Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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.

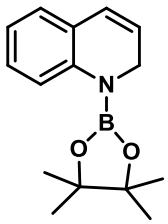
General procedures for hydroboration of N-heteroarenes

In a glove box, ^{t}BuOK (5 mol%) or KH (10 mmol%) was added to a solution containing quinoline (0.1 mmol) in 0.5 mL C_6D_6 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 ºC 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

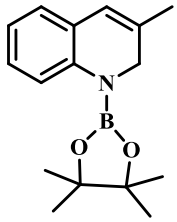
In a glove box, KH (0.05 mmol) was added to a 2 mL THF solution of pyridine (0.5 mmol) in 10 mL flask. Then, the pinacolborane HBpin (0.55 mmol) was added to the resulting mixture. After taken out of the glovebox and heated at 100 ºC for specified time, it was measured by NMR spectroscopy. The reaction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

2. Characterization data

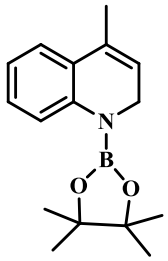


1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline

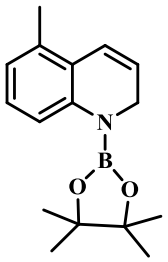
(4a) : white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.82 (d, J = 10 Hz, 1H, H_{Ar}), 7.08 (td, J_1 = 9 Hz, J_2 = 5 Hz, 1H, H_{Ar}), 6.84 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H, H_{Ar}), 6.79 (td, J_1 = 7.5 Hz, J_2 = 0.5 Hz, 1H, H_{Ar}), 6.25 (d, J_1 = 10 Hz, 1H, H_{Ar}), 5.55-5.59 (m, 1H, H_{Ar}), 4.17 (dd, J_1 = 4 Hz, J_2 = 1.5 Hz, 2H, CH_2), 1.04 (s, 12H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 141.9, 127.8, 126.7, 126.6, 124.2, 121.6, 120.9, 82.5, 43.3, 24.3. ^{11}B NMR (160 MHz, C_6D_6) δ 23.9.



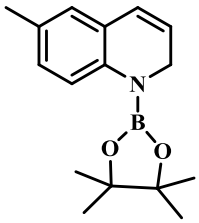
3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroqui noline **(4c)**: white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.88 (d, J = 10 Hz, 1H, H_{Ar}), 7.10 (td, J_1 = 13 Hz, J_2 = 1.5 Hz, 1H, H_{Ar}), δ 6.88 (dd, J_1 = 7.5 Hz, J_2 = 2 Hz, 1H, H_{Ar}), 6.84 (td, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 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_6D_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_6D_6): δ 24.1.



4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroqui noline **(4d):** white solid. ^{1}H NMR (500 MHz, C_6D_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_6D_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_6D_6) δ 23.9.

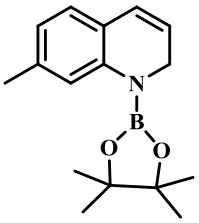


5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroqui noline **(4e):** white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.71 (d, J = 10 Hz, 1H, H_{Ar}), 7.04 (t, J = 10 Hz, 1H, H_{Ar}), 6.68 (d, J = 7.5 Hz, 1H, H_{Ar}), 5.67-5.71 (m, 1H, H_{Ar}), 4.12 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 2H, CH_2), 2.08 (s, 3H, CH_3), 1.05 (s, 12H, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 142.0, 133.2, 127.3, 124.1, 123.5, 123.5, 119.3, 82.4, 42.6, 24.4, 18.7. ^{11}B NMR (160 MHz, C_6D_6) δ 23.9.

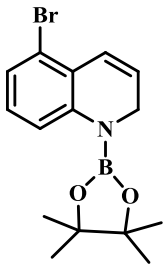


6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroq uinoline **(4f)**: white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.75 (d, J = 8.5 Hz, 1H, H_{Ar}), 6.93 (d, J = 8.0 Hz, 1H, H_{Ar}), 6.27 (d, J = 9.5 Hz, 1H, H_{Ar}), 5.60-5.63 (m, 1H, H_{Ar}), 4.18 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 2H, CH_2), 2.01 (s, 3H, CH_3), 1.05 (s,

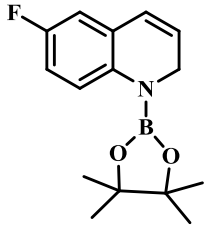
12H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 139.4, 130.4, 128.4, 126.7, 126.6, 124.3, 120.8, 121.9, 81.4, 43.4, 24.4, 20.3. ^{11}B NMR (160 MHz, C_6D_6) δ 23.9.



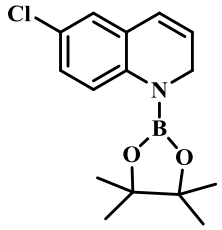
7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline **(4g)** : white solid. ^1H NMR (500 MHz, C_6D_6) δ 7.64 (s, 1H, H_{Ar}), 6.81 (d, J = 7.5 Hz, 1H, H_{Ar}), 6.65 (d, J = 7.5 Hz, 1H, H_{Ar}), 6.30 (d, J = 9.5 Hz, 1H, H_{Ar}), 5.56-5.60 (m, 1H, H_{Ar}), 4.18 (dd, J_1 = 4.0 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_6D_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_6D_6) δ 24.0.



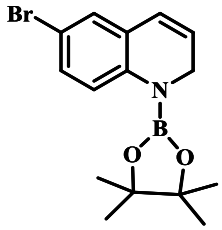
5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline **(4j)** : white solid. ^1H NMR (500 MHz, C_6D_6) δ 7.53 (d, J = 9.0 Hz, 1H, H_{Ar}), 7.17 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H, H_{Ar}), 6.95 (d, J = 10.0 Hz, 1H, H_{Ar}), 5.43-5.47 (m, 1H, H_{Ar}), 4.03 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 2H, CH_2), 1.00 (s, 12H, CH_3). ^{13}C NMR (126 MHz, C_6D_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_6D_6) δ 23.8.



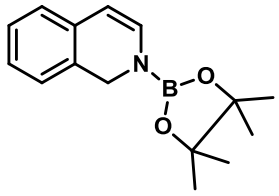
6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline **(4k)** : white solid. ^1H NMR (500 MHz, C_6D_6) δ 7.60 (m, 1H, H_{Ar}), 6.70 (td, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H, H_{Ar}), 6.52 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H, H_{Ar}), 6.00 (d, J = 9.5 Hz, 1H, H_{Ar}), 5.51-5.54 (m, 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_6D_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_6D_6) δ 23.9. ^{19}F NMR (471 MHz, C_6D_6) δ -122.69.



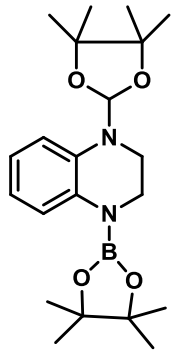
6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline **(4l)** : white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.59 (d, *J* = 9.0 Hz, 1H, H_{Ar}), 7.03 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H, H_{Ar}), 6.80 (d, *J* = 2.5 Hz, 1H, H_{Ar}), 5.45-5.49 (m, 1H, H_{Ar}), 4.04 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H, CH_2), 1.01 (s, 12H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 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_6D_6) δ 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_6D_6) δ 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_6D_6) δ 140.8, 130.4, 129.1, 128.5, 125.4, 122.4, 113.9, 82.7, 43.1, 24.3. ^{11}B NMR (160 MHz, C_6D_6) δ 23.8.

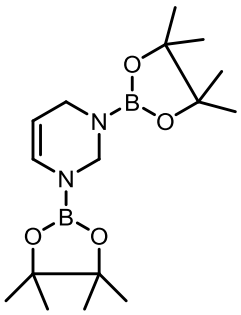


2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline **(6)** : white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.00 (t, *J* = 7.5 Hz, 1H, H_{Ar}), 6.87 (t, *J* = 7.5 Hz, 1H, H_{Ar}), 6.85 (d, *J* = 7.5 Hz, 1H, H_{Ar}), 6.81 (d, *J* = 7.5 Hz, 1H, H_{Ar}), 6.53 (d, *J* = 7.5 Hz, 1H, H_{Ar}), 4.64 (s, 2H, CH_2), 1.02 (s, 12H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 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_6D_6) δ 23.8.

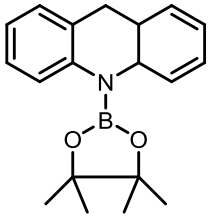


1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline **(7)** : white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 8.13-8.16 (m, 2H, H_{Ar}), 6.95-6.98 (m, 2H, H_{Ar}), 3.61 (s, 4H, CH_2), 1.05 (s, 24H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 132.9,

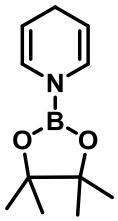
121.2, 120.8, 82.3, 43.9, 24.3. ^{11}B NMR (160 MHz, C_6D_6) δ 24.1.



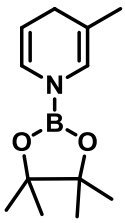
1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine **(8)**: colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ 6.82 (dt, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, H_{Ar}), 4.82 (s, 2H, CH_2), 4.63-4.66 (m, 1H, H_{Ar}), 3.81-3.82 (m, 2H, CH_2), 1.06 (s, 12H, CH_3), 1.01 (s, 12H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 129.3, 102.2, 82.5, 82.0, 55.8, 41.8, 24.5. ^{11}B NMR (160 MHz, C_6D_6) δ 23.9.



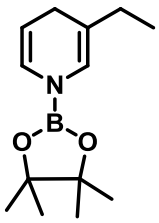
10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9,9a,10-tetrahydroacridine **(9)** white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.15-7.18 (m, 2H, H_{Ar}), 6.93-7.01 (m, 4H, H_{Ar}), 3.55 (s, 2H, CH_2), 1.06 (s, 12H, CH_3), ^{13}C NMR (126 MHz, C_6D_6) δ 142.4, 130.2, 127.1, 126.1, 123.3, 122.6, 82.9, 33.7, 24.3. ^{11}B NMR (160 MHz, C_6D_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 (500MHz, C_6D_6) δ 6.55 (m, 2H), 4.57 (m, 2H), 2.81 (m, 2H, CH_2), 0.96 (s, 12H, CH_3), ^{13}C NMR (126 MHz, C_6D_6). ^{11}B NMR (160 MHz, C_6D_6) δ 23.0.

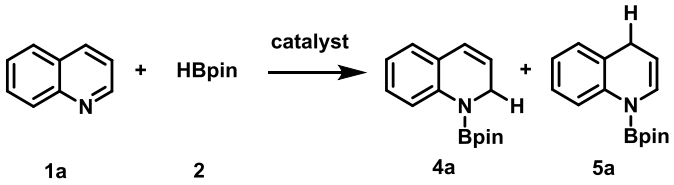


3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine **(10s)** white solid. ^{1}H NMR (500MHz, C_6D_6) δ 6.63 (m, 1H), 6.42 (m, 1H), 4.67 (m,1H), 2.73 (m, 2H, CH_2). 1.41 (s, 3H, CH_3), 1.00 (s, 12H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 126.6, 121.8, 110.4, 101.7, 82.9, 28.0, 24.2, 20.4. ^{11}B NMR (160 MHz, C_6D_6) δ 24.1.



3-ethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (**10t)** colorless oil. ^{1}H NMR (500MHz, C_6D_6) δ 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_6D_6) δ 126.8, 120.9, 115.9, 101.9, 82.9, 28.0, 26.0, 24.3, 11.4. ^{11}B NMR (160 MHz, C_6D_6) δ 24.1.

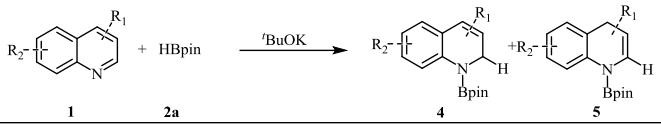
3. Table S1 Optimization of Reaction Conditions[a]



Entry	Cat	Temp	solvent	Conv (%)[b]	**4a**[b]	**5a**[b]
1	LiCl	RT	C_6D_6	0	0	0
2	NaCl	RT	C_6D_6	0	0	0
3	KCl	RT	C_6D_6	0	0	0
4	Li_2CO_3	RT	C_6D_6	0	0	0
5	Na_2CO_3	RT	C_6D_6	0	0	0
6	K_2CO_3	RT	C_6D_6	0	0	0
7	^{t}BuOLi	RT	C_6D_6	10	10	0
8	^{t}BuONa	RT	C_6D_6	31	31	0
9	LiH	RT	C_6D_6	0	0	0
10	NaH	RT	C_6D_6	0	0	0
11	KH	RT	C_6D_6	0	0	0
12	LiH	50 ºC	C_6D_6+THF[c]	99	70	29
13	NaH	50 ºC	C_6D_6+THF[c]	99	94	5
14	**KH**	**50** ºC	C_6D_6+THF[c]	**100**	**97**	**3**

[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_6D_6 + 0.15 mL THF

4. Table S2 Scope of the ^{t}BuOK-catalyzed hydroboration of *N*-Heteroarenes.[a]

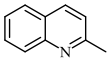


1 2a 4 5

1a

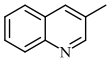
Conversion of **1a:** 99%
yield of **4a**: 96%
yield of **5a**: 3%

1b



Conversion of **1b:** 0%
yield of **4b**: 0%
yield of **5b**: 0%

1c



Conversion of **1c:** 99%
yield of **4c**: 99%
yield of **5c**: 0%

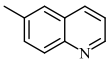
1d

Conversion of **1d:** 99%
yield of **4d**: 99%
yield of **5d**: 0%

1e

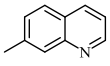
Conversion of **1e:** 99%
yield of **4e**: 86%
yield of **5e**: 13%

1f



Conversion of **1f:** 100%
yield of **4f**: 90%
yield of **5f**: 10%

1g



Conversion of **1g:** 100%
yield of **4g**: 96%
yield of **5g**: 4%

1h

Conversion of **1h:** 0%
yield of **4h**: 0%
yield of **5h**: 0%

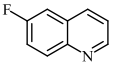
1i

Conversion of **1i:** 0%
yield of **4i**: 0%
yield of **5i**: 0%

1j

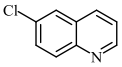
Conversion of **1j:** 100%
yield of **4j**: 93%
yield of **5j**: 7%

1k



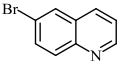
Conversion of **1k:** 100%
yield of **4k**: 95%
yield of **5k**: 5%

1l



Conversion of **1l:** 100%
yield of **4l**: 98%
yield of **5l**: 2%

1m

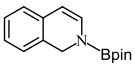


Conversion of **1m:** 96%
yield of **4m**: 93%
yield of **5m**: 3%

1n

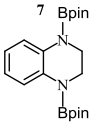
Conversion of **1n:** 99%
yield of **6**: 99%

6



1o[b]

7



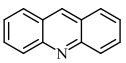
Conversion of **1o:** 99%
yield of **7**: 99%

1p[b]

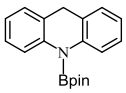
8

Conversion of **1p:** 92%
yield of **8**: 92%

1q



9

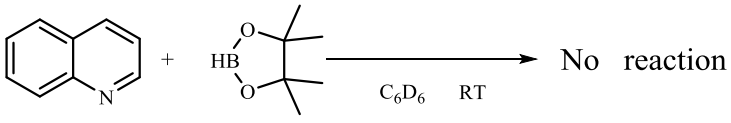


Conversion of **1q:** 92%
yield of **9**: 92%

[a] Conditions: substrates (0.1 mmol), HBpin (0.2 mmol), ^{t}BuOK (5 mol%), C_6D_6 0.5 mL + THF 0.15 mL heated at 50 °C for 48 h, Both conversion and product yields were determined by ^{1}H NMR analysis. [b] 0.4 mmol HBpin was used

5. Mechanistic studies of the reaction catalyzed by ^{t}BuOK

5.1 Reaction of 1a with 2a



1a **2a**

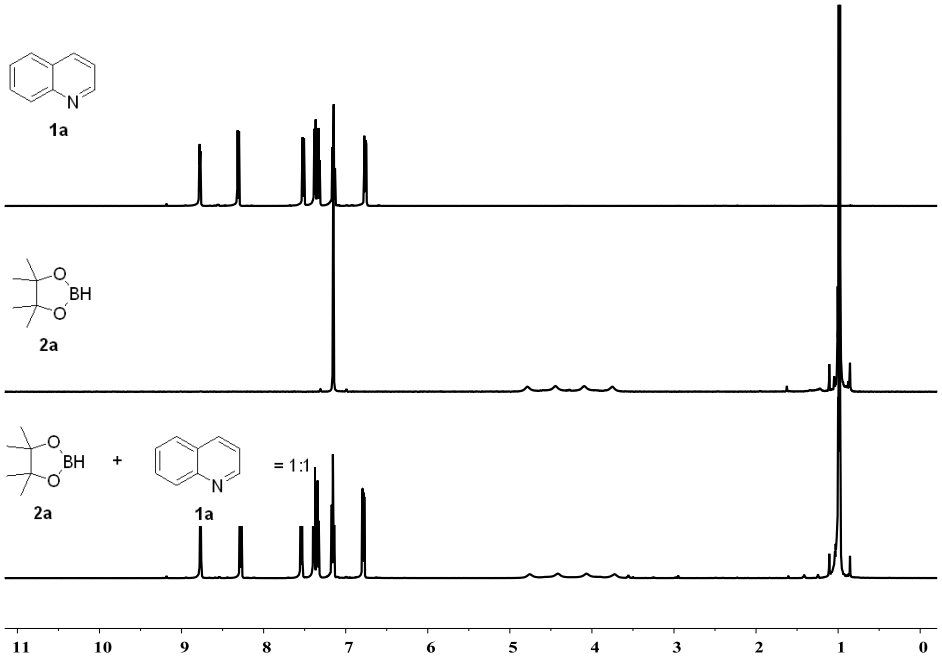
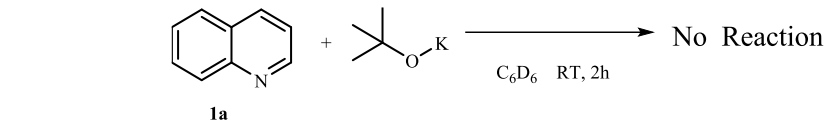


Figure S1. Overlay of ^{1}H NMR spectra for (a) quinoline **1a** (b) Pinacolborane (c) quinoline: Pinacolborane=1:1.

5.2 Reaction of 1a with ^{t}BuOK



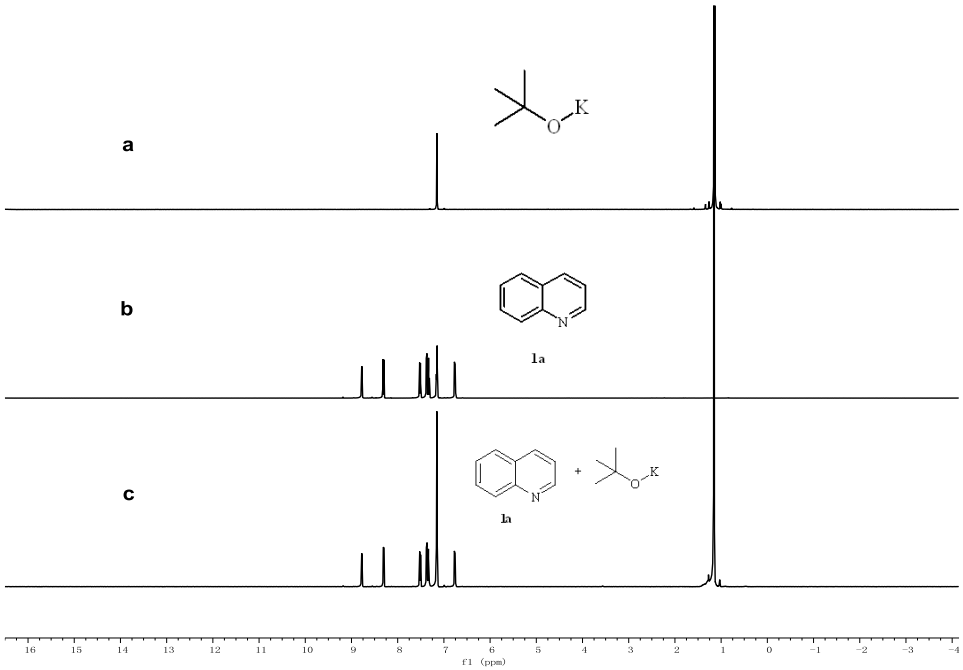
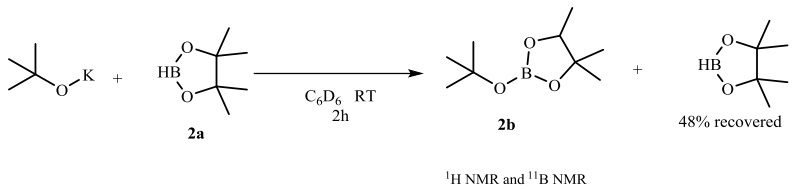


Figure S2. Overlay of ^{1}H NMR spectra for (a) ^{t}BuOK (b) quinoline (c) quinoline: ^{t}BuOK =1:1.

5.3 Reaction of ^{t}BuOK with 2a



^{1}H NMR and ^{11}B NMR

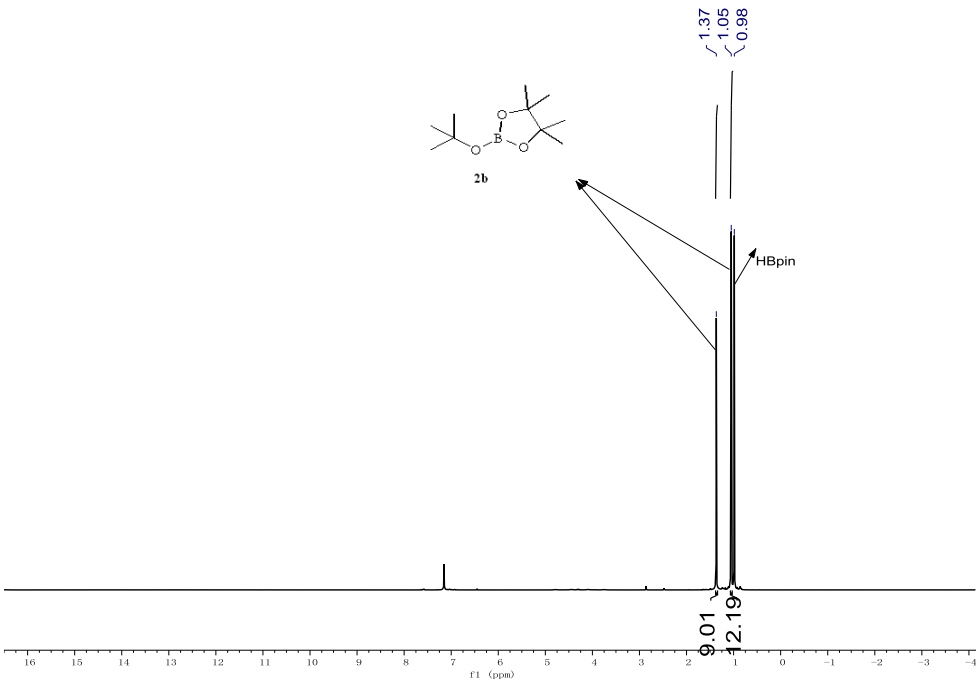


Figure S3. ^{1}H NMR spectrum for reaction of **2a** with ^{t}BuOK

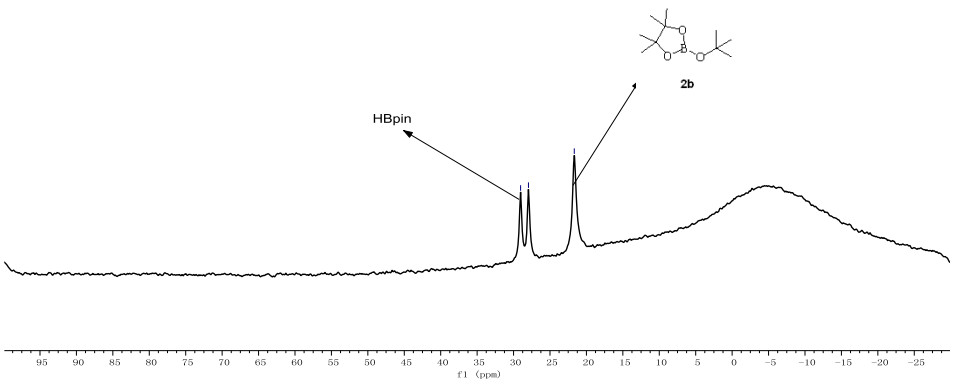
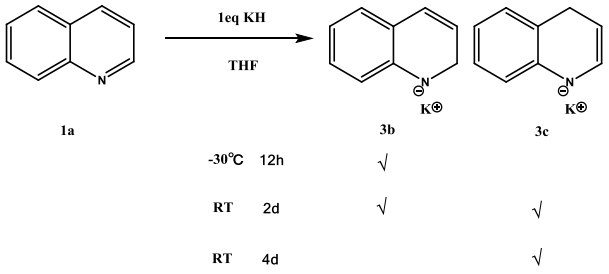


Figure S4. ^{11}B NMR spectrum for reaction of **2a** with ^{t}BuOK.

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 ℃ 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.

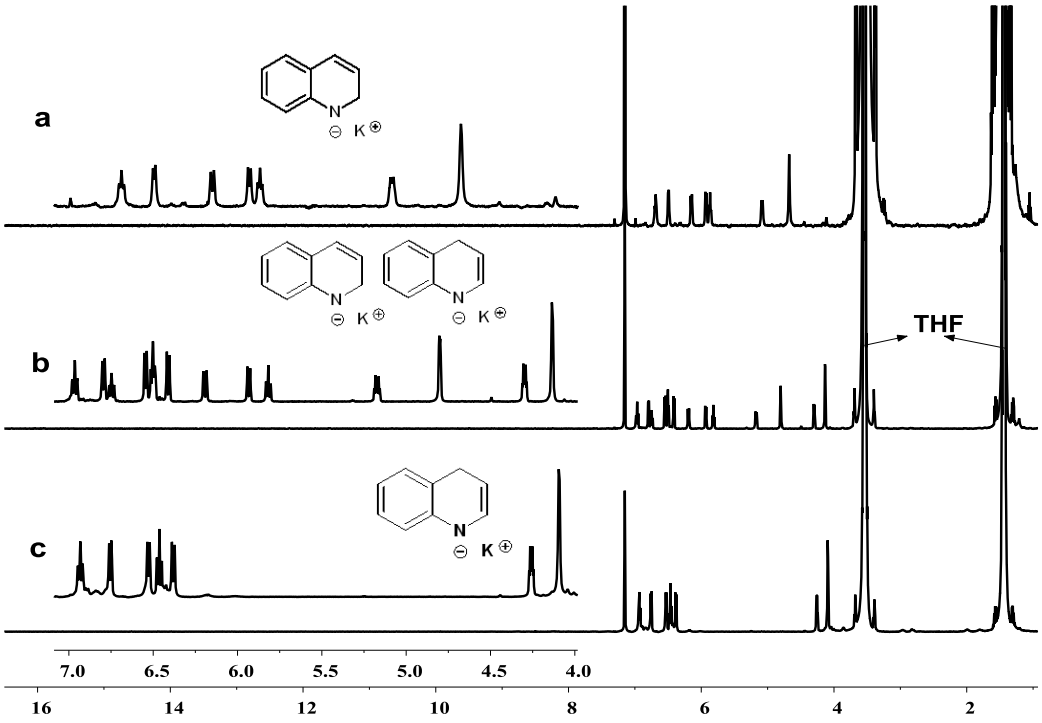
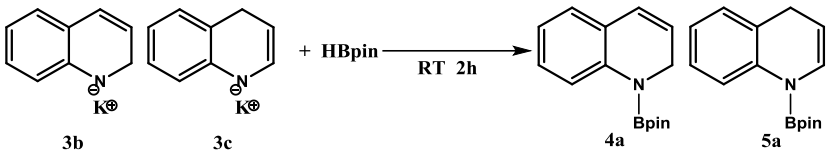


Figure S5. Overlay of ^{1}H NMR spectra for (a) intermediate **3b**, (b) mixture of **3b** and **3c**, (c) intermediate **3c**.

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



3b 3c 4a 5a

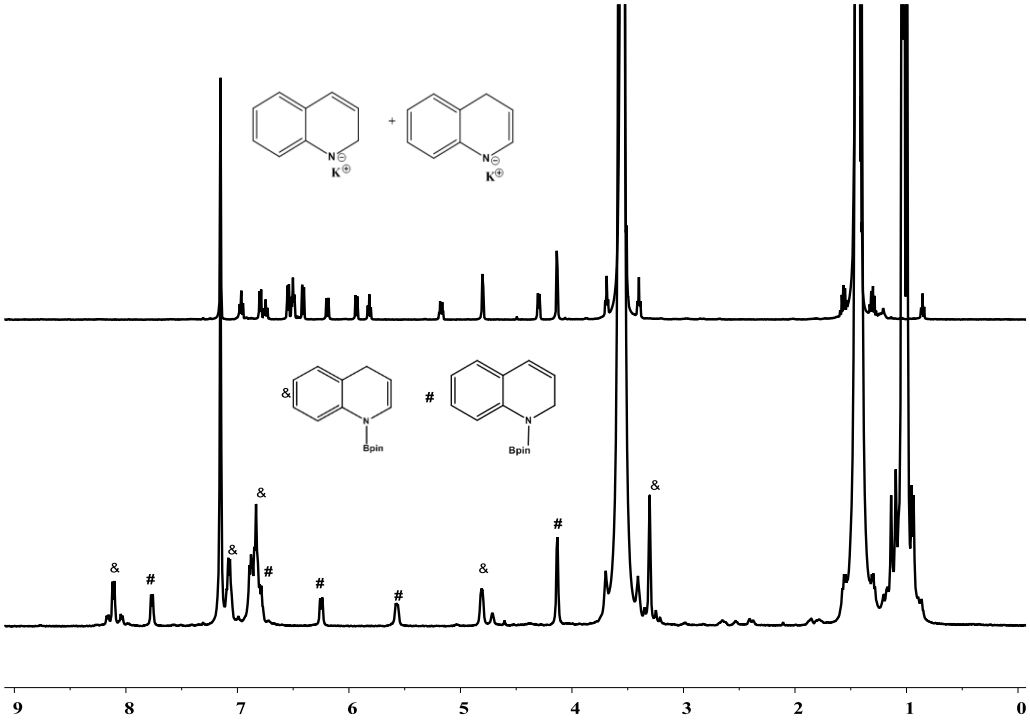
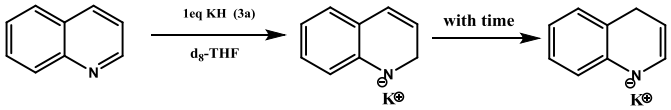


Figure S6. Overlay of the ^{1}H NMR spectra for the mixture of **3b** and **3c** (top) and the reaction of HBpin with the mixture **3b** and **3c** (bottom)

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.

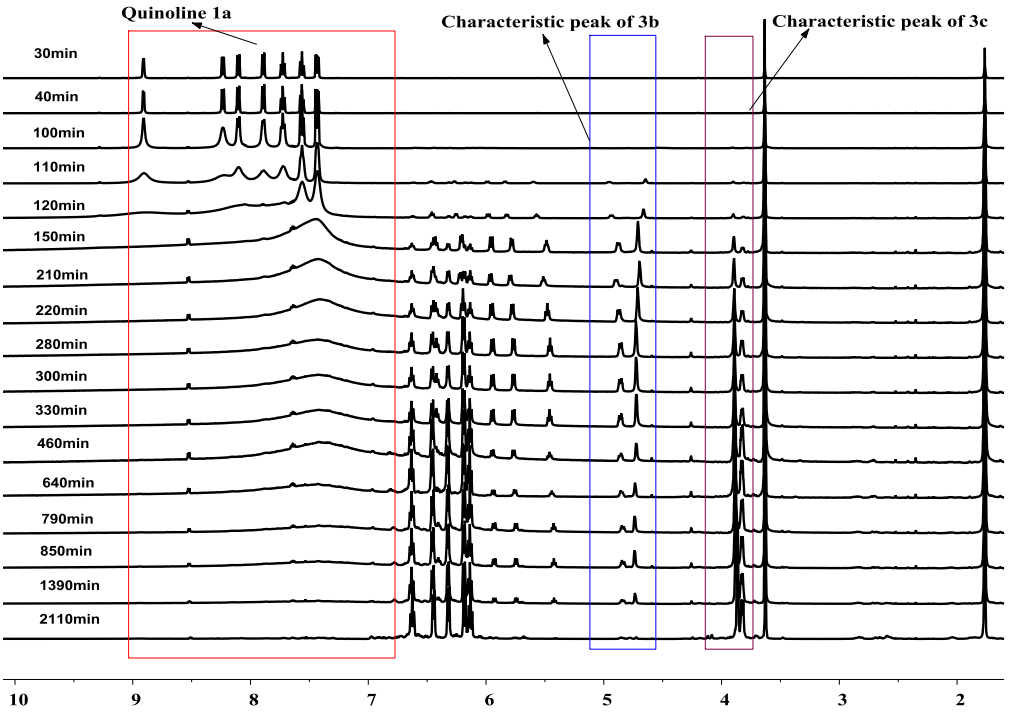
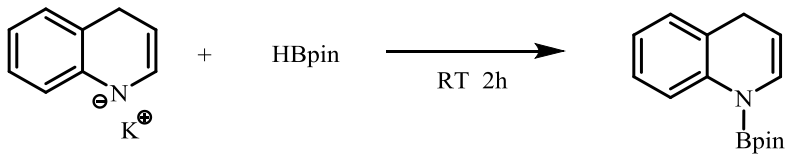


Figure S7. Overlay of ^{1}H NMR spectra for the reaction of **1a** with KH at RT for different time interval.

7. Reaction of thermodynamics intermediate 3c with HBpin



3c **5a**

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 C_6D_6 and THF.

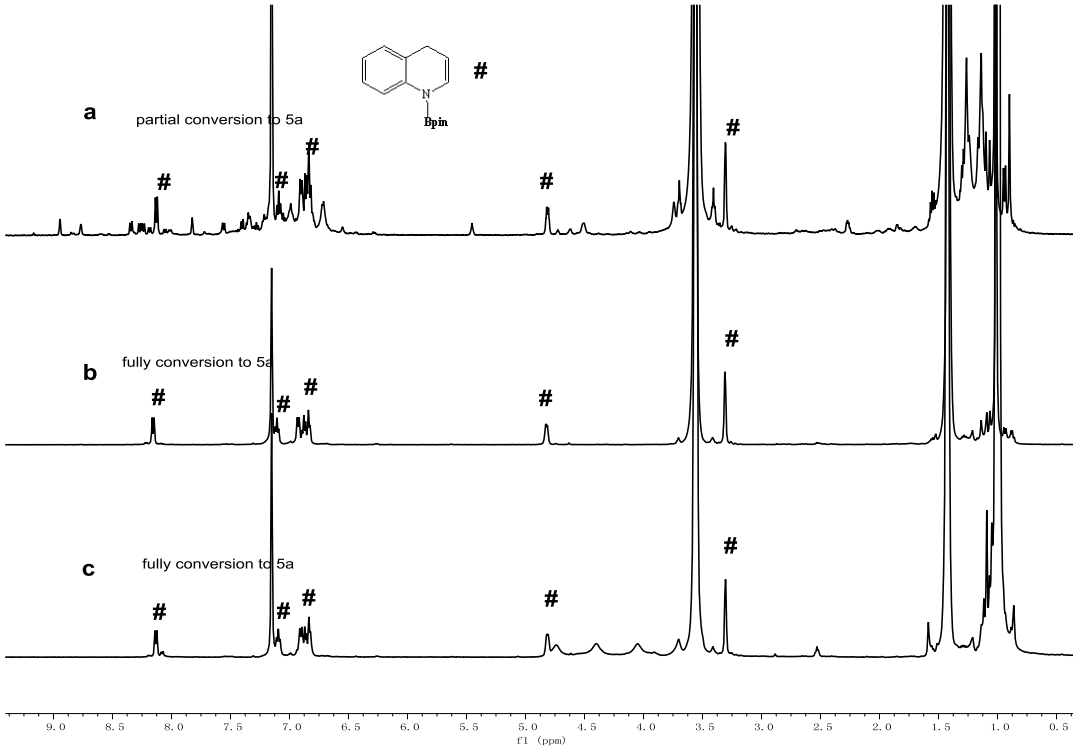


Figure S8. Overlay of ^{1}H NMR spectra for the reaction thermodynamics intermediate **3c** with HBpin in different ratios

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_6D_6 in a J. Young-type NMR tube and heated at 50 ℃ for 24 h (Figure S9a) and 48 h (Figure S9b). After heating at 80 ℃ for 48 h (Figure S9c), the addition of 0.1 mL THF to the mixture did not transform **4a** to **5a** (Figure S9d).

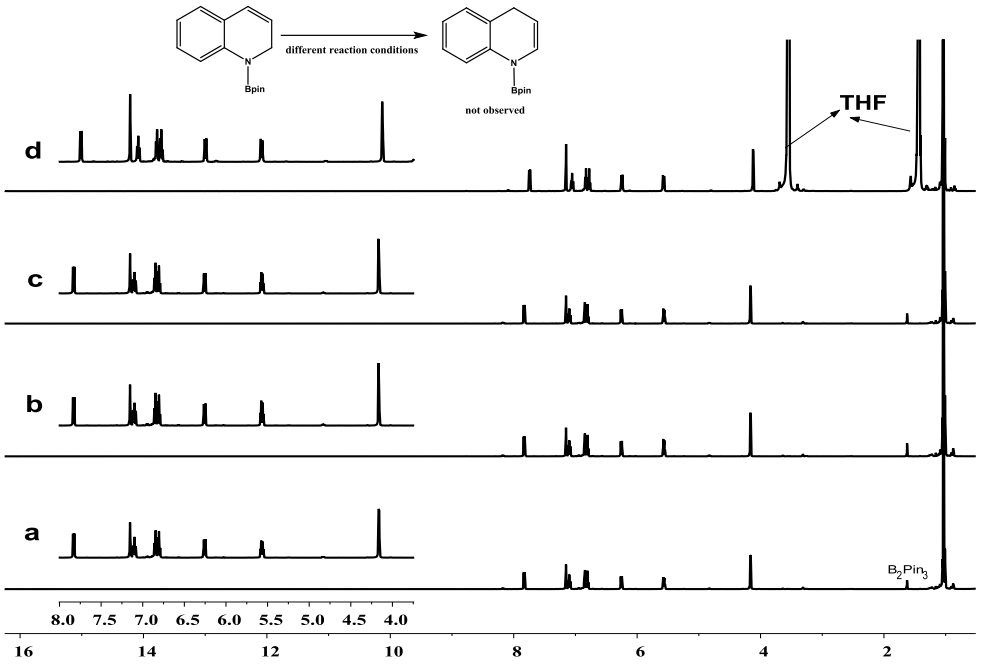


Figure S9. Overlay of ^{1}H NMR spectra for the reaction heating at (a) T=50 ℃, t=24 h，in 0.5 mL C_6D_6. (b) T=50 ℃, t=48 h，in 0.5 mL C_6D_6. (c) T=80 ℃, t=48 h，in 0.5 mL C_6D_6. (d) T=80 ℃, t=48 h，addition of 0.1 mL THF to 0.5 mL C_6D_6.

(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_6D_6 and 0.1 mL THF in a J. Young type NMR tube and heated at 50 ℃ for 24 h (Figure S10a) and 48 h (Figure S10b). Heating at 80 ℃ for 48 h did not transform **4a** into **5a** (Figure S10) (Figure S10c).

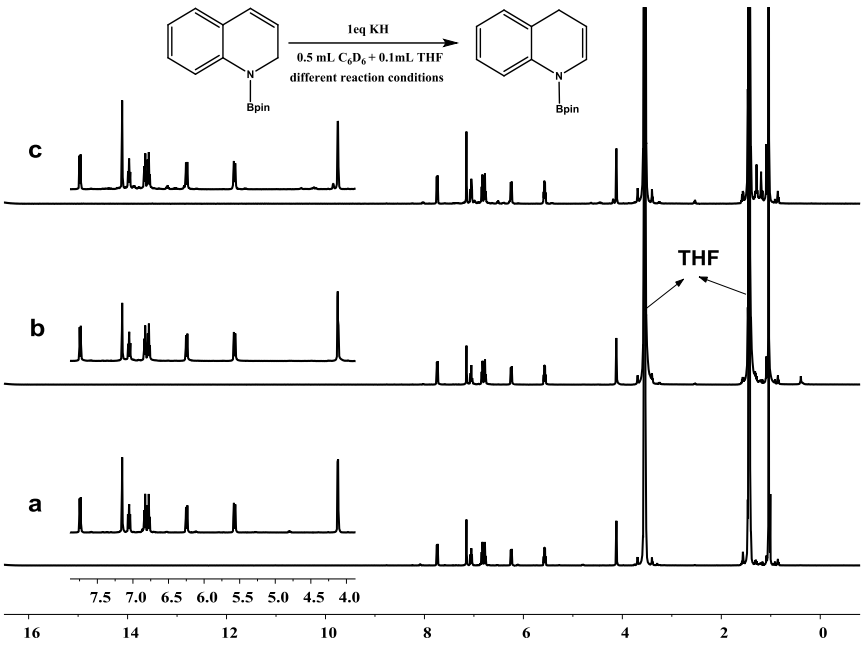


Figure S10. Overlay of ^{1}H NMR spectra for reaction heating at (a) T=50 ℃, t=24 h. (b) T=50 ℃, t=48 h. (c)

T=80 ℃, 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 C_6D_6 and 0.1 mL THF in a J. Young type NMR tube and heated at 50 ℃ for 24 h (Figure S11a) and 48 h (Figure S11b). Heating at 80 ℃ for 48 h did not transform **4a** to **5a** (Figure S11c).

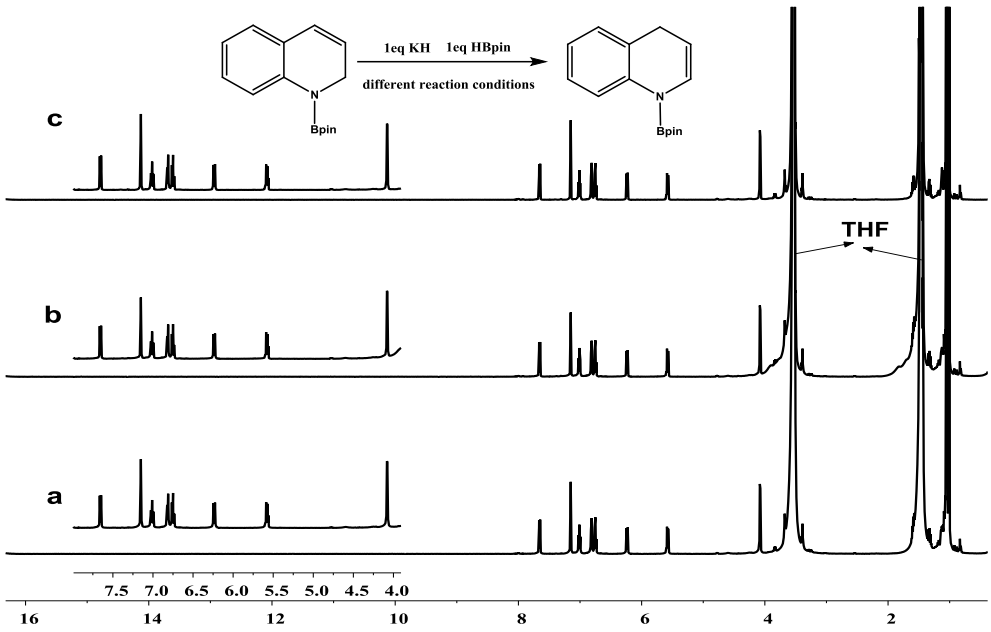
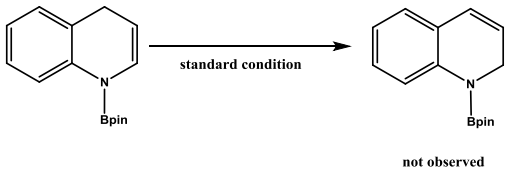


Figure S11. Overlay of ^{1}H NMR spectra for reaction carried out in the mixed solvents of 0.5 mL C_6D_6 and 0.15 mL THF (a). T=50 ℃, t=24 h (b) T=50 ℃, t=48 h.(c) T=80 ℃, t=48 h.

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 C_6D_6 and 0.15 mL THF in a J.Young type NMR tube. After heating at 50 ℃ 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**.

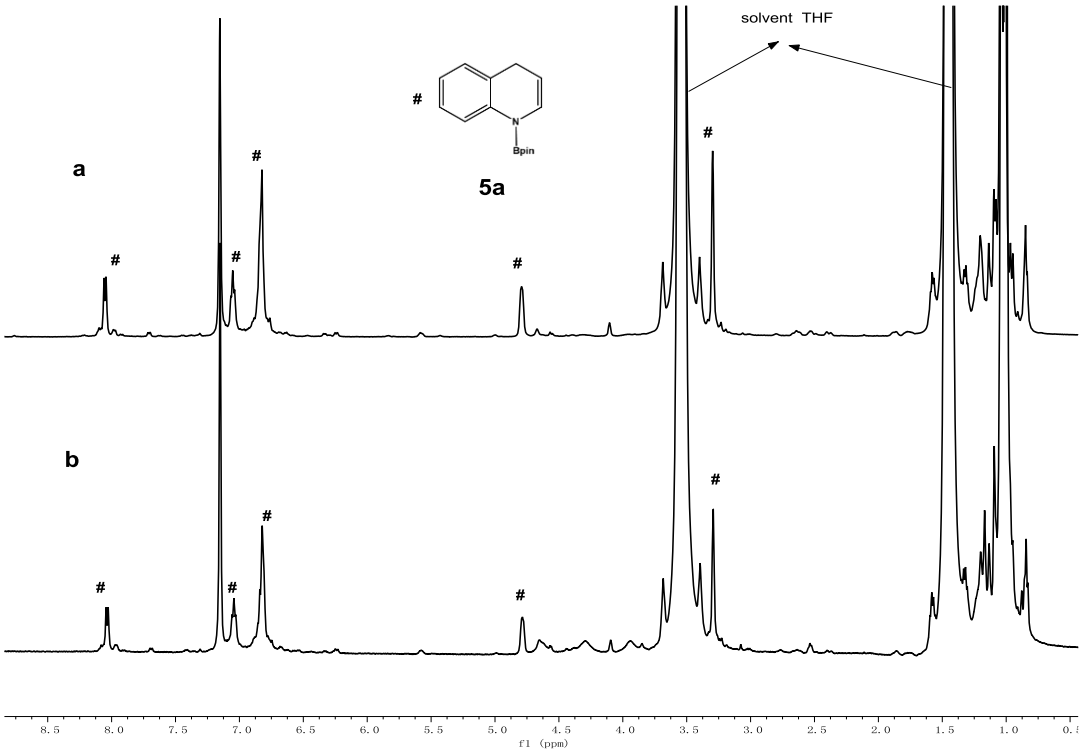
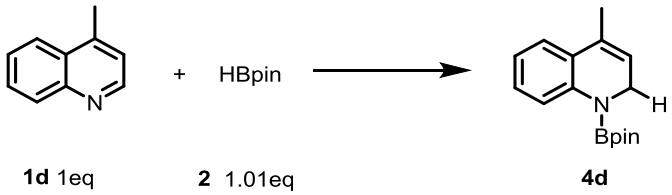


Figure S12. Overlay of ^{1}H NMR spectra for (a) **5a** in the mixed solvents. (b) HBpin and KH were added to (a) and then heated at 50 ℃ for 24 h.

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 ℃ for 24 h for recrystallization. Pure products was obtained as white solids (2.53 g, 93% yield).

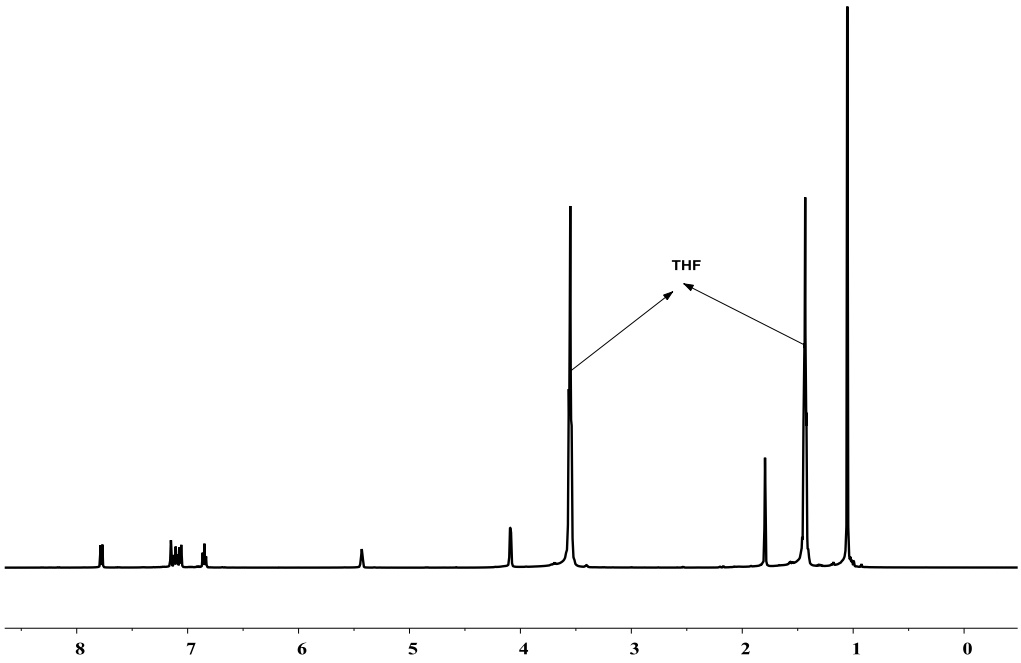
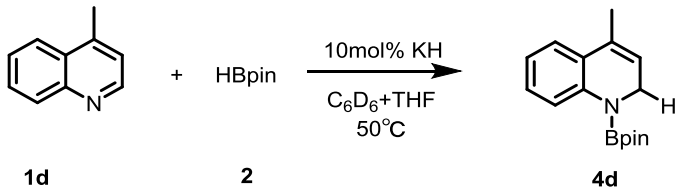


Figure S13. ^{1}H NMR spectrum of the reaction mixture of preparative scale experiment.

10. **Long-life catalytic performance of the KH-catalyzed hydroboration of 1d**



1d **2** **4d**

In a glovebox, KH (10 mol%, 0.4 mg) was added to a solution (0.5 mL C_6D_6 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 ℃ for 24 h and NMR measurement, another batch of 4-methylquinoline, HBpin and mesitylene in 0.075 mL C_6D_6 and 0.025 mL THF were added to the reaction system and continue screening the catalytic activity. This process was repeated 7 times.

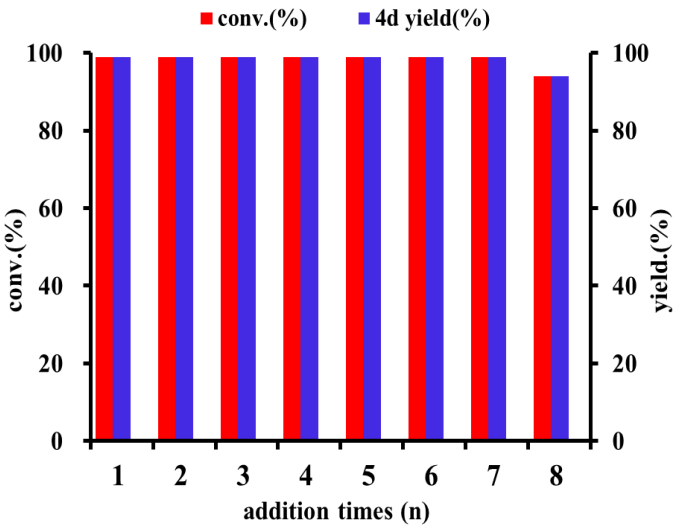
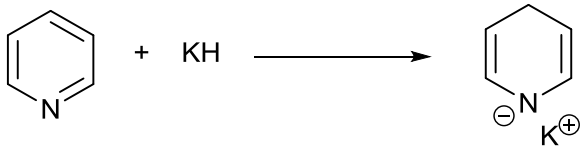


Figure S14 Long-life catalytic performance of the KH-catalyzed hydroboration of **1d**

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 ℃ 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**.



1r 3g

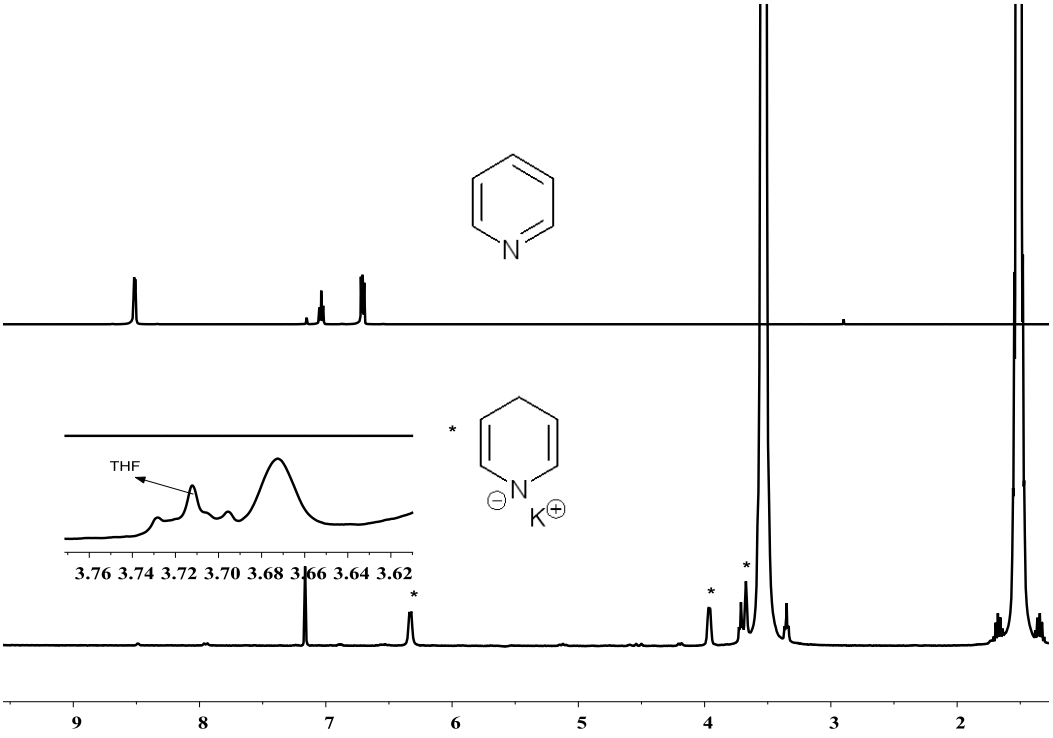
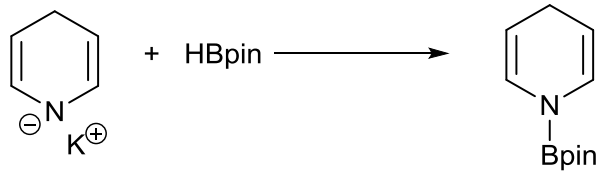


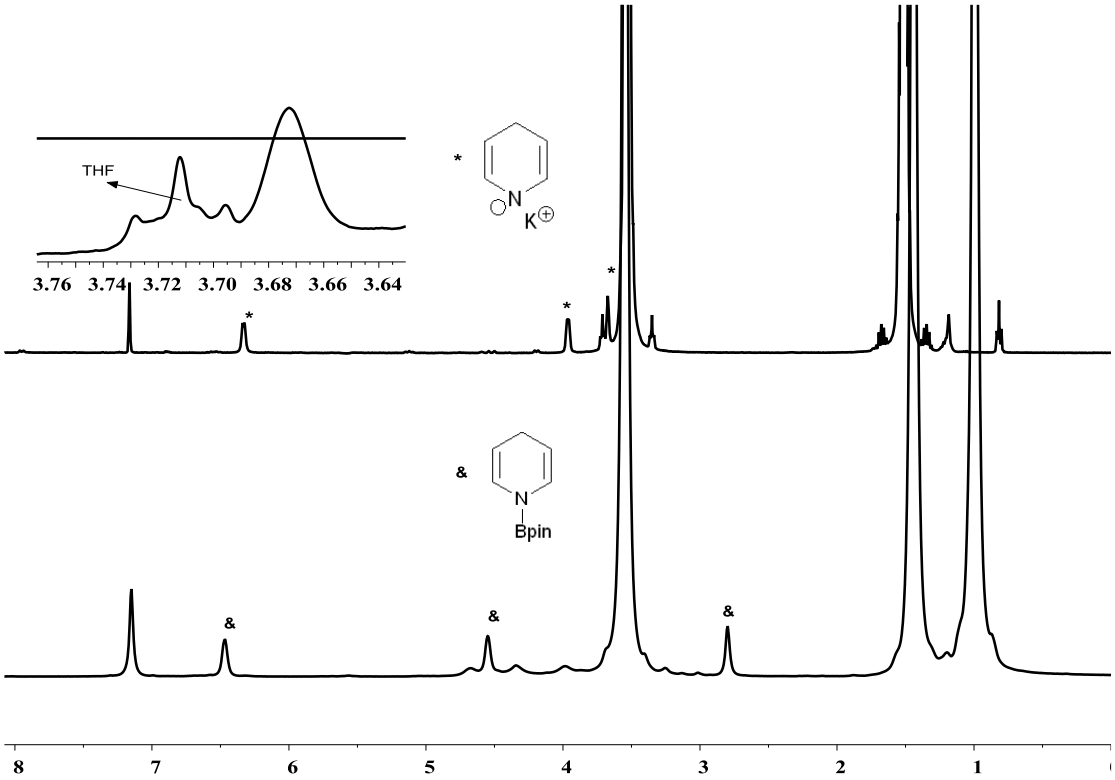
Figure S15. Overlay of ^{1}H NMR spectra for **1r** (top) and the reaction of **1r** and KH (bottom).

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**.

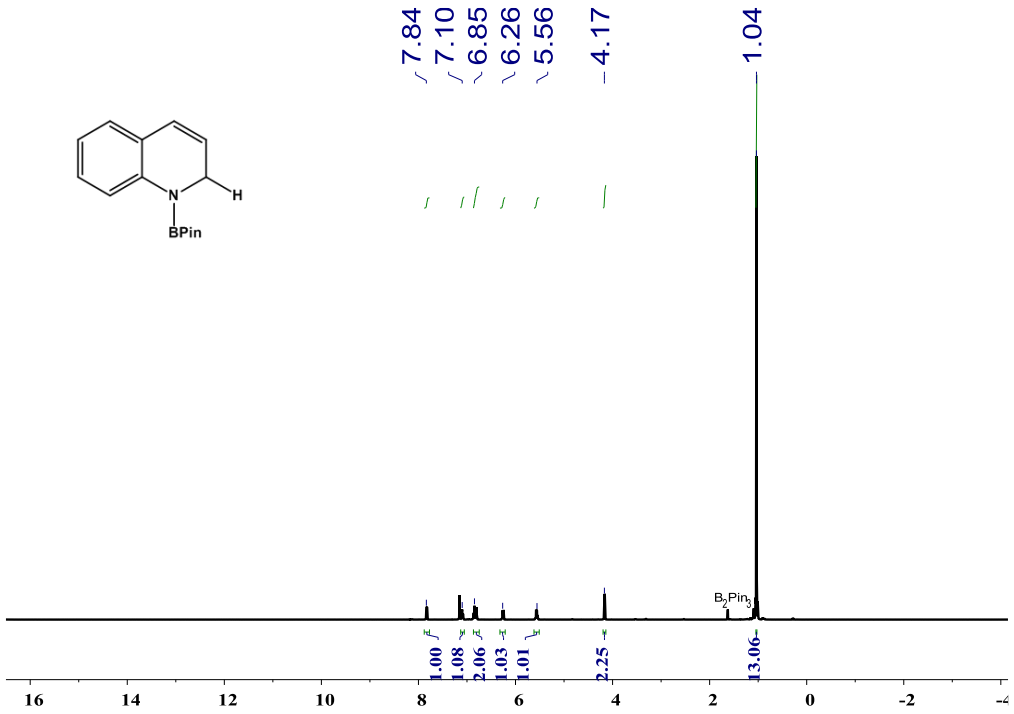


3g 2a 7a

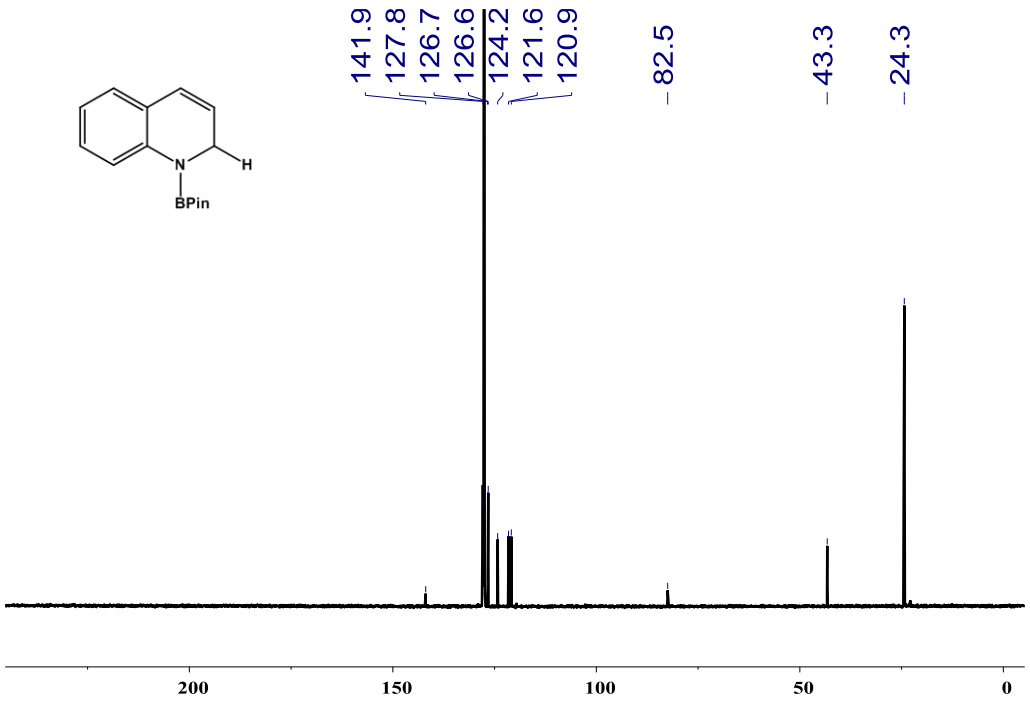


FigureS16 [1]H NMR spectrum for intermediate **3g** in-situ generated from the reaction of **1r** and KH (top) and reaction of intermediate **3g** with HBpin (bottom)

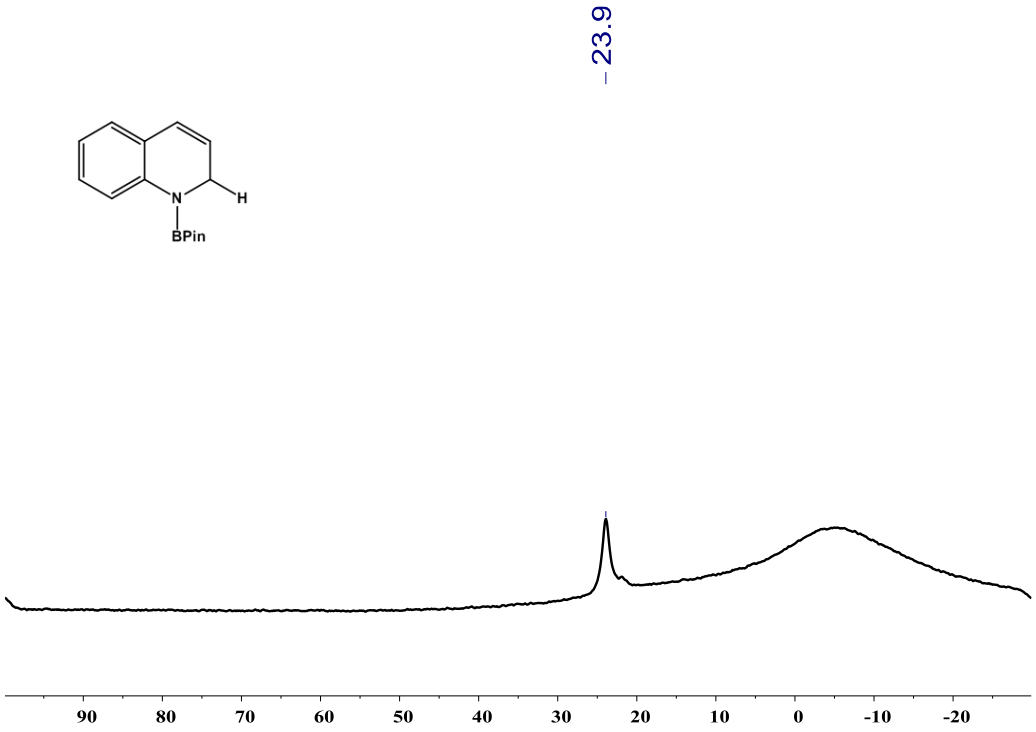
13. NMR spectra



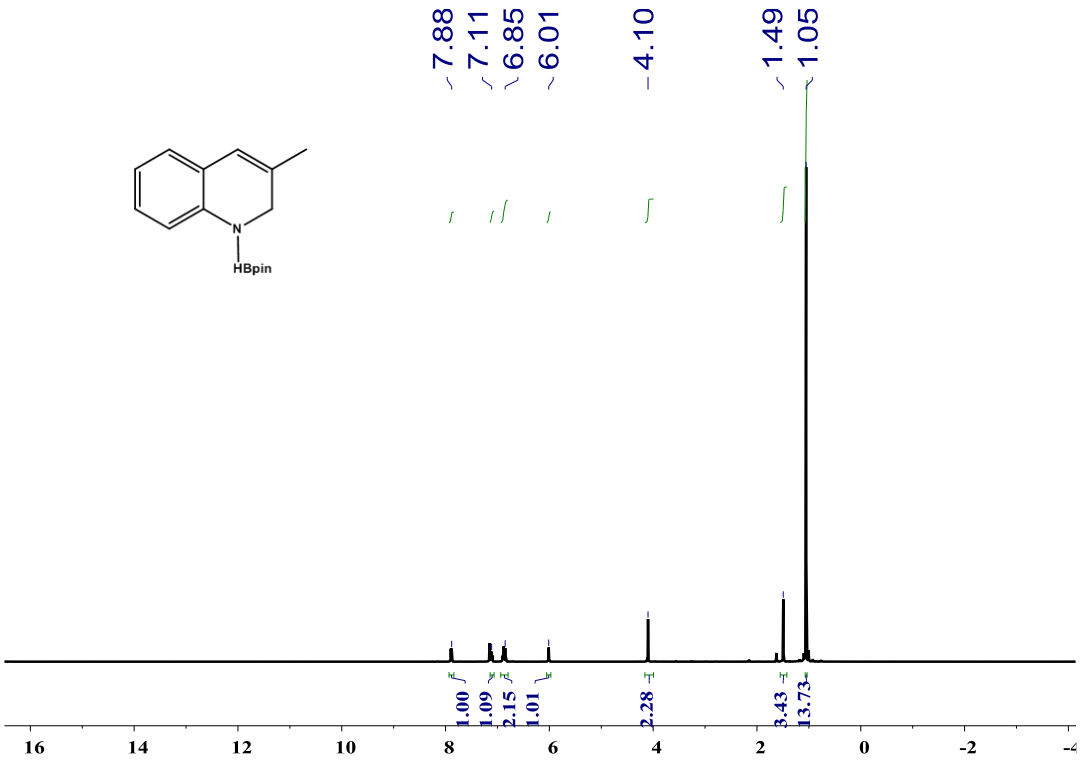
[1]H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl-1,2-dihydroquinoline (**4a**) (500 MHz, C_6D_6)



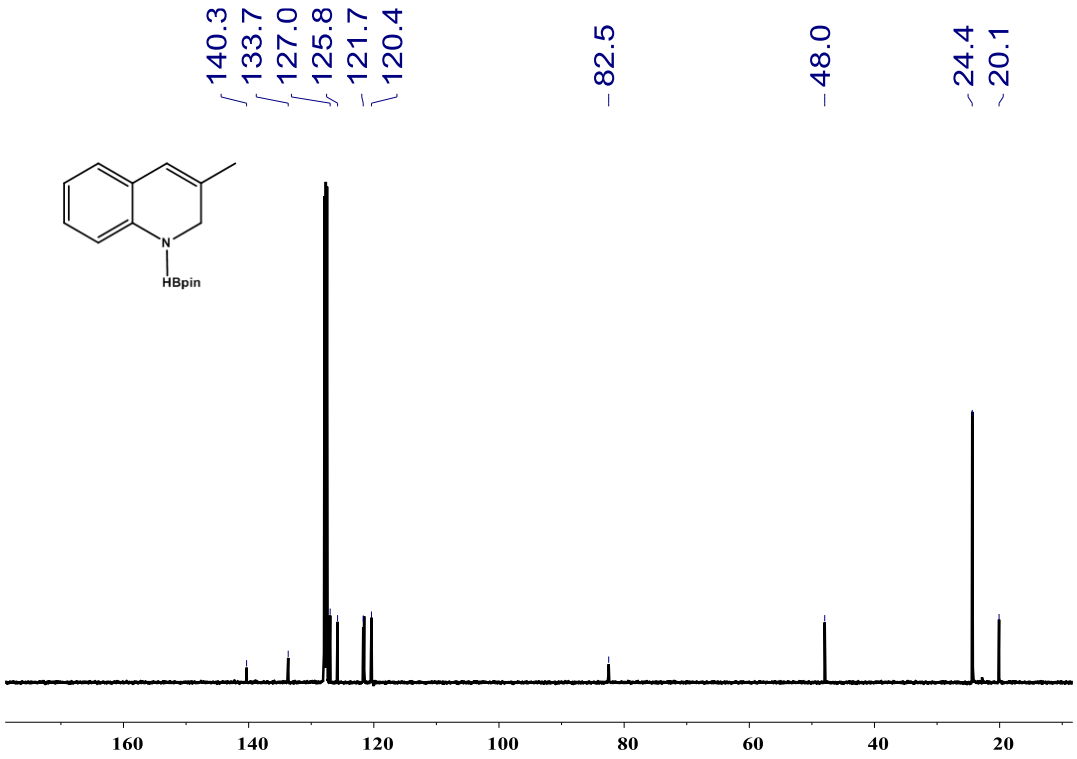
^{13}C NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -1,2-dihydroquinoline (**4a**) (126 MHz, C_6D_6)



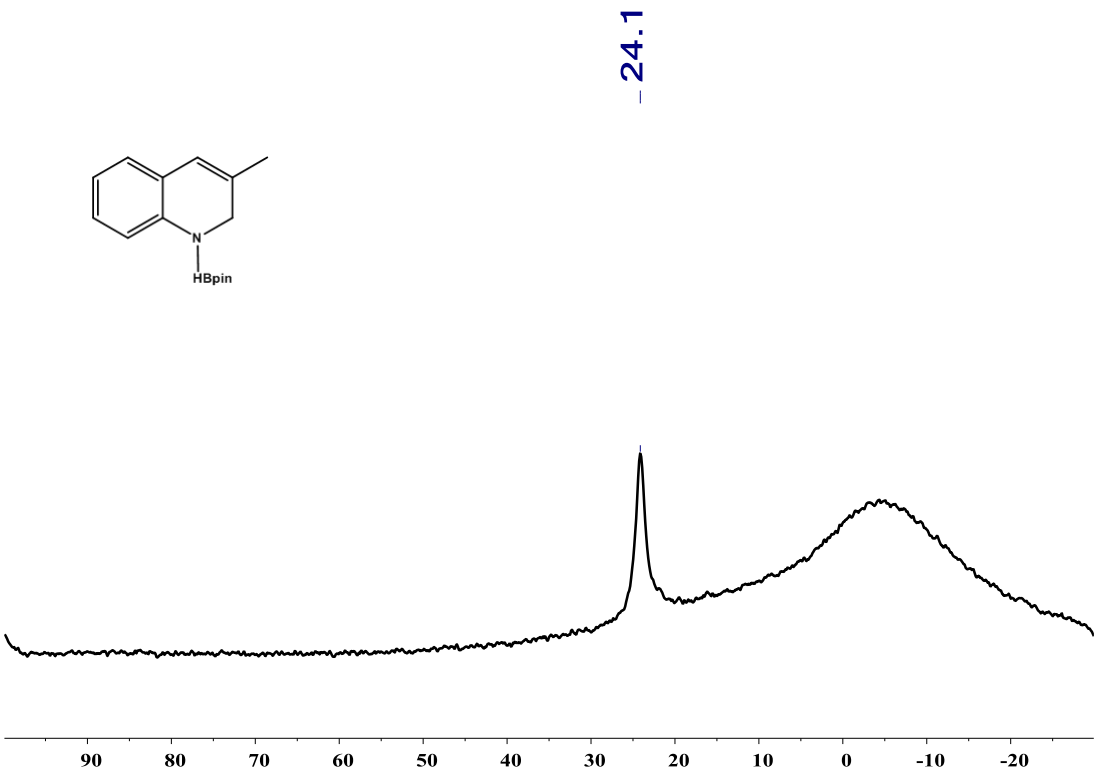
^{11}B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4a**) (160 MHz, C_6D_6).



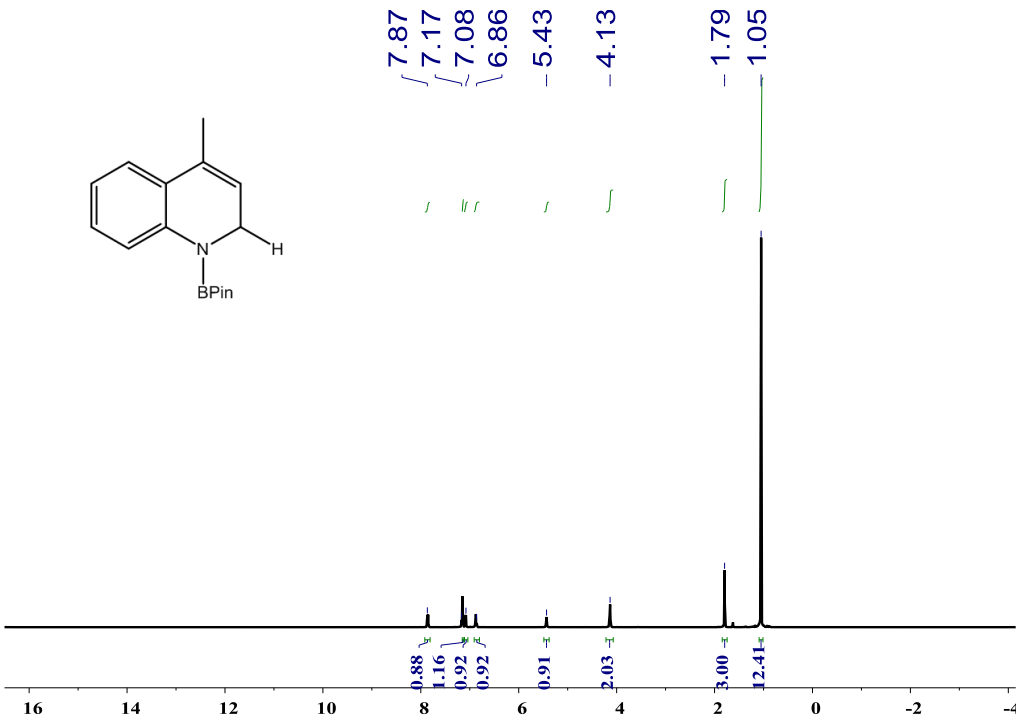
^{1}H NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4c**) (500 MHz, C_6D_6



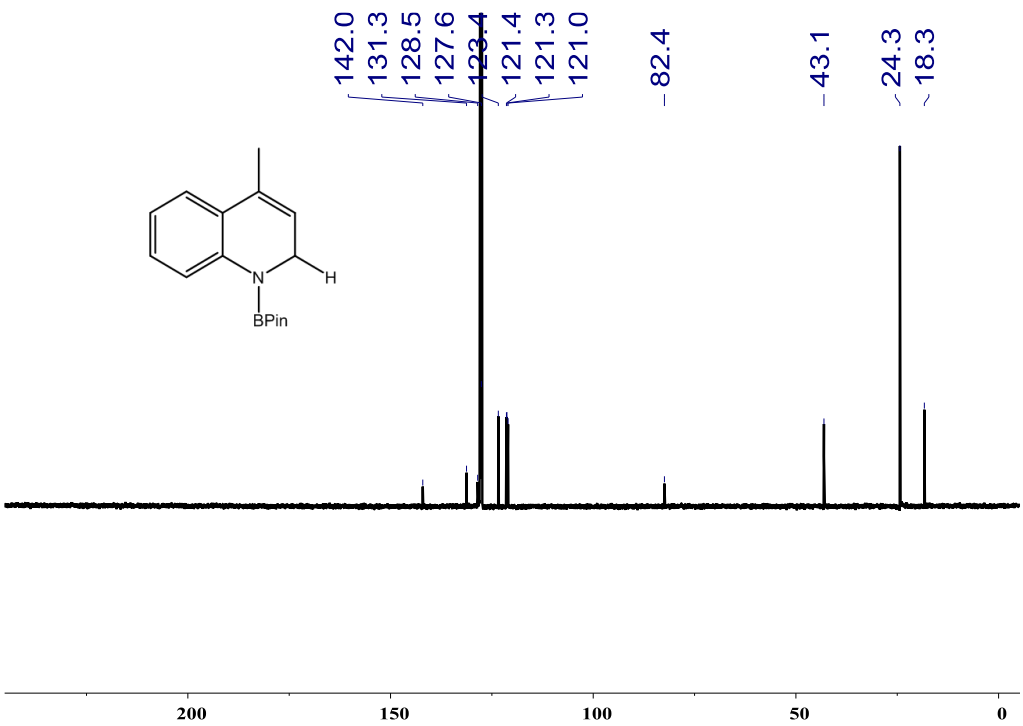
^{13}C NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydro quinoline (**4c**) (126 MHz, C_6D_6)



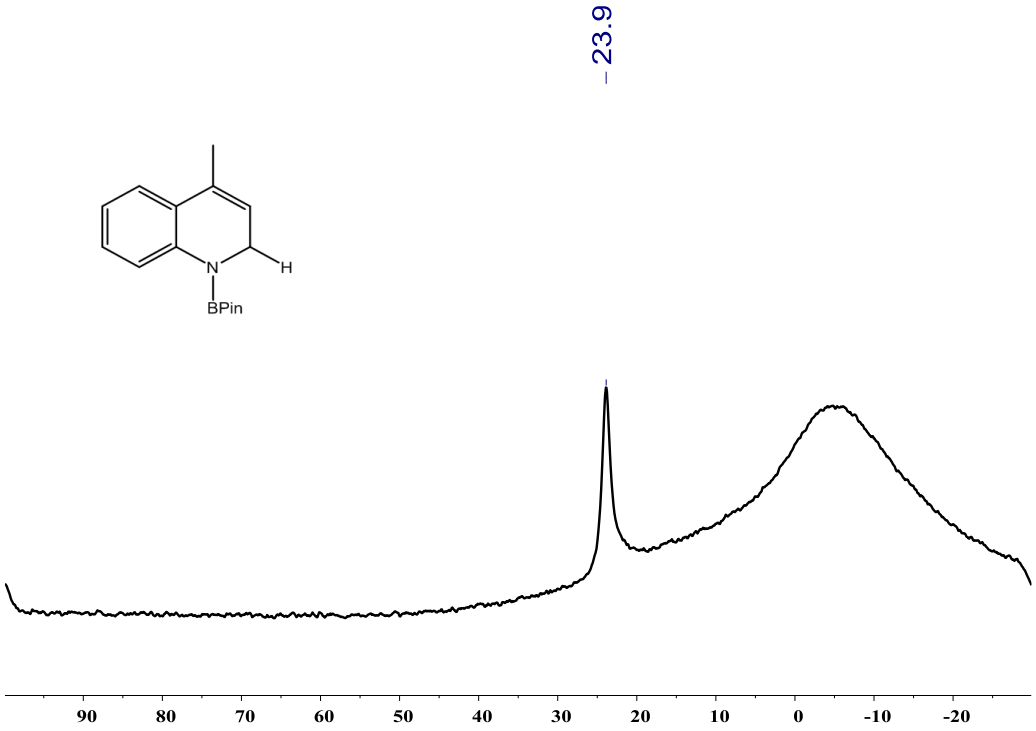
[11]B NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydro quinoline (**4c**) (160 MHz, C_6D_6,).



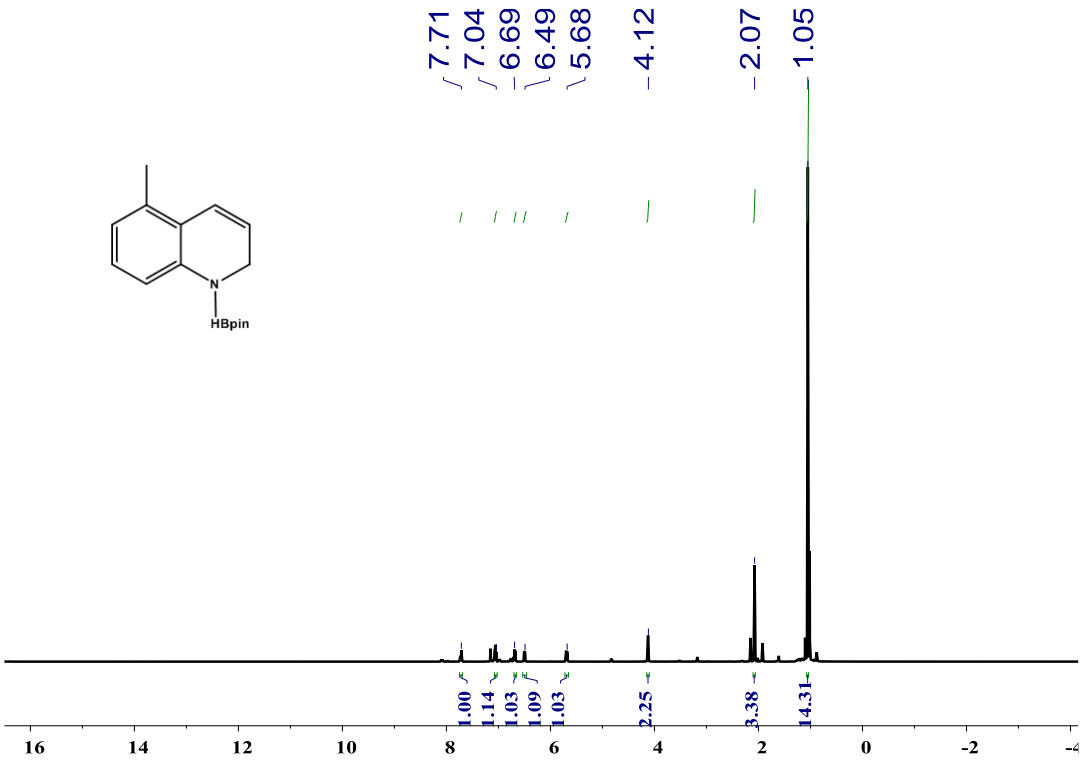
[1]H NMR spectrum of 4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4d**) (500 MHz, C_6D_6)



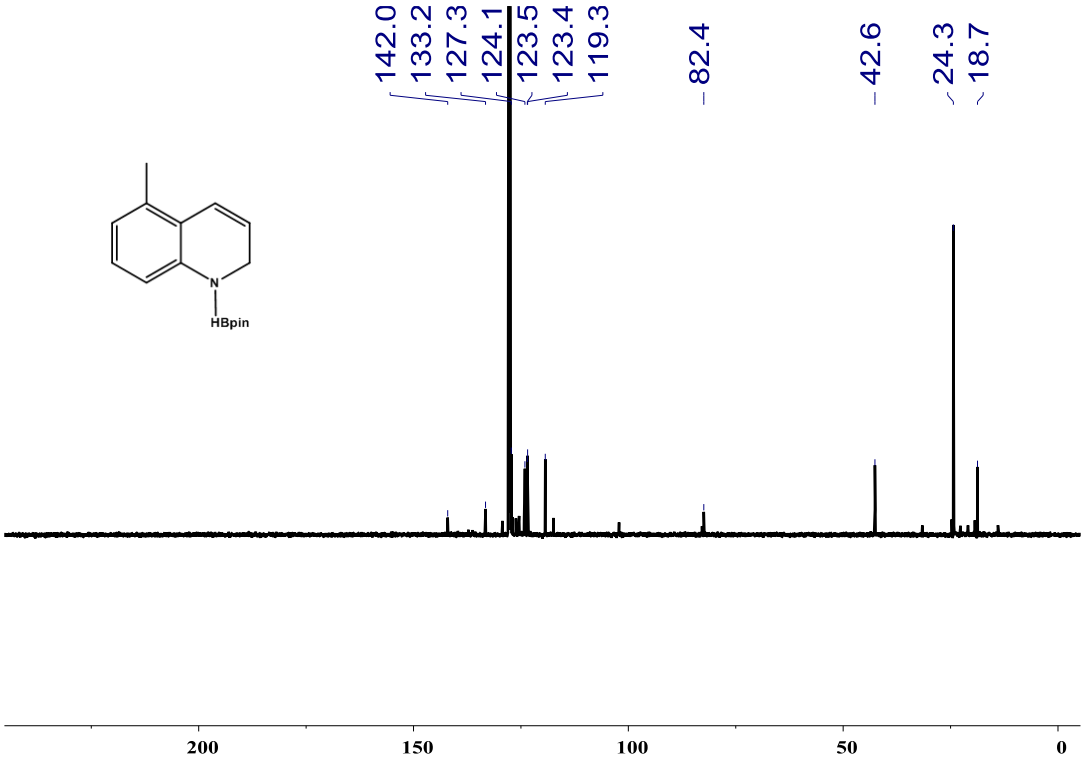
^{13}C NMR spectrum of 4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4d**) (126 MHz, C_6D_6)



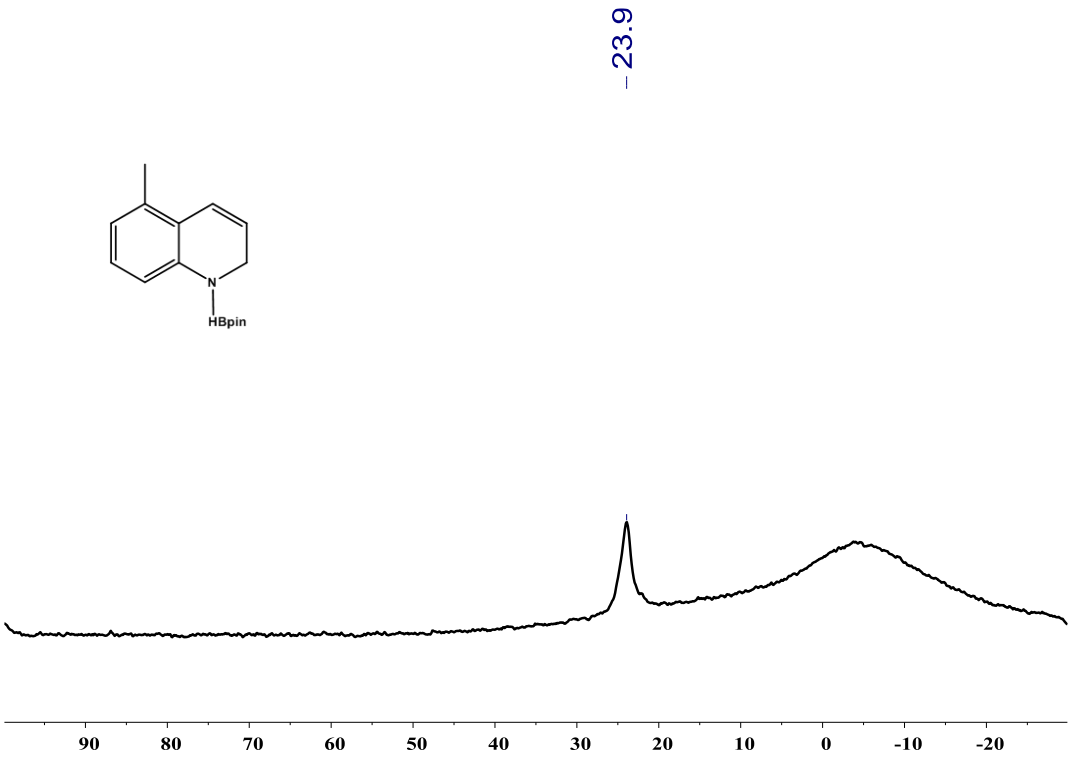
^{11}B NMR spectrum of 4-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4d**) (160 MHz, C_6D_6,).



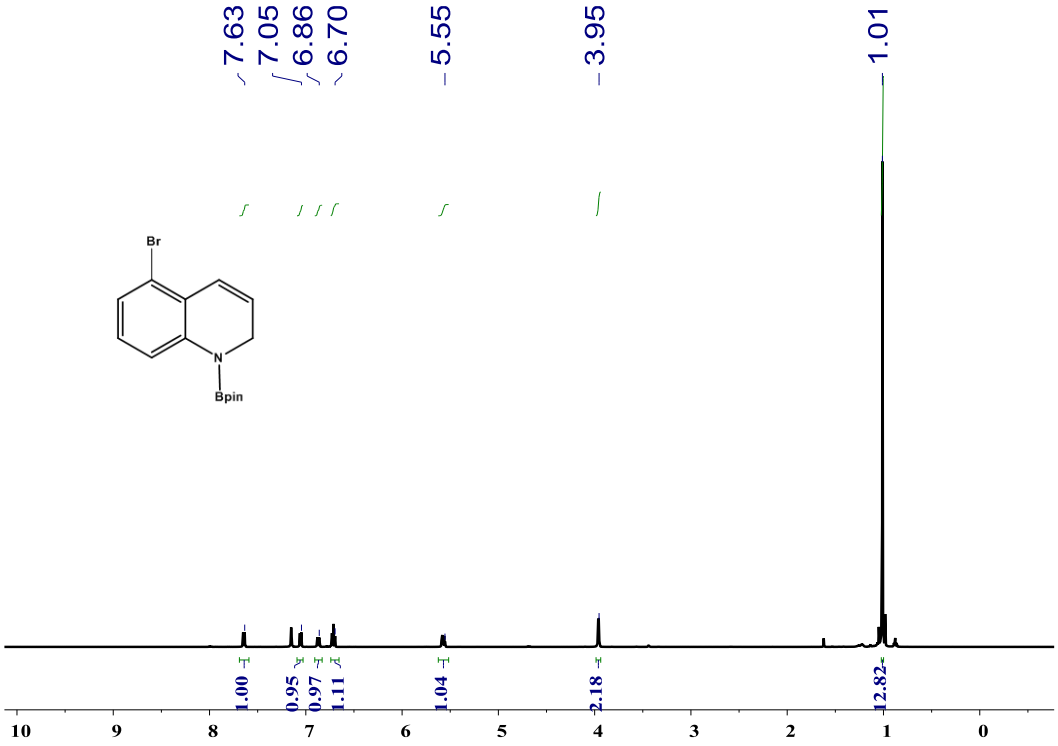
^{1}H NMR spectrum of 5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4e**) (500 MHz, C_6D_6)



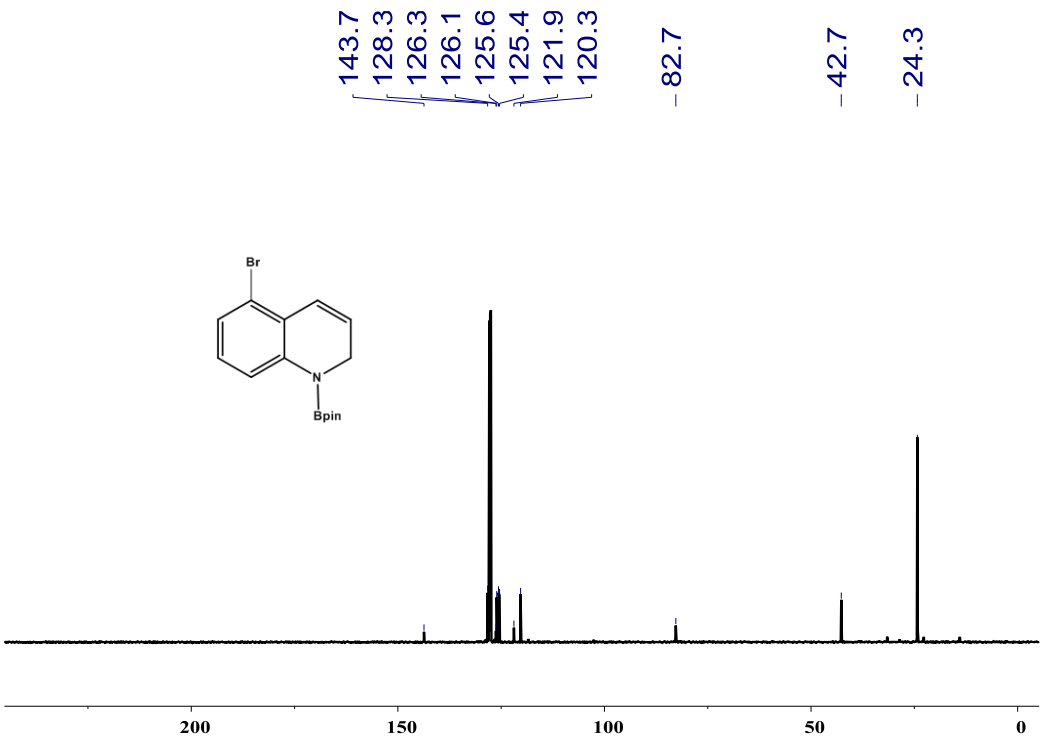
^{13}C NMR spectrum of 5- methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4e**) (126 MHz, C_6D_6)



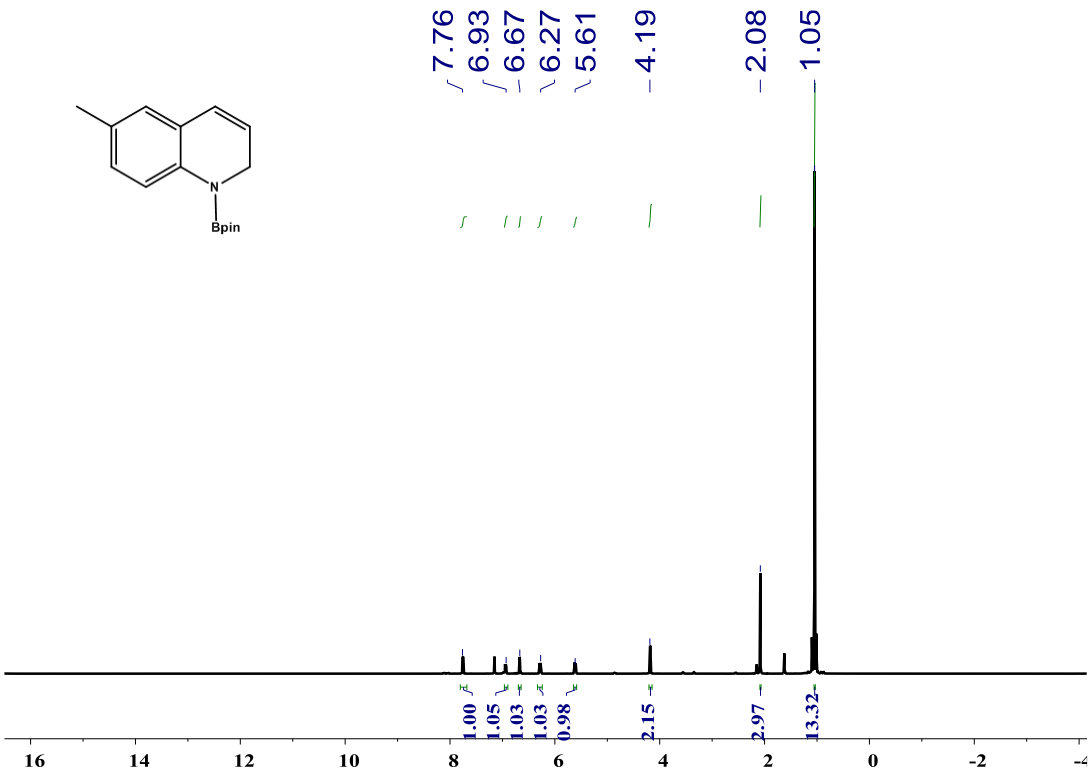
^{11}B NMR spectrum of 5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4e**) (160 MHz, C_6D_6).



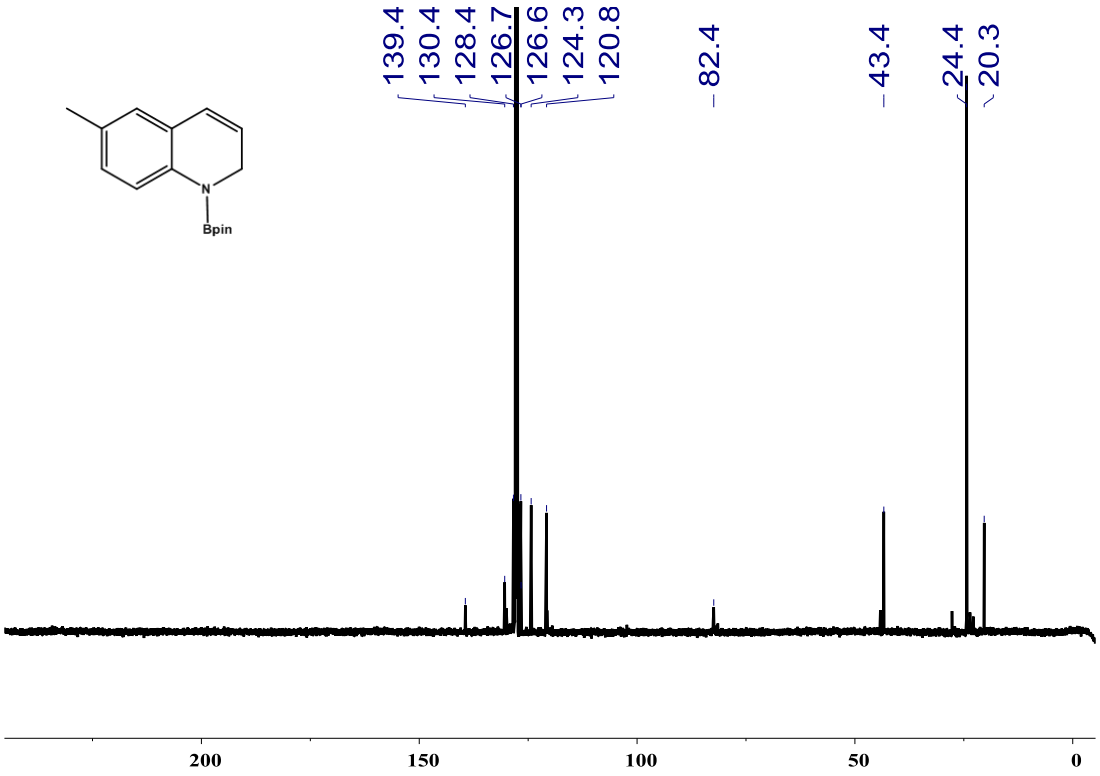
^{1}HNMR spectrum of 5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4j**) (500 MHz, C_6D_6)



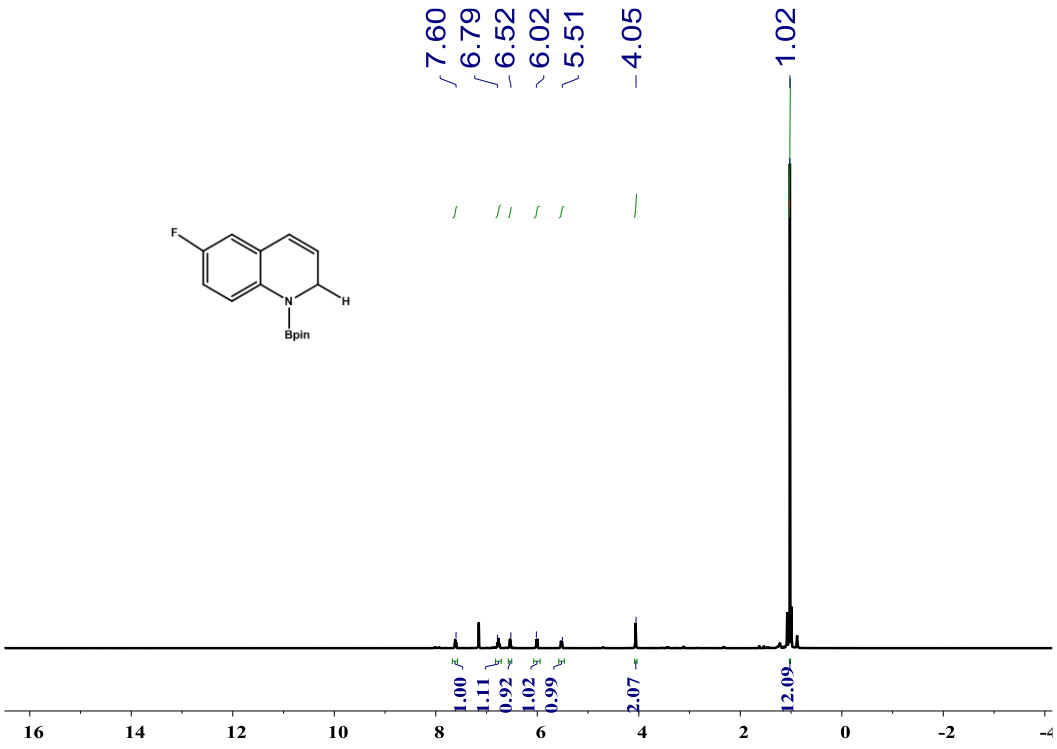
^{13}C NMR spectrum of 5-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4j**) (126 MHz, C_6D_6)



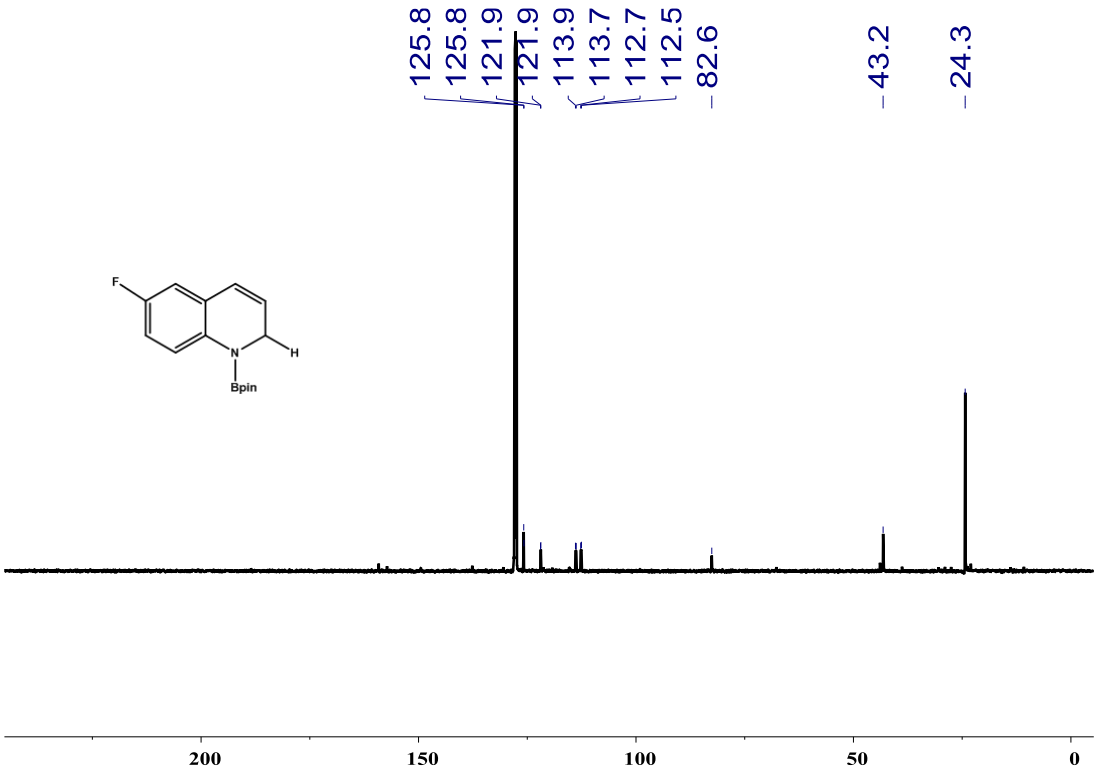
^{1}H NMR spectrum of 6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4f**) (500 MHz, C_6D_6)



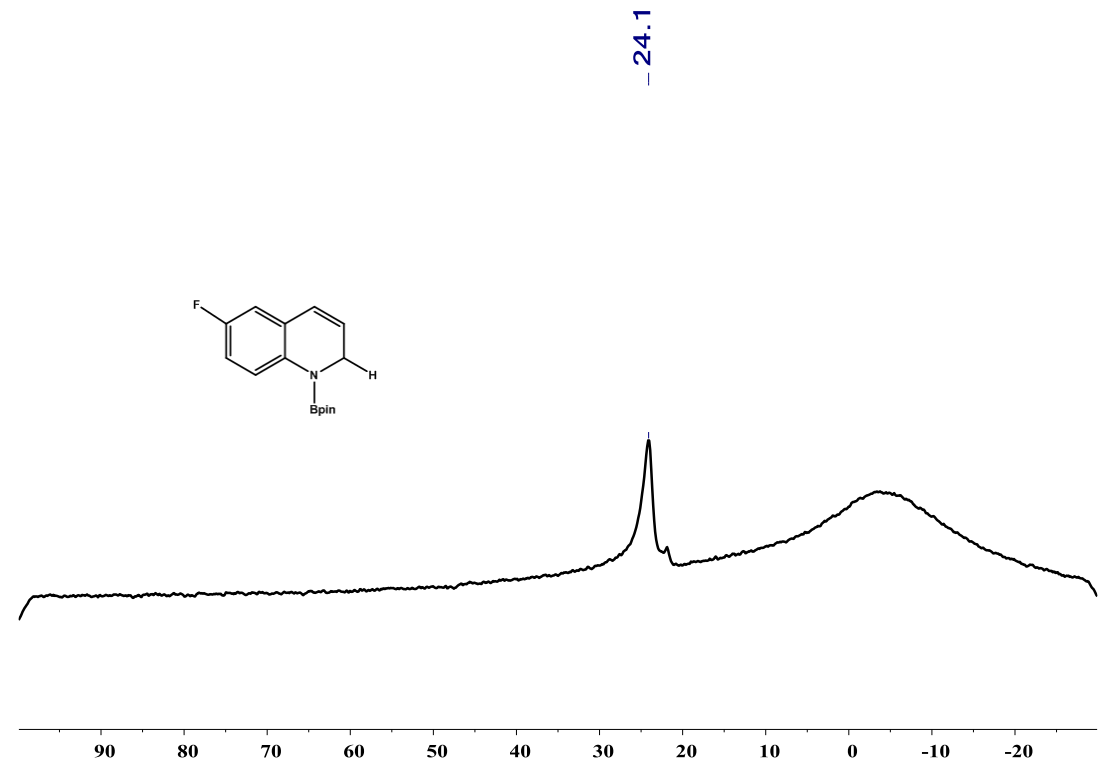
^{13}C NMR spectrum of 6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4f**) (126 MHz, C_6D_6)



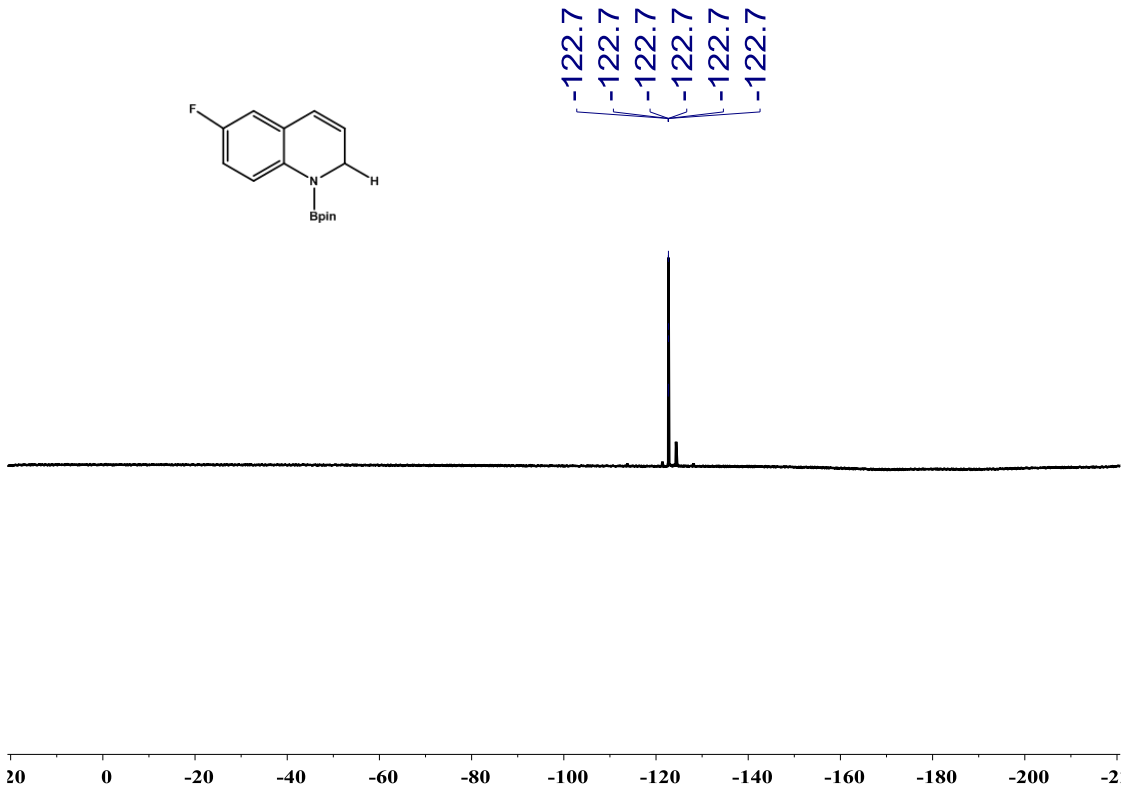
^{1}H NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4k**) (500 MHz, C_6D_6)



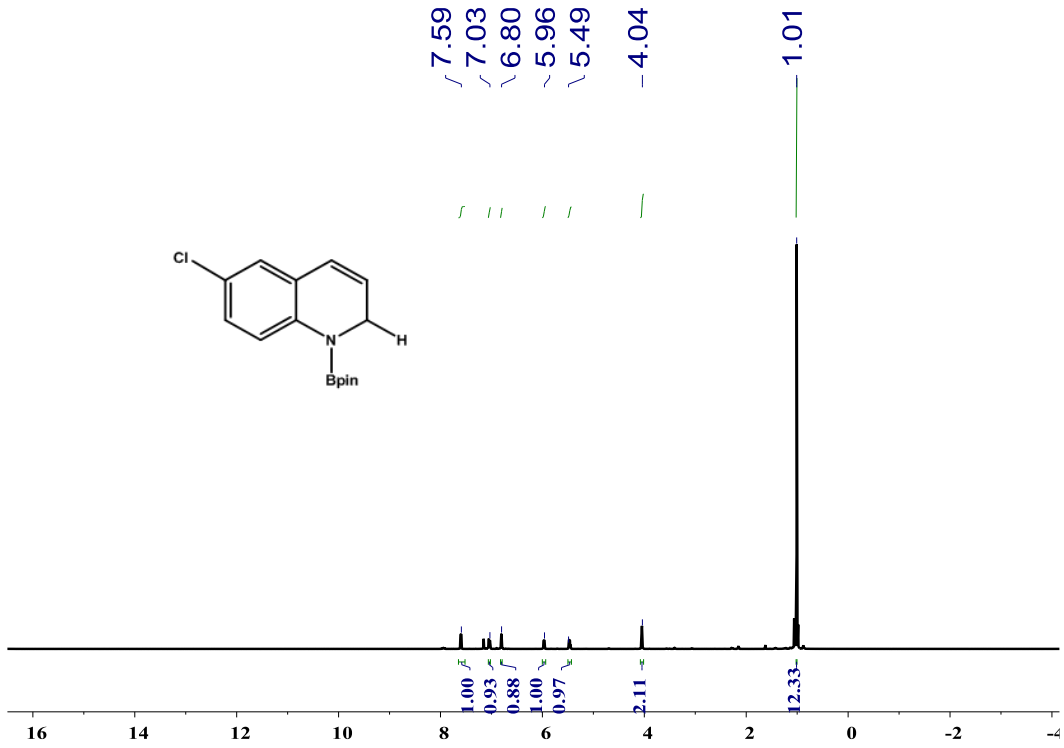
^{3}C NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4k**) (126 MHz, C_6D_6)



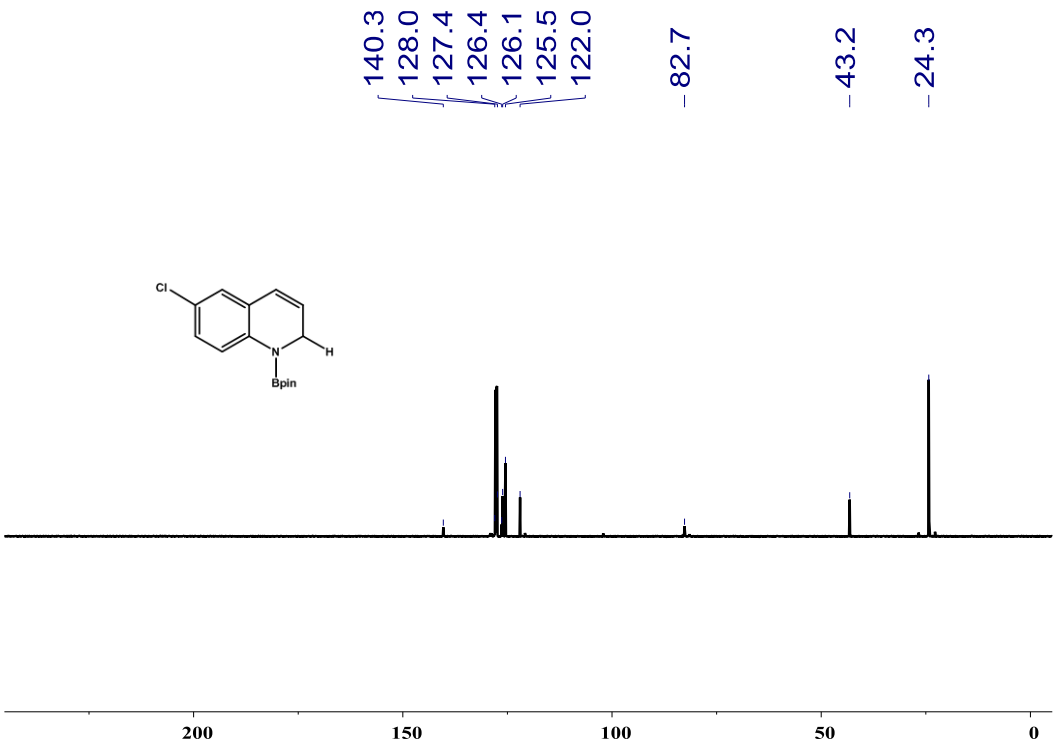
^{11}B NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl-1,2-dihydroquinoline (**4k**) (160 MHz, C_6D_6).



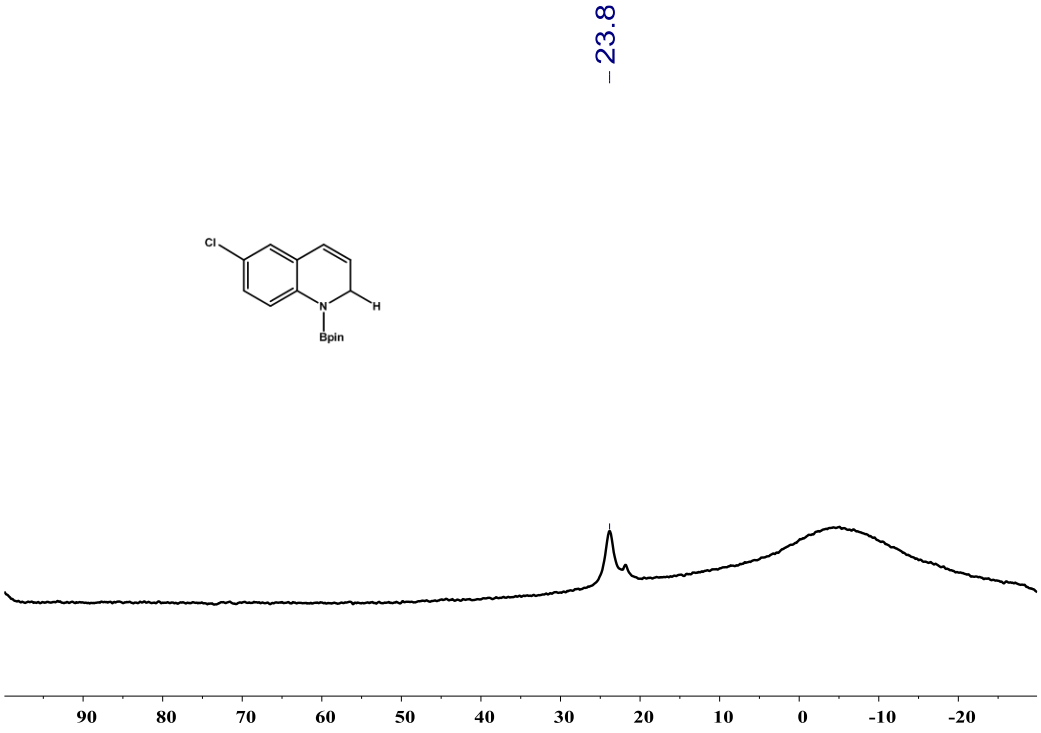
^{19}F NMR spectrum of 6-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4k**) (147 MHz, C_6D_6).



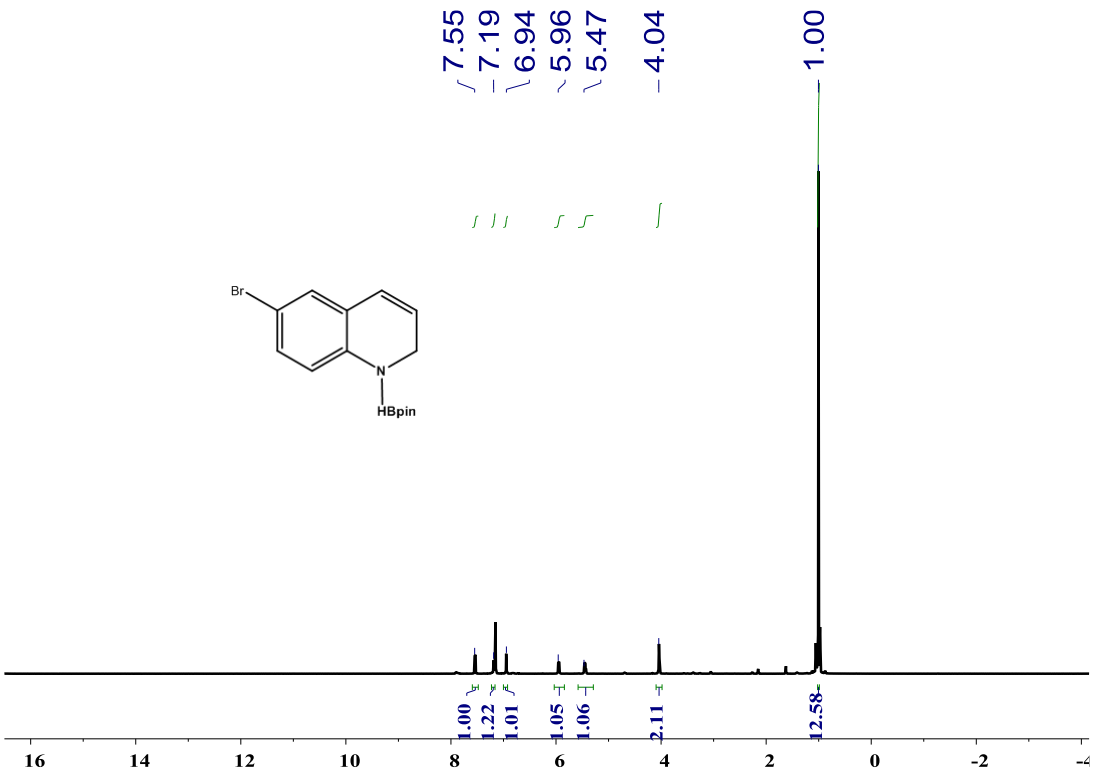
^{1}HNMR spectrum of 6-chloro -1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4l**) (500 MHz, C_6D_6)



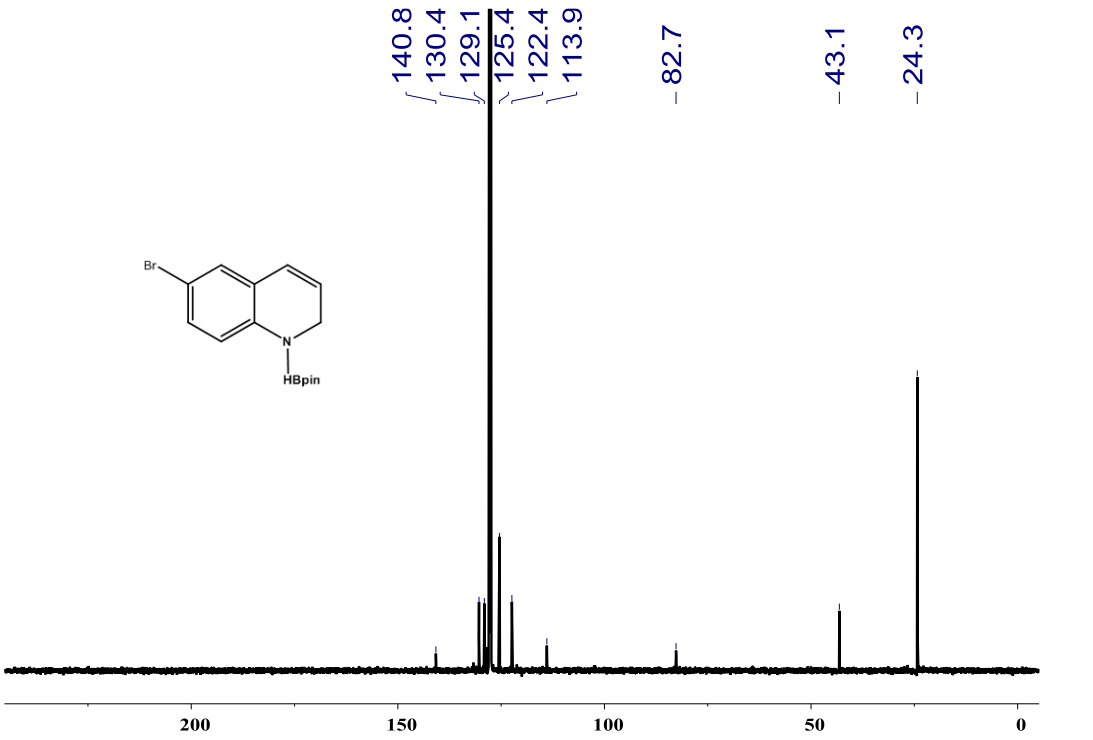
^{13}C NMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl-1,2-dihydroquinoline (**4l**) (126 MHz, C_6D_6)



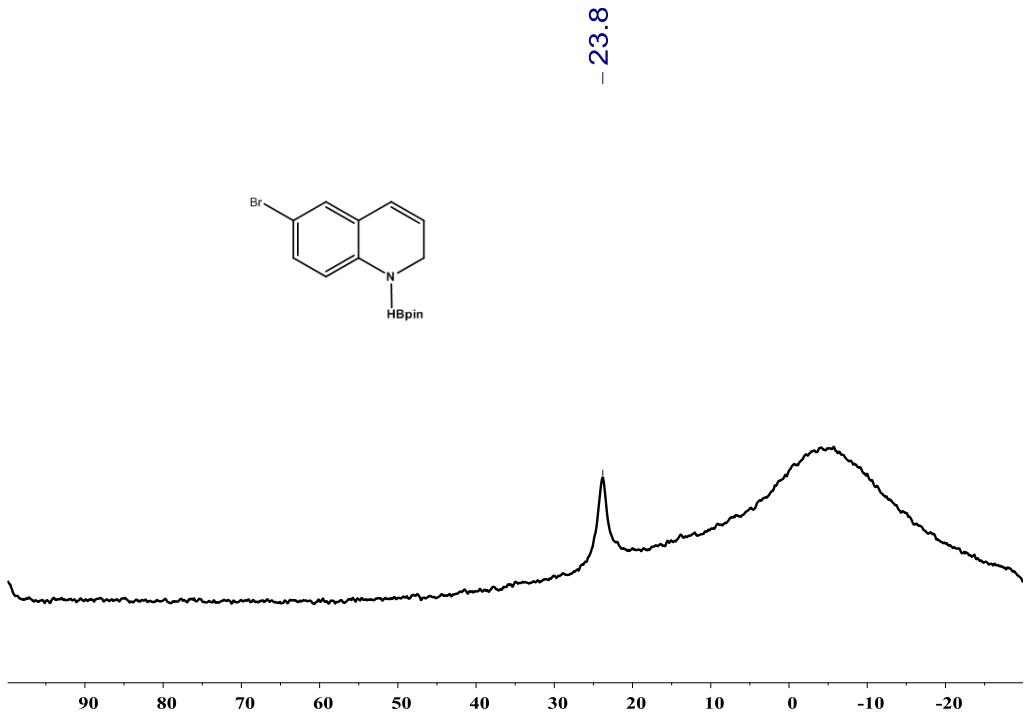
^{11}B NMR spectrum of 6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4l**) (160 MHz, C_6D_6).



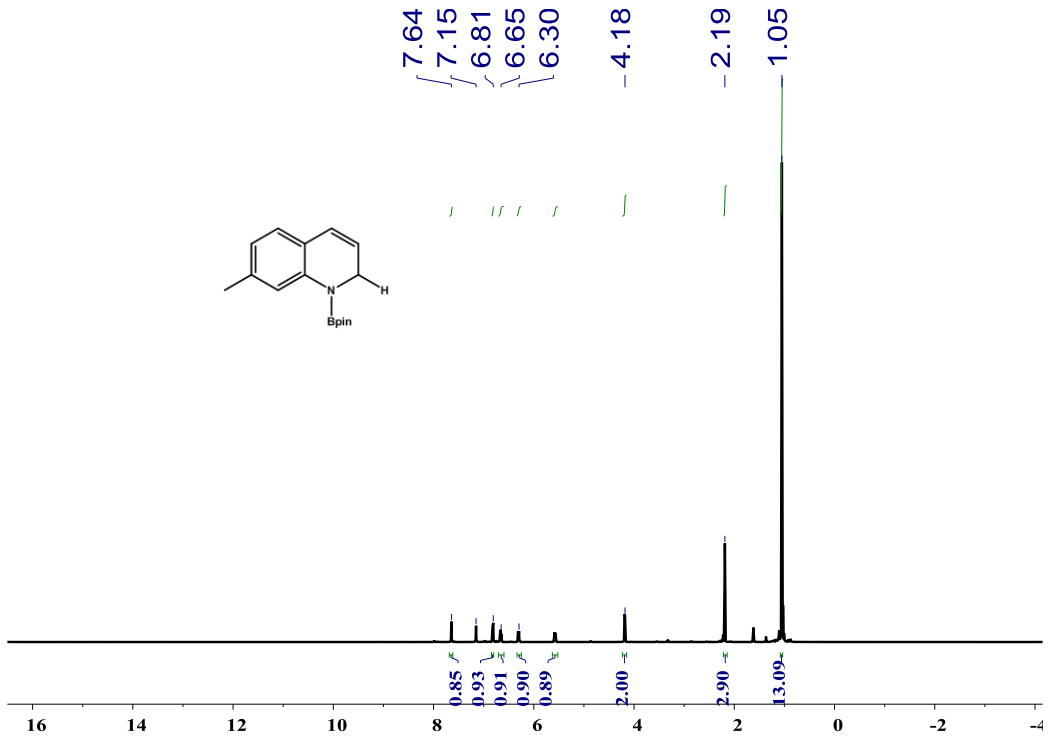
^{1}H NMR spectrum of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4m**) (500 MHz, C_6D_6)



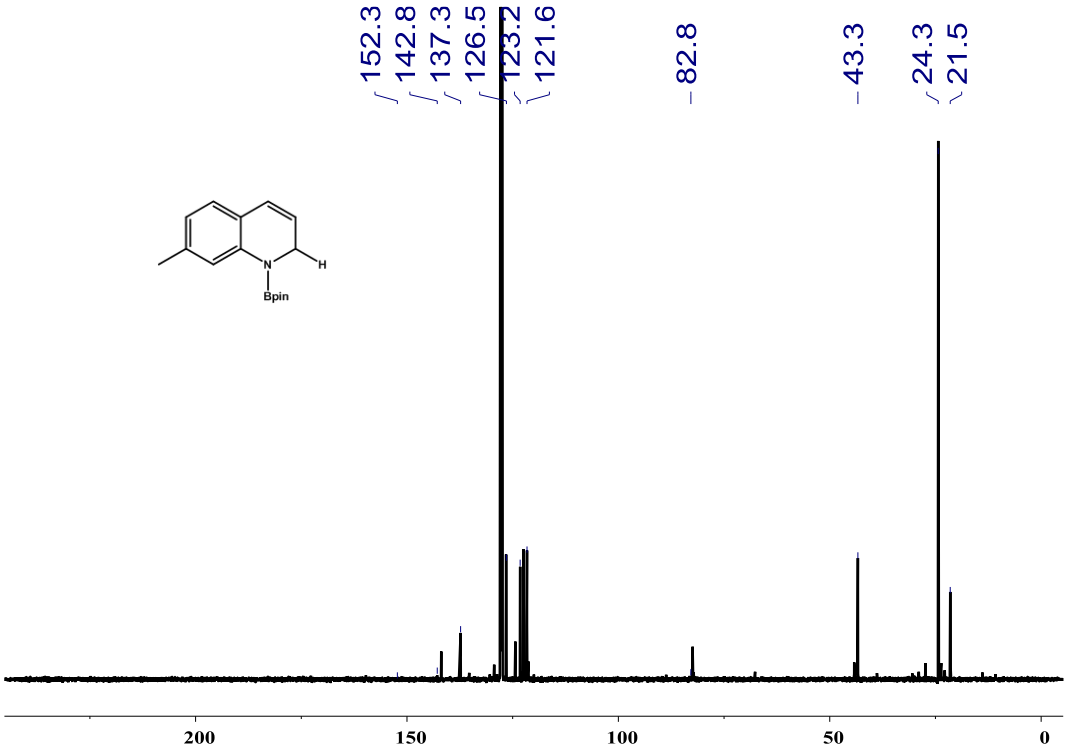
^{13}C NMR spectrum of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4m**) (126 MHz, C_6D_6)



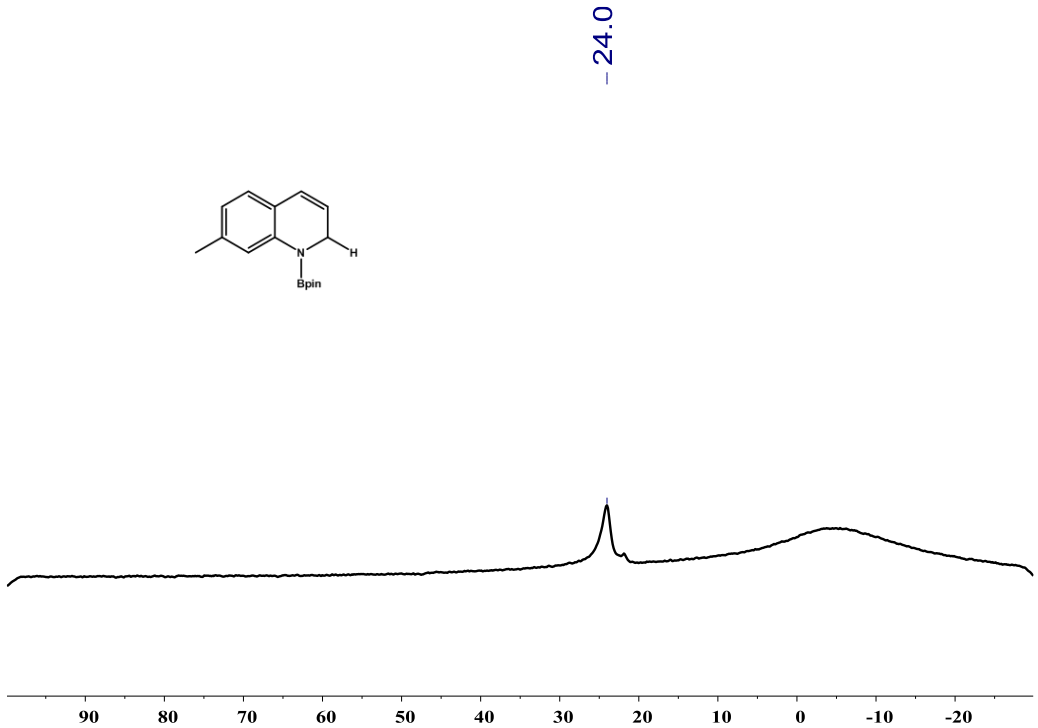
^{11}B NMR spectrum of 6-bromo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4m**) (160 MHz, C_6D_6).



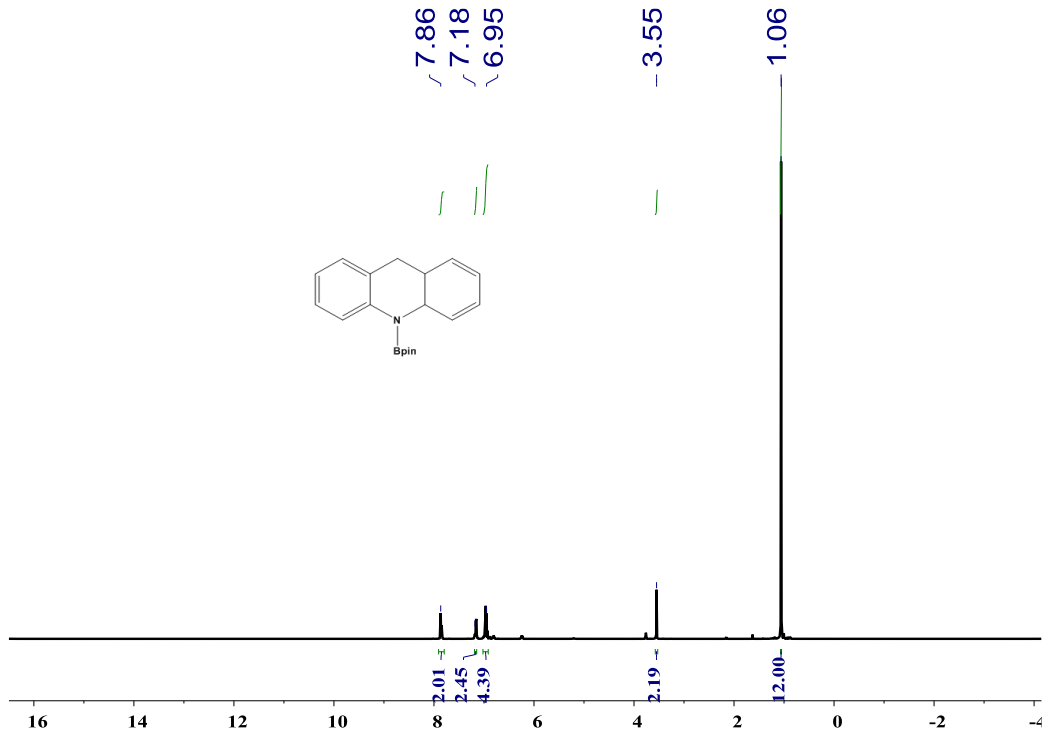
^{1}H NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4g**) (500 MHz, C_6D_6)



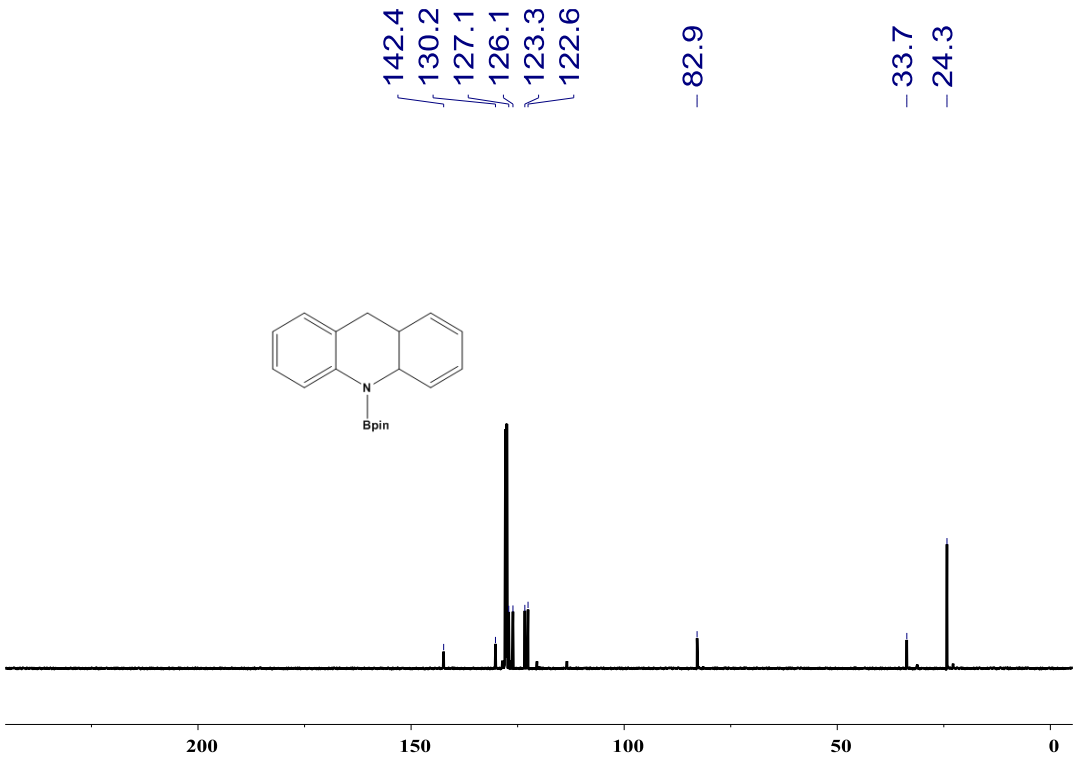
^{13}C NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4g**) (126 MHz, C_6D_6)



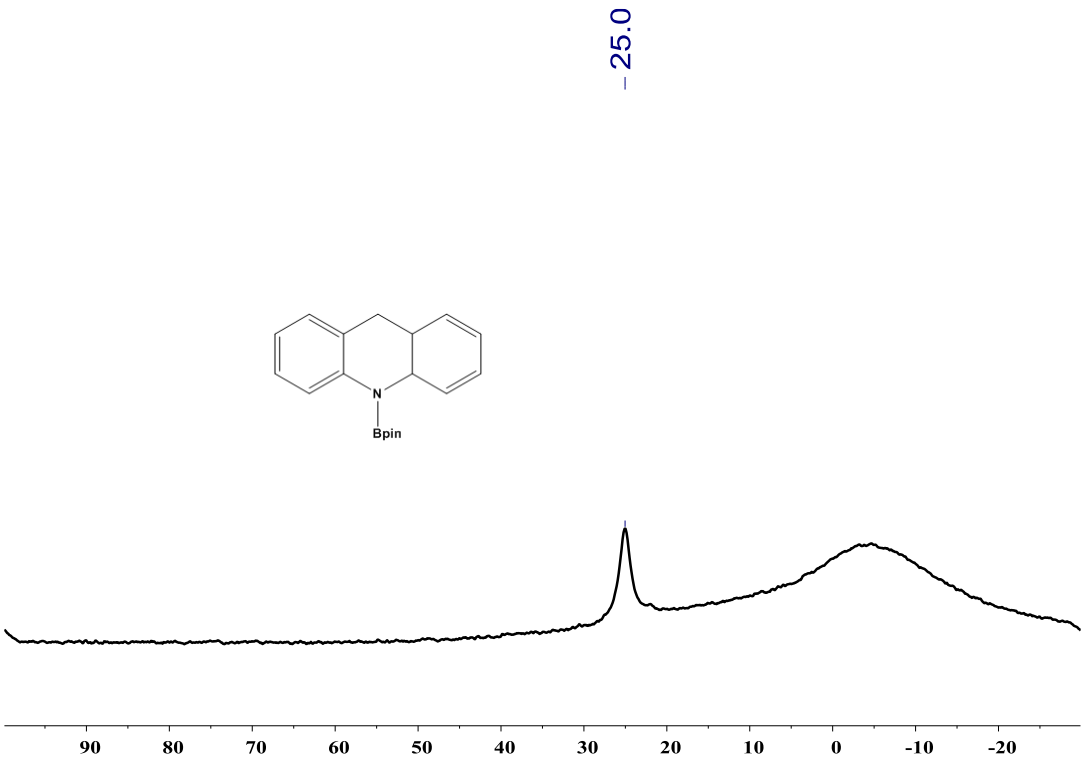
^{11}B NMR spectrum of 7-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline (**4g**) (160 MHz, C_6D_6).



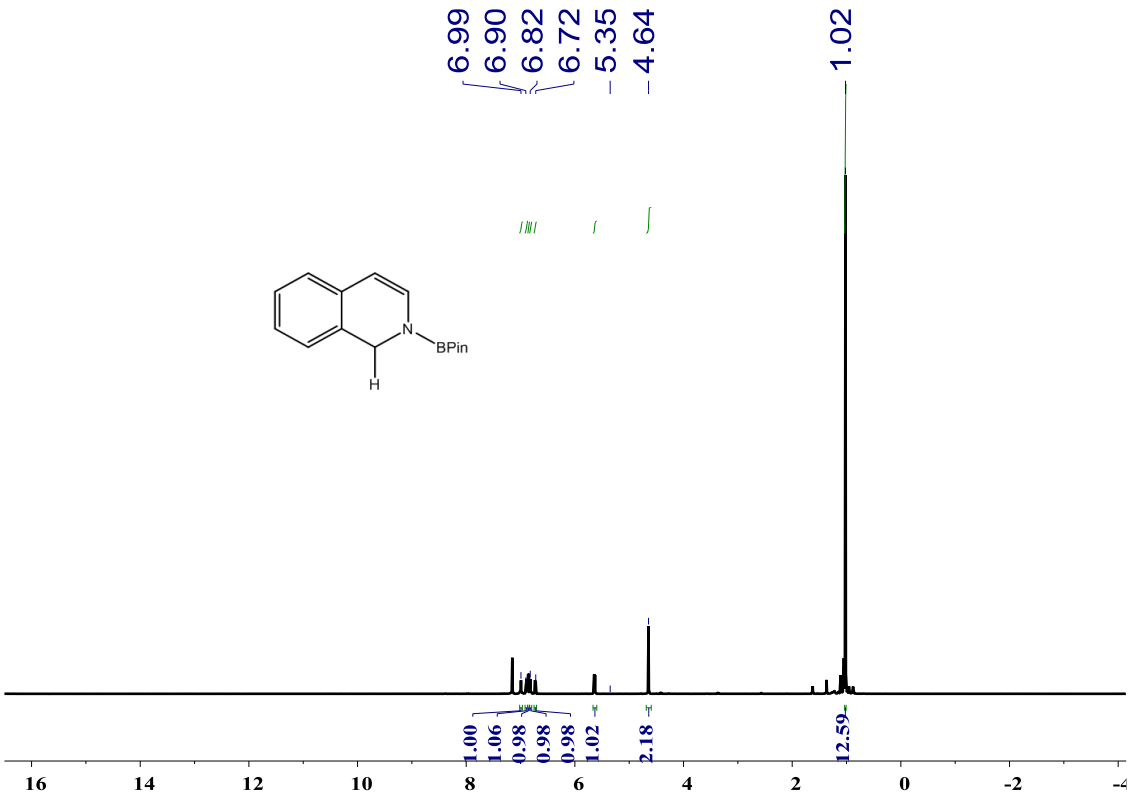
^{1}H NMR spectrum of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9,9a,10-tetrahydroacridine (**9**) (500 MHz, C_6D_6)



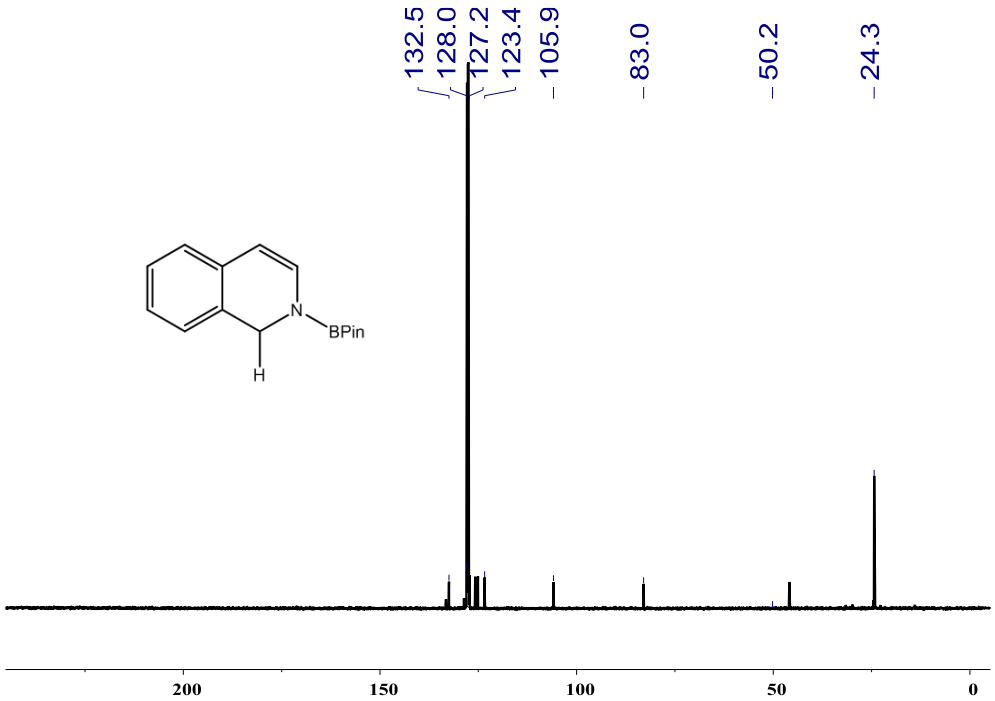
^{13}C NMR spectrum of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9,9a,10-tetrahydroacridine (**9**) (126 MHz, C_6D_6)



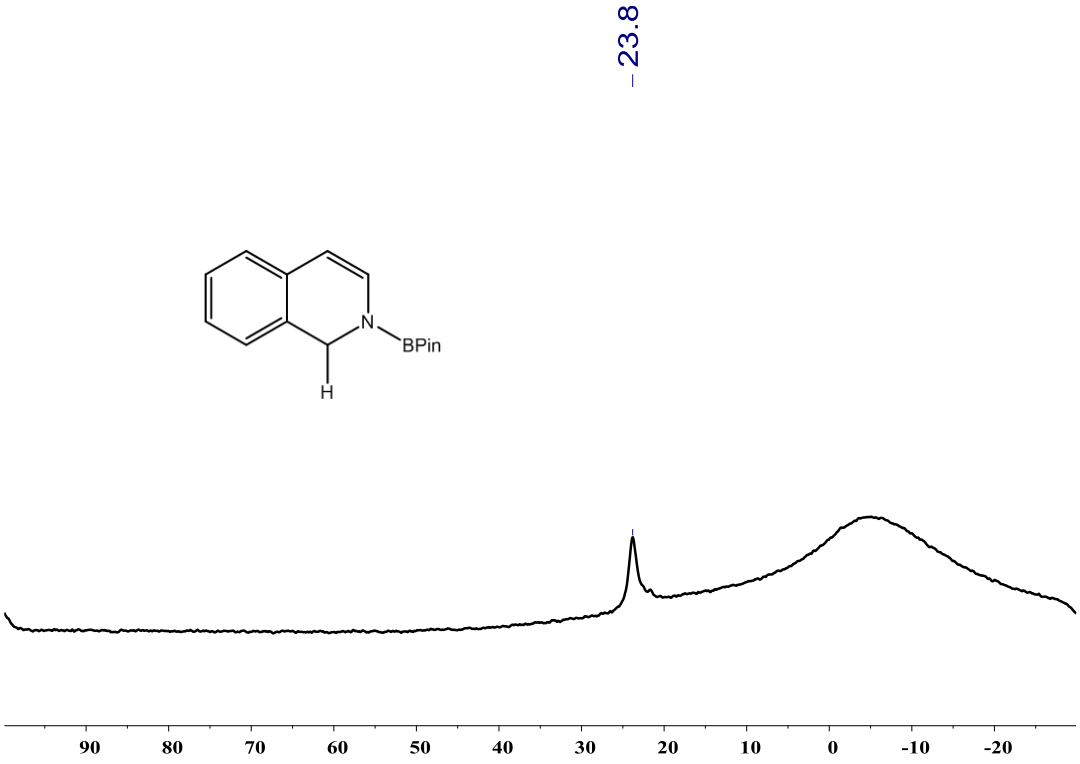
^{11}B NMR spectrum of 10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4a,9,9a,10-tetrahydroacridine (**9**) (160 MHz, C_6D_6).



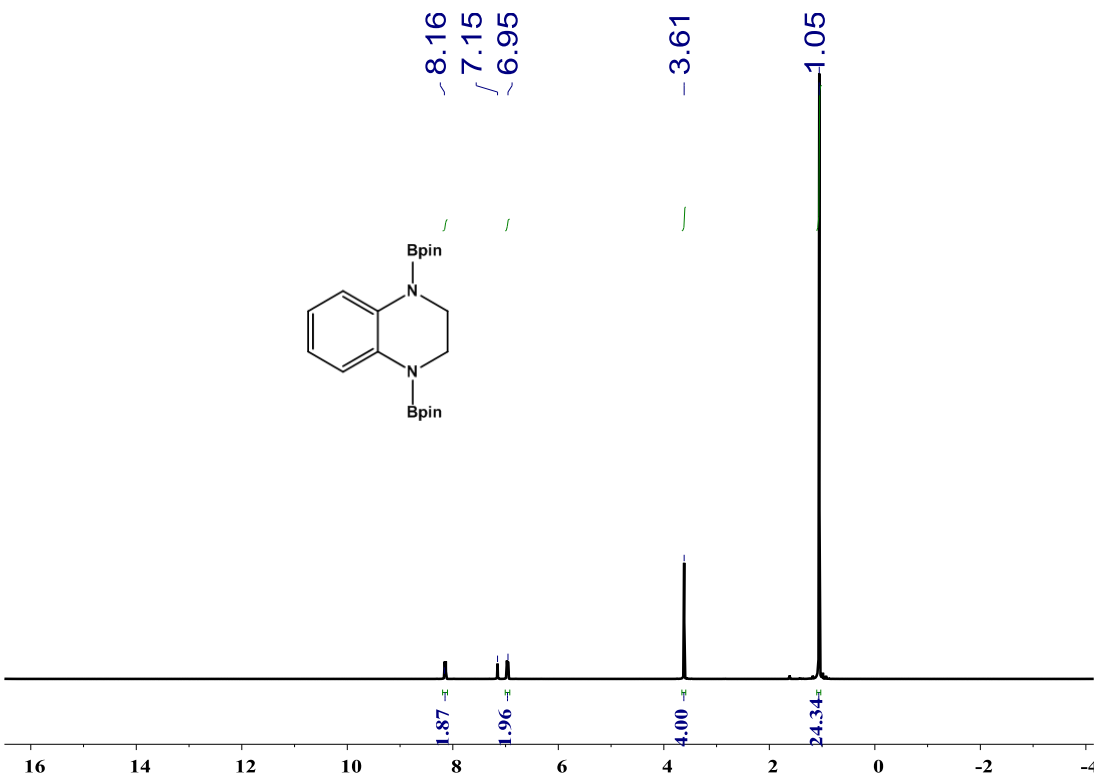
^{1}HNMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (**6**) (500 MHz, C_6D_6)



^{13}C NMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (**6**) (126 MHz, C_6D_6)

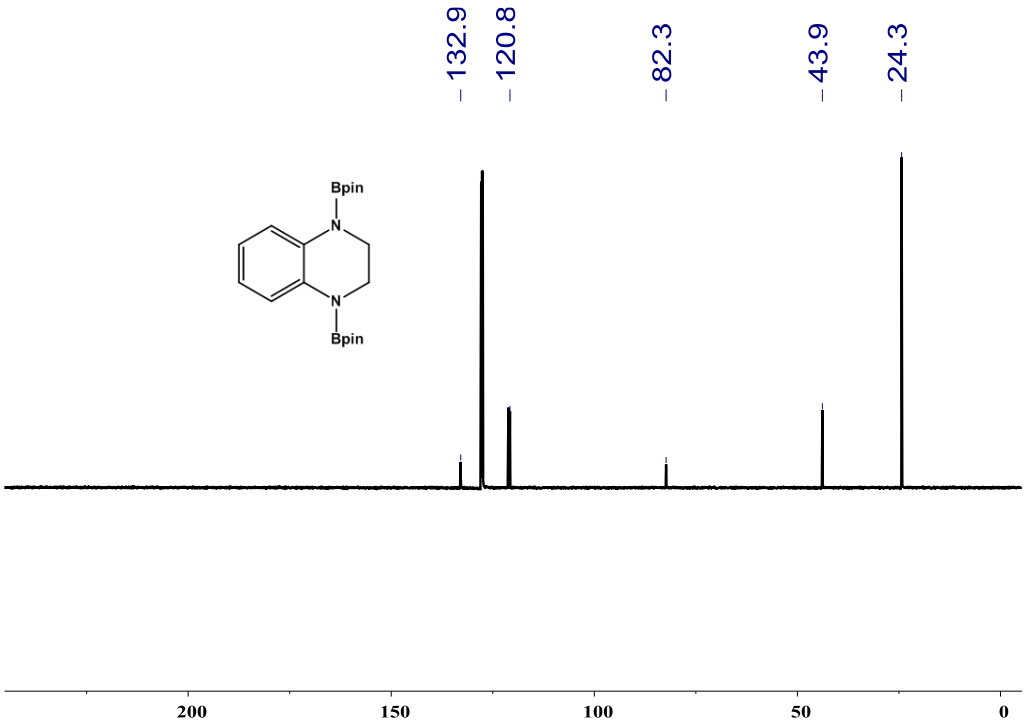


^{11}B NMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroisoquinoline (**6**) (160 MHz, C_6D_6).



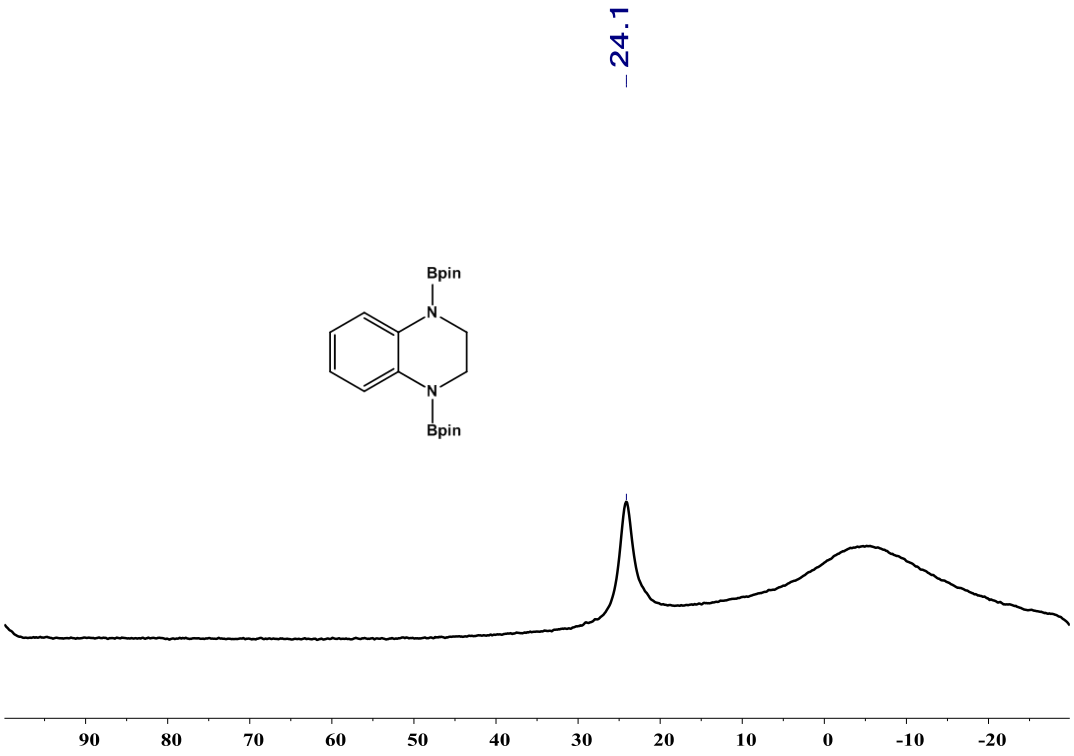
^{1}H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)

-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (**7**) (500 MHz, C_6D_6)

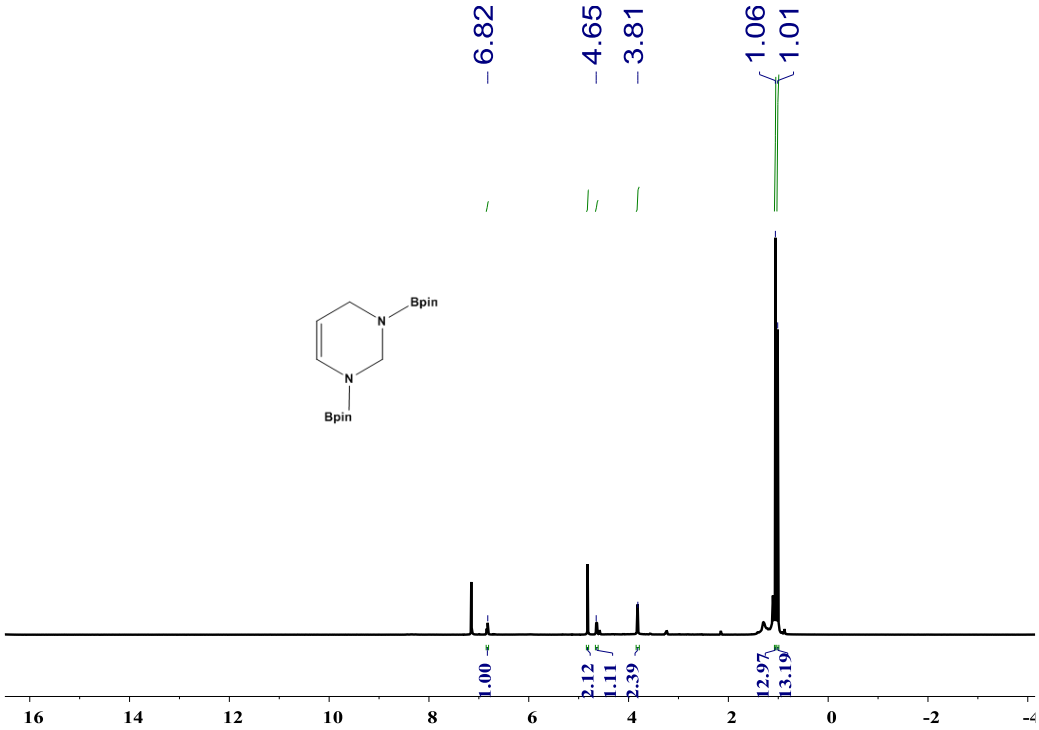


^{13}C NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)

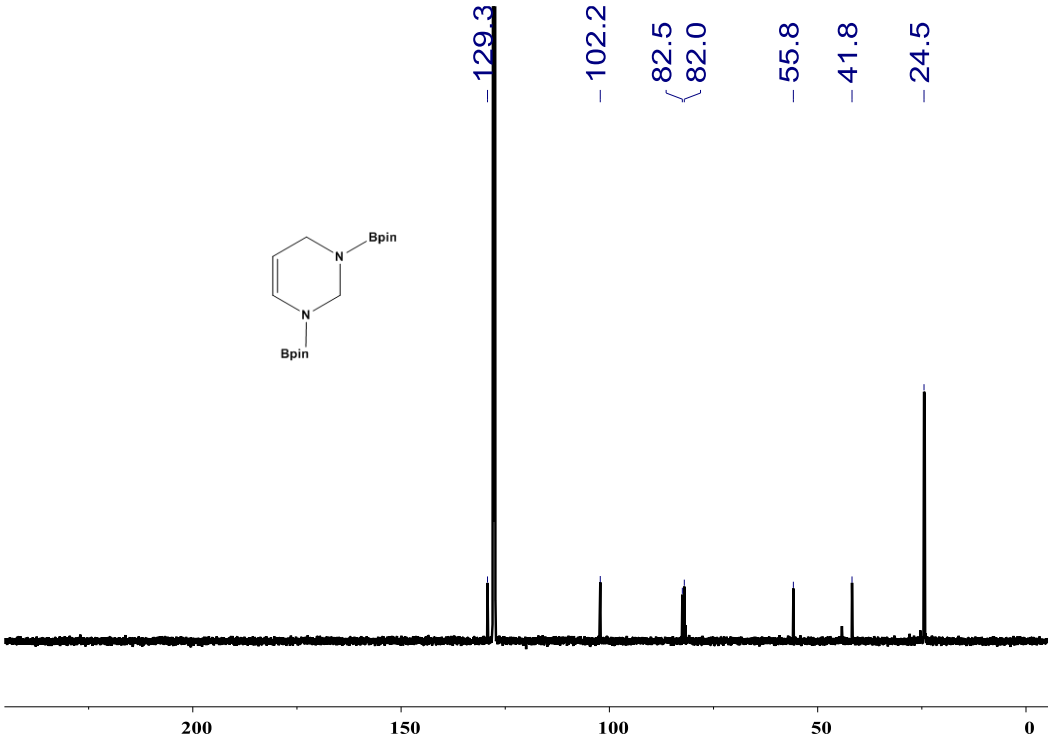
-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (**7**) (126 MHz, C_6D_6)



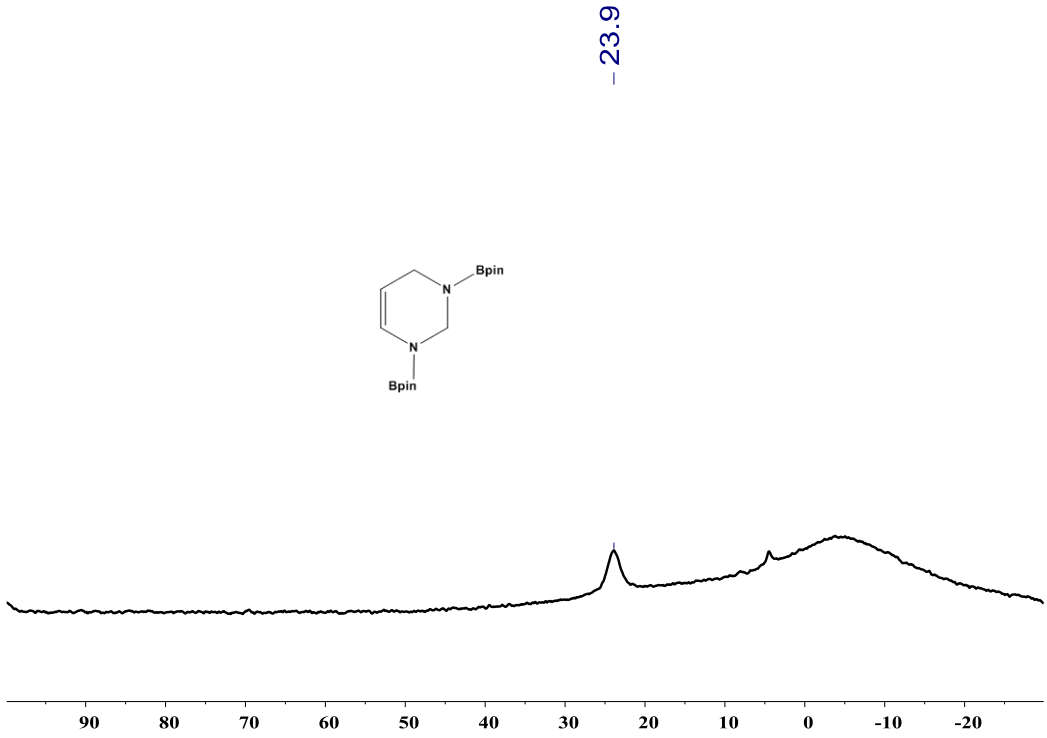
^{11}B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (**7**) (160 MHz, C_6D_6).



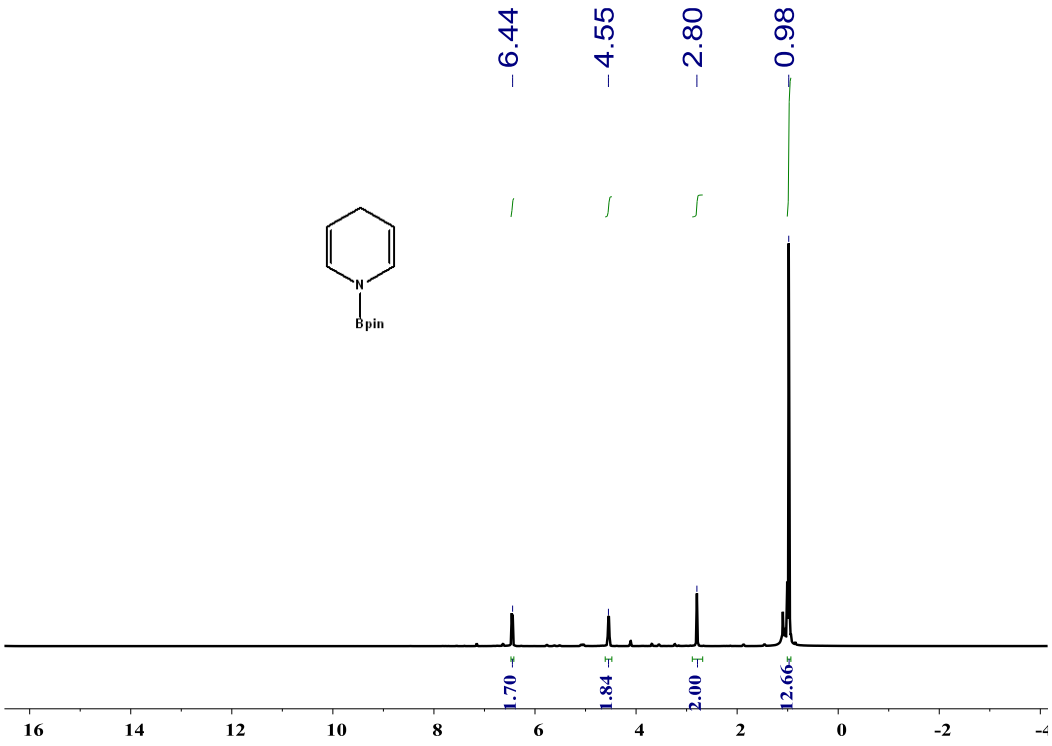
^{1}H NMR spectrum of 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (**8**) (500 MHz, C_6D_6)



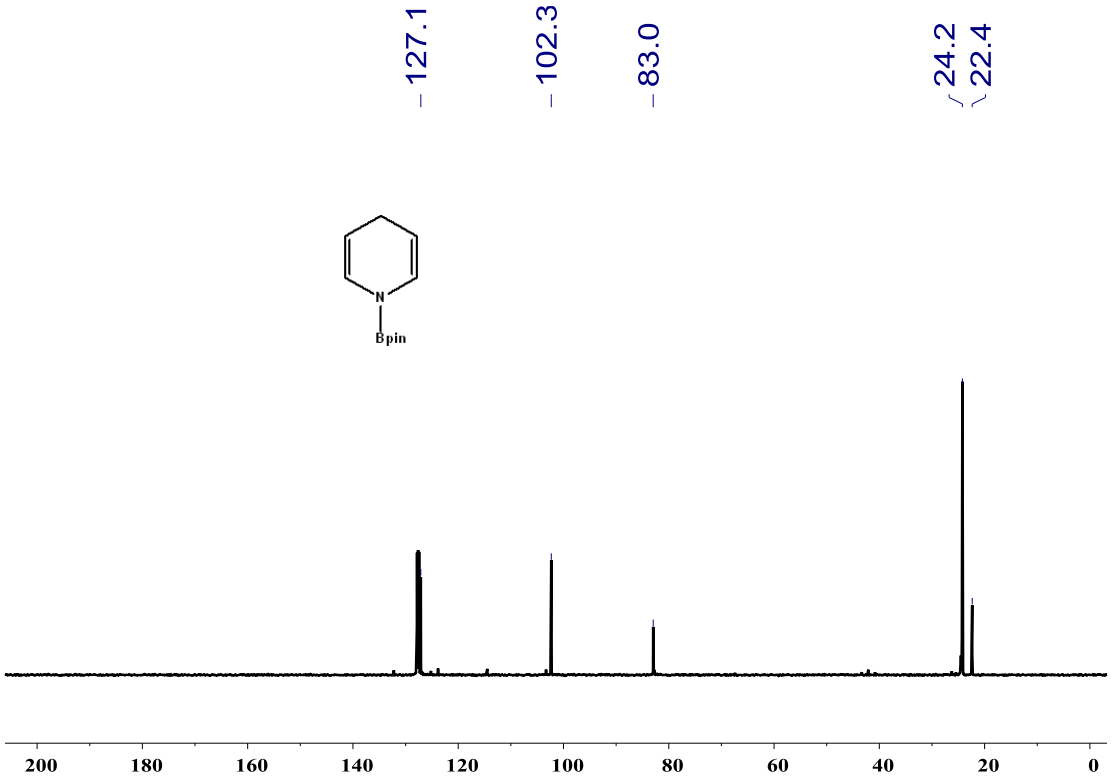
^{13}C NMR spectrum of 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (**8**) (126 MHz, C_6D_6)



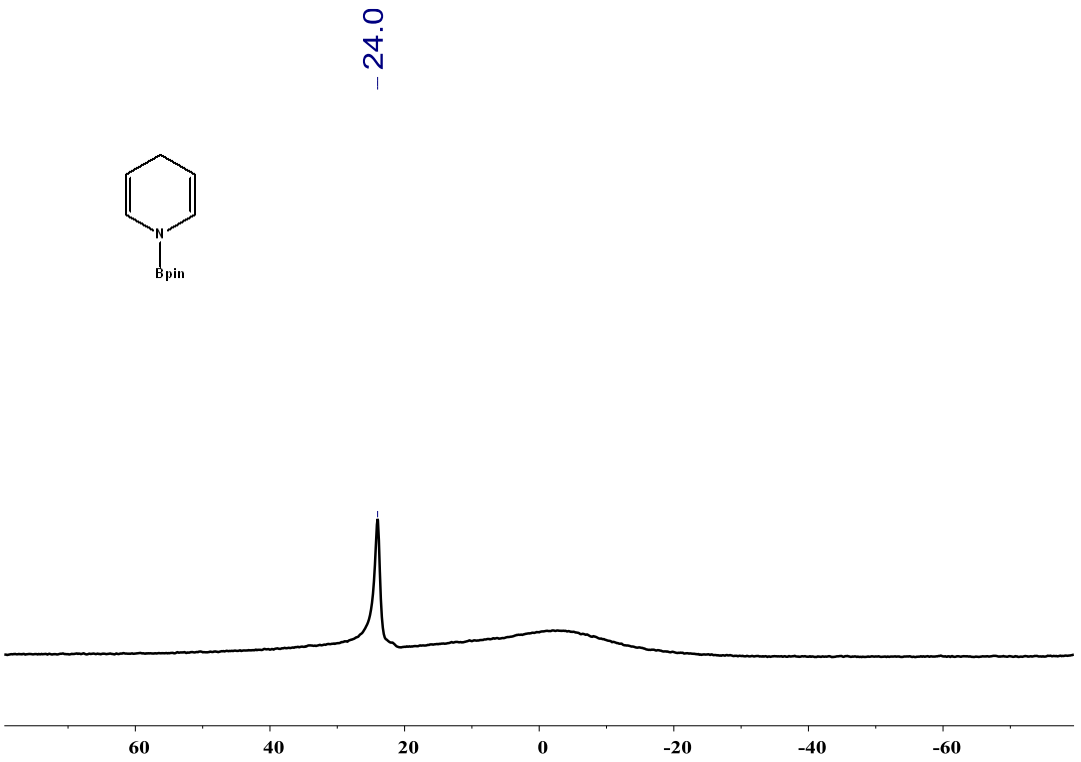
^{11}B NMR spectrum of 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydropyrimidine (**8**) (160 MHz, C_6D_6).



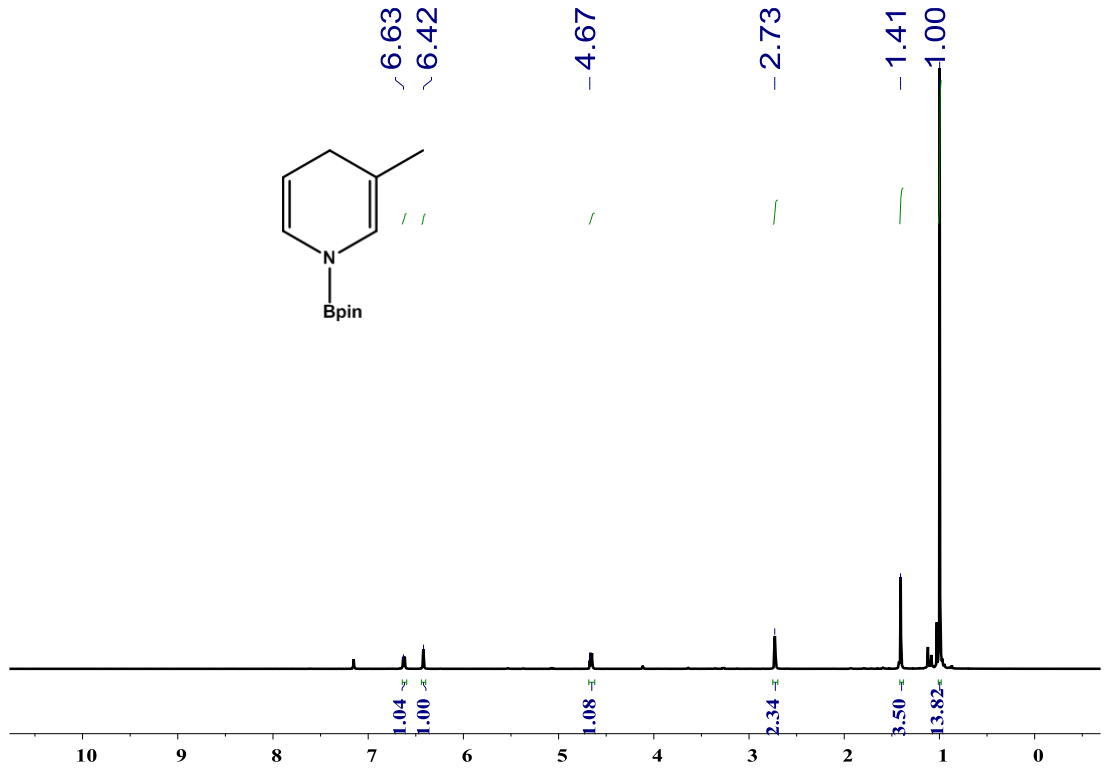
^{1}H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (**10r**) (500 MHz, C_6D_6)



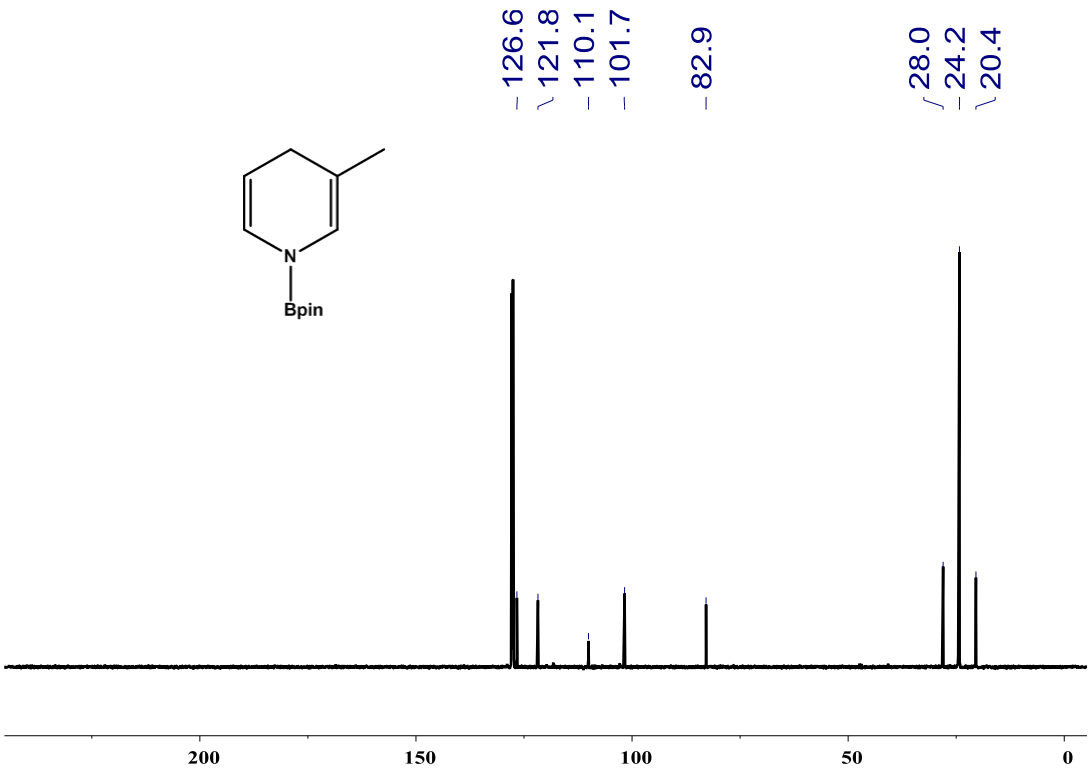
^{13}C NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (**10r**) (126 MHz, C_6D_6)



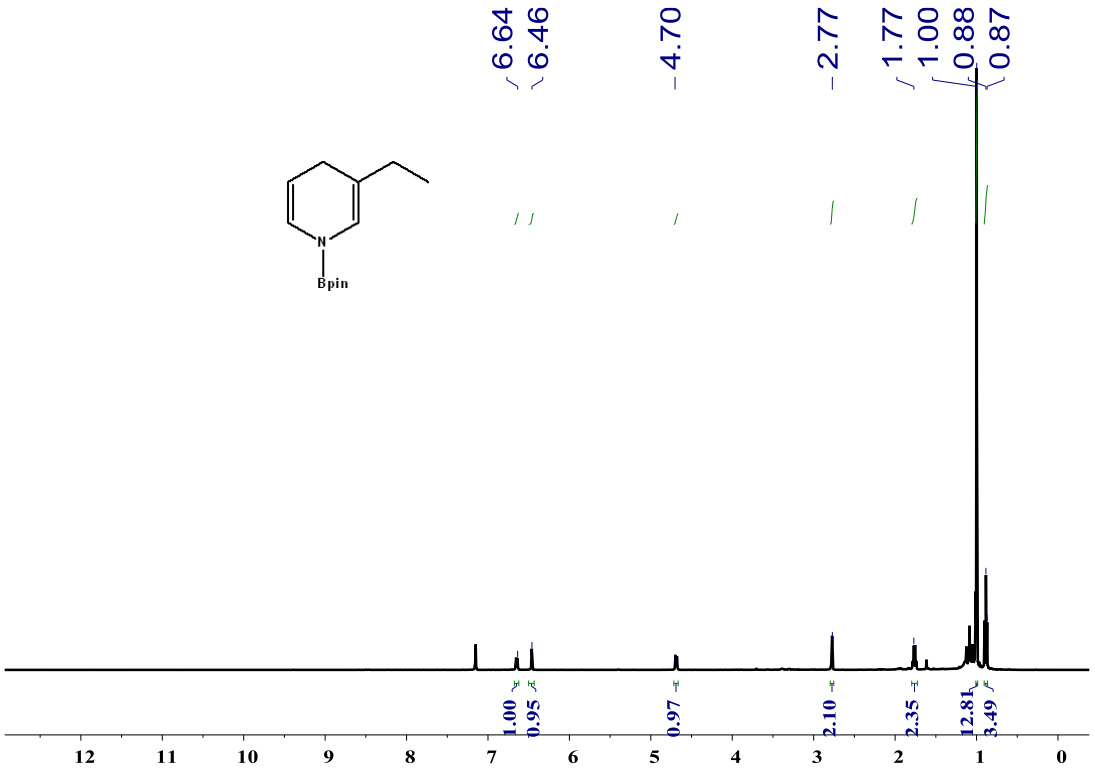
^{11}B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (**10r**) (160 MHz, C_6D_6).



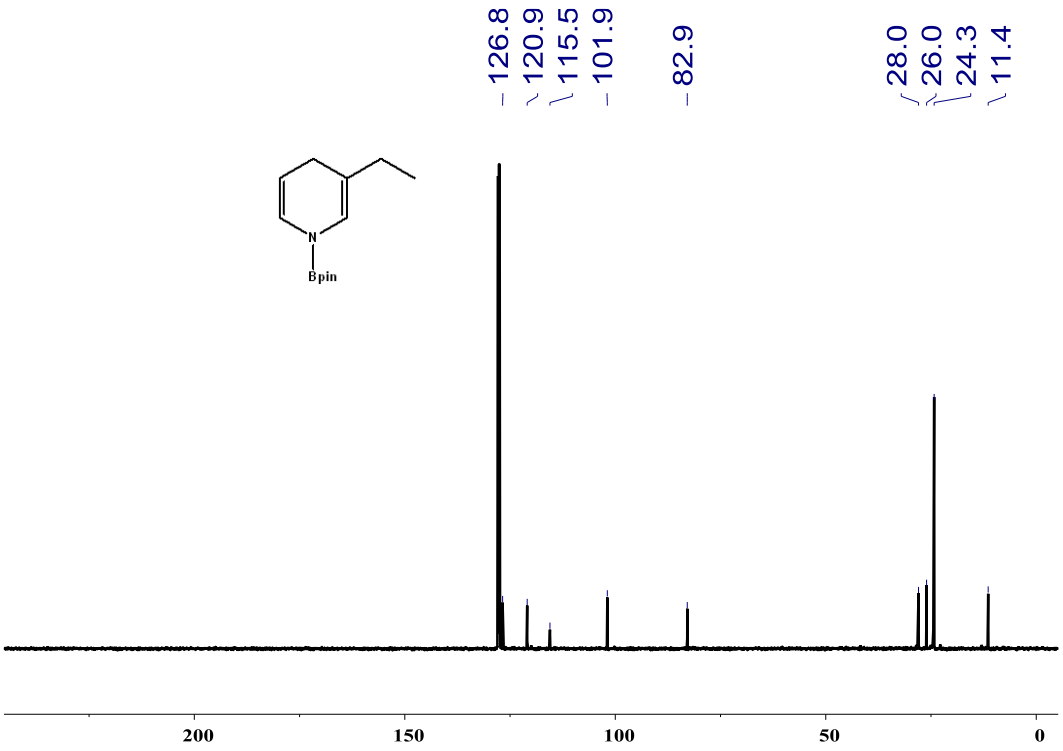
^{1}H NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (**10s**) (500 MHz, C_6D_6)



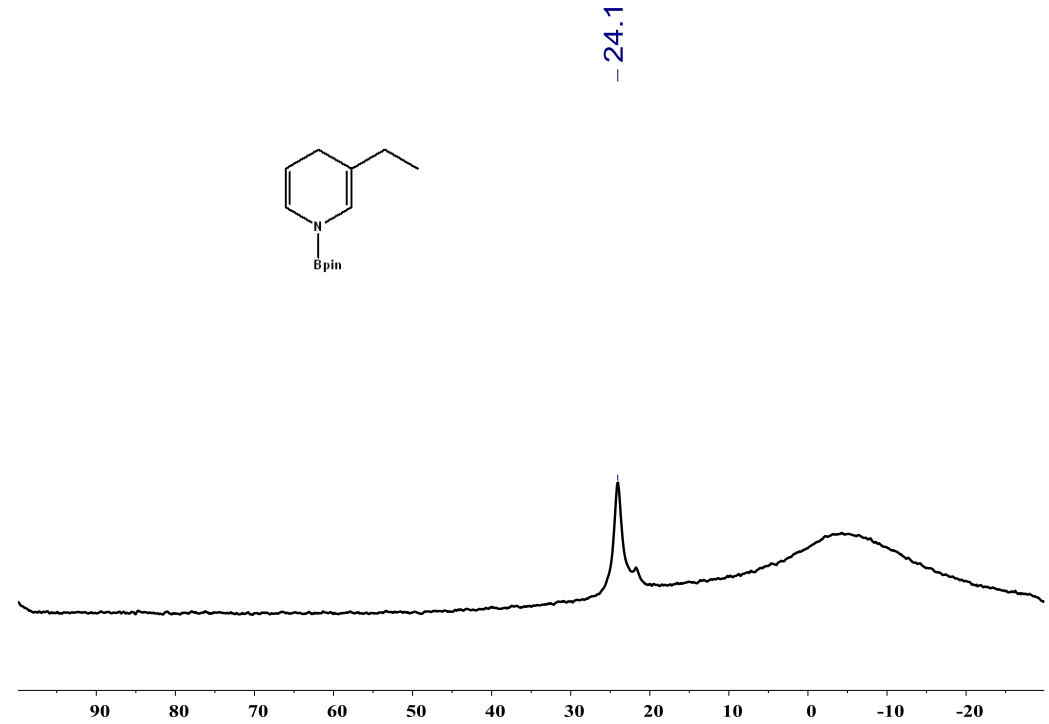
^{13}C NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (**10s**) (126 MHz, C_6D_6)



^{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_6D_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_6D_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_6D_6).