A Dynamic Supramolecular System Exhibiting Substrate Selectivity in the Catalytic Epoxidation of Olefins

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Electronic Supplementary Information (ESI)

General:
All commercial chemicals were used as received, unless otherwise noted. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves. PhIO was prepared by hydrolysis of iodobenzene I,I-diacetate following a literature procedure.[1] NMR spectra were recorded on a Bruker DRX400 NMR spectrometer in $CDCl_3$ at ambient temperature, ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, unless otherwise stated. Chemical shifts are reported in ppm relative to an internal standard of residual chloroform (δ = 7.27 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR). IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. Melting points were recorded on a Sanyo Gallenkamp Melting Point Apparatus and are uncorrected. Elemental analyses were performed by A. Kolbe, Mikroanalytisches Laboratorium, Germany.

Synthesis and characterization of key compounds

***N,N'*-Bis(3-*tert*-butyl-5-[4-hexyl-2-oxo-3-pentyl-1,2-dihydro-quinolin-7-yl]-salicylidene)-(1*R*,2*R*)-1,2-Bis-(4-decyloxy-phenyl)-ethane-1,2-diamine (12):**
3-*tert*-Butyl-5-(4-hexyl-2-oxo-3-pentyl-1,2-dihydro-quinolin-7-yl)-2-hydroxy-benzaldehyde (751 mg, 1.58 mmol) and (1*R*,2*R*)-1,2-bis(4-decyloxy-phenyl)-ethane-1,2-diamine (419 mg, 0.79 mmol) were suspended in a mixture of ethanol (30 mL) and toluene (15 mL). The mixture was heated to reflux upon which solution was achieved and bright yellow color developed. Reflux was maintained for 10h. Upon cooling, the solvents were evaporated under reduced pressure and the residue was purified by chromatography on silica gel using heptane / ethyl acetate 4:1 as eluent, affording 803 mg of **12** (70% yield).
Bright yellow solid. Mp 115-116°C. Rf (Heptane / EtOAc 1:1) 0.65. $[\alpha]^{19}_D$ 62° (c 0.542 in $CHCl_3$). ^{1}H NMR: δ (ppm) 14.04 (s, 2 H, OH), 10.47 (br. s, 2 H, NH), 8.44 (s, 2 H, C*H*=N), 7.66 (d, *J* = 8.6 Hz, 2 H, ArH), 7.55 (s, 2 H, ArH), 7.32-7.23 (m, 6 H, ArH), 7.15 (d, *J* = 8.7 Hz, 4 H, ArH), 6.80 (d, *J* = 8.7 Hz, 4 H, ArH), 4.73 (s, 2 H, ArC*H*-N), 3.91 (t, *J* = 6.6 Hz, 4 H, $ArOCH_2$), 2.87 (t, *J* = 7.7 Hz, 4 H, $ArCH_2$), 2.70 (t, *J* = 7.7 Hz, 4 H, $ArCH_2$), 1.76 (tt, *J* = 6.6, *J* = 6.6 Hz, 4 H, $ArOCH_2CH_2$), 1.68-1.20 (m, 56 H, alkyl-H), 1.45 (s, 18 H, tBu-CH_3), 0.97-0.80 (m, 18 H, alkyl-CH_3). ^{13}C NMR: δ (ppm) 166.4, 163.4, 160.4, 158.5, 147.2, 141.6, 137.9, 137.4, 131.2, 130.9, 129.5, 129.0, 128.5, 128.4, 128.2, 124.8, 120.9. 118.8, 114.4, 112.8, 79.5, 68.0, 35.0, 32.2, 31.9, 31.6, 30.0, 29.9, 29.57, 29.55, 29.41, 29.31, 29.26, 29.10, 28.93, 27.0, 26.0, 25.7, 22.67, 22.62, 22.57, 14.11, 14.08, 14.03. IR (KBr): 2925, 2854, 1653, 1618, 1511, 1466, 1441, 1247, 1171, 830 cm^{-1}. HRMS (FAB+): *m/z* calcd. for $C_{96}H_{134}N_4O_6$ $[M+1]^+$ 1440.0382; found: 1440.0382. Anal. calcd. for $C_{96}H_{134}N_4O_6$: C, 80.06; H, 9.38; N, 3.89; found C, 79.96; H, 9.35; N, 3.93.

[*N,N'*-Bis(3-*tert*-butyl-5-[4-hexyl-2-oxo-3-pentyl-1,2-dihydro-quinolin-7-yl]-salicylidene)-(1*R*,2*R*)-1,2-Bis-(4-decyloxy-phenyl)-ethane-1,2-diamine]manganese(III))chloride (2):
Manganese(II) acetate tetrahydrate (382 mg, 1.56 mmol) was added to a suspension of salen ligand **12** (748 mg, 0.52 mmol) in a mixture of ethanol (25 mL) and chloroform (10 mL). The mixture immediately developed a brown color, darkening upon heating. It was refluxed for 1h under a stream of air, followed by addition of lithium chloride (110 mg, 2.6 mmol) and a further hour of refluxing. Upon cooling to room temperature, a dark brown precipitate formed under a light brown supernatant. Partial evaporation under reduced pressure decreased the chloroform content of the solvent mixture, leaving the supernatant almost colorless. The precipitate was collected by filtration and washed 3x with water and 2x with ether, providing, after careful drying in vacuo, 746 mg of analytically pure **2** (94% yield).

Brown solid, mp 213-214°C. Rf ($CHCl_3$ / MeOH 19:1) 0.22. $[\alpha]^{20}_D$ 2990° (c 0.157 in $CHCl_3$). IR (KBr) 2925, 2854, 1647, 1602, 1539, 1513, 1432, 1390, 1317, 1253, 1177, 818, 574 cm^{-1}. HRMS (FAB+): *m/z* calcd. for $C_{96}H_{132}MnN_4O_6$ $[M\text{-}Cl]^+$ 1491.9527; found 1491.9535. Anal. calcd. for $C_{96}H_{132}ClMnN_4O_6$: C, 75.44; H, 8.70; N, 3.67; found: C, 75.51; H, 8.78; N, 3.72.

5,15-bis[3-(2-benzyloxypyrid-4-yl)-5-decyloxyphenyl]-10,20-bis(4-decyloxy-2,6-dimethylphenyl)porphyrin (13).

3-Decyloxy-5-(2-benzyloxy-pyrid-4-yl)-benzaldehyde (3.13 g; 7.02 ml) and 5-(4-decyloxy-2,6-dimethylphenyl)dipyrromethane (2.86 g; 7.02 mmol) were added in dichloromethane (702 ml) and TFA (0.928 ml; 12.5 mmol) was added in one portion. The resulting reaction mixture was stirred at room temperature for 3h. To the brown dark solution was added DDQ (1.59 g; 7.02 mmol) in one portion, the green solution was stirred at room temperature for 1h before to be filtered on a pad of dry neutral alumina (∅=6 cm, h=10 cm) and was eluted with dichloromethane (800 ml) until the eluent was clear green. The solvent was evaporated under reduced pressure and the residue (2.903 g) was dissolved in tolune (140 ml) with an addtional amount of DDQ (1.59 g; 7.02 mmol), the purple orange solution was refluxed for 1h and after cooling to room temperature it was filtered on a pad of dry neutral alumina (∅=6 cm, h=10 cm) and was eluted with dichloromethane (750 ml) unitl the eluent was almost colorless. The solvent was evaporated under reduced pressure giving 1.388 g of purple solid (23.8%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.94 (4 H, d, J = 4.5 Hz) 8.79 (4 H, d, J = 4.5 Hz), 8.31 (2 H, d, J = 5.4 Hz), 8.14 (2 H, s), 7.91 (2 H, s), 7.63 (2 H, s), 7.57-7.48 (4 H, m) 7.44-7.29 (10 H, m), 7.08 (4 H, s), 5.48 (4 H, s), 4.35 - 4.20 (8 H, m), 2.08-1.85 (20 H, m), 1.74-1.20 (56 H, m), 1.02-0.85 (12 H, m), -2.57 (2 H, bs).^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 164.45, 158.99, 158.04, 141.14, 147.33, 143.98, 140.86, 140.79, 140.71, 137.59, 137.28, 133.62, 131.33, 130.38, 128.46, 127.98, 127.82, 125.94, 121.55, 118.55, 118.32, 115.91, 112.83, 112.66, 109.26, 68.54, 68.06, 67.80, 31.96, 31.87, 29.69-29.30 (10C), 26.28, 26.12, 22.73, 22.65, 22.05, 14.16, 14.10. IR (KBr): 2922.0, 2852.5, 1598.9, 1548.7 cm^{-1}. UV (11.55 μM, Ether): λ (nm) 418 (ε = 4000), 513 (ε = 26521.74), 546 (ε = 21565.22), 591 (ε = 20695), 648 (ε = 19391)

5,15-Bis(3-decyloxy-5-[2-oxo-pyrid-4-yl]phenyl)-10,20-bis(4-decyloxy-2,6-dimethylphenyl)-porphyrin (4):

The required amount of TFA was added to dissolve **13** (1.39 g; 0.835 mmol) then thioanisol (0.794 ml; 6.715 mmol) was added in one portion to the green mixture. The resulting mixture was stirred at room temperature for 24h. TFA was evaporated under reduced presure to give a green residue. It was dissolved in ether and triethylamine was added dropwise until the solution became purple. The solvent was removed under reduced pressure and the purple solid was triturated successively with methanol, water and methanol and dried under reduced pressure to give 1.249 g of purple solid (quantitative). Purple solid. ^{1}H NMR (3.2 mM in $CDCl_3$): δ (ppm) 8.94-8.77 (m, 4 H), 877-8.62 (m, 4 H), 8.09-7.96 (m, 2 H), 7.93-7.84 (m, 2 H), 7.60-7.49 (m, 2 H), 7.47-7.37 (m, 2 H), 7.10-6.95 (m, 2 H), 6.80-6.69 (m, 2 H), 4.33-4.12 (m, 8 H) 2.06-1.76 (m, 20 H), 1.73-1.11 (m, 56 H), 1.00-0.74 (m, 12 H), -2.80 – (-2.72) (m, 2H). ^{13}C NMR (100 MHz) δ (ppm) 165.61, 158.97, 158.03, 153.82, 144.00, 140.85, 140.76, 140.66, 136.96, 134.52, 134.34, 133.53, 125.82, 125.77, 122.01, 118.37, 118.30, 112.82, 112.45, 106,82, 68.59, 68.05, 31.94, 31.86, 29.67, 29.63, 29.59, 29.54, 29.42, 29.38, 29,29, 26.26, 26.10, 22.71, 22.64, 22.00. IR (KBr): 3313.5, 2923.9, 2850.6, 1651, 1600.8 cm^{-1}. UV: λ (nm) 417 (ε = 142184), 515 (ε = 16564), 549 (ε = 6591), 590 (ε = 5863. HRMS (FAB+): *m/z* calcd for $C_{98}H_{124}N_6O_6$ $[M]^+$ 1480.9582; found 1480.9595. Anal. calcd. for $C_{98}H_{124}N_6O_6$: C, 79.42; H, 8.43; N, 5.67; found C, 79.28; H, 8.49; 5.57.

[5,15-Bis(3-decyloxy-5-[2-oxo-pyrid-4-yl]phenyl)-10,20-bis(4-decyloxy-2,6-dimethylphenyl)-porphyrinato(2-)]zinc(II) (3):

4 (110.5 mg; 0.075 mmol) and zinc acetate dihydrate (40.9 mg; 0.186 mmol) were dissolved in chloroform/methanol (9:1; 74 ml) and it was heated under reflux for 1h. The reaction mixtiure was cooled to room temperature and was extracted several times with 10% $NaHCO_3$, dried with $MgSO_4$ and the solvent was removed under reduced pressure to give 115.91 mg of purple solid (quantitative). Purple solid. ^{1}H NMR (4.6 mM in $CDCl_3$/Pyridine-d_5; (95:5): δ (ppm) 8.94-8.77 (m, 4 H), 8.77-8.62 (m, 4 H), 8.09-7.96 (m, 2 H), 7.93-7.84 (m, 2 H), 7.60-7.49 (m, 2 H), 7.47-7.37 (m, 2 H), 7.10-6.95 (m, 2 H), 6.80-6.69 (m, 2 H), 4.33-4.12 (m, 8 H) 2.06-1.70 (m, 20 H), 1.73-1.11 (m, 56 H), 1.00-0.74 (m, 12 H). ^{13}C NMR (100MHz) 165.59, 158.56, 157.67, 154.10, 150.18, 149.51, 145.51, 140.55, 136.37, 134.55, 131.78, 130.58, 128.46,

126.10,122.08, 118.51, 117.11, 114.27, 112.54, 111.79, 106.97, 68.47, 67.98, 31.91, 31.84, 29.66, 29.62, 29.55, 29.51, 29.41, 29.36, 29.27, 28.37, 26.29, 26.08, 25.99, 22.68, 22.62, 22.08, 14.12, 14.06. IR (KBr): 3413.8, 2920.0, 2850.6, 1651, 1600.8 cm^{-1}. UV: λ (nm) 428 (ε = 134092), 560 (ε = 18336), 599 (ε = 5492). HRMS (FAB+): *m/z* calcd for $C_{98}H_{122}N_6O_6Zn$ $[M]^+$ 1542.8717; found 1542.8716. Anal. calcd. for $C_{98}H_{122}N_6O_6Zn$: C, 76.16; H, 7.96; N, 5.44; found C, 75.86; H, 8.08; N, 5.33.

Substrates 5-7:
All three cis-disubstituted olefin substrates were prepared from the corresponding phenyl ketones via their enamines, following the procedure of H. C. Brown for hydroboration-elimination of enamines.[2, 3]

1,4-Diphenyl-1-*cis*-butene (5):
Colorless liquid. Rf (Heptane / EtOAc 4:1) 0.62. ^{1}H NMR: δ (ppm) 7.35-7.19 (m, 10 H, ArH), 6.46 (d, *J* = 11.7 Hz, 1 H, PhC*H*=C), 5.72 (dt, *J* = 11.7, *J* = 7.1 Hz, 1 H, PhCH=C*H*), 2.78 (m, 2 H, PhCH_2), 2.69 (m, 2 H, PhCH_2CH_2). ^{13}C NMR: δ (ppm) 141.7, 137.5, 131.8, 129.4, 128.7, 128.5, 128.3, 128.1, 126.6, 125.9, 36.1, 30.4. IR (neat film): 2922, 2855, 1601, 1493, 1452 cm^{-1}. HRMS (FAB+): *m/z* calcd. for $C_{16}H_{16}$ $[M]^+$ 208.1252; found: 208.1251. Anal. calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74; found C, 92.13; H, 7.76.

4-(4-Phenyl-*cis*-but-3-enyl)-pyridine (6):
Colorless liquid. Rf (EtOAc) 0.35. ^{1}H NMR: δ (ppm) 8.49 (d, *J* = 6.0 Hz, 2 H, Pyr-2,6H), 7.37-7.29 (m, 2 H, ArH), 7.26-7.19 (m, 3 H, ArH), 7.11 (d, *J* = 6.0 Hz, 2 H, Pyr-3,5 H), 6.48 (d, *J* = 11.6 Hz, 1 H, PhC*H*=C), 5.65 (dt, *J* = 11.6, *J* = 7.0 Hz, 1 H, PhCH=C*H*), 2.77 (m, 2 H, PhCH_2), 2.68 (m, 2 H, PhCH_2CH_2). ^{13}C NMR: δ (ppm) 150.6, 149.6, 137.2, 130.6, 130.2, 128.6, 128.2, 126.8, 123.9, 35.3, 29.0. IR (neat film): ν 1601, 1558, 1493, 1446, 1413 cm^{-1}. HRMS (EI+): *m/z* calcd. for $C_{15}H_{15}N$ $[M]^+$ 209.1204; found 209.1208. Anal. calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69; found C, 85.92; H, 7.16; N 6.73.

4-(5-Phenyl-*cis*-pent-4-enyl)-pyridine (7):
Colorless liquid. Rf (EtOAc) 0.38. ^{1}H NMR: δ (ppm) 8.46 (d, *J* = 6.0 Hz, 2 H, pyr-2,6H), 7.35-7.21 (m, 5 H, ArH), 7.06 (d, *J* = 5.9 Hz, 2 H, pyr-3,5H), 6.48 (d, *J* = 11.6 Hz, 1 H PhC*H*=C), 5.67 (dt, *J* = 11.6, *J*=7.3 Hz, 1 H, PhCH=C*H*), 2.63 (t, *J* = 7.6 Hz, 2 H, PyrCH_2), 2.38 (dtt, *J* = 7.4, *J* = 7.3, *J* = 1.7 Hz, 2 H, CH=CHCH_2), 1.80 (tt, *J* = 7.4, *J* = 7.3 Hz, 2 H, PyrCH$_2$CH_2). ^{13}C NMR: δ (ppm) 151.1, 149.6, 131.8, 129.7, 128.7, 128.2, 126.6, 123.9, 34.6, 30.5, 27.8. IR (neat film): ν 2934, 2858, 1601, 1558, 1493, 1446, 1413 cm^{-1}. HRMS (FAB+): *m/z* calcd. for $C_{16}H_{18}N$ $[M+1]^+$ 224.1439; found 224.1431. Anal. calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27; found C, 85.88; H, 7.63; N 6.34.

4-(4-*tert*-Butylphenyl)-pyridine *N*-oxide (11):
Prepared by Suzuki coupling between 4-*tert*-butylphenylboronic acid and 4-bromopyridine, followed by MTO catalyzed N-oxidation of the coupling product with hydrogen peroxide.[4]
Off-white solid, mp 147-148°C (benzene / hexane). ^{1}H NMR: δ (ppm) 8.24 (bs, 2 H, pyr-2,6H), 7.6-7.4 (bs, 6 H, ArH, pyrH), 1.37 (s, 9 H, CH_3). ^{13}C NMR: δ (ppm) 152.7, 139.5, 138.8, 133.1, 126.3, 126.1, 123.3, 34.7, 31.2. IR (KBr): ν 1481, 1246 cm^{-1}. HRMS (FAB+): *m/z* calcd. for $C_{15}H_{18}NO$ $[M+1]^+$ 228.1383; found 228.1388. Anal. calcd. for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16; found C, 79.20; H, 7.62; N 6.19.

Typical procedure for competition reaction (Table 2):
Typically 7 reactions were run in one batch. The Mn(III)salen catalyst **2** (0.0030 mmol) was weighed into 7 2 mL glass vials. The receptor Zn(II)porphyrin **3** or any other appropriate additive* was added to each of the vials. A 2.00 mL stock solution of benzyl benzoate (internal standard (IS), 0.12 mmol), 4-(4-*tert*-butylphenyl)-pyridine *N*-oxide **11**# (0.084 mmol) and 2 substrates (0.24 mmol each) in CH_2Cl_2 was prepared. 250 μL of the stock solution were transferred to each vial followed by 350 μL of CH_2Cl_2. Homogeneous solution was obtained after ultrasonication. Into another set of vials, 12 μmol of PhIO were weighed and the reaction solutions were transferred to the PhIO containing vials.
A typical reaction mixture thus contained the following: Substrate **5** (0.030 mmol), substrate **6** (0.030 mmol), **2** (0.0030 mmol), **3** (0.0030 mmol), PhIO (0.012 mmol), *N*-oxide **11** (0.012 mmol) and benzyl benzoate (0.015 mmol), and CH_2Cl_2 (0.60 mL).

After stirring overnight at rt, each reaction mixture was evaporated under reduced pressure, suspended in 1 mL of EtOAc, then applied to a dry 1.2 g silica pad and eluted with 25 mL EtOAc. After evaporation of the

solvent under reduced pressure, the residue was dissolved in 1 mL of ether and filtered through a membrane filter to remove any residual catalyst. The ether was evaporated and the residue dissolved in $CDCl_3$ (0.80 mL) for NMR analysis. An aliquot was taken for GC analysis.

The selectivity was determined as the ratio of initial rates of formation of the two *cis*-epoxides **9** vs. as represented by the distribution of the starting materials and the products after 20% conversion of the total amount of alkenes.

The selectivity was determined as the ratio of initial rates of formation of the two *cis*-epoxides (**9** vs. **8**, **9** vs. **10** and **10** vs. **8**) (by GC), (**9** vs. **8** and **10** vs. **8**) (by NMR), and as consumption of the two alkenes **6** vs. **5**, **6** vs. **7** and **7** vs. **5**) (by ^{1}H NMR) as represented by the distribution of products and starting alkenes after 20% conversion of the total amount of alkene.

One of the reactions in any experiment was run with only **2** as catalyst, and was used as a reference. Product ratios based on the signals from *cis*-epoxide products in GC or NMR were normalized to those of the reference reaction to obtain selectivity values. This normalization cancels out any systematic error such as deviation from equal amounts of substrates in stock solution or differences in response factors in GC (*vide infra*).
All reported selectivites were based on two reaction runs and each run was analysed three times by GC and once by NMR.

*Additives and respective amounts: Zn(II)porphyrin **3** (0.0030 mmol), metal free porphyrin **4** (0.0030 mmol), Zn(II)TPP (0.0030 mmol), Pyridine *N*-oxide (0.012 mmol), 4-ethylpyridine 0.090 mmol).
#To the reaction containing pyridine *N*-oxide as additive, the stock solution was added before dissolving **11** in the stock solution.

Gas-chromatographic analysis (GC):
GC chromatography was performed on a Perkin-Elmer Autosystem XL Gas Chromatograph. Column: Varian FactorFour capillary column, VR-1 ms, 30 m*0.25 mm*0.25 μm. Detector: FID. Carrier gas: Helium. Flow gradient: 0.5 mL/min to 3 mL/min ramp 0.1. Oven program: 140 °C to 185 °C ramp 3, then to 250 °C ramp 10 °C/min, then hold 3.5 minutes. Total time: 25 minutes. The resulting chromatograms were analyzed using Perkin-Elmer Turbochrom Navigator ver. 6.1.1.0.0:K20 software. Retention times of substrates and internals standard were as follows: IS: 12.7 min, **5**: 12.5 min, **6**: 14.7 min, **7**: 16.7 min. *Cis*-epoxide products had the following retention times: **8**: 14.9 min, **9**: 16.7 min, **10**: 18.2 min. *Cis*-epoxide peaks consistently accounted for approximately 70 % of total area of all detectable product peaks. The other product peaks were too small to give consistent results in our analysis. Reactions containing Zn(II)TPP could not be analyzed by GC due to difficulties in removing the porphyrin from the sample. Competition experiments between substrates **6** and **7** could not be analyzed by GC because of overlap of epoxide **9** and substrate **7** peaks.

Quantitative NMR analysis:
^{1}H NMR spectra were recorded and evaluated on a Bruker Avance DRX500 NMR spectrometer using the XWINNMR software ver. 2.6. Resonance frequency for proton was 500.2 MHz and all experiments were performed using a 5 mm inverse broadband probe. Acquisition time used was 3 sec and the relaxation delay was set to 7 sec. 0.0030 mmol of Zn(II)TPP was added to the NMR samples before analysis to induce a small downfield shift in the chemical shift of the pyridine containing substrate, making it possible to separate and accurately integrate the otherwise overlapping signals of the two different substrates/products The following signals were used in analysis of experiments involving competition between **6** or **7** vs. **5**:

IS (benzyl benzoate) 5.39 (s).
Substrate **5** 5.72 (dt, J = 11.7, J = 7.1 Hz).
Substrate **6** 5.55 (dt, J = 11.6, J = 7.0 Hz).
Substrate **7** 5.62 (dt, J = 11.6, J = 7.3 Hz).
Product **8** 4.09 (d, J = 4.3 Hz); 3.26 (dt, J = 6.3, J = 4.3 Hz).

Product **9** 4.01 (d, J = 4.2 Hz); 3.11 (dt, J = 6.2, J = 4.4 Hz).
Product **10** 4.06 (d, J = 4.3 Hz); 3.18 (dt, J = 6.3, J = 4.4 Hz).

The IS peak integral was always calibrated to 1. Product ratios were directly measured from integrals of the proton resonances of the product peaks (*cis*-epoxide only), and also calculated from the amounts of consumed substrates.

When analyzing the competition reaction between substrates **6** vs. **7**, the proton resonances from the vinyl group of the substrates **6** and **7**, could not be separated and neither could the proton resonances of the epoxide group of the product **9** and **10**. The addition of Zn(II)TPP was of no help in this case. Instead the following proton resonances were used for the analysis of disappearance of substrates **6** vs. **7** (as compared to IS).

Substrate **6** 2.82-2.72 (m).
Substrate **7** 2.38 (dtt, J = 7.4, J = 7.3, J = 1.7 Hz).
Both substrates (overlapping peaks) 6.48 (d, J = 11.6 H); 5.74-5.58 (m) (gives the total amount of **6** and **7**)

Signals from both *trans*-epoxide and ketone (Lewis acid-catalyzed ring-opening of epoxide, identified by Long-range H-C 2D correlation experiment, showing correlation to a carbonyl carbon) products were detected in the NMR spectra but were too small to be reproducibly integrated.

Treatment of data.
We need the ratio of measured areas for product signals to represent the product ratio and, ultimately, the ratio of initial rates. But it is not entirely so, as shown in the following formula;

$$\frac{A_{an}}{A_{bn}} = \frac{x_a \cdot [P]_{an}}{x_b \cdot [P]_{bn}} = \frac{x_a \cdot k_{an} \cdot [S]_{a0}}{x_b \cdot k_{bn} \cdot [S]_{b0}}$$

where A is the integrated area of a measurement signal, x is any factor of systematic error (for example Response factor in FID detector in GC), [P] is product concentration in the sample, k is an initial rate constant, $[S]_0$ is initial substrate concentration in reaction. Subscripts a and b refer to different substrates. Subscripts n and 1 refer to reactions (1 is the reference reaction).
Normalizing the product signal ratio of a reaction n to that of a reference reaction 1 cancels out all factors, giving a number corresponding directly to the normalized product ratio and normalized ratio of initial rates:

$$\frac{\dfrac{A_{an}}{A_{bn}}}{\dfrac{A_{a1}}{A_{b1}}} = \frac{\dfrac{x_a \cdot [P]_{an}}{x_b \cdot [P]_{bn}}}{\dfrac{x_a \cdot [P]_{a1}}{x_b \cdot [P]_{b1}}} = \frac{[P]_{an} \big/ [P]_{bn}}{[P]_{a1} \big/ [P]_{b1}}$$

$$\frac{\dfrac{A_{an}}{A_{bn}}}{\dfrac{A_{a1}}{A_{b1}}} = \frac{\dfrac{x_a \cdot k_{an} \cdot [S]_{a0}}{x_b \cdot k_{bn} \cdot [S]_{b0}}}{\dfrac{x_a \cdot k_{a1} \cdot [S]_{a0}}{x_b \cdot k_{b1} \cdot [S]_{b0}}} = \frac{k_{an} \big/ k_{bn}}{k_{a1} \big/ k_{b1}}$$

Since systematic error factors are cancelled out, GC and NMR data are rendered compatible with each other and do not have to be treated separately necessarily.

In the analysis of NMR data, product ratios were obtained not only from the integrals of product signlas, but also from disappearance of substrates. Since all NMR integrals are normalized to that of the IS, we can state that:

$$\frac{[P]_{an}}{[P]_{bn}} = \frac{[S]_{a0} - [S]_{an}}{[S]_{b0} - [S]_{bn}}$$

given that the product distribution is the same for both substrates, which it indeed is. Substrate consumption was not used in the selectivity analysis from GC data due to the large uncertainty, introduced by using two measured values instead of one.

Estimation of the inherent selectivity of pure 1 and association constant for the system 2 + 3 ⇌ 1 from experimental selectivity data

In any of the reactions, the rate constant for formation of each product can be treated as a linear combination of the two rate constants corresponding to the two different catalysts present: the free Mn(III)salen **2** and the H-bonded macrocycle **1**. Thus, a formula for the observed selectivity can be derived as follows:

$$sel = \frac{k_a}{k_b} = \frac{\%\mathbf{1} \cdot k_{a1} + \%\mathbf{2} \cdot k_{a2}}{\%\mathbf{1} \cdot k_{b1} + \%\mathbf{2} \cdot k_{b2}}$$

Where k is rate constant, %**1** and %**2** are mole fractions of catalysts **1** and **2**, derived from the association constant K=[**1**]/[**2**][**3**] and total concentrations of **2** and **3** according to Equation 1 (C_2 and C_3 denote total concentration of respective compound). Subscripts *a* and *b* refer to different substrates, subscripts 1 and 2 refer to the different catalysts.

$$\%\mathbf{1} = \frac{\left(C_2K + C_3K + 1\right) - \sqrt{\left(C_2K + C_3K + 1\right)^2 - 4C_2C_3K^2}}{2C_2K} \qquad (1)$$

$$\%\mathbf{2} = 1 - \%\mathbf{1}$$

Now the observed selectivity is normalized to that of the reference reaction (see bottom of page S2), where %**1**=0 and %**2**=1:

$$norm.sel = \frac{k_a / k_b}{k_{aref} / k_{bref}} = \frac{k_a / k_b}{k_{a2} / k_{b2}} = \frac{\frac{\%\mathbf{1} \cdot k_{a1} + \%\mathbf{2} \cdot k_{a2}}{\%\mathbf{1} \cdot k_{b1} + \%\mathbf{2} \cdot k_{b2}}}{\frac{k_{a2}}{k_{b2}}} = \frac{\%\mathbf{1} \cdot k_{a1}k_{b2} + \%\mathbf{2} \cdot k_{a2}k_{b2}}{\%\mathbf{1} \cdot k_{b1}k_{a2} + \%\mathbf{2} \cdot k_{b2}k_{a2}}$$

Rearrangement gives:

$$norm.sel = \frac{\%\mathbf{1} \cdot \frac{k_{a1}/k_{b1}}{k_{a2}/k_{b2}} + \%\mathbf{2} \cdot k_{b2}/k_{b1}}{\%\mathbf{1} + \%\mathbf{2} \cdot k_{b2}/k_{b1}} = \frac{\%\mathbf{1} \cdot norm.sel(\mathbf{1}) + \%\mathbf{2} \cdot k_{b2}/k_{b1}}{\%\mathbf{1} + \%\mathbf{2} \cdot k_{b2}/k_{b1}} \qquad (2)$$

So we now have a way to estimate values for the normalized selectivity of pure **1** (*norm.sel*(**1**)), association constant *K* and the ratio of initial rates for transformation of substrate *b* by the two different catalysts (k_{b2}/k_{b1}), by non-linear curve fitting of Equation 2 (same as Equation 1 in the communication) to experimental selectivity data.

Fig. 1 shows %**1** (dotted line) as a function of total concentration of porphyrin **3** (C_3) (C_2 fixed at 0.0050 M). Three points in this graph represent actual experimental data points for substrates **6** vs. **5**: C_3 = 0, C_3 = 0.0050 M and C_3 = 0.015 M in the competitive reactions: The normalized observed selectivities of these three reactions are presented as black boxes. The calculated selectivities are shown by a solid line.

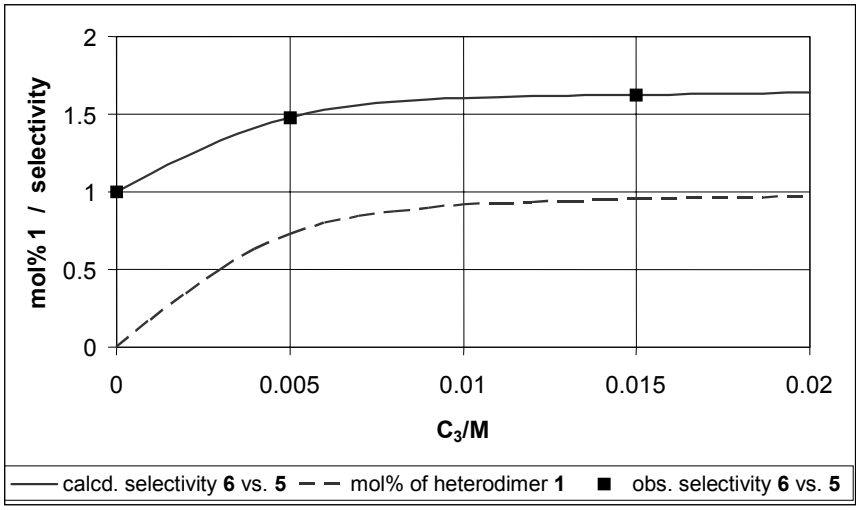

Figure 1: Competition experiment 6 vs. 5: Calculated and observed selectivities for 6 vs. 5and mol% of dimer 1, respectively, as a function of concentration of porphyrin 3 (Keeping the concentration of Mn(III)salen 2 constant at 0.005 M).

The result of the curve fitting was as follows:
$K = 2 \cdot 10^3\ M^{-1}$
norm.sel(**1**) = 1.658
$k_{b2}/k_{b1} =$ 0.9945.

The last figure suggests that epoxidation of substrate b (**5** in the experimental case) is catalyzed more or less equally fast by both catalysts. The estimated value for *K* suggests that %**1** = 0.73 (≈ 70%) at standard reaction conditions ($C_3 = C_3 = 0.0050$ M).

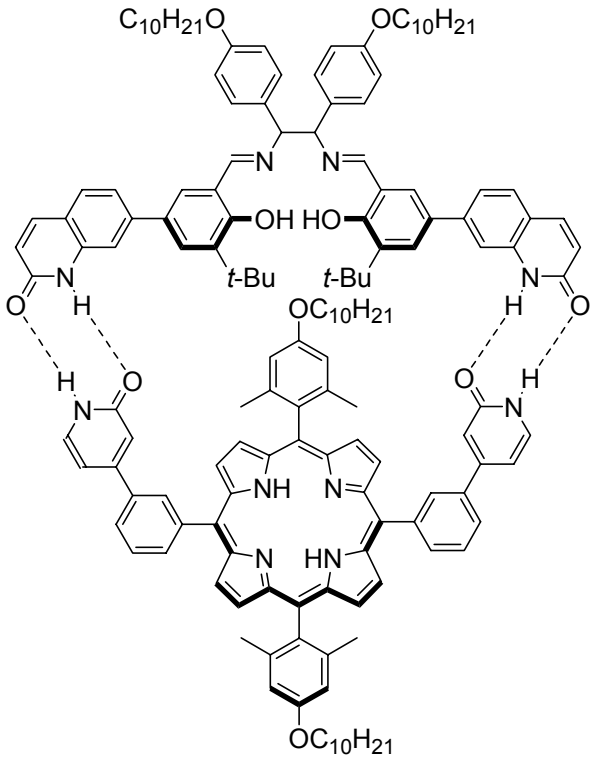

Figure 2. Salen-porphyrin dimer used in NMR dilution experiment

NMR titration of an analogous Salen-porphyrin dimer

The *K* estimated above can be compared to a *K* value estimated by NMR titration of an analogous salen-porphyrin heterodimer, used in another project (see structure in Fig. 2). The association constant for the latter dimer was estimated to $K = 3.6 \cdot 10^3$ M^{-1} in $CDCl_3$ (see below). Care must be exercised when comparing these values, because there are considerable differences between the two systems. (1) The solvent is not the same. In some cases, association constants for hydrogen bonded complexes can be as much as 2-3x higher in CH_2Cl_2 than $CHCl_3$. (2) Some of the alkyl chains in **1** are not present in Fig. 2. Particularly those on the quinolones might lead to lower *K* for **1**. (3) There are no metals present in Fig. 2. Due to solubility reasons and the paramagnetic nature of Mn(III)salens, the NMR titration was performed on metal-free ligands. This means higher degree of freedom, thus lowering of *K* for the dimer in Fig. 2. However, the structures are very similar and their association constants are expected to be in the same order of magnitude, in spite of the above differences.

In the titration, the only signal moving considerably was the pyridone/quinolone N-H proton signal. The chemical shift of this signal is a weighed average of the corresponding N-H shifts of the free salen (S), the free porphyrin (P) and of the dimer (D). Thus we decided to carry out a dilution experiment of a 1:1 mixture of S and P instead of titrating one with the other. Then [P] = [S] = [M], where M is the concentration of monomer, is true in all data points and $K = [D]/[P][S]$ becomes $K = [D]/[M]^2$. Further, $[D] = C - [M]$, where *C* = total concentration of monomer. This leads to the equation:

$$\delta_{obs} = (\delta_D - \delta_M)\left(1 + \left(1 - \frac{\sqrt{4KC+1}}{2KC}\right)\right) + \delta_M \qquad (3)$$

Equation 3 was used in non-linear curve fitting to the experimental NMR data, shown in Figure 3: observed chemical shifts as black boxes, calculated shifts as a continuous line.

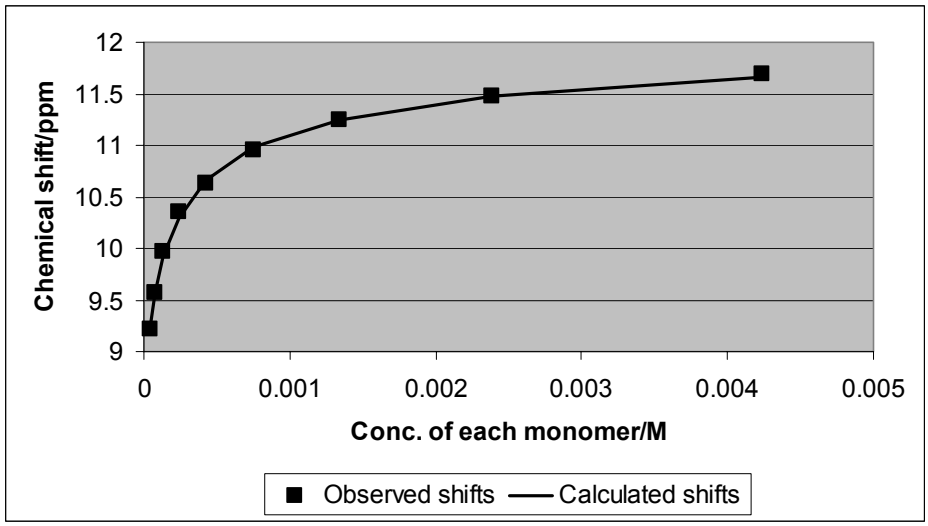

Figure 3. Observed and calculated chemical shifts in NMR dilution experiment of sytem in Fig 2 of ESI.

The values estimated by curve fitting were:
$\delta_M = 8.49$ ppm
$\delta_D = 12.28$ ppm
$K = 3.6 \cdot 10^3$ M^{-1}
In parallel, the dimerization constant of 2-quinolone was estimated to $K = 1.7 \times 10^2$ M^{-1}.[5, 6] This represents the microscopic association constant (or K_{ref})[7], describing the strength of each of many identical association events holding together a molecular aggregate. The indefinite self association constant (K_E) of a compound containing two quinolone groups represents the equilibrium constant of adding one monomer to either end of an oligomer of n monomers. K_E can never be larger than K_{ref} multiplied by a statistical factor determined by the symmetry of the monomer and oligomers (in this case, 4 for n = 1 and 2 for n > 1, n being the order of the aggregate). Indeed, the indefinite self association constant for the salen ligand S was estimated to be $K_E = 3.5 \times 10^2$ M^{-1}.[6] Self aggregation of S thus only results in indefinite linear oligomers. The K resulting from the mixture of S and P is much to high (approx 20 * K_{ref}) to be explained by statistical factors. It can only be explained by the involvement of an association stronger than that of a linear oligomer, that is, a macrocyclic heterodimer of S and P (The order of a discrete aggregate can be determined from the steepness of the titration curve, but the curves of a dimer and a linear oligomer have identical form. The titration curve for S + P could only be fitted to dimer or indefinite models, thus, a discrete aggregate in this case would have to be a dimer). Although the presence of oligomers to some degree is not excluded, the presence of a dimer is clear. The effective molarity (EM) is a useful concept in this respect. EM is a measure of the concentration at which open polymeric structures start to compete with a closed cyclic self-assembled structure.[7] For a discrete aggregate of order n, $EM = K / K_{ref}^{n}$. In the case of S and P, $EM = 3600 / 170^2 = 0.125$ M. This is more than 10 times the total concentration of the salen and porphyrin components **2** and **3** in the catalytic experiments, and thus the closed, macrocyclic heterodimer **1** should prevail under these conditions.

Discussion on kinetics.
The Mn(III)-salen catalyzed epoxidation of olefins is known to be a very fast reaction. Thus it is important to make sure that all the association equilibria involved in the catalytic system under discussion, also are very fast, and preferably faster than the reaction, so that bottlenecks are not created in the process, resulting in diminished selectivity.

Based on a rough estimate from Palucki et al,[8] epoxidation using the combination of *m*CPBA/NMO as the terminal oxidant, has a pseudo-first order rate constant of $k = 10^4$ $M^{-1}s^{-1}$ at 25°C. The rate of substrate binding should be comparable to that determined for pyridine binding to Zn(II)TPP in chlorobenzene at 25°C,[9] $k_{ass} = 10^9$ $M^{-1}s^{-1}$, $k_{diss} = 2 \cdot 10^6$ s^{-1}. Concerning the assembly kinetics of the macrocyclic cavity **1**, we

can give a lower limit of $k_{diss} \geq 10^3$ s^{-1} from the fact that NMR shows only averaged signals with no line broadening at 25°C, and an upper limit of $k_{ass} = 2 \cdot 10^9$ $M^{-1}s^{-1}$, $k_{diss} = 2 \cdot 10^7$ s^{-1}, from the kinetics of 2-pyridone self-association.[10]
So it is fair to say that the assembly processes involved in the catalytic system are not slower than the reaction being catalyzed, so a low observed selectivity should not be a result of that.

Discussion on ligand coordination to the metal centres.
In the catalytic experiments described in this commumication, there are two metal centers present, one Mn(III)salen and one Zn(II)porhyrin, and two labile potential ligands present, one pyridine containing substrate and one pyridine *N*-oxide derivative. It is assumed that the pyridine containing substrate only coordinates to the receptor Zn(II)porphyrin **3**, and the the pyridine *N*-oxide derivative, only coordinates to the Mn(III)salen **2**. This assumption is based on the following analysis:

Pyridine binds to Zn(II)TPP $2 \cdot 10^3$ times more strongly than it does to Mn(III)Cl TPP.[11] Further, pyridine has been shown to bind to Zn(II)TPP 10 times stronger than neutral oxygen ligands (tetramethylurea) do.[12] Although no association constants for pyridine *N*-oxide derivatives coordinating to either Zn or Mn complexes could be found in the literature, the harder Mn center can be expected to have a higher affinity to the harder N-oxide ligand than for the pyridine derivative.

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