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**A Highly General Catalyst for the Enantioselective Reaction of  
Aldehydes with Diethylzinc.**

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**Preparation and Characterization of 2,5-Dihexyloxyphenylboronic acid, 4.** (a) Preparation of 1,4-dihexyloxy-2-bromobenzene, **A**. Under N<sub>2</sub>, to a solution of 1,4-dihexyloxy-2,5-dibromobenzene (25.92 g, 59.45 mmol) in THF (150 mL) was added n-BuLi (23.8 mL, 2.5M in hexanes) at -78 °C over 30 min. After the addition, the reaction mixture was stirred at -78 °C for 1 h and was then quenched with aq. NH<sub>4</sub>Cl at -78 °C. Usual workup gave **A** as a pale yellow liquid (97% yield). (b) Preparation of **4**. To a solution of **A** (10.71 g, 30 mmol) in THF (100 mL) was added n-BuLi (12 mL, 2.5 M in hexanes) at -78 °C over 10 min. After the addition, the reaction mixture was stirred at -78 °C for 30 min and was then cannulated into a solution of triethylborate (3 equiv., 15 mL) in THF (80 mL) at -78 °C. The mixture was stirred at -78 °C for 2 h and then at r.t. for overnight. Hydrolysis of the resulting product solution with 2N HCl at r.t. for 2 h followed by usual workup and column chromatography on silica gel (hexanes/EtOAc = 5/1) gave **4** as a pure white solid in 68% yield. m.p. 85-7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 3.4 Hz, 1H), 6.95 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.53 (s, 1H), 6.44 (s, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.82 (m, 2H), 1.75 (m, 2H), 1.33-1.45 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 158.28, 153.32, 121.34, 119.41, 112.19, 69.07, 68.67, 31.69, 31.58, 29.45, 29.38, 25.80, 25.78, 22.71, 22.62, 14.15, 14.08. FT-IR (cm<sup>-1</sup>) 3462 (m), 2936 (s), 2864 (m), 1495 (s), 1468 (s), 1422 (s), 1333 (s), 1217 (s), 1146 (m), 1044 (s), 908 (s), 735 (s). Anal. Calcd for C<sub>18</sub>H<sub>31</sub>BO<sub>4</sub>: C, 67.08; H, 9.63. Found: C, 67.37; H, 9.75.

**Preparation and Characterization of (*R*)-3,3'-Bis(2",4"-dihexyloxyphenyl)-1,1'-binaphthol, (*R*)-2.** (a) Preparation of (*R*)-2,2'-bis(methoxymethoxy)-3,3'-bis(2",4"-dihexyloxyphenyl)-1,1'-binaphthyl, (*R*)-**B**. Under N<sub>2</sub>, to a solution of (*R*)-**3** (2.63 g, 4.21 mmol) and **4** (4.07 g, 12.63 mmol) in THF (50 mL) were added Pd[(PPh<sub>3</sub>)<sub>4</sub>] (250 mg) and K<sub>2</sub>CO<sub>3</sub> (aq. 2 M, 20 mL, degassed with N<sub>2</sub>) sequentially. The reaction mixture was heated at reflux for 22 h and then quenched with brine at r.t. Usual workup followed by column chromatography on silica gel (hexanes/EtOAc = 10/1) gave (*R*)-**B** as a colorless oil in 88% yield. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 7.88 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.33-7.41 (m, 4H), 7.24-7.29 (m, 2H), 7.03 (d, *J* = 2.7 Hz, 2H), 6.88 (s, 2H), 6.86 (d, *J* = 2.7 Hz, 2H), 4.46 (d, *J* = 5.6 Hz, 2H), 4.41 (d, *J* = 5.6 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 4H), 3.89 (t, *J* = 6.9 Hz, 4H), 2.35 (s, 6H), 1.77 (m, 4H), 1.64 (m, 4H), 1.45 (m, 4H), 1.16-1.35 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 6H), 0.77 (t, *J* = 6.9 Hz, 6H). (b) Preparation of (*R*)-**2**. To a solution of (*R*)-**B** (3.0 g) in a mixed solvent (10 mL CH<sub>2</sub>Cl<sub>2</sub> and 30 mL EtOH) was added conc. HCl (5 mL). The reaction mixture was heated at reflux under N<sub>2</sub> for 16 h. The volatile component was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 10/1) to give (*R*)-**2** as a colorless oil in 85% yield. [α]<sub>D</sub> = 95.0 (c = 0.962, THF). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 7.96 (s, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.25-7.38 (m, 6H), 7.12 (d, *J* = 2.5 Hz, 2H), 6.96 (s, 2H), 6.94 (d, *J* = 2.7 Hz, 2H), 6.32 (s, 2H), 3.99 (t, *J* = 6.5 Hz, 4H), 3.92 (t, *J* = 6.7 Hz, 4H), 1.81 (m, 4H), 1.63 (m, 4H), 1.49 (m, 4H), 1.33-1.40 (m, 8H), 1.21-1.28 (m, 4H), 1.11-1.26 (m, 8H), 0.93 (t, *J* = 6.9 Hz, 6H), 0.76 (t, *J* = 6.9 Hz, 6H). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>) δ 154.10, 150.36, 149.95, 133.75, 131.02, 129.27, 129.17, 129.11, 128.26, 126.55, 124.97, 123.72, 118.52, 116.67, 115.16, 114.94, 70.75, 68.76, 31.72, 31.52, 29.47, 29.34, 25.86, 25.56, 22.74, 22.51, 14.18, 14.05. FT-IR (cm<sup>-1</sup>) 3530 (m), 2930 (s), 2870 (s), 1499 (s), 1470 (s), 1445 (s), 1387 (m), 1265 (s), 1211 (s), 1119 (m), 1038 (m), 909 (s), 787 (m), 735 (s). MS (DIP) *m/z* (relative intensity) 839 (M+H<sup>+</sup>, 9), 755 (M+H<sup>+</sup>-C<sub>6</sub>H<sub>12</sub>, 2), 652 (M-OC<sub>6</sub>H<sub>13</sub>-C<sub>6</sub>H<sub>13</sub>, 2), 585 (M+H<sup>+</sup>-2C<sub>6</sub>H<sub>13</sub>-C<sub>6</sub>H<sub>12</sub>, 0.4), 568

(M+H<sup>+</sup>-OC<sub>6</sub>H<sub>13</sub>-2C<sub>6</sub>H<sub>13</sub>, 2), 484 (M+H<sup>+</sup>-OC<sub>6</sub>H<sub>13</sub>-2C<sub>6</sub>H<sub>13</sub>-C<sub>6</sub>H<sub>12</sub>, 7). Anal. Calcd for C<sub>56</sub>H<sub>70</sub>O<sub>6</sub>: C, 80.19; H, 8.35. Found: C, 79.89; H, 8.80.

### Conditions for the Analysis of Chiral Secondary Alcohols

Chiral Capillary GC: Supelco  $\beta$ - Dex 120<sup>TM</sup> column 30 m x 0.25 mm (i.d.), 0.25  $\mu$ m film. Carrier gas: He (1.05 mL/min). Detector: FID, 280 °C. Injector: 220 °C.

Chiral HPLC: Chiracel OD or Chiracel AD column, hexane/isopropanol 9/1, 1.0 mL/min, 254 nm UV detector.

The racemic alcohol products were obtained by either addition of Et<sub>2</sub>Zn to aldehydes in the presence of 2-pyridylcarbinol catalyst or addition of EtMgBr to aldehydes. The retention time of the racemic alcohol products under the given conditions is listed below.

**1-Phenylpropanol:** t<sub>R</sub> = 7.45 min, t<sub>S</sub> = 8.80 min (HPLC OD column).

**1-(*p*-Methylphenyl)propanol:** t<sub>R</sub> = 32.18 min, t<sub>S</sub> = 34.11 min (GC. 100 °C to 150 °C, 1 °C/min).

**1-(*p*-Methoxyphenyl)propanol:** t<sub>R</sub> = 8.70 min, t<sub>S</sub> = 9.48 min (HPLC AD column).

**1-(*p*-Chlorophenyl)propanol:** t<sub>R</sub> = 6.25 min, t<sub>S</sub> = 7.20 min (HPLC OD column).

**1-(*m*-Chlorophenyl)propanol:** The *ee* was measured by analyzing its acetate with GC: t<sub>R</sub> = 17.46 min, t<sub>S</sub> = 16.79 min (135 °C to 160 °C, 1 °C/min).

**1-(*m*-Methoxyphenyl)propanol:** t<sub>R</sub> = 10.00 min, t<sub>S</sub> = 10.73 min (HPLC OD column).

**1-(*o*-Fluorophenyl)propanol:** t<sub>R</sub> = 26.74 min, t<sub>S</sub> = 28.02 min (GC. 100 °C to 140 °C, 1 °C/min).

**1-(*o*-Methoxyphenyl)propanol:** t<sub>R</sub> = 45.73 min, t<sub>S</sub> = 44.05 min (GC. 100 °C to 150 °C, 1 °C/min).

**1-( $\alpha$ -Naphthyl)propanol:** t<sub>R</sub> = 16.08 min, t<sub>S</sub> = 8.83 min (HPLC OD column).

**1-( $\beta$ -Naphthyl)propanol:** t<sub>R</sub> = 11.87 min, t<sub>S</sub> = 10.40 min (HPLC OD column).

**1-(2'-Furyl)propanol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 22.23$  min,  $t_S = 21.31$  min (80  $^{\circ}\text{C}$  to 120  $^{\circ}\text{C}$ , 1  $^{\circ}\text{C}/\text{min}$ ).

**3-Octanol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 32.03$  min,  $t_S = 30.75$  min (60  $^{\circ}\text{C}$  to 100  $^{\circ}\text{C}$ , 1  $^{\circ}\text{C}/\text{min}$ ).

**3-Nonanol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 33.54$  min,  $t_S = 32.43$  min (70  $^{\circ}\text{C}$  to 110  $^{\circ}\text{C}$ , 1  $^{\circ}\text{C}/\text{min}$ ).

**3-Undecanol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 28.82$  min,  $t_S = 28.07$  min (100  $^{\circ}\text{C}$  to 140  $^{\circ}\text{C}$ , 1  $^{\circ}\text{C}/\text{min}$ ).

**1-Cyclohexylpropanol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 21.00$  min,  $t_S = 20.34$  min (100  $^{\circ}\text{C}$  to 130  $^{\circ}\text{C}$ , 1  $^{\circ}\text{C}/\text{min}$ ).

**5-Methyl-3-hexanol:** The *ee* was measured by analyzing its benzoate with GC.  $t_R = 48.87$  min,  $t_S = 47.71$  min (110  $^{\circ}\text{C}$  to 135  $^{\circ}\text{C}$ , 0.4  $^{\circ}\text{C}/\text{min}$ ).

**(E)-1-Phenyl-pent-1-en-3-ol:**  $t_R = 9.08$  min,  $t_S = 13.40$  min (HPLC OD column).

**(E)-1-Phenyl-2-methyl-pent-1-en-3-ol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 33.17$  min,  $t_S = 32.26$  min (140  $^{\circ}\text{C}$ ).

**(E)-Hex-4-en-3-ol:**  $t_R = 20.42$  min,  $t_S = 22.09$  min (60  $^{\circ}\text{C}$ ).

**5-Methyl-hex-4-en-3-ol:**  $t_R = 11.06$  min,  $t_S = 13.88$  min (GC. 85  $^{\circ}\text{C}$ ).

**(E)-4-Methyl-hex-4-en-3-ol:**  $t_R = 22.46$  min,  $t_S = 26.64$  min (GC. 75  $^{\circ}\text{C}$ ).

**2-(n-Butyl)-pent-1-en-3-ol:** The *ee* was measured by analyzing its acetate with GC.  $t_R = 23.04$  min,  $t_S = 22.13$  min (90  $^{\circ}\text{C}$ ).

**1-Phenyl-pent-1-yn-3-ol:**  $t_R = 7.27$  min,  $t_S = 15.40$  min (HPLC OD column).