Synthesis and Structural Studies of Novel Aminophosphine Ligands and Their Derivatives

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MASTER OF SCIENCE

By

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Declaration

I hereby declare that the matter embodied in this report is the 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 wherever the work described is based on the findings of other investigators.

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Approval Sheet

This thesis entitled **Synthesis and Structural Studies of Novel Aminophosphine Ligands and Their Derivatives** by **Shakil Ahmed** is approved for the degree of Master of Science from IIT Hyderabad.

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Dedicated to

My Beloved Parents,

Family and

Respected Teachers

Abstract

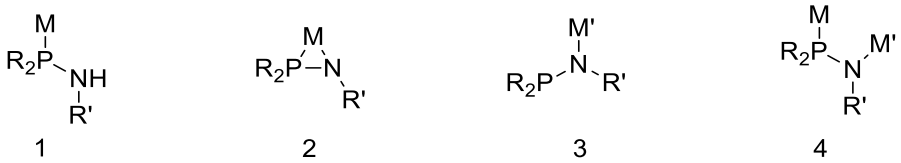
Three novel aminophosphine ligands (containing direct P-N bond), *tert*-butyl-NH(Ph_2P), 2-picolyl-NH(Ph_2P) and 2-picolyl-N(Ph_2P)$_2$, have been synthesized via aminolysis reaction of PPh_2Cl and *tert*-butyl amine and 2-picolyl amine(in case of mono derivative reaction carried out in 1:1 and in case of di derivative in 2:1 ration) respectively. Oxidation of the aminophosphines with elemental selenium gave the corresponding selenides 2-picolyl -NH(Ph_2P=Se) and 2-picolyl-N(Ph_2P=Se)$_2$. The borane derivatives were synthesized by reaction of the aminophosphines and $BH_3.SMe_2$. The bromides of *tert*-butyl-NH(Ph_2P) were prepared by the oxidation of it by bromine. The new compounds were characterised by NMR, IR spectroscopy. Furthermore, representative solid-state structures of the compounds were determined using single crystal X-ray diffraction analysis

Contents

1.1 Introduction

The chemistry of aminophosphine lignads of type R_2PNHR' concerning direct P-N bonds is one of the interesting and challenging area in the organometallic chemistry. In recent years the research in organophosphorus chemistry is mainly focused on the design and synthesis of numerous novel phosphorus based phosphine ligands for synthesizing newer and better metal complexes with improved catalytic activities. Aminophosphines are one of the phosphorus and nitrogen based ligand class. Although this aminophosphine chemistry is now known for many years and well established one, it continues to attract considerable attention from chemists due to its wide application in diverse fields[1, 2]. The phosphorus chemistry at its initial phase is mostly dominated by compounds containing P-C and P-O bonds, but the situation has changed recently. In last two decades compounds containing direct P-N bonds enjoyed intense attention from chemists owing to the presence of polar P-N bond which, in principle, can be the cause of exhibiting additional reactivity for these ligands. This class of ligands is now an emerging and expanding itself into diverse fields. The polar nature of the P-N bond make these ligands extremely sensitive to air and moisture. In spite of that the research in this field is gaining momentum day by day mainly due one reason - the polar nature of the P-N bond make this class of ligand very rich in their ligand behavior and subsequently their uses in catalysis. In few cases due to their unstable nature mainly to protic acid, they found their limited utility. But in last few decades several new class of aminophosphine ligands containing direct P-N bond with substantial stability had been synthesized and these had been investigated to be one of the most promising ligand class. This ligand class enjoyed additional advantage due to their well-defined structure, structural diversity in their metal complexes andrelatively higher stability. Their facile synthesis and their capability to act as

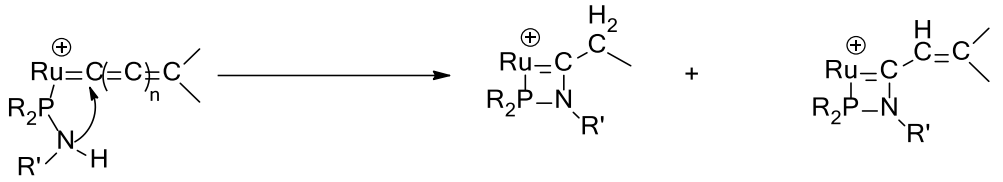
catalyst in various reactions make them more special ligand class. Variations of electronic, steric, and stereochemical parameters may be achieved through the functionalization of aminophosphine ligands with additional donor/functional groups attached to the amine or phosphine, in a very simple manner via their straight forward synthetic routes. Aminophosphine ligands exhibit various coordination modes to the metal centres in their complexes due to the fact they contain multiple donor atoms as well as the presence of the acidic -NH proton. The various possible coordination modes are shown in **Scheme 1**.



Scheme 1. Most common binding modes of aminophosphine and amidophosphine ligands

In case of middle/late transition metal (M), aminophosphine lgands usually coordinates to the metal centre k^1 (P) fashion as in 1[3], while k^1 (N) type coordination is not known till date. While aminophosphine (PR_2NHR') ligands are deprotonated, anionic amidophosphines $[PR_2NR']^-$ are readily obtained which shows a higher affinity toward electropositive metals because of their increased nucleophilicity at the N-site than the parent aminophosphine ligands. In case of early transition metals M', amidophosphine ligands were found to exhibit k^2 (P, N) coordination as shown in 2, and, although, less common, also k^1 (N)-coordination to the metal centres in these case are known as shown in 3, while in the presence of both early and middle/late transition metals, amidophosphine ligands were shown to act as μ^2 bridging ligand thereby forming heterobimetallic complexes of the type 4[4, 5]. In addition to their interesting structural features, aminophosphine ligands exhibits numerous reactivities creating a range of synthetically useful transformations[6].

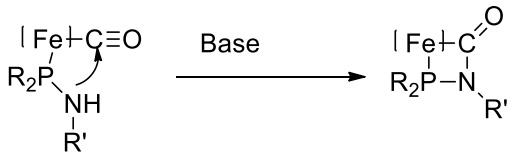
For examples, in case of vinylidene and allenylidene complexes $[RuCp(PPh_2NHR)_2(=C=(C)_n=CHR')]^+$ and $[RuTp(PPh_2NHR)_2(=C=(C)_n=CHR')]^+$ (n = 0,1; R = Ph, n-Pr; R'= alkyl, aryl; Tp = trispyrazoloylborate) an intramolecular addition of the NHR' moiety to the α-carbon of the cumulene moiety had been observed (**Scheme 2**) resulting in the formation of novel four-membered aza-phospha-carbenes .



Scheme 2. Intramolecular addition of the NHR' moiety of an aminophosphine to the α-carbon of a cumulene moiety.

Complexes of the types $[RuCp(PPh_2NHPh)(CH_3CN)_2]^+$ and $[RuCp^*(PR_2NHR')(CH_3CN)_2]^+$ (R = Ph, i-Pr, R' = Ph, C_6F_5) have been shown to react with terminal alkynes and diynes to result in amido butadiene complexes involving PR_2NHR' ligand migration[7,8]. Bunten et al. reported[9] the synthesis of the dinuclear ruthenium complex $[Ru_2(CO)_3(\mu^2\text{-}PPh_2)(\mu^2\text{-}Ph_2PNMePPh_2)(k^2(C,P)\text{-}C(=O)NMePPh_2)]$ containing a carboxamido-phospha-ruthenacyclic moiety. Herberhold et al. reported the preparation of half sandwich complexes of the type $[MCp(CO)_2(C(=O)N(S\text{-}NHPtBu_2)PtBu_2)]$ (M = Cr, Mo, W) by reacting $[MCp(CO)_3H]$ with $PtBu_2PN=S=NPtBu_2$.[10] In addition, iron complexes, $[FeCp(CO)_2(PPh_2NHNMe_2]^+$ bearing a hydrazinophosphine ligand, which is very similar to PR_2NHR' ligands, was investigated to react with nBuLi to give the carboxamido-phospha-ferracycle $[FeCp(-CO)(k^2(C,P)\text{-}(C=O)\text{-}NNMe_2\text{-}PPh_2)]$[11]. Öztopcu et al.

reported the synthesis of iron (II) complexes containing aminophosphine ligands of the type PR_2NHR' where R = Ph, *i*Pr, R'= *i*Pr, *t*Bu, Cy and described the reactivity of these complexes. They have shown that these complexes when treated with strong bases, formed a novel cyclic four-membered carboxamido-phospha-ferracycle via the intramolecular addition of the amine moiety of the bifunctional aminophosphine ligand according to (**Scheme 3**)[12].



$\lfloor Fe \rfloor = Fe(CO)_2Br_2(PR_2NHR')$, $\lfloor FeCp(CO)_2 \rfloor^+$

Scheme 3. Intramolecular addition of the NHR' moiety of an aminophosphine ligand to coordinated CO.

The aminophosphine ligands that contain P–N units such as phosphoraneiminates $[R_3PN]^-$, phosphinimines $[R_2PNR']$, diphosphanylamides $[R_2PNPR_2]^-$, and iminophosphonamides $[(R_2P(NR')_2]^-$ are well known today as ligands and many group demonstrated their potency into main-group and transition-metal chemistry. Previously our group have reported the chemistry of some aminophosphine ligands that contain direct P-N bonds in lanthanide and main group chemistry. Our group's work is focused towards the exploration of this aminophosphine ligands chemistry. Our group recently have reported the synthesis of N-(diphenylphosphino)-2, 6-dimethylaniline $[Ph_2PNH\ (2,\ 6\text{-}Me_2C_6H_3)]$, $[Ph_2PNH(CHPh_2)]$, $[Ph_2PNH\ (CPh_3)]$, their chalcogenides $[Ph_2P(O)NH\ (2,\ 6\text{-}Me_2C_6H_3)]$, $[Ph_2P(S)NH\ (2,\ 6\text{-}Me_2C_6H_3)]$, $[Ph_2P(Se)NH(CHPh_2)]$, $[Ph_2P(Se)NH\ (CPh_3)]$, and their alkali earth metal complexes. This unique

class can potentially bind through hard nitrogen, phosphorus donor atom and as well as via soft donor atom selenium and sulfur.

Now we turn our focus to the the bis(diphenylphosphino)alkyl/aryl amine and their derivatives. Among various aminophosphine ligands, bis(diphenylphosphino)alkyl/aryl amine and their derivatives are getting special attention because of their simple synthetic procedures, relatively higher stability than the usual aminophosphine ligands and their ability to form complexes with transition metals such as palladium, platinum, copper [13, 14]. The presence of the bulky groups attached to the phosphorus center renders the aminophosphine more stable against hydrolysis [15]. These ligands can be further functionalized via the introduction of additional donor groups to the amine or phosphine backbones. They are definitely very attracting as the functional group can be changed to modify the chemical and physical properties of the final product. Many aminophosphine ligands, their derivatives and their complexes have been very useful as co-catalysts in a number of catalytic reactions [16, 17]. In addition, some aminophosphines and their derivatives have also been investigated to act as anticancer drugs [18], herbicides as well as antimicrobial agents; many even as neuroactive agents also [19, 20].

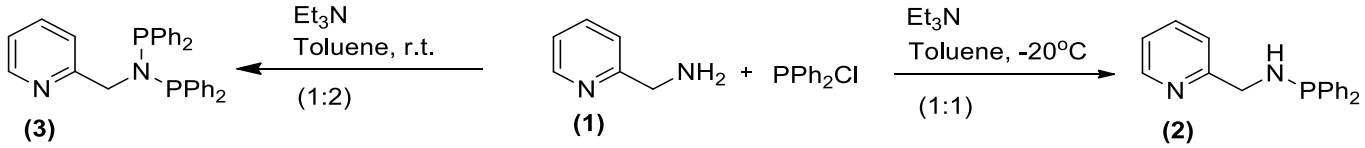
1.2 Scope of the Work

Our group have recently reported the series of phosphine amines [Ph_2PNHR] (R = 2, 6-$Me_2C_6H_3$, $CHPh_2$, CPh_3) and their chalcogen derivatives [$Ph_2P(O)NHR$], [$Ph_2P(S)NHR$], and [$Ph_2P(Se)NHR$] into the chemistry of alkali metals and the heavier alkaline-earth metals. Homoleptic and heteroleptic alkaline-earth-metal complexes are very interesting due to their wide application in various catalytic reactions, including the ring-opening polymerization of various cyclic esters,[21, 22] the polymerization of styrene and dienes,[23] and the hydroamination and hydrophosphination of alkenes and alkynes.[24] Determining the structures and reactivities of alkaline-earth-metal species is an important step toward the design and development of efficient catalysts; however, full realization of the catalytic potential of these elements still requires substantial advances in the understanding of their basic coordination and organometallic chemistry. These alkaline-earth-metal complexes are more oxophilic and electropositive in nature in comparison to those complexes formed from early transition metals. To stabilize these extremely oxophilic and electropositive metals, a wide variety of nitrogen based ancillary ligands, such as tris(pyrazolyl)borates,[25] aminotroponiminates,[26] β-diketiminates, [27] iminopyrroles,[28] and 1,4-diaza-1,3-butadiene,[29] have been introduced to prepare well-defined alkaline-earth-metal complexes. And the catalytic activity and the selectivity of these alkaline-earth-metal complexes can be controlled via a well-defined nitrogen-based ligand architecture. These alkaline-earth-metal complexes can also be stabilize by aminophosphine ligands. Aminophosphines can coordinate to metals through the hard nitrogen and phosphorus donor atoms, forming a highly strained three-membered metallacycle, as reported by Roesky and others.[30,31] The aminophosphine chalcogenides can form either a four-membered metallacycle, if the nitrogen and the chalcogen

atoms (O, S, Se) coordinate to the metal center, or two fused three-membered metallacycles to stabilize the metal complexes, which is what we observed in alkali-metal and heavier alkaline-earth-metal complexes.[32] Thus, due to the presence of three adjacent potential donor atoms, the polymetallacyclic structural motif of the metal complexes was explored. To enrich this chemistry we turned our focus on synthesizing new aminophosphine ligand (containing direct P-N bonds) bis(diphenylphosphino)alkyl/aryl amine and their derivatives which can stabilize the complexes via donation through hard nitrogen and phosphorus donor atom and in case of their chalcogen derivatives extra stabilization comes from the donation of additional soft donor atom (S,Se).

1.3 Results and Discussion :

The novel N-(diphenylphosphino)-2-picolyl amine and N,N-bis(diphenylphosphino)-2-picolyl amine were synthesized by the treatment of chlorodiphenylphosphine with 2-picolylamine in toluene in 1:1 and 2:1 equivalents at -20^{o}C and at room temperature respectively (aminolysis reaction) (**Scheme 4**). The compound **2** and **3** were characterized by analytical/spectroscopic techniques.



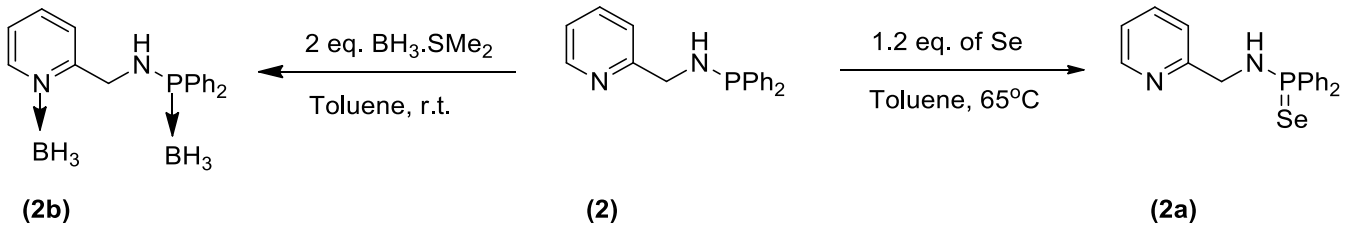
Scheme 4. Synthetic route of ligand **2** ad **3**.

The absorption peak of N-H in FT-IR spectrum in case of **2** is present as in case of starting amine **1**. As expected the absorption peak at 800 cm^{-1} is observed in case of **2** which indicates the formation of new P-N bond. The stretching frequency observed at 1432 cm^{-1} accounts for the presence of P-Ph bond stretching. In ^{1}H spectra N-H proton peak is observed at 3.34 ppm which is also present in the starting 2-picolylamine. The multiplate signals at 7.51-7.46 ppm is due to the proton present in 2-position of pyridine ring of picolyl group. The multiplate signal at 7.39 ppm is due to the presence of proton in 4-position. The other multiplate at 7.32-7.14 ppm accounts for the aromatic protons attached to phosphorus centre. The triplet at 2.30 ppm is observed due to CH_2 protons. The chemical shift value in ^{31}P {1H} NMR is observed at 43.35 ppm. This signal is considerably shielded than that of PPh_2Cl

(81.5 ppm) due the electron donating property of nitrogen (bonding of phosphorus and nitrogen, delocalization of nitrogen non-bonded lone pair into the vacant 3d orbital of phosphorus).

In case of **3** N-H peak is absent which was present in **1** and the presence of stretching frequency at 798 cm^{-1} accounts for the newly formed P-N-P bond. The absence of N-H peak in ^{1}H NMR also proves the formation of **3**. In case of **3**, in the ^{1}H spectra peaks in the region 8.03-7.10 ppm can be assigned as the protons peaks of the aromatic protons, among which the peaks in the 8.03-7.89 ppm region belongs to the aromatic protons of the picolyl group and the peaks in 7.71-7.10 ppm region belongs to the other aromatic protons. The peaks at 3.33 and 2.06 ppm corresponds to the protons of –NH and –CH_2 group. In the ^{31}P {1H} NMR the chemical shift value is observed at 56.89 ppm. This signal appears in somewhat deshielding zone than **2** (43.35 ppm). This is due to the fact that the electron donation from nitrogen is getting shared between two phosphorus atoms (much more delocalization of electrons, making each of the phosphorus centre comparatively less rich in electron density than its mono analogue **2**).

The selenium derivative **2a** of ligand **2** was prepared by oxidation of ligand **2** with the elemental selenium at 65^{o}C in toluene and the borane derivative **2b** was synthesized by reaction of $BH_3.SMe_2$ with ligand **2** in toluene at room temperature respectively (**Scheme 5**).



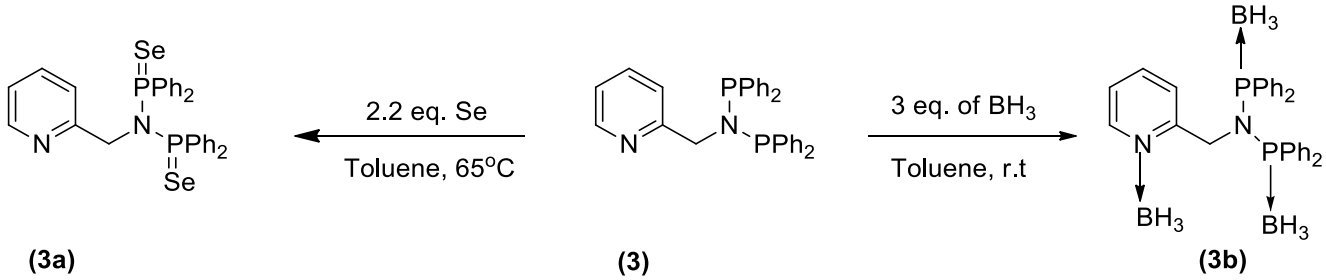
Scheme 5. Synthetic route for selenium and borane derivative of ligand **2**.

IR stretching frequency at 798 cm^{-1} accounts for the P-N bond stretching in selenium derivative **2a** of ligand **2**. Another stretching at 569 cm^{-1} (characteristic for P=Se stretching) indicates the formation of new P=Se in the **2a**. In the ^{1}H spectra of this ligand, the peaks observed in the region 7.75-7.70 ppm represents the proton peaks of aromatic proton of pyridine moiety of the picolyl group, the peaks observed in the region 7.50-7.26 arises due to the aromatic protons of the phenyl group attached to phosphorus centre, the peaks at 5.29, 1.58 ppm can be assigned as the proton peak for –NH, $-CH_2$ group respectively. In the ^{31}P {1H} NMR spectra a signal at 53.76 ppm is observed. This chemical shift value is much more deshielded than that of its parent ligand **2** (43.35 ppm). This reflects the fact that in this case the phosphorus electrons are further delocalized in the phosphorus and selenium double bond (P=Se).

The stretching frequency at 839 cm^{-1} accounts for the P-N bond stretching in selenium derivative **2b** of ligand **2**. The characteristic absorption peaks in the FT-IR spectra at 604 cm^{-1} and 2381 cm^{-1} are also observed which can be assigned as the peak for the P-B bond stretching and B-H bond stretching respectively. In the ^{1}H spectra of this ligand, the peaks observed in the region 7.84-7.69 ppm can be assigned as the proton peaks of aromatic proton of pyridine moiety of the picolyl group, the peaks observed in the region 7.48-7.11 accounts for the aromatic protons of the phenyl group attached to phosphorus centre, the triplet at 3.09 ppm and the signal at 2.27 ppm corresponds to the protons of –NH, $-CH_2$ group and the chemical shift value at 1.21 ppm represents the protons of $-BH_3$ group. In the ^{31}P {1H} spectra one signal is observed at 57.66 ppm is observed as a doublet which indicates the coupling between phosphorus and boron. Again this chemical shift value is observed in deshielding zone than that of its parent ligand **2** due to the electron donating property of phosphorus to the electron deficient boron atom (i.e., delocalization of phosphorus non-bonded electrons in the P-B dative bond).

In ^{11}B {1H} spectra of this ligand chemical shift value appears at -13.5 and -34.3 ppm respectively. The presence of two peaks indicates that there is two types of boron which is actually the case. The chemical shift value appeared as a doublet at -34.4 ppm. This indicates that this signal arises due to the boron centre attached with phosphorus centre, as the signal is doublet due to coupling between phosphorus and boron atom. The signal at -13.5 ppm corresponds to the boron centre attached with the nitrogen of the pyridine moiety of picolyl group. This signal is more deshielded than that of boron attached to phosphorus.

The synthesis of selenium derivative **3a** of **3** is achieved by oxidation of ligand **3** with 2.2 eq. of elemental Se at 65°C in toluene and the borane derivative **3b** of **3** is prepared by the reaction of ligand **3** with 3 eq. of $BH_3.SMe_2$ at room temperature in toluene respectively (**Scheme 6**).



Scheme 6. Synthetic route for selenium and borane derivative of N, N-(diphenylphosphino)-2-picolylamine.

In FT-IR spectrum of **3a** the absorption peak at 794 cm^{-1} is observed which proves the formation of P-N-P bond and the characteristic strong absorption peak at 559 cm^{-1} indicates the formation of new P=Se bond which was not present in the parent ligand **3**. In the ^{1}H spectra of this ligand, the peaks observed in the region 8.00-7.95 ppm arises due to the protons of aromatic proton of pyridine moiety of the picolyl group, the peaks observed in the region 7.49-7.26 accounts for the aromatic protons of

the phenyl group attached to phosphorus centre, the triplet at 3.74 ppm and the signal at 2.35 ppm corresponds to the protons of –NH, -CH_2 group respectively. In ^{31}P {1H} spectra one triplet signal (with satellite peak) is observed at 71.95 ppm observed. This proves the formation of P=Se as the satellite peak is observed due to the coupling between phosphorus and selenium atom. The chemical shift value which appears considerably in the deshielding zone than its parent ligand **3** (56.89 ppm) indicates the further delocalization of phosphorus electrons in the phosphorus and selenium double bond (P=Se). This chemical shift value is even much more deshielded than its mono analogue **2a** (53.76 ppm) which is expected one as the extent of delocalization is more in this case (the nitrogen non-bonded lone pair electrons are getting shared by two phosphorus centre and then again the delocalization of phosphorus own electrons in the double bond between phosphorus and selenium (P=Se)). The solid-state structure of compound **3a** is established by single crystal X-ray diffraction analysis.

Compound **3a** crystallizes in the monoclinic space group $P2_1/n$ having 6 independent molecules in the unit cell. The P-Se distance 2.094(2) Å which is in good agreement to the reported value of P=Se which in turn proves the presence of double bond between P and Se in **3a**. The P2-N2 and P1-N2 bond length is 1.710(6) Å and 1.719(6) respectively, which is slightly longer than the parent aminophosphine ligand **3** (P2-N2 bond length = 1.702(3) Å). The C6-N2 bond length is 1.497(8) Å which is slightly longer than the parent ligand **3** (C6-N2 bond length = 1.468(5) Å). The details of the structural parameters are given in **Table 1**. The solid-state structure of complex 2 is given in **Figure 1**.

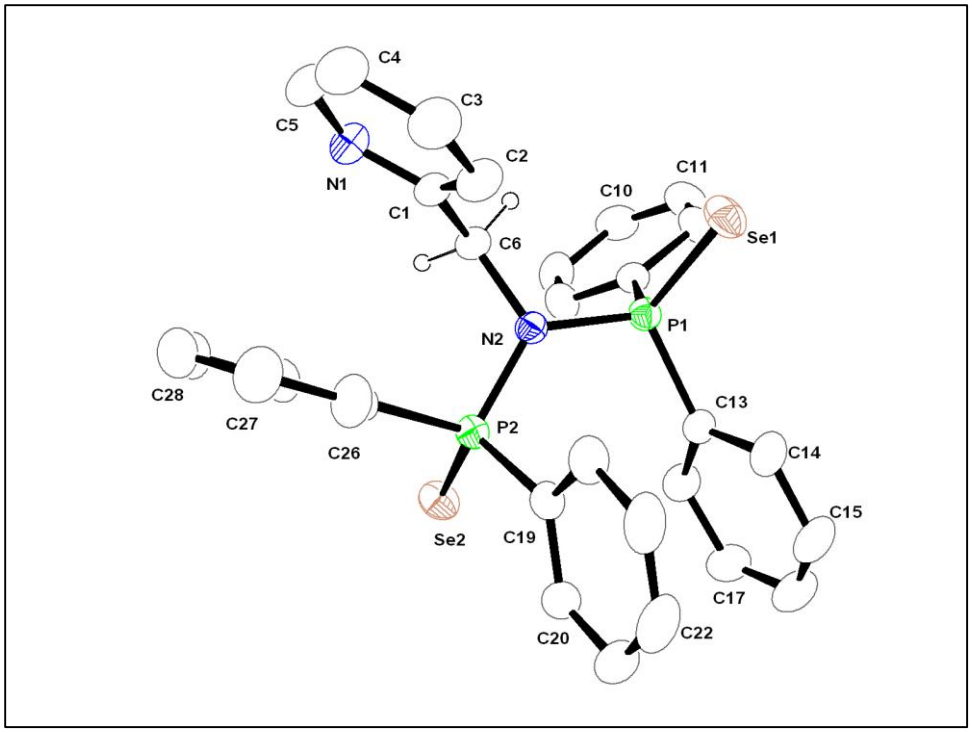


Figure 1. ORTEP drawing of **3a** with thermal displacement parameters drawn at the 30% probability level. Hydrogen atoms except (H1, H2) are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Se2-P2 = 2.1007(19), Se1-P1 = 2.094(2), P2-N2 = 1.710(6), P1-N2 = 1.719(6), N2-C6 = 1.497(8) Å, P2-C19 = 1.834(7), P2-C26 = 1.785(7), P1-C7 = 1.807(7), P1-C13 = 1.824(7), P1-N2-P2 = 127.2(3), C6-N2-P2 = 117.0(5),C6-N2-P1 = 112.4(5),N2-P2-Se2= 116.5(2), N2-P1-Se1= 113.3(2),C26-P2-C19 = 105.8(3),C13-P1-C7 = 106.0(3),C26-P2-Se2 = 112.1(3), C19-P2-Se2 = 112.0(2), C13-P1-Se1 = 114.9(3), C7-P1-Se1 = 109.9(3).

In FT-IR spectrum of ligand **3b** the characteristic absorption peak at 603 cm^{-1} and 2376 cm^{-1} are observed which can be assigned as the peak for the P-B bond stretching and B-H bond stretching respectively. In the ^{1}H spectra of this ligand, the peaks observed in the region 8.31-7.73 ppm arises due to the protons of aromatic proton of pyridine moiety of the picolyl group, the peaks observed in the region 7.39-6.91 accounts for the aromatic protons of the phenyl group attached to phosphorus centre, the triplet at 5.36 ppm and the signal at 2.70 ppm corresponds to the protons

of –NH, -CH_2 group respectively. The chemical shift value at 1.11 ppm arises due to the protons of -BH_3 group. In ^{31}P {1H} spectrum of **3b** one signal at 73.10 ppm is observed. This chemical shift value shifted towards the deshielding zone comparatively to the ligand **3** (56.89 ppm), which account for the fact that the phosphorus non-bonded lone pair of electrons are donated to electron deficient boron centre (further delocalization of phosphorus electrons in the phosphorus and boron dative bond, making the phosphorus centre electronically less rich). In ^{11}B {1H} spectra of this ligand chemical shift value appears at -13.5 and -34.5 ppm respectively. The presence of two kind of boron peaks indicates that there is two types of boron which is actually the case. The chemical shift value appeared as a doublet at -34.5 ppm. This indicates that this signal arises due to the boron centre attached with phosphorus centre. The signal is doublet because of coupling between phosphorus and boron atom. The signal at -13.5 ppm corresponds to the boron centre attached with the nitrogen of the pyridine moiety of picolyl group. This signal appears in more deshielded region than that of boron attached to phosphorus.

The solid-state structure of compound **3b** is established by single crystal X-ray diffraction analysis. Compound **3b** crystallizes in the orthorhombic space group Pbca having 12 independent molecules in the unit cell. The P2-B2 bond length is 1.922(5) Å and the P1-B3 bond distance is 1.924(5) Å. They both are in well agreement with the reported value of 2.1019(8) Å for [{$Ph_2P(BH_3)$}$_2CH_2$] which clearly indicates that the bond between phosphorus and boron is a dative bond. The N1-B1 bond length is 1.599(8) Å which is considerably shorter than that of P-B bond distances which indicates that the bond between N-B is much stronger than the P-B bond. This is due to the fact that relatively more electron donating nature of nitrogen than that of phosphorus makes the N-B bond stronger than P-B. Also the better matching of orbital energies which are involved in overlapping in N-B bond than that of P-B case accounts for this observed shorter length in N-B

case. The P2-N2 and P1-N2 bond lengths are 1.704(3) Å and 1.717(3) Å respectively which are in well agreement to the value of P-N bond length in the parent ligand **3** (P2-N2 bond length = 1.702(3) Å). Also the C6-N2 bond distance is 1.496(4) Å which is slightly longer than the parent ligand **3** (C6-N2 bond length = 1.468(5) Å). The details of the structural parameters of this ligand is given in **Table 1**. The solid-state structure of complex 2 is given in **Figure 2**.

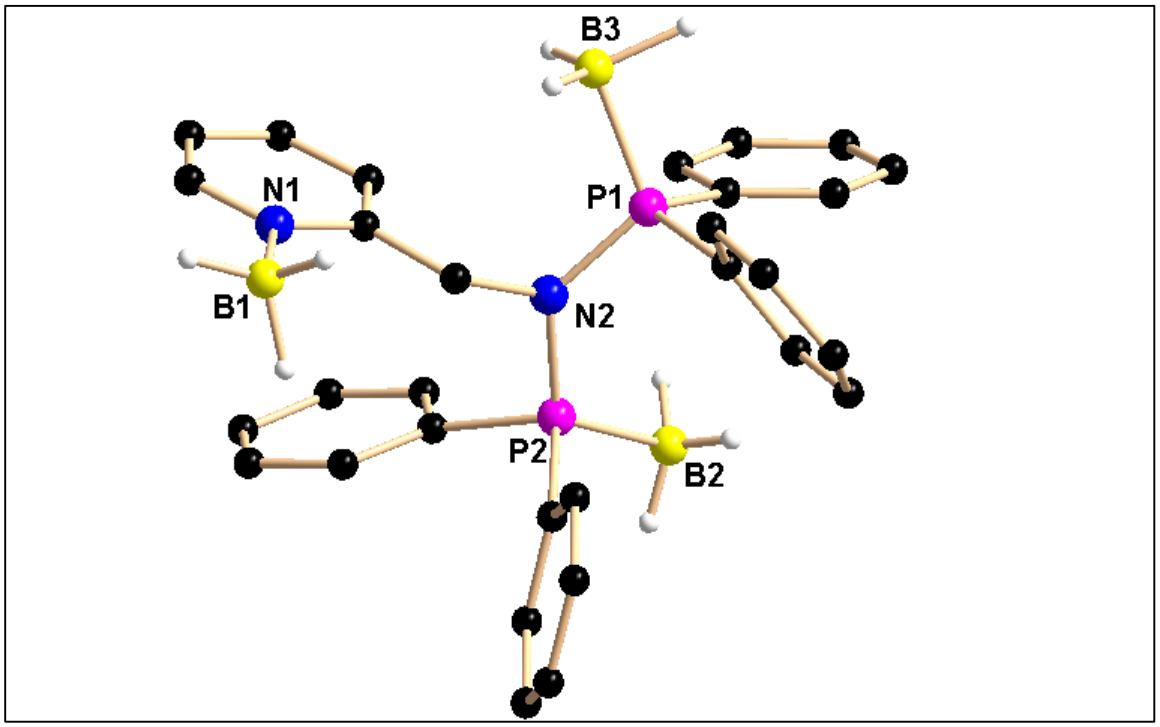
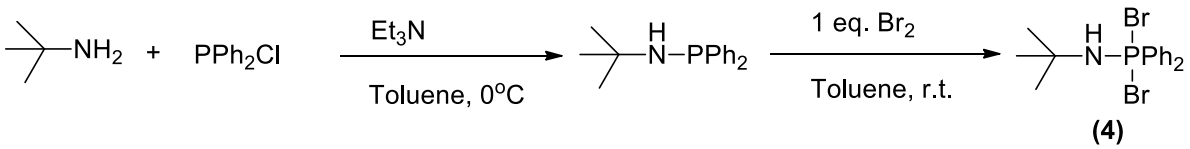


Figure 2. DIAMOND drawing of **3b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): P2-B2 = 1.922(5), P1-B3 = 1.924(5), N2-B1 = 1.599(8), C6-N2 = 1.496(4), P1-N2 = 1.717(3), P2-N2 = 1.704(3),C7-P1 = 1.806(4), C25-P1 = 1.795(5), C13-P2 = 1.794(4), C19-P2 = 1.806(4), P1-N2-P2 = 128.16(17), N2-P1-B3 = 111.1(2), N2-P2-B2 = 119.3(2), C6-N2-P1 = 113.3(2), C6-N2-P2 = 115.2(2), C13-P2-B2 = 110.2(2), C19-P2-B2 = 111.1(2), C7-P1-B3 = 112.9(2), C25-P1-B3 = 107.7(3), C19-P2-N2 = 102.88(15), C13-P2-N2 = 107.86(18).

The N-(diphenylphosphino)*tert*-butyl amine bromide was synthesized by the treatment of 1 eq. of bromine to the N-(diphenylphosphino)*tert*-butylamine (formed in the aminolysis reaction of chlorodiphenylphosphine with 2-picolylamine, in toluene in 1:1 equivalents at 0^oC) in toluene at room temperature (Scheme 7).



Scheme 7. Synthetic route for ligand **4**.

In ^{1}H NMR spectra of **4** a broad peak at 9.58 ppm is observed due to the presence of –NH proton which was also present in the starting amine. The chemical shift values at 7.88-7.83, 7.72-7.67, 7.51-7.39 ppm can be assigned for the para, meta, ortho protons to the phosphorus atom of the aromatic rings attached to the phosphorus respectively. The sharp singlet signal at 1.24 ppm arises due to the presence of protons of $–CH_3$ group. In the ^{13}C {1H} NMR the peaks at 32.03 and 27.85 ppm arises due to the presence of tertiary carbon of (-C $(CH_3)_3$) and primary carbon of - CH_3 group respectively. And the peaks at 133.82, 132.25, 131.45, 129.37 ppm can be assigned as the peak for aromatic carbons. In ^{31}P {1H} spectrum one signal at 34.58 ppm was observed which is accompanied by 2 satellite peaks. This is due to the presence of 2 –Br group which are attached to the phosphorus atom, and they coupled with the phosphorus to give satellite peaks.

1.3.1 Single-Crystal X-ray Structure Determination:

Single crystals of compound 5a and 5b were grown from a solution of DCM under inert atmosphere at -41^{o}C. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 293 K. All measurements were made on a Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic CuKα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in Table 1. The structures were solved by direct methods (SIR92)[42] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97[43]. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were located in the difference Fourier map and subsequently refined. The function minimized was [$\Sigma w (F_o^2 - F_c^2)^2$] ($w = 1/[\sigma^2 (F_o^2) + (aP)^2 + bP]$), where P = (Max($F_o^2$,0) +2$F_c^2$)/3 with $\sigma^2(F_o^2)$ from counting statistics. The functions R1 andwR2 were $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules.

Table 1. Crystallographic data for **3a** and **3b**

Crystal	**3a**	**3b**
Empirical formula	$C_{23}H_{15}N_2O_{0.17}PSe$	$C_{23}H_{13}B_3Cl_{0.08}N_2P_2$
Formula weight	431.97 g/mol	414.68 g/mol
T (K)	293(2)	293(2)
λ (Å)	1.54184	1.54184
Crystal system	Monoclinic	Orthorhombic
Space group	P 2_1/n	P b c a
a (Å)	9.7110(2)	20.6326(7)
b (Å)	17.4530(3)	15.4062(8)

c (Å)	17.5618(4)	20.7287(8)
α(^{o})	90	90.00
β(^{o})	100.015(2)	90.00
γ(^{o})	90	90.00
V ($Å^3$)	2931.13(10)	6589.03(50)
Z	6	12
D_{calc} g cm^{-3}	1.46823	1.254
μ (mm^{-1})	3.450	1.972
F (000)	1304.0	2537.0
Theta range for data collection	7.2 to 142.34°	8.34 to 141.96°
Limiting indices	$-11 \leq h \leq 9$, $-21 \leq k \leq 14$, $-20 \leq l \leq 21$	$-24 \leq h \leq 12$, $-15 \leq k \leq 18$, $-24 \leq l \leq 25$
Reflections collected / unique	8846/ 4939 [R(int) = 0.0194]	17337/ 6262 [R(int) = 0.0518]
Completeness to theta = 71.25	98.07%	98.55%
Refinement method	Full - matrix least-squares on F^2	Full – matrix least-squares on F^2
Data / restraints / parameters	4939/0/325	6262/0/397
Goodness-of-fit on F^2	2.013	1.006
Final R indices [I>2sigma(I)]	R_1 = 0.0786, wR_2 = 0.2674	R_1 = 0.0831, wR_2 = 0.2346
R indices (all data)	R_1 = 0.0884, wR_2 = 0.2776	R_1 = 0.1238, wR_2 = 0.2939
Largest diff. peak and Hole (e $Å^{-3}$)	3.76/-0.99	0.28/-0.49

1.4 Experimental

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 argonfilled M. Braun glovebox. THF was predried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and n-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glovebox. ^{1}H (400 MHz), ^{13}C {1H} (100 MHz), ^{11}B {1H} (128.4 MHz), and ^{31}P {1H} NMR (161.9 MHz) spectra were recorded on a Bruker AVANCE III-400 spectrometer. A Bruker ALPHA FT-IR instrument was used for the FT-IR measurements. Elemental analyses were performed on a Bruker EURO EA instrument at the Indian Institute of Technology Hyderabad. The phosphine amine [Ph_2PNH(picolyl)] compounds were prepared according to the literature procedures. [BH3·SMe2], elemental sulfur and selenium were purchased from Sigma Aldrich and used without further purification. NMR solvents $CDCl_3$ and C_6D_6 were purchased from Sigma Aldrich and dried by either molecular sieves ($CDCl_3$) or a Na/K alloy (C_6D_6) prior to use.

1.4.1 Preparation of 1, 1-diphenyl-N-(pyridin-2-ylmethyl)phosphinamine (2):

In a dry Schlenk tube 2.388g of chlorodiphenylphosphine (10.82 mmol) was added dropwise to a solution of 1.17 g of 2-picolylamine (10.82 mmol) and 1.0952g of triethylamine (10.82 mmol) in

toluene (20 mL) at room temperature -20°C under argon atmosphere. The whole mixture was then stirred for another10 h. The solvent was removed under reduced pressure. The solid was washed with hexane to get a white solid. Yield: 2.23 g, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51-7.46 (m, 4H, Ar*H* of Picolyl group), 7.32-7.14 (m, 10H, Ar*H*), 3.34 (s, 1H, -N*H*), 2.30 (d, 2H, -CH_2). ^{31}P {1H} NMR (161.9 MHz, $CDCl_3$) δ (ppm): 43.35. Selected FT-IR peak (cm^{-1}): 800(P-N), 1432(P-Ph).

1.4.2 Preparation of P, P-diphenyl-N-(pyridin-2-ylmethyl)phosphinoselenoic amide (2a):

In a dry Schlenk tube 0.123 g of ligand 2 (0.420 mmol) and elemental 0.033g of elemental Se (0.420 mmol) were stirred in toluene (10 mL) for 6 h at 55°C. The reaction mixture was filtered. The filtrate was concentrated under reduced pressure and n-hexane (5 mL) was added to wash and to yield it as a pale white solid. Yield: 0.091g, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75-7.70 (m, 4H, Ar*H* of Picolyl), 7.50-7.49 (m, 4H, o to P, Ar*H*), 7.46-7.44 (m, 4H, m to P, Ar*H*), 7.26(m, 2H, p to P, Ar*H*), 5.29 (s, 2H, - CH_2). ^{31}P {1H} NMR (161.9 MHz, $CDCl_3$) δ (ppm): 53.76. Selected FT-IR peaks (cm^{-1}): 794 (P-N), 1456(P-Ph), 1635(C=C).

1.4.3 Preparation of 1, 1-diphenyl-N-(pyridin-2-ylmethyl)phosphinamine-borane (2b):

In a dry Schlenk tube 0.123 g of ligand 2 (0.420 mmol) and 0.0638 g of $BH_3.SMe_2$ (0.840 mmol) were stirred in toluene (20 mL) for 6 h at room temperature. The reaction mixture was concentrated to ca. under reduced pressure and n-hexane (20 mL) was added to wash the solid. Then it was recrystallized from hot toluene to give a pale yellow crystalline solid. Yield: 1.2 g, 78%. ^{1}H NMR

(400 MHz, $CDCl_3$) δ (ppm): 7.84-7.81 (m, 1H, Ar*H* of 2nd position to N of Picolyl), 7.79 (m, 2H, Ar*H* of 3rd position to Nof Picolyl group), 7.69 (m, 1H, Ar*H* of 4th position to N of Picolyl group), 7.48-7.11 (m, 10H, Ar*H*), 3.09 (s, 1H, -N*H*), 2.27(d, 2H, -CH_2), 1.21 (s, 6H, -BH_3); ^{31}P {1H} NMR (161.9 MHz, $CDCl_3$) δ (ppm): 57.66, ^{11}B {1H} (128.4 MHz, $CDCl_3$) δ (ppm): -13.5 (B attached to N), -34.5 (B attached to P); Selected FT-IR peaks (cm^{-1}): 839 (P-N), 1436 (P-Ph), 1619 (aromatic C=C).

1.4.4 Preparation of N-(diphenylphosphino)-1, 1-diphenyl-N-(pyridin-2-ylmethyl)phosphinamine (3):

In a dry Schlenk tube 2.388 g of chlorodiphenylphosphine (10.82 mmol) was added slowly to a solution of 0.585 g of 2-picolylamine (5.41 mmol) and 1.0952g of triethylamine (10.82 mmol) in toluene (20 mL) at room temperature. The resulting white suspension was stirred for 8 h, and the solvent was removed under reduced pressure. The solid was washed with hexane to yield it as a white solid (yield: 2.0512g, 80%; m.p.: 160–162ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03-7.89 (m, 4H, Ar*H* of Picolyl), 7.71-7.10 (m, 20H, Ar*H*), 3.33 (s, 1H, -N*H*), 2.06 (d, 2H, -CH_2). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ (ppm): (C_{Arm}: 159.8; 148.6; 139.2; 135.7; 132.8; 128.8; 128.1; 121.5), (C_{CH2}: 57.9). ^{31}P {1H} NMR (161.9 MHz, $CDCl_3$) δ (ppm): 56.89. Selected IR, m (cm^{-1}): 799(P–N–P), 1427(P-Ph).

1.4.5 Preparation of N-(diphenylphosphoroselenoyl)-P, P-diphenyl-N-(pyridin-2-ylmethyl)phosphinoselenoic amide (3a):

In a dry Schlenk tube 0.20 g of ligand 4 (0.420 mmol) and elemental 0.066 g of elemental Se (0.840 mmol) were stirred in toluene (10 mL) for 6 h at 65^{o}C. The precipitate was filtered. The reaction mixture was concentrated under reduced pressure and n-hexane (5 mL) was added to wash the white solid and then it was recrystallized from dichloromethane to yield it as a white crystal. Yield: 0.1702g, 63%; m.p.-283-285^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00-7.95 (m, 4H, Ar*H* of Picolyl), 7.49-7.26 (m, 20 H, Ar H); 3.74 (t, 1H, -N*H*), 2.35 (s, 2H, CH_2); 31P {1H} NMR (161.9 MHz, $CDCl_3$) δ (ppm): 71.95. Selected IR peaks (cm^{-1}): 794 (P–N–P), 559 (P=Se).

1.4.6 Preparation of N-(diphenylphosphino)-1, 1-diphenyl-N-(pyridin-2-ylmethyl)phosphinamine-borane (3b):

In a dry Schlenk tube 0.20 g of ligand 4 (0.420 mmol) and 0.09572g of $BH_3.SMe_2$ (1.26 mmol) were stirred in toluene (20 mL) for 6 h at room temperature. The reaction mixture was concentrated to ca. under reduced pressure and n-hexane (20 mL) was added to wash the solid. Then it was recrystallized from hot toluene to pale yellow crystalline solid.Yield-2.2089g, 78.83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31(m, 1H, Ar*H* of 2nd position to N of Picolyl), 7.98 (m, 2H, Ar*H* of 3rd position to N of Picolyl), 7.73 (m, 1H, Ar*H* of 4th position to N of Picolyl), 7.39-6.91 (m, 20H, Ar*H*), 5.36 (t, 1H, -N*H*) 2.70 (s, 2H, -CH_2), 1.11 (s,9H, -BH_3). ^{31}P {1H} (161.9 MHz, $CDCl_3$) δ (ppm): 73.10 ppm. ^{11}B {1H} (128.4 MHz, $CDCl_3$) δ (ppm): -13.5 (B attached to N), -35.9 (B attached to P); FT-IR Selected peak (cm^{-1}): 604 (P-B), 2376(B-H), 1433(P-Ph).

1.4.7 Preparation of 1, 1-dibromo-N-(*tert*-butyl)-1, 1-diphenyl phosphoranamine (4):

In a dry Schlenk tube 4.1985 g of Ph_2PCl (19.03 mmol) was added slowly to a solution of 1.392 g of *tert*-butyl amine (19.03 mmol) and 1.89256 g of triethylamine (19.03 mmol) in Toluene (20 mL) at room temperature under argon atmosphere. The resulting white suspension was stirred for 8 h, then filtered. To the filtrate hexane was washed and the all volatiles were removed under reduced pressure to result a white solid. To a solution of this white solid in 10 ml of toluene, 1.5205 g of bromine (19.03 mmol) was added. The whole mixture was then stirred for another10 h. The solvent was removed under reduced pressure. The solid was washed with hexane and kept for recrystallization in methanol.Yield:6.9g, 87%. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) = 7.69-7.49 (m, 1H, p to P, Ar*H*), 7.44-7.40 (m, 2H, m to P, Ar*H*), 7.36-7.18 (m, 2H, o to P, Ar*H*), 1.24(s, 9H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ (ppm): 133.82(ipso to P), 132.25(o to P), 131.45(m to P), 129.37(p to P), 32.03 ($-C_{(CH3)3}$), 27.85 (CH_3) ^{31}P {1H} (161.9 MHz, $CDCl_3$) δ (ppm) = 34.59 ppm.

1.5 Conclusion

In conclusion we have successfully reported the facile, straight forward synthesis of novel mono(diphenylphosphino)picolyl amine and bis(diphenylphosphino)picolyl amine and their selenium and borane derivatives. In addition we also successfully synthesized mono(diphenylphosphino)*tert*butyl amine bromide. The compounds are characterized by NMR, FT-IR spectroscopic analysis and by the Single Crystal X-Ray Analysis.

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1.7 Supporting Information

1.

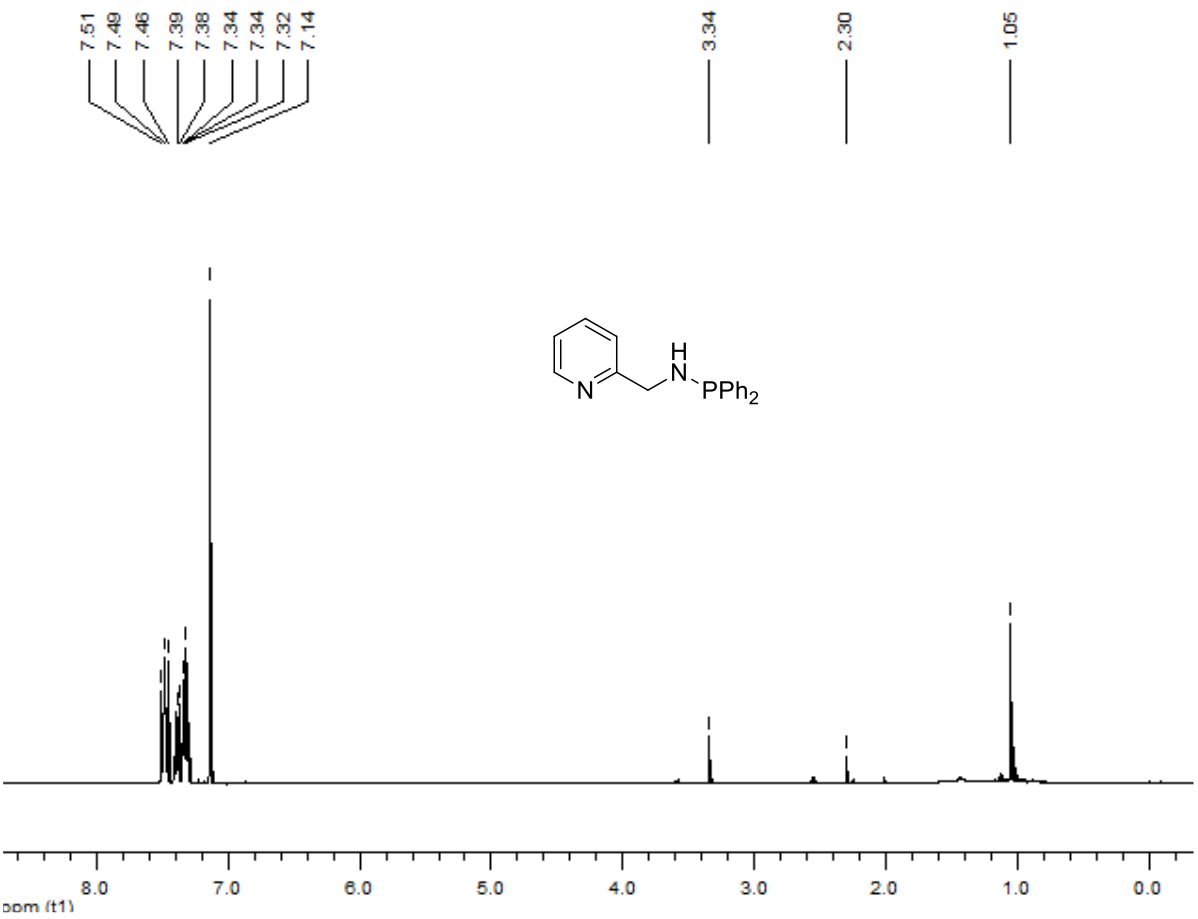

Fig. 1. ^{1}H NMR spectra of Ligand **2**

2.

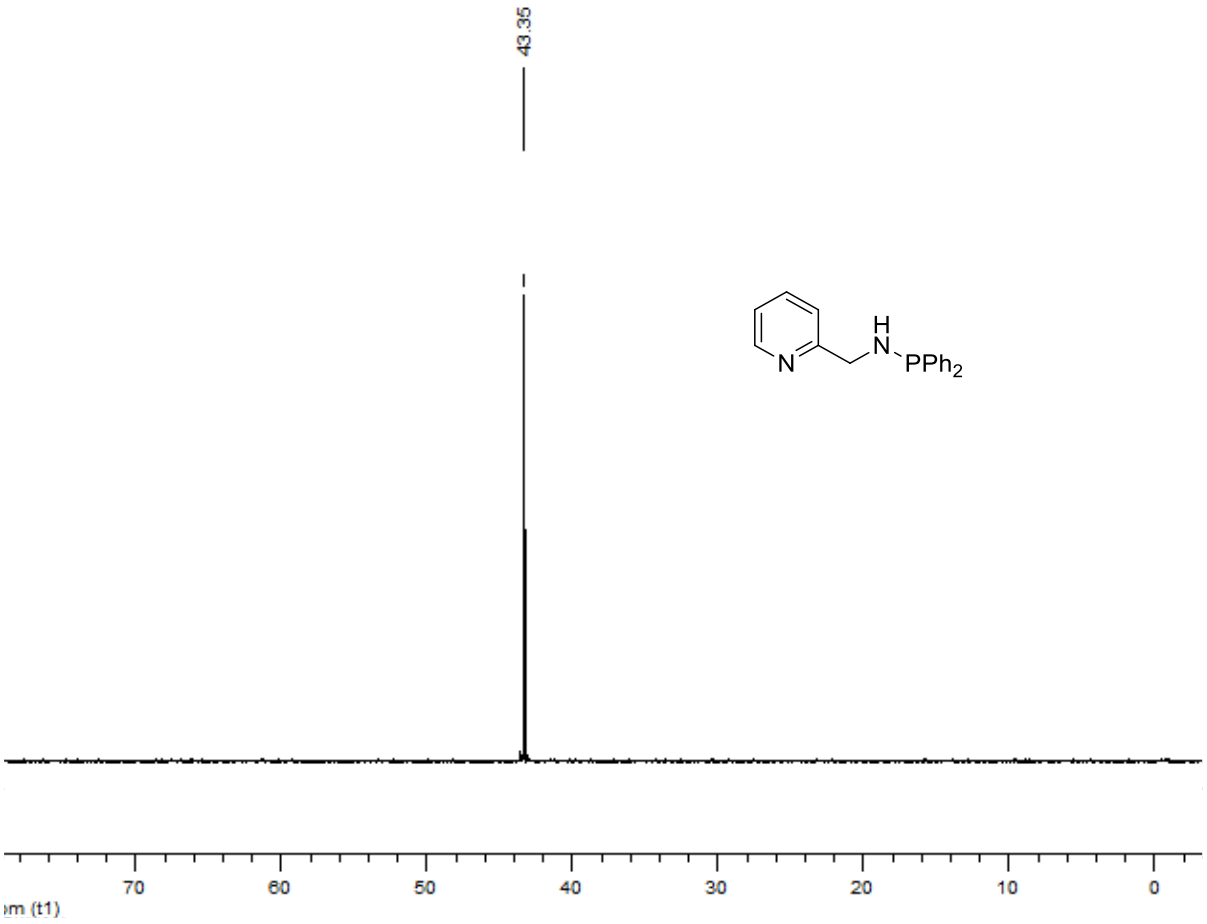

Fig. 2. ^{31}P {1H} spectra of Ligand **2**

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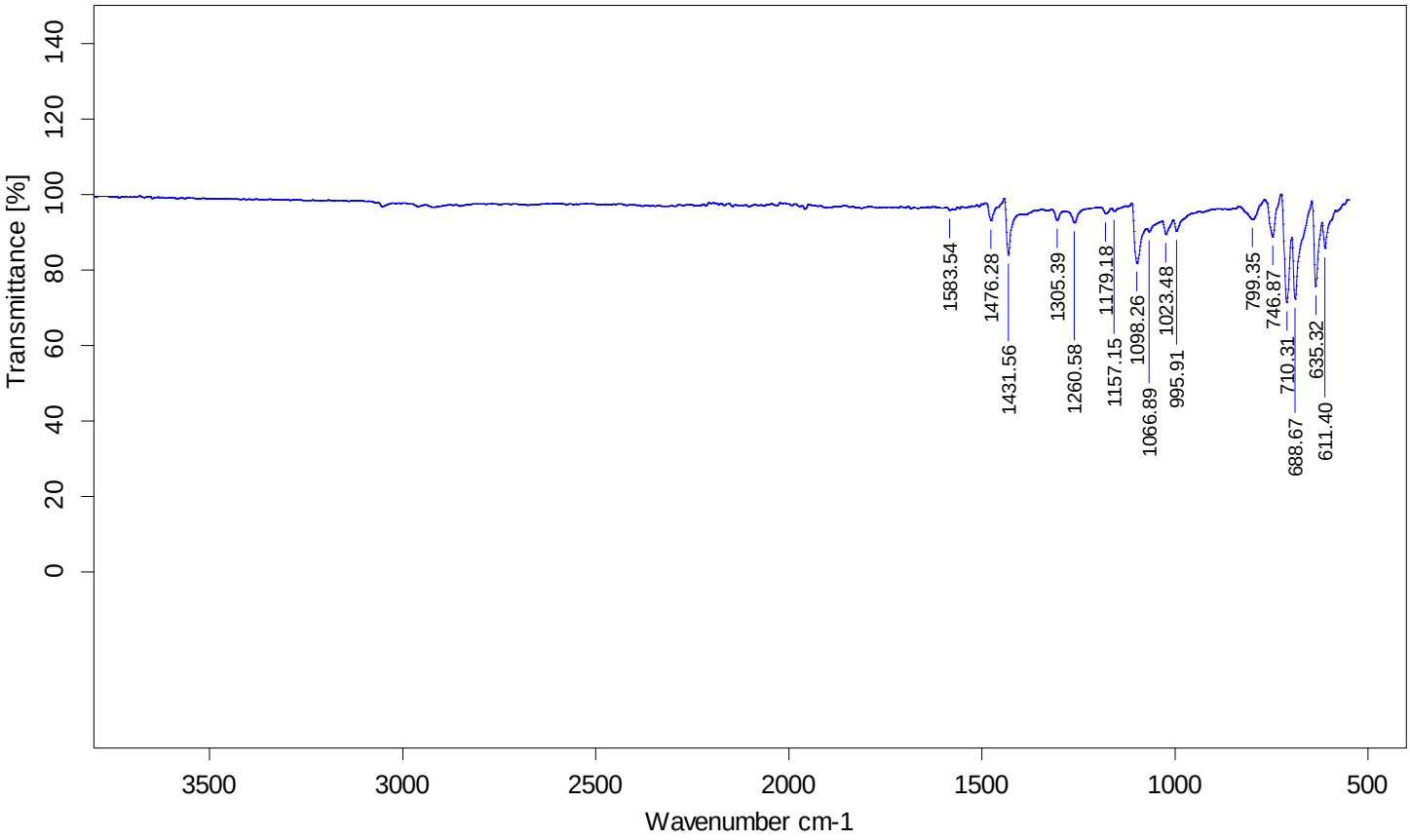

Fig. 3. FT-IR spectra of ligand **2**

4.

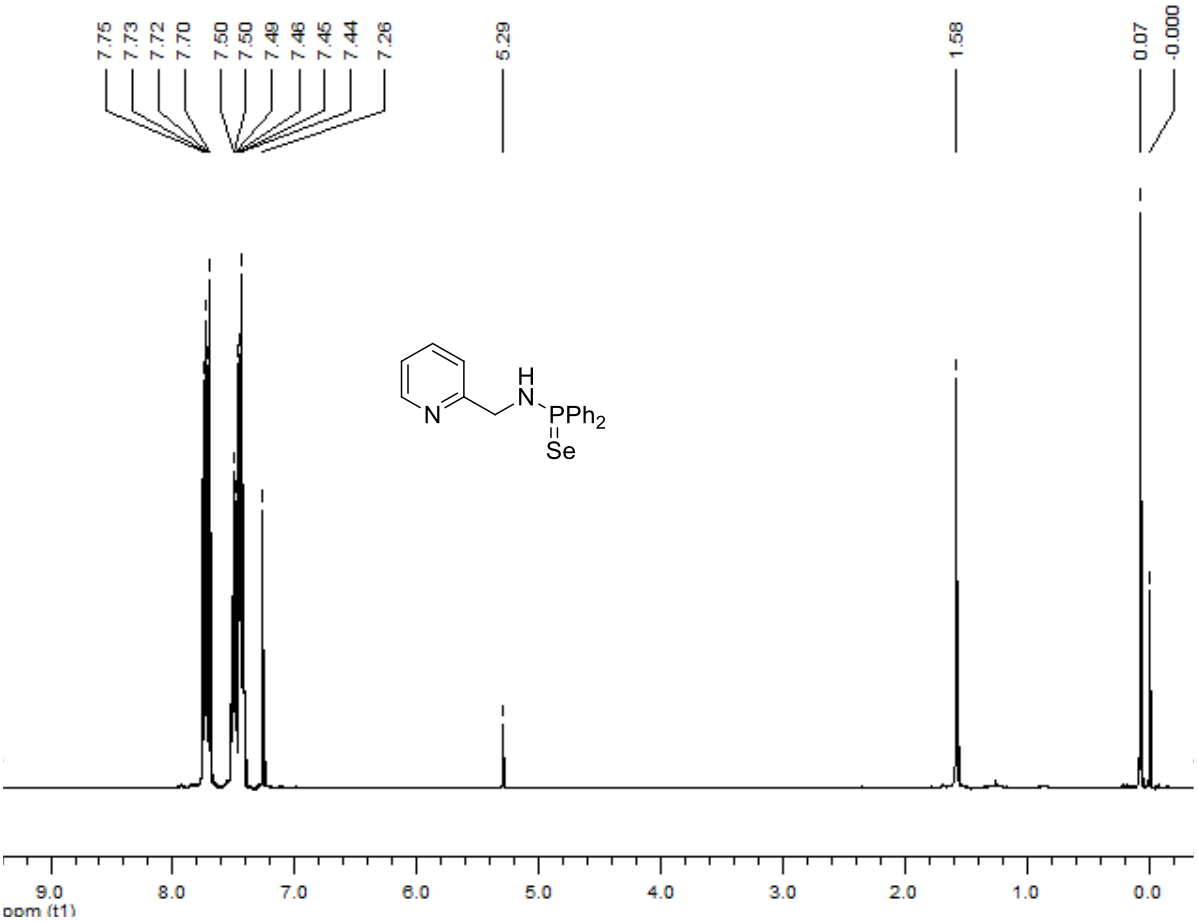

Fig. 4. ^{1}H NMR spectra of Ligand **3a**

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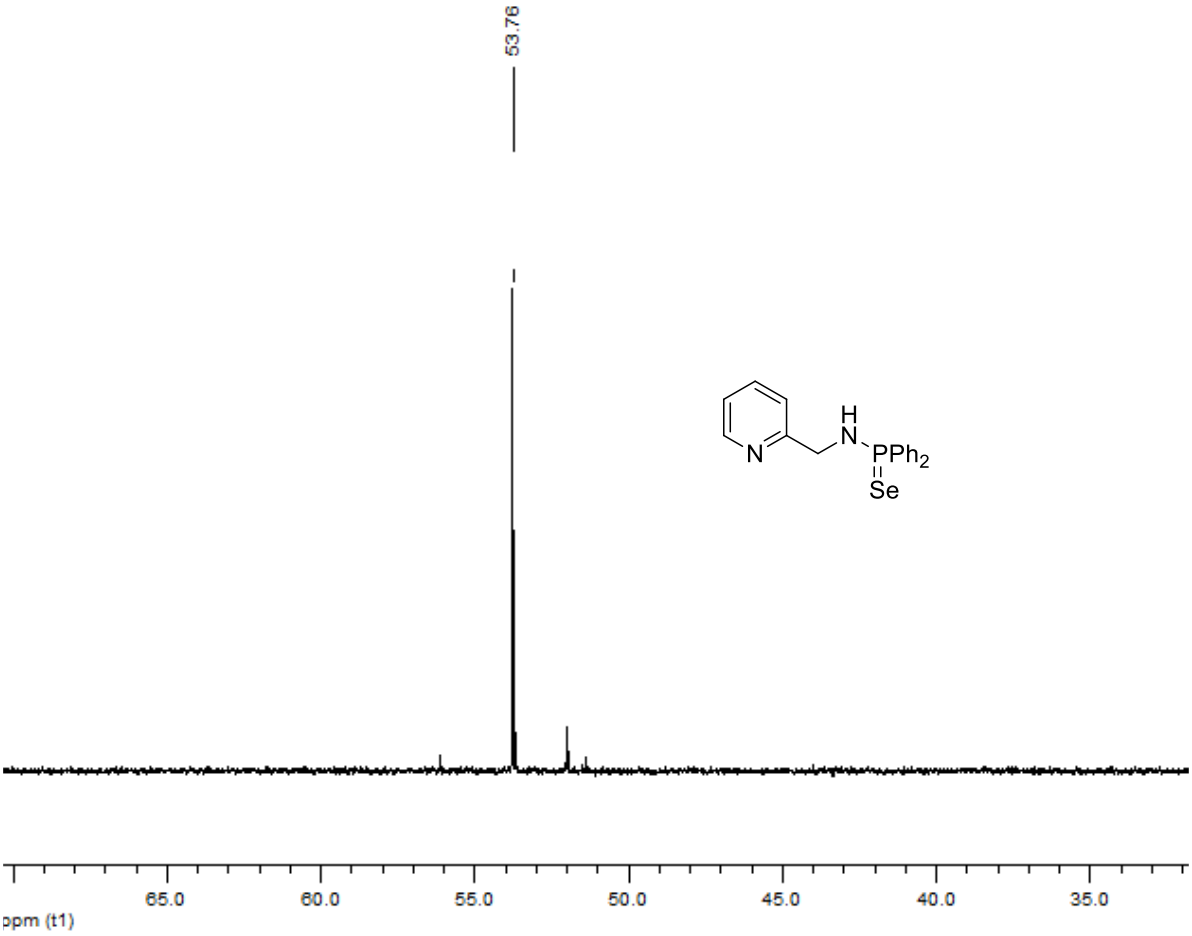

Fig. 5. ^{31}P {1H} spectra of Ligand **3a**

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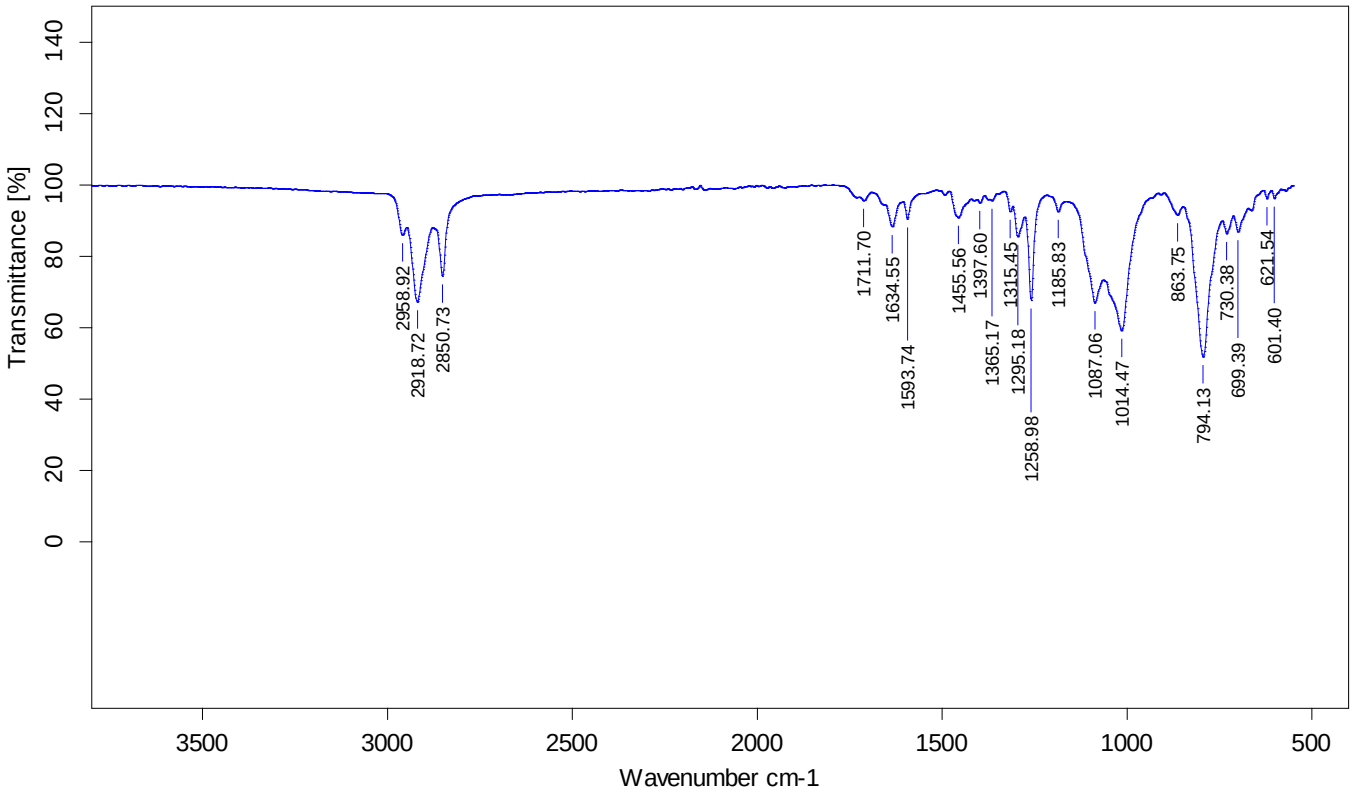

Fig. 6. FT-IR spectra of ligand **3a**

7.

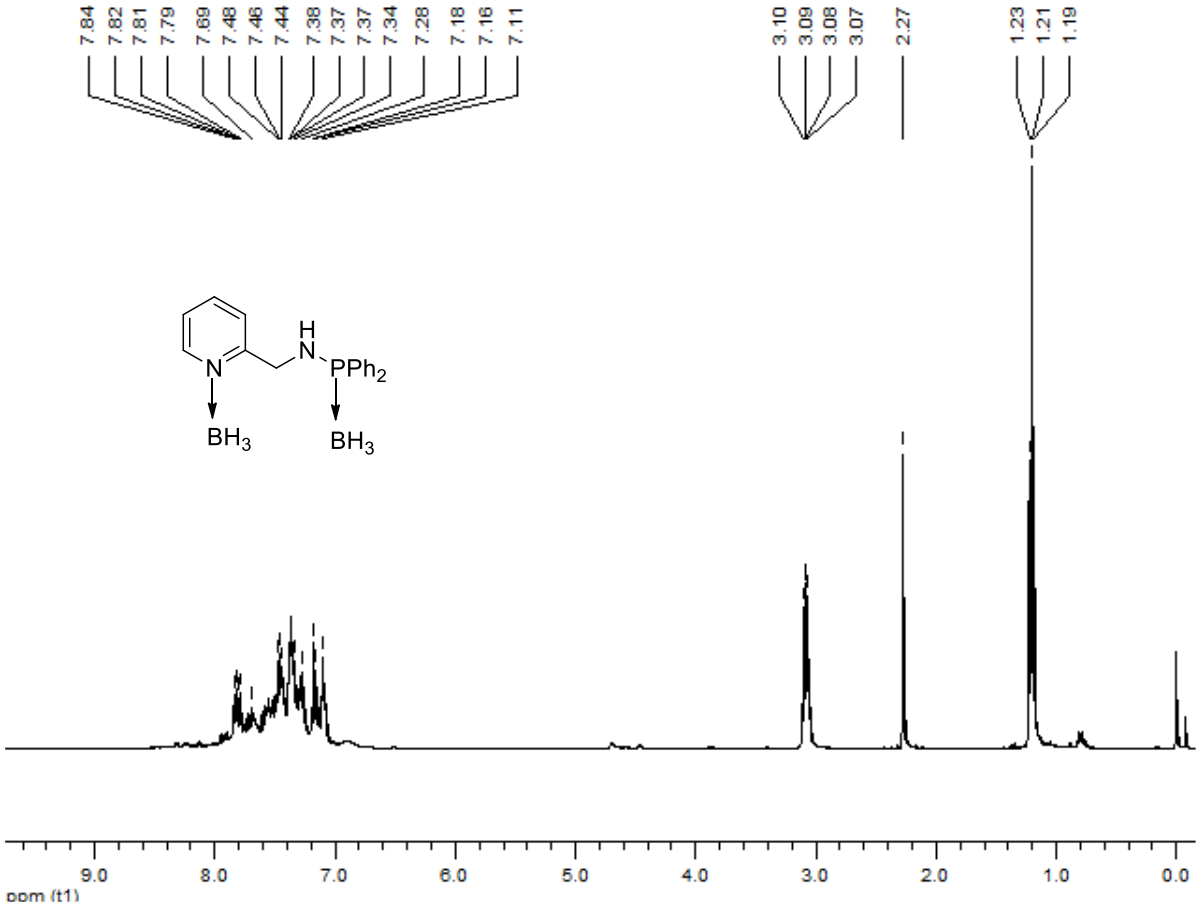

Fig. 7. ^{1}H NMR spectra of ligand **3b**

8.

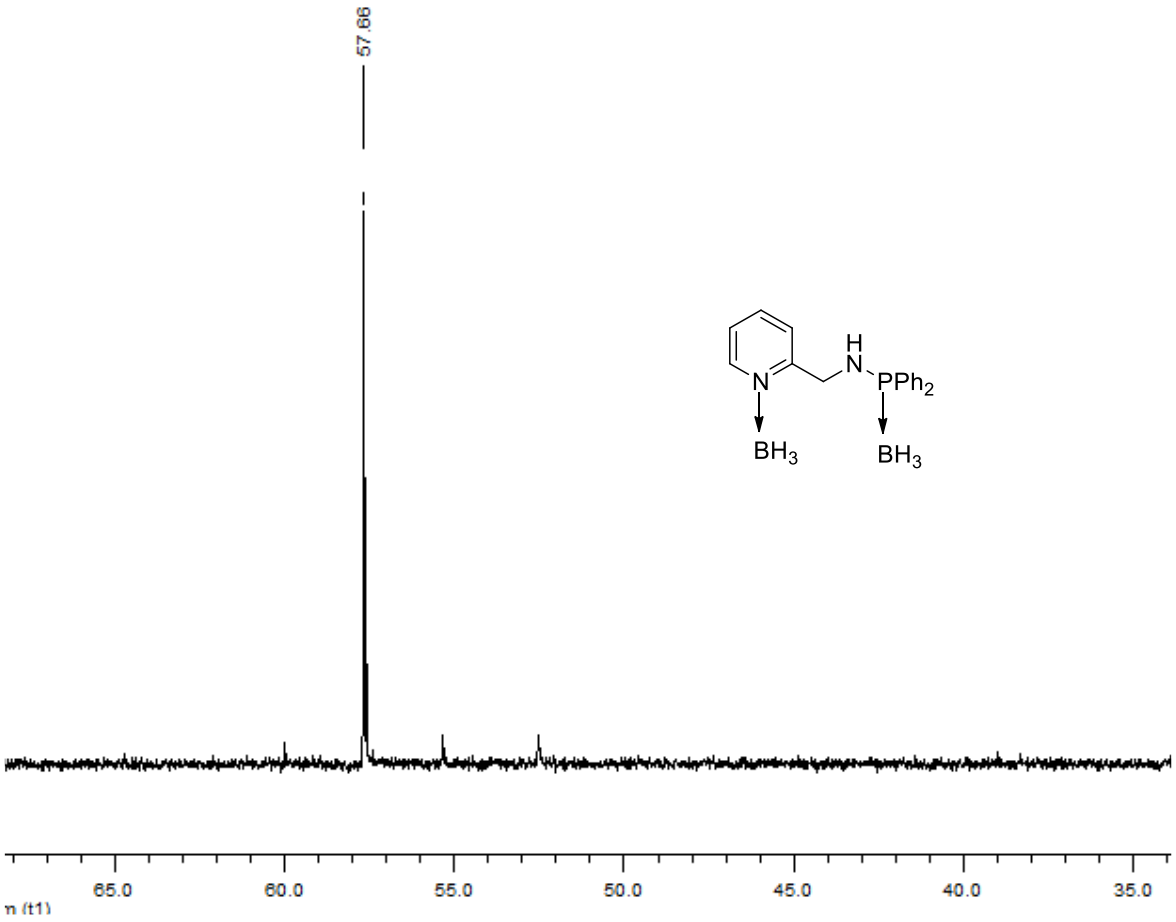

Fig. 8. ^{31}P {1H} spectra of ligand **3b**

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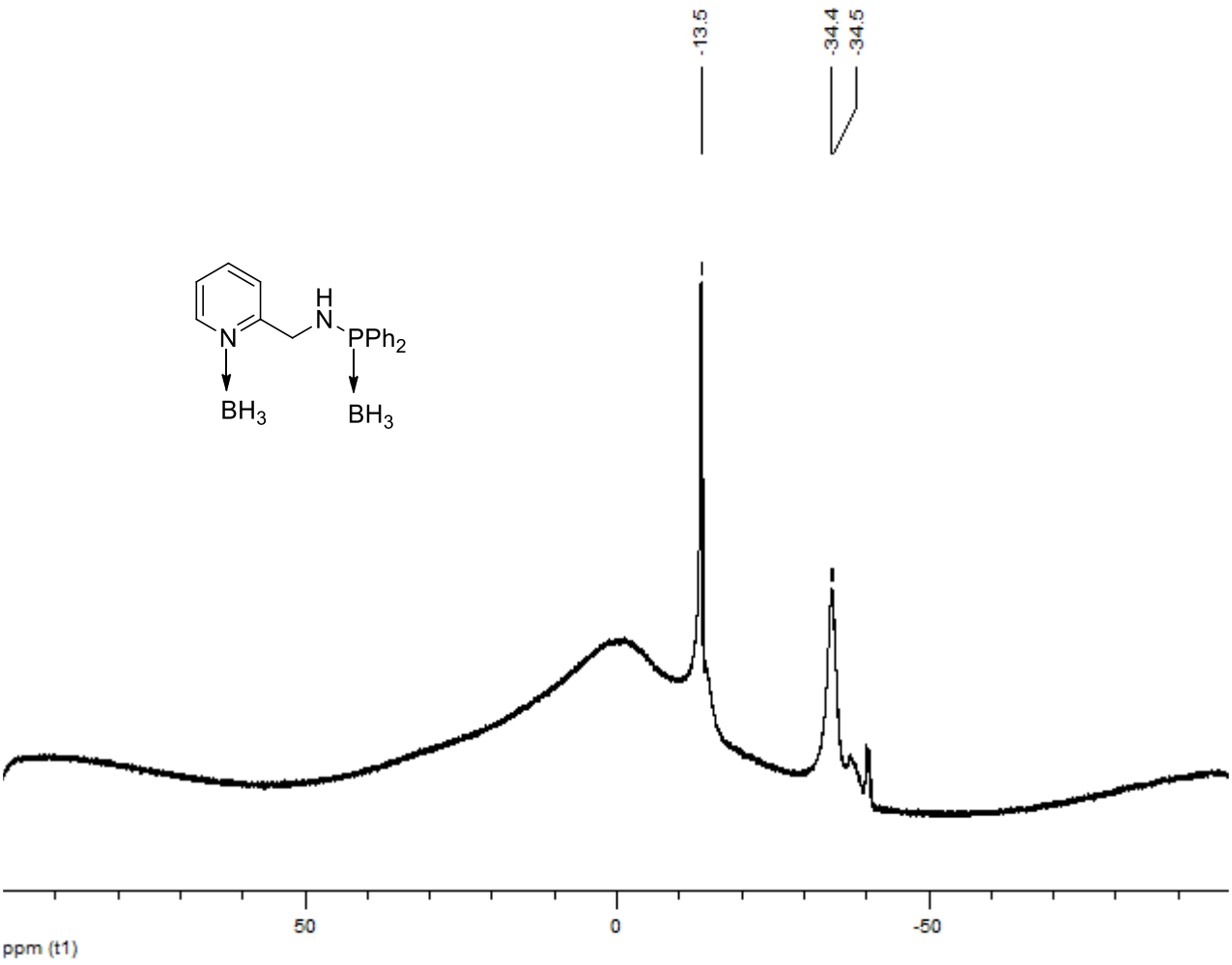

Fig. 9. ^{11}B {1H} spectra of ligand **3b**

10.

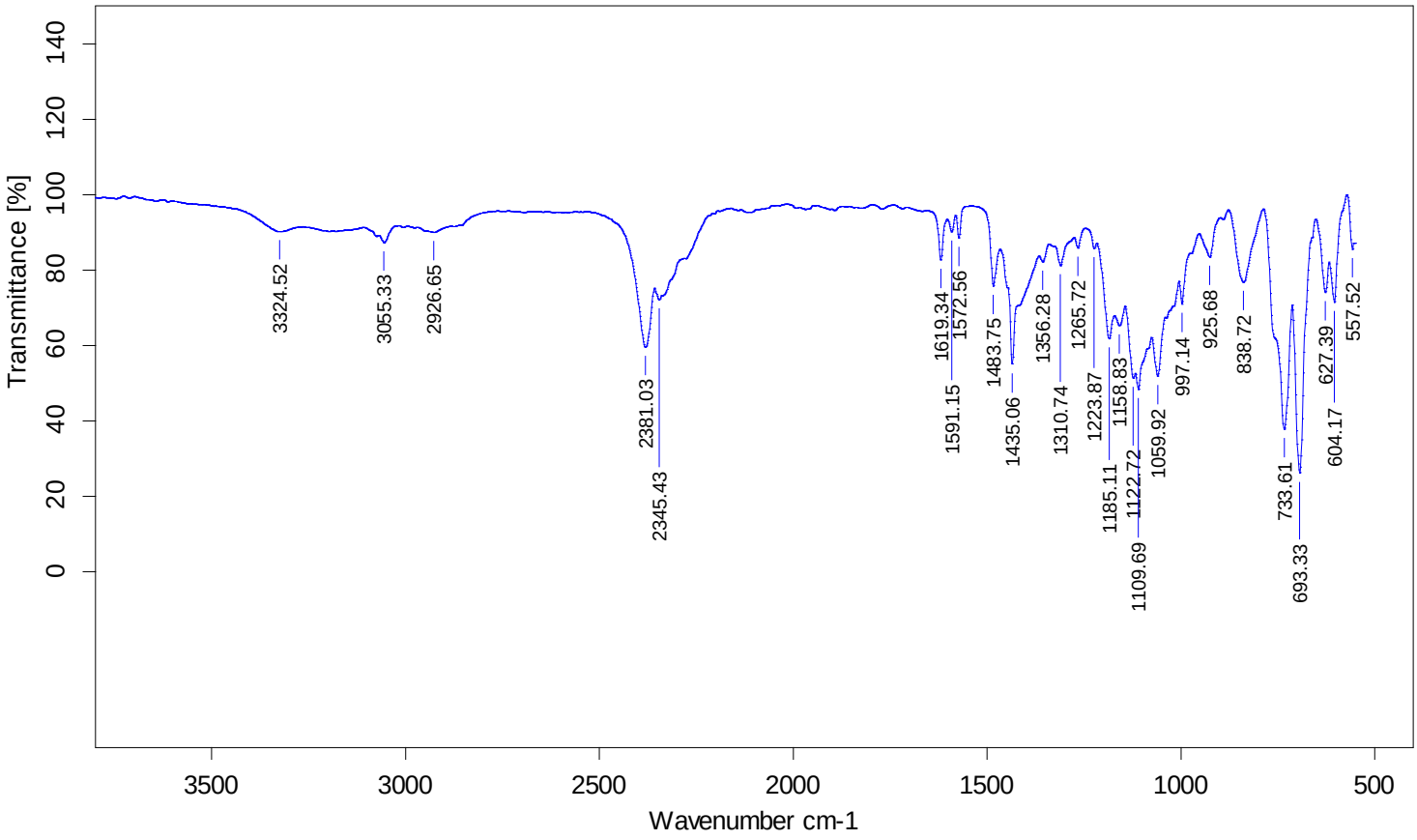

Fig. 10. FT-IR spectra of ligand **3b**

11.

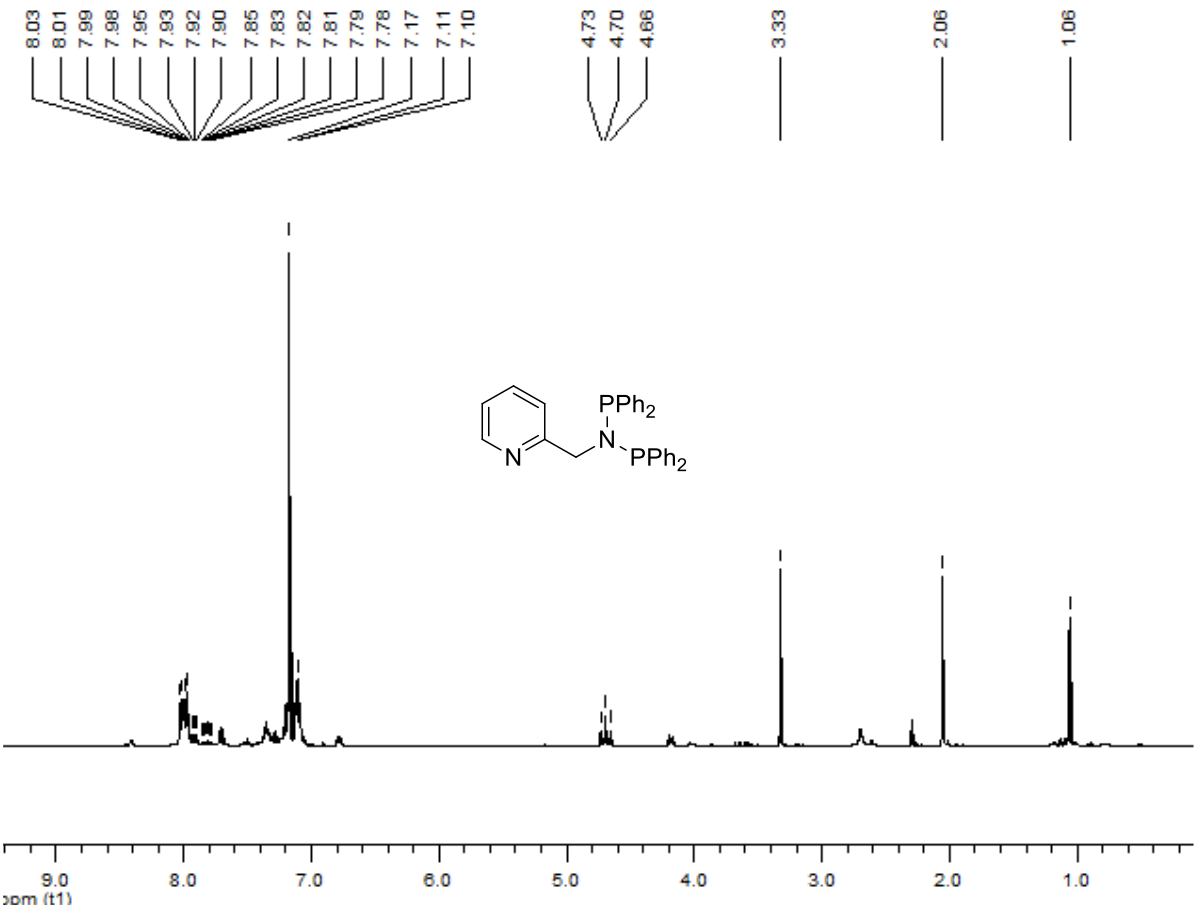

Fig. 11. ^{1}H NMR spectra of **4**

12.

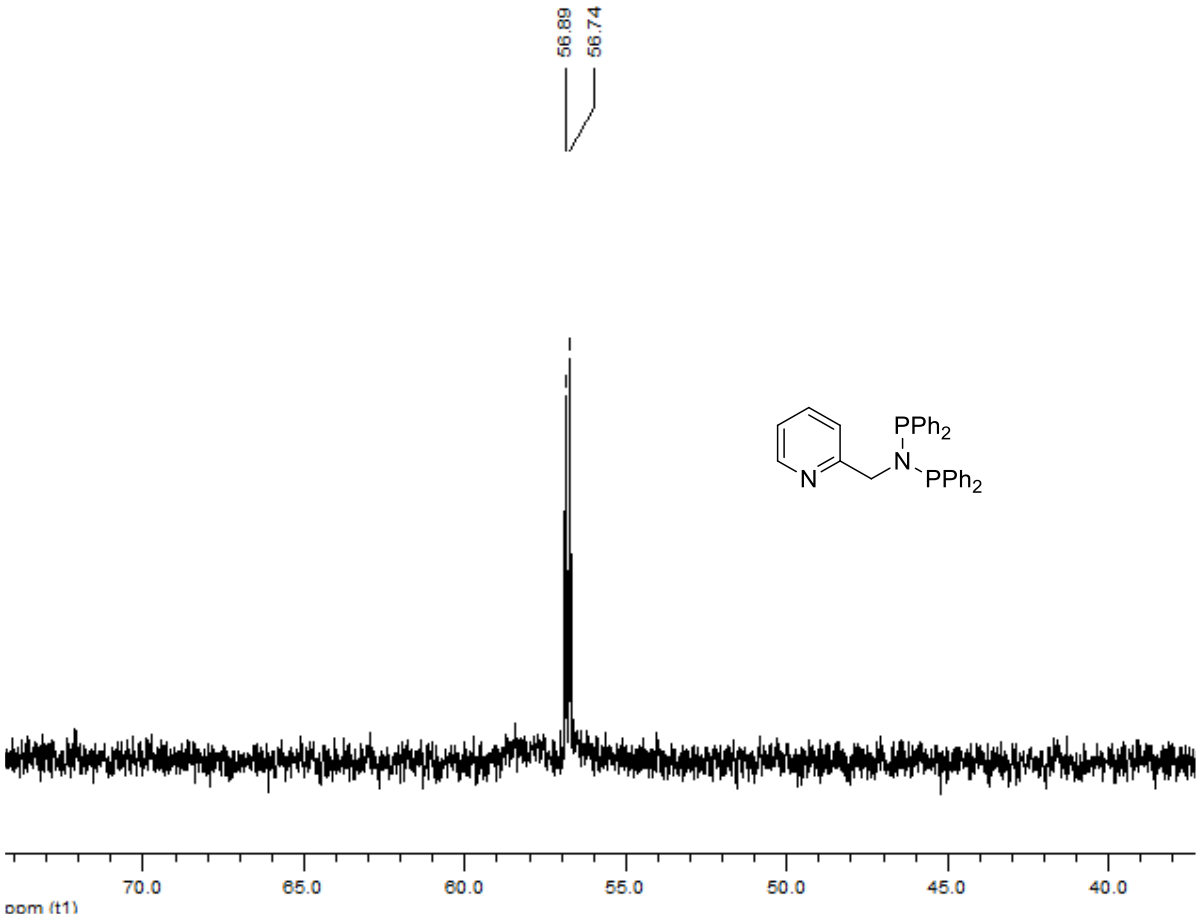

Fig. 12. ^{31}P {1H} spectra of **4**

13.

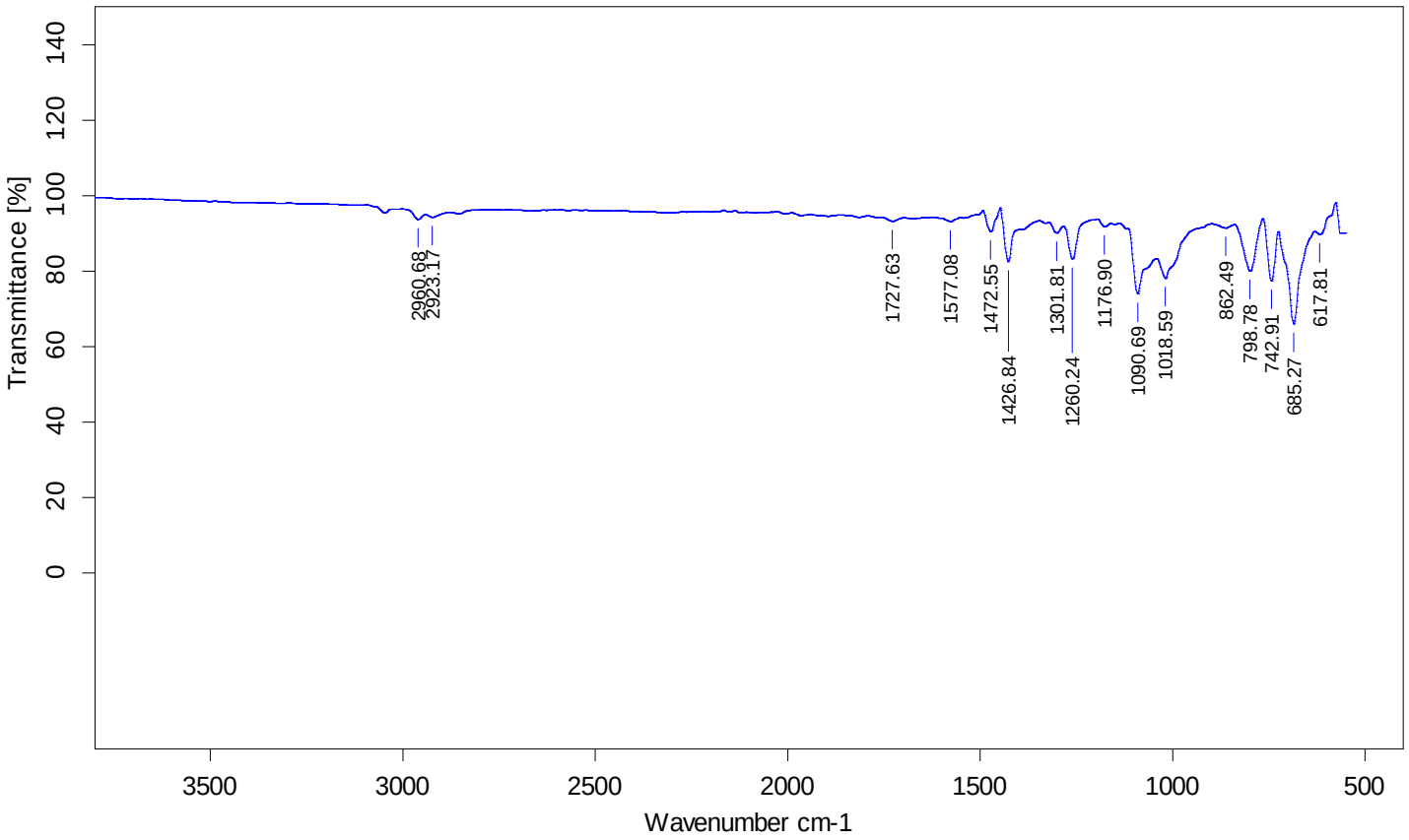

Fig. 13. FT-IR spectra of ligand **4**

14.

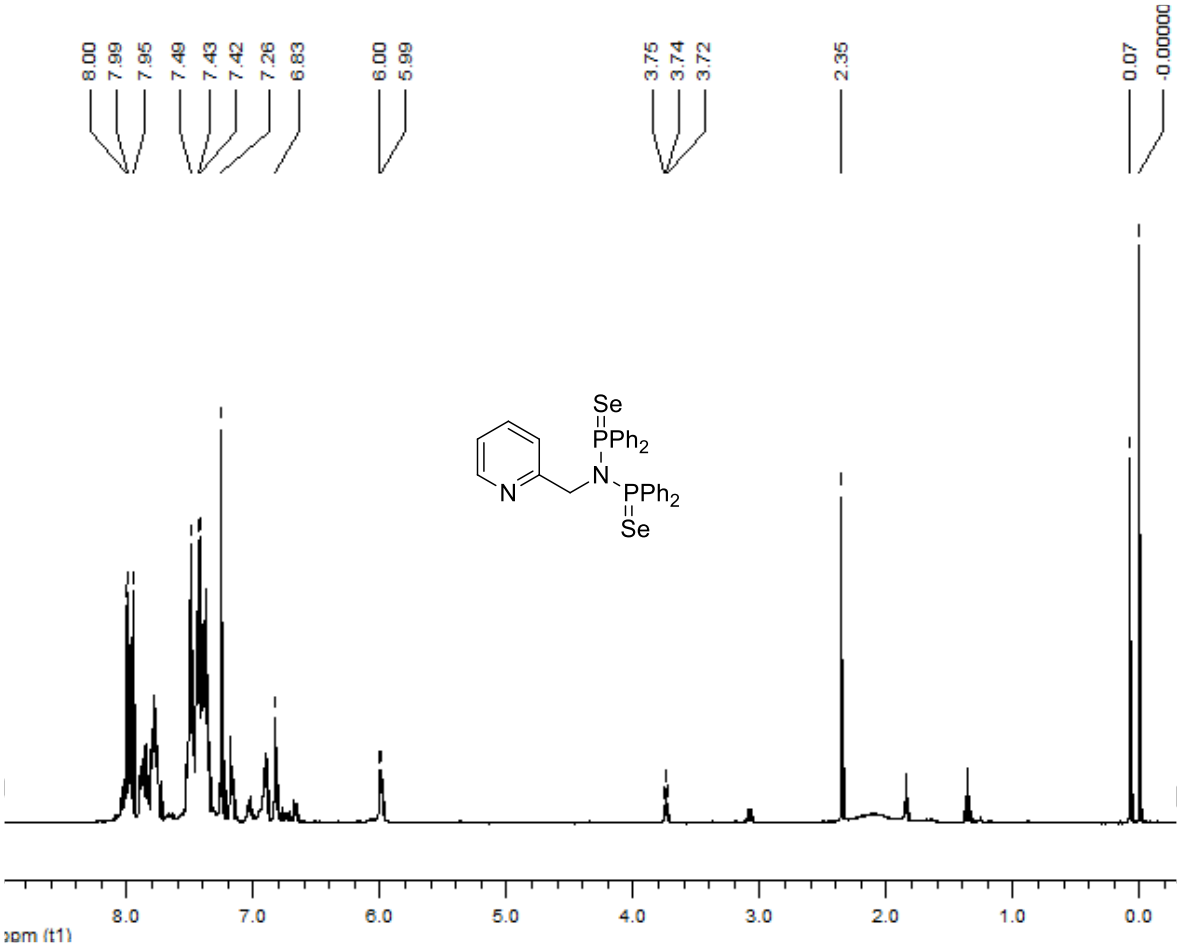

Fig. 14. ^{1}H NMR spectra of **5a**

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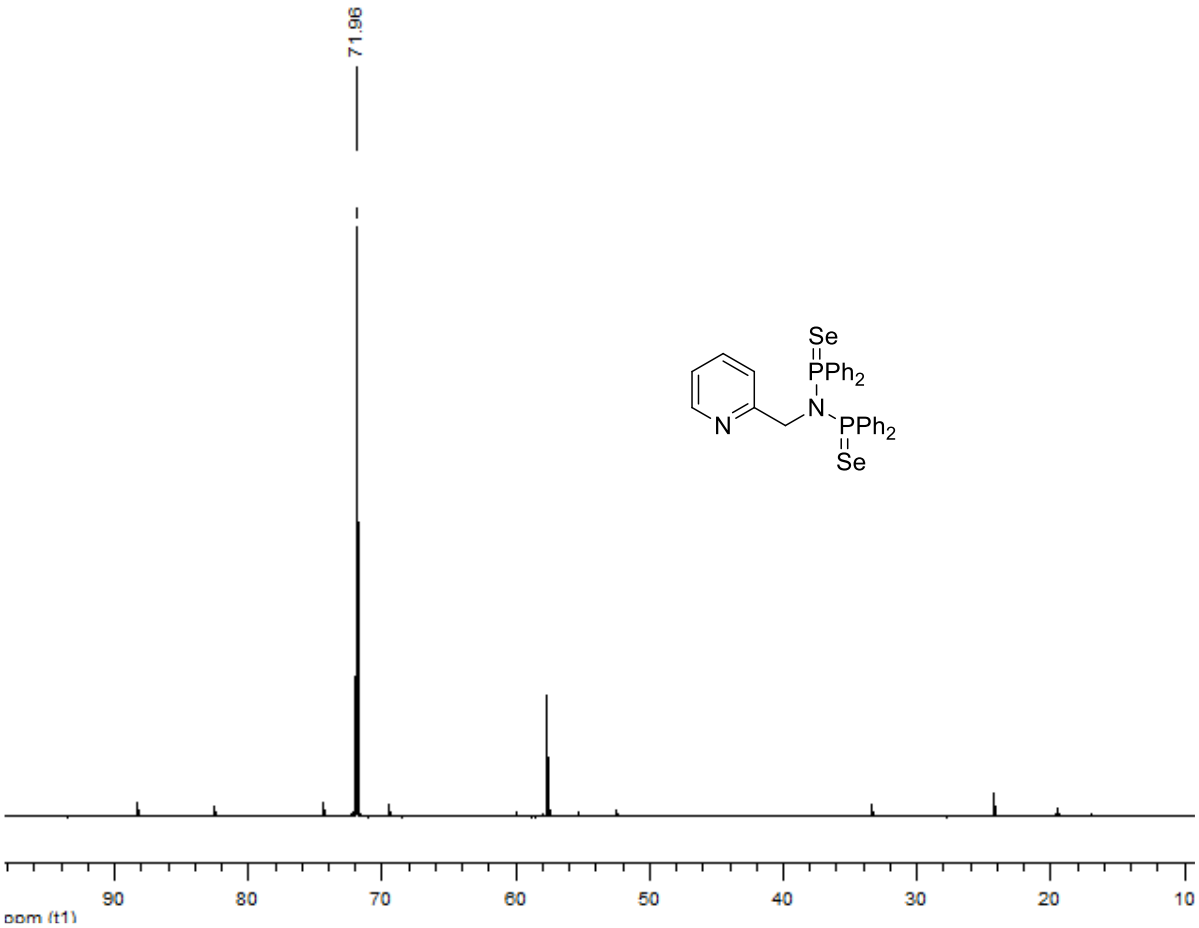

Fig. 15. ^{31}P {1H} spectra of **5a**

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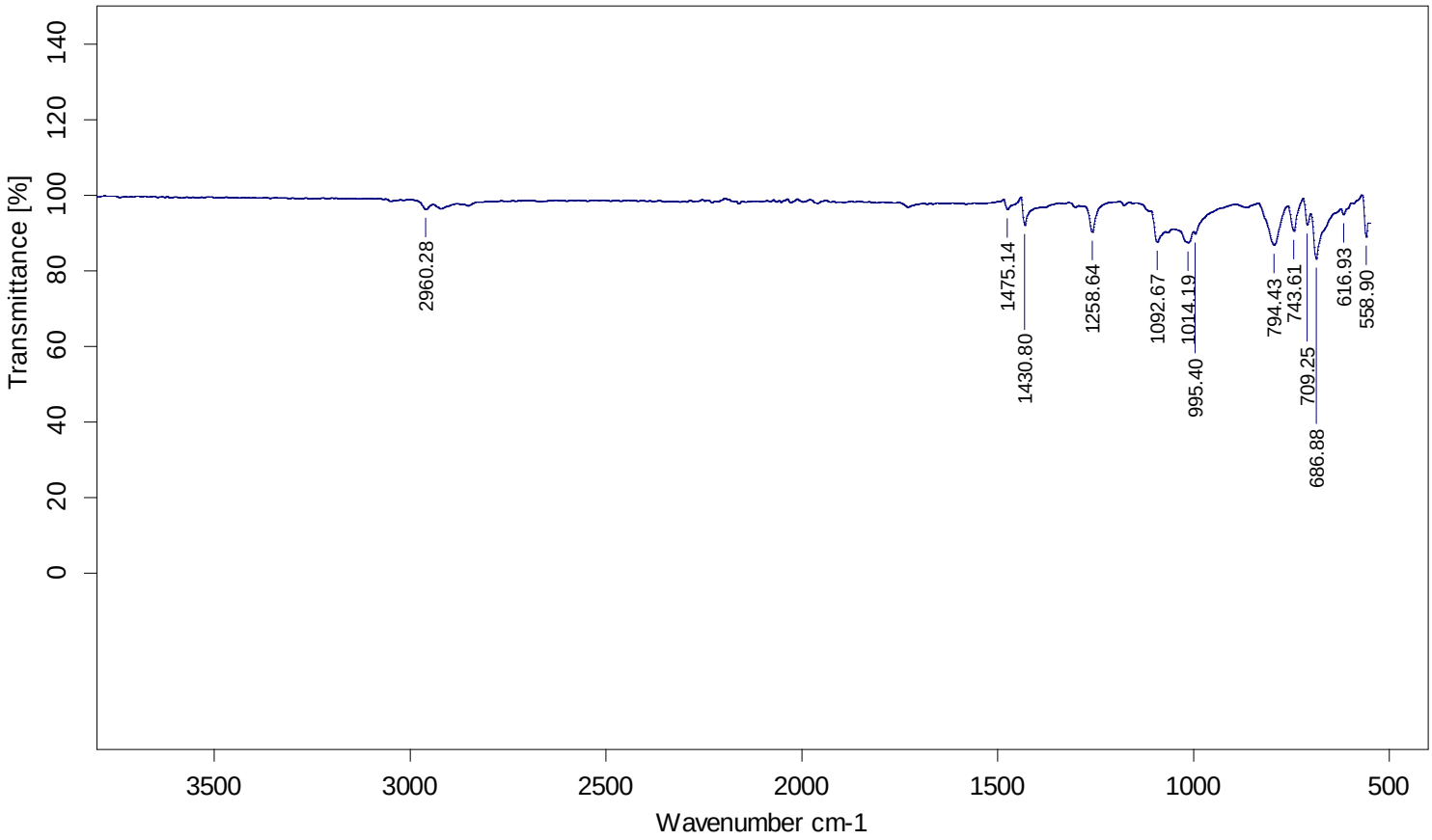

Fig. 16. FT-IR spectra of ligand **5a**

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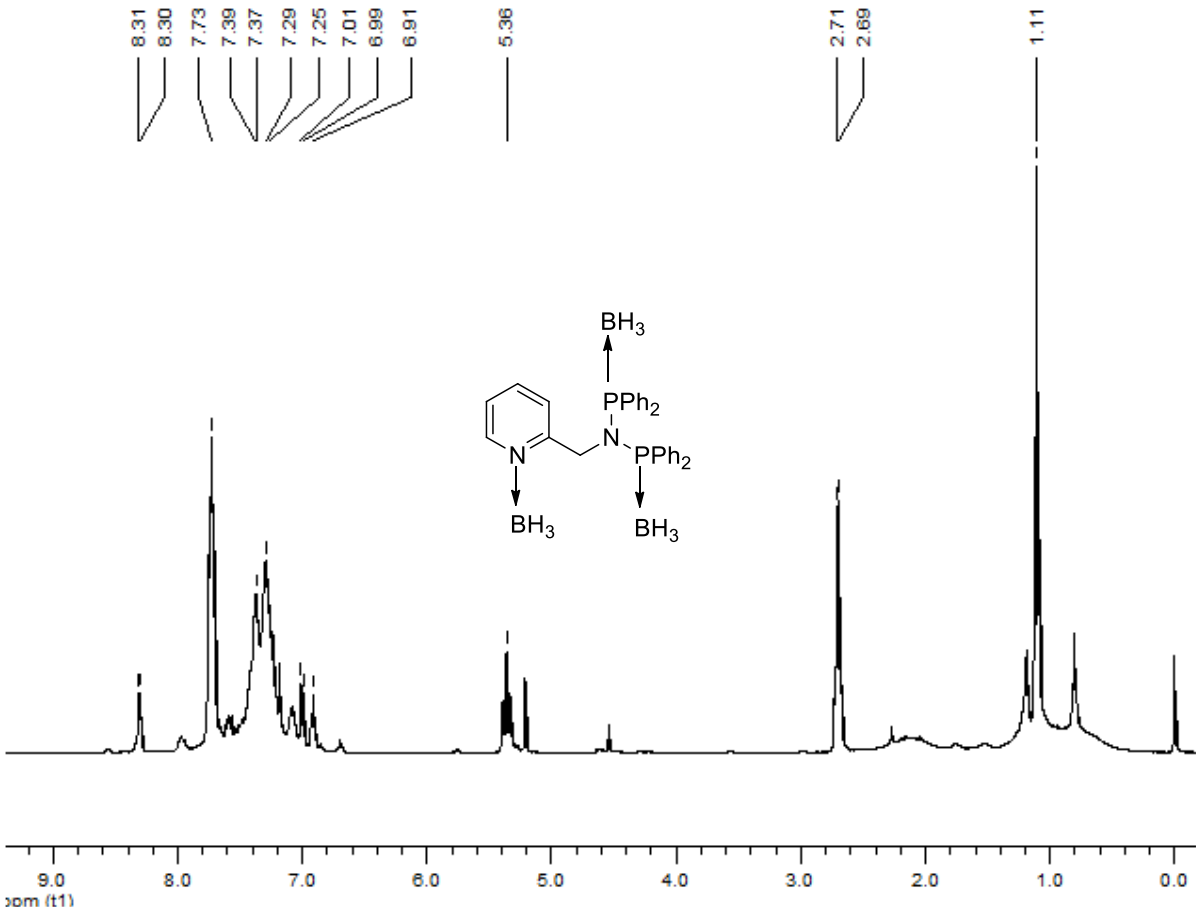

Fig. 17. ^{1}H NMR spectra of **5b**

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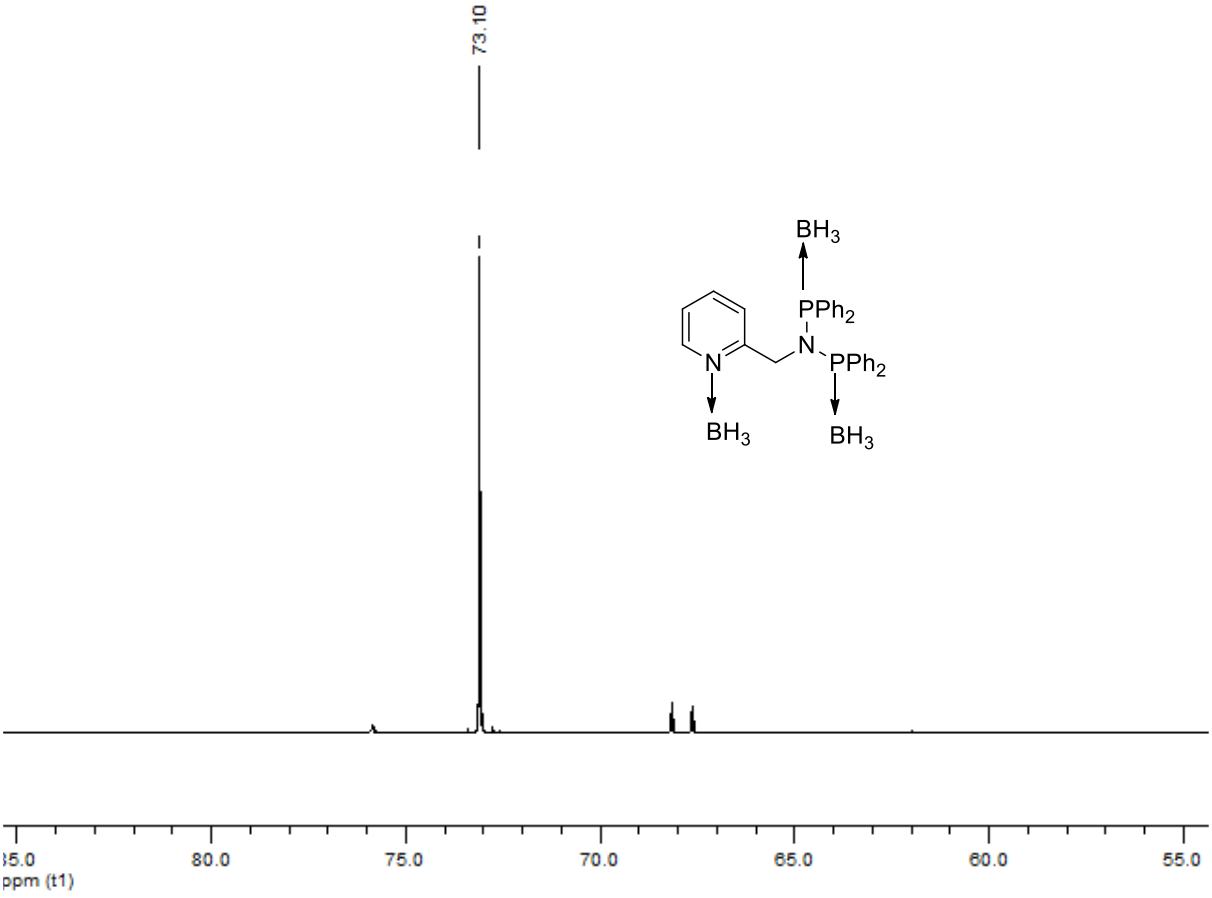

Fig. 18. ^{31}P {1H} spectra of **5b**

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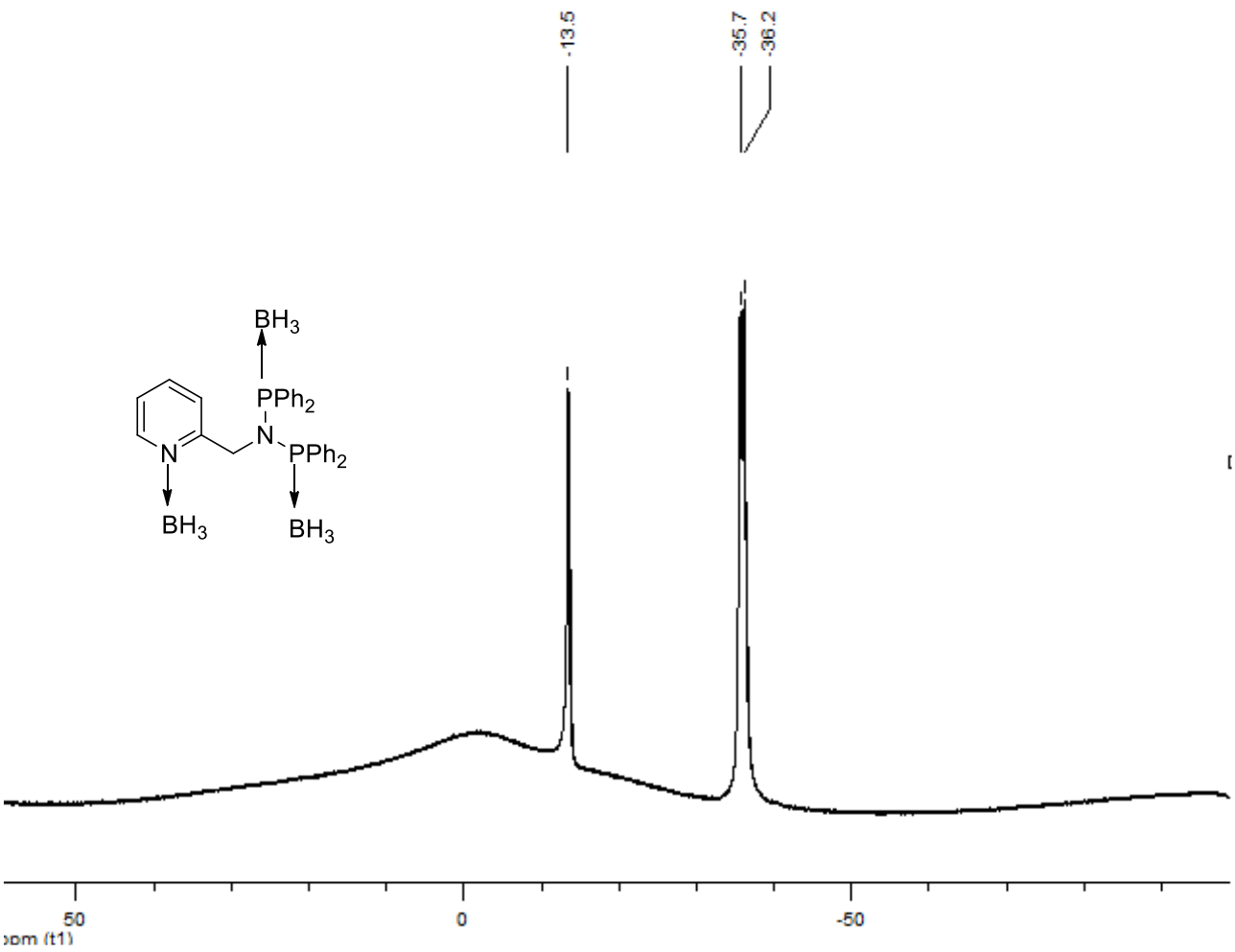

Fig. 19. ^{11}B {1H} spectra of ligand **3b**

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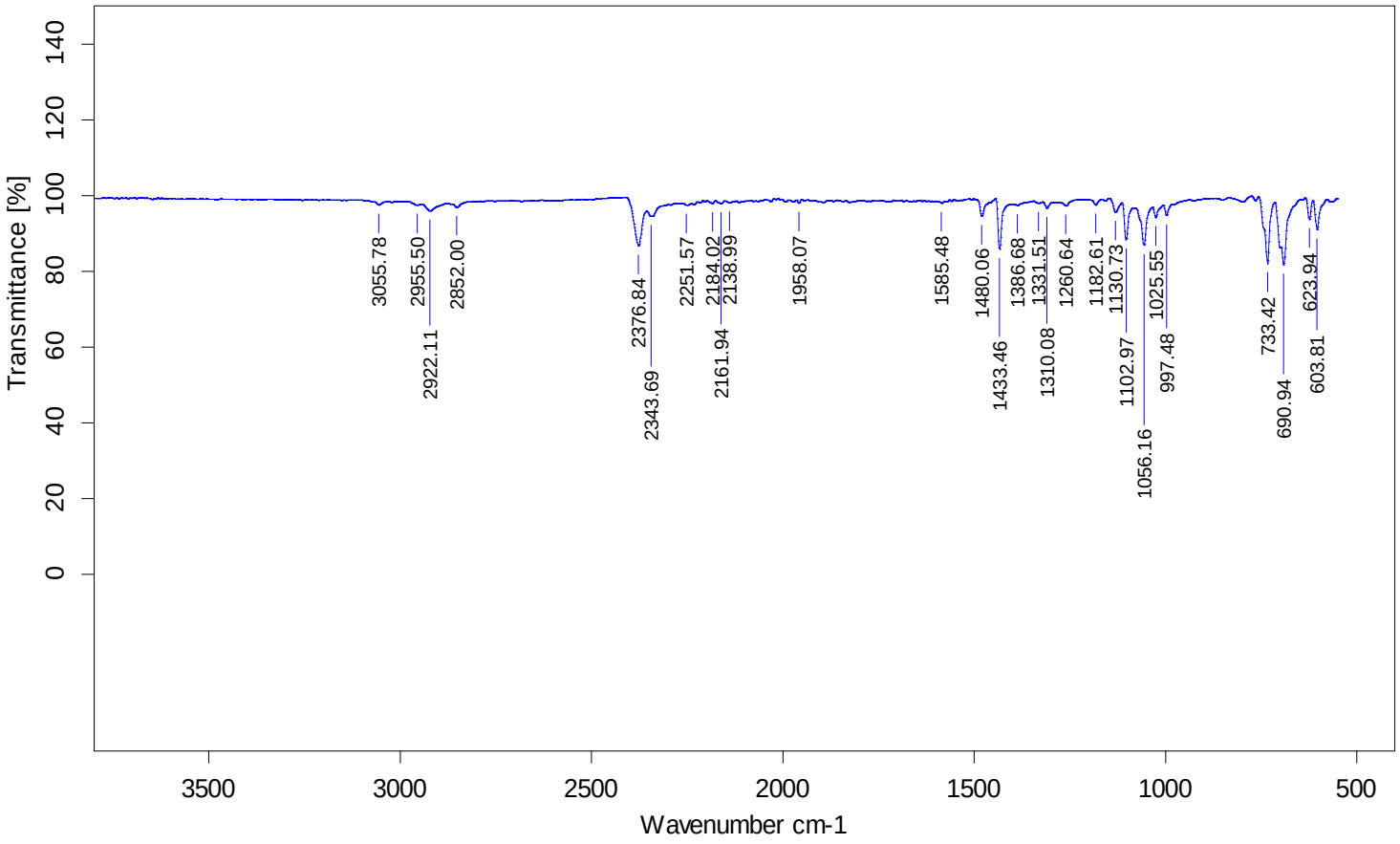

Fig. 20. FT-IR spectra of ligand **5b**

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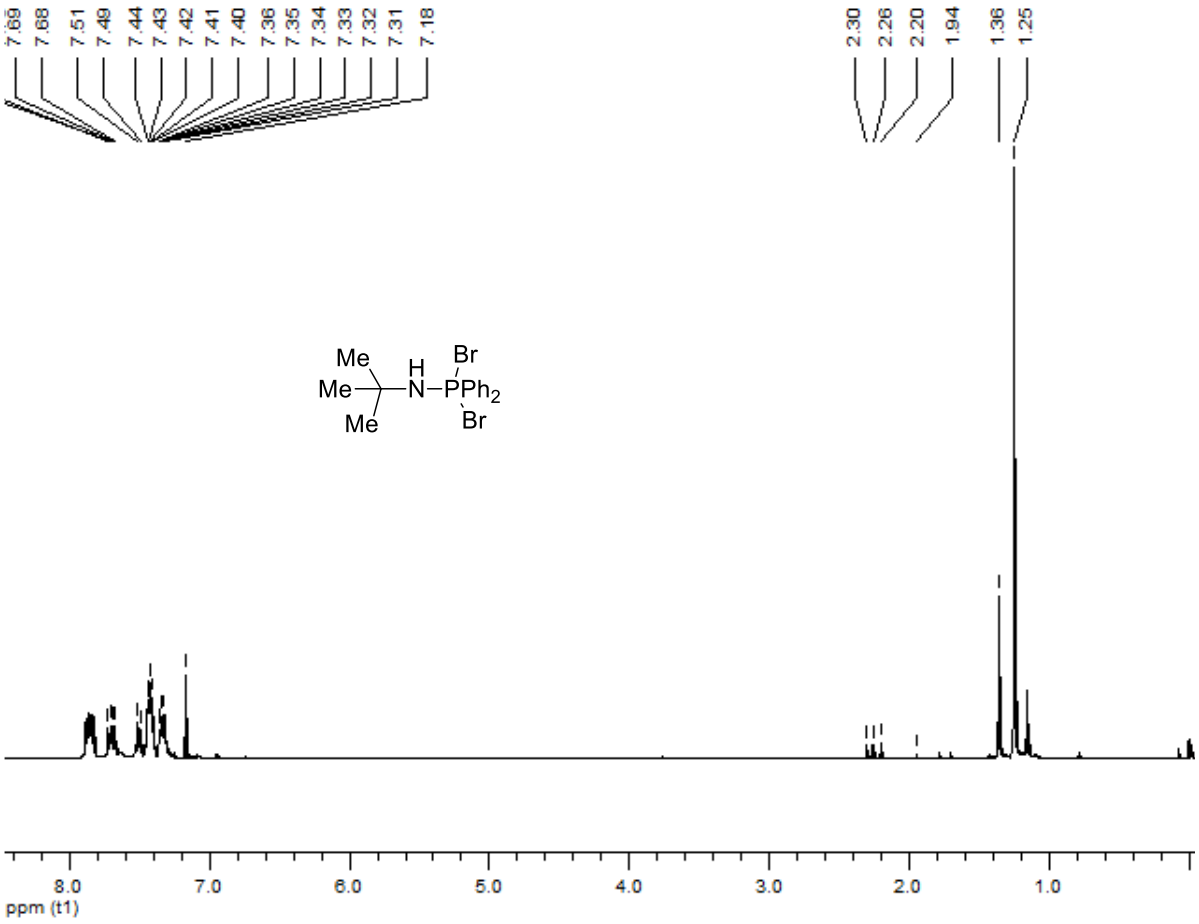

Fig. 21. ^{1}H NMR spectra of **6**

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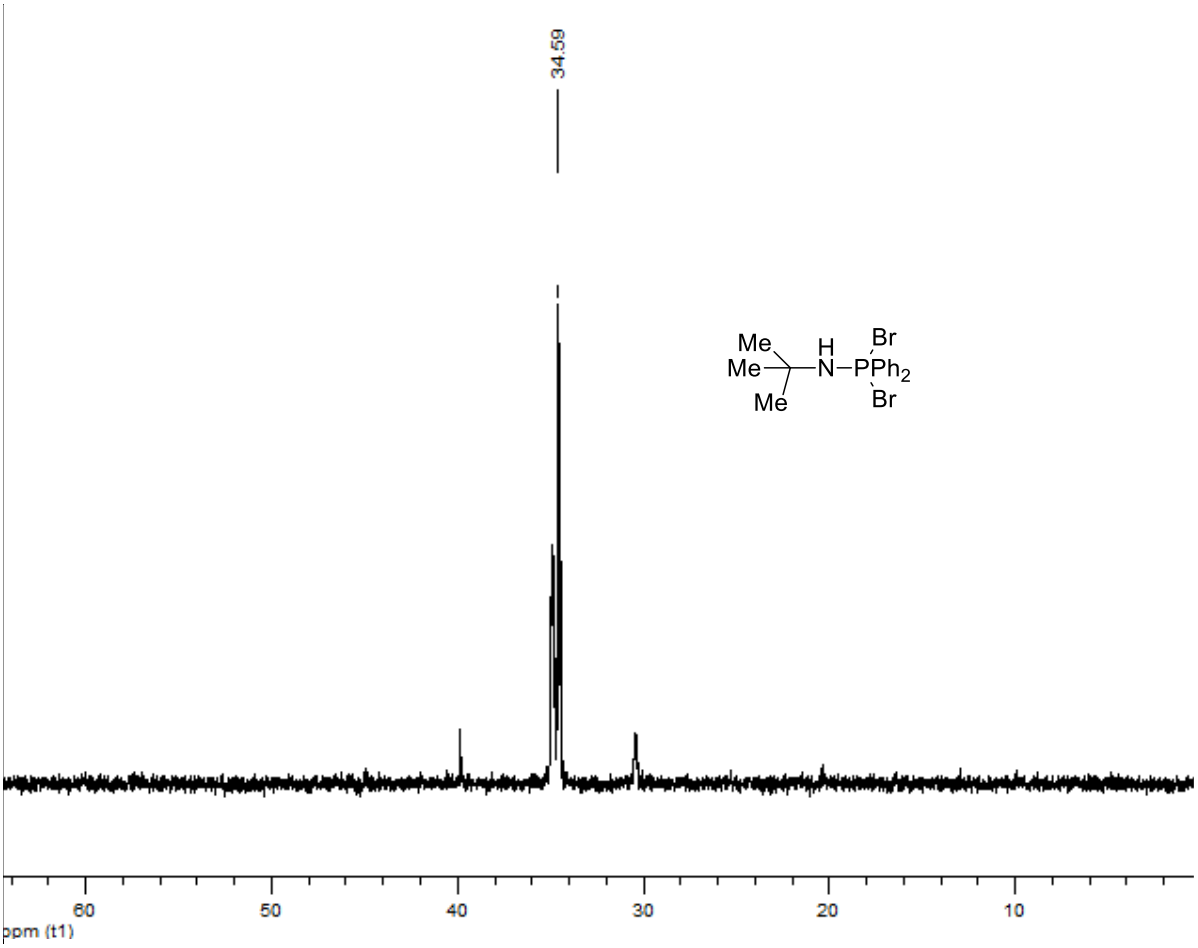

Fig. 22. ^{31}P {1H} spectra of **6**

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