

Supporting Information for

**La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub>-catalyzed reduction of esters to alcohols with  
pinacolborane**

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# 1. $^1\text{H}$ NMR Monitoring of the reaction between $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ and HBpin.

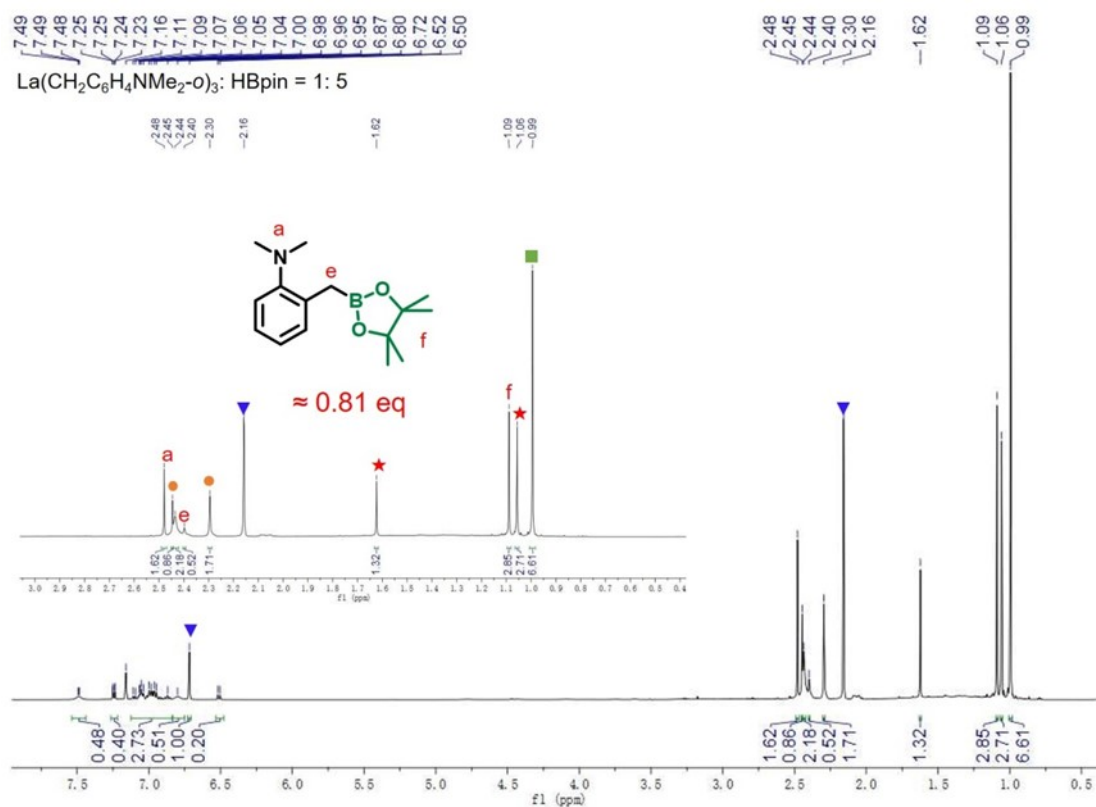
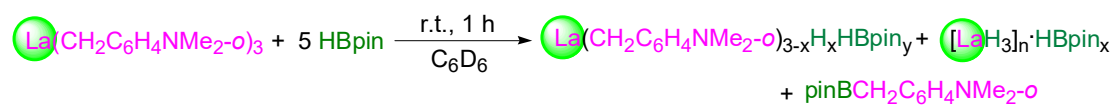


Fig. S1.  $^1\text{H}$  NMR spectrum of the reaction of  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  with 5 equiv HBpin for 1 h, ● =  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_{3-x}\text{H}_x\text{HBpin}_y$ , ★ =  $\text{B}_2(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})_3$ , ■ = excess HBpin, ▼ = 1,3,5-trimethylbenzene (500 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

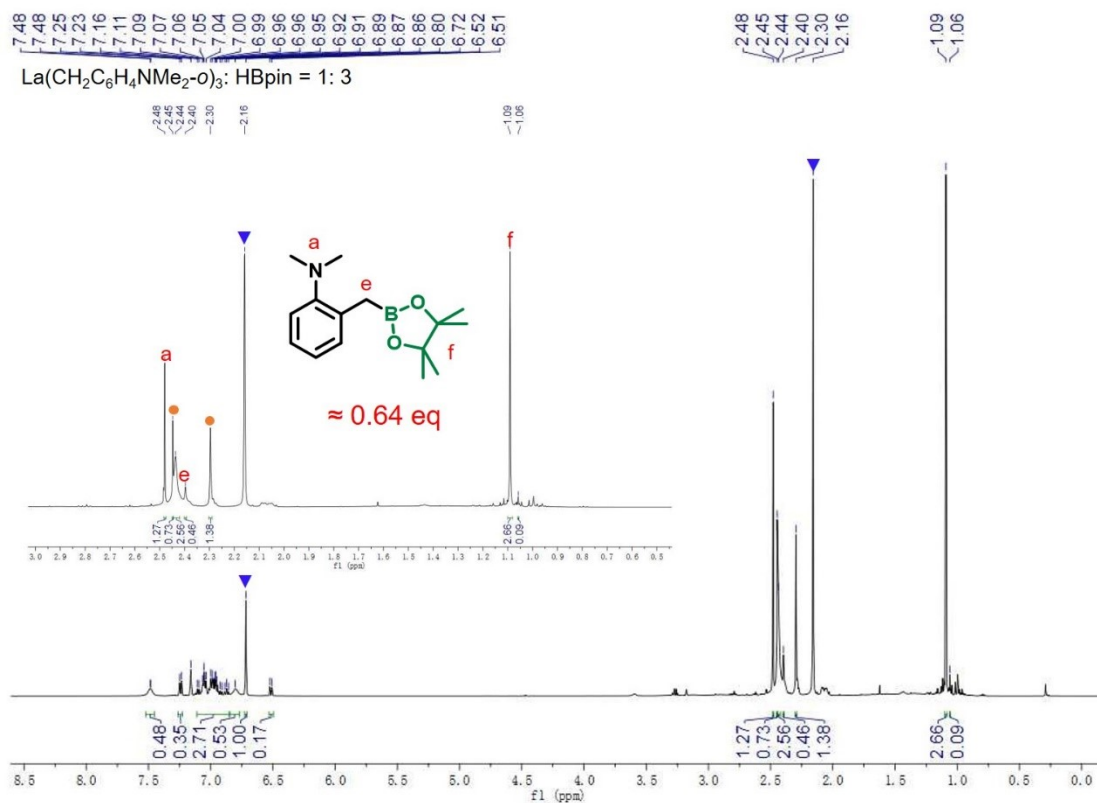


Fig. S2.  $^1\text{H}$  NMR spectrum of the reaction of  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  with 3 equiv HBpin for 1 h,  $\bullet$  =  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_{3-x}\text{H}_x\text{HBpin}_y$ ,  $\blacktriangledown$  = 1,3,5-trimethylbenzene (500 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ).

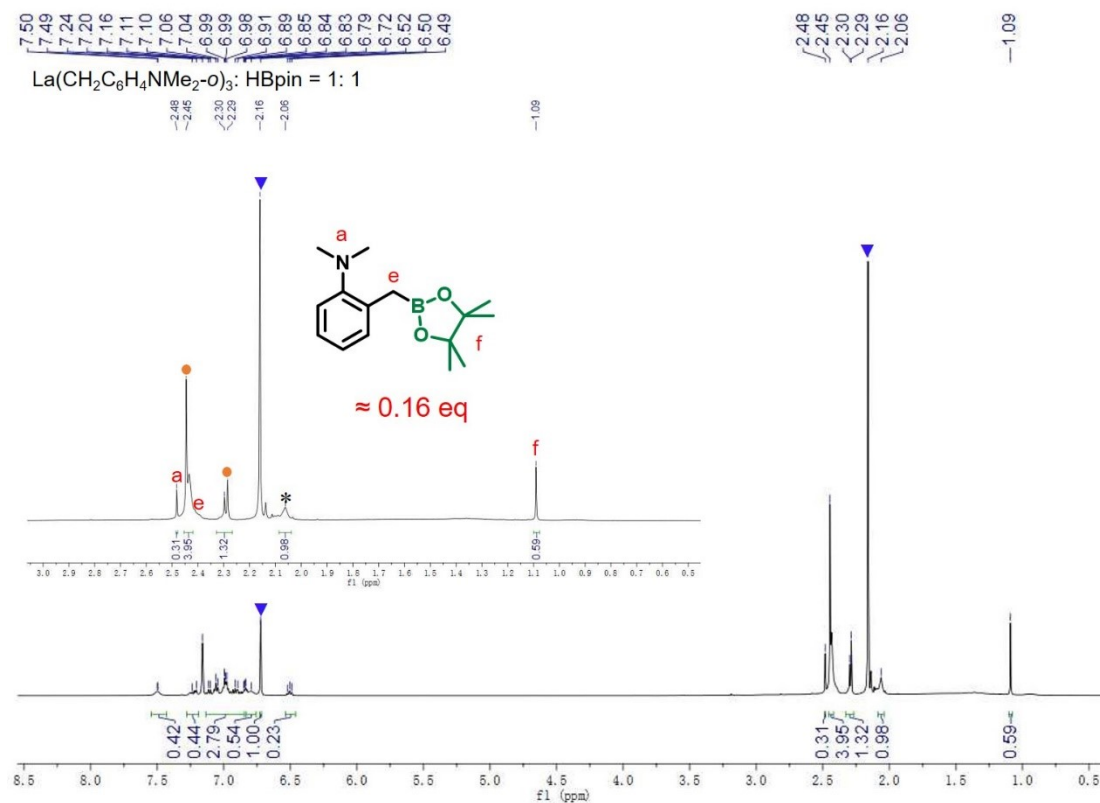


Fig. S3.  $^1\text{H}$  NMR spectrum of the reaction of  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  with 1 equiv HBpin for 1 h, ● =  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_{3-x}\text{H}_x\text{HBpin}_y$ , \* =  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ , ▼ = 1,3,5-trimethylbenzene (500 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

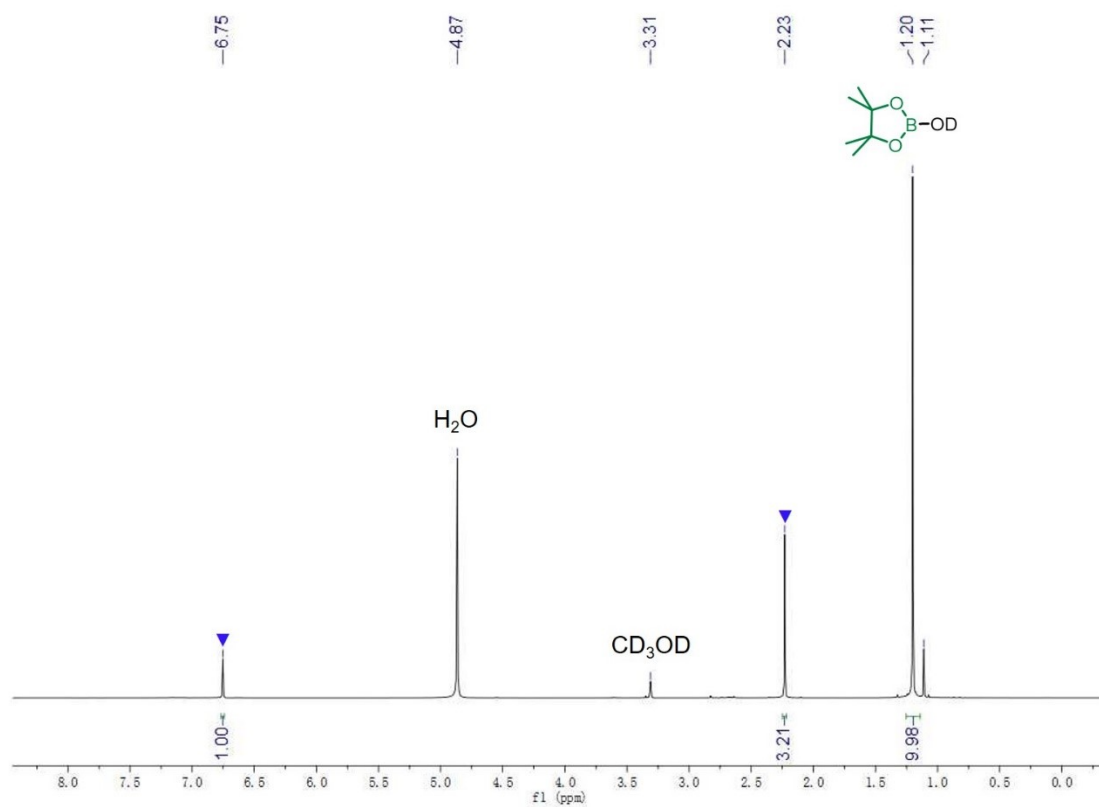


Fig. S4. <sup>1</sup>H NMR spectrum of the hydrolysis product of the insoluble material with CD<sub>3</sub>OD. ▼ = 1,3,5-trimethylbenzene (500 MHz, CD<sub>3</sub>OD, 25 °C).

## 2. Characterization of hydroboration products.

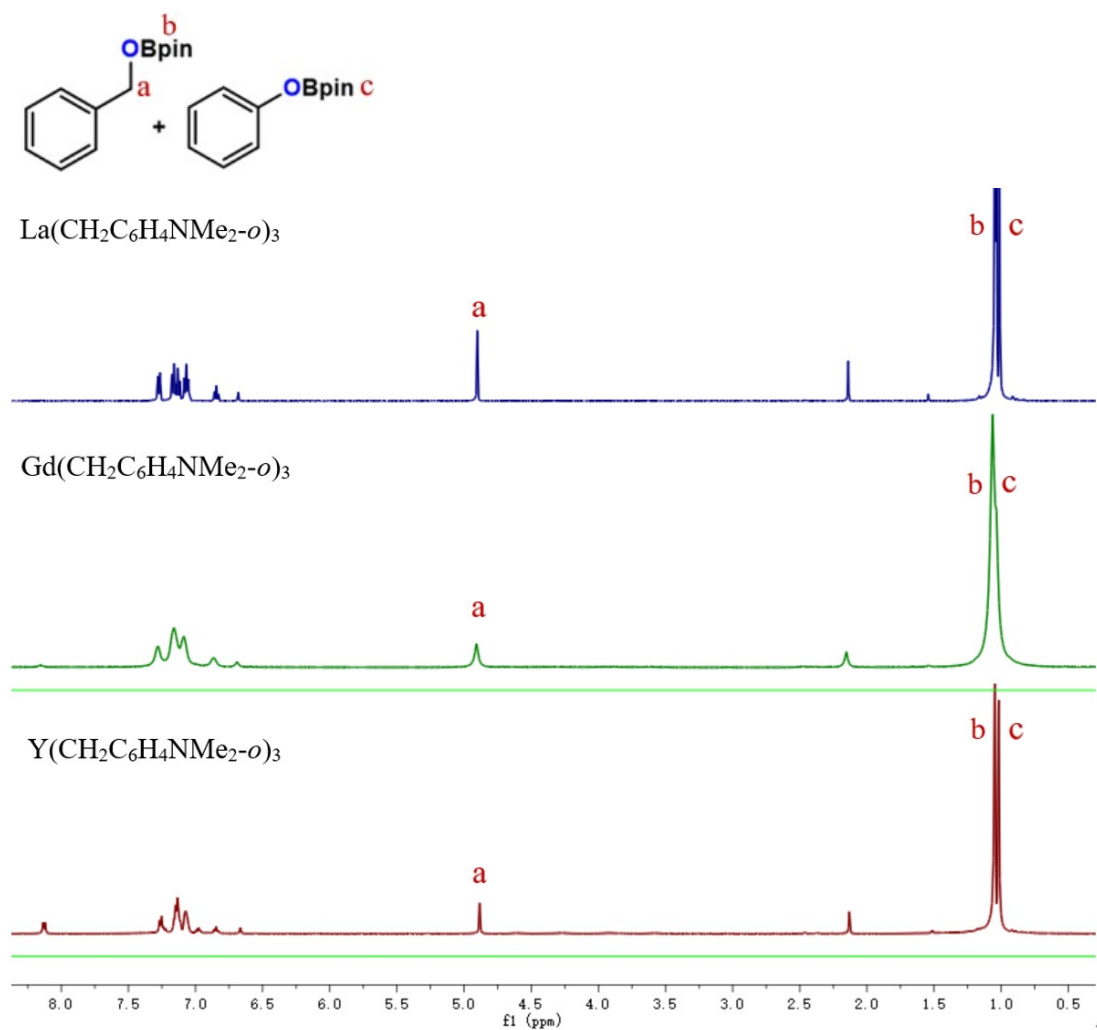


Fig. S5. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of Phenyl benzoate (0.5 mmol) catalyzed by 0.5 mol% Ln(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> at 60 °C for 3 h in C<sub>6</sub>D<sub>6</sub> (1 mL total volume). Ln = La, Gd, Y. HBpin (1.1 mmol, 2.2 equiv). (entry 4, 5, 6, Table 1).

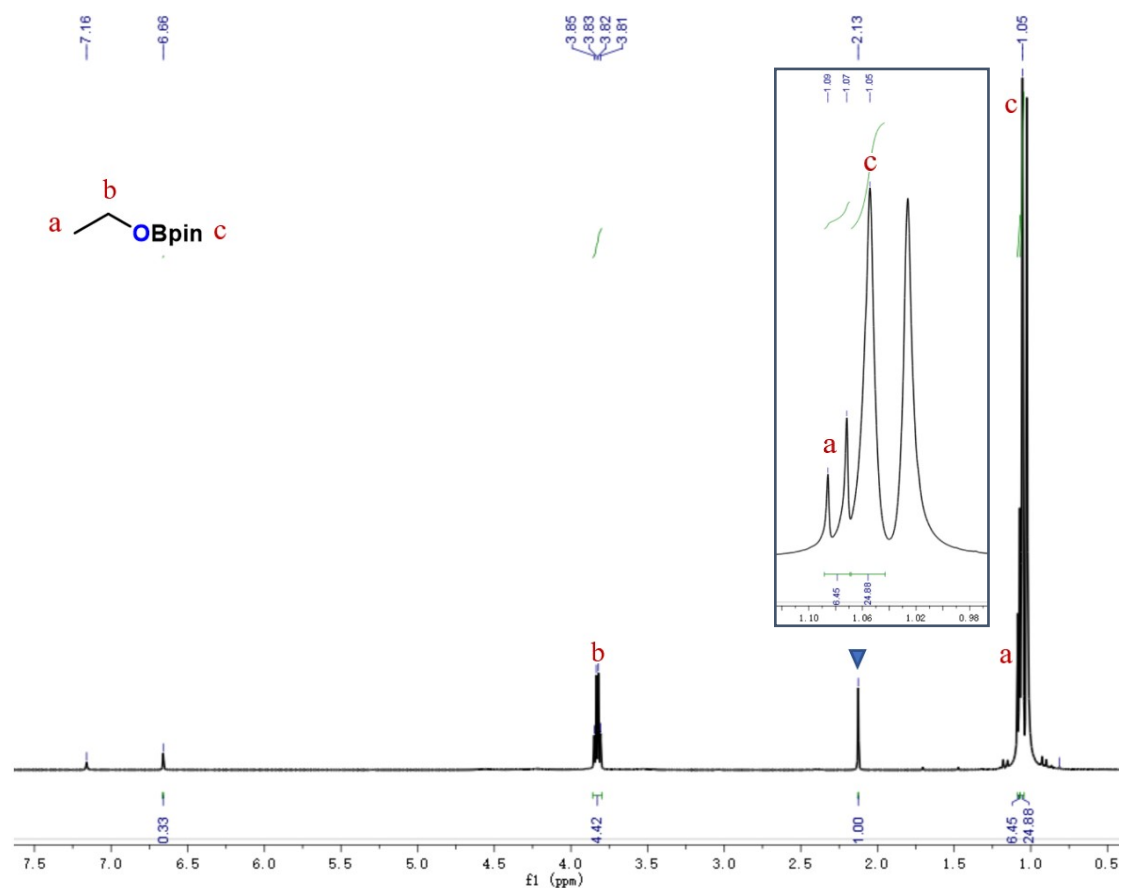


Fig. S6. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of ethyl acetate (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.1 mol%) at 25  $^\circ\text{C}$  for 0.5 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown$  = 1,3,5-trimethylbenzene (7  $\mu\text{L}$ , 0.05 mmol). (entry 1, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  3.83 (q,  $J = 7.0$  Hz, 2H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.08 (d,  $J = 7.0$  Hz, 3H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.05 (s, 12H, EtOBpin).

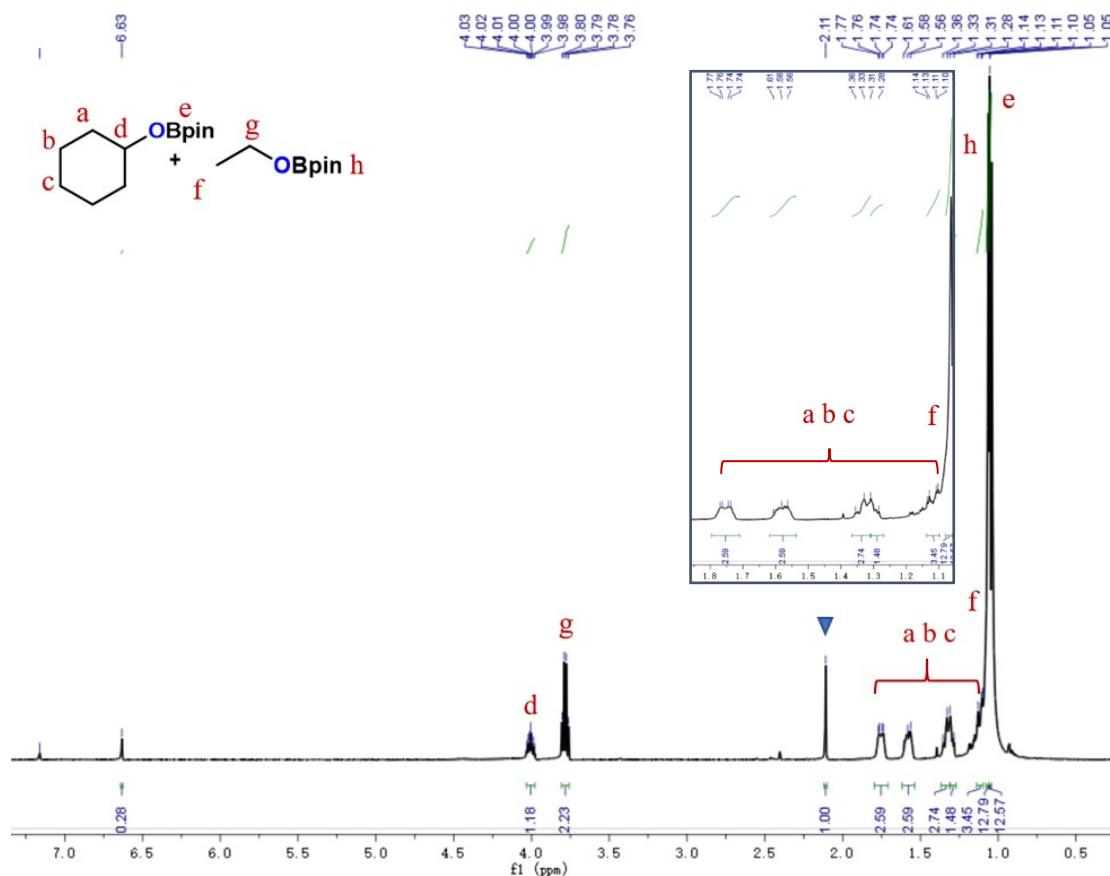


Fig. S7. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of cyclohexyl acetate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>3</sub> (0.5 mol%) at 25 °C for 1 h, HBpin (1.1mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 2, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 4.03-3.98 (m, 1H, CyOBpin), 3.78 (q, *J* = 7.0 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>OBpin), 1.77-1.74 (m, 2H, CyOBpin), 1.61-1.56 (m, 2H, CyOBpin), 1.33-1.31 (m, 2H, CyOBpin), 1.29-1.28 (m, 1H, CyOBpin), 1.14-1.11 (m, 3H, CyOBpin). 1.08 (d, 3H, CH<sub>3</sub>CH<sub>2</sub>OBpin), 1.06 (s, 12H, CyOBpin), 1.05 (s, 12H, CH<sub>3</sub>CH<sub>2</sub>OBpin).



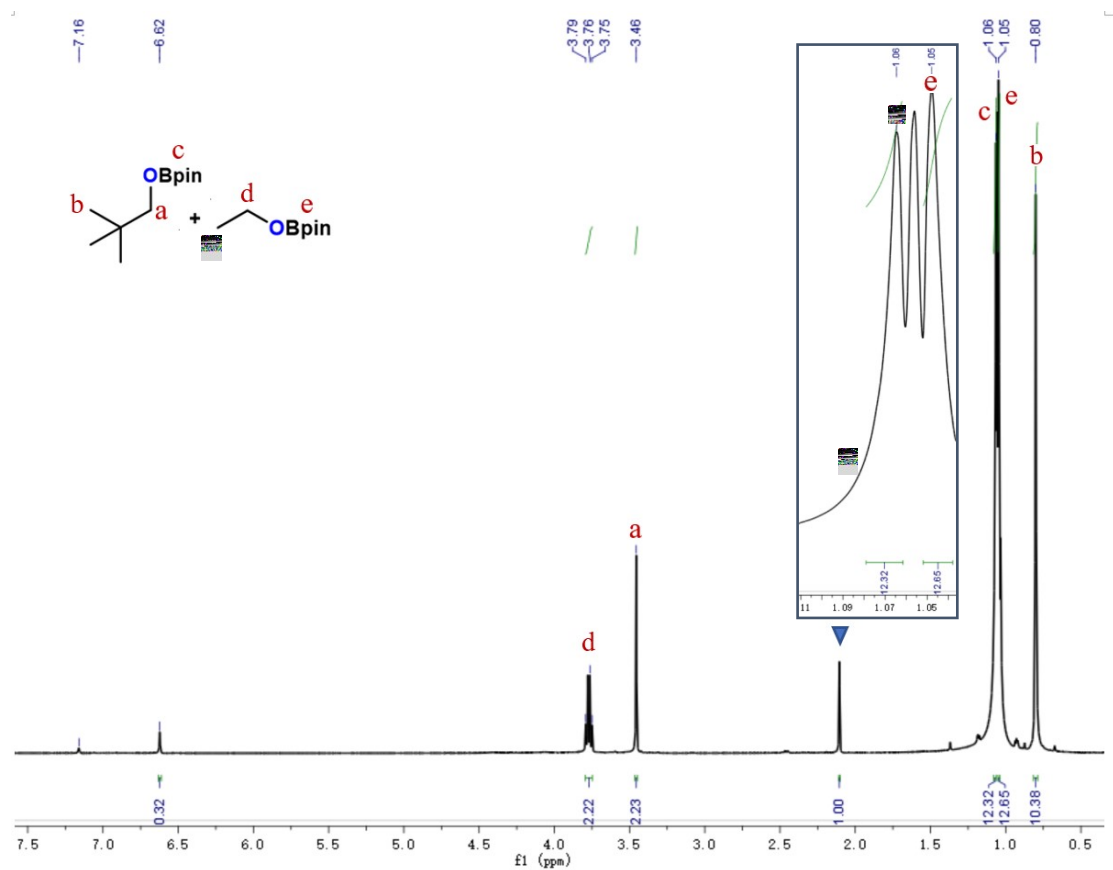


Fig. S8. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of ethyl trimethylacetate (0.5 mmol) catalyzed by La (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 25 °C for 0.5 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 3, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 3.77 (q, *J* = 7.0 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>OBpin), 3.46 (s, 2H, (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OBpin), 1.08 (d, 3H, CH<sub>3</sub>CH<sub>2</sub>OBpin) 1.06 (s, 12H, (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OBpin), 1.05 (s, 12H, EtOBpin), 0.88 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OBpin).

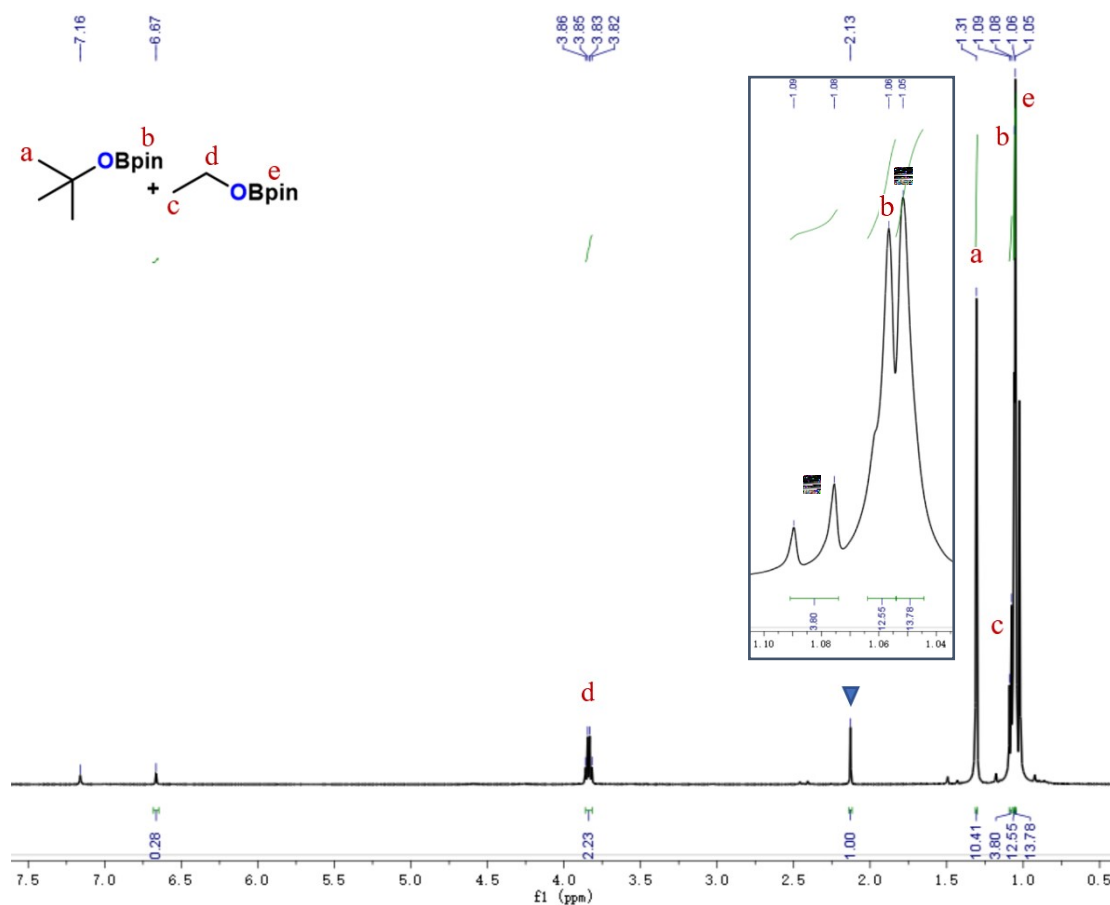


Fig. S9. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of tert-Butyl acetate (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.5 mol%) at 25 °C for 15 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown = 1,3,5\text{-trimethylbenzene}$  (7  $\mu\text{L}$ , 0.05 mmol). (entry 4, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  3.84 (q,  $J = 7.0$  Hz, 2H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.31 (s, 9H,  $(\text{CH}_3)_3\text{CCH}_2\text{OBpin}$ ), 1.08 (d,  $J = 7.0$  Hz, 3H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.06 (s, 12H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.05 (s, 12H,  $(\text{CH}_3)_3\text{CCH}_2\text{OBpin}$ ).

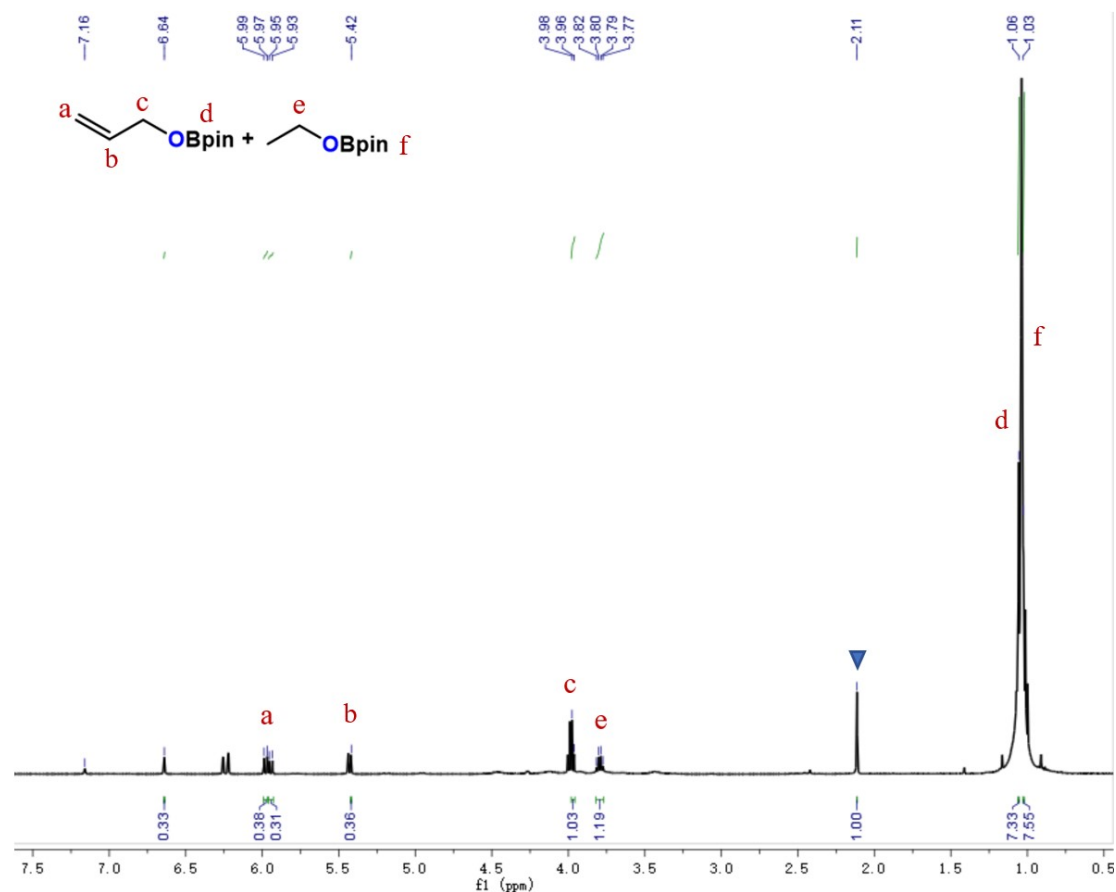


Fig. S10. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of ethyl acrylate (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.5 mol%) at 25 °C for 3 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown$  = 1,3,5-trimethylbenzene (7  $\mu\text{L}$ , 0.05 mmol). (entry 5, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  5.98 (d,  $J$  = 10.4 Hz, 1H,  $\text{CH}_2=\text{CHCH}_2\text{OBpin}$ ), 5.94 (d,  $J$  = 10.4 Hz, 1H,  $\text{CH}_2=\text{CHCH}_2\text{OBpin}$ ), 5.42 (d, 1H,  $\text{CH}_2=\text{CHCH}_2\text{OBpin}$ ), 3.97 (m,  $J$  = 7.1 Hz, 2H,  $\text{CH}_2=\text{CHCH}_2\text{OBpin}$ ), 3.79 (q,  $J$  = 7.0 Hz, 2H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.08 (d, 3H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ), 1.06 (s, 12H,  $\text{CH}_2=\text{CHCH}_2\text{OBpin}$ ), 1.03 (s, 12H,  $\text{CH}_3\text{CH}_2\text{OBpin}$ ).

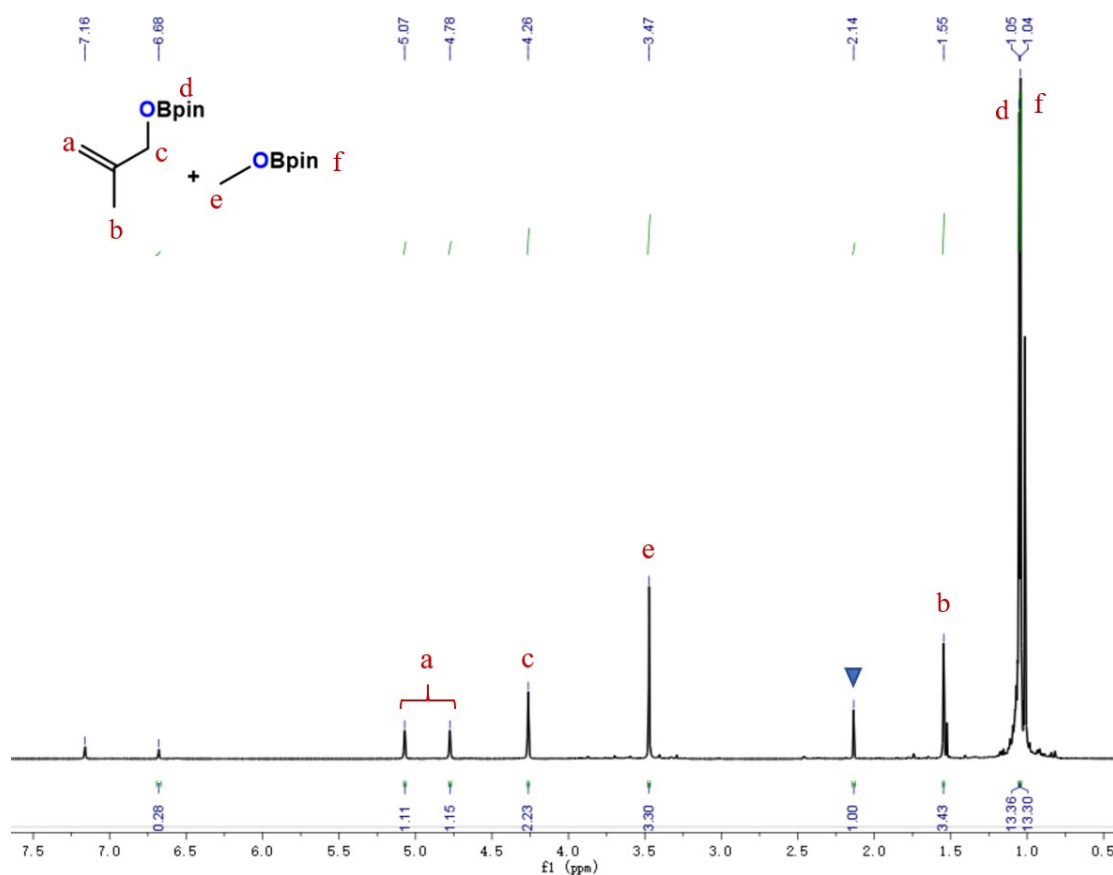


Fig. S11. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of methyl methacrylate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 25 °C for 16 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 6, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 5.07 (s, 1H, CH<sub>2</sub>=CCH<sub>3</sub>CH<sub>2</sub>OBpin), 4.78 (s, 1H, CH<sub>2</sub>=CCH<sub>3</sub>CH<sub>2</sub>OBpin), 4.26 (s, 2H, CH<sub>2</sub>=CCH<sub>3</sub>CH<sub>2</sub>OBpin), 3.47 (s, 3H, CH<sub>3</sub>OBpin), 1.55 (s, 3H, CH<sub>2</sub>=CCH<sub>3</sub>CH<sub>2</sub>OBpin), 1.05 (s, 12H, CH<sub>2</sub>=CCH<sub>3</sub>CH<sub>2</sub>OBpin), 1.04 (s, 12H, CH<sub>3</sub>OBpin).

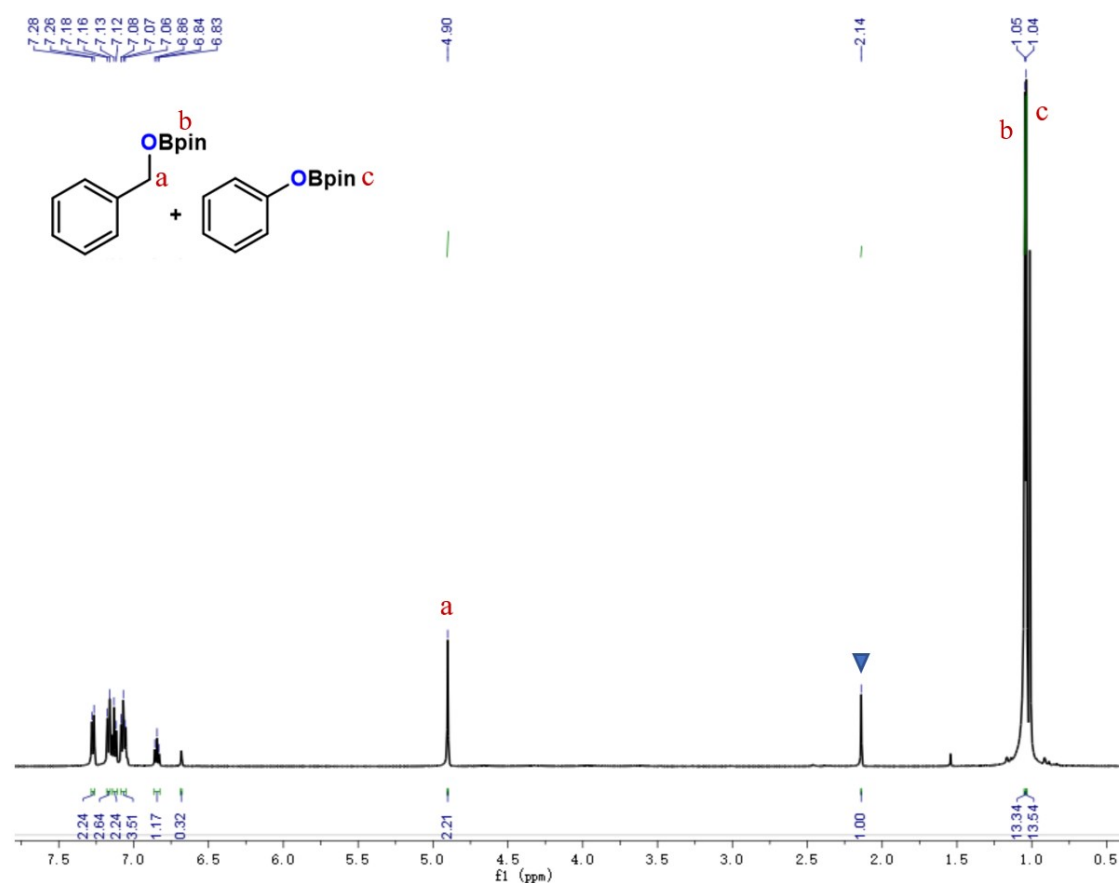


Fig. S12. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of phenyl benzoate catalyzed (0.5 mmol) by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 60 °C for 3 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 7, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.27 (d, *J* = 7.6 Hz, 2H, PhCH<sub>2</sub>OBpin), 7.17 (d, *J* = 7.7 Hz, 2H, PhOBpin), 7.12 (d, *J* = 7.7 Hz, 2H, PhCH<sub>2</sub>OBpin), 7.07 (t, *J* = 6.9 Hz, 3H, PhCH<sub>2</sub>OBpin/PhOBpin), 6.84 (t, *J* = 7.4 Hz, 1H, PhOBpin), 4.90 (s, 2H, PhCH<sub>2</sub>OBpin), 1.05 (s, 12H, PhCH<sub>2</sub>OBpin), 1.04 (s, 12H, PhOBpin).



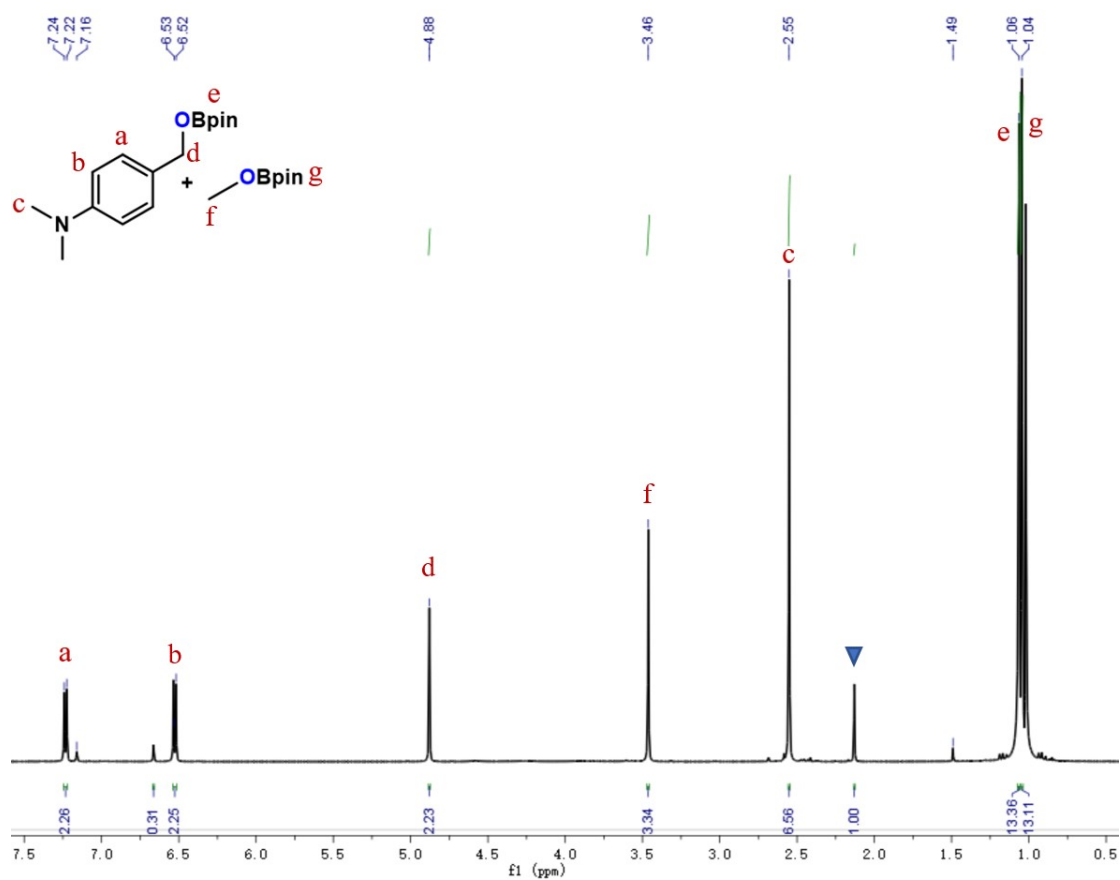


Fig. S14. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of methyl 4-dimethylaminobenzoate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 60 °C for 3 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 9, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.23 (d, *J* = 8.7 Hz, 2H, Me<sub>2</sub>NPhCH<sub>2</sub>OBpin), 6.52 (d, *J* = 6.8 Hz, 2H, Me<sub>2</sub>NPhCH<sub>2</sub>OBpin), 4.88 (s, 2H, Me<sub>2</sub>NPhCH<sub>2</sub>OBpin), 3.46 (s, 3H, CH<sub>3</sub>OBpin), 2.55 (s, *J* = 7.0 Hz, 6H, Me<sub>2</sub>NPhCH<sub>2</sub>OBpin), 1.05 (s, 12H, PhOBpin), 1.05 (s, 12H, EtOBpin).

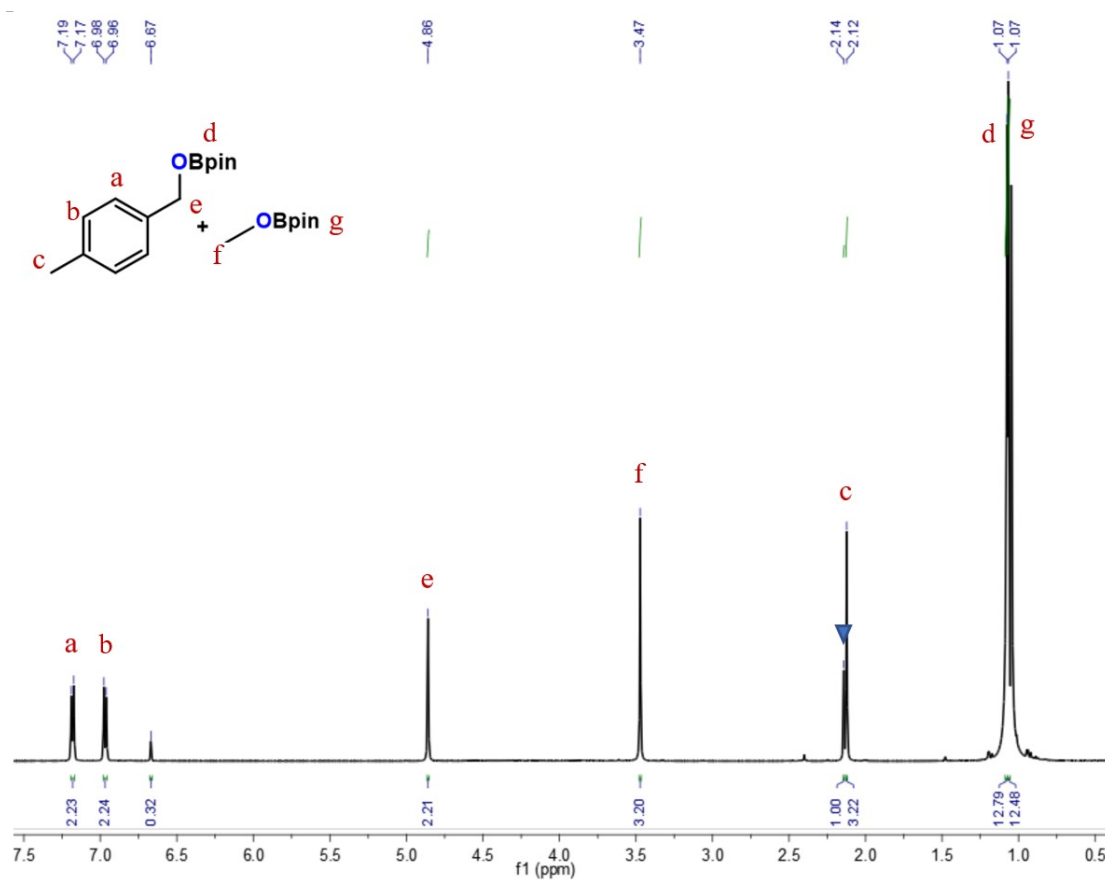


Fig. S15. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of methyl 4-methylbenzoate (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.5 mol%) at 25 °C for 1 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown$  = 1,3,5-trimethylbenzene (7  $\mu\text{L}$ , 0.05 mmol). (entry 10, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  7.18 (d,  $J = 7.9$  Hz, 2H,  $\text{MePhCH}_2\text{OBpin}$ ), 6.69 (d,  $J = 7.9$  Hz, 2H,  $\text{MePhCH}_2\text{OBpin}$ ), 4.86 (s, 2H,  $\text{MePhCH}_2\text{OBpin}$ ), 3.47 (s, 3H, MeOBpin), 2.12 (s, 3H,  $\text{MePhCH}_2\text{OBpin}$ ), 1.07 (s, 12H,  $\text{MePhCH}_2\text{OBpin}$ ), 1.05 (s, 12H, MeOBpin).



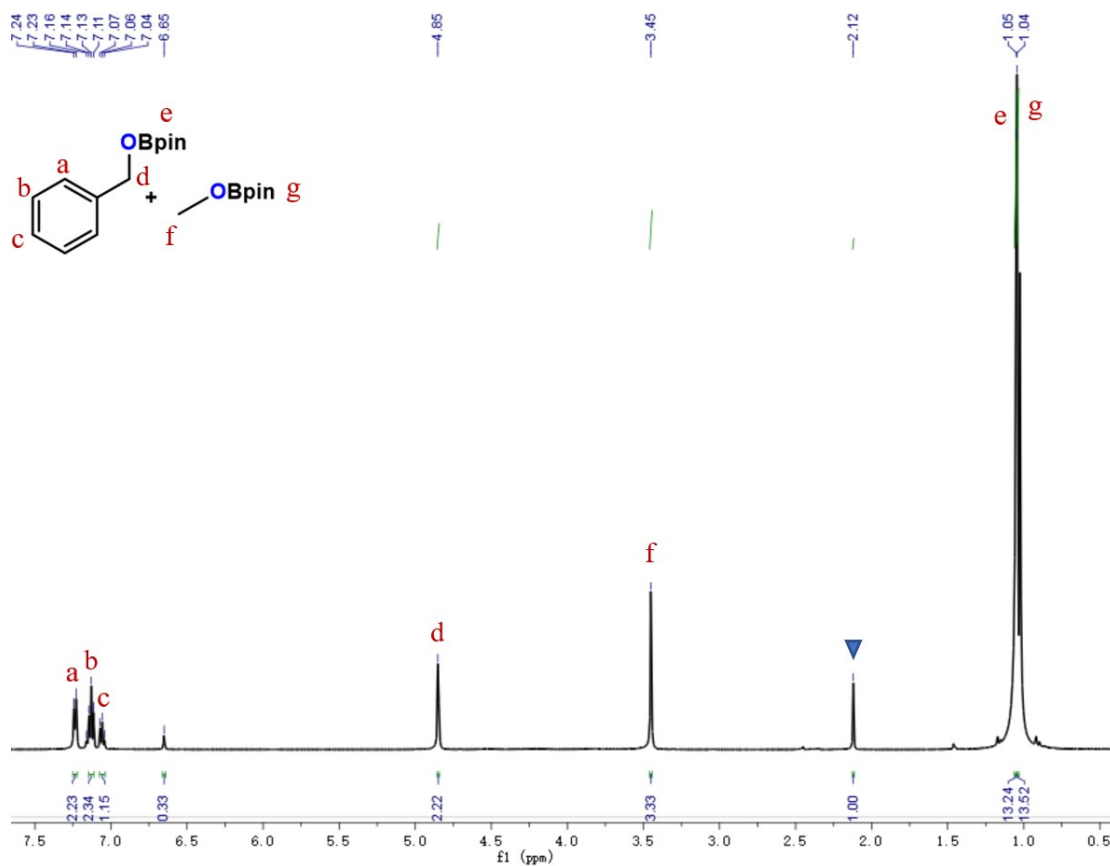


Fig. S16. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of methyl benzoate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 25 °C for 0.75 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 11, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.24 (d, *J* = 7.6 Hz, 2H, PhCH<sub>2</sub>OBpin), 7.13 (t, *J* = 7.5 Hz, 2H, PhCH<sub>2</sub>OBpin), 7.06 (t, *J* = 7.3 Hz, 1H, PhCH<sub>2</sub>OBpin), 4.85 (s, 2H, PhCH<sub>2</sub>OBpin), 3.45 (s, 3H, MeOBpin), 1.05 (s, 12H, PhCH<sub>2</sub>OBpin), 1.04 (s, 12H, MeOBpin).

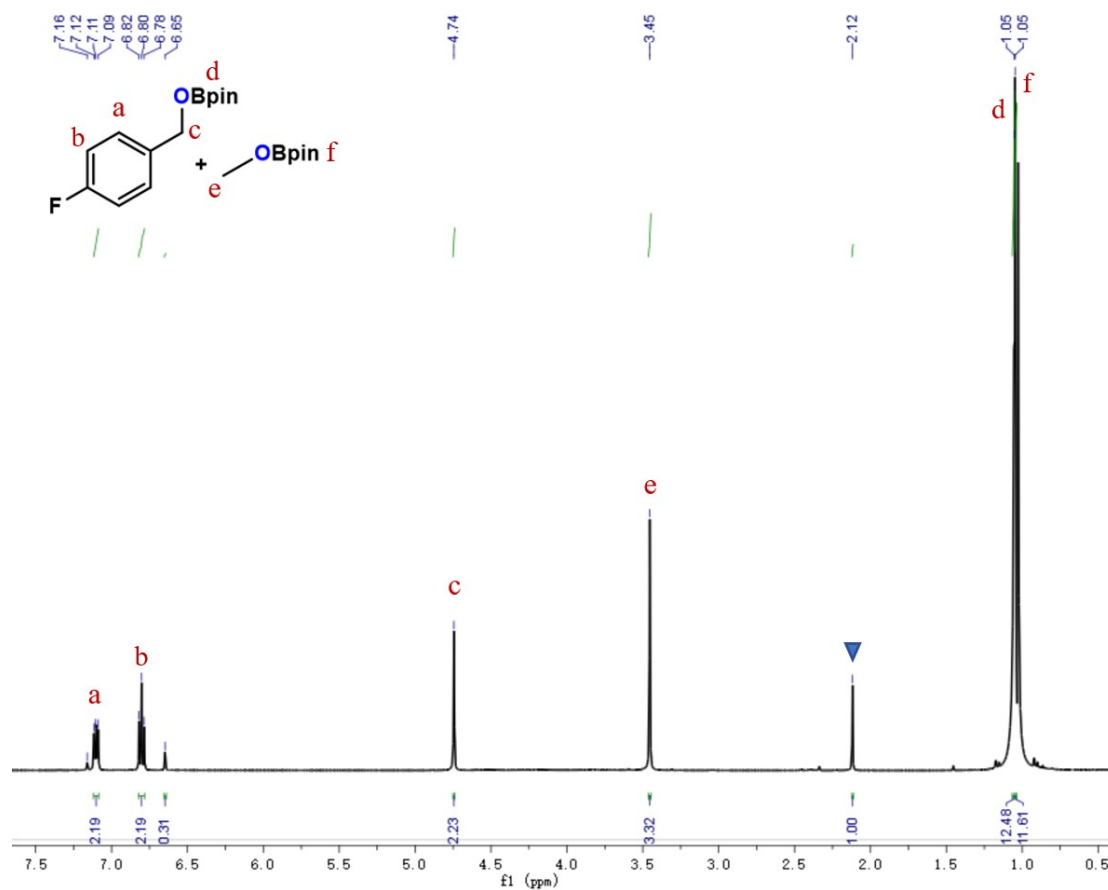


Fig. S17. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of methyl 4-fluorobenzoate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol% ) at 25 °C for 0.5 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 12, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.12-7.08 (m, 2H, FPhCH<sub>2</sub>OBpin), 6.80 (t, *J* = 8.7 Hz, 2H, FPhCH<sub>2</sub>OBpin), 4.74 (s, 2H, FPhCH<sub>2</sub>OBpin), 3.45 (s, 3H, MeOBpin), 1.05 (s, 12H, FPhCH<sub>2</sub>OBpin), 1.05 (s, 12H, MeOBpin).

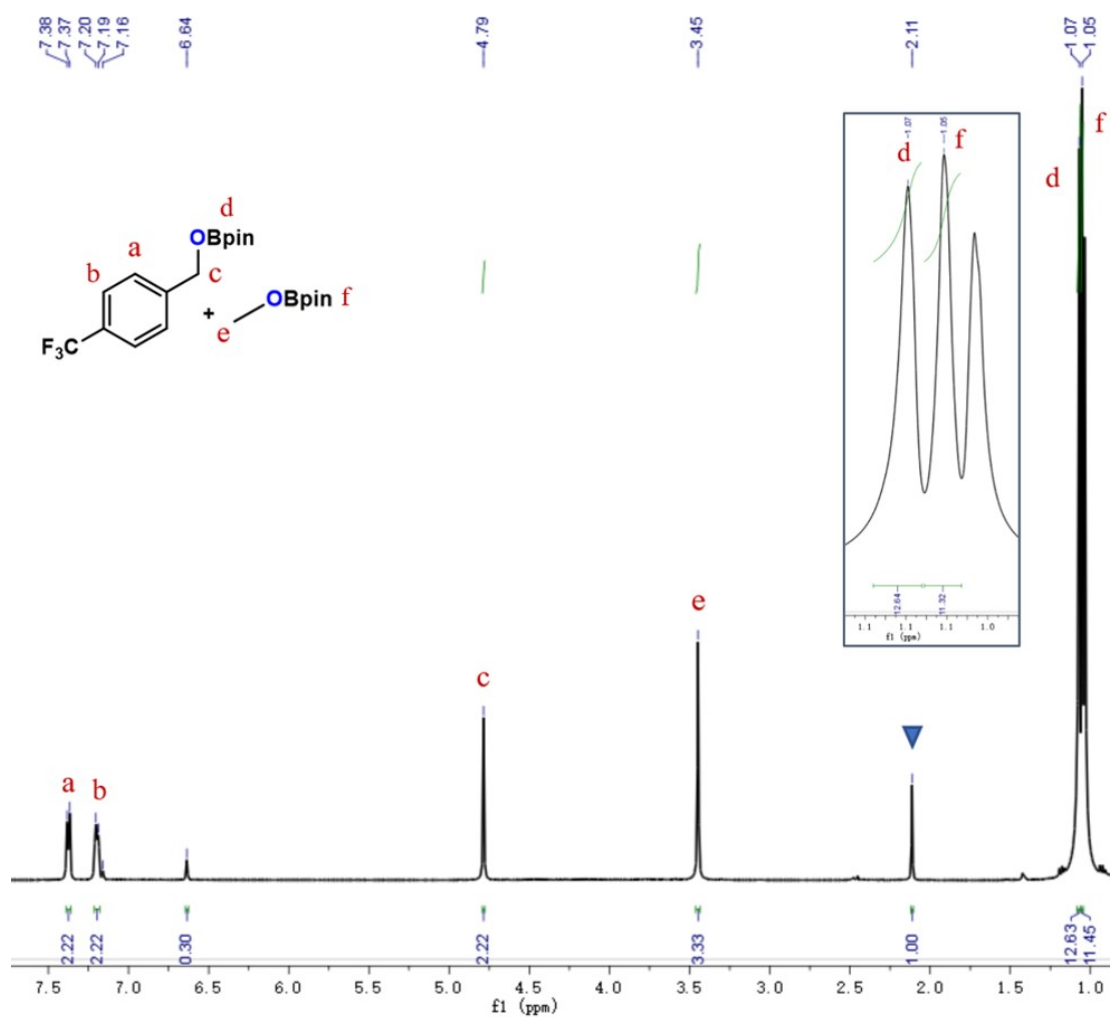


Fig. S18. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of methyl 4-trifluoromethylbenzoate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 25 °C for 0.25 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 13, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.37 (d, *J* = 8.0 Hz, 2H, CF<sub>3</sub>PhCH<sub>2</sub>OBpin), 7.20 (d, *J* = 7.5 Hz, 2H, CF<sub>3</sub>PhCH<sub>2</sub>OBpin), 4.79 (s, 2H, CF<sub>3</sub>PhCH<sub>2</sub>OBpin), 3.45 (s, 3H, MeOBpin), 1.07 (s, 12H, CF<sub>3</sub>PhCH<sub>2</sub>OBpin), 1.05 (s, 12H, MeOBpin).

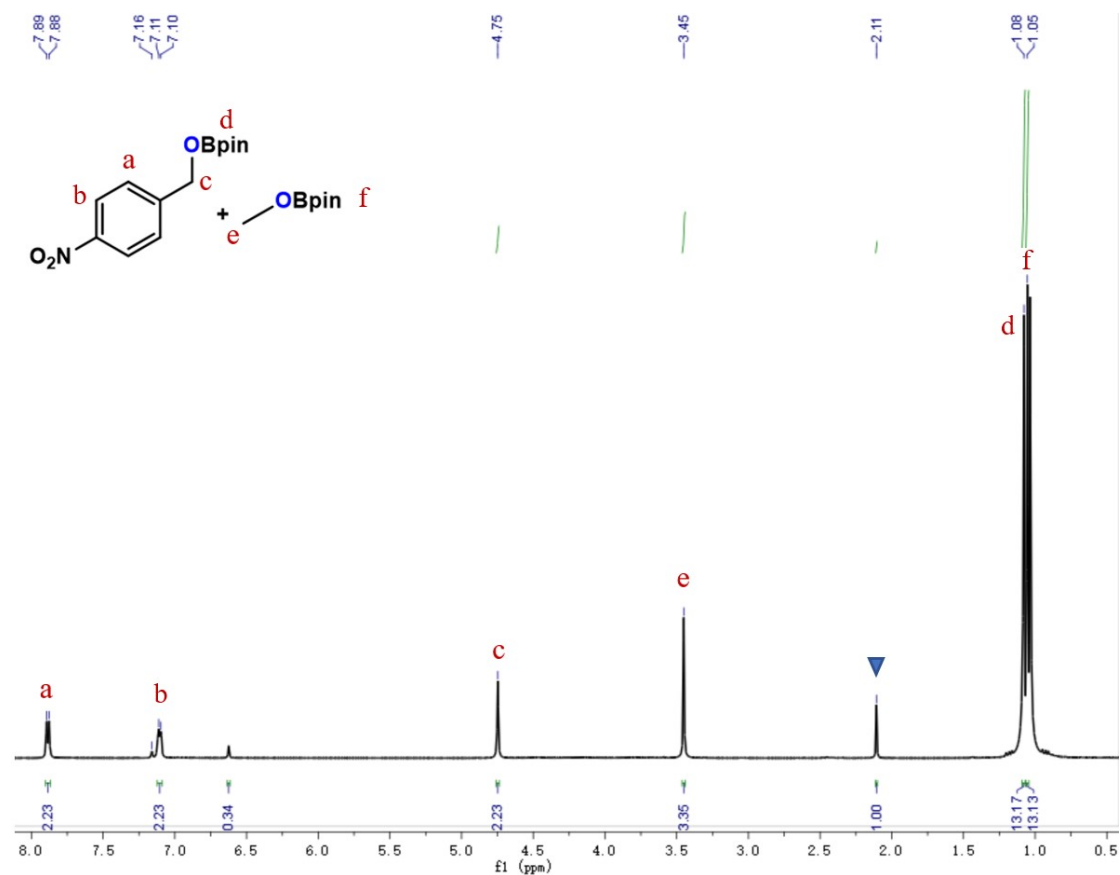


Fig. S19. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of methyl 4-nitrobenzoate (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (0.5 mol%) at 25 °C for 0.25 h, HBpin (1.1 mmol, 2.2 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 14, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.89 (d, *J* = 8.3 Hz, 2H, NO<sub>2</sub>PhCH<sub>2</sub>OBpin), 7.10 (d, *J* = 7.6 Hz, 2H, NO<sub>2</sub>PhCH<sub>2</sub>OBpin), 4.75 (s, 2H, NO<sub>2</sub>PhCH<sub>2</sub>OBpin), 3.45 (s, 3H, MeOBpin), 1.08 (s, 12H, NO<sub>2</sub>PhCH<sub>2</sub>OBpin), 1.05 (s, 12H, MeOBpin).

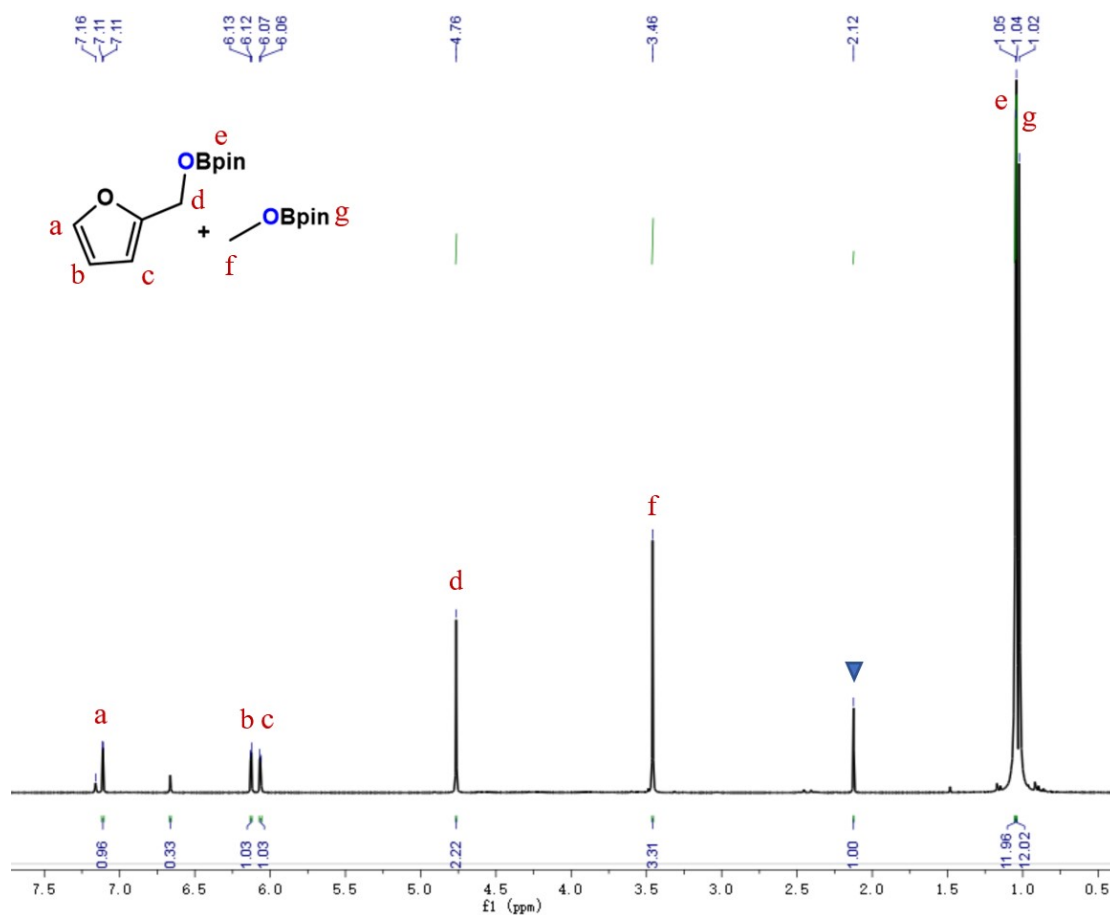


Fig. S20. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of methyl 2-furoate (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.5 mol%) at 25 °C for 0.5 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown$  = 1,3,5-trimethylbenzene (7  $\mu\text{L}$ , 0.05 mmol). (entry 15, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  7.11 (d,  $J$  = 2.7 Hz, 1H,  $\text{C}_4\text{H}_3\text{OCH}_2\text{OBpin}$ ), 6.13 (d,  $J$  = 3.8 Hz, 1H,  $\text{C}_4\text{H}_3\text{OCH}_2\text{OBpin}$ ), 6.06 (d,  $J$  = 5.1 Hz, 1H,  $\text{C}_4\text{H}_3\text{OCH}_2\text{OBpin}$ ), 4.76 (s, 2H,  $\text{C}_4\text{H}_3\text{OCH}_2\text{OBpin}$ ), 3.31 (s, 3H, MeOBpin), 1.05 (s, 12H,  $\text{C}_4\text{H}_3\text{OCH}_2\text{OBpin}$ ), 1.04 (s, 12H, MeOBpin).

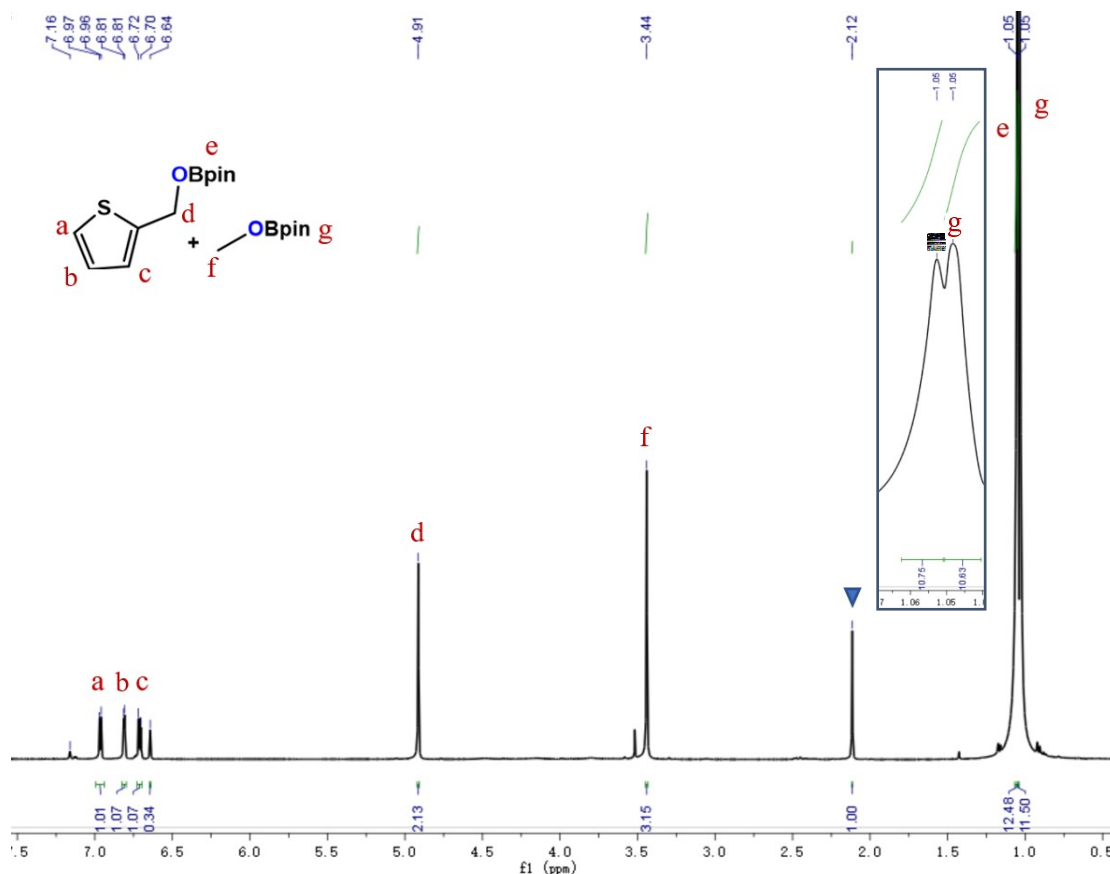


Fig. S21. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of methyl thiophene-2-carboxylate (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.5 mol%) at 25 °C for 0.5 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown$  = 1,3,5-trimethylbenzene (7  $\mu\text{L}$ , 0.05 mmol). (entry 16, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  6.97 (d,  $J$  = 6.1 Hz, 1H,  $\text{C}_4\text{H}_3\text{SCH}_2\text{OBpin}$ ), 6.81 (d,  $J$  = 3.4 Hz, 1H,  $\text{C}_4\text{H}_3\text{SCH}_2\text{OBpin}$ ), 6.71 (d,  $J$  = 8.5 Hz, 1H,  $\text{C}_4\text{H}_3\text{SCH}_2\text{OBpin}$ ), 4.91 (s, 2H,  $\text{C}_4\text{H}_3\text{SCH}_2\text{OBpin}$ ), 3.44 (s, 3H, MeOBpin), 1.05 (s, 12H,  $\text{C}_4\text{H}_3\text{SCH}_2\text{OBpin}$ ), 1.05 (s, 12H, MeOBpin).

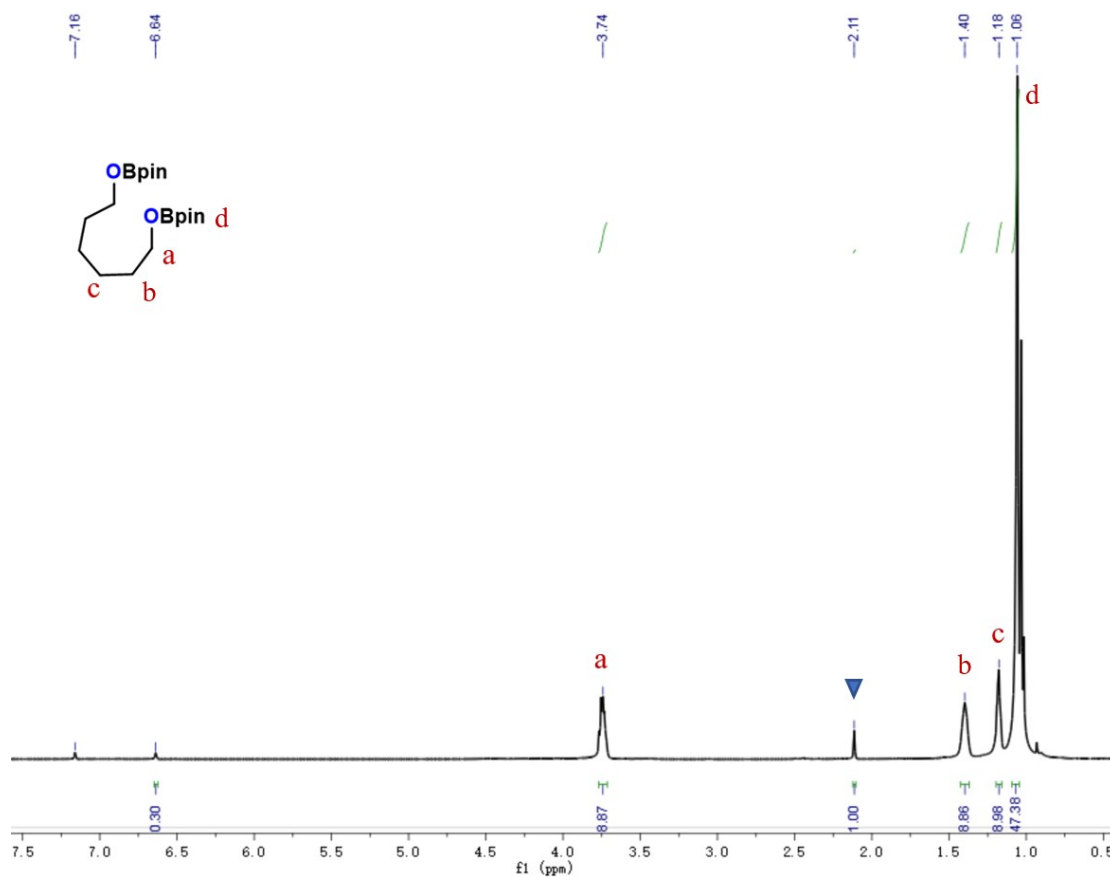


Fig. S22. Quantitative  $^1\text{H}$  NMR spectrum of the products of the hydroboration of  $\epsilon$ -caprolactone (0.5 mmol) catalyzed by  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (0.5 mol%) at 25  $^\circ\text{C}$  for 0.25 h, HBpin (1.1 mmol, 2.2 equiv),  $\blacktriangledown$  = 1,3,5-trimethylbenzene (3.5  $\mu\text{L}$ , 0.025 mmol). (entry 17, Table 2).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  3.74 (m, 4H, pinBO(CH $_2$ ) $_6$ OBpin), 1.40 (s, 4H, pinBO(CH $_2$ ) $_6$ OBpin), 1.18 (s, 4H, pinBO(CH $_2$ ) $_6$ OBpin), 1.06 (s, 24H, pinBO(CH $_2$ ) $_6$ OBpin).

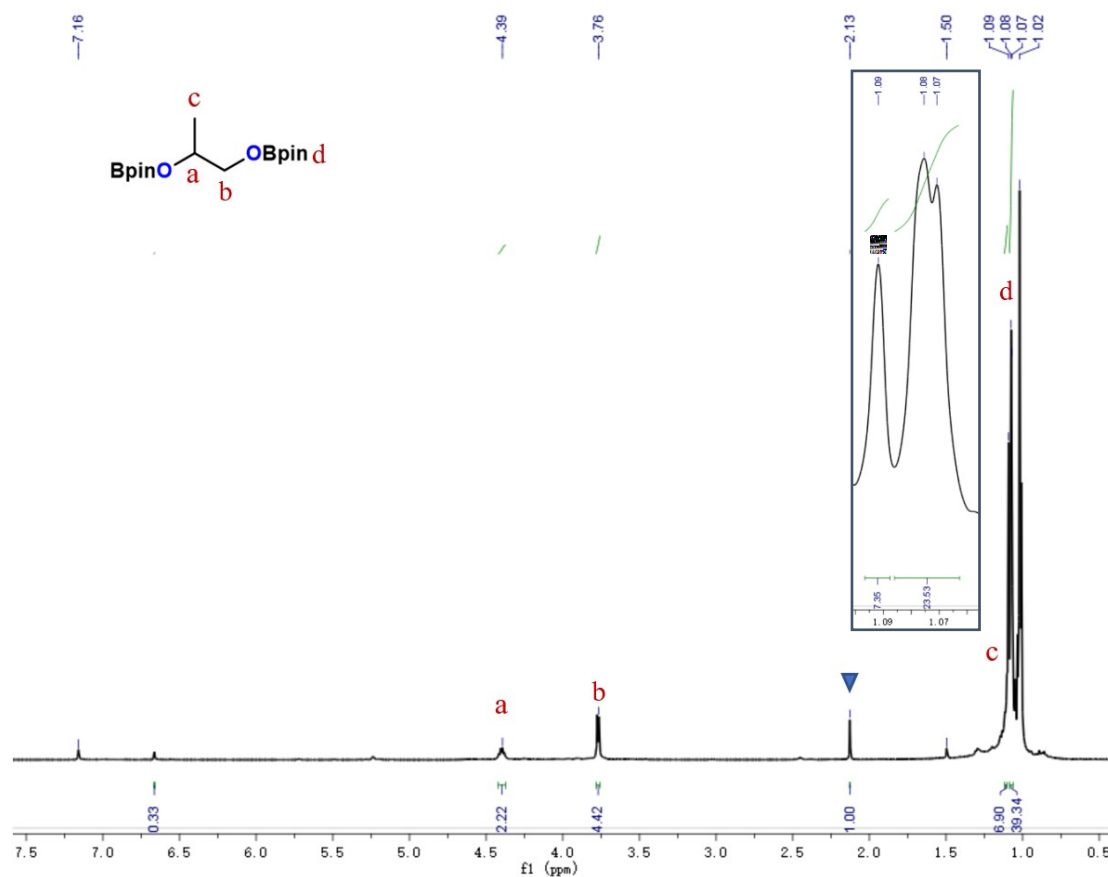


Fig. S23. Quantitative <sup>1</sup>H NMR spectrum of the products of the hydroboration of L-LA (0.5 mmol) catalyzed by La(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>3</sub> (1 mol%) at 60 °C for 3 h, HBpin (2.2 mmol, 4.4 equiv), ▼ = 1,3,5-trimethylbenzene (7 μL, 0.05 mmol). (entry 18, Table 2).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 4.43-4.37 (m, 1H, MeCH), 3.76 (d, *J* = 5.7 Hz, 2H, CH<sub>2</sub>OBpin), 1.09 (s, 3H, MeCH), 1.18, 1.07 (s, 24H, BOCMe<sub>2</sub>).



### 3. Representative gram-scale ester hydroboration.

In a glovebox a mixture of Methyl 4-trifluoromethylbenzoate (1.02 g, 5 mmol), pinacolborane (1.41 g, 11 mmol) in Toluene (15 mL) was added into a 50 mL flask equipped with a magnetic stirring bar. Then, the  $\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (14 mg, 0.025 mmol, 0.5 mol%) was added into the flask. The reaction mixture was stirred at room temperature until the ester was fully converted to the product. The resulting boron ester was quenched with aq. NaOH (1 M) solution, then the crude compound was dried over sodium sulfate. The compound was purified by column chromatography, and characterized by  $^1\text{H}$  NMR.

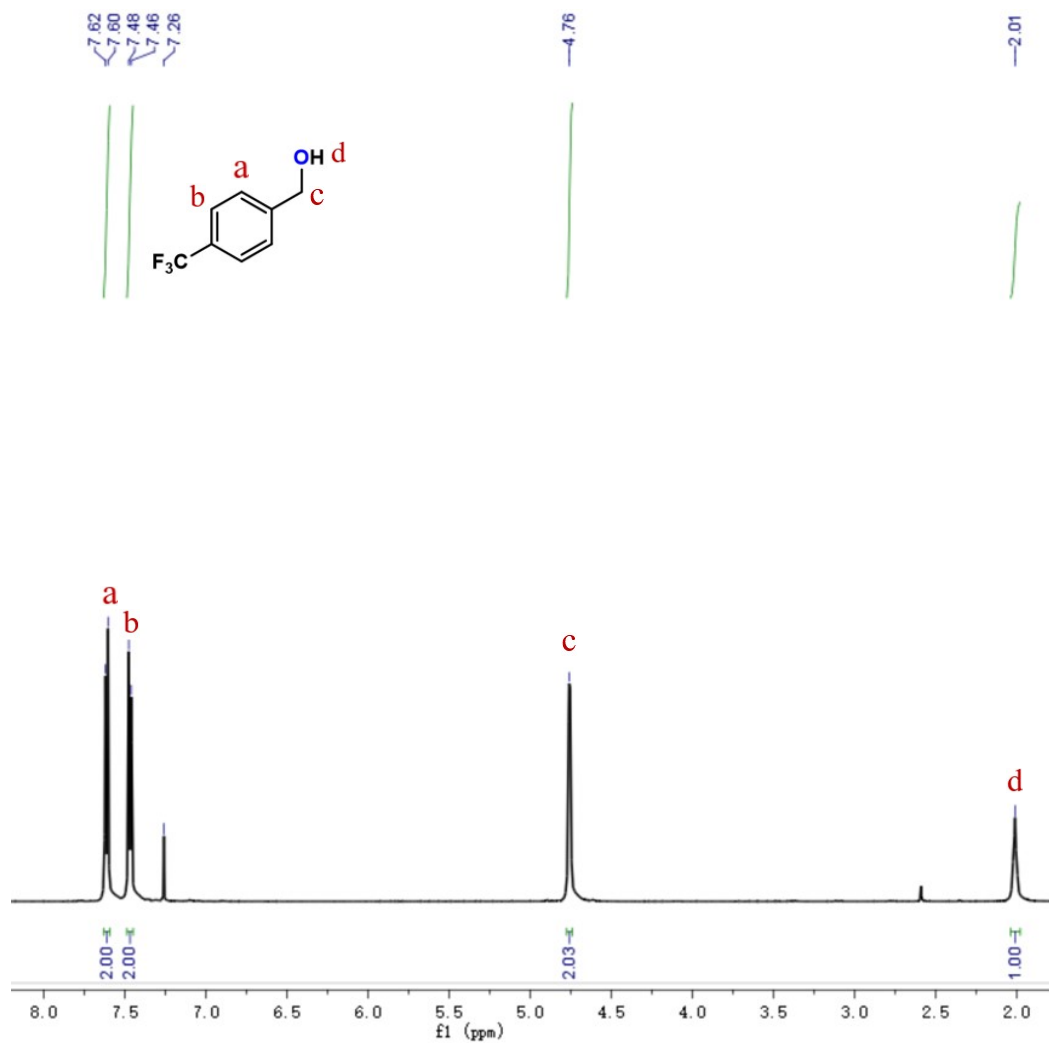
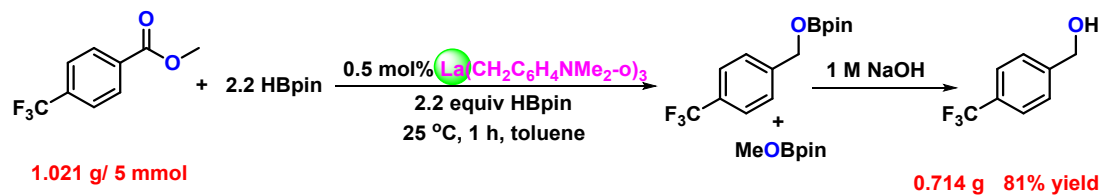


Fig. S24.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.61 (d,  $J = 8.1$  Hz, 2H,  $\text{CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ ), 7.47 (d,  $J = 8.1$  Hz, 2H,  $\text{CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ ), 4.76 (s, 2H,  $\text{CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ ), 2.01 (s, 1H,  $\text{CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ ) (Scheme 1).