

**Sterically Rigid Unsymmetrical Acenaphthenene Imine
(Ar-BIAN) Ligands in Zinc Coordination Sphere
– Synthesis and Structures**

A Project Report

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Master of Science

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 acknowledgement has been made whenever the work described is based on the findings of other investigators.

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Approval Sheet

This thesis entitled “**Sterically Rigid Unsymmetrical Acenaphthene Imine (Ar-BIAN) Ligands and its Metal Complexes – Synthesis and Structures**” by Kulsum Bano is approved for the degree of Master of Science from IIT Hyderabad.



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(Chairman)

Dedicated

To

My Beloved Parents

Who have devoted all their lives to my Education

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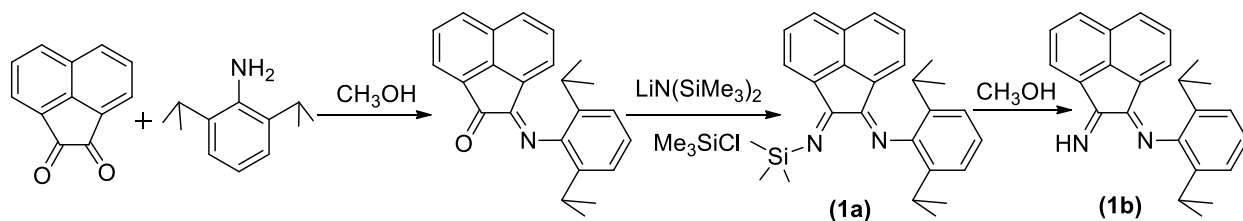
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Abstract

First part of my M.Sc. thesis I have described the synthesis of (Dipp-BIAN-silyl) i.e. N-2-((2,6-diisopropyl)imino)acenaphthylen-1(2H)-ylidene)-1,1,1-trimethylsilanamine ligand (**1a**), which was prepared from reaction of corresponding Ar-BIAO ligands with lithium-bis(trimethylsilanamine) ($\text{LiN}(\text{Si}(\text{CH}_3)_3)_2$) and stir at $50\text{ }^\circ\text{C}$ for $1\frac{1}{2}$ h, then cooled at room temperature, and followed by Me_3SiCl in toluene under reflux at $80\text{ }^\circ\text{C}$. The ligand N-(2-iminoacenaphthylen-1(2H)-ylidene)-2,6-diisopropylaniline (Ar-BIAN-H) (**1b**) was obtained from desilylation of ligand **1a** under reflux condition in methanol at $50\text{ }^\circ\text{C}$ for 2-3 h. The synthesized ligands **1a** and **1b** were characterized by FT-IR, UV-visible, ^1H , ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. The solid state structures of compounds **1a** and **1b** were established by single crystal X-ray diffraction analysis.

In the last part of my thesis I have described the synthesis of zinc complex having formula $[\text{ZnCl}_2(\text{Ar-BIANH})]$ (**2b**) which was prepared from reaction of **1b** with ZnCl_2 in dichloromethane at ambient temperature under inert condition. The synthesized metal complexes **2b** was characterized by FT-IR, UV-visible, ^1H , ^{13}C $\{^1\text{H}\}$ -NMR spectroscopy. The solid state structures of compounds **2b** was established by single crystal X-ray diffraction analysis. The molecular structure of metal complex **2b** is four fold coordination to adopt distorted tetrahedral geometry.



Scheme 1. Overall Synthesis of **1a** and **1b**.

1. Introduction:

The rigid bidentate nitrogen based di-imine ligand bis(*N*-arylimino)acenaphthene (**Ar-BIAN**), which was first introduced by *van Asselt* and *Elsevier* in the early 1990s^[1], was used in various catalytic processes in transition metal chemistry.^[2-6] He explained the various Pd-complex chemistry into the formation of C-C bond (i.e., carbon-carbon coupling reaction). The use of bidentate and tridentate ligands received significant attention by many research groups due to their wide application as auxiliary ligands in catalysis.^[7-11] To improve the catalytic activity of the metal complexes, proper ligand design is most important. The presence of two exocyclic imines to the heteroaromatic ring system lead to better σ -donating and better π -accepting properties than that of 2,2'-bipyridine and 1,10-phenanthroline ligands.^[12-14] This property allows (Ar-BIAN) ligands to stabilize both the higher and lower oxidation states of the coordinated metal ions. In addition, the rigid acenaphthenene backbone prevents rotation around the imine carbon-carbon bond and forces the imine nitrogen atoms to remain in a fixed *cis*- orientation, favoring chelating coordination to a central metal atom.

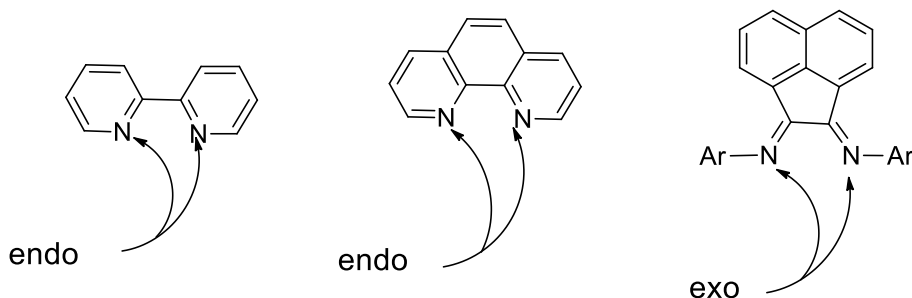


Figure 1. Difference between exo- and endo-imine.

Transition metal complexes with 1,3-diaza-1,4-butadiene ligands,^[15] in particular, acenaphthene-1,2-diimine (BIAN) derivatives, have attracted more attention due to a number of interesting chemical properties of these complexes. These compounds exhibit catalytic activity in alkyne hydrogenation^[16], C-C bond formation^[17,18], cyclo-isomerization,^[19] and, particularly, in polymerization of various olefins^[20-24] and acrylic monomers,^[25] and copolymerization of CO₂ with methylenecyclopropane^[26] and of ethylene with norbornene.^[27] Recently, it was studied at

developing new reactions of organic molecules with acenaphthenediimine complexes of main-group metals.

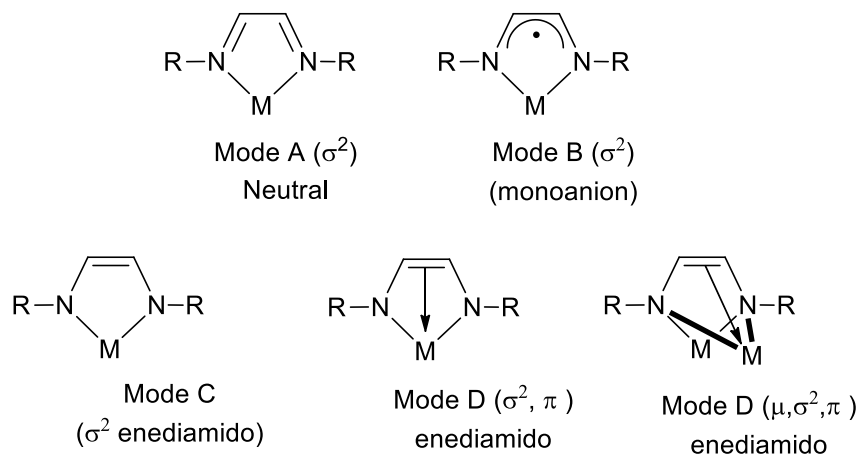


Figure 2. Coordination modes of 1,4-diaza-1,3-butadiene ligands to transition metals.

Till date, neither main-group metal complexes with BIAN ligands nor the compounds containing BIAN in the anionic form were known. Acenaphthene-1,2-diimines have the following distinguishing features as the ligands: (1) conformational rigidity of the chelating diimine fragment; (2) presence of the lone electron pairs of the nitrogen atoms serving as centers of metal-atom coordination and proton-acceptor centers; (3) presence of the π -system, which can act as an electron reservoir.^[28]

Van Asselt and *Elsevier*, have described the palladium complexes of the *cis*-fixed bidentate nitrogen ligand bis(phenylimino)acenaphthene (Ph-BIAN) are excellent catalysts for the carbon-carbon coupling reactions between various organic halides and organo- magnesium, zinc, and tin reagents. The palladium-catalyzed cross-coupling reaction has become a versatile tool in organic synthesis, and a wide variety of organic electrophiles and transmetalating reagents can be used. The nature of the ligands coordinated to the palladium center is expected to have a pronounced influence on the carbon-carbon cross-coupling reaction, because it has been shown that oxidative addition and reductive elimination (and probably also transmetalation) are strongly dependent on the type of ligands coordinated to the metal center. Their investigations concerning the reactivity and catalytic activity of zerovalent (**1**) and divalent (**2**) Palladium complexes containing the *cis*-fixed bidentate nitrogen ligands bis(arylimino)-acenaphthene (e.g. Ph- BIAN).

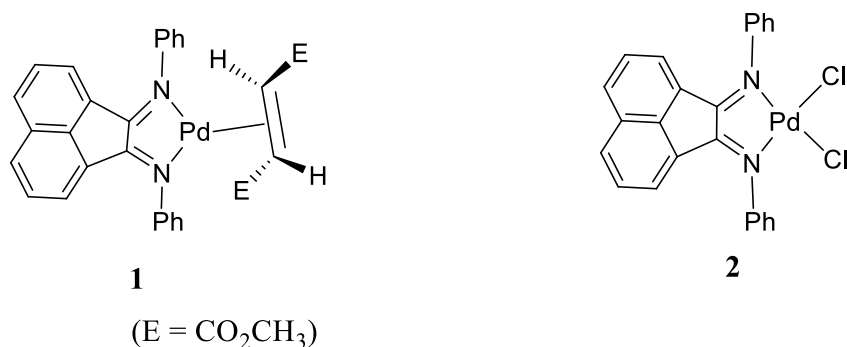


Figure 3. Palladium complexes having oxidation state (0) and (II).

Both higher and lower oxidation states, it is necessary in an alternating sequence of oxidative addition and reductive elimination, for stabilized. Furthermore, the diorganopalladium (II) complex formed after transmetalation has both organic groups in a fixed *cis* orientation, facilitating reductive elimination from this type of complex. Apart from the anticipated behavior it appears, those zerovalent [Pd(Ar-BIAN)(alkene)] complexes are also active as catalysts in the homogeneous hydrogenation of electron-poor alkenes. They report that palladium complexes of the types **1** and **2** are indeed active in a variety of carbon-carbon bond-forming reactions under mild conditions using several organic electrophiles (including acyl, aryl, benzyl, vinyl, and 1,2-dienyl halides) with organomagnesium, -zinc, and -tin reagents. The cross-coupling reaction between organic halides and organomagnesium and -zinc reagents readily takes place in tetrahydrofuran (THF) at 20 °C, and conversion of the organic electrophile is generally complete within several hours with 1% of compound **1** or **2** as the catalyst. The Palladium-(II) and (IV) species active catalysts in C-C bond-forming reactions have been stabilized by adding phenanthroline as a ligand.^[29] Palladium (IV) complexes have been postulated as intermediates in coupling reactions. In addition to the recently prepared complexes^[30], some penta fluorophenyl derivatives described few years ago must be regarded as the first examples of palladium (IV) complexes have been postulated as intermediates in coupling reactions.

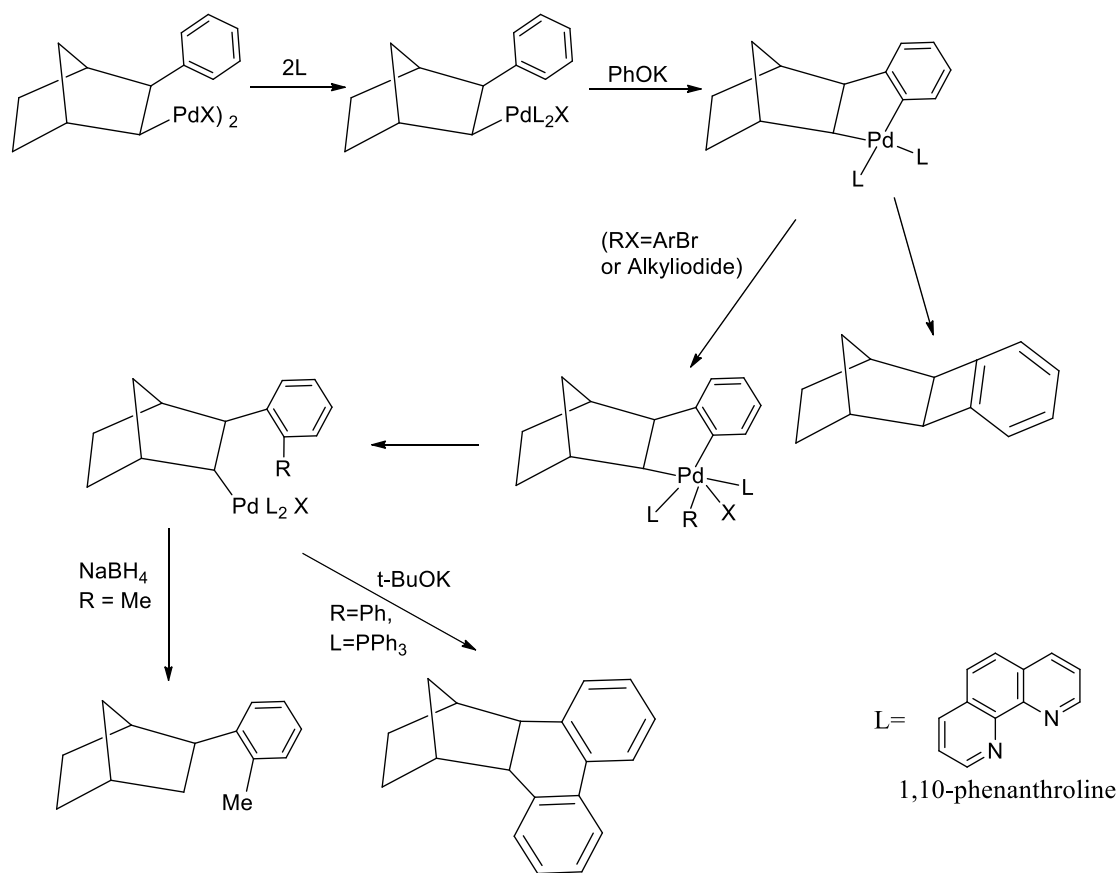


Figure 4. An example of a C-C coupling reaction using palladium (IV) as a catalyst.

2. Scope of the work:

In recent study of various kinds of α -diimine type moieties are known to stabilize a number of transition metal ions using their various coordination modes and those are successfully used in olefin polymerization. Our group have already done rigid bi-dentate [NO] based ligand system and the metal complexes of $ZnCl_2$, ZnI_2 and $ZnBr_2$ with the [NO] based Ar-BIAN/ Ar-BIAO ligands. Now our aim to synthesize the unsymmetrical Ar-BIAN ligand which contain imine-silyl group in one side and other side of the imine nitrogen will contain aryl group. This modified Ar-BIAN ligand is less steric than the Ar-BIAN ligands reported by *Van Asselt and Elsevier* and can show moderate difference in electronic and steric environment. The example of our target ligands are shown below.

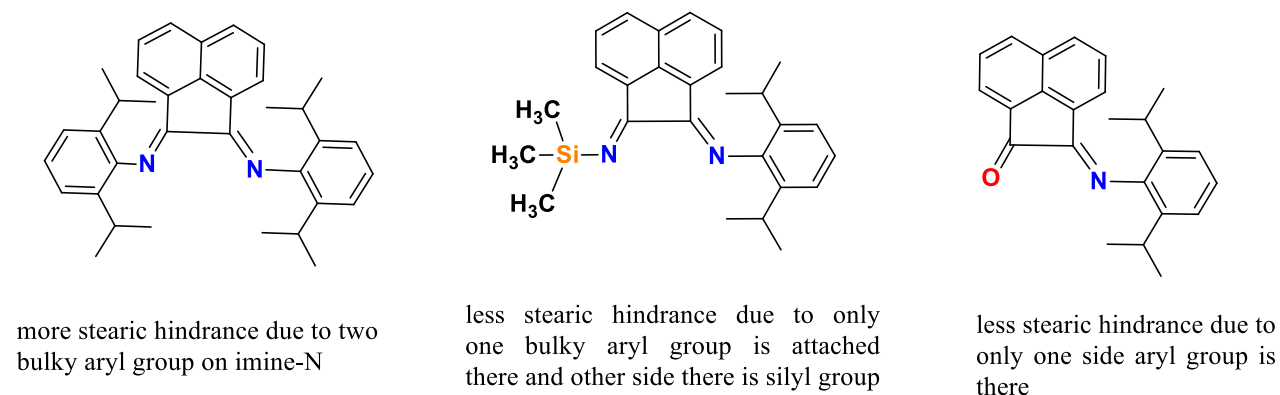


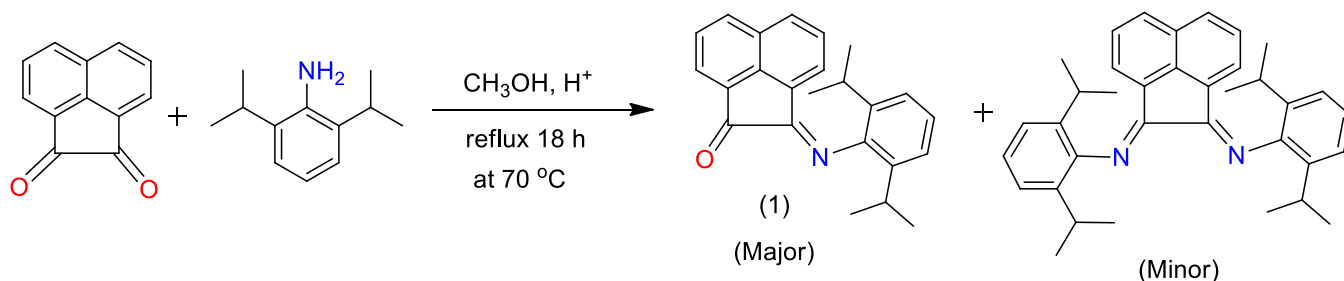
Figure 5. Comparison between BIAN and BIAO Ligands

The Ar-BIAN ligands reported previously have more steric hindrance than Ar-BIAN ligands containing one side silyl group and another side containing aryl group. The introduction of silyl group at the imine nitrogen can enhance the solubility of these ligand systems in hydrocarbons like pentane, hexane, etc.

3. Results and Discussion:

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

The ligands (Ar-BIAO) have been already prepared in our group and various metal-complexes like copper, zinc with these ligands are reported.^[31, 32] To extend the diversity of the BIAO ligand, we wanted to introduce the silyl group into this rigid unsymmetrical system. Such system can be thought of as Ar-BIAN-silyl (**1a**) and Ar-BIANH (**1b**) ligands. The Ar-BIAO ligands were successfully synthesized by our group as a major product and the side product is corresponding (Ar-BIAN) ligand in minor. The synthesis of (Ar-BIAO) ligand is simply single condensation with corresponding arylamine in methanol and catalytic amount of acetic acid was used to reflux at 70 °C for 18 h.



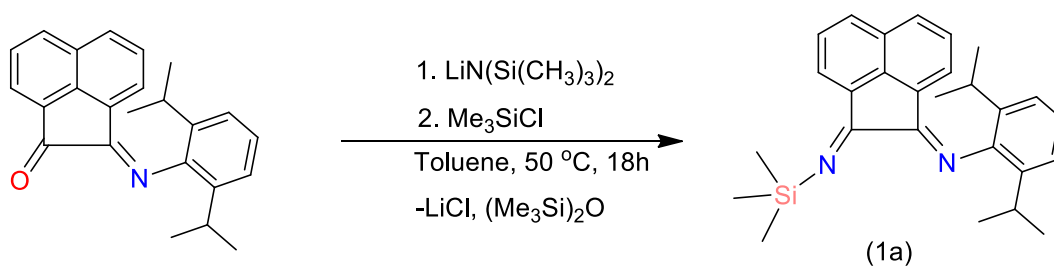
Scheme 2. Synthesis of (Ar-BIAO) ligand starting material for (Ar-BIAN-silyl) ligand (**1a**).

The re-synthesis of Ar-BIAO has been done by our group member previously and characterized by FT-IR, UV-visible, ¹H, ¹³C {¹H} NMR spectroscopy. The spectral data are in agreement with previously reported values.

3.1. Synthesis of N-2-((2,6-diisopropyl)imino)acenaphthylen-1(2H)-ylidene)-1,1,1-trimethylsilanamine ligand (Ar-BIAN-silyl) (**1a**):

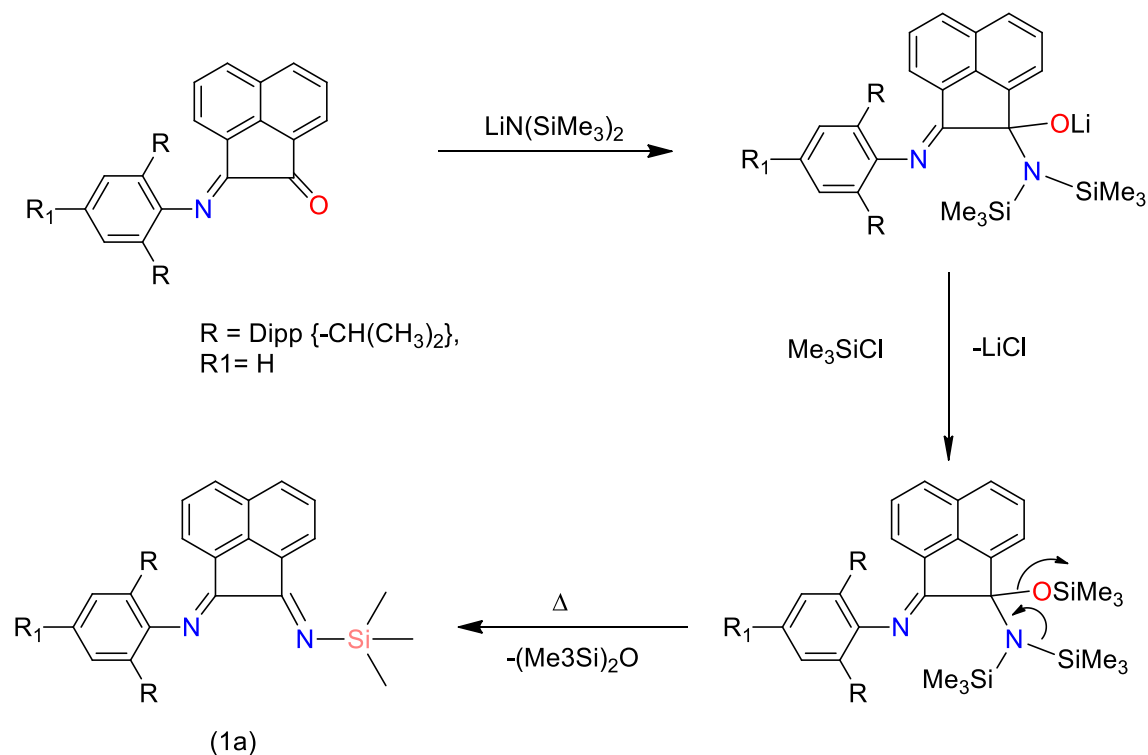
The ligand **1a** was prepared successfully as a major product by the reaction of Ar-BAIO ligand with $(\text{Me}_3\text{Si})_2\text{NLi}$ and Me_3SiCl in toluene solvent under reflux at $80\text{ }^\circ\text{C}$ in inert atmosphere. After 20 h of stirring the solvent was evaporated through rotatory evaporator and then the solid residue was washed with pentane and the title compound was re-crystallized from dichloromethane at $0\text{ }^\circ\text{C}$.

In FT-IR spectra of compound **1a** two strong absorptions was observed at 1625 cm^{-1} and 1658 cm^{-1} for the two different C=N bond stretching due to their different electronic environment, whereas the C=N stretching in 1,2-bis[(trimethylsilyl)imino]acenapthenene^[33] was observed at 1673 cm^{-1} and the expected value of C=N stretching should be $1700\text{-}1600\text{ cm}^{-1}$. The C=N bond stretching of **1a** ligand was observed at low frequency in comparison to reference compound due to resonance in both side C=N bond together and they are in different environment as one side has Me_3Si - group and another side is 2,6-diisopropylphenyl (Dipp). Strong absorptions at 1585 , 1460 , 1435 cm^{-1} can be assigned to the sp^2 C=C bond stretching of aromatic ring. The absorption of C=N bond stretching takes place at higher wavelength than C=C bond due to high electronegativity of Nitrogen. The absorption at 2961 cm^{-1} is for sp^3 hybridized C-H bond stretching and at 849 cm^{-1} is for C-H bond deforming.



Scheme 3. Synthesis of N-2-((2,6-diisopropyl)imino)acenaphthylen-1(2H)-ylidene)-1,1,1-trimethylsilanamine (Ar-BIAN-silyl) ligand (**1a**).

In the ^1H NMR spectrum of compound **1a**, the strong signal at 0.64 ppm can be assigned the presence of silyl group which is more shielded than alkyl group, and the reference compound 1,2-Bis[(trimethylsilyl)imino]acenaphthene^[33] displays the resonance signal for Me_3Si group at 0.43 ppm. The two doublets in 1:1 ratio were observed at 0.80 ppm and 1.12 ppm for CH_3 protons of isopropyl moiety in the aromatic ring, but they are slightly at different region due to having different chemical environments. A septet signal was observed at 2.93 ppm for CH proton of isopropyl group which indicates that the presence of tertiary carbon on the aromatic ring. The aromatic moiety show the resonance from 6.5-8.0 ppm. In $^{13}\text{C}\{^1\text{H}\}$ NMR, the resonance signal observed at 166.6 ppm indicates the presence of $\text{C}=\text{N}$ moiety which is further attached to aromatic group where as another peak absorbed at 160 ppm is also for $\text{C}=\text{N}$ but this is attached to $\text{Si}(\text{CH}_3)_3$, later Carbon of $\text{C}=\text{N}$ is more shielded than previous one due to presence of more shielding $\text{Si}(\text{CH}_3)_3$ group than less shielding aromatic ring. The conversion from (Ar-BIAO) to (Ar-BIAN- $\text{Si}(\text{CH}_3)_3$) have been shown in the above reaction and the possible mechanism of the above reaction is shown below.



Scheme 4. Proposed Mechanism of **1a** (Ar-BIAN-silyl).

The mechanism of this conversion taking place through nucleophilic attack on the carbonyl carbon. The Lithium-Hexamethyldisilazane i.e. $\text{LiN}(\text{Si}(\text{CH}_3)_3)_2$, here it acts as a nucleophile due to nitrogen have more electronegative nature than lithium metal in spite if this more polarity in between the Li^+ ion an N^- ion and the bond in between them is ionic in nature.

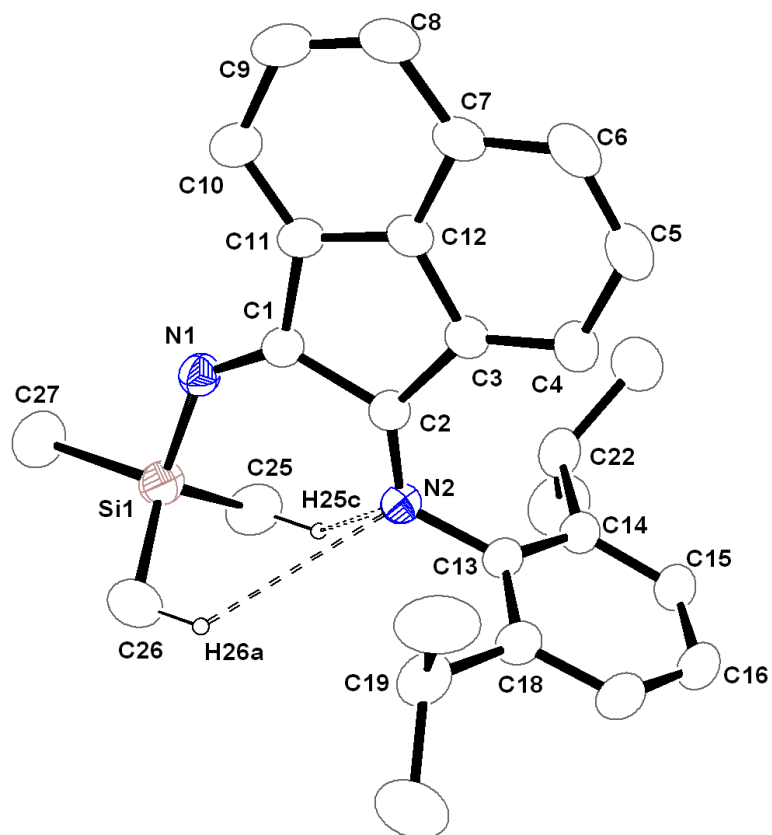


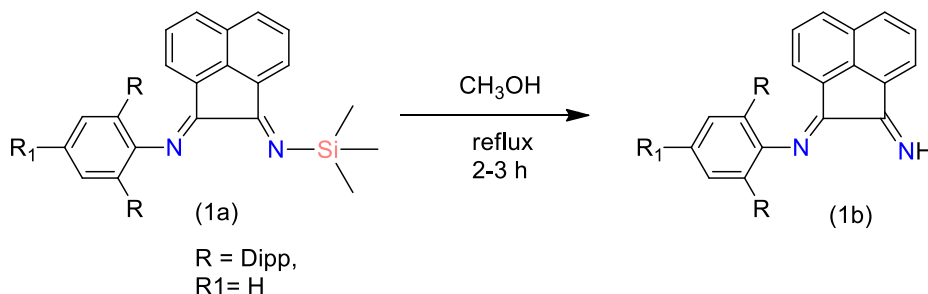
Figure 6. Solid-state structure of compound **1a** showing the atom labelled scheme. Selected bond lengths (Å): N(1)-C(1) 1.261(5), N(1)-Si(1) 1.740(4), N(2)-C(2) 1.270(5), N(2)-C(13) 1.432(5), C(2)-C(1) 1.538(6), C(2)-C(3) 1.490(6), C(1)-C(11) 1.485(6); Selected bond angles (°): C(2)-N(2)-C(13) 119.8(4), C(1)-N(1)-Si(1) 136.4(3), N(2)-C(2)-C(3) 132.2(4), N(1)-C(1)-C(11) 125.8(4), C(3)-C(2)-C(1) 106.7(4), C(11)-C(1)-C(2) 105.0(4), N(1)-C(1)-C(2) 129.1(4), N(2)-C(2)-C(1) 121.1(4).

So, the nitrogen attacking on the carbonyl carbon and the negative charge goes to oxygen which is stabilize through lithium. Then there is an attack of trimethylsilylchloride {Me₃SiCl} from which the elimination of LiCl takes place. Now there is -OSiMe₃ which is good leaving group, due to which on heating the elimination of disilylether (Me₃Si-O-SiMe₃) takes place i.e. Hexamethyldisiloxane and formation of **1a** takes place. This ligand is unstable in air because, apparently, of N-Si bond hydrolysis.

The solid state structure of compound **1a** was determined by single crystal X-ray diffraction analysis. Compound **1a** crystallizes in triclinic space group *P*-1 with four molecules per unit cell. The structural parameters for compound **1a** are given in Table 1. The molecular structure of compound **1a** is shown in Figure 6. The distance between C2-C3 1.490(6) Å and C1-C11 1.485(6) Å is almost similar and these bond values are smaller than actual value of C-C single covalent bond 1.54 Å and greater than the actual value of C=C double bond 1.33 Å it means its containing a single bond. The bond between C1-C2 is 1.538(6) Å which is clearly indicating that the observed bond is a single bond which is nearly identical to C-C single bond, the bond between C1-N1 1.261(5) Å and C2-N2 1.270(5) Å are comparable with corresponding the C-N bond lengths (1.2702(19) and 1.2637(19) Å) in Ar-BIAN(SiMe₃)₂ [33] and corresponding 1,2-bis[(2,6-diisopropyl-phenyl)imino]acenaphthene (both bond lengths are 1.282(4) Å)^[34], and these bond length are smaller than the actual value of C=N bond 1.35 Å and greater than the actual value of C≡N bond 1.16 Å which is indicating that the bonds containing a double bond. The dihedral angle between plane containing naphthalene backbone i.e. C11-C1-C2 and imine aryl moiety i.e. C14-C13-C18 is 84.92° which is indicating that the two planes are orthogonal to each other due to steric hindrance of bulky aryl group on N2. The Centre C1 is making a plane with atom C11, C2, and N1 and its bond angles are N(1)-C(1)-C(11) 125.8(4)°, C(11)- C(1)-C(2) 105.0(4)°, N(1)-C(1)-C(2) 129.1(4)° which is indicating that the Centre C1 showing distorted trigonal planar geometry. Similarly, C2 Centre is also showing distorted trigonal planar geometry due to containing same plane and their bond angles are almost similar to trigonal planar geometry. The two interactions are observed between N2-H25c 2.568 Å, N2-H26a 2.906 Å which is intramolecular H-bonding.

3.2 Synthesis of N-(2-iminoacenaphthylen-1(2H)-ylidene)-2,6-diisopropylaniline (Ar-BIAN-H) Ligand (**1b**):

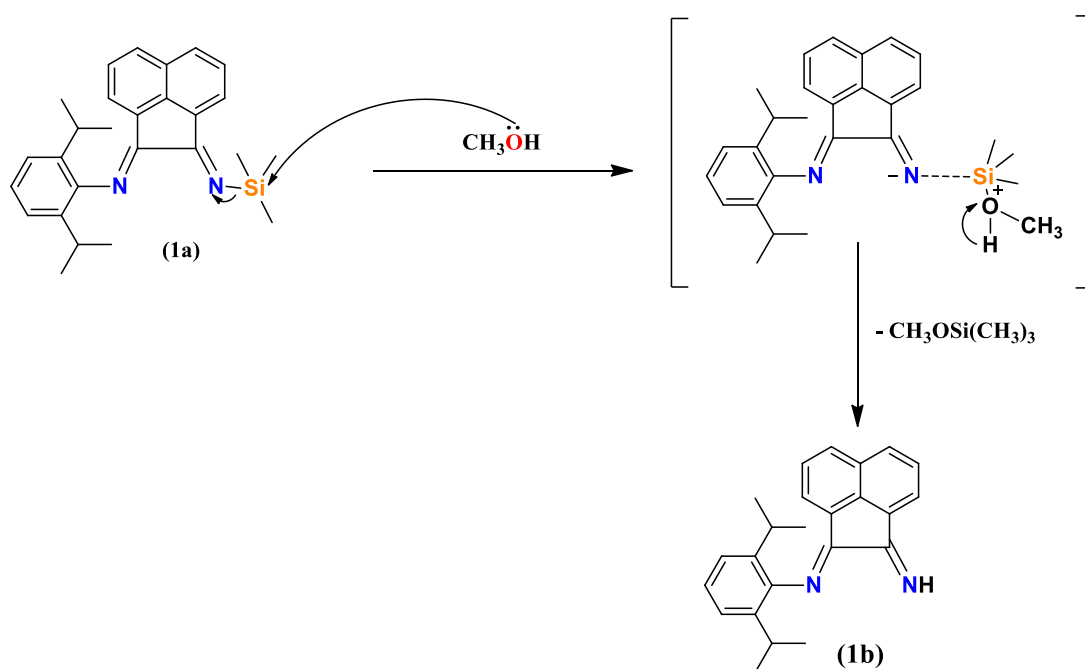
The ligand **1b** has been synthesized successfully, by reaction in the presence of methanol under reflux for 2-3 h. In presence of methanol nucleophilic attack of oxygen lone pair on silicon takes place due to polar nature of N-Si bond. This ligand **1a** is not inert in air. The electronegativity of N is 3.0 and of Si 1.9 which is designating that nitrogen is more electronegative than silicon due to this cause the bond between them is more polar and the electronegativity difference is more in between them and specifying, N-Si bond is weak. More polar bonds means it is ionic in nature and the bond strength of ionic bond is weaker than covalent bond due to which the nitrogen of imine moiety behaves as anionic ligand and they undergo hydrolysis readily. This is an unsymmetrical rigid BAIN-ligand which is containing one side aryl group i.e. 2,6-diisopropylphenyl and other side -Si(CH₃)₃. And both substituting groups showing different electronegativity i.e. N-C bond are less polar than N-Si, and stable in air due to less electronegativity difference between N-C bond.



Scheme 5: Synthesis of Ar-BIANH (**1b**).

In FT-IR spectra of compound **1b**, a strong absorption at 1725 cm⁻¹ and 1636 cm⁻¹ for two different C=N bond stretching i.e. C=N-aryl and C=N-H respectively, whereas the general absorption takes place 1700-1600 cm⁻¹. The absorption of C=N-aryl is at higher frequency than the C=N-H because of the delocalization in the aryl ring when the nitrogen donates its lone pair to the ring and causing -R effect. The absorption observed at 3054 cm⁻¹ for -NH stretching and the generally the absorption of imine group takes place at around 3300-3000 cm⁻¹ frequency. The absorption at 2958 cm⁻¹ is for aromatic C-H (sp²) stretching and at 2866 cm⁻¹ for isopropyl C-H (sp³) stretching. The absorptions around 1591, 1518, 1488, 1460, and 1428 cm⁻¹ is for aromatic C=C (sp²) stretching. The absorption at 779 cm⁻¹ is due to C-H bending.

In ^1H NMR spectrum of ligand **1a**, the two doublet at 0.91 ppm and at 1.16 ppm in 1:1 ratio are obtained, which can be assigned as methyl protons attached to isopropyl groups on the aromatic ring. The septet obtained at $\delta = 2.79$ ppm for methyl protons attached with tertiary carbon atom for **1a**. The absorptions at 7.25, 7.36, 7.78, 7.98, and 8.25 ppm indicating the aromatic protons. A sharp singlet absorbed at 11.16 ppm is for imine proton indicating that the imine proton is deshielded. In ^{13}C $\{^1\text{H}\}$ NMR spectra of ligand **1a**, peaks at $\delta = 23.13, 23.18$ ppm is for aromatic ring which can be assigned as methyl carbon attached to isopropyl groups on the aromatic ring. The absorption at 28.40 ppm is for tertiary carbon of isopropyl group in the aromatic ring. The absorption at 157.07 ppm and 169.98 ppm indicating the presence of imine carbon having different C=N moiety. The prior δ value is for C=NH due to more shielding effect than the later δ value which is for C=N-(2,6-diisopropylphenyl). The mechanism of above reaction is showing below Scheme 6.



Scheme 6: Proposed Mechanism of **(1b)**.

In this mechanism the desilylation takes place. The oxygen from methyl, acts as a nucleophile, occurs nucleophilic attack on the silicon atom of silylimine ruptures the N-Si bond and the proton is abstracted by imine nitrogen and hence, leading to imine and silylmethylether. The proton on

nitrogen in imine group acts as an acidic in nature and N-H bond ionic in nature due to electronegativity difference between them due to which it can easily replace through any other substituent which is containing transition metals and main group metals complexes.

The solid-state structure of ligand **1b** was established by single crystal X-ray diffraction analysis. The structural parameters of ligand **1b** are given in Table 1. The solid state molecular structure is shown below in figure 7. The compound **1b** crystallize in the triclinic and space group *P*-1 having one independent molecule in asymmetric unit. The bond length between C1-C11 1.475(6) Å, C2-C3 1.482(6) Å both are almost similar together and similar to the compound **1a** i.e. containing single bond; bond length between C2-N2 1.283(5) Å, C1-N1 1.273(6) Å also similar to compound **1a** and showing double bond, having similar bond length corresponding 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (both bond lengths are 1.282(4) Å).^[34] and the bond between C1-C2 1.528(6) Å is a single bond in comparison to compound **1a**. The Centre C1 and C2 both are showing distorted trigonal geometry similar to ligand **1a**, having all atoms in one plane and almost similar bond angles.

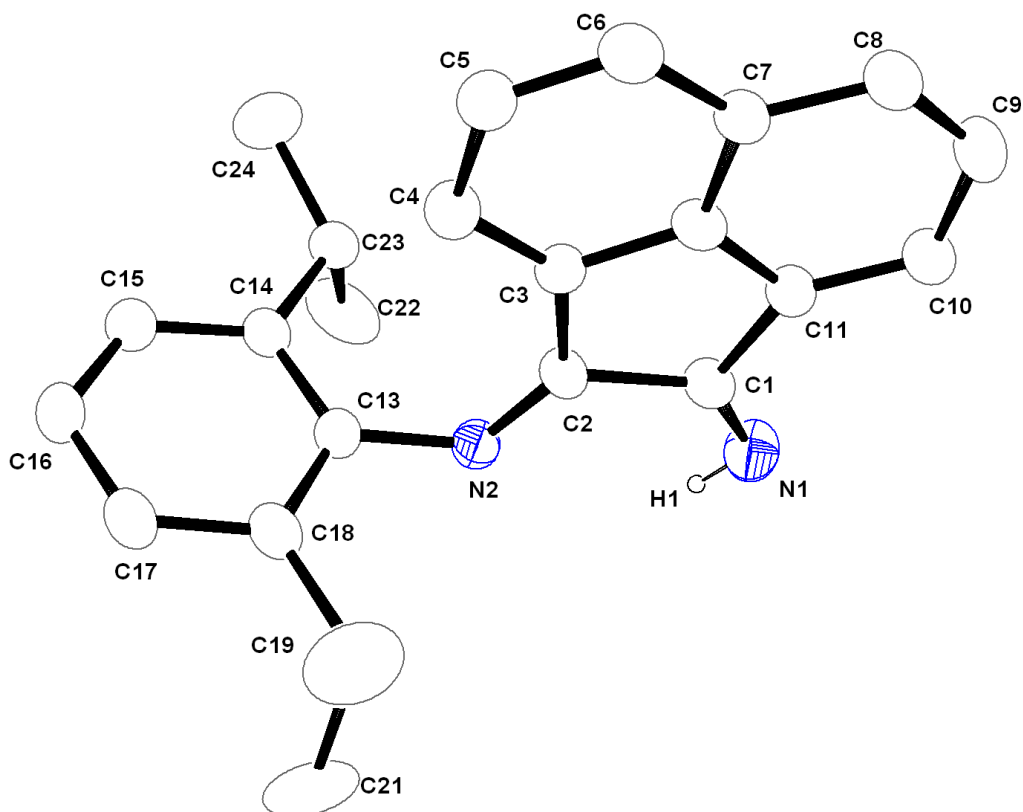
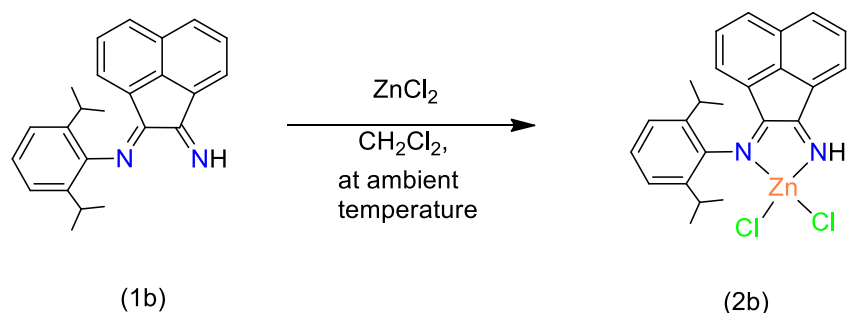


Figure 7. Solid-state structure of compound **1b** showing the atom labelled scheme. Selected bond lengths (Å): N(1)-C(1) 1.273(6), N(2)-C(2) 1.283(5), C(2)-C(1) 1.528(6), C(3)-C(2) 1.482(6), C(1)-C(11) 1.475(6), N(2)-C(13) 1.423(6), N(1)-H(1) 0.7500; Selected bond angles (°): N(2)-C(2)-C(1) 134.4(4), N(2)-C(2)-C(3) 105.9(4), N(2)-C(2)-C(13) 120.3(4), N(1)-C(1)-C(11) 126.4(5), N(1)-C(1)-C(2) 127.4(4), C(11)-C(1)-C(2) 106.2(4), C(1)-N(1)-H(1) 109.5, C(2)-N(2)-C(13) 120.3(4).

The dihedral angle between two planes C3-C2-C1 and C14-C13-C18 is 86.67°, which is indicating the two planes are orthogonal to each other due to steric hindrance repulsion. The bond between N1-H1 0.75 Å indicating that there is electrostatic interaction which indicates that the bond is ionic in nature.

3.3. Zinc complex with (Ar-BIANH) ligand:

The formation of zinc (II)-complex takes place in presence of dichloromethane on constant stirring and kept overnight at ambient temperature. Then evaporate the solvent under high vacuum. And then double layered through n-pentane and kept for crystallization for 2-3 days. And then re-crystallized it through dichloromethane at 0 °C.



Scheme 7: synthesis of [ZnBr₂-(Ar-BIAN-H)] (**2b**).

In FT-IR spectra of compound **2b**, a strong absorption at 1630 cm⁻¹ and 1519 cm⁻¹ for two different C=N bond stretching i.e. C=N-aryl and C=NH respectively, whereas the general absorption takes place 1700-1600 cm⁻¹. The absorption of C=N-aryl is at higher frequency than the C=NH because of the delocalization in the Dipp ring when the nitrogen donates its lone pair to the ring and causing -R effect. The absorption observed at 3219 cm⁻¹ for -NH stretching and the generally the absorption of imine group takes place at around 3300-3000 cm⁻¹ frequency. The absorption at 2963 cm⁻¹ is for aromatic C-H (sp²) stretching and at 2870 cm⁻¹ for isopropyl C-H (sp³) stretching. The absorptions around 1519, 1429, and 1387 cm⁻¹ is for aromatic C=C (sp²) stretching. The absorption at 847 cm⁻¹ is due to C-H bending. ¹H NMR spectrum of the compound **2b** in CDCl₃ shows two doublet at 1.36 ppm and 0.86 ppm for methyl proton in isopropyl of aromatic ring. These are more shielded than the corresponding ligand **1b**. The resonances of the protons of acenaphthene back-

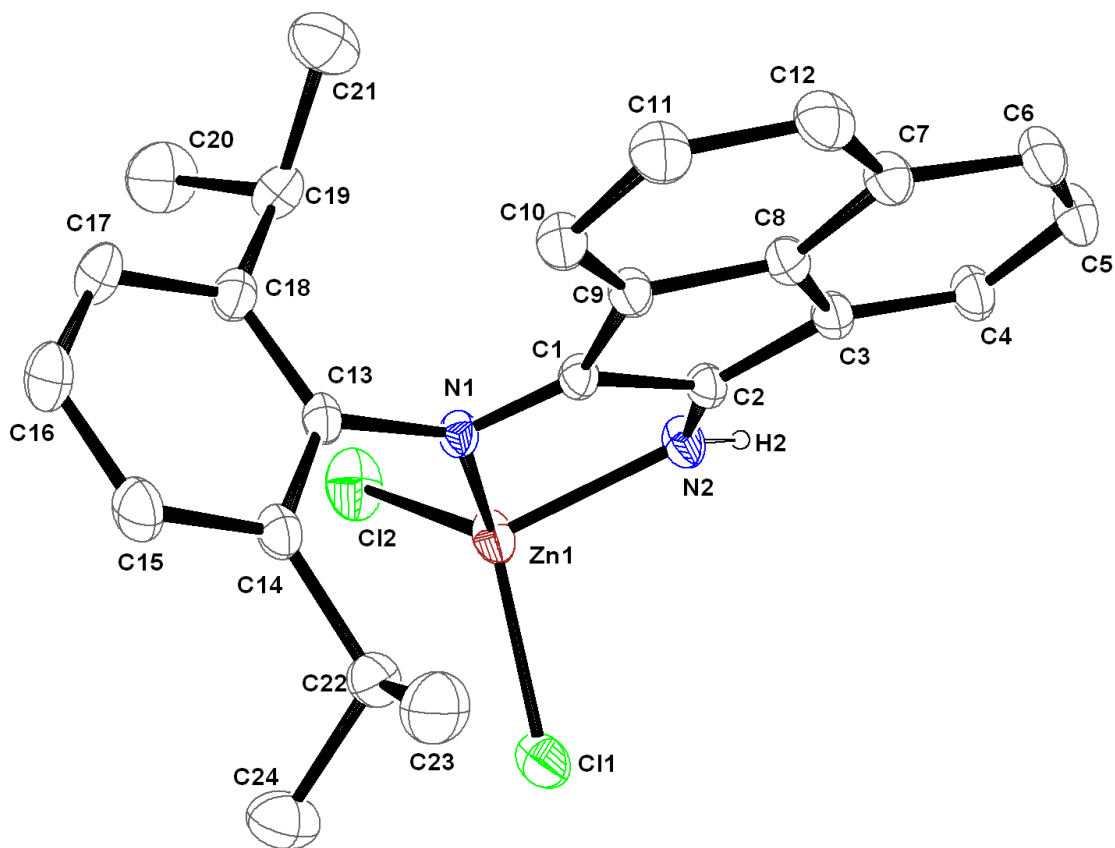


Figure 8. Solid-state structure of compound **2b** showing the atom labelled scheme. Selected bond lengths (Å): Zn(1)-N(2) 2.060(2), Zn(1)-N(1) 2.1114(19), Zn(1)-Cl(2) 2.1703(11), Zn(1)-Cl(1) 2.2203(11), N(1)-C(1) 1.273(3), N(1)-C(13) 1.447(3), N(2)-C(2) 1.262(3), N(2)-H(2) 0.8600, C(1)-C(9) 1.464(3), C(1)-C(2) 1.520(3), C(2)-C(3) 1.458(3); Selected bond angles (°): N(2)-Zn(1)-N(1) 81.11(8), N(2)-Zn(1)-Cl(2) 123.40(8), N(1)-Zn(1)-Cl(2) 115.23(6), N(2)-Zn(1)-Cl(1) 102.60(7), N(1)-Zn(1)-Cl(1) 108.38(6), Cl(2)-Zn(1)-Cl(1) 119.40(5), C(1)-N(1)-C(13) 120.1(2), C(1)-N(1)-Zn(1) 109.91(15), C(13)-N(1)-Zn(1) 130.01(15), C(2)-N(2)-Zn(1) 111.82(17), C(2)-N(2)-H(2) 124.1, Zn(1)-N(2)-H(2) 124.1, N(1)-C(1)-C(9) 134.9(2), N(1)-C(1)-C(2) 118.1(2), C(9)-C(1)-C(2) 106.99(19), N(2)-C(2)-C(3) 135.2(2), N(2)-C(2)-C(1) 118.0(2), C(3)-C(2)-C(1) 106.7(2).

bone and aryl ring are in the expected region in between 6.5-8.6 ppm and in well agreement all the chemical shift values shifted to high field region i.e. deshielded. The peak at 11.79 ppm can be

assigned for the imine proton and chemical shift value shifted to downfield than the corresponding ligand **1b**. In ^{13}C $\{^1\text{H}\}$ NMR spectrum of the compound **2b**, the chemical shift at 170.29 ppm and 166 ppm are the indication of formation of imine groups C=N-Ar and C=N-H respectively. The both shift falls on the downfield region than the corresponding ligand.

The solid state structure of Zinc (II) complex **2b** was established by single crystal X-ray diffraction analysis. The structural parameters are given in Table 1. The molecular structure of the compound **2b** is shown in figure 8. The compound **2b** was crystallized in dichloromethane solvent as a monomer. The compound **2b** crystallize in the monoclinic space group $P2_1/c$ having four molecule in the asymmetric unit. General coordination number of zinc (II) is from 4 as a result of which the geometry will be best described as a distorted tetrahedral geometry with N1, N2, Cl1, and Cl2. The bond angle of N1-Zn1-N2 $81.11(8)^\circ$, which is unlike with the tetrahedral geometry and this deviation of bond angle is because of two different -N donor sites are rigidly bind with acenapthenene moiety. The Zn (1)-N(1) bond distance $2.1114(19) \text{ \AA}$ which is comparable with the reported one as $2.106(5) \text{ \AA}$ [$\text{ZnCl}_2(\text{mes-BIAO})$]^[35,36] and the Zn(1)-N(2) bond distance is $2.060(2) \text{ \AA}$ which is almost comparable with the reported one Zn(1)-O(1) $2.123(4) \text{ \AA}$ in the complex [$\text{EtZn}\{\text{N}(\text{t-Bu})\text{CH}_2\text{C}(\text{NEt})\text{O}\}_2$]^[37]. There is a five membered metallacyclic ring Zn1-N1-C1-C2-N2 which is formed through ligation by the lone pairs of both neutral imine nitrogen. The C1-N1 and C2-N2 bond distances are respectively $1.273(3) \text{ \AA}$ and $1.262(3) \text{ \AA}$, which are similar and unperturbed compare to that of respective ligand. The C1-C2 bond distance is $1.520(3) \text{ \AA}$, which is indicating that the bond is a C-C single bond. The acenapthenene plane and the plane containing N1, N2, and Zn1 atoms are almost coplanar.

UV-Vis spectra of Ligands and Zinc-metal complex:

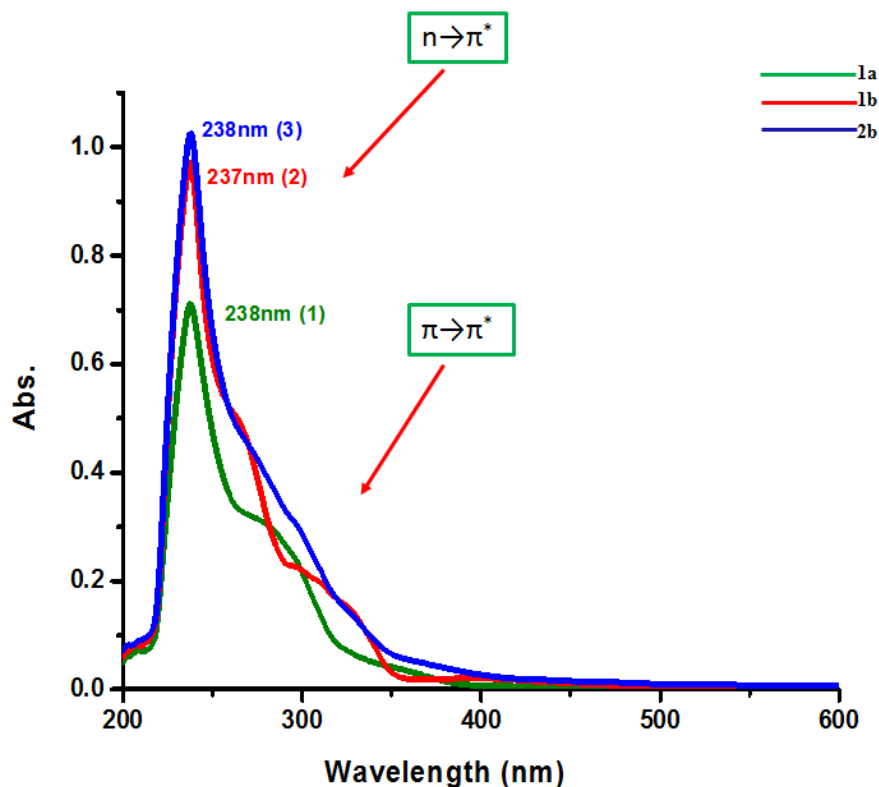


Figure 9. UV- Vis spectrum of **1a**, **2a**, and **2b** in CH_2Cl_2 .

UV-visible absorption spectra of **1a**, **1b** and **2b** (Fig.6) were measured in dichloromethane at room temperature and showing comparable $\pi \rightarrow \pi^*$ absorption peaks at 203-303 nm, $n \rightarrow \pi^*$ absorption peaks from 250-350 nm. The $\pi \rightarrow \pi^*$ transition represents the promotion of π electrons to an antibonding π orbital, i.e., π^* orbital. Similarly when an n -electron (non-bonding) is promoted to antibonding π orbital, i.e., π^* orbital. The $\pi \rightarrow \pi^*$ transition are more intense in comparison to $n \rightarrow \pi^*$ transitions. Here, we are comparing the UV-visible spectra of two different precursor of the ligand. On changing the $-\text{NSiMe}_3$ moiety into $-\text{NH}$ clearly indicated the hyperchromic shift due to changing the more electron-withdrawing substituents to less electron- withdrawing substituent. Whenever in case of metal complex **2b** there is clearly indication of bathchromic shift (red shift) due to changing of electron environment around the metal centre. The respective ν_{max} values of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are given in Table.2.

The transitions with the values of (molar absorptivity) ν_{\max} , more than 10^4 are usually indicates the allowed transitions in the observed compound. They generally arise due to $\pi \rightarrow \pi^*$ transitions. The value of ν_{\max} below to 10^4 for $n \rightarrow \pi^*$ transitions which indicates the forbidden transitions in the reported compounds.

4. Experimental section:

4.1. General Information

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glove box. Dichloromethane and diethyl- ether were dried with P_2O_5 followed by distillation and kept under molecular sieves prior to use. Methanol were also dried under nitrogen from sodium and kept under molecular sieves prior to use. Hydrocarbon solvents i.e. toluene and *n*-pentane were distilled under nitrogen from $LiAlH_4$ and stored in glove box. 1H NMR (400 MHz) and ^{13}C {H} NMR (C100 MHz) spectra were recorded with a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed with a BRUKER EURO EA at Indian Institute of Technology Hyderabad. $ZnCl_2$ was purchased from Sigma Aldrich and used without any purification.

4.2. Preparation of N-2-((2,6-diisopropyl)imino)acenaphthylen-1(2H)-ylidene)-1,1,1-trimethylsilanamine (Ar-BIAN-silyl) ligand (1a):

In a dry degassed Schlenk tube, the re-prepared ligand **1** (1g, 2.937mmol) was taken and around 10 mL of toluene was added into it and stir it till completely dissolved under inert atmosphere. In another dry degassed Schlenk tube $LiN(SiMe_3)_2$ (492mg, 2.937mmol) was taken and into it 10 mL toluene was added and stir it till the completely dissolved under inert atmosphere. Then the $LiN(SiMe_3)_2$ reaction mixture was added drop wise with stirring into the ligand **1** Schlenk tube because whole reaction mixture get react. The resulting reaction mixture heated with continuous stirring for 1.5 h and then take it out and cooled it at room temperature. After this into it the reagent

Me₃SiCl (320mg, 0.4mL, and 2.937mmol) was added drop wise with constant stirring under inert atmosphere. And then heat it for 20h with constant stirring at 90 °C. After this filtered the filtrate with cannula technique, evaporate the solvent through rotatory evaporator under inert condition and then washed with n-pentane. A pale yellow color compound was crystallized in CH₂Cl₂, **1a**: Yield: 350mg, 30 %. FT-IR (selected frequency in cm⁻¹): ν = 2961(*sp*³ C-H str.), 1625 (C=N str.), 1585, 1460, 1435(aromatic C=C str.), 849(C-H deforming), 1322 (*sp*³ C-H bending). ¹H NMR (400 MHz, CDCl₃): δ = 7.98 (d, 1H, Ar-*H*), 7.35 (d, 1H, Ar-*H*), 7.29 (d, 1H, Ar-*H*), 7.16 (t, 3H, Ar-*H*), 7.08 (s, 1H, Ar-*H*), 6.74 (t, 1H, Ar-*H*), 6.65 (d, 1H, Ar-*H*), 2.93 (Sept., 2H, CH(CH₃)₂), 1.12 (d, 6H, CH(CH₃)₂), 0.803 (d, 6H, CH(CH₃)₂), 0.65 (s, 9H, Si(CH₃)₃); ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ = 166.57 (C=N-Ar), 159.98 (C=N-silyl), 28.55 (CH(CH₃)₂), 24.35 (CH(CH₃)₂), 24.04 (CH(CH₃)₂), 1.88 (CH₃ (silyl)).

4.3. Preparation of N-(2-iminoacenaphthylen-1(2H)-ylidene)-2,6-diisopropylaniline (Ar-BIAN-H) ligand (**1b**):

In a dry 100 mL round bottomed flask, ligand **1a** (862mg, 2 mmol) was taken and kept it under high vacuum for 1 h. Then 20 mL of dry methanol was added through syringe technique under inert atmosphere. The compound should be dissolved completely. This reaction mixture was reflux for 2-3 h with constant stirring at 70 °C. After this evaporate the solvent through rotatory evaporator and washed with n- pentane. The pale yellow color ligand was crystallized in dichloromethane, **1b**: Yield: 265mg, 92%. FT-IR (selected frequency in cm⁻¹): ν = 3054 (N-H str.), 2958 (*sp*³ C-H str.), 1725 (N-H deforming), 1637 (C=N str.), 1591, 1518, 1488 (aromatic C=C str.), 1356 (*sp*³ C-H bending). ¹H NMR (400 MHz, CDCl₃): δ = 11.16 (s, 1H, NH), 8.25 (d, 1H, Ar-*H*), 8.01 (d, 1H, Ar-*H*), 7.92 (d, 1H, Ar-*H*), 7.78 (t, 1H, Ar-*H*), 7.36 (t, 1H, Ar-*H*), 7.25 (s, 3H, Ar-*H*), 6.6 (d, 1H, Ar-*H*), 2.790 (Sept., 2H, CH(CH₃)₂), 1.16 (d, 6H, CH(CH₃)₂), 0.91 (d, 6H, CH(CH₃)₂); ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ = 169.98 (C=N-Ar), 157.07 (C=N-H), 28.40 (CH(CH₃)₂), 23.18 (CH(CH₃)₂), 23.13 (CH(CH₃)₂).

4.4. Preparation of Zinc-metal complex with ligand **1b**:

In a dry degassed Schlenk tube, ligand **1b** (100mg, 0.293mmol) was taken into it added ZnCl₂ (40.02mg, 0.293mmol) and kept it under high vacuum for 1 h to remove the remaining moisture from the compound, and then 10 mL dichloromethane (CH₂Cl₂) was added and stirred it continuously for overnight. A change in color from dark yellow to light pale yellow was observed. Filtered the filtrate through cannula technique then evaporate the half solvent under high vacuum and then double-layered with n-pentane and kept it at -40 °C for 2 days. The yellowish color crystals was observed, **2b**: Yield: 50 mg, 70 %. FT-IR (selected frequency in cm⁻¹): ν = 3220 (N-H str.), 2964 (*sp*³ C-H str.), 1630 (C=N str.), 1587, 1520, 1429 (aromatic C=C str.), 1324 (*sp*³ C-H bending). ¹H NMR (400 MHz, CDCl₃): δ = 11.8 (s, 1H, NH), 8.67 (d, 1H, Ar-H), 8.14 (d, 1H, Ar-H), 8.07 (d, 1H, Ar-H), 7.85 (t, 1H, Ar-H), 7.46 (t, 1H, Ar-H), 7.25 (s, 3H, Ar-H), 6.6 (d, 1H, Ar-H), 3.17 (Sept., 2H, CH(CH₃)₂), 1.36 (d, 6H, CH(CH₃)₂), 0.86 (d, 6H, CH(CH₃)₂); ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ = 170.29 (C=N-Ar), 166 (C=N-H), 28.79 (CH(CH₃)₂), 25.05 (CH(CH₃)₂), 24.51 (CH(CH₃)₂).

5. Conclusion:

In conclusion, we have successfully synthesized and structurally characterized the ligands (Ar-BIAN-silyl) (**1a**) and (Ar-BIAN-H) (**1b**) by reported procedures. With ligand **1b**, we have successfully prepared the monomeric zinc complex, [(Ar-BIANH) ZnCl₂] (**2b**) which was spectroscopically characterized by the IR, NMR and its molecular structure was established by X-ray diffraction analysis. In the solid state, the zinc complex shows four fold coordination and adopts a distorted tetrahedral geometry. Further reactions to prepare zinc alkyls and amides with these ligand systems are in progress in our laboratory.

Table 1: Crystallographic data for compounds **1a**, **1b**, and **2b**.

Compound	1a	1b	2b
Identification code	exp-3671	exp-3943	exp-4465
Empirical formula	C ₂₇ H ₃₂ N ₂ Si	C ₂₄ H ₂₄ N ₂	C ₂₄ H ₂₄ Cl ₂ N ₂ Zn
Formula weight	412.64	340.45	443.86
Temperature(K)	293(2)	293(2)	293(2)
Wavelength (Å°)	0.71073	1.54184	1.54184
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
a (Å°)	11.7251(9)	8.9164(10)	10.7797(2)
b (Å°)	13.0093(9)	12.8023(17)	11.6483(2)
c (Å°)	17.3664(14)	18.020(2)	23.5361(5)
α (°)	79.035(7)	73.863(11)	90
β (°)	79.131(7)	85.674(10)	102.129(2)
γ (°)	79.251(6)	85.436(10)	90
Volume (Å ³)	2522.6(3)	1966.6(4)	2889.34(10)
Z	4	4	5
D _{calc.} mg m ⁻³	1.086	1.150	1.275
Absorption coefficient, μ(mm ⁻¹)	0.108	0.512	3.023
F(000)	888	728	1152
Theta range for data collection	1.61 to 25.82	3.60 to 71.33	3.84 to 71.07
Limiting indices	-14<=h<=12, -15<=k<=13, -21<=l<=20	-10<=h<=10, -15<=k<=14, -22<=l<=19	-9<=h<=13, -14<=k<=13, -28<=l<=25

Reflection collected / unique	18963 / 9465 [R(int)=0.0433]	11724 / 6429 [R(int)=0.0571]	12378 / 5461 [R(int)=0.0301]
Data / restraints / parameters	9465 / 0 / 555	6429 / 0 / 480	5461 / 0 / 321
R indices (R₁; wR₂)	(0.0688; 0.2086)	(0.0889; 0.2222)	(0.0592; 0.1349)

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

<i>Compound</i>	<i>Electron excitation</i>	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
1a	Wavelength of maximum absorption (nm)	275	238
	Absorbance	0.311	1.026
	Molar absorptivity ($M^{-1}cm^{-1}$)	6.2×10^3	2.05×10^4
1b	Wavelength of maximum absorption (nm)	289	238
	Absorbance	0.226	0.711
	Molar absorptivity ($M^{-1}cm^{-1}$)	4.5×10^3	1.42×10^4
2b	Wavelength of maximum absorption (nm)	226	237
	Absorbance	0.462	0.971
	Molar absorptivity ($M^{-1}cm^{-1}$)	9.2×10^3	1.92×10^4

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Appendix:

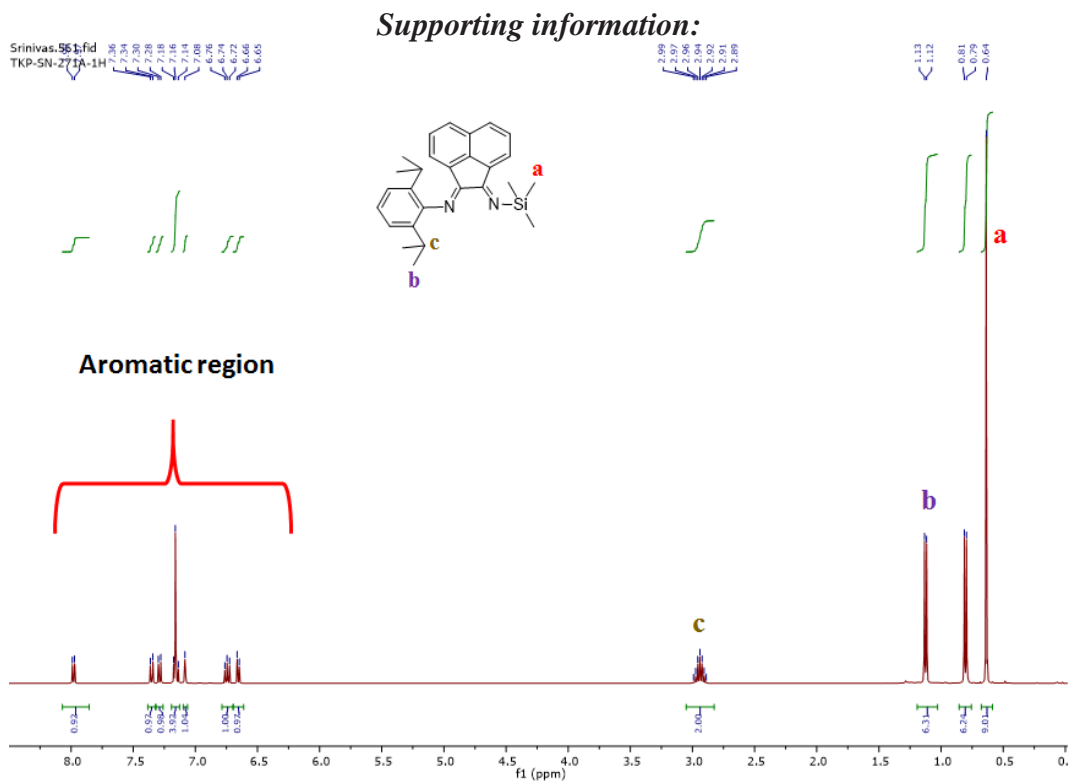


Figure 10: ¹H NMR Spectra of **1a**.

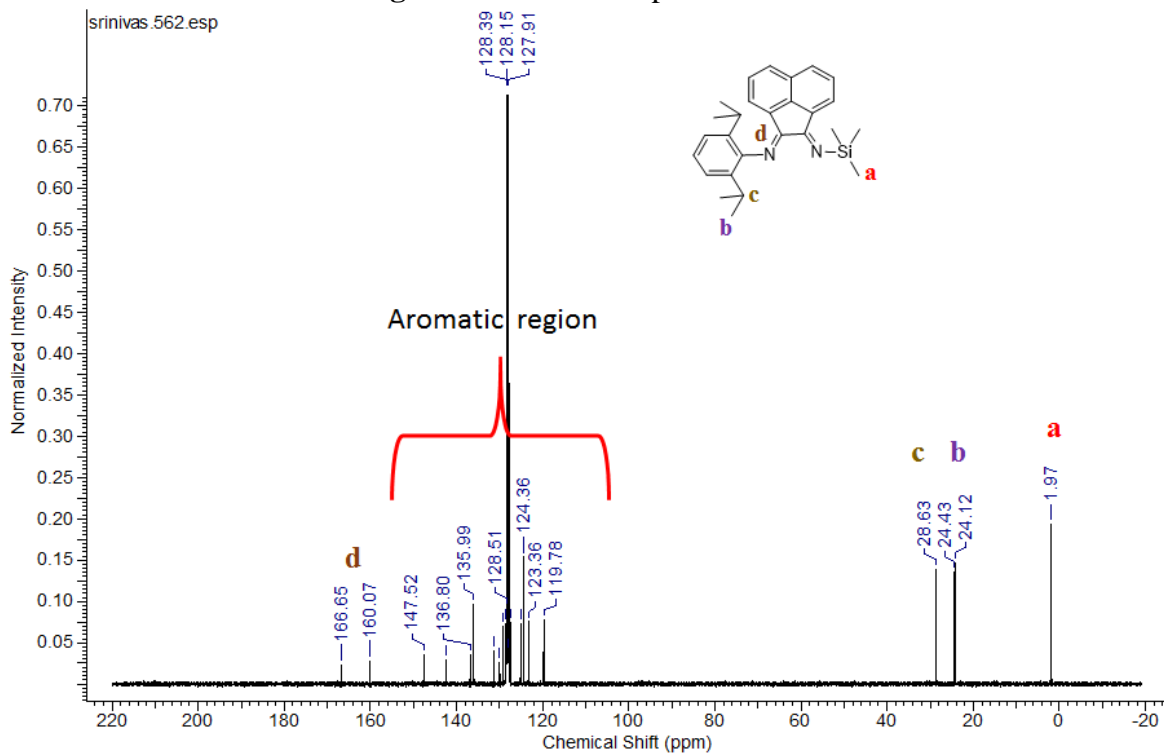
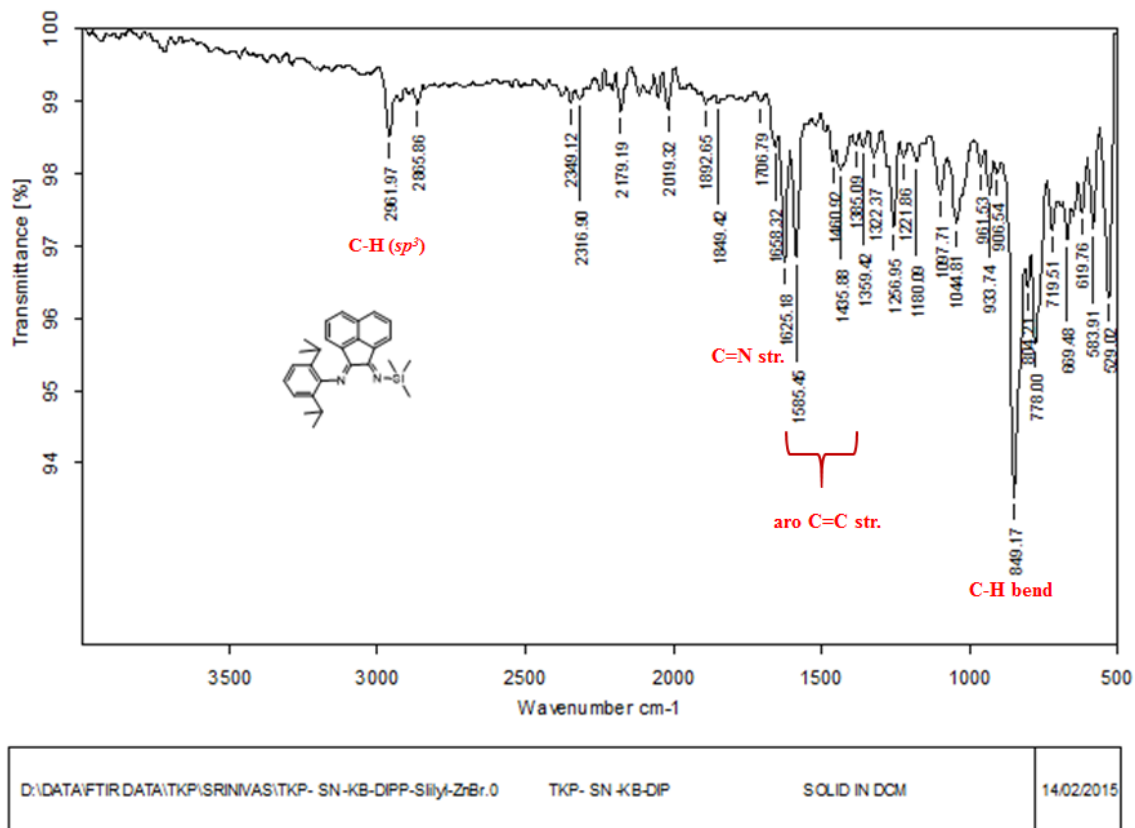


Figure 11: ¹³C {¹H} NMR Spectra of **1a**.



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Figure 12: FT-IR Spectra of 1b.

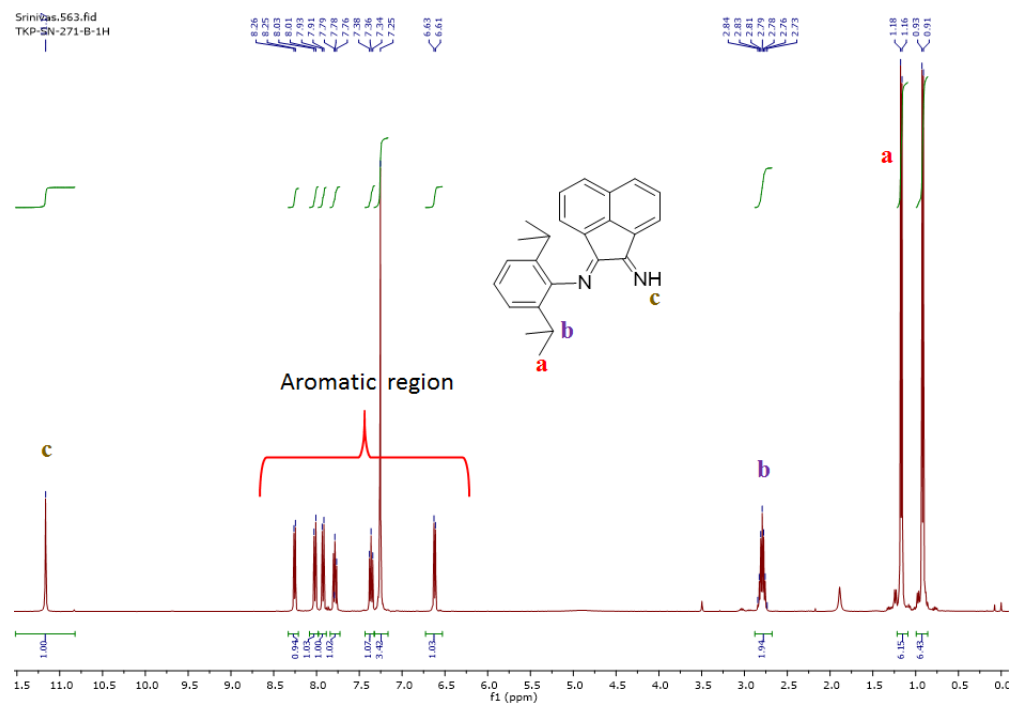


Figure 13: ¹H NMR Spectra of 1b.

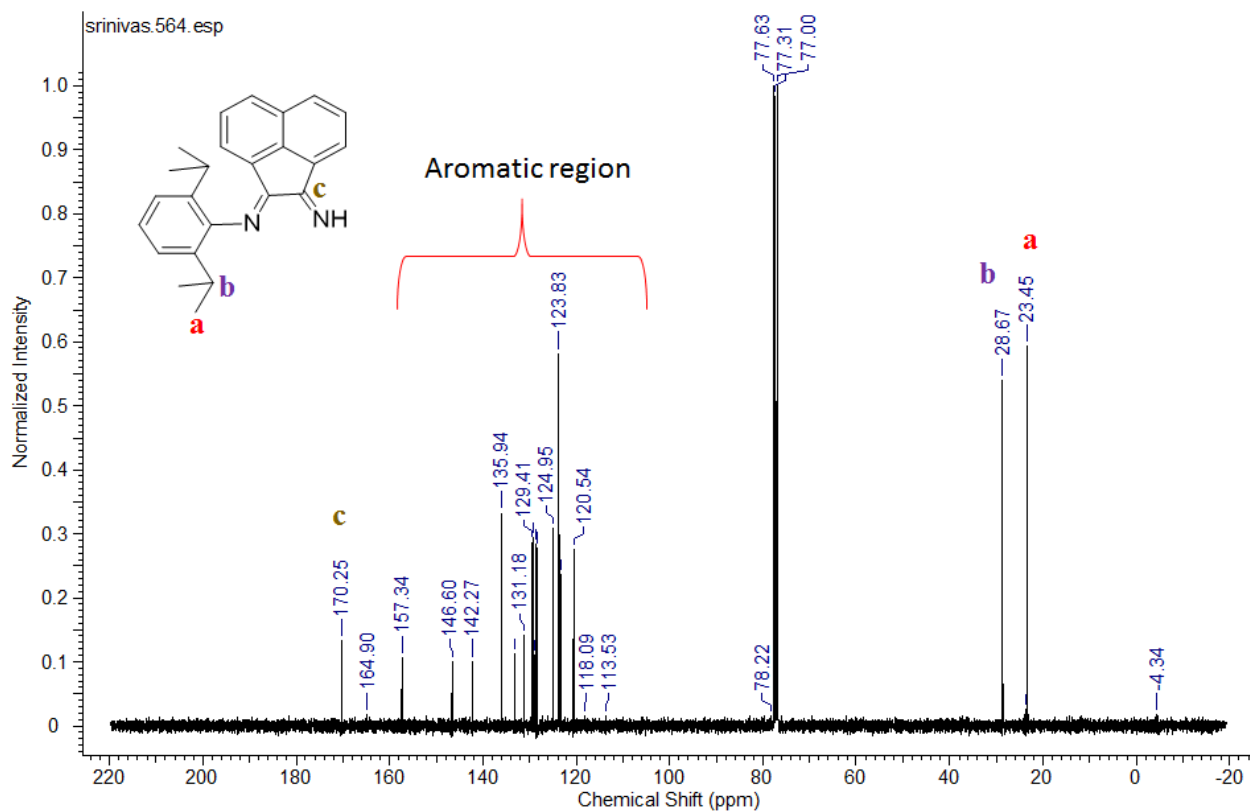
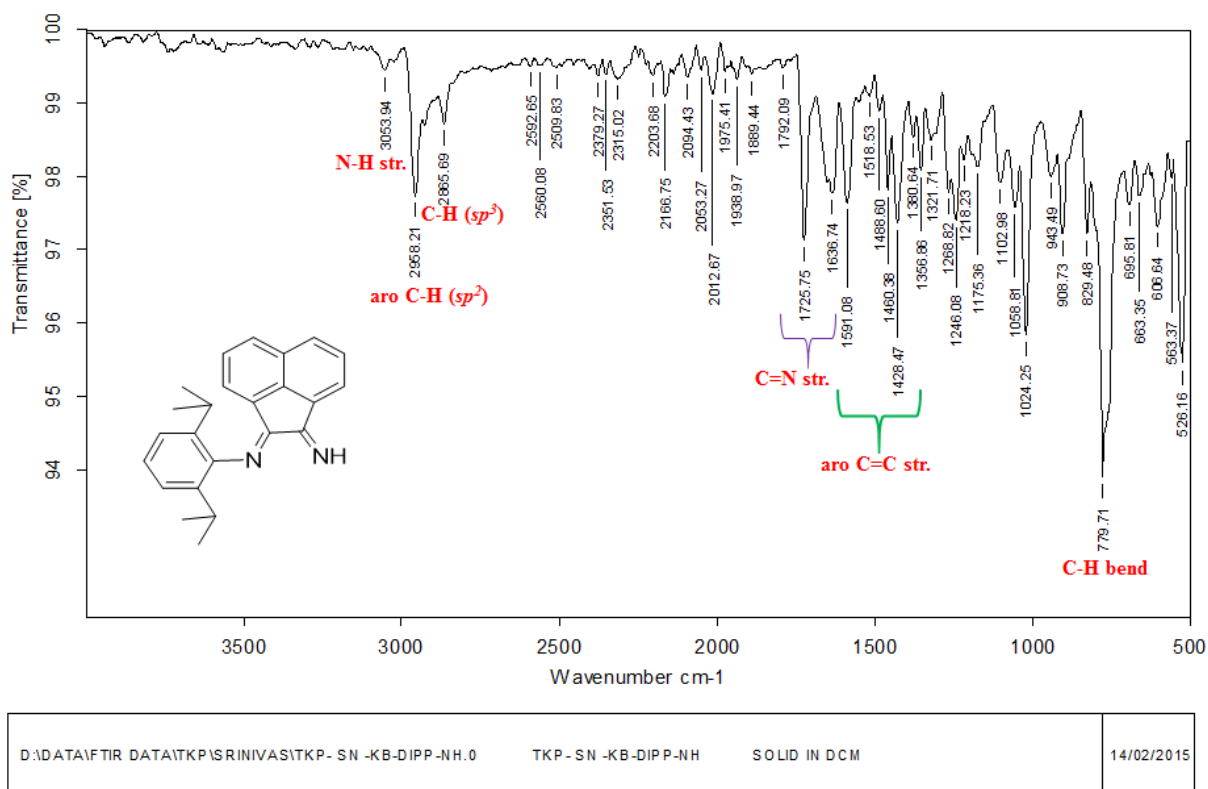


Figure 14. ^{13}C $\{^1\text{H}\}$ NMR Spectra of **1b**.



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Figure 15. FT-IR Spectra of **1b**.

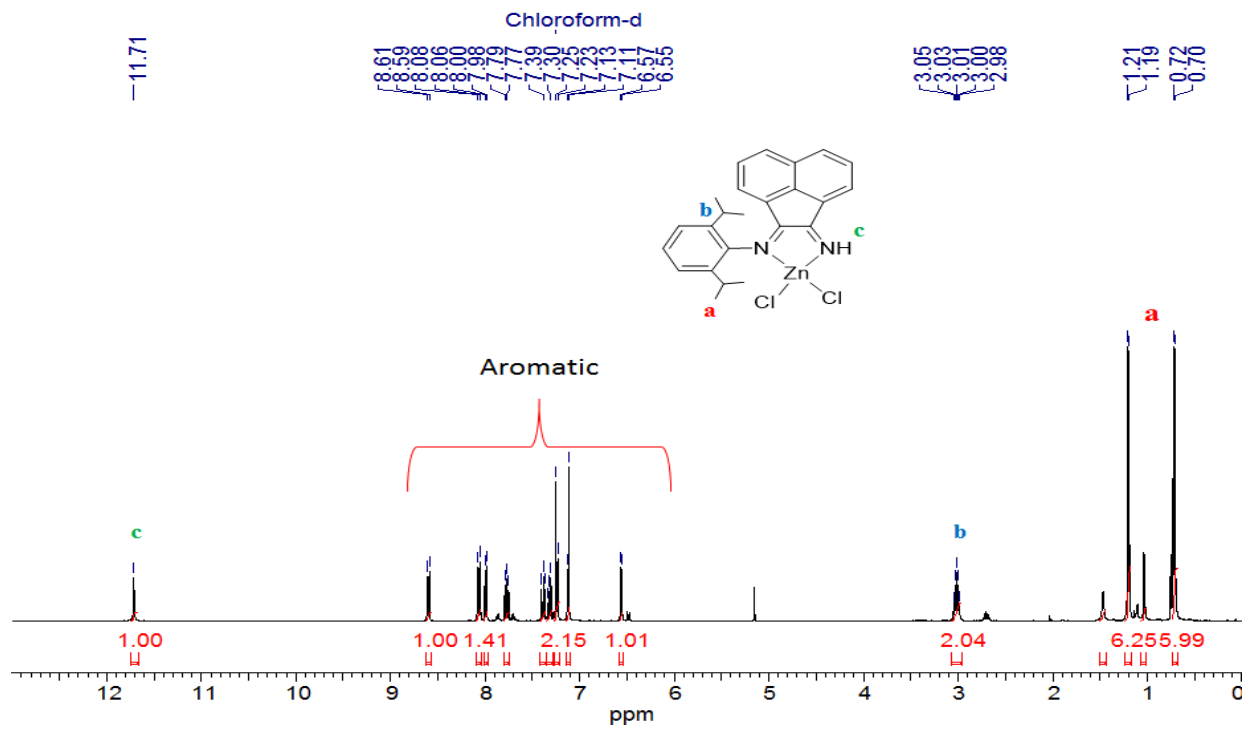


Figure 16: ^1H NMR Spectra of compound **2b**.

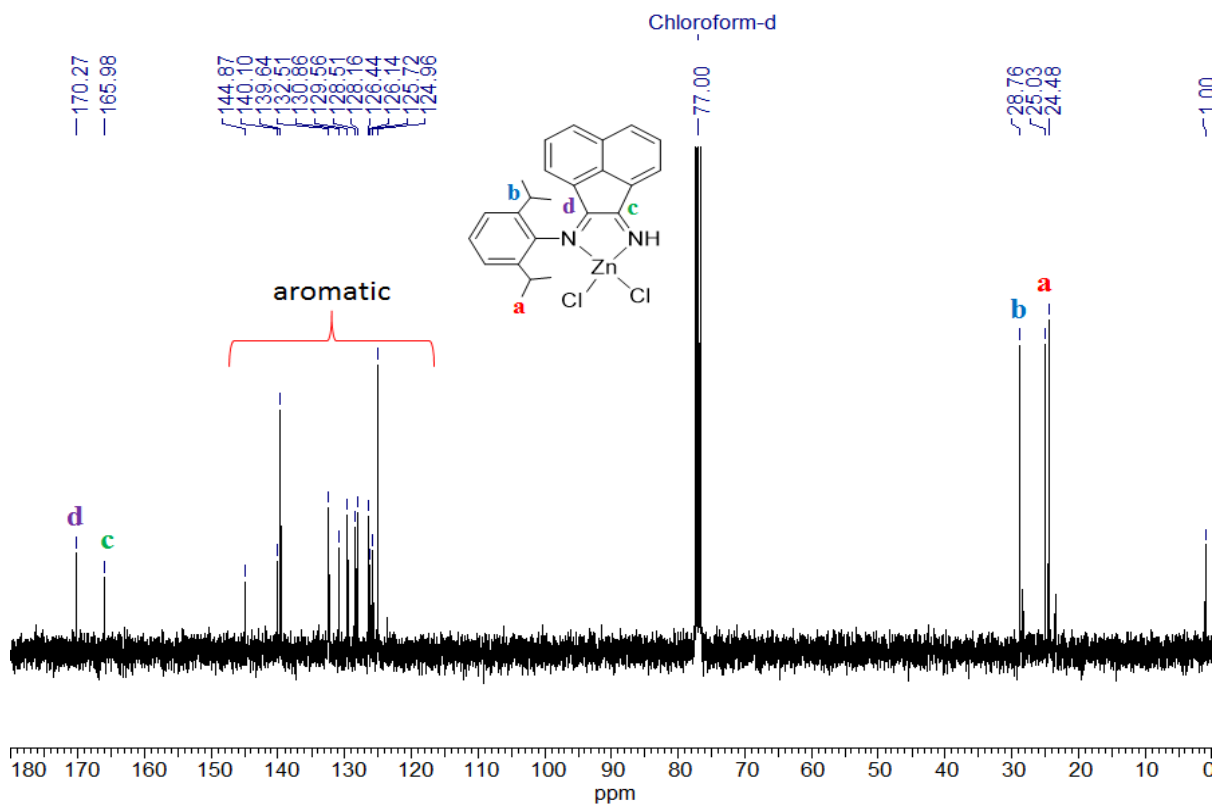
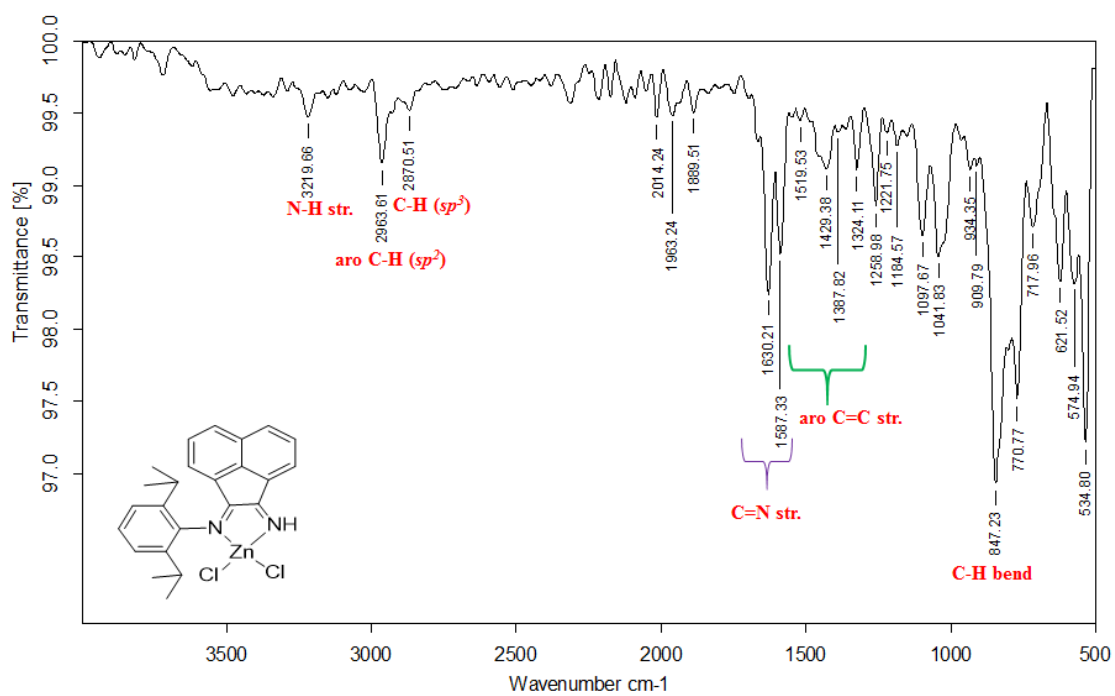


Figure 17. ^{13}C $\{^1\text{H}\}$ NMR Spectra of **2b**.



D:\DATA\FTIR DATA\TKP\SRINIVAS\TKP- SN -KB-DIPP-NH-ZnCl2.0	TKP- SN -KB-DIPP-NH-ZnCl2	SOLID IN DCM	14/02/2015
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Figure 18. FT-IR Spectra of **2b**.

Curriculum Vitae

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