Functionalization of Imidazolin-2-imine by Phenyl isocyanate and Chlorodiphenylphosphine- Syntheses and Reactivity Study

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.

Abhinanda Kundu

(Signature)

Abhinanda Kundu

(Student Name)

Tarun Kanta Panda

Signature of the supervisor

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(Roll No)

Acknowledgement

I have taken enormous efforts in this project. With my appreciative mind, abilities and insatiable curiosity I have learned a lot. However, it would not have been possible without the kind support and help of many individuals and organizations. I would like to extend my sincere thanks to all of them.

I express my deep sense of gratitude and profound feeling of admiration to my thesis supervisor Dr. Tarun K. Panda who gave me constant moral support and guided me in different matters regarding the project topic from the very beginning. Not only this, he has inspired me if I even show a very simple result and has influenced me how to convert that into a bigger achievement. He had been very kind and patient while suggesting me the outlines of this project and clearing my doubts. I sincerely thank him for his overall supports.

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I am very thankful to every research scholars in the Department of Chemistry IIT Hyderabad who all supported me and helped me a lot in gathering different information, record the spectroscopic data, for I have completed my project within this limited time.

I would like to thank the Department of Chemistry of -IIT Hyderabad for providing me all possible lab and equipment facilities. I also cherish the sweet memories of all of my classmates at IIT Hyderabad which I carry forward throughout my life.

Lastly, I offer my regards to all of those who supported me in any respect during the completion of the project.

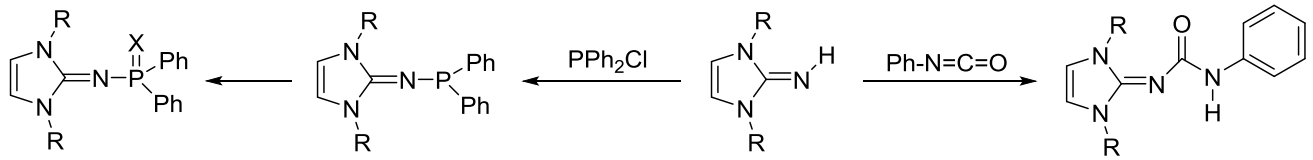
Dedicated

To

My Beloved Parents

Abstract

The thesis work describes the functionalization of imidazolin-2-imine (**1a**, **1b** and **1c**) on the exocyclic nitrogen (the imine nitrogen) by phenyl isocyanate and chlorodiphenylphosphine. We prepared *N*-(1,3-di-*tert*-butylimidazole-2-ylidene)-*N*'-phenylurea **2a,** *N*-(1,3-dimesitylimidazole-2-ylidene)-*N*'-phenylurea **2b**, *N*-(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-*N*'-phenylurea **2c** ligands by reacting imidazoline-2-imine with phenyl isocyanate at ambient temperature. To expand imidazolin-2-imine into the novel imidazolin-2-ylidene-1,1-diphenylphosphinamine ligand family we prepared 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine **3b** and 1,3-bis-**(**2,6-diisopropylphenyl)-imidazolin-2-ylidene-1,1-diphenylphosphinamine **3c** ligands by reacting imidazolin-2-imine with chlorodiphenylphosphine in THF:CH_2Cl_2 mixture at ambient temperature. Further functionalization was done on the imidazolin-2-ylidene-1,1-diphenylphosphinamine by making its chalcogenides. Reaction of 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine with H_2O_2, elemental sulphur and selenium affords corresponding oxide, sulphide and selenide derivatives, 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinicamide **4b,** 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinothioicamide **5b** and 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinoselenoicamide **6b** respectively in good yield. Compound **2a**, **2b** and **2c** are introduced in the late transition metal chemistry to prepare nickel complexes (**7a** and **7b**) and to explore its possible application in organic transformation. All the compounds are characterized by spectroscopically such as NMR, IR, UV and solid state structure established by XRD.



4b : R= mesityl, X= O
5b : R=mesityl, X= S
6b : R=mesityl, X= Se

3b : R= mesityl
3c : R= 2,6-diisopropyl phenyl

1a : R= ^{t}Bu
1b : R= mesityl
1c : R= 2,6-diisopropyl phenyl

2a : R= ^{t}Bu
2b : R= mesityl
2c : R= 2,6-diisopropyl phenyl

Scheme 1.

Contents:

1. Introduction

Ancillary ligands with nitrogen as the coordinating atom are used extensively in homogeneous catalysts, either as neutral or as anionic amido and imido donors[1,2]. Alternative to the cyclopentadienyl derivatives, amidinate $[RC(NR')_2]^-$ and guanidinate $[R_2NC(NR')_2]^-$ ligands now find use as bidentate ligands to metals across the periodic table[3]. Another class of important ligand in organometallic chemistry is carbenes. The isolation of 1,3-bis-(adamantyl)imidazol-2-ylidene (IAd), the first crystallographically authenticated carbene, by Arduengo and co-workers constitutes a landmark discovery in organometallic chemistry[4]. The strong electron-donating capacity and high nucleophilicity of these carbenes (NHC's) can be attributed to the capability of the imidazolium ring to effectively stabilize a positive charge. N-heterocyclic carbenes are strong σ donor than the classical Fischer and Schrock carbenes[5]. This NHC's upon metal coordination forms complexes of the type (Im)MLn (Fig 1.) which has many application such as homogeneous catalysis[6], materials science[7] and in medicinal chemistry[8]. The same principle applies to organic imidazoline derivatives ImX containing an exo-cyclic atom or organic moiety X attached at the 2-position of the N-heterocycle, so that species such as 2-methylen-, 2-imino-, 2-oxo- and 2-thioimidazolines (X = CH_2, NH, O, S) can be prepared[9]. More recently, the reactivity of these carbene centres towards azides was exploited by Matthias Tamm and his co-workers to prepare imidazol-2-imines[10,11], a new class of ligand, particularly basic and nucleophilic a subclass of guanidines type of ligand.

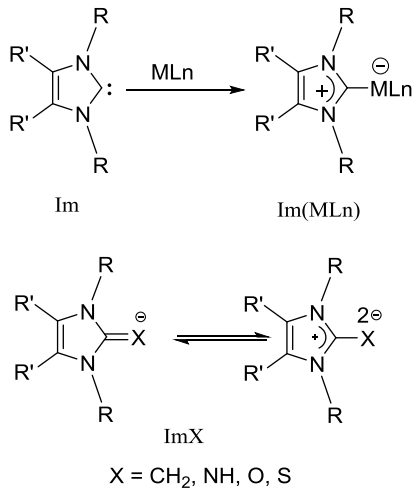


Fig 1. Resonance structure of imidazole based ligands.

Deprotonation of imidazolin-2-imine (ImNH) affords monoanionic imidazolin-2-iminato ligand (ImN^-) which can be act as 2σ, 4π electron donors. These types of ligands are closely related to phosphoraneiminato ligands (R_3PN^-), in which the N-heterocyclic carbene (Im) is replaced by a phosphine moiety and also isolobal with cyclopentadienyl ligand[12,13](Scheme 2). It is known in literature that the coordination chemistry of imidazolin-2-imine ligand with early to late transition metal, rare earth metals and transition metals in high oxidation state and has many applications in catalytic transformation[14,15] such as olefin polymerization and alkene metathesis reactions, has proved to be more active than metallocene catalyst.

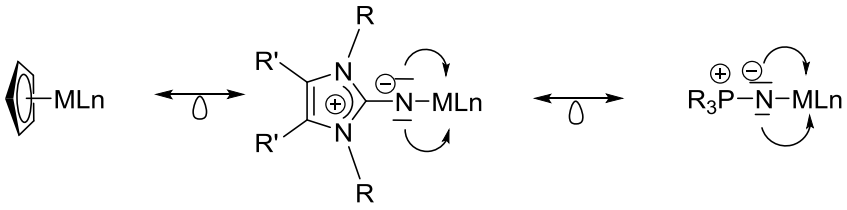


Fig 2. Isolobal relationship of imidazolin-2-imine with phosphoraneiminato and cyclopentadienyl ligand.

Imidazoin-2-imine ligand is now one of the important areas in organometallic research field, continuously research going on to modify or functionalized this ligand to increase more of its application and activity. Imidazolin-2-imine can be functionalized by varying substituent on the imidazole nitrogen, on the olefinic part and on the exocyclic imine nitrogen. It is known in literature compounds having a number of substituents on both imidazole nitrogen atoms such as *tert*-butyl, 2, 4, 6-tri methyl phenyl, 2, 6-diisopropyl etc. Monoanionic imidazolin-2-imine can act as a monodentate ligand (I), by adding substituent on the exocyclic imine nitrogen this ligand can be changed from monodentate to bidentate, tridentate and bridging [16](Fig 3). Adding a functional group X (where X is nitrogen, oxygen donor moiety) on exocyclic nitrogen made it bidentate (II), linking two imidazolin-2-imine fragments made it also bidentate (III), adding one functional group X between two imidazolin-2-imine fragment made it tridentate (IV).

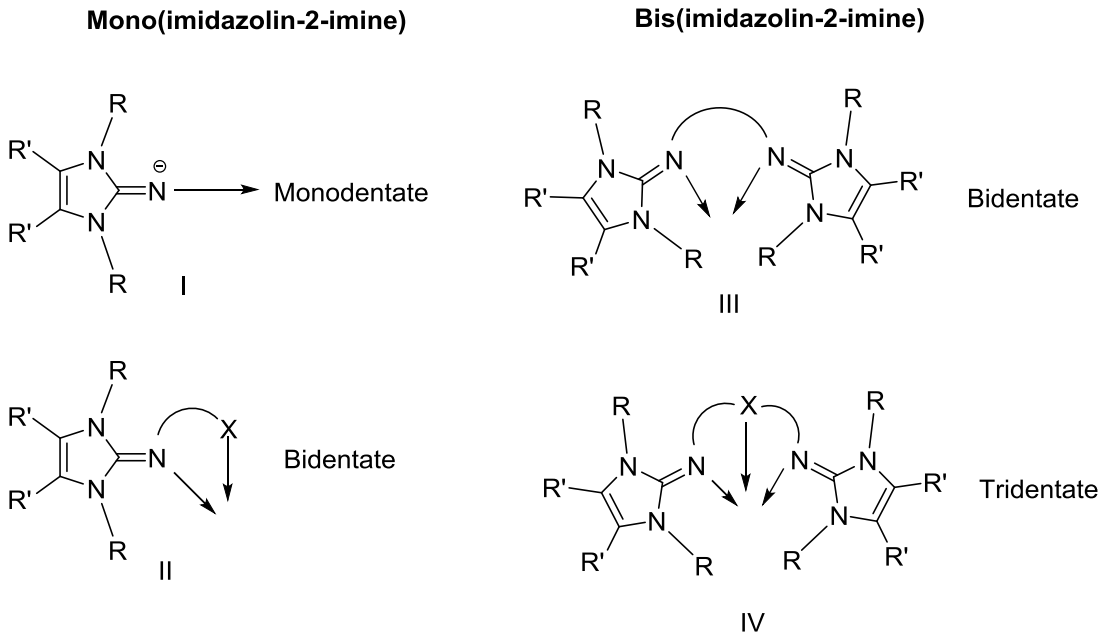


Fig 3. Coordination modes of modified imidazolin-2-imines.

So far in literature many functionalized mono and bidentate imidazolin-2-imine ligands are reported, some selected example are shown in (Fig 4). From early to late transition metal and rare earth metals already has been reported with imidazolin-2-imine. In our group the imidazole-2-imido group 4 metal complexes and their reactivity are explicitly studied[17], in continuation with this study we are focusing to functionalize the imidazolin-2-imine moiety with phenyl isocyanate to prepare *N*-imidazol-2-ylidene-*N*'-phenylureate ligand[18] which is a tridentate ligand can coordinate through both nitrogen and oxygen atoms (Fig 5) and with chlorodiphenylphosphine to prepare imidazolin-2-ylidene-1,1-diphenylphosphinamine type of ligands. P-N ligands are of another class of important ligand. Use of various P–N ligands is one of the alternatives to using cyclopentadienyl ligands. P-N ligand systems, such as monophosphanylamides (R_2PNR')[18-20], diphosphanylamides [$(Ph_2P)_2N$][19], phosphoraneiminato (R_3PN)[20], phosphiniminomethanides [$(RNPR'_2)_2CH$][21], phosphiniminomethandiides [$(RNPR'_2)_2C$][22] and diiminophosphinates [$R_2P(NR')$] are well known today as ligands and have proved their potency in transition and rare earth metal chemistry. Some of the early transition-metal complexes having P–N ligands in the coordination sphere have applications in areas such as the activation of small poorly reactive molecules, homogeneous catalysis or organic synthesis. Roesky[23] and co-workers introduced one chiral

phosphinamine [HN(CHMePh)(PPh_2)] into the early transition metal chemistry as well as in lanthanide chemistry.

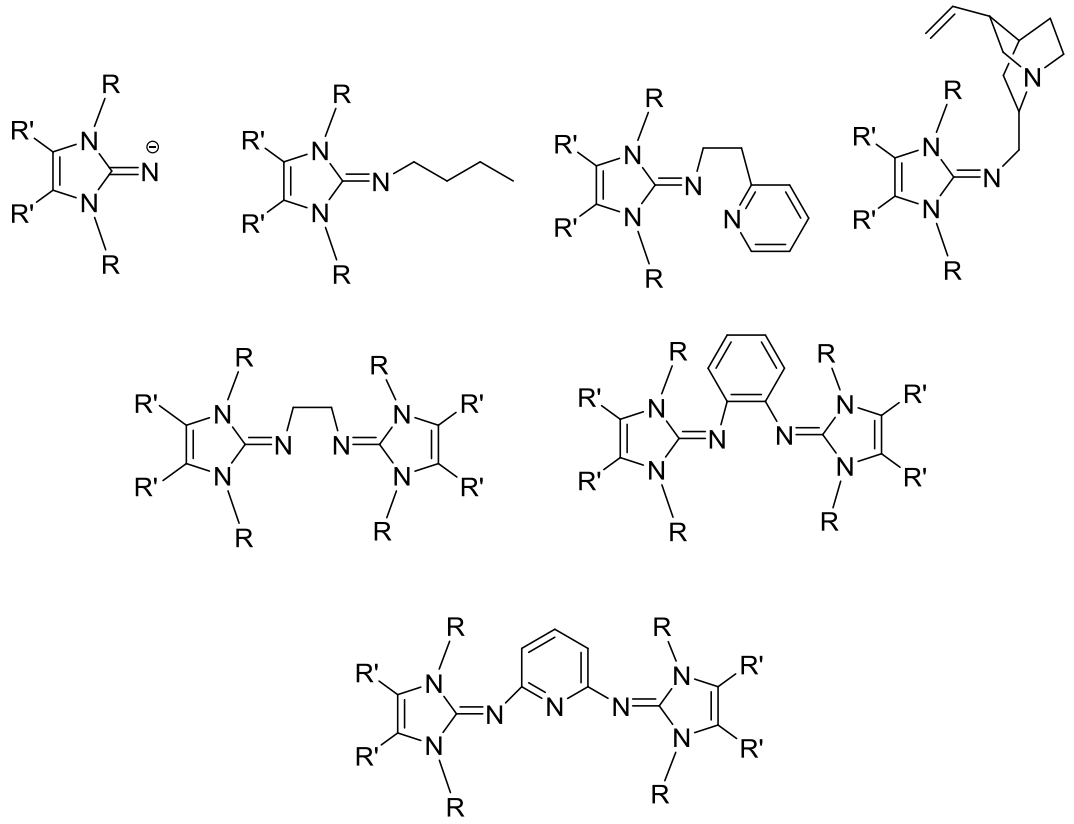


Fig 4. Selected example of imine nitrogen fuctionalized imidazolin-2-imine.

In our group, *N*-(diphenylphosphine)-2,6-dimethylaniline [$Ph_2PNH(2,6\text{-}Me_2C_6H_3)$] and their chalcogenides and their complexes with alkali metals already has been synthesized[24]. Imidazolin-2-iminodiphenylphosphine type of ligand are capable of coordinate via three donor atoms (N, P) and soft donor atom like (S, Se) with heavier alkaline earth metals (Fig 5). Only one report is known where imidazolin-2-imine was functionalized on the imine nitrogen by *p*-tolyl isocyanate and thioisocyanate to prepare *N*-imidazol-2-ylidene-*N′*-*p*-tolylureate and thioureate ligands and metal complexes with titanium, nickel and palladium[18]. Similar kind of compounds are reported where authors used imidazoiln-2-imido-metal (M= Sc, Mo, Ti) complexes with isocyanate, CS_2, XyNCS etc[25].

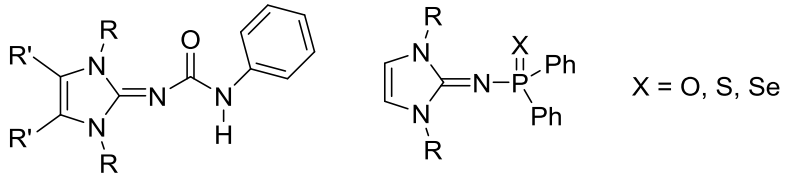


Fig 5.

For each metal the binding mode of ligand is not same (Fig 6), where scandium binding through *NN*' position, titanium binds through nitrogen and sulphur. Similar kind of ligand reported with titanium where instead of higher oxidation state of titanium ligand coordinated through sulphur and nitrogen. Depending on reaction conditions coordination mode of ligand can be vary. So far best of our knowledge only few reports are there for nickel with functionalized imidazolin-2-imine whereas the other transition metals are more explored[18].

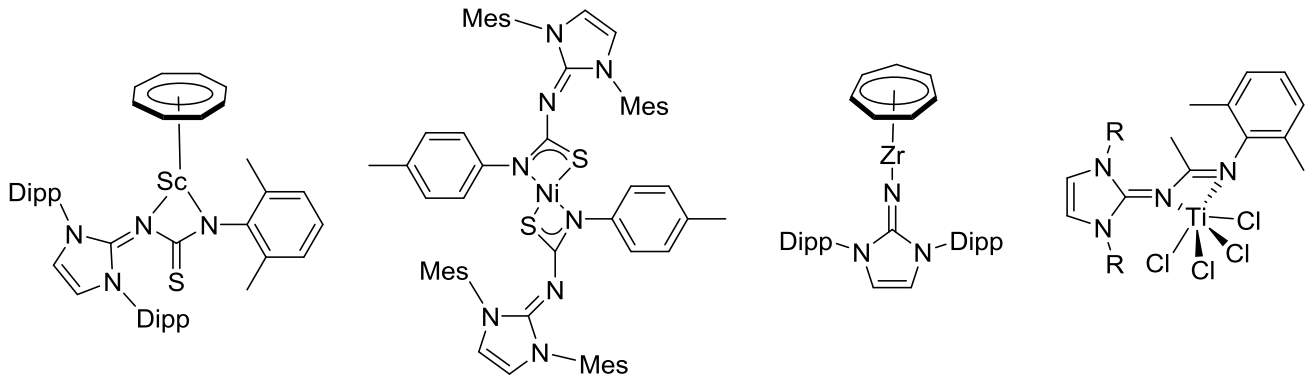


Fig 6. Rare earth and transition metal complexes with functionalized imidazolin-2-imines.

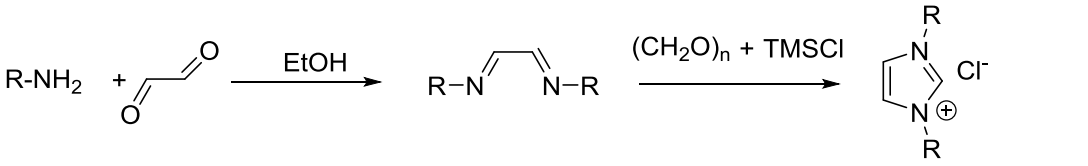
2. Aim of the project:

Imidazolin-2-imine ligand is now one of the important areas in organometallic research field, continuously research going on to modify or functionalized this ligand to increase more of its application and activity. To enrich this family of ligand we focused to design a new ligand system including the imidazolin-2-imine fragment in the ligand structure to prepare *N*-(1,3-di-*tert*-butylimidazole-2-ylidene)-*N*'-phenylureate **2a,** *N*-(1,3-dimesitylimidazole-2-ylidene)-*N*'-phenylureate **2b**, *N*-(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-*N*'-phenylureate **2c** ligands by reacting imidazoline-2-imine with phenyl-isocyanate at ambient temperature.

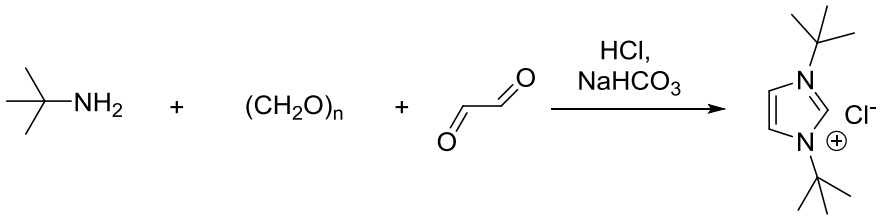
Also we were interested to extend the imidazolin-2-imine ligand by phosphine group to get related imidazolin-2-ylidene-1,1-diphenylphosphinamine and its chalcogenides (O, S, Se) 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b**, 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinothioicamide **5b**, 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinoselenoicamide **6b**. Due to various coordination mode of **2a**, **2b** and **2c** varying reaction condition with the metal precursor we are interested to study the geometry and reactivity of this ligands in the coordination sphere of nickel. To prepare the nickel complex as metal precursor we used $Ni(acac)_2$ and *N*-imidazole-*N*'-phenylureate ligand in THF. These metal complexes can show high reactivity towards catalysis in alkene polymerization or metathesis reactions.

3. Results and Discussion:

3.1 Synthesis of *N*-imidazol-2-ylidene-*N*'-phenylureate ligand : 1,3-Dimesitylimidazolium hydrochloride and 1,3-bis-(2,6-diisopropyl)imidazolium hydrochloride was prepared by the conventional procedure using 1,4-diazabutadiene with *p*-formaldehyde and chlorotrimethylsilane (TMSCl) (Scheme 2). Corresponding 1,3-di-*tert*-butylimidazolium hydrochloride was prepared by one pot synthesis of *tert*-butyl amine with *p*-formaldehyde and glyoxal (Scheme 3). Free *N*-heterocyclic carbene was prepared by reacting imidazolium hydrochloride with potassium *tert*-butoxide (Scheme 4)[18]. The free carbene undergoes Staudinger-type reaction by treatment with trimethylsilyl azide in boiling toluene to give the corresponding N-silylated product. Desilylation was accomplished by stirring in methanol under ambient temperature to obtain the corresponding imines (**1a**, **1b** and **1c**)[10,11] (Scheme 4).

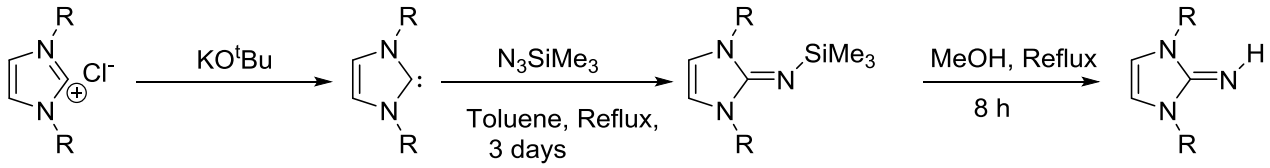


Scheme 2. Preparation of 1,3-substituted-imidazolium hydrochloride

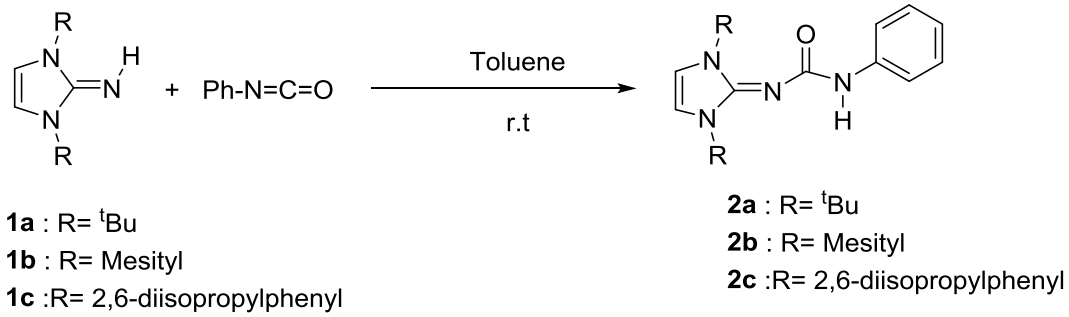


Scheme 3. Preparation of 1,3-di-*tert*-butylimidazolium hydrochloride

Compound **2a**, **2b**, **2c** can be achieved by the treatment of ligand **1a**, **1b**, **1c** in toluene with phenyl isocyanate at ambient temperature (Scheme 5). Compound **2a**, **2b** and **2c** was characterized by analytical/spectroscopic techniques and the molecular structures of these compounds were confirmed by single crystal X-ray diffraction analysis.



Scheme 4. Preparation of Imidazolin-2-imine.

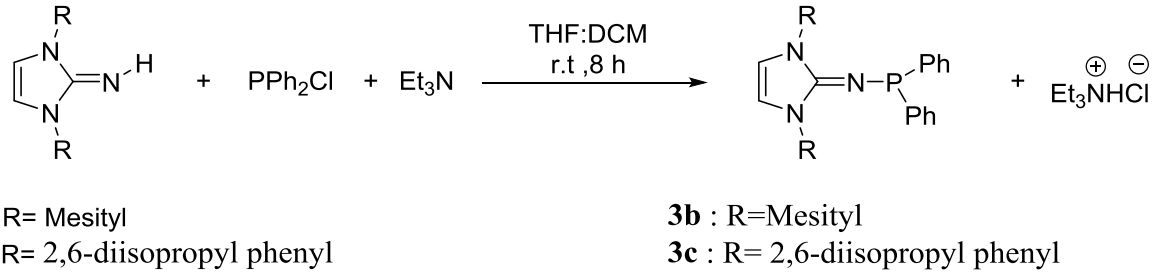


Scheme 5. Preparation of *N*-(imidazole-2-ylidene)-*N*'-phenylureate ligand.

A strong absorption at 1627 cm^{-1} for **2a**, 1648 cm^{-1} for **2b,** 1650 cm^{-1} for **2c** in the FT-IR spectrum proves the formation of new C=O bond, however the acyl stretching frequency in **2a, 2b** and **2c** are substantially lower than the that of the free phenyl isocyanate (2167 cm^{-1}) indicating a marked decrease in C−O bond strength upon formation of the urea. This observed stretching frequency is also slightly lower than that of commonly observed in organic amides, a manifestation of the electron delocalization from the azole ring to the acyl group, resulting in further decreasing the C−O bond order. The absorbance for C=N bond stretching are well in the expected region (1550-1600) cm^{-1}.The imidazolium backbone protons of **2a** resonate as a singlet in the ^{1}H NMR spectrum at δ 6.22, a downfield shift from that of the imidazol-2-imine **1a** (δ 5.94 ppm). For **2b** down field shift of olefinic protons was observed at 5.80 ppm from that of **1b** (δ 5.71 ppm). In case of **2c** also down field shift of olefinic protons was observed at 5.87 ppm from that of **1c** (δ 6.21 ppm). The *o* and *m*-CH protons of parent phenyl isocyanate experience a downfield shift from δ 7.17 and 6.92 ppm in phenyl isocyanate to 7.87 and 7.27 ppm in **2a**. ^{1}H NMR clearly shows that downfield shifting of –NH peak which is observed in 4.28-5.00 ppm region for compound **1a**, **1b** and **1c** to 5.8-6.2 ppm for compound **2a, 2b**

and **2c** due to adjacent carbonyl group, proves formation of new N-H group adjacent to carbonyl. In ^{13}C NMR of **2a**, **2b**, **2c** C=O signal observed at 157 ppm, whereas imidazolin-2-ylidene (N*C*N) observed at 150 ppm same for all three compounds.

3.2 Synthesis of various *N*-imidazolin-2-ylidene-1,1-diphenylphosphinamine ligand: The synthesis of novel *N*-imidazolin-2-ylidene-1,1-diphenylphosphinamine ligand **3b** and **3c** can be achieved by the treatment of 1,3-dimesityl-imidazolin-2-imine and 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-imine with chlorodiphenylphosphine in THF:CH_2Cl_2 mixture (3:1) at ambient temperature (Scheme 6). The compounds **3b** and **3c** were characterized by analytical/spectroscopic techniques and the molecular structure of **3b** and **3c** were confirmed by single crystal X-ray diffraction analysis.



1b : R= Mesityl
1c : R= 2,6-diisopropyl phenyl

3b : R=Mesityl
3c : R= 2,6-diisopropyl phenyl

Scheme 6. Synthesis of 1,3-substituted-imidazolin-2-ylidene-1,1-diphenylphosphinamine.

The strong absorption band for N-H in the compound **1b** and **1c** is absent for compound **3b** and **3c** in the FT-IR spectra. Moreover a strong absorption around 924 cm^{-1} (for compound **3b**) and 916 cm^{-1} (compound **3c**) indicates the evidence of newly formed P-N bond into the ligand precursor. The absorption band for P-Ph (1128 cm^{-1}) and C=N (1653 cm^{-1}) bond stretching are well in the expected ranges. In ^{1}H NMR spectra, the imine proton of the imidazolin-2-imine ligand which was present in the range between 4.20 and 4.77 ppm is absent for compound **3b** and **3c**. The multiplets signals at δ-6.95-6.72, 8.01-7.89 and 7.21-7.07 ppm can be assigned for the two phenyl ring attached to the phosphorus centre. The olefinic protons present in the imidazolium ring in case of both **3b** and **3c** are found to be same with that of **1b** and **1c** respectively at 6.28 ppm. In case of **3c** the two 2,6-diisopropylphenyl ring on the *N*-substituted imidazolin ring is not in the same plane and shows two

different singlet in ^{1}H NMR spectra at 1.13 ppm and 1.31 ppm. In case of compound **3b** the four *o*-methyl groups are equivalent and separate singlet observed for *o*- and *p*-methyl protons. In ^{31}P-{1H} NMR spectra, in compound **3c** shows only one signal is observed at 41.2 ppm representing one phosphorous atom present in the molecule. The significantly high frequency shift of the phosphorus atom compare to free chlorodiphenylphosphine (81.5 ppm) can be explained due to higher electron donating capability of imido nitrogen to the phosphorus atom.

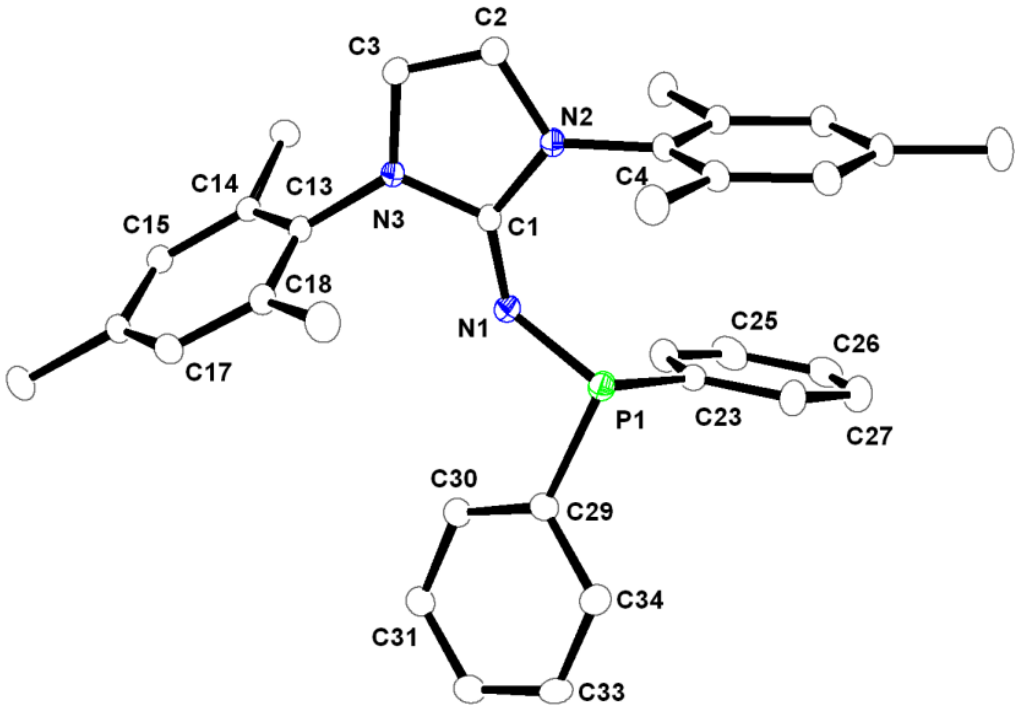
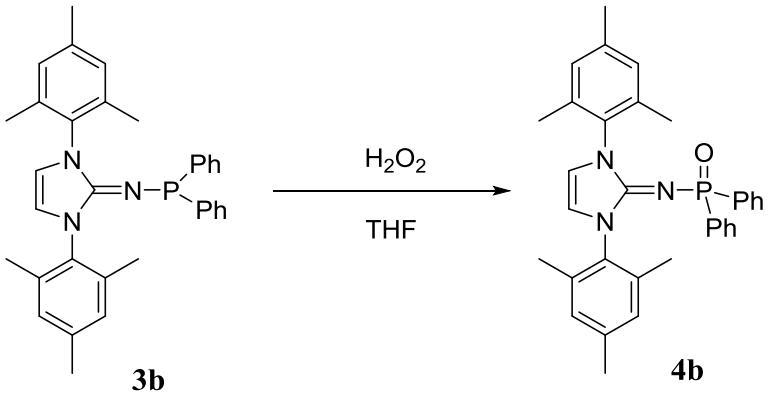


Figure 7.Solid state structure of compound **3b**. Selected bond lengths (Å) and bond angles (^{o}) are given. P(1)-N(1) 1.674(2), P(1)-C(29) 1.840(2), P(1)-C(23) 1.848(3), N(3)-C(1) 1.384(3), N(1)-C(1) 1.301(3), N(2)-C(1) 1.376(3), N(3)-C(3) 1.395(3), N(3)-C(13) 1.436(3), N(2)-C(4) 1.438(3), N(1)-P(1)-C(29) 98.43(10), N(1)-P(1)-C(23) 104.99(11), C(29)-P(1)-C(23) 97.06(10), C(1)-N(1)-P(1) 124.58(17), N(1)-C(1)-N(3) 122.8(2), N(1)-C(1)-N(2) 132.5(2), N(2)-C(1)-N(3) 104.65(18), C(1)-N(3)-C(13) 124.52(18), C(1)-N(2)-C(4) 125.86(18).

The solid state structure of compound **3b** was determined by X-ray diffraction analysis. Compound **3b** crystallizes in triclinic space group *P*-1with two molecules per unit cell. Structural parameters for

compound **3b** are given in Table 2. The molecular structure of compound **3b** is shown in Fig 7. In compound **3b** C(1)-N(1) bond distance 1.301(3) Å remains almost same to that of imidazolin-2-imine (1.298(1) Å) and clearly fall in the range expected for a C-N double bond (1.28 Å). This is also supported by the fact that the imidazole heterocycles in compound **3b** shows no significant change having N(2)-C(1)-N(3) 104.65(18)^{o}, from the imidazole heterocycle of the compound **1b**, which have 105.0(1)^{o}. The P-N bond distances in compound **3b**, P(1)-N(1) 1.674(2) Å shows a slightly shorter of bond length compare to normal P-N bond distances 1.656(3) Å observed for [2,6-$Me_2C_6H_3NHPPh_2$][24] reported by our group. The angle C(1)-N(1)-P(1) is 124.58(17)^{o} is deviated from linearity presumably due to the steric crowding between the phenyl groups over phosphorus atom and the mesityl groups present in the imidazolium ring.



Scheme 7. Synthesis of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b**.

1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b** was synthesized by reacting **3b** in THF with equivalent amount of H_2O_2 (Scheme 7). In this reaction nascent oxygen generated which is bind with P(III) to convert it to P(V). Strong absorption band at 1260 cm^{-1} can be assigned as characteristic P=O bond stretching in the FT-IR spectra of compound **4b**. Stretching frequency for P-Ph observed in the expected region between 1130-1090 cm^{-1} and for P-N (915 cm^{-1}), C=N (1623 cm^{-1}) similar with that of compound **3b** is that no significant change by the oxygen on phosphorus. The ^{1}H NMR spectra of compound **4b** shows that the two phenyl group on phosphorus has same chemical shift in the expected region 7.19-7.07, 7.05-6.97 ppm. Four *o*-methyl groups on mesityl are equivalent from same chemical shift value in the region 1.97 ppm. The olefinic protons present in the

imidazolium ring are observed in same chemical shift value with that of compound - **3b** and **1b**. In the ^{31}P-{^{1}H} NMR spectra one signal is observed at 4.8 ppm indicating one phosphorus atom present in the molecule. The significantly high frequency shift of the phosphorus atom compare to free chlorodiphenylphosphine (81.5 ppm) can be explained due to higher electron donating capability of imine nitrogen to the phosphorus atom.

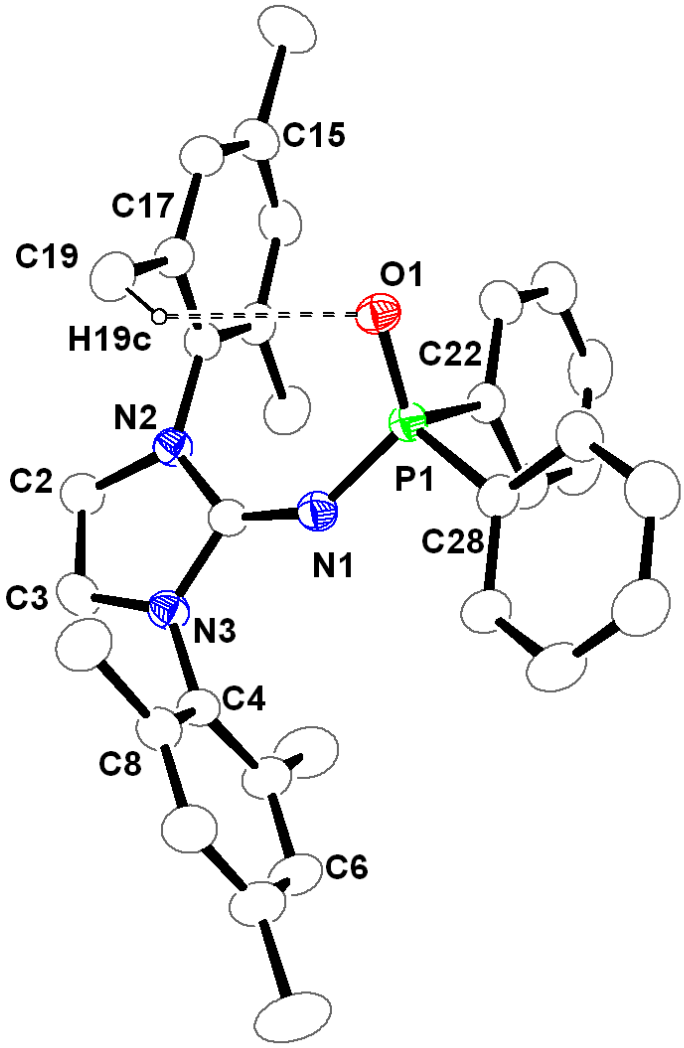
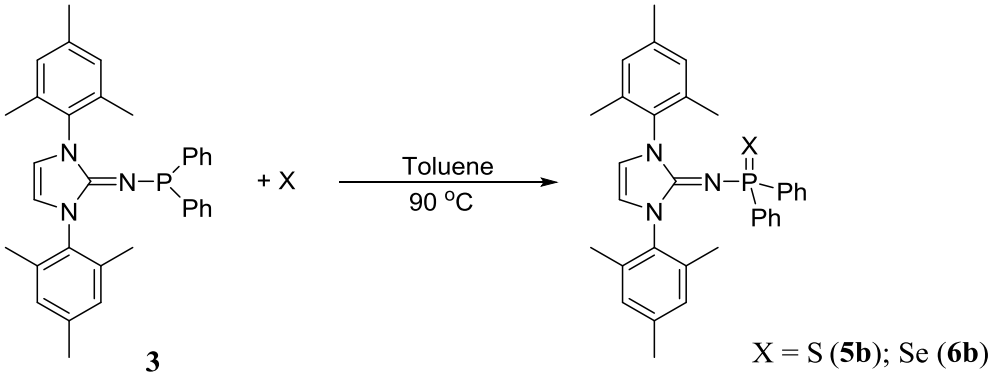


Figure 8. Solid state structure of compound **4b**. Selected bond lengths (Å) and bond angles (^{o}) are given. P(1)-O(1) 1.476(2), P(1)-N(1) 1.597(3), P(1)-C(22) 1.808(3), P(1)-C(28) 1.807(4), N(3)-C(4) 1.427(4), N(2)-C(2) 1.398(5), O(1)-P(1)-N(1) 120.44(16), O(1)-P(1)-C(22) 109.98(15), N(1)-P(1)-C(22) 108.43(16), O(1)-P(1)-C(28) 109.56(16), N(1)-P(1)-C(28) 101.32(17), C(22)-P(1)-C(28) 109.57(15), C(1)-N(2)-C(2) 110.3(3), N(1)-C(1)-N(3) 121.9(3), N(1)-C(1)-N(2) 133.2(3), N(3)-C(1)-N(2) 104.9(3).

Compound **4b** crystallizes in the monoclinic space group *P* 2_1/c with four molecules per unit cell. Structural parameters for compound **4b** are given in Table 2. The P(1)-N(1) bond distance in the compound is 1.597(3) Å, shorter than the corresponding sulfide and selenide complex 1.612(18) Å. The P(1)-C(22) and P(1)-C(28) values are 1.808(3) Å, 1.807(4) Å respectively similar to the values reported in the literature. The P–O distances 1.476(2) Å are in good agreement for considering the P–O bond as double bond and is comparable with the literature [1.4736(19) Å in 2,6-$^{i}Pr_2C_6H_3NHP(O)Ph_2$][24]. The phosphorus atom is also sp^3 hybridized and adopts a tetrahedral geometry, and the bond angles of O(1)-P(1)-C(28) 109.56(19)^o, O(1)-P(1)-C(22) 109.98(15)^o, O(1)-P(1)-N(1) 120.44(16)^o, N(1)-P(1)-C(28) 101.32(17)^o approximately similar to ideal bond angle 109.45^o. The solid state structure of the compound reveals that intramolecular hydrogen bonding present between O(1)-H(19c).

1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinothioicamide **5b** was prepared by reacting compound **3b** in THF:CH_2Cl_2 mixture in (3:1) ratio with elemental sulphur in 1:2 molar ratio respectively at 90 ^{o}C (Scheme 8). In FT-IR spectrum of the compound **5b**, the strong absorption at 666 cm^{-1} is observed, which can be assigned as characteristic P=S bond stretching, P-N stretching observed at (917 cm^{-1}), P-Ph (1435 cm^{-1}), are positioned well in the expected region and similar with the compound [$Ph_2P(S)NH(2,6\text{-}Me_2C_6H_3)$] previously reported by our group[24]. The ^{1}H NMR spectra of compound **5b** shows two sharp singlet of *o*- and *p*-methyl group on mesityl at 2.18 and 2.30 ppm respectively. Phenyl protons on phosphorus observed in the expected range. In the ^{31}P {^{1}H} NMR spectra one signal observed at 35.8 ppm, downfield shift compare to the compound **4b**. 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinoselenoicamide **6b** was prepared by reacting compound **3b** in THF/CH_2Cl_2 mixture in (3:1) ratio with elemental sulphur in 1:4 molar ratio respectively at 90^{o}C (Scheme 8). In the FT-IR spectra of compound **6b** absorption at 965 cm^{-1} characteristic of P=Se bond stretching. In the ^{31}P-{^{1}H} NMR spectra one signal observed at 25.7 ppm, up field shift compare to the compound **5b**.



Scheme 8. Synthesis of imidazolin-2-ylidene-1,1-diphenylphosphinamineo chalcogenides **5b** and **6b**.

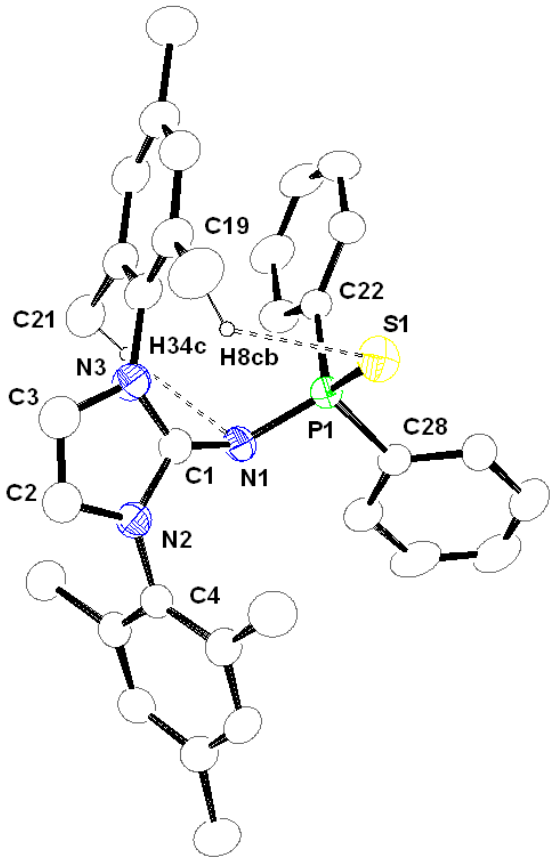


Figure 9. Solid state structure of compound **5b**. Selected bond lengths (Å) and bond angles (°) are given. P(1)-N(1) 1.612(18), P(1)-C(28) 1.824(2), P(1)-C(22) 1.828(2), P(1)-S(1) 1.952(8), N(1)-C(1) 1.311(3), N(2)-C(4) 1.437(3), N(2)-C(1) 1.359(3), N(1)-P(1)-C(28) 102.18(10), N(1)-P(1)-C(22)

108.66(10), C(28)-P(1)-C(22) 101.83(9), N(1)-P(1)-S(1) 119.36(7), C(28)-P(1)-S(1) 111.10(8), C(22)-P(1)-S(1) 111.91(8), C(1)-N(1)-P(1) 130.92(18), N(2)-C(1)-N(3) 106.09(17), C(1)-N(2)-C(4) 124.45(17).

Compound **5b** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell. Structural parameters for compound **5b** are given Table 2. P(1)-S(1) bond distance in the compound is 1.952(8) Å, similar to the compound reported in our group $[Ph_2P(S)NH(2,6\text{-}Me_2C_6H_3)]$[24] (1.951(8)) Å, and normal P-S double bond length is (1.86 Å). The C(1)-N(1) bond distance 1.311(3) Å, P(1)-N(1)-C(1) bond angle 130.92(18)^o are almost same with compound **3b** is that not effected by sulphur atom. P(1)-N(1) bond distance 1.612(18) Å same with compound **3b** and **4b**. Like compound **4b** phosphorus is in tetrahedral geometry. The solid state structure reveals hydrogen bonding between S(1) and H(8cb) and between N(1)-C(21) hydrogen.

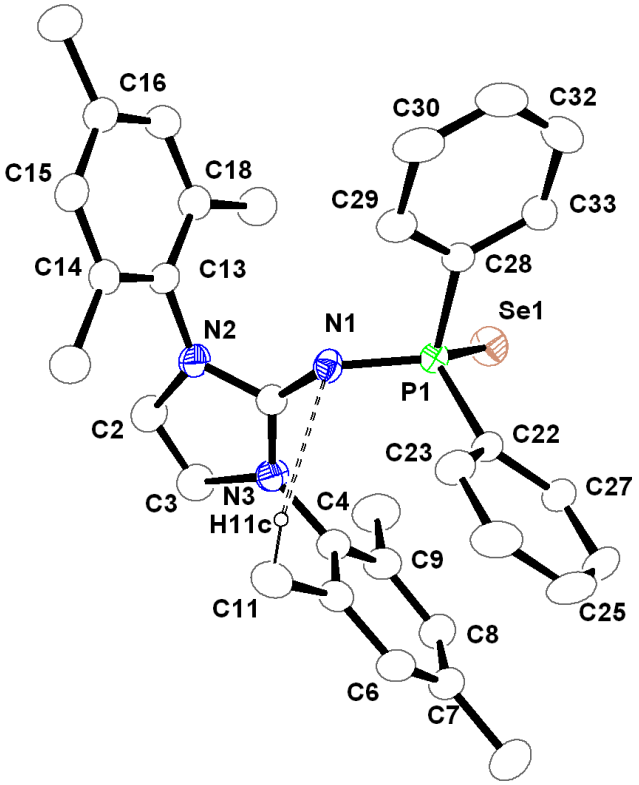


Figure 10. Solid state structure of compound **6b**. Selected bond lengths (Å) and bond angles (^{o}) are given. Se(1)-P(1) 2.108(9), P(1)-N(1) 1.609(3), P(1)-C(22) 1.821(3), P(1)-C(28) 1.824(3), N(1)-C(1)

1.306(4), N(3)-C(4) 1.445(4), N(1)-P(1)-C(22) 109.57(15), N(1)-P(1)-C(28) 102.69(14), N(1)-P(1)-Se(1) 118.08(10), C(22)-P(1)-C(28) 101.47(13), C(22)-P(1)-Se(1) 112.40(12), C(28)-P(1)-Se(1) 110.92(11), C(1)-N(1)-P(1) 132.3(3).

Compound **6b** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell. Structural parameters for compound **6b** are given Table 2. The P–Se distance of 2.108(9) Å is in agreement with the reported value and can be considered as a P–Se double bond. P(1)–N(1) 1.609(3) Å, C(1)–N(1) 1.306(4) Å are also similar to that of compound **5b**. Like compound **5b**, the phosphorus geometry is tetrahedral and the bond angles around the phosphorus atom are also similar. However, hydrogen bonding was observed in the selenium compound between nitrogen N(1) and H(11c) of mesityl substituent.

Table 1. Selected NMR values of compound **3b**, **4b**, **5b**, **6b**.

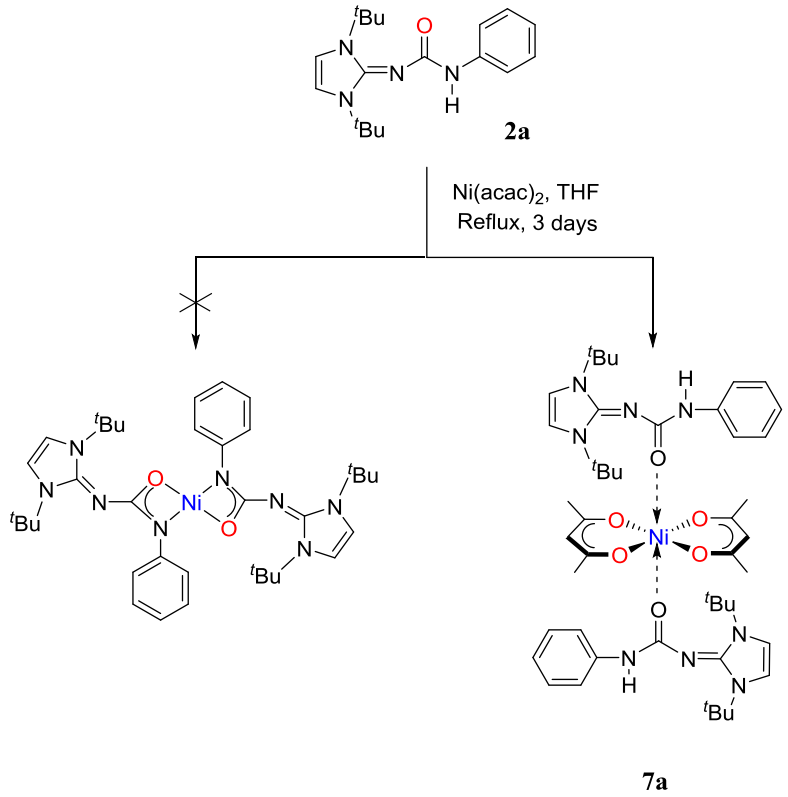
Compound	**^{1}H NMR(ppm)**				**^{31}P {^{1}H} NMR(ppm)**
	o-CH_3	*p*-CH_3	NCH	*m*-$CH_{(mesityl)}$	
3b	2.21	2.43	6.01	6.80	42.5
4b	1.97	2.29	6.40	6.82	4.8
5b	2.18	2.30	6.58	6.77	35.8
6b	2.21	2.30	6.60	6.77	25.7

3.3 Nickel complexes :

Recently, the ligand is introduced in transition metal chemistry, it is observed that the titanium compounds are highly active as polymerization catalyst[26,27]. As we have synthesized a number of *N*-imidazole-*N*'-phenylureate based ligands we are interested to explore its chemistry towards late transition metal chemistry and the possible application in organic transformations.

Synthesis of bis-[*N*-(1,3-di-*tert*-butyl imidazole-2-ylidene)-*N*'-phenyl-ureato]Ni(acac)$_2$ **7a** can be achieved by treatment of **2a** in THF with Ni(acac)$_2$, the reaction mixture was kept under reflux for 3 days. Filtered over celite and recrystallized from CH_2Cl_2 (Scheme 9). The small decrease in the C=O stretching frequency (1588 cm^{-1}) from that of the free ligand **2a** ($\nu_{C=O}$ 1627 cm^{-1}) is however

consistent with a neutral binding mode of the ligand by oxygen lone pair. Broad N-H stretching frequency observed at 3338 cm^{-1}, C-O stretching frequency observed at 1258 cm^{-1}.



Scheme 9. Synthesis of bis-[*N*-(1,3 ditertbutylimidazole-2-ylidene)-*N*'-phenylureato]Ni(acac)$_2$ **7a**.

We expected, a Ni-O bond present in Ni(acac)$_2$ cleavage will occur to produce acetyl-acetonate by loosing N-H proton of the neutral ligand **2a** to afford the monoanionic form to coordinate with nickel ion in bi-dentate fashion. However to our surprise, it was observed that instead of Ni-O bond breakage, a hexacoordinated complex **7a** is formed by coordination of two ligands **2a**, to the Ni(acac)$_2$. This can be attributed to the fact that N-H proton is not much acidic to afford monoanionic ligand. Due to bulkiness of the ligand the exocyclic nitrogen of the imidazolin-2-imine fragment not coordinating, instead of more electronegativity of oxygen is coordinating with its lone pair, easily proved by the low carbonyl stretching frequency in the metal complex than from the ligand **2a**.

Compound **7a** was recrystallized from CH_2Cl_2 and crystallizes in triclinic space group *P*-1 having one molecule per unit cell. The solid state structure of the complex **7a** is given in Fig 11. The

coordination polyhedron of the complex **7a** is formed by the chelation of four oxygen atoms of the two acetylacetonate ligand moiety along with two oxygen atoms from the *N*-imidazole-*N*'-phenylureate ligand. In the nickel complex the nickel atom is surrounded by a tetragonally distorted octahedron, with acetylacetonate oxygen Ni(1)-O(2) and Ni(1)-O(3) are 2.015 and 1.998 Å respectively and with ligand Ni(1)-O(1) bond length is 1.023 Å. Ni-O bond distance are in the range of found in diaquabisacetylacetonatonickel(II)[28] complex. In diaquabisacetylacetonatonickel(II) the acetyl acetonate residue is plannar with a mean deviation of seven atoms from the least-squares plane of 0.04 Å. In case of other acetylacetonate fragment, the nickel atom did not lie in the same plane but 0.32 Å above of it. In complex **7a** nickel atom is coplanar with the four oxygen atoms. The solid state structure revels hydrogen bonding interaction between N-H and acetylacetonate oxygen atoms, also between carbonyl oxygen of the ligand and CH_3 proton is that between O(1)-H(10a).

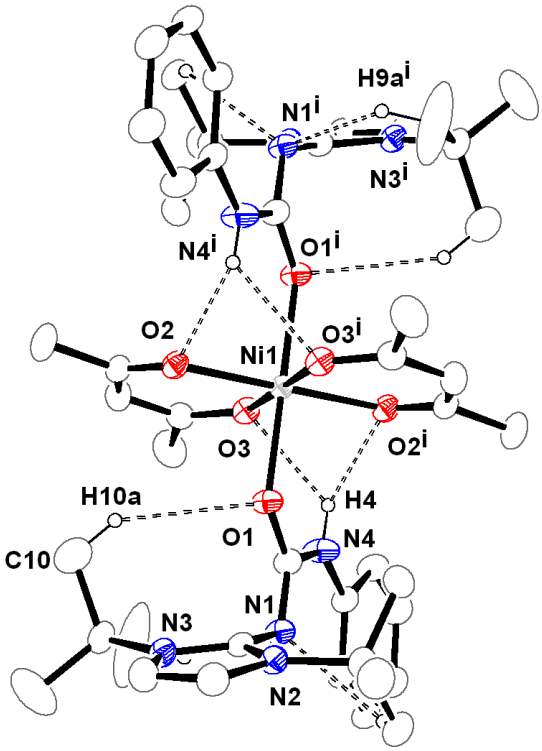
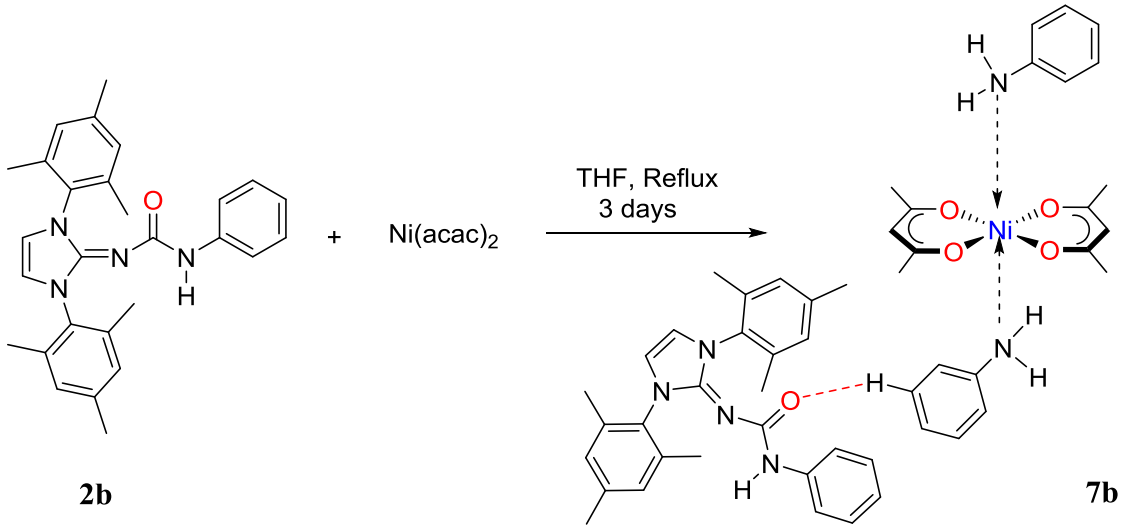


Figure 11. Solid state structure of compound **7a**. Selected bond lengths (Å) and bond angles (^{o}) are given. Ni(1)-O^i(3) 1.998(2), Ni(1)-O(3) 1.998(2), Ni(1)-O(2) 2.015(2), Ni(1)-O^i(2) 2.015(2), Ni(1)-O^i(1) 2.103(2), Ni(1)-O(1) 2.103(2), O(1)-C(12) 1.280(4), O^i(3)-Ni(1)-O(3) 180.0, Oi(3)-Ni(1)-O(2)

87.81(9), O(3)-Ni(1)-O(2) 92.19(9), O^{i}(3)-Ni(1)-O^{i}(2) 92.19(9), O(2)-Ni(1)-O^{i}(2) 180.00(13), O^{i}(3)-Ni(1)-O^{i}(1) 89.96(9), O(3)-Ni(1)-O^{i}(1) 90.04(9), O(2)-Ni(1)-O^{i}(1) 90.96(9), O(3)-Ni(1)-O(1) 89.96(9).

We have done a separate reaction with changing the substituent on the imidazole ring nitrogen from tertiary butyl to mesityl by maintaining the same reaction condition but the crystal structure shows C-N bond is breaking due to may presence of some moisture and amine is coordinating with $Ni(acac)_2$, the whole ligand is attached due to H-bonding interaction of carbonyl oxygen and benzene hydrogen (Scheme 10).



Scheme 10. Synthesis of bis-[*N*-(1,3-dimesitylimidazole-2-ylidene)-*N*'-phenylureato]$Ni(acac)_2$ **7b**.

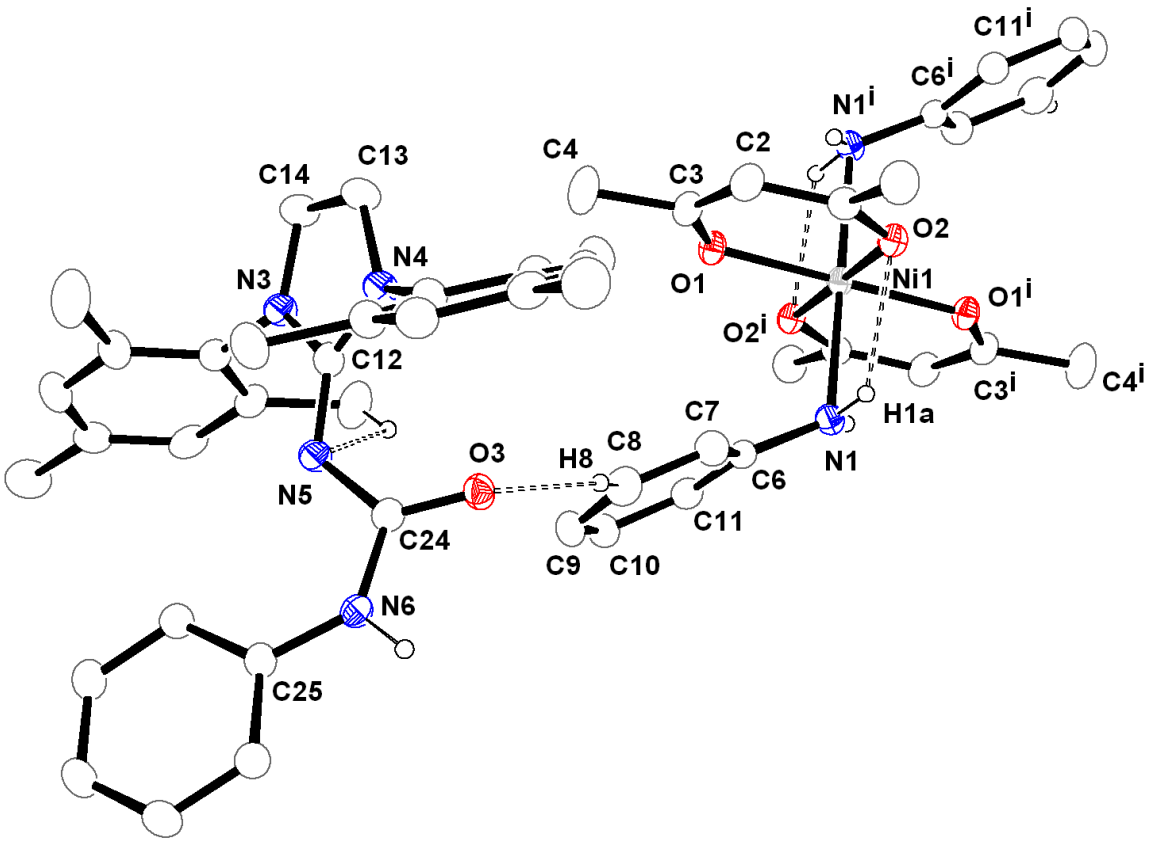


Figure 12. Solid state structure of compound **7b**. Selected bond lengths (Å) and bond angles (°) are given. Ni(1)-O(1)^{i} 2.007(12), Ni(1)-O(1) 2.007(12), Ni(1)-O(2) 2.023(12), Ni(1)-O(2)^{i} 2.023(12), Ni(1)-N(1)^{i} 2.160(15), Ni(1)-N(1) 2.160(15), O(1)-C(3) 1.260(2), N(1)-C(6) 1.424(2), O(1)^{i}-Ni(1)-O(1) 180.0(5), O(1)^{i}-Ni(1)-O(2) 88.06(5), O(1)-Ni(1)-O(2) 91.94(5), O(1)^{i}-Ni(1)-O(2)^{i} 91.94(5), O(1)-Ni(1)-O(2)^{i} 88.06(5), O(2)-Ni(1)-O(2)^{i} 180.0, C(6)-N(1)-Ni(1) 119.43(11), C(1)-O(2)-Ni(1) 124.61(11), O(1)-Ni(1)-N(1) 94.02(5), N(1)^{i}-Ni(1)-O(1) 85.98(5).

Compound **7b** was recrystallized from CH_2Cl_2 and crystallizes in triclinic space group *P*-1 having one molecule per unit cell. The solid state structure of the complex **7b** is given in Fig 12. The coordination polyhedron of the complex **7b** is formed by the chelation of four oxygen atoms of the two acetylacetonate ligand moieties along with two nitrogen atoms from aniline. In the nickel complex the nickel atom is surrounded by a tetragonally distorted octahedron, with acetylacetonate oxygen Ni(1)-O(2) and Ni(1)-O(1) are 2.007 and 2.023 Å respectively and with ligand Ni(1)-N(1) bond length is 2.160 Å greater than Ni-N bond Å lengths found in some Schiff base complex[29] of nickel with nitrogen donor ligand (1.835 Å) -O(1)-Ni(1)-N(1) angle is 94.02(5)°, N(1)^{i}-Ni(1)-O(1)

angle is 85.98(5)^{o}, In plane O(2)-Ni(1)-O(1)^{i} angle is 88.06(5)^{o} similar to 90^{o} ideal angle of octahedral geometry.

UV-Vis spectra of nickel complexes:

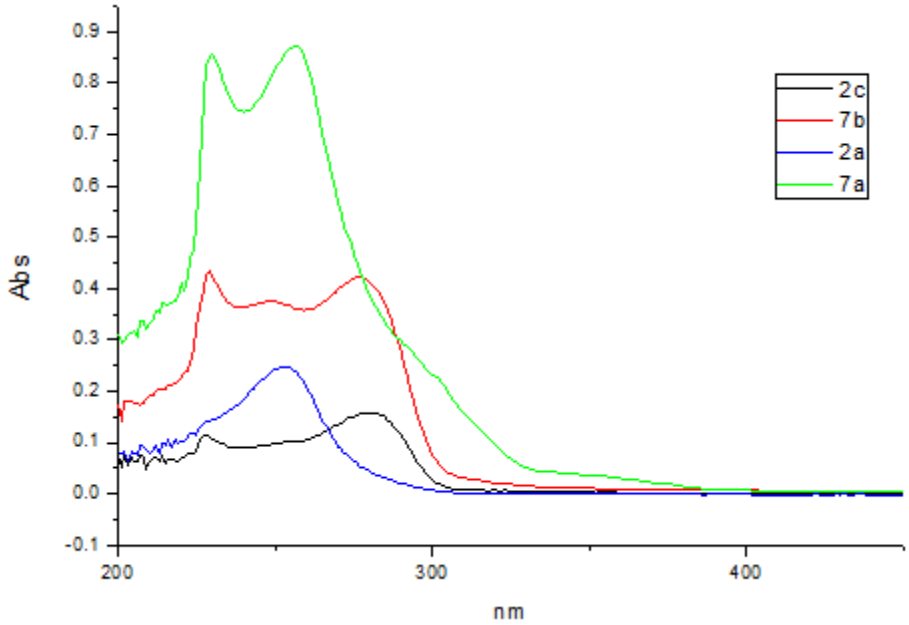


Figure 13. Uv-Vis spectrum (10^{-2}M) of **2a, 2c, 7a** and **7b** in CH_2Cl_2.

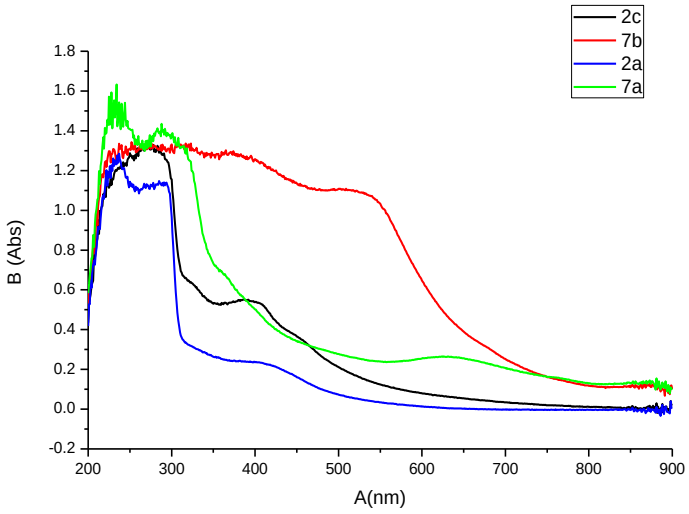


Figure 14. Solid state UV-Vis spectrum of **2a**, **2c**, **7a** and **7b**.

UV-visible absorption spectra of **2a**, **2c**, **7a** and **7b** were measured in CH_2Cl_2 at room temperature and displayed a nearly comparable absorption pattern at 230, 280, 260, 210 nm. Upon complexation of Ni(II) to **2a** as shown in Fig. 13, the increase in the absorption peak at 230 nm was observed, while it was not increased much for compound **7b**. The solid-state UV-visible absorption spectra of **2a**, **2c**, **7a** and **7b** were significantly different from that of solution (Fig. 14). A broad absorption peak from 200-400 nm in the solid state UV-visible spectra of **2a** and **2c** were attributed to the π to π^* transition of ligand. In the solid state UV-visible spectra in case of **7b** storng absorption band observed at 550 nm which is not observed in compound as due to strong ligand field splitting as nitrogen donor ligand coordinating with nickel(II).

4. Experimental Part:

General Information: All manipulations of air sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line. THF, dioxane, was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. CH_2Cl_2 was dried with calcium hydride and phosphorus pentoxide and kept with molecular shives. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^1H NMR (400 MHz), ^{13}C-{^1H} (100 MHz) and ^{31}P-{1H} NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Phenyl-isocyanate was prepared according to the literature procedure[30].

Synthesis of *N*-(1,3-di-*tert*-butylimidazole-2-ylidene)-*N*'-phenylurea (2a) :

To a toluene solution of 1,3-di-*tert*-butylimidazole-2-imine **1a** (300 mg, 0.949 mmol), 5% excess of phenyl-isocyanate (0.990 mmol) was added and the reaction mixture was stirred for 2 h. The solvent was evaporated in vacuum, and the recovered solid was purified by an *n*-pentane wash to afford spectroscopically pure white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-$CH_{(phenyl)}$), 7.25 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *m*-$CH_{(phenyl)}$), 6.90 (t, $^3J_{HH}$ = 8.0 Hz, 1H, *p*-$CH_{(phenyl)}$), 6.22 (s, 2H, NCHCHN), 1.49 (s, 18 H, C*C*H_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 158.3 (C=O), 150.4 (C=N), 142.1 ($C_{ipso(phenyl)}$), 128.6 (*o*-$CH_{(phenyl)}$), 120.1 (*p*-$CH_{(phenyl)}$), 117.2 (*m*-$CH_{(phenyl)}$), 112.3 (NCHCHN), 58.6 (N*C*Me), 29.1 (C*C*H_3) ppm, FTIR selected peaks (cm^{-1}): 1627 (C=O), 2979 (sp^3 CH), 3155 (aromatic CH), 3287 (N-H).

Synthesis of *N*-(1,3-dimesitylimidazole-2-ylidene)-*N*'-phenylurea (2b) :

To a toluene solution of 1,3-dimesitylimidazole-2-imine **1b** (300 mg, 0.949 mmol), $Ni(acac)_2$ was added and the reaction mixture was stirred for 12 h. The solvent was evaporated in vacuum, and the recovered solid was purified by an *n*-pentane wash to afford spectroscopically pure orange solid. ^1H NMR (400 MHz, C_6D_6) : δ 7.10 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-$CH_{(phenyl)}$), 6.91 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *m*-$CH_{(phenyl)}$), 6.72 (s, 4H, m-$CH_{(mesityl)}$), 6.62 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *p*-$CH_{(phenyl)}$), 5.80 (s, 2H, NCHCHN), 5.68 (br s, 1H, NH), 2.24 (s, 12H, *o*-$CH_{3(mesityl)}$), 2.04 (s, 16H, *p*-$CH_{3(mesityl)}$). FTIR selected peaks (cm^{-1}): 1580 (C=N), 1647 (C=O), 2916 (sp^3 CH).

Synthesis of *N*-(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-*N*'-phenylurea (2c) :

To a toluene solution of 1,3-dimesitylimidazole-2-imine **1b** (300 mg, 0.949 mmol), $Ni(acac)_2$ was added and the reaction mixture was stirred for 12 h. The solvent was evaporated in vacuum, and the residue washed by *n*-pentane to obtain orange solid and recrystallized from toluene. ^{1}H NMR (400 MHz, C_6D_6) : δ 7.42 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *p*-$CH_{(Dipp)}$), 7.26 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-$CH_{(Dipp)}$), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-$CH_{(phenyl)}$), 6.88 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *m*-$CH_{(phenyl)}$), 6.75 (t, $^3J_{HH}$ = 8.0 Hz, 2H,*p*-$CH_{(phenyl)}$), 6.61 (s, 2H, NCHCHN), 6.21 (br s, 1H, NH), 2.95 (sept., 4H, C*H*Me), 1.30 (d, 12H, CH_3), 1.19 (d, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 157.2 (C=O), 150.5 (N*C*N), 146.4 ($C_{ipso(dipp)}$), 140.6 ($C_{ipso(Phenyl)}$), 133.0 (*o*-$C_{(dipp)}$), 123.9 (*o*-$CH_{(phenyl)}$), 120.6 (*p*-$CH_{(phenyl)}$), 118.5 (*m*-$CH_{(phenyl)}$), 116.7 (NCHCHN), 28.8 (*C*HMe), 24.6 (CH*C*H_3), 23.3 (CH*C*H_3) ppm. FTIR selected peaks (cm^{-1}) : 1580 (C=N), 1650 (C=O), 2962 (sp^3 CH), 3053 (aromatic CH), 3419 (N-H).

Synthesis of 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine (3b) :

In a dry Schlenk tube (200 mg, 0.626 mmol) of 1,3-di mesitylimidazolin-2-imine dissolved in 10 ml THF:CH_2Cl_2 mixture (3:1), to it 0.1 ml (0.626 mmol) chlorodiphenylphosphine, 0.8 ml (0.626 mmol) triethylamine added. The reaction mixture was kept in ambient temperature for 2 h under stirring. Filtration and evaporation under vacuum afford orange colour solid. The title compound was recrystallized from THF/pentane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 6H, *m*-CH+ *p*-$CH_{(phenyl)}$), 7.28 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *o*-$CH_{(phenyl)}$), 6.82 (s, 4H, *m*-$CH_{(mesityl)}$), 6.01 (s, 2H, NCHCHN), 2.43 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.21 (s, 12H, *o*-$CH_{3(mesityl)}$). $^{31}P\text{-}\{^1H\}$ NMR (161.96 MHz, $CDCl_3$) δ 42.5 ppm. FT-IR selected peak (cm^{-1}): 924 (P-N), 1128 (P-Ph), 1653 (C=N), 3050 (aromatic C-H).

Synthesis of 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine (3c) :

In a dry Schlenk tube (200 mg, 0.495 mmol) of 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-imine **1c** dissolved in 10 ml THF: CH_2Cl_2 mixture (3:1), to it 0.09 ml (0.495 mmol) chlorodiphenylphosphine, 0.06 ml (0.495 mmol) triethyl amine added. The reaction mixture was kept in ambient temperature for 2 h under stirring. Filtration and evaporation under vacuum afford orange colour solid. The title compound was crystallized from THF/pentane. ^{1}H NMR (400 MHz, C_6D_6) : δ 7.49 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *p*-$CH_{(Dipp)}$), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-$CH_{(Dipp)}$), 5.97 (s, 2H, NCHCHN), 3.12 (sept., 4H,

C*H*Me), 1.31 (d, 12H, CH_3), 1.13 (d, 12H, CH_3). ^{31}P-{^1H} NMR (161.96 MHz, $CDCl_3$) δ 41.2 ppm. FT-IR selected peak (cm^{-1}): 916 (P-N), 1110 (P-Ph), 1617 (C=N), 3055 (aromatic C-H).

Synthesis of 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinicamide (4b):

In a dry Schlenk (160 mg, 0.318 mmol) of 1,3-dimesitylimidazolin-2-iminediphenylphosphine dissolved in 4 ml of THF, to it 0.1 ml H_2O_2 added and kept for 4 h in room temparature under stirring. Solvent evaporated in vacuum and the crude product purified by column chromatography. Recrystallize from EtOAc/pentane at room temperature. ^1H NMR (400 MHz, $CDCl_3$), δ 7.08 (m, 6H, *m*-CH+ *p*-$CH_{(phenyl)}$), 6.97 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *o*-$CH_{(phenyl)}$), 6.82 (s, 4H, *m*-$CH_{(mesityl)}$), 6.40 (s, 2H, NCHCHN), 2.29 (s, 6H, *p*-$CH_{3(mesityl)}$), 1.97 (s, 12H, *o*-$CH_{3(mesityl)}$). ^{31}P-{1H} NMR (161.96 MHz, $CDCl_3$), δ 4.85 ppm. FT-IR selected peak (cm^{-1}): 915 (P-N), 1109 (P-Ph), 1260 (P=O), 1623 (C=N), 3052 (aromatic C-H).

1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinothioicamide (5b) :

In a dry Schlenk (100 mg, 0.198 mmol) of 1,3-dimesitylimidazolin-2-iminediphenylphosphine dissolved in 3 ml of toluene, to it (6.36 mg, 0.198 mmol) elemental sulphur added and kept at 90 ^oC for 12 h under stirring. Solvent evaporated in vacuum and the crude product purified by column chromatography and recrystallized from CH_2Cl_2/pentane at room temparature. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.19 (m, 6H, *m*-CH+ *p*-$CH_{(phenyl)}$), 6.99 (d, $^3J_{HH}$= 8.0 Hz, 4H, *o*-$CH_{(phenyl)}$), 6.71(s, 4H, *m*-$CH_{(mesityl)}$), 6.58 (s, 2H, NCHCHN), 2.30 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.18 (s, 12H, *o*-$CH_{3(mesityl)}$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 146.7 (N*C*N), 146.6 (P attached Ph*C*), 141.3 (P attached Ph*C*), 140.3 ($C_{ipso(mesityl)}$), 138.9 (*o*-*C*$CH_{3(mesiyl)}$), 136.6 (*p*-*C*$CH_{3(mesiyl)}$), 130.7 (P attached *o*-Ph*C*), 130.6 (P attached *o*-Ph*C*), 129.02(P attached *m*-Ph*C*), 128.8 (P attached *m*-Ph*C*), 128.7 (*m*-$CH_{(mesityl)}$), 126.9 (P attached *p*-Ph*C*), 126.8 (P attached *p*-Ph*C*), 115.7 (NCHCHN), 21.07 (*p*-C*C*$H_{3(mesityl)}$), 18.7 (*o*-C*C*$H_{3(mesityl)}$). ^{31}P {^1H} NMR (161.96 MHz, $CDCl_3$) δ 35.83 ppm. FT-IR selected peak (cm^{-1}): 710 (P=S), 911 (P-N), 1434 (P-Ph), 1561 (C=N), 3052 (aromatic C-H).

Synthesis of 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinoselenoicamide (6b) :

In a dry Schlenk (100 mg, 0.198 mmol) of 1,3-dimesitylimidazolin-2-iminediphenylphosphine dissolved in 3 ml of toluene, to it (18.76 mg, 0.396 mmol) elemental selenium added and kept at 90

°C for 12 h under stirring. Solvent evaporated in vacuum and the crude product purified by column chromatography and recrystallized from CH_2Cl_2/pentane at room temparature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 6H, *m*-CH and *p*-$CH_{(phenyl)}$), 7.14 (d, $^3J_{HH}$= 8.0 Hz, 4H, *o*-$CH_{(phenyl)}$), 6.77 (s, 4H, *m*-$CH_{(mesityl)}$), 6.06 (s, 2H, NCHCHN), 2.30 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.21 (s, 12H, *o*-$CH_{3(mesityl)}$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 146.7 (N*C*N), 146.6 (P attached Ph*C*), 141.3 (P attached Ph*C*), 140.3 ($C_{ipso(mesityl)}$), 138.9 (*o*-*C*$CH_{3(mesiyl)}$), 136.6 (*p*-*C*$CH_{3(mesiyl)}$), 132.7 (P attached *o*-Ph*C*), 130.7 (P attached *o*-Ph*C*), 129.0 (P attached *m*-Ph*C*), 128.8 (P attached *m*-Ph*C*), 128.7 (*m*-$CH_{(mesityl)}$), 126.9 (P attached *p*-Ph*C*), 126.8 (P attached *p*-Ph*C*), 115.7 (NCHCHN), 21.07 (*p*-C*C*$H_{3(mesityl)}$), 18.7 (*o*-C*C*$H_{3(mesityl)}$). ^{31}P {1H} NMR (161.96 MHz, $CDCl_3$) δ 25.77 ppm. FT-IR selected peak (cm^{-1}) : 965 (P=Se), 917 (P-N), 1615 (C=N), 3049 (aromatic C-H).

Synthesis of bis-[*N*-(1,3-ditertbutylimidazole-2-ylidene)-*N*'-phenylureato]Ni(acac)$_2$ (7a) :

To a solution of 1a (200 mg, 0.636 mmol) in THF, Ni(acac)$_2$ (163.39 mg, 0.636 mmol) was added and kept under reflux for 3 days. The solution was filtered over celite and concentrated under vacuum, crystallize from CH_2Cl_2. FTIR selected peaks (cm^{-1}): 1588 (C=O), 3338 (N-H), 3050 (aromatic CH), 1258 (C-O).

Synthesis of bis-[*N*-(1,3-dimesity imidazole-2-ylidene)-*N*'-phenyl ureato]Ni(acac)$_2$ (7b) :

To a solution of 2a (200 mg, 0.636 mmol) in THF, Ni(acac)$_2$ (163.39 mg, 0.636 mmol) was added and kept under reflux for 3 days. The solution was filtered over celite and concentrated under vacuum, crystallize from CH_2Cl_2. FTIR selected peaks (cm^{-1}): 1553 (C=O), 3048 (aromatic CH), 1263 (C-O), 2961(sp^3 CH).

Table 2: Crystallographic data for compounds **3b-6b.**

Crystal	**3b**	**4b**	**5b**	**6b**
CCDC No	-	-	-	-
Empherical Formula	$C_{33}H_{34}N_3P$	$C_{37}H_{42}N_3O_3P$ (**4b**. Dioxane)	$C_{33}H_{34}N_3PS$	$C_{33}H_{34}N_3PSe$
Formula weight	503.60	607.71	535.67	583.57
T (K)	150(2)	293(2)	293(2)	293(2)
λ (Å)	1.54184	1.54184	1.54184	1.54184

Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P*-1	*P* 2_1/c	*P*2_1 2_1 2_1	*P*2_1 2_1 2_1
a (Å)	8.8079(6)	8.4818(4)	8.7492(4)	8.9524(3)
b (Å)	10.3470(8)	31.2129(18)	18.4412(11)	18.2570(8)
c (Å)	16.7289(8)	14.0448(9)	18.4412(11)	18.5025(8)
α (^{o})	89.195(6)	90	90	90
β (^{o})	80.155960	103.174(6)	90	90
γ (^{o})	69.595(7)	90	90	90
V (Å^3)	1406.17(18)	3620.4(4)	2977.6(3)	3024.1(2)
Z	2	4	4	4
D_{calc} g cm^{-3}	1.189	1.115	1.195	1.282
μ (mm^{-1})	1.051	0.957	1.660	2.366
F (000)	536	1296	1136	1212
Theta range for data collection	4.57 to 70.56 deg	3.53 to 70.75 deg.	3.39 to 70.79 deg	3.40 to 71.11 deg
Limiting indices	-10<=h<=10 12<=k<=12 20<=l<=15	-10<=h<=10 37<=k<=37 12<=l<=17	-10<=h<=6 20<=k<=20 22<=l<=20	-10<=h<=6 22<=k<=18 22<=l<=13
Reflections collected/ unique	9935 / 5287 [R(int) = 0.0220]	16013 / 6827 [R(int) = 0.0314]	6407 / 4510 [R(int) = 0.0208]	8084 / 4885 [R(int) = 0.0243]
Completeness to theta = 70.56	97.7 %	98.1 %	88.5 %	97.8 %
Final R indices [I>2sigma(I)]	R1 = 0.0633, wR2 = 0.1822	R1 = 0.0828, wR2 = 0.2317	R1 = 0.0368, wR2 = 0.1027	R1 = 0.0381, wR2 = 0.0989
R indices (all data)	R1 = 0.0674, wR2 = 0.1867	R1 = 0.0905, wR2 = 0.2411	R1 = 0.0384, wR2 = 0.1050	R1 = 0.0444, wR2 = 0.1059
Largest diff. peak and hole	0.715 and -0.547 e.Å^{-3}	0.435 and -0.296 e.Å^{-3}	0.187 and -0.197 e.Å^{-3}	0.148 and -0.342 e.Å^{-3}

Table 3 : Comparison between theoretical and practical values of compound **3b**.

The structure of compound **3b** was freely optimized without any geometrical constraints using density functional theory (B3LYP 6-311+G(2d,p)). The optimized structures were in excellent agreement with those established with X-Ray diffraction analyses.

Bond Length[Å]/angle[^{o}]	Experimental	B3LYP/6-311+G(2d,p)
P1-N1	1.674	1.698
P1-C29	1.840	1.855
P1-C23	1.848	1.864
N3-C1	1.384	1.393
N3-C3	1.395	1.392
N3-C13	1.436	1.432
N1-C1	1.301	1.287
N2-C1	1.376	1.397
N2-C4	1.438	1.435
N1-P1-C29	98.43	99.686
N1-P1-C23	104.99	102.856
C29-P1-C23	97.06	98.190
C1-N3-C3	110.14	110.404
C1-N3-C13	124.52	124.552
C1-N1-P1	124.58	127.671
C1-N2-C2	109.64	109.706
C1-N2-C4	125.86	127.924
C2-N2-C4	123.95	122.189
N1-C1-N2	132.52	133.573
N1-C1-N3	122.82	122.314
N2-C1-N3	104.65	104.105
C3-C2-N2	108.12	108.078
C2-C3-N3	107.52	107.707

Table 4. Comparison between theoretical and practical values of compound **4b**.

The structure of compound **4b** were freely optimized without any geometrical constraints using density functional theory (B3LYP 6-311+G(2d,p)). The optimized structure was in excellent agreement with those established with X-Ray diffraction analyses.

Bond Length[Å]/angle[^{o}]	Experimental	B3LYP/6-311+G(2d,p)
P1-N1	1.597	1.635
P1-C28	1.807	1.828
P1-C22	1.808	1.834
P1-O1	1.476	1.493
N1-C1	1.292	1.292
N2-C1	1.371	1.387
N2-C2	1.398	1.397
N3-C4	1.427	1.434
C1-N3	1.368	1.386
C2-C3	1.350	1.344
C3-N3	1.399	1.391
NI-PI-C28	101.32	102.69
NI-PI-C22	108.43	106.76
C28-P1-C22	105.97	105.36
N1-P1-O1	120.44	120.52
C28-P1-O1	109.56	110.60
C22-P1-O1	109.98	110.54
C1-N1-P1	138.9	135.19
C1-N2-C2	110.3	109.53
C1-N3-C4	126.10	124.63
N1-C1-N2	133.2	133.36
N2-C1-N3	104.9	104.66
C3-N3-C4	126.8	125.06

Table 5. Comparison between theoretical and practical values of compound **5b**.

The structure of compound **5b** were freely optimized without any geometrical constraints using density functional theory (B3LYP 6-311+G(2d,p)). The optimized structure was in excellent agreement with those established with X-Ray diffraction analyses.

Bond Length[Å]/angle[^{o}]	Experimental	B3LYP/6-311+G(2d,p)
P1-N1	1.612	1.632
P1-C28	1.824	1.837
P1-C22	1.828	1.843
P1-S1	1.952	1.918
N1-C1	1.311	1.298
N2-C1	1.359	1.381
N2-C2	1.390	1.388
N2-C4	1.437	1.436
C1-N3	1.365	1.383
C13-N3	1.434	1.438
C2-C3	1.320	1.345
C3-N3	1.400	1.393
NI-PI-C28	102.18	103.21
NI-PI-C22	108.66	108.40
C28-P1-C22	101.83	101.90
N1-P1-S1	119.36	118.32
C28-P1-S1	111.10	111.35
C22-P1-S1	111.91	112.09
C1-N1-P1	130.92	133.54
C1-N2-C2	109.32	110.23
C1-N2-C4	124.45	124.82
C2-N2-C4	126.10	124.93
N1-C1-N2	122.32	123.43

N1-C3-N3	131.32	131.63
N2-C1-N3	106.09	104.79
C1-N3-C3	108.82	109.62
C1-N3-C13	126.60	127.31
C3-N3-C13	123.62	122.64

Table 6. Comparison between theoretical and practical values of compound **6b**.

The structure of compound **6b** were freely optimized without any geometrical constraints using density functional theory (B3LYP 6-311+G(2d,p)). The optimized structure was in excellent agreement with those established with X-Ray diffraction analyses.

Bond Length[Å]/angle[^{o}]	Experimental	B3LYP/6-311+G(2d,p)
P1-N1	1.609	1.630
P1-C28	1.824	1.837
P1-C22	1.821	1.845
P1-Se1	2.108	2.149
N1-C1	1.306	1.299
N2-C1	1.365	1.381
N2-C2	1.396	1.388
N3-C4	1.445	1.439
C1-N3	1.356	
C2-C3	1.327	1.345
C3-N3	1.403	1.393
NI-PI-C28	102.69	103.41
NI-PI-C22	109.57	108.94
C28-P1-C22	105.97	101.72
N1-P1-Se1	118.08	117.98

C28-P1-Se1	110.92	110.02
C22-P1-Se1	112.40	112.22
C1-N1-P1	132.2	134.46
C1-N2-C2	109.0	110.20
C3-N3-C4	123.0	122.55
C1-N3-C4	126.7	127.38
N1-C1-N2	122.0	123.56
N2-C1-N3	106.2	104.83
C3-N3-C4	128.0	

5. Conclusion : We have demonstrated the functionalization of imidazolin-2-imine at the imine end of the ligand by phenyl-isocyanate and chlorodiphenylphosphine. The phosphine derivatives were further used to synthesis various chalcogenides compounds (O, S, Se). *N*-imidazol-2-imine-*N*'-phenylureate ligands were introduced into the nickel chemistry and two nickel complexes were prepared. It is observed that the ligand is not enough acidic to be deprotonated rather coordinate through oxygen atoms of the ligands to the nickel center. The structure of all compound were confirmed by X-ray diffraction analysis. The nickel complexes are potentially active to be used as a olefin polymerization or in various organic transformations.

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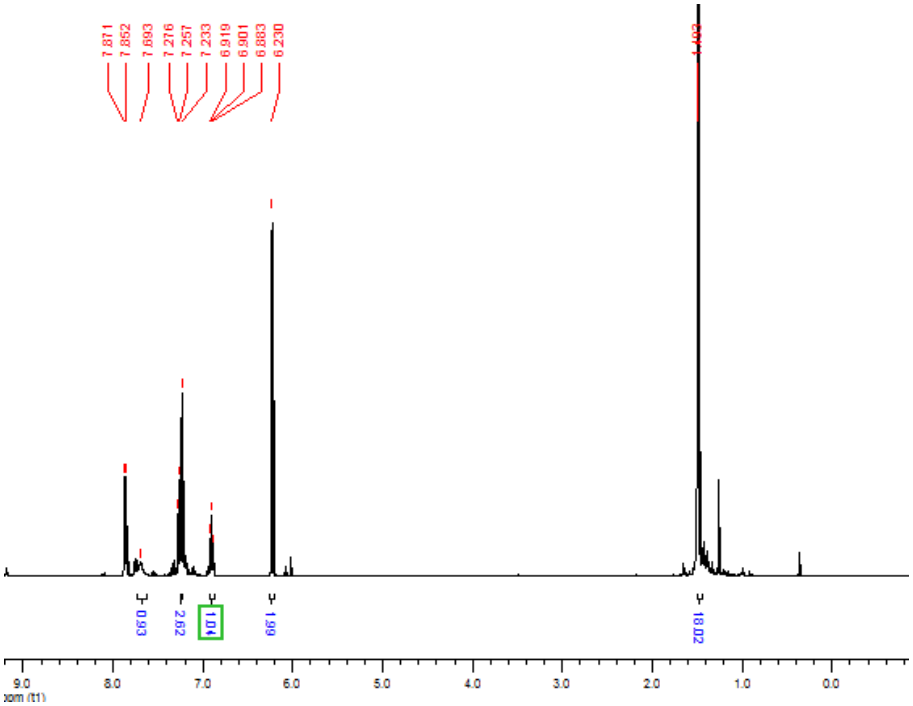
Appendix:

Supporting information:



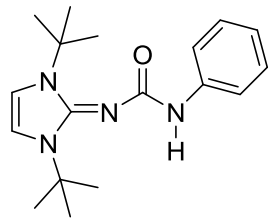
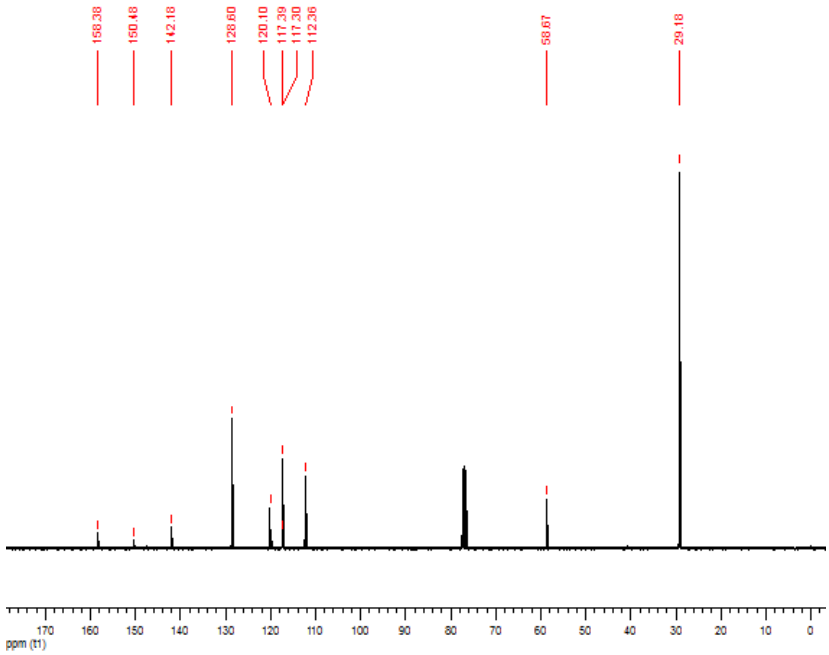


Figure 1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of *N*-(1,3-di-*tert*-butylimidazole-2-ylidene)-*N*'phenylureate **2a.**



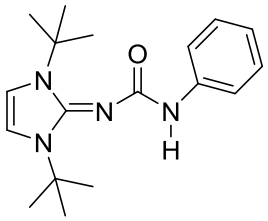


Figure 2. ^{13}C NMR spectra of *N*-(1,3-di-*tert*-butylimidazole-2-ylidene)-*N*'phenylureate **2a.**

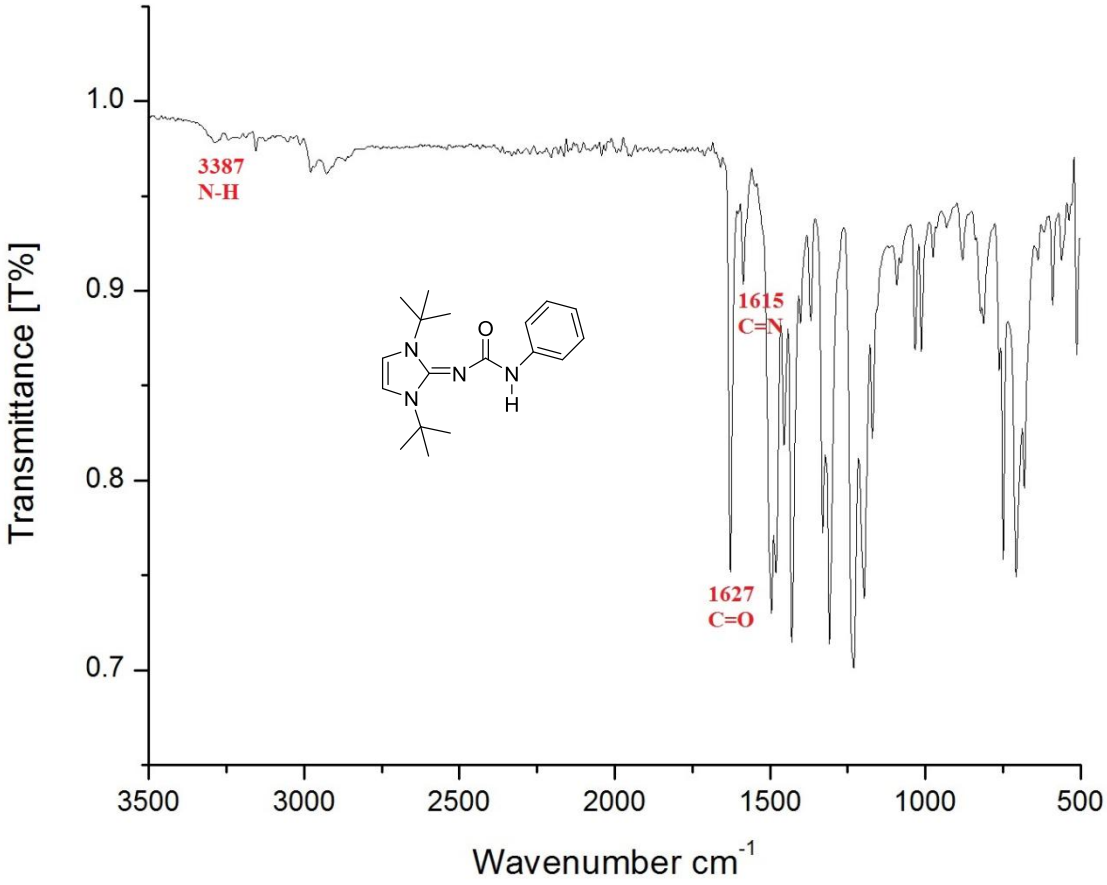


Figure 3. FT-IR spectra of *N*-(1,3-di-*tert*-butylimidazole-2-ylidene)-*N*'phenylureate **2a.**

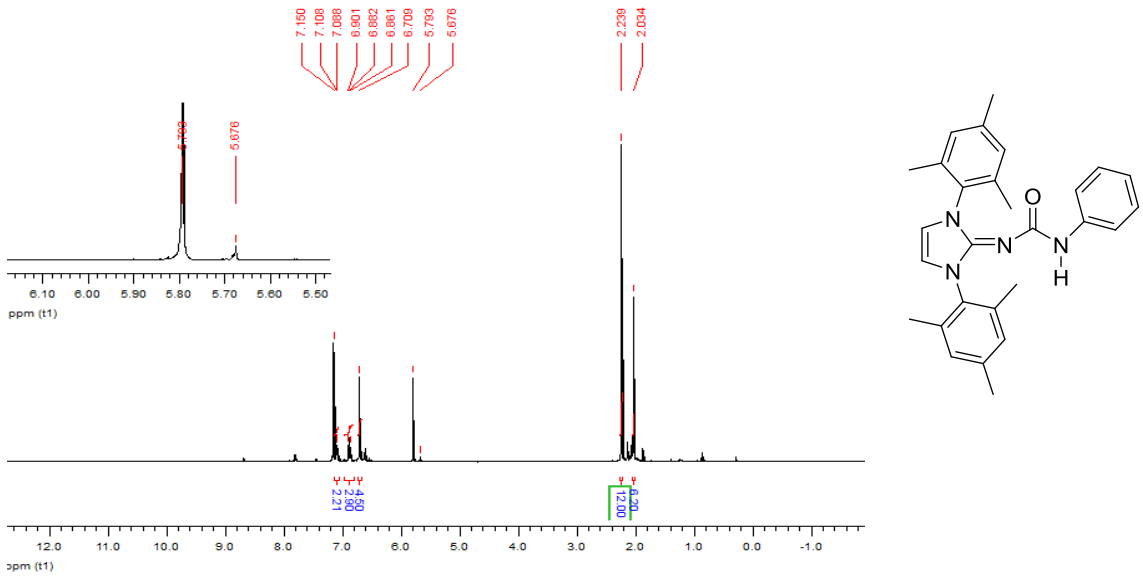


Figure 4. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of *N*-(1,3-dimesitylimidazole-2-ylidene)-*N*' phenylureate **2b.**

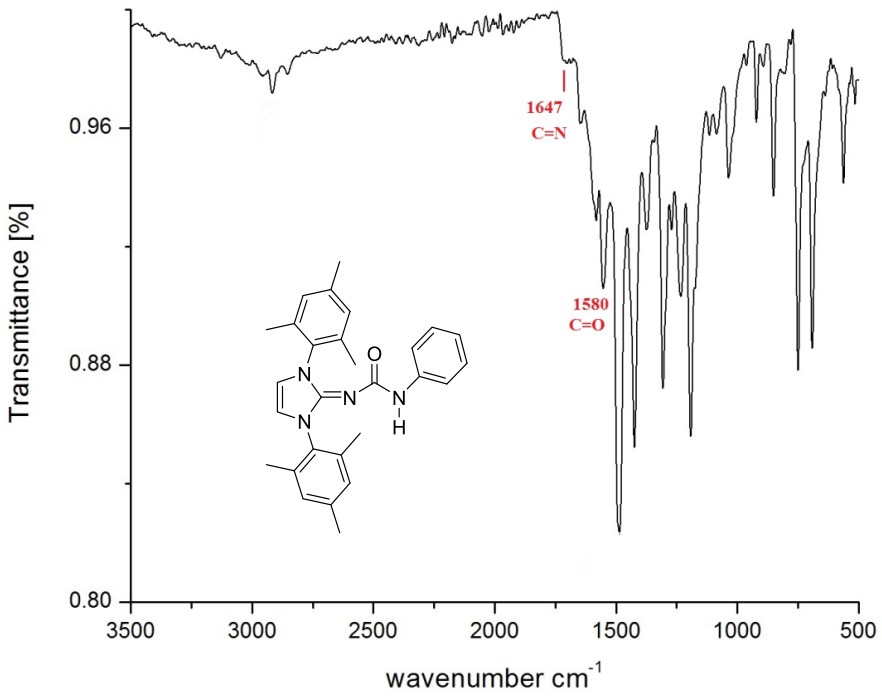


Figure 5. FT-IR spectra of *N*-(1,3-dimesitylimidazole-2-ylidene)-*N*' phenylureate **2b.**

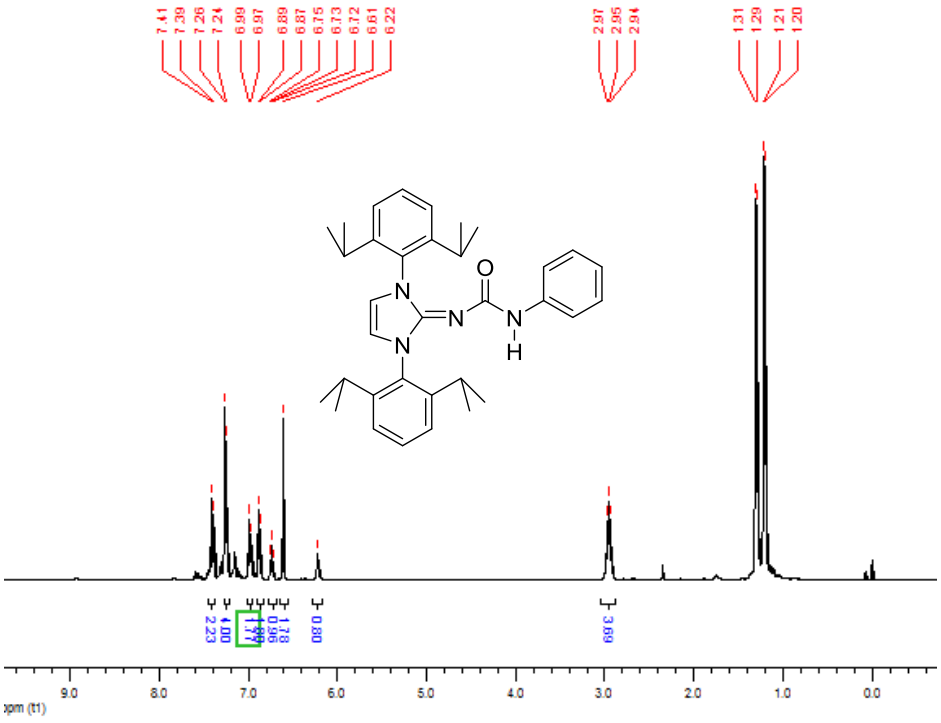


Figure 6. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of *N*-(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-*N*'-phenylurea **2c**.

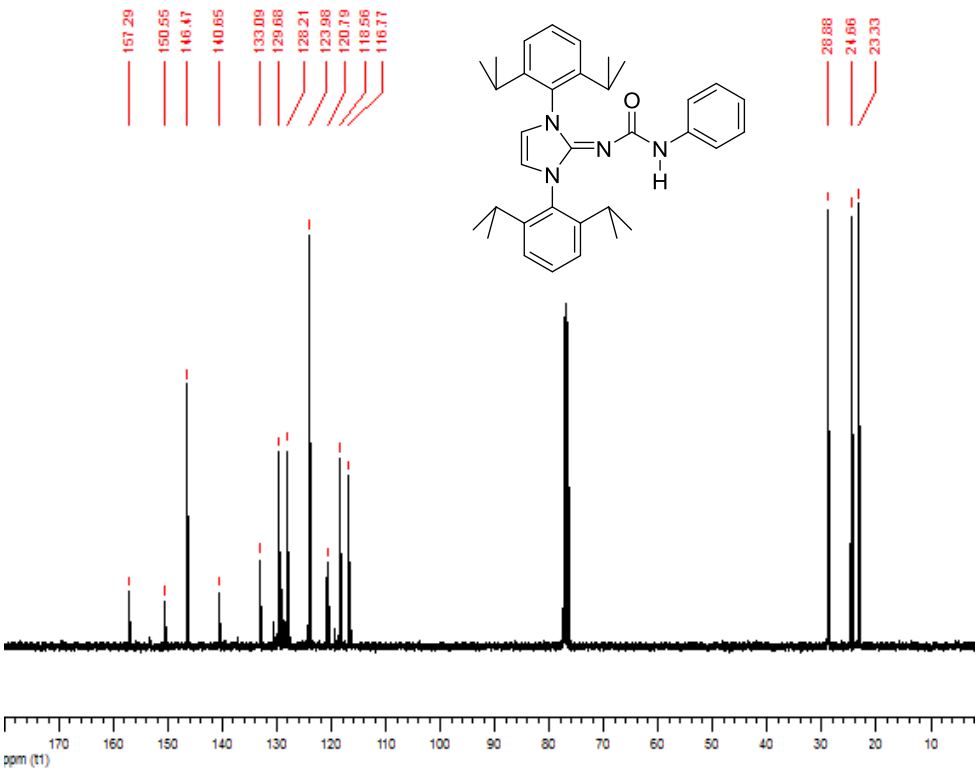


Figure 7. ^{13}C NMR spectra of *N*-(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-*N*'-phenylurea **2c**.

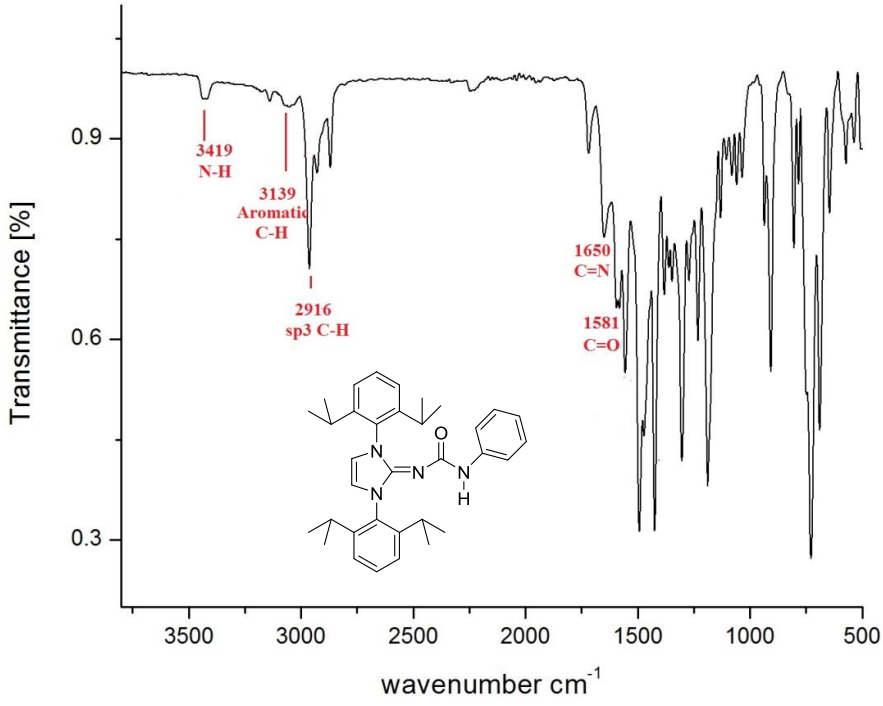


Figure 8. FT-IR spectra of *N*-(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene)-*N*'-phenylurea **2c**.

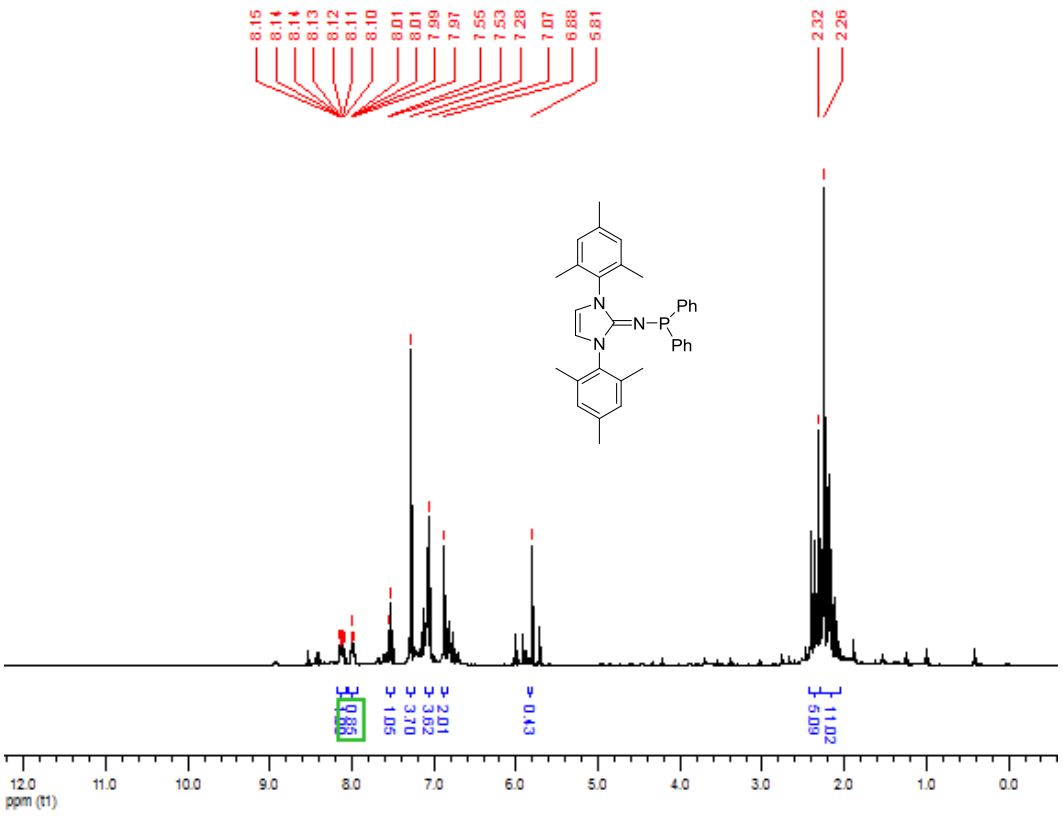


Figure 9. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) of 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine **3b**.

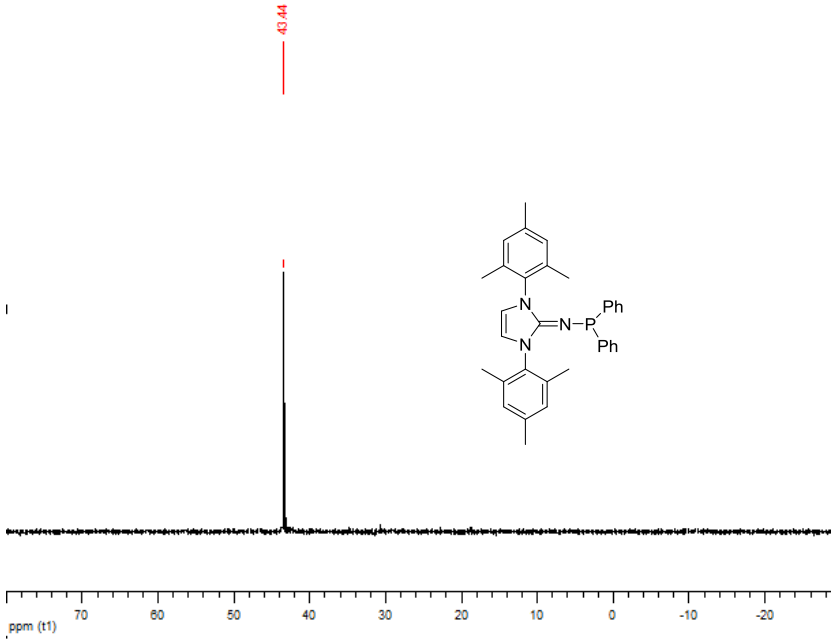


Figure 10. ^{31}P-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine **3b**.

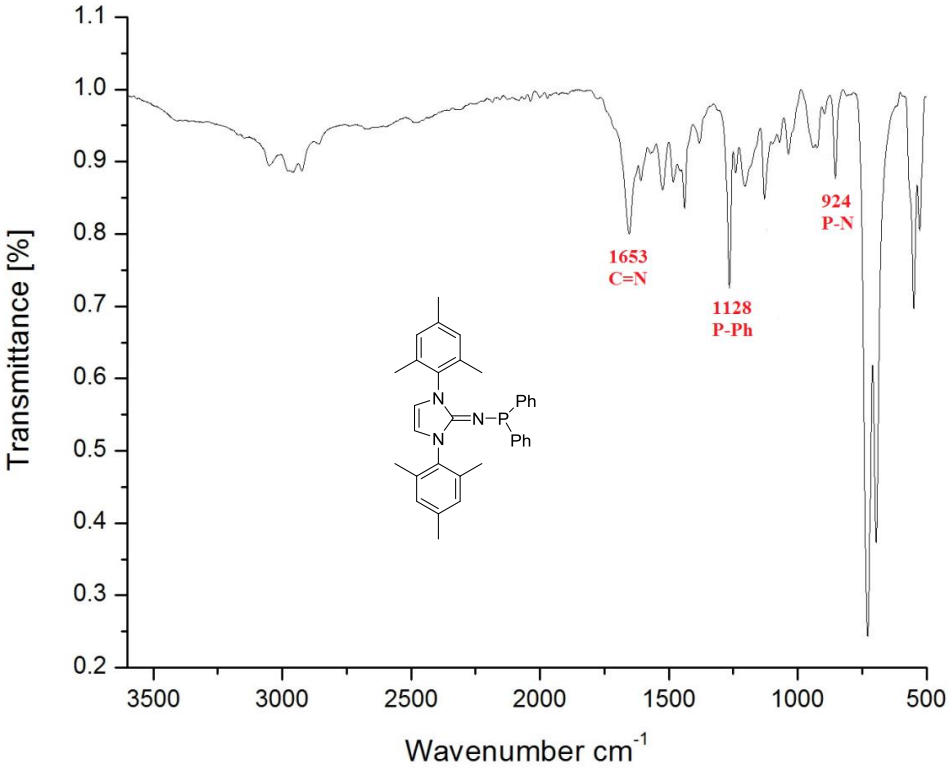


Figure 11. FT-IR spectra of 1,3-dimesitylimidazolin-2-ylidene-1,1-diphenylphosphinamine **3b**.

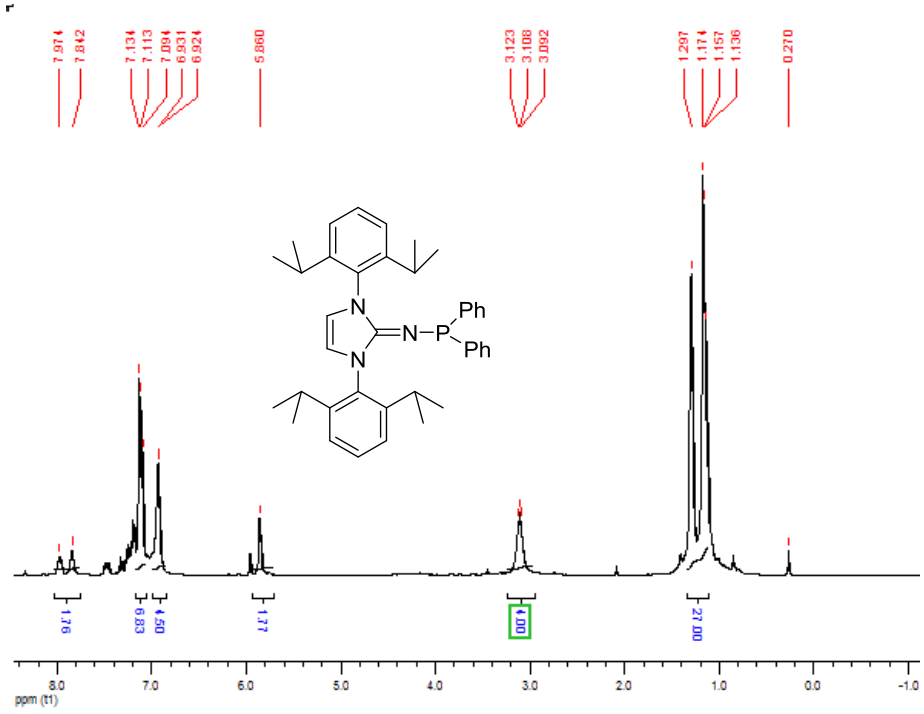


Figure 12. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of 1,3-bis-**(**2,6-diisopropylphenyl)-imidazolin-2-ylidene-1,1-diphenylphosphinamine **3c**.

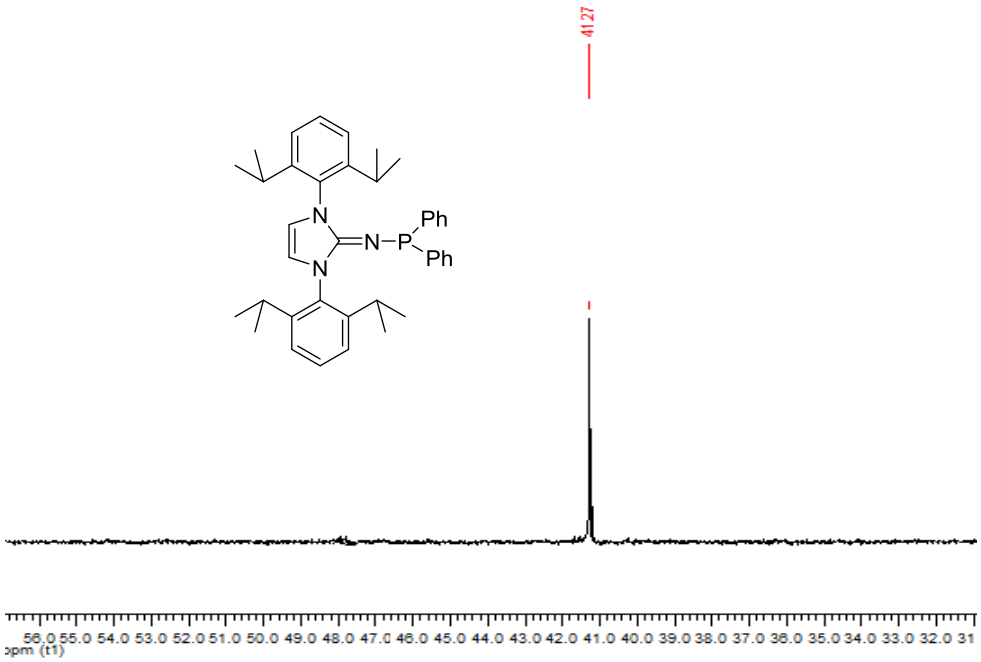


Figure 13. ^{31}P-{^{1}H} NMR of 1,3-bis-**(**2,6-diisopropylphenyl)-imidazolin-2-ylidene-1,1-diphenylphosphinamine **3c**.

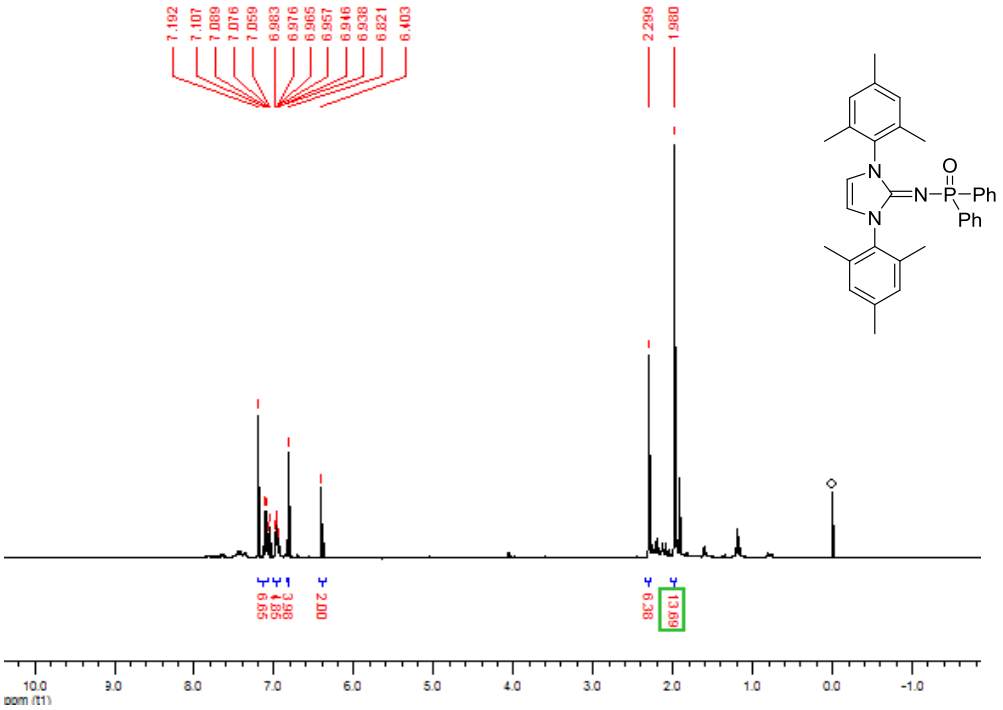


Figure 14. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b**.

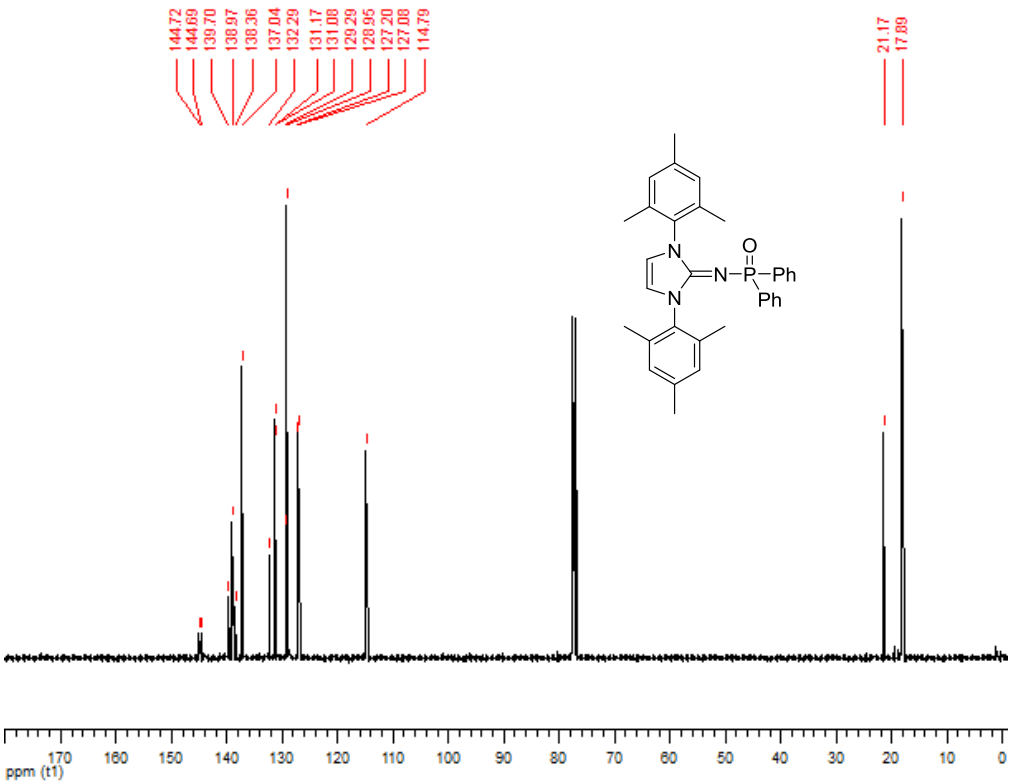


Figure 15. ^{13}C-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b**.

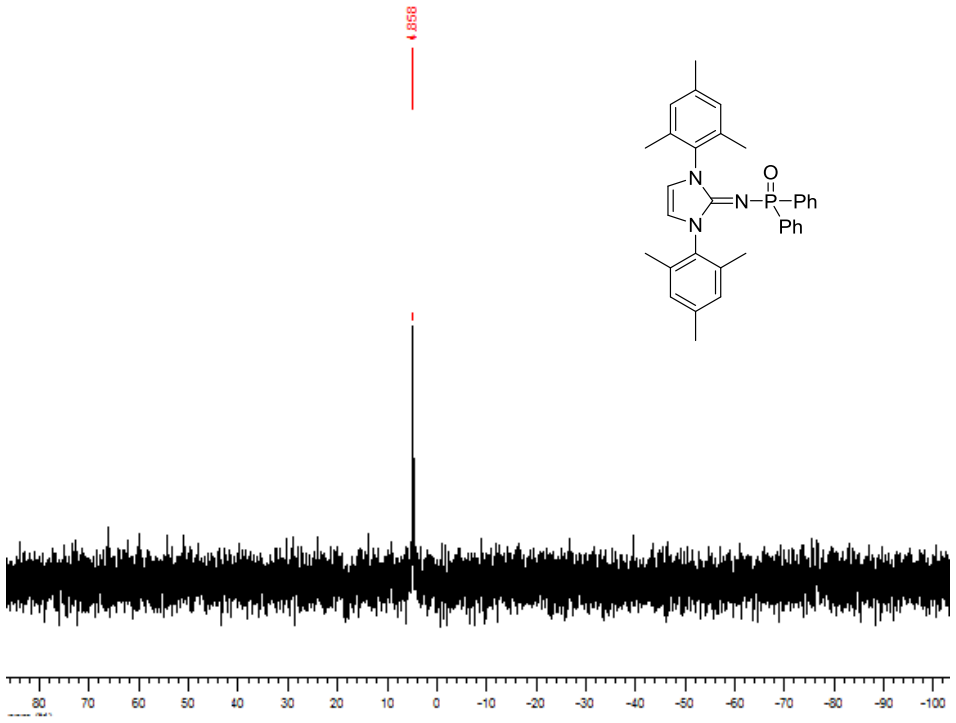


Figure 16. ^{31}P-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b**.

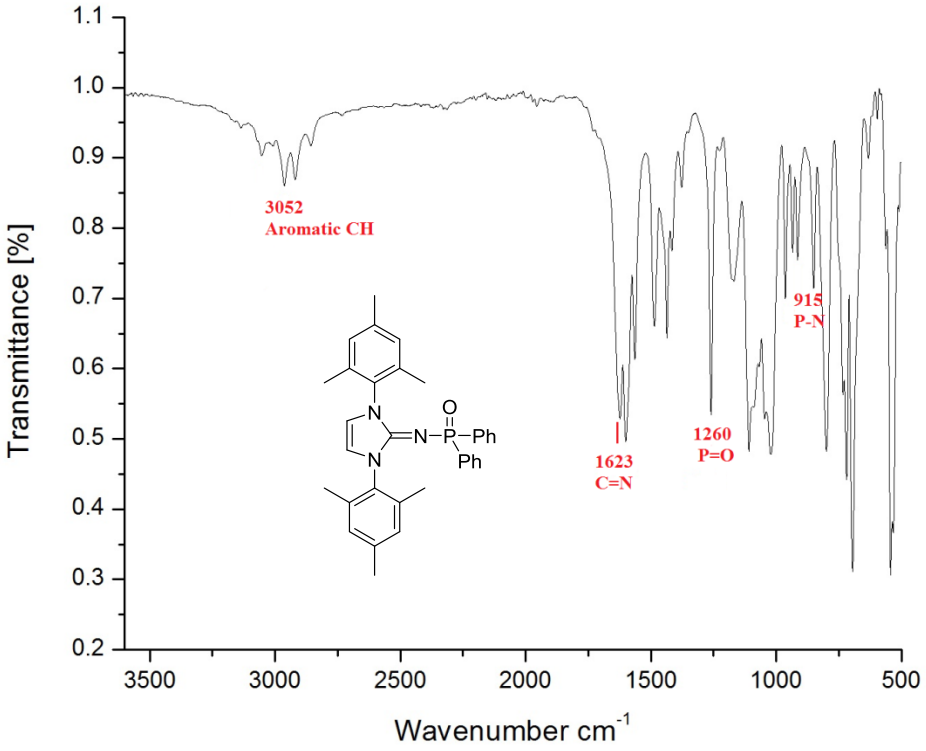


Figure 17. FT-IR spectra of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinicamide **4b**.

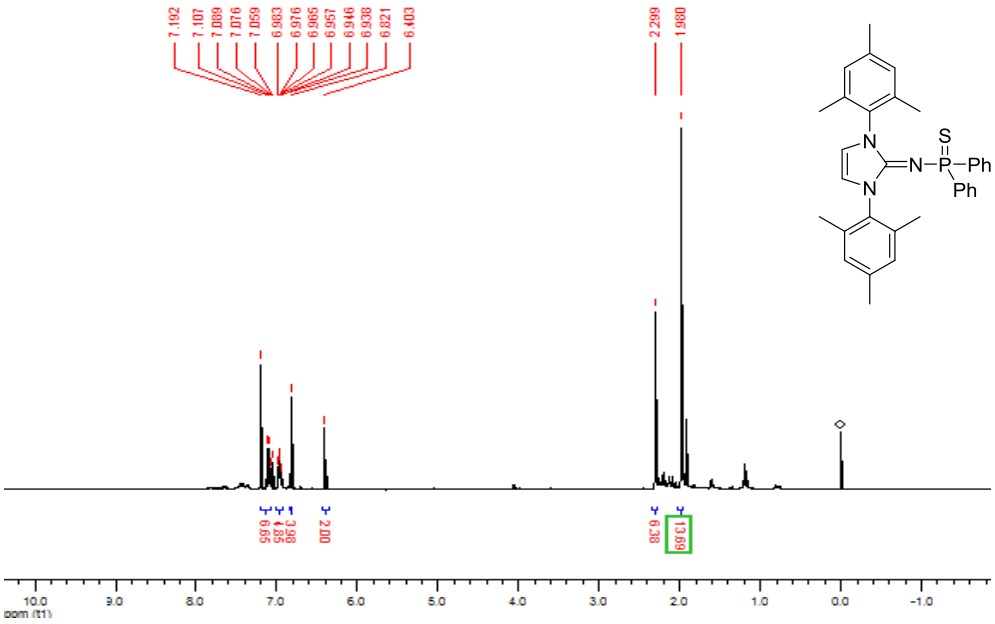


Figure 18. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinothioicamide **5b**.

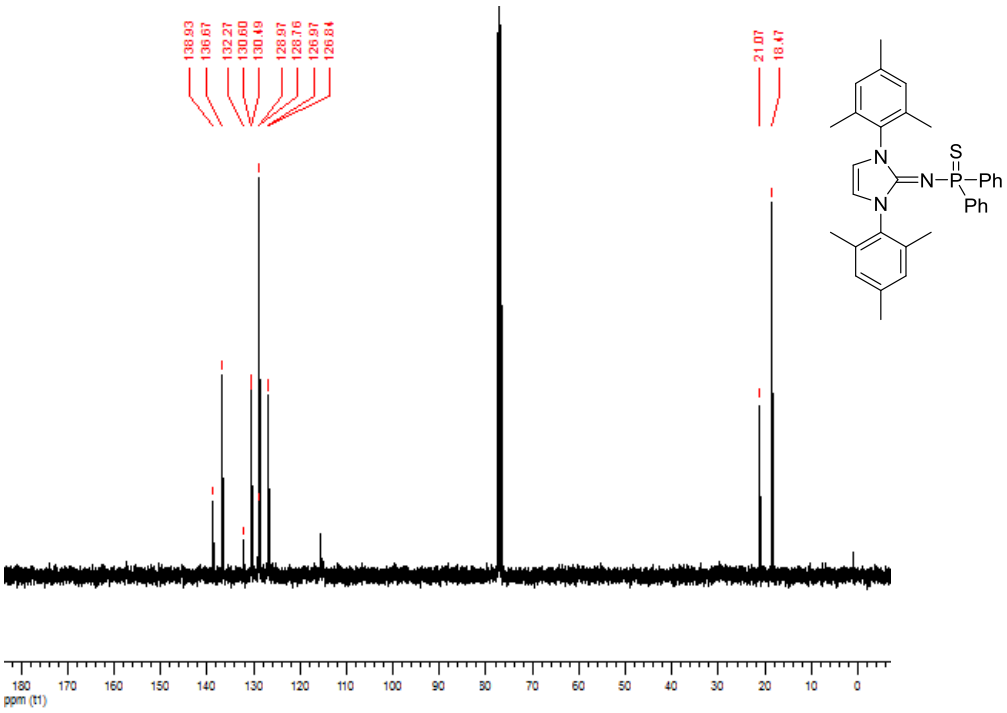


Figure 19. ^{13}C-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinothioicamide **5b**.

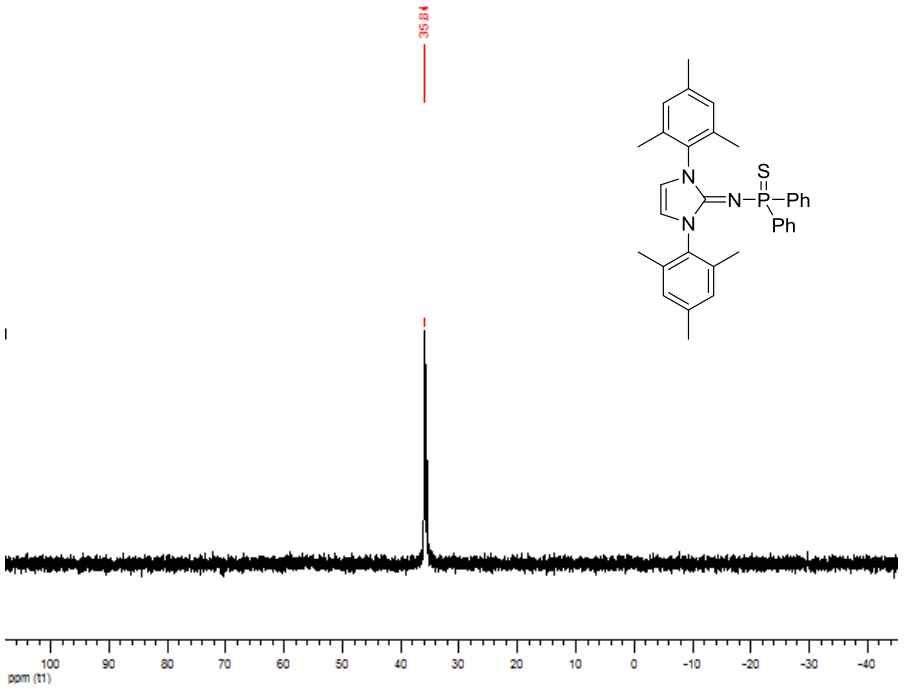


Figure 20. ^{31}P-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinothioicamide **5b**.

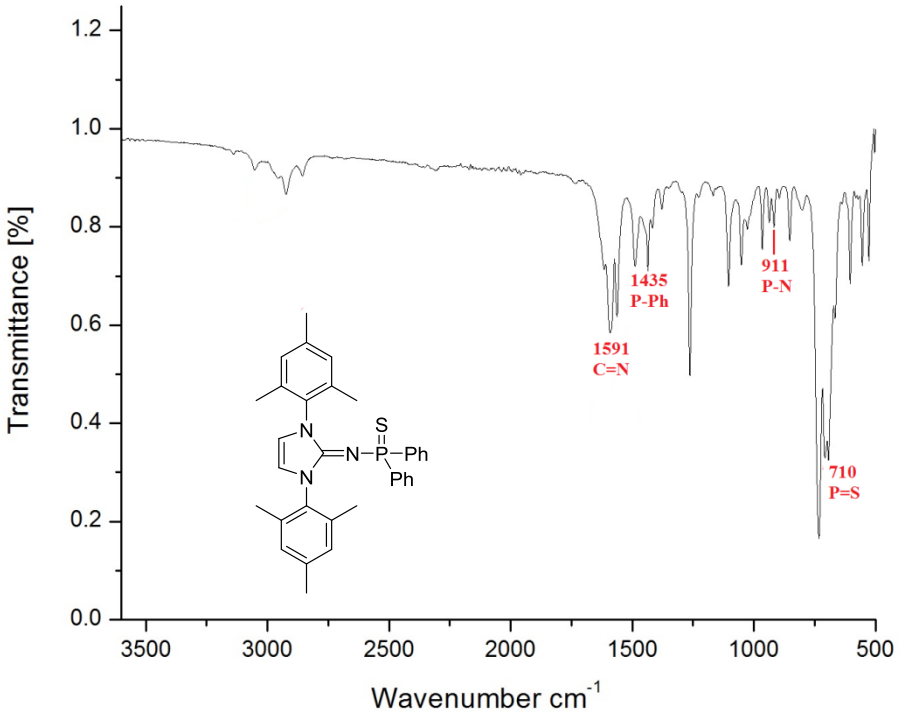


Figure 21. FT-IR spectra of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinothioicamide **5b**.

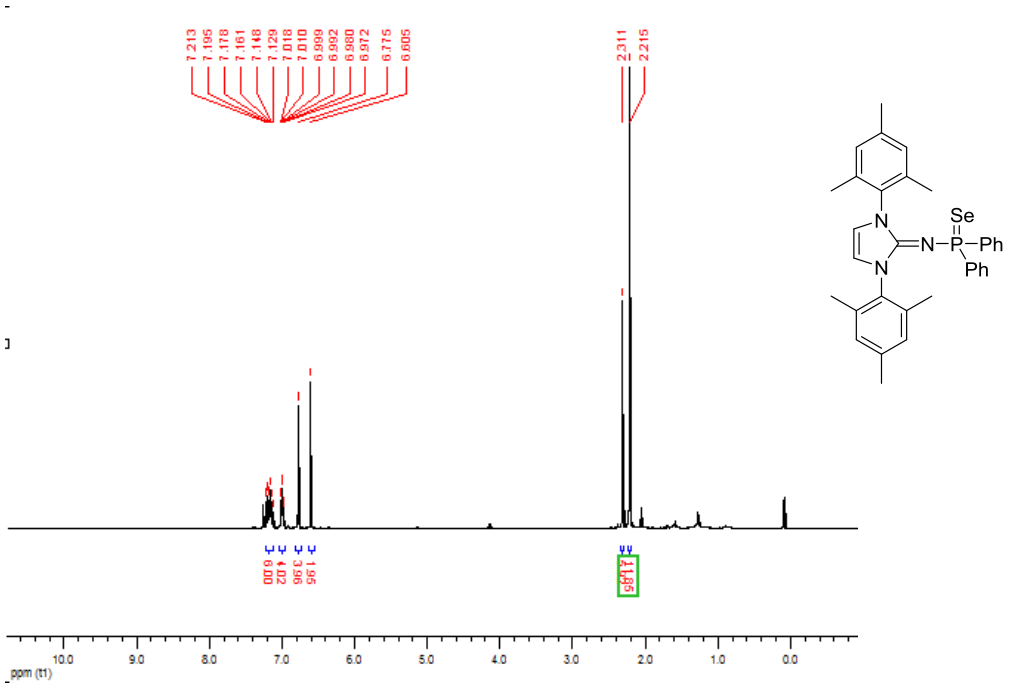


Figure 22. ^{1}H NMR ($CDCl_3$, 400 MHz, 25^{o}C) of 1,3-dimesitylimidazolidiphenylphosphinoselenoicamide **6b**.

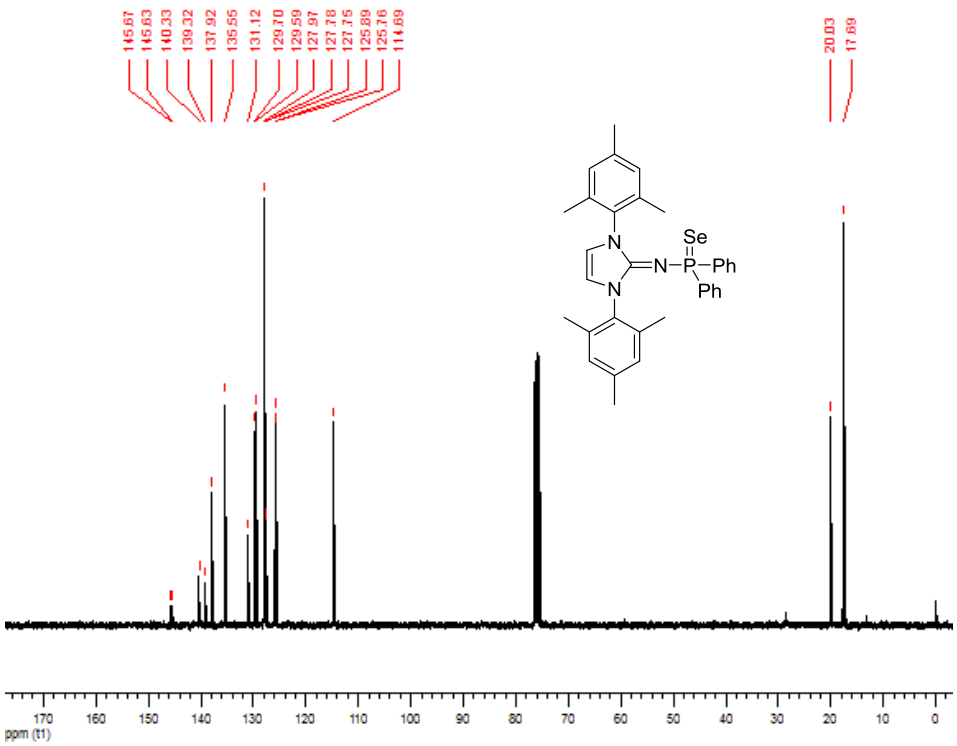


Figure 23. ^{13}C-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinoselenoicamide **6b**.

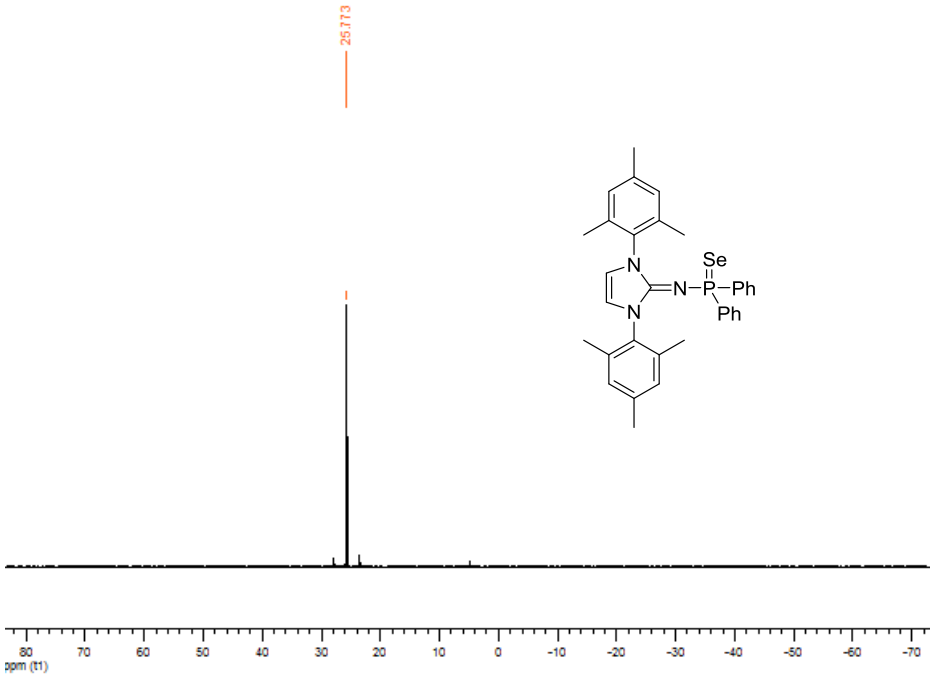


Figure 24. ^{31}P-{^{1}H} NMR of 1,3-dimesitylimidazolin-2-ylidene-*P*,*P*-diphenylphosphinoselenoicamide **6b**.

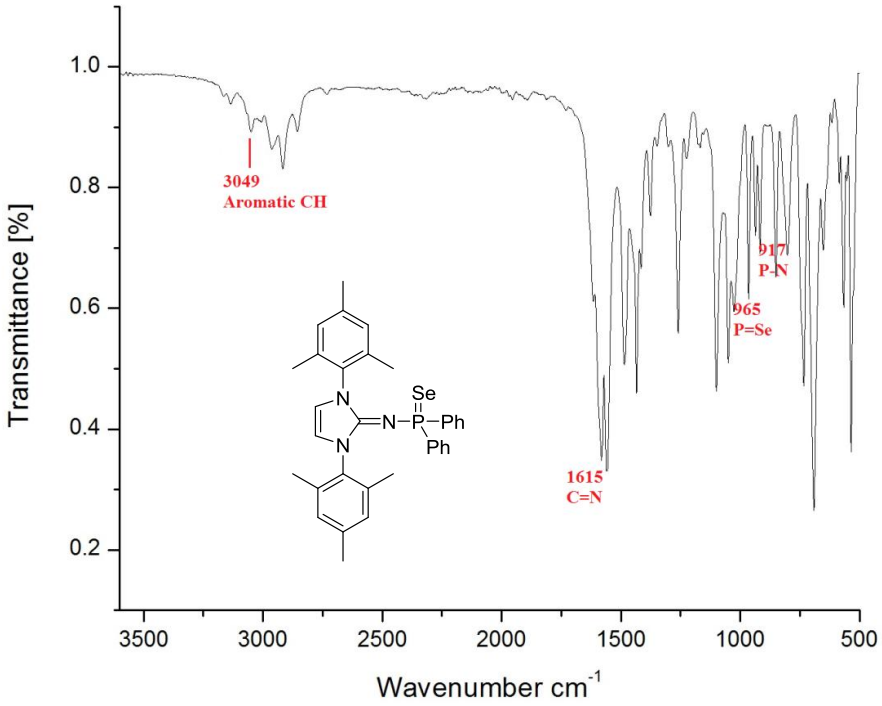


Figure 25. FT-IR spectra of 1,3-dimesitylimidazolin-2-ylidene-*P,P*-diphenylphosphinoselenoicamide **6b**.

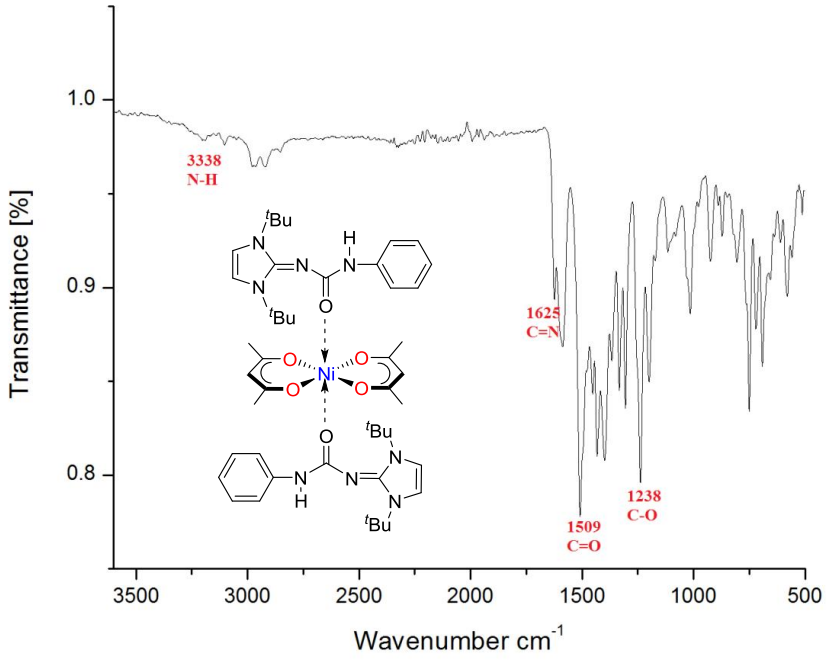


Figure 26. FT-IR spectra of bis-[*N*-(1,3-di-*tert*-butyl imidazole-2-ylidene)-*N*'-phenyl-ureato]Ni(acac)$_2$ **7a**.

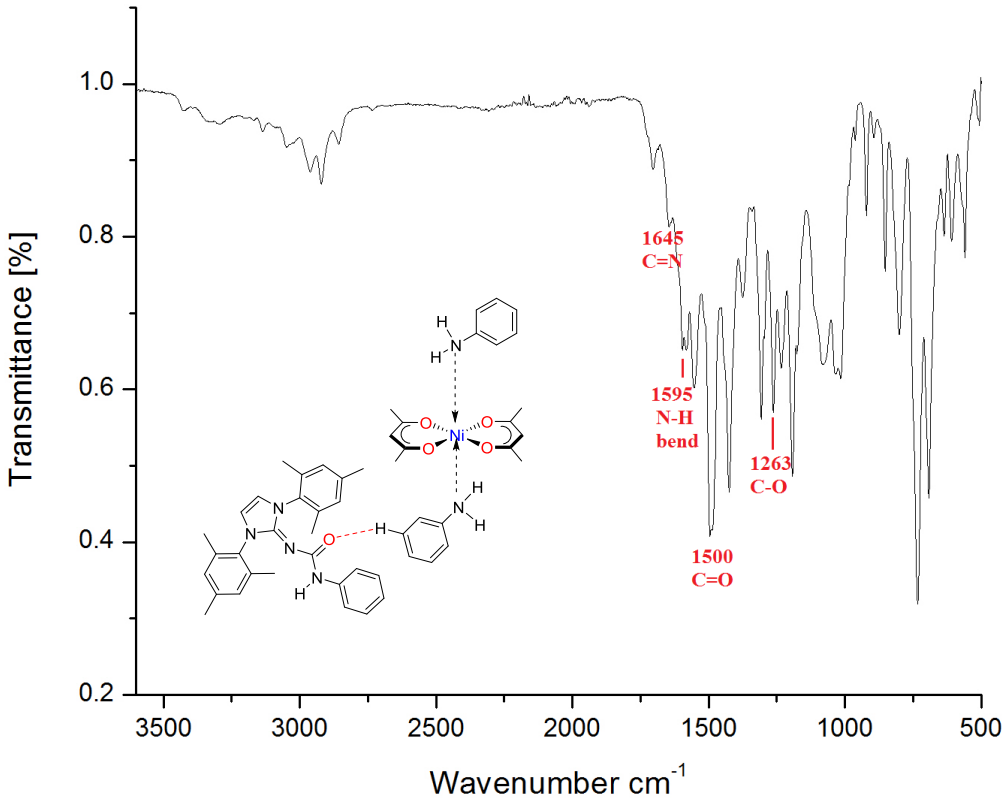


Figure 27. FT-IR spectra of bis-[*N*-(1,3-dimesity imidazole-2-ylidene)-*N*'-phenyl ureato]Ni(acac)$_2$ **7b**

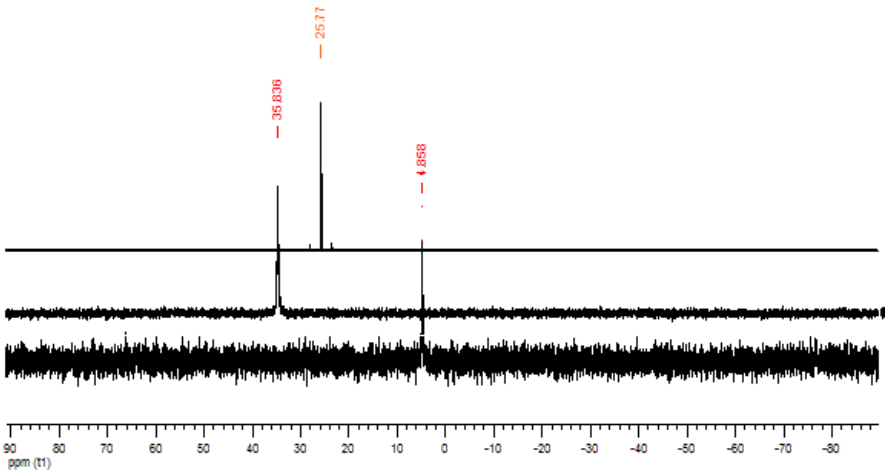


Figure 28. Comparison of ^{31}P-{^{1}H} spectra of **4b**, **5b**, **6b**.

Curriculum Vitae

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Secondary (10th)	West Bengal Board Of Secondary Education	Ramesh Chandra Girls' High school	First, 73%	2007
Higher Secondary (10+2)	West Bengal Council Of Higher Secondary Education	Ramesh Chandra Girls' High school	First, 80%	2009
B.Sc Honours	University of Calcutta.	Serampore college	First, 67%	2012
M.Sc	IIT Hyderabad.	IIT Hyderabad	9.65 (till 3rd sem)	2014

Awards and Honours:

- Awarded for 2nd in the college in Bachelor of Science (B.Sc)
- Qualified JAM 2012 (All india rank : 225)
- Received academic excellence award at IIT Hyderabad in 2013 and M.C.M scholarship.
- Qualified Graduate Aptitude Test in Engineering.