Supporting Information

Regioselective 1, 2-Hydroboration of N-Heteroarenes by Potassium-Based Catalyst

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1. Materials, Reagents, and Methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or an argon-filled glovebox. THF and hexane were refluxed over sodium/potassium alloy distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. Benzene-$d_6$ and THF-$d_8$ were dried over molecular sieves 4 Å. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, $^1$H; 126 MHz, $^{13}$C; 471 MHz, $^{19}$F; 160 MHz, $^{11}$B) instrument at room temperature (RT). Chemical shifts for $^1$H and $^{13}$C spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe$_4$, whereas $^{19}$F NMR spectra were referenced to external CFCl$_3$. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes. It should be noted that all new compounds reported in the manuscript were characterized by $^1$H, $^{13}$C, and $^{11}$B NMR spectroscopy without HRMS or elemental analyses, due to their extreme sensitivity to air and moisture.

Quinoline, 2-methylquinoline, 3-methylquinoline, 4-methylquinoline, 5-methylquinoline, 6-methylquinoline, 7-methylquinoline, 8-methylquinoline, 5-bromoquinoline, 6-bromoquinoline, 6-fluoroquinoline, 6-chloroquinoline, pyridine, 3-methylpyridine, 3-ethylpyridine, 3-bromopyridine, 4-methylpyridine isoquinoline, quinoxaline, Pyrimidine, acridine and Pinacolborane (HBpin) were purchased from Energy Chemical, potassium hydride and potassium tert-butanol were purchased from J&K, it is note that potassium hydride was 30 wt % dispersion in mineral oil, use dry hexane wash off the mineral oil and then dried in vacuo to afford pure KH. All chemicals were used as received unless otherwise specified.
General procedures for hydroboration of N-heteroarenes

In a glove box, 'BuOK (5 mol%) or KH (10 mmol%) was added to a solution containing quinoline (0.1 mmol) in 0.5 mL C₆D₆ and 0.15 mL THF in a J. Young type NMR tube. Then, pinacolborane HBpin (0.2 mmol) was added to the resulting mixture. After taken out of the glovebox and heated at 50 °C for specified time, it was measured by NMR spectroscopy. The reaction mixture was concentrated under vacuum and the solid was obtained after crystallization, followed by dried in vacuo.

General procedures for the hydroboration of pyridine

In a glove box, KH (0.05 mmol) was added to a 2 mL THF solution of pyridine (0.5 mmol) in 10 mL flask. Then, the pinacolborane HBpin (0.55 mmol) was added to the resulting mixture. After taken out of the glovebox and heated at 100 °C for specified time, it was measured by NMR spectroscopy. The reaction mixture was concentrated under vacuum and the solid was obtained after crystallization, followed by dried in vacuo.

2. Characterization data

![Chemical Structure](image)

1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4a): white solid. ¹H NMR (500 MHz, C₆D₆) δ 7.82 (d, J = 10 Hz, 1H, H₄), 7.08 (td, J₁ = 9 Hz, J₂ = 5 Hz, 1H, H₃), 6.84 (dd, J₁ = 7.5 Hz, J₂ = 1.5 Hz, 1H, H₅), 6.79 (td, J₁ = 7.5 Hz, J₂ = 0.5 Hz, 1H, H₆), 6.25 (d, J₁ = 10 Hz, 1H, H₇), 5.55-5.59 (m, 1H, H₈), 4.17 (dd, J₁ = 4 Hz, J₂ = 1.5 Hz, 2H, CH₂), 1.04 (s, 12H, CH₃). ¹³C NMR (126 MHz, C₆D₆) δ 141.9, 127.8, 126.7, 126.6, 124.2, 121.6, 120.9, 82.5, 43.3, 24.3. ¹¹B NMR (160 MHz, C₆D₆) δ 23.9.
3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4c): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.88 (d, $J = 10$ Hz, 1H, H$_{Ar}$), 7.10 (td, $J_1 = 13$ Hz, $J_2 = 1.5$ Hz, 1H, H$_{Ar}$), δ 6.88 (dd, $J_1 = 7.5$ Hz, $J_2 = 2$ Hz, 1H, H$_{Ar}$), 6.84 (td, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H, H$_{Ar}$), 6.01 (s, 1H, H$_{Ar}$), 2.28 (s, 2H, CH$_2$), 1.49 (s, 3H, CH$_3$), 1.05 (s, 12H, CH$_3$), $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 140.3, 133.7, 127.4, 127.0, 125.8, 121.7, 120.4, 82.5, 48.0, 24.4, 20.1. $^{11}$B NMR (160 MHz, C$_6$D$_6$): δ 24.1.

4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4d): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.85 (d, $J = 10$ Hz, 1H, H$_{Ar}$), 7.14 (m, 1H, H$_{Ar}$), 6.86 (t, $J = 7.5$ Hz, 1H, H$_{Ar}$), 5.43 (s, 1H, H$_{Ar}$), 4.13 (d, $J = 2.0$ Hz, 2H, CH$_2$), 1.80 (s, 1H, CH$_3$), 1.05 (s, 12H, CH$_3$), $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 142.1, 131.3, 128.5, 127.6, 123.4, 121.4, 121.3, 121.0, 82.4, 43.1, 24.4, 18.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 23.9.

5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4e): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.71 (d, $J = 10$ Hz, 1H, H$_{Ar}$), 7.04 (t, $J = 10$ Hz, 1H, H$_{Ar}$), 6.68 (d, $J = 7.5$ Hz, 1H, H$_{Ar}$), 5.67-5.71 (m, 1H, H$_{Ar}$), 4.12 (dd, $J_1 = 4.5$ Hz, $J_2 = 1.5$ Hz, 2H, CH$_2$), 2.08 (s, 3H, CH$_3$), 1.05 (s, 12H, CH$_3$), $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 142.0, 132.3, 127.3, 124.1, 123.5, 123.5, 119.3, 82.4, 42.6, 24.4, 18.7. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 23.9.

6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4f): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.75 (d, $J = 8.5$ Hz, 1H, H$_{Ar}$), 6.93 (d, $J = 8.0$ Hz, 1H, H$_{Ar}$), 6.27 (d, $J = 9.5$ Hz, 1H, H$_{Ar}$), 5.60-5.63 (m, 1H, H$_{Ar}$), 4.18 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.5$ Hz, 2H, CH$_2$), 2.01 (s, 3H, CH$_3$), 1.05 (s,
7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4g): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.64 (s, 1H, H$_{Ar}$), 6.81 (d, $J = 7.5$ Hz, 1H, H$_{Ar}$), 6.65 (d, $J = 7.5$ Hz, 1H, H$_{Ar}$), 6.30 (d, $J = 9.5$ Hz, 1H, H$_{Ar}$), 5.56-5.60 (m, 1H, H$_{Ar}$), 4.18 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.5$ Hz, 1H, CH$_2$), 2.19 (s, 3H, CH$_3$), 1.05 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 141.9, 137.3, 126.6, 126.5, 124.4, 123.2, 122.4, 121.6, 82.4, 43.3, 24.3, 21.5. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 24.0.

5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4j): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.53 (d, $J = 9.0$ Hz, 1H, H$_{Ar}$), 7.17 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz, 1H, H$_{Ar}$), 6.95 (d, $J = 10.0$ Hz, 1H, H$_{Ar}$), 5.43-5.47 (m, 1H, H$_{Ar}$), 4.03 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.5$ Hz, 2H, CH$_2$), 1.00 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 143.7, 128.3, 126.3, 126.1, 125.6, 125.4, 120.3, 121.9, 82.7, 42.7, 24.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 23.8.

6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4k): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.60 (m, 1H, H$_{Ar}$), 6.70 (td, $J_1 = 9.0$ Hz, $J_2 = 3.0$ Hz, 1H, H$_{Ar}$), 6.52 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.5$ Hz, 1H, H$_{Ar}$), 6.00 (d, $J = 9.5$ Hz, 1H, H$_{Ar}$), 5.51-5.54 (m, 1H, H$_{Ar}$), 2.26 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.5$ Hz, 1H, CH$_2$), 1.02 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 125.8, 125.8, 121.9, 121.9, 113.9, 113.7, 112.7, 112.5, 82.6, 43.2, 24.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 23.9.

$^{19}$F NMR (471 MHz, C$_6$D$_6$) δ -122.69.
6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4i): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 7.59 (d, $J = 9.0$ Hz, 1H, H$_{Ar}$), 7.03 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz, 1H, H$_{Ar}$), 6.80 (d, $J = 2.5$ Hz, 1H, H$_{Ar}$), 5.45-5.49 (m, 1H, H$_{Ar}$), 4.04 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.5$ Hz, 1H, CH$_2$), 1.01 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 140.1, 128.0, 127.4, 126.4, 126.1, 125.1, 125.5, 122.0, 82.7, 43.2, 24.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) $\delta$ 23.8.

6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4m): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 7.53 (d, $J = 8.5$ Hz, 1H, H$_{Ar}$), 7.17 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.5$ Hz, 1H, H$_{Ar}$), 6.94 (d, $J = 2.5$ Hz, 1H, H$_{Ar}$), 5.94 (d, $J = 9.5$ Hz, 1H, H$_{Ar}$), 5.43-5.47 (m, 1H, H$_{Ar}$), 4.03 (dd, $J_1 = 4.0$ Hz, $J_2 = 2.0$ Hz, 1H, CH$_2$), 1.01 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 140.8, 130.4, 129.1, 128.5, 125.4, 113.9, 82.7, 43.1, 24.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) $\delta$ 23.8.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (6): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 7.00 (t, $J = 7.5$ Hz, 1H, H$_{Ar}$), 6.87 (t, $J = 7.5$ Hz, 1H, H$_{Ar}$), 6.85 (d, $J = 7.5$ Hz, 1H, H$_{Ar}$), 6.81 (d, $J = 7.5$ Hz, 1H, H$_{Ar}$), 6.53 (d, $J = 7.5$ Hz, 1H, H$_{Ar}$), 4.64 (s, 2H, CH$_2$), 1.02 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 132.2, 132.5, 128.6, 127.2, 127.2, 123.4, 105.9, 83.0, 50.2, 24.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) $\delta$ 23.8.

1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (7): white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 8.13-8.16 (m, 2H, H$_{Ar}$), 6.95-6.98 (m, 2H, H$_{Ar}$), 3.61 (s, 4H, CH$_2$), 1.05 (s, 24H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 132.9,
121.2, 120.8, 82.3, 43.9, 24.3. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 24.1.

1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (8): colorless oil. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 6.82 (dt, $J_1$ = 8.0 Hz, $J_2$ = 2.0 Hz, 1H, H$_{Ar}$), 4.82 (s, 2H, CH$_2$), 4.63-4.66 (m, 1H, H$_{Ar}$), 3.81-3.82 (m, 2H, CH$_2$), 1.06 (s, 12H, CH$_3$), 1.01 (s, 12H, CH$_3$).

$^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 129.3, 102.2, 82.5, 82.0, 55.8, 41.8, 24.5.

$^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 23.9.

10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9,9a,10-tetrahydroacridine (9) white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.15-7.18 (m, 2H, H$_{Ar}$), 6.93-7.01 (m, 4H, H$_{Ar}$), 3.55 (s, 2H, CH$_2$), 1.06 (s, 12H, CH$_3$), $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 129.3, 102.2, 82.5, 82.0, 55.8, 41.8, 24.5. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 25.0.

1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10r) white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 6.55 (m, 2H), 4.57 (m, 2H), 2.81 (m, 2H, CH$_3$), 0.96 (s, 12H, CH$_3$), $^{13}$C NMR (126 MHz, C$_6$D$_6$). $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 23.0.

3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10s) white solid. $^1$H NMR (500 MHz, C$_6$D$_6$) δ 6.63 (m, 1H), 6.42 (m, 1H), 4.67 (m, 1H), 2.73 (m, 2H, CH$_2$), 1.41 (s, 3H, CH$_3$), 1.00 (s, 12H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 126.6, 121.8, 110.4, 101.7, 82.9, 28.0, 24.2, 20.4. $^{11}$B NMR (160 MHz, C$_6$D$_6$) δ 24.1.
3-ethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (101) colorless oil. $^1$H NMR (500MHz, C$_6$D$_6$) $\delta$ 6.64 (m, 1H), 6.46 (m, 1H), 4.70 (m, 1H), 2.77 (m, 2H, CH$_2$), 1.77 (m, 2H, CH$_2$), 1.00 (s, 12H, CH$_3$), 0.88 (t, $J$ = 7.5 Hz, 3H, CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 126.8, 120.9, 115.9, 101.9, 82.9, 28.0, 26.0, 24.3, 11.4. $^{11}$B NMR (160 MHz, C$_6$D$_6$) $\delta$ 24.1.

3. Table S1 Optimization of Reaction Conditions$^a$

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$^a$ Conditions: quinoline 1a (0.1 mmol), HBpin (0.2 mmol), KH (10 mol%) for 24 h. $^b$ Conversion and product yields were determined by $^1$H NMR analysis. $^c$ 0.5 mL C$_6$D$_6$ + 0.15 mL THF
4. Table S2 Scope of the 'BuOK-catalyzed hydroboration of N-Heteroarenes.\textsuperscript{a}

$$\begin{align*}
1 & \quad 2a & \quad \text{BuOK} & \quad 4 & \quad 5 \\
\text{Conversion of } 1a: & 99\% & \text{Conversion of } 1b: & 0\% & \text{Conversion of } 1c: & 99\% & \text{Conversion of } 1d: & 99\% & \text{Conversion of } 1e: & 99\% & \text{Conversion of } 1f: & 100\% & \text{Conversion of } 1g: & 100\% \\
yield of 4a: & 96\% & \text{yield of 4b:} & 0\% & \text{yield of 4c:} & 99\% & \text{yield of 4d:} & 99\% & \text{yield of 4e:} & 86\% & \text{yield of 4f:} & 90\% & \text{yield of 4g:} & 96\% \\
yield of 5a: & 3\% & \text{yield of 5b:} & 0\% & \text{yield of 5c:} & 0\% & \text{yield of 5d:} & 4\% & \text{yield of 5e:} & 13\% & \text{yield of 5f:} & 10\% & \text{yield of 5g:} & 4\% \\
\end{align*}$$

5. Mechanistic studies of the reaction catalyzed by 'BuOK

5.1 Reaction of 1a with 2a

$$\begin{align*}
\text{1a} & \quad + \quad \text{2a} & \quad \text{C}_6\text{D}_6 & \quad \text{RT} & \quad \text{No reaction} \\
\end{align*}$$

\textsuperscript{a} Conditions: toluene (0.1 mmol), HBpin (0.2 mmol), 'BuOK (5 mmol), C_6D_6 0.5 mL. - THF 0.15 mL. Heated at 55 °C for 48 h. Both conversion and product yields were determined by 31P NMR analysis. \textsuperscript{1} 6a (4 mmol) HBpin was used.
5.2 Reaction of 1a with 'BuOK

Figure S1. Overlay of $^1$H NMR spectra for (a) quinoline 1a (b) Pinacolborane (c) quinoline: Pinacolborane=1:1.

Figure S2. Overlay of $^1$H NMR spectra for (a) 'BuOK (b) quinoline (c) quinoline: 'BuOK =1:1.
5.3 Reaction of 'BuOK with 2a

\[ \text{O} - \text{K} + \text{O} - \text{O} \rightarrow \text{O} - \text{O} + \text{H} \]

\( 2a \rightarrow 2b \)

Figure S3. \(^1\)H NMR spectrum for reaction of 2a with 'BuOK

Figure S4. \(^{11}\)B NMR spectrum for reaction of 2a with 'BuOK.
6. Reaction of 1a with KH

6.1 Reaction of 1a with KH

In a glove box, quinoline (1a) (51.6 mg, 0.4 mmol) was dissolved in 2 mL THF in a schlenk flask, then KH (16 mg, 0.4 mmol) was added with stirring. This flask was held at -30 °C for 12 h. Then, a 0.2 mL aliquot was taken out for NMR measurement, only trace amount of potassium 2H-quinolin-1-ide (3b) was observed in $^1$H NMR spectrum. Another flasks containing the same feed of starting materials was held at RT for 2 day and then a 0.2 mL aliquot was taken out for NMR measurement, 1a was all converted to a mixture of 3b and potassium 4H-quinolin-1-ide (3c). When held for 4 days, only 3c could be observed.
6.2 Reaction of HBpin with the mixture of 3b and 3c

The mixture of 3b and 3c (1 mmol 170 mg) was added to a 2 mL THF solution of HBpin (2.2 mmol, 282 mg) at RT in a flask. After 2 h, 0.2 mL aliquot was taken out for NMR measurement.
Figure S6. Overlay of the $^1$H NMR spectra for the mixture of $3b$ and $3c$ (top) and the reaction of HBpin with the mixture $3b$ and $3c$ (bottom)

6.3. Isomerization between $3b$ and $3c$

In a glove box, quinoline (1a) (12.9 mg, 0.1 mmol) was dissolved in 0.5 mL $d_8$-THF in a J. Young-type NMR tube, then KH (4 mg, 0.1 mmol) was added.
7. Reaction of thermodynamics intermediate 3c with HBpin

Thermodynamics intermediates 3c (1 mmol 170 mg) was added to a 2 mL THF solution containing a predetermined amount of HBpin at RT in three different flasks (a, HBpin (1 mmol 128 mg); b, HBpin (2.2 mmol 281.6 mg); c, HBpin (5 mmol 640 mg)). After 2h, 0.2 mL aliquot was withdrawn from each flask for NMR measurement. It turned out that 3c was completely converted to 5a, which is the same with the direct reaction of 3c with HBpin in the mixed solvents of C₆D₆ and THF.
Figure S8. Overlay of $^1$H NMR spectra for the reaction thermodynamics intermediate 3c with HBpin in different ratios

8. Control experiments

8.1 Test whether 4a could be transformed into 5a

(i) In a glove box, 4a (25.7 mg, 0.1 mmol) was added to 0.5 mL C$_6$D$_6$ in a J. Young-type NMR tube and heated at 50 °C for 24 h (Figure S9a) and 48 h (Figure S9b). After heating at 80 °C for 48 h (Figure S9c), the addition of 0.1 mL THF to the mixture did not transform 4a to 5a (Figure S9d).
Figure S9. Overlay of $^1$H NMR spectra for the reaction heating at (a) $T=50 \, ^\circ C$, $t=24 \, h$, in 0.5 mL C$_6$D$_6$. (b) $T=50 \, ^\circ C$, $t=48 \, h$, in 0.5 mL C$_6$D$_6$. (c) $T=80 \, ^\circ C$, $t=48 \, h$, in 0.5 mL C$_6$D$_6$. (d) $T=80 \, ^\circ C$, $t=48 \, h$, addition of 0.1 mL THF to 0.5 mL C$_6$D$_6$.

(ii) 4a (25.7 mg, 0.1 mmol) and KH (4 mg, 0.1 mmol) was added to the mixed solvents of 0.5 mL C$_6$D$_6$ and 0.1 mL THF in a J. Young type NMR tube and heated at 50 °C for 24 h (Figure S10a) and 48 h (Figure S10b). Heating at 80 °C for 48 h did not transform 4a into 5a (Figure S10) (Figure S10c).

Figure S10. Overlay of $^1$H NMR spectra for reaction heating at (a) $T=50 \, ^\circ C$, $t=24 \, h$. (b) $T=50 \, ^\circ C$, $t=48 \, h$. (c)
T=80 °C, t=48 h.

(iii) 4a (25.7 mg, 0.1 mmol), KH (4 mg, 0.1 mmol) and HBpin (12.8 mg, 0.1 mmol) was added to the mixed solvents of 0.5 mL C₆D₆ and 0.1 mL THF in a J. Young type NMR tube and heated at 50 °C for 24 h (Figure S11a) and 48 h (Figure S11b). Heating at 80 °C for 48 h did not transform 4a to 5a (Figure S11c).

Figure S11. Overlay of ¹H NMR spectra for reaction carried out in the mixed solvents of 0.5 mL C₆D₆ and 0.15 mL THF (a). T=50 °C, t=24 h (b) T=50 °C, t=48 h. (c) T=80 °C, t=48 h.

8.2 Test whether 5a could be transformed into 4a

In a glove box, 5a (12.9 mg, 0.05 mmol), KH (10 mol%, 0.4 mg) and HBpin (12.8 mg, 0.1 mmol) was added to 0.5 mL C₆D₆ and 0.15 mL THF in a J. Young type NMR tube. After heating at 50 °C for 24 h, a 0.2 mL of aliquot was taken out for NMR reaction. It turned out that 5a was not transformed into 4a.
9. **Preparative scale synthesis of 4d**

In a glove box, 4-methylquinoline (1d, 1.43 g 10 mmol), KH (0.1 mmol 4 mg) and HBpin (10.1 mmol 1.29 g) were mixed in 8mL THF in a 20 mL schlenk flask. After heating at 50 ºC for 24 h, a 0.2 mL aliquot was taken out for NMR measurements (yield of 4d is 98%). After filtration, the filtrate was concentrated in vacuo and added with 10 mL hexane, then held in a refrigerator at -40 ºC for 24 h for recrystallization. Pure products was obtained as white solids (2.53 g, 93% yield).
10. Long-life catalytic performance of the KH-catalyzed hydroboration of 1d

In a glovebox, KH (10 mol%, 0.4 mg) was added to a solution (0.5 mL C₆D₆ and 0.15 mL THF) containing 4-methylquinoline (14.3 mg, 0.1 mmol), HBpin (25.6 mg, 0.2 mmol) and mesitylene (12 mg, 0.1 mmol) in a 2 mL J. Young type NMR tube. After heating at 50 °C for 24 h and NMR measurement, another batch of 4-methylquinoline, HBpin and mesitylene in 0.075 mL C₆D₆ and 0.025 mL THF were added to the reaction system and continue screening the catalytic activity. This process was repeated 7 times.
Figure S14 Long-life catalytic performance of the KH-catalyzed hydroboration of 1d

11. Reaction of 1r with KH

In a glove box, pyridine (1r) (79 mg, 1 mmol) was dissolved in 2 mL THF in a schlenk flask, then KH (40 mg, 1 mmol) was added. After heating at 100 °C for 24 h, a 0.2 mL aliquot was withdrawn for NMR measurement. It turned out that near quantitative of 1r was converted to 3g.

\[
\begin{align*}
\text{1r} & \quad \stackrel{\text{KH}}{\longrightarrow} \quad \text{3g}
\end{align*}
\]
12. Reaction of intermediate 3g and HBpin

3g (23.8 mg, 0.2 mmol) was dissolved in 0.5 mL THF in a schlenk flask, then HBpin (89.6 mg, 0.7 mmol) was added at RT. After 2h, a 0.2 mL aliquot was withdrawn for NMR measurement. It turned out that near quantitative 3g was converted to 7a.
Figure S16 $^1$H NMR spectrum for intermediate 3g in-situ generated from the reaction of 1r and KH (top) and reaction of intermediate 3g with HBpin (bottom)

13. NMR spectra

$^1$H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4a) (500 MHz, CdCl₃)
$^{13}$C NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4a) (126 MHz, C$_6$D$_6$).

$^{11}$B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4a) (160 MHz, C$_6$D$_6$).
$^1$H NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4c) (500 MHz, CD$_6$D$_6$)

$^{13}$C NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydro quinoline (4c) (126 MHz, CD$_6$D$_6$)
$^1$B NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y1)-1,2-dihydro quinoline (4e) (160 MHz, C$_6$D$_6$).

$^1$H NMR spectrum of 4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y1)-1,2-dihydroquino line (4d) (500 MHz, C$_6$D$_6$).
$^{13}$C NMR spectrum of 4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4d) (126 MHz, C$_6$D$_6$).

$^{11}$B NMR spectrum of 4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4d) (160 MHz, C$_6$D$_6$).
$^1$H NMR spectrum of 5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4e) (500 MHz, C$_6$D$_6$)

$^{13}$C NMR spectrum of 5- methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4e) (126 MHz, C$_6$D$_6$)
$\text{\textsuperscript{11}B NMR spectrum of 5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4e) (160 MHz, C$_6$D$_6$).}$

$\text{\textsuperscript{1}HNMR spectrum of 5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4j) (500 MHz, C$_6$D$_6$).}$
$^1$C NMR spectrum of 5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4j) (126 MHz, C$_6$D$_6$)

$^1$H NMR spectrum of 6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4f) (500 MHz, C$_6$D$_6$)
\(^{13}\)C NMR spectrum of 6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4f) (126 MHz, CD\(_6\)D\(_6\))

\(^1\)H NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4k) (500 MHz, CD\(_6\)D\(_6\))
$^3$C NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4k) (126 MHz, C$_6$D$_6$).

$^{11}$B NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4k) (160 MHz, C$_6$D$_6$).
$^{19}$F NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4k) (147 MHz, C$_6$D$_6$).

$^1$HNMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4l) (500 MHz, C$_6$D$_6$)
\textsuperscript{13}C NMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4l) (126 MHz, C\textsubscript{6}D\textsubscript{6})

\textsuperscript{11}B NMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4l) (160 MHz, C\textsubscript{6}D\textsubscript{6}).
$^1$H NMR spectrum of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4m) (500 MHz, C$_6$D$_6$)

$^{13}$C NMR spectrum of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4m) (126 MHz, C$_6$D$_6$)
$^{11}$B NMR spectrum of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4m) (160 MHz, C$_6$D$_6$).

$^1$H NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4g) (500 MHz, C$_6$D$_6$)
$^{13}$C NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4g) (126 MHz, C$_6$D$_6$).

$^{11}$B NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (4g) (160 MHz, C$_6$D$_6$).
$^1$H NMR spectrum of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9a,10-tetrahydroacridine (9) (500 MHz, C$_6$D$_6$)

$^{13}$C NMR spectrum of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9a,10-tetrahydroacridine (9) (126 MHz, C$_6$D$_6$)
$^{11}$B NMR spectrum of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9,9a,10-tetrahydroacridine (9) (160 MHz, CD$_6$D$_6$).

$^1$HNMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (6) (500 MHz, CD$_6$D$_6$)
$^{13}$C NMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (6) (126 MHz, C$_6$D$_6$).

$^{11}$B NMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (6) (160 MHz, C$_6$D$_6$).
$^1$H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (7) (500 MHz, C$_6$D$_6$)

$^{13}$C NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (7) (126 MHz, C$_6$D$_6$)
$^1$H NMR spectrum of 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (8) (500 MHz, C$_6$D$_6$)

$^{13}$B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (7) (160 MHz, C$_6$D$_6$).
$^{13}$C NMR spectrum of 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (8) (126 MHz, CdD$_6$).

$^{11}$B NMR spectrum of 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (8) (160 MHz, CdD$_6$).
$^1$H NMR spectrum of 1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10r) (500 MHz, C$_6$D$_6$)

$^{13}$C NMR spectrum of 1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10r) (126 MHz, C$_6$D$_6$)
$^1$B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10r) (160 MHz, C$_6$D$_6$).

$^1$H NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10s) (500 MHz, C$_6$D$_6$)
$^1$C NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10s) (126 MHz, C$_6$D$_6$)

$^1$H NMR spectrum of 3-ethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10t) (500 MHz, C$_6$D$_6$)
$^{13}$C NMR spectrum of 3-ethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10t) (126 MHz, C$_6$D$_6$)

$^{11}$B NMR spectrum of 3-ethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (10t) (160 MHz, C$_6$D$_6$).