Bis-NHC-based Manganese(I) complex catalyzed amide and CO_2 hydroboration

A Thesis

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by

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Certificate

This is to certify that this thesis entitled **Bis-NHC-based Manganese(I) complex catalyzed amide and CO_2 hydroboration**, towards the partial fulfillment of the MSc. degree program at the Indian Institute of Science Education and Research, Pune, represents research work carried out by **Prabhakar Tiwari (20226215)** at the Indian Institute of Science Education and Research under the supervision of **Dr. Shabana Khan**, Department of Chemistry, during the academic year 2023 - 2024.

Shabana Khan

Dr. Shabana Khan

Committee:

Dr. Shabana Khan

Dr. R Boomi Shankar

Dedicated to **Family** and **Friends**

Declaration

I hereby declare that the matter embodied in the report entitled **Bis-NHC based Manganese(I) complex catalyzed amide and CO_2 hydroboration** 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.

Prabhakar Tiwari

Prabhakar Tiwari

12-04-2024

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Acknowledgments:

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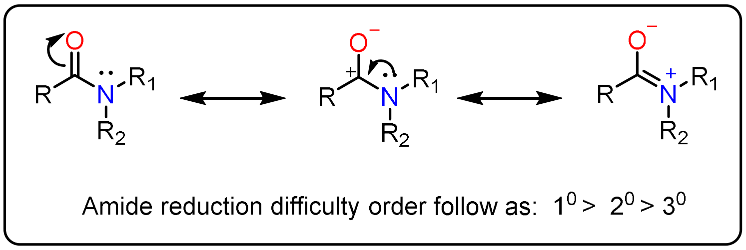
1. Abstract:

The reductive modification of the C=O moiety in cyclic/acyclic amides, and even involving carbon dioxide, determines a formidable challenge but holds crucial significance for synthesizing value-added chemicals. This process harbors the potential to unveil new avenues for utilizing non-fossil feedstocks. Earth-abundant, environment-friendly, and cost-effective metal catalysts could play a crucial role in driving the advancement of sustainable synthetic processes grounded on this principle. Manganese bis-(NHC) complexes' activity in the reducing challenging carbonyl (C=O) group and carbon dioxide (CO_2) has been attributed to the strong σ-donating and weak π-accepting properties of the bis-(NHC) carbene. Herein, we have employed the bis-NHC-based manganese complexes as effective catalysts for the hydroboration of both primary and secondary amides, which are quite difficult to reduce due to better resonance within the amide system and obtained moderate to excellent yield. Additionally, we employed these complexes to reduce carbon dioxide (CO_2) under solvent-free conditions, yielding moderate yields.

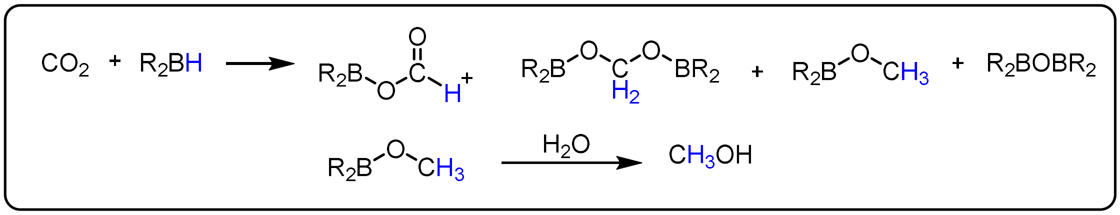
2. Introduction

The intrinsic low reactivity of the carbonyl (C=O) bond in amides renders the reduction of amides to amines a challenging organic transformation. (**Scheme 1**). Numerous methods exist to synthesize amines; however, many of these methods are often associated with complexities or limitations in their synthesis protocols.[1,2] Reducing carbon dioxide (CO_2) to methoxyborane is an economical step due to the formation of methanol (MeOH) (**Scheme 2**). As we all know, Carbon dioxide (CO_2) stands as a prominent greenhouse gas, raising environmental concerns due to its escalating atmospheric concentration driven by the expanding use of fossil fuels. However, the unique characteristics of carbon dioxide (CO_2), such as its cost-effectiveness, non-toxicity, non-flammability, and abundant availability as a suitable precursor to many important catalytic transformations, make it tempting for chemists to concentrate on developing C1-products from sustainable sources.[3] The carbonyl (C=O) group catalytic reduction present in carboxylic acids (RCO_2H), amides (RCO_2NH_2) and their derivatives, and even carbon dioxide (CO_2) is currently a topic of significant interest for advancing sustainable chemical processes. These processes have the potential to open up a large number of new synthetic routes by altering functional groups, particularly in the realms of fine chemicals, agrochemicals, and pharmaceutical synthesis. This alignment with the principles of Green Chemistry signifies their environmentally friendly impact. [4-6] These transformations hold significant importance in utilizing alternative feedstocks derived from carbon dioxide[7-10] or biomass.[11-13] One of the desirable outcomes of carbon dioxide reduction is the production of methanol (MeOH), which boasts an annual worldwide[14] production exceeding ninety-five million metric tons. Methanol serves various purposes, such as a fuel additive, bulk chemical, and solvent. Additionally, it can function as an energy carrier, achieved through either reforming or catalytic dehydrogenation to generate hydrogen on demand. In this context, first-row transition metal complexes are increasingly receiving attention as suitable catalysts for a large number of reduction reactions within this framework.[15-26]



Scheme 1: Amide stabilization via resonance (R_1 and R_2: H, alkyl or aryl)

Transition metal-based molecular complexes are commonly utilized for CO_2 reduction and for systematic exploration of reaction mechanisms owing to their abundant structural and electronic adaptability. Typically, in the initial stage of CO_2 hydroboration, a hydride gets transferred to the carbon atom of CO_2. Various catalysts, including metal hydride complexes, can facilitate this process, including ambiphilic compounds, strong Lewis bases, or hydroborate compounds.[27,28] Previous studies have illustrated instances of transition metal hydride complexes enabling selective CO_2 hydroboration to yield methoxyboranes.



Scheme 2: Full Range of Expected Products in CO_2 Hydroboration

In 2010, Guan and collaborators reported the first POCOP pincer-type ligand [POCOP = 2,6-$(tBu_2PO)_2C_6H_3$] co-ordinated Ni hydrido complex. This complex demonstrated catalytic activity in the hydroboration of CO_2 with HBcat (catecholborane), resulting in the formation of CH_3OBcat [CH_3OBcat = methoxycatecholborane] with a TON of 495.[29] In 2012, Sgro and Stephan applied a Ru hydrido complex accompanying the properties of frustrated-Lewis pair (FLP) and featuring the ligand backbone $N[(CH_2)_2NHP^iPr_2)(CH_2)_2NP^iPr_2)(CHCH_2NHP^iPr_2)]$ as a catalyst in this reaction, employing HBpin (pinacolborane). This led to the formation of CH_3OBpin [CH_3OBpin = methoxypinacolborane] and $O(Bpin)_2$. They achieved an average Turnover Number (TON) of 9.[30]

During the same year, Sabo-Etienne, Bontemps, and their team introduced $[Ru(H)_2(H_2)_2(PCy_3)_2]$ as a catalyst in conjunction with HBpin in deuterated benzene

(C_6D_6). They successfully produced CH_3OBpin with a yield of 39%.[31] After that, many rare metal complexes and earth-crust abundant metal complexes were utilized as efficient catalysts for the selective hydroboration of carbon dioxide to methoxyboranes (**Chart 1**).[27-36]

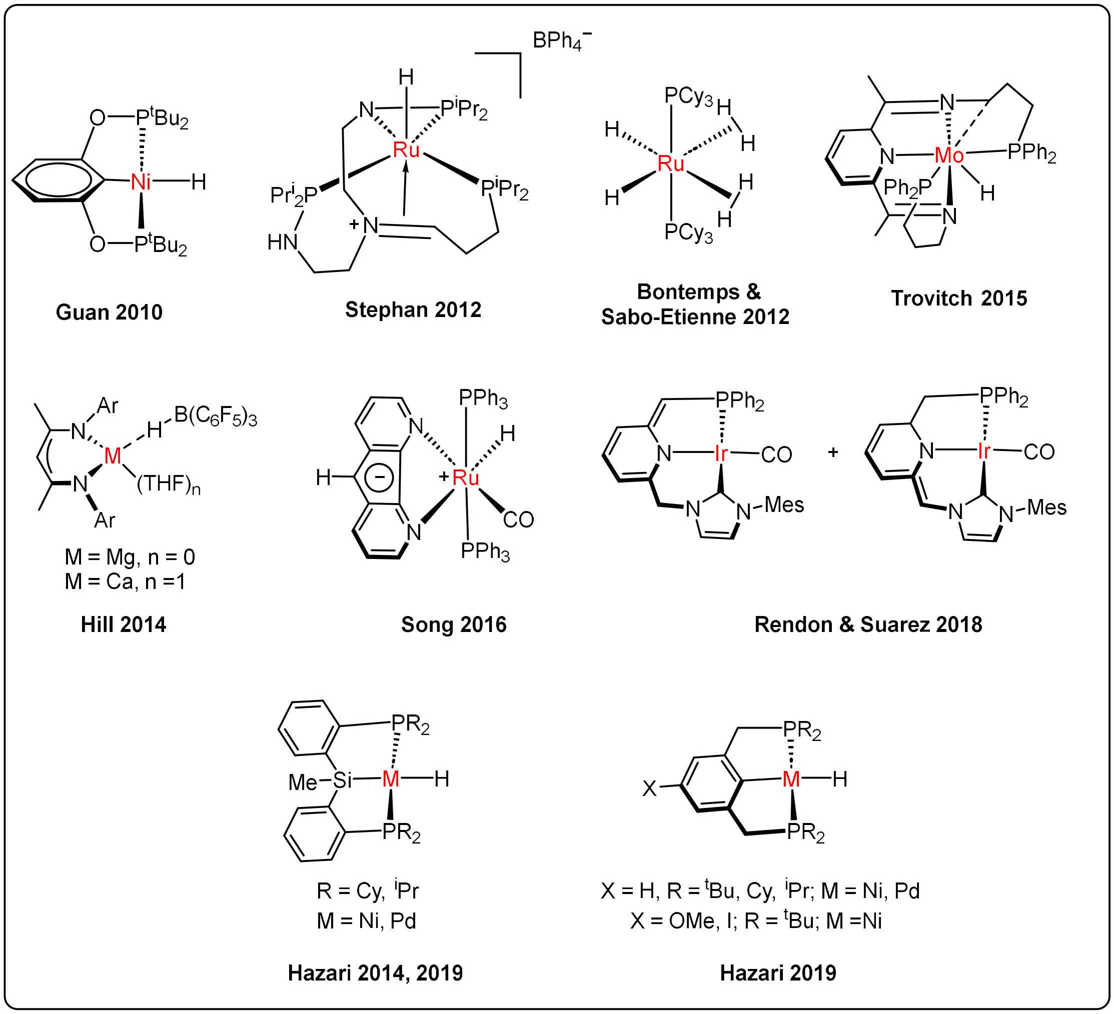


Chart 1: Examples of distinct metal complexes having various types of ligand backbone for the selective conversion of CO_2 to methoxyborane through hydroboration

Historically, a lot of metal complexes of the platinum group have already been utilized as catalysts for carbon dioxide hydroboration.[37,38] However, over the past decade, a sector of the chemistry community has redirected its efforts towards exploring more economical catalysts derived from earth-abundant metals to improve process sustainability. Significant success was observed in CO_2 hydroboration reactions catalyzed by $[Fe(H_2)(dmpe)]$ (dmpe = 1,2-bis(dimethylphosphine)ethane)[39a], alongside iron and copper catalysts[39b] incorporating phosphine and phosphinite based ligands as $PhSi\{CH_2PPh_2\}_3$ and $PhSi\{OPPh_2\}_3$, as documented. Manganese, ranked as the third Earth’s crust's most abundant metal, has attracted considerable interest in homogeneous catalysis, particularly in CO_2 reduction processes.[40] To our knowledge, there are relatively few reports available detailing Mn(I) complexes as efficient catalysts for CO2 hydroboration (**Chart 2**).

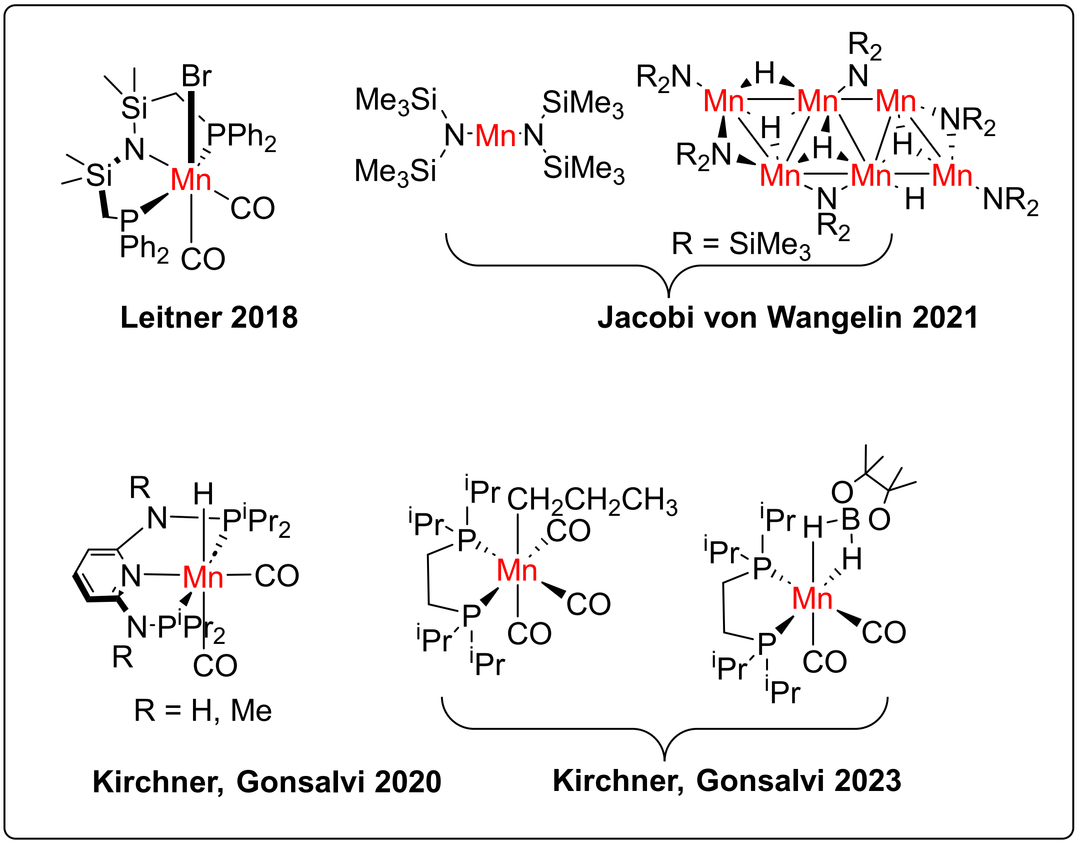


Chart 2: Hydroboration of CO_2 using Mn(I) complexes as efficient catalysts

In 2018, Leitner and colleagues presented the inaugural instance of such utilization. Employing the manganese-based complex $[MnBr\{(Ph_2PCH_2SiMe_2)_2NH\}(CO)_2]$, they achieved the selective formation of methoxyborane with a high TON of 883 using HBpin with very little catalyst loading (0.036 mol%), and additive (NaO^tBu) Under neat conditions at a moderate temperature of 100°C.[41] They have also employed this manganese base catalyst to hydroborate other challenging substrates that contain the carbonyl (C=O) group. The reaction mechanism was subsequently investigated by other authors through Density Functional Theory (DFT) calculations.[42] In 2020, Kirchner and Gonsalvi reported the catalytic reduction of CO_2 to methoxyboranes using well-characterized manganese complex [MnH(PNP^{NR}-^{i}Pr)(CO)$_2$] (where R = H or Me). They employed HBpin and 9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonane) along with borates as Lewis acid additives. High yields of CH_3OBpin (up to 78%) were attained within 24 hours under relatively gentle reaction parameters in THF-d_8. As a co-catalyst, Lewis acid additive [B(OPh)$_3$] was employed.[43] In 2021, Ghosh and Jacobi von Wangelin detailed the hydroboration of CO_2 at around 1 bar and 80°C, obtaining complete selectivity towards methoxyborane with the utilization of HBpin and catalysts [Mn(hmds)$_2$] and [MnH(hmds)]$_6$ (where hmds = hexamethyldisilazane).[44] Recently, In 2023, Kirchner and Gonsalvi utilized earth-abundant transition metal catalysts, including well-explored, bench-stable Mn(I) non-pincer ligand-based complexes like alkylcarbonyl Mn(I) bis(phosphine) complexes fac-[Mn($CH_2CH_2CH_3$)(dippe)(CO)$_3$], [dippe = 1,2-bis(di isopropylphosphino)ethane], as well as [Mn(dippe)(CO)$_2${(μ-H)$_2$(Bpin)}], have been identified for the CO_2 reduction to boryl-protected methanol in the presence of HBpin. Remarkably, under mild reaction conditions without the requirement for any base or additives, quantitative yields were achieved.[45]

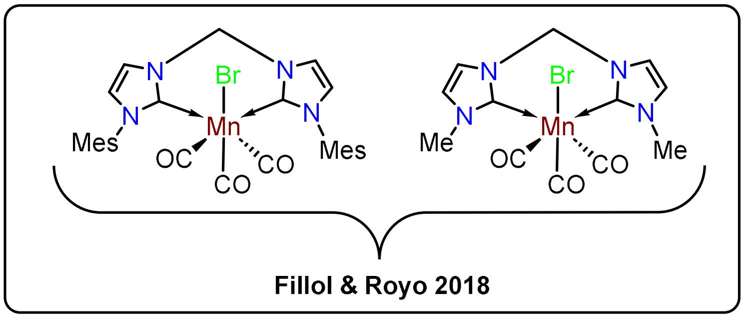


Chart 3: Bis-NHC-based manganese complexes

Herein, we have successfully employed the bis-NHC ligand-based manganese complexes as effective catalysts for the hydroboration of primary and secondary amides as well as carbon dioxide. These bis-NHC-based manganese complexes have shown promise as electrocatalysts for CO_2 reduction to CO, as employed by Fillol and co-workers in 2018 and by Duan and co-workers in 2020.[46,47] These manganese complexes are also successfully employed for the catalytic ketones reduction with silanes and catalytic N-formylation/N-methylation of amines using carbon dioxide and phenylsilane by Royo and co-workers in 2018 and 2023,[48,49] respectively (**Chart 3**).

❖ The reasons behind choosing bis-NHC carbene as a suitable ligand backbone

❖ Bis-(N-heterocyclic carbene) ligands are preferred for many metal catalysts due to several advantageous characteristics:

- **Enhanced Chelating Ability**: Bis-NHC ligands consist of two NHC units connected by a linker, providing a bidentate chelating coordination mode to the metal center. This chelating effect typically leads to increased stability of the resulting metal complexes, which can enhance catalyst activity and selectivity.
- **Rigidity and Steric Bulk**: The rigid backbone and bulky substituents of bis-NHC ligands provide a controlled steric environment around the metal center. This sterically demanding environment can influence the reactivity of the metal complex, favoring certain reaction pathways and improving selectivity in catalytic transformations.
- **Facilitated Catalyst Design**: The modular nature of bis-NHC ligands allows for facile synthesis and tuning of their properties. Modifications of the NHC backbone, linker nature, and substituents on the NHC units allow for precise adjustment of the ligand's electronic and steric characteristics, thus optimizing catalyst performance for specific reactions.
- **Increased Catalyst Stability**: The chelating bis-NHC ligands often lead to more stable metal complexes, improving catalyst longevity and enabling catalysis under harsh reaction conditions. This enhanced stability can result in higher turnover numbers and better overall catalytic performance.
- **Diverse Metal Coordination**: Bis-NHC ligands have been successfully employed with a wide range of metal centers across the periodic table, including metals of transition and main group. This versatility enables their application in various catalytic reactions, ranging from cross-coupling reactions to hydrogenation and beyond.
- **Broad Synthetic Utility**: Bis-NHC ligands have found widespread use in numerous catalytic transformations, including organic synthesis, polymerization, and organometallic chemistry. Their robustness,

tunability, and ability to stabilize reactive intermediates make them valuable tools for synthetic chemists.

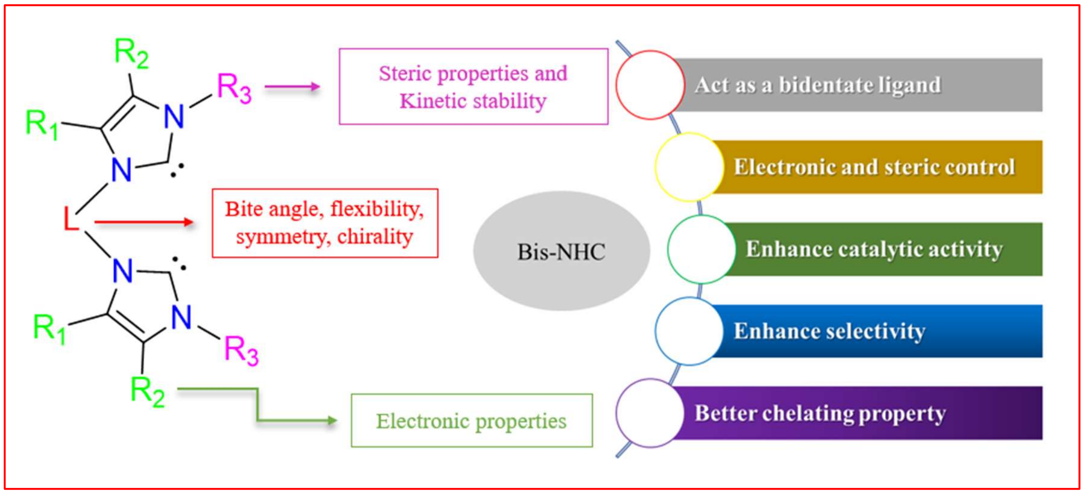
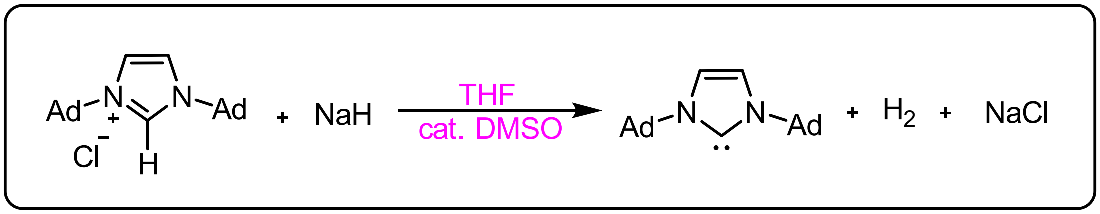


Chart 4: An overview of bis(N-heterocyclic carbene)

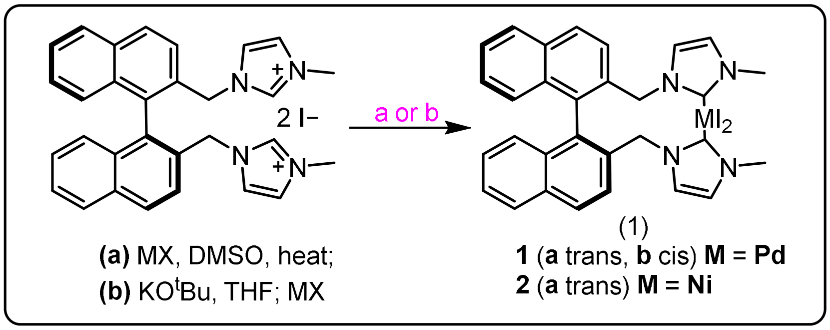
The collective attributes of enhanced chelating capability, rigidity, steric bulk, streamlined catalyst design, heightened stability, versatile metal coordination, and extensive synthetic applicability render bis-NHC ligands exceptionally well-suited for numerous metal catalysts across a diverse array of catalytic processes (**Chart 4**).

In 1991, Arduengo and collaborators first isolated *N*-heterocyclic carbene with extraordinary stability:[50]



Scheme 3: Synthesis of the first storable active NHC

In 2000, RajanBabu and collaborators synthesized the first chelated chiral *N*-heterocyclic bis-carbene complex:[51]



(a) MX, DMSO, heat;
(b) KO^{t}Bu, THF; MX

1 (**a** trans, **b** cis) **M** = **Pd**
2 (**a** trans) **M** = **Ni**

Scheme 4: Synthesis of the first chelated chiral bis-NHC complex

3. Motivation:

Acknowledging the distinctive electronic characteristics of bis-NHC carbene following the concise overview of *N*-heterocyclic carbene-based metal complexes, this project aims to explore the utility of bis-NHC-based manganese(I) complexes in metal-mediated catalysis targeting hydroboration of challenging carbonyl (C=O) groups and even carbon dioxide (CO_2).

The motivation behind borylation reaction catalysis lies in its potential to provide efficient access to a broad range of valuable boron-containing compounds, thereby driving innovation in various scientific and industrial applications like the development of new drugs, agrochemicals, materials, and other functional molecules.

The objectives of this project:

Borylation of carbonyl (C=O) containing challenging group and Carbon dioxide (CO_2) by bis-NHC-based manganese complex as an efficient catalyst

4. Materials and Methods:

4.1 Common Consideration:

All procedures were conducted under an inert gas atmosphere of argon utilizing the standard Schlenk technique and within an argon-filled MBRAUN MB 150-GI glovebox. All glassware was dried overnight at 130°C and then cooled to room temperature before being used in the experiments. All solvents sustain purification using the MBRAUN MB SPS-800 solvent purification system. The distillation of toluene, THF, and n-hexane was conducted following the standard literature protocol, which involves using sodium metal and benzophenone to generate a dark blue color solution, indicating ketyl radical formation. Deuterated solvent $CDCl_3$ was dried over calcium hydride, distilled in an inert atmosphere, and stored in sealed Schlenk flasks. Another deuterated solvent, like DMSO-d^6, was used as received from the supplier.

4.2 Starting Materials:

All commercially available starting materials were purchased and utilized as received from Sigma Aldrich, Alfa-aesar, BLD Pharma, and TCI. The starting material of mesitylene-substituted bis-imidazolium salt was synthesized with the help of previously reported protocols.

4.3 Analytical Methods:

4.3.1 Nuclear Magnetic Resonance (NMR) Measurements:

NMR samples for air- and moisture-sensitive compounds were prepared under an inert atmosphere. Subsequently, maintaining the inert environment, the samples were sealed in oven-dried NMR tubes for measurements. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using an ARX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100.61 MHz) from Bruker. Additionally, ^{11}B-NMR spectra were recorded using an ARX 400 spectrometer (^{11}B, 128.38 MHz) from Bruker.

The following abbreviations have been used to denote NMR signal multiplicity:

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br - broad signal

4.3.2 Mass Spectrometry:

Mass spectra of compounds were recorded using the AB Sciex 4800 plus HRMS instrument. To maintain the sample integrity, samples for sensitive compounds were freshly prepared in an inert atmosphere in an Eppendorf wrapped with parafilm/Teflon. The mass spectra were recorded as a plot of relative intensity versus *m/z* value.

4.3.3 Infrared Spectroscopy:

The IR spectra of specific compounds were recorded using ALPHA-II ECO ATR, Bruker instrument. Spectra were recorded as a plot of transmittance (%) versus wavenumber (cm^{-1}).

4.3.4 Crystallographic Data:

Crystallographic reflections were collected on a Bruker Smart Apex Duo diffractometer at 150 K using Mo Kα radiation (λ=0.71073 Å) for the structure of complex **Mn2**. The structure was solved by the direct method and refined by full-matrix least square methods against F2 (SHELXL-2014/6).

4.4. Synthesis and characterization:

4.4.1 Synthesis of bis-imidazolium salt 1:[52,53]

First, we have synthesized mesitylene substituted imidazole precursor by following previously reported protocols. Further, under the atmosphere of nitrogen, a microwave (Monowave 300) tube (G30) was charged with acetonitrile solution (5 ml) containing mesitylene substituted imidazole (1.862 g, 10.0 mmol) and dibromomethane (0.6 ml, 8.0 mmol). This solution mixture was heated for 1 hour at 160 ^{0}C under microwave radiation. A dark brown solid precipitated from the solution mixture. The precipitate was filtered off and rinsed with cold THF until it transformed into a colorless solid. Subsequently, it was dried under vacuum to yield the desired hygroscopic bis-NHC salt, achieving approximately 70% yield. The obtained product was then characterized with proton NMR spectroscopy.

^{1}H NMR (400 MHz $CDCl_3$): δ 11.35 (s, 2H), 9.84 (s, 2H), 7.95 (s, 2H), 7.22 (s, 2H), 7.03 (s, 4H), 2.35 (s, 6H), 2.05 (s, 12H).

ESI-MS: (*m/z*) Found: 386.2421, Calculated: 386.5419.

4.4.2 Synthesis of bis-imidazolium salt 2:[52]

Under the atmosphere of nitrogen, a microwave (Monowave 300) tube (G30) was charged with acetonitrile solution (5 ml) containing methyl-substituted imidazole (0.80 ml, 10.0 mmol) and dibromomethane (0.6 ml, 8.0 mmol). This solution mixture was heated for 1 hour at 140 ^{0}C under microwave radiation. A colorless solid with a slightly yellowish tinch precipitated from the solution mixture. The precipitate was filtered and rinsed with cold THF until it transformed into a white solid. Subsequently, it was dried under vacuum to yield the desired hygroscopic bis-NHC salt, achieving approximately 65% yield. The obtained product was then characterized with proton NMR spectroscopy.

^{1}H NMR (400 MHz DMSO-d$_6$): *δ* 9.53 (s, 2H), 8.07 (s, 2H), 7.82 (s, 2H), 6.76 (s, 2H), 3.91 (s, 6H).

^{13}C NMR (100 MHz DMSO-d$_6$): *δ* 143.38, 143.14, 129.54, 127.16, 63.13, 41.47.

ESI-MS: (*m/z*) Found: 338.3418 [M+2H], Calculated: 335.9657.

4.4.3 Synthesis of bis-NHC-based manganese catalyst Mn1:[53]

Under a nitrogen atmosphere and in the absence of light, basic manganese precursor $Mn(CO)_5Br$ (70 mg, 0.26 mmol) was dissolved in dry THF (20 mL), followed by the addition of KO^{t}Bu (52 mg, 0.46 mmol). The reaction mixture was then heated at 60°C, and mesitylene substituted imidazolium salt **1** (120 mg, 0.22 mmol) was slowly added to the suspended solution. The resulting suspension was stirred at 60°C for 24 hours. Upon cooling the mixture to room temperature, the solvent THF was evaporated under a vacuum, yielding an orange-yellow residue. This residue was suspended in DCM (25 mL) and then filtered in a vacuum. The orange-yellow filtrate obtained was subsequently evaporated under vacuum to afford the crude product. Purification has been done by washing multiple times with diethyl ether. Finally, yellow powder was obtained. The obtained product was then characterized with proton NMR spectroscopy.

^{1}H NMR (400 MHz DMSO-d_6): *δ* 7.84 (br, s, 2H), 7.37 (br, s, 2H), 7.02 (br, s, 2H), 6.97 (br, s, 2H), 6.84−6.75 (br, d, 2H), 6.47−6.37 (br, d, 2H), 2.29 (br, s, 6H), 2.08 (br, s, 6H), 1.82 (br, s, 6H).

ESI-MS: (*m/z*) Found: 303.0539 [M+H], Calculated: 302.5364.

FTIR υ_{CO} 2006.51 (s), 1923.05 (s), 1889 (s).

4.4.4 Synthesis of bis-NHC-based manganese catalyst Mn2:[46]

Under a nitrogen atmosphere and in the absence of light, basic manganese precursor $Mn(CO)_5Br$ (164.94 mg, 0.6 mmol) was dissolved in dry THF (20 mL), followed by the addition of KOtBu (135 mg, 1.15 mmol). The reaction mixture was then heated at 60°C, and methyl-substituted imidazolium salt **2** (170 mg, 0.5 mmol) was slowly introduced into the suspended solution. The resulting suspension was stirred at 60°C for 24 hours. Upon cooling the mixture to room temperature, the solvent THF was evaporated under a vacuum, yielding an orange-yellow residue. This residue was suspended in DCM (25 mL) and then filtered in a vacuum. The orange-yellow filtrate obtained was subsequently evaporated under vacuum to afford the crude product. Purification has been done by washing multiple times with ether. Finally, yellow powder was obtained. The prepared catalyst is characterized by single-crystal XRD and FTIR.

^{1}H NMR (400 MHz DMSO-d_6): *δ* 7.57 (s, 2H), 7.43 (s, 2H), 6.62 (d, 2H), 6.03 (d, 2H), 3.98 (s, 6H)

ESI-MS: (*m/z*) Found: 397.0826 [M+2H], Calculated: 395.0939

FTIR υ_{CO} 2008 (s), 1911 (s), 1889 (s).

4.5 Catalytic application:

4.5.1 General method for hydroboration of primary amides:

A catalysis Schlenk tube was charged with 0.2 mmol of primary amide with 1.8 ml HBpin (4.5 equiv.) (0.5 M solution in toluene) and 5 mol% catalyst loading (**Mn1**, 6 mg). This mixture was heated at 100 ^{0}C temperature for 24 hours. After cooling it down to room temperature, the solvent evaporated under vacuum. Further, the obtained crude product was dissolved in 0.5 ml $CDCl_3$ with 27 μl mesitylene as an internal standard, and yield was calculated by integrating proton NMR with respect to mesitylene.

4.5.2 General method for hydroboration of secondary amides:

A catalysis Schlenk tube was charged with 0.2 mmol of secondary amide with 1.35 ml HBpin (3.3 equiv.) (0.5 M solution in toluene) and 2 mol% catalyst loading (**Mn1**, 2.5 mg). This mixture was heated at 100 ^{0}C temperature for 24 hours. After cooling it down to room temperature, the solvent evaporated under vacuum. Further, the obtained crude product was dissolved in 0.5 ml $CDCl_3$ with 27 µl mesitylene as an internal standard, and yield was calculated by integrating proton NMR with respect to mesitylene.

4.5.3 General method for CO_2 hydroboration:

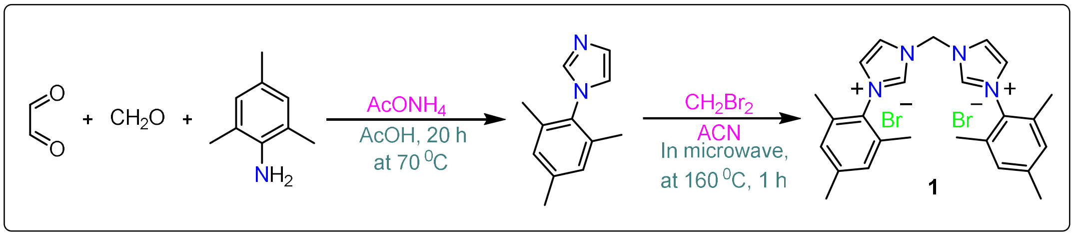
A catalysis Schlenk tube was charged with 0.2 mmol of HBpin with 5 mol% catalyst (**Mn2**, 4 mg) loading in solvent-free conditions. CO_2 was purged in a Schlenk tube containing the reaction mixture. After properly shielding, heated this mixture at 100 ^{0}C for 24 hours. After cooling it down to room temperature, 0.5 ml $CDCl_3$ and mesitylene (9 µl) were added as an internal standard, and yield was calculated by integrating proton NMR with respect to mesitylene.

5. Result and Discussion:

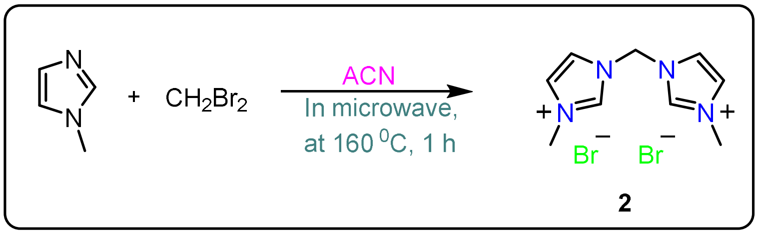
5.1 Bis-NHC carbene and their corresponding Mn(I) metal complexes synthesis:

The selection of ligands in chemical reactions or catalytic processes depends on several factors, including the reaction's specific demands and the desired results. Among the various ligands available, bis-NHC ligands are frequently favored in certain catalytic processes for several compelling reasons. One key advantage is the tunability of bis-carbene ligands' structure, allowing for precise control over their steric and electronic properties. This tunability makes them highly versatile for a broad range of applications.

Furthermore, the chelating nature of bis-NHC ligands enables the formation of stable, five- or six-membered metal-chelate rings. These chelates contribute to metal complexes' enhanced stability and reactivity, thereby promoting efficient catalytic processes. Bis-NHC ligands can facilitate various catalytic transformations with improved selectivity and catalytic activity by forming such stable chelate rings. Overall, the unique structural and electronic properties of bis-NHC ligands make them valuable tools in the development of efficient and selective catalytic systems.



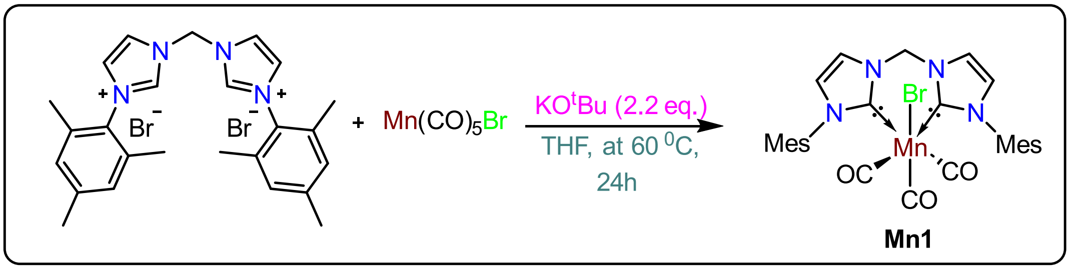
Scheme 5: Synthesis of bis-NHC carbene salt **1**



Scheme 6: Synthesis of bis-NHC carbene salt **2**

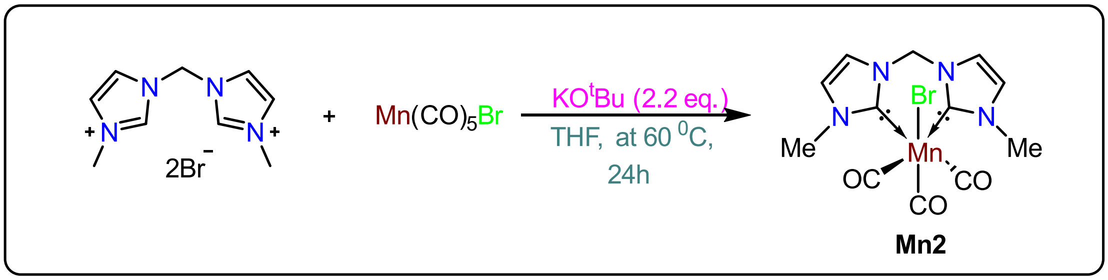
Using previously reported literature, we synthesized mesitylene substituted imidazole precursor at the previously optimized reaction conditions and used these substituted imidazole precursors with dibromomethane in acetonitrile solvent stirred for 1 hour at 160 ^{0}C in the microwave to synthesize bis-NHC salt **1** (**Scheme 5**) and **2** (**Scheme 6**).

We have synthesized bis-NHC coordinated manganese complex **Mn1** by following previously reported protocols by Duan and coworkers in 2020.[53]



Scheme 7: A schematic representation for the synthesis of bis-NHC coordinated manganese(I) complex **Mn1**

We have synthesized bis-NHC coordinated manganese complex **Mn2** by following previously reported protocols by Fillol and co-workers in 2018.[46]



Scheme 8: A schematic representation for the synthesis of bis-NHC coordinated manganese complex **Mn2**

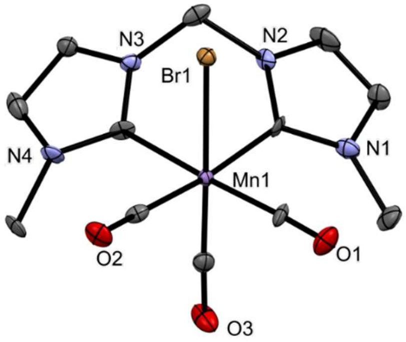


Figure 1: The crystal structure of **Mn2** complex.

Chart 5: Selected bond distances of complex **Mn2**

Bond Distances {Å}	
Mn1-Br1	2.5744(3)
Mn1-C1	2.0412(19)
Mn1-C6	2.043(2)
Mn1-C10	1.782(2)
Mn1-C12	1.810(2)
Mn1-C13	1.819(2)

Chart 6: Selected bond angles of complex **Mn2**

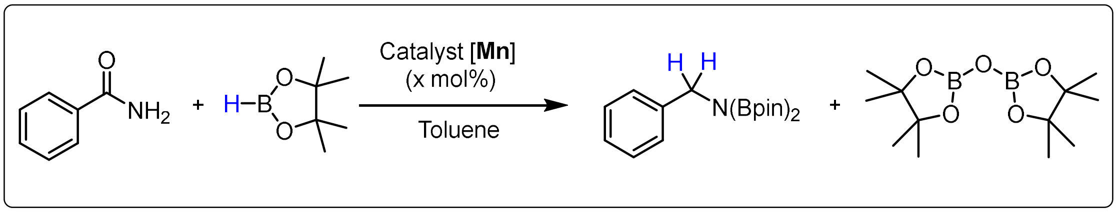
Bond Angles {°}	
C1-Mn1-Br1	89.21(5)
C6-Mn1-Br1	87.52(5)
C10-Mn1-Br1	178.96(7)
C1-Mn1-C6	85.11(8)
C12-Mn1-C6	177.29(9)
C10-Mn1-C6	91.90(8)
C13-Mn1-C1	178.84(8)
C12-Mn1-C1	92.65(9)
C10-Mn1-C1	91.60(9)
C12-Mn1-C13	88.12(9)
C10-Mn1-C13	89.26(9)
C10-Mn1-C12	89.69(9)

5.2 Amides hydroboration to the borylated amines

Our investigation commenced with the examination of the deoxygenation reaction of benzamide employing HBpin in the presence of manganese complexes **Mn1** and **Mn2** as catalysts. Remarkably, we observed that employing 5 mol% of the catalyst **Mn1** at 100°C, alongside 4.5 equivalents of HBpin over a duration of 24 hours, resulted in a nearly good quantitative yield (**Entry 1**, **Table 1**).

Throughout the optimization process outlined in (**Table 1**), notable variations in the yields of hydroborated products were observed across different reaction conditions. Notably, all reactions were conducted using toluene as the reaction solvent.

Table 1: Reaction conditions optimization for manganese catalyst-based deoxygenation of 1° amides.



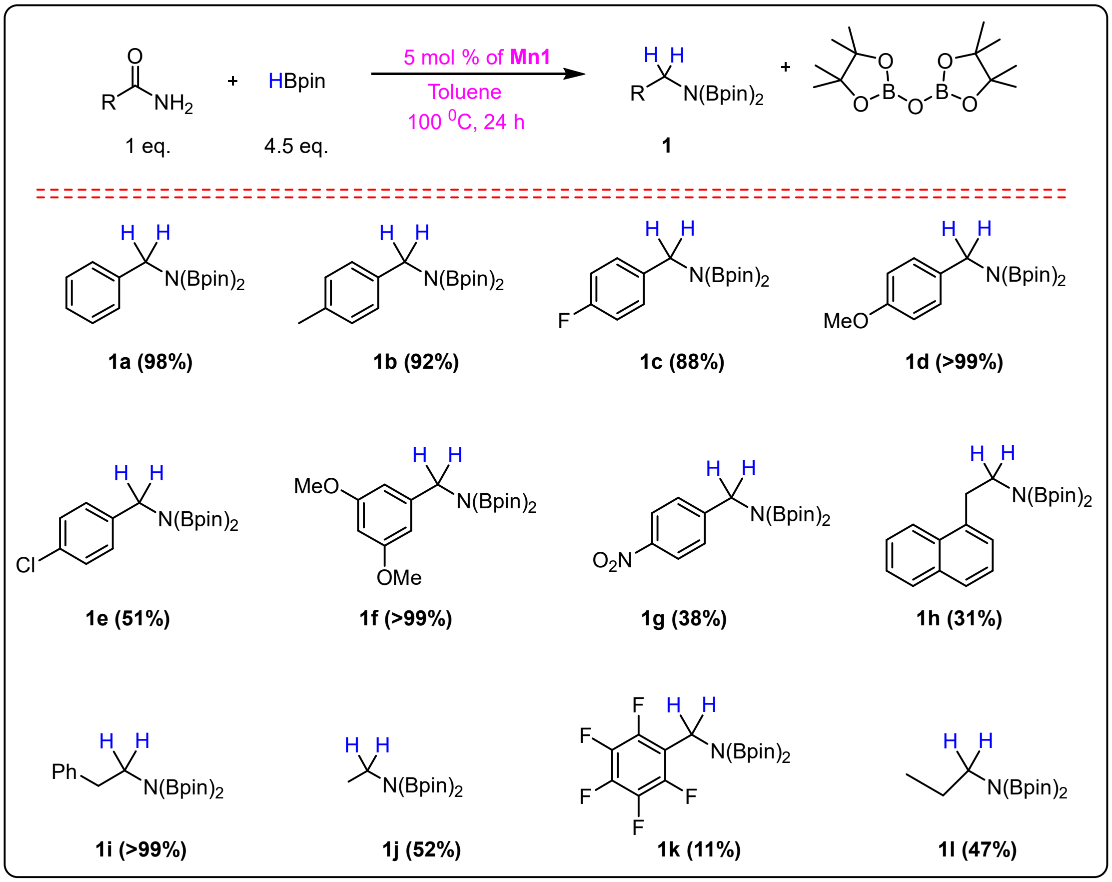
Entry	[Mn] catalyst	Catalyst mol % (x)	Eqv. of HBpin	Temp. (°C)	Time (h)	Yield* (%)
1.	Mn1	5	4.5	100	24	98
2.	Mn2	5	4.5	100	24	31
3.	Mn2	5	4.5	100	36	45
4.	Mn1	1	4.5	100	24	24
5.	Mn1	2	4.5	100	24	45
6.	Mn1	3	4.5	100	24	63
7.	Mn1	4	4.5	100	24	85
8.	Mn1	5	4.5	RT	24	Trace
9.	Mn1	5	4.5	55	24	6
10.	Mn1	5	4.5	70	24	21
11.	Mn1	5	4.5	85	24	54
12.	Mn1	5	4.5	100	4	7
13.	Mn1	5	4.5	100	8	53
14.	Mn1	5	4.5	100	12	67

15.	Mn1	5	4.5	100	16	75
16.	Mn1	5	4.5	100	20	84
17.	Mn1	5	3	100	24	43
18.	Bis-NHC salt	5	4.5	100	24	20
19.	-	-	4.5	100	24	<5
20 [b]	Mn1	5	4.5	100	24	34

[a] Benzaimde (24.5 mg, 0.2 mmol), HBpin (0.5 M solution in toluene), all product yields were calculated by integrating proton NMR spectra with mesitylene as an internal standard; solvent = Toluene. [b] Solvent = THF.

After the successful completion of the optimization of benzamide with manganese catalyst **Mn1**, we have further studied the substrate scope.

Table 2: Deoxygenation of primary amides



1a (98%) **1b (92%)** **1c (88%)** **1d (>99%)**

1e (51%) **1f (>99%)** **1g (38%)** **1h (31%)**

1i (>99%) **1j (52%)** **1k (11%)** **1l (47%)**

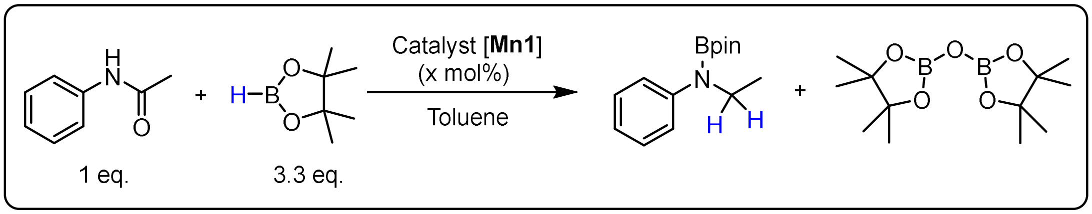
Reaction conditions: Amides (0.2 mmol, 1 equiv.), HBpin (1.8 ml, 4.5 equiv., 0.5 M solution in toluene), **Mn1** (6 mg, 5 mol%), 100 ^{0}C, 24 h. All substrate yields were calculated by integrating proton NMR spectra by taking mesitylene as an internal standard.

After completion of the substrate scope, we observed that in the case of the electron-withdrawing group, the substrate yield was much less than that of the substrate with electron-donating ability. This means that the deoxygenation of amides is facilitated when the carbonyl (C=O) bond is weakened.

Further, we have commenced an investigation into the deoxygenation of acetanilide employing HBpin in the presence of manganese complexes **Mn1** as the catalyst. Remarkably, we observed that employing 2 mol% of the catalyst **Mn1** at 100°C, alongside 3.3 equivalents of HBpin over a duration of 24 hours, resulted in a nearly good quantitative yield (**Entry 1**, **Table 3**).

Throughout the optimization process outlined in (**Table 3**), notable variations in the yields of hydroborated products were observed across different reaction conditions. Notably, all reactions were conducted using toluene as the reaction solvent.

Table 3: Reaction conditions optimization for manganese catalyst-based deoxygenation of 2° amides.



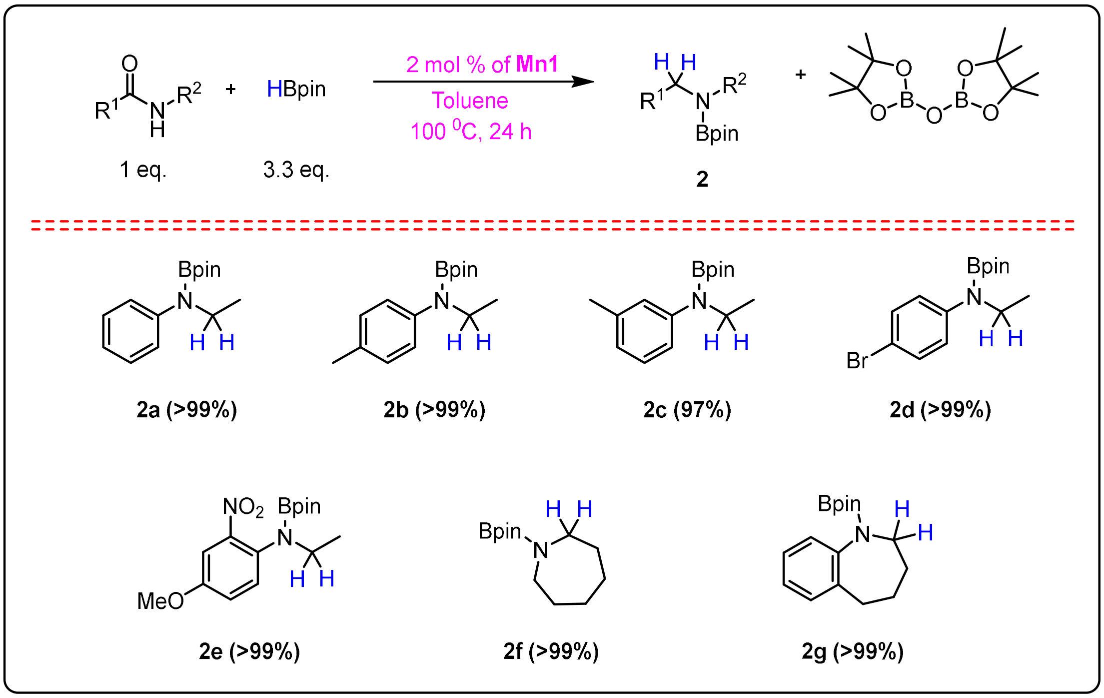
Entry	Catalyst mol% (x)	Temp. (°C)	Time (h)	Yield* (%)
1.	2	100	24	>99
2.	3	100	24	87
3.	4	100	24	75
4.	5	100	24	66
5.	2	40	24	trace
6.	2	60	24	12
7.	2	80	24	40
8.	2	100	6	trace
9.	2	100	12	7

10.	2	100	18	20
11.	Bis-NHC salt	100	24	18
12.	-	100	24	trace

Reaction conditions: Acetanilide (27.04 mg, 0.2 mmol), catalyst **Mn1** (2 mol%, 2.5 mg), HBpin (1.35 ml, 3.3 equiv., 0.5 M solution in toluene), all product yields were calculated by integrating proton NMR spectra with mesitylene as an internal standard

After the successful completion of the optimization of acetanilide with manganese catalyst **Mn1**, we have conducted the deoxygenation of secondary amides substrate scope under optimized reaction conditions:

Table 4: Deoxygenation of secondary amides

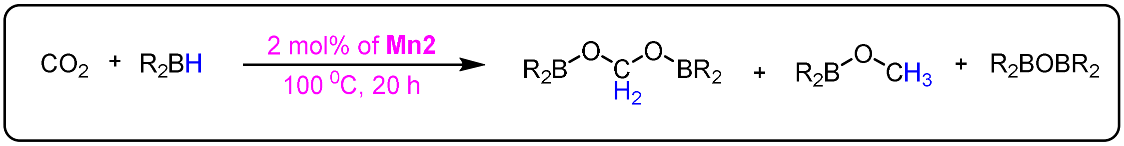


Reaction conditions: Amides (0.2 mmol, 1 equiv.), HBpin (1.35 ml, 3.3 equiv., 0.5 M solution in toluene), **Mn1** (2.5 mg, 2 mol%), 100 ^{0}C, 24 h. All substrate yields were determined by integrating proton (^{1}H) NMR spectra by taking mesitylene as an internal standard.

For secondary amides, we have not observed any observable effect on product yield based on the electronic properties of the alkyl or aryl group attached to the nitrogen atom. We observed excellent yield in the case of secondary amides borylation catalyzed by **Mn1** catalyst.

Further, we have utilized these manganese catalysts **Mn1** and **Mn2** for the reductive hydroboration of carbon dioxide (CO_2). We observed that catalyst **Mn2** transformed carbon dioxide into methoxyboranes with a better yield than catalyst **Mn1** (**Scheme 7**)

Scheme 9: Reductive borylation of CO_2 to methoxyborane



Reaction conditions: Mn2 (0.01 mmol), HBpin (0.5 mmol), CO_2 (1 bar), 100 ^{0}C, 24 h. Yield was determined by integrating proton NMR spectra with mesitylene as an internal standard.

The advantage of this reaction is the absence of solvent requirement. This eliminates the need for a solvent during the course of the reaction, simplifying the process and reducing the environmental impact associated with solvent usage. Additionally, solvent-free reactions can offer practical benefits such as easier product isolation and reduced purification steps.

Here, we have compared turn over no. and turn over frequency of this manganese catalyst with previously reported manganese-based catalysts:

Table 5: Comparison of TON and TOF with previously reported catalyst:[41,43]

Catalyst	**Mol %**	**Product**	**Yield* %**	**TON**	**Time (h)**	**TOF (h^{-1})**
$[Mn^{I}H(PNP^{NH}\text{–}{}^{i}Pr)(CO)_2]$	1	CH_3-OBpin	78.3	26	24	1.08
$[Mn^{I}(Ph_2PCH_2SiMe_2)_2NH(CO)_2Br]$	0.036	CH_3-OBpin	96	883	14	49.78
fac-$[Mn^{I}(bis\text{-}{}^{Mes}NHC)(CO)_3Br]$ **(This work)**	2	CH_3-OBpin	70	35	20	1.75

6. Conclusion and future plans:

In this project, we synthesized bis-N-heterocyclic-based manganese complexes **Mn1** and **Mn2**. We successfully utilized manganese complex **Mn1** as an efficient and selective catalyst for primary and secondary amide deoxygenative reduction and obtained moderate to excellent yield. We employed complex **Mn2** as an efficient catalyst for the catalytic transformation of carbon dioxide to boryl-protected methanol and achieved a moderate yield. Moving forward, our aim is to enhance the yield of this process in future endeavors. Through continued exploration and refinement of reaction conditions, including catalyst modification and optimization. This commitment underscores our dedication to advancing the efficacy and sustainability of the reduction of carbon dioxide using bis-NHC-based manganese complexes.

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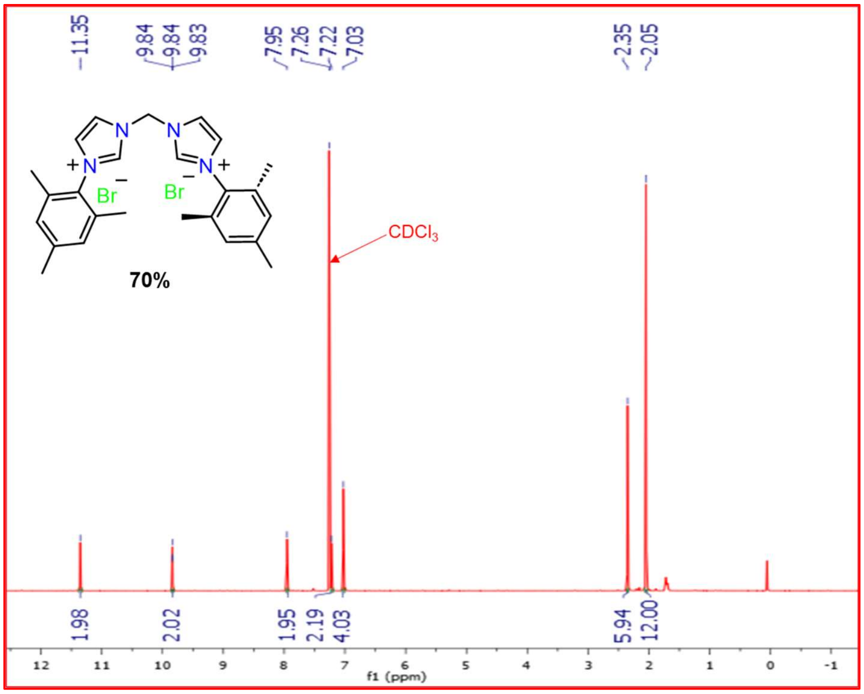
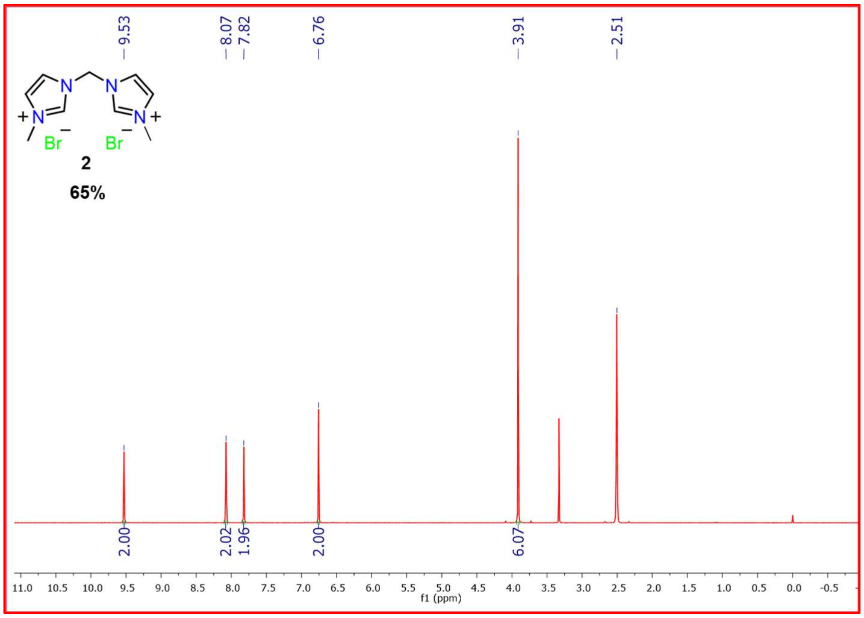
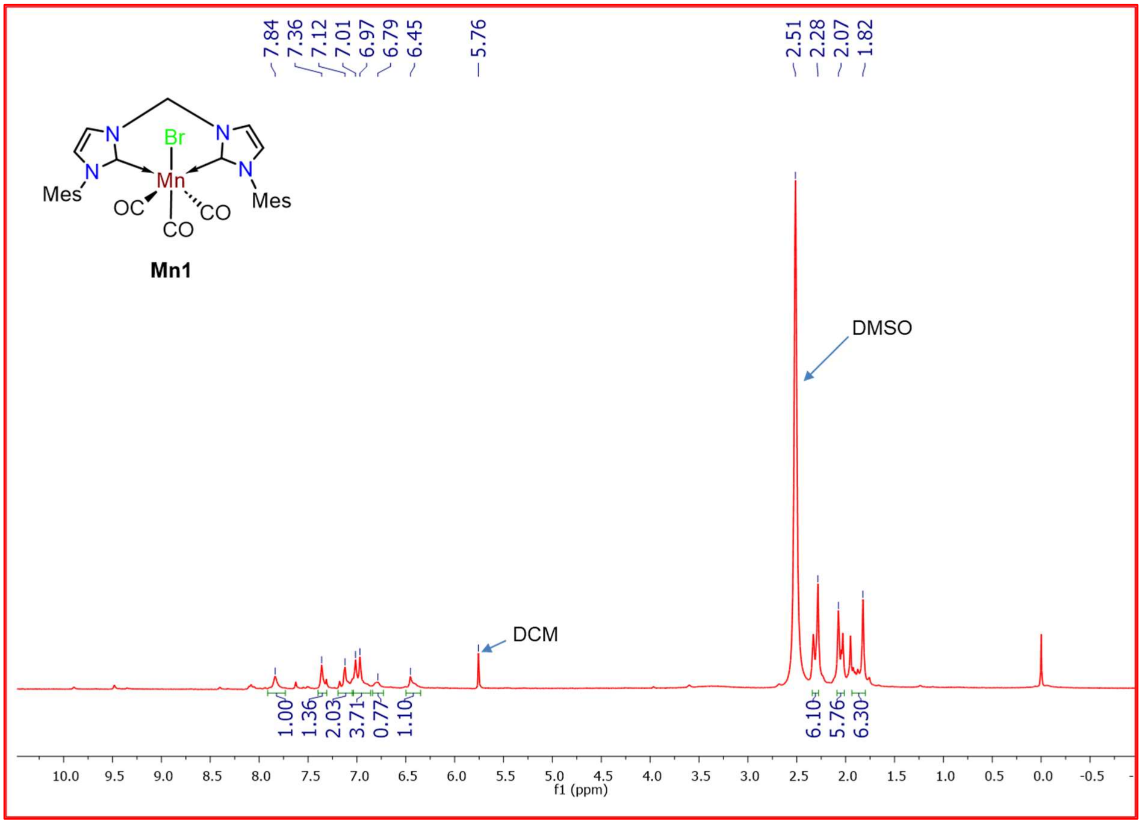
8. Appendix:

- **Containing data:(a) Proton and Carbon NMR data (b) FTIR spectra**
- **Proton (^{1}H) NMR Data:** Complexes **Mn1** and **Mn2** synthesis related



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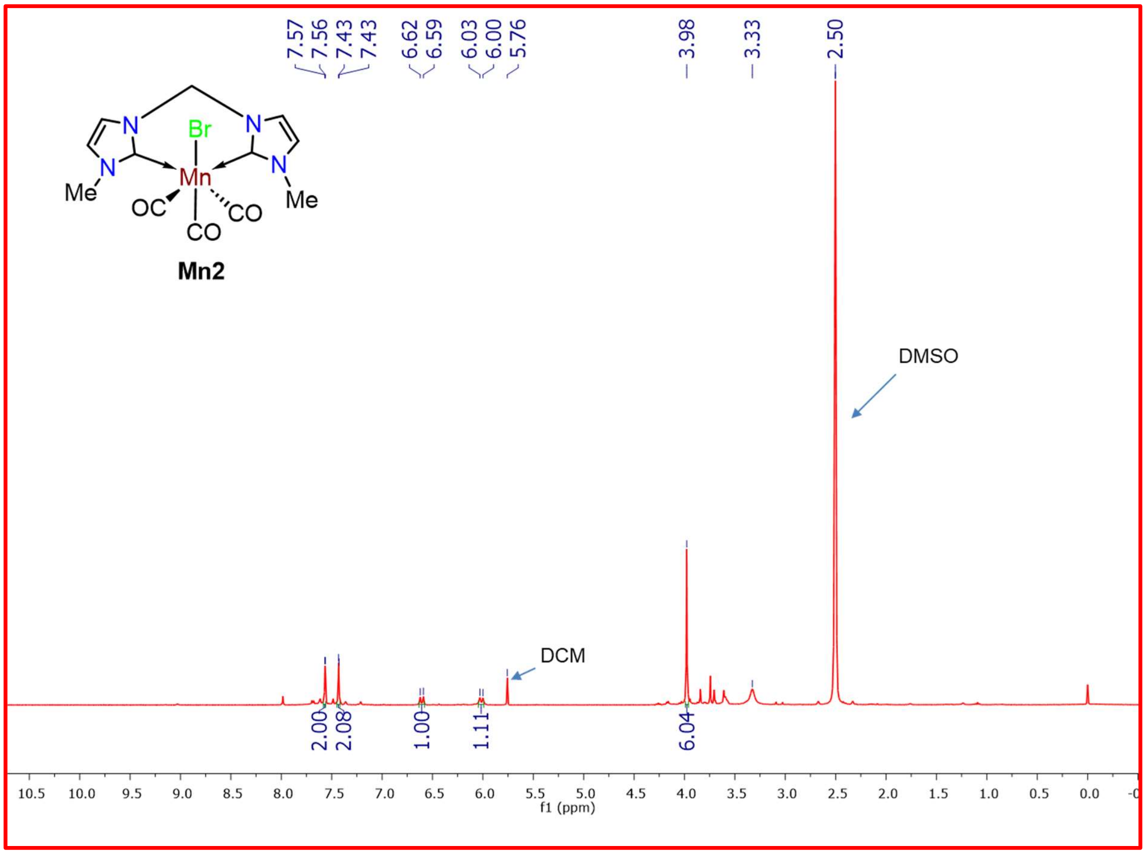
7.12
7.01
6.97
6.79
6.45
5.76
2.51
2.28
2.07
1.82
N
N
N
N
Br
Mn
Mes
Mes
OC
CO
CO
Mn1
DMSO
DCM
1.00
1.36
2.03
3.71
0.77
1.10
6.10
5.76
6.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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7.56
7.43
7.43
6.62
6.59
6.03
6.00
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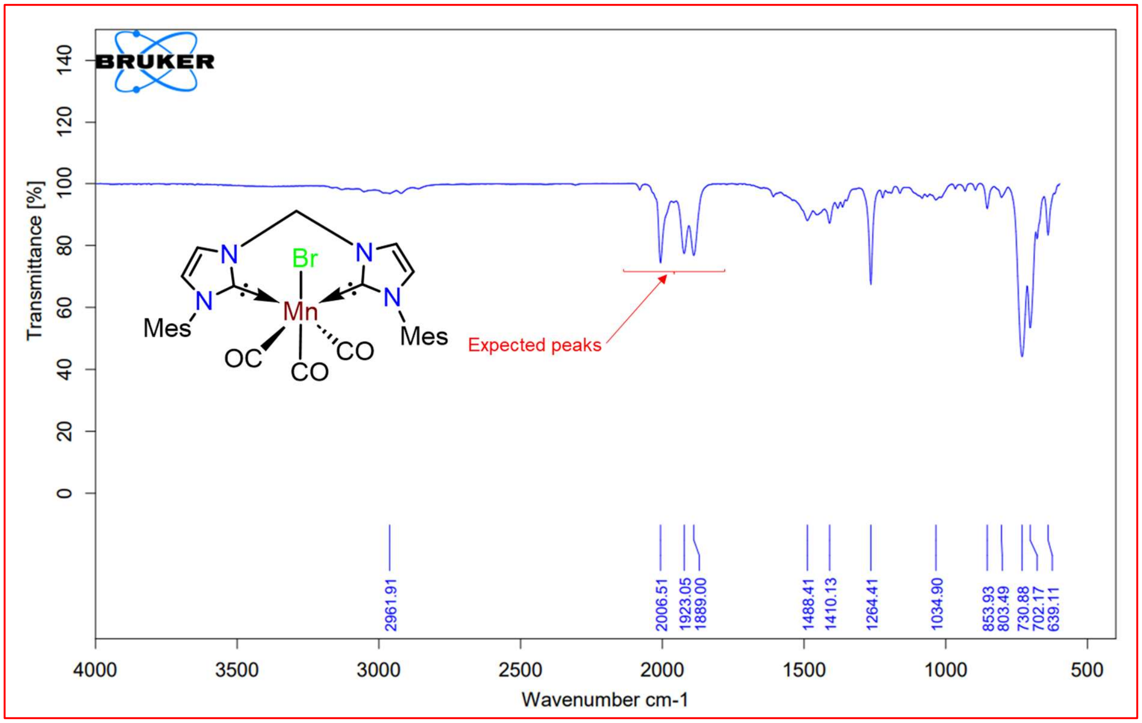
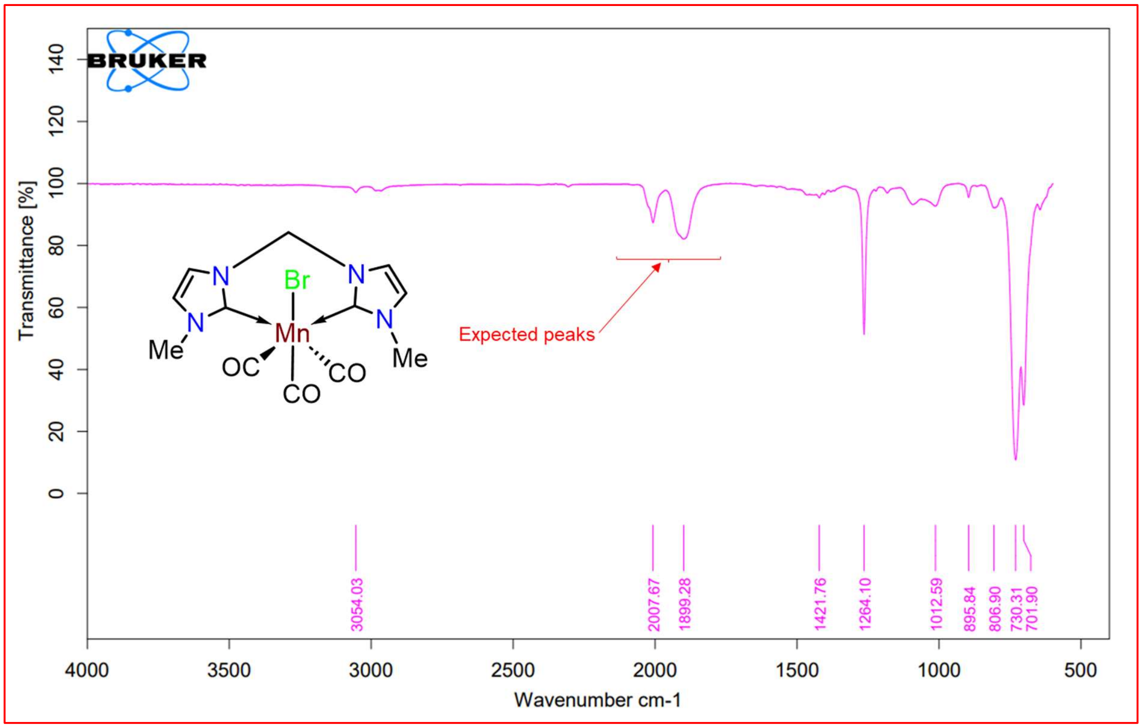
3.98
3.33
2.50
N
N
N
N
Br
Mn
Me
Me
OC
CO
CO
Mn2
DMSO
DCM
2.00
2.08
1.00
1.11
6.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

- **FTIR Data:** For complexes **Mn1** and **Mn2**

FTIR spectra of **Mn1**

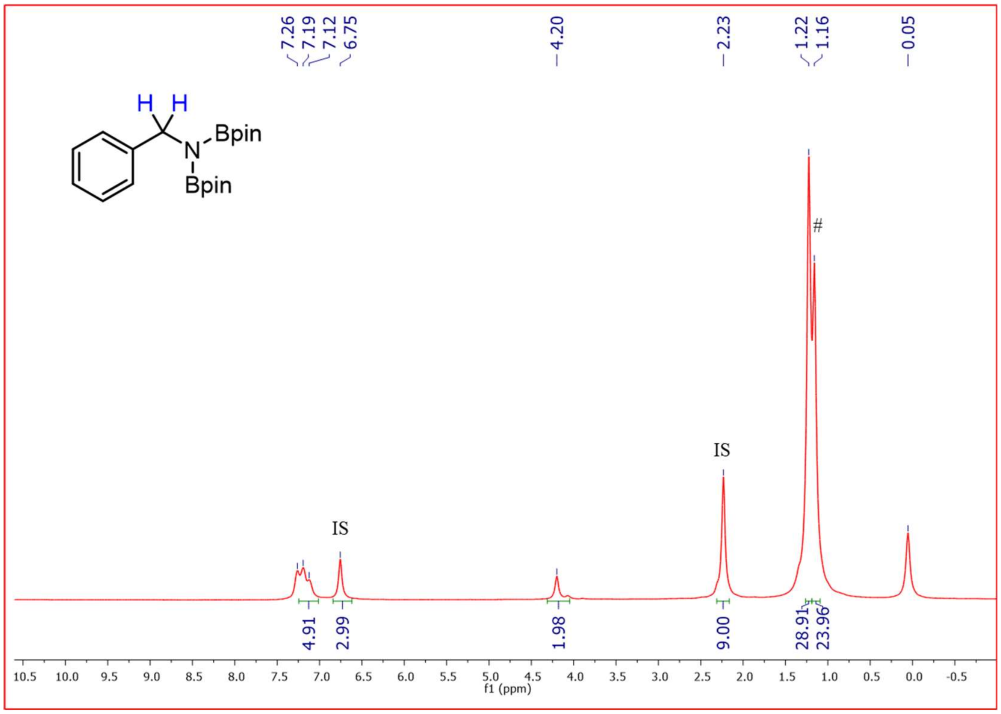


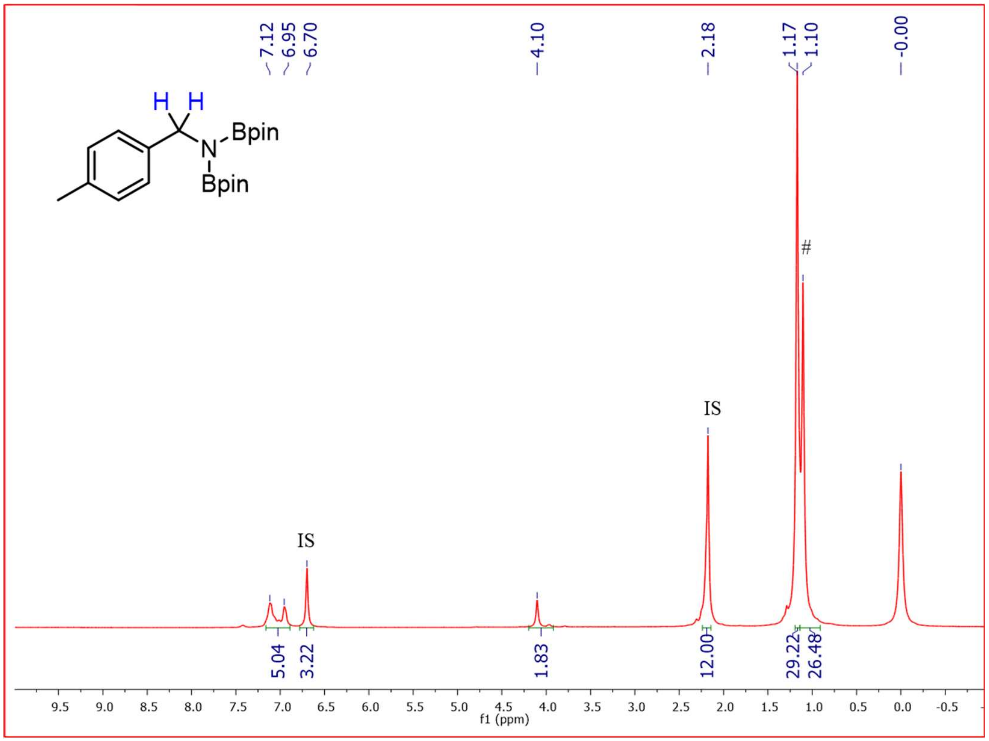
FTIR spectra of **Mn2**

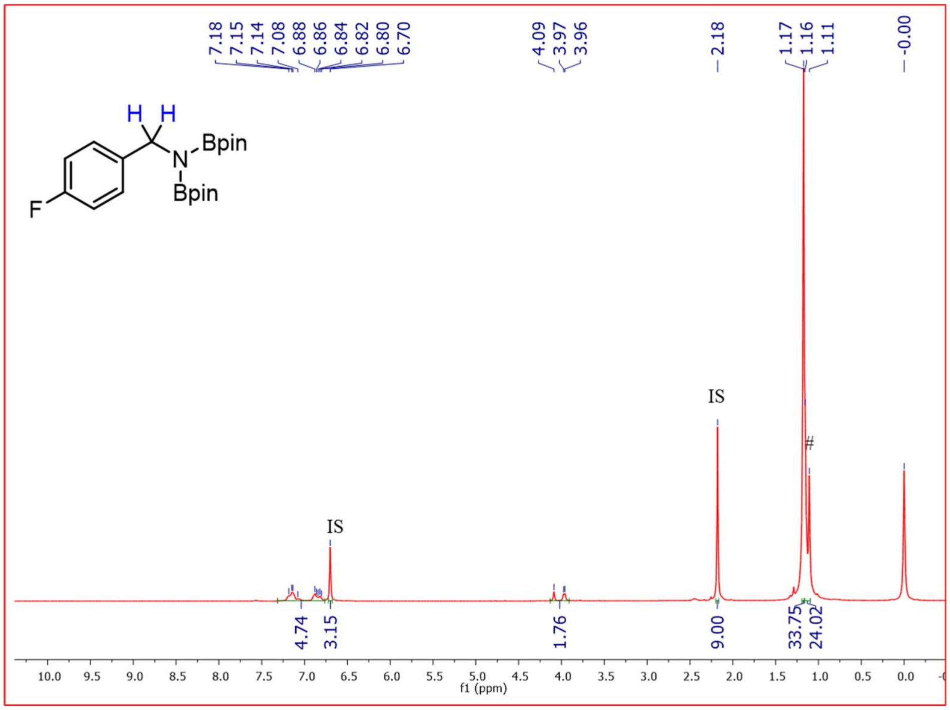


NMR of Substrate scope:

IS = Internal standard (Mesitylene), # = O(Bpin)$_2$ peak



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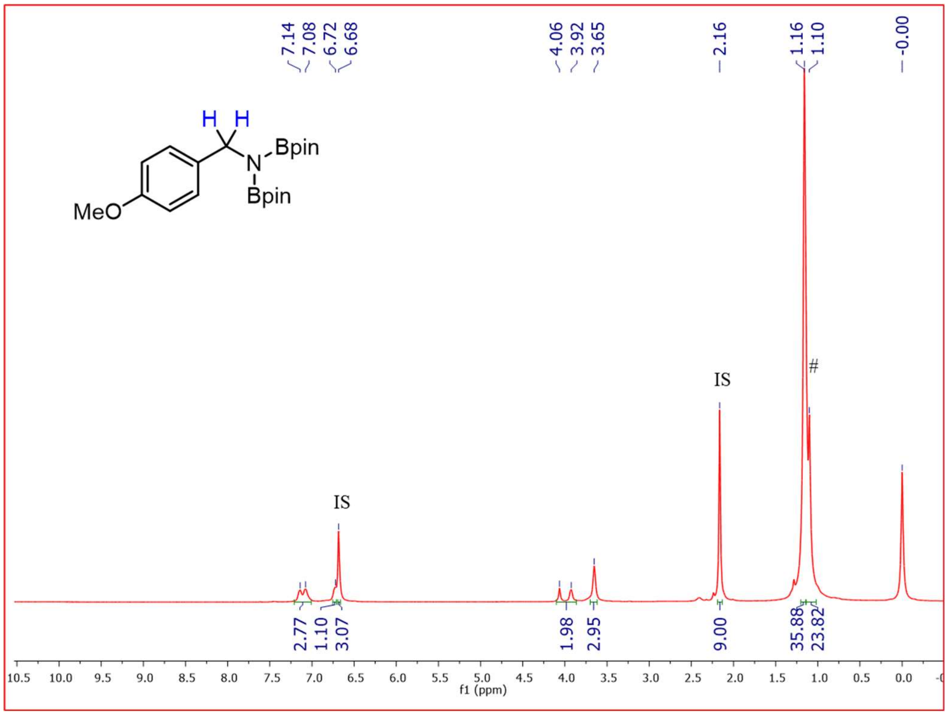
6.84
6.82
6.80
6.70
4.09
3.97
3.96
2.18
1.17
1.16
1.11
-0.00
H H
Bpin
N
Bpin
F
IS
IS
#
4.74
3.15
1.76
9.00
33.75
24.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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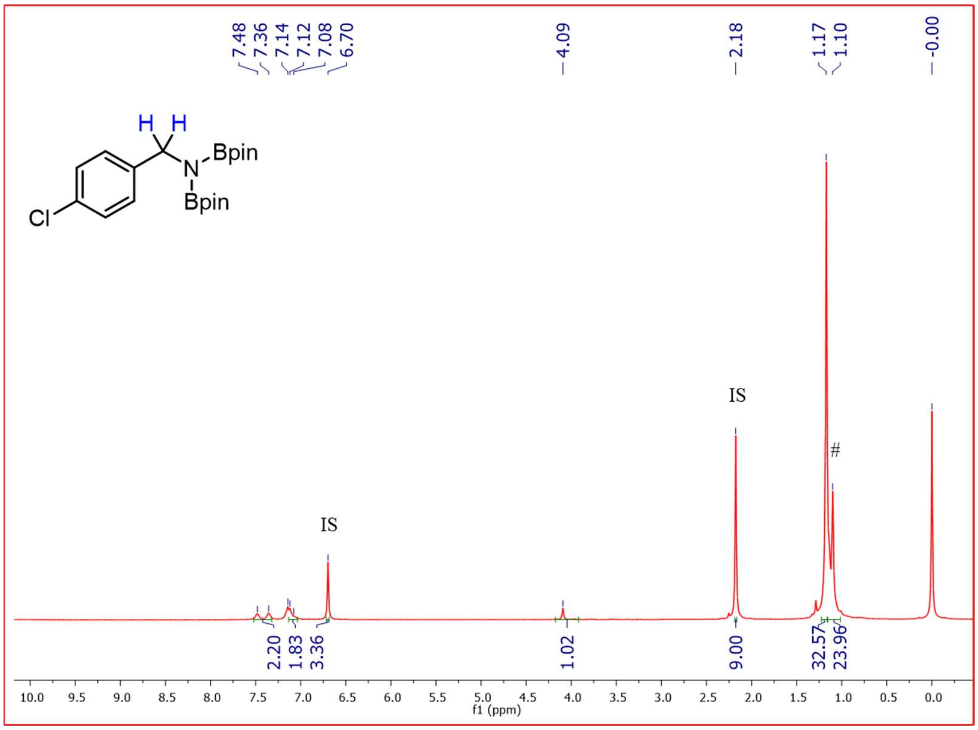
2.16
1.16
1.10
-0.00
H H
Bpin
N
Bpin
MeO
IS
IS
#
2.77
1.10
3.07
1.98
2.95
9.00
35.88
23.82
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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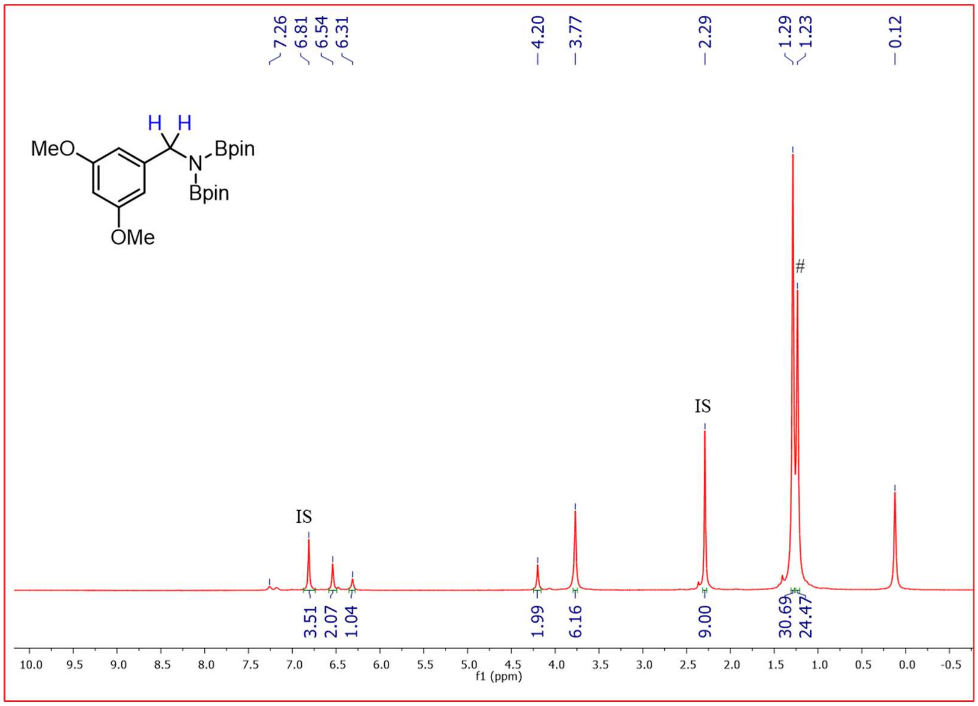
7.36
7.14
7.12
7.08
6.70
4.09
2.18
1.17
1.10
-0.00
H H
N
Bpin
Bpin
Cl
IS
IS
#
2.20
1.83
3.36
1.02
9.00
32.57
23.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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6.54
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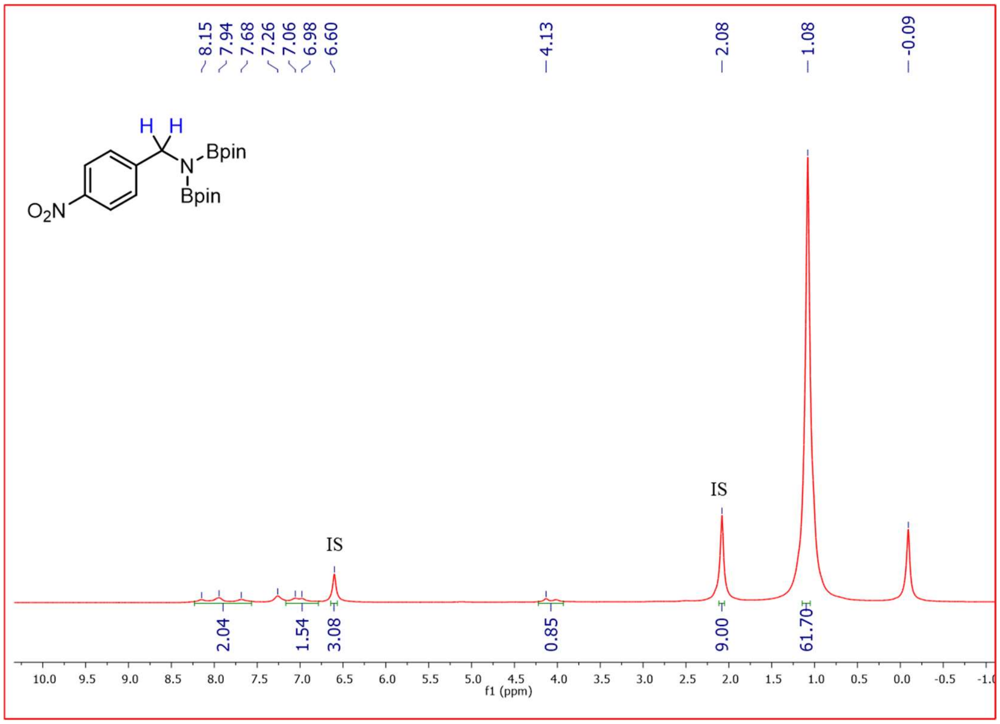
3.77
2.29
1.29
1.23
0.12
H H
MeO
N
Bpin
Bpin
OMe
IS
IS
#
3.51
2.07
1.04
1.99
6.16
9.00
30.69
24.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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7.68
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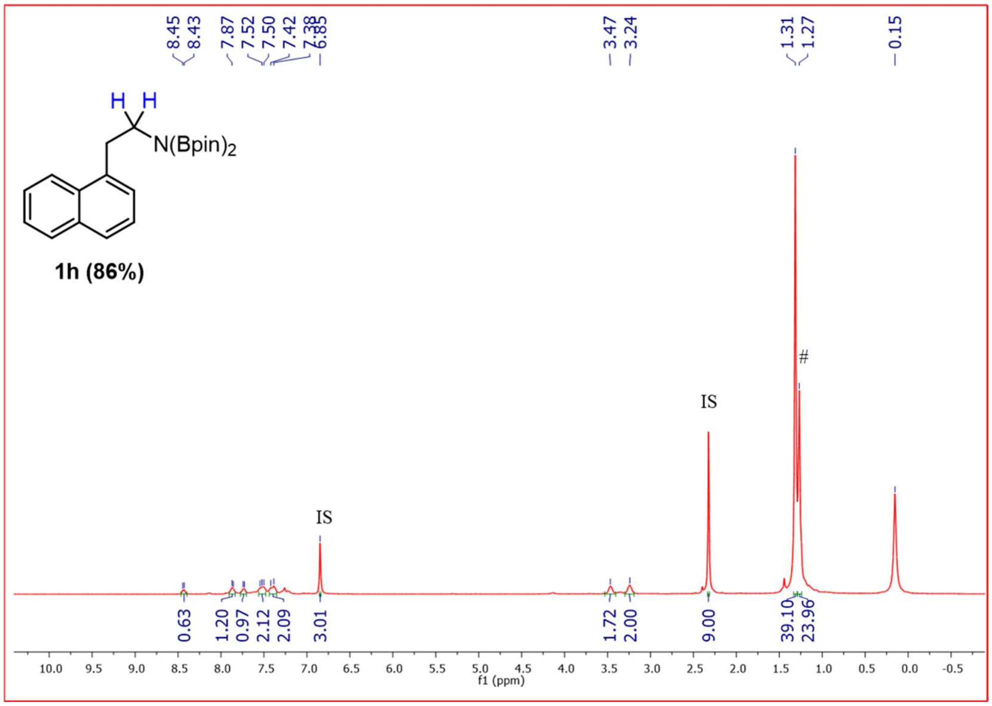
7.06
6.98
6.60
4.13
2.08
1.08
-0.09
H H
N
Bpin
Bpin
O2N
IS
IS
2.04
1.54
3.08
0.85
9.00
61.70
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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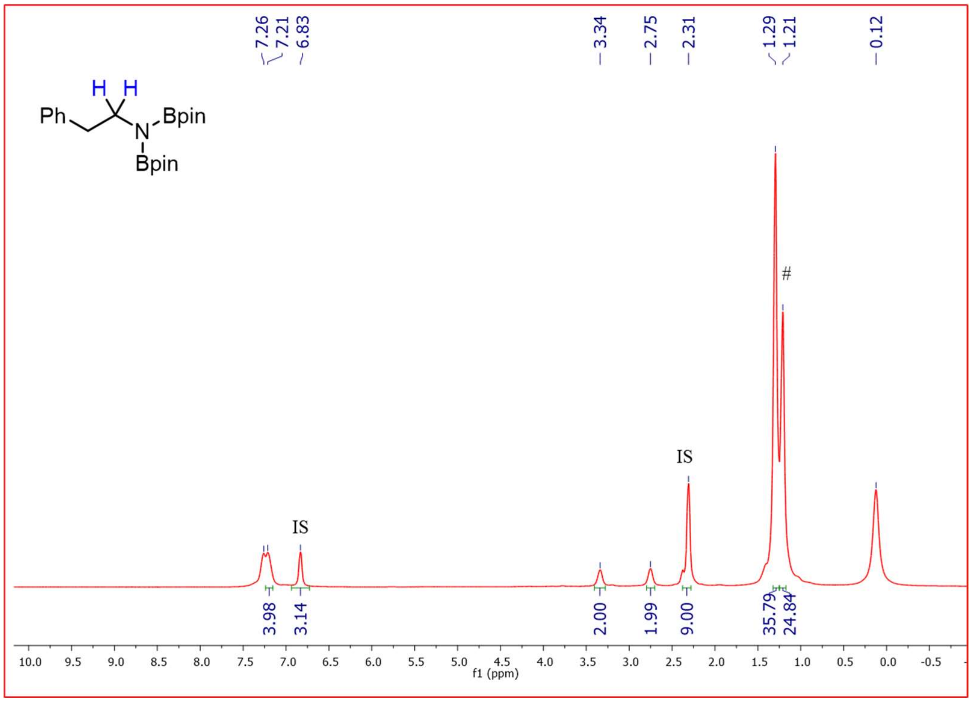
7.50
7.42
7.38
6.85
3.47
3.24
1.31
1.27
0.15
H H
N(Bpin)2
IS
IS
#
0.63
1.20
0.97
2.12
2.09
3.01
1.72
2.00
9.00
39.10
23.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

1h (86%)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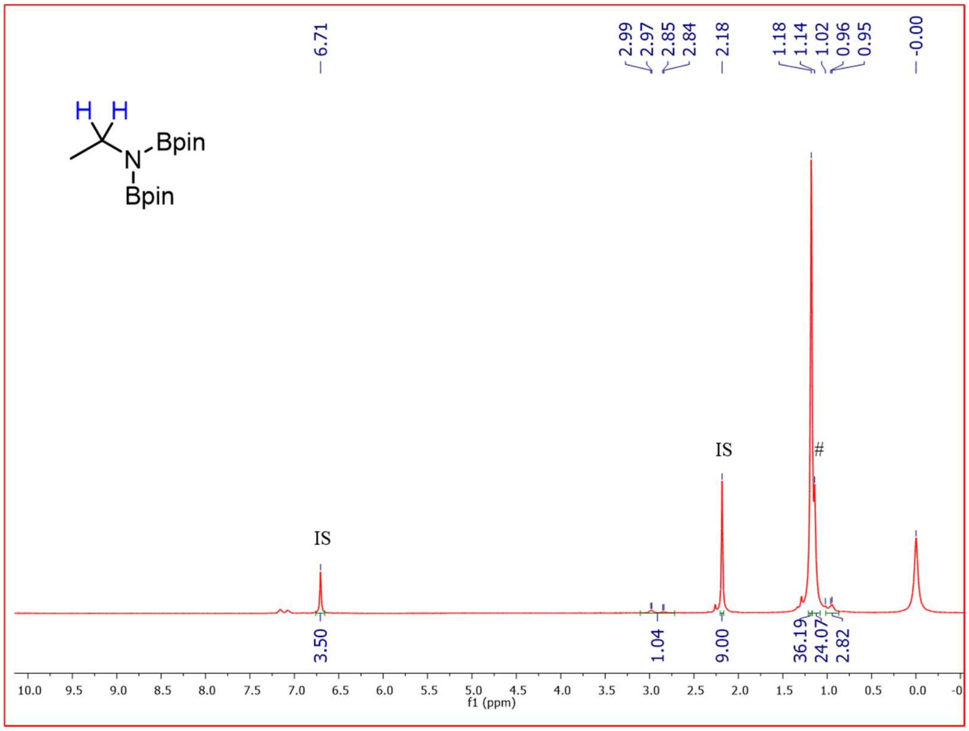
7.21
6.83
3.34
2.75
2.31
1.29
1.21
0.12
H H
Ph
N
Bpin
Bpin
#
IS
IS
3.98
3.14
2.00
1.99
9.00
35.79
24.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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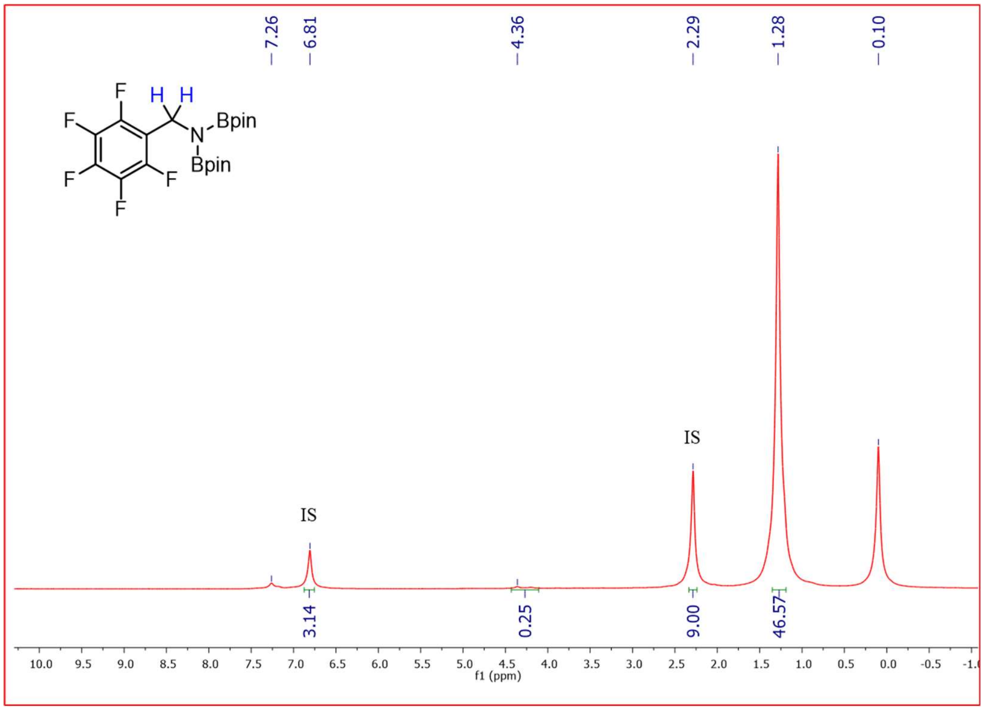
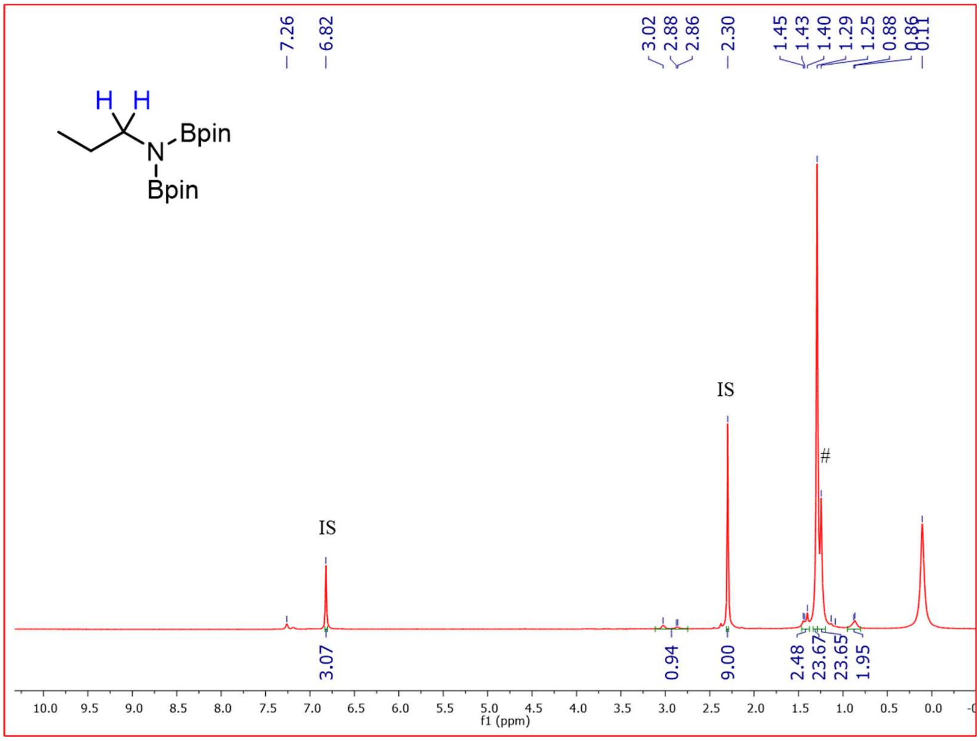
2.97
2.85
2.84
2.18
1.18
1.14
1.02
0.96
0.95
-0.00
H H
N
Bpin
Bpin
IS
IS
#
3.50
1.04
9.00
36.19
24.07
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



7.26
6.81
4.36
2.29
1.28
0.10
F
F
F
F
F
H H
N
Bpin
Bpin
IS
IS
3.14
0.25
9.00
46.57
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



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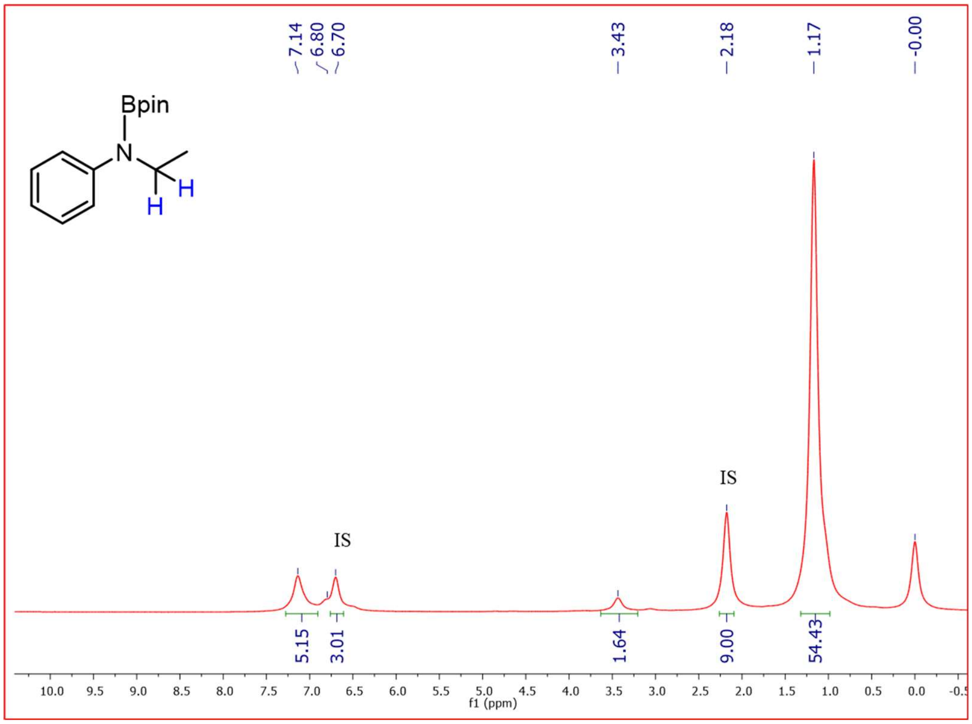
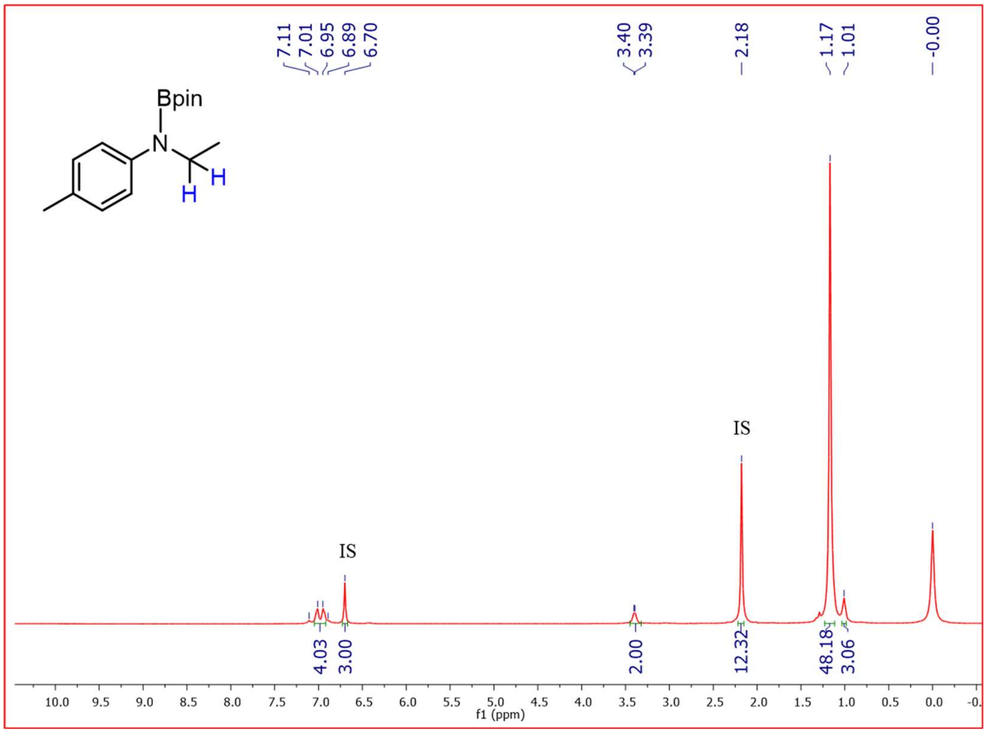
6.82
3.02
2.88
2.86
2.30
1.45
1.43
1.40
1.29
1.25
0.88
0.86
0.11
H H
N
Bpin
Bpin
IS
IS
#
3.07
0.94
9.00
2.48
23.67
23.65
1.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.14
6.80
6.70
3.43
2.18
1.17
-0.00
Bpin
N
H
H
IS
IS
5.15
3.01
1.64
9.00
54.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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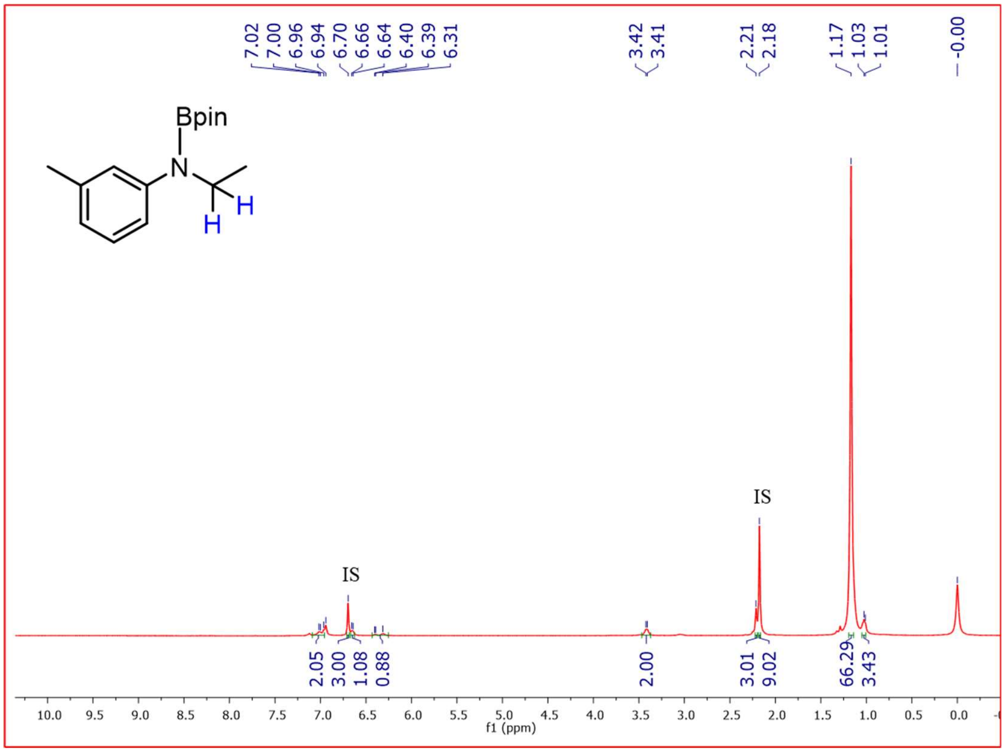
3.39
2.18
1.17
1.01
-0.00
Bpin
N
H
H
IS
IS
4.03
3.00
2.00
12.32
48.18
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.00
6.96
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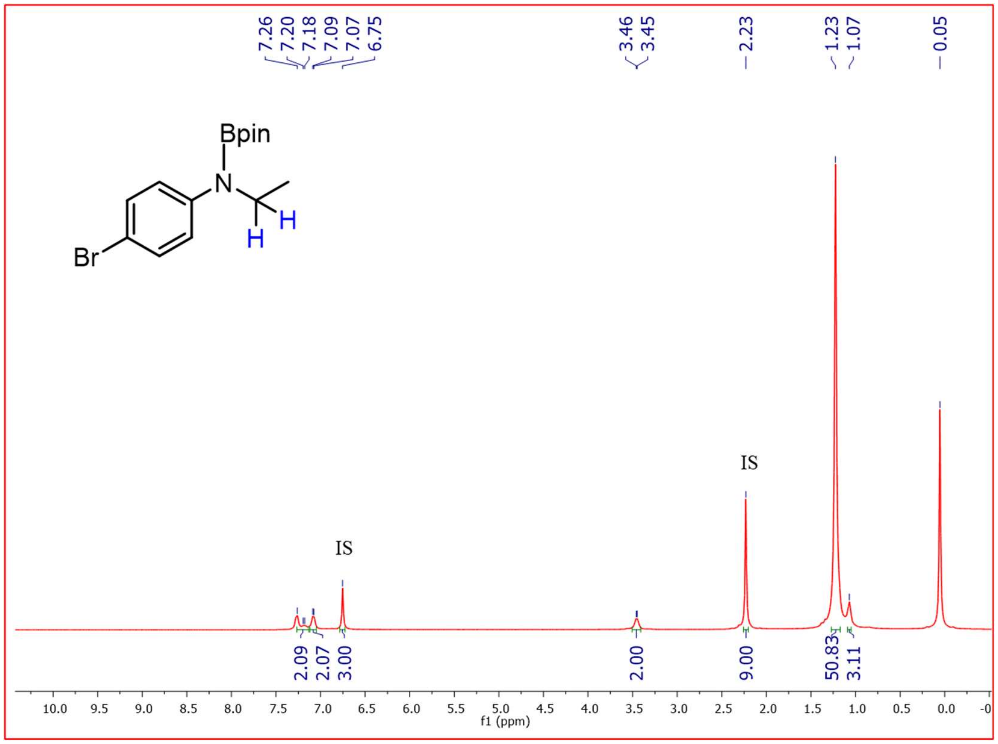
6.70
6.66
6.64
6.40
6.39
6.31
3.42
3.41
2.21
2.18
1.17
1.03
1.01
-0.00
Bpin
N
H
H
IS
IS
2.05
3.00
1.08
0.88
2.00
3.01
9.02
66.29
3.43
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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7.20
7.18
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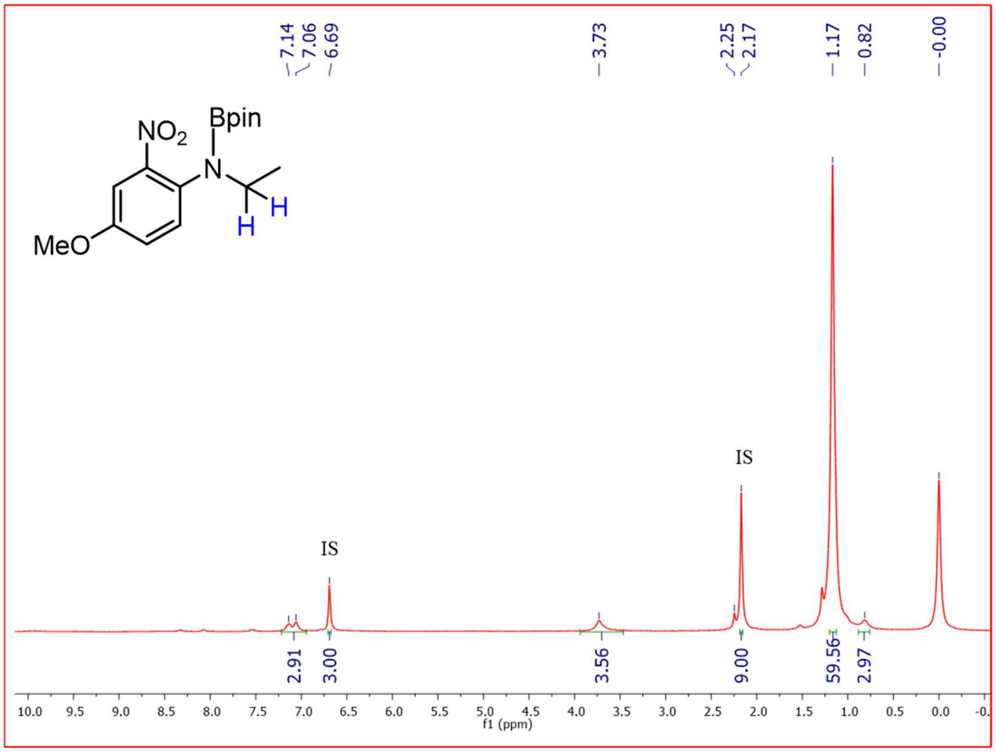
7.07
6.75
3.46
3.45
2.23
1.23
1.07
0.05
Bpin
N
H
H
Br
IS
IS
2.09
2.07
3.00
2.00
9.00
50.83
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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7.06
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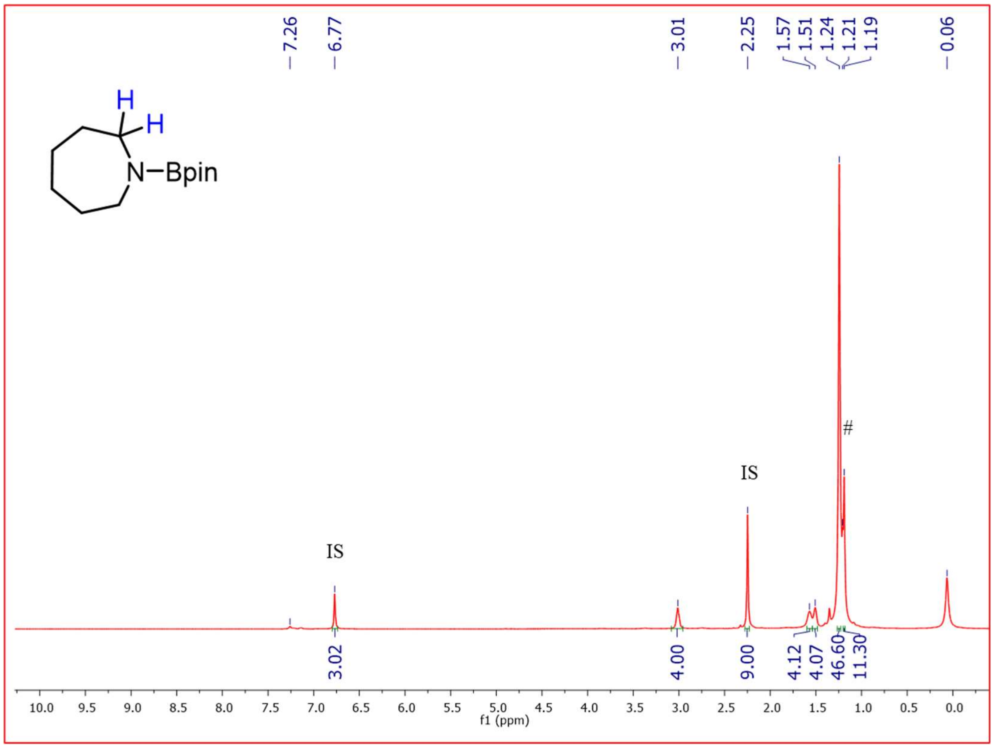
1.17
0.82
-0.00
NO2
Bpin
N
H
H
MeO
IS
IS
2.91
3.00
3.56
9.00
59.56
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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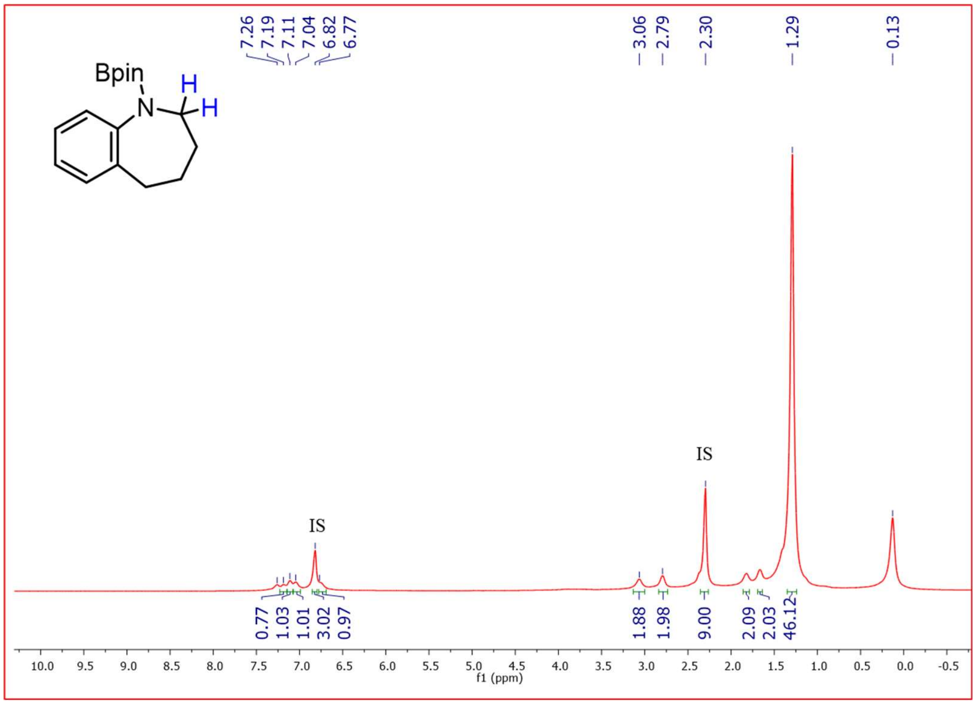
6.77
3.01
2.25
1.57
1.51
1.24
1.21
1.19
0.06
H
H
N–Bpin
IS
IS
#
3.02
4.00
9.00
4.12
4.07
46.60
11.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.26
7.19
7.11
7.04
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6.77
3.06
2.79
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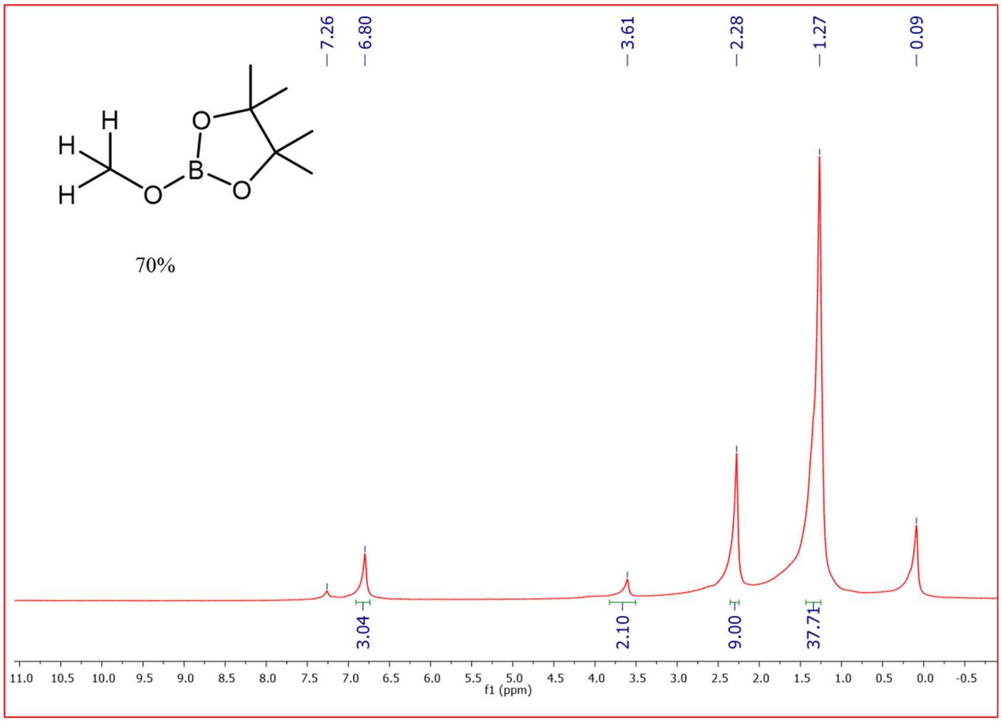
1.29
0.13
Bpin
N
H
H
IS
IS
0.77
1.03
1.01
3.02
0.97
1.88
1.98
9.00
2.09
2.03
46.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.26
6.80
3.61
2.28
1.27
0.09
H
H
H
O
B
O
O
70%
3.04
2.10
9.00
37.71
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)