Supporting Information

Preparation of the catalysts and their precursors

3,3'-dichlorobenzophenone

12.5 mL of n-butyllithium (1.6 M in hexane) was added to a solution of 2.35 mL (20 mmol) of 3-bromochlorobenzene in 45 mL of dry THF at –100 ˚C under nitrogen. The mixture was stirred for 30 min. and then 0.956 mL (10 mmol) of freshly distilled ethyl chloroformate in 10 mL of dry THF was added and the solution was stirred for 2 hours at –80 ˚C. 100 mL of cooled MeOH was added to the cold solution, which was then warmed to 0 ˚C and 50 mL of 3 M HCl was slowly added. The organic phase was separated and the aqueous phase was extracted with ether. The combined organic phases were washed with $NaHCO_3$, dried with Na_2SO_4, and the solvent was evaporated. Crystallization from hot methanol resulted in 1.63 g (65 %) of white crystals, mp 121-124 ˚C (lit.:[1] 123.8-124.9 ˚C); ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.75 (unresolved singlet, 2H), 7.61 (unresolved triplet, 4H), 7,42 (t, J = 8.2 Hz, 2H); HRMS (EI): e/z 245.9955 (23.09 %), calculated for $C_{13}H_8Cl_2O$: 249.9952.

Bis(3-phenyl)-dichloromethane

1.3 g (5.2 mmol) of 3,3'-dichlorobenzophenone and 1.6 g (7.8 mmol) of PCl_5 were heated to 150 ˚C and the flask was fitted with a distillation head and the $POCl_3$ was removed at atmospheric pressure. After 2 hours, the solution was distilled under high vacuum, resulting in 1.49 g (94%) of the product as a white solid. mp 55-60 ˚C; ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.61 (unresolved singlet, 1H), 7.43 (unresolved doublet, 2H), 7.36 (m, 1H), 7.32 (unresolved singlet, 2H), 7.29 (s, 1H), 7.24 (m, 1H); MS (EI): e/z 306 (6%).

(4R,5R)-4,5-bis(diethylcarboxylate)-2,2-bis(3-phenyl)-1,3-dioxolane

A mixture of 1.49 g (4.8 mmol) of (2R,3R)-(+)-diethyl tartarate, 1.25 mL (7.3 mmol) of bis(3-phenyl)-dichloromethane and 10 mL of 1,2-dichlorobenzene was heated to reflux under nitrogen, until the evolution of HCl deceased (36 h). After evaporation, the unreacted compounds were removed by distillation under high vacuum and the remained compound was dissolved in CH_2Cl_2 and decolorized with activated carbon. Evaporation of the solvent resulted

in 1.60 g (76%) of the product. ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7,52 (s, 2H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.26 (m, 4H), 4.92 (s, 2H), 4.14 (m, 4H), 1.22 (t, *J* = 6.6 Hz, 6H).

(4S,5S)-4,5-bis(hydroxymethyl)-2,2-bis(3-phenyl)-1,3-dioxolane

To a suspension of 0.28 g (7.3 mmol) $LiAlH_4$ in 20 mL of dry THF under nitrogen, a solution of 1.6 g (3.6 mmol) of (4R,5R)-4,5-diethyl ester-2,2-(3,3'diphenyl)-1,3-dioxolane in 15 mL of dry THF was added dropwise. After three hours of heating to reflux, 5 mL of ethyl acetate was added at room temperature and the reaction mixture was cooled to 0 ˚C. After successive additions of water, NaOH, and water, the white precipitate was removed by filtration, and the water phase was extracted twice with diethyl ether. The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Crystallization from hot hexane resulted in 0.65 g (51%) of the product. mp 104-107 ˚C; ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.47 (s, 2H), 7.32 (m, 2H), 7.26 (m, 4H), 4.18 (s, 2H), 3.83 (d, *J* = 5.6 Hz, 2H), 3.72 (d, *J* = 6.2 Hz, 2H).

(4S,5S)-4,5-bis(*p*-tosyloxy)methyl-2,2-bis(3-phenyl)-1,3-dioxolane

To a -10 ˚C solution of 0.67 g (1.8 mmol) (4S,5S)-4,5-bis(hydroxymethyl)-2,2-bis(3-phenyl)-1,3-dioxolane in 10 mL of dry pyridine, 1.37 g (7.2 mmol) of *p*-toluene-sulfonylchloride was added at once. The mixture was stirred for 12 h at 0 ˚C, followed by slow addition of water to the reaction mixture. Once crystals began to form, water was added more rapidly up to 20 mL. The solid product was collected, washed with 95% ethanol, and recrystallized by benzene/heptane to afford 0.97 g (81%) of the product. mp 115-120 ˚C; $[\alpha]_D^{20}$ +5.1^o (c = 0.02, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.70 (d, *J* = 8.2 Hz, 4H), 7.27 (m, 12H), 4.11 (s, 2H), 4.03 (m, 4H), 2.44 (s, 6H); HRMS (EI): e/z 662.0530 (0.98 %), calculated for $C_{13}H_8Cl_2O$: 662.0603.

Synthesis of 3-H_2

217 mg (1.6 mmol) of solid K_2CO_3 was added to a 100 ˚C solution of 65 mg (0.087 mmol) of 5,10,15,20 tetrakis(2,6-dihydroxyphenyl)porphyrin and 288 mg (0.42 mmol) of (4S,5S)-4,5-bis(*p*-tosyloxy)methyl-2,2-bis(3-phenyl)-1,3-dioxolane in 12 mL of dry DMF under a nitrogen atmosphere. After 24 hours at 100 ˚C, the cool reaction mixture was diluted with 20 mL CH_2Cl_2 and washed with 40 mL H_2O. After drying with Na_2SO_4 and evaporation the resulting

solid was loaded on alumina. The side products were eluted with EtOAc/hexane (40:60), and elution with CH_2Cl_2 afforded one fast moving fraction. By crystallization from $CHCl_3$/heptane 47 mg (26.7%) of **3**-H_2 were obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.22 (d, *J* =4.63 Hz, 4H), 8.19 (d, *J* = 4.49 Hz, 4H), 7.66 (m, 4H), 7.21 (d, *J* =8.00 Hz, 8H), 7.06 (t, *J* =1.80 Hz, 4H), 7.03 (dd, J^1 =7.90 Hz, J^2 =1.19 Hz, 4H), 6.93 (t, *J* =7.92 Hz, 4H), 6.70 (dt, J^1 =7.81 Hz, J^2 =1.56 Hz, 4H), 6.15 (t, *J* =1.75 Hz, 4H), 5.33 (dd, J^1 =5.93 Hz, J^2 =1.98 Hz, 4H), 5.20 (dd, J^1 =7.86 Hz, J^2 =1.97 Hz, 4H), 4.74 (dd, J^1 =8.30 Hz, J^2 =2.60 Hz, 4H), 4.39 (dd, J^1 =7.13 Hz, J^2 =2.27 Hz, 4H), 4.32 (t, *J* =9.05 Hz, 4H), 4.16 (m, 8H), 4.07 (dm, J^1 =8.26 Hz, 4H), 2.84 (m, 4H), -1.54 (s, 2H); λ_{max} (CH_2Cl_2, nm): 440 (Soret), 536, 576; FAB MS: m/z: 2019.7 ($[M-H]^-$, 100%).

3-Ru(CO)

A solution of 20 mg. (0.009 mmol) of **3**-H_2 in 3 ml of 1,2-dichlorobenzene (freshly distilled) was stirred and heated to reflux under argon. Then 38 mg. (0.054 mmol) of $Ru_3(CO)_{12}$ was added in eight aliquots over two hours. After reflux for over night, flash chromatography (alumina, CH_2Cl_2/hexane 70:30) and recrystallization from $CHCI_3$/heptane, 8.7 mg (42 %) of **3**-Ru(CO) were obtained as orange solids. R_f = 0.72 (alumina, CH_2Cl_2/hexane 70:30); λ_{max} (CH_2Cl_2): 428 (Soret), 552 nm. MS (FAB): e/z 2146.3 (38%), 2020.5 (100%); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.25 (two unresolved doublets, 6H), 8.14 (d, *J* =4.6 Hz, 2H), 7.63 (m, 4H), 7.33 (s, 2H), 7.04 - 7.23 multiplet cover by peak solvent, 6.81 (d, *J* =8.3 Hz, 2H), 6.65 (s, 2H), 6.40 (d, *J* =7.3 Hz, 2H), 6.05 (d, *J* =7.6 Hz, 2H), 6.01 (s, 2H), 5.91 (d, *J* =7.9 Hz, 2H), 5.58 (m, 6H), 4.90 (d, *J* =10.5 Hz, 2H), 4.84 (d, *J* =10.9 Hz, 2H), 4.31 (m, 12H), 4.15 (m, 4H), 4.03 (m, 4H), 3.25 (t, 2H), 2.90 (m, 2H).

3-Ru(O)$_2$

Samples of the *trans*-dioxoruthenium(VI) porphyrin **3**-Ru(O)$_2$ were freshly prepared by adding 0.54 mg (3 μmol) of *m*-CPBA to a solution of 2.7 mg (1 μmol) of **3**-Ru(CO) in 1 mL of CH_2Cl_2. After flash chromatography (alumina, CH_2Cl_2/EtOAc 80:20), 2.6 mg (99 %) of the product were isolated. λ_{max} (CH_2Cl_2): 444 (Soret), 538 nm; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.53 (d, *J* =4.6 Hz, 4H), 8.45 (d, *J* =4.7 Hz, 4H), 7.77 (t, *J* =8.2 Hz, 2H), 7.69 (t, *J* =8.4 Hz, 2H), 7.31 (d, *J* =8.3 Hz, 4H), 7.18 (d, *J* =8.6 Hz , 4H), 7.08 (t, *J* =1.8 Hz, 4H), 6.99

(d, J =9.5 Hz , 4H), 6.87 (t, J =7.9 Hz, 4H), 6.66 (d, J =8.1 Hz , 4H), 6.44 (t, J =1.8 Hz , 4H), 5.83 (dd, J^1 =7.9 Hz , J^2 =3.8 Hz , 4H), 4.87 (dd, J^1 =9.5 Hz , J^2 =2.5 Hz , 4H), 4.75 (d, J =7.7 Hz , 4H), 4.48 (m, 8H), 4.29 (d, J =8.8, 4H), 4.18 (d, J =7.5, 4H), 3.88 (t, J =7.8, 4H), 3.01 (m, 4H).

Catalytic Oxidations

a. epoxidation

The ruthenium porphyrin catalysts was added in one portion to a well-stirred argon-purged solution of accurate amounts of olefin, nitrobenzene (internal standard), and oxidant. Reactions were stopped by freezing the reaction mixture by liquid N_2. For determination of the chemical yields, aliquots from the reaction mixtures were injected into a non-chiral GC column (HP-5) without any treatment, and the ratio of products compared to the internal standard. Enantiomeric excesses were determined after separation of the reaction products from the catalyst and any unreacted oxidant by bulb-to-bulb vacuum distillation, by GC, using a Cyclodex -B chiral capillary column for the ring-substituted styrenes, Chiraldex A-TA for *trans*--β-methylstyrene, and by HPLC— using a (s,s)-whelk-01 (5mm) column— for *trans*-stilbene oxide.. The reaction times, yields, turnover numbers, and ee's for the catalyzed reactions are compiled in each table, together with all the other variables.

b. Oxidations with Pyridine-*N*-Oxides and $HCl_{(g)}$

A small amount (10 mL/L) of a saturated HCl solution in benzene was added to the well-stirred argon-purged benzene solution of accurate amounts of alkane, oxidant, nitrobenzene (internal standard), and catalyst. Reactions were stopped by freezing the reaction mixture with external liquid N_2. For determination of the chemical yields, aliquots from the reaction mixtures were injected into a non-chiral GC column (HP-5) (after addition of K_2CO_3 and filtration), and the ratio of products was compared to the internal standard. The ee's were determined by GC, using a Cyclodex-B capillary column, after separation of the reaction products from the catalyst and any unreacted oxidant by bulb-to-bulb vacuum distillation. The reaction times, yields, turnover numbers, are compiled in each table, together with all the other variables

c. Hydroxylation with Pyridine-*N*-Oxides and $HBr_{(l)}$

After the addition of an aqueous solution of HBr (48%) to the well-stirred argon-purged benzene solution of accurate amounts of alkane, oxidant, nitrobenzene (internal standard), and 4 A molecular sieves, the catalyst was added. Reactions were stopped by freezing the reaction mixture with external liquid N_2. The chemical yields and ee's were determined as described in the previous paragraph. The reaction times, yields, turnover numbers, are compiled in each table, together with all the other variables.

d. Absolute configurations of the products

The absolute configurations of the products were determined for styrene oxide and 3-chlorostyrene oxide, by GC comparison with the commercially available pure enantiomers (Aldrich, (*S*)-(-) and (*R*)-(+), respectively). In both cases, the enantiomer in excess at the reaction conditions of Table 1 was (*R*)-(+).

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[1] Haller, H. L.; Bartlett, P. D.; Drake, N. L.; Newman, M. S.; Cristol, S.J.; Eaker, C. M.; Hayes, R. A.; Kilmer, G. W.; Magerlein, B.; Meuller, G. P.; Schneider, A.; Whealey, W. *J. Amer. Chem. Soc.* **1945**, *67*, 1591.