Electronic Supplementary Material (ESI) for ChemComm.

Remarkable increase in the rate of the catalytic epoxidation of electron deficient styrenes through the addition of Sc(OTf)3 to the MnTMTACN catalyst

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Electronic Supporting Information

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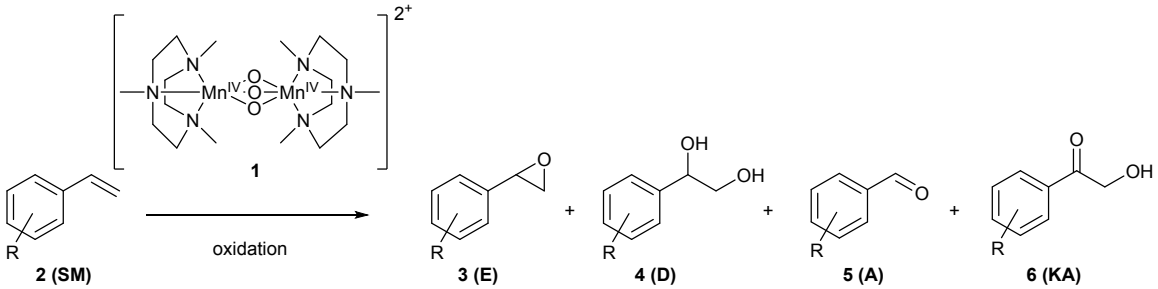
The ^{1}H NMR spectra of the oxidation of 4-fluorostyrene under identical conditions used to optimise reaction conditions for styrene epoxidation are presented. This is because over-oxidation products were not separable by HPLC for the styrene oxidation and consequently could not be identified satisfactorily; in the case of 4-fluorostyrene clear separation occurred. As can clearly be seen in the presence of 0.5 mol% co-catalyst the reaction conversion and styrene selectivity was very high. In comparison, when 10 mol% $Sc(OTf)_3$ was employed, significant amounts of starting material (SM) remain as well as products resulting from over-oxidation, keto alcohol (KA) and epoxide ring-opening (D) and the reaction was also significantly slower. Moreover, the pure epoxide is not completely stable under these conditions, and a stability test of pure 4-fluorostyrene oxide showed that after 3 minutes 87% of the epoxide remained unreacted. The ^{1}H NMR spectrum of the styrene reaction was similarly complex for 10 mol% of the Lewis acid additive and essentially a single epoxide product when 0.5 mol% was employed.



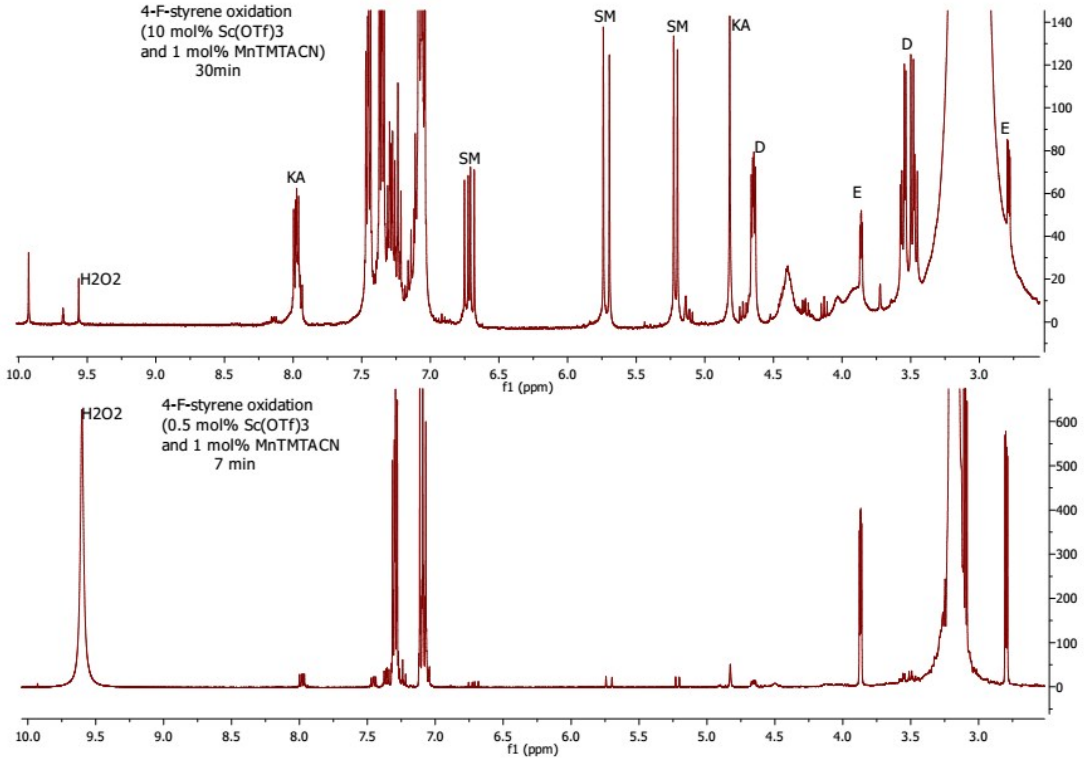


Figure ES1. The ^{1}H NMR spectra of the catalytic oxidation of 4-fluorostyrene performed in MeCN-d_3.

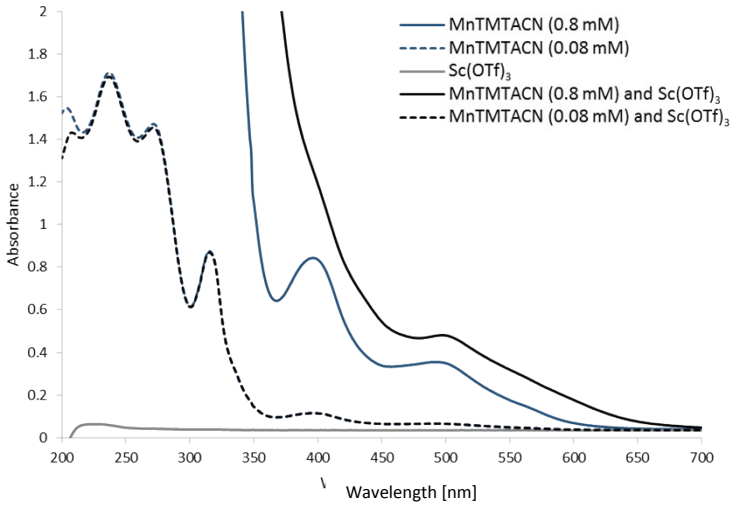


Figure ES2. The UV-VIS spectra of **1** and the mixtures with $Sc(OTf)_3$ in MeCN at different concentrations.

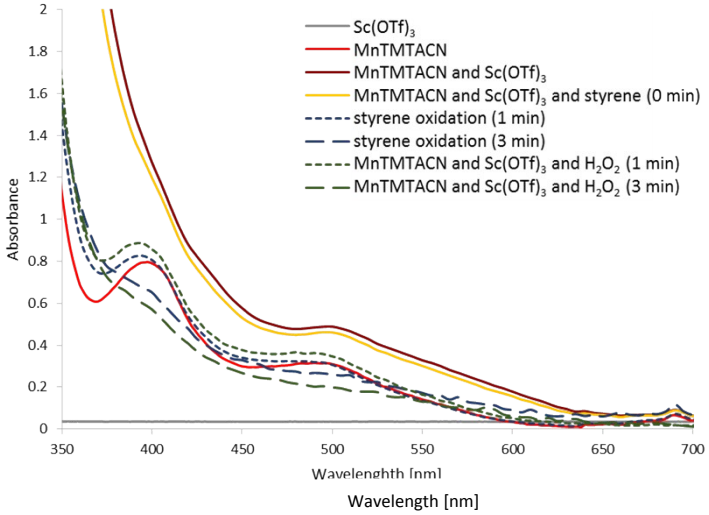


Figure ES3. UV-VIS spectra of a range of reactant mixtures

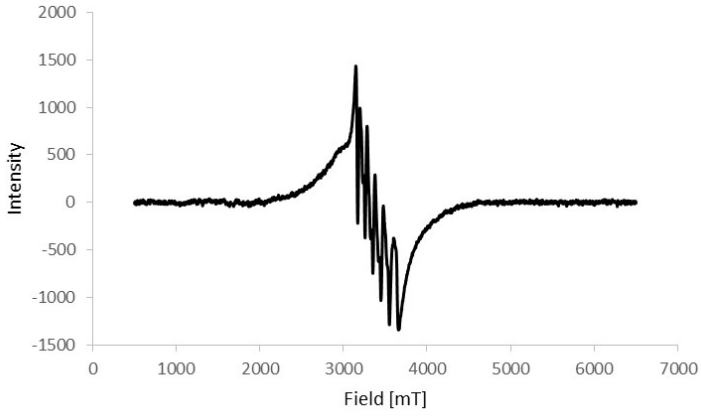


Figure ES4. EPR spectrum of **1** (1 mol%) and $Sc(OTf)_3$ (0.5 mol%) with styrene and hydrogen peroxide in acetonitrile solution after 3 minutes measured at 100 K

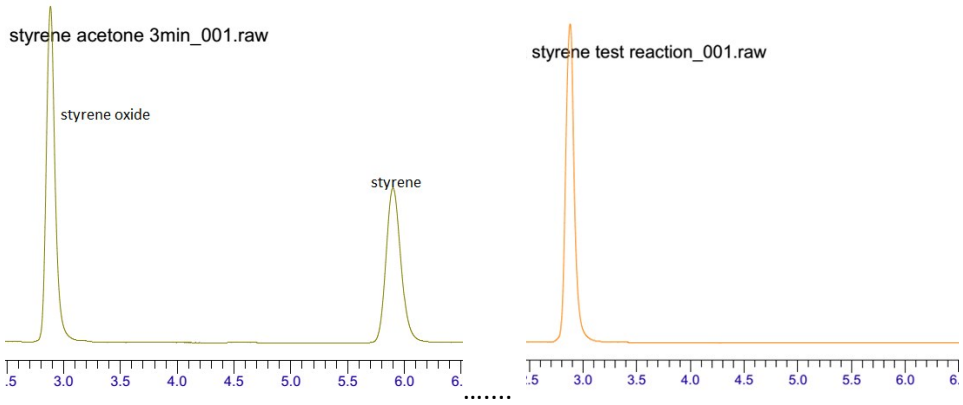


Figure ES5. Chromatograms of styrene oxidation in acetone (left) and in MeCN (right) after 3 minutes without work-up.

General experimental details

All reagents were purchased from Sigma-Aldrich, Acros Organics, or Alfa Aesar and were used without further purification unless otherwise stated. The hydrogen peroxide used in the epoxidation procedures was bought from Sigma Aldrich as a 30% (w/w) solution in water with stabilizer. Acetonitrile was refluxed over CaH_2 and freshly distilled under a nitrogen atmosphere prior to use.‡ ^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AV400 or a Bruker AMX400 at 400 MHz and at 100.2 MHz respectively and referenced to the signal of tetramethylsilane (TMS) or residual protonated solvent. UV-Vis spectra were obtained on an HP 8453 spectrophotometer, absorption maxima (λ_{max}) are expressed in nm, the molar extinction coefficients (ε) are expressed in L $mol^{-1}cm^{-1}$. EPR experiments were carried out using an X-band Bruker Elexsys E500 Spectrometer (Bruker BioSpin GmbH, Germany) equipped with a closed-cycle cryostat (Cryogenic Ltd, UK). The magnetic field was calibrated at room temperature with a Bruker strong pitch sample (g = 2.0028). Measurements were carried out in an X-band split-ring resonator module with 2 mm sample access (ER 4118X-MS2). All measurements were recorded at 100 K with a 7 G modulation amplitude and 2 mW microwave power. The reaction solution was flash-frozen in liquid nitrogen prior to use. Electrospray ionisation mass spectrometry was obtained from the EPSRC National Mass Spectrometry Service, University of Wales, Swansea on a Thermofisher LTQ Orbitrap XL. High Performance Liquid Chromatography was performed on a Perkin Elmer Series 200 instrument equipped with UV-Vis detector using an reverse phase ZORBAX Eclipse Plus C18 (4.6×150 mm, 5 µm) column.

General epoxidation procedure

A solution containing scandium(III) triflate (0.005 M, 500 µL) in dry MeCN‡ was delivered to a capped microwave reaction vial with closed-top seal and silicone septum followed by a solution of catalyst **1** (0.01 M, 500 µL) in dry MeCN and the mixture was stirred for 5 min. Then a solution of the styrene (0.50 M, 1000 µL, 1.0 equiv.) in dry MeCN were added to the reaction vial and the mixture allowed to equilibrate for 10 min at room temperature. In the meantime, a solution of H_2O_2 (30% aq. w/w 855 µL, 10 equiv.) in MeCN (3000 µL) was prepared and after 5 min it was added to the reaction mixture in one portion. After 3 min the addition of the hydrogen peroxide a small amount of silver powder was added to an aliquot and after approximately 2 minutes biphenyl (internal standard, 0.10 M, 500 µL) in dry MeCN was added and a sample (200 µL) was taken and filtered through a short pad of silica and $MgSO_4$ using MeCN (3 mL) as eluent. The aliquot was then analysed by HPLC.

‡It is essential to use freshly distilled dry acetonitrile; HPLC grade acetonitrile should not be used.

Table ES1. ^{1}H NMR data for epoxides prepared in this study

Substituted styrene oxide, R =	Ref	Retention time [min][a]	^{1}H NMR (400 MHz, $CDCl_3$)
H	[1]	2.84	δ 7.29 – 7.11 (m, 5H), 3.74 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.02 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.68 (dd, *J* = 5.5, 2.6 Hz, 1H).
α-Me	[1]	3.39	δ 7.34 – 7.12 (m, 5H), 2.91 (d, *J* = 5.4 Hz, 1H), 2.73 (d, *J* = 5.4 Hz, 1H), 1.65 (s, 3H).
β-*trans*-Me	[1]	3.41	δ 7.43 – 7.24 (m, 5H), 3.60 (d, *J* = 2.0 Hz, 1H), 3.07 (qd, *J* = 5.1, 2.1 Hz, 1H), 1.48 (d, *J* = 5.2 Hz, 3H).
β-*cis*-Me	[2]	5.81[b]	δ 7.34 – 7.08 (m, 5H), 3.99 (d, *J* = 4.2 Hz, 1H), 3.36 – 3.12 (m, 1H), 1.01 (d, *J* = 5.4 Hz, 3H).
cis-stilbene (β-*cis*-Ph)	*cis*[3] *trans*[1]	*cis*: 6.36, *trans*:9.76	*cis*-stilbene oxide δ 7.24 – 7.11 (m, 10H), 4.37 (s, 2H); *trans*-stilbene oxide δ 7.44 – 7.30 (m, 10H), 3.88 (s, 2H).
4-F	[1]	2.89	δ 7.32 – 7.22 (m, 2H), 7.10 – 6.97 (m, 2H), 3.85 (dd, *J* = 3.9, 2.7 Hz, 1H), 3.14 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.77 (dd, *J* = 5.4, 2.6 Hz, 1H).
4-Cl	[1]	3.93	δ 7.25 – 7.14 (m, 2H), 7.14 – 7.04 (m, 2H), 3.72 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.03 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.64 (dd, *J* = 5.5, 2.5 Hz, 1H).
4-Br	[1]	4.35	δ 7.48 – 7.44 (m, 2H), 7.17 – 7.12 (m, 2H), 3.82 (dd, *J* = 3.9, 2.6 Hz, 1H), 3.14 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.75 (dd, *J* = 5.5, 2.5 Hz, 1H).
4-NO_2	[4]	2.61	δ 8.29 – 8.19 (m, 2H), 7.50 – 7.40 (m, 2H), 3.99 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.25 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.80 (dd, *J* = 5.5, 2.5 Hz, 1H)
4-AcO	[5]	2.26	δ 7.31 – 7.26 (m, 2H), 7.10 – 7.04 (m, 2H), 3.86 (dd, *J* = 3.9, 2.7 Hz, 1H), 3.13 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.77 (dd, *J* = 5.5, 2.6 Hz, 1H), 2.29 (s, 3H).
4-CN	[5]	2.16	δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 3.90 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.20 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.75 (dd, *J* = 5.5, 2.5 Hz, 1H).
3-NO_2	[4]	2.60	δ 8.18 – 8.09 (m, 2H), 7.66 – 7.46 (m, 2H), 3.97 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.22 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.81 (dd, *J* = 5.4, 2.5 Hz, 1H).
4-Me	[1]	3.72	δ 7.21 – 7.09 (m, 4H), 3.88 – 3.77 (m, 1H), 3.13 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.35 (s, 3H).
2,4,6-triMe	[6]	7.39	δ 6.83 (s, 2H), 3.91 (t, *J* = 3.3 Hz, 1H), 3.17 (ddd, *J* = 5.5, 4.1, 0.5 Hz, 1H), 2.75 (ddd, *J* = 5.6, 2.9, 0.5 Hz, 1H), 2.38 (s, 6H), 2.28 (s, 3H).

[a] analysis condition: ZORBAX Eclipse Plus C18 (4.6 × 150 mm, 5 µm) column, eluent program: 30% H_2O/70% MeOH eluent; flow 1mL/min, λ=212 nm; [b] eluent program: 7 min - 40% H_2O/60% MeOH, then 30% H_2O/70% MeOH

NMR data for [1-(2-phenylcyclopropyl)ethenyl]benzene[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.27 – 7.05 (m, 8H), 5.29 (s, 1H), 4.97 (s, 1H), 1.97 – 1.85 (m, 2H), 1.33 (ddd, *J* = 8.6, 6.1, 5.1 Hz, 1H), 1.20 (dt, *J* = 8.5, 5.4 Hz, 1H); ^{13}C NMR (100.2 MHz, $CDCl_3$) δ 148.5, 142.7, 141.2, 128.6, 128.4, 127.7, 126.3, 125.9, 109.5, 28.0, 26.6, 16.0.

NMR data for 2-phenyl-2-(2-phenylcyclopropyl)oxirane (2 diastereomers)[8]

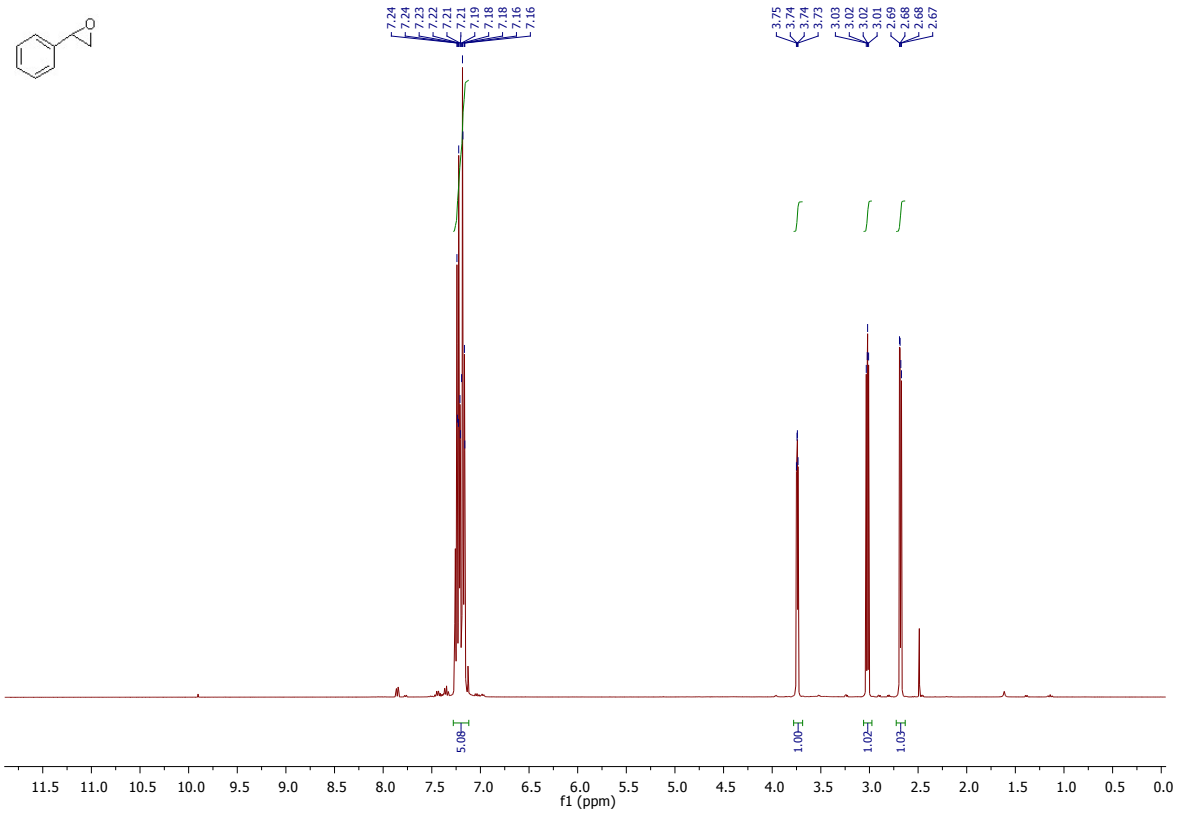
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.04 (m, 10H), 3.01 (d, *J* = 5.5 Hz, 1H), 2.90 (d, *J* = 5.5 Hz, 0.6H *diastereomer 1*), 2.84 (d, *J* = 5.3 Hz, 0.4H *diastereomer 2*), 2.08 – 1.96 (m, 1H), 1.90 (s, 1H), 1.11 (s, 1.4H *diastereomer 2*), 1.00 – 0.92 (m, 0.6H *diastereomer 1*); ^{13}C NMR (100.2 MHz, $CDCl_3$, 2 disastereomers) δ 142.3, 142.1, 140.4, 140.2, 128.6, 128.5, 128.4, 127.8, 126.2, 126.1, 126.1, 126.0, 125.8, 59.1, 58.5, 55.1, 54.8, 25.9, 25.7, 21.0, 20.3, 12.9, 11.4; GC-MS (EI) *m/z* 236 (M^+), 129 (100%), 115, 91, 71, 44, 128, 207.

NMR data for 2,5-diphenyl-3,6-dihydro-2H-pyran

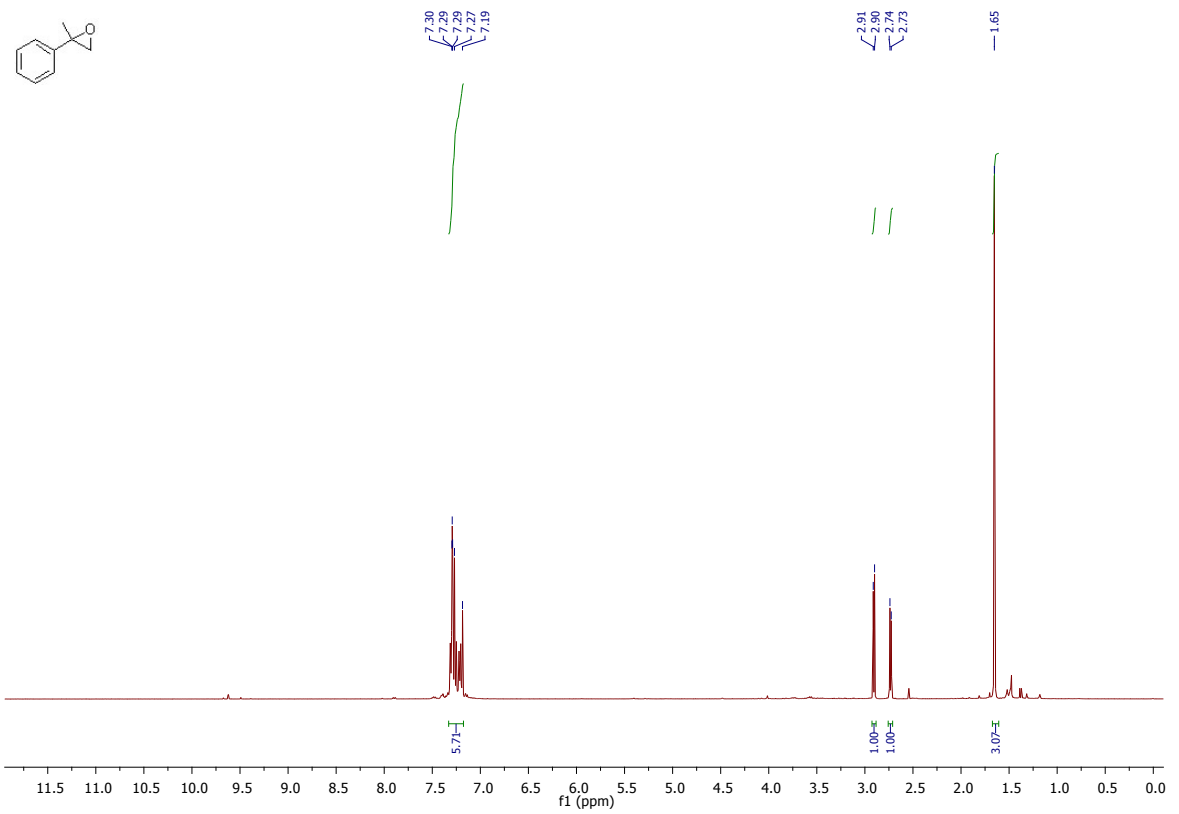
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.43 – 7.26 (m, 8H), 5.94 (t, *J* = 8.6 Hz, 1H), 4.82 (dt, *J* = 9.2, 4.6 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 11.9 Hz, 1H), 2.78 (dt, *J* = 14.2, 8.5 Hz, 1H), 2.72 – 2.62 (m, 1H), ^{13}C NMR (100.2 MHz, $CDCl_3$) δ 144.2, 142.8, 141.7, 128.6, 128.5, 127.82, 127.80, 127.3, 126.2, 125.8, 73.0, 59.8, 38.6.

Spectra of epoxides

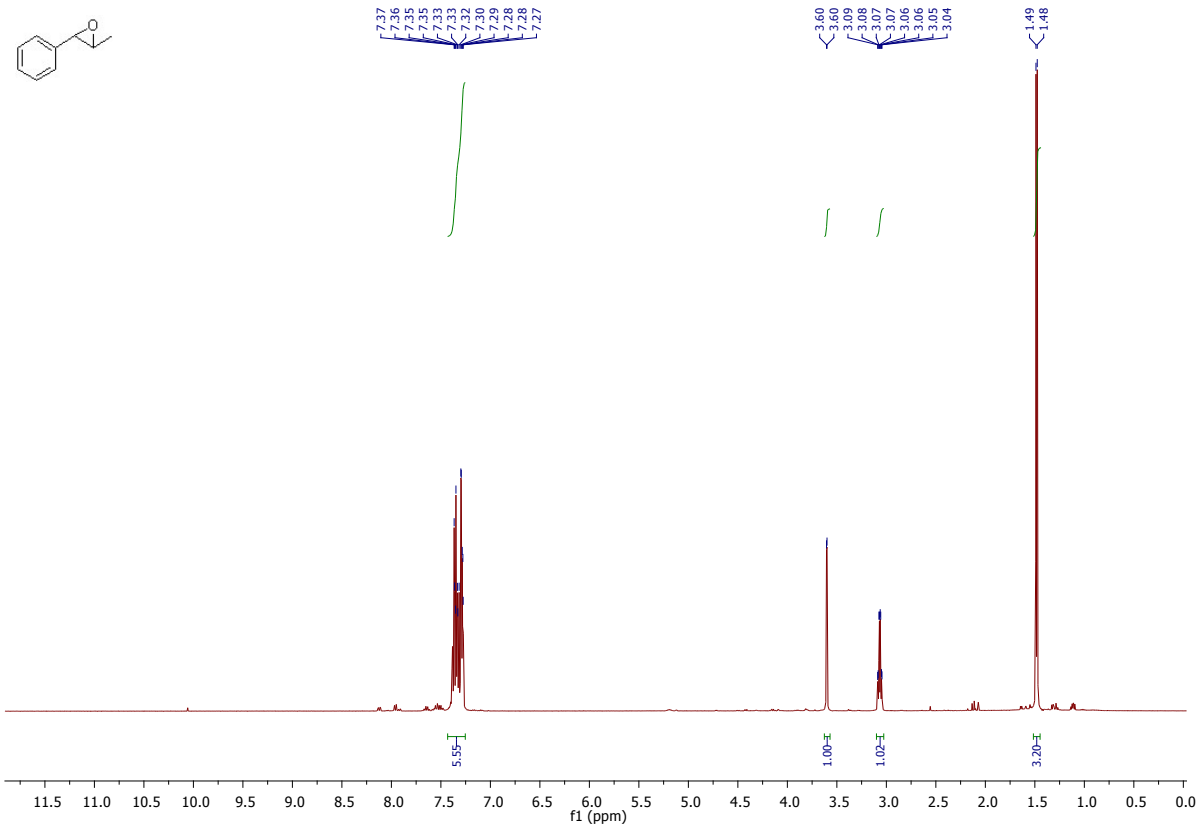
Styrene oxide[1]



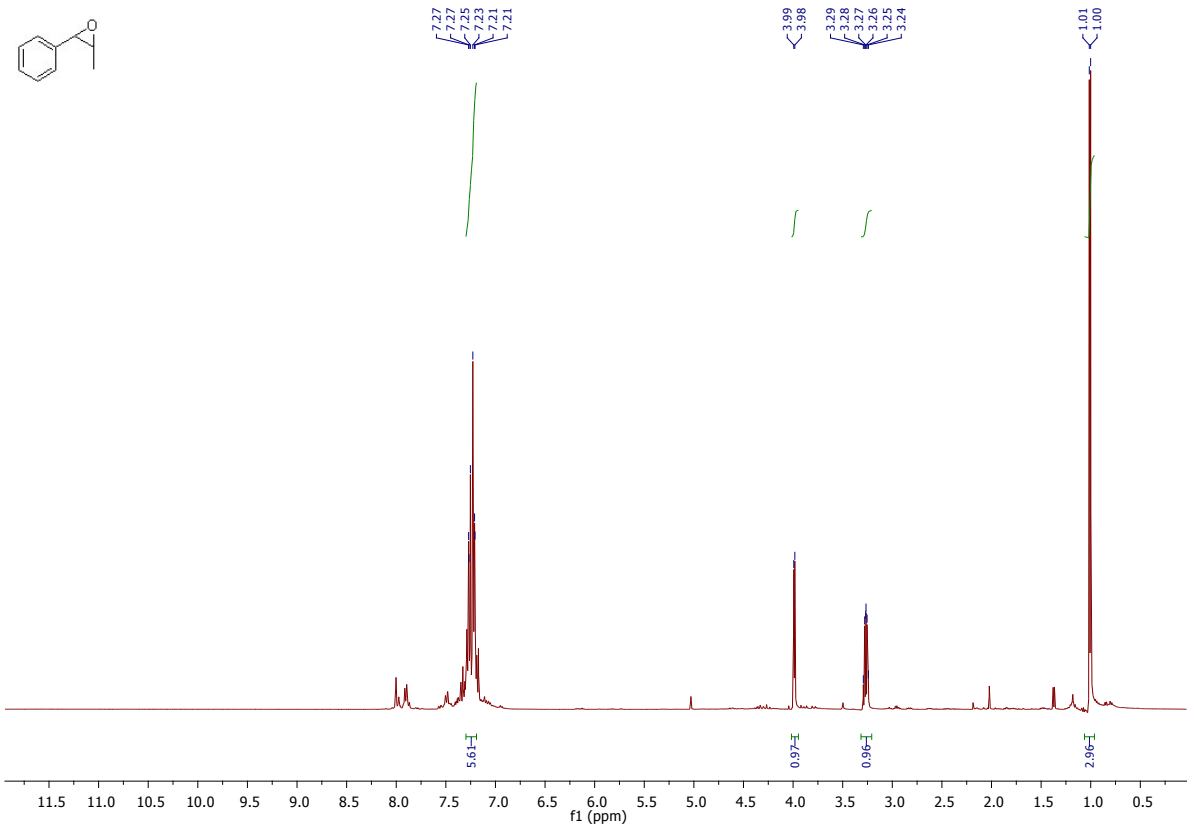
α-Methylstyrene oxide[1]



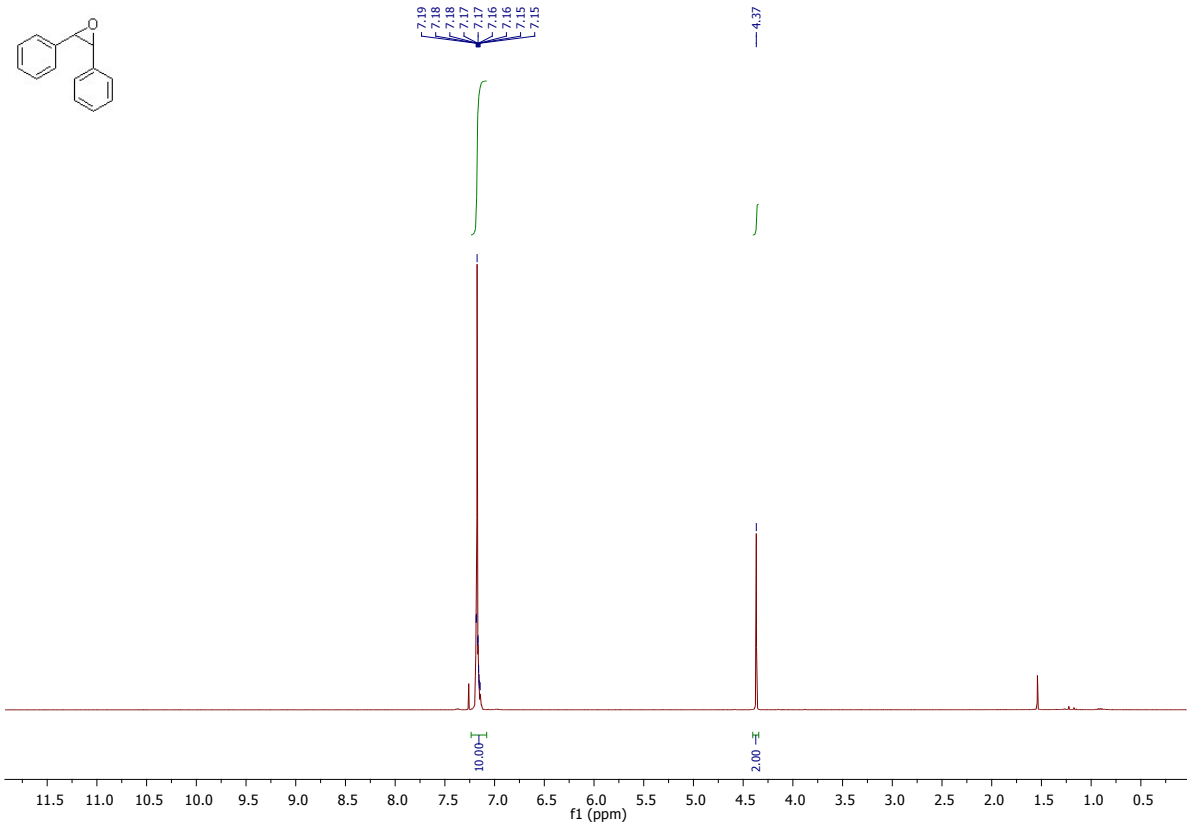
β-*trans*-Methylstyrene oxide[1]



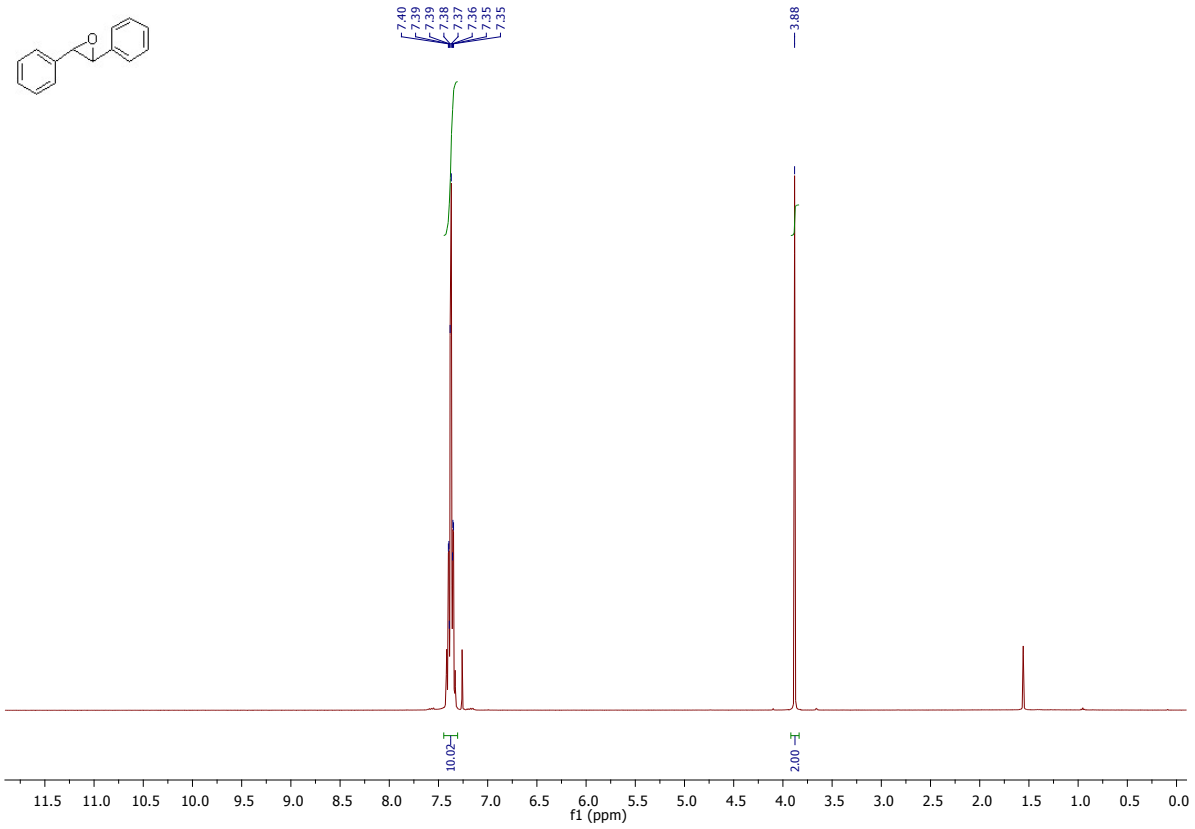
β-*cis*-Methylstyrene oxide[2]



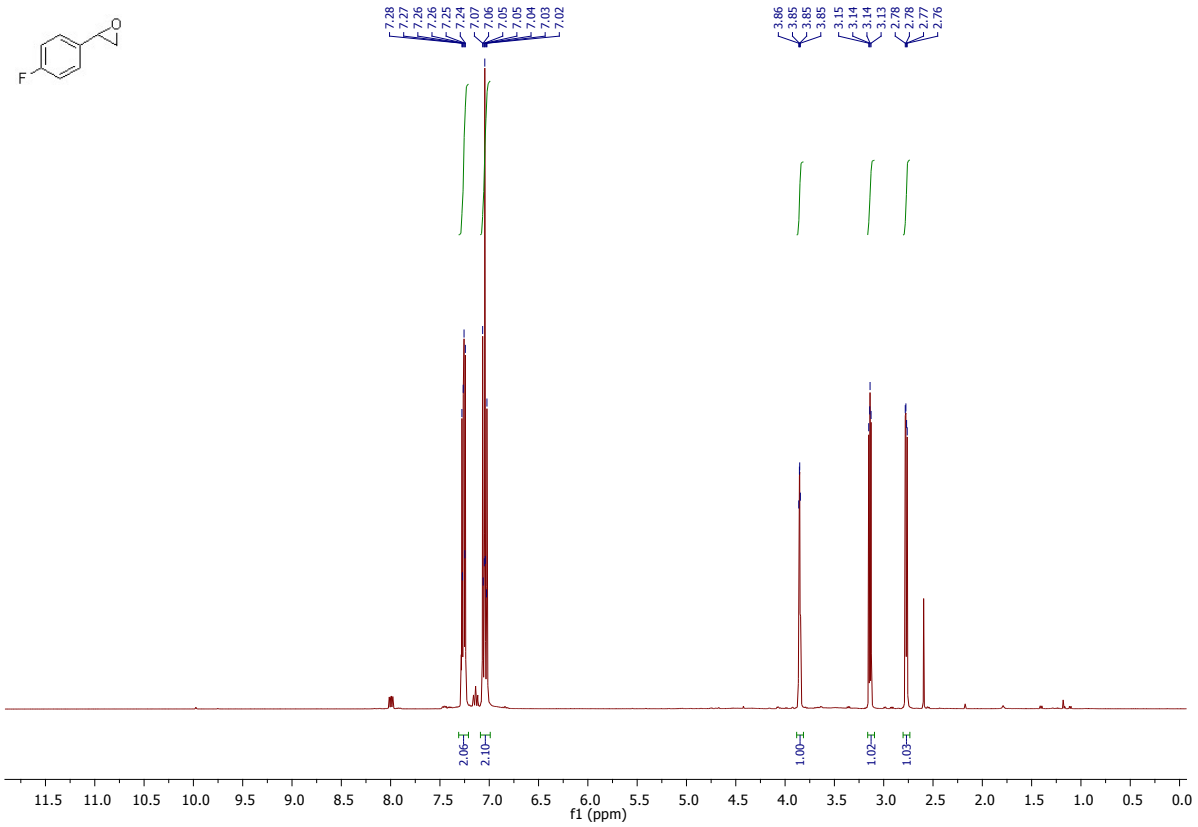
cis-Stilbene oxide[3]



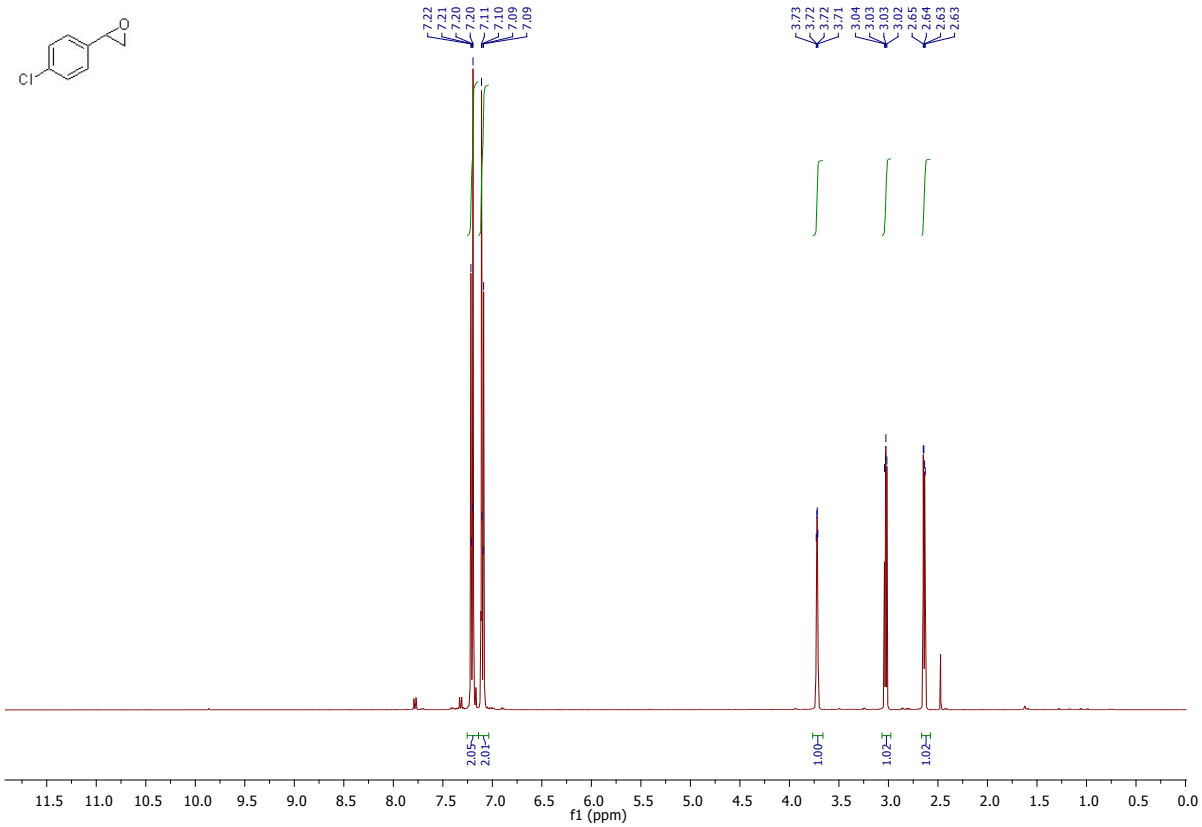
trans-Stilbene oxide[1]



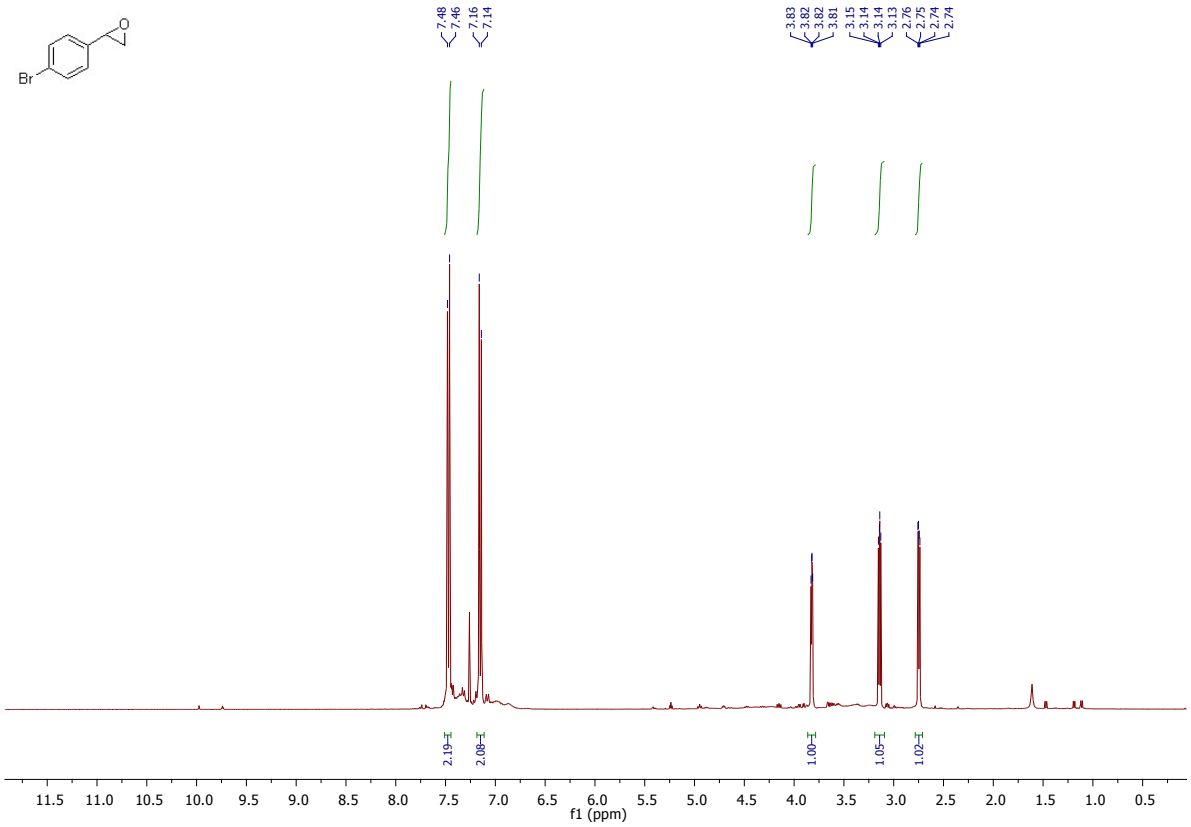
4-Fluorostyrene oxide[1]



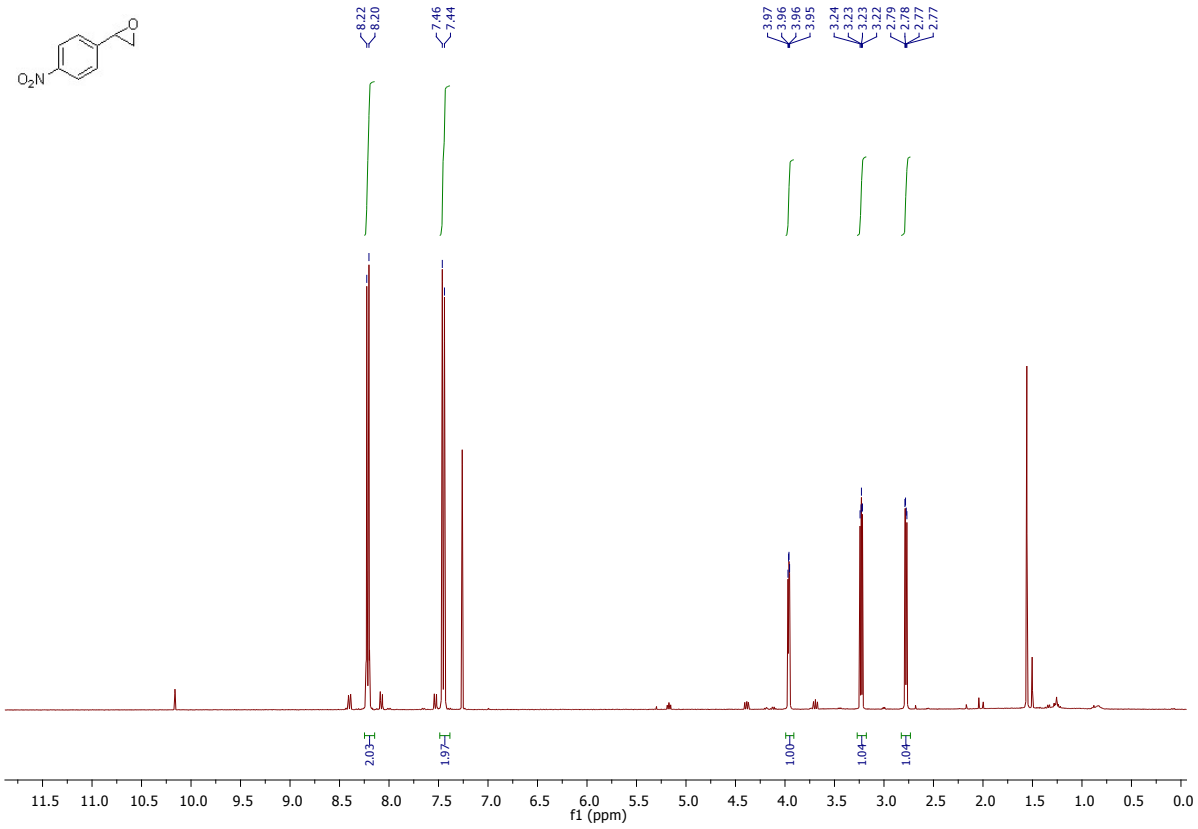
4-Chlorostyrene oxide[1]



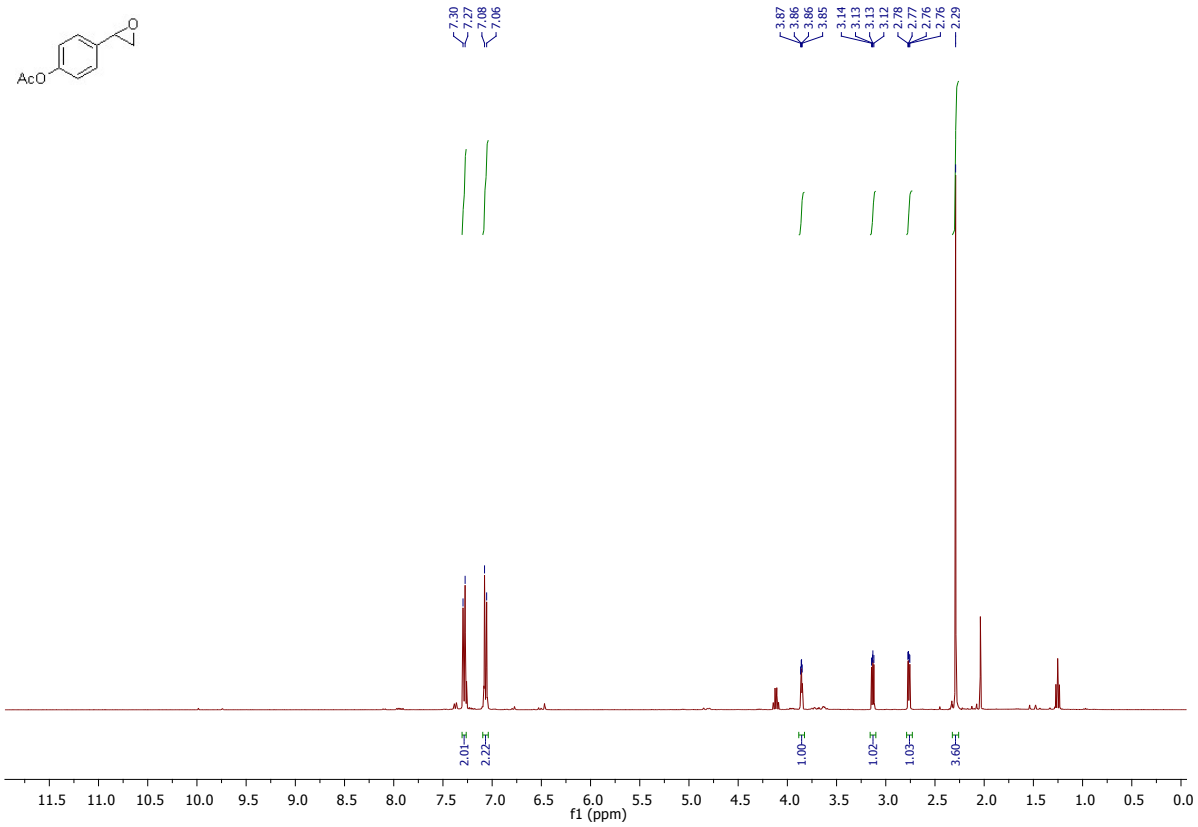
4-Bromostyrene oxide[1]



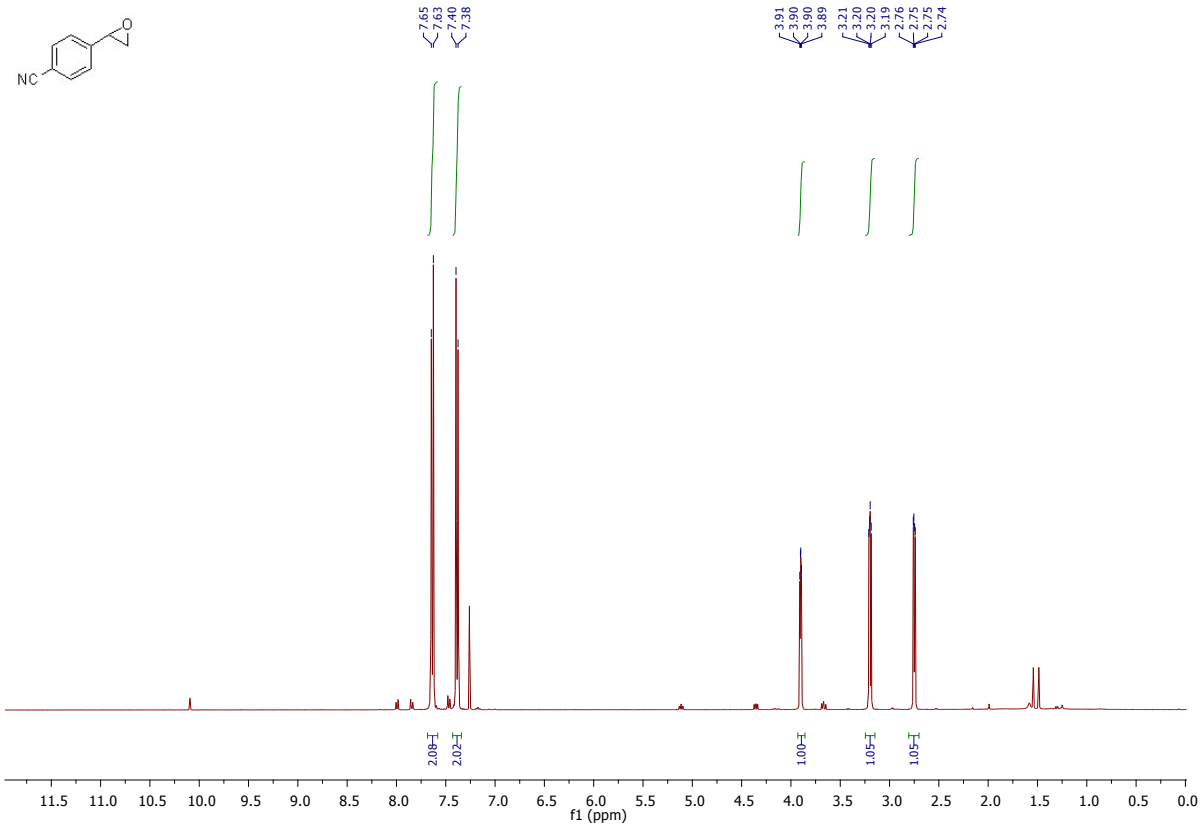
4-Nitrostyrene oxide[4]



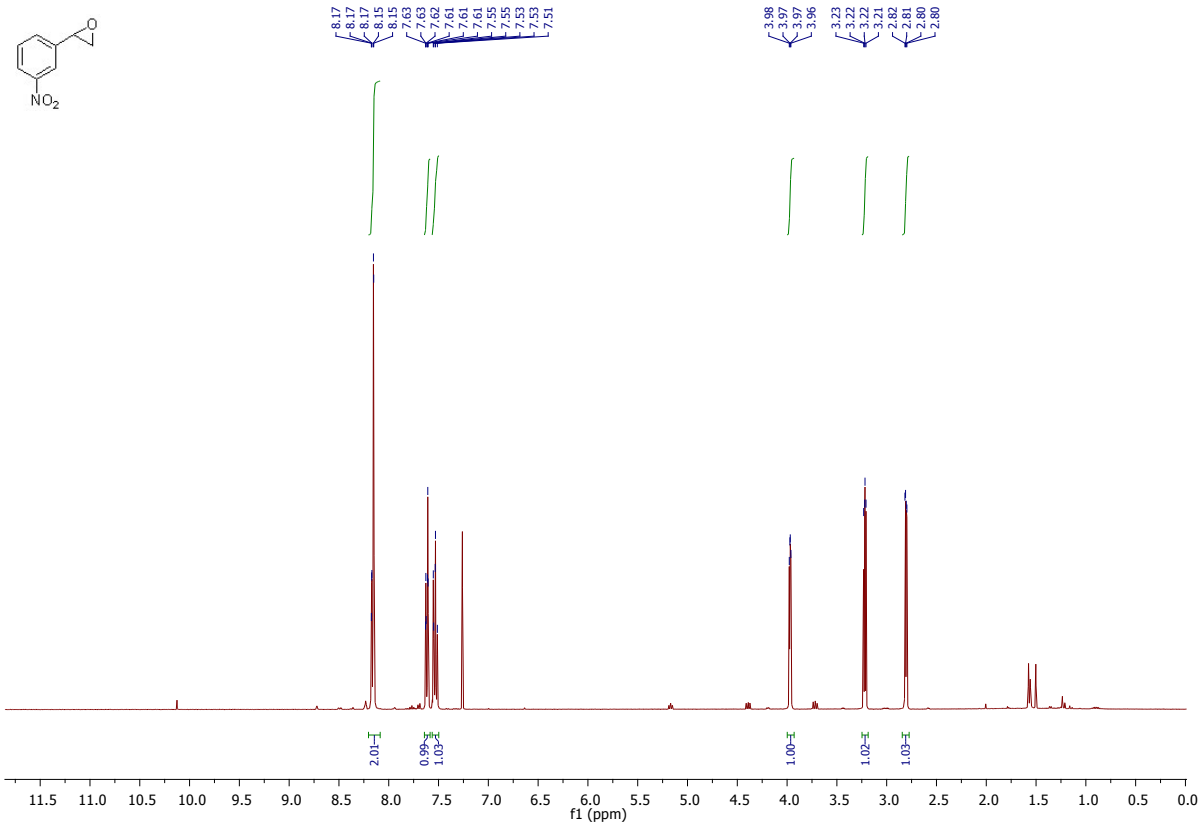
4-Acetoxystyrene oxide[5]



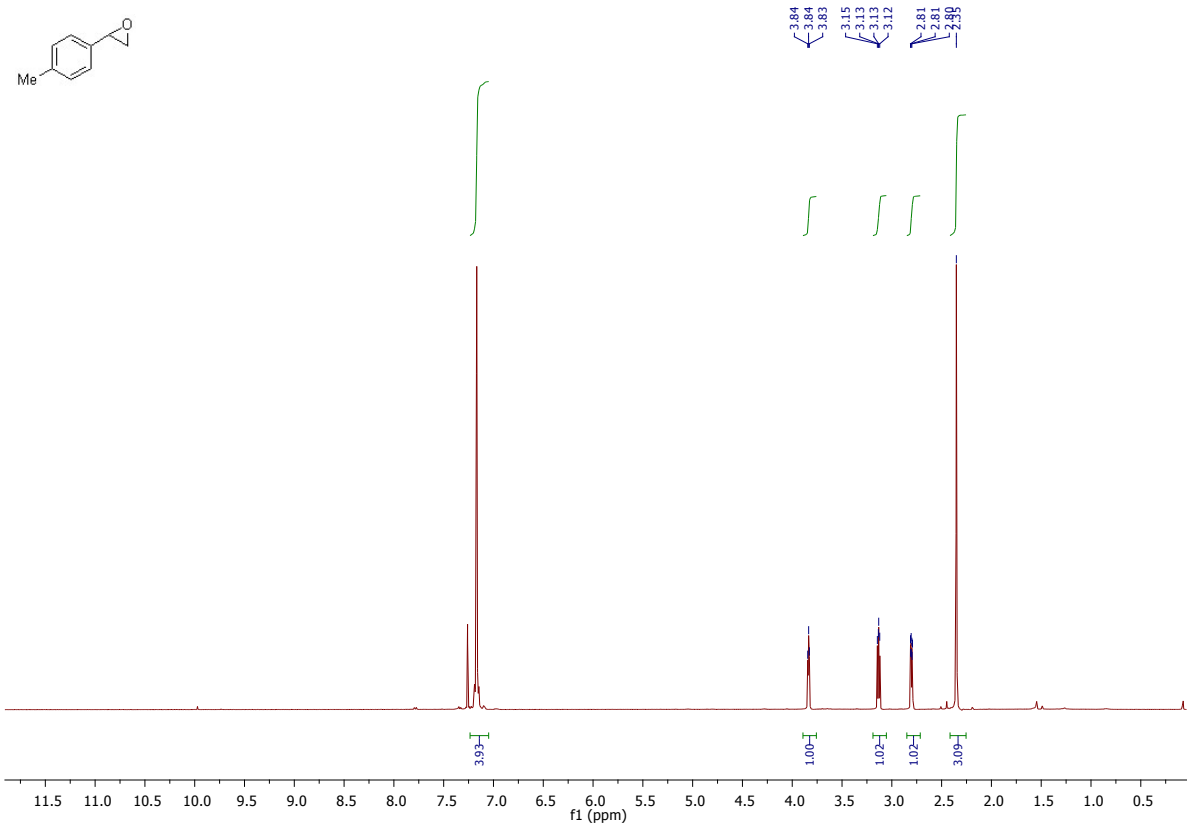
4-Cyanostyrene oxide[5]



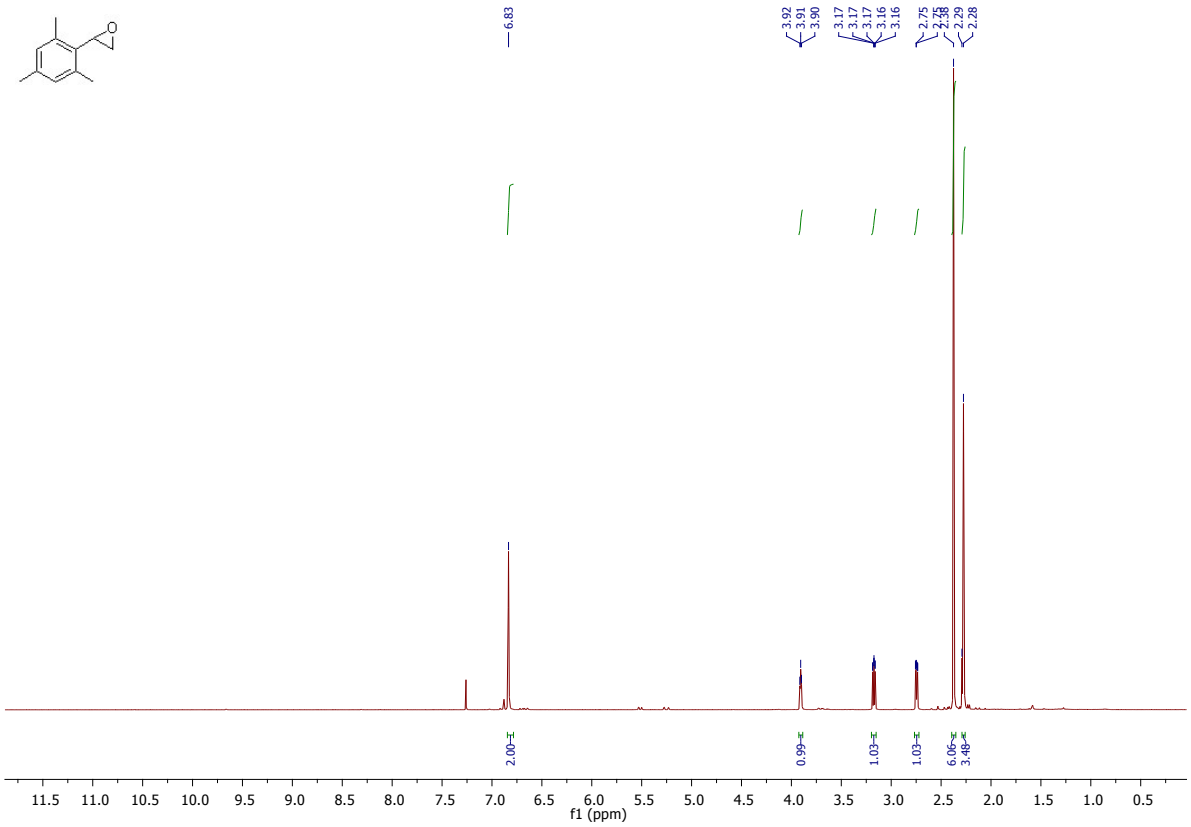
3-Nitrostyrene oxide[4]



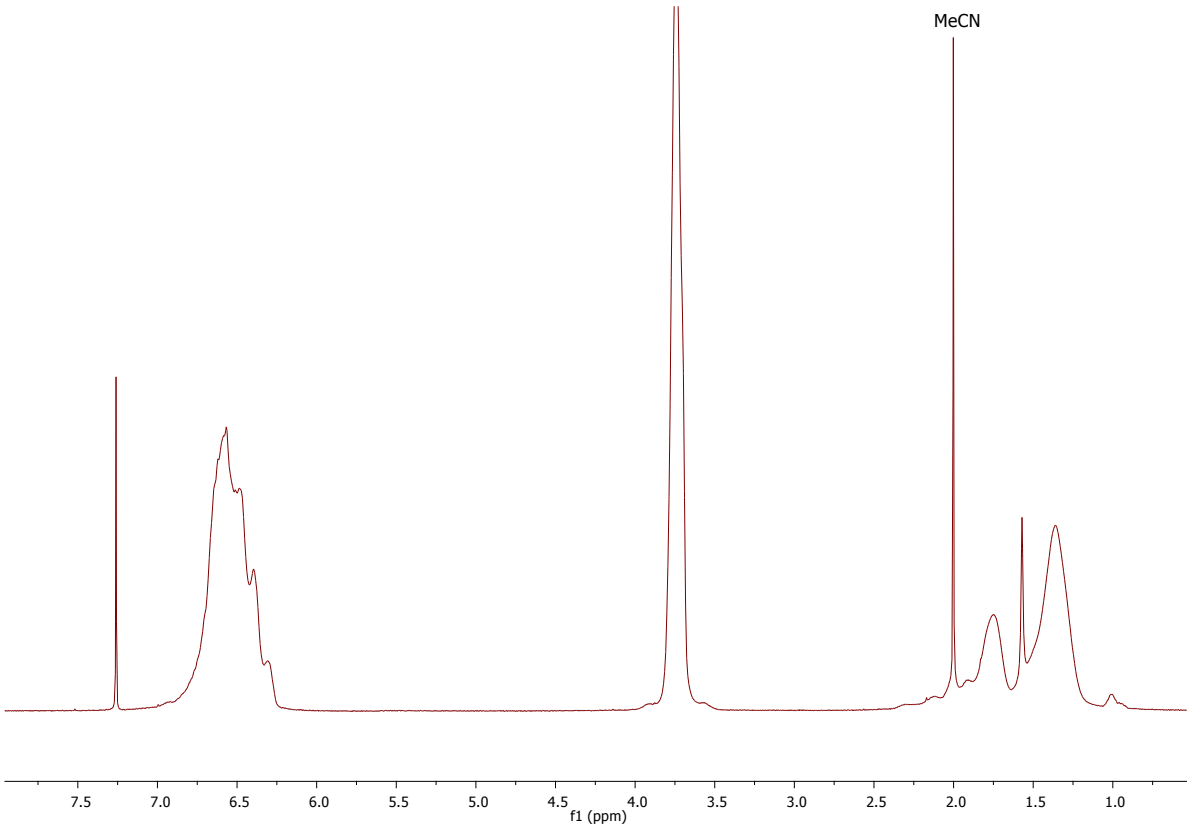
4-Methylstyrene oxide[1]



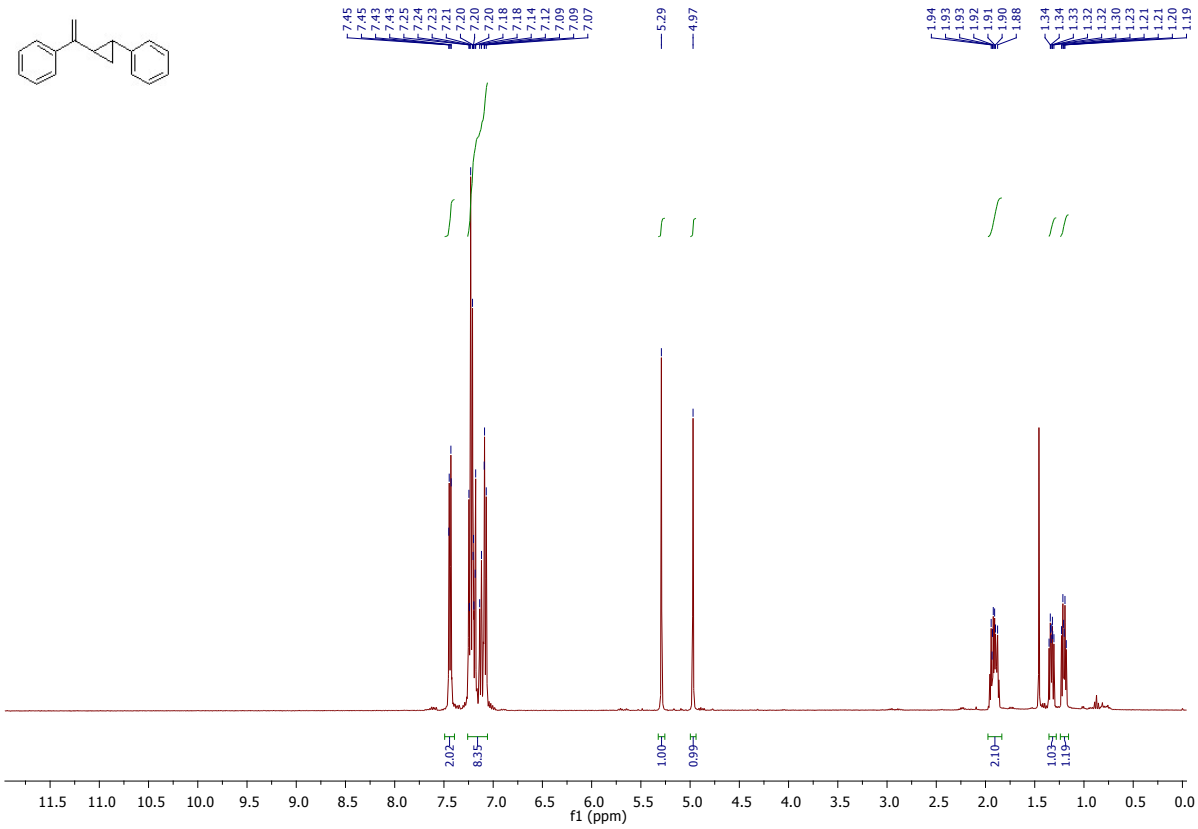
2,4,6-Trimethylstyrene oxide[6]



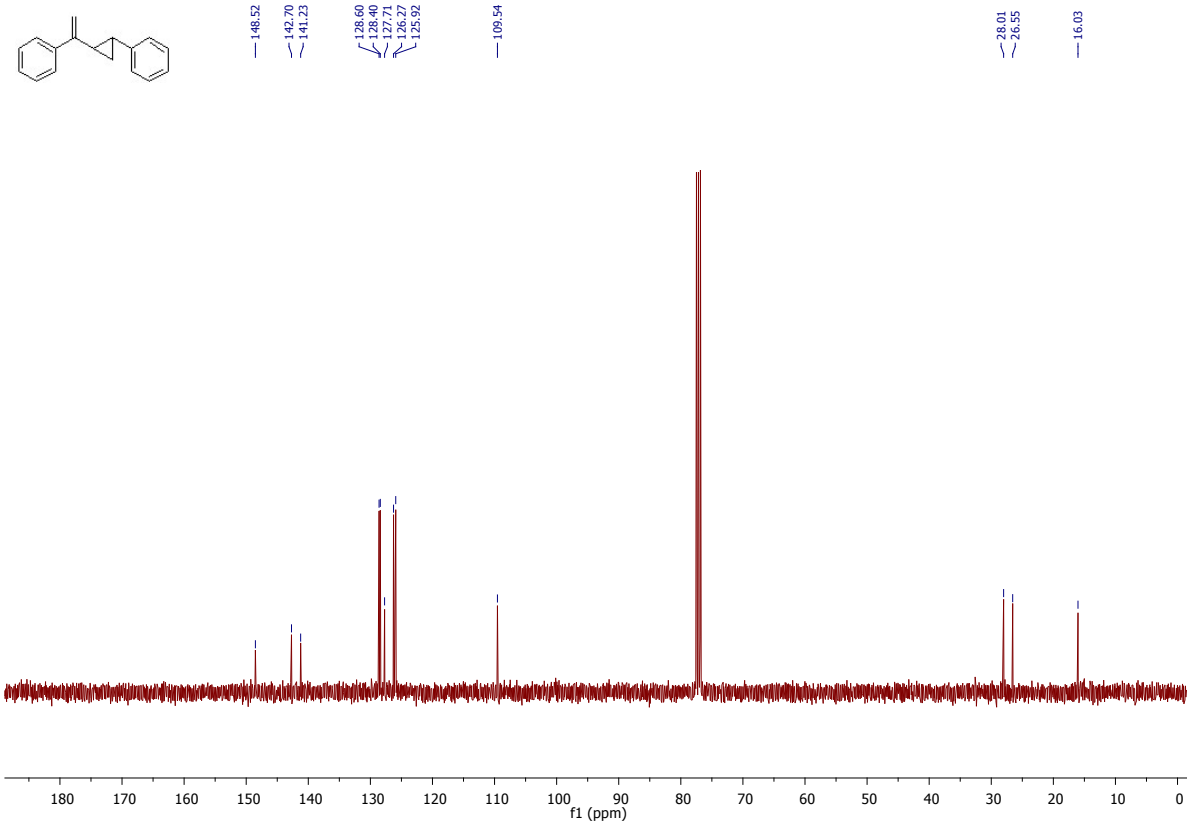
^{1}H NMR spectrum of polymerised 4-methoxystyrene[9]



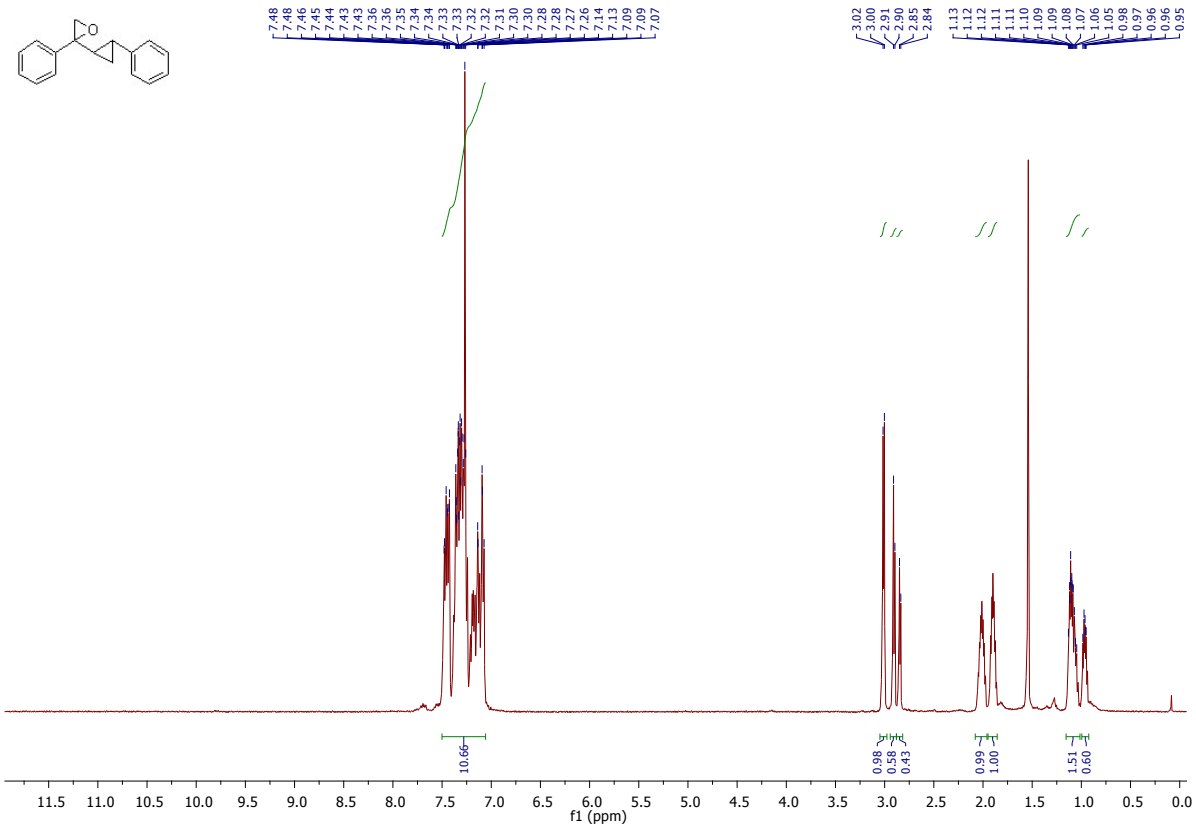
^{1}H NMR spectrum of [1-(2-phenylcyclopropyl)ethenyl]benzene[7]



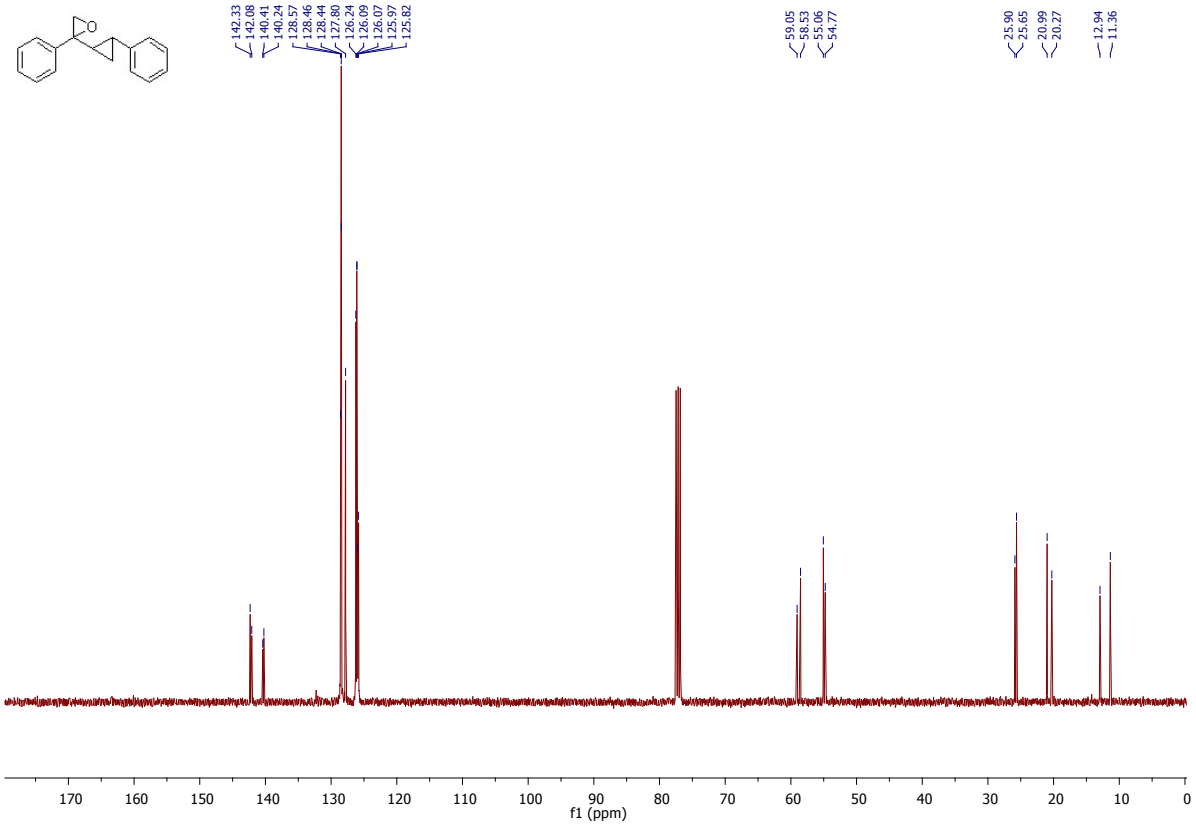
^{13}C NMR spectrum of [1-(2-phenylcyclopropyl)ethenyl]benzene[7]



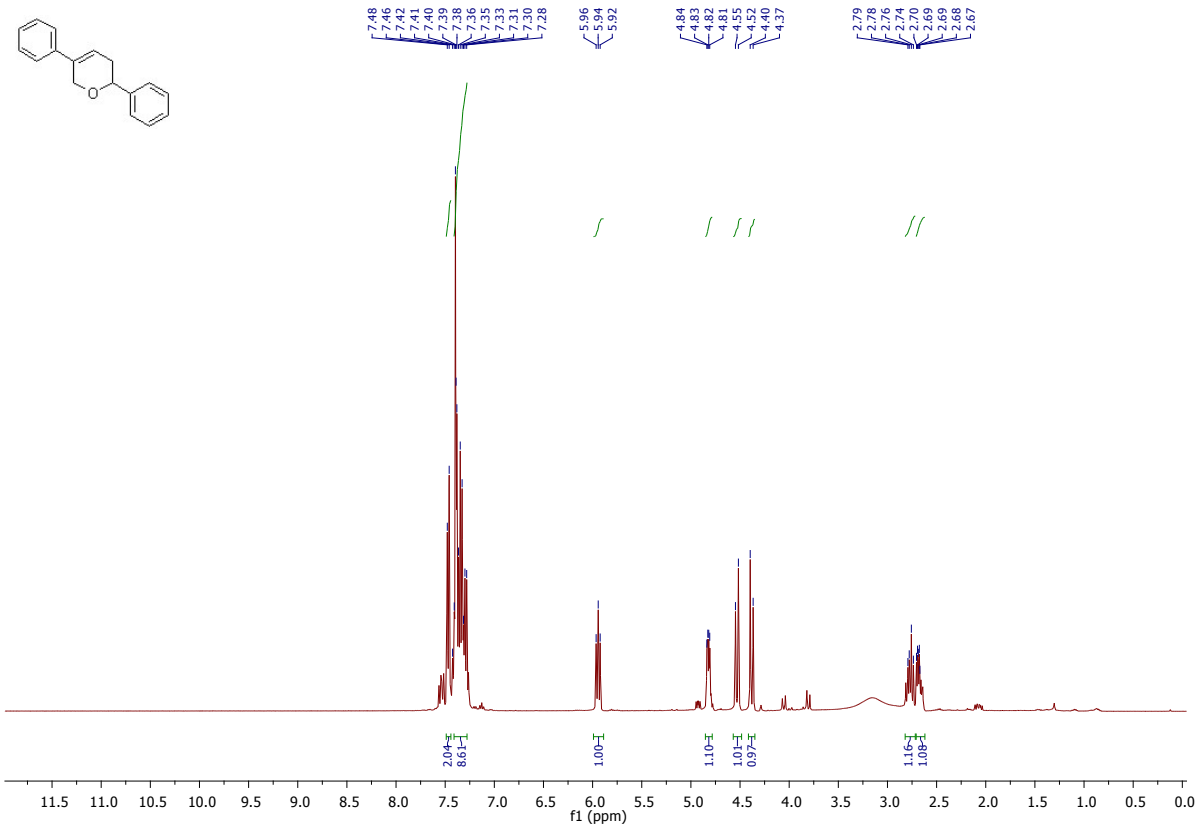
^{1}H NMR spectrum of 2-phenyl-2-(2-phenylcyclopropyl)oxirane (2 diastereomers)[8]



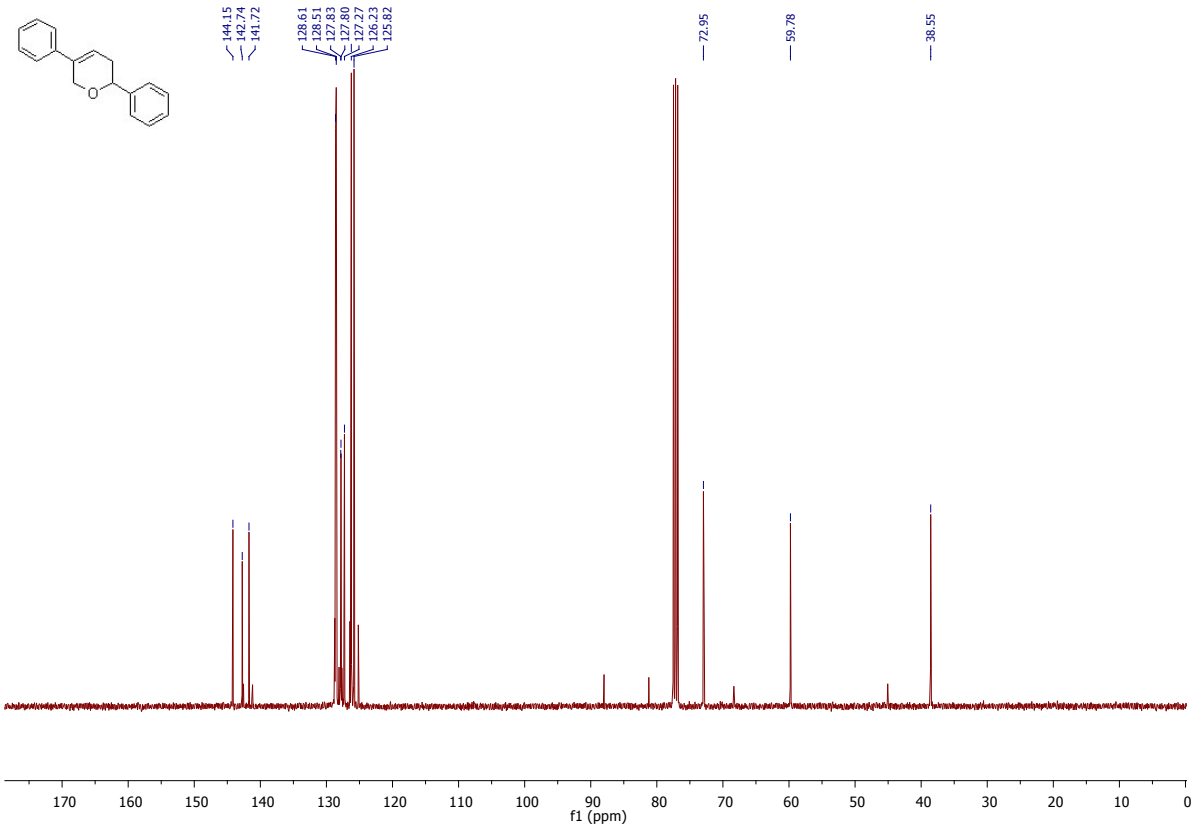
^{13}C NMR spectrum of 2-phenyl-2-(2-phenylcyclopropyl)oxirane (2 diastereomers)[8]



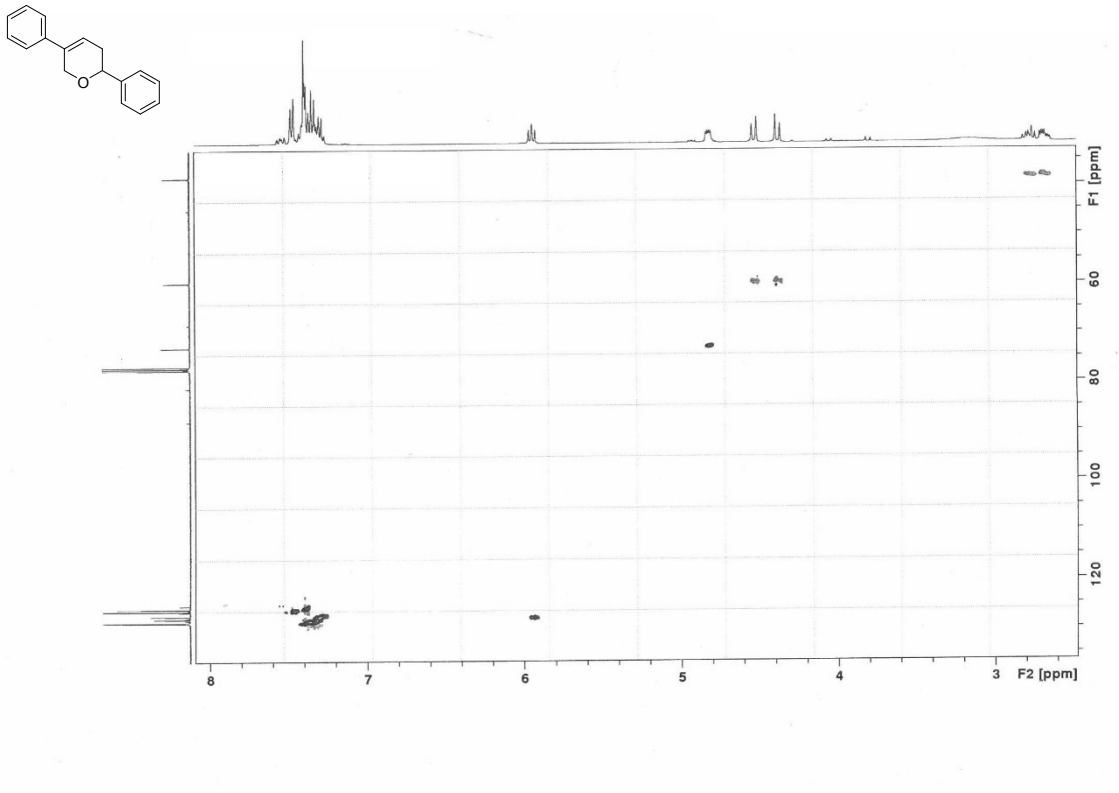
^{1}H NMR spectrum of 2,5-diphenyl-3,6-dihydro-2H-pyran



^{13}C NMR spectrum of 2,5-diphenyl-3,6-dihydro-2H-pyran



^{1}H-^{13}C NMR spectrum of 2,5-diphenyl-3,6-dihydro-2H-pyran



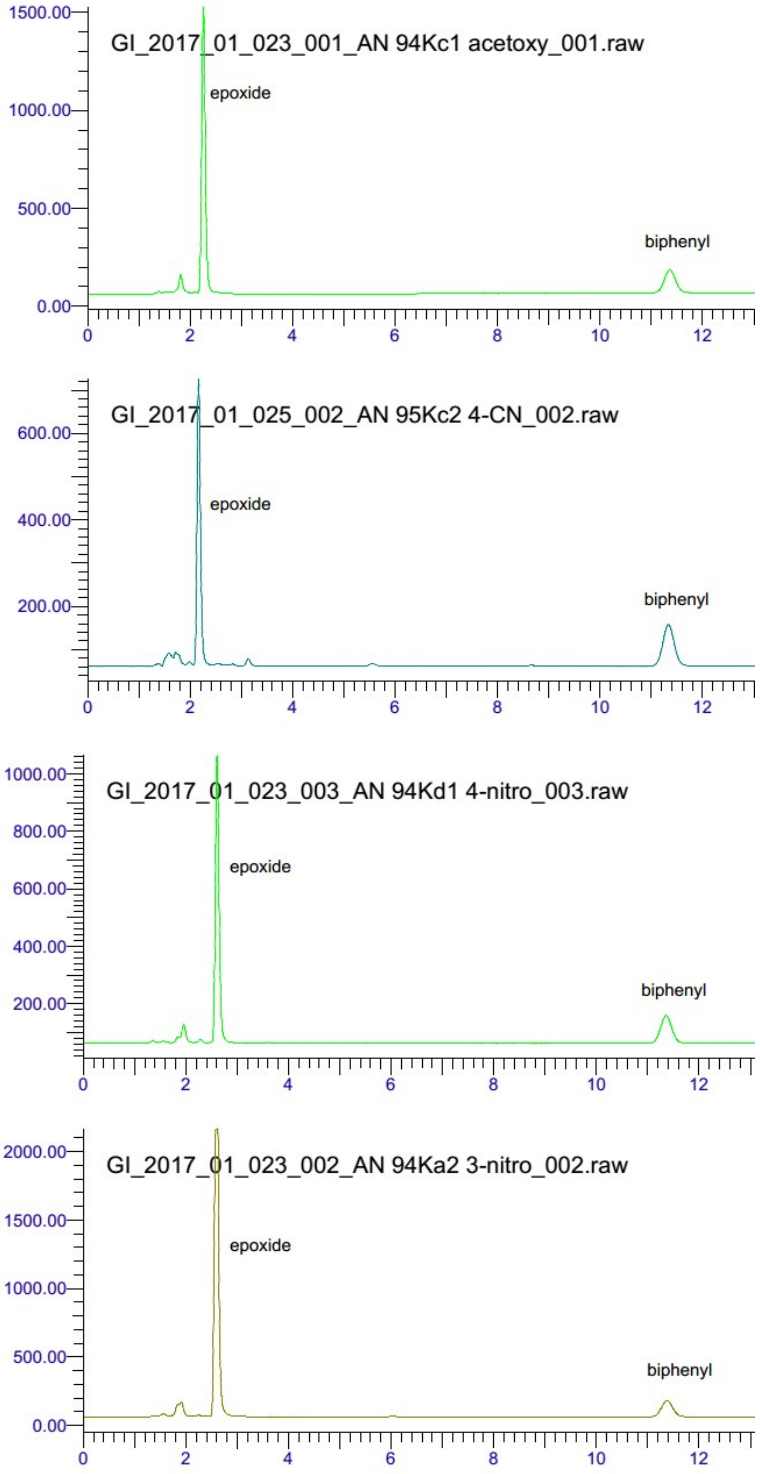


Figure ES6. Chromatograms of reaction mixtures of the oxidation of 4-acetoxystyrene, 4-cyanostyrene, 4-nitrostyrene and 3-nitrostyrene.

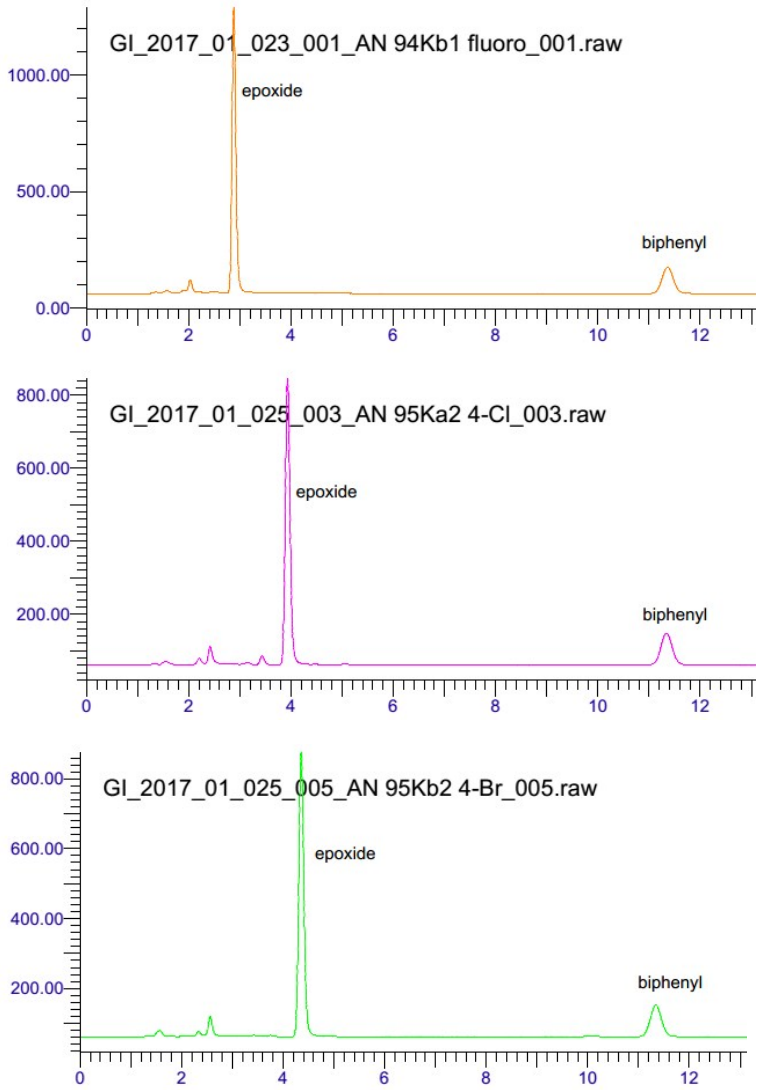


Figure ES7. Chromatograms of reaction mixtures of the oxidation of 4-fluorostyrene, 4-chlorostyrene and 4-bromostyrene.

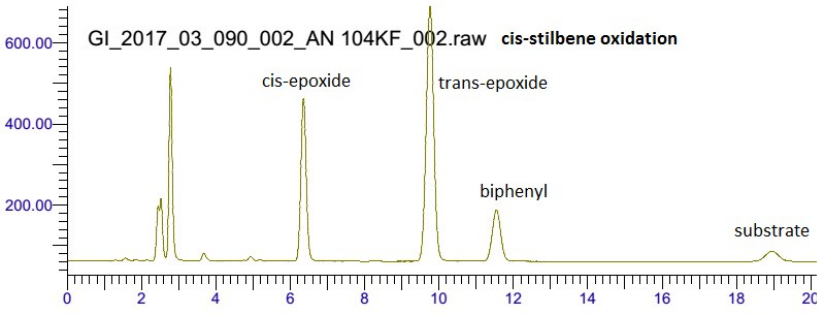


Figure ES8. Chromatogram of the reaction mixture of *cis*-stilbene oxidation.

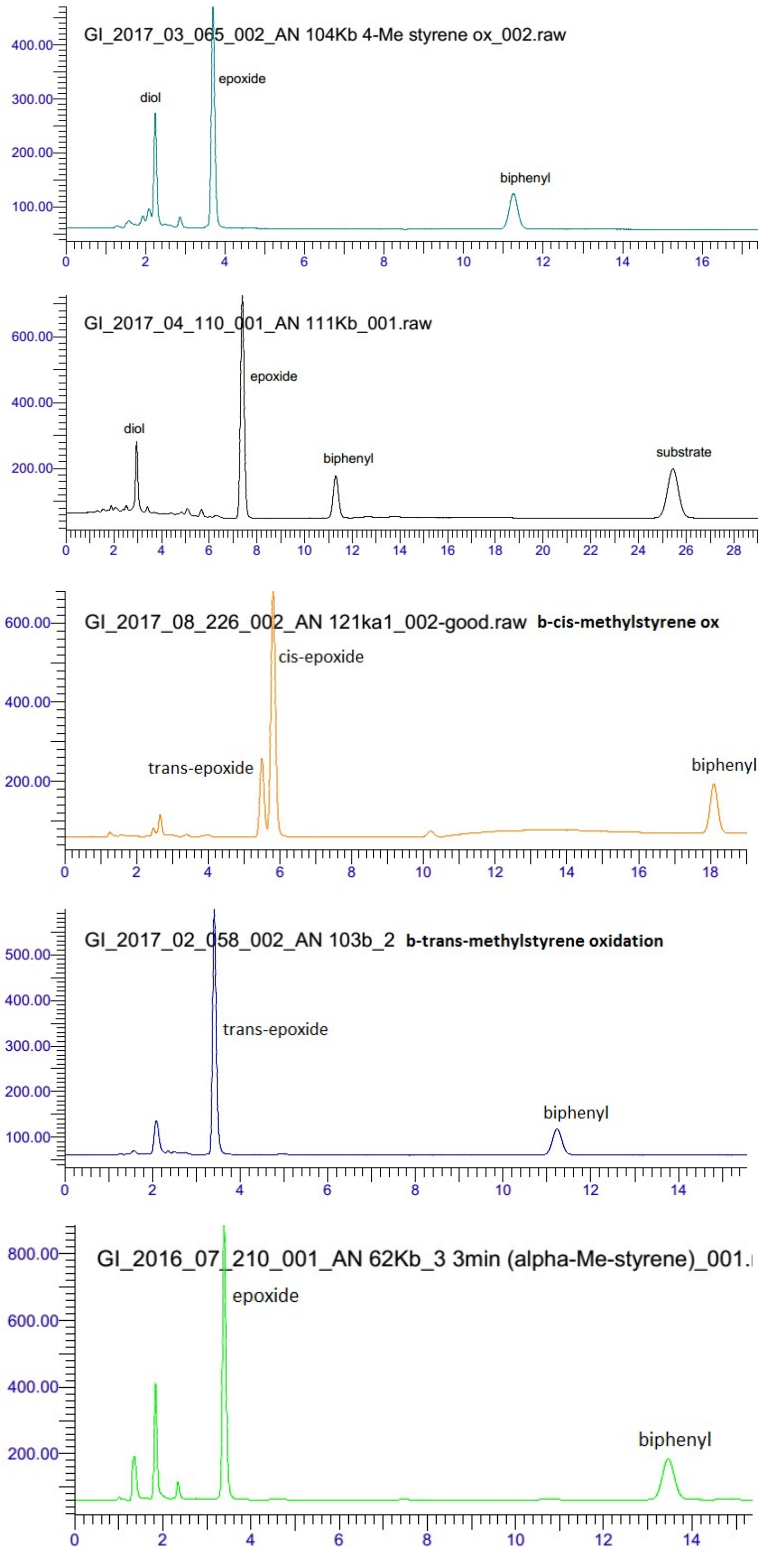


Figure ES9. Chromatograms of reaction mixtures of the oxidation of 4-methylstyrene, 2,4,6-trimethylstyrene, β-*cis*-methylstyrene, β-*trans*-methylstyrene and α-methylstyrene.

Calibrations

Standard solutions of styrene or substituted styrene (0.50 M) in MeCN, corresponding styrene oxide (0.50 M) in MeCN and biphenyl (0.10 M) in MeCN were prepared. Biphenyl solution (500 µL) was then delivered into six volumetric flasks to which solutions of the corresponding 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 MeCN (1.0 mL) and analysed by HPLC to obtain standard calibration plots.[10] The retention times for epoxides and HPLC conditions are given in Table ES1.

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