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

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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. Anisole 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.
H-Styrene calibration plot
\[ y = 0.0384x \]
\[ R^2 = 0.9998 \]

H-Styrene oxide calibration plot
\[ y = 3.0833x \]
\[ R^2 = 0.9999 \]

p-OMe-styrene calibration plot
\[ y = 0.0261x \]
\[ R^2 = 0.9898 \]

p-OMe-styrene oxide calibration plot
\[ y = 2.0338x \]
\[ R^2 = 0.9958 \]

p-Me-styrene calibration plot
\[ y = 2.53E+02x \]
\[ R^2 = 9.94E+01 \]

p-Me-Styrene oxide calibration plot
\[ y = 2.47E+00x \]
\[ R^2 = 9.94E+01 \]

p-F-styrene calibration plot
\[ y = 0.0572x \]
\[ R^2 = 0.9942 \]

p-F-Styrene oxide calibration plot
\[ y = 1.6437x \]
\[ R^2 = 0.9987 \]
Figure ES1 Calibration 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.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Styrene</th>
<th>HPLC conditions: Reverse phase Eclipse C18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H-Styrene</td>
<td>Flow: 1 mL min(^{-1}); Solvent: H(_2)O (30%) MeOH (70%); (\lambda = 252) nm; (R_t(\text{styrene}) = 5.88) min, (R_t(\text{anisole}) = 3.54) min, (R_t(\text{styrene epoxide}) = 2.83) min.</td>
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<tr>
<td>2</td>
<td>(p)-OMe-styrene</td>
<td>Flow: 1 mL min(^{-1}); Solvent: H(_2)O (35%) MeOH (65%); (\lambda = 252) nm; (R_t(4\text{-methoxystyrene}) = 9.26) min, (R_t(\text{anisole}) = 5.31) min, (R_t(4\text{-methoxystyrene epoxide}) = 3.28) min.</td>
</tr>
<tr>
<td>3</td>
<td>(p)-Me-styrene</td>
<td>Flow: 0.80 mL min(^{-1}); Solvent: H(_2)O (40%) MeOH (60%) over 10 min to H(_2)O (30%) MeOH (70%) with curve 2, then over 3 min to H(_2)O (40%) MeOH (60%) with curve 2, then over 5 min to H(_2)O (40%) MeOH (60%); (\lambda = 252) nm; (R_t(4\text{-methylstyrene}) = 23.42) min, (R_t(\text{anisole}) = 7.39) min, (R_t(4\text{-methylstyrene epoxide}) = 6.64) min.</td>
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<tr>
<td>4</td>
<td>(p)-F-styrene</td>
<td>Flow: 1 mL min(^{-1}); Solvent: H(_2)O (30%) MeOH (70%); (\lambda = 252) nm; (R_t(4\text{-fluorostyrene}) = 10.98) min, (R_t(\text{anisole}) = 5.27) min, (R_t(4\text{-fluorostyrene epoxide}) = 4.10) min.</td>
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<tr>
<td>5</td>
<td>(p)-Cl-styrene</td>
<td>Flow: 1 mL min(^{-1}); Solvent: H(_2)O (40%) MeOH (60%) over 20 min to H(_2)O (10%) MeOH (90%) with curve 2, then over 5 min to H(_2)O (40%) MeOH (60%) with curve 1, then over 5 min to H(_2)O (40%) MeOH (60%); (\lambda = 252) nm; (R_t(4\text{-chlorostyrene}) = 15.44) min, (R_t(\text{anisole}) = 6.54) min, (R_t(4\text{-chlorostyrene epoxide}) = 5.28) min.</td>
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<tr>
<td>6</td>
<td>(p)-Br-styrene</td>
<td>Flow: 1 mL min(^{-1}); Solvent: H(_2)O (40%) MeOH (60%) over 20 min to H(_2)O (10%) MeOH (90%) with curve 2, then over 5 min to H(_2)O (40%) MeOH (60%) with curve 1, then over 5 min to H(_2)O (40%) MeOH (60%); (\lambda = 252) nm; (R_t(4\text{-bromostyrene}) = 16.78) min, (R_t(\text{anisole}) = 7.55) min, (R_t(4\text{-bromostyrene epoxide}) = 5.31) min.</td>
</tr>
<tr>
<td></td>
<td>Epoxide</td>
<td>Flow:</td>
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</tr>
<tr>
<td>7</td>
<td>p-NO₂-styrene</td>
<td>0.80 mL min⁻¹</td>
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<tr>
<td>8</td>
<td>p-CN-styrene</td>
<td>0.70 mL min⁻¹</td>
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</table>

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