**Supplementary Data for:**

**Stoichiometric Reductions of Alkyl-Substituted Ketones and Aldehydes to Borinic Esters**
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**Materials and Methods**

**General Considerations:** All reactions and work-up procedures were performed under an inert atmosphere of dry N\(_2\) using standard Schlenk techniques or a glovebox (MBraun glovebox equipped with a -35 °C freezer). Pentane and toluene (Aldrich) were dried using an Innovative Technologies solvent system. Deuterated solvents (CD\(_2\)Cl\(_2\), d\(_8\)-toluene, C\(_6\)D\(_5\)Br) were purchased from Cambridge Isotope Laboratories, Inc. and stored over activated 4Å molecular sieves prior to use. Ketones and aldehydes were purchased from either Sigma-Aldrich or Alfa Aesar, B(C\(_6\)F\(_5\))\(_3\) was purchased from Boulder Scientific, BPh\(_3\) was purchased from Strem, and C\(_{10}\)H\(_6\)(PPh\(_2\))\(_2\) was prepared from a known literature procedure. All were used without further purification. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssureTM gas purifier.

NMR spectra were obtained on a Bruker Avance III 400 MHz, Varian Mercury 300 MHz, Agilent DD2 600 MHz, or Agilent DD2 500 MHz spectrometer. Spectra were referenced to residual solvent of d\(_8\)-toluene (\(^1\)H = 2.08 for methyl; \(^{13}\)C = 20.40 for CH\(_3\)), CD\(_2\)Cl\(_2\) (\(^1\)H = 5.32, \(^{13}\)C = 54.0), or C\(_6\)D\(_5\)Br (\(^1\)H = 7.28 ppm for meta proton; \(^{13}\)C = 122.4 ppm for ipso carbon). Chemical shifts are listed in ppm and coupling constants are listed in Hz. NMR assignments are supported by additional 2D experiments. High-resolution mass spectrometry (HRMS) was performed in house.

**Syntheses and Characterizations**

*In general, borinic esters and boron enolates synthesized for this communication were highly prone to decomposition upon isolation. Boron enolates have been characterized in solution, and attempts to isolated borinic ester 5b cleanly were unsuccessful (see below). These materials are stable in their crude reaction mixture for days; for those products which were isolated successfully, they were stored in a -35 °C freezer.*

**General Synthesis – Ketone Hydrogenation (NMR scale):** The ketone (0.05 mmol), B(C\(_6\)F\(_5\))\(_3\) (0.05 mmol), and 1,3,5-tri-tert-butylbenzene (internal standard, 0.02-0.03 mmol) were combined in 0.4 mL of d\(_8\)-tol or C\(_6\)D\(_5\)Br and transferred to a J-Young tube. The tube was degassed by three freeze-pump-thaw cycles on a vacuum/H\(_2\) Schlenk line and filled with H\(_2\) (4 atm) at -196 °C. The tube was then heated to 110 °C until the reaction was complete, as evidenced by \(^1\)H, \(^{19}\)F, and \(^{11}\)B NMR. NMR yields were calculated using \(^1\)H integration and a known amount of internal standard (1,3,5-tri-tert-butylbenzene). For isolation, the reaction was repeated without internal standard and, once the reaction was complete, the solvent was removed in vacuo, the resulting material was dissolved in
pentane and filtered over celite. The filtrate was concentrated yielding the borinic ester product.
*These products are sensitive to air and moisture, and were unstable in dichloromethane (with the exception of 2a). Once isolated, the materials were stored in a -35 °C freezer under a N\textsubscript{2} atmosphere.*

**General Synthesis – Ketone Hydrogenation (large scale):** The ketone (0.5 mmol) was quantitatively transferred to a vial containing B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (0.5 mmol) with 1 mL toluene. The resulting solution was quantitatively transferred to a 50 mL Schlenk bomb equipped with a magnetic stir bar using 3 mL toluene. The reaction vessel was degassed by three freeze-pump-thaw cycles on a vacuum/H\textsubscript{2} Schlenk line and filled with H\textsubscript{2} (4 atm) at -196 °C. The reaction was heated to 110 °C for the required reaction time, after which the volatiles were removed *in vacuo* and the resulting material was dissolved in minimal pentane and filtered over celite. The solution was concentrated, yielding the desired products as clear or faint yellow oils.

**General Synthesis – Boron Enolate Synthesis:** The aldehyde (0.05 mmol) and borane (0.05 mmol) were combined in 0.5 mL of d\textsubscript{8}-tol or C\textsubscript{6}D\textsubscript{5}Br and heated to 110 °C until the reaction was complete, as evidenced by \textsuperscript{1}H, \textsuperscript{19}F (where applicable), and \textsuperscript{11}B NMR. Isolation attempts were unsuccessful, as the materials decompose upon concentration. They are therefore characterized from the crude reaction mixtures.

**General Synthesis – Boron Enolate Hydrogenation:** A crude reaction mixture containing 4a or 4b was added to a vial containing B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (0.01 mmol). The resulting solution was combined with phosphine (0.01 mmol) and the reaction was transferred to a J-Young tube. The tube was degassed by three freeze-pump-thaw cycles on a vacuum/H\textsubscript{2} Schlenk line and filled with H\textsubscript{2} (4 atm) at -196 °C. The tube was then heated to 110 °C until the reaction was complete, as evidenced by \textsuperscript{1}H, \textsuperscript{19}F, \textsuperscript{31}P, and \textsuperscript{11}B NMR. NMR yields were calculated using \textsuperscript{1}H integration and a known amount of internal standard (1,3,5-tri-tert-butylbenzene). The reaction was repeated without internal standard, and the reactions (upon completion) were concentrated, dissolved in minimal pentane and filtered to remove the phosphine. Successive washings with cold pentane yielded the pure product 5a or 5b.

\[
\begin{align*}
\text{O} & \quad \text{B(C}_6\text{F}_5)_2 \\
& \quad \text{2a}
\end{align*}
\]

2a: Reaction time: 24 h. Isolated as a faint yellow oil (228 mg, 99%).

\textsuperscript{1}H NMR (400 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): \textit{\delta} 4.21 (quintet, \textit{\textit{J}}_{H-H} = 6.0 Hz, 1H, OCH), 1.70-1.55 (m, 4H, 2xCH\textsubscript{2}), 1.47-1.36 (m, 2H, CH\textsubscript{2}), 1.33-1.22 (m, 2H, CH\textsubscript{2}), 0.88 (t, \textit{\textit{J}}_{H-H} = 7.3 Hz, 6H, CH\textsubscript{3}).

\textsuperscript{19}F NMR (377 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): \textit{\delta} -132.3 (dd, \textit{\textit{J}}_{F-F} = 23.2 Hz, \textit{\textit{J}}_{F-F} = 9.5 Hz, 2F, o-C\textsubscript{6}F\textsubscript{5}), -150.8 (t, \textit{\textit{J}}_{F-F} = 20.1 Hz, 1F, p-C\textsubscript{6}F\textsubscript{5}), -161.8 - -162.0 (m, 2F, m-C\textsubscript{6}F\textsubscript{5}).

\textsuperscript{11}B NMR (128 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): \textit{\delta} 39.3 (br s).

\textsuperscript{13}C\{(\textsuperscript{1}H)\} NMR (101 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): \textit{\delta} 148.0 (dm, \textit{\textit{J}}_{C-F} = 249 Hz, C\textsubscript{6}F\textsubscript{5}), 138.0 (dm, \textit{\textit{J}}_{C-F} = 254 Hz, C\textsubscript{6}F\textsubscript{5}), 82.5 (s, OCH), 38.6 (s, CH\textsubscript{2}), 18.7 (s, CH\textsubscript{2}), 14.3 (s, CH\textsubscript{3}).

HRMS (EI) calcd for C\textsubscript{19}H\textsubscript{15}BF\textsubscript{10}O 460.1056, found 460.1067.
Figure S1: $^1$H NMR spectrum of 2a.

Figure S2: $^{19}$F NMR spectrum of 2a.
Figure S3: $^{11}$B NMR spectrum of 2a.

Figure S4: $^{13}$C{¹H} NMR spectrum of 2a.
2b: Reaction time: 24 h. Isolated as a clear oil (213 mg, 99%). Unidentified impurities in the $^{19}$F NMR spectrum were recurrent but minor (Figure S6).

$^1$H NMR (300 MHz, 298 K, C$_6$D$_5$Br): $\delta$ 3.97-3.89 (m, 1H, OCH), 1.64-1.42 (m, 4H, 2xCH$_2$), 0.83 (t, $^3$J$_{H,H}$ = 7.4 Hz, 6H, 2xCH$_3$).

$^{19}$F NMR (282 MHz, 298 K, C$_6$D$_5$Br): $\delta$ $-$131.4 (dd, $^3$J$_{F,F}$ = 24.4 Hz, $^4$J$_{F,F}$ = 9.7 Hz, 2F, $o$-C$_6$F$_5$), $-$149.0 (t, $^3$J$_{F,F}$ = 20.9 Hz, 1F, $p$-C$_6$F$_5$), -160.1 - -160.3 (m, 2F, $m$-C$_6$F$_5$).

$^{11}$B NMR (128 MHz, 298 K, C$_6$D$_5$Br): $\delta$ 39.2 (br s).

$^{13}$C{$^1$H} NMR (126 MHz, 298 K, d$_8$-tol), partial: $\delta$ 147.7 (dm, $^1$J$_{C,F}$ ~ 245 Hz, C$_6$F$_5$), 143.0 (dm, $^1$J$_{C,F}$ ~ 256 Hz, C$_6$F$_5$), 137.6 (dm, $^1$J$_{C,F}$ ~ 255 Hz, C$_6$F$_5$), 84.5 (s, OCH), 28.7 (s, CH$_2$), 9.3 (s, CH$_3$).

HRMS (EI) calcd for C$_{17}$H$_{11}$BF$_{10}$O 432.0743, found 432.0727.

Figure S5: $^1$H NMR spectrum of 2b.
Figure S6: $^{19}$F NMR spectrum of 2b.

Figure S7: $^{11}$B NMR spectrum of 2b.
2c: Reaction time: 21 h. Isolated as a clear oil (168 mg, 83%). Unidentified impurities in the $^{19}$F NMR were recurrent but minor (Figure S10).

$^1$H NMR (400 MHz, 298 K, d$_8$-tol): δ 4.17 (septet, $^3$J$_{H-H}$ = 6.0 Hz, 1H, OCH), 1.09 (d, $^3$J$_{H-H}$ = 6.0 Hz, 6H, 2xCH$_3$).

$^{19}$F NMR (377 MHz, 298 K, d$_8$-tol): δ -133.0 (dd, $^3$J$_{F-F}$ = 23.5 Hz, $^4$J$_{F-F}$ = 9.3 Hz, 2F, o-C$_6$F$_5$), -149.4 (br t, $^3$J$_{F-F}$ = 20.5 Hz, 1F, p-C$_6$F$_5$), -161.1 (br s, 2F, m-C$_6$F$_5$).

$^{11}$B NMR (128 MHz, 298 K, d$_8$-tol): δ 39.3 (br s).

$^{13}$C($^1$H) NMR (100 MHz, 298 K, d$_8$-tol), partial: δ 74.6 (s, OCH), 24.1 (s, 2xCH$_3$).

HRMS (EI) calcd for C$_{14}$H$_7$BF$_3$O 404.0430, found 404.0438.
Figure S9: $^1$H NMR spectrum of 2c.

Figure S10: $^{19}$F NMR spectrum of 2c.
Figure S11: $^{11}$B NMR spectrum of 2c.

Figure S12: $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 2c.
2d: Reaction time: 120 h. NMR yield 94%.

$^1$H NMR (400 MHz, 298 K, d$_8$-tol): $\delta$ 4.26 (pentet, $^3J_{H-H} = 6.2$ Hz, 1H, OCH), 1.68-1.51 (m, 4H, 2xCH$_2$), 1.38-1.31 (m, 2H, 2xCH), 0.79 (d, $^3J_{H-H} = 6.5$ Hz, 6H, 2xCH$_3$), 0.72 (d, $^3J_{H-H} = 6.4$ Hz, 6H, 2xCH$_3$).

$^{19}$F NMR (377 MHz, 298 K, d$_8$-tol): $\delta$ -132.2 (br s, 2F, o-C$_6$F$_5$), -149.3 (br s, 1F, p-C$_6$F$_5$), -161.1 (br s, 2F, m-C$_6$F$_5$).

$^{11}$B NMR (128 MHz, 298 K, d$_8$-tol): $\delta$ 39.3 (br s).

$^{13}$C{${^1}$H} NMR (126 MHz, 298 K, d$_8$-tol), partial: $\delta$ 147.8 (dm, $^1J_{C-F} \sim 240$ Hz, C$_6$F$_5$), 143.1 (dm, $^1J_{C-F} \sim 259$ Hz, C$_6$F$_3$), 137.7 (dm, $^1J_{C-F} \sim 255$ Hz, C$_6$F$_5$), 79.2 (s, OCH), 45.7 (s, CH$_2$), 24.5 (s, CH), 22.8 (s, CH$_3$), 22.4 (s, CH$_3$).

HRMS (EI) calcd for C$_{21}$H$_9$BF$_{10}$O 488.1369, found 488.1364

Figure S13: $^1$H NMR spectrum of 2d.
Figure S14: $^{19}$F NMR spectrum of 2d.

Figure S15: $^{11}$B NMR spectrum of 2d.
Figure S16: $^{13}$C{$^{1}$H} NMR spectrum of 2d.

2e: Reaction time: 24 h. NMR yield: 97%. Isolated as a faint yellow oil (from cyclohexanone: 201 mg, 91%; from cyclohexenone: 208 mg, 94%).

$^1$H NMR (400 MHz, 298 K, C$_6$D$_5$Br): $\delta$ 4.26 (br, 1H, OCH), 1.77-1.58 (m, 6H, Cy), 1.33-1.21 (m, 4H, Cy).

$^{19}$F NMR (377 MHz, 298 K, C$_6$D$_5$Br): $\delta$ -131.9 (dd, $^3$J$_{F-F}$ = 23.8 Hz, $^4$J$_{F-F}$ = 9.7 Hz, 2F, o-C$_6$F$_5$), -149.5 (br s, 1F, p-C$_6$F$_5$), -160.7 (br s, 2F, m-C$_6$F$_5$).

$^{11}$B NMR (128 MHz, 298 K, C$_6$D$_5$Br): $\delta$ 39.1 ppm (br s).

$^{13}$C{$^{1}$H} NMR (126 MHz, 298 K, C$_6$D$_5$Br), partial: $\delta$ 79.1 (s, OCH), 34.1 (s, CH$_2$), 25.3 (s, CH$_2$), 23.0 (s, CH$_2$).

HRMS (EI) calcd for C$_{18}$H$_{11}$BF$_{10}$O 444.0743, found 444.0739.
Figure S17: $^1$H NMR spectrum of $2e$.

Figure S18: $^{19}$F NMR spectrum of $2e$. 
Figure S19: $^{11}$B NMR spectrum of 2e.

Figure S20: $^{13}$C{${}^1$H} NMR spectrum of 2e.
2f: Reaction time: 65 h. NMR yield: 85%.

$^1$H NMR (400 MHz, 298 K, $d_8$-tol): $\delta$ 3.92-3.86 (m, 1H, OCH), 1.58-1.47 (m, 1H, $i$Pr CH), 1.12 (d, $^3$J$_{H-H}$ = 6.3 Hz, 3H, OCH-CH$_3$), 0.88 (d, $^3$J$_{H-H}$ = 6.7 Hz, 3H, $i$Pr CH$_3$), 0.78 (d, $^3$J$_{H-H}$ = 6.8 Hz, 3H, $i$Pr CH$_3$).

$^{19}$F NMR (377 MHz, 298 K, $d_8$-tol): $\delta$ -132.6 (dd, $^3$J$_{F-F}$ = 23.5 Hz, $^4$J$_{F-F}$ = 9.3 Hz, 2F, $o$-C$_6$F$_5$), -149.4 (br s, 1F, $p$-C$_6$F$_5$), -161.1 (br s, 2F, $m$-C$_6$F$_5$).

$^{11}$B NMR (128 MHz, 298 K, $d_8$-tol): $\delta$ 39.4 (br s).

$^{13}$C{$^1$H} NMR (101 MHz, 298 K, $d_8$-tol), partial: $\delta$ 147.8 (dm, $^1$J$_{C-F}$ ~ 248 Hz, C$_6$F$_5$), 137.7 (dm, $^1$J$_{C-F}$ ~ 256 Hz, C$_6$F$_5$), 82.9 (s, OCH), 34.3 (s, $i$Pr CH), 19.8 (s, OCH-CH$_3$), 18.4 (s, $i$Pr CH$_3$), 16.7 (s, $i$Pr CH$_3$).

HRMS (EI) calcd for C$_{17}$H$_{11}$BF$_{10}$O 432.0743, found 432.0750.

Figure S21: $^1$H NMR spectrum of 2f.
Figure S22: $^{19}$F NMR spectrum of 2f.

Figure S23: $^{11}$B NMR spectrum of 2f.
Figure S24: $^{13}$C{$^{1}$H} NMR spectrum of 2f.

2g: Reaction time: 68 h. NMR yield: >99%.

$^{1}$H NMR (300 MHz, 298 K, d$_{8}$-tol): $\delta$ 3.74 (dt, $^{3}J_{H-H} = 8.4$, 4.7 Hz, 1H, OCH), 1.74-1.34 (m, 3H, CH$_2$ and iPr CH), 0.86 (d, $^{3}J_{H-H} = 6.8$ Hz, 3H, CH$_3$), 0.82-0.77 (m, 6H, 2xCH$_3$).

$^{19}$F NMR (377 MHz, 298 K, CD$_2$Cl$_2$): $\delta$ -132.0 (dd, $^{3}J_{F-F} = 23.5$ Hz, $^{4}J_{F-F} = 9.3$ Hz, 2F, o-C$_6$F$_5$), -150.9 (t, $^{3}J_{F-F} = 20.6$ Hz, 1F, p-C$_6$F$_5$), -161.9 - -162.1 (m, 2F, m-C$_6$F$_5$).

$^{11}$B NMR (96 MHz, 298 K, d$_{8}$-tol): $\delta$ 39.5 (br s).

$^{13}$C{$^{1}$H} NMR (100 MHz, 298 K, d$_{8}$-tol), partial: $\delta$ 87.9 (s, OCH), 32.2 (s, i-Pr CH), 26.0 (s, CH$_2$), 18.3 (s, CH$_3$), 16.8 (s, CH$_3$), 9.5 (s, CH$_3$).

HRMS (El) calcd for C$_{18}$H$_{13}$BF$_{10}$O 446.0900, found 446.0903.
Figure S25: $^1$H NMR spectrum of 2g.

Figure S26: $^{19}$F NMR spectrum of 2g.
Figure S27: $^{11}$B NMR spectrum of 2g.

Figure S28: $^{13}$C$^{1}$H NMR spectrum of 2g.
4a: Reaction time: 24 h. Characterized from the crude reaction mixture with HC$_6$F$_5$.

$^1$H NMR (400 MHz, 298 K, d$_8$-tol): δ 6.37 (s, 1H, alkene CH), 2.29 (q, $^3$J$_{H-H}$ = 7.6 Hz, 2H, CH$_2$), 1.77 (qd, $^3$J$_{H-H}$ = 7.5 Hz, $^1$J$_{H-H}$ = 1.4 Hz, 2H, CH$_2$), 1.02 (t, $^3$J$_{H-H}$ = 7.6 Hz, 3H, CH$_3$), 0.82 (t, $^3$J$_{H-H}$ = 7.5 Hz, 3H, CH$_3$). HC$_6$F$_5$: δ 5.86-5.77 (m, 1H).

$^{19}$F NMR (376 MHz, 298 K, d$_8$-tol): δ -131.9 (d, $^3$J$_{F-F}$ = 22.7 Hz, 2F, o-C$_6$F$_5$), -148.1 (t, $^3$J$_{F-F}$ = 21.0 Hz, 1F, p-C$_6$F$_5$), -160.9 - -161.0 (m, 2F, m-C$_6$F$_5$). HC$_6$F$_5$: δ -139.2 - -139.3 (m, 2F), -154.3 (t, $^3$J$_{F-F}$ = 19.9 Hz, 1F), -162.4 - -162.6 (m, 2F).

$^{11}$B NMR (128 MHz, 298 K, d$_8$-tol): δ 39.8 (br s).

$^{13}$C{$^1$H} NMR (100 MHz, 298 K, d$_8$-tol), partial: δ 148.3 (dm, $^1$J$_{C-F}$ ~ 245 Hz, C$_6$F$_5$), 143.6 (dm, $^1$J$_{C-F}$ ~ 254 Hz, C$_6$F$_5$), 133.6 (dm, $^1$J$_{C-F}$ ~ 251 Hz, C$_6$F$_5$), 133.5 (s, alkene CH), 133.5 (s, quat. C), 24.3 (s, CH$_2$), 20.9 (s, CH$_2$), 12.7 (s, CH$_3$), 12.4 (s, CH$_3$). HC$_6$F$_5$, partial: δ 100.5 (td, $^2$J$_{C-F}$ = 23.1 Hz, $^3$J$_{C-F}$ = 3.5 Hz, CH).

HRMS (EI) calcd for C$_{18}$H$_{11}$BF$_{10}$O 444.0743, found 444.0730.

Figure S29: $^1$H NMR spectrum of 4a.
Figure S30: $^{19}$F NMR spectrum of 4a with HC$_6$F$_5$.

Figure S31: $^{11}$B NMR spectrum of 4a.
Figure S32: $^{13}$C{$^{1}$H} NMR spectrum of 4a.

4b: Reaction time: 24 h. Characterized from the crude reaction mixture with C$_6$H$_6$.

$^1$H NMR (400 MHz, 298 K, d$_8$-tol): $\delta$ 7.73-7.71 (m, 4H, o-CH), 7.24-7.19 (m, 6H, m-CH + p-CH), 6.61 (br t, $^4$$J_{H-H}$ = 1.2 Hz, 1H, alkene CH), 2.41 (q, $^3$$J_{H-H}$ = 7.6 Hz, 2H, CH$_2$), 1.80 (qd, $^3$$J_{H-H}$ = 7.4 Hz, $^4$$J_{H-H}$ = 1.2 Hz, 2H, CH$_2$), 1.10 (t, $^3$$J_{H-H}$ = 7.6 Hz, 3H, CH$_3$), 0.87 (t, $^3$$J_{H-H}$ = 7.4 Hz, 3H, CH$_3$). C$_6$H$_6$: $\delta$ 7.12 (s).

$^{11}$B NMR (128 MHz, 298 K, d$_8$-tol): $\delta$ 45.2 (br s).

$^{13}$C{$^{1}$H} NMR (101 MHz, 298 K, d$_8$-tol): $\delta$ 135.8 (s, alkene CH), 135.3 (s, o-CH), 130.8 (s, p-CH), 127.9 (s, m-CH), 127.8 (s,quat. C), 24.5 (s, CH$_2$), 21.0 (s, CH$_2$), 13.1 (s, CH$_3$), 12.7 (s, CH$_3$). C$_6$H$_6$: $\delta$ 128.5.

HRMS (EI) calcd for C$_{18}$H$_{21}$BO 264.1685, found 264.1686.
Figure S33: $^1$H NMR spectrum of 4b.

Figure S34: $^{11}$B NMR spectrum of 4b.
Figure S35: $^{13}$C{$^1$H} NMR spectrum of 4b.

5a: Reaction time: 24 h. NMR yield: 79%.

**$^1$H NMR** (600 MHz, 298 K, d$_8$-tol): $\delta$ 3.88 (d, $^3$J$_{H-H}$ = 4.5 Hz, 1H, OCH$_2$), 1.38-1.23 (m, 5H, CH + 2xCH$_2$), 0.77 (t, $^3$J$_{H-H}$ = 7.4 Hz, 6H, 2xCH$_3$).

**$^{19}$F NMR** (377 MHz, 298 K, d$_8$-tol): $\delta$ -132.5 - -132.6 (m, 2F, o-C$_6$F$_5$), -148.9 (br s, 1F, p-C$_6$F$_5$), -160.9 (br s, 2F, m-C$_6$F$_5$).

**$^{11}$B NMR** (128 MHz, 298 K, d$_8$-tol): $\delta$ 40.0 (br s).

**$^{13}$C{$^1$H} NMR** (101 MHz, 298 K, d$_8$-tol), partial: $\delta$ 72.0 (s, OCH$_2$), 42.6 (s, CH), 23.2 (s, 2xCH$_2$), 11.1 (s, 2xCH$_3$).

**HRMS** (El) calcd for C$_{18}$H$_{13}$BF$_{10}$O 446.0900, found 446.0891.
Figure S36: $^1$H NMR spectrum of 5a.

Figure S37: $^{19}$F NMR spectrum of 5a.
**Figure S38:** $^{11}$B NMR spectrum of 5a.

**Figure S39:** $^{13}$C\{H\} NMR spectrum of 5a.
5b: Reaction time: 24 h. NMR yield: 70%.
*NMR spectra contain residual pentane from washes. Attempts to remove the solvent resulted in decomposition.*

H NMR (400 MHz, 298 K, d8-tol): δ 7.67-7.64 (m, 4H, o-CH), 7.25-7.21 (m, 6H, m-CH and p-CH), 3.95 (d, 3J_H-H = 4.4 Hz, 2H, OCH2), 1.43-1.31 (m, 5H, CH and 2xCH2), 0.79 (t, 3J_H-H = 7.2 Hz, 6H, 2xCH3).

NMR (128 MHz, 298 K, d8-tol): δ 45.7 (br s).

C{H} NMR (126 MHz, 298 K, d8-tol), partial: δ 134.6 (s, o-CH), 130.2 (s, p-CH), 127.9 (s, m-CH), 69.6 (s, OCH2), 43.4 (s, CH), 23.6 (s, 2xCH2), 11.4 (s, 2xCH3).

HRMS (EI) calcd for C18H23BO 266.1842, found 266.1846.

Figure S40: 1H NMR spectrum of 5b (contains residual pentane).
Figure S41: $^1$H NMR spectrum of 5b after attempts to remove residual pentane.

Figure S42: $^{11}$B NMR spectrum of 5b.
Figure S43: $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 5b (contains residual pentane).

Figure S44: $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 5b after attempts to remove residual pentane.
