Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Catalytic and mechanistic studies into the epoxidation of styrenes using manganese complexes of structurally similar polyamine ligands.

Gennadiy Ilyashenko, Giorgio De Faveri, Thomas Follier, Rawan Al-Safadi, Majid Motevalli and Michael Watkinson*

The Joseph Priestley Building, School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London, E1 4NS, UK.

Email m.watkinson@qmul.ac.uk

Calibrations

The calibration procedure used allows for the simultaneous calibration of substrate and product, thus reducing error. Standard solutions of styrene (0.50 M) in MeCN, styrene oxide (0.50 M) in MeCN and anisole (0.10 M) in MeCN were prepared. Ansiole solution (500 μL) was then delivered into six volumetric flasks to which solutions of styrene and styrene oxide were added in the following ratios: 1000 μL:0 μL; 800 μL:200 μL; 600 μL:400 μL; 400 μL:600 μL; 200 μL:800 μL; 0 μL:1000 μL. The solutions were then diluted with MeCN to give an overall volume of 5.0 mL. Each solution (100 μL) was then transferred into a HPLC sample vial and diluted with THF (1.0 mL) and analysed by HPLC to obtain standard calibration plots (**Figure ES1**). **Note** that 1,2-dichlorobenzene DCB was used for the calibration of 4-nitrilestyrene. Table 1 listing HPLC conditions and retention times for each styrene substrate is given below.

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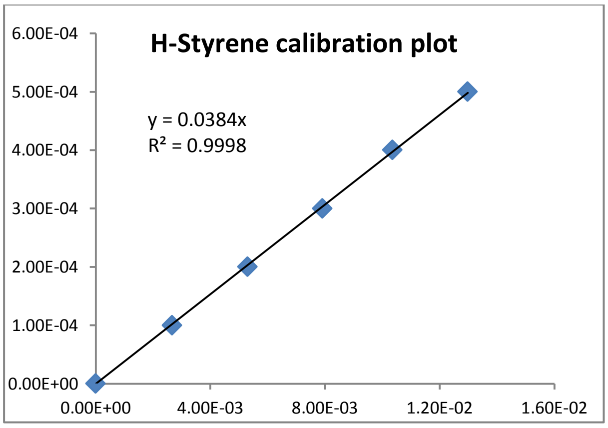

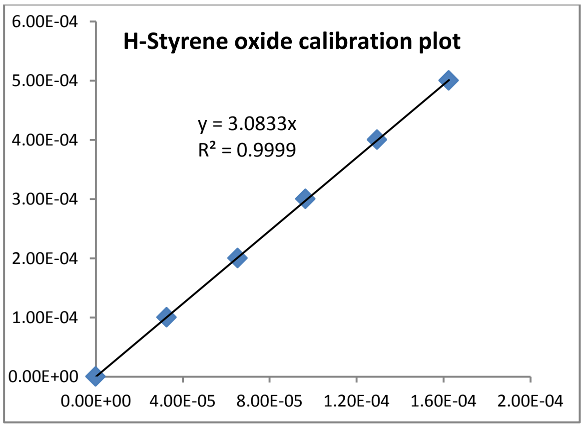

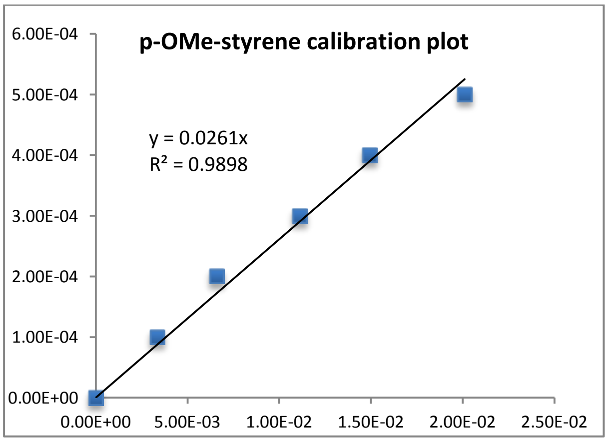

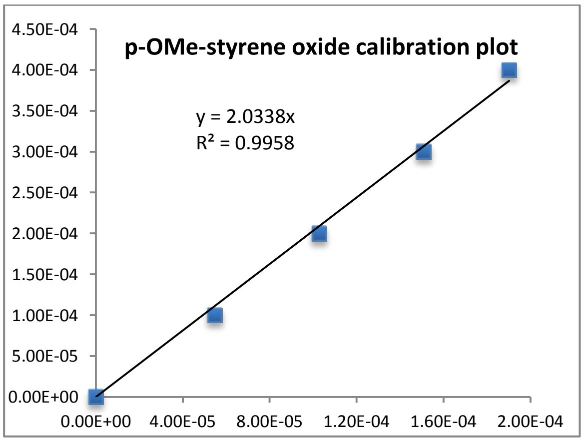

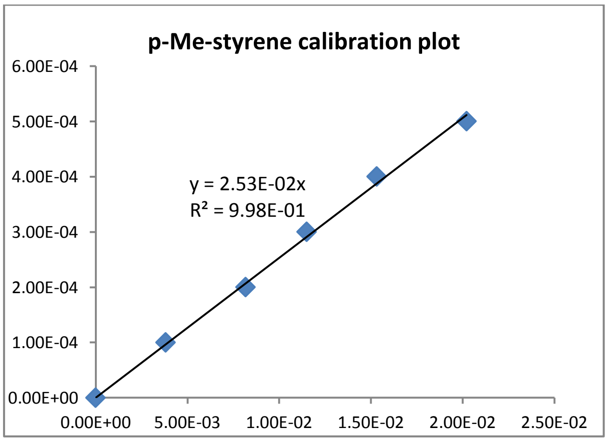

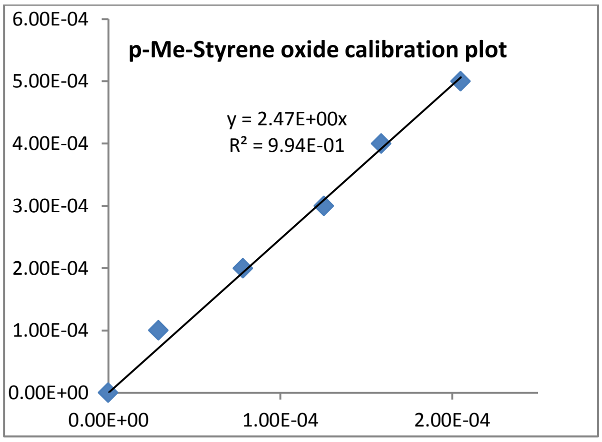

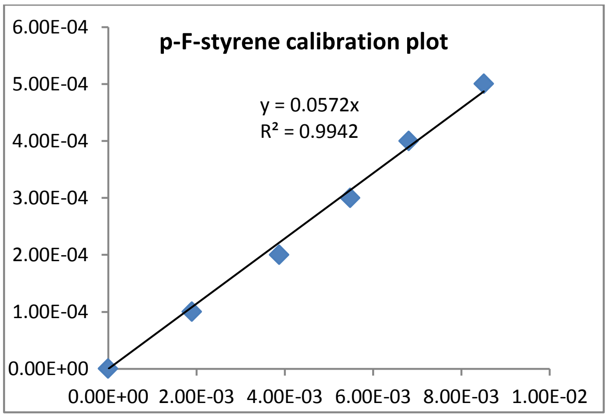

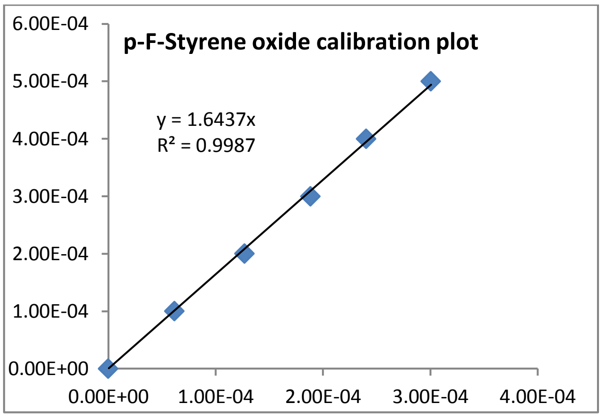

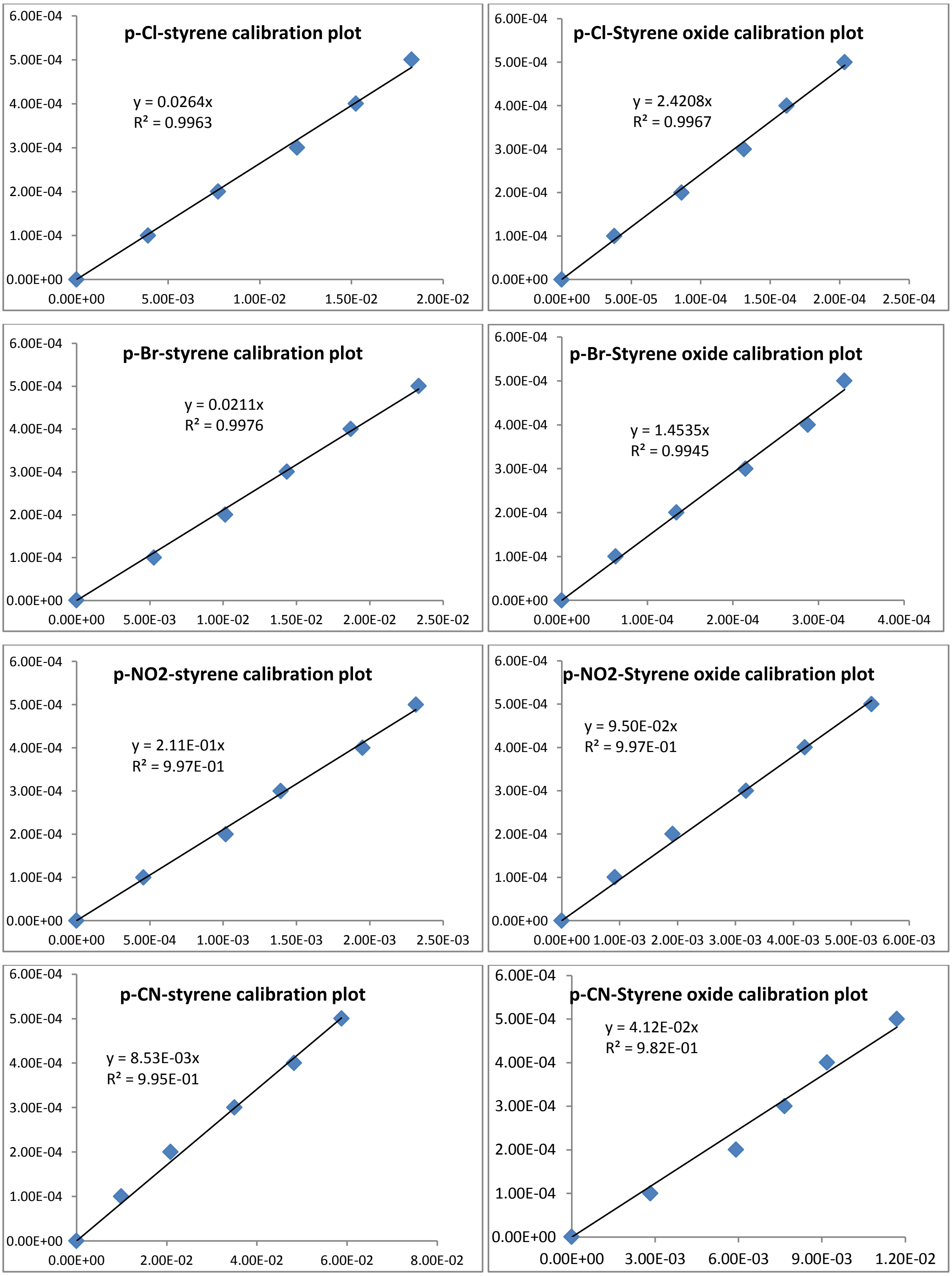

Figure ES1 Callibration graphs for all styrenes and corresponding epoxides used in this study: y axis is the number of moles of styrene/epoxide expected, x axis is the number of moles of styrene/epoxide observed. The slope is correction factor. Note that DCB was used for the *p*-CN-styrene calibration.

Entry	**Styrene**	**HPLC conditions: Reverse phase Eclipse C18**
1	H-Styrene	Flow: 1 mL min^{-1}; Solvent: H_2O (30%) MeOH (70%); λ = 252 nm; $R_{t(styrene)}$ = 5.88 min, $R_{t(anisole)}$ = 3.54 min, $R_{t(styrene\ epoxide)}$ = 2.83 min.
2	*p*-OMe-styrene	Flow: 1 mL min^{-1}; Solvent: H_2O (35%) MeOH (65%); λ = 252 nm; $R_{t(4\text{-}methoxystyrene)}$ = 9.26 min, $R_{t(anisole)}$ = 5.31 min, $R_{t(4\text{-}methoxystyrene\ epoxide)}$ = 3.28 min.
3	*p*-Me-styrene	Flow: 0.80 mL min^{-1}; Solvent: H_2O (40%) MeOH (60%) over 10 min to H_2O (30%) MeOH (70%) with curve 2, then over 3 min to H_2O (40%) MeOH (60%) with curve 2, then over 5 min to H_2O (40%) MeOH (60%); λ = 252 nm; $R_{t(4\text{-}methylstyrene)}$ = 23.42 min, $R_{t(anisole)}$ = 7.39 min, $R_{t(4\text{-}methylstyrene\ epoxide)}$ = 6.64 min.
4	*p*-F-styrene	Flow: 1 mL min^{-1}; Solvent: H_2O (30%) MeOH (70%); λ = 252 nm; $R_{t(4\text{-}fluorostyrene)}$ = 10.98 min, $R_{t(anisole)}$ = 5.27 min, $R_{t(4\text{-}fluorostyrene\ epoxide)}$ = 4.10 min.
5	*p*-Cl-styrene	Flow: 1 mL min^{-1}; Solvent: H_2O (40%) MeOH (60%) over 20 min to H_2O (10%) MeOH (90%) with curve 2, then over 5 min to H_2O (40%) MeOH (60%) with curve 1, then over 5 min to H_2O (40%) MeOH (60%); λ = 252 nm; $R_{t(4\text{-}chlorostyrene)}$ = 15.44 min, $R_{t(anisole)}$ = 6.54 min, $R_{t(4\text{-}chlorostyrene\ epoxide)}$ = 5.28 min.
6	*p*-Br-styrene	Flow: 1 mL min^{-1}; Solvent: H_2O (40%) MeOH (60%) over 20 min to H_2O (10%) MeOH (90%) with curve 2, then over 5 min to H_2O (40%) MeOH (60%) with curve 1, then over 5 min to H_2O (40%) MeOH (60%); λ = 252 nm; $R_{t(4\text{-}bromostyrene)}$ = 16.78 min, $R_{t(anisole)}$ = 7.55 min, $R_{t(4\text{-}bromostyrene\ epoxide)}$ = 5.31 min.

7	*p*-NO_2-styrene	Flow: 0.80 mL min^{-1}; Solvent: H_2O (40%) MeOH (60%); λ = 252 nm; $R_{t(4\text{-nitrostyrene})}$ = 8.99 min, $R_{t(\text{anisole})}$ = 6.68 min, $R_{t(4\text{-nitrostyrene epoxide})}$ = 4.43 min.
8	*p*-CN-styrene	Flow: 0.70 mL min^{-1}; Solvent: H_2O (65%) MeOH (35%) over 5 min with curve 1, then over 15 min to H_2O (25%) MeOH (75%) with curve 2, then over 5 min to H_2O (50%) MeOH (50%) with curve 1; λ = 252 nm; $R_{t(4\text{-nitrilestyrene})}$ = 20.12 min, $R_{t(\text{DCB})}$ = 25.06 min, $R_{t(4\text{-nitrilestyrene epoxide})}$ = 4.87 min.

Table ES1. HPLC conditions used for monitoring progress of the epoxidation reactions.