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1. Methods and Materials

1.1. Experimental Considerations

All manipulations were performed under an inert atmosphere using standard Schlenk-line, and glovebox techniques. Glassware was flame dried prior to use. Dry THF, diethyl ether, toluene, and pentane were obtained using Innovative Technologies anhydrous engineering solvent purification systems and subsequently degassed. DME, pyridine, and hexane were dried over Na or K, purified by distillation. *o*DFB was dried over CaH_2 and purified by distillation. Pyr-d_5, THF-d_8, C_6D_6, were dried over activated 3 Å molecular sieves. All solvents were stored over activated 3 Å molecular sieves.

Red phosphorus, naphthalene, catechol borane, pinacol borane, HBBN dimer, borane dimethyl sulfide, 18-crown-6, sodium triflate, 2-methyl pyridine, 2-methoxy pyridine, 3-methoxy pyridine, 3-chloro pyridine, 3,5-dimethyl pyridine, 4-methyl pyridine, 4-tert-butyl pyridine, quinoline, 6-methyl quinoline, 6-methoxy quinoline, 6-bromo quinoline, 8-methyl quinoline, 8-methoxy quinoline, 8-bromo quinoline, acridine, N-benzylideneaniline, N-(1-phenylethylidene)aniline, benzonitrile, 4-bromobenzonitrile, 4-methoxybenzonitrile, cyclohexylcarbonitrile, butrylnitrile, pyridine-3-carbonitrile, trityl tetrakis(pentafluorophenyl)borate were purchased from a commercial source (Sigma-Aldrich, Alfa Aesar, Fuorochem, Tokyo Chemical Industry, Thermo Fisher Scientific, and Acros Organics) and used without purification. Elemental sodium and elemental potassium were cleaned by removal of the oxide layers and washing with toluene and hexane. Clusters $[Na(DME)_x]_3P_7$, K_3P_7, $(Me_3Si)_3P_7$, $[Na(18\text{-}c\text{-}6)]_2[HP_7]$, $[K(18\text{-}c\text{-}6)]_2[HP_7]$, $[Na(18\text{-}c\text{-}6)]_2[(BBN)P_7]$ and $[K(18\text{-}c\text{-}6)]_2[(BBN)P_7]$ were synthesized using modified literature procedures.[1-3] N-phenyl-1-(p-tolyl)methanimine, 1-(4-bromophenyl)-N-phenylmethanimine, 1-(4-methoxyphenyl)-N-phenylmethanimine, N-methyl-1-(p-tolyl)methanimine, N-methyl-1-(4-methoxyphenyl)methanimine, N-methyl-1-(4-methoxyphenyl)methanimine, N-t-butyl-1-phenylmethanimine, N-(cyclohexylmethylene)-2-methylpropan-2-amine, N-(2,4,6-trimethylphenyl)-1-phenylmethanimine, N-(2-pyridylmethylidene)methylamine, 2-(phenyliminomethyl)pyridine were synthesized using modified literature procedures.[4, 5]

1.2. Analytical Considerations

NMR Spectroscopy. ^{1}H, ^{1}H COSY, ^{11}B, ^{11}B{^{1}H}, ^{13}C{^{1}H}, ^{31}P NMR and ^{31}P COSY spectra were recorded on a Bruker AVIII 400 spectrometer (operating frequencies: 399.78 MHz, 128.36 MHz, 100.53 MHz and 161.83 MHz for ^{1}H, ^{11}B, ^{13}C, and ^{31}P, respectively). ^{1}H and ^{13}C{^{1}H} NMR chemical shifts were internally referenced to the residual solvent resonances (C_6D_6 (benzene-d_6): ^{1}H δ = 7.16 ppm, ^{13}C{^{1}H} δ = 128.02 ppm, THF-d_8 (tetrahydrofuran-d_8): ^{1}H δ = 3.58, 1.73 ppm, ^{13}C{^{1}H} δ = 67.57, 25.37 ppm, Pyr-d_5 (pyridine-d_5): ^{1}H δ = 8.74, 7.58, 7.22 ppm, ^{13}C{^{1}H} δ = 150.35, 135.91, 123.87 ppm. ^{11}B, ^{31}P chemical shifts were externally referenced to $BF_3{\cdot}Et_2O$, H_3PO_4, respectively. Solution phase NMR samples were prepared under an inert atmosphere in 5 mm J Young NMR tubes. NMR data was analyzed using MestReNova V14.0.0 software or Topspin V3.6.1 software.

Mass spectrometry. Mass spectrometry samples were measured by the mass spectrometry service of the University of Manchester using an electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) equipped Thermo Orbitrap Executive Plus Extended Mass Range mass spectrometer. Samples were prepared under a nitrogen atmosphere, unless stated after hydrolysis and directly injected into the ionization source of the mass spectrometer.

1.3. X-ray Diffraction Studies

Data collection: X-ray diffraction data for compounds **2b'** and **2b''** were collected using a dual wavelength Rigaku FR-X rotating anode diffractometer using CuKα (λ = 1.54146 Å) radiation, equipped with an AFC-11 4-circle kappa goniometer, VariMAX^{TM} microfocus optics, a Hypix-6000HE detector and an Oxford Cryosystems 800 plus nitrogen flow gas system, at a temperature of 100K. Data were collected and reduced using CrysAlisPro v42. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.

Crystal structure determination and refinements: The crystal structures were solved and refined against all F^2 values using the SHELX and Olex2 suite of programmes.[6, 7] All atoms were refined anisotropically. Hydrogen atoms for both models were freely refined with isotropic atomic displacement parameters.

Crystallographic data have been deposited with the CCDC (CCDC 2260639-2260640).

2. Catalytic hydroboration of N-Heteroarenes

2.1. Initial investigations

During the synthesis of $[(BBN)P_7]^{2-}$ ($[\mathbf{1}]^{2-}$)[3]: To a mixture of $[Na(18\text{-c-}6)]_2[HP_7]$ (250 mg, 0.64 mmol, 1 eq.) and $(HBBN)_2$ (116 mg, 0.48 mmol, 1.5 eq.) THF (20 mL) was added and allowed to react for 1 h. After complete consumption of $(HBBN)_2$, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of THF and upon slow diffusion of hexane into the concentrated THF solution red crystals formed. If advantage pyridine was present in the $[Na(18\text{-c-}6)]_2[HP_7]$, minor amounts of clear crystals could be detected under a microscope, and were found to be suitable for single crystal X-ray diffraction analysis. Two different crystals were obtained.

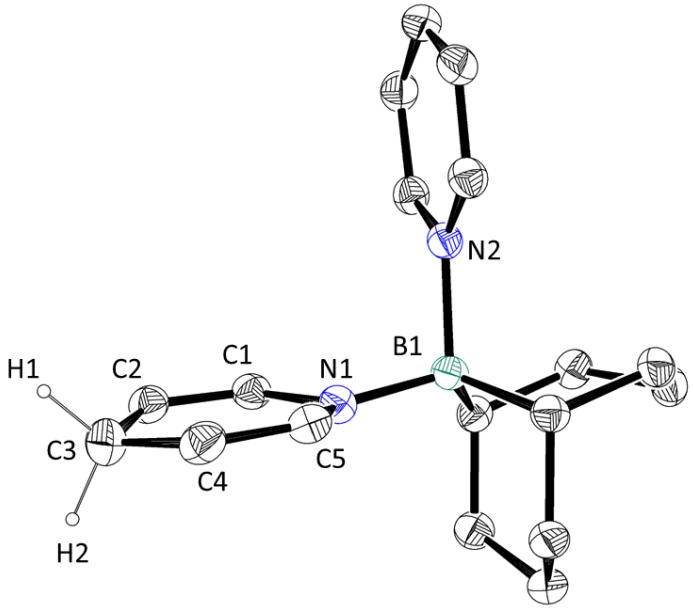


Figure S1. Molecular structure of **2b'**. Anisotropic displacement ellipsoids pictured at 50% probability. Only selected hydrogen atoms shown for clarity. Boron: green; carbon: black; nitrogen: blue, hydrogen: white. Selected bond length [Å]: B1–N1 1.5440(13), B1–N2 1.6779(13), C1–C2 1.3402(14), C2–C3 1.5044(16); selected bond angles [deg]: C2–C3–C4 109.22(9).

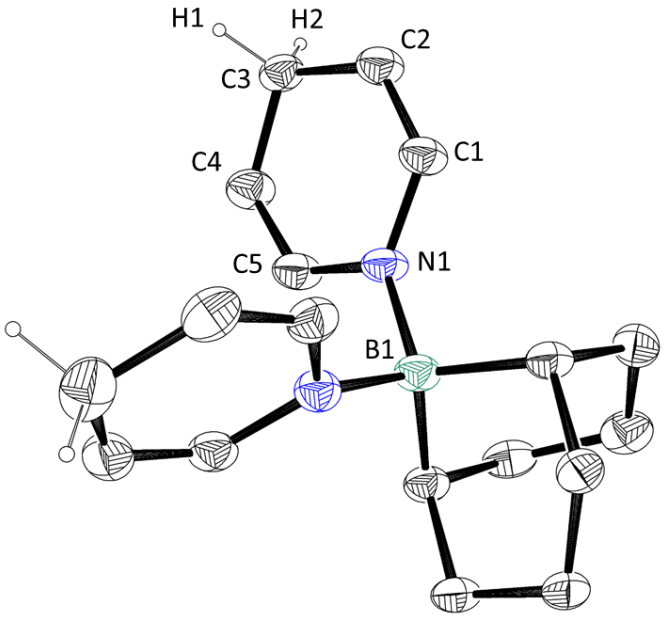
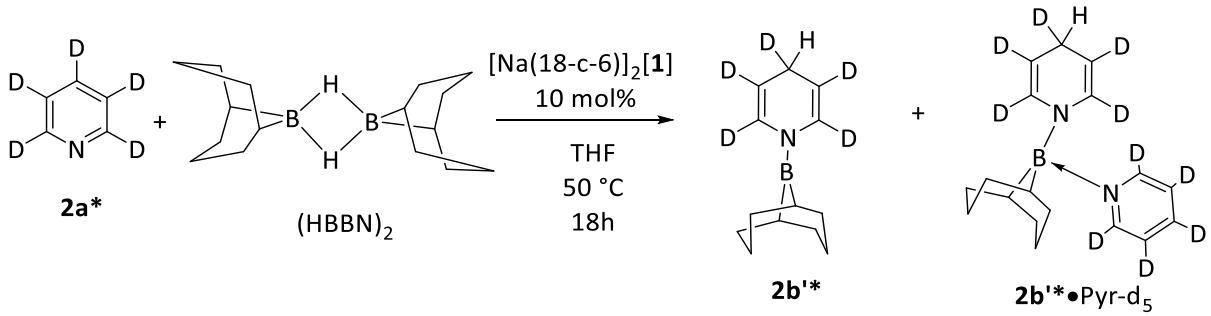


Figure S2. Molecular structure of **2b''** in the $[Na(THF)_2(18\text{-c-}6)][\mathbf{2''}]$ salt. Anisotropic displacement ellipsoids pictured at 50% probability. Only selected hydrogen atoms shown and $[Na(THF)_2(18\text{-c-}6)]^+$ cation omitted for clarity. Boron: green; carbon: black; nitrogen: blue; hydrogen: white. Selected bond length [Å]: B1–N1 1.581(3), B1–N2 1.582(2), C1–C2 1.345(3), C2–C3 1.501(3); selected bond angles [deg]: C2–C3–C4 109.04(18).

2.2. Deuterium labelled studies



To a solution of $[Na(18\text{-c-}6)]_2[\mathbf{1}]$ (25 mg, 0.027 mmol, 0.1 eq.) and $(HBBN)_2$ (33 mg, 0.135 mmol, 0.5 eq.) in THF (0.5 mL), pyridine-d_5 (22 µL, 0.27 mmol, 1 eq.) was added and allowed to react at 50 °C for 18 h. The reaction was monitored by ^1H, ^2H, ^{11}B and $^{11}B\{^1H\}$ NMR. After complete consumption of $(HBBN)_2$ the solvent was removed under

reduced pressure. The residue was extracted using C_6D_6. Resonances corresponding to **2b'*** are picked below.

^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 2.76 (t, $^2J_{HD}$ = 3.1 Hz, CD*H*) ppm.

^{2}H NMR (61 MHz, 298 K, C_6D_6): δ = 6.51 (bs, NC*D*$_2$CD$_2$), 4.68 (bs, NCD$_2$C*D*$_2$), 2.67 (bs, C*D*H) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 52.42 (s, **2b'***), 0.45 (s, **2b'*** •Pyr) ppm.

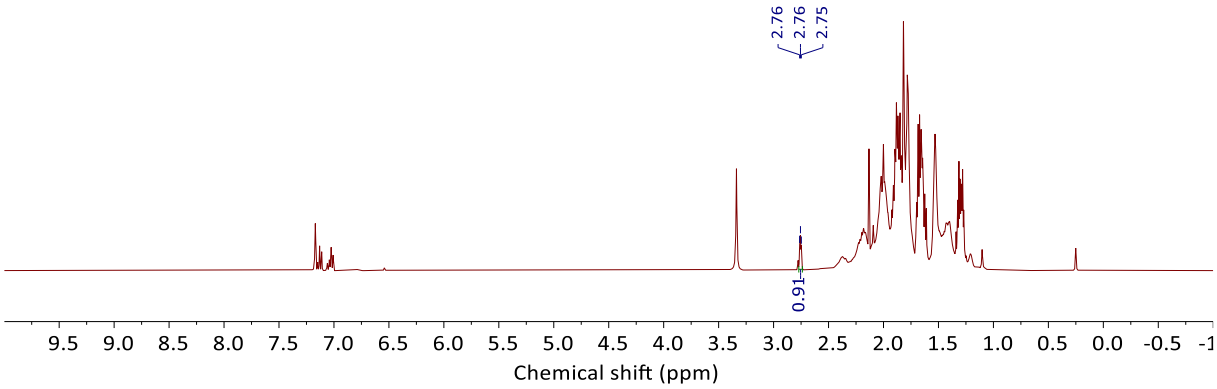


Figure S3. ^{1}H NMR spectrum (C_6D_6) of deuterium labelled studies.

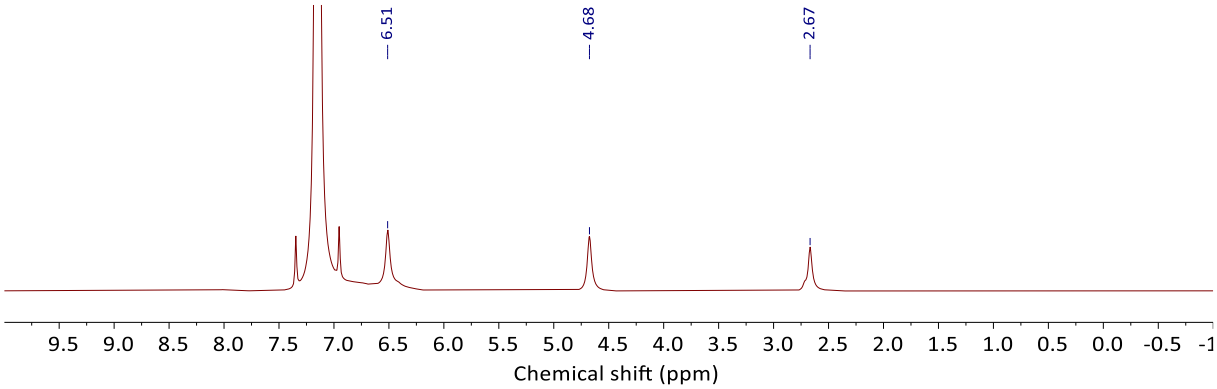


Figure S4. ^{2}H NMR spectrum (C_6D_6) of deuterium labelled studies.

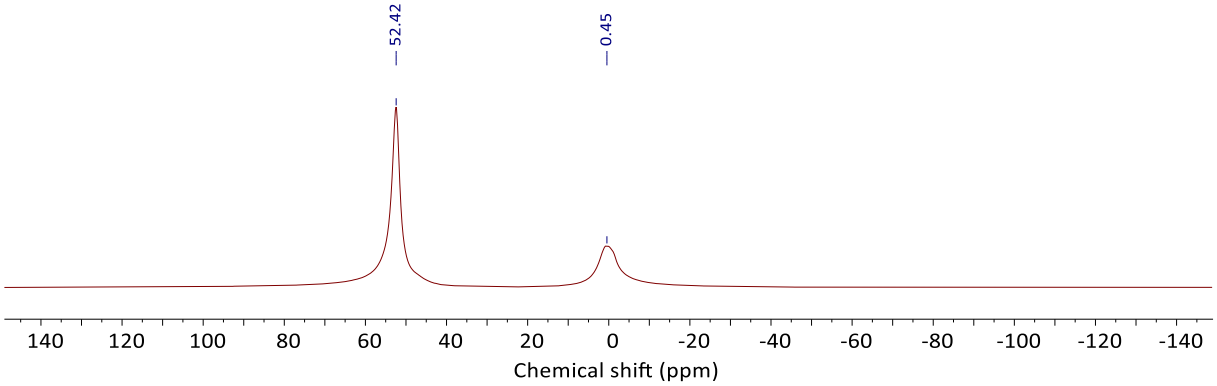


Figure S5. ^{11}B NMR spectrum (C_6D_6) of deuterium labelled studies.

2.3. Screening and controls

To a solution of catalyst and borane (B–H, 0.27 mmol, 1 eq.) in solvent (0.5 mL), pyridine (22 µL, 0.27 mmol, 1eq.) was added and allowed to react at the specified temperature for 24 h. The reaction was monitored by ^{1}H NMR, ^{11}B NMR and ^{11}B{^{1}H} NMR. When *o*DFB was employed as a solvent, the ^{1}H NMR spectrum was referenced to toluene. Crude NMR conv. was determined by integration using the resonances of the 18-crown-6 in [**1**]$^{2-}$ as internal standard or the crude NMR conv. was determined by integration using toluene (^{1}H δ = 2.31 ppm) as internal standard (25 µL, 0.24 mmol, toluene).

2.4. Control $[P_7]^{3-}$ as pre-catalyst

Following the procedure described in section 2.3. above, the reaction of $[Na(DME)]_3[P_7]$ with HBpin and pyridine in the presence of 18-c-6 as shown in Table 2 in the manuscipt resulted in a functionalized cluster observed by ^{31}P NMR spectroscopy (Figure S6, top spectrum). The five major resonances (highlighted below) are consistent with a $[P_7]$ cage having a mirror plane and κ^2-substitution as reported for the $[(BBN)P_7]^{2-}$ cluster we previously reported. Reaction of $[Na(DME)]_3[P_7]$ with an excess of HBpin and 18-c-6 did not show any new resonances in the ^{31}P NMR spectrum. It was suspected that substrate must be present to accept the hydride from HBpin. This need for a hydride acceptor was further probed by the addition of tritylium tetrakis(pentafluorophenyl)borate as a stoichiometric hydride acceptor in place of the substrate, ^{31}P NMR in Figure S6, middle spectrum. The ^{31}P NMR spectrum from the *in situ* generated $[(Bpin)P_7]^{2-}$ from reaction of $[Na(18\text{-}c\text{-}6)]_2[HP_7]$ and HBpin reveals similar resonances (Figure S6, bottom spectrum), along with formation of polyphosphide (labelled by *) decomposition products and $[(HBpin)(Bpin)P_7]^{2-}$ (labelled by #).

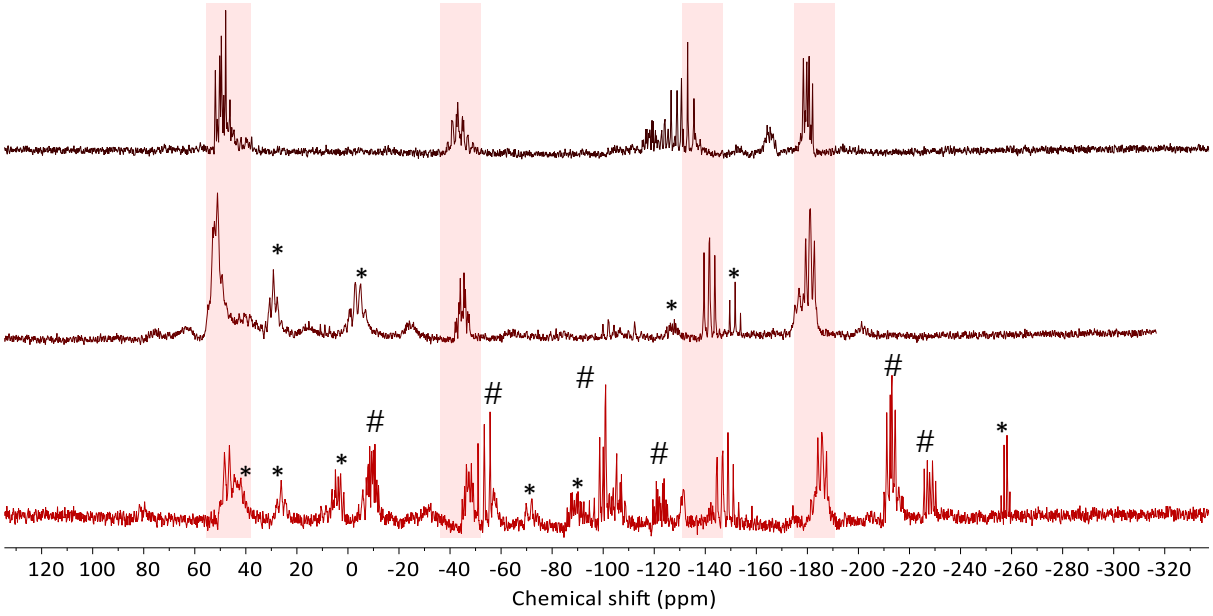


Figure S6. Stacked ^{31}P NMR spectra (*o*DFB) of control experiments $[P_7]^{3-}$ as pre-catalyst: top: reaction mixture HBpin + $[Na(DME)_x]_3[P_7]$ + 18-c-6 + pyridine, middle: reaction mixture HBpin + $[Na(DME)_x]_3[P_7]$ + 18-c-6 + $[Ph_3C][B(C_6F_5)_4]$, bottom: reaction mixture $[Na(18\text{-}c\text{-}6)]_2[HP_7]$ + HBpin. Polyphosphide: labelled by * and $[(HBpin)(Bpin)P_7]^{2-}$ labelled by #.

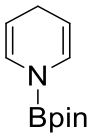
2.5. General procedure for hydroboration of heteroarenes

To a solution of $[Na(18\text{-}c\text{-}6)]_2$[**1**] (10 mg, 11 µmol, 0.05 eq.) and pinacolborane (HBpin; 28 mg, 32 µL, 0.22 mmol, 1 eq.) in *o*DFB (0.5 mL), N-heteroarenes (0.22 mmol, 1 eq.) and toluene (25 µL, 0.24 mmol) was added and allowed to react at 50 °C for 18–48 h. The reaction was monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using toluene (^{1}H δ = 2.31 ppm) as an internal standard. The reaction mixture was worked-up by removal of volatiles and extraction by pentane to remove catalyst and any possible residual HBpin, unless stated otherwise below. In the crude NMR spectra, the resonances used for the calculation of the conversion has been picked and integrated, unless isolation was not possible, then all resonances identified for the products are picked and integrated.

2.6. Characterization data hydroboration of heteroarenes

We validated our analysis of most hydroborated heteroarenes by comparison to various literature sources and found all data to be in agreement with those previously reported.[8, 9]

2.6.1. 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine and 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydropyridine

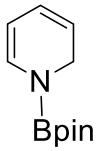


^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.52 (dt, $^{3}J_{HH}$ = 8.7, $^{4}J_{HH}$ = 1.8 Hz, 2H, alkene-*H*), 4.63 – 4.48 (m, 2H, alkene-*H*), 2.81 (tt, $^{3}J_{HH}$ = 3.3, $^{4}J_{HH}$ = 1.7 Hz, 2H, CH_2), 0.97 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 23.9 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 127.54 (s), 103.83 (s), 83.38 (s), 24.62(s), 22.79 (s) ppm.

NMR Conv.: 83%



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.70 (dt, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 1.3 Hz, 1H, alkene-*H*), 5.85 – 5.71 (m, 1H, alkene-*H*), 5.17–5.08 (m, 2H, alkene-*H*), 4.15 (dt, $^{3}J_{HH}$ = 4.2, $^{4}J_{HH}$ = 1.4 Hz, 2H, C*H*$_2$), 1.00 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 23.9 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 132.66 (s), 124.28 (s), 114.94 (s), 102.83 (s), 83.17 (s), 42.55 (s), 24.72 (s) ppm.

NMR Conv.: 16%

Mass spectrometry (APCI): $C_{11}H_{18}BNO_2$+Na ([M+Na]$^{+}$): calcd: 207.1431; found: 207.1428.

Isolated Yield after work up both isomers: 90%

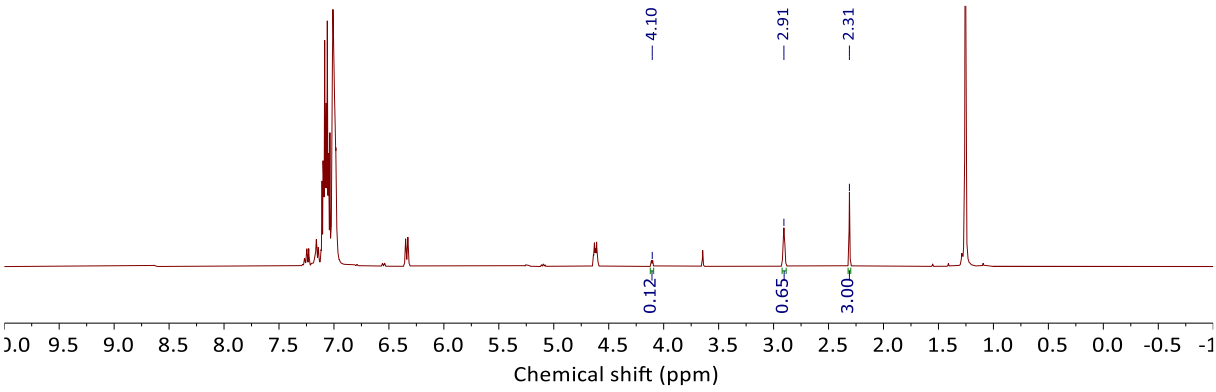


Figure S7. ^{1}H NMR spectrum (*o*DFB) of crude **2b** and **2c**.

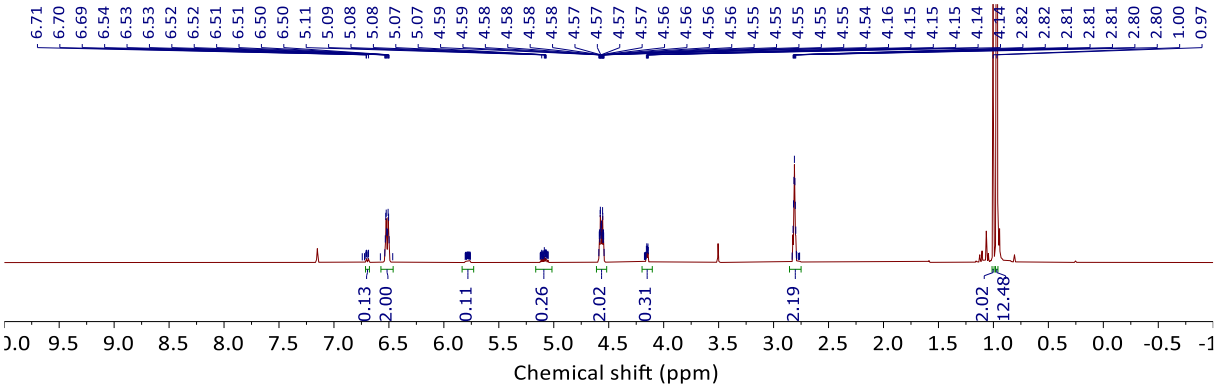


Figure S8. ^{1}H NMR spectrum (C_6D_6) of **2b** and **2c**.

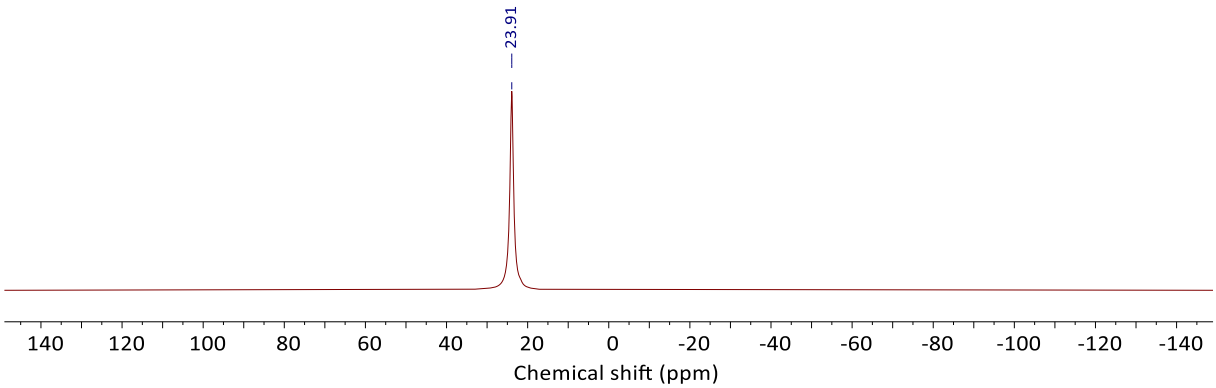


Figure S9. ^{11}B NMR spectrum (C_6D_6) of **2b** and **2c**.

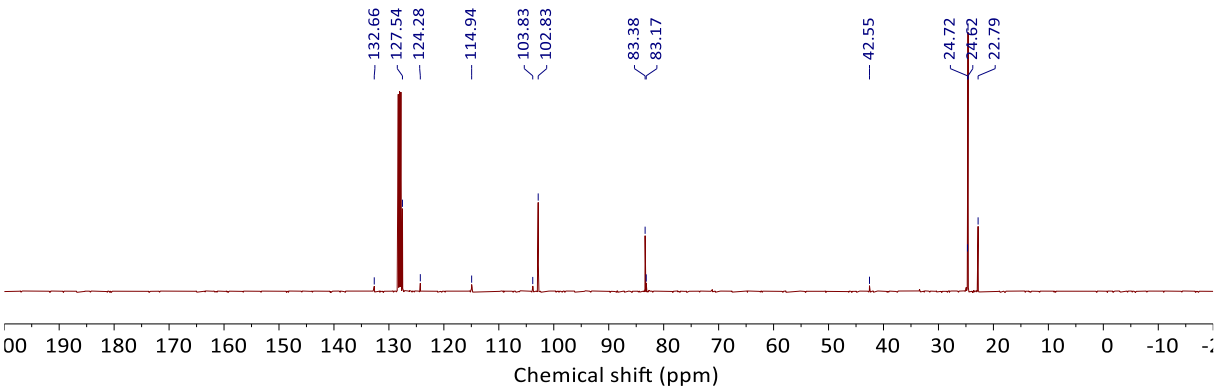
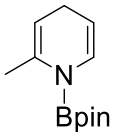


Figure S10. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **2b** and **2c**.

2.6.2. 2-methyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.81 (dt, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.6 Hz, 1H, alkene-*H*), 4.75 – 4.69 (m, 1H, alkene-*H*), 4.51 – 4.44 (m, 1H, alkene-*H*), 2.85 (tt, $^3J_{HH}$ = 3.3, $^4J_{HH}$ =1.6 Hz, 2H, C*H*$_2$), 2.10 – 2.07 (m, 3H, *Me*) , 0.97 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6**):** δ = 24.2 (s) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 135.70 (s, alkene-*C*), 129.82 (s, alkene-*C*), 102.88 (s, alkene-*C*), 102.52 (s, alkene-*C*), 83.64 (s, *NBpin*), 24.46 (s, *NBpin*), 23.93 (s, *C*H$_2$), 22.41 (s, *Me*) ppm.

Mass spectrometry (APCI): $C_{12}H_{20}BNO_2$+H ($[M+H]^+$): calcd: 222.1662; found: 222.1667.

NMR Conv.: 53%

Isolated Yield: 46%

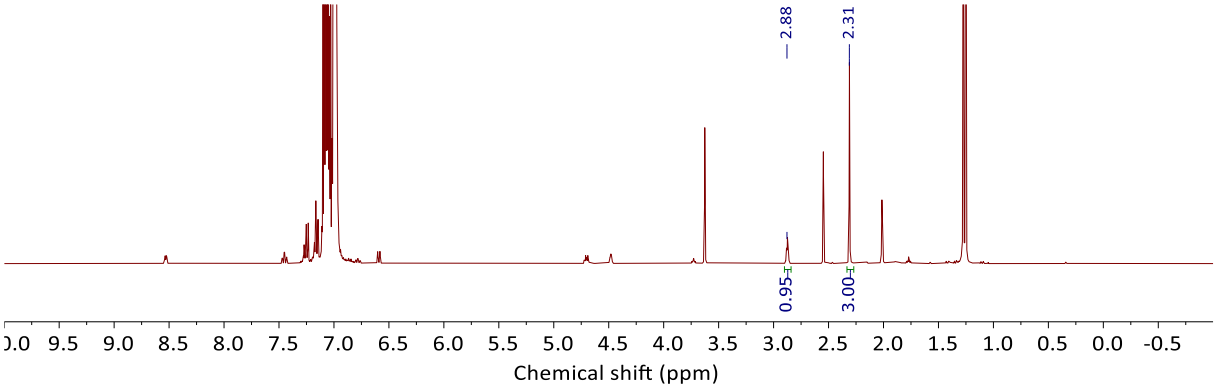


Figure S11. ^{1}H NMR spectrum (*o*DFB) of crude **3b**.

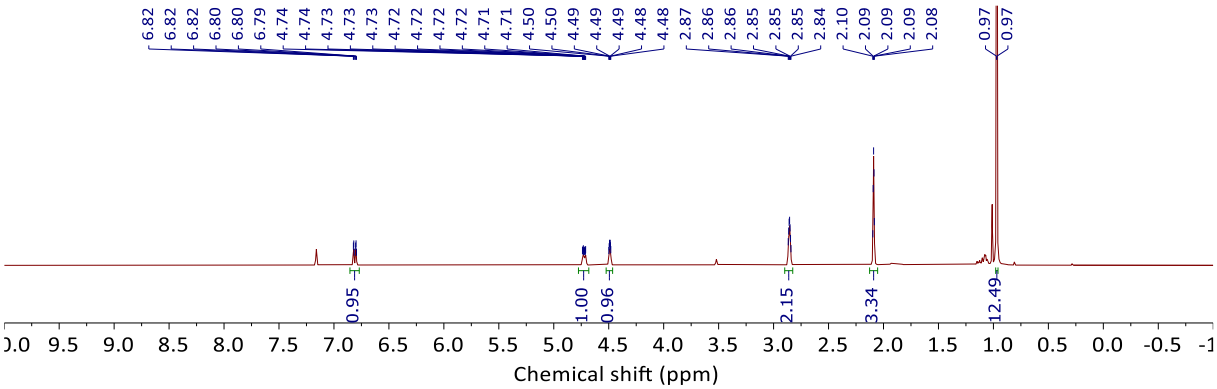


Figure S12. ^{1}H NMR spectrum (C_6D_6) of **3b**.

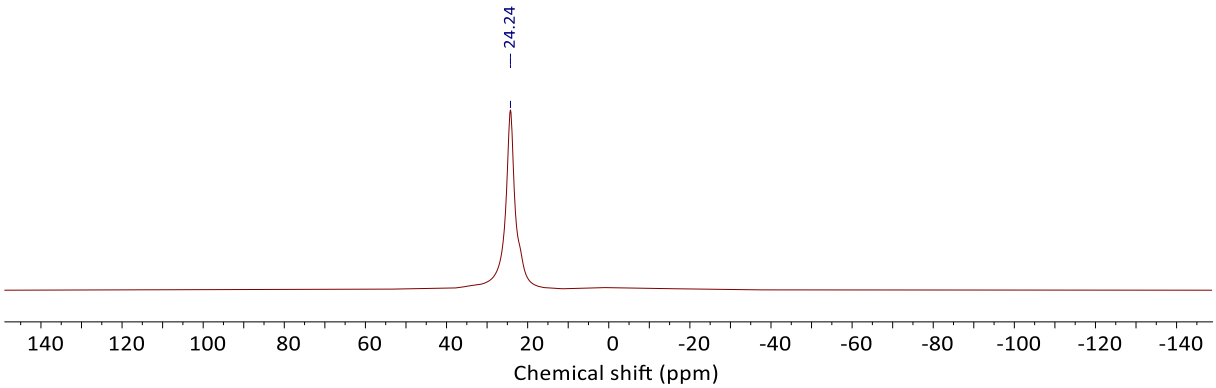


Figure S13. ^{11}B NMR spectrum (C_6D_6) of **3b**.

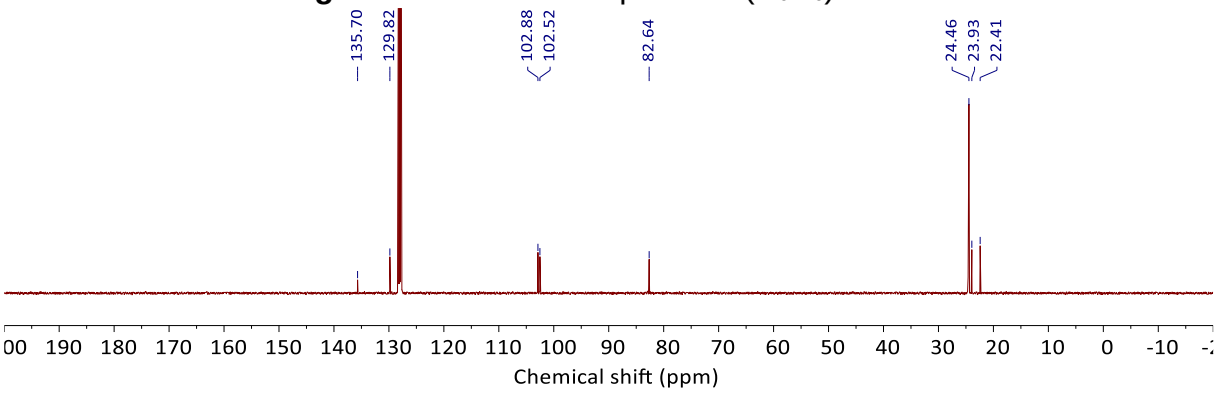
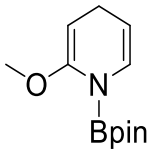


Figure S14. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **3b**.

2.6.3. 2-methoxyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.51 (dt, $^{3}J_{HH}$ = 8.3, $^{4}J_{HH}$ = 0.9 Hz, 1H, alkene-*H*), 3.76 (s, 3H, O*Me*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.8 (s) ppm.

Mass spectrometry (APCI): $C_{12}H_{20}BNO_3$+H ([M+H]$^{+}$): calcd: 238.1609; found: 238.1619.

NMR Conversion: 1%

Note: Resonances corresponding to the NBpin moiety could not be observed due to low concentration. Isolation of the product was not possible due to the low conversion.

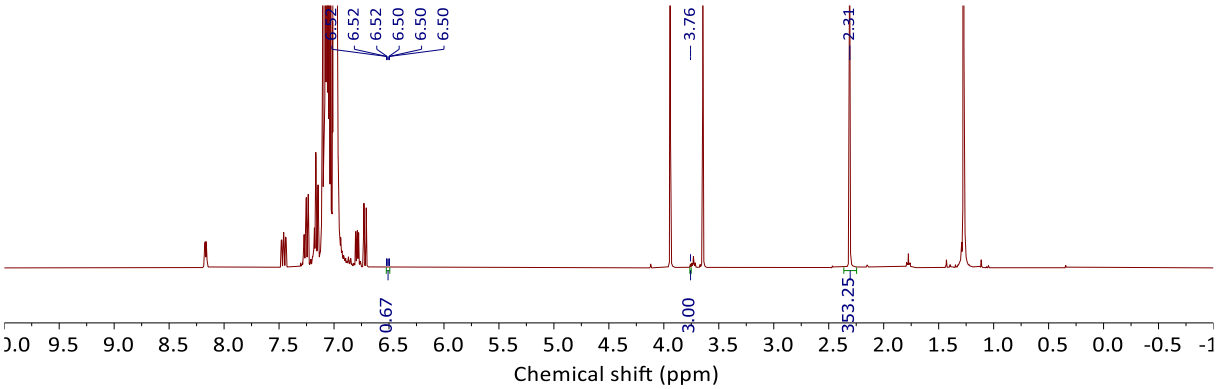


Figure S15. ^{1}H NMR spectrum (*o*DFB) of crude **4b**.

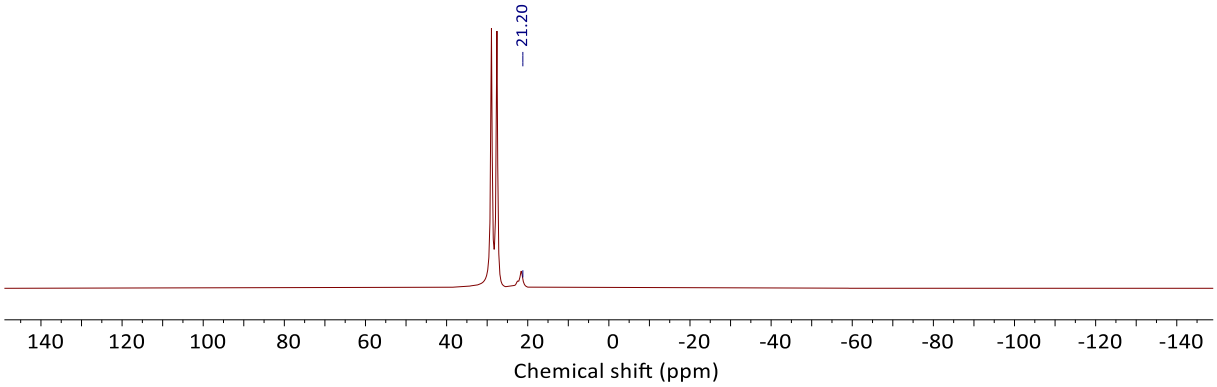
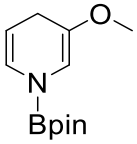


Figure S16. ^{11}B NMR spectrum (*o*DFB) of crude **4b**.

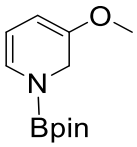
2.6.4. 3-methoxyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine, 3-methoxyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydropyridine and 3-methoxyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydropyridine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.44 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, alkene-*H*), 5.98 (s, 1H, alkene-*H*), 4.71 (dt, $^{3}J_{HH}$ = 8.0, 3.4 Hz, 1H, alkene-*H*), 3.42 (s, 3H, O*Me*), 3.05 (dt, $^{3}J_{HH}$ = 3.0, $^{4}J_{HH}$ = 1.4 Hz, 2H, CH_2), 1.29 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.8 (s) ppm.

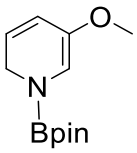
NMR Conv.: 40%



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.32 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, alkene-*H*), 5.11 (dd, $^{3}J_{HH}$ = 7.1, 6.3 Hz, 1H, alkene-*H*), 4.93 (d, $^{3}J_{HH}$ = 6.2 Hz, 1H, alkene-*H*), 4.15 (d, $^{4}J_{HH}$ = 0.9 Hz, 2H, CH_2), 3.52 (s, 3H, O*Me*), 1.27 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.8 (s) ppm.

NMR Conv.: 14%



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.16 (s, 1H, alkene-*H*), 5.38 (s, 1H), 4.17 (d, $^{4}J_{HH}$ = 1.1 Hz, 2H, CH_2), 3.47 (s, 3H, O*Me*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 21.2 (s) ppm.

NMR Conv.: 3%

Note: Resonances corresponding to the NBpin moiety and alpha alkene-*H could not be observed due to low concentration. Isolation of the product was not possible due to the low conversion and difficulties to remove **5a**.*

Mass spectrometry (APCI): $C_{12}H_{20}BNO_3$+H ([M+H]$^{+}$): calcd: 238.1609; found: 238.1614.

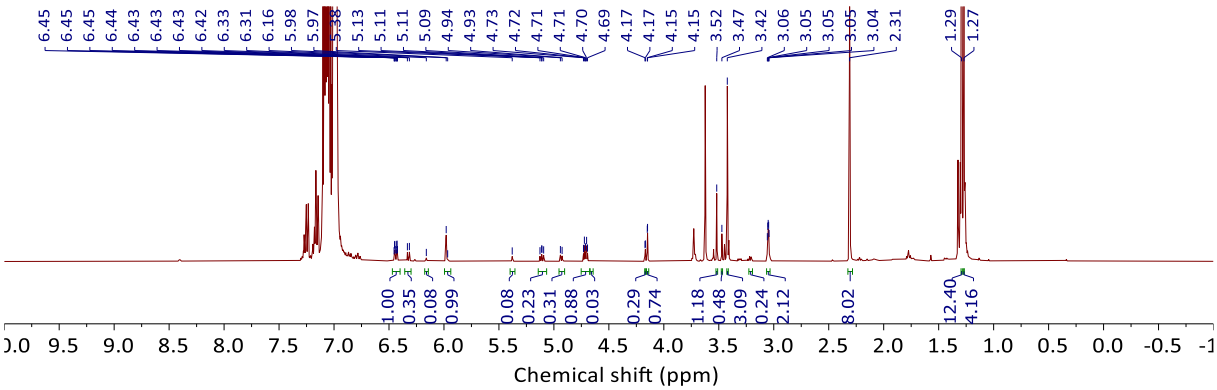


Figure S17. ^{1}H NMR spectrum (*o*DFB) of crude **5b**, **5c** and **5d**.

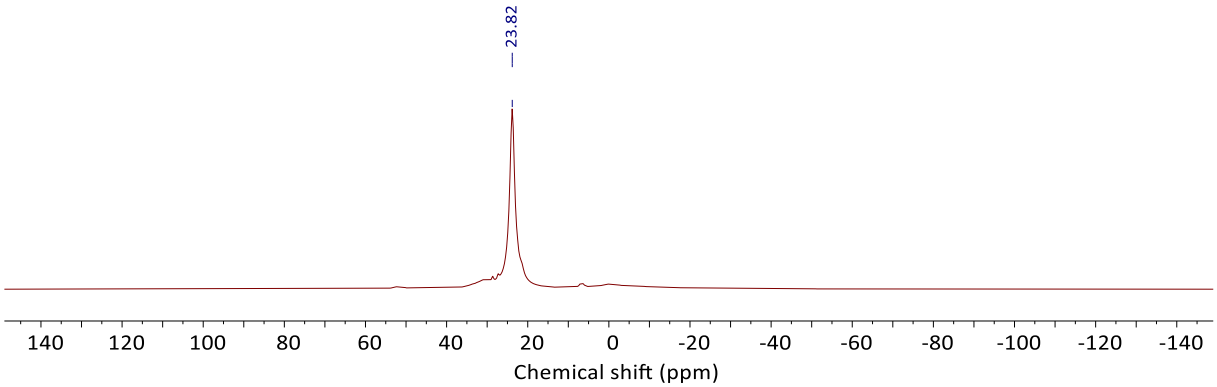
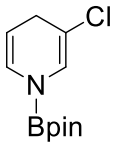


Figure S18. ^{11}B NMR spectrum (*o*DFB) of crude **5b**, **5c** and **5d**.

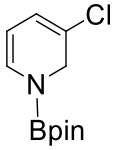
2.6.5. 3-chloro-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine and 3-chloro-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydropyridine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.54 (d, $^{4}J_{HH}$ = 1.2 Hz, 1H, alkene-*H*), 6.29 (ddt, $^{3}J_{HH}$ = 8.1, $^{4}J_{HH}$ =1.6 Hz, 1H, alkene-*H*), 4.61 (dt, $^{3}J_{HH}$ = 8.1, 3.3 Hz, 1H, alkene-*H*), 3.10 (dt, $^{3}J_{HH}$ = 3.2, $^{4}J_{HH}$ =1.5 Hz, 2H, C*H*$_2$), 1.27 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.7 (s) ppm.

NMR Conv.: 18%



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.44 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, alkene-*H*), 5.89 (ddt, $^{3}J_{HH}$ = 6.1, $^{4}J_{HH}$ = 1.4, 1.4 Hz, 1H, alkene-*H*), 4.93 (dd, $^{3}J_{HH}$ = 7.3, 6.1 Hz, 1H, alkene-*H*), 4.25 (d, $^{4}J_{HH}$ = 1.4 Hz, 2H, C*H*$_2$), 1.26 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.7 (s) ppm.

NMR Conv.: 9%

Mass spectrometry (APCI): $C_{11}H_{17}BClNO_2$+H ([M+H]$^+$): calcd: 242.1116; found: 242.0935.

*Note: Isolation of the product was not possible due to the low conversion and difficulties to remove **6a**.*

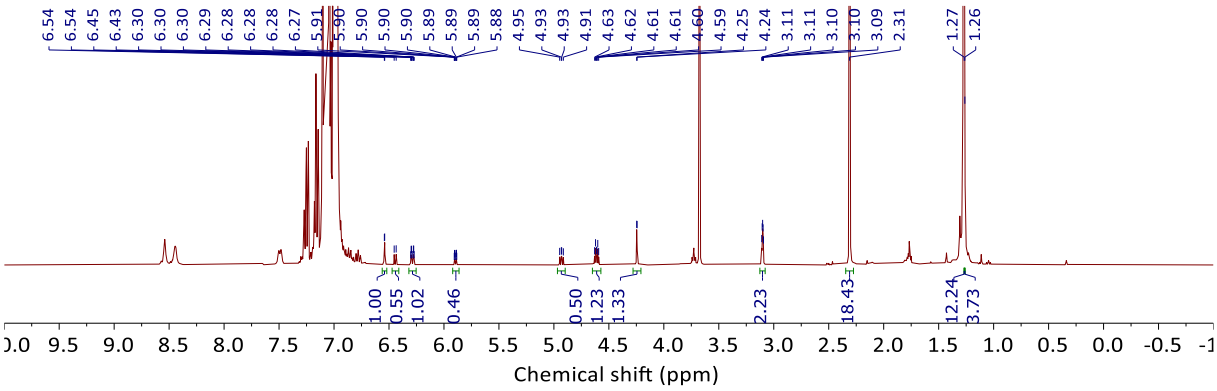


Figure S19. ^{1}H NMR spectrum (*o*DFB) of crude **6b** and **6c**.

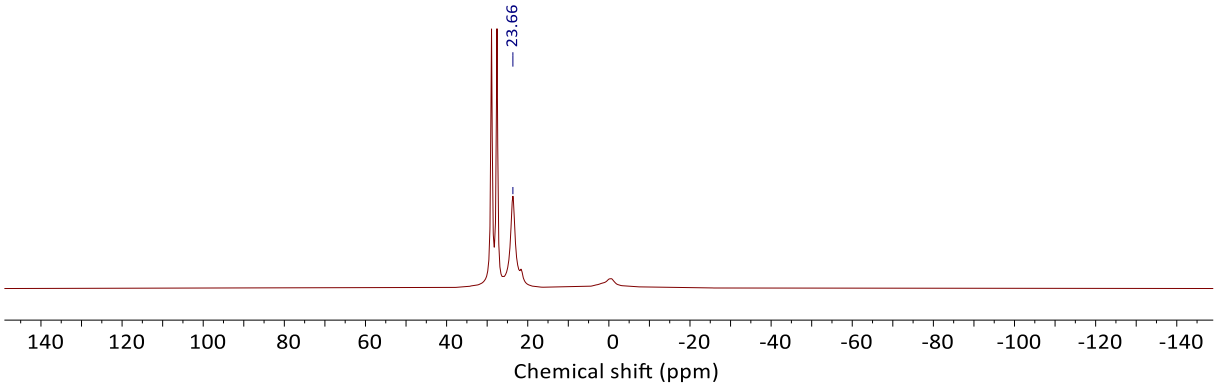
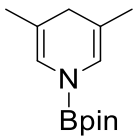


Figure S20. ^{11}B NMR spectrum (*o*DFB) of crude **6b** and **6c**. Resonance observed at –0.1 ppm is coordination of **6a** to **6b** and **6c**.

2.6.6. 3,5-dimethyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.27 (s, 2H, alkene-*H*), 2.60 (s, 2H, C*H*$_2$), 1.56 (s, 6H, *Me*), 1.31 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.8 (s) ppm.

Mass spectrometry (APCI): $C_{13}H_{22}BNO_2$+H ([M+H]$^+$): calcd: 236.1819; found: 236.1817.

NMR Conv.: 35%

*Note: Isolation of the product was not possible due to the low conversion and difficulties to remove **7a**.*

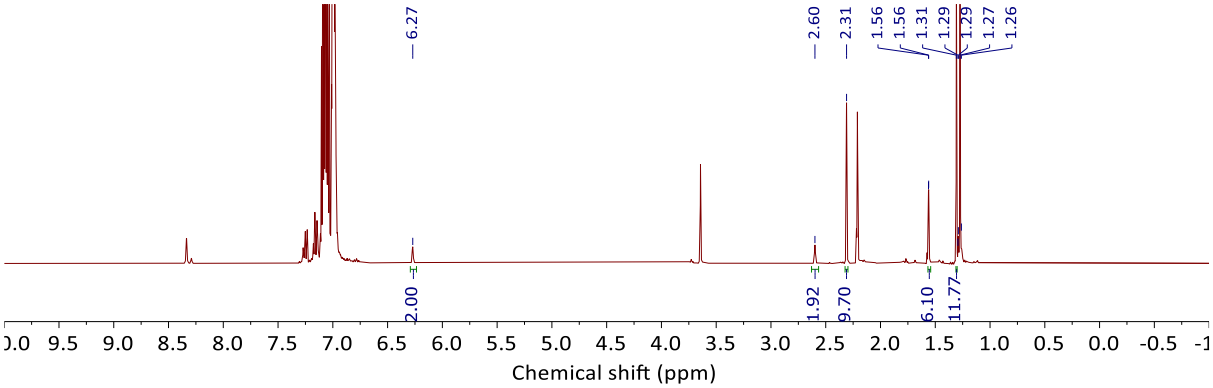


Figure S21. ^{1}H NMR spectrum (*o*DFB) of crude **7b**.

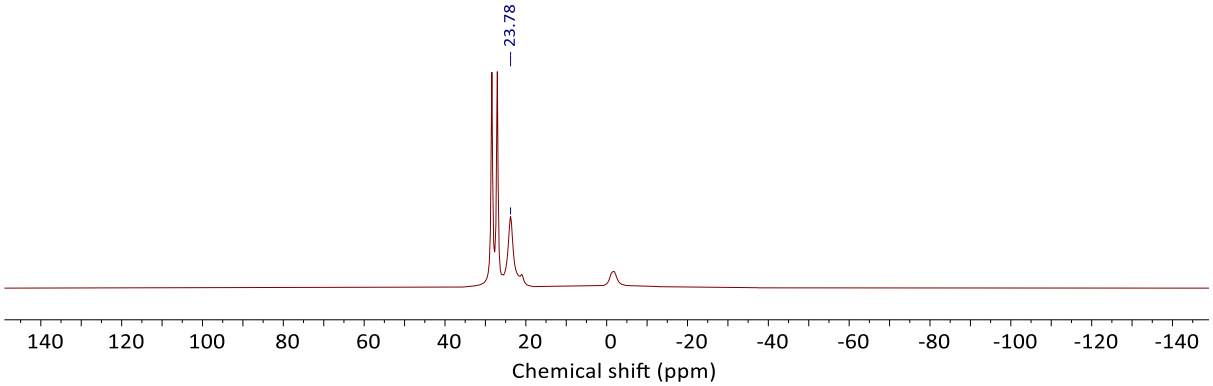
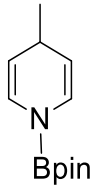


Figure S22. ^{11}B NMR spectrum (*o*DFB) of crude **7b**. Resonance observed at –0.1 ppm is coordination of **7a** to **7b**.

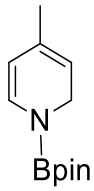
2.6.7. 4-methyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine and 4-methyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydropyridine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.39 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ =1.4 Hz, 1H, alkene-*H*), 4.64 (dd, $^3J_{HH}$ = 8.5, 3.3 Hz, 1H, alkene-*H*), 3.09 (dtq, $^3J_{HH}$ = 6.8, 3.4, $^4J_{HH}$ = 1.7 Hz, 1H, CH_2), 1.29 (s, 6H, *NBpin*), 1.26 (s, 6H, *NBpin*), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 3H, *Me*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.8 (s) ppm.

NMR Conv.: 15%



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 6.57 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, alkene-*H*), 4.99 (dd, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 1.6 Hz, 1H, alkene-*H*), 4.10 (dd, $^{3}J_{HH}$ = 4.0, $^{4}J_{HH}$ = 1.7 Hz, 1H, C*H*$_2$), 3.28 (t, $^{3}J_{HH}$ = 4.7 Hz, 1H, alkene-*H*), 1.58 (s, 3H, *Me*), 1.26 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 23.8 (s) ppm.

NMR Conv.: 15%

Mass spectrometry (APCI): $C_{12}H_{20}BNO_2$+H ([M+H]$^{+}$): calcd: 222.1662; found: 222.1667.

*Note: Isolation of the product was not possible due to the low conversion and difficulties to remove **8a**.*

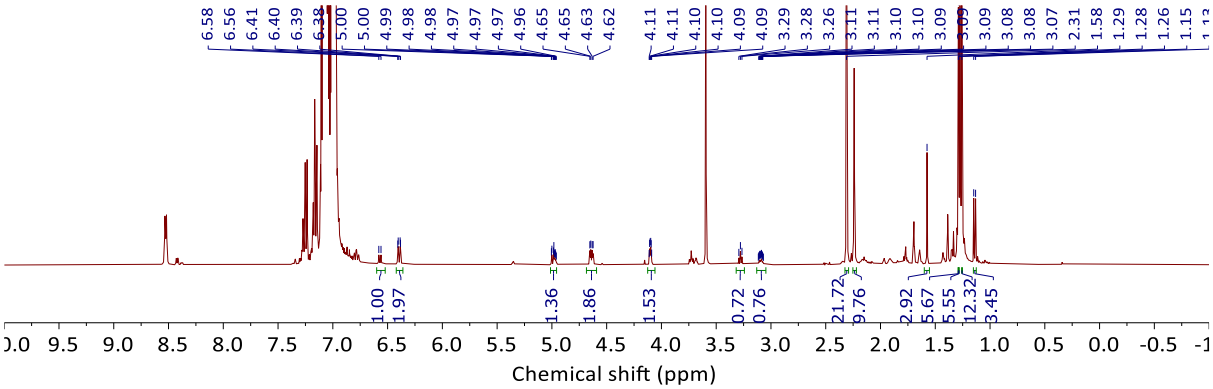


Figure S23. ^{1}H NMR spectrum (*o*DFB) of crude **8b** and **8c**.

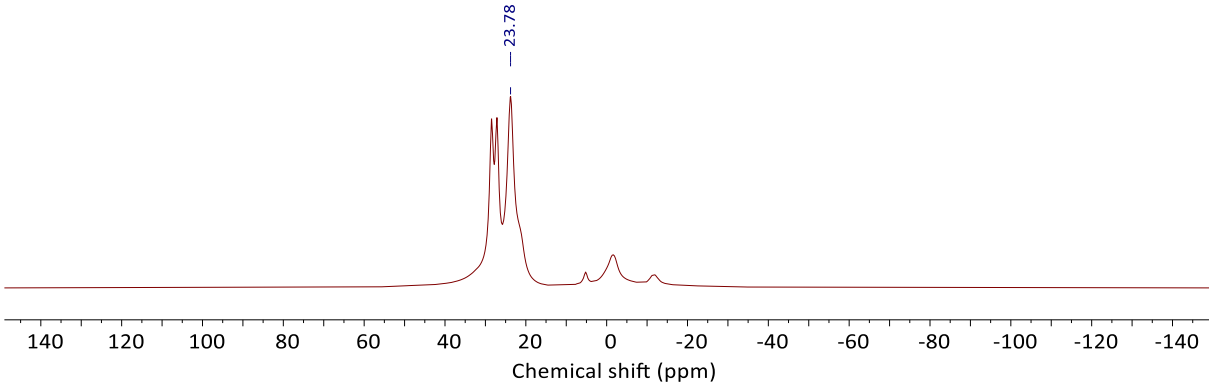
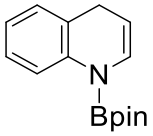


Figure S24. ^{11}B NMR spectrum (*o*DFB) of crude **8b** and **8c**. Resonance observed at –0.1 ppm is coordination of **8a** to **8b** and **8c**.

2.6.8. 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoline and 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline

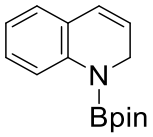


^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 8.17 (dd, $^{3}J_{HH}$ = 8.3, $^{4}J_{HH}$ = 1.3 Hz, 1H, *Ar*), 7.17 – 7.07 (m, 2H, *Ar*), 6.99 – 6.80 (m, 2H, *Ar* and alkene-*H*), 4.83 (dt, $^{3}J_{HH}$ = 8.1, 4.2, $^{4}J_{HH}$ = 3.1 Hz, 1H, alkene-*H*), 3.44 (dd, $^{3}J_{HH}$ = 3.6, $^{4}J_{HH}$ = 1.6 Hz, 2H, CH_2), 1.01 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.5 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 139.82 (s, *Ar*), 129.39 (s, *Ar*), 129.08 (s, *Ar*), 129.08 (s, *Ar*), 126.55 (s, *Ar*), 122.89 (s, *Ar*), 119.61 (s, alkene-*C*), 102.64 (s, alkene-*C*), 82.93 (s, *NBpin*), 27.03 (s, *C*H$_2$), 24.23 (s, *NBpin*) ppm.

NMR Conv.: 87%



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.82 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, *Ar*), 7.17 – 7.07 (m, 2H, *Ar*), 6.99 – 6.80 (m, 1H, *Ar*), 6.25 (dd, $^{3}J_{HH}$ = 9.7 Hz, 1H, alkene-*H*), 5.57 (dt, $^{3}J_{HH}$ = 9.6, 4.2, $^{3}J_{HH}$ = 1.1 Hz, 1H, alkene-*H*), 4.16 (dt, $^{3}J_{HH}$ = 4.2, $^{4}J_{HH}$ = 1.5 Hz, 2H, CH_2), 1.03 (s, 12H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.5 (s) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 139.82 (s, *Ar*), 129.08 (s, *Ar*), 126.58 (s, *Ar*), 124.26 (s, *Ar*), 123.84 (s, *Ar*), 121.58 (s, *Ar*), 120.91 (s, alkene-*C*), 102.64 (s, alkene-*C*), 82.50 (s, *NBpin*), 43.28 (s, *C*H_2), 24.35 (s, *NBpin*) ppm.

NMR Conv.: 12%

Mass spectrometry (APCI): $C_{15}H_{20}BNO_2$+H ($[M+H]^+$): calcd: 258.1663; found: 258.1666.

Isolated Yield after work up both isomers: 89%

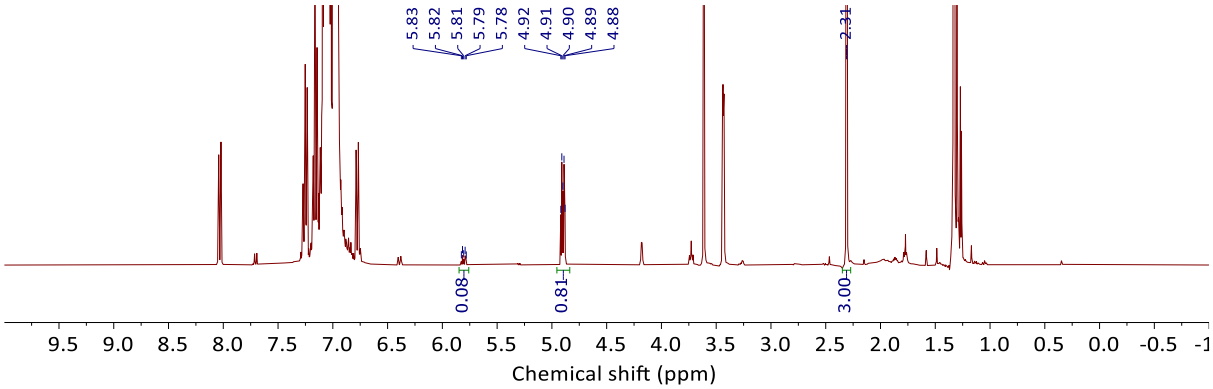


Figure S25. ^{1}H NMR spectrum (*o*DFB) of crude **9b** and **9c**.

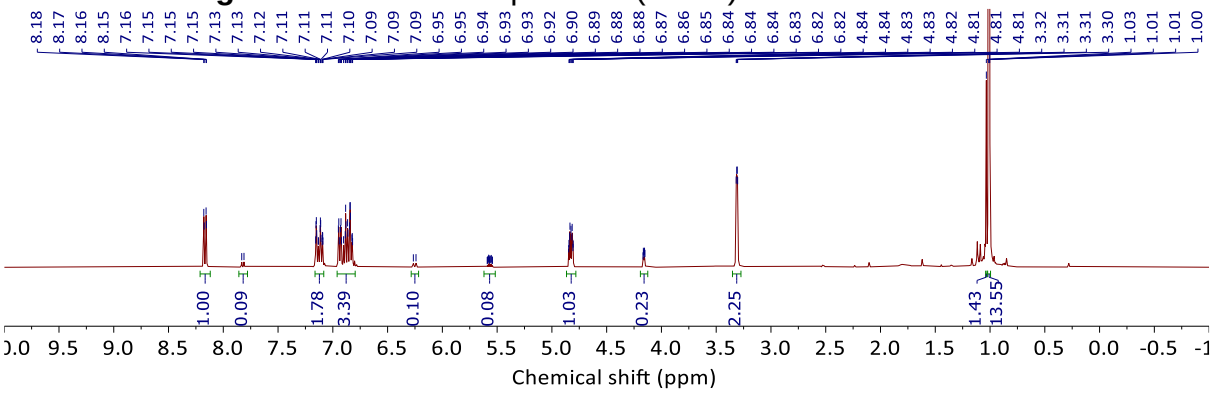


Figure S26. ^{1}H NMR spectrum (C_6D_6) of **9b** and **9c**.

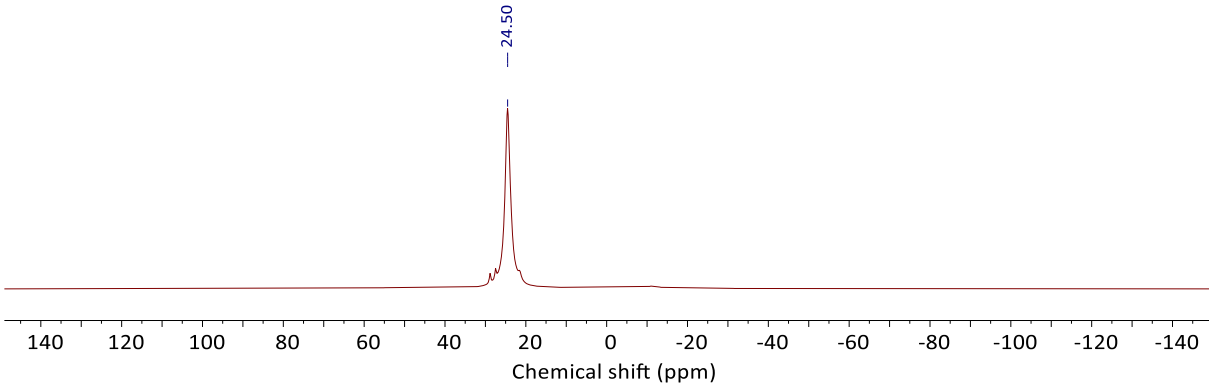


Figure S27. ^{11}B NMR spectrum (C_6D_6) of **9b** and **9c**.

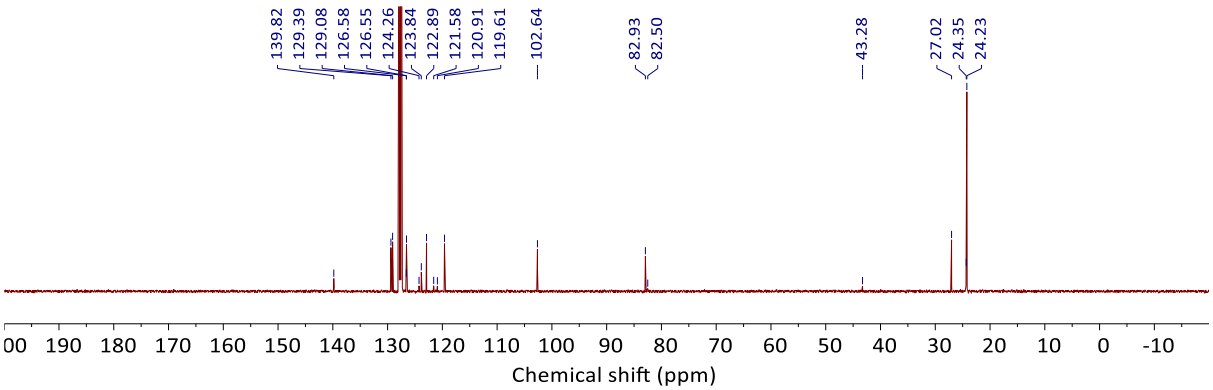
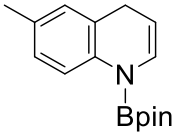


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6) of **9b** and **9c**.

2.6.9. 6-methyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoline and 6-methyl-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline

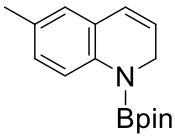


^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 8.17 – 8.10 (m, 1H, *Ar*), 7.02 – 6.93 (m, 2H, *Ar*), 6.64 (d, $^{3}J_{HH}$ = 7.8 Hz, alkene-*H*), 4.86 (dt, $^{3}J_{HH}$ = 7.8, 3.7 Hz, 1H, alkene-*H*), 3.34 (dd, $^{3}J_{HH}$ = 3.6, $^{4}J_{HH}$ = 1.8 Hz, 2H, CH_2), 2.09 (s, 3H, *Me*), 1.01 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.8 (s) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 137.34 (s, *Ar*), 131.80 (s, *Ar*), 129.68 (s, *Ar*), 129.50 (s, *Ar*), 127.21 (s, *Ar*), 123.60 (s, *Ar*), 119.50 (s, alkene-*C*), 102.38 (s, alkene-*C*), 82.86 (s, NB*pin*), 27.07 (s, *C*H_2), 24.26 (s, NB*pin*), 20.33 (s, *Me*) ppm.

NMR Conv.: 92%



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.76 (dd, $^{3}J_{HH}$ = 8.2, $^{4}J_{HH}$ = 2.1 Hz, 1H, *Ar*), 6.70 – 660 (m, 2H, *Ar*), 6.28 (dd, $^{3}J_{HH}$ = 9.6, $^{4}J_{HH}$ = 2.2 Hz, 1H, alkene-*H*), 5.61 (dt, $^{3}J_{HH}$ = 9.0, 4.2 Hz, 1H, alkene-*H*), 4.18 (dd, $^{3}J_{HH}$ = 4.2, $^{4}J_{HH}$ = 1.8 Hz, 2H, CH_2), 2.15 (d, $^{3}J_{HH}$ = 3.1 Hz, 3H, *Me*), 1.04 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.8 (s) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 131.35 (s, *Ar*), 130.43 (s, *Ar*), 128.41 (s, *Ar*), 126.69 (s, *Ar*), 124.37 (s, *Ar*), 124.30 (s, *Ar*), 120.82 (s, alkene-*C*), 108.50 (s, alkene-*C*), 82.86 (s, NB*pin*), 43.36 (s, *C*H_2), 24.26 (s, NB*pin*), 20.33 (s, *Me*) ppm.

NMR Conv.: 5%

Mass spectrometry (APCI): $C_{16}H_{22}BNO_2$+H ([M+H]$^+$): calcd: 272.1819; found: 272.1808.

Isolated Yield after work up both isomers: 91%

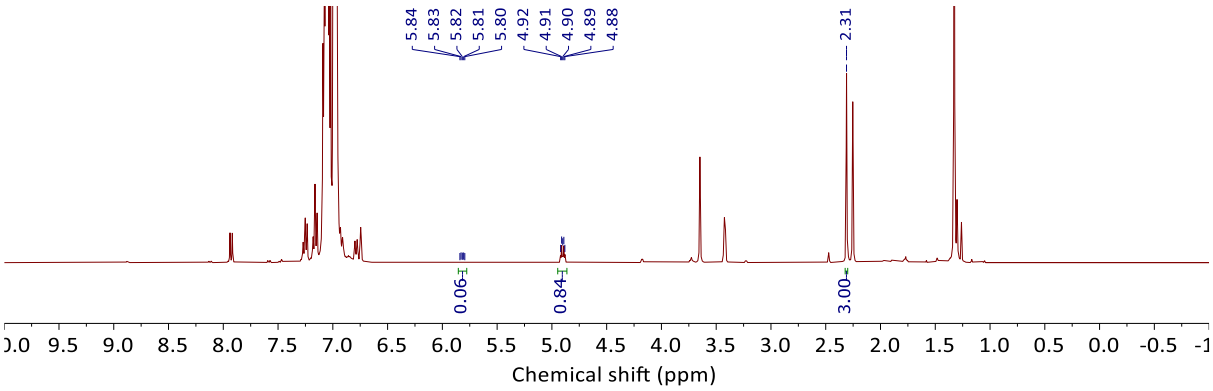


Figure S29. ^{1}H NMR spectrum (*o*DFB) of crude **10b** and **10c**.

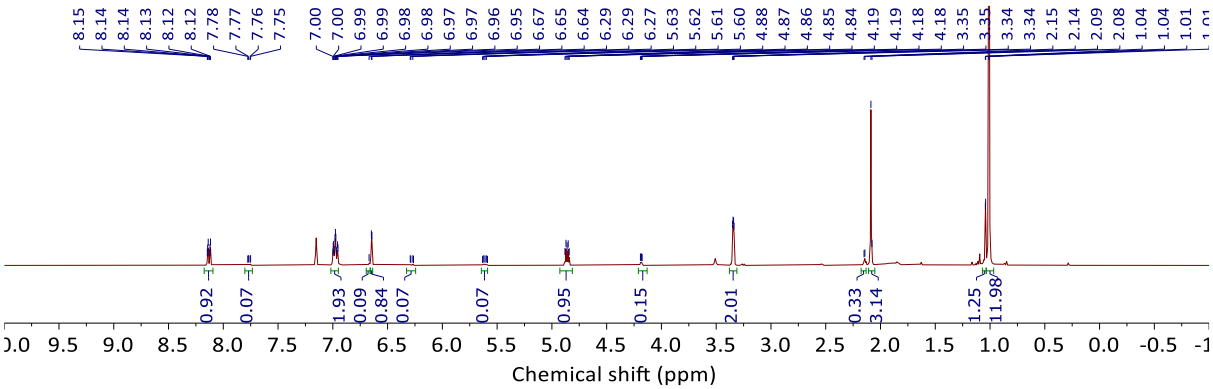


Figure S30. ^{1}H NMR spectrum (C_6D_6) of **10b** and **10c**.

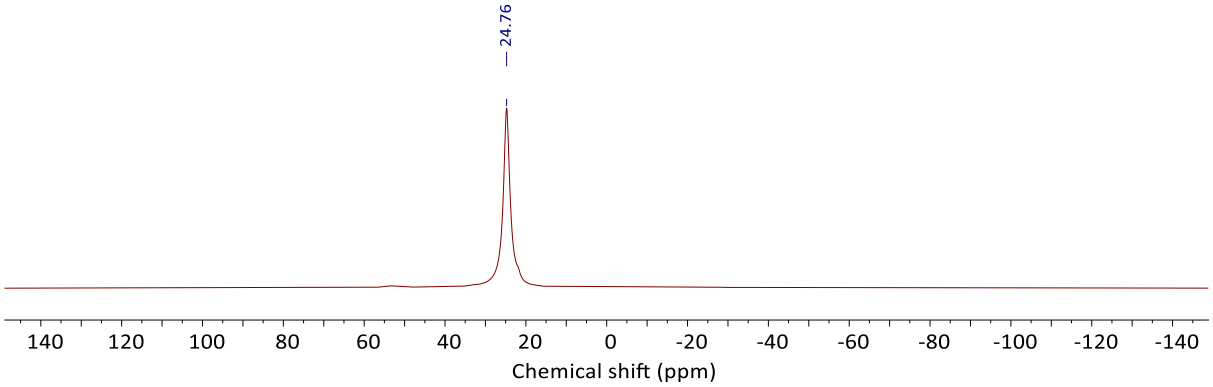


Figure S31. ^{11}B NMR spectrum (C_6D_6) of **10b** and **10c**.

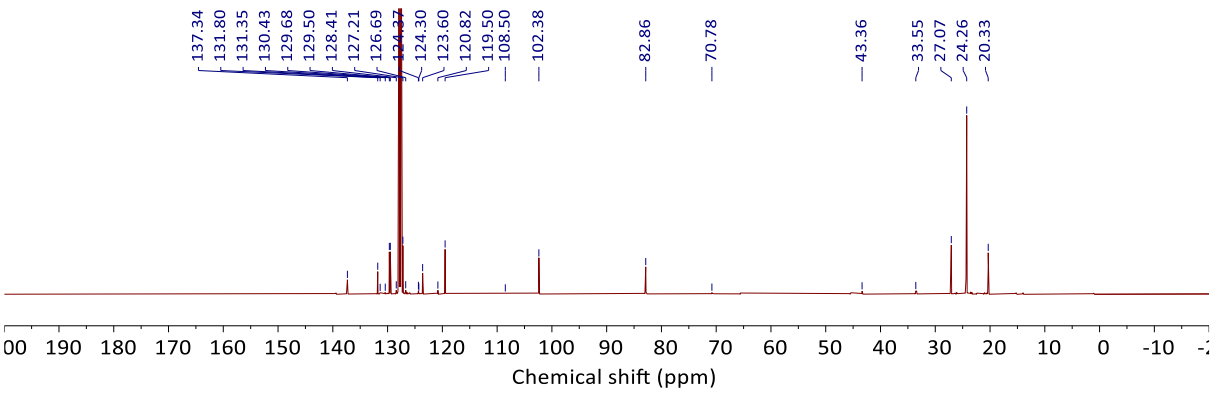
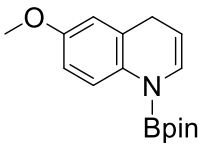


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6) of **10b** and **10c**.

2.6.10. 6-methoxy-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoline and 6-methoxy-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline

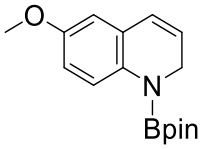


^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 8.13 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *Ar*), 7.00 – 6.96 (m, 1H, *Ar*), 6.75 (dd, $^{3}J_{HH}$ = 9.0, $^{4}J_{HH}$ = 3.0 Hz, 1H, *Ar*), 6.49 (d, $^{4}J_{HH}$ = 3.0 Hz, 1H, alkene-*H*), 4.85 – 4.77 (m, 1H, alkene-*H*), 3.34 – 3.32 (m, 2H, C*H*$_2$), 3.31 (s, 3H, O*Me*), 1.02 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.7 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 155.63 (s, *Ar*), 133.13 (s, *Ar*), 129.51 (s, *Ar*), 124.93 (s, *Ar*), 120.64 (s, *Ar*), 113.61 (s, *Ar*), 112.44 (s, alkene-*C*), 101.59 (s, alkene-*C*), 82.85 (s, NB*pin*), 54.50 (s, O*Me*), 27.39 (s, *C*H$_2$), 24.28 (s, NB*pin*) ppm.

NMR Conv.: 96%



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.72 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, *Ar*), 6.80 – 6.90 (m, 2H, *Ar*), 6.23 (d, $^{3}J_{HH}$ = 9.6 Hz, 1H, alkene-*H*), 5.63 (dt, $^{3}J_{HH}$ = 9.1, 4.2 Hz, 1H, alkene-*H*), 4.15 (dd, $^{3}J_{HH}$ = 4.3, $^{4}J_{HH}$ = 1.7 Hz, 2H, C*H*$_2$), 3.37 (s, 3H, O*Me*), 1.05 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.7 (s) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 147.91 (s, *Ar*), 133.87 (s, *Ar*), 131.56 (s, *Ar*), 126.61 (s, *Ar*), 121.95 (s, *Ar*) 121.11 (s, *Ar*), 108.09 (s, alkene-*C*), 105.00 (s, alkene-*C*), 82.85 (s, NB*pin*), 54.64 (s, O*Me*), 43.35 (s, *C*H_2), 24.28 (s, NB*pin*) ppm.
NMR Conv.: 4%

Mass spectrometry (APCI): $C_{16}H_{22}BNO_3$+H ($[M+H]^+$): calcd: 288.1768; found: 288.1756.

Isolated Yield after work up both isomers: 90%

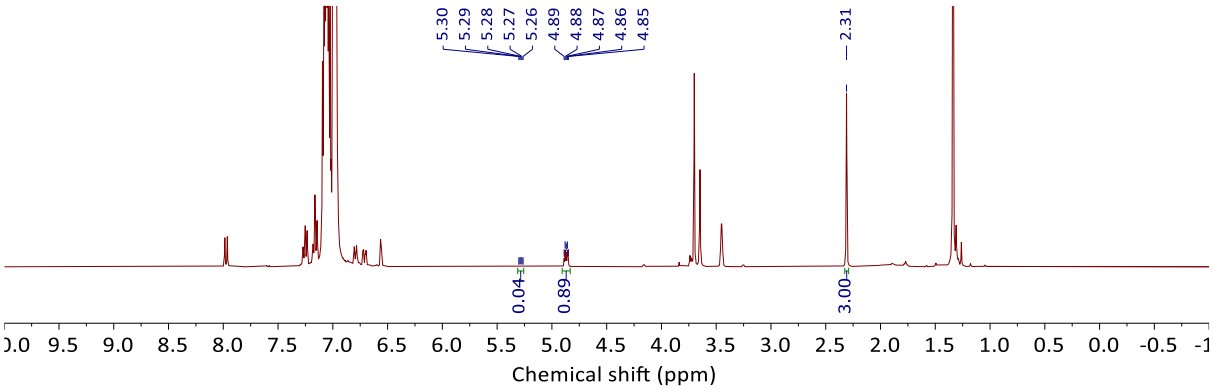


Figure S33. ^{1}H NMR spectrum (*o*DFB) of crude **11b** and **11c**.

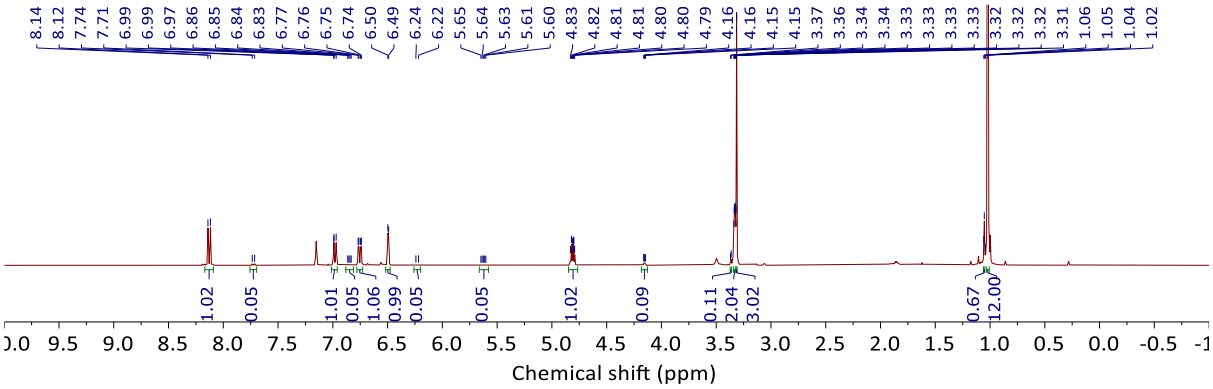


Figure S34. ^{1}H NMR spectrum (C_6D_6) of **11b** and **11c**.

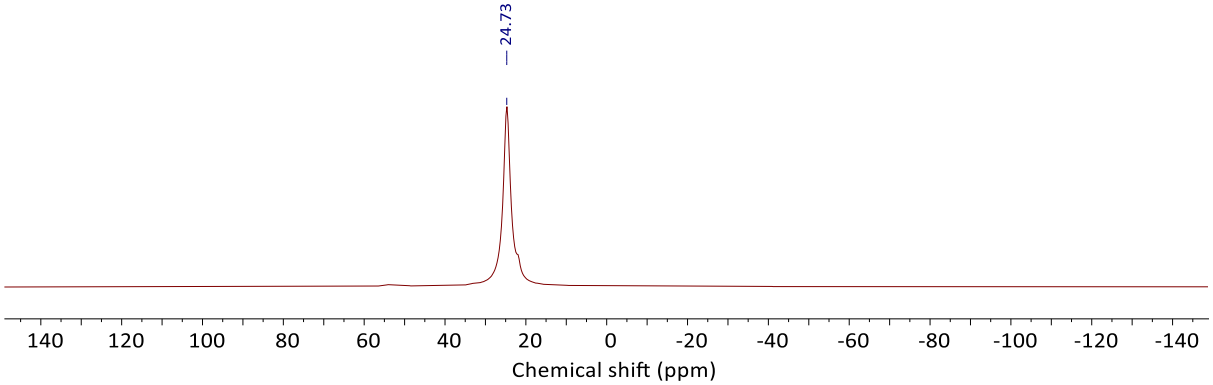


Figure S35. ^{11}B NMR spectrum (C_6D_6) of **11b** and **11c**.

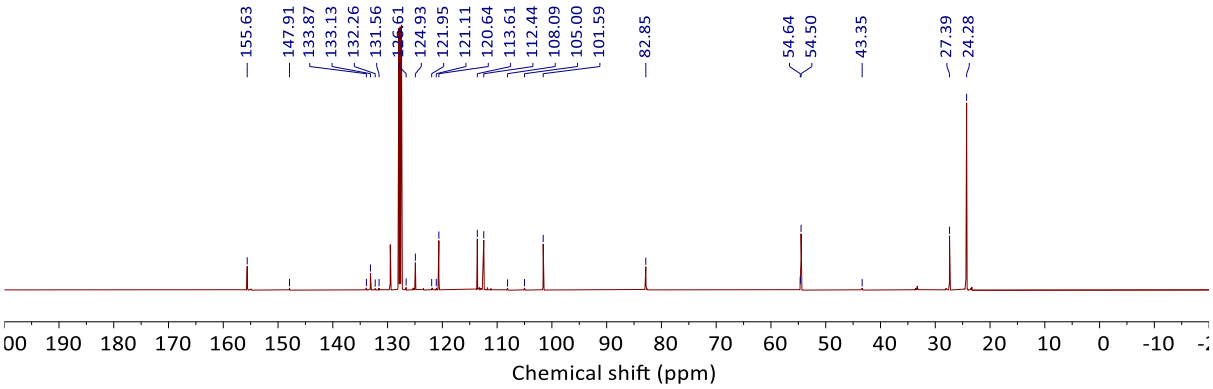
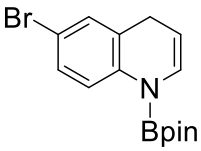


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6) of **11b** and **11c**.

2.6.11. 6-bromo-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoline and 6-bromo-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline

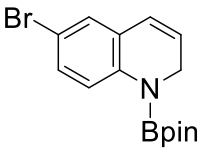


^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.89 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, *Ar*), 7.22 – 7.13 (m, 2H, *Ar and* alkene-*H*), 6.81 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, *Ar*), 4.69 (dt, $^{3}J_{HH}$ = 7.7, 3.7 Hz, 1H, alkene-*H*), 3.05 (ddd, $^{3}J_{HH}$ = 3.8, $^{4}J_{HH}$ = 1.9, 1.0 Hz, 2H, C*H*$_2$), 0.97 (s, 12H, N*Bpin*).

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.6 (s) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 138.87 (s, *Ar*), 131.73 (s, *Ar*), 129.37 (s, *Ar*), 129.01 (s, *Ar*), 126.21 (s, *Ar*), 121.24 (s, *Ar*), 115.28 (s, alkene-*C*), 102.28 (s, alkene-*C*), 83.14 (s, N*Bpin*), 26.62 (s, *C*H$_2$), 24.20 (s, N*Bpin*) ppm.

NMR Conv.: 96%



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.54 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, *Ar*), 6.94 (d, $^{3}J_{HH}$ = 2.6 Hz, 1H, *Ar*), 6.92 (s, 1H, *Ar*), 5.95 (dt, $^{3}J_{HH}$ = 9.6, $^{4}J_{HH}$ = 1.9 Hz, 1H, alkene-*H*), 5.45 (dt, $^{3}J_{HH}$ = 9.3, 4.2 Hz, 1H, alkene-*H*), 4.04 (dd, $^{3}J_{HH}$ = 4.3, $^{4}J_{HH}$ = 1.8 Hz, 2H, C*H*$_2$), 0.99 (s, 12H, N*Bpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.6 (s) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 150.53 (s, *Ar*), 140.81 (s, *Ar*), 134.16 (s, *Ar*), 132.46 (s, *Ar*), 130.36 (s, *Ar*), 129.37 (s, *Ar*), 122.44 (s, alkene-*C*), 113.93 (s, alkene-*C*), 83.14 (s, N*Bpin*), 43.15 (s, *C*H$_2$), 24.20 (s, N*Bpin*) ppm

NMR Conv.: 4%

Mass spectrometry (APCI): $C_{16}H_{19}BBrNO_2$+H ([M+H]$^+$): calcd: 336.0791; found: 336.0768.

Isolated Yield after work up both isomers: 87%

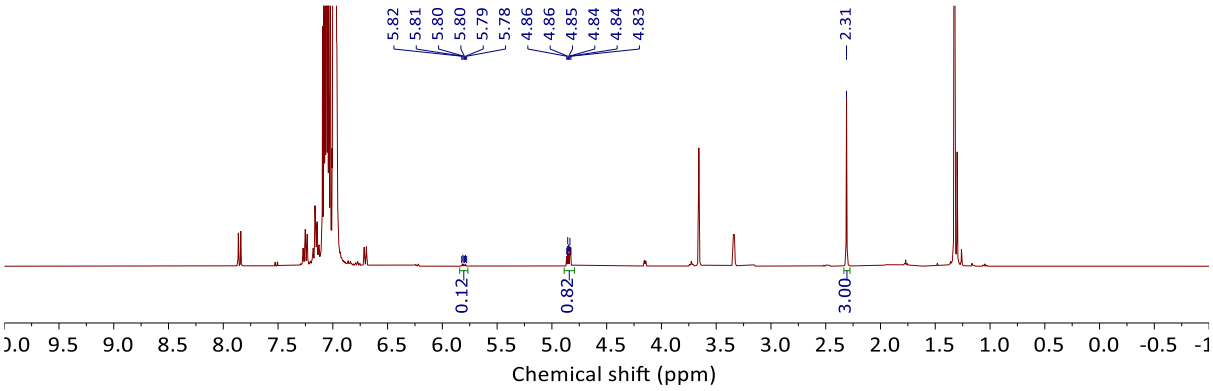


Figure S37. ^{1}H NMR spectrum (*o*DFB) of crude **12b** and **12c**.

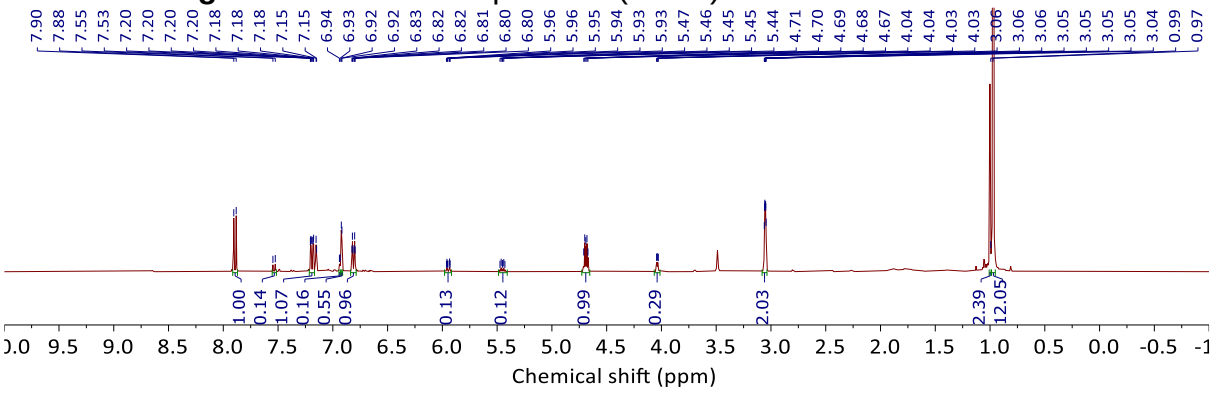


Figure S38. ^{1}H NMR spectrum (C_6D_6) of **12b** and **12c**.

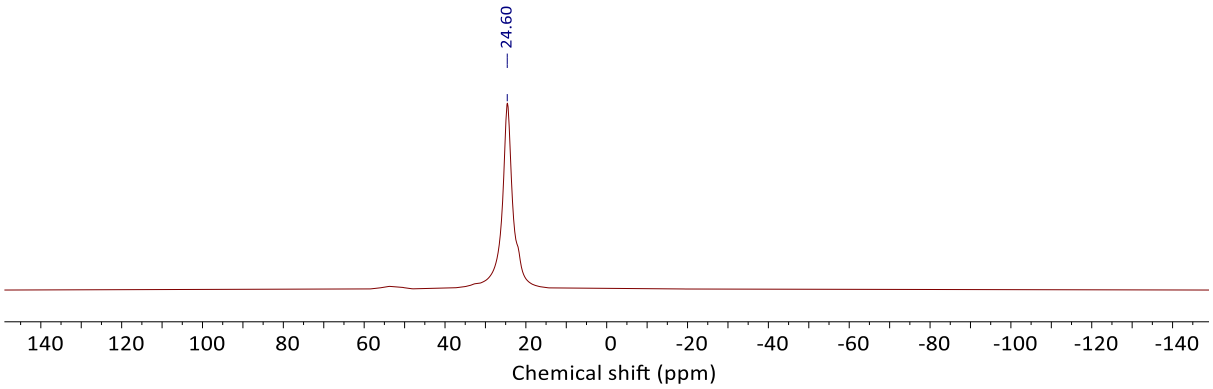


Figure S39. ^{11}B NMR spectrum (C_6D_6) of **12b** and **12c**.

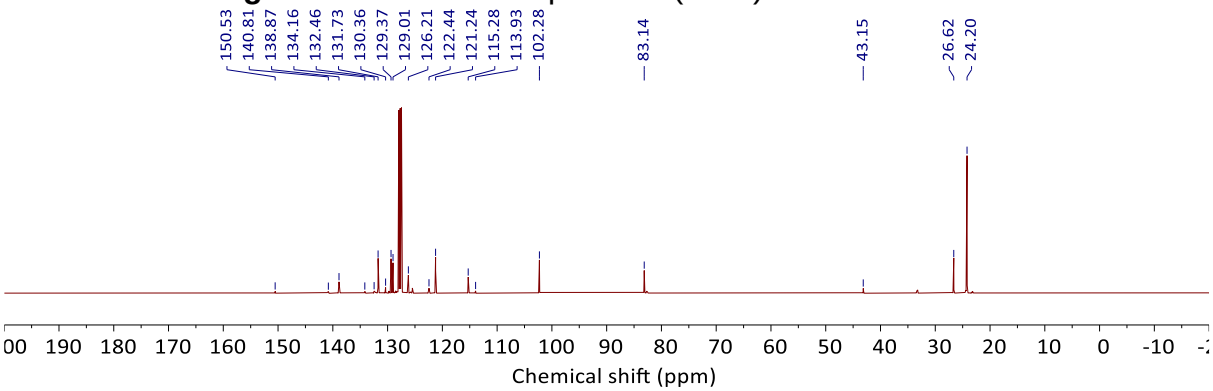
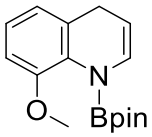


Figure S40. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **12b** and **12c**.

2.6.12. 8-methoxy-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoline



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.02 (dt, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.3 Hz, 1H, *Ar*), 6.90 (dd, $^3J_{HH}$ = 7.6 Hz, 1H, *Ar*), 6.56 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3 Hz, 1H, *Ar*), 6.51 (d, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.3 Hz, 1H, alkene-*H*), 4.93 (dt, $^3J_{HH}$ = 7.6, 3.9 Hz, 1H, alkene-*H*), 3.39 (s, 3H, O*Me*), 3.15 (d, $^3J_{HH}$ = 3.9 Hz, 2H, CH_2), 1.12 (s, 12H, N*Bpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.8 (s) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 150.67 (s, *Ar*), 131.73 (s, *Ar*), 130.29 (s, *Ar*), 129.53 (s, *Ar*), 123.53 (s, *Ar*), 120.28 (s, *Ar*), 109.15 (s, alkene-*C*), 104.89 (s, alkene-*C*), 82.42, (s, N*Bpin*), 54.51 (s, O*Me*), 27.72 (s, *C*H_2), 24.43 (s, N*Bpin*) ppm.

Mass spectrometry (APCI): $C_{16}H_{22}BNO_3$+H ($[M+H]^+$): calcd: 288.1768; found: 288.1765.

NMR Conv.: 89%

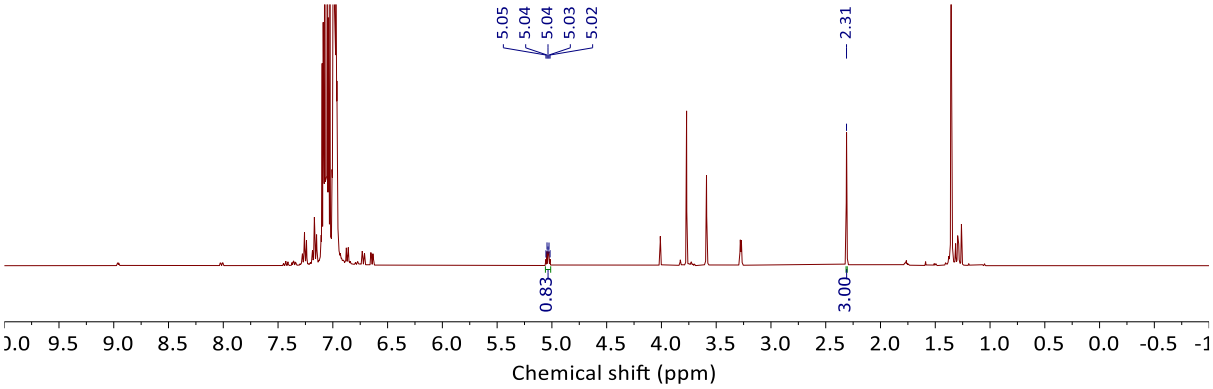


Figure S41. ^{1}H NMR spectrum (*o*DFB) of crude **13b** and **13c**.

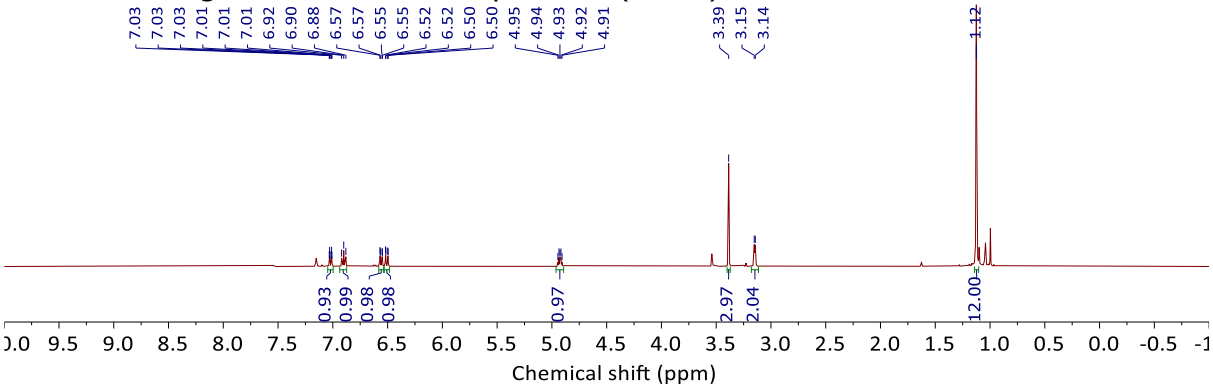


Figure S42. ^{1}H NMR spectrum (C_6D_6) of **13b** and **13c**.

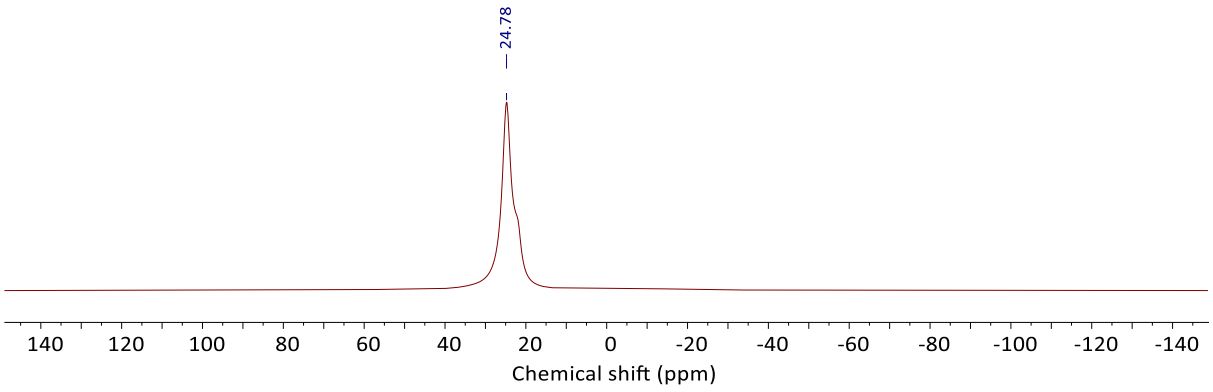


Figure S43. ^{11}B NMR spectrum (C_6D_6) of **13b** and **13c**.

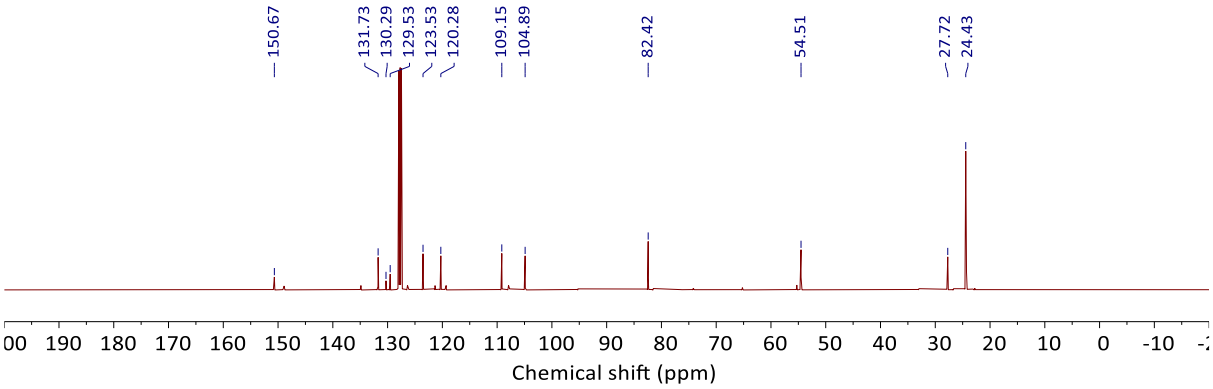
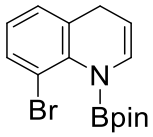


Figure S44. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **13b** and **13c**.

2.6.13. 8-bromo-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoline and 8-bromo-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dihydroquinoline

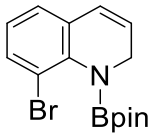


^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.36 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, *Ar*), 6.91 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H, alkene-*H*), 6.59 – 6.49 (m, 2H, *Ar*), 4.93 (dt, $^{3}J_{HH}$ = 6.7, 4.0 Hz, 1H, alkene-*H*), 2.93 (d, $^{3}J_{HH}$ = 4.0 Hz, 2H, C*H*$_2$), 1.13 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.1 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 139.86 (s, *Ar*), 132.47 (s, *Ar*), 132.32 (s, *Ar*), 131.34 (s, *Ar*), 126.94 (s, *Ar*), 124.66 (s, *Ar*), 116.65 (s, alkene-*C*), 107.63 (s, alkene-*C*), 83.37 (s, NB*pin*), 28.33 (s, *C*H$_2$), 24.65 (s, NB*pin*) ppm.

NMR Conv.: 96%



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.33 – 7.30 (m, 1H, *Ar*), 6.79 – 6.72 (m, 1H, *Ar*), 6.68 – 6.61 (m, 1H, *Ar*), 6.39 – 6.31 (m, 1H, alkene-*H*), 5.68 (dt, $^{3}J_{HH}$ = 9.0, 4.1 Hz, 1H, alkene-*H*), 3.30 – 3.27 (m, 2H , C*H*$_2$), 1.13 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.1 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 135.52 (s, *Ar*), 132.90 (s, *Ar*), 129.94 (s, *Ar*), 128.93 (s, *Ar*), 126.52 (s, *Ar*), 124.30 (s, *Ar*), 121.51 (s, alkene-*C*), 96.53 (s, alkene-*C*), 83.37 (s, NB*pin*), 43.48 (s, *C*H$_2$), 24.30 (s, NB*pin*) ppm.

NMR Conv.: 4%

Mass spectrometry (APCI): $C_{16}H_{19}BBrNO_2$+H ([M+H]$^{+}$): calcd: 336.0757; found: 336.0768.

Isolated Yield after work up both isomers: 90%

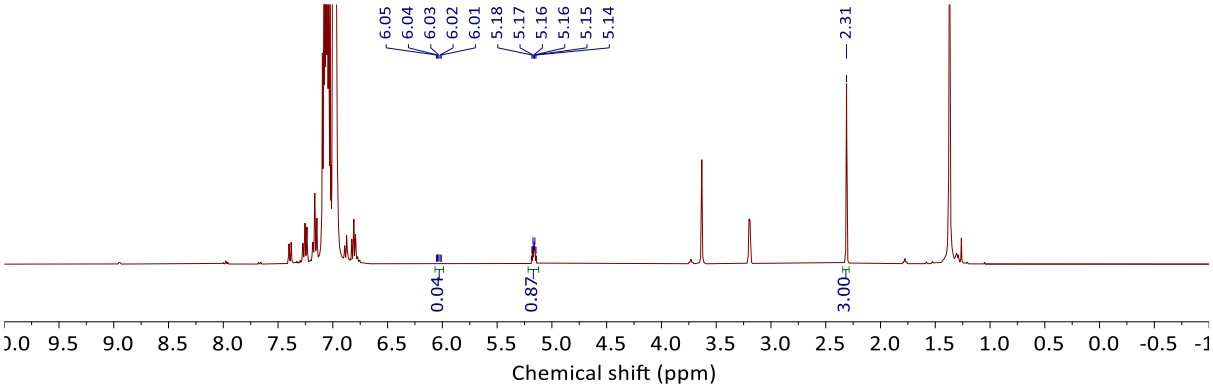


Figure S45. ^{1}H NMR spectrum (*o*DFB) of crude **14b** and **14c**.

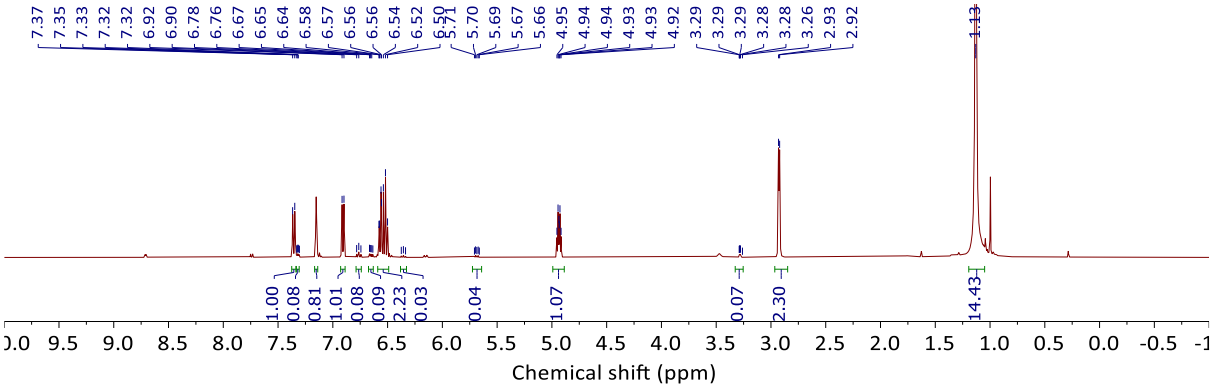


Figure S46. ^{1}H NMR spectrum (C_6D_6) of **14b** and **14c**.

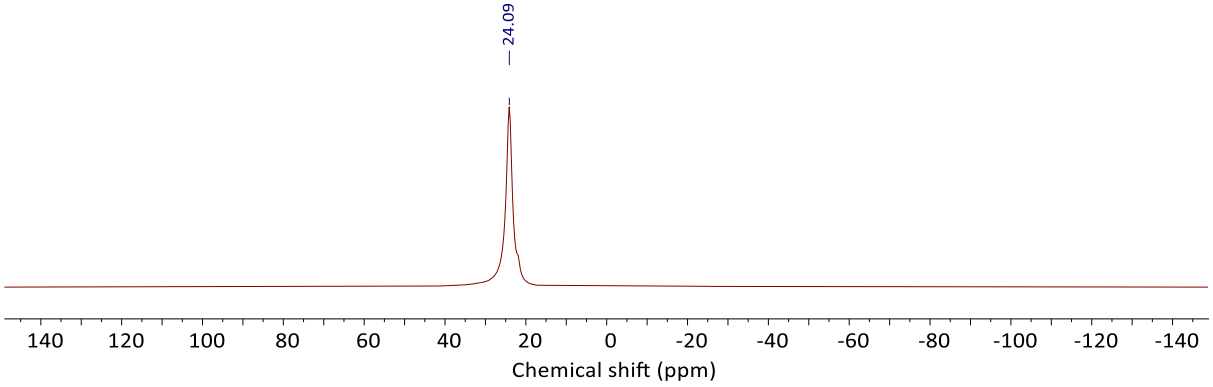


Figure S47. ^{11}B NMR spectrum (C_6D_6) of **14b** and **14c**.

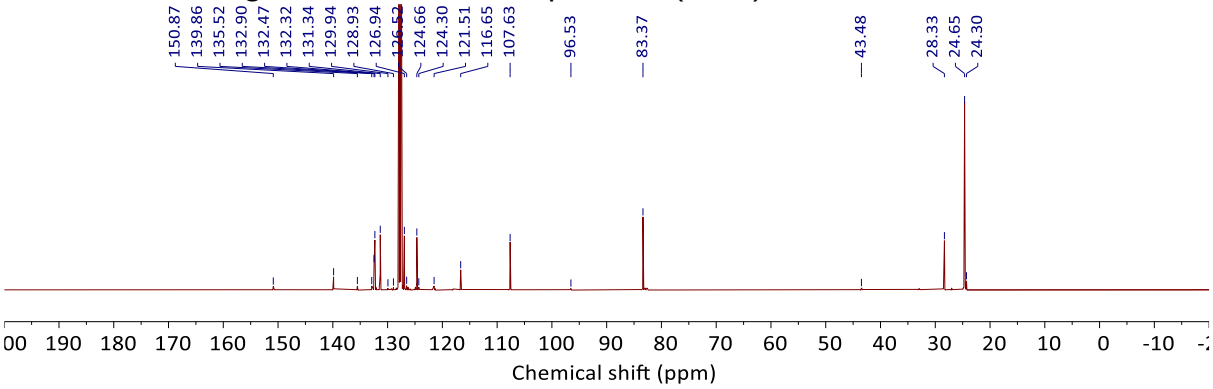
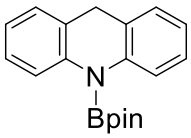


Figure S48. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **14b** and **14c**.

2.6.14. 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroacridine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.89 – 7.85 (m, 2H, *Ar*), 7.20 – 7.15 (m, 2H, *Ar*), 6.99 – 6.93 (m, 4H, *Ar*), 3.54 (s, 2H, C*H*$_2$), 1.05 (s, 12H, N*Bpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.0 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 142.38 (s, *Ar*), 130.24 (s, *Ar*), 127.14 (s, *Ar*), 126.15 (s, *Ar*), 123.36 (s, *Ar*), 122.60 (s, *Ar*), 82.92 (s, N*Bpin*), 33.69 (s, *C*H$_2$), 24.28 (s, N*Bpin*) ppm.

Mass spectrometry (APCI): $C_{19}H_{20}BNO_2$+H ([M+H]$^+$): calcd: 306.1661; found: 306.1661.

NMR Conv.: 93%

Isolated Yield: 86%

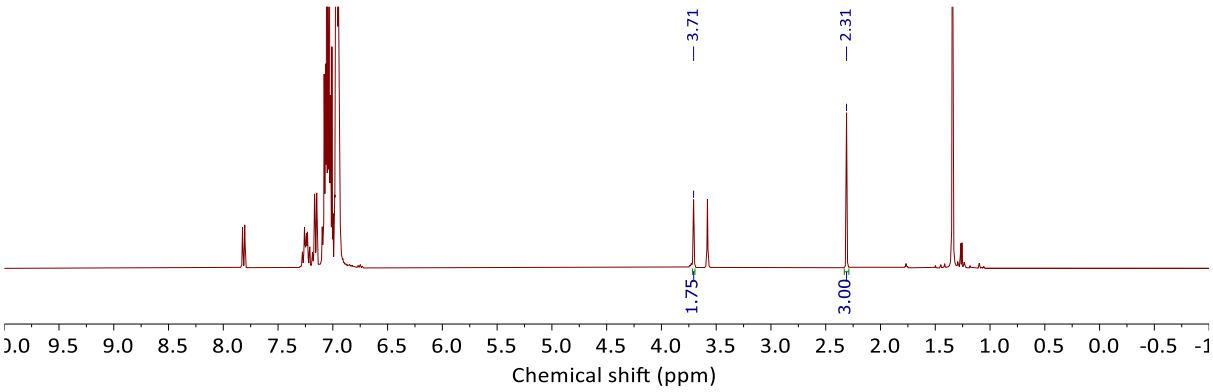


Figure S49. ^{1}H NMR spectrum (*o*DFB) of crude **15b** and **15c**.

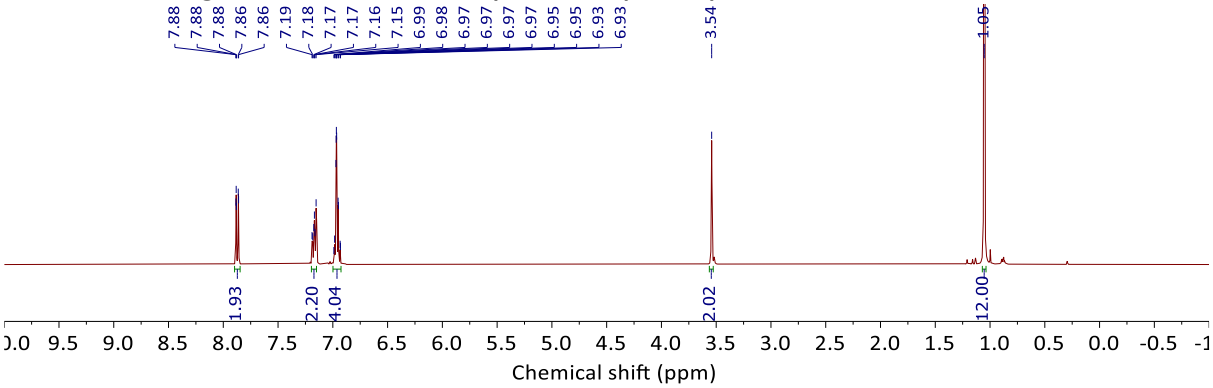


Figure S50. ^{1}H NMR spectrum (C_6D_6) of **15b** and **15c**.

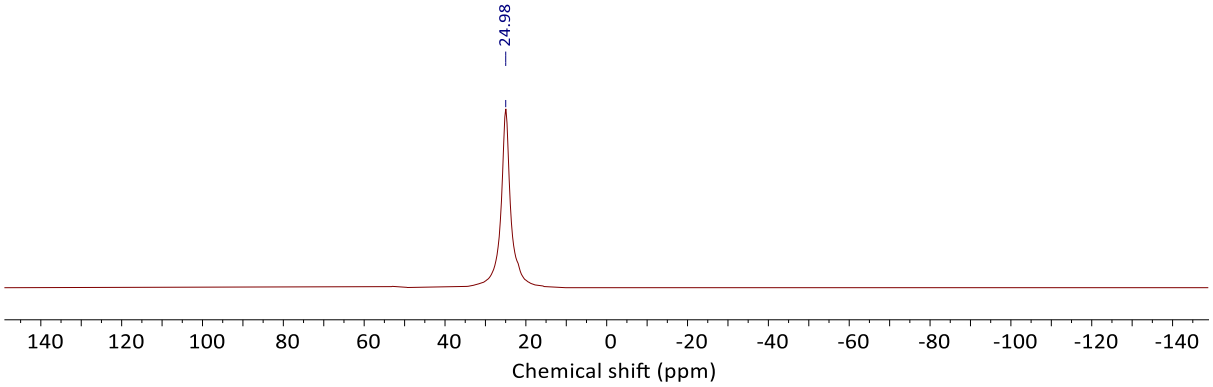


Figure S51. ^{11}B NMR spectrum (C_6D_6) of **15b** and **15c**.

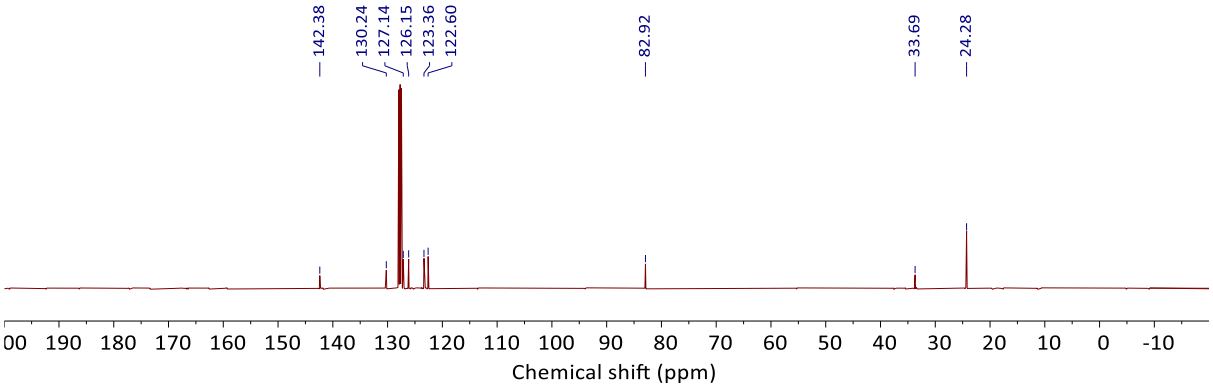


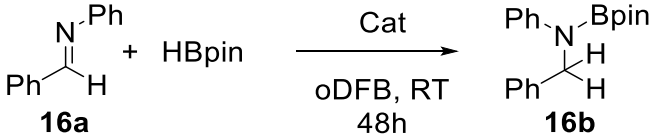
Figure S52. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **15b** and **15c**.

3. Catalytic hydroboration of imines

3.1. Screening and controls

To a solution of catalyst and HBpin (32 µL, 0.22 mmol, 1 eq.) in solvent (0.5 mL), N-benzylideneaniline (40 mg, 0.22 mmol, 1 eq.) and toluene (25 µL, 0.24 mmol) were added and allowed to react at RT for 48 h. The reaction was monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using the resonances of the toluene (^{1}H δ = 2.31 ppm) as internal standard. The reaction mixture was worked-up by removal of volatiles and extraction by pentane to remove catalyst and any possible residual HBpin.

Table S1. Optimization hydroboration of N-benzylideneaniline



16a **16b**

Entry	Catalyst	Loading (mol%)	Solvent	Conv. (%)[a]
1	[Na(18-c-6)]$_2$[**1**]	1	THF-d$_8$	20
2	[Na(18-c-6)]$_2$[**1**]	2.5	THF-d$_8$	62
3	[Na(18-c-6)]$_2$[**1**]	1	*o*DFB	35
4	[Na(18-c-6)]$_2$[**1**]	2.5	*o*DFB	98

[a] Determined by ^{1}H NMR spectroscopy, based on C–H bond formation.

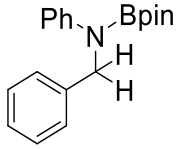
3.2. General procedure hydroboration of imines

To a solution of [Na(18-c-6)]$_2$[**1**] (5 mg, 5.5 µmol, 0.025 eq.) and HBpin (28 mg, 32 µL, 0.22 mmol, 1 eq.) in *o*DFB (0.5 mL), the imine (0.22 mmol, 1 eq.) and toluene (25 µL, 0.24 mmol) were added and allowed to react at RT for 48 h. The reaction was monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using toluene (^{1}H δ = 2.31 ppm) as an internal standard. The reaction mixture was worked-up by removal of volatiles and extraction by pentane to remove catalyst and any possible residual HBpin. In the crude NMR spectra, the resonances used for the calculation of the conversion has been picked and integrated.

3.3. Characterization data hydroboration of imines

We validated our analysis of most hydroborated imines by comparison to various literature sources and found all data to be in agreement with those previously reported.[10, 11]

3.3.1. N-benzyl-N-phenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.50 – 7.44 (m, 2H, *Ar*), 7.25 – 7.20 (m, 2H, *Ar*), 7.17 – 7.07 (m, 4H, *Ar*), 7.01 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *Ar*), 6.84 – 6.77 (m, 1H, *Ar*), 4.77 (s, 2H, C*H*$_2$NBpin), 1.07 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.2 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 146.44 (s, *Ar*), 140.59 (s, *Ar*), 128.53 (s, *Ar*), 128.36 (s, *Ar*), 126.40 (s, *Ar*), 126.32 (s, *Ar*), 121.39 (s, *Ar*), 120.62 (s, *Ar*), 82.64 (s, NB*pin*), 51.16 (s, *C*H$_2$NBpin), 24.26 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_{13}H_{13}N$+H ([M+H]$^+$): calcd: 184.1121; found: 184.1118.

NMR Conv.: 98%

Isolated Yield: 86%

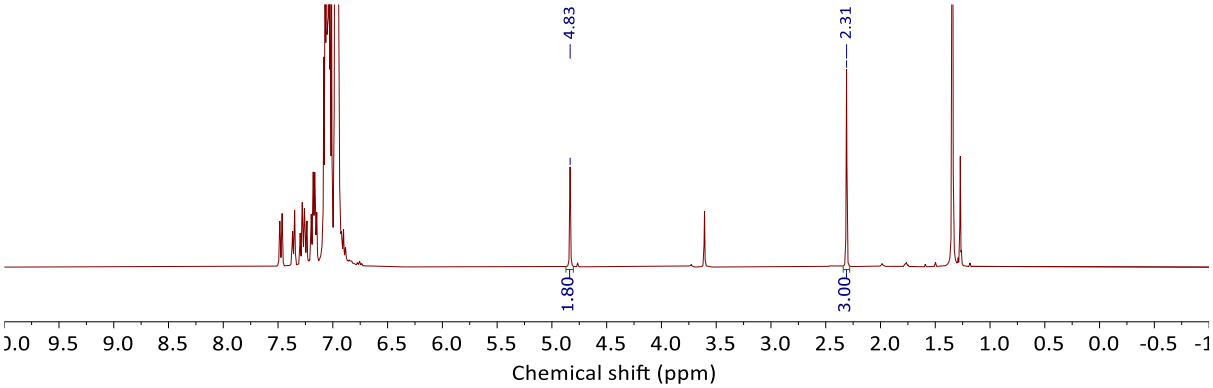


Figure S53. ^{1}H NMR spectrum (*o*DFB) of crude **16b**.

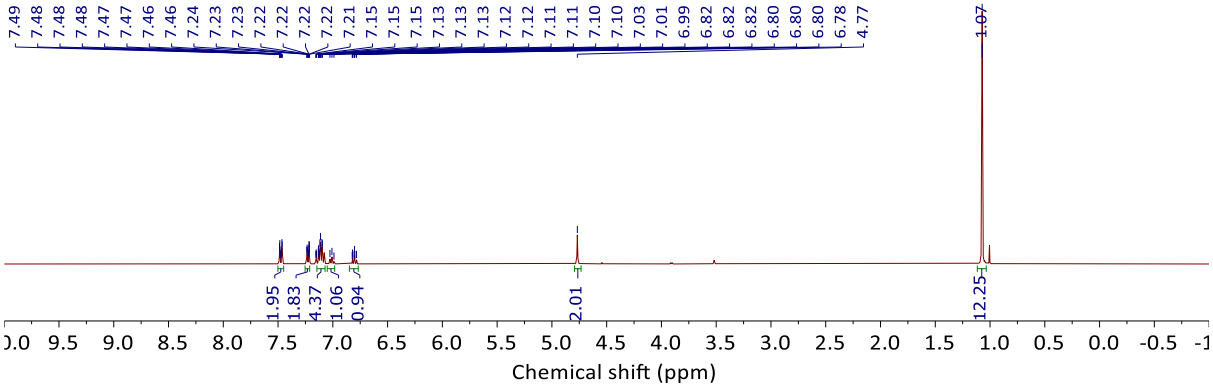


Figure S54. ^{1}H NMR spectrum (C_6D_6) of **16b**.

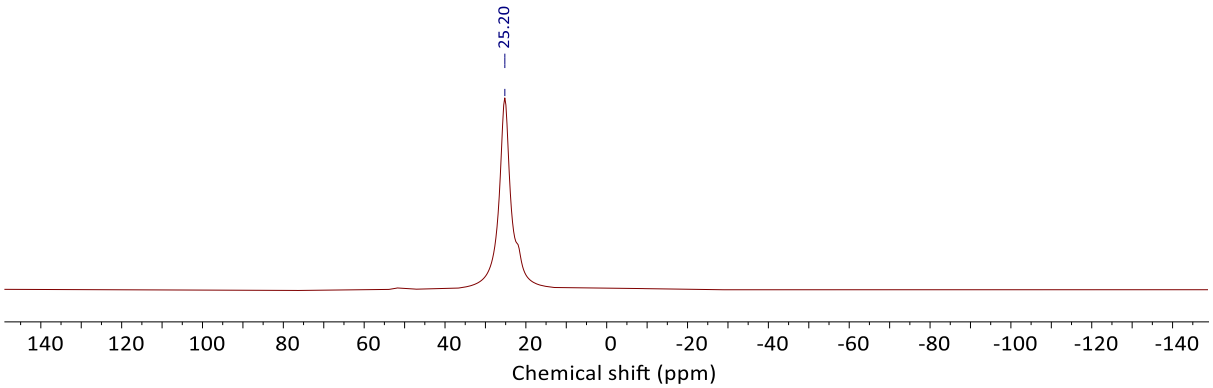


Figure S55. ^{11}B NMR spectrum (C_6D_6) of **16b**.

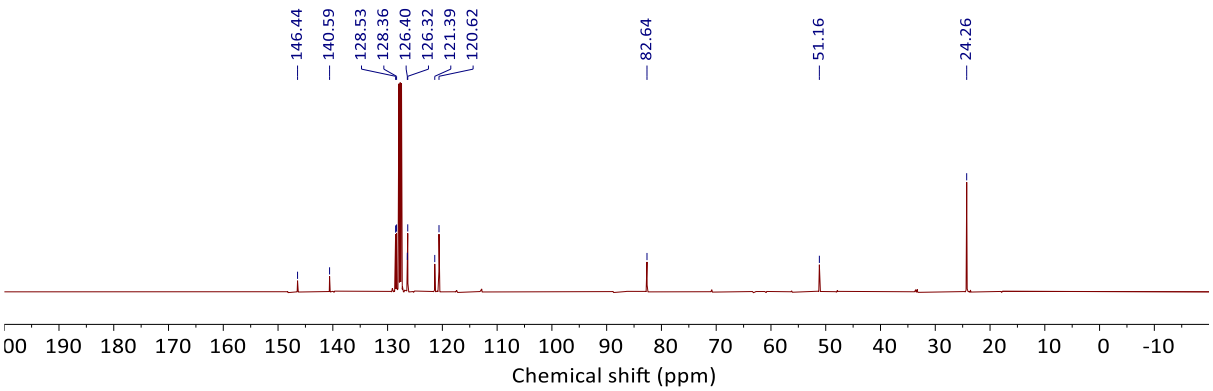
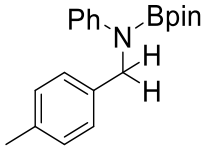


Figure S56. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **16b**.

3.3.2. N-(4-methyl)benzyl-N-phenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.51 (dd, $^{3}J_{HH}$ = 8.8, $^{4}J_{HH}$ = 1.1 Hz, 2H, *Ar*), 7.20 – 7.15 (m, 2H, *Ar*), 7.11 (dd, $^{3}J_{HH}$ = 8.7, 7.3 Hz, 2H, *Ar*), 6.98 – 6.92 (m, 2H, *Ar*), 6.85 – 6.78 (m, 1H, *Ar*), 4.78 (s, 2H, C*H*$_2$NBpin), 2.06 (s, 3H, *Me*), 1.09 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.2 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 146.51 (s, *Ar*), 137.57 (s, *Ar*), 135.61 (s, *Ar*), 129.09 (s, *Ar*), 128.50 (s, *Ar*), 126.35 (s, *Ar*), 121.37, (s, *Ar*) 120.75 (s, *Ar*), 82.60 (s, NB*pin*), 50.95 (s, *C*H$_2$NBpin), 24.27 (s, NB*pin*), 20.66 (s, *Me*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_{14}H_{15}N$+H ([M+H]$^{+}$): calcd: 198.1277; found: 198.1272.

NMR Conv.: 86%

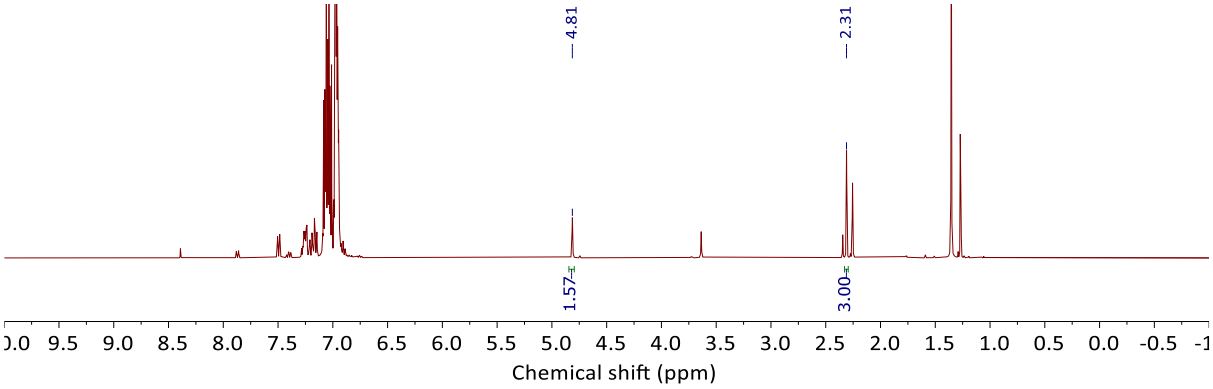


Figure S57. ^{1}H NMR spectrum (*o*DFB) of crude **17b**.

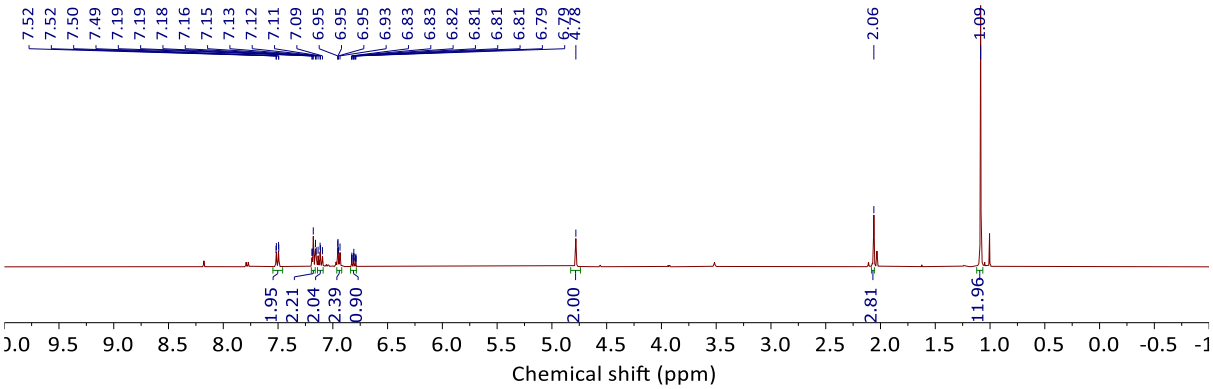


Figure S58. ^{1}H NMR spectrum (C_6D_6) of **17b**.

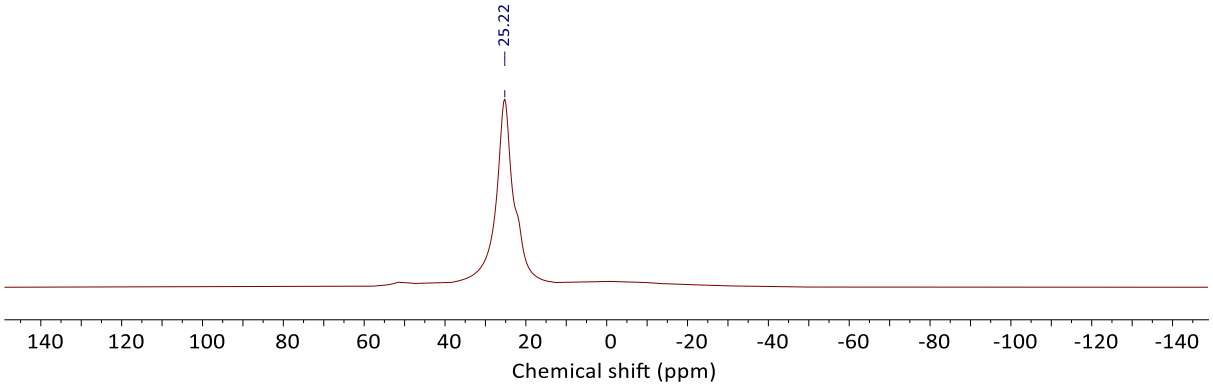


Figure S59. ^{11}B NMR spectrum (C_6D_6) of **17b**.

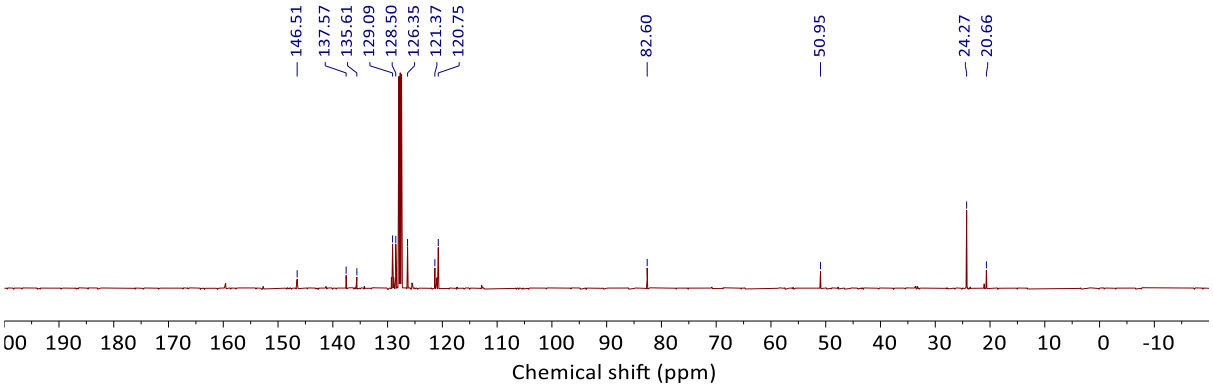
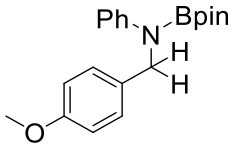


Figure S60. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **17b**.

3.3.3. N-(4-methoxy)benzyl-N-phenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.55 – 7.46 (m, 2H, *Ar*), 7.19 – 7.06 (m, 4H, *Ar*), 6.82 (tt, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.1 Hz, 1H, *Ar*), 6.77 – 6.65 (m, 2H, *Ar*), 4.75 (s, 2H, C*H*$_2$NBpin), 3.26 (s, 3H, O*Me*), 1.10 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.2 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 158.61 (s, *Ar*), 146.47 (s, *Ar*), 132.41 (s, *Ar*), 128.51 (s, *Ar*), 127.54 (s, *Ar*), 121.43 (s, *Ar*), 120.91 (s, *Ar*), 113.90 (s, *Ar*), 82.60 (s, NB*pin*), 54.34 (s, O*Me*), 50.60 (s, *C*H$_2$NBpin), 24.29 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_{14}H_{15}NO$+H ([M+H]$^+$): calcd: 214.1226; found: 214.1219.

NMR Conv.: 94%

Isolated Yield: 81%

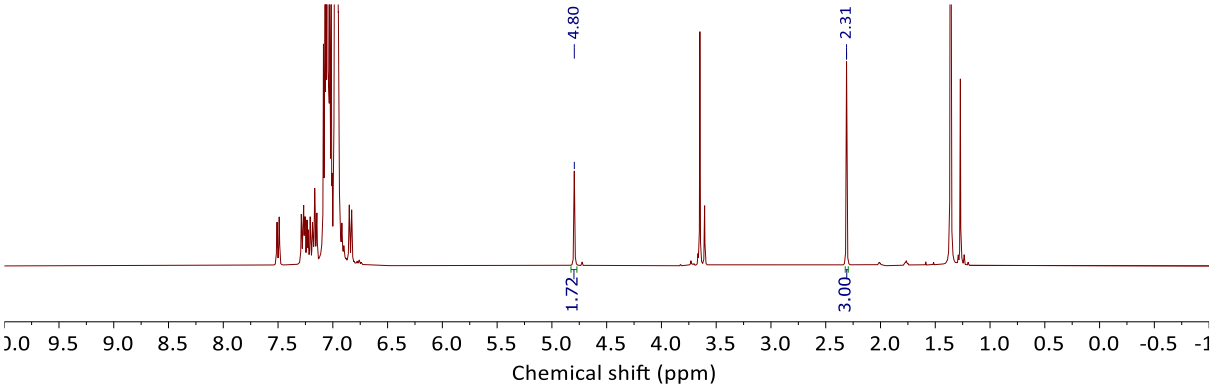


Figure S61. ^{1}H NMR spectrum (*o*DFB) of crude **18b**.

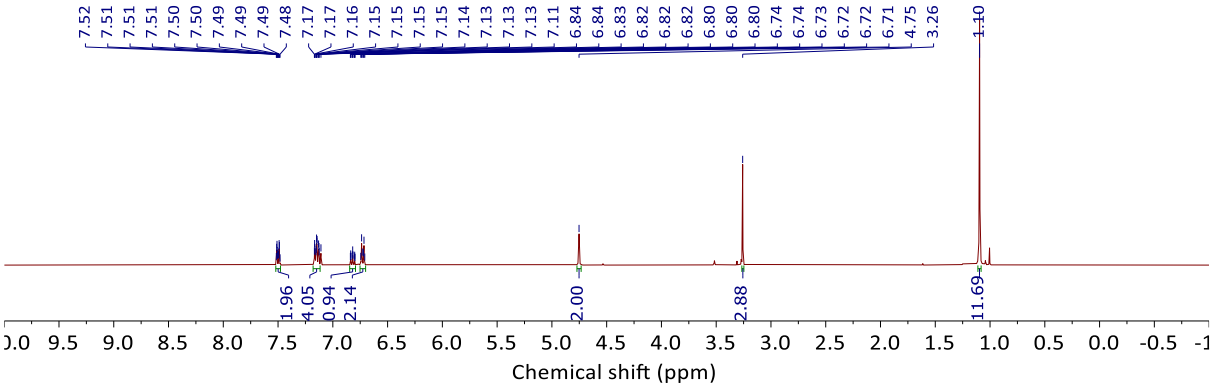


Figure S62. ^{1}H NMR spectrum (C_6D_6) of **18b**.

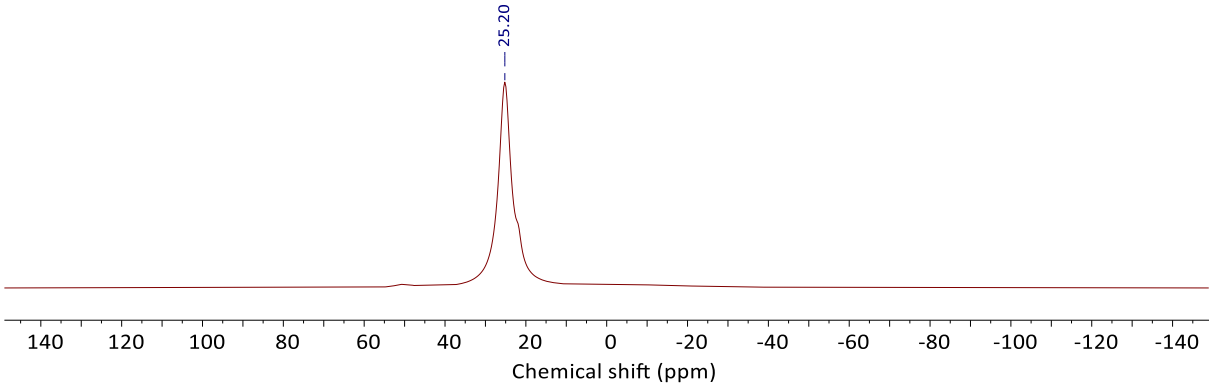


Figure S63. ^{11}B NMR spectrum (C_6D_6) of **18b**.

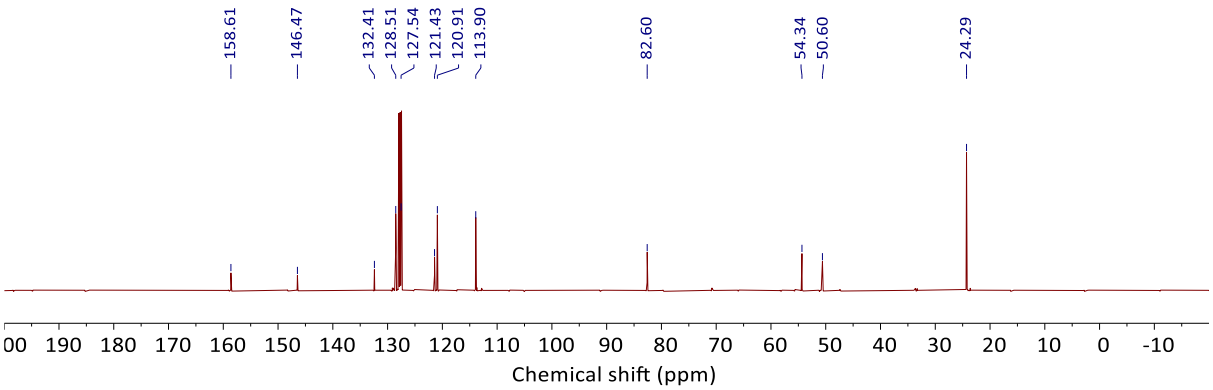
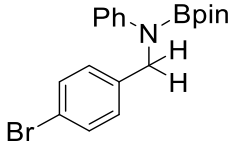


Figure S64. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **18b**.

3.3.4. N-(4-bromo)benzyl-N-phenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.40 – 7.36 (m, 2H, *Ar*), 7.20 – 7.16 (m, 2H, *Ar*), 7.14 – 7.08 (m, 2H, *Ar*), 6.88 – 6.80 (m, 3H, *Ar*), 4.56 (s, 2H, C*H*$_2$NBpin), 1.05 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.2 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 146.08 (s, *Ar*), 139.53 (s, *Ar*), 131.42 (s, *Ar*), 128.61 (s, *Ar*), 128.10 (s, *Ar*), 121.62 (s, *Ar*), 120.53 (s, *Ar*), 120.21 (s, *Ar*), 82.74 (s, NB*pin*), 50.52 (s, *C*H$_2$NBpin), 24.23 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_{13}H_{12}NBr+H$ ($[M+H]^+$): calcd: 262.0226; found: 262.0217.

NMR Conv.: 97%

Isolated Yield: 85%

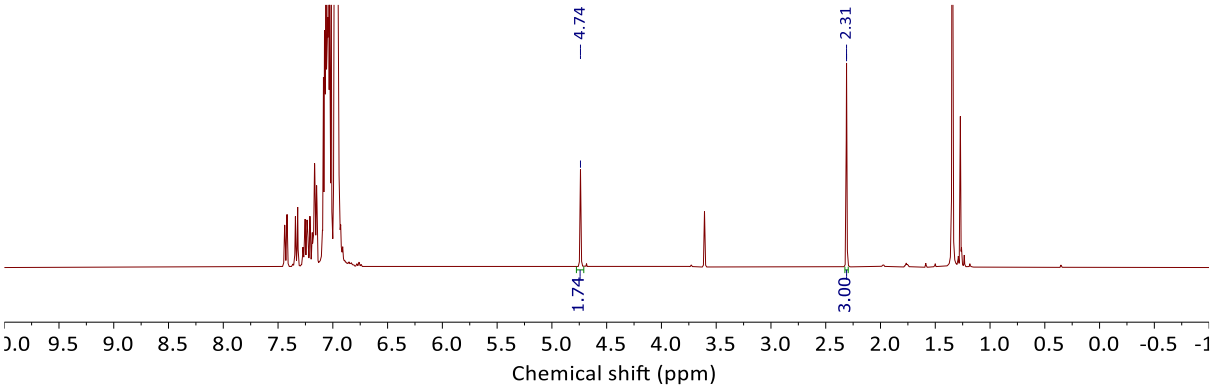


Figure S65. ^{1}H NMR spectrum (*o*DFB) of crude **19b**.

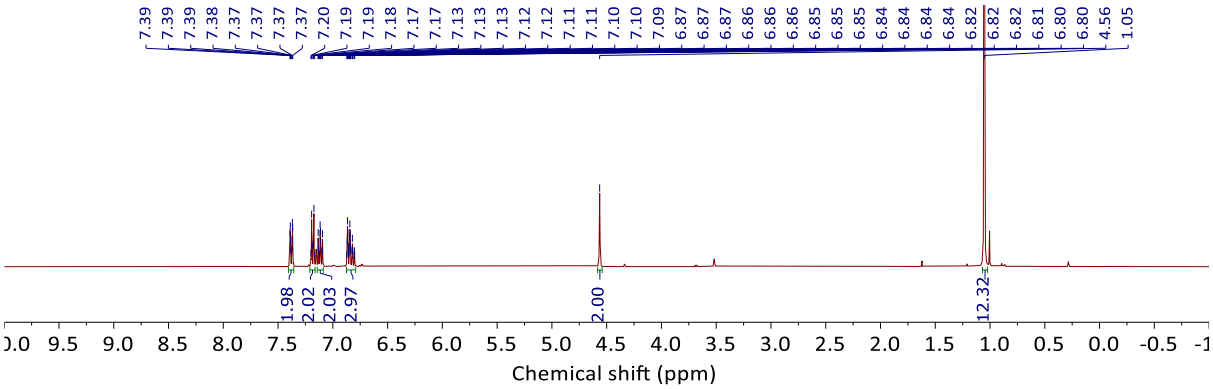


Figure S66. ^{1}H NMR spectrum (C_6D_6) of **19b**.

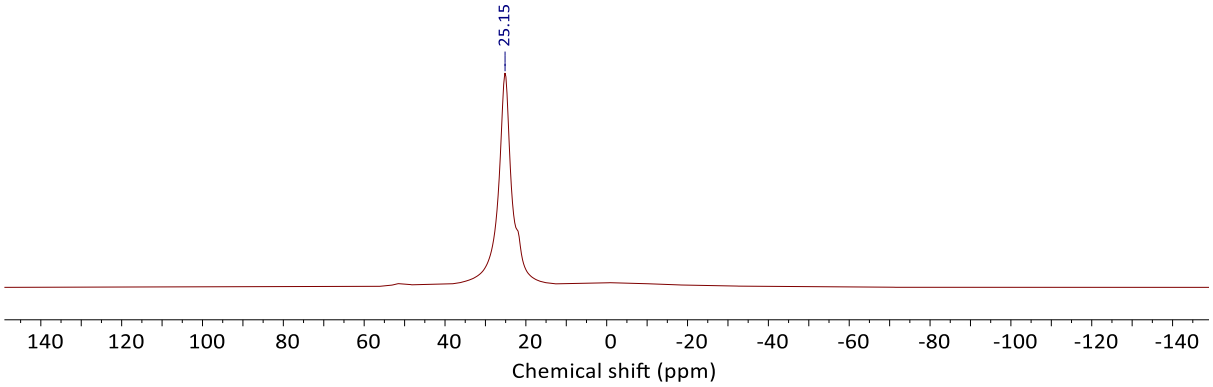


Figure S67. ^{11}B NMR spectrum (C_6D_6) of **19b**.

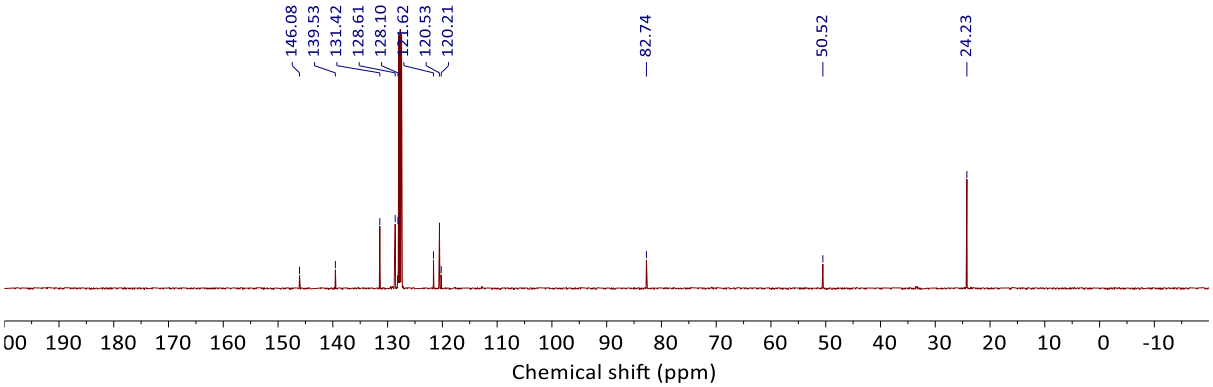
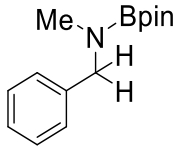


Figure S68. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **19b**.

3.3.5. N-benzyl-N-methyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.28 – 7.24 (m, 2H, *Ar*), 7.21 – 7.16 (m, 2H, *Ar*), 7.11 – 7.05 (m, 1H, *Ar*), 4.14 (s, 2H, C*H*$_2$NBpin), 2.58 (s, 3H, N*Me*), 1.14 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.1 (s) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 140.40 (s, *Ar*), 128.26 (s, *Ar*), 127.71 (s, *Ar*), 126.64 (s, *Ar*), 82.05 (s, NB*pin*), 52.89 (s, *C*H$_2$NBpin), 32.97 (s, N*Me*), 24.48 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_8H_{12}N$+H ($[M+H]^+$): calcd: 122.0964; found: 122.0965.

NMR Conv.: 93%

Isolated Yield: 86%

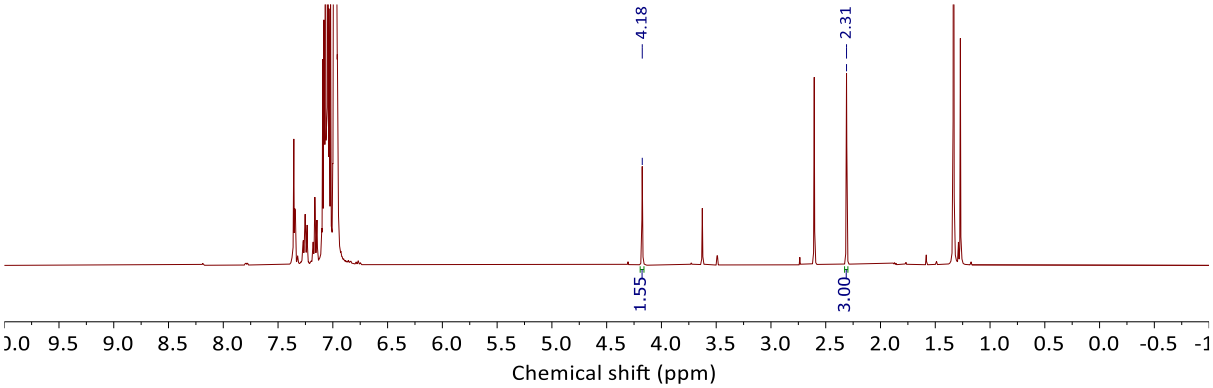


Figure S69. ^{1}H NMR spectrum (*o*DFB) of crude **20b**.

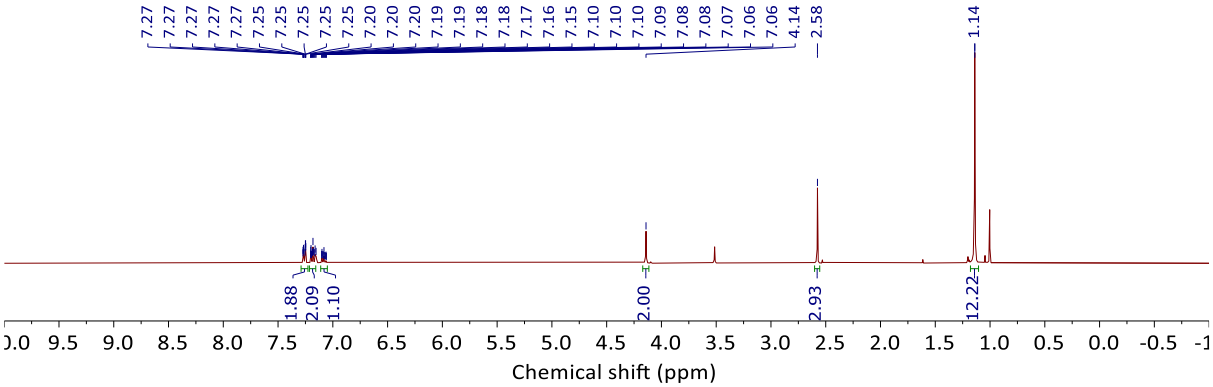


Figure S70. ^{1}H NMR spectrum (C_6D_6) of **20b**.

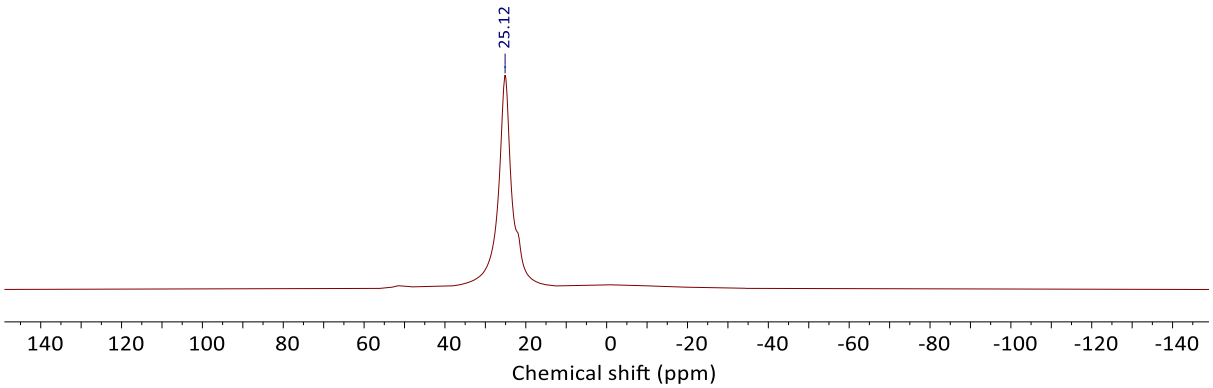


Figure S71. ^{11}B NMR spectrum (C_6D_6) of **20b**.

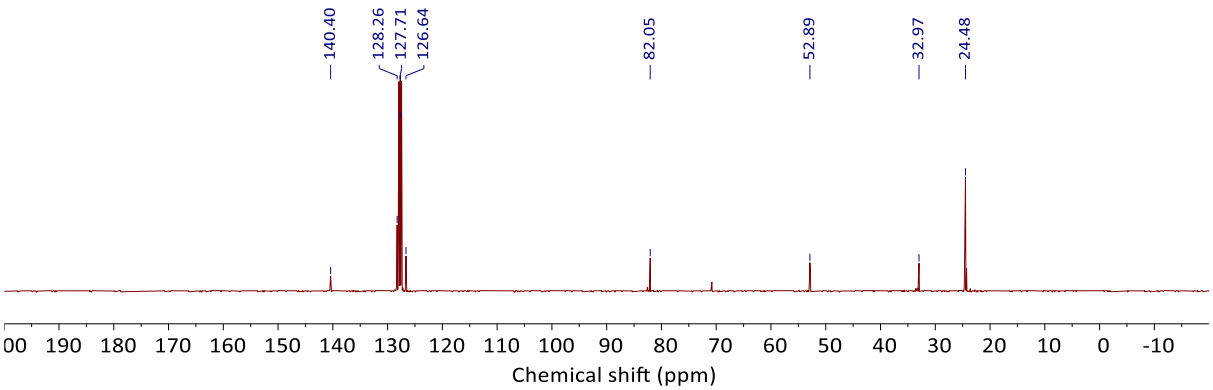
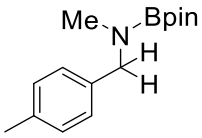


Figure S72. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **20b**.

3.3.6. N-(4-methyl)benzyl-N-methyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.20 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, *Ar*), 7.01 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, *Ar*), 4.15 (s, 2H, C*H*$_2$NBpin), 2.61 (s, 3H, N*Me*), 2.13 (s, 3H, *Me*), 1.15 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.7 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 137.41 (s, *Ar*), 135.86 (s, *Ar*), 128.97 (s, *Ar*), 127.79 (s, *Ar*), 82.01 (s, NB*pin*), 52.63 (s, *C*H$_2$NBpin), 32.92 (s, N*Me*), 24.49 (s, NB*pin*), 20.73 (s, *Me*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_9H_{13}N$+H ($[M+H]^+$): calcd: 136.1121; found: 136.1118.

NMR Conv.: >99%

Isolated Yield: 87

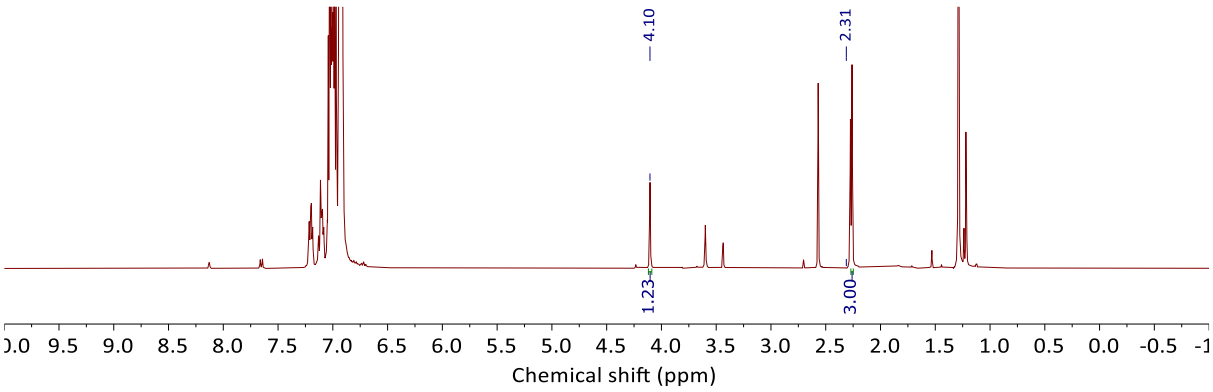


Figure S73. ^{1}H NMR spectrum (*o*DFB) of crude **21b**.

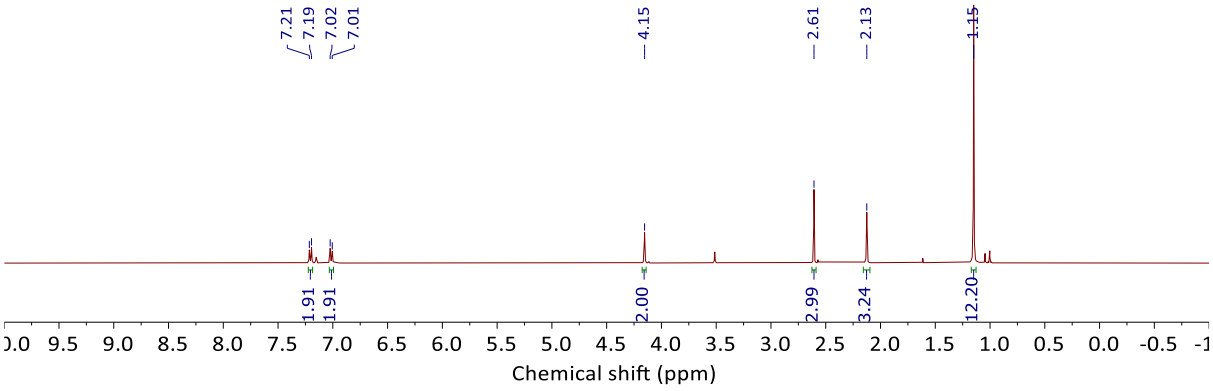


Figure S74. ^{1}H NMR spectrum (C_6D_6) of **21b**.

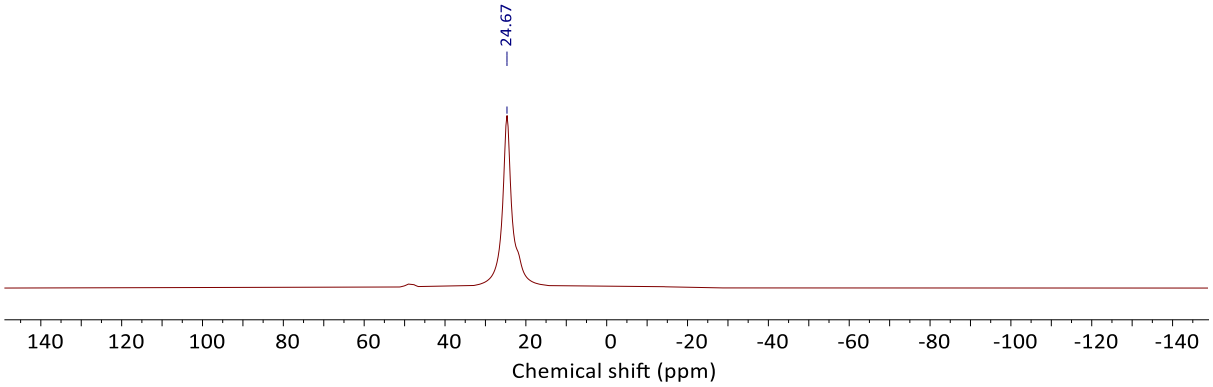


Figure S75. ^{11}B NMR spectrum (C_6D_6) of **21b**.

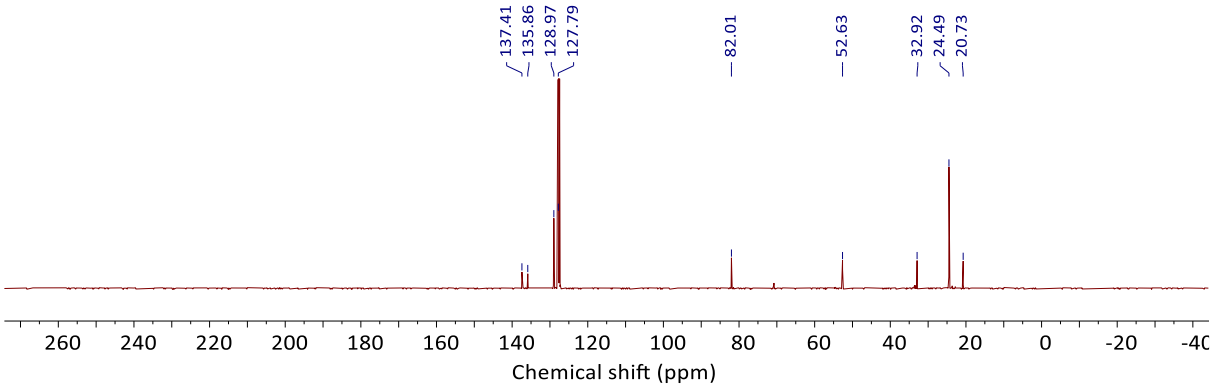
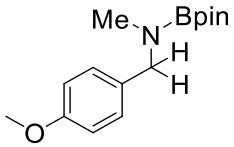


Figure S76. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **21b**.

3.3.7. N-(4-methoxy)benzyl-N-methyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.20 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *Ar*), 6.80 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *Ar*), 4.13 (s, 2H, C*H*$_2$NBpin), 3.32 (s, 3H, O*Me*), 2.61 (s, 3H, N*Me*), 1.15 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.7 (s) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, 298 K, C_6D_6): δ = 158.88 (s, *Ar*), 132.38 (s, *Ar*), 128.93 (s, *Ar*), 113.77 (s, *Ar*), 82.00 (s, NB*pin*), 54.41 (s, O*Me*), 52.29 (s, *C*H$_2$NBpin), 32.82 (N*Me*), 24.50 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_9H_{13}NO$+H ([M+H]$^+$): calcd: 152.1070; found: 152.1068.

NMR Conv.: 85%

Isolated Yield: 84%

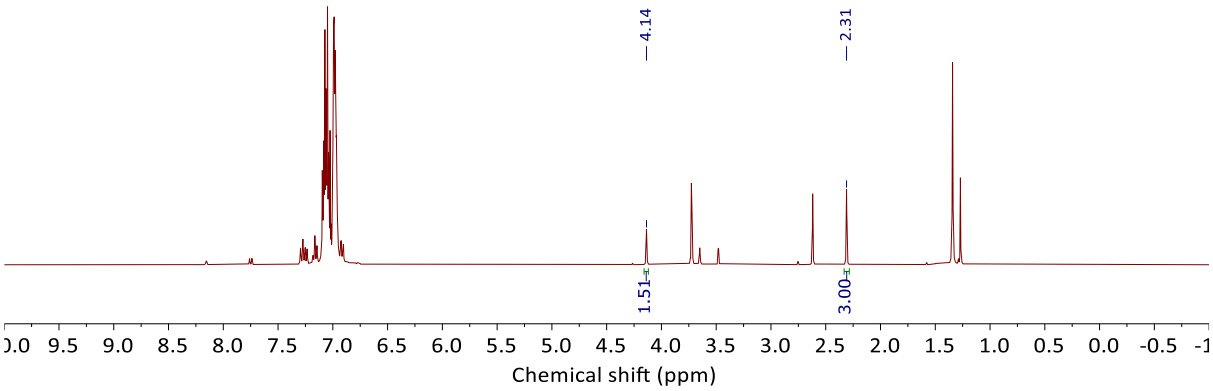


Figure S77. ^{1}H NMR spectrum (*o*DFB) of crude **22b**.

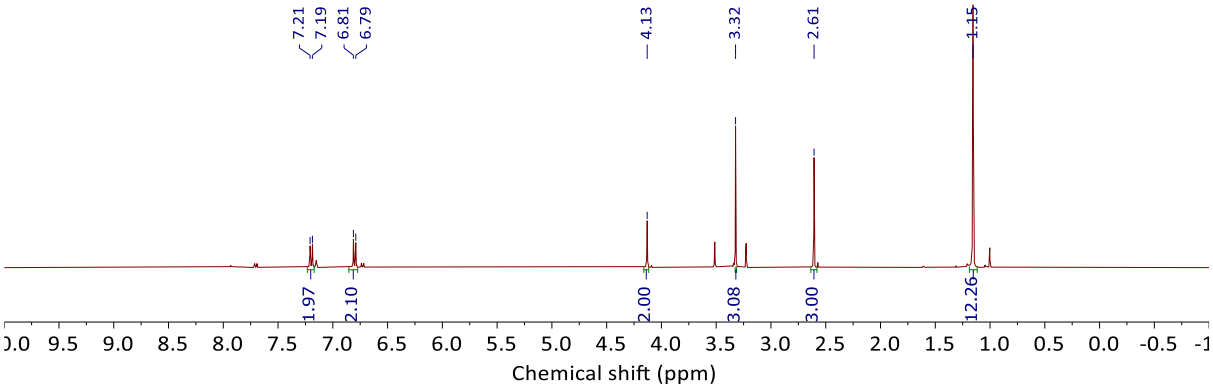


Figure S78. ^{1}H NMR spectrum (C_6D_6) of **22b**.

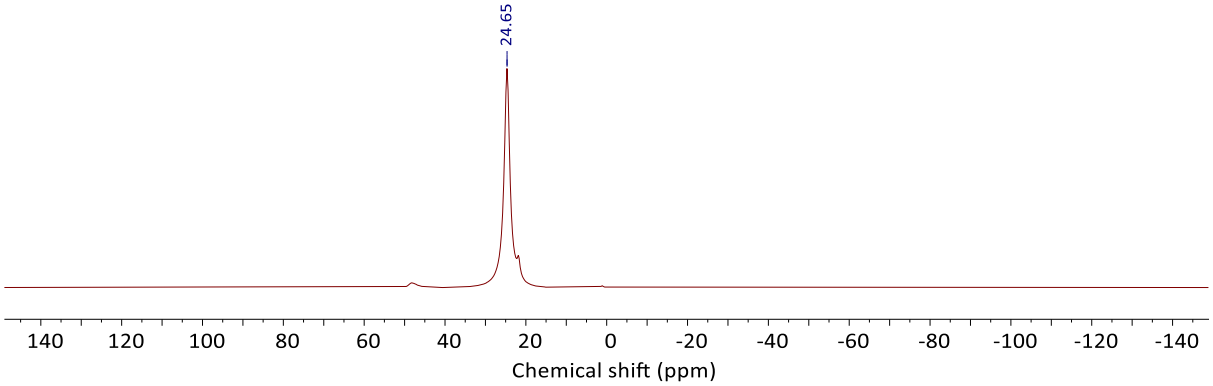


Figure S79. ^{11}B NMR spectrum (C_6D_6) of **22b**.

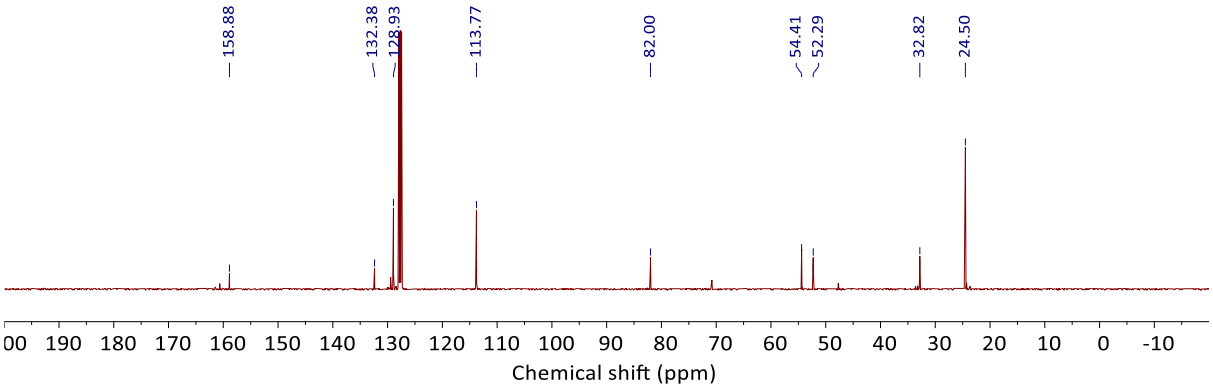
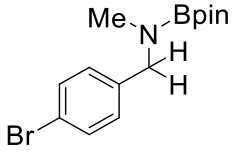


Figure S80. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **22b**.

3.3.8. N-(4-bromo)benzyl-N-methyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.25 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *Ar*), 6.88 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *Ar*), 3.93 (s, 2H, C*H*$_2$NBpin), 2.48 (s, 3H, N*Me*), 1.12 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.6 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 139.33 (s, *Ar*), 131.34 (s, *Ar*), 129.38 (s, *Ar*), 120.47 (s, *Ar*), 82.15 (s, NB*pin*), 52.17 (s, *C*H$_2$NBpin), 32.93 (s, N*Me*), 24.45 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_8H_{10}NBr$+H ($[M+H]^+$): calcd: 200.0069; found: 200.0064.

NMR Conv.: 97%

Isolated Yield: 82%

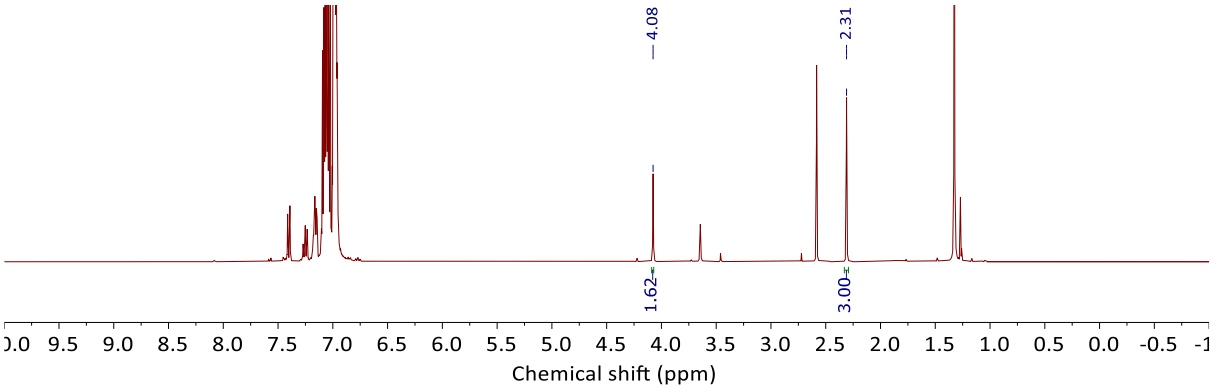


Figure S81. ^{1}H NMR spectrum (*o*DFB) of crude **23b**.

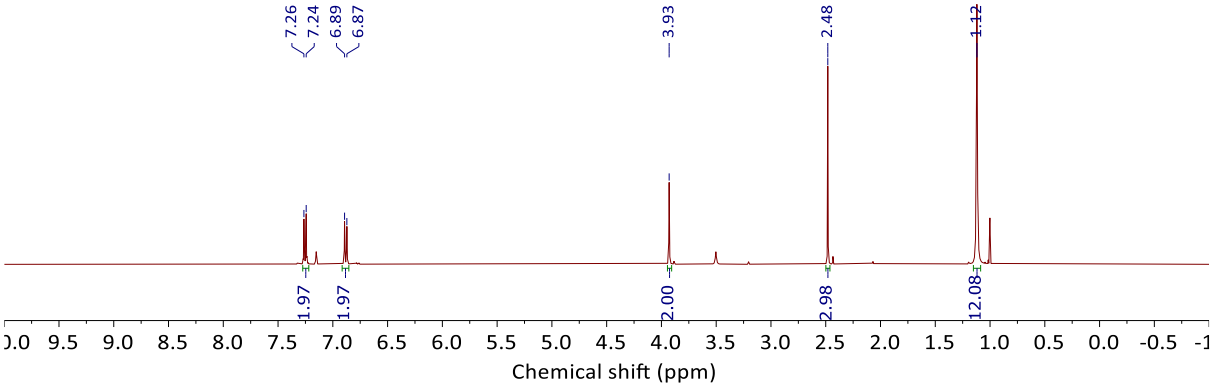


Figure S82. ^{1}H NMR spectrum (C_6D_6) of **23b**.

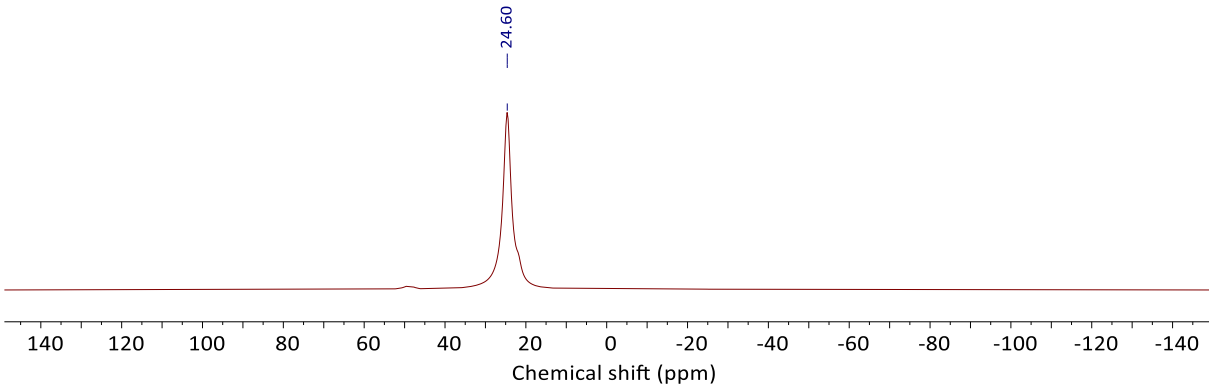


Figure S83. ^{11}B NMR spectrum (C_6D_6) of **23b**.

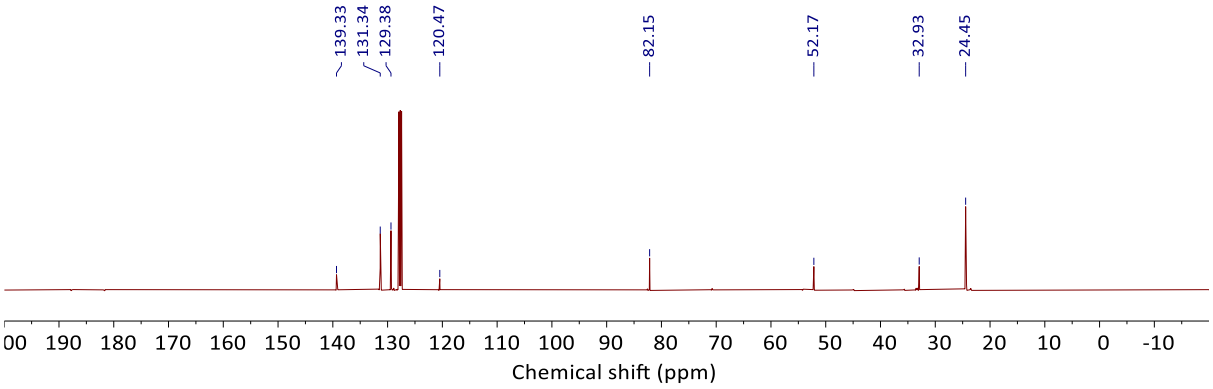
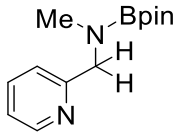


Figure S84. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **23b**.

3.3.9. N-(2-pyridineethyl)-N-methyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 8.46 (ddd, $^{3}J_{HH}$ = 4.9, 1.8, $^{4}J_{HH}$ = 1.2 Hz, 1H, *Ar*), 7.20 (dt, $^{3}J_{HH}$ = 7.9, $^{4}J_{HH}$ = 1.2 Hz, 1H, *Ar*), 7.15 – 7.10 (m, 1H, *Ar*), 6.65 – 6.59 (m, 1H, *Ar*), 4.47 (s, 2H, C*H*$_2$NBpin), 2.68 (s, 3H, N*Me*), 1.13 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.8 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 160.91 (s, *Ar*), 149.21 (s, *Ar*), 135.64 (s, *Ar*), 121.16 (s, *Ar*), 120.45 (s, *Ar*), 82.10 (s, NB*pin*), 55.08 (s, *C*H$_2$NBpin), 33.68 (s, N*Me*), 24.47 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_7H_{10}N_2$+H ([M+H]$^{+}$): calcd: 123.0917; found: 123.0918.

NMR Conv.: 97%

Isolated Yield: 82%

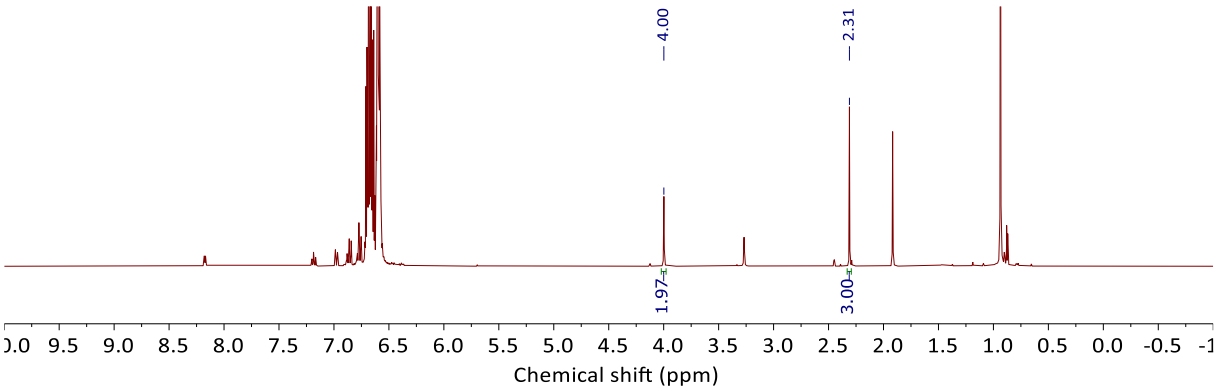


Figure S85. ^{1}H NMR spectrum (*o*DFB) of crude **24b**.

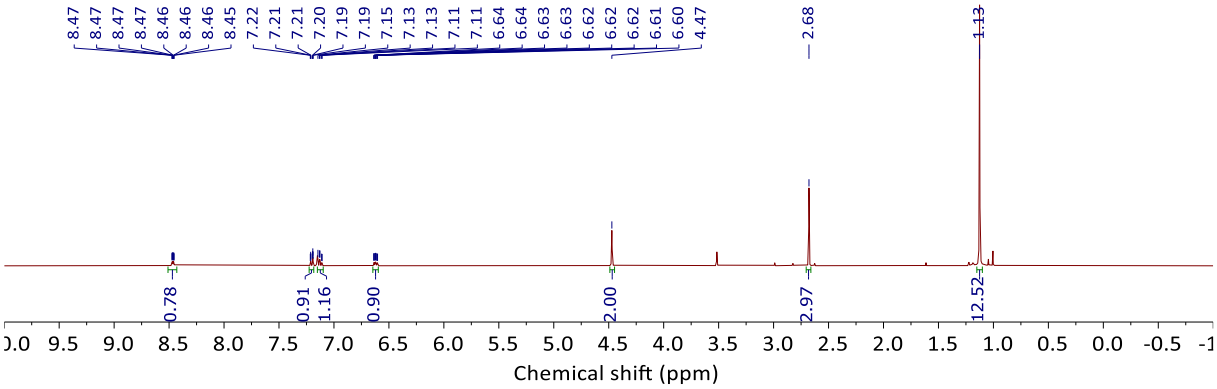


Figure S86. ^{1}H NMR spectrum (C_6D_6) of **24b**.

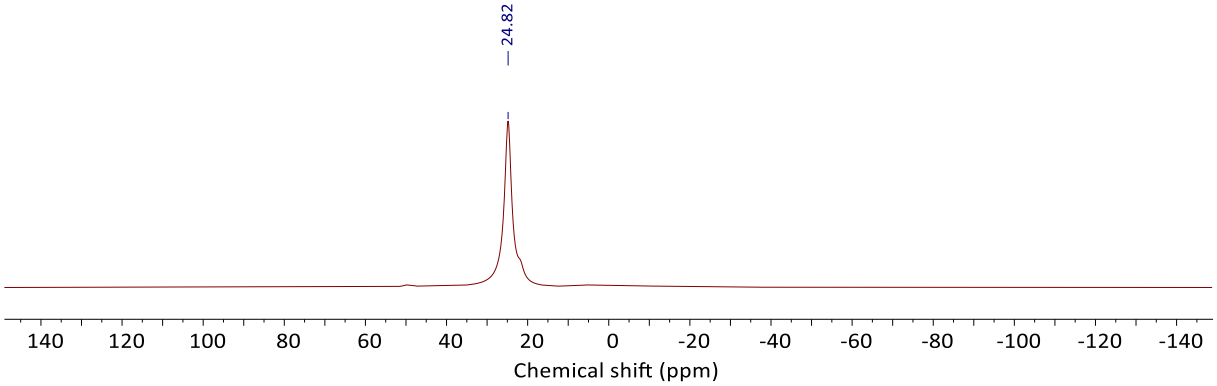


Figure S87. ^{11}B NMR spectrum (C_6D_6) of **24b**.

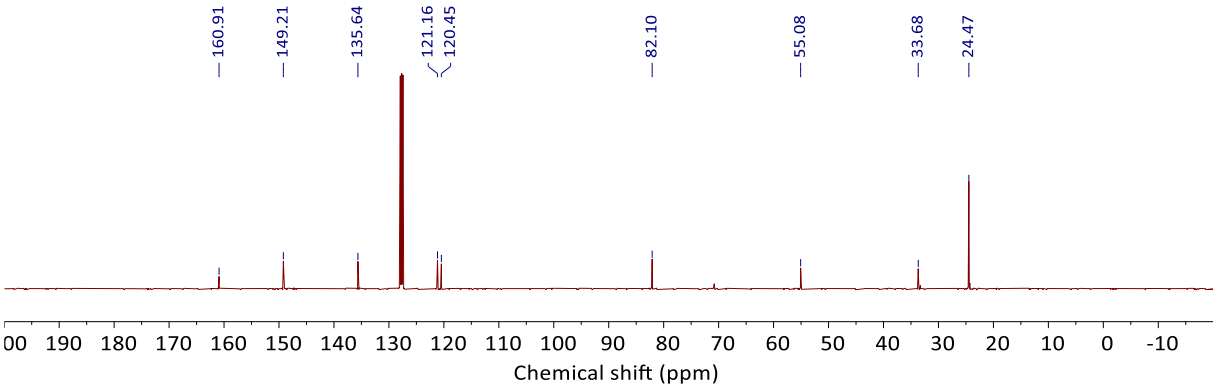
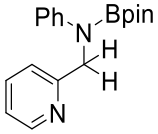


Figure S88. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **24b**.

3.3.10. N-(2-pyridineethyl)-N-phenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 8.45 (ddd, $^{3}J_{HH}$ = 4.9, 1.9, $^{4}J_{HH}$ = 1.0 Hz, 1H, *Ar*), 7.64 – 7.49 (m, 2H, *Ar*), 7.16 – 7.14 (m, 1H, *Ar*), 7.13 – 7.07 (m, 2H, *Ar*), 7.02 (dt, $^{3}J_{HH}$ = 7.7, 1.8 Hz, 1H, *Ar*), 6.78 (tt, $^{3}J_{HH}$ = 7.5, $^{4}J_{HH}$ = 1.1 Hz, 1H, *Ar*), 6.56 (ddd, $^{3}J_{HH}$ = 7.5, 4.8, $^{4}J_{HH}$ = 1.1 Hz, 1H, *Ar*), 5.09 (s, 2H, C*H*$_2$NBpin), 1.07 (s, 12H, NB*pin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 25.2 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 160.73 (s, *Ar*), 149.27 (s, *Ar*), 146.38 (s, *Ar*), 135.76 (s, *Ar*), 128.60 (s, *Ar*), 121.16 (s, *Ar*), 121.14 (s, *Ar*), 119.91 (s, *Ar*), 82.71 (s, NB*pin*), 53.22 (s, *C*H$_2$NBpin), 24.26 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_{12}H_{12}N_2$+H ([M+H]$^{+}$): calcd: 185.1073; found: 185.1070.

NMR Conv.: 97%

Isolated Yield: 82%

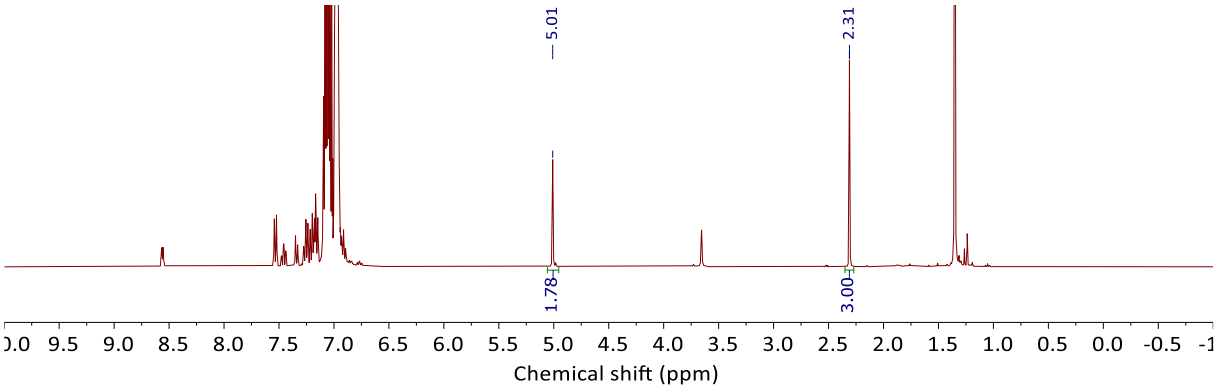


Figure S89. ^{1}H NMR spectrum (*o*DFB) of crude **25b**.

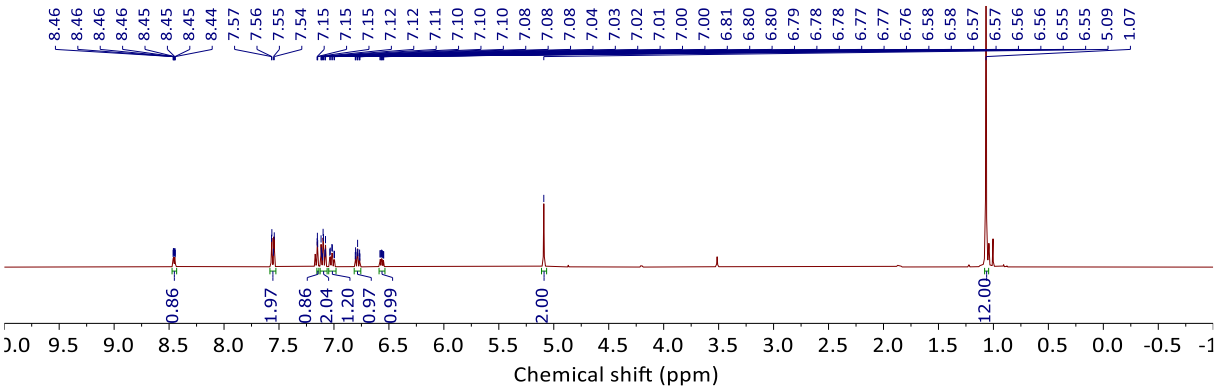


Figure S90. ^{1}H NMR spectrum (C_6D_6) of **25b**.

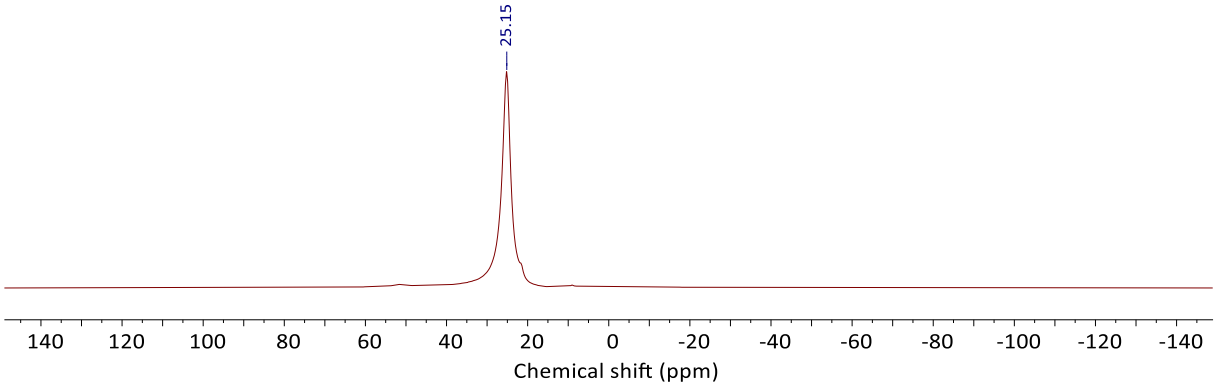


Figure S91. ^{11}B NMR spectrum (C_6D_6) of **25b**.

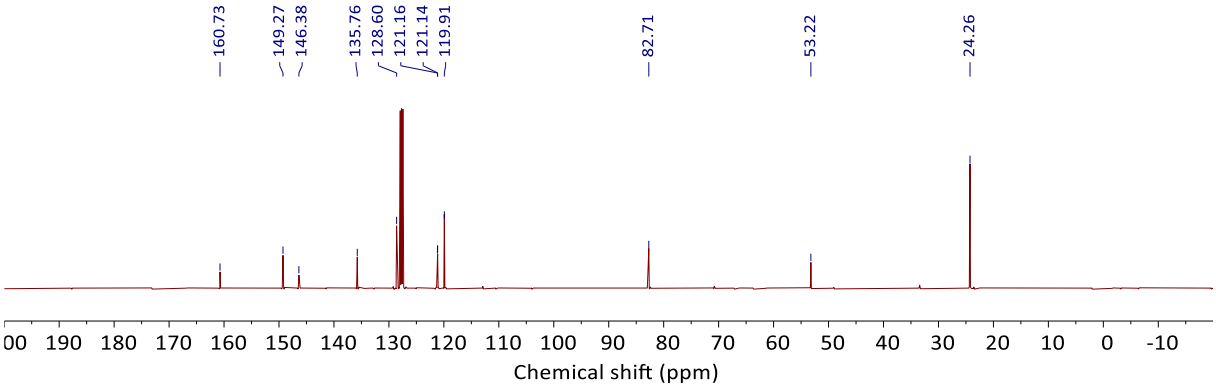
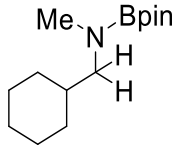


Figure S92. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **25b**.

3.3.11. N-(cyclohexyl)ethyl-N-methyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 2.87 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*$_2$NBpin), 2.65 (s, 3H, N*Me*), 1.73 – 1.57 (m, 6H, *Cy*), 1.50 (ddt, $^3J_{HH}$ = 11.1, 7.1, 3.6 Hz, 1H, NCH$_2$C*H*), 1.22 – 1.14 (m, 2H, Cy), 1.12 (s, 12H, NB*pin*), 0.96 – 0.84 (m, 2H, *Cy*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 24.5 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 81.63 (s, NB*pin*), 55.26 (s, *C*H$_2$Bpin), 35.33 (s, N*Me*), 33.50 (s, *Cy*), 30.64 (s, *Cy*), 26.86 (s, *Cy*), 26.07 (s, *Cy*), 24.47 (s, NB*pin*) ppm.

Mass spectrometry after hydrolysis (APCI): $C_8H_{17}N$+H ([M+H]$^+$): calcd: 128.1434; found: 128.1433.

NMR Conv.: 92%

Isolated Yield: 89%

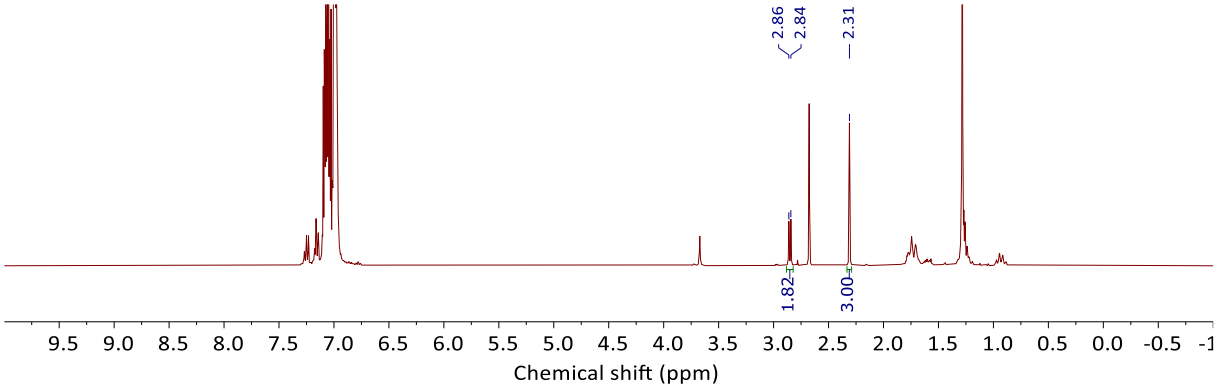


Figure S93. ^{1}H NMR spectrum (*o*DFB) of crude **26b**.

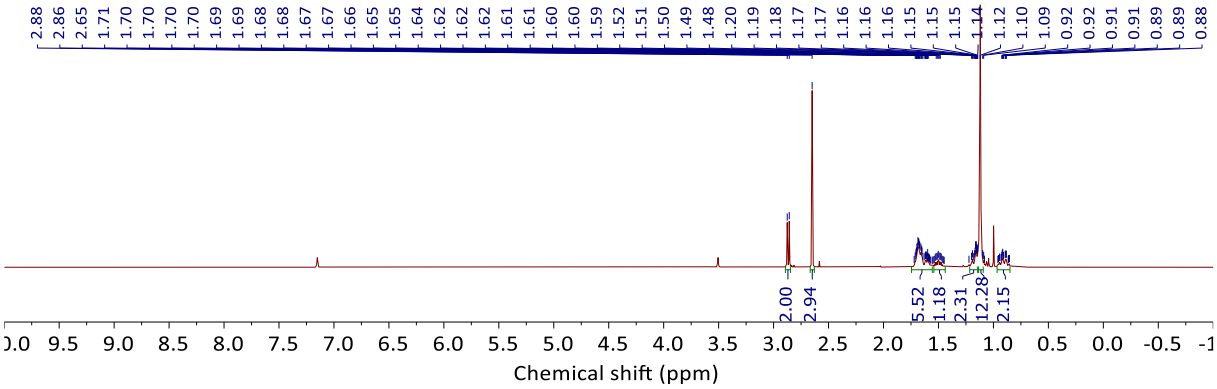


Figure S94. ^{1}H NMR spectrum (C_6D_6) of **26b**.

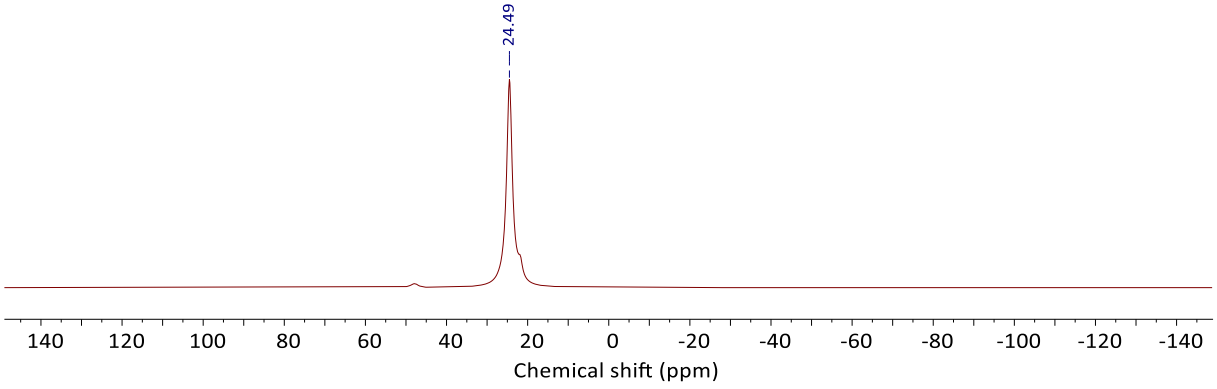


Figure S95. ^{11}B NMR spectrum (C_6D_6) of **26b**.

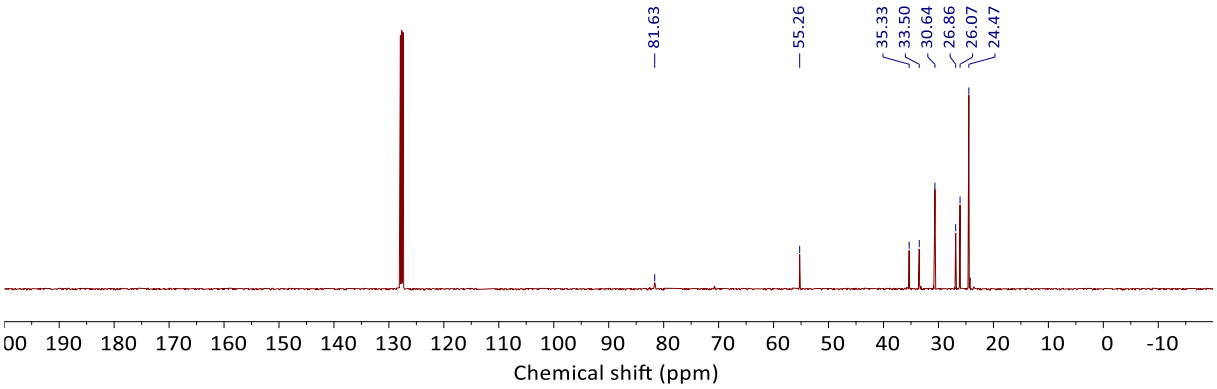


Figure S96. ^{13}C{^{1}H} NMR spectrum (C_6D_6) of **26b**.

4. Catalytic Hydroboration Carbonitriles

4.1. Screening and controls

To a solution of catalyst and HBpin (64 µL, 0.44 mmol, 2 eq.) in solvent (0.5 mL), benzonitrile (23 µL, 0.22 mmol, 1 eq.) and toluene (25 µL, 0.24 mmol) were added and allowed to react at the specified temperature for 48 h. The reaction was monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using the resonances of the toluene (^{1}H δ = 2.31 ppm) as internal standard.

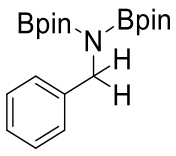
4.2. General procedure for hydroboration of Carbonitriles

To a solution of [Na(18-c-6)]$_2$[**1**] (10 mg, 11 µmol, 0.05 eq.) and HBpin (56 mg, 64 µL, 0.44 mmol, 2eq.) in *o*DFB (0.5 mL), carbonitriles (0.22 mmol, 1eq.) and toluene (25 µL, 0.24 mmol) were added and allowed to react at 50 °C for 48 h. The reaction monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using toluene (^{1}H δ = 2.31 ppm) as internal standard. The reaction mixture was worked-up by removal of volatiles and extraction by pentane to remove catalyst and any possible residual HBpin.

4.3. Characterization data hydroboration of nitriles

We validated our analysis of most hydroborated nitriles by comparison to various literature sources and found all data to be in agreement with those previously reported.[12, 13]

4.3.1. N-benzyl-N,N-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 7.57 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, *Ar*), 7.24 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, *Ar*), 7.11 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, *Ar*), 4.59 (s, 2H, C*H*$_2$NBpin), 1.02 (s, 24H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, C_6D_6): δ = 26.8 (s) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, C_6D_6): δ = 143.41 (s, *Ar*), 127.97 (s, *Ar*), 127.68 (s, *Ar*), 126.27 (s, *Ar*), 82.20 (s, NB*pin*$_2$), 47.45 (s, *C*H$_2$), 24.35 (s, NB*pin*$_2$) ppm.

Mass spectrometry after hydrolysis (APCI): C_7H_9N+H ([M+H]$^+$): calcd: 108.0813; found: 107.0823.

NMR Conv.: 97%

Isolated Yield: 85%

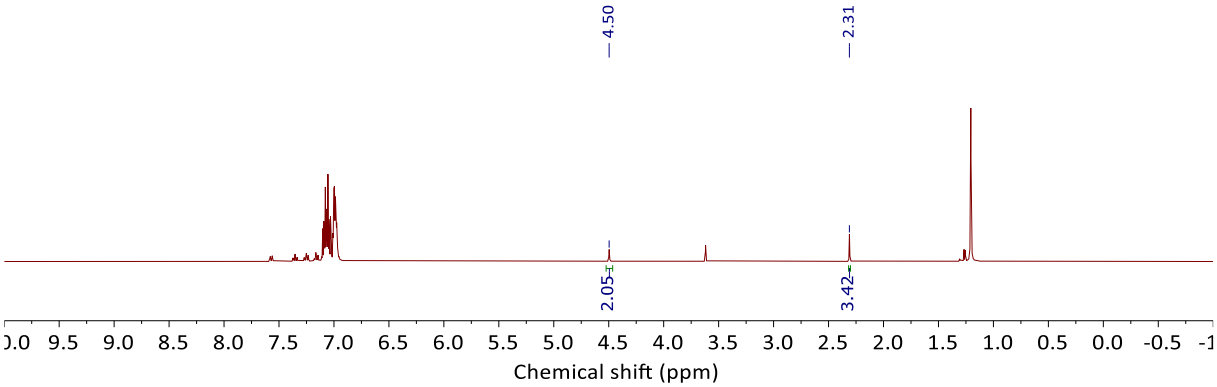


Figure S97. ^{1}H NMR spectrum (*o*DFB) of crude **27b**.

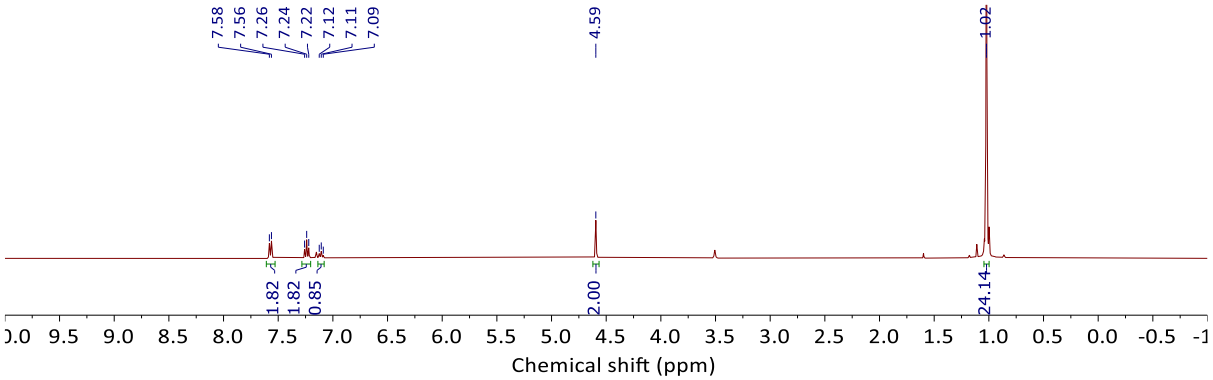


Figure S98. ^{1}H NMR spectrum (C_6D_6) of **27b**.

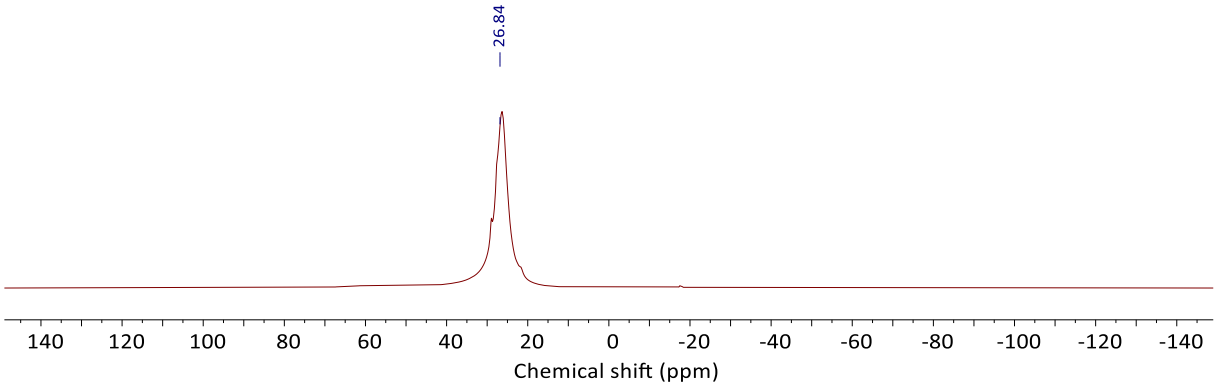


Figure S99. ^{11}B NMR spectrum (C_6D_6) of **27b**.

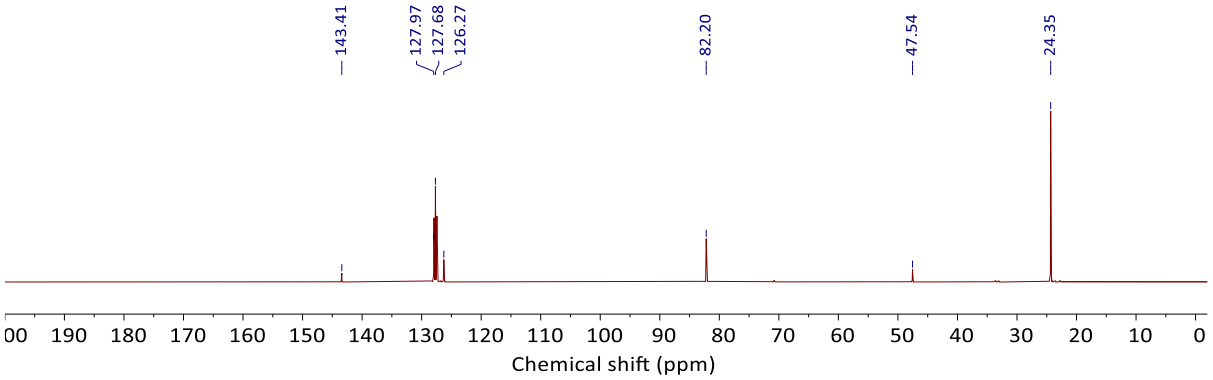
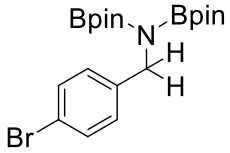


Figure S100. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **27b**.

4.3.2. N-(4-bromo)benzyl-N,N-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 7.42 – 7.40 (m, 2H, *Ar*), 7.26 – 7.23 (m, 2H, *Ar*), 4.39 (s, 2H, C*H*$_2$NBpin), 1.21 (s, 24H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 26.2 (s) ppm.

Mass spectrometry after hydrolysis (APCI): C_7H_8BrN+H ($[M+H]^+$): calcd: 185.9918; found: 185.9909.

NMR Conv.: 65%

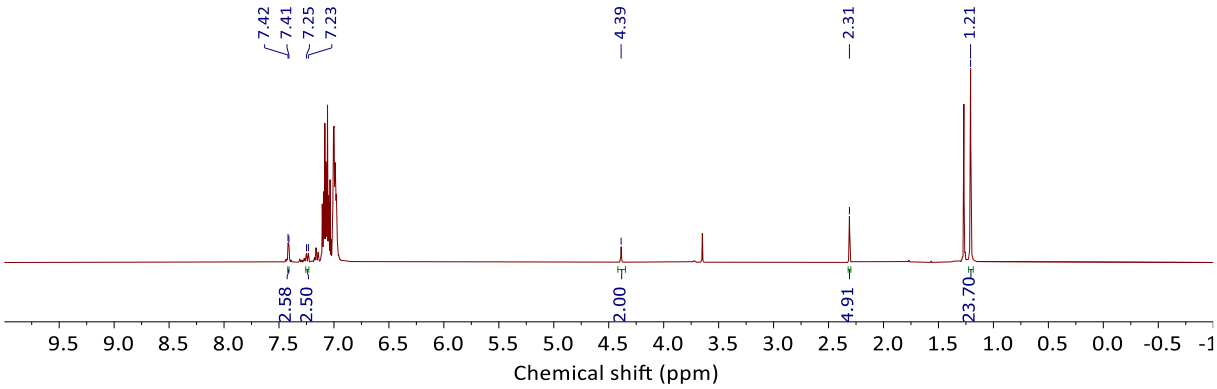


Figure S101. ^{1}H NMR spectrum (*o*DFB) of crude **28b**.

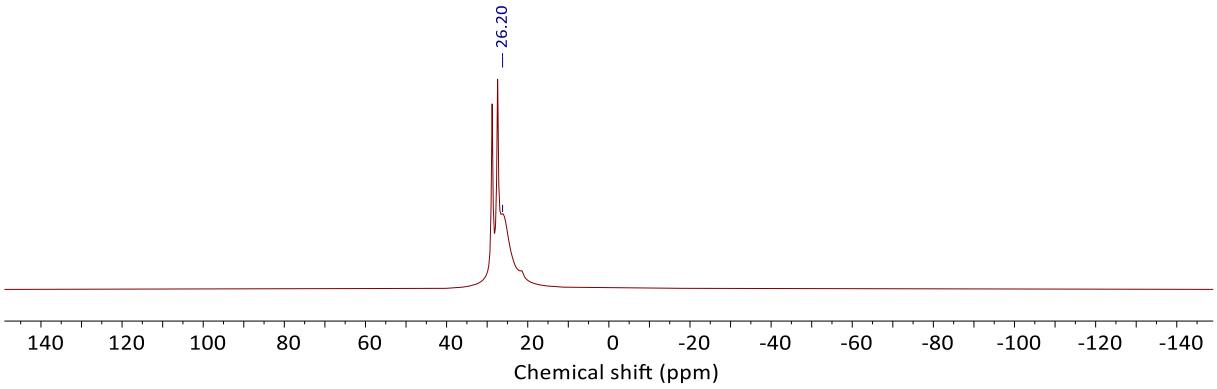
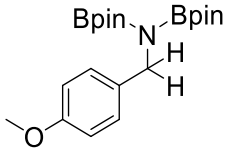


Figure S102. ^{11}B NMR spectrum (*o*DFB) of crude **28b**.

4.3.3. N-(4-methoxy)benzyl-N,N-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 7.53 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, *Ar*), 6.93 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, *Ar*), 4.44 (s, 2H, C*H*$_2$NBpin), 3.73 (s, 3H, O*Me*), 1.22 (s, 24H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 26.1 (s) ppm.

Mass spectrometry after hydrolysis (APCI): $C_8H_{11}NO$+H ([M+H]$^+$): calcd: 138.0919; found: 138.0923.

NMR Conv.: 82%

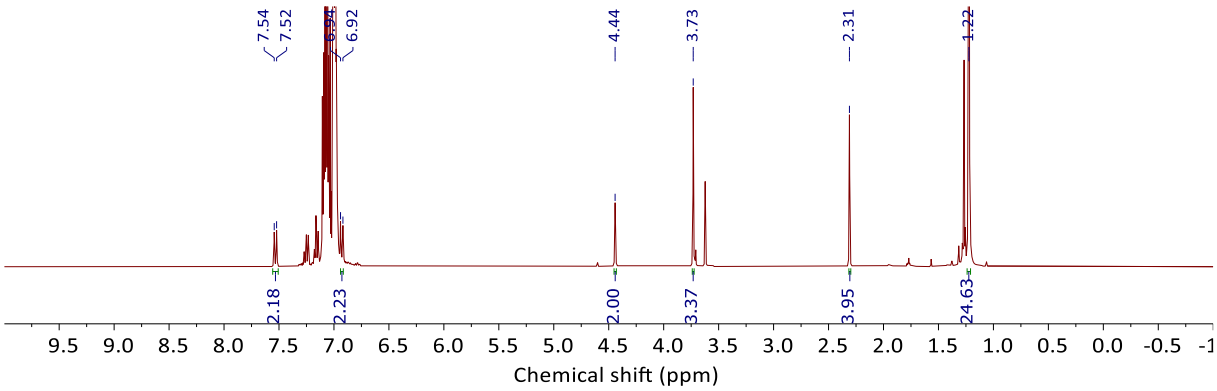


Figure S103. ^{1}H NMR spectrum (*o*DFB) of crude **29b**.

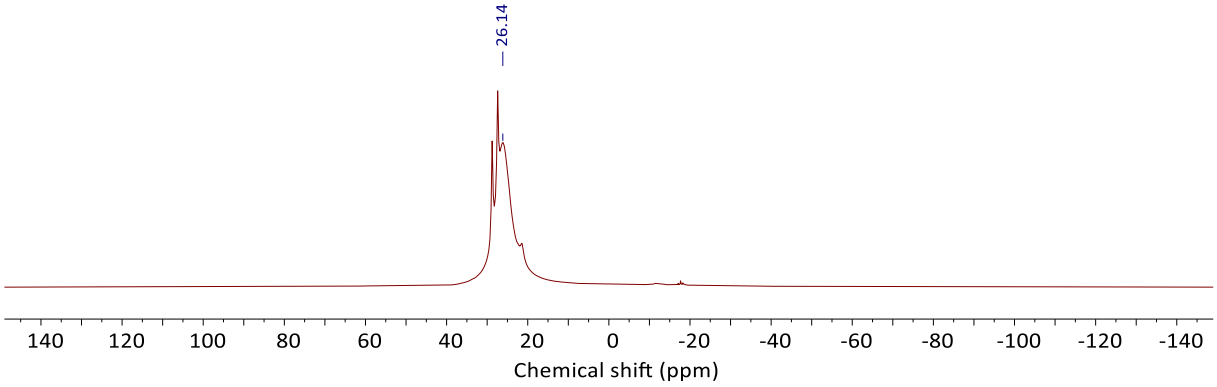
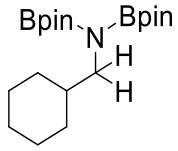


Figure S104. ^{11}B NMR spectrum (*o*DFB) of crude **29b**.

4.3.4. N-(cyclohexyl)ethyl-N,N-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 3.18 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H, C*H*$_2$NBpin), 1.24 (s, 24H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 26.0 (s) ppm.

Mass spectrometry after hydrolysis (APCI): $C_7H_{15}N$+H ($[M+H]^+$): calcd: 114.1283; found: 114.1279.

NMR Conv.: 43%

Note: Significant overlap is observed in the ^{1}H NMR spectrum with starting material, which prevented assignment of the Cy protons of the product.

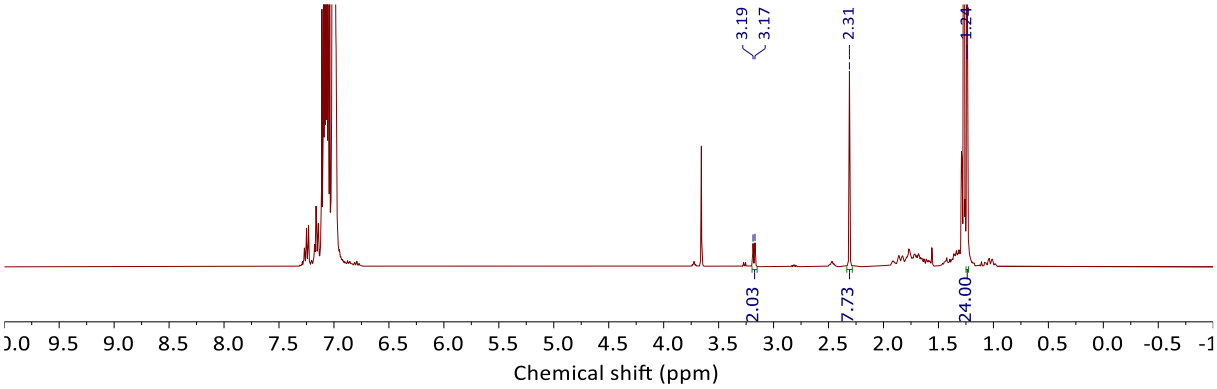


Figure S105. ^{1}H NMR spectrum (*o*DFB) of crude **30b**.

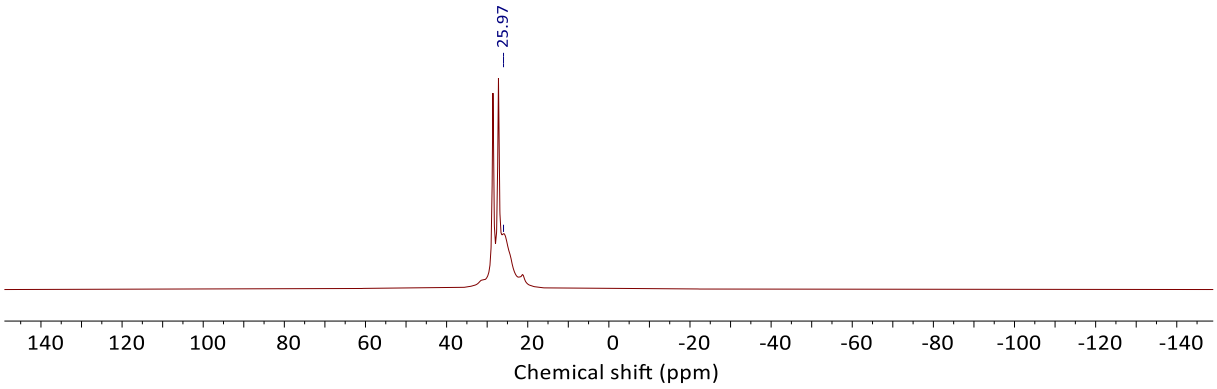
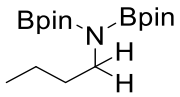


Figure S106. ^{11}B NMR spectrum (*o*DFB) of crude **30b**.

4.3.5. N-butyl-N,N-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 3.32 (t, $^{3}J_{HH}$ = 7.0 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.33 – 1.29 (m, 4H, NCH$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.23 (s, 24H, *NBpin*), 0.92 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 21.6 (s) ppm.

Mass spectrometry after hydrolysis (APCI): $C_4H_{11}N$+H ([M+H]$^{+}$): calcd: 74.0970; found: 74.0965.

NMR Conv.: 29%

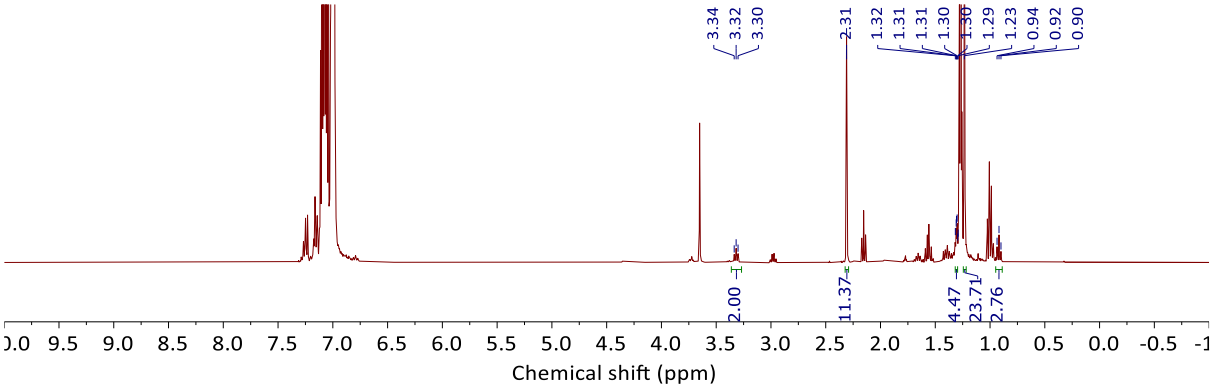


Figure S107. ^{1}H NMR spectrum (*o*DFB) of crude **31b**.

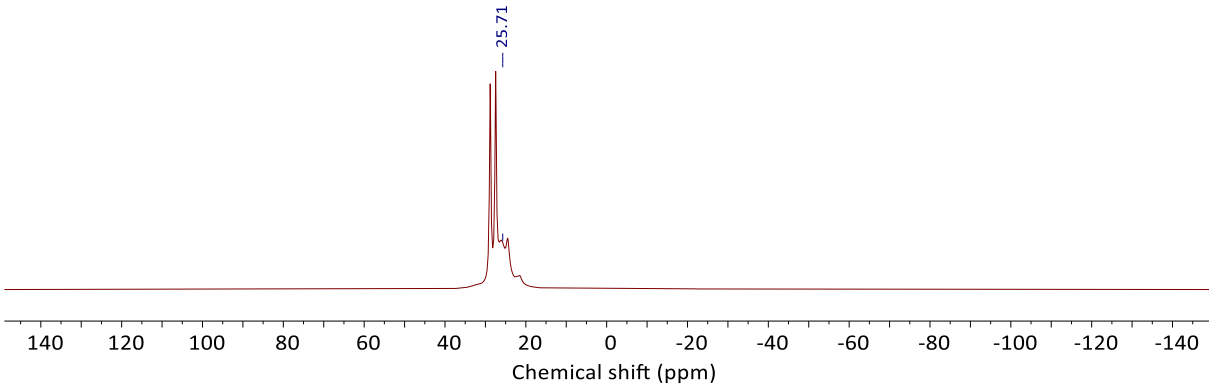
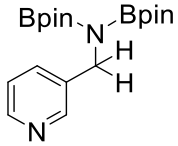


Figure S108. ^{11}B NMR spectrum (*o*DFB) of crude **31b**.

4.3.6. N-(3-pyridineethyl)-N,N-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-amine



^{1}H NMR (400 MHz, 298 K, Reaction mixture): δ = 8.65 (dd, $^{3}J_{HH}$ = 5.5, $^{4}J_{HH}$ = 1.7 Hz, 1H, *Ar*), 8.56 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H, *Ar*), 7.58 (dd, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.8 Hz, 1H, *Ar*), 7.39 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, *Ar*), 4.74 (s, 2H, CH_2NBpin), 1.20 (s, 24H, *NBpin*) ppm.

^{11}B NMR (128 MHz, 298 K, Reaction mixture): δ = 21.6 (s) ppm.

Mass spectrometry after hydrolysis (APCI): $C_6H_8N_2$+H ($[M+H]^+$): calcd: 109.0766; found: 109.0745.

NMR Conv.: 5%

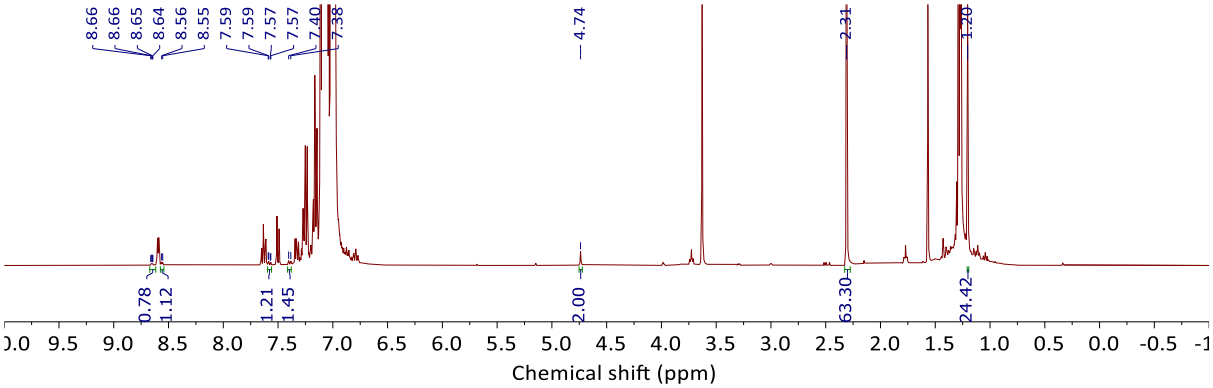


Figure S109. ^{1}H NMR spectrum (*o*DFB) of crude **32b**.

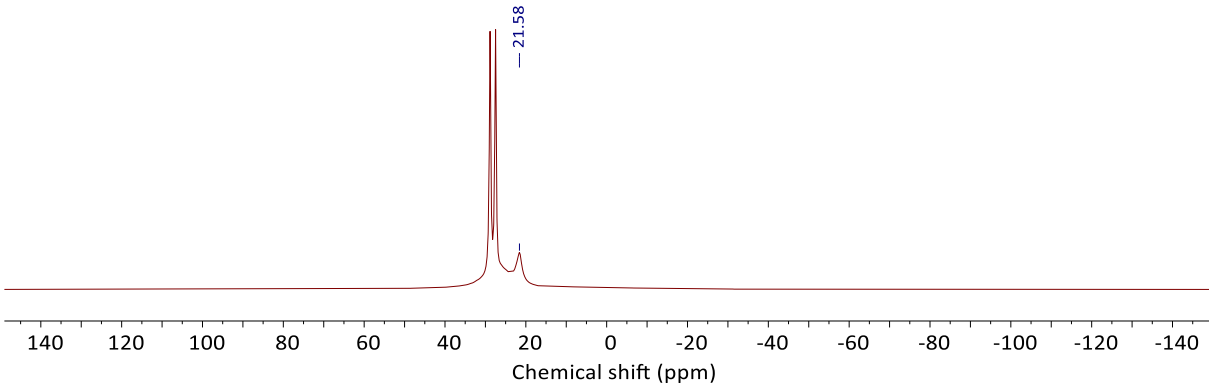
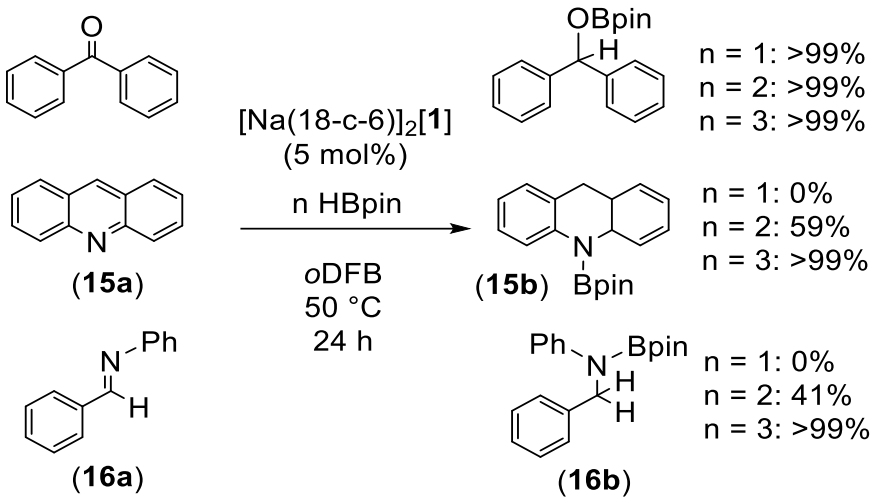


Figure S110. ^{11}B NMR spectrum (*o*DFB) of crude **32b**.

5. Selectivity, recycling and scale-up experiments

5.1. Competition experiments



In three different NMR tubes, to a solution of $[Na(18\text{-c-}6)]_2$[**1**] (5 mg, 5.5 µmol, 0.05 eq.) in *o*DFB (0.5 mL), acridine (20 mg, 0.11 mmol, 1 eq.), *N*-benzylideneaniline (20 mg, 0.11 mmol, 1 eq.), benzophenone (20 mg, 0.11 mmol, 1 eq.), and toluene (25 µL, 0.24 mmol) was added. One NMR tube was charged with pinacolborane (HBpin; 14 mg, 16 µL, 0.11 mmol, 1 eq.), another NMR tube was charged with pinacolborane (HBpin; 28 mg, 32 µL, 0.22 mmol, 2 eq.), and the last NMR tube was charged with pinacolborane (HBpin; 42 mg, 48 µL, 0.33 mmol, 3 eq.). All reactions were allowed to react at 50 °C for 24 h. The reactions were monitored by ^{1}H NMR (referenced to toluene). Crude NMR conv. was determined by integration using toluene (^{1}H δ = 2.31 ppm) as an internal standard. Hydroborated benzophenone product (^{1}H δ = 6.41 ppm), **15b** (^{1}H δ = 4.84 ppm), and **16b** (^{1}H δ = 3.71 ppm).

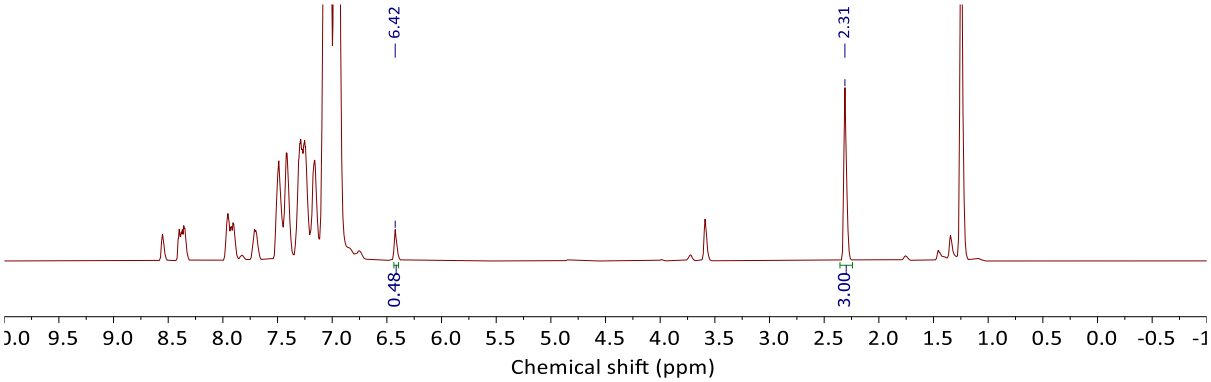


Figure S111. ^{1}H NMR spectrum (*o*DFB) of crude competition reaction between benzophenone, **15a**, and **16a** using 1 eq. of HBpin.

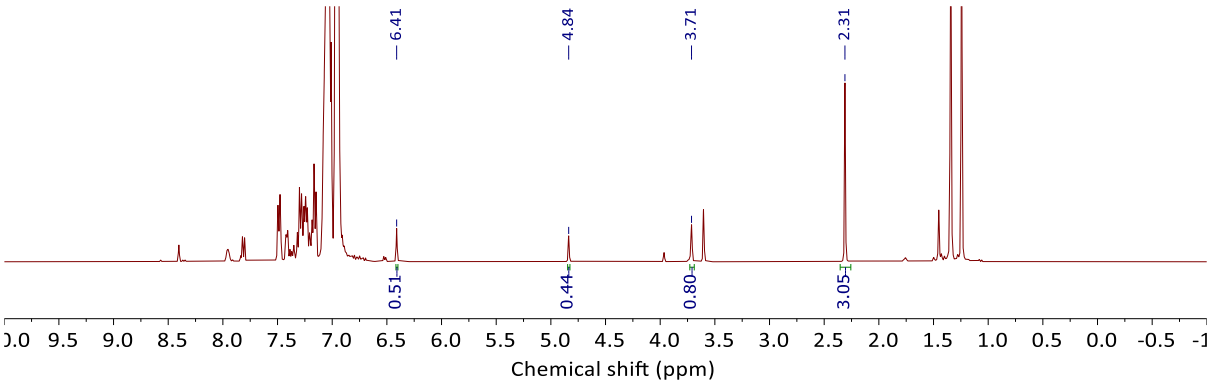


Figure S112. ^{1}H NMR spectrum (*o*DFB) of crude competition reaction between benzophenone, **15a**, and **16a** using 2 eq. of HBpin.

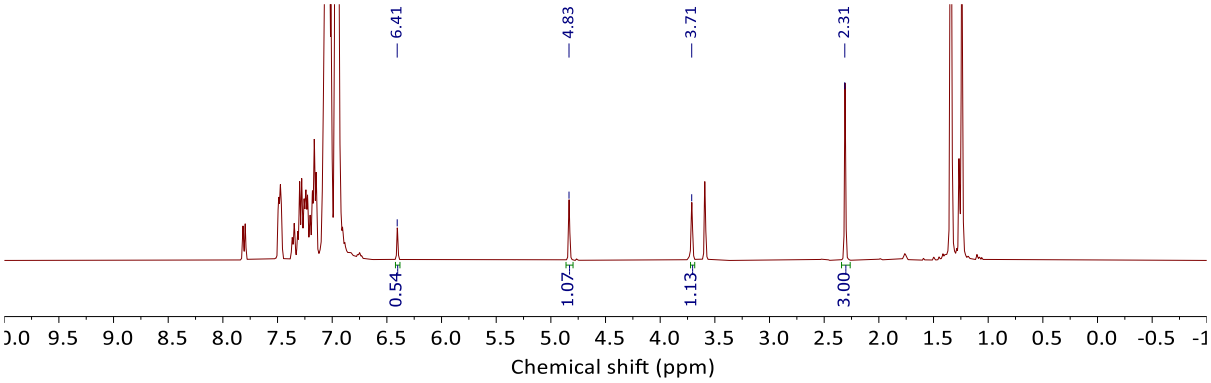
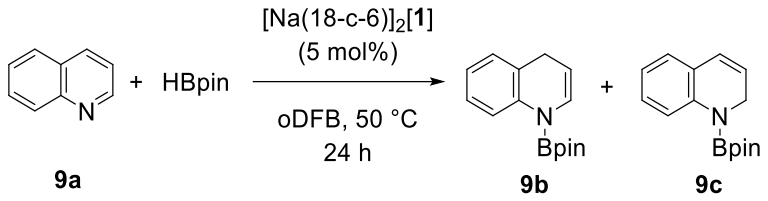


Figure S113. ^{1}H NMR spectrum (*o*DFB) of crude competition reaction between benzophenone, **15a**, and **16a** using 3 eq. of HBpin.

5.2. Recycling hydroboration of quinoline



To a solution of $[Na(18\text{-c-}6)]_2$[**1**] (10 mg, 11 µmol) and HBpin (28 mg, 32 µL, 0.22 mmol) in *o*DFB (0.5 mL), quinoline (0.22 mmol) and toluene (25 µL, 0.24 mmol) were added and allowed to react at 50 °C for 18 h. The reaction monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using toluene (^{1}H δ = 2.31 ppm) as an internal standard. The tube was reloaded with HBpin (28 mg, 32 µL, 0.22 mmol) and quinoline (0.22 mmol). This process was performed a total of 9 times. No loss of catalyst performance was observed. Overall the turnover number is 200. The selectivity of the reaction slowly increased from a ratio **9b**:**9c** of 92:8 after the first 5 cycles to 95:5 after the 10th cycle.

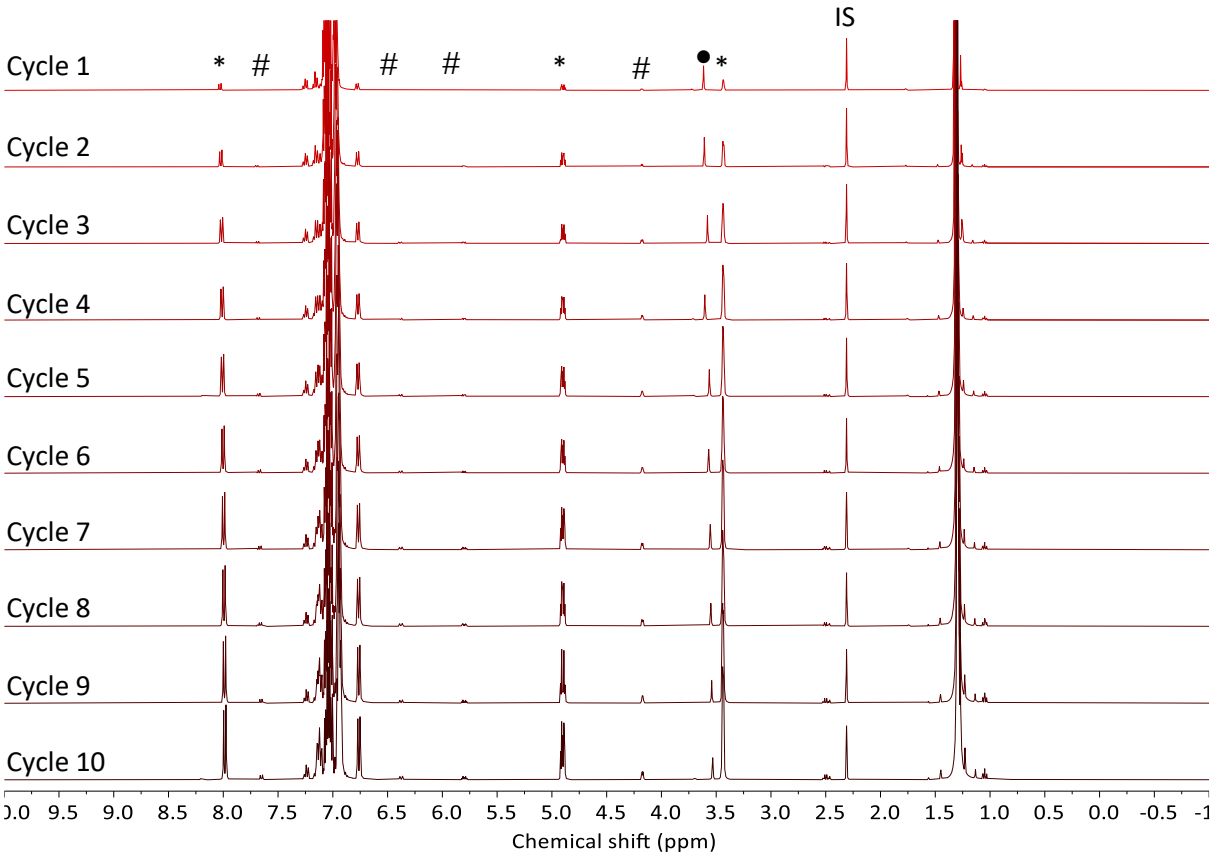


Figure S114. Stacked ^{1}H NMR spectra (*o*DFB) of catalyst recycling in the hydroboration of quinoline. Toluene internal standard is marked by IS, **9b** marked by *, and **9c** marked by #. [**1**]$^{2-}$ marked by ●. Resonances associated with the BBN moiety on [**1**]$^{2-}$ could not be observed due to overlap with the Bpin resonances of **9b** and **9c**.

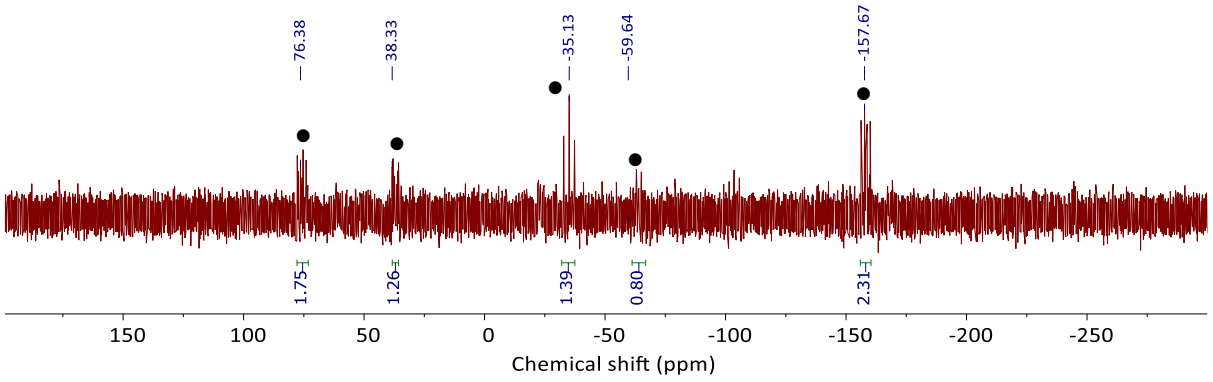
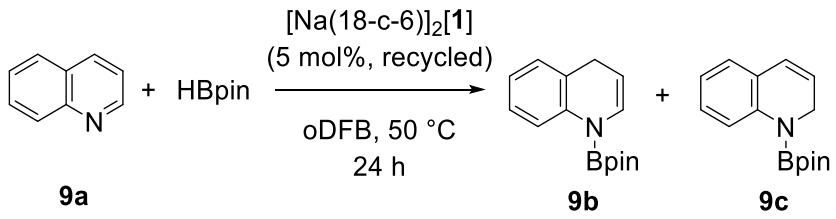


Figure S115. ^{31}P NMR spectrum (*o*DFB) of after recycling cycles in the hydroboration of quinoline. [**1**]$^{2-}$ marked by ●.

5.3. Recovery of catalysts and reuse in the hydroboration of quinoline



After the 10th cycle in the recycling in the hydroboration of quinoline (**9a**) (section 5.1. above), the catalyst was isolated from the reaction mixture by removal of volatiles, and washing with pentane. The catalysts was dried and then dissolved in *o*DFB (0.5 mL). To this solution HBpin (28 mg, 32 µL, 0.22 mmol), quinoline (0.22 mmol) and toluene (25 µL, 0.24 mmol) were added and allowed to react at 50 °C for 48 h. The reaction monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using toluene (1H δ = 2.31 ppm) as internal standard and found to be 95%.

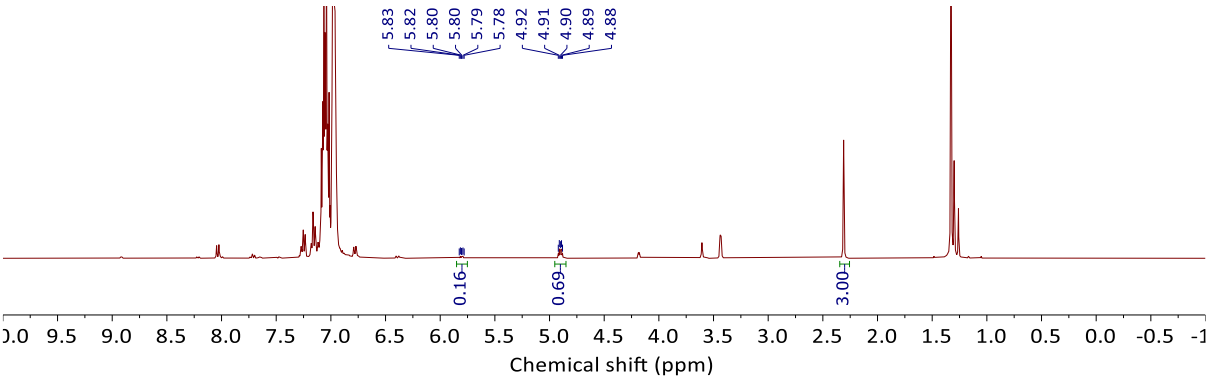


Figure S116. ^{1}H NMR spectrum (*o*DFB) of using recovered catalysts in the hydroboration of **9a**.

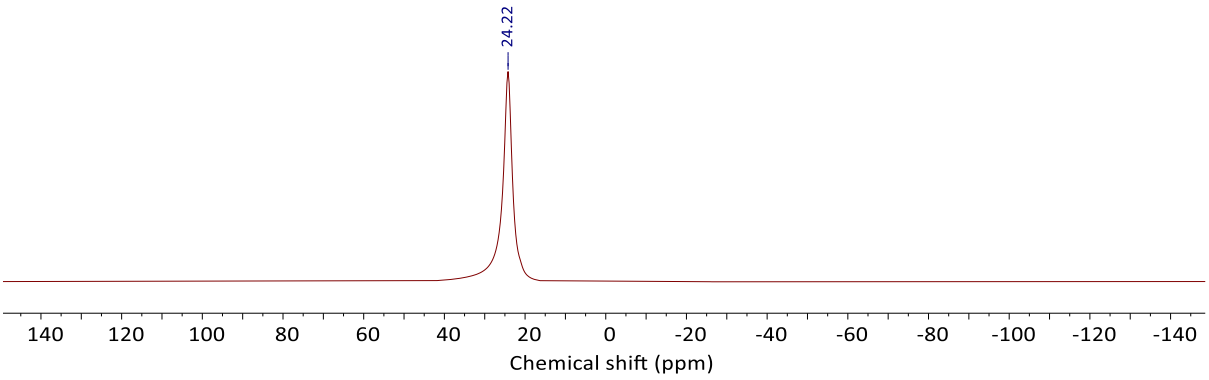
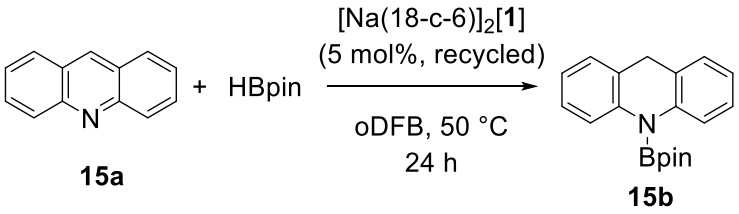


Figure S117. ^{11}B NMR spectrum (*o*DFB) of using recovered catalysts in the hydroboration of **9a**.

5.4. Recovery of catalysts and reuse mixed hydroboration



First the hydroboration of benzaldehyde was performed as described previously using benzaldehyde (0.22 mmol), HBpin (0.22 mmol) and [Na(18c6)][**1**] (2.2 µmol).[3] NMR spectra identical to that reported, with a conversion of 99% as determined by ^{1}H NMR spectroscopy. The catalyst was isolated from the reaction mixture by removal of volatiles, and washing with pentane. The catalysts was dried and then dissolved in *o*DFB (0.5 mL). To this solution HBpin (5.6 mg, 6.4 µL, 0.044 mmol), acridine (7.9 mg, 0.044 mmol) and toluene (25 µL, 0.24 mmol) were added and allowed to react at 50 °C for 24 h. The reaction monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using toluene (1H δ = 2.31 ppm) as internal standard and found to be 86%.

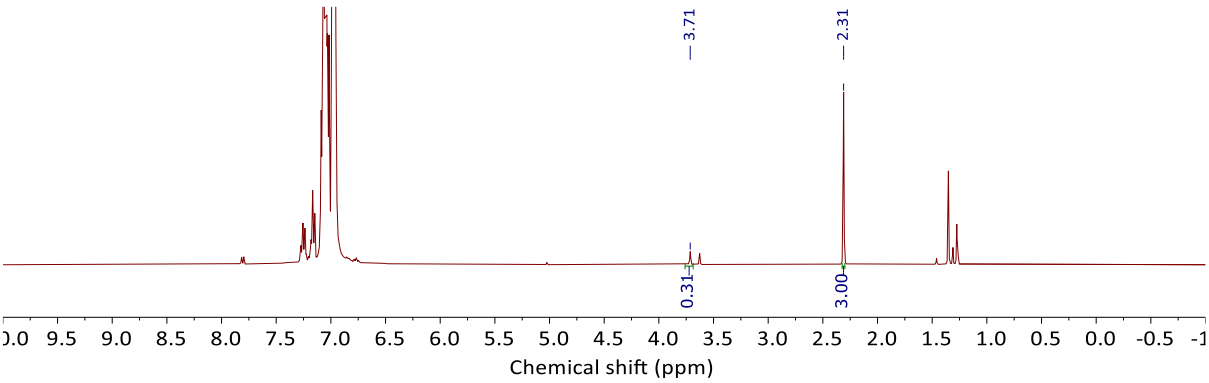
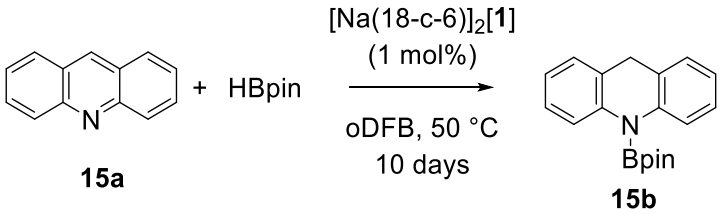


Figure S118. ^{1}H NMR spectrum (*o*DFB) of using recovered catalysts in the hydroboration of **15a**.

Further NMR data was identical to that presented in section 2.6.14.

5.5. Scale-up hydroboration of acridine



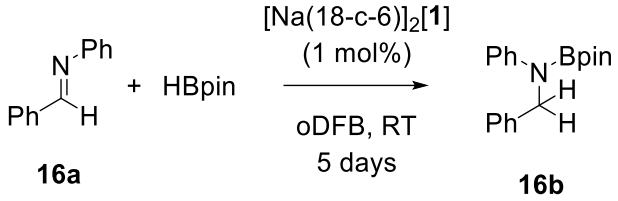
15a **15b**

To a solution of [Na(18-c-6)]$_2$[**1**] (50 mg, 0.056 mmol) and HBpin (714 mg, 5.58 mmol) in *o*DFB (5 mL), acridine (1002 mg, 5.58 mmol) was added and allowed to react at 50 °C for 10 days. The volatiles were removed in vacuo and the remaining solid was extracted with hexane (3x50 mL). Removal of volatiles from the hexane extract yielded **15b** as a white powder.

Yield: 1452 mg, 85%.

NMR data was identical to that presented in section 2.6.14.

5.6. Scale-up hydroboration of *N*-Benzylideneaniline



16a **16b**

To a solution of [Na(18-c-6)]$_2$[**1**] (50 mg, 0.056 mmol) and HBpin (714 mg, 5.58 mmol) in *o*DFB (5 mL), N-Benzylideneaniline (1011 mg, 5.58 mmol) was added and allowed to react at RT for 5 days. The volatiles were removed in vacuo and the remaining solid was extracted with hexane (1x50 mL). Removal of volatiles from the hexane extract yielded **16b** as a white powder.

Yield: 1675 mg, 97%.

NMR data was identical to that presented in section 3.3.1.

6. Control hidden catalysis

Thomas *et al.* have previously reported that BH_3 can play in hydroboration catalysis as hidden catalysis, when HBpin is used as the hydroborating agent in the presence of a Lewis acid catalyst.[14] The pinacol borane was investigated by NMR spectroscopy for contaminants, none were found.

6.1. TMEDA addition controls

First, N-benzylideneaniline (**16a**), benzonitrile (**27a**) and pyridine (**2a**) were converted using catalysts $[Na(18\text{-}c\text{-}6)]_2$[**1**] as descibed above (**16a**: 2.5 mol%, RT, 1 eq. HBpin, 48h; **27a**: 5 mol%, 50 °C, 2 eq. HBpin, 48h; **2a**: 5 mol%, 50 °C, 1 eq. HBpin, 48h). The reaction mixture was investigated by ^{11}B NMR spectroscopy. Next, an excess (>2 eq. compared to HBpin) of tetramethylethylenediamine (TMEDA) was added to the reaction mixture and investigated by ^{11}B NMR spectroscopy. No evidence of BH_3 was detected during the catalysis. When TMEDA was present during the reaction (Figure S120), the catalysis was not inhibited and no BH_3 could be observed.

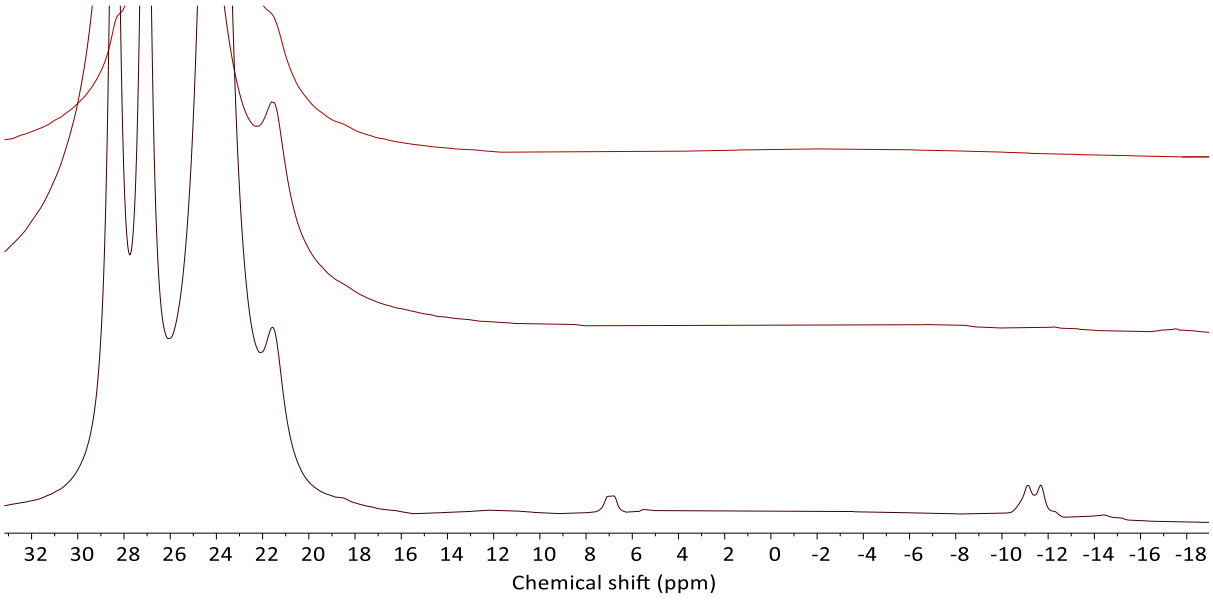


Figure S119. ^{11}B NMR spectrum (reaction mixture) of addition of TMEDA to the

hydroboration after the reaction of: top: N-benzylideneaniline; middle: benzonitrile; bottom: pyridine. Resonances observed at 7 and –11 ppm are believed to be TMEDA and/or pyridine adducts of HBpin or species involved in the catalysis.

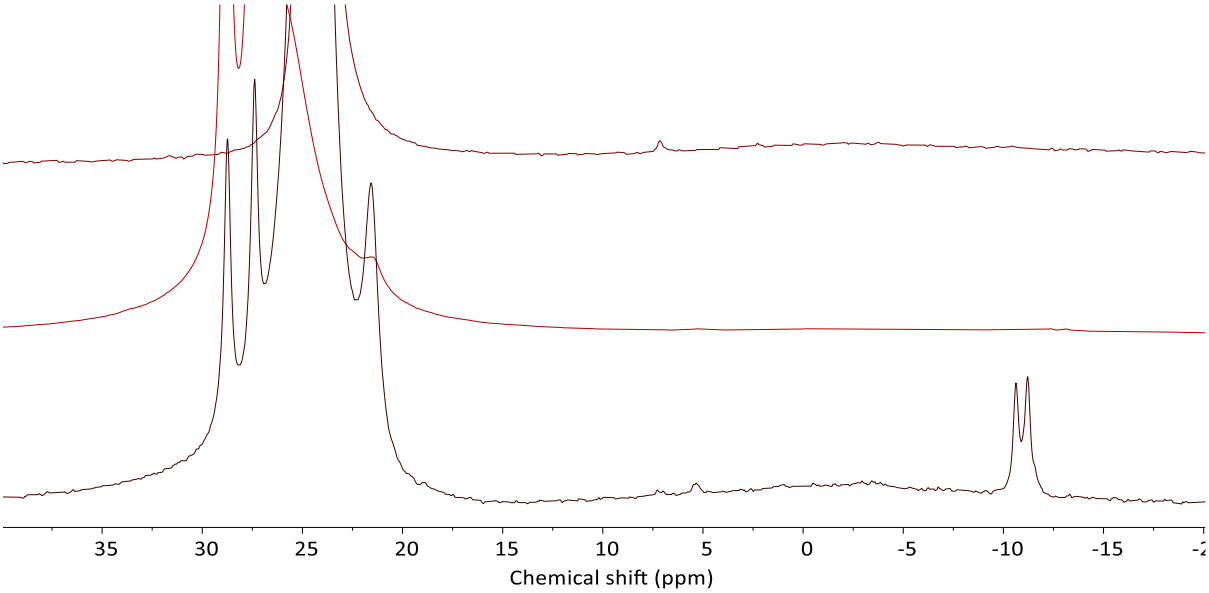


Figure S120. ^{11}B NMR spectrum (reaction mixture) of addition of TMEDA to the hydroboration during the reaction of: top: N-benzylideneaniline; middle: benzonitrile; bottom: pyridine. Resonances observed at 7 and –11 ppm are believed to be TMEDA and/or pyridine adducts of HBpin or species involved in the catalysis.

Next, we reacted [Na(18-c-6)]$_2$[**1**] with HBpin while mimicking our harshest conditions (50 °C, 48h). The reaction mixture was investigated by NMR spectroscopy. Next, an excess of TMEDA was added to the reaction mixture and investigated by NMR spectroscopy. No evidence of BH_3 was detected.

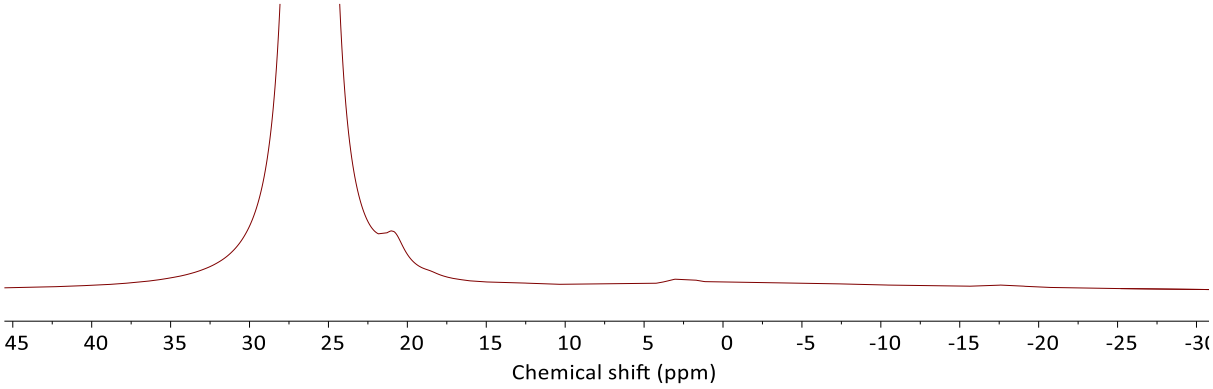
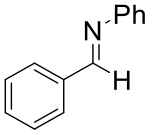
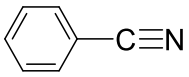


Figure S121. ^{11}B NMR spectrum (reaction mixture) of addition of TMEDA to [Na(18-c-6)]$_2$[**1**] after 50 °C, 48h.

6.2. Catalysis controls using BH_3•SMe_2

To a solution of BH_3•SMe_2 (0.84 mg, 1.0 µL, 11 µmol) and HBpin in *o*DFB (0.5 mL) substrate (0.219 mmol) and toluene (0.235 mmol) was added and allowed to react at the specified temperature for 48 h. The reaction monitored by ^{1}H NMR (referenced to toluene), ^{11}B NMR and ^{11}B{^{1}H} NMR. Crude NMR conv. was determined by integration using the resonances of the toluene (^{1}H δ = 2.31 ppm) as an internal standard. These studies confirm that BH_3 is a worse catalyst for these transformations when compared to [Na(18-c-6)]$_2$[**1**].

Table S2. Catalysis controls using BH_3•SMe_2

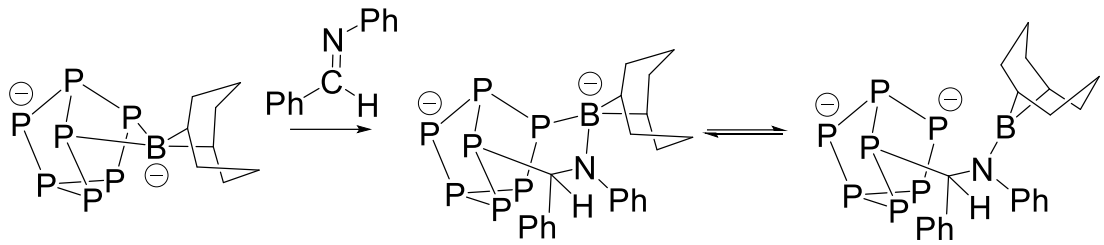
Entry	Substrate	Temp. (°C)	Eq. HBpin	BH_3•SMe_2 Catalyst Loading (mol%)	Solvent	Conv.[a]
1		RT	1	5	*o*DFB	12
2		50	2	5	*o*DFB	54
3		50	1	5	*o*DFB	0

[a] Determined by ^{1}H NMR spectroscopy, based on C–H bond formation.

7. Experimental Mechanistic Investigations

Addition of pyridine to [Na(18-c-6)]$_2$[**1**] does not result in any observed reactivity by NMR spectroscopy. Furthermore, we have previously reported the NMR spectroscopic data of [Na(18-c-6)]$_2$[**1**] in pyrdine-d$_5$/THF-d$_8$ which is identical to NMR spectroscopic data recorded in *o*DFB.[3]

7.1. Addition N-benzylideneaniline to [Na(18-c-6)]$_2$[1].



To a J Young NMR tube a solution of [Na(18-c-6)]$_2$[**1**] (25 mg, 0.027 mmol, 1 eq.) in *o*DFB and N-benzylideneaniline (3.2 mg, 0.027 mmol, 1 eq.) were added. The reaction was monitored by ^{11}B, ^{11}B{^{1}H} and ^{31}P NMR.

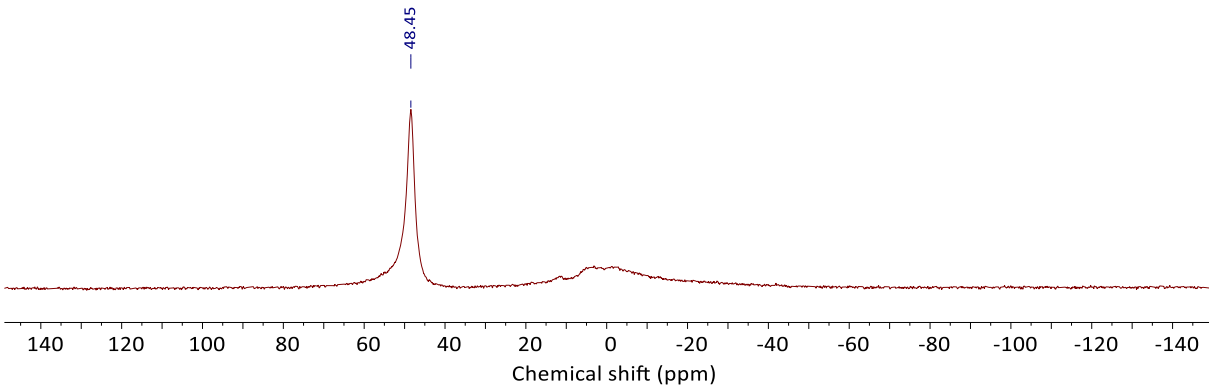


Figure S122. ^{11}B NMR spectrum (reaction mixture) of Addition N-benzylideneaniline to [Na(18-c-6)]$_2$[**1**].

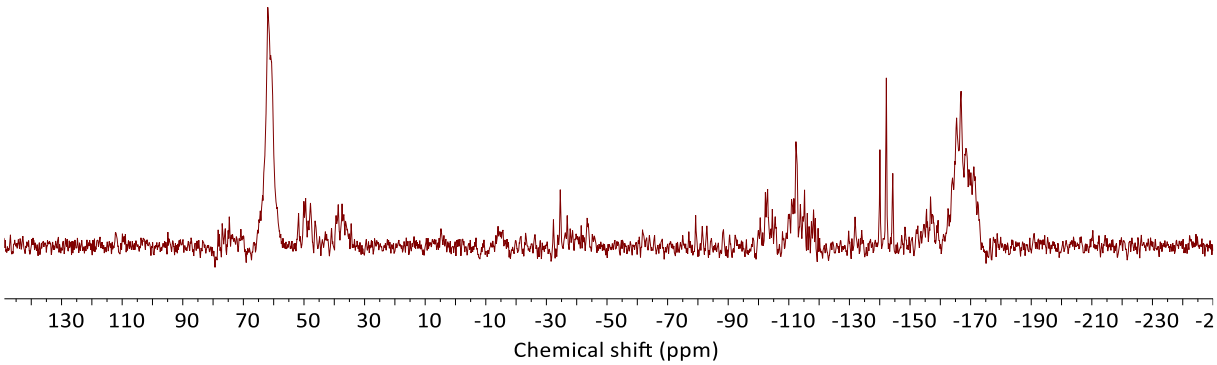
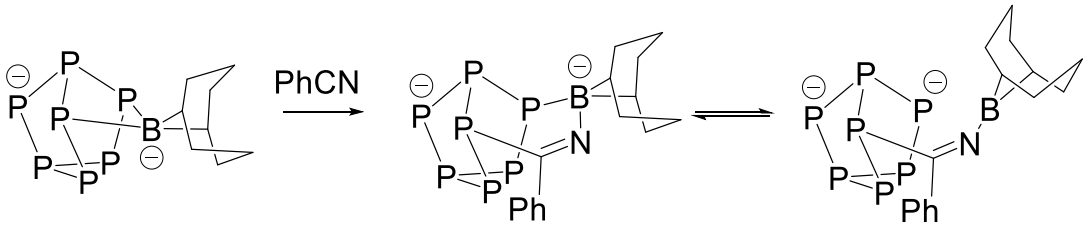


Figure S123. ^{31}P NMR spectrum (reaction mixture) of Addition N-benzylideneaniline to [Na(18-c-6)]$_2$[**1**].

7.2. Addition benzonitrile to [Na(18-c-6)]$_2$[1].



To a J Young NMR tube a solution of [Na(18-c-6)]$_2$[**1**] (25 mg, 0.027 mmol, 1 eq.) in *o*DFB and benzonitrile (3.2 mg, 0.027 mmol, 1 eq.) were added. The reaction was monitored by ^{11}B, ^{11}B{^{1}H} and ^{31}P NMR.

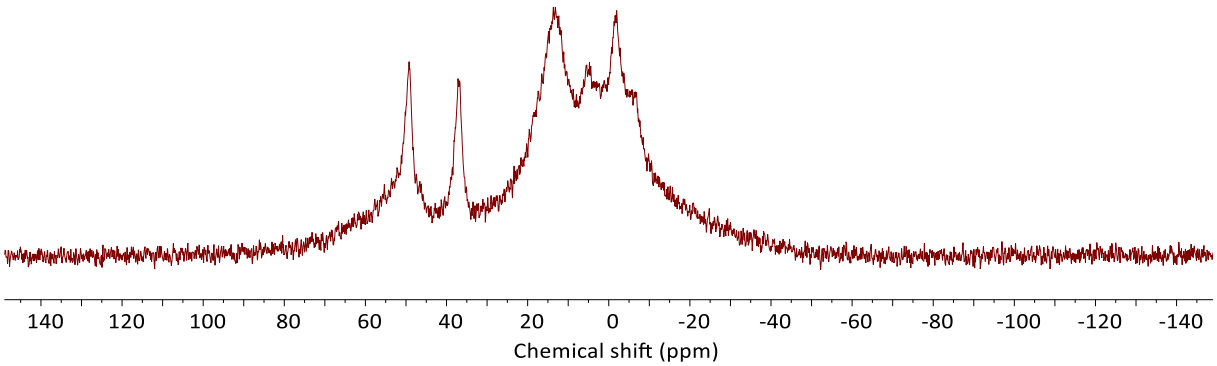


Figure S124. ^{11}B NMR spectrum (reaction mixture) of addition benzonitrile to [Na(18-c-6)]$_2$[**1**].

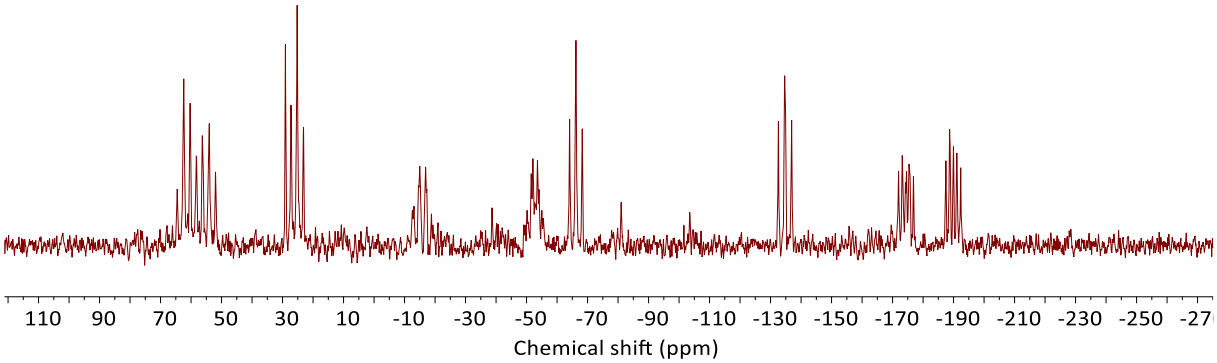
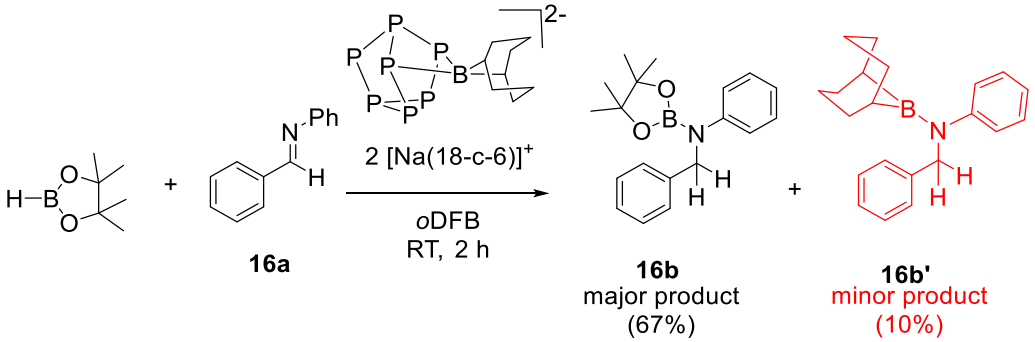


Figure S125. ^{31}P NMR spectrum (reaction mixture) of addition benzonitrile to [Na(18-c-6)]$_2$[**1**].

7.3. Stoichiometric hydroboration of N-benzylideneaniline



To a J Young NMR tube a solution of [Na(18-c-6)]$_2$[1] (25 mg, 0.027 mmol, 1.0 eq.) in oDFB, HBpin (4.0 µL, 0.027 mmol, 1.0 eq.), N-benzylideneaniline (4.9 mg, 0.027 mmol, 1.0 eq.), and toluene (25 µL, 0.24 mmol) was added. The reaction was monitored by 1H, ^{11}B, ^{11}B{^{1}H} and ^{31}P NMR. Using the toluene as an internal standard, the reaction gave an overall conversion of 77% conversion. Product conv. distribution was 67%:10% **16b**:**16b'**. The ^{31}P NMR spectrum recorded after the reaction shows compound [**1**]$^{2-}$ and potentially N-benzylideneaniline inserted product and [(Bpin)P$_7$]$^{2-}$

.

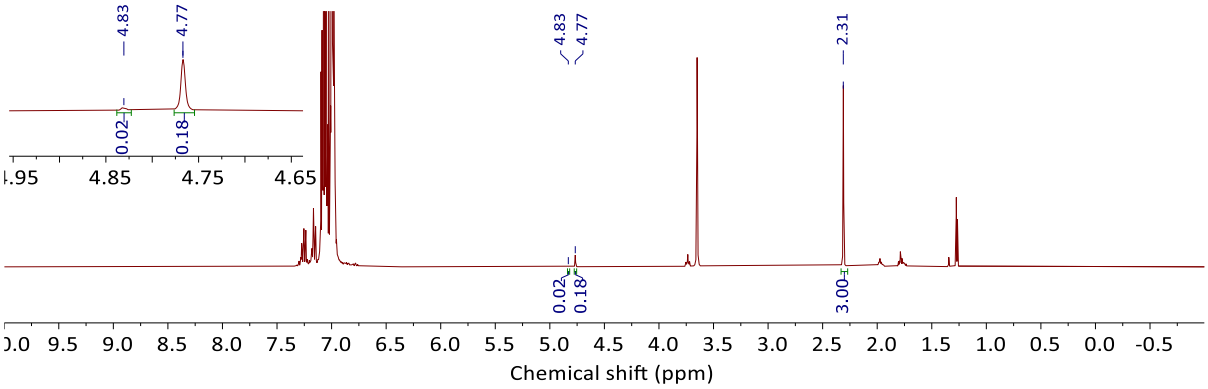


Figure S126. ^{1}H NMR spectrum (reaction mixture) of the stoichiometric hydroboration of N-benzylideneaniline using [Na(18-c-6)]$_2$[**1**].

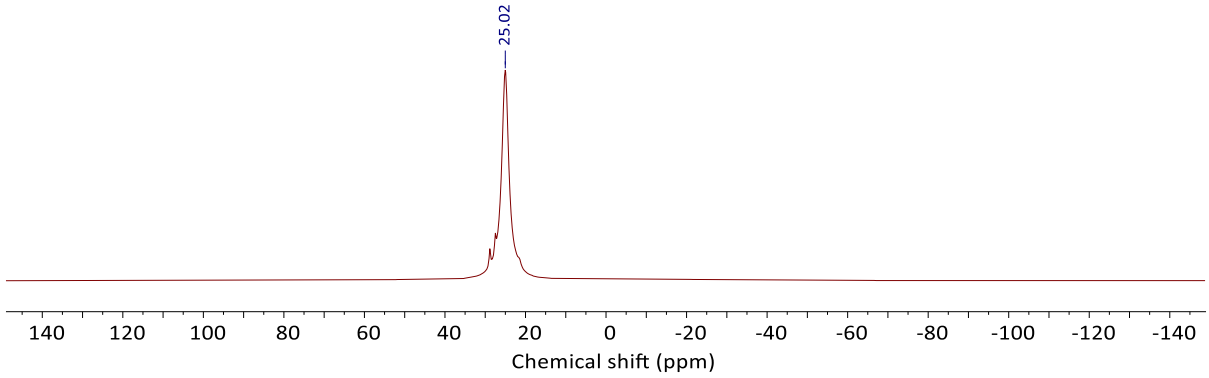


Figure S127. ^{11}B NMR spectrum (reaction mixture) of the stoichiometric hydroboration of N-benzylideneaniline using [Na(18-c-6)]$_2$[**1**].

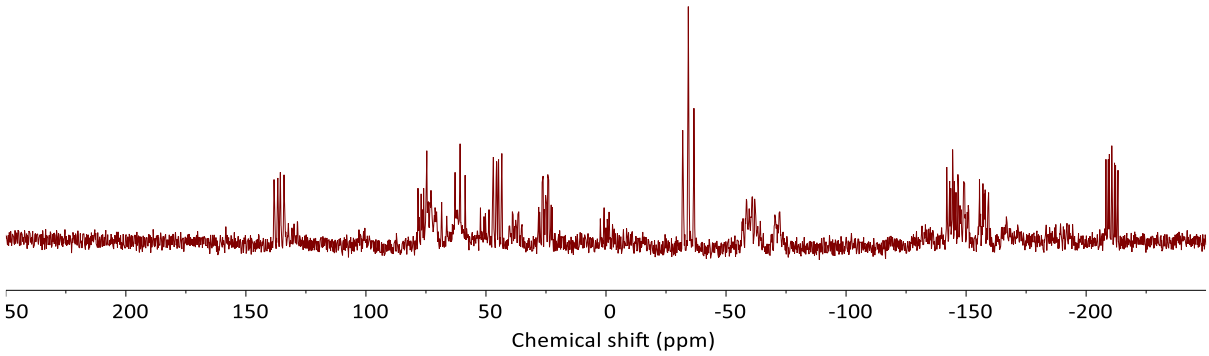
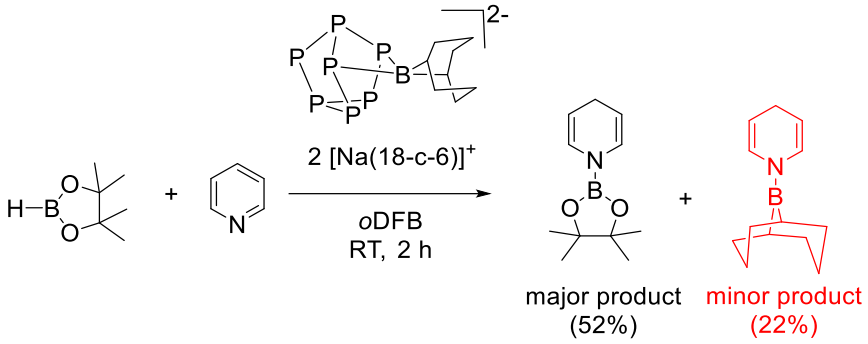


Figure S128. ^{31}P NMR spectrum (reaction mixture) of the stoichiometric hydroboration of N-benzylideneaniline using [Na(18-c-6)]$_2$[**1**].

7.4. Stoichiometric hydroboration of Pyridine



To a J Young NMR tube a solution of $[Na(18\text{-c-}6)]_2$[**1**] (25 mg, 0.027 mmol, 1.0 eq.) in *o*DFB, HBpin (4.0 µL, 0.027 mmol, 1.0 eq.), pyridine (2.2 mg, 0.027 mmol, 1.0 eq.), and toluene (25 µL, 0.24 mmol) was added. The reaction was monitored by ^{1}H (referenced to toluene), ^{11}B, ^{11}B{^{1}H} and ^{31}P NMR. Using the toluene as an internal standard, the reaction gave an overall conversion of 74% conversion. Product conv. distribution was 52%:22% **2b**:**2b'**. The ^{31}P NMR spectrum recorded after the reaction shows compound [**1**]$^{2-}$.

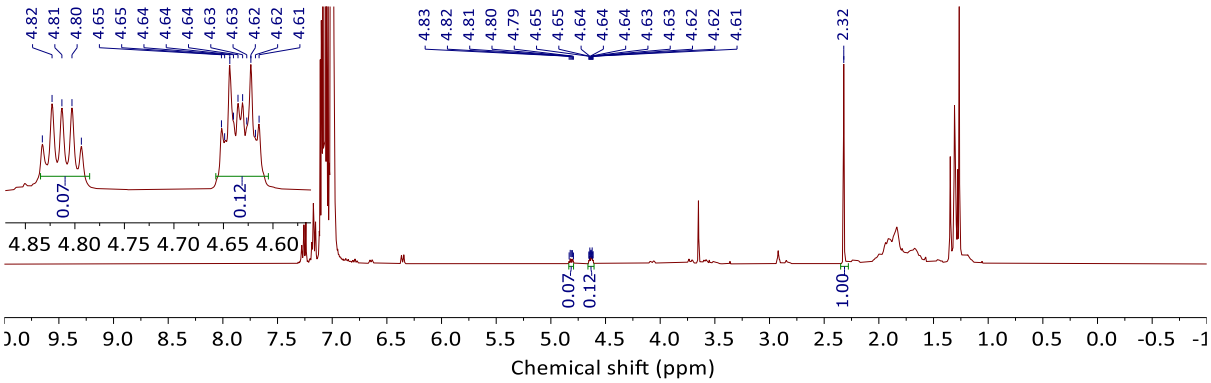


Figure S129. ^{1}H NMR spectrum (reaction mixture) of the stoichiometric hydroboration of pyridine using $[Na(18\text{-c-}6)]_2$[**1**].

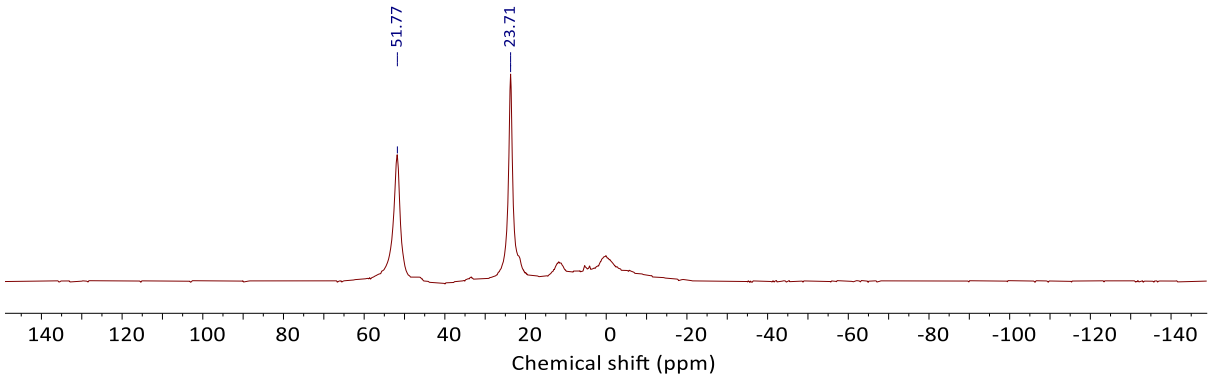


Figure S130. ^{11}B NMR spectrum (reaction mixture) of the stoichiometric hydroboration of pyridine using [Na(18-c-6)]$_2$[**1**].

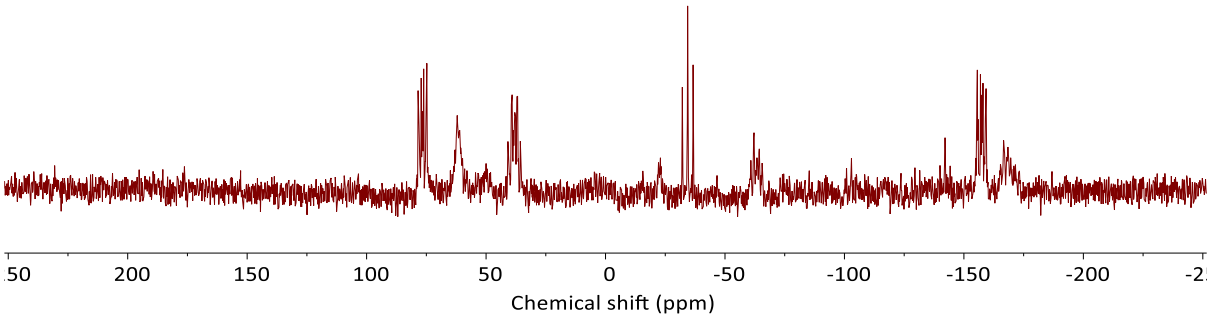
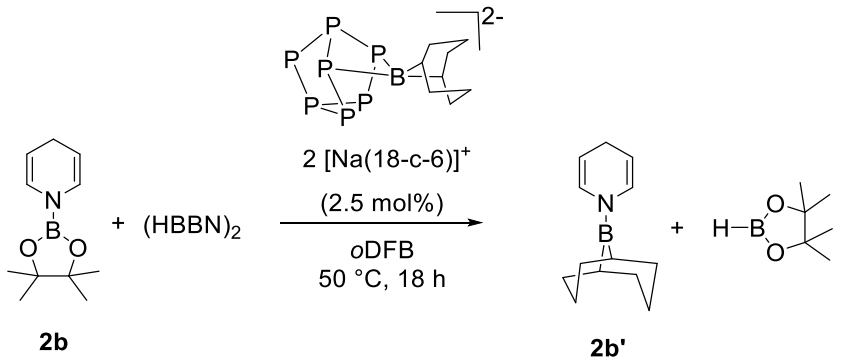


Figure S131. ^{31}P NMR spectrum (reaction mixture) of the stoichiometric hydroboration of pyridine using [Na(18-c-6)]$_2$[**1**].

7.5. Scrambling boron-substituents



To a J Young NMR tube a solution of $[Na(18\text{-}c\text{-}6)]_2$[**1**] (5 mg, 5.5 µmol, 0.025 eq.) in *o*DFB, HBpin (32 µL, 0.22 mmol, 1.0 eq.), pyridine (17.7 µL, 0.22 mmol, 1.0 eq.), and toluene (25 µL, 0.24 mmol) was added and allowed to react overnight at 50 °C. ^{11}B NMR spectroscopy confirmed full consumption of the HBpin. To the reaction was added $(HBBN)_2$ (26.8 mg, 0.11 mmol, 1 eq. H–B) and the reaction was allowed to react overnight at 50 °C.

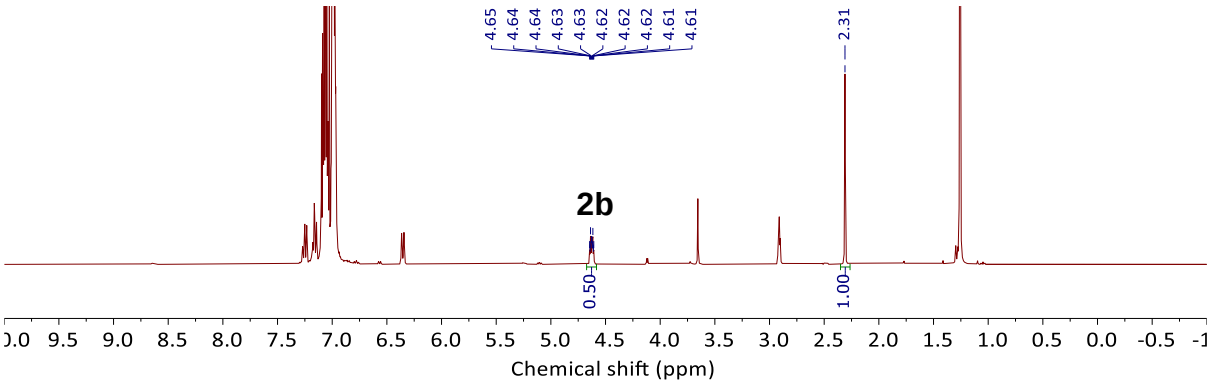


Figure S132. ^{1}H NMR spectrum (reaction mixture) of the boron scrambling before adding $(HBBN)_2$.

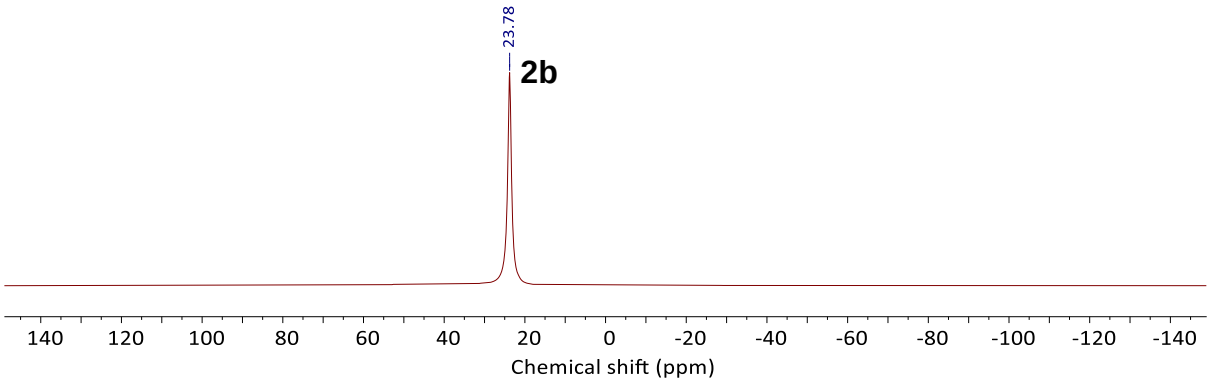


Figure S133. ^{11}B NMR spectrum (reaction mixture) of the boron scrambling before adding $(HBBN)_2$.

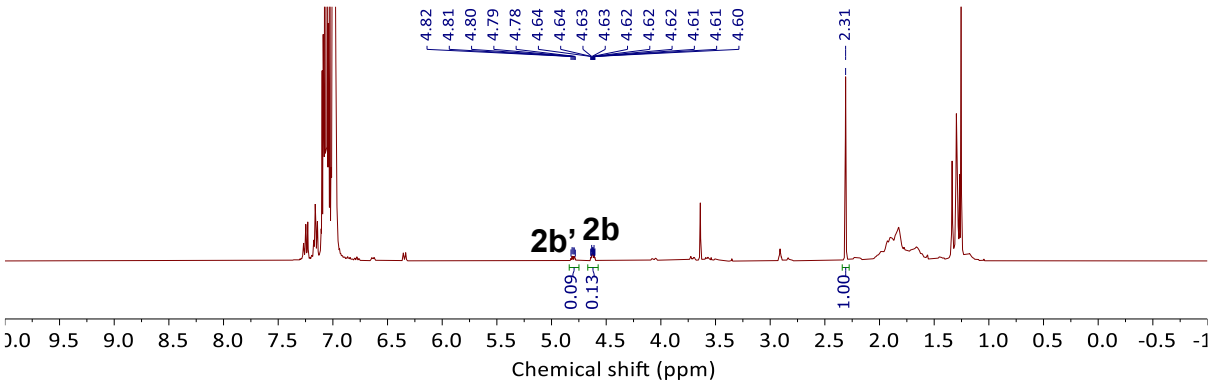


Figure S134. ^{1}H NMR spectrum (reaction mixture) of the boron scrambling after adding $(HBBN)_2$.

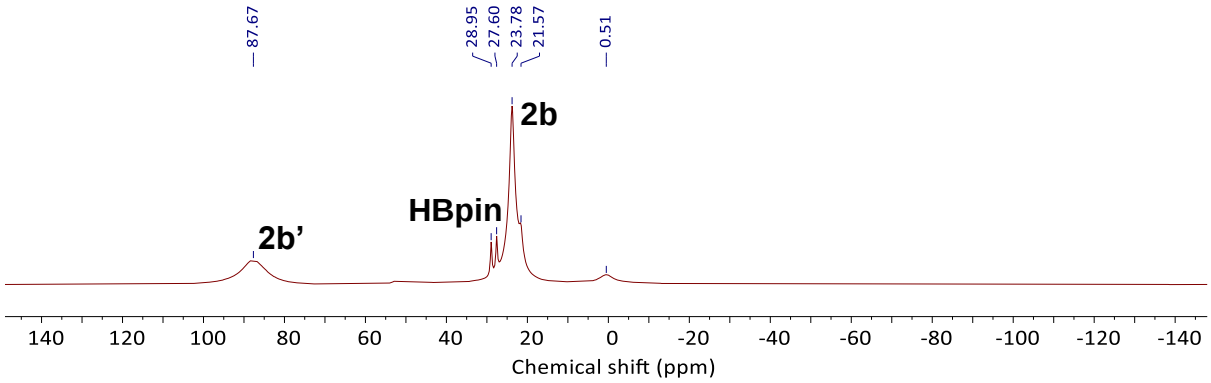
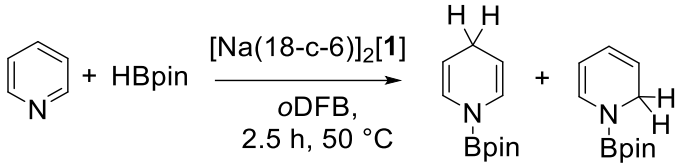


Figure S135. ^{11}B NMR spectrum (reaction mixture) of the boron scrambling after adding $(HBBN)_2$.

7.6. Variable Time Normalisation Analysis (VTNA)



Variable time normalization analysis was applied to better understand the order of the hydroboration reaction of pyridine. Reaction profiles were tracked by performing the reaction in a NMR spectrometer. Samples were loaded into the NMR spectrometer within 2-2.5 min. Concentrations of the product (^{1}H δ = 2.91 ppm), HBpin (^{1}H δ = 1.28 ppm), and pyridine (^{1}H δ = 8.62 ppm) were calculated by integration of the ^{1}H NMR spectrum using toluene as an internal standard (^{1}H δ = 2.31 ppm). Following the variable time normalization analysis as described by Burés,[15, 16] the reaction order can be obtained via a graphical representation using the expression shown below, Formula 1. The analysis supports a fitting of a zero order in the concentration of pyridine and a first order in the concentration of HBpin and catalyst, represented in Formula 2.

Formula 1. $[P] = k \int [Pyridine]^{\alpha} \times [HBpin]^{\beta} \times [Catalyst]^{\gamma}$

Formula 2. $[P] = k \int [Pyridine]^{0} \times [HBpin]^{1} \times [Catalyst]^{1}$

Table S3. VTNA analysis reactions.

Exp	Added pyridine (mmol) (A)	Added HBpin (mmol) (B)	Added Catalyst (mmol) (Cat)	Total Volume (µL)
1 (▲)	0.11	0.11	0.0055	600
2 (●)	0.055	0.11	0.0055	596
3 (■)	0.11	0.055	0.0055	592
4 (◆)	0.11	0.11	0.0077	625
5 (⬢)	0.11	0.11	0.0033	575

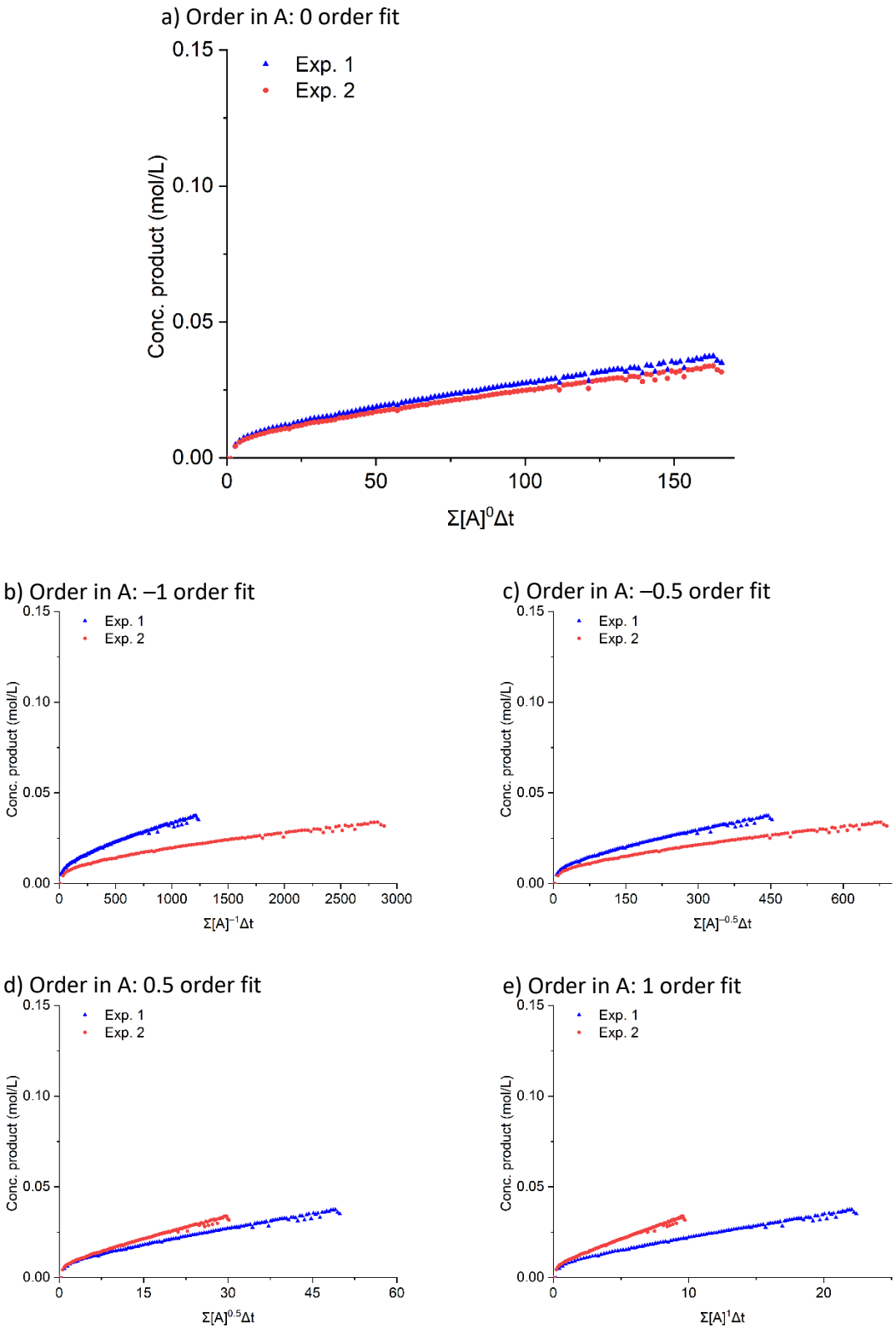


Figure S136. VTNA hydroboration pyridine using HBpin a reducing agent and [Na(18-c-6)]$_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration pyridine ([A]) using the concentration of the product, obtained from the analysis.

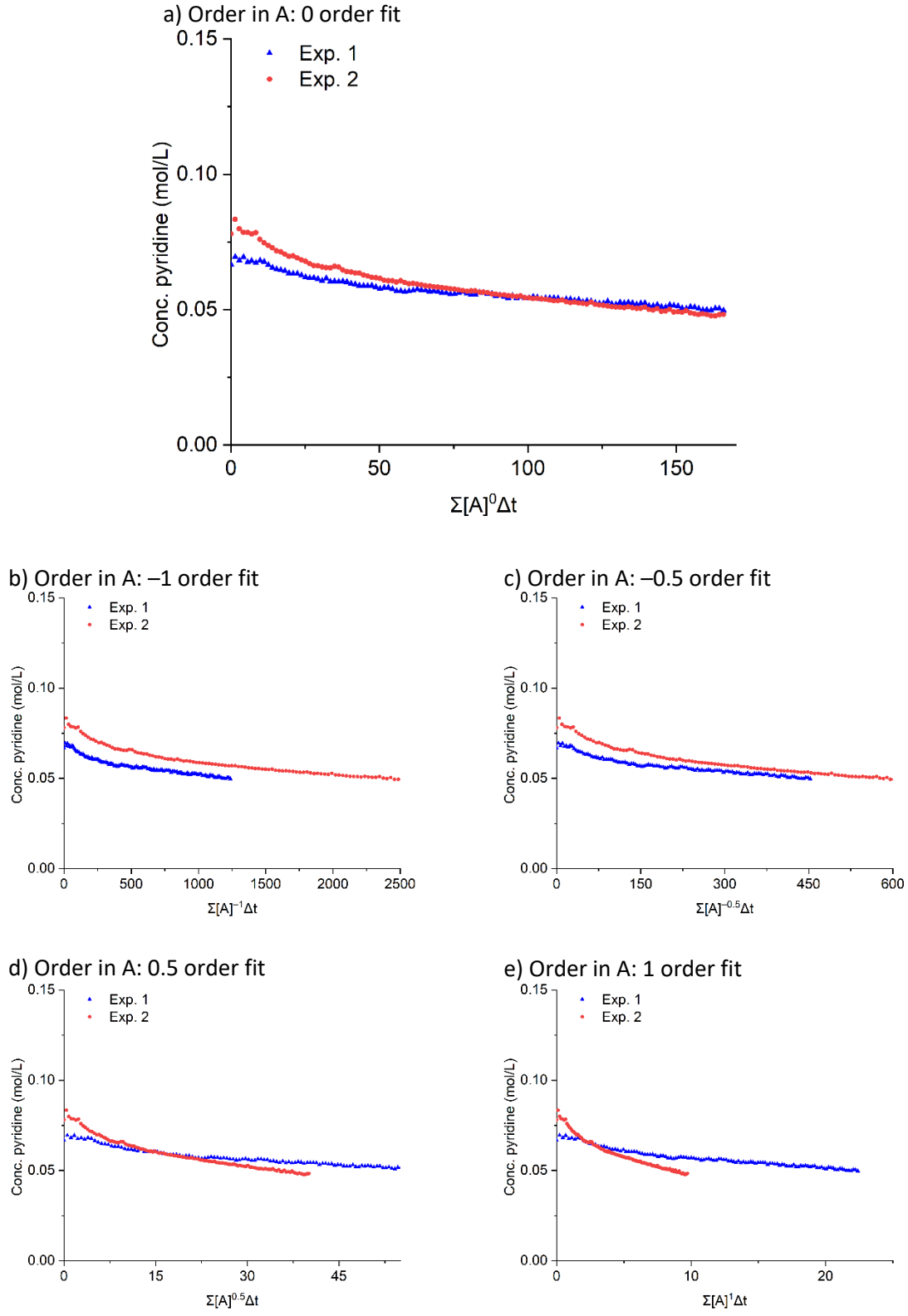


Figure S137. VTNA hydroboration pyridine using HBpin a reducing agent and [Na(18-c-6)]$_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration pyridine ([A]) using the concentration of pyridine ([A]), obtained from the analysis.

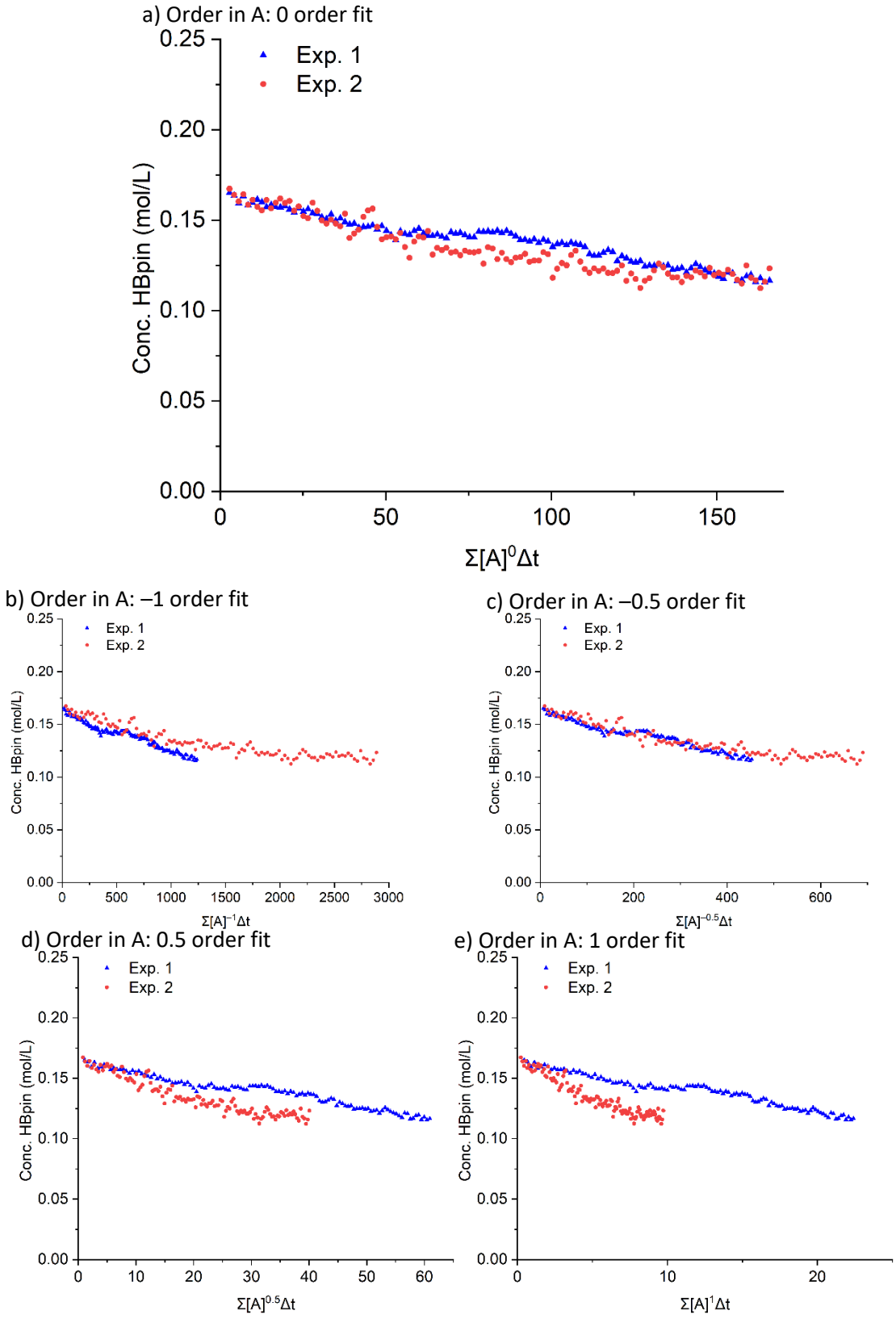


Figure S138. VTNA hydroboration pyridine using HBpin a reducing agent and $[Na(18\text{-c-}6)]_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration pyridine ([A]) using the concentration of HBpin ([B]), obtained from the analysis.

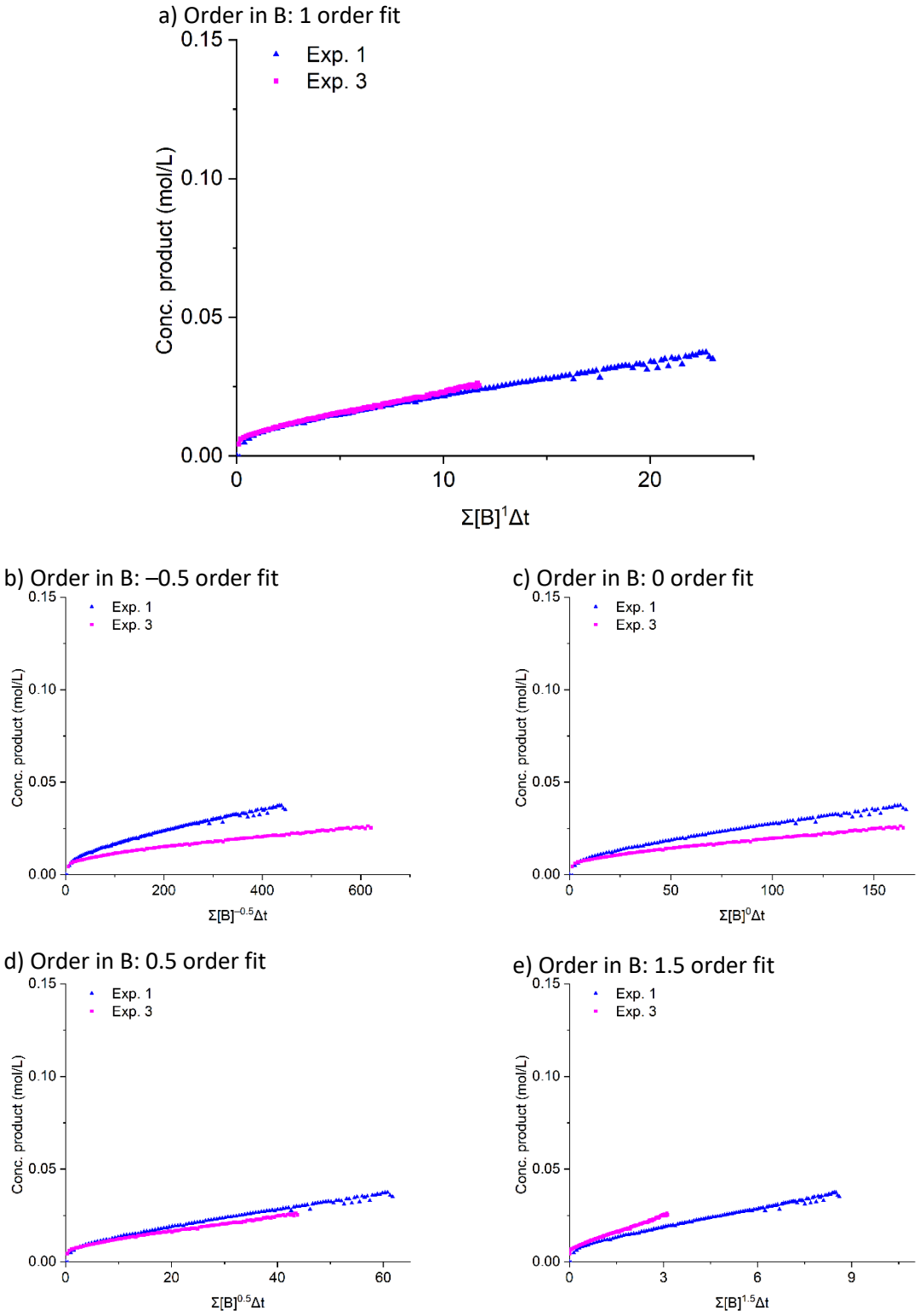


Figure S139. VTNA hydroboration pyridine using HBpin a reducing agent and [Na(18-c-6)]$_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration HBpin ([B]) using the concentration of the product, obtained from the analysis.

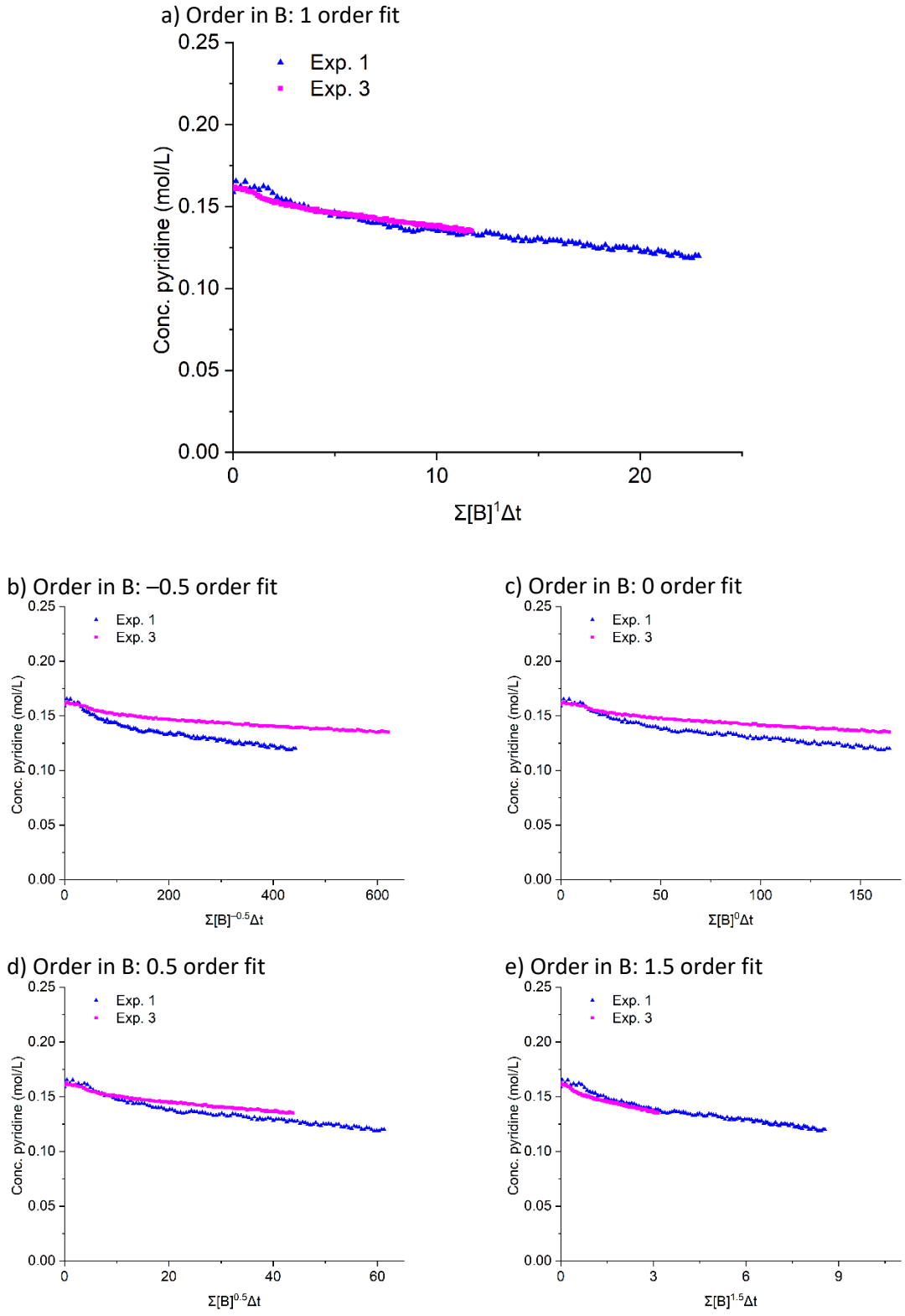


Figure S140. VTNA hydroboration pyridine using HBpin a reducing agent and $[Na(18\text{-c-}6)]_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration HBpin ([B]) using the concentration of pyridine ([A]), obtained from the analysis.

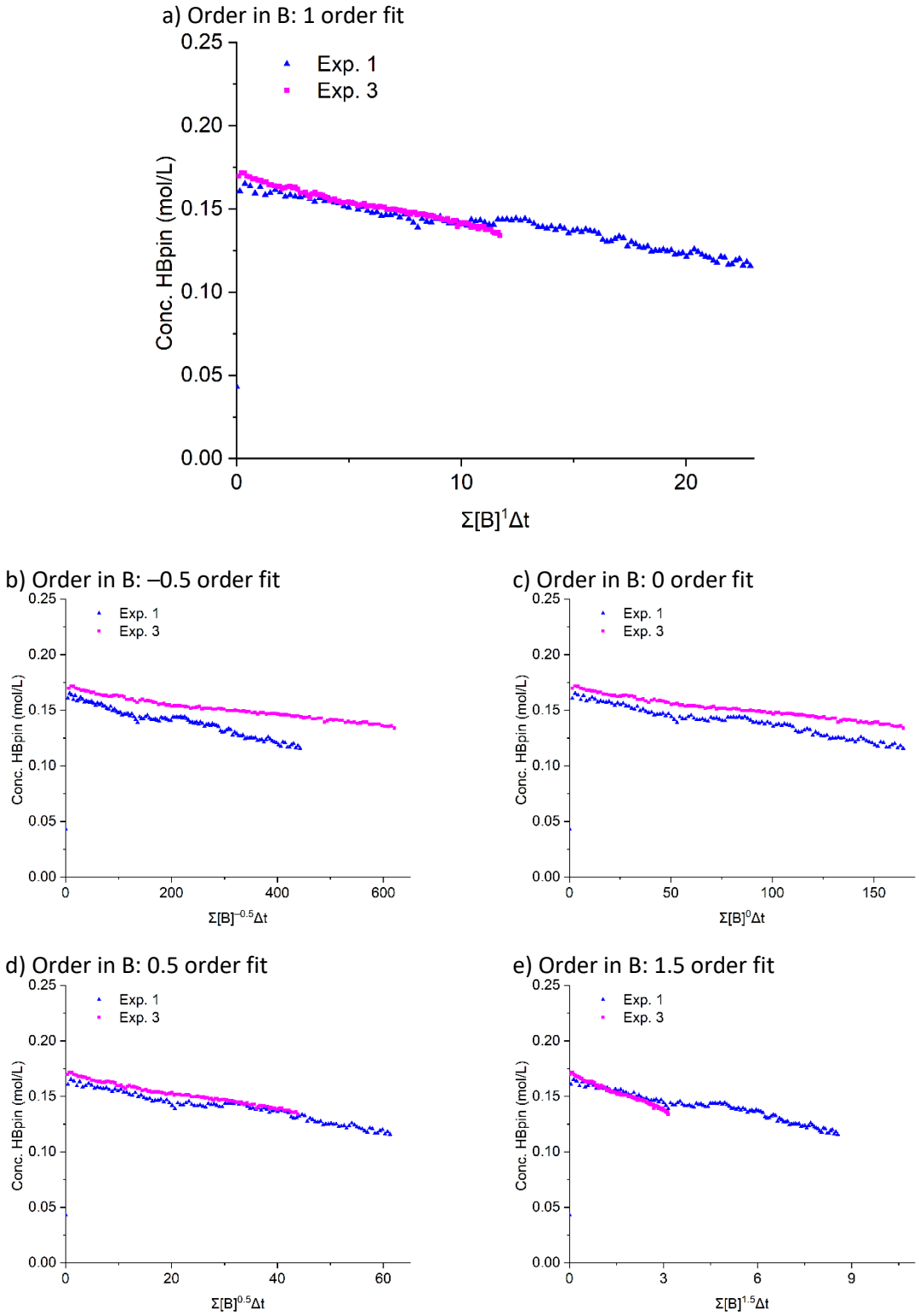


Figure S141. VTNA hydroboration pyridine using HBpin a reducing agent and [Na(18-c-6)]$_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration HBpin ([B]) using the concentration of HBpin ([B]), obtained from the analysis.

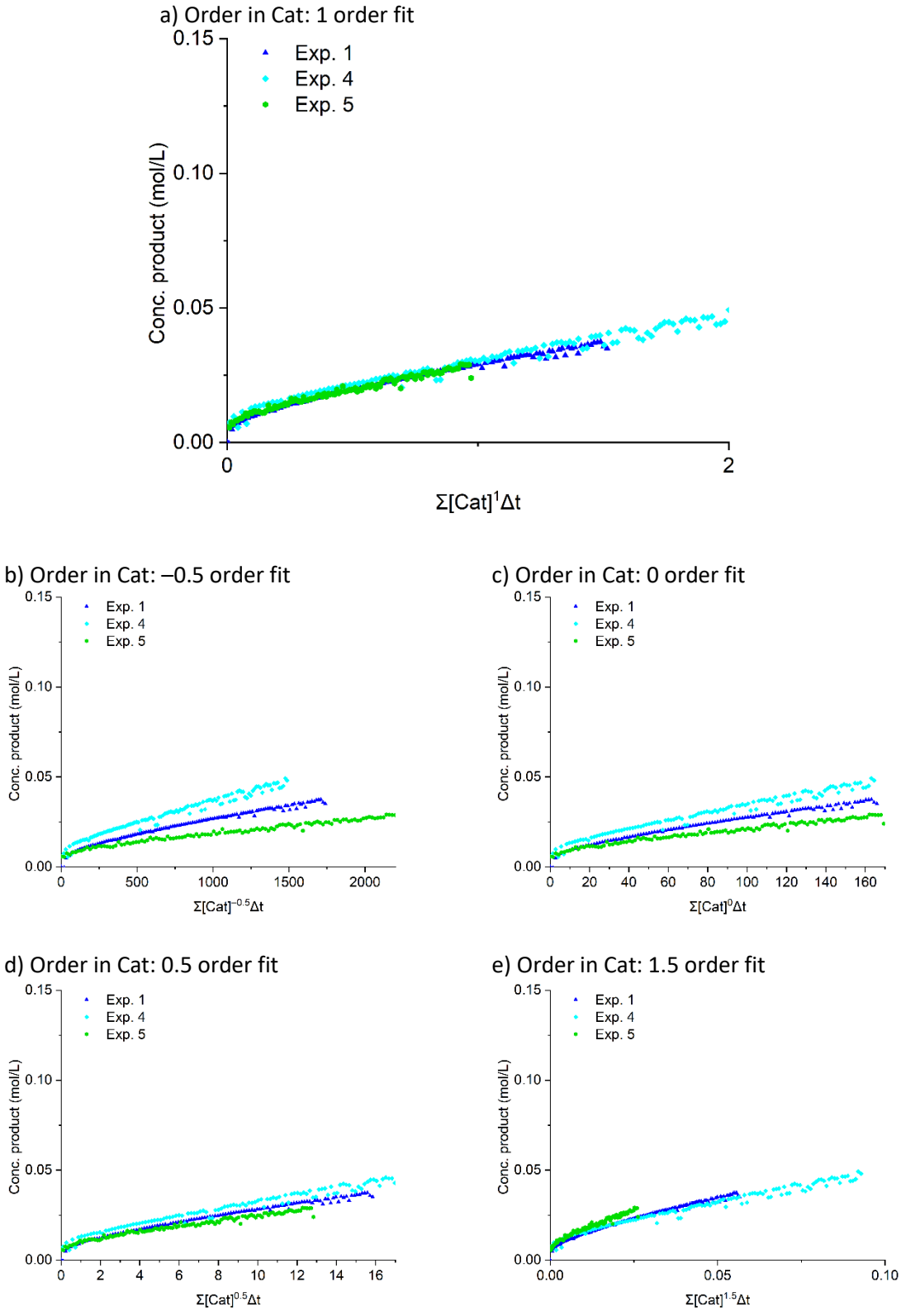


Figure S142. VTNA hydroboration pyridine using HBpin a reducing agent and $[Na(18\text{-c-}6)]_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration catalyst ([Cat]) using the concentration of the product, obtained from the analysis.

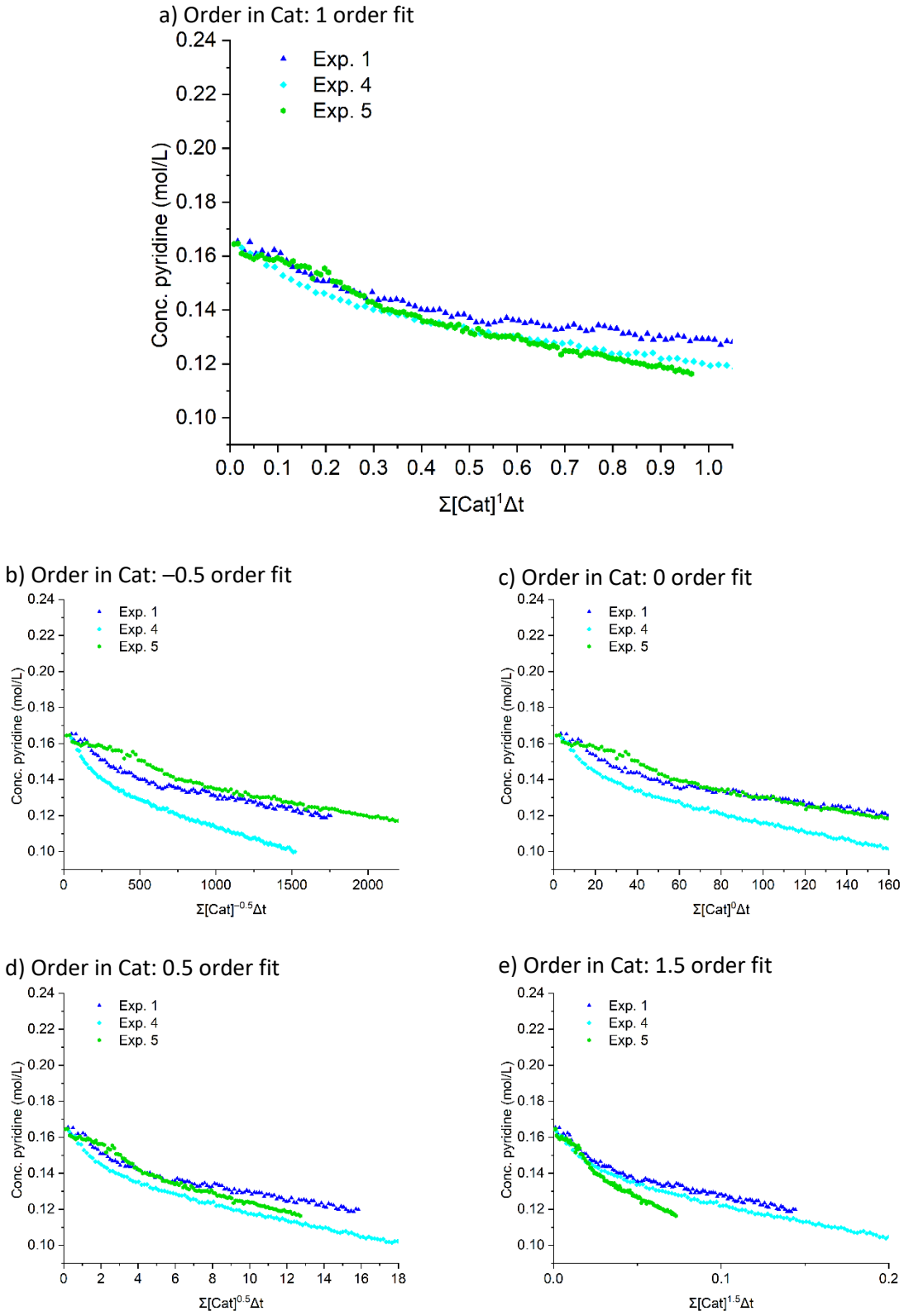


Figure S143. VTNA hydroboration pyridine using HBpin a reducing agent and $[Na(18\text{-c-}6)]_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration catalyst ([Cat]) using the concentration of pyridine ([A]), obtained from the analysis.

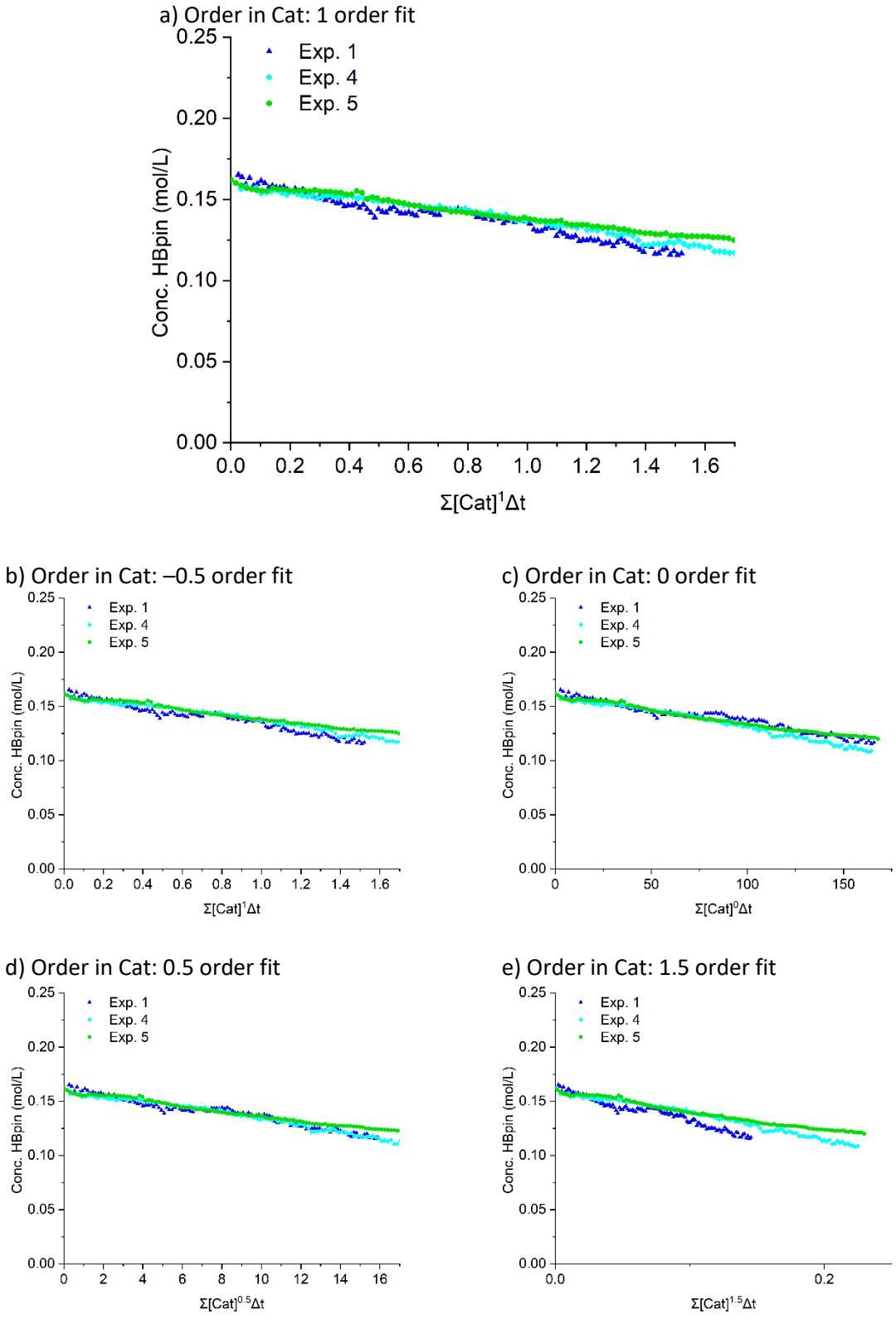


Figure S144. VTNA hydroboration pyridine using HBpin a reducing agent and [Na(18-c-6)]$_2$[**1**] as catalyst. Graphs a, b, c, d, and e are the graphical representation of different orders in concentration catalyst ([Cat]) using the concentration of HBpin ([B]), obtained from the analysis.

7.7. Reaction monitoring speciation catalysts

To a solution of $[Na(18\text{-c-}6)]_2$[**1**] (20 mg, 22 µmol, 0.05 eq.) and pinacolborane (HBpin; 28 mg, 32 µL, 0.22 mmol, 1 eq.) in *o*DFB (0.5 mL), Pyridine (17 mg, 18 µL, 0.22 mmol, 1 eq.) was added. The reaction heated to 50 °C in a NMR spectrometer and was monitored by ^{1}H and ^{31}P NMR spectroscopy.

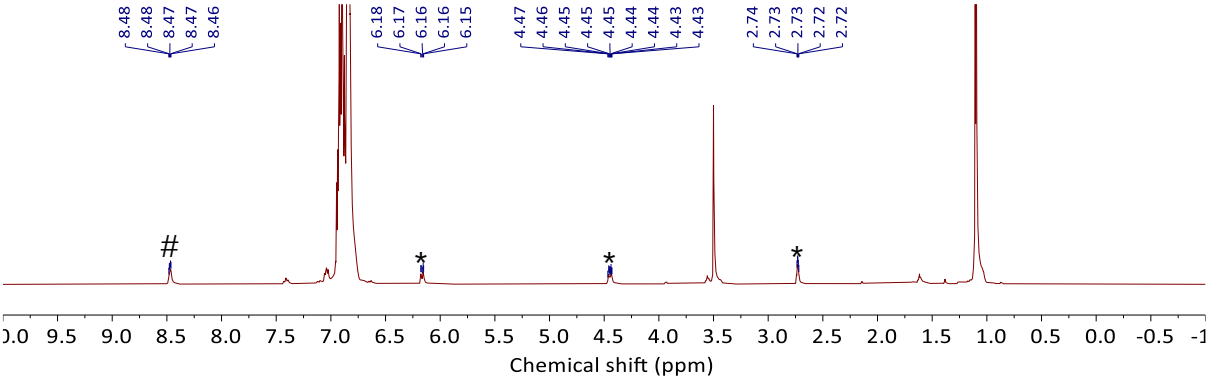


Figure S145. ^{1}H NMR spectrum (reaction mixture) of the catalytic hydroboration of pyridine using $[Na(18\text{-c-}6)]_2$[**1**]. Pyridine labelled with #. **2b** labelled *.

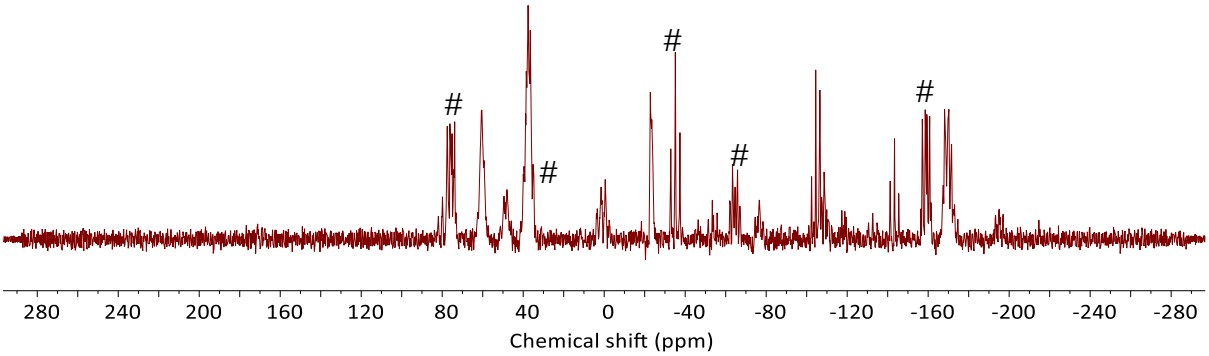


Figure S146. ^{1}H NMR spectrum (reaction mixture) of the catalytic hydroboration of pyridine using $[Na(18\text{-c-}6)]_2$[**1**]. [**1**]$^{2-}$ labelled with #.

8. Crystallography Tables

Identification code	**2b'**	**2b''**
Empirical formula	$C_{18}H_{25}BN_2$	$C_{38}H_{66}BN_2NaO_8$
Formula weight	280.21	712.72
Temperature/K	99.9(4)	100.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	9.52937(8)	14.9715(4)
b/Å	12.24923(11)	12.8581(3)
c/Å	13.53962(11)	21.3987(5)
α/°	90	90
β/°	93.9457(7)	105.047(3)
γ/°	90	90
Volume/Å^3	1576.70(2)	3978.10(17)
Z	4	4
ρ_{calc}g/cm^3	1.180	1.190
μ/mm^{-1}	0.513	0.746
F(000)	608.0	1552.0
Crystal size/mm^3	0.171 × 0.1 × 0.047	0.162 × 0.095 × 0.016
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.302 to 152.366	6.114 to 152
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -17 ≤ l ≤ 16	-18 ≤ h ≤ 16, -15 ≤ k ≤ 5, -26 ≤ l ≤ 26
Reflections collected	19524	18533
Independent reflections	3244 [R_{int} = 0.0234, R_{sigma} = 0.0163]	7823 [R_{int} = 0.0411, R_{sigma} = 0.0558]
Data/restraints/parameters	3244/0/290	7823/0/716
Goodness-of-fit on F^2	1.074	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0971	R_1 = 0.0443, wR_2 = 0.0992
Final R indexes [all data]	R_1 = 0.0383, wR_2 = 0.0992	R_1 = 0.0732, wR_2 = 0.1115
Largest diff. peak/hole / e Å^{-3}	0.34/-0.18	0.24/-0.19
CCDC	2260639	2260640

9. Density Functional Theory Studies

9.1 Computational Methods

All density functional theory calculations were performed using the Gaussian 16 (G16) suite of programmes, revision C.01,[17] using the same methodology as in our recent study of C=O reductions.[3] The wB97XD functional was used throughout, along with the def2-TZVP basis set on all atoms.[18] A superfine integration grid was used, and the influence of the solvent was modelled using the SMD model with parameters appropriate to fluorobenzene (a convenient model for *o*DFB).[19] Free energies were computed using the unscaled vibrational frequencies. It is well established that this protocol provides an over-estimate of the entropic contributions, so we report the electronic energies (ΔE) throughout the manuscript, with free energies (ΔG) given in parenthesis.

9.2 Total energies (*E* and *G*) and optimized cartesian coordinates (Å) for all stationary points reported in the text.

[1]$^{2-}$ (literature[3])

E = -2728.01768724 au *G* = -2727.836340 au

P	3.351642000	0.815324000	0.000064000
P	1.539444000	1.449172000	1.122458000
P	1.539231000	1.449577000	-1.122060000
P	0.419321000	-0.392667000	-1.498413000
P	1.353350000	-1.717249000	-0.000214000
P	0.419787000	-0.393171000	1.498676000
P	3.450650000	-1.330421000	-0.000410000
C	-2.113002000	-1.343515000	-0.000202000
H	-1.661846000	-2.343079000	-0.000412000
C	-2.953081000	-1.245408000	1.287229000
H	-3.749984000	-2.001590000	1.281753000
H	-2.299358000	-1.498956000	2.128185000

C	-3.585455000	0.127115000	1.560546000
H	-3.914479000	0.163686000	2.604657000
H	-4.494584000	0.232214000	0.966494000
C	-2.658786000	1.320839000	1.289076000
H	-3.261114000	2.239497000	1.290076000
H	-1.961451000	1.416357000	2.128955000
C	-1.822370000	1.227637000	0.000361000
H	-1.152109000	2.095097000	0.000621000
C	-2.658473000	1.321464000	-1.288557000
H	-3.260902000	2.240036000	-1.289221000
H	-1.960886000	1.417376000	-2.128164000
C	-3.585033000	0.127750000	-1.560827000
H	-3.913647000	0.164770000	-2.605059000
H	-4.494384000	0.232763000	-0.967096000
C	-2.952857000	-1.244871000	-1.287769000
H	-2.298968000	-1.498296000	-2.128640000
H	-3.749776000	-2.001041000	-1.282664000
B	-0.990708000	-0.162674000	-0.000027000

H[B] = HB(OCH$_2$CH$_2$O) (literature[3])

E = -254.623618704 au *G* = -254.572125 au

H	2.414189000	-0.000336000	-0.000016000
B	1.224861000	-0.000155000	-0.000012000
O	0.483758000	1.141397000	0.040354000
O	0.483453000	-1.141523000	-0.040334000
C	-0.898576000	0.767633000	-0.044312000

C	-0.898781000	-0.767402000	0.044305000
H	-1.300079000	1.129145000	-0.992176000
H	-1.445625000	1.235132000	0.773923000
H	-1.445931000	-1.234752000	-0.773946000
H	-1.300416000	-1.128799000	0.992159000

I1 (note that this is not the same as I1 from ref *J. Am. Chem. Soc.* **2022**, *144*, 21213–21223)

E = -2982.6499823 au *G* = -2982.394498 au

P	3.592895	-1.198417	-0.753337
P	2.561126	0.656269	-1.456217
P	1.530785	-1.323955	-1.555541
P	0.323394	-1.508590	0.235702
P	1.518634	-0.330830	1.631248
P	2.031618	1.477051	0.492872
P	3.451755	-1.268072	1.406887
C	-2.314336	-0.276022	1.080894
H	-1.782920	0.286339	1.858472
C	-3.503760	0.600434	0.649720
H	-4.190862	0.774182	1.490681
H	-3.096713	1.579504	0.378269
C	-4.317366	0.078739	-0.544232
H	-4.951475	0.888848	-0.922476
H	-5.009596	-0.692912	-0.203768
C	-3.469765	-0.472811	-1.700012
H	-4.135473	-1.006060	-2.394072
H	-3.054916	0.371938	-2.261706

C	-2.289875	-1.365012	-1.274816
H	-1.737900	-1.608122	-2.192518
C	-2.726952	-2.704490	-0.655785
H	-3.409365	-3.240467	-1.330884
H	-1.835009	-3.333377	-0.566942
C	-3.390611	-2.613150	0.728501
H	-3.388403	-3.608442	1.186310
H	-4.444094	-2.354379	0.608038
C	-2.732986	-1.619353	1.699165
H	-1.834350	-2.086434	2.116936
H	-3.413805	-1.463729	2.548386
B	-1.373940	-0.503024	-0.231513
C	-1.183372	3.709968	-0.801790
C	-1.342882	3.770113	0.716630
O	0.091348	3.095317	-0.995915
O	-0.442045	2.774641	1.203728
B	0.402911	2.443326	0.172426
H	-1.190397	4.693954	-1.271046
H	-2.355834	3.543210	1.048337
H	-1.046604	4.741936	1.122265
H	-1.948226	3.081875	-1.266642
H	-1.034997	0.568607	-0.728575

TS1

E = -2982.6235543 au *G* = -2982.369423 au

P	2.006355	-3.090433	-0.463395

P	2.024104	-1.152168	-1.627512
P	0.129042	-2.325655	-1.367479
P	-0.933740	-1.493265	0.338938
P	0.753312	-0.817069	1.571768
P	1.814800	0.202046	0.003126
P	1.955530	-2.616567	1.636818
C	-2.175775	1.255072	0.719195
H	-1.258027	1.577776	1.226805
C	-2.746329	2.503966	0.022554
H	-3.017066	3.273488	0.760381
H	-1.940379	2.932431	-0.583545
C	-3.960131	2.258541	-0.887544
H	-4.106135	3.135215	-1.528742
H	-4.862495	2.194617	-0.277307
C	-3.858149	1.006395	-1.771385
H	-4.847429	0.811693	-2.210757
H	-3.187629	1.227896	-2.609620
C	-3.312151	-0.248667	-1.065997
H	-3.221247	-1.025067	-1.837947
C	-4.257882	-0.806692	0.011766
H	-5.259514	-0.987595	-0.404246
H	-3.874293	-1.787267	0.311514
C	-4.408374	0.054275	1.277075
H	-4.851423	-0.558827	2.069603
H	-5.131812	0.850178	1.090717
C	-3.101120	0.671300	1.798455

H	-2.539638	-0.103996	2.332806
H	-3.353987	1.431225	2.551645
B	-1.858229	0.149034	-0.435598
C	3.510798	3.810139	-0.725476
C	3.193290	3.929433	0.766848
O	3.289802	2.431835	-1.028721
O	2.392456	2.783268	1.054613
B	2.547928	1.904184	0.005596
H	4.542228	4.073959	-0.960666
H	2.634284	4.833882	1.008094
H	4.097140	3.894699	1.381405
H	2.839074	4.419910	-1.335845
H	-1.114305	0.612963	-1.298315

I2 (note that this is the same as I1 from ref *J. Am. Chem. Soc.* **2022**, *144*, 21213–21223)

E = -2982.64783594 au *G* = -2982.394835 au

P	2.005507000	2.488087000	-0.008994000
P	1.576405000	1.107084000	1.702150000
P	-0.061956000	2.286902000	0.768459000
P	-1.018941000	0.998027000	-0.706990000
P	0.694007000	-0.217971000	-1.297620000
P	1.303554000	-0.836766000	0.738802000
P	2.146297000	1.290546000	-1.794758000
C	-2.698124000	-1.513990000	-0.348461000
H	-1.818477000	-2.118491000	-0.603896000
C	-3.532385000	-2.357596000	0.633272000

H	-3.879231000	-3.285652000	0.155902000
H	-2.863081000	-2.663021000	1.445207000
C	-4.748477000	-1.647659000	1.249335000
H	-5.093629000	-2.222813000	2.115899000
H	-5.578008000	-1.670451000	0.540580000
C	-4.495482000	-0.196075000	1.684279000
H	-5.466487000	0.273294000	1.899857000
H	-3.944358000	-0.208509000	2.631267000
C	-3.683084000	0.651973000	0.689172000
H	-3.514890000	1.623707000	1.173075000
C	-4.430847000	0.938595000	-0.624228000
H	-5.413567000	1.388273000	-0.421616000
H	-3.859529000	1.695906000	-1.171386000
C	-4.634933000	-0.271190000	-1.550641000
H	-4.902410000	0.090398000	-2.549645000
H	-5.498698000	-0.845977000	-1.211512000
C	-3.421587000	-1.206170000	-1.669438000
H	-2.693847000	-0.745203000	-2.347351000
H	-3.746910000	-2.133410000	-2.162344000
B	-2.278576000	-0.138729000	0.420921000
C	5.402849000	-1.305689000	0.435183000
C	4.898512000	-2.458754000	-0.442765000
O	4.223991000	-0.755843000	1.025568000
O	3.484524000	-2.272571000	-0.512039000
B	3.139411000	-1.277239000	0.367893000
H	5.895241000	-0.527679000	-0.151944000

H	5.103803000	-3.436883000	-0.000782000
H	5.316415000	-2.430449000	-1.449528000
H	6.079581000	-1.639255000	1.222641000
H	-1.705958000	-0.375950000	1.483306000

Pyridine

E = -248.2940704 au *G* = -248.231871 au

C	1.138207	-0.717844	0.000204
C	-1.138328	-0.717660	0.000203
C	1.191316	0.667518	0.000012
H	2.053772	-1.300400	0.000262
C	-1.191204	0.667719	0.000037
H	-2.053996	-1.300055	0.000200
H	2.146980	1.175050	0.000171
H	-2.146787	1.175405	0.000149
C	0.000117	1.374868	-0.000156
H	0.000217	2.457922	-0.000145
N	-0.000120	-1.407933	-0.000348

TS2

E = -3230.8998936 au *G* = -3230.556742 au

P	-0.170924	4.132225	0.000378
P	-1.213788	3.362238	1.729067
P	-2.086742	3.073982	-0.245454
P	-1.629358	1.110581	-1.169994
P	0.530309	0.836113	-1.312001

P	1.418012	1.014973	0.699697
P	1.467631	2.723237	-0.699109
C	-1.685996	-1.763257	-0.126462
H	-0.595592	-1.803575	-0.249850
C	-2.009016	-2.658175	1.082459
H	-1.727442	-3.702513	0.881295
H	-1.372776	-2.324844	1.909215
C	-3.472476	-2.635353	1.551480
H	-3.529457	-3.073812	2.554312
H	-4.066161	-3.294483	0.915415
C	-4.116943	-1.241139	1.579887
H	-5.201631	-1.364543	1.714456
H	-3.755436	-0.710969	2.467722
C	-3.809622	-0.352925	0.360837
H	-4.259416	0.627243	0.570265
C	-4.440613	-0.860025	-0.946908
H	-5.524189	-1.004876	-0.827796
H	-4.322755	-0.071611	-1.698051
C	-3.841045	-2.157657	-1.514961
H	-4.154099	-2.262563	-2.559808
H	-4.277132	-3.013672	-0.996576
C	-2.308372	-2.252031	-1.442765
H	-1.883873	-1.649335	-2.253670
H	-2.016229	-3.291608	-1.653425
B	-2.185711	-0.253593	0.235234
C	5.261711	-0.444275	0.794536

C	5.192763	-0.048652	-0.684775
O	4.063075	0.071345	1.357321
O	3.819871	0.240172	-0.919016
B	3.168219	0.236751	0.305252
H	6.124324	-0.017791	1.308389
H	5.522374	-0.853176	-1.345697
H	5.785439	0.845522	-0.898904
H	5.279499	-1.532382	0.917491
C	1.943821	-2.528845	1.264449
C	2.253287	-2.457906	-1.001584
C	1.304184	-3.753503	1.188185
H	2.079813	-2.022366	2.213590
C	1.627386	-3.681071	-1.174772
H	2.635284	-1.891006	-1.842602
H	0.927250	-4.225097	2.085434
H	1.511120	-4.095175	-2.167289
C	1.146572	-4.341588	-0.056188
H	0.639811	-5.293497	-0.154627
N	2.411041	-1.897395	0.192652
H	-1.673064	0.158151	1.274033

I3

E = -3230.9060992 au *G* = -3230.561898 au

P	0.159601	4.054557	-0.010264
P	-0.910202	3.392060	1.748466
P	-1.868194	3.212197	-0.197096

P	-1.663612	1.222657	-1.157811
P	0.454039	0.717702	-1.346137
P	1.424964	0.793429	0.619940
P	1.619682	2.484217	-0.765481
C	-1.821904	-1.641255	-0.090323
H	-0.732693	-1.699767	-0.213061
C	-2.165423	-2.506956	1.134124
H	-1.899928	-3.560727	0.958086
H	-1.530216	-2.165482	1.958545
C	-3.632150	-2.449597	1.591191
H	-3.703895	-2.861872	2.604083
H	-4.230290	-3.115815	0.966836
C	-4.257805	-1.045400	1.580986
H	-5.346109	-1.153128	1.699456
H	-3.904707	-0.504088	2.465277
C	-3.918914	-0.181399	0.352588
H	-4.353668	0.809473	0.541137
C	-4.544065	-0.696094	-0.955055
H	-5.633455	-0.805069	-0.852281
H	-4.387577	0.071931	-1.720024
C	-3.975514	-2.022572	-1.484474
H	-4.285344	-2.149188	-2.527934
H	-4.433225	-2.854064	-0.945240
C	-2.446504	-2.144915	-1.400645
H	-2.007649	-1.564159	-2.220695
H	-2.171912	-3.193542	-1.590625

B	-2.291982	-0.115293	0.246828
C	5.271549	-0.078480	0.835659
C	5.156016	-0.397776	-0.650718
O	3.983668	-0.340173	1.351150
O	3.810591	-0.101961	-0.958323
B	3.055880	-0.334025	0.240085
H	5.531736	0.976500	0.989069
H	5.372502	-1.460193	-0.837756
H	5.821989	0.204769	-1.272402
H	6.017990	-0.696522	1.342710
C	1.977396	-2.461446	1.264867
C	2.133650	-2.395874	-1.043174
C	1.287085	-3.652639	1.223162
H	2.211882	-1.958410	2.192746
C	1.447325	-3.587462	-1.158623
H	2.494403	-1.840041	-1.896315
H	0.958224	-4.110728	2.144934
H	1.248785	-3.994507	-2.139803
C	1.012735	-4.224260	-0.009521
H	0.457659	-5.151259	-0.071844
N	2.389325	-1.850640	0.148835
H	-1.778374	0.278497	1.291575

TS3

E = -3230.854927 au *G* = -3230.518959 au

P	0.645665	3.792864	0.002771

P	-0.137225	3.040638	1.871017
P	-1.361820	2.885977	0.085536
P	-1.181868	1.007017	-1.087977
P	0.902577	0.473154	-1.366797
P	2.110861	0.683280	0.436260
P	2.060153	2.304303	-1.040885
C	-3.103548	-1.321965	-1.304687
H	-2.565873	-1.572757	-2.227253
C	-3.649155	-2.638870	-0.721046
H	-4.425715	-3.044132	-1.382743
H	-2.844679	-3.377822	-0.740339
C	-4.230634	-2.557636	0.704629
H	-4.227184	-3.561271	1.143047
H	-5.282635	-2.278371	0.640679
C	-3.524146	-1.593121	1.674381
H	-4.200106	-1.401971	2.517724
H	-2.651500	-2.090314	2.106451
C	-3.053593	-0.259263	1.066411
H	-2.479835	0.265579	1.837635
C	-4.224936	0.663266	0.667237
H	-4.885741	0.821809	1.529170
H	-3.811744	1.646242	0.421382
C	-5.064280	0.181493	-0.524089
H	-5.685030	1.011838	-0.875596
H	-5.765219	-0.587364	-0.195614
C	-4.236072	-0.349439	-1.700631

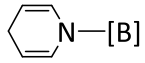
H	-3.788897	0.500982	-2.224311
H	-4.909924	-0.835289	-2.417963
B	-2.163991	-0.548563	-0.239622
C	5.625370	-1.065431	0.545730
C	5.319914	-1.602877	-0.846956
O	4.370771	-1.029858	1.181589
O	4.027501	-1.112430	-1.123532
B	3.364650	-0.937564	0.141003
H	6.057068	-0.056287	0.484504
H	5.326024	-2.703104	-0.847114
H	6.025149	-1.253728	-1.605815
H	6.316944	-1.702708	1.104721
C	1.555817	-2.026667	1.567909
C	1.584415	-2.591579	-0.687378
C	0.255322	-2.371116	1.686514
H	2.143783	-1.714224	2.421348
C	0.290445	-2.990571	-0.646357
H	2.188374	-2.687826	-1.579740
H	-0.220730	-2.351499	2.657201
H	-0.159439	-3.447247	-1.517439
C	-0.522174	-2.635150	0.494779
H	-1.428404	-3.206135	0.641295
N	2.219984	-2.029262	0.374592
H	-1.165665	-1.455593	0.157715

I4

E = -3230.9026089 au *G* = -3230.561066 au

P	-0.440692	3.932034	0.249856
P	-1.528930	2.933350	1.828900
P	-2.356091	2.940421	-0.168897
P	-1.741731	1.169950	-1.390142
P	0.434987	0.862340	-1.529184
P	1.242161	0.754491	0.496441
P	1.271782	2.656973	-0.576753
C	-1.708941	-1.780671	-0.581986
H	-0.740124	-1.774544	-1.087972
C	-1.440873	-2.188051	0.884604
H	-0.999945	-3.190110	0.908005
H	-0.674746	-1.512174	1.277318
C	-2.658431	-2.136367	1.814252
H	-2.308611	-2.194888	2.849093
H	-3.280293	-3.019330	1.663210
C	-3.506361	-0.868220	1.656789
H	-4.450980	-0.990378	2.199703
H	-2.976734	-0.038722	2.137304
C	-3.796206	-0.441126	0.199054
H	-4.313330	0.521923	0.241661
C	-4.696750	-1.410707	-0.599803
H	-5.652700	-1.541034	-0.079023
H	-4.933274	-0.927309	-1.554621
C	-4.087667	-2.788504	-0.889753
H	-4.692363	-3.285251	-1.654841

H	-4.164380	-3.416488	-0.002574
C	-2.629924	-2.741861	-1.364905
H	-2.615909	-2.427748	-2.414891
H	-2.208304	-3.753710	-1.344045
B	-2.405162	-0.367356	-0.538707
C	4.837011	1.163242	0.627110
C	4.917100	0.814021	-0.857778
O	4.011956	0.164222	1.170047
O	3.689244	0.189216	-1.142588
B	3.085792	-0.206992	0.114715
H	4.388877	2.157777	0.765043
H	5.751814	0.123761	-1.049716
H	5.051939	1.698955	-1.487820
H	5.813922	1.154671	1.119144
C	2.539443	-2.346532	1.372414
C	2.322679	-2.381484	-0.956239
C	2.063787	-3.591820	1.495080
H	2.806338	-1.764685	2.246430
C	1.835328	-3.628478	-0.952094
H	2.427280	-1.825510	-1.879426
H	1.950670	-4.004628	2.490583
H	1.542583	-4.069424	-1.897676
C	1.677351	-4.438326	0.308965
H	2.286384	-5.354523	0.265947
N	2.729853	-1.696754	0.169962
H	0.642601	-4.799189	0.412147



E = -502.9495457 au *G* = -502.811824 au

C	-3.080783	0.759030	0.109070
C	-3.080824	-0.759034	-0.108618
O	-1.715213	1.147111	-0.063301
O	-1.715166	-1.147096	0.063156
B	-0.965168	0.000005	-0.000159
H	-3.399003	1.027441	1.119116
H	-3.399567	-1.027620	-1.118445
H	-3.703024	-1.287211	0.613067
H	-3.703332	1.287322	-0.612227
C	1.195183	1.192665	-0.013072
C	1.195191	-1.192671	0.012530
C	2.523410	1.232502	-0.013075
H	0.596505	2.093273	-0.022169
C	2.523420	-1.232499	0.013240
H	0.596522	-2.093293	0.021121
H	3.006291	2.201610	-0.022772
H	3.006307	-2.201604	0.022991
C	3.382996	0.000007	0.000400
H	4.051181	-0.009390	-0.869776
N	0.459266	-0.000013	-0.000407
H	4.050567	0.009420	0.871058

I4_iso

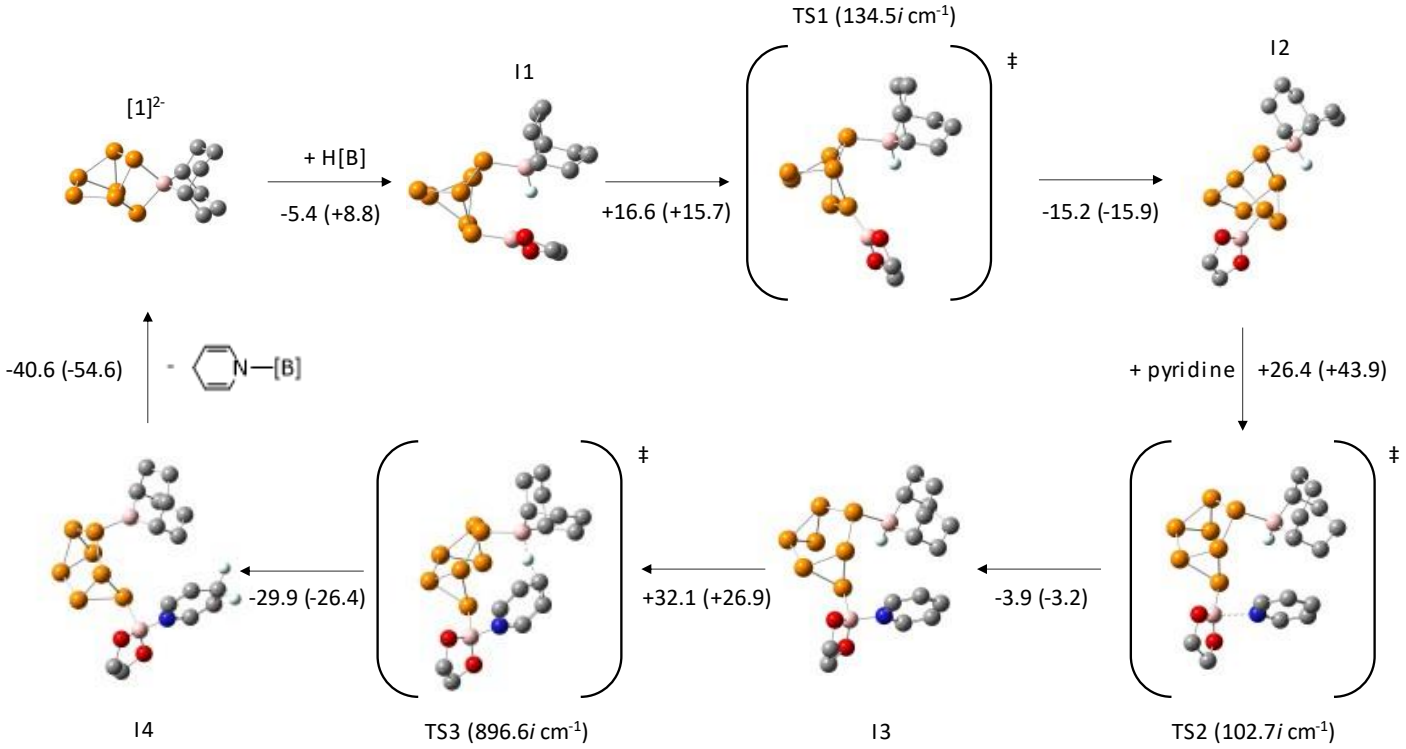
E = -3230.9111784 au *G* = -3230.572496 au

P	-1.060038	-3.450471	-0.131723
P	-0.099153	-2.769284	1.676843
P	0.899743	-2.457296	-0.232350
P	0.524843	-0.467358	-1.101915
P	-1.596005	-0.014135	-1.085687
P	-2.692110	-0.529481	0.787836
P	-2.610669	-1.952769	-0.885930
C	2.033597	2.178682	-1.178500
H	2.300647	1.887035	-2.201701
C	0.697240	2.926527	-1.291931
H	0.811701	3.818543	-1.922594
H	-0.003881	2.275716	-1.825501
C	0.059137	3.348952	0.038624
H	-0.994314	3.591631	-0.136994
H	0.519807	4.278972	0.376385
C	0.140883	2.298114	1.156415
H	-0.063406	2.795818	2.113954
H	-0.668890	1.578740	1.021585
C	1.454400	1.505931	1.249871
H	1.273560	0.722921	1.995466
C	2.625524	2.367644	1.766931
H	2.364395	2.818832	2.733564
H	3.481747	1.714514	1.960757
C	3.075761	3.483219	0.813515
H	4.046565	3.866020	1.146426

H	2.388126	4.326226	0.893950
C	3.188424	3.055774	-0.657044
H	4.119085	2.492047	-0.781474
H	3.294504	3.956746	-1.276787
B	1.885261	0.889852	-0.191763
C	-6.452235	0.911670	-0.213197
C	-5.721631	2.199185	0.187833
O	-5.523002	-0.136504	0.073681
O	-4.358121	1.804244	0.350576
B	-4.301645	0.433458	0.327400
H	-6.690478	0.887308	-1.278863
H	-6.086247	2.604241	1.134765
H	-5.785364	2.974451	-0.575947
H	-7.367026	0.750901	0.357652
C	3.532084	-0.693697	0.995037
C	3.941969	-0.221832	-1.243408
C	4.595209	-1.502291	1.083416
H	2.861525	-0.593546	1.837953
C	5.021564	-1.013819	-1.276712
H	3.599791	0.261046	-2.149686
H	4.754720	-2.037441	2.011968
H	5.529622	-1.149406	-2.224351
C	5.554285	-1.717759	-0.056961
H	6.563005	-1.356124	0.198701
N	3.174478	0.031661	-0.125202
H	5.683931	-2.791161	-0.254480

9.3 Alternative representation of Scheme 4.

Computed mechanism for the [**1**]$^{2-}$-catalysed hydroboration of pyridine. Electronic energies (kcal/mol) and, in parentheses, Gibbs energies are given for the individual steps. Imaginary wavenumbers are given for the transition states. Only key H atoms are shown.



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