

**The Mechanistic Basis for Electronic Effects on Enantioselectivity  
in the (salen)Mn(III)-Catalyzed Epoxidation Reaction**

**SUPPORTING INFORMATION**

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**General Procedure for the Preparation of the Ligand Precursors to 2: (*R,R*)-2,2'-[(1,2-Diphenyl-1,2-ethanediyl)bis(nitrilomethylidene)]-bis[4-methoxy-6-(1,1-dimethylethyl)phenol] (ligand precursor to 2a)** To a solution of diphenylethylenediamine (356 mg, 2.00 mmol) in 10 mL of EtOH was added a solution of 3-*t*-butyl-5-methoxysalicylaldehyde (832 mg, 4.00 mmol) in 10 mL of EtOH. The resulting yellow solution was heated to reflux for 1 hour and the heating bath removed. Upon standing overnight, a yellow crystals formed which was collected and washed with cold 70% EtOH to yield the title compound (1.12 g, 95% yield). IR (KBr) 2984, 1595, 1456, 1429, 1333, 1236, 1150, 1059, 839 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.41 (s, 18H), 3.65 (s, 6H), 4.70 (s, 2H), 6.46 (d, *J* = 2.9 Hz, 2H), 6.91 (d, *J* = 2.9 Hz, 2H), 7.18 (m, 10H), 8.32 (s, 2H), 13.40 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 29.2, 34.9, 55.5, 80.1, 111.5, 117.7, 118.6, 127.5, 127.9, 128.3, 138.7, 139.3, 151.1, 154.7, 166.7; mp 84-86 °C. Anal. calc'd. for (C<sub>38</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>) C, 77.00; H, 7.48; N, 4.73; found: C, 76.72; H, 7.55; N, 4.59.

**(*R,R*)-2,2'-[(1,2-Diphenyl-1,2-ethanediyl)bis(nitrilomethylidene)] bis[4-methyl-6-(1,1-dimethylethyl)phenol] (ligand precursor to 2b)** The general procedure was followed on 5 mmol scale.

After the reflux period, the volume of the reaction mixture was reduced to 25 mL by distillation and water (5 mL) was then added. Upon cooling to room temperature, a yellow precipitate formed which was collected to yield the title compound (2.67 g, 95% yield). IR (KBr) 2952, 2870, 1630, 1441, 1211, 1165, 1022, 864  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.42 (s, 18H), 2.17 (s, 6H), 4.67 (s, 2H), 6.76 (d,  $J = 1.5$  Hz, 2H), 7.04 (d,  $J = 7.6$  Hz, 2H), 7.12-7.21 (m, 10H), 8.29 (s, 2H), 13.52 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.5, 29.4, 34.7, 80.2, 118.2, 126.5, 127.4, 128.0, 128.3, 130.0, 130.6, 136.7, 139.5, 157.9, 166.9; mp 137-138 °C. Anal. calc'd. for ( $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2$ ) C, 81.39; H, 7.91; N, 5.00; found C, 81.44; H, 7.93; N, 4.96.

**(*R,R*)-2,2'-[(1,2-Diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)] bis[6-(1,1-dimethylethyl)phenol]** (ligand precursor to 2c) The general procedure was followed on 1 mmol scale. Water (5 mL) was added dropwise to the reaction mixture. The oil that separated solidified upon standing. Recrystallization from MeOH/H<sub>2</sub>O afforded 485.8 mg (0.910 mmol, 91% yield) of the title compound, mp 117-117.5 °C. IR (KBr) 2957, 1618, 1483, 1433, 1389, 1306, 1198, 1144, 1028, 847, 770, 750, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.42 (s, 18H), 4.70 (s, 2H), 6.69 (t,  $J = 7.6$  Hz, 2H), 7.20 (d,  $J = 7.6$  Hz, 2H), 7.16-7.19 (m, 10H), 7.24 (d,  $J = 7.6$  Hz, 2H), 8.33 (s, 2H), 13.80 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.3, 34.8, 80.1, 117.8, 118.5, 127.5, 127.9, 128.3, 129.6, 130.1, 137.0, 139.4, 160.2, 166.8. Anal. calc'd. for  $\text{C}_{36}\text{H}_{40}\text{N}_2\text{O}_2$ ) C, 81.17; H, 7.60; N, 5.26; found C, 81.17; H, 7.60; N, 5.25.

**(*R,R*)-2,2'-[(1,2-Diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)] bis[4-chloro-6-(1,1-dimethylethyl)phenol]** (ligand precursor to 2d) The general procedure was followed on 5 mmol scale. Water (10 mL) was added dropwise to the reaction mixture. The mixture was allowed to cool to room temperature, and the resulting solid was collected by filtration. Recrystallization from 80% EtOH afforded 2.786 g of the title compound (4.65 mmol, 93% yield), mp 89-91 °C. IR (KBr) 2957, 1628, 1580, 1453, 1431, 1271, 1175, 1028, 870  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.40 (s, 18H), 4.70 (s, 2H), 6.93 (d,  $J = 2.3$  Hz, 2H), 7.17-7.26 (m, 12H), 8.22 (s, 2H), 13.75 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.0, 35.0, 80.0, 119.0, 122.6, 127.8, 127.9, 128.5, 128.7, 129.9, 138.8, 139.5, 158.8, 165.8. Anal. calc'd. for  $\text{C}_{36}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_2$ ) C, 71.87; H, 6.37; N, 4.66; found C, 71.81; H, 6.37; N, 4.73.

**(*R,R*)-2,2'-[(1,2-cyclohexandiyl)bis(nitrilomethylidene)]bis[4-chloro-6-(1,1-dimethylethyl)phenol]**

**(ligand precursor to 3d).** To a solution of (*R,R*)-cyclohexanediamine-mono-(+)-tartrate salt<sup>1</sup> (68.4 mg, 0.269 mmol) in 10 mL of EtOH and 1 mL of H<sub>2</sub>O was added K<sub>2</sub>CO<sub>3</sub> (71.5 mg, 0.517 mmol) and 3-*t*-butyl-2-hydroxy-5-chlorobenzaldehyde (110 mg, 0.517 mmol). The resulting yellow mixture heated at reflux for 1 h. The reaction was cooled to room temperature and the solvents removed under vacuum to afford a yellow slurry. Distilled water (15 mL) was added, and the resulting yellow precipitate was isolated by filtration, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), washed sequentially with brine (20 mL) and water (20 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent removed by filtration and 595 mg of product (85% yield) was isolated as a yellow powder after removal of the solvent. IR (CCl<sub>4</sub>) 2957, 2943, 1632, 1432, 1202, 1175, 871 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.38 (s, 18H), 1.40-1.49 (m, 2H), 1.72-1.75 (m, 2H), 1.88-2.00 (m, 6H), 3.31 (dd, *J* = 4.0, 5.9 Hz, 2H), 6.94 (d, *J* = 2.7 Hz, 2H), 7.18 (d, *J* = 2.8 Hz, 2H), 8.17 (s, 2H), 13.8 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.2, 29.1, 32.8, 35.0, 72.3, 119.1, 122.5, 128.5, 129.5, 139.4, 158.9, 164.5. This material was used without further purification.

**(*R,R*)-2,2'-[(1,2-cyclohexandiyl)bis(nitrilomethylidene)]bis[4-nitro-6-(1,1-dimethylethyl)phenol]**

**(ligand precursor to 3e)** To a solution of (*R,R*)-cyclohexanediamine-mono-(+)-tartrate salt (315 mg, 1.19 mmol) in 75 mL of EtOH and 5 mL of H<sub>2</sub>O was added K<sub>2</sub>CO<sub>3</sub> (328 mg, 2.38 mmol) and the mixture heated at 50 °C for 10 min. 3-*t*-Butyl-2-hydroxy-5-nitrobenzaldehyde (2.38 mmol) was then added to the solution and resulting yellow mixture heated at reflux for 30 minutes. The reaction was cooled to room temperature and the solvents removed under vacuum. The residue was dissolved in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed with 100 mL of brine, 100 mL H<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent removed by filtration and the product (595 mg, 85% yield) was isolated as a yellow powder after removal of the solvent. IR (CCl<sub>4</sub>) 2945, 1636, 1616, 1483, 1329, 1286, 1110, 784 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.40 (s, 18H), 1.50-1.56 (m,

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2H), 1.80 (d,  $J = 8.5$  Hz, 2H), 1.96-2.11 (m, 4H), 3.46-3.49 (m, 2H), 8.00 (d,  $J = 2.7$  Hz, 2H), 8.15 (d,  $J = 2.8$  Hz, 2H), 8.35 (s, 2H), 12.6 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.0, 28.8, 32.5, 35.2, 71.3, 116.8, 125.0, 126.1, 138.7, 139.6, 164.5, 167.1. HRMS (FAB)  $m/z$ : calc'd ( $\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_6$ ) 525.273 ( $\text{M}+\text{H}^+$ ), found 525.2717.

**Chloro-(*R,R*)-[[2,2'-[(1,2-cyclohexandiyl)bis(nitrilomethylidene)]bis[4-Nitro-6-(1,1-dimethyl ethyl)phenolato]]-*N,N'O,O'*]manganese(III) (3e).** A 3 necked round bottom flask equipped with a reflux condenser, addition funnel and glass stopper was charged with the salen ligand (0.209 g, 0.400 mmol) and 20 mL of EtOH. The mixture was heated to reflux and a solution of  $\text{Mn}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$  dissolved in 2 mL of 50% EtOH/  $\text{H}_2\text{O}$  was added whereupon the solution immediately turned brown. After refluxing for 30 minutes, 1 mL of brine was added and the resulting solution refluxed for an additional 30 minutes. After cooling to room temperature, the solvents were removed and 50 mL of  $\text{CH}_2\text{Cl}_2$  was added. The solution was then washed with 50 mL of brine followed by 50 mL of  $\text{H}_2\text{O}$  and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the drying agent followed by concentration of the filtrate resulted in a brown powder which was chromatographed (5% EtOH/ $\text{CH}_2\text{Cl}_2$ ) affording the product (0.220 g, 90% yield). IR ( $\text{CCl}_4$ ) 2955, 1628, 1598, 1565, 1510, 1330, 1311, 1296, 1271, 1116, 706, 698, 690  $\text{cm}^{-1}$ ; mp > 400 °C. HRMS (FAB)  $m/z$ : calc'd ( $\text{C}_{28}\text{H}_{34}\text{ClMnN}_4\text{O}_6$ ) 577.1859 ( $\text{M}-\text{Cl}^+$ ), found 577.1849.