

Silylene Supported Ni Complex and Its Catalytic Application in C-N Coupling Reactions

A Thesis

Submitted to

Indian Institute of Science Education and Research, Pune in partial fulfillment
of the requirements for the BS-MS Dual Degree Programme

by

Rakesh Kumar Meena



Indian Institute of Science Education and Research, Pune

Dr. Homi Bhabha Road,

Pashan, Pune 411008, INDIA

October 2022

Supervisor: Dr. Shabana Khan

All rights reserved

Certificate

This is to certify that this dissertation entitled “Silylene supported Ni Complex and Its Catalytic Application in C-N coupling reactions” towards the partial fulfillment of the BS-MS dual degree program at the Indian Institute of Science Education and Research, Pune represents the study and work carried out by Rakesh Kumar Meena under the supervision of Dr. Shabana Khan, Department of Chemistry, during the academic year 2021-2022.



Dr. Shabana Khan

Committee:

Dr. Shabana Khan

Dr. Sakya Sen

This thesis is dedicated

to

"My Mother"

Declaration

I hereby declare that the matter embodied in the report entitled "Silylene Supported Ni Complex and Its Catalytic Application in C-N coupling reactions" are the results of the work carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. Shabana Khan and the same has not been submitted elsewhere for any other degree.

Rakesh Meena

Rakesh Kumar Meena

Date: 30th October 2022

Abstract

The chemistry of N-heterocyclic silylenes (NHSis) [a higher analogue of NHC], is one of the hottest research topics in current low-valent organometallic chemistry. In this work, a hybrid N-heterocyclic silylene (NHSi) and phosphine-based compound was developed and used as a ligand in transition metal-catalyzed homogeneous catalysis. We will be discussing the development and electronic as well as steric properties of silylenes especially NHSi ligands to achieve the potential catalyst for transition metal-catalyzed organic transformation. The electronic and steric properties of the newly synthesized silylene- and phosphine-based hybrid ligand are described. Further, the application of the ligand-supported Ni^{II} complex in the C-N coupling reactions as potent catalyst is described. Next section will cover the synthesis and characterization of the NHSi and phosphine-based ligand and its Ni^{II} metal complex.

Acknowledgments

I would like to express my sincere gratitude to Dr. Shabana Khan for her continuous guidance, encouragement, and granting of academic freedom throughout my master's thesis work.

I sincerely thank Dr. Sakya Sen for his continued guidance and suggestions during my project tenure. A special thanks to Mr. Sandeep H. Kaulage for leading me throughout my project with his friendly attitude and moral support during the difficult phase of my thesis work. I would also like to thank my all-lab members, Mr. M. Javed, Miss Nilanjana Sen, Miss Moushaki Ghosh, Miss Ruksana Akhtar, Mr. Brij Shah, Miss Prachi Gothe, Mr. Vijay Mandal, Mr. Kumar Gaurav, and Mr. Rahul Verma for their continuous support and being lovely mates throughout the project.

I am also thankful to the Director of IISER Pune, Prof. Jayant B. Udgaonkar, the chemistry chairperson, Prof. Niramalya Bhallav, and all the chemistry department faculties for assisting me in achieving my objective at IISER Pune. Finally, I convey my heart full thanks to my family and friends for backing me up throughout my journey.

Abbreviations

Ar	Aryl
°C	Celsius degree
br	broad
cod, COD	1,5-cyclooctadiene
equiv.	equivalent(s)
h	hour(s)
HOMO	highest occupied molecular orbital
Hz	Hertz
LUMO	lowest occupied molecular orbital
M	Metal
MHz	Megahertz
mmol	millimole
m/z	mass/charge
NHSi	N-heterocyclic silylene
NHC	N-heterocyclic carbene
Ph	Phenyl
<i>i</i> Pr	isopropyl
r. t.	room temperature
THF	tetrahydrofuran
TMS	tetramethylsilane
δ	chemical shift
Dipp	2,6- <i>i</i> Pr ₂ C ₆ H ₃

Table of Content

1. INTRODUCTION	10
1.1 Silylenes: Divalent compounds of silicon	10
A. Cyclic silylenes	10
N-heterocyclic silylenes (NHSis)	10
B. Acyclic silylenes	13
1.2 Silylene- and Phosphine-based hybrid donor ligands	13
1.3 Electronic properties of silylene ligands	18
1.4 Silylene- and phosphine-based hybrid donor ligands in catalysis	18
A. C-C bond formation reactions	19
B. C-X (X = N, Si) bond-making reactions	20
C. Reduction reactions	21
2. MOTIVATION	23
3. RESULT AND DISCUSSION:	24
3.1 Synthesis of Silylene- and Phosphine-based hybrid ligand system and its corresponding Ni ^{II} metal complex	24
3.2 C-N coupling reactions catalyzed by silylene- and phosphine-based hybrid donor ligand Ni ^{II} complex	27
4. MATERIALS AND METHODS	32
4.1 General Consideration	32
4.2 Starting materials	32
4.3 Analytical Methods	32
Nuclear Magnetic Resonance (NMR) Measurements	32
Mass Spectrometry:	33
4.4 Synthesis and characterization of all compounds	33
A. Synthesis of silylene- and phosphine-based hybrid ligand	33
Synthesis of compound a	33
Synthesis of compound b	34
Synthesis of L1:	34
B. Coordination of NiBr ₂ ·(DME) complex with the ligand L1	35
5. REFERENCES	36
6. APPENDIX	40

List of Schemes

Scheme 1: Synthetic route of the first NHSi I-2	11
Scheme 2: Some examples of the NHSis	11
Scheme 3: Synthetic path of the NHSi I-16	11
Scheme 4: NHSi Ni complex I-11 reactivity towards HX	12
Scheme 5: Synthetic pathways to the NHSi I-14	12
Scheme 6: Some selected examples of acyclic silylenes I-15 – I-18	13
Scheme 7: Synthesis of Au(I) complex with aurophilic interaction.	15
Scheme 8: Synthetic route for the heavier tetrylenes-phosphane compounds.	15
Scheme 9: Synthesis of Phosphine- and silylene-based hybrid-donor ligand I-24	16
Scheme 10: Synthesis of ligands I-25 – I-26 and corresponding Ni ⁰ metal complexes.....	17
Scheme 11: Synthesis of I-27 and I-28 using amidinato chlorosilylene.....	17
Scheme 12: Modifications in σ -donation properties of silylenes with different donor sites and X- substitutions	18
Scheme 13: Selected silylene-based metal complexes utilized in C-C bond-making reactions	20
Scheme 14: Selected examples of silylene ligand-bearing metal complexes utilized in C-X (X = N, Si) bond-making reactions	21
Scheme 15: Selected examples of silylene ligand-based metal complexes utilized in reduction reactions.	22
Scheme 16: Synthesis of phosphine substituted compound b	24
Scheme 17: Synthesis of hybrid ligand L1 and its corresponding Ni ^{II} complex 1	24

1. Introduction

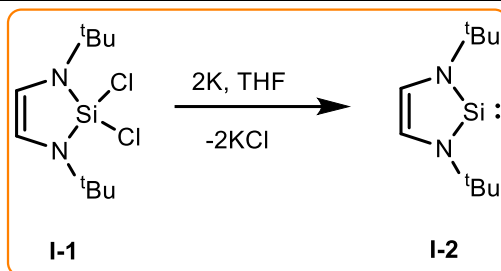
1.1 Silylenes: Divalent compounds of silicon

The heavier analogous of carbenes are silylenes, having divalent silicon atoms. Silylenes and carbenes are both Lewis acids and Lewis bases because of empty 3p orbitals and the presence of a lone pair of electrons respectively.^[1] In silylenes, silicon atoms prefer to remain in a singlet ground state. Silylenes are highly reactive species that before the 1980s, these species noticed spectroscopically at low temperatures and could be isolated as silylene metal complexes. The first stable Si^{II} compound, decamethylsilicocene, was isolated by Jutzi et al. in 1986 to draw attention to silylene chemistry. With the progress of silylene chemistry, many other silylenes having thermodynamic and kinetic stabilization (e.g., cyclic alkyl (amino) silylenes, cyclic dialkyl silylenes (CAASi), N-heterocyclic silylenes (NHSis), and acyclic silylenes) were isolated by different groups. These stable silylenes showed their potential in unreactive bond activation and provide stability to compounds with low-valent main-group atoms, and as ligands in transition metals-based catalysis. This chapter we will be discussing the chemistry of the silylenes as ligand in Ni^{II} support complex and their potential properties in homogeneous catalysis.

A. Cyclic silylenes

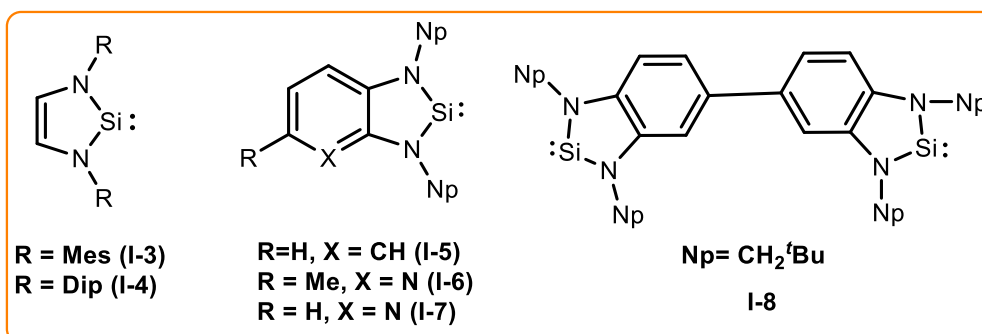
N-heterocyclic silylenes (NHSis)

The first N-heterocyclic silylene (NHSis) was obtained by West and Denk in 1994 by the reduction of N-heterocyclic dichlorosilane by potassium in THF.^[2] The two adjacent nitrogen atoms having bulky substituents provides the stability to these moieties.



Scheme 1: Synthetic route of the first NHSi **I-2**

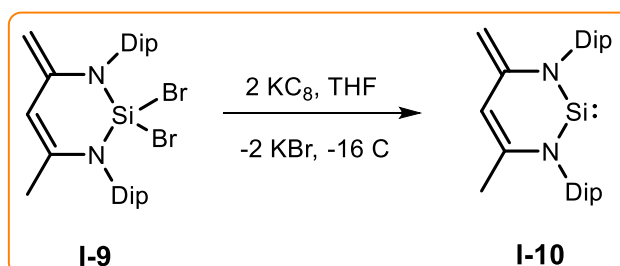
In some coming years, NHSis with different substituent groups on N (e.g., **I-3**, **I-4**) have been obtained and reported by different research groups.^[3]



Scheme 2: Some examples of the NHSis

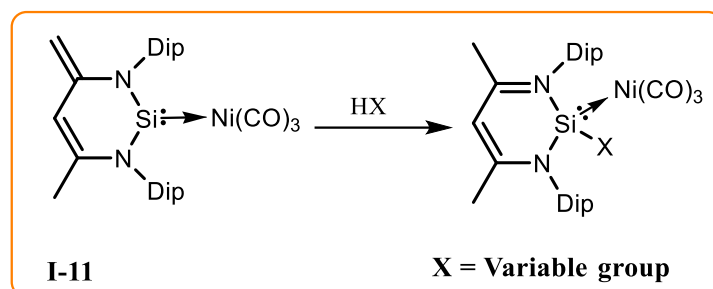
Further, Pyrido- and benzo-fused backbone stabilized N-heterocyclic silylenes (e.g., **I-5**, **I-6**, and **I-7**) were also obtained.^[4] Following this, Lappert et al. reported the bis-silylene-based biphenyl moiety **I-8** in 2005.^[5]

Driess et al. reported the first NHSi stabilized by a β -diketiminato-like backbone (**I-10**) in 2006.^[6] This species was obtained by reacting dibromosilane **I-9** with potassium graphite in THF and obtained as yellowish crystals.



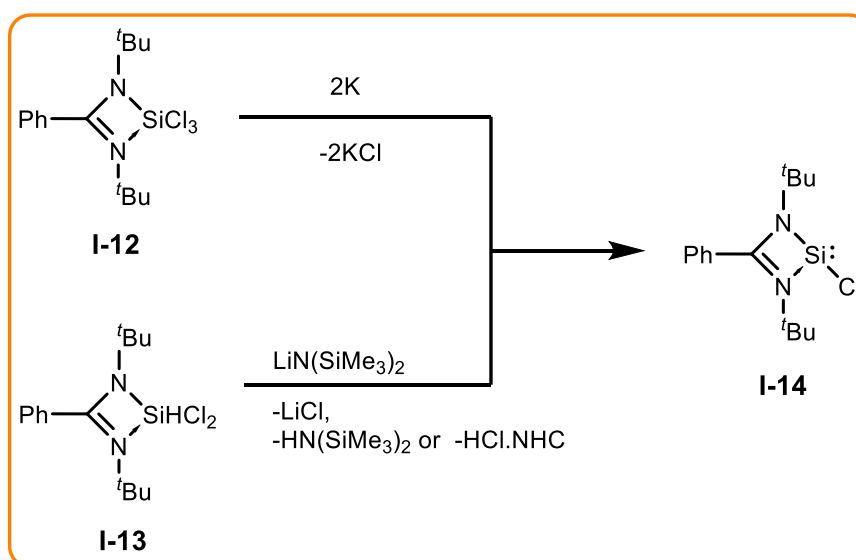
Scheme 3: Synthetic path of the NHSi **I-10**

In presence of arenes, **I-10** reacts with $[\text{Ni}(\text{cod})_2]$ providing the corresponding Ni^0 (η^6 -arene) complexes. The reaction of Ni^0 complex with CO provided silylene complex **I-11**. After reacting **I-11** with HX (HX = H_2O , HOTf, HCl, H_2S , NH_3 , and $\text{NH}_2(\text{iPr})$), 1,4-addition products were obtained.^[7]



Scheme 4: NHSi Ni complex **I-11** reactivity towards HX

After the successful isolation of NHSi **I-10**, the *N, N*-di(*tert*-butyl)amidinato NHSi **I-14** was obtained by Roeskey and co-workers. This group synthesized this by two pathways. First, by reducing the trichlorosilane precursor **I-12** with elemental potassium in THF,^[8] This method yielded a low (10%) so they used dichlorosilane **I-13** as a precursor. Another pathway, reacting **I-13** $\text{LiN}(\text{SiMe}_3)_2$ in toluene provided considerably higher yields (90%) which encouraged further research on **I-14** and its derived compounds in catalysis as ligands.^[9]

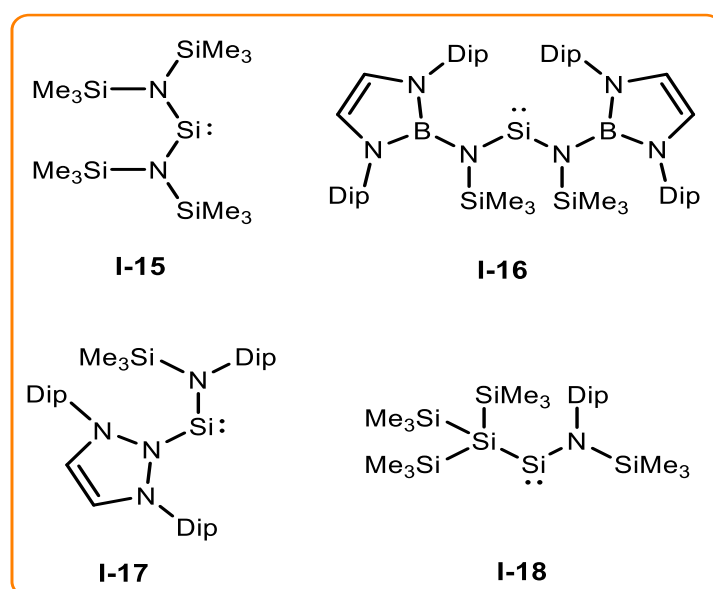


Scheme 5: Synthetic pathways to the NHSi **I-14**

B. Acyclic silylenes

By reducing of the corresponding dibromosilane with the potassium graphite generated the acyclic silylene **I-15**.^[24] However, this species persisted only for 10 to 12 hours at -20 °C. The introduction of the bulkier substituents led to the stabilization of acyclic silylenes **I-16**, **I-17**, and **I-18**.(Scheme 6)^[25]

Remarkably, acyclic silylene **I-17** underwent H₂ activation at r.t. because of the small LUMO-HOMO gap assisted by the wide bond angle at the Si center and the strong σ -donation property.^[10]



Scheme 6: Some selected examples of acyclic silylenes **I-15 – I-18**

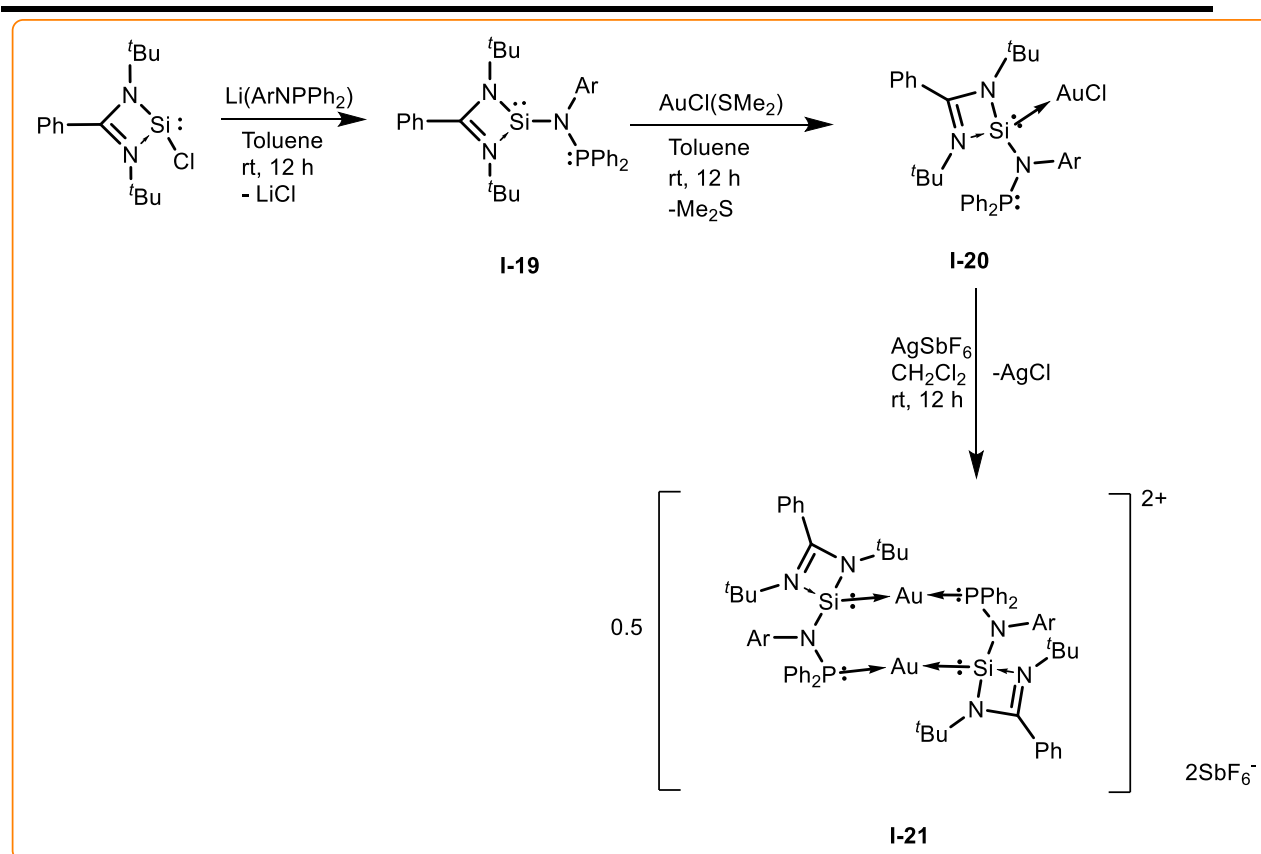
1.2 Silylene- and Phosphine-based hybrid donor ligands

Various NHSis stabilized by different donor atoms have been obtained and demonstrated for their coordination properties towards the main-group elements and transition metals.^[11, 13] The hybrid two-donor center ligands can provide more reliable stability than ligands with one donor sight; hence, the substantial number of NHSi- and phosphine-based hybrid ligands were synthesized with different donor atoms incorporated with the divalent Si

center.^[13] These hybrid bidentate systems, because of two donor sites, have the potential to stabilize transition metal complexes and many other reactive species.^[12,14,15] This new strategy of hybrid bidentate ligands has increased faith in obtaining new moieties for small molecule activation and metal-mediated homogeneous catalysis.

There are some literature on bidentate hybrid silylenes ligands coordination to Ni halide complexes. Surprisingly, much attention is not given to the complexes of Ni^{II} metal halides with such a hybrid Si^{II}-P^{III} system.

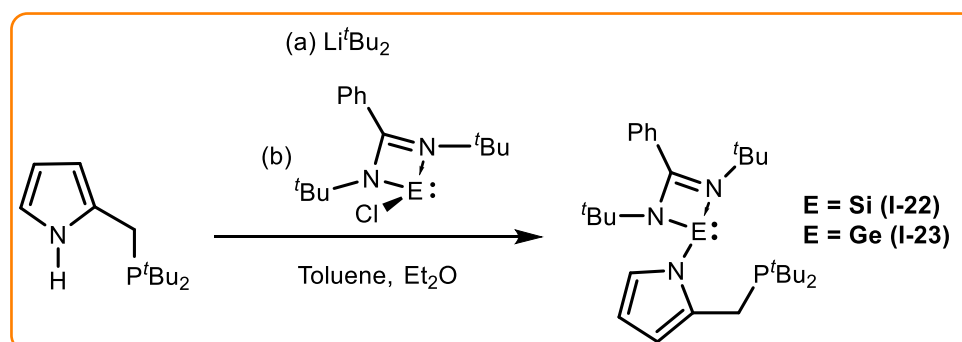
In 2016, Khan and co-workers reported a new dinuclear gold^I cation system supported with a silylene with aurophilic interaction.^[14a] The silylene (PhC(N^tBu)₂SiN(PPh₂)(2,6-ⁱPr₂-C₆H₃)) **I-19** was synthesized from previously reported (PhC(N^tBu)₂SiCl) salt elimination pathway. The reaction of **I-19** with AuCl(SMe₂) afforded **I-20**. Furthermore, chloride abstraction from **I-20** by AgSbF₆ lead to dinuclear Au(I) cationic complex **I-21** formation, possesses an intramolecular Au...Au interaction.



Scheme 7: Synthesis of Au(I) complex with aurophilic interaction.

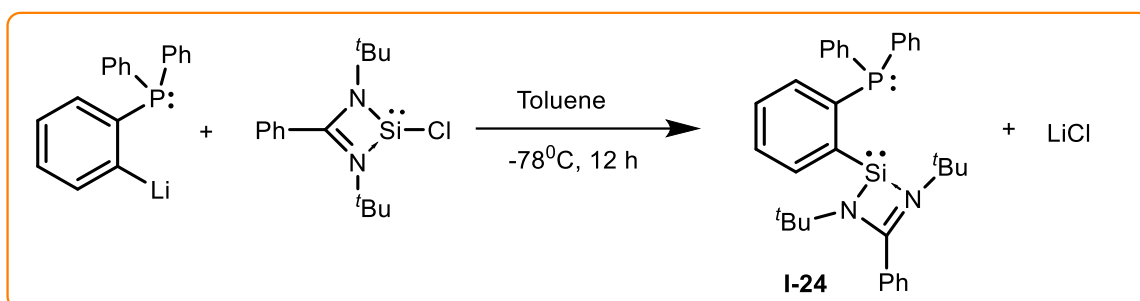
Carlos and coworkers reported the synthesis of phosphane decorated silylenes and germynes **I-22**, **I-23** and their reaction with group 10 metals in 2020.^[14c]

These tetrylenes, having phosphane side-arm synthesized by reaction of amidinatotetrylenes with $\text{Li}^t\text{Bu}_2\text{P}^t\text{Bu}_2$.



Scheme 8: Synthetic route for the heavier tetrylenes-phosphane compounds.

The reaction of **I-22** and **I-23** with selected M(0) metal precursors has provided the synthetic path for corresponding metal complexes showing outstanding Ge, P- and Si, P-chelating properties of ligands **I-22** and **I-23**.^[14c]

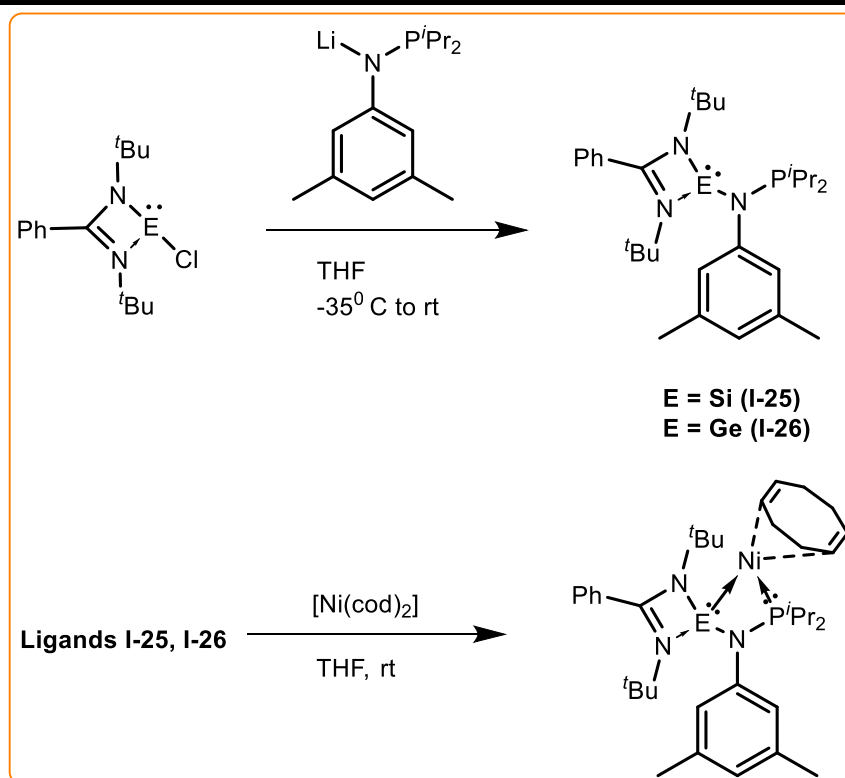


Scheme 9: Synthesis of Phosphine- and silylene-based hybrid-donor ligand **I-24**

In 2021, Roeskey et al. reported a new hybrid bi-dentate ligand with P and Si donor atom sites and its coordination behaviour.^[14b] The ligand **I-24** was obtained reacting chlorosilylene (PhC(NtBu)₂SiCl) with *ortho*-lithiated diphenylphosphinobenzene (LiC₆H₄PPh₂).

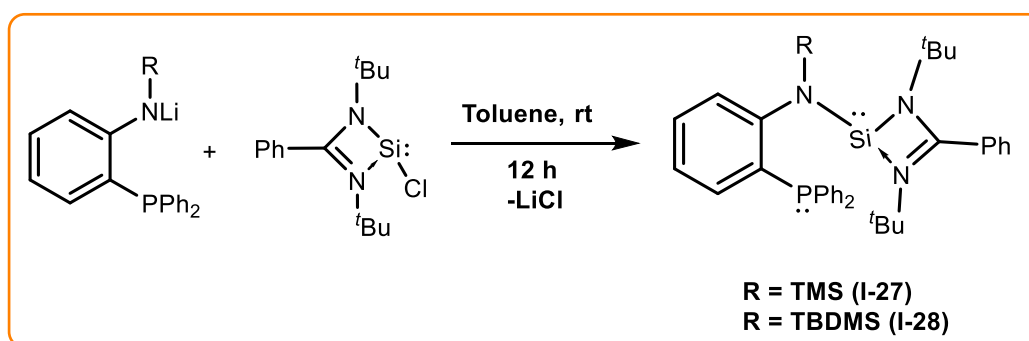
Further treatment of ligand **I-24** with various metal complexes afforded the corresponding metal precursor complexes.

In the same year, Xi and co-workers reported the synthesis and reactivity of side-arm phosphine functionalized amidinato-silylene- and amidinato-germylene and their corresponding Ni⁰ complexes.^[14d]



Scheme 10: Synthesis of ligands **I-25** – **I-26** and corresponding Ni^0 metal complexes

Very recently, Khan et al. reported complexes of phosphine-silylene-based hybrid ligands with first-row transition metals.^[15] They prepared new hybrid silylene-phosphine-based ligands $\text{Si}\{\text{N}(\text{R})\text{C}_6\text{H}_4(\text{PPh}_2)\}\{\text{PhC}(\text{N}^t\text{Bu})_2\}$ [$\text{R} = \text{TMS}$ {trimethylsilyl} (**I-27**) and $\text{R} = \text{TBDMS}$ {*tert*-butyldimethylsilyl} (**I-28**) with two donor sites. Further, the reaction of ligands with base metal halides afforded the corresponding metal complexes of **I-27** and **I-28**.

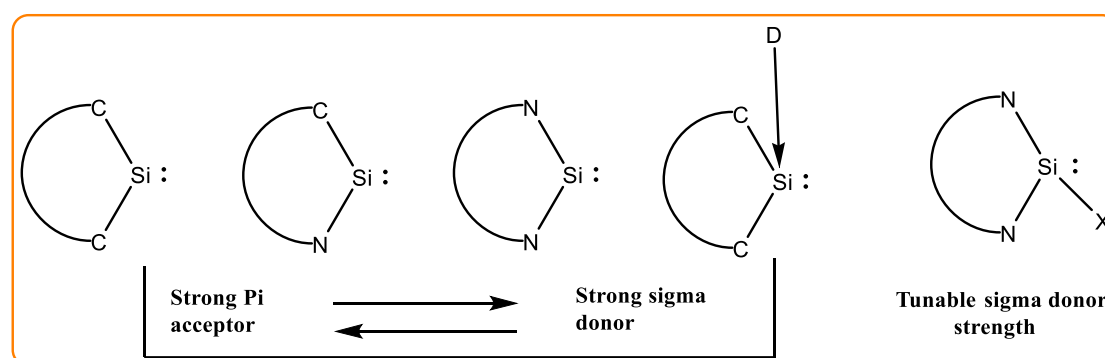


Scheme 11: Synthesis of **I-27** and **I-28** using amidinato chlorosilylene

1.3 Electronic properties of silylene ligands

Different-different backbones of the silylenes are the factor behind the varying electronic properties of the silylene ligands. The dialkylsilylene ligands have the most electronically poor two-coordinate Si^{II} center with an up-field ²⁹Si NMR shift than other silylenes. The π-donation from the nitrogen atom makes cyclic alkyl (amino) silylenes with a more shielded Si^{II} nucleus.^[16]

The three-coordination donor site provides extra stabilization to three-coordinate silylenes with more electron-rich Si^{II} centre. Among three-coordinate silylenes, silylenes having β-diketiminato and *N,N*-di(*tert*-butyl)amidinato backbones facilitates the balance of the σ-donor strength by easily modifying X substitutions.



Scheme 12: Modifications in σ -donation properties of silylenes with different donor sites and X-substitutions

The *N,N*-di(*tert*-butyl)amidinato backbone-based silylene ligands are easy to modify relative to silylene ligands with β -diketiminato backbones.

1.4 Silylene- and phosphine-based hybrid donor ligands in catalysis

NHSis with two-coordinate silicon are both Lewis acids and bases, because of the presence of an empty 3p orbital and a lone pair of electrons, respectively. The remarkable discovery of two-coordinate isolable silylenes stabilizes the

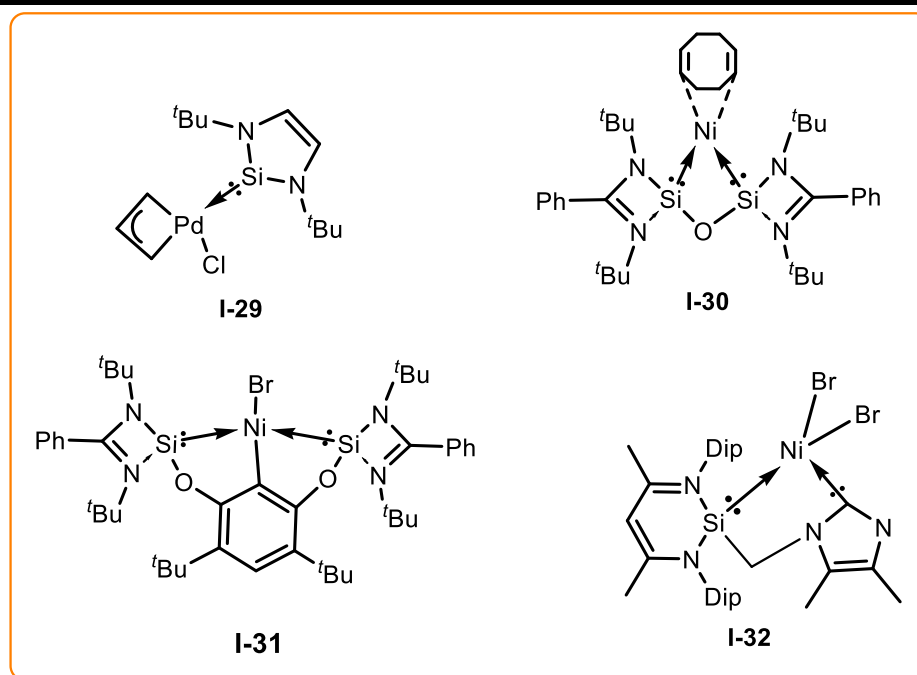
reactive Si^{II} atom providing symbiotic thermodynamic and kinetic stabilization with the advantage of transition metal stabilization support.^[17]

Since the last two decades, silylene, especially isolable NHSi, has been demonstrated to act as a promising ligand in different metal-catalyzed reactions including C-C bond-making reactions, C-X (X = N, Si) bond-making reactions, and reduction reactions.^[12a] Current literature indicates that efficiencies of various catalytic organic transformations can be enhanced by silylene ligands due to their stronger σ -donation ability. The properties can also promote excellent regio-selectivity, stereo-selectivity, and chemo-selectivity in the metal-catalyzed transformation reactions of organic substrates.^[26]

A. C-C bond formation reactions

Some selected examples of NHSi-supported transition-metal complexes showing their potential in catalytic C-C bond formation reactions have been demonstrated in **Scheme 1-15**. Complexes **I-29** and **I-30** were obtained by the reaction of NHSi ligands with corresponding metal complexes via ligand exchange. Complex **I-29** was found useful in the Suzuki coupling reactions. In 2008, Roesky et al. found the catalytic activity of **I-30** in the Heck coupling reactions.^[18]

Complex **I-31** was synthesized by reaction of NHSi ligand with NiBr₂·(DME) metal complex via an aromatic C-H activation in the presence of NEt₃. The Ni^{II} complex **I-31** was demonstrated as active precatalyst in the Sonogashira coupling reactions.^[18a] The Ni complex **I-32** synthesized by the reaction of *N*-heterocyclic silylcarbene with NiBr₂·(DME) via proton migration in toluene. Complex **I-32** was found to be a potent catalyst in Kumada-Tamao-Corriu coupling reactions with excellent catalytic yields.^[18b]

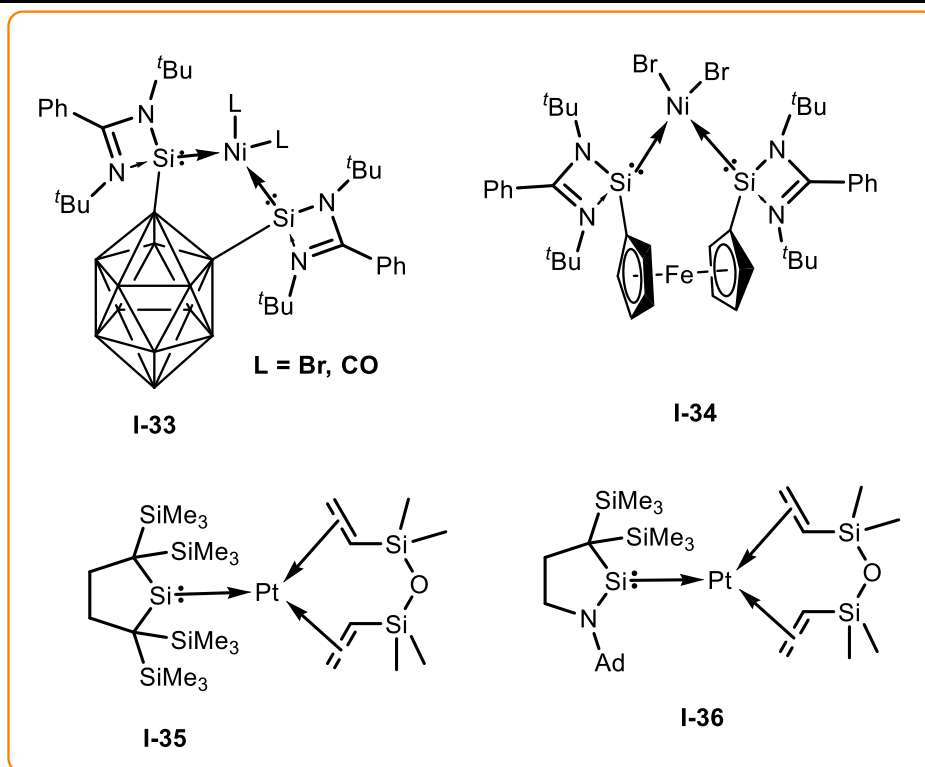


Scheme 13: Selected silylene-based metal complexes utilized in C-C bond-making reactions

B. C- X (X = N, Si) bond-making reactions

In 2016, Driess et al. reported Ni complexes **I-33a**, **I-33b**, and **I-35** promotes Buchwald-Hartwig amination reactions of aryl halides with secondary amines with excellent catalytic activity.^[19c] Iwamoto and coworkers reported the Pt⁰-complex **I-35** having a cyclic dialkyl silylene as a ligand and demonstrated it as a catalyst in the olefin hydrosilylation reactions in the same year. Additionally, **I-35** was also found potent pre-catalyst in the hydrosilylation of terminal alkenes.^[19a]

In 2017, the same group reported a related Pt⁰ complex **I-36** with CAASi ligand which was found effective in olefin hydrosilylation.^[19b]

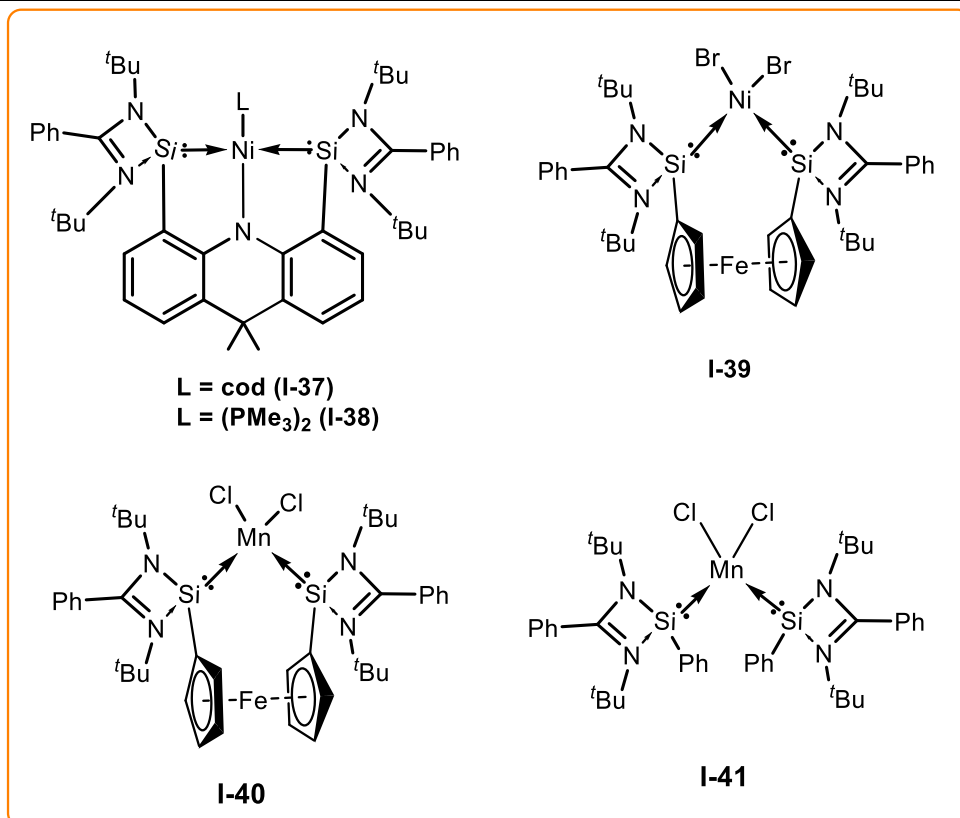


Scheme 14: Selected examples of silylene ligand-bearing metal complexes utilized in C-X (X = N, Si) bond-making reactions

C. Reduction reactions

In 2017, Driess et al. reported Ni(cod)-complex **I-37** (cod=cyclooctadiene) decorated with a xanthane-based bis-N-heterocyclic silylene. This Ni⁰ complex was demonstrated as potent catalyst in the hydrogenation of olefin at room temperature. The Ni(PMe₃)₂-complex **I-38** was also demonstrated catalytically active in the same reactions, but with less efficiency and with different functional group tolerance.^[20c] η⁶-arene Fe⁰ complex **I-39** was found catalytically active in the hydrogenation of aldehydes and ketones.^[20b]

Complex **I-40** and **I-41** reported by Driess et al., are Mn metal complexes bearing silylene ligand which was first found catalytically active in the hydrogenation of unsaturated hydrocarbons with excellent yields.^[20a]



Scheme 15: Selected examples of silylene ligand-based metal complexes utilized in reduction reactions.

2. Motivation

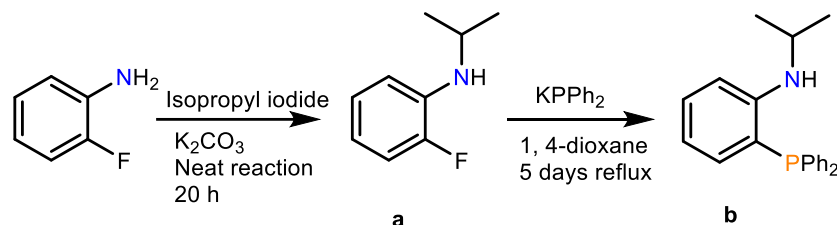
We are aware of the unique electronic properties of NHSis after the brief introduction to silylenes. Considering these potential properties of the silylenes this project is to study the application of NHSi- and phosphine-based hybrid ligand in metal-mediated catalysis.

The objectives of this project are:

- 1) Synthesizing the NHSi- and phosphine-based hybrid donor sites ligand and its corresponding Ni^{II} metal complex.
- 2) Application of NHSi-based hybrid ligand in C-N bond formation reactions under various reaction conditions.

3. Result and Discussion:

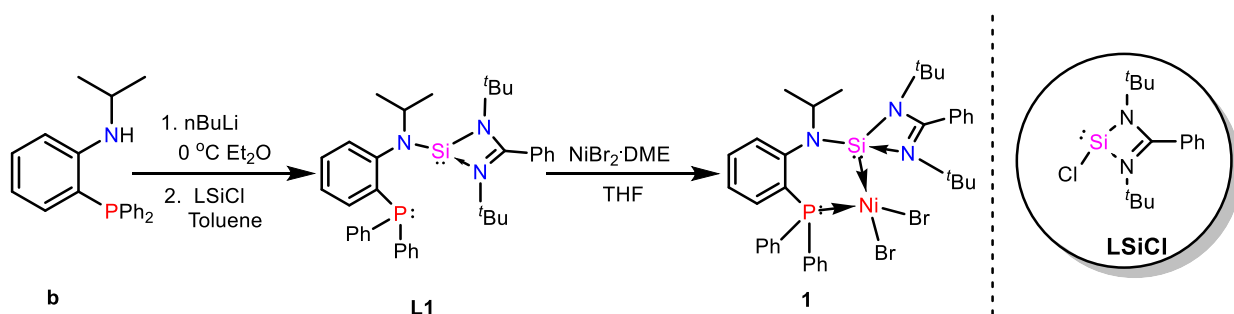
3.1 Synthesis of Silylene- and Phosphine-based hybrid ligand system and its corresponding Ni^{II} metal complex



Scheme 16: Synthesis of phosphine substituted compound **b**

The neat reaction of 2-fluoroaniline with isopropyl iodide in presence of K₂CO₃ for 20 hours afforded compound **a** with 30% yield after purification by using column chromatography. Reflux of **a** with KPPH₂ in Dioxane for 5 days afforded diphenylphosphine-decorated compound **b** with 50% yield. Compound **b** was characterized by regular spectroscopic techniques.

The lithiation of secondary amine was done in diethyl ether at 0 °C. Lithiated salt of compound **b** and chlorosilylene (**LSiCl**) was added to the reaction flask at ambient temperature and stirred for 12 h in toluene. After filtration through frit afforded the expected **L1** in pale yellow solid. The hybrid donor ligand **L1** was characterized with ¹H NMR, ¹³C NMR, ²⁹Si NMR, ³¹P NMR, and mass spectrometry. However, due to the very low melting point, we are not able to crystallize ligand **L1**.



Scheme 17: Synthesis of hybrid ligand **L1** and its corresponding Ni^{II} complex **1**

^{31}P NMR shifts for the ligand are $\delta = -20.64$ ppm (s); ^{29}Si NMR shifts are $\delta = -15.36 - -15.65$ ppm (d).

ESI: HRMS- mass calculated for **L1**: m/z 578.3120; found: m/z 578.3191

Stirring 1:1 equivalents of ligand **L1** and $\text{NiBr}_2 \cdot (\text{DME})$ metal complex in Schlenk flask at room temperature in THF afforded deep red/brownish compound **1** with 90% yield.

^{31}P NMR shift for Complex **1** is $\delta = 20.10$ ppm (s); ^{29}Si NMR shift is $\delta = 10.74 - 9.50$ ppm (d).

We can notice a downfield shift in the ^{31}P NMR and ^{29}Si NMR of complex **1** compare to the ligand **L1** showing the coordination of the Ni^{II} metal center to the donating Si and P atom centers. A downfield shift in NMR shows the electron donation from the hybrid donor centers to the Ni metal.

Crystallization of complex **1** was performed in THF/n-hexane solvent at room temperature and we obtained red colour needle like crystals of complex **1**. Important bond parameters and angles are mentioned in **Table 1** and **Table 2**.

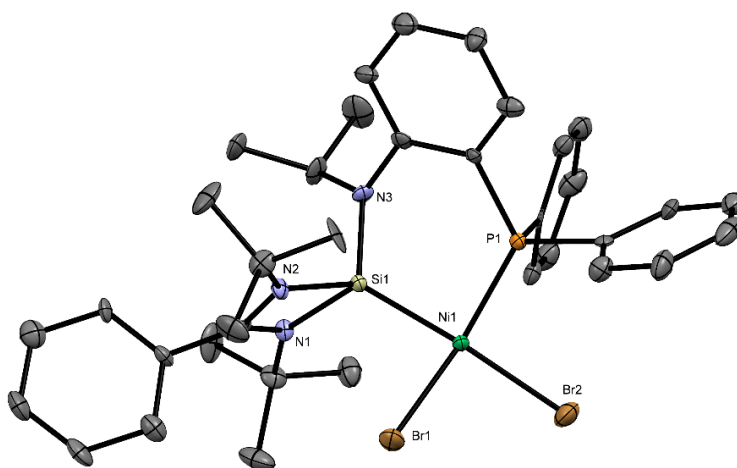


Figure 1. The molecular structure of complex **1**. Hydrogen atoms and solvent molecules are omitted for the better clarity.

Table 1. Selected bond distances [Å] of complex **1**

Bond distances [Å]	
N3-Si1	1.744(5)
Si1-Ni1	2.152(2)
P1-Ni1	2.129(2)
Ni1-Br1	2.315(1)
Ni1-Br2	2.258(1)

Table 2. Selected bond angles [°] of complex **1**

Bond angles [°]	
N3-Si1-Ni2	118.6(2)
P1-Ni1-Si1	87.76(6)
Br1-Ni1-Br2	96.58(4)
Si1-Ni1-Br1	88.51(5)
P1-Ni1-Br2	92.16(5)

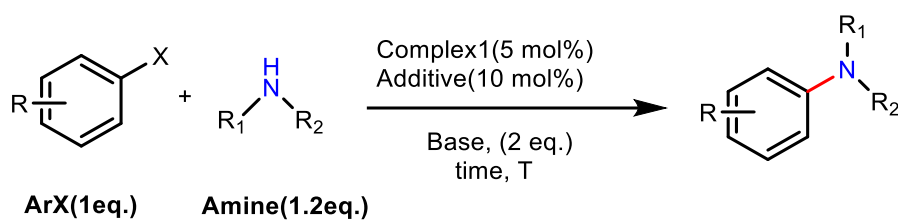
The complexation of **L1** with NiBr₂·(DME) provides complex **1**, which crystallize in the triclinic P1 space group. It's always tricky to analyse the geometry (tetrahedral and square planner) for tetrahedral complexes. However, analysing the previous reports of Ni^{II} tetrahedral complexes we can predict that the complex **1** shows a distorted square planner geometry with the bond angles P1-Ni1-Si1, Br1-Ni1-Br2, Si1-Ni1-Br1, and P1-Ni1-Br2 of 87.76(6), 96.58(4), 88.51(5), and 92.16(5), respectively. This kind of distortion in the geometry of Ni^{II} complexes was also observed in the previously reports of analogous Ni^{II} complexes.^[15, 27]

3.2 C-N coupling reactions catalyzed by silylene- and phosphine-based hybrid donor ligand Ni^{II} complex

Carbon-Nitrogen bond-forming reaction is usually catalyzed by the palladium-based complexes and named as Buchwald-Hartwig amination reactions. These amination reactions are important in organic transformations since a huge number of medical and biochemical important molecules contain amine species.^[21] However, in the last two decades, for decreasing the dependency on expensive and less earth-abundant elements, much attention is given to the development of less expensive and with good abundance on earth first-row transition metal complexes as an alternative. Among transition metals, nickel is a promising replacement metal that could make facile the initial addition step of various substrates at the Ni metal center.^[22]

In recent years, either based on structure or in situ obtained Ni metal complexes are chosen by various researchers as pre-catalyst in Buchwald-Hartwig amination reactions. Taking the strong σ -donating properties of NHSi ligands into account, the integration of NHSis with Ni metal complexes would further make facile the oxidative addition step, thus the development of new NHSi ligand systems for C-N coupling reactions is demanding.^[23]

Initial optimization revealed that 5 mol % of complex **1** can catalyze the desired C-N bond formation reactions providing good to excellent yields after 24 hours at 100 °C using the catalytic amounts of AgSbF₆ and K^tBuO (2 equiv.) used as base. (**Table 3**) The reaction without AgSbF₆ ended up with lower conversions (10-40%). When K₂CO₃, NaHCO₃, and Cs₂CO₃ were utilized, the reactions provided very low conversions (5-20%). Na^tBuO provided better conversions (20-30%), but not to promising levels because of side product formation.

Table 3. The complex **1** C-N coupling using different reaction conditions^[a]

Sr. no.	Additive	Base	Solvent	Time (h)	Temp.(°C)	Conv. ^[b] (%)
1	-	NaHCO ₃	Toluene	12	80	5
2	-	NaHCO ₃	Dioxane	12	80	10
3	AgSbF ₆	K ₂ CO ₃	Toluene	12	100	10
4	AgSbF ₆	K ₂ CO ₃	Dioxane	16	100	15
5	AgSbF ₆	Cs ₂ CO ₃	Toluene	24	100	15
6	AgSbF ₆	Cs ₂ CO ₃	Dioxane	24	100	20
7	AgSbF ₆	Na ^t BuO	Toluene	24	100	25
8	AgSbF ₆	Na ^t BuO	Dioxane	24	100	30
9	AgSbF ₆	K ^t BuO	Toluene	24	100	45
10	AgSbF ₆	K ^t BuO	Dioxane	24	100	95

[a] Reaction conditions: ArX (1 mmol), Amine (1.2 mmol), complex **1** (5 mol%), Additive (10 mol%), base (2 eq.), T=80-100 °C, Solvent = 3mL, t = 12-24 h.

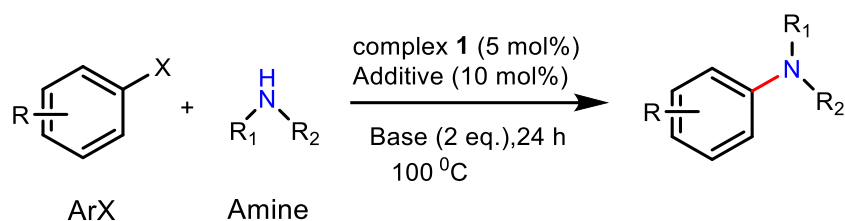
[b] The conversions and yields are calculated taking ArX (X = Cl, Br) substrate as reference.

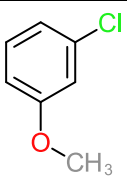
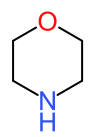
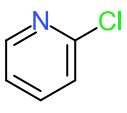
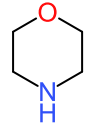
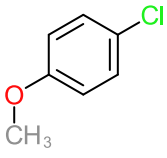
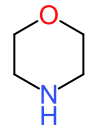
Aryl halides having electron-withdrawing groups on the para- and meta-position of the ring increased the overall reaction rate (Me < H < NH₂ < OMe; **Table 4**). It shows that the electronic properties of starting material used in the reaction determines the overall reaction rate. A substituent at the ortho-positions gave

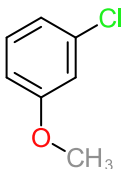
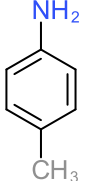
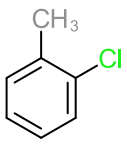
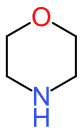
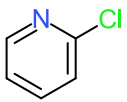
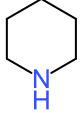
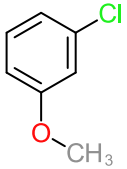
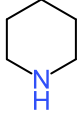
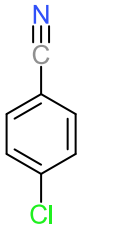
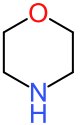
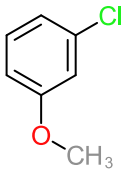
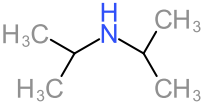
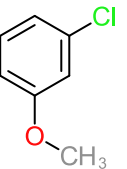
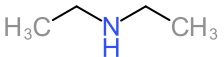
lower conversions compared to *meta*- and *para*-positions of aryl halides suggesting the steric impact.

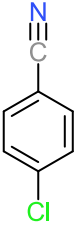
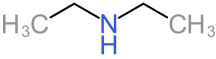
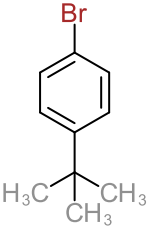
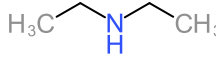
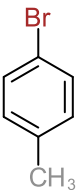
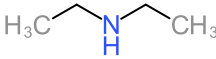
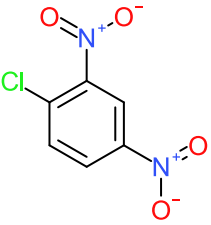
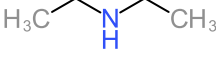
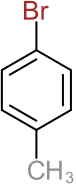
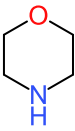
The catalytic potential of complex **1** was verified using different amine substrates with different substituents to reach the various steric and electronic properties. It was observed that the amination of aryl halides provided good to excellent yields (**Table 3**) as a result of the steric and electronic properties of amine substrates. Usually, anilines and secondary amines with a bulky group (e.g. Diisopropylamine) gave lower yields than secondary amines with less steric substituents. (e.g., Diethyl amine).

Table 4. Some C-N coupled products catalyzed by complex **1**



Entry	ArX	Amine	t (h)	Conv. ^[b] (%)	Isolated yield (%)
1			24	99	85
2			24	90	80
3			24	92	83

4			24	85	78
5			24	85	76
6			24	88	82
7			24	95	85
8			24	97	88
9			24	85	80
10			24	99	90

11			24	98	88
12			12	97	85
13			12	95	86
14			24	90	82
15			12	92	84

[b] The conversions and yields are calculated taking ArX (X = Cl, Br) substrate as reference.

4. Materials and Methods

4.1 General Consideration

All reactions and manipulations were carried out using standard Schlenk techniques and all the sensitive reactions were performed in an oxygen-free environment i.e. in using nitrogen/argon-filled glovebox. All the glassware were dried at 140 °C and cooled down to ambient temperature prior to use and purged with nitrogen/argon gas. The handling of the sensitive solid samples were carried out in inert gas filled glovebox with maintained O₂ and H₂O levels below 0.5 ppm.

All solvents were distilled and purified under an N₂ atmosphere prior to use using appropriate methods and stored in Schlenk flasks. The purification and distillation of Benzene, toluene, and n-hexane were carried out using Na/benzophenone. KOH were added to Et₂O and THF to get pre-dried solvents and then distillation were carried out from Na/benzophenone.

4.2 Starting materials

All starting materials were commercially available and used as received. The important precursor [*N*, *N'*-di-tert-butyl(phenylamidinato)chlorosilylene],^[9] were synthesized according to reported procedure.

4.3 Analytical Methods

Nuclear Magnetic Resonance (NMR) Measurements: For all these moisture/air-sensitive compounds NMR samples were prepared under an inert environment and maintaining the inert environment the samples were sealed-off in dried NMR tubes for measurements. All the deuterated solvents i.e., C₆D₆, toluene-d₆, and CDCl₃ were dried over sodium, distilled in inert atmosphere (N₂/Ar) and stored into sealed schlenk flasks. Using ARX 400 (¹H, 400 MHz; ¹³C, 100.46 MHz)

spectrometers from the Bruker, all these ^{13}C -NMR and ^1H -NMR spectra were recorded. Using ARX 400 (^{29}Si , 79.490 MHz) spectrometer, ^{29}Si -NMR spectra were recorded.

The short notations for the multiplicity of the signals are as follows: br = broad, m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet and sept = septet.

Mass Spectrometry: Mass spectra of all isolated compounds - recorded using AB Sciex, 4800 plus HRMS on the Waters Synapt, USA. A sealed glass tube were used to record the melting points of samples. The N_2/Ar filled glovebox were used to prepare all the sensitive solid samples and solution of sample was prepared freshly before the measurement into the inert atmosphere. The presentation of the mass spectra is in the standard form, m/z.

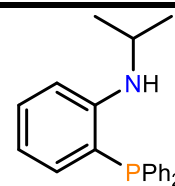
4.4 Synthesis and characterization of all compounds

A. Synthesis of silylene- and phosphine-based hybrid ligand

Synthesis of compound **a**: 2-Fluorobenzamine (11.5 g, 103 mmol, 1 equiv.) and 2-Iodopropane (52.5 g, 309 mmol, and 3.0 equiv.) were added to a 100 mL Schlenk flask. With stirring, potassium carbonate (15.5 g, 113 mmol, 1.1 equiv.) was added to the flask. After 24 hours of reflux of this neat reaction, we got an off-white solution. Added some DI water and DCM to the reaction mixture and separated organic and aqueous layers using a separating funnel. Dried organic layer under vacuum and separated the pure product using column chromatography. Compound **a** was isolated with 30 % yield and characterized with ^1H NMR.

^1H NMR (400 MHz, CDCl_3) δ 6.94 – 6.83 (m, 2H), 6.62 (td, $J = 8.5, 1.5$ Hz, 1H), 6.53 – 6.47 (m, 1H), 3.68 – 3.48 (m, 1H), 1.16 (d, $J = 6.2$ Hz, 6H).

Synthesis of compound **b**: **1** (4.28 g, 27.93 mmol, 1equiv.) and KPPH_2 (55.86 mL, 27.93 mmol, 1 equiv.) was added to a 250 mL schlenk flask. Around 80 ml of **1**, 4-dioxane was added to the flask as solvent.



The reaction mixture was set for 5 days of reflux at 110 °C. After 5 days of reflux, the workup of the reaction mixture in DCM was followed by drying of DCM under a vacuum. Compound **b** was isolated with 50 % yield. Then we added some amount of ethanol for recrystallization but no crystals were obtained with ethanol. Then we dried ethanol and tried recrystallization in n-pentane.

^1H NMR (400 MHz, CDCl_3) δ = 7.22 (d, J = 2.4 Hz, 9H), 7.15 – 7.11 (m, 1H), 6.77 – 6.72 (m, 1H), 6.55 (dd, J = 8.1, 4.8 Hz, 1H), 6.48 (t, J = 7.4 Hz, 1H), 3.51 (m, J = 11.0, 5.5 Hz, 1H), 0.97 (d, J = 6.3 Hz, 6H).

^{31}P NMR (162 MHz, CDCl_3) δ = -20.58 ppm (s).

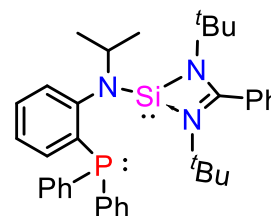
Synthesis of **L1**: **2** (10.2 g, 31.5 mmol, 1 equiv.) was suspended in 50 mL Et_2O in a 100 mL Schlenk flask. Flask was set up in a container filled with ice and $n\text{-BuLi}$ (12.6 mL, 31.5 mmol, 1 eq.) was slowly added to the flask with stirring. After the addition flask was packed and removed from the ice container then left for 12 h of stirring. After 12 hrs reaction, added some amount of hexane was for recrystallization. Lithiated salt (1 g, 2.11 mmol, 1 eq.) and chlorosilylene LSiCl (0.624 g, 2.11 mmol, 1 eq.) were suspended in toluene in a 100 mL schlenk flask. After overnight stirring, toluene was reduced under vacuum and some amount of hexane was added for recrystallization.

^1H NMR (400 MHz, C_6D_6) δ = 7.30 (m, J = 7.7, 3.2, 1.7 Hz, 1H), 7.22 – 7.16 (m, 1H), 6.89 (d, J = 7.6 Hz, 10H), 6.79 (d, J = 0.7 Hz, 5H), 6.68 – 6.62 (m, 1H), 6.40 – 6.31 (m, 1H), 1.05 (s, 18H), 0.64 – 0.61 (m, 1H).

^{13}C NMR (101 MHz, C_6D_6) δ = 137.13 (d, J = 2.4 Hz), 136.67 (s), 132.72 (dt, J = 14.7, 9.8 Hz), 132.06 (d, J = 10.5 Hz), 129.45 (s), 128.23 – 126.95 (m), 126.95 – 125.99 (m), 125.06 (s), 124.62 (d, J = 22.5 Hz), 124.50 (s), 123.02 (s), 51.99 (d, J = 8.3 Hz), 31.38 (s), 31.01 (d, J = 10.5 Hz), 30.32 (dd, J = 42.4, 15.3 Hz), 21.50 (d, J = 5.6 Hz), 20.25 (s).

^{31}P NMR (162 MHz, C_6D_6) δ = -20.64 ppm (s).

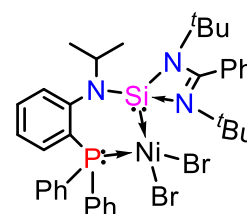
^{29}Si NMR (80 MHz, C_6D_6) δ = -15.51 (d, J = 22.9 Hz) ppm.



B. Coordination of $\text{NiBr}_2\cdot(\text{DME})$ complex with the ligand L1

Ligand **L1** (1.49 g, 2.16 mmol, 1 equiv.) and $\text{NiBr}_2\cdot(\text{DME})$ (0.665 g, 2.16 mmol, 1 equiv.) were weighed in a 100 mL Schlenk flask. THF was added as a solvent and the reaction mixture was stirred for 3 hours at room temperature. After 3 hours, some amount of THF was reduced under vacuum and the flask was kept at -20°C for crystallization.

Due to the paramagnetic nature of the Ni metal center, ^1H NMR of complex **1** got denatured or there is a widening in the peaks.



^{31}P NMR (202 MHz, CDCl_3) δ = 20.10 ppm (s).

^{29}Si NMR (99 MHz, CDCl_3) δ = 10.74 – 9.50 ppm (d).

5. References

- [1] a) T. Iwamoto, S. Ishida, in *Organosilicon Compounds*, Academic Press, **2017**, pp. 361-532; b) S. S. Sen, S. Khan, S. Nagendran, H. W. Roesky, *Acc. Chem. Res.* **2012**, 45, 578-587; c) S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, 30, 1748-1767.
- [2] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, 116, 2691-2692.
- [3] a) P. Zark, A. Schäfer, A. Mitra, D. Haase, W. Saak, R. West, T. Müller, *J. Organomet. Chem.* **2010**, 695, 398-408; b) H. Cui, Y. Shao, X. Li, L. Kong, C. Cui, *Organometallics* **2009**, 28, 5191-5195.
- [4] a) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Organomet. Chem.* **1996**, 521, 211-220; b) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, D. Blaser, *J. Chem. Soc., Chem. Commun.* **1995**, 1931-1932; c) M. Denk, J. C. Green, N. Metzler, M. Wagner, *J. Chem. Soc., Dalton Trans.* **1994**, 2405-2410.
- [5] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2005**, 631, 1383-1386.
- [6] M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, 128, 9628-9629.
- [7] a) A. Meltzer, S. Inoue, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2010**, 132, 3038-3046; b) A. Meltzer, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2009**, 131, 7232-7233.

-
- [8] C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, 45, 3948-3950.
- [9] S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, 132, 1123-1126.
- [10] B. D. Reken, T. M. Brown, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2012**, 134, 6504-6507.
- [11] a) G. Tavcar, S. S. Sen, R. Azhakar, A. Thorn, H. W. Roesky. *Inorg. Chem.* **2010**, 49, 10199–10202. b) K. Junold, J. A. Baus, C. Burschka, R. Tacke. *Angew. Chem., Int. Ed.* **2012**, 51, 7020–7023. c) M. Stoelzel, C. Präsang, S. Inoue, S. Enthaler, M. Driess. *Angew. Chem., Int. Ed.* **2012**, 51, 399–403. d) M. J. Krahfuss, U. Radius. *Inorg. Chem.* **2020**, 59, 10976–10985.
- [12] a) S. Raoufmoghaddam, Y. Zhou, Y. Wang, M. Driess. *J. Organomet. Chem.* **2017**, 829, 2–10. b) S. Fujimori, S. Inoue. *Eur. J. Inorg. Chem.* **2020**, 3131–3142.
- [13] C. So, H. W. Roesky, J. Magull, R. B. Oswald. *Angew. Chem., Int. Ed.* **2006**, 45, 3948–3950. b) S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmüller, A. Pal, R. Herbstlirmer. *Organometallics* **2008**, 27, 5459–5463.
- [14] a) S. Khan, S. Pal, N. Kathewad, I. Purushothaman, S. De, P. Parameswaran. *Chem. Commun.* **2016**, 52, 3880–3882. b) M. Nazish, M. M. Siddiqui, S. K. Kumar Sarkar, A. Münch, C. M. Legendre, R. Herbstlirmer, D. Stalke, H. W. Roesky. *Chem. Eur. J.* **2021**, 27, 1744–1752. c) J. A. Cabeza, P. García-Álvarez, C. J. Laglera-Gándara, E. Pérez-Carreño. *Dalton Trans.* **2020**, 49, 8331–8339. d) M. Zhong, J. Wei, W. Zhang, Z. Xi. *Organometallics* **2021**, 40, 310–313.
- [15] R. Akhtar, S. H. Kaulage, M. P. Sangole, S. Tothadi, P. Parvathy, P. Parameswaran, K. Singh, S. Khan. *Inorg. Chem.* **2022**, 61, 13330–13341.

[16] T. Troadec, A. Prades, R. Rodriguez, R. Mirgalet, A. Baceiredo, N. SaffonMerceron, V. Branchadell, T. Kato, *Inorg. Chem.* **2016**, 55, 8234-8240.

[17] a) S. K. Grumbine, T. D. Tilley, F. P. Arnold, A. L. Rheingold, *J. Am. Chem. Soc.* **1994**, 116, 5495-5496. b) S. D. Grumbine, T. D. Tilley, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, 115, 358-360.

[18] a) M. Stoelzel, C. Präsang, B. Blom, M. Driess, *Aust. J. Chem.* **2013**, 66, 1163-1170. b) G. Tan, S. Enthaler, S. Inoue, B. Blom, M. Driess, *Angew. Chem. Int. Ed.* **2015**, 54, 2214-2218.

[19] a) T. Iimura, N. Akasaka, T. Iwamoto, *Organometallics* **2016**, 35, 4071-4076. b) T. Iimura, N. Akasaka, T. Kosai, T. Iwamoto, *Dalton Trans.*, **2017**, 46, 8868-8874. c) Y.-P. Zhou, S. Raoufmoghaddam, T. Szilvási, M. Driess, *Angew. Chem. Int. Ed.* **2016**, 55, 12868-12872.

[20] a) Y. P. Zhou, Z. Mo, M. P. Luecke, M. Driess, *Chem. Eur. J.*, **2018**, 24, 4780-4784. b) M.-P. Luecke, D. Porwal, A. Kostenko, Y. P. Zhou, S. Yao, M. Keck, C. Limberg, M. Oestreich, M. Driess, *Dalton Trans.*, **2017**, 46, 16412-16418.

[21] a) D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, 47, 6338-6361. b) J. F. Hartwig, *Acc. Chem. Res.* **2008**, 41, 1534-1544.

[22] a) R. M. Bullock, *Science* **2013**, 342, 1054-1055. b) S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, *Acc. Chem. Res.* **2015**, 48, 1995-2003. c) P. J. Chirik, *Acc. Chem. Res.* **2015**, 48, 1687-1695.

[23] V. Ritleng, M. Henrion, M. J. Chetcuti, *ACS Catal.* **2016**, 6, 890-906.

[24] G.-H. Lee, R. West, T. Müller, *J. Am. Chem. Soc.* **2003**, 125, 8114-8115.

[25] a) T. J. Hadlington, J. A. B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones, *Chem. Commun.* **2016**, 52, 1717-1720; b) A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. References 150 Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Angew. Chem. Int. Ed.* **2013**, 52, 568-571.

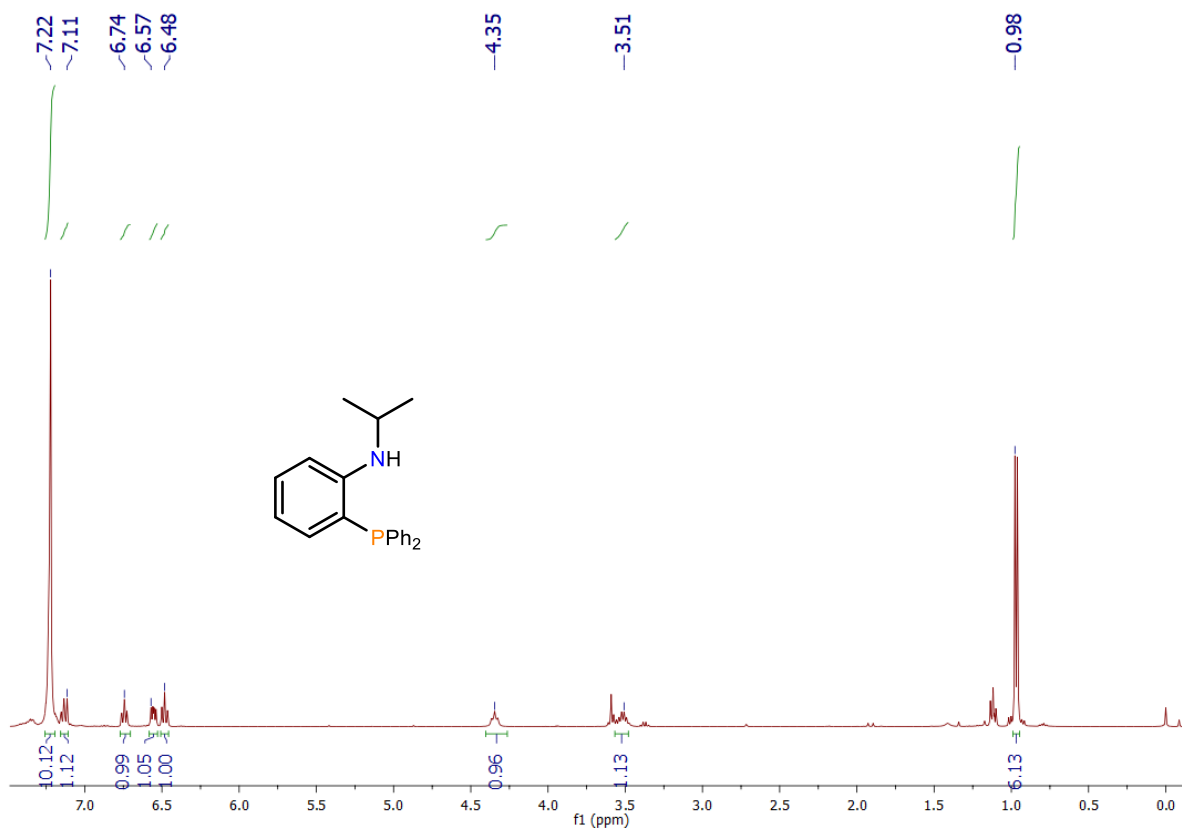
[26] Yu-Peng Zhou, M. Driess, *Angew.Chem.Int.Ed.* **2019**,58,3715 –3728.

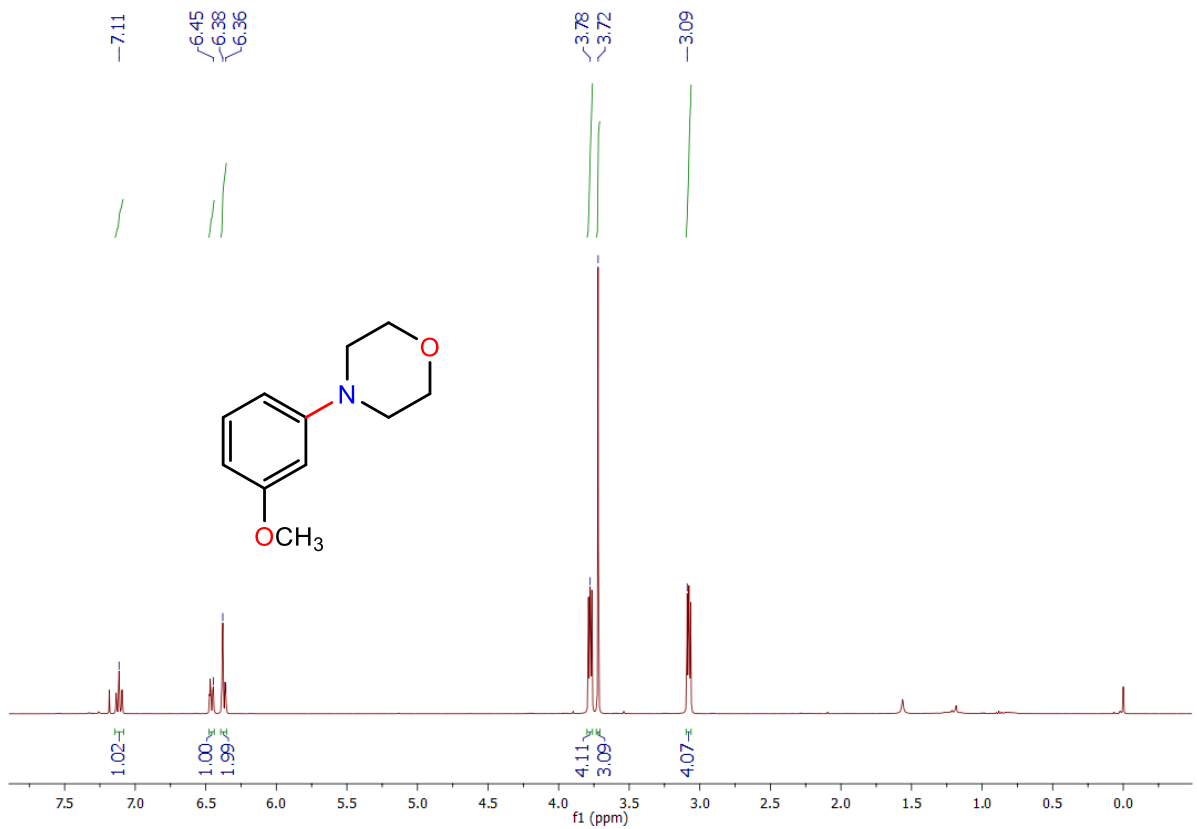
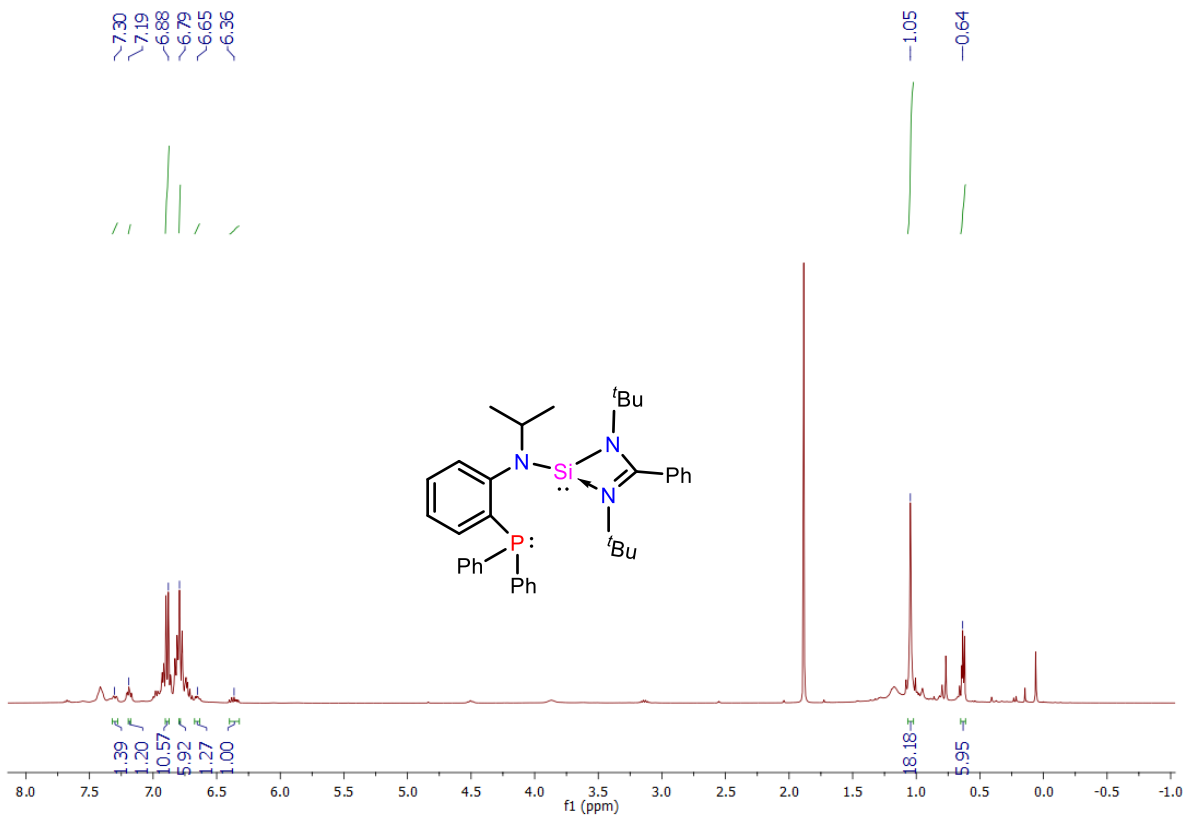
[27] a) J. Baus, F. M. Mück, H. Schneider, R. Tacke, *Chem. Eur. J.* **2017**, 23, 296–303; b) G. Tan, S. Enthaler, S. Inoue, B. Blom, M. Driess, *Angew. Chem., Int. Ed.* **2015**, 54, 2214–2218. c)

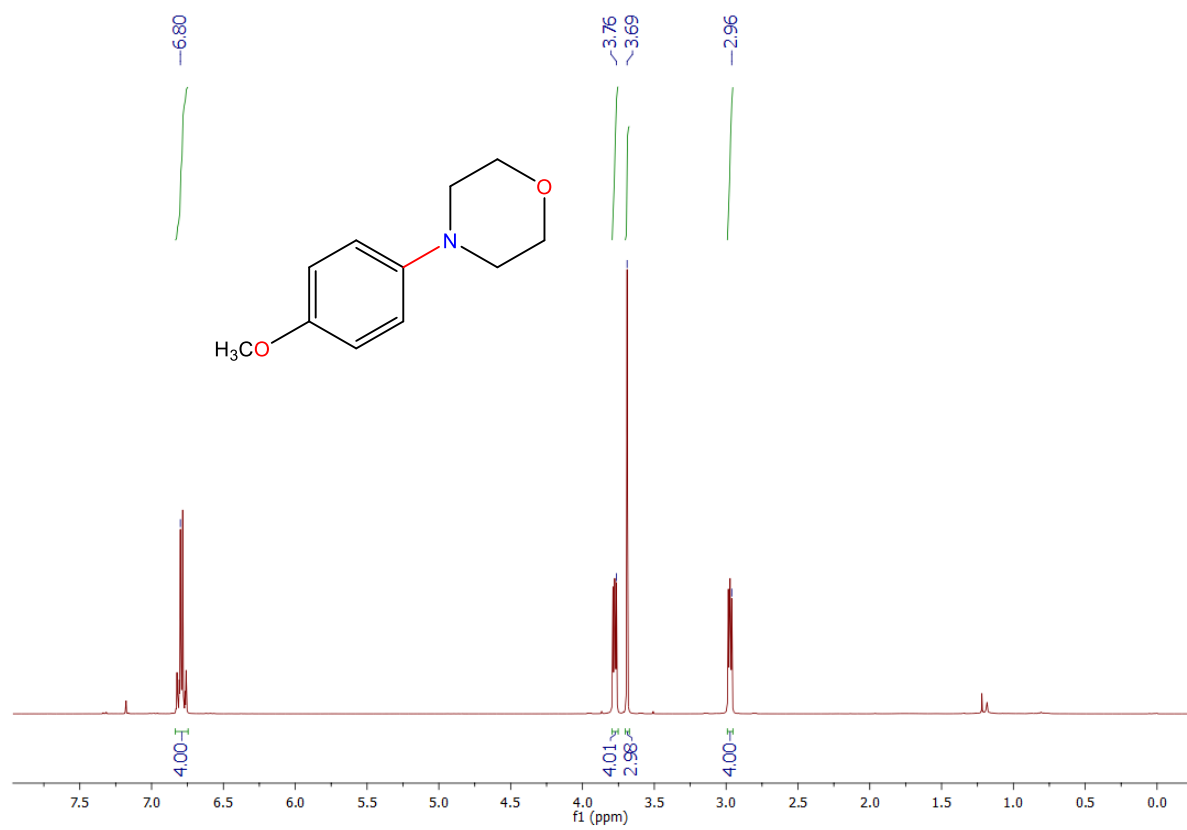
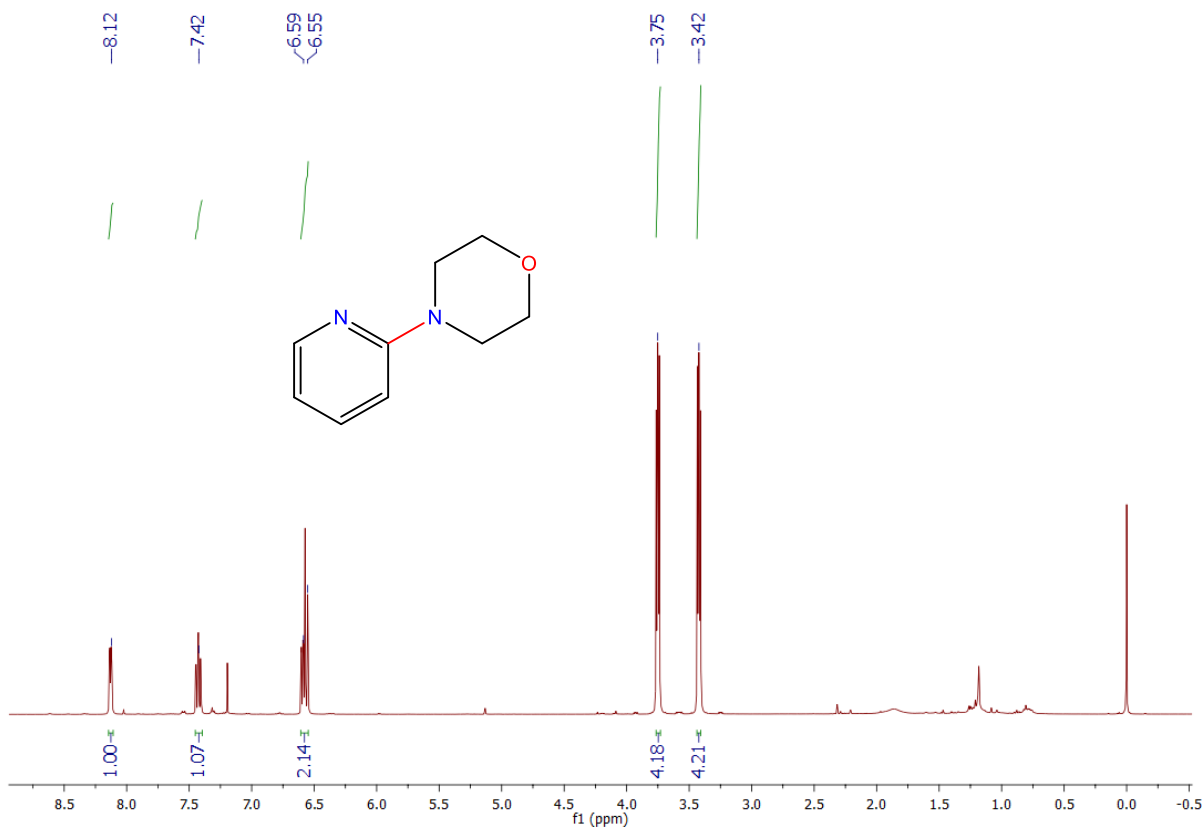
6. Appendix

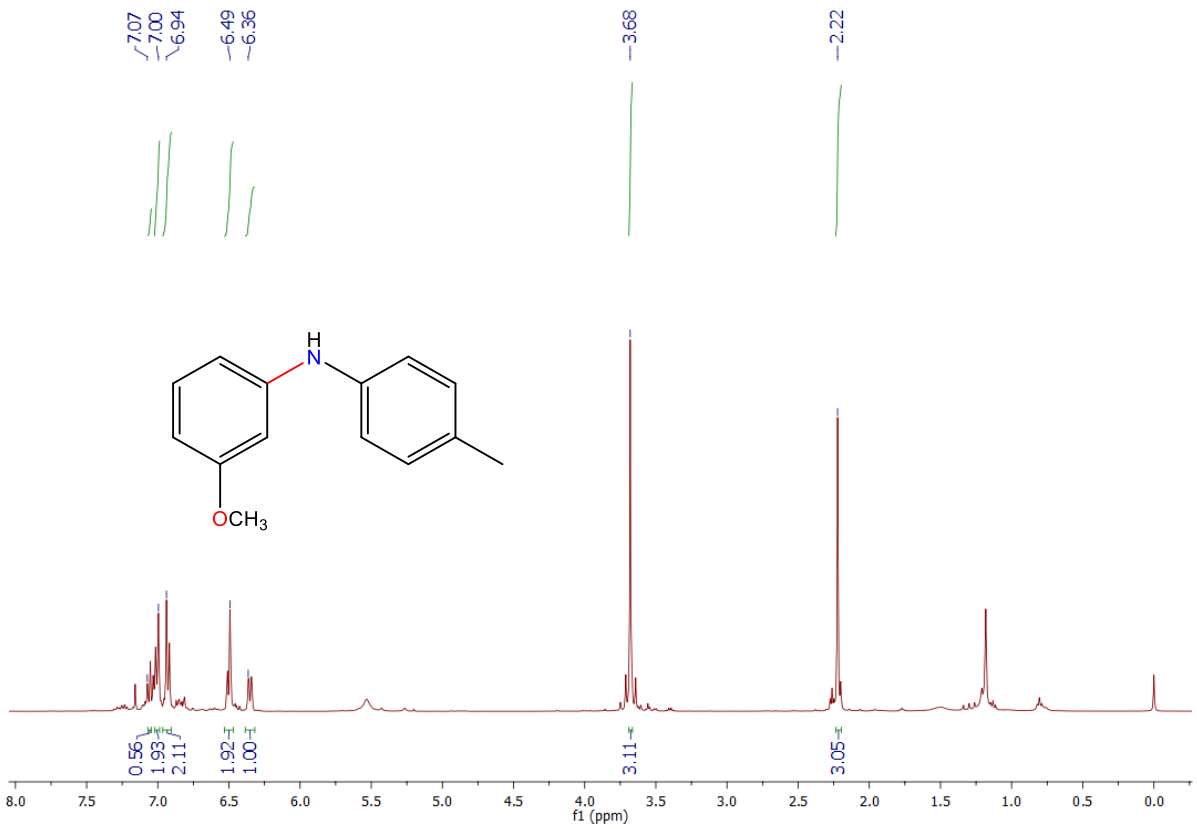
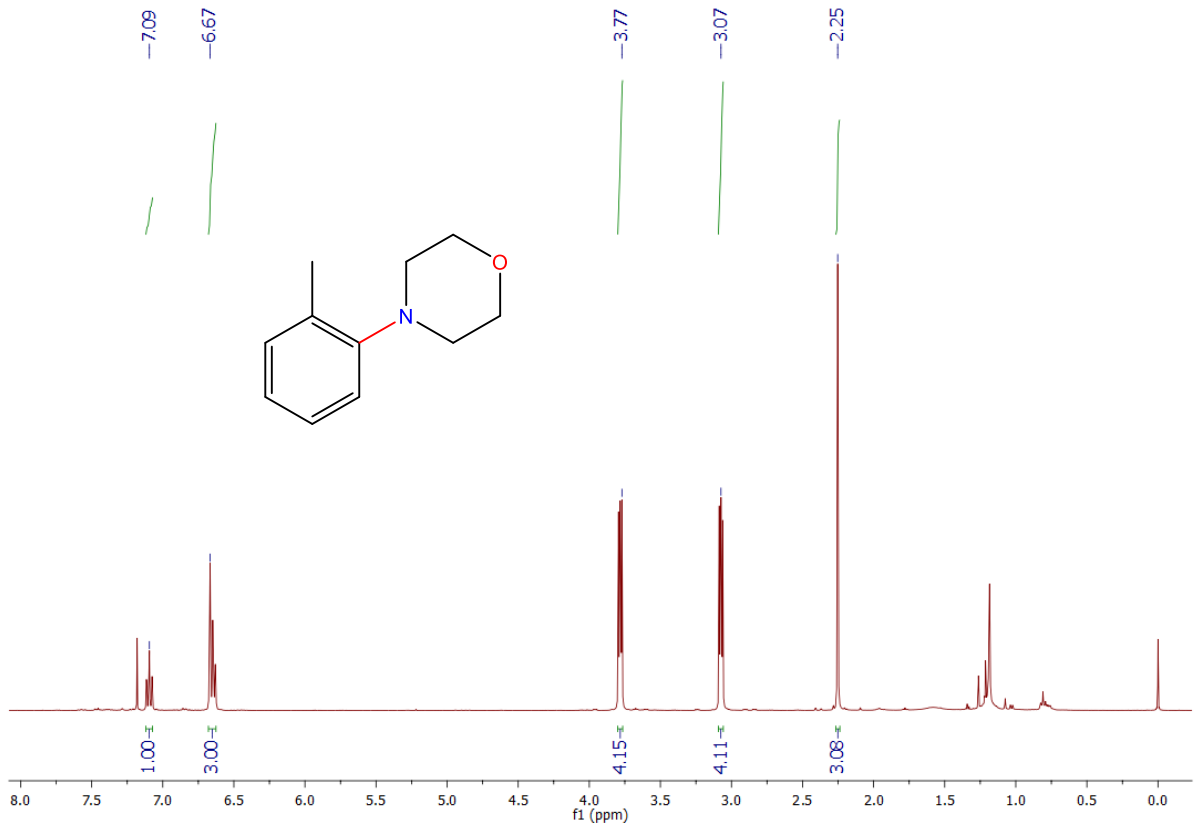
NMR data

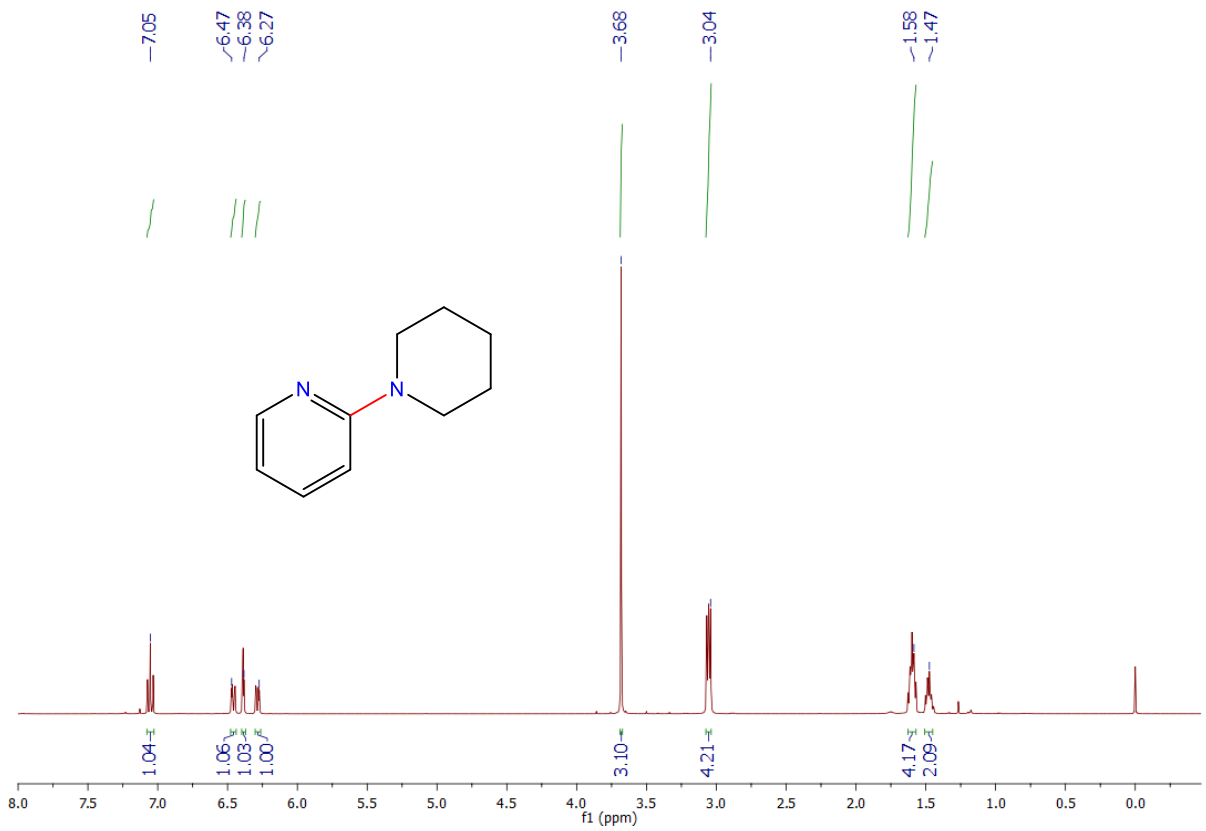
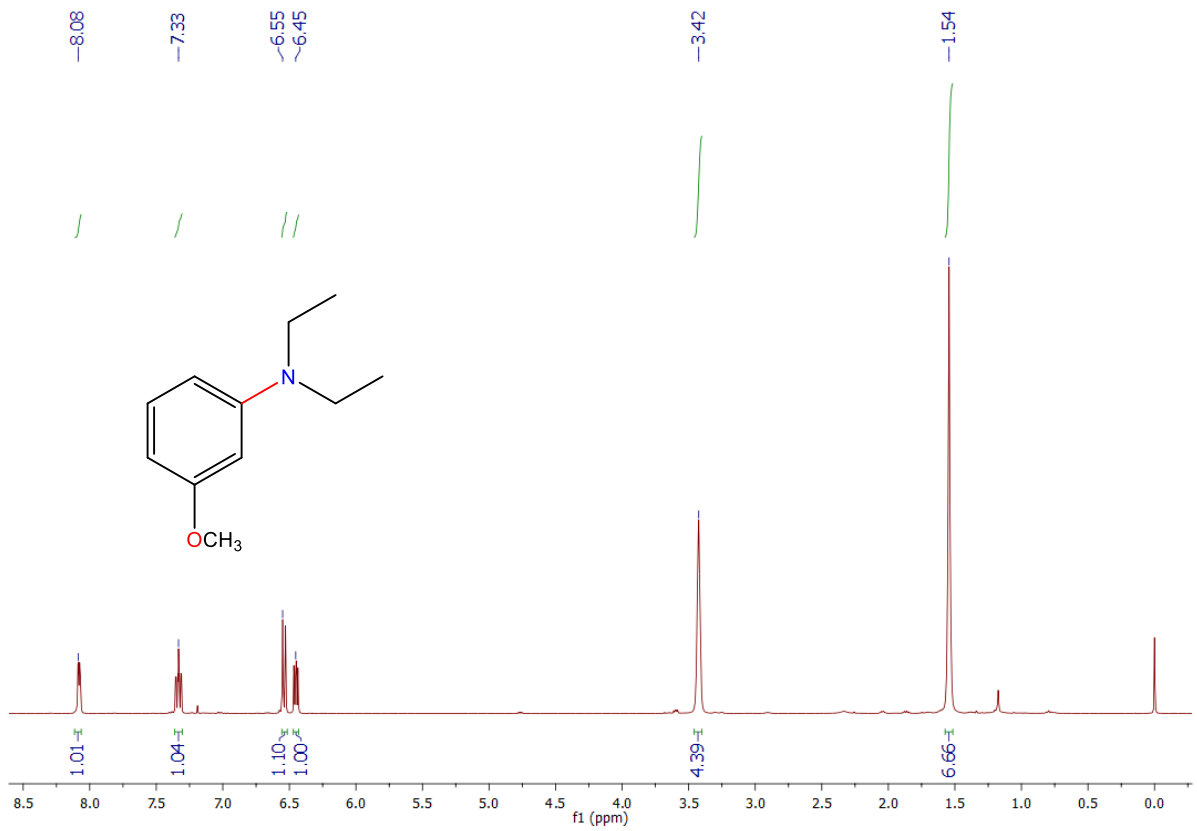
^1H NMR data

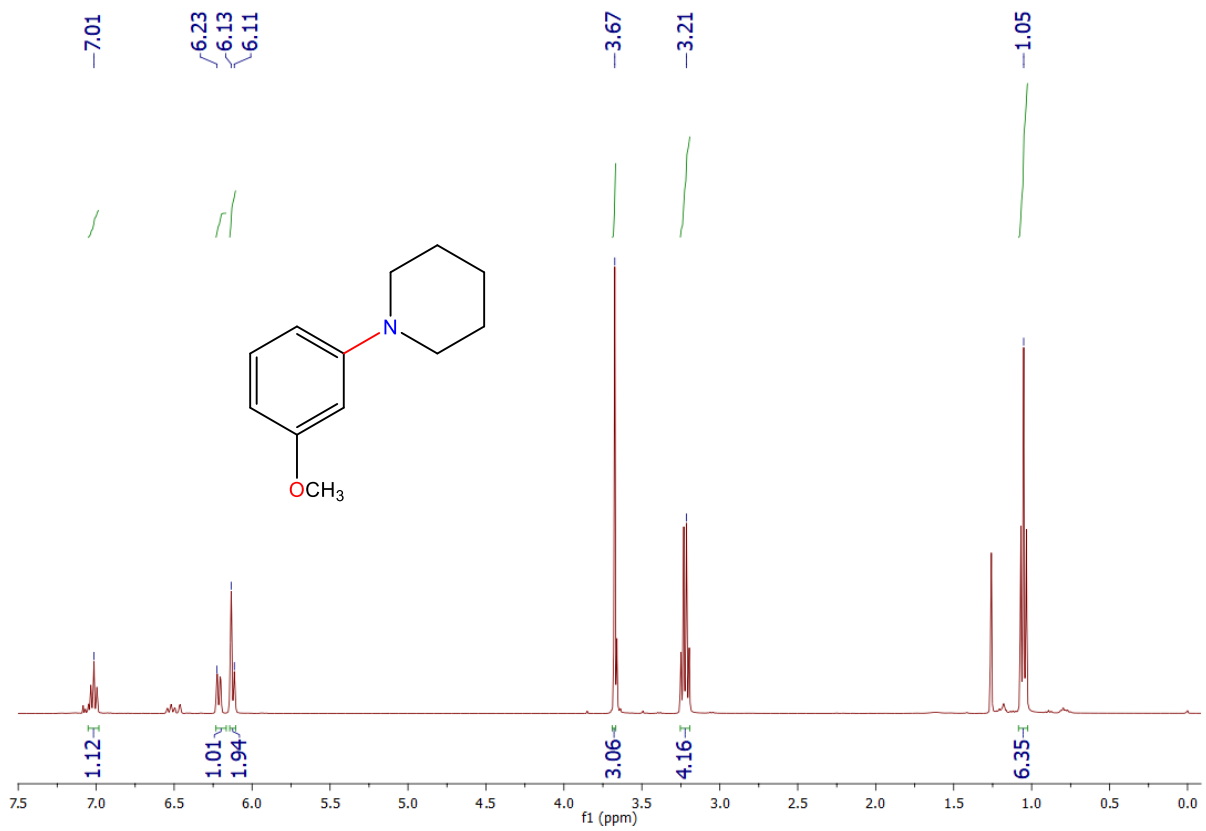
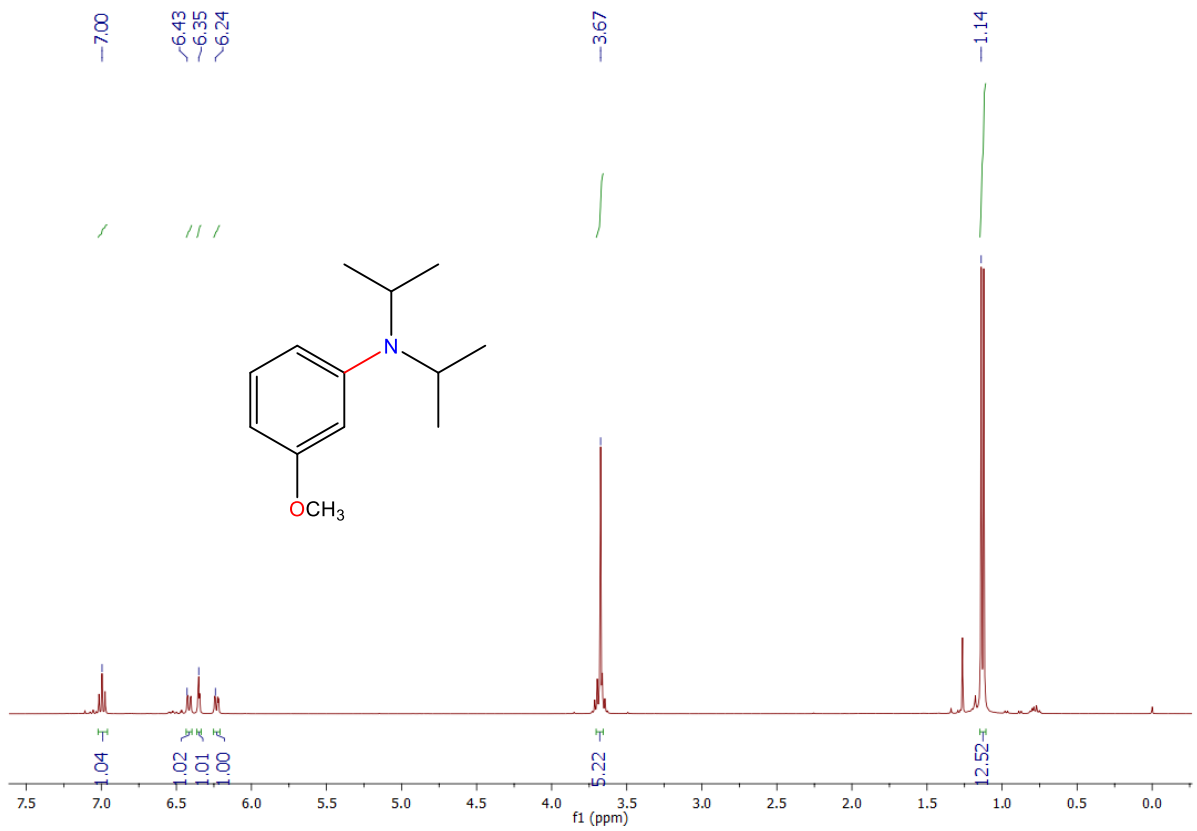


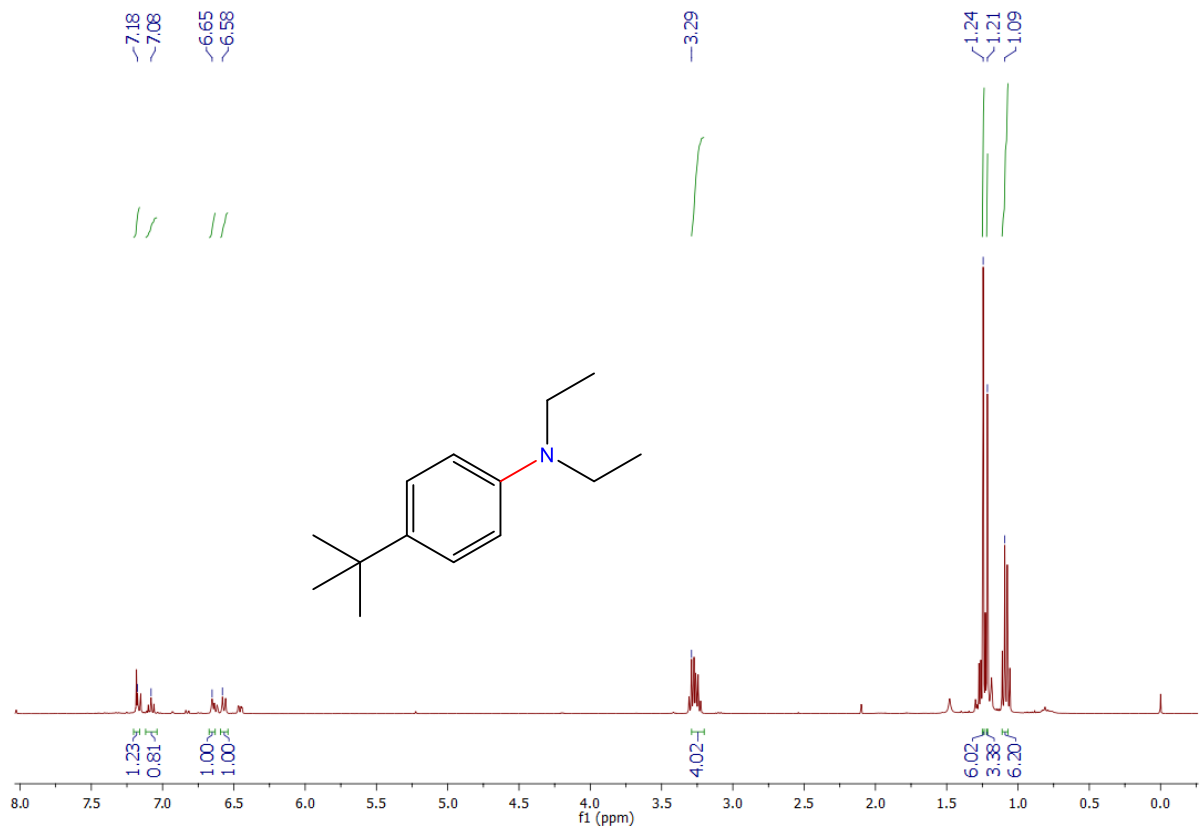
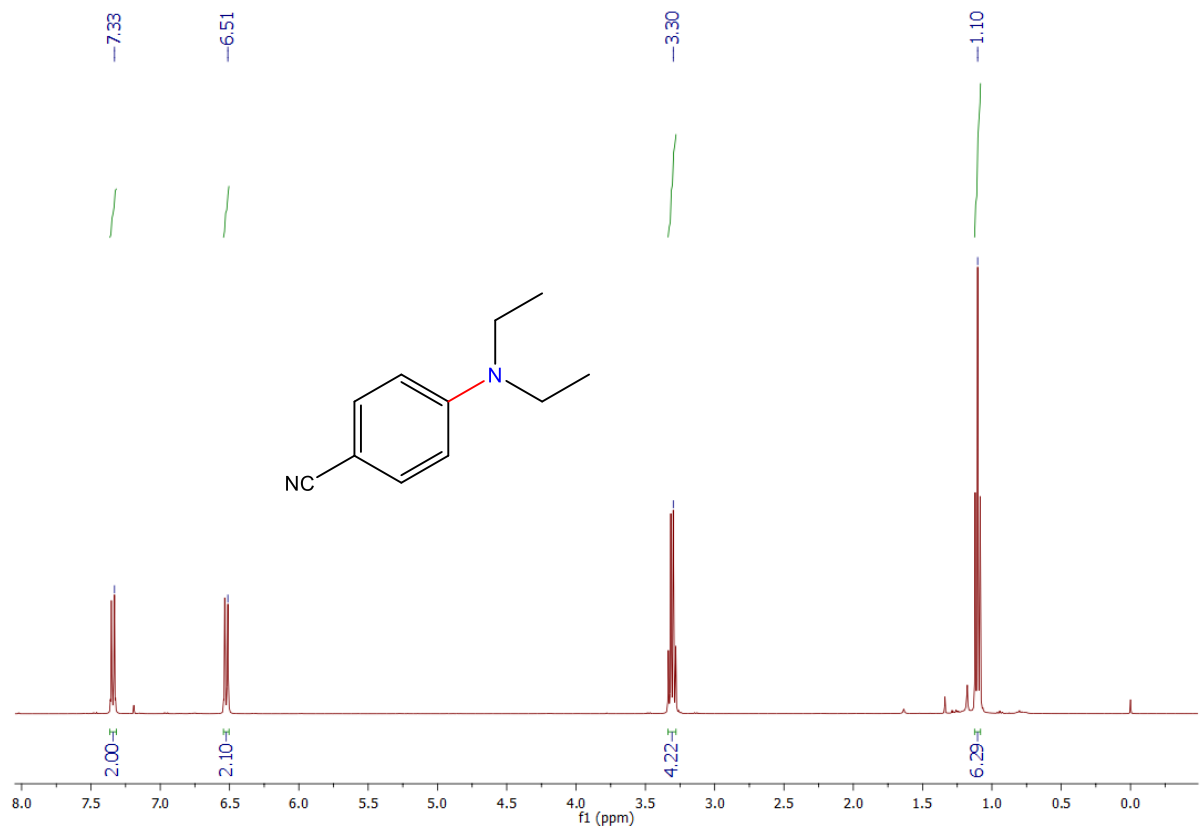


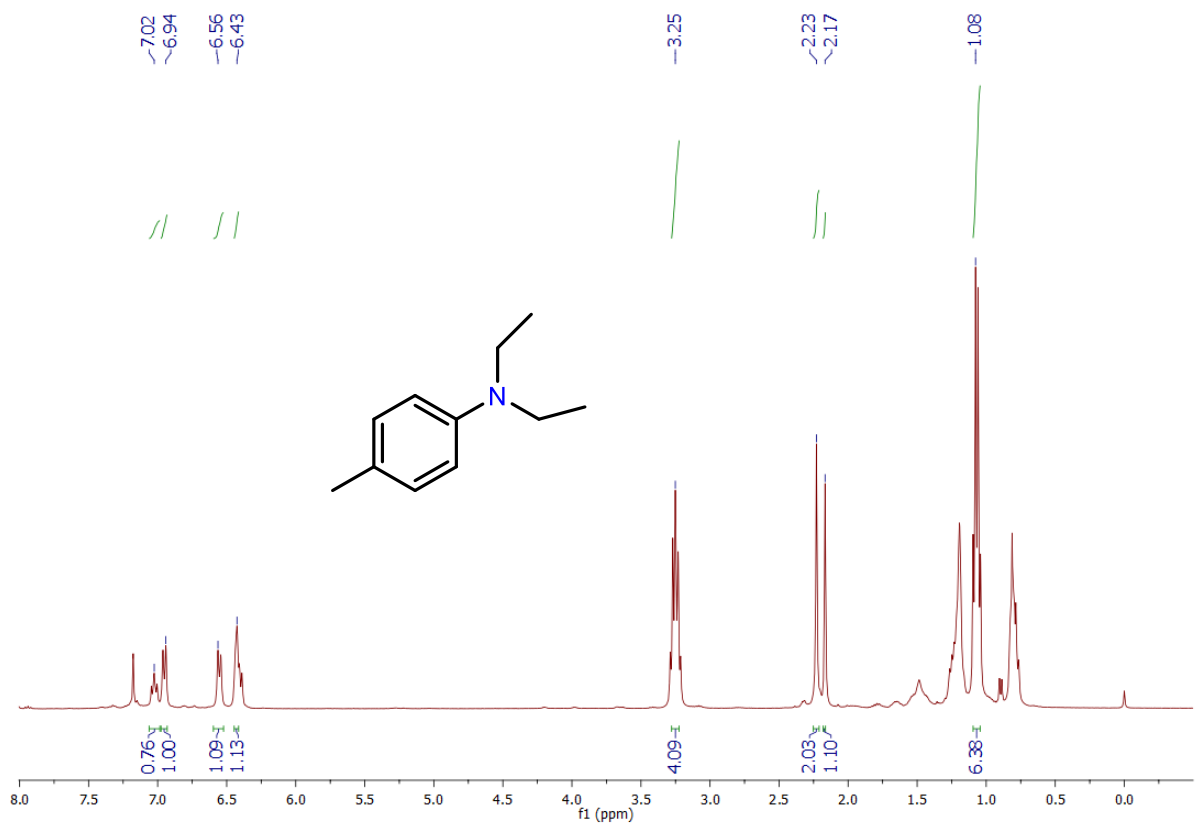
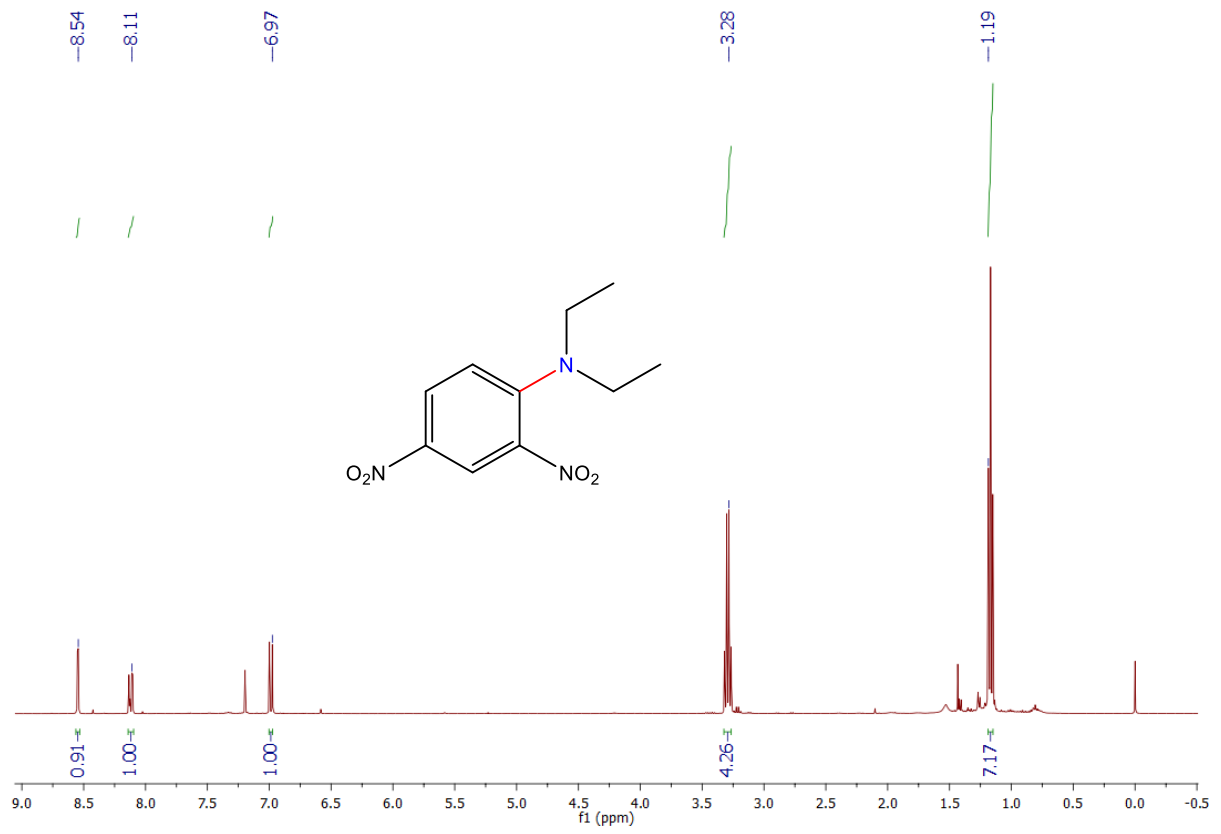


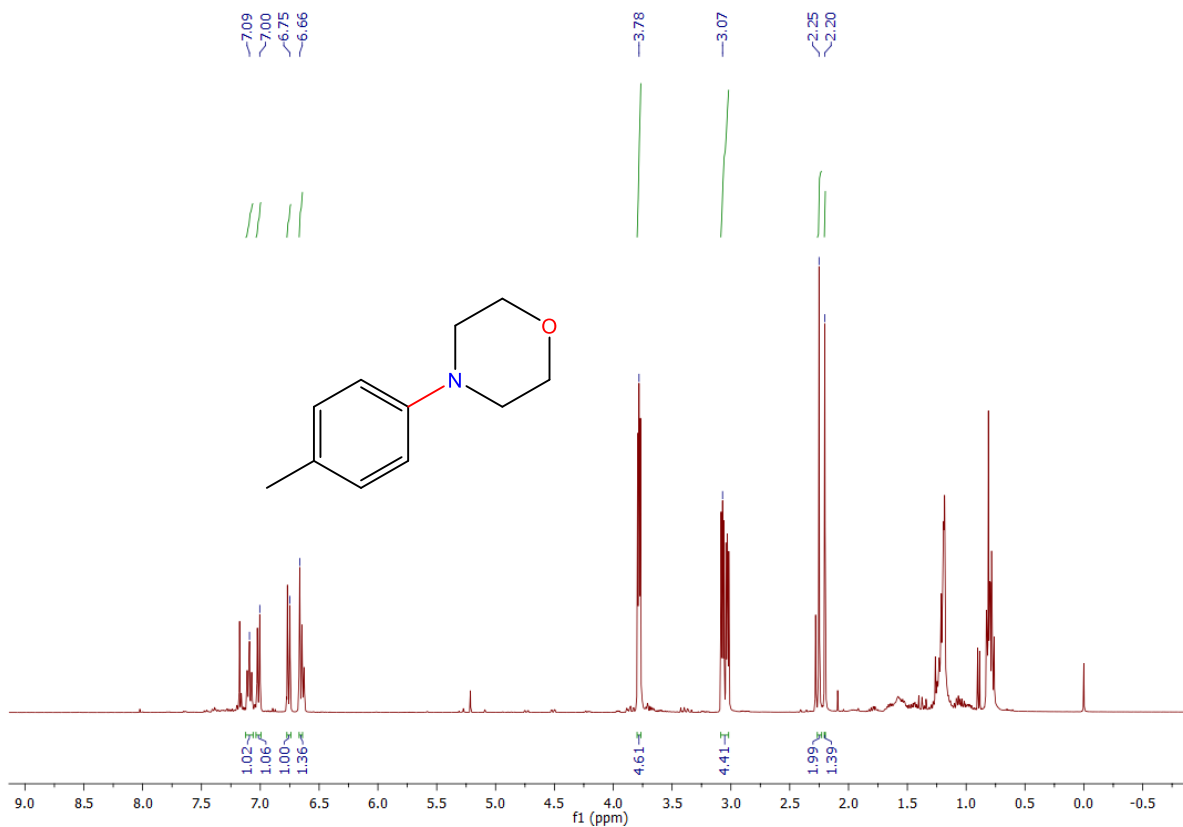




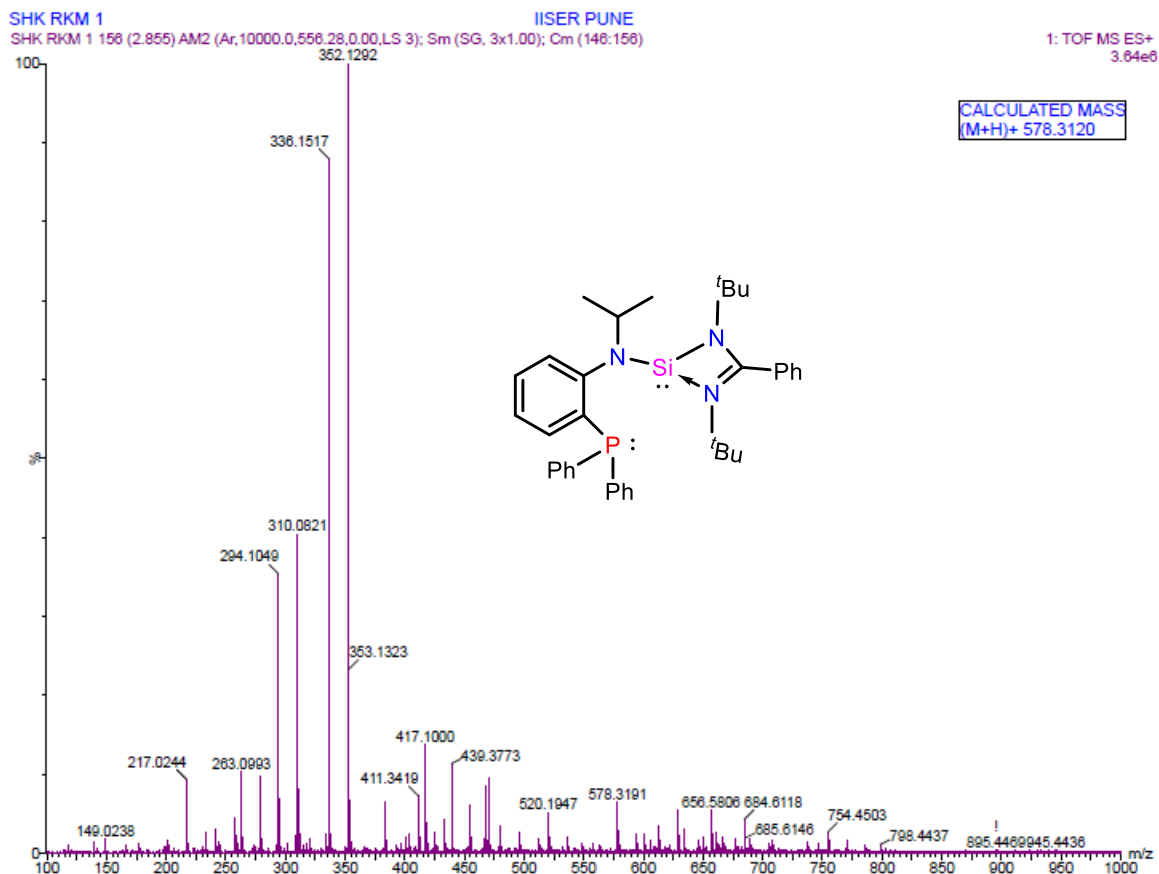








HRMS Data

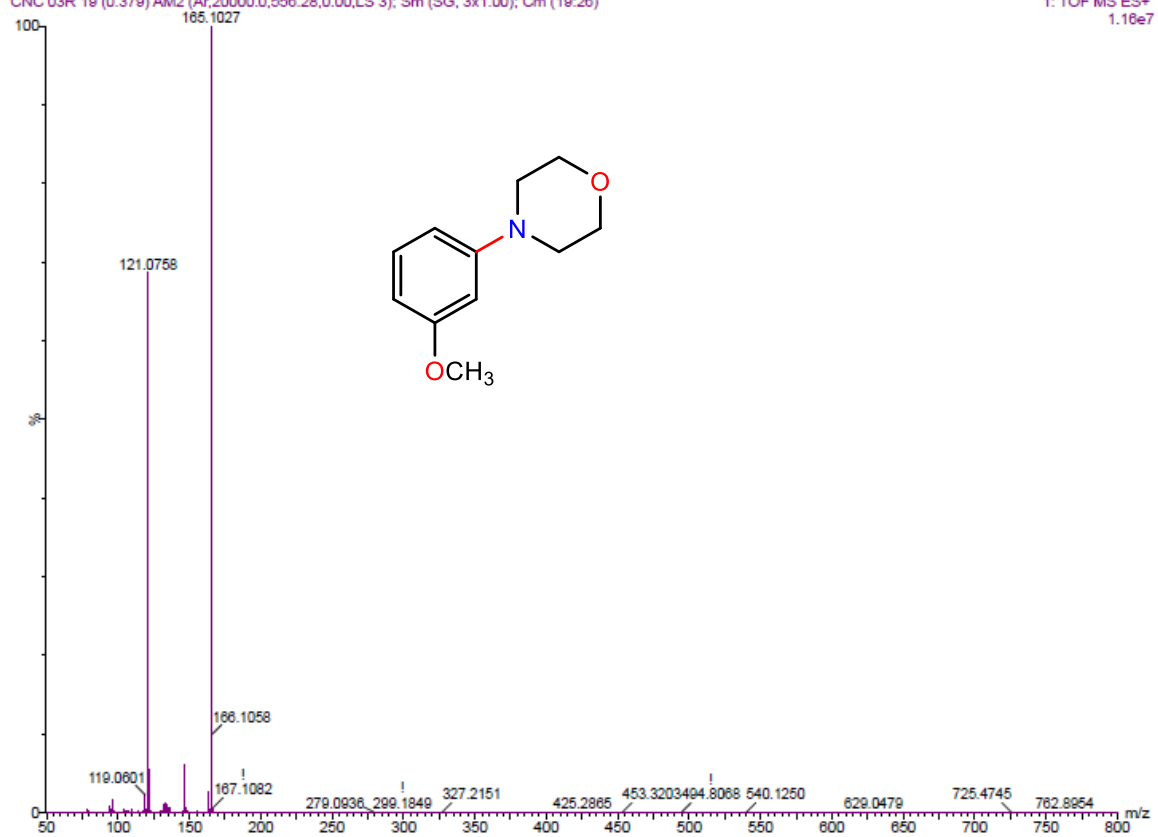


CNC 03R

IISER PUNE

CNC 03R 19 (0.379) AM2 (Ar,20000,0,556.28,0,0,LS 3); Sm (SG, 3x1.00); Cm (19:26)

1: TOF MS ES+
1.16e7

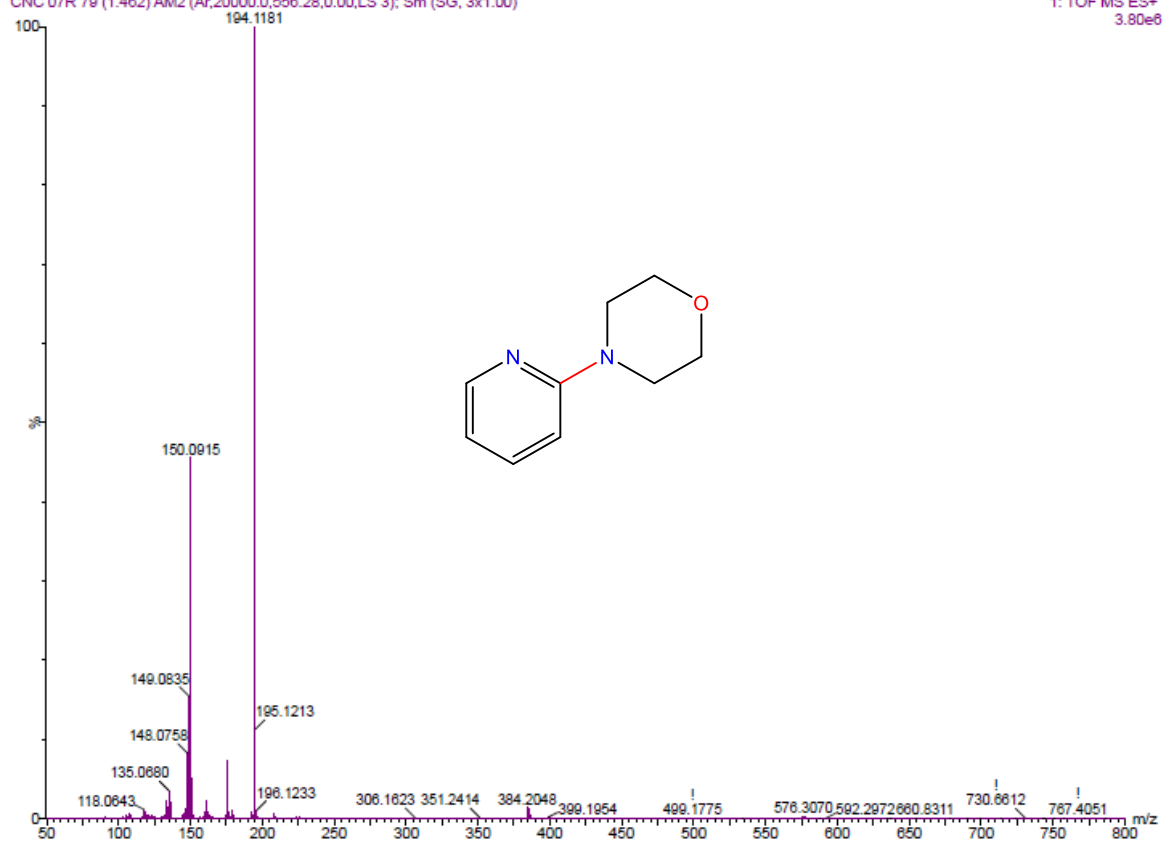


CNC 07R

IISER PUNE

CNC 07R 79 (1.462) AM2 (Ar,20000,0,556.28,0,0,LS 3); Sm (SG, 3x1.00)

1: TOF MS ES+
3.80e6

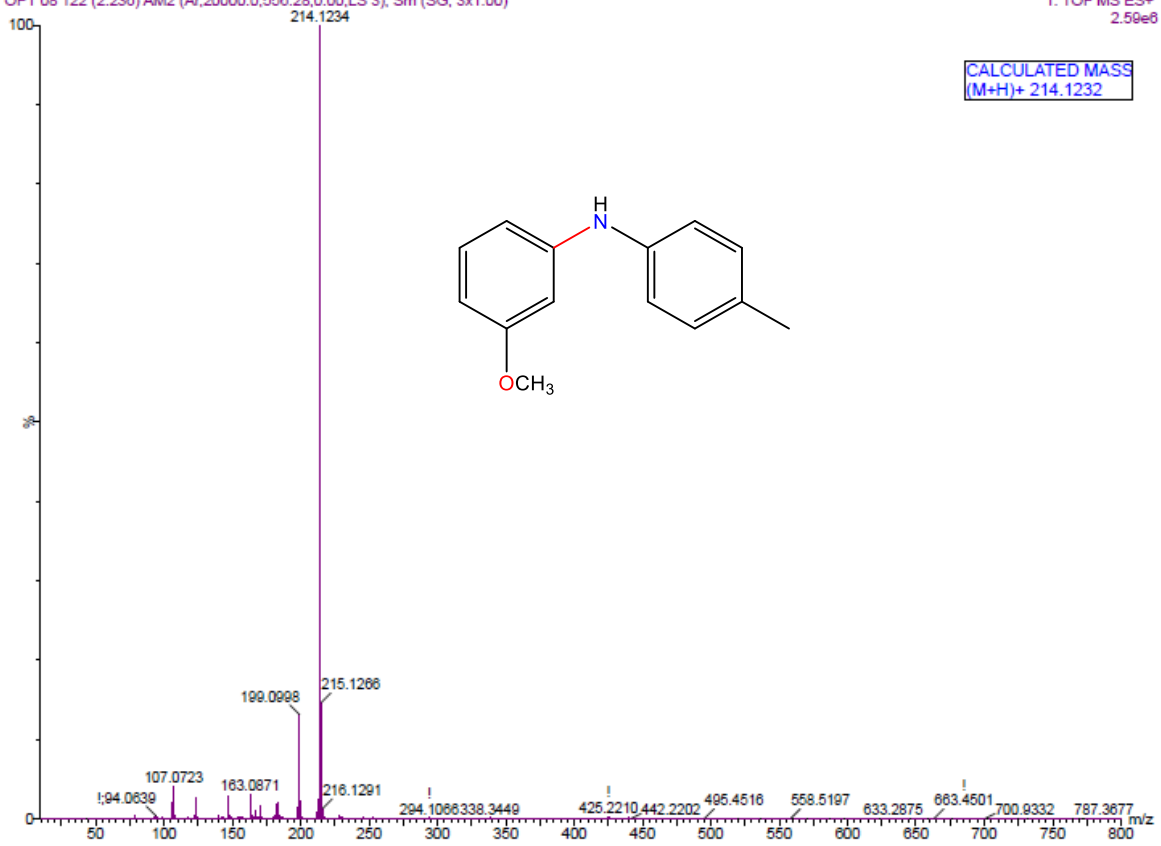


OPT 08

OPT 08 122 (2.238) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
2.59e6

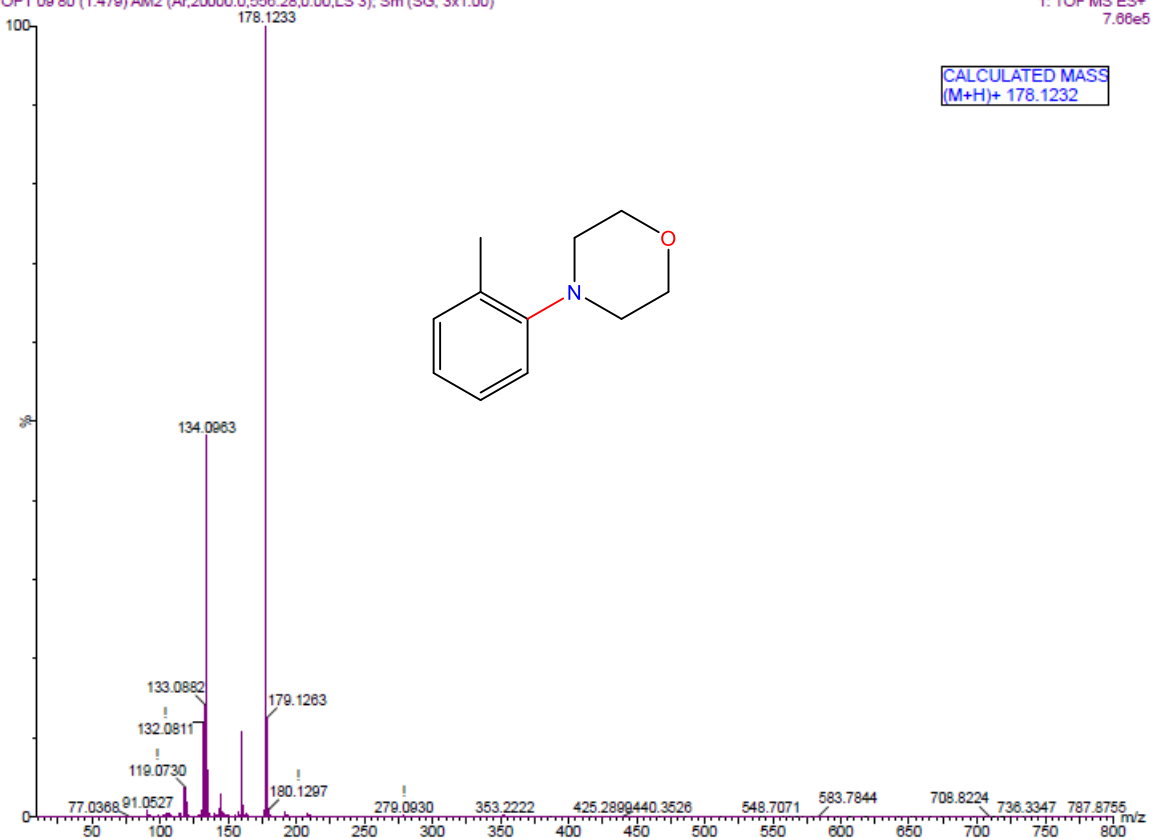


OPT 09

OPT 09 80 (1.479) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
7.86e5

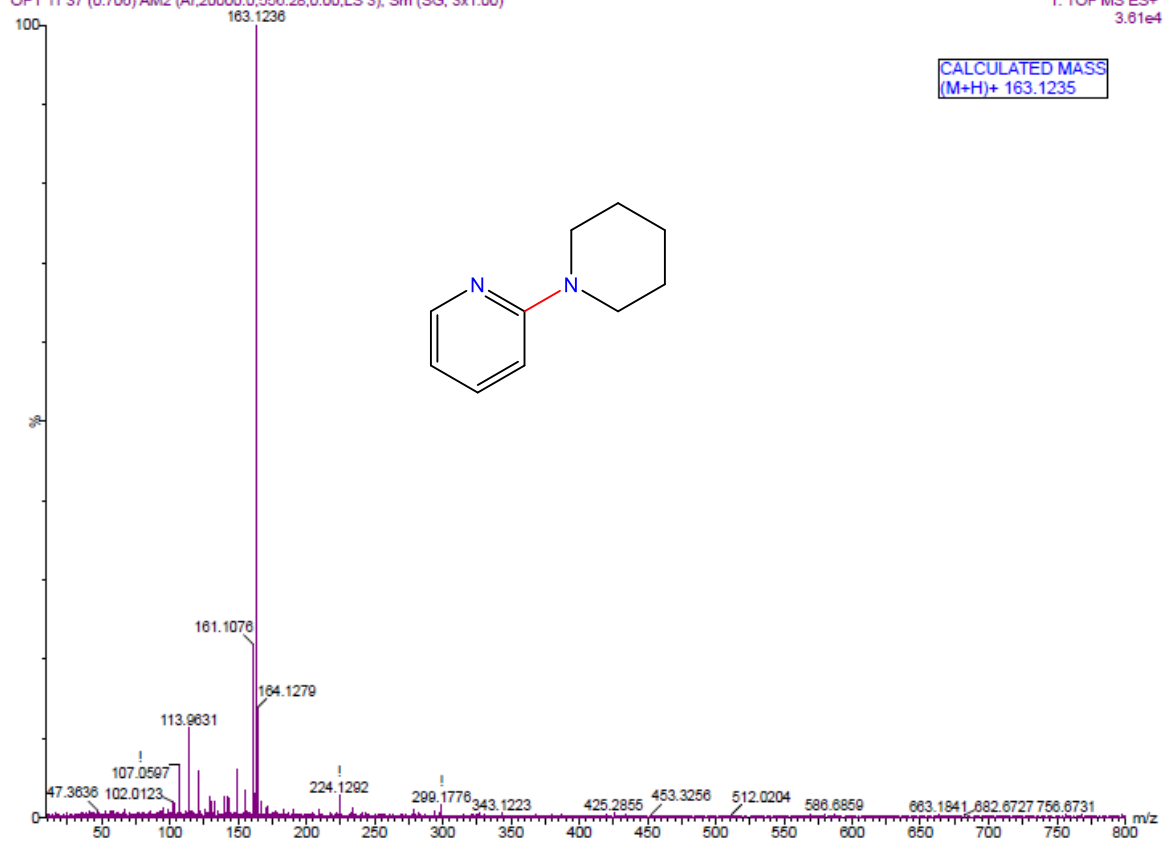


OPT 11

OPT 11 37 (0.708) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
3.81e4

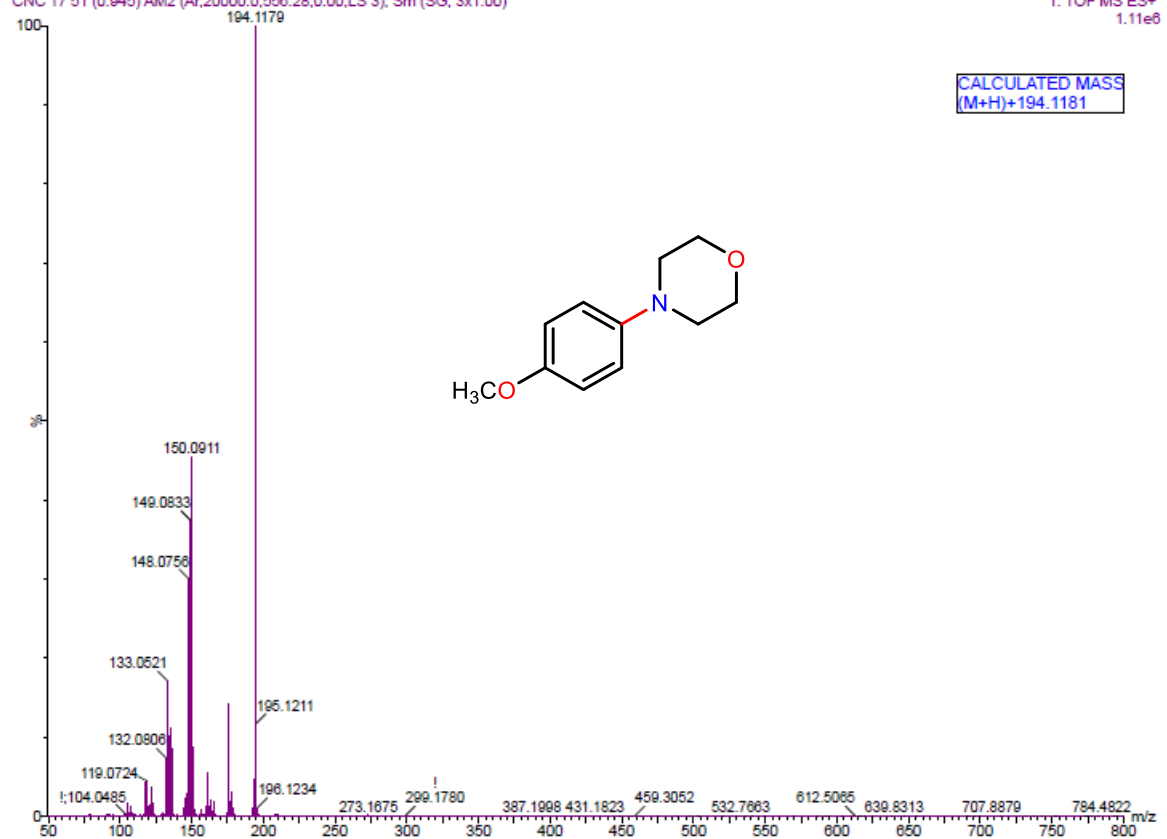


CNC 17

CNC 17 51 (0.945) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
1.11e6

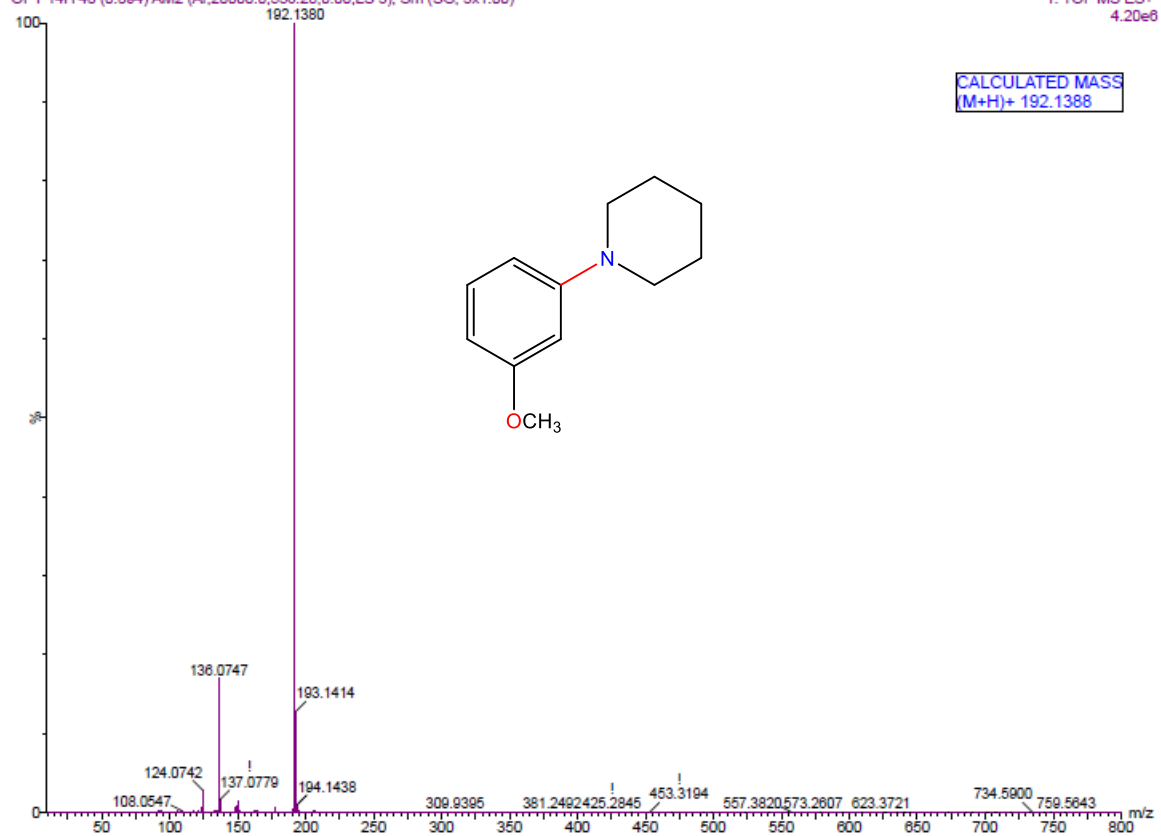


OPT 14H

OPT 14H 48 (0.894) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
4.20e8

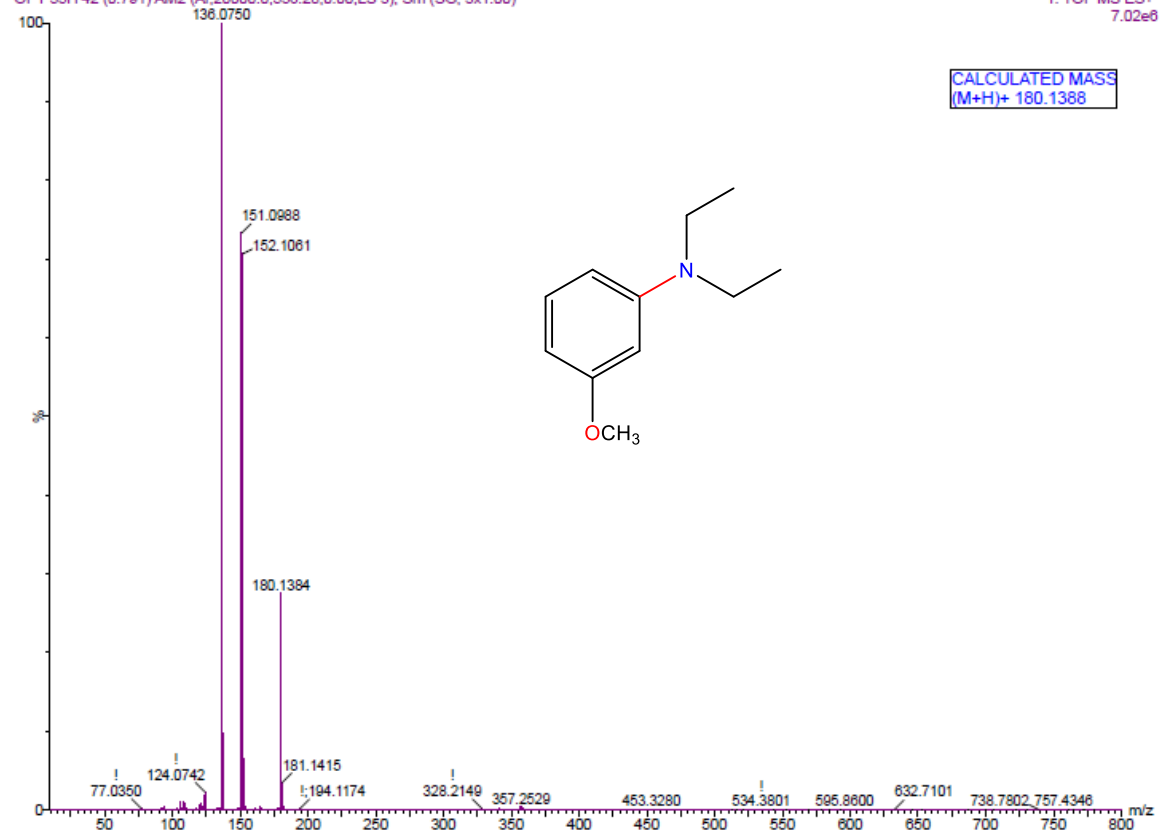


OPT 35H

OPT 35H 42 (0.791) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
7.02e8

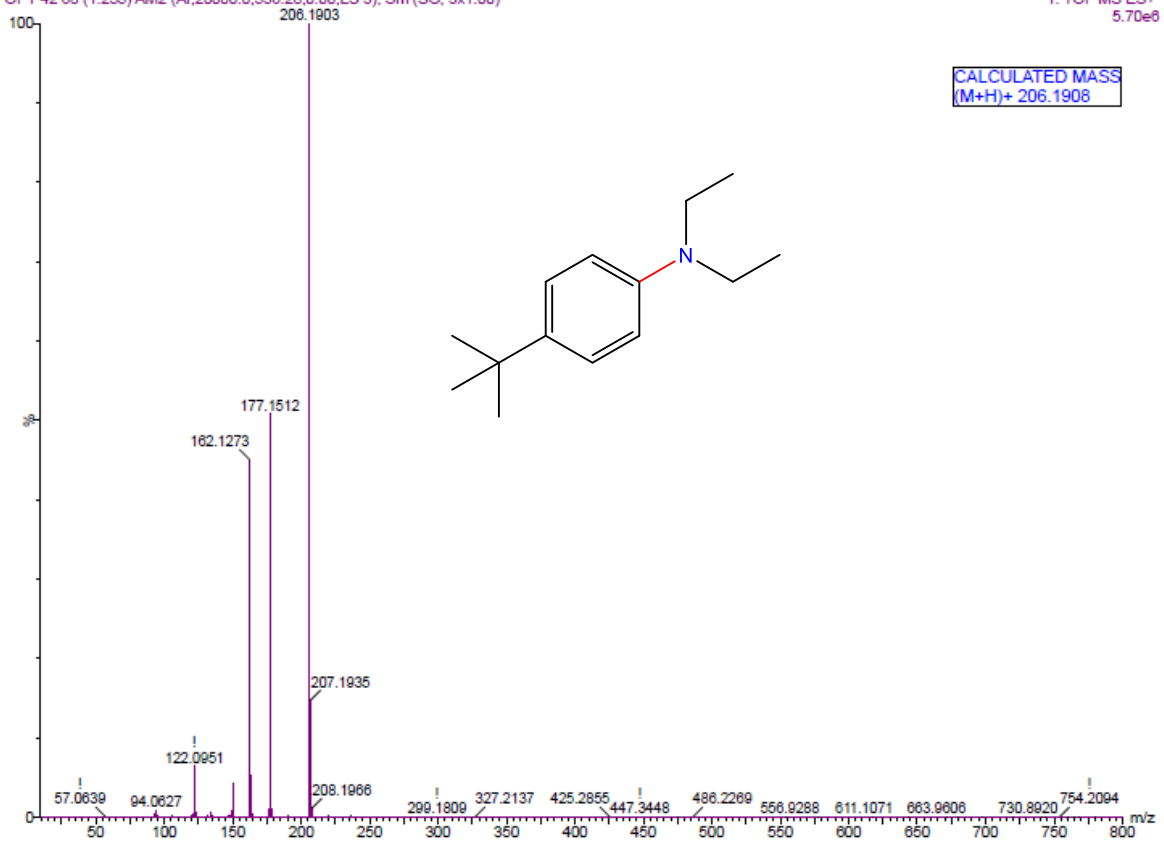


OPT 42

OPT 42 68 (1.255) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
5.70e8

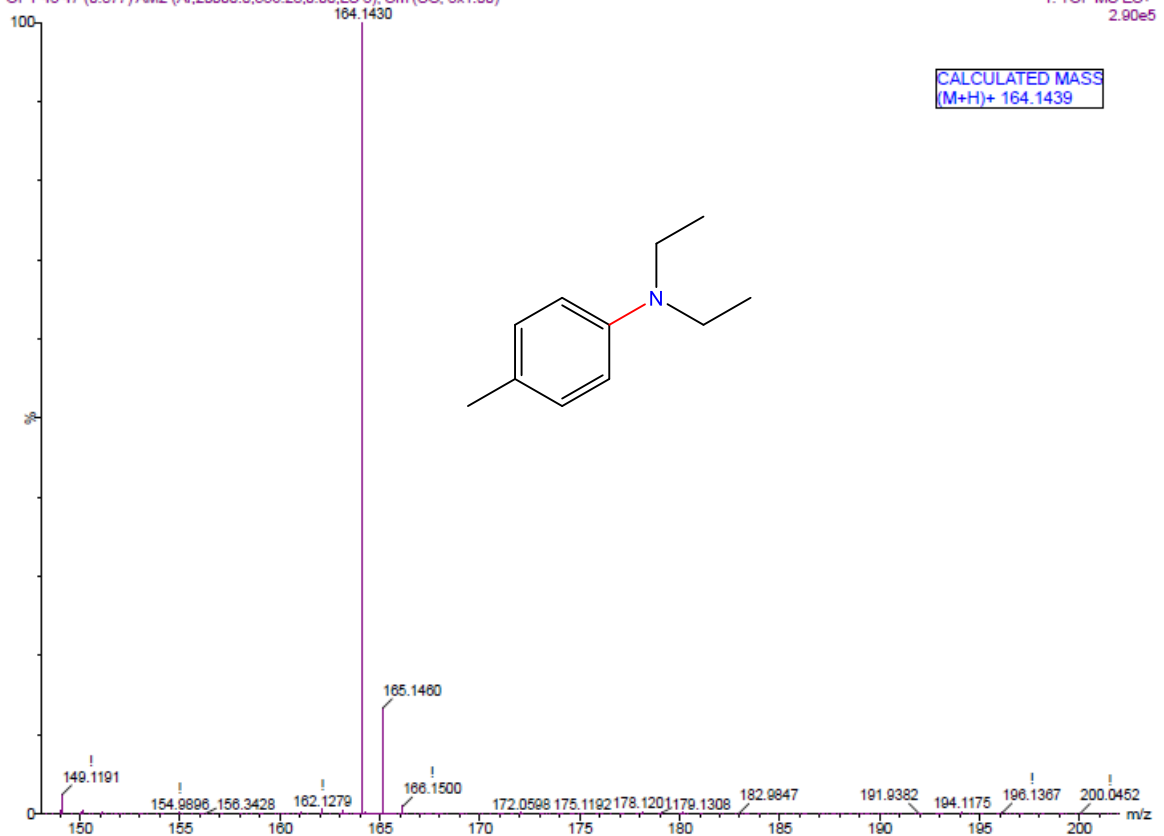


OPT 43

OPT 43 47 (0.877) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
2.90e5

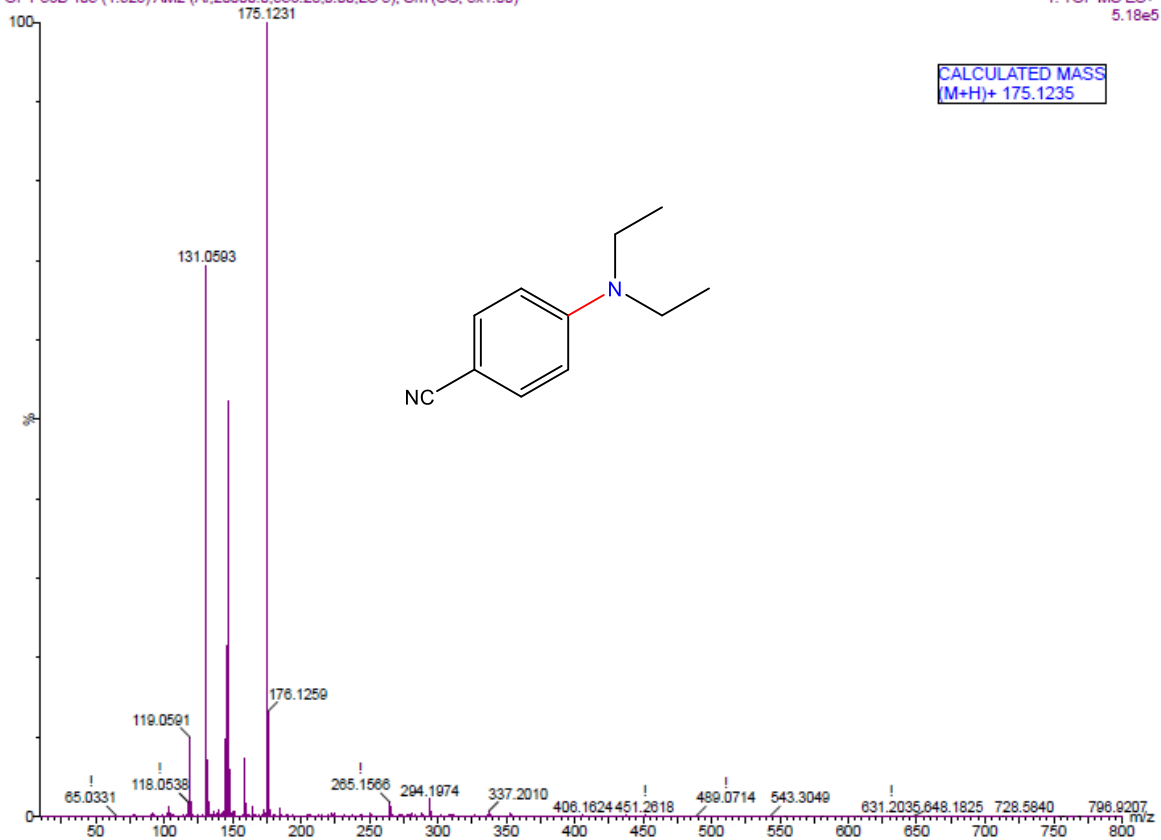


OPT 36B

OPT 36B 105 (1.928) AM2 (Ar,20000,0,556.28,0,0,LS 3); Sm (SG, 3x1.00)

IISER PUNE

1: TOF MS ES+
5.18e5

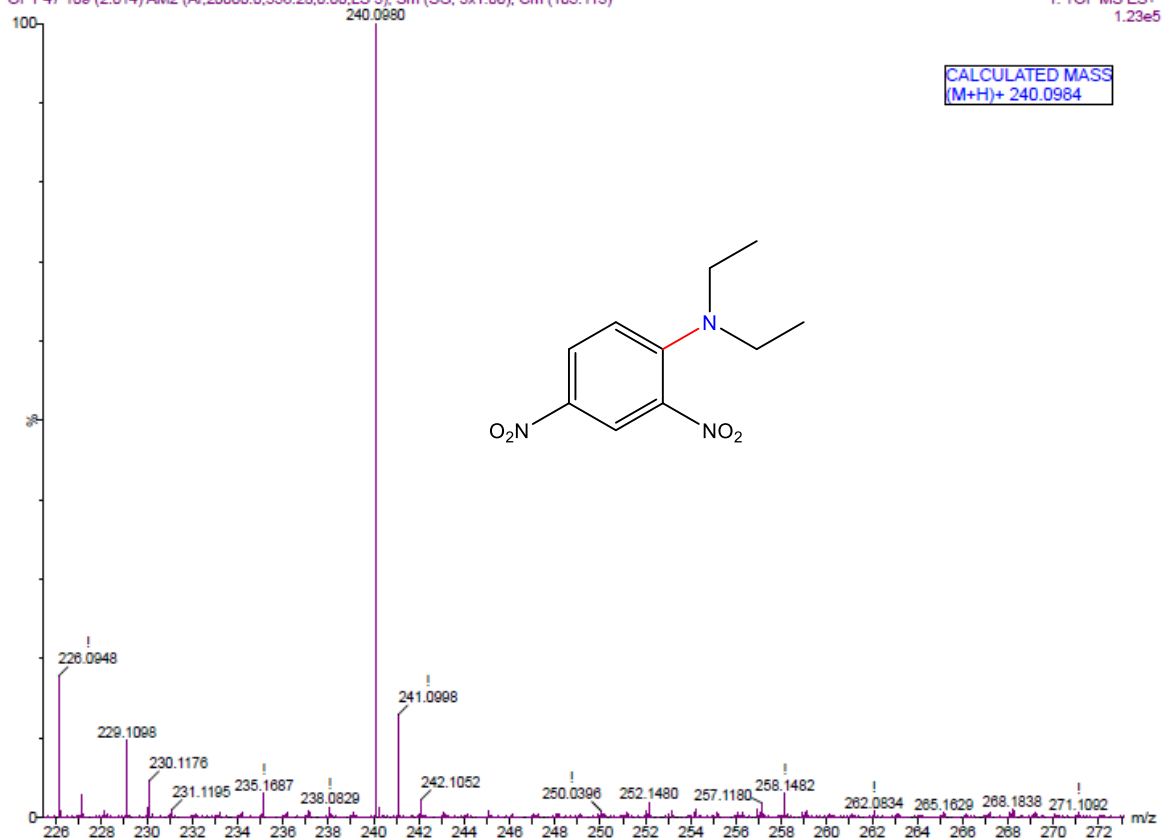


OPT 47

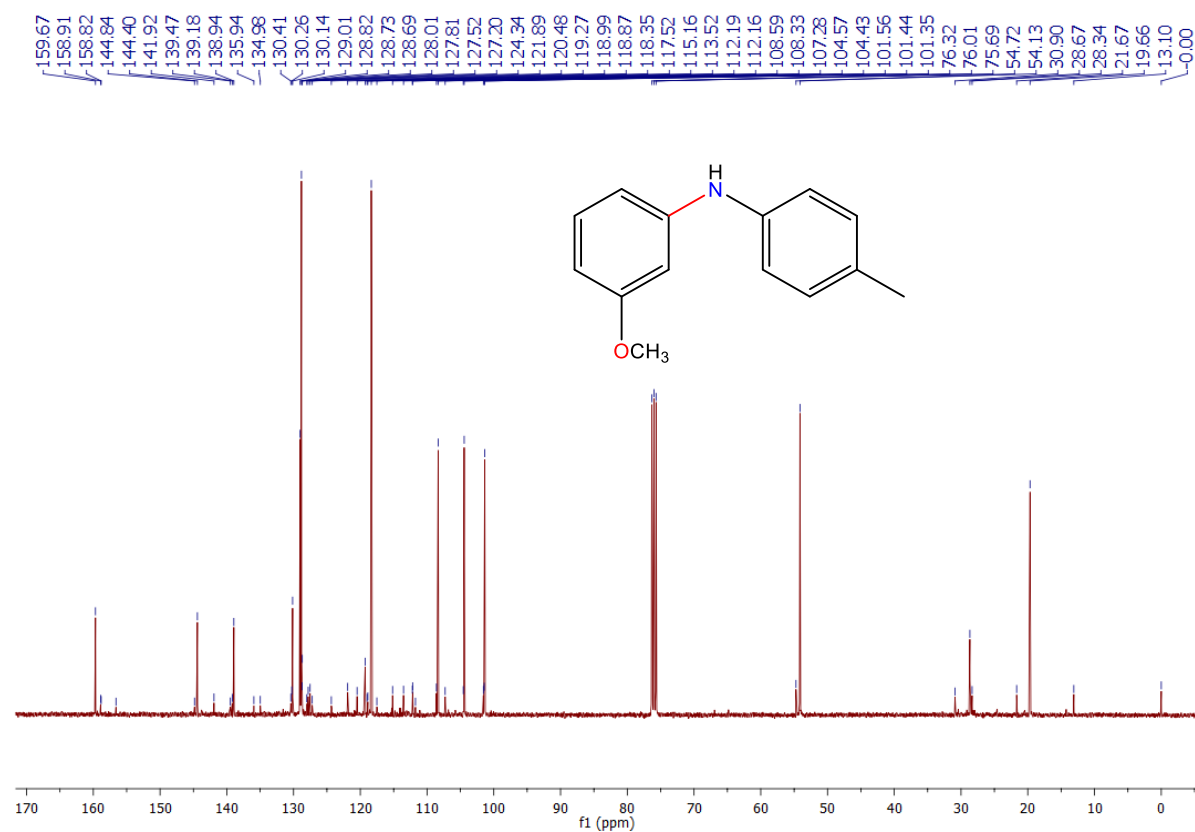
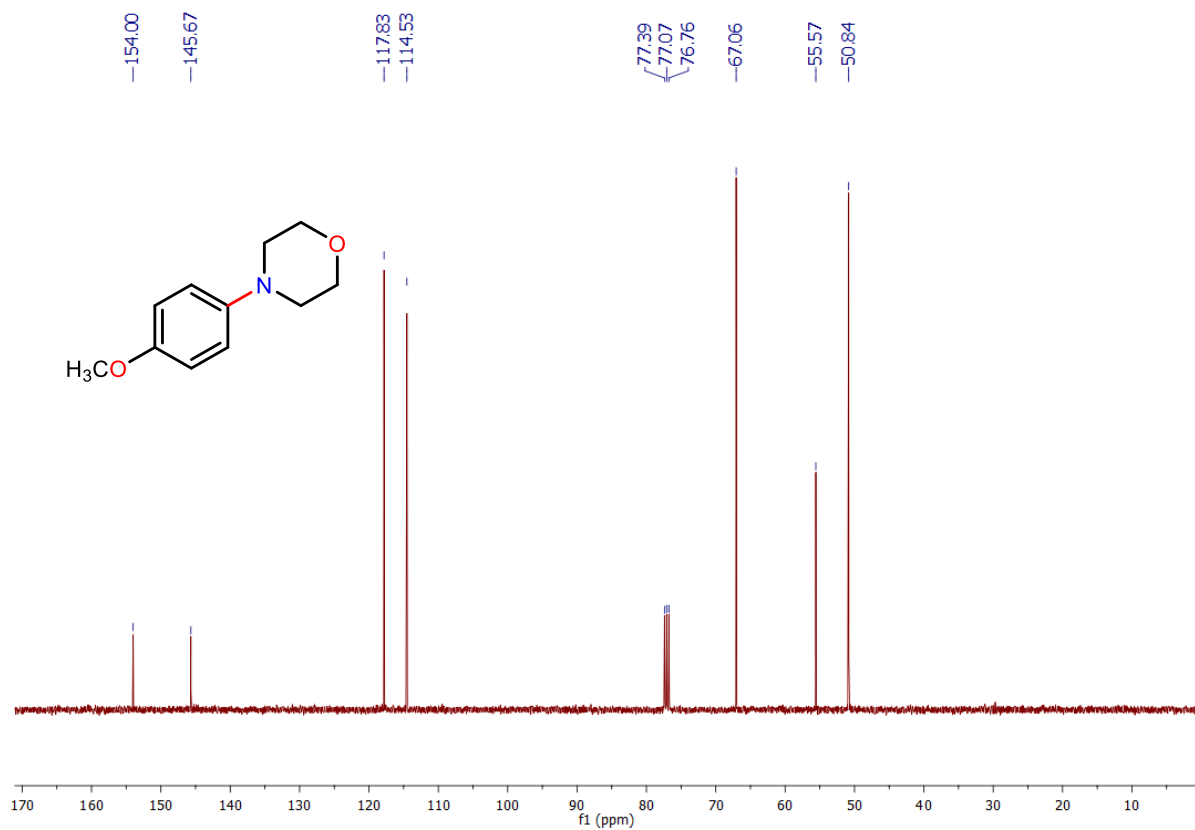
OPT 47 109 (2.014) AM2 (Ar,20000,0,556.28,0,0,LS 3); Sm (SG, 3x1.00); Cm (105:113)

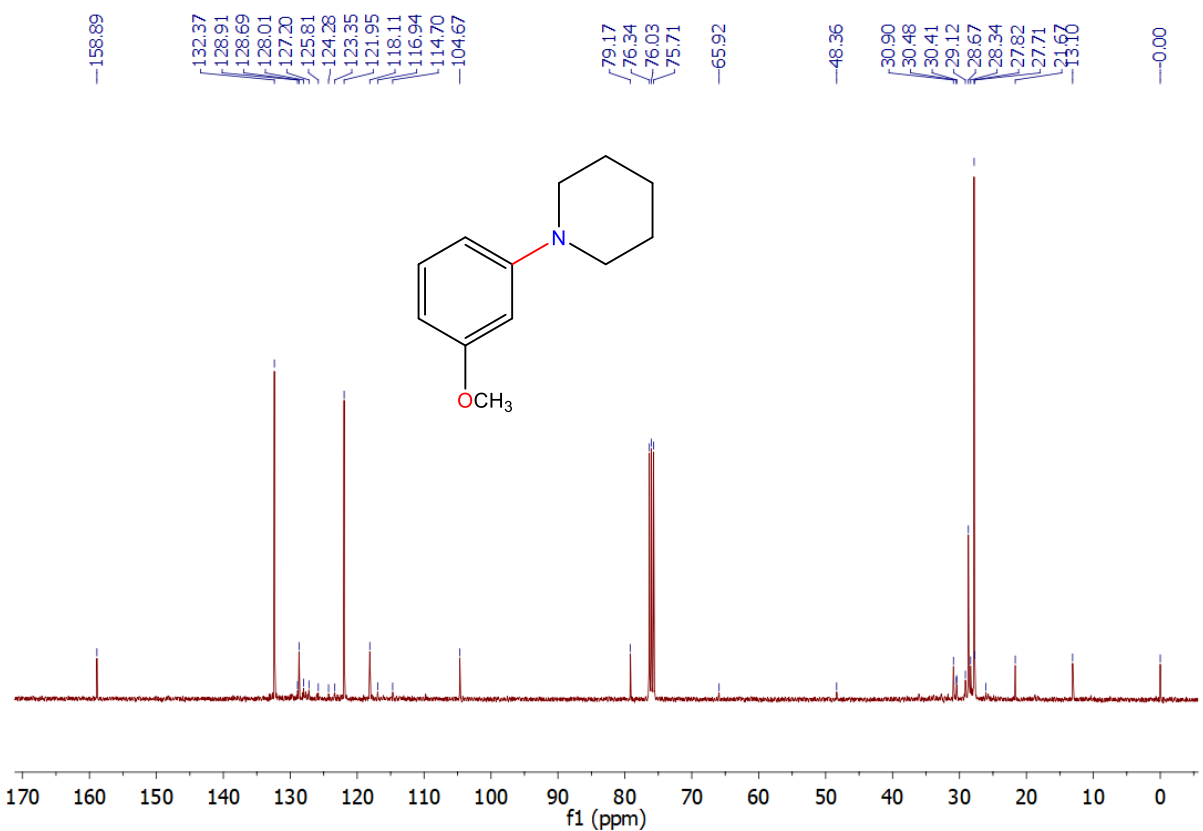
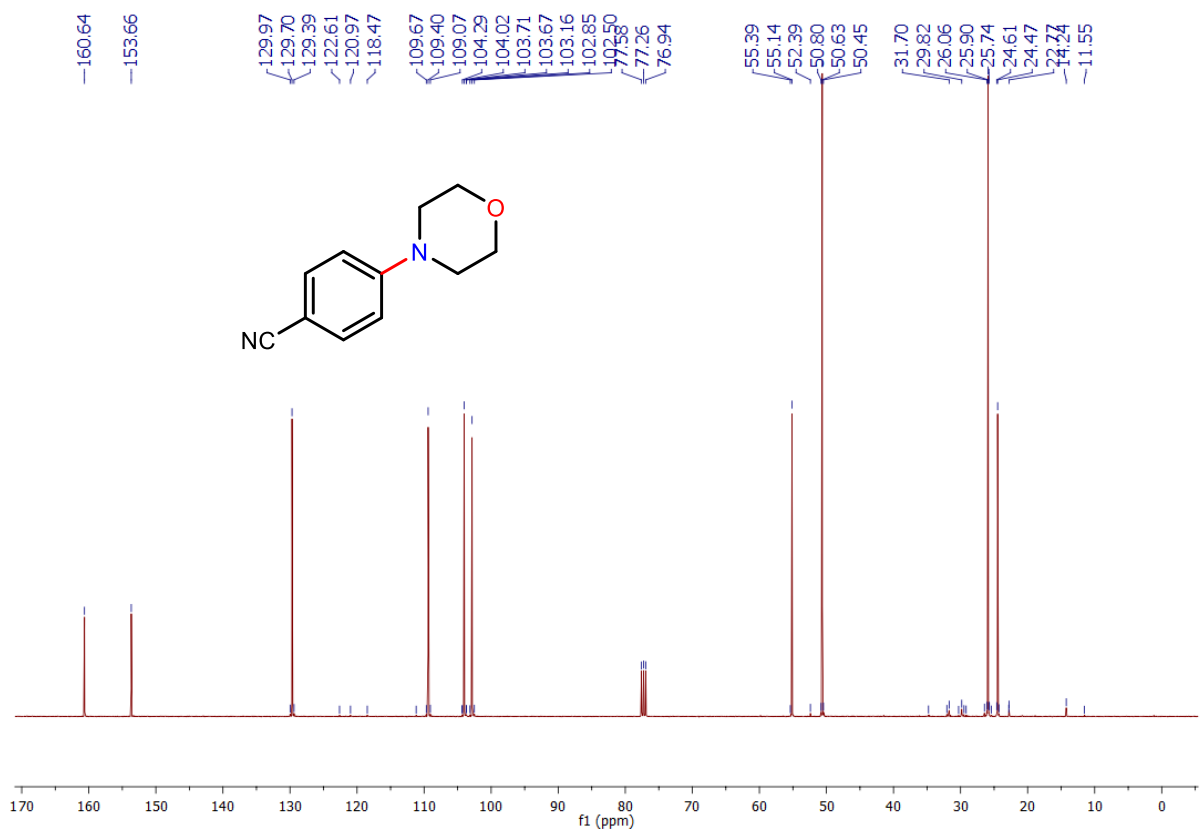
IISER PUNE

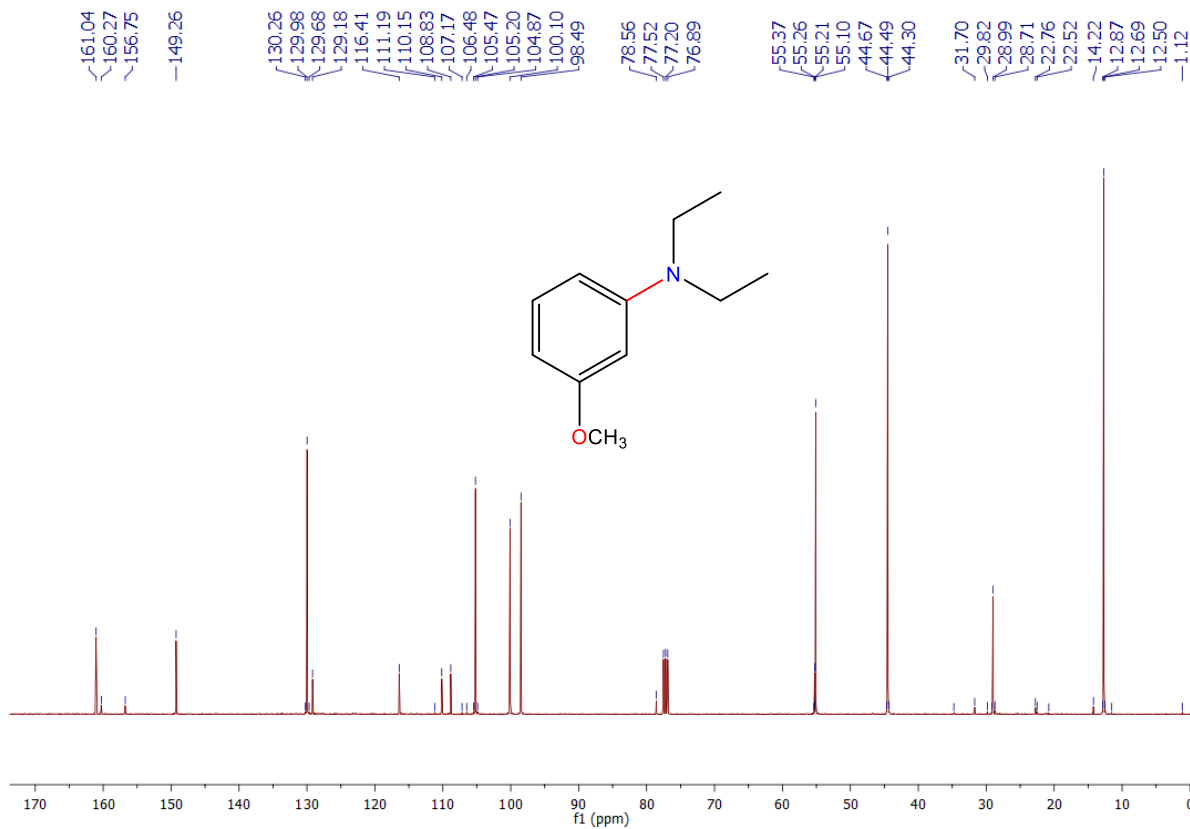
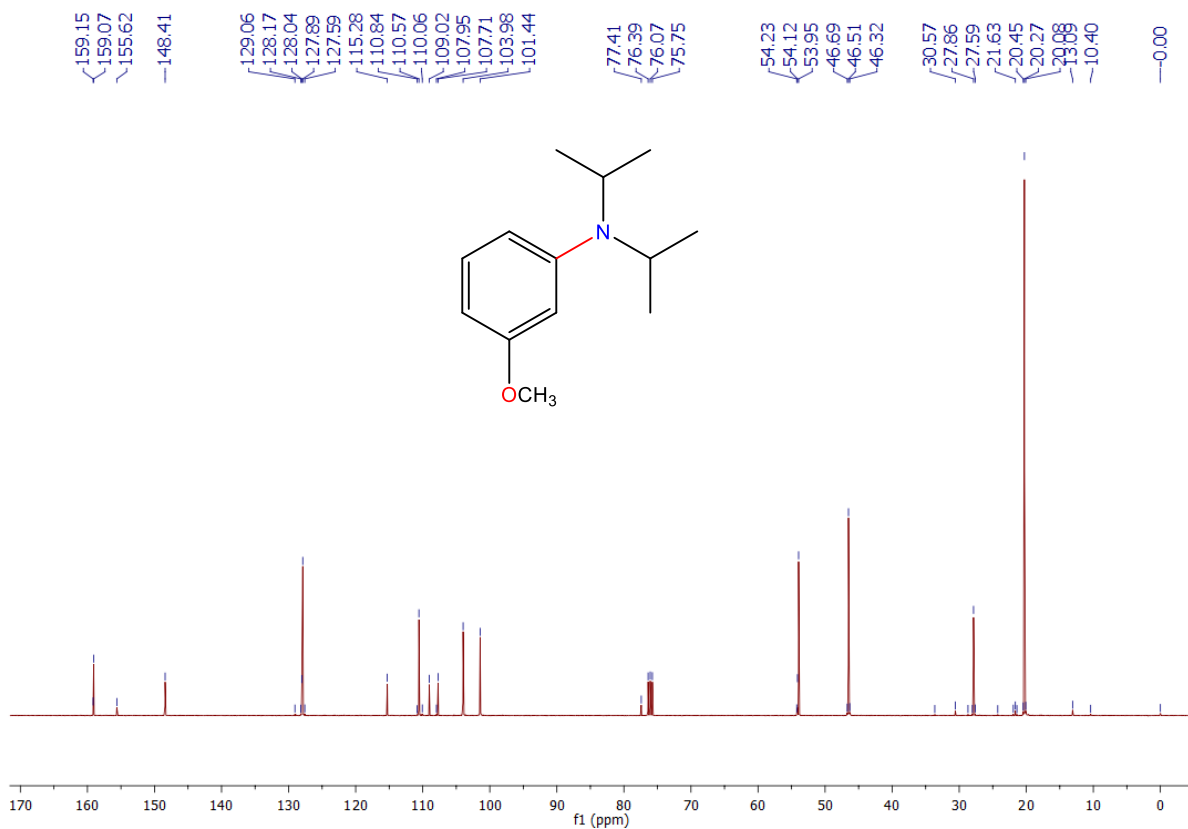
1: TOF MS ES+
1.23e5

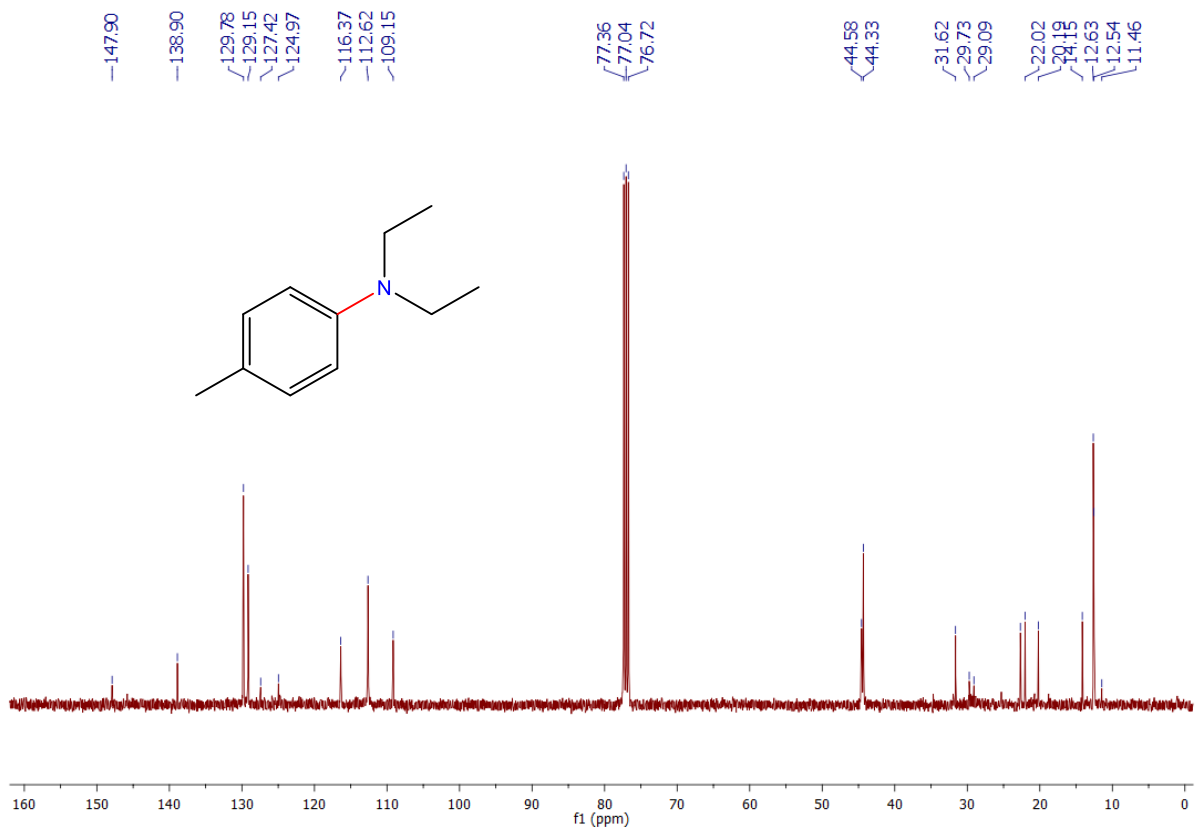
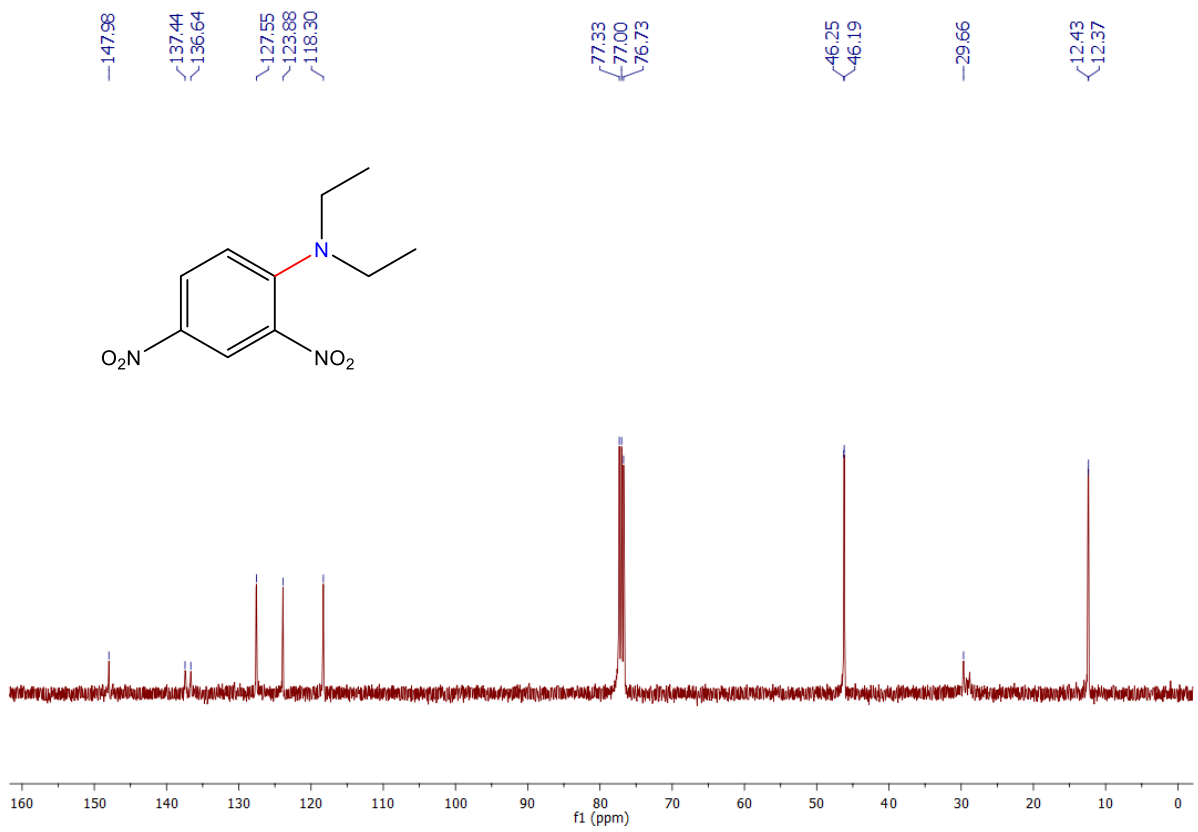


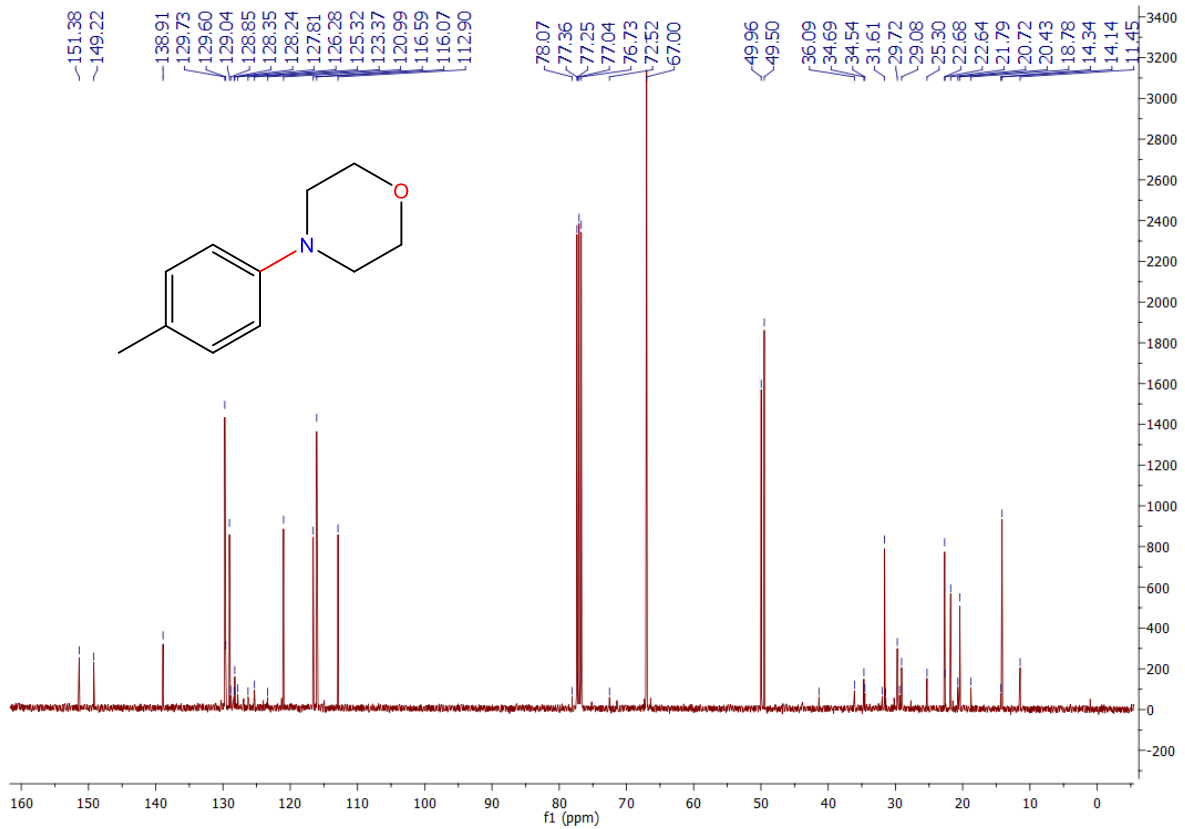
¹³C NMR Data





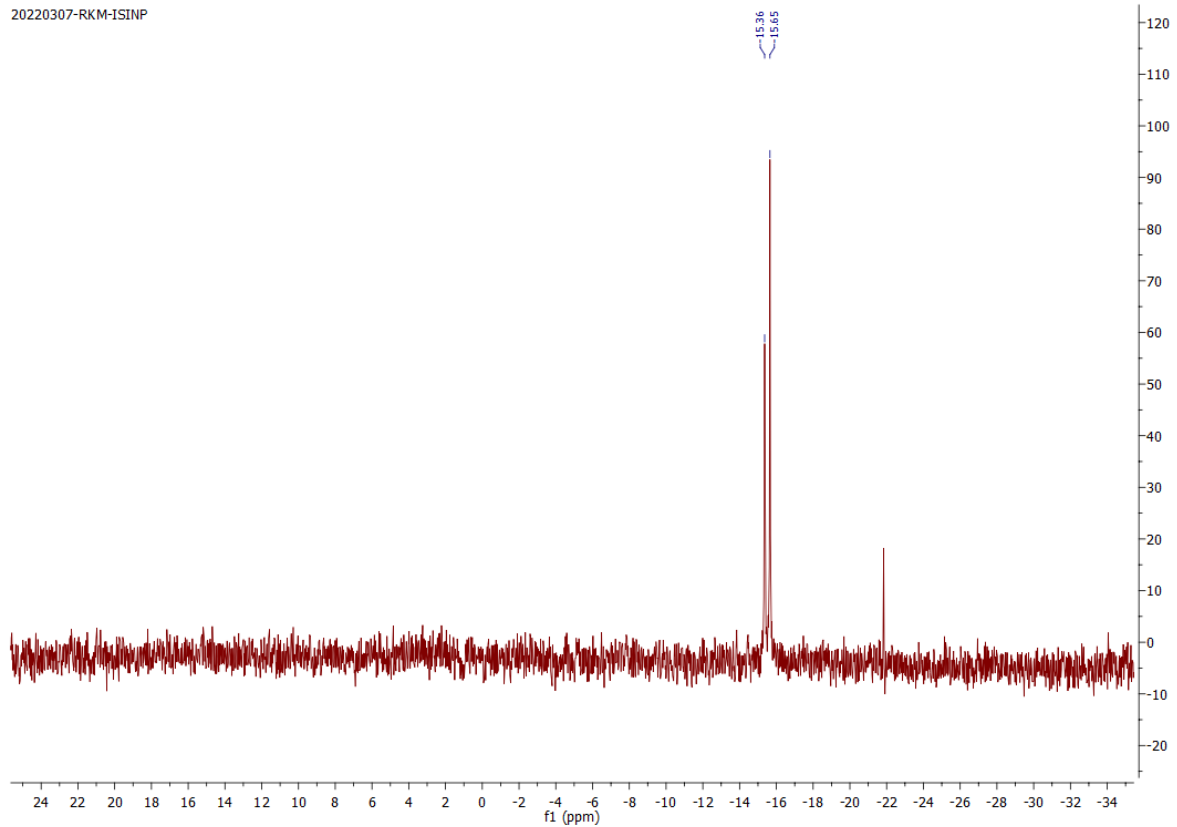




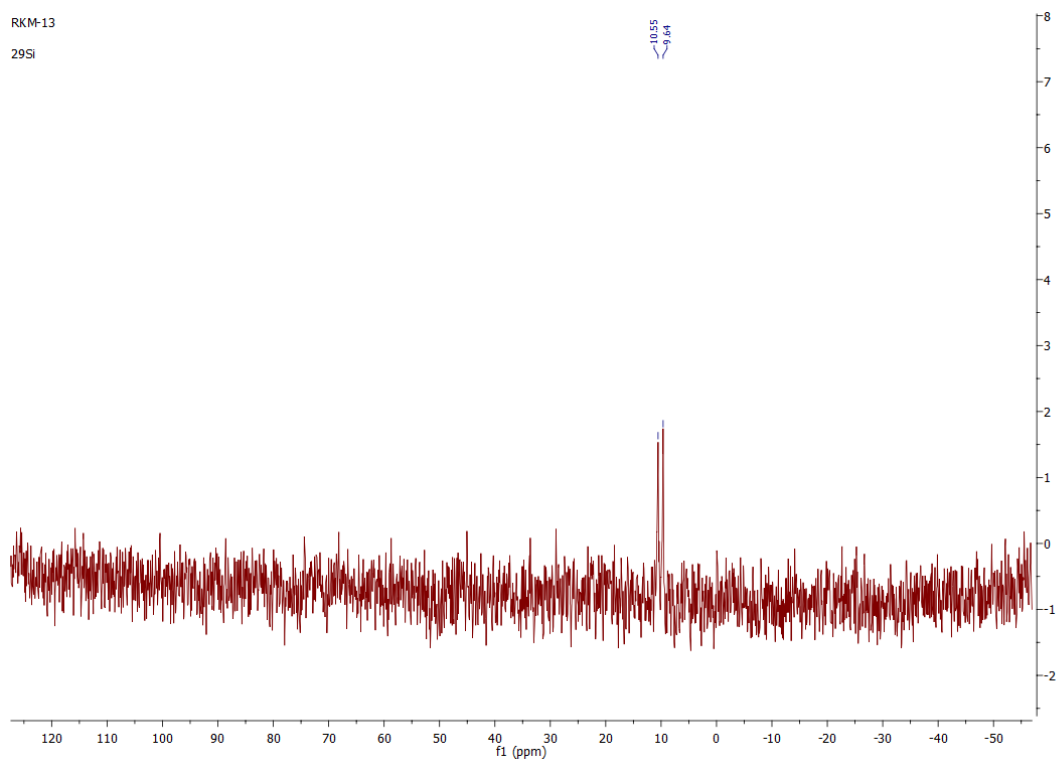


²⁹Si NMR of ligand L1

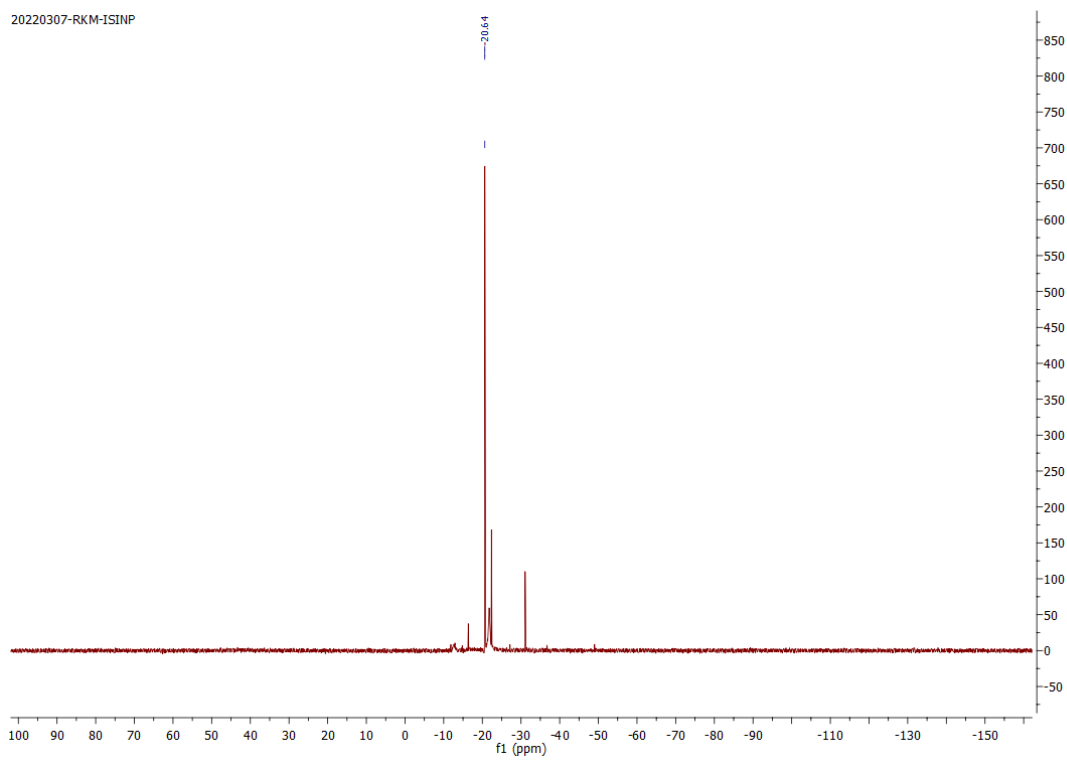
20220307-RKM-ISINP



^{29}Si NMR of complex **1**



^{31}P NMR of ligand **L1**



^{31}P NMR of complex 1

RKM-13

^{31}P Decoupled

