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Syntheses and Characterization of a New Cyano-Substituted Bis(pyrazolyl)borate and its
Thallium (I) Complex

A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfilment

of the requirements for the degree

Master of Science in Chemistry

by

Chris Acquah

December 2016

Dr. Ismail O. Kady, Chair

Dr. Cassandra Eagle

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Keywords: Cyanoscorpionates, Bis pyrazole, Poly(pyrazolyl)borate

ABSTRACT

Syntheses and Characterization of a New Cyano-Substituted Bis(pyrazolyl)borate and its Thallium (I) Complex

by

Chris Acquah

Scorpionates are versatile and flexible ligands with a wide range of applications including catalysis, C-H bond activation, formation of new class of materials, and mimicking enzymatic reactions. This is as a result of its steric and electronic properties, and due to the relative ease with which the 3, and 5-positions of the pyrazole ring can be functionalized. In this work, we report the synthesis of a new class of scorpionate ligands known as cyanoscorpionates which can crosslink various metal centers. Thus, bis (4-cyano-3,5-diphenylpyrazolyl)borate $\text{Bp}^{\text{Ph}_2,4\text{CN}}$ was synthesized and fully characterized by ^1H NMR and FT-IR. Coordination of bis (4-cyano-3,5-diphenylpyrazolyl)borate $\text{Bp}^{\text{Ph}_2,4\text{CN}}$ to thallium (I) metal was performed and characterized and we are looking to elucidating its molecular structure by X-ray crystallography in future.

DEDICATION

I dedicate this work to the Almighty God for his care, strength, guidance and protection,
My Parents Mr. and Mrs. Acquah and my uncle Mr. Charles Percy Amoako.

ACKNOWLEDGEMENTS

I want to thank the Almighty God for his care, protection guidance and abundant grace throughout my degree. I would also like to give special thanks to my research advisor Dr Ismail Kady for taking me as his research student and providing me with excellent advice and guidance throughout this research.

Thanks to Dr Cassandra Eagle for helping me throughout my difficult times and serving as my committee member. I also use this opportunity to thank all the professors in the ETSU chemistry department especially Dr Abbas Shilabin for serving on my committee and Dr Ray Mohseni for his immense help with instrumentation for this research.

I also express my deepest gratitude to my family for their constant support and prayers. Lastly, a big thank you to all the graduate students in the ETSU chemistry department especially my good friends Adetola Opeyemi, Fanah Joy Selorm and Mrs Conerlia Yeboah.

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LIST OF ABBREVIATIONS

Bp	Bis Pyrazole
Cp	Cyclopentadienyl
DCM	Dichloromethane
DMSO	Dichloromethane
FT-IR	Fourier Transform Infra-red
GC-MS	Gas Chromatography-mass Spectrometry
KBH ₄	Potassium Borohydride
min	Minutes
m.p	Melting point
NMR	Nuclear Magnetic Resonance
ppm	Parts per million
PLED's	Polymer Light Emitting Diodes
ROMP	Ring Opening Metathesis Polymerization
Rf	Retention factor
TLC	Thin Layer Chromatography
Tp	Tris Pyrazole
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

Trofimenko, in 1966, reported the first polypyrazolylborates ligand also known as scorpionate ligand.¹ The general structure of a scorpionate ligand is a multidentate ligand consisting of a pyrazole ring; a five membered heterocyclic and polydentate compound with three carbon and two nitrogen atoms.¹ One of the nitrogen donor atoms attaches to a boron atom and the other becomes a donor site for other ligands which result in the formation of a polypyrazolylborates ligand with improved steric and electronic properties (Fig 1).² This is due to the fact that the number and position of the substituents on the pyrazole ring, mostly the 3 and 5 position, can be varied and functionalize relatively easily.² The term scorpionate comes from the nature of its bonding which resembles a scorpion attacking its prey using its pincers and sting. It binds to a metal with its two donor nitrogen atoms with a final and third donor point, which is either another pyrazole ring or an 'R' group attached to the boron, reaching over the plane to sting the metal (Fig 2).² However, this is not obligatory especially because the Tp ligand for instance can only be bidentate sometimes as seen in complexes such as Pd(II) and Rh(I).²

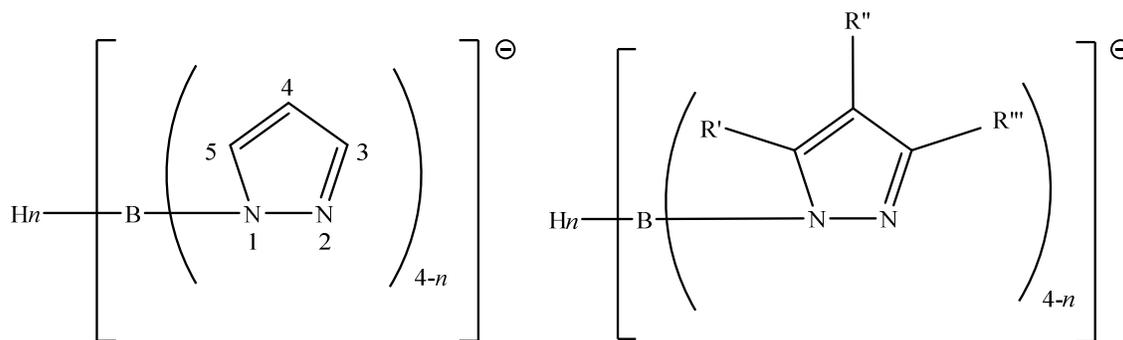


Fig 1: General Structure of Polypyrazolylborates (Scorpionates) Ligand, where n can be 0, 1, or 2 and R can be and alkyl or aryl group.^{1,2}

There are three forms of scorpionate ligands depending on the number of pyrazole rings (Fig 3). These include the dihydrobis(pyrazolyl)borates (Bp), hydrotris(pyrazolyl)borates (Tp), and tetrakis(pyrazolyl)borates (pzTp), with the Tp being the most popular and also the first to be discovered and synthesized by Trofimenko.¹ They all carry a negative charge and can simply be synthesized by reacting a borohydride ion with excess pyrazole under different ratios and controllable conditions (Fig 4).^{1,2} Since their discovery, scorpionate ligands are deemed to be one of the most useful ligands in inorganic chemistry with applications in organic chemistry, bioinorganic chemistry, organometallics as well as in new materials such as polymer light emitting diodes (PLEDs).¹ Applications include catalysis of polymerization and oligomerization reactions,³ modelling and mimicking of enzymatic reactions such as metalloenzymes,⁴ investigating of the active sites of biomolecules as seen in bromoperoxidase,⁵ and C-H bond activation or functionalization.¹

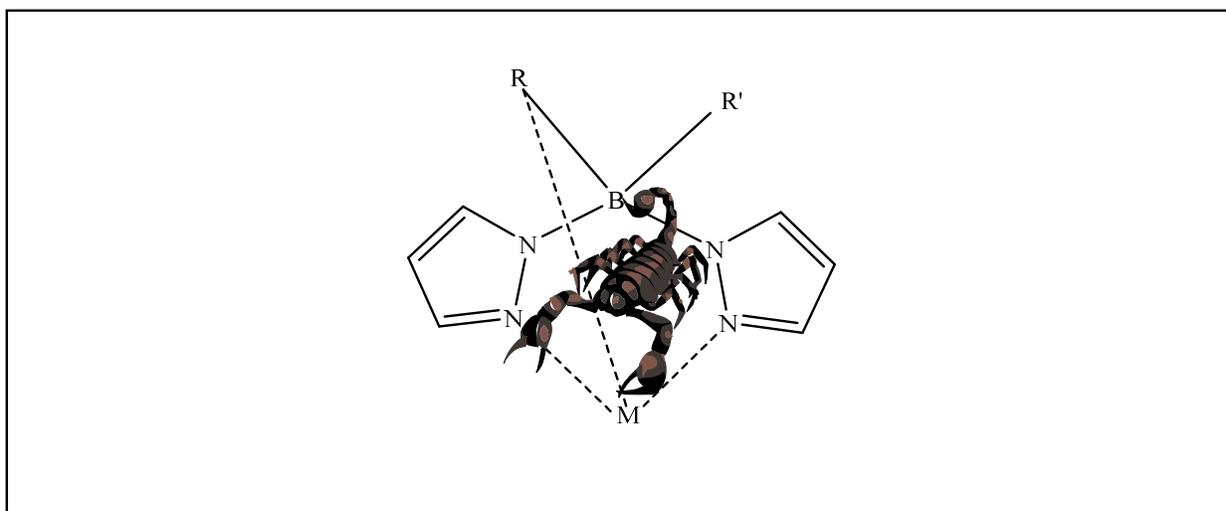


Fig 2: Structure of bonding in polypyrazolylborates (Scorpionate) ligands.¹

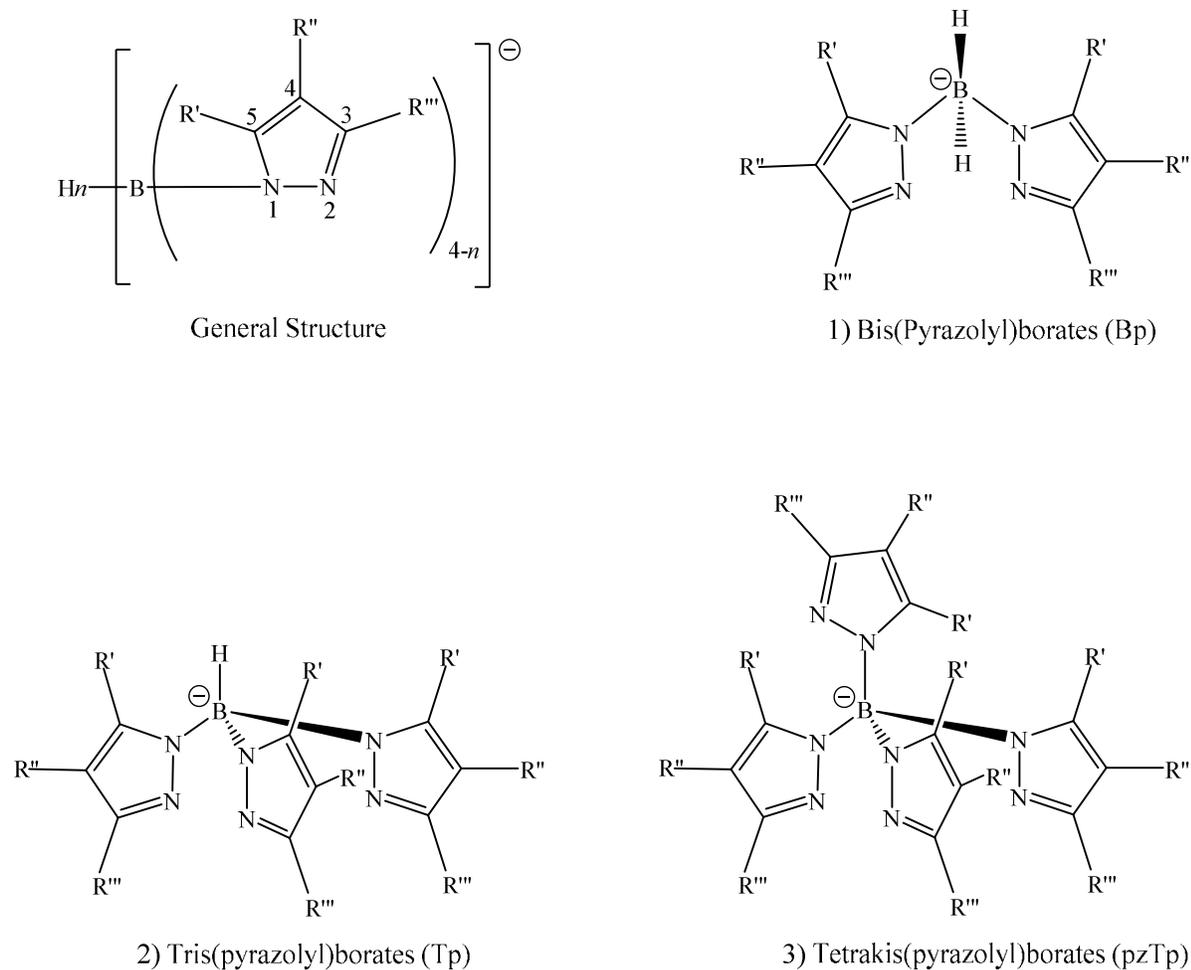


Fig 3: The three forms of polypyrazolylborates anions.¹

Most pyrazole derivatives are known to show biological activity. For instance, the complex 4-acetyl-3-amino-5-methyl pyrazole (aamp) has an outstanding biological activity and can be used to mimic enzymatic reactions.⁶ Tp complexes are also used to model mononuclear molybdenum cofactors of molybdoenzyme enzymes such as nitrate reductase and sulphite oxidase.² Also, the combination of Tp complexes with AlCl_3 are used to catalyze polymerization and oligomerization reactions such as the ring opening metathesis polymerization (ROMP) of cyclooctene.^{2,7}

Neutral Ru(II) complex such as $\text{TpRuCl}(\text{PPh}_3)_2$ can also be used to dimerized terminal alkynes with similar activity occurring with molybdenum complex.^{2,8}

$\text{TpRu}(\text{=C=CHPh})(\text{Cl})(\text{PPh}_3)$ can be used to catalyze the ROMP of norbornene.⁹ Photolysis of the $\text{Tp}^*\text{Rh}(\text{CO})_2$ complex followed by the loss of CO and oxidative addition of R-H or Ar-H is used in the activation of C-H bonds in aliphatic and aromatic hydrocarbon molecules.^{2,10}

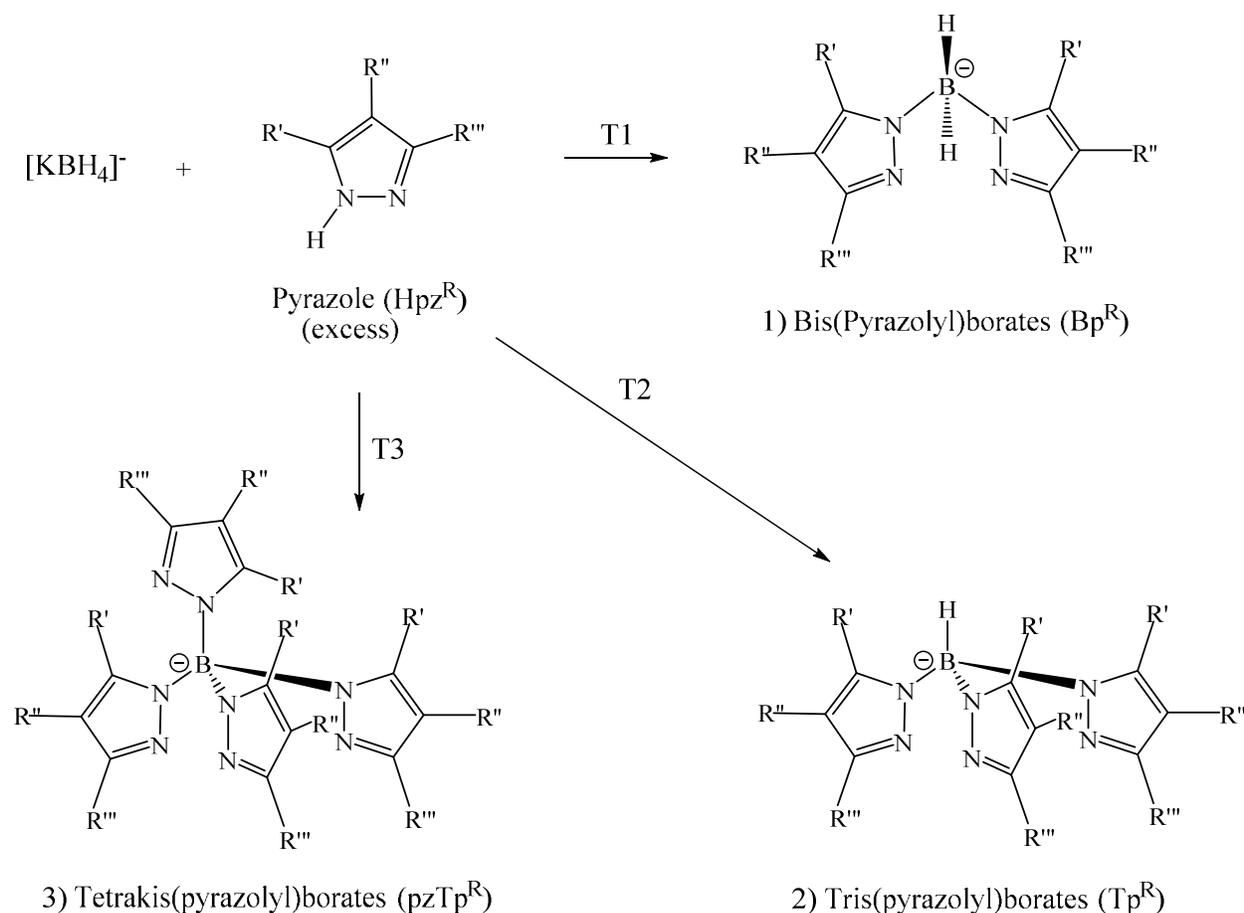


Fig 4: Synthesis of Poly(pyrazolyl)borate ligands under different ratios (of KBH_4 to pyrazole) and temperatures (T1, T2 & T3).^{1,2}

Another application of scorpionate ligand can be seen in carbene and nitrene transfer reactions. The reactions of olefins with ethyl diazoacetate is catalyzed by the complex $\text{Tp}^{\text{R}}\text{Cu}(\text{ethylene})$ to form cyclopropanes which also catalyzes the transfer of nitrene from

PhI=NTs arizidines.¹¹⁻¹³ Diaz et al researched into different Tp^R complexes as a catalyst for the conversion of olefins and ethyl diazoacetate into cyclopropanes. They find out that The $Tp^{Ms}Cu$ complex gave the highest diaste-reomeric excesses, that in the case of styrene, of ca.96% as compared to other catalyst which gave a maximum diastereomeric excess (de) of 84% for styrene.^{11,13} Scorpionate ligands have also been applied in the development of new materials. The most recent being the fusion of Tp coordinated lanthanide complexes in electroluminescent lights which was reported by the Boncella group.^{1,14} Polymer light emitting diodes have been incorporated with lanthanide complex containing Tp^R ligands coordinated to tetraphenylporphyrin. Tetraphenylporphyrin shows diode-like behavior and binds to the lower half of the lanthanide metal while the Tp^* ligand binds the top half leading to the enclosing of the lanthanide ion and shielding it from outside interactions (Fig 5).¹⁴ This improves the effectiveness of luminescence compared with analogous containing mono and bidentate ligands.^{1,14}

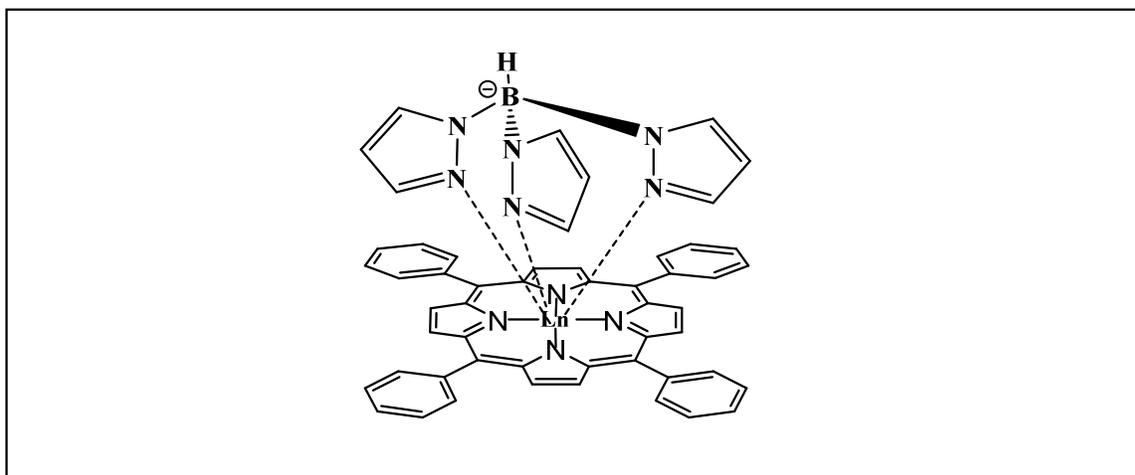


Fig 5: An electroluminescent lanthanide complex containing a Tp ligand coordinated to tetraphenylporphyrin in tripodal fashion.¹

The Tp ligand is widely used because it is similar in a way to the cyclopentadienyl (Cp) ligand although both can either be a five electron donor which represents the covalent model ligands or a six electron donor representing the ionic model ligands.¹ The difference, however, is that the Tp ligands are more bulky and have a comparatively weaker donor properties as compared to the Cp ligand. This is because the Tp ligands are weak field δ -N donors and form octahedral complexes in a “fac” manner while Cp is 5 fold π donors and form tetrahedral complexes.¹

The naming of the scorpionate ligands poly(pyrazolyl)borates is done with emphasis on the pyrazole ring. This has been grouped into four different cases. The default position is the 3 position on the pyrazole ring and a substituent ‘R’ at this position is denoted or represented by a superscript “R”. Hence for Bp, we have Bp^R, Tp, Tp^R etc. For example, hydrobis(3-phenylpyrazolyl) borate is written as Bp^{Ph}; hydrotris(3-methylpyrazolyl)borate is denoted as Tp^{Me} etc. The next position of interest is the 5-position which follows the 3-position. In this case, substituents are named as a superscript separated by a coma.¹⁵ Example, hydrobis(3-phenyl-5-methylpyrazolyl)borate is written as Bp^{Ph,Me}.

Thirdly, in the case where both R substituents on 3 and 5 positions are identical, it is represented by a superscript R, followed by 2. For example, hydrobis(3,5-dimethylpyrazolyl)borate is denoted by Bp^{Me2}. Lastly, a substituent, R at 4-position is represented by a superscript 4R.¹⁵ For instance, tetrakis (4-cyano-3-phenylpyrazolyl)borate is denoted by pzTp^{Ph,4CN}.

Recent research shows that varying the substituent at 3- and 5-positions of the pyrazole rings with strong electron withdrawing groups such as cyano groups or sterically hindered alkyl and aryl groups will not only affect the coordination geometry but also its electronic properties.¹⁶

The ease at which the substituents on the 3- and 5-positions on the Pyrazolyl ring of the scorpionate ligands can be modified leads to three main generations of scorpionates with different electronic and steric properties.¹⁷ The first generation of scorpionates involved small and less bulky substituent such as methyl (CH₃) group. These are readily available and inexpensive, and they coordinate in tridentate fashions.¹

However, the bid to improve the catalytic ability of scorpionate ligands led to the synthesis of the second generation of scorpionates. They have bulkier substituents such as phenyl (Ph), tert-butyl (t-Bu)¹⁸ etc. These substituents can be either on 3-position or a combination of the 3, 4, and 5-positions of the pyrazole ring.¹ Bulkier substituents such as phenyl groups at 3-position give rise to low coordination ligands, mainly due to steric hindrance.¹⁹

Eichorn et al made several research into the effects of bulky substituents on poly(pyrazolyl)borate ligand complexed with Fe(II) (Table 1).^{20,21} Their findings showed that bulky substituents have erroneous effects on the Fe-N bond lengths, the spin state as well as the redox potential of the complexes.²¹ The octahedral Fe(II) metal which has a 3d⁶ electronic configuration has been a model for investigating low spin, high spin, and spin crossover complexes with 3d⁶ configuration.²¹ Table 1 shows that as the substituent gets bulkier the Fe-N bond gets longer. This is because there is a crystal field above which Iron (II) acts as a low spin t_{2g}^6 (¹A_{1g}) complex and below which its acts as a high spin with $t_{2g}^4 e_g^2$ (⁵T_{2g}) configuration.

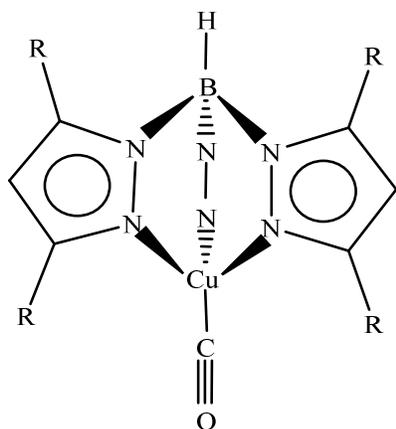
Table 1: Effects of substituents on the electronic properties of Tp coordinated Iron (II) complex.^{20,21}

	(Tp) ₂ Fe	Tp(^{Me}) ₂ Fe	Tp(^{Ph}) ₂ Fe
Fe – N Bond (Å)	1.97	2.17	2.25
Spin State	Spin Crossover T _c > 395 K	Spin Crossover T _c > 395 K	High Spin T > 2 K
Redox Potential	0.1V	N/A	0.86V

Hence, there is an increase in metal-ligand bond length as we go from a t_{2g}^6 low spin state to a $t_{2g}^4 e_g^2$ high spin state.²¹ Increasing the bulkiness of the substituent however elongates the Fe-N bond length resulting in high spin complex as shown in table 1. The redox potential also increases with increasing bulkiness of substituent. Another effect is also seen in the spin crossover which by definition is basically the movement of an electron from one orbital to the next and is highly dependent on temperature.^{16,20} The more bulky the substituent, the lesser the temperature needed for spin crossover to occur.²⁰

Finally, the third generation scorpionates; this is made of electronically active and high electron withdrawing substituents such as CN and CF₃.^{22,23} Years of extensive research by Diaz et al into the third generation scorpionates showed that the electronically active and high electron withdrawing substituents have a major effect on the magnetic, electronic and structural properties of the metal complexes.²⁴ They also improve the thermal stability, oxidation resistance, volatility and the solubility of the metal complexes.²⁵

Table 2: Effect of different substituent on tris(pyrazolyl)boratocopper(I) carbonyl complexes.²³



R	ν_{CO} (cm ⁻¹)	Cu-C (Å)
CF ₃	2137	1.808(4)
Ph	2086	
H	2083	1.765(14)
CH ₃	2066	
<i>i</i> -Pr	2056	1.769(8)

Table 2, gives a detailed description of the effects of several electron withdrawing substituents on tris(pyrazolyl)boratocopper(I) carbonyl complexes.²³ It was reported that, as the electron rich substituents increase (from iso-propyl to CF₃) the electron density of the pyrazole ring (and in turn the coordinated metal) is reduced, which results in weakening the metal-nitrogen bond. This enhances the interaction between the carbonyl (a strong π acceptor ligand) and the metal, mostly due to π back bonding, this leads to an increase in the metal carbon (Cu-C) bond as well as an increase in the CO stretching frequency.^{23,24}

Cyanoscorpionates

Cyanosubstituted scorpionates or simply cyanoscorpionates fall under the third generation scorpionates. In spite of the strong electron withdrawing ability of the cyano group, cyanoscorpionates can coordinate to metal ions through the nitrogen in the cyano group. They can also serve as ligands to form coordination bonds with a second transition metal²⁶ through the nitrogen of the pyrazole ring. Thus, cyanoscorpionates can be cross-linked to different metal complexes by a conjugated pathway (Fig 6) connecting the nitrile coordinated metal and the

pyrazole of a second cyanosubstituted scorpionate forming an array of coordinated polymer chain.^{2,27} Expanding of this cross-linked coordination leads to polymeric coordination complexes with improved conductivity and magnetism properties.²⁷ In this polymer, different metal moieties can “chat” with each other allowing magnetic interactions and electronic communication.¹⁵ This permits electron movement along multidimensional polymer chains leading to the formation of conductive polymers. The cyano-substituent which is normally at the 4-position of the pyrazole ring is affected by other substituents at the 3- and 5-position. In 2000, Trofimenko first synthesized and published the Bp^{4CN} ligand with no substituent in the 3-, and 5 positions. Intractable polymer was formed, and the effect of the CN substituent was not yet known and fully explored.^{15,29}

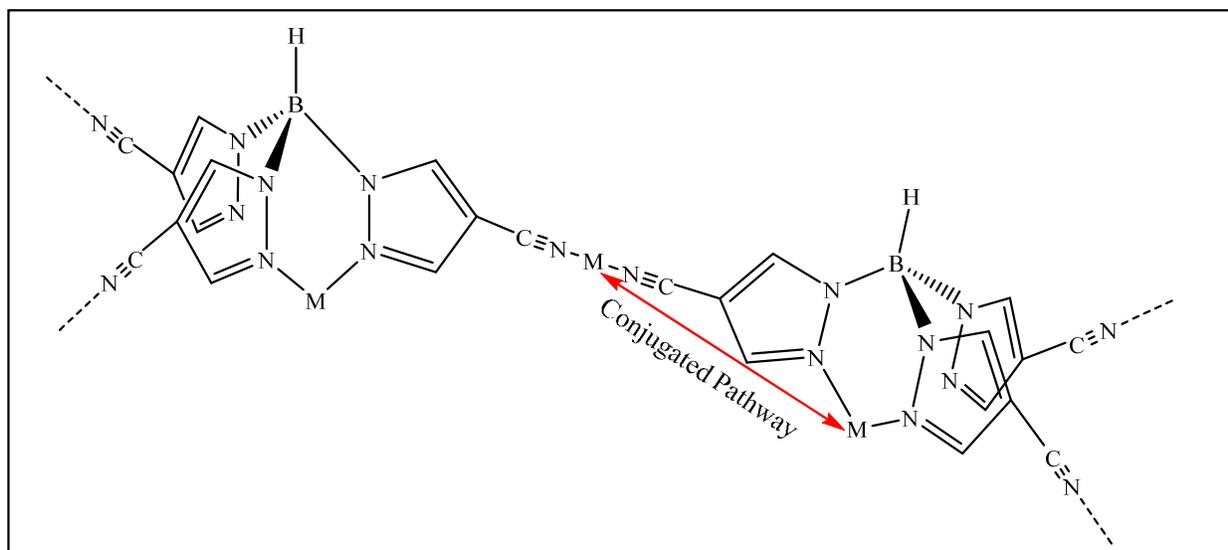


Fig 6: Cyano bridged coordination polymer of cyanoscorpionates via a conjugated pathway.¹⁵

Recent works by Eichorn et al focused on the $\text{Bp}^{4\text{CN}}$ ligand but with bulky alkyl substituent. They successfully synthesized the homoscorpionate complexes $(\text{Bp}^{\text{Ph},4\text{CN}})_2\text{Co}$ and $(\text{Bp}^{\text{Ph},4\text{CN}})_2\text{Cu}$.^{27,29} They then concluded that, the cyano substituent did not have a significant effect on the introduction of a bulky substituent on the 3- or 5- positions of the ligand, though the effect of the electron withdrawal properties of the cyano group on the ligand was not studied.²⁷ Other significant findings from the Eichhorn's group also confirmed the cyano-scorpionate polymer formation.^{28,29} Formation of a red precipitate after mixing $(\text{Bp}^{\text{Ph},4\text{CN}})_2\text{Co}$ with $\text{Rh}_2(\text{CF}_3\text{COO})_4$ in CH_2Cl_2 , which gave two infrared CN stretches at 2285 cm^{-1} and 2234 cm^{-1} and has a m/z of 761 peak in the mass spectrum.^{15,28,29} The two CN stretches indicate polymer formation and the coordination of the CN group to the Rh ion.^{15,29}

Siemer et al also synthesized a cyano-substituted hydrobis(pyrazolyl)borate complex, $\text{Bp}^{4\text{CN}}$, but were unable to isolate the monomeric homoleptic complex of the Bp ligand due to formation of polymeric species as a result of the cross-linked coordination between the cyano group and the metal of a neighboring $\text{M}(\text{Bp}^{4\text{CN}})$ complex.²⁹

The goal of this research is to synthesize and structurally characterize bis cyano-substituted scorpionate ligands with symmetric phenyl substituents at the 3- and 5-positions $(\text{Bp}^{\text{Ph}_2,4\text{CN}})$ and to synthesize their metal (Thallium) complex. This is more advantageous than the asymmetric substituents due to the fact that the symmetrical substitution provides protection of the B-H group and prevents ligand degradation; this also provides steric congestion due to rearrangement, as seen in asymmetric derivatives.³⁰

CHAPTER 2

METHODOLOGY

Materials and Methods

All reagents used in this research were obtained from Alfa Aesar, Fischer Scientific, Sigma-Aldrich, and Acros Organics which were used without further purification unless otherwise stated. Glassware used were cleaned by soaking them in a base bath, rinsed with distilled water and dried in an isotemp oven from Fischer Scientific. The base bath was prepared by a combination of potassium hydroxide (KOH) and a 2:1 isopropanol/water solution. Toluene was further dried by distilling over sodium lumps and benzophenone. Reduction of solvents under reduced pressure and mass measurements were carried out using a 19A BUCHI SWITZERLAND ROTAVAPOR RII and a METTLER TOLEDO PB403-S/FACT analytical balance respectively. NMR, FT-IR, GC-MS were the techniques used for structural elucidation and characterization of results. A SHIMADZU 1R PRESTIGE-21 FT-IR spectrometer was used in recording IR Spectra. ¹H NMR were conducted on 400MHZ JOEL-NMR Eclipse Spectrophotometer with a TMS standard. Singlet (s), doublet (d), and triplet (t) were the terms used to describe splitting patterns with chemical shifts reported in parts per million (ppm). GC-MS Spectra were recorded on a SHIMADZU GCMS-QP210 PLUS GC system spectrometer. Melting points were recorded with a MELTEMP 50/60 CYCLES melting point apparatus. Column Chromatography and Thin Layer Chromatography were conducted to purify products. A 100-200 mesh silica gel was used with a 3:1 Dichloromethane (DCM)/Hexane mixture as the solvent. Silica active TLC plates were used for TLC and spots viewed with a 254nm UV lamp.

Bp^{Ph₂,4CN} Ligand

The Bp^{Ph₂,4CN} was first reported by Trofimenko and has been synthesized by Eichhorn et al. Though after synthesizing both the Bp^{t-butyl,4CN} and Bp^{Ph,4CN} ligands and successfully complexing with a metal, they concluded that the bulky nature of the tert-butyl tend to push the metal further away from the nitrogen therefore increasing the bond length but that wasn't seen in the Bp^{Ph,4CN} ligand as the less bulky phenyl group (as compared to tert-butyl) did not sterically hinder the complexation of the metal to the nitrogen hence resulting in a shorter bond length. However, in order to study very well the effects of the bulky substituents on the electronic properties of the ligand, we decided to increase the phenyl group substituent on the pyrazole ring hence the synthesis of the Bp^{Ph₂,4CN} ligand, which seeks to broaden our understanding on the effects of both di-substituted and tri-substituted poly(Pyrazolyl)borates ligands on the magnetic and electronic properties of the ligands and their contribution to the ligand metal bond distances as well as their ability to form coordination polymers.

The Bp^{Ph₂,4CN} has never been reported and synthesized though its analogous Tp ligand has been successfully reported, synthesized and structurally characterized using the X-ray diffractometer after complexation with Thallium (I) metal. Thallium (I) metal is larger and very stable due to inert pair effect and should be easily crystallized as compared to other metals. The starting material which is the pyrazole (Hpz^{Ph₂,4CN}) was previously synthesized with a technique which was toxic and explosive. Hence, a modified version courtesy Bray and Tupper as described by Zhao¹⁵ was used. The general scheme for the synthesis of the Bp^{Ph₂,4CN} is shown in Fig 7.

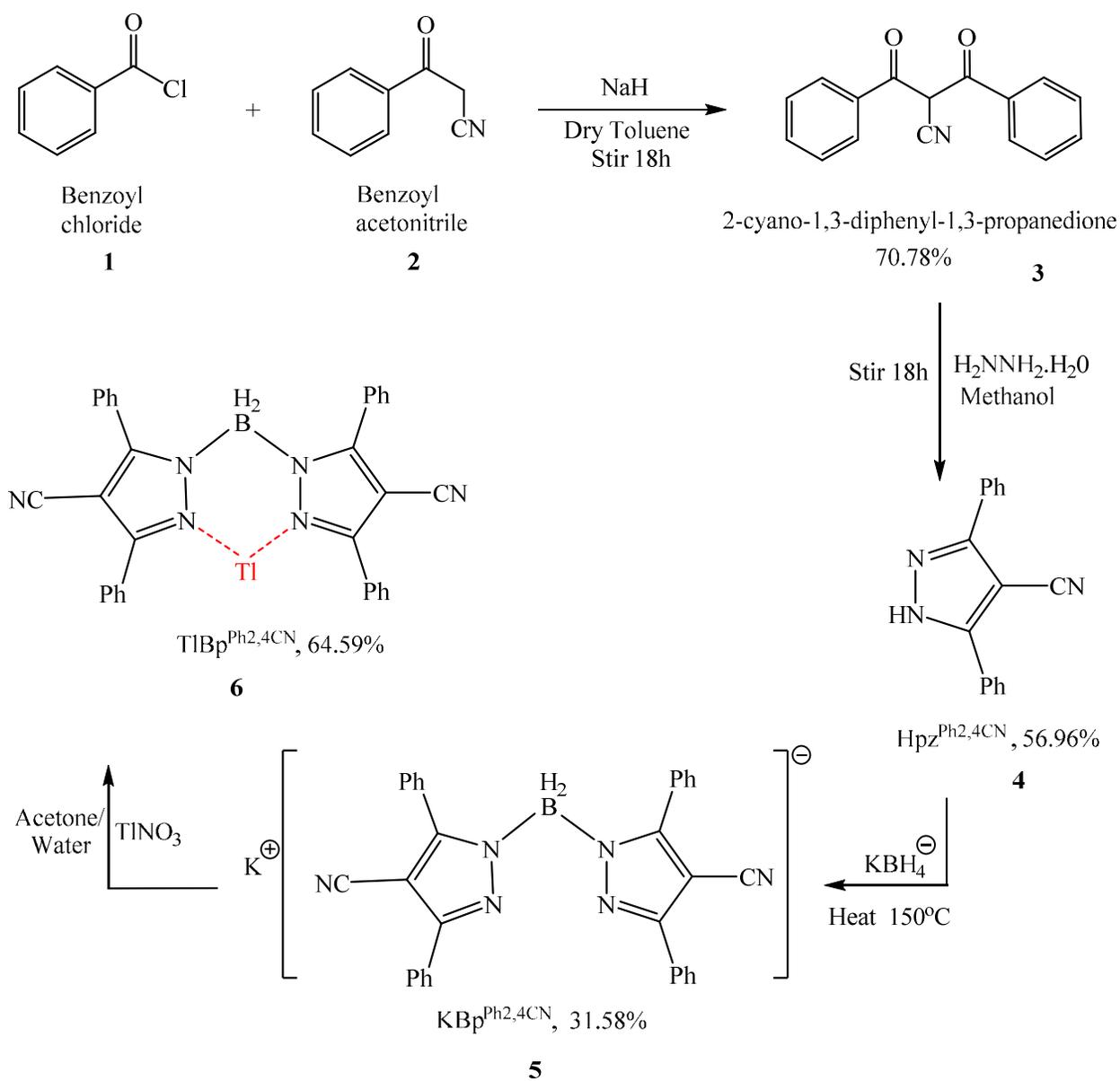


Figure 7: General scheme for the synthesis of Bp^{Ph₂,4CN} ligand (Ph = Phenyl)

Synthesis of 4-cyano-3,5-diphenylpyrazole (Hpz^{Ph₂,4CN}) (4)

Sodium hydride (0.690 g, 0.01724 mole), as 60% dispersion in mineral oil, was suspended in 100ml dry toluene. Benzoylacetoneitrile (2.500 g, 0.01724 mole) was then added to

the suspension which resulted in the immediate appearance of small bubbles. The solution was placed under nitrogen, cooled in ice bath and stirred for 18 hours, forming a cloudy solution. Benzoyl chloride (2.420 g, 0.0172 mole) was added dropwise to the solution and stirred overnight resulting in a yellowish solution. The solution was then transferred into a separatory funnel and extracted three times with 3x100 mL of 0.2 M sodium hydroxide. The aqueous layers were combined and neutralized with 6 M HCl. The acidified solution was re transferred to the separatory funnel and extracted with three portions of 100 mL of ethyl acetate. The combined yellow organic layer was dried over anhydrous magnesium sulphate, then evaporated under reduced pressure on a rotary evaporator to yield 3.500 g of the crude product. The product was recrystallized from ethanol to give 3.027g (70% yield) of yellowish crystals, 2-cyano-1,3-diphenyl-1,3-propanedione, **3**.

The recrystallized **3** (3.027 g, 0.01216 mole) was stirred over night with hydrazine monohydrate (0.609 g, 0.0121 mole) in 100 mL of methanol. The solution was concentrated to 25 mL under reduced pressure and chromatographed on a 100-200 mesh silica gel column, using 3:1 dichloromethane/hexane mixture as an eluent. Several fractions were collected and TLC showed the first 10 fractions to have one spot with identical R_f value. These fractions were combined and the solvent was evaporated under reduced pressure. The solid product was recrystallized from ethanol to give 1.697 g (56% yield) , 4-cyano-3,5-diphenylpyrazole (**4**), as yellowish crystals. M.p. 130 °C. $^1\text{H NMR}$ (DMSO- d_6), δ : 7.90 (d,4H), 7.67 (t,2H), and 7.57 (t,4H). FT-IR (cm^{-1}): 3300 cm^{-1} (N-H Stretch) and 2210 cm^{-1} ($\text{C}\equiv\text{N}$ stretch). GC-MS (m/z): 245 and 77.

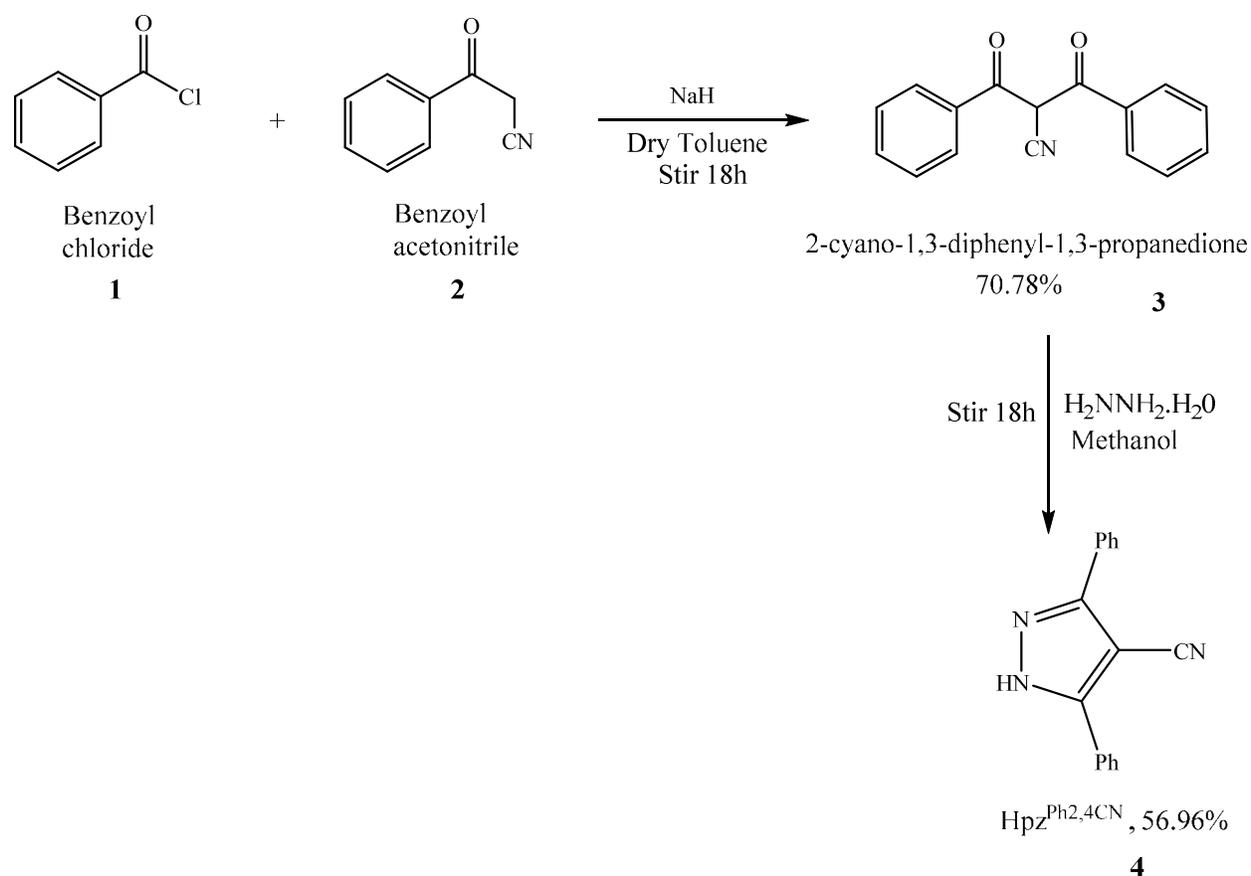


Figure 8: Scheme for the synthesis of 4-cyano-3,5-diphenylpyrazole (Hpz^{Ph2,4CN}) complex.

Synthesis of Potassium bis (4-cyano-3,5-diphenylpyrazole)borate (KBp^{Ph2,4CN}) (**5**)

Compound **4** (1.042 g, 0.00425 mole) was reacted with 0.5 equivalent of potassium borohydride (0.114 g, 0.002125 mole) in a round bottom flask fitted with a reflux condenser. The mixture was stirred and heated gradually in an oil bath to 150 °C for 1 hour. The reaction mixture began to melt at 130°C, giving off hydrogen gas, and completely melted at 150 °C after 1 hour. The melted pyrazole/potassium borohydride mixture was allowed to cool at room temperature for 45 min to form solid. The solid was dissolved in acetonitrile (50 mL) and

filtered to remove any excess KBH_4 . The solvent was evaporated under reduced pressure and the residue was washed (trituated) with toluene (10 mL) to remove any unreacted pyrazole.

Filtration and drying gave a dark yellow powder of potassium bis (4-cyano-3,5-diphenylpyrazole)borate ($\text{KBp}^{\text{Ph}_2,4\text{CN}}$), **5** (0.525 g, 31% yield). M.p: 240 °C, ^1H NMR: 8.07 ppm (d,8H), 7.65 ppm (t,4H), 7.55 ppm (t,8H). FT-IR, cm^{-1} : 2350 and 2250, representing the B-H and $\text{C}\equiv\text{N}$ bonds, respectively.

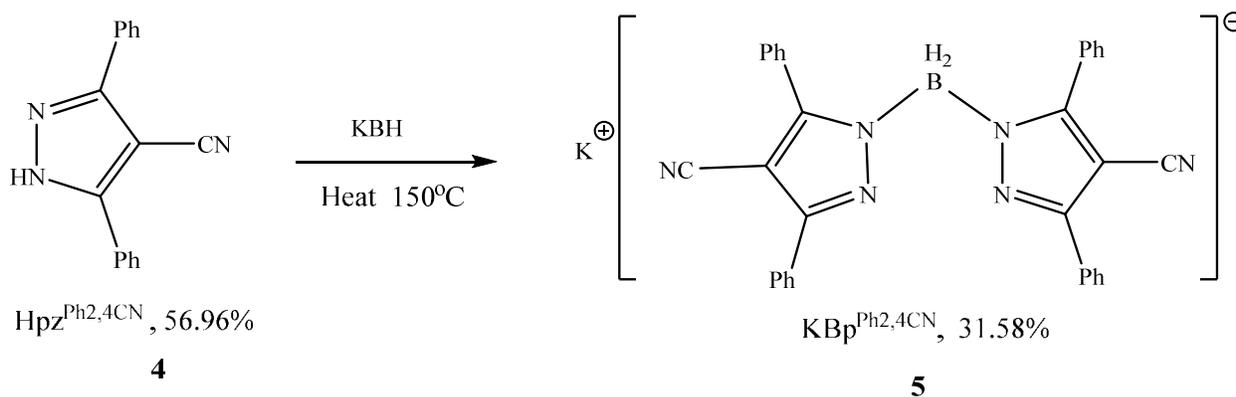


Figure 9: Scheme for the synthesis of potassium bis(4-cyano-3,5-diphenylpyrazole)borate ($\text{KBp}^{\text{Ph}_2,4\text{CN}}$), **5**.

Synthesis of Thallium bis (4-cyano-3,5-diphenylpyrazolyl) borate ($\text{TlBp}^{\text{Ph}_2,4\text{CN}}$), **6**

Compound **5** (0.425 g, 0.00084 mole) was dissolved in 20 mL of acetone. The solution was then added to TlNO_3 (0.220 g, 0.00084 mole) dissolved in 20 mL of 50/50 (v/v) of water/acetone. After stirring for 1 hour the solvent was evaporated under reduced pressure. The yellow solid residue was washed with water (20 mL) to remove any unreacted TlNO_3 , then dried. A lightly yellow powder, **6** (0.385 g, 64%) was obtained. M.p: 280 °C, ^1H NMR, δ : 7.95 (d,8H),

7.72 (t,8H), 7.61 (t,4H). FT-IR, cm^{-1} : 2350 and 2220, confirming the presence of both B-H and $\text{C}\equiv\text{N}$ bonds, respectively.

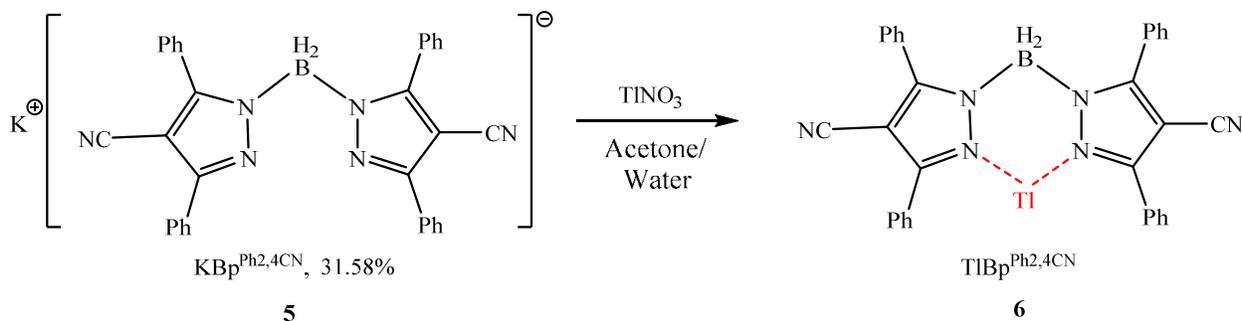


Figure 10: Scheme for the synthesis of thallium bis (4-cyano-3,5-diphenylpyrazolyl) borate $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$, **6**

Growing of thallium bis (4-cyano-3,5-diphenylpyrazolyl) borate $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ crystals

X-Ray quality crystals can be grown with different techniques including slow evaporation and liquid-liquid diffusion. Both techniques were attempted, but at least in our hands, the latter seems to give better quality crystals. A typical recrystallization involved layering a saturated solution of ligand (**5**) in acetone over a saturated solution of TlNO_3 in 50/50 (v/v) water/acetone in a test tube covered with paraffin film. This was repeated with different concentrations of ligand: 1/4, 1/8, 1/16, 1/20 of the original solution in acetone. The layered solutions were kept in a cool dry place for a month. The tubes were opened after the first two weeks when crystals start to grow in order to expedite crystal growth. An illustration of the crystallization technique is shown in Fig 11.

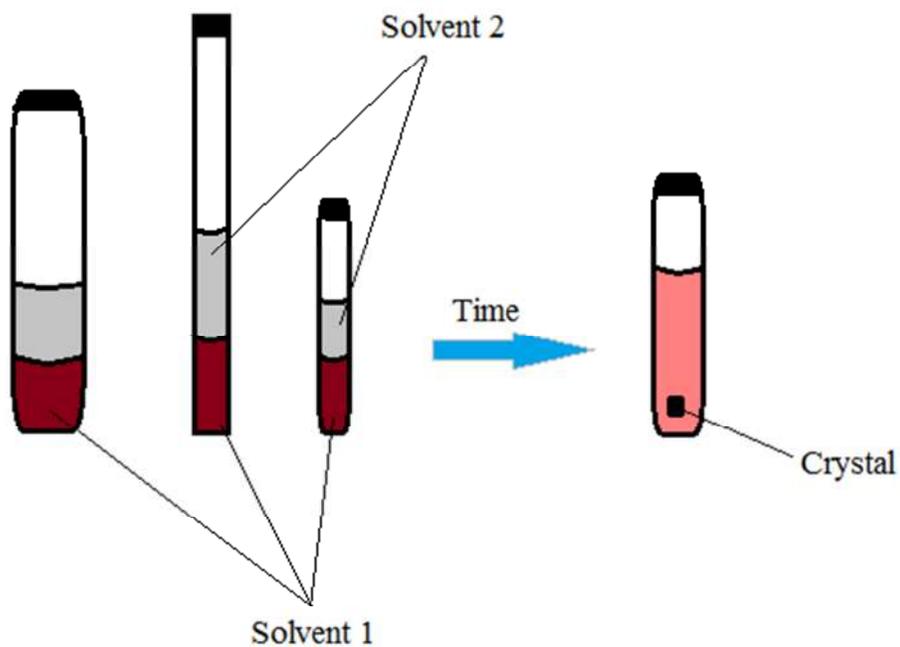


Figure 11: Layering crystallization (or liquid-liquid diffusion) technique for crystal growth³¹

‘Image modified from’

http://www.chemistryviews.org/details/education/2538941/Tips_and_Tricks_for_the_Lab_Growing_Crystals_Part_3.html.³¹

Solvent 1 contains TlNO_3 in 50/50 acetone/water while solvent 2 contains $\text{KBp}^{\text{Ph}_2,4\text{CN}}$ in acetone.

CHAPTER 3

RESULTS AND DISCUSSION

Various cyano-substituted pyrazolyl derivatives have been synthesized for potential applications in catalysis, bioinorganic and organic chemistry. In this research we successfully synthesized $\text{Bp}^{\text{Ph}_2,4\text{CN}}$ and its thallium (I) complex, $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$. Our attempts to grow x-ray quality crystals were promising but the diffraction results were inconclusive. As a result, we were not able to obtain acceptable X-ray crystal structures of such complexes. The synthesized compounds were purified by utilizing a combination of column chromatography and recrystallization; and their structures were elucidated by NMR, FT-IR and GC-MS.

4-cyano-3,5-diphenylpyrazole, $\text{Hpz}^{\text{Ph}_2,4\text{CN}}$, **4**

This compound was synthesized using the reported method in figure 8. Benzoyl chloride and benzoylacetone were reacted in dry toluene in the presence of sodium hydride as a base to deprotonate the benzoylacetone, to form 2-cyano-1,3-diphenyl-1,3-propanedione,**3** in good yield. This was further reacted with hydrazine to form the substituted pyrazole product. The lightly yellow crude product was recrystallized from ethanol, to give 70% yield of **4** with a melting point of 150 °C. FT-IR gave two characteristic absorptions at 3300 cm^{-1} (for N-H bond) and at 2210 cm^{-1} (for $\text{C}\equiv\text{N}$ bond). This is consistent with the pyrazole being substituted with $\text{C}\equiv\text{N}$.³² GC-MS also confirmed the structure of compound **4** as indicated by m/z peak of 245 and a phenyl cation fragment peak of 77. ¹H NMR spectrum of **4** gave three peaks, a doublet and two triplets in the chemical shift range of 8-7.5 ppm, corresponding to the hydrogens (protons) in the aromatic phenyl group. Individual peak integration showed a ratio of 2:1:2 for

the protons in the aromatic region for the ortho, para and meta protons of the phenyl group, appearing at 7.90 ppm (d,4H), 7.67 ppm (t,2H) and 7.57 ppm (t,4H), respectively. The down field shift of the ortho protons is attributed to the fact that they are highly deshielded by the nearby electron withdrawing cyano group. The meta and para protons, however, are less deshielded than the ortho protons, thus their signals appear relatively upfield. The signal of the amino group proton was not observed since it undergoes deuterium exchange with the solvent. The peak at 3.7 ppm is due to water impurities in DMSO-d₆. (Refer to spectra in **appendix A, B, C1 and C2**).

Potassium bis (4-cyano-3,5-diphenylpyrazolyl)borate, KBp^{Ph₂,4CN} .5

KBp^{Ph₂,4CN} scorpionate was synthesized according to the general scheme shown in Fig 9 . A portion of pyrazole **4** was heated with KBH₄ in a 2:1 ratio to a melting temperature without use of solvent. Upon melting in the range of 130 -150 °C, the reaction proceeded by giving off hydrogen gas. Slight excess of pyrazole **4** was used to ensure complete reaction of KBH₄. FT-IR spectra of the compound (**5**) shows B-H stretch at 2350 cm⁻¹ and C≡N stretch at 2250 cm⁻¹. The B-H stretching frequency of compound **5** was slightly lower than those of other analogous (KBp^{Ph₂,4CN}) observed by Eichhorn et al (Table 3). This is as a result of the introduction of another bulky phenyl substituent on 5-position of the pyrazole ring as well as the presence of the strongly electron withdrawing cyano group. This attributes to weakening of the B-H bond lowering its stretching frequency. The absence of the N-H absorption indicates the bonding of two pyrazole rings to boron. ¹H NMR of spectrum of (**5**) showed three peaks in 7.5 - 8.1 ppm range, doublet and two triplets, which correspond to the protons on the aromatic groups. The singlet at 7.25 ppm is the chloroform-d solvent peak. Individual peak integration gave a ratio of

4:2:4 for the aromatic protons due to the highly symmetrical nature of compound. The eight ortho protons of the phenyl groups gave a doublet at 8.07 ppm. The other two triplets at 7.55 ppm and 7.60 ppm represent the para (4H) and the meta (8H) protons, respectively. These are shifted upfield compared to the ortho protons due to the fact that they are less deshielded. (Refer to spectra in **appendix D, E1 and E2**).

Table 3: Comparison of B-H and C≡N stretches of different synthesized Bp Ligand.

Compound	B-H (cm ⁻¹)	C≡N (cm ⁻¹)	Reference
KBp ^{Ph₂,4CN}	2350	2250	This work
KBp ^{Ph,4CN}	2421	2225	27

Thallium bis(4-cyano-3,5-diphenylpyrazolyl)borates, TIBp^{Ph₂,4CN} **6**

The choice of thallium (I) metal is due to its ability to form generally stable complexes due to its inert pair effect (oxidation state that are two less than the group oxidation) and for its relatively low price. Furthermore, most thallium based pyrazole complexes are widely employed in ligand exchange reactions,³³ and have potential applications in catalysis. Since ligand **5** is insoluble in water, it has to be dissolved in acetone during complexation reaction with TlNO₃. After work up, the thallium complex, TIBp^{Ph₂,4CN} **6** was obtained in good yield (64%). FT-IR spectrum of **6** shows the B-H stretch at 2350 cm⁻¹ and the C≡N stretch at 2210 cm⁻¹. We also noticed a C=O stretch at 1600 cm⁻¹, apparently coming from trace amount of acetone. Although the B-H stretch remained unchanged from the FT-IR of starting material **5**, there was a slight change in the C≡N stretch as it shifted from 2250 cm⁻¹ to 2220 cm⁻¹. This may be attributed to the change in the molecular geometry of the complex and to the ionic radii differences of

thallium (I) metal ion due to possible complexation. ^1H NMR gave three peaks, a doublet and two triplets at chemical shifts of 7.95 ppm, 7.72 ppm, and 7.61 ppm, corresponding to the ortho (d,8H), para (t,4H) and meta (t,8H) protons of the phenyl groups, respectively. (Refer to spectra in **appendix F, G1** and **G2**). However, the NMR and FT-IR results does not indicate a successful complexation and position of complexation of the thallium metal to the $\text{Bp}^{\text{Ph}_2,4\text{CN}}$ ligand though the melting points are different; thus the structure of the $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ complex is left open.

Thallium bis(4-cyano-3,5-diphenylpyrazolyl)borates, $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ (**6**) crystals

X-ray quality crystals were grown using the layering or liquid-liquid diffusion technique. Although we tried other techniques such as slow evaporation, the liquid-liquid diffusion technique proved to be the most effective. Slow crystallization, over a month period, provided shiny colorless crystals. Structural characterization of the compound **6** crystals by X-ray crystallography proved inconclusive as the data obtained from the X-ray indicated an unsuccessful crystallization. The X-ray crystallographic data obtained for our harvested crystals was similar to that of TlNO_3 crystals suggesting that our Bp ligand couldn't crystallize hence an unsuccessful complexation of the Tl metal to the Bp ligand. Melting point of the crystals gave $206\text{ }^\circ\text{C}$ which was similar to the theoretical melting point of TlNO_3 which is $207\text{ }^\circ\text{C}$. This however confirmed that the crystals isolated or harvested were indeed TlNO_3 crystals and not our $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ complex.

CHAPTER 4

CONCLUSION

Since their initial discovery by Trofimenko, the scorpionates have attracted significant interest due to their versatile applications in various fields. We succeeded to synthesize substituted pyrazole derivatives that vary in their functionalities. This opened a new way that may lead to future investigation into how new scorpionate ligands can be synthesized and how their electronic properties can be modified. Cyanoscorpionates have become very valuable in modern inorganic chemistry for their ability to form transition metal complexes and fully conjugated coordination polymers.

In this work, we successfully synthesized new cyanoscorpionate ligands, 4-cyano-3,5-diphenylpyrazole, $\text{Hpz}^{\text{Ph}_2,4\text{CN}}$, bis(4-cyano-3,5-diphenylpyrazolyl)borate, $\text{Bp}^{\text{Ph}_2,4\text{CN}}$ and their thallium (I) complex. These were synthesized by modifying literature procedures. Thallium (I) complex of $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ was synthesized and crystallized using the layering liquid-liquid diffusion technique. Structural determination of the thallium complexes of the new scorpionates by X-ray crystallography is in progress; however initial attempts were inconclusive due to poor diffraction of the crystals. Further attempts also proved unsuccessful as it was established that the isolated crystals was however TlNO_3 crystals instead of our $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ complex.

Future work would involve further attempts to resolve the structures of thallium complexes of the newly synthesized ligands by X-ray. We also will seek to improve the synthesis of cyanoscorpionates by optimizing reaction conditions to improve reactions yield; and to prepare coordination polymers involving cyanoscorpionates as well as ways to successfully grow $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ crystals.

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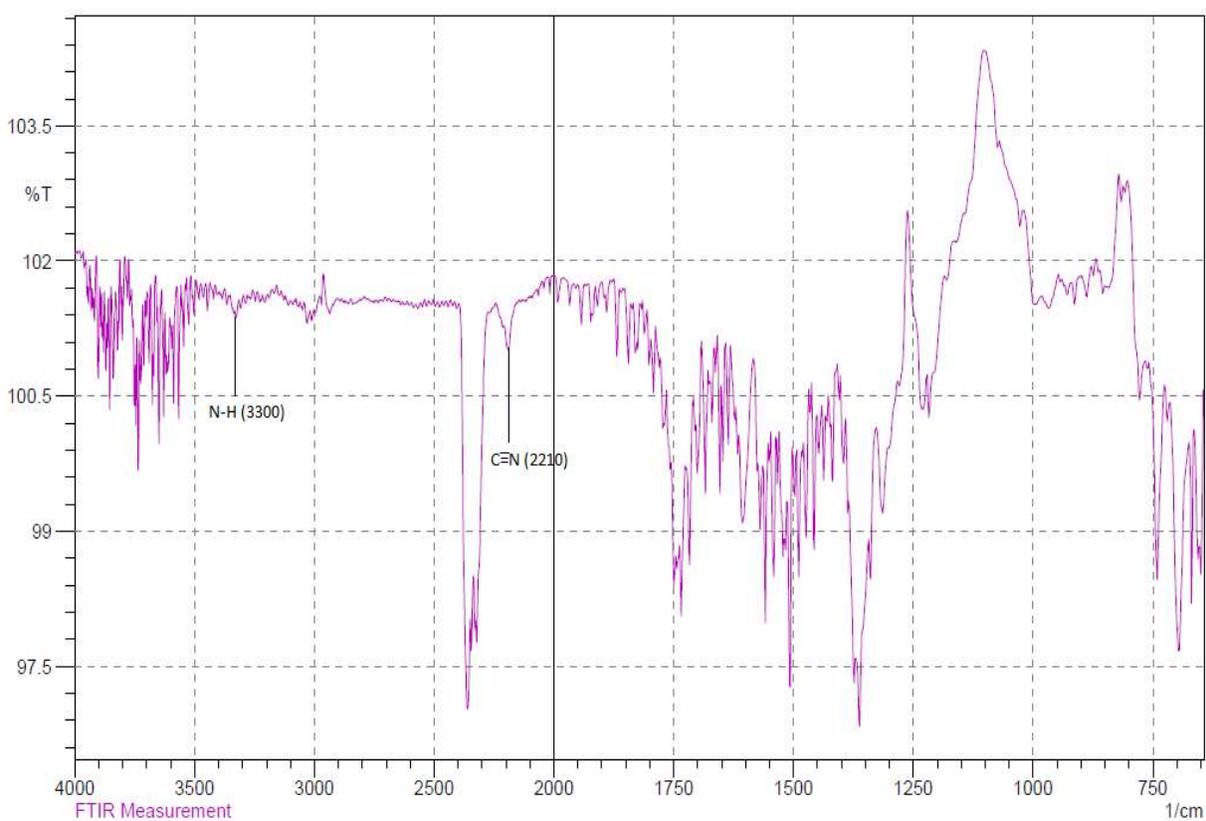
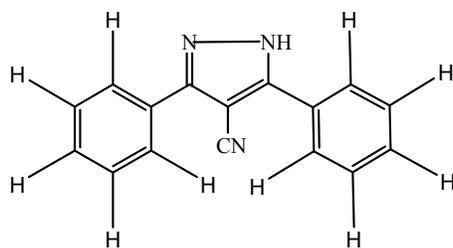
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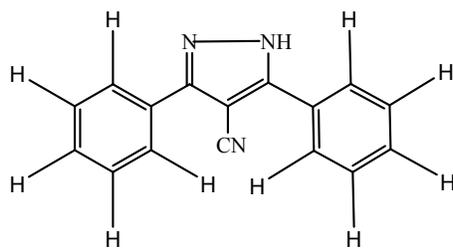
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APPENDICES

Appendix A: FT-IR spectrum of Hpz^{Ph₂,4CN} (4)



Appendix B: Mass spectrum of Hpz^{Ph2,4CN} (4)



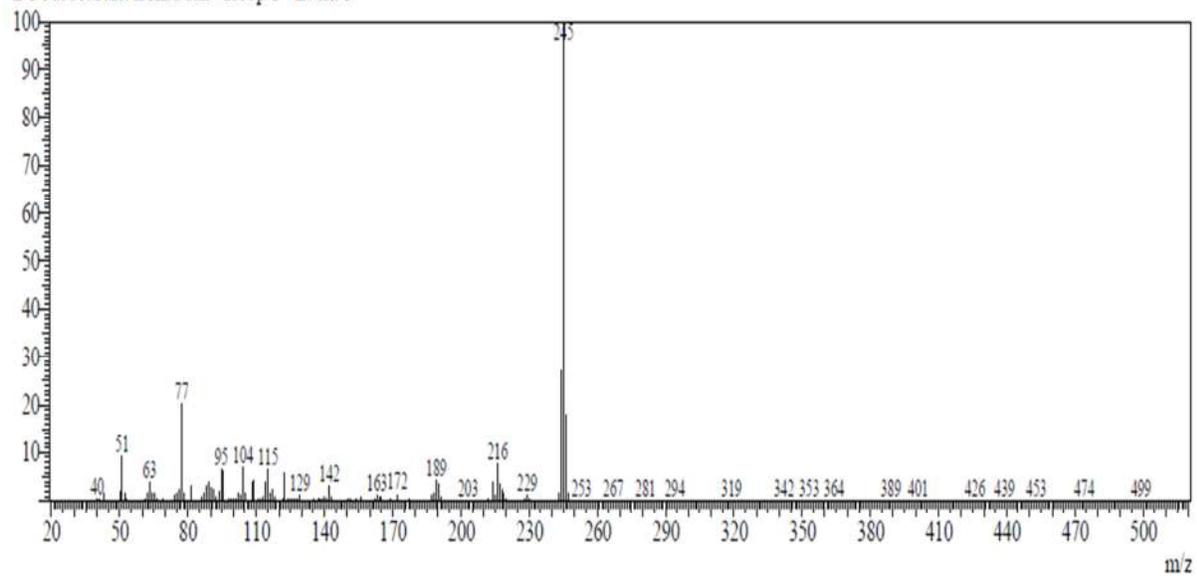
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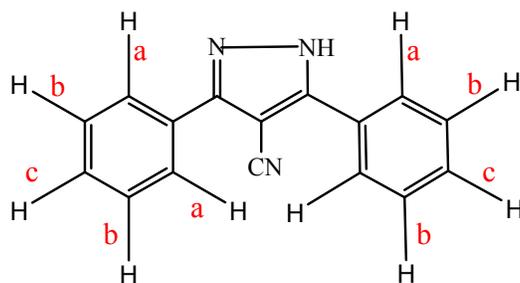
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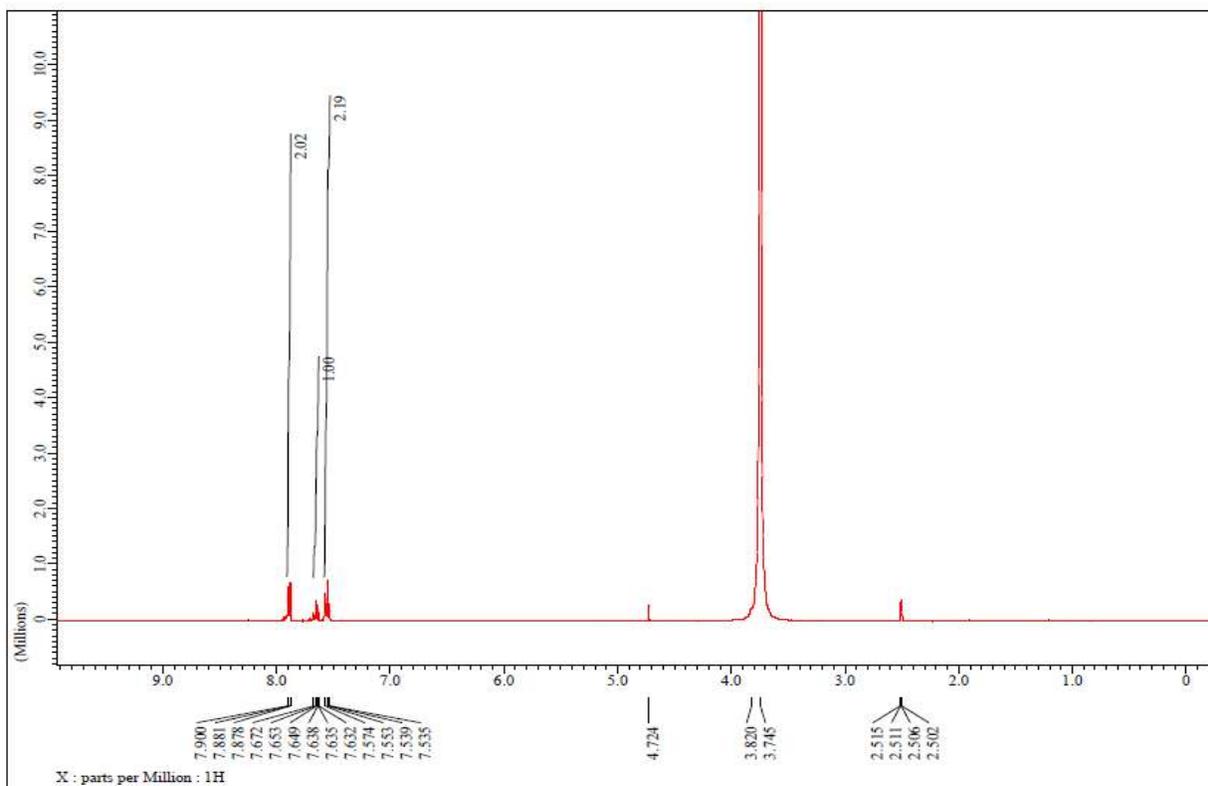
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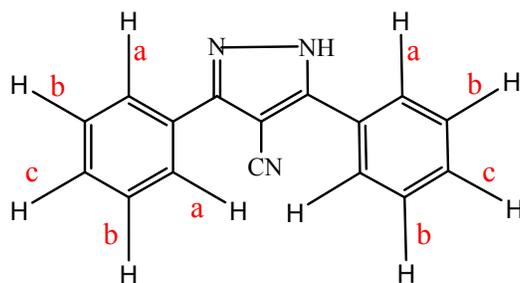
Appendix C1 : ^1H NMR spectrum of $\text{Hpz}^{\text{Ph}_2,4\text{CN}}$ (**4**) (DMSO-d₆)



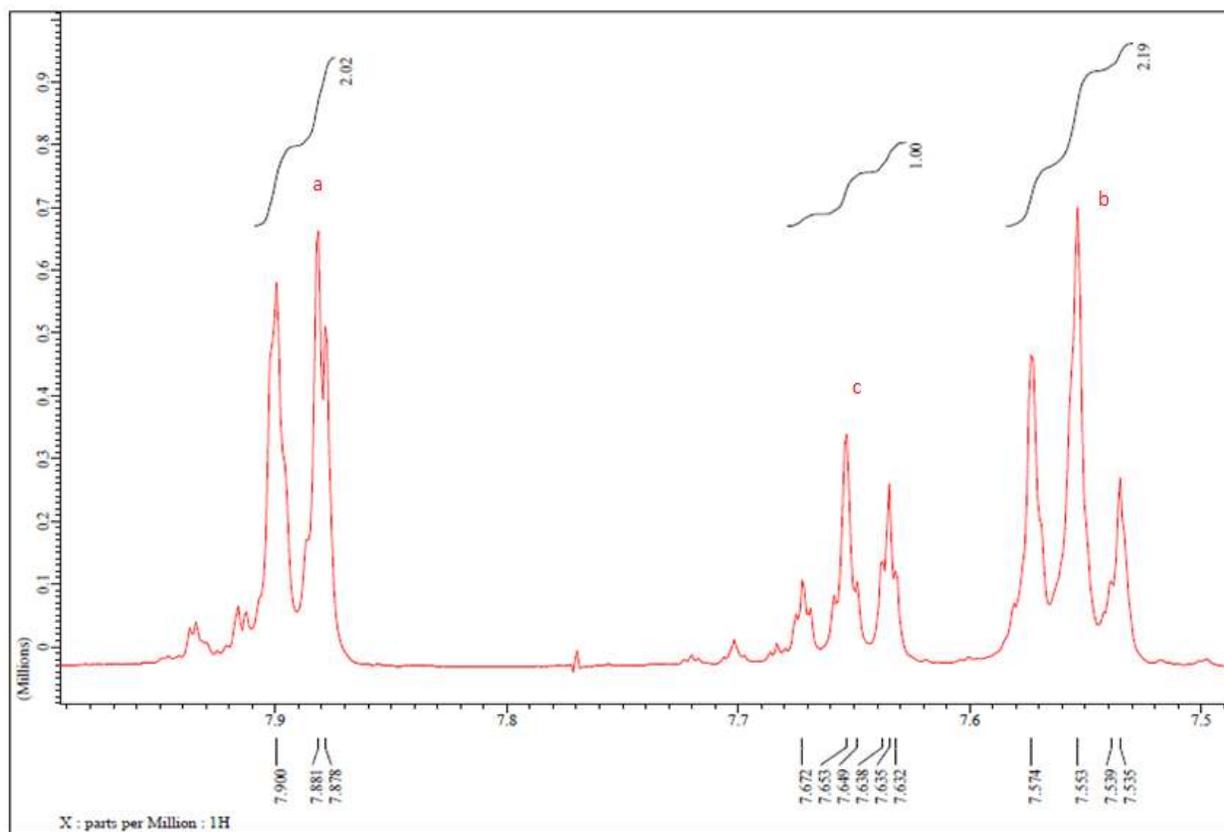
a = ortho, b = para, & c = meta protons



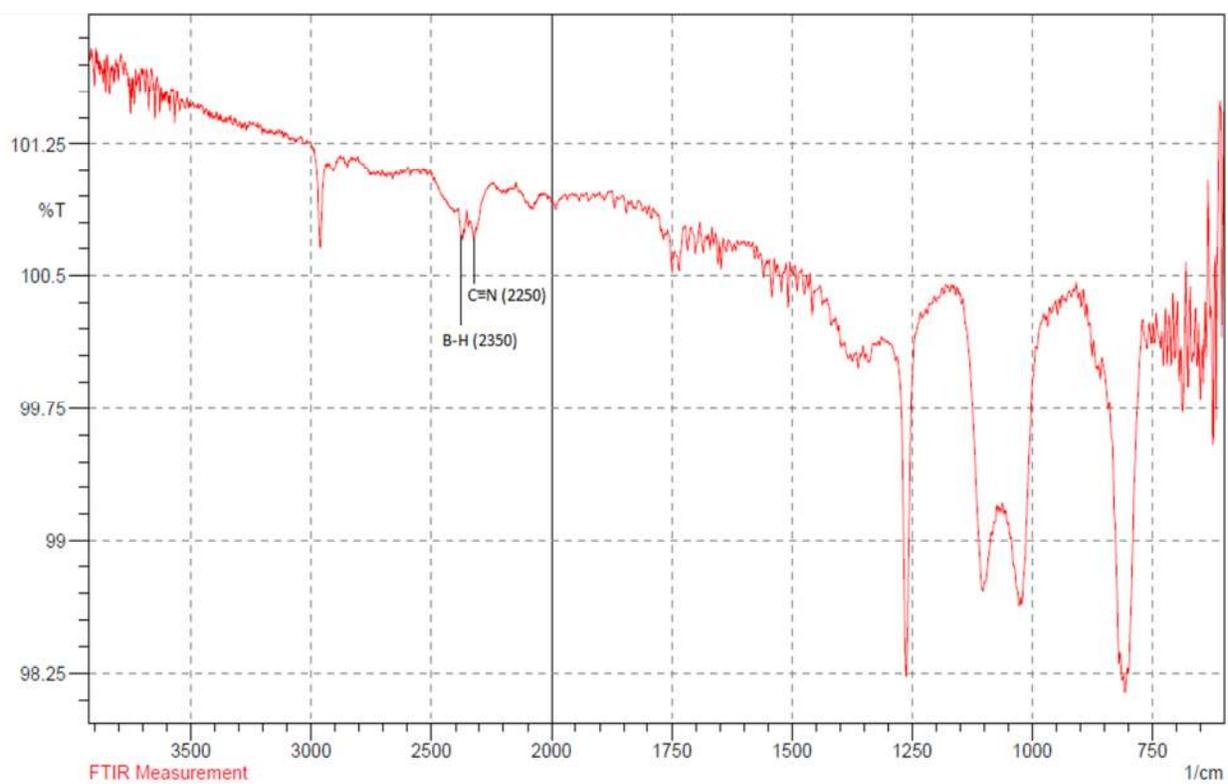
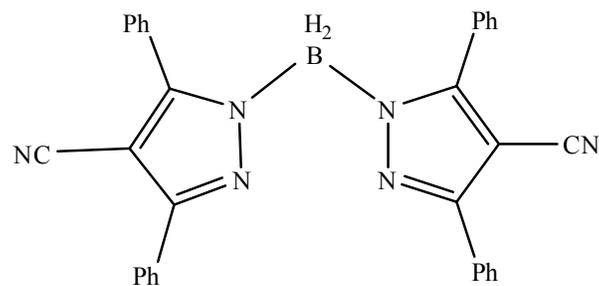
Appendix C2: Extended ^1H NMR spectrum of $\text{Hpz}^{\text{Ph}_2,4\text{CN}}$ (**4**) (DMSO- d_6)



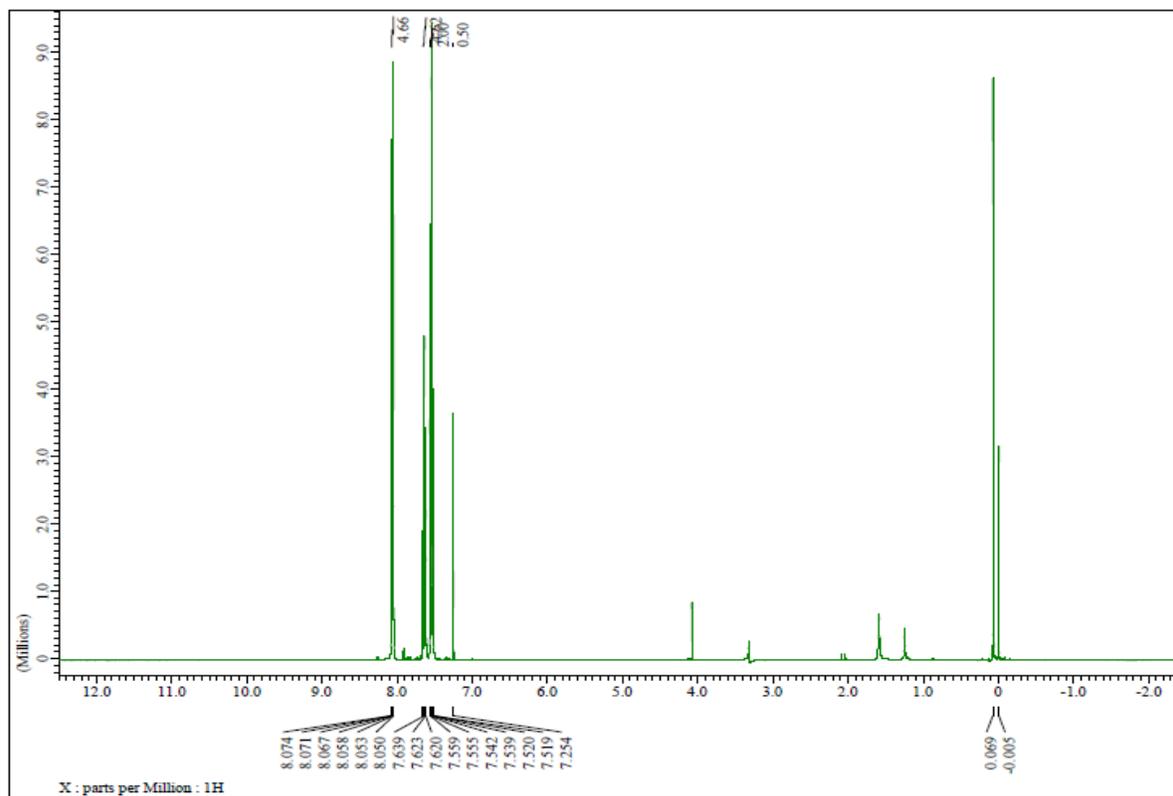
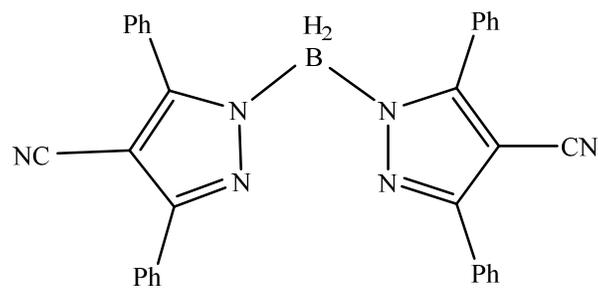
a = ortho, b = para, & c = meta protons



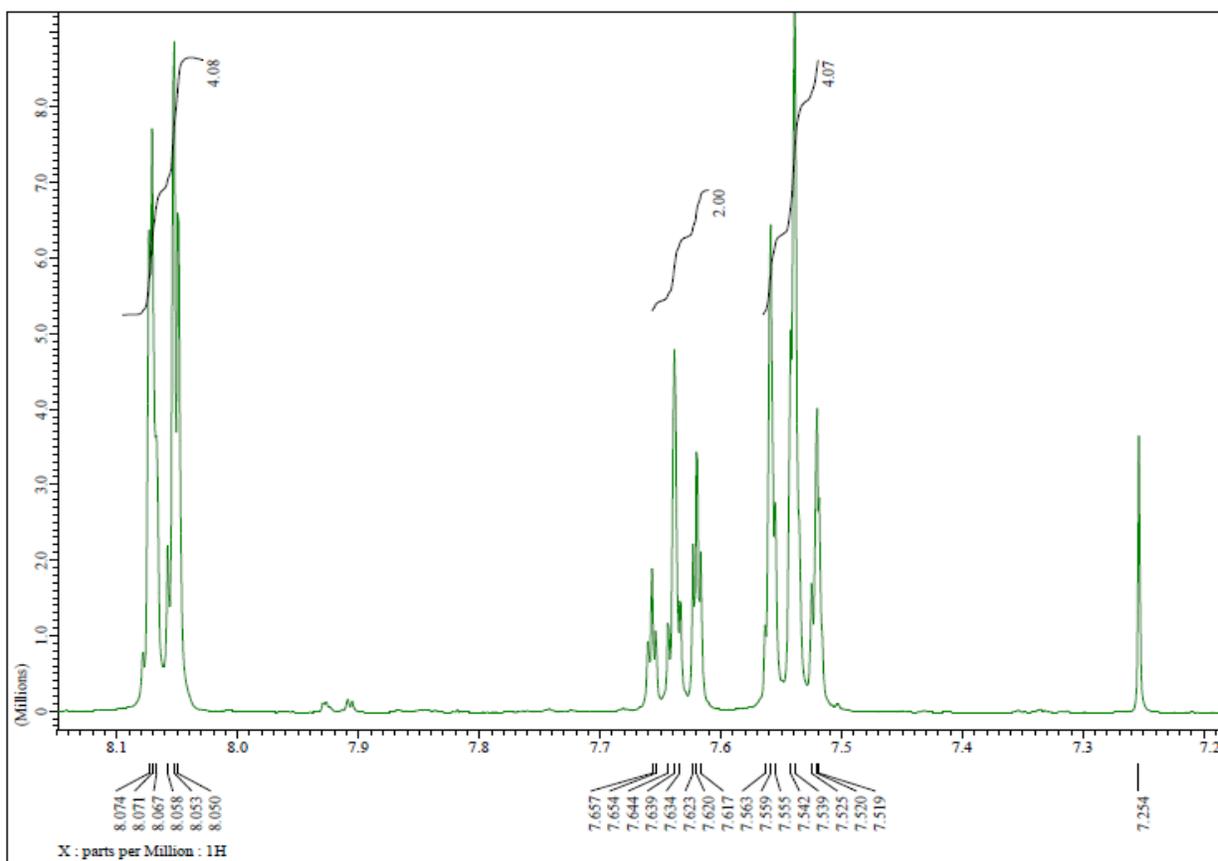
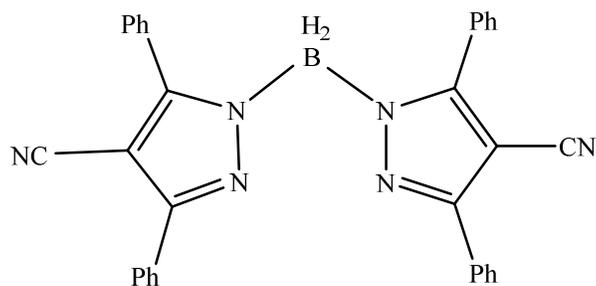
Appendix D: FT-IR spectrum of Bp^{Ph₂,4CN} (**5**)



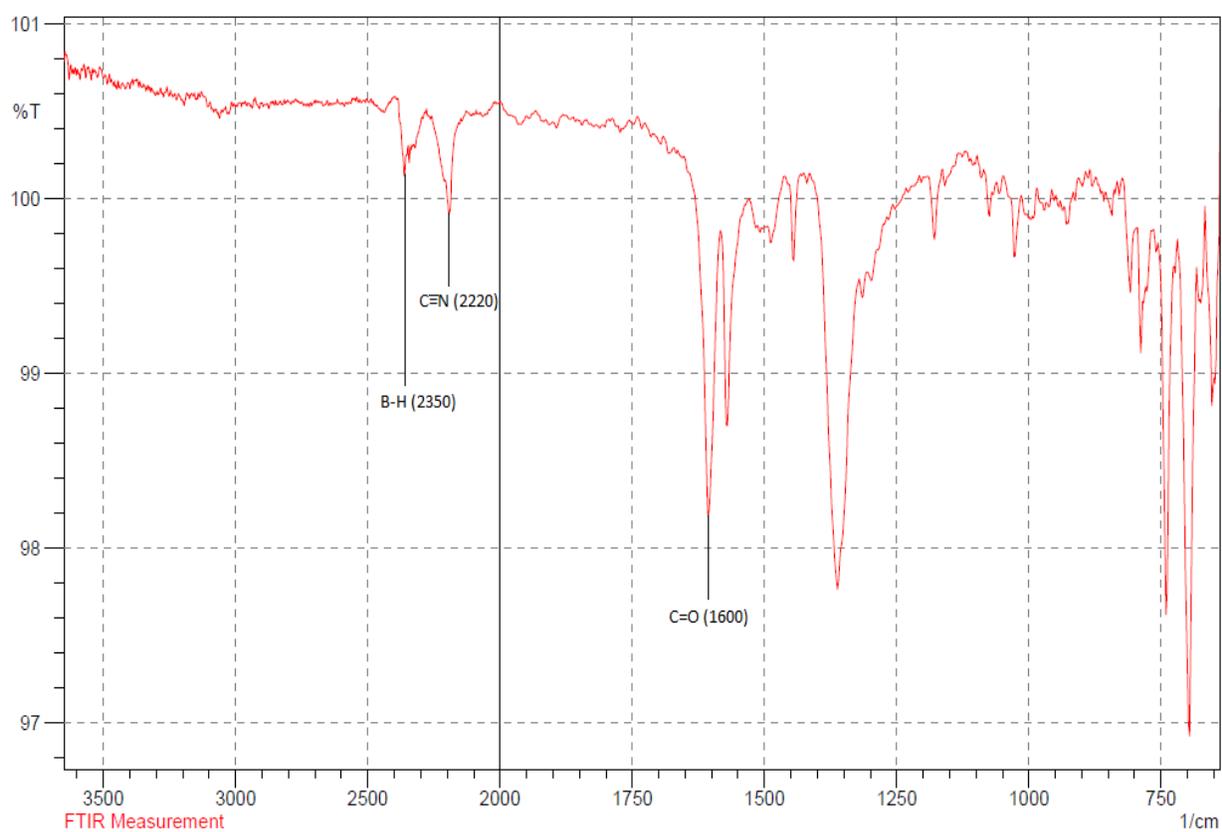
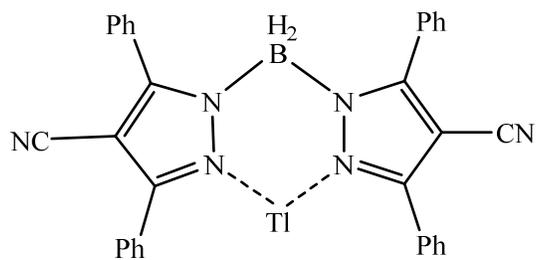
Appendix E1: ^1H NMR spectrum of $\text{KBp}^{\text{Ph}_2,4\text{CN}}$ (**5**) (Chloroform-d)



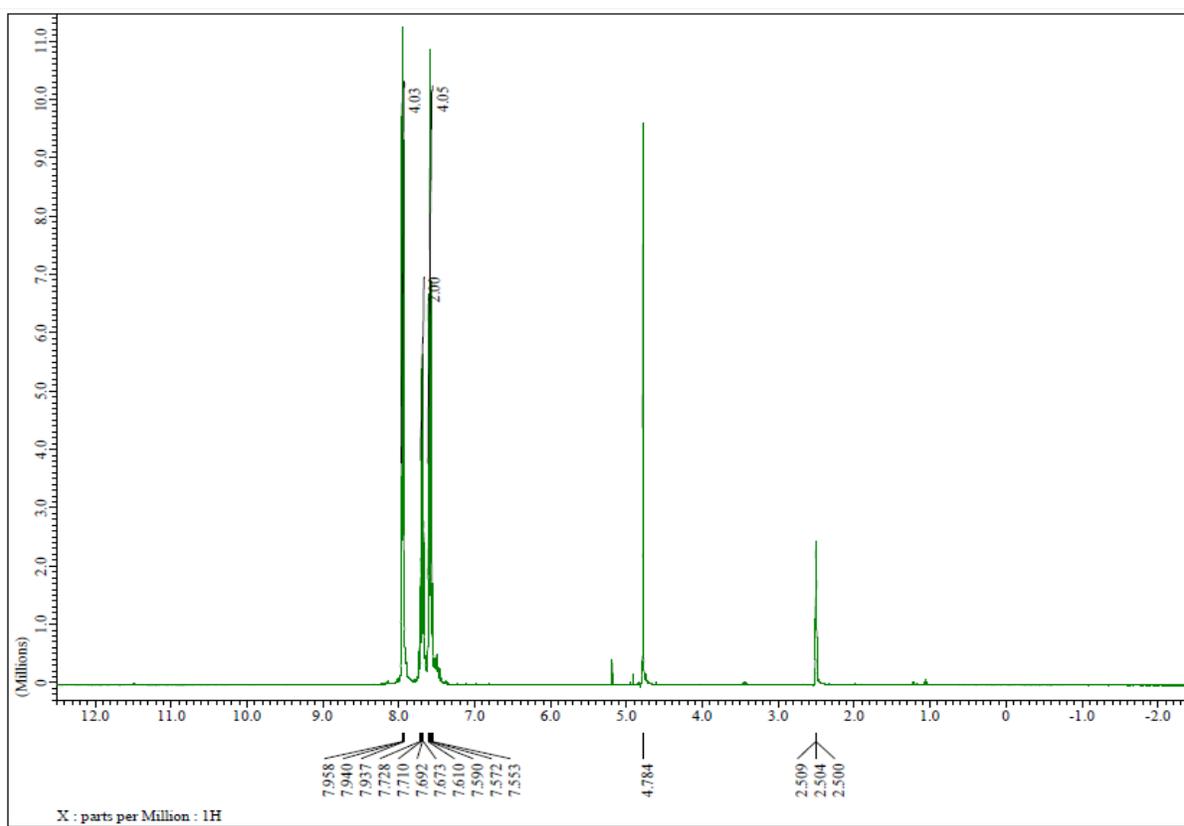
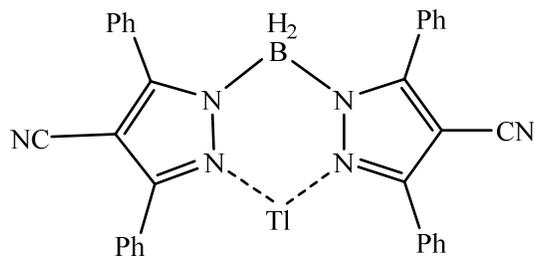
Appendix E2: Extended ^1H NMR spectrum of $\text{Bp}^{\text{Ph}_2,4\text{CN}}$ (**5**) (Chloroform-d)



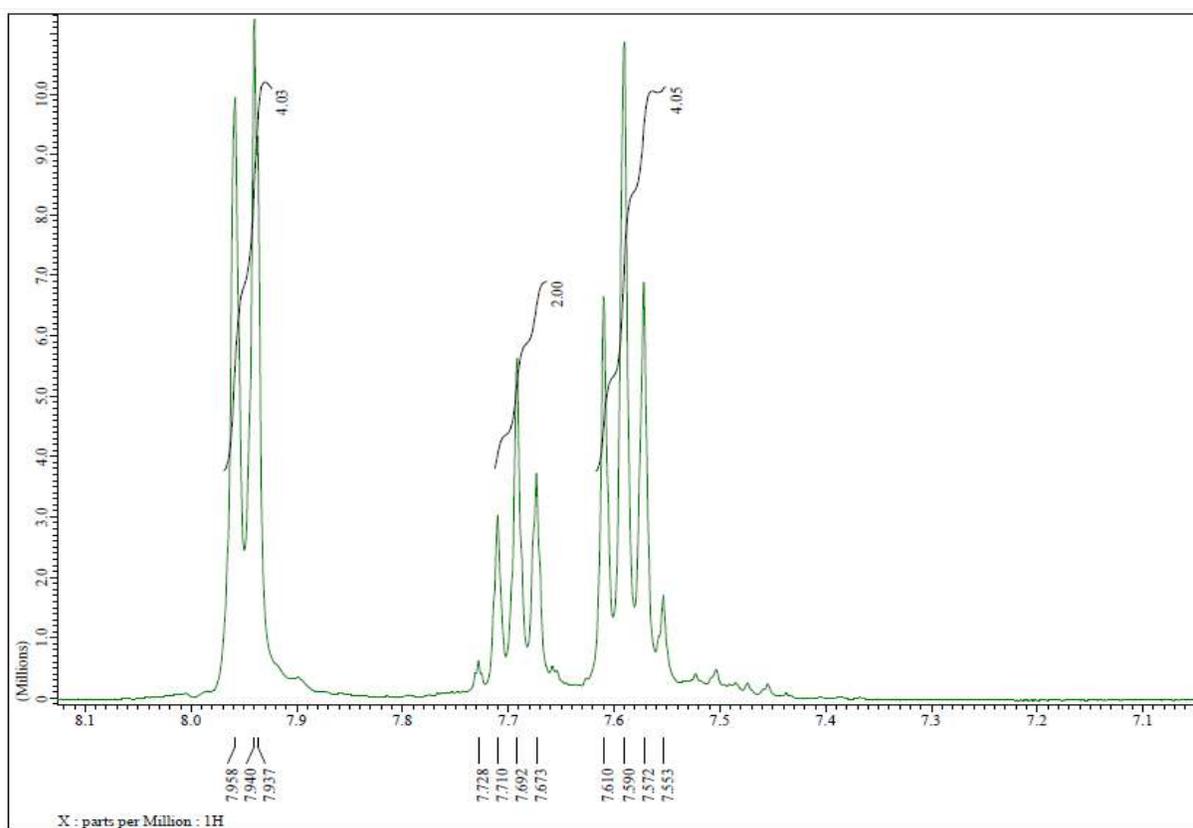
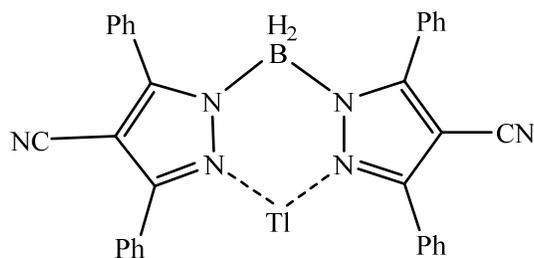
Appendix F: FT-IR spectrum of $\text{TlBp}^{\text{Ph}_2,4\text{CN}}$ (6)



Appendix G1: ^1H NMR spectrum of $\text{TIBp}^{\text{Ph}_2,4\text{CN}}$ (**6**) (DMSO-d₆)



Appendix G2: Extended ^1H NMR spectrum of TIBp^{Ph₂,4CN} (**6**) (DMSO-d₆)



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