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Aluminum-Catalyzed Selective Hydroboration of Nitriles and Alkynes: A Multifunctional Catalyst

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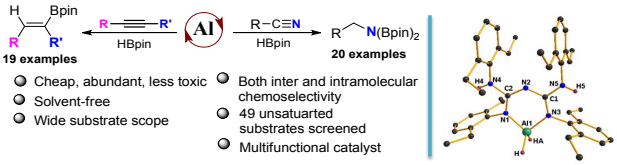
ABSTRACT: The reaction of LH [L= {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar =2,6-Et_2-C_6H_3] with commercially available alane amine adduct ($H_3Al{\cdot}NMe_2Et$) in toluene resulted in the formation of a conjugated bis-guanidinate (CBG) supported aluminum dihydride complex, *i.e.*, $LAlH_2$ (**1**) in good yield. The new complex has been thoroughly characterized by multinuclear magnetic resonance, IR, mass and elemental analyses, including single-crystal structural studies. Further, we have demonstrated the aluminum-catalyzed hydroboration of a variety of nitriles and alkynes. Moreover, aluminum-catalyzed hydroboration is expanded to more challenging substrates such as alkene, pyridine, imine, carbodiimide, and isocyanides. More importantly, we have shown the aluminum dihydride catalyzed both intra- and intermolecular chemoselective hydroboration of nitriles and alkynes over other reducible functionalities for the first time.



INTRODUCTION

Aluminum is the third most abundant metallic element after oxygen and silicon in the Earth's crust and also cheaper, less toxic when compared to transition or lanthanide elements. The sustainable and environmentally friendly aluminum-based reagents/molecules are ideal for applications in catalysis.[1] Hence, the development of well-defined aluminum-based catalysts is quite attractive.[2] In recent years there has been substantial progress in the development of the main group- or transition metal-catalyzed hydroboration of carbonyl compounds;[3,4] however, relatively few examples of the main group catalyzed nitrile and alkyne hydroboration have been documented. Nonetheless, aluminum-catalyzed reduction of organic nitriles has been rarely documented. In 2016, Hill *et al.* reported the first main-group catalyzed, Nacnac Mg alkyl catalyzed hydroboration of nitriles.[5] Recently, Okuda,[6] Thomas,[4i] Ma[7] research groups independently reported the main group catalyzed hydroboration of nitriles. During the preparation of this manuscript, Yang,[8] and Roesky[9] and co-workers reported Nacnac supported aluminum dialkyl and dihydride complexes as (pre)catalysts for the hydroboration of nitriles and also, Panda[10] et al. reported aluminum alkyl as a pre-catalyst for the hydroboration of nitriles. There have been several reports on the main-group,[4g,7,11] transition[12] metal-catalyzed hydroboration of alkynes, while a few reports on aluminum[13] catalyzed hydroboration of alkynes. Moreover, very few reports of aluminum catalyzed hydroboration of alkene[4i,13a,14] carbodiimide[9,15]and imines.[4g,16]

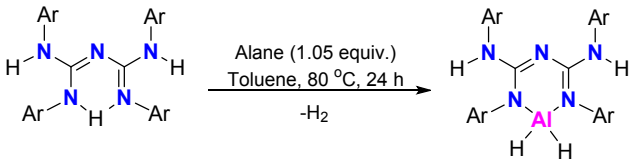
The reports mentioned above are having drawbacks such as very limited substrate scope, high catalyst loading, ligand containing elements other than C, H, and N, etc.

Therefore, the design of a sustainable catalyst is very desirable because catalysts should be easily accessible, efficient, and tolerance of more functional groups. Moreover, to our knowledge, there are no reports on aluminum catalyzed hydroboration of pyridine,[17] and isonitrile[18] functionalities. Thus, herein, we report well-defined aluminum dihydride complex bearing conjugated bis-guanidinate ligand catalyzed selective reduction of a wide range of nitriles and alkynes. Moreover, this protocol further extended to other reducible functionalities such as alkene, carbodiimide, imine, isocyanide and pyridine. To the best of our knowledge, this is the first report of aluminum-based multifunctional catalysts for the hydroboration of unsaturated organic substrates.

RESULTS AND DISCUSSION

Treatment of the free conjugated bis-guanidine (CBG), LH[19] ligand with one equiv. of alane, $H_3Al{\cdot}NMe_2Et$ in toluene at room temperature and followed by heating at 80 °C cleanly yields the CBG supported aluminum dihydride complex (**1**) in good yield (84%) (Scheme 1).

Scheme 1. Synthesis of Conjugated Bis-Guanidinate(CBG) Supported Aluminum-Dihydride Complex (**1**).



The new complex **1** was fully characterized by multinuclear (^1H, ^{13}C, and ^{27}Al) NMR, infrared, mass, and elemental analyses. In addition, the crystallographic analysis

confirmed the solid-state structure of **1**, which is monomeric (Figure 1).

The ^{1}H NMR spectrum reveals a complete disappearance of a free ligand N–*H*–N peak at 12.97 ppm, which indicates the formation of complex **1**. Moreover, a singlet resonance displayed at 5.14 ppm, which corresponds to two protons of side arm ArN–*H* moieties. Besides, other expected signals for the CBG ligand were observed. The ^{13}C{^{1}H} NMR spectrum exhibits a characteristic N_3C peak at 158.6 ppm, which is downfield when compared to free ligand (155.0 ppm). The Al–H resonances were not obtained in ^{1}H NMR spectroscopy of compound (**1**) because of quadrupolar broadening on the ^{27}Al center (nuclear spin = 5/2).[20] Nonetheless, the existence of an Al−H bond was established by IR spectroscopy, which shows two broad bands at 1813 and 1926 cm^{-1}, referred to the Al−H stretching frequencies.[4l,21]

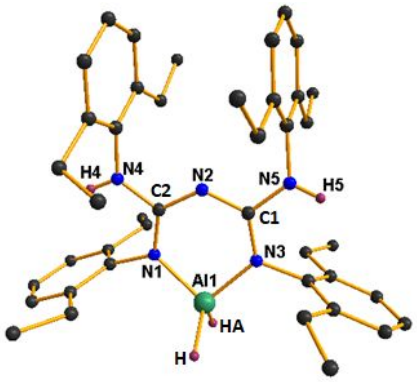


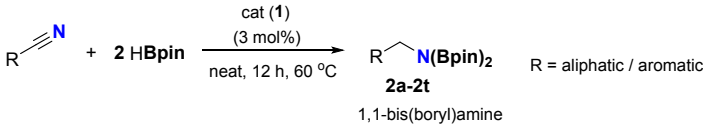
Figure 1. Molecular structure of catalyst **1**. Selected bond distances (Å) and angles (deg): C1-N2 1.332(4), C1-N5 1.351(4), C1-N3 1.326(4), N3-Al1 1.894(3), N1-Al1 1.879(3), C2-N1 1.336(4), C2-N2 1.342(4), C2-N4 1.355(4), Al1-H 1.411(3), Al1-HA 1.622(3). N2-C1-N3 127.0(3), N2-C1-N5 113.7(3), N3-C1-N5 119.2(3), N1-C2-N2 126.6(3), N2-C2-N4 114.5(3), N1-C2-N4 118.9(3), N3-Al1-N1 94.73(12), N3-Al1-H 112.516(18), N1-Al1-H 113.93(9), N3-Al1-HA 110.88(12), N1-Al1-HA 117.12(12), H-Al1-HA 107.220(21).

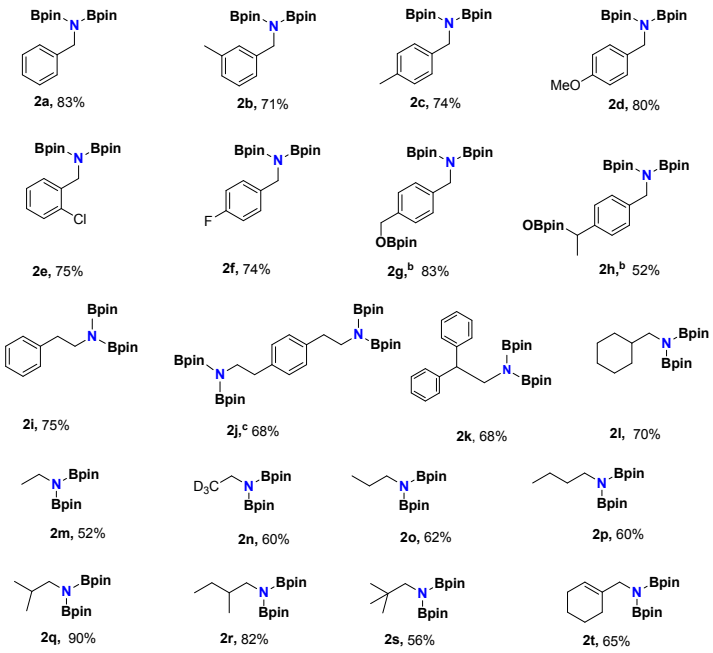
Nitrile Hydroboration

We began by examining the role of aluminum dihydride compound (**1**) in the catalytic hydroboration of benzonitrile with 2 equiv. HBpin. At a loading of 5 mol % of **1** in benzene-d_6 at 60 °C, benzonitrile was hydroborated to afford 1,1-bis(boryl) amine in 98 % yield within 12 h (Table S1, Supporting Information). No reaction took place at similar reaction conditions in the absence of catalyst **1**, showing that the aluminum dihydride compound is responsible for this conversion. Also, the same reaction was carried out under similar conditions by utilizing lower catalyst loadings (1 mol % and 3 mol %). We observed the formation of 1,1-bis(boryl) amine in 50 % and 97 % yields, respectively. However, the same reaction was accomplished under solvent-free conditions by using 3 mol % catalyst; in this case, we noticed the formation of the desired product in quantitative yield.

Therefore, we investigated the reduction of a wide range of organic nitriles with HBpin by using 3 mol % of catalyst **1** under neat conditions (Table 1). Aryl nitriles with electron-donating or electron-withdrawing groups undergo reduction efficiently, yielding the corresponding 1,1-bis(boryl) amine products. Functional groups such as OMe, Cl, and F were all found to be tolerant under reaction conditions. Primary, secondary, and tertiary alkyl nitriles were efficiently reduced to corresponding 1,1-bis(boryl) amines in 52-80 % yields (**2m-2s**). More importantly, we have explored the intramolecular chemoselective hydroboration reaction by choosing 1-cyanocyclohexene (or cyclohexene-1-carbonitrile) substrate, as an example — the reaction of 1-cyanocyclohexene with two equiv. HBpin and catalyst **1** (3 mol %) in neat condition at 60 °C was executed. The ^{1}H NMR analysis of this reaction mixture illustrated the chemoselective hydroboration of nitrile with the quantitative conversion over alkene (**2t**). Unsurprisingly, substrates bearing reducible carbonyl functional group (**2g** and **2h**) were not tolerated under the conditions.

Table 1. Hydroboration of Nitriles Catalyzed by $LAlH_2$Complex (**1**)[a]



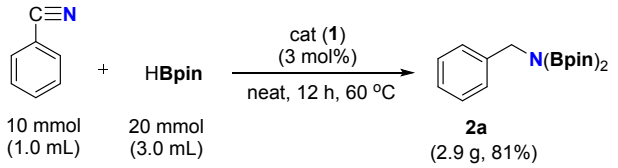


[a]Reaction conditions: nitrile (1.0 mmol, 1.0 equiv.), pinacolborane (2.0 mmol, 2.0 equiv.), catalyst (**1**) (3 mol%), 12 h at 60 °C under N_2. Reported numbers are the isolated yields. [b]For 2g and 2h, pinacolborane (3.0 equiv.) used and precursors 4-Formylbenzonitrile and 4-Acetylbenzonitrile, respectively. [c]For 2j pinacolborane (4.0 equiv.).

All 1,1-bis(boryl)amine products were characterized by multinuclear (^{1}H, ^{13}C, and ^{11}B) NMR spectroscopy. HRMS confirmed purity of new 1,1-bis(aryl) amines. Further, compound **2i** was confirmed by a single X-ray crystal structural analysis (see Supporting Information). Notably, this protocol also works for large scale synthesis as

established by 10 mmol scale reaction of benzonitrile under optimized conditions producing corresponding 1,1-bis(boryl) amine (**2a**) in 82% isolated yield (Scheme 2).

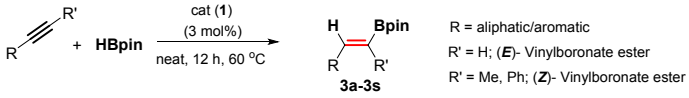
Scheme 2. Large-Scale Hydoboration of Benzonitrile with HBpin

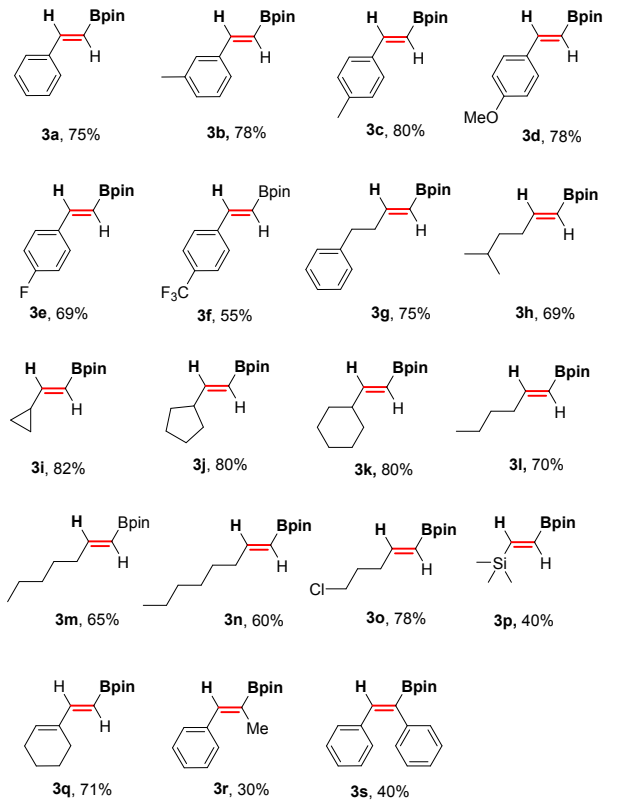


Alkyne Hydroboration

Next, we decided to explore the catalytic activity of compound **1** for the hydroboration of alkynes. We chose phenylacetylene as a substrate for the hydroboration with 1 equiv. HBpin. At a loading of 5 mol % catalyst **1** in benzene-d6 at 60 °C, phenylacetylene hydroborated to afford the cis-hydroborated product, (***E***)-vinyl boronate ester in quantitative yield within 12 h (Table S2, Supporting Information).

Table 2. Hydroboration of Alkynes Catalyzed by $LAlH_2$ Complex (**1**)[a]





[a]Reaction conditions: alkyne (1.0 mmol, 1.0 equiv.), pinacolborane (1.0 mmol, 1.0 equiv.), catalyst (**1**) (3 mol%), 12 h at 60 °C under N_2. Products are isolated after column chromatography. The ***E*** selectivity was determined by NMR spectroscopy except for **3r** and **3s**, which show ***Z*** selectivity.

No conversion took place in the absence of catalyst **1**. Further, when the same reaction was performed at lower catalyst loadings, lesser conversion observed (1 mol %, 70% yield, and 3 mol %, 95 % yield). However, a quantitative conversion was displayed when the same reaction operated under solvent-free conditions by using a 3 mol % catalyst.

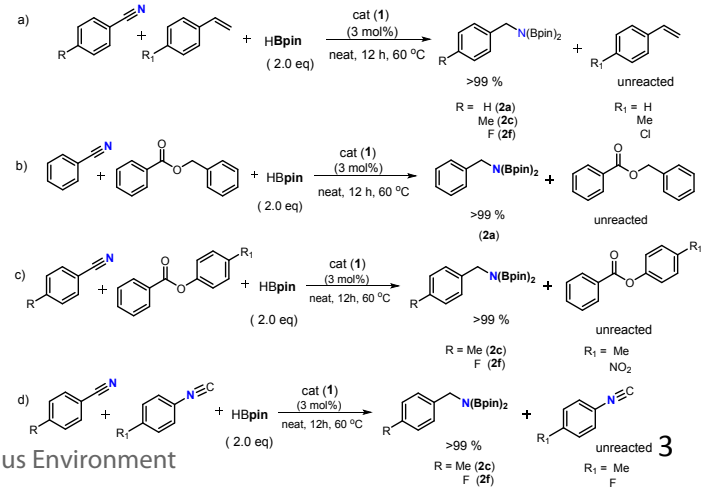
With the optimized reactions conditions in hand, we investigated the scope of the aluminum-catalyzed hydroboration of terminal alkynes (Table 2). We began examining different phenylacetylene derivatives and were satisfied to see that substituents with electron-donating or electron-withdrawing groups on the aromatic ring did not influence the catalytic activity (**3a-3e,** 69-80 %). However, a slightly lower yield obtained for the phenylacetylene derivative **3f,** containing CF_3 at the para position of the aromatic ring.

Subsequently, we considered the scope of the transformation by employing terminal alkynes bearing alkyl substituents (**3g-3o**), which performed similarly to the corresponding phenylacetylene derivatives (60-80%). Hydroboration of trimethylsilylacetylene took place, providing **3p** in 40 % yield. More importantly, another interesting intramolecular chemoselective hydroboration of terminal alkyne by choosing 1-ethynylcyclohexene, as an example was carried out. Hydroboration took place smoothly, providing **3q** in 71 % yield, in which C=C tolerated. To further broaden the substrate scope, we decided to test the aluminum catalyzed hydroboration of internal alkyne. Hydroboration of unsymmetrical and symmetrical internal alkynes, like 1-phenyl-1-propyne and diphenylacetylene, took place, providing (***Z***)-vinyl boronate esters in 30% and 40 % yields, respectively. It is interesting to note that CBG supported aluminum dihydride catalyzes the challenging substrates such as symmetrical and unsymmetrical internal alkynes, in contrast to previously reported Nacnac AlH_2, which is less effective to reduce the internal alkynes.[13c]

Nitrile Intermolecular Chemoselectivity:

More importantly, we have displayed aluminum dihydride **1** catalyzed intermolecular chemoselective hydroboration of nitriles over alkenes containing both electron-donating and electron-withdrawing substituents, esters and isonitriles.

Scheme 3. Nitrile Intermolecular Chemoselective Reactions Catalyzed by **1**



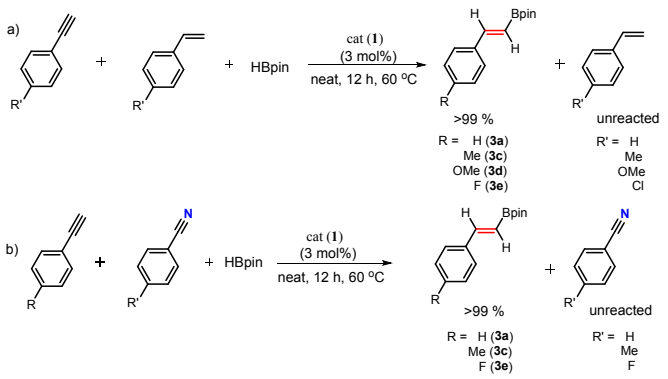
The reaction of 1 equiv. of benzonitrile, 1 equiv. styrene and 2 equiv. HBpin were mixed with catalyst **1** (3 mol %) under solvent-free conditions at 60 °C, which produced the diborylated product 1,1-bis(boryl)amine in the quantitative conversion of benzonitrile, in preference to the alkene (Supporting Information). Similarly, either the reaction of aryl nitrile containing electron-donating group, 4-methyl benzonitrile, or electron-withdrawing group, 4-Fluro benzonitrile gives corresponding 1,1-bis(boryl) amine in preference to the alkene. Moreover, the reaction of 1 equiv. benzonitrile, 1 equiv. benzyl benzoate and 2 equiv. HBpin were allowed to react with catalyst **1** (3 mol %) under solvent-free conditions at 60 °C, which yielded the diborylated product 1,1-bis(boryl) amine in the quantitative conversion of benzonitrile over benzyl benzoate. Similarly, 4-methyl benzonitrile and 4-Fluro benzonitrile gave the corresponding 1,1-bis(boryl) amines in preference to the esters (Scheme 3). Further, at similar reaction conditions, 4-methyl benzonitrile and 4-fluoro benzonitrile yielded the corresponding 1,1-bis(boryl) amines over aryl isonitriles.

Alkyne Intermolecular Chemoselectivity:

The reaction of equimolar amounts of phenylacetylene, styrene, and HBpin was reacted together with catalyst **1** (3 mol %) under neat conditions at 60 °C, which afforded the (*E)* vinyl boronate ester in preference to the alkene. Similarly, 4-methyl phenylacetylene, 4-methoxy phenylacetylene, 4-fluoro phenylacetylene were hydroborated at the same reaction conditions over alkenes (Scheme 4).

The reaction of equimolar amounts of phenylacetylene, benzonitrile, and HBpin was reacted together with catalyst **1** under neat conditions at 60 °C, which yielded the (***E***)-vinyl boronate ester over nitrile functionality. Similarly, equimolar amounts of aryl alkynes and aryl nitrile with either electron-donating or electron-withdrawing groups, and HBpin were reacted together, independently, in which exclusively alkyne hydroborated over nitrile.

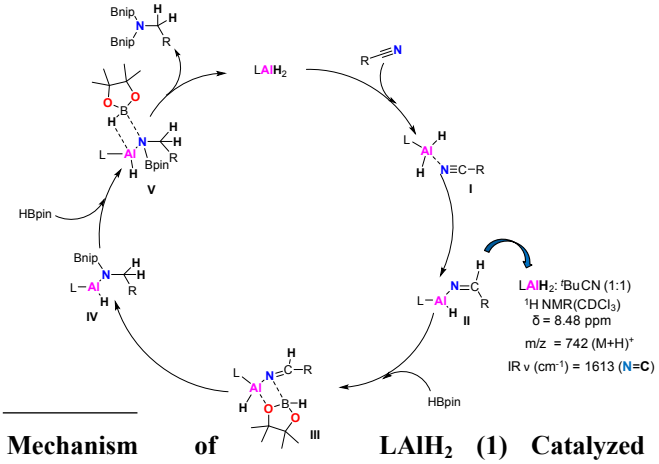
Scheme 4. Alkyne Intermolecular Chemoselective Reaction Catalyzed by **1**.



Mechanism of $LAlH_2$(1) Catalyzed Hydroboration of Nitrile:

Initially, catalyst **1** reacts with the nitrile to form transition species (I), and followed by sigma bond metathesis to yield the corresponding imine (II). This imine complex further reacts with HBpin to produce the four-membered species (III), which rearranges to give boryl amine (IV). Further, it reacts with one more molecule of HBpin to yield intermediate species (V), which undergoes sigma bond metathesis to yield the product 1,1-bis(boryl) amine and regeneration of the ligated aluminum dihydride catalyst (Scheme 5). Moreover, the aluminum imine species (II) was confirmed by ^{1}H and ^{13}C NMR analyses by the stoichiometric reaction between catalyst **1** and trimethylacetonitrile in $CDCl_3$ at 70 °C. The ^{1}H NMR spectrum exhibits a characteristic imine, Al-N=C*H*-R peak at 8.48 ppm, while the Al-H signal was silent. The ^{13}C {^{1}H} NMR spectrum displays a typical Al-N=*C*-HR peak at the far downfield region at 160.4 ppm.

Scheme 5. Proposed Mechanism for Hydroboration of Nitrile.



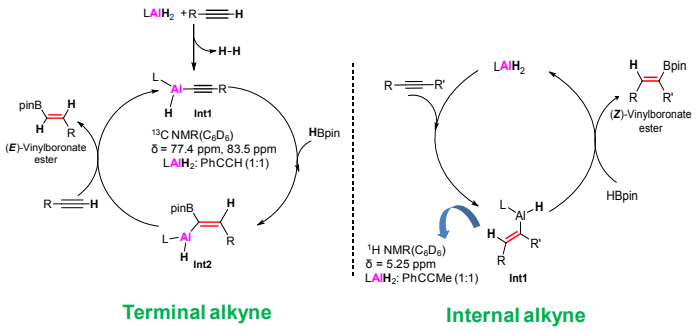
Mechanism of $LAlH_2$ (1) Catalyzed Hydroboration of Alkyne:

Considering the previously established mechanisms of aluminum-catalyzed hydroboration of terminal alkynes [13a,c] we propose that the hydroboration reaction proceeds according to the mechanism shown in Scheme 6. First, the deprotonation of alkyne with aluminum-dihydride **1** leads to the formation of aluminum acetylide (Int 1). Further, a stoichiometric reaction of catalyst **1** and phenylacetylene in C_6D_6 at 70 °C was carried out to confirm the formation of Int 1. ^{1}H and ^{13}C NMR analyses confirmed the formation of aluminum acetylide, LAl(H)CCPh. The ^{1}H NMR shows side arm ArN*H* resonance at 4.90 ppm, which upfield region compared the $LAlH_2$ (ArN*H* 5.13 ppm). The ^{13}C {^{1}H} NMR displays two peaks at 77.4 and 83.5 ppm, which corresponding to Al-*CC*Ph carbon atoms, respectively. The second step involves the cycloaddition reaction, in which the B-H bond of HBpin adds to the C-C triple of Int 1 that leads alkene Int 2. In the third step, Int 2 reacts with another molecule of phenylacetylene, in which sigma bond metathesis occurs that leads to the formation of product and regeneration of the active catalyst Int 1.

A different mechanism is operative for the internal alkynes, which is previously reported by Thomas, Cowley and coworkers.[13b] Accordingly, we propose the catalytic cycle starting with Al-H insertion in alkyne CC triple bond to form Int 1, which undergoes transmetallation to regenerate the

catalyst and (***Z***)-vinyl boronate ester. Further, a controlled reaction was carried out to confirm the proposed reaction mechanism. Thus, the treatment of catalyst **1** with 1-phenyl-1-propyne in 1:1 ratio in C_6D_6 at 80 °C resulted in the formation of Int 1, which is confirmed by ^1H and ^{13}C NMR spectroscopy analyses. The ^1H NMR reveals two singlets at 1.85 and 5.25 ppm, which correspond to methyl and H signals of Al-C*Me*=C*H*Ph moiety. The $^{13}C\{^1H\}$ NMR spectrum shows a typical signal at the upfield region at 3.2 ppm, which corresponds to the carbon atom of Al-C*Me*=CHPh moiety.

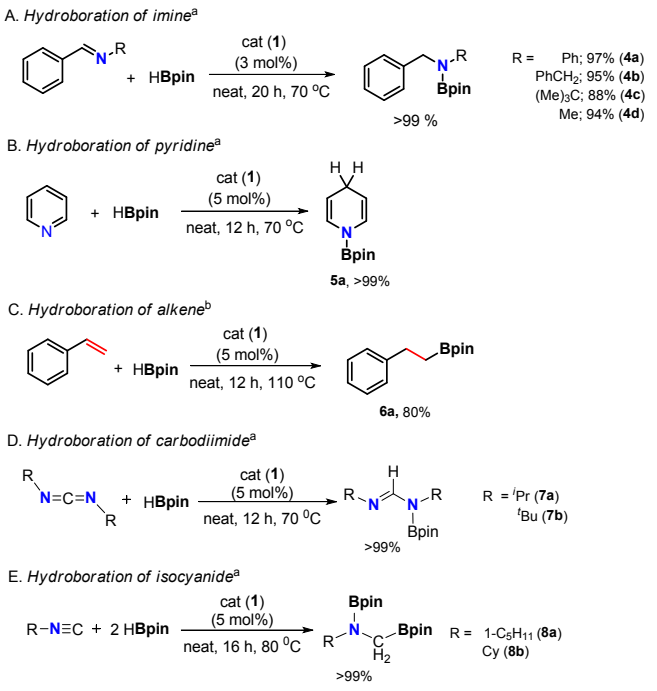
Scheme 6. Proposed Mechanism for Hydroboration of Alkyne.



Aluminum Catalyzed Hydroboration of Imines, Alkene, Pyridine, Carbodiimides, and Isonitriles

To the best of our knowledge, there have been no reports on aluminum-catalyzed hydroboration of heterocycles and isonitriles. To further establish the relevance of this procedure, we utilized aluminum-dihydride catalyzed hydroboration to more challenging substrates.

Scheme 7. Hydroboration of Imines, Alkene, Pyridine, Carbodiimide, and Isonitriles by using Al Complex (**1**) as a Catalyst.[a]



[a]Reaction conditions: all reactions were done on 1.0 mmol scales. For isocyanide, 2.0 mmol of pinacolborane used. Conversion based on ^1H NMR spectroscopy. For imine, the yield was determined by using nitromethane as an internal standard.[b]Isolated yield of alkene hydroboration based on column chromatography.

To our delight, compound **1** efficiently catalyzes the hydroboration of imine, pyridine, alkene, carbodiimide, and isonitrile substrates at neat and mild reaction conditions (Scheme 7). Hydroboration of imine was successfully achieved for aldimines like N-Benzylideneaniline by 3 mol % of catalyst **1** at 70 °C within 20 h. Similarly, other imines such as benzyl, *t*butyl, and methyl were also hydroborated at the same reaction conditions (**4a-4d**). The reaction of equimolar amounts of pyridine and HBpin were reacted together with catalyst **1** in C_6D_6, which afforded exclusively N-borylated 1,4- reduced product (**5a**). Next, using catalyst **1** (5 mol %) and HBpin (1.0 equiv), the hydroboration of styrene proceeded in an 80 % yield to give the anti-Markovnikov (linear) alkyl boronic ester (**6a**) within 12 h at 110 °C. Further compound **1** catalyzed the more challenging organic substrates such as carbodiimides and isonitriles has been investigated. Aliphatic substrates such as *N, N′*-diisopropyl carbodiimide and *N, N′*-ditertbutyl carbodiimide reduced to corresponding monohydroborated ester (**7a-7b**) when treated with 1eq. of HBpin. Following this, the inert isocyanides such as acyclic and cyclic alkyl isonitriles, *i.e.*, 1-pentylisoniitrile and cycloisonitrile and efficiently converted to corresponding hydroborated amines (**8a-8b**).

CONCLUSION

In summary, we have demonstrated a newly synthesized *β*-diketiminate analogue of well-defined conjugated bis-guanidinate (CBG) supported aluminum dihydride (**1**) catalyzed dihydroboration of a large number of organonitriles with HBpin. We noticed that catalyst **1** is more efficient for the hydroboration of nitriles than that of *β*-diketiminate(Nacnac)supported aluminum dihydride complex. Further, compound **1** catalyzed hydroboration of both terminal and internal alkynes with HBpin has been investigated. In contrast to Nacnac Al dihydride catalysis, two different mechanisms are operative for CBG aluminum dihydride catalyzed alkyne hydroboration reaction.

Further, compound **1** catalyzed hydroboration of alkene, pyridine, imine, carbodiimide, and isocyanide substrates with HBpin has been studied. Overall compound **1** was found to be a highly efficient (low catalyst loadings and mild reaction conditions) and multifunctional catalyst with a broad substrate scope. Further studies on the aluminum-dihydride catalyzed other organic transformations are ongoing in our laboratory.

EXPERIMENTAL SECTION

All air and moisture sensitive reactions were carried out by using standard Schlenk line and glovebox techniques under an inert atmosphere of dinitrogen. The precursor LH[19][LH = {(ArHN)(ArHN)C=N C= NAr(NHAr)}; Ar = 2, 6-Et_2 - C_6H_3] was prepared by using method developed in our laboratory. Alane-N,N-dimethyl ethyl amine complex (0.5 M) in toluene were purchased from Sigma-Aldrich and used as received. Anhydrous solvents such as toluene, benzene, and n- hexane were collected from the MBraun solvent purification system, degassed and stored under an atmosphere of dinitrogen before use. The ^1H, ^{13}C, ^{11}B &^{27}Al

NMR spectra were acquired on 400 MHz (Bruker or JEOL) and 700MHz Bruker spectrometers using dried deuterated solvents with chemical shift given in parts per million. Dry deuterated benzene (C_6D_6), chloroform ($CDCl_3$) solvents were used for NMR measurements; chemical shift values (δ) were reported in parts per million (ppm) relatives to the residual signals of their respective solvents. High-resolution mass spectra (HRMS) were recorded on Bruker micrOTOF-Q II spectrometer. IR spectrum of compound **1** was recorded on the Perkin-Elmer FTIR spectrometer. Elemental analysis for compound **1** was performed by EuroEA3000-CHNS-Analyzer.

Synthesis of $LAlH_2$(1): To a solution of LH (1.0 g, 1.58 mmol) in toluene (~30 mL) at room temperature was added dropwise a solution of alane-N,N-dimethylethylamine complex (0.5 M) in toluene (3.32 mL, 1.66 mmol). The reaction mixture was heated at 80 °C and stirred for a further 24 h. The reaction mixture was allowed to attain room temperature and filtered through a Celite. Then volatiles were removed in vacuo to yield a colorless solid. The residue was extracted into toluene and colorless crystals suitable for X-ray diffraction studies, were obtained from the storage of a saturated solution in toluene at 5 °C. A second crop of crystals was obtained on further concentration of the supernatant solution at -30 °C.(0.87 g, yield 84%). ^{1}H NMR (C_6D_6, 400 MHz, 273K): δ (ppm) 0.94 (t, $^3J_{HH}$ = 8 Hz, 12H, PhCH$_2$C*H*$_3$), 1.36 (t, $^3J_{HH}$ = 8 Hz, 12H, PhCH$_2$C*H*$_3$), 2.20 – 2.24 (m, 4H, PhC*H*$_2$CH$_3$), 2.32 – 2.34 (m, 4H, PhC*H*$_2$CH$_3$), 2.84 – 2.86 (m, 4H, PhC*H*$_2$CH$_3$), 3.33 – 3.37 (m, 4H, PhC*H*$_2$CH$_3$), 5.13 (s, 2H, Ar N*H*), 6.61– 6.63 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar*H*), 6.87 (t, $^3J_{HH}$ = 8 Hz, 2H, Ar*H*), 7.00 – 7.05 (m, 2H, Ar*H*), 7.12 – 7.14 (m, 2H, Ar*H*), 7.15 – 7.16 (m, 2H, Ar*H*); ^{13}C {^{1}H} NMR (101 MHz, C_6D_6, 273K): δ 14.4, 14.5, 23.8, 25.1, 125.4, 126.8, 127.0, 127.5, 134.6, 138.0, 141.3, 141.3, 158.6. ^{27}Al NMR (104 MHz, C_6D_6, 273K) δ 56.35. Mp - 260 – 264 °C. IR (Nujol mull) ν (cm^{-1}): 1813 and 1926 (br, Al-H). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{56}AlN_5$ 658.4797; Found 658.4424. Elemental analysis (%) for $C_{42}H_{56}AlN_5$: Calcd C 76.67 H 8.58 N 10.64; Found C 76.20 H 8.42 N 10.86.

General Procedure for Catalytic Hydroboration of Nitriles. In a sealed vial 19 mg (0.03 mmol) of catalyst **1**, 304.7 µL (2.1 mmol) of pinacolborane was then added, followed by 1.0 mmol of nitrile in a neat condition. This mixture was then transferred to an oil bath at 60 °C for 12 h. The residue was redissolved in the minimum volume of *n*-hexane and left to crystallize in the freezer overnight. The product was isolated *via* filtration (**2a**–**2t**).

*N-{B(OMe$_2$)$_2$}$_2$–phenylmethanamine(**2a**)*[22]*. Yield: 298 mg (83%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.60 – 7.59 (m, 2H, o-H), 7.25 (t, *J* = 8.0 Hz, 2H, m-H), 7.15 – 7.12 (d, *J* = 8.0 Hz, 1H, p-H), 4.62 (s, 2H, NCH$_2$), 1.03 (s, 24H, OC(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 143.4, 131.6, 128.4, 126.2, 82.2, 47.5, 24.3. ^{11}B NMR (128 MHz, C_6D_6) δ 29.45.

N-{B(OMe$_2$)$_2$}$_2$–m-tolylmethanamine *(**2b**)*[22]*. Yield: 264 mg (71%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.47 – 7.43 (m, 1H, *o-H*), 7.29 – 7.25 (m, 1H, *p-H*), 7.04 – 6.95 (m, 2H, *m-H*), 4.60 (s, 2H, NC*H*$_2$), 2.30 (s, 3H, PhC*H*$_3$), 1.14 (s, 24H, OC(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 143.2, 137.0, 128.5, 127.9, 126.9, 124.6, 82.1, 47.4, 24.3, 21.1. ^{11}B NMR (128 MHz, C_6D_6) δ 29.92.

N-{B(OMe$_2$)$_2$}$_2$–p-tolylmethanamine *(**2c**)*[22]*. Yield: 277 mg (74%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.56– 7.54 (d, *J* = 8.0 Hz, 2H, *o-H*), 7.10 – 7.08 (d, *J* = 8.0 Hz, 2H, *m-H*), 4.63 (s, 2H, NC*H*$_2$), 2.16 (s, 3H, PhC*H*$_3$), 1.05 (s, 24H, OC(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 140.5, 135.3, 128.6, 127.7, 82.1, 47.2, 24.3, 20.7. ^{11}B NMR (128 MHz, C_6D_6) δ 29.68.

*N-{B(OMe$_2$)$_2$}$_2$–p-methoxymethanamine *(**2d**)*[23]*. Yield: 311 mg (80%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.17 (d, *J* = 8.0 Hz, 2H, *o-H*), 6.86 – 6.84 (d, *J* = 8.0 Hz, 2H, *m-H*), 4.03 (s, 2H, NC*H*$_2$), 3.76 (s, 3H, PhOC*H*$_3$), 1.24 (s, 24H, OC(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.3, 135.0, 127.9, 113.7, 82.1, 55.2, 44.6, 24.5.

*N-{B(OMe$_2$)$_2$}$_2$–o-chlorobenzylamine *(**2e**)*[24]*. Yield: 294 mg (75%, colorless liquid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.08 (d, *J* = 8.0 Hz, 1H,*o-H*), 7.03 (t, *J* = 8.0, 1H, *o-H*), 6.56 (t, *J* = 8.0, 1H,*p-H*), 6.19 – 6.13 (m, 1H, *o-H*), 4.50 (s, 2H), 1.00 (s, 24H, OC(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 136.9, 130.5, 128.3, 127.2, 127.1, 126.4, 82.2, 65.0, 24.3. ^{11}B NMR (128 MHz, C_6D_6) δ 29.92.

*N-{B(OMe$_2$)$_2$}$_2$–p-fluorobenzylamine *(**2f**)*[5]*. Yield: 277 mg (74%, white solid). ^{1}H NMR (700 MHz, C_6D_6) δ 7.38 (t, *J* = 8.0, 2H, *o-H*), 6.87 (t, *J* = 8.0 Hz, 2H, *m-H*), 4.41 (s, 2H, NC*H*$_2$), 1.01 (s, 24H, OC(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 162.4, 161.1, 139.1 (d, *J* = 3.0 Hz), 129.4 (d, *J* = 7.6 Hz), 114.6 (d, *J* = 21.0 Hz), 82.2, 46.7, 24.3.

*N-{B(OMe$_2$)$_2$}$_2$–O-B(OCMe$_2$)$_2$–(4-(aminomethyl)phenyl)methanol *(**2g**)*[23]*. Yield: 428 mg (83%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.49 – 7.48(d, *J* = 4.0 Hz, 2H, *o-H*), 7.31 – 7.30(d, *J* = 4.0 Hz, 2H, *p-H*),4.92 (s, 2H, OC*H*$_2$), 4.50 (s, 2H, NC*H*$_2$), 1.04 (s, 12H, OC(C*H*$_3$)$_2$), 1.01 (s, 24H, OC(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 142.5, 137.6, 127.9, 126.6, 82.2, 82.1, 66.5, 47.2, 24.3, 24.3. ^{11}B NMR (128 MHz, C_6D_6) δ 28.32, 22.79.

*N-{B(OMe$_2$)$_2$}$_2$-O-B(OCMe$_2$)$_2$–(4-(aminomethyl)phenyl)ethanol *(**2h**)*[12d]*. Yield: 275 mg (52%, white solid). ^{1}H NMR (700 MHz, C_6D_6) δ 7.57– 7.55 (d, *J* = 8.0 Hz, 2H, *o-H*), 7.43 – 7.41 (d, *J* = 8.0 Hz, 2H, *m-H*), 5.47 – 5.43 (q, *J* = 8.0 Hz, 1H,PhC*H*CH$_3$), 4.59 (s, 2H,NC*H*$_2$), 1.49 – 1.47(d, *J* =8.0 Hz, 3H, C*H*$_3$), 1.03 (s, 24H, OC(C*H*$_3$)$_2$), 1.01 (s, 12H, OC(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 143.0, 142.2, 128.2, 125.1, 82.5, 82.1, 72.5, 44.9, 25.3, 24.3, 24.2.

*N-{B(OMe$_2$)$_2$}$_2$–2-phenylethanamine *(**2i**)*[22]*. Yield: 280 mg (75%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.29 – 7.27(d, *J* = 8.0 Hz, 2H, *o-H*), 7.18 – 7.14 (m, 3H, *m-H, p-H*), 3.67 (t, *J* = 8.0 Hz, 2H, NC*H*$_2$), 2.99 (t, *J* = 8.0 Hz, 2H, PhC*H*$_2$), 1.04 (s, 24H, OC(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 140.7, 129.7, 129.0, 126.1, 82.3, 46.0, 40.2, 24.7. ^{11}B NMR (128 MHz, C_6D_6) δ 29.85.

*[N-{B(OMe$_2$)$_2$}$_2$-O-B(OCMe$_2$)–(4-(aminoethylphenyl)]$_2$ *(**2j**)*[23]*. Yield: 454 mg (68%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 7.23 (s, 4H, Ar*H*), 3.67 – 3.63 (m, 4H, NC*H*$_2$CH$_2$), 3.00 – 2.93(m, 4H, NC*H*$_2$CH$_2$), 1.04 (s, 48H, OC(C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 137.7, 129.1, 81.9, 45.8, 39.6, 24.3. Reaction has been performed for 48 h in dry benzene.

*N-{B(OCMe$_2$)$_2$}$_2$–diphenylacetoamine (**2k**)*[5]*.* Yield: 305 mg (68%, white solid) ^{1}H NMR (400 MHz, C_6D_6) δ 7.42 – 7.40 (d, *J* = 8.0 Hz, 4H, *o-H*), 7.07 – 7.02 (m, 4H, *m-H*), 6.95 – 6.93 (m, 2H, *p-H*), 4.62 (t, *J* = 8.0 Hz, 1H, Ph_2CH), 4.09 – 4.07(d, *J* = 8.0 Hz, 2H, NCH_2), 1.01 (s, 24H, $OC(CH_3)_2$).$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 143.9, 129.2, 128.6, 126.4 82.9, 54.8, 49.2, 24.8. Reaction has been performed for 48 h in dry benzene.

*N-{B(OCMe$_2$)$_2$}$_2$–cyclohexylmethanamine (**2l**)*[5]*.* Yield: 255 mg (70%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 3.31 – 3.29 (d, *J* = 8.0 Hz, 2H, NCH_2), 1.90 – 1.87(m, 2H, NCH_2CH),1.73 – 1.30 (m, 10H, Cy-*H*), 1.07 (s, 24H, $OC(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 82.2, 50.5, 40.9, 31.2, 27.2, 26.6, 24.7. ^{11}B NMR (128 MHz, C_6D_6) δ 29.48.

*N-{B(OCMe$_2$)$_2$}$_2$–ethanamine (**2m**)*[22]*.* Yield: 155 mg (52%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 3.48 – 3.43 (q, *J* = 8.0 Hz, 2H, NCH_2), 1.33 (t, *J* = 8.0 Hz, 3H, CH_2CH_3), 1.15 (s, 24H, $OC(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 81.7, 38.6, 24.3, 18.6. ^{11}B NMR (128 MHz, C_6D_6) δ 28.80.

*N-{B(OCMe$_2$)$_2$}$_2$–ethanamine(D3) (**2n**)*[23]*.* Yield: 180 mg (60%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 3.32 (s, 2H, NCH_2), 1.02 (s, 24H, $OC(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 82.1, 38.8, 24.6, 18.3– 17.7 (m, CD_3). ^{11}B NMR (128 MHz, C_6D_6) δ 29.75.

*N-{B(OCMe$_2$)$_2$}$_2$–propan-1-amine (**2o**)*[22]*.* Yield: 195 mg (62%, pale yellow solid). ^{1}H NMR (400 MHz, C_6D_6) δ 3.30 (t, *J* = 8.0 Hz, 2H, NCH_2), 1.68 – 1.63 (m, 2H, CH_2CH_3), 1.02 (s, 24H, $OC(CH_3)_2$), 0.88 (t, *J* = 8.0 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 81.7, 45.6, 26.3, 24.3, 11.0. ^{11}B NMR (128 MHz, C_6D_6) δ 29.31.

*N-{B(OCMe$_2$)$_2$}$_2$–butan-1-amine (**2p**)*[25]*.* Yield: 195 mg (60%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (t, *J* = 8.0 Hz, 2H, NCH_2), 2.66 – 2.62(m, 2H, CH_2CH_3), 1.52 – 1.44 (m, 2H, CH_2CH_3), 1.10 (s, 24H, $OC(CH_3)_2$), 0.80 (t, *J* = 8.0 Hz, 3H, CH_2CH_3).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 81.6, 40.6, 35.5, 24.3, 19.9, 13.6.

*N-{B(OCMe$_2$)$_2$}$_2$–2-methylpropan-1-amine (**2q**)*[22]*.* Yield: 293 mg (90%, pale yellow oil). ^{1}H NMR (400 MHz, C_6D_6) δ 3.20 – 3.18 (d, *J* = 8.0 Hz, 2H, NCH_2), 2.02 – 1.95 (m, 1H, $CH(CH_3)_2$), 1.07 (s, 24H, $OC(CH_3)_2$), 0.98 – 0.96 (d, *J* = 8.0 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 82.5, 52.0, 31.4, 25.0, 20.6. ^{11}B NMR (128 MHz, C_6D_6) δ 29.53.

*N-{B(OCMe$_2$)$_2$}$_2$–2-methylbutan-1-amine (**2r**).* Yield: 277 mg (82%, pale yellow solid). ^{1}H NMR (400 MHz, C_6D_6) δ 3.27 – 3.09(m, 2H, NCH_2), 1.79 – 1.72 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.03 (s, 24H, $OC(CH_3)_2$), 0.95 – 0.87 (m, 8H, $CH(CH_3)(CH_2CH_3)$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 81.8, 49.8, 37.4, 26.8, 24.3, 16.8, 10.8. ^{11}B NMR (128 MHz, C_6D_6) δ 29.48. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{35}B_2NO_4$ 340.2054; Found: 340.2892.

*N-{B(OCMe$_2$)$_2$}$_2$–2,2-dimethylpropan-1-amine (**2s**)*[22]*.* Yield: 190 mg (56%, white solid). ^{1}H NMR (400 MHz, C_6D_6) δ 3.27 (s, 2H, NCH_2), 1.12 (s, 24H, $OC(CH_3)_2$), 1.03 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 82.1, 54.9, 33.6, 28.0, 24.8. ^{11}B NMR (128 MHz, C_6D_6) δ 29.57.

*N-{B(OCMe$_2$)$_2$}$_2$–cyclohex-1-en-1-ylmethylamine (**2t**).* Yield: 235 mg (65%); white solid; ^{1}H NMR (400 MHz, C_6D_6) δ 6.69 – 6.67 (d, *J* = 18.1 Hz, 1H, C*H*), 4.78 (s, 2H, NCH_2), 2.87 – 2.77 (m, 2H, CH_2), 2.15 – 2.12 (m, 2H, CH_2), 1.85 – 1.80 (m, 2H, CH_2), 1.55 – 1.54 (m, 2H, CH_2,), 1.00 (s, 24H, $OC(CH_3)_2$).$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 141.71, 132.3, 122.9, 82.3, 48.11, 24.2, 23.9, 23.9, 21.82. ^{11}B NMR(128 MHz, C_6D_6) δ 29.85. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{35}B_2NO_4$ 364.2793; Found 364.2832.

General Procedure for Catalytic Hydroboration of Alkynes. In a sealed vial, 19 mg (0.03 mmol) of catalyst **1**, 145μL (1.0 mmol) of pinacolborane was then added, followed by 1.0 mmol of alkyne in a neat condition. This mixture was then transferred to an oil bath at 60 °C for 12 h. The reaction mixture was concentrated and purified by column chromatography over silica gel (100–200 mesh) with *n*-hexane/ethyl acetate (1:5) mixture as an eluent, which provided the pure product which was visualized by UV light at 254 nm (**3a**–**3s**).

*(E)-4,4,5,5-teteramethyl-2-styryl-1,3,2-dioxaborolane (**3a**)*[13b]*.* Yield: 172mg (75%, pale yellow oil). ^{1}H NMR (700 MHz, C_6D_6) δ 7.79 – 7.75(d, *J* = 18.5 Hz, 1H, C*H*), 7.33 – 7.32 (m, 2H, Ar*H*), 7.03 – 7.01(m, 3H, Ar*H*), 6.48 – 6.45 (d, *J* = 18.5 Hz, 1H, C*H*), 1.12 (s, 12H, $OC(CH_3)_2$).$^{13}C\{^1H\}$ NMR (176 MHz, C_6D_6) δ 149.9, 137.7, 128.6, 128.5, 127.0, 116.6 (br, *C*-B), 82.8, 24.6.

*(E)-4,4,5,5-teteramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (**3b**)*[26]*.* Yield: 190 mg (78%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (d, *J* = 18.4 Hz, 1H, C*H*), 7.33 – 7.25 (m, 3H, Ar*H*), 7.14 – 7.12 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.20 – 6.15 (d, *J* = 18.4 Hz, 1H, C*H*), 2.37 (s, 3H, CH_3), 1.34 (s, 12H, $OC(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.6, 138.0, 137.4, 129.7, 128.4, 127.7, 124.2, 83.3, 24.8, 21.4, one resonance not located (*C*-B).

*(E)-4,4,5,5-teteramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (**3c**)*[26]*.* Yield: 195 mg (80%, yellow oil). ^{1}H NMR (700 MHz, C_6D_6) δ 7.82– 7.80 (d, *J* = 18.5 Hz, 1H, *C*H), 7.30 – 7.28 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.86 – 6.85 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.49 – 6.46 (d, *J* = 18.5 Hz, 1H, *C*H), 2.02 (s, 3H, CH_3), 1.14 (s, 12H, $OC(CH_3)_2$).$^{13}C\{^1H\}$ NMR(176 MHz, C_6D_6) δ 150.0, 138.5, 135.1, 129.2, 127.1, 82.8, 24.6, 20.8, one resonance not located (*C*-B).

*(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)*[26]*.* Yield: 202 mg (78%, colorless oil). ^{1}H NMR (400 MHz, C_6D_6) δ 7.78 – 7.73 (d, *J* = 18.5 Hz, 1H, C*H*), 7.29 – 7.27 (d, *J*= 8.0 Hz, 2H, Ar*H*), 6.63 – 6.61 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.36 – 6.32 (d, *J* = 18.5 Hz, 1H, C*H*), 3.23 (s, 3H, OCH_3), 1.15 (s, 12H, $OC(CH_3)_2$).$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 160.8, 149.9, 130.9, 128.8, 114.3(*C*-B), 83.1, 54.7, 25.0.

*(E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaboralane (**3e**)*[13b]*.* Yield: 171 mg (69%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 7.63– 7.60 (d, *J* = 18.5 Hz, 1H, C*H*), 7.05 – 7.04 (m, 2H, Ar*H*), 6.64 (t, *J* = 8.7 Hz, 2H, Ar*H*), 6.29 – 6.26 (d, *J* = 18.5 Hz, 1H, C*H*), 1.13 (s, 12H, $OC(CH_3)_2$).$^{13}C\{^1H\}$ NMR (176 MHz, C_6D_6) δ 163.8, 162.4, 148.5, 133.8 (d, *J* = 3.2 Hz),128.7 (d, *J* = 8.2 Hz),115.4 (d, *J* = 21.0 Hz, *C*-B), 82.9, 24.6.

*(E)-4,4,5,5-tetramethyl-2(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (**3f**)*[26]*.* Yield: 149 mg (55%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 7.57 – 7.54 (dd, *J* = 17.8 Hz, 1H, C*H*), 7.19 – 7.16(d, *J* = 8.0 Hz, 2H, Ar*H*), 7.05 –

7.04 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.38 – 6.34 (m, 1H, C*H*), 1.12 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 147.9, 140.7, 130.34 (q, J = 32 Hz), 127.08, 125.4 (q, J = 4.0 Hz), 83.1, 24.5, one resonance not located (*C*-B).

(E)-2-(4-phenylbut-1-en-1-yl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane ***(3g)***[26]. Yield: 193mg (75%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H,Ar*H*), 7.23 – 7.21 (d, *J* = 8.0 Hz, 3H, Ar*H*), 6.75 (dt, *J* = 17.9, 5.8 Hz, 1H, C*H*), 5.57 – 5.53 (d, *J* = 18.0 Hz, 1H,C*H*), 2.78 (t, *J* = 8.0 Hz, 2H, CH_2), 2.52 (dd, *J* = 15.3, 6.9 Hz, 2H, CH_2), 1.31 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.4, 141.7, 128.4, 125.8, 83.0, 37.5, 34.6, 24.8, one resonance not located (*C*-B).

(E)-4,4,5,5-teteramethyl-2-(5-methylhex-1-en-1-yl)-1,3,2-dioxaborolane ***(3h)***[12d]. Yield: 154mg (69%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (dt, *J* = 17.9, 6.4 Hz, 1H, C*H*), 5.43 – 5.38 (d, *J* = 17.9 Hz, 1H, C*H*), 2.16 (dd, *J* = 14.7, 7.1 Hz, 2H, CH_2), 1.59 – 1.50 (m, 1H, C*H*), 1.31 – 1.27 (m, 2H, CH_2), 1.24 (s, 12H, OC(CH_3)$_2$), 0.86 – 0.84 (d, *J* = 6.6 Hz, 6H, CH_3).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 82.9, 37.3, 33.6, 27.4, 24.7, 22.4, one resonance not located (*C*-B).

(E)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3i)***[13b]. Yield: 159mg (82%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 6.40 – 6.36 (dd, *J*= 17.8, 9.3 Hz, 1H, C*H*), 5.87 – 5.84 (d, *J* = 17.8 Hz, 1H, C*H*), 1.30 – 1.28 (m, 1H, CH_2), 1.10 (s, 12H, OC(CH_3)$_2$), 0.47 – 0.46 (m, 2H, CH_2), 0.29 – 0.28(m, 2H, CH_2).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 158.6, 116.0 (br, *C*-B), 82.4, 24.6, 16.9, 7.61.

2-[(E)-2-cyclopentylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3j)***[12g]. Yield: 182 mg (80%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 17.9, 7.3 Hz, 1H, C*H*), 5.38 – 5.33 (d, *J* = 18.2 Hz, 1H, C*H*), 2.50 (dd, *J* = 15.7, 7.8 Hz, 1H, Cp*H*), 1.75 – 1.73 (m, 2H, Cp*H*), 1.60 – 1.50 (m, 4H, Cp*H*), 1.33 – 1.32 (m, 2H, Cp*H*), 1.22 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.8, 82.9, 46.1, 32.3, 25.2, 24.7, one resonance not located (*C*-B).

(E)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3k)***[26]. Yield: 188mg (80%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (dd, *J* = 18.2, 6.2 Hz, 1H, C*H*), 5.36 – 5.32 (d, *J* = 18.0 Hz, 1H, C*H*), 2.06 – 1.96 (m, 1H, Cy*H*), 1.70 (t, *J* = 8.0 Hz, 4H, Cy*H*), 1.63 – 1.60 (m, 1H, Cy*H*), 1.23 (s, 12H, OC(CH_3)$_2$), 1.07 (t, *J* = 11.6 Hz, 5H, Cy*H*).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.7, 82.9, 43.2, 31.9, 26.1, 25.9, 24.7, one resonance not located (*C*-B).

(E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3l)***[12d]. Yield: 147mg (70%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 6.97– 6.94 (d, *J* = 17.8 Hz, 1H, C*H*), 5.80 – 5.77 (d, *J* = 17.8 Hz, 1H, C*H*), 2.05 – 2.02(q, *J* = 7.0 Hz, 2H, CH_2), 1.26 – 1.25(m, 2H, CH_2), 1.16 – 1.15 (m, 2H, CH_2), 1.10 (s, 12H,OC(CH_3)$_2$), 0.76 (t, *J* = 7.3 Hz, 3H, CH_3).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 154.5, 119.2 (br, *C*-B), 82.5, 35.5, 30.4, 24.6, 22.1, 13.6.

(E)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (***3m***)[13c]. Yield: 145 mg (65%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 6.99– 6.97 (d, *J* = 17.8 Hz, 2H,C*H*), 5.81 – 5.79(d, *J* = 17.8 Hz, 2H, C*H*), 2.06 – 2.03(q, *J* =7.0 Hz, 2H, CH_2), 1.29(m,2H, CH_2), 1.14 (m, 4H, CH_2), 1.10 (s, 12H,OC(CH_3)$_2$), 0.79 (t, *J* = 7.3 Hz, 3H, CH_3).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 154.6,119.2 (br, *C*-B), 82.5, 35.8, 31.3, 28.0, 24.6, 22.4, 13.7.

(E)-2-(oct-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3n)***[13b]. Yield: 142mg (60%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 6.97 – 6.96 (d, *J* = 17.8 Hz, 1H, C*H*), 5.79 – 5.77(d, *J* = 17.8 Hz, 1H, C*H*), 2.07 – 2.04 (q, *J* = 7.0 Hz, 2H, CH_2), 1.31 – 1.28 (m, 4H, CH_2), 1.18 – 1.16 (m, 4H, CH_2), 1.10 (s, 12H, OC(CH_3)$_2$), 0.83 (t, *J* = 7.3 Hz, 3H, CH_3).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 154.6, 119.3(br, *C*-B), 82.5, 35.86, 31.6, 28.8, 28.3, 24.6, 22.5, 13.9.

(E)-2-(5-chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3o)***[26]. Yield: 179mg (78%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 6.75 – 6.73(d, *J* = 17.8 Hz, 1H, C*H*), 5.72 – 5.69 (m, 1H, C*H*), 2.97 (t, *J* = 7.3 Hz, 2H, CH_2), 1.98 – 1.95 (m, 2H, CH_2), 1.46 – 1.42 (m,2H,CH_2), 1.09 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 152.2, 121.1 (br, *C*-B), 82.6, 43.7, 32.5, 30.9, 24.5.

(E)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane ***(3p)***[11f]. Yield: 90mg (40%); colorless oil; ^{1}H NMR (700 MHz, C_6D_6) δ 6.64 – 6.61 (d, *J* = 19.1 Hz, 1H, C*H*), 5.93 – 5.87 (d, *J* = 19.1 Hz, 1H,C*H*), 1.09 (s, 12H, OC(CH_3)$_2$), 0.03 (s, 9H, Si(CH_3)$_3$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 157.5, 141.0 (*C*-B), 82.8, 24.5, -2.20(Si – *C*).

(E)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3q)***[13b]. Yield: 166mg (71%, pale yellow oil). ^{1}H NMR (700 MHz, C_6D_6) δ 7.51 – 7.48 (d, *J* = 18.1 Hz, 1H, C*H*), 5.84 – 5.80 (m, 2H, C*H*), 2.08 – 2.06 (m, 2H, CH_2), 1.87 – 1.84 (m, 2H, CH_2), 1.41 – 1.40 (m, 2H, CH_2), 1.33 – 1.32 (m, 2H, CH_2), 1.12 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 153.5, 137.3, 133.5, 112.5 (br, *C-B*), 82.5, 25.9, 24.6, 23.7, 23.0, 22.2

(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane ***(3r)***[11f]. Yield: 73mg (30%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.36 – 7.30 (m, 1H, Ar*H*), 7.28 – 7.27 (m, 2H, Ar*H*), 5.40 (s, 1H, C*H*), 2.05 (s, 1H, CH_3), 1.30 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.1, 136.4, 131.3, 129.9, 126.7, 123.8, 122.3, 83.3, 24.9, 3.1, one resonance not located (*C*-B).

(Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3s)***[11f]. Yield: 122mg (40%, colorless oil). ^{1}H NMR (700 MHz, C_6D_6) δ 8.17 (s, 1H, C*H*), 7.37 – 7.33 (m, 2H, Ar*H*), 7.23 (s, 3H, Ar*H*), 7.18 (d, *J* = 2.0 Hz, 3H, Ar*H*), 7.12 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.10 (d, *J* = 2.0 Hz, 1H, Ar*H*), 1.11 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (176 MHz, C_6D_6) δ 143.7, 140.1, 135.0, 131.2, 129.6, 128.3, 125.4, 83.3, 24.6, one resonance not located (*C*-B).

General procedure for intermolecular chemoselective catalytic hydroboration. In a sealed vial, 19 mg (0.03 mmol) of catalyst **1**, 1.0 mmol (or 2.0 mmol (for nitrile)) of pinacolborane and 1.0 mmol of reactants were added successively. The progress of the reaction was monitored by ^{1}H NMR analyses, which marked the complete hydroboration of alkyne over unreacted alkene or nitrile and also complete hydroboration of nitrile over unreacted alkene, ester and isocyanide (final spectra are provided) in individual cases.

General procedure for catalytic hydroboration of imines. In a sealed vial, 19 mg (0.03 mmol) of catalyst **1**, 145 μL (1.0 mmol) of pinacolborane was then added, followed by 1.0 mmol of imine in a neat condition. This mixture was then transferred to an oil bath at 70 °C for 20 h. The ^{1}H NMR spectrum confirms the complete disappearance of the starting material and the appearance of a new CH_2 peak. The yield was determined by using nitromethane as an internal standard (**4a**–**4d**).

*N-benzyl-4,4,5,5-tetramethyl-N-phenyl-1,3,2-dioxaborolan-2-amine (**4a**)*[27]. NMR Yield: (97%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 6H, Ar*H*), 7.14 – 7.12 (m, 2H, Ar*H*), 7.09 – 7.05 (m, 2H, Ar*H*), 4.75 (s, 2H, NCH_2), 1.08 (s, 12H, B{OC(CH_3)$_2$}$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.3, 140.5, 128.5, 128.3, 126.4, 121.3, 120.5, 82.9, 51.2, 24.6.

*N,N–dibenzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**4b**)*[27]. NMR Yield: (95%, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H, Ar*H*), 7.78 – 7.74 (m, 4H, Ar*H*), 7.70 – 7.66 (m, 5H, Ar*H*), 4.70 (s, 4H, NCH_2), 1.76 (s, 12H, B{OC(CH_3)$_2$}$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.1, 128.2, 128.0, 126.7, 82.5, 48.3, 24.6.

*N-benzyl-N-(tert-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**4c**)*[27]. NMR Yield: (88%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37– 7.35 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.27– 7.26 (d, *J* = 4.0 Hz, 1H, Ar*H*), 4.34 (s, 2H, NCH_2), 1.33 (s, 12H, B{OC(CH_3)$_2$}$_2$), 1.29 (s, 9H, NC(CH_3)$_3$).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 127.9, 126.7, 125.8, 81.4, 53.0, 48.3, 30.6, 24.5.

*N-benzyl-N-4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (**4d**)*[28]. NMR Yield: (94%, yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 2H, Ar*H*), 7.36 – 7.35 (d, *J* = 4.0 Hz, 2H, Ar*H*), 7.33 – 7.29 (m, 1H, Ar*H*), 4.11 (s, 2H, NCH_2), 2.54 (s, 3H, NCH_3), 1.32 (s, 12H, B{OC(CH_3)$_2$}$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.2, 128.2, 127.6, 126.6, 82.2, 52.8, 33.2, 24.6.

General procedure for catalytic hydroboration of pyridine. In a sealed vial, 32 mg (0.05 mmol) of catalyst **1**, 145 μL (1.0 mmol) of pinacolborane, was then added, followed by 1.0 mmol of pyridine in a neat condition. This mixture was then transferred to an oil bath at 70 °C for 12 h. The course of the reaction was determined by ^{1}H NMR spectroscopy, which explains the complete conversion of pyridine.

*1,4-dihydropyridine (**5a**)*[29]. ^{1}H NMR (400 MHz, C_6D_6) δ 6.53 – 6.52 (m, 2H, Ar*H*), 4.58 – 4.55 (m, 2H, Ar*H*), 2.82 – 2.81 (m, 2H, CH_2), 1.01 (s, 12H, OC(CH_3)$_2$).^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 127.1, 102.4, 83.0, 24.2, 22.4.

General procedure for catalytic hydroboration of alkene. In a sealed vial, 32 mg (0.05 mmol) of catalyst **1**, 145 μL (1.0 mmol) of pinacolborane, was then added, followed by 1.0 mmol of the alkene in a neat condition. This mixture was then transferred to an oil bath at 110 °C for 12 h. The course of the reaction was checked by ^{1}H NMR. Upon completion, the reaction mixture was filtered and evaporated, and the residue was purified by column chromatography over silica gel (100−200 mesh) with ethyl acetate/hexane (1:5).

*4,4,5,5-tetramethyl-2-phenylethyl-1,3,2-dioxaborolane (**6a**)*[4i]. Yield: 185 mg (80%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H, Ar), 7.17 – 7.13 (m, 1H, Ar), 2.75 (t, *J* = 8.0 Hz, 2H, CH_2), 1.22 (s, 12H, OC(CH_3)$_3$), 1.15 (t, *J* = 8.0 Hz, 2H, CH_2).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.4, 128.1, 128.0, 125.5, 83.1, 29.9, 24.8.

General procedure for catalytic hydroboration of carbodiimides. In a sealed vial, 32 mg (0.05 mmol) of catalyst **1**, 145 μL (1.0 mmol) of pinacolborane, was then added, followed by 1.0 mmol of carbodiimide in a neat condition. This mixture was then transferred to an oil bath at 70 °C for 12 h. The ^{1}H NMR spectrum confirms the complete disappearance of the starting material and the appearance of a new CH peak. The yield was determined by ^{1}H NMR spectroscopy (**7a**–**7b**).

*(E)-N,N'-diisopropyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (**7a**)*[15]. NMR Yield: (>99%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H, NC*H*N), 4.41 – 4.34 (dt, *J* = 13.0, 6.4 Hz, 1H, C*H*(CH$_3$)$_2$), 3.26 – 3.20 (dt, *J* = 12.0, 5.8 Hz, 1H, C*H*(CH$_3$)$_2$), 1.16 (s, 12H, NB*pin*), 1.14 – 1.12 (d, *J* = 8.0 Hz, 6H, CH(CH_3)$_2$), 1.03 – 1.02 (d, *J* = 4.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.2 (N*C*HN), 82.4, 56.7, 42.8, 25.1, 24.3, 21.3.

*(E)-N,N'-di-tert-butyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formimidamide (**7b**)*[15]. NMR Yield: (>99%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H, NC*H*N), 1.30 (s, 12H, NB*pin*), 1.22 (s, 9H, N(CH_3)$_2$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.5(N*C*HN), 81.9, 54.4, 30.1, 24.4.

General procedure for catalytic hydroboration of isocyanide. In a sealed vial, 32 mg (0.05 mmol) of catalyst **1**, 290 μL (2.0 mmol) of pinacolborane, was then added, followed by 1.0 mmol of isocyanide in a neat condition. This mixture was then transferred to an oil bath at 80 °C for 16 h. The ^{1}H NMR spectrum confirms the complete disappearance of the starting material and the appearance of a new CH_2 peak. The yield was determined by ^{1}H NMR spectroscopy (**8a**–**8b**).

*4,4,5,5-tetramethyl-N-pentyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,3,2-dioxaborolan-2-amine (**8a**)*[18]. NMR Yield: (>99%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, *J* = 8.0 Hz, 2H, CH$_3$(CH_2)$_4$NBpinCH$_2$Bpin), 2.45 (s, 2H, CH$_3$(CH$_2$)$_4$NBpinCH_2Bpin), 1.36–1.30 (m, 2H, CH$_3$(CH_2)$_4$NBpinCH$_2$Bpin), 1.25–1.20 (m, 4H, CH$_3$(CH_2)$_4$NBpinCH$_2$Bpin), 1.18 (s, 12H, CH$_3$(CH$_2$)$_4$NBpinCH$_2$B*pin*), 1.12 (s, 12H, CH$_3$(CH$_2$)$_4$NB*pin*CH$_2$Bpin), 0.81 (t, *J* = 8.0 Hz, 3H, CH_3(CH$_2$)$_4$NBpinCH$_2$Bpin). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 83.0, 81.6, 48.5, 28.5, 28.0, 24.7, 24.7, 24.4, 22.4, 14.0.

*N-Cyclohexyl-4,4,5,5-tetramethyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,3,2-dioxaborolan-2-amine (**8b**)*[18]. NMR Yield: (>99%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 – 2.89 (m, 1H, Cy*H*), 2.37 (s, 2H, Cy*H*), 1.66 – 1.63 (m, 2H, Cy*H*), 1.56 – 1.52 (m, 2H, Cy*H*), 1.36 – 1.30 (m, 4H, Cy*H*), 1.17 (s, 12H, CyNBpinCH$_2$B*pin*), 1.12 (s, 12H, CyNB*pin*CH$_2$Bpin), 0.96

(m, 2H, Cy*H*). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 82.9, 81.3, 55.7, 31.8, 26.0, 25.7, 24.7, 24.4, 22.5.

ASSOCIATED CONTENT

Detailed optimizations, NMR spectra of the products, and crystallographic data and structure refinement summary (**PDF**).

Crystallographic information files (**CIF**)

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Notes

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