

DESIGN AND SYNTHESIS OF PHOSPHORUS CATIONS AND EXPLORING THEIR REACTIVITY

M.Sc. THESIS

by

Sounak Saha



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE**

May 2026

DESIGN AND SYNTHESIS OF PHOSPHORUS CATIONS AND EXPLORING THEIR REACTIVITY

A THESIS

*Submitted in partial fulfilment of the
requirements for the award of the degree
of
Master of Science*

by
SOUNAK SAHA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE**

May 2026



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Design and Synthesis of Phosphorus Cations and Exploring Their Reactivity** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July, 2025 to May, 2026 under the supervision of Dr. Dipak Kumar Roy, Associate Professor.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Sounak Saha

Signature of the student
(**SOUNAK SAHA**)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of the Supervisor
(**Dr. DIPAK KUMAR ROY**)

SOUNAK SAHA has successfully given his M.Sc. Oral Examination held on **11 May, 2026**.

ACKNOWLEDGEMENTS

Pursuing my M.Sc. at IIT Indore has been one of the best decisions of my life. I am deeply grateful to all the remarkable individuals I have encountered along the way, who have enriched my experiences and broadened my knowledge.

First, I sincerely thank my M.Sc. supervisor, **Dr. Dipak Kumar Roy**, for the opportunity to do the following work in his group. Working under Dr. Roy's guidance has been a privilege, and I will always treasure the invaluable experiences and insights gained during this time.

I am grateful for the support of the Department of Chemistry and the Sophisticated Instrumentation Center (SIC) for their valuable contributions during my journey.

I would like to extend my heartfelt gratitude to my labmates at IIT Indore—Dr. Darakshan Parveen (my mentor), Dr. Rahul Kumar Yadav, Mr. Ritesh Kumar Sahu, Ms. Radhika Shrivastava, Ms. Dimpal Sharma, Mr. Rohit Yadav, Mr. Rahul Kumar, Mr. Aniket Chouhan, Mr. Utkarsh Sengar—for their unwavering support and insightful discussions throughout my research journey.

I would also like to extend my heartfelt thanks to my friends. Finally, I would like to express my deepest gratitude to my family, whose constant support has been the foundation of my accomplishments. I am especially thankful to my mother, Mrs. Tinku Saha and my father, Mr. Sandip Saha for their boundless love, encouragement, and unwavering belief in me. Their constant presence, support, and motivation have been invaluable throughout this journey, and I am truly blessed to have them by my side.

SOUNAK

2403131027

ABSTRACT

Phosphorus cations are a compelling class of main-group species due to their high electrophilicity, potential for novel bonding, and ability to mimic some aspects of transition metal reactivity, especially in small-molecule activation and bond activation chemistry. Diimine ligands or related bidentate/ π -donating ligands can stabilize phosphorus cations through delocalization of positive charge and/ or by π -donation, enabling isolation of otherwise highly reactive or transient species while still retaining reactivity at the phosphorus center. However, diimine-stabilized phosphorus cations remain relatively underexplored in literature because their high electrophilic nature and tendency to undergo undesirable side reactions make them difficult to isolate and handle under normal conditions. Systems with constrained or planar phosphorus centers (often enforced by ligand frameworks) have been predicted and observed to show unusual reactivity: for example, enhanced Lewis acidity, small-molecule activation (e.g. N-H, C-H, halide abstraction), or insertions. Previous works have shown that phosphorus dications with N-heterocyclic imine substituents are isolable. Although NHCs have been employed to stabilize phosphorus cations, their strong σ -donation often over-stabilizes the cation and suppresses electrophilicity. This leaves their reactivity less explored. Diimine ligands and aminotroponimine ligands, by contrast, provide charge delocalization while retaining reactivity, and their chelating nature can enforce unique geometries such as planar phosphorus centers. Thus, the phosphorus cations stabilized by these ligands, offer access to reactivity patterns that are less accessible with NHC stabilization. Motivated by these opportunities, my project aims to synthesize novel diimine and aminotroponimine stabilized phosphorus cations and systematically explore their reactivity.

CONTENTS

1. Title page.....	i
2. Declaration page.....	iii
3. Acknowledgements.....	iv
4. Abstract.....	v
5. List of Schemes.....	viii
6. List of Figures.....	x
7. Abbreviations.....	xii
8. Introduction.....	1
8.1 Importance of Main Group Chemistry.....	1
8.2 Exploration of Ligands in Main Group Chemistry...	3
8.3 Role of ligands in main group chemistry.....	3
8.4 N, N'-based ligands.....	3
8.5 β -diimines.....	6
8.6 Aminotroponimines (ATI).....	9
8.7 Synthesis of amionotroponimine ligand.....	10
8.8 Importance of Phosphorus.....	11
8.9 Phosphorus Cations in Main-Group Chemistry.....	12
9. Objectives.....	16
10. Results and Discussions.....	17
11. Conclusions.....	20
12. Future Scope.....	21
13. Experimental Section.....	22
13.1 Materials and Methods.....	22
13.2 Synthesis of Ligands.....	23

13.3 Synthesis of Phosphorus Cations.....	32
13.4 Reactivity of Phosphorus Cation.....	37
14. Characterization.....	39
14.1 NMR spectra.....	39
14.2 Mass spectra.....	36
15. References.....	66

LIST OF SCHEMES:

- Scheme 1.** O, O-, O, N- and N, N'-based metal complexes.
- Scheme 2.** General routes to metal-amidinate, -guanidinate and - β -diketiminato complexes.
- Scheme 3.** General structure of amidines, guanidines and β -diimines (R = H, alkyl, aryl).
- Scheme 4.** Synthesis of a sterically encumbered β -diimine compound LH.
- Scheme 5.** Examples of (a) bimetallic transition-metal complexes, (b) frustrated Lewis pairs (top) and heterobimetallic main-group complexes (bottom, dative ligands are not shown), and (c) homobimetallic main-group complexes with intermolecular metal-metal bonds, which are in certain cases affected by monomer-dimer equilibria.
- Scheme 6.** Synthetic protocol of ATI ligands
- Scheme 7.** Synthesis of first phosphonium cation **a** by Clermont
- Scheme 8.** Synthesis of first stable phosphenium cation **b** by Fleming
- Scheme 9.** Synthesis of first stable NHC stabilized phosphenium cation **c** by Bertrand
- Scheme 10.** Synthesis of ligand **L1**
- Scheme 11.** Synthesis of ligand **L2**
- Scheme 12.** Synthesis of ligand **L3**
- Scheme 13.** Synthesis of ligand **L4**
- Scheme 14.** Synthesis of ligand **L5**
- Scheme 15.** Synthesis of ligand **L6**
- Scheme 16.** Synthesis of ligand **L7**
- Scheme 17.** Synthesis of ligand **L8**
- Scheme 18.** Synthesis of ligand **L9**
- Scheme 19.** Synthesis of **1**
- Scheme 20.** Synthesis of **2**
- Scheme 21.** Synthesis of **3**
- Scheme 22.** Synthesis of **4**
- Scheme 23.** Synthesis of **5**

Scheme 24. Synthesis of **6**

Scheme 25. Synthesis of **7**

Scheme 26. Synthesis of **8**

LIST OF FIGURES

- **Figure 1.** Possible sites for tuning in diimines and aminotroponimines
- **Figure 2.** Structure of β -diimine, N-heterocyclic carbene (NHC) and Aminotropimine ligands
- **Figure 3.** ^1H NMR of ligand **L1** recorded in CDCl_3
- **Figure 4.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L1** recorded in CDCl_3
- **Figure 5.** ^1H NMR of ligand **L2** recorded in CDCl_3
- **Figure 6.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L2** recorded in CDCl_3
- **Figure 7.** ^1H NMR of ligand **L3** recorded in CDCl_3
- **Figure 8.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L3** recorded in CDCl_3
- **Figure 9.** ^1H NMR of ligand **L4** recorded in CDCl_3
- **Figure 10.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L4** recorded in CDCl_3
- **Figure 11.** ^1H NMR of ligand **L5** recorded in CDCl_3
- **Figure 12.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L5** recorded in CDCl_3
- **Figure 13.** ^1H NMR of ligand **L6** recorded in CDCl_3
- **Figure 14.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L6** recorded in CDCl_3
- **Figure 15.** ^1H NMR of ligand **L7** recorded in CDCl_3
- **Figure 16.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L7** recorded in CDCl_3
- **Figure 17.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L8** recorded in CDCl_3
- **Figure 18.** ^1H NMR of ligand **L8** recorded in CDCl_3
- **Figure 19.** ^1H NMR of ligand **L9** recorded in CDCl_3
- **Figure 20.** $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L9** recorded in CDCl_3
- **Figure 21.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **1** recorded in CDCl_3
- **Figure 22.** ^1H NMR of **1** recorded in CDCl_3
- **Figure 23.** $^{13}\text{C}\{^1\text{H}\}$ NMR of **1** recorded in CDCl_3
- **Figure 24.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **2** recorded in CDCl_3
- **Figure 25.** ^1H NMR of **2** recorded in CDCl_3
- **Figure 26.** $^{13}\text{C}\{^1\text{H}\}$ NMR of **2** recorded in CDCl_3
- **Figure 27.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **3** recorded in CDCl_3
- **Figure 28.** ^1H NMR of **3** recorded in CDCl_3
- **Figure 29.** $^{13}\text{C}\{^1\text{H}\}$ NMR of **3** recorded in CDCl_3
- **Figure 30.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **4** recorded in Toluene

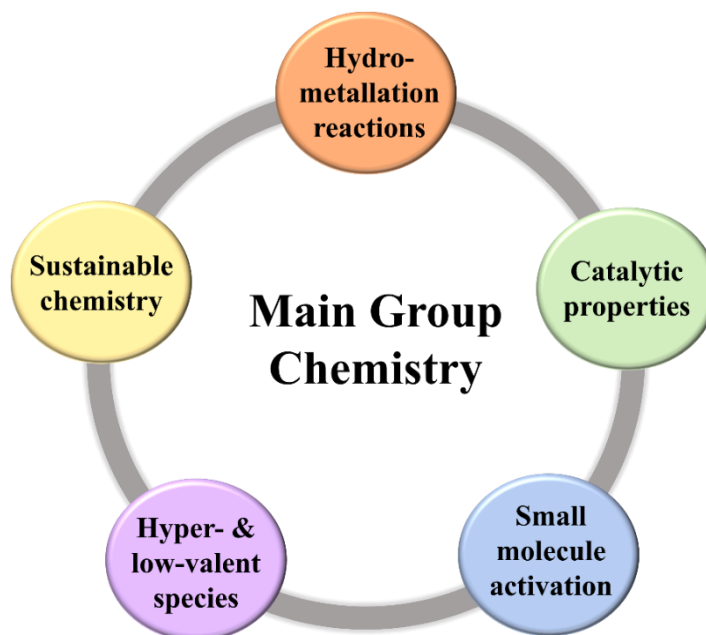
- **Figure 31.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **5** recorded in Toluene
- **Figure 32.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **6** recorded in Toluene
- **Figure 33.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **7** recorded in Toluene
- **Figure 34.** $^{31}\text{P}\{^1\text{H}\}$ NMR of **8** recorded in Toluene
- **Figure 35.** Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR of **8** recorded in Toluene.
- **Figure 36.** HRMS data of ligand **L1**
- **Figure 37.** HRMS data of ligand **L2**
- **Figure 38.** HRMS data of ligand **L3**
- **Figure 39.** HRMS data of ligand **L4**
- **Figure 40.** HRMS data of ligand **L5**
- **Figure 41.** HRMS data of ligand **L6**
- **Figure 42.** HRMS data of ligand **L7**
- **Figure 43.** HRMS data of ligand **L8**
- **Figure 44.** HRMS data of ligand **L9**
- **Figure 45.** HRMS data of **1**
- **Figure 46.** HRMS data of **2** ($[\text{M}]^+$)
- **Figure 47.** HRMS data of **2** ($[\text{M}/2]^+$)
- **Figure 48.** HRMS data of **3** ($[\text{M}]^+$)
- **Figure 49.** HRMS data of **3** ($[\text{M}/2]^+$)
- **Figure 50.** HRMS data of **4**
- **Figure 51.** HRMS data of **5**
- **Figure 52.** HRMS data of **6** ($[\text{M}]^+$)
- **Figure 53.** HRMS data of **6** ($[\text{M}/2]^+$)
- **Figure 54.** HRMS data of **7**

ABBREVIATIONS

°C	Degree Celsius
g	Gram
h	Hour
Mg	Milligram
mmol	Millimoles
min	Minutes
mL	Millilitre
Eq	equivalent
DCM	Dichloromethane
MeOH	Methanol
CDCl ₃	Chloroform-d
NMR	Nuclear Magnetic Resonance
HRMS	High Resolution Mass Spectrometry
ESI	Electrospray Ionization
s	Singlet
d	Doublet
m	Multiplet
sept	Septet
ppm	Parts per million
Hz	Hertz, s ⁻¹

“Dedicated to my Family”

INTRODUCTION



Importance of Main Group Chemistry

Main-group chemistry has undergone significant progress in recent years, largely fueled by the increasing demand for sustainable and environmentally benign alternatives to conventional transition-metal-based systems.[1-3] This transition is especially relevant in catalysis, where transition metals have long dominated a broad spectrum of industrial and synthetic applications.[2] However, growing concerns over their environmental impact, high cost, limited availability, and potential toxicity have encouraged the exploration of main-group elements as viable substitutes. Owing to their natural abundance, lower toxicity, and versatile reactivity, main-group elements have emerged as promising candidates for the development of greener catalytic systems.[4]

Among the key advances in this area is the utilization of N, N'-based bis(diimine) (BDI) ligands, which have demonstrated remarkable efficiency in stabilizing reactive main-group species, particularly those

in unusual oxidation states. These ligands offer a strongly electron-donating environment combined with steric adaptability, enabling the stabilization of highly reactive main-group metal centers.[5-7] Such stabilization enhances their reactivity, allowing them to participate in catalytic transformations that are traditionally associated with transition metals. Furthermore, the tunability of bis(diimine) ligands that is achieved through modification of substituents on the imine nitrogen atoms provides precise control over both electronic and steric parameters, thereby expanding their applicability in catalysis.[6,8]

In addition to bis(diimine) ligands, aminotroponimine (ATI) ligands have emerged as a versatile class of monoanionic, bidentate N, N'-donor ligands featuring a rigid and highly delocalized π -conjugated framework. Owing to their extended 10π -electron delocalization and structural rigidity, ATI ligands provide enhanced electronic stabilization compared to conventional amidines and β -diimines, while maintaining strong N, N'-chelation.[3,4] This unique combination of rigidity and delocalization allows ATI ligands to stabilize highly reactive and electron deficient metal centers without significantly diminishing their intrinsic reactivity.[6] Furthermore, their tunability through substitution at the nitrogen atoms and the conjugated backbone enables fine control over both steric and electronic properties. Recent studies have also highlighted their ability to participate in redox processes and ligand cooperativity, making them particularly promising for stabilizing low-coordinate main-group species, including electrophilic Group 15 cations.[1,6]

Despite these advantages, challenges remain in synthesizing and stabilizing bis(diimine)- and aminotroponimine-based main-group complexes. Many of these species exist in low oxidation states and are prone to side reactions such as oxidation or disproportionation, requiring careful reaction control.[7] However, substantial progress has been achieved, resulting in the successful synthesis of bis(diimine)- and ATI-supported complexes of magnesium, zinc, boron, and other main-group elements. These complexes have demonstrated remarkable catalytic

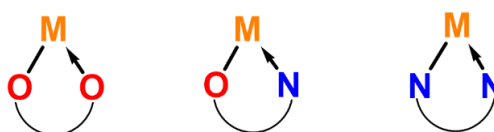
activity in key transformations, highlighting the potential of main-group metals to serve as important alternatives to traditional transition-metal catalysts.[8,9]

The shift towards green chemistry has intensified the search for sustainable, transition-metal free catalytic systems. Main-group elements offer an eco-friendly alternative, reducing reliance on scarce and toxic metals. In this context, bis(diimine)- and aminotroponimine-based complexes show great promise, enabling catalytic transformations where transition metals may be less effective. By bridging fundamental main-group chemistry with practical catalysis, these ligand systems open new avenues for both research and industrial applications, advancing sustainability in chemical processes.

EXPLORATION OF LIGANDS IN MAIN GROUP CHEMISTRY:

Role of ligands in main group chemistry

Based on N and O donor atoms, O, O-, N, O-, and N, N'-ligands are widely utilized in coordination chemistry, including the utilization of main group elements and transition metals.[22-26]



Scheme 1. O, O-, O, N- and N, N'-based metal complexes.

N, N'-based ligands

N, N'-based ligands have become widely prevalent in modern coordination chemistry. The ease with which their steric and electronic properties can be tuned, along with their bidentate coordination behavior, renders them highly suitable for coordination with transition

metals, lanthanides, and main-group elements.[10, 11] While transition metal complexes supported by N, N'-based ligands have long been established and extensively applied in catalysis,[12] interest in main-group element chemistry has grown significantly over the past few decades.[13–15] This increasing focus can be attributed to several important factors. In comparison to transition metals, main-group elements are typically less (bio)toxic, more economical, and, importantly, more abundant in the Earth's crust.[16–18] As a result, complexes of main-group elements featuring N, N'-based ligands are gaining considerable attention, particularly in the context of sustainability.

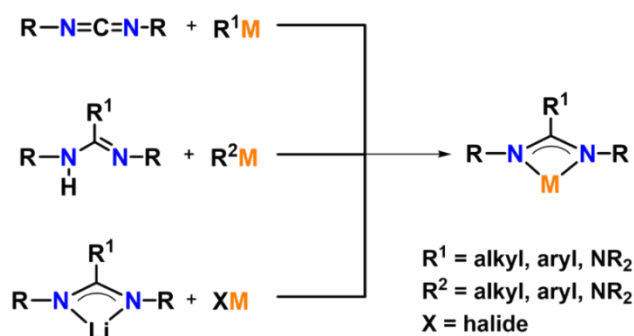
N, N'-based ligands, defined by the presence of two nitrogen donor atoms, are highly versatile and broadly employed in coordination chemistry. They easily form stable complexes with a broad variety of metals while enabling precise tuning of both steric and electronic properties.

Below are some common examples of N, N'-based ligands (**Scheme 1**):

- (a) amidines
- (b) guanidines
- (c) β -diimines (β -diketimines)

Metal amidinate, guanidinate, and β -diiminate complexes are commonly synthesized through one of the following three approaches (**Scheme 2**):

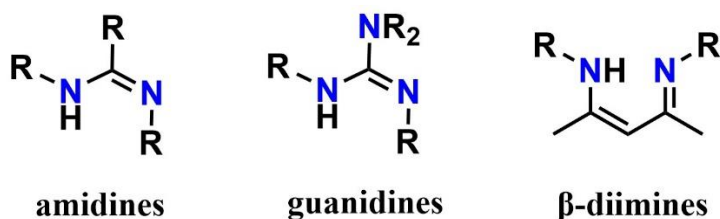
1. insertion of a carbodiimide into a metal–carbon, metal–amide, or metal–phosphide bond;
2. deprotonation of the neutral proligand using a metal–alkyl or metal–amide reagent; and
3. salt metathesis between a metal halide and the lithiated ligand, which is typically generated through method 1 or 2.



Scheme 2. General routes to metal-amidinate, -guanidinate and - β -diiminates complexes.

In modern chemistry, ligands play a crucial role in facilitating the synthesis and stabilization of elusive intermediates and highly reactive species. Among them, N, N'-donor ligands are some of the most widely explored in organometallic and coordination chemistry due to their easy accessibility through simple and highly versatile condensation-based synthetic routes. The steric and electronic properties of these ligands can be readily tuned by modifying substituents on the heteroatoms and within the ligand framework. Such ligands are capable of stabilizing a broad spectrum of metal ions spanning the s-, p-, d-, and f-block elements of the periodic table. Across different oxidation states, these metal complexes often exhibit enhanced catalytic activity, selectivity, and stability in processes such as hydrogenation, olefin polymerization, and cross-coupling reactions. In particular, the study of N, N'-donor ligands with early transition metals has led to significant advances, including the isolation of numerous highly reactive metal–ligand multiple bonds. For instance, β -diimine (BDI) ligands represent an important class of N, N'-donor systems. Using such ligand frameworks, chemists have been able to isolate metal–metal bonded species involving main-group elements that display multiple oxidation states in a manner analogous to transition metals. Moreover, these ligands are capable of stabilizing low-oxidation-state main-group complexes featuring multiple bonds.^[19–21] N, N' donor ligands are also characterized into different classes as BDI, anilido, aminotroponimines, and priso (amidines and guadines) ligands. These ligands play a vital

role in replacing the most expensive transition metal-based catalysts with cheap, earth-abundant, non-toxic main group elements.



Scheme 3. General structure of amidines, guanidines and β-diimines (R = H, alkyl, aryl).

Main group elements also have the potential to activate small molecules like transition metal complexes, and this might be greatly influenced by the ligands.[22,23]

β-diimines (BDI)

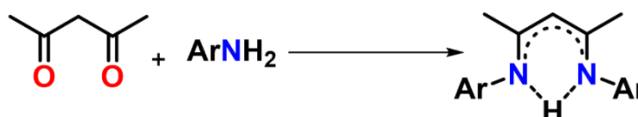
β-diimine ligands have gained significant prominence in coordination chemistry due to their strong metal-binding capability, tunable steric and electronic properties, and diverse coordination modes.[26,27] Structurally analogous to acetylacetonate (acac), β-diimine ligands contain nitrogen donor atoms in place of oxygen, and are often functionalized with alkyl, silyl, or aryl substituents to provide steric protection. The introduction of bulky substituents increases steric protection, thereby modulating the chemical behaviour and properties of the resulting metal complexes.[21–23]

A defining feature of β-diimine ligands is the π -electron delocalization across the NCN backbone, which contributes to enhanced stability and enables effective stabilization of metals in various oxidation states. Their versatility allows fine-tuning of both steric and electronic environments, thereby affecting the geometry, reactivity, and stability of metal complexes.[24–27]

These ligands are particularly valued for their ability to stabilize metal centers, especially those in low oxidation states or highly reactive environments.

The electron-donating nitrogen atoms reduce the electrophilicity of the metal center, increasing stability and facilitating the isolation of unusual oxidation states. Consequently, β -diimine ligands play an important role in catalysis and the development of advanced materials.[28,29] They also provide excellent control over the geometry and coordination environment of metal complexes, allowing precise modulation of steric and electronic properties. Thus, they have been widely employed in catalytic processes such as bond activation, polymerization, and C–H functionalization.[26]

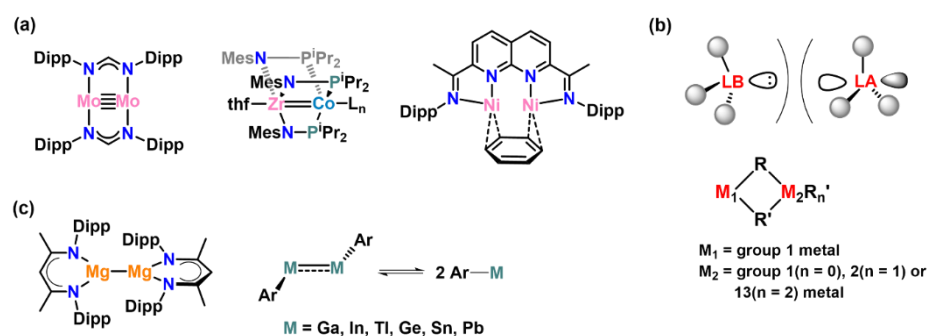
The first β -diimine complexes were reported in the 1960s as homoleptic complexes of cobalt, nickel, copper, and zinc. When the substituent R is small (e.g., H, Me, or SiMe₃), the complexes tend to dimerize and accommodate higher coordination numbers at the metal center. In contrast, bulky aryl substituents on the nitrogen atoms typically favour the formation of monomeric species with lower coordination numbers. The ligand LH can be efficiently synthesized following the method developed by Feldman and his colleagues (**Scheme 4**), involving the direct condensation of 2,4-pentanedione with 2,6-diisopropylaniline in boiling ethanol in the presence of HCl, followed by neutralization with Na₂CO₃ to afford LH as colourless crystals.[30-33]



Scheme 4. Synthesis of a sterically encumbered β -diimine compound LH.

Expanding on the versatility of mono- β -diimine ligands, bis- β -diimine ligands provide greater coordination complexity and enhanced stability. By integrating two β -diimine units within a single framework, these ligands introduce additional metal-binding sites and allow improved control over the geometry and electronic characteristics of metal complexes. The bis(diimine) architecture effectively stabilizes metal centers, particularly in uncommon oxidation states, making it highly

valuable in catalytic applications.[34] Bimetallic complexes derived from such ligands enable cooperative interactions between metal centers, allowing transformations that are not accessible to monometallic systems.[35–38] This cooperative behaviour, reminiscent of metalloenzymes, has driven efforts to emulate nature’s catalytic efficiency and selectivity. These ideas are reflected in the development of a wide range of bimetallic complexes and frustrated Lewis pairs (Scheme 5).[39–42]



Scheme 5. Examples of (a) bimetallic transition-metal complexes, (b) frustrated Lewis pairs (top) and heterobimetallic main-group complexes (bottom, dative ligands are not shown), and (c) homobimetallic main-group complexes with intermolecular metal–metal bonds, which are in certain cases affected by monomer–dimer equilibria.

Bis(diimine) ligands offer several advantages over mono(diimine) systems, such as greater coordination versatility, enhanced stability, and better tuning of the electronic and geometric environment around the metal center. The presence of two metal-binding sites enables stronger and more stable interactions, particularly for stabilizing metals in low oxidation states or highly reactive forms. Their capacity to finely regulate the geometry of metal complexes is especially important in catalysis, where geometric factors strongly influence reactivity and selectivity.[41] Moreover, bis(diimine) ligands are highly effective in stabilizing metals in unusual or otherwise less stable oxidation states.

A major benefit of bis(diimine) ligands is their ability to promote the formation of bimetallic complexes. The close proximity of two metal

centers facilitates cooperative interactions that can drive catalytic transformations, many of which are difficult or inaccessible with monometallic systems. This cooperative behaviour resembles that observed in metalloenzymes, where multiple metal centers work together to enable complex reactions.[42] The combination of enhanced stability, precise control over coordination environments, and the potential for bimetallic cooperation makes bis(diimine) ligands highly versatile. They find broad applications in catalysis, materials science, and the stabilization of reactive intermediates, ultimately enabling more efficient and selective chemical transformations. Consequently, they are considered indispensable tools in modern synthetic chemistry. [43]

Aminotroponimines (ATI)

Aminotroponimine (ATI) ligands constitute an important class of monoanionic, bidentate N, N'-donor ligands distinguished by a rigid, planar, and unsaturated C₇-ring backbone. These ligands feature well-defined N, N' coordination sites and are derived from aminotroponimines through deprotonation. Upon binding to a metal center, ATI ligands typically generate a nearly planar five-membered metallacycle, thereby offering a well-defined coordination environment. A notable structural characteristic of ATI ligands is their seven-membered tropone-based framework, which accommodates a highly delocalized 10 π -electron system extending over the C₇ backbone and the two nitrogen atoms. This extensive π -conjugation provides significant electronic stabilization, decreases their susceptibility to both nucleophilic and electrophilic attack, and allows for fine-tuning through substitution either at the nitrogen atoms or along the ligand backbone. In comparison to classical amidines (4 π systems) and β -diimines (6 π systems), ATI ligands display stronger π -delocalization and a more rigid structural framework, while still maintaining monoanionic N, N'-chelating behaviour.[44-46]

Structurally, ATI ligands can be regarded as linking motifs between established ligand systems such as phenylenediamines and diazadienes,

owing to the presence of both imino and amino functionalities. Although ATI and β -diimine ligands share certain similarities, they are distinctly differentiated by the rigid C₇ backbone, which serves as a defining structural feature of ATI frameworks.[46]

The combination of rigidity, extensive delocalization, and electronic tunability makes ATI ligands particularly well suited for stabilizing highly reactive and electron-deficient metal centers in both transition metal and main group chemistry. They have been extensively utilized in stabilizing cationic Group 13 complexes, in the synthesis of hypo- and hypervalent Group 14 species, and in investigations of spin delocalization in first-row transition metal complexes. Furthermore, ATI-supported systems have been explored in a range of catalytic transformations, including hydroamination, olefin polymerization, epoxidation, and electron transfer processes.[44]

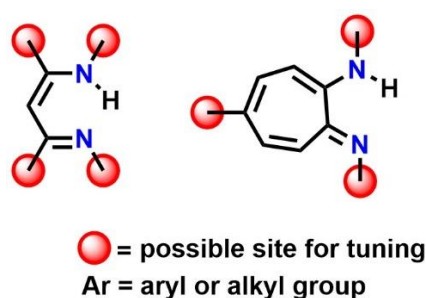
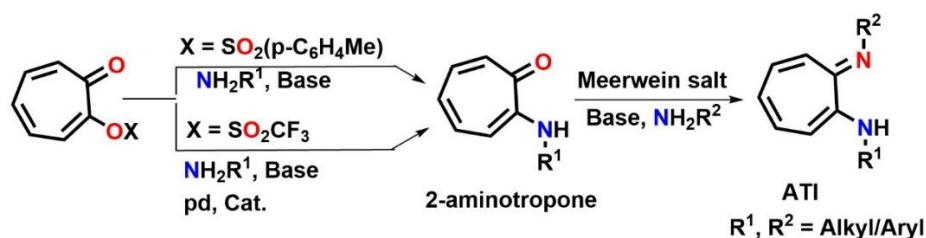


Fig 1. Possible sites for tuning in diimines and aminotroponimines

Synthesis of amionotroponimine ligand

The initial introduction of an NR group onto tropolone is governed by the nucleophilicity of the amine. Bulky amines such as Dipp and Mes exhibit lower nucleophilicity and therefore require a Pd-based catalyst for successful incorporation[45, 46], whereas more nucleophilic amines like tert-butyl and isopropylamine can be introduced without the need for a catalyst. The resulting aminotropones are typically converted into the desired ATI ligands through a one-pot reaction involving the

addition of a Meerwein salt and the corresponding amine.



Scheme 6. Synthetic protocol of ATI ligands

Despite these developments, the chemistry of bis(aminotroponimine) ligands remains relatively underexplored, particularly in the context of Group 15 main-group chemistry, especially for low-coordinate phosphorus cations. These phosphorus cations require ligand systems capable of providing adequate stabilization without completely suppressing their inherent electrophilicity and reactivity.

In this regard, bis-ATI ligands present a promising alternative platform. Their monoanionic yet strongly delocalized π -framework offers both kinetic and electronic stabilization while maintaining the reactive nature of the phosphorus center. The extended conjugation and comparatively softer donor environment of ATI ligands may allow access to phosphorus cations that are sufficiently stable for isolation while still retaining high electrophilicity for reactivity studies.^[47] Moreover, a bis-ATI framework can impose a constrained coordination environment, facilitate charge delocalization, and potentially stabilize unusual oxidation states or bonding motifs in phosphorus chemistry. Consequently, the investigation of bis-ATI-supported phosphorus cations provides an effective strategy to balance instability and over-stabilization, enabling the isolation and study of highly reactive Group 15 cationic species.

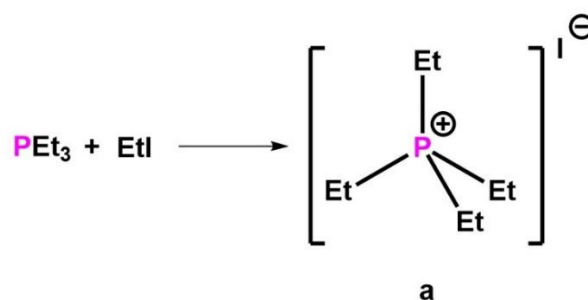
Importance of Phosphorus

Phosphorus, a Group 15 p-block element with electronic configuration $[\text{Ne}]3s^23p^3$, is one of the most chemically versatile non-metals in the periodic table due to its ability to access various oxidation states ranging from $-III$ to $+V$.^[49] Unlike heavier pnictogens, phosphorus exhibits

limited π -bonding because of poor 3p–3p overlap, which leads to a dominance of σ -bonded frameworks and diverse molecular geometries.[49-51] Elemental phosphorus exists in several allotropes such as white, red, violet, and black phosphorus, each displaying distinct structures, reactivities, and applications. Although phosphorus is not as universally encountered in everyday life as carbon or oxygen, it is one of the six biogenic elements—hydrogen, carbon, nitrogen, oxygen, phosphorus, and sulfur—that are essential in large amounts for the formation and sustenance of living organisms on Earth.[50] Phosphorus compounds span a vast range of structural and electronic environments, including phosphines, phosphine oxides, phosphates, phosphazenes, and cationic phosphorus species, enabling applications in catalysis, materials chemistry, agrochemicals, and biochemistry. In agriculture, phosphorus is a key macronutrient, and global food production heavily depends on phosphate-based fertilizers derived from phosphate rock.[52] In synthetic inorganic chemistry, organophosphorus compounds especially tertiary phosphines (PR_3) play central roles as ligands in transition-metal catalysis, enabling hydroformylation, hydrogenation, and cross-coupling reactions.[50,53]

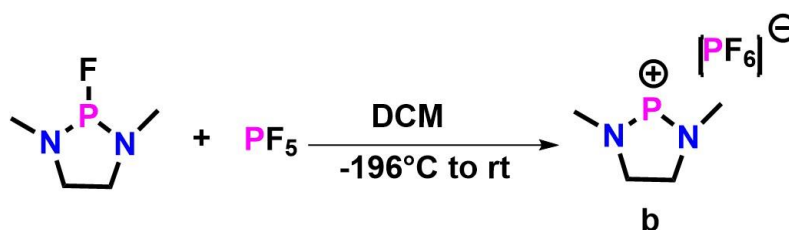
Phosphorus Cations in Main-Group Chemistry

A particularly important and rapidly growing field within modern inorganic and main-group chemistry is the study of phosphorus cations, which exhibit unusual bonding modes and electrophilic behaviour. The most widely studied class is the phosphonium cations (PR_4^+), tetrahedral P(V) species formed by alkylation of tertiary phosphines; these are stable, isolable, and widely applied in phase-transfer catalysis and ionic liquid design.[52] One of the very first stable phosphonium cation **a** was synthesized by Clermont in 1851.



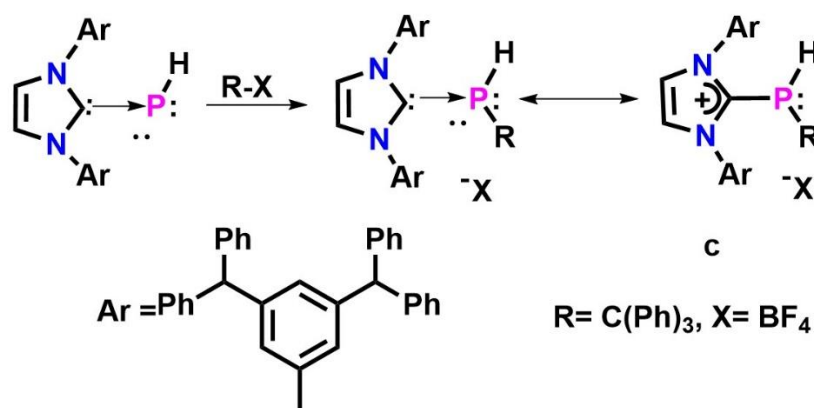
Scheme 7. Synthesis of first phosphonium cation **a** by Clermont

The first stable phosphonium cation **b** was synthesized by Fleming and co-workers in 1972 from halide abstraction of a cyclic urodialkylaminophosphine using BF_3 or PF_5 . These studies demonstrated that phosphorus can adopt stable low-coordinate cationic states when supported by suitable substituents, opening a new field of research into main group cations.[53]



Scheme 8. Synthesis of first stable phosphonium cation **b** by Fleming

Bertrand and co-workers achieved a landmark in 2015 by isolating a NHC-stabilized parent phosphonium **c**, thus proving that even highly reactive phosphorus cations can be stabilized through carbene donation.[55] This breakthrough demonstrated how strong σ -donation from N-heterocyclic carbenes can effectively tame otherwise transient, electron-deficient main-group species. Subsequently, various ligand frameworks have been employed to stabilize phosphorus cations, including N-heterocyclic carbenes (NHCs) which act as strong σ -donors. These advances have collectively expanded the accessible coordination environments of low-valent phosphorus, enabling systematic exploration of their structure–reactivity relationships.[54, 55]



Scheme 9. Synthesis of first stable NHC stabilized phosphonium cation **c** by Bertrand

However, the strong donor ability of NHCs often leads to over-stabilization of the phosphorus center. In many NHC-supported systems, the ligand phosphorus interaction becomes so strong that the intrinsic electrophilic character of the cation is significantly reduced, limiting its reactivity and making these compounds valuable mainly for structural rather than functional studies. For reactive phosphorus cations, successful ligand design requires not only stabilization but also preservation of electrophilicity and substrate accessibility.[54]



Figure 2. Structure of β -diimine, N-heterocyclic carbene (NHC) and aminotroponimine ligands

Recent computational and experimental studies have highlighted that ligand choice critically tunes the stability–reactivity balance, with diimine frameworks often producing highly Lewis acidic, transition-metal-like phosphorus cations capable of halide abstraction, small-molecule activation, and even selective C–H or N–H bond activation.[55, 56]

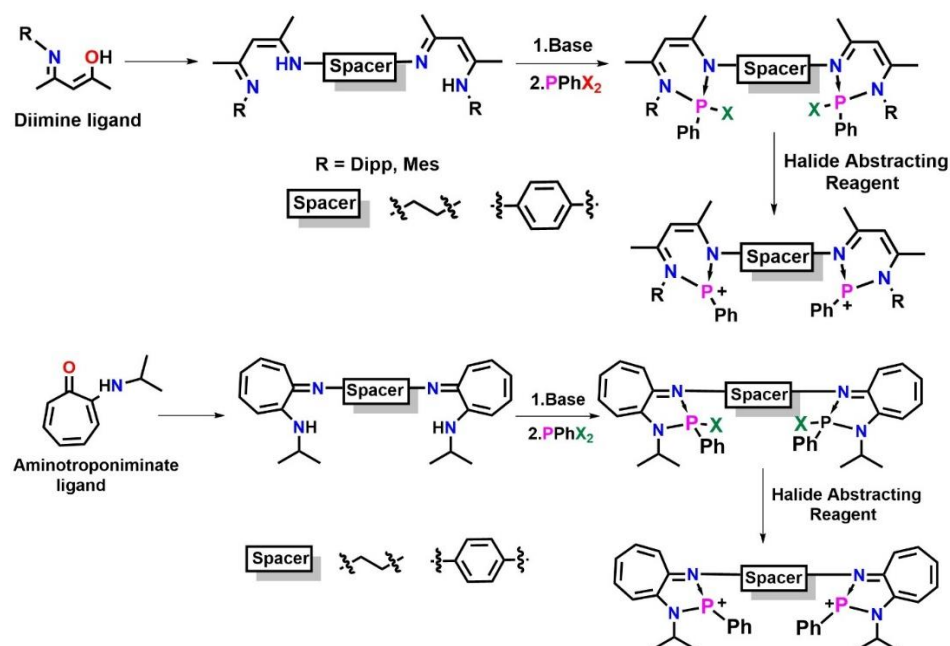
A recent study demonstrated that appropriately designed phosphonium salts can undergo selective monodefluorination of CF_3 groups,

underscoring their synthetic potential.[57] Alongside, theoretical investigations continue to reveal the importance of planarity and charge delocalization in enabling novel bonding modes. Collectively, these findings emphasize that while carbene-stabilized phosphorus cations have been well explored structurally, β -diketiminato and aminotroponimino stabilized systems represent an unexplored area of research with exciting opportunities to uncover unprecedented reactivity.

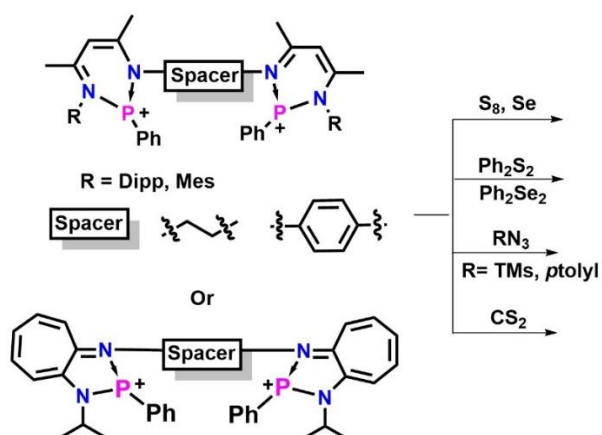
So our main objective is to synthesize β -diimine and aminotroponimine ligands and thereby use them to produce novel β -diketiminato and aminotroponimino stabilized phosphorus cations and systematically explore their reactivity.

OBJECTIVES

Our objective was to synthesize a set of bis-(diimine) and bis-aminotroponimine ligands using spacers such as ethylene and phenyl spacers. Then our aim was to use suitable reagents with our ligands to obtain complexes and then use suitable halide abstracting reagents to obtain phosphorus cations.

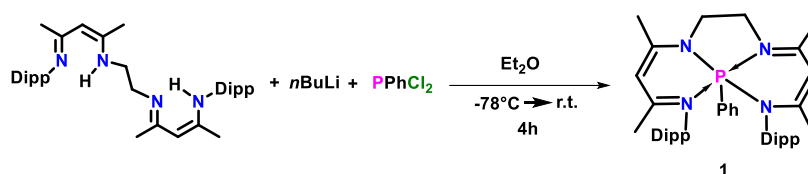


After obtaining phosphorus cations, our aim was to explore their reactivity

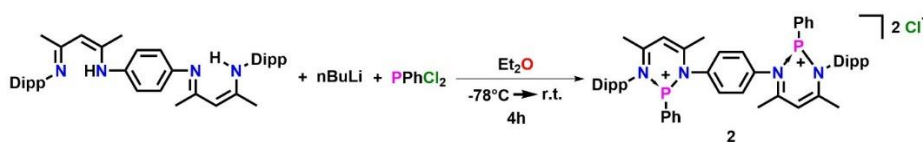


RESULTS AND DISCUSSIONS

Initially bis(diimine) ligand with ethylene bridge was chosen to synthesize phosphorus cations. But the $^{31}\text{P}\{^1\text{H}\}$ NMR showed a singlet peak at a higher upfield shift of -48.46 ppm which indicated higher electron density in the phosphorus centre. The chemical shift value also indicated the formation of a five coordinated saturated phosphorus complex **1** instead of bis phosphorus cation. Moreover, HRMS confirmed the formation of complex **1**. This indicated that on using flexible spacer, a saturated phosphorus complex is getting formed due to bond rotation. The formation of the complex was further confirmed by ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR.

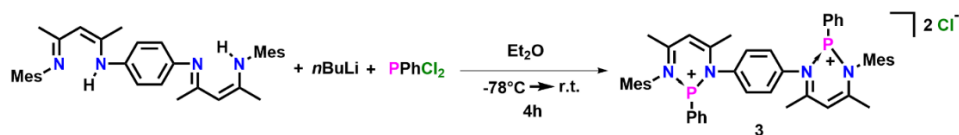


So to avoid bond rotation, a more rigid spacer that is phenyl spacer was selected. The $^{31}\text{P}\{^1\text{H}\}$ NMR showed a singlet peak at a highly downfielded shift of 161.28 ppm which indicated comparatively lower electron density in the phosphorus centre. The chemical shift value also matched with the reported data thereby indicating the formation of bis phosphorus cation **2**. Moreover, in HRMS the simulated data of $[\text{M}]^+$ and $[\text{M}/2]^+$ matched with experimental data thereby indicating the formation of complex **2**. The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR further confirmed that bis phosphorus cation was successfully synthesized.

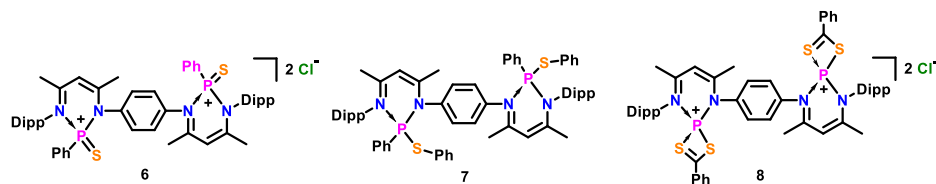


The data was reproducible and it indicated that spacers played a huge role in synthesizing bis phosphorus cations. Then after having good success in synthesizing bis phosphorus cation using Dipp bis(diimine) ligands, it was decided to explore Mes bis(diimine) ligands. Based on previous observations, a rigid spacer (phenyl spacer) was employed to

minimize bond rotation. Then $^{31}\text{P}\{^1\text{H}\}$ NMR was obtained, which showed a highly downfielded peak of 160.23 ppm thereby indicating the formation of phosphorus cation. The ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR and HRMS data further indicated that phosphorus cation **3** was successfully synthesized.



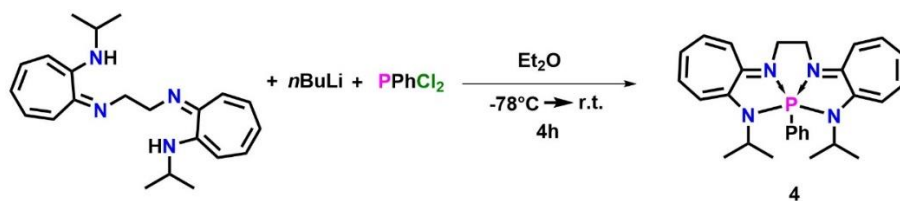
After successfully synthesizing bis(diimine) stabilized phosphorus cations, their reactivity with various reagents was explored. Firstly, sulphur based reagents were used. The phosphorus cation **2** was reacted with S_8 , Ph_2S_2 and CS_2 and obtained products **6**, **7**, **8** respectively. These were characterized by $^{31}\text{P}\{^1\text{H}\}$ NMR and mass data. When phosphorus cation **2** was reacted with S_8 , a peak was obtained at 73.63 ppm in $^{31}\text{P}\{^1\text{H}\}$ NMR. Similarly for Ph_2S_2 and CS_2 , $^{31}\text{P}\{^1\text{H}\}$ NMR peaks around 139.32 ppm and 92.92 ppm were obtained respectively. Further attempts to explore reactivities with selenium based reagents (Se , Ph_2Se_2) were not successful.



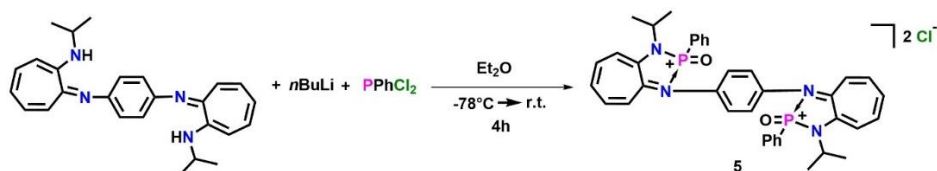
Following the successful synthesis of six-membered phosphorus cations using bis(diimine) ligands, efforts were directed toward the synthesis of five-membered phosphorus cations. For this purpose, aminotroponimine ligands were selected.

Initially, bis(aminotropimine) ligand with ethylene spacer was used. But the $^{31}\text{P}\{^1\text{H}\}$ NMR showed a singlet peak at a higher upfield shift of -49.85 ppm which indicated higher electron density in the phosphorus centre. Upon characterization, the formation of a saturated five coordinate phosphorus complex **4** was confirmed. This observation was

consistent with the results obtained using a bis(diimine) ligand with an ethylene spacer.



To avoid bond rotation and facilitate the formation of the bis phosphorus cation, a phenyl spacer was employed. The ^{31}P $\{^1\text{H}\}$ NMR spectrum showed a singlet at a downfield chemical shift of 160.76 ppm, along with an additional peak around 85.21 ppm. Although the exact nature of the species could not be conclusively established, HRMS data suggested the probable formation of complex **5** containing a $\text{P}=\text{O}$ bond.



Now since the phosphorus centre was fully saturated over here, so it was not possible to explore further reactivity with this complex.

CONCLUSIONS

In this work, five diimine ligands were successfully synthesized in good yields. Initial attempts to generate phosphorus cations using ligand **L2** were unsuccessful, which led to the use of a more rigid ligand **L3**. This modification enabled the successful isolation of a six-membered phosphorus cation **2**. Moreover, ligand **L5** was used to synthesize phosphorus cation **3**. Spectroscopic characterization including $^{31}\text{P}\{^1\text{H}\}$ NMR, ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and HRMS, confirmed the formation of the cationic phosphorus species.

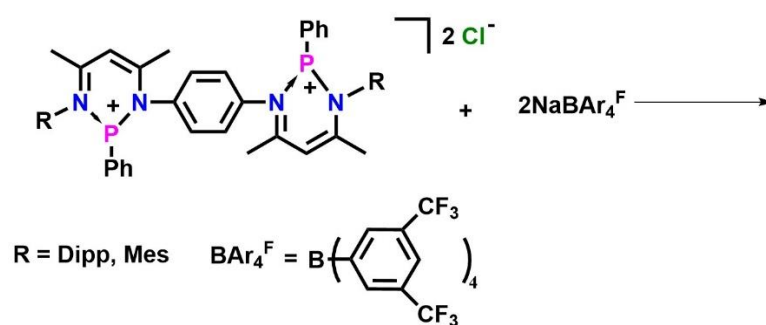
Following its successful synthesis, the reactivity of the phosphorus cation was investigated with various reagents. Promising results were obtained with elemental sulphur and diphenyl disulphide, which further motivated exploration using carbon disulphide.

After successfully synthesizing six membered phosphorus cations with diimine ligands, the focus was shifted towards aminotroponimine ligands with the aim of synthesizing five-membered phosphorus cations. Four aminotroponimine ligands were successfully prepared. Initial attempts to generate phosphorus cations using ligand **L8** were unsuccessful, prompting the use of a more rigid ligand **L9**. Although phosphorus cations were generated using **L9**, the phosphorus center underwent oxidation. Repetition of the reaction yielded similar outcomes.

Overall, these results contribute to a deeper understanding of the design, stabilization, and reactivity of phosphorus cations supported by diimine and aminotroponimine ligands, and highlight their potential for further development in main-group chemistry. In conclusion, this study shows the importance of ligand design, where the balance between rigidity and flexibility significantly influences the stabilization and reactivity of the phosphorus center, thereby governing the successful isolation of the cationic species.

FUTURE SCOPE

Future work will primarily focus on obtaining pure reaction products necessary for complete structural characterization. Although preliminary results suggest successful formation of phosphorus cation **2** and **3**, further purification and characterization are required before drawing definitive conclusions. Efforts should be made towards the crystallization of phosphorus cations **2** and **3** using different solvent systems, with the aim of obtaining suitable single crystals for structural analysis.



In addition, efforts should be directed towards the crystallization and full characterization of phosphorus cations stabilized by aminotroponimate ligands. Further investigations should also be carried out to understand and prevent the oxidation observed in phosphorus cation **5** by using more bulky ligands like 2,3-dimethylphenyl-1,4-diamine.

EXPERIMENTAL SECTION

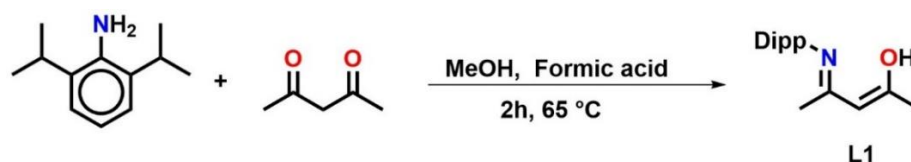
MATERIALS AND METHODS

The reactions were performed either under an Argon-filled Glove box or using standard Schlenk techniques. Chemicals were purchased from Sigma-Aldrich, Spectrochem, or TCI and used as received. All the solvents were purified by distillation using the appropriate drying agents, deoxygenated using three freeze–pump–thaw cycles, and stored over molecular sieves under argon prior to use. Complex and Cations were prepared by following the reported procedure. The deuterated solvents used for NMR spectroscopy were deoxygenated by freeze–pump–thaw cycles and stored under an argon atmosphere over molecular sieves. NMR chemical shifts are reported in ppm and coupling constants in Hz. ^1H , ^{13}C , and ^{31}P NMR spectroscopy data were obtained at ambient temperature using a Bruker 500 NMR spectrometer (operating at 500 MHz for ^1H , 126 MHz for ^{13}C and 202 MHz for ^{31}P). ^1H NMR spectra were referenced *via* residual proton resonances of CDCl_3 (^1H , 7.26 ppm) and C_6D_6 (^1H , 7.16 ppm). ^{13}C NMR spectra were referenced to CDCl_3 (^{13}C , 77.16) and C_6D_6 (^{13}C , 128.06 ppm). LC-HRMS was performed on an Xevo G3 QTOF mass spectrometer coupled with an Acquity H-class plus UPLC with a mass range of 20 to 1500 Daltons in ESI+ ionisation mode.

SYNTHESIS OF LIGANDS

Synthesis of ligand L1

Reaction Scheme:



Scheme 10. Synthesis of ligand L1

Experimental Procedure:

2,6-Diisopropylaniline (15 mL, 81.2 mmol, 1 eq.) was taken in a two neck round bottom flask (r.b.) and minimum amount of methanol (6 mL) and catalytic amount of formic acid (2 mL) was added. The reaction mixture was allowed to run at room temperature (r.t) for 10 mins. Acetylacetone (8.4 mL, 81.2 mmol, 1eq.) was added to the reaction mixture and refluxed for 2h at 65 °C. Then the reaction mixture was cooled to room temperature (r.t.). Methanol was removed using rota vapour. Orangish liquid was cooled to -35 °C to get crystalline product **L1**.

Yield = 80%.

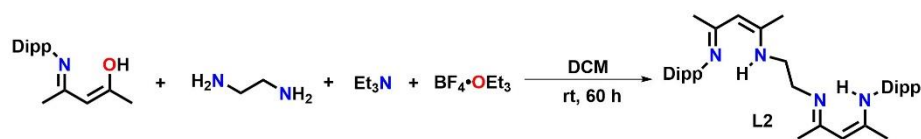
¹H NMR (500 MHz, CDCl₃) δ 12.13 (s, 1H, OH), 7.37 (t, 1H, CH_{Aryl}), 7.25 (d, *J* = 6.1 Hz, 2H, CH_{Aryl}), 5.29 (s, 1H, CH_{pentene}), 3.09 (sept, 2H, (CH₃)₂CH), 2.2 (s, 3H, CH₃), 1.71 (s, 3H, CH₃), 1.29 (d, *J* = 8.4, 6H, (CH₃)₂CH), 1.22 (d, *J* = 8.4, 6H, (CH₃)₂CH).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 195.97, 163.54, 146.30, 133.51, 128.35, 123.61, 95.69, 29.02, 28.54, 24.63, 22.71, 19.21.

HRMS (ESI): Calculated for C₁₇H₂₅NO: 260.2014 [M+H]⁺, found: 260.2032.

Synthesis of ligand L2

Reaction Scheme:



Scheme 11. Synthesis of ligand L2

Experimental Procedure:

4-((2,6-diisopropylphenyl)imino)pent-2-en-2-ol [L1] (3 g, 11.6 mmol, 2 eq.) was taken in a Schlenk tube and vacuumed it for 30 minutes. Then Meerwein salt ($\text{BF}_4 \cdot \text{OEt}_3$) was added to it in Glove Box. The reaction mixture was dissolved in DCM and stirred for overnight. Triethylamine (1.6 mL, 11.56 mmol, 2eq) was added to the reaction mixture after overnight stirring. Then after 20 minutes, ethan-1,2-diamine (0.4 mL, 5.79 mmol, 1eq) was dissolved in triethylamine (12 mL) and added to the reaction mixture. The reaction mixture was stirred for 2 days. Then the reaction mixture was dried in vacuum and extracted in dry toluene. The toluene was dried using rota vapour. Then cold methanol was added and sonication was done to obtain precipitate. Then it was filtered to obtain ligand L2.

Yield: 82%

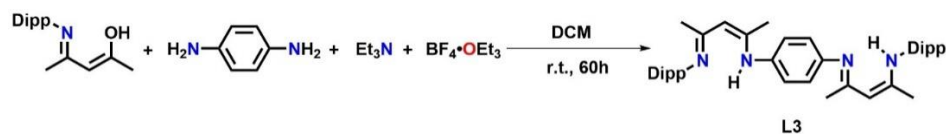
^1H NMR (CDCl_3 , 500 MHz): δ 10.93 (s, 2H, NH), 7.09 (d, J = 7.9 Hz, 4H, CH_{Aryl}), 7.02 (t, 2H, CH_{Aryl}), 4.64 (s, 2H, $\text{CH}_{\text{Pentene}}$), 3.29 (s, 4H, CH_2), 2.84 (sept, 4H, CH_{Dipp}), 1.95 (s, 6H, CH_3), 1.61 (s, 6H, CH_3), 1.14 (d, J = 6.9 Hz, 12H, $\text{CH}_3_{\text{Dipp}}$), 1.09 (d, J = 6.9 Hz, 12H, $\text{CH}_3_{\text{Dipp}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 166.3, 155.4, 146.7, 138.1, 122.8, 122.7, 93.8, 44.5, 28.1, 23.9, 22.8, 21.7, 19.1.

HRMS (ESI): Calculated for $\text{C}_{36}\text{H}_{54}\text{N}_4$: 543.443 $[\text{M}+\text{H}]^+$, found: 543.444

Synthesis of ligand L3

Reaction Scheme:



Scheme 12. Synthesis of ligand L3

Experimental Procedure

4-((2,6-diisopropylphenyl)imino)pent-2-en-2-ol [**L1**] (4 g, 15.4 mmol, 2 eq.) was taken in a Schlenk tube and vacuumed it for 30 minutes. Then Meerwein salt ($\text{BF}_4 \cdot \text{OEt}_3$) (2.9 g, 15.4 mmol, 2 eq) was added to it in Glove Box. The reaction mixture was dissolved in DCM and stirred for overnight. Triethylamine (2.5 mL, 15.4 mmol, 2 eq) was added to the reaction mixture after overnight stirring. Then after 20 minutes, phenyl-1,4-diamine (0.84 g, 7.7 mmol, 1eq) was dissolved in triethylamine (12 mL) and added to the reaction mixture. The reaction mixture was stirred for 2 days. Then the reaction mixture was dried in vacuum and extraction was done in dry toluene. The toluene was dried using rota vapour, Then cold methanol was added and sonication was done to obtain precipitate. Then it was filtered to obtain ligand **L3**.

Yield: 74%

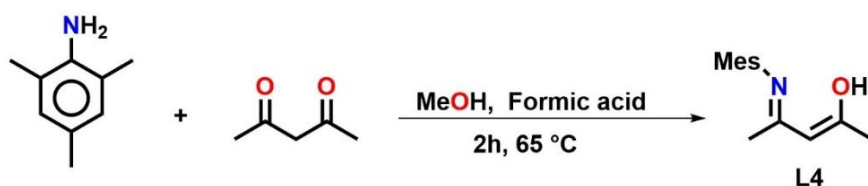
^1H NMR (CDCl_3 , 500 MHz): δ 12.65 (s, 2H, NH), 7.13-7.07 (m, 6H, CH_{Aryl}), 6.85 (s, 4H, $\text{CH}_{\text{Phenyl}}$), 4.84 (s, 2H, $\text{CH}_{\text{Pentene}}$), 2.97 (sept, 4H, CH_{Dipp}), 2.03 (s, 6H, CH_3), 1.68 (s, 6H, CH_3), 1.19 (d, $J = 6.9$ Hz, 12H, $\text{CH}_3_{\text{Dipp}}$), 1.12 (d, $J = 6.8$ Hz, 12H, $\text{CH}_3_{\text{Dipp}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 163.1, 157.1, 142.9, 140.8, 139.8, 124.4, 123.4, 123.0, 95.6, 28.3, 24.2, 22.8, 21.2, 20.8.

HRMS (ESI): Calculated for $\text{C}_{40}\text{H}_{54}\text{N}_4$: 591.4427 $[\text{M}+\text{H}]^+$, found: 591.4436.

Synthesis of ligand L4

Reaction Scheme:



Scheme 13. Synthesis of ligand L4

Experimental Procedure:

2,4,6-Trimethylaniline (9 mL, 64.4 mmol, 1 eq.) was taken in a two neck round bottom flask and minimum amount of methanol (6 mL) and catalytic amount of formic acid (2 mL) was added. The reaction mixture was allowed to run at room temperature (r.t.) for 10 mins. Acetylacetone (10 mL, 96.8 mmol, 1.5 eq.) was added to the reaction mixture and refluxed for 2h at 65 °C. Then the reaction mixture was cooled to room temperature (r.t.). Methanol was removed using rota vapour. Orangish liquid was cooled to -35 °C to get crystalline product **L4**.

Yield = 84%.

¹H NMR (500 MHz, CDCl₃) δ 11.84 (s, 1H, OH), 6.89 (s, 2H, CH_{Mes}), 5.19 (s, 1H, CH_{pentene}), 2.27 (s, 3H, CH₃), 2.15 (s, 6H, CH₃ Mes), 2.09 (s, 3H, CH₃ Mes), 1.62 (s, 3H, CH₃).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 163.24, 137.07, 135.72, 133.88, 128.92, 95.70, 29.01, 20.94, 18.88, 18.15

HRMS (ESI): Calculated for C₁₄H₁₉NO: 218.155 [M+H]⁺, found: 218.156.

Synthesis of ligand L5

Reaction Scheme:



Scheme 14. Synthesis of ligand L5

Experimental Procedure:

4-(mesitylimino)pent-2-en-2-ol [L4] (3 g, 13.8 mmol, 2 eq.) was taken in a Schlenk tube and vacuumed it for 30 minutes. Then Meerwein salt (BF₄•OEt₃) was added to it in Glove Box. The reaction mixture was dissolved in DCM and stirred for overnight. Triethylamine (1.9 mL, 13.8 mmol, 2 eq.) was added to the reaction mixture after overnight stirring. Then after 20 minutes, phenyl-1,4-diamine (0.8 mL, 6.9 mmol, 1 eq) was dissolved in triethylamine (12 mL) and added to the reaction mixture. The reaction mixture was stirred for 2 days. Then the reaction mixture was dried in vacuum and extracted in dry toluene. The toluene was dried using rota vapour. Then cold methanol was added and sonication was done to obtain precipitate. Then it was filtered to obtain ligand L5.

Yield: 76%

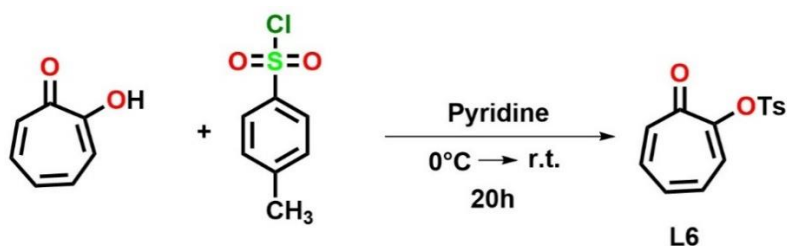
¹H NMR (CDCl₃, 500 MHz): δ 12.50 (s, 2H, NH), 6.87 (s, 4H, CH_{Phenyl}), 6.87 (s, 4H, CH_{Mesl}) 4.85 (s, 2H, CH_{Pentene}), 2.27 (s, 6H, CH₃), 2.11 (s, 12H, CH₃ Mes), 2.03 (s, 6H, CH₃ Mes), 1.68 (s, 3H, CH₃)

¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 161.47, 156.44, 141.58, 139.02, 131.97, 129.56, 127.39, 122.23, 94.60, 19.90, 19.75, 19.63, 19.58, 19.34, 17.32, 14.25

HRMS (ESI): Calculated for C₃₄H₄₂N₄: 507.349 [M+H]⁺, found: 507.350

Synthesis of ligand L6

Reaction Scheme:



Scheme 15. Synthesis of ligand L6

Experimental Procedure:

4-methylbenzenesulfonyl chloride (6.2 g, 32.8 mmol, 1 eq.) was taken in a two neck round bottom flask. Then pyridine was added at 0 °C. After that 2-hydroxycyclohepta-2,4,6-trien-1-one (4 g, 32.8 mmol, 1 eq.) was added. The reaction mixture was stirred continuously overnight from 0 °C to room temperature. After the completion of the reaction, add deionized water to the reaction mixture as a result, a white precipitate formed, and filtration was done to get the white solid product **L6**.

Yield: 82%

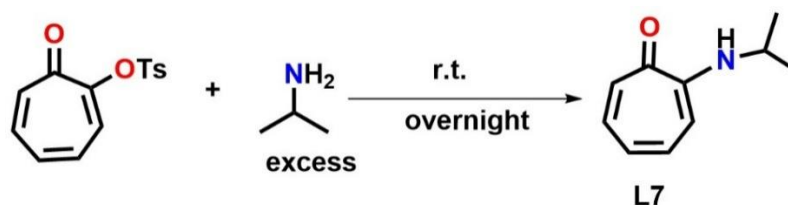
¹H NMR (CDCl₃, 500 MHz): δ 7.65 (m, 4H, CH_{Aryl tosyl}), 7.25 (m, 5H, CH_{Aryl}), 2.37 (s, 3H, CH_{3 tosyl})

¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 179.43, 155.16, 145.54, 141.23, 136.38, 134.67, 133.42, 129.64, 128.60, 21.78

HRMS (ESI): Calculated for C₁₄H₁₂O₄S₁: 277.054 [M+H]⁺, found: 277.055.

Synthesis of ligand L7

Reaction Scheme:



Scheme 16. Synthesis of ligand **L7**

Experimental Procedure

In a Schlenk tube, 2-(tosyloxy)cyclohepta-2,4,6-trien-1-one (3 g, 10.8 mmol, 1 eq.) was kept under vacuum for 30 minutes. After that isopropylamine (10 mL, 1.7 mmol, 15 eq.) was added in excess amount to the reaction mixture. After the completion of the reaction, the solvent was dried under vacuum. Then the mixture was quenched by 2N NaOH and then the product **L7** was extracted in DCM.

Yield: 73%

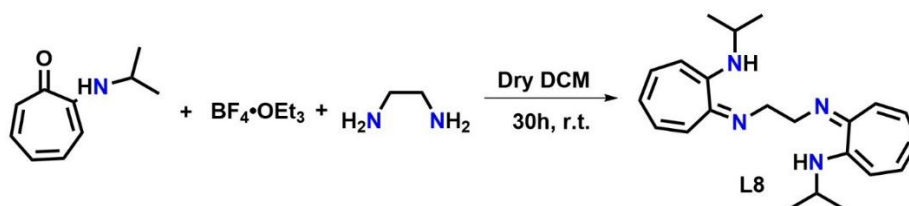
¹H NMR (CDCl₃, 500 MHz): δ 7.15 (m, 5H, CH_{Aryl}), 6.8 (s, 1H, NH), 3.76 (septet, 1H, CH_{isopropyl}), 1.25 (d, 6H, CH₃ isopropyl)

¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 176.67, 154.77, 137.27, 136.38, 128.34, 121.92, 108.96, 43.89, 22.10

HRMS (ESI): Calculated for C₁₀H₁₃NO: 164.108 [M+H]⁺, found: 164.109.

Synthesis of ligand L8

Reaction Scheme:



Scheme 17. Synthesis of ligand L8

Experimental Procedure

2-(isopropylamino)cyclohepta-2,4,6-trien-1-one [L7] (1.1 g, 15.4 mmol, 2 eq.) was taken in a Schlenk tube and vacuumed it for 30 minutes. Then Meerwein salt ($\text{BF}_4 \cdot \text{OEt}_3$) (2.6 g, 13.8 mmol, 2 eq) was added to it in Glove Box. The reaction mixture was dissolved in DCM and stirred for 6h at room temperature. Then ethylene diamine (0.2 mL, 3.5 mmol, 0.5 eq.) was added and the reaction mixture was stirred for 24h. After completion of the reaction, the solvent was dried under vacuum. Then the mixture was quenched by 2N NaOH and then the product L8 was extracted in DCM. Then the solvent was dried and the dark brown solid product L8 was collected.

Yield: 76%

^1H NMR (CDCl_3 , 500 MHz): δ 6.66 (m, 4H, CH_{Aryl}), 6.47 (d, 2H, CH_{Aryl}), 6.23 (d, 4H, CH_{Aryl}), 6.13 (s, 2H, NH), 3.82 (septet, 2H, $\text{CH}_{\text{isopropyl}}$), 3.71 (s, 4H, CH_2CH_2), 1.25 (d, 12H, $\text{CH}_{3\text{isopropyl}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 152.99, 150.20, 132.14, 131.62, 116.41, 111.60, 106.82, 47.18, 44.04, 22.07

HRMS (ESI): Calculated for $\text{C}_{22}\text{H}_{30}\text{N}_4$: 351.255 $[\text{M}+\text{H}]^+$, found: 351.257

Synthesis of ligand L9

Reaction Scheme:



Scheme 18. Synthesis of ligand **L9**

Experimental Procedure

2-(isopropylamino)cyclohepta-2,4,6-trien-1-one [**L7**] (0.7 g, 4.3 mmol, 1 eq.) was taken in a Schlenk tube and vacuumed it for 30 minutes. Then Meerwein salt ($\text{BF}_4 \cdot \text{OEt}_3$) (1.6 g, 8.6 mmol, 2 eq) was added to it in Glove Box. The reaction mixture was dissolved in DCM and stirred for 6h at room temperature. Then phenyl-1,4-diamine (0.2 mL, 2.1 mmol, 0.5 eq.) was added and the reaction mixture was stirred for 24h. After completion of the reaction, the solvent was dried under vacuum. Then the mixture was quenched by 2N NaOH and then the product **L10** was extracted in DCM. Then the solvent was dried and the solid product **L9** was collected.

Yield: 79%

^1H NMR (CDCl_3 , 500 MHz): δ 6.66 (m, 4H, CH_{Aryl}), 6.47 (d, 2H, CH_{Aryl}), 6.23 (d, 4H, CH_{Aryl}), 7.64 (s, 2H, NH), 3.82 (septet, 2H, $\text{CH}_{\text{isopropyl}}$), 6.24 (3, 4H, CH_{Aryl}), 1.25 (d, 12H, CH_3 isopropyl).

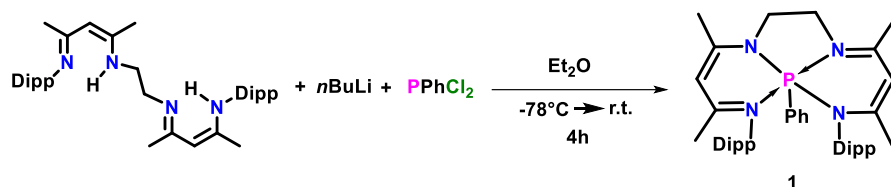
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 155.38, 150.26, 146.49, 133.92, 132.91, 122.21, 120.72, 119.14, 105.04, 43.90, 22.47

HRMS (ESI): Calculated for $\text{C}_{26}\text{H}_{30}\text{N}_4$: 399.255 $[\text{M}+\text{H}]^+$, found: 399.258

SYNTHESIS OF PHOSPHORUS CATIONS

Synthesis of 1

Reaction Scheme:



Scheme 19. Synthesis of **1**

Experimental Procedure:

In a Schlenk tube, **L2** (300 mg, 0.54 mmol, 1eq) was taken and diethyl ether (7 mL) was added. Then the reaction mixture was cooled to -78°C and $n\text{BuLi}$ (0.7 mL, 1.2 mmol, 2.1 eq) was added. Reaction mixture was allowed to warm to room temperature while the stirring was on. This took around 30 minutes (for the reaction mixture to come to room temperature). Then the reaction mixture was stirred for another 1h. Again, the reaction mixture was cooled to -78°C and PPhCl_2 (0.2 mL, 1.1 mmol, 2 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and further stirred for 3h. After being stirred for 3h, liquid from the reaction mixture removed via filter cannula and remaining solid was dried in vacuum to obtain orangish brown solid as a product **1**.

Yield: 76%

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ -48.46 (s)

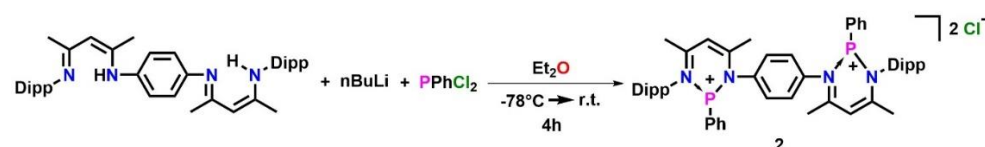
^1H NMR (CDCl_3 , 500 MHz): δ 7.7 (d, 2H, $J=7.2$, $\text{CH}_{\text{Phenyl}}$), 7.3-7.2(m, 3H, CH_{Aryl}), 7.2(d, 4H, $J=7.6$, CH_{Aryl}), 7.1(t, 2H, CH_{Aryl}), 5.1(s, 2H, $\text{CH}_{\text{Pentene}}$), 3.7(s, 4H, $\text{CH}_{\text{Ethylene}}$), 2.91(sept, 4H, CH_{Dipp}), 2.25(s, 6H, CH_3), 1.75(s, 6H, CH_3), 1.25(d, $J=6.9$ Hz, 12H, $\text{CH}_{3\text{Dipp}}$), 1.14(d, $J=6.9$ Hz, 12H, $\text{CH}_{3\text{Dipp}}$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 164.38, 163.77, 145.96, 137.6, 135.95, 130.36, 128.10, 127.58, 95.90, 94.49, 45.18, 28.38, 24.66, 21.07, 19.79.

HRMS (ESI): Calculated for $\text{C}_{42}\text{H}_{57}\text{N}_4\text{P}$: 649.4399 $[\text{M}+\text{H}]^+$, found: 649.4402

Synthesis of 2

Reaction Scheme:



Scheme 20. Synthesis of 2

Experimental Procedure:

In a Schlenk tube, **L3** (300 mg, 0.54 mmol, 1 eq) was taken and diethyl ether (7 mL) was added. Then the reaction mixture was cooled to -78°C and *n*BuLi (0.7 mL, 1.07 mmol, 2.1 eq) was added. Reaction mixture was allowed to warm to room temperature while the stirring was on. This took around 30 minutes (for the reaction mixture to come to room temperature). Then the reaction mixture was stirred for another 1h. Again the reaction mixture was cooled to -78°C and PPhCl_2 (0.2 mL, 1.1 mmol, 2 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and further stirred for 3h. After being stirred for 3h, liquid from the reaction mixture removed via filter cannula and remaining solid was dried in vacuum to obtain yellow solid as a product **2**.

Yield: 78%

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 161.29 (s)

^1H NMR (CDCl_3 , 500 MHz): δ 7.7 (d, 4H, $\text{CH}_{\text{Phenyl}}$), 7.3 (t, 4H, CH_{Aryl}), 7.32-7.31 (m, 4H, CH_{Aryl}), 7.2 (d, 4H, CH_{Aryl}), 7.1 (t, 2H, CH_{Aryl}), 5.3 (s, 2H, $\text{CH}_{\text{Pentene}}$), 3.0 (sept, 4H, CH_{Dipp}), 1.95 (s, 6H, CH_3), 1.86 (s, 6H, CH_3), 1.27 (d, 12H, $\text{CH}_3_{\text{Dipp}}$), 1.21 (d, $J=6$, 12H, $\text{CH}_3_{\text{Dipp}}$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 164.99, 145.77, 137.58, 130.34, 129.14, 128.33, 128.03, 127.56, 124.14, 94.47, 28.41, 24.68, 24.58, 21.57, 21.45, 21.34

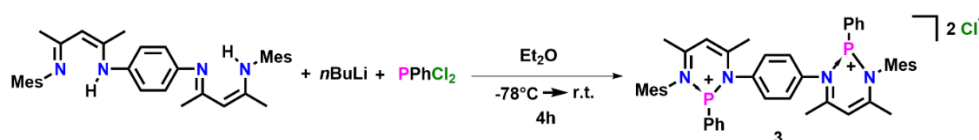
HRMS (ESI):

For $[\text{M}]^+$ Calculated for $\text{C}_{52}\text{H}_{62}\text{N}_4\text{P}_2$: 805.4528, found: 805.4546

For $[\text{M}/2]^+$ Calculated for $\text{C}_{52}\text{H}_{62}\text{N}_4\text{P}_2$: 403.2303, found: 403.2312

Synthesis of 3

Reaction Scheme:



Scheme 21. Synthesis of 3

Experimental Procedure:

In a Schlenk tube, **L5** (300 mg, 0.6 mmol, 1 eq.) was taken and diethyl ether (15 mL) was added. Then the reaction mixture was cooled to -78°C and $n\text{BuLi}$ (0.6 mL, 1.2 mmol, 2.1 eq) was added. Reaction mixture was allowed to warm to room temperature while the stirring was on. This took around 30 minutes (for the reaction mixture to come to room temperature). The reaction mixture was stirred for another 1h. Again, the reaction mixture was cooled to -78°C and PPhCl_2 (0.2 mL, 1.2 mmol, 2 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and further stirred for 3h. After being stirred for 3h, liquid from the reaction mixture removed via filter cannula and remaining solid was dried in vacuum to obtain yellow solid as product **3**.

Yield: 76%

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 160.23 (s)

^1H NMR (CDCl_3 , 500 MHz): δ 12.32 (s, 2H, NH), 6.70 (s, 4H, $\text{CH}_{\text{Phenyl}}$), 6.87 (s, 4H, CH_{Mesl}) 4.85 (s, 2H, $\text{CH}_{\text{Pentene}}$), 2.32 (s, 6H, CH_3), 2.18 (s, 12H, CH_3_{Mes}), 2.14 (s, 6H, CH_3_{Mes}), 1.63 (s, 3H, CH_3)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 161.52, 157.32, 143.58, 138.74, 132.93, 128.42, 122.23, 94.60, 19.90, 19.75, 19.46, 19.58, 19.52, 17.64, 14.42

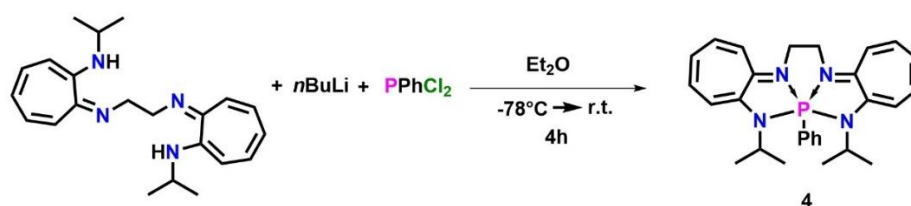
HRMS (ESI):

For $[\text{M}]^+$ Calculated for $\text{C}_{46}\text{H}_{50}\text{N}_4\text{P}_2$: 721.359, found: 721.359

For $[\text{M}/2]^+$ Calculated for $\text{C}_{46}\text{H}_{50}\text{N}_4\text{P}_2$: 361.183, found: 361.181

Synthesis of 4

Reaction Scheme:



Scheme 22. Synthesis of **4**

Experimental Procedure:

In a Schlenk tube, **L8** (381 mg, 1.1 mmol, 1 eq.) was taken and diethyl ether (7 mL) was added. Then the reaction mixture was cooled to -78°C and $n\text{BuLi}$ (1.4 mL, 2.3 mmol, 2.1 eq) was added. Reaction mixture was allowed to warm to room temperature while the stirring was on. This took around 30 minutes (for the reaction mixture to come to room temperature). Then the reaction mixture was stirred for another 1h. Again the reaction mixture was cooled to -78°C and PPhCl_2 (0.3 mL, 2.2 mmol, 2 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and further stirred for 3h. After being stirred for 3h, liquid from the reaction mixture removed via filter cannula and remaining solid was dried in vacuum to obtain orangish yellow solid as a product **4**.

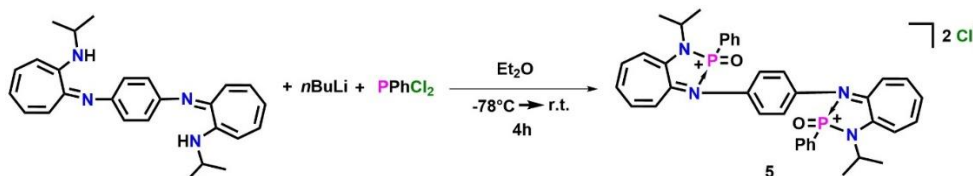
Yield: 71%

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ -49.85 (s)

HRMS (ESI): For $[\text{M}]^+$ Calculated for $\text{C}_{28}\text{H}_{33}\text{N}_4\text{P}$: 457.252, found: 457.253

Synthesis of 5

Reaction Scheme:



Scheme 23. Synthesis of **5**

Experimental Procedure:

In a Schlenk tube, **L9** (150 mg, 0.38 mmol, 1 eq) was taken and diethyl ether (7 mL) was added. Then the reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and $n\text{BuLi}$ (0.4 mL, 0.8 mmol, 2.1 eq) was added. Reaction mixture was allowed to warm to room temperature while the stirring was on. This took around 30 minutes (for the reaction mixture to come to room temperature). Then the reaction mixture was stirred for another 1h. Again the reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and PPhCl_2 (0.1 mL, 0.75 mmol, 2 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature and further stirred for 3h. After being stirred for 3h, liquid from the reaction mixture removed via filter cannula and remaining solid was dried in vacuum to obtained olive green solid as product **5**.

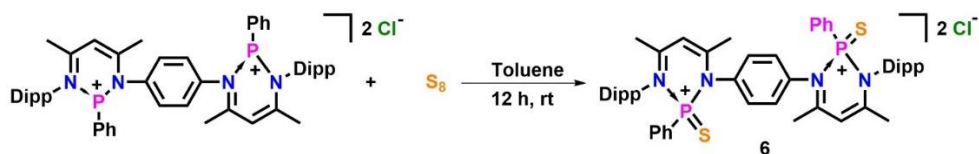
Yield: 74%

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 160.77 (s), 85.21 (s)

HRMS (ESI): For $[\text{M}]^+$ Calculated for $\text{C}_{38}\text{H}_{38}\text{N}_4\text{P}_2\text{O}_2$: 645.255, found: 645.265

REACTIVITY OF PHOSPHORUS CATIONS

1. With elemental S₈



Scheme 24. Synthesis of complex **6**

Experimental Procedure:

In a J Young NMR tube, **2** (40 mg, 0.05 mmol, 1 eq) and elemental sulphur (3.2 mg, 0.01 mmol, 0.25 eq) were taken and then toluene was added to the reaction mixture. The entire reaction was performed in the J Young NMR tube inside the Glove Box. This led to the formation of product **6**.

³¹P{¹H} NMR: δ 73.64 (s)

¹H NMR (CDCl₃, 500 MHz): δ 7.7 (d, 4H, CH_{Phenyl}), 7.3(t, 4H, CH_{Aryl}), 7.32-7.31(m, 4H, CH_{Aryl}), 7.2(d, 4H, CH_{Aryl}), 7.1(t, 2H, CH_{Aryl}), 5.3(s, 2H, CH_{Pentene}), 3.0(sept, 4H, CH_{Dipp}), 1.95(s, 6H, CH₃), 1.86(s, 6H, CH₃), 1.27(d, 12H, CH_{3Dipp}), 1.21(d, 12H, CH_{3Dipp})

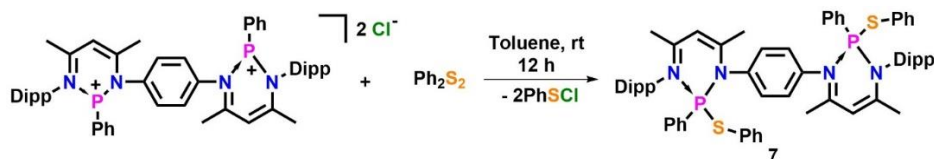
¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 164.99, 145.77, 137.58, 130.34, 129.14, 128.33, 128.03, 127.56, 124.14, 94.47, 28.41, 24.68, 24.58, 21.57, 21.45, 21.34

HRMS (ESI):

For [M]⁺ Calculated for C₅₂H₆₂N₄P₂S₂: 869.3969, found: 869.3961

For [M/2]⁺ Calculated for C₅₂H₆₂N₄P₂S₂: 435.2024, found: 435.2039

2. With elemental Ph₂S₂



Scheme 25. Synthesis of **7**

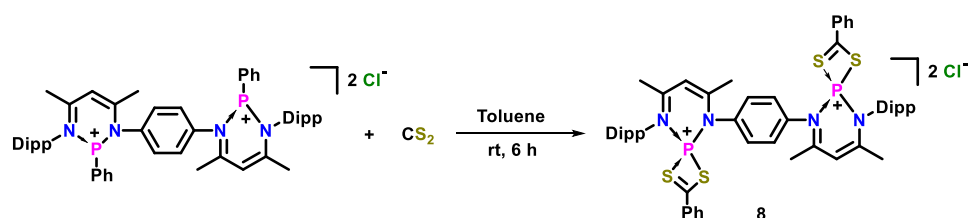
Experimental Procedure:

In a J Young NMR tube, **2** (50 mg, 0.06 mmol, 1 eq) and diphenyl disulphide (27 mg, 0.12 mmol, 2 eq) were taken and then toluene was added. After that, toluene was added to the reaction mixture. The entire reaction was performed in J Young NMR tube inside the Glove Box. This led to the formation of product **7**.

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 139.32 (s)

HRMS (ESI): Calculated for $\text{C}_{64}\text{H}_{72}\text{N}_4\text{P}_2\text{S}_2$: 1022.4673 $[\text{M}]^+$, found: 1022.4591.

3. With elemental CS_2



Scheme 26. Synthesis of **8**

Experimental Procedure:

In a J Young NMR tube, to the solution of **2** (40 mg, 0.05 mmol, 1 eq) in toluene, carbon disulphide (0.01 ml, 0.01 mmol, 2 eq) was added. We are expecting the formation of **8**.

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 160.96 (s), 92.92 (s)

NMR SPECTRA

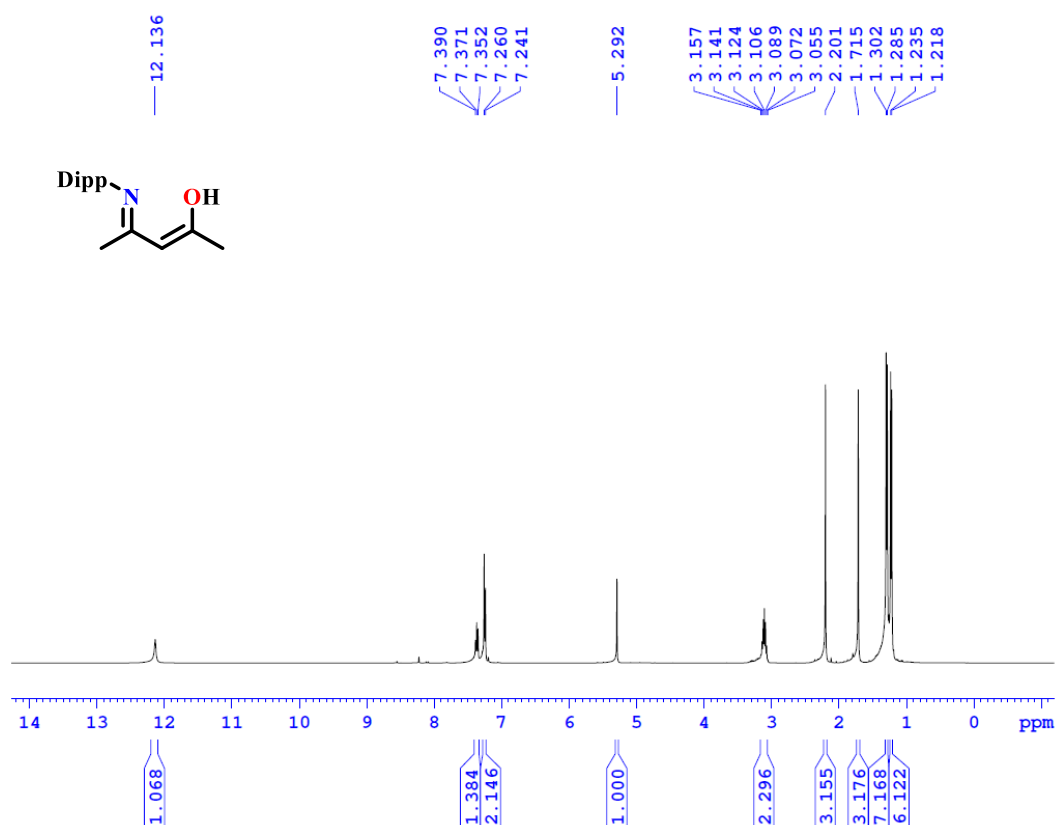


Figure 3. ¹H NMR of ligand **L1** recorded in CDCl₃

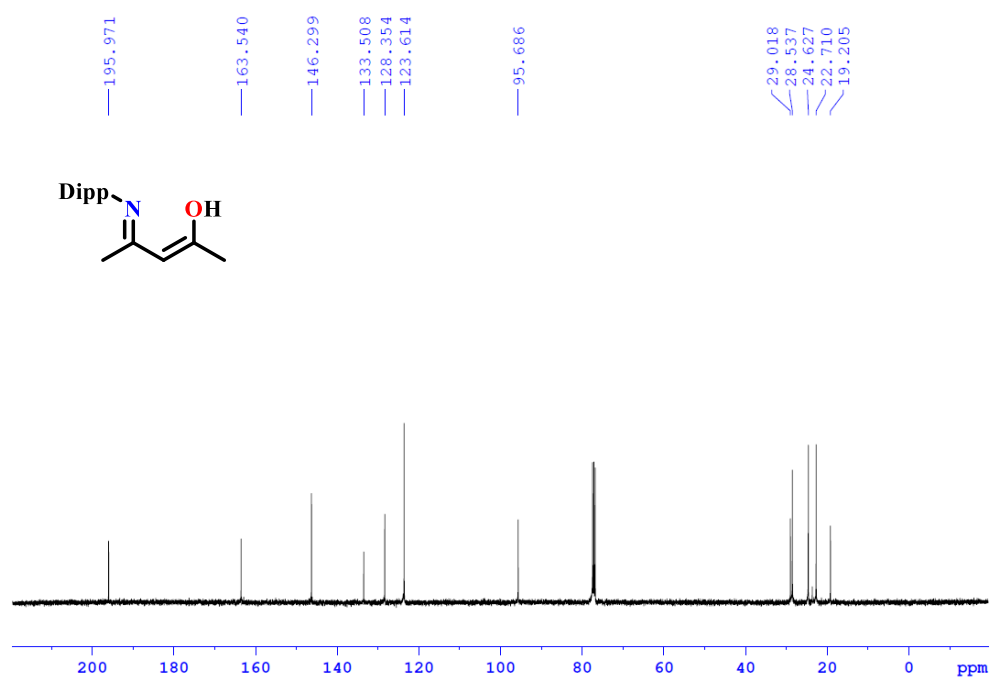


Figure 4. ¹³C{¹H} NMR of ligand **L1** recorded in CDCl₃

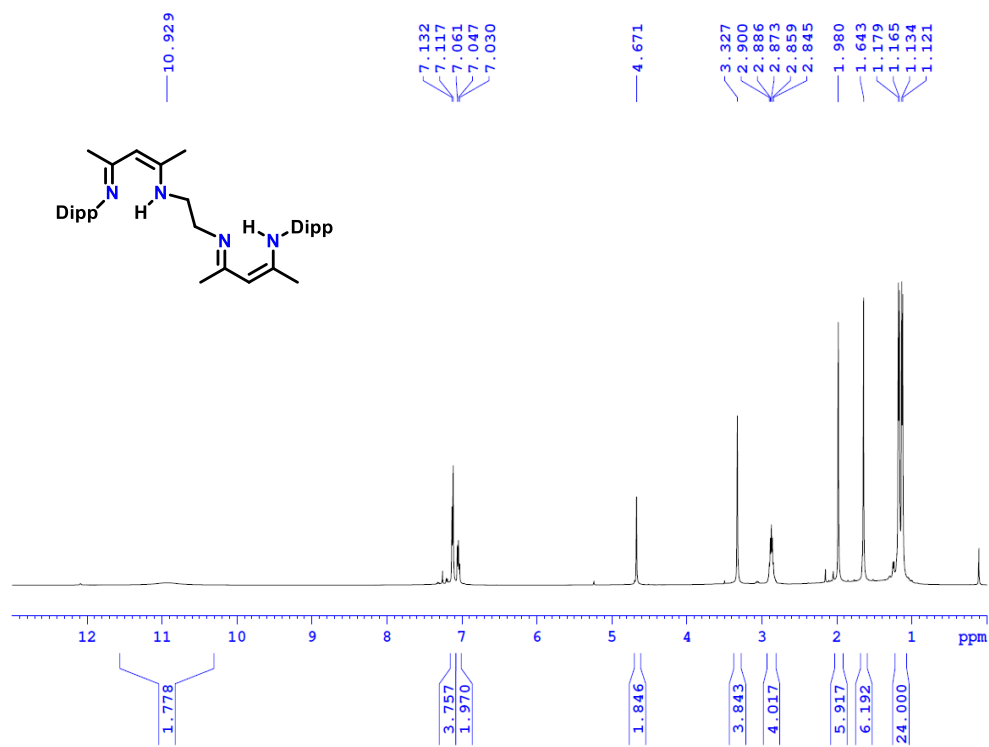


Figure 5. ¹H NMR of ligand **L2** recorded in CDCl₃

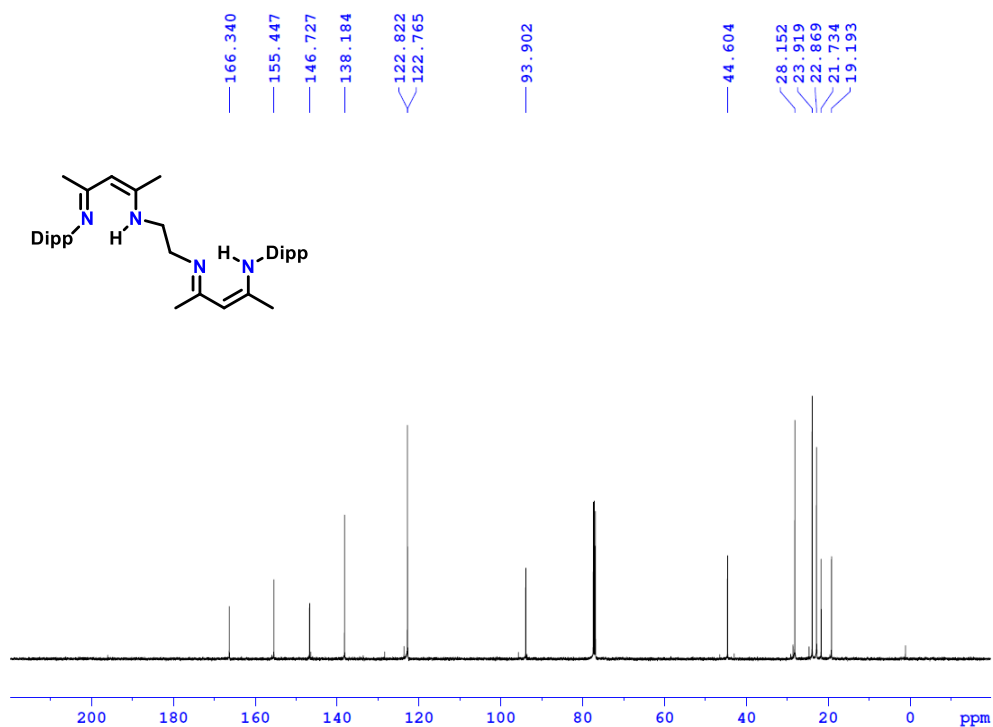


Figure 6. ¹³C{¹H} NMR of ligand **L2** recorded in CDCl₃

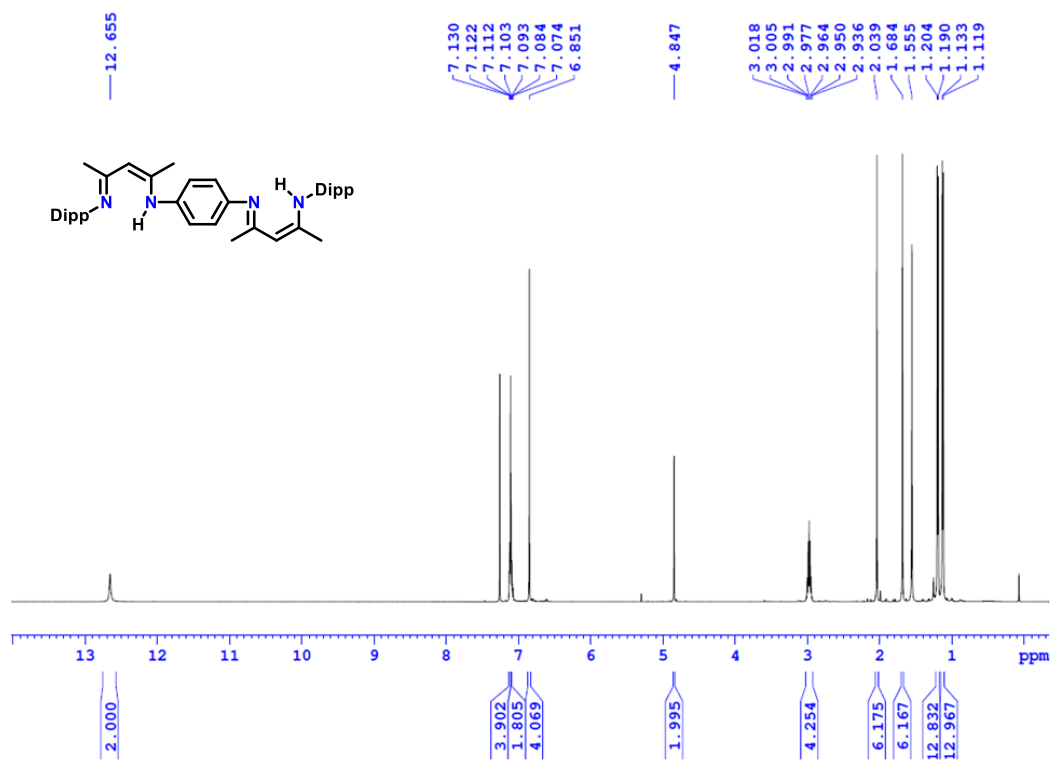


Figure 7. ¹H NMR of ligand **L3** recorded in CDCl₃

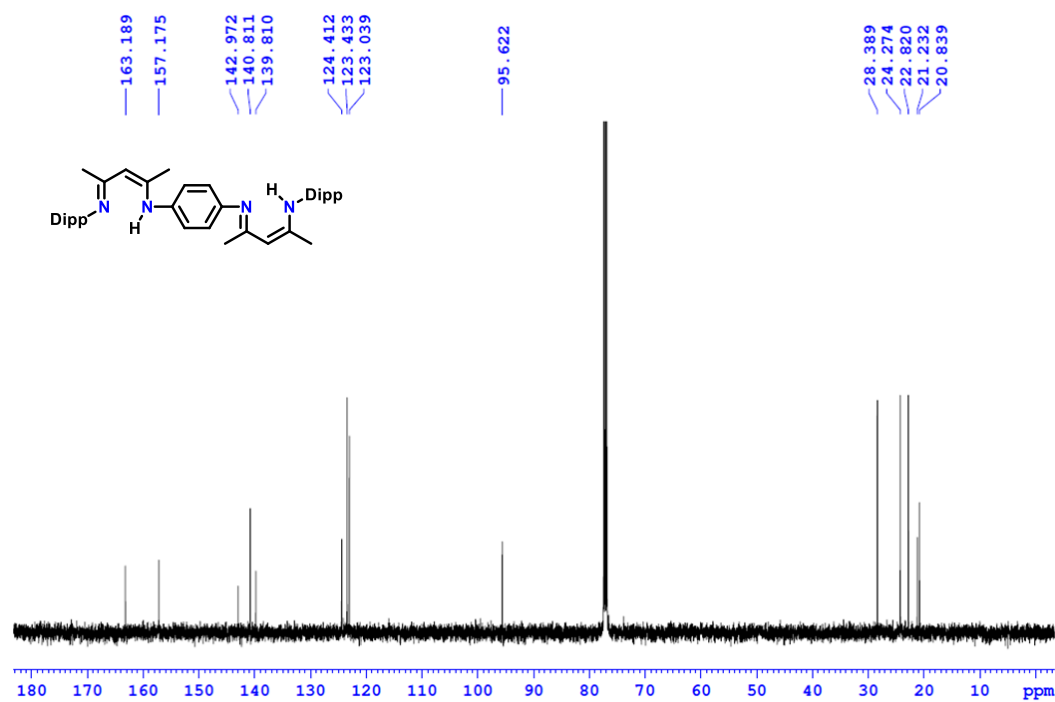


Figure 8. ¹³C{¹H} NMR of ligand **L3** recorded in CDCl₃

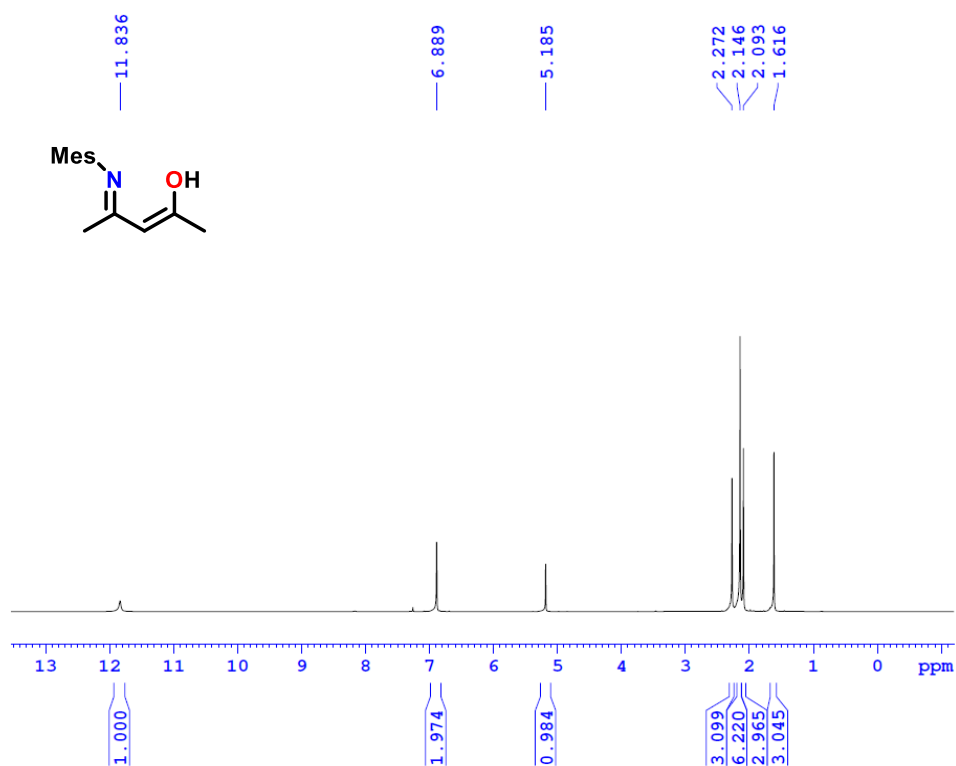


Figure 9. ¹H NMR of ligand **L4** recorded in CDCl₃

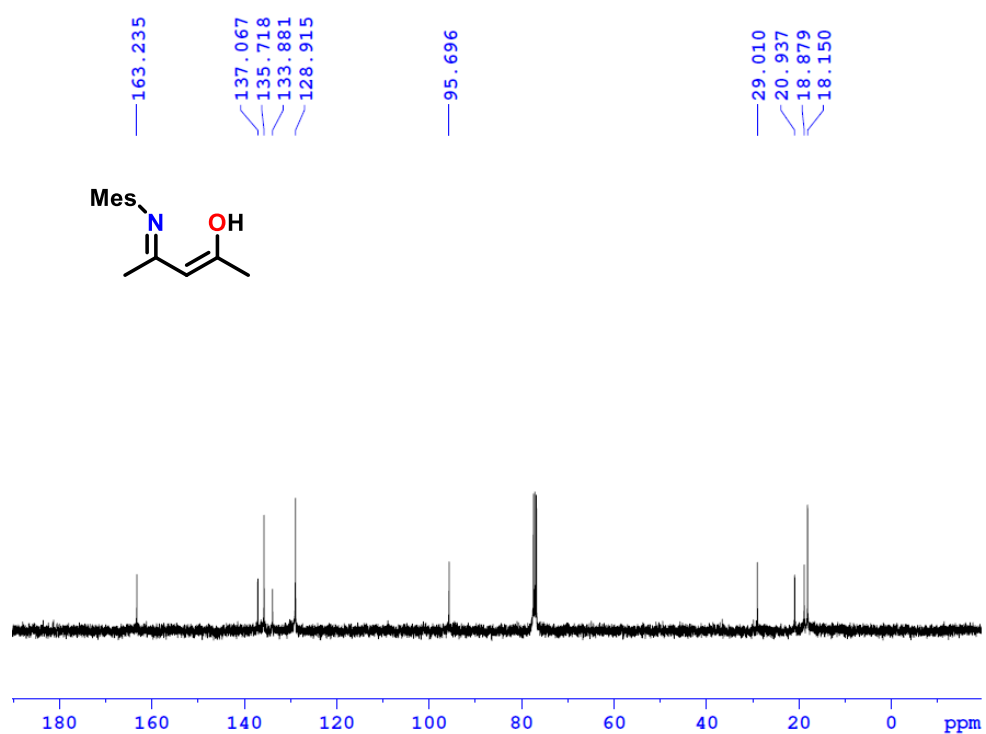


Figure 10. ¹³C{¹H} NMR of ligand **L4** recorded in CDCl₃

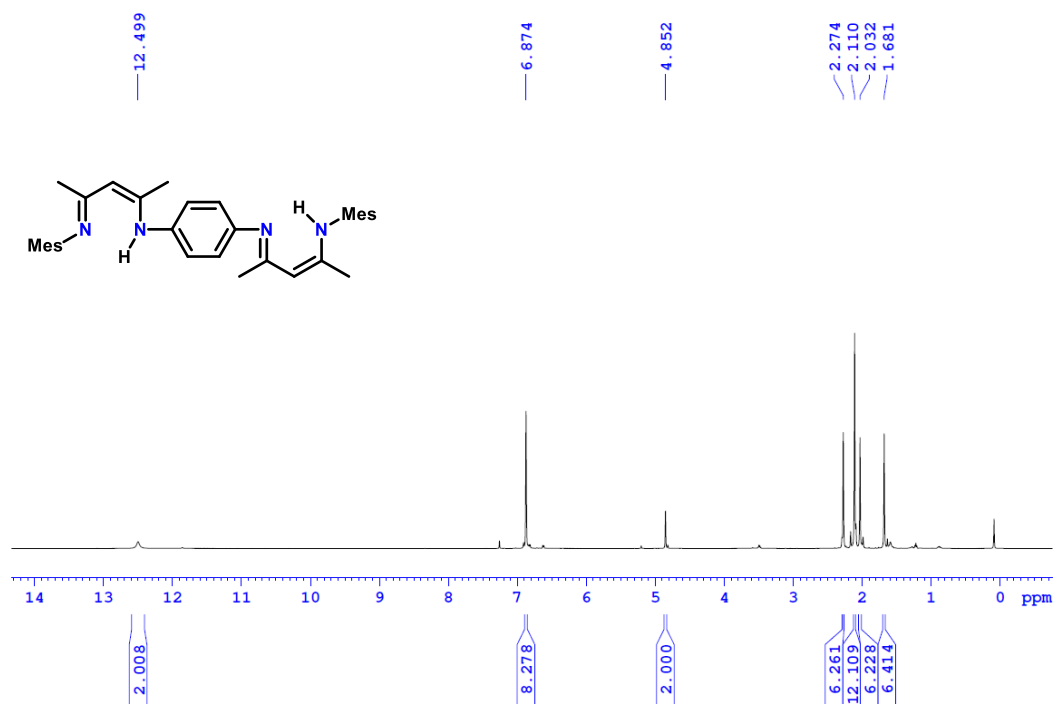


Figure 11. ^1H NMR of ligand **L5** recorded in CDCl_3

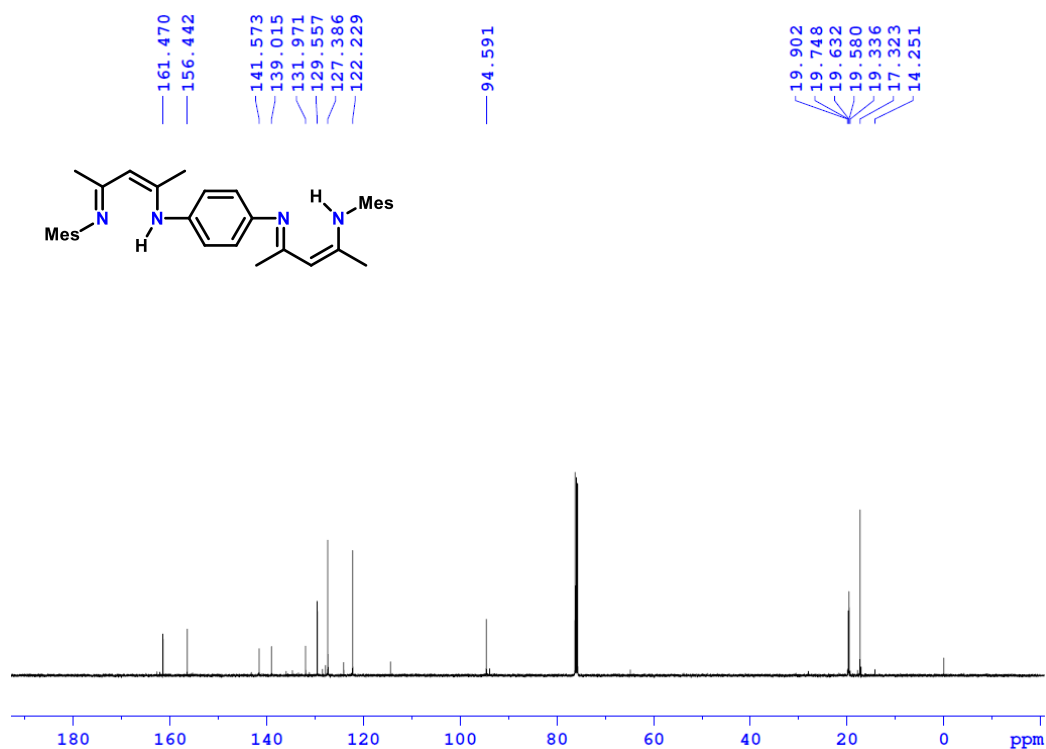


Figure 12. $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L5** recorded in CDCl_3

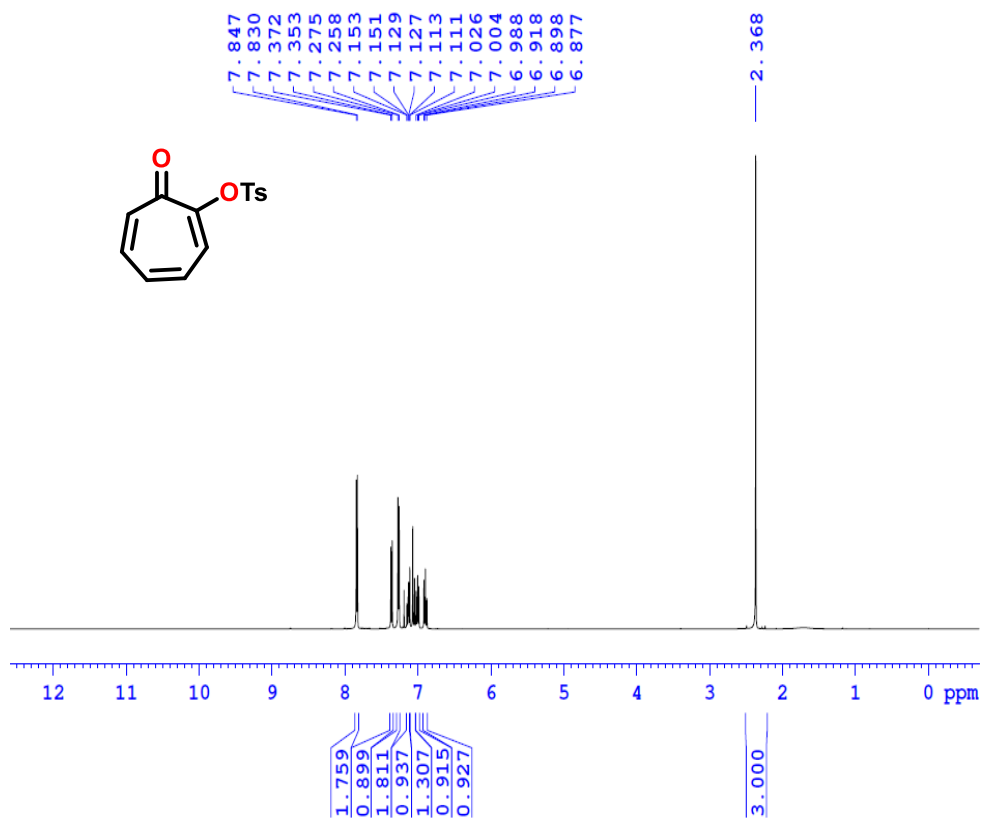


Figure 13. ¹H NMR of ligand **L6** recorded in CDCl₃

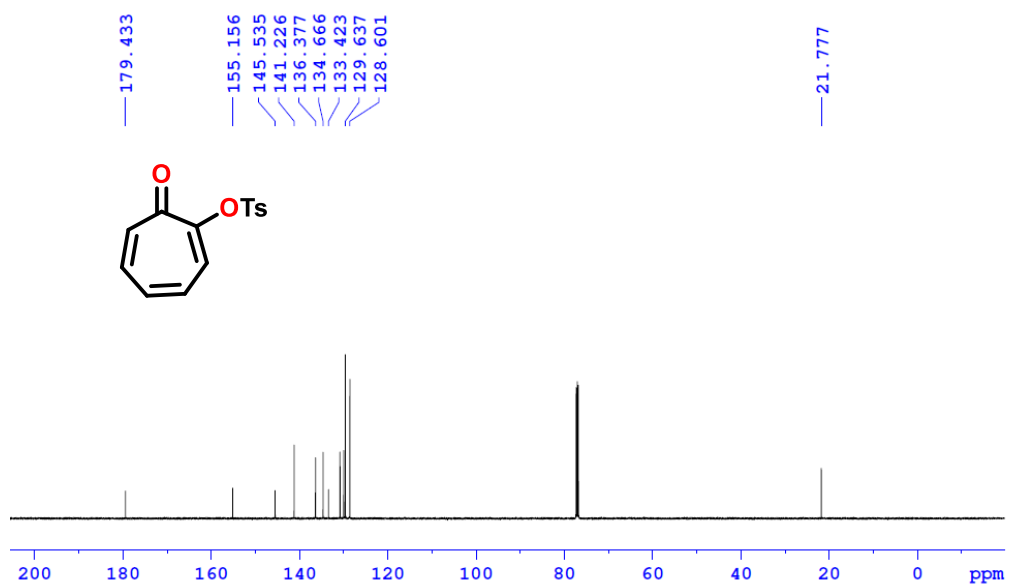


Figure 14. ¹³C{¹H} NMR of ligand **L6** recorded in CDCl₃

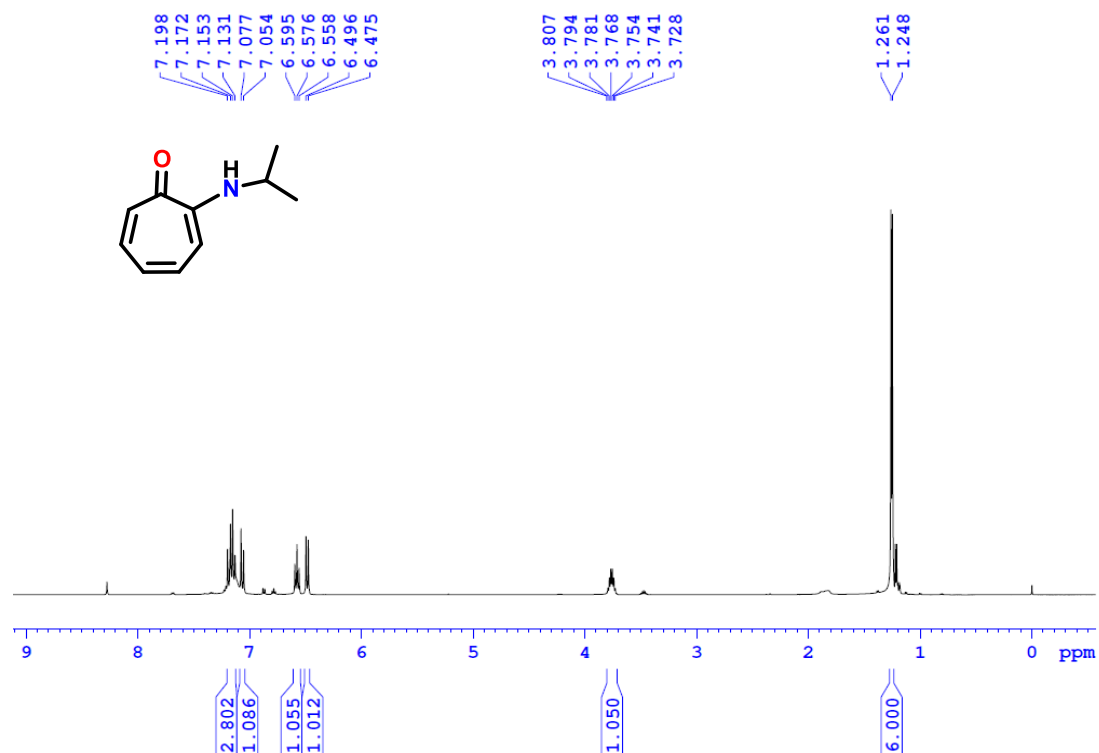


Figure 15. ¹H NMR of ligand L7 recorded in CDCl₃

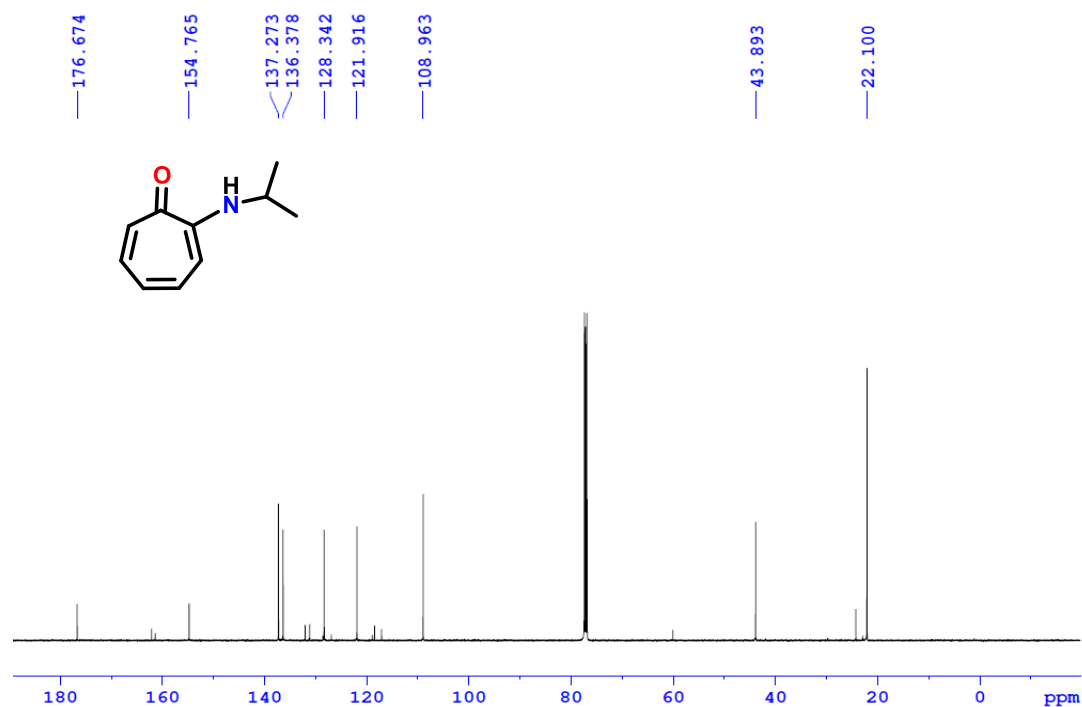


Figure 16. ¹³C{¹H} NMR of ligand L7 recorded in CDCl₃

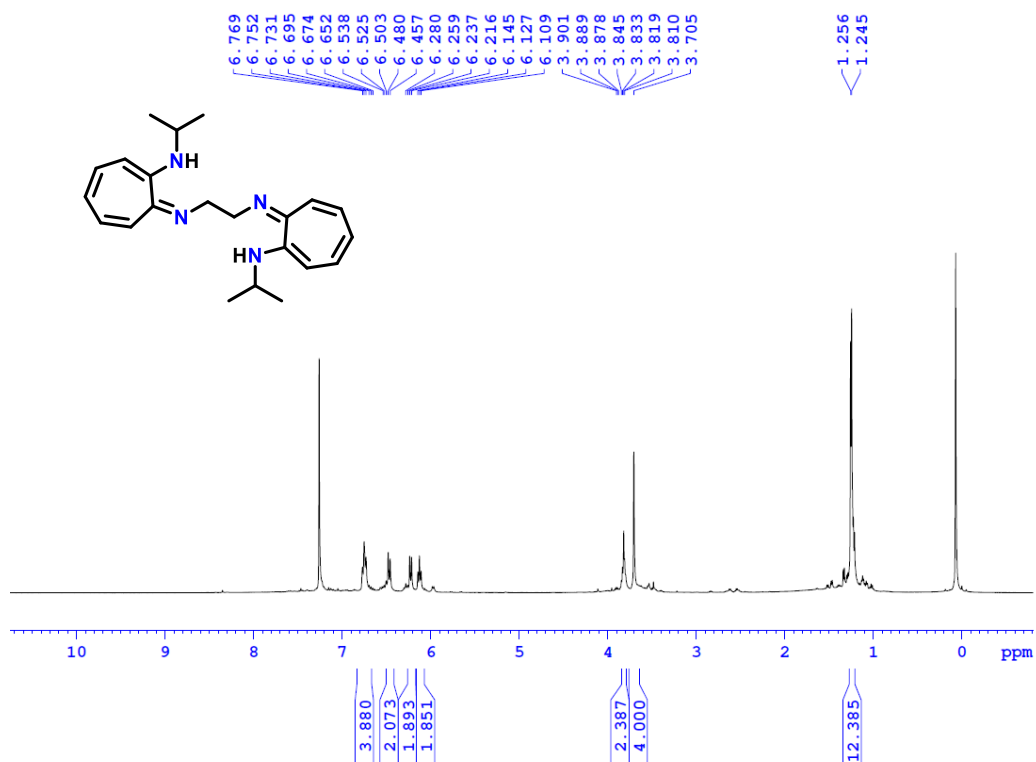


Figure 17. ^1H NMR of ligand **L8** recorded in CDCl₃

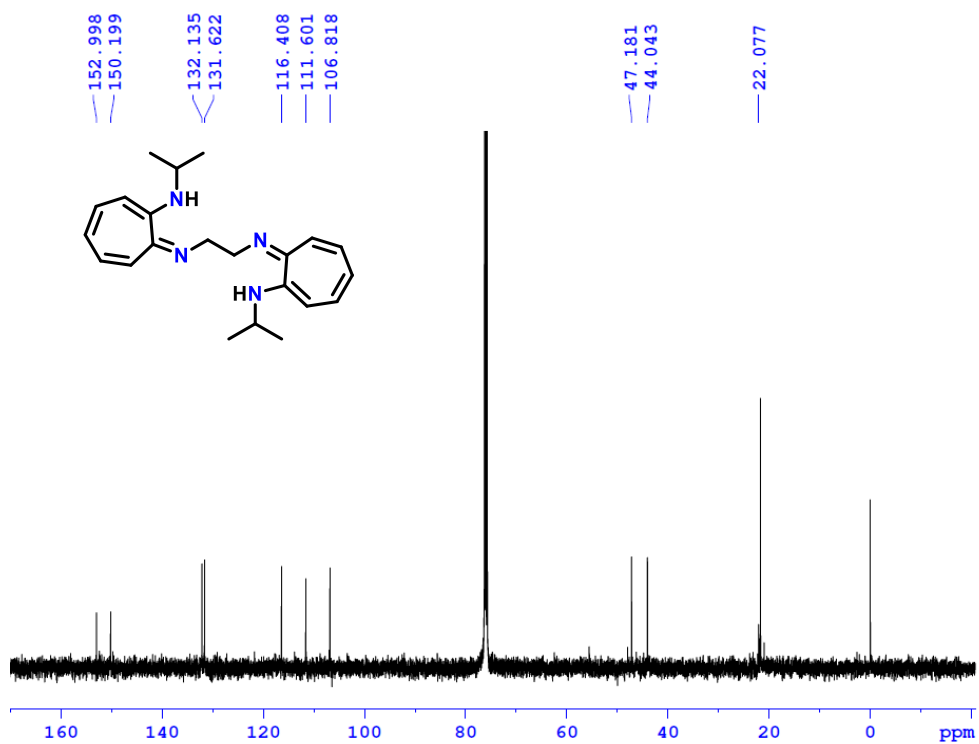


Figure 18. $^{13}\text{C}\{^1\text{H}\}$ NMR of ligand **L8** recorded in CDCl₃

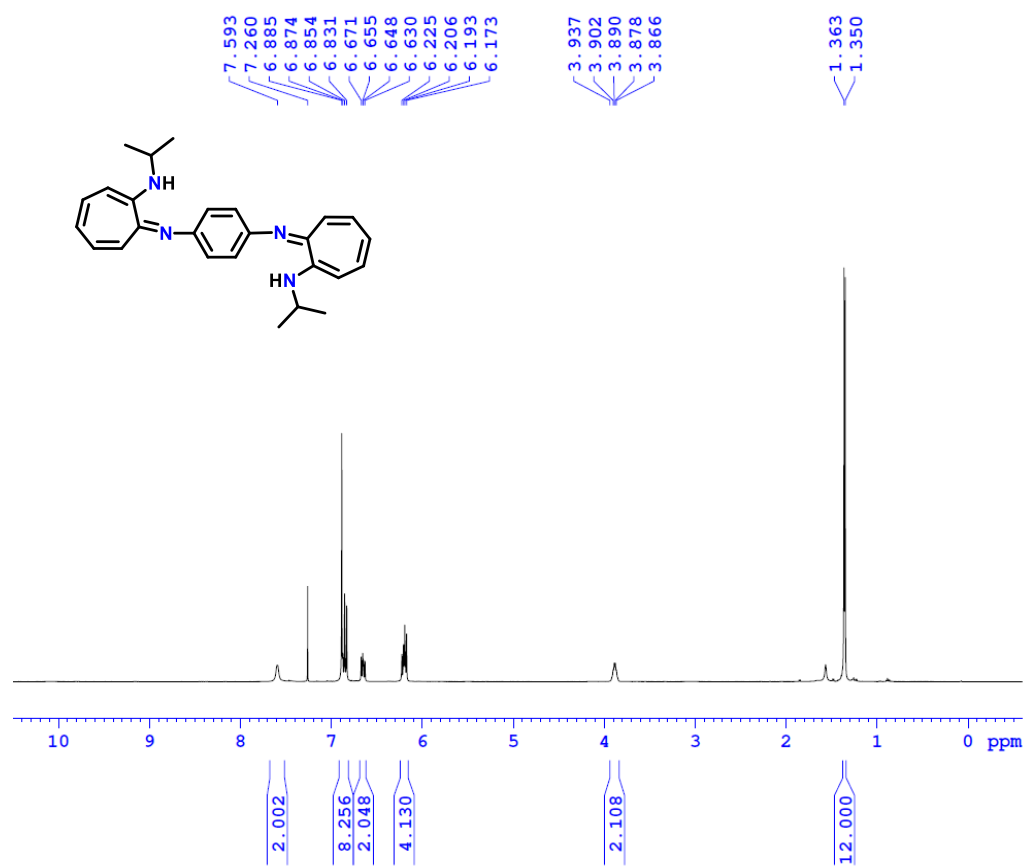


Figure 19. ¹H NMR of ligand L9 recorded in CDCl₃

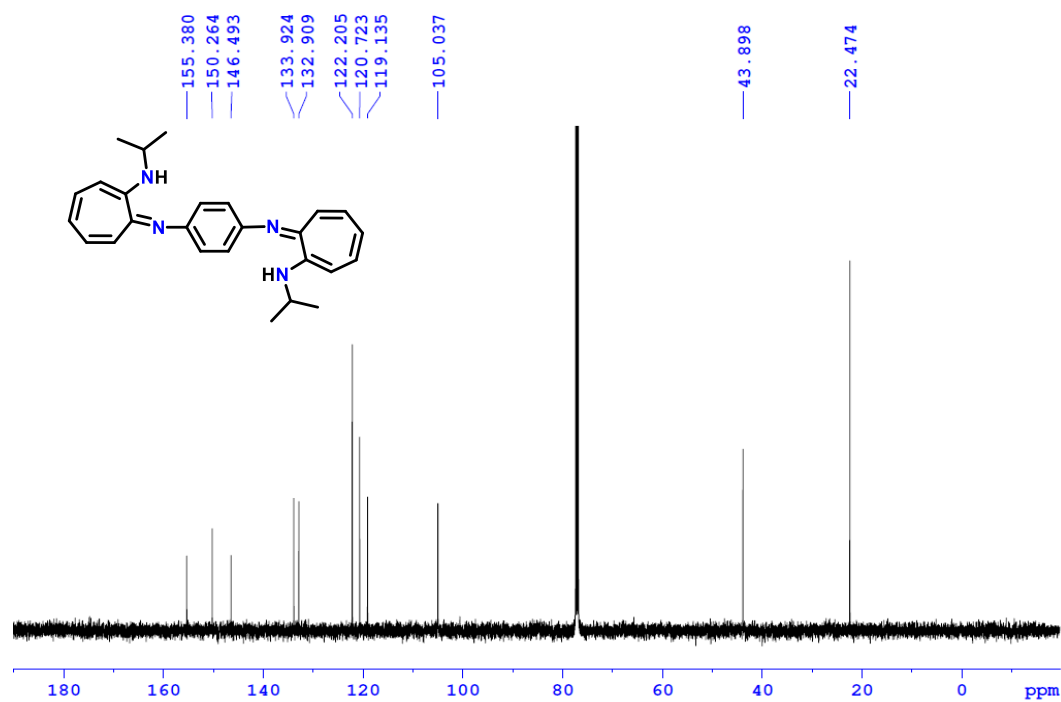


Figure 20. ¹³C{¹H} NMR of ligand L9 recorded in CDCl₃

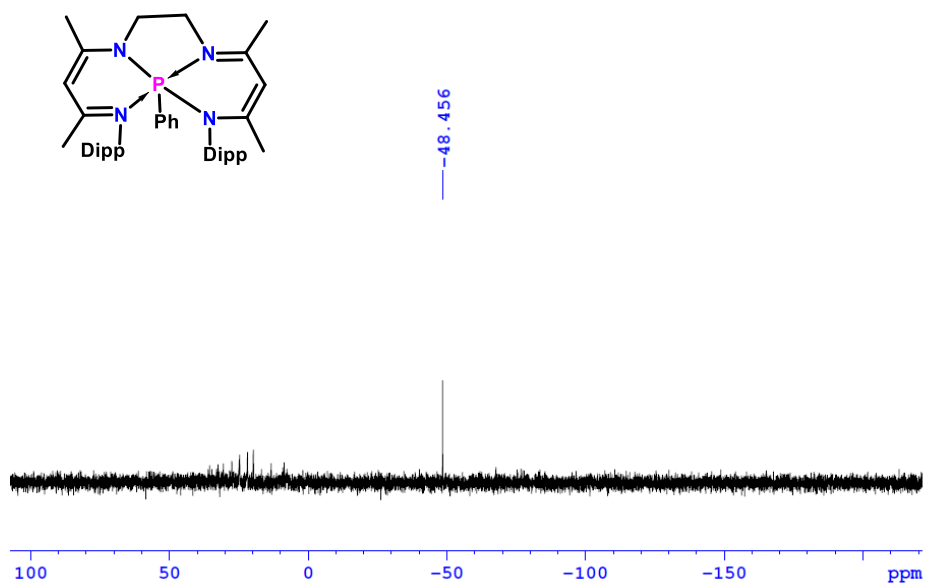


Figure 21. $^{31}\text{P}\{^1\text{H}\}$ NMR of **1** recorded in CDCl_3

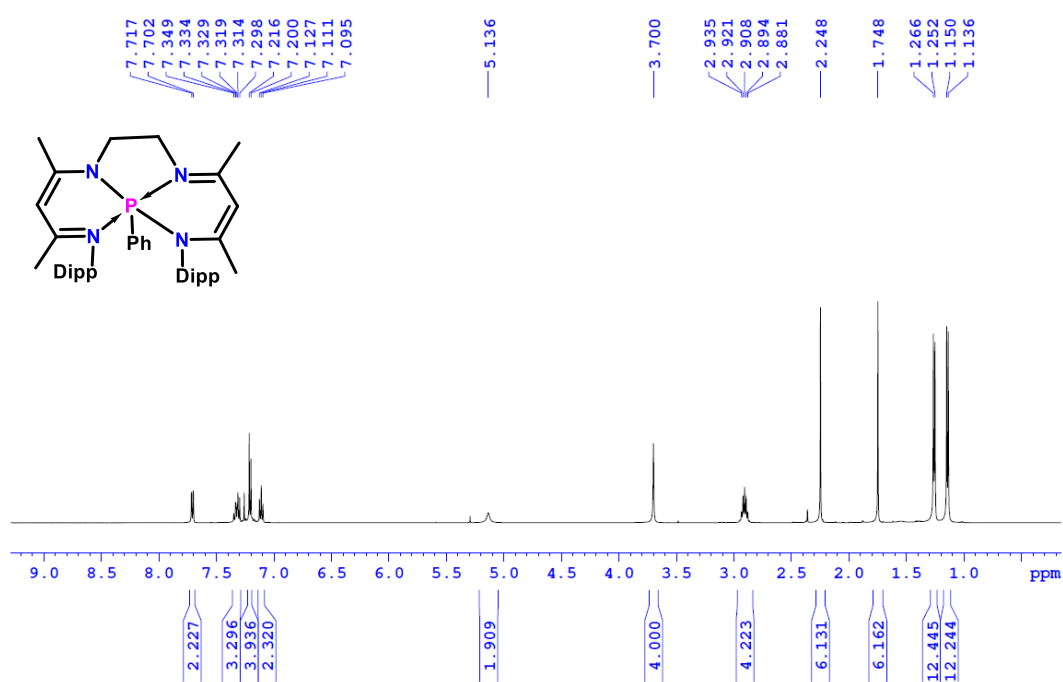


Figure 22. ^1H NMR of **1** recorded in CDCl_3

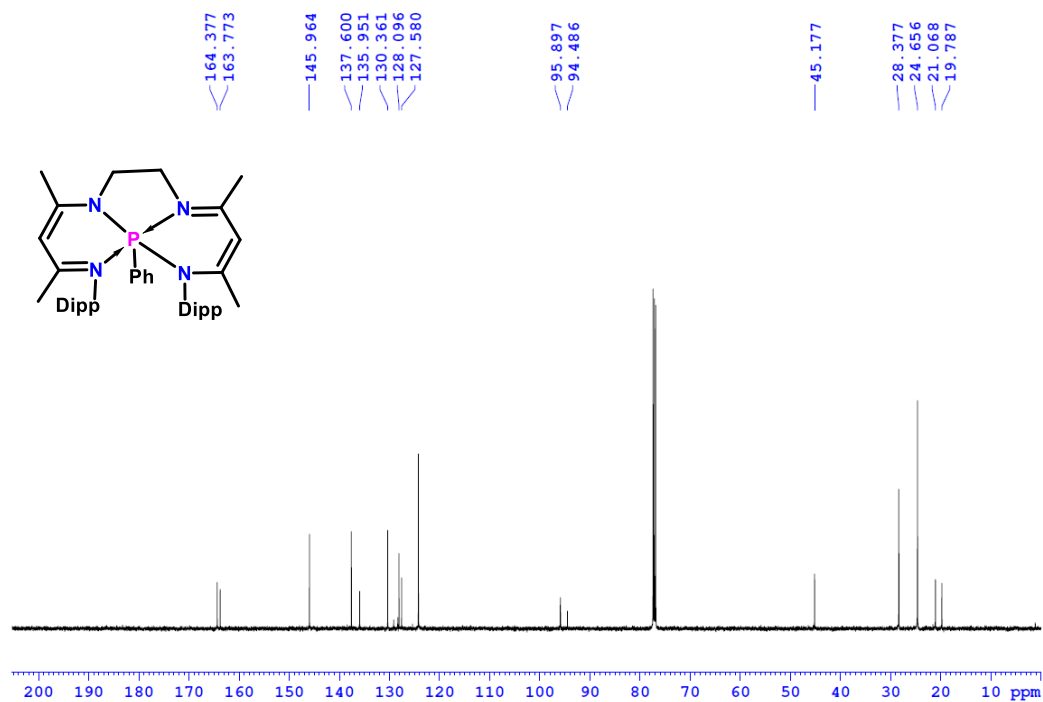


Figure 23. $^{13}\text{C}\{^1\text{H}\}$ NMR of **1** recorded in CDCl_3 .

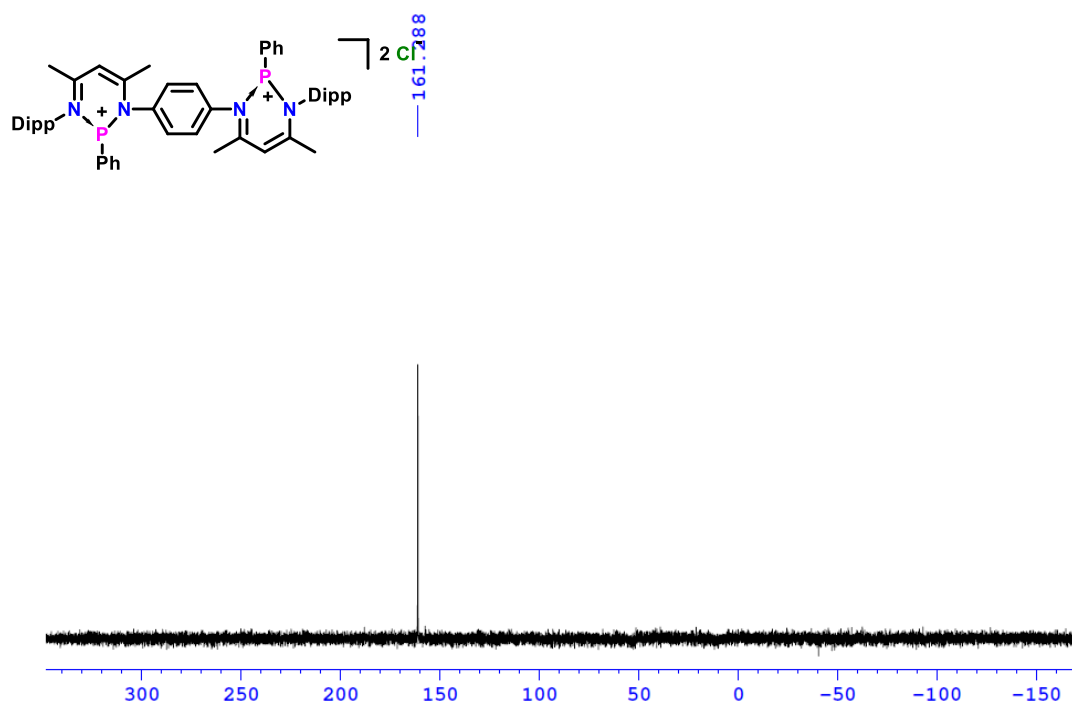


Figure 24. $^{31}\text{P}\{^1\text{H}\}$ NMR of **2** recorded in CDCl_3 .

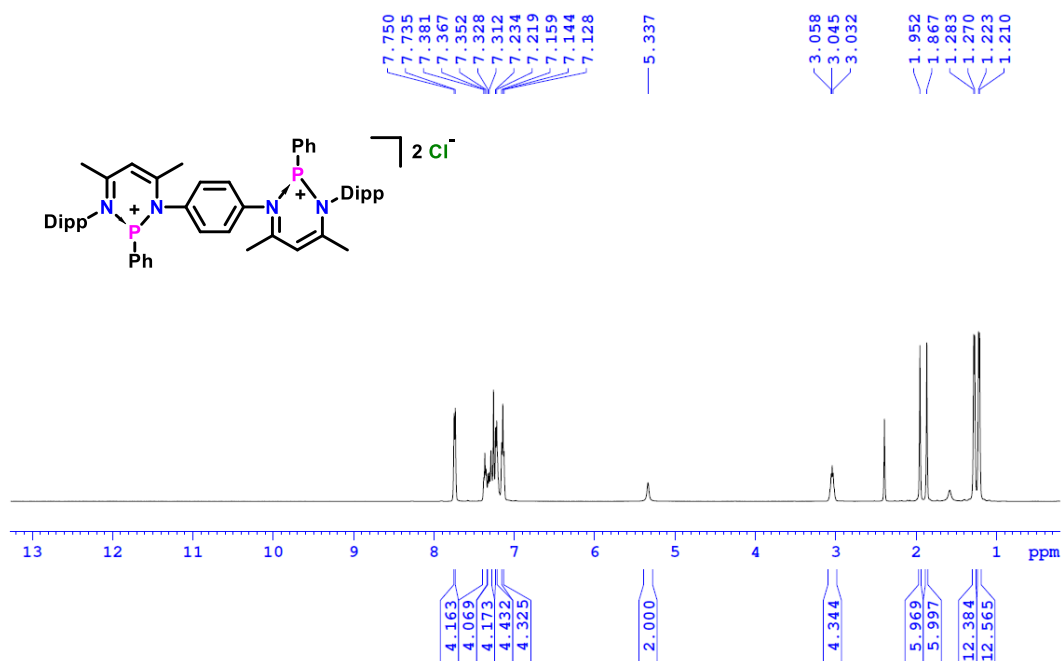


Figure 25. ^1H NMR of **2** recorded in CDCl_3 .

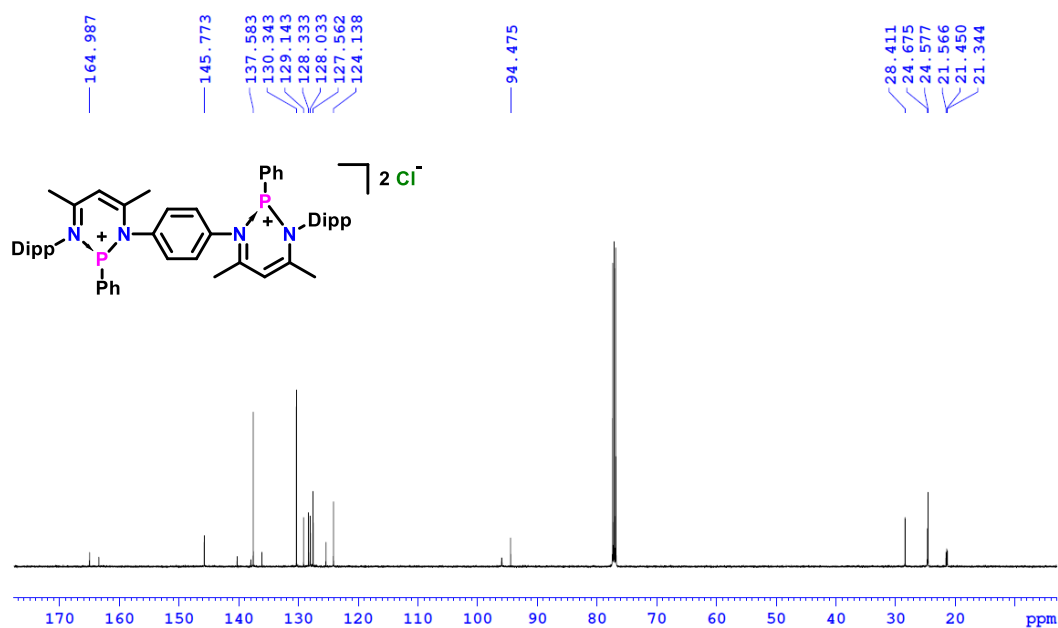


Figure 26. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2** recorded in CDCl_3 .

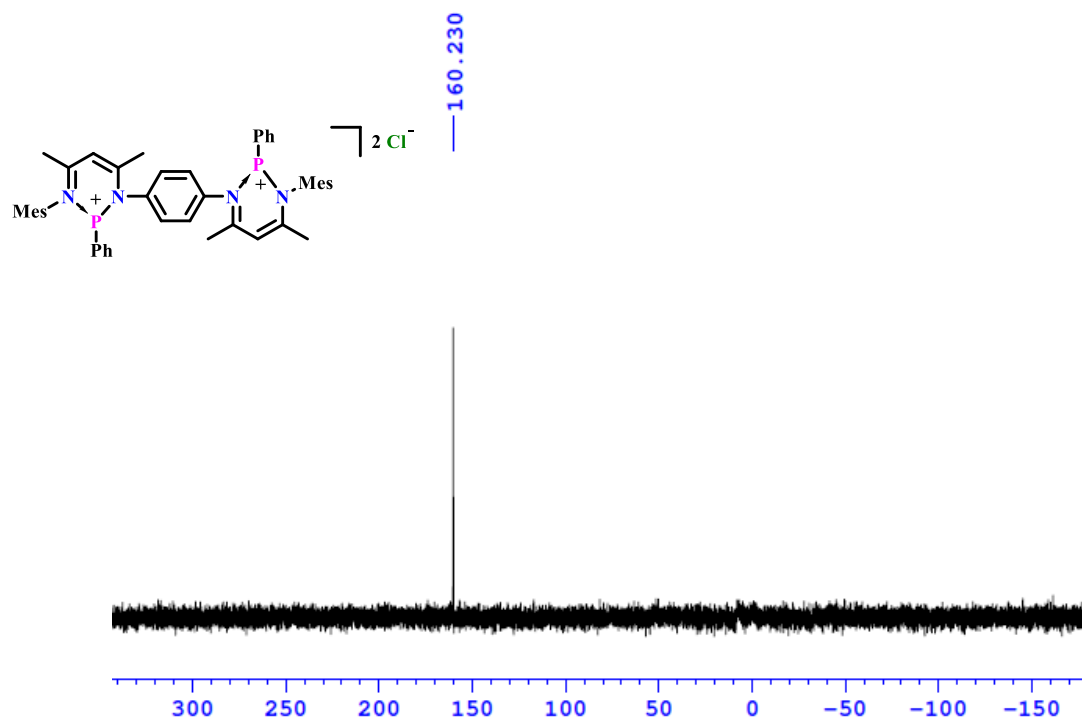


Figure 27. $^{31}\text{P}\{^1\text{H}\}$ NMR of **3** recorded in CDCl_3

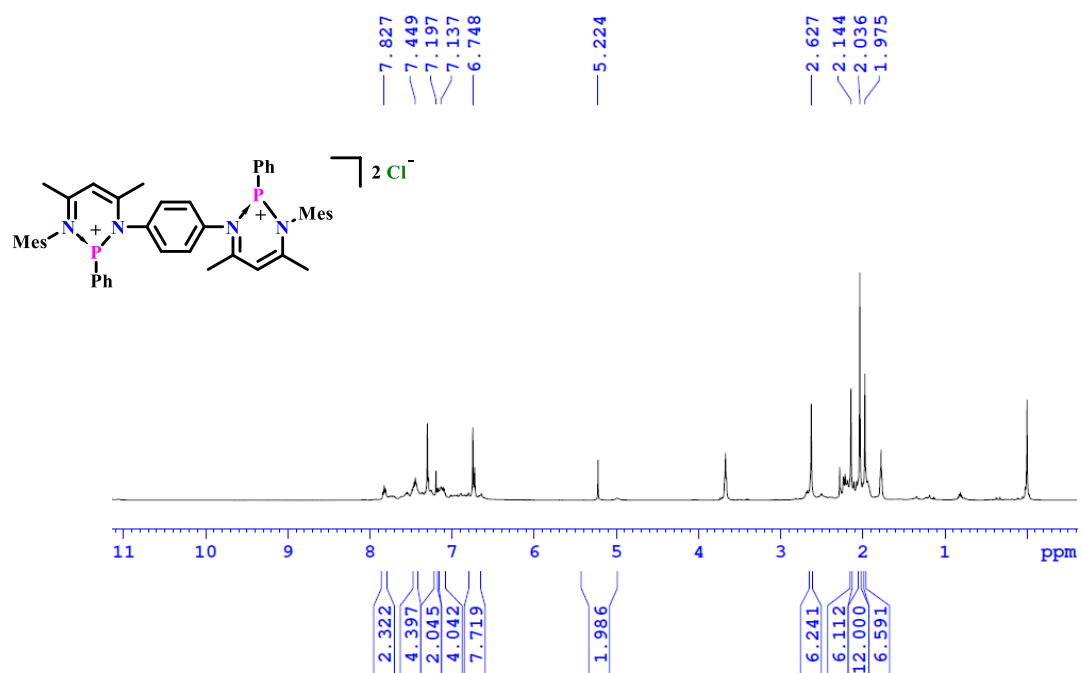
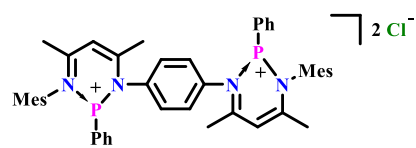


Figure 28. ^1H NMR of **3** recorded in CDCl_3 .

[illegible]

52

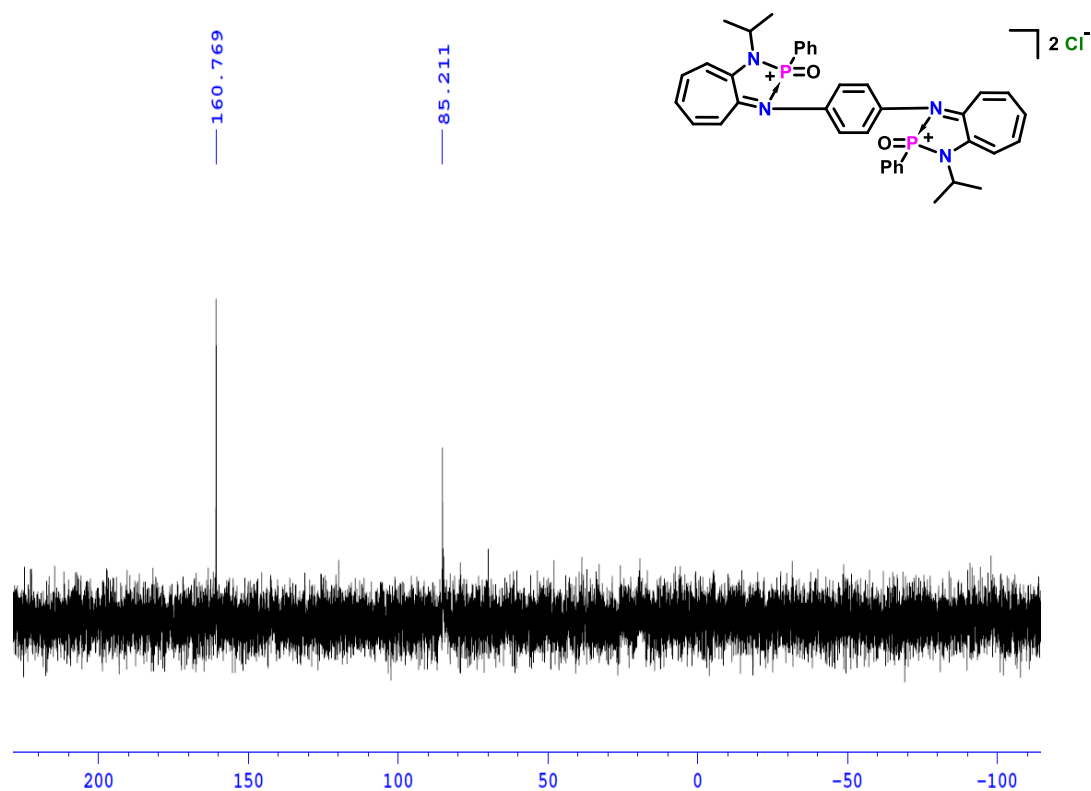


Figure 31. $^{31}\text{P}\{^1\text{H}\}$ NMR of **5** recorded in Toluene

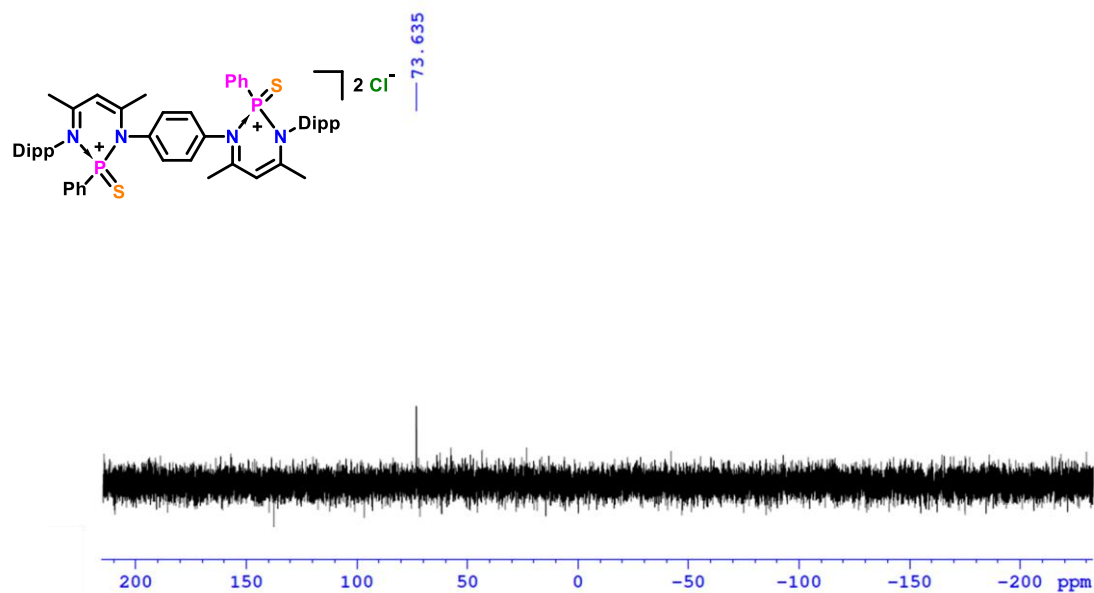


Figure 32. $^{31}\text{P}\{^1\text{H}\}$ NMR of **6** recorded in Toluene.

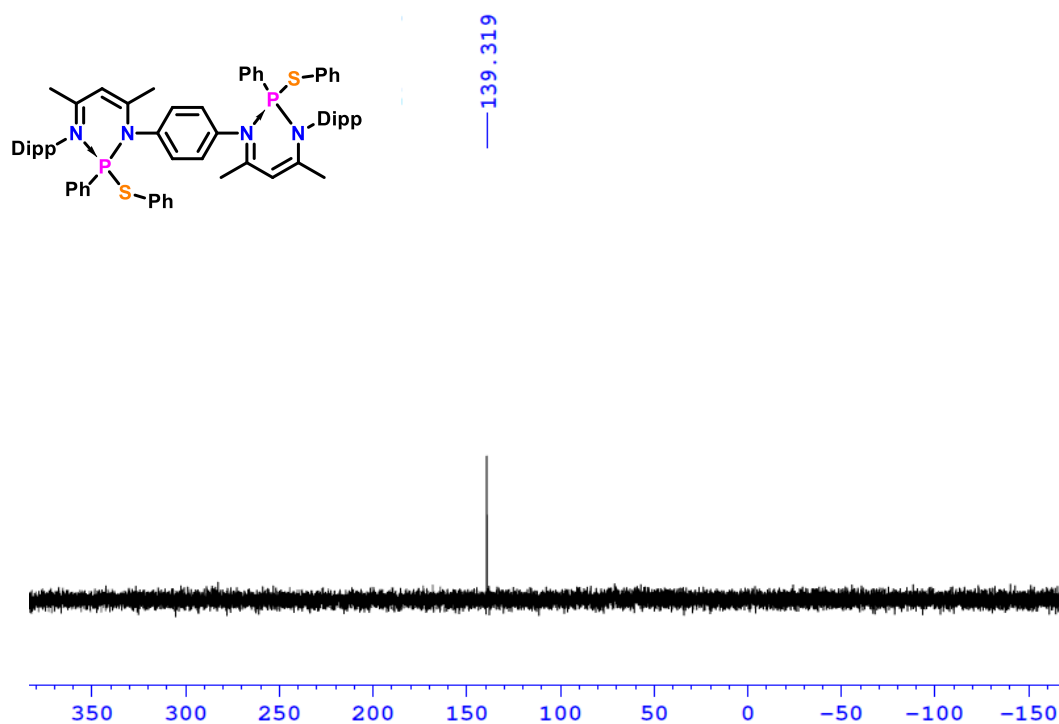


Figure 33. $^{31}\text{P}\{^1\text{H}\}$ NMR of **7** recorded in Toluene

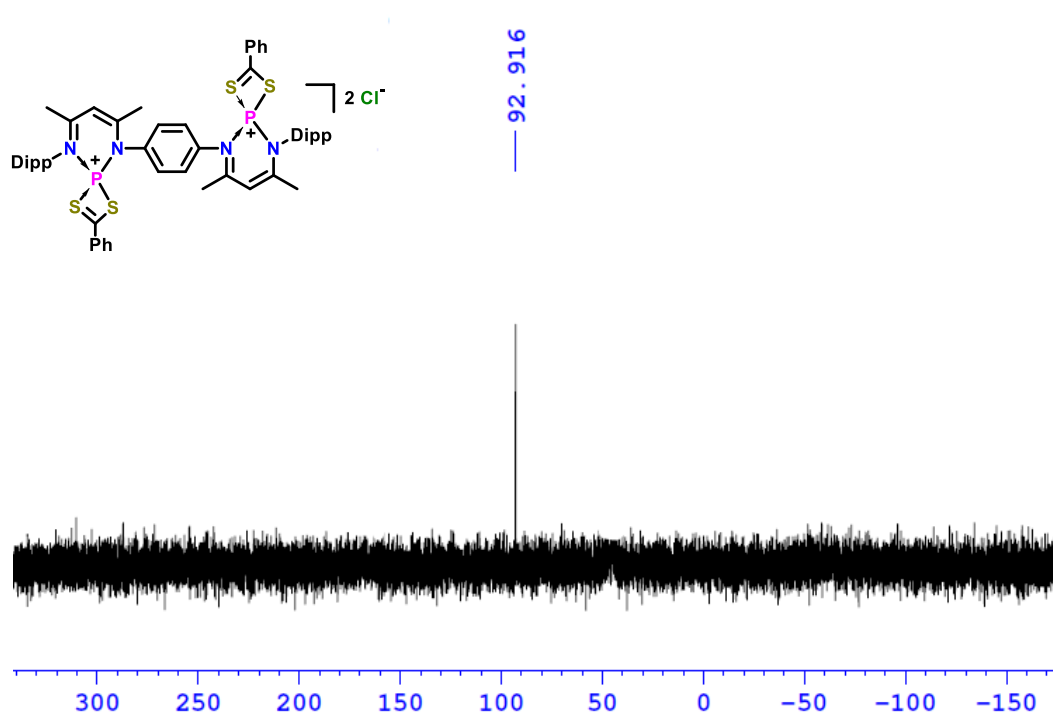


Figure 34. $^{31}\text{P}\{^1\text{H}\}$ NMR of **8** recorded in Toluene.

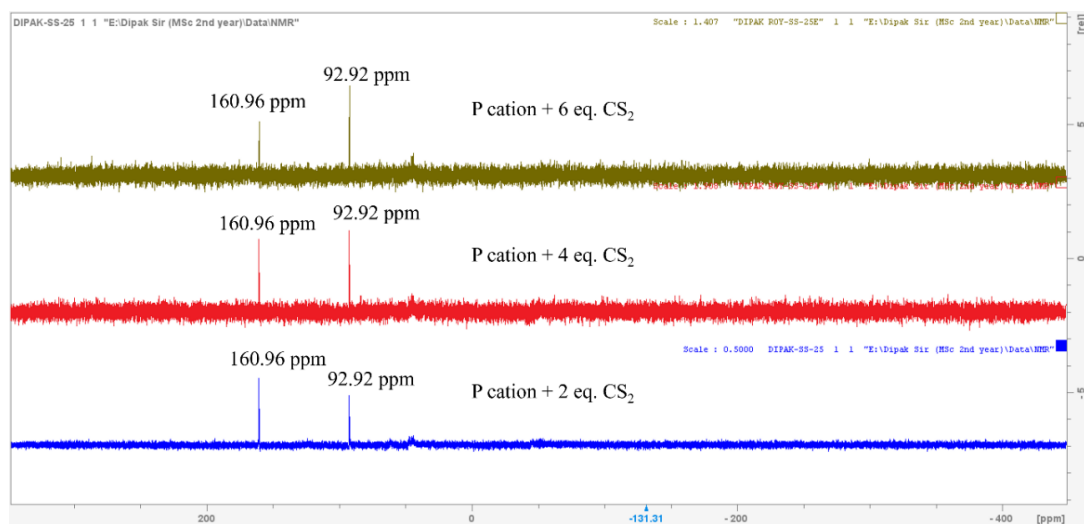


Figure 35. Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR of **8** recorded in Toluene.

MASS SPECTRA

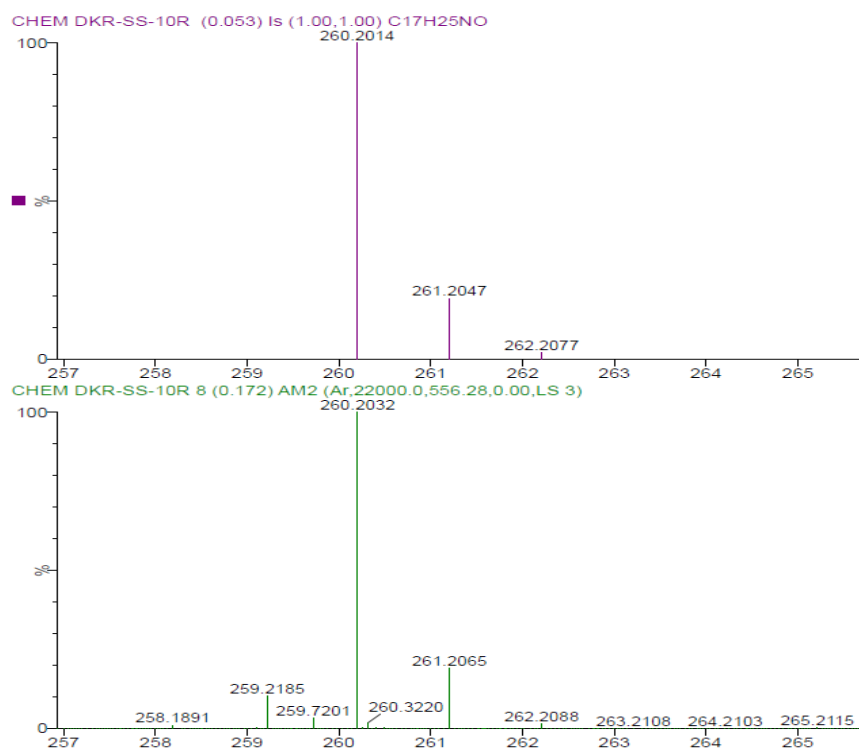


Figure 36. HRMS data of ligand L1

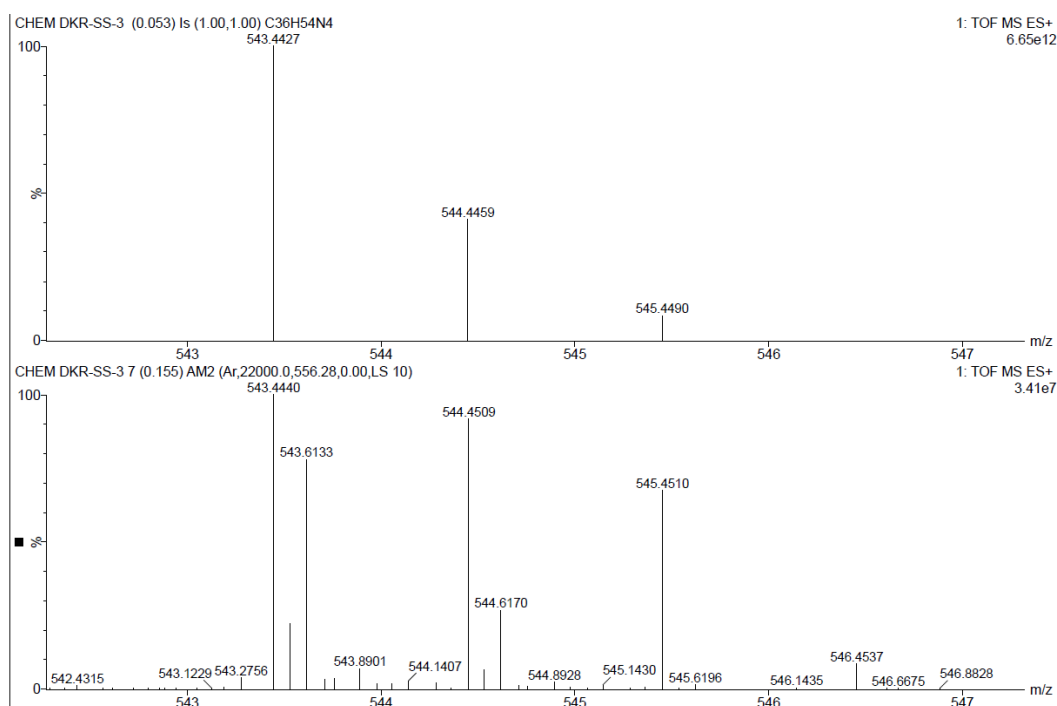


Figure 37. HRMS data of ligand L2

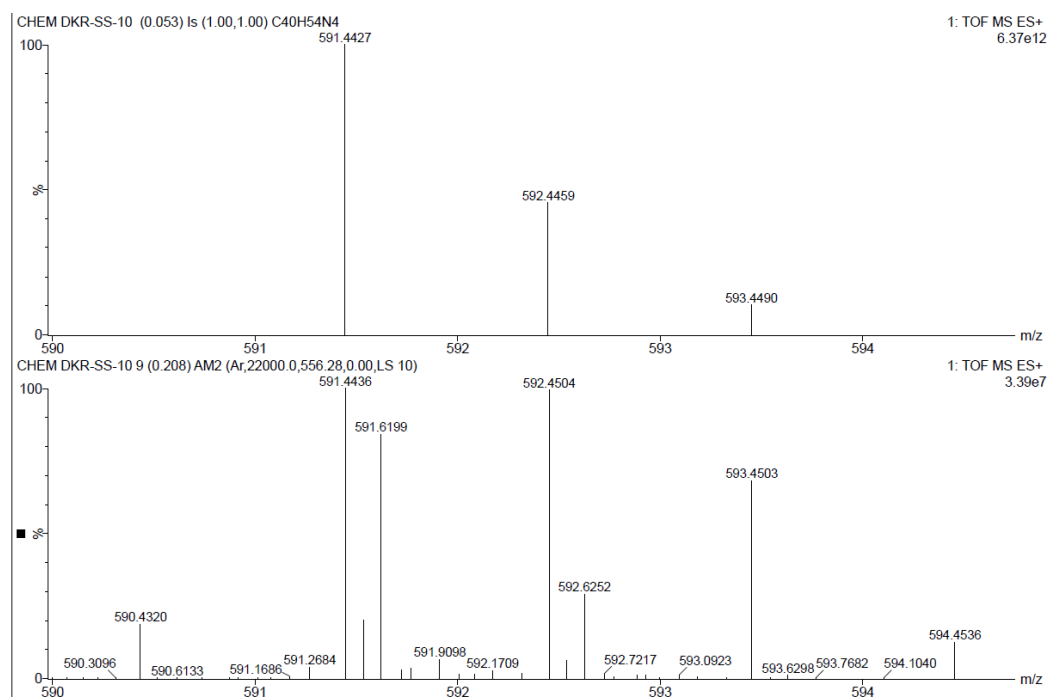


Figure 38. HRMS data of ligand L3

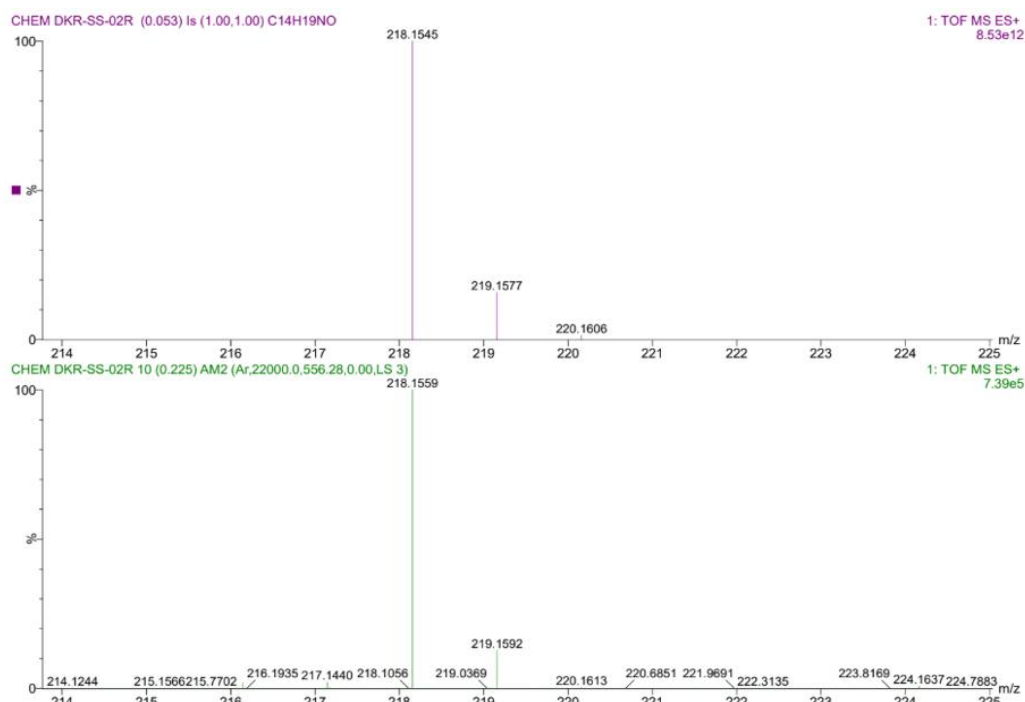


Figure 39. HRMS data of ligand L4

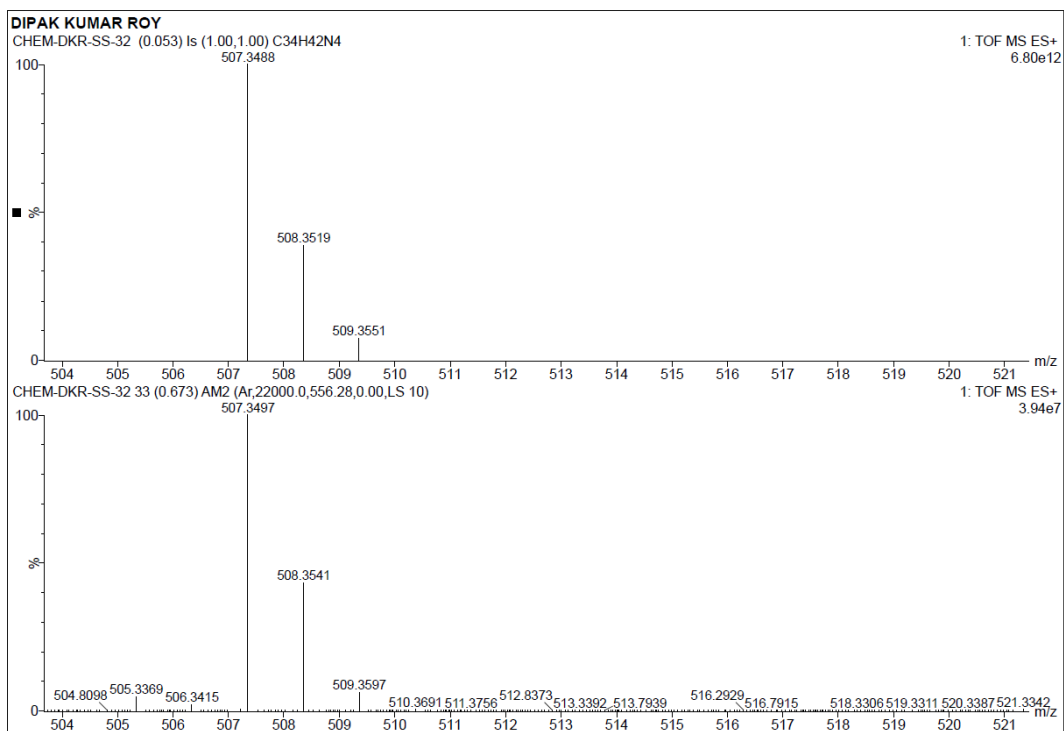


Figure 40. HRMS data of ligand L5

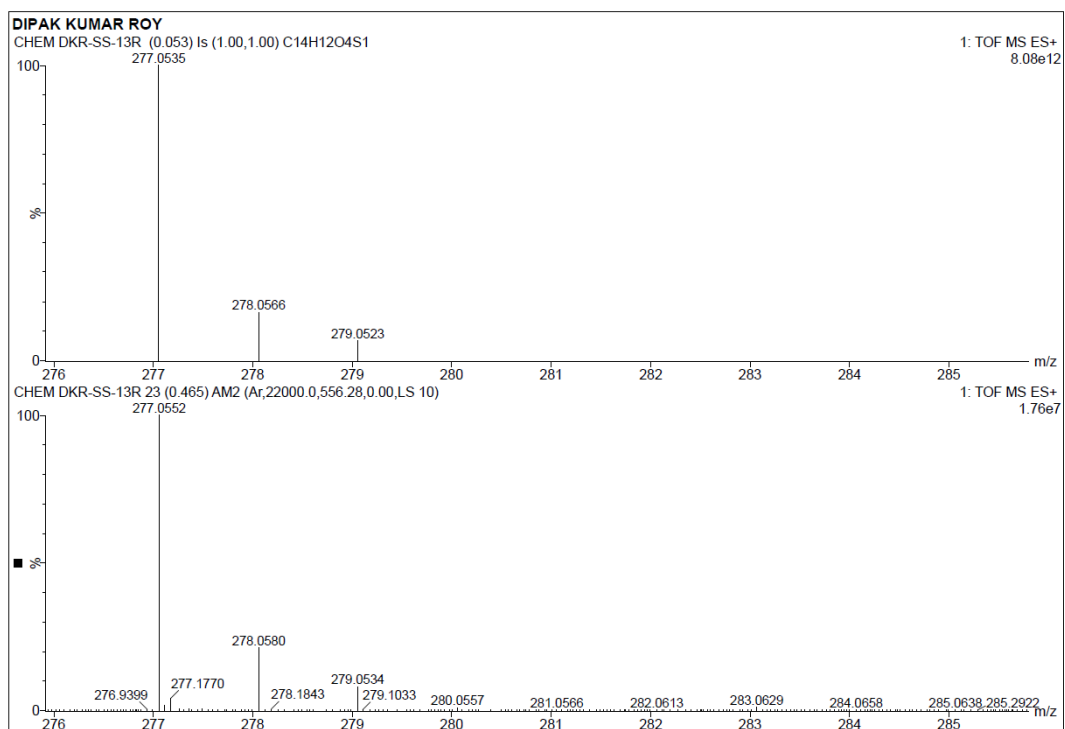


Figure 41. HRMS data of ligand L6

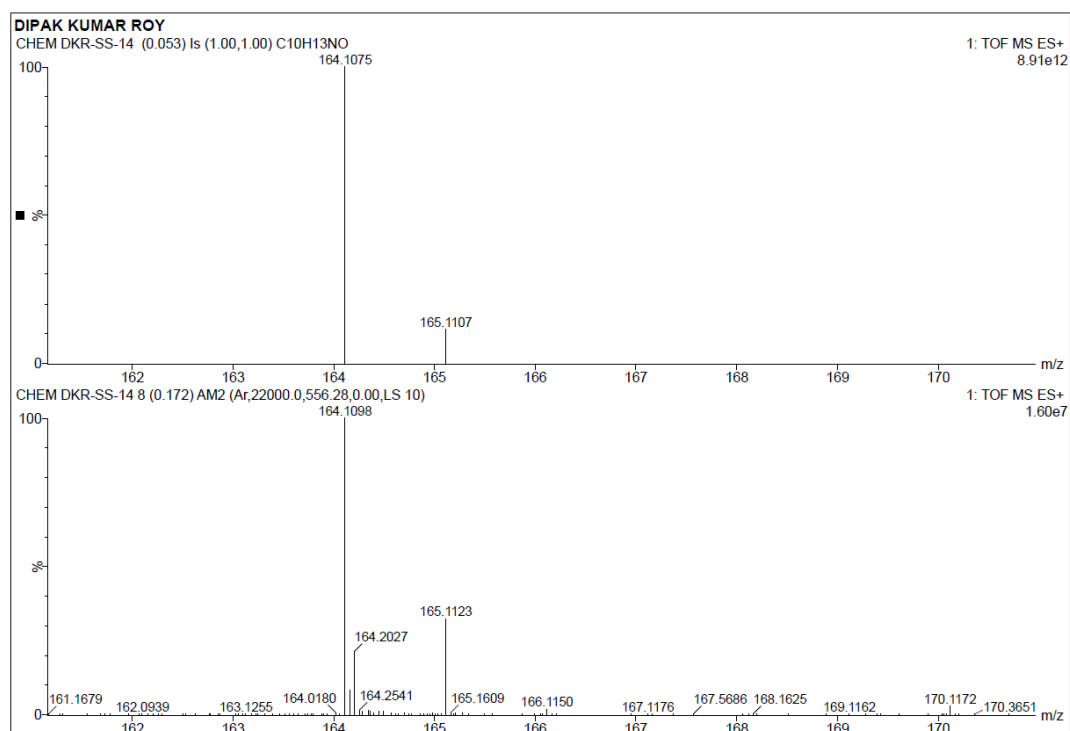


Figure 42. HRMS data of ligand L7

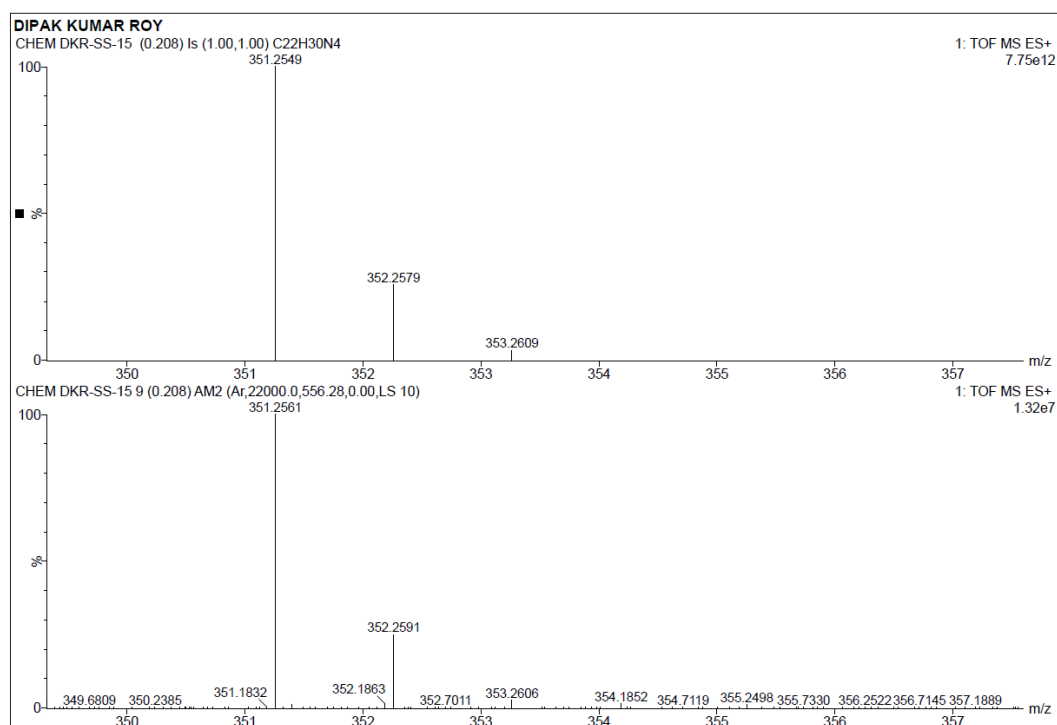


Figure 43. HRMS data of ligand L8

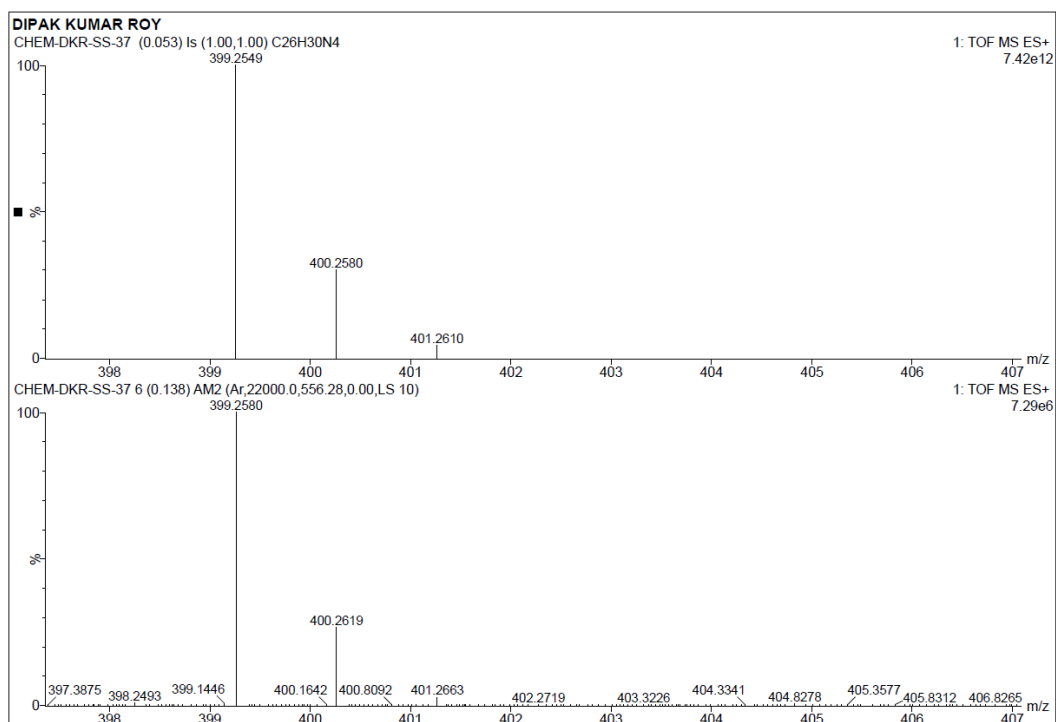


Figure 44. HRMS data of ligand L9

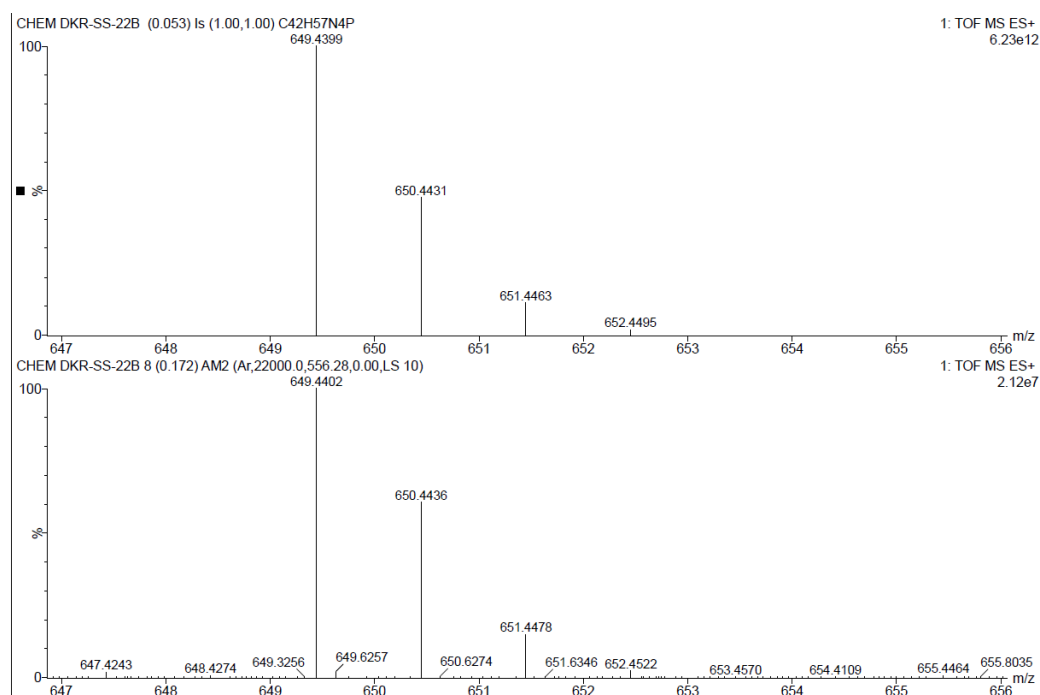


Figure 45. HRMS data of 1

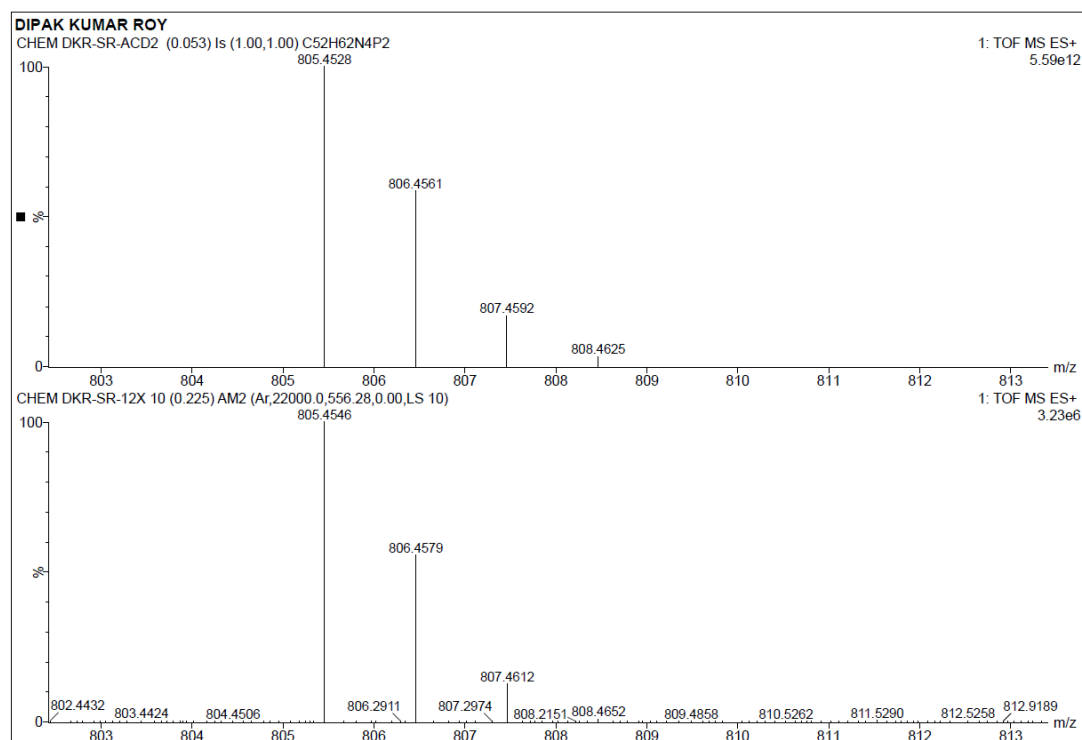


Figure 46. HRMS data of **2** ($[M]^+$).

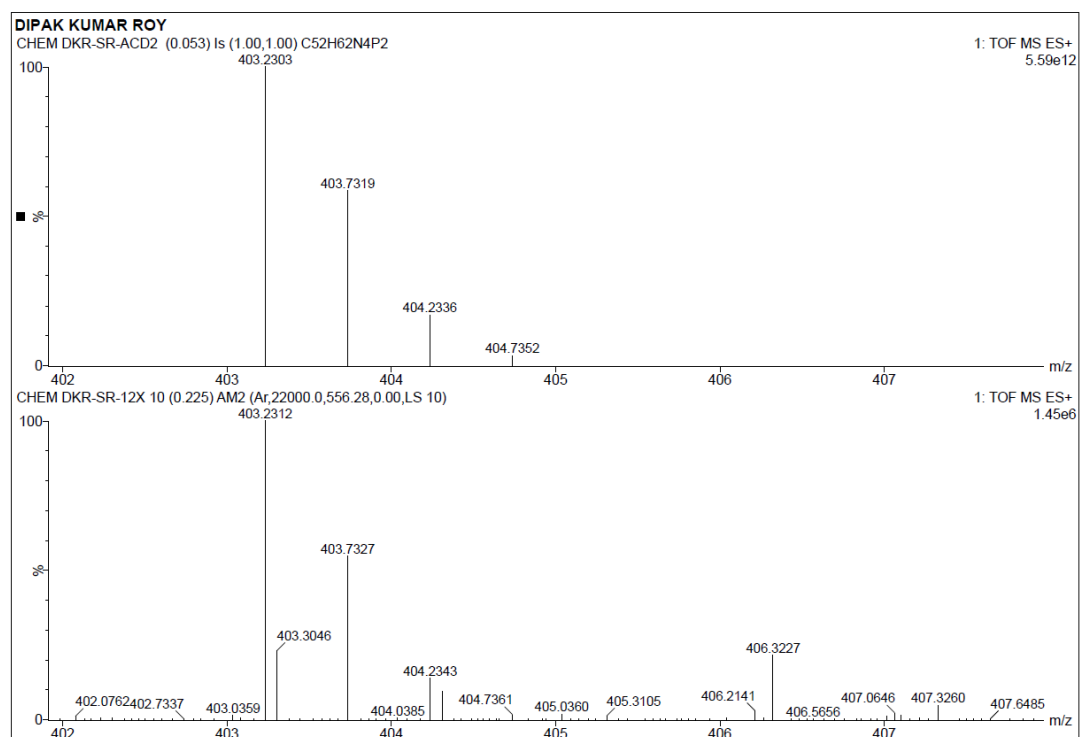


Figure 47. HRMS data of **2** ($[M/2]^+$).

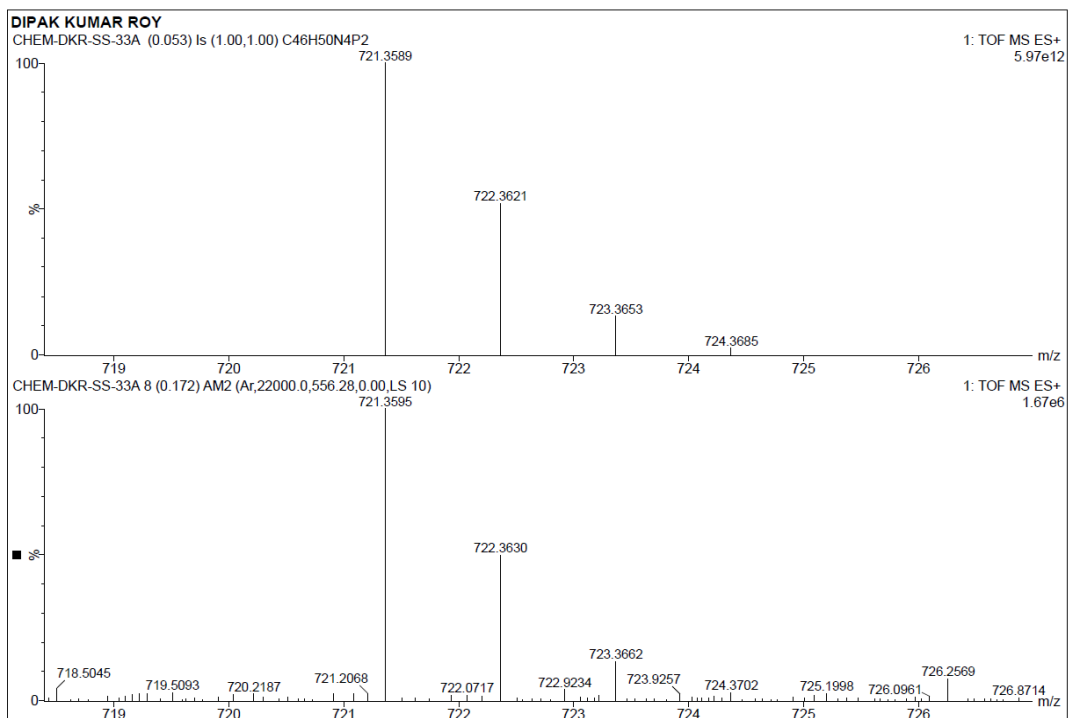


Figure 48. HRMS data of **3** ($[M]^+$).

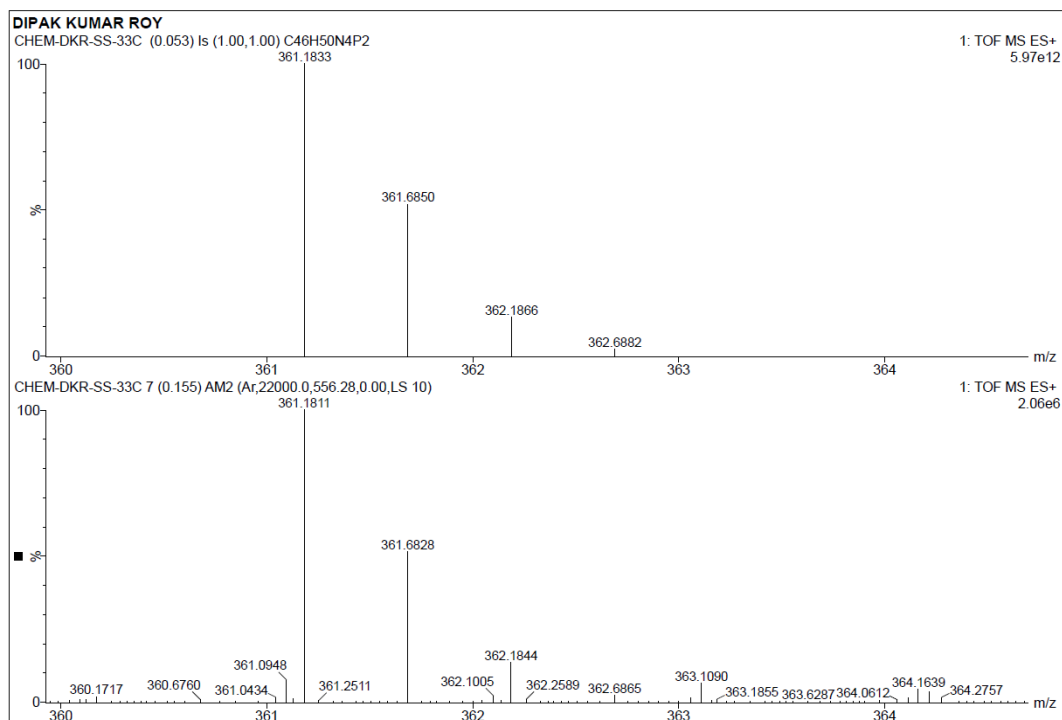


Figure 49. HRMS data of **3** ($[M/2]^+$).

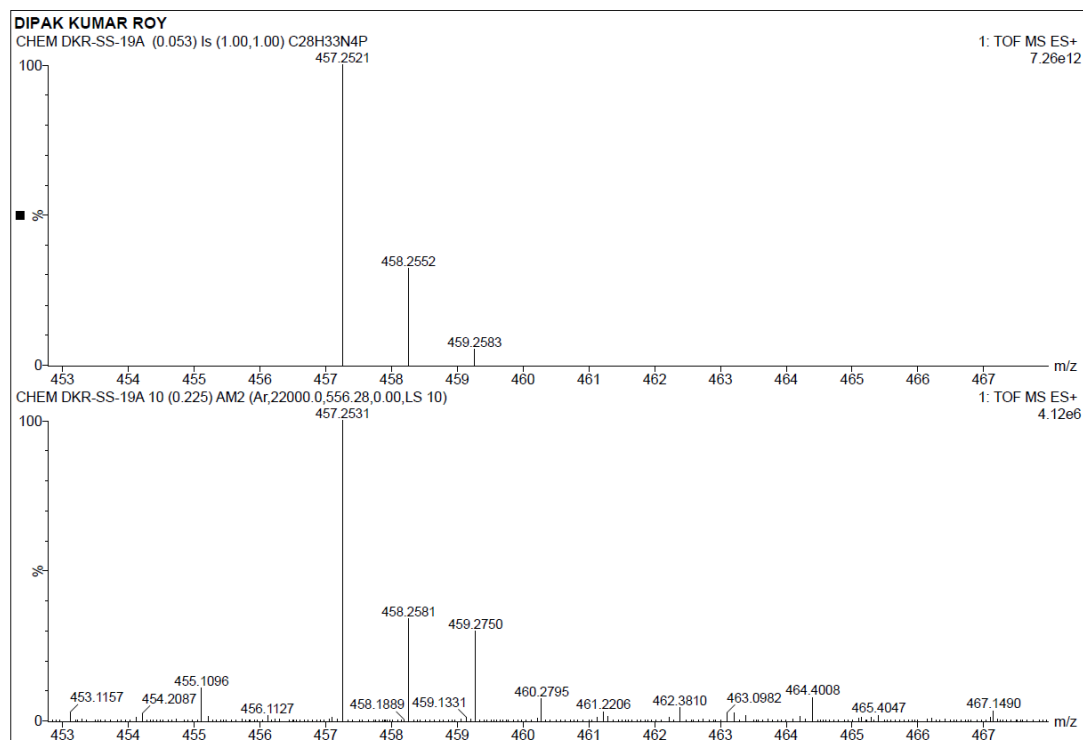


Figure 50. HRMS data of 4

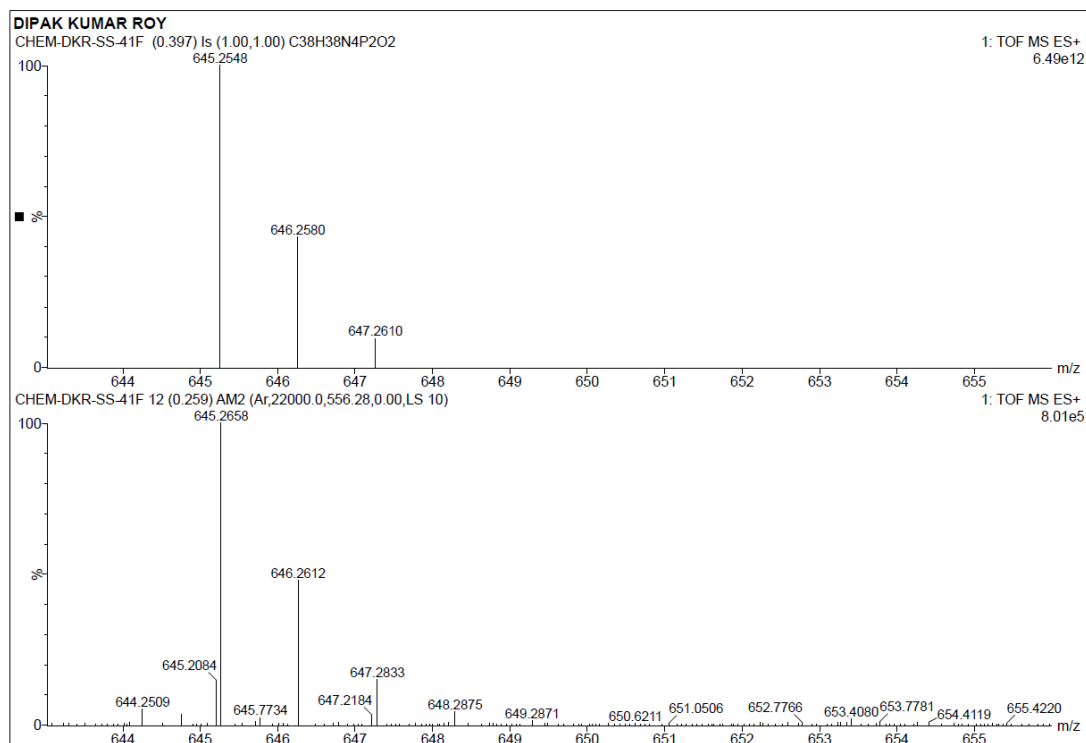


Figure 51. HRMS data of 5

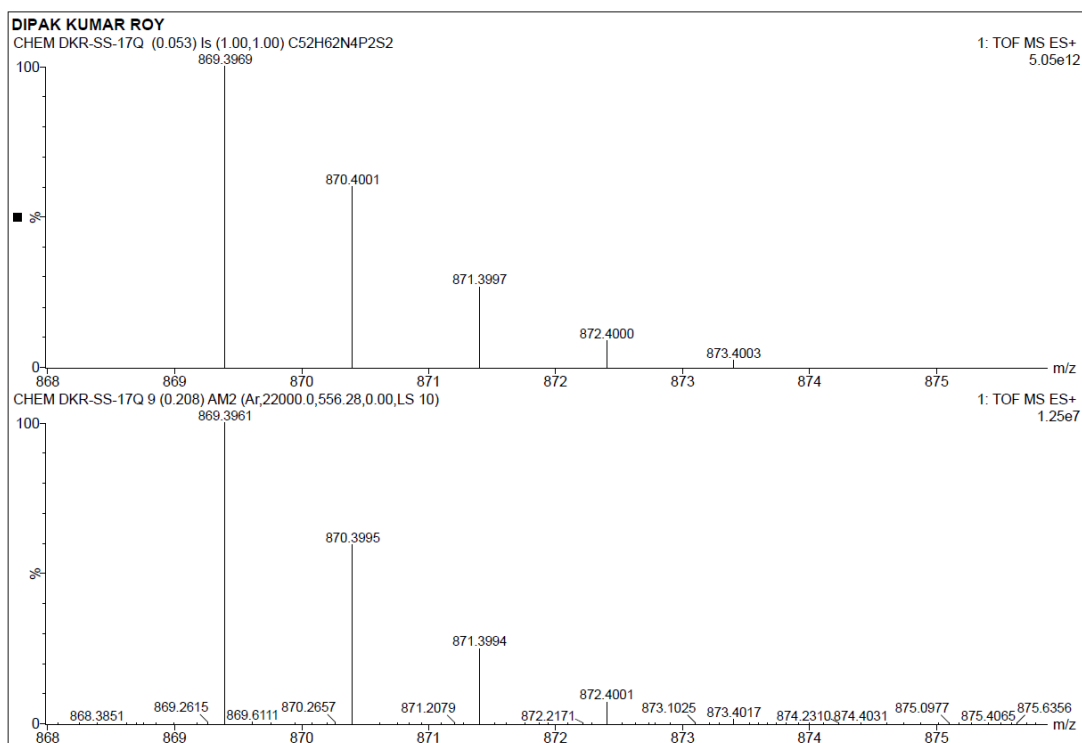


Figure 52. HRMS data of **6** ($[M]^+$).

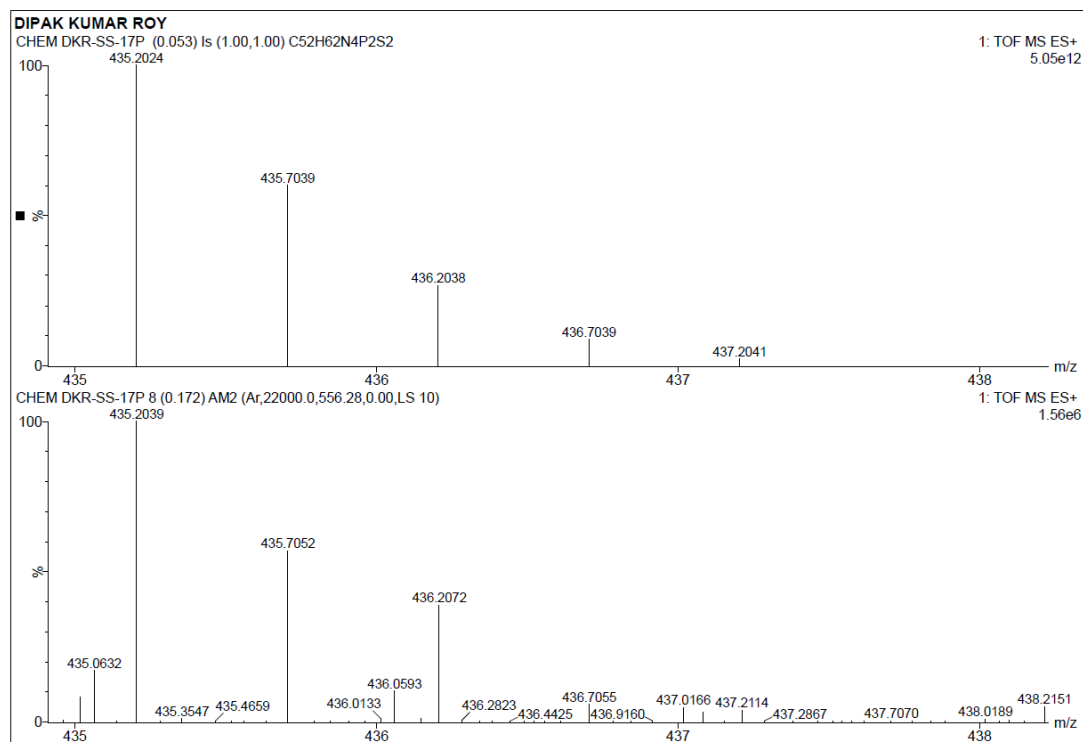


Figure 53. HRMS data of **6** ($M/2^+$).

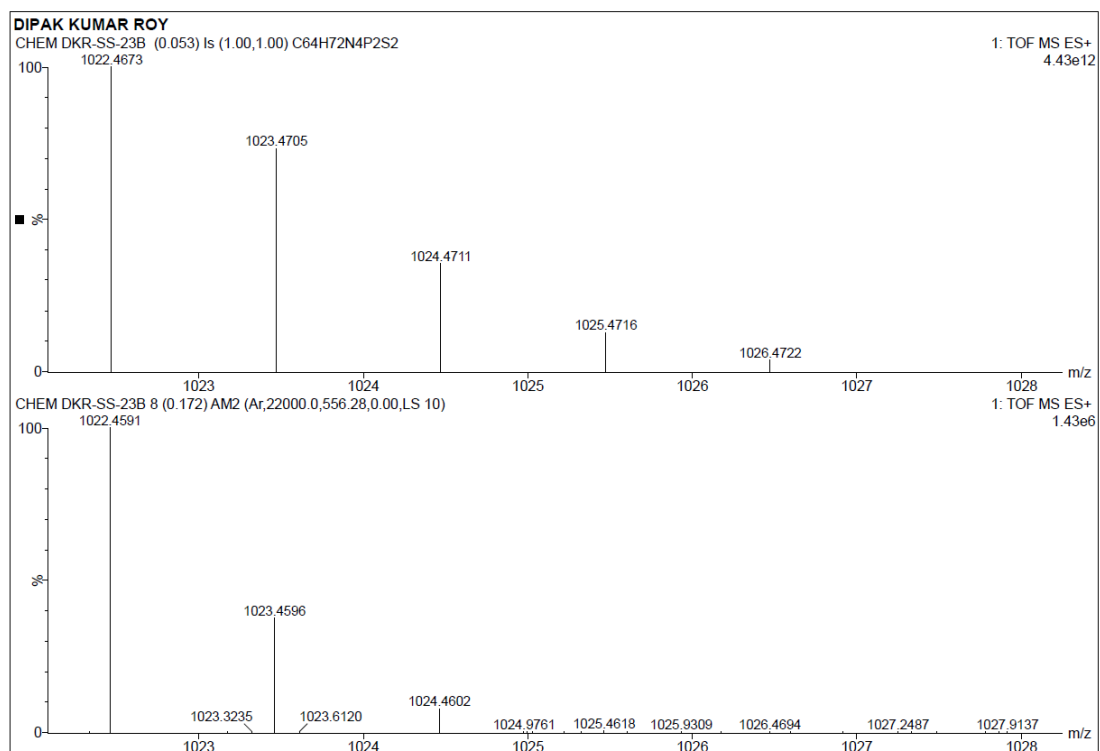


Figure 54. HRMS data of **7**

REFERENCES

1. Power P. P. (2010), Main-group elements as transition metals, *Nature.*, 463, 171-177 (DOI: 10.1038/nature08634)
2. Inoue S., Melen R. L., Harder S. (2020), Main Group Catalysis, *Eur. J. Inorg. Chem.* 32, 3019–3030 (DOI: 10.1002/ejic.202000460)
3. Gil-Negrete J. M., Hevia E. (2020), Main Group Bimetallic Partnerships for Cooperative Catalysis, *Chem. Sci.*, 11, 1982–1992 (DOI: 10.1039/D0SC05116K)
4. Webster R. L. (2017), β -Diketiminato Complexes of the First Row Transition Metals: Applications in Catalysis, *Dalton Trans.* 46, 4483–4498 (DOI: 10.1039/C7DT00319F)
5. Zhong M., Sinhababu S., Roesky H. W. (2020), The Unique β -Diketiminato Ligand in Aluminum(I) and Gallium(I) Chemistry, *Dalton Trans.*, 49, 1351–1364 (DOI: 10.1039/C9DT04763H)
6. Dias H. V. R., Wang Z., Jin, W. (1998), Aminotroponiminato Complexes of Silicon, Germanium, Tin and Lead, *Coord. Chem. Rev.*, 176, 67–86 (DOI: 10.1016/S0010-8545(98)00112-X)
7. Hanft A., Rottschäfer D., Wieprecht N., Geist F., Radacki K., Lichtenberg, C. (2021), Aminotroponiminates: Impact of the NO₂ Functional Group on Coordination, Isomerisation, and Backbone Substitution, *Chem. Eur. J.*, 27, 14250–14262 (DOI: 10.1002/chem.202102324)
8. Pop L. C., Axet M. R., Silaghi-Dumitrescu R., Saffon N. (2011), Aminotroponiminato and Aminotroponate Complexes of Group 15 (P, As) Elements: Synthesis, X-ray Diffraction Analysis and Reactivity, *Eur. J. Inorg. Chem.*, 31, 3357–3364 (DOI: 10.1002/ejic.201100131)
9. Merle L.B., Lappert M. F., Severn J. R. (2002), The chemistry of β -diketiminatometal complexes, *Chem. Rev.*, 102, 3031–3066 (DOI: 10.1021/cr010424r)

10. Mehrotra R. C., Bohra R., Gaur D. P. (2001), Metal β -diketonates and allied derivative, Dalton Trans., 20, 3792-3799. (DOI: 10.1021/om050309x)
11. Holm R. H., Everett G. W., Chakravorty C. (1996), Metal complexes of Schiff bases and β -ketoamines, Inorg. Chem., 7, 83. (DOI: 10.1002/9780470166086.ch3)
12. Wilkinson G., Gillard R. D., McCleverty J. A. Comprehensive coordination chemistry, The synthesis, reactions, properties and applications of coordination compounds. Dalton Trans., 41, 5586-5594 (DOI: 10.1039/D0SC05116K)
13. Tsai Y.-C. (2012), The chemistry of univalent metal β -diketiminates, Coord. Chem. Rev., 256, 722-758 (DOI: 10.1016/j.ccr.2011.12.012)
14. Zhang Y., Ma Y., Cheng A.L., Yue Q., Sun Q., Gao E.Q. (2011), Synthesis, structures, and magnetic properties of transition metal compounds with 2,2'-dinitrobiphenyl-4,4'-dicarboxylate and N, N'-chelating ligands, Dalton Trans., 40, 7221-7227 (DOI: 10.1039/C1DT10158G)
15. Webster R. L. (2017), β -Diketiminato complexes of the first row transition metals: Applications in catalysis, Dalton Trans., 46, 4483-4498 (DOI: 10.1039/C7DT00319F)
16. Barba L. F. S., Hughes D. L., Humphrey S. M., Bochmann M. (2005), New bis(allyl)(diketiminato) and tris(allyl) lanthanide complexes and their reactivity in the polymerization of polar monomers, Organometallics, 24, 3792-3799 (DOI: 10.1021/om050309x)
17. Liu P., Chen H., Zhang Y., Xue M., Yao Y., Shen Q. (2014), Synthesis of γ -amidine-functionalized dianionic β -diketiminato lanthanide amides and trianionic β -diketiminato Na/Sm heterobimetallic complexes and their reactivity in polymerization of L-lactide, Dalton Trans., 43, 5586-5594 (DOI: 10.1039/C3DT52706A)
18. Desat M. E., Kretschmer R. (2019), Dinuclear aluminum halide complexes based on bis(β -diketiminato) ligands: Synthesis,

- structures, and electrochemical characterization, *Inorg. Chem.*, 58, 16302-16311 (DOI: 10.1021/acs.inorgchem.9b02868)
19. Merle L. B., Lappert M. F., Severn J. R. (2002), The chemistry of β -diketiminate metal complexes, *Chem. Rev.*, 102, 3031–3065 (DOI: 10.1021/cr010424r)
 20. Rahim M., Taylor N. J., Xin S., Collins S. (1998), Synthesis and structure of acyclic bis(ketenimine) complexes of zirconium, *Organometallics*, 17, 1315–1323 (DOI: 10.1021/om970862h)
 21. Roesky H. W., Singh S., Jancik V., Chandrasekhar V. (2004), A paradigm change in assembling OH functionalities on metal centers, *Acc. Chem. Res.*, 37, 969–981 (DOI: 10.1021/ar0402154)
 22. Zhong M., Sinhababu S., Roesky H. W. (2020), The unique β -diketimate ligand in aluminum(I) and gallium(I) chemistry, *Dalton Trans.*, 49, 1351-1364 (DOI: 10.1039/C9DT04763H)
 23. Jones D. D. L., Watts S., Jones C. (2021), Synthesis and characterization of super bulky β -diketiminate group 1 metal complexes, *Inorganic Chemistry*, 9, 72-81 (DOI: 10.3390/inorganics9090072)
 24. Bourne C., Dong H., McKai, K., Mayer L. C., McKay A. P., Cordes D. B., Slawin A. M. Z., Stasch A. (2024), Alkyl backbone variations in common β -diketimate ligands and applications to N-heterocyclic silylene chemistry, *Dalton Trans.*, 53, 9887-9895 (DOI: 10.1039/D4DT01298D)
 25. Zhu D., Budzelaar P. H., M. N-Aryl (2013), β -diiminate complexes of the platinum metals, *Dalton Trans.*, 42, 11343-11354 (DOI: 10.1039/C3DT50715G)
 26. Chen C., Bellows S. M., Holland P. L. (2015), Tuning steric and electronic effects in transition-metal β -diketimate complexes, *Dalton Trans.*, 44, 16654-16670 (DOI: 10.1039/C5DT02215K)
 27. Hohloch S., Kriegel B. M., Bergman R. G., Arnold J. (2016), Group 5 chemistry supported by β -diketimate ligands, *Dalton Trans.*, 45, 15725-15745 (DOI: 10.1039/C6DT01770C)

28. Hobson K., Carmalt C. J., Bakewell C. (2020), Recent advances in low oxidation state aluminium chemistry, *Chem. Sci.*, 11, 6942-6956 (DOI: 10.1039/D0SC02686G)
29. McGeachin S. G. (1968), Synthesis and properties of some β -diketimines derived from acetylacetone, and their metal complexes, *Can. J. Chem.*, 46, 1903–1912 (DOI: 10.1139/v68-315)
30. Barry W. J., Finar I. L., Mooney E. F. (1965), A comparison of the structures of some dianils with those of analogous diazepines, *Spectrochim. Acta*, 21, 1095–1099 (DOI: 10.1016/0371-1951(65)80189-8)
31. Bonnett R., Bradley D. C., Fisher K. J. (1968), Bis-(NN'-diethylbutane-2, 4-di-iminato) cobalt (II), a tetrahedral cobalt derivative of a new nitrogen chelate group *J. Chem. Soc. Chem. Commun.*, 65, 886–887 (DOI: 10.1039/C19680000886)
32. Hohloch S., Kriegel, B. M. Bergman, R. G. Arnold, J. (2016), Group 5 chemistry supported by β -diketiminate ligands. *Dalton Trans.*, 45, 15725-15745 (DOI: 10.1039/C6DT01770C)
33. McGeachin S. G. (1968), Synthesis and properties of some β -diketimines derived from acetylacetone, and their metal complexes, *Can. J. Chem.*, 46, 1903–1912 (DOI: 10.1139/v68-315)
34. Bonnett R., Bradley D. C., Fisher K. J., Rendall I. F. (1971), Metallo-organic compounds containing metal–nitrogen bonds. Synthesis and properties of bis-(NN'-diethylbutane-1,3-di-iminato) derivatives of cobalt(II) and zinc, *J. Am. Chem. Soc.*, 82, 1622-1627. (DOI: 10.1039/J19710001622)
35. Parks J. E., Holm R. H. (1968), Synthesis, solution stereochemistry, and electron delocalization properties of bis(β iminoamino)nickel(II) complexes, *Inorg. Chem.*, 7, 1408–1416 (DOI: 10.1021/ic50065a029)
36. Cotton F. A., DeBoer B. G., Pipal J. R. (1970), Crystal and molecular structure of bis(3,3',5,5'-

- tetramethyldipyrrromethenato)nickel(II), *Inorg. Chem.*, 9, 783–788 (DOI: 10.1021/ic50086a018)
37. Matsunaga S., Shibasaki M. (2014), Recent advances in cooperative bimetallic asymmetric catalysis: Dinuclear Schiff base complexes. *Chem. Commun.*, 50, 1044-1057 (DOI: 10.1039/C3CC47587E)
38. Navarro M., Moreno J. J., Jiménez M. P., Campos J. (2022), Small molecule activation with bimetallic systems: A landscape of cooperative reactivity, *Chem. Commun.*, 58, 11220-11235 (DOI: 10.1039/D2CC04296G)
39. Ward T. R. (2009), Bio-inspired Catalysts; Topics in organometallic chemistry, 25, 645 (DOI: 10.1002/ejoc.200400389)
40. Liao K., Negretti S., Musaev D. G., Bacsá J., Davies H. M. L. (2016), Site-selective and stereoselective functionalization of unactivated C-H bonds, *Nature.*, 533, 230-234 (DOI: 10.1038/nature17651)
41. Stephan D. W., Erker G. (2010), Frustrated lewis pairs: Metal-free hydrogen activation and more, *Angew. Chem. Int. Ed.*, 49, 46-76. (DOI: 10.1002/anie.200903708)
42. Stephan D. W., Erker, G. (2015) Frustrated Lewis pair chemistry: Development and perspectives, *Angew Chem Int. Ed.*, 54, 6400-6441 (DOI: 10.1002/anie.201409800)
43. Claramunt R. M., Sanz D., Torralba M. P., Pinilla E., Torres M. R., Elguero J. (2004), Solid-State Structure and Tautomerism of 2-Aminotroponimines Studied by X-ray Crystallography and Multinuclear NMR Spectroscopy, *Eur. J. Org. Chem.*, 4452–4466 (DOI: 10.1002/ejoc.200400389)
44. Korolev A. V., Ihara E., Guzei I., A., Young V. G., Jordan, R. (2001), Cationic Aluminum Alkyl Complexes Incorporating Aminotroponimate Ligands, *J. Am. Chem. Soc.*, 123, 8291–8309 (DOI: 10.1021/ja010242e)

45. Dias H. V. R., Wang Z., Jin, W. (1998), Aminotroponiminato complexes of silicon, germanium, tin and lead, *Coord. Chem. Rev.*, 176, 67-86 (DOI: 10.1016/S0010-8545(98)00112-X)
46. Roesky P. W. (2000), The co-ordination chemistry of aminotroponiminates, *Chem. Soc. Rev.*, 29, 335-345 (DOI: 10.1039/A906763I)
47. Dagorne S., Atwood D. A. (2008), Synthesis, Characterization, and Applications of Group 13 Cationic Compounds. *Chem. Rev.*, 108, 4037-4071 (DOI: 10.1021/cr078351k)
48. Dielmann F., Mehlmann P, Witteler T., and Wilm L. F. B. (2019), Isolation, characterization and reactivity of three-coordinate phosphorus dications isoelectronic to alanes and silylium cations *Nat. Chem.*, 11, 1139–1143 (DOI: 10.1038/s41557-019-0348-0)
49. Dillon A. C., Butle, A., Cahoon J., Holmes J. D., Smalley R. E. (2014), Structure and Reactivity of Phosphorus Allotropes, *Chem. Rev.*, 114, 10819–10859 (DOI:10.1021/cr500289m)
50. Tawiński J., Bauer W., Ziolkowski J. et al (2013), Phosphonium and Phosphenium Ions in Synthesis, *Chem. Soc. Rev.*, 42, 640–674 (DOI:10.1039/c2cs35209c)
51. Fleming S., Lupton M. K., Jekot K. (1972), Synthesis of a Cyclic Fluorodialkylaminophosphine and Its Coordination with Boron Acids: Formation of a Unique Dialkylaminophosphine Cation, *Inorg. Chem.*, 11, 2534–2540.
52. Krachko E., Daniliuc C. G. (2018), Microreview: Stabilization of Phosphorus Cations by Lewis-bases, *Eur. J. Inorg. Chem.*, 2705–2718 (DOI:10.1002/ejic.201800331)
53. Liu L. L., Ruiz D. A., Dahcheh F., Bertrand G. (2015), Isolation of the Parent Phosphenium Cation: A Carbene-Stabilized Electron-Deficient Phosphorus Center. *Chem. Commun.*, 51, 12732–12735 (DOI:10.1039/C5CC05241F)
54. Wagner H. K., Romanov A. S., Borger J. E. (2020), Halide Abstraction from Phosphine Complexes: A Route to Cationic Phosphorus Species, *Angew. Chem. Int. Ed.*, 59, 150–163 (DOI:10.1002/anie.201910789)

55. Holthausen M. H., Schulz C. (2021), Phosphorus Cation Chemistry: Advances and New Directions. *Chem. Eur. J.*, 27, 11974–11986 (DOI:10.1002/chem.202100555)
56. Shoji Y., Matsuo T., Kawaguchi H. (2017), Generation of Reactive Phosphorus Cations by Halide Abstraction. *J. Am. Chem. Soc.*, 139, 17397–17400 (DOI:10.1021/jacs.7b10519)
57. Yadav R. K., Parveen D., Jangra P., Mondal B., Roy D. K. (2025), Synthesis, Characterization, and Reactivity of Aminotroponimate-Based Difluoroboranes: A Pathway toward Bore(boro)nium Cations, *Inorg. Chem.*, 64, 10780–10791 (DOI: 10.1021/acs.inorgchem.5c00451)