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Article

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Ytterbium-Catalyzed Hydroboration of Aldehydes and Ketones

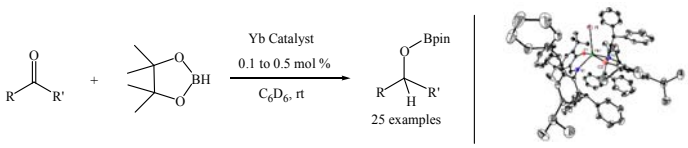
Weifan Wang,[†] Xingchao Shen,[†] Fengyi Zhao,[†] Huan Jiang,[†] Weiwei Yao,[‡] Sumod A. Pullarkat,[§] Li Xu,[†] and Mengtao Ma*[,†]

[†]College of Science, Nanjing Forestry University, Nanjing 210037, People's Republic of China

[‡]College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023, People's Republic of China

[§]Division of Chemistry & Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Supporting Information Placeholder



ABSTRACT: The well-defined heavy rare earth ytterbium iodide complex **1** (L_2YbI) has been successfully employed as an efficient catalyst for the hydroboration of a wide range of aldehydes and ketones with pinacolborane (HBpin) at room temperature. The protocol requires low catalyst loadings (0.1−0.5 mol %) and proceeds rapidly (>99% conversion in <10 min). Additionally, the catalyst **1** shows good functional group tolerance even towards the hydroxyl and amino moieties and displays chemoselective hydroboration of aldehydes over ketones under mild conditions.

INTRODUCTION

Catalytic hydroboration of unsaturated organic compounds is a key transformation in commodity and fine chemical production, materials synthesis, and preparation of complex molecules. Among the hydroboration of unsaturated bonds such as C=C, C=N, and C=O double bonds, as well as C≡C triple bonds, the catalytic reduction of carbonyl compounds has been extensively studied.[1,2] The common methods of hydroboration involve equimolar addition of a borane reagent to carbonyl compounds to form borates, which can be subsequently hydrolyzed to yield alcohols. Borates are excellent organic intermediates in organic synthesis. Thus, a number of catalytic methods are employed for the synthesis of borate derivatives. Commonly, hydroboration reduction of carbonyl compounds is achieved by the use of transition metal complexes.[3] During the past several years, the main group metal and non-metal catalyzed hydroboration has also attracted considerable attention.[4] To our surprise, examples of rare earth metals catalyzed hydroboration are very few.[5-7] To the best of our knowledge, there are only two reports about hydroboration of carbonyl compounds catalyzed by rare earth metal complexes to date. One is the rapid, clean hydroboration of ketones and aldehydes with HBpin achieved using the homoleptic lanthanum amido catalyst $La[N(SiMe_3)_2]_3$ reported by Lohr, Marks and coworkers in early 2017.[6] The reaction rates of ketones in the hydroboration were generally faster than for aldehydes. This observation was contrary to what has been observed previously, where aldehydes are more reactive than ketones. The other report involves a series of tri(cyclopentadienyl)lanthanide complexes Cp_3Ln (Ln = La, Nd, Sm, Yb, and Y) that can be employed as excellent catalysts for the hydroboration of various carbonyl compounds reported by Xue, Yao, Shen and coworkers very recently.[7] However, the reactivity toward aldehydes was higher than that of ketones in this instance. This trend is consistent with previously reported transition and main group metal complexes but opposite to that reported by Marks et al.

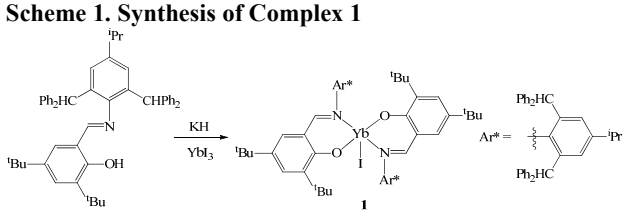
Schiff-base ligands are popular in coordination chemistry and catalytic chemistry by virtue of their ease of preparation, high yield, and good complexing ability by reaction with metal ions.[8,9] Recently, we used sterically bulky Schiff-base ligands to synthesize a series of the corresponding magnesium complexes and investigated their catalytic effect in the hydrosilylation of ketones.[10] While most catalysts are efficient for the reduction of aldehydes, they usually perform poorly with ketones, requiring long reaction times, high catalyst loadings, or elevated temperatures. Compared to the above-mentioned light rare earth metal (La),[6,7] the catalytic hydroboration of heavy rare earth metal remains unexplored and therefore deserves attention. Herein, we report the facile preparation of the Schiff-base heavy rare earth ytterbium halide complex (L_2YbI) which can catalyze the hydroboration of various aldehydes and ketones with pinacolborane with low catalyst loadings and excellent reaction rates at room temperature to afford alkoxypinacolboronate esters.

RESULTS AND DISCUSSION

The reaction of the extremely bulky ligand 2-((2,6-dibenzhydryl-4-isopropylphenylimino)methyl)-4,6-di-tert-butylphenol (LH) with one equiv KH in THF produced the potassium salt of Schiff-base ligand. Subsequently, the resultant potassium salt was treated with YbI_3 in THF to generate the corresponding ytterbium iodide complex **1** (L_2YbI) as yellow crystals in moderate yield (Scheme 1). The formation and molecular

structure of **1** was confirmed by single-crystal X-ray diffraction (Figure S1). In complex **1**, the ytterbium atom is in a five coordinate distorted trigonal bipyramid environment in which one iodine atom and two nitrogen atoms define the equatorial plane and the two oxygen atoms of Schiff-base ligands occupy the apical position.

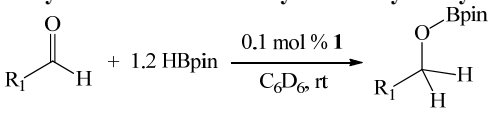
Scheme 1. Synthesis of Complex 1



It well known that the rare earth metal atom radius has a considerable effect on the catalytic activity.[11] In the aforementioned two examples of rare earth catalyzed hydroboration of carbonyl compounds, the lanthanum metal of both $La[N(SiMe_3)_2]_3$ and Cp_3La catalysts is light rare earth element.[6,7] The heavy rare earth metal catalyzed hydroboration of aldehydes and ketones is not introduced in detail in literature although Shen et al. briefly mentioned the test of Cp_3Yb during the optimization of hydroboration reaction conditions.[7] We found that the heavy rare earth ytterbium iodide complex **1** was a very efficient catalyst for the hydroboration of aldehydes and ketones. This is contrary to that observed with the precursor of the manganese alkyl complexes reported by Zhang et al., namely the manganese chloride, which is not an active catalyst for the hydroboration of carbonyl compounds.[3g] Therefore, we used the heavy rare earth ytterbium halide complex **1** as catalyst to investigate the hydroboration of aldehydes and ketones in detail.

As expected, the catalyst-free hydroboration of benzaldehyde displayed little conversion.[6] In contrast, when we began our investigation with the addition of only 0.5 mol % of catalyst **1** to the mixture of benzaldehyde and HBpin, we observed the formation of $PhCH_2OBpin$ in quantitative yield within less than 10 min at room temperature. Encouraged by this we then decreased the catalyst loading to 0.1 mol %, and noted that the catalyst could still give full conversion in the same reaction time (Table 1, entry 1). Therefore, we proceeded to explore the hydroboration of a wide range of aldehydes by using 0.1 mol % catalyst loading at room temperature as optimized condition. Progress of the hydroboration reaction was monitored by ^1H NMR of the reaction mixture, which confirmed the quantitative formation of boronate esters. Table 1 summarizes the full scope of aldehydes substrates investigated in this report. It should be noted that the reactivity of catalyst **1** toward aldehydes is higher than that of the reported $La[N(TMS)_2]_3$ complex and in some instances are indeed better than that of Cp_3La.[6,7] The position of halogen on the phenyl ring has an important effect on the reactivity, as demonstrated by the clean hydroboration of 2/3/4-chlorobenzaldehyde or 2/3/4-fluorobenzaldehyde (Table 1, entries 3-7). It can be seen that the presence of the chloride or fluoride groups in the *ortho* position of benzaldehyde led to full conversion in less than 10 min of the parent benzaldehyde. However, the *meta*/*para*-halide-substituted benzaldehyde needs a slightly longer time to achieve full conversion when compared to the *ortho* substituted analogue. This substituent effect is different from that observed for the Cp_3La based protocol wherein the substituent position (*o, m, p*) on the benzene ring have no significant

Table 1. Hydroboration of Aldehydes Catalyzed by 1



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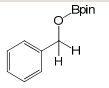
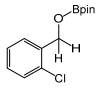
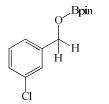
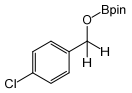
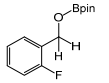
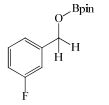
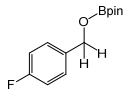
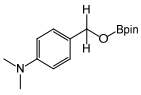
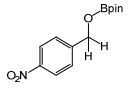
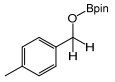
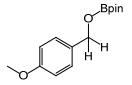
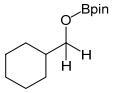
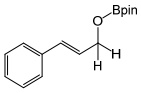
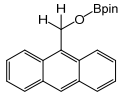
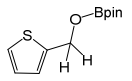
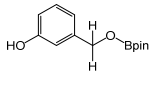
1		2a	<10	>99
2		2b	<10	>99
3		2c	120	>99
4		2d	80	>99
5		2e	<10	>99
6		2f	120	>99
7		2g	50	>99
8		2h	<10	>99
9		2i	<10	>99
10		2j	<10	>99
11		2k	<10	>99
12		2l	<10	>99
13		2m	<10	>99
14		2n	<10	>99
15		2o	60	>99
16		2p	<10	>99

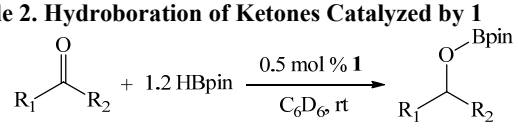
[a] Yield was determined by ^1H NMR spectroscopy.

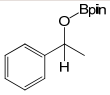
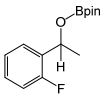
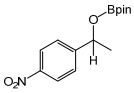
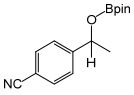
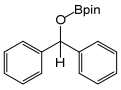
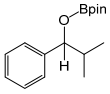
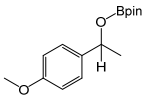
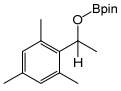
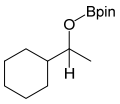
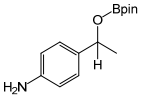
impact on the reactivity.[7] Under the same reaction conditions, both electron withdrawing and electron donating groups such as Me_2N-, O_2N-, Me- and MeO-substituted benzaldehydes underwent the reaction rapidly with equal efficiency (Table 1, entries 8-11). Aliphatic aldehyde, cinnamaldehyde and 9-anthraldehyde were also hydroborated in full conversion with 0.1 mol % catalyst loading in less than 10 min (Table 1, entries 12-14). It needs to be noted that for α, β-unsaturated cinnamaldehyde, the catalytic activity of the ytterbium complex **1** is higher than that of observed when employing $La[N(TMS)_2]_3$ and Cp_3La catalysts. Furthermore, those procotols need 1.0 mol % catalyst, 15 min reaction time and 0.1 mol % catalyst, 120 min reaction time, respectively.[6,7] No dearomatization of the thiophene ring was obtained when 2-thiophenecarboxaldehyde was used, underscoring the catalyst selectivity towards the C=O functionality (Table 1, entry 15). Surprisingly, when 3-hydroxybenzaldehyde was used, hydroboration occurred at the aldehyde functional group instead of hydroxylborane dehydrocoupling (Table 1, entry 16). However, in the absence of catalyst, the dehydrocoupling of HBpin was achieved albeit with low yield when the same reaction is carried out as reported by Bertrand and co-workers.[12] No rare earth metal catalyst has so far been reported to show tolerance towards the phenolic OH group.

As expected, the Yb-catalyzed hydroboration of more sterically bulky ketonic carbonyl functions normally required slightly higher catalyst loadings than that of aldehydes to achieve similar results (Table 2). This observation is consistent with the aforementioned Cp_3La based protocol, but contrary to that reported for the $La[N(TMS)_2]_3$ catalyst.[6,7] Initial investigation on the hydroboration of acetophenone catalyzed by **1** with pinacolborane at room temperature under different catalyst loading was carried out. We observed that the acetophenone was clearly converted into the corresponding borate ester in 30 min at 1 mol % catalyst loading while the 0.5 mol % catalyst loading in 50 min gave the same conversion (Table 2, entry 1). Encouraged by this result, a wide range of aromatic and aliphatic ketones were investigated for hydroboration activity with HBpin at room temperature using catalyst loadings as low as 0.5 mol % (Table 2). We chose the 0.5 mol % catalyst loading for the conversion since the reaction time is almost the same and the catalyst loading is relatively lower compared to 1.0 mol %. In most cases, the reaction was completed within 1 h in quantitative yields. For the hydroboration of aromatic ketones with electron withdrawing or electron donating group (Table 2, entries 2−8), quantitative conversion was obtained. 4-Acetylbenzonitrile and 4-aminoacetophenone (Table 2, entries 4, 11) need a slightly longer time since it will react with HBpin leading to the uncatalyzed amine-borane blocking catalytic C=O hydroboration. Comparison of the reactivity of acetophenone and 2,4,6-trimethylacetophenone once again highlighted the im portance of steric factors in these hydroboration reactions (Table 2, entry 8). Under the same reaction conditions, dialkyl ketones were independently reacted with an equimolar amount of HBpin in full yields in a very short time (Table 2, entries 9, 10). The reaction showed excellent functional group tolerance toward NH functionality: for 4-aminoacetophenone, the reaction with HBpin led to the corresponding borate ester instead of dehydrocoupling product[13] (Table 2, entry 11).

The challenging chemoselective hydroboration of aldehydes over the ketones using catalyst **1** was also explored. Equimolar amounts of benzaldehyde, acetophenone, and pinacolborane were treated with 0.1 mol % **1**. It resulted in 99 % conversion of benzaldehyde in 20 min. The acetophenone remained almost intact. 1H NMR analysis indicated the presence of more than 99 % of unreacted acetophenone in the reaction mixture. Such functional group selectivity for aldehyde versus ketone hydroboration with pinacolborane is similar to that previously reported using lanthanum, ruthenium and aluminum catalysts.[3a,5e,6,7] Similar intermolecular chemoselectivity is also observed in competitive catalytic hydroboration reactions of 2-fluorobenzaldehyde over 2-fluoroacetophenone and cyclohexanecarbaldehyde over cyclohexyl methyl ketone (Scheme 2).

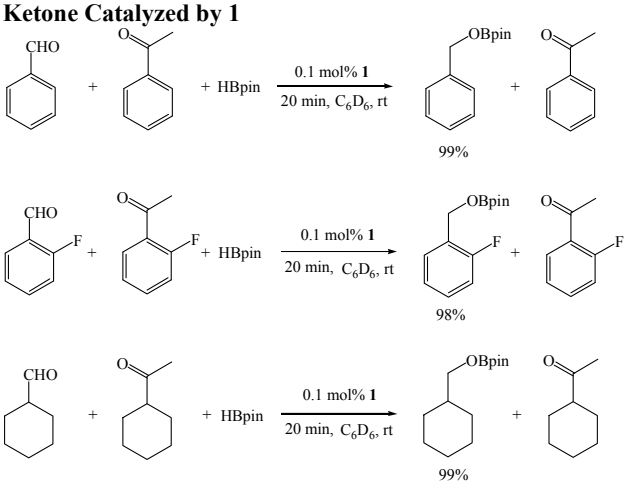
Table 2. Hydroboration of Ketones Catalyzed by 1



Entry	Product		Time (min)	Yield (%)[a]
1		3a	50	>99
2		3b	15	>99
3		3c	15	>99
4		3d	180	92
5		3e	60	>99
6		3f	<10	>99
7		3g	50	>99
8		3h	48*60	99
9		3i	<10	>99
10		3j	<10	>99
11		3k	4.5*60	>99

[a] Yield was determined by ^1H NMR spectroscopy.

Scheme 2. Chemoselective Hydroboration of Aldehyde / Ketone Catalyzed by 1



CONCLUSION

In summary, we have demonstrated that Schiff-base heavy rare earth ytterbium halide complex **1** was an efficient catalyst for the hydroboration of ketones and aldehydes with HBpin. It demonstrated higher reactivity than that reported for the similar amidinato calcium iodide complex that typically needed higher catalyst loading (0.5-3 mol %) and longer reaction time (40 min to 5 h).[5j] The newly developed protocol also shows good functional group tolerance even towards OH and NH groups. High chemoselectivity for aldehyde hydroboration over ketones and C=C double bond is also observed. As known, the lanthanide halide is also a very useful precursor for other lanthanide derivatives. Hence further investigations of the potential of the ytterbium iodide **1**, such as the preparation of the corresponding ytterbium alkyl and amide complexes etc. and their catalytic behavior, are currently in progress.

EXPERIMENTAL SECTION

General Information. All air-sensitive compounds were carried out using standard Schlenk-line or glove box techniques under high-purity argon. Toluene, THF and hexane were dried and distilled from molten sodium. C_6D_6 was dried over sodium mirror and freeze–thawed twice prior to use. ^1H, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra were recorded at 25 °C on Bruker Avance III 600 MHz spectrometer in deuterated solvents and were referenced to the resonances of the solvent used. IR Spectrum for complex **1** was recorded in Perkin–Elmer FT–IR spectrometer. Microanalyses were performed by the Elemental Analysis Laboratory of the Advanced Analysis and Testing Center at Nanjing Forestry University. Melting points were determined in sealed capillaries under dinitrogen and are uncorrected. Ligand was prepared according to a literature procedure.[14] Chemicals were purchased from Sigma–Aldrich, Alfa–Aesar, and Acros and used without further purification.

Experimental Procedure. *Synthesis of Complex **1***. KH (0.07 g, 1.75 mmol) in THF (5 mL) was added dropwise to a solution of ligand 2-((2,6-dibenzhydryl-4-isopropylphenyl imino)methyl)-4,6-di-tert-butylphenol (1.00 g, 1.46 mmol) in THF (40 mL) at −80 °C. The suspension was warmed to room temperature and stirred for 3 hours. Then the solution of YbI_3 (0.81 g, 1.46 mmol) in THF (20 mL) was added dropwise to the solution at −80 °C. The suspension was warmed to room temperature and stirred overnight. The resultant solution was filtered, all volatiles were removed in vacuo, and the residue was extracted with toluene (20 mL). The solution was concentrated to ca. 5 mL. Complex **1** was obtained as yellow crystals at −30 °C after several days (0.82 g, 60%). M.p. 282−284 °C. Anal Calcd for $C_{100}H_{104}IN_2O_2Yb$: C, 72.10; H, 6.29; N, 1.68. Found C, 72.58; H, 6.63; N, 1.32. IR (KBr, cm^{-1}): 3429, 3061, 3028, 2960, 2867, 1626 (C=N), 1602, 1571, 1535, 1445, 1400, 1253, 1162, 1117, 1076, 1022, 803, 758, 699, 604. Note: NMR data for **1** could not be obtained due to paramagnetic character.

General Procedure for Catalytic Hydroboration of Aldehydes. In a glove box, catalyst **1** (0.1 mol %) was added to a solution of aldehyde (1 mmol) and pinacolborane (1.2 mmol) in a J. Young NMR tube equipped with a Teflon screw cap, which was charged with C_6D_6 (0.5 mL). The progress of the reaction was monitored by ^1H NMR, ^{13}C NMR and ^{11}B NMR, which indicated the completion of the reaction by the disappearance of aldehyde (RCHO) proton and appearance of a new CH_2 resonance.

Spectroscopic Data for Aldehyde Hydroboration Products. *2-(Benzyloxy)pinacolborane (**2a**).*[4] ^1H NMR (600 MHz, C_6D_6): δ 7.30 (d, $^3J_{HH}$ = 7.2 Hz, 2 H), 7.13 (t, $^3J_{HH}$ = 7.2 Hz, 2 H), 7.05 (t, $^3J_{HH}$ = 7.2 Hz, 1 H), 4.95 (s, 2 H), 1.04 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 140.1, 128.6, 127.6, 127.1, 82.7, 67.0, 24.7. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.82.

*2-(2-Chlorobenzyloxy)pinacolborane (**2b**).*[7] ^1H NMR (600 MHz, C_6D_6): δ 7.55 (d, $^3J_{HH}$ = 7.2 Hz, 1 H), 7.08 (d, $^3J_{HH}$ = 7.2 Hz, 1 H), 6.92 (t, $^3J_{HH}$ = 7.2 Hz, 1 H), 6.77 (t, $^3J_{HH}$ = 7.2 Hz, 1 H), 5.14 (s, 2 H), 1.04 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 137.6, 132.2, 129.3, 128.1, 127.9, 127.0, 82.9, 64.4, 24.7. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.80.

*2-(3-Chlorobenzyloxy)pinacolborane (**2c**).*[7] ^1H NMR (600 MHz, C_6D_6): δ 7.30 (s, 1 H), 7.00 (t, $^3J_{HH}$ = 6.6 Hz, 2 H), 6.82 (t, $^3J_{HH}$ = 7.8 Hz, 1 H), 4.74 (s, 1 H), 1.03 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 142.1, 134.5, 129.8, 127.6, 127.1, 124.9, 82.9, 66.0, 24.6. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.76

*2-(4-Chlorobenzyloxy)pinacolborane (**2d**).*[5e] ^1H NMR (600 MHz, C_6D_6): δ 7.07 (d, $^3J_{HH}$ = 8.4 Hz, 2 H), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 2 H), 4.76 (s, 2 H), 1.03 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 138.5, 133.4, 128.7, 128.4, 82.9, 66.1, 24.7. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.73.

*2-(2-Fluorobenzyloxy)pinacolborane (**2e**).*[5i] ^1H NMR (600 MHz, C_6D_6): δ 7.41−7.44 (m, 1 H), 6.85−6.81 (m, 2 H), 6.76−6.73 (m, 1 H), 5.09 (s, 2 H), 1.04 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 161.5, 159.9, 129.2, 124.3, 115.3, 115.1, 82.9, 61.0, 24.7. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.81.

*2-(3-Fluorobenzyloxy)pinacolborane (**2f**).*[5i] ^1H NMR (600 MHz, C_6D_6): δ 7.05−6.68 (m, 5 H), 4.79 (s, 2 H), 1.03 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 130.1, 130.0, 122.24, 122.21, 114.4, 114.1, 113.9, 113.6, 82.8, 66.0, 24.6. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.74.

*2-(4-Fluorobenzyloxy)pinacolborane (**2g**).*[6] ^1H NMR (600 MHz, C_6D_6): δ 7.09−7.06 (m, 2 H), 6.78−6.75 (m, 2 H), 4.79 (s, 2 H), 1.04 (s, 12 H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 163.4, 161.8, 135.8, 128.9, 115.4, 115.3, 82.8, 66.2, 24.7. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.73.

*2-(4-N,N-Dimethylaminobenzyloxy)pinacolborane (**2h**).*[5e] ^1H NMR (600 MHz, C_6D_6): δ 7.34 (d, $^3J_{HH}$ = 8.4 Hz, 2 H), 6.56 (d, $^3J_{HH}$ = 8.4 Hz, 2 H), 5.00 (s, 2 H), 2.50 (s, 6 H), 1.07 (s, 12 H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 150.6, 129.0, 112.8, 82.5, 67.2, 40.3, 24.8. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.80.

2-((4-Methylbenzyl)oxy)pinacolborane ***(2i)***.[6,7] ^{1}H NMR (600 MHz, C_6D_6): δ 7.26 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H), 6.97 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H), 4.96 (s, 2 H), 2.08 (s, 3 H), 1.05 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 137.2, 137.0, 129.3, 127.3, 82.7, 66.9, 24.7, 21.1. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.82.

2-(4-Nitrophenyl) pinacolborane ***(2j)***.[5j] ^{1}H NMR (600 MHz, C_6D_6): δ 7.80 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 6.93 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H), 4.69 (s, 1 H), 1.05 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 147.6, 146.6, 126.8, 123.6, 83.2, 65.6, 24.7. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.71.

2-(4-Methoxybenzyloxy)pinacolborane ***(2k)***.[6] ^{1}H NMR (600 MHz, C_6D_6): δ 7.26 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H), 6.75 (d, $^{3}J_{HH}$ = 7.8 Hz, 2 H), 4.93 (s, 1 H), 3.30 (s, 3 H), 1.05 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 159.7, 132.2, 128.9, 114.1, 82.7, 66.8, 54.8, 24.7. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.80.

2-(Cyclohexylmethoxy)pinacolborane ***(2l)***.[5e] ^{1}H NMR (600 MHz, C_6D_6): δ 3.77 (d, $^{3}J_{HH}$ = 6.6 Hz, 2 H), 1.73−1.59 (m, 4 H), 1.55−1.51 (m, 2 H), 1.15−1.09 (m, 3 H), 1.07 (s, 12 H), 0.92−0.90 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 82.4, 70.6, 39.9, 29.7, 26.9, 26.2, 24.8. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.55.

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(2m)***.[5e] ^{1}H NMR (600 MHz, C_6D_6): δ 7.18−7.17 (m, 2 H), 7.10−7.07 (m, 2 H), 7.03−7.00 (m, 1 H), 6.62−6.59 (m, 1 H), 6.19−6.15 (m, 1 H), 4.53 (d, $^{3}J_{HH}$ = 5.4 Hz, 2 H), 1.07 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 137.4, 130.9, 128.8, 127.7, 127.5, 126.9, 82.7, 65.5, 24.7. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.74.

2-(Anthracen-9-ylmethoxy)pinacolborane ***(2n)***.[6] ^{1}H NMR (600 MHz, C_6D_6): δ 8.58 (d, $^{3}J_{HH}$ = 9.0 Hz, 2 H), 8.12 (s, 1 H), 7.75 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 7.33 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 7.23 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 5.90 (s, 2 H), 1.01 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 132.0, 131.2, 130.5, 129.3, 128.8, 126.2, 125.2, 125.1, 82.8, 59.7, 24.7. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.86.

2-(Thiophen)pinacolborane ***(2o)***.[6] ^{1}H NMR (600 MHz, C_6D_6): δ 6.86-6.66 (m, 3 H), 5.00 (s, 2 H), 1.04 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 142.8, 126.8, 126.1, 125.7, 82.9, 61.8, 24.7. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.78.

2-(Phenol)pinacolborane ***(2p)***.[5j] ^{1}H NMR (600 MHz, C_6D_6): δ 7.12−7.03 (m, 2 H), 6.96−6.75 (m, 2 H), 5.86 (s, 1 H), 4.91 (s, 2 H), 1.03 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 157.1, 141.5, 129.8, 118.7, 114.9, 114.1, 82.1, 66.9, 24.6. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 21.98.

General Procedure for Catalytic Hydroboration of Ketones. In a glove box, catalyst 1 (0.5 mol %) was added to a solution of ketone (1 mmol) and pinacolborane (1.2 mmol) in a J. Young NMR tube equipped with a Teflon screw cap, which was charged with C_6D_6 (0.5 mL). The progress of the reaction was monitored by ^{1}H NMR, ^{13}C NMR and ^{11}B NMR, which indicated the completion of the reaction by the appearance of a new CH resonance.

Spectroscopic Data for Ketone Hydroboration Products. *2-(Phenylethoxy)pinacolborane* ***(3a)***.[4] ^{1}H NMR (600 MHz, C_6D_6): δ 7.36 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 7.14 (t, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 7.05 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H), 5.40 (q, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 1.45 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H), 1.03 (s, 6 H), 1.00 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 145.4, 128.5, 127.4, 125.7, 82.5, 73.0, 25.8, 24.7, 24.6. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.51.

2-(1-(2-Fluorophenyl)ethoxy)pinacolborane ***(3b)***.[5k,7] ^{1}H NMR (600 MHz, C_6D_6): δ 7.63−7.60 (m, 1 H), 6.87−6.84 (m, 2 H), 6.77−6.74 (m, 1 H), 5.86 (q, $^{3}J_{HH}$ = 6.6, 1 H), 1.49 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H), 1.02 (s, 6 H), 1.00 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 160.5, 132.5, 128.7, 127.1, 124.5, 115.3, 82.7, 67.0, 25.0, 24.6, 24.6. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.48.

2-(1-(4-Nitrophenyl)ethoxy)pinacolborane ***(3c)***.[5j,7] ^{1}H NMR (600 MHz, C_6D_6): δ 7.81 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 7.02 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 5.19 (q, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 1.26 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H), 1.04 (s, 6 H), 1.01 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 151.8, 147.5, 126.1, 123.6, 82.9, 71.6, 25.3, 24.6. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.39.

2-(1-(4-Benzonitrile)ethoxy)pinacolborane ***(3d)***.[15] ^{1}H NMR (600 MHz, C_6D_6): δ 7.03 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 6.97 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 5.15 (q, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 1.24 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H), 1.03 (s, 6 H), 1.00 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 149.8, 132.2, 126.0, 118.9, 111.6, 82.5, 72.1, 25.3, 24.6, 24.6. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.41.

2-(Diphenylmethoxy)pinacolborane ***(3e)***.[7] ^{1}H NMR (600 MHz, C_6D_6): δ 7.45−7.44 (m, 4 H), 7.11−7.08 (m, 4 H), 7.02−6.99 (m, 2 H), 6.43 (s, 1 H), 0.98 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 143.9, 128.6, 127.6, 127.0, 82.9, 78.5, 24.2. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.84.

2-(2-Methyl-1-phenylpropoxy)pinacolborane ***(3f)***.[3a] ^{1}H NMR (600 MHz, C_6D_6): δ 7.33 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 7.14 (t, $^{3}J_{HH}$ = 7.8 Hz, 2 H), 7.05 (t, $^{3}J_{HH}$ = 7.8 Hz, 1 H), 5.03 (d, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 1.97 (q, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 1.01 (s, 6 H), 0.98 (s, 6 H), 0.97 (d, $^{3}J_{HH}$ = 3.6 Hz, 3 H), 0.84 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 143.2, 127.4, 126.9, 82.1, 81.9, 35.8, 24.62, 24.59, 19.1, 17.8. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.66.

2-(1-(4-Methoxyphenyl)ethoxy)pinacolborane ***(3g)***.[7] ^{1}H NMR (600 MHz, C_6D_6): δ 7.30 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 6.76 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 5.41 (q, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 3.30 (s, 3H), 1.48 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H), 1.04 (s, 6 H), 1.02 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 159.4, 137.5, 127.0, 114.0, 82.5, 72.7, 54.8, 25.7, 24.7, 24.6. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.56.

2-(Mesitylmethoxy)pinacolborane ***(3h)***.[7] ^{1}H NMR (600 MHz, C_6D_6): δ 6.72 (s, 2 H), 5.85 (q, $^{3}J_{HH}$ = 7.2 Hz, 1 H), 2.47 (s, 6 H), 2.09 (s, 3 H), 1.53 (d, $^{3}J_{HH}$ = 7.2 Hz, 3 H), 0.99 (s, 6 H), 0.96 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 137.4, 136.1, 135.8, 130.3, 82.4, 70.3, 24.7, 24.5, 22.0, 20.8. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.51.

2-(Cyclohexyloxy)pinacolborane ***(3i)***.[5f] ^{1}H NMR (600 MHz, C_6D_6): δ 4.20 (sept, $^{3}J_{HH}$ = 4.2 Hz, 1 H), 1.89−1.87 (m, 2 H), 1.62−1.59 (m, 2 H), 1.50−1.44 (m, 2 H), 1.30−1.27 (m, 2 H), 1.16−1.10 (m, 2 H), 1.07 (s, 12 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 82.2, 72.7, 34.8, 25.8, 24.7, 24.1. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.32.

2-(Cyclohexylmethoxy)pinacolborane ***(3j)***.[5f] ^{1}H NMR (600 MHz, C_6D_6): δ 4.12 (q, $^{3}J_{HH}$ = 6.0 Hz, 1 H), 1.88−1.86 (m, 1 H), 1.68−1.63 (m, 3 H), 1.57−1.55 (m, 1 H), 1.33−1.29 (m, 1 H), 1.18 (d, $^{3}J_{HH}$ = 6.0 Hz, 3 H), 1.15−1.11 (m, 2 H), 1.08 (s, 12 H), 1.06−1.03 (m, 2 H), 0.98−0.96 (m, 1 H). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ 82.2, 75.0, 44.7, 29.1, 28.6, 26.9, 26.6, 26.5, 24.75, 24.70, 20.1. $^{11}B\{^{1}H\}$ NMR (193 MHz, C_6D_6): δ 22.41.

2-(1-(4-Aminophenyl)ethoxy)pinacolborane ***(3k)***.[5j] ^{1}H NMR (600 MHz, C_6D_6): δ 7.22 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 6.35 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H), 5.38 (q, $^{3}J_{HH}$ = 6.6 Hz, 1 H), 2.93 (s, 2 H), 1.51 (d, $^{3}J_{HH}$ = 6.6 Hz, 3 H), 1.03 (s, 6 H), 1.01 (s, 6 H). $^{13}C\{^{1}H\}$

NMR (151 MHz, C_6D_6): δ 146.5, 134.8, 126.9, 126.6, 117.9, 114.9, 82.4, 72.9, 25.7, 24.7, 24.6. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_6): δ 22.49.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
NMR spectra of hydroboration products (PDF)
Crystallographic data for the complex **1** (CIF)

AUTHOR INFORMATION

Corresponding Author

*Email: mengtao@njfu.edu.cn

Notes

The authors declare no competing financial interest.

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