Oxidation of primary and secondary benzylic alcohols with hydrogen peroxide and *tert*-butyl hydroperoxide catalyzed by a "helmet" phthalocyaninato iron complex in the absence of added organic solvent

Supplemental information: experimental details for alcohol oxidation reactions

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Equipment and materials: All solvents (HPLC grade or higher) were purchased from commercial sources and used without drying or distillation. Iron complex **1** was prepared as we have described previously.[22] All other reagents were obtained from commercial sources in the highest available purity and used as received. All HPLC experiments were carried out by use of either a 0.46 x 25 cm Phenomenex Luna phenyl-hexyl reverse phase column or a 0.46 x 7.5 cm Agilent Zorbax XDB phenyl reverse phase column on an Agilent 1100 system equipped with a variable wavelength UV-VIS detector and running the ChemStation software suite, version B.03.02. Methanol/water gradients were used for all HPLC analyses. Products were quantified vs. external standards. Reactions with alcohol substrates that are solids at room temperature were heated on stirring hot plates, using a thermometer inserted directly into the reaction solution to determine the temperature.

Catalysis experiments:

Caution- solutions containing significant concentrations of TBHP or hydrogen peroxide and metal-containing compounds are potentially dangerous, and reactions should be carried out behind adequate protection.

Benzyl alcohol oxidation with hydrogen peroxide: In a typical experiment, a 25 mL round bottomed flask was charged with 1.3 mg (1.6 μmol) of **1** and 5.0 mL benzyl alcohol. After magnetic stirring to dissolve the catalyst, 1.0 mL of 30% hydrogen peroxide solution in water was added via syringe. The contents of the open flask were stirred for 15 minutes at room temperature, then analyzed by HPLC.

Benzyl alcohol oxidation with TBHP (30 min reaction time): In a typical experiment, a 25 mL round bottomed flask was charged with 1.0 mg (1.2 μmol) of **1** and 5.0 mL benzyl alcohol. After magnetic stirring to dissolve the catalyst, 0.3 mL of 70% TBHP solution in water was added via syringe. The contents of the open flask were stirred at room temperature for 30 minutes, then analyzed by HPLC.

Benzyl alcohol oxidation with TBHP (2 h reaction time): In a typical experiment, a 25 mL round bottomed flask was charged with 1.2 mg (1.5 μmol) of **1** and 5.0 mL benzyl alcohol. After magnetic stirring to dissolve the catalyst, 0.3 mL of 70% TBHP solution in water was added via syringe. The contents of the open flask were stirred at room temperature for two hours, then analyzed by HPLC.

4-Chlorobenzyl alcohol oxidation with hydrogen peroxide: In a typical experiment, a 100 mL round bottomed flask was charged with 5.8 g of the solid alcohol and 2.8 mg (3.5 μmol) of **1**. The contents of the flask were then heated on a hot plate with stirring until the alcohol melted and dissolved the catalyst. Then, 1.0 mL of 30% hydrogen peroxide solution in water was added via syringe as the temperature of

the solution was maintained at 72 °C for fifteen minutes. The contents of the flask were then transferred to a volumetric flask, followed by HPLC analysis. A volume of 25 mL EtOH was used to aid in the transfer.

4-Chlorobenzyl alcohol oxidation with TBHP (30 min reaction time): In a typical experiment, a 50 mL round bottomed flask was charged with 5.2 g of the solid alcohol and 1.7 mg (2.1 μmol) of **1**. The contents of the flask were then heated on a hot plate with stirring until the alcohol melted and dissolved the catalyst. Then, 0.3 mL of 70% TBHP solution in water was added via syringe as the temperature of the solution was maintained at 85 °C for thirty minutes. The contents of the flask were then transferred to a volumetric flask, followed by HPLC analysis. A volume of 25 mL EtOH was used to aid in the transfer.

4-Chlorobenzyl alcohol oxidation with TBHP (2 h reaction time): In a typical experiment, a 50 mL round bottomed flask was charged with 5.4 g of the solid alcohol and 1.2 mg (1.5 μmol) of **1**. The contents of the flask were then heated on a hot plate with stirring until the alcohol melted and dissolved the catalyst. Then, 0.3 mL of 70% TBHP solution in water was added via syringe as the temperature of the solution was maintained at 85 °C for two hours. The contents of the flask were then transferred to a volumetric flask, followed by HPLC analysis. A volume of 25 mL EtOH was used to aid in the transfer.

1-Phenylethanol oxidation with hydrogen peroxide: In a typical experiment, a 50 mL round bottomed flask was charged with 1.4 mg (1.7 μmol) of **1** and 10.0 mL 1-phenylethanol. After magnetic stirring to dissolve the catalyst, 1.0 mL of 30% hydrogen peroxide solution in water was added via syringe. The contents of the open flask were stirred for six minutes at room temperature, then analyzed by HPLC.

1-Phenylethanol oxidation with TBHP (30 min reaction time): In a typical experiment, a 50 mL round bottomed flask was charged with 1.9 mg (2.4 μmol) of **1** and 6.0 mL 1-phenylethanol. After magnetic stirring to dissolve the catalyst, 0.3 mL of 70% TBHP solution in water was added via syringe. The contents of the open flask were stirred for thirty minutes at room temperature, then analyzed by HPLC.

1-Phenylethanol oxidation with TBHP (2 h reaction time): In a typical experiment, a 50 mL round bottomed flask was charged with 1.3 mg (1.6 μmol) of **1** and 5.0 mL 1-phenylethanol. After magnetic stirring to dissolve the catalyst, 0.3 mL of 70% TBHP solution in water was added via syringe. The contents of the open flask were stirred for two hours at room temperature, then analyzed by HPLC.

Diphenylmethanol (benzhydrol) oxidation with hydrogen peroxide: In a typical experiment, a 100 mL round bottomed flask was charged with 5.1 g of the solid alcohol and 1.2 mg (1.5 μmol) of **1**. The contents of the flask were then heated on a hot plate with stirring until the alcohol melted and dissolved the catalyst. Then, 1.0 mL of 30% hydrogen peroxide solution in water was added via syringe as the temperature of the solution was maintained at 70 °C for ten minutes. The contents of the flask were then transferred to a volumetric flask, followed by HPLC analysis. A volume of 50 mL EtOH was used to aid in the transfer.

Diphenylmethanol (benzhydrol) oxidation with TBHP (30 min reaction time): In a typical experiment, a 100 mL round bottomed flask was charged with 5.2 g of the solid alcohol and 1.4 mg (1.7 μmol) of **1**. The contents of the flask were then heated on a hot plate with stirring until the alcohol melted and dissolved the catalyst. Then, 0.3 mL of 70% TBHP solution in water was added via syringe as the

temperature of the solution was maintained at 75 °C for thirty minutes. The contents of the flask were then transferred to a volumetric flask, followed by HPLC analysis. A volume of 25 mL EtOH was used to aid in the transfer.

Diphenylmethanol (benzhydrol) oxidation with TBHP (2 h reaction time): In a typical experiment, a 100 mL round bottomed flask was charged with 5.5 g of the solid alcohol and 1.6 mg (2.0 μmol) of **1**. The contents of the flask were then heated on a hot plate with stirring until the alcohol melted and dissolved the catalyst. Then, 0.3 mL of 70% TBHP solution in water was added via syringe as the temperature of the solution was maintained at 68 °C for two hours. The contents of the flask were then transferred to a volumetric flask, followed by HPLC analysis. A volume of 35 mL EtOH was used to aid in the transfer.