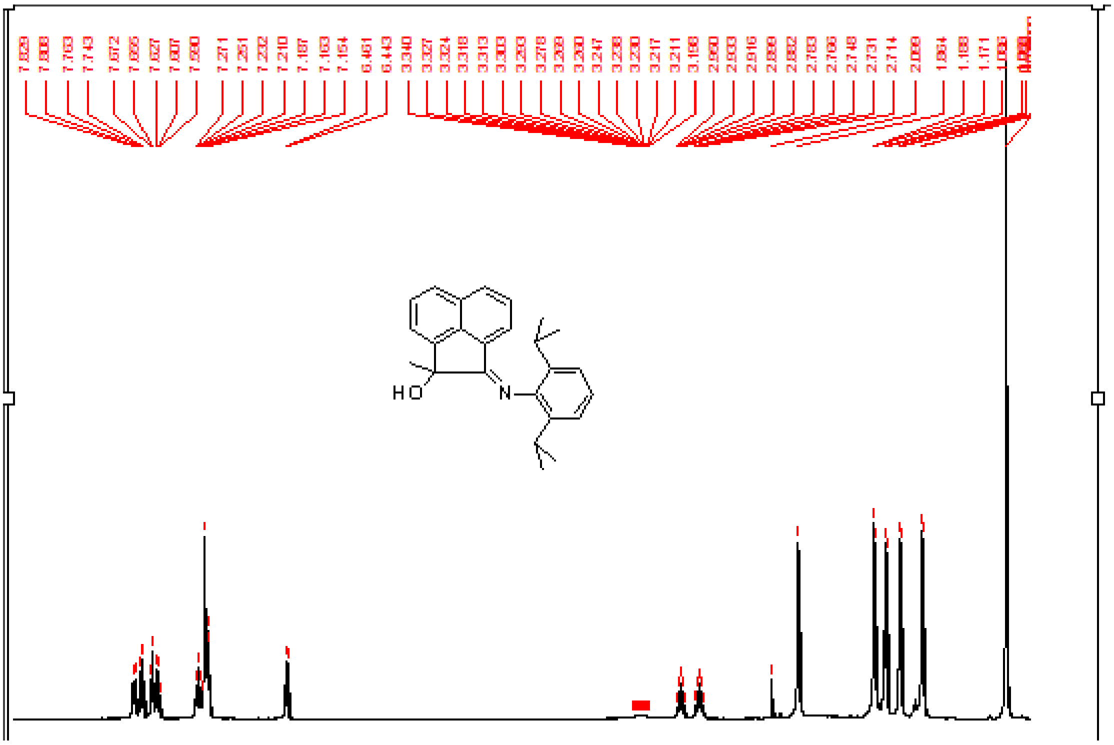

Fig S2: ^{1}H NMR spectra of Compound **1a**

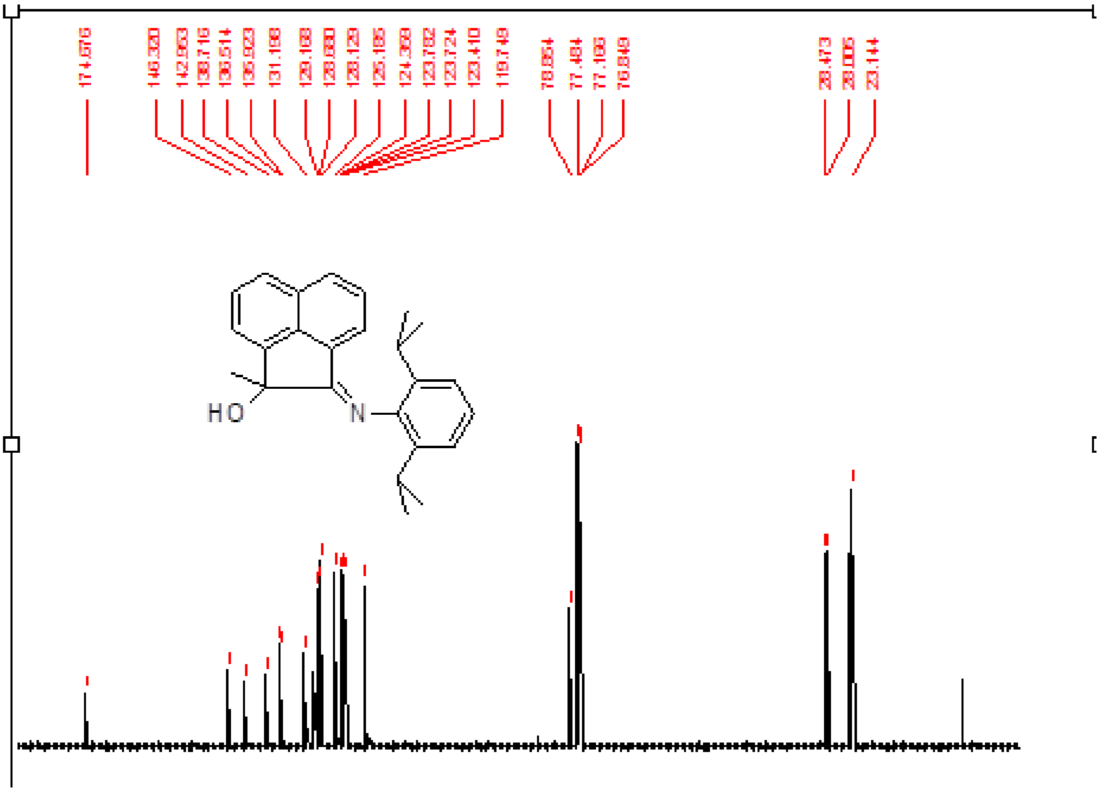

Fig S3: $^{13}C\{^{1}H\}$ NMR spectra of Compound **1a**

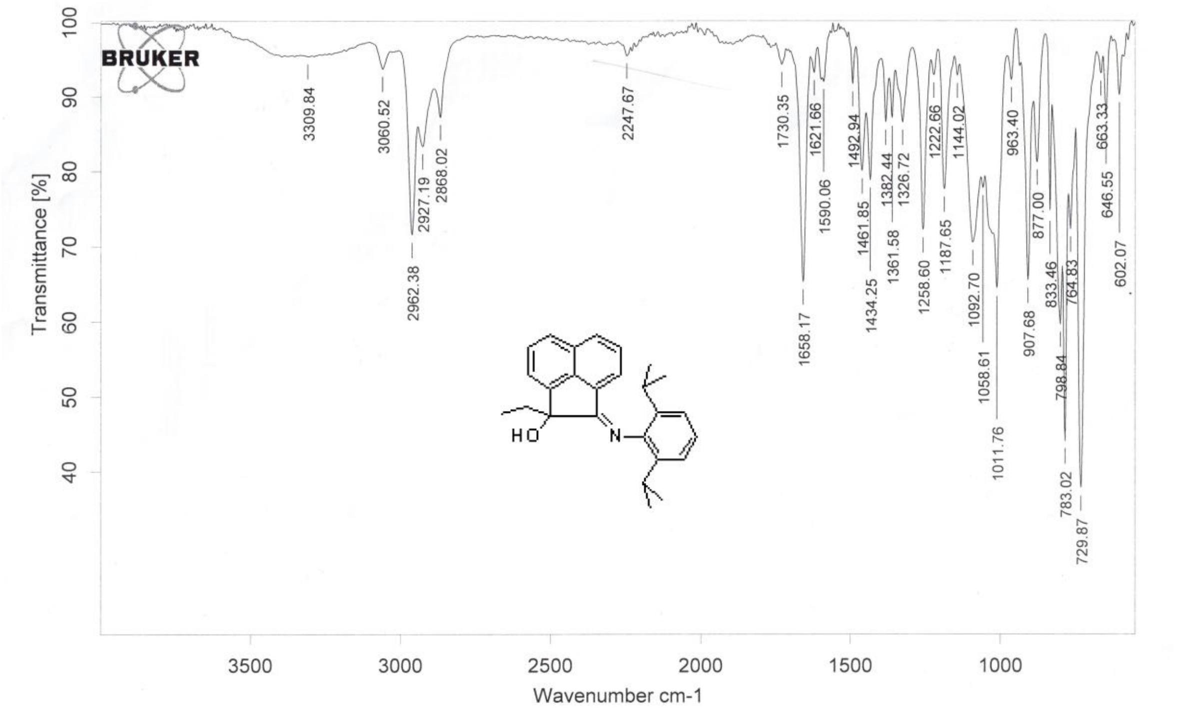

Fig. S4: FT-IR spectra of Compound **1b**

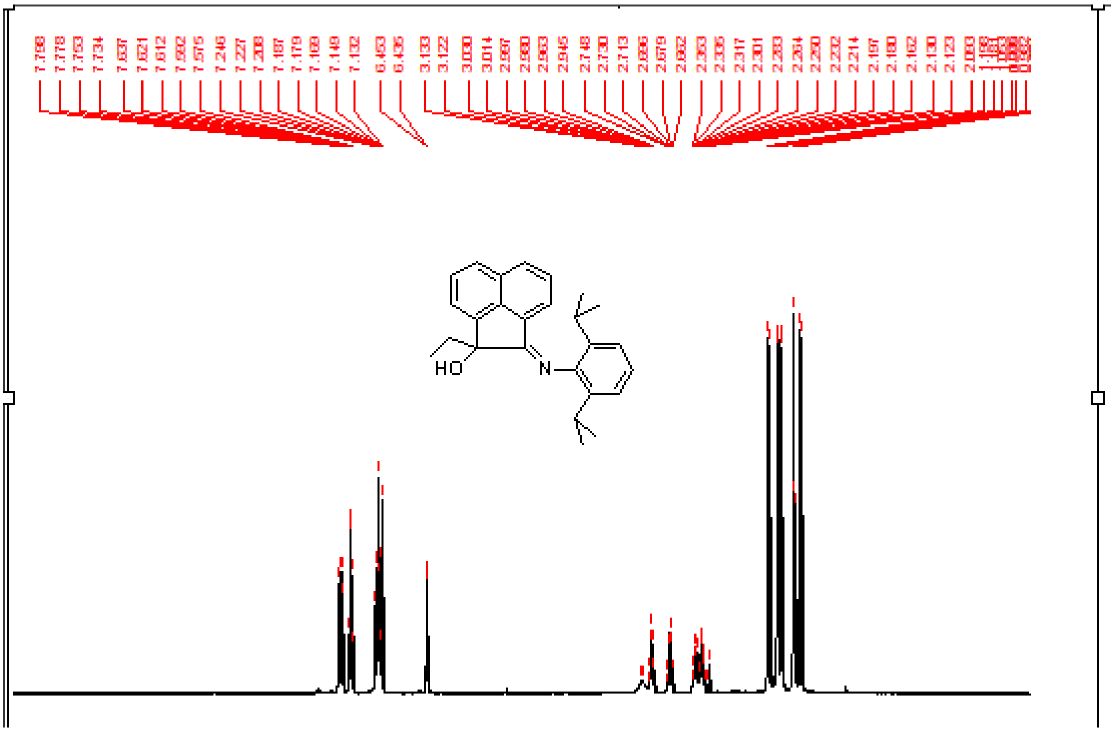

Fig S5: ^{1}H NMR spectra of Compound **1b**

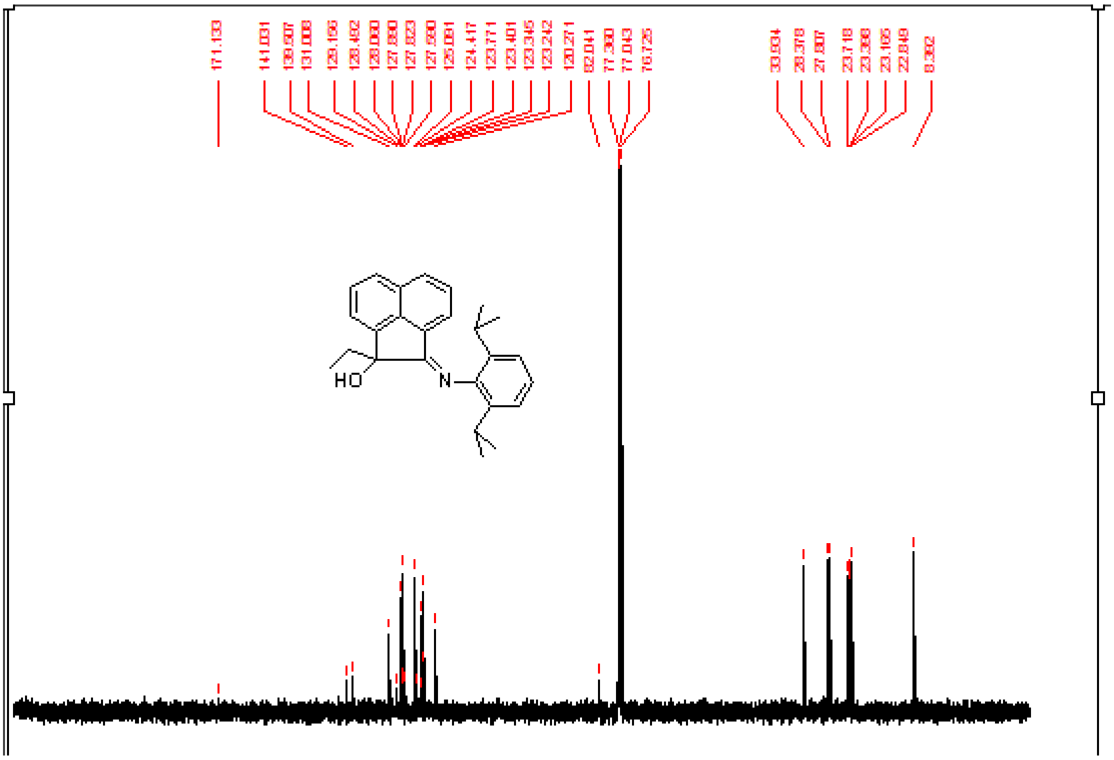

Fig S6: ^{13}C{^{1}H} NMR spectra of Compound **1b**

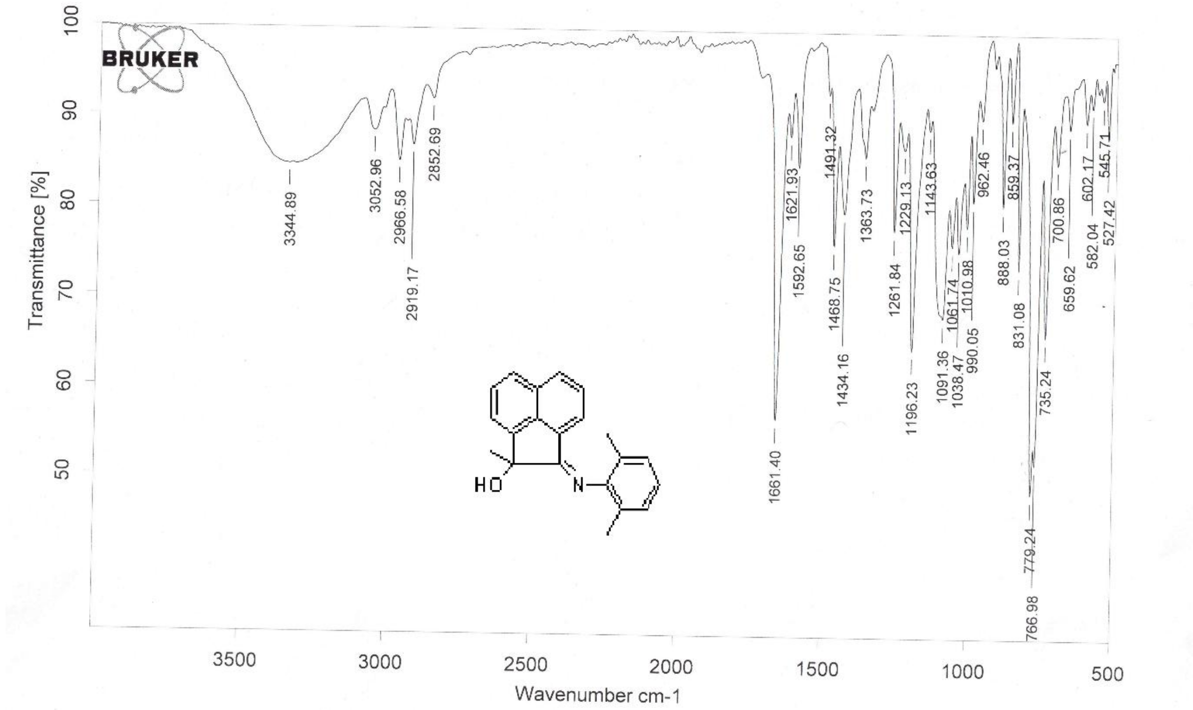

Fig. S7: FT-IR spectra of Compound **2a**

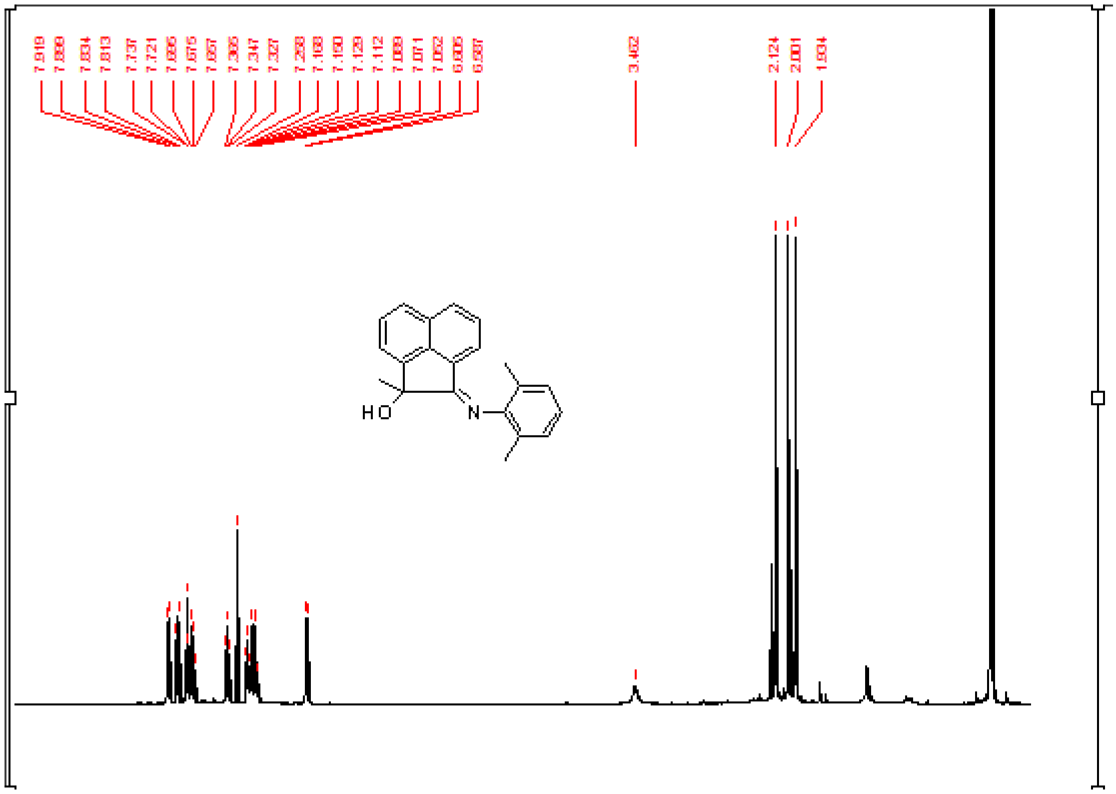

Fig S8: ^{1}H NMR spectra of Compound **2a**

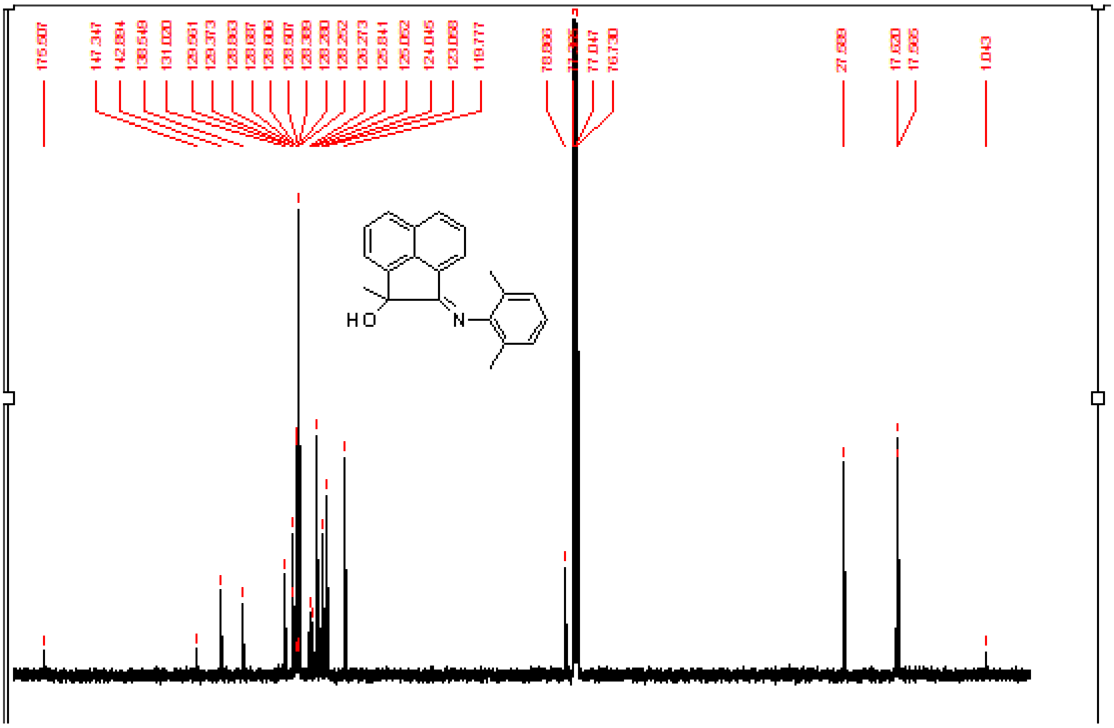

Fig S9: $^{13}C\{^1H\}$ NMR spectra of Compound **2a**

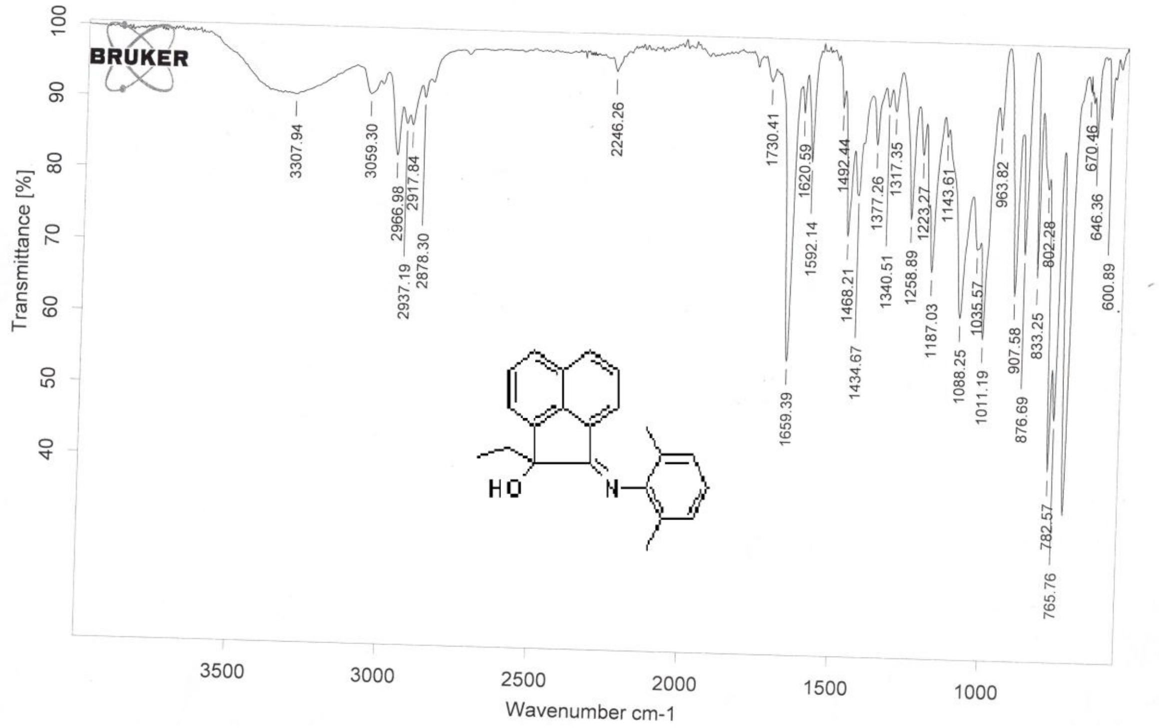

Fig. S10: FT-IR spectra of Compound **2b**

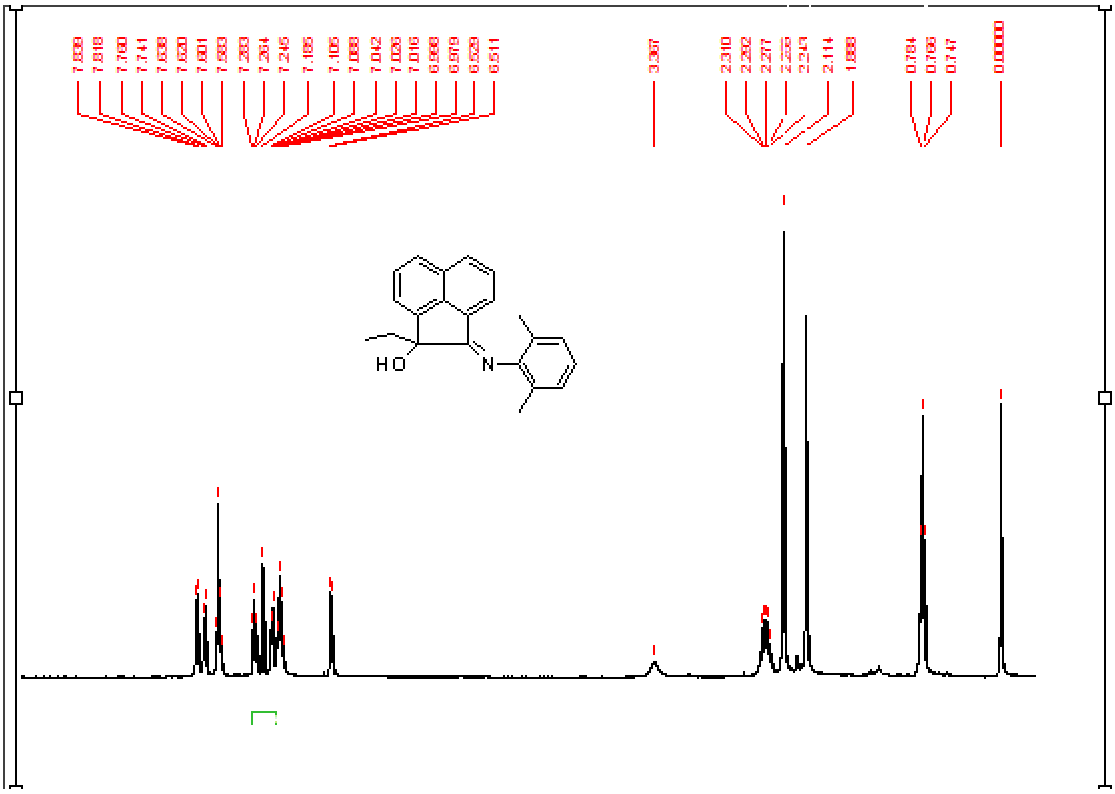

Fig S11: ^{1}H NMR spectra of Compound **2b**

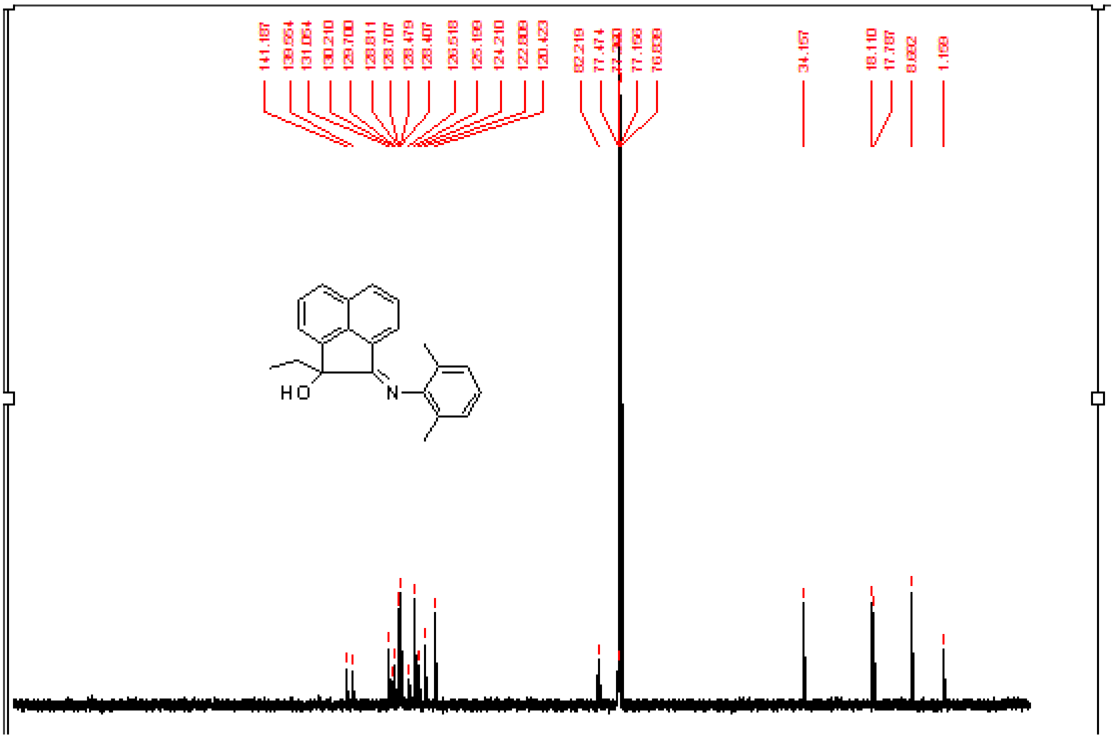

Fig S12: ^{13}C{^{1}H} NMR spectra of Compound **2b**

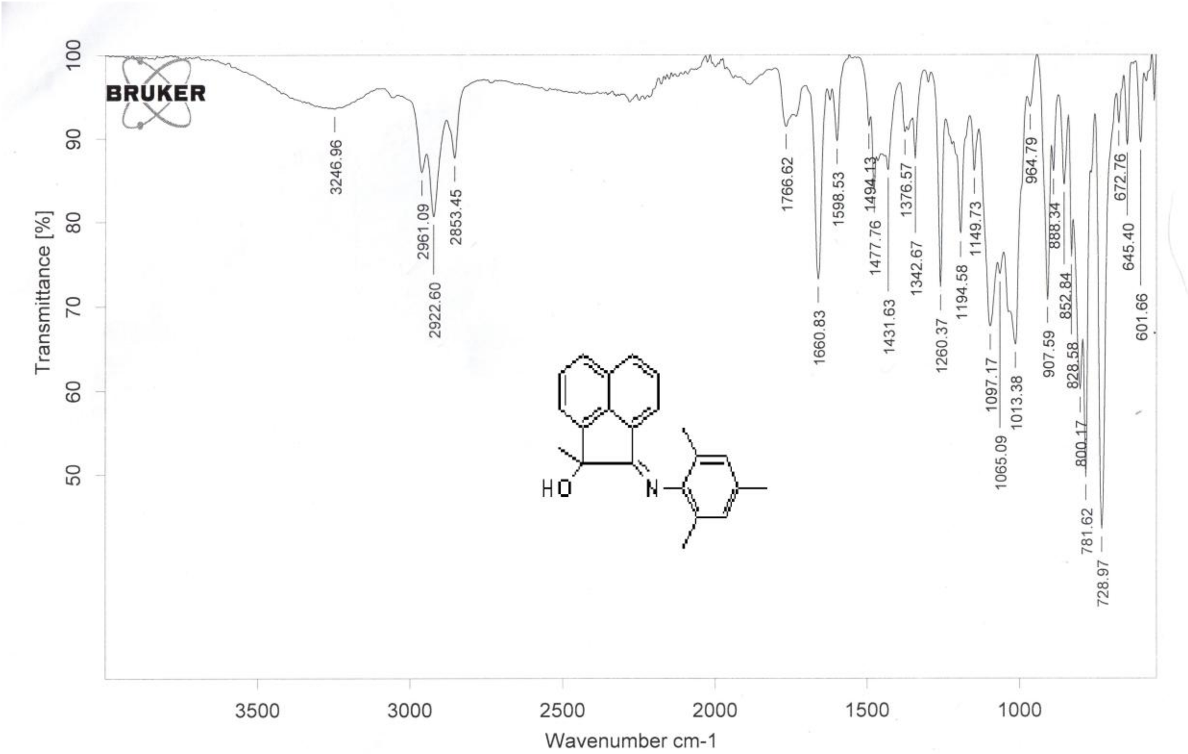

Fig. S13: FT-IR spectra of Compound **2a**

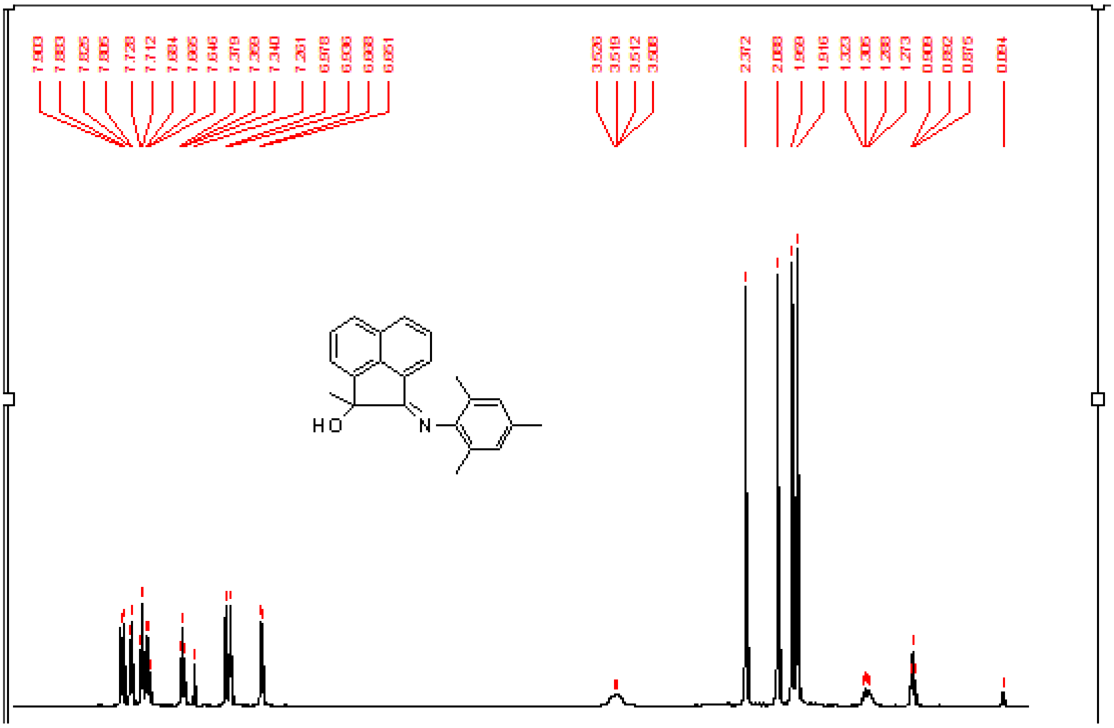

Fig S14: ^{1}H NMR spectra of Compound **3a**

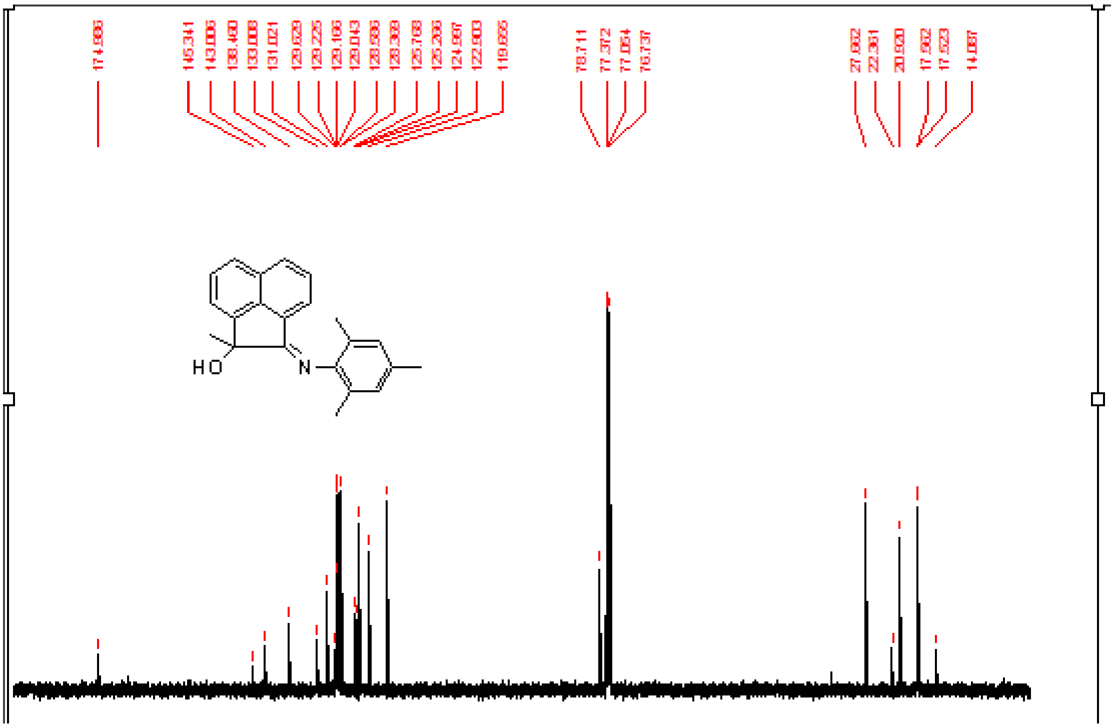

Fig S15: $^{13}C\{^{1}H\}$ NMR spectra of Compound **3a**.

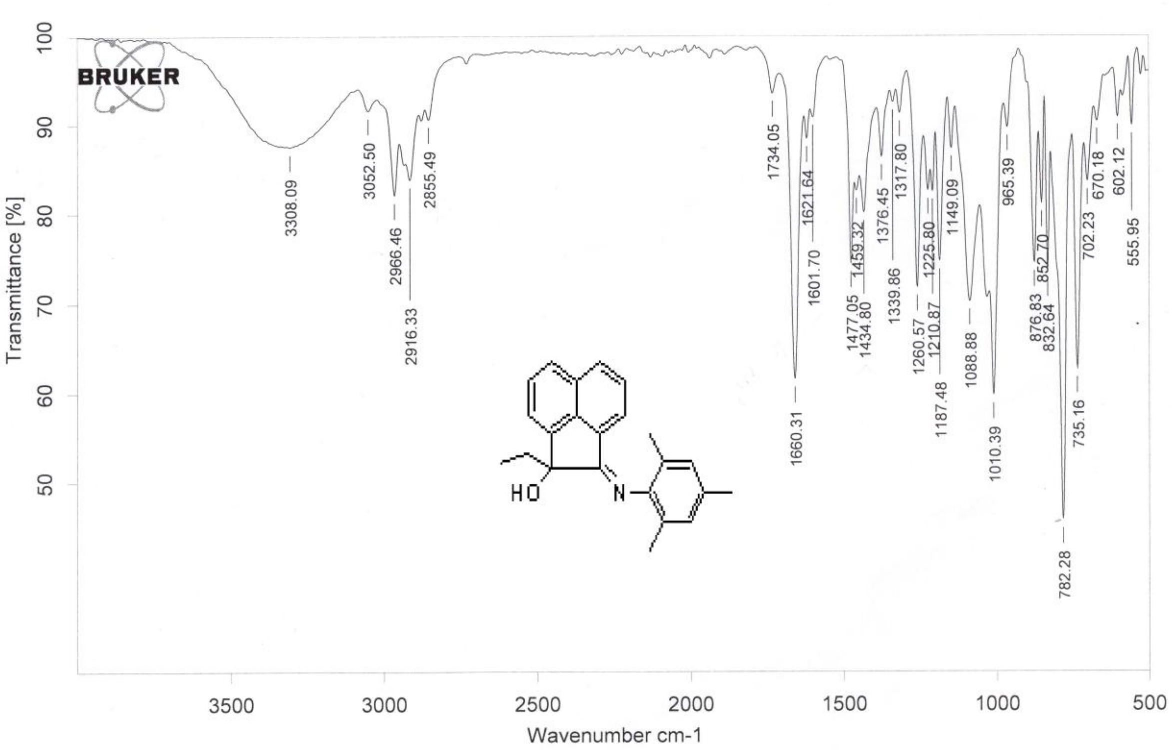

Fig. S16: FT-IR spectra of Compound **3b**

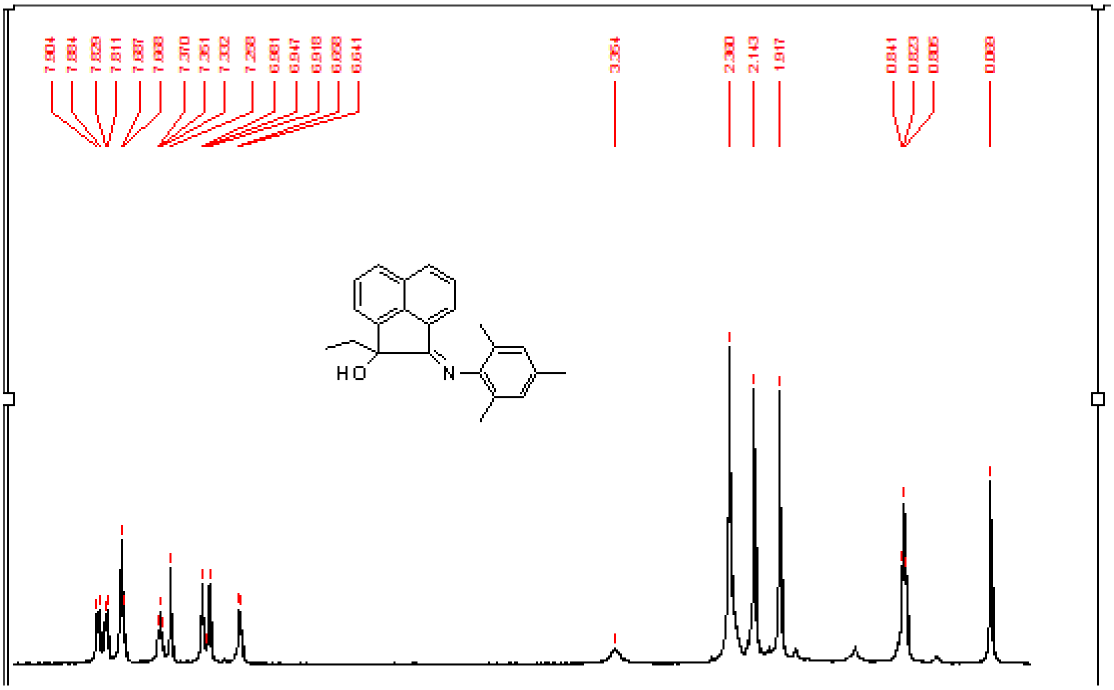

Fig S17: ^{1}H NMR spectra of Compound **3b**

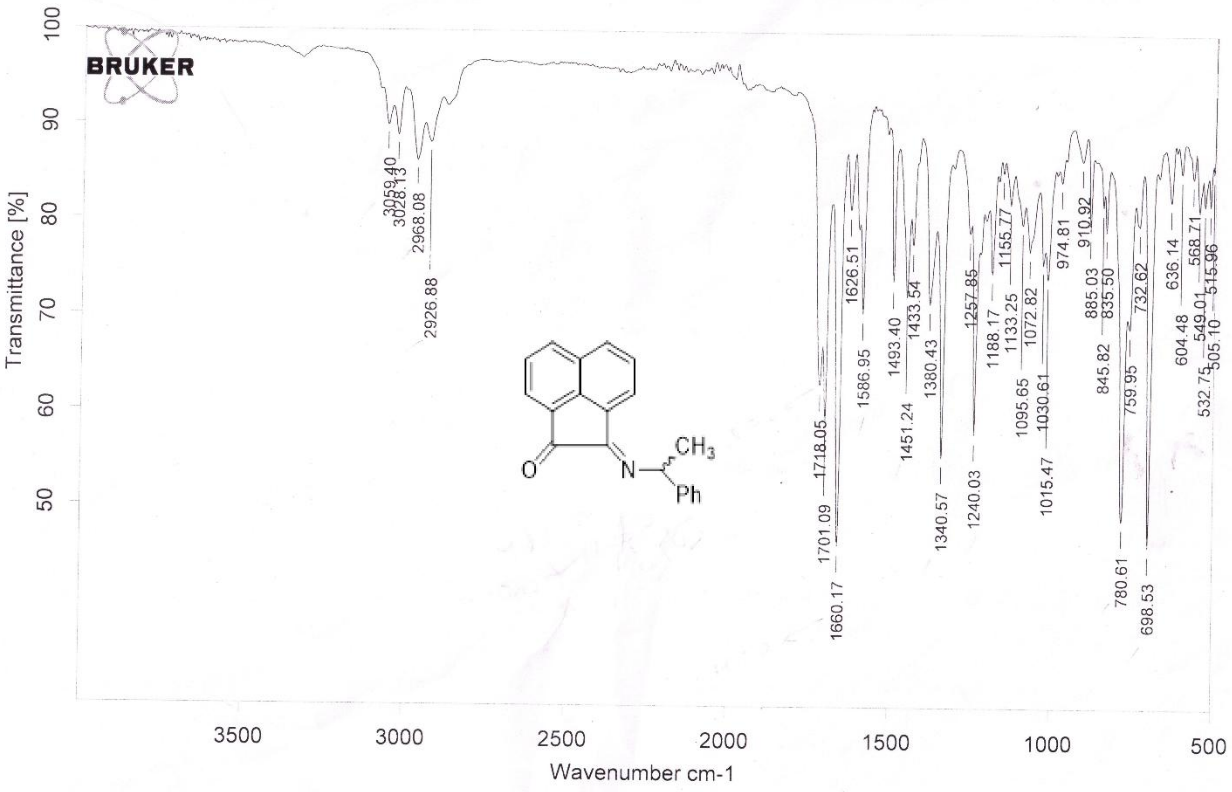

Fig. S18: FT-IR spectra of Compound **4**

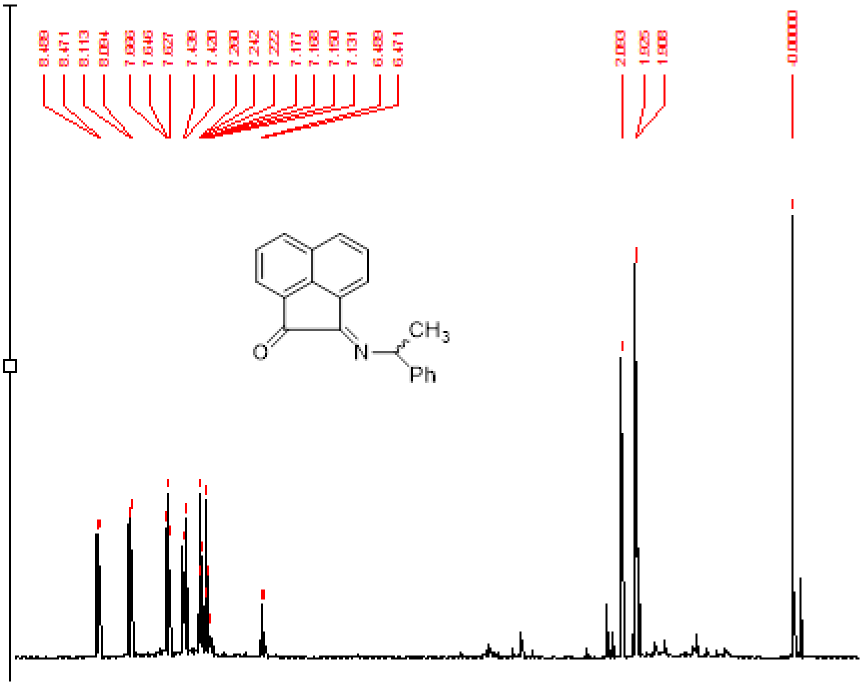

Fig S19: 1H NMR spectra of Compound **4**

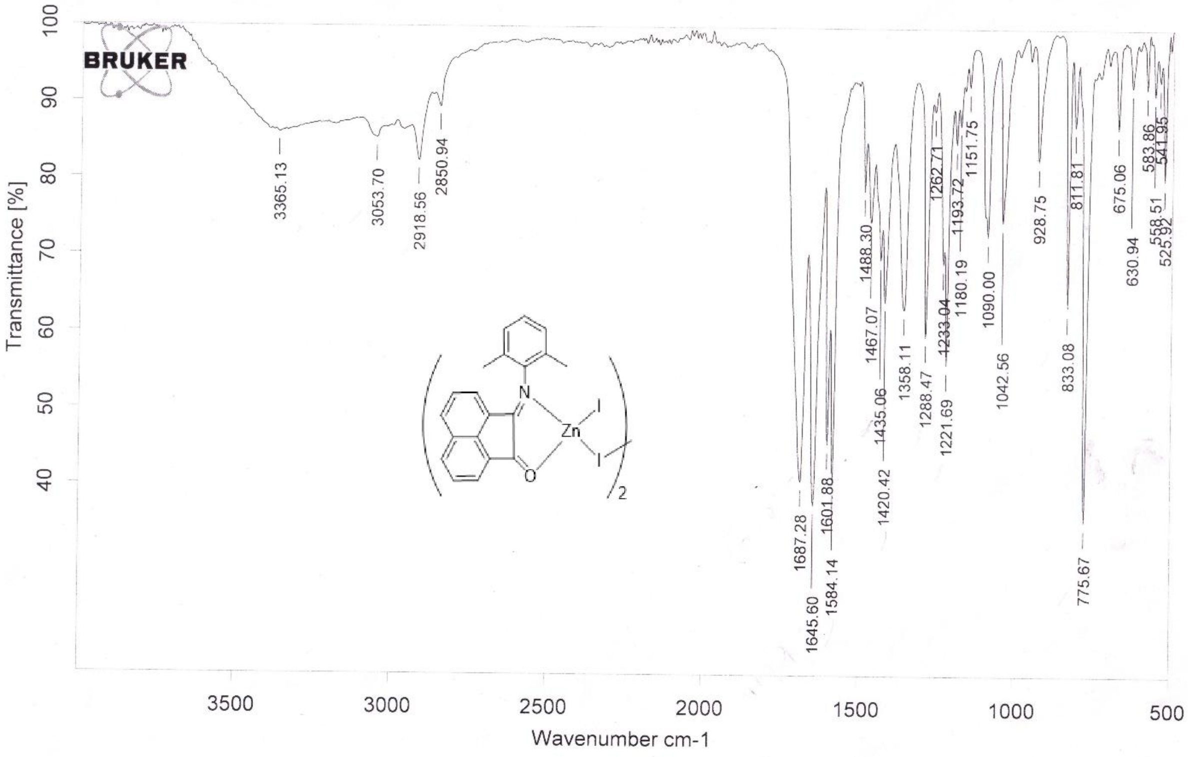

Fig. S20: FT-IR spectra of Compound **6**

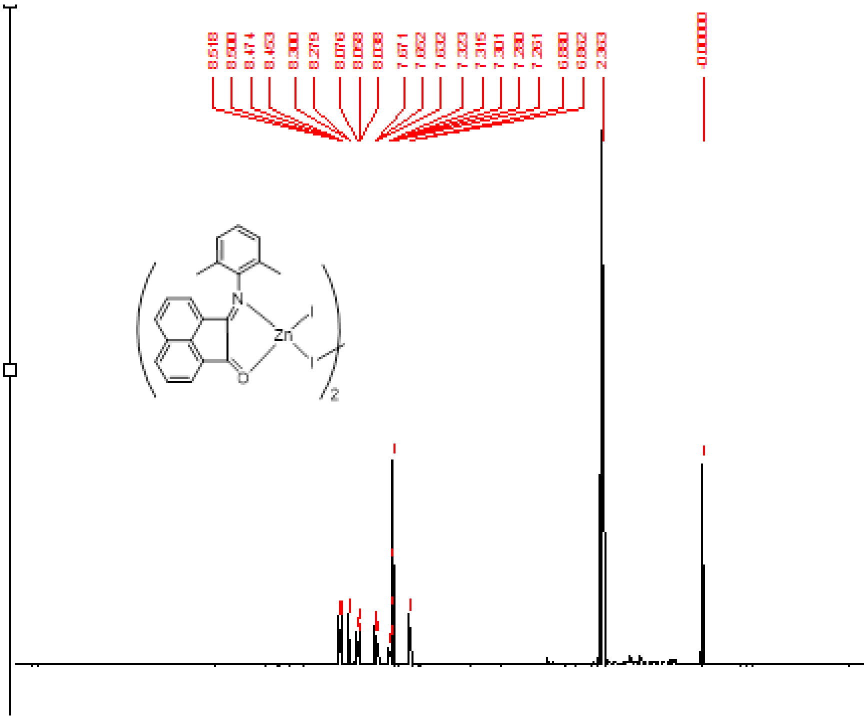

Fig S21: 1H NMR spectra of Compound **6**

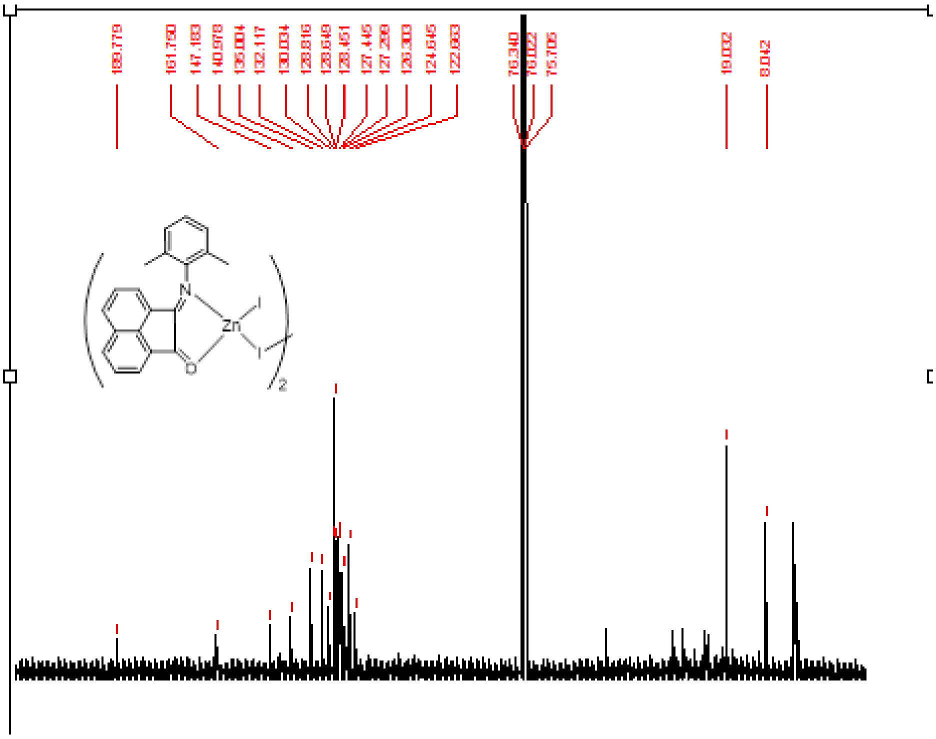

Fig S22: 13C{1H} NMR spectra of Compound **6**

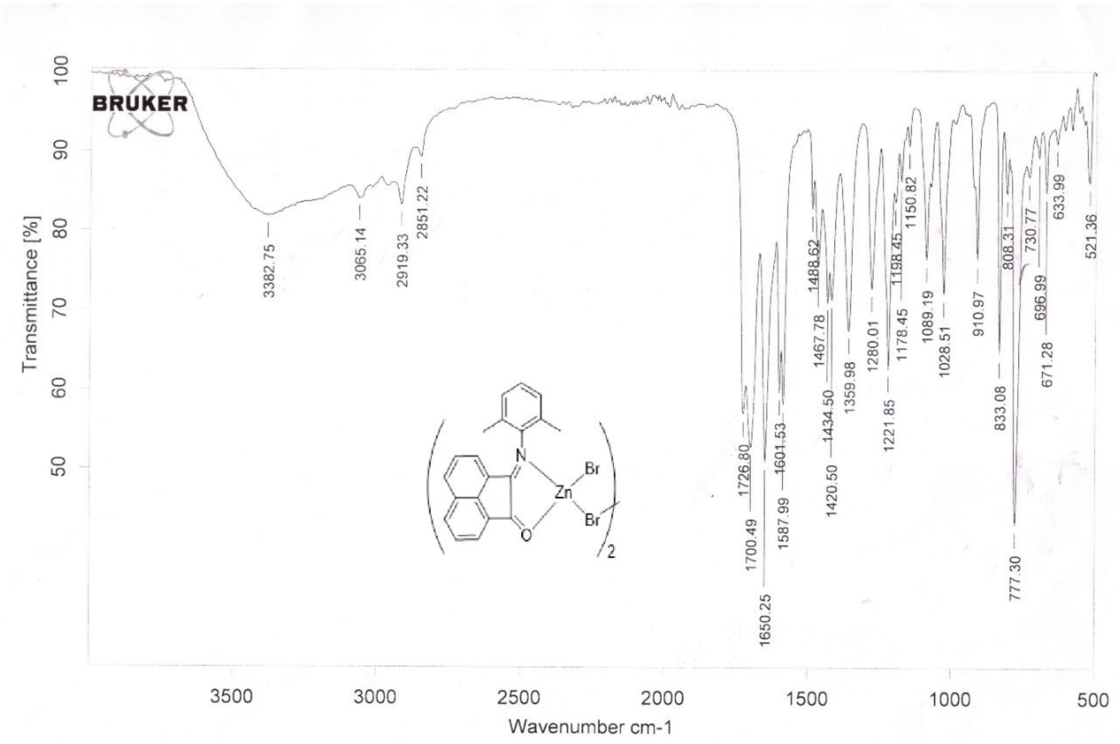

Fig. S23: FT-IR spectra of Compound **7**

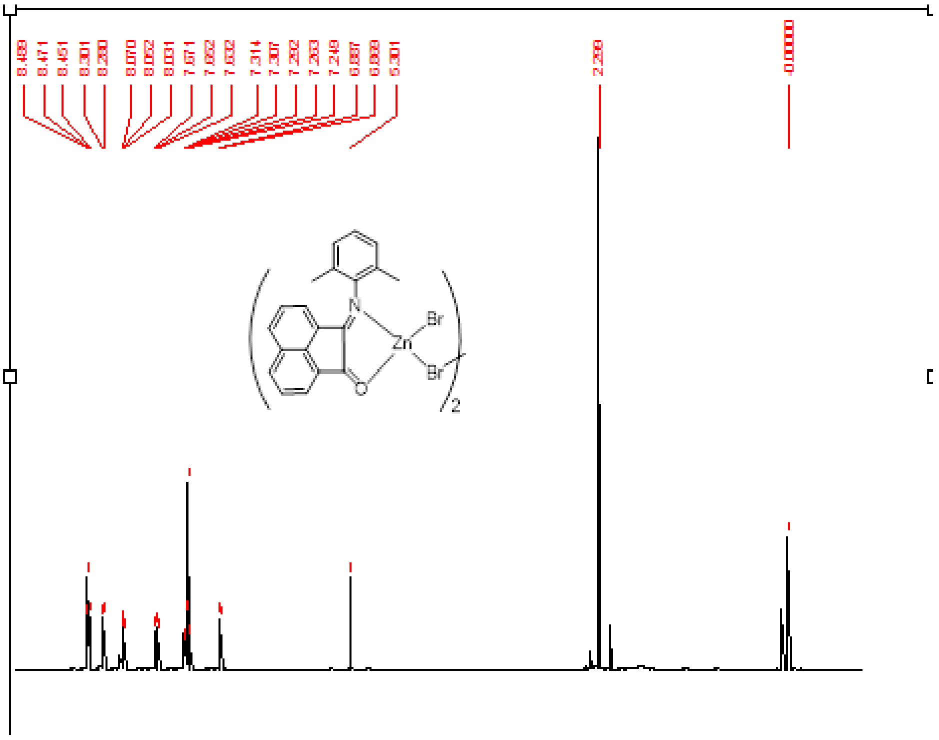

Fig S24: 1H NMR spectra of Compound **7**

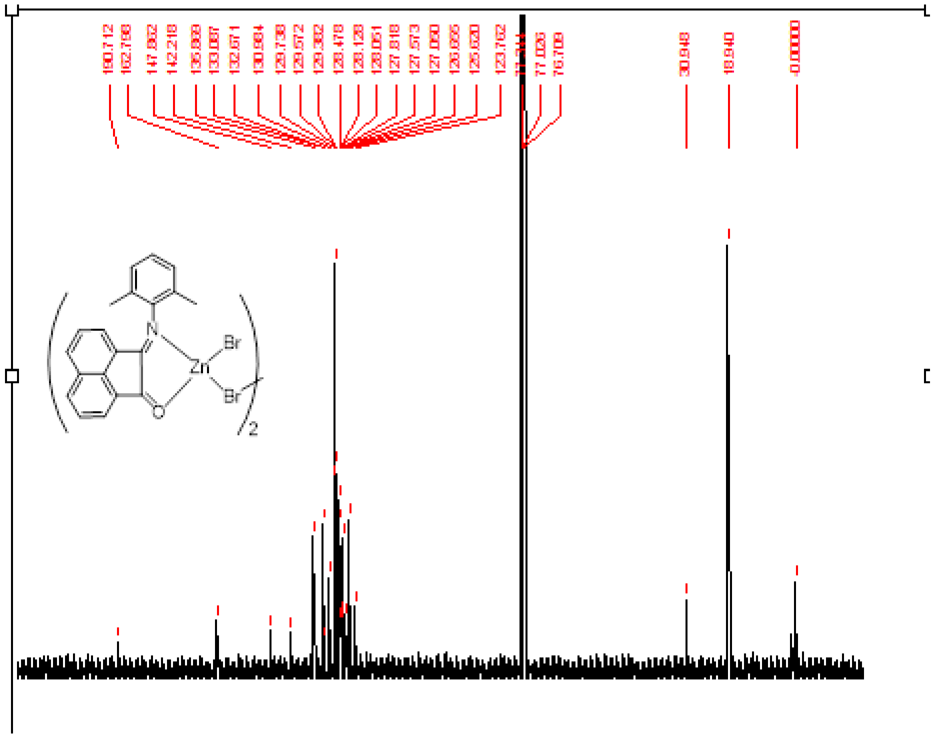

Fig S25: 13C{1H} NMR spectra of Compound **7**

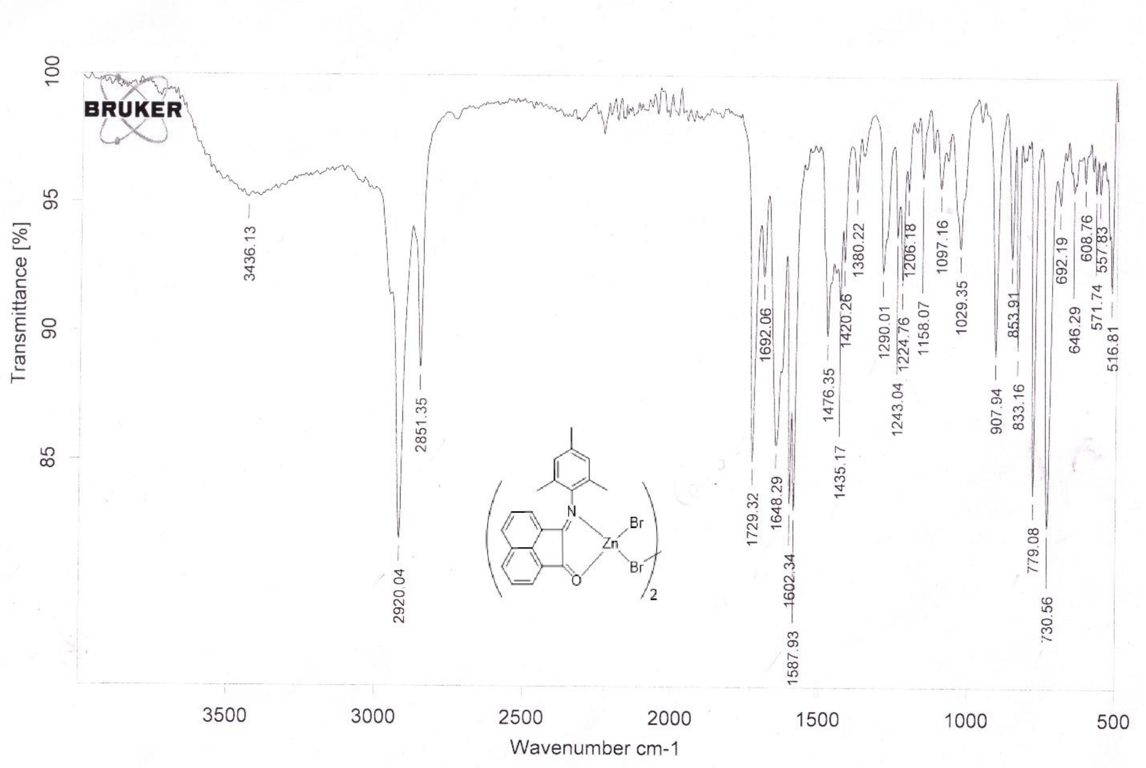

Fig. S26: FT-IR spectra of Compound **8**

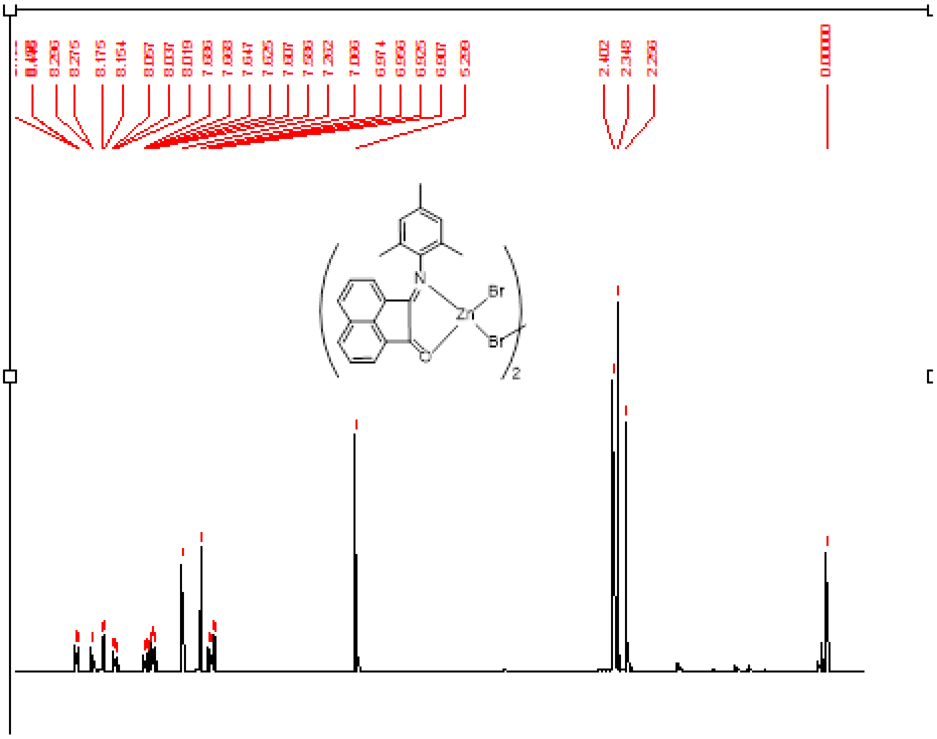

Fig S27: 1H NMR spectra of Compound **8**

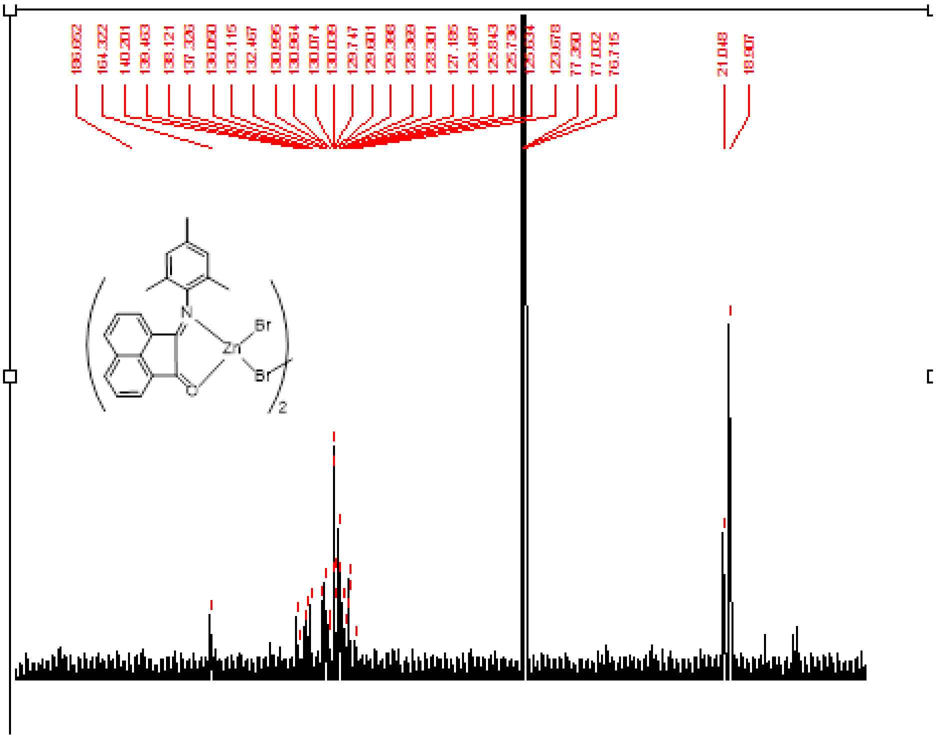

Fig S28: 13C{1H} NMR spectra of Compound **8**

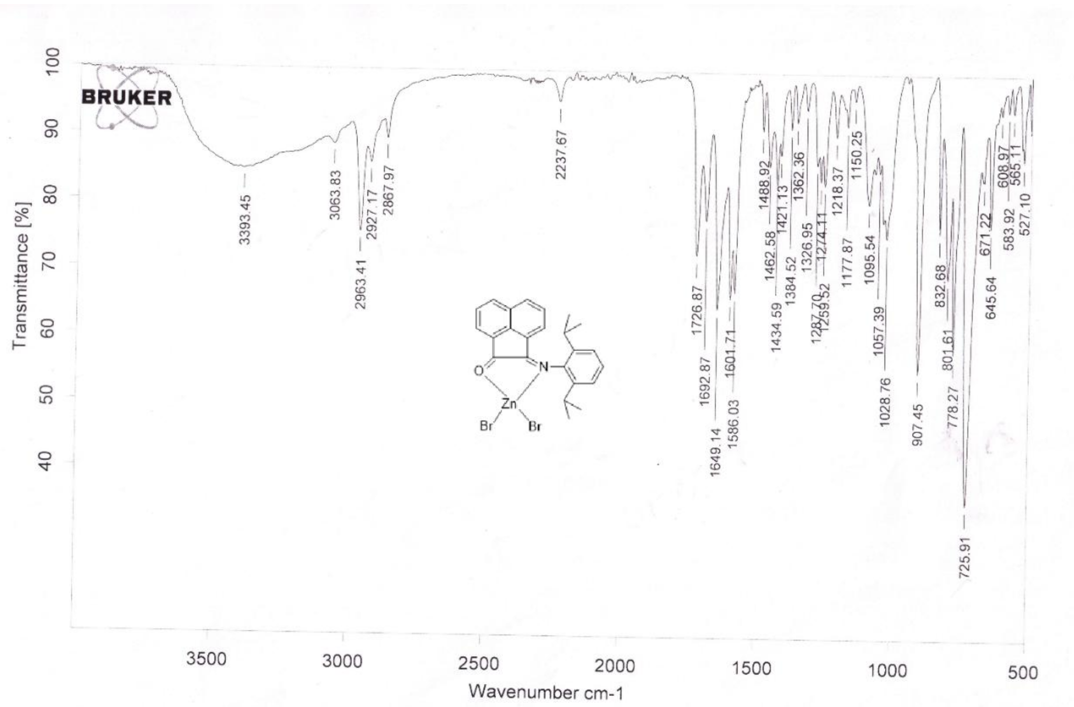

Fig. S29: FT-IR spectra of Compound **9**

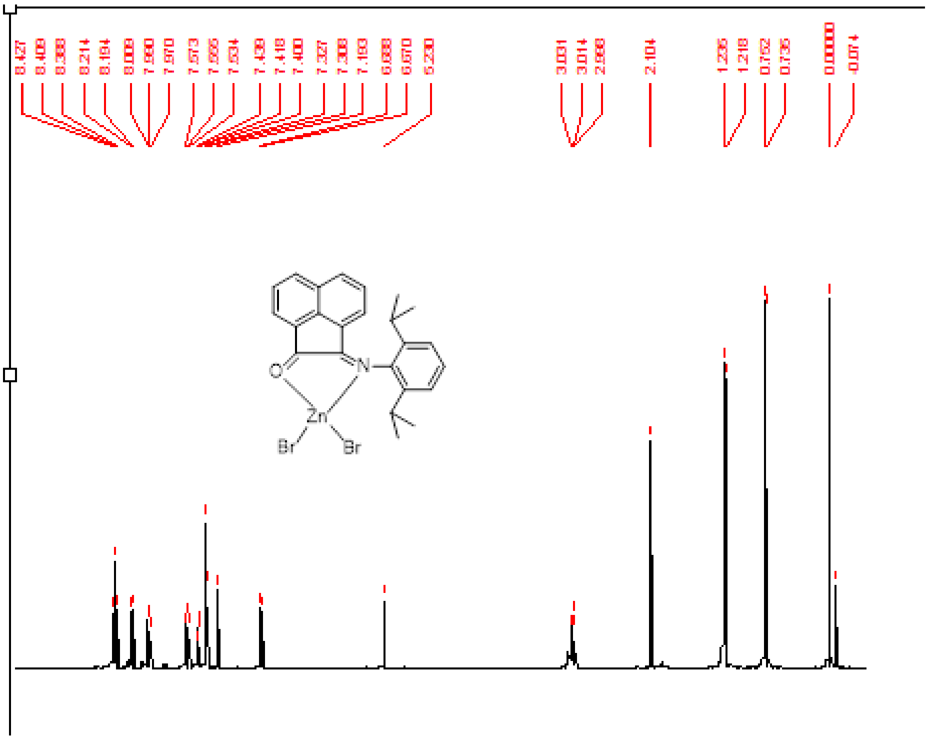

Fig S30: 1H NMR spectra of Compound **9**

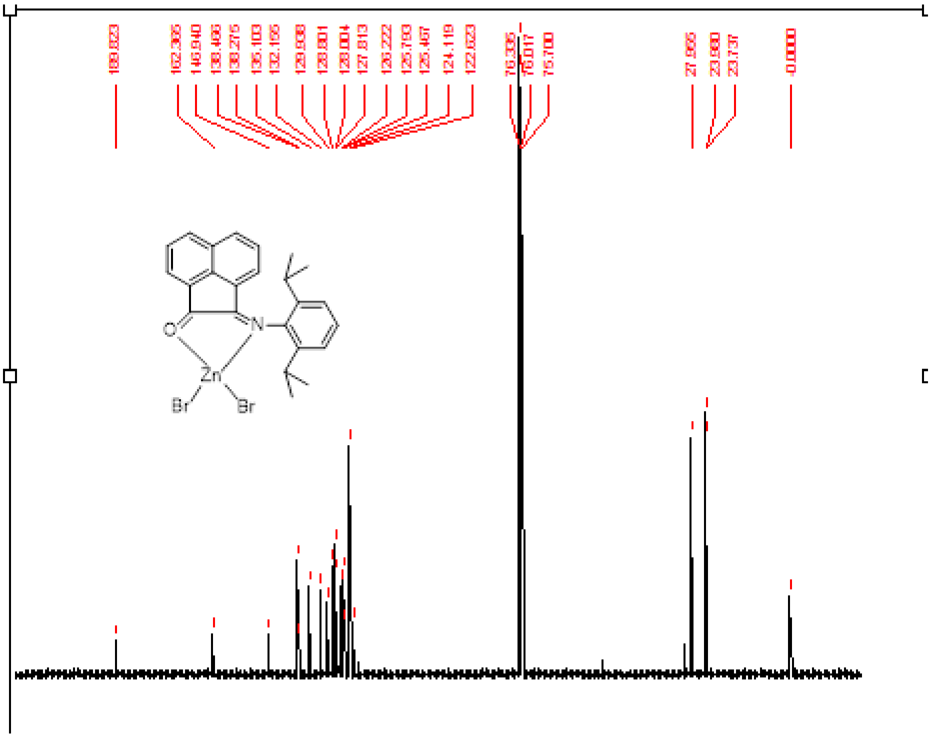

Fig S31: 13C{1H} NMR spectra of Compound **9**

List of Abbreviation:

1. Ar-BIAO: *N*-(Aryl)imino-Acenapthenone
2. Ar-BIAO-ol: 1-alkyl-*N*-(Aryl)imino-Acenaphthylen-1-ol
3. Ar-BIAN: Bis(*N*-aryl)imino-Acenaphthene
4. DAB: Di-Aza-Butadiin
5. Dipp: Diisopropylphenyl
6. Mes: Mesityl.

Curriculum Vitae

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1	M.Sc.	Indian Institute of Technology Hyderabad	Indian Institute of Technology Hyderabad	2014	8.74 (till 3rd Semester)
2	B.Sc. (Hons.)	R. K. Mission Residential College, Narendrapur	Calcutta University	2012	75.25%
3	Higher Secondary	Maldanga R. M. Institution	West Bengal Council of Higher Secondary Education	2009	82%
4	Secondary	Kusumgram Tyeba Institution	West Bengal Board of Secondary Education	2007	85.12%

Awards and Honors:

- Recipient of “M.C.M Scholarship” from the Indian Institute of Technology Hyderabad for Academic Excellence during the M.Sc. course 2012-2014.
- Qualified CSIR-NET with rank 61 in the year of 2013.
- Qualified GATE-2014 (AIR-139).
- Obtained All India Rank 222 in JAM (Joint Admission test for M.Sc) entrance Examination conducted by Indian Institute of Technology in 2012.
- Foundation for Excellence Scholarship, R. K. Mission Residential College Narendrapur, India.
- Stood sixth in College in B.Sc.
- Stood 2nd in 12th standard in school.