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Note

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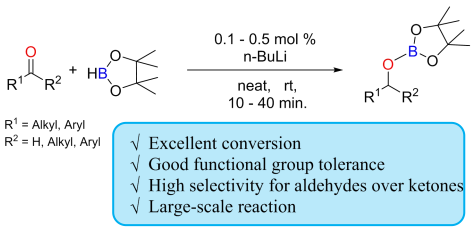
Supporting Information

ABSTRACT: Highly efficient and selective hydroboration of aldehydes and ketones with HBpin is achieved by using the simple and convenient *n*-BuLi as a catalyst. The reaction proceeds rapidly with low catalyst loading (0.1-0.5 mol %) under mild conditions. Key features include the high catalytic efficiency, exceptional functional group compatibility, ample substrate scope and high selectivity for aldehydes over ketones. Computational studies were carried out to provide a mechanistic insight into the *n*-BuLi catalyzed hydroboration of aldehydes/ketones with HBpin.

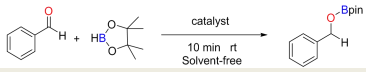


The development of inexpensive and environment-friendly metal catalysts for valuable chemical transformations is of great significance in modern organic synthesis. In contrast to the intense attentions paid to the organic catalytic chemistry driven by precious metals, the application of earth-abundant and biocompatible main group metals is lagged and underdeveloped.[1] Furthermore, the utilization of simple and easily attainable metal catalysts remains limited as the sphere is mostly dominated by complexes stabilized by sterically hindered ligands.[2] In addition, the synthesis of these complexes is cumbersome and labor consuming. Therefore, there is a critical need to develop more efficient and sustainable main group metal based catalysts which could essentially mitigate the environmental concerns and over-exploitation of the less abundant earth elements.

Hydroboration reduction of carbonyl compounds is a vital transformation in organic synthesis as the resultant borates provide an efficient approach to alcohols via hydrolysis.[2a,3] In comparison to the traditional stoichiometric reduction by using light metal hydrides, catalyzed hydroboration of aldehydes and ketones has been realized by means of a vast number of catalysts ranging from transition metals,[1b,c,4-16] main group elements[17-24] as well as lanthanide complexes.[25,26] In most cases, however, these compounds/complexes are either expensive or difficult to be prepared. As noted earlier, studies on the hydroboration reactions driven by simple main group metal catalysts are rather limited. Recently, Zhao's group reported that powder NaOH could catalyze the hydroboration of aldehydes and ketones.[24b] However, the relatively high catalytic demand and the use of deuterated solvents to achieve a better solubility of the powdered alkali hydroxide were obvious drawbacks. During the preparation of this manuscript, Hreczycho's group reported a catalyst- and solvent-free method for the hydroboration of various aldehydes with pinacolborane.[27] Although this scheme was applicable to aldehydes, the ketones were largely ineffective. Besides, a higher temperature was required to get better conversions for aldehyde substrates. Therefore, the development of a general and highly selective hydroboration method based on an easily accessible metal catalyst with great efficiency is desirable to advance the synthetic toolkit. Herein, we report the use of the inexpensive and commercially available *n*-butyllithium (*n*-BuLi) and other lithium anilides as catalysts for the hydroboration of carbonyl compounds with pinacolborane (HBpin). The excellent catalytic performance of *n*-BuLi for the chemoselective hydroboration of aldehydes/ketones was observed. More interestingly, this protocol maintains its high catalytic efficiency when scaled up.

Benzaldehyde and HBpin were initially chosen as model substrates to optimize reaction conditions and the progress was monitored by ^{1}H NMR. The reaction of a 1:1 molar ratio of benzaldehyde and HBpin catalyzed by PhNHLi was carried out at room temperature under neat conditions. A rapid reaction was observed using as little as 0.01 mol % of catalyst loading (Table 1, entry 1). An increase in catalyst loading resulted in a corresponding increase in the yield of product, giving a good yield of 96% with 0.1 mol % of catalyst loading (entries 2 and 3). When a slight excess of HBpin was used relative to benzaldehyde (1:1.1), full conversion was attained (>99%, entry 4). Other lithium compounds such as 2,6-Me_2PhNHLi, 2,6-$^i Pr_2$PhNHLi and *n*-BuLi could also effectively catalyze the hydroboration of benzaldehyde with HBpin (entries 5-7). It was recorded that all lithium anilides and *n*-BuLi exhibited excellent catalytic activity: complete conversions were accomplished under solvent-free condition

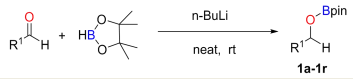
Table 1. Hydroboration of Benzaldehyde Catalyzed by Lithium Anilides and *n*-BuLi[a]

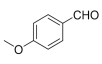
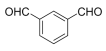
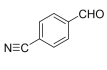
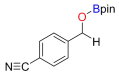
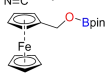


entry	cat. (mol %)	substrate ratio[b]	yield[c] (%)
1	PhNHLi (0.01)	1:1	52
2	PhNHLi (0.05)	1:1	78
3	PhNHLi(0.1)	1:1	96
4	PhNHLi(0.1)	1:1.1	>99
5	2,6-Me_2PhNHLi (0.1)	1:1.1	>99
6	2,6-$^i Pr_2$PhNHLi(0.1)	1:1.1	>99
7	*n*-BuLi (0.1)	1:1.1	>99

[a]Benzaldehyde, HBpin, and lithium compounds at rt. [b]Benzaldehyde, HBpin. [c]Yield was determined by ^{1}H NMR spectroscopy.

Table 2. Hydroboration of Aldehydes Catalyzed by *n*-BuLi[a]



entry	aldehydes	product	cat. (mol %)	t (min)	yields[c] (%)
1			0.1	10	>99
2			0.1	10	>99
3			0.1	10	>99
4			0.1	10	>99
5			0.1	10	>99
6			0.1	10	>99
7			0.1	10	>99
8			0.3 (0.1)	30	>99 (73)
9[b]			0.1	10	>99
10			0.1	10	>99
11			0.1	10	>99
12[d]			0.1	10	>99
13			0.1	10	>99
14			0.1	10	>99
15			0.1	10	>99
16[b]			0.1	10	>99
17[b]			0.1	10	>99
18[b]			0.2	10	>99

[a]Aldehydes (1 mmol), HBpin (1.1 mmol) and *n*-BuLi at rt. [b]THF (0.2 mL) was added as the aldehyde is a solid. [c]Yield of aldehydes based on ^{1}H NMR analysis. [d]HBpin (2.2 mmol) was used.

in 10 min at ambient temperature. Pleasingly, it was observed that these lithium compounds possess comparable catalytic activity to the rare-earth metal catalytic systems.[25] Compared with some known lithium catalysts, the catalytic activity of lithium anilides and *n*-BuLi is found to be better than that of the latest published work,[24d-f] although lower than that of the most active lithium hydridotriphenylborate.[24a] Considering the readily availability and commercial attainability, *n*-BuLi as an ideal catalyst was served for this study.

With the afore-defined reaction conditions in hand, the adaptability of *n*-BuLi with a wide range of aldehydes was explored. As shown in Table 2, almost all of the aldehydes achieved full conversions within 10 min with 0.1 mol % catalyst loading. The presence of halogens had no obvious effect as demonstrated by the clean hydroboration of the *p*-fluoro and *m*-chloro-benzaldehyde substrates (entries 2 and 3). Electron donating aldehydes including *o*-tolualdehyde, *p*-tolualdehyde, 2,4,6-trimethylbenzaldehyde, and *p*-methoxybenzafdehyde all afforded the corresponding borate esters in excellent yields (entries 4-7). Moreover, there was no obvious steric effect with substrates bearing ortho substituents (entries 4 and 6). A higher catalyst loading and longer time were required for the full conversion of cinnamaldehyde and ferrocene carboxaldehyde (entries 8 and 18). Naphthalene-2-carbaldehyde and heterocyclic aldehydes such as 2-acetyl thiophene and 2-pyridinecarboxaldehyde were also compatible with the hydroboration protocol giving full conversions (entries 9-11). Interestingly, an increase in catalyst loading was not required in order to achieve complete conversion for a dialdehyde substrate *m*-phthalaldehyde (entry 12). For aliphatic aldehydes, including cyclic substrate (1-formylcyclohexane), short straight chain (propionaldehyde) and long straight chain (*n*-heptanal), the corresponding borate esters were delivered in excellent yields (entries 13-15). Pleasingly, *n*-BuLi also displayed high chemoselectivity and catalytic efficiency towards the hydroboration of aldehydic substrates containing sensitive unsaturated functional groups such as C=C, C≡C, and C≡N. Notably, these functional groups were left intact after completion of reaction (entries 8, 16 and 17).

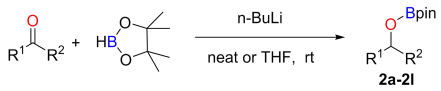
Encouraged by the satisfactory results obtained with aldehydes, the scope was expanded to ketone substrates. As expected, a longer time was required for the hydroboration of ketones compared with aldehydes. This is analogous to previously described methods in which aldehydes were generally more reactive than ketones.[6c,18b,19,20,26] A catalyst loading of 0.1 mol % was sufficient for achieving the full conversions of acetophenone and *p*-fluoroacetophenone in 20 min (Table 3, entries 1 and 2). Similarly, full conversions of most aromatic ketones were achieved within 20 min by employing a catalyst loading of 0.1 mol % (entries 1-9). This showcased better reactivity in comparison with the NaOH catalytic system where the catalyst loading of 5 mol % was required for ketone substrates.[24b] It is worth noting that full conversions were achieved with substrates having either electron-withdrawing or electron-donating substituents such as *p*-F, *p*-Cl, *p*-Br, *p*-NO_2, *p*-CH_3 and *p*-OCH_3 groups. Again, no obvious effect due to steric hindrance was found in this reaction. Furthermore, 3-methyl-2-butanone required 0.2 mol % catalyst loading to achieve full conversion into the corresponding borate ester (entry 10).

In the beginning, the reaction involving 4-aminoacetophenone led to a dehydrogenative byproduct

coupling of the amino group with HBpin.[28] However, by controlling the order of addition of substrates, the complete and favorable formation of the desired borate ester was realized (entry 11). A drug molecule spironolactone was also selectively hydroborated in excellent yield, thus indicating the potential application of the present method in medicinal chemistry (entry 12).

Furthermore, the chemoselective hydroboration of aldehydes over ketones was explored. The reaction of equimolar amounts of benzaldehyde, acetophenone, and HBpin were carried out in the presence of *n*-BuLi (0.1 mol %) under neat conditions at room temperature. This resulted in the preferential conversion of the benzaldehyde into the corresponding boronate ester (96% conversion). A similar trend was also observed with the reactions involving other aldehydes and ketones, but was more pronounced for an aliphatic carbonyl compound where complete selectivity was shown towards the aliphatic aldehyde (Scheme 1a).

Table 3. Hydroboration of Ketones Catalyzed by *n*-BuLi[a]

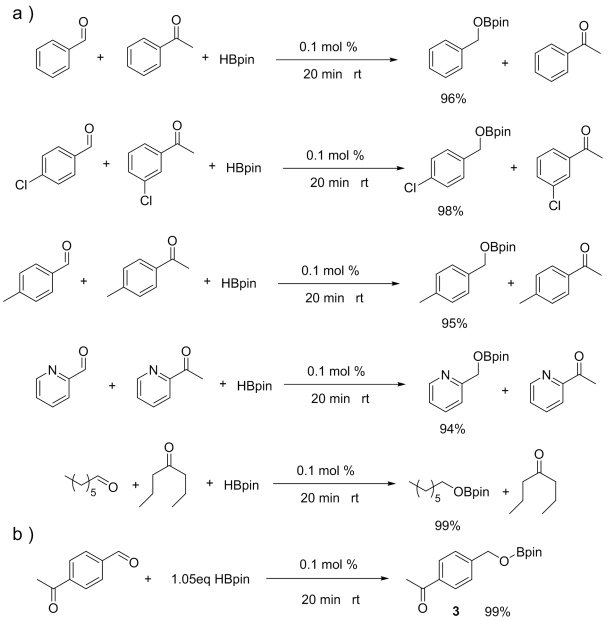


entry	ketones	product	cat. (mol %)	t (min)	yield[c] (%)
1			0.1	20 (10)	>99 (96)
2			0.1	20 (10)	>99 (90)
3			0.1	20	>99
4[b]			0.1	20	>99
5[b]			0.1	20	>99
6			0.1	20	>99
7[b]			0.1	20	>99
8[b]			0.1	20	>99
9			0.1	20	>99
10			0.2	20	>99
11[b]			0.5	20	>99
12[b]			0.5	20	>99

[a]Ketones (1 mmol), pinacolborane (1.1 mmol) and *n*-BuLi at rt. [b]THF (0.2 mL) was added as ketones are solid. [c]Yield of ketones based on ^{1}H NMR analysis.

Importantly, the chemoselectivity towards aldehyde was very noticeable in the hydroboration of 4-acetylbenzaldehyde to give pure 2-(1-(4-acetylphenyl)ethoxy)pinacol borane in a yield of 99% (Scheme 1b).

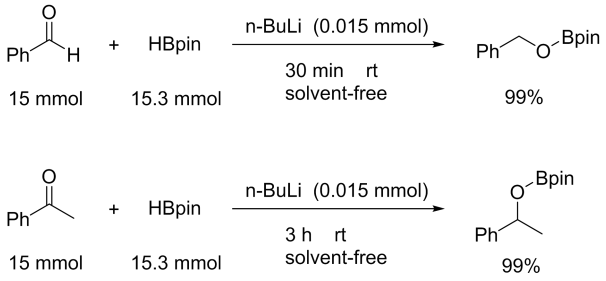
Scheme 1. Chemoselective Hydroboration of Aldehydes Catalyzed by *n*-BuLi



Both hydroboration reactions of benzaldehyde and acetophenone with HBpin (1:1.02) catalyzed by 0.1 mol % of *n*-BuLi under neat conditions were carried out, respectively, on a large scale. Remarkably, complete conversions were obtained in both cases giving 99% yields (Scheme 2).

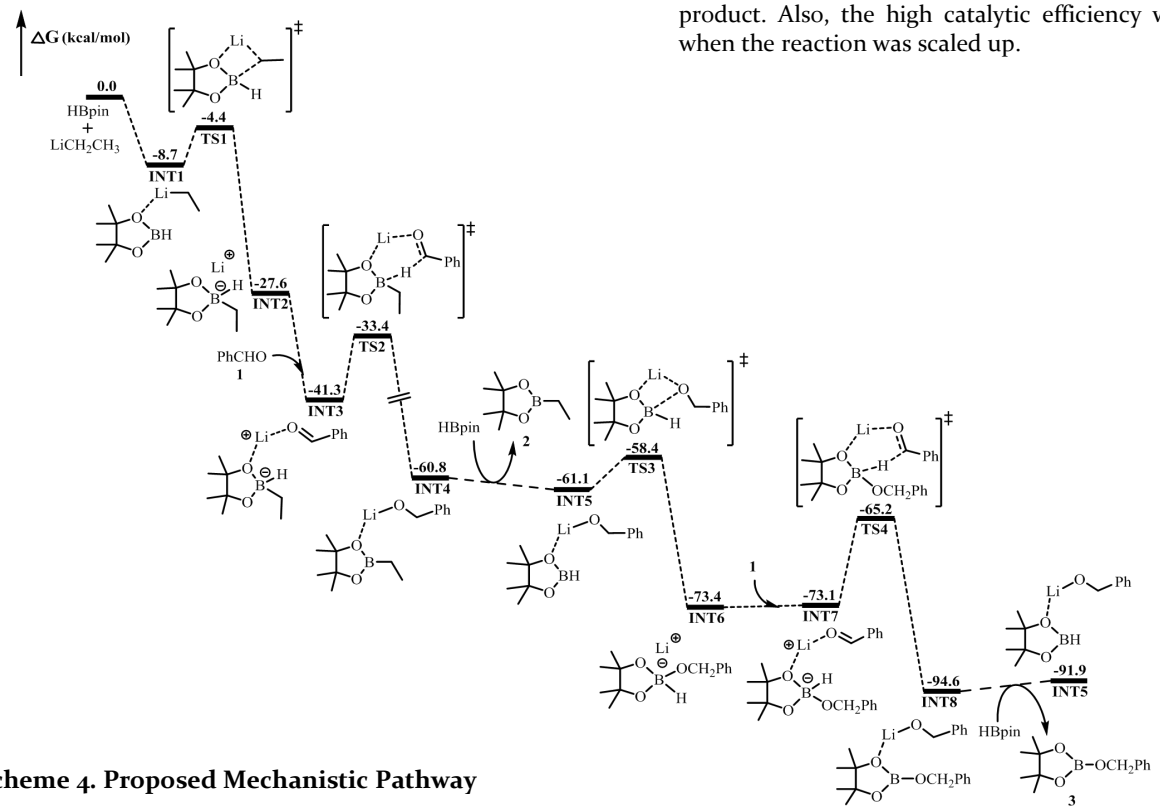
Computational studies were carried out to explore a mechanistic understanding of the *n*-BuLi catalyzed

Scheme 2. Large-scale Reaction of Benzaldehyde/Acetophenone with HBpin

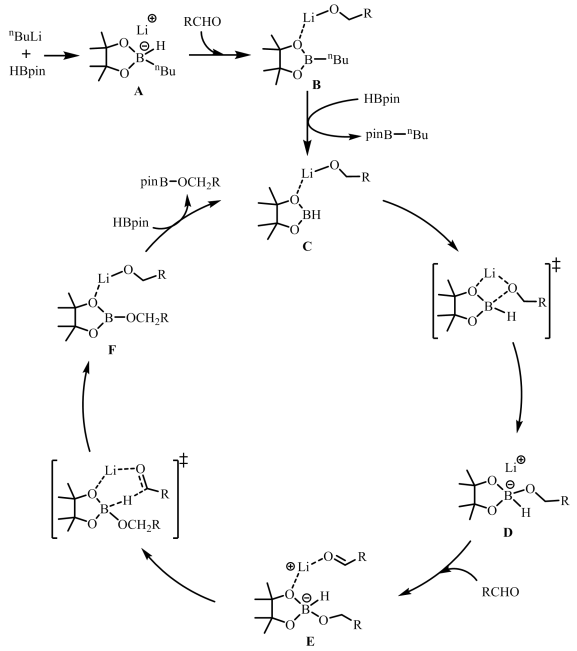


hydroboration of aldehydes with HBpin.[29] Initially, the lithium atom of the catalyst could bind with an oxygen atom of HBpin to form a complex **INT1** (Scheme 3). Subsequently, the alkyl group of the catalyst may attack HBpin to afford the zwitterionic intermediate **INT2** via **TS1**. Next, **INT2** could bind with substrate benzaldehyde to form a complex **INT3**, from which the hydride migration to the carbonyl carbon could occur to yield the intermediate **INT4**.[30] After a ligand exchange step with HBpin, the alkoxy group in the formed intermediate **INT5** could nucleophilically attack the HBpin to generate the zwitterionic intermediate **INT6**. Similarly, another molecule of benzaldehyde could bind with **INT6** to give **INT7**, and a hydride transfer to the carbonyl carbon could follow to form the intermediate **INT8**. Thus, the final product would be obtained after a ligand exchange step with

Scheme 3. Energy Profiles (in kcal/mol) for the *n*-BuLi Catalyzed Hydroboration of PhCHO with HBpin.



Scheme 4. Proposed Mechanistic Pathway



HBpin and the yieled **INT5** is ready for the next catalytic cycle. According to the DFT study, a possible mechanistic pathway is proposed in Scheme 4.

In conclusion, the use of simple *n*-BuLi as an efficient catalyst for the selective hydroboration of aldehydes and ketones is described for the first time. Notable features encompass high catalytic efficiency with low catalyst loading under mild conditions, a wide range of substrates, excellent chemical selectivity, good functional group tolerance, solvent-free, and a controllable manner to obtain full conversion of an amino-containing substrate into target product. Also, the high catalytic efficiency was maintained when the reaction was scaled up.

EXPERIMENTAL SECTION

General Information

All reactions were performed in a glove box under nitrogen-atmosphere. $CDCl_3$ was purchased from TCI chemicals and stored over activated 4Å molecular sieves. HBpin was purchased from Accela and used without further purification. All the liquid ketones and aldehydes were distilled, dried over CaH_2 and degassed prior to use. All the solid ketones and aldehydes were degassed prior to use. ^1H, ^{13}C and ^{11}B spectra were recorded on Bruker AV-400 (^1H: 400 MHz, ^{13}C: 101 MHz, ^{11}B: 128 MHz). NMR chemical shifts were reported in ppm with respect to tetramethylsilane.

General Procedure for the Hydroboration of Aldehydes/Ketones Catalyzed by *n*-BuLi

Aldehyde/ketone (1 mmol, THF (200 ul) for solid substrates), HBpin (1.1 mmol) and a stock solution containing *n*-BuLi (0.05 M) were injected into a pre-dried vial equipped with a magnetic bar. The resultant mixture was stirred at room temperature and the reaction progress was monitored by ^1H NMR. For aldehydes, the disappearance of aldehydic proton signal and appearance of a new -CH_2- proton signal indicate completion of reaction. For ketones, the completion of the reaction was indicated by the appearance of a new -CH- proton signal. After completion of reaction, the solvent and excess HBpin were removed from the mixture by vacuum drying in an oven to afford the corresponding boronate ester without further purification (Note: the catalytic

hydroboration of carbonyl compounds by *n*-BuLi is an exothermic reaction. Large-scale reactions should be carried out under cooling in an ice bath, and *n*-BuLi should be added in a slow dropwise manner).

Spectral Data for Boronate Esters

*2-(benzyloxy)pinacolborane (**1a**).*[25a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.23 (m, 5H, Ar-H), 4.92 (s, 2H, OCH_2), 1.26 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8 (Ar-C), 127.8 (Ar-C), 126.9 (Ar-C), 126.2 (Ar-C), 82.5 (OC), 66.2 (OCH_2), 24.1 (CH_3).

*2-(4-fluorobenzyloxy)pinacolborane (**1b**).*[25b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H, Ar-H), 7.04-6.98 (m, 2H, Ar-H), 4.87 (s, 2H, OCH2), 1.26 (s, 12H, CH3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (ds, Ar-C), 134.5 (d, *J* = 3.2 Hz, Ar-C), 128.1 (d, *J* = 8.1 Hz, Ar-C), 114.6 (ds, Ar-C), 82.5 (OC), 65.6 (OCH_2), 24.1 (CH_3).

*2-(3-chlorobenzyloxy)pinacolborane (**1c**).*[25b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H, Ar-H), 7.28-7.19 (m, 3H, Ar-H), 4.89 (s, 2H, OCH_2), 1.27 (s, 12H,CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (Ar-C), 133.7 (Ar-C), 129.1 (Ar-C), 127.0 (Ar-C), 126.3 (Ar-C), 124.2 (Ar-C), 82.6 (OC), 65.4 (OCH_2), 24.1 (CH_3).

*2-((2-methylbenzyl)oxy)pinacolborane (**1d**).*[26a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dq, *J* = 7.2, 3.6 Hz, 1H,Ar-H), 7.18-7.11 (m, 3H, Ar-H), 4.92 (s, 2H, OCH_2), 2.30 (s, 3H, Ar-CH_3), 1.26 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7 (Ar-C), 135.1 (Ar-C), 129.5 (Ar-C), 126.9 (d, *J* = 25.25, Ar-C), 125.4 (Ar-C), 82.4 (OC), 64.5 (OCH_2), 24.2 (CH_3), 18.2 (CH_3).

*2-((4-methylbenzyl)oxy)pinacolborane (**1e**).*[25b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.22 (m, 2H,Ar-H), 7.13-7.11 (m, 2H, Ar-H), 4.87 (s, 2H, OCH_2), 2.32 (s, 3H, Ar-CH_3), 1.24 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5 (Ar-C), 135.8 (Ar-C), 128.5 (Ar-C), 126.4 (Ar-C), 82.4 (OC), 66.1 (OCH_2), 24.1 (CH_3), 20.7 (CH_3).

*2-(mesitylmethoxy)pinacolborane (**1f**).*[25a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H,Ar-H), 4.96 (s, 2H, OCH_2), 2.38 (s, 6H, Ar-CH_3), 2.25 (s, 3H, Ar-CH_3), 1.26 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2 (Ar-C), 137.1 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 82.3 (OC), 60.7 (OCH_2), 24.1 (CH_3), 20.5 (CH_3), 18.9 (CH_3).

*2-(4-methoxybenzyloxy)pinacolborane (**1g**).*[25b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H,Ar-H), 6.87-6.84 (m, 2H, Ar-H), 4.84 (s, 2H, OCH_2), 3.78 (s, 3H, Ar-CH_3), 1.21 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (Ar-C), 131.0 (Ar-C), 128.0 (Ar-C), 113.2 (Ar-C), 82.4 (OC), 65.9 (OCH_2), 54.7 (OCH_3), 24.1 (CH_3).

*2-(cinnamyloxy)pinacolborane (**1h**).*[25a] Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H, Ar-H), 7.29 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.24-7.20 (m, 1H, Ar-H), 6.62 (d, *J* = 15.9 Hz, 1H, CH), 6.28 (dt, *J* = 15.9, 5.3 Hz, 1H, CH), 4.52 (s, 2H, OCH_2), 1.26 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4 (CH), 130.1 (Ar-C), 128.0 (Ar-C), 127.0 (Ar-C), 126.3 (Ar-C), 126.0 (CH), 82.4 (OC), 64.8 (OCH_2), 24.2 (CH_3).

*2-(2-naphthylmethoxy)pinacolborane (**1i**).*[18b] White solid; mp 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H, Ar-H), 7.49-7.44 (m, 2H, Ar-H), 5.10 (s, 2H, OCH_2), 1.29 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (Ar-C), 132.9 (Ar-C), 132.3 (Ar-C), 127.5 (Ar-C), 127.4 (Ar-C), 127.2 (Ar-C), 125.5 (Ar-C), 125.2 (Ar-C), 124.7 (Ar-C), 124.4 (Ar-C), 82.6 (OC), 66.3 (OCH_2), 24.2 (CH_3).

*2-(pyridine)pinacolborane (**1j**).*[27] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.4 Hz, 1H, Ar-H), 7.91 (t, *J* = 7.7 Hz, 1H, Ar-H), 7.49-7.41 (m, 2H, Ar-H), 5.10 (s, 2H, OCH_2), 1.32 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (Ar-C), 143.7 (Ar-C), 139.6 (Ar-C), 123.4 (Ar-C), 120.1 (Ar-C), 81.0 (OC), 66.5 (OCH_2), 25.5 (CH_3).

*2-(thiophen)pinacolborane (**1k**).*[25b] Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 4.3 Hz, 1H, Ar-H), 7.02-6.94 (m, 2H, Ar-H), 5.04 (s, 2H, OCH_2), 1.27 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (Ar-C), 126.6 (Ar-C), 125.9 (Ar-C), 125.5 (Ar-C), 83.1 (OC), 61.6 (OCH_2), 24.6 (CH_3).

*2-(benzyloxy)dipinacolborane (**1l**).*[4] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 4H, Ar-H), 4.91 (s, 4H, OCH_2), 1.26 (s, 24H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8 (Ar-C), 127.8 (Ar-C), 125.3 (Ar-C), 124.6 (Ar-C), 82.5 (OC), 66.1 (OCH_2), 24.1 (CH_3).

*2-(cyclohexylmethoxy)pinacolborane (**1m**).*[25a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (d, *J* = 6.4 Hz, 2H, OCH_2), 1.57-1.47 (m, 6H, C_6H_{11}), 1.57-1.47 (m, 1H, C_6H_{11}), 1.25 (s, 12H, CH_3), 1.18-1.11 (m, 2H, C), 0.99-0.87 (m, 2H, C_6H_{11}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.0 (OC), 69.8 (OCH_2), 38.8, 28.8, 26.0, 25.2 (C_6), 24.0 (CH_3).

*2-(ethylmethoxy)pinacolborane (**1n**).*[25a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (t, *J* = 6.6 Hz, 2H, OCH_2), 1.63-1.54 (m, 2H, CH_2), 1.25 (s, 12H, CH_3), 0.91 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.0 (OC), 66.0 (OCH_2), 24.1 (CH_3CH_2), 24.1 (CH_3), 9.6 (CH_2CH_3).

*2-(hexylmethoxy)pinacolborane (**1o**).*[26c] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (t, *J* = 8 Hz, 2H, OCH_2), 1.52-1.58 (m, 2H, CH_2), 1.27-1.34 (m, 8H, CH_2), 1.24 (s, 12H, CH_3), 0.87 (t, *J* = 8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.0 (OC), 64.4 (OCH_2), 31.3 (CH_2), 30.9 (CH_2), 28.4 (CH_2), 25.0 (CH_2), 24.0 (CH_3), 22.1 (CH_2), 13.5 (CH_3).

*2-(2-ethynylbenzyloxy)pinacolborane (**1p**).*[25a] Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 19.8, 7.6 Hz, 2H, Ar-H), 7.35 (m, 1H, Ar-H), 7.23 (dd, *J* = 15.9, 8.4 Hz, 1H, Ar-H), 5.12 (s, 2H, OCH_2), 3.30 (s, 1H, CH), 1.27 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 (Ar-C), 131.9 (Ar-C), 128.5 (Ar-C), 126.4 (Ar-C), 125.6 (Ar-C), 119.0 (Ar-C), 82.5 (OC), 81.7 (CHC), 80.4 (CCH), 64.4 (OCH_2), 24.1 (CH_3).

*2-(4-cyanobenzyloxy)pinacolborane (**1q**).*[25a] White solid; mp 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H, Ar-H), 7.46-7.44 (m, 2H, Ar-H), 4.98 (s, 2H, OCH_2), 1.27 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (Ar-C), 131.6 (Ar-C), 126.3 (Ar-C), 118.3 (NC), 110.6 (Ar-C), 82.8 (OC), 65.2 (OCH_2), 24.1 (CH_3).

*2-(ferrocenylmethoxy)pinacolborane (**1r**).*[25a] Brown solid; mp 70-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 3H, Cp-H), 4.24 (s, 2H, OCH_2), 4.14-4.11 (m, 5H, Cp-H), 1.26 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.9 (OC), 82.3, 67.9, 67.7, 62.7 (Cp-C), 24.2 (CH_3).

*2-(phenylethoxy)pinacolborane (**2a**).*[25a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 5H, Ar-H), 5.24 (q, *J* = 6.5 Hz, 1H, OCH), 1.49 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (d, *J* = 11.9 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (Ar-C), 127.7 (Ar-C), 126.6 (Ar-C), 124.9 (Ar-C), 82.3 (OC), 72.1 (OCH), 25.0 (CH_3), 24.0 (d, *J* = 4.5 Hz, CH_3).

*2-(1-(4-fluorophenyl)ethoxy)pinacolborane (**2b**).*[26a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H, Ar-H), 7.02-6.96 (m, 2H, Ar-H), 5.22 (q, *J* = 6.4 Hz, 1H, OCH), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (d, *J* = 11.6 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (ds, Ar-C), 140.3 (d, *J* = 3.1 Hz, Ar-C), 127.0 (d, *J* = 8.0 Hz, Ar-C), 114.9 (ds, Ar-C), 82.8 (OC), 72.0 (OCH), 25.4 (CH_3), 24.5 (d, *J* = 6.1 Hz, CH_3).

*2-(1-(4-chlorophenyl)ethoxy)pinacolborane (**2c**).*[26a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H, Ar-H), 5.21 (q, *J* = 6.4 Hz, 1H, OCH), 1.46 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (d, *J* = 11.6 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (Ar-C), 132.3 (Ar-C), 127.8 (Ar-C), 126.3 (ds, Ar-C), 82.4 (OC), 71.4 (OCH), 24.9 (CH_3), 24.0 (d, *J* = 4.7 Hz, CH_3).

*2-(1-(4-bromophenyl)ethoxy)pinacolborane (**2d**).*[4] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H, Ar-H), 7.26-7.23 (m, 2H, Ar-H), 5.19 (q, *J* = 6.4 Hz, 1H, OCH), 1.46 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (d, *J* = 11.3 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (Ar-C), 130.8 (Ar-C), 126.7 (Ar-C), 120.4 (Ar-C), 82.4 (OC), 71.5 (OCH), 24.9 (CH_3), 24.0 (d, *J* = 4.4 Hz, CH_3).

*2-(1-(4-nitrophenyl)ethoxy)pinacolborane (**2e**).*[25a] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.18 (m, 2H, Ar-H), 7.55-7.52 (m, 2H, CH_3), 5.33 (q, *J* = 6.5 Hz, 1H, OCH), 1.51 (d, *J* = 6.5 Hz, 3H, CH_3), 1.24 (d, *J* = 12.7 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4 (Ar-C), 146.6 (Ar-C), 125.6 (Ar-C), 123.1 (Ar-C), 82.6 (OC), 71.3 (OCH), 24.8 (CH_3), 24.0 (d, *J* = 1.1 Hz, CH_3).

*2-(1-(4-methylphenyl)ethoxy)pinacolborane (**2f**).*[19] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 2H, Ar-H), 7.11-7.13 (m, 2H, Ar-H), 5.21 (q, *J* = 6.4 Hz, 1H, OCH), 2.32 (s, 3H, Ar-CH_3), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (d, *J* = 10.4 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 (Ar-C), 136.2 (Ar-C), 128.4 (Ar-C), 124.8 (Ar-C), 82.2 (OC), 72.0 (OCH), 25.0 (CH_3), 24.1 (d, *J* = 3.7 Hz, CH_3), 20.6 (s, Ar-CH_3).

*2-(1-(4-methoxyphenyl)ethoxy)pinacolborane (**2g**).*[19] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H, Ar-H), 6.86-6.83 (m, 2H, Ar-H), 5.20 (q, *J* = 6.4 Hz, 1H, OCH), 3.77 (s, 3H, OCH_3), 1.47 (d, *J* = 6.4 Hz, 3H, CH_3), 1.22 (d, *J* = 10.4 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (Ar-C), 136.3 (Ar-C), 126.1 (Ar-C), 113.1 (Ar-C), 82.2 (OC), 71.7 (OCH), 54.7 (OCH_3), 24.8 (s, CH_3), 24.0 (d, *J* = 6.2 Hz, CH_3).

*2-(diphenylmethoxy)pinacolborane (**2h**).*[25a] White solid; mp 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.20 (m, 10H, Ar-C), 6.17 (s, 1H, OCH), 1.19 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (Ar-C), 128.2 (Ar-C), 127.3 (Ar-C), 126.5 (Ar-C), 83.0 (OC), 77.9 (OCH), 24.5 (CH_3).

*2-(1-(thiophen-2-yl)ethoxy)pinacolborane (**2i**).*[26a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.18 (m, 1H, Ar-H), 6.97-6.91 (m, 2H, Ar-H), 5.48 (q, *J* = 6.4 Hz, 1H, OCH), 1.60 (d, *J* = 6.4 Hz, 3H, CH_3), 1.24 (d, *J* = 4.9 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7 (Ar-C), 125.9 (Ar-C), 123.6 (Ar-C), 122.8 (Ar-C), 82.4 (OC), 68.1 (OCH), 24.6 (CH_3), 24.0 (d, *J* = 9.8 Hz, CH_3).

*2-(isopropylethoxy)pinacolborane (**2j**).*[19] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (p, *J* = 6.2 Hz, 1H, OCH), 1.66 (dq, *J* = 13.5, 6.8 Hz, 1H, CH_3CH), 1.25 (s, 12H, CH_3), 1.14 (d, *J* = 6.3 Hz, 3H, CH_3), 0.91-0.85 (m, 6H, $CHCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.3 (OC), 75.4 (OCH), 34.2 (OCHCH), 24.5 (d, *J* = 7.4 Hz, CH_3), 19.3 (CH_3), 18.1 (CH_3), 17.7 (CH_3).

*2-(1-(4-aminophenyl)ethoxy)pinacolborane (**2k**).*[19] At the outset, 4-aminoacetophenone (1 mmol, THF (200 ul)) and a stock solution containing *n*-BuLi (0.05 M) were injected into a pre-dried vial equipped with a magnetic bar. Then, the resultant mixture was stirred at room temperature followed by the slow addition of HBpin (1.1 mmol). The reaction progress was monitored by ^{1}H NMR. After completion of reaction, the solvent and excess HBpin were removed from the mixture by vacuum drying in an oven to afford the corresponding boronate ester without further purification as a yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H, Ar-H), 6.63-6.61 (m, 2H, Ar-H), 5.14 (q, *J* = 6.4 Hz, 1H, OCH), 3.62 (s, 2H, NH_2), 1.45 (d, *J* = 6.4 Hz, 3H, CH_3), 1.22 (d, *J* = 9.2 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (Ar-C), 134.2 (Ar-C), 126.1 (Ar-C), 114.3 (Ar-C), 82.1 (OC), 71.9 (OCH), 24.7 (CH_3), 24.0 (d, *J* = 7.1 Hz, CH_3); ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.15.

*2-(spironolactone)pinacolborane (**2l**).*[24b] White solid; mp 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (d, *J* = 8.9 Hz, 1H), 4.60-4.56 (m, 1H), 3.92-3.88 (m, 1H), 2.69-2.65 (m, 1H), 2.58-2.45 (m, 2H), 2.43-2.34 (m, 1H), 2.33 (s, 3H), 2.18 (ddd, *J* = 10.6, 9.1, 3.1 Hz, 1H), 2.07 (dd, *J* = 14.3, 2.6 Hz, 1H), 1.96-1.88 (m, 3H), 1.81-1.69 (m, 3H), 1.61-1.49 (m, 4H), 1.44-1.29 (m, 4H), 1.25 (s, 12H), 1.08 (s, 3H), 0.95 (s, 3H), 0.78 (td, *J* = 11.7, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3 (s), 176.2 (s), 141.3 (s), 125.9 (s), 95.3 (s), 82.1 (s), 69.4 (s), 67.4 (s), 49.2 (s), 45.5, 45.4, 45.0 (s), 38.6 (s), 36.6 (s), 34.7 (s), 34.5 (s), 30.8, 30.7, 28.7 (s), 26.9 (s), 25.1 (s), 24.0 (d, *J* = 13.8 Hz), 21.9 (s), 19.8 (s), 18.4 (s), 14.0 (s); ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.09.

*2-(1-(4-acetylphenyl)ethoxy)pinacolborane (**3**).*[4] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.43 (d, *J* = 8.3 Hz, 2H, Ar-H), 4.99 (s, 2H, OCH_2), 2.59 (s, 3H, $COCH_3$), 1.27 (s, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3 (Ar-CO), 144.1 (Ar-C), 135.7 (Ar-C), 127.9 (Ar-C), 125.9 (Ar-C), 82.7 (OC), 65.5 (OCH_2), 26.1 ($COCH_3$), 24.1 (CH_3); ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.44.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copies of NMR spectra for all the compounds; DFT computational methods (PDF)

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Notes

The authors declare no competing financial interest.

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（29）See SI for computational details. In order to reduce the computational cost, the *n*-butyl group in the *n*-BuLi catalyst was replaced by the ethyl group.

（30）One may wonder if the alkoxy group in **INT4** could nucleophilically attack the boron site via **TS5** to afford the zwitterionic intermediate **INT9**, from which the desired product would be afforded and the catalyst is regenerated via **TS6** (Figure S1). Although the formation of **INT9** is not difficult, the subsequent conversion from **INT9** to the final product has a significantly high energy barrier, suggesting the pathway via **INT9** is not favorable.