Synthesis of pyridine functionalized NHC-Iron(II) complexes and their applications

MS Thesis Report submitted towards the partial fulfillment of

BS-MS dual degree program

By

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Under the guidance of

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CERTIFICATE

This is to certify that this dissertation entitled "**Synthesis of pyridine functionalized NHC-Iron(II) complexes and their applications**" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents work carried out by "Shweta Sunil Hiwase at IISER Pune" under the supervision of "Dr. Shabana Khan" during the academic year 2018-2019.

Date: 20.03.2019

Place: IISER Pune

Supervisor's signature: Shabana

Date: 20.03.2019

Place: IISER Pune

Student's signature: SHiwase

DECLARATION

I hereby declare that the matter embodied in the report entitled "**Synthesis of pyridine functionalized NHC-Iron(II) complexes and their applications**" are the results of the work carried out by me at the Department of Chemistry, IISER Pune, under the supervision of Dr. Shabana Khan and the same has not been submitted elsewhere for any other degree.

Date: 20.03.2019

Place: IISER Pune

Supervisor's signature: Shabana

Date: 20.03.2019

Place: IISER Pune

Student's signature: Shiwas

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-Shweta

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Abbreviations

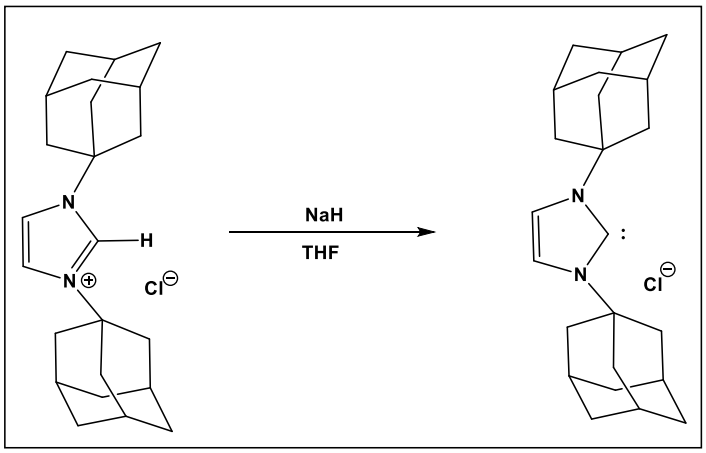
NHC	N-heterocyclic carbene
TM	Transition metal
MeCN	Acetonitrile
DCM	Dichloromethane
THF	Tetrahydrofuran
DMSO	Dimethyl Sulfoxide
HBpin	Pinacolborane
Mes	Mesitylene
Hrs	Hours
NMR	Nuclear magnetic resonance
SCXRD	Single crystal X-ray Diffraction
HRMS	High Resolution Mass Spectroscopy
IS	Internal standard
mg	Milligram
mmol	Millimoles
ppm	Parts per million
RT	Room temperature

Abstract:

Catalytic hydroboration of carbonyl compounds using pinacolborane is an important technique for synthesizing organoboranes and for synthesizing corresponding alcohols in organic chemistry. There is always a quest of better performing catalysts. N-heterocyclic carbene (NHC) based transition metal complexes have shown their great potential in this field. Herein, we present a facile synthesis of Iron(II) complexes of pincer based pyridine functionalized N-heterocyclic carbene, which are successfully characterized by SCXRD analysis and multinuclear NMR spectroscopy. This easily prepared iron catalysts enables hydroboration of aromatic aldehydes with HBpin (pinacolborane) without any additive. The hydroboration reaction gives good yield with low catalyst loading (1-2 mol%) at room temperature and shows wide range of functional group tolerance.

1. INTRODUCTION:

Carbenes are neutral compounds containing a divalent carbon atom with only six-valence electrons, are considered as a highly reactive class of compounds. In NHCs, two nitrogen atoms are adjacent to carbene carbon center and bounded to it by a covalent bond. All atoms are constrained in a ring. The actual idea of formation of stable NHC was first proposed by *Wanzlick et al.* around 1960s.[1] Shortly thereafter, *Wanzlick* and *Ofele* reported transition metals complexes having NHC as a ligand, but they could not isolate the carbene.[2] After almost two decades, the first stable nucleophilic heterocyclic carbene (NHC) 1, 3-bis(l-adamantyl)imidazol-2-ylidene (IAd) was isolated by group of Arduengo in 1991 (Scheme 1).[3] After the discovery of first NHC many different types of NHCs have been synthesized with the various of substituents on both the nitrogen atoms and backbone carbon atoms of imidazolium ring and their properties have been studied extensively.



Scheme.1: Synthesis of the first stable NHC (IAd)

Variations of NHCs are limitless, their electronic as well as steric properties can be tuned easily by altering the substituents on nitrogen atoms as well as the heterocyclic backbone. There are many types of NHC precursors, but thiazolium, triazolium and imidazolium salts are commonly known (Figure 1). Most importantly these salts are stable without decomposition in the air. Also they are easy to synthesize on large scale. Four, six even seven-membered NHCs also exist, but five membered NHCs are most widely used. [4]

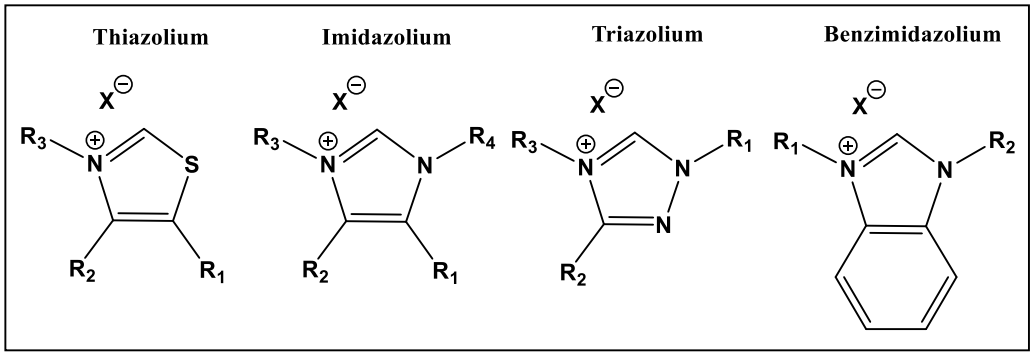
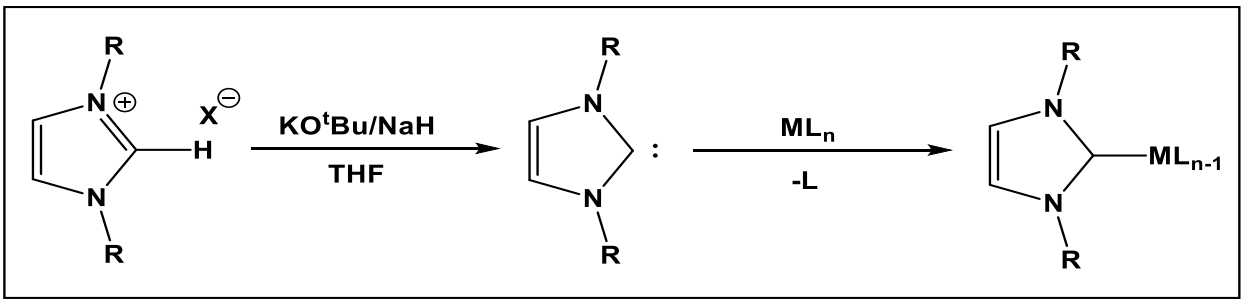
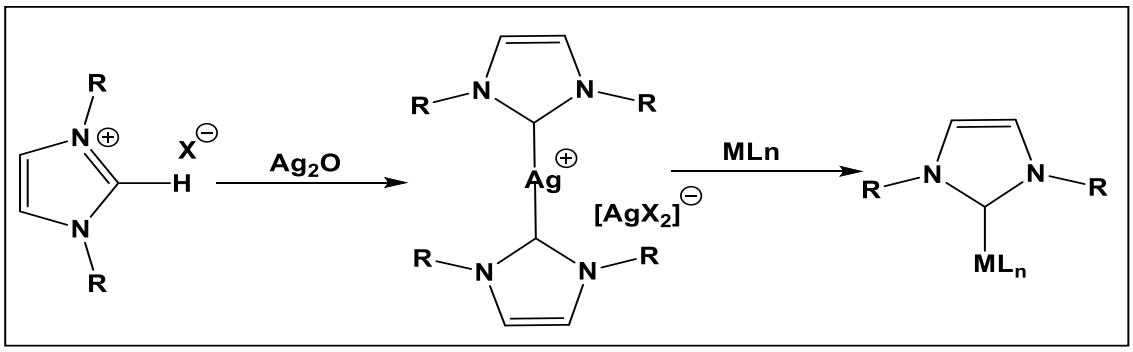


Figure.1: Common types of NHC precursor salts

For synthesis of NHC-TM complexes, various methods of synthesizing are employed and the important part is there is no need of synthesizing free carbene. The synthesis of NHC-TM[5] complexes can generally be done via two routes. 1) Deprotonation of NHC precursor by strong bases like KO^{t}Bu, NaH followed by addition of metal complex (Scheme 2). 2) trans-metalation from NHC-Ag complex[6] (Scheme 3) as the bond between silver and NHC is labile. The insolubility of silver halide (precipitation) is also the driving force of the reaction.



Scheme 2: Schematic representation of the synthesis of NHC-M by deprotonation method



Scheme 3. Schematic representation of the synthesis of NHC-TM by trans-metalation

NHCs are mostly bent having a sp^2 hybridized σ orbital and a p orbital (π) which is orthogonal to sp^2 plane. Stability of carbenes depends upon σ-p_π energy gap. The nitrogen being more electronegative than carbon shows the σ-electron withdrawing effect and stabilizes the σ orbital of carbene carbon, which increases the σ-pπ gap therefore favoring the singlet state. NHCs are also stabilized by a push-push mesomeric effect, both nitrogen have lone pair of electrons, which strongly interact with the empty p_π orbital of the carbene center. The electro-neutrality of the carbene center is maintained by both mesomeic and inductive effects (Figure 2). [7]

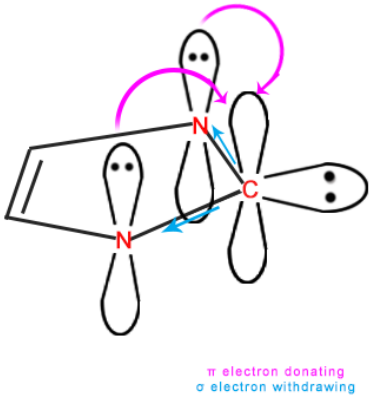
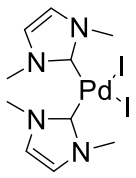


Figure.2: Ground state electronic structure of NHC

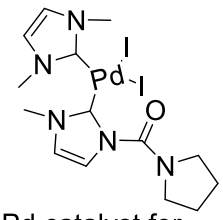
In contrast to classical carbenes like Fisher and Shrock, NHCs do not form double bond with metal as they show very little to no π-backbonding. They form a strong bond with majority of metals. As per rule, strong interaction between NHC and metal means NHC-M bond to be less labile and complexes to be more stable thermally as well as oxidatively, making them robust. NHCs are electron rich and considered as nucleophilic in nature. With these attractive features, NHCs are considered as a versatile ligand. NHCs can form complexes with low and high valent transition metals, alkaline earth metals and lanthanides.[8] The utilization of NHC ligands for making transition metal complexes (TMC) has become widespread and they have found multiple applications in homogeneous catalytic transformations.[9] Even though all NHC type ligands have unique properties depending upon their donors, NHC ligands consisting nitrogen donor are of great interest especially pyridine functionalized NHCs because pyridine can act as a pincer ligand and

it can facilitate binding to the softer oxidation state of metals. It also promotes hemilability hence enhances the catalytic activity.[10]

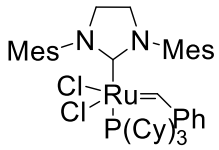
Transition metal complexes containing NHCs as their ligand backbone have been subject of interest for many years and have shown remarkable capabilities in homogeneous catalysis of organic transformations. In year 1995, Herrmann's group first demonstrated the use of NHC-TM in homogeneous catalysis by reporting NHC-Palladium catalyzed Heck coupling reaction.[11] It opened new route to extensive studies of NHC-TM complexes in catalysis. Later numerous of transition metals complexes having NHC as a catalysts have been reported. Though Pd catalyzed C-C coupling reactions (Heck, Suzuki-Miyura[12], Sonagashira[13], Kumada[14] reactions), Ir and Ru catalyzed hydrogenation and hydrogen transfer[15], Rh and Pt catalyzed hydrosilylation[16], gold catalyzed π-bond activation[17] are best known transformations, Ru catalyzed olefin metathesis (Grubbs catalyst)[18] remains the most celebrated achievement in chemistry of NHC-TM complexes. There are also other important transformations like cyanosilylation, hydroboration, hydroformylation transesterification, aryl amination can be catalyzed by NHC-TM complexes.



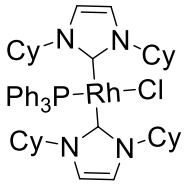
Hermann's Pd catalyst for Heck coupling



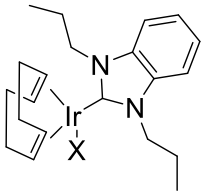
Pd catalyst for Sonagashira coupling



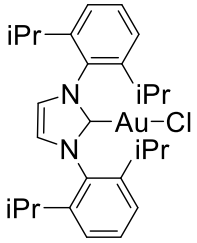
Grubb's Ru catalyst for olefin metathesis



Hermann's Rh catalyst for olefin hydrogenation



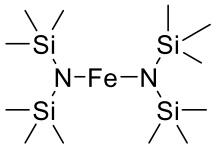
Hahn's Ir catalyst for transfer hydrogenation



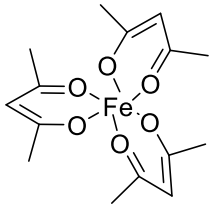
Au catalyst for allylic rearrangement

Chart 1: Some selected examples of NHC-TM catalysts.

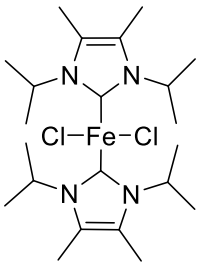
So far, we have discussed the most commonly used catalysts based on nobel/ heavy transition metals like palladium, ruthenium, rhodium, gold, iridium and platinum. Considering the fact that these precious metals are quite expensive, their low abundance and toxicity there is always a search for development of cheap, less toxic and better catalysts that can replace these precious metals and perform important organic transformations. Iron being first row transition metal, it satisfies all the requirements. It is a most abundant earth metal after Aluminium. Owing to its cheap cost and low toxicity Iron based catalysts have received much attention in last two decades.[19] Oxidation states of Iron varies from -2 to +5, but +2 and +3 are most common.



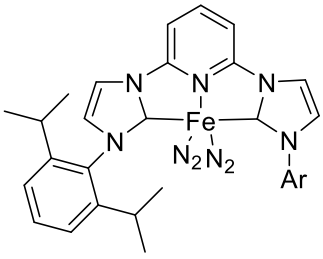
Fe catalyst for hydroboration of carbonyl compounds



$Fe(acac)_3$ catalyst for hydroboration of aldehydes



Fe catalyst for ATRP



Fe catalyst for alkene hydrogenation

Chart 2. Some selected examples of Iron(II) catalysts

In low oxidation states, Iron center can behave as a nucleophile and can catalyze basic organic transformations like nucleophilic additions, hydrosilylation, hydroboration, hydrogenation etc. In recent years, numerous of iron-catalyzed hydroboration of carbonyl compounds[20] reports have been published. Also, iron catalyzed hydrosilylation of alkene and alkynes[21] as well as carbonyl compounds[22] have been reported. Most recent work using iron catalyst includes Bai's report on the hydroboration of carbonyl compounds using $[Fe_2(NPtBu_3)]$ catalyst.[23] Tom baker and coworkers also have synthesized $[Fe\text{-}N_2S_2]_2$ complex and employed it for hydroboration of aldehydes.[24] Findlater et al. has

reported [Fe(acac)$_3$] as a catalyst and used it for hydroboration of aldehydes and ketones at ambient temperature.[25]

In this thesis work N, N'-bis(2-pyridyl)benzene-1, 2-diamine[26] ligand precursor has been used to prepare the carbene salt[27]. This pyridine-functionalized NHC was used to synthesize NHC-metal complexes. Two NHC-Iron(II) complexes were synthesized by treating the pyridine-functionalized NHC salt with Ag_2O forming the NHC–silver complex followed by trans-metalation using $FeCl_2$.THF precursor complex in solvent CH_3CN and DCM respectively. The newly synthesized complexes were characterized by XRD and NMR spectroscopic studies (^{1}H, ^{13}C and ^{19}F NMR). Further, we have employed both the Iron(II)-NHC complexes for hydroboration of aldehydes.

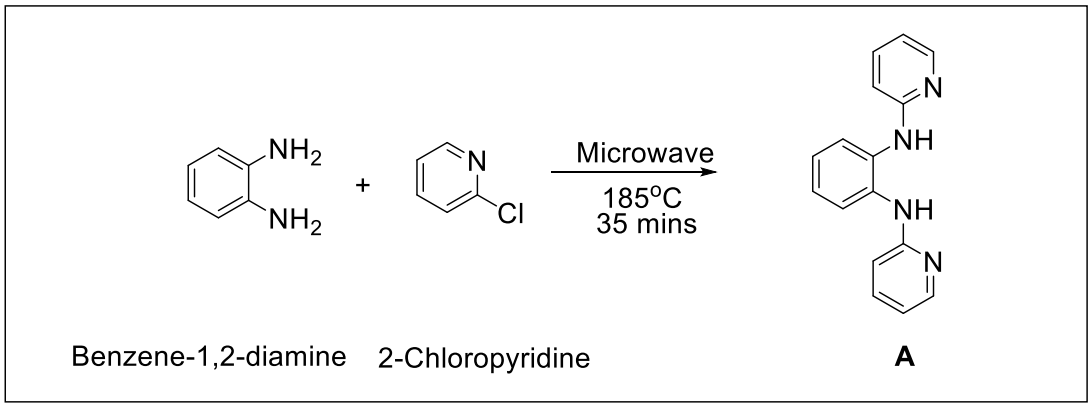
2. EXPERIMENTAL METHODS

2.1 Materials: *o*-Phenylenediamine, 2-Chloropyridine, Silver(I) oxide, Iron(II) chloride, Copper bromide, Tetrafluoroboric acid, Triethyl orthoformate, Benzaldehyde, Pinacolborane, 2-Bromo benzaldehyde, 3-Bromo benzaldehyde, 4-Fluoro benzaldehyde, 4-Cyano benzaldehyde, 4-Nitro benzaldehyde, 4-Methyl benzaldehyde, 3-Methoxy benzaldehyde, 2-Hydroxy benzaldehyde, 2,6-Dimethyl benzaldehyde, Naphthaldehyde, Cinnamaldehyde, Furfuraldehyde were purchased from Sigma-Aldrich chemicals and used without any further purification. Solvents like Acetonitrile, Dichloromethane, Diethyl ether and Chloroform-*d* were dried using P_2O_5, Na and Benzophenone and distilled before use.

General procedures: All experiments were performed under dry argon atmosphere using standard Schlenk techniques and a vacuum-line system unless otherwise stated. Solvents were deoxygenated and dried immediately prior to use. All Ag_2O reactions were carried out in absence of light. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 400 MHz BRUKER/JEOL NMR spectrophotometer at room temperature unless mentioned otherwise. All NMR spectra were recorded in a $CDCl_3$ solvent having TMS as an internal standard unless mentioned otherwise. Mass spectra were recorded using AB Sciex, 4800 plus MALDI TOF/TOF. XRD data were recorded on Bruker Smart Apex Duo diffractometer at 100 K using Mo Kα radiation (λ = 0.710 73 Å).

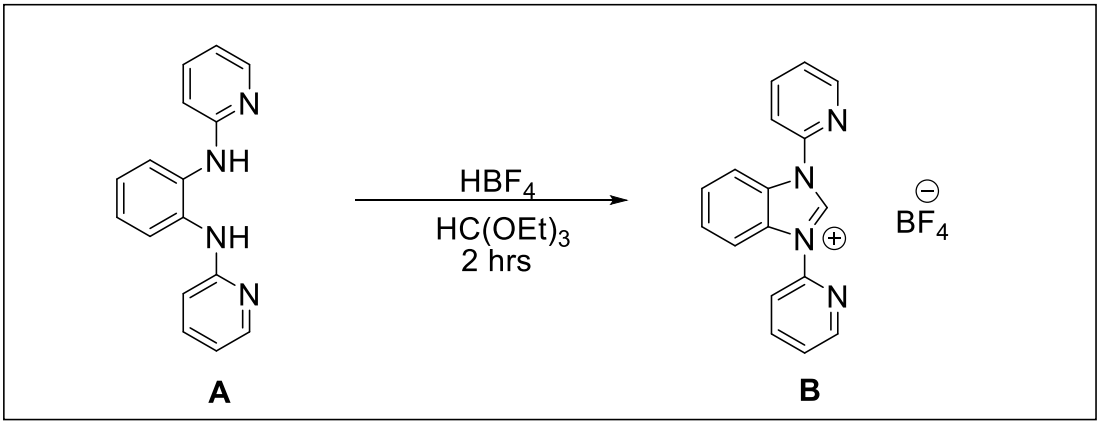
2.2 Synthesis

(a) Synthesis of N,N'-bis(2-pyridyl)benzene-1,2-diamine (A): 1,2-diaminobenzene(1g, 9.24 mmol), 2-Bromopyridine (1.8 g, 19.4 mmol) were taken in microwave vial. The vial was closed with a teflon septum cap then kept in microwave reactor. The reaction mixture was heated at 458 K for 35 minutes (scheme 4). After that the mixture was cooled down to room temperature. This crude reaction mixture was dissolved in water and then added to a solution of concentrated ammonia in water, which caused the formation of pink-red precipitate. Further, this precipitate was filtered off, washed with distilled water and then dried in air to afford the desired product. Recrystallization was done in ethanol to obtain the pure product. Yield = 91% (1.2g). ^{1}H NMR ($CDCl_3$): *δ* ppm = 8.18 (*m*, 2H), 7.72 (*dd*, 2H), 7.44 (*m*, 2H), 7.12 (*dd*, 2H), 6.72(*m*, 2H), 6.71 (*br s*, 2H), 6.61 (*m*, 2H). ^{13}C NMR ($CDCl_3$): δ ppm = 156.6, 148.3, 137.8, 133.4, 123.2, 115.2, 108.9.



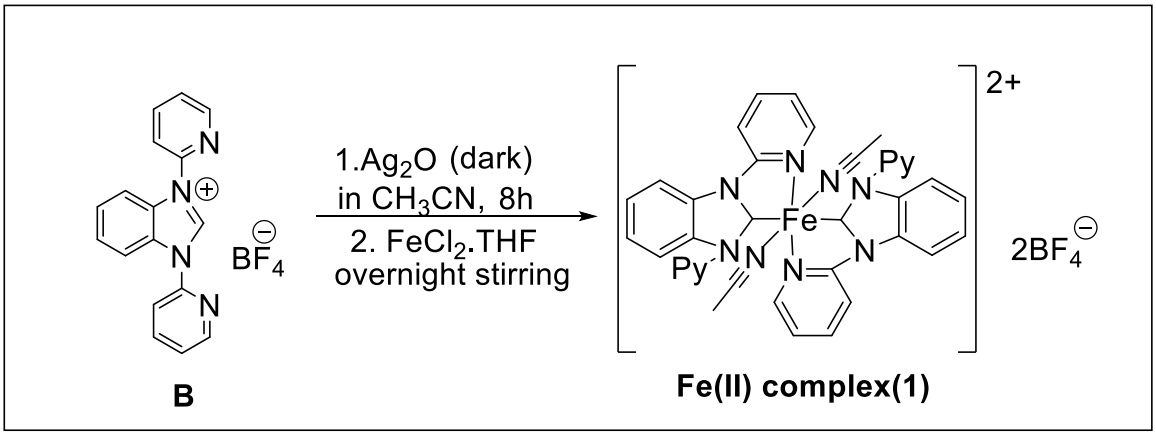
Scheme 4: Synthesis of ligand (**A**)

(b) Synthesis of 1,3-bis(pyridine-2-yl)-1H-benzimidazol-3-ium tetrafluoroborate (B): N, N'-Bis(2-pyridyl)benzene-1, 2-diamine (**A**) (5 g, 19 mmol) was treated with aq. HBF_4 (2.7 ml, 19 mmol) in 50 mL of triethyl orthoformate ($HC(OEt)_3$)(Scheme 5). The resulting reaction mixture was stirred at 323 K for 2 hours and then excess triethyl formate was removed by filtration. The solids were washed with diethyl ether (20 mL) and dried in air to afford pale violet-blue compound. Yield = 4.8 g (70%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* ppm: 10.47 (*s*, 1H), 8.74 (*d*, 2H), 8.56 (*dd,* 2H), 8.36 (*d*, 2H), 8.23 (*m*, 2H), 7.79 (*dd*, 2H), 7.6 (*dd*, 2H).



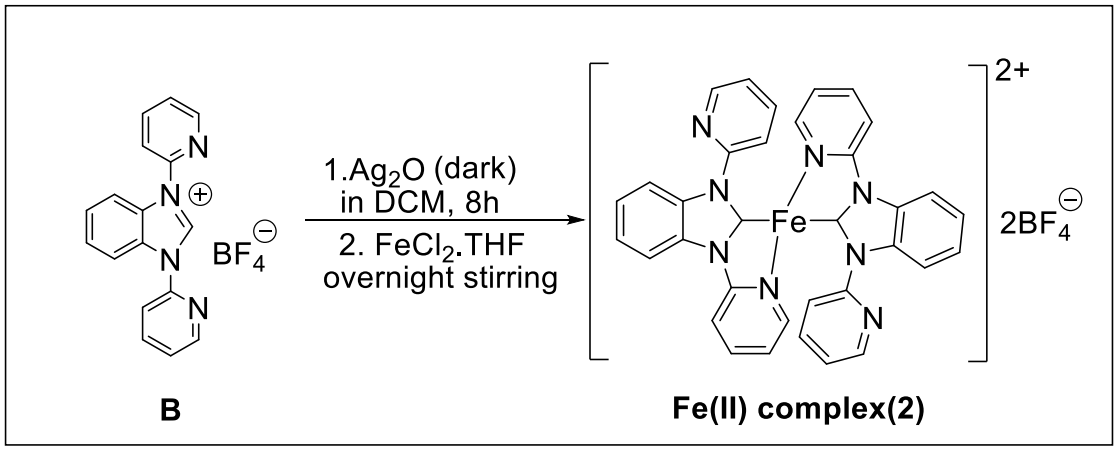
Scheme 5: Synthesis of NHC (**B**)

(c) Synthesis of NHC-Fe(II) complex(1): Silver(I) oxide (192 mg, 0.83 mmol) and carbene salt(B) (600 mg, 1.66 mmol) were mixed in distilled acetonitrile (30 mL) in a schlenk flask. This reaction mixture was covered with aluminium foil and stirred for 8 hours under dark conditions then $FeCl_2$.THF complex (165 mg, 0.83 mmol) was added. The reaction was again kept for stirring for 12 hours. The resultant brown solution was passed through celite plug to get rid of the precipitated AgCl. The red filtrate was reduced to a 4-5 mL under high vacuum. The dropwise addition of 2 mL of diethyl ether to this concentrated solution resulted deep red crystals. Yield = 320 mg (45%). M.P: 223-235ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.8-8.5 (*m*, 24H), 2.04 (*s*, 6H, MeCN). HRMS (positive ESI) m/z for [$C_{38}H_{30}N_{10}FeB_2F_8$]: 889.2767 ($M+H^+$).



Scheme 6: Synthesis of Fe(II)-NHC complex (**1**)

(d) Synthesis of NHC-Fe(II) complex(2): Silver(I) oxide (192 mg, 0.83 mmol) and carbene salt(B) (600 mg, 1.66 mmol) were taken in a Schlenk flask and solubilized in DCM (30 mL). The reaction mixture was stirred for 8 hours at RT under dark conditions then addition of $FeCl_2$.THF precursor complex (165 mg, 0.83 mmol) was done. This reaction mixture was again stirred for overnight under dark conditions. The resulting green solution was paseed through celite plug to get rid of the precipitated AgCl. The green filtrate was reduced to a 4 mL under vacuum and diethyl ether was slowly added to this concentrated solution to obtain dark green crystals. Yield = 260 mg (41%). M.P: 190ºC-205ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.5-8.8 (*m*, 24H). HRMS (positive ESI) m/z for [$C_{34}H_{24}N_8FeB_2F_8$]: 775.5903 ($M+H^+$).



Scheme 7: Synthesis of Fe(II)-NHC complex (**2**)

3. Results and discussion:

3.1. Characterization of compounds A and B: We first prepared the diamine ligand (**A**) then reacted it with fluroboric acid in triethyl orthoformate to afford carbene salt (**B**). NMR studies confirmed the formation of desired products.

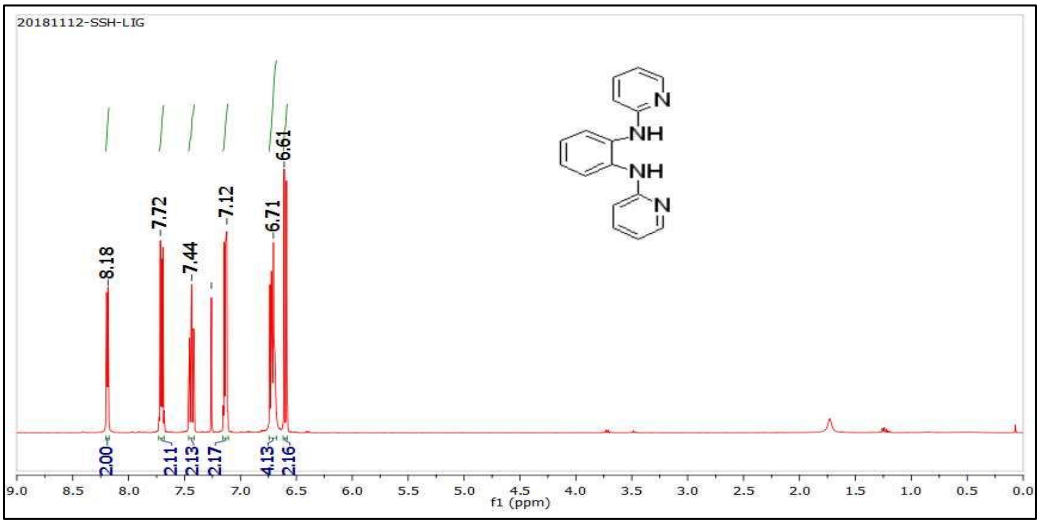


Figure 3[a]: ^{1}H NMR spectrum of **A** in $CDCl_3$

^{1}H NMR ($CDCl_3$): δ ppm = 8.18 (*m*, 2H), 7.72 (*dd*, 2H), 7.44 (*m*, 2H), 7.12 (*dd*, 2H), 6.72(*m*, 2H), 6.71 (*br s*, 2H), 6.61 (*m*, 2H).

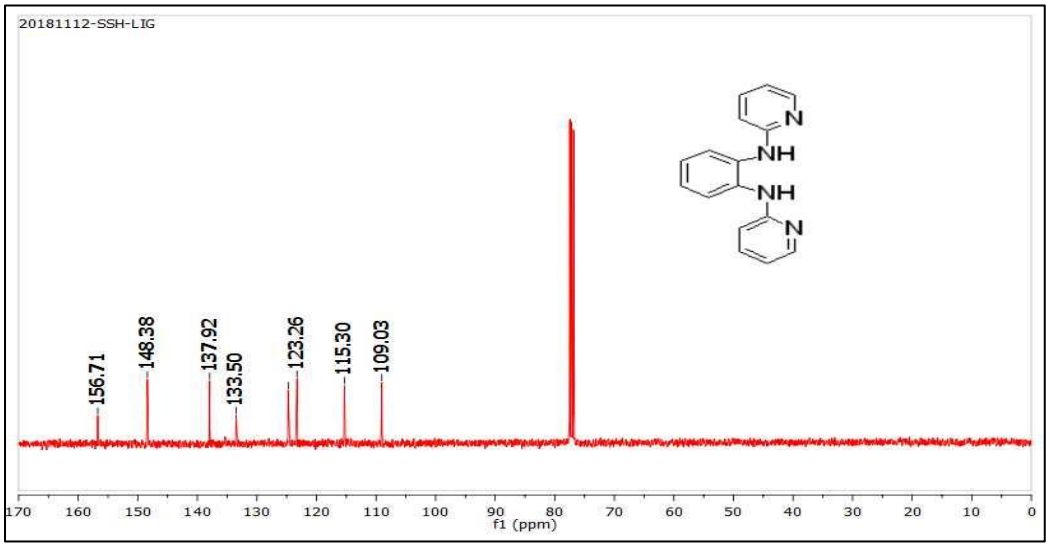


Figure 3[b]: ^{13}C NMR spectrum of **A** in $CDCl_3$

^{13}C NMR ($CDCl_3$): δ ppm =156.7, 148.3, 137.9, 133.5, 123.2, 115.3, 108.9.

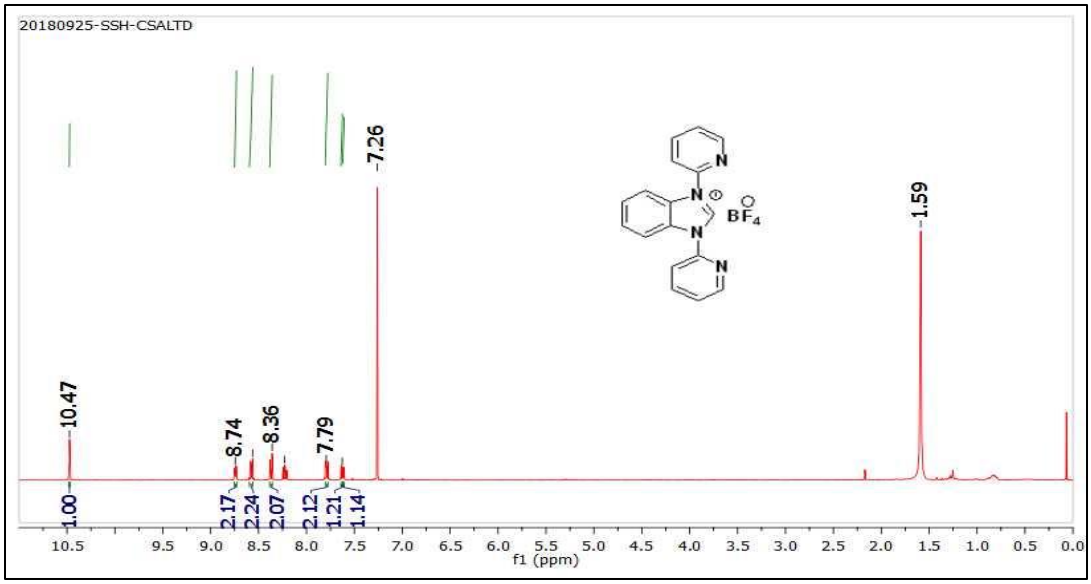


Figure 4[a]: ^{1}H NMR spectrum of **B** in $CDCl_3$

^{1}H NMR ($CDCl_3$) *δ* ppm: 10.47 (*s*, 1H), 8.74 (*d*, 2H), 8.56 (*dd*, 2H), 8.36 (*d*, 2H), 8.23 (*m*, 2H), 7.79 (*dd*, 2H), 7.6 (*dd*, 2H).

The NMR peak at 10.47ppm in figure (4a) represents single imidazolium acidic proton.

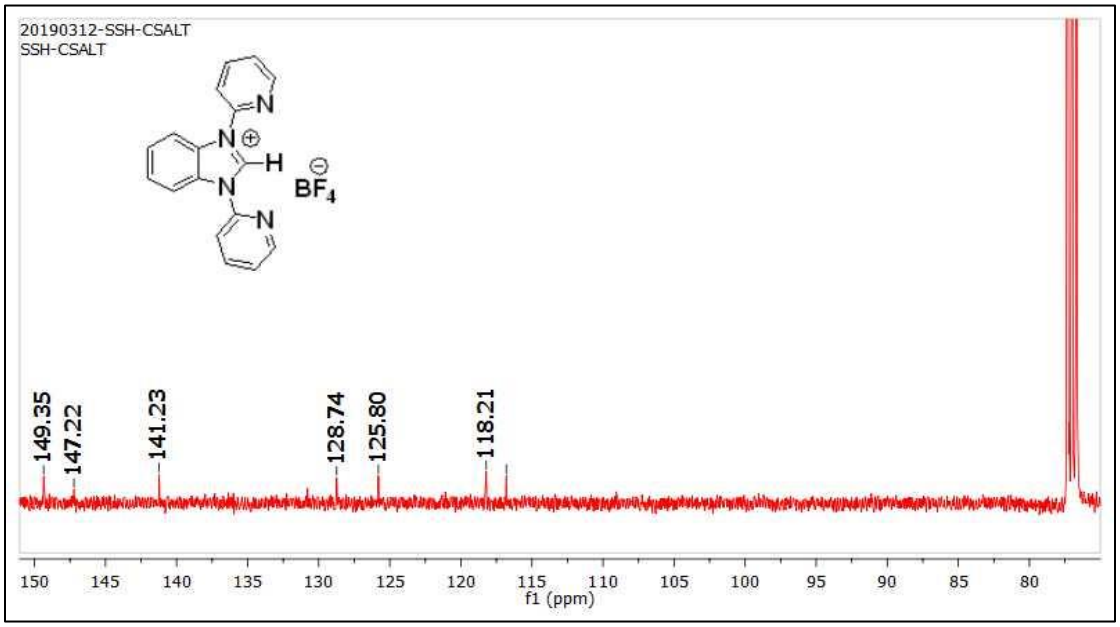


Figure 4[b]: ^{13}C NMR spectrum of **B** in $CDCl_3$

^{13}C ($CDCl_3$) δ ppm: 149.35, 147.22, 141.23, 128.74, 125.80, 118.21, 116.8.

3.2. Characterization of Fe(II)-NHC complexes (1) and (2):

Both complexes [(**1**) and (**2**)] were structurally characterized by multinuclear NMR spectroscopic studies, HRMS spectrometry, and single crystal X-ray structural analysis.

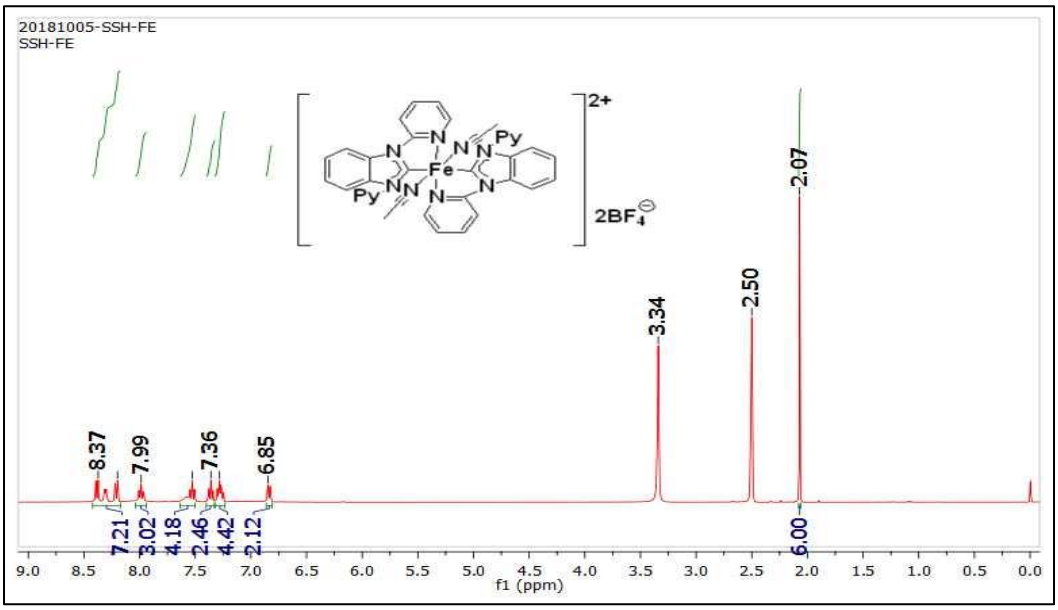


Figure 5[a]: ^{1}H NMR spectrum of (**1**) in DMSO-d_6

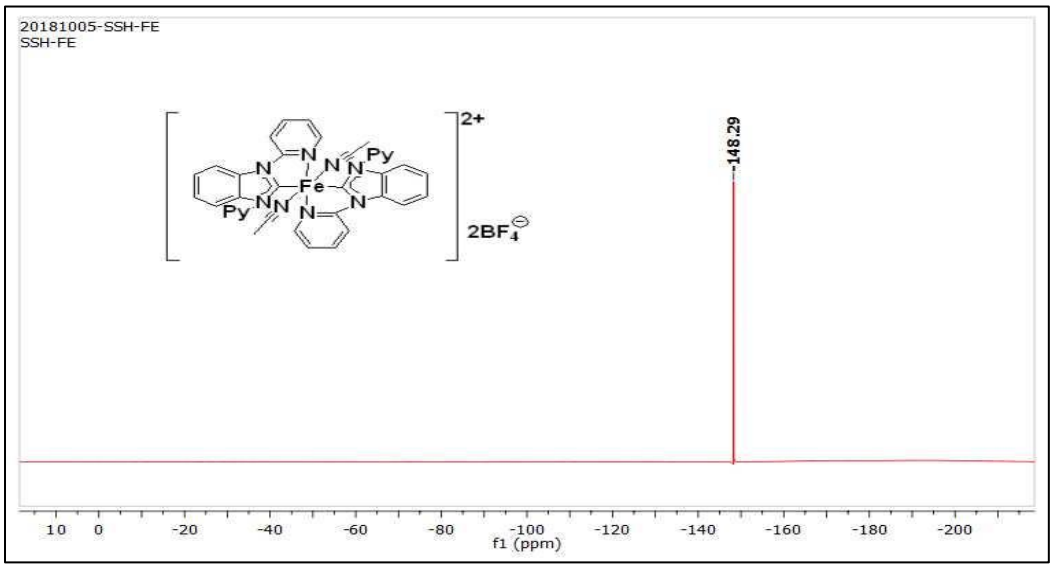


Figure 5[b]: ^{19}F NMR spectrum of (**1**) in DMSO-d_6

In ^{1}H NMR of complex (**1**) (fig.5[a]), peak at 2.07 represents 6 protons of acetonitrile, which is coordinated to Fe(II) atom. Aromatic proton peaks appeared around 6.5-8.5 ppm

and they are matching with the carbene salt (**B**) spectrum. This data indicates the formation of NHC-Fe(II) (**1**) complex. In ^{19}F NMR spectrum of complex (**1**) (fig.5[b]), a peak appears at -148.2 ppm which matches well with the reported value for BF_4 anion (-148 to -150 ppm).

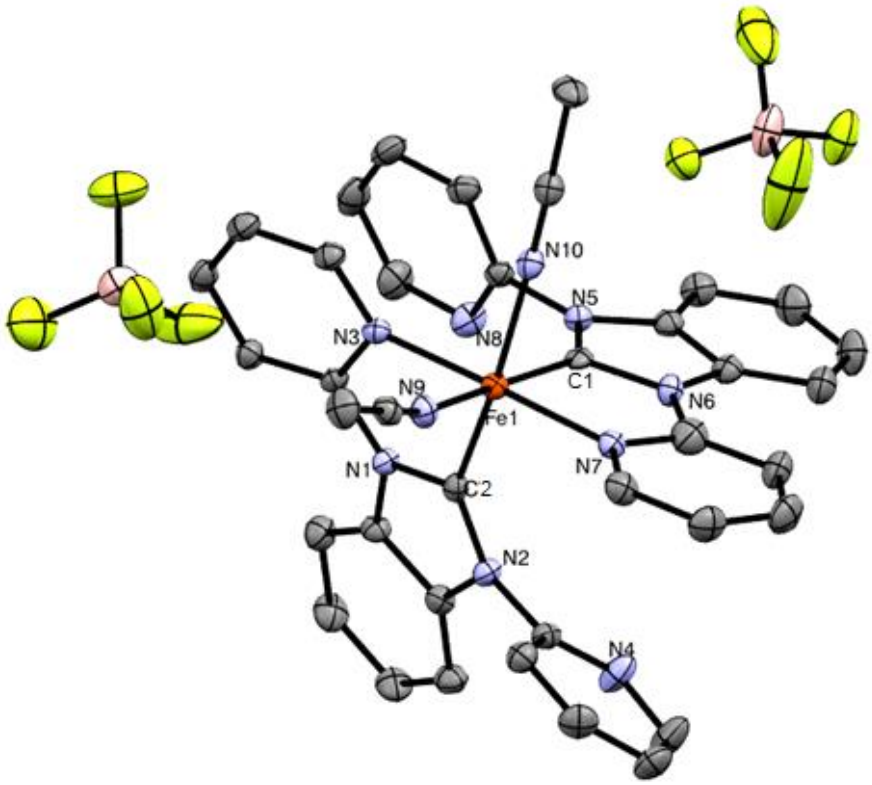


Figure 6: Molecular structure of Fe(II)-NHC complex (**1**), ORTEP style representation with ellipsoids shown at the 50% probability level. Hydrogen atoms are not shown for clarity. Some selected geometrical parameters: Fe1-C1 1.908 Å, Fe1-C2 1.908 Å, Fe1-N3 1.985 Å, Fe1-N7 1.993 Å, Fe1-N9 1.982 Å, Fe1-N10 1.975 Å, N3-Fe1-N7 178.43º.

The complex (**1**) is insoluble in THF, diethyl ether and soluble in acetonitrile. Crystallization was done in acetonitrile-diethyl ether solvent system at room temperature. In the above structure (fig 6), we can clearly see that the formed NHC-Fe(II) complex has six coordination and exhibits distorted octahedral geometry. Iron center is coordinated with bischelating ligand backbone and two acetonitirile moieties. It is extremely stable

towards air and moisture. The Fe-C_{NHC} (Fe1-C1, Fe1-C2) bond distances are 1.908 Å, corresponding well to the previously reported Fe-C_{NHC} bond distances. [28, 29]

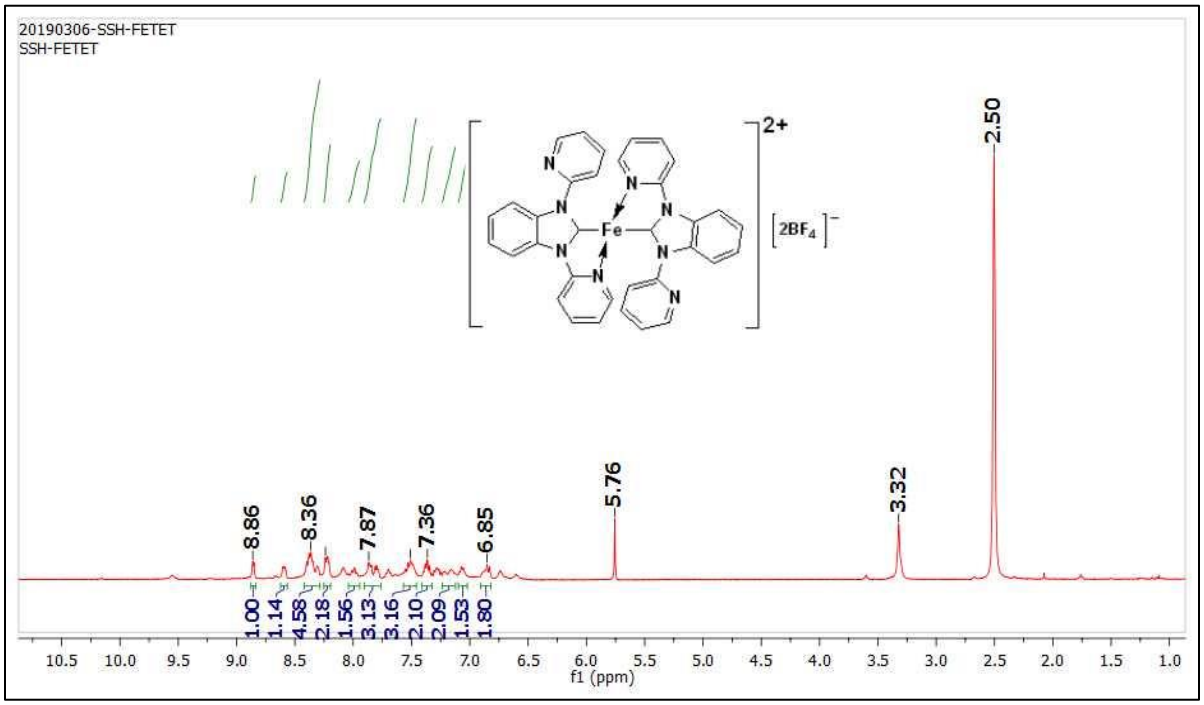


Figure 7[a]: ^{1}H NMR spectrum of (**2**) in DMSO-d_6

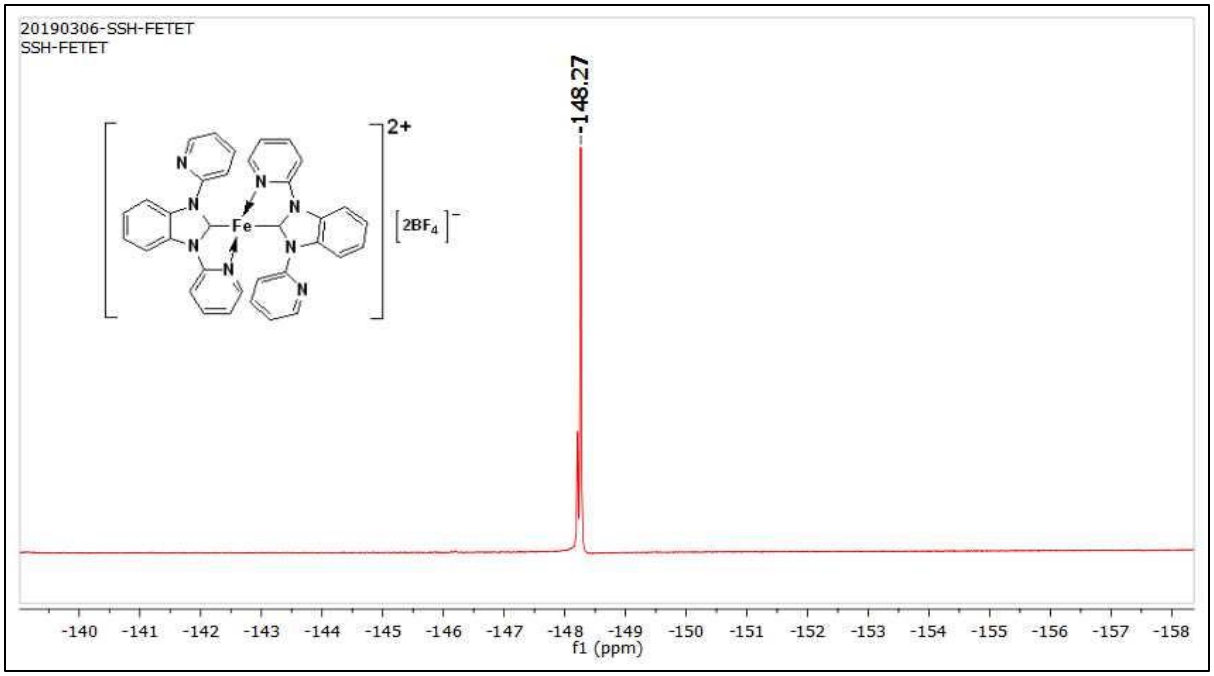


Figure 7[b]: ^{19}F NMR spectrum of (**2**) in DMSO-d_6

^{1}H NMR of complex (**2**) reveals that there is no acetonitrile peak, confirming the absence of coordination from solvent molecules to Fe(II) center. All aromatic proton peaks are present around 6.8-8.5 ppm, matching well with carbene salt (**B**) peaks. The peak of BF_4 anion in ^{19}F NMR is at -148.2 ppm.

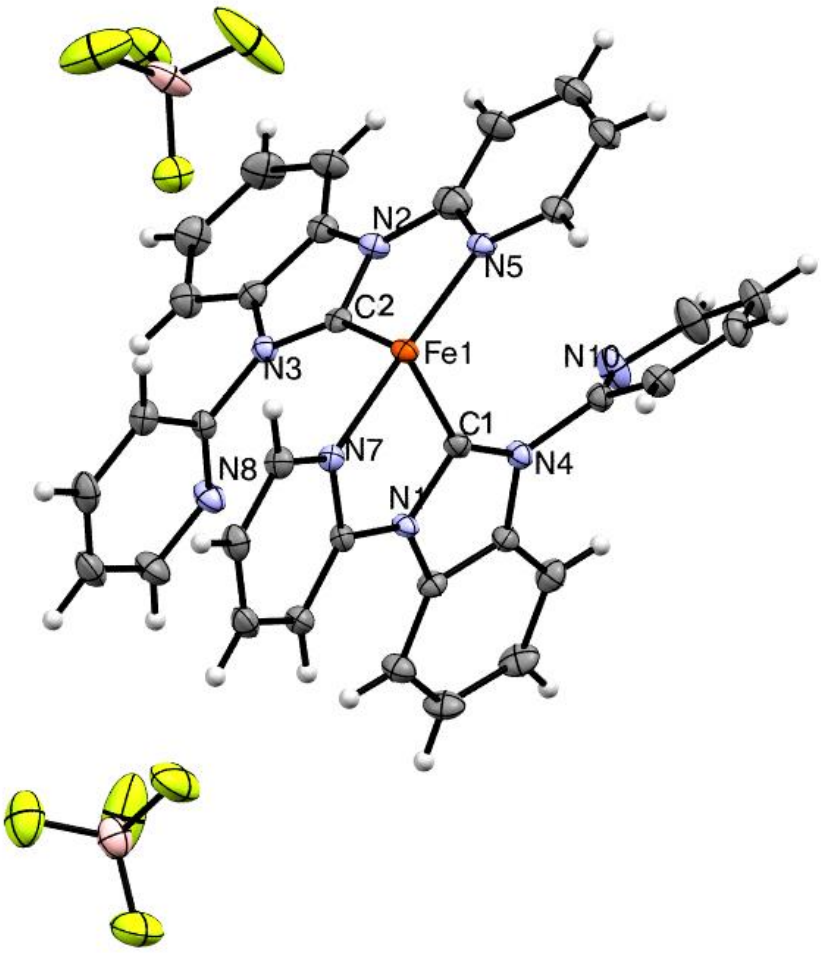


Figure 8: Molecular structure of Fe(II)-NHC complex (**2**), ORTEP style representation with ellipsoids shown at the 50% probability level. Some selected geometrical parameters: Fe1-C1 1.906 Å, Fe1-C2 1.906 Å, Fe1-N5 1.990 Å, Fe1-N7 1.983 Å, N5-Fe1-N7 179.53º, C1-Fe1-C2 87.78º.

Crystals for complex (**2**) were grown in DCM-pentane solvent system. Molecular structure shows that the Fe atom has total four coordination through ligand backbone. The bond

angle between two pyridine nitrogens (N5-Fe1-N7) is almost linear. The complex shows distorted square planar geometry and is pretty stable on exposure to air. Fe-C_{NHC} (Fe1-C1, Fe1-C2) bond distances are 1.906 Å and are quite same as bond distances of complex (**1**).

Both the complexes (**1**) and (**2**) were fully characterized and are probed to catalytic applications. We speculate that the complex (**2**) being square planar in geometry will be more active and a better catalyst than complex (**1**) due to availability of two vacant sites. Reactant species can easily bind to Fe center and catalysis could be much more efficient which is not possible in complex (**1**) where all sites are occupied because of presence of two extra acetonitrile moieties.

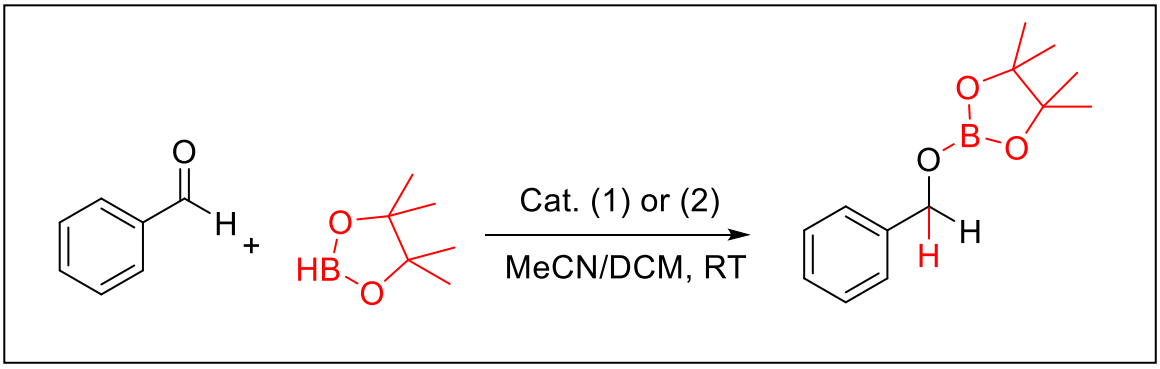
Crystallographic data for complex (1) and (2):

	Complex 1	**Complex 2**
Chemical formula	$C_{38}H_{30}N_{10}FeB_2F_8$	$C_{34}H_{24}N_8FeB_2F_8$
Crystal system	Triclinic	Triclinic
Space group	P 1/2	P 1/2
Unit cell dimensions	a 10.943(5) Å, b 11.255(5) Å, c 16.084(8) Å α 108.817(12), β 92.525(13), γ 90.638(12)	a 10.943(5) Å, b 11.255(5) Å, c 16.084(8) Å α 108.817(12), β 92.525(13), γ 90.638(12)
Cell volume	1872.62 $Å^3$	1872.62 $Å^3$

3.3 Catalytic applications:

Hydroboration of aromatic aldehydes using complex (1) and (2) as a catalyst.

With the two new Fe(II)-NHC complexes, we investigated their potential as hydroboration catalysts for aldehydes. Benzaldehyde was used as a model substrate and HBPin as a source of boron for optimizing the reaction conditions. Both complexes **(1)** and complex **(2)** show fairly good conversion of benzaldehyde to the corresponding borate ester.



Scheme.8: General schematic representation of hydroboration of aldehydes

Table.1 Optimization of reaction conditions for catalyst (**1**) and (**2**)

Entry	Catalyst (mol%)	Time	Solvent	Yield[a] (%)
1	--	0.5h	MeCN	Trace
2	1 (5)	12h	MeCN	>99
3	1 (1)	12h	MeCN	>99
4	1 (1)	6h	MeCN	80
5	1 (2)	6h	MeCN	98
6	2 (5)	12h	DCM	>99
7	2 (1)	12h	DCM	>99
8	2 (1)	1h	DCM	85
9	2 (2)	0.5h	DCM	96

[a]Reaction conditions: Benzaldehyde (0.25 mmol), HBPin (0.25 mmol) and Acetonitrile/Dichloromethane (2 mL) as a solvent at room temperature. [b]Yields were determined by ^{1}H NMR using mesitylene as an internal standard.

First we did the control reaction of benzaldehdye and HBpin without any catalyst, it resulted very low amount of expected borate ester (Entry 1). The reaction of

benzaldehyde and HBpin with 5mol% of catalyst (**1**) gives excellent yield (>99, entry 2). Reducing the catalyst loading to 1mol%, still gave the 99% yield (entry 3). Even with a reduced catalyst (**1**) loading and reduced reaction time (entry 4) good yield was obtained at room temperature. We finalized 2 mol% catalyst loading with 6hrs of reaction time (entry 5) to be best reaction conditions for catalyst (**1**). As expected, catalyst (**2**) is highly active and gives 85% conversion within 60 minutes. For catalyst (**2**), 2 mol% catalyst loading and 30 min reaction time (entry 9) were chosen as an optimized reaction conditions.

NMR data for optimization of reaction conditions using catalyst (1) and (2):

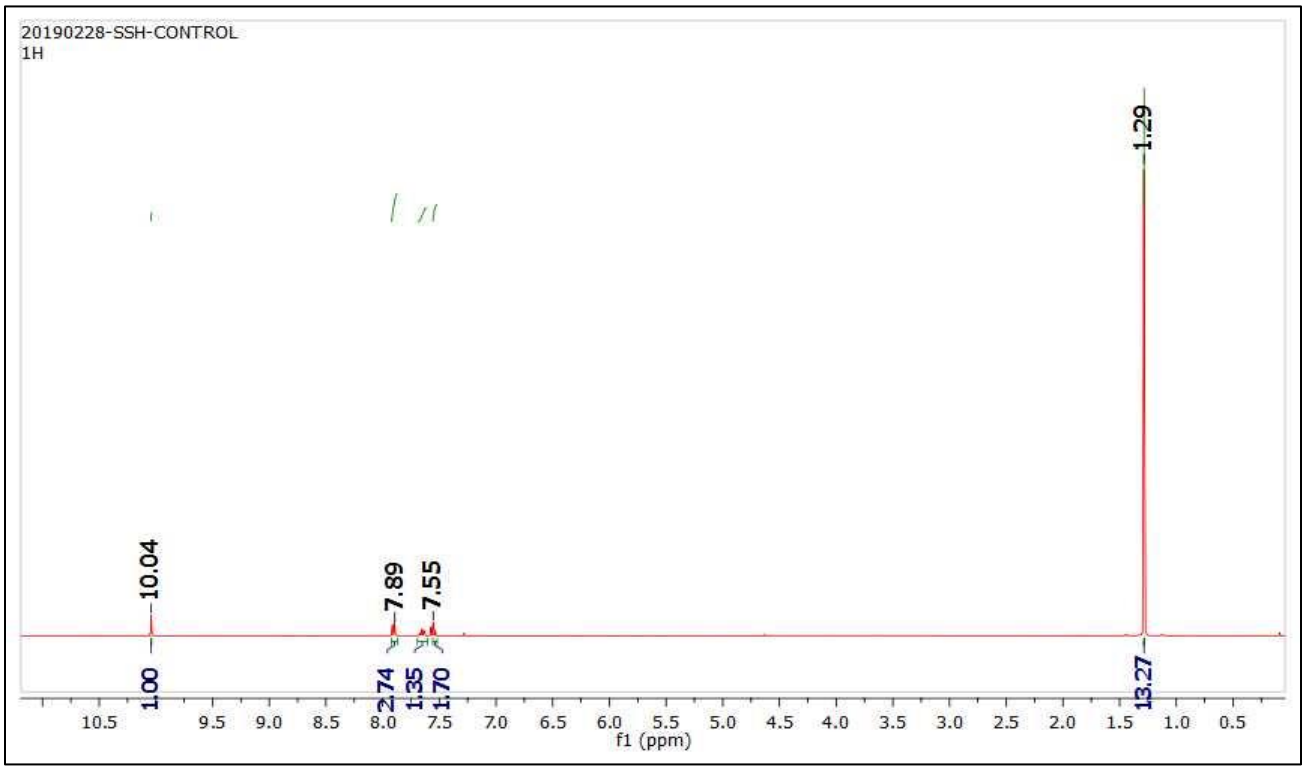


Figure 9. ^{1}H NMR spectrum of control reaction. [Solvent: $CDCl_3$]

The absence of proton peak around 4.8-5.1 ppm shows that there's no product formation.

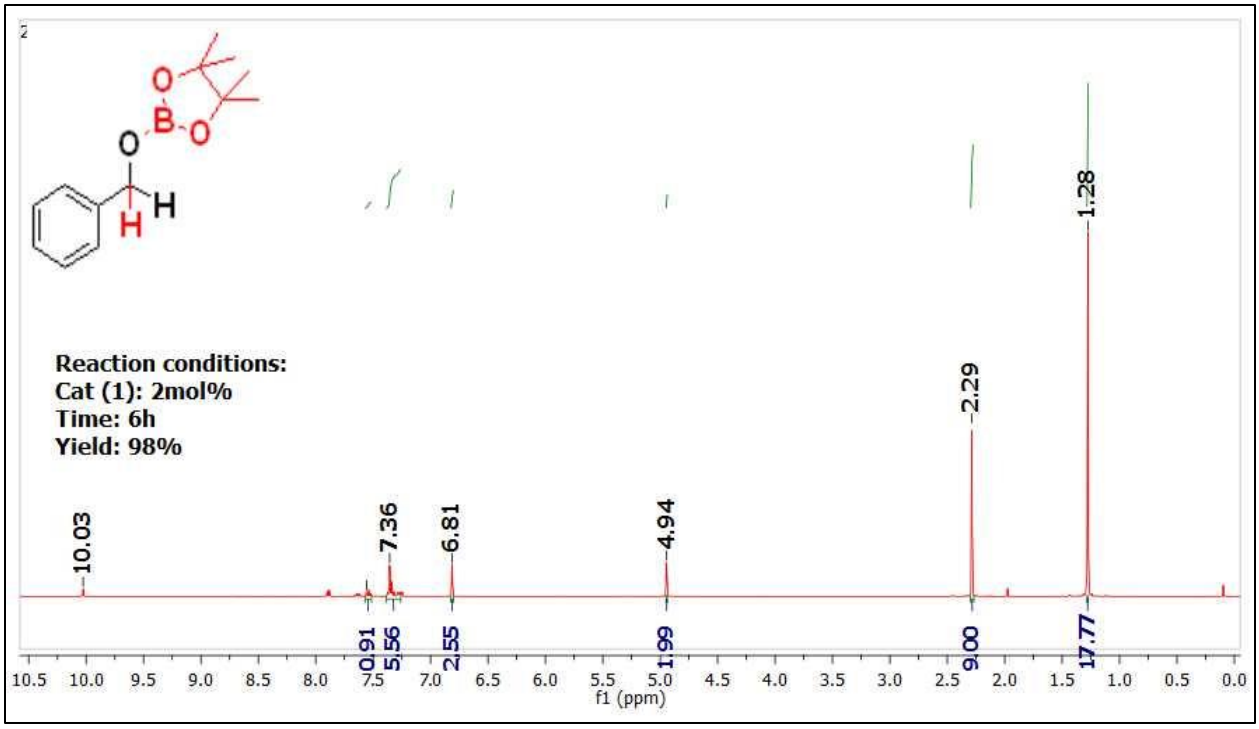


Figure 10. ^{1}H NMR spectrum for entry (5) [Solvent: $CDCl_3$]

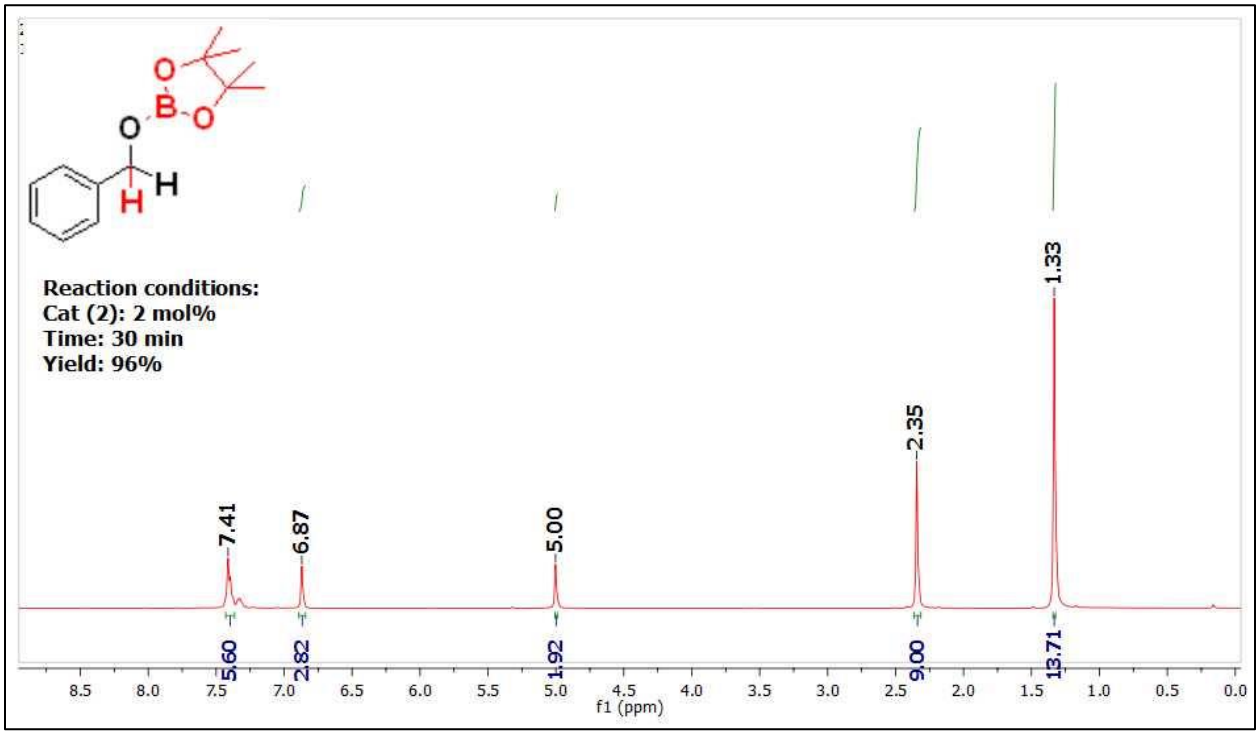


Figure 11. ^{1}H NMR spectrum for entry (9) [Solvent: $CDCl_3$]

After optimization of reaction conditions, we investigated the substrate scope of aromatic aldehydes. All the catalytic hydroboration transformations were monitored by ^{1}H NMR spectroscopy, which confirmed the formation of the corresponding borate esters as desired in good yields.

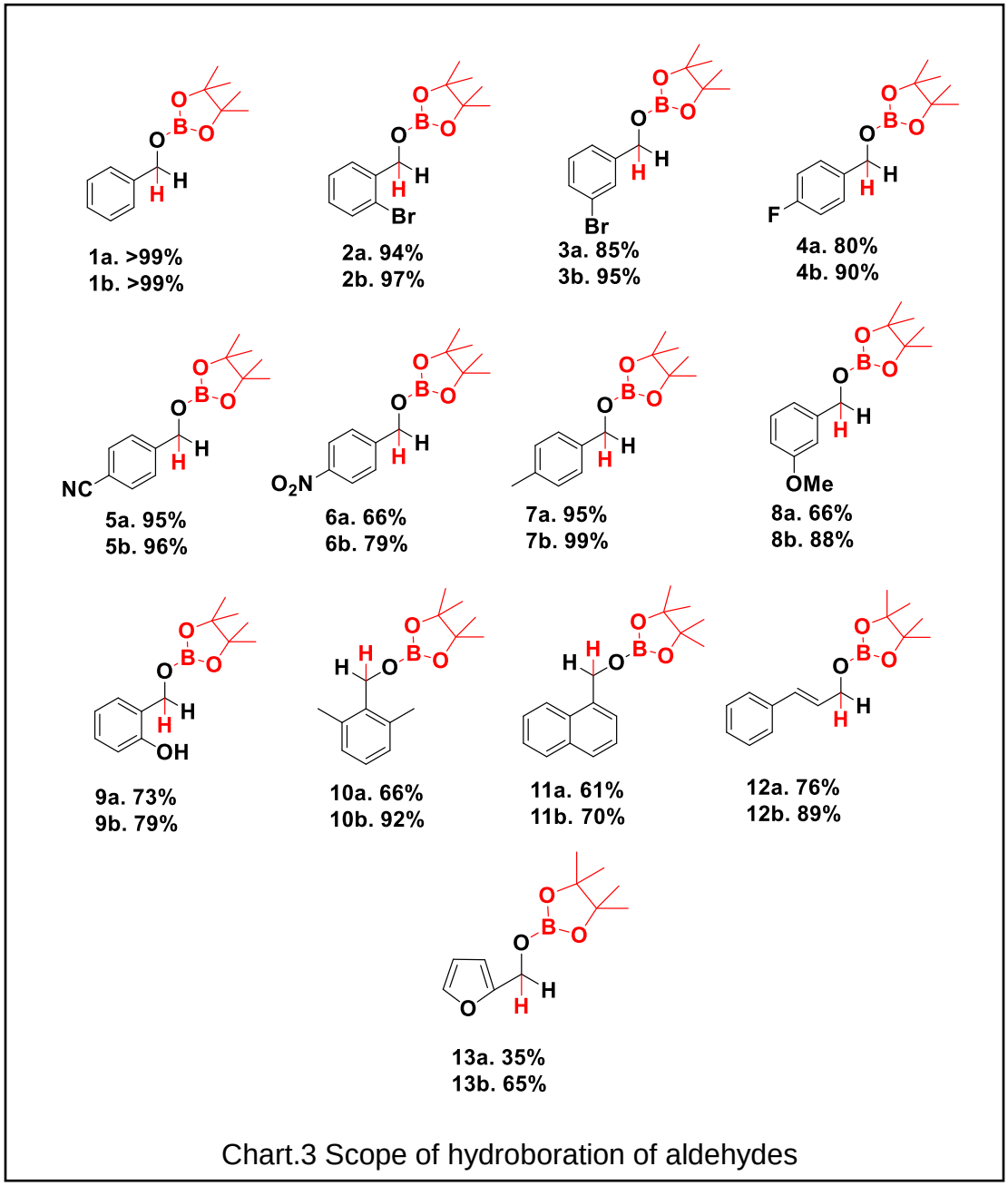


Chart.3 Scope of hydroboration of aldehydes

[a]Reaction conditions: Benzaldehyde (0.25 mmol), HBPin (0.25 mmol) and Acetonitrile(a), Dichloromethane(b) (1.5 mL) as a solvent. Catalyst loading for both (1) and (2) is 2mol%. [b]Yields were determined by ^{1}H NMR using mesitylene as an internal standard and are given below the products (a for catalyst (1) and b for catalyst (2)).

Aldehydes substituted with electron-donating as well as electron-withdrawing groups had undergone hydroboration efficiently showing good yields of the corresponding borate esters. Many important functional groups in organic chemistry like hydroxy, methoxy, nitro, cyano group even halides were tolerated and showed good compatibility under the standardized reaction conditions. Additionally, we carried out catalytic reactions with the α,β-unsaturated aldehyde and heteroatomic aldehyde which also resulted moderate yields of corresponding borate esters. We observed that the assumptions made on the basis of availability of vacant sites are proved to be true. Catalyst (**2**) is way better than the catalyst (**1**), gives products in high yield with less reaction time. Further investigations to find out mechanistic pathway of the catalytic hydroboration reaction are in process.

General procedure for hydroboration reactions catalyzed by catalyst (1) and (2): The hydroboration reaction of differently substituted aldehydes were carried out in schlenk tubes. HBpin (0.25 mmol) and the desired aromatic aldehyde (0.25 mmol) were dissolved in MeCN (for catalyst **1**) or DCM (for catalyst **2**) and were taken in a schlenk tube, and then the exact equivalence of catalyst **1** or **2** was added. The catalytic tube was stirred for a known standardized time (6 hrs/30min) at room temperature. Later the solvents were removed under vacuum and mesitylene and $CDCl_3$ was added to reaction mixture. This reaction solution was taken in NMR tube and then subjected to proton NMR experiment in order to obtain the definite yield of the hydroborated products.

NMR Data for hydroborated products catalyzed by catalyst (1) and (2):

All NMR spectra were recorded at ambient temperature using a Bruker Ascend 400 NMR spectrometer.

1. $PhCH_2OBpin$ - ^1H NMR (400 MHz, ppm): δ 7.4-7.92 (*m*, 5H, *Ph*), 4.98 (*s*, 2H, OCH_2), 1.32 (*s*, 12H, Bpin-CH_3), IS: 6.85 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.33 (*s*, 9H, $(CH_3)_3$)

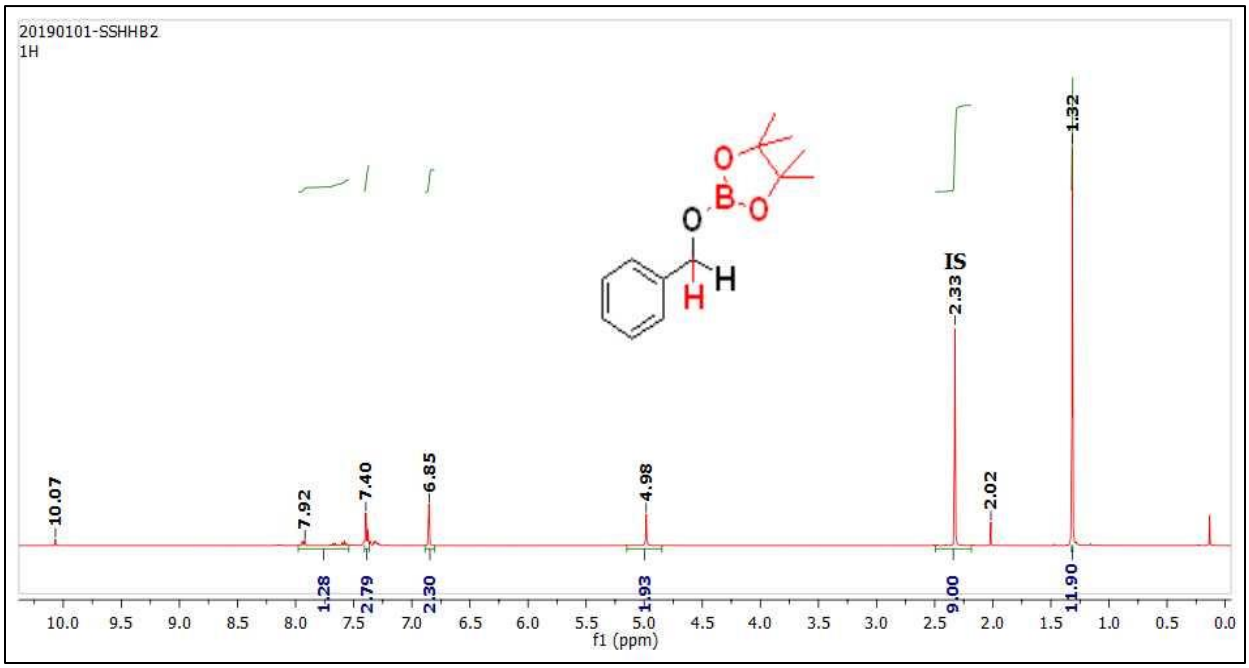


Figure 12a. ^1H NMR spectrum of [1a]. [Solvent: $CDCl_3$, IS: Mesitylene]

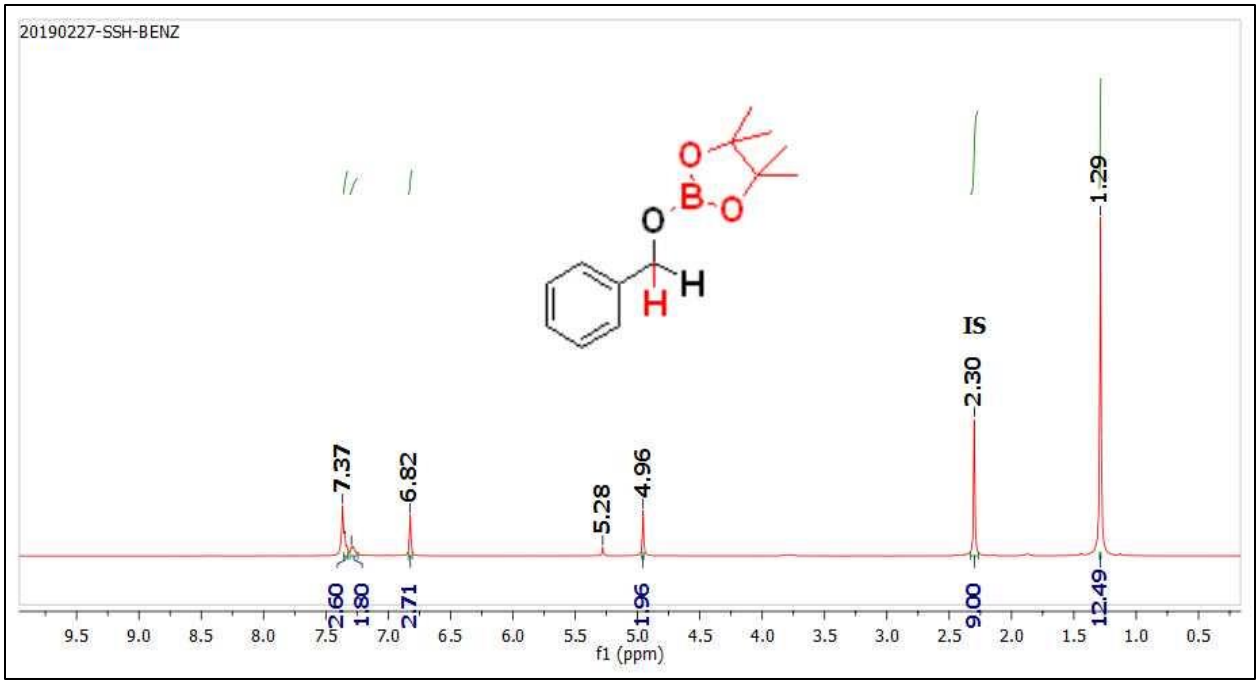


Figure 12b. ^{1}H NMR spectrum of [1b]. [Solvent: $CDCl_3$, IS: Mesitylene]

2. 2-BrPhCH$_2$OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.4-7.92 (*m*, 5H, *Ph*), 4.99 (*s*, 2H, OCH_2), 1.29 (*s*, 12H, Bpin-CH_3), IS: 6.8 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.28 (*s*, 9H, $(CH_3)_3$)

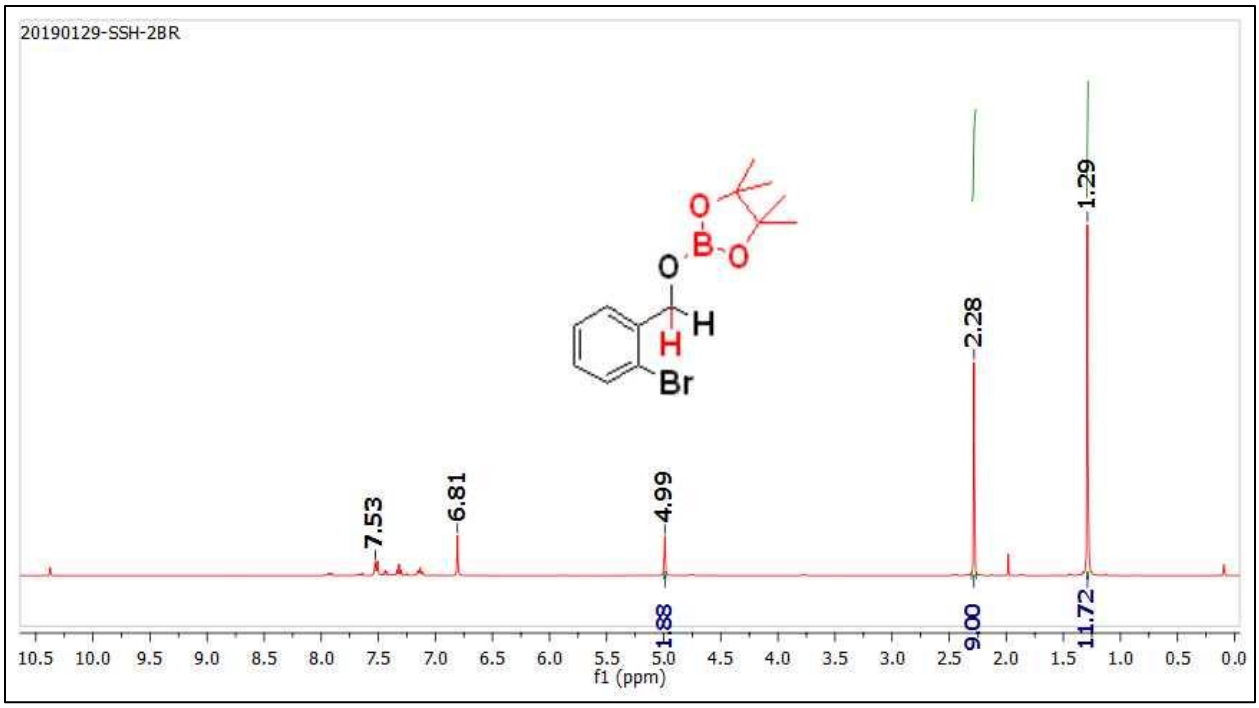


Figure 13a. ^{1}H NMR spectrum of 2[a]. [Solvent: $CDCl_3$, IS: Mesitylene]

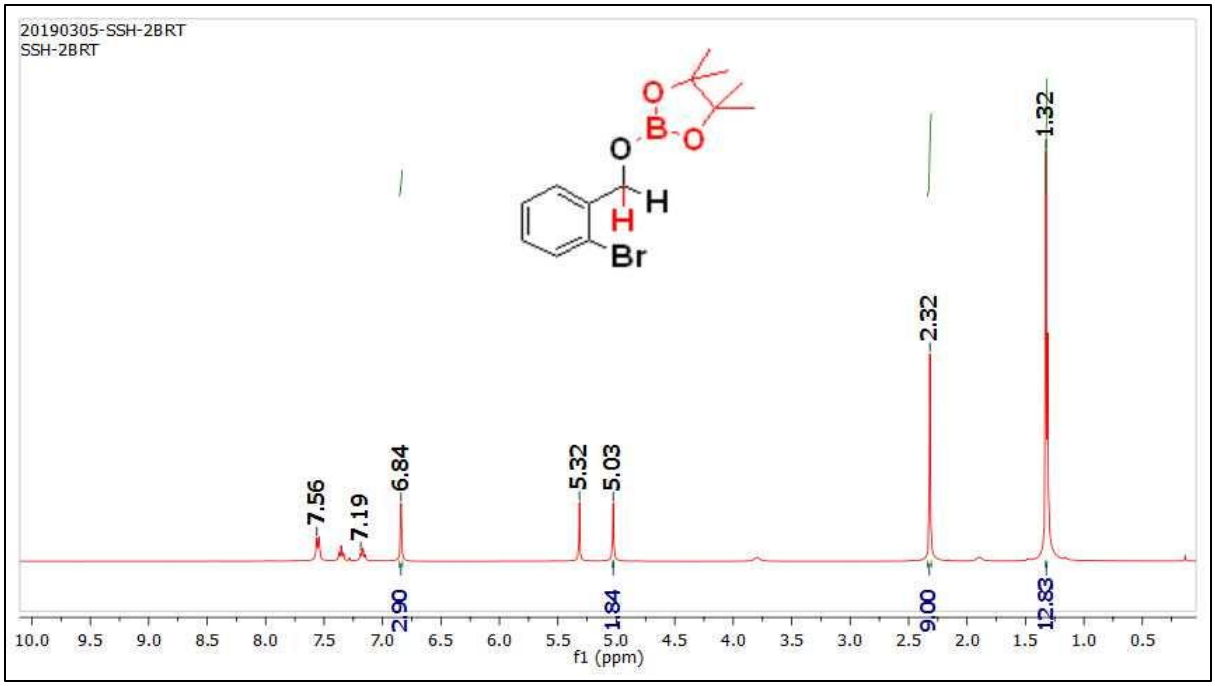


Figure 13b. ^{1}H NMR spectrum of [2b]. [Solvent: $CDCl_3$, IS: Mesitylene]

3. 3-BrPhCH$_2$OBpin -^{1}H NMR (400 MHz, ppm): δ 7.2-7.52 (*m*, 5H, *Ph*), 4.89 (*s*, 2H, OCH_2), 1.27 (*s*, 12H, Bpin-CH_3), IS: 6.8 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.28 (*s*, 9H, $(CH_3)_3$).

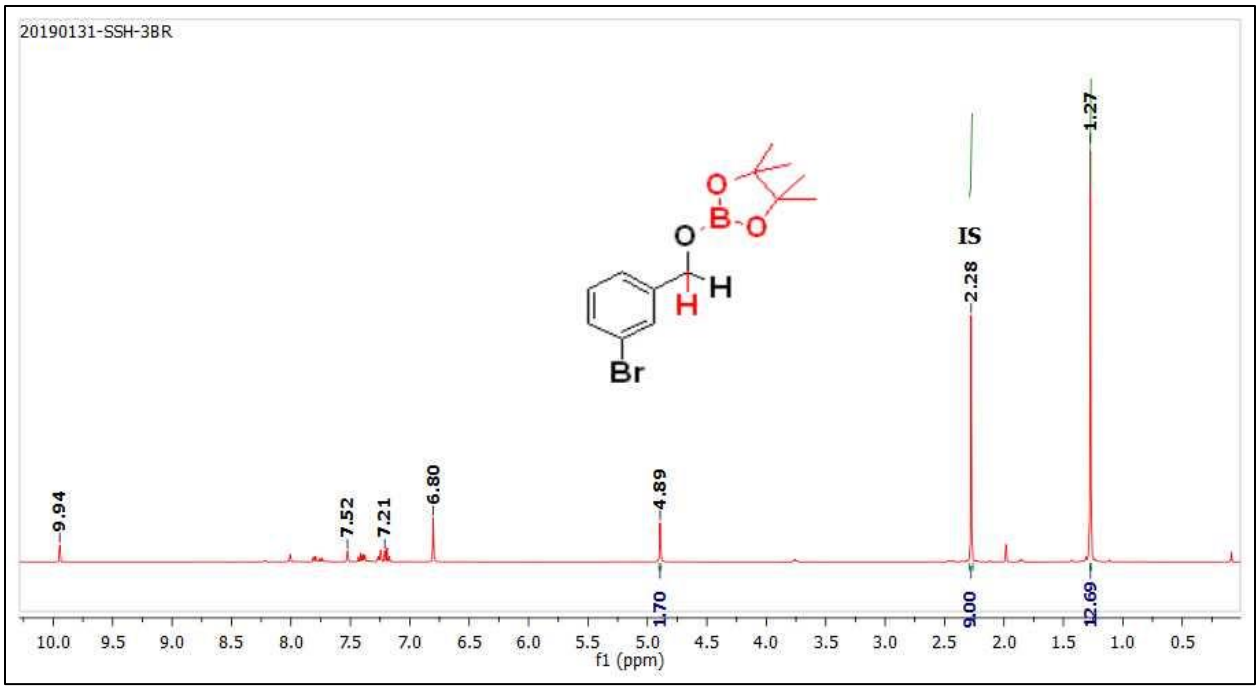


Figure 14a. ^{1}H NMR spectrum of [3a]. [Solvent: $CDCl_3$, IS: Mesitylene]

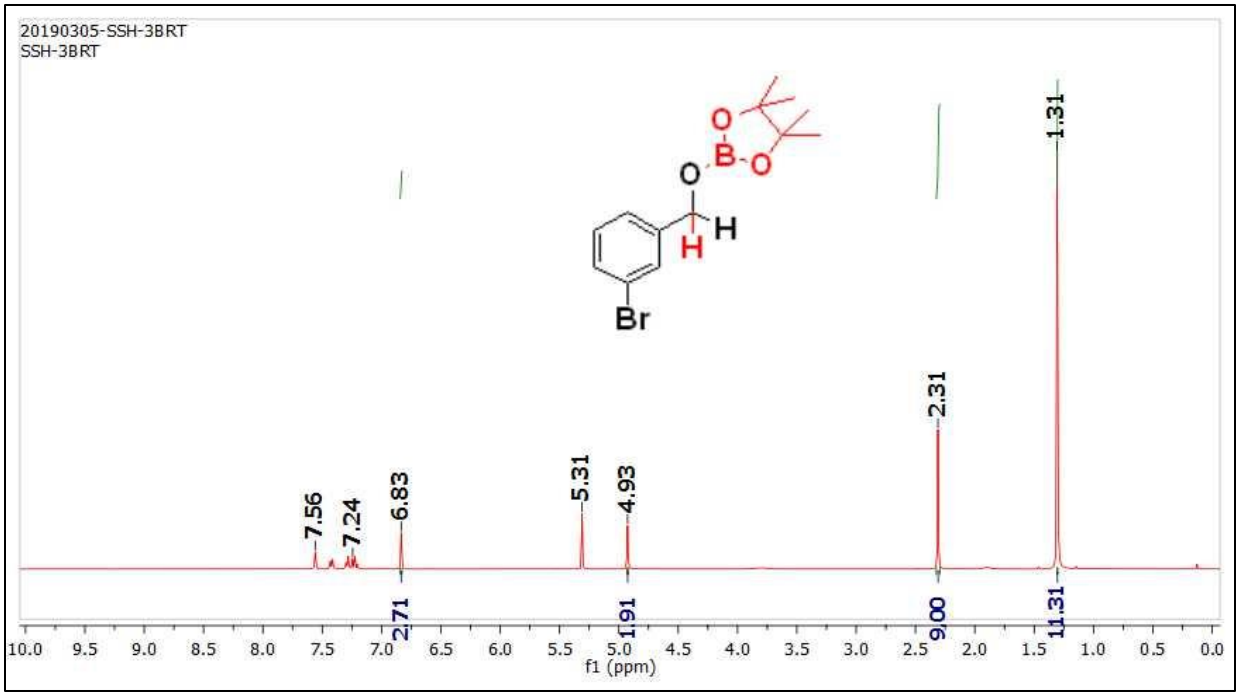


Figure 14b. ^{1}H NMR spectrum of [3b]. [Solvent: $CDCl_3$, IS: Mesitylene]

4. 4-FPhCH$_2$OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.2-7.52 (*m*, 5H, *Ph*), 4.88 (*s*, 2H, OCH_2), 1.26 (*s*, 12H, Bpin-CH_3), IS: 6.8 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.28 (*s*, 9H, $(CH_3)_3$).

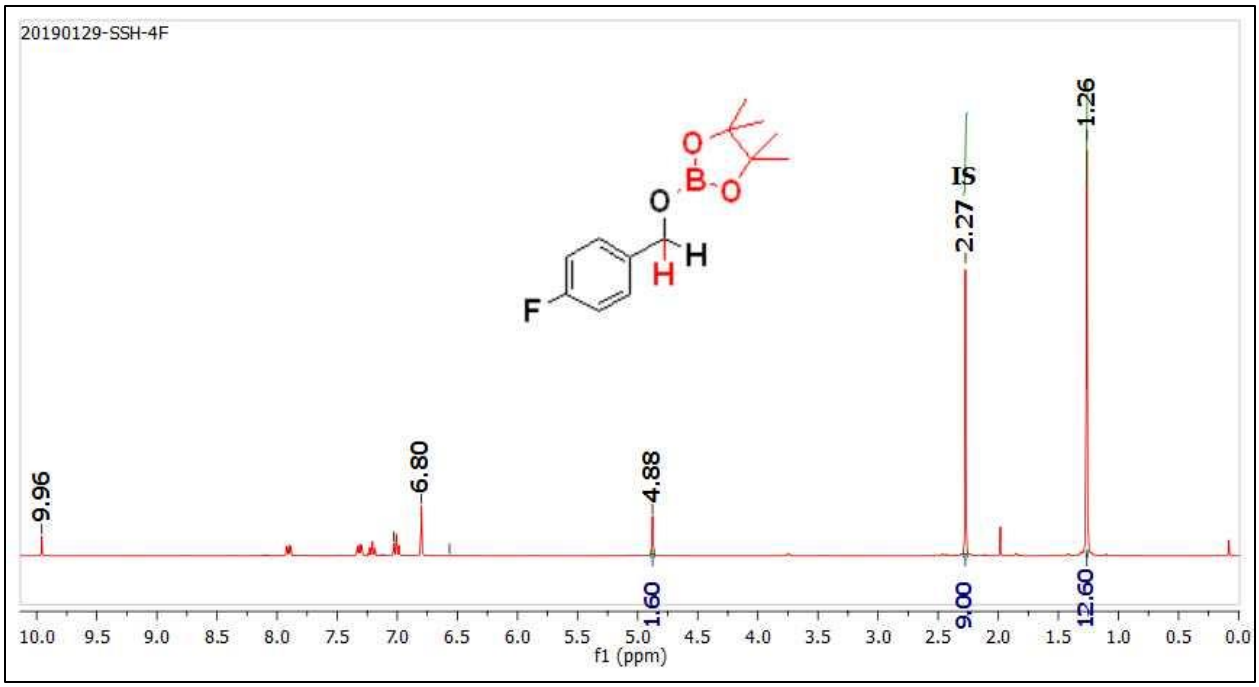


Figure 15a. ^{1}H NMR spectrum of [4a]. [Solvent: $CDCl_3$, IS: Mesitylene]

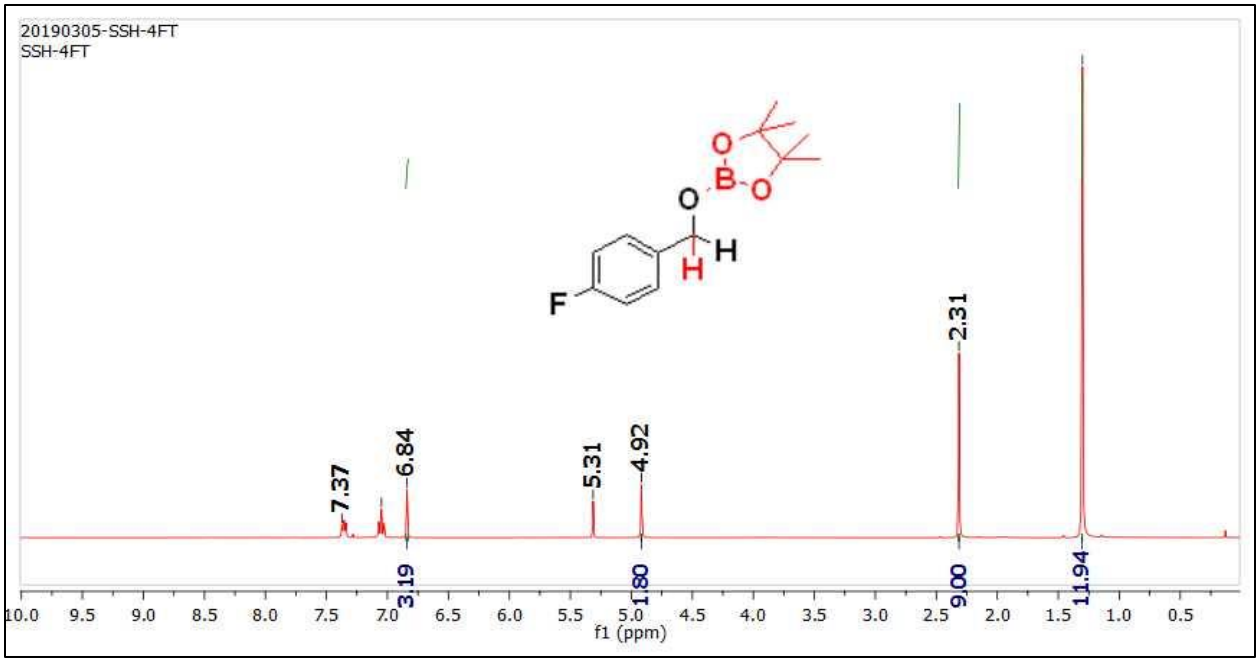


Figure 15b. ^{1}H NMR spectrum of [4b]. [Solvent: $CDCl_3$, IS: Mesitylene]

5. 4CN-PhCH$_2$OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.4-7.52 (*m*, 5H, *Ph*), 4.97 (*s*, 2H, OCH_2), 1.26 (*s*, 12H, Bpin-CH_3), IS: 6.8 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.26 (*s*, 9H, $(CH_3)_3$).

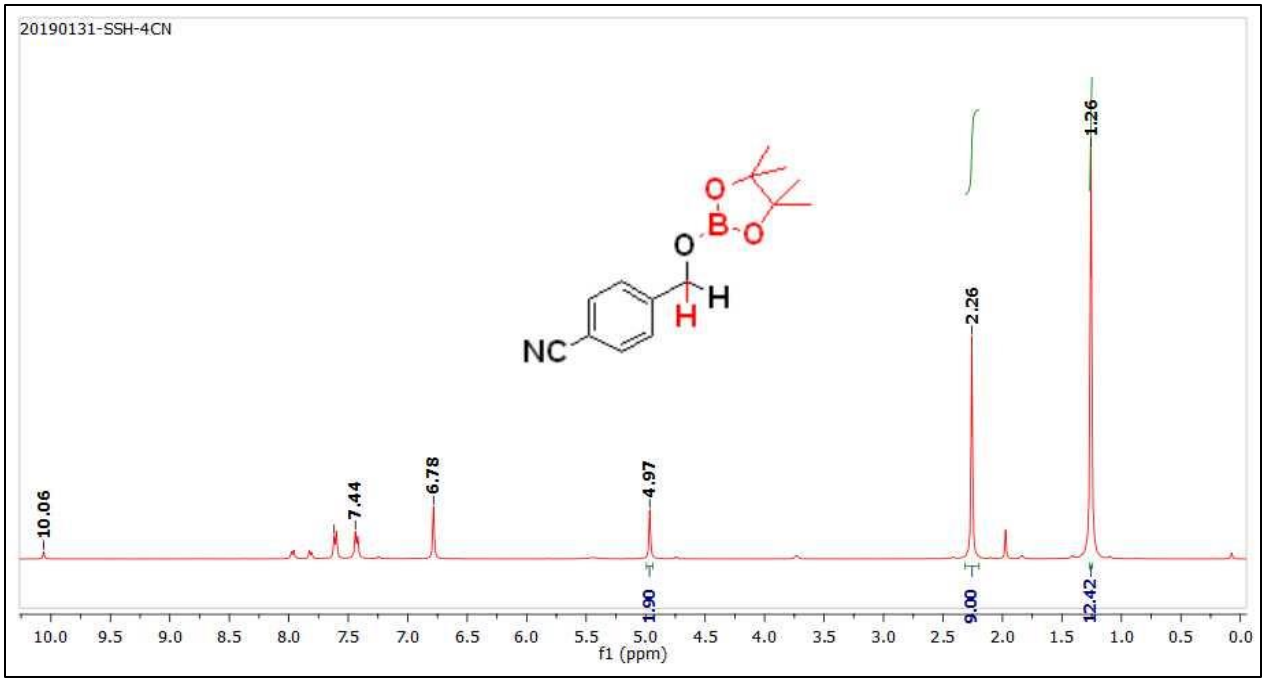


Figure 16a. ^{1}H NMR spectrum of [5a]. [Solvent: $CDCl_3$, IS: Mesitylene]

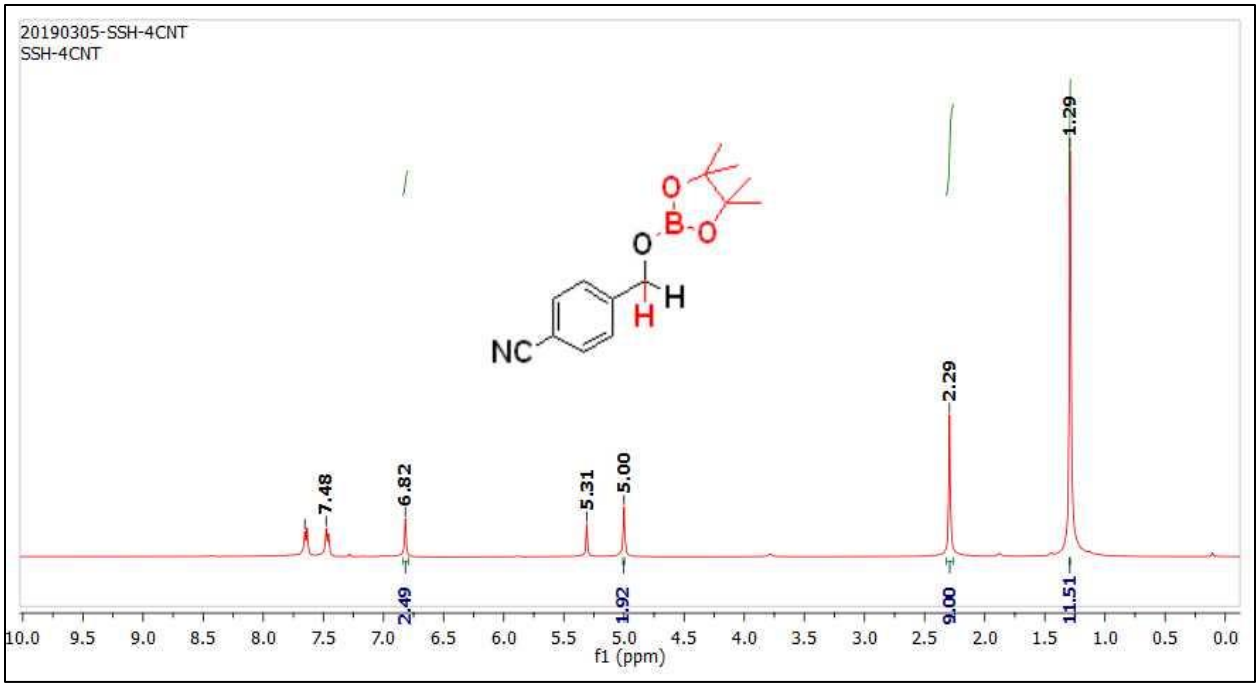


Figure 16b. ^{1}H NMR spectrum of [5b]. [Solvent: $CDCl_3$, IS: Mesitylene]

6. 4-NO_2PhCH_2OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.4-8.06 (*m*, 5H, *Ph*), 5.01 (*s*, 2H, OCH_2), 1.26 (*s*, 12H, Bpin-CH_3), IS: 6.7 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.25 (*s*, 9H, $(CH_3)_3$).

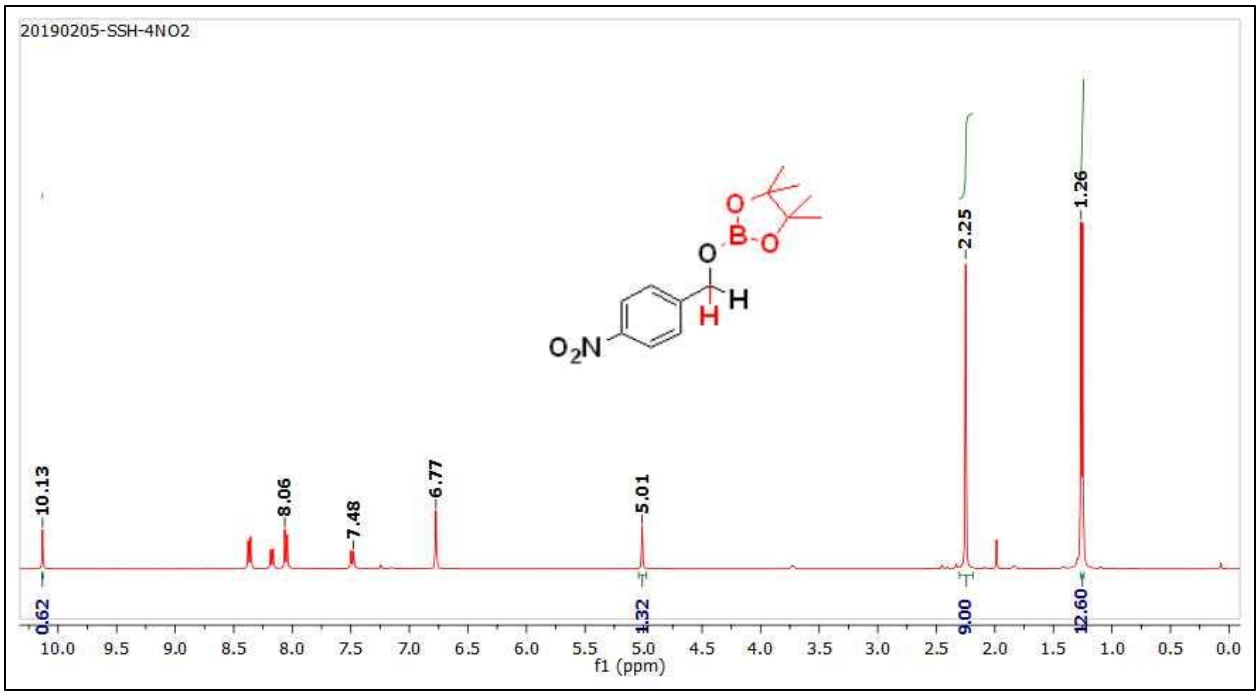


Figure 17a. ^{1}H NMR spectrum of [6a]. [Solvent: $CDCl_3$, IS: Mesitylene]

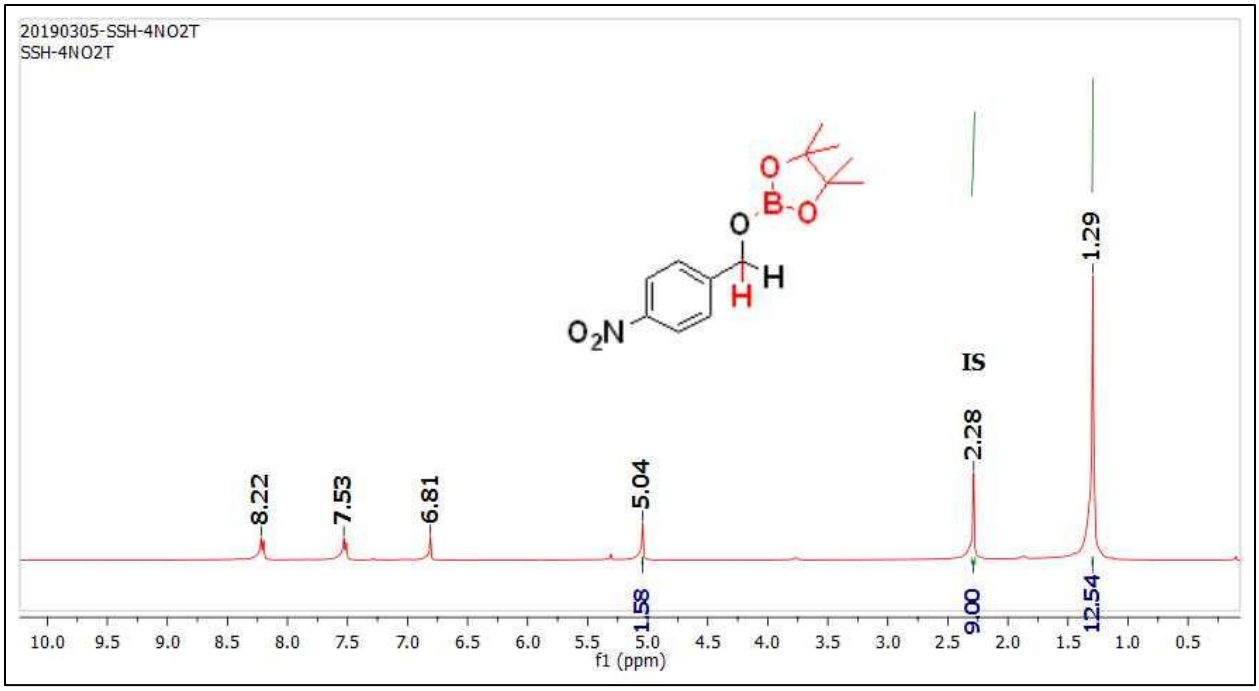


Figure 17b. ^{1}H NMR spectrum of [6b]. [Solvent: $CDCl_3$, IS: Mesitylene]

7. 4-CH_3PhCH_2OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.2-7.5 (*m*, 5H, *Ph*), 4.90 (*s*, 2H, OCH_2), 2.34 (*s*, 3H, $PhCH_3$), 1.27 (*s*, 12H, Bpin-CH_3), IS: 6.8 (*s*, 3H, $C_6H_3(CH_3)_3$), 2.29 (*s*, 9H, $(CH_3)_3$).

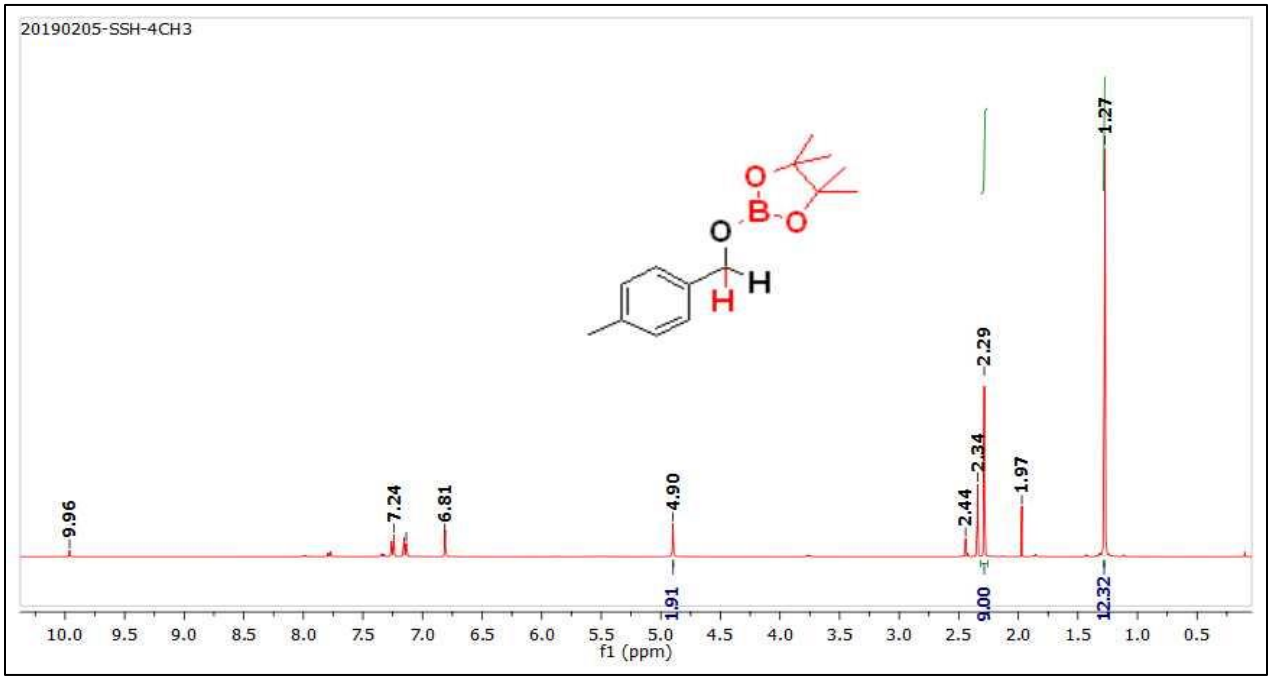


Figure 18a. ^{1}H NMR spectrum of [7a]. [Solvent: $CDCl_3$, IS: Mesitylene]

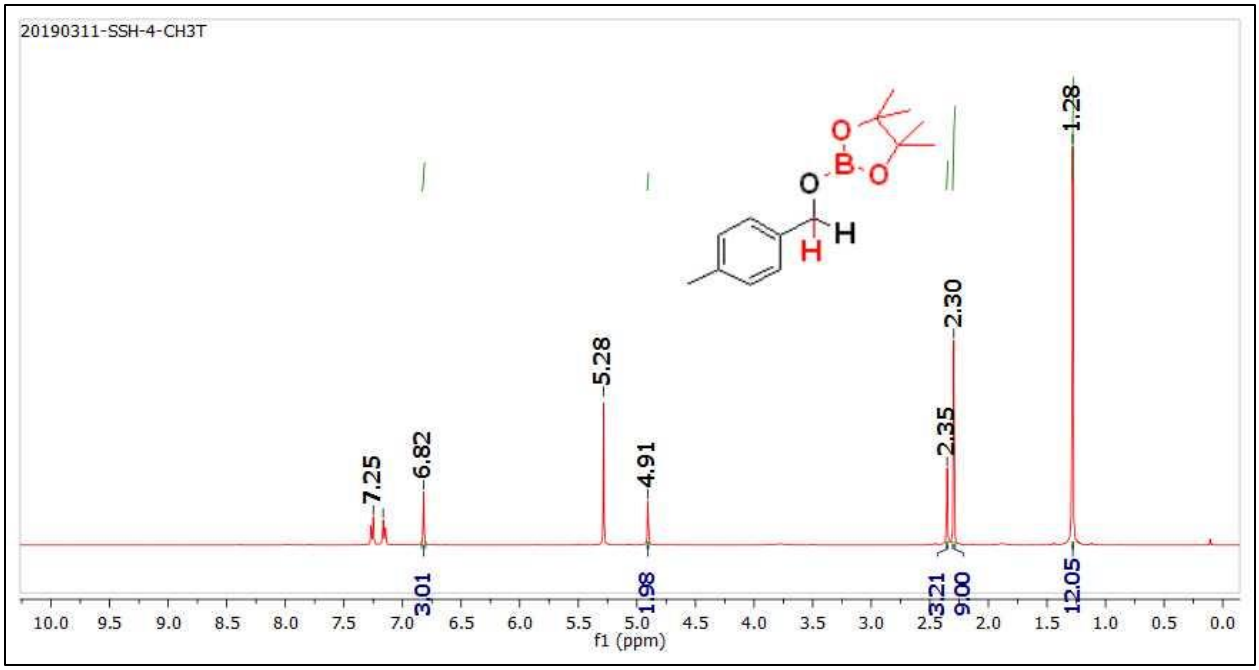


Figure 18b. ^{1}H NMR spectrum of [7b]. [Solvent: $CDCl_3$, IS: Mesitylene]

8. 3-OMePhCH$_2$OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.02-7.51(*m*, 4H, Ph), 4.91(*s*, 2H, pinBOCH$_2$), 3.85 (*s*, 3H, 3-(OCH$_3$)PhCH$_2$OBpin), 1.27 (*s*, 12H, Bpin-CH$_3$), IS: 2.27 (*s*, 9H, Ph(CH$_3$)$_3$), 6.8 (*s*, 3H C$_6$H$_3$(CH$_3$)$_3$).

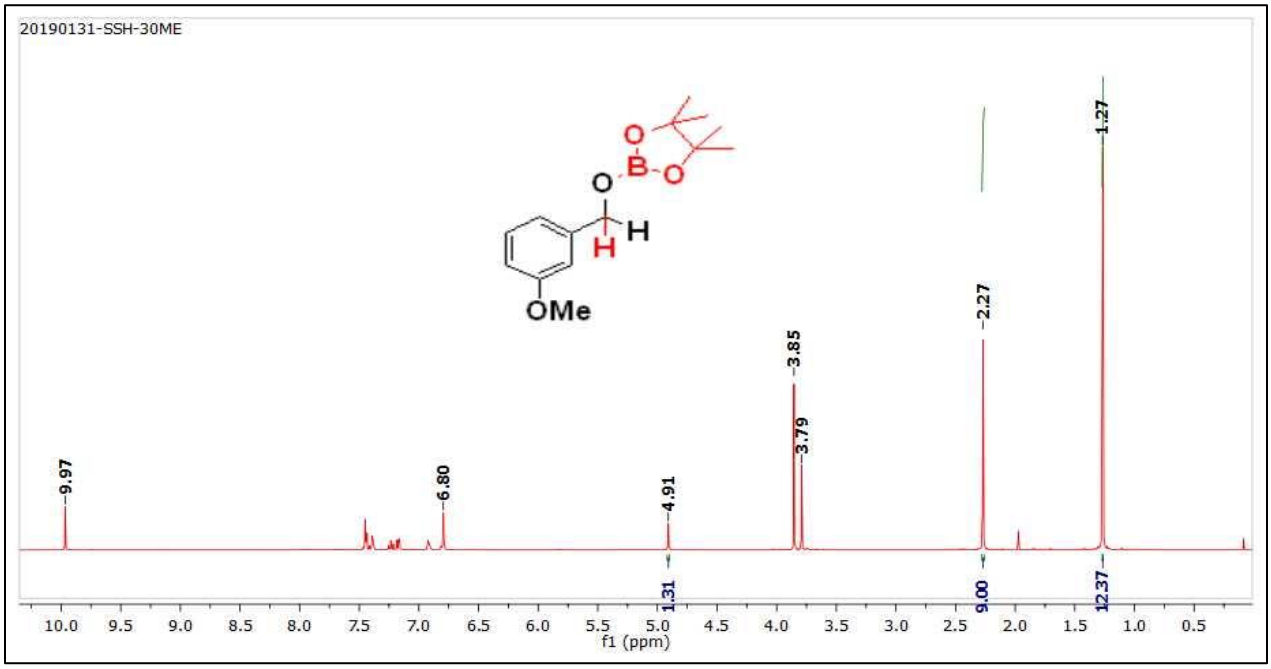


Figure 19a. ^{1}H NMR spectrum of [8a]. [Solvent: $CDCl_3$, IS: Mesitylene]

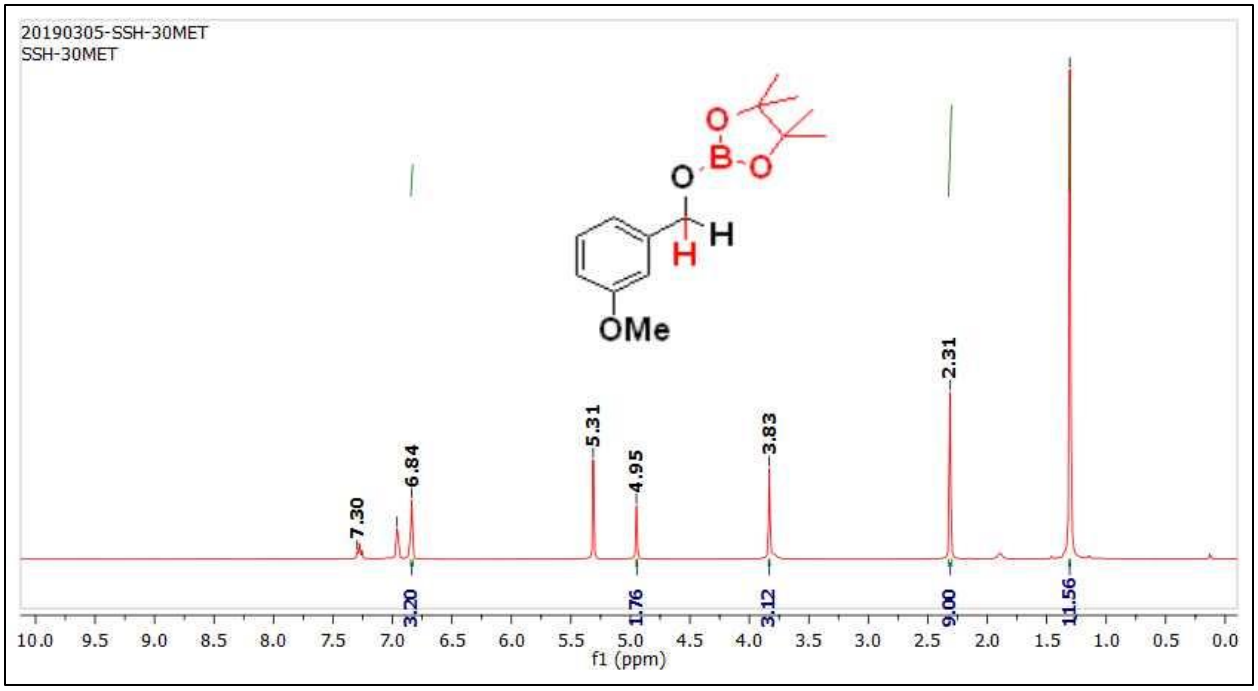


Figure 19b. ^{1}H NMR spectrum of [8b]. [Solvent: $CDCl_3$, IS: Mesitylene]

9. 2-OHPhCH_2OBpin - ^{1}H NMR (400 MHz, ppm): δ 11.03 (*s*, 1H, OH) 6.9-7.2 (*m*, 4H, Ph), 4.98 (*s*, 2H, pinBOCH_2), 1.28 (*s*, 12H, Bpin-CH_3), IS: 2.28 (*s*, 9H, Ph(CH_3)$_3$), 6.81 (*s*, 3H $C_6H_3(CH_3)_3$).

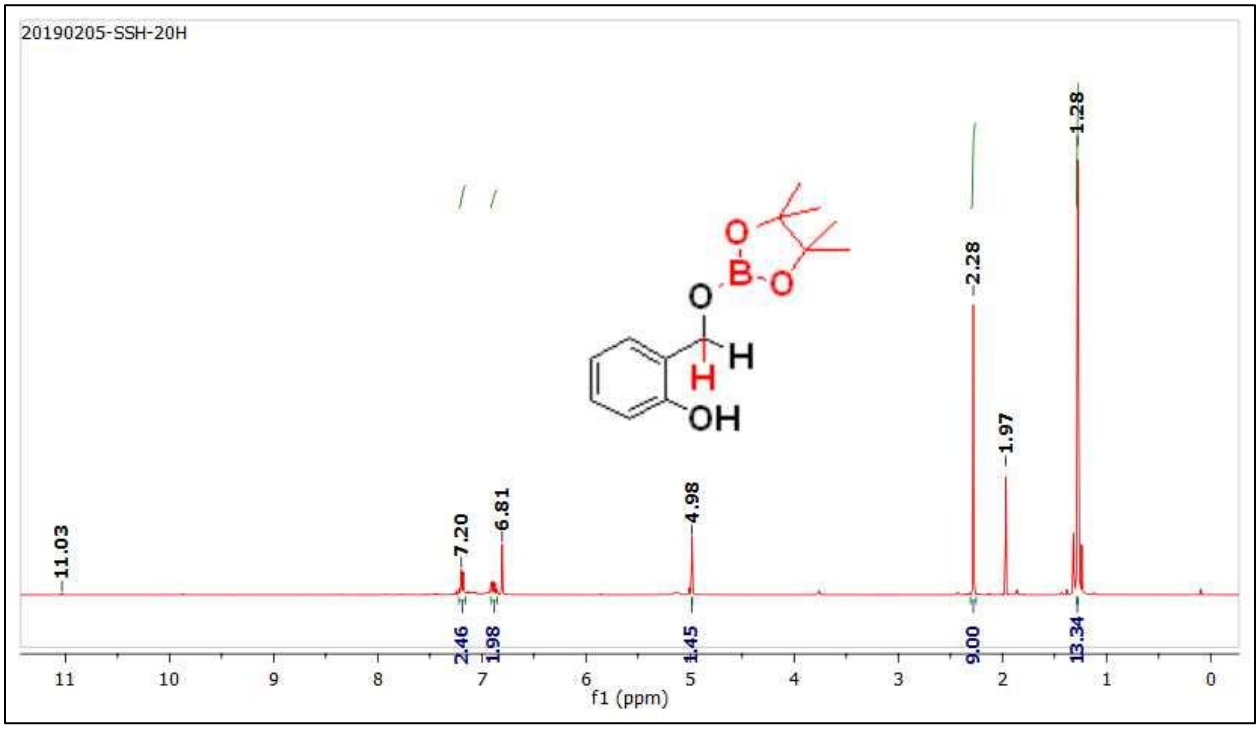


Figure 20a. ^{1}H NMR spectrum of [9a]. [Solvent: $CDCl_3$, IS: Mesitylene]

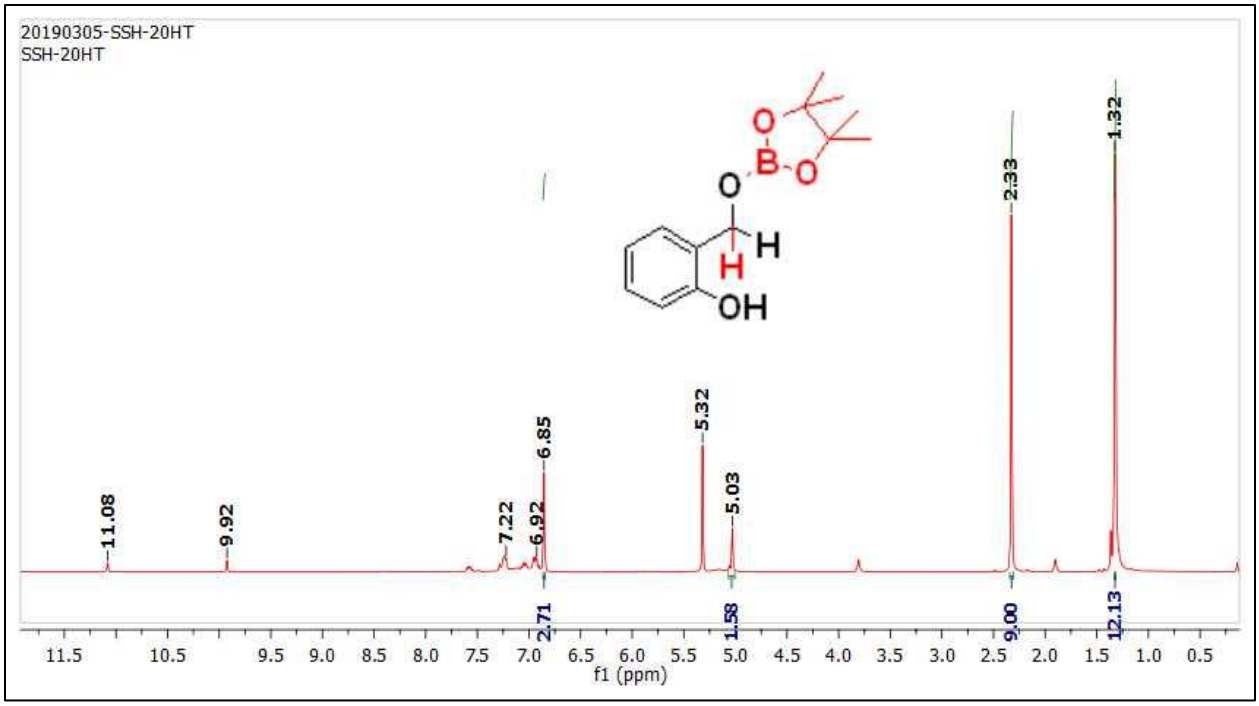


Figure 20b. ^{1}H NMR spectrum of [9b]. [Solvent: $CDCl_3$, IS: Mesitylene]

10. 2,6-$(CH_3)_2$PhCH$_2$OBpin - ^{1}H NMR (400 MHz, ppm): δ 7.06-7.4 (*m*, 4H, Ph), 5.04 (*s*, 2H, pinBOCH$_2$), 2.47 (*s*, 3H, 2-CH$_3$), 2.66 (*s*, 3H, 6-CH$_3$), IS: 1.32 (*s*, 12H, Bpin-CH$_3$), 2.33 (*s*, 9H, Ph(CH$_3$)$_3$), 6.85 (*s*, 3H C$_6$H$_3$(CH$_3$)$_3$).

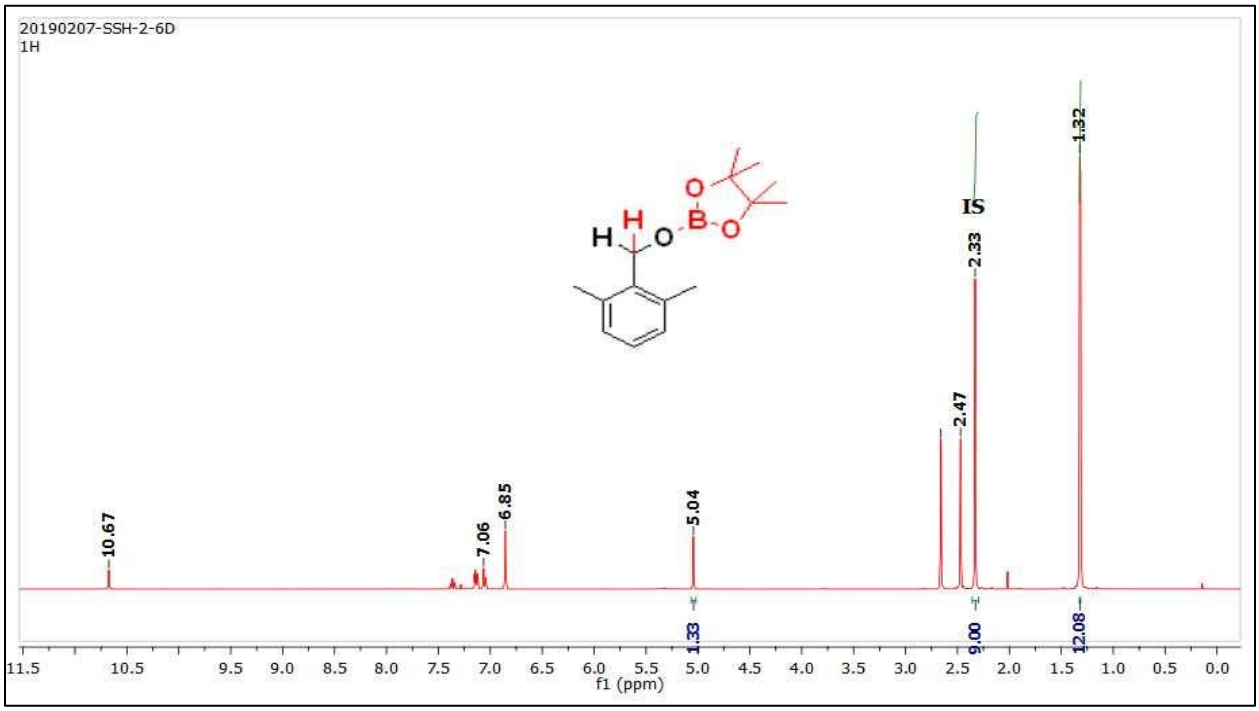


Figure 21a. ^{1}H NMR spectrum of [10a]. [Solvent: $CDCl_3$, IS: Mesitylene]

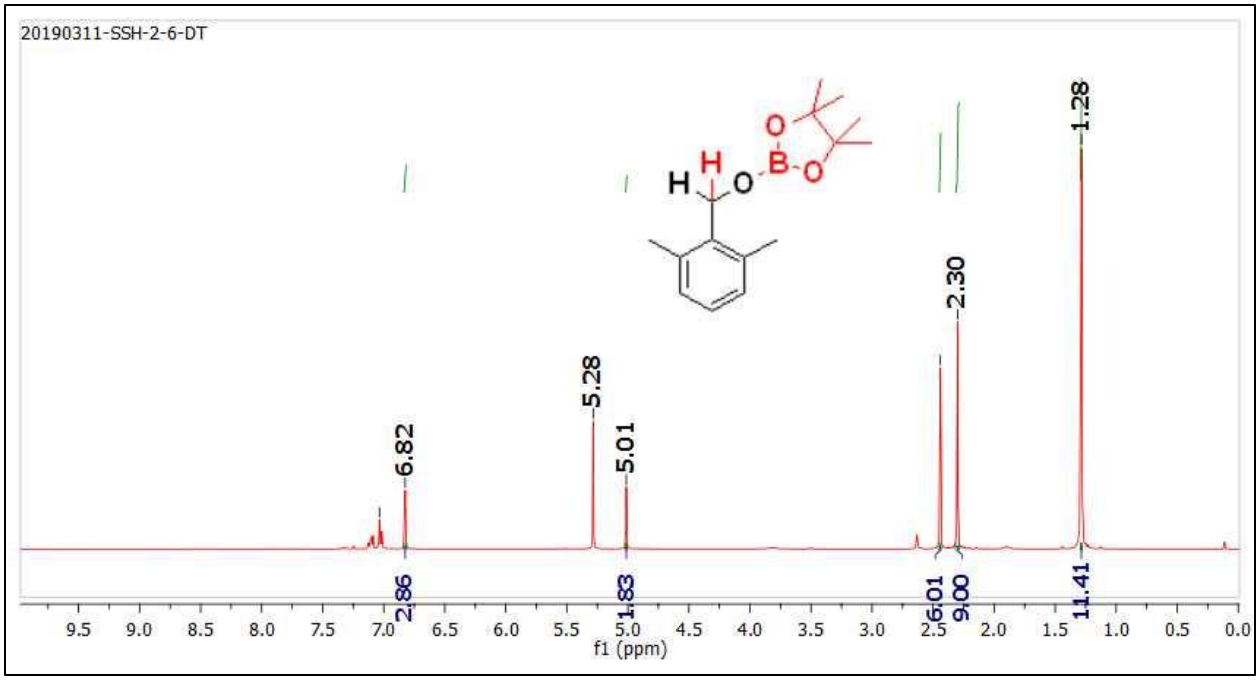


Figure 21b. ^{1}H NMR spectrum of [10b]. [Solvent: $CDCl_3$, IS: Mesitylene]

11.α-$C_{10}H_7CH_2$-OBpin- ^{1}H NMR (400 MHz, ppm): δ 7.5-8.1 (*m*, 7H, Ph), 5.48 (*s*, 2H, pinBOCH_2), 1.34 (*s*, 12H, Bpin-CH_3), IS: 2.34 (*s*, 9H, Ph$(CH_3)_3$), 6.86 (*s*, 3H $C_6H_3(CH_3)_3$).

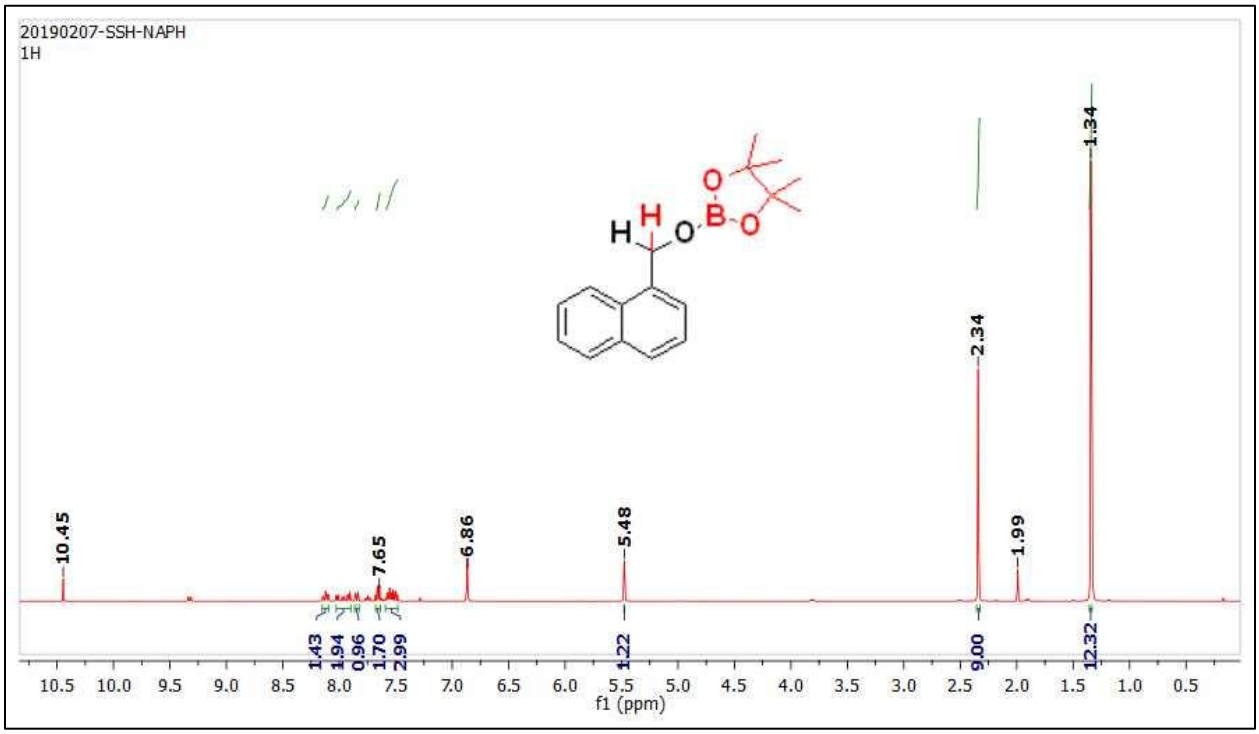


Figure 22a. ^{1}H NMR spectrum of [11a]. [Solvent: $CDCl_3$, IS: Mesitylene]

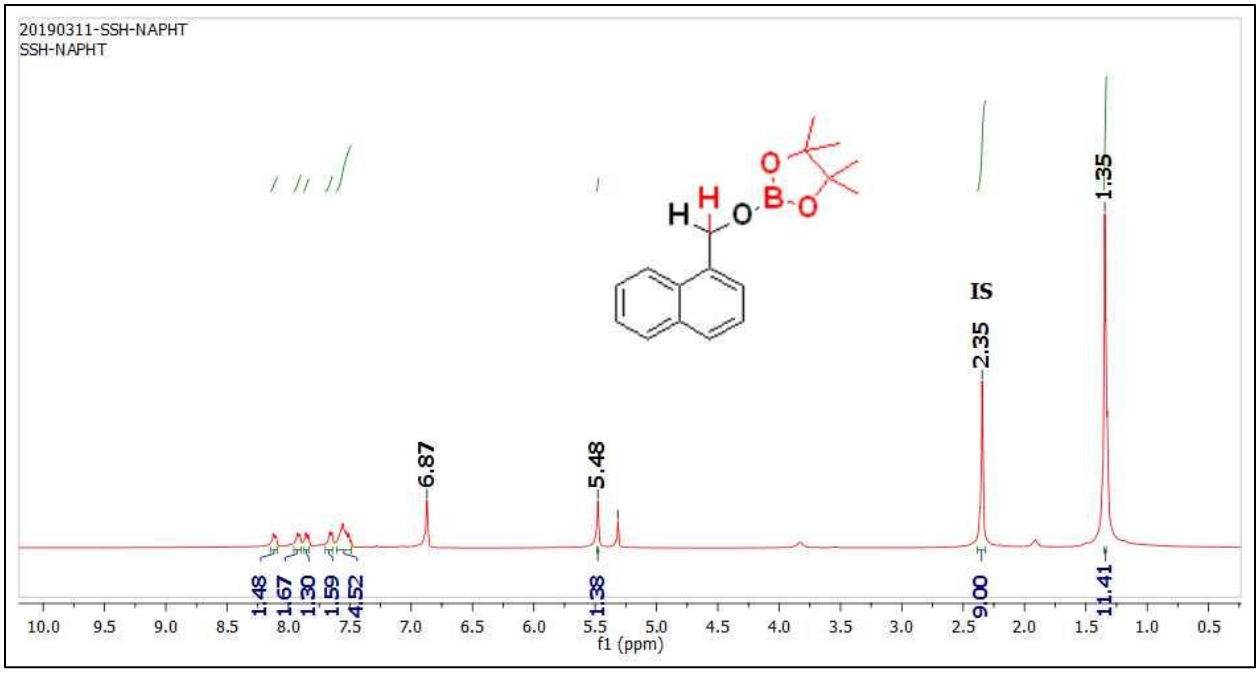


Figure 22b. ^{1}H NMR spectrum of [11b]. [Solvent: $CDCl_3$, IS: Mesitylene]

12. Ph-C3H4OBpin – ^{1}H NMR (400 MHz, ppm): δ 7.32-7.53 (*m*, 5H, Ph), 6.34-6.39 (*dd*, 1H, $PhCHCHCH_2OBpin$), 6.69-6.77 (*m*, 1H, $PhCHCHCH_2OBpin$), 4.62 (*s*, 2H, $pinBOCH_2$), 1.31 (*s*, 12H, Bpin-CH_3) 2.30 (*s*, 9H, $Ph(CH_3)_3$), 6.83 (*s*, 3H $C_6H_3(CH_3)_3$)

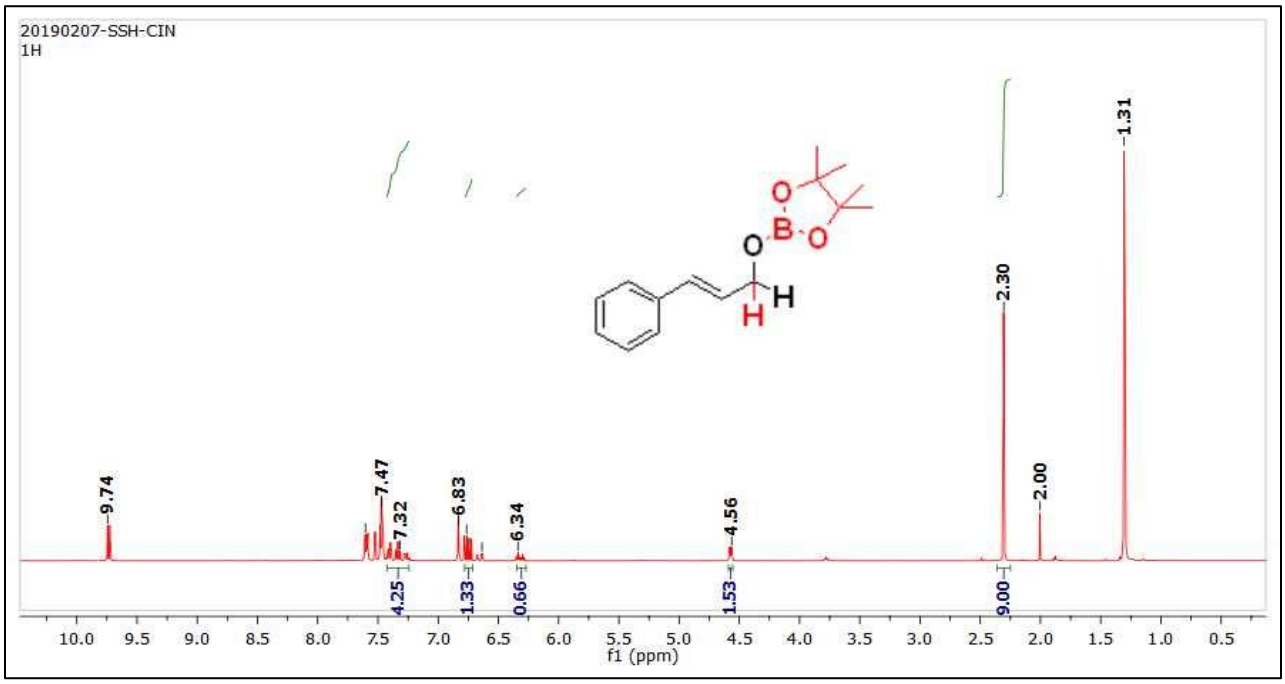


Figure 23a. ^{1}H NMR spectrum of [12a]. [Solvent: $CDCl_3$, IS: Mesitylene]

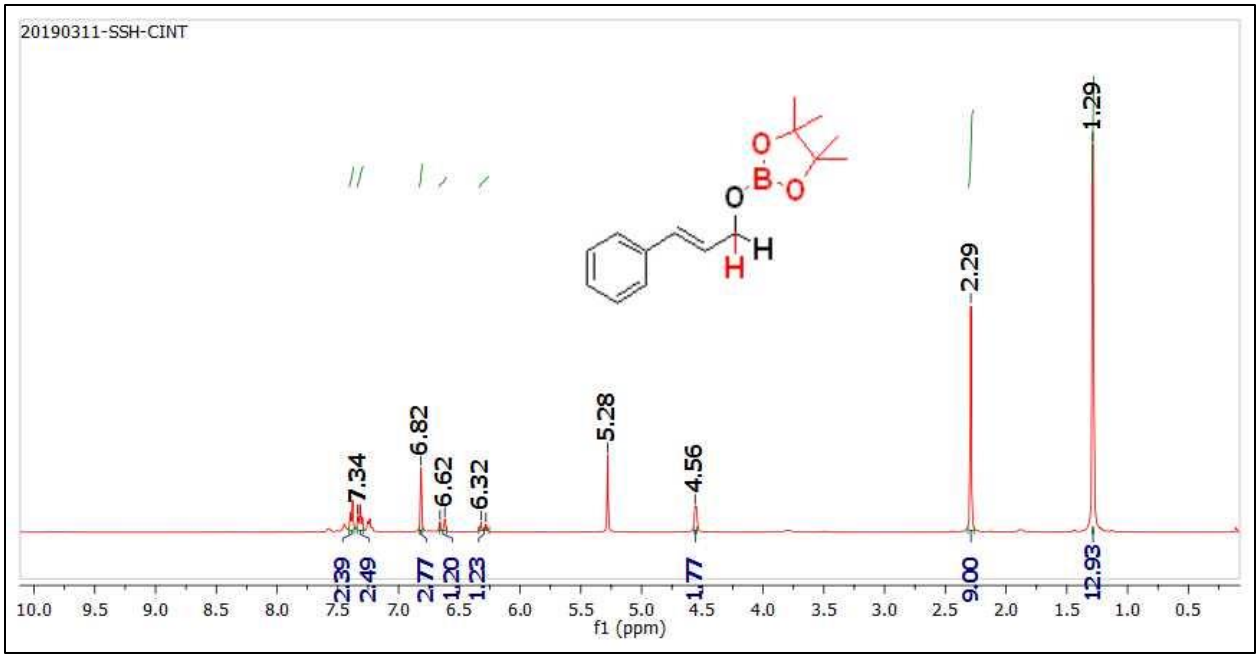


Figure 23b. ^{1}H NMR spectrum of [12b]. [Solvent: $CDCl_3$, IS: Mesitylene]

13. $C_4H_3OCH_2OBpin$ – ^{1}H NMR (400 MHz, ppm): δ 6.36-7.29 (*m*, 3H, CH(heterocycle), 4.86 (*s*, 2H, $pinBOCH_2$), 1.30 (*s*, 12H, Bpin-CH_3) 2.33 (*s*, 9H, $Ph(CH_3)_3$), 6.84 (*s*, 3H $C_6H_3(CH_3)_3$).

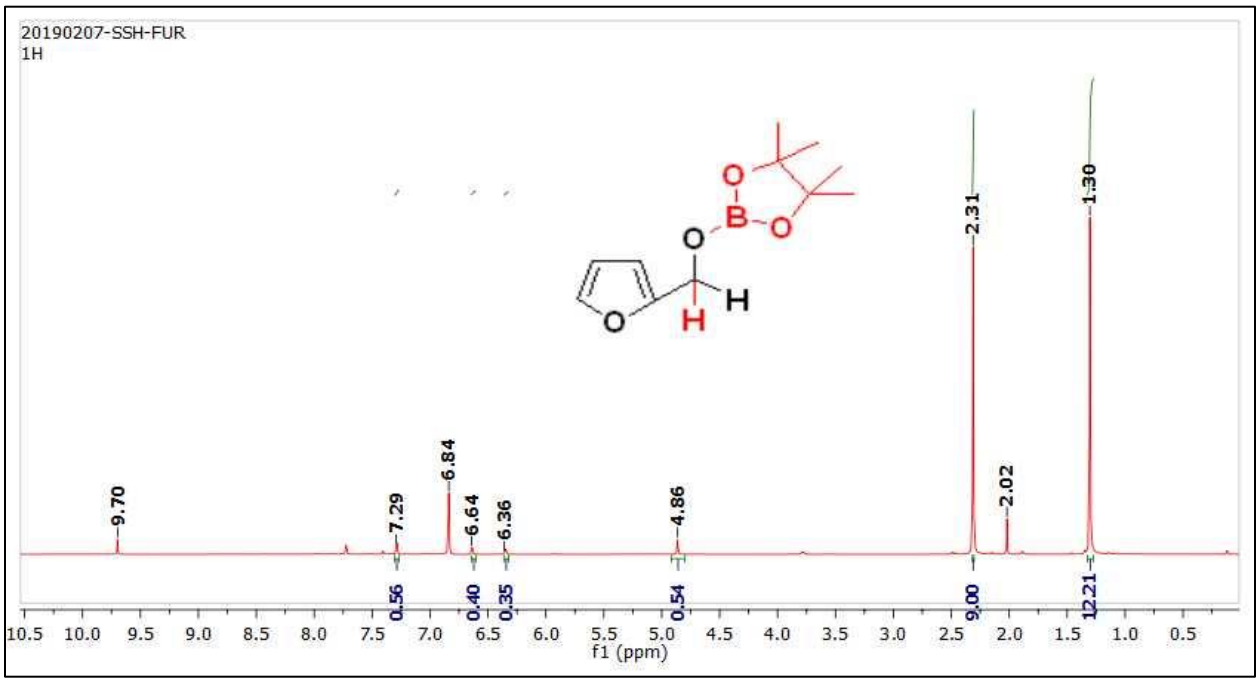


Figure 24a. ^{1}H NMR spectrum of [13a]. [Solvent: $CDCl_3$, IS: Mesitylene]

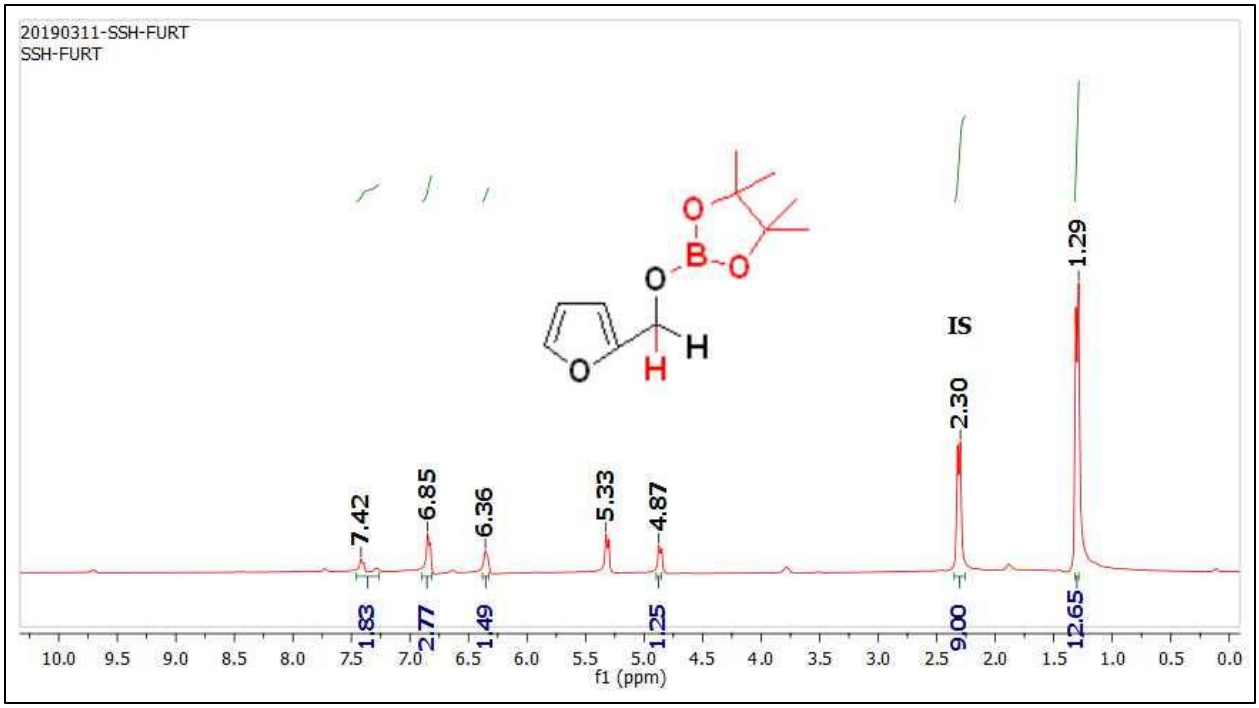


Figure 24b. ^{1}H NMR spectrum of [13b]. [Solvent: $CDCl_3$, IS: Mesitylene]

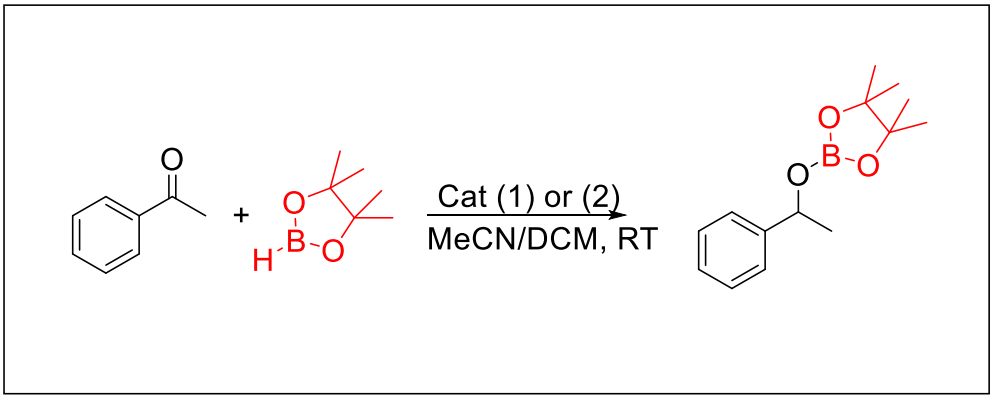
Conclusion

Herein, we have successfully synthesized NHC-supported Iron(II) complexes by trans-metalation pathway. Both the complexes were fully characterized by NMR spectroscopic and mass spectrometric methods. To further confirm the structural features, X-ray structure analysis of both the complexes was carried out. Complex (**1**) has distorted octahedral geometry, bearing two acetonitrile moieties and bischelating NHC backbone whereas, complex (**2**) is square planar having four coordination from ligand backbone. Both the complexes show good catalytic activity for hydroboration of aldehydes. However, complex (**2**) was found to be much more efficient than complex (**1**), owing to its vacant sites. A variety of substrates were found to be converted to their corresponding borate ester derivatives. Further mechanistic investigations to provide a mechanism of catalysis are under way in our laboratory.

Future plans

1. We will be investigating mechanistic pathway of reaction and would try to isolate the reactive intermediate. Also, to gain mechanistic understanding of this efficient iron(II) catalysts we will be doing theoretical and kinetics studies.

2. As we have successfully carried out the hydroboration of aldehydes using both the Fe(II)-NHC complexes, our next motive is to perform hydroboration of ketones.



Scheme 9. Schematic representation of hydroboration of ketones

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