

Supporting Information for

Formoxyboranes as hydroborane surrogates for catalyzed carbonyl reduction through transfer hydroboration

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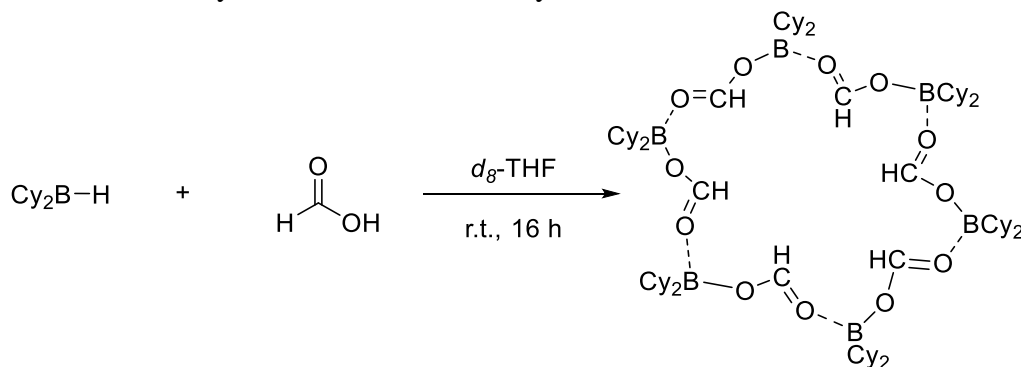
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1 General considerations

Unless otherwise stated, all reactions were performed in a recirculating *mBraun LabMaster DP* inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware were dried overnight at 120 °C. NMR spectra were recorded in a *Bruker Avance Neo 400 MHz* spectrometer. Chemical shifts were reported as ppm downfield from residual solvent peaks. The following calibrations were used: CDCl₃ δ = 7.26 and 77.16 ppm, THF-*d*₈ δ = 3.58, 1.72 and 67.21, 25.31 ppm, C₆D₆ δ = 7.16 and 128.06 ppm, CD₂Cl₂ δ = 5.32 and 53.84 ppm. 4Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Deuterated solvents were dried and stored under molecular sieves. *fac*-[Ru(κ^1 -OAc)(κ^2 -OAc)(κ^3 -PN^HP^{Ph})] (**2a**),^[1] *fac*-[Ru(κ^1 -OAc)(κ^2 -OAc)(κ^3 -PN^{Me}P^{Ph})] (**2a-Me**)^[1] and [Ru(η^1 -OAc)(H)(CO)(*mer*- κ^3 -PN^HP^{Ph})] (**2b**)^[1] were synthesized according to literature procedures. HCO₂H (99 %, highest grade commercially available), triethylamine, quinolone, pyridine and 4-Dimethylaminopyridine (DMAP) were obtained from Acros and degassed prior to use. Sodium formate was purchased from Aldrich, finely ground and dried at 120°C under high vacuum for 2 hours prior to use. 9-Borabicyclo nonane dimer was obtained from Aldrich and dicyclohexylborane^[2] and was synthesized according to literature. Ketones were purchased and used without any further purification. IR spectra was recorded with a Shimadzu IRAffinity-1S equipped with a MIRacle 10 ATR accessory and a demountable FT IR Liquid cell (Pike Technologies). GC data were acquired with a Shimadzu GC-2010 Plus apparatus, equipped with a Supelco column CARBOXEN 1010 PLOT (30 m x 0.53 mm, T = 100 °C) and using argon as a gas carrier.

2 Oligomer synthesis

In a glovebox, a *J. Young* NMR Tube was charged with dicyclohexylborane (0.05 mmol, 1 equiv.), *d*₈-THF and formic acid (1 equiv.). Hydrogen evolution was immediately observed and after 16 h reacting at room temperature, a crystalline insoluble product was observed. Crystals suitable for X-ray diffraction were directly formed from the reaction medium.



Scheme S1. Synthesis of formoxyborane oligomer.

3 Formoxyborane synthesis

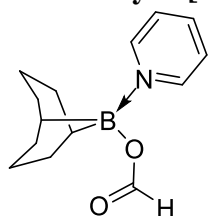
Method A.



Scheme S2. General procedure for the synthesis of formoxyboranes.

In a glovebox, a flame dried round bottom flask equipped with a solv-seal connection and a *J. Young* valve was charged with the corresponding hydroborane (8 mmol, 1 equiv.) and suspended in toluene (20 mL). To this mixture, the Lewis base (16.8 mmol, 1.05 equiv.) and formic acid (19.8 mmol, 1.1 equiv.) were added in that order. The flask was sealed, brought out of the glovebox and stirred at room temperature overnight. After reaction completion, the solvent was removed under reduced pressure. The obtained solid was washed with cold hexane and dried under vacuum to produce the final pure compound.

9-borabicyclo[3.3.1]nonan-9-yl formate pyridine adduct (1a)



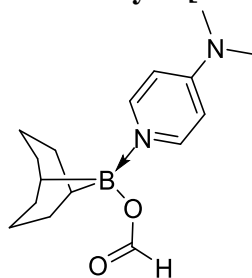
Isolated as a white powder in 98% yield (1.92 g).

$^1\text{H NMR}$ (200 MHz, C_6D_6): δ = 8.44 (d, J = 5.7 Hz, 2H), 8.27 (s, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.33 (t, J = 6.8 Hz, 2H), 2.70-1.27 (m, 14H).

$^{13}\text{C NMR}$ (50 MHz, C_6D_6): δ = 163.5, 145.9, 140.7, 125.0, 32.2, 31.2, 24.9, 22.7 (bs).

$^{11}\text{B NMR}$ (64 MHz, C_6D_6): δ = 7.5

9-borabicyclo[3.3.1]nonan-9-yl formate *N,N*-dimethylaminopyridine adduct (1b)



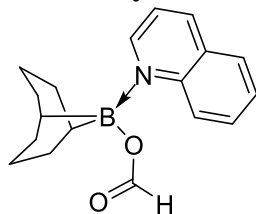
Isolated as a white powder in 96% yield (2.21 g).

$^1\text{H NMR}$ (400 MHz, C_6D_6): δ = 8.51 (s, 1H), 8.22 (d, J = 7.2 Hz, 2H), 5.55 (d, J = 7.3 Hz, 2H), 2.74-2.63 (m, 2H), 2.42-2.26 (m, 4H), 2.18-2.03 (m, 3H), 1.90 (s, 6H), 1.85 (bs, 2H), 1.78-1.59 (m, 3H).

$^{13}\text{C NMR}$ (100 MHz, C_6D_6): δ = 163.7, 155.1, 145.0, 105.8, 38.2, 32.3, 31.7, 25.4, 25.3, 23.1 (bs).

$^{11}\text{B NMR}$ (128 MHz, C_6D_6): δ = 6.0

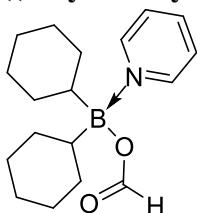
9-borabicyclo[3.3.1]nonan-9-yl formate quinoline adduct



Brown powder. Product obtained impure in low yield.

¹H NMR (200 MHz, *d*₈-THF): δ = 9.09 (d, *J* = 4.8 Hz, 1H), 8.54-7.55 (m, 7H), 2.04-0.70 (m, 14H).

((Dicyclohexylboraneyl)oxy)formaldehyde pyridine adduct (**1c**)



Isolated as a white powder in 82% yield (1.98 g).

¹H NMR (200 MHz, C₆D₆): δ = 8.79 (s, 1H), 8.16 (d, *J* = 5.5 Hz, 2H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.66-6.46 (m, 2H), 1.92-0.4 (m, 22H)

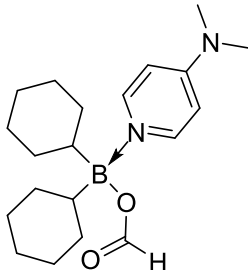
¹³C NMR (50 MHz, C₆D₆): δ = 162.5, 144.1, 139.7, 124.6, 29.6 (bs), 28.9, 28.7, 27.9.

¹¹B NMR (64 MHz, C₆D₆): δ = 9.0.

Additionally, compound **1c** can be obtained from Cy₂BCl through the following procedure:

In a glovebox, a flamed dried round bottom flask equipped with a solv seal connection and a *J. Young* valve was charged with sodium formate (4 mmol, 2 equiv.) and LiCl (0.2 mmol, 20 mol%) and suspended in MeCN (20 mL). To this mixture, pyridine (2.1 mmol, 1.02 equiv.) and a 1M solution of Cy₂BCl in hexanes (2 mmol, 1 equiv.) were sequentially added. The flask was sealed, brought out of the glovebox and stirred at 100 °C. After 20 hours, the solvent was removed under reduced pressure. Toluene (10 mL) was added and the resulting suspension was filtered through Celite. The residue was treated with additional toluene (2 x 5 mL). Solvent evaporation gave **1c** as a white powder in 94% yield (0.57 g).

((Dicyclohexylboraneyl)oxy)formaldehyde *N,N*-dimethylaminopyridine adduct (**1d**)



Isolated as a white powder in 82% yield (2.25 g).

¹H NMR (200 MHz, *d*₈-THF): δ = 8.34 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 2H), 3.14 (s, 6H), 1.9-0.4 (m, 22H)

¹³C NMR (50 MHz, *d*₈-THF): δ = 162.3, 156.1, 143.8, 106.6, 39.1, 29.4, 29.3, 29.1, 28.3.

¹¹B NMR (64 MHz, *d*₈-THF): δ = 5.4.

4 NMR spectra of formoxyboranes

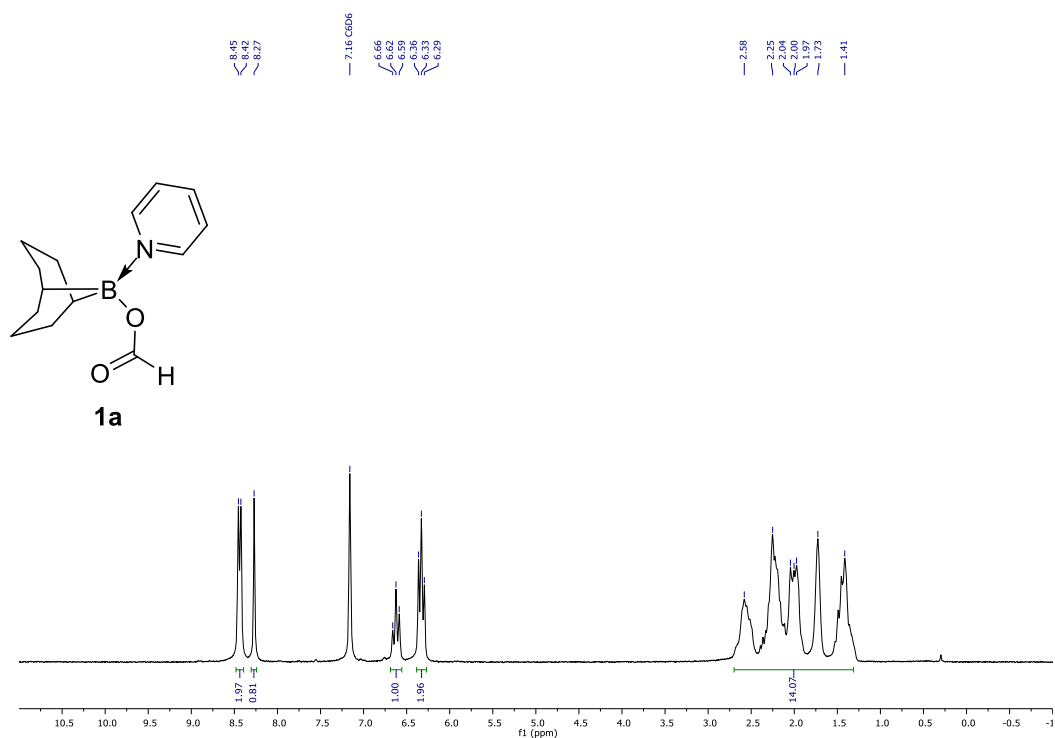


Figure S1. ^1H NMR spectrum obtained in C_6D_6 for formoxyborane **1a**.

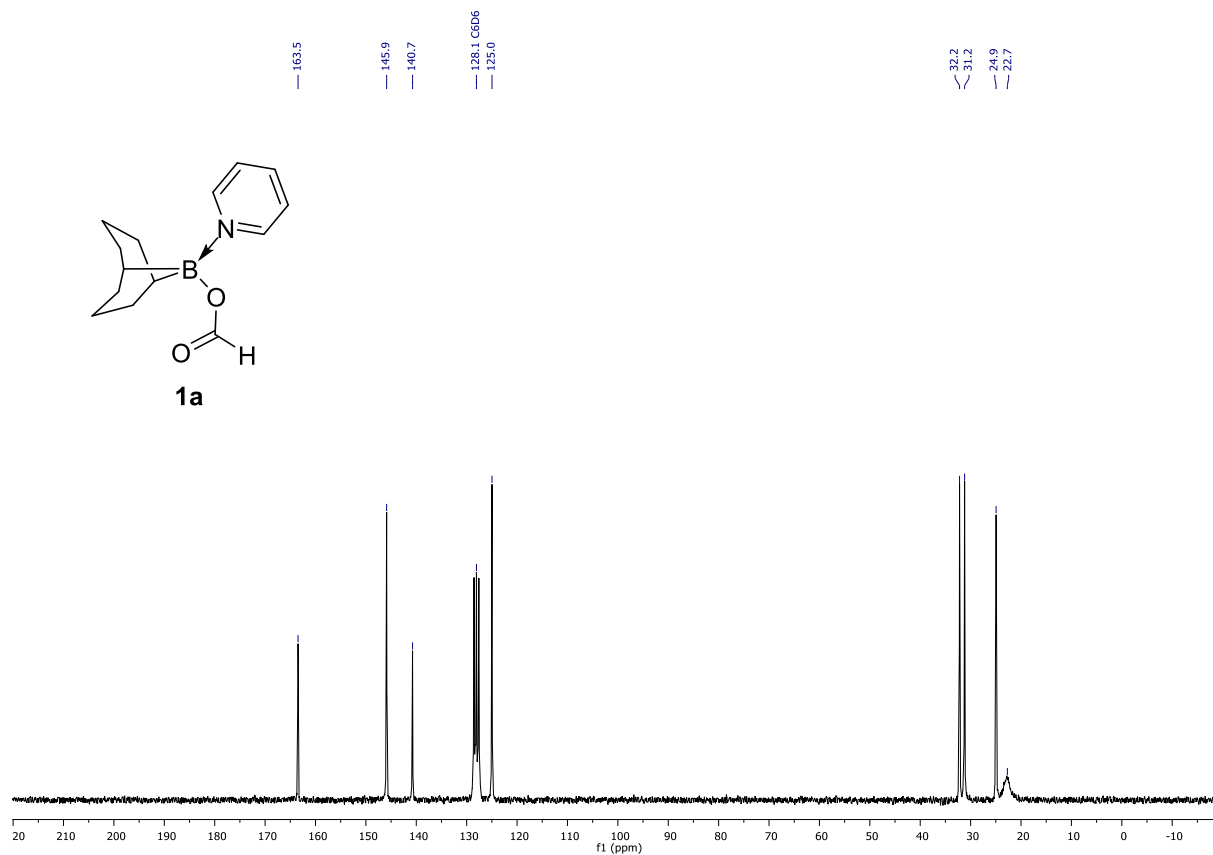


Figure S2. ^{13}C NMR spectrum obtained in C_6D_6 for formoxyborane **1a**.

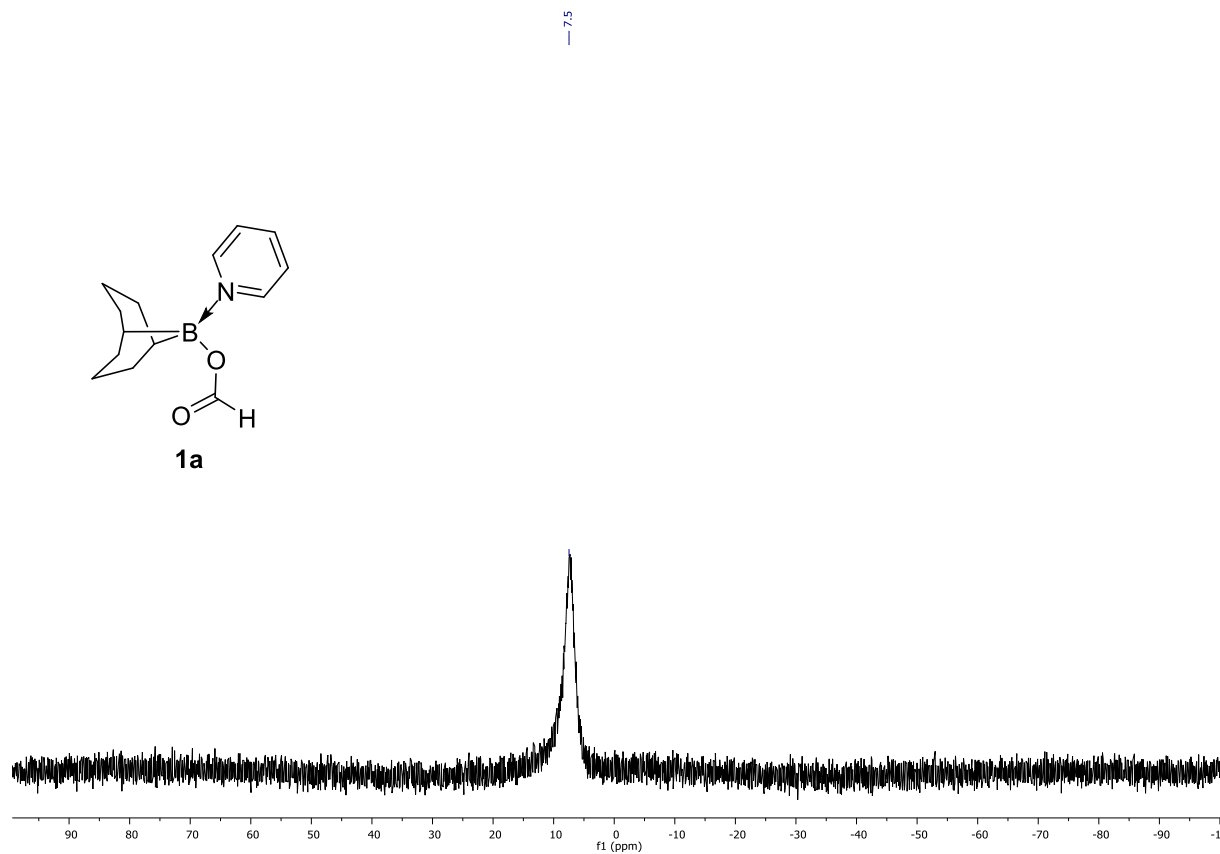


Figure S3. ^{11}B NMR spectrum obtained in C_6D_6 for formoxyborane **1a**.

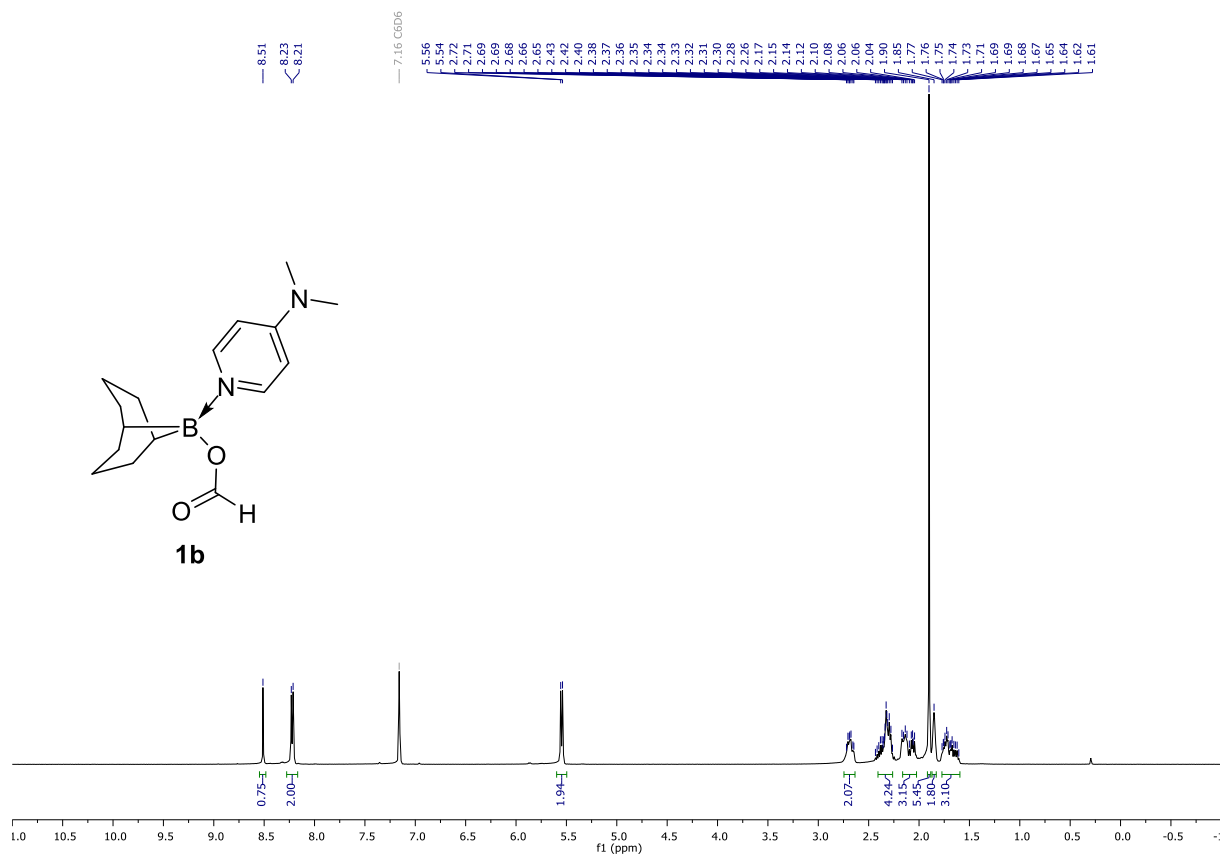


Figure S4. ^1H NMR spectrum obtained in C_6D_6 for formoxyborane **1b**.

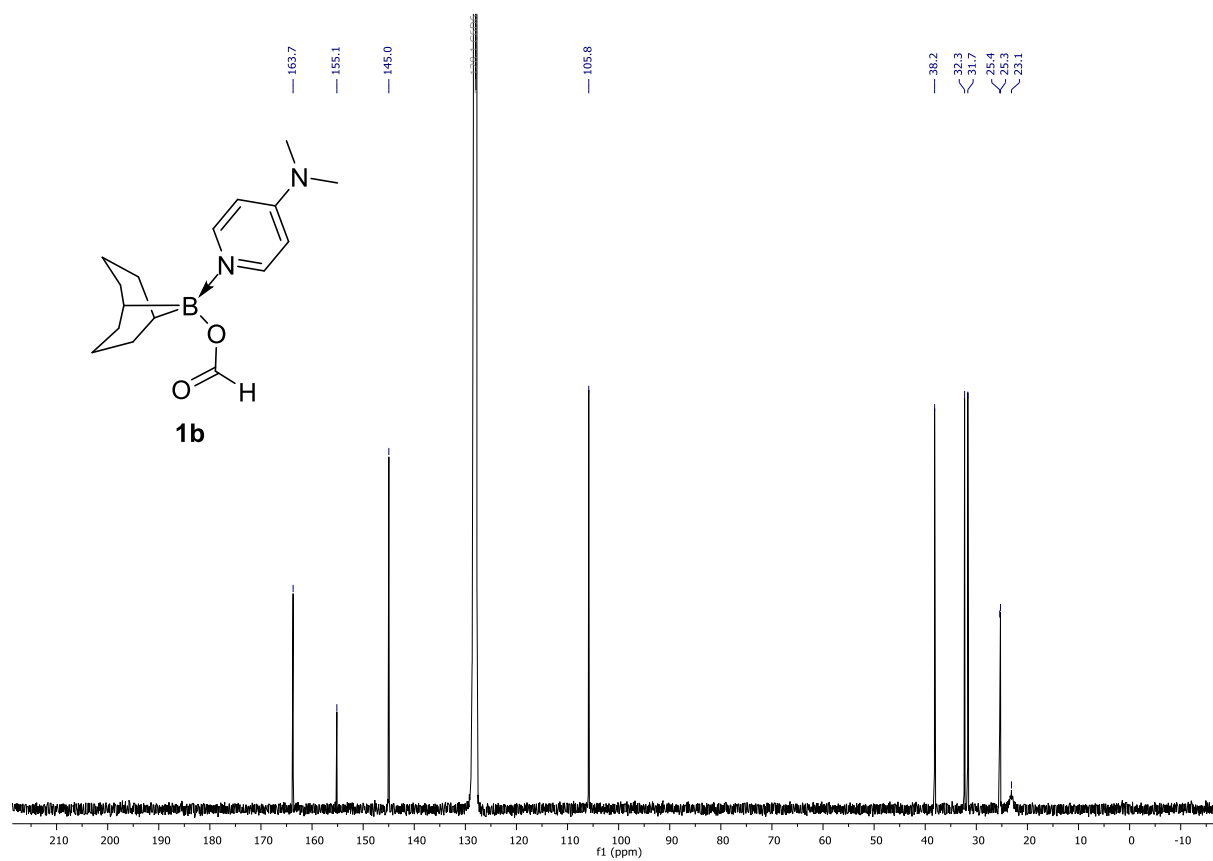


Figure S5. ^{13}C NMR spectrum obtained in C_6D_6 for formoxyborane **1b**.

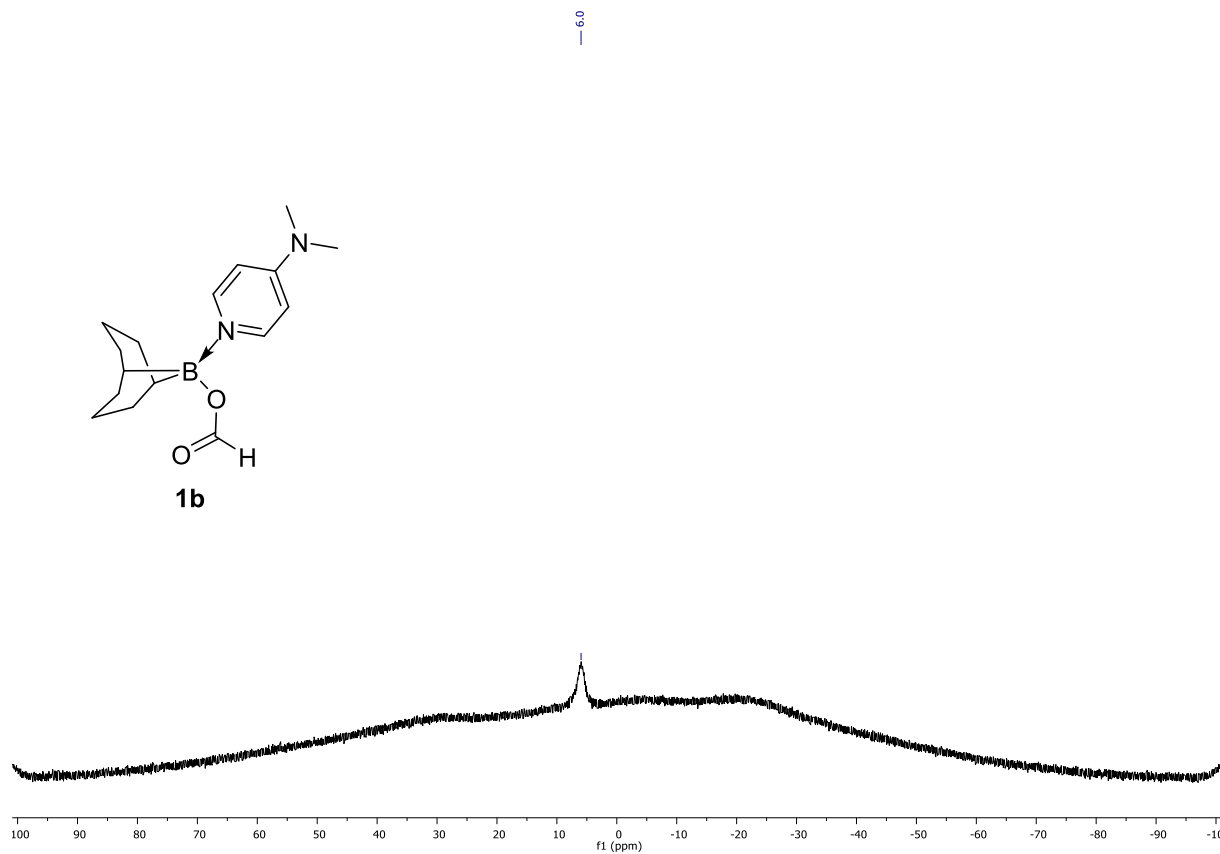


Figure S6. ^{11}B NMR spectrum obtained in C_6D_6 for formoxyborane **1b**.

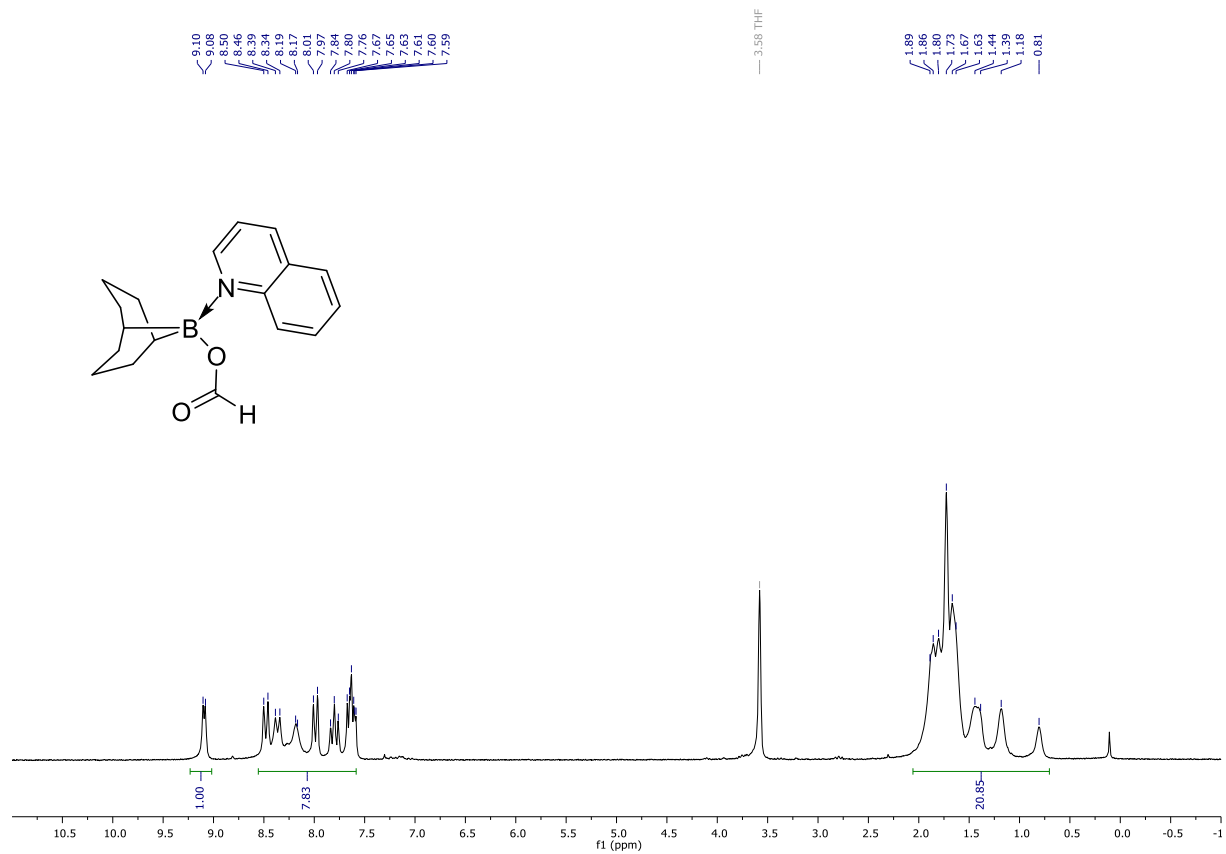


Figure S7. Impure ¹H NMR spectrum obtained in *d*₈-THF for formoxyborane with quinoline.

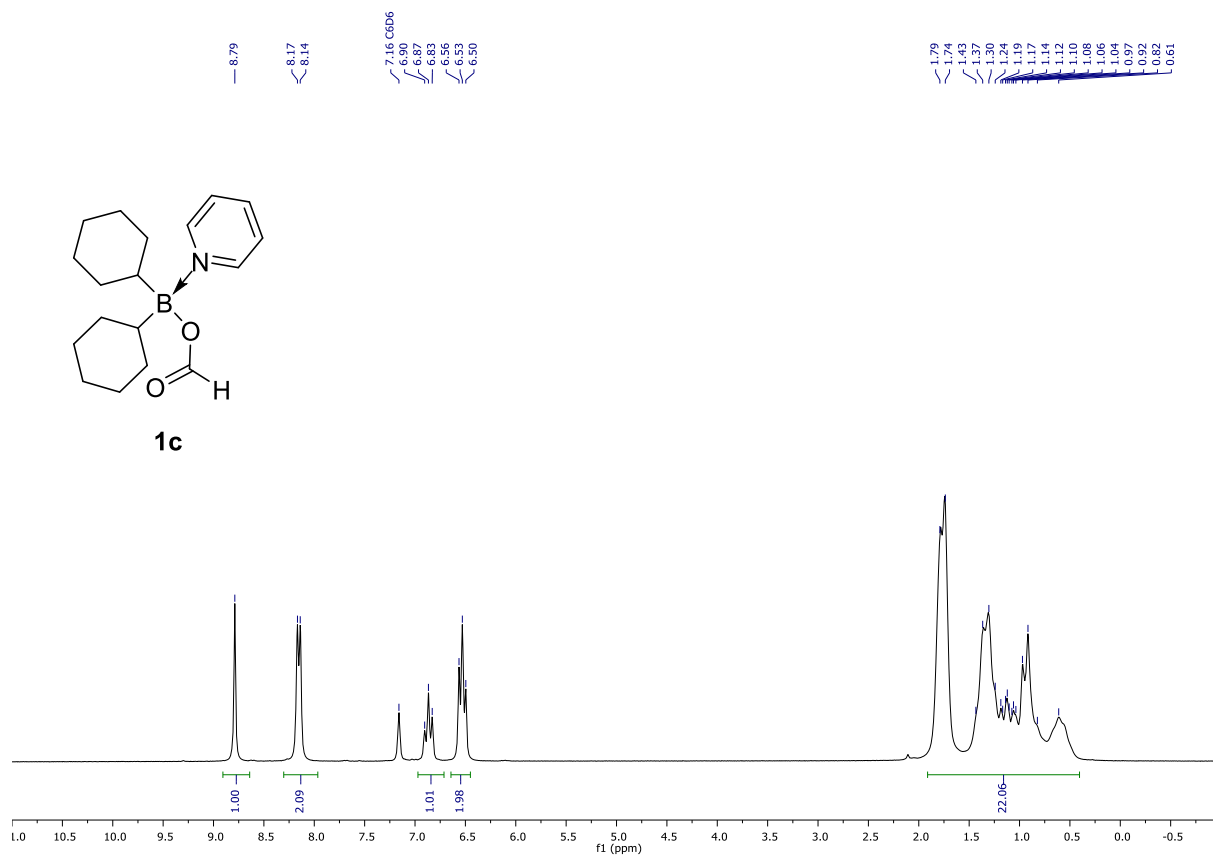


Figure S8. ¹H NMR spectrum obtained in C₆D₆ for formoxyborane **1c**.

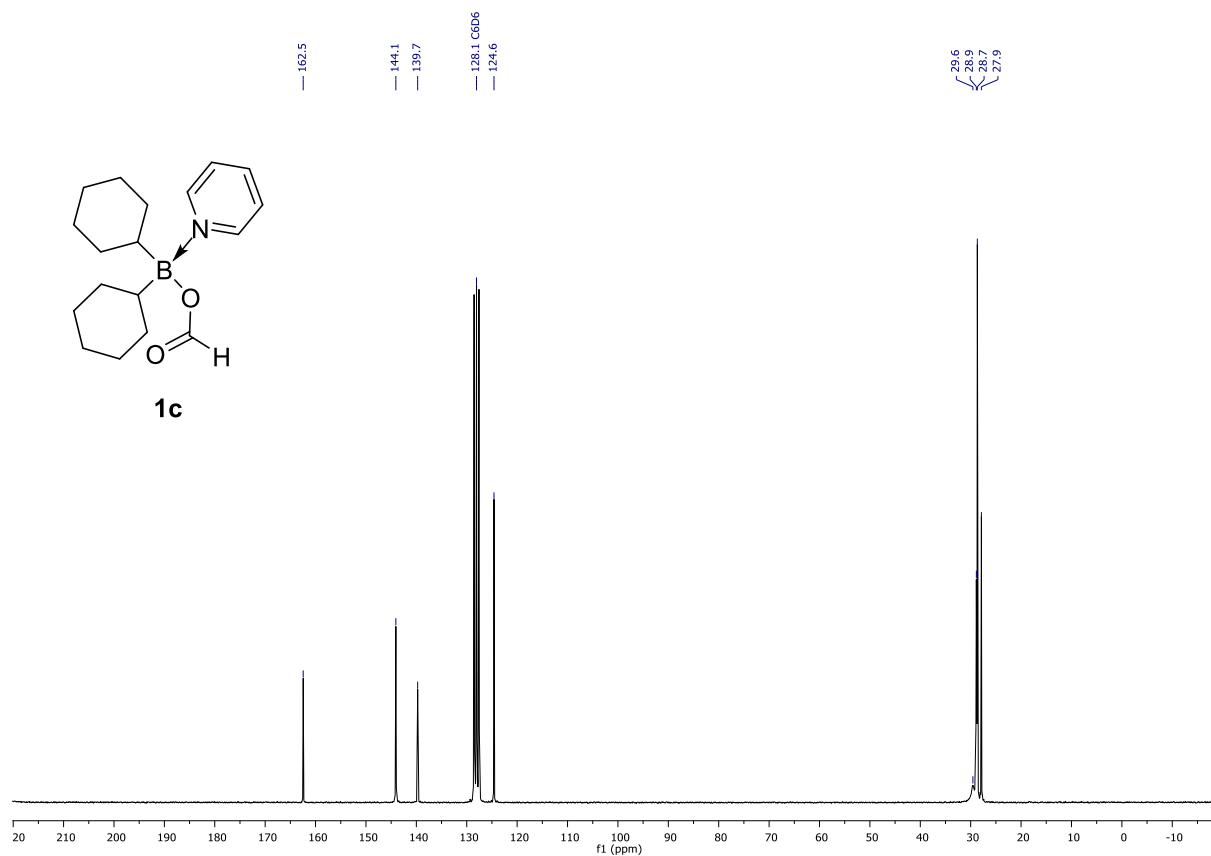


Figure S9. ^{13}C NMR spectrum obtained in C_6D_6 for formoxyborane **1c**.

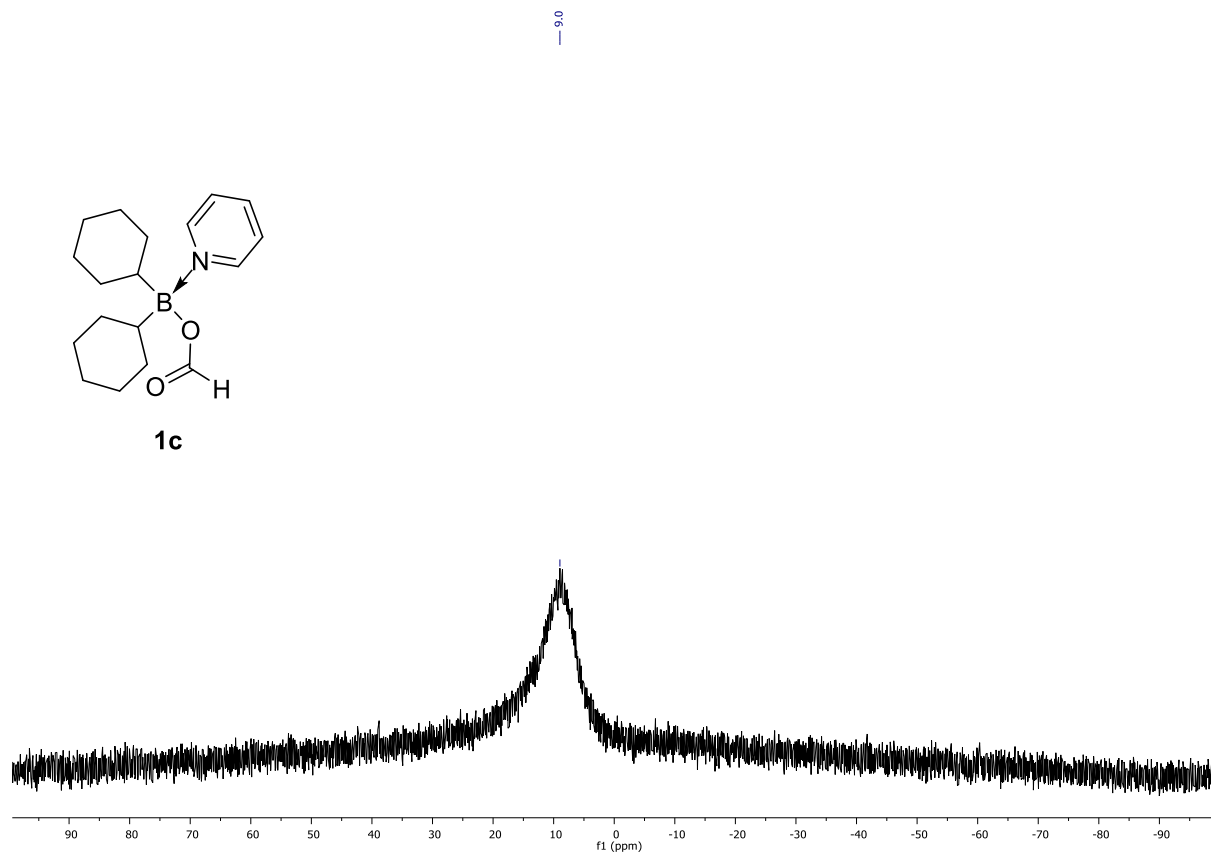


Figure S10. ^{11}B NMR spectrum obtained in C_6D_6 for formoxyborane **1c**.

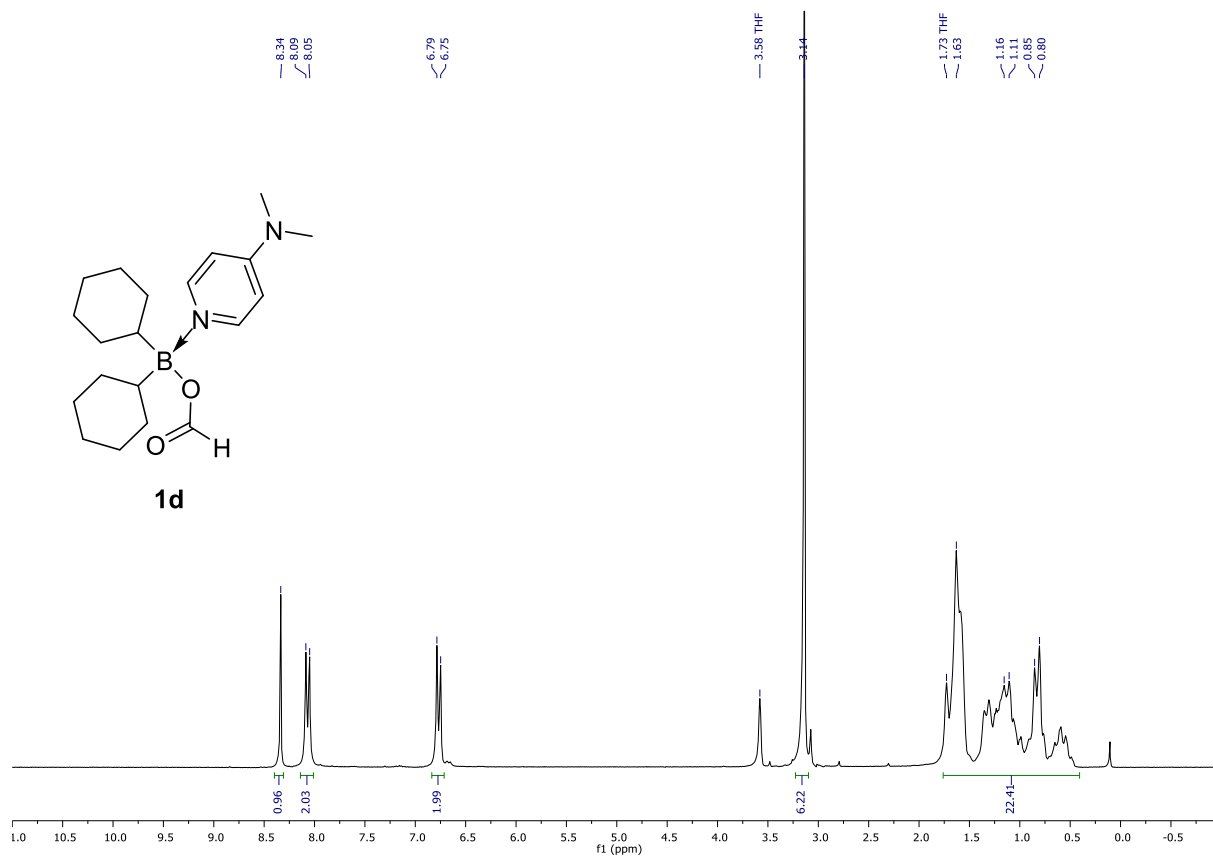


Figure S11. ^1H NMR spectrum obtained in d_8 -THF for formoxyborane **1d**.

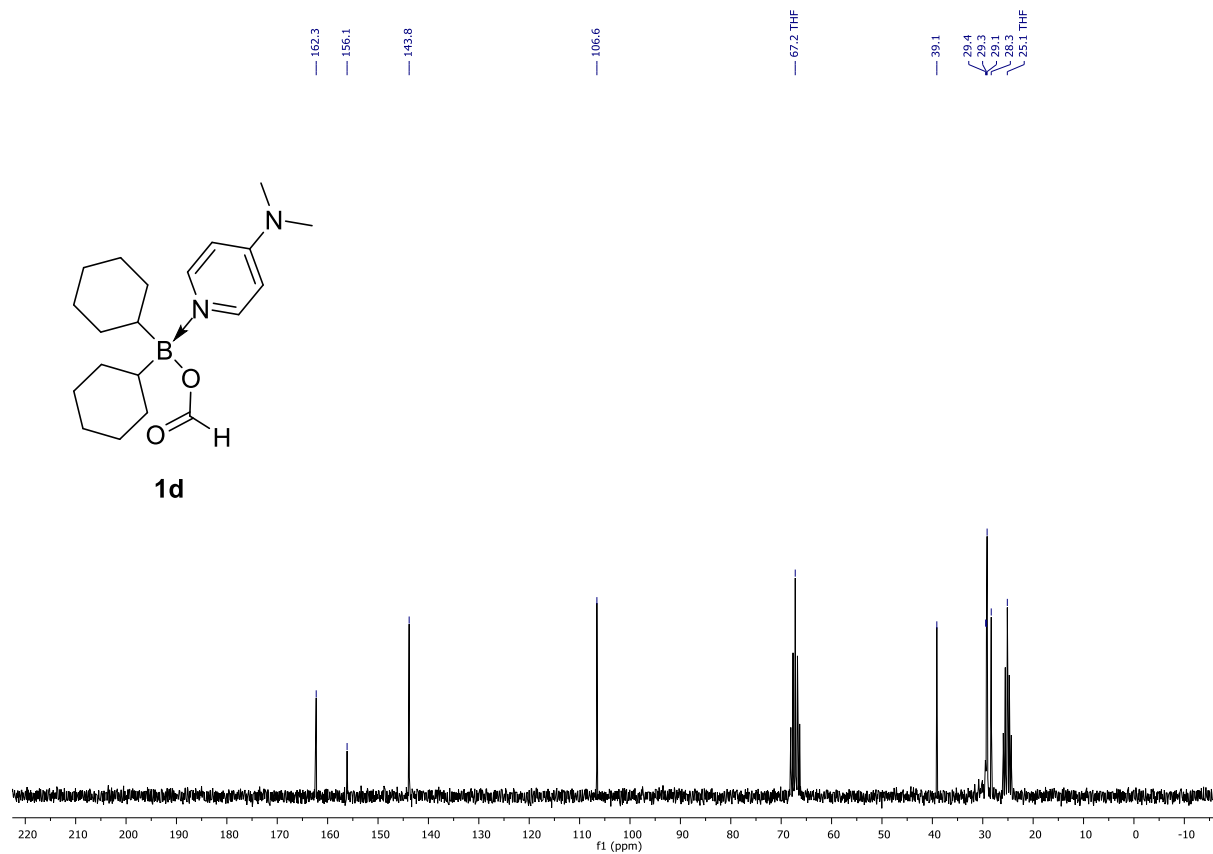


Figure S12. ^{13}C NMR spectrum obtained in d_8 -THF for formoxyborane **1d**.

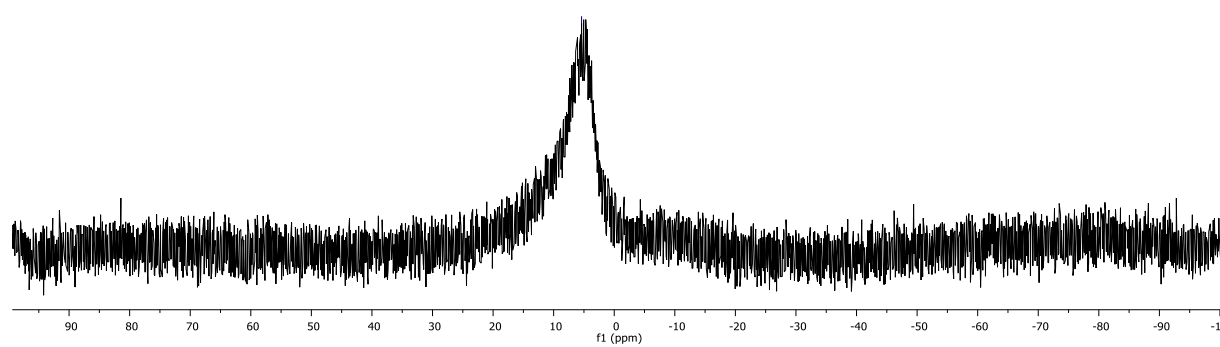
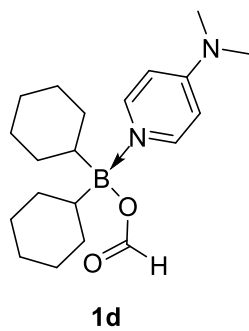


Figure S13. ¹¹B NMR spectrum obtained in *d*₈-THF for formoxyborane **1d**.

5 Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer³ using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ - and ω -scans) were processed with HKL2000.⁴ The structures were solved by intrinsic phasing with SHELXT,⁵ expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL.⁶ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH₃). In the structure of the formoxyborane hexamer, both THF solvent molecules are disordered over two positions sharing either one or two carbon atoms, which have been refined with occupancy parameters constrained to sum to unity and with restraints on bond lengths and displacement parameters. Crystal data and structure refinement parameters are given in Table S1. The molecular plots were drawn with ORTEP-3.⁷

Table S1. Crystal Data and Structure Refinement Details

| | hexamer·4TH | 1a | 1b | 1c | 1d |
|--|---|--|--|--|--|
| chemical formula | C ₉₄ H ₁₇₀ B ₆ O ₁₆ | C ₁₄ H ₂₀ BNO ₂ | C ₁₆ H ₂₅ BN ₂ O ₂ | C ₁₈ H ₂₈ BNO ₂ | C ₂₀ H ₃₃ BN ₂ O ₂ |
| M (g mol ⁻¹) | 1621.15 | 245.12 | 288.19 | 301.22 | 344.29 |
| cryst syst | triclinic | orthorhombic | monoclinic | monoclinic | monoclinic |
| space group | P $\bar{1}$ | Pbca | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ |
| a (Å) | 11.5184(6) | 10.7670(2) | 9.8725(5) | 10.1407(4) | 12.5923(8) |
| b (Å) | 14.6526(7) | 12.8036(5) | 7.3758(4) | 28.0242(11) | 10.8437(6) |
| c (Å) | 16.1480(9) | 18.9389(8) | 21.8820(12) | 12.2214(5) | 14.9151(8) |
| α (deg) | 97.730(3) | 90 | 90 | 90 | 90 |
| β (deg) | 108.931(2) | 90 | 98.551(3) | 94.627(3) | 90.370(5) |
| γ (deg) | 98.573(3) | 90 | 90 | 90 | 90 |
| V (Å ³) | 2500.0(2) | 2610.85(16) | 1575.68(15) | 3461.8(2) | 2036.6(2) |
| Z | 1 | 8 | 4 | 8 | 4 |
| T (K) | 200 | 150 | 100 | 150 | 100 |
| reflns colld | 123007 | 59510 | 70088 | 105117 | 55323 |
| indep reflns | 9438 | 2468 | 2965 | 6562 | 3861 |
| obsd reflns $[I >$ | 7006 | 2140 | 2550 | 5121 | 2652 |
| R_{int} | 0.025 | 0.018 | 0.022 | 0.031 | 0.074 |
| params refined | 588 | 163 | 192 | 397 | 228 |
| R_1 | 0.064 | 0.039 | 0.037 | 0.040 | 0.042 |
| w R_2 | 0.200 | 0.101 | 0.101 | 0.099 | 0.111 |
| S | 1.066 | 1.045 | 1.065 | 1.049 | 0.989 |
| $\Delta\rho_{\text{min}}$ (e Å ⁻³) | -0.48 | -0.18 | -0.21 | -0.17 | -0.20 |
| $\Delta\rho_{\text{max}}$ (e Å ⁻³) | 0.50 | 0.26 | 0.25 | 0.19 | 0.20 |

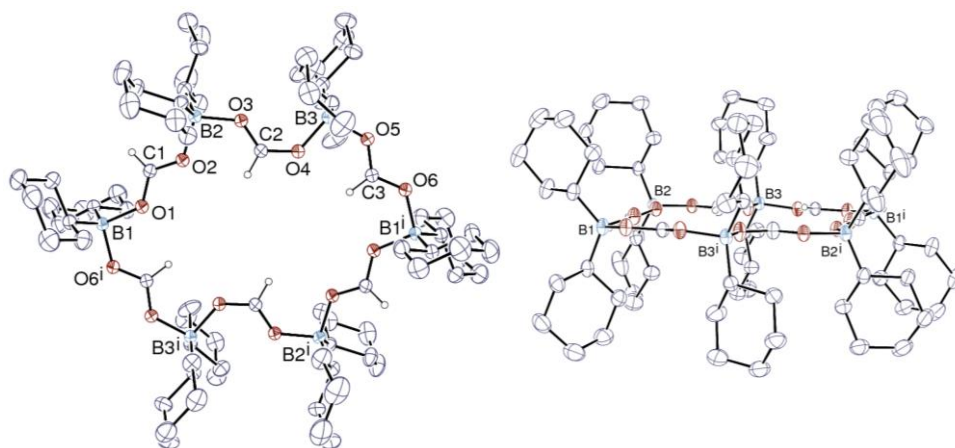


Figure S14. Two views of the formoxyborane hexamer with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted except for those of formate units. Symmetry code: $i = 1 - x, 1 - y, 1 - z$.

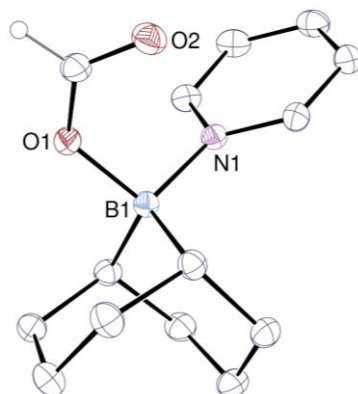


Figure S15. View of **1a** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted except for that of formate.

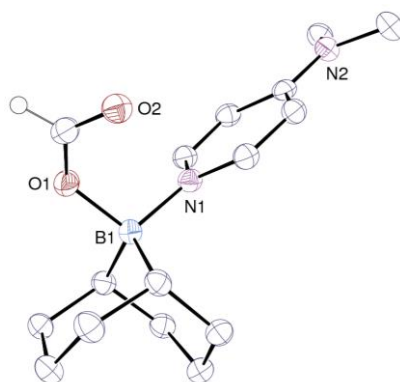


Figure S16. View of **1b** with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted except for that of formate.

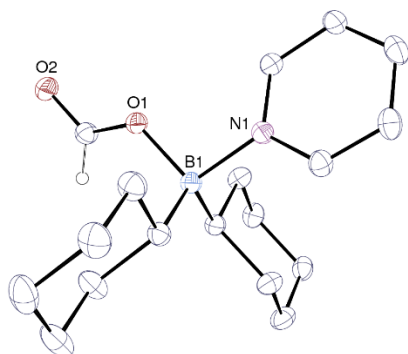


Figure S17. View of one of the two independent molecules in **1c** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted except for that of formate.

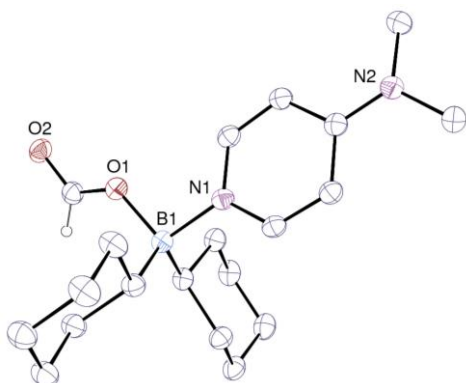


Figure S18. View of **1d** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted except for that of formate.

6 Screening of conditions

In a glovebox, a *J. Young* NMR Tube was charged with Catalyst (2 mol%), solvent (0.4 mL), acetophenone **3a** or 3-pentanone **3b** (0.1 mmol, 1.0 equiv.), trimethoxybenzene (10 mg) and the formoxyborane (1.2 equiv.). The tube was sealed, brought out of the glovebox and heated. The reaction progress was monitored by ¹H NMR spectroscopy. Yields were determined by ¹H NMR integration versus trimethoxybenzene as an internal standard.

Table S1. Screening of conditions. 0.1 mmol scale

$$\text{R-C(=O)-R'} + \text{R}_2\text{B-O-CHO} \xrightarrow[\text{Trimethoxybenzene, Solvent, T, t}]{\text{Catalyst (2 mol\%)}} \text{R-C(OBR}_2\text{)-R'}$$

R = Ph, R' = CH₃ (**3a**)
 R = R' = Et (**3b**)
1a-d (1.2 equiv.)
4

| Entry | Substrate | R | LB | Catalyst | Solvent | T (°C) | t (h) | Yield (%) |
|-------|-----------|------|------|--|---------------------------------|--------|-------|-----------|
| 1 | 3a | 9BBN | Py | - | C ₆ D ₆ | 130 | 48 | 0 |
| 2 | 3a | 9BBN | Py | [Ru(triphos)(OAc) ₂] | C ₆ D ₆ | 110 | 4.5 | 19 |
| 3 | 3a | 9BBN | Py | [Ru(PN ^H P)(H)Cl(CO)] | C ₆ D ₆ | 110 | 4.5 | 56 |
| 4 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 110 | 0.75 | 99 |
| 5 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | <i>d</i> ₈ -THF | 110 | 0.75 | 93 |
| 6 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | CD ₂ Cl ₂ | 110 | 0.75 | 5 |
| 7 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | CD ₃ CN | 110 | 0.75 | 5 |
| 8 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 4 | 99 |
| 9 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 2 | 49 |
| 10 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 70 | 40 | 71 |
| 11 | 3a | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 25 | 40 | 0 |
| 12 | 3a | 9BBN | DMAP | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 3 | 95 |
| 13 | 3a | 9BBN | DMAP | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 2 | 93 |
| 15 | 3a | Cy | DMAP | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 4 | 63 |
| 16 | 3a | Cy | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 3 | 98 |
| 17 | 3a | Cy | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 2 | 95 |
| 18 | 3b | 9BBN | DMAP | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 5 | 92 |
| 19 | 3b | 9BBN | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 5 | 50 |
| 20 | 3b | Cy | Py | [Ru(PN ^H P)(OAc) ₂] (2a) | C ₆ D ₆ | 90 | 5 | 27 |

7 General procedures

7.1 General Procedure for NMR Scale reactions (GP1)

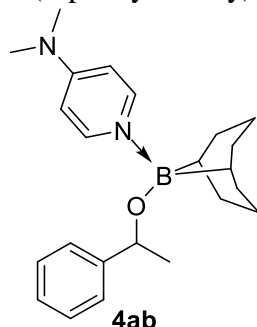
In a glovebox, a *J. Young* NMR Tube was charged with *fac*-[Ru(κ^1 -OAc)(κ^2 -OAc)(κ^3 -PN^HP^{Ph})] (**2a**) (2 mol%), 9-borabicyclo[3.3.1]nonan-9-yl formate *N,N*-dimethylaminopyridine adduct (**1b**) (1.2 equiv.), C₆D₆ (0.4 mL), ketone (0.1 mmol, 1.0 equiv.) and mesitylene (10 μ L) or trimethoxybenzene (10 mg). The tube was sealed, brought out of the glovebox and heated at 90 °C. The reaction progress was monitored by ¹H NMR spectroscopy. Yields of hydroborylated products were determined by ¹H NMR integration versus mesitylene or trimethoxybenzene as an internal standard (δ_{H} = 6.71 and 2.15 ppm in C₆D₆ for mesitylene, δ_{H} = 6.22 and 3.33 ppm in C₆D₆ for trimethoxybenzene).

7.2 General Procedure for product hydrolysis reactions (GP2)

After reaction completion, the mixture was directly concentrate to dryness in the *J. Young* NMR Tube. In a glovebox, *ds*-THF (0.4 mL) and mesitylene (if used as internal standard) (10 μ L) were added. ¹H NMR spectrum was recorded and water (20 mL) was added. The final mixture was stirred for 1h and the reaction progress was monitored by ¹H NMR spectroscopy. To isolate the final alcohol, the mixture was concentrated under reduced pressure and purify directly by column chromatography.

8 Characterization of hydroborylated compounds

9-(1-phenylethoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4ab)



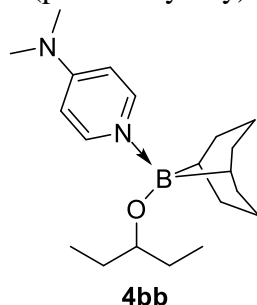
Obtained in 96% NMR Yield with trimethoxybenzene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.96 (d, J = 6.3 Hz, 2H), 7.36 (d, J = 7.3 Hz, 2H), 7.03 (t, J = 7.2 Hz, 2H), 6.96-6.84 (m, 1H), 5.62 (d, J = 6.2 Hz, 2H), 4.88 (q, J = 6.2 Hz, 1H), 2.33-2.12 (m, 10H), 2.06 (s, 6H), 1.88-1.77 (m, 2H), 1.59 (bs, 2H), 1.40 (d, J = 6.2 Hz, 2H),

¹¹B NMR (128 MHz, C₆D₆): δ = 10.4.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[8]

9-(pentan-3-yloxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4bb)



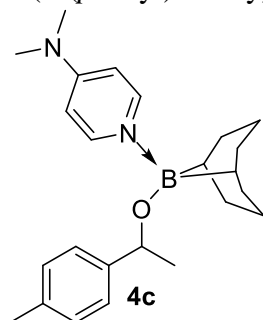
Obtained in 100% NMR Yield with trimethoxybenzene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.31 (d, J = 6.5 Hz, 2H), 8.02 (d, J = 6.4 Hz, 2H), 3.75 (q, J = 5.8 Hz, 1H), 2.22 (s, 6H), 2.05-1.93 (m, 10H), 1.60-1.51 (m, 2H), 1.50-1.38 (m, 6H), 0.88 (t, J = 7.4 Hz, 6H).

¹¹B NMR (128 MHz, C₆D₆): δ = 41.3.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[9]

9-(1-(*p*-tolyl)ethoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4c)



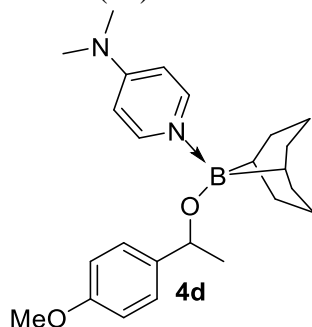
Obtained in 99% NMR Yield with trimethoxybenzene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.00 (d, J = 7.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 7.6 Hz, 2H), 5.66 (d, J = 7.3 Hz, 2H), 4.89 (q, J = 6.3 Hz, 1H), 2.31-2.14 (m, 10H), 2.09 (s, 6H), 2.07 (s, 3H), 1.85-1.77 (m, 2H), 1.58 (bs, 2H), 1.40 (d, J = 6.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 13.4.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[10]

9-(1-(4-methoxyphenyl)ethoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4d)



Obtained in 99% NMR Yield with trimethoxybenzene as internal standard (procedure GP1). After 2.5h, 87% NMR Yield was observed.

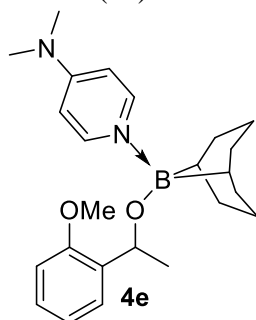
¹H NMR (400 MHz, C₆D₆): δ = 7.98 (d, J = 7.0 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 8.6 Hz, 2H), 5.68 (d, J = 7.1 Hz, 2H), 4.88 (q, J = 6.3 Hz, 1H), 3.31 (s, 3H), 2.33-2.14 (m, 10H), 2.13 (s, 6H), 1.86-1.76 (m, 2H), 1.58 (bs, 2H), 1.42 (d, J = 6.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 12.8.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[11]

9-(1-(2-methoxyphenyl)ethoxy)-9-borabicyclo[3.3.1]nonane adduct (4e)

N,N-dimethylaminopyridine



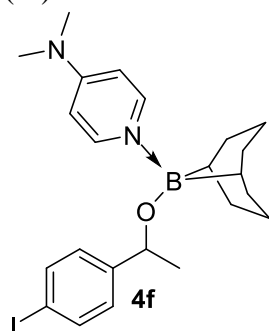
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.11 (d, J = 6.7 Hz, 2H), 7.95 (d, J = 7.4 Hz, 1H), 6.98-6.91 (m, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 8.1 Hz, 1H), 5.70 (d, J = 6.8 Hz, 2H), 5.52 (q, J = 6.2 Hz, 1H), 3.385 (s, 3H), 2.34-2.17 (m, 10H), 2.09 (s, 6H), 1.82-1.75 (m, 2H), 1.65 (bs, 2H), 1.42 (d, J = 6.2 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 13.8.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[12]

9-(1-(4-iodophenyl)ethoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4f)



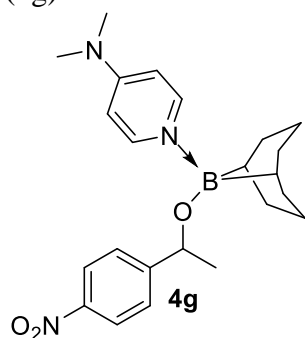
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.76 (d, J = 6.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 5.50 (d, J = 6.8 Hz, 2H), 4.68 (q, J = 6.3 Hz, 1H), 2.42-2.21 (m, 10H), 2.17 (s, 6H), 1.90-1.81 (m, 2H), 1.51 (bs, 2H), 1.38 (d, J = 6.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 9.1.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[13]

9-(1-(4-nitrophenyl)ethoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4g)



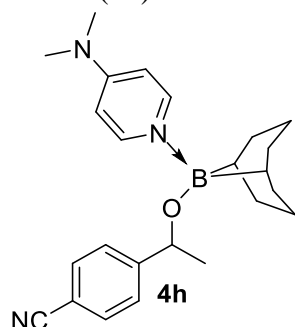
Obtained in 60% NMR Yield with trimethoxybenzene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.88 (d, J = 6.2 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 5.63 (d, J = 6.2 Hz, 2H), 4.69 (q, J = 6.3 Hz, 1H), 2.32-2.16 (m, 10H), 2.12 (s, 6H), 1.88-1.82 (m, 2H), 1.47 (bs, 2H), 1.32 (d, J = 6.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 6.8.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[14]

4-(1-9-Borabicyclo[3.3.1]nonan-9-yl)oxyethyl)benzotrile *N,N*-dimethylaminopyridine adduct (4h)



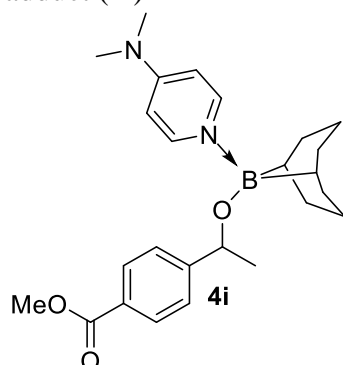
Obtained in 86% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.76 (d, J = 6.5 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 5.51 (d, J = 6.9 Hz, 2H), 4.65 (q, J = 6.3 Hz, 1H), 2.37-2.22 (m, 10H), 2.13 (s, 6H), 1.89-1.81 (m, 2H), 1.47 (bs, 2H), 1.28 (d, J = 6.3 Hz, 2H).

¹¹B NMR (128 MHz, C₆D₆): δ = 7.3.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[14]

Methyl 4-(1-(9-Borabicyclo[3.3.1]nonan-9-yl)oxy)ethyl)benzoate *N,N*-dimethylaminopyridine adduct (4i)



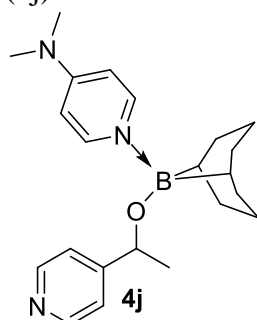
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.81 (d, J = 8.2 Hz, 4H), 7.21 (d, J = 8.2 Hz, 2H), 5.51 (d, J = 7.7 Hz, 2H), 4.80 (q, J = 6.3 Hz, 1H), 3.50 (s, 3H), 2.37-2.17 (m, 10H), 2.08 (s, 6H), 1.90-1.81 (m, 2H), 1.53 (bs, 2H), 1.39 (d, J = 6.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 8.7.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[15]

4-(1-(9-Borabicyclo[3.3.1]nonan-9-yl)oxy)ethyl)pyridine *N,N*-dimethylaminopyridine adduct (4j)



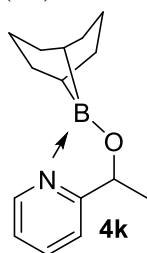
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.28 (d, J = 6.0 Hz, 2H), 7.89 (d, J = 6.9 Hz, 2H), 7.00 (d, J = 6.0 Hz, 2H), 5.62 (d, J = 7.2 Hz, 2H), 4.67 (q, J = 6.4 Hz, 1H), 2.38-2.20 (m, 10H), 2.08 (s, 6H), 1.88-1.79 (m, 2H), 1.51 (bs, 2H), 1.28 (d, J = 6.4 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 7.4.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[16]

2-(1-(9-Borabicyclo[3.3.1]nonan-9-yl)oxy)ethyl)pyridine *N,N*-dimethylaminopyridine adduct (4k)



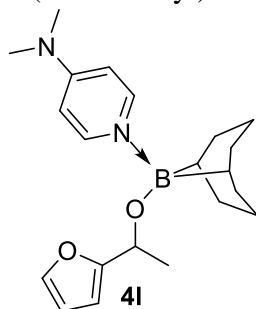
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.41 (d, J = 5.6 Hz, 2H), 8.36 (d, J = 5.7 Hz, 1H), 6.88 (t, J = 7.7 Hz, 1H), 6.47 (d, J = 8.1 Hz, 1H), 6.41 (t, J = 6.5 Hz, 1H), 6.12 (d, J = 5.7 Hz, 2H), 5.14 (q, J = 6.6 Hz, 1H), 2.63-2.32 (m, 8H), 2.28 (s, 6H), 2.25-2.17 (m, 4H), 2.02-1.94 (m, 2H), 2.80 (d, J = 6.6 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 12.1.

This product was not possible to hydrolyze, presumably due to the intramolecular N-B bond.

9-(1-furan-2-yl)ethoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4l)



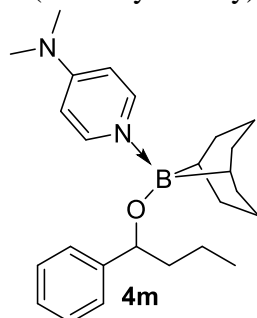
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.05 (d, J = 6.8 Hz, 2H), 7.01 (s, 1H), 6.10 (d, J = 2.9 Hz, 1H), 6.04-6.00 (m, 1H), 5.81 (d, J = 6.8 Hz, 2H), 4.96 (q, J = 6.4 Hz, 1H), 2.33-2.18 (m, 10H), 2.14 (s, 6H), 1.88-1.81 (m, 2H), 1.52 (bs, 2H), 1.41 (d, J = 6.4 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 10.3.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[17]

9-(1-Phenylbutoxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4m)



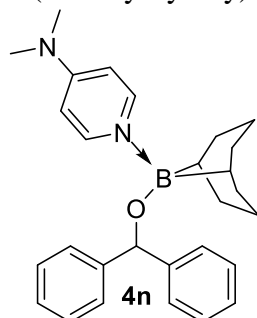
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.90 (d, J = 7.0 Hz, 2H), 7.20 (d, J = 7.2 Hz, 2H), 6.98-6.92 (m, 2H), 6.88-6.82 (m, 1H), 5.60 (d, J = 7.1 Hz, 2H), 4.76 (t, J = 6.3 Hz, 1H), 2.40-1.3 (m, 18H), 2.10 (s, 6H), 0.89 (t, J = 7.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 14.6.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[15]

9-(Benzhydryloxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4n)



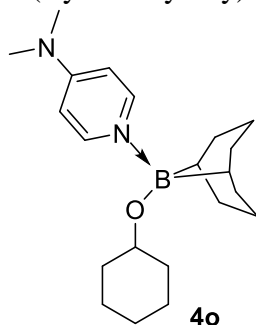
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 7.85 (d, J = 6.4 Hz, 2H), 7.48 (d, J = 7.8 Hz, 4H), 7.04-7.98 (m, 4H), 7.90-6.83 (m, 2H), 5.77 (s, 1H), 5.45 (d, J = 6.6 Hz, 2H), 2.37-2.18 (m, 10H), 2.02 (s, 6H), 1.89-1.82 (m, 2H), 1.65 (bs, 2H).

¹¹B NMR (128 MHz, C₆D₆): δ = 8.8.

Hydrolyzed alcohol product obtained in 97% yield from the borylated compound crude mixture (procedure GP2).^[18]

9-(Cyclohexyloxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4o)



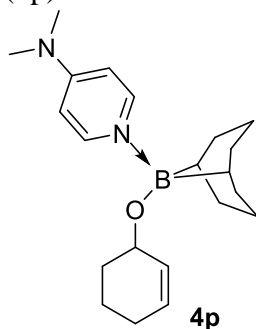
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.24 (d, *J* = 7.0 Hz, 2H), 5.93 (d, *J* = 6.9 Hz, 2H), 3.84-3.72 (m, 1H), 2.14 (m, 6H), 2.32-1.10 (m, 25H).

¹¹B NMR (128 MHz, C₆D₆): δ = 26.1.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[19]

9-(Cyclohex-2-en-1-yloxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4p)



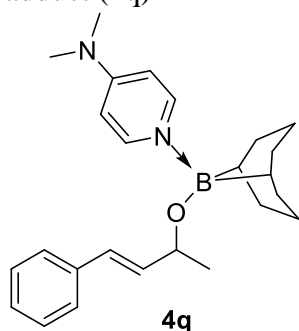
Obtained in 90% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.19 (d, *J* = 6.9 Hz, 2H), 5.90 (d, *J* = 6.8 Hz, 2H), 5.65-5.55 (m, 2H), 4.40-4.30 (m, 1H), 2.14 (m, 6H), 2.35-1.45 (m, 23H).

¹¹B NMR (128 MHz, C₆D₆): δ = 17.2.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[20]

9-(((E)-4-Phenylbut-3-en-2-yl)oxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4q)



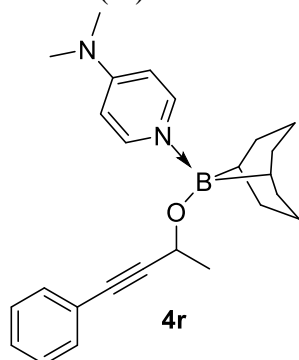
Obtained in 93% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.09 (d, J = 7.0 Hz, 2H), 7.03-6.93 (m, 5H), 6.09 (d, J = 16.0 Hz, 1H), 5.92 (dd, J = 6.9, 16.0 Hz, 1H), 5.72 (d, J = 7.0 Hz, 2H), 4.43-4.33 (m, 1H), 2.40-2.18 (m, 10H), 2.03 (s, 6H), 1.93-1.87 (m, 2H), 1.55 (bs, 2H), 1.41 (d, J = 6.3 Hz, 3H).

¹¹B NMR (128 MHz, C₆D₆): δ = 10.1.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[21]

9-(((4-Phenylbut-3-yn-2-yl)oxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4r)



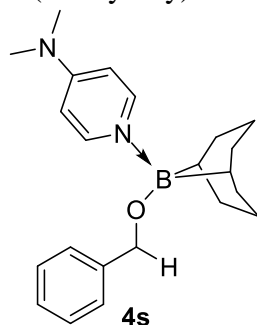
Obtained in 62% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.20-8.14 (m, 2H), 7.07-7.01 (m, 2H), 6.95-6.87 (m, 3H), 5.80 (d, J = 6.3 Hz, 2H), 4.76 (q, J = 6.5 Hz, 1H), 2.47-2.20 (m, 10H), 2.07 (s, 6H), 1.93-1.86 (m, 2H), 1.67 (d, J = 6.5 Hz, 3H), 1.56 (bs, 2H).

¹¹B NMR (128 MHz, C₆D₆): δ = 6.4.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[22]

9-(Benzyloxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4s)



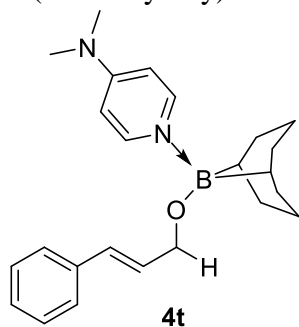
Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.07 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H), 7.21-7.15 (m, 2H), 7.04 (t, J = 7.3 Hz, 1H), 5.71 (d, J = 7.1 Hz, 2H), 4.53 (s, 2H), 2.40-2.22 (m, 10H), 2.06 (s, 6H), 1.96-1.87 (m, 2H), 1.59 (bs, 2H).

¹¹B NMR (128 MHz, C₆D₆): δ = 8.4.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[23]

9-(Cinnamyloxy)-9-borabicyclo[3.3.1]nonane *N,N*-dimethylaminopyridine adduct (4t)



Obtained in 99% NMR Yield with mesitylene as internal standard (procedure GP1).

¹H NMR (400 MHz, C₆D₆): δ = 8.09 (d, J = 7.0 Hz, 2H), 7.20-7.14 (m, 2H), 7.08-7.02 (m, 2H), 6.97 (t, J = 7.3 Hz, 1H), 6.75-6.72 (m, 1H), 6.36 (dt, J = 4.8, 15.8 Hz, 1H), 5.74 (d, J = 7.1 Hz, 2H), 4.20-4.14 (m, 2H), 2.38-2.22 (m, 10H), 2.07 (s, 6H), 1.96-1.88 (m, 2H), 1.57 (bs, 2H).

¹¹B NMR (128 MHz, C₆D₆): δ = 8.7.

Hydrolyzed alcohol product obtained in 99% yield from the borylated compound crude mixture (procedure GP2).^[23]

9 NMR Spectra of hydroborated compounds

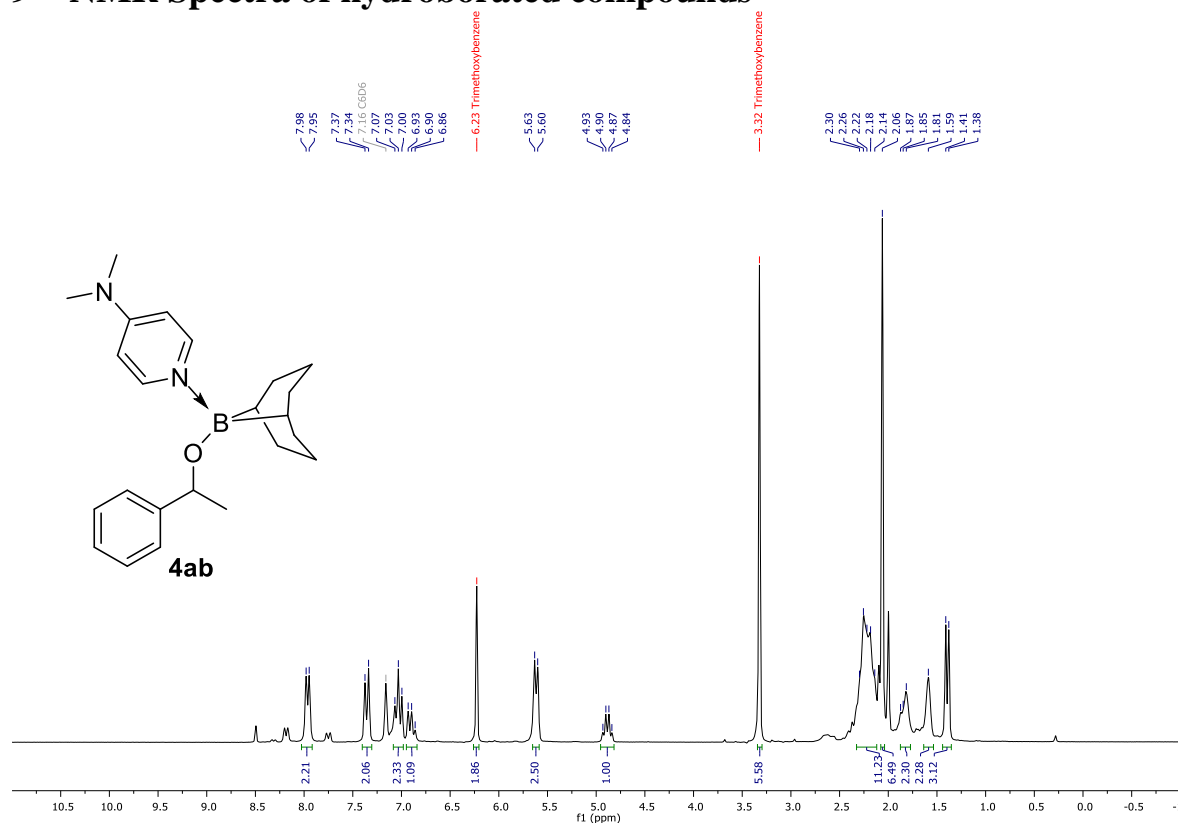


Figure S14. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4ab**. Crude reaction mixture.

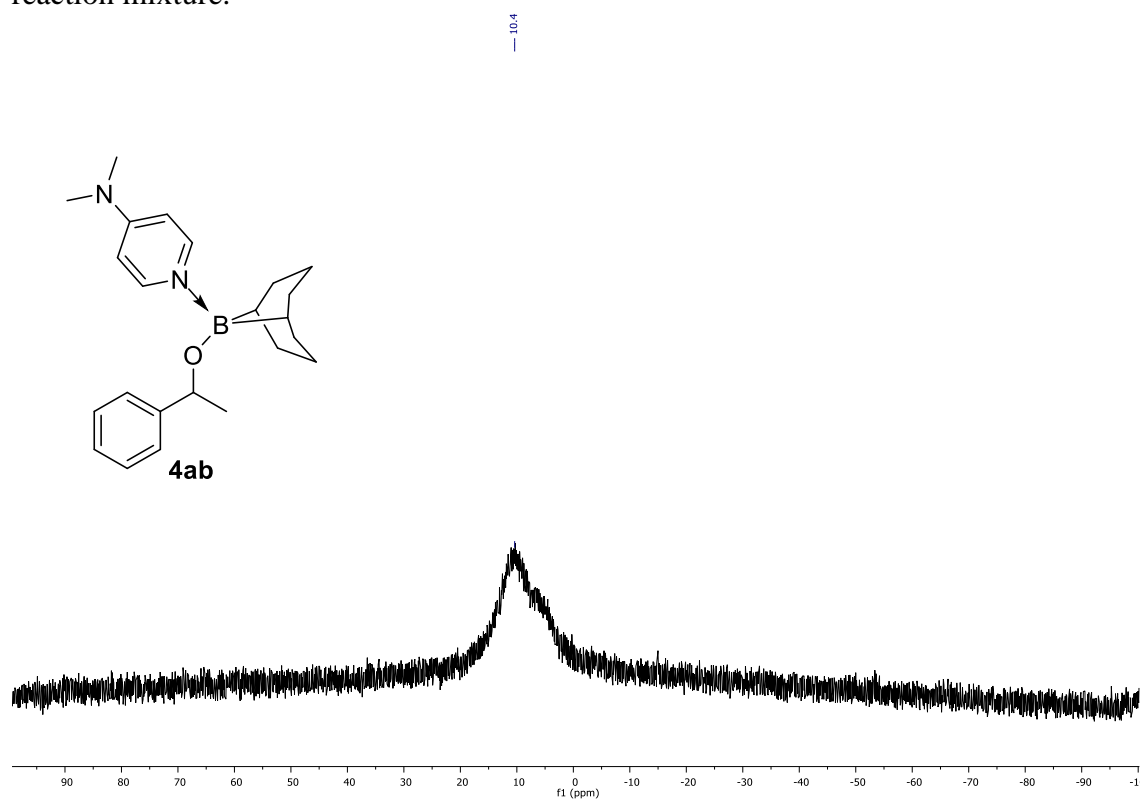


Figure S15. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4ab**. Crude reaction mixture.

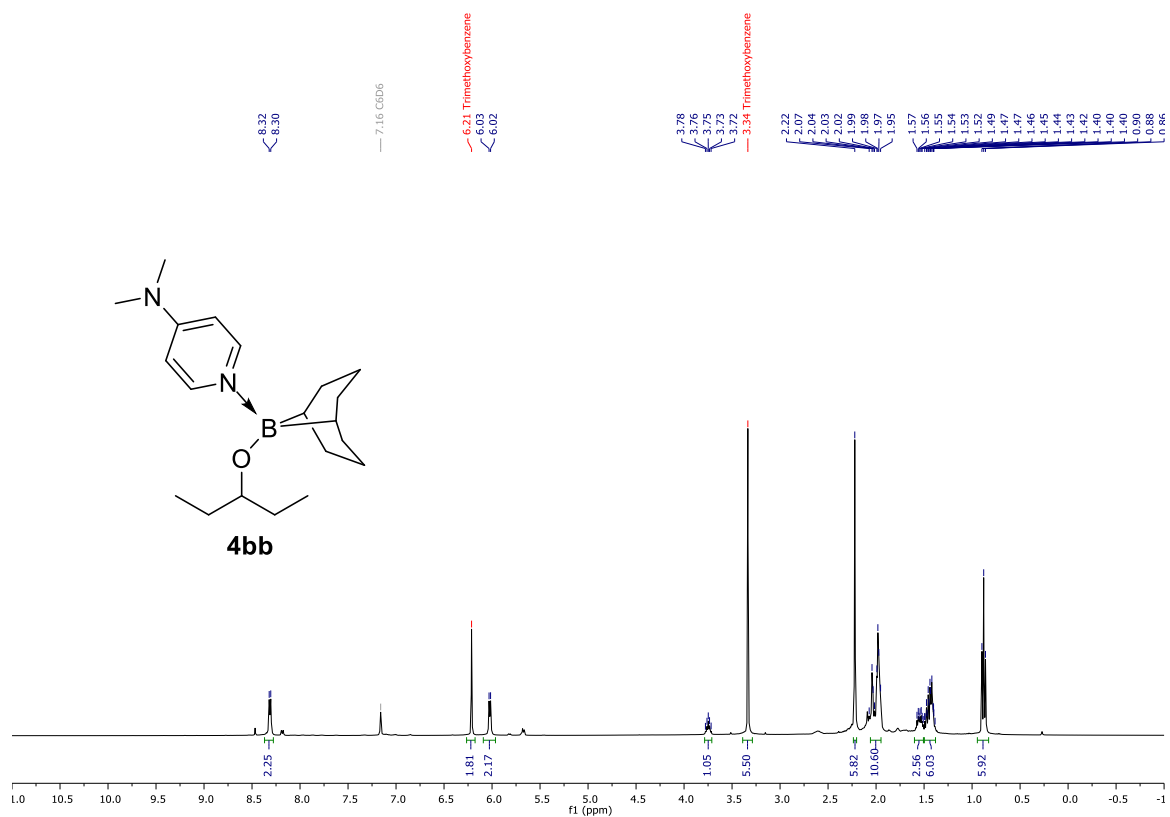


Figure S16. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4bb**. Crude reaction mixture.

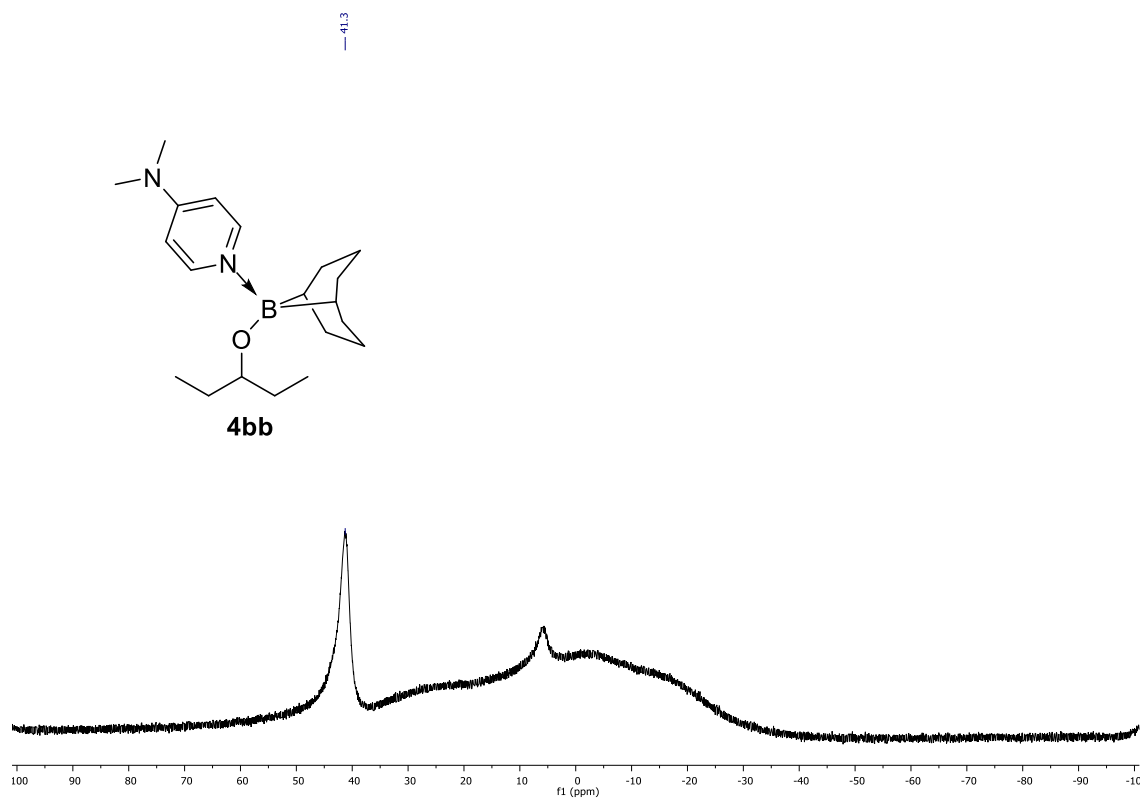


Figure S17. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4bb**. Crude reaction mixture.

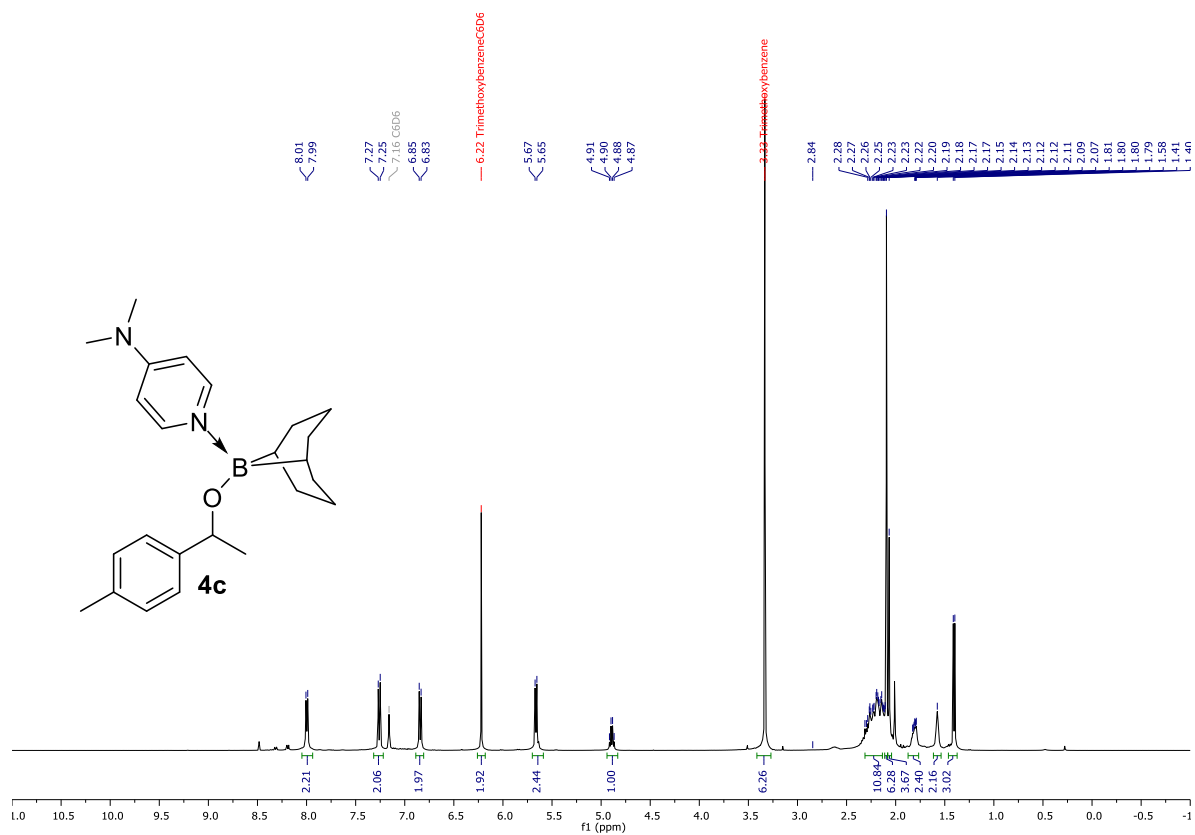


Figure S18. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4c**. Crude reaction mixture.

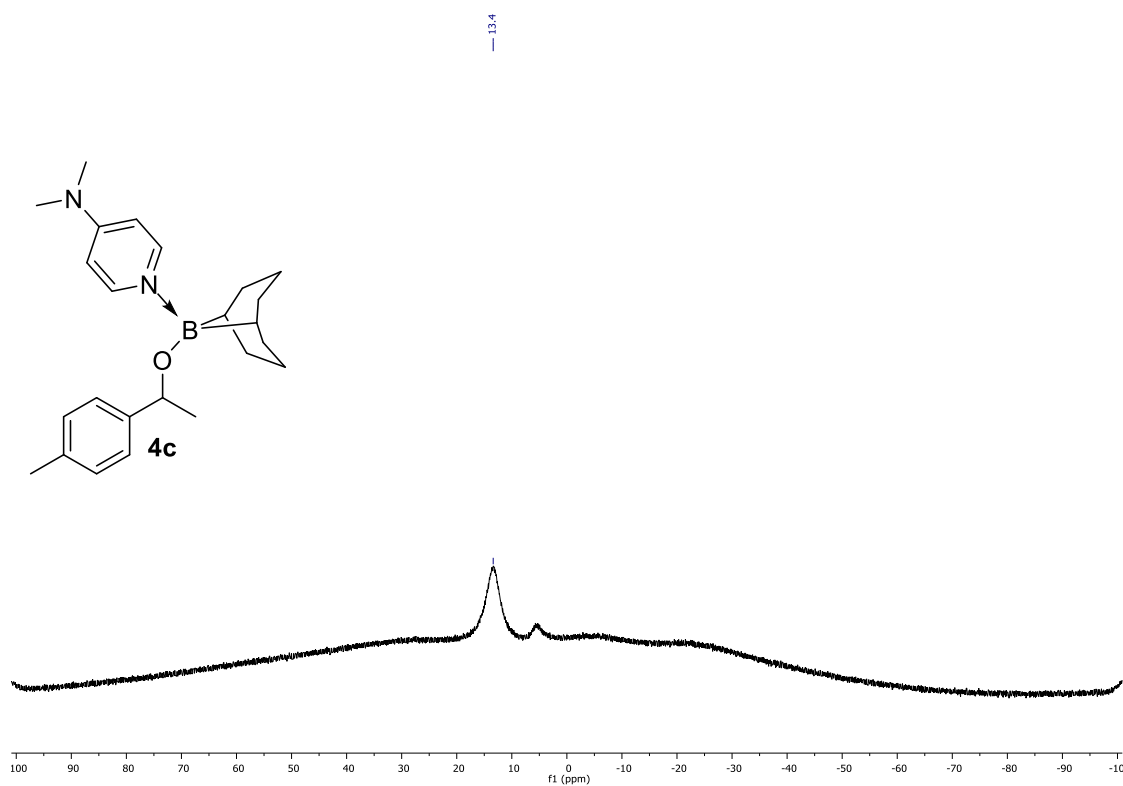


Figure S19. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4c**. Crude reaction mixture.

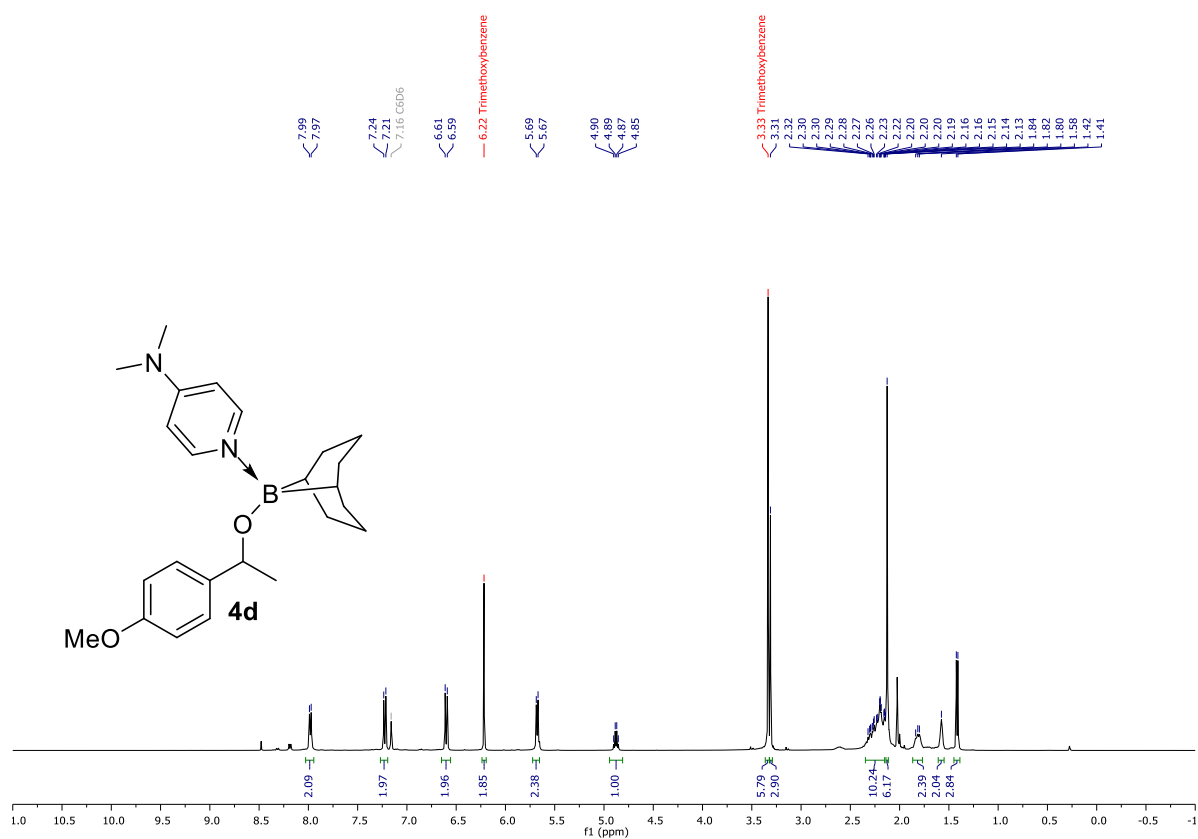


Figure S20. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4d**. Crude reaction mixture.

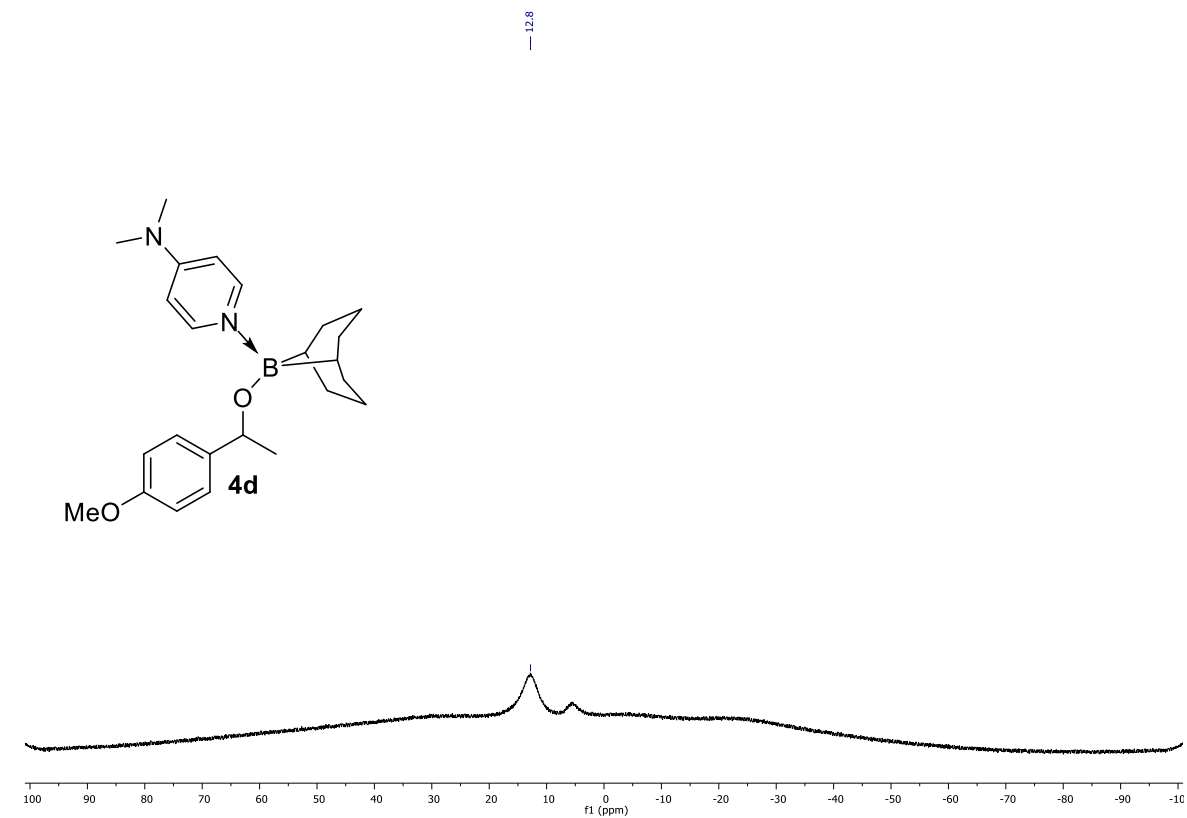


Figure S21. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4d**. Crude reaction mixture.

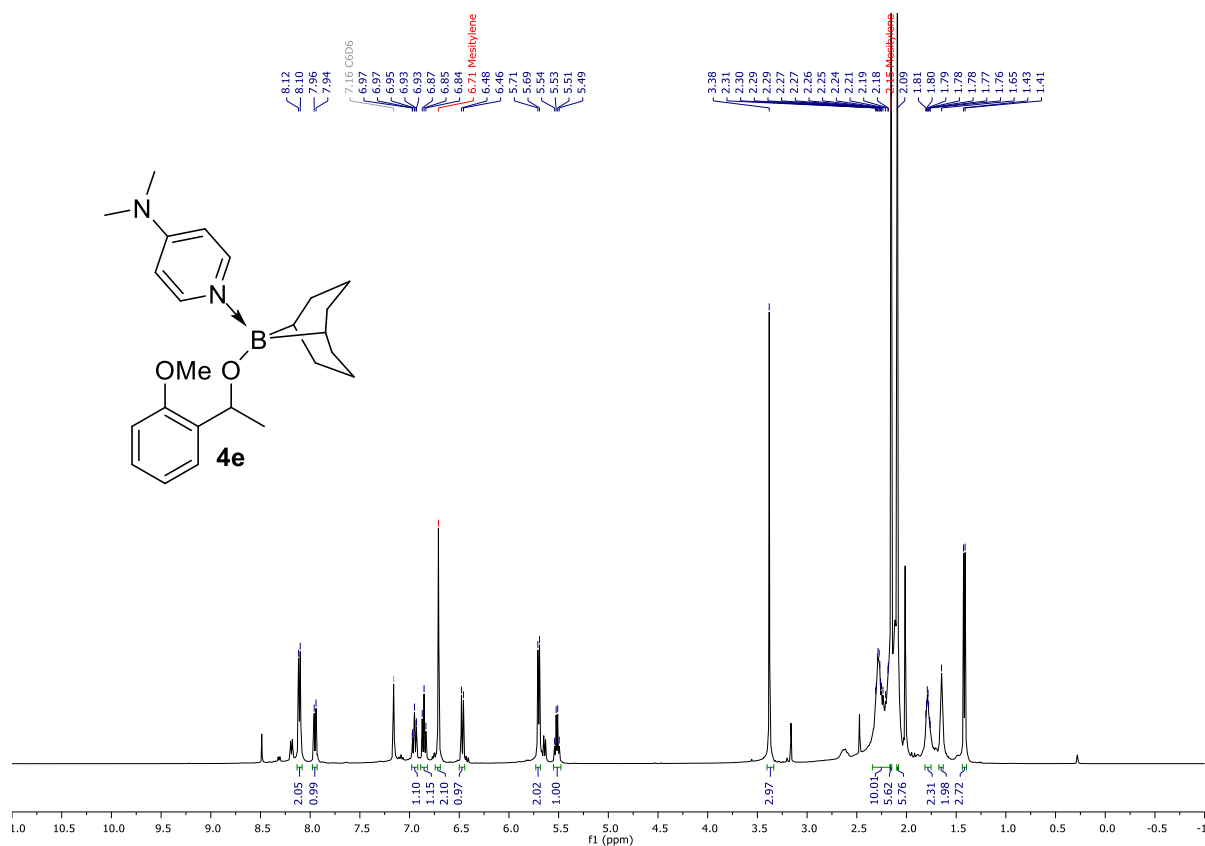


Figure S22. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4e**. Crude reaction mixture.

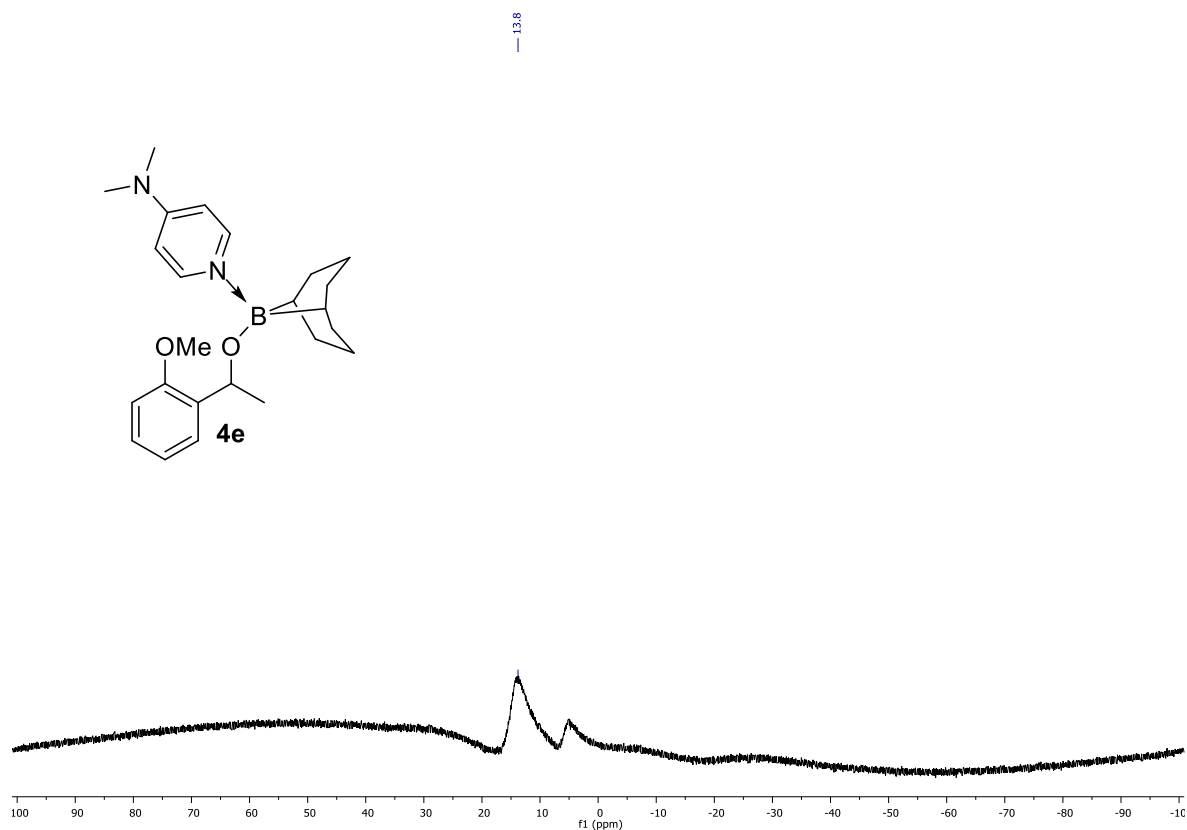


Figure S23. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4e**. Crude reaction mixture.

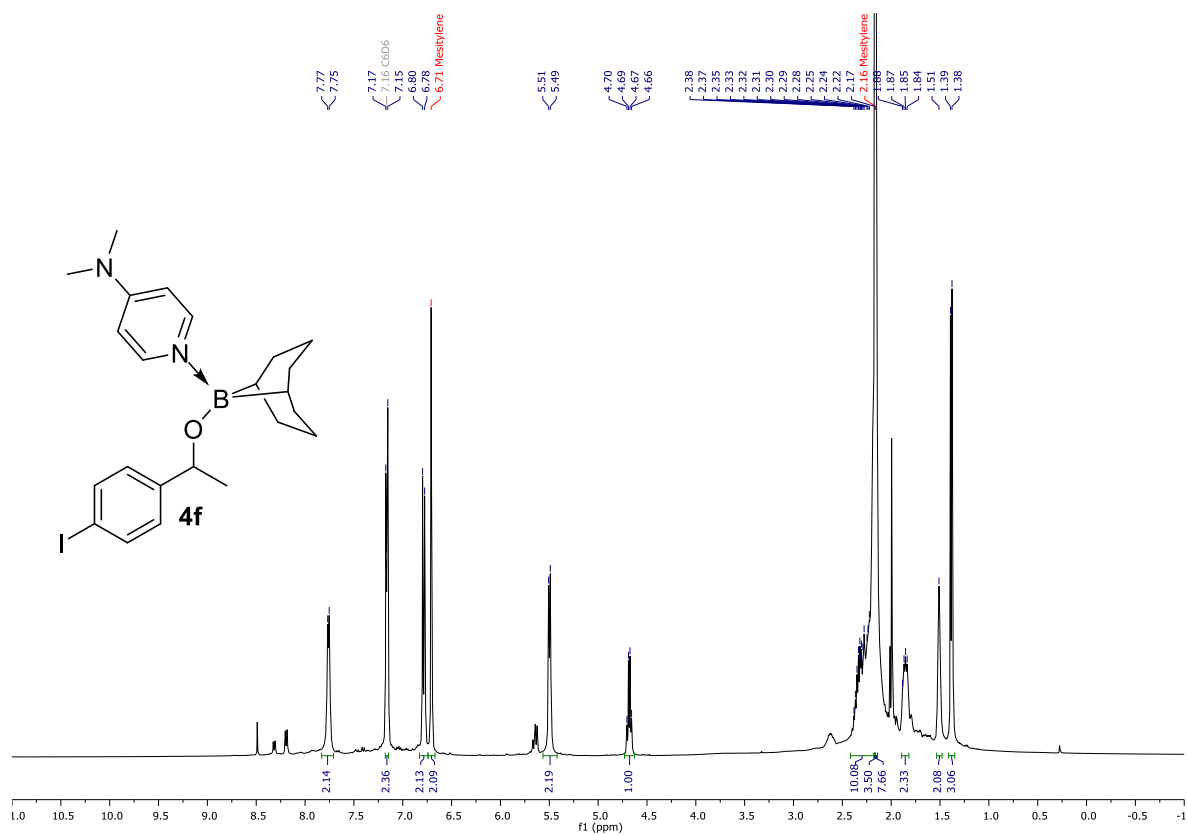


Figure S24. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4f**. Crude reaction mixture.

— 9.1

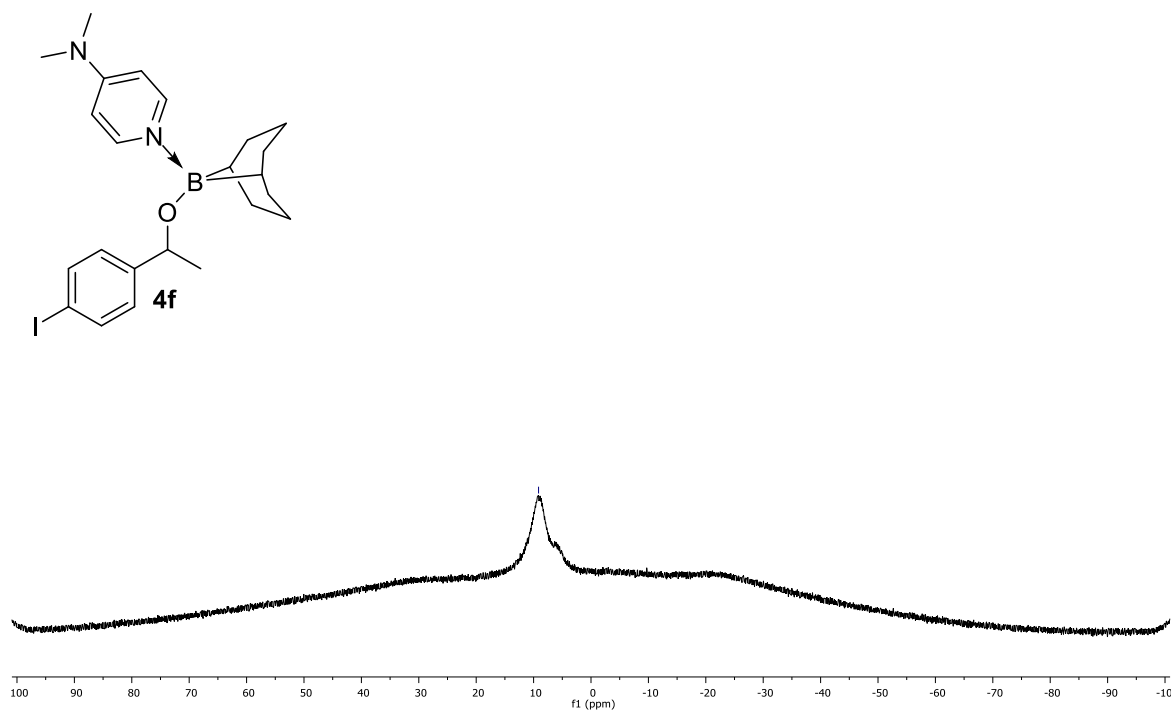


Figure S25. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4f**. Crude reaction mixture.

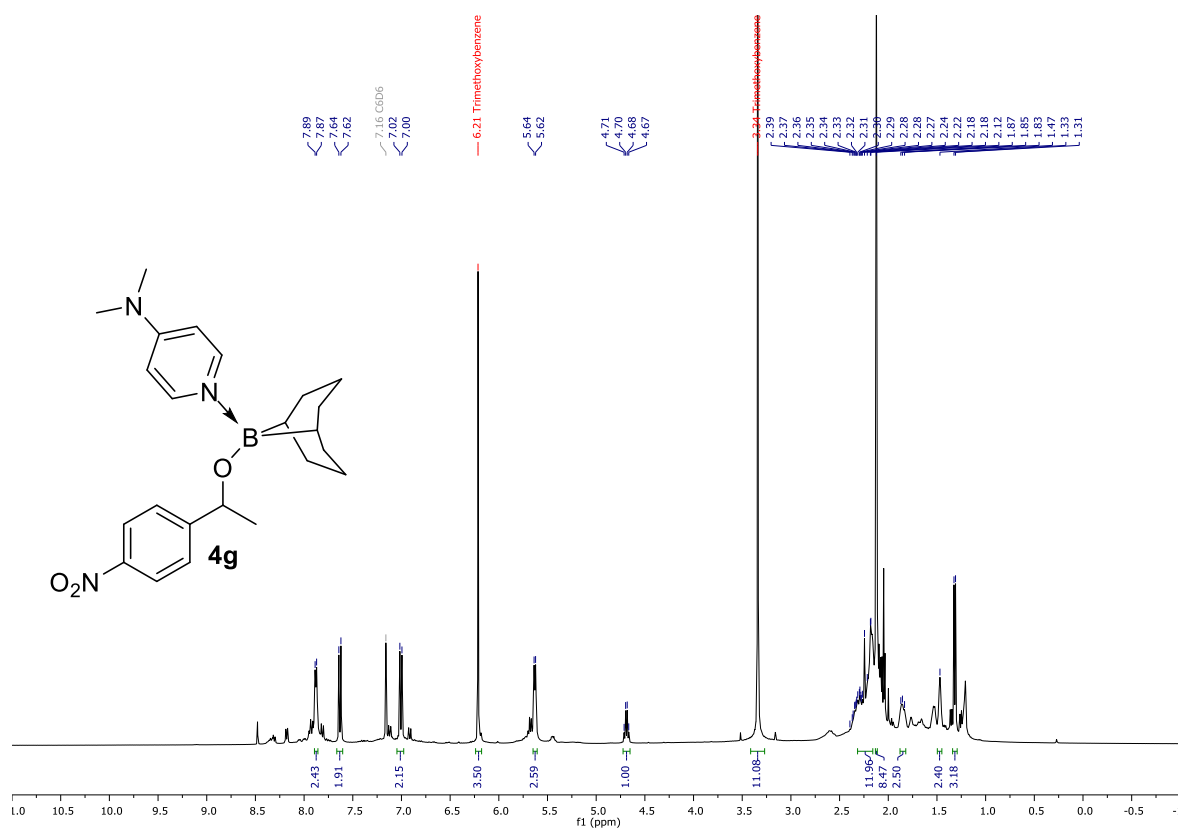


Figure S26. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4g**. Crude reaction mixture.

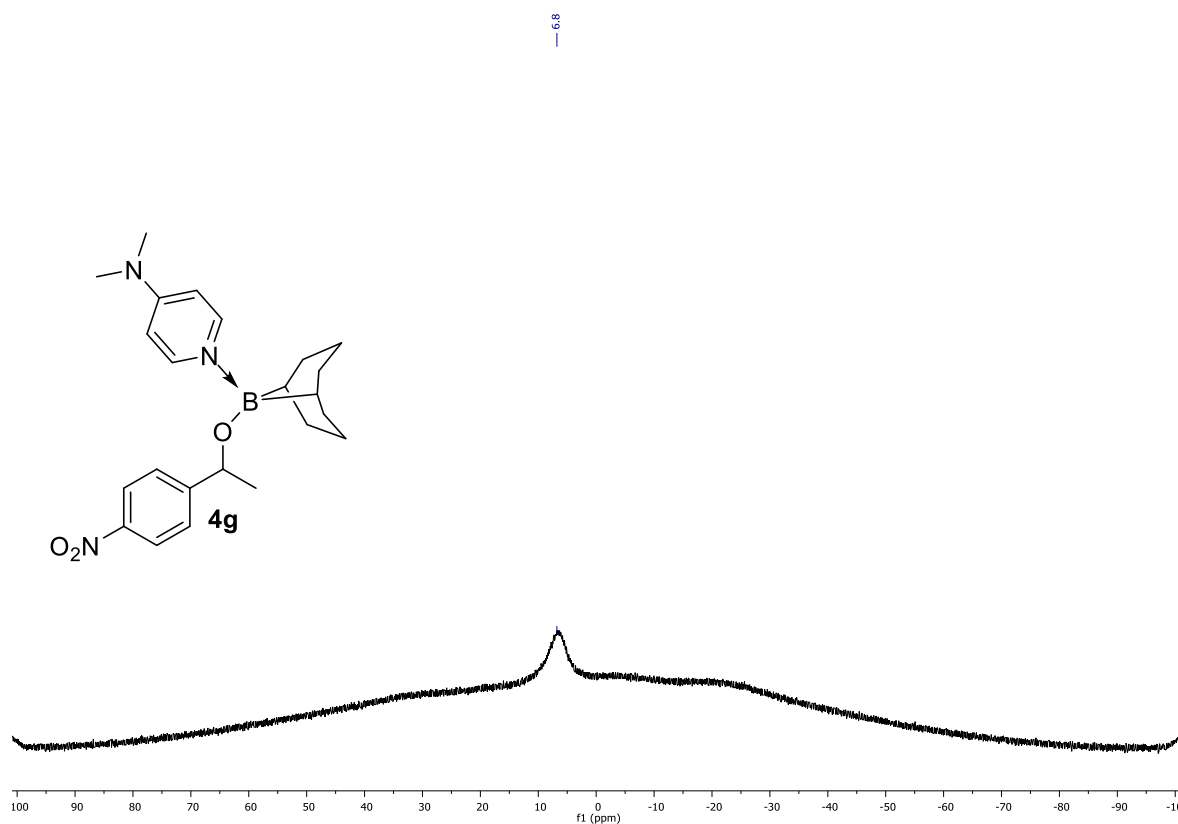
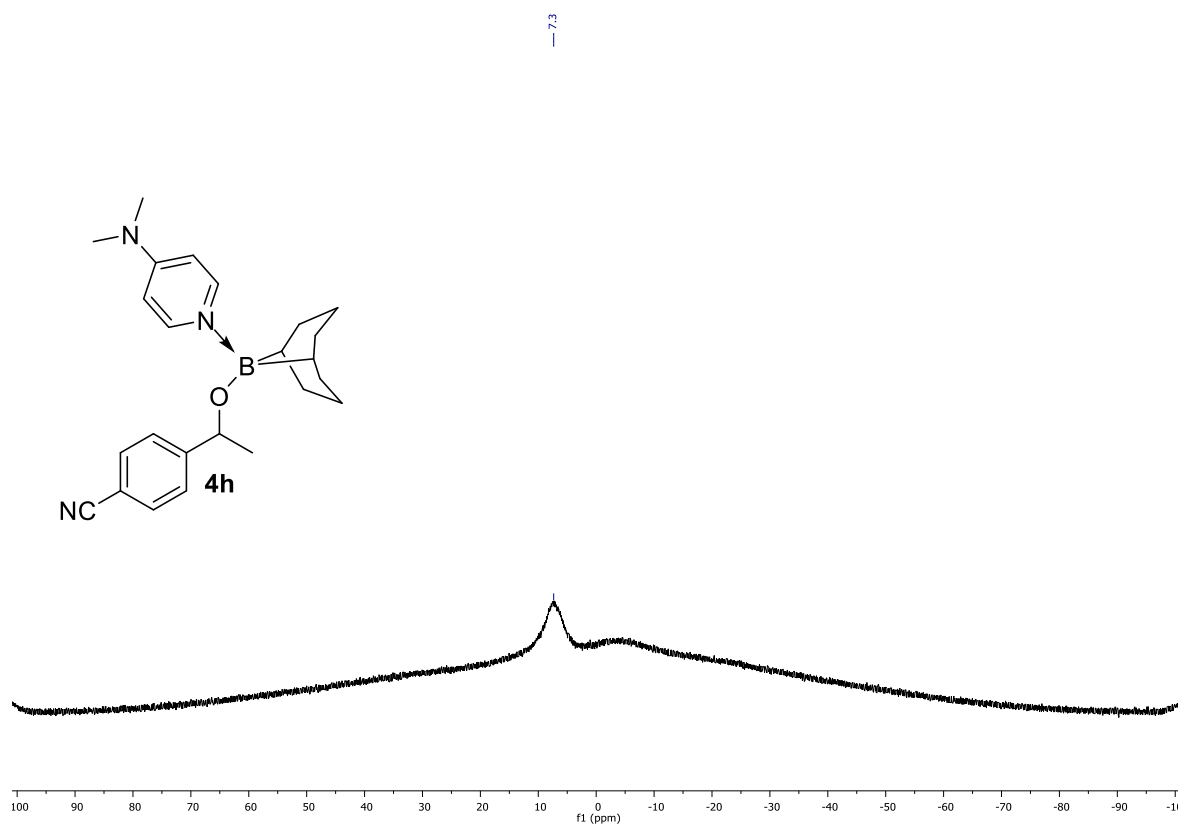
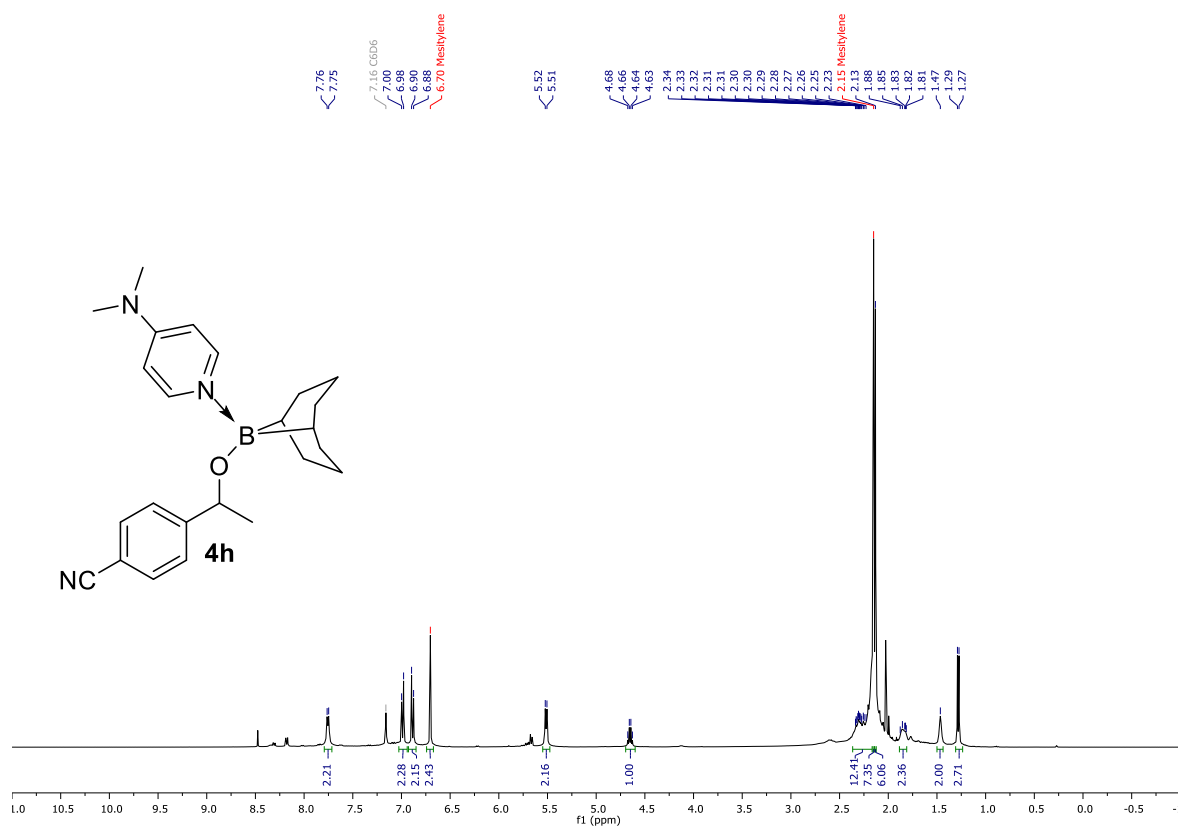


Figure S27. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4g**. Crude reaction mixture.



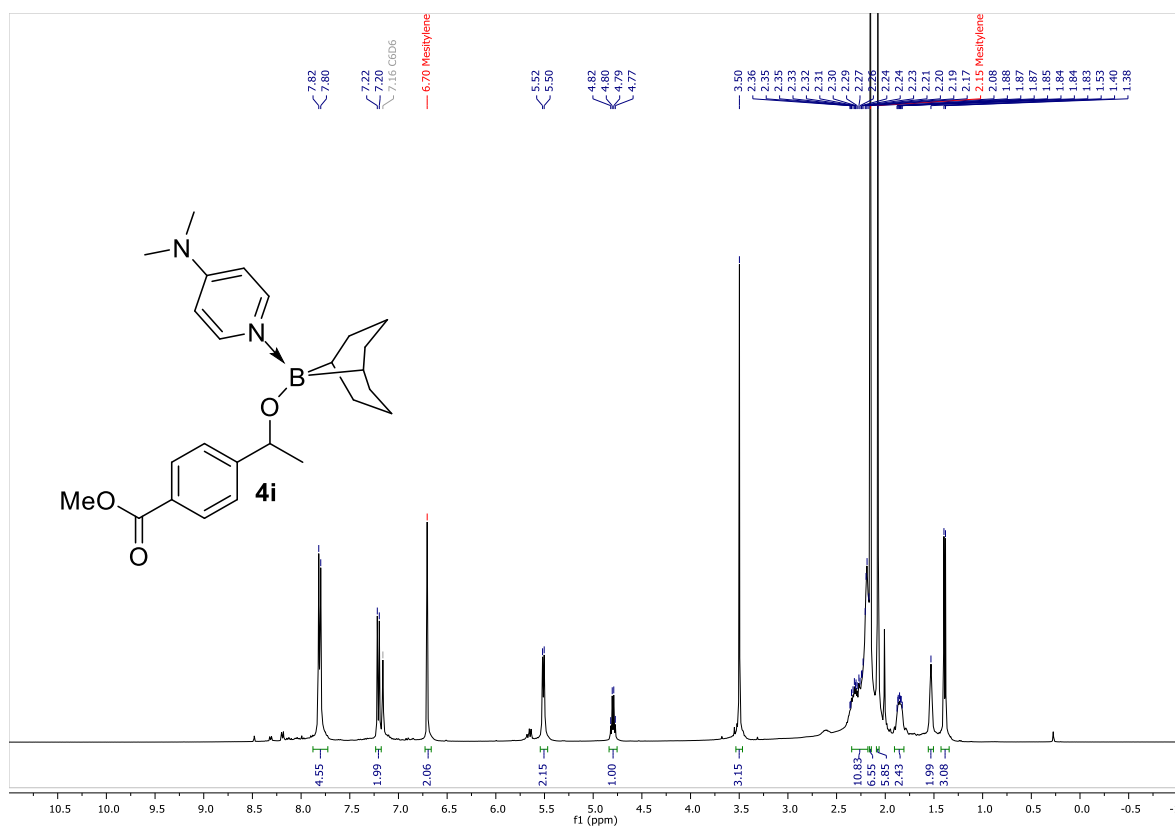


Figure S30. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4i**. Crude reaction mixture.

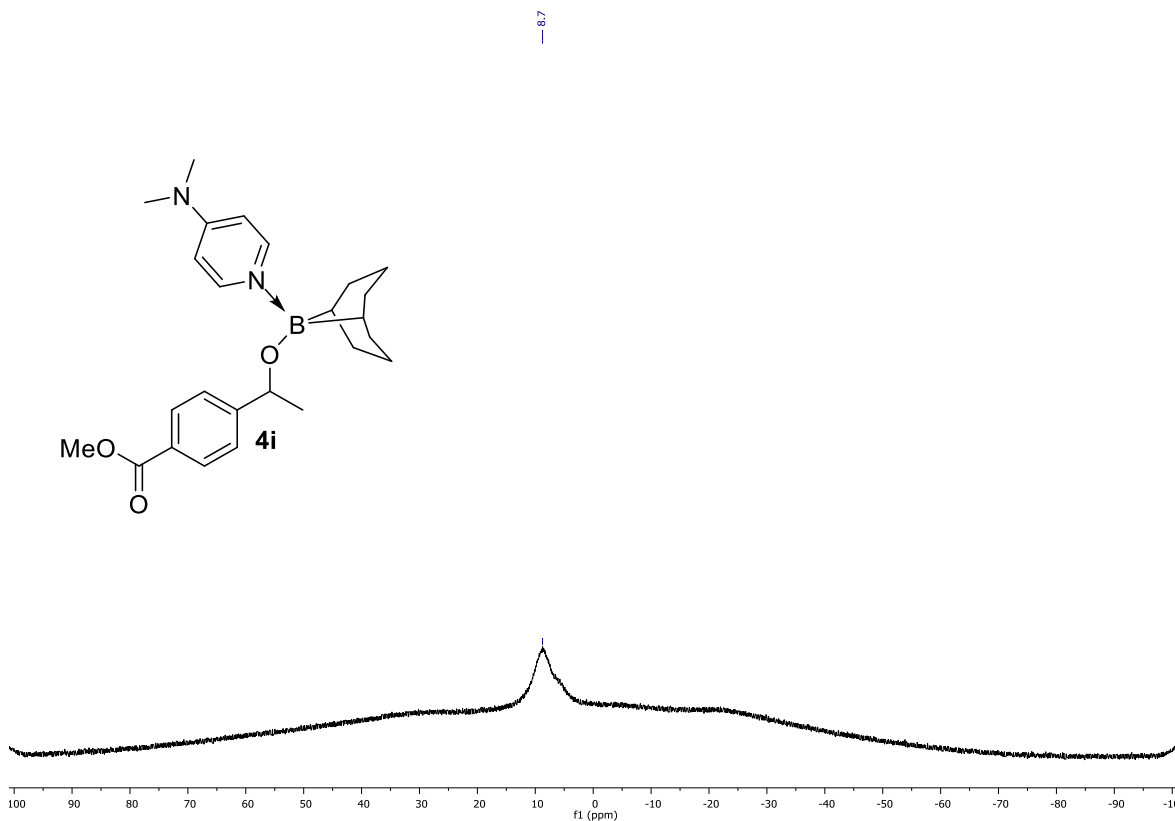


Figure S31. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4i**. Crude reaction mixture.

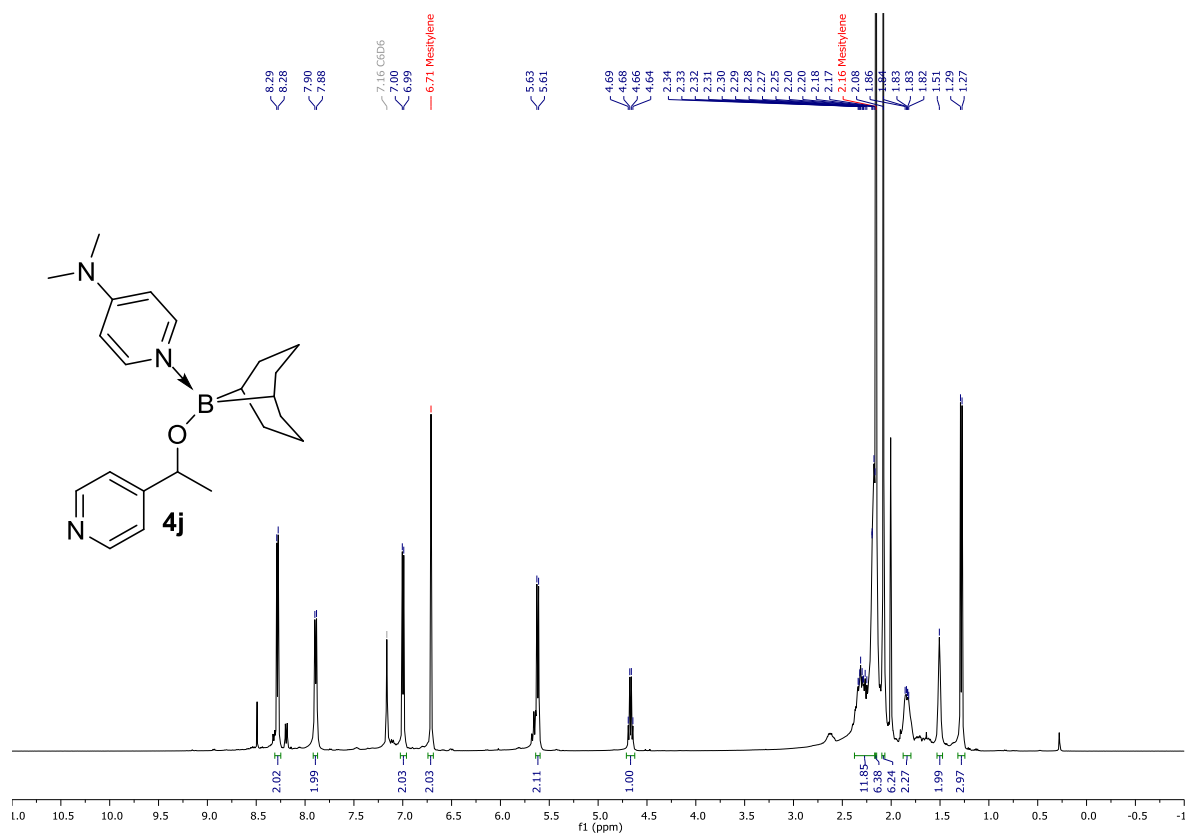


Figure S32. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4j**. Crude reaction mixture.

— 7.4

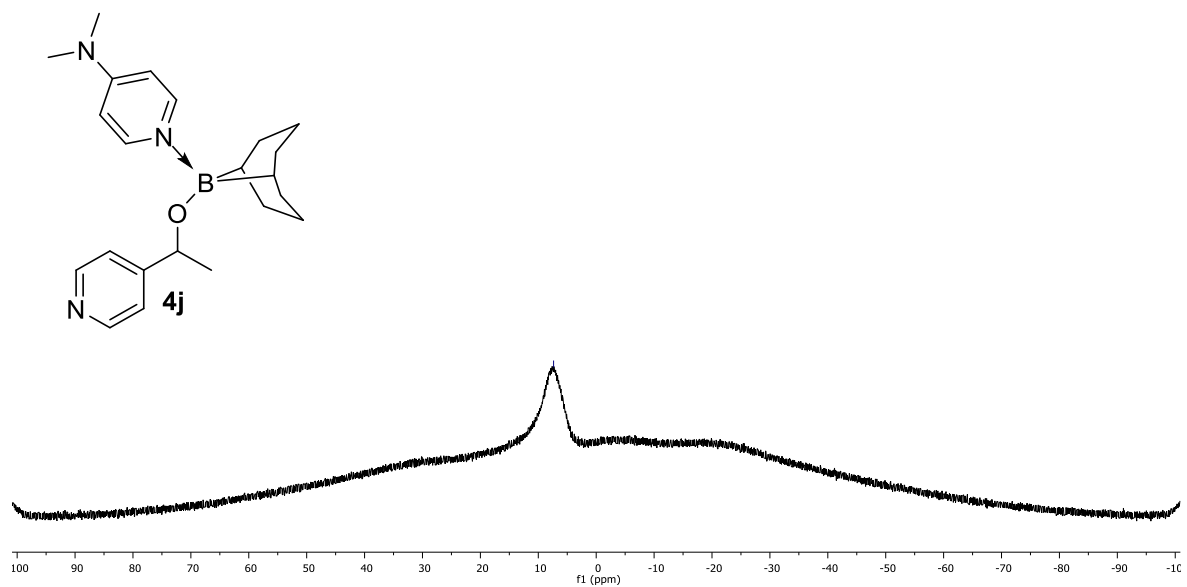


Figure S33. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4j**. Crude reaction mixture.

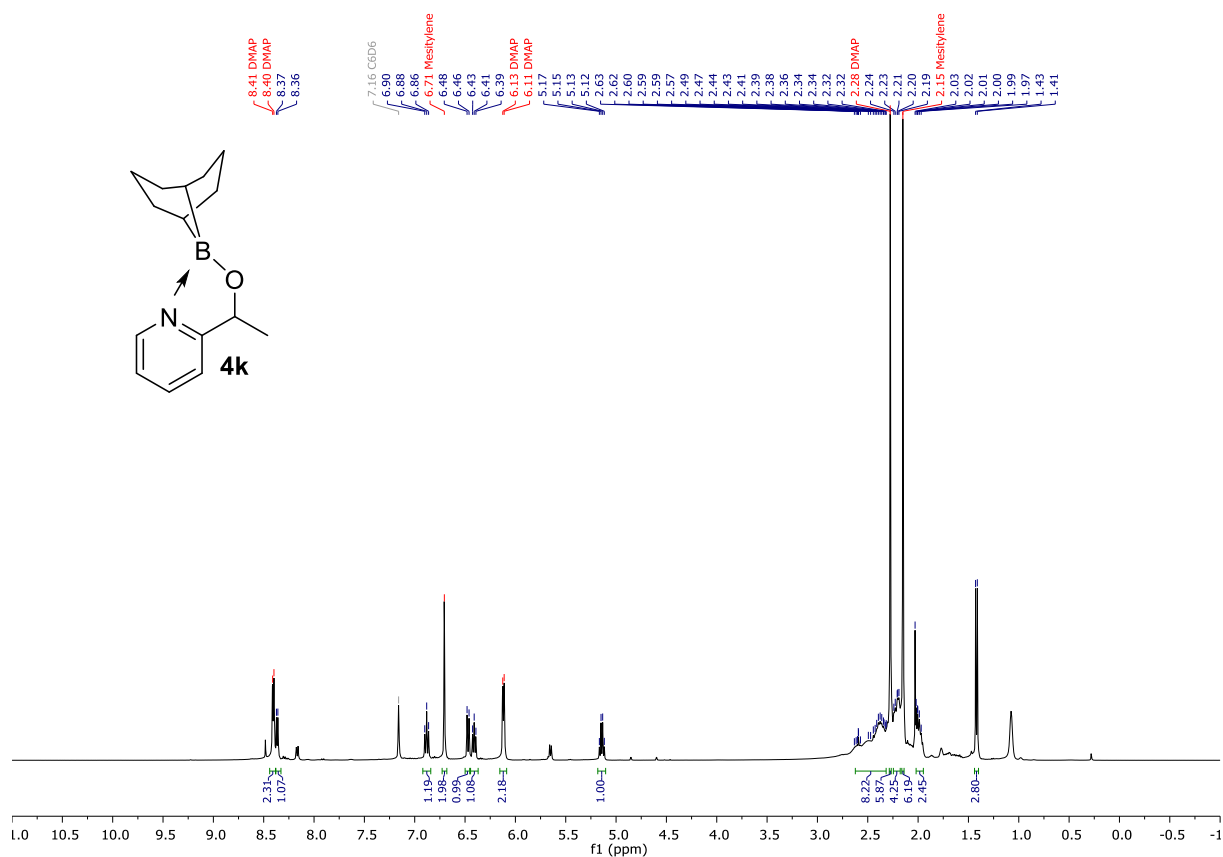


Figure S34. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4k**. Crude reaction mixture.

- 12.1

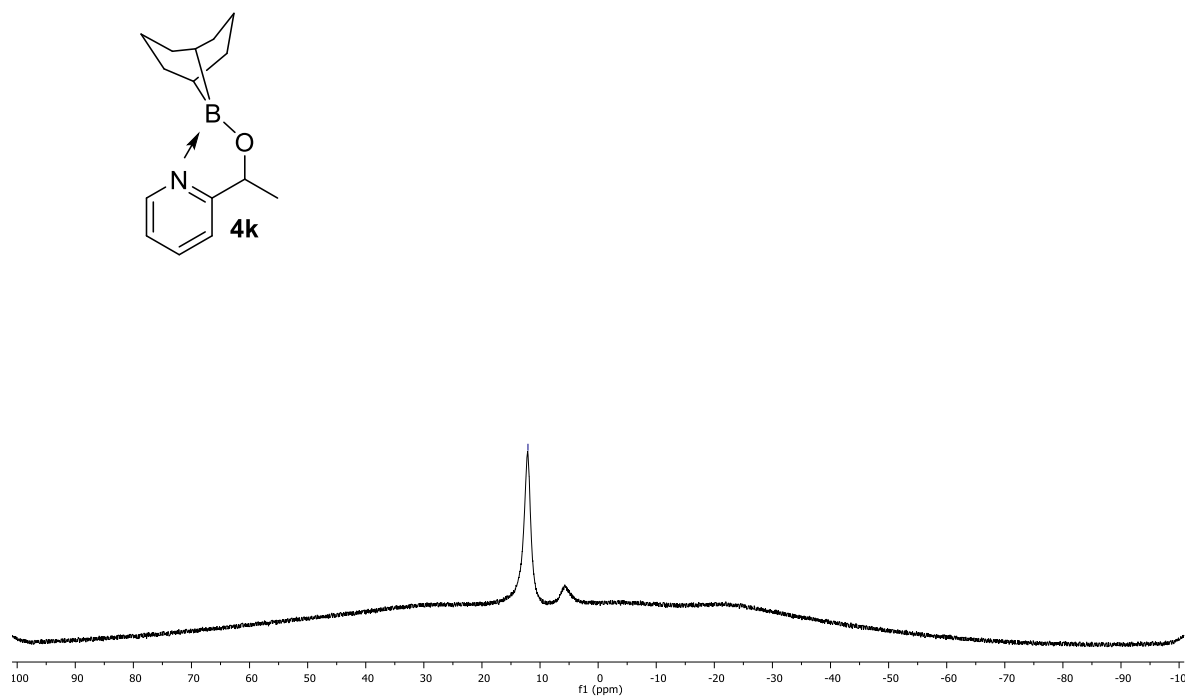
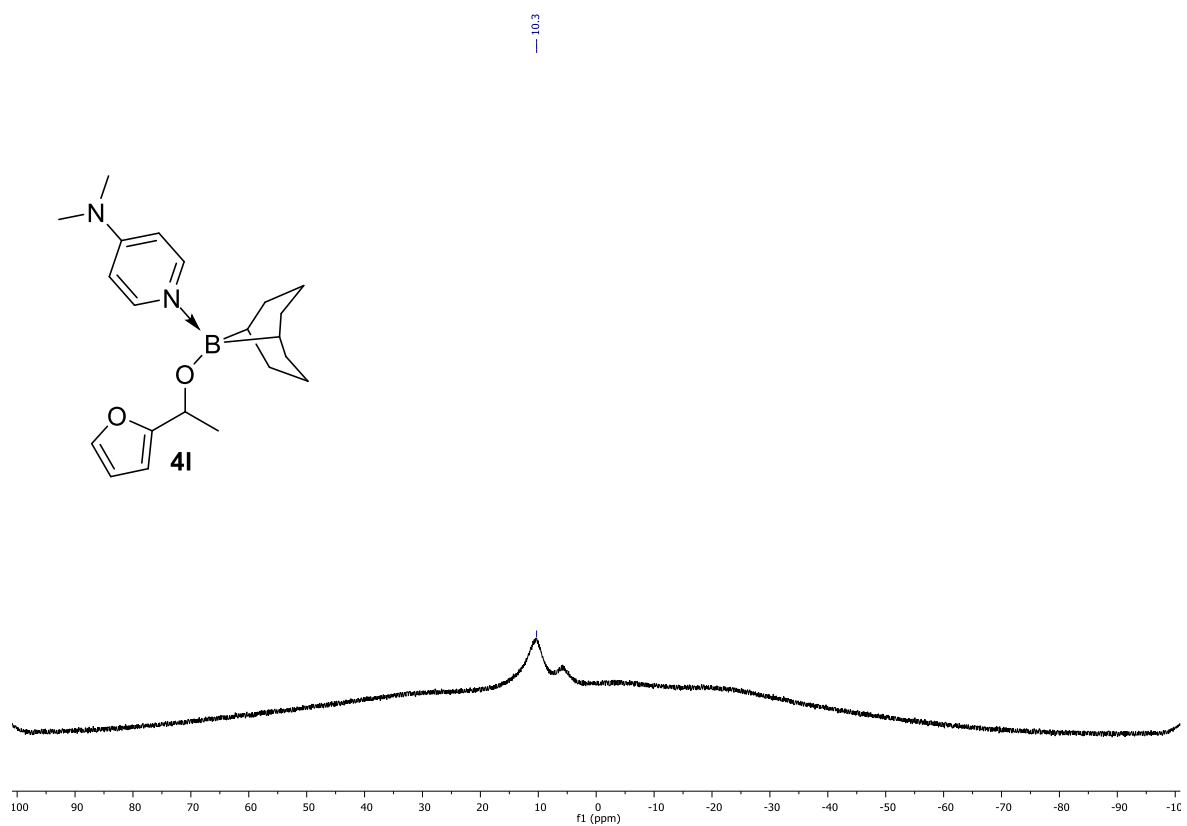
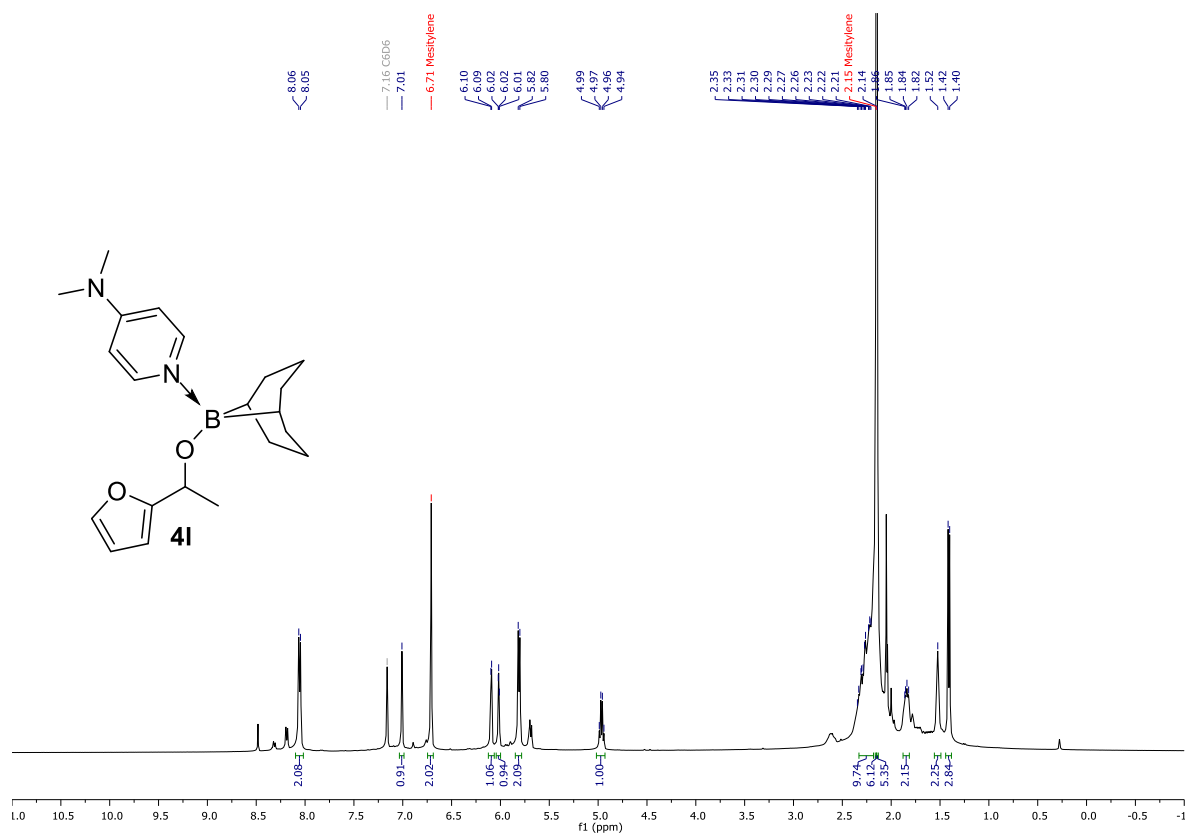


Figure S35. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4k**. Crude reaction mixture.



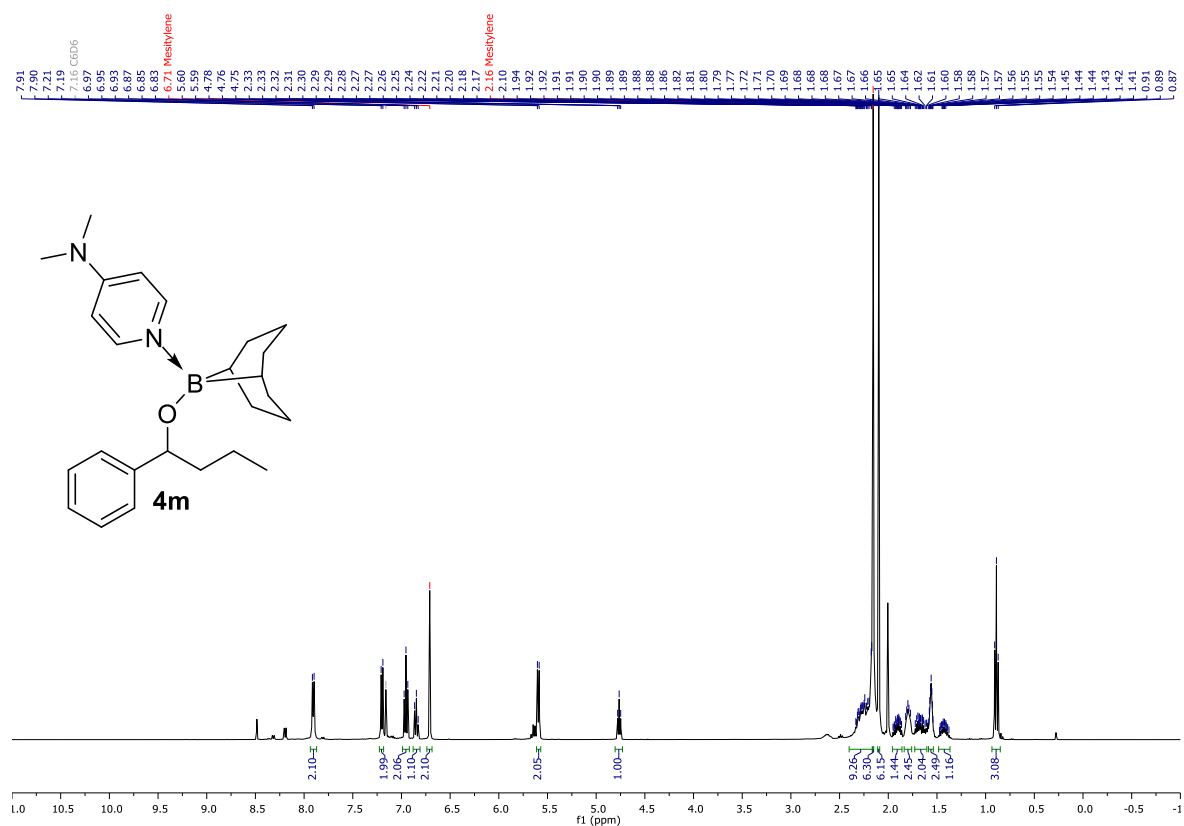


Figure S38. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4m**. Crude reaction mixture.

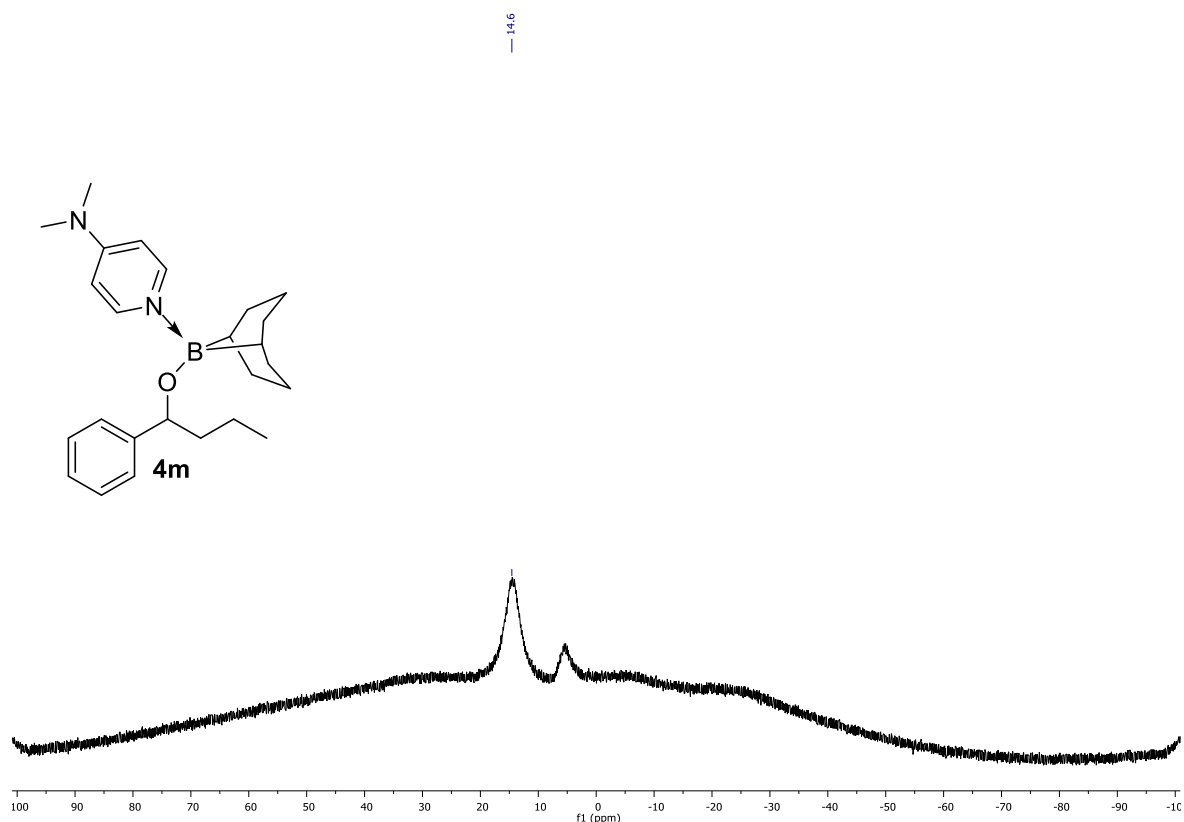


Figure S39. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4m**. Crude reaction mixture.

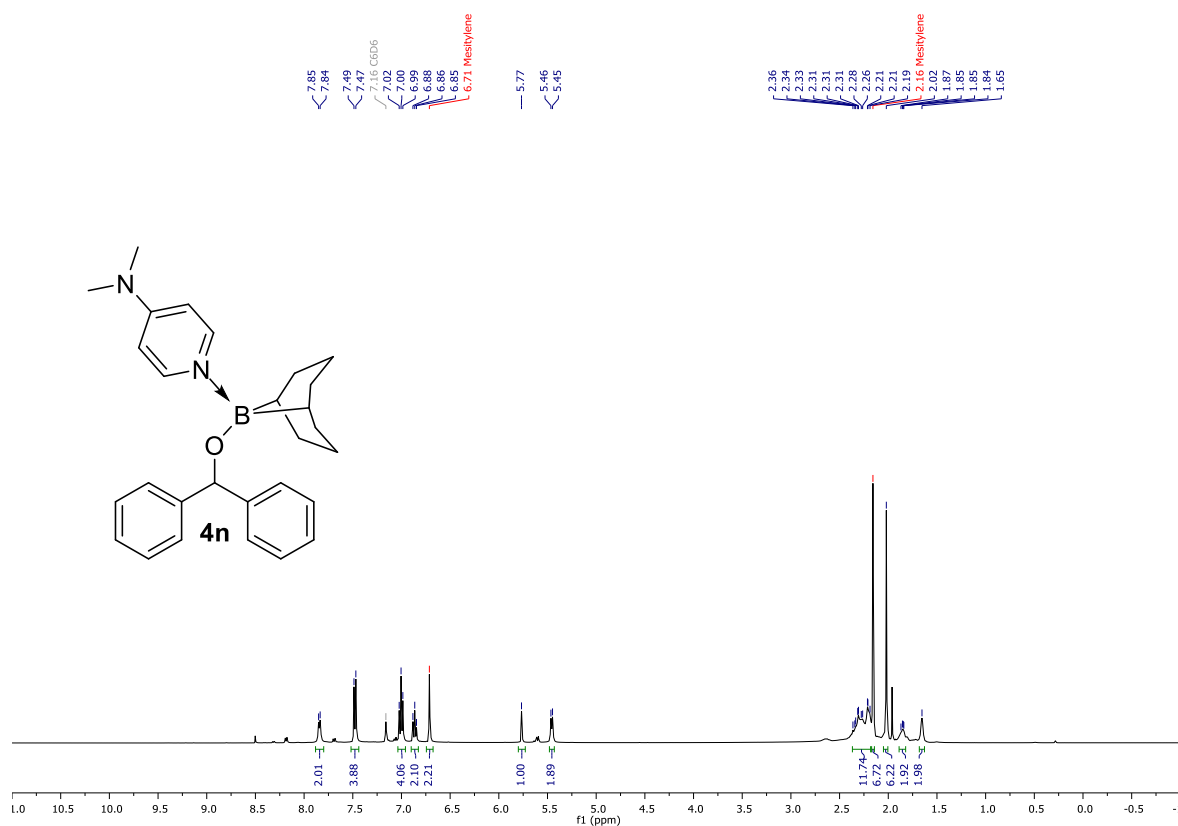


Figure S40. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4n**. Crude reaction mixture.

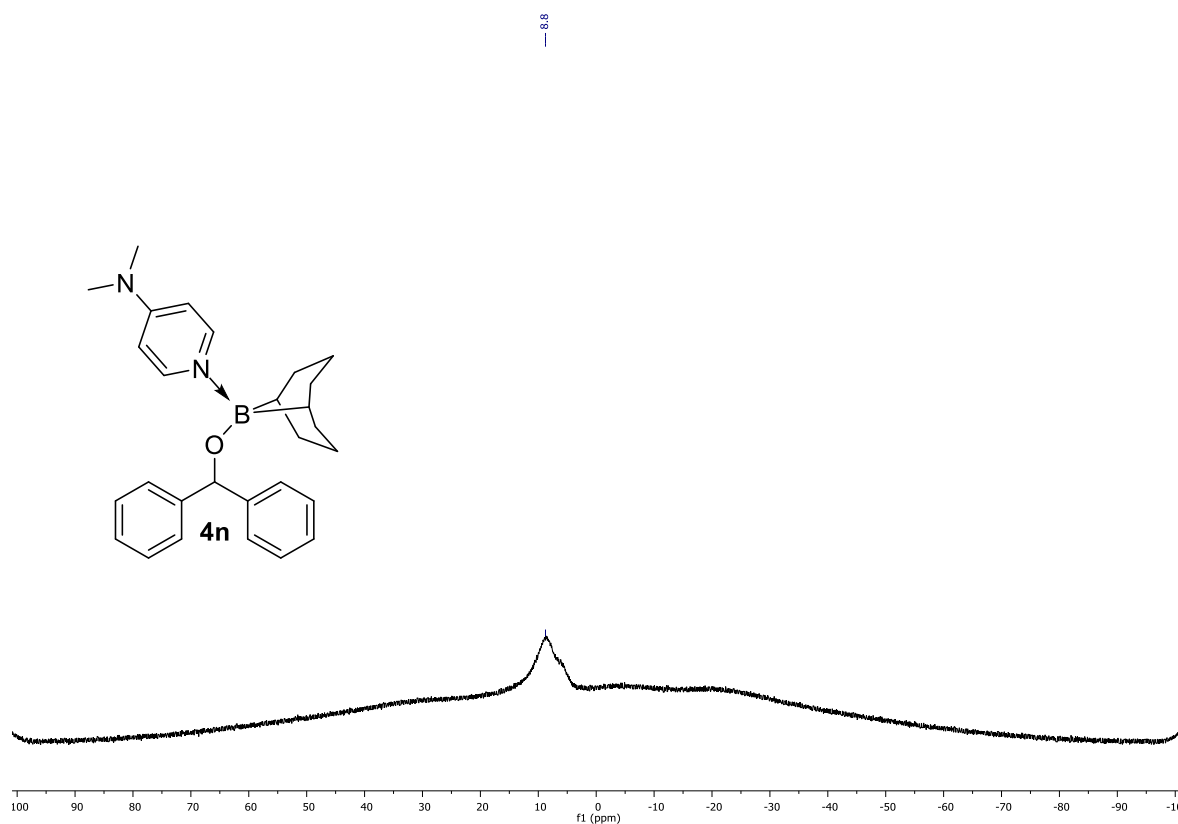


Figure S41. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4n**. Crude reaction mixture.

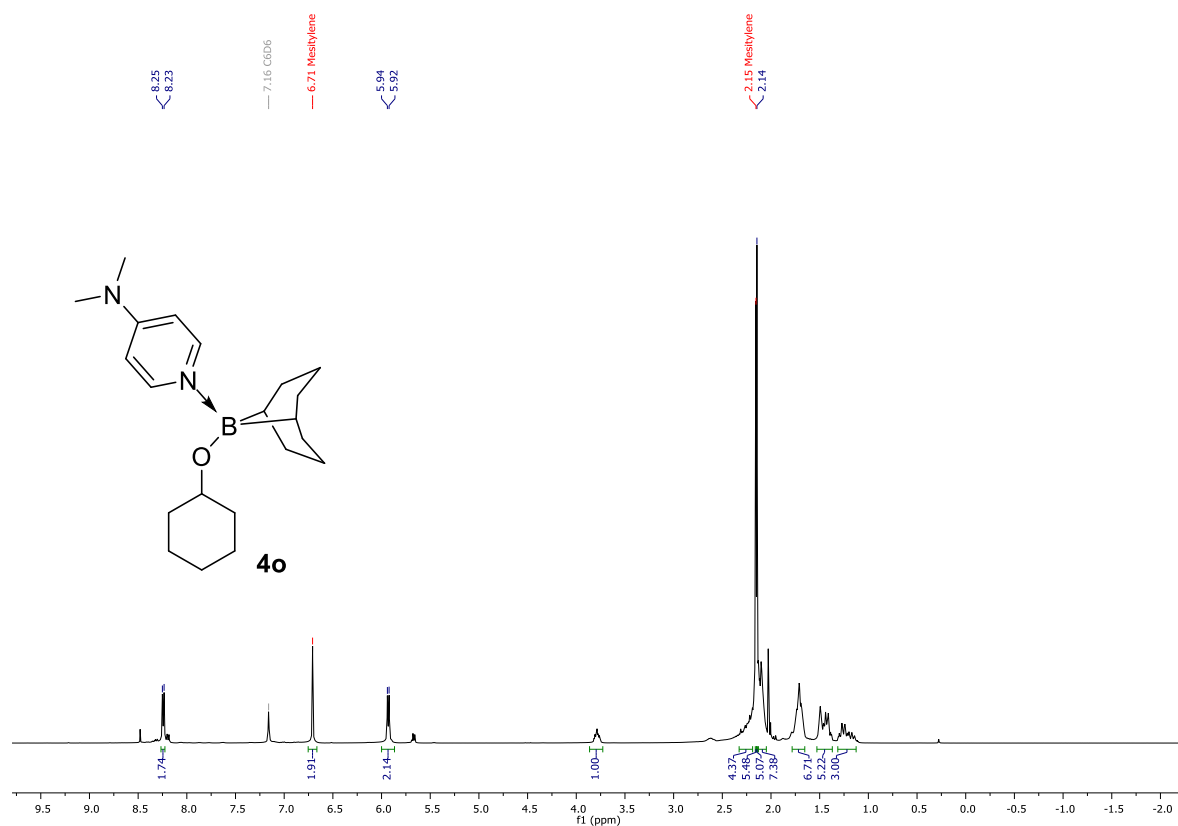


Figure S42. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4o**. Crude reaction mixture.

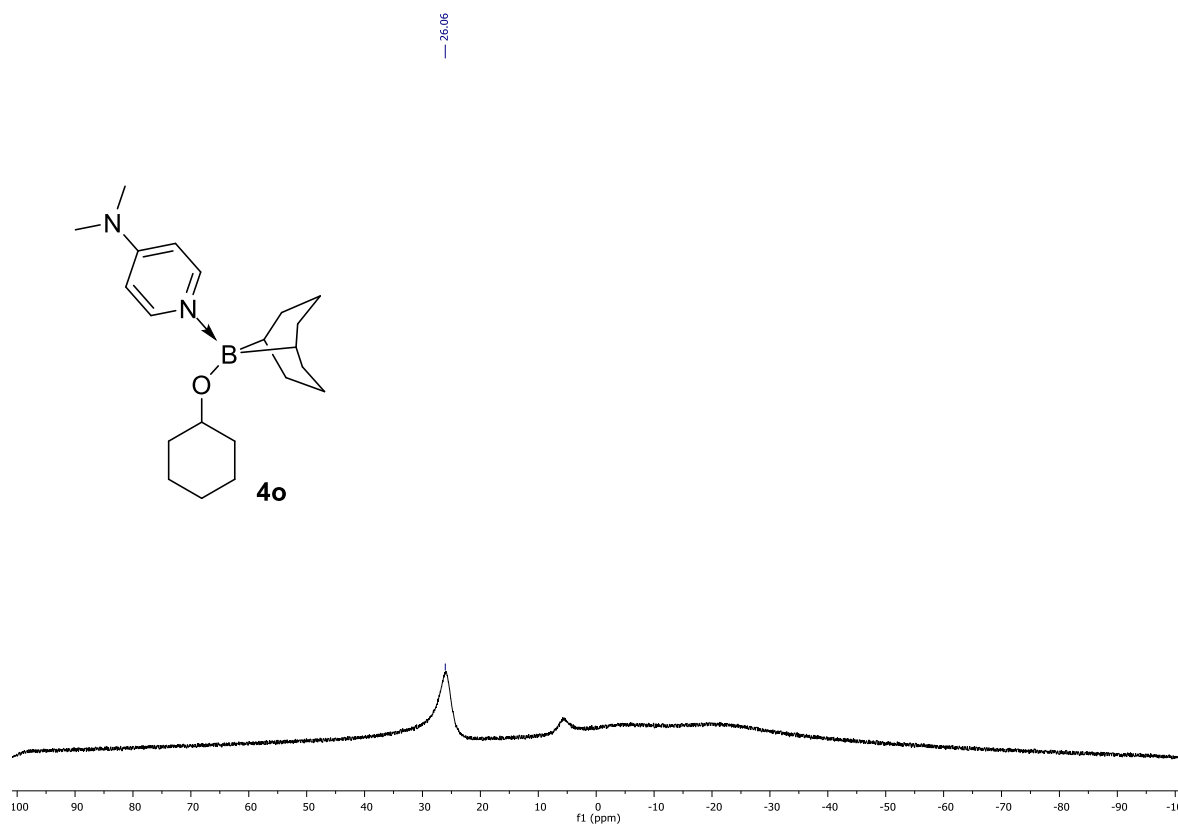
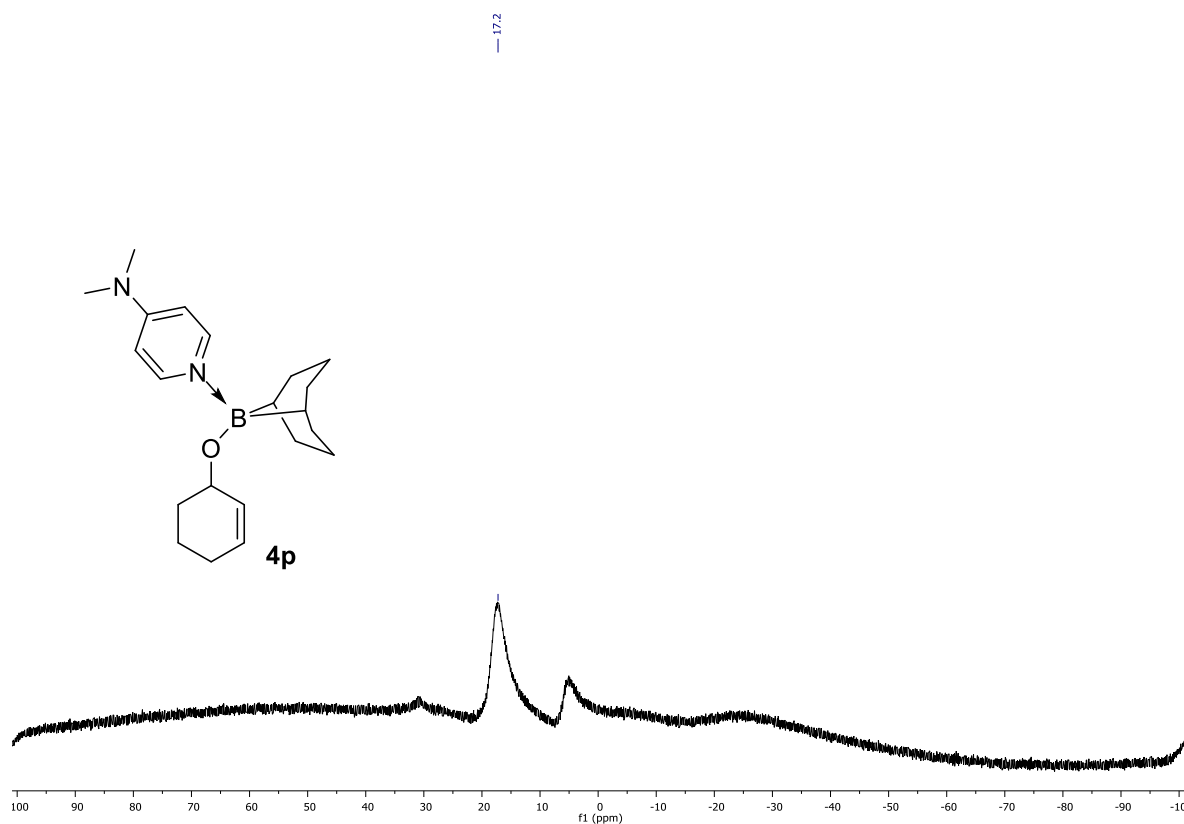
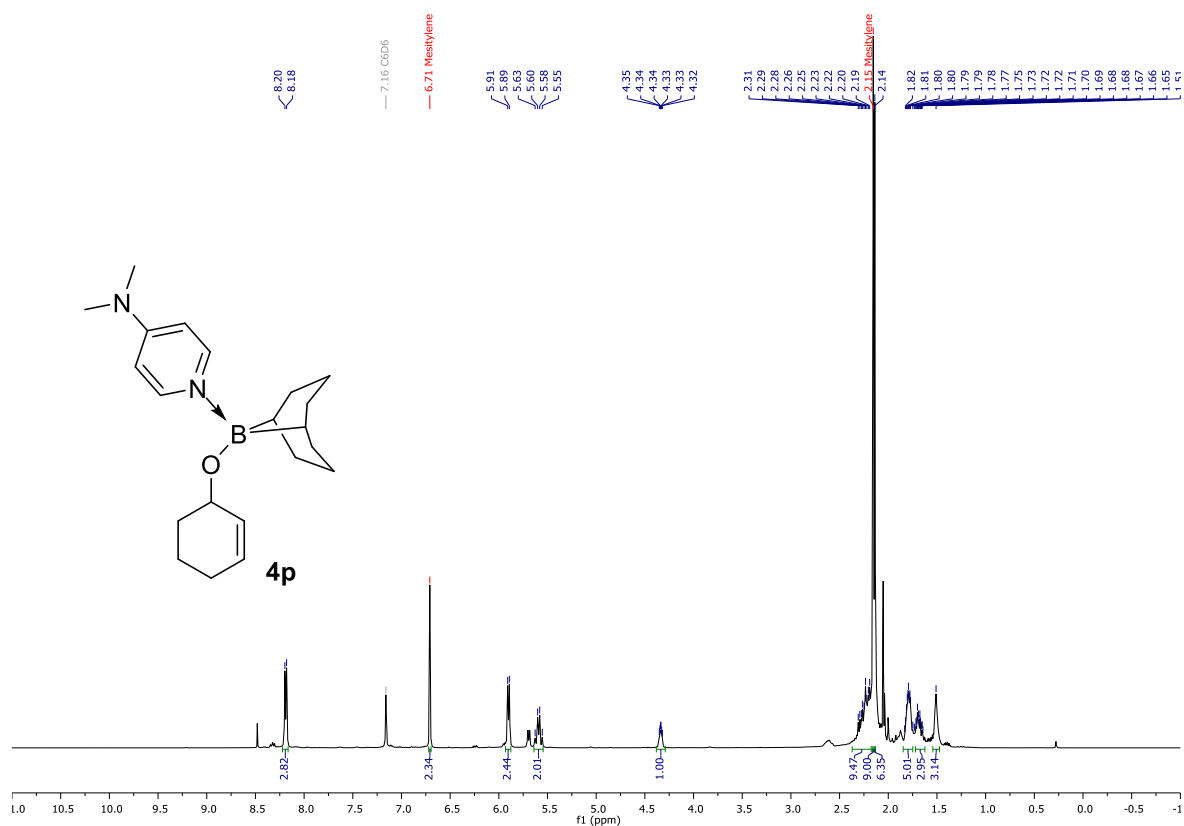


Figure S43. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4o**. Crude reaction mixture.



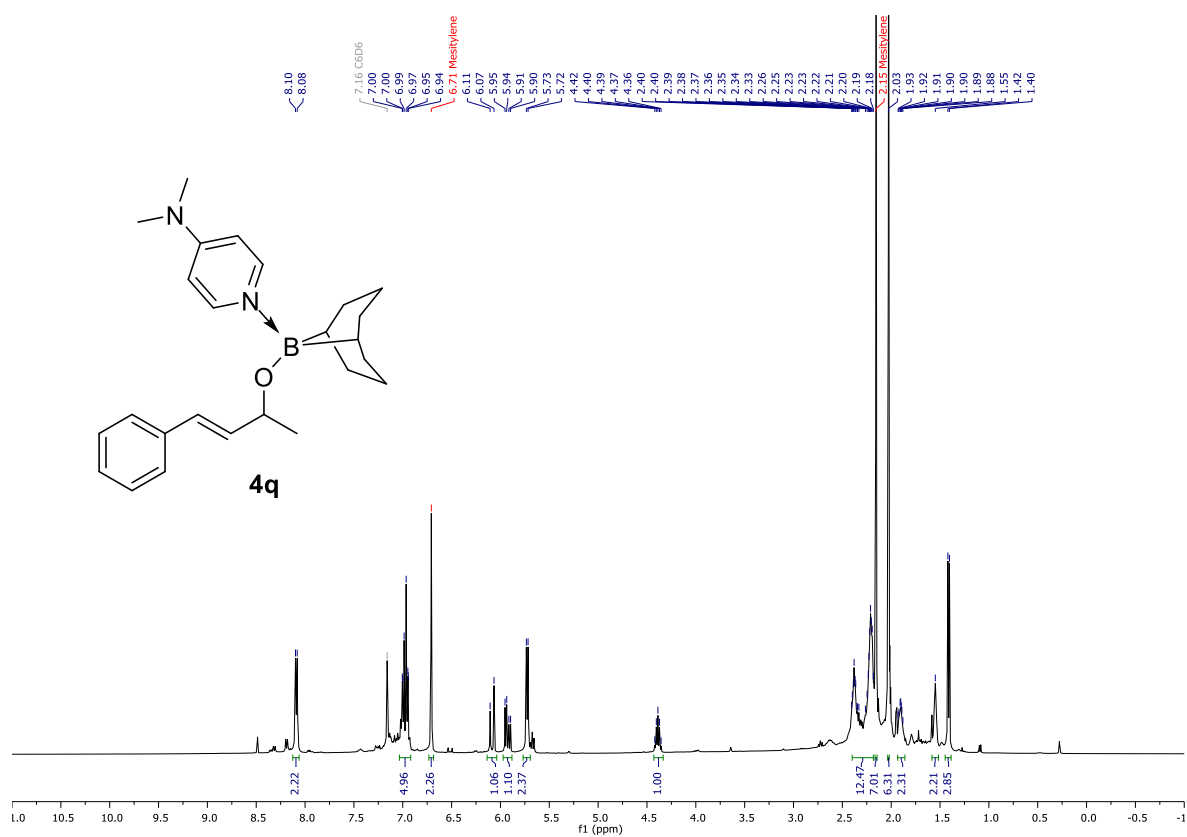


Figure S46. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4q**. Crude reaction mixture.

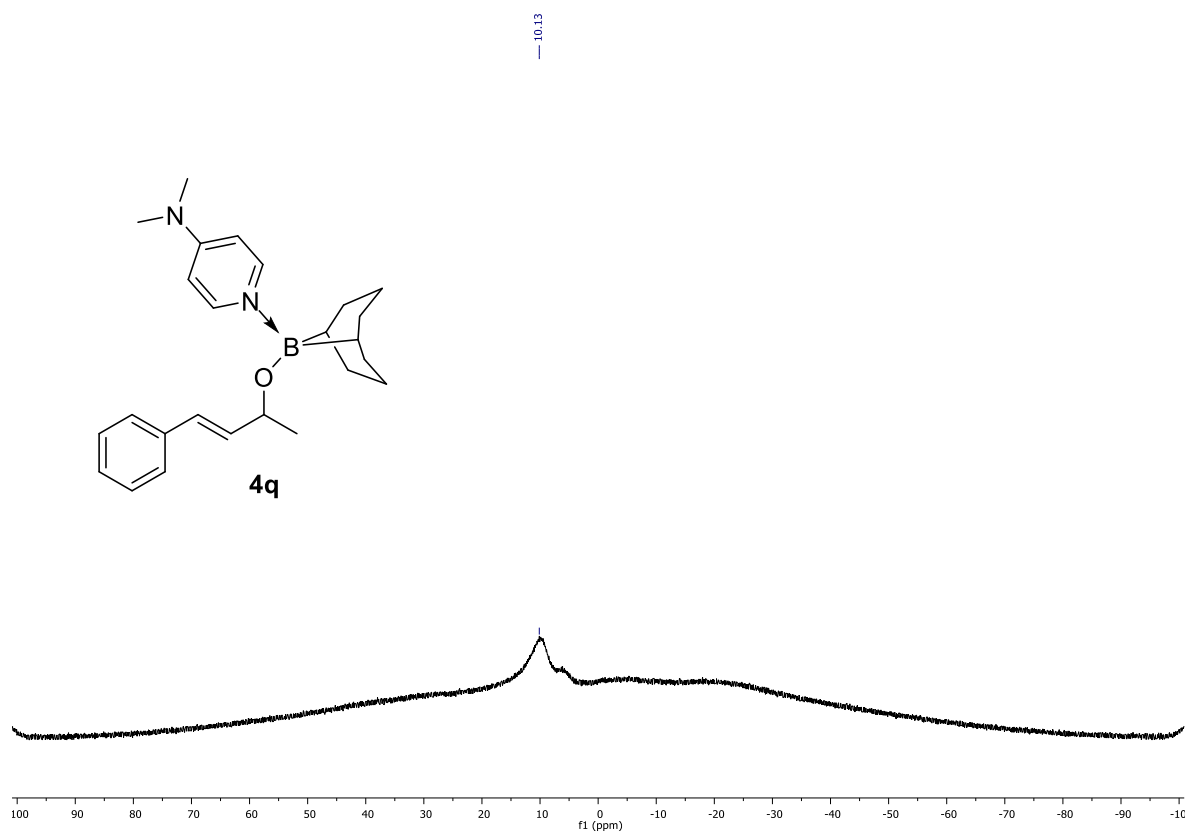


Figure S47. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4q**. Crude reaction mixture.

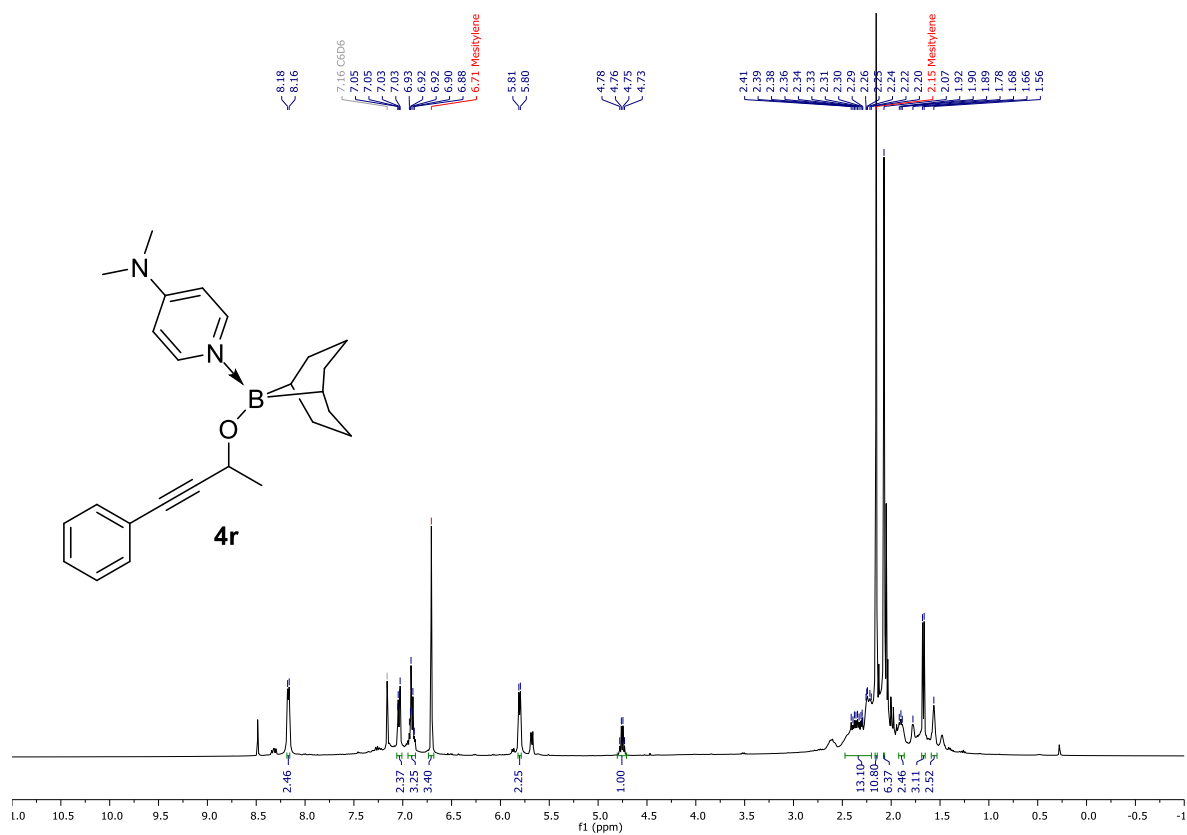


Figure S48. ¹H NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4r**. Crude reaction mixture.

— 6.4

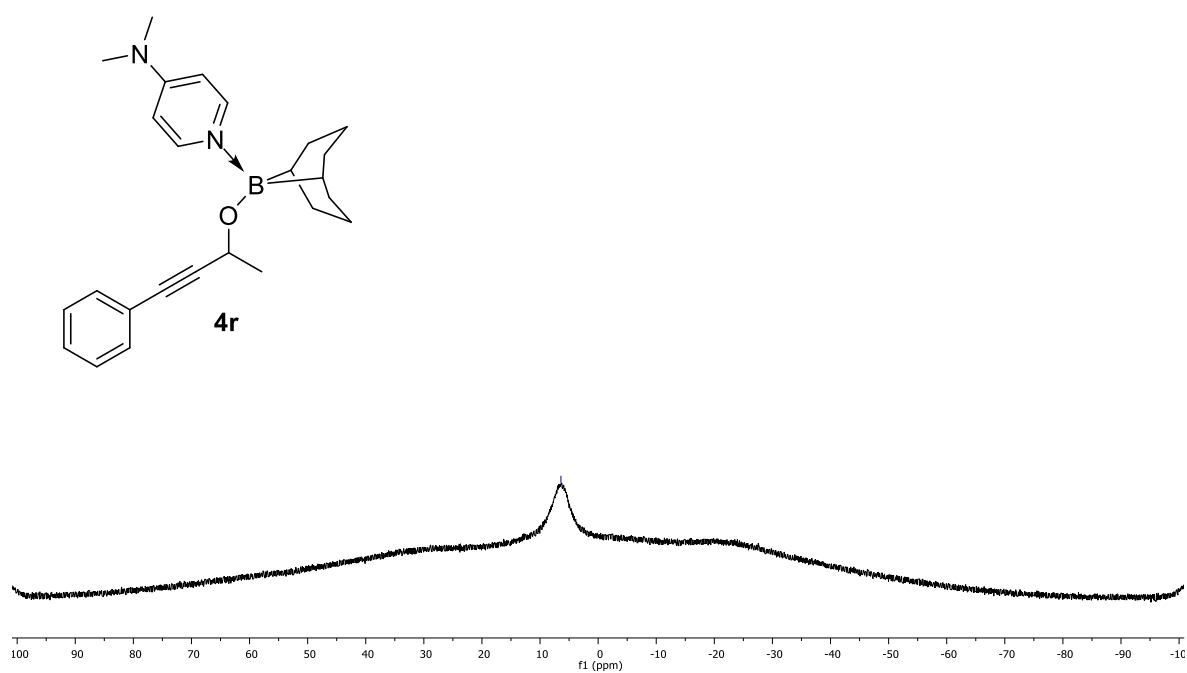


Figure S49. ¹¹B NMR spectrum obtained in C₆D₆ for the transfer hydroboration of **4r**. Crude reaction mixture.

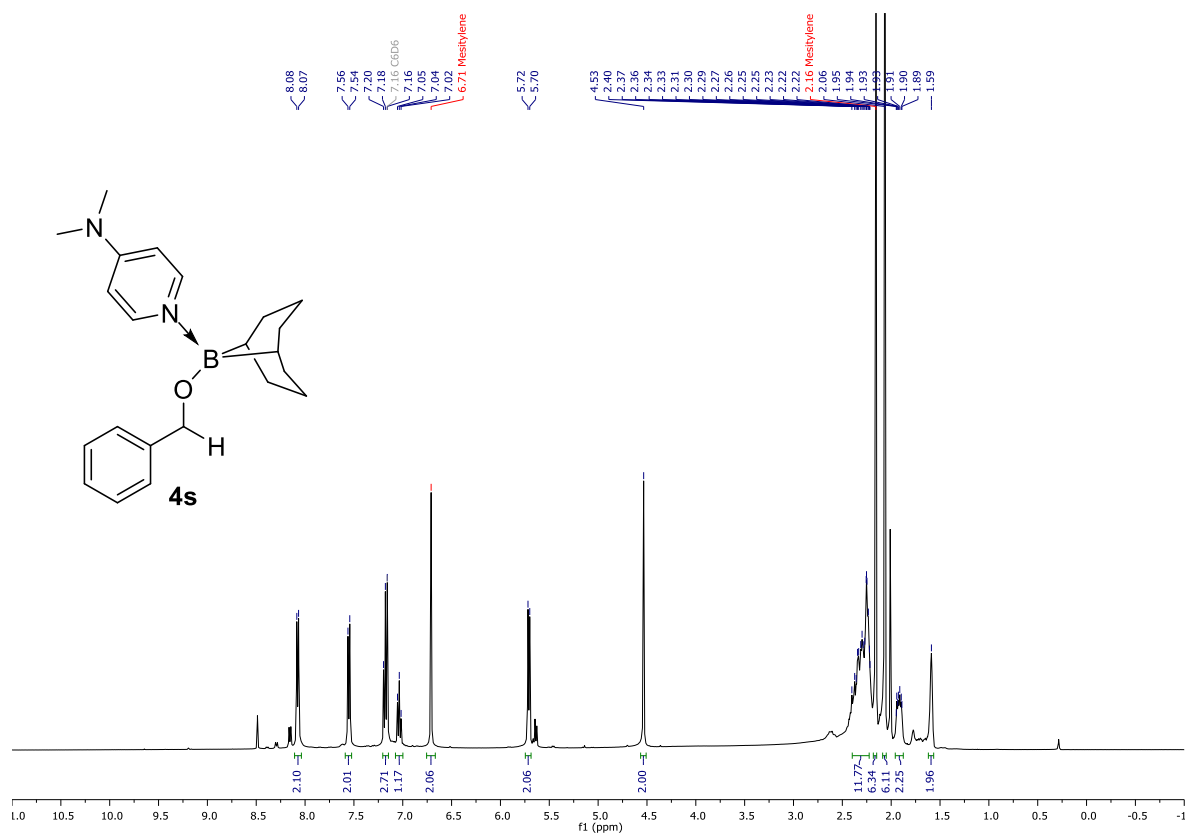


Figure S50. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4s**. Crude reaction mixture.

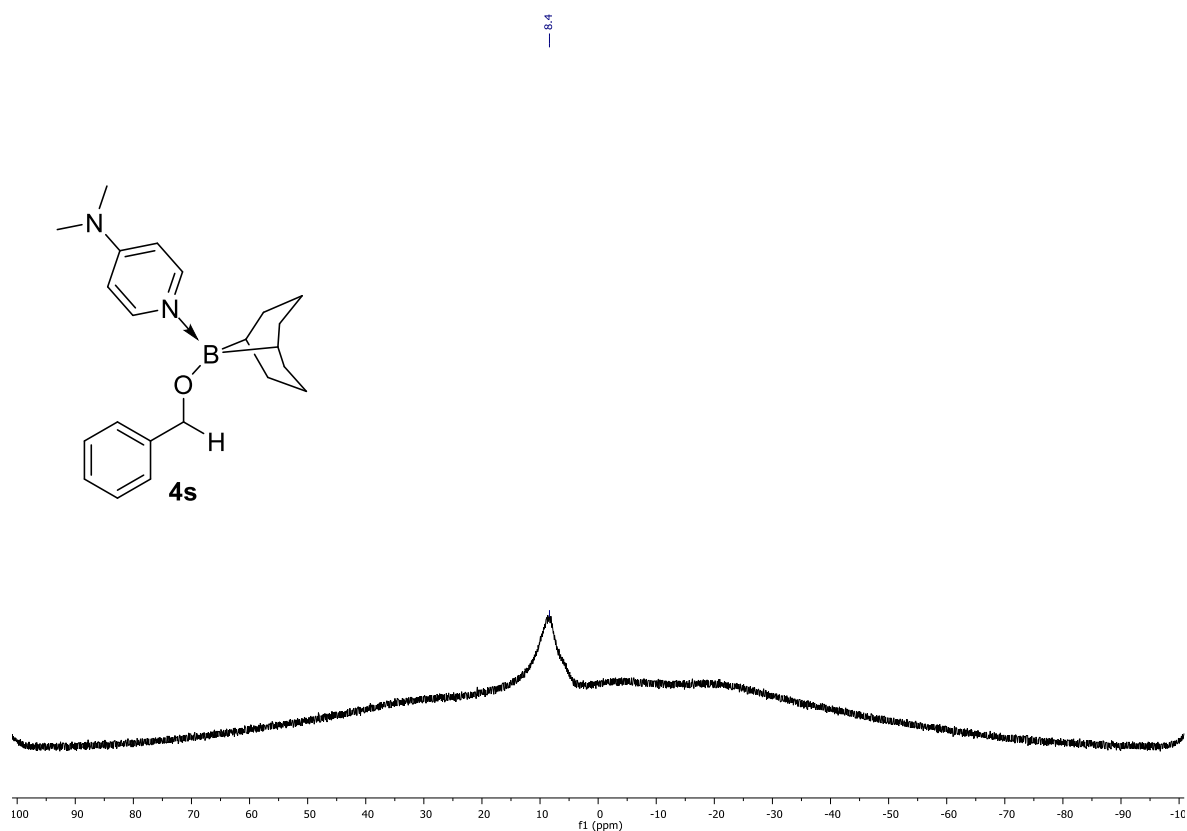


Figure S51. ^{11}B NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4s**. Crude reaction mixture.

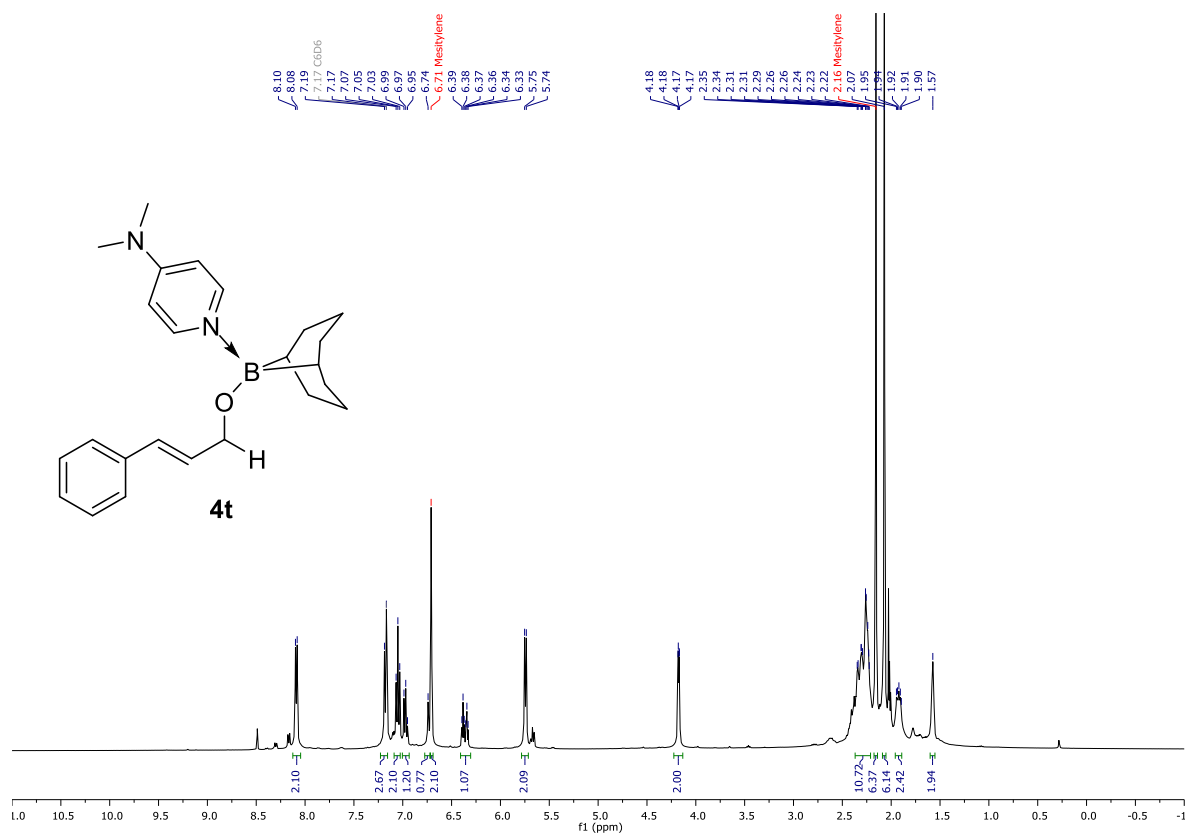
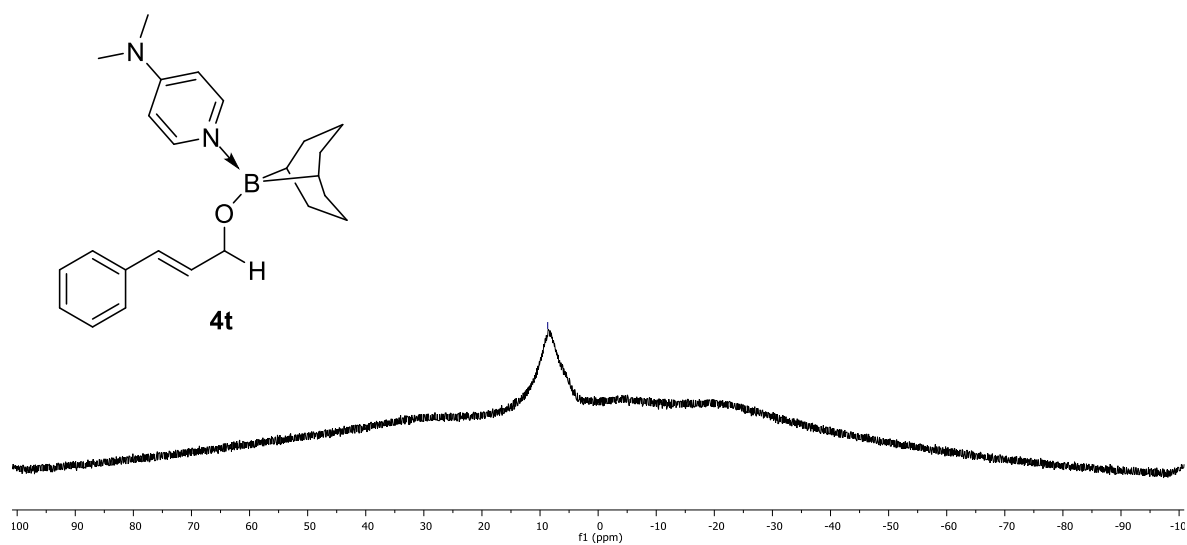


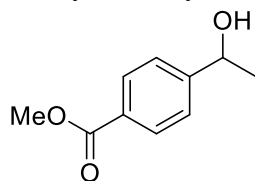
Figure S52. ^1H NMR spectrum obtained in C_6D_6 for the transfer hydroboration of **4t**. Crude reaction mixture.

— 8.7



10 Characterization of isolated hydrolyzed products

Methyl 4-(1-hydroxyethyl)benzoate



Isolated as a colorless oil in 97% yield (17.4 mg) (procedure GP2). Spectroscopic data in accordance with literature.^[15]

¹H NMR (400 MHz, CDCl₃): δ = 8.01 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 4.96 (q, J = 6.3 Hz, 1H), 3.91 (s, 3H), 2.01 (s, 1H), 1.50 (d, J = 6.5 Hz, 3H)

¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 151.1, 130.0, 129.3, 125.4, 70.1, 52.2, 25.4.

11 NMR Spectra of hydrolyzed product

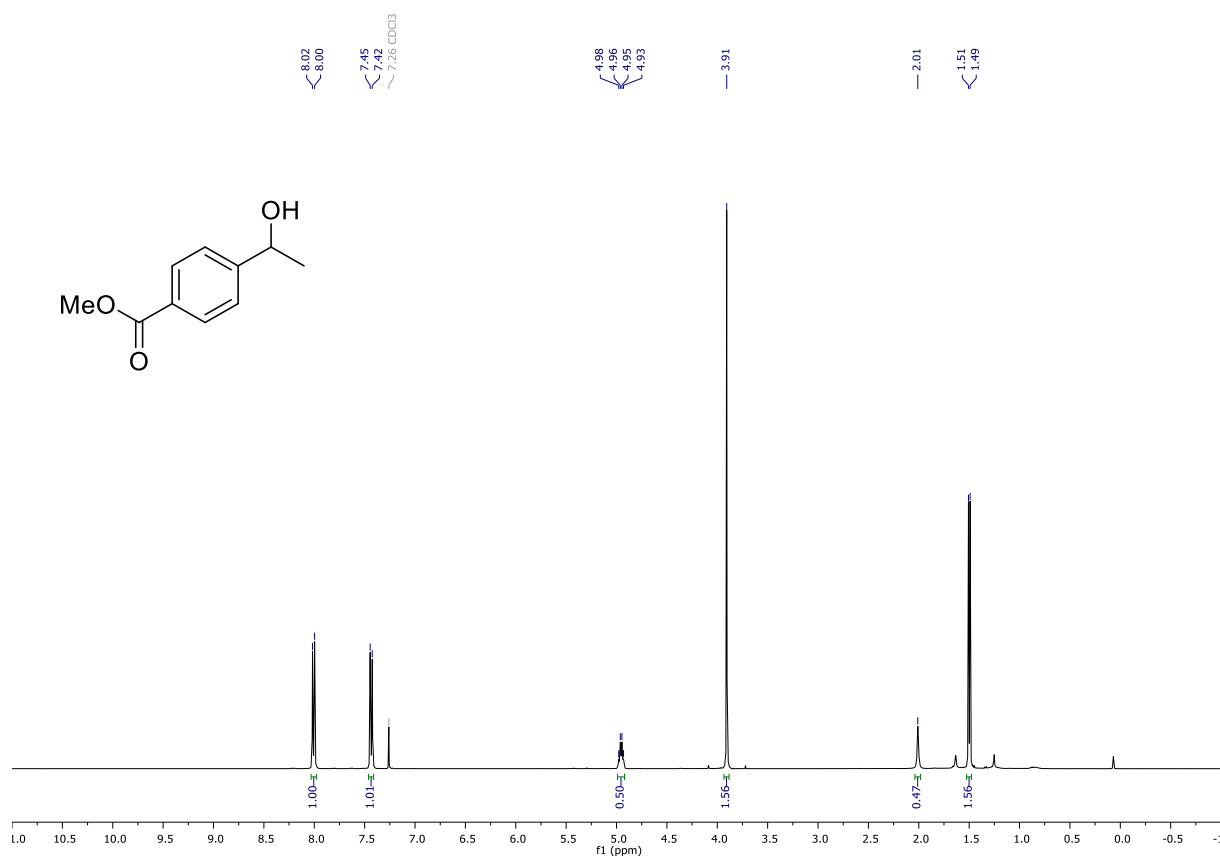


Figure S54. ¹H NMR spectrum obtained in CDCl₃ for isolated alcohol from **4i** hydrolysis.

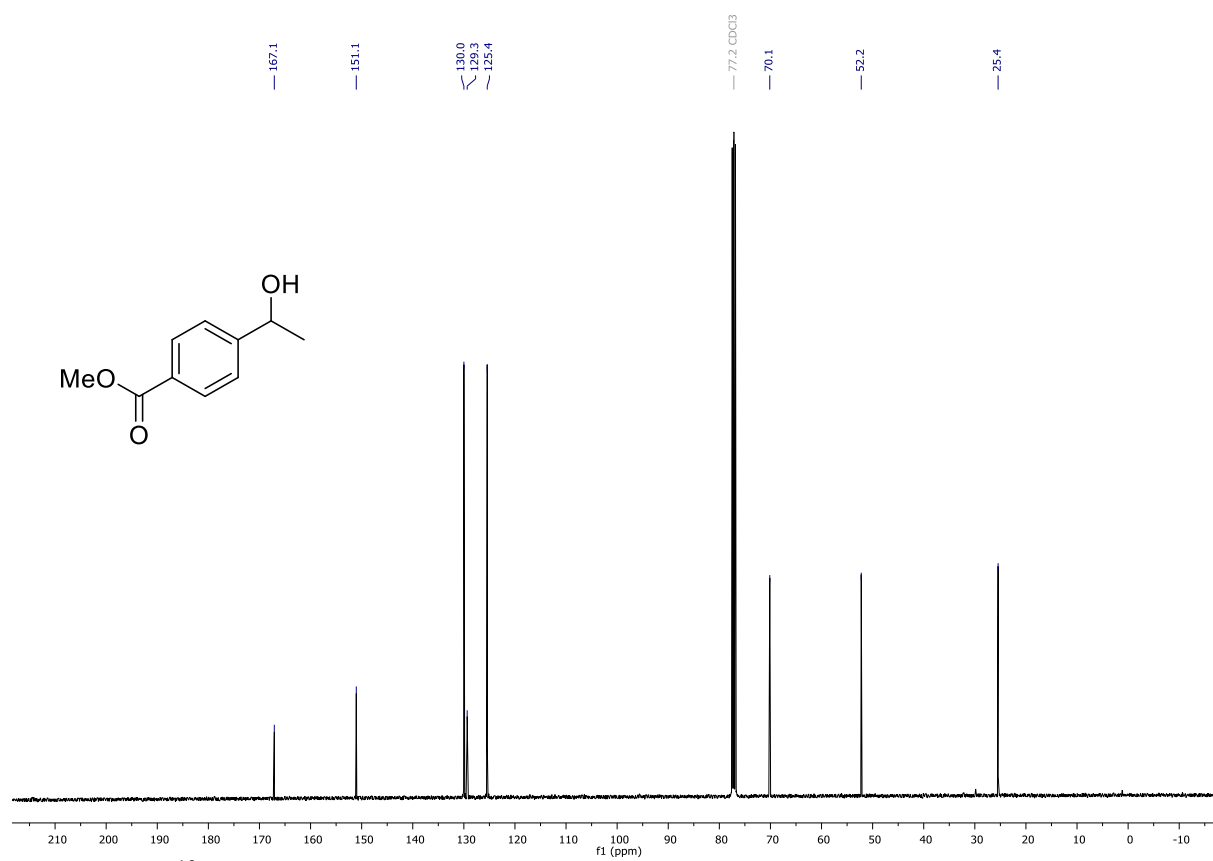


Figure S55. ^{13}C NMR spectrum obtained in CDCl_3 for isolated alcohol from **4i** hydrolysis.

12 Evidence for the formation of CO₂ during the reaction

In order to prove the formation of CO₂ during the reaction, a typical reaction following the general procedure of NMR scale reactions (GP1) was performed, using acetophenone as the ketone. After the reaction, the gas phase was sampled from the headspace of the J. Young tube and injected in GC. The trace presents two peaks: the first is N₂ from air, and the second (5.6 minutes) is CO₂.

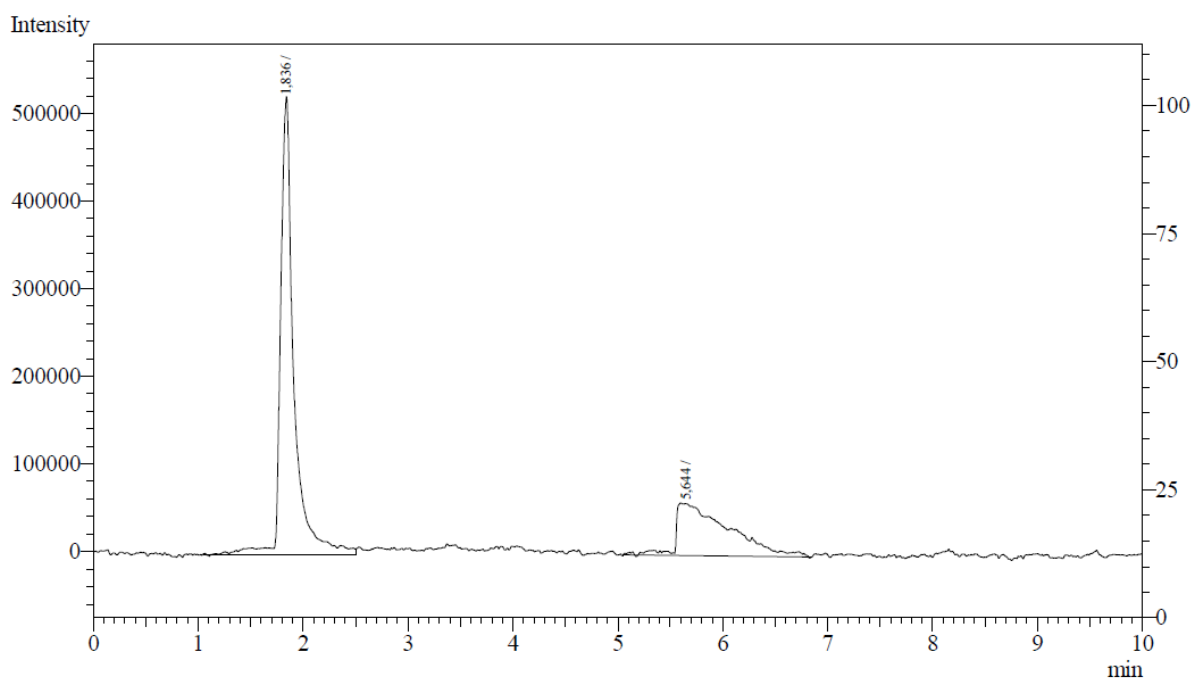


Figure S56. GC trace of the gas phase after reaction.

13 Evidence of the crucial role of the N–H function

In order to prove the importance of the role of the N-H in the hydroboration of ketones, the reaction was performed with catalyst *fac*-[Ru(κ^1 -OAc)(κ^2 -OAc)(κ^3 -PN^{Me}P^{Ph})] (**2a-Me**) following the general procedure of NMR scale reactions (GP1).

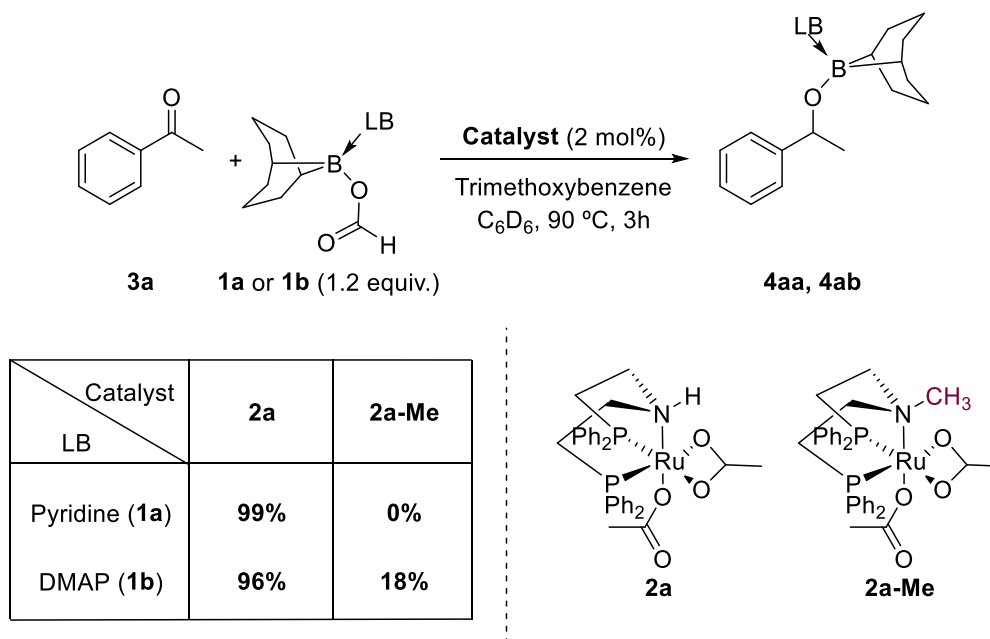


Table S2. Screening Hydroboration reaction of ketone **3a** with catalyst **2a** or **2a-Me** and formoxyboranes **1a** and **1b**.

14 Experimental evidence of ruthenium monohydride species

In a glovebox, a *J. Young* NMR Tube was charged with *fac*-[Ru(κ^1 -OAc)(κ^2 -OAc)(κ^3 -PN^HP^{Ph})] (**2a**) (1 equiv.), 9-borabicyclo[3.3.1]nonan-9-yl formate *N,N*-dimethylaminopyridine adduct (**1b**) (1.2 equiv.), C₆D₆ (0.4 mL) and mesitylene (10 μ L). The tube was sealed, brought out of the glovebox and heated at 90 °C. during 30 seconds. The reaction was monitored by ¹H NMR spectroscopy after 0.5 minutes of reaction (Figure S57, Figure S58), showing the presence of different ruthenium hydrides, including related Ru(PN^HP)(H)(CO)(OAc) (−16.7 ppm). The presence of a CO ligand was further demonstrate by the IR measurement of the solution (1923 cm^{−1}) (Figure S60).

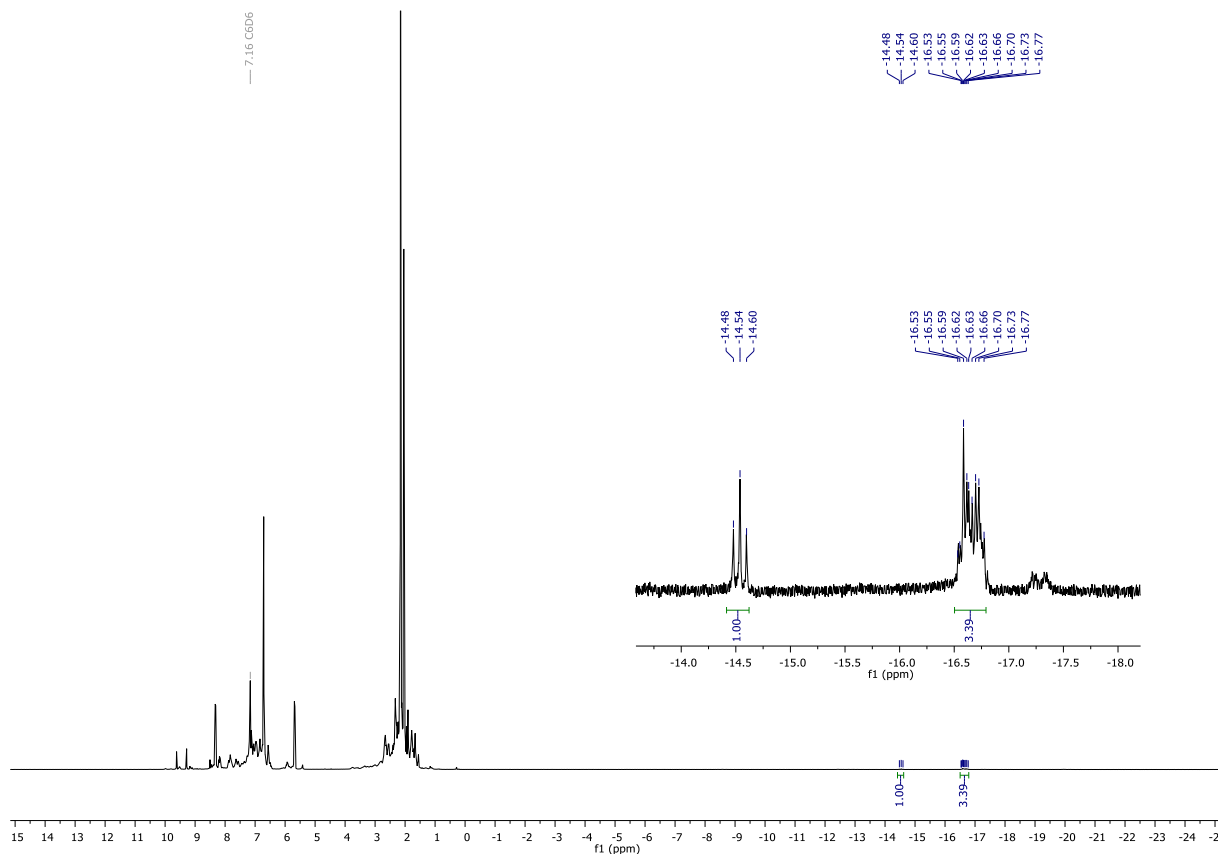


Figure S57. ¹H NMR spectrum from stoichiometric reaction of catalyst **2a** with formoxyborane **1b**.

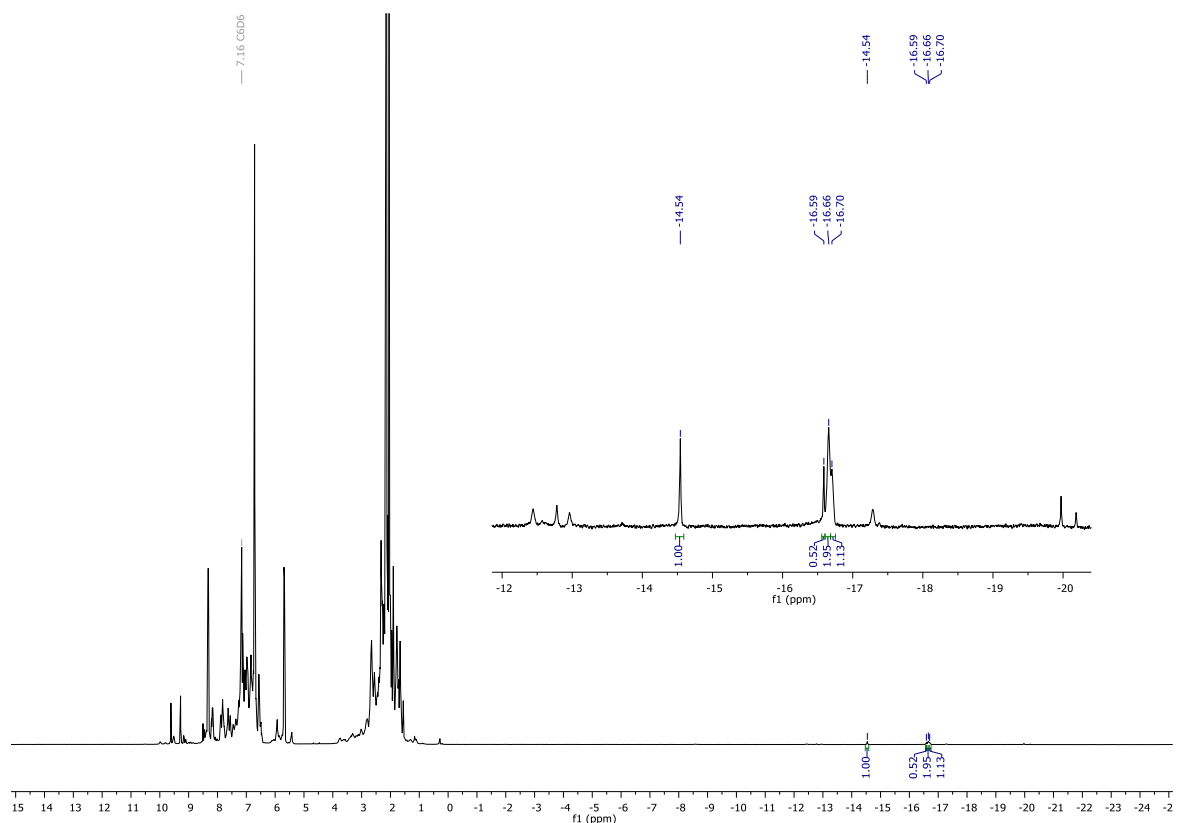


Figure S58. $^1\text{H}[^{31}\text{P}]$ NMR spectrum from stoichiometric reaction of catalyst **2a** with formoxyborane **1b**.

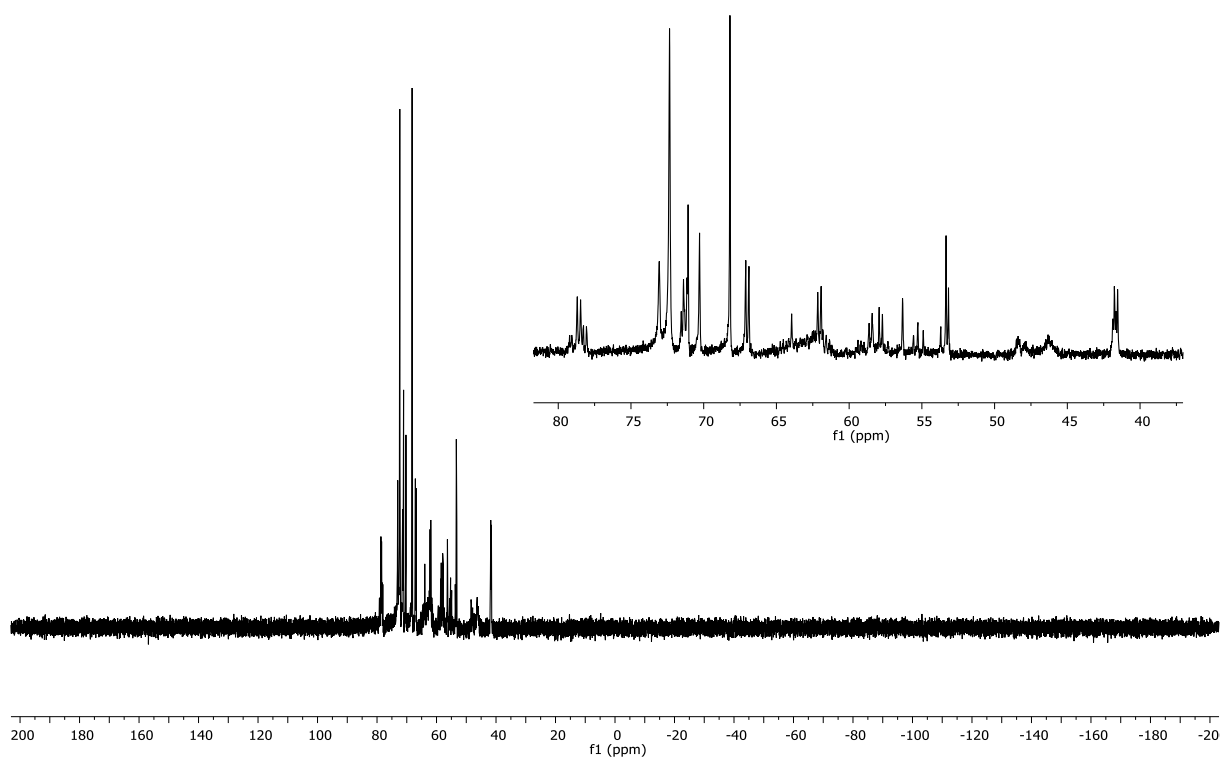


Figure S59. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum from stoichiometric reaction of catalyst **2a** with formoxyborane **1b**.

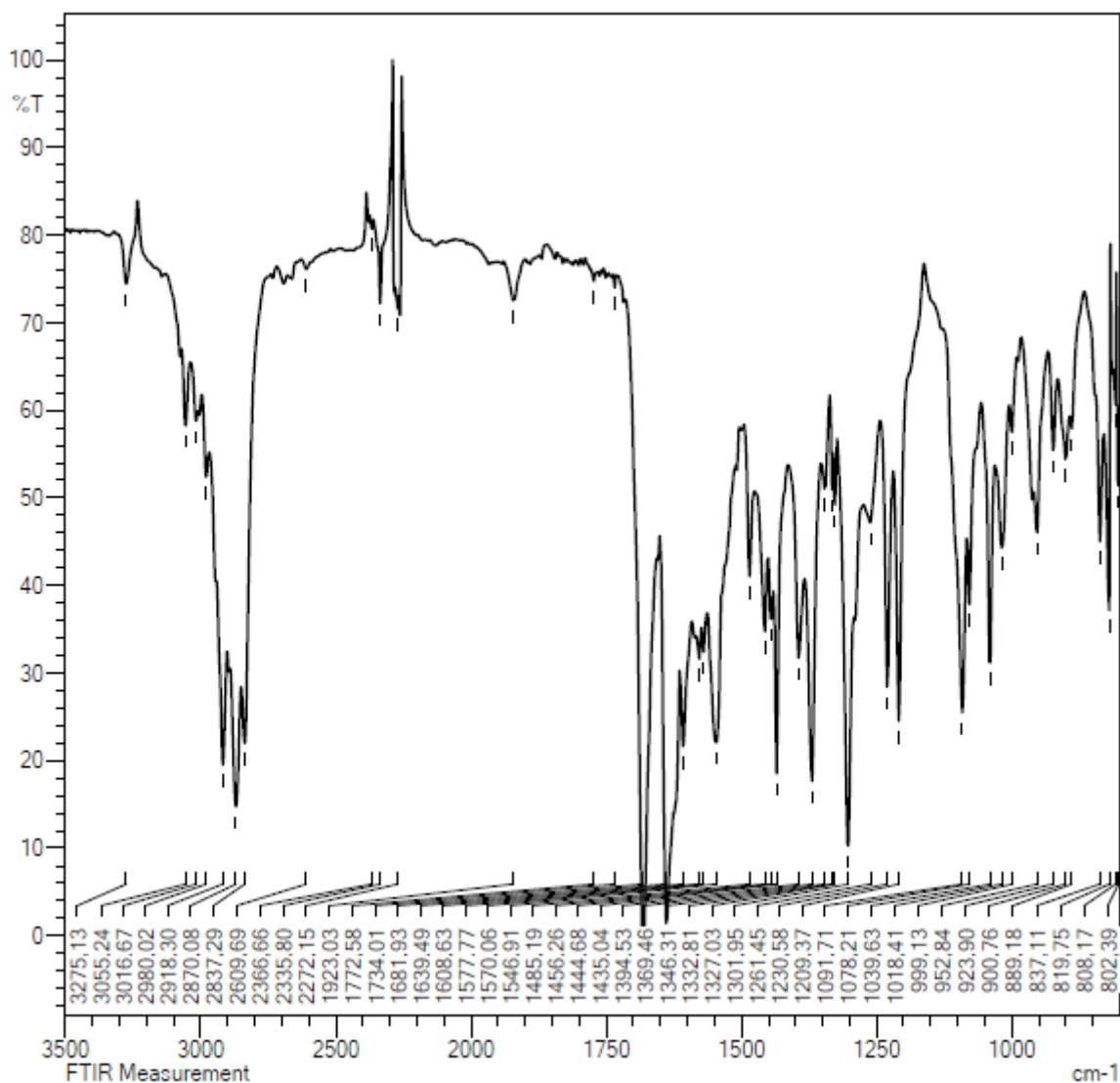


Figure S60. IR spectrum from stoichiometric reaction of catalyst **2a** with formoxyboranes **1b**.

15 Ketone hydroboration with isolated $\text{Ru}(\eta^1\text{-OAc})(\text{H})(\text{CO})(\text{mer-}\kappa^3\text{-PN}^{\text{H}}\text{P}^{\text{Ph}})$ as catalyst

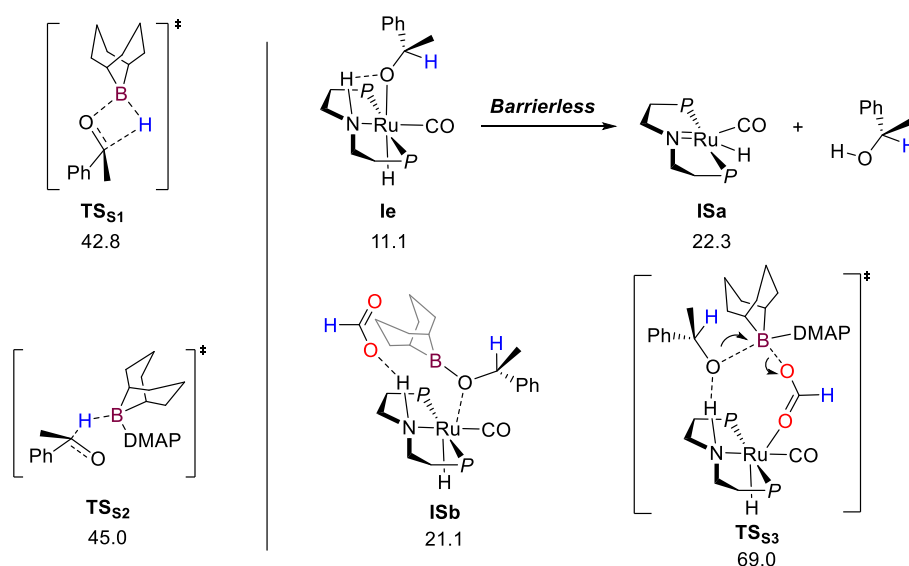
In a glovebox, a *J. Young* NMR Tube was charged $[\text{Ru}(\eta^1\text{-OAc})(\text{H})(\text{CO})(\text{mer-}\kappa^3\text{-PN}^{\text{H}}\text{P}^{\text{Ph}})]$ (**2b**) (2 mol%), 9-borabicyclo[3.3.1]nonan-9-yl formate *N,N*-dimethylaminopyridine adduct (**1b**) (1.2 equiv.), C_6D_6 (0.4 mL), acetophenone (**3a**) (0.1 mmol, 1.0 equiv.) and trimethoxybenzene (10 mg). The tube was sealed, brought out of the glovebox and heated at 90 °C. The reaction progress was monitored by ¹H NMR spectroscopy. After 3 hours of reaction, 99% yield of the hydroborylated product (**4ab**) was obtained versus trimethoxybenzene as an internal standard.

16 Computational details and structures

16.1 General considerations

All the density functional theory calculations were carried out by using the Gaussian16 suite of codes.²⁴ The hybrid functional B3LYP²⁵ was used with Grimme's D3 empirical dispersion.²⁶ Charged species were approximated as isolated contact ion pair unless isolated ionic species are described. The Def2SVP basis set together with the W06 fitting set was used for all atoms.^{27[22]} All the geometries were fully optimized without any symmetry or geometry constrains. Harmonic vibrational analyses were performed to confirm and characterize the structures as minima. Free energies were calculated within the harmonic approximation for vibrational frequencies. Solvent effects were accounted by application of the implicit solvent model SMD (solvent = benzene).²⁸ All relative energies (corrected for ZPE contributions) and Gibbs free energies (T= 298 K, P = 1 atm) are reported below in Hartree.

16.2 Alternative intermediates and transition states



Scheme S3. Computed alternative intermediates and TS for the (catalytic) transfer of hydroboration of acetophenone **3a** with **1b** catalyzed by **Ia** at B3LYP-D3/Def2SVP level of theory and SMD model to account for solvent effect (C₆D₆). Values are given as Gibbs free energies, referenced to **Ia** and the respective organic reagents, and in kcal.mol⁻¹.

These results show that a mechanism involving the generation of a genuine hydroborane is energetically unfavoured (TS_{S1}, TS_{S2} > 40 kcal.mol⁻¹). Moreover, some alternative intermediates (**ISa**, **ISb** > 20 kcal.mol⁻¹), as well as an alternative TS (TS_{S3}) were also computed, they are all higher in energy than the proposed catalytic mechanism reported in Scheme 6.

16.3 Three lowest frequencies and energies for all computed structures

Structures can be found in the xyz document attached. Reports were directly generated from the .log files using the GEAC program.²⁹

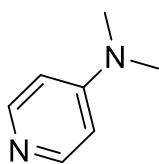
CO₂

| | 1 | 2 | 3 |
|----------------|----------|----------|-----------|
| | PI | PI | SG |
| Frequencies -- | 648.6979 | 648.6979 | 1389.9816 |
| Red. masses -- | 12.8774 | 12.8774 | 15.9949 |
| Frc consts -- | 3.1927 | 3.1927 | 18.2075 |

IR Inten -- 36.6562 36.6562 0.0000

HF = -188.443466993

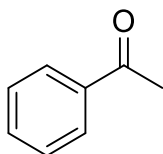
DMAP



| | 1 | 2 | 3 |
|----------------|---------|---------|----------|
| | A | A | A |
| Frequencies -- | 78.8040 | 83.3045 | 157.6830 |
| Red. masses -- | 2.2325 | 2.4375 | 1.8139 |
| Frc consts -- | 0.0082 | 0.0100 | 0.0266 |
| IR Inten -- | 0.8295 | 0.0138 | 0.1626 |

HF = -382.004858777

Acetophenone



| | 1 | 2 | 3 |
|----------------|---------|----------|----------|
| | A | A | A |
| Frequencies -- | 64.8564 | 154.3861 | 187.9477 |
| Red. masses -- | 4.0107 | 4.3875 | 1.0371 |
| Frc consts -- | 0.0099 | 0.0616 | 0.0216 |
| IR Inten -- | 3.2860 | 0.0065 | 0.5022 |

HF = -384.641019152

Et₃SiH

| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 49.6515 | 64.8405 | 67.8831 |
| Red. masses -- | 2.2110 | 1.8932 | 1.9144 |
| Frc consts -- | 0.0032 | 0.0047 | 0.0052 |
| IR Inten -- | 0.0103 | 0.1198 | 0.1253 |

HF = -527.567942729

Et₃SiOCHO

| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 30.4374 | 48.1648 | 58.2381 |
| Red. masses -- | 2.2892 | 2.7537 | 4.1759 |
| Frc consts -- | 0.0012 | 0.0038 | 0.0083 |
| IR Inten -- | 0.1211 | 1.2386 | 2.0125 |

HF = -716.041086164

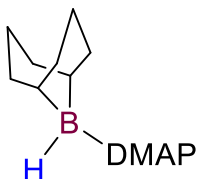
BBNH



| | 1 | 2 | 3 |
|----------------|---------|---------|----------|
| | A | A | A |
| Frequencies -- | 54.6536 | 86.0735 | 231.3540 |
| Red. masses -- | 1.6643 | 2.2196 | 1.6968 |
| Frc consts -- | 0.0029 | 0.0097 | 0.0535 |
| IR Inten -- | 0.6459 | 0.0000 | 0.0414 |

HF = -338.515936054

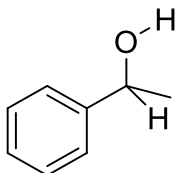
BBNH•DMAP



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 32.2349 | 40.5953 | 97.5936 |
| Red. masses -- | 3.0992 | 3.8524 | 2.0611 |
| Frc consts -- | 0.0019 | 0.0037 | 0.0116 |
| IR Inten -- | 0.0230 | 0.5920 | 0.5313 |

HF = -720.574815540

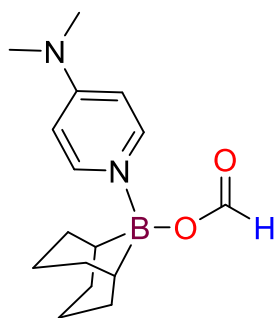
1-phenylethan-1-ol



| | 1 | 2 | 3 |
|----------------|---------|----------|----------|
| | A | A | A |
| Frequencies -- | 38.4218 | 136.5959 | 227.7801 |
| Red. masses -- | 3.6027 | 3.4310 | 2.5136 |
| Frc consts -- | 0.0031 | 0.0377 | 0.0768 |
| IR Inten -- | 2.1779 | 3.4835 | 3.0660 |

HF = -385.838137317

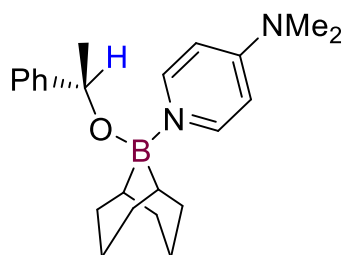
1b



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 33.9797 | 43.2225 | 74.9959 |
| Red. masses -- | 4.1906 | 3.4797 | 6.7499 |
| Frc consts -- | 0.0029 | 0.0038 | 0.0224 |
| IR Inten -- | 0.9086 | 0.3323 | 3.9649 |

HF = -909.063048322

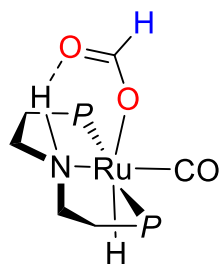
3b



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 23.5174 | 26.0437 | 35.7947 |
| Red. masses -- | 4.1621 | 4.3908 | 3.9028 |
| Frc consts -- | 0.0014 | 0.0018 | 0.0029 |
| IR Inten -- | 0.4812 | 0.5706 | 0.5528 |

HF = -1105.27101844

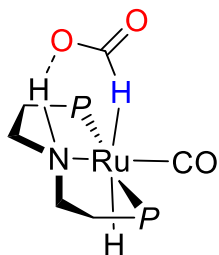
1a



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 12.7970 | 21.5816 | 25.4913 |
| Red. masses -- | 5.2348 | 4.8041 | 5.9175 |
| Frc consts -- | 0.0005 | 0.0013 | 0.0023 |
| IR Inten -- | 0.1340 | 1.0314 | 1.2291 |

HF = -2218.98561854

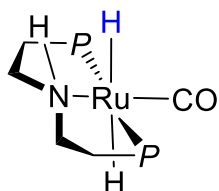
Ib



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 17.1298 | 22.2971 | 23.9990 |
| Red. masses -- | 4.6781 | 5.5782 | 3.8907 |
| Frc consts -- | 0.0008 | 0.0016 | 0.0013 |
| IR Inten -- | 0.1770 | 1.4243 | 0.1909 |

HF = -2218.95903577

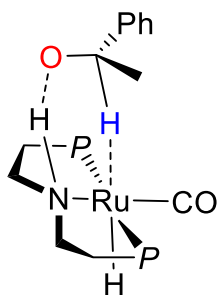
Ic



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 15.2103 | 22.1314 | 32.2900 |
| Red. masses -- | 5.2571 | 6.0580 | 3.9236 |
| Frc consts -- | 0.0007 | 0.0017 | 0.0024 |
| IR Inten -- | 0.0000 | 0.7013 | 0.5699 |

HF = -2030.49325218

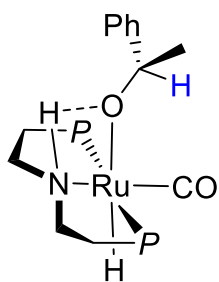
Id



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 15.4261 | 23.5930 | 27.0413 |
| Red. masses -- | 4.6802 | 5.5057 | 5.6326 |
| Frc consts -- | 0.0007 | 0.0018 | 0.0024 |
| IR Inten -- | 0.0152 | 0.4418 | 0.4349 |

HF = -2415.15085612

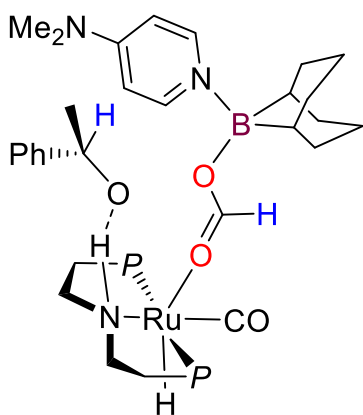
Ie



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 20.3787 | 22.9265 | 28.2409 |
| Red. masses -- | 5.2154 | 4.7101 | 5.2283 |
| Frc consts -- | 0.0013 | 0.0015 | 0.0025 |
| IR Inten -- | 0.0946 | 0.0241 | 0.9639 |

HF = -2415.17184863

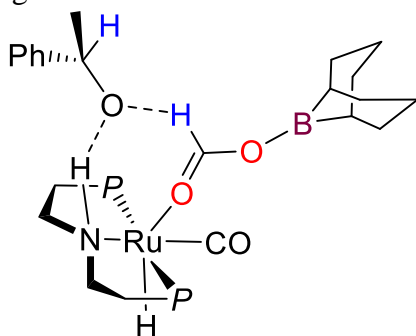
If



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 18.6833 | 23.1767 | 25.1780 |
| Red. masses -- | 5.4464 | 5.3287 | 5.0796 |
| Frc consts -- | 0.0011 | 0.0017 | 0.0019 |
| IR Inten -- | 1.1976 | 1.2064 | 0.4143 |

HF = -3324.26066331

Ig

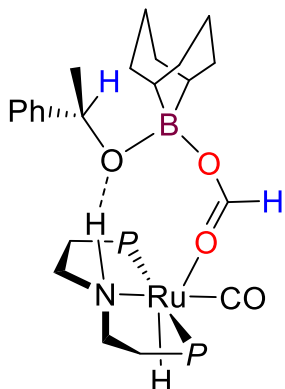


| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 15.7803 | 17.1003 | 22.5022 |
| Red. masses -- | 4.3917 | 5.0338 | 4.9704 |
| Frc consts -- | 0.0006 | 0.0009 | 0.0015 |

IR Inten -- 0.0582 0.0207 0.2050

HF = -2942.19892502

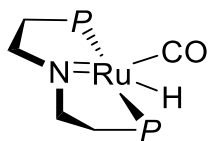
Ih



| | 1 | 2 | 3 |
|----------------|--------|---------|---------|
| | A | A | A |
| Frequencies -- | 5.6719 | 18.5916 | 20.6080 |
| Red. masses -- | 5.4362 | 5.6446 | 5.2772 |
| Frc consts -- | 0.0001 | 0.0011 | 0.0013 |
| IR Inten -- | 0.2153 | 0.4664 | 0.1949 |

HF = -2942.24426868

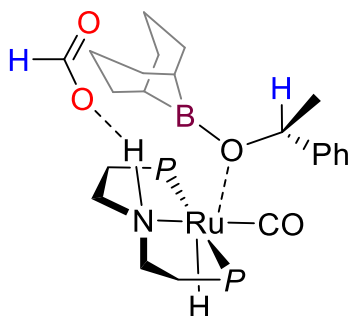
ISa



| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 15.1056 | 17.6231 | 24.7354 |
| Red. masses -- | 5.2542 | 5.1840 | 4.0515 |
| Frc consts -- | 0.0007 | 0.0009 | 0.0015 |
| IR Inten -- | 0.0734 | 0.0049 | 0.0002 |

HF = -2029.28679104

ISb

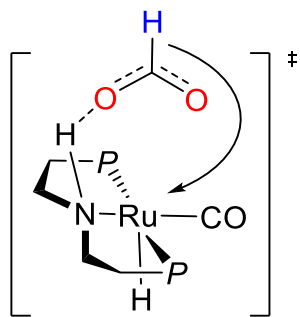


| | 1 | 2 | 3 |
|----------------|---------|---------|---------|
| | A | A | A |
| Frequencies -- | 21.2257 | 28.1963 | 31.2257 |
| Red. masses -- | 5.5810 | 5.1414 | 4.8976 |

| | | | | |
|------------|----|--------|--------|--------|
| Frc consts | -- | 0.0015 | 0.0024 | 0.0028 |
| IR Inten | -- | 1.1682 | 0.6427 | 1.2371 |

HF = -2942.21762119

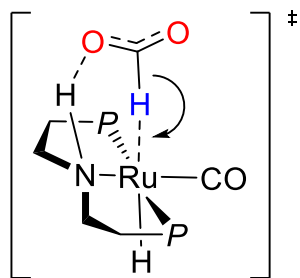
TS_{a-b}



| | | | | |
|-------------|----|-----------|---------|---------|
| | | 1 | 2 | 3 |
| | | A | A | A |
| Frequencies | -- | -336.0741 | 15.2809 | 21.2182 |
| Red. masses | -- | 1.9436 | 4.7771 | 5.1883 |
| Frc consts | -- | 0.1293 | 0.0007 | 0.0014 |
| IR Inten | -- | 2.4063 | 0.1771 | 0.0970 |

HF = -2218.95095349

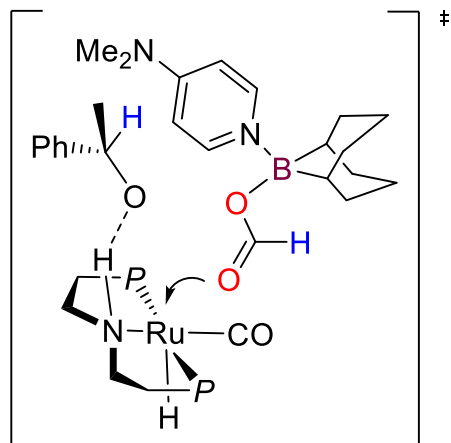
TS_{b-c}



| | | | | |
|-------------|----|-----------|---------|---------|
| | | 1 | 2 | 3 |
| | | A | A | A |
| Frequencies | -- | -316.2353 | 11.8766 | 18.5255 |
| Red. masses | -- | 5.1456 | 4.9844 | 7.2421 |
| Frc consts | -- | 0.3032 | 0.0004 | 0.0015 |
| IR Inten | -- | 1337.4047 | 0.2958 | 1.2200 |

HF = -2218.94463208

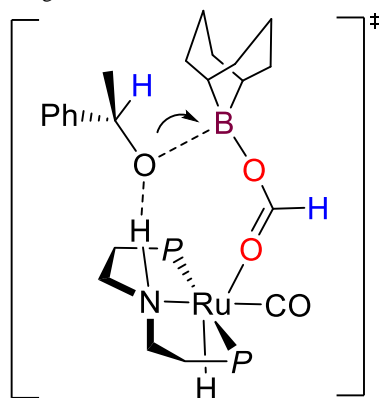
TS_{e-f}



| | 1 | 2 | 3 |
|----------------|----------|--------|---------|
| | A | A | A |
| Frequencies -- | -44.1851 | 7.5919 | 17.0293 |
| Red. masses -- | 7.0229 | 5.3910 | 5.1705 |
| Frc consts -- | 0.0081 | 0.0002 | 0.0009 |
| IR Inten -- | 2.0844 | 0.3843 | 0.6577 |

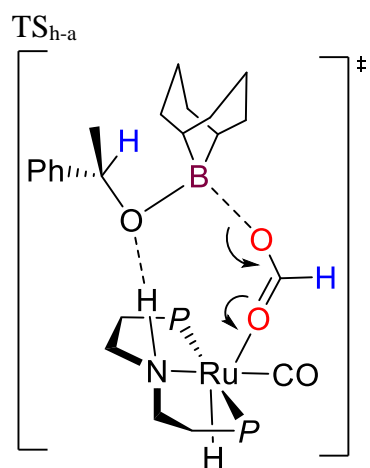
HF = -3324.24910165

TS_{g-h}



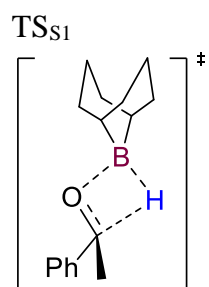
| | 1 | 2 | 3 |
|----------------|----------|---------|---------|
| | A | A | A |
| Frequencies -- | -74.7223 | 16.8769 | 22.5924 |
| Red. masses -- | 5.3974 | 4.9554 | 4.6549 |
| Frc consts -- | 0.0178 | 0.0008 | 0.0014 |
| IR Inten -- | 19.0796 | 0.4007 | 0.1973 |

HF = -2942.19208215



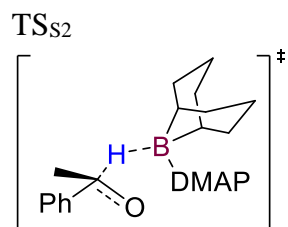
| | 1 | 2 | 3 |
|----------------|----------|--------|---------|
| | A | A | A |
| Frequencies -- | -94.4996 | 8.5759 | 14.0147 |
| Red. masses -- | 6.9277 | 5.4137 | 5.5509 |
| Frc consts -- | 0.0365 | 0.0002 | 0.0006 |
| IR Inten -- | 49.0635 | 0.3227 | 0.1469 |

HF = -2942.23637738



| | 1 | 2 | 3 |
|----------------|-----------|---------|---------|
| | A | A | A |
| Frequencies -- | -256.0949 | 43.1252 | 55.2744 |
| Red. masses -- | 4.9260 | 4.2207 | 3.8461 |
| Frc consts -- | 0.1903 | 0.0046 | 0.0069 |
| IR Inten -- | 181.1370 | 0.0389 | 0.0945 |

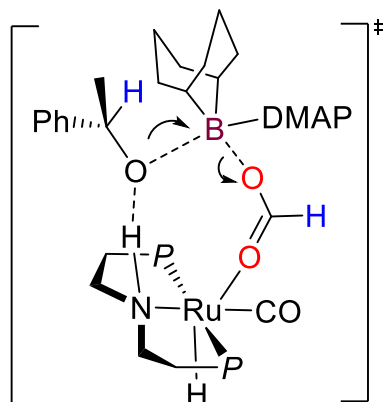
HF = -723.162799624



| | 1 | 2 | 3 |
|----------------|-----------|---------|---------|
| | A | A | A |
| Frequencies -- | -243.7378 | 10.2645 | 36.6520 |
| Red. masses -- | 6.8214 | 4.7554 | 3.9478 |
| Frc consts -- | 0.2388 | 0.0003 | 0.0031 |
| IR Inten -- | 218.5745 | 1.1245 | 0.7416 |

HF = -1105.18898421

TS_{S3}



| | 1 | 2 | 3 |
|----------------|-----------|---------|---------|
| | A | A | A |
| Frequencies -- | -177.7228 | 17.2496 | 19.9769 |
| Red. masses -- | 6.1306 | 5.2144 | 4.9786 |
| Frc consts -- | 0.1141 | 0.0009 | 0.0012 |
| IR Inten -- | 134.0417 | 0.6025 | 0.1741 |

HF = -3324.17676342

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