Electronic Supplementary Information

All manipulations were carried out under dry, O_2-free argon on a vacuum line. The following methods were found to produce the highest yields of **2** (1:1 equivalents of reagents) and **3** (1:2 equivalents of reagents).

§ *Synthesis of* **2**; To a solution of **1** (0.177g, 0.5mmol) in toluene (20ml) was added $FeCl_2$ (0.064g, 0.5 mmol) at 25°C. The reaction mixture turned deep red and was stirred at room temperature (3h). The slightly cloudy solution was then filtered (Celite, P3) and the solvent reduced in volume under vacuum to *ca.* 10ml, whereupon precipitation of a red solid occurred. This solid was redissolved by heating and the solution stored (24h, 5°C) to give deep red crystals of **2**. Yield 0.05g (33%). Decomp. *ca.* 220°C (darkens *ca.* 86°C). IR (Nujol, NaCl), ν/cm^{-1}= *ca.* 3040(w) (aryl, C-H str.), 1577(w), 1548(w), 1091(s), 1023(s), 856(s). ^{1}H NMR (500.20MHz, 300K, d_8-toluene), δ= 8.62(br.d.), 8.51(d., J= 8.4Hz), 8.06(d., 5.5Hz), 7.70(d., 6.8Hz), 7.60(d.), 7.44(d.), 6.72-6.86 (mult.), 6.46(mult.), 6.20(mult.), 5.77(br.s.) [200K; resonances in the region δ= *ca.* 8.51-72 reduce in intensity and the resonance at δ5.77 splits into two multiplets]. UV/visible (25°C, thf, 4.1 x 10^{-5} mol dm^{-3}), ν/cm^{-1}= 19,627cm^{-1} (ε= *ca.* 26,000 mol^{-1} dm^3 cm^{-1}), 27,322 (ε= *ca.* 8,000 mol^{-1} dm^3 cm^{-1}), 23,175 (ε= *ca.* 17,100 mol^{-1} dm^3 cm^{-1}). Cyclic voltametry (CH_2Cl_2, rel. to Ag/AgCl, 0.1mol dm^{-3} ^{n}Bu$_4$NBF$_4$), –0.08V (I_{pa}/I_{pc}= 3.7; ΔE= 209μA), -1.13V (I_{pc}= -3.95μA). Elemental analysis found C 61.0, H 4.7, N 13.5; cald. for **2** C 63.2, H 4.9, N 13.8.

Synthesis of **3**; A solution of **1** (0.71g, 2.0mmol) in thf (20ml) was added dropwise to a solution of Cp_2Mn (0.185g, 1.0mmol) in thf (20ml) at –78°C. The reaction mixture was allowed to warm to room temperature and was stirred (16h) before being brought to reflux (16h). The dark brown solution was filtered (Celite, P3) to give a brown/red solution. The solvent was removed under vacuum and the solid redissolved in thf (5ml). Storage (48h, 5°C) gave colourless crystal of **3**·thf. Yield 0.15g (24%). Decomp. *ca.* 60°C (loss of thf), *ca.* 200°C decomp. to black solid. IR (Nujol, NaCl), ν/cm^{-1}= *ca.* 3060(w) (mult., C-H aryl), 1560(m), 1540(mw) ($C\overset{\cdots}{-}N$ str.). ^{1}H NMR (500.20MHz, 300K, d$_8$-toluene), δ= 8.56 (br. s., C-H aryl), 6.75 (br. s., C-H aryl), 3.59 (br. s., thf), 1.49 (br. s., thf), 1.38 (s., Me-Al); the broadness of the resonances made integration impossible. Elemental analysis found C 62.8, H 5.6, N 12.7; cald. for **3**·thf C 63.6, H 5.6, N 12.6.

¶ The catalytic reaction was carried out in a high-pressure stainless steel catalytic reactor (100 ml) lined with Poly Ether Ether Ketone (PEEK). 20 mg of **2**, stored and handled under inert conditions (nitrogen or argon), was transferred under an inert atmosphere to the catalyst delivery unit, which was subsequently sealed and introduced to the high-pressure reactor (using dry helium). The substrate (styrene) (≈ 25.0 g), and a suitable internal standard (mesitylene) were then introduced into the reactor and the reactor was sealed. The reactor and the inlet and outlet ports were purged with dry nitrogen three times prior to the introduction of dry air (oxidant). A leak test was carried out and the reactor was then pressurized to 45 bar using dry air. The reactor was then heated to the desired temperature and the contents were stirred using a mechanical stirrer at 400 rpm (Where kinetic and rate effects were studied, a mini- robot liquid sampling valve was employed to remove small aliquots of the sample without perturbing the pressure in the reactor). At the end of the reaction, the heating was turned off and the contents of the reactor were cooled (quenched). The reactor was then depressurised. A mass-balance calculation was made at this stage to check for handling and weight losses. The products were analyzed (using a suitable internal standard) by gas chromatography (GC, Varian, Model 3400 CX) employing a

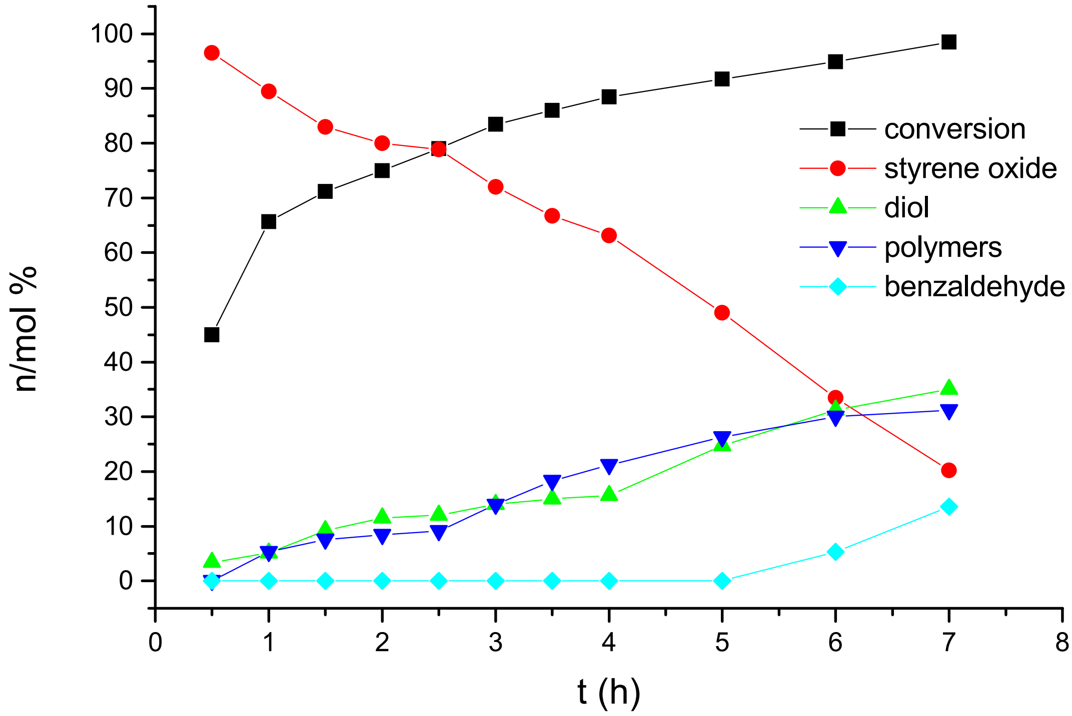
HP-1 capillary column (25 m x 0.32 mm) and flame ionisation detector using a variable ramp temperature program (from 323 K to 493 K). The identities of the products were first confirmed using authenticated standards and their individual response factors were determined using a suitable internal standard (calibration method). The conversions and selectivities were determined as defined by the following equations and the yields were normalized with respect to the response factors obtained as above:

Conv. % = [(moles of initial substrate – moles of residual substrate) / (moles of initial substrate)] x 100

Sel. % = [(moles of individual product) / (moles of total products)] x 100

The identity of the products was further confirmed using LCMS (Shimadzu LCMS-QP8000)

Kinetic plot for the epoxidation of styrene (at 80°C)


n/mol %
t (h)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
conversion
styrene oxide
diol
polymers
benzaldehyde