### Electronic Supplementary materials for:

# Magnesium-catalyzed Hydroboration of Esters via a Zwitterionic Mechanism

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#### **Table of Contents.**

General Experimental Procedures	S-1
Synthesis of Magnesium Compounds	S-2
Catalytic Hydroboration	S-3
Procedures for Kinetic Measurements	S-13
Mechanism and Rate Law Derivations	S-15
Kinetic Plots	S-18
<sup>1</sup> H NMR spectra of catalytic products	S-25
References	S-41

General Experimental Procedures. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, toluene, pentane, diethyl ether, and tetrahydrofuran were dried and deoxygenated using an IT PureSolv system. Benzene- $d_6$  was heated to reflux over Na/K alloy and vacuum-transferred. To<sup>M</sup>MgMe was synthesized according to the literature procedure.<sup>1</sup> Ester substrates were purchased from Sigma-Aldrich and stored under a N<sub>2</sub> atmosphere inside the glovebox. Liquid substrates were distilled from CaH<sub>2</sub> and stored over molecular sieves prior to use. HBpin was purchased from Sigma-Aldrich, stored at –30 °C inside the glovebox, but used without purification. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B NMR spectra were collected on a Bruker AVII 600 or a DRX 400 spectrometer. <sup>15</sup>N chemical shifts were determined by <sup>1</sup>H-

<sup>15</sup>N HMBC experiments on a Bruker AVII 600 spectrometer with a Bruker Z-gradient inverse TXI <sup>1</sup>H/<sup>13</sup>C/<sup>15</sup>N 5mm cryoprobe; <sup>15</sup>N chemical shifts were originally referenced to an external liquid NH<sub>3</sub> standard and recalculated to the CH<sub>3</sub>NO<sub>2</sub> chemical shift scale by adding –381.9 ppm. Catalytic products were identified by comparison to literature spectroscopic values or converted to alcohols and compared to authentic samples including 4,4,5,5-tetramethyl-2-benzyloxy-1,3,2-dioxaborolane/benzyl alcohol, <sup>2</sup> 4,4,5,5-tetramethyl-2-(isobutyroxy)-1,3,2-dioxaborolane /isobutanol,<sup>2</sup> 4-nitrobenzyl alcohol, <sup>3</sup> 4-methylbenzylalcohol,<sup>4</sup> 4-hydroxymethyl benzonitrile, cyclohexanemethanol, thiophenemethanol, 1,2-propopanediol, 2-methyl-2-propen-1-ol, 1,2-benzenedimethanol, 2-hydroxy-benzenepropanol, 2,2-dimethyl-3-(2-methyl-1-propen-1-yl)-cyclopropanemethanol, 5-bromo-1-pentanol, 1-phenyl-1,4-butanediol, 1-hexyl-1,4-butanediol.<sup>5</sup> Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility. X-ray diffraction data was collected on a Bruker APEX II diffractometer.

#### Synthesis of Magnesium Compounds

To<sup>M</sup>MgH<sub>2</sub>Bpin. A benzene solution of To<sup>M</sup>MgMe (0.250 g, 0.593 mmol, 0.297 M) was added in a dropwise fashion to a stirred solution of HBpin (1.3 mL, 8.959 mmol) dissolved in 10 mL of benzene. The mixture was filtered, and the filtrate was evaporated to give a white solid. The solid was washed with pentane  $(3 \times 5 \text{ mL})$  and dried under vacuum to provide analytically pure To<sup>M</sup>MgH<sub>2</sub>Bpin (0.248 g, 0.463 mmol, 78.1%). Pentane diffusion into a concentrated toluene solution of To<sup>M</sup>MgH<sub>2</sub>Bpin at -35 °C provided X-ray quality crystals. <sup>1</sup>H NMR (600 MHz, benzene-d<sub>6</sub>):  $\delta$  1.15 (s, 18 H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 1.42 (br s, 12 H, BOCMe<sub>2</sub>), 3.38 (s, 6 H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 4.19 (br, q, 2 H, MgH<sub>2</sub>B), 7.36 (t,  ${}^{3}J_{HH} = 7.2$  Hz, 1 H, *p*-Ph), 7.54 (t,  ${}^{3}J_{HH} = 7.2$ Hz, 2 H, *m*-Ph), 8.26 (d,  ${}^{3}J_{HH} = 7.8$  Hz, 2 H, *o*-Ph).  ${}^{13}C{}^{1}H{}$  NMR (175 MHz, benzene-*d*<sub>6</sub>):  $\delta$ 25.27 (BOCMe<sub>2</sub>), 28.38 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 66.40 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 80.94 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 83.48 (BOCMe<sub>2</sub>), 126.24 (p-Ph), 127.16 (m-Ph), 136.47 (o-Ph), 142.41 (br, ipso-Ph), 192.49 (br, *C*NCMe<sub>2</sub>CH<sub>2</sub>O). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$  –18.4 (To<sup>M</sup>), 3.4 (t, <sup>1</sup> $J_{BH}$  = 93.5 Hz, MgH<sub>2</sub>B). <sup>15</sup>N NMR:  $\delta$  –161.1. IR (KBr, cm<sup>-1</sup>): 3041 (w), 2971 (s), 2930 (m), 2309 (br, v<sub>BH</sub>), 1581 (s, v<sub>CN</sub>), 1463 (br, m), 1367 (m), 1272 (s), 1195 (s), 1157 (s), 1034 (w), 961 (s), 894 (w), 850 (w), 813 (w), 750 (w), 706 (m), 679 (m), 661 (w), 638 (m), 580 (w). Anal. Calcd. for C<sub>27</sub>H<sub>43</sub>B<sub>2</sub>N<sub>3</sub>O<sub>5</sub>Mg: C, 60.55; H, 8.09; N, 7.85. Found: C, 60.18; H, 7.89; N, 7.77. Mp: 50-60 °C

(dec).

To<sup>M</sup>MgOEt. Ethanol (5.5 µL, 0.942 mmol) was added to a benzene solution of To<sup>M</sup>MgMe (0.387 g, 0.918 mmol, 91.8 mM). The reaction mixture was stirred for 1 h. Evaporation of the volatile materials, pentane washes of the residue  $(3 \times 5 \text{ mL})$ , and drying under vacuum provided analytically pure To<sup>M</sup>MgOEt (0.350 g, 0.775 mmol, 84.4%). X-ray quality single crystals were obtained from a saturated benzene solution standing at ambient temperature. The solid-state structure is dimeric. The spectroscopic data for this species in benzene- $d_6$  were acquired immediately after its formation at room temperature because a material precipitated within 2 h as X-ray quality crystals. That precipitate dissolves and remains soluble in methylene chloride- $d_2$  to give identical spectral data as in situ generated To<sup>M</sup>MgOEt. The <sup>1</sup>H NMR spectra of To<sup>M</sup>MgOEt, acquired in methylene chloride- $d_2$  at temperatures from 296 to 215 K, contained one set of oxazoline resonances and were consistent with a  $C_{3v}$ -symmetric, monomeric solution structure. This assignment is further supported by the solution IR spectrum, acquired in methylene chloride, which contained only one  $v_{CN}$  band at 1598 cm<sup>-1</sup>. However, this geometry is not maintained in the solid state; an IR spectrum of the crystals (KBr) precipitated from benzene contained two  $v_{CN}$ bands at 1629 and 1594 cm<sup>-1</sup>, corresponding to non-coordinated and coordinated oxazoline. <sup>1</sup>H NMR (600 MHz, benzene- $d_6$ ):  $\delta$  1.21 (s, 18 H, CNC $Me_2$ CH<sub>2</sub>O), 1.27 (t,  ${}^{3}J_{HH} = 7.2$  Hz, 3 H, MgOCH<sub>2</sub>CH<sub>3</sub>), 3.54 (s, 6 H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 3.81 (q,  ${}^{3}J_{HH} = 7.2$  Hz, 2 H, MgOCH<sub>2</sub>CH<sub>3</sub>), 7.25 (t,  ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 1 \text{ H}, p\text{-Ph}), 7.46 \text{ (t, } {}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 2 \text{ H}, m\text{-Ph}), 8.08 \text{ (d, } {}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 2 \text{ H}, o\text{-Ph}).$ <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-*d*<sub>6</sub>): δ 22.14 (MgOCH<sub>2</sub>CH<sub>3</sub>), 29.06 (CNC*Me*<sub>2</sub>CH<sub>2</sub>O), 58.54 (MgOCH<sub>2</sub>CH<sub>3</sub>), 66.71 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 78.61 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 125.98 (p-Ph), 127.70 (m-Ph), 134.56 (o-Ph), 147.12 (br, ipso-Ph), 187.94 (br, CNCMe<sub>2</sub>CH<sub>2</sub>O). <sup>11</sup>B NMR (128 MHz, benzene $d_6$ ):  $\delta - 17.4$ . <sup>15</sup>N NMR:  $\delta - 157.1$ . IR (KBr, cm<sup>-1</sup>): 3038 (w), 2966 (s), 2931 (m), 2868 (m), 1629 (m, v<sub>CN</sub>), 1594 (s, v<sub>CN</sub>), 1568 (s, v<sub>CN</sub>), 1463 (m), 1431 (w), 1386 (m), 1369 (m), 1281 (m), 1198 (s), 1154 (s), 1118 (s), 1066 (m), 1003 (s), 969 (s), 930 (w), 896 (m), 880 (w), 842 (w), 810 (w), 764 (w), 753 (w), 713 (m), 702 (m), 655 (m), 638 (w), 618 (w), 595 (w), 560 (m). Anal. Calcd. for C<sub>23</sub>H<sub>34</sub>BN<sub>3</sub>O<sub>4</sub>Mg: C, 61.16; H, 7.59; N, 9.30. Found: C, 60.88; H, 7.79; N, 9.45. Mp: 225-230 °C (dec).

**To<sup>M</sup>Mg{EtO(H)Bpin}.** A toluene- $d_8$  solution of To<sup>M</sup>MgMe (0.016 g, 0.038 mmol) was placed in an NMR tube and cooled to -78 °C. EtOAc (40 µL, 0.407 mmol) and HBpin (120 µL, 0.827 mmol) were added, and the tube was placed in a spectrometer precooled to -10 °C. Although To<sup>M</sup>Mg{EtO(H)Bpin} is the only To<sup>M</sup>-containing species detected, attempts to isolate by crystallization were not successful. <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>): δ 1.14 (s, 18 H, CNC*Me*<sub>2</sub>CH<sub>2</sub>O), 1.33 (s, 6 H, BOCMe<sub>2</sub>), 1.36 (s, 6 H, BOCMe<sub>2</sub>), 1.46 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 3 H, MgOCH<sub>2</sub>CH<sub>3</sub>), 3.39 (s, 6 H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 3.80 (q, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.29 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 1 H, *p*-Ph), 7.45 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 2 H, *m*-Ph), 8.09 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 2 H, *o*-Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, toluene-*d*<sub>8</sub>): δ 17.48 (MgOCH<sub>2</sub>CH<sub>3</sub>), 25.05 (BOC*Me*<sub>2</sub>), 26.26 (BOC*Me*<sub>2</sub>), 27.64 (CNC*Me*<sub>2</sub>CH<sub>2</sub>O), 58.87 (OCH<sub>2</sub>CH<sub>3</sub>), 65.96 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 79.40 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 79.55 (BOCMe<sub>2</sub>), 125.14 (*p*-Ph), 126.22 (*m*-Ph), 135.39 (*o*-Ph), 143.47 (br, *ipso*-Ph), 190.73 (br, CNCMe<sub>2</sub>CH<sub>2</sub>O). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>): δ –18.2 (To<sup>M</sup>), 7.2 (br, Bpin). <sup>15</sup>N NMR: δ –158.8.

**Representative example for gram-scale hydroboration of esters.** Cyclohexylmethyl cyclohexanecarboxylate (0.99 g, 4.413 mol) and HBpin (1.235 g, 9.648 mmol) were added to a benzene solution of  $To^{M}MgMe$  (0.010 g, 0.024 mmol). The resulting mixture was stirred for 12 h at ambient temperature and then quenched with 1 M aqueous solution of NaOH. Extraction with diethyl ether and subsequent evaporation provided cyclohexanemethanol (0.88 g, 7.706 mmol, 87.3%).



**4,4,5,5-tetramethyl-2-(1-cyclohexylmethyloxy)-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  0.92 (m, 2 H, C<sub>6</sub>H<sub>11</sub>), 1.07 (s, 12 H, BOC $Me_2$ ), 1.11 (m, 3 H, C<sub>6</sub>H<sub>11</sub>), 1.53 (m, 2 H, C<sub>6</sub>H<sub>11</sub>), 1.60 (m, 2 H, C<sub>6</sub>H<sub>11</sub>), 1.72 (m, 2 H, C<sub>6</sub>H<sub>11</sub>), 3.78 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 2 H, C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub>OBpin). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene- $d_6$ ):  $\delta$  25.08 (BOC $Me_2$ ), 26.23 (3-C<sub>6</sub>H<sub>11</sub>), 27.02 (4-C<sub>6</sub>H<sub>11</sub>), 29.03 (2-C<sub>6</sub>H<sub>11</sub>), 41.27 (1-C<sub>6</sub>H<sub>11</sub>), 69.02 (C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub>OBpin), 82.44 (BOCMe<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$  22.5.

NMR characterization data for each of the boron ester products is given below. All boranes were converted to alcohol products by treatment with aqueous NaOH, and the identity of the product was further verified by comparison with the appropriate authentic sample.



**4,4,5,5-tetramethyl-2-ethoxy-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  1.06 (s, 12 H, BOC $Me_2$ ), 1.10 (t,  ${}^{3}J_{HH} = 7.0$  Hz, 3 H, C $H_3$ CH<sub>2</sub>OBpin), 3.88 (t,  ${}^{3}J_{HH} = 7.0$  Hz, 2 H, CH<sub>3</sub>CH<sub>2</sub>OBpin).  ${}^{13}$ C{<sup>1</sup>H} NMR (175 MHz, benzene- $d_6$ ):  $\delta$  17.85 (CH<sub>3</sub>CH<sub>2</sub>OBpin), 25.06 (BOC $Me_2$ ), 61.02 (CH<sub>3</sub>CH<sub>2</sub>OBpin), 82.69 (BOC $Me_2$ ). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$  22.6.



**4,4,5,5-tetramethyl-2-(4-methylbenzyloxy)-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): δ 1.05 (s, 12 H, BOC*Me*<sub>2</sub>), 2.08 (s, 3 H, *Me*), 4.97 (s, 2 H, ArylC*H*<sub>2</sub>OBpin), 6.97 (d,  ${}^{3}J_{\text{HH}} = 7.9$  Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.26 (d,  ${}^{3}J_{\text{HH}} = 7.9$  Hz, 2 H, C<sub>6</sub>H<sub>4</sub>).  ${}^{13}C{}^{1}\text{H}$  NMR (175 MHz, benzene-*d*<sub>6</sub>): δ 21.77 (*Me*-C<sub>6</sub>H<sub>4</sub>), 25.07 (BOC*Me*<sub>2</sub>), 66.72 (ArylCH<sub>2</sub>OBpin), 82.75 (BOCMe<sub>2</sub>), 127.13 (2-C<sub>6</sub>H<sub>4</sub>), 129.22 (3-C<sub>6</sub>H<sub>4</sub>), 136.58 (4-C<sub>6</sub>H<sub>4</sub>), 138.11 (1-C<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>): δ 22.5.



**4,4,5,5-tetramethyl-2-(4-nitrobenzyloxy)-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzened<sub>6</sub>):  $\delta$  1.05 (s, 12 H, BOC*Me*<sub>2</sub>), 4.69 (s, 2 H, ArylC*H*<sub>2</sub>OBpin), 6.92 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.80 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-*d*<sub>6</sub>): 25.05 (BOC*Me*<sub>2</sub>), 66.03 (ArylCH<sub>2</sub>OBpin), 83.11 (BOCMe<sub>2</sub>), 125.04 (2-C<sub>6</sub>H<sub>4</sub>), 127.27 (3-C<sub>6</sub>H<sub>4</sub>), 147.79 (4-C<sub>6</sub>H<sub>4</sub>), 149.54 (1-C<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>):  $\delta$  22.8.



**4,4,5,5-tetramethyl-2-(4-cyanobenzyloxy)-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzened<sub>6</sub>):  $\delta$  1.04 (s, 12 H, BOC*Me*<sub>2</sub>), 4.67 (s, 2 H, ArylC*H*<sub>2</sub>OBpin), 6.91 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.03 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-*d*<sub>6</sub>):  $\delta$  25.08 (BOC*Me*<sub>2</sub>), 67.53 (ArylCH<sub>2</sub>OBpin), 83.25 (BOCMe<sub>2</sub>), 111.25 (4-C<sub>6</sub>H<sub>4</sub>), 119.02 (*C*N-C<sub>6</sub>H<sub>4</sub>), 127.22 (2-C<sub>6</sub>H<sub>4</sub>), 132.62 (3-C<sub>6</sub>H<sub>4</sub>), 147.09 (1-C<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>):  $\delta$  22.7.



**2,2'-[1,2,-phenylenebis(methyleneoxy)]bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane].** <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  1.03 (s, 24 H, BOC $Me_2$ ), 5.07 (s, 4 H, - $CH_2OBpin$ ), 7.09 (m, 2 H, C<sub>6</sub> $H_4(CH_2OBpin)_2$ ), 7.51 (m, 2 H, C<sub>6</sub> $H_4(CH_2OBpin)_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene- $d_6$ ):  $\delta$  25.08 (BOC $Me_2$ ), 67.59 (C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OBpin)<sub>2</sub>), 83.22 (BOCMe<sub>2</sub>), 127.44 (2- $C_6H_4(CH_2OBpin)_2$ ), 131.98 (3- $C_6H_4(CH_2OBpin)_2$ ), 136.54 (1- $C_6H_4(CH_2OBpin)_2$ ). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$  22.8.



**4,4,5,5-tetramethyl-2-[2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy]propyl-1,3,2dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): δ 1.07 (m, 3 H, *Me*CH(OBpin)CH<sub>2</sub>OBpin), 1.09 (s, 12 H, BOC*Me*<sub>2</sub>), 1.11 (s, 12 H, BOC*Me*<sub>2</sub>), 3.86 (m, 2 H, MeCH(OBpin)CH<sub>2</sub>OBpin), 4.52 (m, 1 H, MeCH(OBpin)CH<sub>2</sub>OBpin). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-*d*<sub>6</sub>): δ 18.92 (*Me*CH(OBpin)CH<sub>2</sub>OBpin), 25.00 (BOC*Me*<sub>2</sub>), 25.08 (BOC*Me*<sub>2</sub>), 25.11 (BOC*Me*<sub>2</sub>), 25.16 (BOC*Me*<sub>2</sub>), 69.96 (MeCH(OBpin)CH<sub>2</sub>OBpin), 71.12 (MeCH(OBpin)CH<sub>2</sub>OBpin), 82.76 (BOCMe<sub>2</sub>), 82.91 (BOCMe<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>): δ 22.5.



2-{2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy]propyl}-1-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy]benzene. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>):  $\delta$  1.06 (s, 12 H, BOC*Me*<sub>2</sub>), 1.07 (s, 12 H, BOC*Me*<sub>2</sub>), 1.90 (m, 2 H, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 2.75 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 3.90 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 6.82

(m, 1 H, C<sub>6</sub>H<sub>4</sub>), 6.98 (m, 2 H, C<sub>6</sub>H<sub>4</sub>), 7.15 (m, 1 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzened<sub>6</sub>):  $\delta$  25.05 (BOCMe<sub>2</sub>), 25.10 (BOCMe<sub>2</sub>), 25.12 (BOCMe<sub>2</sub>), 25.15 (BOCMe<sub>2</sub>), 25.80 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 33.02 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 68.92 (C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 82.28 (BOCMe<sub>2</sub>), 83.07 (BOCMe<sub>2</sub>), 117.03 (6-C<sub>6</sub>H<sub>4</sub>), 120.90 (4-C<sub>6</sub>H<sub>4</sub>), 126.98 (2-C<sub>6</sub>H<sub>4</sub>), 127.68 (5-C<sub>6</sub>H<sub>4</sub>), 131.32 (3-C<sub>6</sub>H<sub>4</sub>), 154.75 (1-C<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR (128 MHz, benzene-d<sub>6</sub>):  $\delta$  22.4.



**4,4,5,5-tetramethyl-2-[4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy]decyl-1,3,2dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>):  $\delta$  0.84 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 3 H, C<sub>6</sub>*H*<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 1.06 (s, 12 H, BOC*Me*<sub>2</sub>), 1.07 (s, 12 H, BOC*Me*<sub>2</sub>), 1.17-1.34 (m, 9 H), 1.41-1.57 (m, 3 H), 1.67 (m, 2 H, C<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 3.89 (m, 1 H, C<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 4.13 (m, 1 H, C<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-*d*<sub>6</sub>):  $\delta$  14.23 (*C*<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 22.95 (*C*<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 30.04 (*C*<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 30.09 (*C*<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 32.65 (*C*<sub>6</sub>H<sub>13</sub>CH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 34.84  $\begin{array}{ll} (C_{6}H_{13}CH(OBpin)CH_{2}CH_{2}CH_{2}OBpin), & 38.01 & (C_{6}H_{13}CH(OBpin)CH_{2}CH_{2}CH_{2}OBpin), & 68.23 \\ (C_{6}H_{13}CH(OBpin)CH_{2}CH_{2}CH_{2}OBpin), & 71.88 & (C_{6}H_{13}CH(OBpin)CH_{2}CH_{2}CH_{2}OBpin), & 83.01 \\ (BOCMe_{2}). & ^{11}B \ \text{NMR} \ (128 \ \text{MHz}, \ \text{benzene-}d_{6}): \ \delta \ 22.6. \end{array}$ 



4,4,5,5-tetramethyl-2-[1-phenyl-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy]butyl-**1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  1.01 (s, 12 H, BOC $Me_2$ ), 1.04 (s, 12 H,  $BOCMe_2$ ), 1.68 2 H, PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), (m, 1.68 (m, 2 H. PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 1.85 (m, 2 H, PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 3.88 (m, 2 H, PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 5.25 (m, 2 H, PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 7.03 (t,  ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 1 \text{ H}, p-C_{6}\text{H}_{5}), 7.11 \text{ (t, }{}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 2 \text{ H}, m-C_{6}\text{H}_{5}), 7.29 \text{ (d, }{}^{3}J_{\text{HH}} = 7.6 \text{ Hz}, 2 \text{ H}, o C_6H_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-d<sub>6</sub>):  $\delta$  25.04 (BOCMe<sub>2</sub>), 25.08 (BOCMe<sub>2</sub>), 25.12  $(BOCMe_2),$ 25.16  $(BOCMe_2),$ 32.22 (PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 36.88 (PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 69.22 (PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 73.03 (PhCH(OBpin)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 82.88 (BOCMe<sub>2</sub>), 83.06 (BOCMe<sub>2</sub>), 126.83 (p-C<sub>6</sub>H<sub>5</sub>), 127.99 (*m*-C<sub>6</sub>H<sub>5</sub>), 138.27 (*o*-C<sub>6</sub>H<sub>5</sub>), 144.16 (*ipso*-C<sub>6</sub>H<sub>5</sub>). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$ 22.6.



*trans:cis* = 1.77:1

## 4,4,5,5-tetramethyl-2-(2,2-dimethyl-3-(2-methyl-1-propen-1-yl)-cyclopropanemethoxy)-1,3,2-dioxaborolane. The <sup>1</sup>H NMR spectrum of this mixture of isomers is complicated by the overlap of proton resonances. However, the C2-*H* resonances in both *trans* and *cis* isomers are well-resolved, and from this the isomer ratio is determined to be 1.77:1. The <sup>13</sup>C NMR spectrum is very well-resolved and comparable to the literature values for the corresponding alcohol isomers. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): $\delta$ 1.00-1.02 (overlapped multiplets), 1.05 (*trans*-

BOC*Me*<sub>2</sub>), 1.07 (*cis*-BOC*Me*<sub>2</sub>), 1.09 (overlapped peaks), 1.14-1.20 (overlapped multiplets), 1.34-1.36 (overlapped multiplets), 1.61-1.65 (overlapped multiplets), 3.87-391 (overlapped multiplets), 4.01-404 (overlapped multiplets), 4.13-4.19 (overlapped multiplets), 4.94 (d,  ${}^{3}J_{HH} =$  7.7 Hz, 1 H, *trans*-C2-*H*), 5.08 (d,  ${}^{3}J_{HH} =$  7.5 Hz, 1 H, *cis*-C2-*H*).  ${}^{13}C{}^{1}H{}$  NMR (175 MHz, benzene-*d*<sub>6</sub>):  $\delta$  15.99 (*cis*-C-10), 18.73 (*trans*-C-9), 18.93 (*cis*-C-9), 20.80 (*cis*-C-8), 21.88 (*trans*-C-10), 22.18 (*trans*-C-8), 23.16 (*trans*-C-5), 25.07 (BCO*Me*<sub>2</sub>), 25.11 (BCO*Me*<sub>2</sub>), 25.31 (*trans*-C-7), 26.05 (*cis*-C-7), 26.97 (*cis*-C-6), 29.17 (*trans*-C-6), 29.25 (*cis*-C-5), 30.41 (*cis*-C-4), 34.75 (*trans*-C-4), 63.46 (*cis*-C-3), 66.17 (*trans*-C-3), 82.68 (BOCMe<sub>2</sub>), 82.83 (BOCMe<sub>2</sub>), 120.21(*cis*-C-2), 124.60 (*trans*-C-2), 133.16 (*trans*-C-1), 135.17 (*cis*-C-1).  ${}^{11}$ B NMR (128 MHz, benzene-*d*<sub>6</sub>):  $\delta$  22.5.



**4,4,5,5-tetramethyl-2-(2-thiophenylethyloxo)-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  1.05 (s, 12 H, BOC $Me_2$ ), 2.88 (t,  ${}^{3}J_{HH} = 6.6$  Hz, 2 H, (C<sub>4</sub>H<sub>3</sub>S)CH<sub>2</sub>CH<sub>2</sub>OBpin), 4.03 (t,  ${}^{3}J_{HH} = 6.6$  Hz, 2 H, (C<sub>4</sub>H<sub>3</sub>S)CH<sub>2</sub>CH<sub>2</sub>OBpin), 6.67 (d,  ${}^{3}J_{HH} = 5.0$  Hz, 1 H, 2-C<sub>4</sub>H<sub>3</sub>S), 6.70 (m, 1 H, 3-C<sub>4</sub>H<sub>3</sub>S), 6.81 (d,  ${}^{3}J_{HH} = 5.0$  Hz, 1 H, 4-C<sub>4</sub>H<sub>3</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene- $d_6$ ):  $\delta$  25.06 (BOC $Me_2$ ), 32.78 ((C<sub>4</sub>H<sub>3</sub>S)CH<sub>2</sub>CH<sub>2</sub>OBpin), 66.02 (C<sub>4</sub>H<sub>3</sub>S)CH<sub>2</sub>CH<sub>2</sub>OBpin), 82.88 (BOCMe<sub>2</sub>), 124.20 (4-C<sub>4</sub>H<sub>3</sub>S), 126.11 (3-C<sub>4</sub>H<sub>3</sub>S), 127.26 (2-C<sub>4</sub>H<sub>3</sub>S), 141.26 (1-C<sub>4</sub>H<sub>3</sub>S). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$  22.5.



**4,4,5,5-tetramethyl-2-(6-bromohex-1-yloxy)-1,3,2-dioxaborolane.** <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  1.07 (s, 12 H, BOC $Me_2$ ), 1.09 (m, 2 H, Br(CH<sub>2</sub>)<sub>2</sub>C $H_2$ (CH<sub>2</sub>)<sub>2</sub>OBpin), 1.42 (m, 6 H, BrCH<sub>2</sub>C $H_2$ CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 2.91 (t, <sup>3</sup> $J_{HH}$  = 6.9 Hz, 2 H, BrC $H_2$ (CH<sub>2</sub>)<sub>5</sub>OBpin), 3.85 (t, <sup>3</sup> $J_{HH}$  = 6.6 Hz, 2 H, Br(CH<sub>2</sub>)<sub>5</sub>C $H_2$ OBpin). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene- $d_6$ ):  $\delta$  25.09 (BOC $Me_2$ ), 25.44 (Br(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 28.34 (BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OBpin), 32.02 (BrCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>OBpin), 33.31 (Br(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OBpin), 33.91 (BrCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>OBpin), 65.18 (Br(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OBpin), 82.77 (BOCMe<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, benzene- $d_6$ ):  $\delta$  22.5.



**4,4,5,5-tetramethyl-2-(2-methyl-2-propen-1-yloxo)-1,3,2-dioxaborolane**. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): δ 1.06 (s, 12 H, BOC*Me*<sub>2</sub>), 1.56 (m, 3 H, *Me*C(=CH<sub>2</sub>)CH<sub>2</sub>OBpin), 4.32 (m, 2 H, MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin), 4.81 (m, 1 H, MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin), 5.14 (m, 1 H, MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, benzene-*d*<sub>6</sub>): δ 25.03 (BOC*Me*<sub>2</sub>), 25.07 (BOC*Me*<sub>2</sub>), 19.34 (*Me*C(=CH<sub>2</sub>)CH<sub>2</sub>OBpin), 68.83 (MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin), 82.93 (BOC*Me*<sub>2</sub>), 110.48 (MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin), 143.64 (MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>): δ 22.7.

Entry	Substrate	Cat. loading (mol %)	Т °С <sup>[а]</sup>	Timeª	Products	yield (%) <sup>[b]</sup>
1		5 0.5	25 °C 25 °C	15 min 45 min	2 Bpin	>99%
2		5	25 °C	15 min	2 O Bpin	>99% (90%)
3		5	25 °C	15 min	2 OBpin NO <sub>2</sub>	>99% (91%)
4	NC	5 0.5	25 °C 25 °C	15 min 30 min	2 CN	>99% (91%)
5		5 0.5	25 °C 25 °C	15 min 30 min	<sup>2</sup> O <sup>Bpin</sup>	>99% (90%)
6		5 0.5	25 °C 25 °C	15 min 30 min	2 2 Bpin	>99% (87%)
7		5	25 °C	15 min	S + pinB O	>99%
8	Br <sub>(CH<sub>2</sub>)5</sub> O	5	25 °C	15 min	$\frac{\text{Br}(\text{CH}_2)_5 \text{O}^{\text{Bpin}}}{+}$	>99%

**Table S-1.** Magnesium-catalyzed reactions of HBpin and esters.<sup>[a]</sup>

0	0	5	25 °C	15 min	2 S Bpin	>99%
9	Y o Y	0.5	25 °C	45 min	2 Y \0	(90%)
10		5	25 °C	15 min	↓ O Bpin + Bpin	>99%
11		5 0.5	25 °C 25 °C	15 min 2 h	+ Bpin_0	>99%
12		5 0.5	25 °C 25 °C	15 min 30 min	2 O Bpin O Bpin	>99% (88%)
13	-+о-с- <u></u> + О сн <sub>3</sub>	5	25 °C	15 min	n O Bpin O Bpin	>99%
14		5 0.5	25 °C 25 °C	15 min 30 min	Bpin O Bpin	>99%
15		5 0.5	25 °C 25 °C	15 min 30 min	O Bpin Bpin	>99%
16	C <sub>6</sub> H <sub>13</sub> 0 0	5 0.5	25 °C 25 °C	15 min 30 min	Bpin I C <sub>6</sub> H <sub>13</sub> O Bpin	>99%
17	0	5 0.5	25 °C 25 °C	15 min 1 h	O Bpin	>99% (92%)

<sup>[a]</sup>Micromolar scale reactions conditions: benzene- $d_6$ , r.t.. <sup>[b]</sup>Gram-scale reactions are conducted using 0.5 mol% catalyst loading.

General procedure for kinetic measurements. Reactions were monitored by <sup>1</sup>H NMR spectroscopy using a Bruker DRX-400 spectrometer for kinetic studies. The NMR probe was set to desired temperature before each set of experiments and calibrated using 100% CD<sub>3</sub>OD (for temperatures below 300 K). Single-scan <sup>1</sup>H NMR spectra were acquired at preset intervals. The concentration of the To<sup>M</sup>MgMe precatalyst was determined by integration vs. a standard of accurately known concentration prior to the addition of substrate. [HBpin] was not monitored with time because the resonance partially overlaps with that of the product EtOBpin as well as with EtOAc. The initial concentration values of [HBpin] were used in plotting. The concentrations of other species of interest were determined by comparison of corresponding integrated resonances to a known concentration of tetrakis(trimethylsilyl)silane dissolved in toluene-*d*<sub>8</sub> (6.0 mM).

General description of <sup>1</sup>H NMR kinetic experiments for the catalytic hydroboration of EtOAc using HBpin and To<sup>M</sup>MgMe. The samples were prepared by adding a measured volume (0.64 mL) of the stock toluene- $d_8$  solution of Si(SiMe\_3)\_4 to pre-weighed To<sup>M</sup>MgMe giving [Mg]<sub>tot</sub> ranging from 6.6 mM to 25.2 mM. The sample was placed in a septa-capped NMR tube and cooled to -78 °C. A substrate mixture containing 0.22 mL of EtOAc and 0.96 mL of HBpin was prepared and 120 microliters of this mixture was added to the sample through the septa using a microliter syringe. The hole was sealed with silicone grease. The sample was placed in the NMR spectrometer probe, preset and calibrated to 287 K. Single-scan spectra were acquired automatically at preset time intervals. The concentrations of EtOAc and EtOBpin were determined by comparison of weighted integrals of appropriate resonances to the known concentration of the internal standard Si(SiMe\_3)<sub>4</sub>.

**Determination of rate dependence on [EtOAc] under the condition of [EtOAc]**<sub>ini</sub> = 0.30 M and [HBpin]<sub>ini</sub> = 0.85 M. Plots of [EtOAc] vs. time follow a half-order decay. The half-order rate constants ( $k_{obs}$ ) for each [Mg]<sub>tot</sub> were obtained by a nonweighted linear least-squares fit of the data to the integrated half-order rate law:

$$\left[\text{EtOAc}\right]_{t}^{1/2} = \frac{k_{obs}}{2}t$$

Alternatively, a plot of [EtOAc] vs. time was analyzed by non-linear least squares regression to the equation:

$$\left[ \text{EtOAc} \right]_{t} = \left\{ \left[ \text{EtOAc} \right]_{0}^{1/2} - \frac{k}{2} t \right\}^{2}$$

**Determination of rate dependence on [HBpin] under the condition of [EtOAc]\_{ini} = 0.30 M.**  $k_{obs}$  values are equivalent within error at [HBpin] ranging from 0.85 M to 2.4 M while keeping  $[Mg]_{tot}$  invariant. This demonstrates zero-order [HBpin] dependence on the overall rate law.

Determination of rate dependence on  $[Mg]_{tot}$  under the condition of  $[EtOAc]_{ini} = 0.30$  M and  $[HBpin]_{ini} = 0.85$  M. An observed linear correlation between  $[Mg]_{tot}$  and the corresponding  $k_{obs}$  indicates a first-order  $[Mg]_{tot}$  dependence on overall catalytic rate law. The overall three-half order rate constant (k') value was obtained from the nonweighted linear least-square fit on the plot of  $k_{obs}$  vs.  $[Mg]_{tot}$ .

Thus the rate law for the overall catalysis is written as follows:

$$\frac{-d\left[\text{EtOAc}\right]}{dt} = k' \left[Mg\right]^{1} \left[\text{EtOAc}\right]^{1/2} \left[\text{HBpin}\right]^{0}$$



#### Inconsistent mechanisms and their rate laws:

1.  $K_{1} = k_{1}/k_{.1}$   $0.5 \operatorname{RCO}_{2}\operatorname{CH}_{2}\operatorname{R} \xrightarrow{\operatorname{cat. To^{M}MgOCH}_{2}\operatorname{R}} \stackrel{}{\underset{H}{\overset{H}{\overset{}}}_{\operatorname{R}}} \stackrel{}{\underset{R}{\overset{}}} \stackrel{}{\underset{H}{\overset{}}}_{\operatorname{R}}$   $To^{M}\operatorname{MgH} + \stackrel{}{\underset{H}{\overset{H}{\overset{}}}_{\operatorname{R}}} \stackrel{}{\underset{R}{\overset{K_{2} = k_{2}/k_{.2}}{\overset{}}} To^{M}\operatorname{MgOCH}_{2}\operatorname{R}}$   $To^{M}\operatorname{MgOCH}_{2}\operatorname{R} + \operatorname{HBpin} \stackrel{}{\underset{turnover limiting}{\overset{K_{3}}{\underset{turnover limiting}{\overset{}}}} To^{M}\operatorname{MgH} + \operatorname{RCH}_{2}\operatorname{OBpin}$   $-\frac{d[\operatorname{RCH}_{2}\operatorname{O}_{2}\operatorname{CR}]}{dt} = k_{3}[\operatorname{To^{M}MgOCH}_{2}\operatorname{R}][\operatorname{HBpin}] \quad fails; \text{first order in HBpin}$ 

**2.** The alternative, in which  $To^{M}MgH + RCHO$  is turnover-limiting, is unlikely because  $To^{M}MgH$  is unstable and unlikely persistent during catalysis. Thus, this mechanism is inconsistent with other observations.

3.



This mechanism is also first order in HBpin and inconsistent with observations.



This mechanism is first-order in RCO<sub>2</sub>CH<sub>2</sub>R and inconsistent with observations.

**5.** Note that To<sup>M</sup>MgH/HBpin rapidly forms an adduct in the presence of excess HBpin. To<sup>M</sup>MgOCH<sub>2</sub>R/HBpin forms an adduct detected as the only To<sup>M</sup>MgX species present during catalysis. Any mechanism that invokes a second-order To<sup>M</sup>MgX/HBpin interaction must first involve the unlikely sequence of HBpin dissociation from the adduct and then HBpin returning to complete the reactions.

**6.** The observed resting state  $To^MMg\{(RCH_2O)HBpin\}$  could directly eliminate product to give  $To^MMgH$  in a turnover-limiting step. Then  $To^MMgH$  and RCHO insertion and  $To^MMgOCH_2R$  and HBpin adduct formation could be fast. However, such a mechanism would be zero-order in  $RCO_2CH_2R$ .

m1

m2

R

Chisq

-0.0002585

1.138E-5

0.9999

7.176E-7

NA

NA

Figure S1. Kinetic plots of [EtOAc] versus time; non-linear least square fits to the equation  $[EtOAc]_t = \{[EtOAc]_t^{1/2} - t(k/2)\}^2$  are consistent with half-order dependence on [EtOAc]. The plot of [EtOAc] (rather than  $[EtOAc]^{1/2}$ , see Figure S2) vs. time more clearly shows the >3 halflives, but both representations of the data give equal values for  $k_{obs}$ .



Plots of [EtOAc] vs time; variation of [To<sup>M</sup>MgMe]

m1

m2

R

Chisq

-0.0004107

9.547E-6

0.9999

2.016E-6

NA

NA

**Figure S2.** Each curve shows the half-order dependence of the reaction on ethyl acetate concentration, and the [To<sup>M</sup>MgMe] is varied between data sets. This data is also shown in Figure S1, but as [EtOAc] vs. time rather than [EtOAc]<sup>1/2</sup> vs. time shown here. The data are fit to a line using linear least-squares regression analysis, and the slope m2 =  $k_{obs}$ .



**Figure S3.** First-order plot of Ln[EtOAc] vs. time with varying concentrations of  $To^{M}MgMe$  as the precatalyst. In all cases >10 equiv of HBpin (relative to [EtOAc]) are present in the reaction mixture.



**Figure S4.** Second order plot of 1/[EtOAc] vs time with varying concentrations of To<sup>M</sup>MgMe as the precatalyst, showing that the reaction is not second order in [EtOAc]. In all cases >10 equiv of HBpin (relative to [EtOAc]) are present in the reaction mixture.



**Figure S5.** EtOAc cleavage/hydroboration at 287 K. Plot showing first-order dependence on catalyst concentration.



Plot showing [To<sup>M</sup>MgMe]<sup>1</sup> dependence

**Figure S6.** Zero-order HBpin dependence in catalytic ester hydroboration reaction, determined at 287 K in toluene- $d_8$ . Magnesium and EtOAc concentrations are constant for these experiments, and only the [HBpin]<sub>ini</sub> was varied.



**Figure S7.** Zero-order dependences on [HBpin] in its reaction with EtOAc.  $k_{obs}$  values are obtained from plots of [EtOAc] vs. time in Figure S4.



**Figure S8.** <sup>1</sup>H NMR spectrum of  $C_6H_5CH_2OBpin$  in benzene- $d_6$  after catalytic conversion with with To<sup>M</sup>MgMe as the precatalyst



**Figure S9.** <sup>1</sup>H NMR spectrum of p-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OBpin in benzene- $d_6$  after catalytic conversion with To<sup>M</sup>MgMe as the precatalyst. The resonance at 1.00 ppm is assigned to a small amount of residual HBpin that is present before workup.



**Figure S10.** <sup>1</sup>H NMR spectrum of p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OBpin in benzene- $d_6$  after catalytic conversion with To<sup>M</sup>MgMe as the precatalyst. The resonance at 1.00 ppm is assigned to a small amount of residual HBpin that is present before workup.



**Figure S11.** <sup>1</sup>H NMR spectrum of p-NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OBpin in benzene- $d_6$  after catalytic conversion with To<sup>M</sup>MgMe as the precatalyst. The resonance at 1.00 ppm is assigned to a amount of residual HBpin that is present before workup; excess HBpin was used in this experiment to demonstrate the selectivity for ester reduction in favor over the cyano group.



**Figure S12.** <sup>1</sup>H NMR spectrum of  $C_2H_5OBpin$  in benzene- $d_6$  after catalytic conversion with To<sup>M</sup>MgMe as the precatalyst.



**Figure S13.** <sup>1</sup>H NMR spectrum of  $C_6H_{11}OBpin$  in benzene- $d_6$  after catalytic conversion with To<sup>M</sup>MgMe as the catalyst.



**Figure S14.** <sup>1</sup>H NMR spectrum of  $(C_4H_3S)C_2H_4OBpin$  and EtOBpin in benzene- $d_6$  after catalytic conversion of  $(C_4H_3S)CH_2CO_2Et$  with To<sup>M</sup>MgMe as the catalyst. Excess HBpin is present in the reaction mixture (demonstrating the selectivity for ester reduction over thiophene conversion.



**Figure S15.** <sup>1</sup>H NMR spectrum of  $BrC_6H_{12}OBpin$  and EtOBpin in benzene- $d_6$  from catalytic conversion of  $BrC_5H_{10}CO_2Et$  with  $To^MMgMe$  as the catalyst. Excess HBpin was used in this experiment to demonstrate the inert nature of the alkyl halide functionality under catalytic conditions.



**Figure S16.** <sup>1</sup>H NMR spectrum of MeC(=CH<sub>2</sub>)CH<sub>2</sub>OBpin and MeOBpin in benzene- $d_6$  from catalytic conversion of MeC(=CH<sub>2</sub>)CO<sub>2</sub>Me with To<sup>M</sup>MgMe as the catalyst. The resonance at 1.00 ppm is assigned to residual HBpin present before workup.



**Figure S17.** <sup>1</sup>H NMR spectrum in benzene- $d_6$  of C<sub>10</sub>H<sub>17</sub>OBpin and EtOBpin obtained from hydroboration of ethyl chrysanthemate with To<sup>M</sup>MgMe as catalyst. The resonance at 1.00 ppm is assigned to residual HBpin present before workup.



**Figure S18.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum in benzene- $d_6$  of of C<sub>10</sub>H<sub>17</sub>OBpin and EtOBpin obtained from hydroboration of ethyl chrysanthemate.



**Figure S19.** <sup>1</sup>H NMR spectrum in benzene- $d_6$  of pinBOCH<sub>2</sub>CHMeOBpin from lactide hydroboration. A small amount of HBpin is also present.



**Figure S20.** <sup>1</sup>H NMR spectrum in benzene- $d_6$  of pinBOCH(C<sub>6</sub>H<sub>5</sub>)(CH<sub>2</sub>)<sub>3</sub>OBpin from  $\gamma$ -phenyl butyrolactone hydroboration after catalytic conversion with To<sup>M</sup>MgMe. Excess HBpin is also present.



**Figure S21.** <sup>1</sup>H NMR spectrum in benzene- $d_6$  of pinBOC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>OBpin from dihydrocoumarin hydroboration. Excess HBpin is also present.



**Figure S22.** <sup>1</sup>H NMR spectrum in benzene- $d_6$  of pinBOCH(C<sub>6</sub>H<sub>13</sub>)(CH<sub>2</sub>)<sub>3</sub>OBpin from  $\gamma$ -decalactone hydroboration. Excess HBpin is also present.



**Figure S23.** <sup>1</sup>H NMR spectrum in benzene- $d_6$  of C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OBpin)<sub>2</sub> from phthalide hydroboration. Excess HBpin is also present.



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