Supporting Information

Earth-abundant Metal Catalysis Enabled by Counterion Activation
R. Agahi, A.J. Challinor, N.B. Carter and S.P. Thomas

EaStCHEM, School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, U.K. Fax: (+44)-(0)-131-650-6543

Syngenta, Jealott's Hill International Research Centre, Bracknell, Berkshire, RG42 6EX, U.K.
E-mail: stephen.thomas@ed.ac.uk

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General Experimental Information

**Reaction Setup:** All reactions were performed in oven (180 °C) dried glassware under an atmosphere of argon, unless otherwise indicated. All air- and moisture-sensitive reactions were carried out using standard vacuum line and Schlenk techniques, or in a glovebox with a purified argon atmosphere. All glassware was cleaned using base (KOH, iPrOH) and acid (HCl_aq) baths. All reported reaction temperatures correspond to external bath temperatures. Room temperature (rt) was approximately 20°C. “Brine” refers to a saturated solution of sodium chloride in H_2O. For the hydroboration of olefins, the reactions were typically carried out in a glass vial (10 ml, Fisher Scientific, product code 11563680), under an inert atmosphere of argon, unless otherwise stated.

**NMR Spectroscopy:** \(^1^H, \^{13}^C, \text{and}^{11}^B\) NMR spectra were recorded on BrukerAvance III 400 and 500 MHz; Bruker AVI 400 MHz; Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). \(^1^H\) and \(^\text{13}^C\) NMR spectra were referenced to the residual deuterated solvent peak (CHCl\textsubscript{3}: 7.27 ppm, 77.00 ppm; CH\textsubscript{2}Cl\textsubscript{2}: 5.32 ppm, 54.00 ppm; \textit{d}_8\text{-THF:} 1.73 ppm, 25.37 ppm; CD\textsubscript{3}CN: 1.94 ppm, 1.39 ppm). Multiplicities are indicated by app. (apparent), br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet). Coupling constants, \(J\), are reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided. \(^1^H\) and \(^\text{13}^C\) assignments are corroborated through 2-D NMR experiments (COSY, HSQC, HMBC).

**Infrared Spectroscopy:** Infra-red (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR, or Shimadzu IR Affinity-1 spectrometer (serial no. A213749). Peaks are reported in cm\(^{-1}\) with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T), w (weak, 67–100% T), and br. (broad).

**Mass Spectrometry:** Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry Mass Spectrometry Laboratory. High resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

**Melting Points:** Melting points (mp) were determined on a Stuart Scientific SMP10, or Griffin Gallankamp melting point apparatus in capillary tubes and are uncorrected.

**Chromatography:** Analytical thin-layer chromatography was performed on aluminium-backed silica plates (Merck 60 F\textsubscript{254}). Pet. ether refers to petroleum ether 40-60. Product spots were visualised by UV light at 254 nm, and subsequently developed using potassium permanganate solution if appropriate. Flash column chromatography was performed on silica gel (Merck Kielsegel 60, 40-63 μm).

**Solvents:** All solvents for air- and moisture sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Anhydrous \textit{d}_8-tetrahydrofuran was distilled.
from sodium/benzophenone. Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et$_2$O) (Fisher, BHT stabilized ACS grade), and dichloromethane (CH$_2$Cl$_2$) (Fisher, unstabilised HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH$_2$Cl$_2$) (ACS grade), ether (Et$_2$O) (Fisher, BHT stabilized ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60°C, ACS grade).

**Chemicals:** All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics, Tokyo Chemical Industries UK, Fluorochem, Fisher Scientific UK and Apollo Scientific or synthesised within the laboratory. Iron (II) tetrafluoroborate hexahydrate 97% (product number 401668) was purchased from Sigma Aldrich; anhydrous iron (II) chloride 98% was purchased from Strem Chemicals Inc. (UK) (product number 39957, Lot 19226800); cobalt (II) tetrafluoroborate hexahydrate 99% was purchased from Sigma Aldrich (product number 93-2631, Lot MKBX9974V, 44.00000% Fe, expect 44.059%).
Alkene Synthesis

1-(1,2,3,4-tetrahydroisoquinolino)undec-10-en-1-one (2h)

According to a modification of the procedure reported by White and coworkers,\textsuperscript{1} carbonyldiimidazole (3.89 g, 24.0 mmol, 1.20 equiv.) and 10-undecenoic acid (3.61 g, 20.00 mmol, 1.00 equiv.) were dissolved in anhydrous dichloromethane (75 mL) under a nitrogen atmosphere. The mixture was stirred for 3 hours at room temperature, at which time 1,2,3,4-tetrahydroisoquinoline (5.33 g, 40.0 mmol, 2.00 equiv.) was added. The reaction was stirred for 72 hours at ambient temperature. The mixture was concentrated \textit{in vacuo}. The crude product was purified by flash column chromatography (40 g SiO$_2$, 25 mm Ø, wet loaded, EtOAc:pentane 1:1) to give 1-(1,2,3,4-tetrahydroisoquinolino)undec-10-en-1-one (2h) as a yellow oil (5.66 g, 95%).

\textbf{1H NMR:} (500 MHz, CDCl$_3$)

7.24-7.11 (4H, m), 5.87-5.79 (1H, m), 5.03-4.93 (2H, m), 4.75 (1H, s), 4.64 (1H, s) 3.85 (1H, t, $J = 6.0$ Hz), 3.70 (1H, t, $J = 6.0$ Hz), 2.92 (1H, t, $J = 5.9$ Hz), 2.86 (1H, t, $J = 5.9$ Hz), 2.55-2.40 (2H, m), 2.08-2.04 (2H, m), 1.73-1.65 (2H, m), 1.39-1.32 (10H, m)

\textbf{13C NMR:} (126 MHz, CDCl$_3$)

172.0, 139.2, 134.1, 133.7, 129.0, 128.3, 126.7, 126.6, 126.5, 126.3, 114.1, 47.5, 44.2, 43.3, 39.6, 33.8, 29.4, 29.1, 28.9, 25.2

\textbf{IR:} $\nu_{max}$ (neat)

2924 (s), 2852 (s), 1640 (s), 1428, 1206, 908

\textbf{MS:} (EI)

299.2 ([M$^+$], 48)

\textbf{HRMS:} found: 299.22445, [M$^+$]+ C$_{20}$H$_{29}$NO requires 299.22437

\textbf{TLC:} $R_f = 0.50$ (7:3 pentane:EtOAc) [KMnO$_4$]
Ligand and Pre-Catalyst Preparation

2,6-Bis-[1-(2,6-diethylphenylimino)ethyl]pyridine (EtBIP)

According to a previously reported procedure,\textsuperscript{2} 2,6-Diethylaniline (4.50 ml, 27.0 mmol, 2.20 equiv.) was added to a stirred suspension of 2,6-diacetylpyridine (2.00 g, 12.3 mmol, 1.00 equiv.) and p-toluenesulfonic acid (0.110 g, 0.62 mmol, 0.05 equiv.) in anhydrous toluene (25 ml) and heated under Dean-Stark conditions for 18 hours. The mixture was allowed to cool to ambient temperature. The resulting yellow solid was isolated by filtration, washed with cold dichloromethane and recrystallised (CH$_2$Cl$_2$) to give 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine (EtBIP) (3.66 g, 8.61 mmol, 70%) as yellow cuboids.

$^1$H NMR: (500 MHz, CDCl$_3$)

8.51 (2H, d, $J = 7.8$ Hz), 7.95 (1H, t, $J = 7.8$ Hz), 7.16 - 7.14 (4H, m), 7.09 – 7.05 (2H, m), 2.51 – 2.34 (8H, m), 2.28 (6H, s), 1.18 (12H, t, $J = 7.5$ Hz)

$^{13}$C NMR: (126 MHz, CDCl$_3$)

166.9, 155.1, 147.8, 136.9, 131.2, 126.0, 123.4, 122.2, 24.6, 16.8, 13.7

M.P: (CH$_2$Cl$_2$) 196–198 °C; lit 185–186 °C

$^1$H NMR: (500 MHz, CDCl$_3$)

8.51 (2H, d, $J = 7.8$ Hz), 7.95 (1H, t, $J = 7.8$ Hz), 7.16 - 7.14 (4H, m), 7.09 – 7.05 (2H, m), 2.51 – 2.34 (8H, m), 2.28 (6H, s), 1.18 (12H, t, $J = 7.5$ Hz)

$^{13}$C NMR: (126 MHz, CDCl$_3$)

166.9, 155.1, 147.8, 136.9, 131.2, 126.0, 123.4, 122.2, 24.6, 16.8, 13.7

M.P: (CH$_2$Cl$_2$) 196–198 °C; lit 185–186°C

Data were in accordance with those previously reported.\textsuperscript{2}
2,6-Bis[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) tetrafluoroborate (1a)

Iron tetrafluoroborate hexahydrate (0.079 g, 0.235 mmol, 1.00 equiv.) and 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine (0.1 g, 0.235 mmol, 1.00 equiv.) were stirred in THF (5 ml) for 16 hours. The solvent was then removed in vacuo to provide pre-catalyst 1a (0.140 g, 0.214 mmol, 91%) as an amorphous dark red solid. This species was paramagnetic.

\(^1\)H NMR: \((500 \text{ MHz}, \text{CD}_2\text{Cl}_2)\)
\[
23.12, 22.02, 18.39, 17.36, 16.74, 14.79, 8.78, 8.64, 7.50, 7.37, 7.19, 4.20, 3.49, 2.82, 2.76, 2.56, 1.98, 1.32, 1.26, 0.41
\]

\(^{11}\)B NMR: \((160 \text{ MHz}, \text{CD}_2\text{Cl}_2)\)
-0.03

\(^{19}\)F NMR: \((500 \text{ MHz}, \text{d}_8-\text{THF})\)
-145.7, -154.6

See single crystal X-ray analysis data
2,6-Bis[1-(2,6-diethylphenylimino)ethyl]pyridine cobalt(II) tetrafluoroborate (1b)

Cobalt tetrafluoroborate hexahydrate (0.080 g, 0.235 mmol, 1.00 equiv.) and 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine (0.1 g, 0.235 mmol, 1.00 equiv.) were stirred in THF (10 ml) for 16 hours. The solvent was then removed *in vacuo* to provide pre-catalyst 1b (0.145 g, 0.221 mmol, 94%) as an amorphous orange solid. This species was paramagnetic.

\[ ^{11} \text{B NMR:} \quad (160 \text{ MHz, d}_8\text{-THF}) \]
\[ 1.79, -4.19 \]

\[ ^{19} \text{F NMR:} \quad (470 \text{ MHz, d}_8\text{-THF}) \]
\[ -154.9, -150.4 \]

*See single crystal X-ray analysis data*
2,6-Bis[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) tetraphenylborate(1c)

$\text{EtBIPFeCl}_2$ (0.100 g, 0.181 mmol, 1.00 equiv.) and NaBPh$_4$ (0.1 g, 0.235 mmol, 2.00 equiv.) were stirred in THF (5 ml) for 16 hours. The reaction mixture was filtered, eluting with hexane to remove NaCl. The solvent was then removed in vacuo to provide pre-catalyst 1c as an amorphous black solid (0.140 g, 0.214 mmol, 91%).

$\text{^1H NMR:}$ (500 MHz, CD$_2$Cl$_2$)  
7.85, 7.65, 7.49, 7.40, 7.31, 6.56, 3.67, 2.07, 1.24, 0.32

$\text{^11B NMR:}$ (160 MHz, CD$_2$Cl$_2$)  
-6.69
2,6-Bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine cobalt(I) chloride (1d)

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (0.0064 g, 0.05 mmol, 2.00 equiv.) was added to a solution of \( ^{iPr}\text{BIPCoCl}_2 \) (0.015 g, 0.025 mmol, 1.00 equiv.) and TBAT (0.027 g, 0.05 mmol, 2.00 equiv.) in THF (0.8 mL). Upon addition, a colour change from yellow to dark red was observed. After 24 hours, the solvent was removed and replaced with \( \text{C}_6\text{D}_6 \) (0.60 mL). The complex was not isolated but was identified by \(^1\text{H}\) and \(^{13}\text{C}\) NMR.

\(^1\text{H}\) NMR: \((500\,\text{MHz, C}_6\text{D}_6)\)
9.62 (1H, t, \( J = 10.0 \, \text{Hz} \)), 7.90 (2H, m), 7.37 (2H, m), 7.24 (2H, m), 7.02 (2H, m), 3.28 (4H, t), 1.16 (12H, d), 0.98 (12H, d) 0.10 (6H, s)

\(^{13}\text{C}\) NMR: \((126\,\text{MHz, C}_6\text{D}_6)\)
167.1, 152.5, 150.5, 140.4, 126.6, 125.3, 123.9, 114.8, 28.7, 23.7, 23.6, 20.9

Data were in accordance with those previously reported. \(^3\)
General Experimental Procedure

A. General Procedure for the Hydroboration of Olefins

\[
\begin{align*}
\text{R} & \xrightarrow{\text{THF, r.t. 4 h}} \text{R} - \text{H} - \text{BPin} \\
\text{M(BF}_4\text{)}_{\text{2}} & \cdot 6\text{H}_2\text{O (1 mol\%)} \\
\text{BIP (1 mol\%)} & \\
\text{HBPin (1.20 equiv.)} & \\
\end{align*}
\]

In an 8 mL vial equipped with a magnetic stir bar and under an atmosphere of argon, a bis(imino)pyridine ligand (0.01 equiv.) and a metal tetrafluoroborate hexahydrate salt (0.01 equiv.) were dissolved in anhydrous THF (0.5 ml). This mixture was stirred for 1 minute at ambient temperature to form the catalyst. The olefin (0.50 mmol, 1.00 equiv.) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.60 mmol, 1.20 equiv.) were added and the mixture was stirred at ambient temperature for 4 hours. Diethyl ether (3 ml) and water (3 ml) were subsequently added. The aqueous phase was extracted with diethyl ether and the solvent removed \textit{in vacuo}. 1,3,5-Trimethoxybenzene (30.3 mg, 0.18 mmol, 0.20 equiv.) was added for use as a \textsuperscript{1}H NMR (CDCl\textsubscript{3}) internal standard to determine the reaction yield.
Iron and Cobalt-Catalysed Hydroboration Products: Experimental and Analytical Data

Iron-Catalysed Hydroboration Products

Octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 1-Octene (168 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 99:1 pentane:EtOAc, ca. 5 mL fractions) to give the octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a) as a yellow oil.

[Fe] system: 313 mg, 87%, 1.3 mmol
[Co] system: 360 mg, 99%, 1.49 mmol

**¹H NMR:** (500 MHz, CDCl₃)
1.39 (2H, m), 1.34 – 1.27 (10H, m), 1.27 (12H, s), 0.86 (3H, t, J = 6.9 Hz), 0.75 (2H, t, J = 7.8 Hz)

**¹³C NMR:** (125 MHz, CDCl₃)
82.8, 32.4, 31.9, 29.4, 25.0, 24.8, 24.0, 22.7, 14.1

**¹¹B NMR:** (128 MHz, CDCl₃)
34.2

**MS:** (EI⁺)
240.2 ([M⁺], 3)

**TLC:** \( R_f = 0.5 \) (29:1 pentane:EtOAc) [KMnO₄]

Data were in accordance with those previously reported.⁴
2-(4-Phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 4-Phenyl-1-butene (198 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H2O (3 mL), extracted with Et2O (2 x 5 mL) and purified by flash column chromatography (40 g SiO2, 30 mm Ø, wet loaded, 99:1 pentane:EtOAc, ca. 5 mL fractions) to give 2-(4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b) as a yellow oil.

[Fe] system: 254 mg, 65%, 0.98 mmol
[Co] system: 257 mg, 66%, 0.99 mmol

\[ \text{H NMR: (500 MHz, CDCl}_3\] 
7.31 – 7.27 (2H, m), 7.22 – 7.17 (3H, m), 2.65-2.62 (2H, t, \(J = 7.5\) Hz), 1.70 –1.64 (2H, dt, \(J = 15.6, 7.7\) Hz), 1.54 –1.48 (2H, dt, \(J = 15.4\) (obs.), 7.7 Hz), 1.27 (12H, s), 0.86 –0.83 (2H, \(t J = 7.7\) Hz)

\[ \text{C NMR: (126 MHz, CDCl}_3\] 
142.9, 128.4, 128.2, 125.5, 82.9, 35.8, 34.2, 24.8, 23.8

\[ \text{B NMR: (128 MHz, CDCl}_3\] 
34.1

\[ \text{MS: (EI\(^+\))} \]
260.2 ([M\(^+\)], 11)

\[ \text{TLC: } R_f = 0.4 \text{ (29:1 pentane:EtOAc) [KMnO}_4\]}

Data were in accordance with those previously reported.\(^2\)
2-[2-(Cyclohex-3-en-1-yl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 4-Vinylcyclohexene (162 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 29:1 pentane:EtOAc, ca. 5 mL fractions) to give 2-[2-(cyclohex-3-en-1-yl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c) as a yellow oil.

[Fe] system: 249 mg, 70%, 1.05 mmol
[Co] system: 260 mg, 73%, 1.10 mmol

¹H NMR: (500 MHz, CDCl₃)
5.69 – 5.64 (2H, m), 2.16 – 2.08 (1H, m), 2.06 –2.01 (2H, m), 1.80 – 1.74 (1H, m), 1.68 – 1.59 (1H, m), 1.50 – 1.31 (3H, m) 1.27 (12H, s), 1.23 – 1.14 (1H, m), 0.84 – 0.79 (2H, m)

¹³C NMR: (125 MHz, CDCl₃)
127.0, 126.7, 82.9, 35.8, 31.6, 30.7, 28.5, 25.4, 24.8

¹¹B NMR: (128 MHz, CDCl₃)
34.2

MS: (EI⁺)
236.2 ([M]+, 21)

TLC: Rₛ = 0.4 (29:1 pentane:EtOAc) [KMnO₄]

Data were in accordance with those previously reported.²
7-Methyl-3-methylidene-oct-6-enyl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). Myrcene (204 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 29:1 pentane:EtOAc, ca. 5 mL fractions) to give 7-methyl-3-methylidene-oct-6-enyl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d) as a yellow oil.

[Fe] system: 243 mg, 65%, 0.98 mmol
[Co] system: 300 mg, 84%, 1.26 mmol

¹H NMR: (500 MHz, CDCl₃)
5.16 – 5.11 (1H, m), 4.76 – 4.70 (2H, m), 2.18 – 2.03 (6H, m), 1.70 (3H, s), 1.63 (3H, s), 1.26 (12H, s), 0.95 (2H, t, J = 8.1 Hz)

¹³C NMR: (125 MHz, CDCl₃)
151.5, 131.4, 124.4, 107.6, 83.0, 36.3, 30.1, 26.6, 25.7, 24.8, 24.6, 17.7

¹¹B NMR: (128 MHz, CDCl₃)
34.1

MS: (EI⁺)
264.2 ([M]⁺, 3)

TLC: Rf = 0.5 (29:1 pentane:EtOAc) [KMnO₄]

Data were in accordance with those previously reported.⁵
2-(2,4,6-Trimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 2,4,6-Trimethylstyrene (219 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H2O (3 mL), extracted with Et2O (2 x 5 mL) and purified by flash column chromatography (40 g SiO2, 30 mm Ø, wet loaded, 39:1 pentane:EtOAc, ca. 5 mL fractions) to give 2-(2,4,6-trimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e) as a yellow oil.

[Fe] system: 20% (NMR)
[Co] system: 278 mg, 68%, 1.02 mmol

1H NMR: (500 MHz, CDCl3)
6.84 (2H, s), 2.71 - 2.67 (2H, m), 2.32 (6H, s), 2.26 (3H, s), 1.29 (12H, s), 1.00 - 0.95 (2H, m)

13C NMR: (125 MHz, CDCl3)
138.5, 135.6, 134.6, 128.8, 83.1, 24.9, 23.2, 20.8, 19.6

11B NMR: (128 MHz, CDCl3)
33.9

IR: νmax (neat)
2974 (s), 1369 (s), 1308 (s), 1142 (s), 847 (s), 674 (w)

MS: (EI+)
274.2 ([M]+, 28)

TLC: Rf = 0.8 (9:1 pentane:Et2O) [KMnO4]

HRMS: m/z (EI+)
found: 274.21044 (C17H27O2B1) [M]+ requires: 274.20986
2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 4-Fluorostyrene (183 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 19:1 pentane:Et₂O, ca. 5 mL fractions) to give 2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f) as a yellow oil.

[Co] system: 254 mg 68%, 1.02 mmol

**¹H NMR:** (500 MHz, CDCl₃)
- 7.20 – 7.17 (2H, m), 6.97 – 6.94 (2H, m), 2.74 (2H, t, J = 8.1 Hz), 1.23 (12H, s), 1.14 (2H, t, J = 8.1 Hz)

**¹³C NMR:** (125 MHz, CDCl₃)
- 162.1, 160.2, 140.0, 129.3, 114.7, 83.1, 29.2, 24.8

**¹¹B NMR:** (128 MHz, CDCl₃)
- 33.9

**MS:** (EI⁺)
- 250.2 ([M]⁺, 15)

**TLC:** Rₚ = 0.7 (9:1 pentane:Et₂O) [KMnO₄]

Data were in accordance with those previously reported.⁶
2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 4-Methoxystyrene (202 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 9:1 pentane:EtOAc, ca. 5 mL fractions) to give 2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g) as a yellow oil.

[Co] system: 251 mg, 64%, 0.96 mmol

**¹H NMR:** (500 MHz, CDCl₃)
7.17 – 7.14 (2H, dt, J = 9.1, 2.9 Hz), 6.84 – 6.82 (2H, dt, J = 9.1, 2.9 Hz), 3.80 (3H, s), 2.71 (2H, t, J = 8.2 Hz), 1.24 (12H, s), 1.14 (2H, t, J = 8.2 Hz)

**¹³C NMR:** (125 MHz, CDCl₃)
157.6, 136.6, 128.9, 113.6, 83.1, 55.3, 29.1, 24.8

**¹¹B NMR:** (128 MHz, CDCl₃)
34.0

**MS:** (EI⁺)
262.2 ([M⁺], 33)

**TLC:** \( R_f = 0.4 \) (9:1 pentane:Et₂O) [KMnO₄]

Data were in accordance with those previously reported.⁷
(Z)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). Diphenylacetylene (267 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (230 mg, 1.8 mmol, 1.2 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H\textsubscript{2}O (3 mL), extracted with Et\textsubscript{2}O (2 x 5 mL) and purified by flash column chromatography (40 g SiO\textsubscript{2}, 30 mm Ø, wet loaded, 49:1 pentane:EtOAc, ca. 5 mL fractions) to give (Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h) as an amorphous pale yellow solid.

[Fe] system: 321 mg, 70%
[Co] system: 0%

\textbf{\textsuperscript{1}H NMR:} (500 MHz, CDCl\textsubscript{3})
7.40 (1H, s), 7.31 – 7.06 (10H, m), 1.33 (s, 12H)

\textbf{\textsuperscript{13}C NMR:} (125 MHz, CDCl\textsubscript{3})
143.1, 140.5, 137.0, 130.0, 128.9, 128.2, 127.8, 127.6, 126.2, 83.8, 24.3

\textbf{\textsuperscript{11}B NMR:} (128 MHz, CDCl\textsubscript{3})
30.6

\textbf{MS:} (EI\textsuperscript{+})
306.2 ([M\textsuperscript{+}]), 100

\textbf{TLC:} R\textsubscript{f} = 0.41 (29:1 pentane:EtOAc) [KMnO\textsubscript{4}]

Data were in accordance with those previously reported.\textsuperscript{2}
2-(5-(Epoxyhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 1,2-Epoxy-5-hexene (147 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (460 mg, 3.6 mmol, 2.4 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 9:1 pentane:EtOAc, ca. 5 mL fractions) to give 2-(5-(epoxyhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i) as a yellow oil.

[Fe] system: 222 mg, 65%, 0.98 mmol
[Co] system: 136 mg, 40%, 0.60 mmol

1H NMR: (500 MHz, CDCl₃)
2.95 – 2.91 (1H, m), 2.76 (1H, t, \( J = 4.7 \) Hz), 2.48, (dd, \( J = 5.0 \) (obs.), 2.7 Hz), 1.55 – 1.46 (6H, m), 1.27 (12H, s), 0.82 (2H, t, \( J = 7.1 \) Hz)

13C NMR: (125 MHz, CDCl₃)
82.9, 52.4, 47.1, 32.3, 28.6, 24.8, 23.9

11B NMR: (128 MHz, CDCl₃)
34.1

IR: \( \nu_{max} \) (neat)
2932.2 (w), 1373 (s), 1145 (s), 736 (s)

MS: (EI⁺)
226.2 ([M⁺], 1)

TLC: \( R_f = 0.5 \) (19:1 pentane:Et₂O) [KMnO₄]

HRMS: \( m/z \) (EI⁺)
Found: 226.17457, (C₁₂H₂₃O₃B₁) [M⁺] requires: 226.17348
1-(Hexan-5-one)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 5-Hexen-2-one (147 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (460 mg, 3.6 mmol, 2.4 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H2O (3 mL), extracted with Et2O and purified by flash column chromatography (40 g SiO2, 30 mm Ø, wet loaded, CH2Cl2, ca. 5 mL fractions) to give 1-(hexan-5-one)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j) as a yellow oil.

[Co] system: 119 mg, 35%, 0.53 mmol

1H NMR: (500 MHz, CDCl3)
2.43 (2H, t, J = 7.4 Hz), 2.14 (3H, s), 1.63 – 1.57 (2H, m), 1.46 – 1.38 (2H, m), 1.26 (12H, s), 0.80 (2H, t, J = 8.0 Hz)

13C NMR: (125 MHz, CDCl3)
209.2, 83.0, 43.7, 29.8, 26.5, 24.8, 23.7

11B NMR: (128 MHz, CDCl3)
33.9

MS: (EI+)
226.2 ([M]+, 1)

TLC: \( R_f = 0.21 \) (9:1 pentane:Et2O) [KMnO4]

Data were in accordance with those previously reported.8
11-Methylundecanoate-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)

According to General Procedure A, iron or cobalt tetrafluoroborate (5.10 mg, 0.015 mmol, 0.01 equiv.) and EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). Methyl 10-undecenoate (147 mg, 1.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (460 mg, 3.6 mmol, 2.4 equiv.). After stirring for 4 hours at ambient temperature, the reaction mixture was quenched with H₂O (3 mL), extracted with Et₂O (2 x 5 mL) and purified by flash column chromatography (40 g SiO₂, 30 mm Ø, wet loaded, 29:1 pentane:EtOAc, ca. 5 mL fractions) to give 11-methylundecanoate-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k) as a yellow oil.

[Fe] system: 320 mg, 66%, 0.99 mmol
[Co] system: 312 mg, 65%, 0.98 mmol

**¹H NMR:** (500 MHz, CDCl₃)
3.67 (3H, s), 2.32 – 2.29 (2H, t, J = 7.6 Hz), 1.66 – 1.59 (2H, m), 1.43 – 1.38 (2H, m), 1.33 – 1.26 (12H, m), 1.25 (12H, s), 0.79 – 0.76 (2H, t, J = 7.8 Hz)

**¹³C NMR:** (125 MHz, CDCl₃)
174.3, 82.8, 51.4, 34.1, 32.4, 29.5, 29.4, 29.4, 29.2, 29.2, 25.0, 24.8, 24.0

**¹¹B NMR:** (128 MHz, CDCl₃)
34.2

**MS:** (EI⁺)
326.3 ([M⁺], 6)

**TLC:** Rᶠ = 0.3 (29:1 pentane:EtOAc) [KMnO₄]

Data were in accordance with those previously reported.⁹
1-(1,2,3,4-Tetrahydroisoquinolo)undec-11-ol-1-one (3l)

In an 8 mL vial equipped with a magnetic stir bar and under an atmosphere of argon, $\text{EtBIP (6.38 mg, 0.015 mmol, 0.01 equiv.)}$ and cobalt tetrafluoroborate hexahydrate (5.10 mg, 0.015 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). This mixture was stirred for 1 minute at ambient temperature to form the catalyst. The 1-(1,2,3,4-tetrahydroisoquinolo)undec-10-en-1-one (449 mg, 1.50 mmol, 1.0 equiv.) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (522 µL, 3.60 mmol, 2.4 equiv.) were added and the mixture was stirred at ambient temperature for 4 hours. The reaction mixture was cooled to 0 °C, and an aqueous solution of sodium hydroxide (1 M, 6 mL) and hydrogen peroxide (30%wt in water, 4 mL) were added, and the resulting mixture stirred for 0.5 h. The organic phase was then extracted with diethyl ether (3 × 10 mL), washed with a saturated aqueous solution of sodium thiosulfate (10 mL), washed with a saturated solution of sodium chloride (10 mL), dried over magnesium sulfate, and concentrated in vacuo. The title compound was purified by flash column chromatography (40 g SiO$_2$, 30 mm Ø, wet loaded, 4:1 pentane:EtOAc, ca. 5 mL fractions) to give the 1-(1,2,3,4-tetrahydroisoquinolo)undec-11-ol-1-one (3l) as a yellow oil (213 mg, 0.675 mmol, 45%).

$^1$H NMR: (500 MHz, CDCl$_3$) 7.24-7.11 (4H, m), 4.75 (1H, s), 4.64 (1H, s), 3.85 (1H, t, $J = 6.0$ Hz), 3.70 (1H, t, $J = 6.0$ Hz), 3.66 (2H, t, $J = 6.6$ Hz), 2.92 (1H, t, $J = 5.9$ Hz), 2.86 (1H, t, $J = 5.9$ Hz), 2.44-2.40 (2H, m), 1.72-1.65 (3H, m), 1.61-1.55 (2H, m), 1.43-1.28 (12H, m).

$^{13}$C NMR: (125 MHz, CDCl$_3$) 172.2, 135.3, 133.7, 132.8, 130.0, 129.0, 128.3, 126.5, 63.1, 47.5, 44.2, 43.3, 39.7, 33.7, 32.8, 29.5, 28.6, 25.7, 25.3, 24.9

IR: $\nu_{max}$ (neat) 3415 (br), 2918 (m), 2848 (m), 1620 (s), 1449 (m), 1207 (m), 1071 (m)

MS: (EI$^+$) 317.2 ([M]$^+$, 15)

TLC: $R_f = 0.27$ (7:3 Pentane:EtOAc) [KMnO$_4$]

HRMS: Found: 317.23514, (C$_{20}$H$_{31}$O$_2$N) [M]$^+$ requires: 317.23493
Enantioselective Hydroboration of \( \alpha \)-Methylstyrene to give 2-(2-Phenyl-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)

1. Using Fe(BF\(_4\))\(_2\)·6H\(_2\)O
Fe(BF\(_4\))\(_2\)·6H\(_2\)O (8.4 mg, 0.025 mmol, 0.05 equiv.) and (S)-(−)-2,6-diisopropyl-N-(1-(6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)aniline (9.8 mg, 0.025 mmol, 0.05 equiv.) were complexed in THF (0.5 ml) by stirring for 1 minute. \( \alpha \)-Methylstyrene (65\( \mu \)l, 0.50 mmol, 1.00 equiv.) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80\( \mu \)l, 0.55 mmol, 1.10 equiv.) were added. The mixture was stirred for 4 hours at ambient temperature, and then diluted with diethyl ether and passed through a short plug of silica. The filtrate was concentrated to give 3m (>95%). The crude reaction product was purified by flash column chromatography (15 g SiO\(_2\), 25 mm Ø, wet loaded, pentane: Et\(_2\)O 95:5, ca. 5 ml fractions) to give the boronic ester 3m as a colourless oil (103 mg, 0.42 mmol, 83%, 98% ee).

2. Using Co(BF\(_4\))\(_2\)·6H\(_2\)O
Co(BF\(_4\))\(_2\)·6H\(_2\)O (7.2 mg, 0.021 mmol, 0.03 equiv.) and (S)-(−)-2,6-diisopropyl-N-(1-(6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)aniline (8.2 mg, 0.021 mmol, 0.03 equiv.) were complexed in THF (0.5 ml) by stirring for 1 minute. \( \alpha \)-Methylstyrene (91\( \mu \)l, 0.70 mmol, 1.00 equiv.) and 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (112\( \mu \)l, 0.77 mmol, 1.10 equiv.) were added. The mixture was stirred for 4 hours at ambient temperature, and then diluted with diethyl ether and concentrated in vacuo. The crude reaction product was purified by flash column chromatography (16 g SiO\(_2\), 25 mm Ø, wet loaded, pentane: Et\(_2\)O 95:5, ca. 5 ml fractions) to give the boronic ester 3m as a colourless oil (103 mg, 0.42 mmol, 60%, 94% ee).

\(^1\)H NMR: (500 MHz, CDCl\(_3\))
7.30 – 7.26 (4H, m), 7.19 – 7.15 (1H, m), 3.06 (1H, sext. (obs.), \( J = 7.7 \) Hz), 1.31 (3H, d, \( J = 6.9 \) Hz), 1.19 (14H, s)

\(^{13}\)C NMR: (126 MHz, CDCl\(_3\))
142.9, 128.4, 128.2, 125.7, 83.0, 35.8, 24.9, 24.8, 24.7
**^11\text{B} NMR:** (160 MHz, CDCl$_3$)

33.6

**TLC:** $R_f$ 0.5 (pentane:Et$_2$O 95:5) [UV]

See below for HPLC details and spectra (S71).
Data were in accordance with those previously reported.$^{10}$
## Supporting Schemes and Tables

### Table SI.1: Control Reactions for Hydroboration

| Entry | Conditions                                                                 | Result (% Yield 3a) |
|-------|-----------------------------------------------------------------------------|---------------------|
| 1     | $[^{[E^*]}BIPFe(BF_4)_2]$                                                   | 98                  |
| 2     | $[^{[E^*]}BIPFe(BF_4)_2\cdot xH_2O]$                                       | 69                  |
| 3     | Fe(BF_4)_2\cdot 6H_2O + $^{[E^*]}BIP$                                       | 83                  |
| 4     | $^{[E^*]}BIPFeCl_2$ + AgBF_4                                              | 0                   |
| 5     | $^{[E^*]}BIP$                                                              | 0                   |
| 6     | AgBF_4                                                                     | 0                   |
| 7     | $^{[E^*]}BIPFeCl_2$                                                       | 0                   |
| 8     | Fe(BF_4)_2\cdot 6H_2O                                                     | 0                   |
| 9     | $^{[E^*]}BIP$ + AgBF_4                                                    | Trace               |
| 10    | $^{[E^*]}BIPFeCl_2$ + $^{[E^*]}BIP$                                        | 0                   |
| 11    | NH_4BF_4 + $^{[E^*]}BIP$                                                  | 0                   |
| 12    | $^{[E^*]}BIPFe(BF_4)_2$                                                   | 0                   |
| 13    | $^{[E^*]}BIPFe(BF_4)_2$                                                   | 90                  |
| 14    | $^{[E^*]}BIPFe(BF_4)_2$                                                   | >95                 |

**Conditions:** 1-Octene (1.00 equiv.) with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 equiv.), stirred at ambient temperature; a) THF solvent used directly from Winchester bottle; b) THF used from Winchester bottle and degassed prior to use; c) Complex synthesised from 99.99% pure FeCl_2.
### Table SI.2: Optimisation for Hydroboration

| Entry | Metal Salt | Ligand | Catalytic Loading (Equiv.) | Result (% Yield) |
|-------|------------|--------|----------------------------|------------------|
| 1     | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 0.01 | >95 |
| 2     | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | H<sub>2</sub>BIP | 0.01 | 0 |
| 3     | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Mes<sub>2</sub>BIP | 0.01 | 58 |
| 4     | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Mes<sub>2</sub>BIP | 0.01 | 79 |
| 5     | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | iPr<sub>2</sub>BIP | 0.01 | >95 |
| 6     | Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 0.01 | >95 |
| 7     | Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | H<sub>2</sub>BIP | 0.01 | 0<sup>a</sup> |
| 8     | Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Mes<sub>2</sub>BIP | 0.01 | 23 |
| 9     | Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Mes<sub>2</sub>BIP | 0.01 | >95 |
| 10    | Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | iPr<sub>2</sub>BIP | 0.01 | 35 |
| 11    | Fe(OAc)<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 0 |
| 12    | Fe(stearate)<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 16<sup>b</sup> |
| 13    | Fe(ClO<sub>4</sub>)<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 3 |
| 14    | Fe(acac)<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 0 |
| 15    | FeSO<sub>4</sub> | Et<sub>2</sub>BIP | 2 | 0 |
| 16    | FeBr<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 0 |
| 17    | FeCl<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 0 |
| 18    | FeF<sub>2</sub> | Et<sub>2</sub>BIP | 2 | 0 |
| 19    | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 2 | 70 |
| 20    | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 5 | 30<sup>c</sup> |
| 21    | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 1 | >95 |
| 22    | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 0.5 | 77 |
| 23    | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 0.2 | 43 |
| 24    | Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 0.1 | 29 |
| 25    | Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 2 | >95<sup>%</sup> |
| 26    | Cu(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 2 | 0 |
| 27    | Zn(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 2 | 0 |
| 28    | Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O | Et<sub>2</sub>BIP | 2 | 3<sup>d</sup> |

**Conditions:** Olefin (1.00 equiv.) with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 equiv.), and metal salt (0.02 equiv.) stirred in THF (1 M) at ambient temperature; over 24 hours. Yields determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. a) 70% isomerised alkene recovered b) 60% Hydrogenated alkene recovered c) 20% isomerised alkene recovered d) 13% isomerised alkene recovered
Table SI.3: Ligand Screen for Hydroboration

| Metal Salt (X mol%) | Ligand (X mol%) | Metal Salt (X mol%) | Ligand (X mol%) |
|---------------------|-----------------|---------------------|-----------------|
| R - 2a              | 3a              | R - 2a              | 3a              |
| THF, r.t. 24 h      |                 | THF, r.t. 24 h      |                 |

| Ligand | Yield (%) |
|--------|-----------|
| 0%     |           |
| 1%     |           |
| Trace  |           |
| 4%     |           |
| 0%     |           |
| 9%     |           |
| 0%     |           |
| 10%    |           |
| 0%     |           |

**Conditions:** 1-Octene (1.00 equiv.) with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 equiv.), stirred at ambient temperature in THF, yields calculated from 1,3,5-trimethoxybenzene internal standard; a) Myrcene (1.00 equiv.) used as substrate.
Table SI.4: Unreactive Substrates Towards Hydroboration

| Unreactive Substrate | Conditions |
|----------------------|------------|
| **Table SI.4: Unreactive Substrates Towards Hydroboration** |
| ![Diagram](image) |
| THF, rt, 4 h |
| M(BF$_4$)$_2$·6H$_2$O (1 mol%) |
| t-BuB (1 mol%) |
| HBPin (1.20 equiv.) |

**Conditions:** Olefin (1.00 equiv.), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 equiv.) stirred under an atmosphere of argon, ambient temperature. a) alkyne hydrogenation observed.
Table SI.5: Enantioselective Hydroboration of α-Methylstyrene

| Entry | Metal Salt (X equiv.)                                      | Result (% Yield X) |
|-------|------------------------------------------------------------|--------------------|
| 1     | Fe(BF₄)₂·6H₂O (0.05)                                       | >95 (98% ee)       |
| 2     | Co(BF₄)₂·6H₂O (0.01)                                       | 46                 |
| 3     | Co(BF₄)₂·6H₂O (0.03)                                       | (60) (94% ee)      |

**Conditions:** α-Methylstyrene (1.00 equiv.), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 equiv.) stirred in THF, 4 h, ligand A was added in equal amount to metal salt; see below for HPLC details.
SI6: Mechanistic Studies

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-fluoride (7)

![Structure of 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-fluoride (7)](image)

Tetrabutylammonium difluorotriphenylsilicate (270 mg, 0.5 mmol, 1 equiv.) was dissolved in anhydrous THF. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (72.55 µL, 0.5 mmol, 1 equiv.) was then added. The solution was concentrated in vacuo to give the product as an amorphous white solid and analysed by $^{11}\text{B}$ and $^{19}\text{F}$ NMR spectroscopy. Compound 7 was used directly without isolation.

$^{11}\text{B NMR}$: (160 MHz, CDCl$_3$)

5.11

$^{19}\text{F NMR}$: (470 MHz, CDCl$_3$)

-142.7
2,3-Bis(trimethylsilyloxy)-2,3-dimethylbutane (9)

Me$_3$SiCl (6.35 mL, 50.0 mmol) was added dropwise to a stirred solution of pinacol (2.36 g, 20.0 mmol) and Et$_3$N (8.36 mL, 60.0 mmol) in CH$_2$Cl$_2$ (83 mL) at 0 °C and the resultant mixture was allowed to warm to room temperature over 48 h. The mixture was then cooled to 0 °C and sat. aq. NH$_4$Cl (5 mL) was added and the resultant mixture was filtered through a pad of Celite® (eluent CH$_2$Cl$_2$). The filtrate was washed with brine (100 mL), dried and concentrated in vacuo. The residue was triturated with Et$_2$O, then filtered through a pad of Celite® (eluent Et$_2$O) and concentrated in vacuo. Purification via distillation at reduced pressure (14 mmHg) to give the silyl ether 9 as a colourless oil (2.25 g, 43%).

$^1$H NMR: (500 MHz, CDCl$_3$)
1.21 (12H, s), 0.12 (18H, s)

$^{13}$C NMR: (125 MHz, CDCl$_3$)
78.3, 25.0, 2.47

MS: (EI$^+$)
262.2 ([M]$^+$, 11)

Data were in accordance with those previously reported.$^{11}$
(2)-Fluoro-4,4,5,5-tetramethyl-1,3-dioxo-2-boracyclopentane (FBpin)

\[
\begin{align*}
\text{BF}_3\cdot\text{OEt}_2 (90.7 \mu\text{L}, 0.74 \text{ mmol}) \text{ was added in one portion to a stirred solution of } 9 (193 \text{ mg}, 0.74 \text{ mmol}) \text{ in THF (1.40 mL) and the resultant mixture was stirred at this temperature for 5 min. A colourless solution (containing a small amount of an unidentified white precipitate) was produced. The solution was decanted and analysed by } ^{11}\text{B, } ^{19}\text{F NMR spectroscopy. Compound 7 was used directly without isolation.}
\end{align*}
\]

\[ ^{11}\text{B NMR: } (160 \text{ MHz, } d_8\text{-THF}) \]
\[ 21.82, 20.82 \]

\[ ^{19}\text{F NMR: } (470 \text{ MHz, } d_8\text{-THF}) \]
\[ -151.4 \text{ (br)} \]

Data were in accordance with those previously reported.\textsuperscript{11}
Triphenylmethine (8)

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-fluoride (8.8 mg, 0.013 mmol, 1 equiv.) and tritylium hexachloroantimonate (7.6 mg, 0.013 mmol, 1 equiv.) were dissolved in THF (0.6 mL) in a Young’s tap NMR tube. Complete consumption of compound 7 was observed and the presence of triphenylmethine was confirmed by $^1$H NMR spectroscopy.

$^1$H NMR: (500 MHz, THF)

7.45 (6H, t, $J = 7.4$ Hz), 7.37 (3H, t, $J = 7.3$ Hz), 7.31 (6H, d, $J = 7.4$ Hz), 5.77 (1H, s)

Data were in accordance with those previously reported.$^{12}$
**d^1-Triphenylmethine (d^1-8)**

In an 8 mL vial equipped with a magnetic stir bar and under an atmosphere of argon, EtBIP (2.12 mg, 0.01 equiv.) and a metal tetrafluoroborate hexahydrate salt (1.7 mg, 0.005 mmol, 0.01 equiv.) and tritylium hexachloroantimonate (11.6 mg, 0.02 mmol, 0.04 equiv.) were dissolved in anhydrous THF (0.5 ml). 1-octene (76.5 µL, 0.50 mmol, 1.00 equiv.) and 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (86.9 µL, 0.60 mmol, 1.20 equiv.) were added and the mixture was stirred at ambient temperature for 4 hours. Diethyl ether (3 ml) and water (3 ml) were subsequently added. The aqueous phase was extracted with diethyl ether and the solvent removed in vacuo. 1,3,5-Trimethoxybenzene (30.3 mg, 0.18 mmol, 0.20 equiv.) was added for use as a ¹H NMR (CDCl₃) internal standard to determine the reaction yield.

¹H NMR: (500 MHz, CDCl₃)
7.35-7.30 (9H, m), 7.16-7.12 (6H, m)

²H NMR: (61.4 MHz, CHCl₃)
5.72

¹³C NMR: (125 MHz, CDCl₃)
143.9, 139.5, 128.3, 127.9, 127.3, 126.3, 56.9

**NMR study of FBpin formation in situ**

For comparison, EtBIPCo(BF₄)₂ (30 mg, 0.04 mmol), was reacted with HBpin (30 µL, 0.2 mmol) in a solution of THF (0.5 mL) and subjected to ¹¹B and ¹⁹F NMR analysis.
Figure 1 - Formation of FBPin in situ - $^{11}$B NMR

Figure 2 - Formation of FBPin in situ - $^{19}$F NMR
NMR Quenching Studies

According to General Procedure A, cobalt tetrafluoroborate (1.70 mg, 0.005 mmol, 0.01 equiv.) and EtBIP (2.12 mg, 0.005 mmol, 0.01 equiv.) were dissolved in anhydrous THF (1.5 mL). 1-Octene (78.5 µL, 0.5 mmol, 1 equiv.) was then added, followed by 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (86.9 mg, 0.6 mmol, 1.2 equiv.) followed by addition of an additional reagent to quench the reaction.

H$_2$O Quench: H$_2$O (1 mL) was added at the beginning of the reaction or after 30 s, 120 s, 180 s, 300 s, 600 s and 900s, and the yield determined by $^1$H NMR spectroscopy.

Ph$_3$C$^+$ Quench: [Ph$_3$C][SbCl$_6$] (11.6 mg, 0.02 mmol, 0.04 equiv.) was added at the beginning of the reaction or after 30s, 120s, 180s, 300s, 600s and 900s, the reaction left to stir at room temperature for two hours and the yield determined by $^1$H NMR spectroscopy.

| entry | time of H$_2$O addition | % yield |
|-------|-------------------------|---------|
| 1     | 0 s                     | 0       |
| 2     | 30s                     | 8       |
| 3     | 120s                    | 21      |
| 4     | 180s                    | 34      |
| 5     | 300s                    | 64      |
| 6     | 600s                    | 78      |
| 7     | 900s                    | 90      |
Table SI.6.2 – Reaction Quenching with [Ph₃C⁺]

| entry | time of Ph₃C⁺ addition | % yield |
|-------|------------------------|---------|
| 1     | 0 s                    | 0       |
| 2     | 30s                    | 4       |
| 3     | 120s                   | 20      |
| 4     | 180s                   | 30      |
| 5     | 300s                   | 80      |
| 6     | 600s                   | 82      |
| 7     | 900s                   | 88      |
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$^1$H and $^{13}$C NMR Spectra for novel compounds are provided on the following pages
Ligand and (pre-)Catalyst Preparation

2,6-Bis-[1-(2,6-diethylphenylimino)ethyl]pyridine (EtBIP)
2,6-Bis[1-(2,6-diethylphenylimino)ethyl]pyridine iron(II) tetrafluoroborate (1a)
2,6-Bis[1-(2,6-diethylphenylimino)ethyl]pyridine cobalt(II) tetrafluoroborate (1b)
Hydroboration Products
Octyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)

![Chemical Structure](image)

- **Experiment**: e1H
- **Solvent**: CDCl3
- **Holder**: 36 Group
- **THO Email**: ()
- **localpath**: pro39k://snapshot3.2/data/THO/ro/5/Feb0/1001/10
- **archive data**: THO/AleolMaz/AleolMaz_04/1171P_190213_1H_pr500_Feb0/1001
2-(4-Phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)
2-(2-(Cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)
7-Methyl-3-methylidene-oct-6-enyl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)
2-(2,4,6-Trimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)
2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)
2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)
(Z)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)
2-(5-(Epoxhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)
1-(Hexan-5-one)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)
11-Methylundecanoate-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)
1-(1,2,3,4-tetrahydridoisoquinolino)undec-11-ol-1-one (31)
2-(2-Phenyl-propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)
4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-fluoride (7)
Triphenylmethane (8)
d<sup>1</sup>-Triphenylmethane (d<sup>1</sup>-8)
2,3-Bis(trimethylsilyloxy)-2,3-dimethylbutane (9)
HPLC Data

HPLC of (±)-4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane

[Daicel Chiralpak OD-H (2.1 x 150 mm), particle size = 5 μm hexane/iPrOH = 99.50:0.50, v = 0.80 mL min⁻¹, λ = 210 Nm]

| # | Time  | Area  | Height | Width | Area² | Symmetry |
|---|-------|-------|--------|-------|-------|----------|
| 1 | 16.276| 11104.9| 375.3  | 0.4931| 49.904| 0.339    |
| 2 | 21.273| 11147.6| 268.6  | 0.6882| 50.096| 0.305    |
HPLC of (S)(+)-4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane, [Co] System

[Daicel Chiralpak OD-H (2.1 x 150 mm), particle size = 5 μm hexane/iPrOH = 99.50:0.50, v = 0.80 mL min⁻¹, λ = 210 Nm, t (minor) = 16.7 mins, t (major) = 20.9 mins]
HPLC of \((S)(+)-4,4,5,5\text{-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane, [Fe] System}

Daicel Chiralpak OD-H (2.1 x 150 mm), particle size = 5 µm hexane/iPrOH = 99.50:0.50, \(v = 0.80\) mL min\(^{-1}\), \(\lambda = 210\) Nm, \(t\) (minor) = 15.8 mins, \(t\) (major) = 19.7 mins