Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Regioselective 1,4-Hydroboration of Pyridines Catalyzed by an Acid-Initiated Boronium Cation

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SI.1 Experimental Details

All reactions were carried out under a dry, oxygen free nitrogen atmosphere using standard Schlenk and glovebox techniques in dry degassed solvents unless otherwise specified. All solvents were collected freshly distilled over calcium hydride (acetonitrile) or sodium wire (heptane). Deuterated NMR solvents were dried over activated molecular sieves and degassed with dry nitrogen (CD_3CN) or used as purchased in ampules (C_6D_6). 1,2-difluorobenzene, purchased from Fluorochem, was stirred over alumina followed by vacuum transfer from CaH2 and finally stored over activated molecular sieves. Ammonium tetraphenylborate was purchased from Sigma Aldrich and dried overnight under vacuum at 100 °C. HBpin was purchased from Sigma Aldrich, distilled, and stored under dry nitrogen in a Young's flask. All pyridines were stirred over CaH_2, distilled or sublimed, and stored under dry atmosphere.

NMR spectra were recorded at 298.0 K on a Bruker 400 MHz AVIII HD Smart Probe spectrometer (^{1}H at 400 MHz, ^{11}B 128 MHz, ^{13}C 101 MHz) unless otherwise specified. Chemical shifts (δ, ppm) are given relative to residual solvent signals for ^{1}H and ^{13}C, to external $BF_3{\cdot}Et_2O$ for ^{11}B, with coupling constants (J) reported in Hz. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and combinations thereof for highly coupled systems.

High-resolution mass spectra (HRMS) were collected using a Waters Xevo G2-S QTOF mass spectrometer in positive mode using CH_3CN.

Single crystal X-ray diffraction was carried out at 180(2) K on a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec IμS Cu microsource (λ = 1.5418 Å). Structures were solved using SHELXT[1] and refined using full-matrix least squares on F^2 using SHELXL-2014.[2]

SI.2 Synthetic Procedures

General procedure for NMR-scale reactions:

In a glove box, ammonium tetraphenylborate (5mg, 2.5 mol%, 0.0148 mmol) was dissolved/suspended in dry solvent (0.5 mL CD_3CN, C_6D_6, or heptane). This solution was transferred to a J. Young NMR tube. For reactions conducted in heptane, a DMSO-d_6 capillary

was included. The desired pyridine (0.593 mmol) was then added, followed by 1.5 equivalents HBpin (0.13 mL, 0.890 mmol). The NMR tube was sealed, removed from the glove box, shaken and placed in a preheated oil bath.

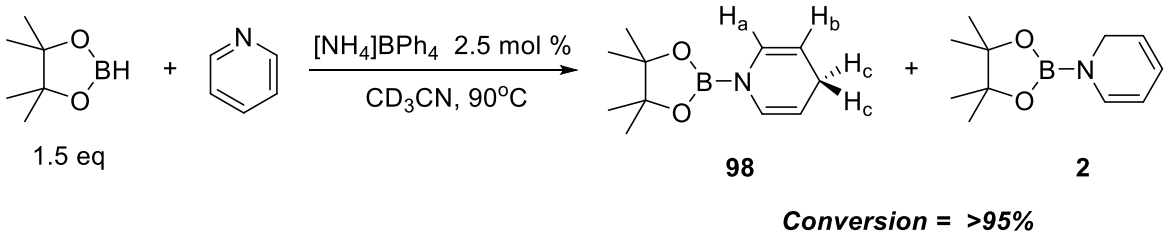
General procedure for preparative-scale reactions:

In a glove box, ammonium tetraphenylborate (28.3 mg, 0.08 mmol) was transferred to an oven-dried J. Young flask equipped with a magnetic stir bar along with the desired pyridine (3.36 mmol) and HBpin (0.73 mL, 5.04 mmol). Dry CH_3CN, heptane, or benzene (5ml) was then added outside of the glovebox. The reaction was then heated in an oil bath. Following heating the volatiles were removed *in vacuo*, and the remaining reaction mixture was suspended in dry pentane (5ml). The solution was then filtered through paper via a cannula filter into a pre-dried Schlenk flask. After removal of the pentane the 1,2- and 1,4-dihydropyridine products were retrieved as oils or waxy solids which can be purified further by reported methods if necessary. Due to the high moisture sensitivity of the products, the reaction was frequently contaminated with a small amount of pinBOH.

SI.3 Spectral characterization

NMR spectra of NMR-scale reactions:

- Pyridine



Characterization of N-boryl-1,4-dihydropyridine:[3]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 6.11 (dt, *J* = 8.5, 1.6 Hz, 2H, $\mathbf{H_a}$), 4.64 – 4.56 (m, 2H, $\mathbf{H_b}$), 2.84 – 2.80 (m, 2H, $\mathbf{H_c}$), 1.23 (s, 12H, pin).

Characterization of N-boryl-1,2-dihydropyridine:

N-boryl-1,2-dihydropyridine could not be fully assigned due to its low concentration in solution. However, it can be identified by the characteristic multiplet at δ 3.92 (dd, J = 4.2, 1.7 Hz, 2H, $\mathbf{H_d}$).

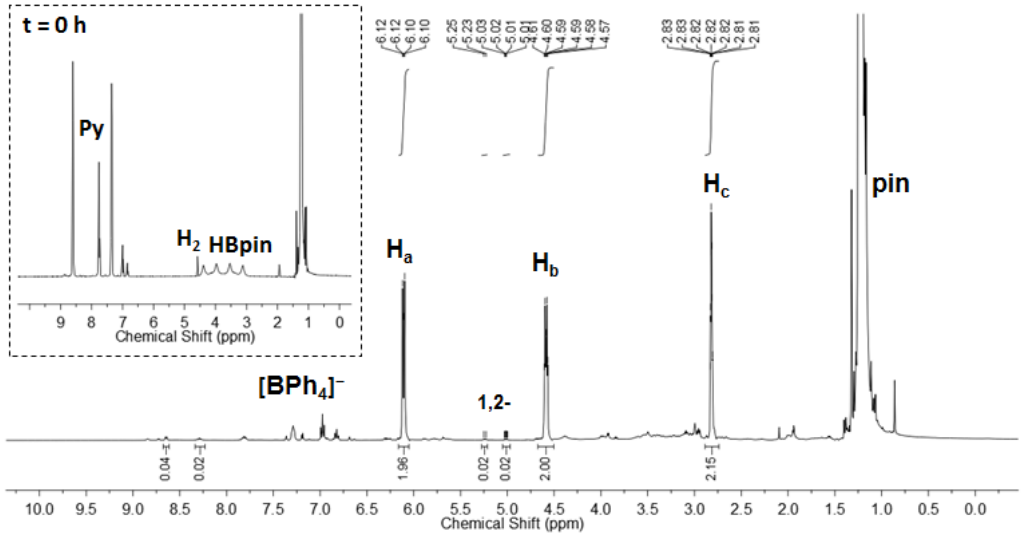


Figure S1. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 24 hours (inset: reaction mixture at t = 0h showing presence of H_2).

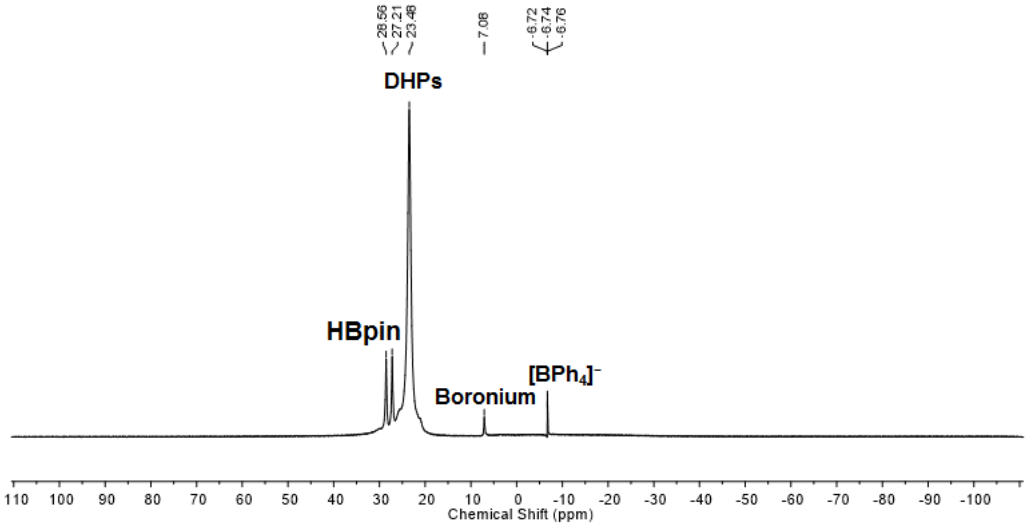


Figure S2. ^{11}B NMR (128 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 24 hours. DHPs = 1,2- and 1,4-dihydropyridine products, Cat = boronium catalyst.[3] This ^{11}B NMR spectrum is typical of the NMR-scale reactions.

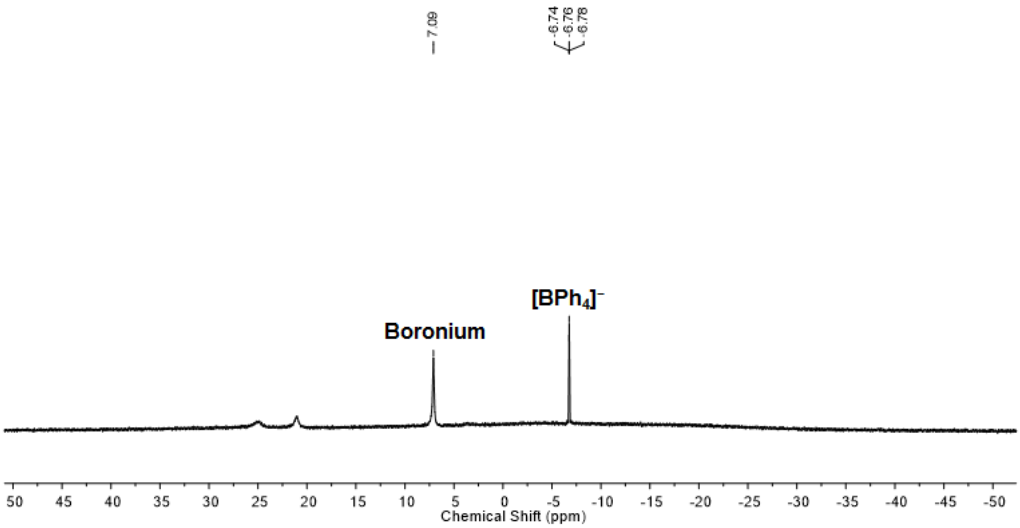


Figure S3. ^{11}B NMR (128 MHz, 298.0 K, CD_3CN) spectrum of isolated crystals of the pinBPy_2BPh_4 salt.

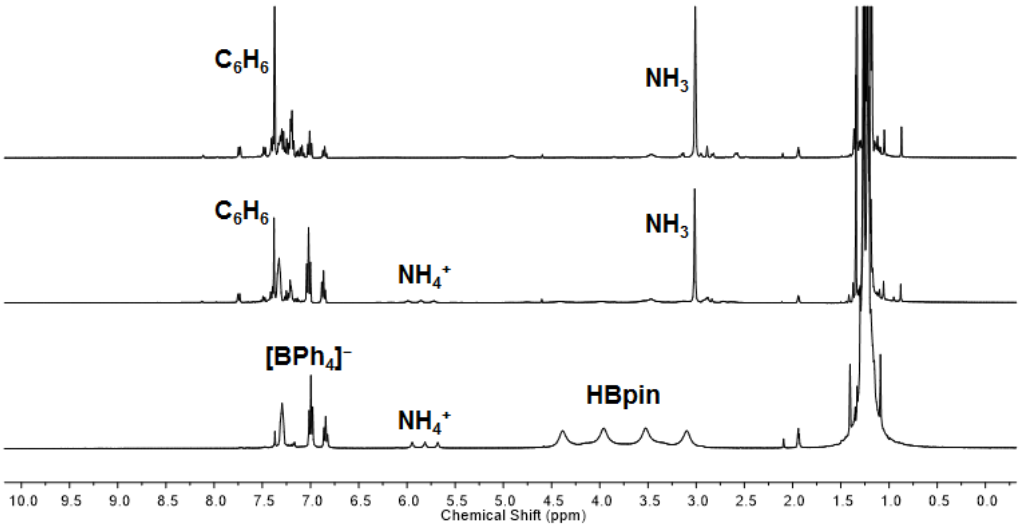


Figure S4. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectra of HBpin and NH_4BPh_4 in acetonitrile. Bottom: freshly prepared reaction mixture; middle: reaction mixture after 4 hours of heating at 90 °C; top: reaction mixture after 24 hours of heating at 90 °C.

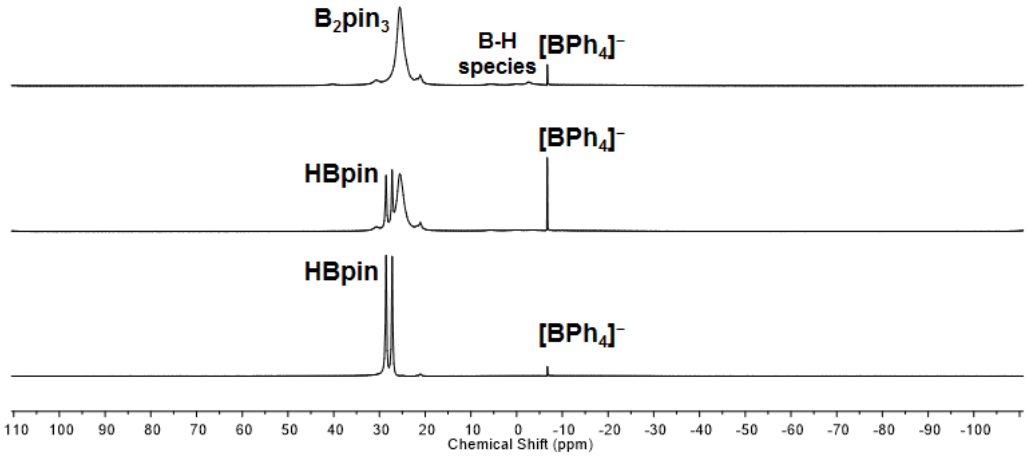
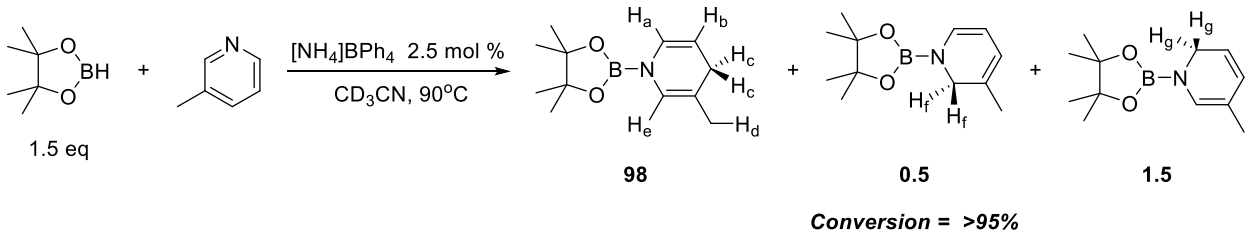


Figure S5. ^{11}B NMR (128 MHz, 298.0 K, CD_3CN) spectra of HBpin and NH_4BPh_4 in acetonitrile. Bottom: freshly prepared reaction mixture; middle: reaction mixture after 4 hours of heating at 90 °C; top: reaction mixture after 24 hours of heating at 90 °C.

- 3-methylpyridine



Characterization of N-boryl-3-methyl-1,4-dihydropyridine:[4,5]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 6.15 (dd, *J* = 8.1, 1.3 Hz, 1H, **H$_a$**), 5.97 – 5.95 (m, 1H, **H$_e$**), 4.63 (dt, *J* = 8.1, 3.3 Hz, 1H, **H$_b$**), 2.77 – 2.68 (m, 2H, **H$_c$**), 1.51 (s, 3H, **H$_d$**), 1.22 (s, 12H, pin).

Characterization of minor products:

N-boryl-3-methyl-1,2-dihydropyridine and *N*-boryl-3-methyl-1,6-dihydropyridine could not be fully assigned due to their low concentration in solution. However, they can be identified as the 1,2- and 1,6-isomers by characteristic multiplets at δ 3.86 (m, 2H, **H$_f$**) and 3.83 (dd, *J* = 4.2, 1.7 Hz, 2H, **H$_g$**), respectively.

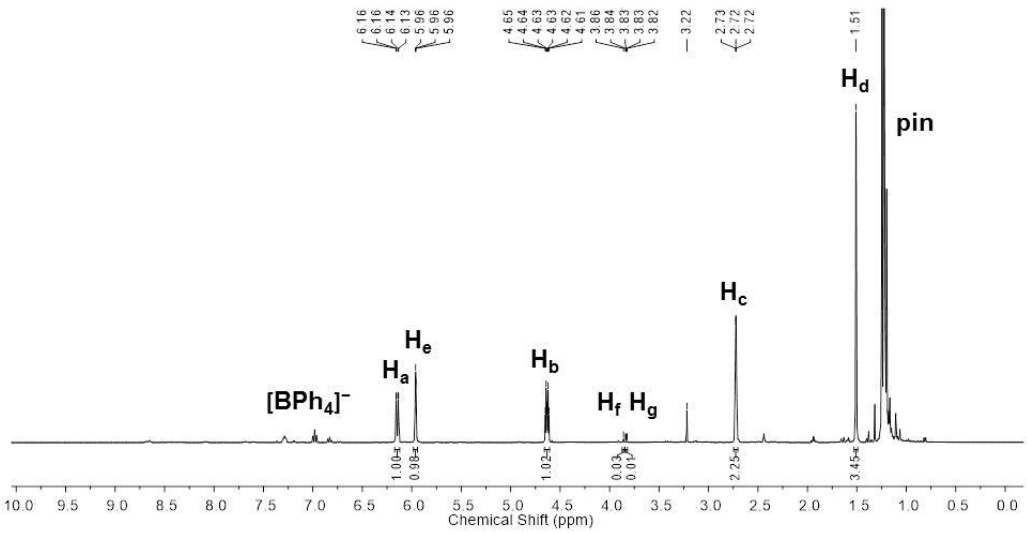


Figure S6. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 42 hours.

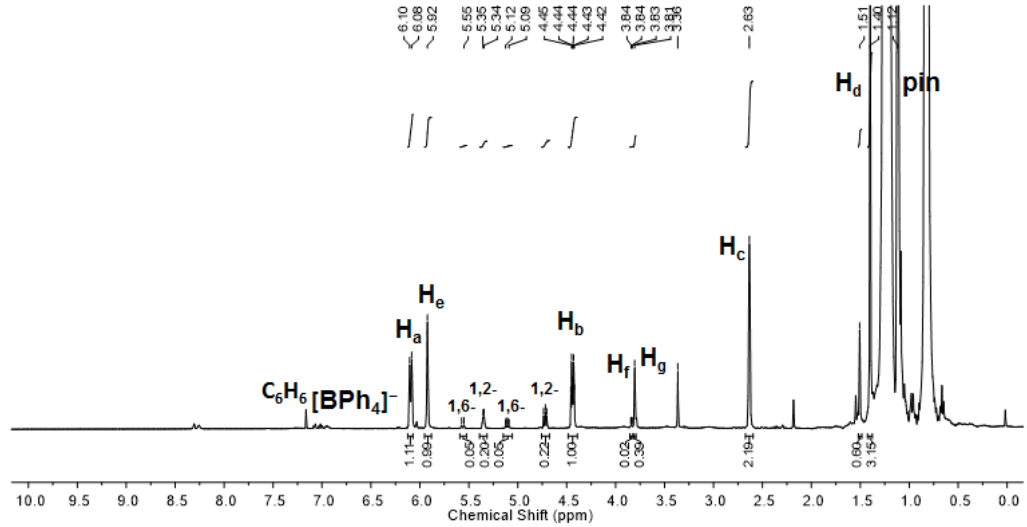
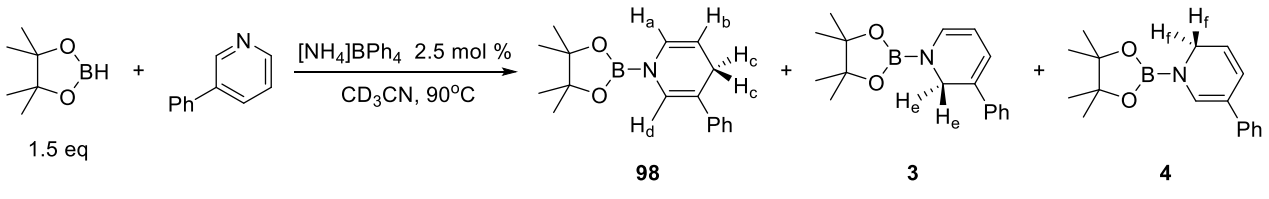


Figure S7. ^{1}H NMR (400 MHz, 298.0 K, heptane) spectrum of the reaction mixture after 98 hours (spectrum referenced to DMSO-d_6 in a glass capillary; C_6H_6 likely resulting from BPh_4^- decomposition).

- 3-phenylpyridine



Conversion = >95%

Characterization of N-boryl-3-phenyl-1,4-dihydropyridine:[3,6]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 7.34 – 7.16 (m, 5H, Ph), 6.81 (s, 1H, **H_d**), 6.29 (dd, *J* = 8.1, 0.8 Hz, 1H, **H_a**), 4.93 – 4.85 (m, 1H, **H_b**), 3.21 – 3.18 (m, 2H, **H_c**), 1.25 (s, 12H, pin).

Characterization of minor products:

N-boryl-3-phenyl-1,2-dihydropyridine and *N*-boryl-3-phenyl-1,6-dihydropyridine could not be fully assigned due to their low concentration in solution. However, they can be identified as the 1,2- and 1,6-isomers by characteristic peaks at δ 4.35 (s, 1H, **H_e**) and 4.01 (dd, *J* = 4.1, 1.6 Hz, 1H, **H_f**), respectively.

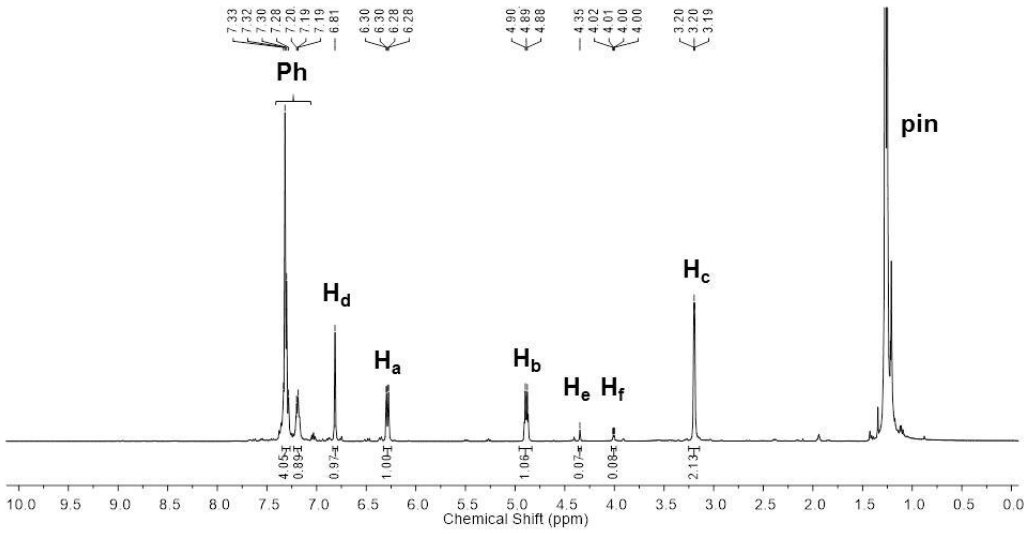
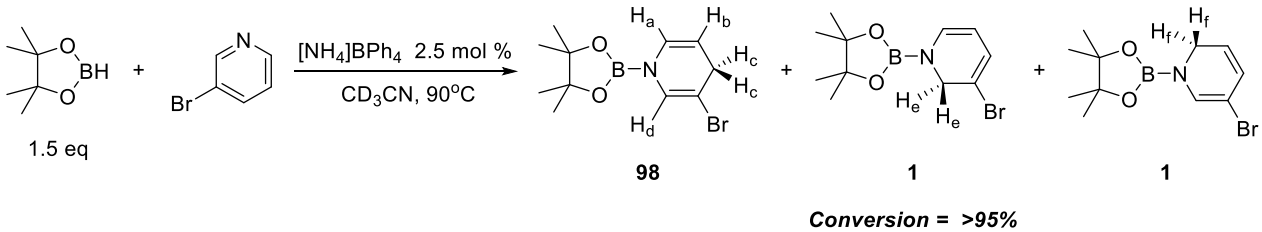


Figure S8. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 20 hours.

- 3-bromopyridine



Characterization of N-boryl-3-bromo-1,4-dihydropyridine:[3,6]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 6.48 (d, *J* = 1.1 Hz, 1H, **H_d**), 6.17 (dd, *J* = 8.1, 1.1 Hz, 1H, **H_a**), 4.63 (dt, *J* = 8.1, 3.3 Hz, 1H, **H_b**), 3.18 (dt, *J* = 3.2, 1.5 Hz, 2H, **H_c**), 1.24 (s, 12H, pin).

Characterization of minor products:

N-boryl-3-bromo-1,2-dihydropyridine and *N*-boryl-3-bromo-1,6-dihydropyridine could not be fully assigned due to their low concentration in solution. However, they can be identified as the 1,2- and 1,6-isomers by characteristic peaks at δ 4.18 (d, *J* = 1.3 Hz, 2H, **H_e**) and 3.91 (dd, *J* = 4.3, 1.8 Hz, 2H, **H_f**), respectively.

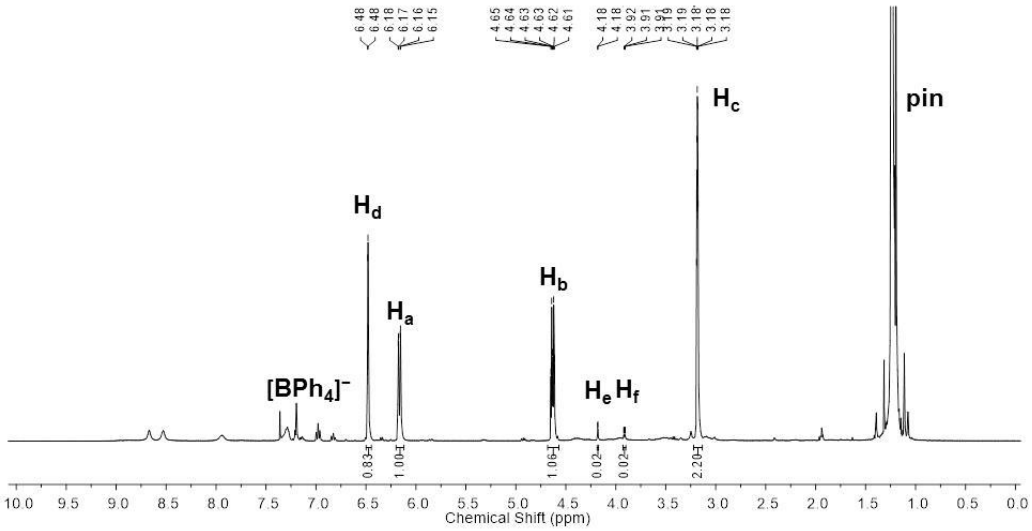
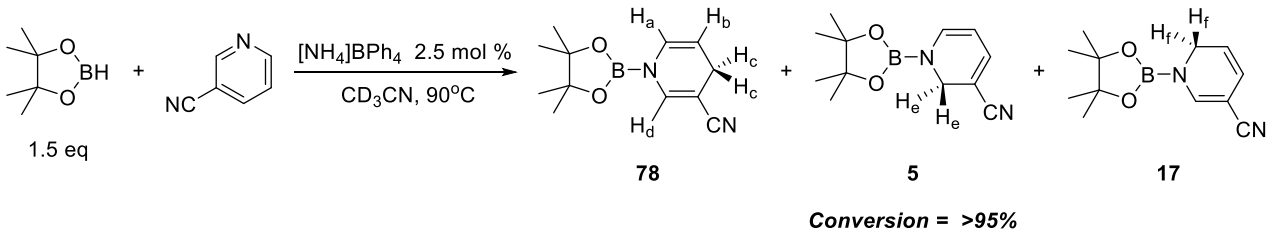


Figure S9. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 24 hours.

- 3-pyridinecarbonitrile



Conversion = >95%

Characterization of N-boryl-3-cyano-1,4-dihydropyridine:[3]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 6.86 (s, 1H, **H_d**), 6.10 (dd, *J* = 8.3, 1.4 Hz, 1H, **H_a**), 4.82 (dt, *J* = 8.1, 3.4 Hz, 1H, **H_b**), 3.00 – 2.98 (m, 2H, **H_c**), 1.24 (s, 12H, pin).

Characterization of minor products:

N-boryl-3-cyano-1,2-dihydropyridine and *N*-boryl-3-cyano-1,6-dihydropyridine could not be fully assigned due to their low concentration in solution. However, they can be identified as the

1,2- and 1,6-isomers by characteristic peaks at δ 4.03 (s, 2H, $\mathbf{H_e}$) and 4.08 (dd, J = 3.8, 1.8 Hz, 2H, $\mathbf{H_f}$), respectively.

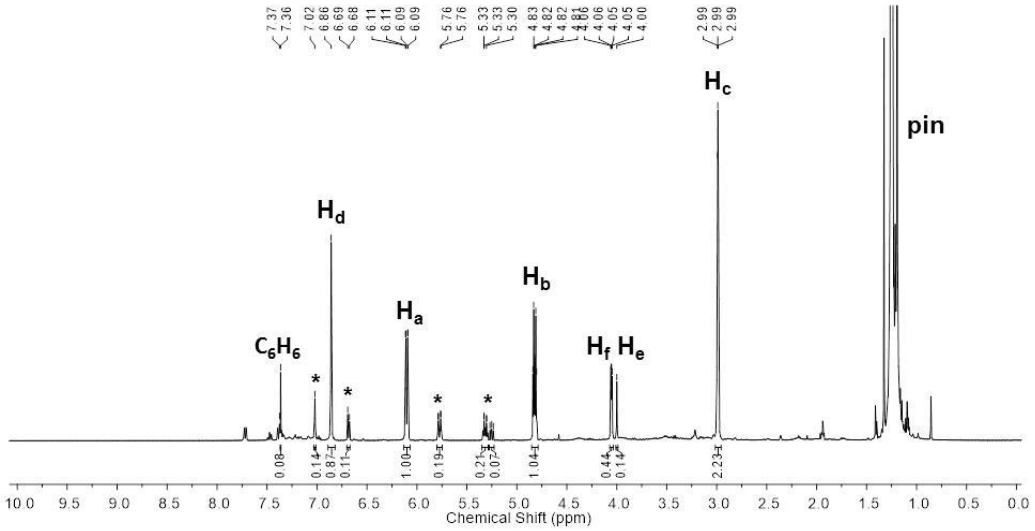
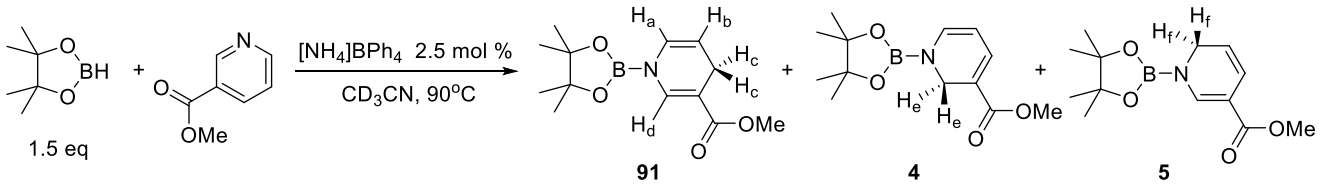


Figure S10. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 19 hours (*peaks arising from the minor 1,2- and 1,6- products; C_6H_6 likely resulting from BPh_4^- decomposition.)

- Methyl nicotinate



Conversion = >95%

Characterization of N-boryl-1,4-dihydropyridine-3-methylcarboxylate:[3]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 7.25 (d, J = 0.7 Hz, 1H, $\mathbf{H_d}$), 6.11 (ddd, J = 8.1, 3.1, 1.7 Hz, 1H, $\mathbf{H_a}$), 4.89 (dt, J = 8.0, 3.4 Hz, 1H, $\mathbf{H_b}$), 3.65 (s, 3H, OCH_3), 3.00 – 2.92 (m, 2H, $\mathbf{H_c}$), 1.26 (s, 12H, pin).

Characterization of minor products:

N-boryl-1,2-dihydropyridine-3-methylcarboxylate and *N*-boryl-1,6-dihydropyridine-3-methylcarboxylate could not be fully assigned due to their low concentration in solution. However, they can be identified as the 1,2- and 1,6-isomers by characteristic peaks at δ 4.12 (d, J = 0.7 Hz, $\mathbf{H_e}$) and 4.05 (dd, J = 3.7, 1.9 Hz, $\mathbf{H_f}$), respectively.

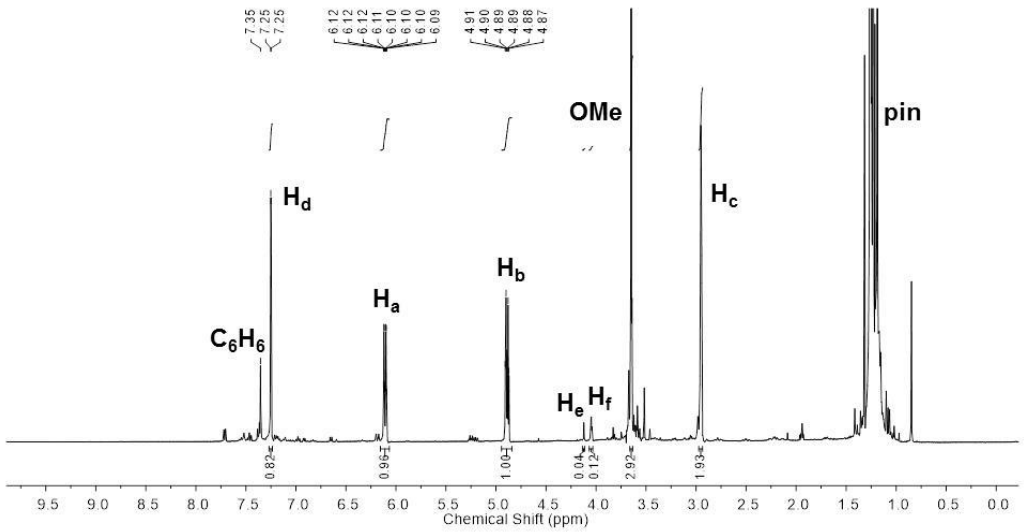
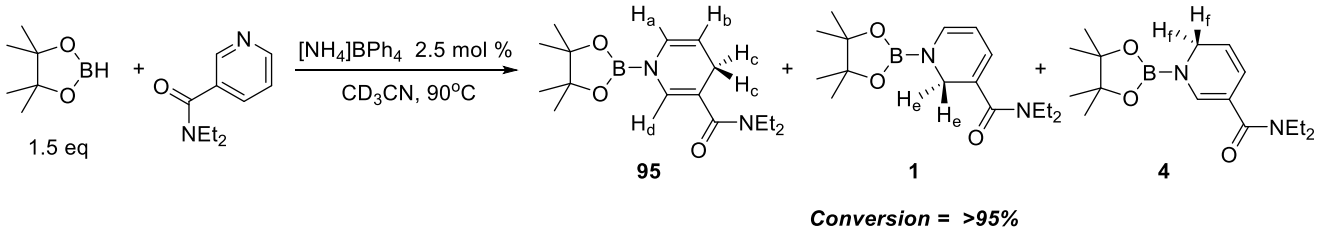


Figure S11. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 18 hours (C_6H_6 likely resulting from BPh_4^- decomposition).

- *N*,*N*-diethylnicotinamide



Characterization of N-boryl-1,4-dihydropyridine-3-(N,N-diethylamide):

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 6.33 (s, 1H, **H_d**), 6.13 (dd, *J* = 8.2, 1.2 Hz, 1H, **H_a**), 4.76 (dt, *J* = 8.0, 3.3 Hz, 1H, **H_b**), 3.35 (q, *J* = 7.1 Hz, 4H, Et), 3.00 – 2.94 (m, 2H, **H_c**), 1.23 (s, 12H, pin), 1.10 (t, *J* = 7.1 Hz, 6H, Et); ^{13}C NMR (101 MHz, 298.0 K, CD_3CN) δ 171.62, 128.06, 126.65, 110.71, 104.20, 84.90, 83.98, 41.88, 24.86, 24.76, 24.45, 14.04; ^{11}B NMR (128 MHz, 298.0 K, CD_3CN) δ 23.70. HRMS (positive mode, CH_3CN) *m/z* calcd for $C_{16}H_{28}BN_2O_3$ ($M+H^+$): 307.2187, found: 307.2177 (-3.2 ppm).

Characterization of minor products:

N-boryl-1,2-dihydropyridine-3-(*N'*,*N'*-diethylamide) and *N*-boryl-1,6-dihydropyridine-3-(*N'*,*N'*-diethylamide) could not be fully assigned due to their low concentration in solution. However, they can be identified as the 1,2- and 1,6-isomers by characteristic peaks at δ 3.98 (d, *J* = 0.5 Hz, **H_e**) and 3.95 (dd, *J* = 4.1, 1.6 Hz, **H_f**), respectively.

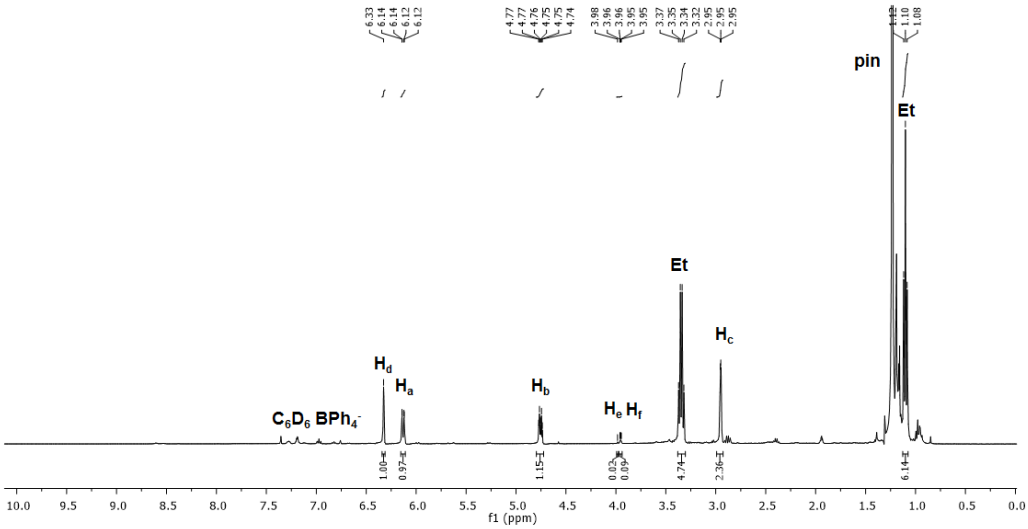
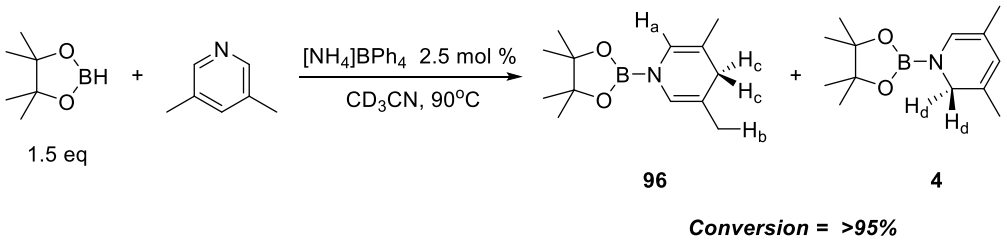


Figure S12. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 25 hours (C_6H_6 likely resulting from minor BPh_4^- decomposition).

- 3,5-leutidine



Characterization of N-boryl-1,4-dihydro-3,5-lutidine:[4]

^{1}H NMR (400 MHz, 298.0 K, CD_3CN) δ 5.99 (s, 2H, $\mathbf{H_a}$), 2.60 (s, 2H, $\mathbf{H_c}$), 1.55 (s, 6H, $\mathbf{H_b}$), 1.22 (s, 12H, pin).

Characterization of N-boryl-1,2-dihydro-3,5-lutidine:

N-boryl-1,2-dihydro-3,5-lutidine could not be fully assigned due to its low concentration in solution. However, it can be identified by the characteristic peak at δ 3.77 (s, 2H, $\mathbf{H_d}$).

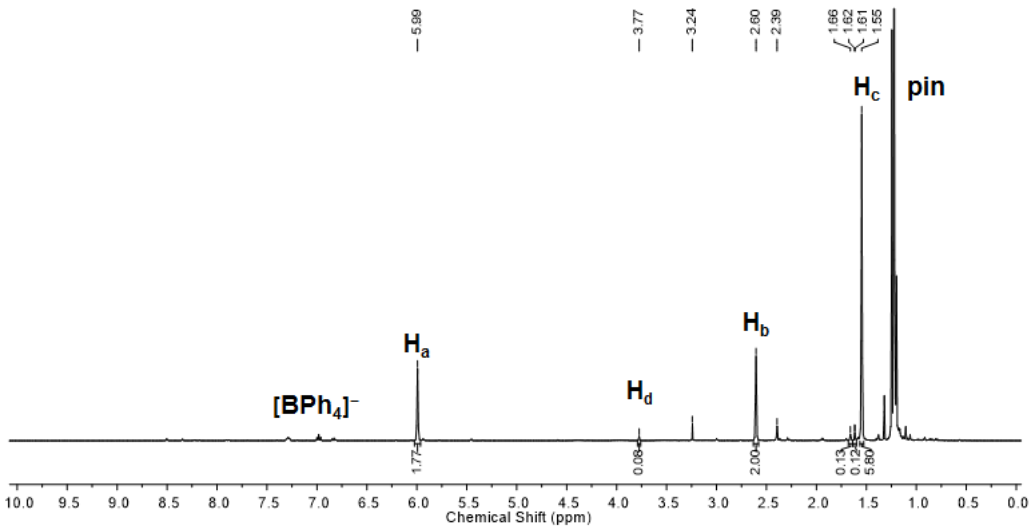
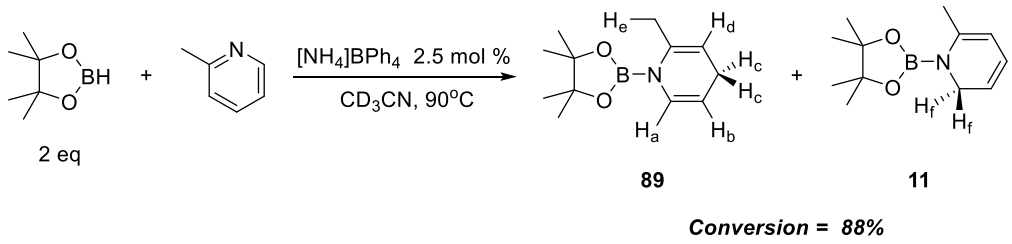


Figure S13. [1]H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 69 hours.

- 2-methylyridine



Characterization of N-boryl-2-methyl-1,4-dihydropyridine:[4]

[1]H NMR (400 MHz, 298.0 K, CD_3CN) δ 6.30 (d, *J* = 8.2 Hz, 1H, $\mathbf{H_a}$), 4.63 (m, 1H, $\mathbf{H_b}$), 4.42 (m, 1H, $\mathbf{H_d}$), 2.77 – 2.71 (m, 2H, $\mathbf{H_c}$), 1.86 (d, *J* = 1.2 Hz, 3H, $\mathbf{H_e}$), 1.22 (s, 12H, pin).

Characterization of N-boryl-2-methyl-1,2-dihydropyridine:

N-boryl-2-methyl-1,2-dihydropyridine could not be fully assigned due to its low concentration in solution. However, it can be identified by a characteristic multiplet at δ 3.79 (d, *J* = 4.2 Hz, 2H, $\mathbf{H_d}$).

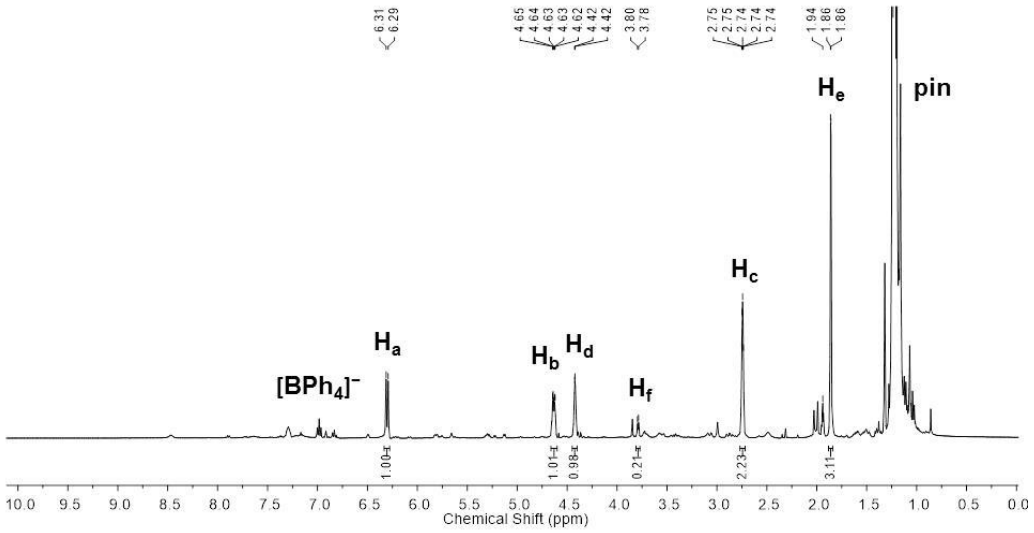
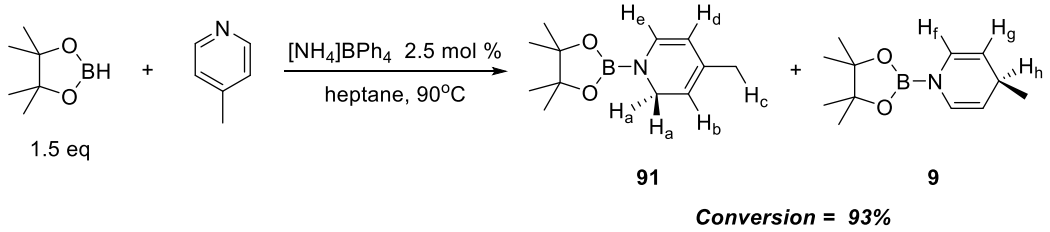


Figure S14. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 17 hours.

- 4-methylpyridine



Characterization of N-boryl-4-methyl-1,2-dihydropyridine:[4]

^{1}H NMR (400 MHz, 298.0 K, heptane) δ 6.23 (d, *J* = 7.4 Hz, 1H, **H_e**), 4.78 (m, 1H, **H_b**), 4.71 (dd, *J* = 7.5, 1.4 Hz, 1H, **H_d**), 3.85 (dd, *J* = 3.8, 1.7 Hz, 2H, **H_a**), 1.54 (d, *J* = 1.4 Hz, 3H, **H_c**), 1.12 (s, 12H, pin).

Characterization of N-boryl-4-methyl-1,4-dihydropyridine:

N-boryl-4-methyl-1,4-dihydropyridine could not be fully assigned due to its low concentration in solution. However, it can be identified by characteristic peaks at δ 6.08 (d, *J* = 7.4 Hz, 2H, **H_f**), 4.39 (dd, *J* = 8.4, 3.2 Hz, 2H, **H_g**), 2.95 – 2.89 (m, 1H, **H_h**).

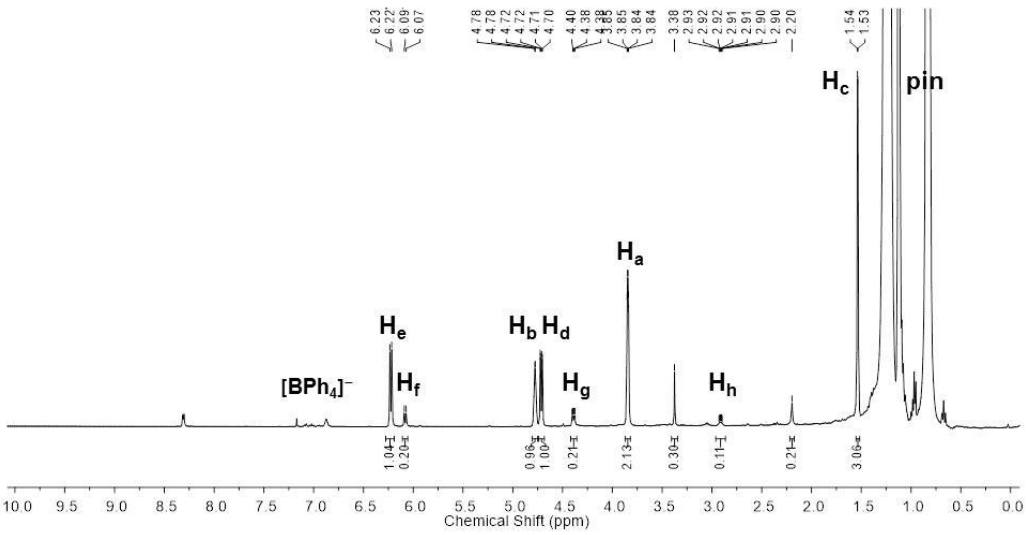


Figure S15. ^{1}H NMR (400 MHz, 298.0 K, heptane) spectrum of the reaction mixture after 41 hours (spectrum referenced to DMSO-d_6 in a glass capillary).

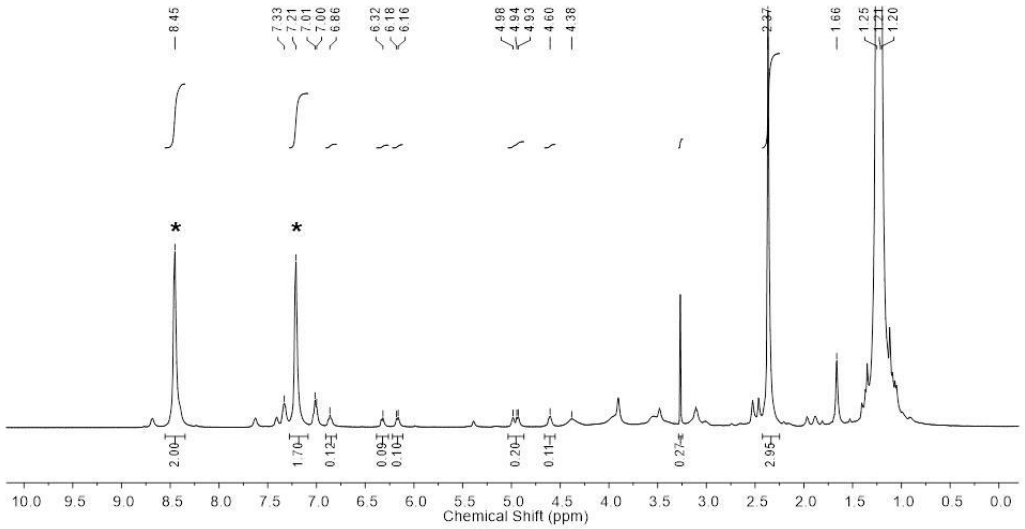


Figure S16. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum of the reaction mixture after 48 hours (* indicates unreacted starting material).

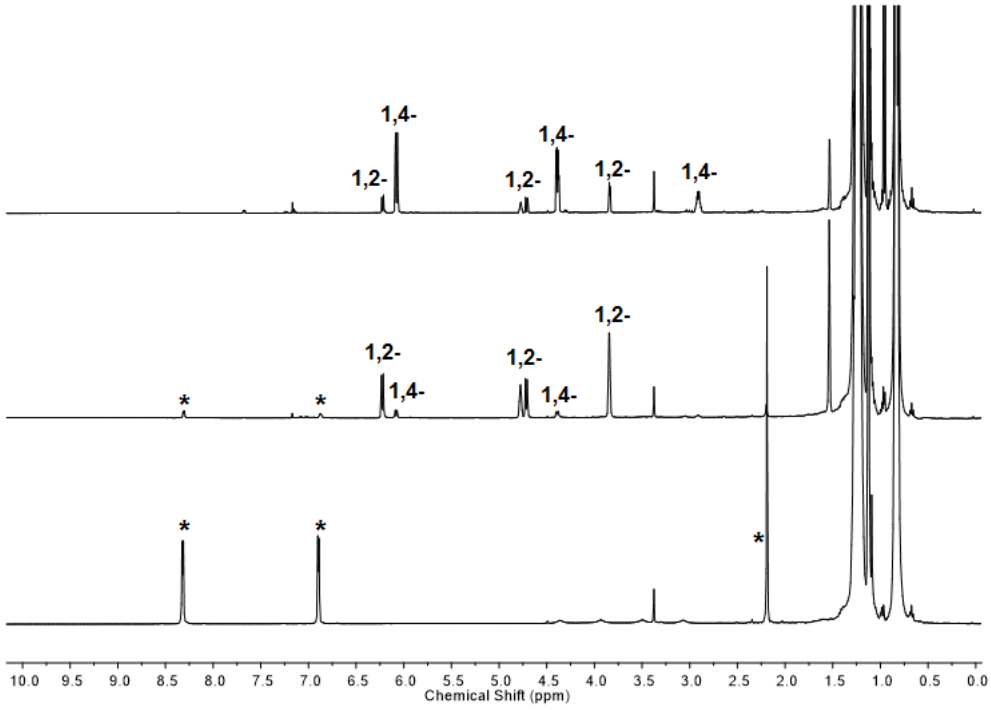
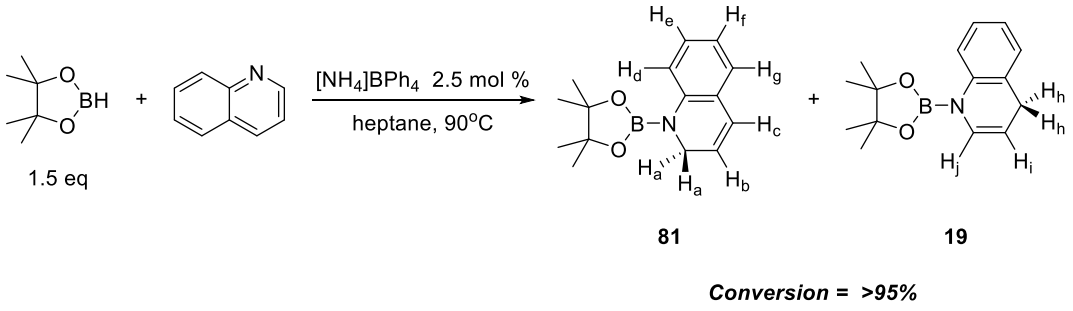


Figure S17. [1]H NMR (400 MHz, 298.0 K, heptane) spectra of *N*-boryl-4-methyl-1,2-dihydropyridine interconversion to *N*-boryl-4-methyl-1,4-dihydropyridine (* indicates starting material). Bottom: 4-methylpyridine; middle: hydroboration reaction mixture after 48 hours at 90 °C; top: hydroboration reaction mixture after subsequent heating at 110 °C for 72 hours.

- Quinoline



Characterization of N-boryl-1,2-dihydroquinoline:[4,7]

[1]H NMR (400 MHz, 298.0 K, heptane) δ 7.24 (d, *J* = 8.2 Hz, 1H, $\mathbf{H_g}$), 6.83 – 6.77 (m, 1H, $\mathbf{H_f}$), 6.66 (m, 1H, $\mathbf{H_d}$), 6.58 (td, *J* = 7.4, 1.1 Hz, 1H, $\mathbf{H_e}$), 6.13 (d, *J* = 9.6 Hz, 1H, $\mathbf{H_c}$), 5.55 (dt, *J* = 9.4, 4.2 Hz, 1H, $\mathbf{H_b}$), 3.90 (dd, *J* = 4.2, 1.7 Hz, 2H, $\mathbf{H_a}$), 1.07 (s, 12H, pin).

Characterization of N-boryl-1,4-dihydroquinoline:

N-boryl-1,4-dihydroquinoline could not be fully assigned due to its low concentration and overlapping signals in solution. However, it can be identified by characteristic peaks at δ 6.43 (dt, J = 8.1, 1.7 Hz, 1H, $\mathbf{H_j}$), 4.64 – 4.60 (m, 1H, $\mathbf{H_i}$), 3.25 (dd, J = 3.3, 1.4 Hz, 2H, $\mathbf{H_h}$).

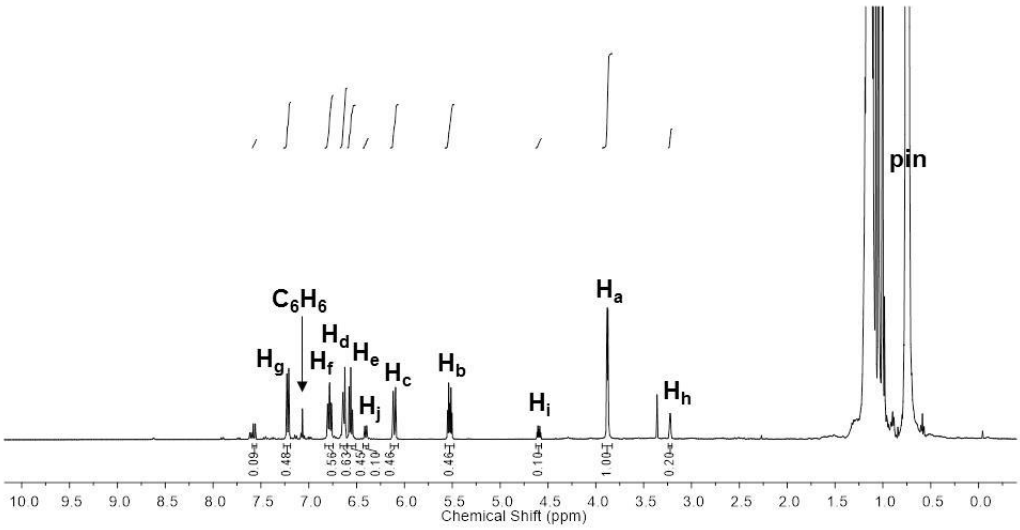


Figure S18. ^{1}H NMR (400 MHz, 298.0 K, heptane) spectrum of the reaction mixture after 20 hours (spectrum referenced to DMSO-d_6 in a glass capillary; C_6H_6 likely resulting from BPh_4^- decomposition).

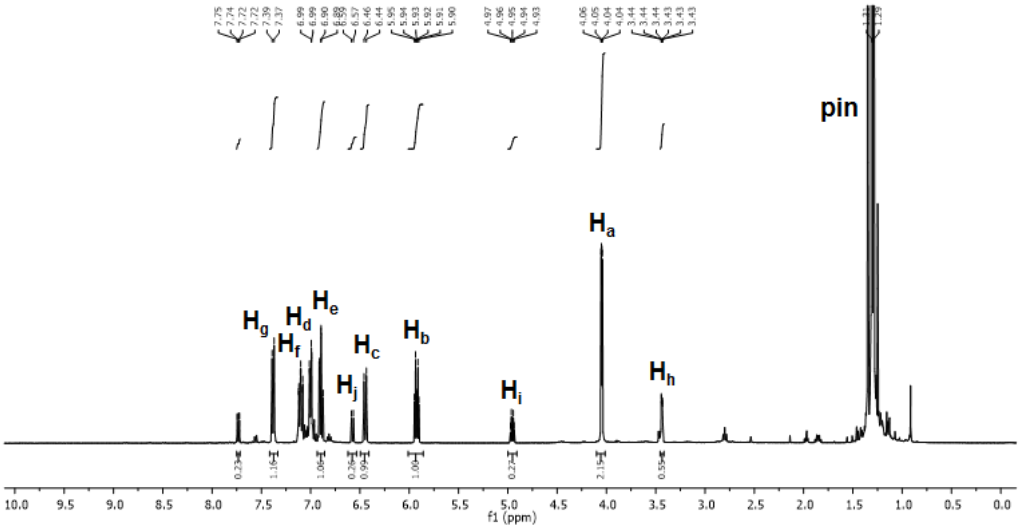
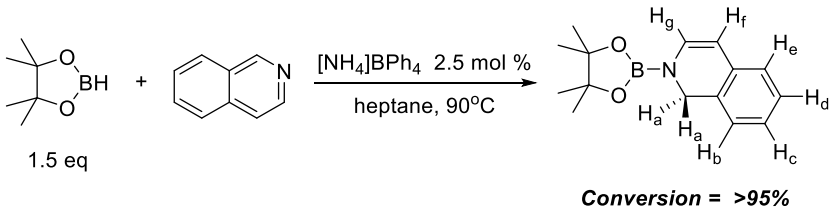


Figure S19. ^{1}H NMR (400 MHz, 298.0 K, CD_3CN) spectrum of the reaction mixture after 21 hours.

- Isoquinoline



Characterization of N-boryl-1,2-dihydroisoquinoline:[4]

^{1}H NMR (400 MHz, 298.0 K, heptane) δ 6.79 (td, *J* = 7.5, 1.3 Hz, 1H, **H$_d$**), 6.73 (d, *J* = 7.4, 1.3 Hz, 1H, **H$_c$**), 6.62 (d, *J* = 7.3 Hz, 1H, **H$_x$**), 6.58 (dd, *J* = 7.4, 0.8 Hz, 1H, **H$_x$**), 6.31 (d, *J* = 7.5 Hz, 1H, **H$_g$**), 5.31 (d, *J* = 7.5 Hz, 1H, **H$_f$**), 4.27 (s, 2H, **H$_a$**), 1.00 (s, 12H, pin).

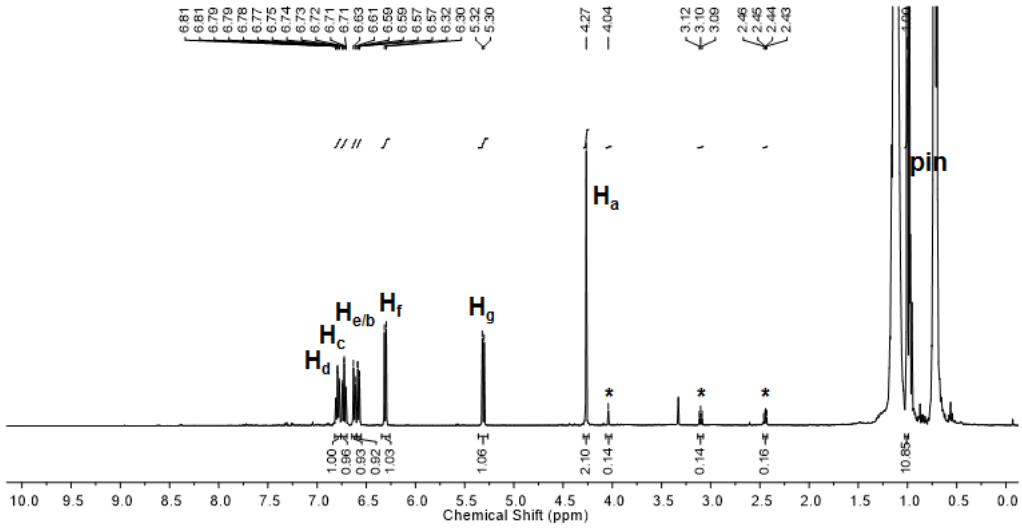


Figure S20. ^{1}H NMR (400 MHz, 298.0 K, heptane) spectrum of the reaction mixture after 18 hours (spectrum referenced to DMSO-d_6 in a glass capillary; * indicates unknown by-product (ca. 6%) hypothesized to be a 1,2,3,4-tetrahydroisoquinoline species).

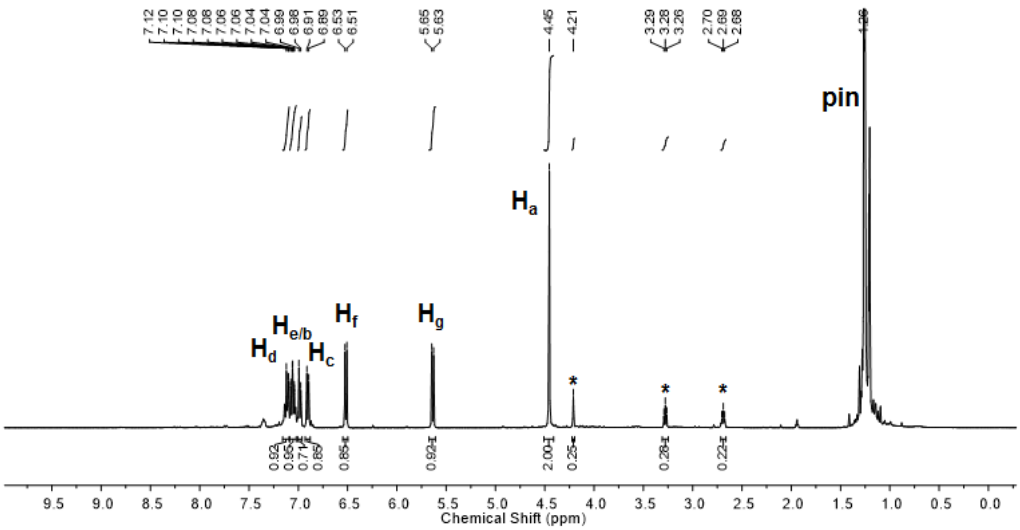


Figure S21. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum of the reaction mixture after 18 hours (* indicates unknown by-product (ca. 11%) hypothesized to be a 1,2,3,4-tetrahydroisoquinoline species).

NMR spectra of products isolated from preparative-scale reactions:

- *N*-boryl-1,4-dihydropyridine

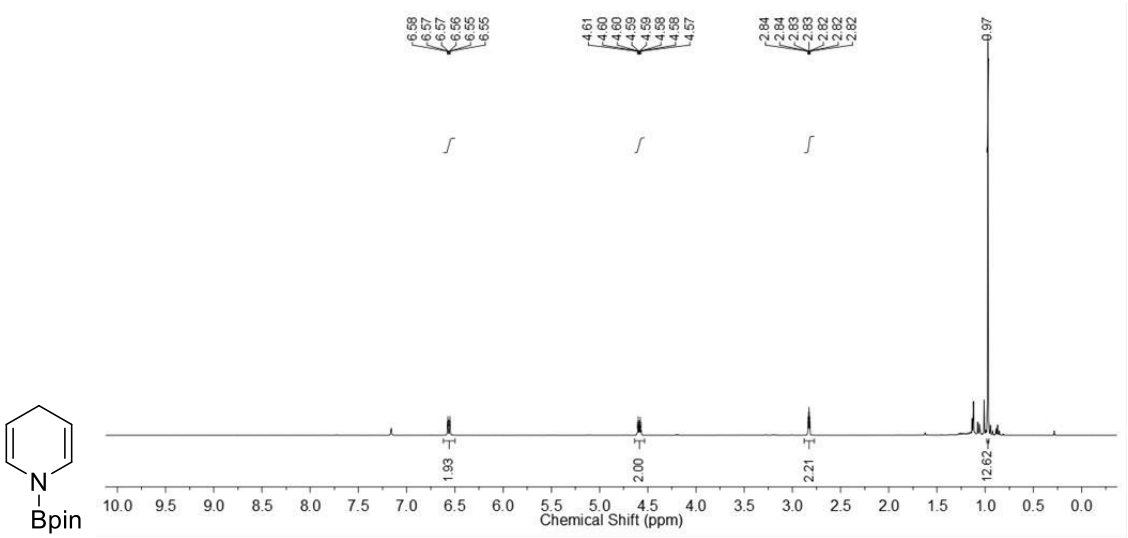


Figure S22. ^{1}H NMR (400 MHz, 298.0 K, C_6D_6) spectrum.

- *N*-boryl-3-methyl-1,4-dihydropyridine

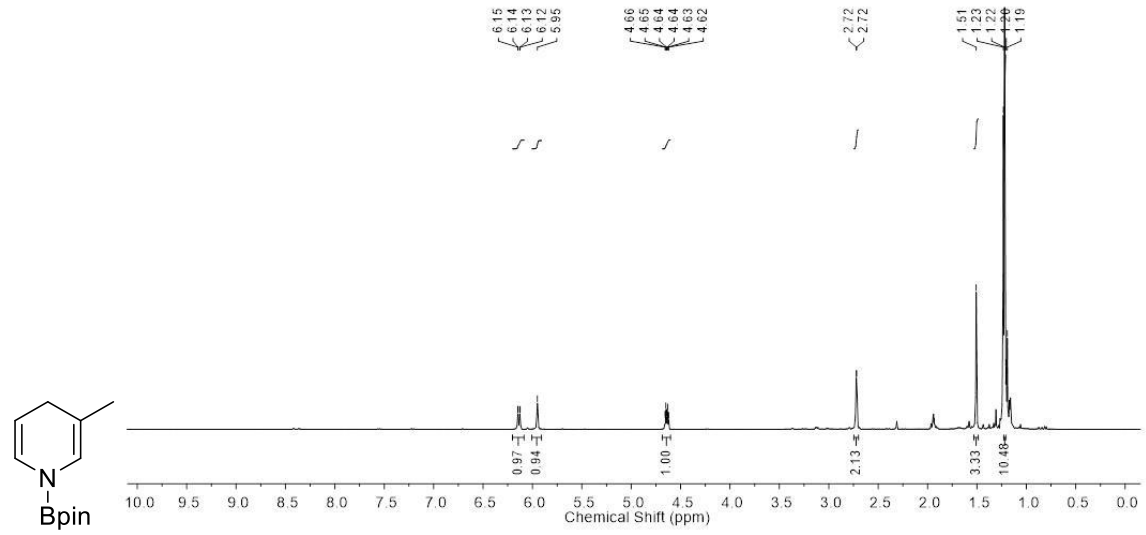


Figure S23. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-3-phenyl-1,4-dihydropyridine

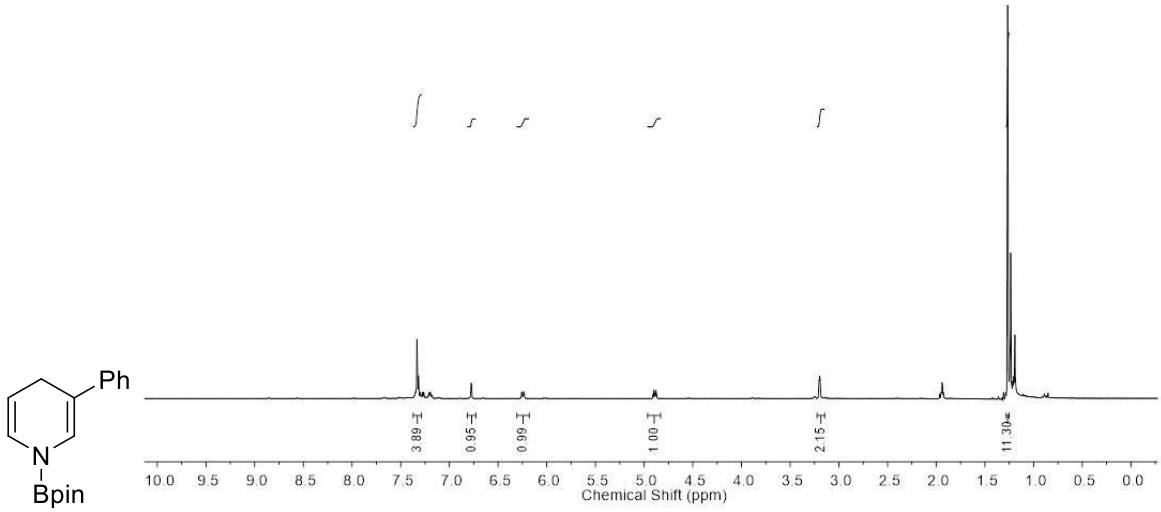


Figure S24. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-3-bromo-1,4-dihydropyridine

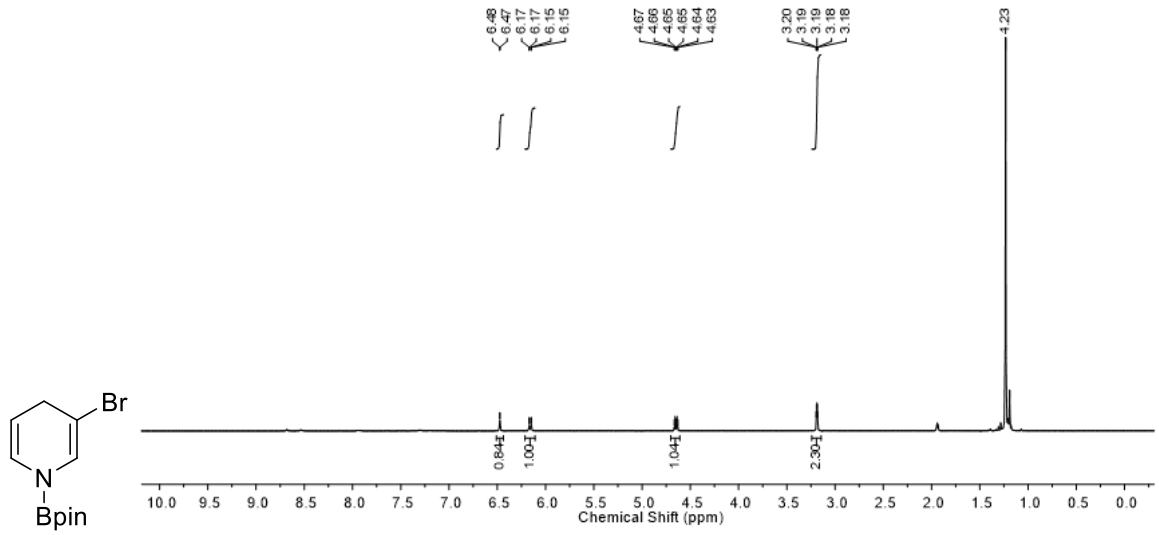


Figure S25. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-3-cyano-1,4-dihydropyridine

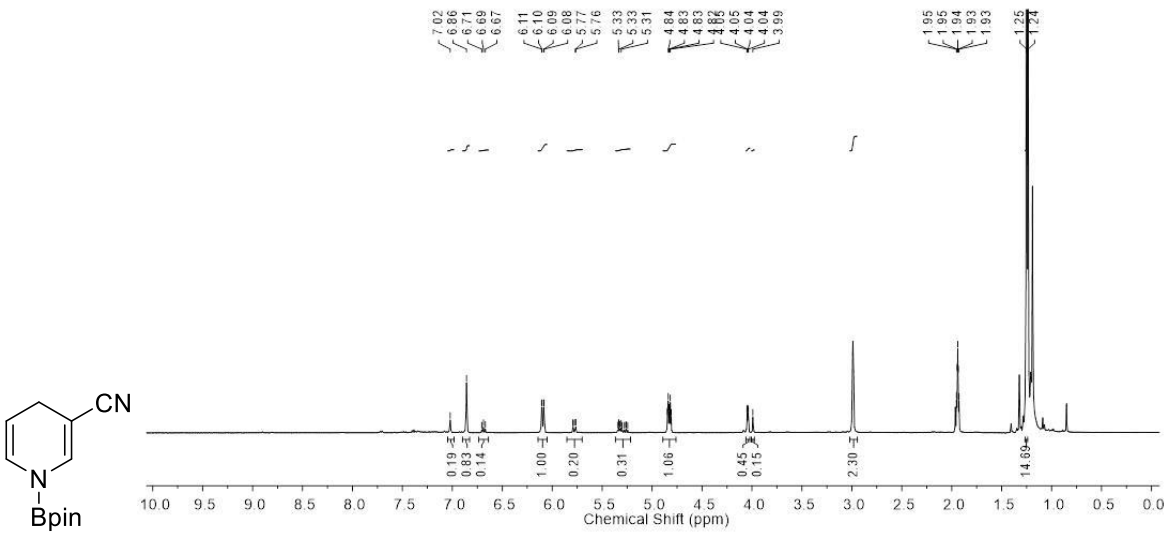


Figure S26. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-1,4-dihydropyridine-3-methylcarboxylate

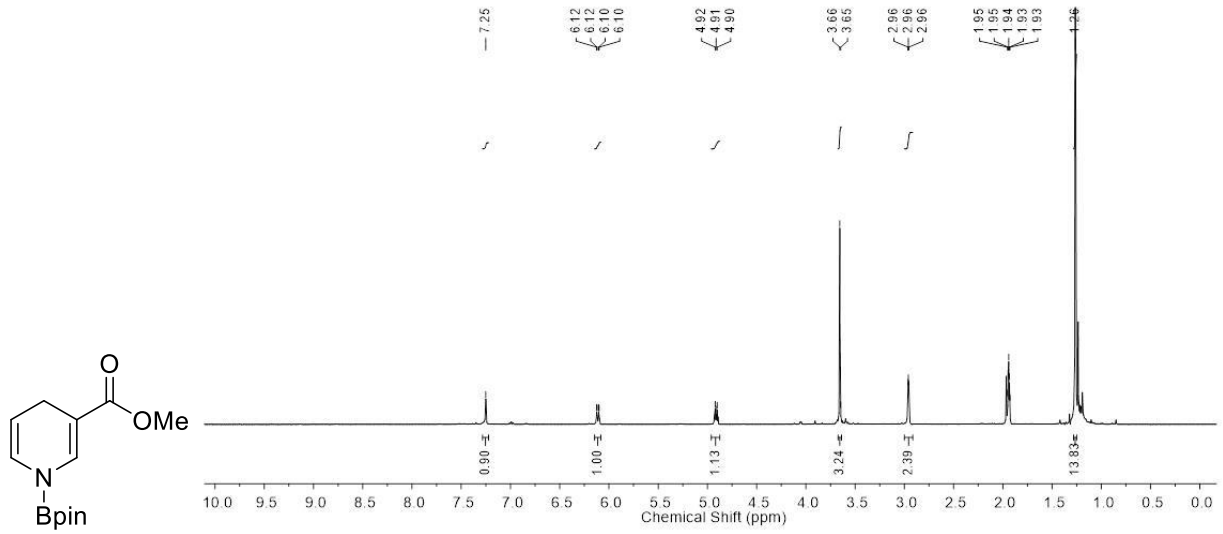


Figure S27. [1]H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-1,4-dihydropyridine-3-(*N'*,*N'*-diethylamide)

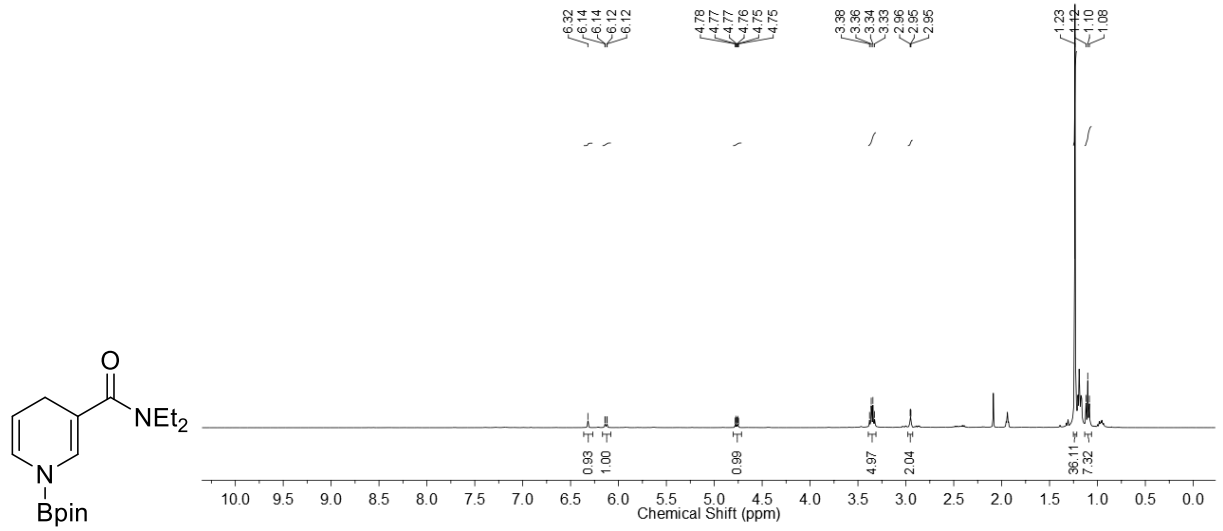


Figure S28. [1]H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

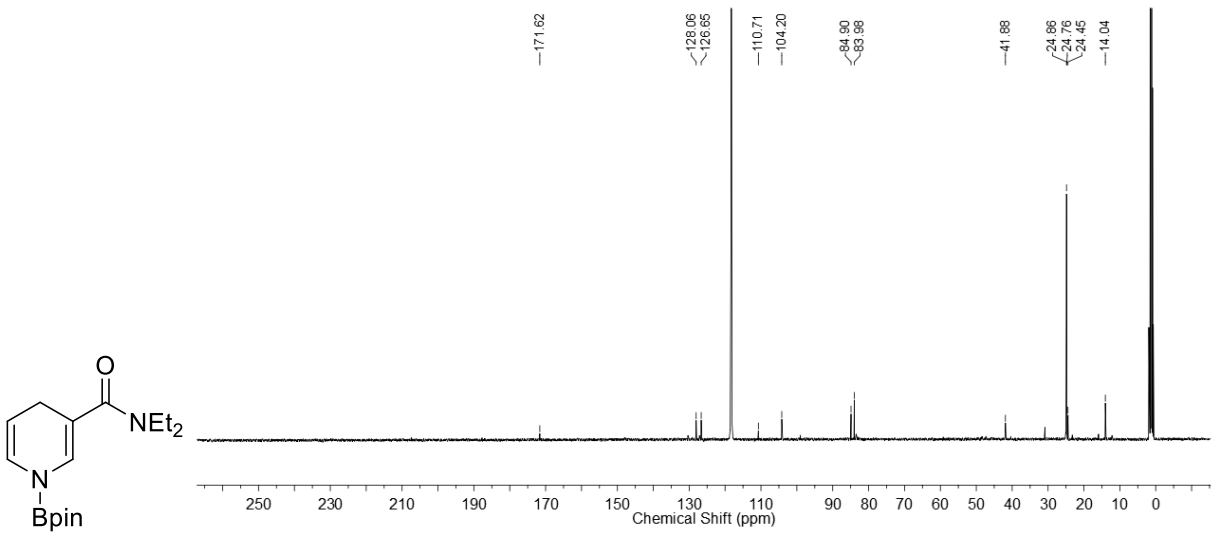


Figure S29. ^{13}C NMR (101 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-1,4-dihydro-3,5-lutidine

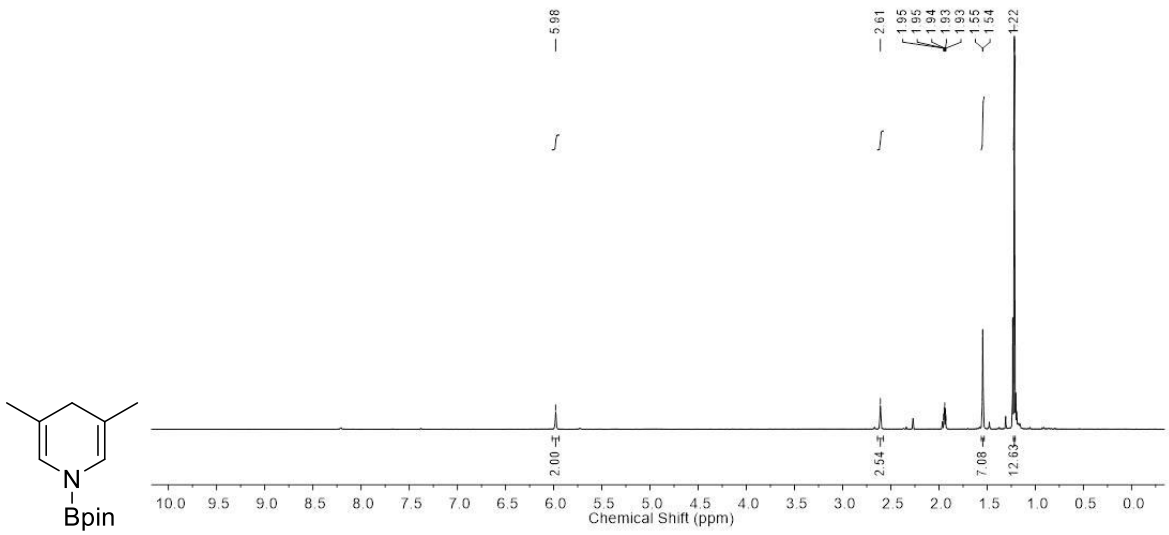


Figure S30. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-2-methyl-1,4-dihydropyridine

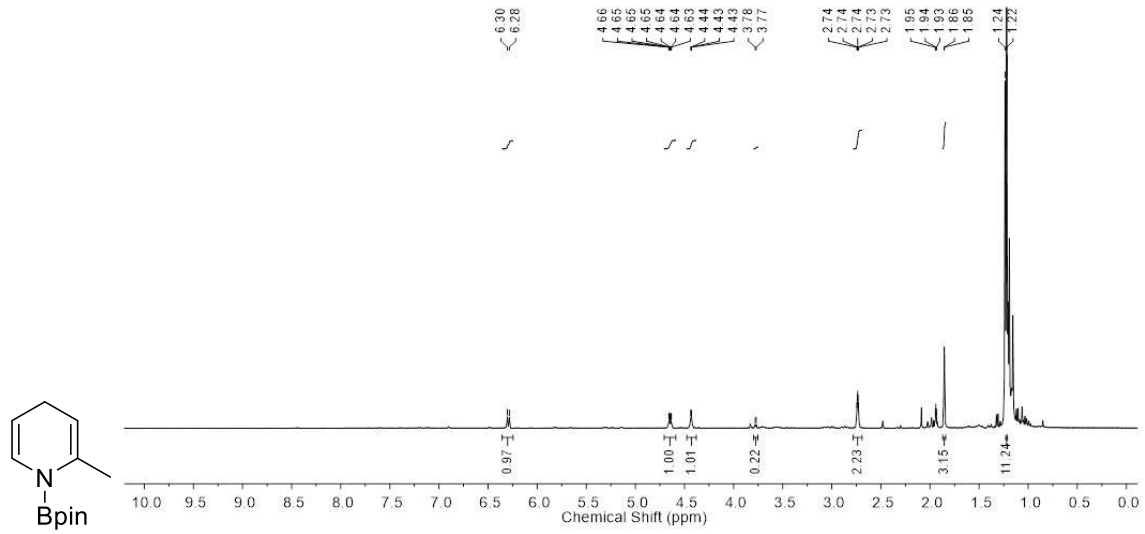


Figure S31. [1]H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-4-methyl-1,2-dihydropyridine

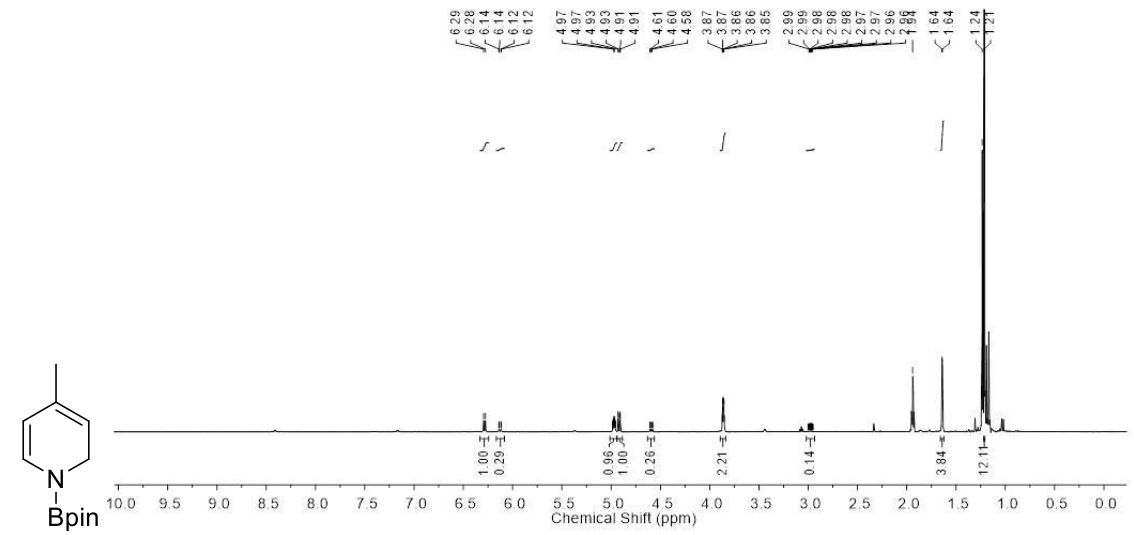


Figure S32. [1]H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-1,2-dihydroquinoline

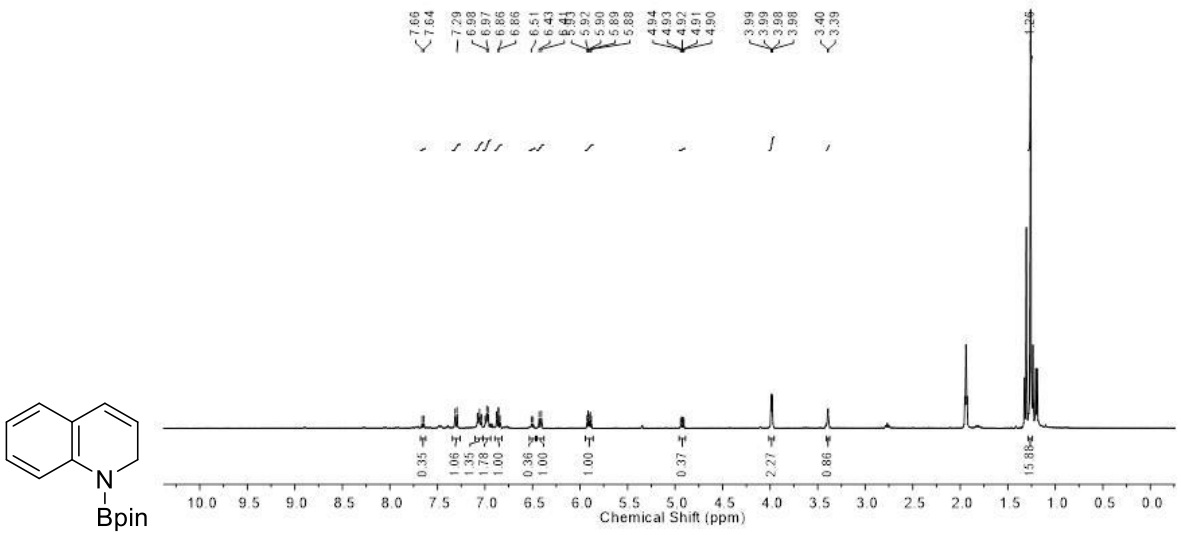


Figure S33. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

- *N*-boryl-1,2-dihydroisoquinoline

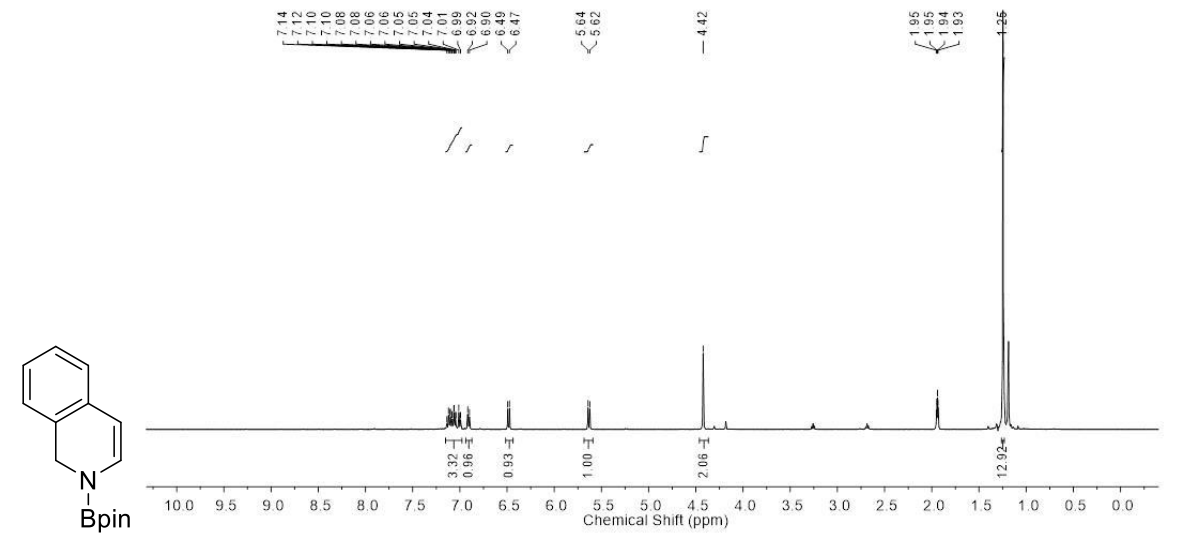


Figure S34. ^{1}H NMR (400 MHz, 298.0 K, CH_3CN) spectrum.

SI.4 Crystallographic Details:

Table 1. Crystal data and structure refinement for $pinBPy_2BPh_4$.

Identification code	DW_B2_0282
Empirical formula	$C_{40}H_{42}B_2N_2O_2$
Formula weight	604.37
Temperature/K	180.0
Crystal system	triclinic
Space group	P-1
a/Å	10.5637(3)
b/Å	10.8714(3)
c/Å	15.2958(4)
α/°	95.1220(10)
β/°	102.8720(10)
γ/°	95.0690(10)
Volume/$Å^3$	1694.99(8)
Z	2
$\rho_{calc}g/cm^3$	1.184
μ/mm^{-1}	0.550
F(000)	644.0
Crystal size/mm^3	0.7 × 0.17 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.964 to 133.832
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-18 \leq l \leq 17$
Reflections collected	32118
Independent reflections	5953 [R_{int} = 0.0737, R_{sigma} = 0.0475]
Data/restraints/parameters	5953/74/470
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0604, wR_2 = 0.1381
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1525
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.24

SI.5 References:

(1) Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3.

(2) Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.

(3) Fan, X.; Zheng, J.; Li, Z. H.; Wang, H. *J. Am. Chem. Soc.* **2015**, *137* (15), 4916–4919.

(4) Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Köhn, G.; Weetman, C. *Organometallics* **2011**, *30* (21), 5556–5559.

(5) Oshima, K.; Ohmura, T.; Suginome, M. *J. Am. Chem. Soc.* **2012**, *134* (8), 3699–3702.

(6) Dudnik, A. S.; Weidner, V. L.; Motta, A.; Delferro, M.; Marks, T. J. *Nat. Chem.* **2014**, *6* (12), 1100–1107.

(7) Intemann, J.; Lutz, M.; Harder, S. *Organometallics* **2014**, *33* (20), 5722–5729.