

**Utilization of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$  as a Catalyst for the Hydroboration of  
Organic Substrates: Scope and Mechanistic Aspect**

विद्या वाचस्पति की  
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

A thesis submitted in partial fulfilment of the requirements of the degree of  
Doctor of Philosophy

द्वारा / By  
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भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे  
INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

2023



*Dedicated*

*To*

***Ammi & Abbu***

*and*

*Family Members*

*For their Love, Support and Encouragement...*

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Indian Institute of Science Education and Research (IISER), Pune

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### Certificate

It is hereby certified that the work described in this thesis entitled ***“Utilization of  $Ce[N(SiMe_3)_2]_3$  as a Catalyst for the Hydroboration of Organic Substrates: Scope and Mechanistic Aspect”*** submitted by ***Mr. Md Javed Hossain*** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.

Date: 27.10.2023

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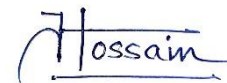
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## Synopsis

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The thesis entitled ***“Utilization of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> as a Catalyst for the Hydroboration of Organic Substrates: Scope and Mechanistic Aspect”*** is predominantly pivoted upon widespread experimental research of organo-lanthanide-catalysed hydroboration reaction of organic molecules using borating reagents e.g., pinacolborane (HBpin) and catecholborane (HBcat) to develop new synthetic methodologies for various organic transformations.

***“The development of a rational view of the nature of catalysis was thus absolutely dependent on the creation of the rate of chemical reaction.”***

-Wilhelm Ostwald (1853-1932), German Chemist, Nobel Prize-1909

Highly effective catalysts are indispensable in various applications, enhancing reaction outcomes and resource efficiency, with a growing resurgence of homogeneously catalyzed processes due to their mild reaction conditions and improved selectivity in industries. An efficient catalyst is of fundamental interest in the lanthanide-based catalytic hydroboration reactions. Throughout my Ph.D tenure, I dedicated significant effort to developing synthetic strategies and experimental exploration of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> with versatile catalytic applications in hydroboration reactions.

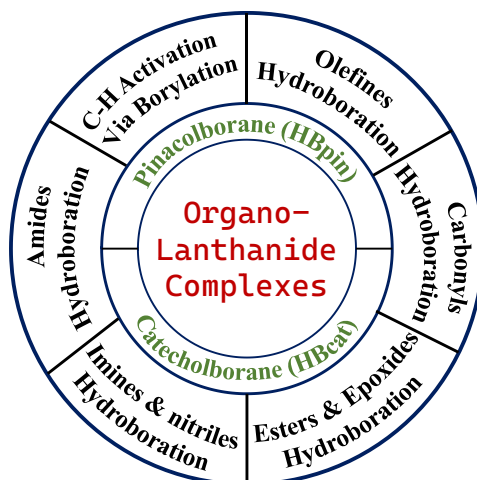
The proposed thesis comprises four chapters, which are mentioned below.

### **Chapter 1: Introduction of lanthanide complexes in hydroboration reaction**

In recent years, there has been significant interest in organo-lanthanide complexes that catalyze the organic transformations. Among these transformations, the hydroboration of olefins, carbonyl compounds, esters, epoxides, imines, nitriles or amides has been emerged as a crucial strategy for the preparation of organoborane compounds. These organoborane compounds are very emergent intermediates in synthetic chemistry to prepare value-added products.

After a brief introduction, this chapter will focus on organo-lanthanides as catalysts for (i) hydroboration of alkenes, (ii) hydroboration of carbonyl compounds, (iii) hydroboration of esters and epoxides, (iv) hydroboration of imines and nitriles, (v) hydroboration of amides and (vi) C–H bond activation using pinacolborane. The deliberation will delve into the catalytic performance of organo-lanthanide catalysts, kinetic analysis and mechanistic insights associated with these hydroboration reactions. The aim is to highlight the variations in catalytic

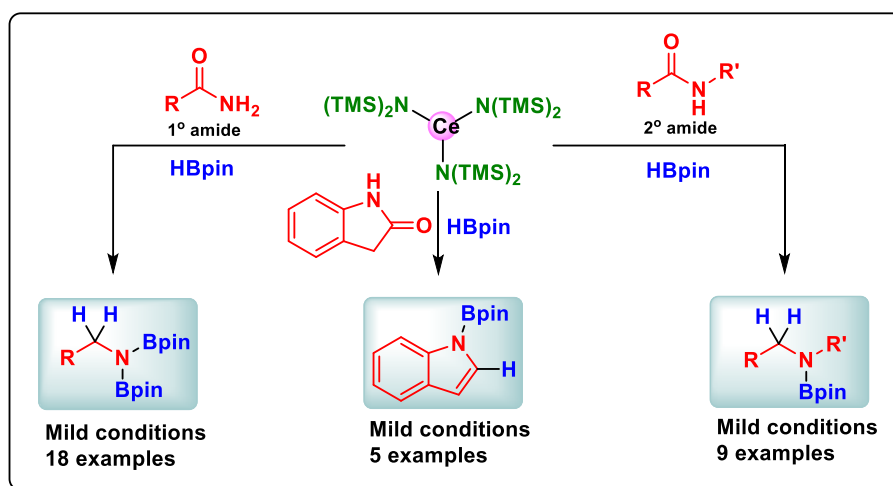
behaviour among different organo-lanthanide catalysts, emphasizing their unique characteristics and activities in synthetic organic chemistry.



Furthermore, this brief discussion will touch upon the challenges encountered in this field and outline potential future directions and motivation of my work. The study of organo-lanthanides in the context of hydroboration of olefins, carbonyl compounds, esters, epoxides, imines, nitriles or amides holds great promise for advancing the field of organic synthesis.

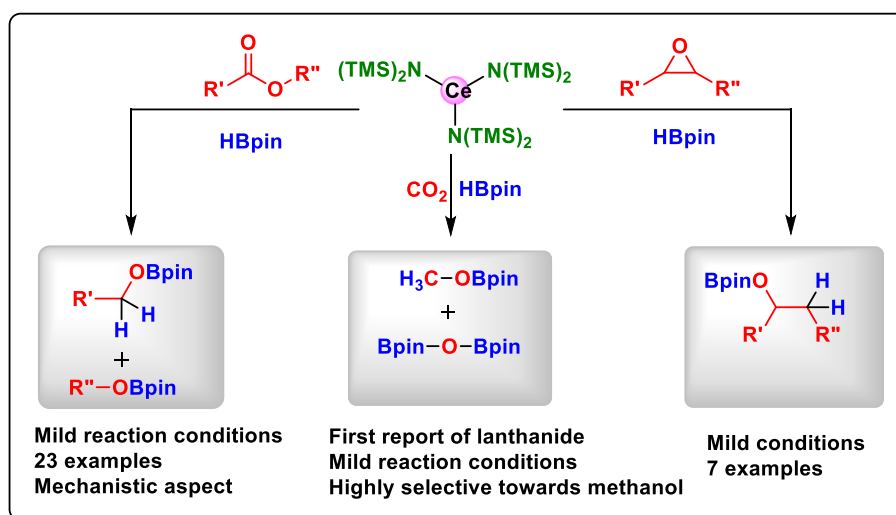
## Chapter 2: Deoxygenation of 1° and 2° amides with $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ under mild conditions

The pursuit of sustainable methods for synthesizing amines using readily available or easily synthesized catalysts under mild reaction conditions is a modern focal point in catalysis. Achieving a convenient, mild and straightforward approach to amide-to-amine reduction has long been a sought-after goal in catalysis. In this research, we harnessed the easily accessible  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst for the hydroboration of both 1° and 2° amides under mild conditions, leading to the formation of corresponding amines in high yields. It's worth noting that 1° amides are notoriously challenging to reduce and typically necessitate high temperatures. Furthermore, this methodology extends to the synthesis of indole derivatives and has been successfully demonstrated on a gram-scale, showcasing the wide-ranging applicability of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. To gain a deeper understanding of the mechanistic aspects of the  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed amide hydroboration reaction, we conducted an in-depth experimental study, which revealed that the formation of a tris-amidate species plays a decisive role in the catalytic pathway.



### Chapter 3: Reduction of esters, epoxides and $\text{CO}_2$ using $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ as a catalyst

In this chapter, we successfully achieved the challenging activation of the C–O bond using a readily synthesized and verily accessible homoleptic bis(trimethylsilyl) amides of cerium(III) complex under mild reaction conditions. Reduction of C–O bonds in esters and epoxides with  $\text{HBpin}$  was efficiently accomplished using just 1-2 mol% of the catalyst at 60 °C within a time frame of 5-12 hours, yielding borylated alcohols that can easily be hydrolysed into alcohols, which has significant industrial demand.

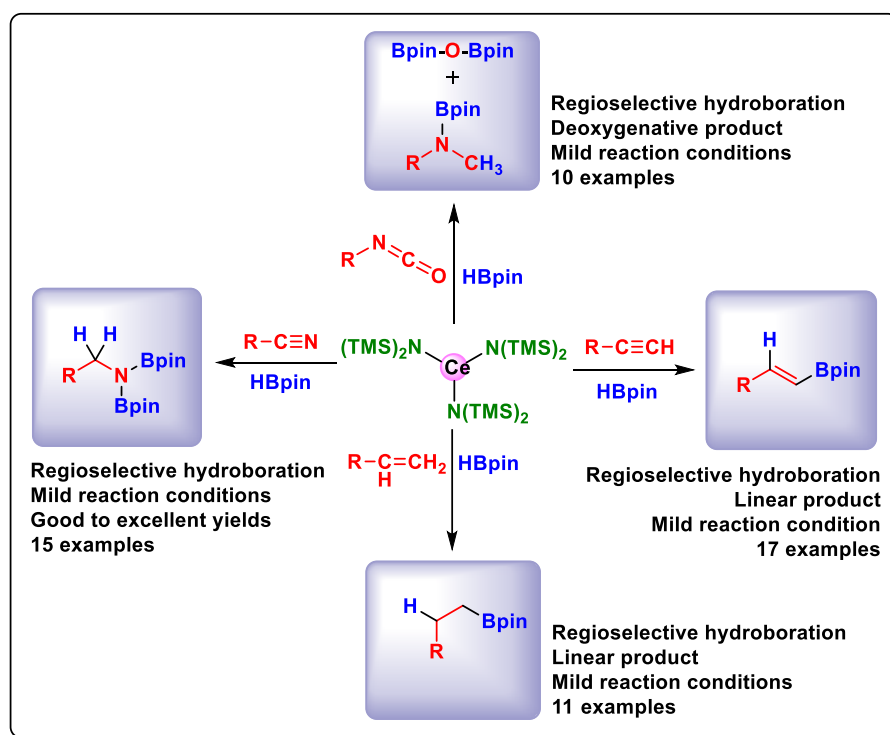


One of the most demanding and promising reactions involve the reduction of  $\text{CO}_2$  to highly selective borylated methanol, which was achieved using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. We investigated the impact of temperature on the hydroboration of  $\text{CO}_2$  at four different levels (25 °C, 45 °C, 65 °C and 85 °C). Remarkably, up to 99% yield was reached within 3 hours at 85 °C temperature. This exceptional efficiency was quantified with a turnover number (TON)

of 1145.8 and a turnover frequency (TOF) of  $\sim 382 \text{ h}^{-1}$  for the formation of borylated methanol from the reduction of  $\text{CO}_2$  with HBpin.

#### Chapter 4: Organo-lanthanide-catalysed hydroboration of multiple bonds ( $\text{C}=\text{C}$ , $\text{C}\equiv\text{C}$ , $\text{C}\equiv\text{N}$ and $\text{N}=\text{C}=\text{O}$ )

In this chapter, we have demonstrated the efficiency of organo-cerium  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst for the selective reduction of unsaturated and unactivated bonds e.g.,  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}\equiv\text{N}$  and  $\text{N}=\text{C}=\text{O}$  bonds in the presence of pinacolborane (HBpin) under comparatively mild reaction conditions. The hydroboration of alkenes and alkynes is associated with the formation of corresponding linear borylated products. The nitrile hydroboration reaction afforded corresponding borylated amines in the presence of 2 equiv. of HBpin. Surprisingly, the hydroboration of isocyanates delivered deoxygenated product *N*-boryl methyl amines with 3 equiv. of HBpin. Although, we treated the isocyanate with 1 equiv. and 2 equiv. of HBpin in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , but observed only deoxygenated products instead of monohydroborated or dihydroborated products.



In summary, we've showcased the efficacy of the readily synthesized and available complex  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a highly efficient catalyst for the hydroboration of diverse organic substrates, affording valuable chemicals.

## Abbreviations

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|                               |                                        |
|-------------------------------|----------------------------------------|
| acac                          | Acetylacetonate                        |
| CCDC                          | Cambridge Crystallographic Data Centre |
| CDCl <sub>3</sub>             | Deuterated chloroform                  |
| C <sub>6</sub> D <sub>6</sub> | Deuterated benzene                     |
| Cp*                           | 1,2,3,4,5-Pentamethylcyclopentadiene   |
| DFT                           | Density functional theory              |
| DIBAL-H                       | Diisobutylaluminium hydride            |
| DMAP                          | 4-(Dimethylamino)pyridine              |
| ee                            | Enantioselective                       |
| eq.                           | Equation                               |
| eqv.                          | Equivalent                             |
| equiv.                        | Equivalent                             |
| h                             | Hour                                   |
| HBcat                         | Catecholborane                         |
| HBpin                         | Pinacolborane                          |
| HRMS                          | High resolution mass spectrometry      |
| <i>i</i> Pr                   | Isopropyl                              |
| KIE                           | Kinetic isotope effect                 |
| Ln                            | Lanthanide                             |
| Me                            | Methyl                                 |
| Mes                           | 2,4,6-trimethylbenzene                 |
| MHz                           | Megahertz                              |
| min                           | Minute                                 |
| mL                            | Millilitre                             |
| mmol                          | Millimole                              |
| NMR                           | Nuclear magnetic resonance             |
| OTf                           | Triflate (trifluoromethanesulfonate)   |
| Ph                            | Phenyl                                 |
| Py                            | Pyridine                               |
| RDS                           | Rate determining step                  |
| RT                            | Room temperature                       |

|                        |                                      |
|------------------------|--------------------------------------|
| <i>t</i> Bu            | <i>tert</i> -butyl                   |
| tfc                    | 1,1,1-Trifluoro-3-(octylthio)acetone |
| THF                    | Tetrahydrofuran                      |
| TMEDA                  | Tetramethylethylenediamine           |
| TOF                    | Turnover frequency                   |
| Toluene-d <sub>8</sub> | Deuterated toluene                   |
| TON                    | Turnover number                      |
| XRD                    | X-ray diffraction                    |
| μL                     | Microlitre                           |
| 9-BBN                  | 9-Borabicyclo[3.3.1]nonane           |

## Publications

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1. **Hossain, M. J.**; Shah, B. K.; Khan, S. Deoxygenation of 1° and 2° Amides with Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> under Mild Conditions. *ACS Catal.* **2023**, *13*, 13577-13587.
2. **Hossain, M. J.**; Gopinath, J. S.; Tothadi, S.; Parameswaran, P.; Khan, S. NHSi/NHGe-Supported Copper Halide and Pseudohalide Complexes: Synthesis and Application. *Organometallics* **2022**, *41*, 3706-3717.
3. **Hossain, M. J.**; Parvin, N.; Shah, B. K.; Khan, S. Four-Coordinate Germylene and Stannylene and Their Reactivity Towards Se & Te\*\*. *Z. Anorg. Allg. Chem.* **2022**, *648*, e202200164. (*Special issue*)
4. **Hossain, M. J.**; Akhtar, R.; Khan, S. Luminescent Coinage Metal Complexes of Carbene. *Polyhedron* **2021**, *201*, 115151. (*Review article*)
5. Parvin, N.; **Hossain, M. J.**; George, A.; Parameswaran, P.; Khan, S. *N*-heterocyclic Silylene Stabilized Monocordinated Copper(I)–Arene Cationic Complexes and Their Application in Click Chemistry. *Chem. Commun.* **2020**, *56*, 273-276.
6. Parvin, N.; Mishra, B.; George, A.; Neralkar, M.; **Hossain, M. J.**; Parameswaran, P.; Hotha, S.; Khan, S. *N*-Heterocyclic Silylene/Germylene Ligands in Au(I) Catalysis. *Chem. Commun.* **2020**, *56*, 7625-7628.

## ***Chapter 1***

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# **Introduction of lanthanide complexes in hydroboration reactions**

---

## 1.1. Properties of lanthanides

*“Lanthanides...are crucial for everyday technologies”<sup>1</sup>*

Dr. Louise Natrajan

The *f*-block elements (lanthanides (**Figure 1.1**) and actinides) are collectively known as “*inner transition metals*”.<sup>2</sup> But the properties of the *f*-block elements are far away from the regular transition metals. The lanthanides are electropositive in nature and their complexes generally occur as Ln(III) with empty, half-filled or full-filled *f*-subshells.<sup>2</sup> “*Lanthanide contraction*” is an alluring property of the lanthanides.<sup>3</sup> Usually, lanthanides exhibit large flexible coordination numbers due to the presence of inner 4*f*-orbitals. Transition metal-based complexes typically demonstrate oxidative addition and reductive elimination reactions, whereas lanthanide complexes primarily participate in 1,2-insertion and  $\sigma$ -bond metathesis.<sup>4</sup>

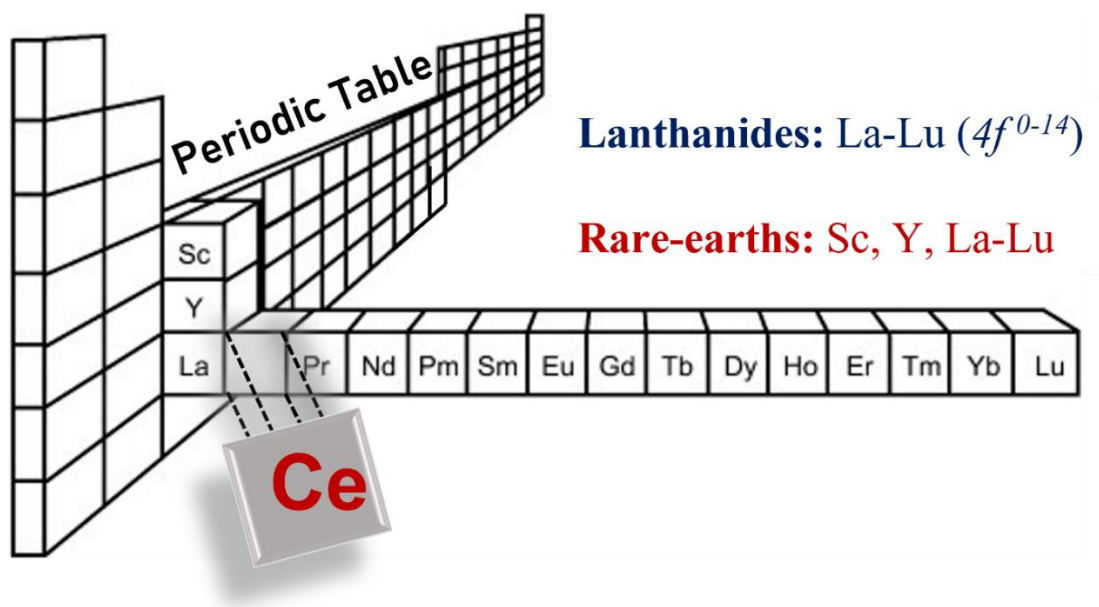


**Figure 1.1.** Rare-earth metals highlighted periodic table and the position of cerium among lanthanides.

The lanthanide complexes are less explored as compared to the transition metal complexes and main-group element compounds as catalysts in homogeneous catalysis. In certain areas of study, lanthanide complexes have gained popularity, particularly in the field of photoluminescence<sup>5</sup> and magnetism,<sup>6</sup> owing to their inherent paramagnetic properties. However, the lanthanides are less exposed as catalysts in homogeneous catalysis. Although a few complexes based on Yttrium (Y), Lanthanum (La), Praseodymium (Pr), Neodymium (Nd),

Samarium (Sm), Gadolinium (Gd), Dysprosium (Dy), Erbium (Er) and Ytterbium (Yb) have been reported as catalysts in polymerization,<sup>7</sup> hydroamination,<sup>8</sup> hydrofunctionalization<sup>9</sup> and hydroboration reactions.<sup>4,10</sup>

## 1.2. Importance of the hydroboration reaction

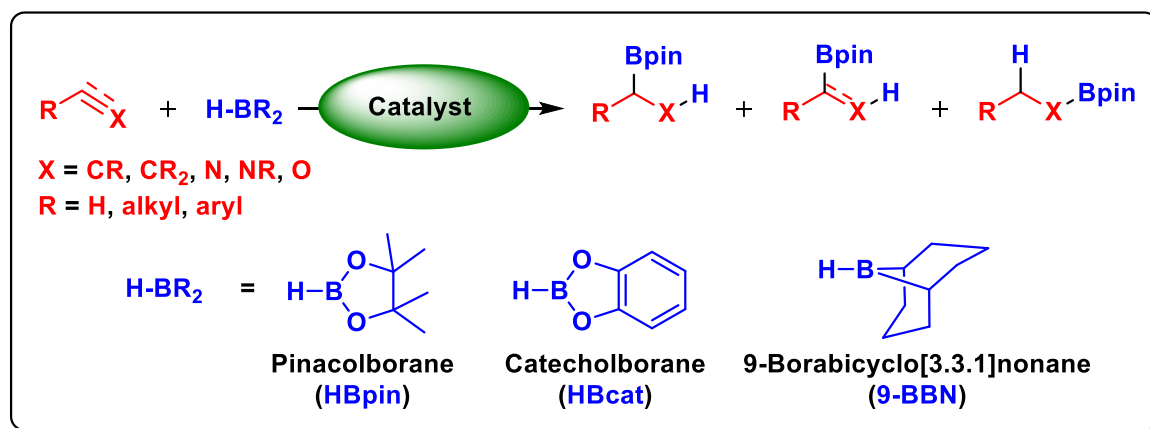
There are variant norms of synthetic organic methodologies which are well developed in homogeneous catalysis, *e.g.*; C-H activation,<sup>11</sup> hydrogenation,<sup>12</sup> cyclization,<sup>13</sup> alkylation,<sup>14</sup> cyanosilylation,<sup>15</sup> C-N coupling,<sup>16</sup> C-C coupling,<sup>17</sup> borylation,<sup>18</sup> hydrosilylation,<sup>19</sup> hydroboration<sup>20</sup> *etc.* Hydroboration reaction is one of the famous and juvenile in organic synthesis. This is also known as hydroborylation or hydrofunctionalization reaction. The hydroboration reaction is an atom-efficient reaction and generally mild reaction conditions are required to complete the reaction.<sup>10,20</sup> The catalysed products of the hydroboration reactions are immensely useful in industries as well as academia.<sup>4,10</sup> A general hydroboration reaction is displayed below (**Scheme 1.1**).

Hydroboration is indeed a valuable synthetic method in organic chemistry known for its efficiency and selectivity under mild conditions. Here are some key reasons why hydroboration is highly regarded for its efficiency and selectivity:

- **Regioselectivity:** Hydroboration typically proceeds with *anti*-Markovnikov addition, which means the boron atom added to the less substituted centres which is highly desirable for the synthesis of specific compounds.
- **Stereochemistry:** Hydroboration usually occurs with *syn*-addition, which means that the boron and hydrogen atoms are added to the same face.
- **Mild reaction conditions:** Hydroboration reactions are generally carried out under mild conditions, often at or near room temperature and atmospheric pressure, which minimizes the risk of side reactions or undesired chemical transformations.
- **High yield:** Hydroboration reactions tend to have high yields and the boron substituents can be easily modified or converted into other functional groups, making it versatile for further synthetic steps.
- **Compatibility with other functional groups:** Hydroboration is compatible with a wide range of functional groups, including carbonyls, halides and esters, making it useful in complex molecule synthesis.

- **Reductive workup:** After the hydroboration reaction, the boron compounds can be easily converted to the desired product by reductive workup, typically using alkaline hydrogen peroxide (*e.g.*, NaOH/H<sub>2</sub>O<sub>2</sub>). This step is generally straightforward and efficient.
- **Wide applicability:** Hydroboration reactions find applications in various areas of organic chemistry, including the synthesis of pharmaceuticals, agrochemicals and fine chemicals.

Overall, hydroboration is a highly efficient and selective method for the preparation of organoboron compounds, which can serve as valuable intermediates for the synthesis of a wide range of organic molecules. Its mild reaction conditions, regioselectivity and compatibility with other functional groups contribute to its widespread use in synthetic chemistry.



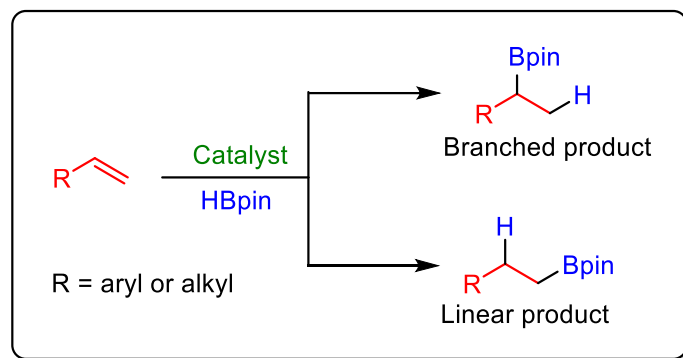
**Scheme 1.1.** General hydroboration reaction.

Pinacolborane (HBpin) is the most common reagent for hydroboration reactions due to its availability and lower price. Where catecholborane (HBcat) and 9-borabicyclo[3.3.1]nonane (3-BBN) are also used. The hydroboration process can reduce aldehyde, ketone, ester, alkene, alkyne, nitrile, amide etc. using pinacolborane (HBpin) or catecholborane (HBcat) to afford corresponding borylated products, which are easily hydrolysed.<sup>10</sup>

### 1.3. Lanthanide complexes in the hydroboration of alkenes

Alkene hydroboration is one of the most synthetically valuable methods for the preparation of myriad organic molecules of commercial and medicinal importance.<sup>21</sup> There are two possible products of the alkene hydroboration reaction with HBpin (**Scheme 1.2**). (i) Branched product

and (ii) Linear product. The selectivity of these products depends upon the catalyst and sometimes depends upon the substituent (R) *e.g.*, alkyl or aryl.



**Scheme 1.2.** Possible catalysed products of alkene hydroboration reaction with HBpin.<sup>21</sup>

In 1992, Marks and co-workers first reported the organo-lanthanides-catalysed hydroboration of alkenes using catecholborane (HBcat).<sup>22</sup> They demonstrated that the cyclopentadienyl-mediated lanthanum and samarium complexes **1-4** (**Chart 1.1**) are highly efficient catalysts for the hydroboration of olefin with HBcat for the synthesis of corresponding alcohols.<sup>22</sup> This cyclopentadienyl-lanthanides-catalysed hydroboration of olefins took place at room temperature and the internal alkene hydroboration also performed at the same ambient temperature. The cyclopentadienyl-lanthanum complex elucidated the effective catalytic rate  $\text{TOF} = 200 \text{ h}^{-1}$  (for 1-hexene with 25 to 100-fold stoichiometric excess) and  $\text{TOF} = 50 \text{ h}^{-1}$  (for cyclohexene with 25 to 100-fold stoichiometric excess) by using HBcat to produce 1-hexanol and phenol, respectively (**Scheme 1.3**). The catalysed products were highly regioselective followed by *anti*-Markovnikov rule. The authors hypothesized that the rate of the hydroboration reaction was dependent on both the size of the metal ions (larger size, higher rate) and the size of the ligands (more open ancillary ligation, higher rate). Also, higher rates of the reaction were observed for the terminal alkenes as compared to the di- or tri-substituted or internal alkenes.<sup>22</sup> The proposed mechanism of organo-lanthanide-catalysed alkene hydroboration with HBcat was disclosed by Marks and co-workers by forming an active species, lanthanide hydride (**1a**), henceforth *anti*-Markovnikov alkene insertion to form **1b** (**Scheme 1.4**).

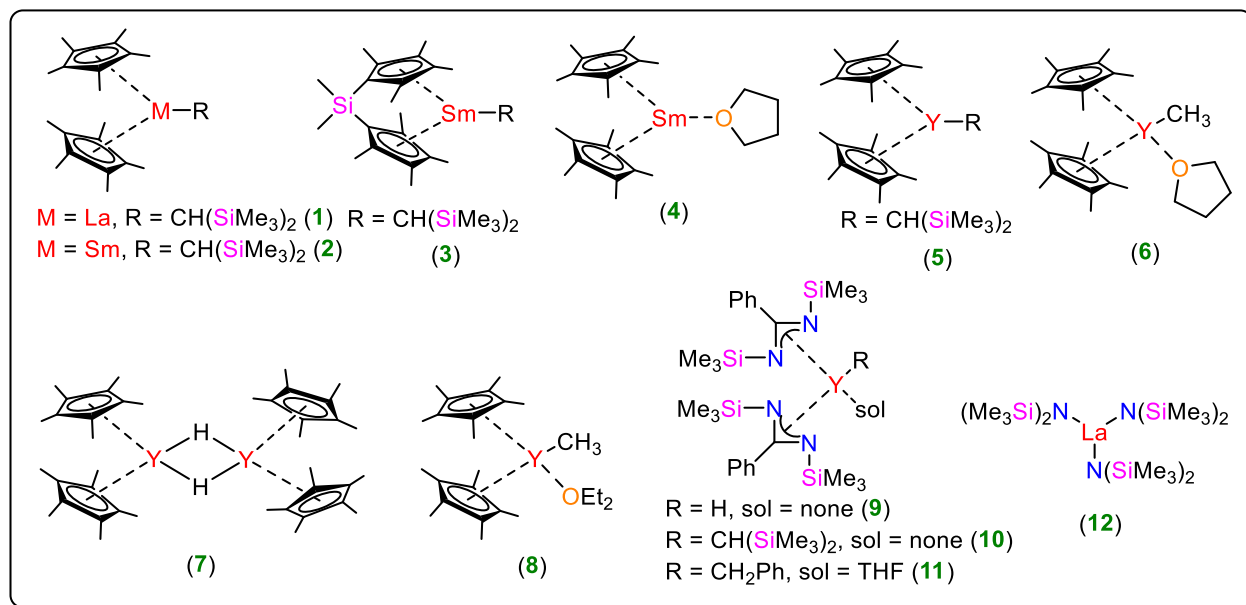
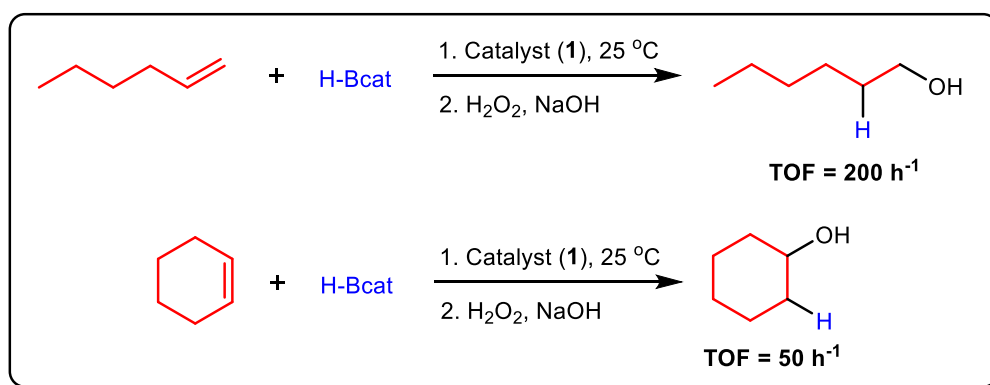
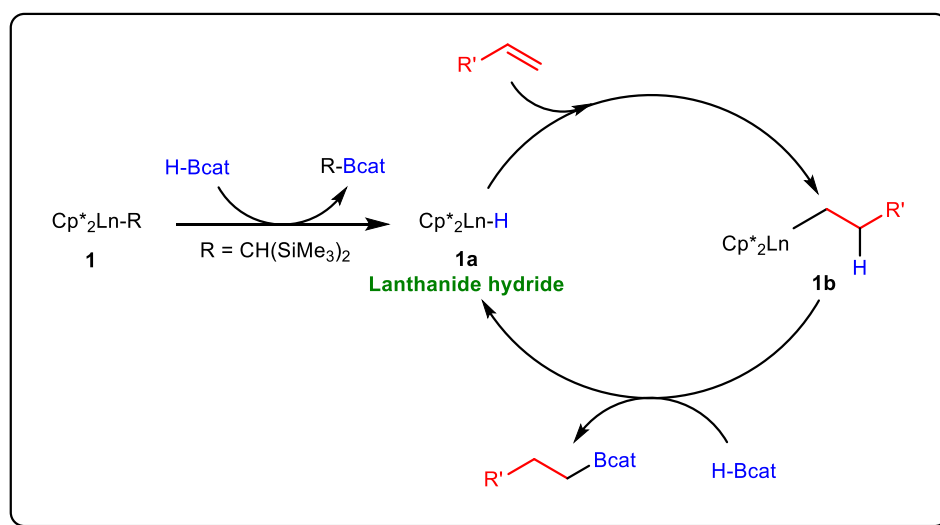


**Chart 1.1.** Reported organo-lanthanide complexes in alkenes hydroboration reaction.



**Scheme 1.3.** Hydroboration of 1-hexene and cyclohexene with HBcat using complex 1.<sup>22</sup>



**Scheme 1.4.** Mechanistic pathway of organolanthanide-catalysed alkene hydroboration using HBcat proposed by Marks and co-workers in 1992.<sup>22</sup>

In 1993, Evans and co-workers manifested the easily accessible  $\text{SmI}_3$ ,  $\text{NdI}_3$ ,  $\text{PrI}_3$ ,  $\text{LuI}_3$ ,  $(t\text{BuO})\text{SmI}_2$ ,  $\text{Sm}(\text{OiPr})_3$ ,  $\text{Eu}(\text{tfc})_3$  and  $\text{ScI}_3$ -catalysed olefins hydroboration with catecholborane (HBcat) at ambient temperature in 18 hours in THF solvent to afford the corresponding products, whereas  $\text{SmBr}_3$ ,  $\text{SmCl}_3$ ,  $\text{SmF}_3$ , and  $\text{Sm}(\text{OTf})_3$  were off towards olefin hydroboration reaction.<sup>23</sup>

Tueben and co-workers introduced a series of yttrium complexes based on pentamethylcyclopentadienyl (**5-8**) and benzamidinate (**9-11**) ligand backbone, which behaved as active catalysts for hydroboration of 1-hexene with HBcat.<sup>24</sup> But, all the complexes (**5-11**) were comparatively less effective than complex **1** because of the smaller size of yttrium and their increased  $\sigma$ -bond metathesis transition state energy.<sup>10</sup> They also proposed the mechanism of 1-hexene hydroboration with HBcat *via* hydride formation.<sup>24</sup>

The conventional reactivity pattern in the hydroboration of alkenes is dependent upon the steric effect of the alkene and it emulates the order as mono- > di- > tri- > tetra-substituted carbon-carbon double bonds. In 1995, Villiers and Ephritikhine disclosed a completely contradictory result, which was observed in  $\text{UCl}_4$ - and  $\text{NdCl}_3$ -catalysed hydroboration of alkenes in the presence of the  $\text{LiBH}_4$  reactions.<sup>25</sup>

Livinghouse and co-workers first time applied the homoleptic lanthanum amide, tris[bis(trimethylsilyl)amide] (**12**) as a catalyst for the hydroboration of alkenes with pinacolborane (HBpin) as a hydroborating agent.<sup>26</sup> The electron-donating group (*e.g.*,  $\text{OCH}_3$ ) substituted styrene afforded a relatively higher yield than the electron-withdrawing group (*e.g.*,  $\text{CF}_3$ ) substituted styrene, whereas upon increasing the alkene substitution the rate of the hydroboration reaction was curtailed.<sup>26</sup> In this literature, authors alluded to the lanthanum-catalysed alkene hydroboration with HBpin also imitated *via* lanthanum-hydride formation.

**Cyclization/boration reaction of 1,5- and 1,6-dienes:**

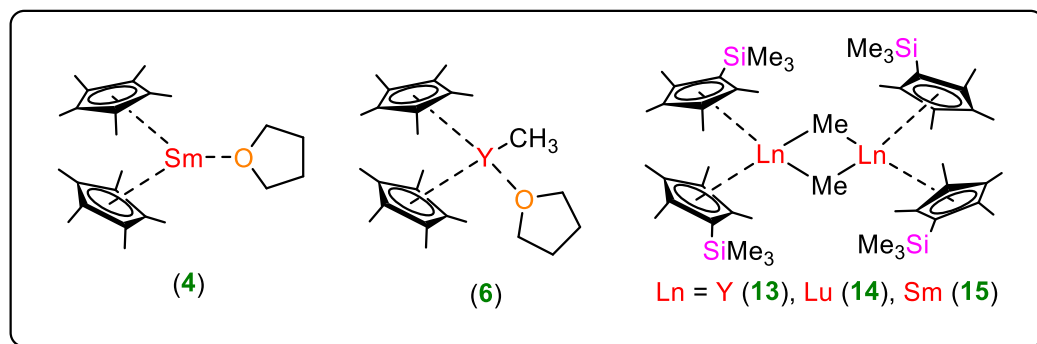
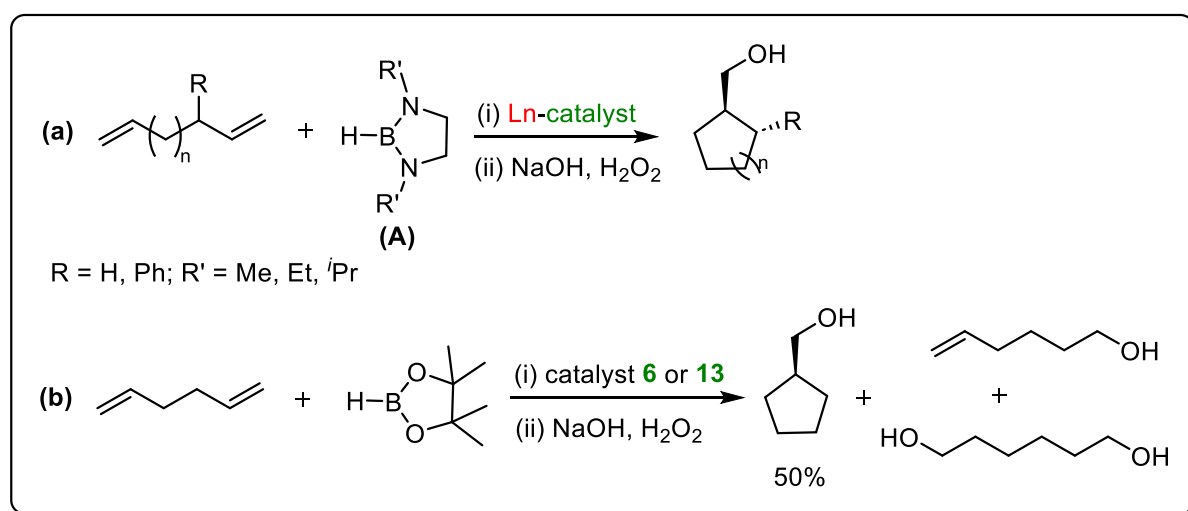


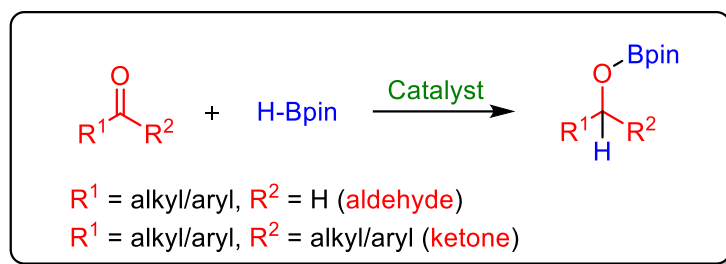
**Chart 1.2.** Reported organo-lanthanide complexes for cyclization/boration of 1,5- and 1,6-dienes.

In 2001, Molander and co-workers established a protocol for cyclization/boration reaction (**Scheme 1.5**) catalysed by organo-lanthanide complexes **4**, **6**, **13-15** (**Chart 1.2**).<sup>27</sup> This reaction resulted in the formation of primary alcohols containing five- and six-membered rings after oxidative workup. In the presence of HBcat and HBpin, complex **4** was ineffective towards cyclization/boration reaction, but in the presence of organoborane (**A**), complex **4** was effective towards cyclization/boration of 1,5-hexadiene (**Scheme 1.5a**). Whereas, complex **6** was inactive towards cyclization/boration reaction in the presence of organoborane (**A**), but active towards cyclization/boration reaction in the presence of HBpin (**Scheme 1.5b**). After that, they synthesized complexes **13-15**, which were highly efficient towards cyclization/boration reaction in the presence of **A** and delivered good yields.



**Scheme 1.5.** Ln-catalysed cyclization/boration of 1,5- and 1,6-dienes using borane.<sup>27</sup>

## 1.4. Lanthanide complexes in the hydroboration of aldehydes and ketones



**Scheme 1.6.** Hydroboration of carbonyl compounds with HBpin.

The reduction of carbonyl compounds is evermore an essential transformation in synthetic organic chemistry. The direct hydrogenation method is well explored and using a strong base like  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$  and  $\text{B}_2\text{H}_6$  sometimes hampers the reaction and shows intolerance in the other substituted functional group, which reduces the selectivity of the reaction.<sup>28</sup> The hydroelementation (*e.g.*, hydrosilylation, hydroboration) reactions are quite renowned in this field.<sup>29</sup> The reaction involving the hydroboration of ketones and aldehydes with HBpin resulted in the formation of borylated alcohols (**Scheme 1.6**). The catalyzed hydroborated products are used in the synthesis of fine chemicals, drug discovery and valuable renewable sources of fuels and chemical feedstocks.<sup>30</sup> The *s*-*p*-*d*-block metal-catalyzed hydroboration reactions have been broadly investigated over the last two decades.<sup>31</sup> Marks and co-workers reported the first instances of carbonyl hydroboration mediated by organo-lanthanide complexes in 2017. In this groundbreaking work, they achieved the swift and efficient hydroboration of ketones and aldehydes using HBpin to afford eco-friendly alcohols in the presence of homoleptic lanthanide amide complexes.<sup>32</sup> The catalyst **12** exhibited remarkable efficiency in the hydroboration of carbonyl compounds, up to turnover frequency (TOF)  $40,000 \text{ h}^{-1}$ . Complexes **16-18** exhibited as efficient catalysts for carbonyl hydroboration, albeit with a relatively lower yield rate as compared to complex **12**. Excellent yields were observed for all substrates of aldehydes and ketones in the presence of very low catalyst loading (0.01-1 mol%) at room temperature within a few minutes (15-90 min), irrespective of electron withdrawing and electron donating group substituted substrates, along with weak functional group tolerance.

The rate laws for hydroboration of ketones and aldehydes were determined separately, employing dicyclohexyl ketone and cyclohexanecarbaldehyde as substrates, respectively and established the overall rate equations (Eq. 1 & 2).

$$\text{rate} = k[\mathbf{12}]^1[\text{ketone}]^1[\text{HBpin}]^1 \quad (\text{Eq. 1})$$

$$\text{rate} = k[\mathbf{12}]^1[\text{aldehyde}]^0[\text{HBpin}]^0 \quad (\text{Eq. 2})$$

Suggesting, *first-order* dependence in **[12]**, **[ketone]** and **[HBpin]**, declaring all the components played a role in the turnover-limiting step of the ketone hydroboration reaction. First-order dependence with respect to catalyst **12** was observed, but surprisingly, *zeroth-order* dependence with respect to aldehyde and HBpin was audited for the aldehyde hydroboration reaction.

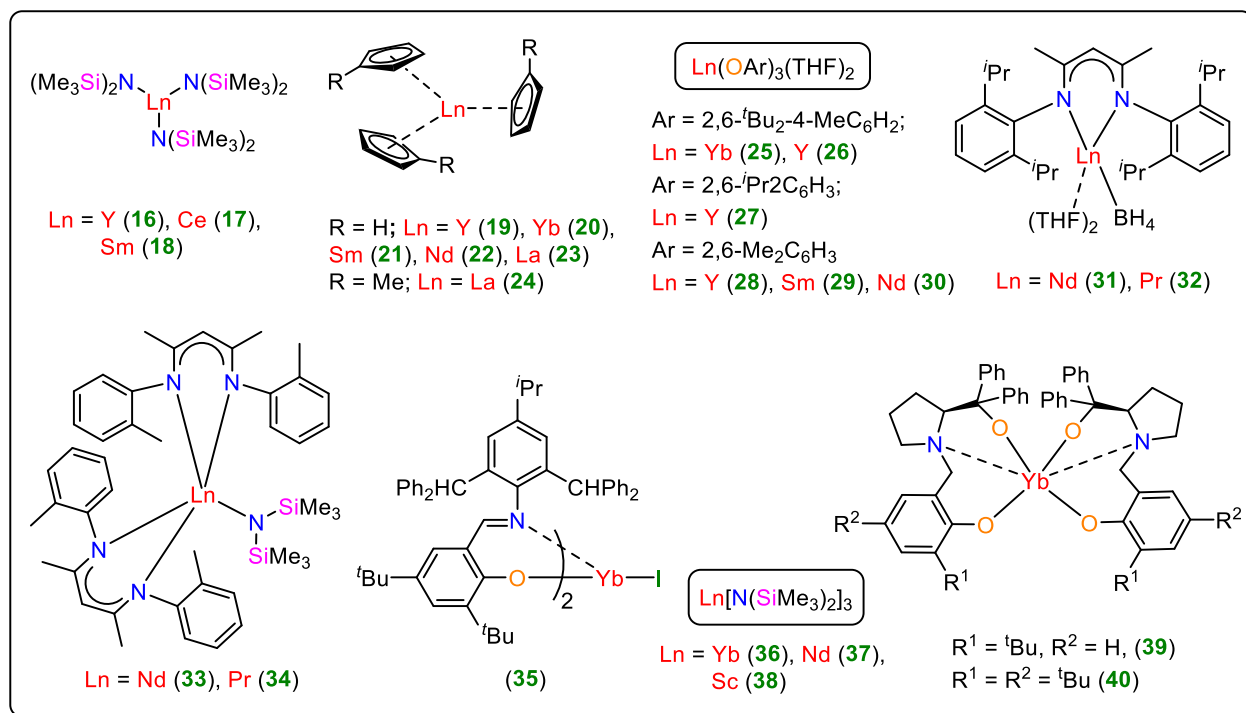
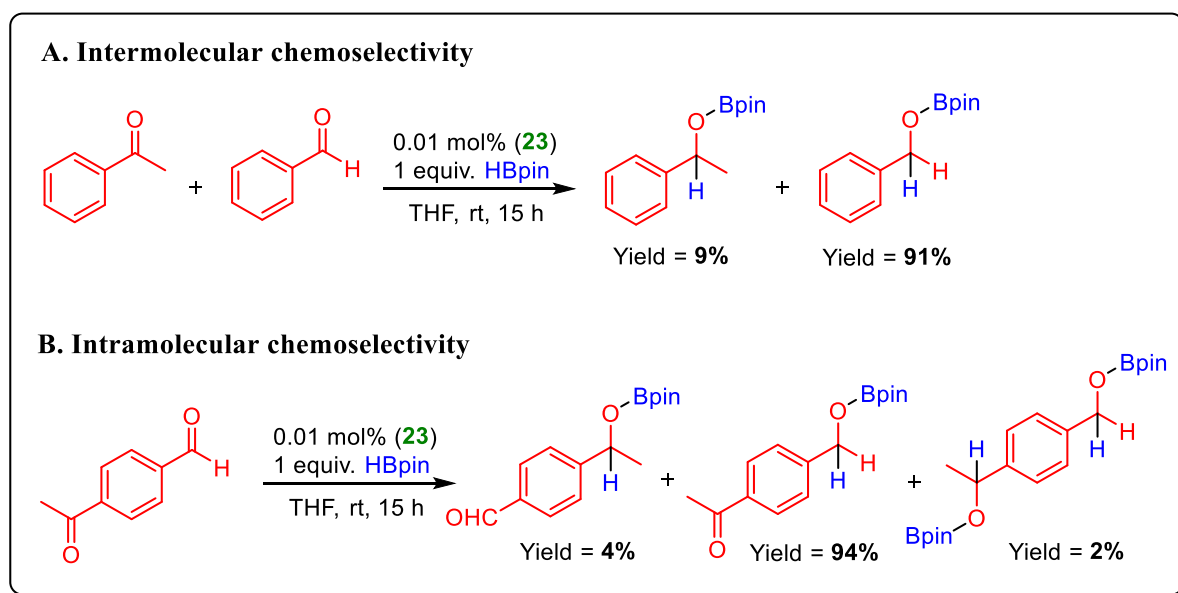


**Chart 1.3.** Reported lanthanide complexes in aldehydes and ketones hydroboration reaction.

Xue, Bao, Shen and their co-workers introduced homoleptic cyclopentadienyl lanthanide complexes **19-24** (**Chart 1.3**) and demonstrated exceptional catalytic performance in the hydroboration of carbonyl compounds using HBpin as the borating agent in 2017-2018.<sup>33</sup> These complexes exhibited remarkable selectivity, effectively hydroborating the carbonyl bond while remaining unreactive toward other functional groups, such as halides and nitro groups. Possibly owing to the less electrophilicity and increased steric hindrance around the carbonyl centre in ketones, they typically exhibited slower reaction rates when compared to their aldehyde counterparts. Authors observed aldehydes are preferentially reduced over ketones under identical reaction conditions (**Scheme 1.7**).<sup>33</sup>



**Scheme 1.7.** Comparative investigation of aldehyde/ketone hydroboration selectivity.<sup>33</sup>

The kinetic studies revealed first-order dependence on catalyst **23**, aldehyde/ketone and HBpin, which is demonstrated in the Equations 3 and 4.

$$\text{rate} = k[\mathbf{23}]^1[\text{ketone}]^1[\text{HBpin}]^1 \quad (\text{Eq. 3})$$

$$\text{rate} = k[\mathbf{23}]^1[\text{aldehyde}]^1[\text{HBpin}]^1 \quad (\text{Eq. 4})$$

In 2018, Xue, Bao, and co-workers synthesized a series of lanthanide aryloxide complexes **25-30** (**Chart 1.3**) and utilized them as catalysts in the hydroboration of carbonyl compounds with HBpin.<sup>34</sup> They suggested that in the hydroboration reaction, complexes that contain bulkier ligands exhibit superior catalytic activities when compared to complexes with less sterically hindered ligands. This finding implies that the steric properties of the ligands in the catalyst play a crucial role in enhancing the reactivity and efficiency of the catalytic process.

The use of bulkier ligands can have several beneficial effects in catalysis:

1. Increased selectivity: Bulkier ligands can help to control the selectivity of the reaction by shielding certain parts of the catalyst from reacting with unwanted substrates. This can lead to improved selectivity of the desired product.
2. Enhanced catalyst stability: Bulkier ligands can provide a protective environment around the catalytically active centre, preventing undesired side reactions or catalyst degradation.
3. Improved substrate accessibility: While bulky ligands may hinder substrate approach in some cases, they can also create well-defined and sterically favourable environments

for specific reactions, facilitating the binding of substrates and accelerating the reaction rate.

4. Greater coordination flexibility: Bulkier ligands can offer more flexible coordination geometries, allowing the catalyst to adapt to the specific requirements of the reaction.

Overall, the choice of ligands in a catalytic system can significantly impact its performance, and sometimes, bulkier ligands may be preferred to enhance the catalytic activity and selectivity for particular reactions.

In 2018, Xue, Shen and co-workers introduced two types of lanthanide complexes,  $\beta$ -diimide bivalent lanthanide borohydride complexes (**31-32**) and bis( $\beta$ -diimide) lanthanide complexes (**33-34**), as catalysts for the hydroboration reaction of carbonyl compounds (aldehydes and ketones) using HBpin to synthesize alcohols.<sup>10</sup> Ma and co-workers utilized the ytterbium iodide complex **35** as an efficient catalyst for aldehyde and ketone hydroboration.<sup>35</sup> They demonstrated that the hydroboration of more sterically bulky ketone substrates was less effective and required higher catalyst loading compared to aldehyde substrates. This observation is expected and can be attributed to the steric hindrance caused by the bulky groups attached to the ketone molecule. Steric hindrance occurs when the bulky substituents on a molecule hinder or block the approach of other molecules, including reactants and catalysts. In the context of hydroboration reactions, the presence of bulky groups on ketones can make it more challenging for the borating agent and the catalyst to access and react with the carbonyl group of the ketone. As a result, higher catalyst loading or higher reaction temperature or longer reaction time is often required to overcome this steric hindrance and promote the reaction to proceed at a reasonable rate. In contrast, aldehydes typically have less steric hindrance around the carbonyl group compared to ketones because they have one fewer substituent. Therefore, they are often more reactive and require lower catalyst loading for efficient hydroboration. Overall, this observation highlights the importance of considering steric effects when designing and optimizing catalytic reactions, especially when dealing with bulky substrates.

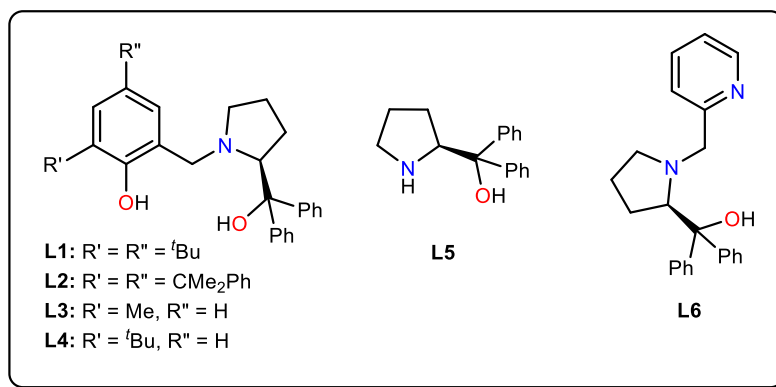
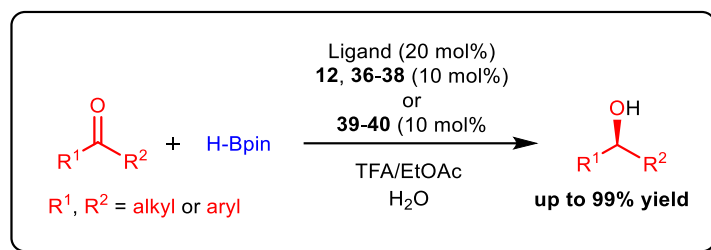


**Chart 1.4.** Ligands for the enantioselective hydroboration of ketones.<sup>36</sup>

In 2018, Yao, Zhao, and co-workers unveiled a notable achievement, which is the sole example of an enantioselective reduction of ketones catalysed by lanthanide complexes (**12**, **36-40**) featuring phenoxy-modified chiral prolinols (**Chart 1.4**, **Scheme 1.8**).<sup>36</sup> This finding represents a significant contribution to the field of asymmetric catalysis, showcasing the potential of lanthanide complexes in promoting selective ketone hydroboration with the assistance of chiral prolinols. Also, they introduced complex **39** as a catalyst due to its structural resemblance to the in situ formed active species and better yields of up to 99% and *ee* value of up to 95%. Complex **40** was an efficient catalyst for the enantioselective hydroboration of  $\alpha, \beta$ -unsaturated ketone to alcohol with up to 99% yield and up to 87% *ee* value.<sup>36</sup>



**Scheme 1.8.** Hydroboration of ketones an enantioselective approach.<sup>36</sup>

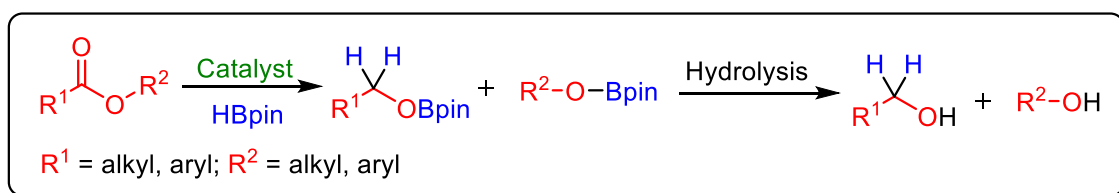
## 1.5. Lanthanide complexes in the hydroboration of esters and epoxides

### Ester hydroboration with HBpin using lanthanide catalyst:

The selective reduction of esters is indeed an important transformation in organic chemistry. It involves the conversion of ester functional groups ( $\text{R}^1\text{COOR}^2$ ) into alcohols ( $\text{ROH}$ ) or aldehydes ( $\text{RCHO}$ ). There are several synthetic methodologies are reported for selective esters reduction.

- a) **Using strong reducing agents:**  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ ,  $\text{BH}_3$  etc., which can reduce esters to primary alcohols. DIBAL-H (diisobutylaluminum hydride), amalgamated zinc ( $\text{Zn-Hg}$ ) etc. are used for the selective reduction of esters to aldehydes.<sup>37</sup>
- b) **Direct hydrogenation method:** Selectively esters can be reduced to alcohols in the presence of the metal catalyst and hydrogen gas.<sup>38</sup>
- c) **Hydroelementation reaction:** Hydrosilylation (used silane) and hydroboration (used borating agent) are well known for the reduction of esters to alcohols.<sup>39</sup>

The choice of reducing agent and conditions depends on the specific ester and the desired product. Selective reduction of esters is a fundamental transformation in organic synthesis, as it allows chemists to modify and functionalize molecules for various applications, including drug discovery, material science and the production of fine chemicals.<sup>40</sup> Main-group element<sup>41</sup>-catalyzed ester hydroboration has been introduced from the last decade (**Scheme 1.9**).



**Scheme 1.9.** Hydroboration of ester with HBpin to alcohol.

In 2019, Sadow and co-workers introduced homoleptic tris(alkyl)lanthanum complex  $\text{La}[\text{C}(\text{SiHMe}_2)_3]_3$ , which is highly efficient toward C-O bond cleavage in the hydroboration of esters and epoxides.<sup>42</sup> Alkyl esters, alkyl benzoates and aryl benzoates were reduced to borylated alcohols using **41** (5 mol%) as a catalyst (**Chart 1.5**) at room temperature with excellent yields. The catalyst **41** was highly chemoselective towards esters hydroboration with HBpin. Electron-withdrawing group substituted esters afforded higher yields as compared to electron-donating group substituted esters. They demonstrated the reactivity of catalyst **41** and HBpin can lead to the formation of lanthanum hydride species. However, those lanthanum hydride species exhibited notable efficiency towards ketones but not esters. The authors described the mechanistic pathway of ester hydroboration with HBpin using catalyst  $\text{La}[\text{C}(\text{SiHMe}_2)_3]_3$  by *in-depth* kinetic studies. They established the experimental rate law with a ternary-order rate constant ( $k'$ ) in Equation 5.

$$\text{rate} = k'[\mathbf{41}]^1[\text{ester}]^1[\text{HBpin}]^1 \quad (\text{Eq. 5})$$

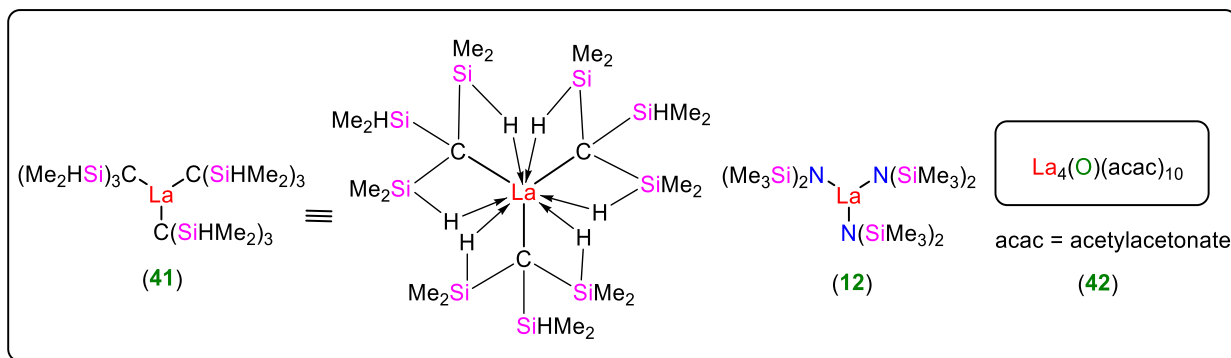
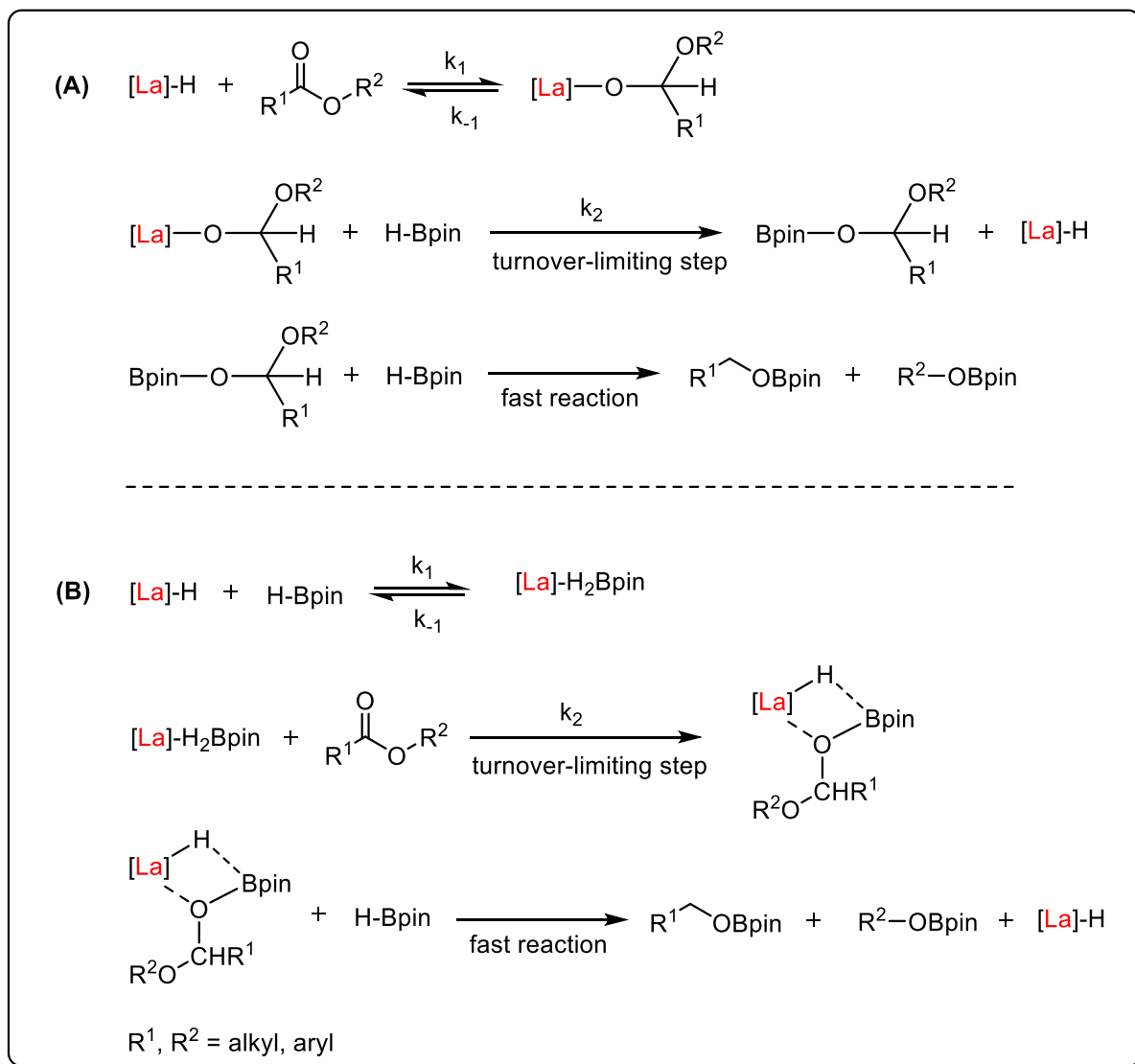


**Chart 1.5.** Reported lanthanide complexes for ester and epoxide hydroboration reaction. Catalyst **41** for ester & epoxide hydroboration and catalyst **12** for ester hydroboration.

Sadow and co-workers introduced two possible reaction mechanisms consisting of experimental rate law. (a) “Ester-first” mechanistic pathway: A reversible interaction of  $[\text{La}]-\text{H}$  with the ester to form  $[\text{La}]-\text{OCHR}^1(\text{OR}^2)$  and the irreversible reaction of  $[\text{La}]-\text{OCHR}^1(\text{OR}^2)$  with HBpin (**Scheme 1.10A**). (b) “HBpin-first” mechanistic pathway: A reversible formation of lanthanum hydridoborate  $[\text{La}]-\text{H}_2\text{Bpin}$  from  $[\text{La}]-\text{H}$  and HBpin and irreversible binding of  $[\text{La}]-\text{H}_2\text{Bpin}$  with ester (**Scheme 1.10B**). Both the mechanistic pathways A and B are in accordance with the results of kinetic experiments, notwithstanding, pathway A is considered less possible due to the reactivity of in-situ produced hydridolanthum species. They concluded that lanthanum hydride is effective for the chemical transformation of ketones, likely involving processes such as carbonyl insertion and alkoxide transfer to boron. Nevertheless, for the more complex and challenging reduction of esters, the presence of  $[\text{La}]-\text{H}_2\text{Bpin}$  is required to facilitate the reactions.



**Scheme 1.10.** Mechanistic pathway of ester hydroboration using catalyst **41**.<sup>42</sup>

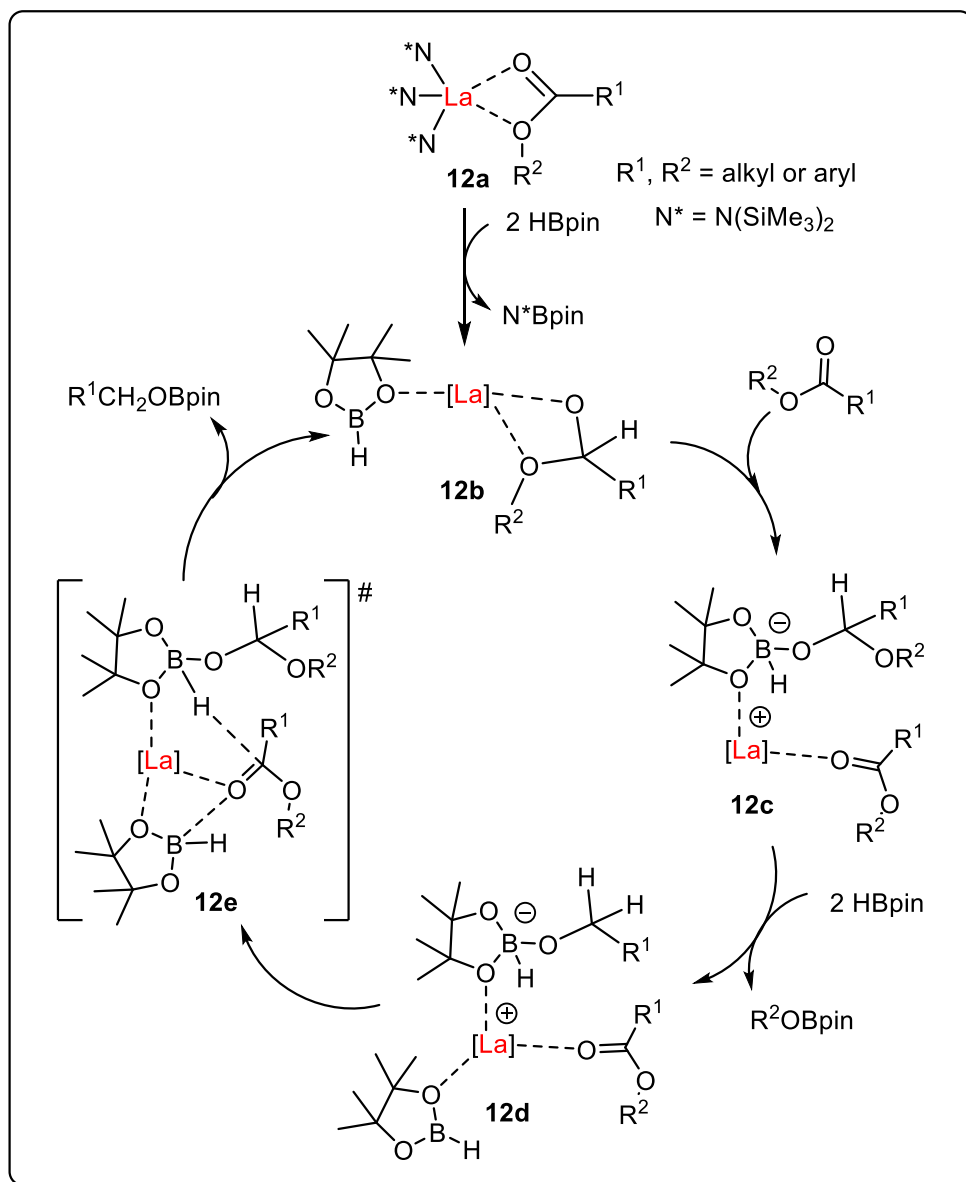
In 2019, Marks and co-workers introduced a synthetic methodology to synthesize alcohols from the reduction of esters with HBpin by using a highly active, very efficient and selective catalyst **12**.<sup>43</sup> A wide range of esters were used for hydroboration reactions using 1 mol% of catalyst **12** at ambient reaction conditions. Steric hindrance at the alkoxy position ( $\text{R}^2$ ) had a notable negative impact on reaction time for hydroboration of esters, increasing the bulkiness at the alkoxy position of the ester, reduces the reaction rate. In contrast, steric hindrance at the acetyl position ( $\text{R}^1$ ) had minimal influence on the reactivity of the hydroboration reaction. In addition to the steric effect, there was a noteworthy increase in turnover number observed for substrates that had electron-withdrawing substituents at the acetyl position ( $\text{R}^1$ ). Furthermore, the electron density on the alkoxy position ( $\text{R}^2$ ) was found to be a crucial factor in determining reactivity toward hydroboration reaction. Specifically, the introduction of a phenyl group at the

R<sup>2</sup> position led to a significant reduction in reaction rate. They demonstrated that catalyst **12** is highly selective towards the ester group for the reaction. The kinetic studies of the ester hydroboration reaction unveiled that the reaction rate is *first-order* with respect to catalyst **12** and *zeroth-order* concerning both HBpin and ester. This relationship is accurately described by the rate law expressed in Equation 6.

$$rate = k[\mathbf{12}]^1[ester]^0[HBpin]^0 \quad (\text{Eq. 6})$$

Based on the control experiments and DFT (density functional theory) calculations, a plausible mechanism was proposed in **Scheme 1.11**. The proposed mechanism:

- (i) Activation of the ester coordinated complex **12a** with HBpin initiates the reaction.
- (ii) Coordination of another molecule of HBpin results in the formation of the hemiacetal active species **12b**.
- (iii) In this intermediate, the HBpin molecule promotes the dissociation of the La-O bond and the formation of the B-O bond, giving rise to intermediate **12c**. This intermediate was simultaneously stabilized by ester molecule.
- (iv) Intramolecular rearrangement occurs, leading to the formation of the product R<sup>2</sup>OBpin.
- (v) Subsequently, there was coordination of another HBpin molecule, resulting in intermediate **12d**.
- (vi) The final step involves hydride transfer from the boron atom of the hydroborate-lanthanum complex to the coordinated ester **12e**, regenerating the active species **12a**.
- (vii) Simultaneously, the product R<sup>1</sup>CH<sub>2</sub>OBpin was released.

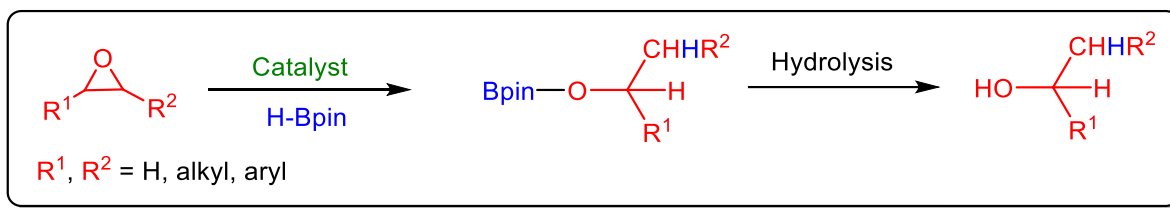


**Scheme 1.11.** Proposed mechanistic cycle of ester hydroboration.<sup>43</sup>

This proposed mechanism outlines the series of chemical transformations that occur during the hydroboration reaction, providing insights into the reaction pathway and the role of various intermediates and reagents.

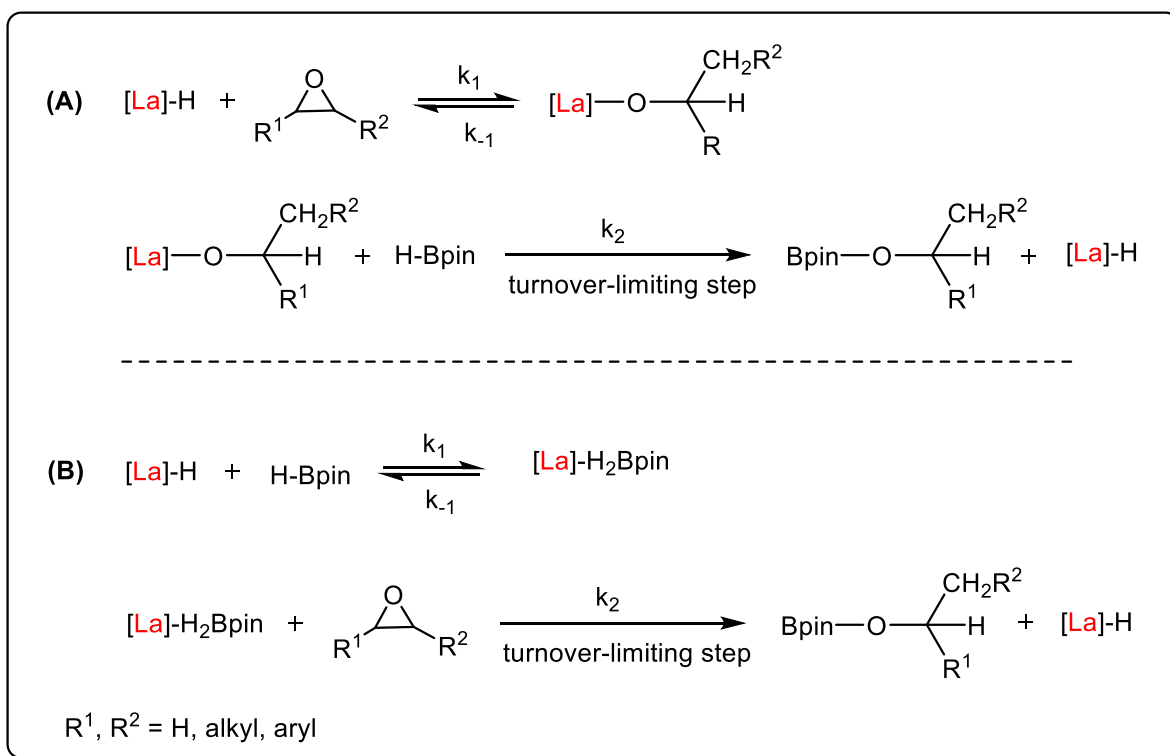
### Epoxide hydroboration with HBpin using lanthanide catalyst:

Hydroboration of epoxides are also a process of C-O bond activation (**Scheme 1.12**).<sup>41</sup> The hydroboration of epoxides is very uncommon in synthetic organic chemistry. There is only one report on lanthanide-catalyzed hydroboration of epoxides.



**Scheme 1.12.** Hydroboration of epoxide with HBpin using lanthanide as catalyst.

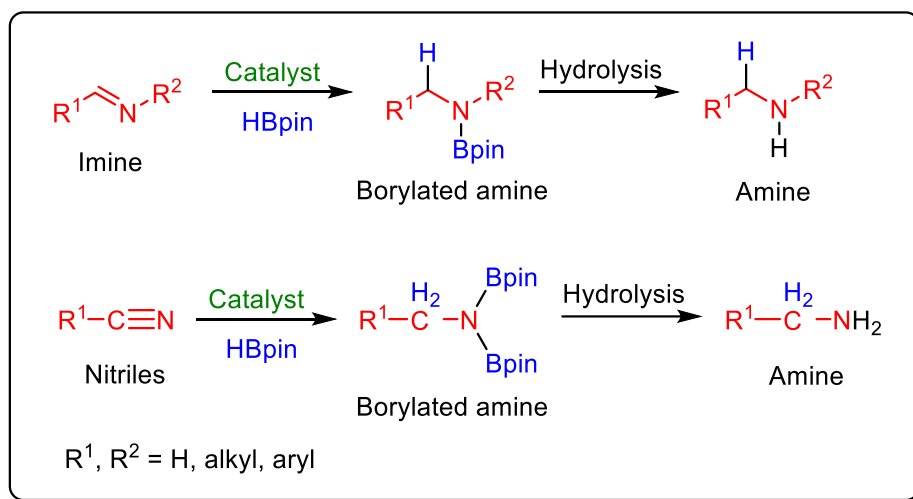
Sadow and co-workers disclosed the epoxide hydroboration reaction using catalyst **41**, which is very active, regioselective and highly efficient towards epoxides hydroboration with HBpin.<sup>42</sup> 5 mol% of the catalyst **41** with 1.3 equivalent HBpin at 25-60 °C temperature in 24 hours was the optimized reaction conditions for epoxide hydroboration and they demonstrated a series of examples of different type of epoxide hydroboration at the optimized reaction conditions. The relatively slower rate of epoxide hydroboration has constrained the scope of comprehensive kinetic investigations. Furthermore, it's important to note that the mechanism of this reaction differs significantly from that of ester hydroboration. Although, they demonstrated two different reaction pathways for epoxide hydroboration. (a) “Ester-first” mechanistic pathway (**Scheme 1.13A**) and (b) “HBpin-first” mechanistic pathway (**Scheme 1.13B**). Hence, the authors introduced the mechanism outlined in **Scheme 1.13B** is favoured due to their alignment with analogous rate laws.<sup>42</sup>



**Scheme 1.13.** Mechanistic pathway for epoxide hydroboration using catalyst **41**.<sup>42</sup>

There is no such report on lanthanide-catalysed hydroboration of epoxide using HBpin.

## 1.6. Lanthanide complexes in the hydroboration of imines and nitriles



**Scheme 1.14.** Hydroboration of imine and nitrile with HBpin.

Imines and nitriles are emergent functional groups in organic chemistry, their reduction is indeed an eventual methodology in synthetic organic chemistry to synthesize primary and secondary amines, which have wide applications in diverse fields. The reduction of imines and nitriles and its motive are:

- **Reduction of imines:** Imines are C=N bond-containing compounds and can be reduced to amines.<sup>44</sup>
- **Reduction of nitriles:** Nitriles are C≡N bond-containing compounds and can be reduced to primary amines.<sup>44</sup>
- **Natural product synthesis:** Natural products, *e.g.*, alkaloids, peptides and antibiotics containing amine functional groups and the reduction of imines and nitriles provide a key step in the synthesis of those compounds.<sup>45</sup>
- **Drug discovery:** Amines are verily used in pharmaceuticals. Hence, the reduction of imines and nitriles is a golden tool in the progression of drugs and pharmaceuticals.<sup>45</sup>
- **Polymer science:** The various polymers (*e.g.*, polyamides and polyurethanes) can be synthesized using primary and secondary amines. The reduction of nitriles can be a crucial step in the preparation of these monomers.<sup>45</sup>
- **Industrial and academics:** This methodology is extensively utilized in both industrial processes and research laboratories for amines synthesis. It enables chemists to access

diverse amine-containing molecules, contributing to the advancement of chemical science and technology.<sup>45</sup>

There are several synthetic methodologies were reported for imines and nitriles reduction (**Scheme 1.14**), e.g., direct hydrogenation,<sup>46</sup> using strong reducing agents ( $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ ,  $\text{BH}_3$  etc.)<sup>47</sup> and hydroelementation reaction (hydrosilylation,<sup>48</sup> hydroboration<sup>49</sup>). However, all the broadly reported synthetic strategies have some disadvantages over hydroboration reaction for the reduction of imines and nitriles to amines.

- **Direct hydrogenation method:** Using  $\text{H}_2$  gas in the presence of the metal catalyst, the storage and handling of  $\text{H}_2$  gas is highly risky.<sup>30</sup>
- **Using strong reducing agents:** The metal hydrides ( $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ ) possess very strong reducing properties, which sometimes hampers the other functional group and gives less selectivity towards imines and nitriles hydroboration reaction.<sup>30</sup>
- **Hydrosilylation reaction:** The hydrosilylation reaction is atom efficient and uses generally mild reaction conditions, but most of the silanes are costly as compared to HBpin. So, the hydrosilylation reaction is economically less favourable.<sup>30</sup>

Whereas, hydroboration reactions have good advantages; (i) It is atom efficient, (ii) Usually mild reaction conditions are used, (iii) high efficiency and high selectivity and (iv) the hydroborating agents are comparatively cheaper.<sup>50</sup> Consequently, the hydroboration reaction has enticed more academic and industrial amenities for two decades.

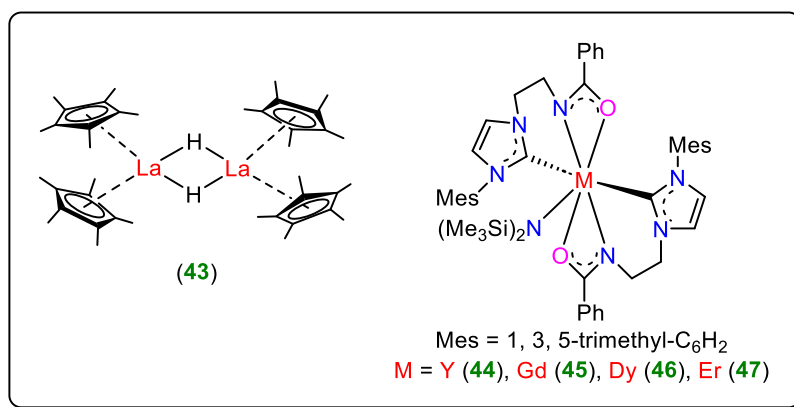
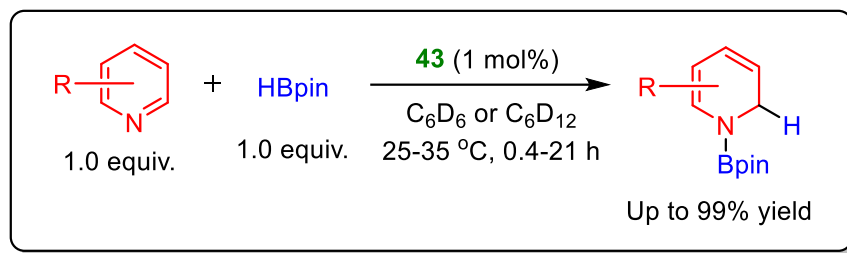


**Chart 1.6.** Reported lanthanide complexes in imines and nitriles hydroboration reaction.

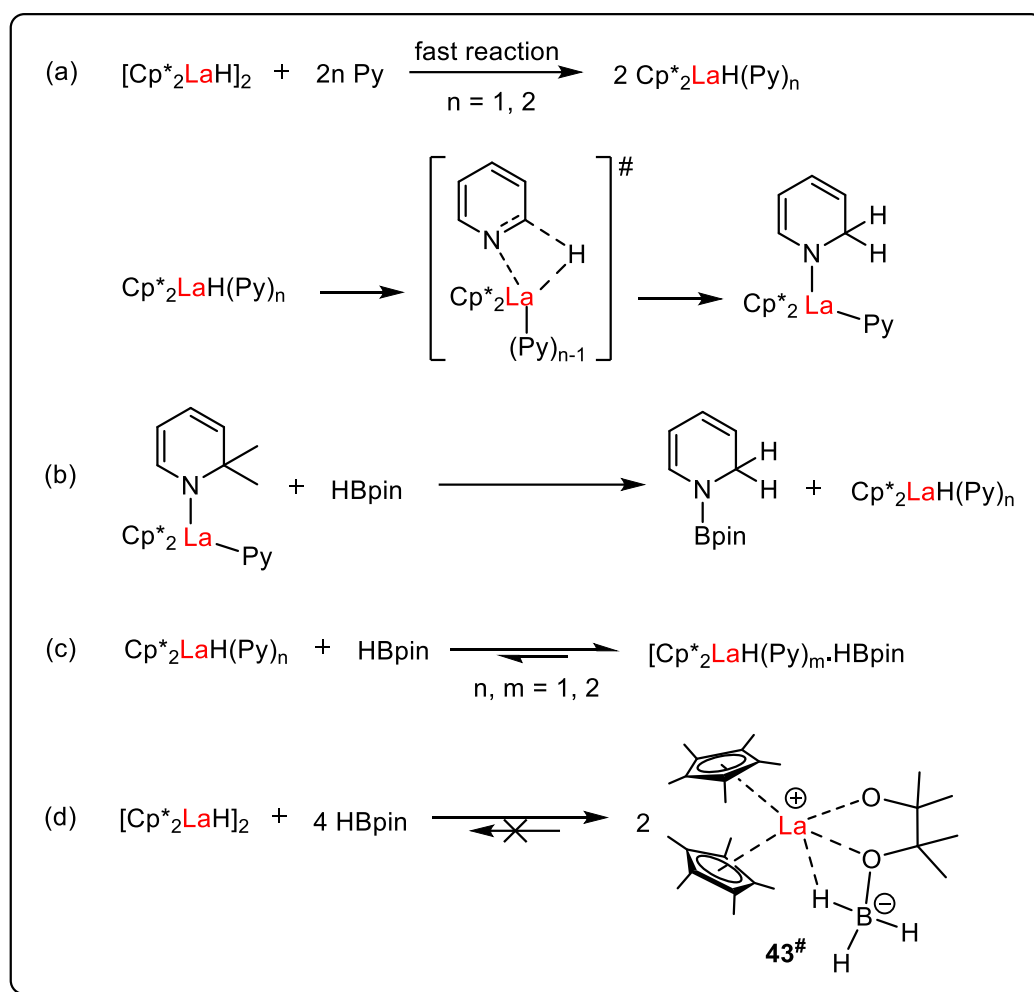
The transition metal catalysed hydroboration reaction is extensively introduced in organic transformation; but there are very less reports on lanthanide-catalysed hydroboration of imines and nitriles compounds.



**Scheme 1.15.** Lanthanide hydride-catalysed 1,2-hydroboration of pyridine with HBpin.

In 2014, Marks and co-workers first disclosed the organo-lanthanide-catalysed hydroboration of a C=N moiety of pyridines.<sup>51</sup> In this work, they demonstrated the regioselective 1,2-dearomatization of pyridines with HBpin by using lanthanum hydride complex **43** (**Chart 1.6**) as a catalyst to afford 1,2-dihydropyridines (**Scheme 1.15**). This report confers various advantages, including the utilization of deliberately available, non-toxic, cost-effective lanthanide hydride complex **43**. This complex exhibited exceptional atom efficiency and demonstrated remarkable 1,2-regioselectivity even with at low catalyst loading (1 mol%) under mild reaction conditions (**Scheme 1.15**). This synthetic methodology demonstrated excellent functional group tolerance, despite the inherent electrophilic nature of the lanthanide centre. In presence of the electron-withdrawing group at the substrates delivered a higher reaction rate as compared to the electron-donating group substituted substrates. Other than pyridines, other benzofused N-heterocycles, e.g., quinoline and isoquinoline underwent rapid hydroboration yielding the corresponding 1,2-dearomatized products with very good yields. Mechanistic studies have unveiled an experimental rate law characterized by a variable dependence on pyridine concentration and a rather unusual inverse first-order dependence on HBpin.

$$rate = k_{obs}[43]^1[pyridine]^1[HBpin]^{-1} \quad (\text{Eq. 7})$$



**Scheme 1.16.** Plausible fundamental reaction order for pyridine dearomatization reaction with HBpin using **43** as catalyst.<sup>51</sup>

Experimental investigation of the reaction mechanism (**Scheme 1.16**) revealed a decisive and dispersive role of catalyst **43** for pyridine dearomatization reaction.

- When catalyst **43** was treated with excess pyridine, afforded  $[\text{Cp}^*_2\text{La}(\text{NC}_5\text{H}_6)(\text{Py})]$  complex (**Scheme 1.16a**)
- The addition of 1 equivalent of HBpin subsequently leads to the formation of the dearomatized B–N product (**Scheme 1.16b**)
- The inverse order with respect to [HBpin] suggests that there is kinetic inhibition, which is competing with the turnover-limiting step in the reaction (**Scheme 1.16c**). These results indicate that the catalyst’s “resting state” may be a mononuclear species related to  $[\text{Cp}^*_2\text{LaH(Py)}_n]$  and the turnover-limiting step likely involves intramolecular C=N insertion.

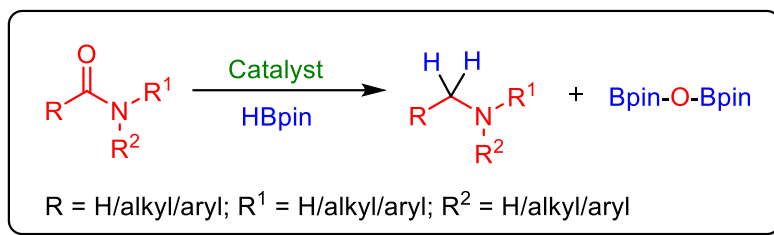
- Upon stoichiometric reaction of catalyst **43** with HBpin (4 equiv.) delivered a rapid and irreversible formation of catalytically inactive zwitterionic complex **43<sup>#</sup>** (**Scheme 1.16d**).

In 2018, Wang and co-workers reported a significant advancement by achieving the hydroboration of a wide range of imines and nitriles using amide-functionalized N-heterocyclic carbene-mediated rare-earth complexes **44-47** (**Chart 1.6**) as catalysts.<sup>52</sup> This significant research likely contributed to the development of efficient methods for the synthesis of valuable amines from imines and nitriles. They introduced these complexes, which exhibited remarkable catalytic activity in N-benzylideneaniline hydroboration reaction, yielding the desired hydroborated product in high yields. These complexes **44-47** displayed catalytically higher reactivities towards hydroboration reaction than other amido-metal complexes, e.g.,  $\text{NaN}(\text{SiMe}_3)_2$ ,  $\text{KN}(\text{SiMe}_3)_2$ ,  $\text{Gd}[\text{N}(\text{SiMe}_3)_2]_3$  and  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  (where, Ln = Y, Dy, Er). This observation highlights the significance of the carbene moiety in enhancing the catalytic activity of these complexes. An exception was observed in the reaction involving a compound with a strong electron-withdrawing nitro group present in imine. In this case, a poor yield was obtained due to the coordination of the nitrogen atom to the rare-earth metal centre, which affected the reaction outcome. Expanding the substrate scope to nitrile compounds, it was found that both aliphatic and aromatic nitriles could undergo double hydroboration in the presence of these catalysts irrespective of the electronic or steric properties of the substrates, resulting in the formation of dihydroborated products with excellent yields.

## 1.7. Lanthanide complexes in the hydroboration of amides

Reduction of amide to amine is always a significant and emergent process in synthetic organic chemistry. Because amides are verily abundant in nature (protein, peptide, plant), on the other hand, amines are fundamental organic compounds with wide-ranging applications in the pharmaceuticals, agrochemical products, preparation of material dye, textile industry, production of rubber, cutting oil and for  $\text{CO}_2$  capture.<sup>50</sup> In peptide chemistry, the conversion of amides to amines is very important for modifying peptide structures, creating peptide mimetics and developing bioactive compounds. Several methodologies have been reported for amide reduction in the last few decades by using the direct hydrogenation method, transition metal catalyst, main-group element catalyst and harsh reducing agents.<sup>50</sup> Recently, researchers

developed a new synthetic strategy for amide reduction, known as deoxygenation of amide by using lanthanide as a catalyst (**Scheme 1.17**).



**Scheme 1.17.** Deoxygenation of amide to amine using HBpin.

In 2020, Findlater and co-workers unveiled polyoxometalate lanthanum-catalysed hydroboration of amides with HBpin.<sup>53</sup> Where they demonstrated the direct deoxygenation of amides using polynuclear lanthanum-diketonato cluster **42** (**Chart 1.7**) in the presence of HBpin. Complex **42** was exhibited to be a remarkably versatile hydroboration catalyst, effectively facilitating the hydroboration of primary (1°), secondary (2°) and tertiary (3°) amides. Notably, this methodology offers a straightforward approach that exhibits tolerance for a broad spectrum of functional groups and heteroatoms.

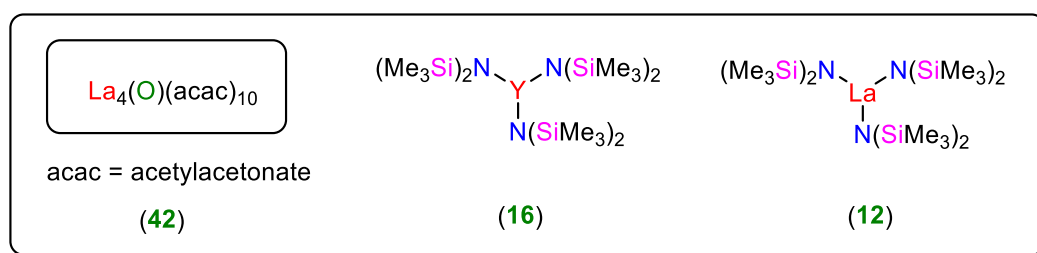
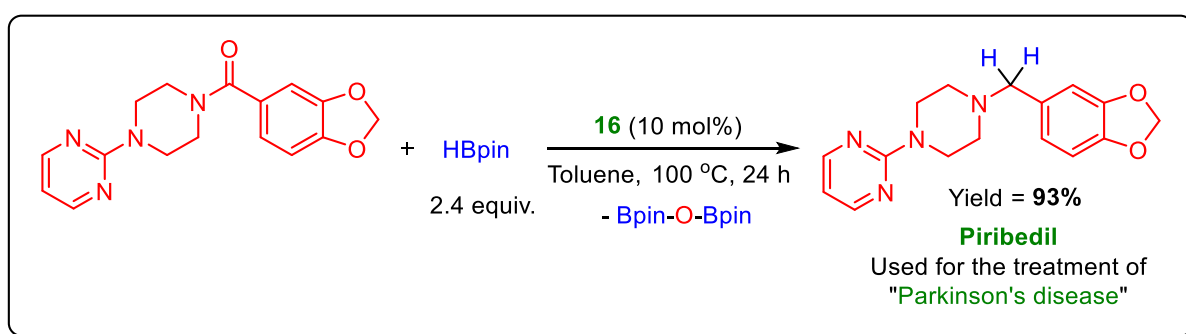


**Chart 1.7.** Reported lanthanide complexes in amides hydroboration reaction

In 2020, Chen and co-workers introduced rare-earth metal-catalysed deoxygenation of secondary and tertiary amides using HBpin.<sup>54</sup> They displayed homoleptic bis(trimethylsilyl)amides of yttrium complex **16** (**Chart 1.7**) behave as an efficient catalyst for hydroboration of secondary and tertiary amides to corresponding amines in the presence of HBpin. They showed a capacious substrate scope of secondary and tertiary amides hydroboration with various functional group substituted examples including electron-donating and electron-withdrawing groups in good to excellent yields. By utilizing this synthetic methodology, they synthesized indole and its derivatives, which have a great impact on the biological field:

- It is used as an antimicrobial, anticancer agent, anti-hypertensive and anti-inflammatory agent.
- Used as an intercellular signal molecule.

Further showcased this efficient synthetic methodology through the successful execution of a gram-scale synthesis of piribedil (**Scheme 1.18**), a compound used in the treatment of Parkinson's disease, achieving an impressive isolated yield of 93%. To investigate whether the rate-determining step (RDS) involved B-H activation by **48**, performed the kinetic isotope effect (KIE). The KIE value 1.32, indicating that RDS was not associated with B-H activation in this reaction.<sup>54</sup>



**Scheme 1.18.** “Gram-scale” synthesis of piribedil using HBpin.

In the same year, Marks and co-workers reported homoleptic La-catalysed hydroboration of secondary and tertiary amide with HBpin under mild reaction conditions.<sup>55</sup> The hydroboration reaction of amides afforded borylated amines and O(Bpin)<sub>2</sub> catalysed by [La(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> **12** in presence of HBpin. This reaction methodology exhibited excellent tolerance for nitro, halide and amino functional groups. Importantly, this amide reduction process is highly chemoselective with no competing inter- or intramolecular alkene/alkyne hydroboration reactions was observed. Kinetic studies suggested that the reduction of tertiary amides followed an unconventional *mixed-order* rate law, which was believed to arise from the saturation of the catalyst with HBpin. The rate law equations were:

(a) At low HBpin concentration

$$\text{rate} = k[\mathbf{12}]^1[\text{amide}]^0[\text{HBpin}]^1 \quad (\text{Eq. 8})$$

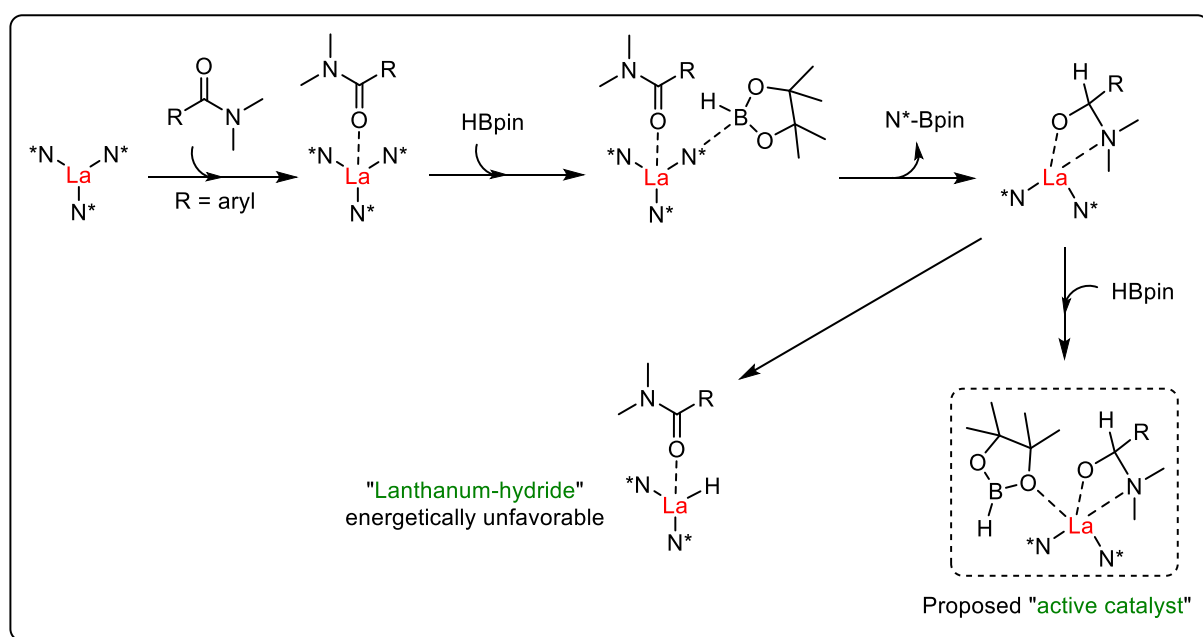
(b) At high HBpin concentration

$$\text{rate} = k[\mathbf{12}]^1[\text{amide}]^0[\text{HBpin}]^0 \quad (\text{Eq. 9})$$

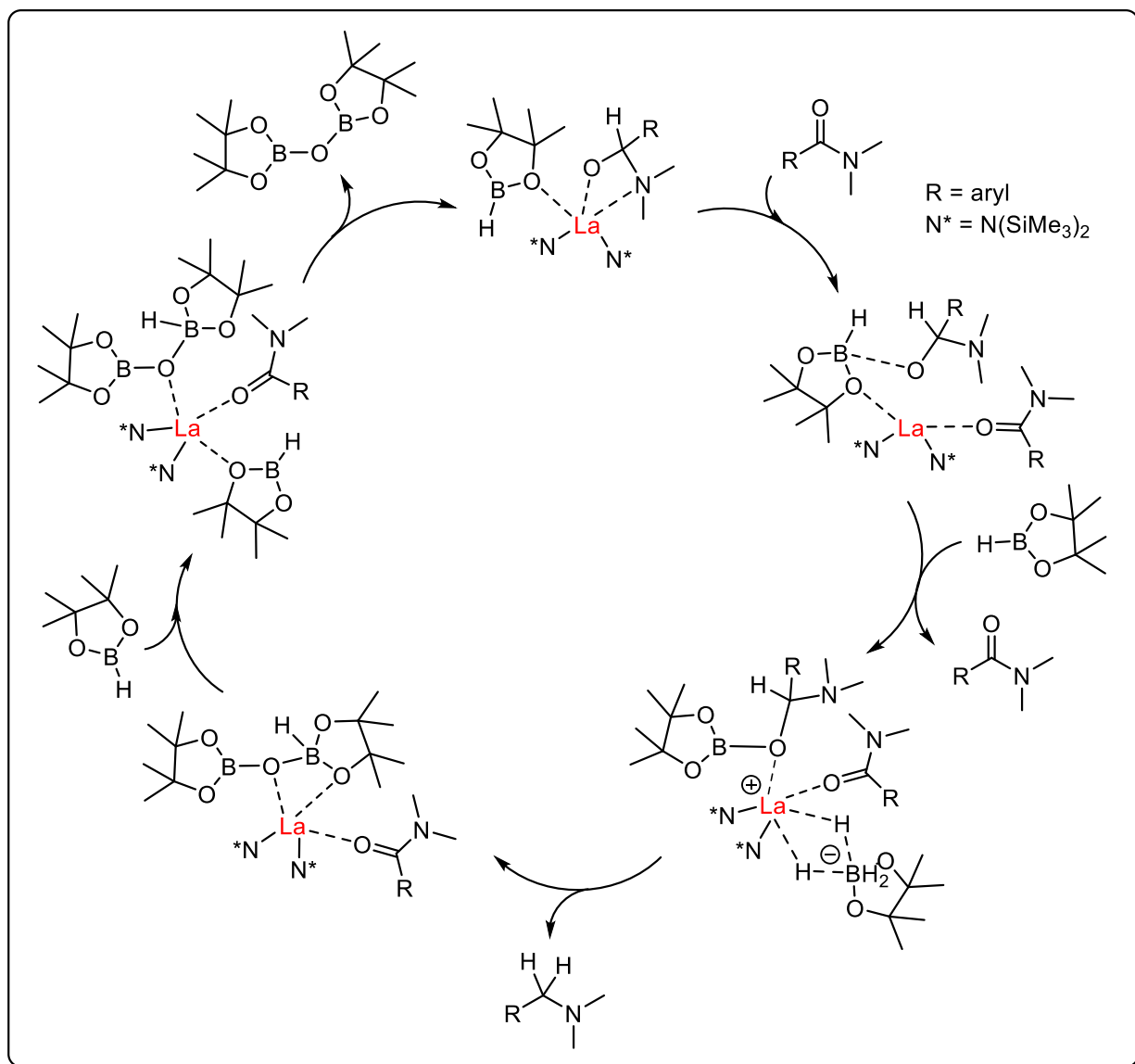
They also performed Hammett plot from the reduction of *para*-substituted N-benzoylpyridines with HBpin and established the Hammett equation (Eq. 10), where, Hammett constant  $\rho = 0.56$ .

$$\log(k/k_H) = \rho\sigma = 0.56\sigma \quad (\text{Eq. 10})$$

Marks and co-workers very beautifully and systematically described the catalyst activation process in the presence of **12**, amide and HBpin (**Scheme 1.19**) via theoretical studies. They demonstrated that the formation of “lanthanum -hydride” was energetically not favourable and “lanthanum-hemiaminal” species was proposed as an “active catalyst” for tertiary amide hydroboration with HBpin.<sup>55</sup> Also, they disclosed a catalytic reaction cycle by using density functional theory (DFT) calculations (**Scheme 1.20**).



**Scheme 1.19.** Proposed “active catalyst” for tertiary amide hydroboration using **12**.<sup>55</sup>

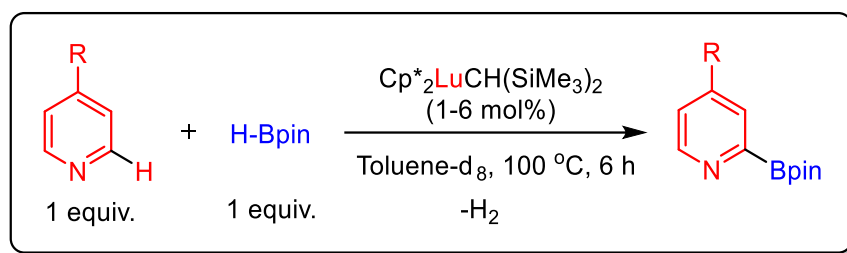


**Scheme 1.20.** DFT-calculated proposed mechanistic pathway of tertiary amide hydroboration catalysed by **12**.<sup>55</sup>

### 1.8. Lanthanide complexes in C–H bond activation via borylation reaction

Chemodivergent strategies play a crucial role in synthetic organic chemistry by enabling the efficient introduction of structural diversity into value-added organic products through straightforward chemical alterations. These methodologies provide chemists with versatile tools to access a wide range of compounds with diverse structures and properties, making them invaluable in the design and synthesis of complex molecules for various applications in pharmaceuticals, material science and chemical research.<sup>56</sup> To achieve these objectives,

numerous effective chemodivergent strategies make use of adjustments such as varying additives, solvents and catalysts, making slight substrate modifications and employing other tactical approaches. Regarding catalyst modification, it is well-documented that altering the choice of metal, especially within a transition-metal series, can have a profound impact on catalytic selectivity. However, it is often observed in lanthanide/rare-earth catalytic chemistry that making incremental changes in the ionic radius typically leads to only modest and gradual variations in catalytic activity.



**Scheme 1.21.** Lanthanide-catalysed  $\alpha$ -C–H borylation of substituted pyridine.

Hence, the development of more efficient and selective methods for the  $\alpha$ -functionalization of pyridine and related azines would represent a significant advancement in synthetic methodology.<sup>57</sup> There are few reports on transition-metal-catalysed  $\alpha$ -functionalization,<sup>58</sup> but rare-earth metal catalysts are an infant in  $\alpha$ -functionalization of organic substrate.

Recently, Marks and co-workers reported chemodivergent Lu-catalysed  $\alpha$ -C–H borylation of pyridines with HBpin (**Scheme 1.21**).<sup>59</sup> Previously, Marks and co-workers introduced the 1,2-dearomatization of pyridines with HBpin using  $[\text{Cp}^*_2\text{LaH}]_2$  (**39**) as a catalyst.<sup>51</sup> Ther after, they hypothesized that  $\alpha$ -C–H borylation of pyridines with HBpin occurred in the presence of smaller lanthanides (such as  $\text{Lu}^{3+}$  with ionic radius 0.995 Å), whereas 1,2-dearomatization of pyridines with HBpin happened in presence of larger lanthanides (such as  $\text{La}^{3+}$  with ionic radius 1.250 Å) (**Scheme 1.22**).<sup>59</sup>

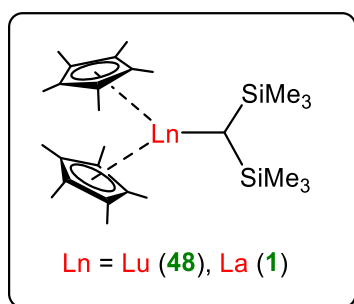
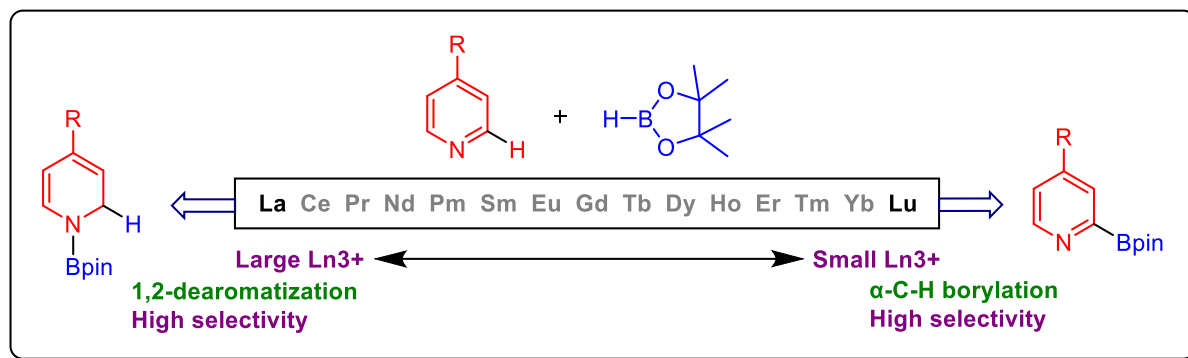
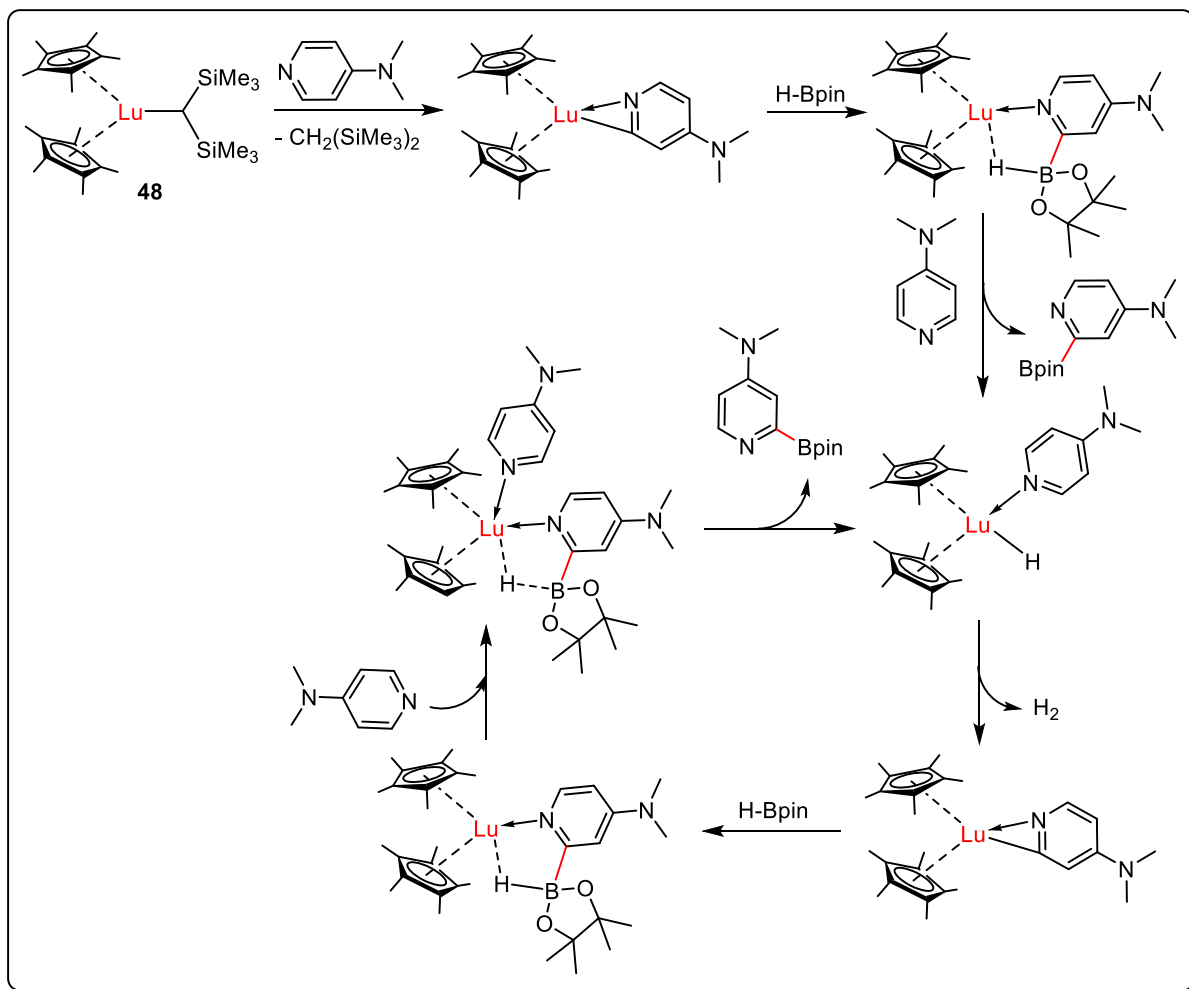


**Chart 1.8.** Reported lanthanide complexes in  $\alpha$ -C-H bond activation of pyridine via borylation reaction.



**Scheme 1.22.** Chemodivergent Ln-catalysed regioselective 1,2-dearomatization or  $\alpha$ -C-H bond activation of pyridine.<sup>59</sup>

They demonstrated a significant number of pyridine substrates including electron-donating and electron-withdrawing group substituted substrates and all the substrates afforded good yields under optimized reaction conditions (1-6 mol% catalyst, toluene- $d_8$ , 100 °C and 6 h). They displayed the reaction mechanistic of  $\alpha$ -C-H borylation of pyridines by taking DMAP with HBpin using  $[\text{Cp}^*_2\text{Lu}\{\text{CH}(\text{SiMe}_3)_2\}]$  (**48**) (**Chart 1.8**) as a catalyst (**Scheme 1.23**).<sup>59</sup>



**Scheme 1.23.** Proposed mechanistic pathway for  $\alpha$ -C–H borylation of DMAP with HBpin by using Lu-catalyst **48**.<sup>59</sup>

## 1.9. Motivation and objectives

Lanthanides possess immense coordinating properties in the absence of orbital interactions due to “lanthanide contraction” and it displays a large flexible coordination number for the presence of  $4f$  orbitals. On the other hand, lanthanides are highly reactive in nature and behave as a reducing agent in synthetic chemistry. Upon reviewing the existing literatures on lanthanide-catalysed hydroboration reactions, it becomes evident that there is a notable gap in research pertaining to cerium-catalysed hydroboration reactions. It’s worth noting that cerium, being the most abundant and cost-effective among the lanthanides, presents an intriguing and potentially valuable avenue for exploration in homogeneous catalysis. The advantages of the lanthanide-catalysed hydroboration reactions in synthetic organic chemistry: (i) atom efficient

reaction, (ii) selectivity, (iii) control stereochemistry, (iv) good functional group tolerance, (v) applications in pharmaceuticals and green chemistry.

In summary, lanthanide-catalysed hydroboration reactions are versatile tools in organic synthesis, allowing for selective functionalization of molecules and enabling the creation of complex structures with controlled stereochemistry.

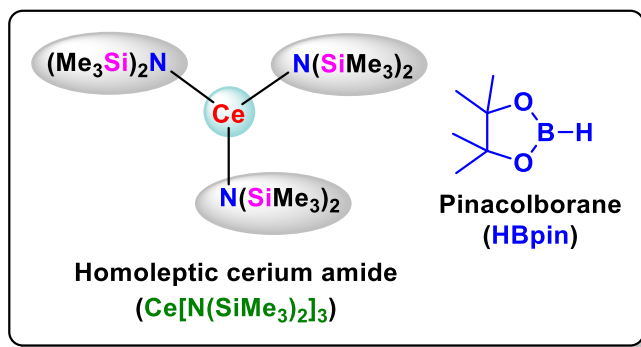


**Figure 1.2.** Homoleptic bis(trimethylsilyl)amides of cerium complex  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ .

Taking all of those factors into consideration, we synthesized homoleptic bis(trimethylsilyl)amides of cerium complex (**Figure 1.2**),<sup>60</sup> which have some magnificent properties:

- ✓ Commercially available
- ✓ Less air and moisture sensitive
- ✓ Comparatively cheaper
- ✓ High abundance
- ✓ Low toxicity

Having successfully synthesized  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , it serves as a catalyst for wide range of organic transformations in presence of HBpin, e.g., deoxygenation of primary and secondary amides, hydroboration of esters and epoxides, reduction of  $\text{CO}_2$  to methanol, reduction of  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{N}$  bonds and selective deoxygenation of isocyanates to form N-boryl methyl amines.

## 1.10. References

1. Natrajan, L.; Hunt, A. (Ed.) (2013). F-block elements recovery: Chapter 6. In *RSC Green Chemistry Series, Element Recovery and Sustainability* (1 ed., Vol. 1, pp. 160-177). Royal Society of Chemistry.
2. Atkins, P. W.; Overton, T. L.; Rourke, J. P.; Weller, M. T.; Armstrong, F. A. (2010), *Shriver and Atkins' Inorganic Chemistry*, Fifth Edition. ISBN 978-1-42-921820-7.
3. Gschneider Jr., K. A.; Eyring, L. (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, North-Holland, Amsterdam, Vol. 1, (1978) to Vol. 21, (1995).
4. Dicken, R. D.; Motta, A.; Marks, T. J. Homoleptic Lanthanide Amide Catalysts for Organic Synthesis: Experiment and Theory. *ACS Catal.* **2021**, *11*, 2715-2734.
5. (a) Bunzli, J. -C. G.; Piguet, C. Taking Advantage of Luminescent Lanthanide Ions. *Chem. Soc. Rev.* **2005**, *34*, 1048-1077. (b) Eliseeva, S. V.; Bunzli, J. -C. G. Lanthanide Luminescence for Functional Materials and Bio-Sciences. *Chem. Soc. Rev.* **2010**, *39*, 189-227. (c) Bunzli, J. -C. G. Lanthanide Luminescence for Biomedical Analyses and Imaging. *Chem. Rev.* **2010**, *110*, 2729-2755. (d) Bunzli, J. -C. G. On the Design of Highly Luminescent Lanthanide Complexes. *Coord. Chem. Rev.* **2015**, *293-294*, 19-47.
6. (a) Prsa, K.; Nehrkorn, J.; Corbey, J. F.; Evans, W. J.; Demir, S.; Long, J. R.; Guidi, T.; Waldmann, O. Perspectives on Neutron Scattering in Lanthanide Based Single Molecule Magnets and a Case Study of the Tb<sub>2</sub>(μ-N<sub>2</sub>) System. *Magnetochemistry* **2016**, *2*, 45. (b) Jena, R.; Benner, F.; Delano, F.; Holmes, D.; McCracken, J.; Demir, S.; Odom, A. L. *Chem. Sci.* **2023**, *14*, 4257-4264. (c) Benner, F.; Droitte, L. L.; Cador, O.; Guennic, B. L.; Demir, S. Magnetic Hysteresis and Large Coercivity in Bisbenzimidazole Radical-Bridged Dilanthanide Complexes. *Chem. Sci.* **2023**, *14*, 5577-5592.
7. (a) Liu, D.; Wang, M.; Chai, Y.; Wan, X.; Cui, D. Self-Activated Coordination Polymerization of Alkoxy-styrenes by a Yttrium Precursor: Stereocontrol and Mechanism. *ACS Catal.* **2019**, *9*, 2618-2625. (b) Schmidt, B. M.; Pindwal, A.; Venkatesh, A.; Ellern, A.; Rossini, A. J.; Sadow, A. D. Zwitterionic Trivalent (Alkyl)lanthanide Complexes in Ziegler-Type Butadiene Polymerization. *ACS Catal.* **2019**, *9*, 827-838. (c) Gçttker-Schnetmann, I.; Kenyon, P.; Mecking, S. Coordinative Chain Transfer Polymerization of Butadiene with Functionalized Aluminum Reagents. *Angew. Chem., Int. Ed.* **2019**, *58*, 17777-17781.
8. Escorihuela, J.; Lledós, A.; Ujaque, G. Anti-Markovnikov Intermolecular Hydroamination of Alkenes and Alkynes: A Mechanistic View. *Chem. Rev.* **2023**, *123*, 9139-9203. (b) Nguyen, H. N.; Hultsch, K. C. Rare-Earth Metal-Catalyzed Kinetic

- Resolution of Chiral Aminoalkenes via Hydroamination: The Effect of the Silyl Substituent of the Binaphtholate Ligand on Resolution Efficiency. *Eur. J. Org. Chem.* **2019**, 2592-2601.
9. (a) Selikhov, A. N.; Plankin, G. S.; Cherkasov, A. V.; Shavyrin, A. S.; Louyriac, E.; Maron, L.; Trifonov, A. A. Thermally Stable Ln(II) and Ca(II) Bis(benzhydryl) Complexes: Excellent Precatalysts for Intermolecular Hydrophosphination of C-C Multiple Bonds. *Inorg. Chem.* **2019**, *58*, 5325-5334. (b) Basiouny, M. M. I.; Dollard, D. A.; Schmidt, J. A. R. Regioselective Single and Double Hydrophosphination and Hydrophosphinylation of Unactivated Alkynes. *ACS Catal.* **2019**, *9*, 7143-7153. (c) Lapshin, I. V.; Basalov, I. V.; Lyssenko, K. A.; Cherkasov, A. V.; Trifonov, A. A. Ca<sup>II</sup>, Yb<sup>II</sup> and Sm<sup>II</sup> Bis(Amido) Complexes Coordinated by NHC Ligands: Efficient Catalysts for Highly Regio- and Chemoselective Consecutive Hydrophosphinations with PH<sub>3</sub>. *Chem. Eur. J.* **2019**, *25*, 459-463. (d) Su, J.; Zhou, Y.; Xu, X. Hydroaminoalkylation of Sterically Hindered Alkenes with N, N-dimethyl Anilines Using a Scandium Catalyst. *Org. Biomol. Chem.* **2019**, *17*, 2013-2019.
10. Liu, H.; Eisen, M. S. Organo-*f*-Complexes for Efficient and Selective Hydroborations. *Synthesis* **2020**, *52*, 629-644.
11. (a) Crabtree, R. H. Introduction: CH Activation. *Chem. Rev.* **2017**, *117*, 8481-8482. (b) Shilov, A. E.; Shul'pin, G. B. Activation of C-H Bonds by Metal Complexes. *Chem. Rev.* **1997**, *97*, 2879-2932.
12. Zhang, L.; Zhou, M.; Wang, A.; Zhang, T. Selective Hydrogenation Over Supported Metal Catalysts: From Nanoparticles to Single Atoms. *Chem. Rev.* **2020**, *120*, 683-733.
13. (a) Langer, P.; Freiberg, W. Cyclization Reactions of Dianions in Organic Synthesis. *Chem. Rev.* **2004**, *104*, 4125-4149. (b) Chen, C.; Zhao, J.; Shi, X.; Liu, L.; Zhu, Y. -P.; Sun, W.; Zhu, B. Recent Advances in Cyclization Reactions of Unsaturated Oxime Esters (Ethers): Synthesis of Versatile Functionalized Nitrogen-Containing Scaffolds. *Org. Chem. Front.* **2020**, *7*, 1948-1969.
14. (a) Irrgang, T.; Kempe, R. 3d-Metal Catalyzed N- and C-Alkylation Reactions via Borrowing Hydrogen or Hydrogen Autotransfer. *Chem. Rev.* **2019**, *119*, 2524-2549. (b) Poulsen, T. B.; Jørgensen, K. A. Catalytic Asymmetric Friedel-Crafts Alkylation Reactions Copper Showed the Way. *Chem. Rev.* **2008**, *108*, 2903-2915.
15. (a) Pahar, S.; Kundu, G.; Sen, S. S. Cyanosilylation by Compounds with Main-Group Elements: An Odyssey. *ACS Omega* **2020**, *5*, 25477-25484. (b) Sen, N.; Khan, S. Heavier Tetrylenes as Single Site Catalysts. *Chem Asian J.* **2021**, *16*, 705-719.

16. Bariwalab, J.; Van der Eycken, E. C–N Bond Forming Cross-Coupling Reactions: An Overview. *Chem. Soc. Rev.* **2013**, *42*, 9283-9303.
17. Yin, L.; Liebscher, J. Carbon-Carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. *Chem. Rev.* **2007**, *107*, 133-173.
18. (a) Ros, A.; Fernandez, R.; Lassaletta, J. M. Functional Group Directed C–H Borylation. *Chem. Soc. Rev.* **2014**, *43*, 3229-3243. (b) Bisht, R.; Haldar, C.; Hassan, M. M. M.; Hoque, M. E.; Chaturvedi, J.; Chattopadhyay, B. Metal-Catalysed C–H Bond Activation and Borylation. *Chem. Soc. Rev.* **2022**, *51*, 5042-5100.
19. (a) Nakajima, Y.; Shimada, S. Hydrosilylation Reaction of Olefins: Recent Advances and Perspectives. *RSC Adv.* **2015**, *5*, 20603-20616. (b) Diez-Gonzalez, S.; Nolan, S. P. Copper, Silver, and Gold Complexes in Hydrosilylation Reactions. *Acc. Chem. Res.* **2008**, *41*, 349-358.
20. (a) Geier, S. J.; Vogels, C. M.; Melanson, J. A.; Westcott, S. A. The Transition Metal-Catalysed Hydroboration Reaction. *Chem. Soc. Rev.* **2022**, *51*, 8877-8922. (b) Shegavi, M. L.; Bose, S. K. Recent Advances in the Catalytic Hydroboration of Carbonyl Compounds. *Catal. Sci. Technol.* **2019**, *9*, 3307-3336.
21. Magre, M.; Szewczyk, M.; Rueping, M. s-Block Metal Catalysts for the Hydroboration of Unsaturated Bonds. *Chem. Rev.* **2022**, *122*, 8261-8312.
22. Harrison, K. N.; Marks, T. J. Organolanthanide-Catalyzed Hydroboration of Olefins. *J. Am. Chem. Soc.* **1992**, *114*, 9220-9221.
23. Evans, D. A.; Muci, A. R.; Stiirmer, R. Samarium(III)-Catalyzed Hydroboration of Olefine with Catecholborane. A General Approach to the Synthesis of Boronate Esters. *J. Org. Chem.* **1993**, *58*, 5307-5309.
24. Bijpost, E. A.; Duchateau, R.; Teuben, J. H. Early Transition Metal Catalyzed Hydroboration of Alkenes. *J. Mol. Catal A: Chem.* **1995**, *95*, 121-128.
25. Villiers, C.; Ephritikhine, M. Novel Hydroboration of Highly Substituted Alkenes catalysed by Borohydride Complexes of Uranium, Neodymium and Zirconium. *J. Chem. Soc., Chem. Commun.* **1995**, 979-980.
26. Horino, Y.; Livinghouse, T.; Stan, M. Alkene-Pinacolborane Hydroborations Catalyzed by Lanthanum Tris[bis(trimethylsilyl)amide]. *Synlett* **2004**, *14*, 2639-2641.
27. Molander, G. A.; Pfeiffer, D. Organolanthanide-Catalyzed Cyclization/Boration of 1,5- and 1,6-Dienes. *Org. Lett.* **2001**, *3*, 361-363.

28. (a) Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115*, 6621-6686. (b) Volkov, A.; Tinnis, F.; Slagbrand, T.; Trilloa, P.; Adolfsson, H. Chemoselective reduction of carboxamides. *Chem. Soc. Rev.* **2016**, *45*, 6685-6697.
29. (a) Kuciński, K.; Hreczycho, G. Hydrosilylation and Hydroboration in a Sustainable Manner: From Earth-Abundant Catalysts to Catalyst-Free Solutions. *Green Chem.* **2020**, *22*, 5210-5224. (b) Tamang, S. R.; Findlater, M. Emergence and Applications of Base Metals (Fe, Co, and Ni) in Hydroboration and Hydrosilylation. *Molecules* **2019**, *24*, 3194.
30. Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, *5*, 3238-3259.
31. (a) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. Magnesium hydridotriphenylborate  $[Mg(thf)_6][HBPh_3]_2$ : A Versatile Hydroboration Catalyst. *Chem. Commun.* **2016**, *52*, 13155-13158. (b) Zhang, G.; Zeng, H.; Wu, J.; Yin, Z.; Zheng, S.; Fetting, J. C. Highly Selective Hydroboration of Alkenes, Ketones and Aldehydes Catalyzed by a Well Defined Manganese Complex. *Angew. Chem., Int. Ed.* **2016**, *55*, 14369-14372. (c) Mukherjee, D.; Osseili, H.; Spaniol, T. P.; Okuda, J. Alkali Metal Hydridotriphenylborates  $[(L)M][HBPh_3]$  ( $M = Li, Na, K$ ): Chemoselective Catalysts for Carbonyl and  $CO_2$  Hydroboration. *J. Am. Chem. Soc.* **2016**, *138*, 10790-10793.
32. Weidner, V. L.; Barger, C. J.; Delferro, M.; Lohr, T. L.; Marks, T. J. Rapid, Mild, and Selective Ketone and Aldehyde Hydroboration/ Reduction Mediated by a Simple Lanthanide Catalyst. *ACS Catal.* **2017**, *7*, 1244-1247.
33. (a) Chen, S.; Yan, D.; Xue, M.; Hong, Y.; Yao, Y.; Shen, Q. Tris(cyclopentadienyl)lanthanide Complexes as Catalysts for Hydroboration Reaction toward Aldehydes and Ketones. *Org. Lett.* **2017**, *19*, 3382-3385. (b) Yan, D.; Dai, P.; Chen, S.; Xue, M.; Yao, Y.; Shen, Q.; Bao, X. Highly Efficient Hydroboration of Carbonyl Compounds Catalyzed by Tris(methylcyclopentadienyl)lanthanide Complexes. *Org. Biomol. Chem.* **2018**, *16*, 2787-2791.
34. Zhu, Z.; Dai, P.; Wu, Z.; Xue, M.; Yao, Y.; Shen, Q.; Bao, X. Lanthanide Aryloxides Catalyzed Hydroboration of Aldehydes and Ketones. *Catal. Commun.* **2018**, *112*, 26-30.
35. Wang, W.; Shen, X.; Zhao, F.; Jiang, H.; Yao, W.; Pullarkat, S. A.; Xu, L.; Ma, M. Ytterbium-Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2018**, *83*, 69-74.

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36. Song, P.; Lu, C.; Fei, Z.; Zhao, B.; Yao, Y. Enantioselective Reduction of Ketones Catalyzed by Rare-Earth Metals Complexed with Phenoxy Modified Chiral Prolinols. *J. Org. Chem.* **2018**, *83*, 6093-6100.
37. Nystrom, R. F.; Brown, W. G. Reduction of Organic Compounds by Lithium Aluminum Hydride. III. Halides, Quinones, Miscellaneous Nitrogen Compounds. *J. Am. Chem. Soc.* **1948**, *70*, 3738-3740.
38. Werkmeister, S.; Junge, K.; Beller, M. Catalytic Hydrogenation of Carboxylic Acid Esters, Amides, and Nitriles with Homogeneous Catalysts. *Org. Process Res. Dev.* **2014**, *18*, 289-302.
39. Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev.* **2018**, *2*, 15-34.
40. Wu, L.; Moteki, T.; Gokhale, A. A.; Flaherty, D. W.; Toste, F. D. Production of Fuels and Chemicals from Biomass: Condensation Reactions and Beyond. *Chem* **2016**, *1*, 32-58.
41. Sarkar, N.; Sahoo, R. K.; Nembenna, S. Aluminium Catalyzed Selective Hydroboration of Esters and Epoxides to Alcohols: C-O Bond Activation. *Chem. Eur. J.* **2023**, *29*, e202203023.
42. Patnaik, S.; Sadow, A. D. Interconverting Lanthanum Hydride and Borohydride Catalysts for C=O Reduction and C-O Bond Cleavage. *Angew. Chem., Int. Ed.* **2019**, *58*, 2505-2509.
43. Barger, C. J.; Motta, A.; Weidner, V. L.; Lohr, T. L.; Marks, T. J. La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-Catalyzed Ester Reductions with Pinacolborane: Scope and Mechanism of Ester Cleavage. *ACS Catal.* **2019**, *9*, 9015-9024.
44. Kaithal, A.; Chatterjee, B.; Gunanathan, C. Ruthenium-Catalyzed Selective Hydroboration of Nitriles and Imines. *J. Org. Chem.* **2016**, *81*, 11153-11161.
45. Lawrence, S. A. Amines: Synthesis, Properties and Applications. Cambridge University Press: Cambridge, 2005.
46. Choi, J. -H.; Precht, M. H. G. Tuneable Hydrogenation of Nitriles into Imines or Amines with a Ruthenium Pincer Complex under Mild Conditions. *ChemCatChem* **2015**, *7*, 1023-1028.
47. Elsen, H.; Langer, J.; Ballmann, G.; Wiesinger, M.; Harder, S. Insights into LiAlH<sub>4</sub> Catalyzed Imine Hydrogenation. *Chem. Eur. J.* **2021**, *27*, 401-411.
48. Gutsulyak, D. V.; Nikonov, G. I. Chemoselective Catalytic Hydrosilylation of Nitriles. *Angew. Chem., Int. Ed.* **2010**, *49*, 7553-7556.
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49. Wang, X.; Xu, X. Hydroboration of Nitriles and Imines by Highly Active Zinc Dihydride Catalysts. *RSC Adv.* **2021**, *11*, 1128-1133.
50. Dicken, R. D.; Motta, A.; Marks, T. J. Homoleptic Lanthanide Amide Catalysts for Organic Synthesis: Experiment and Theory. *ACS Catal.* **2021**, *11*, 2715-2734.
51. Dudnik, A. S.; Weidner, V. L.; Motta, A.; Delferro, M.; Marks, T. J. Atom-Efficient Regioselective 1,2-De aromatization of Functionalized Pyridines by an Earth-Abundant Organolanthanide Catalyst. *Nat. Chem.* **2014**, *6*, 1100-1107.
52. Huang, Z.; Wang, S.; Zhu, X.; Yuan, Q.; Wei, Y.; Zhou, S.; Mu, X. Well-Defined Amidate-Functionalized N-Heterocyclic Carbene-Supported Rare-Earth Metal Complexes as Catalysts for Efficient Hydroboration of Unactivated Imines and Nitriles. *Inorg. Chem.* **2018**, *57*, 15069-15078.
53. Tamang, S. R.; Singh, A.; Bedi, D.; Bazkiaei, A. R.; Warner, A. A.; Glogau, K.; McDonald, C.; Unruh, D. K.; Findlater, M. Polynuclear lanthanide-Diketonato Clusters for the Catalytic Hydroboration of Carboxamides and Esters. *Nat. Catal.* **2020**, *3*, 154-162.
54. Ye, P.; Shao, Y.; Ye, X.; Zhang, F.; Li, R.; Sun, J.; Xu, B.; Chen, J. Homoleptic Bis(trimethylsilyl)amides of Yttrium Complexes Catalyzed Hydroboration Reduction of Amides to Amines. *Org. Lett.* **2020**, *22*, 1306-1310.
55. Barger, C. J.; Dicken, R. D.; Weidner, V. L.; Motta, A.; Lohr, T. L.; Marks, T. J. La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-Catalyzed Deoxygenative Reduction of Amides with Pinacolborane. Scope and Mechanism. *J. Am. Chem. Soc.* **2020**, *142*, 8019-8028.
56. Beletskaya, I. P.; Najera, C.; Yus, M. Chemodivergent reactions. *Chem. Soc. Rev.* **2020**, *49*, 7101-7166.
57. Crabtree, R. H. The Organometallic Chemistry of the Transition Metals. 3<sup>rd</sup> ed.; John Wiley & Sons, **2009**.
58. Dutta, U.; Maiti, S.; Bhattacharya, T.; Maiti, D. Arene Diversification Through Distal C(sp<sup>2</sup>)-H Functionalization. *Science* **2021**, *372*, 701.
59. Rothbaum, J. O.; Motta, A.; Kratish, Y.; Marks, T. J. Chemodivergent Organolanthanide-Catalyzed C-H  $\alpha$ -MonoBorylation of Pyridines. *J. Am. Chem. Soc.* **2022**, *144*, 17086-17096.
60. Bradley, D. C.; Ghotra, J. S.; Hart, F. A. Low Co-ordination Numbers in Lanthanide and Actinide Compounds. Part I. The Preparation and Characterization of Tris{bis(trimethylsilyl)amido}lanthanides. *J. Chem. Soc., Dalton Trans.* **1973**, 1021-1023.

## *Chapter 2*

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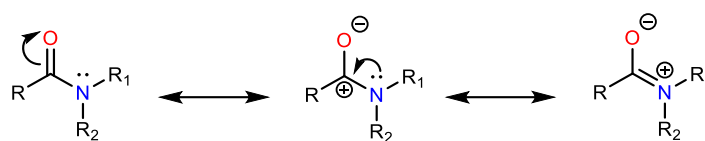
### **Deoxygenation of 1° and 2° Amides with Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> under Mild Conditions**

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## 2.1. Introduction

The reduction of amides to amines is a challenging organic transformation due to the amides' less reactive carbonyl bond (C=O) (**Scheme 2.1**). Several methods are known for the synthesis of amines, but they lack the ease of synthesis.<sup>1-2</sup> The direct hydrogenation of amides to amines (using H<sub>2</sub>) in the presence of late-transition metal catalysts is well explored but requires high temperature and pressure.<sup>3</sup> Similarly, strong reducing agents like LiAlH<sub>4</sub>, B<sub>2</sub>H<sub>6</sub>, etc. require stoichiometric amounts and sometimes hamper the other functional group and display poor chemo- and site-selectivity.<sup>4</sup> Other methods like transfer hydrogenation<sup>5</sup> and hydrosilylation<sup>6</sup> are also known for reducing amides but are still in their infancy. Additionally, silanes cost much more than boron reagents. Hence, hydroboration can serve as an alternative route for the reduction of amides. It is evident from the literature that the reduction of 1° amides with pinacolborane is more difficult compared to 2° and 3° amides.<sup>7,8</sup> There is only one example of a simple and easily available compound that can be utilized for the hydroboration of 1° amides.<sup>8a</sup> But, that requires harsh conditions (120°C), which are undesirable for chemo- and site-selective reductions (**Chart 2.1**).<sup>8a</sup>

Recently, significant attention has been paid to the less explored rare-earth metal-based-catalysts for the hydroboration of amides to the corresponding amines.<sup>8a,8b</sup> In 2020, Chen and co-workers introduced the hydroboration of 2° and 3° amides to amines using Y[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> as a catalyst at 100-120 °C temperature (**Scheme 2.2**).<sup>8b</sup> They also tried the hydroboration of 1° amides, but the attempts were unsuccessful.



The difficulty order of amide reduction: 1° > 2° > 3°

**Scheme 2.1.** Resonance stabilization of amide (R<sub>1</sub> and R<sub>2</sub>: H, alkyl or aryl).

| Y[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> | La[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> | Ca[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (THF) <sub>2</sub> |
|-----------------------------------------------------|------------------------------------------------------|-------------------------------------------------------------------------|
| Chen and co-workers                                 | Marks and co-workers                                 | Luo and co-workers                                                      |
| 2020                                                | 2020                                                 | 2021                                                                    |
| 2° and 3° amides                                    | 2° and 3° amides                                     | 1° and 2° amides                                                        |
| 10 mol% of catalyst                                 | 5 mol% of catalyst                                   | 120°C, 36 h                                                             |
| 2.4-6 eqv. of HBpin                                 | 5 eqv. of HBpin                                      | 5 mol% of catalyst                                                      |
| 100-120 °C, 24-48 h                                 | 25-60 °C, 1-48 h                                     | 5 eqv. of HBpin                                                         |
|                                                     |                                                      | 3° amide (25 °C, 4 h)                                                   |

**Chart 2.1.** Reported homoleptic bis(trimethylsilyl)amide catalysts for amide reduction.

$R_1 = R_2 = H$  (1° amide);  $R_1 = \text{aryl/alkyl}, R_2 = H$  (2° amide);  $R_1 = R_2 = \text{aryl/alkyl}$  (3° amide)

| Findlater and co-workers, 2019                                                                                                                                                                                                                                                                                   | Chen and co-workers, 2020                                                                                                                                                                                                                                                                                                                                                    | Marks and co-workers, 2020                                                                                                                                                                                                                                                                                                                                                | This work                                                                                                                                                                                                                                                                                                                                                                                                                 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>Hydroboration of 1°, 2° &amp; 3° amides</li> <li>1.5-3 mol% of <math>\text{La}_4(\text{O})(\text{acac})_{10}</math></li> <li>3-4 eqv. of HBpin</li> <li>Benzene as a solvent</li> <li>50-110 °C temperature</li> <li>7-24 h reaction time</li> <li>50 examples</li> </ul> | <ul style="list-style-type: none"> <li>Hydroboration of 2° and 3° amides</li> <li>10 mol% of <math>\text{Y}[\text{N}(\text{SiMe}_3)_2]_3</math></li> <li>2.4-6 eqv. of Hbpin</li> <li>Toluene as a solvent</li> <li>100-120 °C temperature</li> <li>24-48 h reaction time</li> <li>46 examples</li> <li>Commercially available catalyst</li> <li>Indole synthesis</li> </ul> | <ul style="list-style-type: none"> <li>Hydroboration of 2° &amp; 3° amides</li> <li>5 mol% of <math>\text{La}[\text{N}(\text{SiMe}_3)_2]_3</math></li> <li>5 eqv. of HBpin</li> <li><math>\text{C}_6\text{D}_6</math> as a solvent</li> <li>25-60 °C temperature</li> <li>0.5-96 h reaction time</li> <li>15 examples</li> <li>Commercially available catalyst</li> </ul> | <ul style="list-style-type: none"> <li>Hydroboration of 1° &amp; 2° amides</li> <li>2-5 mol% of <math>\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3</math></li> <li>4.5 eqv. of HBpin</li> <li>Toluene/<math>\text{C}_6\text{D}_6</math> as solvent</li> <li>60-70 °C temperature</li> <li>4-36 h reaction time</li> <li>29 examples</li> <li>Commercially available catalyst</li> <li>Indole synthesis</li> </ul> |

**Scheme 2.2.** Reported organo-lanthanide catalysts for the hydroboration of amides.

In the same year, Marks and co-workers also reported the reduction of 2° and 3° with pinacolborane under mild conditions at 25-60 °C temperature using  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$  as a catalyst (**Scheme 2.2**),<sup>8c</sup> but they were also not successful in reducing 1° amides using HBpin. However, they explained the catalyst's activation and mechanistic pathways in detail. Another significant contribution in this line was made by Findlater and co-workers, who introduced the polynuclear lanthanide–diketonato clusters as a promising catalyst for the hydroboration of amides (1°, 2°, and 3°) and esters.<sup>9</sup> Recently, Sen and co-workers demonstrated the reduction of amides (1° and 2°) to their corresponding borylated amines in a neat reaction using harsh conditions with an excess of HBpin (at 100 °C).<sup>10</sup>

Encouraged by the previous studies on homoleptic bis(trimethylsilyl)amides as catalysts, we envisioned using a less explored and easily available  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. In this work, we have demonstrated the deoxygenation of 1° and 2° amides with HBpin in the presence of easily available  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  under mild conditions. Further, we have shown a broad substrate scope of 1° and 2° amides with different functional group tolerance. Several experiments and kinetic studies were performed to understand the mechanistic aspects of the hydroboration reaction of amides using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . Our detailed results are discussed herein.

## 2.2. Experimental section

**2.2.1. General information:** All manipulations were carried out under an inert gas atmosphere of argon using the standard Schlenk technique and in an argon-filled MBRAUN MB 150-GI glovebox. All solvents were purified by MBRAUN MB SPS-800 solvent purification system. All other chemicals were purchased from Sigma Aldrich, Alfa-aesar and BLD Pharma. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  using a Bruker 400 MHz spectrometer. Mass spectra were recorded using an AB Sciex 4800 plus HRMS. The IR spectra were recorded by using ALPHA-II ECO ATR, Bruker.  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  was synthesized by using reported synthetic procedure.<sup>11</sup>

**2.2.2. Catalytic reaction procedure:** The hydroboration of the primary amide (benzamide) was carried out in Schlenk tubes and NMR tubes using the Schlenk line. The benzamide (0.2 mmol) was taken in a Schlenk tube and added 0.5 M of HBpin solution in toluene. The reaction mixture was kept for heating in an oil bath for the mentioned time period. After the completion of the reaction, the solvent was dried under the vacuum, and mesitylene (0.2 mmol) was added. To this mixture, 0.5 mL of  $\text{CDCl}_3$  was added to record the NMR spectrum. The yield of the borylated product was determined by integrating the corresponding  $^1\text{H}$  NMR spectrum normalized by mesitylene as an internal standard. In some cases, we used  $\text{C}_6\text{D}_6$  as a solvent due to the products' volatile nature or low boiling point. We have calculated the yield of the product by considering the two protons at the reduced carbon centre (**Figure 2.1**).

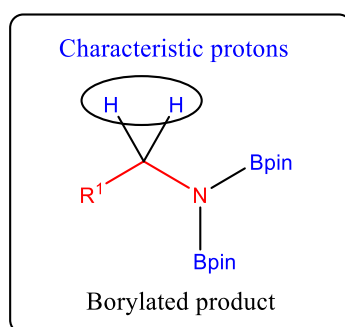


**Figure 2.1.** The general structure of the borylated amine as a product of hydroboration of the primary amide.

## 2.3. Results and discussion

**2.3.1. Reaction optimization:** We started the investigation of the deoxygenation of benzamide (1° amide) with pinacolborane (HBpin) in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. We observed that 5 mol% of the catalyst at 70 °C with 4.5 equivalent of HBpin in 36 hours led to almost quantitative deoxygenation of benzamide (**Entry 2, Table 2.1**). During optimization (**Table 2.1**), a significant change in the yields of the hydroborated products was observed under varying reaction conditions. All the reactions are performed in toluene or benzene- $\text{d}_6$  solvent. After optimizing the reaction conditions for the deoxygenation of benzamide, we moved towards the deoxygenation of secondary amides (acetanilide) with HBpin (**Table 2.2**). We found that 2 mol% of the catalyst at 70 °C temperature in 12 hours with 4.5 equivalent of HBpin are the fruitful conditions to attain the corresponding hydroborated product of acetanilide in good yields (**Entry 3, Table 2.2**). After that, we tried to get the deoxygenated product of a tertiary amide by varying several reaction conditions (up to 100 °C temperature in 48 hours). Unfortunately, we could not get the desired product from 3° amides. This was a surprising observation, as two previous reports on organolanthanides-catalyzed deoxygenation of 2° and 3° amides have already been documented.<sup>8a,8b</sup>

During optimization of the reaction conditions (**Table 1** and **Table 2.2**), it was noticed that the equivalency of the HBpin greatly influences the deoxygenation of 1° and 2° amides. Conceptually, 3.0 equivalent of HBpin is required to accomplish the deoxygenative reduction of 2° amides, but for the completion of the reaction with a higher yield, it requires 4.5 equivalent of HBpin. Similar observations are made in the previous lanthanide-based catalysts, where it is presumed that the excess of HBpin compensates for the possible formation of transient amide-borane/amine-borane adducts during the reaction.<sup>8b</sup>

**Table 2.1.** Optimization of reaction conditions for  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalyzed deoxygenation of 1° amides.

0.2 mmol      y mmol       $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (X mol%)      Product      +      Byproduct

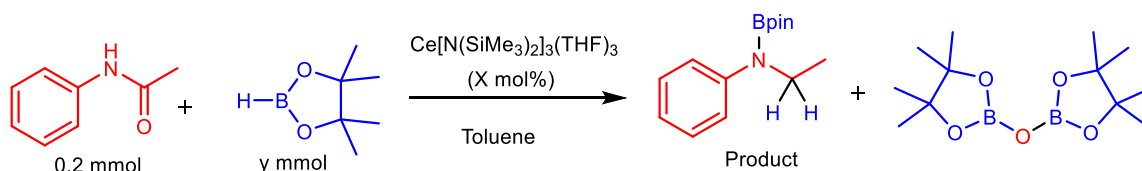
Toluene

| Entry | Mol% (X)<br>of catalyst        | Eqv. of<br>HBpin | Temp.<br>(°C) | Time<br>(h) | Yield*<br>(%) |
|-------|--------------------------------|------------------|---------------|-------------|---------------|
| 1.    | 5[ $\text{Ce}^{\text{NTMS}}$ ] | 4.5              | 70            | 24          | 63            |

|     |                        |     |    |    |                 |
|-----|------------------------|-----|----|----|-----------------|
| 2.  | 5[Ce <sup>NTMS</sup> ] | 4.5 | 70 | 36 | 95.5            |
| 3.  | 2[Ce <sup>NTMS</sup> ] | 4.5 | 70 | 36 | 30              |
| 4.  | 4[Ce <sup>NTMS</sup> ] | 4.5 | 70 | 36 | 49              |
| 5.  | 5[Ce <sup>NTMS</sup> ] | 4.5 | rt | 36 | 18.5            |
| 6.  | 5[Ce <sup>NTMS</sup> ] | 4.5 | 50 | 36 | 40.5            |
| 7.  | 5[Ce <sup>NTMS</sup> ] | 4.5 | 60 | 36 | 72.5            |
| 8.  | 5[Ce <sup>NTMS</sup> ] | 3.5 | 70 | 36 | 54.5            |
| 9.  | 5[Ce <sup>NTMS</sup> ] | 4.5 | 70 | 36 | 17 <sup>#</sup> |
| 10. | -                      | 4.5 | 70 | 36 | 13              |
| 11. | 10[CeCl <sub>3</sub> ] | 4.5 | 70 | 36 | 22              |
| 12. | 5[La <sup>NTMS</sup> ] | 4.5 | 70 | 36 | 17              |
| 13. | 5[Yb <sup>NTMS</sup> ] | 4.5 | 70 | 36 | 44              |

[\*Yields were determined by the integration of the corresponding <sup>1</sup>H NMR spectra normalized with an internal standard (mesitylene); <sup>#</sup>Reaction in neat condition; Ln<sup>NTMS</sup>: Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (where, Ln = Ce, La, Yb)]

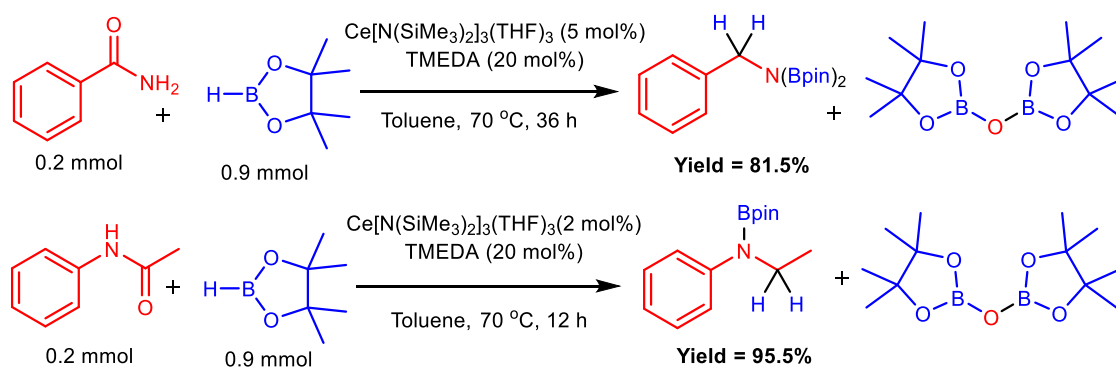
**Table 2.2.** Optimization of reaction conditions for Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>-catalyzed deoxygenation of 2° amides.



| Entry | Mol% (X)<br>of catalyst | Eqv. of<br>HBpin | Temp.<br>(°C) | Time<br>(h) | Yield*<br>(%) |
|-------|-------------------------|------------------|---------------|-------------|---------------|
| 1.    | 2[Ce <sup>NTMS</sup> ]  | 4.5              | 70            | 24          | >99           |
| 2.    | 2[Ce <sup>NTMS</sup> ]  | 3                | 70            | 24          | 80            |
| 3.    | 2[Ce <sup>NTMS</sup> ]  | 4.5              | 70            | 12          | 98            |
| 4.    | 2[Ce <sup>NTMS</sup> ]  | 4.5              | 70            | 8           | 69            |
| 5.    | 1[Ce <sup>NTMS</sup> ]  | 4.5              | 70            | 12          | 58            |
| 6.    | 2[Ce <sup>NTMS</sup> ]  | 4.5              | rt            | 12          | 17            |
| 7.    | 2[Ce <sup>NTMS</sup> ]  | 4.5              | 50            | 12          | 68            |
| 8.    | -                       | 4.5              | 70            | 12          | <3            |
| 9.    | 10[CeCl <sub>3</sub> ]  | 4.5              | 70            | 12          | <5            |

[\*Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene)]

After finalizing the optimized reaction conditions, we further performed some control reactions to elucidate the role of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and HBpin for the deoxygenation of  $1^\circ$  and  $2^\circ$  amides (**Table 1** and **Table 2.2**). For  $1^\circ$  amide (benzamide), when the reaction was performed without a catalyst, a 13% yield of the product was observed (**Table 2.1**). Similarly, 10 mol% of  $\text{CeCl}_3$  as a catalyst led to the formation of 22% hydroborated product (**Table 2.1**). To exclude the hidden catalysis by  $\text{BH}_3$ , we performed the catalytic reaction in the presence of 20 mol% of TMEDA.<sup>12,13</sup> This reaction afforded 81.5% yield of the product, confirming a minor impact of  $\text{BH}_3$  in this  $1^\circ$  amide hydroboration reaction (**Scheme 2.3**). However, for  $2^\circ$  amide (acetanilide), the same set of control experiments afforded a significantly less yield of the product (3-5%) (**Entry 8-9, Table 2.2**). The presence of 20 mol% of TMEDA in this reaction gave a 95.5% yield of the product, representing an insignificant role of  $\text{BH}_3$  in  $2^\circ$  amide hydroboration reaction (**Scheme 2.3**).

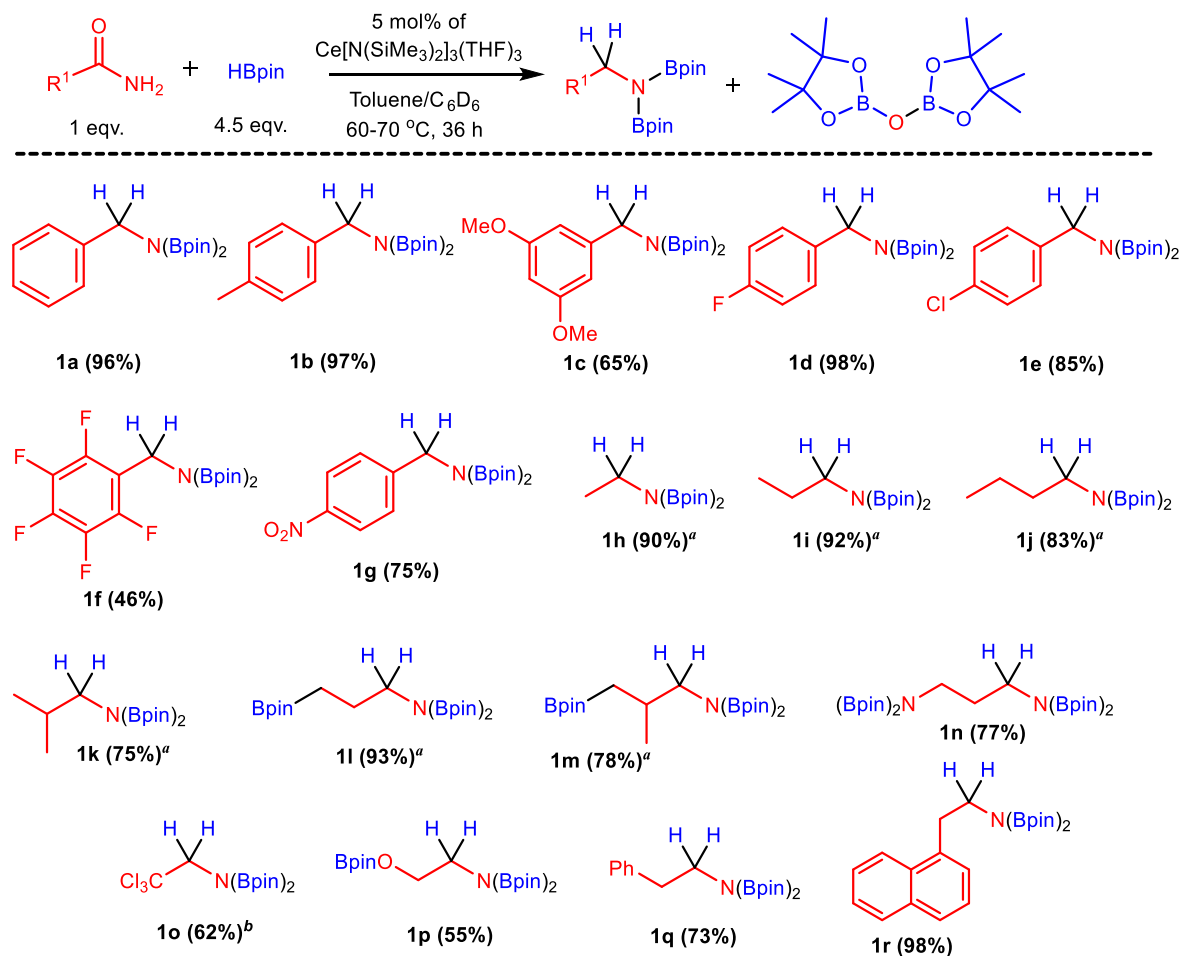


**Scheme 2.3.** Hydroboration of  $1^\circ$  and  $2^\circ$  amides in the presence of TMEDA, a test for “hidden catalysis”.

**2.3.2. Substrate scope of deoxygenation of amides:** After optimizing the reaction conditions, we moved toward the substrate scope to study the influence of different electron-withdrawing and electron-donating groups on the aromatic and aliphatic primary amides (**Scheme 2.4**). The aromatic amides are observed to offer more prolific yields as compared to the aliphatic amides. The electron-withdrawing and electron-donating groups play an unambiguous preface to afford the corresponding hydroborated amines.

The electron-withdrawing groups substituted primary amides are conferring comparatively less yields (**1f** with pentafluoro group, **1g** with  $-\text{NO}_2$  group, **1n** with  $-\text{CN}$  group, **1o** with trichloro

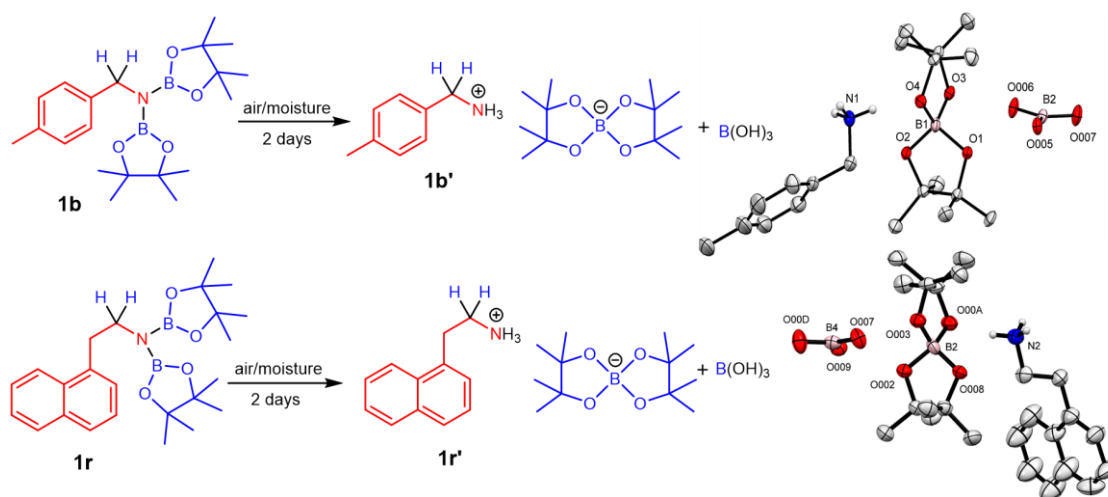
groups, **1p** with -OH groups). Surprisingly, **1c** shows less yield (65%) than the other substrates, possibly due to the two methoxy groups at the *meta*-position (**Scheme 2.4**).



**Scheme 2.4.** Substrate scope of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed primary amide hydroboration reaction. [<sup>a</sup> $\text{C}_6\text{D}_6$  as solvent. <sup>b</sup>72 hours reaction time. Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene).]

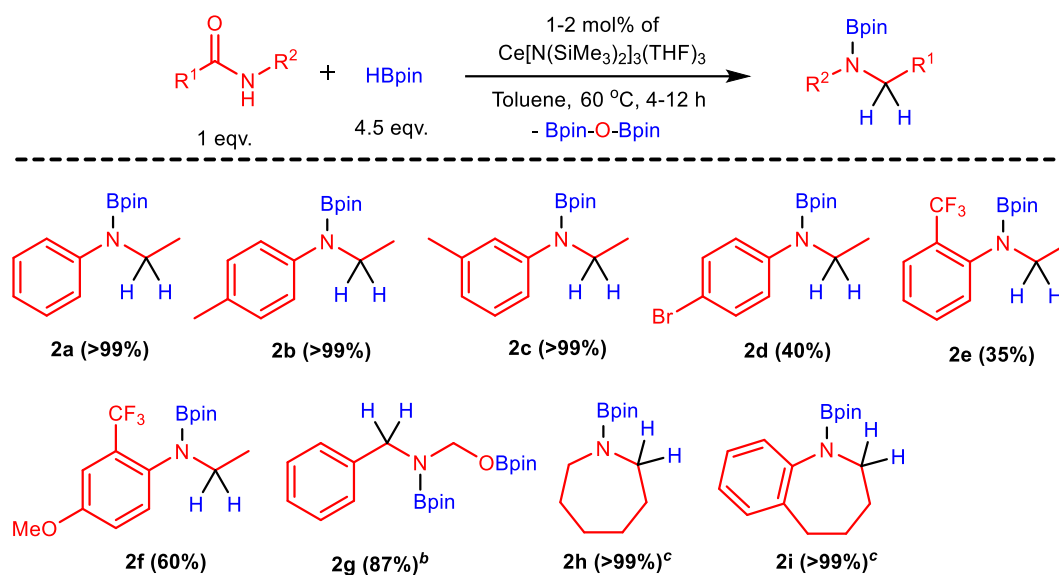
We used  $\text{C}_6\text{D}_6$  as a solvent (instead of toluene) for six substrates (**1h–1m**) as the boiling points of the desired products in these cases were less. **1a** and **1b** were obtained in almost similar yields, there is no significant effect of the  $-\text{CH}_3$  group at the *para* position of benzamide. The yield of **1e** (yield = 85%;  $-\text{Cl}$  group at *para* position) was slightly less than **1d** (yield = 98%;  $-\text{F}$  group at *para* position), but a trichloro-substituted group in acetamide afforded 62% of **1o**. Due to the presence of  $-\text{OH}$  and  $\text{C}=\text{C}$  groups, yields of the hydroborated products, **1p**, **1l**, and **1m**, were reduced. The phenyl group substituted acetamide (**1q**) afforded less yield than the naphthyl group substituted acetamide (**1r**), though there is not much electronic difference in the substrate. Important to note that **1p** is utilized to scrub the combusted fuel emissions to remove  $\text{CO}_2$  and  $\text{H}_2\text{S}$  gases. We examined the stability of the borylated products in the presence

of air/moisture, which caused the hydrolysis of the borylated product to the corresponding amine salt with a cationic boron counterpart (**Scheme 2.5**). These amine salts were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and the single crystal X-ray diffraction technique (CCDC: 2264469 (**1b'**) and 2264470 (**1r'**) and confirmed the expected reduction of amides.



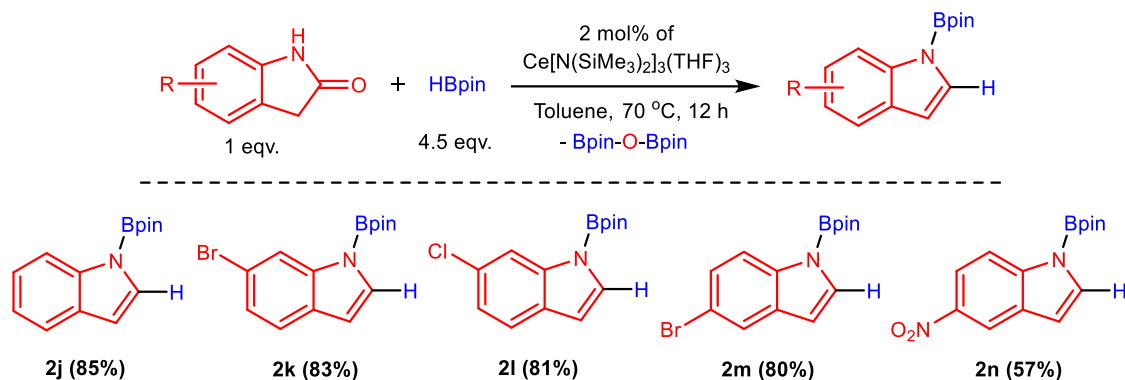
**Scheme 2.5.** Unexpected hydrolysed products of **1b** and **1r**.

The optimized reaction conditions for the deoxygenation of 2° amide (acetanilide) are much more energetically favorable and less time-consuming compared to 1° amide (benzamide). All the desired products were observed in good to excellent yields under the same optimized conditions (**Scheme 2.6**), except **2g** was obtained in 87% with a long reaction time (24 hours). On the other hand, cyclic 2° amides ( $\epsilon$ -caprolactam and its derivative) required lower catalyst loading (1 mol%) and a shorter reaction time (4 hours) to complete the reaction, leading to excellent yields of **2h** and **2i**. The corresponding amine of **2h** is an industrially useful compound, which is being used as an impregnating agent for  $\text{CO}_2$  capture and drug discovery.<sup>14</sup>



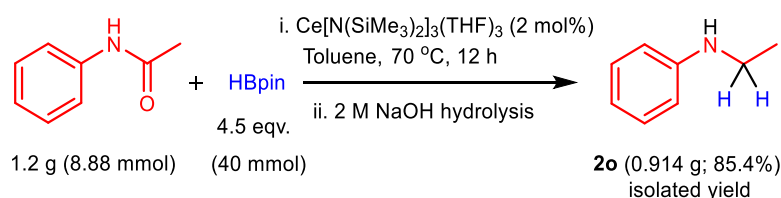
**Scheme 2.6.** Substrate scope of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalyzed hydroboration reaction of 2° amides. [<sup>b</sup>24 hrs reaction time. <sup>c</sup>1 mol% of the catalyst and 4 hrs reaction time. Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene)].

**2.3.3. Substrate scope of borylated indoles:** Synthesis of indoles and their derivatives is in high demand due to their significant biological role in the human body.<sup>15</sup> They have wide applications as anti-microbial, anti-cancer, anti-hypertensive, antiproliferative, and anti-inflammatory agents.<sup>15</sup> The most suitable condition for the hydroboration of indolin-2-one to borylated indole was found to be 4.5 equivalent of HBpin in the presence of 2 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  at 70 °C in 12 hours (**Scheme 2.7**). A mixture of borylated indole and borylated indoline products was observed upon increasing the reaction temperature or the reaction time. The presence of the halide group (-Cl and -Br at 5- and 6-position) on the substrate did not hamper the completeness of the reaction and displayed almost the same yields of the products (83% for **2k**, 81% for **2l**, and 80% for **2m**) (**Scheme 2.7**). But, in the presence of nitro group (-NO<sub>2</sub>) at the 5<sup>th</sup>-position, the formation of borylated indole product was reduced (57%) (**Scheme 2.7**).



**Scheme 2.7.** Synthesis of borylated indole and its derivatives. [Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene)].

**2.3.4. Gram-scale amine synthesis:** Bulk-scale synthesis is always one of the crucial challenges for industrial purposes. Hence, we tried a gram scale reaction to see the feasibility of the bulk scale synthesis and a reaction of 1.2 gm (8.88 mmol) of acetanilide with 4.5 equivalent HBpin (40 mmol) using 2 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  at the optimized reaction conditions was performed (**Scheme 2.8**). The borylated product was hydrolyzed using a 2 M NaOH solution, which afforded corresponding *N*-ethylaniline in 85.4% isolated yield (0.914 gm). The smooth scaling up of this reaction confirms the suitability of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst for the potential bulk-scale synthesis.



**Scheme 2.8.** Synthesis of *N*-ethylaniline from a gram scale reaction of acetanilide.

### 2.3.5. Analytical data of substrates scope:

**1a:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.32-7.26 (m, 4H, *Ph*), 7.19-7.18 (m, 1H, *Ph*), 6.82 (*mesitylene*), 4.26 (s, 2H,  $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 2.30 (*mesitylene*), 1.29 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.22 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  143.1 (*Ph*), 137.7 (*mesitylene*), 132.1 (*Ph*), 127.8 (*Ph*), 127.55 (*Ph*), 126.9 (*mesitylene*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 82.3 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 47.3 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{19}\text{H}_{31}\text{B}_2\text{NO}_4$ :  $m/z$  359.2439. Found  $m/z$  359.3704 ( $[\text{M}]^+$ ).

**1b:**  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.23-7.14 (m, 2H, *Ph*), 7.07-7.05 (m, 2H, *Ph*), 6.81 (*mesitylene*), 4.21 (s, 2H,  $\text{ArCH}_2(\text{Bpin})_2$ ), 2.36 (s, 3H,  $\text{CH}_3$ ), 2.29 (*mesitylene*), 1.28 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.21 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.5 MHz, 298 K):  $\delta$  143.6 (*Ph*), 137.6 (*mesitylene*), 131.9 (*Ph*), 129.4 (*Ph*), 128.0 (*Ph*), 126.9 (*mesitylene*), 82.5 ( $\text{O}(\text{Bpin})_2$ ), 82.0 ( $\text{ArCH}_2\text{N}(\text{Bpin})_2$ ), 44.9 ( $\text{ArCH}_2\text{N}(\text{Bpin})_2$ ), 24.7 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{ArCH}_2\text{N}(\text{Bpin})_2$ ), 21.1 (*mesitylene*), 21.0 (*MePh*) ppm. ESI-MS: Calculated for  $\text{C}_{20}\text{H}_{33}\text{B}_2\text{NO}_4$ :  $m/z$  374.2629. Found  $m/z$  397.5423 ( $[\text{M}+\text{Na}]^+$ ).

**1c:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.81 (*mesitylene*), 6.54 (s, 2H, *Ph*), 6.31 (broad, 2H, *Ph*), 4.19(s, 2H,  $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 3.77 (s, 6H,  $\text{OCH}_3$ ), 2.29 (*mesitylene*), 1.28 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.23 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  160.5 (*PhOMe*), 145.5 (*Ph*), 137.7 (*mesitylene*), 128.2 (*Ph*), 126.9 (*mesitylene*), 105.4 (*Ph*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 82.4 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 55.2 (*PhOMe*), 47.5 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{21}\text{H}_{35}\text{B}_2\text{NO}_6$ :  $m/z$  419.2650. Found  $m/z$  419.2766 ( $[\text{M}]^+$ ).

**1d.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.31-7.27 (t, 2H, *Ph*), 6.95- 6.91 (t, 2H, *Ph*), 6.81 (*mesitylene*), 4.19 (s, 2H,  $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 2.29 (*mesitylene*), 1.28 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.21 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  162.8 (*PhF*), 138.9 (*Ph*), 137.7 (*mesitylene*), 129.3 (*Ph*), 128.3 (*Ph*), 127.0 (*mesitylene*), 114.6 (*Ph*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 82.4 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 46.6 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{19}\text{H}_{30}\text{B}_2\text{FNO}_4$ :  $m/z$  377.2345. Found  $m/z$  414.2418 ( $[\text{M}+\text{K}]^+$ ).

**1e:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.35-7.32 (m, 2H, *Ph*), 7.30-7.24 (m, 2H, *Ph*), 6.81 (*mesitylene*), 3.92 (s, 2H,  $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 2.29 (*mesitylene*), 1.26 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.20 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.5 (*mesitylene*), 133.1 (*Ph*), 129.3 (*Ph*), 128.7 (*Ph*), 128.1 (*Ph*), 126.8 (*mesitylene*), 82.4 ( $\text{O}(\text{Bpin})_2$ ), 82.0 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 44.6 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 24.7 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 21.1 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{19}\text{H}_{30}\text{B}_2\text{ClNO}_4$ :  $m/z$  393.2049. Found  $m/z$  415.2115 ( $[\text{M}+\text{Na}]^+$ ).

**1f:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.81 (*mesitylene*), 4.36 (s, 2H,  $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 2.29 (*mesitylene*), 1.28 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.21 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  145.6 (*Ph*), 143.1 (*Ph*), 139.0 (*Ph*), 137.8 (*mesitylene*), 127.0 (*mesitylene*), 125.4 (*Ph*), 83.2 ( $\text{O}(\text{Bpin})_2$ ), 82.6 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ), 33.8 ( $\text{PhCH}_2\text{N}(\text{Bpin})_2$ ) 24.6

(O(*Bpin*)<sub>2</sub>), 24.2 (PhCH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 21.3 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>19</sub>H<sub>26</sub>B<sub>2</sub>F<sub>5</sub>NO<sub>4</sub>: *m/z* 449.1968. Found *m/z* 488.7883 ([M+K]<sup>+</sup>).

**1g:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 8.19-8.16 (d, 2H, *Ph*), 7.47- 7.44 (d, 2H, *Ph*), 6.81 (*mesitylene*), 4.23 (s, 2H, PhCH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 2.29 (*mesitylene*), 1.28 (s, 24H, N(*Bpin*)<sub>2</sub>), 1.23 (s, 24H, O(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 150.6 (*Ph*), 147.3 (*Ph*), 137.6 (*mesitylene*), 129.0 (*Ph*), 126.9 (*mesitylene*), 123.5 (*Ph*), 82.6 (O(*Bpin*)<sub>2</sub>), 82.4 (PhCH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 44.7 (PhCH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.7 (O(*Bpin*)<sub>2</sub>), 24.6 (PhCH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 21.1 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>19</sub>H<sub>30</sub>B<sub>2</sub>N<sub>2</sub>O<sub>6</sub>: *m/z* 404.2290. Found *m/z* 405.1199 ([M+H]<sup>+</sup>).

**1h:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 6.62 (*mesitylene*), 2.92-2.87 (q, 2H, CH<sub>2</sub>), 2.10 (*mesitylene*), 1.09 (s, 24H, N(*Bpin*)<sub>2</sub>), 1.06 (s, 24H, O(*Bpin*)<sub>2</sub>), 0.88-0.84 (t, 3H, CH<sub>3</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 137.7 (*mesitylene*), 127.0 (*mesitylene*), 83.1 (O(*Bpin*)<sub>2</sub>), 82.0 (CH<sub>3</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 38.6 (CH<sub>3</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.6 (O(*Bpin*)<sub>2</sub>), 24.6 (CH<sub>3</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 18.7 (CH<sub>3</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>) ppm. ESI-MS: Calculated for C<sub>14</sub>H<sub>29</sub>B<sub>2</sub>NO<sub>4</sub>: *m/z* 297.2283. Found *m/z* 297.2383 ([M]<sup>+</sup>).

**1i:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 3.44-3.28 (t, 2H, CH<sub>2</sub>), 1.68-1.52 (m, 2H, CH<sub>2</sub>), 1.11 (s, 24H, N(*Bpin*)<sub>2</sub>), 0.77-0.72 (t, 3H, CH<sub>3</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 137.7 (*mesitylene*), 127.0 (*mesitylene*), 83.1 (O(*Bpin*)<sub>2</sub>), 82.0 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 45.4 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 26.1 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.6 (O(*Bpin*)<sub>2</sub>), 24.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 21.2 (*mesitylene*), 11.2 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>) ppm. ESI-MS: Calculated for C<sub>15</sub>H<sub>31</sub>B<sub>2</sub>NO<sub>4</sub>: *m/z* 311.2439. Found *m/z* 311.2540 ([M]<sup>+</sup>).

**1j:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 6.59 (*mesitylene*), 2.86-2.83 (t, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 2.07 (*mesitylene*), 1.50-1.40 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 1.23- 1.20 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 1.07 (s, 24H, N(*Bpin*)<sub>2</sub>), 1.04 (s, 24H, O(*Bpin*)<sub>2</sub>), 0.69-0.72 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 137.3 (*mesitylene*), 126.7 (*mesitylene*), 82.7 (O(*Bpin*)<sub>2</sub>), 81.6 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 42.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.7 (O(*Bpin*)<sub>2</sub>), 24.3 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 22.5 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 20.9 (*mesitylene*), 19.4 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 13.8 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>) ppm. ESI-MS: Calculated for C<sub>16</sub>H<sub>33</sub>B<sub>2</sub>NO<sub>4</sub>: *m/z* 325.2596. Found *m/z* 325.1259 ([M]<sup>+</sup>).

**1k.**  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.67 (*mesitylene*), 2.70-2.67 (d, 2H,  $\text{CH}_2\text{N}(\text{Bpin})_2$ ), 2.13 (*mesitylene*) 1.50 (broad, 1H, CH), 1.05 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.01 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 0.76-0.74 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 126.9 (*mesitylene*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 81.9 ( $((\text{CH}_3)_2\text{CHCH}_2\text{N}(\text{Bpin})_2)$ ), 51.0 ( $((\text{CH}_3)_2\text{CHCH}_2\text{N}(\text{Bpin})_2)$ ), 34.9 ( $((\text{CH}_3)_2\text{CHCH}_2\text{N}(\text{Bpin})_2)$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.4 ( $((\text{CH}_3)_2\text{CHCH}_2\text{N}(\text{Bpin})_2)$ ), 21.2 (*mesitylene*), 19.6 ( $((\text{CH}_3)_2\text{CHCH}_2\text{N}(\text{Bpin})_2)$ ) ppm. ESI-MS: Calculated for  $\text{C}_{16}\text{H}_{33}\text{B}_2\text{NO}_4$ :  $m/z$  325.2596. Found  $m/z$  347.6984 ( $[\text{M}+\text{Na}]^+$ ).

**1l.**  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.64 (*mesitylene*), 2.88-2.85 (t, 2H,  $\text{CH}_2\text{N}(\text{Bpin})_2$ ), 2.12 (*mesitylene*), 1.12 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.09 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.05-1.04 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.73-0.69 (t, 2H,  $\text{CH}_2\text{Bpin}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 127.0 (*mesitylene*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 82.1 ( $\text{N}(\text{Bpin})_2$ ), 82.0 ( $\text{CH}_2(\text{Bpin})$ ), 45.4 ( $\text{CH}_2\text{N}(\text{Bpin})_2$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.6 ( $\text{N}(\text{Bpin})_2$ ), 24.5 ( $\text{CH}_2(\text{Bpin})$ ), 22.8 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 21.3 (*mesitylene*), 11.2 ( $\text{CH}_2(\text{Bpin})$ ) ppm. ESI-MS: Calculated for  $\text{C}_{21}\text{H}_{42}\text{B}_3\text{NO}_6$ :  $m/z$  437.3291. Found  $m/z$  437.3507 ( $[\text{M}]^+$ ).

**1m:**  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.64 (*mesitylene*), 3.05-3.03 (d, 2H,  $\text{CH}_2\text{N}(\text{Bpin})_2$ ), 2.11 (*mesitylene*) 1.49-1.52 (m, 1H, CH), 1.04 (s, 12H,  $\text{CHCH}_2(\text{Bpin})$ ), 1.02 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.01 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 0.88-0.86 (d, 3H,  $\text{CHCH}_3$ ), 0.75-0.73 (d, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.4 (*mesitylene*), 126.8 (*mesitylene*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 83.0 ( $\text{N}(\text{Bpin})_2$ ), 82.9 ( $\text{CH}_2(\text{Bpin})$ ), 67.8 ( $\text{CH}_2\text{N}(\text{Bpin})_2$ ), 25.5 ( $\text{CH}_2(\text{Bpin})$ ) 24.7 ( $\text{O}(\text{Bpin})_2$ ), 24.4 ( $\text{N}(\text{Bpin})_2$ ), 24.4 ( $\text{CH}_2(\text{Bpin})$ ), 24.2 ( $\text{CH}_2\text{CHCH}_2$ ) 22.6 ( $\text{CH}_3$ ), 21.0 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{22}\text{H}_{44}\text{B}_3\text{NO}_6$ :  $m/z$  451.3448. Found  $m/z$  453.3172 ( $[\text{M}+2\text{H}]^+$ ).

**1n:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.65 (*mesitylene*), 3.23-3.05 (t, 4H,  $(\text{Bpin})_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{Bpin})_2$ ), 2.12 (*mesitylene*), 1.50-1.45 (m, 2H,  $(\text{Bpin})_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{Bpin})_2$ ), 1.08 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.02 (s, 48H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*mesitylene*), 127.0 (*mesitylene*), 83.2 ( $\text{O}(\text{Bpin})_2$ ), 82.6 ( $\text{N}(\text{Bpin})_2$ ), 39.9 ( $\text{CH}_2\text{N}(\text{Bpin})_2$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.6 ( $\text{N}(\text{Bpin})_2$ ), 22.8 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 21.3 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{29}\text{H}_{58}\text{B}_4\text{N}_2\text{O}_6$ :  $m/z$  574.4667. Found  $m/z$  574.2328 ( $[\text{M}]^+$ ).

**1o:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298K):  $\delta$  6.78 (*mesitylene*), 4.39 (s, 2H,  $\text{CH}_2$ ), 2.26 (*mesitylene*), 1.25 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.22 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 127.0 (*mesitylene*), 101.7 ( $\text{CCl}_3\text{CH}_2$ ), 83.1

(O(*Bpin*)<sub>2</sub>), 82.9 (N(*Bpin*)<sub>2</sub>), 61.3 (CCl<sub>3</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.6 (O(*Bpin*)<sub>2</sub>), 24.5 (N(*Bpin*)<sub>2</sub>), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>14</sub>H<sub>26</sub>B<sub>2</sub>Cl<sub>3</sub>NO<sub>4</sub>: *m/z* 399.1114. Found *m/z* 400.0898 ([M+H]<sup>+</sup>).

**1p:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): 6.77 (*mesitylene*), 4.34 (broad, 1H, CH<sub>2</sub>OH), 3.74-3.71 (t, 2H, CH<sub>2</sub>OH), 3.24-3.19 (t, 2H, CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 2.24 (*mesitylene*), 1.24 (s, 24H, N(*Bpin*)<sub>2</sub>), 1.20 (s, 24H, O(*Bpin*)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 137.4 (*mesitylene*), 126.8 (*mesitylene*), 82.8 (O(*Bpin*)<sub>2</sub>), 81.7 (N(*Bpin*)<sub>2</sub>), 67.7 (CH<sub>2</sub>(OBpin)), 44.7 (CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.7 (O(*Bpin*)), 24.5 (O(*Bpin*)<sub>2</sub>), 24.4 (N(*Bpin*)<sub>2</sub>), 21.0 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>20</sub>H<sub>40</sub>B<sub>3</sub>NO<sub>7</sub>: *m/z* 439.3084. Found *m/z* 439.3766 ([M]<sup>+</sup>).

**1q:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 7.28-7.24 (m, 2H, *Ph*), 7.21-7.19 (m, 3H, *Ph*), 6.81 (*mesitylene*), 3.34-3.31 (t, 2H, PhCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 2.76-2.72 (t, 2H, PhCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 2.29 (*mesitylene*), 1.28 (s, 24H, N(*Bpin*)<sub>2</sub>), 1.20 (s, 24H, O(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 139.9 (*Ph*), 137.7 (*mesitylene*), 129.0 (*Ph*), 128.3 (*Ph*), 126.9 (*mesitylene*), 126.0 (*Ph*), 83.0 (O(*Bpin*)<sub>2</sub>), 82.0 (PhCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 42.4 (PhCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 39.9 (PhCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.6 (O(*Bpin*)<sub>2</sub>), 24.5 (CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>20</sub>H<sub>33</sub>B<sub>2</sub>NO<sub>4</sub>: *m/z* 373.2596. Found *m/z* 373.2271 ([M]<sup>+</sup>).

**1r:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 7.84-7.80 (m, 1H, *Naphthalene*), 7.71-7.67 (m, 1H, *Naphthalene*), 7.51-7.44 (m, 2H, *Naphthalene*), 7.38-7.32 (m, 2H, *Naphthalene*), 7.17-7.15 (m, 1H, *Naphthalene*), 6.79 (*mesitylene*), 3.43-3.35 (t, 2H, ArCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 3.21-3.15 (t, 2H, ArCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 2.27 (*mesitylene*), 1.26 (s, 24H, N(*Bpin*)<sub>2</sub>), 1.21 (s, 24H, O(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 137.7 (*Mesitylene*), 136.6 (*Naphthalene*), 133.9 (*Naphthalene*), 132.6 (*Naphthalene*), 129.1 (*Naphthalene*), 128.2 (*Naphthalene*), 127.1 (*Naphthalene*), 126.9 (*Mesitylene*), 126.2 (*Naphthalene*), 125.4 (*Naphthalene*), 123.8 (*Naphthalene*), 122.5 (*Naphthalene*), 83.1 (O(*Bpin*)<sub>2</sub>), 82.2 (CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 45.0 (ArCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 37.3 (ArCH<sub>2</sub>CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 24.6 (O(*Bpin*)<sub>2</sub>), 24.5 (CH<sub>2</sub>N(*Bpin*)<sub>2</sub>), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>24</sub>H<sub>35</sub>B<sub>2</sub>NO<sub>4</sub>: *m/z* 422.2789. Found *m/z* 445.1338 ([M+Na]<sup>+</sup>).

**2a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 7.24-7.22 (m, 2H, *Ph*), 6.87 (*mesitylene*), 6.79-6.75 (m, 1H, *Ph*), 6.70-6.67 (m, 1H, *Ph*), 3.24-3.19 (q, 2H, CH<sub>2</sub>), 2.35 (*mesitylene*), 1.34 (s, 12H, PhN(*Bpin*)CH<sub>2</sub>CH<sub>3</sub>), 1.34 (s, 24H, O(*Bpin*)<sub>2</sub>), 1.32-1.30 (t, 3H, PhN(*Bpin*)CH<sub>2</sub>CH<sub>3</sub>) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 148.4 (*Ph*), 137.6 (*mesitylene*), 129.1 (*Ph*),

127.0 (*mesitylene*), 117.3 (*Ph*), 113.0 (*Ph*), 83.0 ( $\text{O}(\text{Bpin})_2$ ), 82.1 ( $\text{N}(\text{Bpin})$ ), 38.5 ( $\text{CH}_2\text{NBpin}$ ), 24.7 ( $\text{O}(\text{Bpin})_2$ ), 24.4 ( $\text{N}(\text{Bpin})$ ), 21.2 (*mesitylene*), 14.8 ( $\text{CH}_2\text{CH}_3$ ) ppm. ESI-MS: Calculated for  $\text{C}_{14}\text{H}_{22}\text{BNO}_2$ :  $m/z$  247.1744. Found  $m/z$  270.1641 ( $[\text{M}+\text{Na}]^+$ ).

**2b.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.00-6.98 (d, 2H, *Ph*), 6.81 (*mesitylene*), 6.55-6.53 (d, 2H, *Ph*), 3.16-3.11 (q, 2H,  $\text{CH}_2$ ), 2.29 (*mesitylene*), 2.25 (s, 3H, *Me*), 1.28 (s, 12H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ), 1.24 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.08-1.12 (t, 3H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  146.2 (*Ph*), 137.7 (*mesitylene*), 129.7 (*Ph*), 128.2 (*Ph*), 126.9 (*mesitylene*), 113.3 (*Ph*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 82.9 ( $\text{N}(\text{Bpin})$ ), 39.0 ( $\text{CH}_2\text{NBpin}$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.1 ( $\text{N}(\text{Bpin})$ ), 21.2 (*mesitylene*), 20.4 (*PhMe*), 14.9 ( $\text{CH}_2\text{CH}_3$ ) ppm. ESI-MS: Calculated for  $\text{C}_{15}\text{H}_{24}\text{BNO}_2$ :  $m/z$  261.1900. Found  $m/z$  262.1547 ( $[\text{M}+\text{H}]^+$ ).

**2c.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.19-7.08 (m, 3H, *Ph*), 6.85 (*mesitylene*), 6.81 (s, 1H, *Ph*), 3.58-3.53 (q, 2H,  $\text{CH}_2$ ), 2.36 (s, 3H, *Me*), 3.32 (*mesitylene*), 1.32 (s, 12H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ), 1.31 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.17-1.15 (t, 3H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  148.6 (*Ph*), 138.6 (*mesitylene*), 129.1 (*Ph*), 125.0 (*mesitylene*), 118.1 (*Ph*), 113.6 (*Ph*), 83.2 ( $\text{O}(\text{Bpin})_2$ ), 82.5 ( $\text{N}(\text{Bpin})$ ), 38.5 ( $\text{CH}_2\text{NBpin}$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{N}(\text{Bpin})$ ), 21.7 (*PhMe*), 21.5 (*mesitylene*), 15.0 ( $\text{CH}_2\text{CH}_3$ ) ppm. ESI-MS: Calculated for  $\text{C}_{15}\text{H}_{24}\text{BNO}_2$ :  $m/z$  261.1900. Found  $m/z$  299.1825 ( $[\text{M}+\text{K}]^+$ ).

**2d.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.26-7.24 (d, 2H, *Ph*), 7.07-7.04 (d, 2H, *Ph*), 6.73 (*mesitylene*), 3.46- 3.40 (q, 2H,  $\text{CH}_2$ ), 2.21 (*mesitylene*), 1.21 (s, 12H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ), 1.20 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.06-1.03 (t, 3H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  145.2 (*Ph*), 137.4 (*mesitylene*), 131.9 (*Ph*), 131.5 (*Ph*), 122.5 (*mesitylene*), 114.3 (*Ph*), 83.2 ( $\text{O}(\text{Bpin})_2$ ), 82.8 ( $\text{N}(\text{Bpin})$ ), 38.5 ( $\text{CH}_2\text{NBpin}$ ), 24.7 ( $\text{O}(\text{Bpin})_2$ ), 24.6 ( $\text{N}(\text{Bpin})$ ), 22.8 (*mesitylene*), 15.2 ( $\text{CH}_2\text{CH}_3$ ) ppm. ESI-MS: Calculated for  $\text{C}_{14}\text{H}_{21}\text{BBrNO}_2$ :  $m/z$  325.0849. Found  $m/z$  325.1229 ( $[\text{M}]^+$ ).

**2e.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.60-7.58 (d, 1H, *Ph*), 7.45-7.41 (m, 1H, *Ph*), 7.24-7.15 (m, 2H, *Ph*), 3.19-3.13 (q, 2H,  $\text{CH}_2$ ), 1.23 (s, 12H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ), 1.04-1.00 (t, 3H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  144.4 (*Ph*), 137.7 (*mesitylene*), 133.2 (*Ph*), 132.6 (*Ph*), 132.3 (*Ph*), 127.0 (*mesitylene*), 126.0 ( $\text{PhCF}_3$ ), 115.7 (*Ph*), 111.8 (*Ph*), 83.1 ( $\text{O}(\text{Bpin})_2$ ), 82.6 ( $\text{N}(\text{Bpin})$ ), 38.2 ( $\text{CH}_2\text{NBpin}$ ), 24.6 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{N}(\text{Bpin})$ ), 21.2 (*mesitylene*), 15.7 ( $\text{CH}_2\text{CH}_3$ ) ppm. ESI-MS: Calculated for  $\text{C}_{15}\text{H}_{21}\text{BF}_3\text{NO}_2$ :  $m/z$  315.1617. Found  $m/z$  316.1695 ( $[\text{M}+\text{H}]^+$ ).

**2f.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.22-7.20 (m, 1H, *Ph*), 7.15-7.12 (m, 2H, *Ph*), 6.77 (*mesitylene*), 3.82 (s, 3H, *OMe*), 3.77- 3.75 (q, 2H,  $\text{CH}_2$ ), 2.24 (*mesitylene*), 1.24 (s, 12H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ), 1.21 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.19-1.16 (t, 3H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  155.0 (*Ph*), 137.6 (*mesitylene*), 129.0 (*Ph*), 128.2 (*Ph*), 127.0 (*mesitylene*), 125.3 ( $\text{PhCF}_3$ ), 123.9 ( $\text{PhCF}_3$ ), 123.2 ( $\text{PhCF}_3$ ), 108.5 (*Ph*), 83.0 ( $\text{O}(\text{Bpin})_2$ ), 82.0 ( $\text{N}(\text{Bpin})$ ), 55.8 (*OMe*), 37.8 ( $\text{CH}_2\text{NBpin}$ ), 24.5 ( $\text{O}(\text{Bpin})_2$ ), 24.5 ( $\text{N}(\text{Bpin})$ ), 21.2 (*mesitylene*), 14.5 ( $\text{CH}_2\text{CH}_3$ ) ppm. ESI-MS: Calculated for  $\text{C}_{15}\text{H}_{23}\text{BN}_2\text{O}_5$ :  $m/z$  322.1700. Found  $m/z$  323.1522 ( $[\text{M}+\text{H}]^+$ ).

**2g.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.32-7.30 (d, 1H, *Ph*), 7.17-7.13 (m, 2H, *Ph*), 7.08-7.06 (m, 2H, *Ph*) 6.70 (*mesitylene*), 3.76 (s, 2H,  $\text{CH}_2\text{OH}$ ), 2.91 (s, 2H,  $\text{PhCH}_2$ ), 2.18 (*mesitylene*), 1.16 (s, 12H,  $\text{PhN}(\text{Bpin})\text{CH}_2\text{CH}_3$ ), 1.09 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.4 (*mesitylene*), 134.2 (*Ph*), 131.0 (*Ph*), 128.1 (*Ph*), 127.1 (*Ph*), 126.7 (*mesitylene*) 83.0 ( $\text{O}(\text{Bpin})_2$ ), 82.9 ( $\text{N}(\text{Bpin})$ ), 67.7 ( $\text{CH}_2\text{OH}$ ), 49.4 ( $\text{PhCH}_2\text{NBpin}$ ), 24.7 ( $\text{O}(\text{Bpin})_2$ ), 24.3 ( $\text{N}(\text{Bpin})$ ), 21.0 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{14}\text{H}_{22}\text{BNO}_3$ :  $m/z$  263.1693. Found  $m/z$  285.1663 ( $[\text{M}+\text{Na}]^+$ ).

**2h.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.76 (*mesitylene*), 3.01-2.98 (t, 4H,  $\text{CH}_2\text{N}(\text{Bpin})\text{CH}_2$ ), 2.24 (*mesitylene*), 1.57-1.53 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.50-1.48 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.23 (s, 24H,  $\text{O}(\text{Bpin})_2$ ), 1.18 (s, 12H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})\text{CH}_2\text{CH}_2\text{CH}_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 126.9 (*mesitylene*), 82.4 ( $\text{O}(\text{Bpin})_2$ ), 81.0 ( $\text{N}(\text{Bpin})$ ), 47.0 ( $((\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2\text{N}(\text{Bpin}))$ ), 31.1 ( $((\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2\text{N}(\text{Bpin}))$ ), 27.3 ( $((\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2\text{N}(\text{Bpin}))$ ), 24.8 ( $\text{O}(\text{Bpin})_2$ ), 24.7 ( $\text{N}(\text{Bpin})$ ), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $\text{C}_{12}\text{H}_{24}\text{BNO}_2$ :  $m/z$  225.1900. Found  $m/z$  248.1964 ( $[\text{M}+\text{Na}]^+$ ).

**2i.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.17-7.02 (m, 4H, *Ph*), 6.84 (*mesitylene*), 2.80-2.77 (t, 2H,  $\text{PhN}(\text{Bpin})\text{CH}_2(\text{CH}_2)_3\text{Ph}$ ), 2.31 (*mesitylene*), 1.80-1.76 (m, 2H,  $\text{PhCH}_2(\text{CH}_2)_3\text{N}(\text{Bpin})\text{Ph}$ ), 1.68-1.67 (m, 2H,  $\text{PhNCH}_2\text{CH}_2(\text{CH}_2)_2\text{PhN}(\text{Bpin})$ ), 1.46-1.42 (m, 2H,  $\text{PhN}(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{PhN}$ ), 1.31 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) 1.28 (s, 12H,  $\text{PhN}(\text{Bpin})(\text{CH}_2)_2\text{Ph}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  150.1 (*Ph*), 137.6 (*mesitylene*), 133.9 (*Ph*), 130.7 (*Ph*), 127.0 (*mesitylene*), 126.5 (*Ph*), 121.1 (*Ph*), 119.6 (*Ph*), 83.0 ( $\text{O}(\text{Bpin})_2$ ), 82.1 ( $\text{N}(\text{Bpin})$ ), 48.9 ( $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})$ ), 35.9 ( $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})$ ), 31.8 ( $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})$ ), 26.9 ( $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Bpin})$ ), 24.5 ( $\text{O}(\text{Bpin})_2$ ), 24.5

(N(*Bpin*)), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $C_{16}H_{24}BNO_2$ :  $m/z$  273.1900. Found  $m/z$  273.1664 ( $[M]^+$ ).

**2j.**  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  7.68-7.66 (d, 1H, PhN(*Bpin*)CHCHPh), 7.45-7.43 (d, 1H, *Ph*), 7.24-7.19 (m, 2H, *Ph*), 7.15-7.12 (m, 1H, *Ph*), 6.84 (*mesitylene*), 6.57-6.56 (d, 1H, PhN(*Bpin*)CHCHPh), 2.32 (*mesitylene*), 1.30 (s, 24H, O(*Bpin*)<sub>2</sub>), 1.28 (s, 12H, PhN(*Bpin*)(CH)<sub>2</sub>Ph) ppm;  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 135.9 (*Ph*), 127.9 (*Ph*), 127.0 (*mesitylene*), 124.5 (PhCHCHN(*Bpin*)), 121.7 (*Ph*), 120.6 (*Ph*), 119.5 (*Ph*), 111.3 (*Ph*), 102.1 (PhCHCHN(*Bpin*)), 83.2 (O(*Bpin*)<sub>2</sub>), 82.9 (N(*Bpin*)), 24.6 (O(*Bpin*)<sub>2</sub>), 24.2 (N(*Bpin*)), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $C_{14}H_{19}BNO_2$ :  $m/z$  243.1431. Found  $m/z$  282.2215 ( $[M+K]^+$ ).

**2k.**  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  7.67 (s, 1H, *Ph*), 7.57-7.55 (d, 1H, PhN(*Bpin*)CHCHPh), 7.34-7.32 (d, 1H, *Ph*), 7.28-7.25 (m, 1H, *Ph*), 6.89 (*mesitylene*), 6.57-6.56 (s, 1H, PhN(*Bpin*)CHCHPh), 2.36 (*mesitylene*), 1.34 (s, 24H, O(*Bpin*)<sub>2</sub>), 1.32 (s, 12H, PhN(*Bpin*)(CH)<sub>2</sub>Ph) ppm;  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 136.9 (*Ph*), 129.1 (*Ph*), 127.0 (*mesitylene*), 125.7 (PhCHCHN(*Bpin*)), 125.4 (*Ph*), 122.6 (*Ph*), 121.6 (*Ph*), 114.5 (*Ph*), 102.1 (PhCHCHN(*Bpin*)), 83.2 (O(*Bpin*)<sub>2</sub>), 82.1 (N(*Bpin*)), 24.6 (O(*Bpin*)<sub>2</sub>), 24.1 (N(*Bpin*)), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for  $C_{14}H_{17}BBrNO_2$ :  $m/z$  321.0536. Found  $m/z$  321.3149 ( $[M]^+$ ).

**2l.**  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  7.85-7.82 (d, 1H, *Ph*), 7.71-7.71 (d, 1H, *Ph*), 7.39-7.38 (d, 1H, PhN(*Bpin*)CHCHPh), 7.33-7.30 (d, 1H, *Ph*), 6.81 (*mesitylene*), 6.53-6.53 (d, 1H, PhN(*Bpin*)CHCHPh), 2.29 (*mesitylene*), 1.28 (s, 24H, O(*Bpin*)<sub>2</sub>), 1.25 (s, 12H, PhN(*Bpin*)(CH)<sub>2</sub>Ph) ppm;  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 129.7 (*Ph*), 129.1 (*Ph*), 128.3 (*Ph*), 127.0 (*mesitylene*), 124.6 (PhCHCHN(*Bpin*)), 121.6 (*Ph*), 117.7 (*Ph*), 116.4 (*Ph*), 106.9 (PhCHCHN(*Bpin*)), 84.7 (O(*Bpin*)<sub>2</sub>), 83.2 (N(*Bpin*)), 24.8 (O(*Bpin*)<sub>2</sub>), 24.6 (N(*Bpin*)), 21.3 (*mesitylene*) ppm. ESI-MS: Calculated for  $C_{14}H_{17}BBrNO_2$ :  $m/z$  321.0536. Found  $m/z$  321.2610 ( $[M]^+$ ).

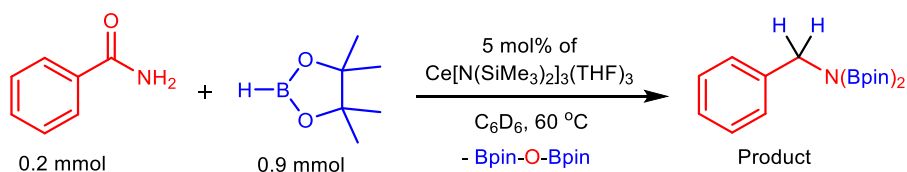
**2m.**  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  7.55-7.53 (d, 1H, PhN(*Bpin*)CHCHPh), 7.42 (s, 1H, *Ph*), 7.21-7.20 (d, 1H, *Ph*), 7.09-7.07 (m, 1H, *Ph*), 6.82 (*mesitylene*), 6.52 (d, 1H, PhN(*Bpin*)CHCHPh), 2.29 (*mesitylene*), 1.28 (s, 24H, O(*Bpin*)<sub>2</sub>), 1.25 (s, 12H, PhN(*Bpin*)(CH)<sub>2</sub>Ph) ppm;  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*mesitylene*), 136.3 (*Ph*), 127.7 (*Ph*), 127.0 (*Ph*), 126.6 (*mesitylene*), 125.1 (PhCHCHN(*Bpin*)), 121.5 (*Ph*), 120.4 (*Ph*), 111.3 (*Ph*), 102.5 (PhCHCHN(*Bpin*)), 83.3 (O(*Bpin*)<sub>2</sub>), 82.0 (N(*Bpin*)), 24.8

(O(*Bpin*)<sub>2</sub>), 24.6 (N(*Bpin*)), 21.3 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>14</sub>H<sub>17</sub>BClNO<sub>2</sub>: *m/z* 277.1041. Found *m/z* 277.0624 ([M]<sup>+</sup>).

**2n.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 8.11-8.00 (d, 1H, *Ph*), 7.53-7.47 (d, 1H, *Ph*), 7.24-7.16 (m, 2H, PhN(*Bpin*)CHCHPh), 6.80 (*mesitylene*), 6.74 (s, 1H, PhN(*Bpin*)CHCHPh), 2.28 (*mesitylene*), 1.28 (s, 24H, O(*Bpin*)<sub>2</sub>), 1.25 (s, 12H, PhN(*Bpin*)(CH)<sub>2</sub>Ph) ppm; <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 137.6 (*mesitylene*), 134.5 (*Ph*), 130.3 (*Ph*), 126.9 (*mesitylene*), 125.5 (PhCHCHN(*Bpin*)), 124.4 (*Ph*), 123.0 (*Ph*), 116.1 (*Ph*), 112.8 (*Ph*), 101.7 (PhCHCHN(*Bpin*)), 84.6 (O(*Bpin*)<sub>2</sub>), 83.2 (N(*Bpin*)), 24.7 (O(*Bpin*)<sub>2</sub>), 24.5 (N(*Bpin*)), 21.2 (*mesitylene*) ppm. ESI-MS: Calculated for C<sub>14</sub>H<sub>17</sub>BClNO<sub>2</sub>: *m/z* 277.1041. Found *m/z* 277.0624 ([M]<sup>+</sup>). ESI-MS: Calculated for C<sub>14</sub>H<sub>17</sub>BN<sub>2</sub>O<sub>4</sub>: *m/z* 288.1281. Found *m/z* 289.1295 ([M+H]<sup>+</sup>).

## 2.4. Kinetic studies

### 2.4.1. Rate equation of deoxygenation of benzamide:



To investigate the mechanism of this reaction, the rate law for catalytic benzamide reduction was determined by a combination of initial rates analysis at various catalyst concentrations. Firstly, we found initial rates (*k<sub>obs</sub>*) of the reaction from [product] vs. time plot and then plotted log<sub>10</sub>(*k<sub>obs</sub>*) vs. log<sub>10</sub>(conc. of x) (where, x = catalyst or HBpin or benzamide) to get the order of the reaction.<sup>16</sup>

Order of reaction with respect to the catalyst: Initial rates (*k<sub>obs</sub>*) were determined from the plot [product] vs. time (**Figure 2.2**) by using various concentrations of the catalyst (8 mM, 16 mM, 24 mM, and 40 mM) while keeping the concentration of benzamide (0.4 M) and HBpin (1.8 M) constant (**Table 2.3**). Further, the order of the reaction with respect to the catalyst was observed from the plot log<sub>10</sub>(*k<sub>obs</sub>*) vs. log<sub>10</sub>(conc. of catalyst) (**Figure 2.5a**), which was found to be 0.46. This fractional order indicates that the rate of deoxygenative reduction increases upon increasing the initial concentration of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> on the hydroboration of benzamide with HBpin.<sup>16a</sup>

**Table 2.3.** Initial rates ( $k_{obs}$ ) for the hydroboration reaction of benzamide with HBpin carried out under varying concentrations of  $Ce[N(SiMe_3)_2]_3(THF)_3$ .

| Sl. No. | $Ce[N(SiMe_3)_2]_3(THF)_3$<br>(mM) | [HBpin]<br>(M) | [Benzamide]<br>(M) | $k_{obs} (\times 10^{-4})$ |
|---------|------------------------------------|----------------|--------------------|----------------------------|
| 1.      | 8                                  | 1.8            | 0.4                | 1.67                       |
| 2.      | 16                                 | 1.8            | 0.4                | 2.30                       |
| 3.      | 32                                 | 1.8            | 0.4                | 3.20                       |
| 4.      | 40                                 | 1.8            | 0.4                | 3.38                       |

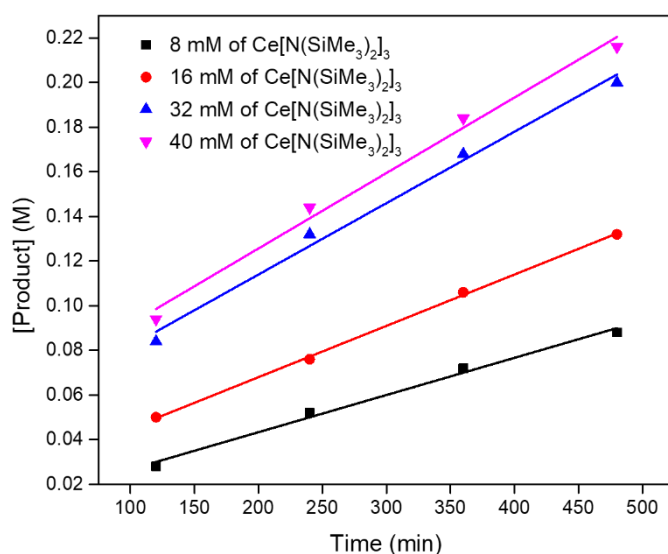


**Figure 2.2.** The plot of [Product] vs. time (best linear fitted) used for the determination of the initial rate ( $k_{obs}$ ) values of benzamide hydroboration carried out with various concentrations of  $Ce[N(SiMe_3)_2]_3(THF)_3$ .

Order of reaction with respect to HBpin: Initial rates ( $k_{obs}$ ) were determined from the plot [product] vs. time (**Figure 2.3**) by using various concentrations of HBpin (0.8 M, 1.2 M, 1.6 M, and 2.0 M) while keeping the concentration of catalyst (20 mM) and benzamide (0.4 M) constant (**Table 2.4**). After that, the order of the reaction with respect to HBpin was calculated from the plot  $\log_{10}(k_{obs})$  vs.  $\log_{10}(\text{conc. of HBpin})$  (**Figure 2.5b**). The fractional order (0.8) of the reaction involving HBpin indicates that more than one path is operative for the hydroboration reaction,<sup>15a</sup> revealing a significant impact of the HBpin on hydroboration of the benzamide in the presence of  $Ce[N(SiMe_3)_2]_3(THF)_3$ .

**Table 2.4.** Initial rates ( $k_{obs}$ ) for the hydroboration reaction of benzamide were carried out under varying concentrations of HBpin.

| Sl. No. | Ce[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (THF) <sub>3</sub><br>(mM) | [HBpin]<br>(M) | [Benzamide]<br>(M) | $k_{obs}$ ( $\times 10^{-4}$ ) |
|---------|---------------------------------------------------------------------------------|----------------|--------------------|--------------------------------|
| 1.      | 20                                                                              | 0.8            | 0.4                | 1.96                           |
| 2.      | 20                                                                              | 1.2            | 0.4                | 2.60                           |
| 3.      | 20                                                                              | 1.6            | 0.4                | 3.20                           |
| 4.      | 20                                                                              | 2.0            | 0.4                | 4.10                           |

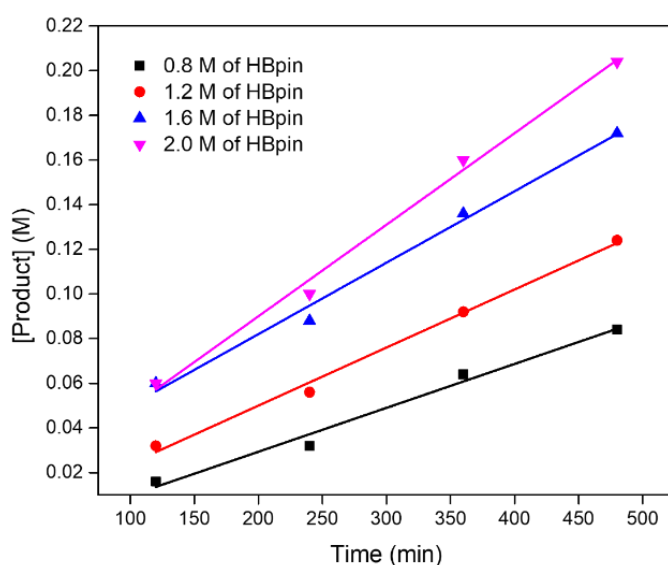


**Figure 2.3.** Plot of [product] vs. time (best linear fitted) used for the determination of the initial rate ( $k_{obs}$ ) values of benzamide hydroboration carried out with various concentrations of HBpin.

Order of reaction with respect to benzamide: Initial rates ( $k_{obs}$ ) were determined from plot [product] vs. time (**Figure 2.4**) by using various concentrations of benzamide (0.2 M, 0.3 M, 0.4 M and 0.5 M), keeping the concentration of the catalyst (20 mM) and HBpin (1.8 M) constant (**Table 2.5**). The order of reaction with respect to benzamide was calculated from the plot  $\log_{10}(k_{obs})$  vs.  $\log_{10}(\text{conc. of benzamide})$  (**Figure 2.5c**). The fractional positive rate-order of 0.42 with respect to benzamide suggests an eventual role of the benzamide on the hydroboration reaction in the presence of HBpin and Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>.<sup>16b</sup>

**Table 2.5.** Initial rates ( $k_{obs}$ ) for the hydroboration reaction of benzamide were carried out under varying concentrations of benzamide.

| Sl. No. | Ce[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (THF) <sub>3</sub><br>(mM) | [HBpin]<br>(M) | [Benzamide]<br>(M) | $k_{obs}$ ( $\times 10^{-4}$ ) |
|---------|---------------------------------------------------------------------------------|----------------|--------------------|--------------------------------|
| 1.      | 20                                                                              | 1.8            | 0.2                | 2.43                           |
| 2.      | 20                                                                              | 1.8            | 0.3                | 2.77                           |
| 3.      | 20                                                                              | 1.8            | 0.4                | 3.17                           |
| 4.      | 20                                                                              | 1.8            | 0.5                | 3.57                           |

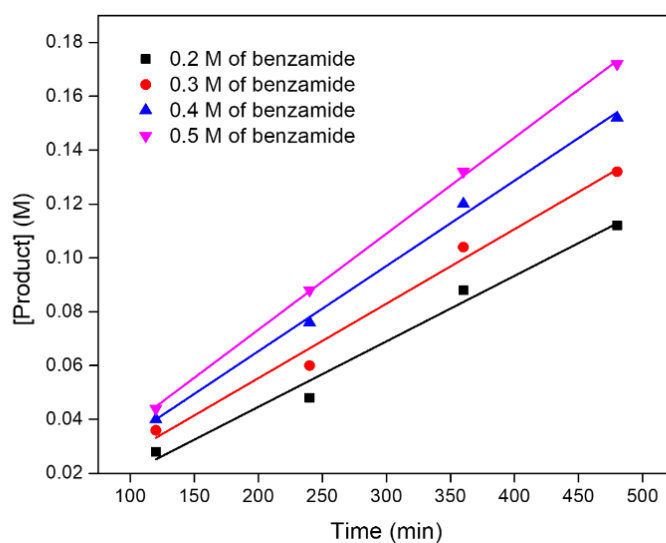
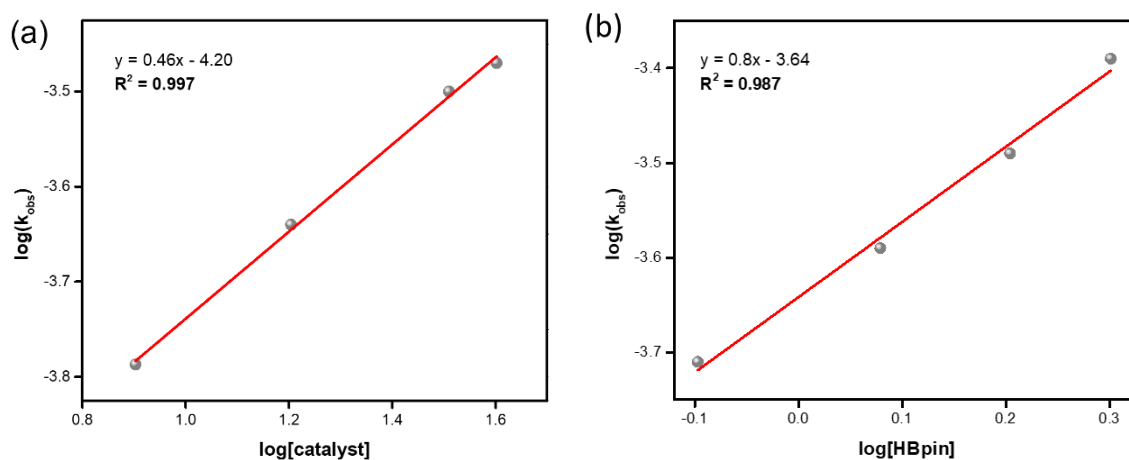


**Figure 2.4.** Plot of [product] vs. time (best linear fitted) used for the determination of the initial rate ( $k_{obs}$ ) values of benzamide hydroboration carried out with various concentrations of benzamide.



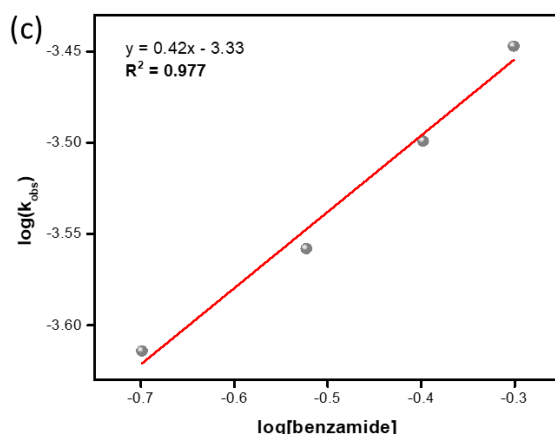


**Figure 2.5.** (a) Plot of  $\log_{10}(k_{obs})$  vs  $\log_{10}(\text{conc. of catalyst})$ . (b) Plot of  $\log_{10}(k_{obs})$  vs  $\log_{10}(\text{conc. of HBpin})$ . (c) Plot of  $\log_{10}(k_{obs})$  vs  $\log_{10}(\text{conc. of benzamide})$ .

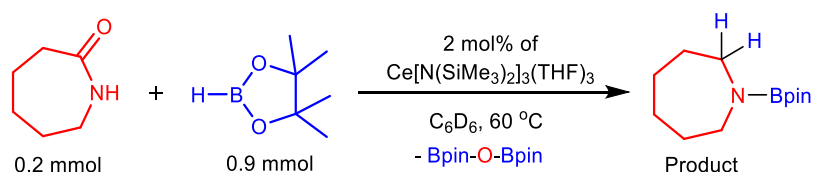
The rate equation of the reaction:

$$\text{rate} = k[\text{catalyst}]^{0.46}[\text{benzamide}]^{0.42}[\text{HBpin}]^{0.8} \quad (\text{Eq. 1})$$

#### 2.4.2. Reaction profile of hydroboration of $\epsilon$ -caprolactam:

The kinetics of the hydroboration reaction of  $\epsilon$ -caprolactam was also investigated to explore the reactivity pattern of  $\epsilon$ -caprolactam with HBpin in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . The kinetic experiment was done by taking 0.2 mmol of  $\epsilon$ -caprolactam and 0.9 mmol of HBpin in  $\text{C}_6\text{D}_6$  in the presence of 2 mol% of the catalyst at  $60^\circ\text{C}$ . The progress of the hydroboration reaction was monitored by  $^1\text{H}$  NMR spectra taken at certain intervals (**Table 2.6**). We considered the beginning point at time  $t = 0$  when the product yield was zero. The reaction profile of the hydroboration of  $\epsilon$ -caprolactam with HBpin using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst over a period of 3 hours was obtained (**Figure 2.6**). The [product] vs. time plot demonstrated that the hydroboration of  $\epsilon$ -caprolactam was promoted firmly, and a fetching point was seen between 30-45 min of the reaction indicating the formation of *in situ* active catalyst.<sup>16b,16c</sup>

**Table 2.6.**  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyzed hydroboration of  $\epsilon$ -caprolactam with various time intervals.



| Time (min) | [product] (M) |
|------------|---------------|
| 0          | 0             |
| 15         | 0.06          |
| 30         | 0.12          |
| 45         | 0.316         |
| 60         | 0.344         |
| 75         | 0.356         |
| 90         | 0.36          |
| 120        | 0.364         |
| 180        | 0.372         |

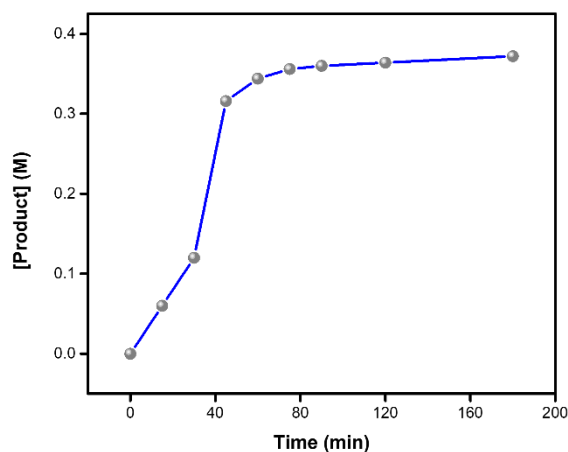
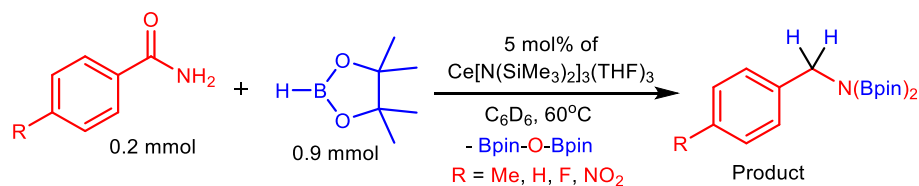


**Figure 2.6.** Reaction profile for the  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed hydroboration of  $\epsilon$ -caprolactam with HBpin.

### 2.4.3. Hammett Plot:

**Table 2.7.** The  $k_{\text{obs}}$  of the *para*-substituted benzamide for Hammett plot.



| Sl. No. | Substrate (0.4 M) | $\sigma$ -value | $k_{\text{obs}}$ |
|---------|-------------------|-----------------|------------------|
| 1.      | benzamide         | 0.000           | 0.0266           |

|    |                   |        |        |
|----|-------------------|--------|--------|
| 2. | 4-methylbenzamide | -0.170 | 0.0314 |
| 3. | 4-fluorobenzamide | +0.062 | 0.0262 |
| 4. | 4-nitrobenzamide  | +0.778 | 0.0154 |

Hammett plot was also performed to understand the effect of the substituents on the deoxygenation of 1° amides with HBpin using *para*-substituted benzamide (**Figure 2.7**). A meager increase in activity was audited for the electron-donating group substituted at the *para*-position of benzamide with a mediocre negative value of Hammett parameter  $\rho = -0.324$ . This  $\rho = -0.324$  value hints that the reaction builds up a positive charge (or loses a negative charge) at the transition state (or the rate-determining step) as the electron density decreases at the reaction site. Because this positive charge builds up by  $\sigma^+$  substituent in the transition state, an electron-donating group can facilitate the reaction rate affording a higher yield.<sup>16d</sup> On the contrary, an electron-withdrawing group can slow down the reaction rate causing a lower yield. The substrate scope of scheme 2.4 supported that electron-withdrawing group substituted substrates led to lower yields but electron-donating group substituted substrates afforded higher yields.

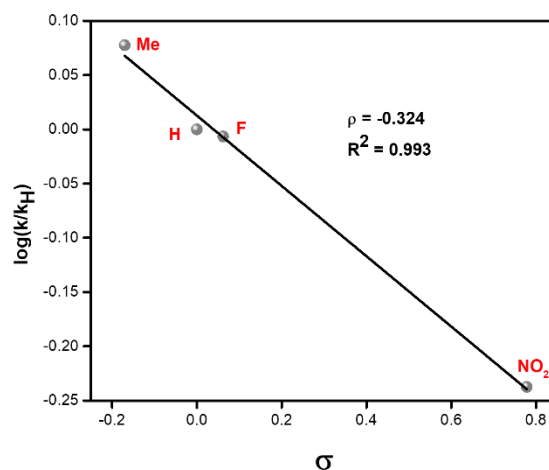


**Figure 2.7.** Hammett plot of deoxygenation of *para*-substituted benzamide with HBpin. The  $k_{\text{obs}}$  were determined by the integration of the corresponding  $^1\text{H}$  NMR spectrum in the presence of an internal standard (mesitylene).

Hammett equation:

$$\log(k/k_H) = \rho\sigma = -0.324\sigma \quad (\text{Eq. 2})$$

## 2.5. Experimental mechanistic aspects

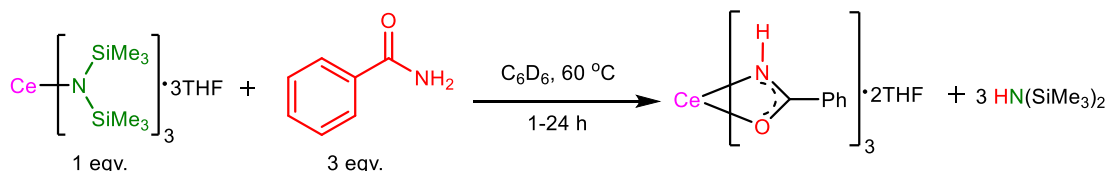
We performed several experimental studies to understand the mechanistic pathway of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyzed  $1^\circ$  and  $2^\circ$  amides hydroboration reaction as previous organo-lanthanide compounds did not catalyze the reduction of  $3^\circ$  amides.<sup>8b,8c</sup> Also,  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  could not catalyze the hydroboration of tertiary amides (*N,N*-dimethyl benzamide), albeit the hydroboration of  $3^\circ$  amides is much easier with HBpin among the other amides. This unusual behavior of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst prompted us to get more insight into the actual reaction pathway.

To understand the course of the reaction, first, we performed a reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with benzamide in a 1:1 molar ratio. The  $^1\text{H}$  NMR spectrum of this mixture was inconclusive, but a small peak at 725.49 was observed in the mass spectrum of 1:1 mixture of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with benzamide, which corresponds to the cerium mono-amidate complex with two THF molecules attached to it. This reaction mixture was further treated with 4.5/13.5 equivalents of HBpin at  $60^\circ\text{C}$  for 36 hours, respectively. However, we did not observe any significant product peak in  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra by using 4.5 equivalent of HBpin but noticed a 73% yield with 13.5 equivalent of HBpin. This indicates that the 1:1 molar ratio of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and benzamide does lead to the most active intermediate species.

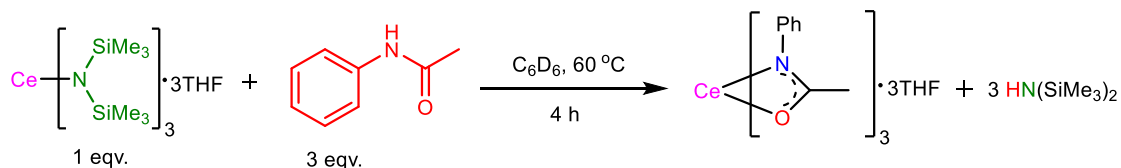
Subsequently, we tried the reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with benzamide ( $1^\circ$  amide) in a 1:3 molar ratio, which afforded a cerium tris-amidate species. The formation of the tris-amidate species was confirmed by  $^1\text{H}$  NMR,  $^{29}\text{Si}$  NMR, and mass spectrometry (**Scheme 2.9**). However, even after repeated attempts, we could not isolate the crystals of this tris-amidate species. The  $^1\text{H}$  NMR spectrum of the 1:3 reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with benzamide displayed a new peak at  $\delta$  0.10 ppm, assigned for  $\text{HN}(\text{SiMe}_3)_2$ . The  $^{29}\text{Si}$  NMR spectrum also revealed a peak at  $\delta$  1.94 ppm, confirming the formation of  $\text{HN}(\text{SiMe}_3)_2$ .<sup>8c,17</sup> The mass spectrometric data showed an intense peak at  $m/z$  645.5652, which matches well with the mass of the cerium tris-amidate complex of benzamide with two THF molecules. A similar tris-amidate species was also observed by Marks and co-workers in the case of  $[\text{La}(\text{N}(\text{TMS})_2)_2]_3$ -catalyzed hydroboration of  $2^\circ$  amides.<sup>8c</sup> They proved the formation of lanthanum tris-amidate species by monitoring the  $^1\text{H}$  NMR spectrum and also used it for further catalytic reaction. This species was proven to be catalytically active, but the reaction progress was slow. However, Chen and co-workers did not mention such tris-amidate formation in their experimental work

of 2° and 3° amides hydroboration reaction.<sup>8b</sup> Subsequently, the reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with acetanilide (2° amide) in a 1:3 molar ratio in  $\text{C}_6\text{D}_6$  revealed the formation of a cerium tris-amidate complex of acetanilide (**Scheme 2.9b**), which was also confirmed by NMR spectroscopy and mass spectrometry. To check the reaction of 3'-methyl acetanilide and  $\epsilon$ -caprolactam (a cyclic 2° amide) with  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , we adopted the same method and observed the formation of a similar species. Important to mention that we did not observe any reaction of *N,N*-dimethylbenzamide (3° amide) with  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , which is presumably due to the lack of hydrogen in 3° amides (**Scheme 2.9c**).

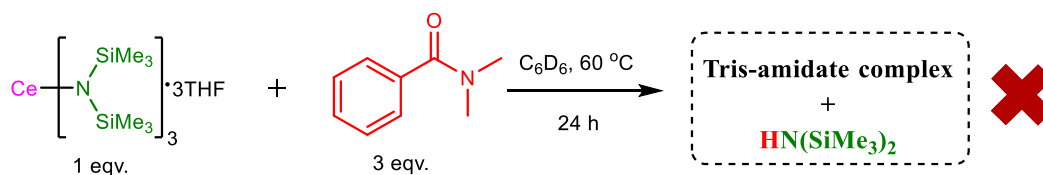
(a) Formation of tris-amidate species of benzamide



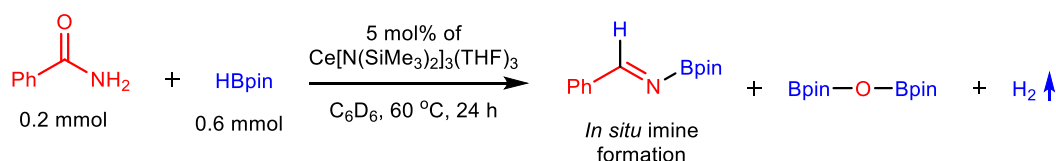
(b) Formation of tris-amidate species of acetanilide



(c) No formation of tris-amidate species of *N,N*-dimethylbenzamide



(d) *In situ* imine formation and  $\text{H}_2$  molecule evolution



**Scheme 2.9.** Control experiments for the mechanistic aspects of hydroboration of amides. (a) Formation of tris-amidate species of benzamide (1° amide); (b) Formation of tris-amidate species of acetanilide (2° amide); (c) No formation of tris-amidate species of *N,N*-

dimethylbenzamide (3° amide); (d) *In situ* imine formation and H<sub>2</sub> molecule evolution in hydroboration reaction.

Further, we also performed the reaction of benzamide with 3 equivalents of HBpin in the presence of 5 mol% of the catalyst in C<sub>6</sub>D<sub>6</sub> (**Scheme 2.9d**) and observed a peak for H<sub>2</sub> in the <sup>1</sup>H NMR spectrum ( $\delta$  4.47 ppm) along with a peak for imine at  $\delta$  10.35 ppm, indicating the possibility of *in-situ* formation of imine species in amide hydroboration reaction. The formation of imine was further confirmed by the characteristic peak of imine group carbon at  $\delta$  168.74 ppm in <sup>13</sup>C{<sup>1</sup>H} NMR spectrum.

Luo and co-workers mentioned that the calcium bis-amidate complex of 4-methylbenzamide was insoluble in the common organic solvents and found to be inactive towards hydroboration reaction.<sup>8a</sup> Similarly, we also observed that the cerium tris-amidate complex of benzamide was initially insoluble in CDCl<sub>3</sub>, but upon the addition of HBpin, dissolution of the solid was observed (**Figure 2.8**).

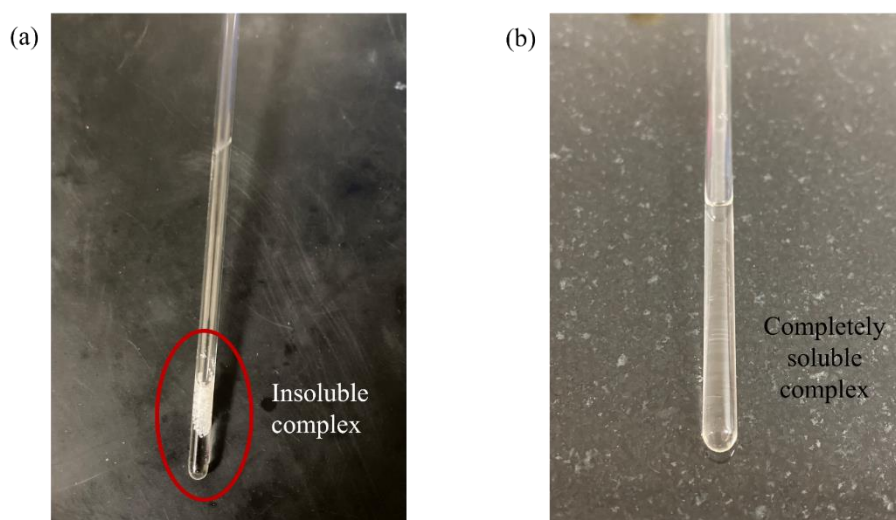
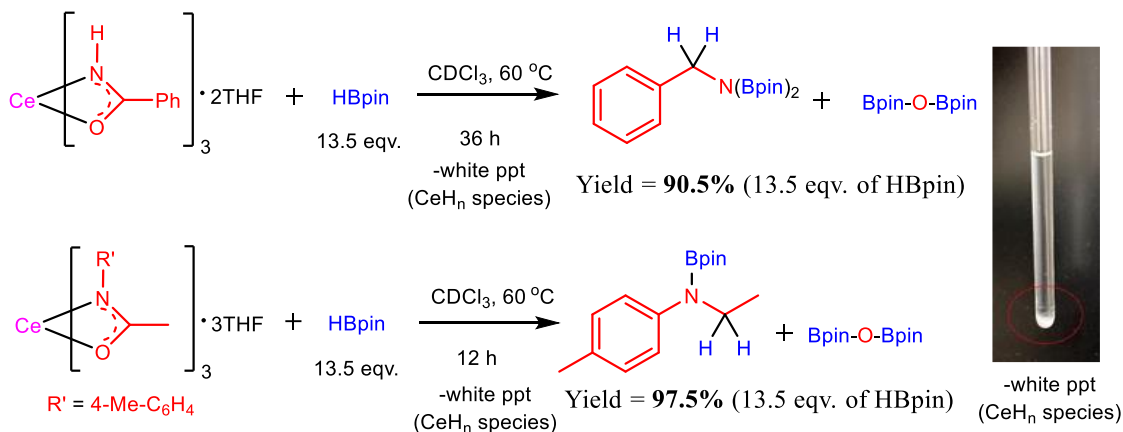


**Figure 2.8.** Images of cerium tris-amidate complex of benzamide in CDCl<sub>3</sub> (a) before addition of HBpin and (b) after 1 hour of the addition of HBpin (13.5 equiv).

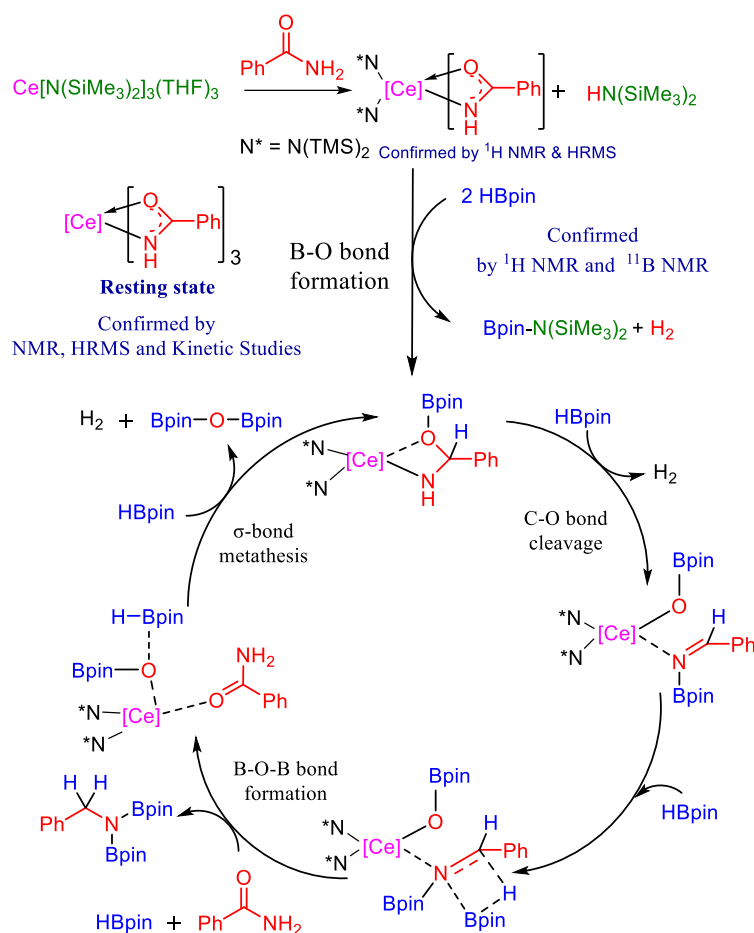
To check the catalytic activity of the tris-amidate complex, we reacted the cerium tris-amidate complex of benzamide with 13.5 equivalent of HBpin in CDCl<sub>3</sub> at 60 °C, which led to the formation of borylated product in 90.5% yield (**Scheme 2.10**). Likewise, treating cerium tris-amidate complex of 4-methylacetanilide with 13.5 equivalent of HBpin gave the corresponding borylated amine product in 97.5% yield (**Scheme 2.10**). To understand the role of the cerium tris-amidate complex in the catalytic cycle, we performed some kinetic experiments, which revealed it to be a resting state. These experiments showed that the most probable first step is

the formation of cerium-amidate complex, which is a crucial step for the hydroboration of 1° and 2° amides. It also explains that due to the absence of hydrogen, 3° amide does not form a cerium-amidate complex, which is the most reasonable explanation for the inactivity of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  towards 3° amides. Moreover, we also observed a white precipitation after the completion of the reaction, which was found insoluble in  $\text{CDCl}_3$  and other common solvents (**Scheme 2.10**). The Raman spectrum of the white precipitate shows a distinct peak at  $1444.2\text{ cm}^{-1}$ , which matches well with the reported Ce-H values.<sup>18</sup>



**Scheme 2.10.** Reaction of tris-amidate complexes with HBpin.

Eventually, based on all these experiments and previous reports,<sup>8c,19</sup> we propose a plausible mechanistic pathway of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalyzed deoxygenative reduction of primary amides with HBpin in Scheme 2.11.



**Scheme 2.11.** Plausible mechanistic pathway of 1° amide hydroboration reaction.

## 2.6. Conclusion

We have demonstrated the use of less explored and easily available  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as catalyst for the hydroboration of 1° and 2° amides with HBpin. Previously reported lanthanide amides, *e.g.*,  $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$  and  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ , could only perform the hydroboration of 2° and 3° amides using HBpin but were unable to reduce 1° amides. On the contrary,  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  was found highly efficient for the hydroboration of 1° and 2° amides under mild reaction conditions and low catalyst loading. Moreover, various functional group tolerance and a gram-scale reaction were also demonstrated in the substrate scope using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. Systematic experimental studies and kinetic experiments supported the formation of a tris-amidate complex as a crucial active species, which is vital for the catalytic cycle. This is the first use of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst showing excellent catalytic performance towards reducing 1° and 2° amides. The easy access of

$\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  makes it a suitable candidate for bulk-scale synthesis and industrial application.

## 2.7. NMR Spectra

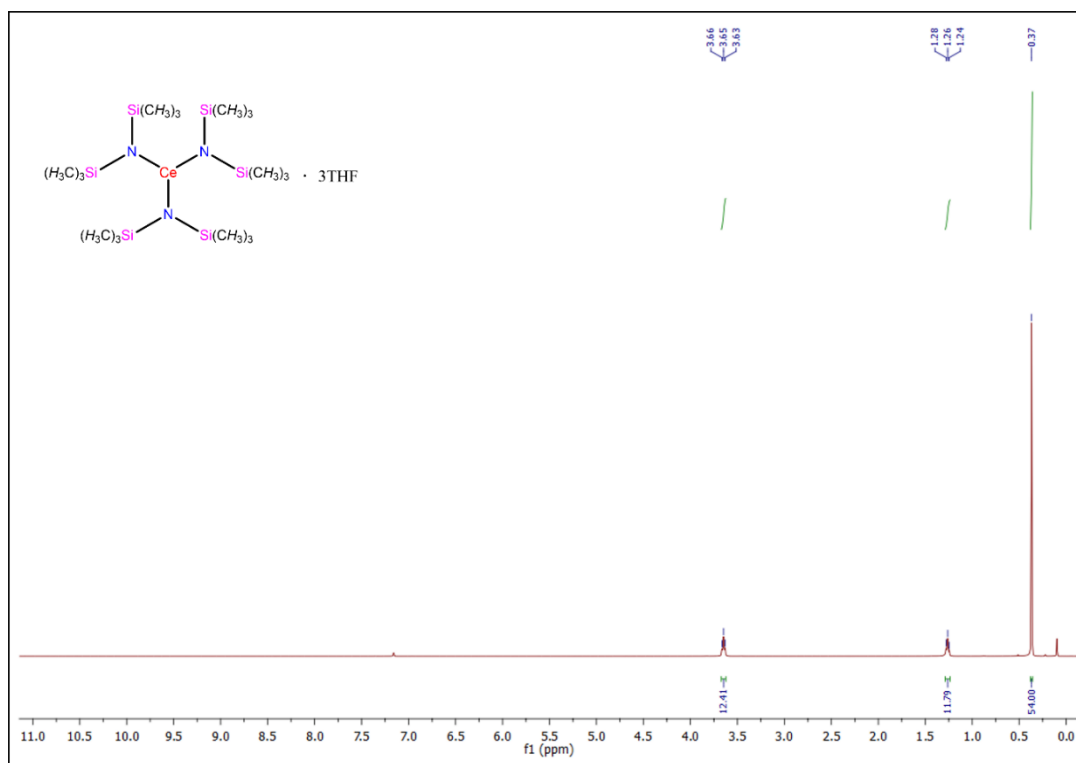


**Figure 2.9.**  $^1\text{H}$  NMR spectrum of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3 \cdot 3\text{THF}$  in  $\text{C}_6\text{D}_6$  [400 MHz, 298 K].

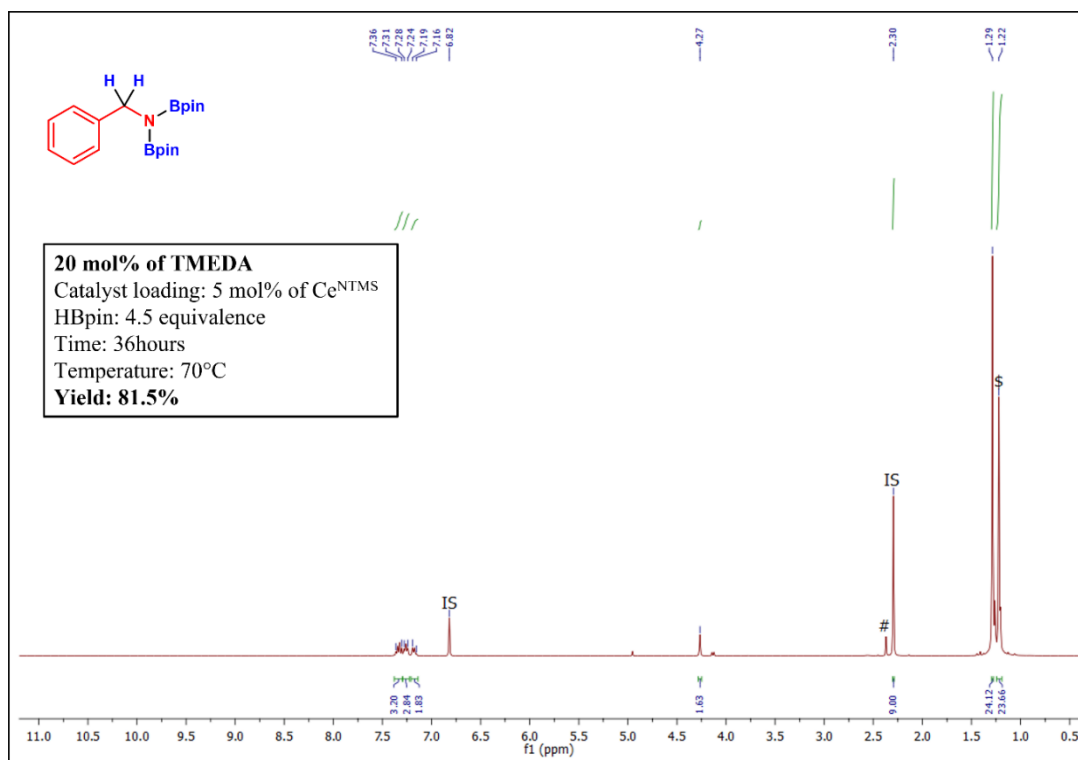


**Figure 2.10.**  $^1\text{H}$  NMR (400 MHz) spectrum for hydroboration reaction of benzamide with 4.5 eq. of HBpin in toluene using 5 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst in presence of 20 mol% of TMEDA for 36 hours at 70°C temperature. [Solvent:  $\text{CDCl}_3$ , 298 K; IS: mesitylene;  $^{\text{S}}$ Peak for  $\text{O}(\text{Bpin})_2$ ;  $^{\text{H}}$ Peak for toluene].

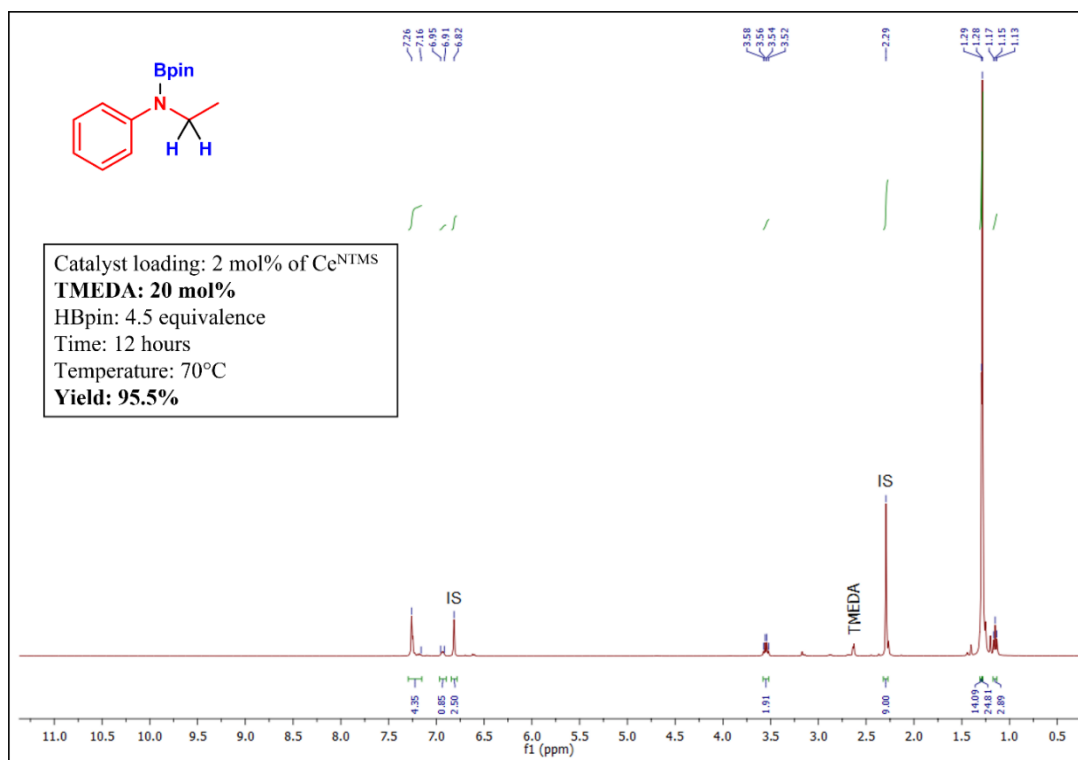


**Figure 2.11.**  $^1\text{H}$  NMR (400 MHz) spectrum for hydroboration reaction of acetanilide with 4.5 eq. of HBpin in toluene using 2 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst in presence of 20 mol% of TMEDA for 12 hours at  $50^\circ\text{C}$  temperature. [Solvent:  $\text{CDCl}_3$ , 298 K; IS: mesitylene].

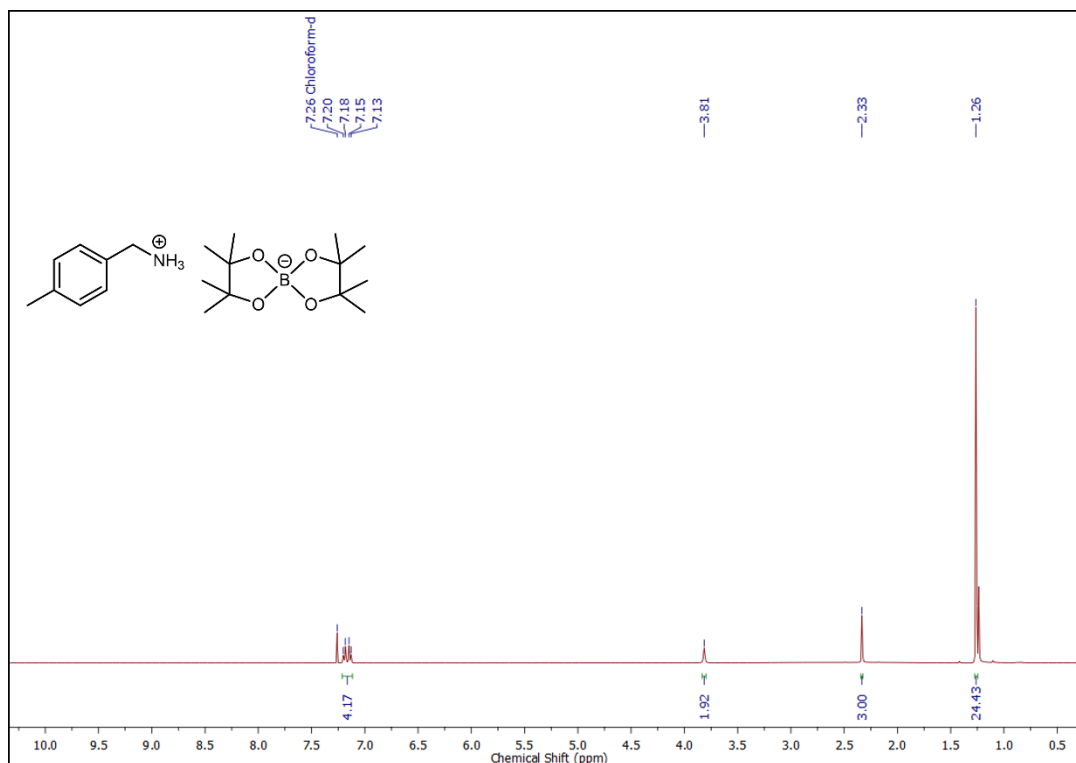


**Figure 2.12.**  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectra of **1b'**.

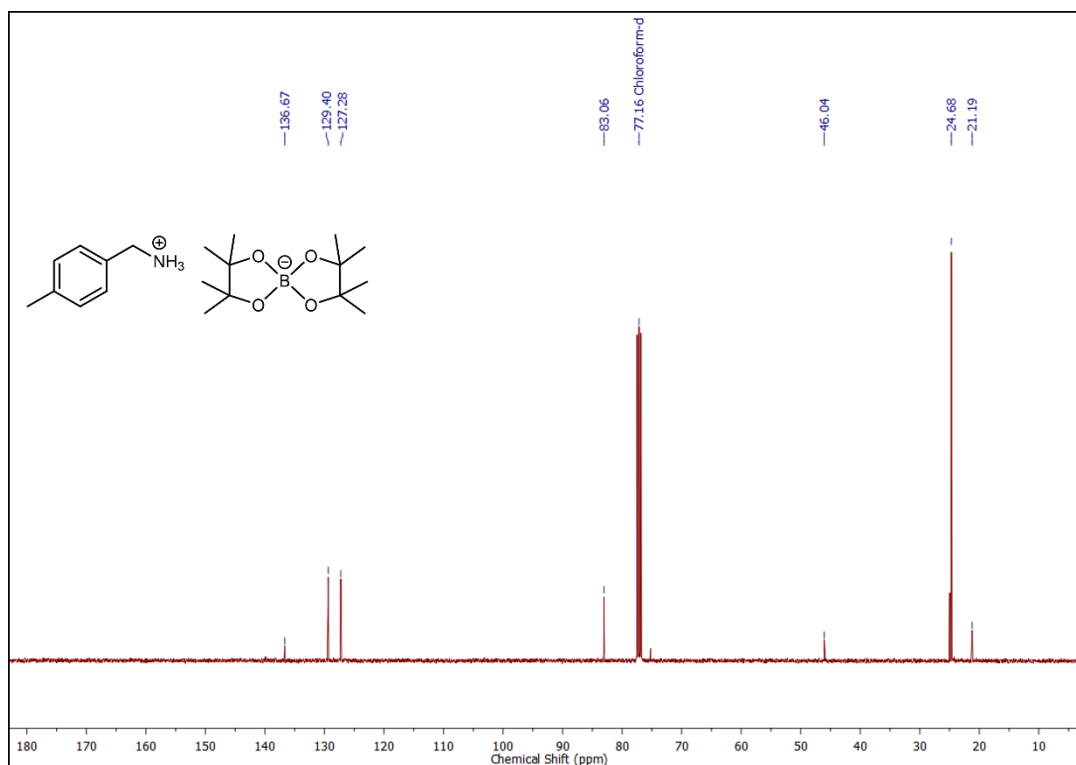
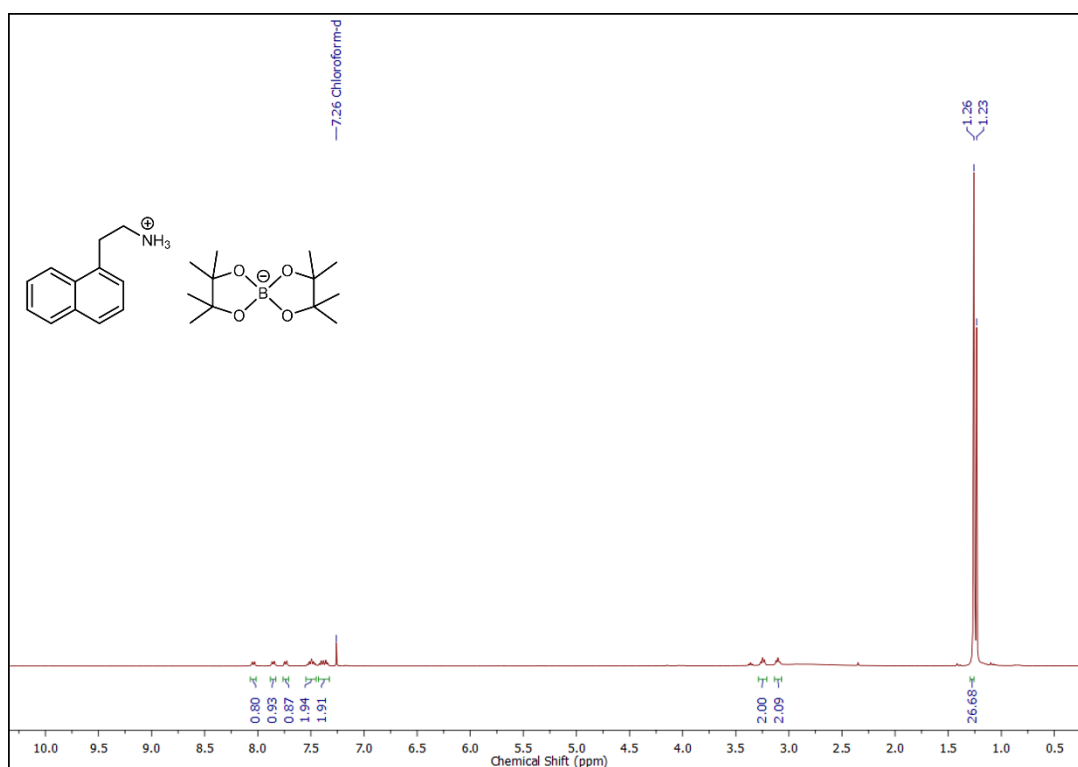
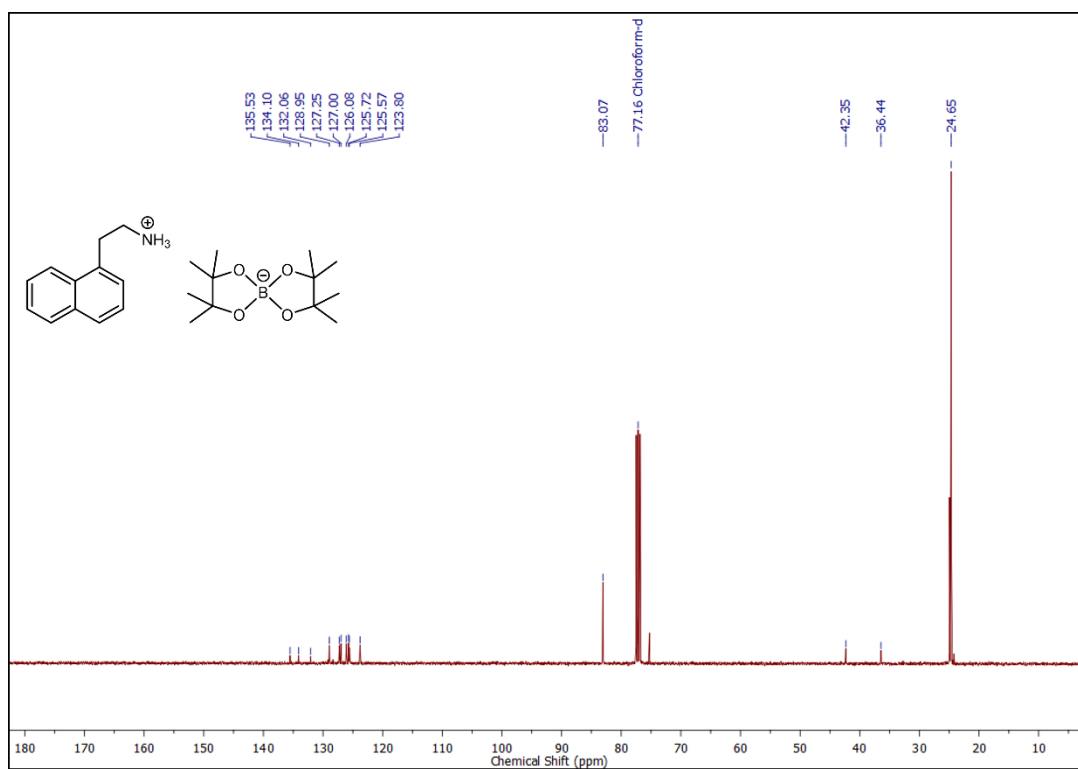


**Figure 2.13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR [ $\text{CDCl}_3$ , 100.613 MHz, 298 K] spectra of **1b'**.**Figure 2.14.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectra of **1r'**.**Figure 2.15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR [ $\text{CDCl}_3$ , 100.613 MHz, 298 K] spectra of **1r'**.

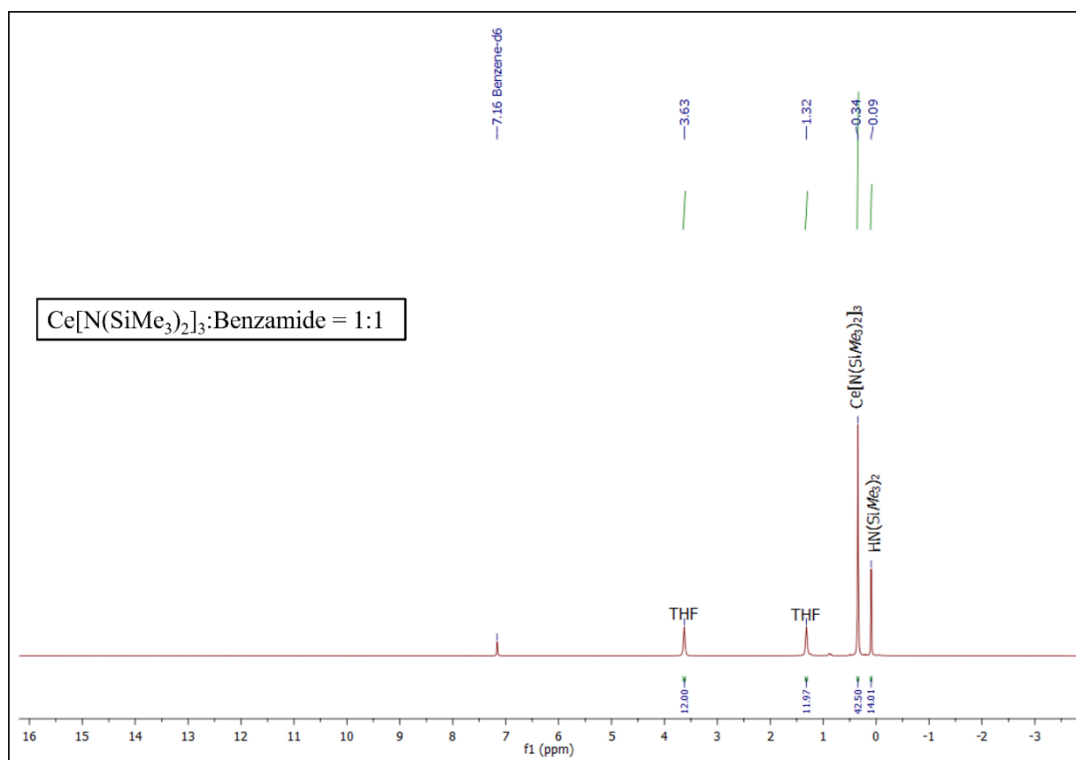


**Figure 2.16.**  $^1\text{H}$  NMR [ $\text{C}_6\text{D}_6$ , 400 MHz, 298 K] spectrum of the reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and benzamide (1:1 ratio).

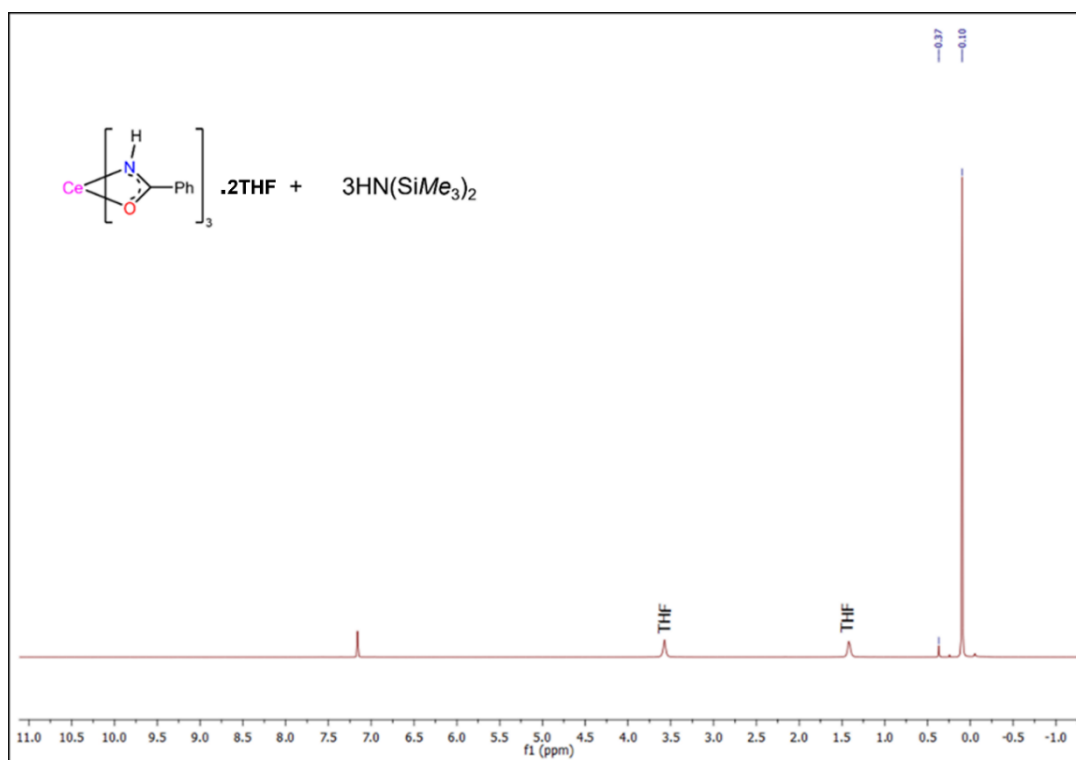


**Figure 2.17.**  $^1\text{H}$  NMR [400 MHz, 298K] spectrum of *in situ* formed active catalyst (cerium tris-amidate species of benzamide) by releasing  $\text{HN}(\text{SiMe}_3)_2$  ( $\delta$  0.10 ppm) in benzene- $\text{d}_6$ .

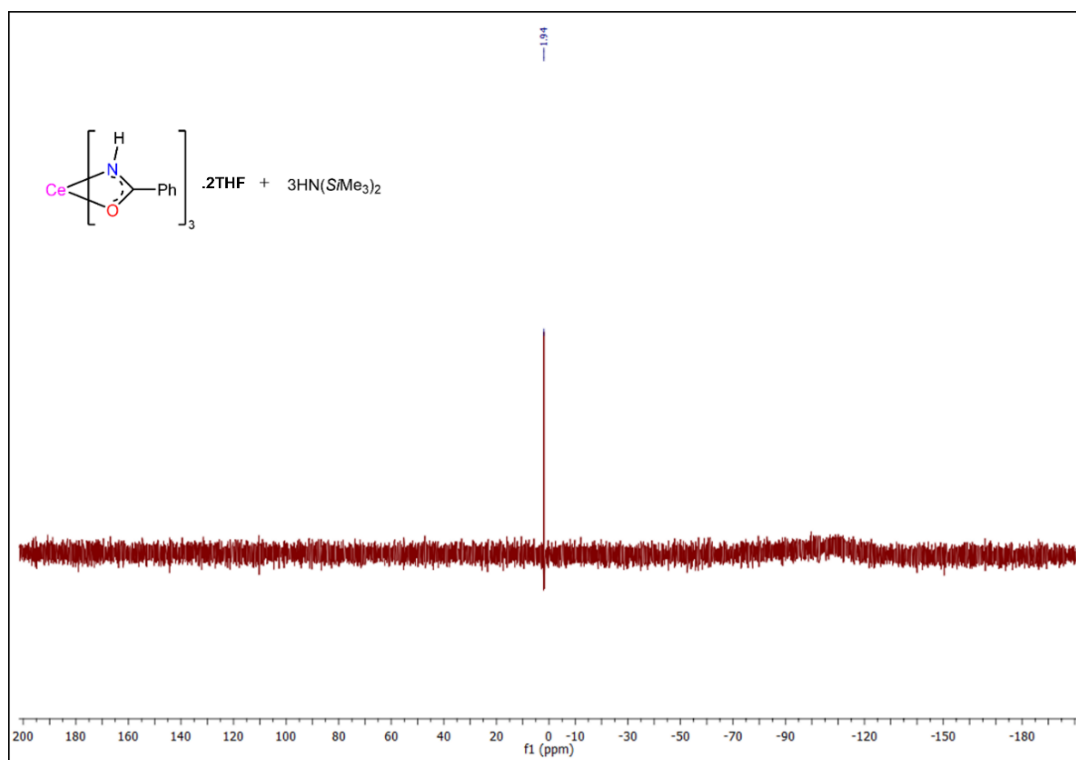


**Figure 2.18.**  $^{29}\text{Si} \{^1\text{H}\}$  NMR [79.495 MHz, 298 K] spectrum of *in situ* formed active catalyst (cerium tris-amidate species of benzamide) by releasing  $\text{HN}(\text{SiMe}_3)_2$  ( $\delta$  1.94 ppm) in benzene- $\text{d}_6$ .

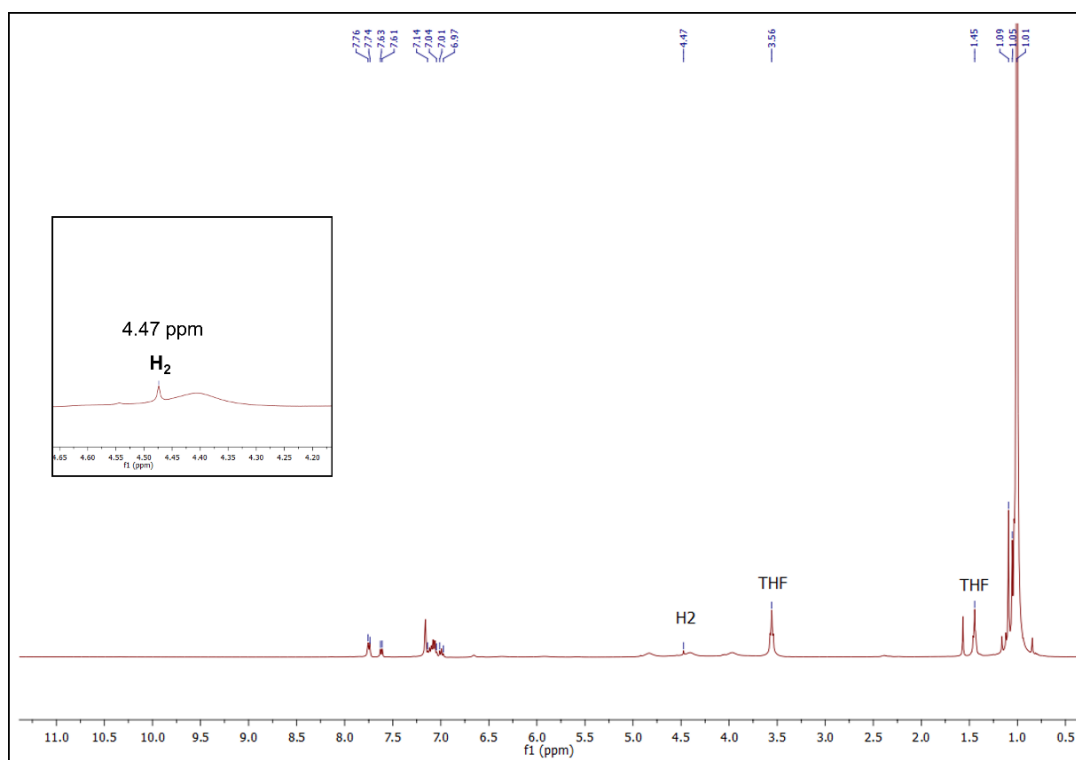


**Figure 2.19.**  $^1\text{H}$  NMR spectrum of molecular hydrogen ( $\text{H}_2$ ) for benzamide hydroboration [ $\text{C}_6\text{D}_6$ , 400 MHz, 298 K].

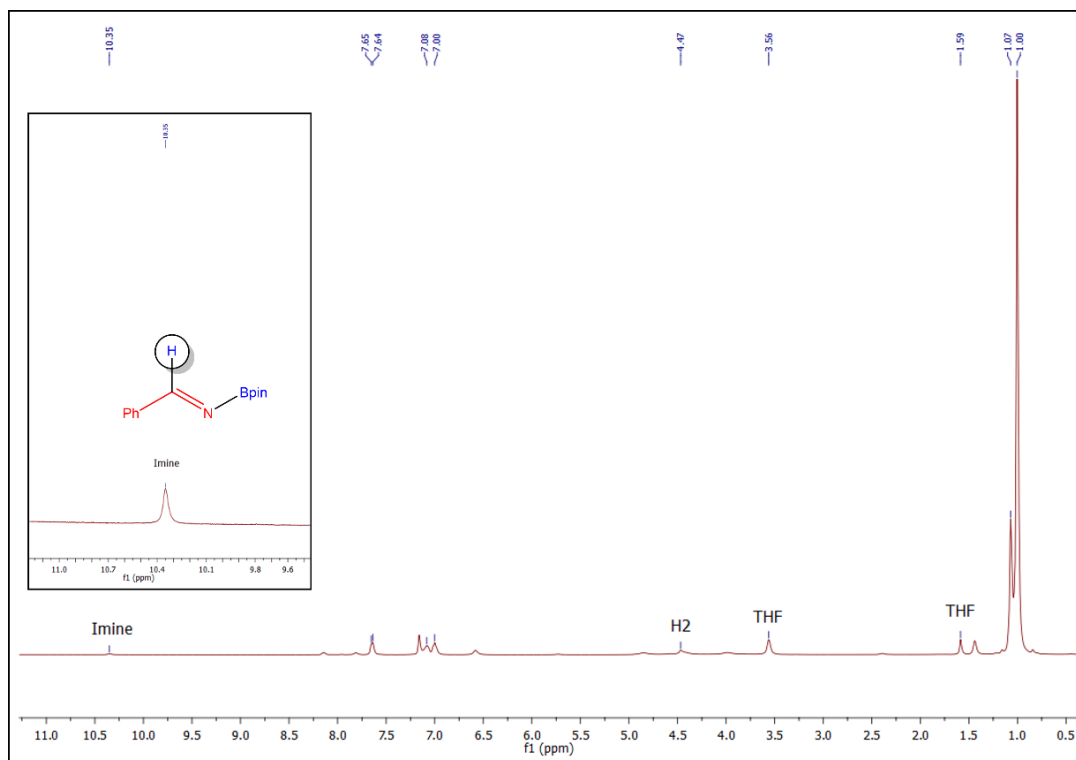


**Figure 2.20.**  $^1\text{H}$  NMR spectrum of *in situ* generated *N*-borylated imine [ $\text{C}_6\text{D}_6$ , 400 MHz, 298 K].

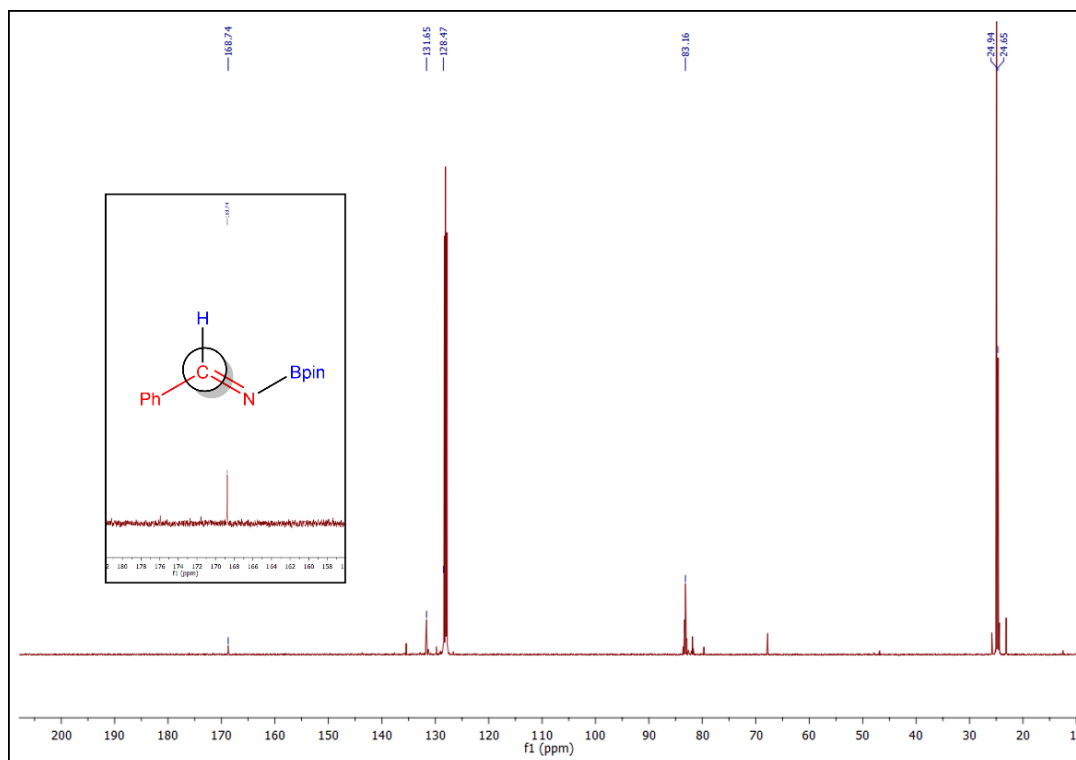


**Figure 2.21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of *in situ* generated *N*-borylated imine [ $\text{C}_6\text{D}_6$ , 100.613 MHz, 298 K].

## 2.8. References

1. (a) Ricci, A. *Modern Amination Method*; Wiley, New York, **2000**; pp 1-258. (b) Lawrence, S. A. *Amines: Synthesis, Properties and Applications*; Cambridge University Press: Cambridge, UK, **2004**. (c) Magano, J.; Dunetz, J. R. Large-Scale Carbonyl Reductions in the Pharmaceutical Industry. *Org. Process Res. Dev.* **2012**, *16*, 1156-1184.
2. (a) Fasano, V.; Radcliffe, J. E.; Ingleson, M. J.  $\text{B}(\text{C}_6\text{F}_5)_3$ -Catalyzed Reductive Amination using Hydrosilanes. *ACS Catal.* **2016**, *6*, 1793-1798. (b) Tang, S.; Li, Z.; Shao, Y.; Sun, J. Ir-Catalyzed Regiocontrolled Allylic Amination of Di-/Trienyl Allylic Alcohols with Secondary Amines. *Org. Lett.* **2019**, *21*, 7228-7232. (c) Liu, Y.; Afanasenko, A.; Elangovan, S.; Sun, Z.; Barta, K. Primary Benzylamines by Efficient *N*-Alkylation of Benzyl Alcohols Using Commercial Ni Catalysts and Easy-to-Handle Ammonia Sources. *ACS Sustainable Chem. Eng.* **2019**, *7*, 11267-11274. (d) Huang, L. B.; Arndt, M.; Gooßen, K.; Heydt, H.; Gooßen, L. J. Late Transition Metal-Catalyzed Hydroamination and Hydroamidation. *Chem. Rev.* **2015**, *115*, 2596-2697. (e) Hong, S.; Marks, T. J. Organolanthanide-Catalyzed Hydroamination. *Acc. Chem. Res.* **2004**, *37*, 673-686. (f) Liu, Y. E.; Lu, Z.; Li, B.; Tian, J.; Liu, F.; Zhao, J.; Hou, C.; Li, Y.; Niu, L.; Zhao, B. Enzyme-Inspired Axially Chiral Pyridoxamines Armed with a Cooperative Lateral Amine Chain for Enantioselective Biomimetic Transamination. *J. Am. Chem. Soc.* **2016**, *138*, 10730-10733. (g) Xie, Y.; Pan, H.; Liu, M.; Xiao, X.; Shi, Y. Progress in asymmetric biomimetic transamination of carbonyl compounds. *Chem. Soc. Rev.* **2015**, *44*, 1740-1748. (h) Trowbridge, A.; Walton, S. M.; Gaunt, M. J. New Strategies for the Transition Metal Catalyzed Synthesis of Aliphatic Amines. *Chem. Rev.* **2020**, *120*, 2613-2692. (i) Han, B.; Zhang, J.; Jiao, H.; Wu, L. Zirconium-Hydride-Catalyzed Site-Selective Hydroboration of Amides for the Synthesis of Amines: Mechanism, Scope, and Application. *Chin. J. Catal.* **2021**, *42*, 2059-2067. (j) Kehner, R. A.; Zhang, G.; Bayeh-Romero, L. Mild Divergent Semireductive Transformations of Secondary and Tertiary Amides via Zirconocene Hydride Catalysis. *J. Am. Chem. Soc.* **2023**, *145*, 4921-4927. (k) Adilkhanova, A.; Frolova, V. F.; Yessengazin, A.; Öztöpcü, Ö.; Gudun, K. A.; Segizbayev, M.; Matsokin, N. A.; Dmitrienko, A.; Pilkington, M.; Khalimon, A. Y. *Dalton Trans.* **2023**, *52*, 2872-2886. (l)

- Geier, S. J.; Vogels, C. M.; Melanson, J. A.; Westcott, S. A. The Transition Metal-Catalysed Hydroboration Reaction. *Chem. Soc. Rev.* **2022**, *51*, 8877-8922.
3. Direct hydrogenation of amides: (a) Wojcik, B.; Adkins, H. Catalytic Hydrogenation of Amides to Amines. *J. Am. Chem. Soc.* **1934**, *56*, 2419- 2424. (b) Stein, M.; Breit, B. Catalytic Hydrogenation of Amides to Amines under Mild Conditions. *Angew. Chem., Int. Ed.* **2013**, *52*, 2231- 2234. (c) Sitte, N. A.; Bursch, M.; Grimme, S.; Paradies, J. Frustrated Lewis Pair Catalyzed Hydrogenation of Amides: Halides as Active Lewis Base in the Metal-Free Hydrogen Activation. *J. Am. Chem. Soc.* **2019**, *141*, 159-162.
  4. (a) Gribble, G. W. Sodium Borohydride in Carboxylic Acid Media: A Phenomenal Reduction System. *Chem. Soc. Rev.* **1998**, *27*, 395-404. (b) Seyden-Penne, J. Reductions by the Alumino and Borohydrides in Organic Synthesis; Wiley-VCH, New York, 2nd ed, **1997**; pp 224. (c) Dodds, D. L.; Cole-Hamilton, D. J. In Sustainable Catalysis; Wiley, Hoboken, NJ, **2013**; pp 1-36.
  5. Transfer hydrogenation of amides: (a) Pan, Y.; Luo, Z.; Han, J.; Xu, X.; Chen, C.; Zhao, H.; Xu, L.; Fan, Q.; Xiao, J. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-Catalyzed Deoxygenative Reduction of Amides to Amines with Ammonia Borane. *Adv. Synth. Catal.* **2019**, *361*, 2301-2308. (b) Pan, Y.; Luo, Z.; Xu, X.; Zhao, H.; Han, J.; Xu, L.; Fan, Q.; Xiao, J. Ru-Catalyzed Deoxygenative Transfer Hydrogenation of Amides to Amines with Formic Acid/Triethylamine. *Adv. Synth. Catal.* **2019**, *361*, 3800-3806.
  6. Hydrosilylation of amides: (a) Cheng, C.; Brookhart, M. Iridium-Catalyzed Reduction of Secondary Amides to Secondary Amines and Imines by Diethylsilane. *J. Am. Chem. Soc.* **2012**, *134*, 11304-11307. (b) Zhou, S. L.; Junge, K.; Addis, D.; Das, S.; Beller, M. A. A Convenient and General Iron-Catalyzed Reduction of Amides to Amines. *Angew. Chem., Int. Ed.* **2009**, *48*, 9507-9510. (c) Das, H. S.; Das, S.; Dey, K.; Singh, B.; Haridasan, R. K.; Das, A.; Ahmed, J.; Mandal, S. K. Primary Amides to Amines or Nitriles: A Dual Role by a Single Catalyst. *Chem. Commun.* **2019**, *55*, 11868-11871. (d) Fernandez-Salas, J. A.; Manzini, S.; Nolan, S. P. Facile and Efficient KOH-Catalysed Reduction of Esters and Tertiary Amides. *Chem. Commun.* **2013**, *49*, 9758-9760. (e) Xie, W.; Zhao, M.; Cui, C. Cesium Carbonate-Catalyzed Reduction of Amides with Hydrosilanes. *Organometallics* **2013**, *32*, 7440-7444. (f) Ni, J.; Oguro, T.; Sawazaki, T.; Sohma, Y.; Kanai, M. Hydroxy Group Directed Catalytic Hydrosilylation of Amides. *Org. Lett.* **2018**, *20*, 7371-7374. (g) Li, Y.; Molina de La Torre, J. A.; Grabow, K.; Bentrup, U.; Junge, K.; Zhou, S.; Bruckner, A.; Beller, M. Selective Reduction of Amides to Amines by Boronic Acid Catalyzed Hydrosilylation. *Angew. Chem., Int. Ed.* **2013**, *52*, 11577-11580. (h) Mukherjee, D.;

- Shirase, S.; Mashima, K.; Okuda, J. Chemoselective Reduction of Tertiary Amides to Amines Catalyzed by Triphenylborane. *Angew. Chem., Int. Ed.* **2016**, *55*, 13326-13329. (i) Kehner, R. A.; Zhang, G.; Bayeh-Romero, L. Mild Divergent Semireductive Transformations of Secondary and Tertiary Amides via Zirconocene Hydride Catalysis. *J. Am. Chem. Soc.* **2023**, *145*, 4921-4927.
7. (a) Lampland, N. L.; Hovey, M.; Mukherjee, D.; Sadow A. D. Magnesium-Catalyzed Mild Reduction of Tertiary and Secondary Amides to Amines. *ACS Catal.* **2015**, *5*, 4219-4226. (b) Bhunia, M.; Sahoo, S. R.; Das, A.; Ahmed, J.; Sreejyothi P.; Mandal, S. K. Transition Metal-Free Catalytic Reduction of Primary Amides Using an Abnormal NHC Based Potassium Complex: Integrating Nucleophilicity with Lewis Acidic Activation. *Chem. Sci.* **2020**, *11*, 1848-1854. (c) Magre, M.; Szewczyk, M.; Rueping, M. s-Block Metal Catalysts for the Hydroboration of Unsaturated Bonds. *Chem. Rev.* **2022**, *122*, 8261-8312. (d) Zhang, G.; Wu, J.; Zheng, S.; Neary, M. C.; Mao, J.; Flores, M.; Trovitch, R. J.; Dub, P. A. Redox Noninnocent Ligand-Supported Vanadium Catalysts for the Chemoselective Reduction of C=X (X = O, N) Functionalities. *J. Am. Chem. Soc.* **2019**, *141*, 15230-15239. (e) Dicken, R. D.; Motta, A.; Marks, T. J. Homoleptic Lanthanide Amide Catalysts for Organic Synthesis: Experiment and Theory. *ACS Catal.* **2021**, *11*, 2715-2734. (f) Lee, C. W.; Ko, H. M. Metal-Free Catalytic Reduction of Amides: Recent Progress. *Asian J. Org. Chem.* **2023**, *12*, e202300098. (g) Yi, J.; Kim, H. T.; Jaladi, A. K.; An, D. K. Deoxygenative Hydroboration of Primary, Secondary and tertiary Amides: Catalyst-Free Synthesis of Various Substituted Amines. *Bull. Korean Chem. Soc.* **2022**, *43*, 129-132.
8. (a) Yu, C.; Guo, C.; Jiang, L.; Gong, M.; Luo, Y. Deoxygenation of Primary Amides to Amines with Pinacolborane Catalyzed by  $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ . *Organometallics* **2021**, *40*, 1201-1206. (b) Ye, P.; Shao, Y.; Ye, X.; Zhang, F.; Li, R.; Sun, J.; Xu, B.; Chen, J. Homoleptic Bis(trimethylsilyl)amides of Yttrium Complexes Catalyzed Hydroboration Reduction of Amides to Amines. *Org. Lett.* **2020**, *22*, 1306-1310. (c) Barger, C. J.; Dicken, R. D.; Weidner, V. L.; Motta, A.; Lohr, T. L.; Marks, T. J.  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ -Catalyzed Deoxygenative Reduction of Amides with Pinacolborane. Scope and Mechanism. *J. Am. Chem. Soc.* **2020**, *142*, 8019-8028.
9. Tamang, S. R.; Singh, A.; Bedi, D.; Bazkiaei, A. R.; Warner, A. A.; Glogau, K.; McDonald, C.; Unruh, D. K.; Findlater, M. Polynuclear lanthanide–diketonato clusters for the catalytic hydroboration of carboxamides and esters. *Nat. Catal.* **2020**, *3*, 154-162.

10. Kumar, R.; Bisai, M. K.; Jain, S.; Vanka, K.; Sen, S. S. Deoxygenative Hydroboration of Primary and Secondary Amides: A Catalyst-Free and Solvent-Free Approach. *Chem. Commun.* **2021**, 57, 10596-10599.
11. Bradley, D. C.; Ghotra, J. S.; Hart, F. A. Low Co-ordination Numbers in Lanthanide and Actinide Compounds. Part I. The Preparation and Characterization of Tris{bis(trimethylsilyl)-amido}lanthanides. *J. Chem. Soc., Dalton Trans.* **1973**, 1021-1023.
12. Bage, A. D.; Hunt, T. A.; Thomas, S. P. Hidden Boron Catalysis: Nucleophile Promoted Decomposition of HBpin. *Org. Lett.* **2020**, 22, 4107-4112.
13. Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. The Hidden Role of Boranes and Borohydrides in Hydroboration Catalysis. *ACS Catal.* **2020**, 10, 13479-13486.
14. Zha, G. -F.; Rakesh, K. P.; Manukumar, H. M.; Shantharam, C. S.; Long, S. Pharmaceutical Significance of Azepane Based Motifs for Drug Discovery: A critical Review. *Eur. J. Med. Chem.* **2019**, 162, 465-494.
15. (a) Humphrey, G. R.; Kuethe, J. T. Practical Methodologies for the Synthesis of Indoles. *Chem. Rev.* **2006**, 106, 2875-2911. (b) Kumar, S.; Ritika A Brief Review of the Biological Potential of Indole Derivatives. *Futur. J. Pharm. Sci.* **2020**, 6, 121. (c) Kaushik, N. K.; Kaushik, N.; Attri, P.; Kumar, N.; Kim, C. H.; Verma, A. K.; Choi, E. H. Biomedical Importance of Indoles. *Molecules* **2013**, 18, 6620-6662.
16. (a) Hossain, J.; Gopinath, J. S.; Tothadi, S.; Parameswaran, P.; Khan, S. NHSi/NHGe-Supported Copper Halide and Pseudohalide Complexes: Synthesis and Application. *Organometallics* **2022**, 41, 3706-3717. (b) Khake, S. M.; Jain, S.; Patel, U. N.; Gonnade, R. G.; Vanka, K.; Punji, B. Mechanism of Nickel(II)-Catalyzed C(2)-H Alkynylation of Indoles with Alkynyl Bromide. *Organometallics* **2018**, 37, 2037-2045. (c) Patel, U. N.; Jain, S.; Pandey, D. K.; Gonnade, R. G.; Vanka, K.; Punji, B. Mechanistic Aspects of Pincer Nickel(II) Catalyzed C-H Bond Alkylation of Azoles with Alkyl Halides. *Organometallics* **2018**, 37, 1017-1025. (d) Khake, S. M.; Jagtap, R. A.; Dangat, Y. B.; Gonnade, R. G.; Vanka, K.; Punji, B. Mechanistic Insights into Pincer-Ligated Palladium-Catalyzed Arylation of Azoles with Aryl Iodides: Evidence of a Pd<sup>II</sup>-Pd<sup>IV</sup>-Pd<sup>II</sup> Pathway. *Organometallics* **2016**, 35, 875-886.
17. Stanlake, L. J. E.; Beard, J. D.; Schafer, L. L. Rare-Earth Amidate Complexes. Easily Accessed Initiators for  $\epsilon$ -Caprolactone Ring-Opening Polymerization. *Inorg. Chem.* **2008**, 47, 8062-8068.

18. (a) Wu, Z.; Cheng, Y.; Tao, F.; Daemen, L.; Foo, G. S.; Nguyen, L.; Zhang, X.; Beste, A.; Ramirez-Cuesta, A. J. Direct Neutron Spectroscopy Observation of Cerium Hydride Species on a Cerium Oxide Catalyst. *J. Am. Chem. Soc.* **2017**, *139*, 9721-9727. (b) Fang, Z.; Thanthiriwatte, K. S.; Dixon, D. A.; Andrews, L.; Wang, X. Properties of Cerium Hydroxides from Matrix Infrared Spectra and Electronic Structure Calculations. *Inorg. Chem.* **2016**, *55*, 1702-1714. (c) Kondo, Y.; Goto, Y.; Kobayashi, M.; Akama, T.; Norob, T.; Taketsugu, T. All-electron Relativistic Spin–Orbit Multireference Computation to Elucidate the Ground State of CeH. *Phys. Chem. Chem. Phys.* **2020**, *22*, 27157-27162.
19. Gao, Q; Li, Y. -H.; Chen, D. -Z.; Liu, J. -B. Exploration of Ligand-Centered Hydride Transfer in La/Y-Catalyzed Deoxygenative Reduction of Tertiary Amides with Pinacolborane. *Inorg. Chem.* **2023**, *62*, 1580-1590.

## *Chapter 3*

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### **Reduction of esters, epoxides and CO<sub>2</sub> using Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst**

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### 3.1. Introduction

The activation of the C–O bond is the key factor for the reduction of ester, epoxide and CO<sub>2</sub>. The reduction of esters, epoxides and CO<sub>2</sub> procreates valuable functionalized alcohols, which are utilized in the synthesis of fine chemicals, drug discovery, chemical feedstocks and valuable renewable sources of fuel.<sup>1</sup> The common reduction method involves aggressive reducing agents (e.g., LiAlH<sub>4</sub>, LiBH<sub>4</sub>, NaBH<sub>4</sub> and BH<sub>3</sub>), which possesses cabalistic drawback on the selectivity and the functional group tolerance.<sup>2</sup> On the other hand, an atom-efficient direct hydrogenation method demands high pressure and high temperature for the C–O bond reduction.<sup>3</sup> The alternative hydroelementation reactions (e.g., hydrosilylation or hydroboration) are striking tactics for the reduction of esters and epoxides. There are plenty of reports on metal-catalysed hydrosilylation of esters,<sup>4</sup> but, fewer reports on the hydroboration of esters.<sup>5</sup> Important to note that, there are very less reports on the hydroboration of epoxides.<sup>5d,6</sup>

The organo-*f*-element-catalysed hydroboration of esters<sup>7</sup> is juvenile in the organic transformation, whereas hydroboration of epoxides<sup>7a</sup> is an infant (**Chart 3.1**). In 2019, Marks and co-workers reported the hydroboration of esters using homoleptic lanthanum amide La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> as a catalyst and explained a detailed mechanistic pathway supported by experimental as well as theoretical studies.<sup>7b</sup> In the same year, Sadow and co-workers introduced the hydroboration of ester and epoxide using homoleptic tris(alkyl) lanthanum La[C(SiHMe<sub>2</sub>)<sub>3</sub>]<sub>3</sub> as a catalyst, where they investigated the reaction pathway by kinetic experiments.<sup>7a</sup> Later, Eisen and co-workers revealed the catalytic hydroboration of ester using thorium and uranium amide complexes as catalysts and proposed a plausible mechanistic pathway based on the stoichiometric reactions and DFT calculations.<sup>7c</sup>

Although the hydroboration of epoxides produces eco-friendly and industrially useful alcohol, reports on it are scarce.<sup>1</sup> Transition metal (Fe, Ni)-catalysed hydroboration of epoxides was reported by the group of Love<sup>6a</sup> and Wang<sup>6b</sup> in 2017. In 2022, Nembenna and co-workers introduced the aluminium-catalysed epoxide hydroboration.<sup>5d</sup> First lanthanide-catalysed hydroboration of epoxides was reported by Sadow and co-workers in 2019, where they showed the use of homoleptic tris(alkyl)lanthanum La[C(SiHMe<sub>2</sub>)<sub>3</sub>]<sub>3</sub> as a catalyst under mild reaction conditions (5-10 mol% of the catalyst, 1.3 equiv. of HBpin, 25-60 °C, 24 h).

The hydroboration reaction is widely explored in the field of the most important and most challenging CO<sub>2</sub> reduction process.<sup>8</sup> The catalysed products (e.g., formic acid derivatives,

diols, methanol) are in high demand in the industries.<sup>1</sup> There has been a gradual increase in the reports concerning the hydroboration of CO<sub>2</sub>, catalyzed by both transition metal-based catalysts and main-group catalysts.<sup>8</sup> However, the lanthanide-catalysed hydroboration of CO<sub>2</sub> using HBpin by the homogenous catalytic process is not known in the literature till to date.

In this chapter, we have demonstrated the reduction of esters, epoxides and CO<sub>2</sub> with HBpin using easily available Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst. The hydroboration of esters afforded good to excellent yields under mild reaction conditions (1 mol% of the catalyst, 60°C temperature and 4-12 hours reaction time). The hydroboration of cyclic esters delivered an excellent yield (up to >99%) under the same reaction conditions. A detailed kinetic experiments and stoichiometric reactions elaborated the mechanistic pathway of ester hydroboration reaction. The hydroboration of epoxides also led to excellent yields of selective borylated alcohol products under mild reaction conditions.

It is of note that we have also first time unveiled the reduction of CO<sub>2</sub> with HBpin to afford the borylated methanol catalysed by homoleptic lanthanide-amide complex as a catalyst. The Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>-catalysed hydroboration of CO<sub>2</sub> is highly selective towards the borylated methanol synthesis. It gives up to >99% yield at room temperature in 24 hours, whereas >99% yield was observed at 85°C temperature in 3 hours by using 0.087 mol% of the catalyst. The observed maximum TON was ~1146 and the TOF was ~382 h<sup>-1</sup> for the hydroboration of CO<sub>2</sub> to borylated methanol at 85°C.

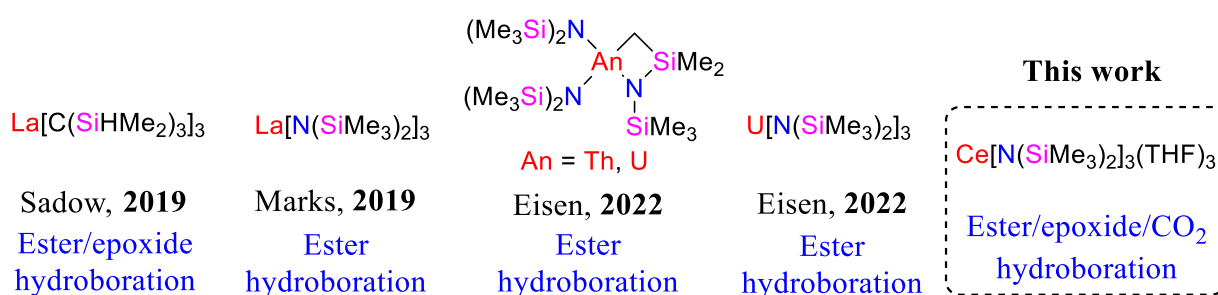


**Chart 3.1.** Organo-*f*-complexes for selective ester/epoxide hydroboration reaction with HBpin.

### 3.2. Experimental section

All manipulations were carried out under an inert gas atmosphere of argon using the standard Schlenk technique and in an argon-filled MBRAUN MB 150-GI glovebox. All solvents were purified by the MBRAUN MB SPS-800 solvent purification system. All other chemicals were

purchased from Sigma Aldrich, Alfa-Aesar, ChemScene and BLD Pharma. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  using a Bruker 400 MHz spectrometer. Mass spectra were recorded using an AB Sciex 4800 plus HRMS.  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  was synthesized by using the reported synthetic procedure.<sup>9</sup>

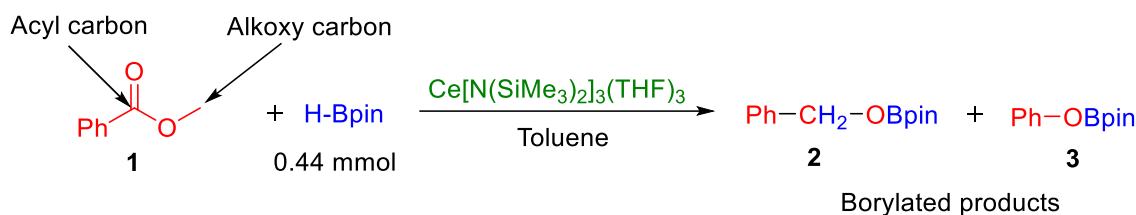
**General catalytic reaction procedure of ester hydroboration:** The  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyst was taken into a 25 mL Schlenk tube inside the glovebox and added ester (0.2 mmol) and 0.88 mL of HBpin solution (0.5 M). The reaction mixture was stirred for 5 h at 60 °C temperature. After that, the solvent was dried under a high vacuum. Then, mesitylene (0.2 mmol) was added as an internal standard into the tube and added 0.5 mL of  $\text{CDCl}_3$  and the crude reaction mixture was submitted for  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The yield of the products was calculated by integrating the mesitylene as an internal standard in  $^1\text{H}$  NMR spectra. We have calculated the yield of the product by considering the two protons at the reduced carbon centre.

**General catalytic reaction procedure of epoxide hydroboration:** The  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyst was taken into a 25 mL Schlenk tube inside the glovebox and added epoxide (0.2 mmol) and 0.88 mL of HBpin solution (0.5 M). The reaction mixture was stirred for 5 h at 60 °C temperature. After that, the solvent was dried under a high vacuum. Then, mesitylene (0.2 mmol) was added as an internal standard into the tube and added 0.5 mL of  $\text{CDCl}_3$  and the crude reaction mixture was submitted for  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The yield of the products was calculated by integrating the mesitylene as an internal standard in  $^1\text{H}$  NMR spectra.

**General catalytic reaction procedure of  $\text{CO}_2$  hydroboration:** We have taken 1 mg (0.0012 mmol) of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst in a 25 mL Schlenk tube inside the argon-filled glovebox. After that, 300  $\mu\text{L}$  (2.06 mmol) of HBpin was added into the tube by using the Schlenk line under an inert atmosphere. Then, the  $\text{CO}_2$  gas was purged into the tube for 5 minutes from the  $\text{CO}_2$  cylinder and packed the tube under the  $\text{CO}_2$  atmosphere and kept it for 1 h, 2 h, 3 h, 4 h, 6 h, 8 h, 12 h, 16 h and 24 h at 25 °C, 45 °C, 65 °C and 85 °C temperature accordingly. After completion of the reaction, added 95  $\mu\text{L}$  (0.67 mmol) of mesitylene and  $\text{CDCl}_3$  as solvent and recorded the  $^1\text{H}$  NMR (400 MHz, 298 K). Calculated the yields of the borylated methanol by integration of mesitylene peak in  $^1\text{H}$  NMR spectra.<sup>9a</sup>

### 3.3. Results and discussion of ester hydroboration reaction

#### 3.3.1. Reaction optimization



**Scheme 3.1.** Hydroboration of ester with HBpin using  $\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3$  as a catalyst.

The esters hydroboration with HBpin in the presence of  $\text{Ce[N(SiMe}_3)_2\text{]}_3$  as a catalyst is selective towards  $\text{C}_{\text{acyl}}\text{-O}$  bond cleavage, which afforded products **2** and **3** (**Scheme 3.1**). 1 mol% of  $\text{Ce[N(SiMe}_3)_2\text{]}_3$  at 60 °C in 5 hours is the optimized reaction condition for the selective reduction of ester (methyl benzoate) with HBpin to achieve a productive yield of borylated alcohol. At room temperature, the hydroboration of the phenyl benzoate led to the formation of product in only 46% yield in 12 hours. We performed three experiments to understand the preface of the catalyst: (i) without catalyst (**Table 3.1; Entry 8**): Demonstrated 27% yield at 60 °C temperature in 5 hours; (ii) 10 mol%  $\text{CeCl}_3$  as a catalyst (**Table 3.1; Entry 9**): Afforded 24% yield at the optimized conditions; (iii) 20 mol% of TMEDA (tetramethylethylenediamine) as an additive with 1 mol% of the catalyst (**Table 3.1; Entry 10**): Delivered 89% yield, which indicated the negligible impact of “hidden  $\text{BH}_3$  catalysis”<sup>10</sup> in the ester hydroboration reaction. All these three distinguish experiments notified that  $\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3$  behaves as an efficient catalyst for the ester reduction with HBpin under mild reaction conditions.

**Table 3.1.** Reaction optimization of methylbenzoate hydroboration reaction.

| $\text{Ph-C(=O)OCH}_3 + \text{H-Bpin} \xrightarrow[\text{Toluene}]{\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3 \text{ (x mol\%)}}$ |                                                 |      |            |          |           |
|--------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|------|------------|----------|-----------|
| $\text{Ph-CH}_2\text{-O-Bpin} + \text{Ph-O-Bpin}$                                                                                    |                                                 |      |            |          |           |
| Borylated product                                                                                                                    |                                                 |      |            |          |           |
| Sl. No.                                                                                                                              | Catalyst                                        | Mol% | Temp. (°C) | Time (h) | Yield*(%) |
| 1.                                                                                                                                   | $\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3$ | 0.5  | 60         | 12       | 45        |
| 2.                                                                                                                                   | $\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3$ | 1    | 60         | 12       | >99       |
| 3.                                                                                                                                   | $\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3$ | 1    | 60         | 5        | >99       |
| 4.                                                                                                                                   | $\text{Ce[N(SiMe}_3)_2\text{]}_3\text{(THF)}_3$ | 1    | 60         | 3        | 79        |

|    |                                                                                                                |    |    |   |     |
|----|----------------------------------------------------------------------------------------------------------------|----|----|---|-----|
| 5. | Ce[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (THF) <sub>3</sub>                                        | 1  | rt | 5 | 5   |
| 6. | Ce[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (THF) <sub>3</sub>                                        | 1  | 50 | 5 | 86  |
| 7. | -                                                                                                              | -  | 60 | 5 | 22  |
| 8. | CeCl <sub>3</sub>                                                                                              | 10 | 60 | 5 | 20  |
| 9. | Ce[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (THF) <sub>3</sub> (in<br>presence of 20 mol% of<br>TMEDA | 1  | 60 | 5 | 100 |

[Yields were determined by integrating <sup>1</sup>H NMR spectra in the presence of an internal standard (mesitylene).]

### 3.3.2. Substrate scope of ester hydroboration

Broad substrates were carried out using Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst at optimized reaction conditions. The electron-withdrawing and electron-donating group substituted aromatic esters afforded very good yields in 5 hours (**Scheme 3.2**). The methylbenzoate with -OH and -OMe group substitutions unexpectedly exhibited a lower yield compared to the others (**2g** and **2i**; **Scheme 3.2**). We achieved good to excellent yields of borylated products from aliphatic ester hydroboration within a 12 hours timeframe. An electron-withdrawing group containing methylbenzoate also provided a decent yield of the borylated alcohol product in the presence of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst. All the substrates demonstrated the kinetically labile cleavage of the C<sub>acyl</sub>-O bond in the ester group neglecting the C<sub>alkoxy</sub>-O bond cleavage in the presence of electrophilic Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst. A complete list of the products is mentioned in **Table 3.2**.

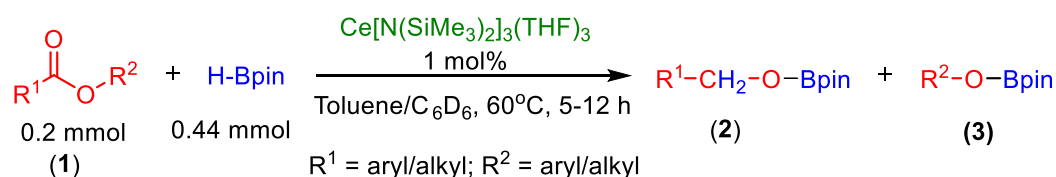
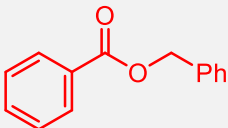
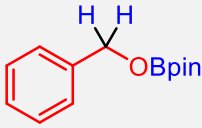
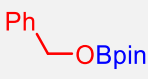
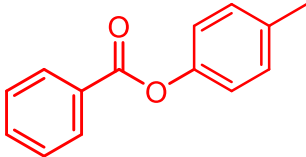
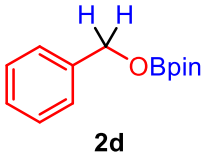
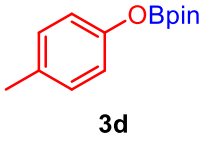
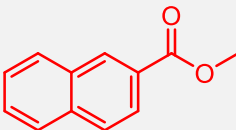
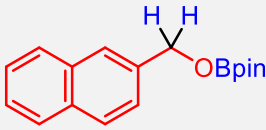
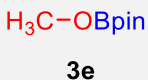
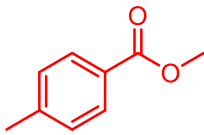
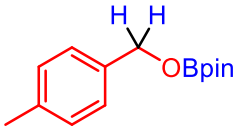
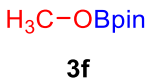
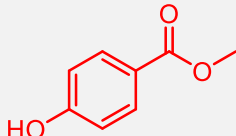
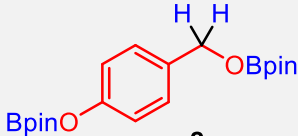
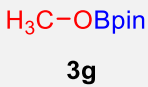
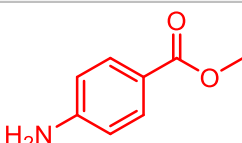
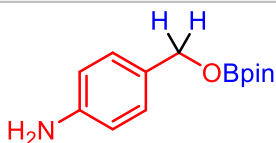
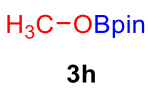
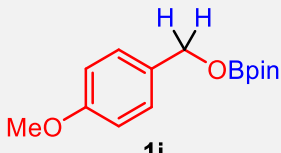
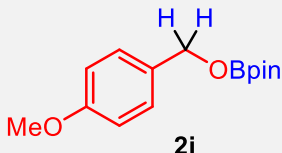
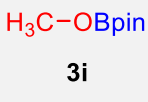
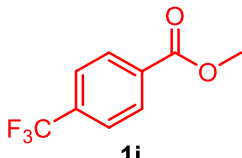
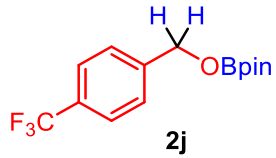
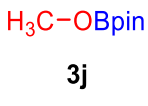
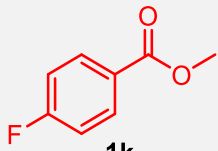
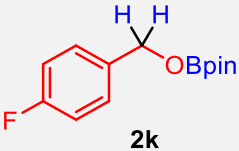
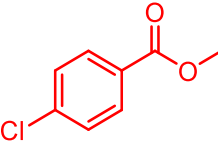
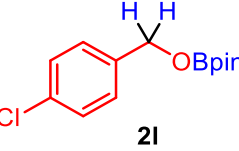
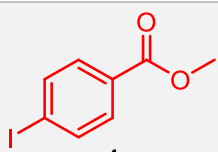
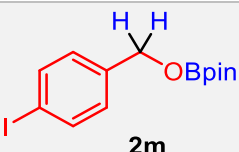
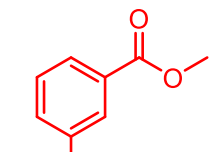
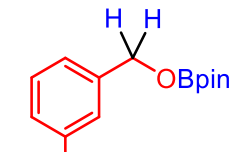
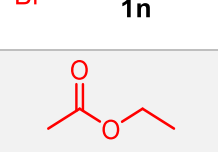
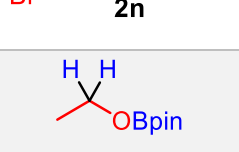
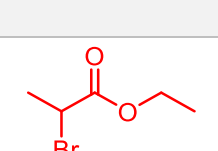
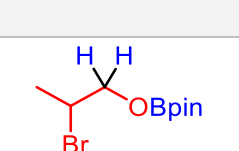
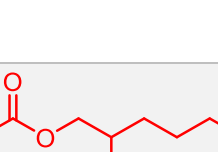
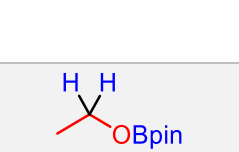
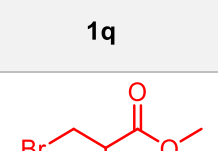
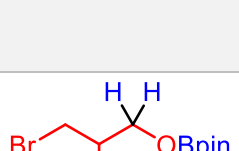


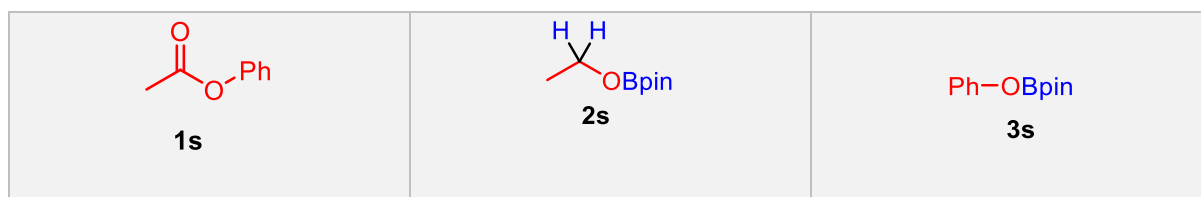
**Table 3.2.** Substrate scope of esters hydroboration.



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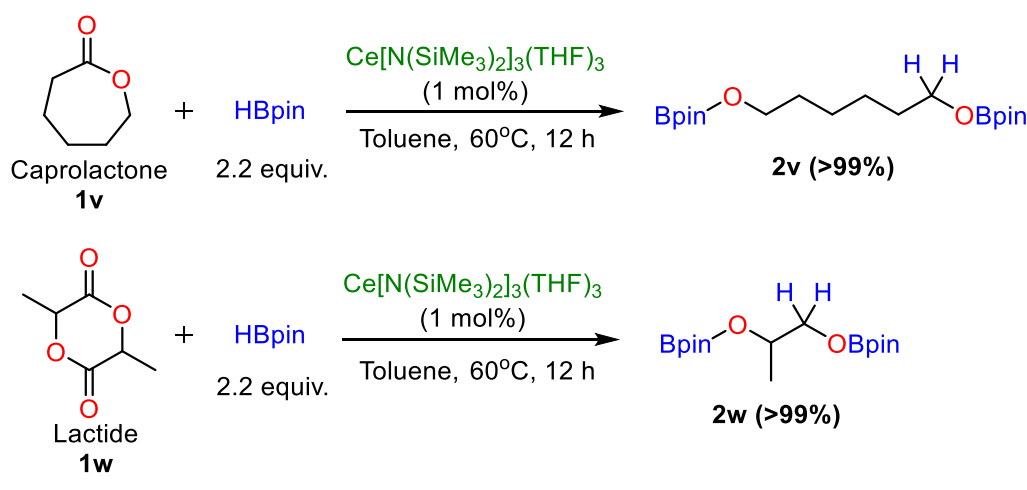
|                                                                                                  |                                                                                                  |                                                                                                    |
|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| <br><b>1c</b>   | <br><b>2c</b>   | <br><b>3c</b>   |
| <br><b>1d</b>   | <br><b>2d</b>   | <br><b>3d</b>   |
| <br><b>1e</b>   | <br><b>2e</b>   | <br><b>3e</b>   |
| <br><b>1f</b>   | <br><b>2f</b>   | <br><b>3f</b>   |
| <br><b>1g</b> | <br><b>2g</b> | <br><b>3g</b> |
| <br><b>1h</b> | <br><b>2h</b> | <br><b>3h</b> |
| <br><b>1i</b> | <br><b>2i</b> | <br><b>3i</b> |
| <br><b>1j</b> | <br><b>2j</b> | <br><b>3j</b> |

|                                                                                                  |                                                                                                  |                                                                                                    |
|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| <br><b>1k</b>   | <br><b>2k</b>   | $\text{H}_3\text{C}-\text{OBpin}$<br><b>3k</b>                                                     |
| <br><b>1l</b>   | <br><b>2l</b>   | $\text{H}_3\text{C}-\text{OBpin}$<br><b>3l</b>                                                     |
| <br><b>1m</b>   | <br><b>2m</b>   | $\text{H}_3\text{C}-\text{OBpin}$<br><b>3m</b>                                                     |
| <br><b>1n</b>   | <br><b>2n</b>   | $\text{H}_3\text{C}-\text{OBpin}$<br><b>3n</b>                                                     |
| <br><b>1o</b> | <br><b>2o</b> | $\text{H}_3\text{C}-\text{CH}_2-\text{OBpin}$<br><b>3o</b>                                         |
| <br><b>1p</b> | <br><b>2p</b> | $\text{H}_3\text{C}-\text{CH}_2-\text{OBpin}$<br><b>3p</b>                                         |
| <br><b>1q</b> | <br><b>2q</b> | <br><b>3q</b> |
| <br><b>1r</b> | <br><b>2r</b> | $\text{H}_3\text{C}-\text{CH}_2-\text{OBpin}$<br><b>3r</b>                                         |



[<sup>a</sup>12 h reaction time. <sup>b</sup>C<sub>6</sub>D<sub>6</sub> as a solvent. Yields were determined by the integration of the corresponding <sup>1</sup>H NMR spectra normalized on the internal standard (mesitylene)]

We took two cyclic esters *e.g.*,  $\epsilon$ -caprolactone and lactide, which are very popular and common monomers for polymerization reactions to deliver polycaprolactone (PCL) and polylactic acid (PLA).<sup>11</sup> Surprisingly in the presence of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> hydroboration of caprolactone and lactide with HBpin afforded borylated alcoholic products instead of polymerized products (**Scheme 3.3**). Both the cyclic esters, showed an excellent yield of the corresponding borylated alcohol products (>99%).



**Scheme 3.3.** Substrate scope of catalytic hydroboration of cyclic esters with HBpin using catalyst Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>. [Yields were determined by the integration of the corresponding <sup>1</sup>H NMR spectra normalized on the internal standard (mesitylene)]

#### Analytical data of borylated alcohol:

**2a + 3a:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K):  $\delta$  7.28-7.22 (m, 4H, *Ph*), 7.19-7.15 (m, 1H, *Ph*), 6.72 (s, 3H, *mesitylene*), 4.85 (s, 2H, CH<sub>2</sub>), 3.83 (s, 3H, CH<sub>3</sub>), 2.19 (s, 9H, *mesitylene*), 1.18 (s, 12H, OBpin) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K):  $\delta$  139.2 (*Ph*), 137.7 (*mesitylene*), 129.6 (*Ph*), 128.3 (*Ph*), 127.4 (*mesitylene*), 126.9 (*Ph*), 83.0 (OBpin), 66.7 (CH<sub>2</sub>), 24.6 (OBpin), 21.2 (*mesitylene*) ppm.

**2b + 3b:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.25-7.20 (m, 4H, 2Ph), 7.17-7.14 (m, 2H, 2Ph), 7.09-7.07 (m, 2H, 2Ph), 6.76-6.75 (m, 2H, 2Ph), 6.69 (s, 3H, *mesitylene*), 4.84 (s, 2H,  $\text{CH}_2$ ), 2.17 (s, 9H, *mesitylene*), 1.16 (s, 24H, 2OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  139.2 (Ph), 137.7 (*mesitylene*), 129.5 (Ph), 128.3 (Ph), 127.5 (*mesitylene*), 127.0 (Ph), 126.8 (Ph), 121.8 (Ph), 120.2 (Ph), 115.5 (Ph), 83.3 (OBpin), 83.1 (OBpin), 66.8 ( $\text{CH}_2$ ), 24.6 (OBpin), 24.5 (OBpin), 21.2 (*mesitylene*) ppm.

**2c:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.26-7.20 (m, 8H, 2Ph), 7.17-7.13 (m, 2H, 2Ph), 6.70 (s, 3H, *mesitylene*), 4.83 (s, 4H, 2 $\text{CH}_2$ ), 2.18 (s, 9H, *mesitylene*), 1.16 (s, 24H, 2OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*mesitylene*), 133.1 (Ph), 129.8 (Ph), 128.7 (Ph), 128.4 (Ph), 127.0 (*mesitylene*), 83.0 (OBpin), 66.8 ( $\text{CH}_2$ ), 24.7 (OBpin), 21.3 (*mesitylene*) ppm.

**2d + 3d:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.26-7.20 (m, 5H, Ph), 6.97-6.95 (m, 2H,  $\text{CH}_3\text{Ph}$ ), 6.89-6.87 (m, 2H,  $\text{CH}_3\text{Ph}$ ), 6.70 (s, 3H, *mesitylene*), 4.84 (s, 2H,  $\text{CH}_2$ ), 2.18 (s, 3H,  $\text{PhCH}_3$ ), 2.18 (s, 9H, *mesitylene*), 1.21 (s, 12H, OBpin), 1.18 (s, 12H, OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  151.3 (Ph), 139.3 (Ph), 137.7 (*mesitylene*), 132.5 (Ph), 129.8 (Ph), 128.3 (Ph), 127.4 (*mesitylene*), 127.0 (Ph), 126.8 (Ph), 119.3 (Ph), 83.5 (OBpin), 83.0 (OBpin), 66.8 ( $\text{CH}_2$ ), 24.7 (OBpin), 24.6 (OBpin), 21.3 (*mesitylene*), 20.7 ( $\text{CH}_3$ ) ppm.

**2e + 3e:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.74-7.68 (m, 4H, *Naphthalene*), 7.48-7.39 (m, 1H, *Naphthalene*), 7.35-7.33 (m, 2H, *Naphthalene*), 6.69 (s, 3H, *mesitylene*), 4.99 (s, 2H,  $\text{CH}_2$ ), 3.50 (s, 3H,  $\text{CH}_3\text{OBpin}$ ), 2.17 (s, 9H, *mesitylene*), 1.17 (s, 12H, OBpin), 1.15 (s, 12H,  $\text{CH}_3\text{OBpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 135.6 (*Naphthalene*), 132.5 (*Naphthalene*), 131.1 (*Naphthalene*), 129.4 (*Naphthalene*), 128.3 (*Naphthalene*), 128.2 (*Naphthalene*), 127.8 (*Naphthalene*), 127.0 (*mesitylene*), 126.7 (*Naphthalene*), 125.8 (*Naphthalene*), 125.3 (*Naphthalene*), 83.1 (OBpin), 66.8 ( $\text{CH}_2$ ), 52.3 ( $\text{CH}_3\text{OBpin}$ ), 24.5 (OBpin), 21.2 (*mesitylene*) ppm.

**2f + 3f:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.16-7.14 (m, 2H, Ph), 7.05-7.03 (m, 2H, Ph), 6.71 (s, 3H, *mesitylene*), 4.79 (s, 2H,  $\text{CH}_2$ ), 2.24 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.18 (s, 9H, *mesitylene*), 1.17 (s, 12H, OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 137.0 ( $\text{CH}_3\text{Ph}$ ), 136.3 ( $\text{CH}_3\text{Ph}$ ), 129.7 ( $\text{CH}_3\text{Ph}$ ), 129.0 ( $\text{CH}_3\text{Ph}$ ), 126.9 (*mesitylene*), 83.1 (OBpin), 83.0 (OBpin), 66.6 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3\text{OBpin}$ ), 24.6 (OBpin), 24.5 (OBpin), 21.2 (*mesitylene*) ppm.

**2g + 3g:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.95-7.93 (d, 2H, *Ph*), 6.95-6.93 (d, 2H, *Ph*), 6.82 (s, 3H, *mesitylene*), 4.85 (s, 2H,  $\text{CH}_2$ ), 2.24 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.29 (s, 9H, *mesitylene*), 1.29 (s, 12H, *OBpin*), 1.28 (s, 12H,  $\text{PhOBpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  155.7 (*PhOH*), 137.7 (*mesitylene*), 131.9 (*PhOH*), 128.8 (*PhOH*), 126.9 (*mesitylene*), 115.5 (*PhOH*), 83.3 (*OBpin*), 83.2 (*OBpin*), 66.7 ( $\text{CH}_2$ ), 52.0 ( $\text{CH}_3\text{OBpin}$ ), 24.6 (*OBpin*), 24.5 (*OBpin*), 21.2 (*mesitylene*) ppm.

**2h + 3h:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.82 (s, 3H, *mesitylene*), 6.66-6.61 (m, 4H, *Ph*), 4.81 (s, 2H,  $\text{CH}_2$ ), 2.30 (s, 9H, *mesitylene*), 1.28 (s, 12H, *OBpin*), 1.27 (s, 12H, *NBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  146.0 ( $\text{PhNH}_2$ ), 137.7 (*mesitylene*), 131.6 ( $\text{PhNH}_2$ ), 128.7 ( $\text{PhNH}_2$ ), 126.9 (*mesitylene*), 113.7 ( $\text{PhNH}_2$ ), 83.1 (*OBpin*), 82.8 (*OBpin*), 66.8 ( $\text{CH}_2$ ), 51.5 ( $\text{CH}_3\text{OBpin}$ ), 24.6 (*OBpin*), 24.5 (*OBpin*), 21.2 (*mesitylene*) ppm.

**2i + 3i:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.33-7.31 (d, 2H, *Ph*), 6.91-6.89 (d, 2H, *Ph*), 6.84 (s, 3H, *mesitylene*), 4.89 (s, 2H,  $\text{CH}_2$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ), 2.31 (s, 9H, *mesitylene*), 1.30 (s, 12H, *OBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  159.1 ( $\text{PhOMe}$ ), 137.7 (*mesitylene*), 131.7 ( $\text{PhOMe}$ ), 128.6 ( $\text{PhOMe}$ ), 127.0 (*mesitylene*), 113.7 ( $\text{PhOMe}$ ), 83.1 (*OBpin*), 82.9 (*OBpin*), 66.5 ( $\text{CH}_2$ ), 55.3 ( $\text{OMe}$ ), 51.9 ( $\text{CH}_3\text{OBpin}$ ), 24.7 (*OBpin*), 24.6 (*OBpin*), 21.2 (*mesitylene*) ppm.

**2j + 3j:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.62-7.60 (d, 2H, *Ph*), 7.49-7.47 (d, 2H, *Ph*), 6.82 (s, 3H, *mesitylene*), 5.01 (s, 2H,  $\text{CH}_2$ ), 2.30 (s, 9H, *mesitylene*), 1.30 (s, 12H, *OBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  143.3 ( $\text{PhCF}_3$ ), 137.8 (*mesitylene*), 130.1 ( $\text{PhCF}_3$ ), 127.0 (*mesitylene*), 126.7 ( $\text{PhCF}_3$ ), 125.3 ( $\text{PhCF}_3$ ), 83.3 (*OBpin*), 66.0 ( $\text{CH}_2$ ), 52.6 ( $\text{CH}_3\text{OBpin}$ ), 24.7 (*OBpin*), 24.6 (*OBpin*), 21.3 (*mesitylene*) ppm.

**2k + 3k:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.30-7.30 (d, 2H, *Ph*), 6.81 (s, 3H, *mesitylene*), 4.90 (s, 2H,  $\text{CH}_2$ ), 2.29 (s, 9H, *mesitylene*), 1.28 (s, 12H, *OBpin*), 1.27 (s, 12H,  $\text{CH}_3\text{OBpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  161.1 (*FPh*), 137.7 (*mesitylene*), 129.1 (*FPh*), 128.3 (*FPh*), 127.0 (*mesitylene*), 125.4 (*FPh*), 83.1 (*OBpin*), 82.8 (*OBpin*), 66.1 ( $\text{CH}_2$ ), 52.6 ( $\text{CH}_3\text{OBpin}$ ), 24.6 (*OBpin*), 24.5 (*OBpin*), 21.2 (*mesitylene*) ppm.

**2l + 3l:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.36-7.33 (m, 2H, *Ph*), 7.06-7.01 (m, 2H, *Ph*), 6.83 (s, 3H, *mesitylene*), 4.91 (s, 2H,  $\text{CH}_2$ ), 2.30 (s, 9H, *mesitylene*), 1.29 (s, 12H, *OBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 135.1 ( $\text{ClPh}$ ), 132.2 ( $\text{ClPh}$ ), 128.7 ( $\text{ClPh}$ ), 127.0 (*mesitylene*), 115.1 ( $\text{ClPh}$ ), 83.1 (*OBpin*), 83.0 (*OBpin*), 66.1 ( $\text{CH}_2$ ), 52.2 ( $\text{CH}_3\text{OBpin}$ ), 24.7 (*OBpin*), 24.6 (*OBpin*), 21.2 (*mesitylene*) ppm.

**2m + 3m:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.69-7.67 (m, 2H, *Ph*), 7.13-7.11 (m, 2H, *Ph*), 6.83 (s, 3H, *mesitylene*), 4.89 (s, 2H,  $\text{CH}_2$ ), 2.31 (s, 9H, *mesitylene*), 1.29 (s, 12H, *OBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*IPh*), 137.7 (*IPh*), 137.4 (*mesitylene*), 131.1 (*IPh*), 128.7 (*IPh*), 127.0 (*mesitylene*), 83.2 (*OBpin*), 83.1 (*OBpin*), 66.1 ( $\text{CH}_2$ ), 52.3 ( $\text{CH}_3\text{OBpin}$ ), 24.7 (*OBpin*), 24.6 (*OBpin*), 21.3 (*mesitylene*) ppm.

**2n + 3n:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.61-7.59 (m, 1H, *Ph*), 7.46-7.42 (m, 1H, *Ph*), 7.33-7.28 (m, 2H, *Ph*), 6.83 (s, 3H, *mesitylene*), 4.95 (s, 2H,  $\text{CH}_2$ ), 4.50 (s, 2H,  $\text{BrCH}_2\text{Ph}$ ), 2.30 (s, 9H, *mesitylene*), 1.30 (s, 12H, *OBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  138.3 ( $\text{BrCH}_2\text{Ph}$ ), 137.8 (*mesitylene*), 133.5 ( $\text{BrCH}_2\text{Ph}$ ), 130.8 ( $\text{BrCH}_2\text{Ph}$ ), 130.2 ( $\text{BrCH}_2\text{Ph}$ ), 129.6 ( $\text{BrCH}_2\text{Ph}$ ), 129.0 ( $\text{BrCH}_2\text{Ph}$ ), 127.0 (*mesitylene*), 83.2 (*OBpin*), 66.3 ( $\text{CH}_2$ ), 52.3 ( $\text{CH}_3\text{OBpin}$ ), 32.5 ( $\text{BrCH}_2\text{Ph}$ ), 24.7 (*OBpin*), 24.6 (*OBpin*), 21.3 (*mesitylene*) ppm.

**2o + 3o:**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 298 K):  $\delta$  6.67 (s, 3H, *mesitylene*), 3.94-3.84 (m, 4H,  $\text{CH}_2$ ), 2.14 (s, 9H, *mesitylene*), 1.02 (s, 24H, *OBpin*), 0.98-0.94 (t, 6H,  $\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.613 MHz, 298 K):  $\delta$  137.6 (*mesitylene*), 127.3 (*mesitylene*), 83.2 (*OBpin*), 60.1 ( $\text{CH}_2$ ), 25.0 (*OBpin*), 21.3 (*mesitylene*), 17.5 ( $\text{CH}_3$ ) ppm.

**2p + 3p:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.76 (s, 3H, *mesitylene*), 4.06-4.02 (m, 1H,  $\text{BrCH}$ ), 3.96-3.89 (m, 4H,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2 + \text{CH}_3\text{CH}_2$ ), 2.23 (s, 9H, *mesitylene*), 1.50-1.48 (d, 3H,  $\text{CH}_3\text{CHBr}$ ), 1.19-1.17 (t, 3H,  $\text{CH}_3\text{CH}_2$ ), 1.15 (s, 12H, *OBpin*), 1.13 (s, 12H, *OBpin*) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.613 MHz, 298 K):  $\delta$  137.5 (*mesitylene*), 127.3 (*mesitylene*), 83.2 (*OBpin*), 70.2 ( $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2$ ), 60.6 ( $\text{CH}_3\text{CH}_2$ ), 48.4 ( $\text{CH}_3\text{CHBr}$ ), 25.0 (*OBpin*), 24.7 (*OBpin*), 22.1 ( $\text{CH}_3\text{CHBr}$ ), 21.3 (*mesitylene*), 17.5 ( $\text{CH}_3\text{CH}_2$ ) ppm.

**2q + 3q:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.82 (s, 3H, *mesitylene*), 3.82-3.75 (m, 4H,  $\text{CH}_3\text{CH}_2 + \text{CHCH}_2$ ), 2.30 (s, 9H, *mesitylene*), 1.40-1.39 (d, 1H,  $\text{CH}$ ), 1.36-1.31 (m, 8H,  $(\text{CH}_2)_4$ ), 1.27 (s, 24H, *OBpin*), 0.92-0.88 (t, 9H,  $(\text{CH}_3)_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*mesitylene*), 127.0 (*mesitylene*), 82.7 (*OBpin*), 67.1 ( $\text{CHCH}_2\text{OBpin}$ ), 60.8 ( $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 41.1 ( $\text{CH}$ ), 30.1 ( $\text{CH}_2$ ), 29.1 ( $\text{CH}_2$ ), 24.7 (*OBpin*), 23.4 ( $\text{CH}_2$ ), 23.2 ( $\text{CH}_2$ ), 21.3 (*mesitylene*), 17.3 ( $\text{CH}_3\text{CH}_2$ ), 14.2 ( $\text{CH}_3\text{CH}_2\text{CH}$ ), 11.2 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ) ppm.

**2r:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.81 (s, 3H, *mesitylene*), 3.78-3.77 (d, 4H,  $(\text{BrCH}_2)_2$ ), 3.74-3.70 (m, 4H,  $\text{CHCH}_2 + \text{CH}_2\text{CH}_3$ ), 3.23-3.17 (m, 1H,  $\text{CH}$ ), 2.29 (s, 9H, *mesitylene*), 1.29 (s, 24H, *OBpin*), 1.26-1.25 (t, 3H,  $\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 126.9 (*mesitylene*), 83.2 (*OBpin*), 52.6 ( $\text{CHCH}_2\text{OBpin}$ ), 48.6 ( $(\text{BrCH}_2)_2\text{CH}$ ), 30.5 ( $(\text{BrCH}_2)_2\text{CH}$ ), 24.5 (*OBpin*), 21.2 (*mesitylene*) ppm.

**2s:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.83 (s, 3H, *mesitylene*), 3.88-3.85 (m, 2H,  $\text{CH}_2$ ), 2.31 (s, 9H, *mesitylene*), 1.28 (s, 12H, *OBpin*), 0.94-0.91 (t, 3H,  $\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100.613 MHz, 298 K):  $\delta$  137.5 (*mesitylene*), 127.3 (*mesitylene*), 83.2 (*OBpin*), 82.9 (*OBpin*), 60.6 ( $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 25.0 (*OBpin*), 24.6 (*OBpin*), 21.3 (*mesitylene*), 14.1 ( $\text{CH}_3\text{CH}_2\text{OBpin}$ ) ppm.

### 3.3.3. Kinetic studies

All the kinetic experiments were accomplished by  $^1\text{H}$  NMR (400 MHz) spectroscopic data using *mesitylene* (0.4 M) as an internal standard in  $\text{C}_6\text{D}_6$  as a solvent. All the yields (in molar concentration) were determined using  $^1\text{H}$  NMR spectra by integrating the corresponding peak of the internal standard (*mesitylene*).

We started the kinetic experiments to determine the overall order and the rate equation of the hydroboration reaction of methyl benzoate with HBpin using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. We started the investigation one by one: (i) the order of the hydroboration reaction with respect to the catalyst, (ii) the order of the hydroboration reaction with respect to HBpin, and (iii) the order of the hydroboration reaction with respect to methyl benzoate.

Representative procedure for the methyl benzoate hydroboration reaction carried out with various concentrations of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ : The order of dependence of the catalyst ( $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  for hydroboration reaction of methyl benzoate with HBpin was determined by the methods of initial rates.<sup>12</sup> Initial rate ( $k_{\text{obs}}$ ) were determined using various concentrations of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (1 mM, 2 mM, 4 mM, and 6 mM) by keeping the concentration of HBpin (0.88 M) and methyl benzoate (0.4 M) constant. We recorded four  $^1\text{H}$  NMR spectra at a certain interval time (60 min) and plotted [product] vs time graph by using OriginPro 9.0 software (**Figure 3.1**). We observed  $k_{\text{obs}}$  values of the reaction from [product] vs time plot, which was equal to the slope of the linear fit lines (**Table 3.3**). The experimental procedure that has been used is described below.

At first, the catalyst (in different concentrations, 1 mM, 2 mM, 4 mM, and 6 mM) was added to the NMR tube inside the glove box, and then the methyl benzoate (0.4 M), HBpin (0.88 M) and  $\text{C}_6\text{D}_6$  (as solvent) were added to the NMR tube under argon atmosphere by using Schlenk line. After that, the  $^1\text{H}$  NMR spectra were recorded at various time intervals. The varying catalyst concentration and the concentration of HBpin and methyl benzoate for each set of experiments are given in **Table 3.3** and represent the data graphically.

**Table 3.3.** Initial rates ( $k_{obs}$ ) for the hydroboration reaction of methyl benzoate with HBpin carried out under varying concentrations of  $Ce[N(SiMe_3)_2]_3(THF)_3$ .

| Sl. No. | $[Ce[N(SiMe_3)_2]_3(THF)_3]$<br>(mM) | [HBpin]<br>(M) | [Benzamide]<br>(M) | $k_{obs} (\times 10^{-4})$ |
|---------|--------------------------------------|----------------|--------------------|----------------------------|
| 1.      | 1                                    | 0.88           | 0.4                | 1.80                       |
| 2.      | 2                                    | 0.88           | 0.4                | 3.07                       |
| 3.      | 4                                    | 0.88           | 0.4                | 8.53                       |
| 4.      | 6                                    | 0.88           | 0.4                | 12.70                      |

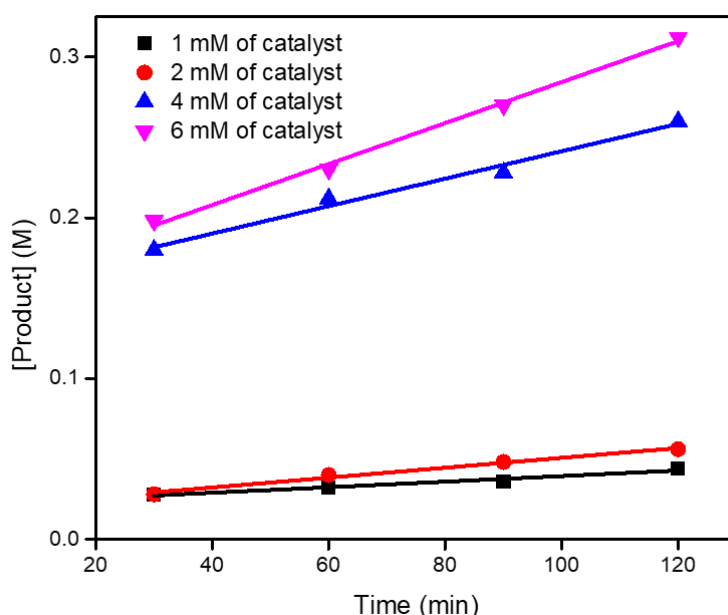


**Figure 3.1.** The plot of [Product] vs. time (best linear fitted) used for the determination of the initial rate ( $k_{obs}$ ) values of methyl benzoate hydroboration carried out with various concentrations of  $Ce[N(SiMe_3)_2]_3(THF)_3$ .

Representative procedure for the methyl benzoate hydroboration reaction carried out with various concentrations of HBpin: Initial rate ( $k_{obs}$ ) was determined using various concentrations of HBpin (0.4 M, 0.6 M and 0.8 M) by keeping the concentration of  $Ce[N(SiMe_3)_2]_3(THF)_3$  (4 mM) and benzamide (0.4 M) constant. We recorded four  $^1H$  NMR spectra at a certain interval time (60 min) and plotted [product] vs time graph by using OriginPro 9.0 software (**Figure 3.2**). We observed  $k_{obs}$  values of the reaction from [product] vs time plot, which was equal to the slope of the linear fit lines (**Table 3.4**). The experimental procedure that has been used is described below.

At first,  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (4 mM) was added to the NMR tube inside the glove box, and then the benzamide (0.4 M), HBpin (in different concentrations, 0.4 M, 0.6 M and 0.8 M) and  $\text{C}_6\text{D}_6$  (as solvent) were added to the NMR tube under argon atmosphere by using Schlenk line. After that, the  $^1\text{H}$  NMR spectra were recorded at various time intervals. The varying HBpin concentration and the constant concentration of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and benzamide for each set of experiments are given in **Table 3.4** and represent the data graphically.

**Table 3.4.** Initial rates ( $k_{\text{obs}}$ ) for the hydroboration reaction of benzamide were carried out under varying concentrations of HBpin.

| Sl. No. | $[\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3]$<br>(mM) | [HBpin]<br>(M) | [Benzamide]<br>(M) | $k_{\text{obs}} (\times 10^{-4})$ |
|---------|------------------------------------------------------------------|----------------|--------------------|-----------------------------------|
| 1.      | 4                                                                | 0.4            | 0.4                | 4.00                              |
| 2.      | 4                                                                | 0.6            | 0.4                | 5.13                              |
| 3.      | 4                                                                | 0.8            | 0.4                | 6.00                              |

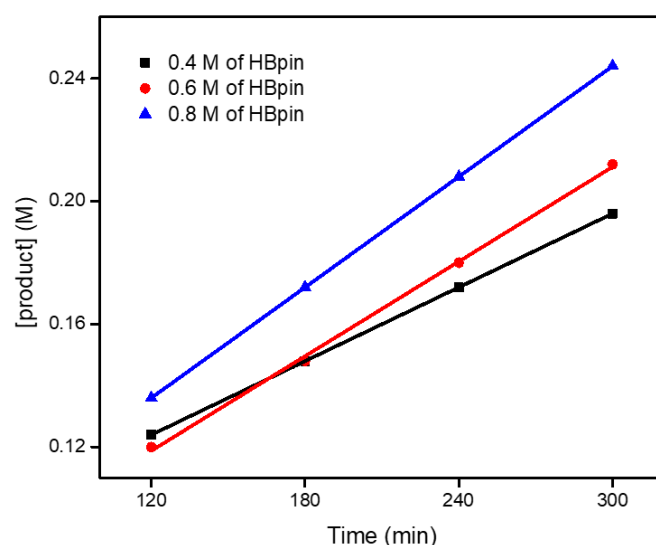


**Figure 3.2.** Plot of [product] vs. time (best linear fitted) used for the determination of the initial rate ( $k_{\text{obs}}$ ) values of methyl benzoate hydroboration carried out with various concentrations of HBpin.

Representative procedure for the methyl benzoate hydroboration reaction carried out with various concentrations of methyl benzoate: Initial rates ( $k_{\text{obs}}$ ) were determined using various concentrations of methyl benzoate (0.4 M, 0.6 M, and 0.8 M) by keeping the concentration of

$\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (4 mM) and HBpin (0.88 M) constant. We recorded four  $^1\text{H}$  NMR spectra at a certain interval time (60 min) and plotted [product] vs. time graph by using OriginPro 9.0 software (**Figure 3.3**). We observed  $k_{\text{obs}}$  values of the reaction from [product] vs. time plot, which was equal to the slope of the linear fit lines (**Table 3.5**). The experimental procedure that has been used is described below.

At first,  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (4 mM) was added to the NMR tube inside the glove box, and then the methyl benzoate (in different concentrations, 0.4 M, 0.6 M, and 0.8 M), HBpin (0.88 M) and  $\text{C}_6\text{D}_6$  (as solvent) were added to the NMR tube under argon atmosphere by using Schlenk line. After that, the  $^1\text{H}$  NMR spectra were recorded at various time intervals. The varying methyl benzoate concentration and the constant concentration of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and HBpin for each set of experiments are given in **Table 3.5** and represent the data graphically.

**Table 3.5.** Initial rates ( $k_{\text{obs}}$ ) for the hydroboration reaction of methyl benzoate were carried out under varying concentrations of methylbenzoate.

| Sl. No. | $[\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3]$<br>(mM) | [HBpin]<br>(M) | [methylbenzoate]<br>(M) | $k_{\text{obs}} (\times 10^{-4})$ |
|---------|------------------------------------------------------------------|----------------|-------------------------|-----------------------------------|
| 1.      | 4                                                                | 0.88           | 0.4                     | 8.73                              |
| 2.      | 4                                                                | 0.88           | 0.6                     | 8.33                              |
| 3.      | 4                                                                | 0.88           | 0.8                     | 8.33                              |

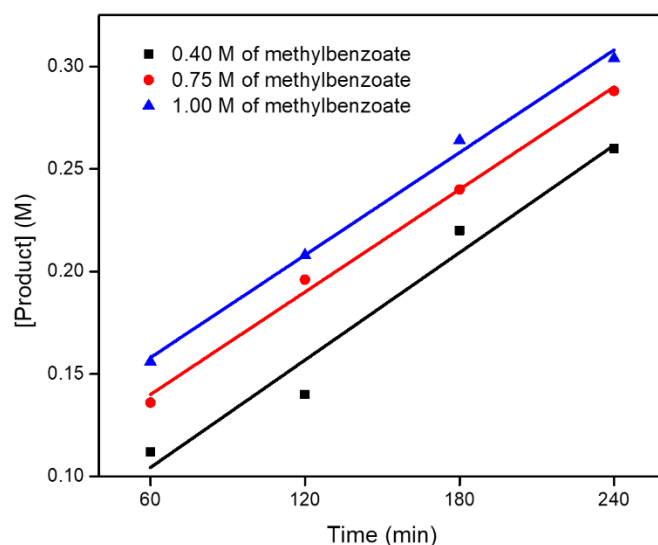
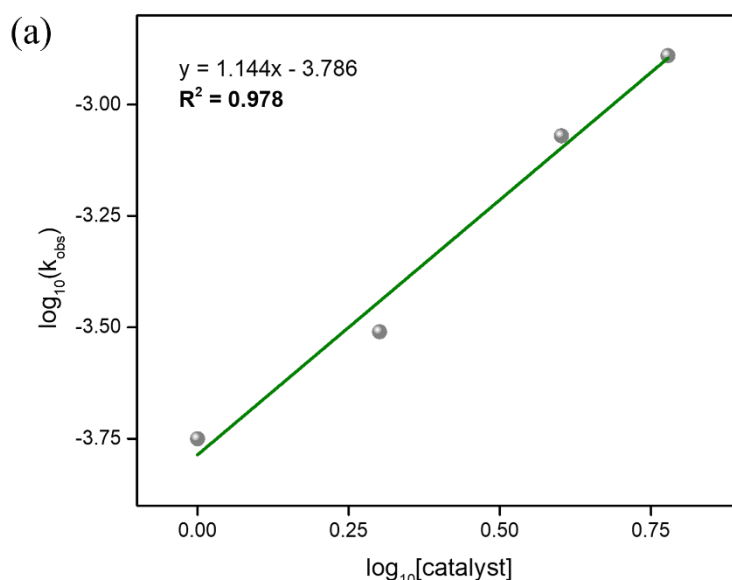


**Figure 3.3.** Plot of [product] vs. time (best linear fitted) used for the determination of the initial rate ( $k_{obs}$ ) values of methyl benzoate hydroboration carried out with various concentrations of methylbenzoate.

The rate constants were determined using the method of initial rates by varying the initial concentration of catalyst, HBpin and methyl benzoate, which conferred a brief concept about the reaction pathway of the ester hydroboration reaction.<sup>12</sup> The plot  $\log_{10}(k_{obs})$  vs.  $\log_{10}[\text{catalyst}]$  (**Figure 3.4a**) displays a slope of 1.1, indicating an approximately first-order dependence with respect to catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  for the hydroboration of ester with HBpin, which also suggests a strong involvement of the catalyst in the rate-determining step.<sup>12a</sup> Upon increasing the initial concentration of the catalyst increases the rate of the reaction. A slope of 0.6 was attained from the plot of  $\log_{10}(k_{obs})$  vs.  $\log_{10}[\text{HBpin}]$  (**Figure 3.4b**), declaring a fractional order hydroboration reaction dependence on HBpin. This positive rate order with respect to HBpin would mean the HBpin reacts in more than one step by the ester hydroboration reaction.<sup>12b</sup> A slope of -0.027 was obtained from the plot of  $\log_{10}(k_{obs})$  vs.  $\log_{10}[\text{methylbenzoate}]$  (**Figure 3.4c**) demonstrating the rate of the hydroboration reaction was independent on the initial concentration of methylbenzoate and displayed a zeroeth order with respect to methylbenzoate.<sup>12a</sup>

The rate equation of the ester hydroboration with HBpin:

$$\text{rate} = k[\text{catalyst}]^{1.1}[\text{HBpin}]^{0.6}[\text{methylbenzoate}]^{-0.02} \quad (\text{Eq. 3.1})$$



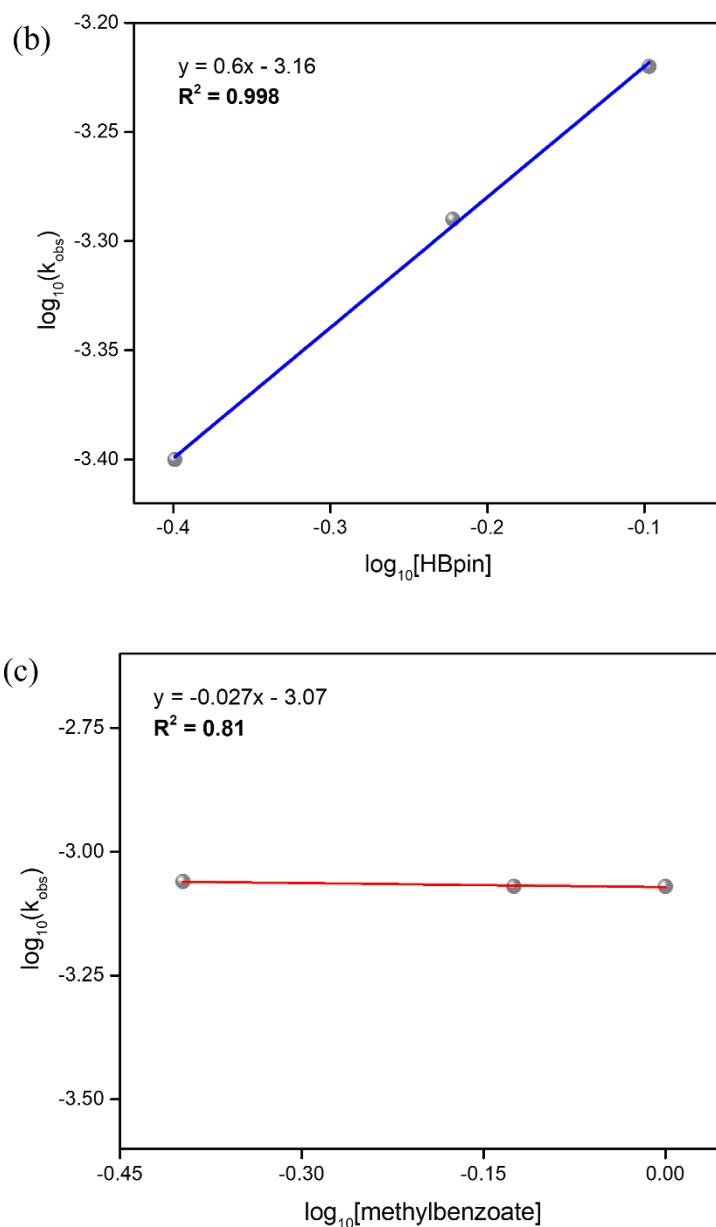
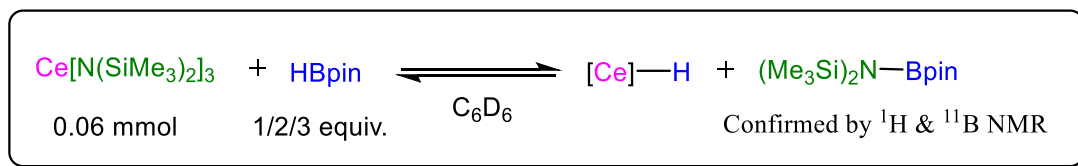


**Figure 3.4.** (a) Plot of  $\log_{10}(k_{obs})$  vs  $\log_{10}[\text{catalyst}]$ . (b) Plot of  $\log_{10}(k_{obs})$  vs  $\log_{10}[\text{HBpin}]$ . (c) Plot of  $\log_{10}(k_{obs})$  vs  $\log_{10}[\text{methylbenzoate}]$ . [Rates were determined *via* integration of product  $^1\text{H}$  NMR spectra relative to a mesitylene as an internal standard.]

### 3.3.4. Control experiments for mechanistic investigation

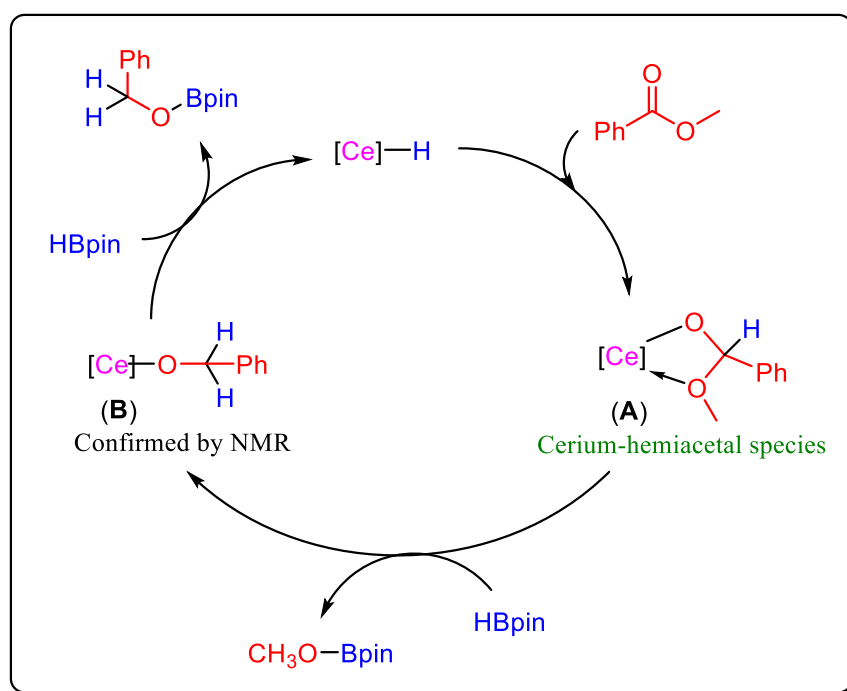
Upon treatment of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (1 equiv.) with HBpin (1/2/3 equiv.), formation of  $(\text{SiMe}_3)_2\text{N-Bpin}$  (**Scheme 3.3**) was observed.  $(\text{SiMe}_3)_2\text{N-Bpin}$  was characterized by a signal at  $\delta$  25.65 in the  $^{11}\text{B}$  NMR spectrum. We didn't notice any off-cycle products as reported by Marks and co-workers.<sup>7b</sup> Following this, we added methyl benzoate (1 equiv.) into the reaction mixture and recorded  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT-135 and HSQC NMR spectra, audited a new peak in  $^1\text{H}$

NMR spectrum at  $\delta$  5.18 ppm, which indicates the formation of  $[\text{Ce}]\text{OCH}_2\text{Ph}$  species (**B**) via the cerium-hemiacetal species (**A**) formation (**Scheme 3.4**).<sup>7a,7b,7e</sup> The HSQC NMR spectrum also displayed a 2D-correlation of the signal at  $\delta$  5.18 ppm ( $^1\text{H}$  NMR) with a signal at  $\delta$  66.46 ppm ( $^{13}\text{C}$  NMR), corresponding to the  $[\text{Ce}]\text{OCH}_2\text{Ph}$  species (**B**).



**Scheme 3.3.** Reversible reaction between  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and HBpin with cerium-hydride and  $(\text{Me}_3\text{Si})_2\text{N}-\text{Bpin}$ .

Furthermore, we commenced the investigation by taking methylbenzoate and  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (1:1 ratio) in  $\text{C}_6\text{D}_6$  and recorded  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, but did not observe any significant changes in the NMR spectra. However, when we treated methyl benzoate, HBpin and  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (1:2:1 ratio reaction, respectively) in  $\text{C}_6\text{D}_6$ , first the formation of  $[\text{Ce}]\text{OCH}_2\text{Ph}$  species (**B**) was observed, which was followed by the cerium-hemiacetal species (**A**), as indicated by  $^{13}\text{C}$ , DEPT-135 and HSQC NMR spectra. A sharp single peak at  $\delta$  25.60 ppm in the  $^{11}\text{B}$  NMR spectrum manifested  $(\text{SiMe}_3)_2\text{N}-\text{Bpin}$  as a side product.<sup>7b</sup> Based on these experiments, we proposed a plausible mechanistic cycle for the hydroboration of ester with HBpin by using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst (**Scheme 3.4**).



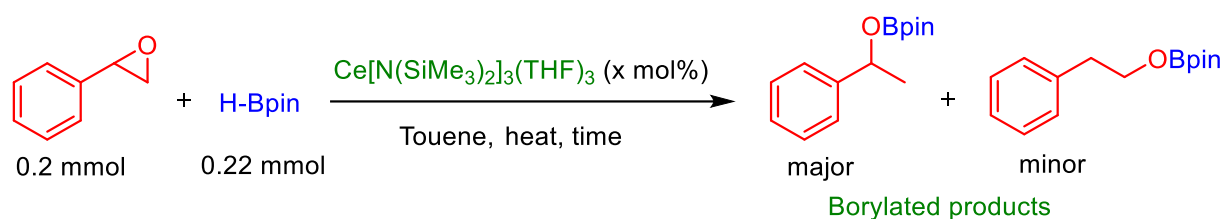
**Scheme 3.4.** Plausible mechanistic pathway for ester hydroboration reaction using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ .

### 3.4. Results and discussion of epoxide hydroboration reaction

#### 3.4.1. Reaction optimization

We started our examination by taking styrene (0.2 mmol) and 1.2 equivalent of HBpin with 1 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  in toluene. After that, we varied the mol% of the catalyst, reaction temperature and time and finally observed that 1 mol% of the catalyst at 60 °C temperature in 12 hours were the fertile reaction conditions for the epoxide hydroboration. We have also done one blank reaction without the catalyst, which led to only a trace yield of the product (**Entry 6; Table 3.6**). We have also performed a reaction in the presence of 20 mol% of TMEDA (tetramethylethylenediamine) to check the “*hidden BH<sub>3</sub> catalysis*”.<sup>10</sup> But we found an 87% yield of the borylated product, which denoted that there is a very less impact of BH<sub>3</sub> in the epoxide hydroboration reaction in the presence of the catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (**Entry 7; Table 3.6**).

**Table 3.6.** Reaction optimization of ester hydroboration reaction.



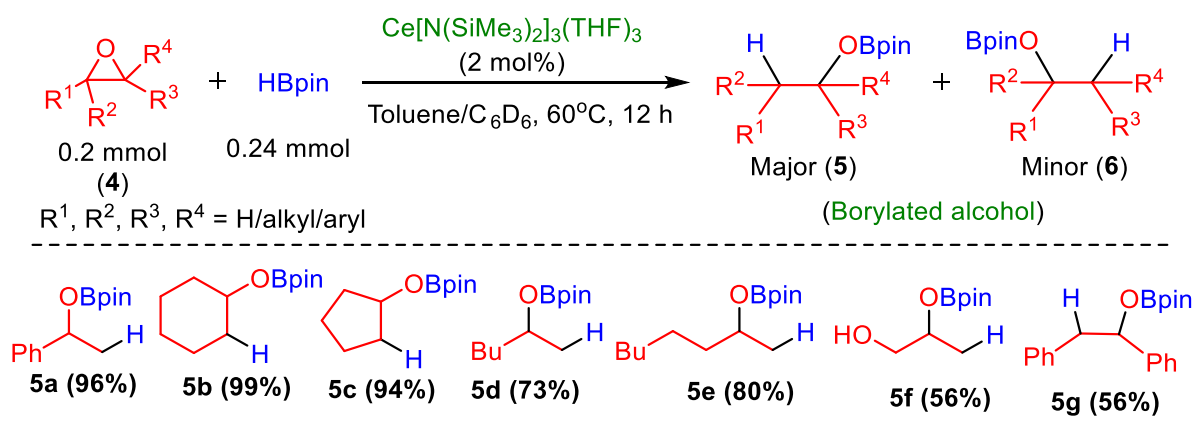
| Sl. No. | Catalyst                                               | Mol% | Temp. (°C) | Time (h) | Yield*(%) |
|---------|--------------------------------------------------------|------|------------|----------|-----------|
| 1.      | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ | 2    | 60         | 12       | 96        |
| 2.      | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ | 2    | 60         | 8        | 75        |
| 3.      | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ | 1    | 60         | 12       | 53        |
| 4.      | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ | 2    | rt         | 12       | 4         |
| 5.      | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ | 2    | 50         | 12       | 82        |
| 6.      | -                                                      | -    | 60         | 12       | trace     |

|    |                                                                                                                 |   |    |    |    |
|----|-----------------------------------------------------------------------------------------------------------------|---|----|----|----|
| 7. | Ce[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (THF) <sub>3</sub><br>(in presence of 20 mol%<br>of TMEDA) | 2 | 60 | 12 | 87 |
|----|-----------------------------------------------------------------------------------------------------------------|---|----|----|----|

[Yields were determined by integrating <sup>1</sup>H NMR spectra in the presence of an internal standard (mesitylene).]

### 3.4.2. Substrate scope of epoxide hydroboration

After the optimization of reaction conditions, we extended our research towards the different substrate scope to obtain ring-opening epoxides using HBpin. Good to excellent yields (>99%) were observed for the selective hydroboration of epoxide substrates (**Scheme 3.5**) and only mixture products were noticed for hydroboration of styrene oxide (90:10 ratio) under the same reaction conditions. Other substrate scope provided single-side C–O bond activation to afford branched selective hydroboration of epoxides. The cyclic substrates (**4b** and **4c**) exhibited comparatively higher yields compared to the acyclic substrates (**4d** and **4e**). However, substrate **4f** afforded less yield (56%) due to the presence of electron-withdrawing hydroxyl group (-OH).



**Scheme 3.5.** Substrate scope of catalytic hydroboration of epoxides with HBpin using catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . [Yields were determined by the integration of the corresponding <sup>1</sup>H NMR spectra normalized on the internal standard (mesitylene)]

#### Analytical data of borylated alcohols:

**5a:** <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.39–7.37 (m, 2H, Ph), 7.34–7.30 (m, 2H, Ph), 7.24–7.22 (m, 1H, Ph), 6.81 (s, 3H, mesitylene), 5.29–5.24 (q, 1H,  $\text{PhCH}(\text{OBpin})\text{CH}_3$ ), 4.09–4.05 (t, 2H,  $\text{CH}_2\text{OBpin}$ ), 2.91–2.87 (t, 2H,  $\text{CH}_2\text{Ph}$ ), 2.29 (s, 9H, mesitylene), 1.52–1.50 (d, 3H,  $\text{CH}_3$ ),

1.25 (s, 12H, OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  144.7 (Ph), 137.8 (mesitylene), 128.3 (Ph), 127.2 (Ph), 127.0 (mesitylene), 125.4 (Ph), 82.8 (OBpin), 72.7 (PhCH(OBpin)CH<sub>3</sub>), 25.5 (CH<sub>3</sub>), 24.6 (OBpin), 21.3 (mesitylene) ppm.

**5b:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.81 (s, 3H, mesitylene), 4.03-3.99 (m, 1H, CH(OBpin)), 2.28 (s, 9H, mesitylene), 1.86-1.84 (m, 2H, CH<sub>2</sub>), 1.75-1.72 (m, 2H, CH<sub>2</sub>), 1.53-1.50 (m, 2H, CH<sub>2</sub>), 1.40-1.32 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 1.26 (s, 12H, OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (mesitylene), 127.0 (mesitylene), 82.5 (OBpin), 72.7 (CHOBpin), 34.3 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>), 24.6 (OBpin), 23.9 (CH<sub>2</sub>), 21.2 (mesitylene) ppm.

**5c:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.81 (s, 3H, mesitylene), 3.85-3.82 (m, 1H, CH(OBpin)), 2.28 (s, 9H, mesitylene), 1.76 (b, 2H, CH<sub>2</sub>), 1.60-1.54 (m, 2H, CH<sub>2</sub>), 1.44-1.33 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 1.26 (s, 12H, OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (mesitylene), 127.0 (mesitylene), 82.9 (OBpin), 65.1 (CHOBpin), 34.8 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 24.7 (OBpin), 23.2 (CH<sub>2</sub>), 21.3 (mesitylene) ppm.

**5d:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.82 (s, 3H, mesitylene), 4.22-4.14 (m, 1H, CH(OBpin)), 2.30 (s, 9H, mesitylene), 1.36-1.31 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 1.29 (b, 2H, CH<sub>2</sub>), 1.27 (s, 12H, OBpin), 1.22-1.20 (d, 3H, CH(OBpin)CH<sub>3</sub>), 0.93-0.90 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (mesitylene), 127.0 (mesitylene), 82.5 (OBpin), 71.0 (CHOBpin), 38.0 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 24.7 (CH<sub>2</sub>), 24.6 (OBpin), 22.7 (CH<sub>3</sub>), 21.3 (mesitylene), 14.2 (CH<sub>3</sub>) ppm.

**5e:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.82 (s, 3H, mesitylene), 4.20-4.16 (m, 1H, CH(OBpin)), 2.30 (s, 9H, mesitylene), 1.57-1.49 (m, 2H, CH<sub>2</sub>), 1.45-1.38 (m, 2H, CH<sub>2</sub>), 1.32-1.29 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.27 (s, 12H, OBpin), 1.21-1.20 (d, 3H, CH(OBpin)CH<sub>3</sub>), 0.92-0.89 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (mesitylene), 127.0 (mesitylene), 82.5 (OBpin), 71.0 (CHOBpin), 38.3 (CH<sub>2</sub>), 32.0 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 24.7 (CH<sub>2</sub>), 24.6 (OBpin), 22.7 (CH<sub>3</sub>), 21.3 (mesitylene), 14.2 (CH<sub>3</sub>) ppm.

**5f:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.33-7.29 (m, 2H, Ph), 7.17-7.16 (m, 8H, Ph), 6.80 (s, 3H, mesitylene), 5.30-5.27 (t, 1H, PhCH(OBpin)), 3.01-3.00 (d, 2H, PhCH<sub>2</sub>), 2.28 (s, 9H, mesitylene), 1.27 (s, 12H, OBpin) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  134.5 (Ph), 129.6 (Ph), 128.6 (Ph), 128.5 (Ph), 127.9 (Ph), 127.6 (Ph), 127.0 (Ph), 126.0 (Ph), 83.3 (OBpin), 75.5 (PhCHOBpin), 46.2 (CH<sub>2</sub>), 24.7 (OBpin) ppm.

**5g:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.82 (s, 3H, *mesitylene*), 4.35-4.28 (m, 1H,  $\text{CH}(\text{OBpin})$ ), 3.54-3.51 (t, 2H,  $\text{CH}_2\text{OBpin}$ ), 2.29 (s, 9H, *mesitylene*), 1.28 (s, 12H, *OBpin*), 1.26 (s, 12H, *OBpin*), 1.20-1.18 (d, 3H,  $\text{CH}(\text{OBpin})\text{CH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.7 (*mesitylene*), 127.0 (*mesitylene*), 83.1 (*OBpin*), 82.8 (*OBpin*), 70.4 ( $\text{CHOBpin}$ ), 69.2 ( $\text{BpinOCH}_2$ ), 24.7 (*OBpin*), 24.6 (*OBpin*), 21.3 (*mesitylene*), 18.6 ( $\text{CH}_3$ ) ppm.

### 3.4.3. Kinetic studies

The kinetic experiments of the epoxide hydroboration reaction were performed by taking styrene oxide and cyclohexene oxide with HBpin in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. The reaction kinetic data ( $^1\text{H}$  NMR spectra) were recorded after every 60 minutes time interval for 5 hours. Only the zeroth-order plot ( $[\text{product}]$  vs time) was linear with both the substrates ( $R^2 = 0.992$  for styrene oxide and  $R^2 = 0.997$  for cyclohexene oxide) (**Figure 3.5** and **Figure 3.6**), indicating that the epoxide hydroboration reaction in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  follows the zeroth-order reaction.<sup>7b</sup>

**For styrene oxide:** We have taken 0.4 M of styrene oxide and 0.88 M of HBpin in an NMR tube and also added 0.4 M of *mesitylene* as an internal standard in solvent  $\text{C}_6\text{D}_6$  (0.5 mL). After that, the NMR tube was kept in heating at 60 °C and recorded the  $^1\text{H}$  NMR (400 MHz, 298 K) in every 60 min interval. Then, we calculated the yield of the product by integration of the *mesitylene* peak and converted the yield into molar concentration.

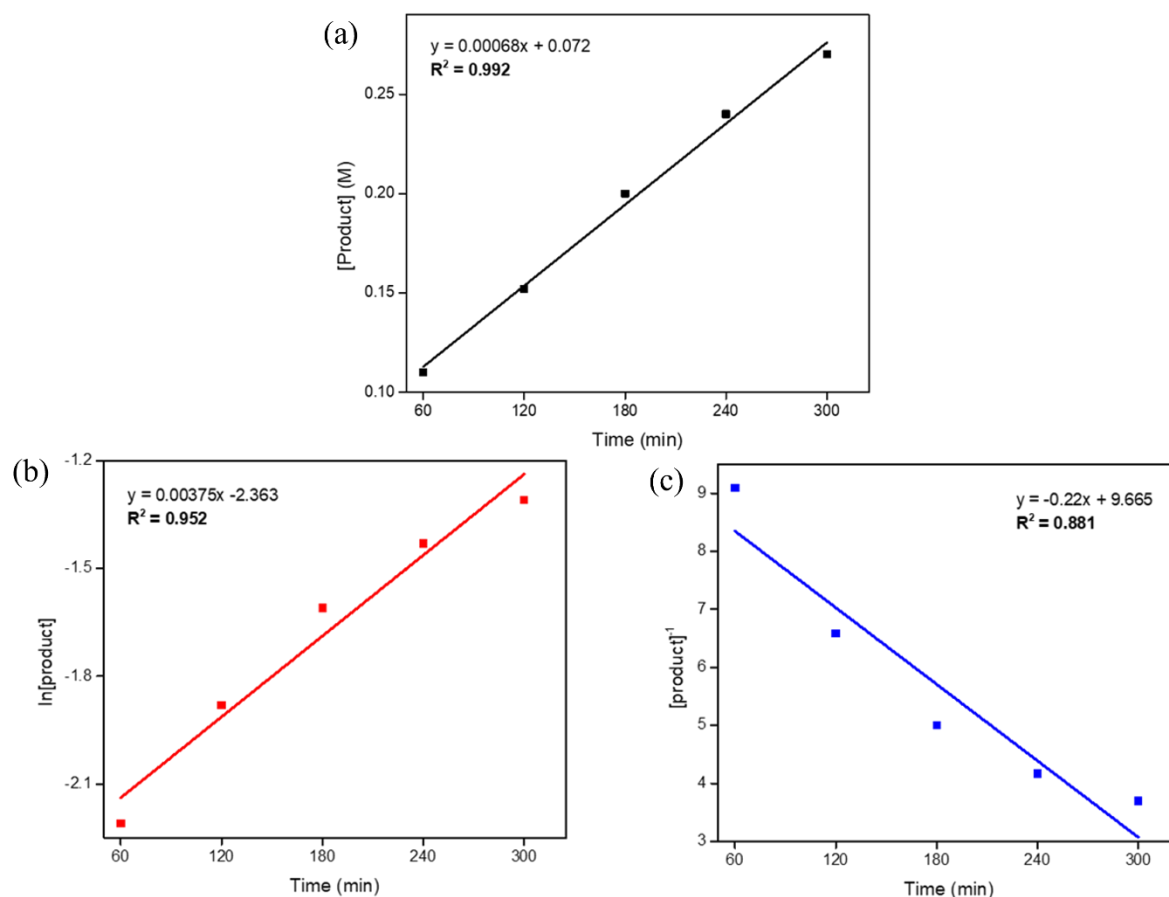


**Figure 3.5.** (a) Plot [product] vs. time with  $R^2 = 0.992$ . Indicating the hydroboration of epoxide with HBpin follows *zeroth-order* reaction. (b) Plot  $\ln[\text{product}]$  vs. time with  $R^2 = 0.952$ . Indicating the hydroboration of epoxide with HBpin not follows *first-order* reaction. (c) Plot  $[\text{product}]^{-1}$  vs. time with  $R^2 = 0.881$ . Indicating the hydroboration of epoxide with HBpin not follows *second-order* reaction.<sup>7b</sup>

**For cyclohexene oxide:** We have taken 0.4 M of cyclohexene oxide and 0.88 M of HBpin in an NMR tube and also added 0.4 M of mesitylene as an internal standard in solvent  $\text{C}_6\text{D}_6$  (0.5 mL). After that, the NMR tube was kept in heating at 60 °C and recorded the  $^1\text{H}$  NMR (400 MHz, 298 K) in every 60 min interval. Then, we calculated the yield of the product by integration of the mesitylene peak and converted the yield into molar concentration.

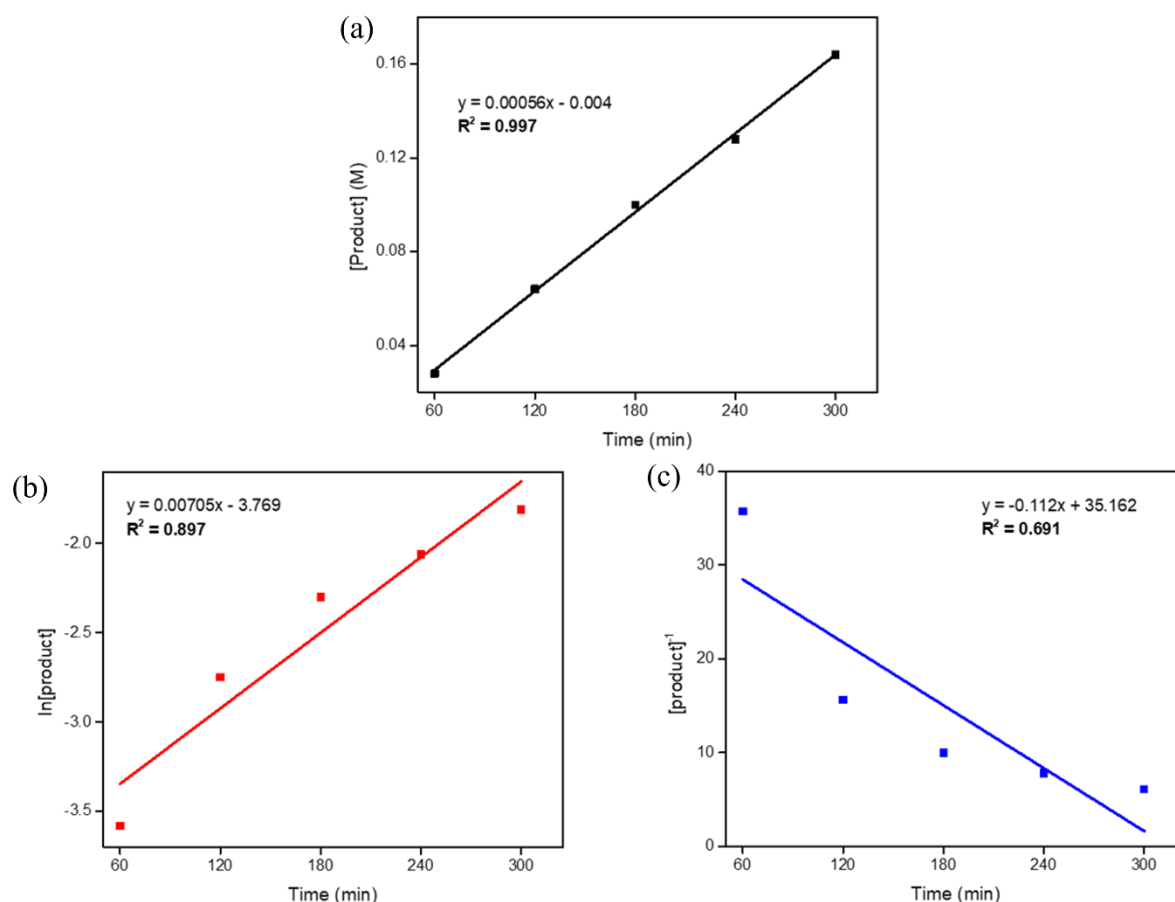


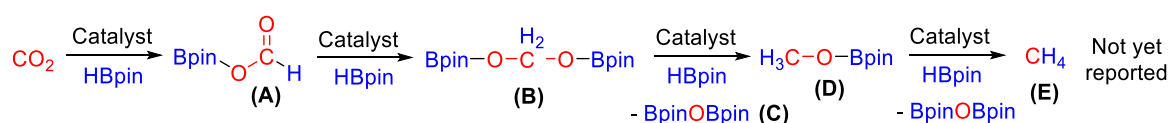
**Figure 3.6.** (a) Plot [product] vs. time with  $R^2 = 0.997$ . Indicating the hydroboration of epoxide with HBpin follows *zeroth-order* reaction. (b) Plot  $\ln[\text{product}]$  vs. time with  $R^2 = 0.897$ . Indicating the hydroboration of epoxide with HBpin not follows *first-order* reaction. (c) Plot  $[\text{product}]^{-1}$  vs. time with  $R^2 = 0.691$ . Indicating the hydroboration of epoxide with HBpin not follows *second-order* reaction.<sup>7b</sup>

### 3.4.4. Control experiments for mechanistic investigations

We bestowed our effort to unveil the reaction mechanistic pathway of the reduction of epoxide-catalysed by the  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with HBpin by putting equimolar reaction between styrene oxide, HBpin and  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , but didn't observe any cabbalistic shift in  $^1\text{H}$  as well as  $^{13}\text{C}$  NMR spectra. Hence, we are unable to demonstrate a plausible reaction mechanistic pathway of the reduction of epoxide with HBpin using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst.

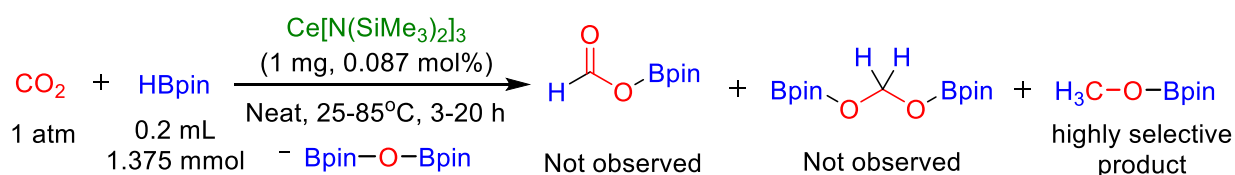
### 3.5. Results and discussion of CO<sub>2</sub> hydroboration

The hydroboration process is an infant in the field of the most important and most challenging CO<sub>2</sub> reduction process.<sup>13</sup> Transition metal-catalysed hydroboration of CO<sub>2</sub> is more explored as compared to the main-group catalysed CO<sub>2</sub> hydroboration reaction, but the lanthanide-catalysed hydroboration of CO<sub>2</sub> is not known in the literature till to date. Herein, we have demonstrated the highly selective hydroboration reaction of CO<sub>2</sub> towards the borylated methanol. This fresh methodology of the CO<sub>2</sub> reduction with HBpin in the presence of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst selectively led to the formation of only borylated methanol, which is one of the most valuable feedstocks of CO<sub>2</sub> reduction.<sup>14</sup>



**Scheme 3.6.** Stepwise CO<sub>2</sub> hydroboration with HBpin and expected products.

The stepwise hydroboration of CO<sub>2</sub> with HBpin pay produces borylated formic acid, borylated methanediol, borylated methanol and methane (yet not reported), respectively (**Scheme 3.6**).<sup>15</sup> Selectivity makes a catalyst extraordinary by producing a specific product. Here, Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-catalysed CO<sub>2</sub> reduction with HBpin afforded only borylated methanol (**Scheme 3.7**). The hydroboration of CO<sub>2</sub> with HBpin was taken place in the presence of 0.087 mol% (1 mg) of the Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> as a catalyst, which delivered a 99% yield of borylated methanol at room temperature in 24 hours.



**Scheme 3.7.** Selective borylated methanol synthesis by CO<sub>2</sub> hydroboration with HBpin using catalyst Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>. [Yields were determined by the integration of the corresponding <sup>1</sup>H NMR spectra normalized on the internal standard (mesitylene).]

The Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-catalysed hydroboration of CO<sub>2</sub> with HBpin was accomplished at various reaction temperatures (25 °C, 45 °C, 65 °C and 85 °C) to afford the percentage yield of the borylated methanol and turn-over frequency (TOF) (**Figure 3.7**). It was well-acquainted that the percentage yield and TOF of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-catalysed CO<sub>2</sub> reduction with HBpin were immensely effective on the reaction temperature, which gradually increased upon increasing

the reaction temperature of CO<sub>2</sub> hydroboration reaction (yield<sup>25°C</sup> = >99% in 20 hours, yield<sup>45°C</sup> = >99% in 12 hours, yield<sup>65°C</sup> = >99% in 8 hours and yield<sup>85°C</sup> = >99% in 3 hours). The turn-over number (TON) of the hydroboration of CO<sub>2</sub> to borylated methanol is 1146. However, the TOF of the hydroboration of CO<sub>2</sub> varies depending on both the reaction time and the reaction temperature. The reaction time rendering a very emergent role in maximizing the formation of borylated methanol product (**Figure 3.8**). The TOF (h<sup>-1</sup>) vs. Temperature (°C) plot (**Figure 3.7**) elucidates the influence of both the reaction temperature and the reaction time on Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-catalysed CO<sub>2</sub> reduction with HBpin to borylated methanol product.<sup>16</sup>

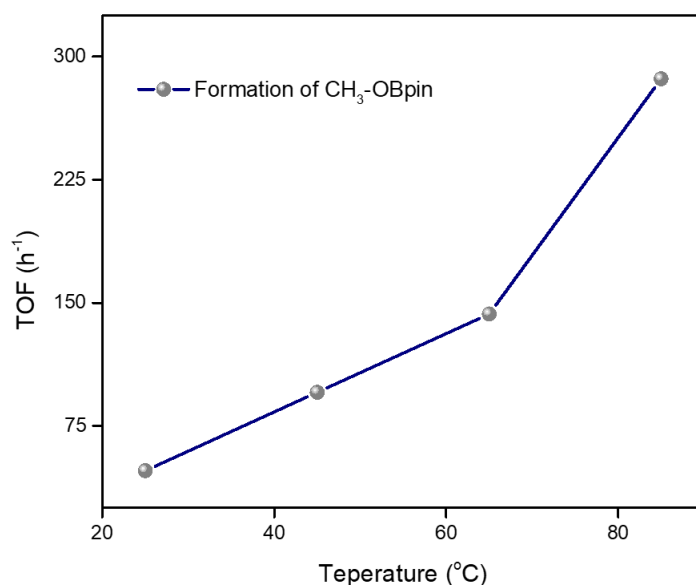


**Figure 3.7.** Effect of temperature on TOF (h<sup>-1</sup>) to the formation of CH<sub>3</sub>-OBpin by CO<sub>2</sub> reduction with HBpin. [The TOF was calculated in units of h<sup>-1</sup> according to the equation  $\text{TOF} = (n_{\text{product}}/n_{\text{catalyst}}) \times (1/t)$ , where  $n_{\text{product}}$  is the number of moles of the corresponding product,  $n_{\text{catalyst}}$  is the number of moles of catalyst and  $t$  is the reaction time in hours.]<sup>16</sup>

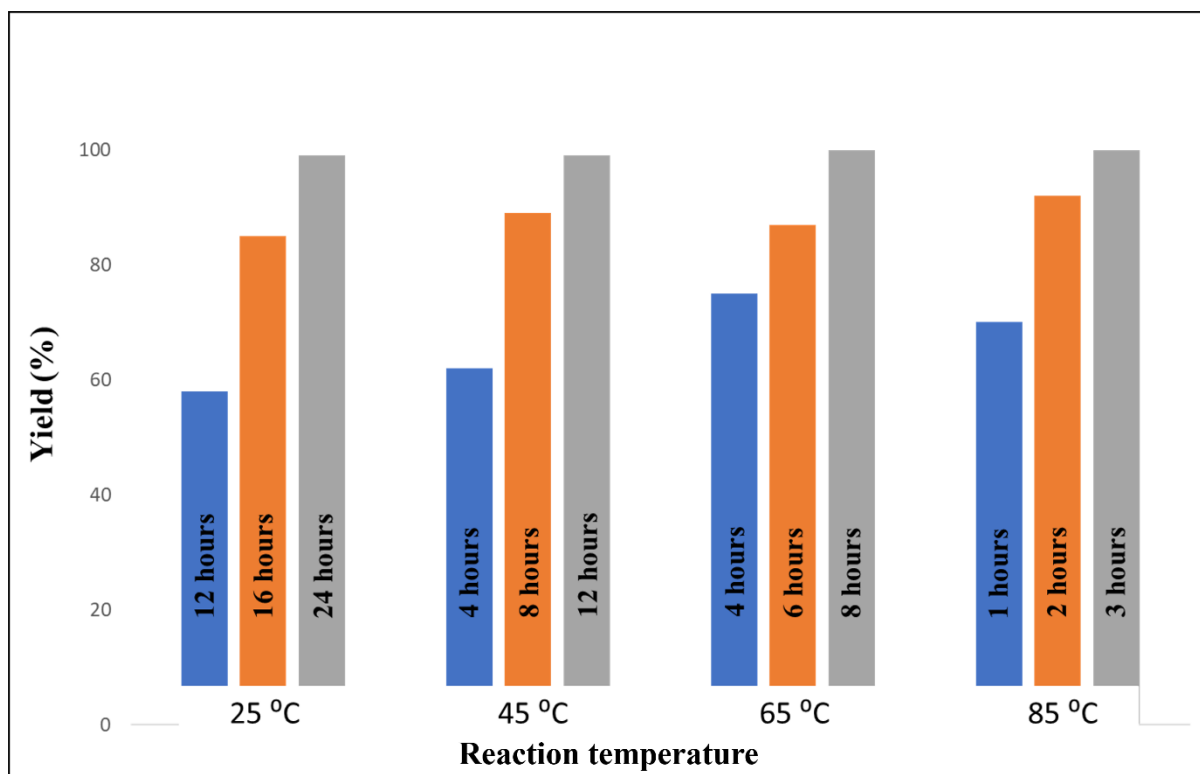


**Figure 3.8.** Bar plot for temperature dependent CO<sub>2</sub> conversion to borylated methanol.

### 3.6. Conclusion

In this report, we have demonstrated the catalytic activity of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  towards the reduction of esters, epoxides and CO<sub>2</sub> under mild reaction conditions. Previously, Marks and co-workers introduced homoleptic lanthanum amide  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ -catalysed hydroboration of ester only, whereas the hydroboration of esters and epoxides was reported by Sadow and co-workers by using homoleptic tris(alkyl) lanthanum  $\text{La}[\text{C}(\text{SiHMe}_2)_3]_3$  as a catalyst. Herein, first time we have explored the catalytic efficiency of the lanthanide amide complex  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  for the reduction of CO<sub>2</sub> with HBpin to borylated methanol synthesis. The kinetic experiments elaborated the order of reaction, where demonstrated first-order dependence with respect to catalyst with a slope of 1.1 and a slope of 0.6 described a fractional order dependence with respect to HBpin and the rate of the hydroboration reaction was independent on the initial concentration of the ester, shown *zeroth*-order reaction with respect to ester. A plausible mechanistic pathway was revealed for the hydroboration of esters using  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst, based on the kinetic studies, control experiments and the reported literature. We demonstrated an affordable and riskless synthetic methodology

for the selective conversion of CO<sub>2</sub> to methanol using HBpin (instead of risky H<sub>2</sub> gas) and verily available catalyst Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>. The effect of temperature on TOF (h<sup>-1</sup>) for the CO<sub>2</sub> reduction with HBpin to borylated methanol was investigated, where maximum TOF was observed ~382 h<sup>-1</sup> at 85°C reaction temperature. Overall, Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> behaves as an efficient catalyst for the C–O activation under the mild reaction conditions.

### 3.7. NMR spectra

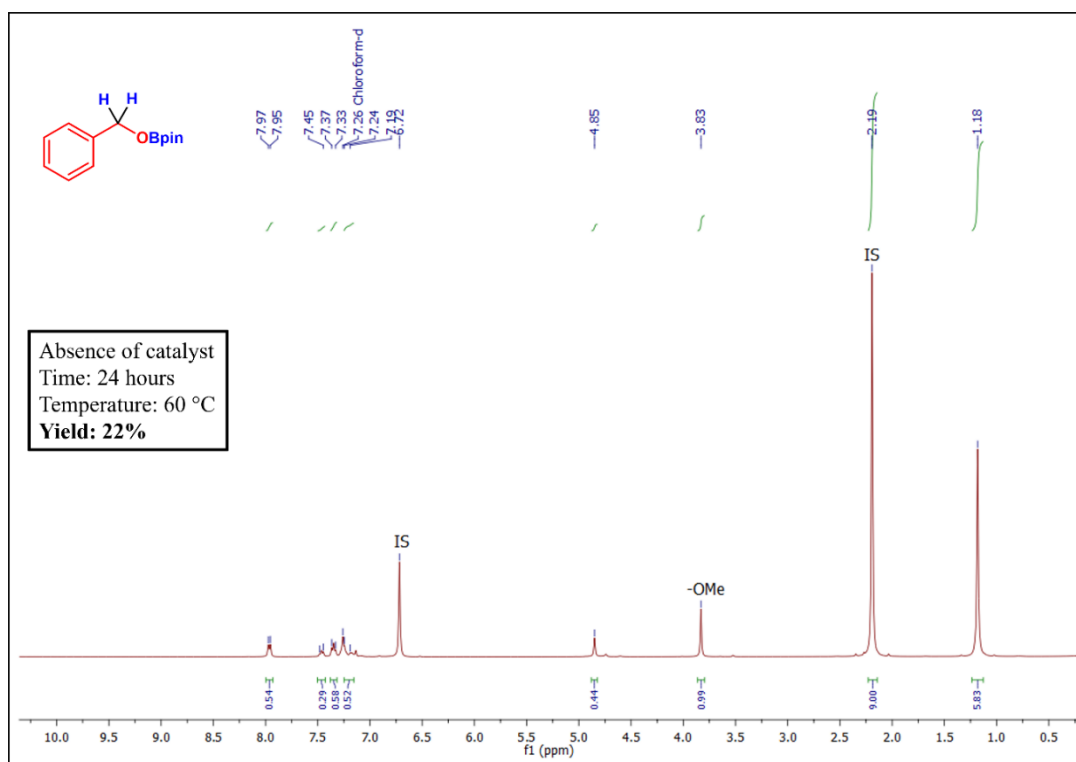


**Figure 3.9.** <sup>1</sup>H NMR (400 MHz) spectrum for hydroboration of methylbenzoate with 2.2 equivalent of HBpin in toluene. [Solvent: CDCl<sub>3</sub>, IS: Internal standard as mesitylene]

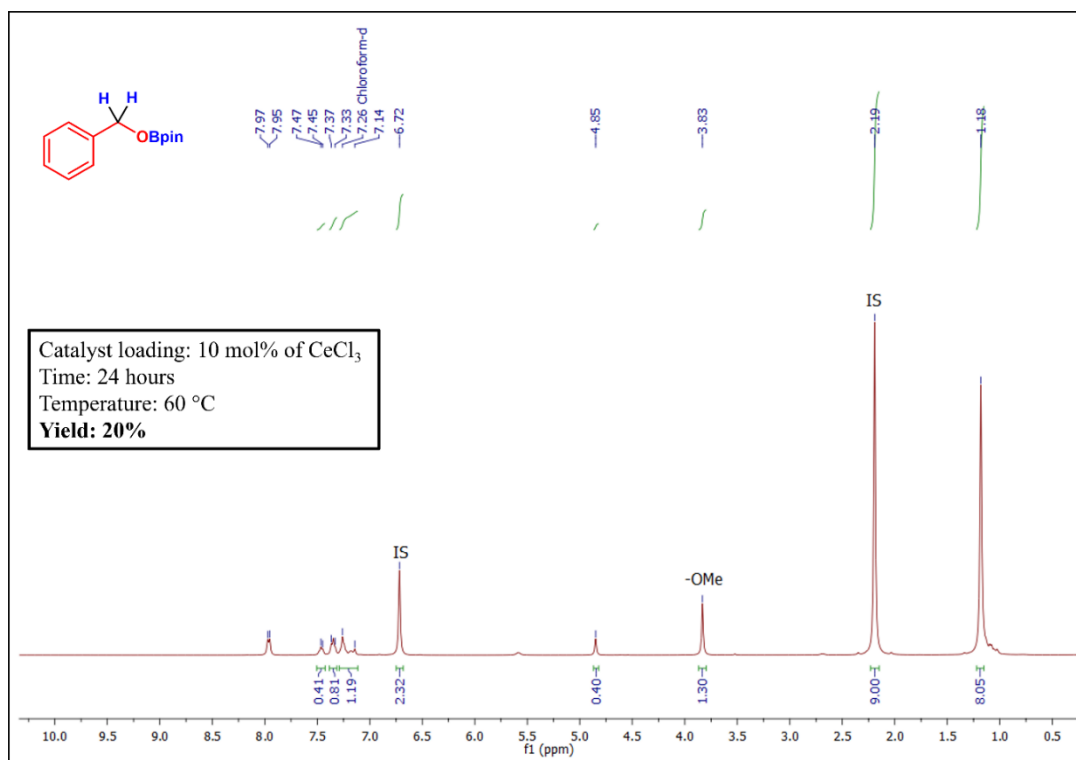


**Figure 3.10.** <sup>1</sup>H NMR (400 MHz) spectrum for hydroboration of methylbenzoate with 2.2 equivalent of HBpin in toluene. [Solvent:  $\text{CDCl}_3$ , IS: Internal standard as mesitylene]

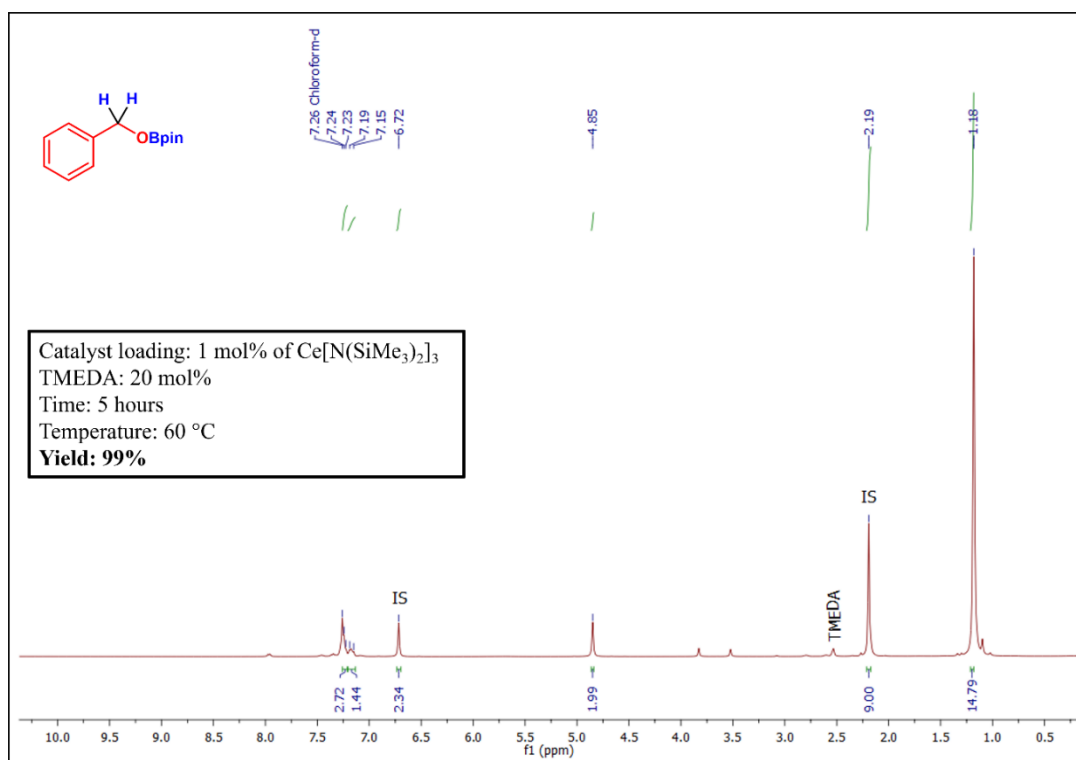


**Figure 3.11.**  $^1\text{H}$  NMR (400 MHz) spectrum for hydroboration of methylbenzoate with 2.2 equivalent of HBpin in toluene in presence of 20 mol% TMEDA. [Solvent:  $\text{CDCl}_3$ , IS: Internal standard as mesitylene]

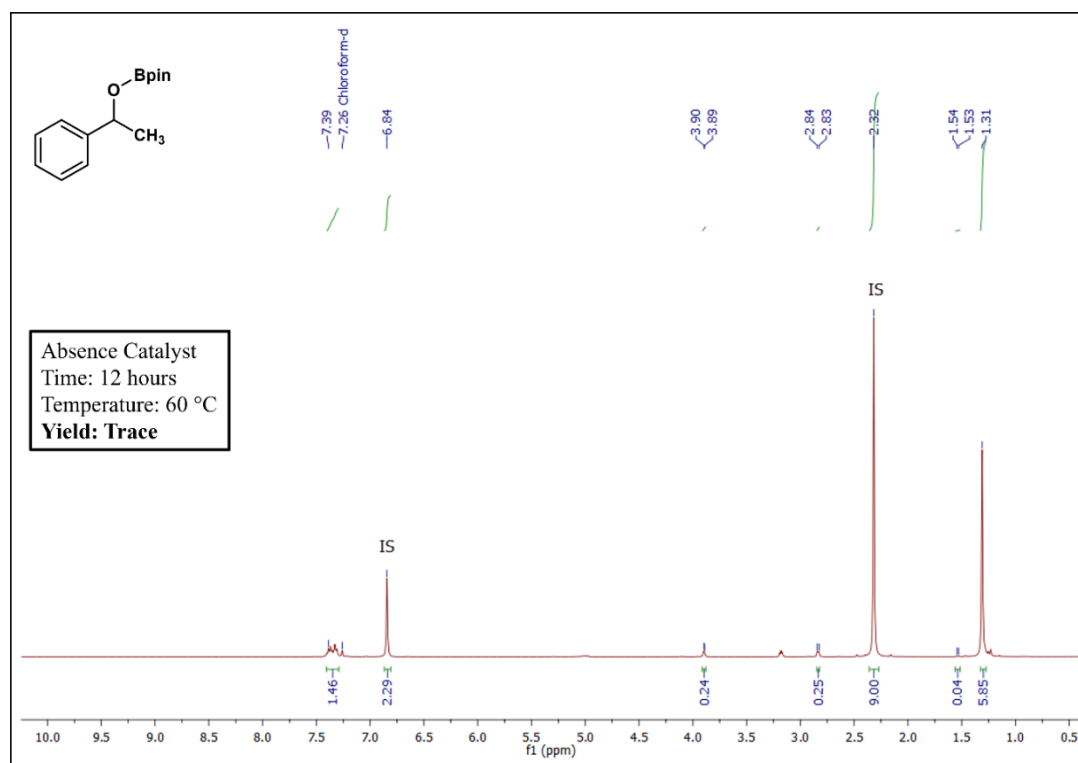


**Figure 3.12.**  $^1\text{H}$  NMR (400 MHz) spectrum for hydroboration of styrene oxide with 1.2 equivalent of HBpin in toluene. [Solvent:  $\text{CDCl}_3$ , IS: Internal standard as mesitylene]

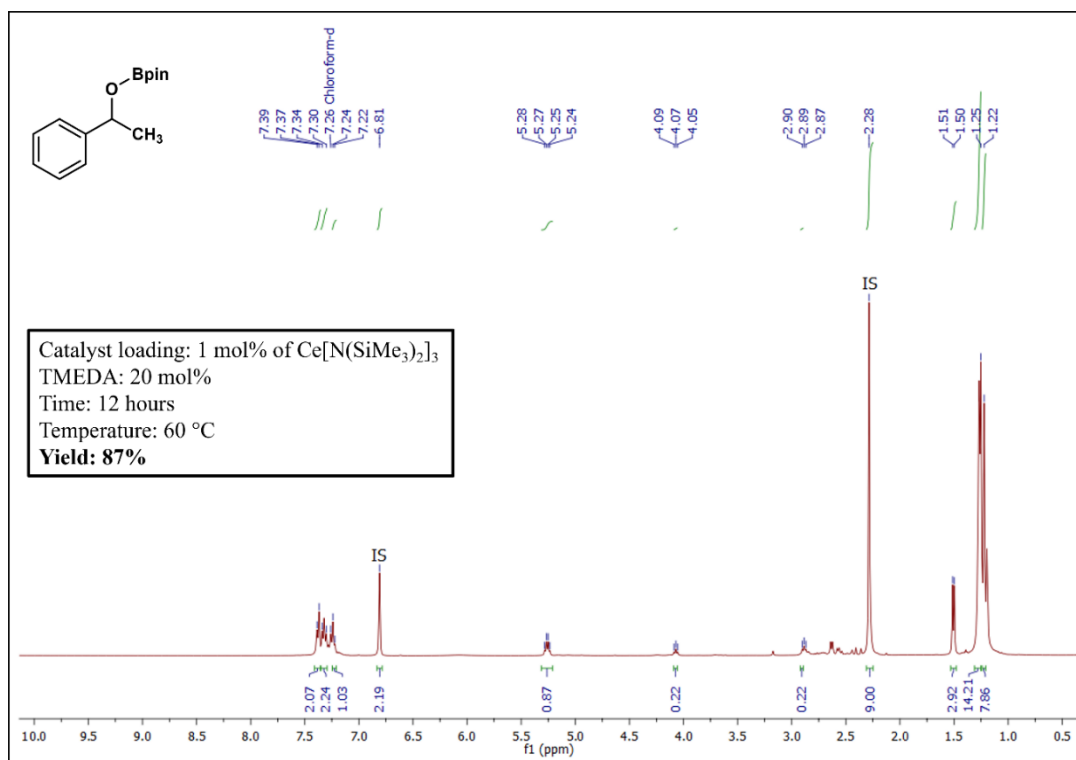


**Figure 3.13.**  $^1\text{H}$  NMR (400 MHz) spectrum for hydroboration of styrene oxide with 1.2 equivalent of HBpin in toluene in presence of 20 mol% of TMEDA. [Solvent:  $\text{CDCl}_3$ , IS: Internal standard as mesitylene]

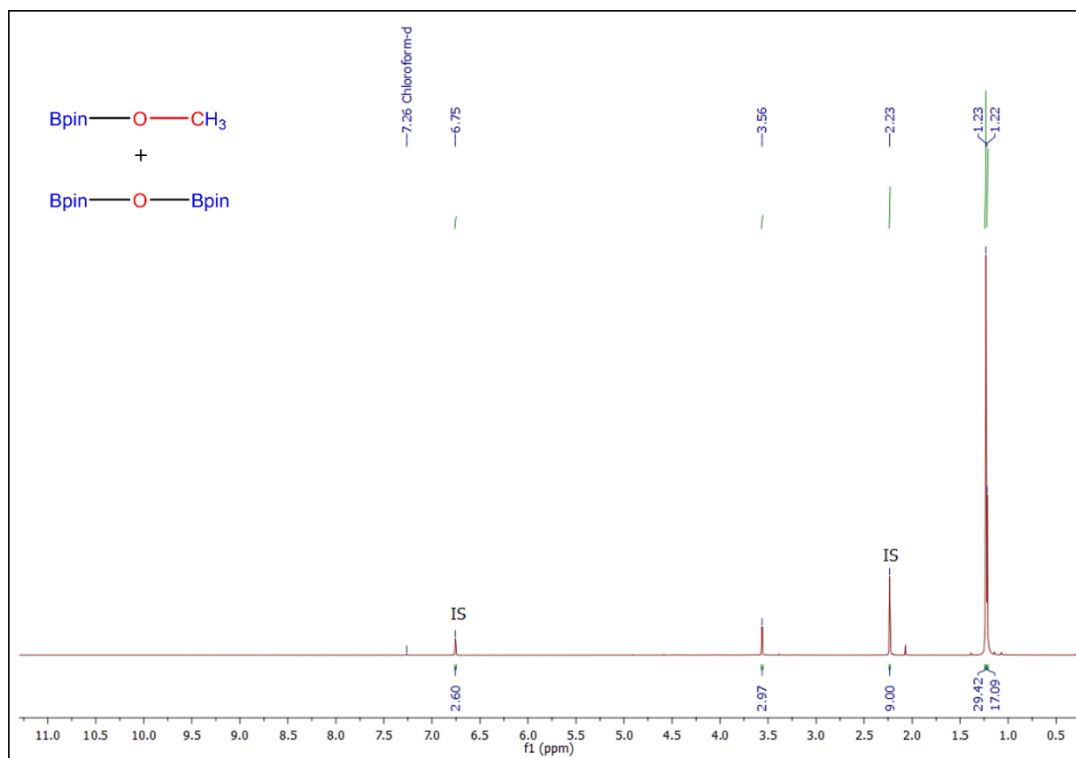


**Figure 3.14.**  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ , 298 K] spectrum of hydroboration of  $\text{CO}_2$  at 25  $^\circ\text{C}$  temperature in 24 hours reaction time in presence of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . The peak at 3.56 ppm is corresponding to  $\text{CH}_3$  of borylated methanol.

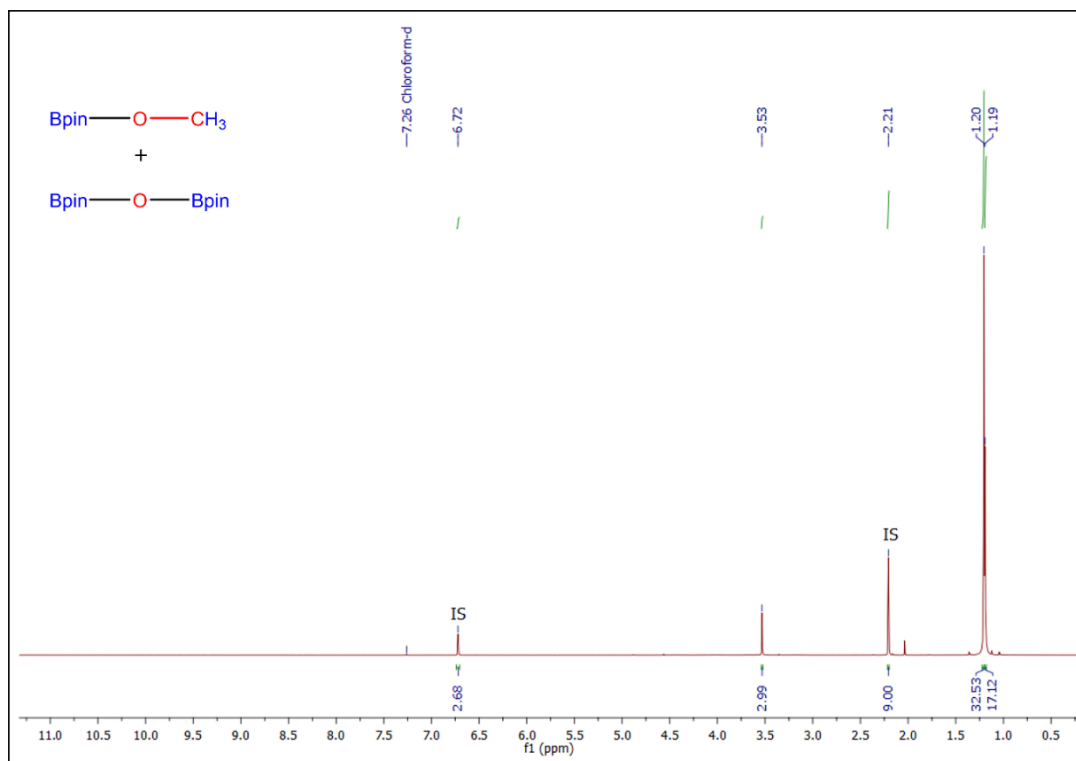


**Figure 3.15.**  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ , 298 K] spectrum of hydroboration of  $\text{CO}_2$  at 45  $^\circ\text{C}$  temperature in 12 hours reaction time in presence of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . The peak at 3.53 ppm is corresponding to  $\text{CH}_3$  of borylated methanol.

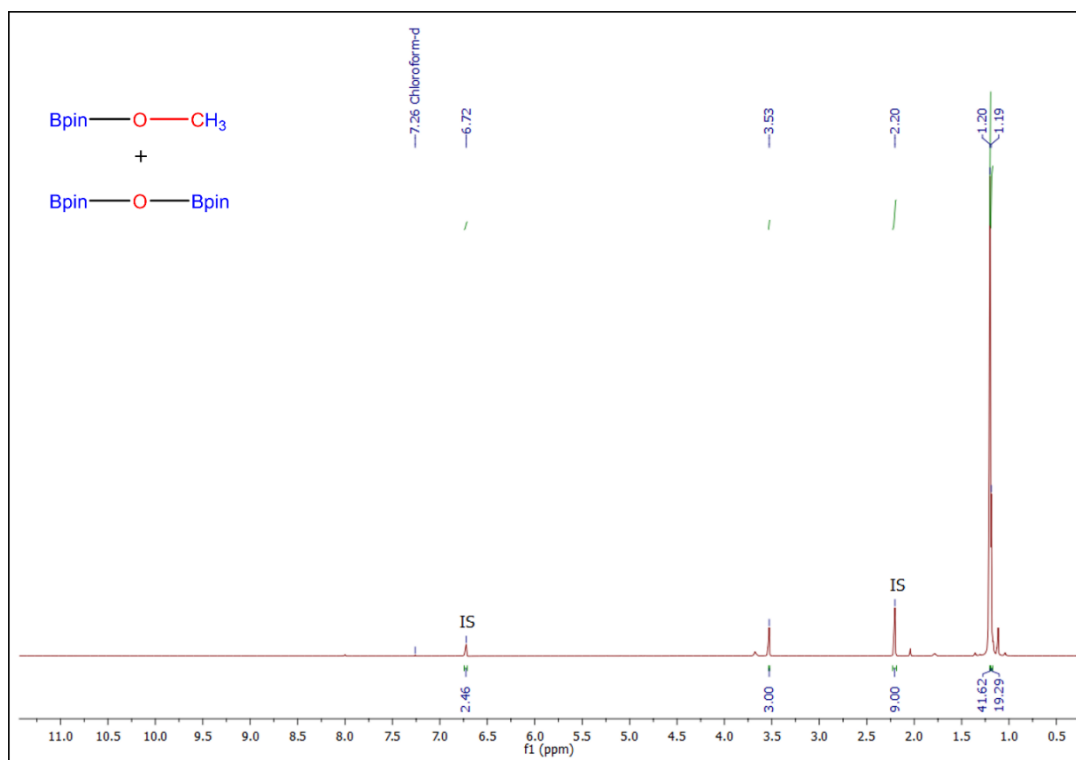


**Figure 3.16.**  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ , 298 K] spectrum of hydroboration of  $\text{CO}_2$  at 65 °C temperature in 8 hours reaction time in presence of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . The peak at 3.53 ppm is corresponding to  $\text{CH}_3$  of borylated methanol.

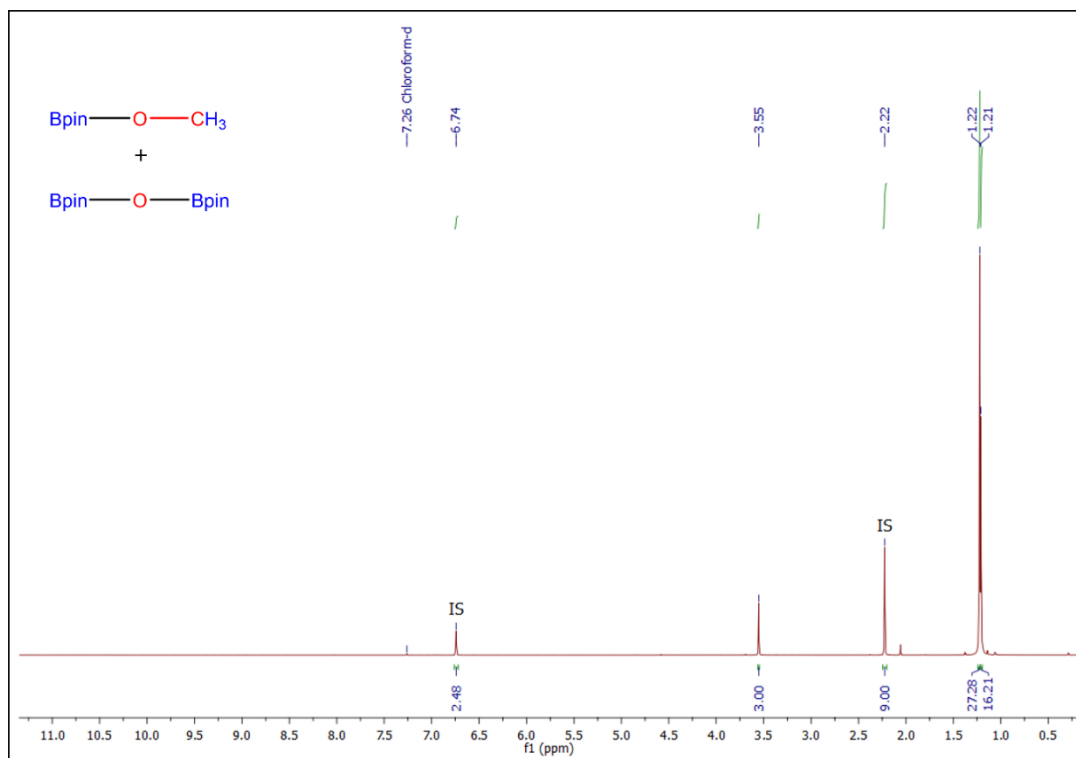


**Figure 3.17.**  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ , 298 K] spectrum of hydroboration of  $\text{CO}_2$  at 85  $^\circ\text{C}$  temperature in 3 hours reaction time in presence of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . The peak at 3.55 ppm is corresponding to  $\text{CH}_3$  of borylated methanol.

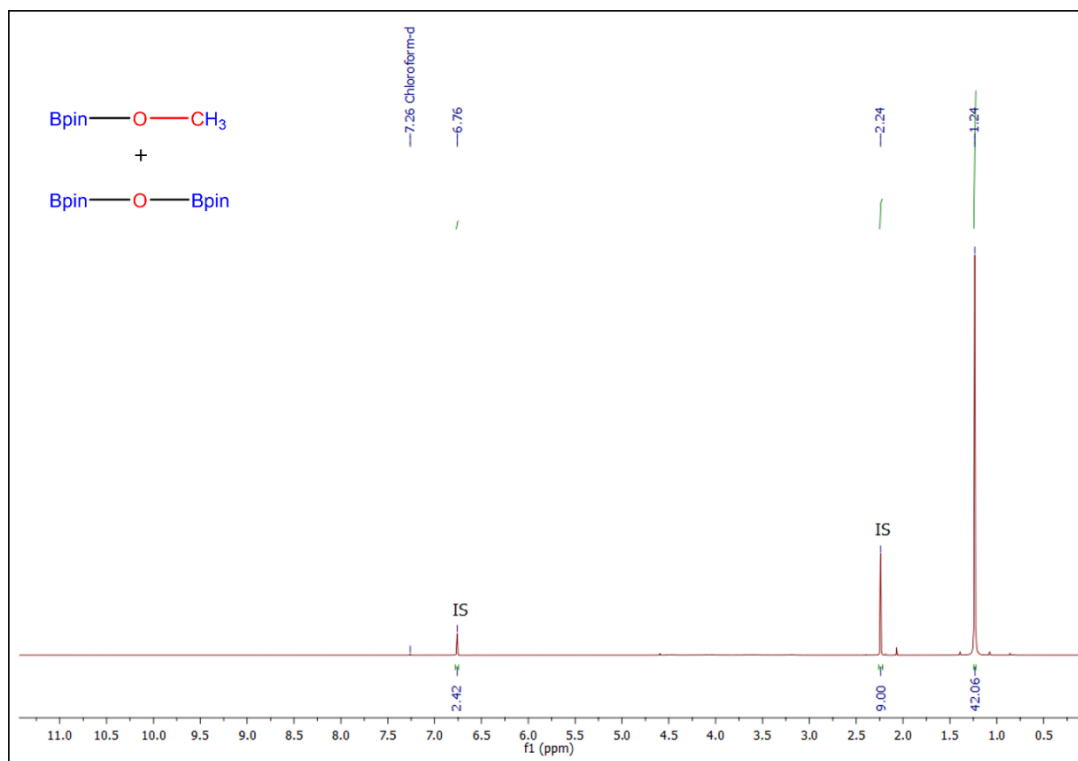


**Figure 3.18.**  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ , 298 K] spectrum of hydroboration of  $\text{CO}_2$  at 85  $^\circ\text{C}$  temperature in 3 hours reaction time in absence of catalyst.

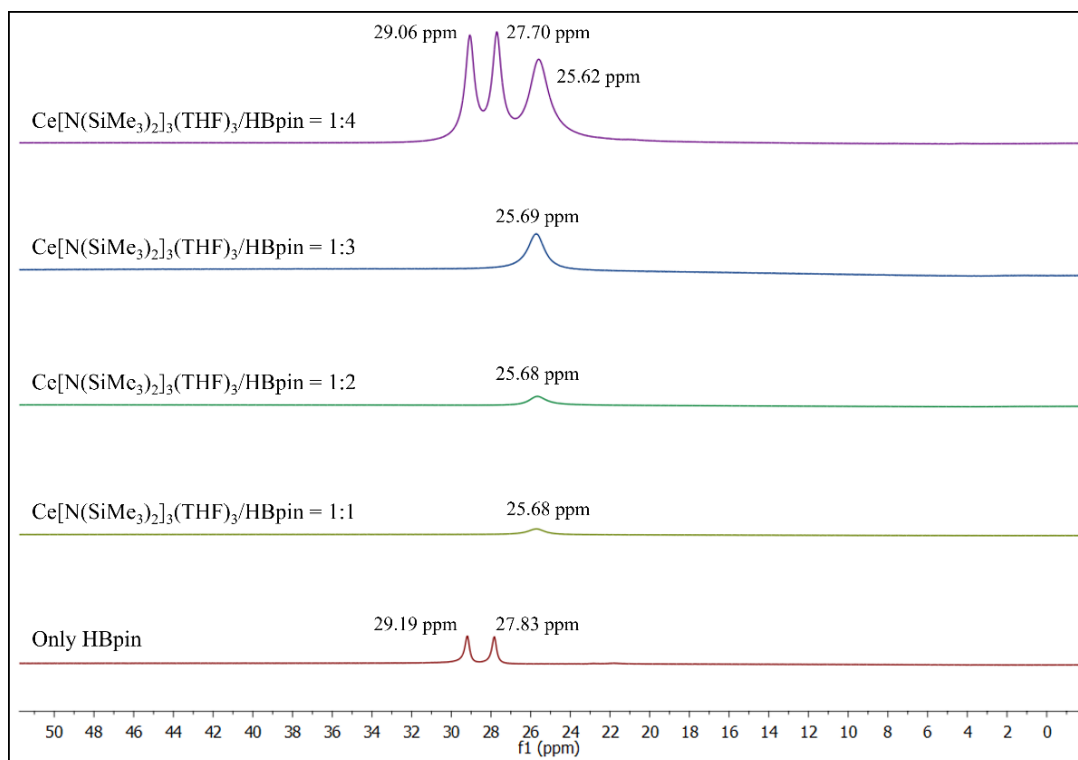


**Figure 3.19.**  $^{11}\text{B}$  NMR spectra of the reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with different equivalent of HBpin.

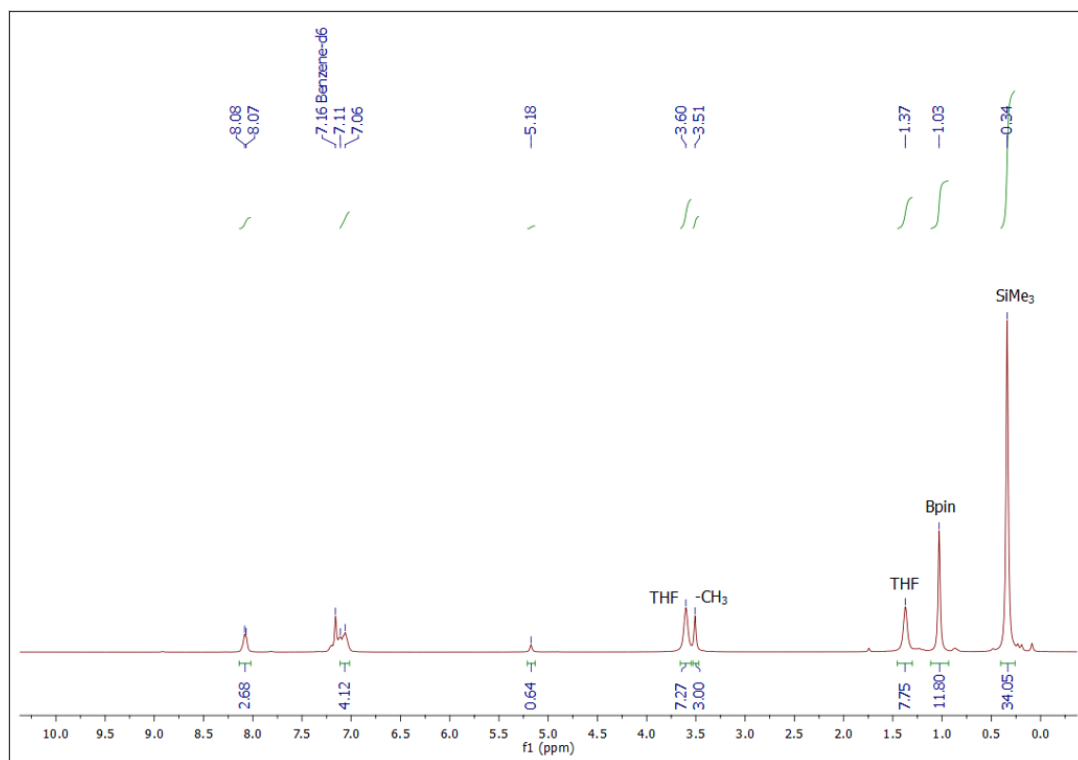


**Figure 3.20.**  $^1\text{H}$  NMR [400 MHz,  $\text{C}_6\text{D}_6$ , 298 K] spectrum of 1:2:1 ratio reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , HBpin and methylbenzoate.

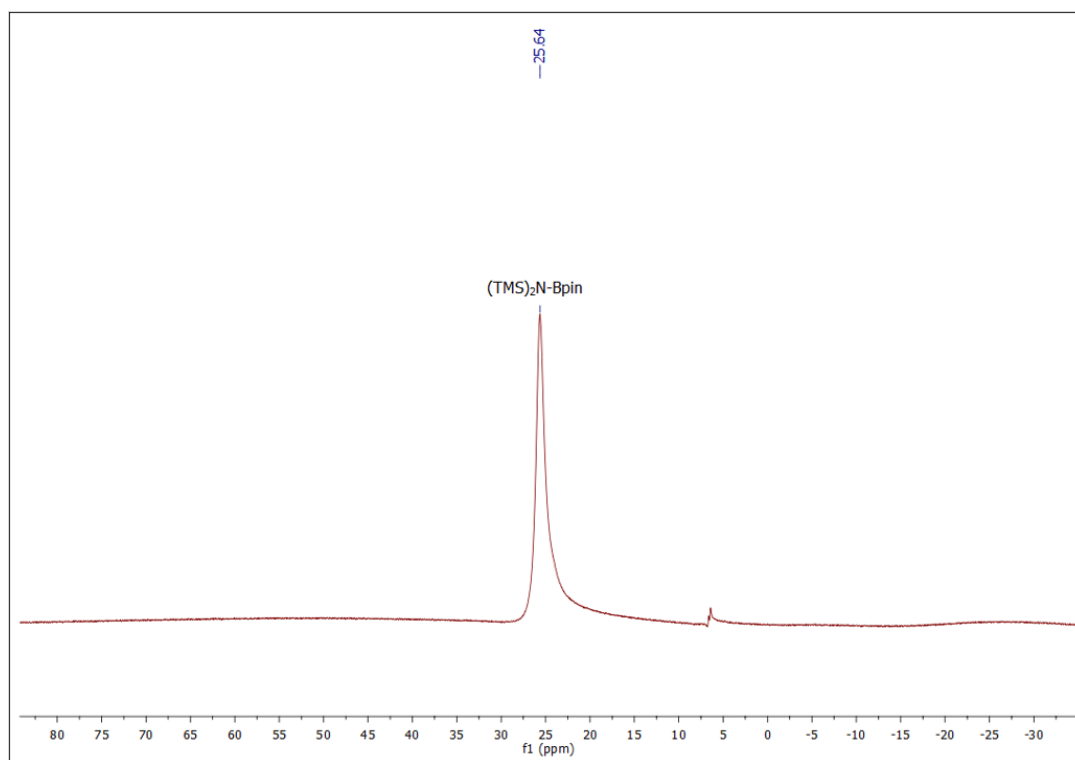


**Figure 3.21.**  $^{11}\text{B}$  NMR [128.3 MHz,  $\text{C}_6\text{D}_6$ , 298 K] spectrum of 1:2:1 ratio reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , HBpin and methylbenzoate.

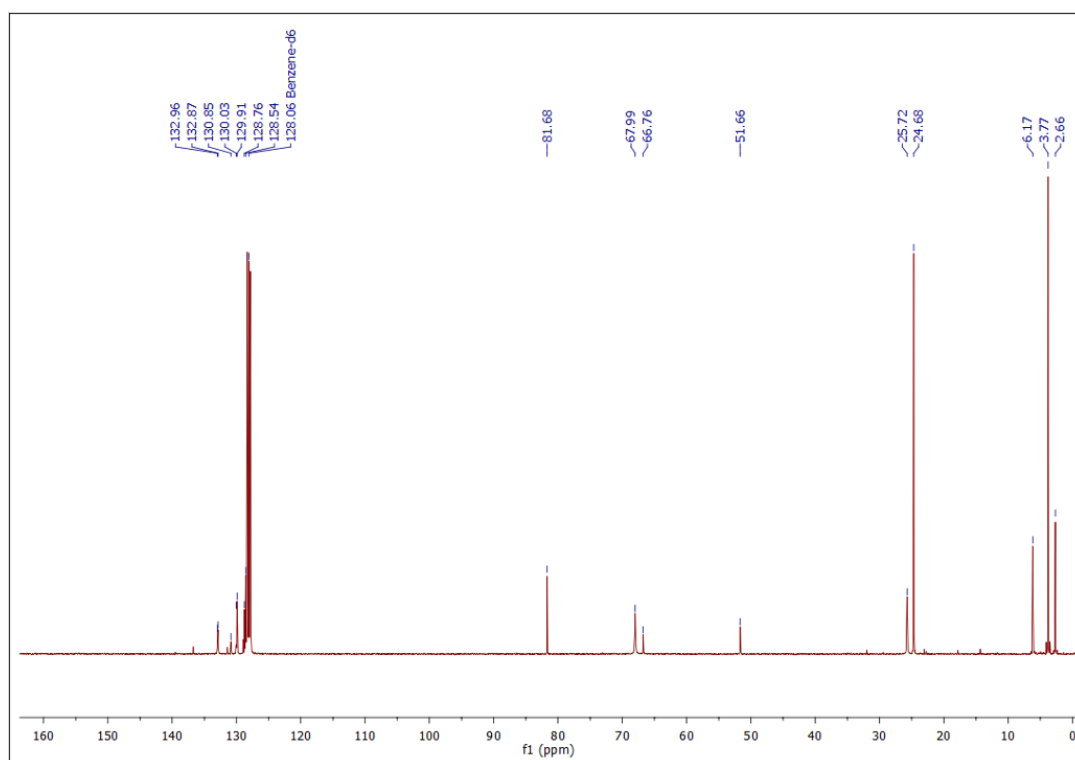


**Figure 3.22.**  $^{13}\text{C}$  NMR [100.613 MHz,  $\text{C}_6\text{D}_6$ , 298 K] spectrum of 1:2:1 ratio reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , HBpin and methylbenzoate.

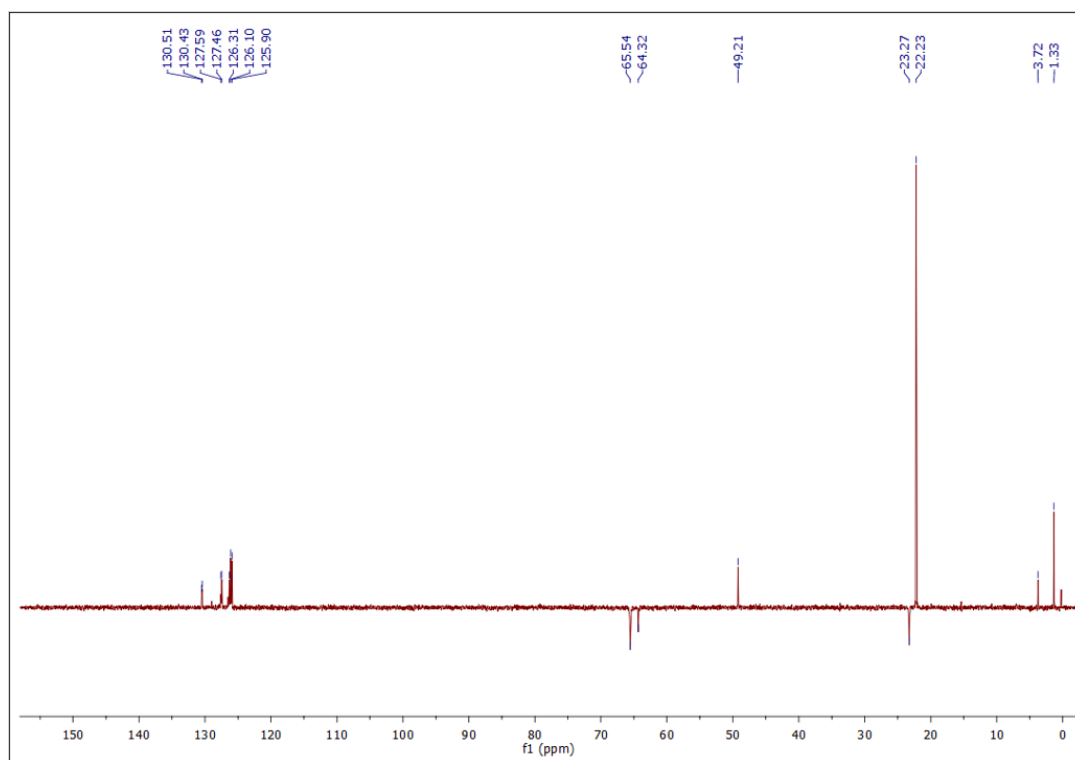


**Figure 3.23.** DEPT-135 NMR [100.613 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K] spectrum of 1:2:1 ratio reaction of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>, HBpin and methylbenzoate.

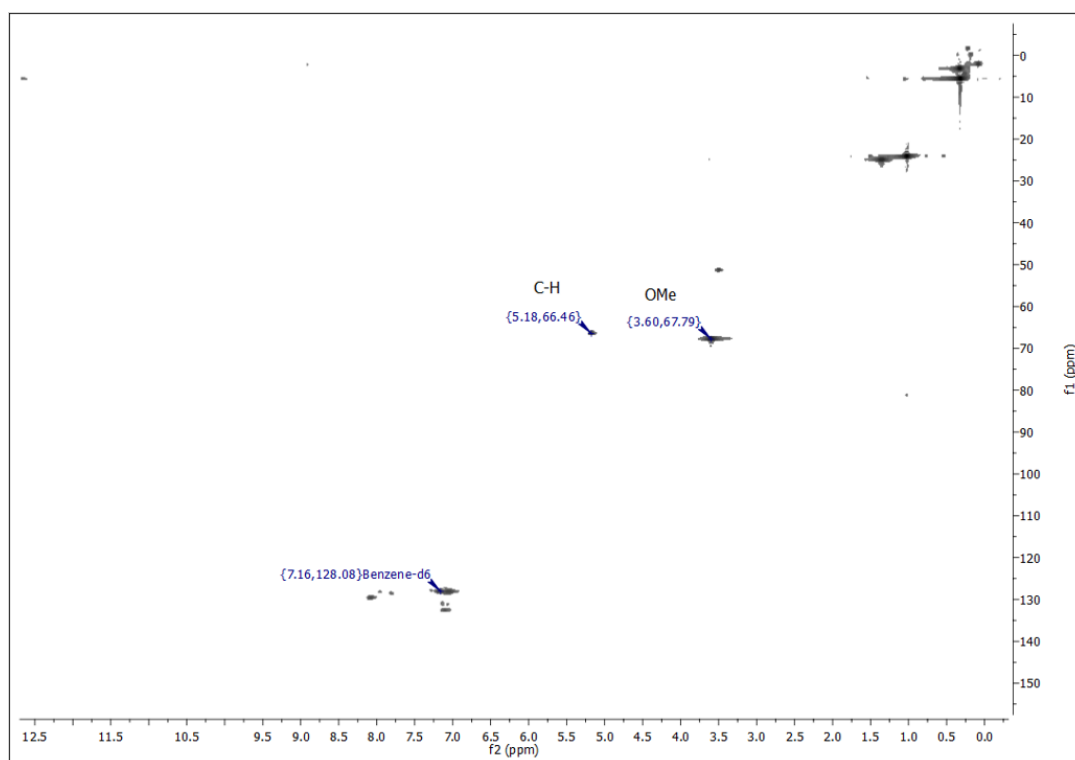


**Figure 3.24.** HSQC-NMR [C<sub>6</sub>D<sub>6</sub>, 298 K] spectrum of 1:2:1 ratio reaction of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>, HBpin and methylbenzoate.

### 3.8. References

1. (a) Turek, T.; Trimm, D. L.; Cant, N. W. The Catalytic Hydrogenolysis of Esters to Alcohols. *Catal. Rev.: Sci. Eng.* **1994**, 36 (4), 645-683; (b) Magano, J.; Dunetz, J. R. Large-Scale Carbonyl Reductions in the Pharmaceutical Industry. *Org. Process Res. Dev.* **2012**, 16, 1156-1184; (c) Lohr, T. L.; Li, Z.; Marks, T. J. Thermodynamic Strategies for C-O Bond Formation and Cleavage via Tandem Catalysis. *Acc. Chem. Res.* **2016**, 49, 824-834; (d) Wu, L.; Moteki, T.; Gokhale, A. A.; Flaherty, D. W.; Toste, F. D. Production of Fuels and Chemicals from Biomass: Condensation Reactions and Beyond. *Chem* **2016**, 1, 32-58. (e) Cornils, B.; Hermann, W. A.; Beller, M.; Paciello, R. Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2017; Vol. 4. (f) Andersson, P. G.; Munslo, I. J. Modern Reduction Methods; Wiley: New York, 2008.
2. (a) Nystrom, R. F.; Brown, W. G. Reduction of Organic Compounds by Lithium Aluminum Hydride. III. Halides, Quinones, Miscellaneous Nitrogen Compounds. *J. Am. Chem. Soc.* **1948**, 70, 3738-3740. (b) Walker, E. R. H. The Functional Group Selectivity of Complex Hydride Reducing Agents. *Chem. Soc. Rev.* **1976**, 5, 23-50. (c) H. C. Brown and S. Krishnamurthy, Forty Years of hydride reductions. *Tetrahedron* **1979**, 35, 567-607. (d) Piers, E.; Chong, J. M. New Powerful Catalysts for the Reduction of Esters by Lithium Borohydride. *J. Org. Chem.* **1982**, 47, 1604-1606. (e) Smith, M. B.; March, J. Advanced Organic Chemistry: Reactions, Mechanisms, and Structure. 6<sup>th</sup> ed.; Wiley: 2007; pp 1786-1840.
3. (a) Pritchard, J.; Filonenko, G. A.; van Putten, R. Hensen, E. J. M.; Pidko, E. A. Heterogeneous and Homogeneous Catalysis for the Hydrogenation of Carboxylic Acid Derivatives: History, Advances and Future Directions. *Chem. Soc. Rev.* **2015**, 44, 3808-3833. (b) Farrar-Tobar, R. A.; Wozniak, B.; Savini, A.; Hinze, S.; Tin, S.; de Vries, J. G. Base-Free Iron Catalyzed Transfer Hydrogenation of Esters Using EtOH as Hydrogen Source. *Angew. Chem., Int. Ed.* **2019**, 58, 1129-1133; (c) Gusev, D. G. Revised Mechanisms of the Catalytic Alcohol Dehydrogenation and Ester Reduction with the Milstein PNN Complex of Ruthenium. *Organometallics*, **2020**, 39, 258-270.

4. (a) Roy, A. K. A Review of Recent Progress in Catalyzed Homogeneous Hydrosilation (Hydrosilylation). *Adv. Organomet. Chem.* **2007**, 55, 1-59. (b) Diez-Gondlez, S.; Nolan, S. P. Organic Preparations and Procedures International: The New Journal for Organic Synthesis. *Org. Prep. Proced. Int.* **2007**, 39, 523-559. (c) Yang, J.; Tilley, T. D. Efficient Hydrosilylation of Carbonyl Compounds with the Simple Amide Catalyst  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ . *Angew. Chem., Int. Ed.* **2010**, 49, 10186-10188. (d) Das, S.; Mçller, K.; Junge, K.; Beller, M. Zinc-Catalyzed Chemoselective Reduction of Esters to Alcohols. *Chem. Eur. J.* **2011**, 17, 7414-7417. (e) Trovitch, R. J. The Emergence of Manganese-Based Carbonyl Hydrosilylation Catalysts. *Acc. Chem. Res.* **2017**, 50, 2842-2852.
5. (a) Mukherjee, D.; Ellern, A.; Sadow, A. D. Magnesium-Catalyzed Hydroboration of Esters: Evidence for a New Zwitterionic Mechanism. *Chem. Sci.* **2014**, 5, 959-964. (b) Barman, M. K.; Baishya, A.; Nembenna, S. Magnesium Amide Catalyzed Selective Hydroboration of Esters. *Dalton Trans.* **2017**, 46, 4152-4156. (c) Bisai, M. K.; Gour, K.; Das, T.; Vanka, K.; Sen, S. S. Readily Available Lithium Compounds as Catalysts for the Hydroboration of Carbodiimides and Esters. *J. Organomet. Chem.* **2021**, 949, 121924. (d) Sarkar, N.; Sahoo, R. K.; Nembenna, S. Aluminium-Catalyzed Selective Hydroboration of Esters and Epoxides to Alcohols: C–O Bond Activation. *Chem. Eur. J.* **2022**, e202203023.
6. (a) Desnoyer, A. N.; Geng, J.; Drover, M. W.; Patrick, B. O.; Love, J. A. Catalytic Functionalization of Styrenyl Epoxides via 2-Nickela(II)oxetanes. *Chem. Eur. J.*, **2017**, 23, 11509-11512. (b) Song, H.; Ye, K.; Geng, P.; Han, X.; Liao, R.; Tung, C. -H.; Wang, W. Activation of Epoxides by a Cooperative Iron-Thiolate Catalyst: Intermediacy of Ferrous Alkoxides in Catalytic Hydroboration. *ACS Catal.* **2017**, 7, 7709-7717.
7. (a) Patnaik, S; Sadow, A. D. Interconverting Lanthanum Hydride and Borohydride Catalysts for C=O Reduction and C–O Bond Cleavage. *Angew. Chem., Int. Ed.* **2019**, 58, 2505-2509. (b) Barger, C. J.; Motta, A.; Weidner, V. L.; Lohr, T. L.; Marks, T. J.  $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ -Catalyzed Ester Reductions with Pinacolborane: Scope and Mechanism of Ester Cleavage. *ACS Catal.* **2019**, 9, 9015-9024. (c) Liua, H.; Eisen, M. S. Organo-*f*-Complexes for Efficient and Selective Hydroborations. *Synthesis* **2020**, 52, 629-644. (d) Dicken, R. D.; Motta, A.; Marks, T. J. Homoleptic Lanthanide Amide Catalysts for Organic Synthesis: Experiment and Theory. *ACS Catal.* **2021**, 11, 2715-

2734. (e) Makarov, K.; Kaushansky, A.; Eisen, M. S. Catalytic Hydroboration of Esters by Versatile Thorium and Uranium Amide Complexes. *ACS Catal.* **2022**, *12*, 273-284.
8. (a) Erken, C.; Kaithal, A.; Sen, S.; Weyhermüller, T.; Hölscher, M.; Werlé, C.; Leitner, W. Manganese-Catalyzed Hydroboration of Carbon Dioxide and Other Challenging Carbonyl Groups. *Nat. Commun.* **2018**, *9*, 4521. (b) Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, *5*, 3238-3259. (c) Sen, A.; Ansari, M.; Rajaraman, G. Mechanism of Hydroboration of CO<sub>2</sub> Using an Fe Catalyst: What Controls the Reactivity and Product Selectivity? *Inorg. Chem.* **2023**, *62*, 3727-3737. (d) Espinosa, M. R.; Charboneau, D. J.; de Oliveira A. G.; Hazari, N. Controlling Selectivity in the Hydroboration of Carbon Dioxide to the Formic Acid, Formaldehyde, and Methanol Oxidation Levels. *ACS Catal.* **2019**, *9*, 301-314. (e) Wang, X.; Chang, K.; Xu, X. Hydroboration of Carbon Dioxide Enabled by Molecular Zinc Dihydrides†. *Dalton Trans.* **2020**, *49*, 7324-7327. (f) Li, C. -Q.; Leng, G.; Li, W. Hydroboration of Carbon Dioxide with Pinacolborane Catalyzed by Various Aluminum Hydrides: A Comparative Mechanistic Study†. *Catal. Sci. Technol.* **2022**, *12*, 6129-6141. (g) Chia, C. -C.; Teo, Y. -C.; Cham, N.; Ho, S. Y. -F.; Ng, Z. -H.; Toh, H. -M.; Mézailles, N.; So, C. -W. Aluminum-Hydride-Catalyzed Hydroboration of Carbon Dioxide. *Inorg. Chem.* **2021**, *60*, 4569-4577. (h) Kostera, S.; Peruzzini, M.; Kirchner, K.; Gonsalv, L. Mild and Selective Carbon Dioxide Hydroboration to Methoxyboranes Catalyzed by Mn(I) PNP Pincer Complexes. *ChemCatChem* **2020**, *12*, 4625-4631.
9. Bradley, D. C.; Ghotra, J. S.; Hart, F. A. Low Co-ordination Numbers in Lanthanide and Actinide Compounds. Part 1. The Preparation and Characterization of Tris{bis(trimethylsilyl)-amido}Lanthanides. *J. Chem. Soc., Dalton Trans.* **1973**, 1021-1023.
10. Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. The Hidden Role of Boranes and Borohydrides in Hydroboration Catalysis. *ACS Catal.* **2020**, *10*, 13479-13486.
11. Appavoo, D.; Spencer, L. C.; Guzei, I. A.; Gomez-Garcia, C. J.; van Wyka, J. L.; Darkwa, J. Ring Opening Polymerization of D, L-Lactide and  $\epsilon$ -Caprolactone Catalysed by (Pyrazol-1-yl)Copper(II) Carboxylate Complexes. *RSC Adv.* **2021**, *11*, 13475-13485.
12. (a) Jagtap, R. A.; Samal, P. P.; Vinod, C. P.; Krishnamurthy, S.; Punji, B. Iron-Catalyzed C(sp<sup>2</sup>)-H Alkylation of Indolines and Benzo[h]quinoline with Unactivated Alkyl

- Chlorides through Chelation Assistance. *ACS Catal.* **2020**, *10*, 7312-7321. (b) Hossain, J.; Gopinath, J. S.; Tothadi, S.; Parameswaran, P.; Khan, S. NHSi/NHGe Supported Copper Halide and Pseudohalide Complexes: Synthesis and Application. *Organometallics* **2022**, *41*, 3706-3717. (c) Hossain, M. J.; Shah, B. K.; Khan, S. Deoxygenation of 1° and 2° Amides with Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> under Mild Conditions. *ACS Catal.* **2023**, *13*, 13577-13587.
13. (a) Sun, Z.; Ma, T.; Tao, H.; Fan, Q.; Han, B. Fundamentals and Challenges of Electrochemical CO<sub>2</sub> Reduction Using Two-Dimensional Materials. *Chem* **2017**, *3*, 560-587. (b) Navarro-Jaen, S.; Virginie, M.; Bonin, J.; Robert, M.; Wojcieszak, R.; Khodakov, A. Y. Highlights and Challenges in the Selective Reduction of Carbon Dioxide to Methanol. *Nat. Rev. Chem.* **2021**, *5*, 564-579. (c) Johnson, D.; Qiao, Z.; Djire, A. Progress and Challenges of Carbon Dioxide Reduction Reaction on Transition Metal Based Electrocatalysts. *ACS Appl. Energy Mater.* **2021**, *4*, 8661-8684.
14. (a) Marlin, D. S.; Sarron, E.; Sigurbjörnsson, O. Process Advantages of Direct CO<sub>2</sub> to Methanol Synthesis. *Front. Chem.* **2018**, *6*, 446. (b) Bowker, M. Methanol Synthesis from CO<sub>2</sub> Hydrogenation. *ChemCatChem* **2019**, *11*, 4238-4246. (c) Zhang, X.; Zhang, G.; Song, C.; Guo, X. Catalytic Conversion of Carbon Dioxide to Methanol: Current Status and Future Perspective. *Front. Energy Res.* **2021**, *8*, 6211.
15. Murphy, L. J.; Hollenhorst, H.; McDonald, R.; Ferguson, M.; Lumsden, M. D.; Turculet, L. Selective Ni-Catalyzed Hydroboration of CO<sub>2</sub> to the Formaldehyde Level Enabled by New PSiP Ligation. *Organometallics* **2017**, *36*, 3709-3720.
16. Chen, C.; Mo, Q.; Huang, Y.; Zhang, L. Selective Reduction of CO<sub>2</sub> to Methanol via Hydrosilylation Boosted by a Porphyrinic Metal-Organic Framework. *ACS Catal.* **2023**, *13*, 6837-6845.

## *Chapter 4*

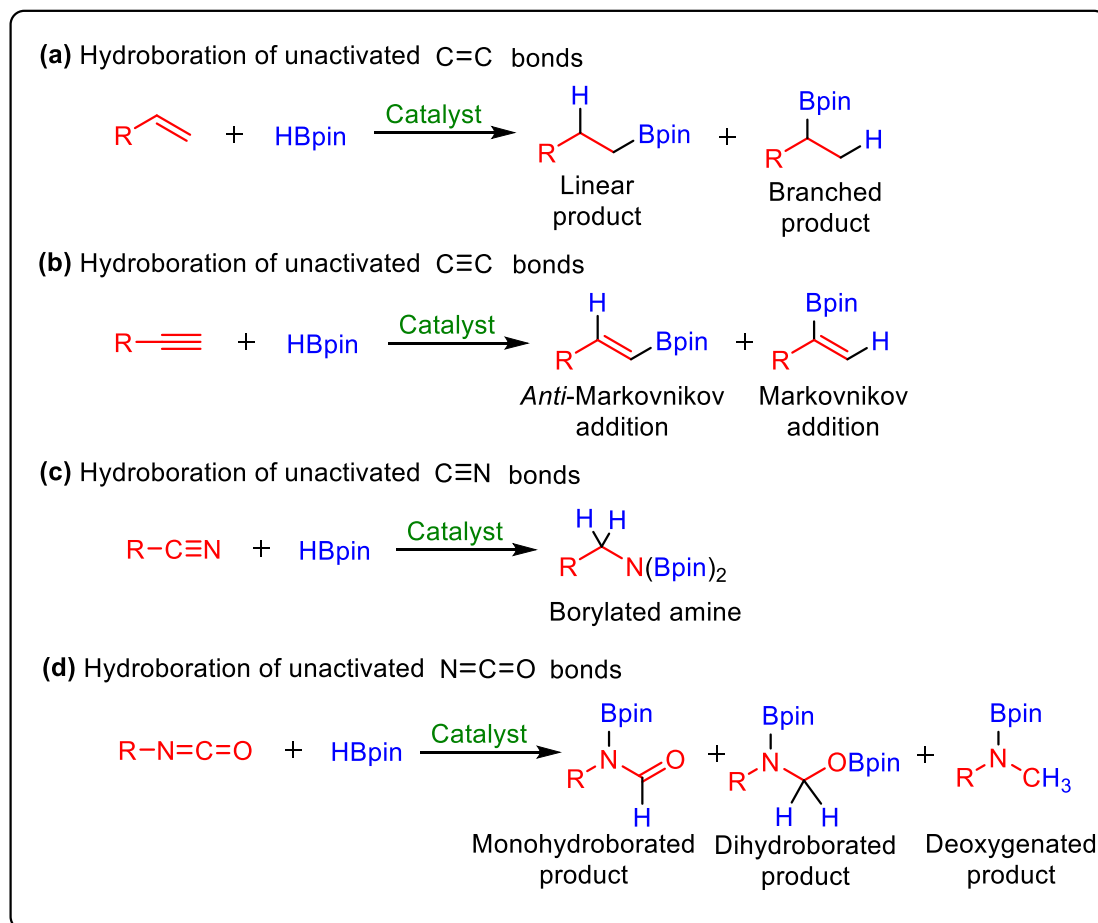
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### **Homoleptic cerium amide-catalysed hydroboration of multiple bonds (C=C, C≡C, C≡N and N=C=O)**

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## 4.1. Introduction

A fundamental research goal in contemporary science is to prioritize environmental friendliness and promote development of the sustainable catalysts and synthetic methodologies. Regioselective hydroboration of unsaturated organic compounds containing C=C, C $\equiv$ C, C $\equiv$ N and N=C=O groups is of paramount importance, as it plays a crucial role in the preparation of pharmaceutical intermediates, fragrances, fine chemicals and various bulk products.<sup>1</sup> Specially, catalytic reduction of unsaturated bonds using pinacolborane (HBpin) under ambient reaction conditions stands out as an economical, atom-efficient and environmentally friendly transformation.<sup>2</sup> There are plenty of heterogeneous methodologies reported for the reduction of unsaturated bonds using harsh reaction conditions (high pressure and high temperature), which demonstrated functional group tolerance and suboptimal selectivity.<sup>3</sup> Several homogeneous catalysts are also well explored for this purpose, which were found to be highly diligent and abuzz, but mostly transition metal-based catalysts.<sup>4</sup> From the last two decades, researchers have become more curious about the synthesis of fascinating main-group element-based catalysts for the reduction of unsaturated bonds as a sustainable option.<sup>5</sup> However, the lanthanides are infants in the field of homogenous catalysis for the organic transformation reactions. Apart from direct hydrogenation reaction of unsaturated bonds,<sup>6</sup> transfer hydrogenation,<sup>7</sup> hydrosilylation<sup>8</sup> and hydroboration<sup>9</sup> reactions are much more convenient due to the mild reaction conditions for the reduction of alkynes to alkenes, alkenes to alkanes, nitrile to imines or amines and isocyanates to amides or amines (**Scheme 4.1**). Hydrosilylation reactions are widely investigated in synthetic organic chemistry, but hydroboration reaction is still less explored. The hydroboration is cost effective over the hydrosilylation reaction because the hydroborating reagents are comparatively cheaper than silanes.



**Scheme 4.1.** Hydroboration of unactivated C=C, C≡C, C≡N and N=C=O bonds using HBpin.

In 1992, Marks and co-workers reported the catalytic hydroboration of alkenes using catecholborane in the presence of lanthanum (La) and samarium (Sm)-based organo-lanthanides **1-4** (**Chart 4.1**).<sup>10</sup> After that, groups of Evans (1993),<sup>11</sup> Tueben (1995),<sup>12</sup> Villiers and Ephritikhine (1995)<sup>13</sup> disclosed the rare-earth-catalysed (Sc, Y, Pr, Nd, Sm and Lu) hydroboration of olefins using HBcat. In 2004, Livinghouse and co-workers introduced homoleptic lanthanum amide (**5**)-catalysed (3 mol% of catalyst) olefins hydroboration using 2 equivalents of pinacolborane (HBpin) at 90 °C temperature in 19-25 hours.<sup>14</sup>

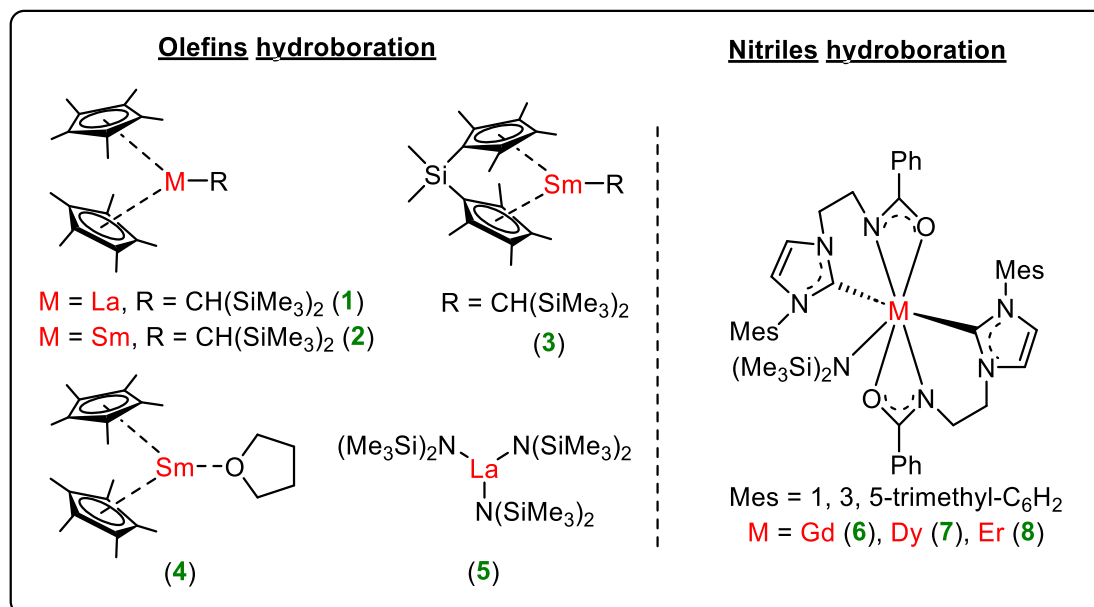


**Chart 4.1.** Reported lanthanide complexes for the olefins and nitriles hydroboration reaction.

In 2018, Wang and co-workers made a significant breakthrough by successfully enabling the hydroboration of a diverse array of nitriles and imines through the utilization of amide-functionalized N-heterocyclic carbene-ligated lanthanide complexes **6-8** (Chart 4.1) as catalysts with 2 mol% of the catalyst and 3 equivalents of HBpin at 110 °C temperature.<sup>15</sup> But, there are no reports on lanthanide-catalysed hydroboration of alkynes and isocyanate compounds using HBpin. The isocyanates are affordable and readily available feedstock, highly valuable in a wide array of organic transformations.<sup>16</sup> Our study commenced with an exploration of the reaction conditions for the homoleptic cerium amide-catalysed hydroboration reaction of isocyanates.

Herein, we have developed the homoleptic cerium bis(trimethylsilyl)amides complex and manifested the highly regioselective hydroboration of unactivated C=C, C≡C, C≡N and N=C=O bonds using HBpin under mild reaction conditions. The noteworthy aspects of the current synthetic strategy include: (i) atom efficient hydroboration reaction, (ii) use of HBpin, (iii) high regioselectivity in the reduction of unactivated and unsaturated bonds (C=C, C≡C, C≡N and N=C=O bonds), (iv) easily synthesized  $Ce[N(SiMe_3)_2]_3(THF)_3$  (also commercially available  $Ce[N(SiMe_3)_2]_3$ ), (v) use of the most abundant lanthanide cerium as a catalyst, (vi) comparatively cheaper among the other lanthanides (vii) low toxicity of cerium, (viii) mild reaction conditions (60-80 °C temperature, 12-36 h reaction time) and (ix) broad substrates scope.

## 4.2. Experimental section

All manipulations were carried out under an inert gas atmosphere of argon using the standard Schlenk technique and in an argon-filled MBRAUN MB 150-GI glovebox. All solvents were purified by the MBRAUN MB SPS-800 solvent purification system. All other chemicals were purchased from Sigma Aldrich, Alfa-Aesar, ChemScene and BLD Pharma. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  using a Bruker 400 MHz spectrometer. Mass spectra were recorded using an AB Sciex 4800 plus HRMS.  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  was synthesized by using the reported synthetic procedure.<sup>17</sup>

**General catalytic reaction procedure of alkene ( $\text{C}=\text{C}$ ) hydroboration:** The  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyst was taken into a 25 mL Schlenk tube inside the glovebox and added alkene (0.2 mmol) and 0.44 mL of HBpin solution (0.5 M). The reaction mixture was stirred for 36 h at 80 °C temperature. After that, the solvent was dried under high a vacuum. Then, mesitylene (0.2 mmol) was added as an internal standard into the tube and added 0.5 mL of  $\text{CDCl}_3$  and the crude reaction mixture was submitted for  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The yield of the products was calculated by integrating the mesitylene as an internal standard in  $^1\text{H}$  NMR spectra.

**General catalytic reaction procedure of alkyne ( $\text{C}\equiv\text{C}$ ) hydroboration:** The  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyst was taken into a 25 mL Schlenk tube inside the glovebox and added alkyne (0.2 mmol) and 0.44 mL of HBpin solution (0.5 M). The reaction mixture was stirred for 12 h at 70 °C temperature. After that, the solvent was dried under a high vacuum. Then, mesitylene (0.2 mmol) was added as an internal standard into the tube and added 0.5 mL of  $\text{CDCl}_3$  and the crude reaction mixture was submitted for  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The yield of the products was calculated by integrating the mesitylene as an internal standard in  $^1\text{H}$  NMR spectra.

**General catalytic reaction procedure of nitrile ( $\text{C}\equiv\text{N}$ ) hydroboration:** The  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyst was taken into a 25 mL Schlenk tube inside the glovebox and added nitrile (0.2 mmol) and 0.88 mL of HBpin solution (0.5 M). The reaction mixture was stirred for 24 h at 80 °C temperature. After that, the solvent was dried under a high vacuum. Then, mesitylene (0.2 mmol) was added as an internal standard into the tube and added 0.5 mL of  $\text{CDCl}_3$  and the crude reaction mixture was submitted for  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The yield of the products was calculated by integrating the mesitylene as an internal standard in  $^1\text{H}$  NMR spectra.

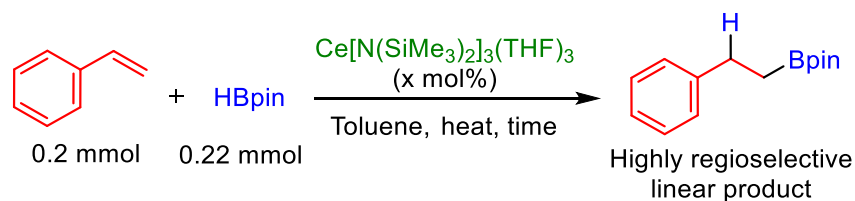
**General catalytic reaction procedure of deoxygenation of isocyanate (N=C=O):** The  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  catalyst was taken into a 25 mL Schlenk tube inside the glovebox and added isocyanate (0.2 mmol) and 0.44 mL of HBpin solution (0.5 M). The reaction mixture was stirred for 24 h at 80 °C temperature. After that, the solvent was dried under a high vacuum. Then, mesitylene (0.2 mmol) was added as an internal standard into the tube and added 0.5 mL of  $\text{CDCl}_3$  and the crude reaction mixture was submitted for  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments. The yield of the products was calculated by integrating the mesitylene as an internal standard in  $^1\text{H}$  NMR spectra.

### 4.3. Results and discussion of alkene (C=C) hydroboration reaction

#### 4.3.1. Reaction optimization:

Our investigation commenced with the hydroboration of styrene (0.2 mmol) using pinacolborane (HBpin, 0.24 mmol) in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. The yield of the borylated product undergoes substantial variations upon altering the catalyst's mol% in conjunction with the changes in the reaction temperature and duration (**Table 4.1**). Our observations revealed that utilizing 2 mol% of the catalyst at 80 °C temperature, along with 1.1 equivalents of HBpin over a span of 36 hours, resulted in nearly complete hydroboration of styrene. We did two control experiments: (i) without catalyst at 80 °C in 36 hours, but we didn't observe any significant yield of the borylated product, which suggests a pivotal role of the catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  in alkene hydroboration reaction (**Entry 8; Table 4.1**); (ii) hidden  $\text{BH}_3$  catalysis test: 2 mol% of catalyst in presence of 20 mol% of TMEDA (tetramethylethylenediamine) at 80 °C in 36 hours, we observed 87% yield of the borylated product (**Entry 9; Table 4.1**), which indicates negligible effect of  $\text{BH}_3$  in the alkene hydroboration reaction.<sup>18</sup>

**Table 4.1.** Optimization of reaction conditions for alkene hydroboration.



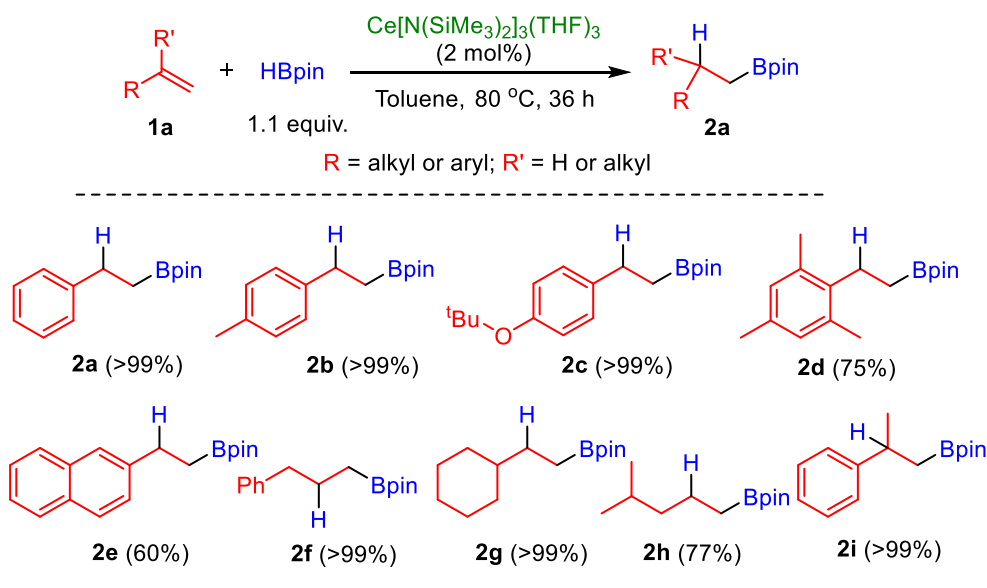
| Entry | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ | Temperature | Time | Yield* |
|-------|--------------------------------------------------------|-------------|------|--------|
|-------|--------------------------------------------------------|-------------|------|--------|

|    | (mol%)                                 | (°C) | (h) | (%)   |
|----|----------------------------------------|------|-----|-------|
| 1. | 1                                      | 80   | 12  | 27    |
| 2. | 2                                      | 80   | 12  | 40    |
| 3. | 2                                      | 80   | 24  | 66    |
| 4. | 2                                      | 80   | 36  | >99   |
| 5. | 2                                      | 60   | 36  | 41    |
| 6. | 2                                      | rt   | 36  | trace |
| 7. | 2                                      | 70   | 36  | 83    |
| 8. | -                                      | 80   | 36  | 8     |
| 9. | 2 (in presence of 20<br>mol% of TMEDA) | 80   | 36  | 87    |

[Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene).]

#### 4.3.2. Substrate scope:

Following the optimization of reaction conditions, our investigation expanded to explore the substrate scope, aiming to examine the impact of various electron-donating and the electron-withdrawing groups on aromatic and aliphatic alkenes. Both aromatic and aliphatic substituted terminal alkenes afforded good to excellent yields for the products. However, a noticeable decrease in the yield of electron-withdrawing group substituted terminal alkenes was observed, whereas electron-donating group substituted terminal alkenes delivered higher yields of the products (**Scheme 4.2**). We observed highly regioselective linear borylated products for all the substrates. In an effort to broaden the catalytic scope, naturally occurring terpenes like R-limonene and disubstituted  $\alpha$ -methylstyrene were investigated for the selective hydroboration of their C=C bonds.  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed hydroboration of R-limonene afforded >99% yield with 5 mol% of catalyst loading (**Scheme 4.2**). Also, disubstituted terminal alkene ( $\alpha$ -methylstyrene) yielded >99% in the presence of 5 mol% of the catalyst at 80 °C in 36 hours instead of optimized 2 mol% of the catalyst (**Scheme 4.2**).



**Scheme 4.2.** Substrate scope of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed alkene hydroboration reaction. [Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene)]

#### Analytical data of the borylated products:

**2a:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.28-7.23 (m, 4H, *Ph*), 7.19-7.15 (m, 1H, *Ph*), 6.83 (s, 3H, *mesitylene*), 2.8-2.76 (t, 2H,  $\text{PhCH}_2$ ), 2.30 (s, 9H, *mesitylene*), 1.24 (s, 12H,  $\text{OBpin}$ ), 1.20-1.16 (t, 2H,  $\text{CH}_2\text{OBpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  144.5 (*Ph*), 137.8 (*mesitylene*), 128.3 (*Ph*), 128.1 (*Ph*), 127.0 (*mesitylene*), 125.6 (*Ph*), 83.2 ( $\text{OBpin}$ ), 30.1 ( $\text{CH}_2\text{Bpin}$ ) 24.9 ( $\text{CH}_2\text{Bpin}$ ), 24.7 ( $\text{CH}_2\text{Ph}$ ) 21.2 (*mesitylene*) ppm.

**2b:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.03-7.01(d, 2H, *Ph*), 6.98-6.96 (d, 2H, *Ph*), 6.71 (s, 3H, *mesitylene*), 2.64-2.60 (t, 2H,  $\text{CH}_2\text{Ph}$ ), 2.21 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.18 (s, 9H, *mesitylene*), 1.13 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 1.06-1.02 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  141.5 (*Ph*), 137.8 (*mesitylene*), 134.9 (*Ph*), 129.0 (*Ph*), 128.0 (*Ph*), 127.0 (*mesitylene*), 83.1 (*Bpin*), 29.6 ( $\text{CH}_2\text{Bpin}$ ), 24.9 (*Bpin*), 24.6 ( $\text{CH}_2\text{Ph}$ ), 21.3 (*mesitylene*), 21.1 ( $\text{CH}_3\text{Ph}$ ) ppm.

**2c:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.02-7.00(d, 2H, *Ph*), 6.80-6.78 (d, 2H, *Ph*), 6.71 (s, 3H, *mesitylene*), 2.65-2.61 (t, 2H,  $\text{CH}_2\text{Ph}$ ), 2.19 (9H, s, *mesitylene*), 1.23 (s, 9H,  $\text{PhOC}(\text{CH}_3)_3$ ), 1.10 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 1.07-1.03 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  153.1 ( $\text{tBuOPh}$ ), 139.3 (*Ph*), 137.8 (*mesitylene*), 128.4 (*Ph*), 127.0 (*mesitylene*), 124.1 (*Ph*), 83.1 (*Bpin*), 78.0 ( $\text{OC}(\text{CH}_3)_3$ ), 29.3 ( $\text{CH}_2\text{Bpin}$ ), 28.9 ( $\text{OC}(\text{CH}_3)_3$ ), 24.9 (*Bpin*), 24.7 ( $\text{CH}_2\text{Ph}$ ), 21.3 (*mesitylene*) ppm.

**2d:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.86 (s, 2H, *Ph*), 6.85 (s, 3H, *mesitylene*), 2.74-2.70 (t, 2H,  $\text{CH}_2\text{Ph}$ ), 2.34 (s, 6H,  $\text{CH}_3\text{Ph}$ ), 2.32 (s, 9H, *mesitylene*), 2.28 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 1.31 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 1.03-0.98 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  138.8 (*Ph*), 137.8 (*mesitylene*), 135.7 (*Ph*), 134.7 (*Ph*), 128.9 (*Ph*), 127.0 (*mesitylene*), 83.2 (*Bpin*), 31.8 ( $\text{CH}_2\text{Bpin}$ ), 25.0 (*Bpin*), 23.4 ( $\text{CH}_3\text{Ph}$ ), 21.3 (*mesitylene*), 20.9 ( $\text{CH}_3\text{Ph}$ ), 19.8 ( $\text{CH}_2\text{Ph}$ ) ppm.

**2e:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.72-7.64 (m, 3H, *Ph*), 7.55 (s, 1H, *Ph*), 7.34-7.27 (m, 3H, *Ph*), 6.71 (s, 3H, *mesitylene*), 2.85-2.81 (t, 2H,  $\text{CH}_2\text{Ph}$ ), 2.18 (s, 9H, *mesitylene*), 1.12 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 1.09-1.04 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  142.1 (*Naphthyl*), 137.8 (*mesitylene*), 133.9 (*Naphthyl*), 132.1 (*Naphthyl*), 128.1 (*Naphthyl*), 127.8 (*Naphthyl*), 127.7 (*Naphthyl*), 127.5 (*Naphthyl*), 127.4 (*Naphthyl*), 127.0 (*mesitylene*), 125.8 (*Naphthyl*), 125.0 (*Naphthyl*), 83.3 (*Bpin*), 30.2 ( $\text{CH}_2\text{Bpin}$ ), 24.9 ( $\text{CH}_2(\text{Naphthyl})$ ), 24.6 (*Bpin*), 21.3 (*mesitylene*) ppm.

**2f:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  7.17-7.15 (d, 2H, *Ph*), 7.09-7.08 (d, 2H, *Ph*), 6.71 (s, 3H, *mesitylene*), 2.54-2.50 (t, 2H,  $\text{CH}_2\text{Ph}$ ), 2.19 (s, 9H, *mesitylene*), 1.67-1.63 (t, 2H,  $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 1.15 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 0.76-0.73 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  142.8 (*Ph*), 137.8 (*mesitylene*), 128.7 (*Ph*), 128.3 (*Ph*), 127.0 (*mesitylene*), 125.7 (*Ph*), 83.0 (*Bpin*), 38.7 ( $\text{CH}_2\text{Ph}$ ), 26.2 ( $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 24.9 ( $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 24.7 ( $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 21.3 (*mesitylene*) ppm.

**2g:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.81 (s, 3H, *mesitylene*), 2.29 (s, 9H, *mesitylene*), 1.75-1.68 (m, 5H,  $\text{CH}_2\text{CH}$ -cyclohexane), 1.26 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 1.20-1.12 (m, 6H,  $\text{CH}_2$ -cyclohexane), 0.90-0.84 (m, 2H,  $\text{CHCH}_2\text{CH}_2\text{Bpin}$ ), 0.80-0.76 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*mesitylene*), 127.0 (*mesitylene*), 82.9 (*Bpin*), 40.1 (CH), 33.1 ( $\text{CH}_2$ ), 31.5 ( $\text{CH}_2$ ), 26.9 ( $\text{CH}_2$ ), 26.6 ( $\text{CH}_2$ ), 24.9 (*Bpin*), 24.6 ( $\text{CH}_2\text{Bpin}$ ), 21.3 (*mesitylene*) ppm.

**2h:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  6.83 (s, 3H, *mesitylene*), 2.30 (s, 9H, *mesitylene*), 1.60-1.51 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.48-1.40 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 1.27 (s, 12H,  $\text{CH}_2\text{Bpin}$ ), 1.21-1.17 (m, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 0.90-0.88 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.80-0.76 (t, 2H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  137.8 (*mesitylene*), 127.0 (*mesitylene*), 83.0 (*Bpin*), 42.1 ( $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 27.9 ( $\text{CH}(\text{CH}_3)_2$ ), 24.9 (*Bpin*), 24.7 ( $\text{CH}(\text{CH}_3)_2$ ), 22.8 ( $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 21.9 ( $\text{CH}_2\text{CH}_2\text{Bpin}$ ), 21.3 (*mesitylene*) ppm.

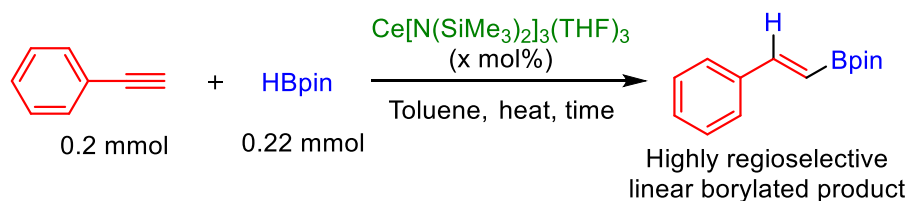
**2i:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K): 7.30-7.25 (m, 3H, *Ph*), 7.20-7.16 (m, 2H, *Ph*), 6.82 (s, 3H, *mesitylene*), 3.11-2.93 (m, 1H,  $\text{PhCHCH}_3$ ), 2.29 (s, 9H, *mesitylene*), 1.31-1.28 (d, 5H,  $\text{Ph}(\text{CH}_3)\text{CHCH}_2\text{Bpin}$ ), 1.17 (s, 12H,  $\text{CH}_2\text{Bpin}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  149.3 (*Ph*), 137.8 (*mesitylene*), 129.1 (*Ph*), 128.3 (*Ph*), 127.0 (*mesitylene*), 125.8 (*Ph*), 83.1 (*Bpin*), 35.9 (CH), 25.0 ( $\text{CH}_3$ ), 24.8 (*Bpin*), 24.6 ( $\text{CH}_2\text{Bpin}$ ), 21.3 (*mesitylene*) ppm.

## 4.4. Results and discussion of alkyne ( $\text{C}\equiv\text{C}$ ) hydroboration reaction

### 4.4.1. Reaction optimization:

While it is recognized that the reduction of  $\text{C}\equiv\text{C}$  bonds is generally more facile than that of  $\text{C}=\text{C}$  bonds, our investigation began by utilizing phenylacetylene (0.2 mmol) with 1.1 equivalents of HBpin in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst. The yield of the borylated product varies with the change in the reaction conditions, which includes mol% of the catalyst, temperature and reaction time (**Table 4.2**). We observed that 1 mol% of the catalyst at 70 °C temperature in 12 hours is the optimized reaction conditions for the hydroboration of phenylacetylene with 1.1 equivalents of HBpin. Similarly, we did two control experiments: (i) without catalyst at 70 °C in 12 hours, but we observed only 26% yield of the corresponding borylated product, suggesting a pivotal role of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  in alkyne hydroboration reaction (**Entry 6; Table 4.2**); (ii) hidden  $\text{BH}_3$  catalysis test: 2 mol% of catalyst in presence of 20 mol% of TMEDA at 70 °C in 12 hours, we observed 94% yield of the borylated product (**Entry 7; Table 4.2**), which suggests the negligible effect of  $\text{BH}_3$  in the phenylacetylene hydroboration reaction and its followed the true catalysis pathway.<sup>18</sup>

**Table 4.2.** Optimization of reaction conditions for phenylacetylene hydroboration.



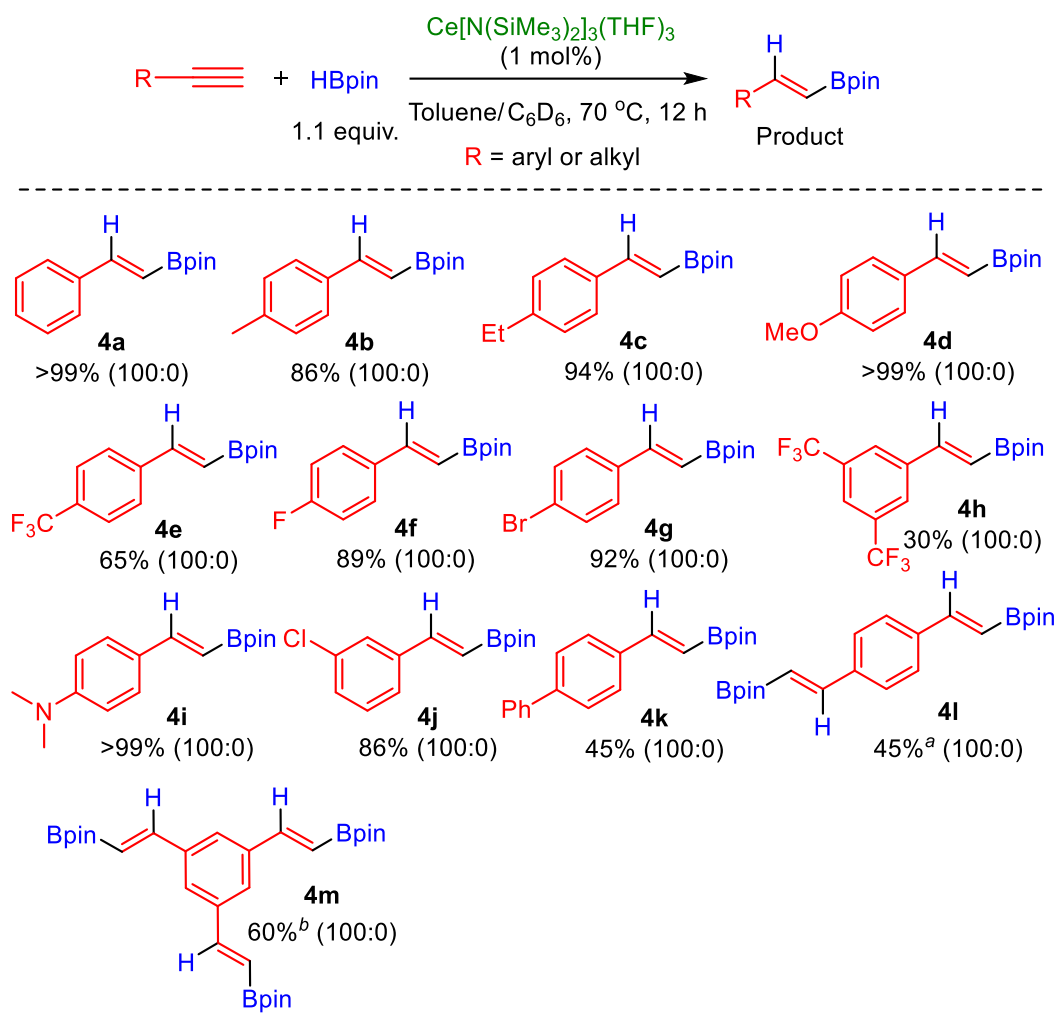
| Entry | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$<br>(mol%) | Temperature<br>(°C) | Time<br>(h) | Yield*<br>(%) |
|-------|------------------------------------------------------------------|---------------------|-------------|---------------|
| 1.    | 1                                                                | 70                  | 12          | 99            |
| 2.    | 0.5                                                              | 70                  | 12          | 85            |

|    |                                        |    |    |    |
|----|----------------------------------------|----|----|----|
| 3. | 1                                      | 70 | 8  | 72 |
| 4. | 1                                      | 60 | 12 | 59 |
| 5. | 1                                      | rt | 12 | <5 |
| 6. | -                                      | 70 | 12 | 26 |
| 7. | 1 (in presence of 20<br>mol% of TMEDA) | 70 | 12 | 94 |

[Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene).]

#### 4.4.2. Substrate scope:

After successfully fine-tuning the reaction parameters for the regioselective hydroboration of the  $\text{C}\equiv\text{C}$  bond in phenylacetylene, we have explored the substrate scope using 1 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  at 70 °C temperature in 12 hours. All the substrates scope delivered moderate to very good yields (**Scheme 4.3**). However, the electron-withdrawing group substituted alkynes afforded comparatively less yields than the electron-donating group substituted alkynes.  $-\text{CF}_3$  group containing alkyne yielded 65% (**4e**), whereas,  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$  and  $-\text{OCH}_3$  group containing alkynes afforded higher yields (up to >99%). On the other hand, the presence of two  $-\text{CF}_3$  groups in the substrate (**4h**) diminished the formation of regioselective linear borylated product (**Scheme 4.3**). We have also performed hydroboration of 1,4-diethynylbenzene and 1,3,5-triethynylbenzene with 2 equivalents and 3 equivalents of HBpin, respectively, to achieve corresponding borylated products (**4l** & **4m**), but afforded less yields (**Scheme 4.3**).



**Scheme 4.3.** Substrate scope of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed alkyne hydroboration reaction. <sup>a</sup>5 mol% of catalyst and 24 h reaction time. <sup>b</sup>5 mol% of catalyst and 48 h reaction time. Ratios in parentheses report the ratio of regioisomers (linear vs. branched). [Yields were determined by integrating <sup>1</sup>H NMR spectra in the presence of an internal standard (mesitylene)]

#### Analytical data of the borylated products:

**4a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.55-7.53 (m, 2H, *Ph*), 7.49-7.44 (d, 1H, *PhCH*), 7.40-7.33 (m, 3H, *Ph*), 6.26-6.21 (*CHBpin*), 6.85 (*mesitylene*), 2.32 (*mesitylene*), 1.36 (*Bpin*) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  149.6 (*PhCH*), 137.8 (*mesitylene*), 137.6 (*Ph*), 129.0 (*Ph*), 128.7 (*Ph*), 127.2 (*Ph*), 127.0 (*mesitylene*), 116.5 (*CHBpin*), 83.4 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4b:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.32-7.27 (m, 3H, *Ph*), 7.05-7.03 (d, 2H, *Ph* + *CHPh*), 6.71 (s, 3H, *mesitylene*), 6.05-6.01 (d, 1H, *CHBpin*), 2.25 (s, 3H, *CH<sub>3</sub>Ph*), 2.18 (s, 9H, *mesitylene*), 1.22 (s, 12H, *Bpin*) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  149.6

(PhCH), 139.0 (*mesitylene*), 137.7 (*Ph*), 134.9 (*Ph*), 129.4 (*Ph*), 127.1 (*Ph*), 127.0 (*mesitylene*), 115.2 (CHBpin), 83.3 (*Bpin*), 24.8 (*Bpin*), 21.4 (CH<sub>3</sub>Ph), 21.2 (*mesitylene*) ppm.

**4c:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.47-7.46 (d, 2H, *Ph*), 7.45-7.42 (d, 1H, PhCH), 7.22-7.20 (d, 1H, *Ph*), 6.85 (s, 3H, *mesitylene*), 6.20-6.15 (d, 1H, CHBpin), 2.71-2.65 (q, 2H, CH<sub>3</sub>CH<sub>2</sub>Ph), 2.32 (s, 9H, *mesitylene*), 1.36 (s, 12H, *Bpin*), 1.29-1.26 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>Ph) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  149.7 (PhCH), 137.8 (*mesitylene*), 135.2 (*Ph*), 132.2 (*Ph*), 128.2 (*Ph*), 127.2 (*Ph*), 127.0 (*mesitylene*), 115.4 (CHBpin), 83.4 (*Bpin*), 28.8 (CH<sub>3</sub>CH<sub>2</sub>Ph), 24.9 (*Bpin*), 21.3 (*mesitylene*), 15.5 (CH<sub>3</sub>CH<sub>2</sub>Ph) ppm.

**4d:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.48-7.46 (d, 2H, *Ph*), 7.42-7.37 (d, 1H, PhCH), 6.90-6.88 (d, 2H, *Ph*), 6.83 (s, 3H, *mesitylene*), 6.08-6.03 (d, 1H, CHBpin), 3.82 (s, 3H, OCH<sub>3</sub>), 2.31 (s, 9H, *mesitylene*), 1.34 (s, 12H, *Bpin*) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  160.4 (*Ph*), 149.2 (PhCH), 137.7 (*mesitylene*), 130.5 (*Ph*), 129.3 (*Ph*), 128.5 (*Ph*), 127.0 (*mesitylene*), 114.0 (CHBpin), 83.3 (*Bpin*), 55.3 (CH<sub>3</sub>OCH<sub>3</sub>), 24.8 (*Bpin*), 21.2 (*mesitylene*) ppm.

**4e:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.62-7.57 (m, 4H, *Ph*), 7.46-7.41 (d, 1H, PhCH), 6.83 (s, 3H, *mesitylene*), 6.31-6.27 (d, 1H, CHBpin), 2.30 (s, 9H, *mesitylene*), 1.29 (s, 12H, *Bpin*) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  147.8 (PhCH), 140.9 (*Ph*), 137.8 (*mesitylene*), 127.3 (*Ph*), 127.0 (*mesitylene*), 125.7 (*Ph*), 125.7 (*Ph*), 122.9 (CF<sub>3</sub>Ph), 120.2 (CHBpin), 83.7 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4f:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.50-7.46 (d, 2H, *Ph*), 7.41-7.36 (d, 1H, PhCH), 7.06-7.02 (d, 2H, *Ph*), 6.82 (s, 3H, *mesitylene*), 6.13-6.08 (d, 1H, CHBpin), 2.30 (s, 9H, *mesitylene*), 1.29 (s, 12H, *Bpin*) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  164.5 (FPh), 148.3 (PhCH), 137.7 (*mesitylene*), 133.8 (*Ph*), 128.8 (*Ph*), 128.7 (*Ph*), 127.0 (*mesitylene*), 115.7 (CHBpin), 83.5 (*Bpin*), 24.8 (*Bpin*), 21.2 (*mesitylene*) ppm.

**4g:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.38-7.36 (d, 2H, *Ph*), 7.26-7.24 (d, 2H, *Ph*), 7.22-7.16 (d, 1H, PhCH), 6.72 (s, 3H, *mesitylene*), 6.09-6.05 (d, 1H, CHBpin), 2.19 (s, 9H, *mesitylene*), 1.23 (s, 12H, *Bpin*) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  148.2 (PhCH), 137.8 (*mesitylene*), 136.5 (*Ph*), 131.9 (*Ph*), 128.6 (*Ph*), 127.0 (*mesitylene*), 123.0 (*Ph*), 117.5 (CHBpin), 83.6 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4h:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.97-7.92 (d, 2H, *Ph*), 7.85-7.82 (d, 1H, *Ph*), 7.48-7.43 (d, 1H, PhCH), 6.84 (s, 3H, *mesitylene*), 6.38-6.34 (d, 1H, CHBpin), 2.31 (s, 9H,

*mesitylene*), 1.36 (s, 12H, *Bpin*) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  146.0 (PhCH), 139.7 (Ph), 137.8 (*mesitylene*), 132.3 (Ph), 132.0 (Ph), 127.0 (*mesitylene*), 124.7 (Ph), 122.1 ( $(\text{CF}_3)_2\text{Ph}$ ), 118.4 (CHBpin), 83.9 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4i:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.42-7.40 (d, 2H, Ph), 7.39-7.34 (d, 1H, PhCH), 6.81 (s, 3H, *mesitylene*), 6.67-6.65 (d, 2H, Ph), 5.97-5.92 (CHBpin), 2.97 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 2.29 (s, 9H, *mesitylene*), 1.32 (s, 12H, *Bpin*) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  151.0 ( $(\text{CH}_3)_2\text{NPh}$ ), 149.9 (PhCH), 137.7 (*mesitylene*), 129.1 (Ph), 128.4 (Ph), 127.0 (*mesitylene*), 126.0 (Ph), 112.0 (CHBpin), 83.0 (*Bpin*), 40.3 ( $(\text{CH}_3)_2\text{NPh}$ ), 24.8 (*Bpin*), 21.2 (*mesitylene*) ppm.

**4j:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.49 (broad, 1H, Ph), 7.39-7.37 (m, 1H, Ph), 7.36-7.34 (d, 1H, PhCH), 9.29-7.28 (m, 2H, Ph), 6.83 (s, 3H, *mesitylene*), 6.23-6.19 (d, 1H, CHBpin), 2.31 (s, 9H, *mesitylene*), 1.35 (s, 12H, *Bpin*) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  150.3 (PhCH), 143.1 (ClPh), 137.6 (*mesitylene*), 135.6 (Ph), 127.5 (Ph), 127.4 (*mesitylene*), 123.1 (Ph), 118.1 (CHBpin), 83.6 (*Bpin*), 24.7 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4k:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.51-7.47 (m, 4H, PhPhCH), 7.35-7.31 (m, 3H, PhPhCH), 7.26-7.22 (m, 2H, PhPhCH), 7.11-7.06 (d, 1H, PhPhCH), 6.70 (s, 3H, *mesitylene*), 6.15-6.10 (d, 1H, CHBpin), 2.18 (s, 9H, *mesitylene*), 1.23 (s, 12H, *Bpin*) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  149.2 (PhPhCH), 141.7 (PhPhCH), 140.7 (PhPhCH), 137.8 (*mesitylene*), 136.6 (Ph), 128.9 (Ph), 128.8 (Ph), 127.7 (Ph), 127.4 (Ph), 127.1 (Ph), 127.0 (*mesitylene*), 116.7 (CHBpin), 83.5 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4l:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.37-7.35 (m, 2H, Ph), 7.32-7.27 (m, 2H, Ph), 7.14-7.09 (d, 2H, CHPhCH), 6.71 (s, 3H, *mesitylene*), 6.12-6.07 (d, 1H, (CHBpin) $_2$ ), 2.18 (s, 9H, *mesitylene*), 1.22 (s, 24H, (*Bpin*) $_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  149.0 (PhCH), 137.8 (*mesitylene*), 132.5 (Ph), 132.1 (Ph), 129.1 (Ph), 127.4 (Ph), 127.0 (*mesitylene*), 117.0 (CHBpin), 83.5 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

**4m:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.34 (s, 2H, Ph), 7.21-7.16 (d, 3H, (PhCH) $_3$ ), 7.05 (s, 1H, Ph), 6.59 (s, 3H, *mesitylene*), 6.01-5.96 (d, 3H, (CHBpin) $_3$ ), 2.06 (s, 9H, *mesitylene*), 1.12 (s, 36H, (*Bpin*) $_3$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  148.1 (PhCH), 137.8 (*mesitylene*), 131.0 (Ph), 127.0 (*mesitylene*), 123.0 (Ph), 115.4 (CHBpin), 83.6 (*Bpin*), 24.9 (*Bpin*), 21.3 (*mesitylene*) ppm.

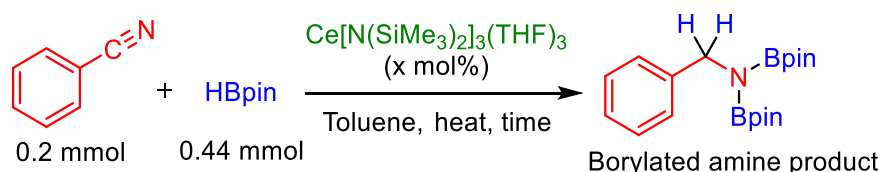
## 4.5. Results and discussion of nitrile (C≡N) hydroboration reaction

### 4.5.1. Reaction optimization:

Nitriles represent a valuable methodology in organic chemistry for the synthesis of primary amines. Primary amines find diverse applications across various fields, adding to their significance.<sup>19</sup> Several synthetic methodologies have been reported for the reduction of nitriles, but hydroboration reaction possesses more advantages due to its atom efficiency and mild reaction conditions.<sup>2</sup> We started the experiment by taking benzonitrile (0.2 mmol) and HBpin (0.44 mmol) in toluene in the presence of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ . Subsequently, we conducted experiments involving variations in catalyst loading, temperature and reaction time. Ultimately, we observed that the optimized conditions for the hydroboration reaction of benzonitrile were achieved with 2 mol% of the catalyst at 80 °C for a duration of 12 hours (**Table 4.3**).

In the same manner, we did two control experiments by taking benzonitrile (0.2 mmol) and HBpin (0.44 mmol): (i) without catalyst at 70 °C in 12 hours, but we observed an 18% yield of the corresponding borylated amine product (**Entry 7; Table 4.3**), suggesting a significant role of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  in benzonitrile hydroboration reaction; (ii) hidden  $\text{BH}_3$  catalysis test: 2 mol% of catalyst in presence of 20 mol% of TMEDA at 70 °C in 12 hours, we observed 94% yield of the borylated product (**Entry 8; Table 4.3**), revealing the negligible effect of  $\text{BH}_3$  in the benzonitrile hydroboration reaction and it followed the true catalysis pathway.<sup>18</sup>

**Table 4.3.** Optimization of reaction conditions for benzonitrile hydroboration.



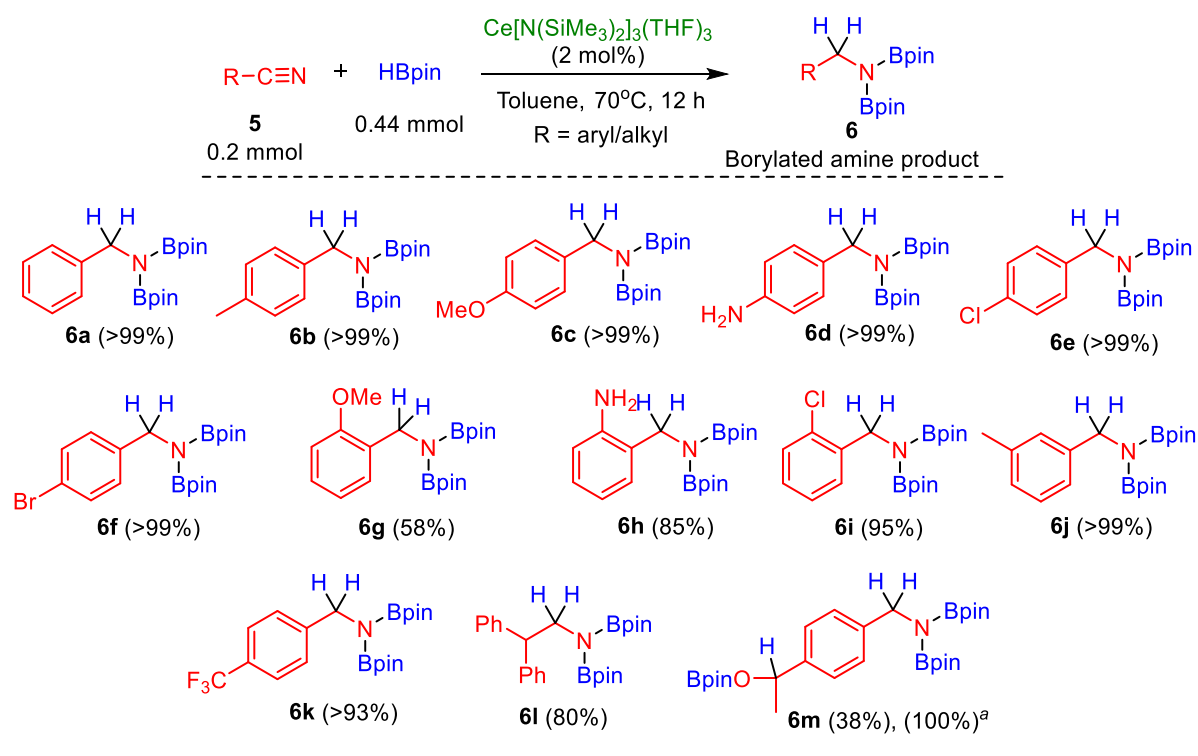
| Entry | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$<br>(mol%) | Temperature<br>(°C) | Time<br>(h) | Yield*<br>(%) |
|-------|------------------------------------------------------------------|---------------------|-------------|---------------|
| 1.    | 2                                                                | 70                  | 24          | >99           |
| 2.    | 2                                                                | 70                  | 12          | >99           |
| 3.    | 1                                                                | 70                  | 12          | 51            |
| 4.    | 2                                                                | 50                  | 12          | 51            |

|    |                                        |    |    |    |
|----|----------------------------------------|----|----|----|
| 5. | 2                                      | 70 | 8  | 45 |
| 6. | 2                                      | rt | 12 | 5  |
| 7. | -                                      | 70 | 12 | 18 |
| 8. | 2 (in presence of 20<br>mol% of TMEDA) | 70 | 12 | 94 |

[Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene).]

#### 4.5.2. Substrate scope:

After finalizing the optimization of the reaction conditions for the hydroboration of benzonitrile with HBpin in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ , we extended our investigation to encompass a wide range of aromatic and aliphatic substrates under these same optimized conditions. We demonstrated a variety of substrates containing electron-withdrawing and electron-donating group substituted nitriles and observed good to excellent yields under the optimized reaction conditions (**Scheme 4.4**). We audited comparatively less yields for the hydroboration of aliphatic nitriles than aromatic nitriles. We observed that the *ortho*- and *meta*-substituted benzonitriles affected more in yield of the borylated amine products (**6g**, **6h**, **6i** & **6l**). In presence of two  $-\text{CF}_3$  group at the *meta*-position of benzonitrile, afforded less yield (42%, **6l**). We also performed the hydroboration of 4-acetylbenzonitrile, which delivered 100% yield corresponding to the hydroboration of the ketone group and 38% yield corresponding to the hydroboration of the nitrile group (**6m**, **Scheme 4.4**).



**Scheme 4.4.** Substrate scope of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed nitriles hydroboration reaction. <sup>a</sup>Hydroboration of ketone. <sup>b</sup> $\text{C}_6\text{D}_6$  as a solvent. [Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (mesitylene)]

#### Analytical data of the borylated products:

**6a:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.34-7.31 (t, 3H, Ph), 7.28-7.24 (m, 2H, Ph), 6.82 (s, 3H, mesitylene), 4.26 (s, 2H,  $\text{PhCH}_2$ ), 2.30 (s, 9H, mesitylene), 1.22 (s, 24H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  143.2 (Ph), 137.8 (mesitylene), 128.4 (Ph), 127.6 (Ph), 127.0 (mesitylene), 126.2 (Ph), 82.4 (Bpin), 47.4 ( $\text{CH}_2\text{Ph}$ ), 24.6 (Bpin), 21.3 (mesitylene) ppm.

**6b:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.23-7.21 (d, 2H, Ph), 7.07-7.05 (d, 2H, Ph), 6.81 (s, 3H, mesitylene), 4.21 (s, 2H,  $\text{CH}_2$ ), 2.31 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.29 (s, 9H, mesitylene), 1.21 (s, 24H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  139.9 (Ph), 137.7 (mesitylene), 129.0 (Ph), 128.5 (Ph), 127.5 (Ph), 127.0 (mesitylene), 82.3 (Bpin), 45.0 ( $\text{CH}_2\text{Ph}$ ), 24.6 (Bpin), 21.2 (mesitylene), 21.1 ( $\text{CH}_3\text{Ph}$ ) ppm.

**6c:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.30-7.28 (d, 2H, Ph), 6.83 (s, 3H, mesitylene), 6.81 (bs, 2H, Ph), 4.20 (s, 2H,  $\text{PhCH}_2$ ), 3.80 (s, 3H,  $\text{PhOCH}_3$ ), 2.31 (s, 9H, mesitylene), 1.24 (s, 24H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  158.4 ( $\text{PhOCH}_3$ ), 137.6

(*mesitylene*), 129.5 (*Ph*), 127.9 (*Ph*), 126.9 (*mesitylene*), 113.7 (*Ph*), 82.1 (*Bpin*), 55.2 (*OCH<sub>3</sub>Ph*), 44.6 (*CH<sub>2</sub>Ph*), 24.7 (*Bpin*), 21.2 (*mesitylene*) ppm.

**6d:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.21-7.19 (d, 2H, *Ph*), 7.01-6.99 (d, 2H, *Ph*), 6.84 (s, 3H, *mesitylene*), 4.18 (s, 2H, PhCH<sub>2</sub>), 2.32 (s, 9H, *mesitylene*), 1.24 (s, 24H, N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 142.0 (*Ph*), 137.7 (*mesitylene*), 128.5 (*Ph*), 127.6 (*Ph*), 126.9 (*mesitylene*), 117.6 (*Ph*), 83.0 (PhN(*Bpin*)<sub>2</sub>), 82.2 (*Bpin*), 44.8 (*CH<sub>2</sub>Ph*), 24.6 (*Bpin*), 21.2 (*mesitylene*) ppm.

**6e:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.28-7.26 (d, 2H, *Ph*), 7.24-7.22 (d, 2H, *Ph*), 6.82 (s, 3H, *mesitylene*), 4.21 (s, 2H, PhCH<sub>2</sub>), 2.30 (s, 9H, *mesitylene*), 1.22 (s, 24H, N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 141.7 (ClPh), 137.8 (*mesitylene*), 131.8 (*Ph*), 129.0 (*Ph*), 128.0 (*Ph*), 127.0 (*mesitylene*), 82.5 (*Bpin*), 46.7 (*CH<sub>2</sub>Ph*), 24.6 (*Bpin*), 21.3 (*mesitylene*) ppm.

**6f:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.41-7.39 (d, 2H, *Ph*), 7.24-7.22 (d, 2H, *Ph*), 6.84 (s, 3H, *mesitylene*), 4.21 (s, 2H, PhCH<sub>2</sub>), 2.32 (s, 9H, *mesitylene*), 1.24 (s, 24H, N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 142.2 (BrPh), 137.7 (*mesitylene*), 131.4 (*Ph*), 130.9 (*Ph*), 129.4 (*Ph*), 127.0 (*mesitylene*), 82.5 (*Bpin*), 46.8 (*CH<sub>2</sub>Ph*), 24.6 (*Bpin*), 21.3 (*mesitylene*) ppm.

**6g:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.59-7.54 (m, 1H, *Ph*), 7.19-7.16 (m, 1H, *Ph*), 7.04-6.98 (m, 1H, *Ph*), 6.93-6.89 (m, 1H, *Ph*), 6.84 (s, 3H, *mesitylene*), 4.32 (s, 2H, PhCH<sub>2</sub>), 3.82 (s, 3H, OCH<sub>3</sub>Ph), 2.31 (s, 9H, *mesitylene*), 1.22 (s, 24H, N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 161.3 (MeOPh), 137.7 (*mesitylene*), 134.4 (*Ph*), 133.8 (*Ph*), 126.9 (*mesitylene*), 120.8 (*Ph*), 120.4 (*Ph*), 111.3 (*Ph*), 82.0 (*Bpin*), 56.0 (OCH<sub>3</sub>Ph), 40.9 (*CH<sub>2</sub>Ph*), 24.6 (*Bpin*), 21.2 (*mesitylene*) ppm.

**6h:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.44-7.31 (m, 3H, *Ph*), 6.82 (s, 3H, *mesitylene*), 6.76-6.72 (m, 1H, *Ph*), 4.49 (s, 2H, PhCH<sub>2</sub>), 2.30 (s, 9H, *mesitylene*), 1.29 (s, 24H, N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 149.8 (*Ph*), 137.7 (*mesitylene*), 134.0 (*Ph*), 132.3 (*Ph*), 126.9 (*mesitylene*), 120.1 (*Ph*), 117.8 (*Ph*), 115.2 (*Ph*), 83.1 (*Bpin*), 43.8 (*CH<sub>2</sub>Ph*), 24.6 (*Bpin*), 21.2 (*mesitylene*) ppm.

**6i:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 7.33-7.31 (m, 2H, *Ph*), 7.24-7.20 (m, 1H, *Ph*), 7.16-7.12 (m, 1H, *Ph*), 6.84 (s, 3H, *mesitylene*), 4.39 (s, 2H, PhCH<sub>2</sub>), 2.31 (s, 9H, *mesitylene*), 1.22 (s, 24H, N(*Bpin*)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 140.1 (*Ph*), 137.7

(*mesitylene*), 132.8 (*Ph*), 129.3 (*Ph*), 128.9 (*Ph*), 128.3 (*Ph*), 127.9 (*Ph*), 127.0 (*mesitylene*), 82.5 (*Bpin*), 45.2 ( $\text{CH}_2\text{Ph}$ ), 24.6 (*Bpin*), 21.3 (*mesitylene*) ppm.

**6j:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.16-7.13 (m, 3H, *Ph*), 6.99-6.97 (d, 1H, *Ph*), 6.81 (s, 3H, *mesitylene*), 4.23 (s, 2H,  $\text{PhCH}_2$ ), 2.32 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.29 (s, 9H, *mesitylene*), 1.22 (s, 24H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  143.0 (*Ph*), 137.7 (*mesitylene*), 128.4 (*Ph*), 127.8 (*Ph*), 127.0 (*mesitylene*), 126.8 (*Ph*), 124.6 (*Ph*), 123.9 (*Ph*), 82.3 (*Bpin*), 47.2 ( $\text{CH}_2\text{Ph}$ ), 24.6 (*Bpin*), 21.4 ( $\text{CH}_3\text{Ph}$ ), 21.2 (*mesitylene*) ppm.

**6k:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.53-7.51 (d, 2H, *Ph*), 7.43-7.41 (d, 2H, *Ph*), 6.81 (s, 3H, *mesitylene*), 4.29 (s, 2H,  $\text{PhCH}_2$ ), 2.29 (s, 9H, *mesitylene*), 1.21 (s, 24H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  147.2 (*Ph*), 137.8 (*mesitylene*), 129.2 (*Ph*), 128.4 (*Ph*), 127.8 (*Ph*), 127.0 (*mesitylene*), 124.9 ( $\text{CF}_3\text{Ph}$ ), 82.6 (*Bpin*), 47.1 ( $\text{CH}_2\text{Ph}$ ), 24.6 (*Bpin*), 21.3 (*mesitylene*) ppm.

**6l:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.36-7.22 (m, 8H, *Ph*), 7.16-7.13 (m, 2H, *Ph*), 6.81 (s, 3H, *mesitylene*), 4.26-4.22 (t, 1H,  $(\text{Ph})_2\text{CHCH}_2$ ), 3.73-3.71 (d, 2H,  $\text{CHCH}_2$ ), 2.29 (s, 9H, *mesitylene*), 1.16 (s, 24H,  $\text{N}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  143.5 (*Ph*), 137.8 (*mesitylene*), 128.8 (*Ph*), 128.2 (*Ph*), 127.0 (*mesitylene*), 126.1 (*Ph*), 82.2 (*Bpin*), 53.6 ( $\text{CHCH}_2\text{Ph}$ ), 48.5 ( $\text{CHCH}_2\text{Ph}$ ), 24.5 (*Bpin*), 21.3 (*mesitylene*) ppm.

**6m:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.34-7.24 (m, 4H, *Ph*), 6.82 (s, 3H, *mesitylene*), 5.28-5.20 (m, 1H,  $\text{PhCH}(\text{OBpin})\text{CH}_3$ ), 4.23 (s, 2H,  $\text{PhCH}_2$ ), 2.29 (s, 9H, *mesitylene*), 1.51-1.48 (d, 3H,  $\text{PhCH}(\text{OBpin})\text{CH}_3$ ), 1.28 (s, 24H,  $\text{N}(\text{Bpin})_2$ ), 1.21 (s, 12H,  $\text{OBpin}$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  143.0 (*Ph*), 141.8 (*Ph*), 137.7 (*mesitylene*), 126.9 (*mesitylene*), 126.6 (*Ph*), 125.4 (*Ph*), 82.7 ( $\text{OBpin}$ ), 82.2 ( $\text{N}(\text{Bpin})_2$ ), 72.4 ( $\text{CH}_3\text{CHOBpin}$ ), 45.0 ( $\text{PhCH}_2$ ), 25.5 ( $\text{CH}_3\text{CHOBpin}$ ), 24.6 ( $\text{OBpin}$ ), 24.5 ( $\text{N}(\text{Bpin})_2$ ), 21.2 (*mesitylene*) ppm.

## 4.6. Results and discussion of deoxygenation of isocyanate ( $\text{N}=\text{C}=\text{O}$ )

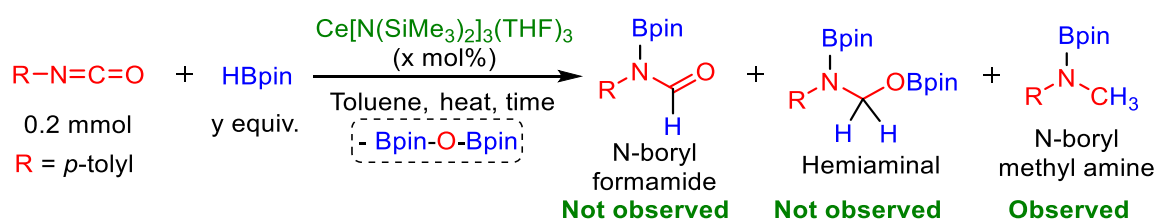
### 4.6.1. Reaction optimization:

We initiated our exploration toward the hydroboration of isocyanate by taking 0.2 mmol of *p*-tolyl isocyanate with 3.3 equivalents of HBpin in the presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as a catalyst afforded highly selective deoxygenated product. After that, we utilized 2.2 and 1.1 equivalents of HBpin to get dihydroborated and monohydroborated products, respectively. But

surprisingly we only noticed the deoxygenated product of *p*-tolyl isocyanate (Entry 4 & 5, **Table 4.4**), which indicates that the catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  is highly selective towards the deoxygenation of isocyanates in presence of HBpin in different concentrations. Thereafter, we examined the reaction conditions for hydroboration of *p*-tolyl isocyanate and found that 2 mol% of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  with 3.3 equivalents of HBpin at 80 °C temperature in 24 hours were the productive parameters for *p*-tolyl isocyanate hydroboration to afford *N*-boryl methyl amine in a quantitative yield (**Table 4.4**).

Similarly, we did two control experiments by taking *p*-tolyl isocyanate (0.2 mmol) and HBpin (0.66 mmol): (i) without catalyst at 80 °C in 24 hours, but we observed 33% yield of the corresponding *N*-boryl methyl amine product (**Entry 10; Table 4.4**), which suggests a cabalistic role of catalyst  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  in isocyanates hydroboration reaction; (ii) hidden  $\text{BH}_3$  catalysis test as a model experiment of hydroboration reaction in presence of HBpin: 2 mol% of catalyst in presence of 20 mol% of TMEDA at 80 °C in 24 hours, we observed 93% yield of the *N*-boryl methyl amine product (**Entry 11; Table 4.4**), intimating that the negligible effect of  $\text{BH}_3$  in the *p*-tolyl isocyanate hydroboration reaction and the hydroboration of isocyanate in presence of HBpin and  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  followed the true catalysis pathway.<sup>18</sup>

**Table 4.4.** Optimization of reaction conditions for *p*-tolyl isocyanate hydroboration.



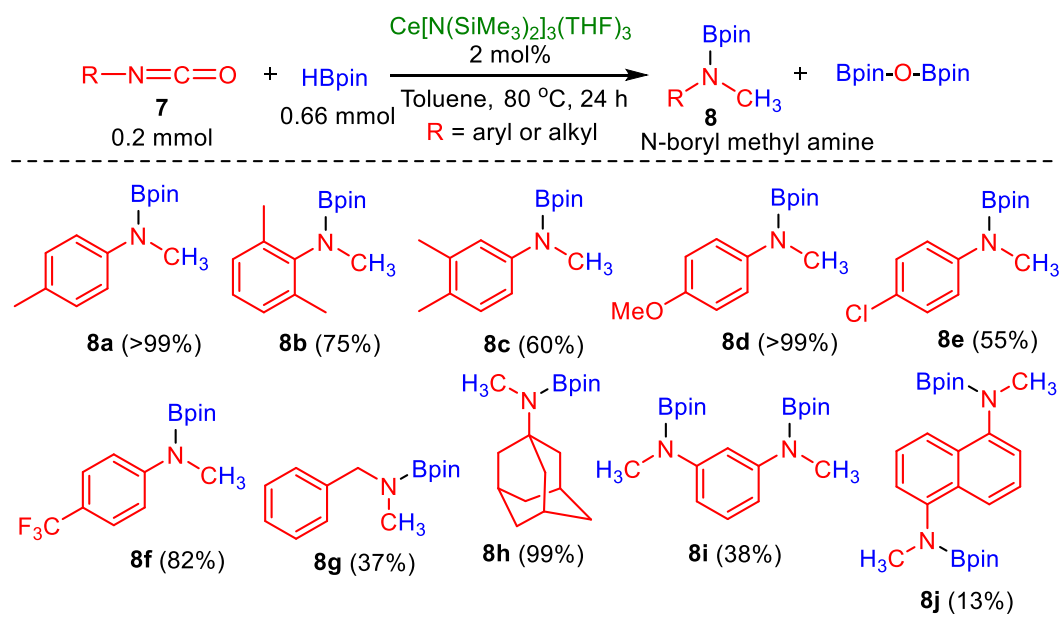
| Entry | $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$<br>(mol%) | HBpin<br>(equiv.) | Temperature<br>(°C) | Time<br>(h) | Yield*<br>(%) |
|-------|------------------------------------------------------------------|-------------------|---------------------|-------------|---------------|
| 1.    | 5                                                                | 3.3               | 80                  | 24          | >99           |
| 2.    | 2                                                                | 3.3               | 80                  | 24          | >99           |
| 3.    | 1                                                                | 3.3               | 80                  | 24          | 57            |
| 4.    | 2                                                                | 2.2               | 80                  | 24          | 80            |
| 5.    | 2                                                                | 1.1               | 80                  | 24          | 25            |
| 6.    | 2                                                                | 3.3               | rt                  | 24          | 20            |
| 7.    | 2                                                                | 3.3               | 70                  | 24          | 72            |

|            |                                        |     |    |    |                 |
|------------|----------------------------------------|-----|----|----|-----------------|
| <b>8.</b>  | 2                                      | 3.3 | 80 | 20 | 95              |
| <b>9.</b>  | 2                                      | 3.3 | 80 | 24 | 85 <sup>#</sup> |
| <b>10.</b> | -                                      | 3.3 | 80 | 24 | 33              |
| <b>11.</b> | 2 (in presence of 20<br>mol% of TMEDA) | 3.3 | 80 | 24 | 93              |

[Yields were determined by integrating <sup>1</sup>H NMR spectra in the presence of an internal standard (dibromomethane).]

#### 4.6.2. Substrate scope:

Having completed the optimization of the hydroboration reaction, we proceeded to investigate the scope of isocyanate substrates. All the substrates yielded deoxygenated N-boryl methyl amine products with moderate to excellent yields (up to >99%). Adamantane substituted isocyanate delivered >99% yield of the deoxygenated N-boryl methyl amine product. So, Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> behaves as an efficient and highly selective catalyst for the hydroboration of isocyanate using HBpin to synthesize deoxygenated N-boryl methyl amine product. In presence of two isocyanate groups in a substrate decreases the yield of the N-boryl methyl product (**8i** & **8j**, **Scheme 4.5**) due to the highly electrophilic nature of the –N=C=O group. In 2022, Khalimon and co-workers reported a catalyst free approach of the isocyanate hydroboration reaction. Which is quite in line with our Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>-catalysed hydroboration of isocyanates (for example **8a**; yield without catalyst was 98% and yield with our catalyst was >99%). Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub>-catalysed hydroboration of **7d** afforded almost complete conversion to **8e** with >99% yield, whereas catalyst-free condition did not work for this substrate **7d**. On the other hand, **7e** and **7g** delivered higher yield at neat and catalyst-free condition, whereas our catalyst was comparatively less reactive toward the substrates **7e** and **7g**. But, at the catalyst-free condition **7g** delivered a mixture of products N-boryl formamide and N-boryl methyl amine. So, we can conclude that always a solvent-free and catalyst-free condition is the best conditions, but for all the substrates its does not work and we need a better catalyst to perform the catalytic reaction, which accelerate to reach the desire products.



**Scheme 4.5.** Substrate scope of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed isocyanate hydroboration reaction. [Yields were determined by integrating  $^1\text{H}$  NMR spectra in the presence of an internal standard (dibromomethane)]

#### Analytical data of the borylated products:

**8a:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.20-7.18 (d, 2H, *Ph*), 7.07-7.05 (d, 2H, *Ph*), 4.92 (s, 2H, *dibromomethane*), 3.04 (s, 3H,  $\text{NCH}_3$ ), 2.28 ( $\text{CH}_3\text{Ph}$ ), 1.29 (s, 12H,  $\text{NBpin}$ ), 1.28 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  147.1 (*Ph*), 129.6 (*Ph*), 124.6 (*Ph*), 112.7 (*Ph*), 82.9 (*Bpin*), 31.0 ( $\text{NCH}_3$ ), 24.5 (*Bpin*), 20.3 ( $\text{CH}_3\text{Ph}$ ), 19.1 (*dibromomethane*) ppm.

**8b:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.17-7.16 (d, 1H, *Ph*), 7.06-7.04 (d, 2H, *Ph*), 4.92 (s, 2H, *dibromomethane*), 3.03 (s, 3H,  $\text{NCH}_3$ ), 2.24 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.19 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 1.28 (s, 12H,  $\text{NBpin}$ ), 1.28 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  147.7 (*Ph*), 130.3 (*Ph*), 120.8 (*Ph*), 114.3 (*Ph*), 83.1 (*Bpin*), 82.6 (*Bpin*), 31.1 ( $\text{NCH}_3$ ), 24.7 (*Bpin*), 24.6 (*Bpin*), 20.2 ( $\text{CH}_3\text{Ph}$ ), 20.1 ( $\text{CH}_3\text{Ph}$ ), 19.1 (*dibromomethane*) ppm.

**8c:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.02 (s, 1H, *Ph*), 7.00-6.96 (m, 2H, *Ph*), 4.90 (s, 2H, *dibromomethane*), 2.79 ( $\text{NCH}_3$ ), 2.29 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 2.23 (s, 3H,  $\text{CH}_3\text{Ph}$ ), 1.26 (s, 12H + 24H,  $\text{NBpin}$  +  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  144.2 (*Ph*), 136.1 (*Ph*), 129.1 (*Ph*), 128.9 (*Ph*), 128.3 (*Ph*), 125.8 (*Ph*), 83.1 (*Bpin*), 82.4 (*Bpin*), 35.5 ( $\text{NCH}_3$ ), 24.6 (*Bpin*), 24.5 (*Bpin*), 19.01 (*dibromomethane*), 18.4 ( $\text{CH}_3\text{Ph}$ ), 17.9 ( $\text{CH}_3\text{Ph}$ ) ppm.

**8d:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  6.79-6.77 (d, 2H, *Ph*), 6.58-6.56 (d, 2H, *Ph*), 4.91 (s, 2H, *dibromomethane*), 3.73 ( $\text{OCH}_3\text{Ph}$ ), 2.78 (s, 3H,  $\text{NCH}_3$ ), 1.25 (s, 12H + 24H,  $\text{NBpin} + \text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  152.2 (*Ph*), 143.6 (*Ph*), 129.0 (*Ph*), 114.8 (*Ph*), 83.0 (*Bpin*), 55.8 ( $\text{CH}_3\text{OPh}$ ), 31.6 ( $\text{NCH}_3$ ), 24.5 (*Bpin*), 19.0 (*dibromomethane*) ppm.

**8e:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.11-7.09 (d, 2H, *Ph*), 6.52-6.49 (d, 2H, *Ph*), 4.92 (s, 2H, *dibromomethane*), 2.78 (s, 3H,  $\text{NCH}_3$ ), 1.25 (s, 12H + 24H,  $\text{NBpin} + \text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  148.0 (*Ph*), 129.0 (*Ph*), 128.3 (*Ph*), 113.6 (*Ph*), 83.2 (*Bpin*), 30.8 ( $\text{NCH}_3$ ), 24.5 (*Bpin*), 19.0 (*dibromomethane*) ppm.

**8f:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.48-7.46 (d, 2H, *Ph*), 7.40-7.37 (d, 2H, *Ph*), 4.92 (s, 2H, *dibromomethane*), 3.06 (s, 3H,  $\text{NCH}_3$ ), 1.29 (s, 12H,  $\text{NBpin}$ ), 1.26 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  150.7 (*Ph*), 126.6 (*Ph*), 125.8 (*Ph*), 118.0 (*Ph*), 111.4 (*Ph*), 83.3 (*Bpin*), 83.2 (*Bpin*), 34.2 ( $\text{NCH}_3$ ), 24.7 (*Bpin*), 24.6 (*Bpin*), 19.0 (*dibromomethane*) ppm.

**8g:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.45-7.43 (m, 1H, *Ph*), 7.33-7.31 (m, 2H, *Ph*), 7.24-7.21 (m, 2H, *Ph*), 4.91 (s, 2H, *dibromomethane*), 4.04 (s, 2H,  $\text{PhCH}_2\text{N}$ ), 2.47 (s, 3H,  $\text{NCH}_3$ ), 1.25 (s, 24H,  $\text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  140.3 (*Ph*), 129.1 (*Ph*), 128.7 (*Ph*), 126.7 (*Ph*), 83.0 (*Bpin*), 82.3 (*Bpin*), 52.9 ( $\text{PhCH}_2$ ), 33.3 ( $\text{NCH}_3$ ), 24.7 (*Bpin*), 24.7 (*Bpin*), 19.0 (*dibromomethane*) ppm.

**8h:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  4.87 (s, 2H, *dibromomethane*), 2.27 (s, 3H,  $\text{NCH}_3$ ), 2.00 (s, 4H,  $(\text{CH}_2)_2$ ), 1.59 (s, 3H,  $(\text{CH})_3$ ), 1.55 (s, 8H,  $(\text{CH}_2)_4$ ), 1.19 (s, 12H + 24H,  $\text{NBpin} + \text{O}(\text{Bpin})_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  83.0 (*Bpin*), 42.0 ( $\text{CNBpin}$ ), 41.7 ( $\text{NCCH}_2$ ), 36.7 ( $\text{CHCH}_2$ ), 29.5 ( $\text{NCH}_3$ ), 24.5 (*Bpin*), 22.6 ( $\text{CHCH}_2$ ), 19.0 (*dibromomethane*) ppm.

**8i:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.30-7.28 (m, 1H, *Ph*), 7.19-7.08 (m, 2H, *Ph*), 6.92-6.68 (m, 1H, *Ph*), 4.93 (s, 2H, *dibromomethane*), 3.05 (s, 3H,  $\text{NCH}_3$ ), 1.28 (s, 24H + 48H,  $(\text{NBpin} + \text{O}(\text{Bpin})_2)_2$ ) ppm;  $^{13}\text{C}$  NMR (100.613 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  147.8 (*Ph*), 128.6 (*Ph*), 119.4 (*Ph*), 112.3 (*Ph*), 83.1 (*Bpin*), 82.5 (*Bpin*), 34.4 ( $\text{NCH}_3$ ), 34.2 ( $\text{NCH}_3$ ), 24.7 (*Bpin*), 24.6 (*Bpin*), 19.1 (*dibromomethane*) ppm.

**8j:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.19-7.08 (m, 4H, *Naphthalene*), (bs, 2H, *Naphthalene*), 4.85 (s, 2H, *dibromomethane*), 2.92 (s, 3H,  $\text{NCH}_3$ ), 1.19 (s, 24H + 48H,  $\{\text{NBpin}$

+ O(*Bpin*)<sub>2</sub>}<sub>2</sub>) ppm; <sup>13</sup>C NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  146.8 (*Naphthalene*), 145.2 (*Naphthalene*), 129.1 (*Naphthalene*), 128.3 (*Naphthalene*), 125.4 (*Naphthalene*), 124.1 (*Naphthalene*), 83.2 (*Bpin*), 31.0 (NCH<sub>3</sub>), 24.6 (*Bpin*), 19.0 (*dibromomethane*) ppm.

## 4.7. Conclusion

In summary, we have utilized Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> complex as an efficient catalyst for the selective reduction of unactivated C=C, C $\equiv$ C, C $\equiv$ N and N=C=O bonds in alkenes, alkynes, nitriles and isocyanates using HBpin under mild conditions. The employment of cost-effective and naturally occurring cerium complex under mild reaction conditions and high selectivity is advantageous for sustainable catalysis. For the first time, we have introduced lanthanide-catalysed hydroboration of alkynes and isocyanates under mild reaction conditions. We have demonstrated the reduction of C $\equiv$ C in alkynes to selective linear borylated alkenes at 70 °C temperature in 12 hours with very good yields. Also, the reduction of isocyanates with HBpin was accomplished in the presence of verily accessible catalyst Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> (2 mol%) at 80 °C temperature in 24 hours reaction time. Similarly, the hydroboration of isocyanates is highly selective towards deoxygenation reaction, which afforded only *N*-boryl methyl amine products. Finally, we can say that Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>3</sub> is a versatile and multi-tasking catalyst for the hydroboration reaction in synthetic organic chemistry.

## 4.8. NMR spectra

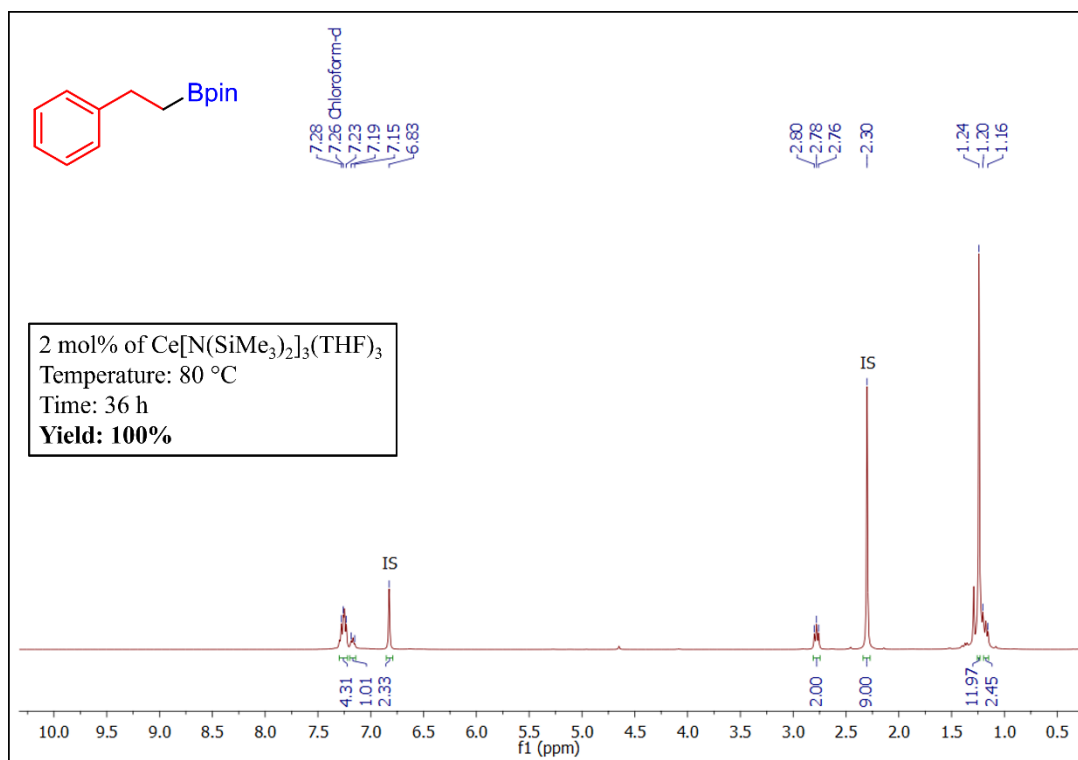


**Figure 4.1.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of styrene (0.2 mmol) with HBpin at 80 °C in 36 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (IS: internal standard mesitylene).

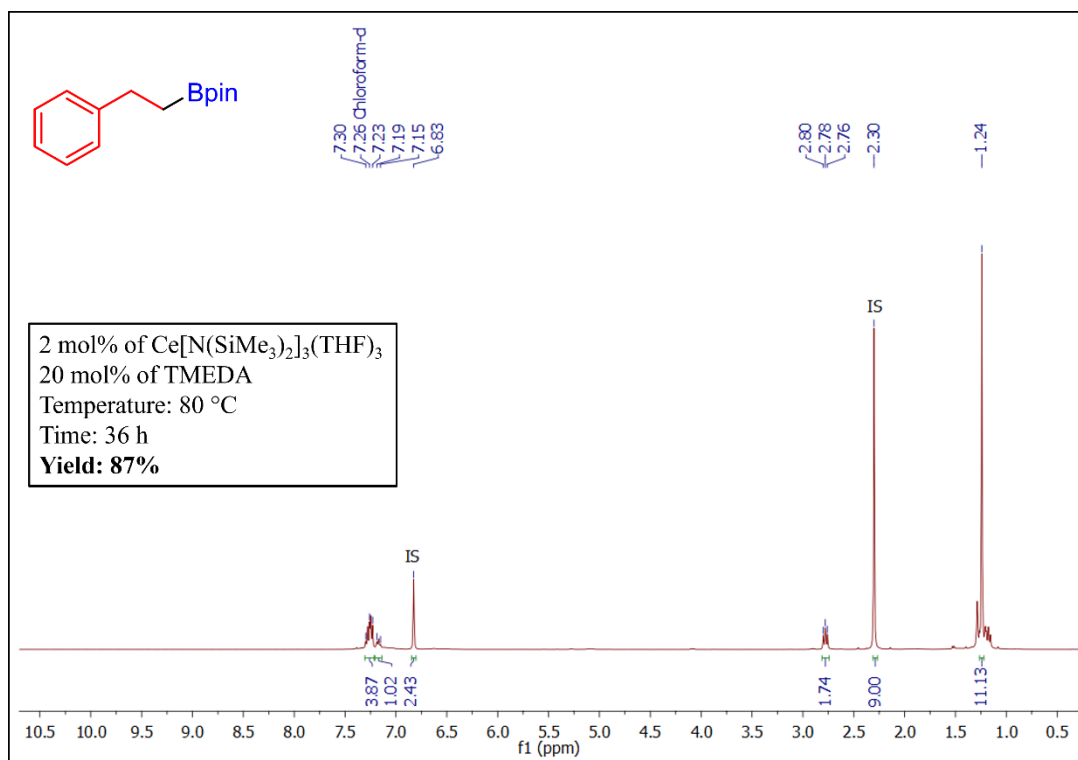


**Figure 4.2.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of styrene (0.2 mmol) with HBpin at 80 °C in 36 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and 20 mol% of TMEDA (IS: internal standard mesitylene).

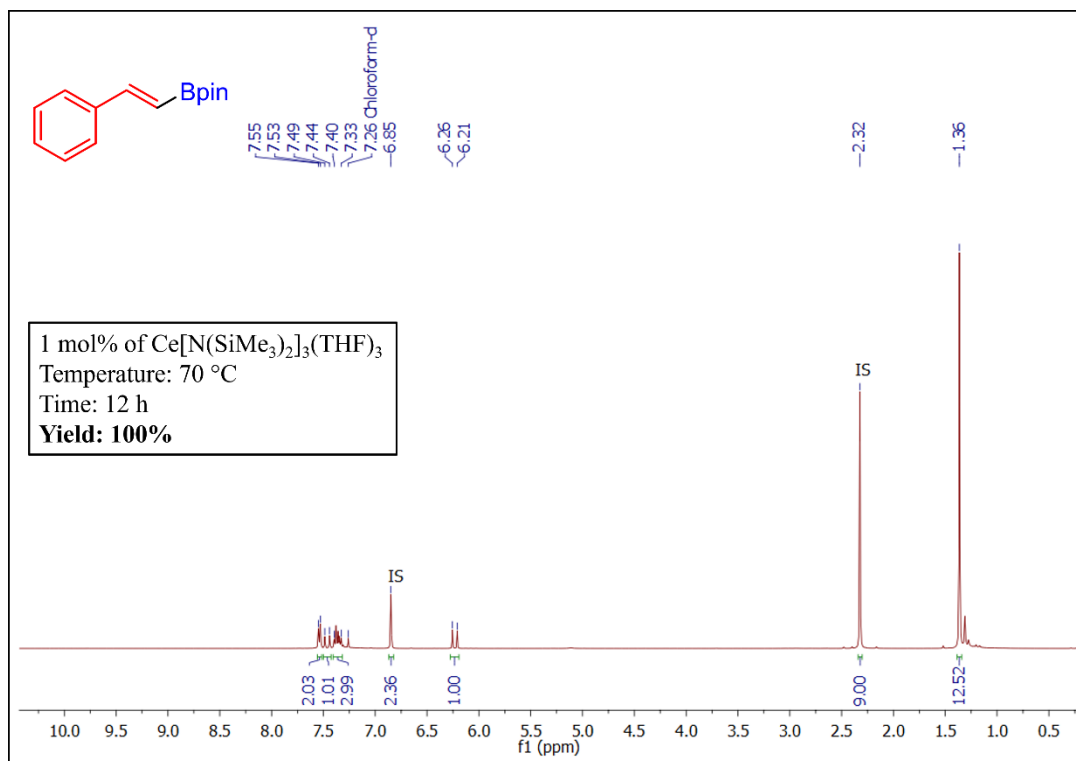


**Figure 4.3.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of phenylacetylene (0.2 mmol) with HBpin at 70 °C in 12 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (IS: internal standard mesitylene).

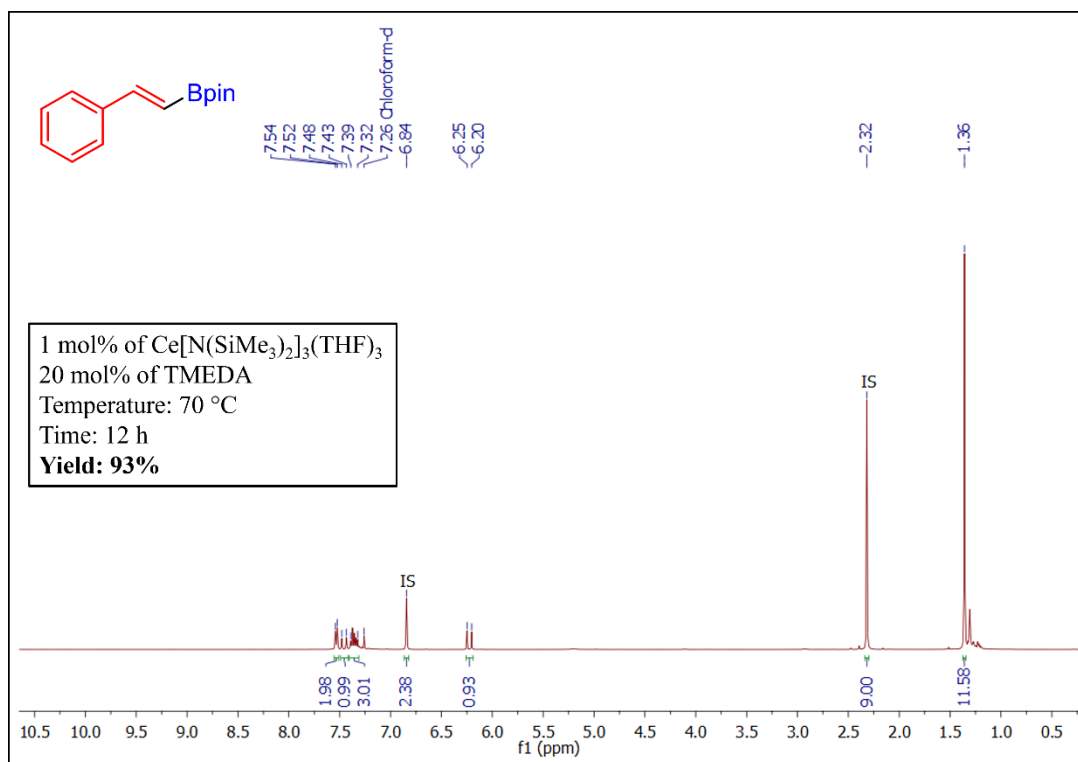


**Figure 4.4.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of phenylacetylene (0.2 mmol) with HBpin at 70 °C in 12 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and 20 mol% of TMEDA (IS: internal standard mesitylene).

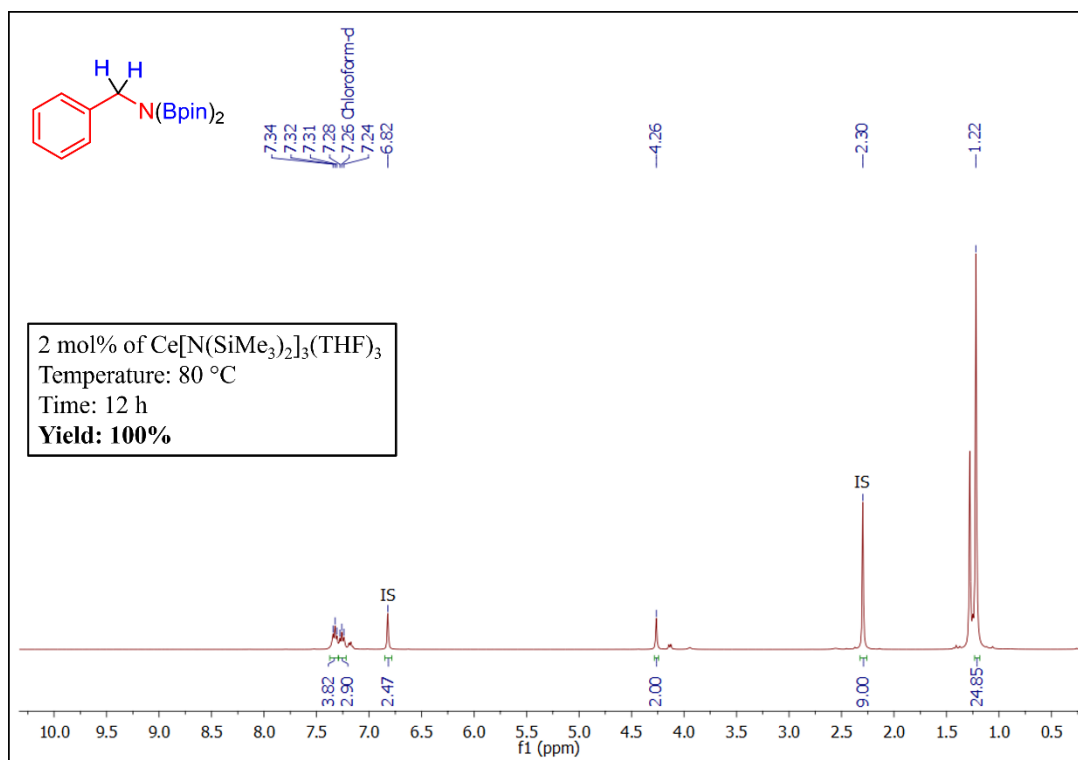


**Figure 4.5.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of benzonitrile (0.2 mmol) with HBpin at 80 °C in 24 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (IS: internal standard mesitylene).

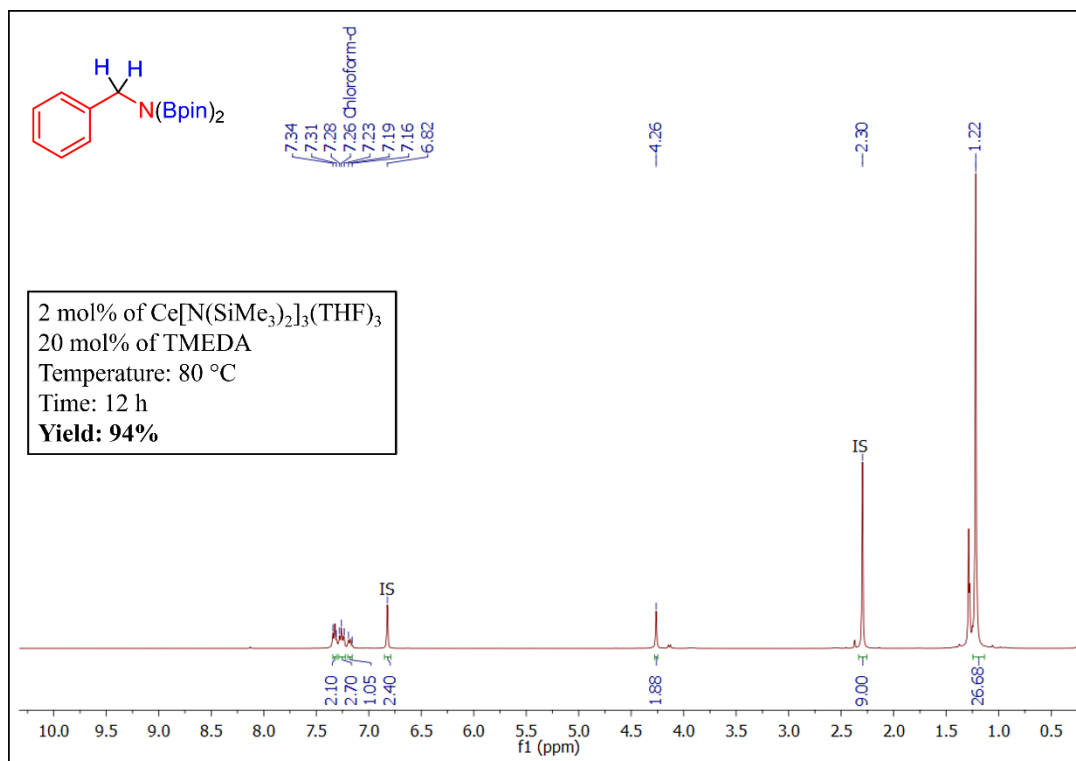


**Figure 4.6.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of benzonitrile (0.2 mmol) with HBpin at 80 °C in 24 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and 20 mol% of TMEDA (IS: internal standard mesitylene).

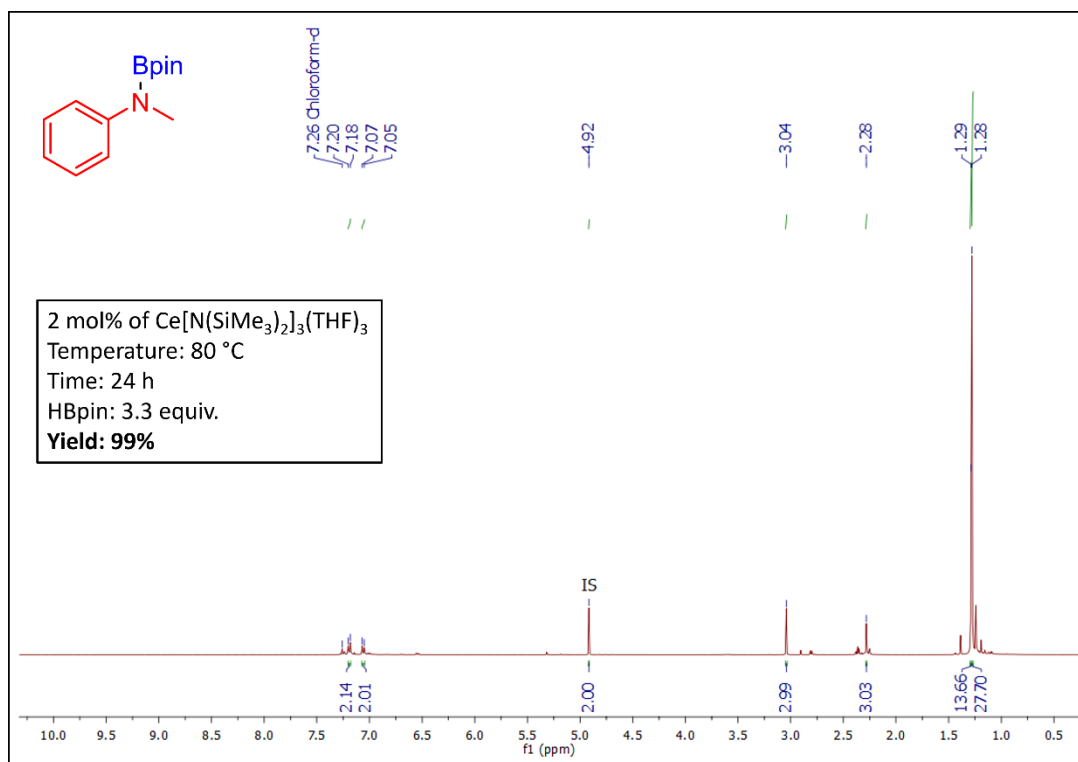


**Figure 4.7.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of *p*-tolyl isocyanate (0.2 mmol) with HBpin at 80 °C in 24 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  (IS: internal standard mesitylene).

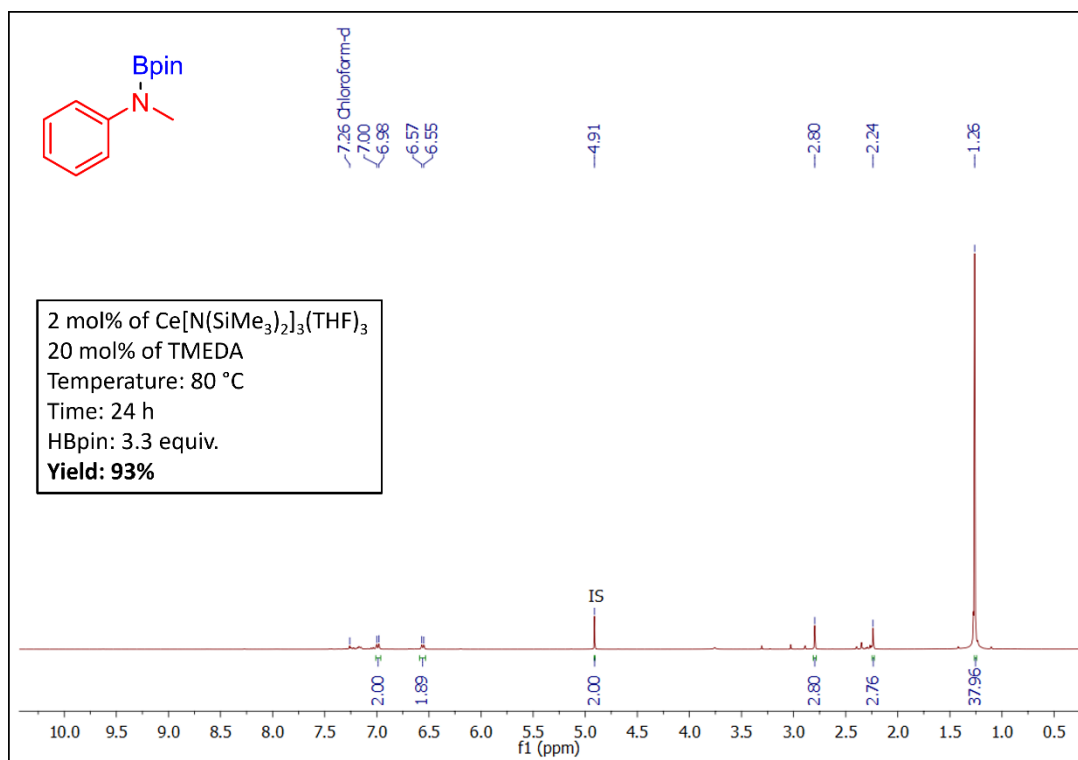


**Figure 4.8.**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz, 298 K] spectrum of hydroboration of *p*-tolyl isocyanate (0.2 mmol) with HBpin at 80 °C in 24 hours in presence of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  and 20 mol% of TMEDA (IS: internal standard mesitylene).

## 4.9. References

1. Lawrence, S. A. *Amines: Synthesis, Properties and Applications*. Cambridge University Press: Cambridge, 2005.
2. Liua, H.; Eisen, M. S. Organo-*f*-Complexes for Efficient and Selective Hydroborations. *Synthesis* **2020**, 52, 629-644.
3. Pritchard, J.; Filonenko, G. A.; Putten, R. van; Hensen, E. J. M.; Pidko, E. A. Heterogeneous and Homogeneous Catalysis for the Hydrogenation of Carboxylic Acid Derivatives: History, Advances and Future Directions. *Chem. Soc. Rev.* **2015**, 44, 3808-3833. (b) Wang, Y.; Wang, M.; Li, Y.; Liu, Q. Homogeneous Manganese-Catalyzed Hydrogenation and Dehydrogenation Reactions. *Chem* **2021**, 7, 1180-1223.
4. Shabade, A. B.; Sharma, D. M.; Bajpai, P.; Gonnade, R. G.; Vanka, K.; Punji, B. Room Temperature Chemoselective Hydrogenation of C=C, C=O and C=N Bonds by Using a Welldefined Mixed Donor Mn(I) Pincer Catalyst. *Chem. Sci.* **2022**, 13, 13764-13773.
5. (a) Kumar, R.; Dutta, S.; Sharma, V.; Singh, P. P.; Gonnade, R. G.; Koley, D.; Sen, S. S. Monomeric Magnesium Catalyzed Alkene and Alkyne Hydroboration. *Chem. Eur. J.* **2022**, 28, e202201896. (b) Kumar, R.; Sharma, V.; Banerjee, S.; Vanka, K.; Sen, S. S. Controlled Reduction of Isocyanates to Formamides Using Monomeric Magnesium. *Chem. Commun.* **2023**, 59, 2255-2258.
6. Choi, J. -H.; Prechtl, M. H. G. Tuneable Hydrogenation of Nitriles into Imines or Amines with a Ruthenium Pincer Complex under Mild Conditions. *ChemCatChem* **2015**, 7, 1023-1028.
7. Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, 115, 6621-6686.
8. Gutsulyak, D. V.; Nikonov, G. I. Chemoselective Catalytic Hydrosilylation of Nitriles. *Angew. Chem., Int. Ed.* **2010**, 49, 7553-7556.
9. Wang, X.; Xu, X. Hydroboration of Nitriles and Imines by Highly Active Zinc Dihydride Catalysts. *RSC Adv.* **2021**, 11, 1128-1133.

10. Harrison, K. N.; Marks, T. J. Organolanthanide-Catalyzed Hydroboration of Olefins. *J. Am. Chem. Soc.* **1992**, *114*, 9220-9221.
11. Evans, D. A.; Muci, A. R.; Stiirmer, R. Samarium(III)-Catalyzed Hydroboration of Olefine with Catecholborane. A General Approach to the Synthesis of Boronate Esters. *J. Org. Chem.* **1993**, *58*, 5307-5309.
12. Bijpost, E. A.; Duchateau, R.; Teuben, J. H. Early Transition Metal Catalyzed Hydroboration of Alkenes. *J. Mol. Catal A: Chem.* **1995**, *95*, 121-128.
13. Villiers, C.; Ephritikhine, M. Novel Hydroboration of Highly Substituted Alkenes catalysed by Borohydride Complexes of Uranium, Neodymium and Zirconium. *J. Chem. Soc., Chem. Commun.* **1995**, 979-980.
14. Horino, Y.; Livinghouse, T.; Stan, M. Alkene-Pinacolborane Hydroborations Catalyzed by Lanthanum Tris[bis(trimethylsilyl)amide]. *Synlett* **2004**, *14*, 2639-2641.
15. Huang, Z.; Wang, S.; Zhu, X.; Yuan, Q.; Wei, Y.; Zhou, S.; Mu, X. Well-Defined Amidate-Functionalized N-Heterocyclic Carbene-Supported Rare-Earth Metal Complexes as Catalysts for Efficient Hydroboration of Unactivated Imines and Nitriles. *Inorg. Chem.* **2018**, *57*, 15069-15078.
16. a) Delebecq, E.; Pascault, J. -P.; Boutevin, B.; Ganachaud, F. On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethane. *Chem. Rev.* **2013**, *113*, 80-118. b) Braunstein, P.; Nobel, D. Transition-Metal-Mediated Reactions of Organic Isocyanates. *Chem. Rev.* **1989**, *89*, 1927-1945. c) Mitchell, S. M.; Sachinethani, K. A. N.; Pulukkody, R.; Pentzer, E. B. 100th Anniversary of Macromolecular Science Viewpoint: Polymerization of Cumulated Bonds: Isocyanates, Allenes, and Ketenes as Monomers. *ACS Macro Lett.* **2020**, *9*, 1046-1059. d) Jurrat, M.; Pointer-Gleadhill, B. J.; Ball, L. T.; Chapman, A.; Adriaenssens, L. Polyurethanes and Polyallophanates via Sequence-Selective Copolymerization of Epoxides and Isocyanates. *J. Am. Chem. Soc.* **2020**, *142*, 8136-8141.
17. Bradley, D. C.; Ghotra, J. S.; Hart, F. A. Low Co-ordination Numbers in Lanthanide and Actinide Compounds. Part 1. The Preparation and Characterization of Tris{bis(trimethylsilyl)-amido}Lanthanides. *J. Chem. Soc., Dalton Trans.* **1973**, 1021-1023.
18. (a) Bage, A. D.; Hunt, T. A.; Thomas, S. P. Hidden Boron Catalysis: Nucleophile Promoted Decomposition of HBpin. *Org. Lett.* **2020**, *22*, 4107-4112. (b) Bage, A. D.;

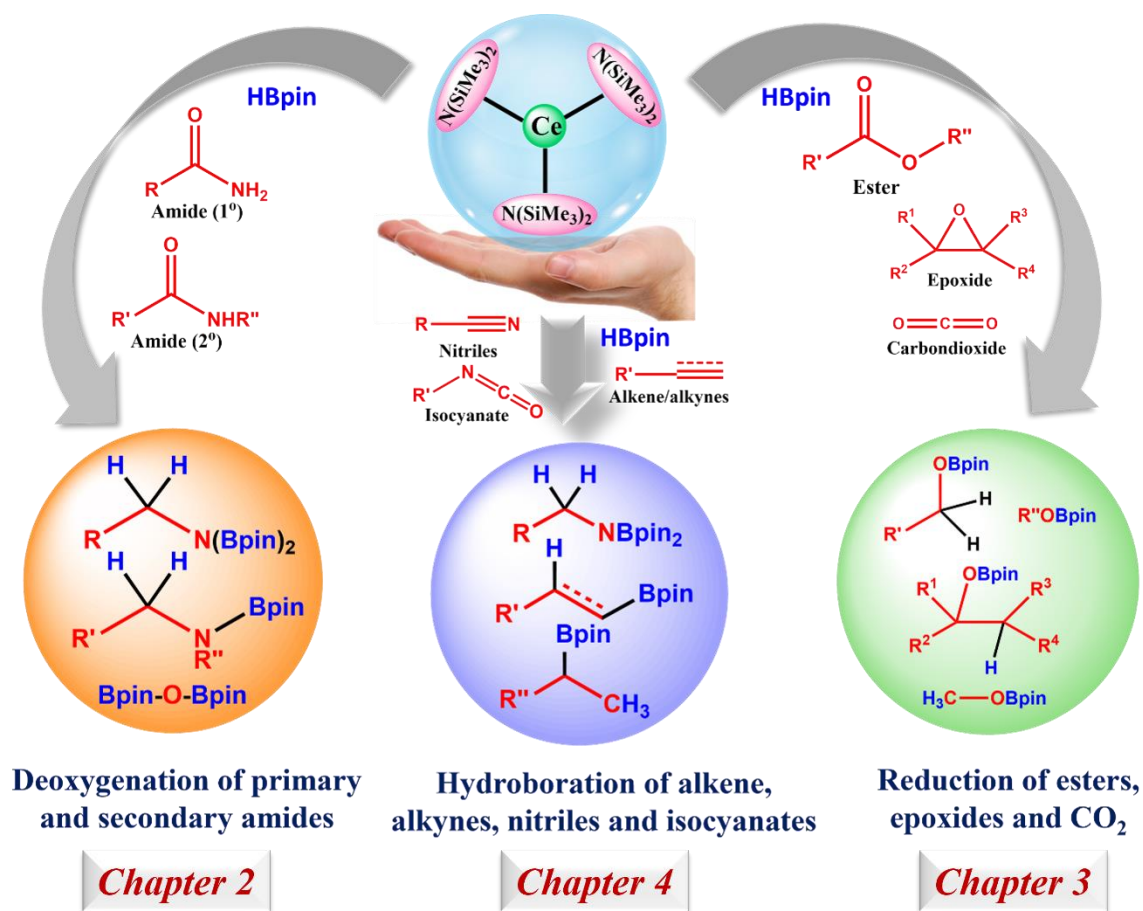
- Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. The Hidden Role of Boranes and Borohydrides in Hydroboration Catalysis. *ACS Catal.* **2020**, *10*, 13479-13486.
19. (a) Hayes, K. S. Industrial processes for manufacturing amines. *Appl. Catal. A-Gen.* **2001**, *221*, 187-195. (b) Pohlki, F.; Doye, S. The catalytic hydroamination of alkynes. *Chem. Soc. Rev.* **2003**, *32*, 104- 114. (c) Lawrence, S. A. *Amines: Synthesis, Properties and Application*; Cambridge University Press: Cambridge, U.K., 2004. (d) Kim, D.; Guengerich, F. P. Cytochrome P450 activation of arylamines and heterocyclic amines. *Annu. Rev. Pharmacol. Toxicol.* **2005**, *45*, 27-49. (e) Severin, R.; Doye, S. The catalytic hydroamination of alkynes. *Chem. Soc. Rev.* **2007**, *36*, 1407-1420. (f) Wang, K.; Guengerich, F. P. Reduction of Aromatic and Heterocyclic Aromatic N-Hydroxylamines by Human Cytochrome P450 2S1. *Chem. Res. Toxicol.* **2013**, *26*, 993-1004.

## Summary

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In the overall conclusion, I can realm that the fundamental object of my wonderful PhD journey was to showcase the utilization of less explored and easily available  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$  as an efficient catalyst for hydroboration reaction. The hydroboration reaction is a very atom-efficient synthetic methodology, which required comparatively mild reaction conditions and the yielded borylated intermediates can easily hydrolysed to afford corresponding products. In my second chapter, we demonstrated the deoxygenation of 1° and 2° amides in the presence of HBpin, whereas comparatively easily reducible 3° amide was unsuccessful by this synthetic methodology. Due to the absence of hydrogen atom at the nitrogen centre in the amide group, which prevented the formation of cerium-amidate species. In the third chapter, I discussed  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{THF})_3$ -catalysed C–O bond cleavage of esters, epoxides and  $\text{CO}_2$  using HBpin, which afforded borylated alcohols. Surprisingly, the selective reduction of  $\text{CO}_2$  in the presence of HBpin produced only borylated methanol with TON was 1146 and TOF was 382  $\text{h}^{-1}$  at 85 °C. In the last chapter, I exhibited that the cerium-amide catalyst was active for the hydroboration of unactivated and unsaturated bonds *e.g.*, C=C, C≡C, C≡N and N=C=O bonds with HBpin. The alkene and alkyne substrates displayed an *anti*-Markovnikov hydroboration and afforded linear products (major). On the other hand, isocyanates delivered selectively deoxygenative products other than monohydroborated or dihydroborated products, upon treatment of 1 or 2 or 3 equivalents of HBpin.

In the nutshell, I have demonstrated that the wide applications of verily accessible  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$  complex as an efficient catalyst for the hydroboration of amides, esters, epoxides,  $\text{CO}_2$ , alkenes, alkynes, nitriles and isocyanates using HBpin under mild reaction conditions. Moreover, its utilization in many challenging and promising organic transformations are under investigation.



*Schematic representation of my doctoral research*

\*\*\*\*\*

## ***Appendix 1***

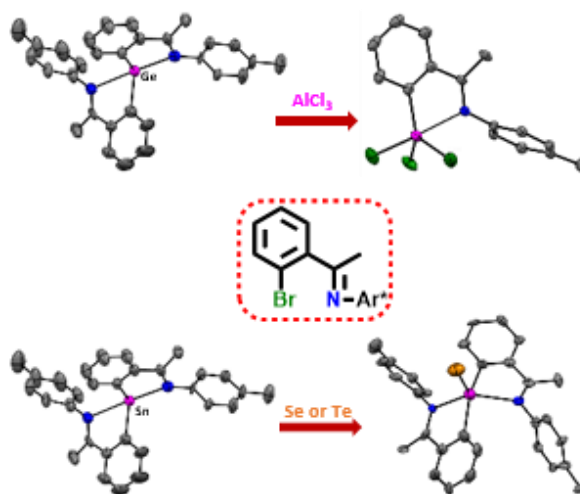
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### **Four-coordinate germylene and stannylene and their reactivity towards Se & Te\*\***

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**Abstract:** In this work, we have prepared a bulky ligand supported chlorogermylene (LGeCl) [L= C<sub>6</sub>H<sub>4</sub>-2-{C(Me)=NAr\*}; Ar\*= (2,6-bis(diphenylmethyl)-4-methylphenyl)] (2), chlorostannylene (LSnCl) (3), four-coordinate germylene (L<sub>2</sub>Ge) (4) and four-coordinate stannylene (L<sub>2</sub>Sn) (5). Subsequently, the reactions of 4 and 5 with elemental selenium and tellurium led to the isolation of respective heavy ketones (7-9). All the compounds are well characterized by multinuclear NMR techniques and single-crystal X-ray diffraction studies.

**Graphical abstract:**



## Introduction:

The “heavy ketones”, which contain a double bond between heavier group 14 and 16 elements, are attractive synthetic targets due to their reactive nature.<sup>1-5</sup> The germanium/tin chalcogenides have already shown their potential as semiconducting materials, which further broadens the scope of these heavy ketones in material chemistry.<sup>6,7</sup> The standard strategy of synthesizing such heavy ketones involves the design of a suitable bulky ligand, which can protect the reactive E=X bond (E = Ge, Sn; X = S, Se, Te).<sup>2e,8,9</sup> Due to their potential application and unprecedented bonding nature, there is always a quest to synthesize the new chalcogenides (**Chart A1.1**).<sup>3,6-9</sup>

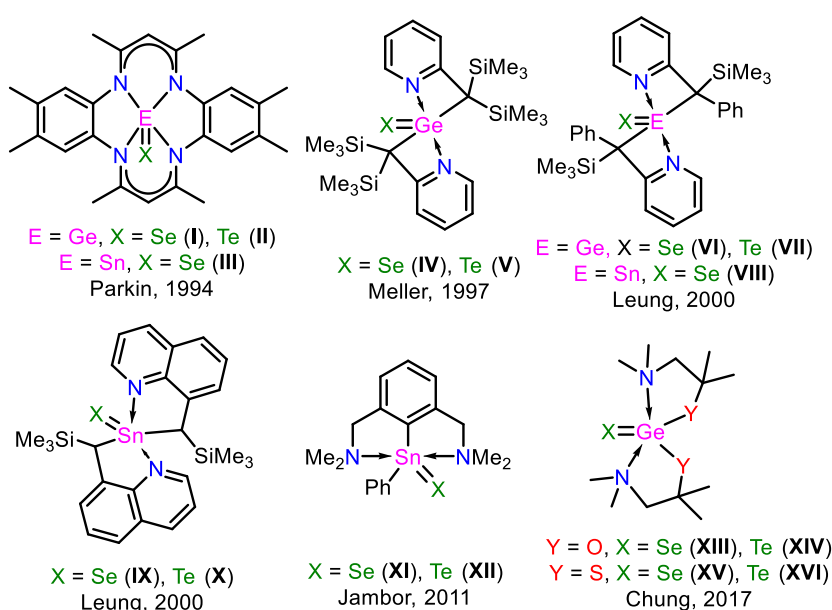


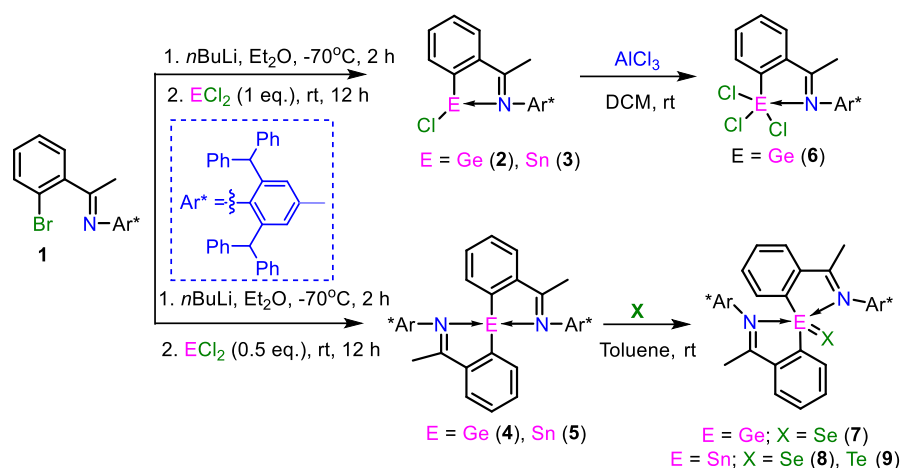
**Chart A1.1.** Previously reported four coordinate germanium/tin chalcogenides.

The synthesis of these heavy ketones is very much dependent upon the bulkiness of the substituents as an increase in bulk favors the stabilization of double-bonded compounds (Ge/Sn=X, X = S, Se, Te), while the decrease in the bulk furnishes cyclic E<sub>2</sub>X<sub>2</sub> moiety (E = Ge, Sn; X = S, Se, Te).<sup>10,11</sup> In order to synthesize the double-bonded chalcogenides, we utilized a bulky ligand **1** ((E)-1-(2-bromophenyl)-N-(2,6-dibenzhydryl-4-methylphenyl)ethan-1-imine) with a sterically crowded Ar\* group [Ar\* = 2,6-(dibenzhydryl-4-methylphenyl)] on the nitrogen atom.<sup>12</sup>

Herein, we report sterically demanding chlorogermylene (**2**), chlorostannylene (**3**), homoleptic germylene (**4**), homoleptic stannylene (**5**), germaselenone (**7**), stannaselenone (**8**), and stannatellurone (**9**). All the compounds were studied by the multinuclear NMR and mass

spectrometry. The molecular structures of **3-7** and **9** are confirmed by single-crystal X-ray diffraction studies.

## Results and discussion:



**Scheme A1.1.** Syntheses of compounds **2-9**.

The treatment of the lithiated salt of **1** with one equivalent of  $\text{ECl}_2$  ( $\text{E} = \text{Ge}$  or  $\text{Sn}$ ) in diethyl ether led to the formation of respective chlorogermylene  $\text{LGeCl}$  (**2**) [ $\text{L} = \text{C}_6\text{H}_4\text{-2-}\{\text{C}(\text{Me})=\text{NAr}^*\}$ ;  $\text{Ar}^* = (2,6\text{-bis(diphenylmethyl)-4-methylphenyl)}$ ] and  $\text{LSnCl}$  (**3**) (**Scheme A1.1**), while the reaction with 0.5 equivalent of  $\text{ECl}_2$  furnished the homoleptic germylene  $\text{L}_2\text{Ge}$  (**4**) and stannylene  $\text{L}_2\text{Sn}$  (**5**) (**Scheme A1.1**).

The  $^{119}\text{Sn}$  NMR spectrum of **3** displays an intense signal at  $\delta$  185.69 ppm, which is comparable to the intramolecular  $\text{N} \rightarrow \text{Sn}$  coordination bonds reported for  $[2,6\text{-(CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3]\text{SnCl}$  ( $\delta$  156 ppm)<sup>13</sup> and  $[2,4\text{-di-}^t\text{Bu-6-}\{(\text{C}_6\text{H}_3\text{-2',6'-}^i\text{Pr}_2)\text{N=CH}\}\text{C}_6\text{H}_2]\text{SnCl}$  ( $\delta$  154.7 ppm),<sup>2e</sup> but significantly upfield shifted than those reported for  $[8\text{-}\{\text{CH}(\text{SiMe}_3)\}\text{C}_9\text{H}_6\text{N}_2]\text{SnCl}$  ( $\delta$  327 ppm),<sup>14</sup>  $[2,6\text{-(NMe}_2)_2\text{C}_6\text{H}_3]\text{SnCl}$  ( $\delta$  380 ppm)<sup>15</sup> and  $[2,4\text{-di-}^t\text{Bu-6-(Et}_2\text{NCH}_2)\text{C}_6\text{H}_2]\text{SnCl}$  ( $\delta$  269.4 ppm).<sup>2e</sup> The molecular structures of **3-5** reveal an intramolecular  $\text{N} \rightarrow \text{Sn}$  coordination bond in **3**, **4**, and **5** (**Figure A1.1-A1.3**). **3** crystallizes (**Figure A1.1**) in a monoclinic  $P21/c$  space group. The  $\text{Sn(II)}$  centre possesses a distorted trigonal pyramidal geometry considering the lone pair of electrons. The  $\text{Sn-N}$  bond distance of **3** is 2.331(4) Å ( $\text{Sn1-N1}$ ), depicting a strong  $\text{N} \rightarrow \text{Sn}$  intramolecular interaction, which resembles those reported in  $[2,4\text{-di-}^t\text{Bu-6-(Et}_2\text{NCH}_2)\text{C}_6\text{H}_2]\text{SnCl}$  ( $\text{Sn1-N1} = 2.345(3)$  Å).<sup>2e</sup>

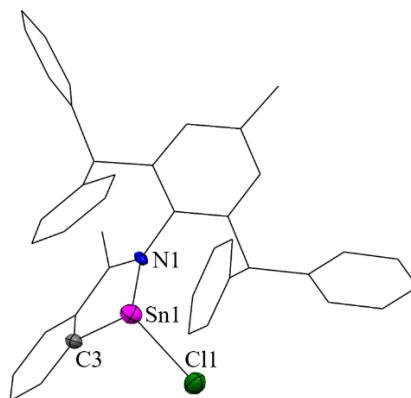


**Figure A1.1.** Molecular structure of **3** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N1-Sn1 2.331(4), C3-Sn1 2.192(5), Sn1-Cl1 2.507(2); N1-Sn1-C3 74.3(2), N1-Sn1-Cl1 96.8(1), C3-Sn1-Cl1 90.1(2).

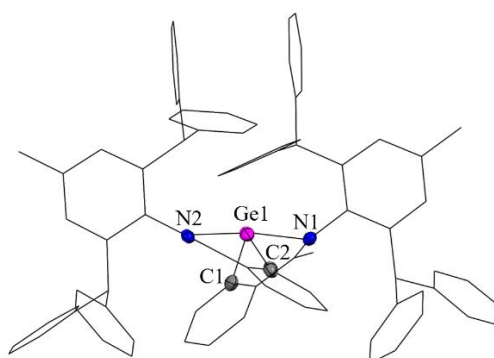


**Figure A1.2.** Molecular structure of **4** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N1-Ge1 2.471(5), Ge1-N2 2.398(4), Ge1-C1 1.990(5), Ge1-C2 1.990(6); N1-Ge1-N2 174.6(1), C2-Ge1-C1 98.9(2), N2-Ge1-C2 75.7(2), N1-Ge1-C1 75.4(2), C2-Ge1-N1 99.73(2), N2-Ge1-C1 102.3(2).

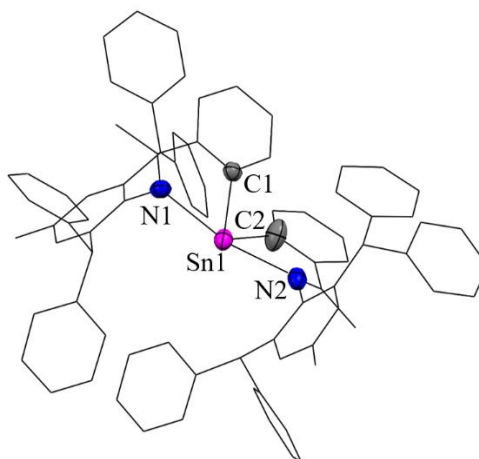


**Figure A1.3.** Molecular structure of **5** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): Sn1-N2 2.593(7), Sn1-N1 2.540(8), C1-Sn1 2.191(8), Sn1-C2 2.20(1); N2-Sn1-N1 169.6(2), C2-Sn1-C1 97.7(4), C1-Sn1-N1 72.0(3), N1-Sn1-C2 102.9(3), C2-Sn1-N2 70.6(3), N2-Sn1-C1 100.4(3).

**4** crystallizes in a triclinic *P*-1 space group. The molecular structure of **4** discloses a distorted square pyramidal geometry at the Ge(II) atom, where the lone pair of electrons is present at the axial position and N1, C1, N2, and C2 atoms are present at the equatorial position (**Figure A1.2**). The Ge-N bond distances in **4** are 2.469(5) Å (Ge1-N1) and 2.393(4) Å (Ge1-N2), which are longer than those found in Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C,N*]Ge(II) (Ge1-N1 2.273(3) Å)<sup>16</sup> and Ge(dmampS)<sub>2</sub> [(dmampS = 1-dimethylamino-2-methylpropane-2-thiolate) (Ge1-N1 2.3052(13) Å and Ge1-N11 2.3596(14) Å)],<sup>6a</sup> indicating a less prominent N→Ge coordination. The molecular structure of **5** (**Figure A1.3**) is similar to **4**. **5** also crystallizes in a triclinic *P*-1 space group and displays a distorted square pyramidal geometry at the tin(II) centre. The bond distances Sn1-N1 and Sn1-N2 in **5** are 2.540(8) Å and 2.593(7) Å, respectively, which are slightly longer than the previously reported N→Sn bonds in [Sn{NPh(py)}<sub>2</sub>] and [Sn{N(SiMe<sub>3</sub>)py}<sub>2</sub>] (2.368–2.416 Å).<sup>17</sup>

Further, we were interested in generating a Ge(II) cation from **2**; Hence we treated **2** with AlCl<sub>3</sub>, which is a well-known Lewis acid for the abstraction of the Cl atom.<sup>18</sup> However, we isolated an oxidized product **6** (**Scheme A1.1**), where Ge(II) centre is oxidized to Ge(IV). The other product could not be identified. The molecular structure of **6** (**Figure A1.4a**) has an orthorhombic *Pmn*2<sub>1</sub> space group, which possesses a vertical plane of symmetry (**Figure A1.4b**). **6** displays a distorted trigonal bipyramidal geometry concerning Ge1, C1, N1, Cl2, and

both Cl1. The Ge1-Cl1 and Ge1-N1 bond distances of **6** are 2.125 (12) Å and 2.471 Å, respectively.

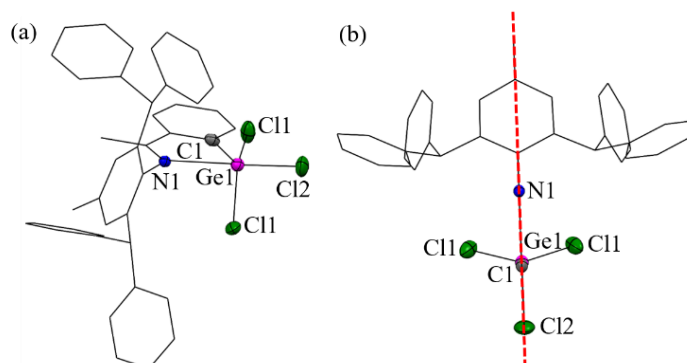


**Figure A1.4.** Molecular structure of **6** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N1-Ge1 2.471, Ge1-Cl1 2.125 (12), Ge1-Cl1 2.125 (12), Ge1-Cl2 2.217 (2), Ge1-C1 1.929 (7); N1-Ge1-C1 75.4, Cl1-Ge1-N1 86.3, Cl1-Ge1-C1 121.9 (7), Cl1-Ge1-C1 121.9 (7), Cl2-Ge1-C1 102.1 (2), Cl1-Ge1-Cl2 95.15 (6), Cl1-Ge1-Cl1 110.98 (9).

Since Ge/Sn=X double-bonded compounds are synthetically challenging,<sup>19</sup> it was interesting to explore the reaction of these newly synthesized homoleptic tetrylenes with the elemental selenium (Se) and tellurium (Te). Consequently, **4** and **5** were treated with selenium powder in toluene to furnish **7** and **8**, respectively. A singlet was observed at  $\delta$  -56.11 ppm in  $^{77}\text{Se}$  NMR spectrum of **7**, which was downfield shifted compared to **IV**, **XIII**, and **XV** ( $^{77}\text{Se}$  NMR at  $\delta$  -97.64 ppm, -391.0 ppm and -129.1 ppm, respectively). Similarly, a peak was observed at  $\delta$  -49.57 ppm in  $^{119}\text{Sn}$  NMR spectrum of **8**, which was upfield shifted compared to that in **5** ( $\delta$  54.06 ppm). Also, a signal was observed at  $\delta$  -265.24 ppm in the  $^{77}\text{Se}$  NMR spectrum of **8**, which is downfield shifted compared to **VIII**, **IX**, and **XI** ( $^{77}\text{Se}$  NMR at  $\delta$  -531.95 ppm, -734.80 ppm, and -570.9 ppm, respectively). Unfortunately, we could not get the suitable crystals of **8** to perform the single-crystal X-ray diffraction studies. However, we established the molecular structure of **7** unambiguously. Due to the poor quality of the crystal data, we are not discussing the bonding parameters of **7** (**Figure A1.5**).

We also treated **4** and **5** with tellurium powder in toluene to obtain the respective compounds (**Scheme A1.1**). However, we could only get the molecular structure of **9** (**Figure A1.6**), while

the reaction of **4** with tellurium led to some unidentified decomposition product. **9** was further characterized by using solution-state NMR spectroscopy and mass spectrometry. The  $^{119}\text{Sn}$  NMR spectrum of **9** displayed a signal at  $\delta$  -278.24 ppm, which is comparable to **X** and **XII** ( $^{119}\text{Sn}$  NMR at  $\delta$  -350.34 ppm and -156.5 ppm, respectively). The  $^{125}\text{Te}$  NMR spectrum of **9** displayed a signal at  $\delta$  -838.21 ppm, which was downfield shifted compared to **X** and **XII** ( $^{125}\text{Te}$  NMR at  $\delta$  -2030.63 ppm and -1393.7 ppm, respectively). **9** crystallizes in a triclinic *P*-1 space group with a distorted square pyramidal geometry concerning Sn1, N1, N2, C1, C2, and Te1, where Sn1 is the central atom situated a little above the basal plane. The Sn1-N1 and Sn1-N2 bond distances of **9** are 2.46(1) Å and 2.46(1) Å, matching well with those found in [{2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}(Ph)Sn=Te] (**XII**) (Sn1-N1 and Sn1-N2: 2.4794(17) Å and 2.4836(17) Å).<sup>6b</sup> The Sn1-Te1 bond distance of **9** is 2.546(2) Å, which is shorter than those found in [{CH(SiMe<sub>3</sub>)C<sub>9</sub>H<sub>6</sub>N-8}<sub>2</sub>Sn=Te] (**X**) (2.618(1) Å)<sup>7a</sup> and [{2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}(Ph)Sn=Te] (**XII**) (2.6139(2) Å),<sup>6b</sup> but matches well with the Sn-Te bond distance of Bbt(Titp)Sn=Te (2.5705(6) Å).<sup>7c</sup>

All the complexes were sparingly soluble in toluene, ether and hexane, but highly soluble in DCM and THF. The UV-vis absorption spectra of all the complexes were recorded in DCM (see SI Table S2 for the summarized data). The colors of compounds **2-9** vary from colorless to orange, which is presumably due to  $n \rightarrow \pi^*$  transitions (transfer of lone-pair from Se/Te to a vacant Ge/Sn d orbital).<sup>7a</sup>

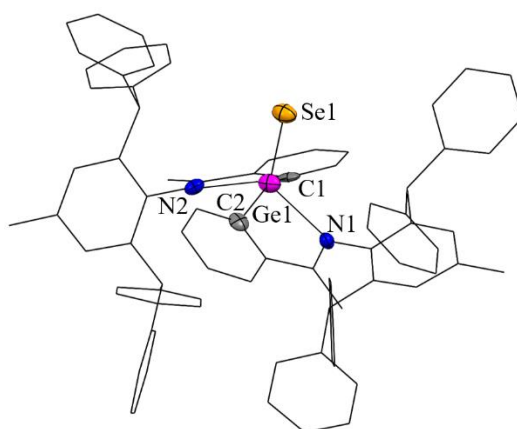


**Figure A1.5.** Molecular structure of **7** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity.

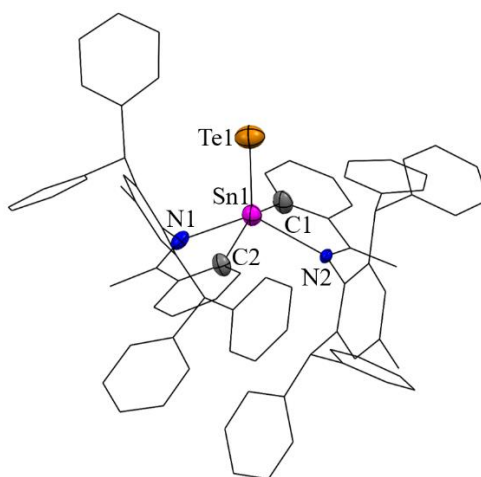


**Figure A1.6.** Molecular structure of **9** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N2-Sn1 2.46(1), C1-Sn1 2.13(2), N1-Sn1 2.46(1), C2-Sn1 2.15(2), Sn1-Te1 2.546(2); N2-Sn1-N1 127.8(4), C2-Sn1-C1 147.1(8), Te1-Sn1-N2 116.0(3), Te1-Sn1-N1 116.3(3), Te1-Sn1-C2 108.0(5), Te1-Sn1-C1 104.9(6), C2-Sn1-N2 91.0(6), C1-Sn1-N1 91.7(6).

### Conclusions:

In summary, we have synthesized a new ligand with a very bulky Ar\* group on the coordinating nitrogen atom and utilized it for the isolation of chlorogermylene (**2**), chlorostannylene (**3**), homoleptic germylene (**4**), and homoleptic stannylene (**5**). Furthermore, the reaction of **4** and **5** with elemental selenium and tellurium afforded heavy ketones **7-9**. All the compounds are well characterized by NMR spectroscopic techniques, mass spectrometry, and single crystal X-ray diffraction studies.

### Experimental Section:

All manipulations were carried out under an inert gas atmosphere of dinitrogen using the standard Schlenk technique and in a dinitrogen-filled MBRAUN MB 150-GI glove box. All solvents were purified by the MBRAUN MB SPS-800 solvent purification system. All other chemicals purchased from Aldrich, Alfa Aesar were used without further purification. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  using a Bruker 400 MHz spectrometer. Mass spectra were recorded using an AB Sciex 4800 plus MALDI TOF/TOF instrument.

**Synthesis of 1.** 2'-bromoacetophenone (4.3 mL, 31.8 mmol) and Ar\*-NH<sub>2</sub> (14 g, 31.8 mmol) were taken in a 500 mL R.B. flask and tetraethyl orthosilicate (~15 mL) and conc. H<sub>2</sub>SO<sub>4</sub> (10 drops, catalytic amount) were added to the flask. Then, this reaction mixture was refluxed for 2 days. After that, the reaction mixture was quenched with KOH<sub>aq</sub> (2 M solution) and 150 mL of MeOH was added to the reaction mixture. The reaction mixture was dried in rota, ethyl acetate was added and the filtrate was washed with the brine solution. The residue was purified by the column chromatography to afford **1** as a colorless crystalline solid. Yield: 71% (14 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 1.30 (s, 3H, NCCH<sub>3</sub>), 2.08 (s, 3H, PhCH<sub>3</sub>), 5.67 (s, 2H, CH), 6.65 (s, 2H, Ph), 6.97-6.99 (m, 3H, Ph), 7.05-7.22 (m, 20H, Ph), 7.45-7.47 (m, 1H, Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 21.44 (NCCH<sub>3</sub>), 22.20 (PhCH<sub>3</sub>), 51.10 (CH), 119.74, 126.16, 127.47, 128.23, 128.41, 129.66, 129.78, 130.02, 132.08, 133.41, 142.62, 143.38, 144.62, 144.91 (Ph), 171.88 (NCCH<sub>3</sub>) ppm. MALDI: Calculated for (C<sub>41</sub>H<sub>34</sub>BrN): *m/z* 619.1875. Found *m/z* 620.5540 [M+H]<sup>+</sup>.

**Synthesis of 2.** Compound **1** (2.5 g, 4 mmol) was taken in a 250 mL Schlenk flask and 80 mL diethyl ether was added to it. To this *n*BuLi (1.6 mL, 2.5 M) was added at -70 °C into the flask and the temperature was maintained from -50 °C to -70 °C for 3 hours. After that, GeCl<sub>2</sub>.dioxane (927 mg, 4 mmol) was added to the solution and left to stir for another 12 hours at room temperature. Then the solution was filtered and concentrated to 10 mL, and stored at room temperature affording light yellow colored crystalline compound **2**. Yield: 55% (1.4 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 0.58 (s, 3H, NCCH<sub>3</sub>), 2.09 (s, 3H, PhCH<sub>3</sub>), 5.24 (s, 2H, CH), 6.60 (s, 2H, Ph), 6.95-6.99 (m, 8H, Ph), 7.07-7.11 (m, 8H, Ph), 7.14-7.16 (m, 4H, Ph), 7.29-7.31 (m, 2H, Ph), 7.50-7.53 (m, 2H, Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 16.65 (NCCH<sub>3</sub>), 20.29 (PhCH<sub>3</sub>), 50.92 (CH), 124.91, 126.00, 126.96, 127.07, 127.22, 127.65, 128.45, 128.99, 130.24, 131.47, 138.18, 141.65, 142.96, 145.46 (Ph), 167.89 (NCCH<sub>3</sub>) ppm. MALDI: Calculated for (C<sub>41</sub>H<sub>34</sub>ClNGe): *m/z* 649.1592. Found *m/z* 672.6220 [M+Na]<sup>+</sup>.

**Synthesis of 3.** **1** (2.5 g, 4 mmol) was taken in a 250 mL Schlenk flask and 80 mL diethyl ether was added to dissolve it. Subsequently, *n*BuLi (1.6 mL, 2.5 M) was added to it at -70 °C and the temperature was maintained from -50 °C to -70 °C for 3 hours. After that SnCl<sub>2</sub> (760 mg, 4 mmol) was added to the solution and it was stirred for another 12 hours at room temperature. After that the solution was filtered and concentrated to 7 mL and stored at room temperature to afford **3** as an orange crystalline solid. Yield: 58% (1.6 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ 0.58 (s, 3H, NCCH<sub>3</sub>), 2.10 (s, 3H, PhCH<sub>3</sub>), 5.24 (s, 2H, CH), 6.60 (s, 2H, Ph), 6.95-6.99 (m, 8H, Ph), 7.08-7.12 (m, 8H, Ph), 7.15-7.18 (m, 4H, Ph), 7.28-7.31 (m, 2H, Ph), 7.51-7.53 (m, 2H, Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K): δ 16.67 (NCCH<sub>3</sub>), 20.29 (PhCH<sub>3</sub>),

50.92 (CH), 124.92, 126.01, 126.96, 127.08, 127.22, 127.66, 128.46, 129.00, 130.25, 131.48, 138.18, 141.65, 142.96, 145.45 (*Ph*), 167.93 (NCCH<sub>3</sub>); <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 149.18 MHz, 298 K):  $\delta$  185.69 ppm. MALDI: Calculated for (C<sub>41</sub>H<sub>34</sub>ClNSn): *m/z* 695.1402. Found *m/z* 695.5196 [M]<sup>+</sup>.

**Synthesis of 4. 1** (2.5 g, 4 mmol) was taken in a 250 mL Schlenk flask and 80 mL diethyl ether was added to it. Then, *n*BuLi (1.6 mL, 2.5 M) was added at -70 °C into the flask and the temperature was maintained from -50 °C to -70 °C for 3 hours. Subsequently, GeCl<sub>2</sub>.dioxane (464 mg, 2 mmol) was added to the solution and it was stirred for 12 hours at room temperature. After that the solution was filtered, concentrated and stored at room temperature to afford **4** as pale yellow crystalline solid. Yield: 69% (1.6 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K):  $\delta$  0.58 (s, 6H, NCCH<sub>3</sub>), 2.09 (s, 6H, PhCH<sub>3</sub>), 5.24 (s, 4H, CH), 6.60 (s, 4H, *Ph*), 6.95-6.98 (m, 16H, *Ph*), 7.07-7.11 (m, 16H, *Ph*), 7.14-7.16 (m, 8H, *Ph*) 7.29-7.30 (m, 4H, *Ph*), 7.50-7.52 (m, 4H, *Ph*); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K):  $\delta$  17.71 (NCCH<sub>3</sub>), 21.36 (PhCH<sub>3</sub>), 51.98 (CH), 125.97, 127.06, 128.02, 128.13, 128.28, 128.71, 129.51, 130.05, 131.30, 132.53, 139.24, 142.70, 144.02, 145.52 (*Ph*), 168.95 (NCCH<sub>3</sub>) ppm. MALDI: Calculated for (C<sub>82</sub>H<sub>68</sub>N<sub>2</sub>Ge): *m/z* 1154.4594. Found *m/z* 1154.0006 [M]<sup>+</sup>.

**Synthesis of 5. 1** (2.5 g, 4 mmol) was taken in a 250 mL Schlenk flask and 80 mL diethyl ether was added to dissolve it. To this solution *n*BuLi (1.6 mL, 2.5 M) was added at -70 °C and the temperature was maintained from -50 °C to -70 °C for 3 hours. After that, SnCl<sub>2</sub> (380 mg, 2 mmol) was added to the solution and it was stirred for 12 hours at room temperature. Then, it was filtered and concentrated to 5 mL to afford light orange colored crystalline compound **5**. Yield: 62% (1.5 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K):  $\delta$  0.58 (s, 6H, NCCH<sub>3</sub>), 2.10 (s, 6H, PhCH<sub>3</sub>), 5.24 (s, 4H, CH), 6.61 (s, 4H, *Ph*), 6.95-6.99 (m, 16H, *Ph*), 7.06-7.12 (m, 16H, *Ph*), 7.15-7.16 (m, 8H, *Ph*), 7.28-7.31 (m, 4H, *Ph*), 7.51-7.53 (m, 4H, *Ph*); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.613 MHz, 298 K):  $\delta$  17.83 (NCCH<sub>3</sub>), 21.47 (PhCH<sub>3</sub>), 52.11 (CH), 126.10, 127.19, 128.14, 128.26, 128.40, 128.83, 129.63, 130.17, 131.42, 132.66, 139.36, 142.83, 144.14, 146.64 (*Ph*), 169.08 (NCCH<sub>3</sub>); <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 149.18 MHz, 298 K):  $\delta$  54.06 ppm. MALDI: Calculated for (C<sub>82</sub>H<sub>68</sub>N<sub>2</sub>Sn): *m/z* 1200.4404. Found *m/z* 1201.8436 [M+H]<sup>+</sup>.

**Synthesis of 6. 2** (300 mg, 0.46 mmol) and AlCl<sub>3</sub> (62 mg, 0.46 mmol) were taken in a 100 mL Schlenk flask and 25 mL DCM was added to it at room temperature. The reaction mixture was stirred for 12 hours at room temperature. After that, the reaction mixture was filtered and concentrated to 6 mL and stored at 0°C temperature, which furnished pale yellow-coloured crystals of **6**. Yield: 66% (220 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K):  $\delta$  0.08 (s, 3H, NCCH<sub>3</sub>), 2.22 (s, 3H, PhCH<sub>3</sub>), 5.90 (s, 2H, CH), 6.83 (s, 2H, *Ph*), 7.05-7.07 (m, 8H, *Ph*), 7.09-7.11 (m,

8H, *Ph*), 7.21-7.23 (m, 4H, *Ph*), 7.61-7.65 (t, 1H, *Ph*), 7.80-7.84 (m, 2H, *Ph*), 8.67-8.68 (m, 1H, *Ph*);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  15.77 ( $\text{NCCH}_3$ ), 20.34 ( $\text{PhCH}_3$ ), 50.23 (*CH*), 125.03, 125.48, 126.88, 127.36, 127.51, 128.42, 129.10, 129.40, 132.19, 134.49, 135.98, 140.39, 140.95, 143.08 (*Ph*), 170.45 ( $\text{NCCH}_3$ ) ppm. MALDI: Calculated for ( $\text{C}_{41}\text{H}_{34}\text{Cl}_3\text{NGe}$ ):  $m/z$  719.0969. Found  $m/z$  720.2171 [ $\text{M}+\text{H}$ ] $^+$ .

**Synthesis of 7.** Compound **4** (300 mg, 0.26 mmol) and selenium powder (21 mg, 0.26 mmol) were taken in a 100 mL Schlenk flask and 25 mL toluene was added to it at room temperature. The reaction mixture was stirred for 24 hours at room temperature. The light yellow coloured crystals of **7** were obtained by storing a concentrated solution at 0°C. Yield: 62% (200 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  0.58 (s, 6H,  $\text{NCCH}_3$ ), 2.08 (s, 6H,  $\text{PhCH}_3$ ), 5.24 (s, 4H, *CH*), 6.60 (s, 4H, *Ph*), 6.95-6.98 (m, 16H, *Ph*), 7.06-7.10 (m, 16H, *Ph*), 7.13-7.15 (m, 8H, *Ph*), 7.28-7.30 (m, 4H, *Ph*), 7.50-7.52 (m, 4H, *Ph*);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  16.65 ( $\text{NCCH}_3$ ), 20.29 ( $\text{PhCH}_3$ ), 50.92 (*CH*), 124.91, 126.00, 126.96, 127.07, 127.22, 127.65, 128.45, 128.99, 130.24, 131.47, 138.18, 141.65, 142.96, 145.46 (*Ph*), 167.89 ( $\text{NCCH}_3$ );  $^{77}\text{Se}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 76.311, 298 K):  $\delta$  -56.11 ppm. MALDI: Calculated for ( $\text{C}_{82}\text{H}_{68}\text{N}_2\text{SeGe}$ ):  $m/z$  1234.3760. Found  $m/z$  1233.8024 [ $\text{M}$ ] $^+$ .

**Synthesis of 8.** Compound **5** (300 mg, 0.25 mmol) and selenium powder (20 mg, 0.25 mmol) were taken in a 100 mL Schlenk flask and 25 mL toluene was added to the it at room temperature. The reaction mixture was stirred for 24 hours at room temperature. After that the reaction mixture was filtered and concentrated to 7 mL. The orange-yellow-coloured crystals of **8** were obtained by storing the concentrated solution at 0°C for 24 hours. Yield: 81% (260 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  0.58 (s, 6H,  $\text{NCCH}_3$ ), 2.09 (s, 6H,  $\text{PhCH}_3$ ), 5.24 (s, 4H, *CH*), 6.60 (s, 4H, *Ph*), 6.95-6.98 (m, 16H, *Ph*), 7.07-7.10 (m, 16H, *Ph*), 7.14-7.16 (m, 8H, *Ph*), 7.29-7.31 (m, 4H, *Ph*), 7.50-7.53 (m, 4H, *Ph*);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  16.65 ( $\text{NCCH}_3$ ), 20.29 ( $\text{PhCH}_3$ ), 50.92 (*CH*), 124.91, 126.00, 126.96, 127.07, 127.22, 127.65, 128.45, 128.99, 130.23, 131.47, 138.18, 141.65, 142.97, 145.46 (*Ph*), 167.88 ( $\text{NCCH}_3$ );  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 149.18 MHz, 298 K):  $\delta$  -49.57;  $^{77}\text{Se}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 76.311, 298 K):  $\delta$  -265.24 ppm. MALDI: Calculated for ( $\text{C}_{82}\text{H}_{68}\text{N}_2\text{SeSn}$ ):  $m/z$  1280.3570. Found  $m/z$  1281.5455 [ $\text{M}+\text{H}$ ] $^+$ .

**Synthesis of 9.** Compound **5** (300 mg, 0.25 mmol) and tellurium powder (32 mg, 0.25 mmol) were taken in a 100 mL Schlenk flask and 25 mL toluene was added to it at room temperature. The reaction mixture was stirred for 48 hours at room temperature. After that, the reaction mixture was filtered, concentrated and a few drops of pentane was added to it. The storage of this solution at 0°C for 24 hours furnished orange-red colored crystals of **9**. Yield: 69% (230

mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  0.58 (s, 6H,  $\text{NCCH}_3$ ), 2.10 (s, 6H,  $\text{PhCH}_3$ ), 5.24 (s, 4H,  $\text{CH}$ ), 6.60 (s, 4H,  $\text{Ph}$ ), 6.95-6.99 (m, 16H,  $\text{Ph}$ ), 7.07-7.11 (m, 16H,  $\text{Ph}$ ), 7.15-7.17 (m, 8H,  $\text{Ph}$ ), 7.29-7.31 (m, 4H,  $\text{Ph}$ ), 7.51-7.57 (m, 4H,  $\text{Ph}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.613 MHz, 298 K):  $\delta$  16.65 ( $\text{NCCH}_3$ ), 20.29 ( $\text{PhCH}_3$ ), 50.93 ( $\text{CH}$ ), 124.92, 126.01, 126.96, 127.08, 127.22, 127.65, 128.46, 129.00, 130.24, 131.48, 138.19, 141.65, 142.97, 145.46 ( $\text{Ph}$ ), 167.90 ( $\text{NCCH}_3$ );  $^{119}\text{Sn}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 149.18 MHz, 298 K):  $\delta$  -278.24;  $^{125}\text{Te}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 126.2 MHz, 298 K):  $\delta$  -838.21 ppm. MALDI: Calculated for ( $\text{C}_{82}\text{H}_{68}\text{N}_2\text{TeSn}$ ):  $m/z$  1330.3467. Found  $m/z$  1353.7108  $[\text{M}+\text{Na}]^+$ .

### Crystallographic Details

Crystallography reflections were collected on a Bruker Smart Apex Duo diffractometer at 150 K using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for **2**, **3**, **4**, **5**, **6**, **7**, **9**.<sup>[20]</sup> The structures were solved by direct method and refined by full-matrix least-squares methods against  $F^2$  (SHELXL-2014/6). Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC no. 2169157 (**2**), 2169081 (**3**), 2169079 (**4**), 2169085 (**5**), 2169083 (**6**), 2169082 (**7**), 2169080 (**9**).

### References:

- [1] (a) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem. Int. Ed.* **2002**, *41*, 1785–1787; *Angew. Chem.* **2002**, *114*, 1863–1865; (b) Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh, *J. Am. Chem. Soc.* **2006**, *128*, 1023–1031; (c) W. Wang, S. Inoue, S. Yao, M. Driess, *Chem. Commun.* **2009**, 2661–2663; (d) S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmiller, A. Pal, R. Herbst-Irmer, *Organometallics* **2008**, *27*, 5459–5463; (e) W.-P. Leung, W.-K. Chiu, K.-H. Chong, T. C. W. Mak, *Chem. Commun.* **2009**, 6822–6824; (f) S. P. Green, C. Jones, P. C. Junk, K. -A. Lippert, A. Stasch, *Chem. Commun.* **2006**, 3978–3980.
- [2] (a) A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930–5931; (b) Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, P. P. Power, *Science* **2009**, *325*, 1668–1670; (c) C. Cui, M. M. Olmstead, J. C. Fettinger, G. H. Spikes, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541; (d) Y. Peng, X. Wang, J. C. Fettinger, P. P. Power, *Chem. Commun.* **2010**, *46*, 943–945; (e) M. Novák, M. Bouška, L. Dostál,

- A. Růžicka, A. Hoffmann, S. Herres-Pawlis, R. Jambor, *Chem. Eur. J.* **2015**, *21*, 7820-7829; (f) W. –P. Leung, W. –H. Kwok, Z. –Y. Zhou, T. C. W. Mak, *Organometallics* **2003**, *22*, 1751-1755.
- [3] P. P. Power, *Nature* **2010**, *463*, 171-177.
- [4] (a) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625-630; (b) Y. Ding, Q. Ma, I. Usón, H. W. Roesky, M. Noltemeyer, H. –G. Schmidt, *J. Am. Chem. Soc.* **2002**, *124*, 8542-8543; (c) L. W. Pineda, V. Jancik, H. W. Roesky, R. Herbst-Irmer, *Angew. Chem. Int. Ed.* **2004**, *43*, 5534–5536; (d) N. Tokitoh, T. Matsumoto, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 2337-2338.
- [5] (a) Y. Matsubashi, N. Tokitoh, Renji Okazaki *Organometallics* **1993**, *12*, 2573-2583; b) M. Saito, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **2004**, *126*, 15572-15582 c) M. Saito, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 11124-11125.
- [6] (a) H. –S. Kim, E. A. Jung, S. H. Han, J. H. Han, B. K. Park, C. G. Kim, T. –M. Chung, *Inorg. Chem.* **2017**, *56*, 4084-4092; (b) B. Mairychova, L. Dostal, A. Ruzicka, M. Fulem, K. Ruzicka, A. Lycka, R. Jambor, *Organometallics* **2011**, *30*, 5904–5910.
- [7] (a) W. –P. Leung, W. –H. Kwok, Z. –Y. Zhou, T. C. W. Mak, *Organometallics* **2000**, *19*, 296-303; b) T. Chivers, D. J. Eisler, J. S. Ritch, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1941-1946; c) T. Tajima, N. Takeda, T. Sasamori, N. Tokitoh, *Organometallics* **2006**, *25*, 3552-3553.
- [8] L. Dostál, R. Jambor, M. Aman, M. Hejda, *ChemPlusChem* **2020**, *85*, 2320 –2340.
- [9] (a) J. Barrau, G. Rima, *Coord. Chem. Rev.* **1998**, *178–180*, 593–622; (b) M. C. Kuchta, G. Parkin, *Coord. Chem. Rev.* **1998**, *176*, 323-372; (c) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625-630 (d) R. Okazaki, N. Tokitoh, *Adv. Organomet. Chem.* **2001**, *47*, 121-166; (e) N. Tokitoh, T. Tajima, N. Takeda, T. Sasamori, *Phosphorus, Sulfur, and Silicon* **2008**, *183*, 948–955.
- [10] (a) Yuanlin Zhou and Darrin S. Richeson *J. Am. Chem. Soc.* **1996**, *118*, 10850-10852; b) P. B. Hitchcock, J. Hu, M. F. Lappert, J. R. Severn, *Dalton Trans.* **2004**, 4193-4201.
- [11] (a) P. B. Hitchcock, E. Jang, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1995**, 3179–3187; b) P. B. Hitchcock, M. F. Lappert, L. J. M. Pierssens, A. V. Protchenko, P. G. H. Uiterweerd, *Dalton Trans.* **2009**, 4578–4585; c) S. M. Mansell, C. A. Russell, D. F. Wass, *Dalton Trans.* **2015**, *44*, 9756– 9765.
- [12] G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Markó, *Dalton Trans.* **2010**, *39*, 1444-1446.

- 
- [13] J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, *Organometallics* **1989**, 8, 1373-1375.
- [14] W. –P. Leung, W. –H. Kwok, F. Xue, T. C. W. Mak, *J. Am. Chem. Soc.* **1997**, 119, 1145-1146.
- [15] C. Drost, P. B. Hitchcock, M. F. Lappert, L. J. –M. Pierssens, *Chem. Commun.* **1997**, 1141-1142.
- [16] G. Ossig, A. Meller, C. Brönneke, O. Müller, M. Schäfer, R. Herbst-Irmer, *Organometallics* **1997**, 16, 2116-2120.
- [17] N. Sen, S. Pal, V. V. Khade, S. Khan, *Eur. J. Inorg. Chem.* **2019**, 4450-4454.
- [18] (a) H. V. R. Dias, Z. Wang, *J. Am. Chem. Soc.* **1997**, 119, 4650-4655; b) M. Stender, A. D. Phillips, P. P. Power, *Inorg. Chem.* **2001**, 40, 5314-5315; c) A. Schfer, W. Saak, D. Haase, T. Müller, *Chem. Eur. J.* **2009**, 15, 3945-3950.
- [19] M. Minoura, T. Kawashima, R. Okazaki, *J. Am. Chem. Soc.* **1993**, 115, 7019-7020.
- [20] (a) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, 26, 615–619; b) D. Stalke, *Chem. Soc. Rev.* **1998**, 27, 171–178; c) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112–122; d) T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelson, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, 42, 885–891; e) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2015**, 48, 3–10.

## *Appendix 2*

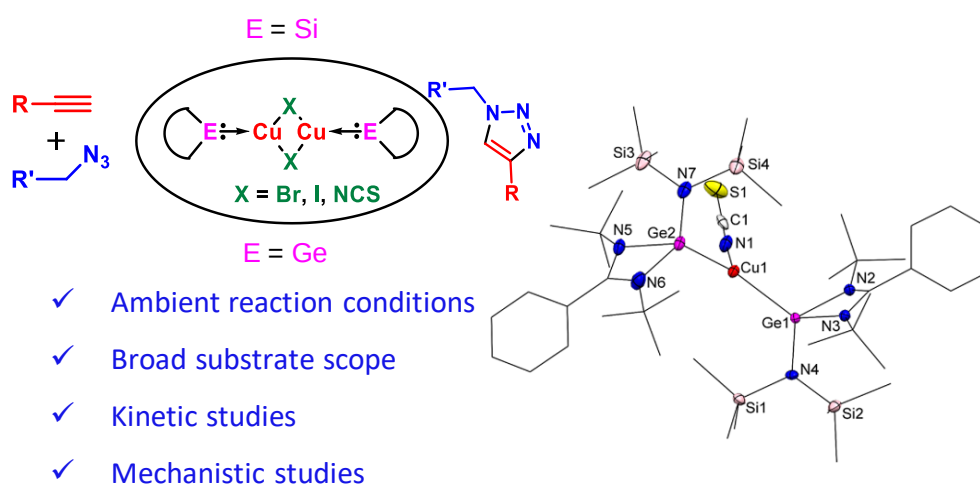
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### **NHSi/NHGe-supported copper halide and pseudohalide complexes: Synthesis and application**

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**Abstract:**

Herein, we have demonstrated the complexation reaction of silylene and germylene [ $\text{PhC}(\text{NtBu})_2\text{EN}(\text{TMS})_2$ ;  $\text{E} = \text{Si}$  (**A**) and  $\text{Ge}$  (**B**)] with several copper(I) salts and further utilized them (**1-6**) as efficient catalysts in CuAAC reaction. The copper complexes (**2, 4-6**) were synthesized from the reaction of [ $\text{PhC}(\text{NtBu})_2\text{EN}(\text{TMS})_2$ ] ( $\text{E} = \text{Si}$  (**A**) or  $\text{Ge}$  (**B**)) and  $\text{CuX}$  ( $\text{X} = \text{Br}, \text{I}, \text{SCN}$ ). The molecular structures of **2, 4, 5**, and **6** were established by single-crystal X-ray diffraction studies. The DFT studies indicate that the bimetallic Cu catalyst facilitate the cycloaddition reaction by anchoring the reactants to the close proximity and reducing the energy gap between the frontier orbitals of dipole and dipolarophile.

**Graphical abstract:**

**Introduction:**

The heavier analogue of N-heterocyclic carbene, namely N-heterocyclic silylene (NHSi), has attracted significant attention as a strong donor ligand in the last two decades.<sup>1-3</sup> The substantial contribution of *N*-heterocyclic silylenes (NHSis) was observed in metal-mediated homogeneous catalysis, where they were utilized as ancillary ligands to tune the reactivity of the metal centre.<sup>4</sup> On the contrary, the use of *N*-heterocyclic germylene (NHGe) as a spectator ligand in the transition metal-based catalysis is relatively scarce.<sup>5</sup> The heavier tetrylenes are mainly explored for Rh, Ni, Pd, Ir, Pt, Fe, Co catalyzed reactions.<sup>4f</sup> The coinage metal complexes of these heavier tetrylenes were not utilized in homogeneous catalysis until recently.<sup>4g</sup> There are only a handful of reports on silylene/germylene-supported coinage metal complexes in catalysis.<sup>6,7</sup> Among them, there are only two reports on copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction (click reaction) (**Chart A2.1, I-III**)<sup>6f,6g</sup> affording 1,2,3-triazole based compounds via the reaction of respective azide and alkyne.<sup>8</sup> In contrast, there are a plethora of examples of CuAAC reactions using *N*-heterocyclic carbenes (NHCs) supported copper(I) complexes.<sup>9</sup> Stalke and co-workers reported the first NHSi-copper(I) cluster catalyzed CuAAC reaction (**Chart A2.1, I & II**),<sup>6f</sup> which was succeeded by our report on NHSi-supported cationic copper complex in click chemistry (**Chart A2.1, III**).<sup>6g</sup> However, our NHSi supported cationic copper catalyst (**III**) is not very stable, and decomposes upon storage for a prolonged time. On the other hand, there is no report on the NHGe-supported copper complex in CuAAC reaction to date. Intrigued by the aforementioned facts, we aimed to prepare NHGe stabilized simple copper(I) complexes and utilize them in CuAAC reaction. For comparison, we have also studied the same reaction with our previously reported analogous NHSi-CuX (X = Br (**1**), I (**3**)) complexes.

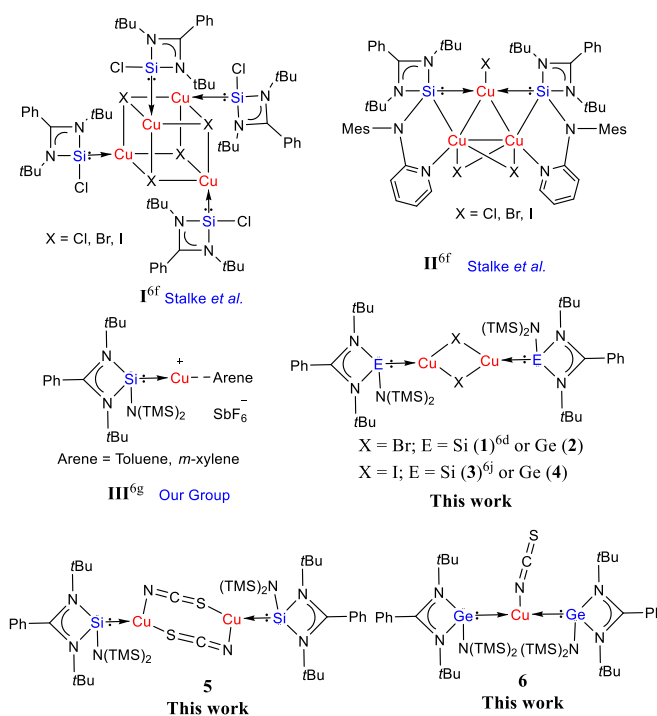


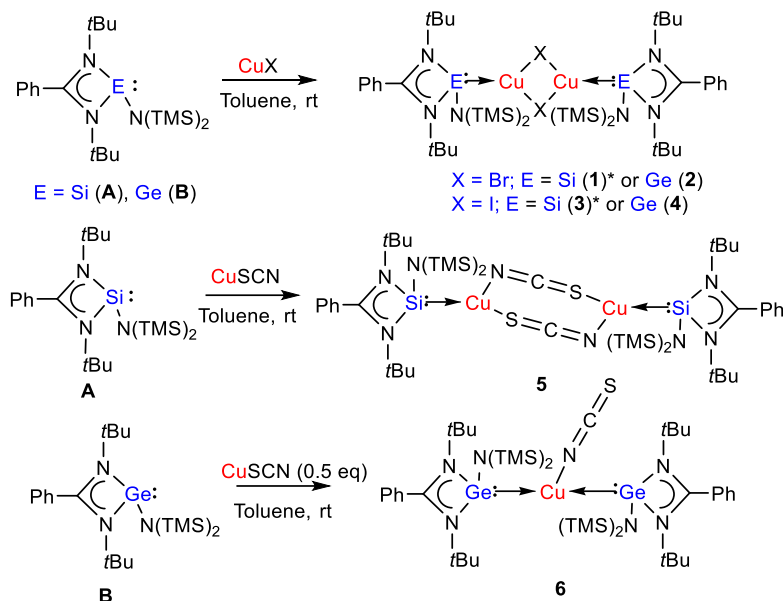
**Chart A2.1.** Reported examples of heavier tetraylene supported copper complexes in CuAAC reaction.

### Result and discussion:

In 2017, we reported the synthesis of **1**.<sup>6d</sup> Using the same synthetic strategy the NHGe-copper bromide, **2** was prepared by the treatment of amidinato germylene  $\text{PhC}(\text{N}^t\text{Bu})_2\text{GeN}(\text{TMS})_2$  (**B**)<sup>6h</sup> with CuBr into a 1:1 ratio in 80% yield (**Scheme A2.1**). In 2015, our group reported NHSi-copper iodide complex **3**,<sup>6j</sup> following the same synthetic protocol, we synthesized the NHGe-copper iodide complex **4** in 76% yield (**Scheme A2.1**). Further, we were interested to extend it to other copper salts. Hence, we chose CuSCN salt to react with **A**<sup>6i</sup> and **B**, as there are no reports on NHSi- and NHGe-supported copper thiocyanate complexes. However, there is one report on cyclic alkyl amino carbene (CAAC) supported copper thiocyanate complexes by Romanov *et al.*<sup>10</sup> The reactions of **A** and **B** with CuSCN afforded NHSi- and NHGe-supported copper thiocyanate complexes, **5** (yield = 73%) and **6** (yield = 79%), respectively. The reaction of **B** with CuSCN afforded the complex **6**, irrespective of the molar ratio of the reaction partners.

The <sup>1</sup>H NMR spectra of complexes **2**, **4**, **5** and **6** displayed a similar pattern of peaks (**2**,  $\delta$  1.19; **4**,  $\delta$  1.24; **5**,  $\delta$  1.22 and **6**,  $\delta$  1.21 ppm for four *CMe*<sub>3</sub> groups) as observed for **1** ( $\delta$  1.19 ppm)<sup>6d</sup> and **3** ( $\delta$  1.33 ppm).<sup>6j</sup> The <sup>29</sup>Si NMR spectrum of **5** displayed the resonances at  $\delta$  5.72, 6.39

ppm (for two  $\text{SiMe}_3$  groups) and  $\delta$  7.29 ppm (for Si(II) centre), respectively. The peak at  $\delta$  7.29 ppm for Si(II) centre is downfield shifted as compared to that of **1** ( $\delta$  5.72 ppm).<sup>6d</sup>



**Scheme A2.1.** Synthesis of NHSi- and NHGe-supported dimeric copper halide (**2** and **4**) and pseudohalide complexes (**5** and **6**). \***1** and **3** were previously reported.

Single-crystal XRD data of complex **2** revealed a discrete dimeric structure of the complex, where two NHGe ligands are connected to the two copper atoms (**Figure A2.1**). The bromide atoms bridge between the two copper centers. The  $\text{Cu}\cdots\text{Cu}$  distance in **2** is 3.037(1) Å, which is shorter than the  $\text{Cu}\cdots\text{Cu}$  distance in **1** (3.255(1) Å).<sup>6d</sup> The Ge–Cu bond distances of **2** are 2.287(1) Å and 2.289(9) Å, respectively, which are in good agreement of the bond distances of  $[\text{PhC}(\text{N}t\text{Bu})_2\text{Ge}(t\text{Bu})\text{CuCl}]_4$  (Cu1–Ge1 2.2765(9) Å).<sup>7j</sup> The four coordinate Ge(II) centers in **2** are similar to the Si(II) centers in **1** and exhibit distorted tetrahedral geometry.

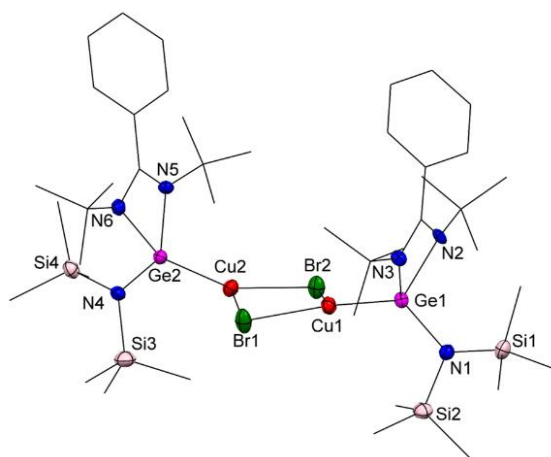


**Figure A2.1.** The molecular structure of **2**. Hydrogen atoms and a solvent molecule (toluene) are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu1-Cu2 3.037(1), Cu1-Ge1 2.287(1), Cu2-Ge2 2.289(9), Cu1-Br1 2.408(8), Cu2-Br1 2.402(9), Cu2-Br2 2.436(8), Cu1-Br2 2.437(9); Br1-Cu1-Br2 101.35(3), Br1-Cu2-Br2 101.54(3), Br2-Cu1-Ge1 128.26(4), Ge1-Cu1-Br1 130.03(4), Ge2-Cu2-Br1 131.53(4), Ge2-Cu2-Br2 126.66(4).

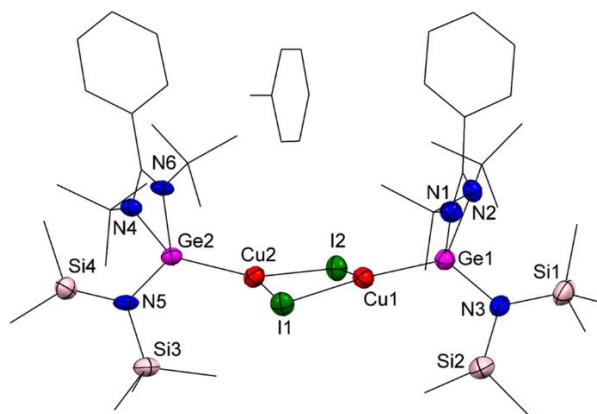


**Figure A2.2.** The molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge2-Cu2 2.324(2), Ge1-Cu1 2.318(2), Cu1-I2 2.595(2), Cu2-I2 2.582(2), Cu2-I1 2.562(2), Cu1-I1 2.565(2), Cu1-Cu2 3.021(2); I2-Cu2-I1 107.42(7), I2-Cu1-I1 106.93(7), Cu2-I2-Cu1 71.39(6), Cu1-I1-Cu2 72.20(6), I2-Cu2-Ge2 124.97(8), Ge2-Cu2-I1 127.41(8), Ge1-Cu1-I2 124.38(8), Ge1-Cu1-I1 128.57(8).

The NHGe-supported copper(I) iodide complex **4** crystallizes in the monoclinic space group  $C2/c$  (**Figure A2.2**). The molecular arrangement of **4** is similar to the complexes **2**, **1**<sup>6d</sup> and **3**.<sup>6j</sup> The Ge(II) center of **4** displays a distorted tetrahedral geometry and the Ge1-Cu1 (2.318(2) Å) and Ge2-Cu2 (2.324(2) Å) bond distances are slightly larger than the Si-Cu bond distances of  $[(\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Si}\{\text{N}(\text{SiMe}_3)_2\})_2\text{Cu}_2\text{I}_2]$ ,<sup>6j</sup> but matches well with those reported for  $[(i\text{Bu})_2\text{ATIGeCl}]_2(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2$ ; Ge1-Cu1 2.345(1) Å] (ATI = aminotroponiminato).<sup>7g</sup> The Cu1-I1 (2.565(2) Å), Cu2-I1 (2.562(2) Å), Cu2-I2 (2.582(2) Å) and Cu1-I2 (2.595(2) Å) bond distances of **4** are significantly smaller than those reported for  $[(i\text{Bu})_2\text{ATIGeCl}]_2(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2$ ; Cu1-I1 (2.733(1) Å) and Cu1\*-I1 (2.651(1) Å).<sup>7g</sup>

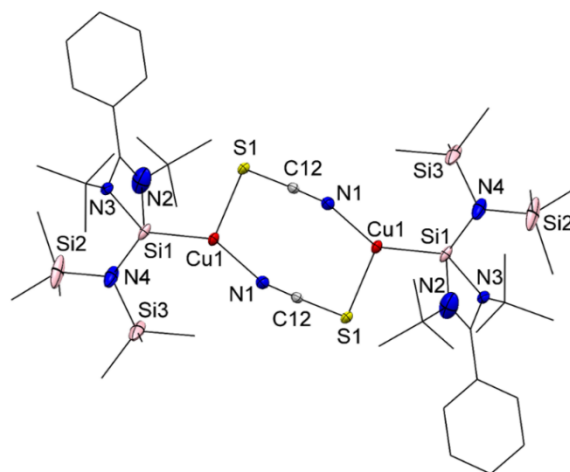


**Figure A2.3.** The molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1-Cu1 2.224(2), Cu1-N1 1.938(5), N1-C12 1.155(7), C12-S1 1.646(5), Cu1-S1 2.362(1), Cu1-Cu1 5.175(2); Si1-Cu1-N1 143.8(1), Si1-Cu1-S1 112.93(6), S1-Cu1-N1 103.3(1), Cu1-N1-C12 161.5(4), N1-C12-S1 177.7(5).

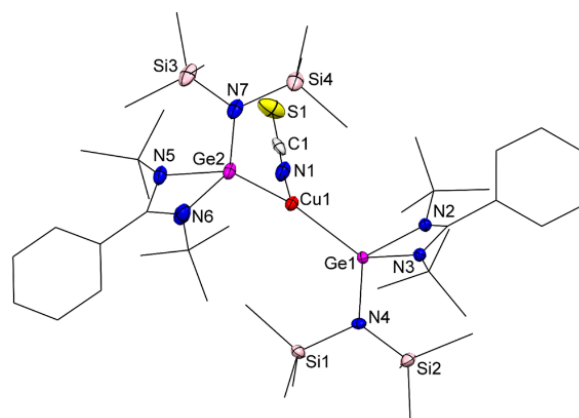


**Figure A2.4.** The molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge2-Cu1 2.3482(9), Ge1-Cu1 2.3469(9), Cu1-N1 1.961(3), N1-C1 1.096(5), C1-S1 1.666(4); Ge2-Cu1-Ge1 141.05(2), Cu1-N1-C1 168.7(3), N1-C1-S1 178.2(3).

The complex **5** crystallizes in the triclinic space group *P*-1 and possesses an *C*<sub>2</sub>-axis. The molecular structure of **5** reveals a dimeric structure (**Figure A2.3**), where copper(I) centre is three-coordinate, displaying the bonding with N-atom of one thiocyanate group and S-atom of another thiocyanate group. The complex **5** is the first report on NHSi-supported copper(I) thiocyanate complex, which displays a structure similar to the CAAC-supported copper(I) thiocyanate complex.<sup>10</sup> The N-bound thiocyanate group displays a signal at  $\delta$  131.86 ppm in <sup>13</sup>C NMR spectrum, which is slightly downfield shifted as compared to the CAAC-supported

copper(I) thiocyanate complex ( $\delta$  134.7 ppm).<sup>10</sup> The IR spectrum of **5** shows a peak at 2104  $\text{cm}^{-1}$ , which also favors the N-bound thiocyanate group to the copper(I) centre (IR stretching frequency of CAAC-copper(I) thiocyanate complex was detected: IR at 2111  $\text{cm}^{-1}$ ).<sup>10</sup> The bond lengths and bond angles of **5** are comparable with those reported for CAAC-copper(I) thiocyanate complex [Cu-N, N=C and C=S bond lengths of **5** are 1.938(5) Å, 1.155(7) Å and 1.646(5) Å, respectively and the Cu-N-C and N-C-S bond angles are 161.5(4)° and 177.7(5)°, respectively; Cu-N, N=C and C=S bond lengths of CAAC-copper(I) thiocyanate complex are 1.9775(11) Å, 1.158(17) Å and 1.659(13) Å, respectively and Cu-N-C and N-C-S bond angles are 158.30(10)° and 178.73(11)°].<sup>10</sup>

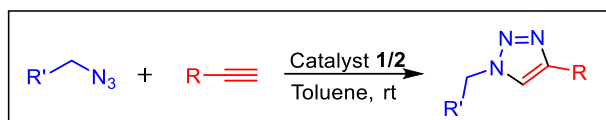
Interestingly, the reaction of copper(I) thiocyanate with NHGe ligand afforded a mononuclear copper(I) thiocyanate complex **6**, which is coordinated to two NHGe ligands (**Figure A2.4**). The chemical shift at  $\delta$  133.76 ppm in the  $^{13}\text{C}$  NMR spectrum of **6** indicates the N-bound thiocyanate complex.<sup>10</sup> The N=C and C=S bond distances of **6** are 1.096(5) and 1.666(4) Å, respectively, which are slightly shorter than those observed in monomeric CAAC-supported copper(I) thiocyanate complex (N=C bond distance = 1.158-1.162 Å and C=S bond distance = 1.619-1.659 Å).<sup>10</sup> The difference in the coordination behavior of these two ligands to CuNCS can be attributed to the strong donation of NHSi ligand compared to the NHGe ligand.

### Catalytic application in click chemistry:

In 2020, our group introduced a NHSi-based cationic copper(I) complex (**III**) as an effective catalyst in click chemistry.<sup>6g</sup> In this work, we utilized 0.5 mol% of the catalyst at room temperature in toluene for CuAAC reaction to afford a moderate to excellent conversion.<sup>6g</sup> However, **III** is not very stable due to its cationic nature and weak arene interaction, which hinders its broad application in large-scale organic synthesis. Therefore, we sought to use a simple silylene -supported copper(I) bromide complex (**1**) as a catalyst, which afforded an excellent conversion for CuAAC reaction (**Table A2.1**). Then, we turned our investigation towards amidinato-germylene-supported copper(I) bromide complex (**2**). We found that **2** is also an effective catalyst for CuAAC reaction but with more catalyst loading as compared to **1** (**Table A2.1**). We also probed complexes **3-6** as catalysts for the comparison purpose. Our results are discussed here.

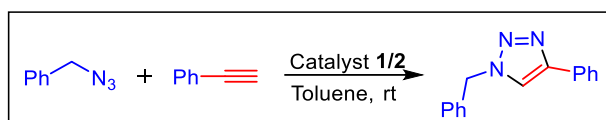
The study was commenced by reacting phenyl acetylene, benzyl azide in presence of **1** or **2** as the catalyst under ambient conditions (**Scheme A2.2**). After optimization of the reaction conditions with different combinations (**Table A2.1**), we found that 0.5 mol% of **1** at room temperature for 8 hours in toluene (Entry 4, **Table A2.2**) is the most efficient condition, which

affords 98% yield of the 1,2,3-triazole product. Slightly higher catalyst loading (2 mol%) and 12 hours reaction time are required for **2** (Entry 8, **Table A2.2**) to catalyze the reaction efficiently. Two sets of the control reactions were performed to understand the role of the catalyst: (i) when the reaction was performed without catalyst (Entry 9, **Table A2.2**), only <1% yield was obtained (ii) when the reaction was carried out with 20 mol% of CuBr as a catalyst, but without any ligand (Entry 10, **Table A2.2**), only <2% yield was detected. These two experiments elucidated the importance of the NHSi and NHGe ligands in CuAAC reaction. Further, we elaborated on the substrate scope of the reaction. Several aromatic and aliphatic alkynes bearing the different functional groups (electron-donating and electron-withdrawing) were probed with a variety of substituted benzyl azides (**Scheme A2.3**) under the optimized conditions (**Chart A2.2-A2.4**). The yields of these reactions range from moderate to excellent (several cases up to >99% yield).



**Scheme A2.2.** General copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction.

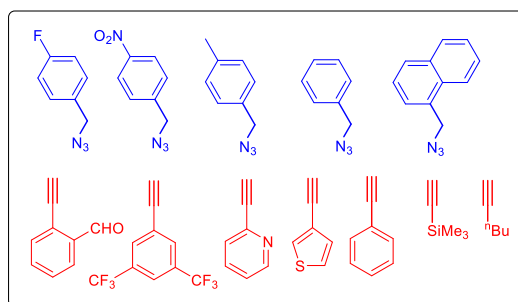
**Table A2.1.** Optimization of the reaction conditions of CuAAC reaction catalyzed by **1** and **2** (for phenyl acetylene and benzyl azide).



| Entry | Catalyst | Mol% | Time (h) | Yield <sup>a</sup> (%) |
|-------|----------|------|----------|------------------------|
| 1.    | 1        | 2    | 12       | >99                    |
| 2.    | 1        | 1    | 12       | >99                    |
| 3.    | 1        | 0.5  | 12       | >99                    |
| 4.    | 1        | 0.5  | 8        | 98                     |
| 5.    | 1        | 0.5  | 6        | 85                     |
| 6.    | 2        | 0.5  | 12       | 41                     |
| 7.    | 2        | 1    | 12       | 65                     |

|     |      |    |    |    |
|-----|------|----|----|----|
| 8.  | 2    | 2  | 12 | 76 |
| 9.  | -    | -  | 12 | <1 |
| 10. | CuBr | 15 | 12 | <2 |

[<sup>a</sup>Yields were determined by the integration of the corresponding <sup>1</sup>H NMR spectra normalized on the internal standard (adamantane)]



**Scheme A2.3.** Various azide and alkyne substrates used to probe substrate scope of CuAAC reaction catalyzed by **1** and **2**.

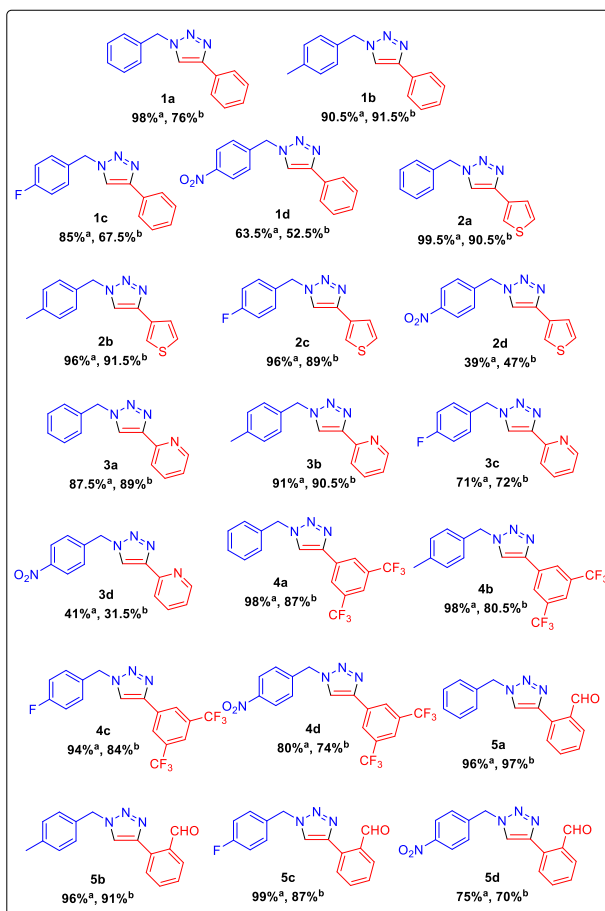


**Chart A2.2.** Substrate scope of CuAAC reaction of aromatic alkynes with different functional group substituted benzyl azides. <sup>a</sup>Catalyst 1 (0.5 mol%, toluene, rt, 8 hours). <sup>b</sup>Catalyst 2 (2 mol%, toluene, rt, 12 hours). \*NMR Yields.

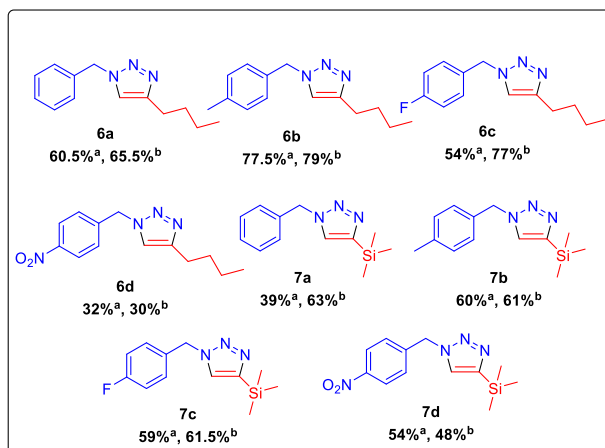


**Chart A2.3.** Substrate scope of CuAAC reaction of aliphatic alkynes with different functional groups substituted benzyl azides. <sup>a</sup>Catalyst 1 (0.5 mol%, toluene, rt, 8 hours). <sup>b</sup>Catalyst 2 (2 mol%, toluene, rt, 12 hours). \*NMR Yields.

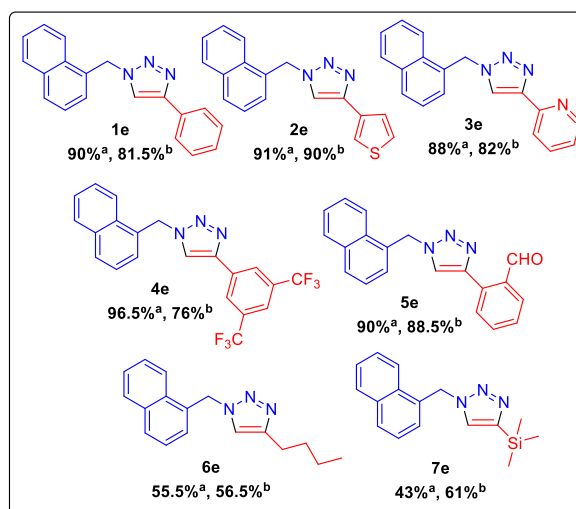


**Chart A2.4.** Substrate scope of CuAAC reaction of aromatic and aliphatic alkynes with 1-(azidomethyl) naphthalene. <sup>a</sup>Catalyst 1 (0.5 mol%, toluene, rt, 8 hours). <sup>b</sup>Catalyst 2 (2 mol%, toluene, rt, 12 hours). \*NMR Yields.

Aromatic alkynes (**Chart A2.2**) led to higher yields with respect to aliphatic alkynes (**Chart A2.3**). To understand the  $\pi$ -electronic displacement from alkynes to the catalyst **1**, absorbance spectra of catalyst **1** in the presence of phenyl acetylene (aromatic alkyne) and ethynyltrimethylsilane (aliphatic alkyne) were investigated. The UV-vis spectra displayed that

the  $\pi$ -electronic displacement is higher in the case of phenyl acetylene as compared to ethynyltrimethylsilane.<sup>11</sup> Strong electron-withdrawing group ( $-\text{NO}_2$ ) substituted benzyl azides give lower yields (**Chart A2.2** and **Chart A2.3**), whereas electron-donating group ( $-\text{CH}_3$ ) substituted benzyl azides render higher yields (**Chart A2.2** and **Chart A2.3**).

We observed that the silylene supported copper bromide complex (**1**) is a better catalyst for the azide-alkyne cycloaddition reactions than the corresponding germylene copper bromide complex (**2**). The UV-vis spectra demonstrated that the  $\pi$ -electronic displacement is higher for **1** than that of **2**,<sup>11</sup> explicating that silylene supported copper complex (**1**) is a better catalyst for azide-alkyne cycloaddition reaction. We have also employed **3**, **4**, **5** and **6** as catalysts for CuAAC reaction and found them to be competent catalysts (**Chart A2.5**). It was observed that the NHSi-supported copper halide complexes exhibit better efficiency as compared to the NHGe-supported copper complexes.

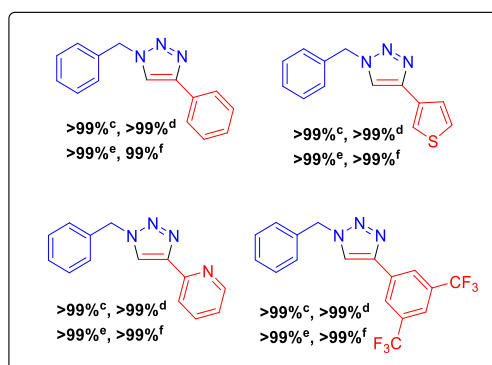


**Chart A2.5.** Substrate scope of CuAAC reaction of aromatic alkynes with benzyl azide using catalysts **3-6**. All are conversion yields. <sup>c</sup>Complex **3** (0.5 mol%, toluene, rt, 4 hours). <sup>d</sup>Complex **4** (2 mol%, toluene, rt, 10 hours). <sup>e</sup>Complex **5** (1 mol%, toluene, rt, 8 hours). <sup>f</sup>Complex **6** (2 mol%, toluene, rt, 12 hours). \*Conversion Yields.

We have compared the efficacy of our catalysts with the previously reported NHSi-supported copper complexes in CuAAC reaction, which is summarized in Table 2. It is important to note that the yields reported for the catalysts **I-III** are conversion yields only. Hence, for the comparison purpose we have used conversion only.

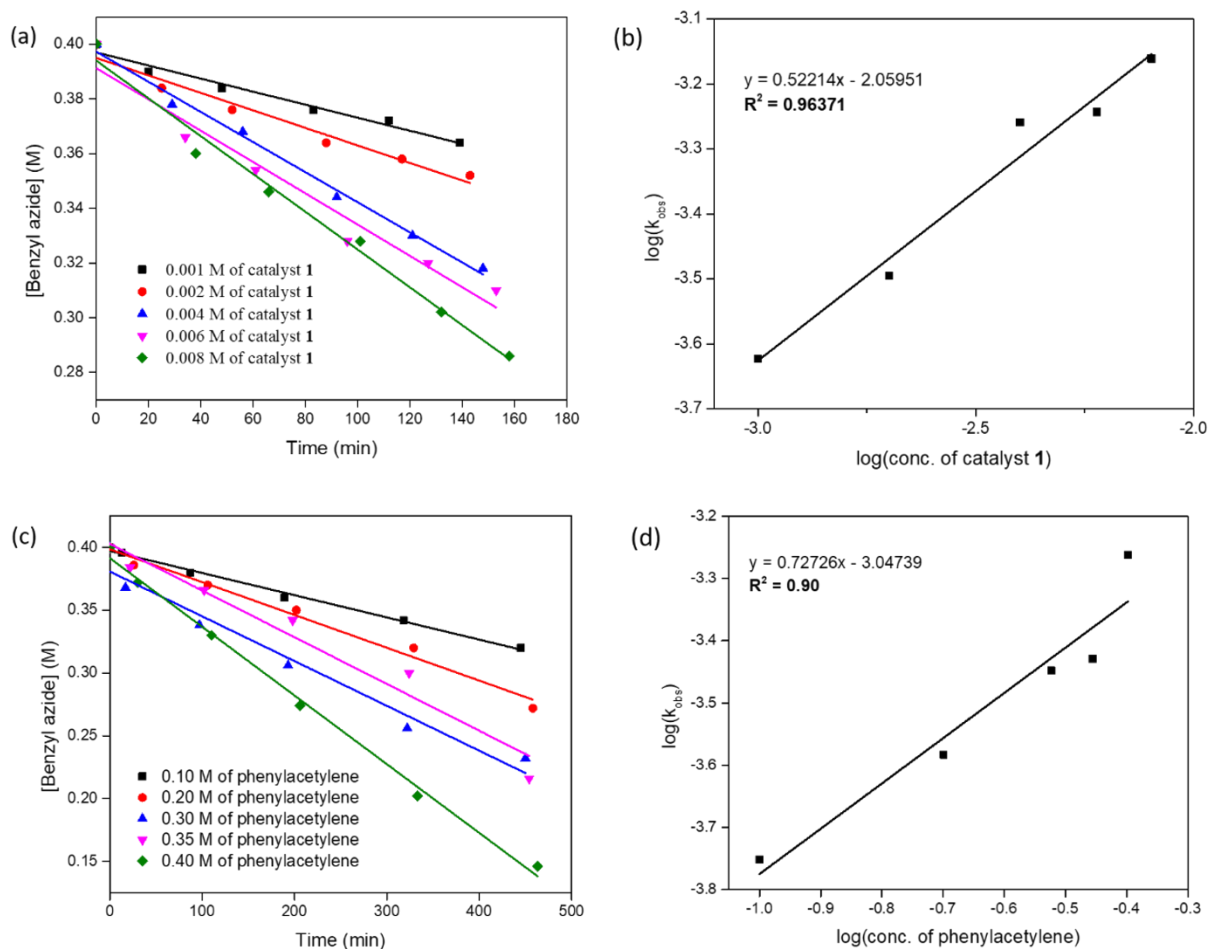
**Table 2.** Comparison with other silylene copper(I) halide complexes (for the reaction of phenyl acetylene and benzyl azide).

| Catalyst   | Mol (%) | Time | Yield (%)                                   | Ref.         |
|------------|---------|------|---------------------------------------------|--------------|
| <b>I</b>   | 1       | 8 h  | 46<br>(conversion)                          | 6f           |
| <b>II</b>  | 1       | 8 h  | >99<br>(conversion)                         | 6f           |
| <b>III</b> | 0.5     | 6 h  | >99<br>(conversion)                         | 6g           |
| <b>1</b>   | 0.5     | 8 h  | >99<br>(conversion)                         | Present work |
| <b>2</b>   | 2       | 12 h | >80<br>(conversion)<br><br>76<br>(Isolated) | Present work |
| <b>3</b>   | 0.5     | 4 h  | >99<br>(conversion)                         | Present work |
| <b>4</b>   | 2       | 10 h | >99<br>(conversion)                         | Present work |
| <b>5</b>   | 0.5     | 8 h  | >99<br>(conversion)                         | Present work |
| <b>6</b>   | 2       | 12 h | >99<br>(conversion)                         | Present work |

### Kinetic studies:

To determine the order of the CuAAC reaction with respect to the catalyst **1**, the initial rate of the reaction was observed (up to ~25-30% consumption of benzyl azide). Initial rate ( $k_{\text{obs}}$ ) was determined using various concentrations of catalyst **1**, while keeping the concentrations of benzyl azide and phenylacetylene constant.<sup>12</sup> The adamantane was used as an internal standard to determine the relative integrations in <sup>1</sup>H NMR spectra. The kinetic studies demonstrated a linear correlation between the concentration of benzyl azide with time (**Figure A2.5a**), where

**Figure A2.5a** benzyl azide concentration gradually decreases with increasing time. Further, another linear correlation is observed in  $\log_{10}(k_{\text{obs}})$  vs.  $\log_{10}(\text{conc. of catalyst 1})$  plot with a slope of 0.52, indicating the rate of CuAAC reaction increases with an increase in the concentration of the catalyst **1**. The obtained fractional order 0.52 can be correlated with the involvement of the binuclear complex as the active catalyst in the CuAAC reaction (**Figure A2.5b**).<sup>12a</sup>



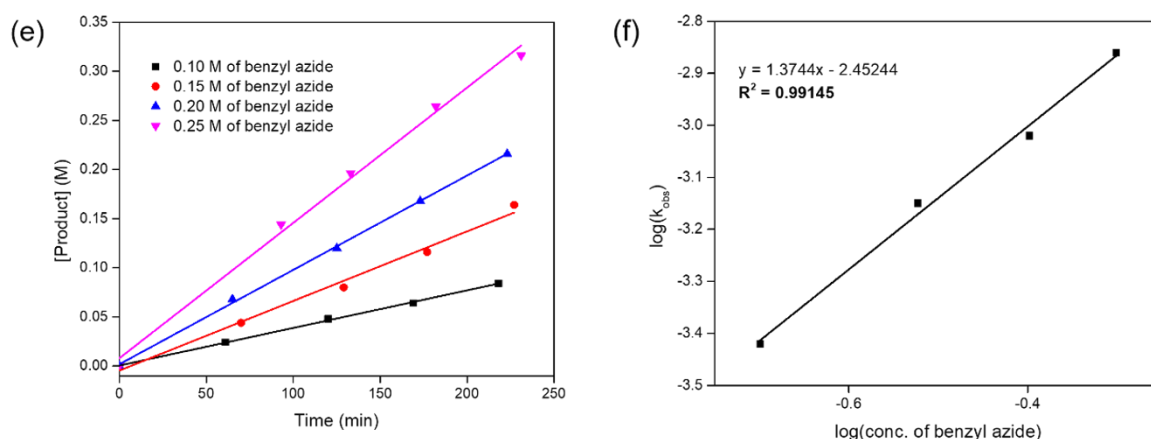


**Figure A2.5.** (a) Plot of [benzyl azide] vs. Time (best linear fitted) used for the determination of the initial rate ( $k_{\text{obs}}$ ) values. (b) Plot of  $\log_{10}(k_{\text{obs}})$  vs.  $\log_{10}(\text{conc. of catalyst } \mathbf{1})$  for the determination of the order of the reaction. (c) Plot of [benzyl azide] vs. Time (best linear fitted) used for the determination of the initial rate ( $k_{\text{obs}}$ ) values. (d) Plot of  $\log_{10}(k_{\text{obs}})$  vs.  $\log_{10}(\text{conc. of phenylacetylene})$  to determine the order of the reaction.

The order of the CuAAC reaction with respect to phenylacetylene was also determined by using the initial rate method by consumption of benzyl azide with time (**Figure A2.5c**). The initial rate ( $k_{\text{obs}}$ ) was determined by using various concentrations of phenylacetylene, while keeping the concentration of benzyl azide and catalyst **1** constant. The rate of the CuAAC reaction increases upon increasing the initial concentration of phenylacetylene with a slope of 0.73 obtained from the plot of  $\log_{10}(k_{\text{obs}})$  vs.  $\log_{10}(\text{conc. of phenylacetylene})$  (**Figure A2.5d**), suggesting the occurrence of more than one pathway.<sup>12b</sup> This observation indicates a decisive and dispersive role of phenylacetylene in the CuAAC reaction.

The order of the CuAAC reaction with respect to benzyl azide was investigated by using the initial rate method by formation of triazole product with time (**Figure A2.5e**). The initial rate ( $k_{\text{obs}}$ ) was determined by using various concentrations of benzyl azide, while keeping the concentration of phenylacetylene and catalyst **1** constant. The rate of CuAAC reaction increases with an increase in the concentration of the benzyl azide, and a slope 1.37 was obtained from plot of  $\log_{10}(k_{\text{obs}})$  vs.  $\log_{10}(\text{conc. of benzyl azide})$  (**Figure A2.5f**), indicating a fractional and complex rate order. This fractional rate order with respect to benzyl azide seems to be logical due to the involvement of the benzyl azide in multiple steps in the CuAAC reaction.<sup>12c</sup>

### Theoretical mechanistic study:

Quantum mechanical calculations were carried out to understand the mechanism of the alkyne azide cycloaddition reaction catalyzed by silylene and germylene-supported Cu(I) complexes. The energetics were carried out at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. The reaction energetics for the uncatalyzed phenylacetylene – benzyl azide cycloaddition was calculated and found to be highly exothermic and exergonic.<sup>13</sup> The mechanism for the CuAAC reactions were studied by group of Sharpless and others.<sup>14,15</sup> One of the well-reported reaction mechanisms is the acetylide formation reaction by Sharpless et al.<sup>14</sup> The group of Díez-Gonzalez discussed various possible reaction pathways for the cycloaddition reaction using mono and bimetallic catalysts.<sup>15</sup>

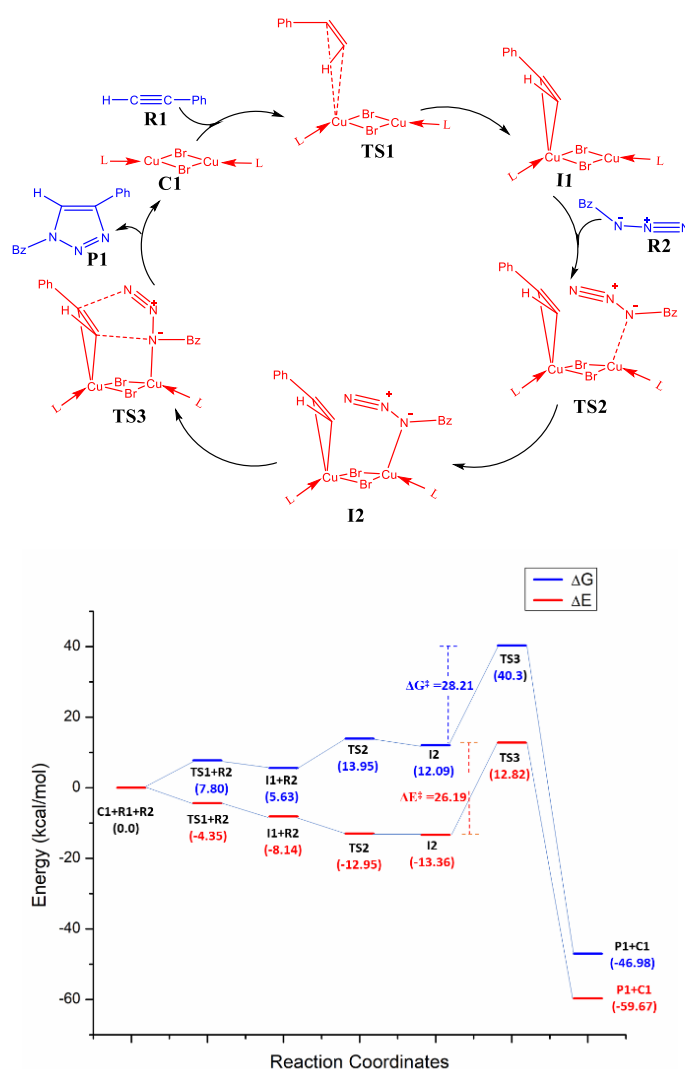
We analyzed multiple reaction pathways by considering mono (LCuBr) and bimetallic ( $L_2Cu_2Br_2$ ) Cu complexes as active catalysts. The monometallic Cu-complex (LCuBr) can be considered as formed by the dissociation of  $L_2Cu_2Br_2$ . The dissociation energy is slightly endothermic and exergonic for  $L = NHSi$  ( $\Delta E = 14.21$  kcal/mol  $\Delta G = -2.52$  kcal/mol) and slightly more endothermic and endergonic for  $L = NHGe$  ( $\Delta E = 19.15$  kcal/mol  $\Delta G = 4.09$  kcal/mol). The energetics for the formation of LCu-acetylide by the elimination of HBr, which is similar to the mechanism suggested by Sharpless, was found to be highly endothermic and endergonic ( $\Delta E = 28.59$  kcal/mol ( $L = NHSi$ ),  $28.76$  kcal/mol ( $L = NHGe$ ) and  $\Delta G = 30.83$  kcal/mol ( $L = NHSi$ ),  $31.80$  kcal/mol ( $L = NHGe$ )). Hence the mechanism involving the LCu-acetylide formation can be excluded. The reaction pathways involving acetylene  $\pi$  complexes are found to be more favourable than the acetylide formation. Among the  $\pi$ -complex reaction pathways, the reaction pathway involving bimetallic Cu-complex is kinetically more favourable than the reaction pathways involving monometallic Cu-complexes. The details of reaction pathway involving bimetallic Cu-complexes are discussed below (**Scheme A2.4**).

In the first step, the alkyne (**R1**) initially forms a weakly bonded  $\pi$ -complex (**I1**) by the interaction of the  $\pi$ -MO of the alkyne with the empty orbital of one of the Cu ( $3d+4p$ ) in the catalyst. The inter electronic repulsion between the  $d^{10}$  Cu and  $\pi$ -electrons of acetylene leads to weakly bonded  $\pi$ -complex (**I1**). Hence, the formation of **I1** is slightly exothermic and slightly endergonic and is more preferable when the ligand is NHSi.

Since the stationary point for the transition states was not located by geometry optimization, we carried out a manual potential energy surface scanning along the reaction coordinates. The highest energy point along the reaction coordinate is taken as transition state geometry (**TS1**). The corresponding barrier was found to be very low (**Scheme A2.4b**) as per the free energy data and barrierless based on the electronic energy.

The C-C bond lengths in intermediates **I1** are elongated (1.246 Å and 1.244 Å) as compared to the free alkyne (1.215 Å). The C-C-C<sub>Ph</sub> and C-C-H bond angles are also reduced to 166° and 160° when L = NHSi and 167° and 160° when L = NHGe. Here, alkyne is anchored on one of the Cu centre by forming  $\pi$ -complex. The tricoordinate Cu centre of **I1** can be bonded with the benzyl coordinated nitrogen of the azide resulting in intermediate **I2**. The formation of **I2** is slightly exothermic and slightly endergonic. We could also locate the transition state (**TS2**) for this step as similar to that employed for obtaining the **TS1**. Here the kinetic barrier is found to be low as per the free energy and barrierless based on the electronic energy.

The N-N<sub>Bz</sub> bond in complex **I2** is slightly elongated (1.239 Å when L = NHSi and 1.240 Å when L = NHGe) as compared to free azide (1.234 Å).



**Scheme A2.4.** (a) Schematic representation of bimetallic CuAAC reaction mechanism calculated at M06/def2-TZVPP//BP86/def2-TZVPP level of theory using toluene as solvent.

Energetics are given in kcal/mol. (b) Reaction energy profile when L = NHGe. The energetics are given in kcal/mol. Reaction energy profile when L = NHSi.

The acetylenic C-C bond lengths and C-C-C<sub>Ph</sub> and C-C-H bond angles in **I2** are similar to those in **I1**. The acetylenic and azide groups are activated and anchored on the nearby Cu centres. This facilitates 1,3-dipolar cycloaddition reaction of acetylenic and azide fragments in **I2** via cyclic 5-membered transition state leading to the formation 1,4 disubstituted triazole and regenerating the catalyst. This step is highly exothermic (-47.02 kcal/mol (NHSi), -46.03 kcal/mol (NHGe)) and highly exergonic (-57.71 kcal/mol (NHSi), -59.06 kcal/mol (NHGe)). The transition state energy barrier for the addition are significantly lower as compared to that obtained for mono metallic Cu-complex as an active catalyst. The transition state barriers are comparable to those reported by Sharpless ( $\Delta G^\ddagger = 26$  kcal/mol) and significantly lower as compared to the uncatalyzed reaction by 8 kcal/mol.

The concerted 1,3-dipolar cycloaddition of azide with acetylene with concomitant dissociation of catalyst can be considered the rate-determining step of the overall reaction. Since the model bimetallic catalyst with CH<sub>3</sub> groups instead of TMS and t-butyl groups was used for the calculations, the activation barrier with the real ligand is expected to be a lower value. Moreover, this activation barrier can be overcome at room temperature with the reported reaction time.

The molecular orbital (MO) analysis of intermediate **I2** indicate that (**Figures A2.6**) the  $\pi$  molecular orbitals of acetylenic and azide fragments are activated as compared to those in free alkyne and azide viz., the eigenvalue of  $\pi$ -bonding molecular orbital increases and that of  $\pi^*$ -antibonding molecular orbital reduces. This corroborates well with the geometrical data and lowering of transition state energy barrier. Hence the bimetallic Cu catalyst facilitate the cycloaddition reaction by anchoring the reactants to the close proximity and reducing the energy gap between the frontier orbitals of dipole and dipolarophile. Since the difference in the transition state barriers for the cycloaddition step as well as overall transition state energy barriers when L = NHSi and L = NHGe are minimal, the better efficiency of NHSi-Cu catalyst would not be attributed to the reaction energetics.

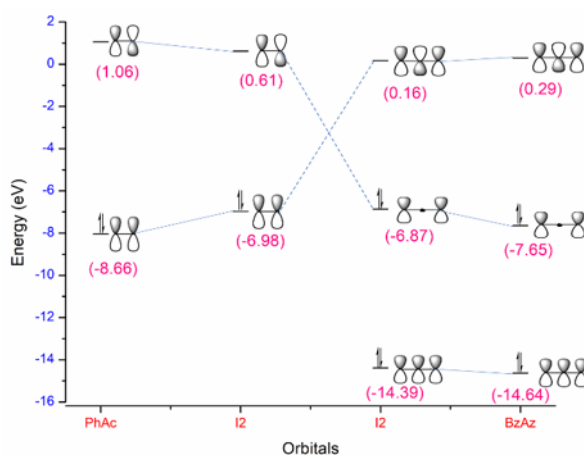


**Figure A2.6.** Important frontier molecular orbitals of phenyl acetylene (PhAc), benzyl azide (BzAz) and corresponding molecular orbitals in I2, when L = NHSi.

### Conclusion:

In summary, we have synthesized four new tetraylene-copper(I) complexes,  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}\text{CuBr}]_2$  (**2**),  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}\text{CuI}]_2$  (**4**),  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Si}\{\text{N}(\text{SiMe}_3)_2\}\text{CuSCN}]_2$  (**5**),  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}2\text{CuSCN}]$  (**6**). It is noteworthy to mention that **5** and **6** are the first examples of NHSi/NHGe based copper thiocyanate complexes. Subsequently, we have demonstrated their use as efficient catalysts in CuAAC reactions. The catalytic activity of silylene copper complexes were found to be superior over germylene copper complexes. Moreover, these catalytic systems are more stable than the previously reported catalyst **III**. We have performed the CuAAC reaction of several alkynes with many organic azides under ambient conditions, affording good to excellent yields of triazoles. The multiple reaction pathways were explored by DFT calculations by considering mono (LCuBr) and bimetallic ( $\text{L}_2\text{Cu}_2\text{Br}_2$ ) Cu complexes as active catalysts. The bimetallic Cu catalyst facilitates the cycloaddition reaction of dipole and dipolarophile.

### Computational methodology:

All geometry optimizations were carried out with a Gaussian09 programming package utilizing the generalized gradient approximation functional of Becke in conjunction with the correlation functional of Perdew (BP86).<sup>16,17</sup> A def2-TZVPP basis set with triple  $\zeta$ -quality, augmented with two sets of polarization function was used for the geometry optimization.<sup>18</sup> All stationary points were characterized on the potential energy hypersurface by vibrational analysis as minima (all real frequencies). Single point calculations were performed on the optimized geometries using the meta-GGA exchange functional M06 with the basis set having triple  $\zeta$ -quality, augmented with two sets of polarization functions (def2-TZVPP).<sup>18,19</sup> The reaction energy ( $\Delta E$ ) was

calculated by adding electronic energy at the M06/def2-TZVPP level of theory with zero-point correction calculated at BP86/def2-TZVPP level of theory. The Gibbs free energy ( $\Delta G$ ) was calculated by adding electronic energy at the M06/def2-TZVPP level of theory with the thermal correction to the Gibbs free energy calculated at BP86/def2-TZVPP level of theory. The solvent effect of toluene was incorporated using the polar continuum model.<sup>20</sup> The bimetallic catalyst was modelled by replacing bulkier TMS and *tert*-butyl groups with CH<sub>3</sub> groups.

### Crystallographic details:

Crystal data for **2** was collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The absorption correction was done using multi-scan method (SADABS). The structures were solved by direct methods and refined by full-matrix least-squares methods against F<sup>2</sup>(SHELXL-2014/6) and Olex1 with the ShelXT2 structure solution program.<sup>21</sup> Attempts to refine peaks of residual electron density as disordered or partial occupancy solvent toluene carbon atoms were unsuccessful. The data were corrected for disordered electron density using the SQUEEZE procedure, as implemented in PLATON.<sup>22</sup> Crystallographic data files for **2-6** have been deposited with the Cambridge Crystallographic Data Centre: 2149671 (**2**), 2203510 (**4**), 2203511 (**5**), 2202740 (**6**).

### References:

1. (a) Haaf, M.; Schmedake, T. A.; West, R. Stable Silylenes. *Acc. Chem. Res.* **2000**, *33*, 704-714. (b) Mizuhata, Y.; Sasamori, T.; Tokito, N. Stable Heavier Carbene Analogues. *Chem. Rev.* **2009**, *109*, 3479-3511. (c) Asay, M.; Jones, C.; Driess, M. N-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands. *Chem. Rev.* **2011**, *111*, 354-396. (d) Mandal, S. K.; Roesky, H. W. Group 14 Hydrides with Low Valent Elements for Activation of Small Molecules. *Acc. Chem. Res.* **2012**, *45*, 298-307. (e) Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. Chemistry of Functionalized Silylenes. *Chem. Sci.* **2012**, *3*, 659-682. (f) Sen, N.; Khan, S. Heavier Tetrylenes as Single Site Catalysts. *Chem. Asian. J.*, **2021**, *16*, 705-719. (g) Ghosh, M.; Khan, S. Silylene Coordinated Coinage Metal Complexes: An Itinerary of Their Utilities. *Adv. Inorg. Chem.*, Academic Press, 2022, ISSN 0898-8838, <https://doi.org/10.1016/bs.adioch.2022.06.001>.
2. (a) Fischer, R. C.; Power, P. P.  $\pi$ -Bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millennium. *Chem. Rev.* **2010**, *110*, 3877-3923. (b) Nagendran, S.; Roesky, H. W. The Chemistry of

- Aluminum(I), Silicon(II), and Germanium(II). *Organometallics* **2008**, *27*, 457-492. (c) Leung, W. –P.; Kan, K. –W; Chong, K. –H. Reactions of Some Organogermanium (II) Chlorides. *Coord. Chem. Rev.* **2007**, *251*, 2253-2265. (d) Kühl, O. *N*-heterocyclic germylenes and related compounds *Coord. Chem. Rev.* **2004**, *248*, 411-427. (e) Dasgupta, R; Das, S.; Hiwase, S; Pati, S. K.; Khan, S. *N*-Heterocyclic Germylene and Stannylene Catalyzed Cyanosilylation and Hydroboration of Aldehydes. *Organometallics* **2019**, *38*, 1429-1435. (f) Ghosh, M.; Sen, N.; Khan, S. Coinage Metal Complexes of Germylene and Stannylene. *ACS Omega* **2022**, *7*, 6449-6454.
3. (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* **2000**, *100*, 39-91. (b) Fremont, P.; Marion, N.; Nolan, S. P. Carbenes: Synthesis, Properties and Organometallic Chemistry. *Coord. Chem. Rev.* **2009**, *253*, 862-892. (c) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An Overview of *N*-Heterocyclic Carbenes. *Nature* **2014**, *510*, 485-496. (d) Hahn, F. E. Introduction: Carbene Chemistry. *Chem. Rev.* **2018**, *118*, 9455-9456. (e) Zhu, D.; Chen, L.; Fan, H.; Yao, Q.; Zhu, S. Recent Progress on Donor and Donor-donor Carbenes. *Chem. Soc. Rev.* **2020**, *49*, 908-950. (f) Sau, S. C.; Hota, P. K.; Mandal, S. K.; Soleilhavoup, M.; Bertrand, G. Stable Abnormal *N*-heterocyclic Carbenes and their Applications. *Chem. Soc. Rev.* **2020**, *49*, 1233-1252. (g) Hossain, J.; Akhtar, R.; Khan, S. Luminescent Coinage Metal Complexes of Carbenes. *Polyhedron* **2021**, *201*, 115151.
4. (a) Fürstner, A.; Krause, H; Lehmann, C. W. Preparation, Structure and Catalytic Properties of a Binuclear Pd(0) Complex with Bridging Silylene Ligands. *Chem. Commun.* **2001**, 2372–2373. (b) Zhang, M.; Liu, X.; Shi, C.; Ren, C.; Ding, Y.; Roesky, H. W. The Synthesis of  $(\eta^3\text{-C}_3\text{H}_5)\text{Pd}\{\text{Si}[\text{N}(\text{tBu})\text{CH}]_2\}\text{Cl}$  and the Catalytic Property for Heck Reaction. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1755–1758. (c) Waterman, R.; Hayes, P. G.; Tilley, T. D. Synthetic Development and Chemical Reactivity of Transition-Metal Silylene Complexes. *Acc. Chem. Res.* **2007**, *40*, 712-719. (d) Blom, B.; Gallego, D.; Driess, M. *N*-heterocyclic Silylene Complexes in Catalysis: New Frontiers in an Emerging Field. *Inorg. Chem. Front.* **2014**, *1*, 134-148. (e) Raoufmoghaddam, S.; Zhou, Y. –P.; Wang, Y.; Driess, M. *N*-heterocyclic Silylenes as Powerful Steering Ligands in Catalysis. *J. Organomet. Chem.* **2017**, *829*, 2-10. (f) Zhou, Y. –P.; Driess, M. Isolable Silylene Ligands Can Boost Efficiencies and Selectivities in Metal-Mediated Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 3715-3728. (g) Ghosh, M.; Khan, S. *N*-Heterocyclic Silylenes in Coinage Metal Chemistry: An Account of Recent Advances. *Dalton Trans.* **2021**, *50*, 10674-10688.

5. (a) Bruck, A.; Gallego, D.; Wang, W.; Irran, E.; Driess, M.; Hartwig, J. F. J. Pushing the  $\sigma$ -Donor Strength in Iridium Pincer Complexes: Bis- (silylene) and Bis(germylene) Ligands are Stronger Donors than Bis(phosphorus(III)) Ligands. *Angew. Chem., Int. Ed.* **2012**, *51*, 11478-11482. (b) Wang, W.; Inoue, S.; Enthaler, S.; Driess, M. Bis(silylenyl)- and Bis(germylenyl)-Substituted Ferrocenes: Synthesis, Structure and Catalytic Applications of Bidentate Silicon(II)–Cobalt Complexes. *Angew. Chem., Int. Ed.* **2012**, *51*, 6167-6171. (c) Gallego, D.; Bruck, A.; Irran, E.; Meier, F.; Kaupp, M.; Driess, M.; Hartwig, J. F. J. From Bis(silylene) and Bis(germylene) Pincer-Type Nickel(II) Complexes to Isolable Intermediates of the Nickel-Catalyzed Sonogashira Cross-Coupling Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 15617-15626. (d) Alvarez-Rodriguez, L.; Cabeza, J. A.; Fernandez-Colinas, J. M.; Garcia-Alvarez, P.; Polo, D. Amidinatogermylene Metal Complexes as Homogeneous Catalysts in Alcoholic Media. *Organometallics* **2016**, *35*, 2516-2523. (e) Sharma, M. K.; Singh, D.; Mahawar, P.; Yadav, R.; Nagendran, S. Catalytic Cyanosilylation Using Germylene Stabilized Platinum(II) Dicyanide. *Dalton Trans.* **2018**, *47*, 5943-5947.
6. (a) Avent, A. G.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. Synthesis and Characterisation of Bis(amino)silylene Nickel(0), Palladium(II), Platinum(0), Platinum(II) and Copper(I) Complexes. *J. Organomet. Chem.* **2003**, *686*, 321-331. (b) Tan, G.; Blom, B.; Gallego, D.; Driess, M. Facile Access to Mono- and Dinuclear Heteroleptic N-Heterocyclic Silylene Copper Complexes. *Organometallics* **2014**, *33*, 363-369. (c) Troadec, T.; Prades, A.; Rodriguez, R.; Mirgalet, R.; Baceiredo, A.; Saffon-Merceron, N.; Branchadell, V.; Kato, T. Silacyclopropylideneplatinum(0) Complex as a Robust and Efficient Hydrosilylation Catalyst. *Inorg. Chem.* **2016**, *55*, 8234-8240. (d) Parvin, N.; Dasgupta, R.; Pal, S.; Sen, S. S.; Khan, S. Strikingly Diverse Reactivity of Structurally Identical Silylene and Stannylene. *Dalton Trans.* **2017**, *46*, 6528-6532. (e) Parvin, N.; Pal, S.; Echeverría, J.; Alvarez, S.; Khan, S. Taming a Monomeric  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$  Complex with Silylene. *Chem. Sci.* **2018**, *9*, 4333. (f) Paesch, A. N.; Kreyenschmidt, A. –K.; Herbst-Irmer, R.; Stalke, D. Side-Arm Functionalized Silylene Copper(I) Complexes in Catalysis. *Inorg. Chem.* **2019**, *58*, 7000-7009. (g) Parvin, N.; Hossain, J.; George, A.; Parameswaran, P.; Khan, S. N-Heterocyclic Silylene Stabilized Monocoordinated Copper(I)–Arene Cationic Complexes and Their Application in Click Chemistry. *Chem. Commun.* **2020**, *56*, 273-276. (h) Samuel, P. P.; Singh, A. P.; Sarish, S. P.; Matussek, J.; Objartel, I.; Roesky, H. W.; Stalke, D. Oxidative Addition Versus Substitution Reactions of Group 14 Dialkylamino Metallylenes with Pentafluoropyridine. *Inorg. Chem.* **2013**, *52*, 1544– 1549. (i) Sen, S. S.; Hey, J.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D. Striking Stability of a Substituted

- Silicon(II) Bis(trimethylsilyl)amide and the Facile Si-Me Bond Cleavage without a Transition Metal Catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 12311–12316; (j) Khan, S.; Ahirwar, S. K.; Pal, S.; Parvin, N.; Kathewad, N. Silicon(II) Bis(trimethylsilyl)amide (LSiN(SiMe<sub>3</sub>)<sub>2</sub>, L = PhC(NtBu)<sub>2</sub>) Supported Copper, Silver, and Gold Complexes. *Organometallics* **2015**, *34*, 5401–5406.
7. (a) Leung, W. –P.; So, C. –W.; Chong, K. –H.; Kan, K. –W.; Chan, H. –S.; Mak, T. C. W. Reactivity of Pyridyl-1-azaallyl Germanium(II) Chloride: Synthesis of Novel Lithium Germinate [(PhC≡C)<sub>3</sub>Ge]<sub>3</sub>GeLi(Et<sub>2</sub>O)<sub>3</sub>] and Ge(II)-M(I) (M = Cu and Au) Adducts. *Organometallics* 2006, *25*, 2851–2858. (b) York, J. T.; Young Jr., V. G.; Tolman, W. B. Heterobimetallic Activation of Dioxygen: Characterization and Reactivity of Novel Cu(I)-Ge(II) Complexes. *Inorg. Chem.* 2006, *45*, 4191–4198. (c) Arii, H.; Nakadate, F.; Mochida, K. Spectroscopic and Structural Characterization of Copper-Germylene Complexes Bearing an Isopropyl-Substituted β-Diketiminato Ligand. *Organometallics* 2009, *28*, 4909–4911. (d) Ferro, L.; Hitchcock, P. B.; Coles, M. P.; Fulton, J. R. Reactivity of Divalent Germanium Alkoxide Complexes Is in Sharp Contrast to the Heavier Tin and Lead Analogues. *Inorg. Chem.* 2012, **51**, 1544–1551. (e) Zhao, N.; Zhang, J.; Yang, Y.; Zhu, H.; Li, Y.; Fu, G. β-Diketiminato Germylene Supported Pentafluorophenyl copper(I) and silver(I) Complexes [LGe(Me)(CuC<sub>6</sub>F<sub>5</sub>)<sub>n</sub>]<sub>2</sub> (n = 1, 2), LGe[C(SiMe<sub>3</sub>)N<sub>2</sub>][AgC<sub>6</sub>F<sub>5</sub>], and {LGe[C(SiMe<sub>3</sub>)N<sub>2</sub>](AgC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>}<sub>2</sub> (L = HC[C(Me)N- 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>): Synthesis and Structural Characterization. *Inorg. Chem.* 2012, **51**, 8710–8718. (f) West, J. K.; Fondong, G. L.; Noll, B. C.; Stahl, L. Heavier Carbene Analogues and Their Derivatives as κ-El, κ<sup>2</sup>-El,N, and κ<sup>2</sup>-N,N' Ligands: Different Reactivity Patterns for Acyclic and Cyclic Diamidogermynes and -Stannylenes. *Dalton Trans.* 2013, *42*, 3835–3842. (g) Yadav, D.; Siwatch, R. K.; Sinhababu, S.; Nagendran, S. Aminotroponiminato(chloro)germylene Stabilized Copper(I) Iodide Complexes: Synthesis and Structure. *Inorg. Chem.*, 2014, **53**, 600–606. (h) Hlina, J.; Arp, H.; Walewska, M.; Floörke, U.; Zangger, K.; Marschner, C.; Baumgartner, J. Coordination Chemistry of Cyclic Disilylated Germynes and Stannylenes with Group 11 Metals. *Organometallics*, 2014, **33**, 7069–7077. (i) Yadav, D.; Siwatch, R. K.; Sinhababu, S.; Karwasara, S.; Singh, D.; Rajaraman, G.; Nagendran, S. Digermylene Oxide Stabilized Group 11 Metal Iodide Complexes. *Inorg. Chem.* 2015, **54**, 11067–11076. (j) Álvarez-Rodríguez, L.; Cabeza, J. A.; García-Álvarez, P.; Polo, D. Amidinatogermylene Complexes of Copper, Silver, and Gold. *Organometallics*, 2015, **34**, 5479–5484. (k) Cabeza, J. A.; Fernández, I.; García-Álvarez, P.; Laglera-Gándara, C. J. A

- Dipyrrromethane-Based Diphosphane–Germylene as Precursor to Tetrahedral Copper(I) and T-Shaped Silver(I) and Gold(I) PGeP Pincer Complexes. *Dalton Trans.* 2019, 48, **13273–13280**.
8. Liang, L.; Astruc, D. The Copper(I)-Catalyzed Alkyne-Azide Cycloaddition (CuAAC) “Click” Reaction and its Applications. An Overview. *Coord. Chem. Rev.* **2011**, 255, 2933–2945.
9. (a) Díez-González, S.; Nolan, S. P. [(NHC)<sub>2</sub>Cu]X Complexes as Efficient Catalysts for Azide–Alkyne Click Chemistry at Low Catalyst Loadings. *Angew. Chem., Int. Ed.* **2008**, 47, 8881–8884. (b) Díez-González, S.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Stevens, E. D.; Slawin, A. M. Z.; Nolan, S. P. [(NHC)CuX] Complexes: Synthesis, Characterization and Catalytic Activities in Reduction Reactions and Click Chemistry. On the Advantage of Using Well-Defined Catalytic Systems. *Dalton Trans.* **2010**, 39, 7595–7606. (c) Saha, S.; Kaur, M.; Bera, J. K. Fluorinated Anions Promoted “on Water” Activity of Di- and Tetranuclear Copper(I) Catalysts for Functional Triazole Synthesis. *Organometallics* **2015**, 34, 3047–3054. (d) Seo, C.; Cheong, Y. –J.; Yoon, W.; Kim, J.; Shin, J.; Yun, H.; Kim, S. – J.; Jang, H. –Y. Mononuclear Copper Complexes with Tridentate Tris(*N*-heterocyclic carbene): Synthesis and Catalysis of Alkyne-Azide Cycloaddition. *Organometallics* **2021**, 40, 16–22.
10. Romanov, A. S.; Becker, C. R.; James, C. E.; Di, D.; Credginton, D.; Linnolahti, M.; Bochmann, M. Copper and Gold Cyclic (Alkyl)(amino)carbine Complexes with Sub-Microsecond Photoemissions: Structure and Substituent Effects on Redox and Luminescent Properties. *Chem. Eur. J.* **2017**, 23, 4625–4637.
11. Ahmed, J.; Chakraborty, S.; Jose, A.; Sreejyothi P; Mandal, S. K. Integrating Organic Lewis Acid and Redox Catalysis: The Phenalenyl Cation in Dual Role. *J. Am. Chem. Soc.* **2018**, 140, 8330–8339.
12. (a) Patel, U. N.; Jagtap, R. A.; Punji, B. Scope and Mechanistic Aspect of Nickel-Catalyzed Alkenylation of Benzothiazoles and Related Azoles with Styryl Bromides. *Organometallics* **2019**, 38, 2422–2430; (b) Khake, S. M.; Jagtap, R. A.; Dangat, Y. B.; Gonnade, R. G.; Vanka, K.; Punji, B. Mechanistic Insights into Pincer-Ligated Palladium-Catalyzed Arylation of Azoles with Aryl Iodides: Evidence of a Pd<sup>II</sup>-Pd<sup>IV</sup>-Pd<sup>II</sup> Pathway. *Organometallics* **2016**, 35, 875–886; (c) Patel, U. N.; Jain, S.; Pandey, D. K.; Gonnade, R. G.; Vanka, K.; Punji, B. Mechanistic Aspects of Pincer Nickel(II)-Catalyzed C-H Bond Alkylation of Azoles with Alkyl Halides. *Organometallics*, **2018**, 37, 1017–1025.

13.  $\Delta E = -59.67$  kcal/mol and  $\Delta G = -46.98$  kcal/mol. The energy barrier for the reaction is  $\Delta E^\ddagger = 24.89$  kcal/mol and  $\Delta G^\ddagger = 36.60$  kcal/mol.
14. Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodleman, L.; Sharpless, K. B.; Fokin, V. V. Copper (I)-catalyzed synthesis of azoles. DFT study predicts unprecedented reactivity and intermediates. *J. Am. Chem. Soc.* **2005**, 127(1), 210-216.
15. Lal, S.; Rzepa, H. S.; Diez-Gonzales, S. Catalytic and Computational Studies of N-Heterocyclic Carbene or Phosphine-Containing Copper(I) Complexes for the Synthesis of 5-Iodo-1,2,3-Triazoles. *ACS Catal.* **2014**, 4, 2274–2287.
16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.
17. Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron gas. *Phys. Rev. B*, **1986**, 33, 8822–8824.
18. Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements : Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor Chem Account* **2008**, 120, 215–241.
19. Weigend, F.; Ahlrichs, R.; Gmbh, F. K. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem Phys.*, **2005**, 7, 3297–3305.
20. Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic Interaction of a Solute with a Continuum. A Direct Utilization of AB Initio Molecular Potentials for the Prevision of Solvent Effects. *Chem. Phys.* **1981**, 55 (1), 117–129.

21. (a) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. (b) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3–8. (c) Kottke, T.; Stalke, D. Crystal Handling at Low Temperatures. *J. Appl. Crystallogr.* **1993**, *26*, 615. (d) Stalke, D. Cryo Crystal Structure Determination and Application to Intermediates. *Chem. Soc. Rev.* **1998**, *27*, 171. (e) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Ruf, M.; Sheldrick, G. M.; Stalke, D. A Comparison of a Microfocus X-ray Source and a Conventional Sealed Tube for Crystal Structure Determination. *J. Appl. Crystallogr.* **2009**, *42*, 885. (f) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* **2015**, *48*, 3.
22. Spek, A. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

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### 1. Chapter 2:

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**Four-Coordinate Germylene and Stannylene and their Reactivity towards Se & Te\*\***

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### 3. Appendix 2

Reprint of **Hossain, J.**; Gopinath, J. S.; Tothadi, S.; Parameswaran, P.; Khan, S. NHSi/NHGe-Supported Copper Halide and Pseudohalide Complexes: Synthesis and Application. *Organometallics* **2022**, 41 (23), 3706-3717.

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