

## Supporting Information

Experimental procedure (described for homoaldol addition to benzaldehyde)

Titanium (IV) isopropoxide (110  $\mu$ l, 0.373 mmol, 0.10 equiv) was added dropwise to a suspension of (R)-2, 2'-binaphthol (0.1046 g, 0.365 mmol, 0.099 equiv, > 99 % ee) in toluene (5 mL) at 0 °C in a Schlenk flask. Immediate formation of an orange-red solution was observed. The reaction mixture was warmed to room temperature and stirred for 3 hours, after which the solvents were removed *in vacuo*. The resulting orange-red solid was dissolved in toluene (2 x 5 mL) and the volatile material removed *in vacuo* after each dissolution. The solid material was dried *in vacuo* for 15 hours, then re-dissolved in a mixture of CD<sub>3</sub>CN and CDCl<sub>3</sub> (6:2 mL) and cooled to 0 °C. Trimethylsilyl triflate (68  $\mu$ L, 0.376 mmol, 0.10 equiv) was added, affording a dark red solution. After 15 minutes, ethoxytrimethylsilyloxycyclopropane (1.12 mL, 5.57 mmol, 1.51 equiv) was added and after 10 minutes, benzaldehyde (430  $\mu$ L, 3.69 mmol, 1 equiv) was added. After 45 minutes, a 500  $\mu$ l aliquot was transferred to an argon filled NMR tube and the reaction monitored by <sup>1</sup>H NMR. After 26 hours at 0 °C, the reaction was quenched by addition of 1 M HCl (10 mL) and the products were extracted into ethyl acetate (3 x 15 mL). The organic layer was washed once with brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude reaction mixture was dissolved in benzene (6 mL), pTsOH (cat.) was added and the reaction mixture stirred overnight. Saturated NaHCO<sub>3</sub> (5 mL) was added and the products extracted into ethyl acetate (3 x 10 mL). The organic layer was washed once with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Purification of the residue by column chromatography on silica gel using 30% hexanes in methylene chloride as eluent afforded 0.590 g of the lactone (99 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, *J* in hertz)  $\delta$  7.24 - 7.39 (m, 5H), 5.46 (dd, 1H, *J* = 7.9, 6.2), 2.54 - 2.67 (m, 3H), 2.04 - 2.22 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  176.8, 139.2, 128.5, 128.2, 125.1, 81.0, 30.7, 28.7; HRMS calcd for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub> (M + H) 163.0759, found 163.0758.

**Homoaldol adduct of Ph-C≡C-CHO.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, *J* in hertz) δ 7.23 – 7.45 (m, 5H), 5.35 (t<sub>app</sub>, 1H, *J*<sub>app</sub> = 5.8), 2.34 – 2.75 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 176.0, 131.7, 129.0, 128.3, 121.5, 87.3, 84.9, 69.5, 29.8, 27.8; HRMS calcd for C<sub>12</sub>H<sub>11</sub>O<sub>2</sub> (M + H) 187.0759, found 187.0758.

**Homoaldol adduct of TMS-C≡C-CHO.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, *J* in hertz) δ 5.07 (t<sub>app</sub>, 1H, *J*<sub>app</sub> = 6.4), 2.43 – 2.66 (m, 3H), 2.23 – 2.31 (m, 1H), 0.14 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 175.9, 100.9, 92.9, 69.2, 29.7, 27.7, - 0.5; HRMS calcd for C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>Si (M + H) 183.0841, found 183.0841.

**Homoaldol adduct of C<sub>4</sub>H<sub>9</sub>CHO.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, *J* in hertz) δ 4.16 (dd, 1H, *J* = 8.9, 6.9), 2.46 – 2.54 (m, 2H), 1.86 – 2.16 (m, 2 H), 0.92 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 177.3, 88.2, 33.8, 29.3, 24.9, 22.9; HRMS calcd for C<sub>8</sub>H<sub>15</sub>O<sub>2</sub> (M + H) 143.1072, found 143.1073.

**Homoaldol adduct of PhCOCH<sub>3</sub>.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.24 – 7.40 (m, 5H), 2.34 – 2.67 (m, 4H), 1.70 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 176.4, 144.2, 128.5, 127.5, 124.0, 86.9, 36.0, 29.3, 28.8; HRMS calcd for C<sub>11</sub>H<sub>13</sub>O<sub>2</sub> (M + H) 177.0916, found 177.0916.

**Homoaldol adduct of p-ClPhCHO.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.30 (d, 2 H, *J* = 8.6), 7.22 (d, 2 H, *J* = 8.6), 5.41 (dd, 1H, *J* = 5.9, 6.4), 2.52 – 2.67 (m, 3H), 2.00 – 2.18 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 176.4, 137.8, 134.0, 128.7, 126.6, 80.3, 30.7, 28.7; HRMS calcd for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>Cl (M + H) 197.0369, found 197.0369.