Supporting Information

Initial rate kinetic studies show an unexpected influence of *para*-substituents on the catalytic behaviour of manganese complexes of TMTACN in the epoxidation of styrenes with H_2O_2.

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General experimental details

All reagents were purchased from Aldrich, Acros, Merck or Fluka 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% solution in water. Acetonitrile and hexane were refluxed over CaH_2 for minimum of 6 h and distilled prior to use. All other solvents that were required to be anhydrous were obtained from an MBRAUN MB SPS-800 solvent purifying system. All water was obtained from an Elga Purelab Option distillation system. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400 MHz and at 100.2 MHz on a Bruker AV400 or a Bruker AMX400 and referenced to the signal of tetramethylsilane (TMS) or residual solvent. IR spectra were recorded on a Perkin Elmer Spectrum 65 IR spectrometer equipped with ATR accessory unless otherwise stated. UV-Vis spectra were obtained on a HP 8453 spectrophotometer, absorption maxima (λ_{max}) are expressed in nm, the molar extinction coefficients (ε) are expressed in L mol^{-1}cm^{-1}. Electrospray ionisation mass spectrometry was obtained from the EPSRC National Mass Spectrometry Service, University of Wales, Swansea on a Thermofisher LTQ Orbitrap XL. Cyclic votammetry was performed on an μAutolab Type III workstation, using $(nBu)_4NPF_6$ as the supporting electrolyte, a carbon working electrode, a silver counter electrode and a silver reference electrode in acetonitrile. Melting points were measured on a Stuart SMP3 melting point apparatus and are uncorrected. High Performance Liquid Chromatography was performed on a Perkin Elmer Series 200 instrument equipped with UV-Vis detector using an Eclips C18 reverse phase column and Chiralcel OJ or Chirlacel OD normal phase chiral columns.

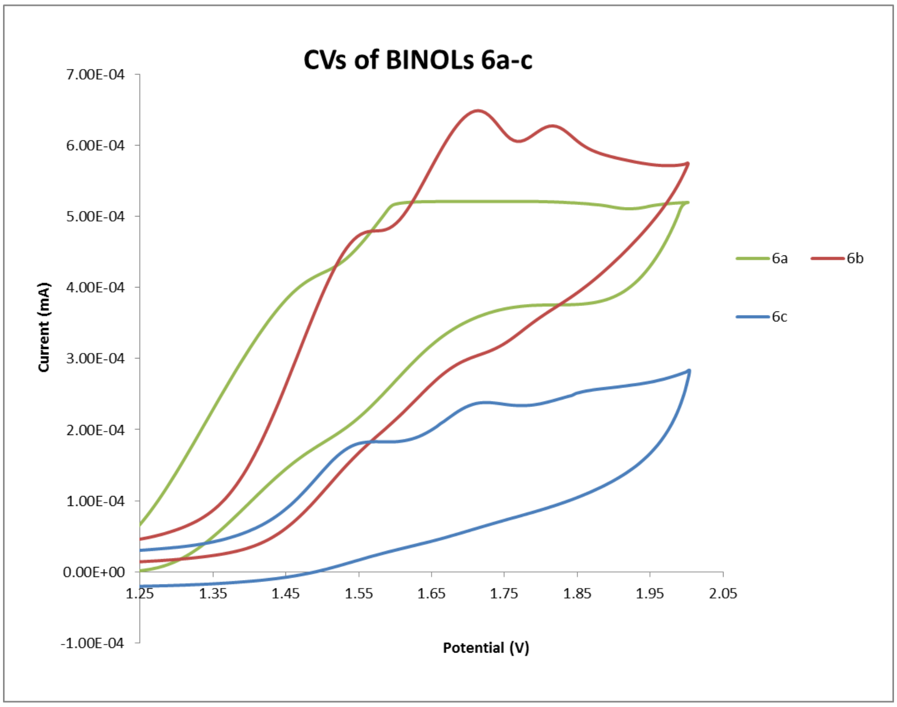


Figure ES1 Selected section of cyclic voltammograms of BINOLS **6** showing their irreversible reductions.

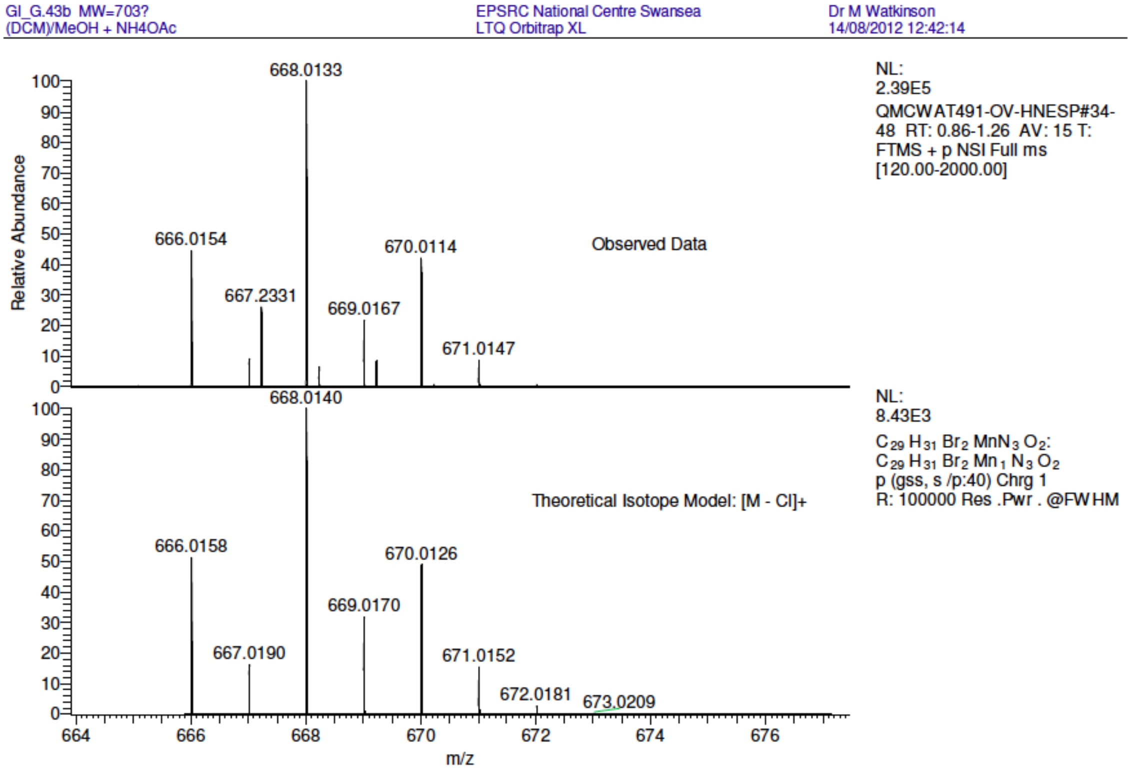


Figure ES2 HRMS of **9** showing the molecular ion with the expected isotopic distribution.

General epoxidation procedure:

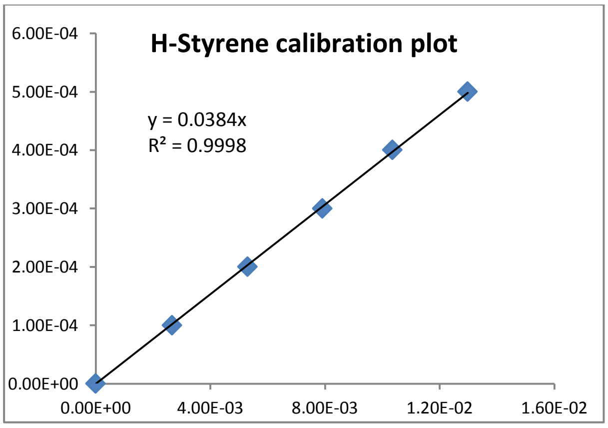
A solution containing catalyst (1 mol% w.r.t. styrene, note 1) in MeCN was delivered to a capped reaction vial following by a solution of the required Binol (1 mol%) in MeCN (500 μL) and the overall volume adjusted to 1500 μL by adding a further portion of MeCN if required (see **note 1**). Solution of styrene in MeCN (0.50 M, 1000 μL, 1.0 equiv.) and Anisole (0.10 M, 500 μL, **note 2**) were then delivered to the reaction vial and mixture allowed to equilibrate for 15 min at room temperature. A solution of H_2O_2 (30% aq. 855 μL, 10 equiv.) in acetone (2500 μL) was then added to the reaction in one portion and the aliquots (50 μL each) were sampled at times 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 35, 40, 50 and 60 min starting from the addition of peroxide. The aliquots were filtered through a short pad of silica and $MgSO_4$ using THF as eluent. The aliquots were then analysed using HPLC of GC and reaction profiles, yields, conversions and e.e. were recorded as appropriate.

Note 1: a) Dimer **1** catalyst solution was prepared by dissolving (19.8 mg) in MeCN (10.00 mL) of which 1000 μL were used to deliver 1 mol% of the catalyst with respect to Mn; no extra MeCN was required in this case. b) For the *in situ* screening two equimolar solutions were prepared: one containing $MnSO_4{\cdot}H_2O$ (8.4 mg) in H_2O (5.00 mL) and other containing TMTACN (8.5 mg) in MeCN (5.00 mL). The solutions were premixed together (500 μL each, thus delivering 1 mol% of catalyst) in the reaction vessel for 15 min prior to the addition of binol); no extra MeCN was required in this case. c) Manganese complex **8** solution was prepared by dissolving (23 mg) in MeCN (5.00 mL) of which 500 μL were used to deliver 1 mol% of the catalyst; a portion of MeCN (1000 μL)/ (500 μL) was required to adjust the overall volume if binol was not/was used. d) Manganese complex **9** solution was prepared by dissolving (34.9 mg) in MeCN (5.00 mL) of which 500 μL were used to deliver 1 mol% of the catalyst; a portion of MeCN (1000 μL) was required to adjust the overall volume.

Note 2: An equivalent amount of 1,2-dichlorobenzene was used as internal standard during the epoxidation of 4-nitrilestyrene due to the overlap of signals on HPLC trace.

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 ES3**). **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
R² = 0.9998
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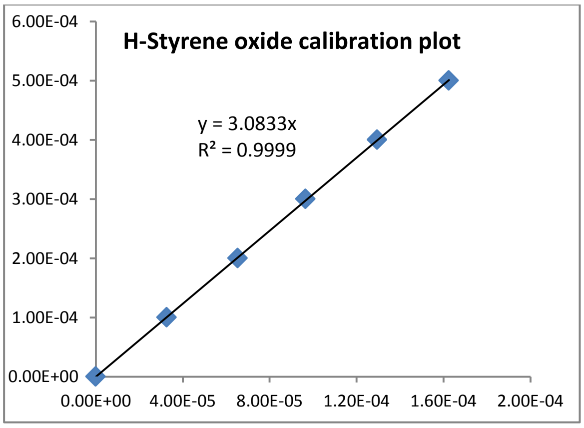
5.00E-04
4.00E-04
3.00E-04
2.00E-04
1.00E-04
0.00E+00
0.00E+00
4.00E-03
8.00E-03
1.20E-02
1.60E-02


H-Styrene oxide calibration plot
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R² = 0.9999
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3.00E-04
2.00E-04
1.00E-04
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0.00E+00
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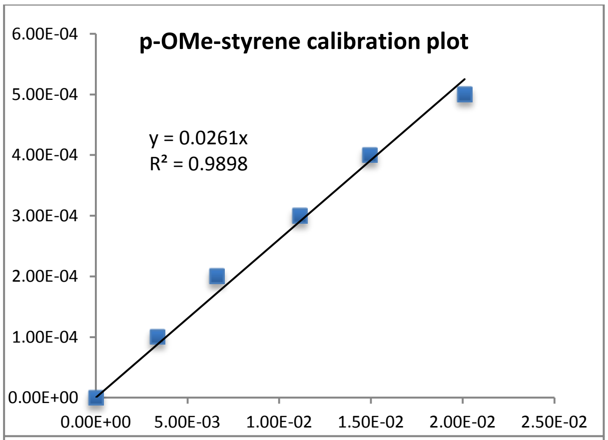
1.20E-04
1.60E-04
2.00E-04


p-OMe-styrene calibration plot
y = 0.0261x
R² = 0.9898
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3.00E-04
2.00E-04
1.00E-04
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0.00E+00
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1.00E-02
1.50E-02
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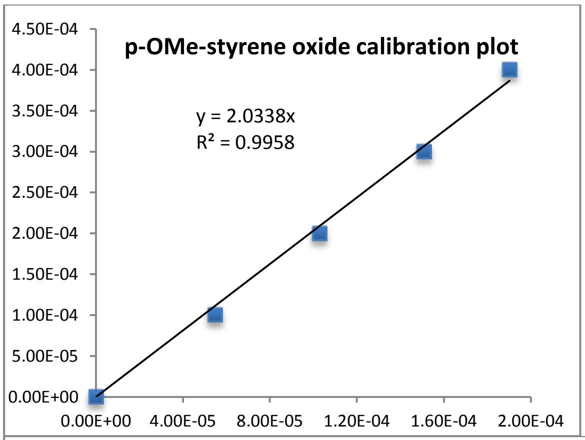
2.50E-02


p-OMe-styrene oxide calibration plot
y = 2.0338x
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3.50E-04
3.00E-04
2.50E-04
2.00E-04
1.50E-04
1.00E-04
5.00E-05
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0.00E+00
4.00E-05
8.00E-05
1.20E-04
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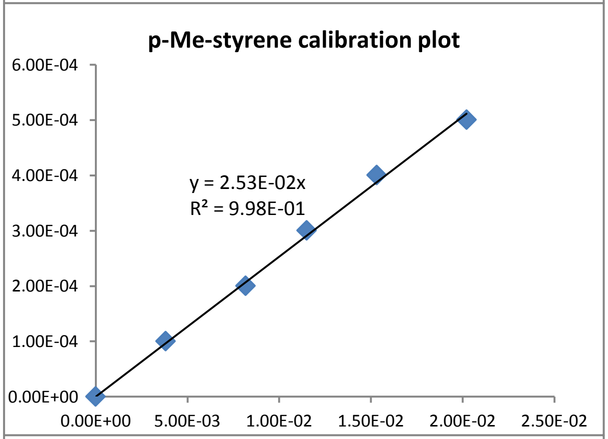
p-Me-styrene calibration plot
y = 2.53E-02x
R² = 9.98E-01
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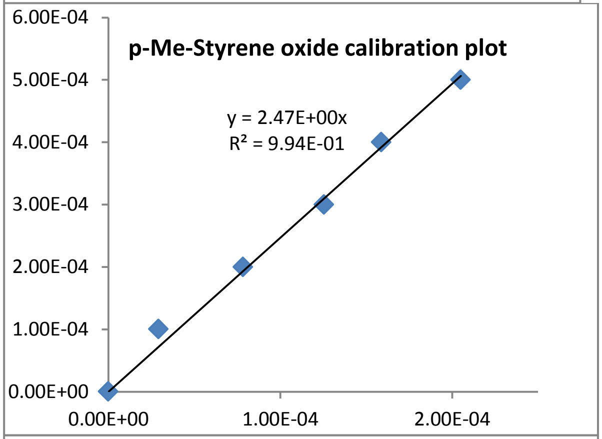
5.00E-04
4.00E-04
3.00E-04
2.00E-04
1.00E-04
0.00E+00
0.00E+00
5.00E-03
1.00E-02
1.50E-02
2.00E-02
2.50E-02


p-Me-Styrene oxide calibration plot
y = 2.47E+00x
R² = 9.94E-01
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4.00E-04
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2.00E-04
1.00E-04
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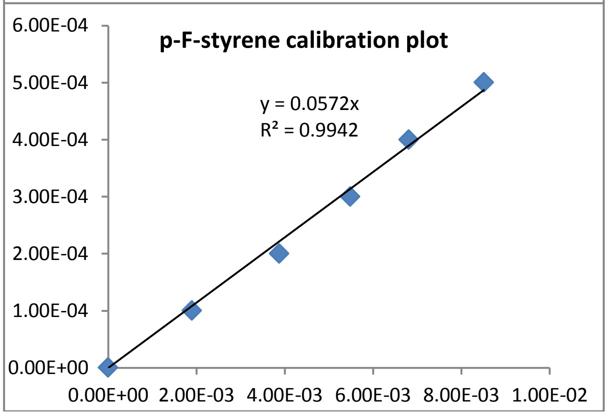
0.00E+00
1.00E-04
2.00E-04


p-F-styrene calibration plot
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R² = 0.9942
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4.00E-04
3.00E-04
2.00E-04
1.00E-04
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0.00E+00
2.00E-03
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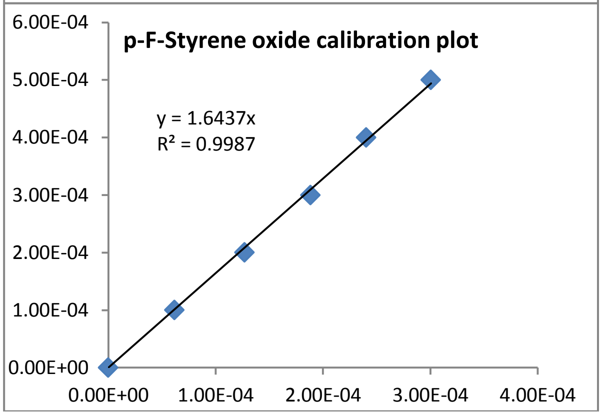
p-F-Styrene oxide calibration plot
y = 1.6437x
R² = 0.9987
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5.00E-04
4.00E-04
3.00E-04
2.00E-04
1.00E-04
0.00E+00
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1.00E-04
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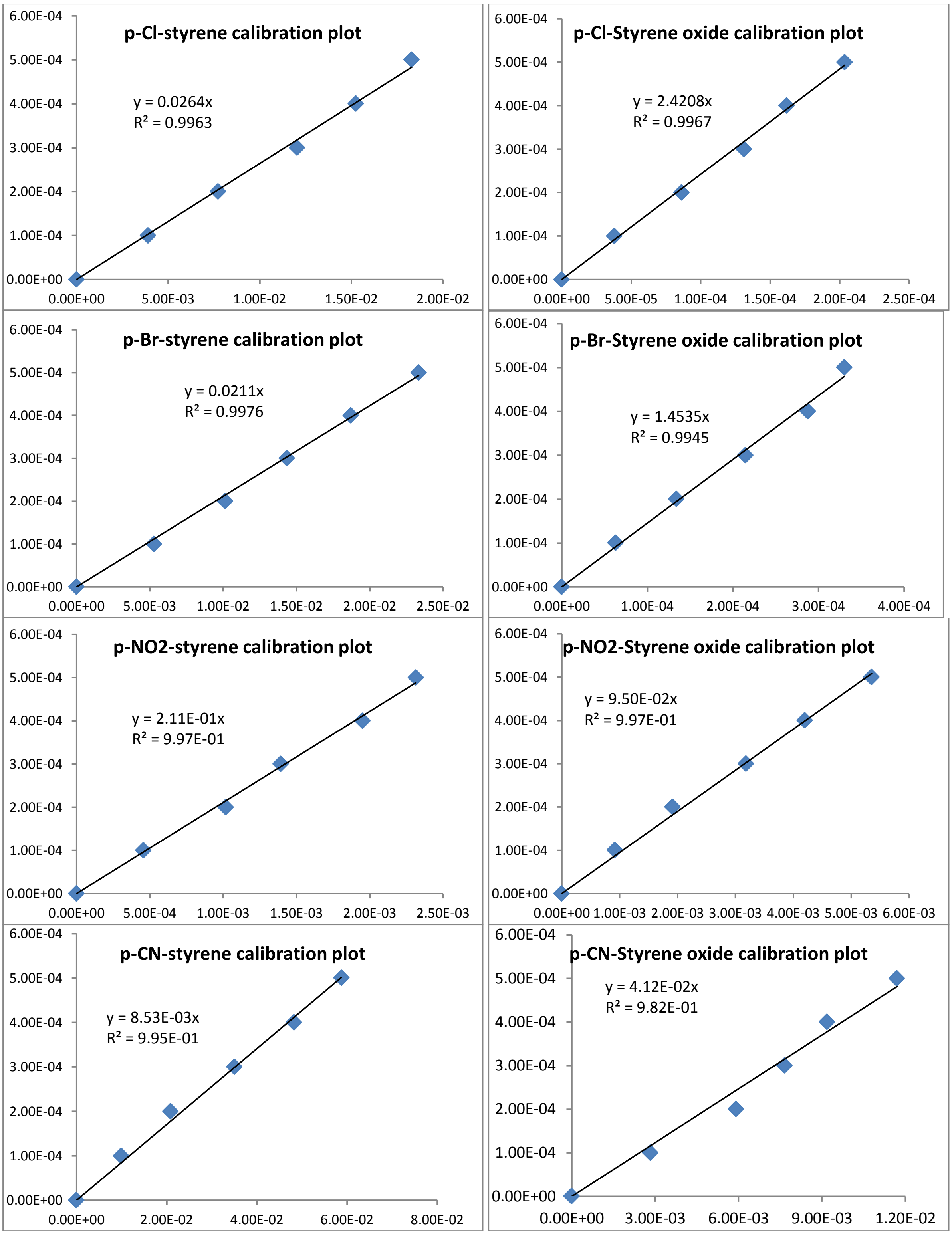


Figure ES3 Callibration graphs for all styrenes and corresponding epoxides used in this study: y axis is the number of moles of styrene/epoxide expected, x axis is the number of moles of styrene/epoxide observed. The slope is the correction factor. Note that DCB was used for the *p*-CN-styrene calibration.

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, $R_{t(anisole)}$ = 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, $R_{t(DCB)}$ = 25.06 min, $R_{t(4\text{-}nitrilestyrene\ epoxide)}$ = 4.87 min.

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

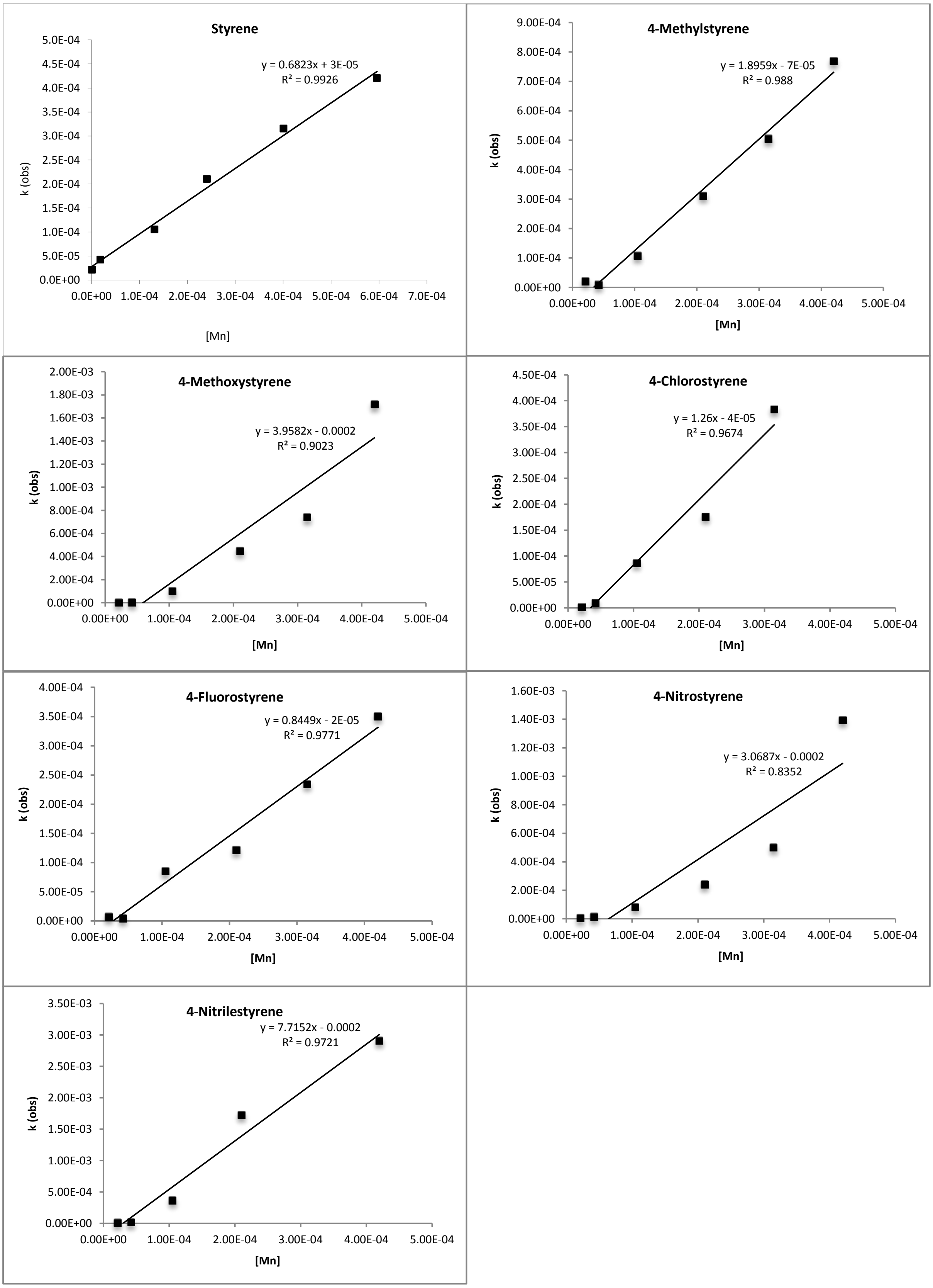


Figure ES4. Plots obtained for k-values for the epoxidation of styrenes with **1**/**6b** system using hydrogen peroxide. y-axis is $k_{(obs)}$ and x-axis is concentration of **1**.

Styrene	**TMTACN/ $MnSO_4$/6b**	**k1**	**k2**	**k3**	**Standard deviation**	**SE for k**	**% SE for K**	**Rates**	**SE for rate**
p-MeO	7.46E-04	7.24E-04	8.36E-04	6.71E-04	6.85E-05	3.96E-05	5.30E+00	1.38E-07	7.32E-09
p-Me	8.45E-04	8.11E-04	9.72E-04	7.61E-04	9.01E-05	5.20E-05	6.16E+00	1.56E-07	9.60E-09
H	1.37E-03	1.23E-03	1.55E-03	1.30E-03	1.36E-04	7.83E-05	5.72E+00	2.53E-07	1.45E-08
p-F	1.12E-03	1.06E-03	1.28E-03	1.01E-03	1.16E-04	6.69E-05	5.97E+00	2.07E-07	1.24E-08
p-Cl	1.86E-03	1.67E-03	2.18E-03	1.77E-03	2.19E-04	1.26E-04	6.78E+00	3.45E-07	2.34E-08
p-Br	1.40E-03	1.32E-03	1.54E-03	1.27E-03	1.19E-04	6.87E-05	4.91E+00	2.59E-07	1.27E-08
p-NO_2	2.60E-03	2.31E-03	2.68E-03	2.26E-03	2.60E-04	1.50E-04	5.76E+00	4.81E-07	2.77E-08
p-CN	5.13E-03	4.36E-03	5.39E-03	4.87E-03	4.91E-04	2.84E-04	5.53E+00	9.50E-07	5.25E-08

Table ESI 2: Standard Error (SE) calculations for initial rate kinetics for TMTACN/$MnSO_4$/**6b**.

Styrene	**9**	**k1**	**k2**	**k3**	**Standard deviation**	**SE for k**	**% SE for K**	**Rates**	**SE for rate**
p-MeO	1.11E-03	1.10E-03	1.24E-03	9.99E-04	1.00E-04	5.79E-05	5.22E+00	2.05E-07	1.07E-08
p-Me	1.31E-03	1.27E-03	1.52E-03	1.18E-03	1.44E-04	8.34E-05	6.37E+00	2.42E-07	1.54E-08
H	1.47E-03	1.43E-03	1.65E-03	1.41E-03	1.10E-04	6.37E-05	4.33E+00	2.72E-07	1.18E-08
p-F	2.03E-03	1.97E-03	2.27E-03	1.83E-03	1.86E-04	1.08E-04	5.30E+00	3.76E-07	1.99E-08
p-Cl	2.21E-03	2.08E-03	2.48E-03	1.99E-03	2.14E-04	1.23E-04	5.58E+00	4.08E-07	2.28E-08
p-Br	2.33E-03	2.26E-03	2.63E-03	2.10E-03	2.24E-04	1.29E-04	5.56E+00	4.30E-07	2.39E-08
p-NO_2	3.04E-03	2.95E-03	3.40E-03	2.95E-03	2.23E-04	1.29E-04	4.24E+00	5.62E-07	2.38E-08
p-CN	3.71E-03	3.49E-03	4.16E-03	3.34E-03	3.58E-04	2.07E-04	5.58E+00	6.86E-07	3.83E-08

Table ESI 3: Standard Error (SE) calculations for initial rate kinetics for **9**.

Styrene	**1/6b**	**k1**	**k2**	**k3**	**Standard deviation**	**SE for k**	**% SE for K**	**Rates**	**SE for rate**
p-MeO	1.72E-03	1.67E-03	1.89E-03	1.55E-03	1.44E-04	8.29E-05	4.82E+00	3.17E-07	1.53E-08
p-Me	6.95E-04	6.74E-04	7.78E-04	6.19E-04	6.64E-05	3.83E-05	5.52E+00	1.29E-07	7.12E-09
H	3.71E-04	3.52E-04	4.16E-04	3.34E-04	3.51E-05	2.03E-05	5.47E+00	6.86E-08	3.75E-09
p-F	5.41E-04	5.25E-04	5.90E-04	4.87E-04	4.31E-05	2.49E-05	4.59E+00	1.00E-07	4.59E-09
p-Cl	7.63E-04	7.40E-04	8.55E-04	7.25E-04	5.88E-05	3.39E-05	4.45E+00	1.41E-07	6.27E-09
p-Br	6.93E-04	6.72E-04	7.76E-04	6.24E-04	6.36E-05	3.67E-05	5.30E+00	1.28E-07	6.79E-09
p-NO_2	1.39E-03	1.25E-03	1.56E-03	1.25E-03	1.49E-04	8.59E-05	6.18E+00	2.58E-07	1.60E-08
p-CN	2.90E-03	2.81E-03	3.36E-03	2.61E-03	3.20E-04	1.85E-04	6.37E+00	5.37E-07	3.42E-08

Table ESI 4: Standard Error (SE) calculations for initial rate kinetics for **1/6b**.

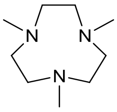
Styrene	8	k1	k2	k3	Standard deviation	SE for k	% SE for K	Rates	SE for rate
p-MeO	9.19E-04	8.91E-04	1.03E-03	8.00E-04	9.52E-05	5.50E-05	5.98E+00	1.70E-07	1.02E-08
p-Me	1.60E-03	1.44E-03	1.79E-03	1.44E-03	1.71E-04	9.89E-05	6.18E+00	2.97E-07	1.84E-08
H	1.77E-03	1.72E-03	1.84E-03	1.59E-03	1.14E-04	6.60E-05	3.73E+00	3.27E-07	1.22E-08
p-F	1.72E-03	1.67E-03	1.93E-03	1.65E-03	1.29E-04	7.45E-05	4.33E+00	3.18E-07	1.38E-08
p-Cl	1.48E-03	1.38E-03	1.66E-03	1.33E-03	1.46E-04	8.44E-05	5.71E+00	2.75E-07	1.57E-08
p-Br	1.69E-03	1.64E-03	1.98E-03	1.52E-03	1.95E-04	1.12E-04	6.65E+00	3.12E-07	2.07E-08
p-NO_2	1.06E-03	1.03E-03	1.19E-03	9.96E-04	8.41E-05	4.86E-05	4.58E+00	1.96E-07	8.98E-09
p-CN	9.95E-03	9.35E-03	1.09E-02	8.96E-03	8.83E-04	5.10E-04	5.12E+00	1.84E-07	9.42E-09

Table ESI 5: Standard Error (SE) calculations for initial rate kinetics for **8**.

Styrene	1/6b	k1	k2	k3	Standard deviation	SE for k	% SE for K
p-MeO	3.96	3.84	4.16	3.56	2.65E-01	1.53E-01	3.86E+00
p-Me	1.89	1.81	2.02	1.70	1.40E-01	8.09E-02	4.28E+00
H	0.682	0.66	0.73	0.61	4.95E-02	2.86E-02	4.19E+00
p-F	0.845	0.82	0.95	0.81	6.34E-02	3.66E-02	4.33E+00
p-Cl	1.26	1.22	1.32	1.13	8.42E-02	4.86E-02	3.86E+00
p-Br							
p-NO_2	3.07	2.98	3.28	2.86	1.83E-01	1.06E-01	3.45E+00
p-CN	7.71	7.48	8.48	7.09	5.85E-01	3.38E-01	4.38E+00

Table ESI 6: Standard Error (SE) calculations for k-values for **1/6b**.

1,4,7-trimethyl-1,4,7-triazacyclononane (L)[1]



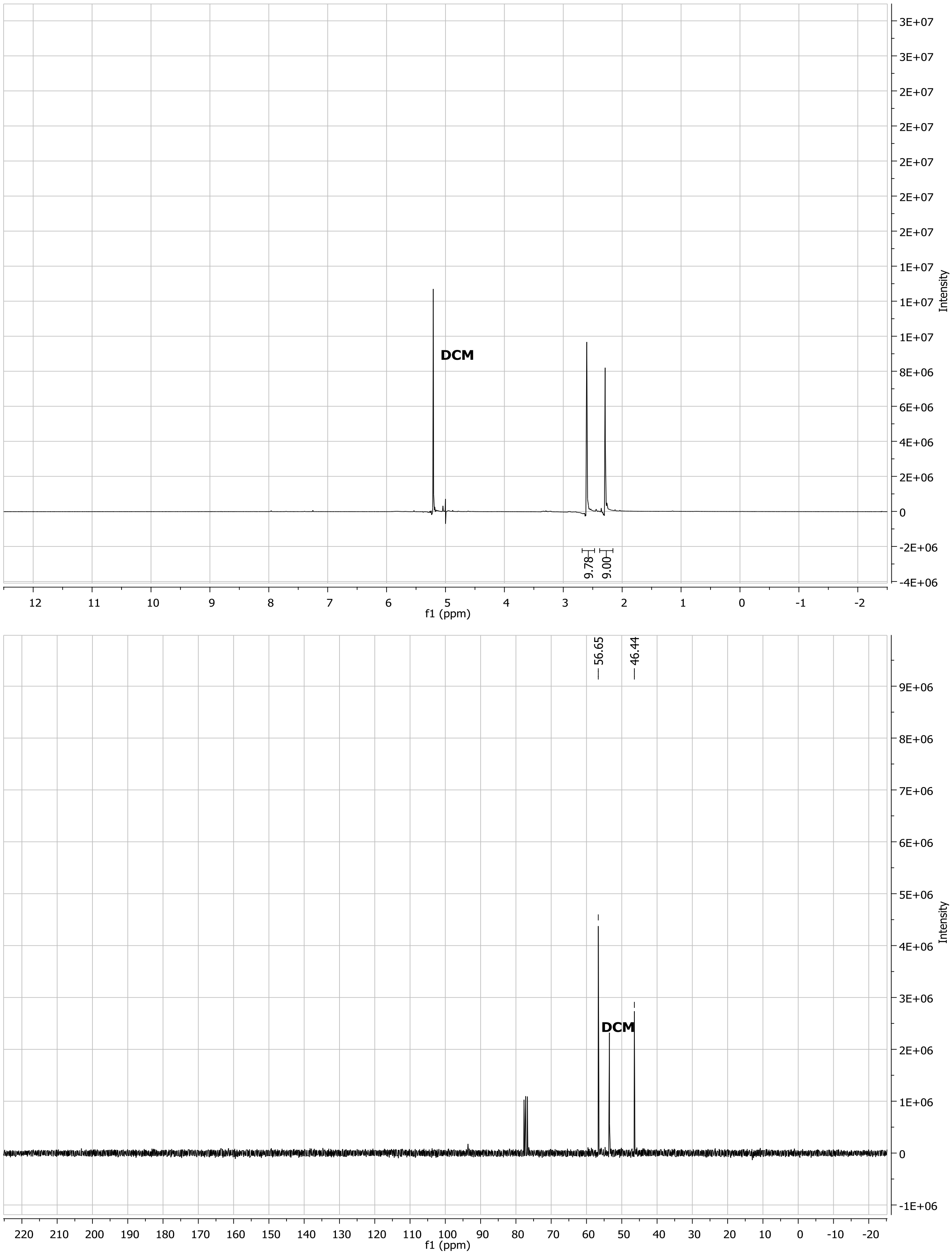
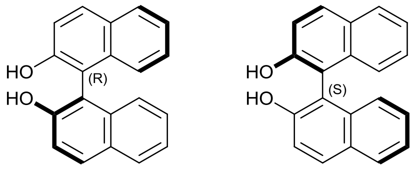


Figure ES5. ^{1}H NMR and ^{13}C NMR spectra of TMTACN ligand used

(***R***, ***R***) and (***S***, ***S***) - 2,2'-dihidroxy-1,1'-bi-naphthol (6a)[2]



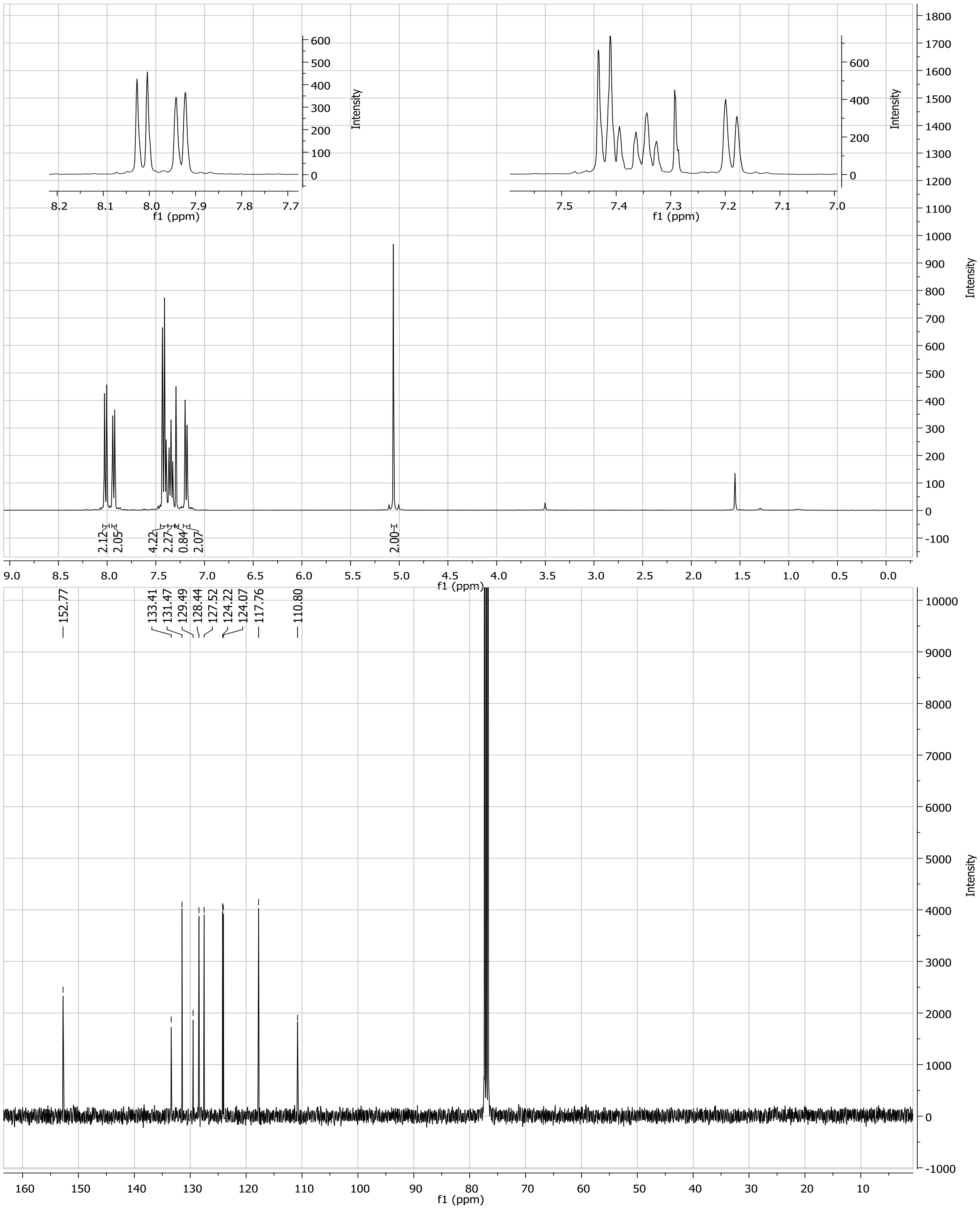
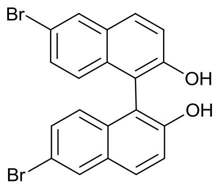


Figure ES6. ^{1}H NMR and ^{13}C NMR spectra of **6a.**

6,6'-dibromo-2,2'-dihidroxy-1,1'-bi-naphthol (6b)[3]



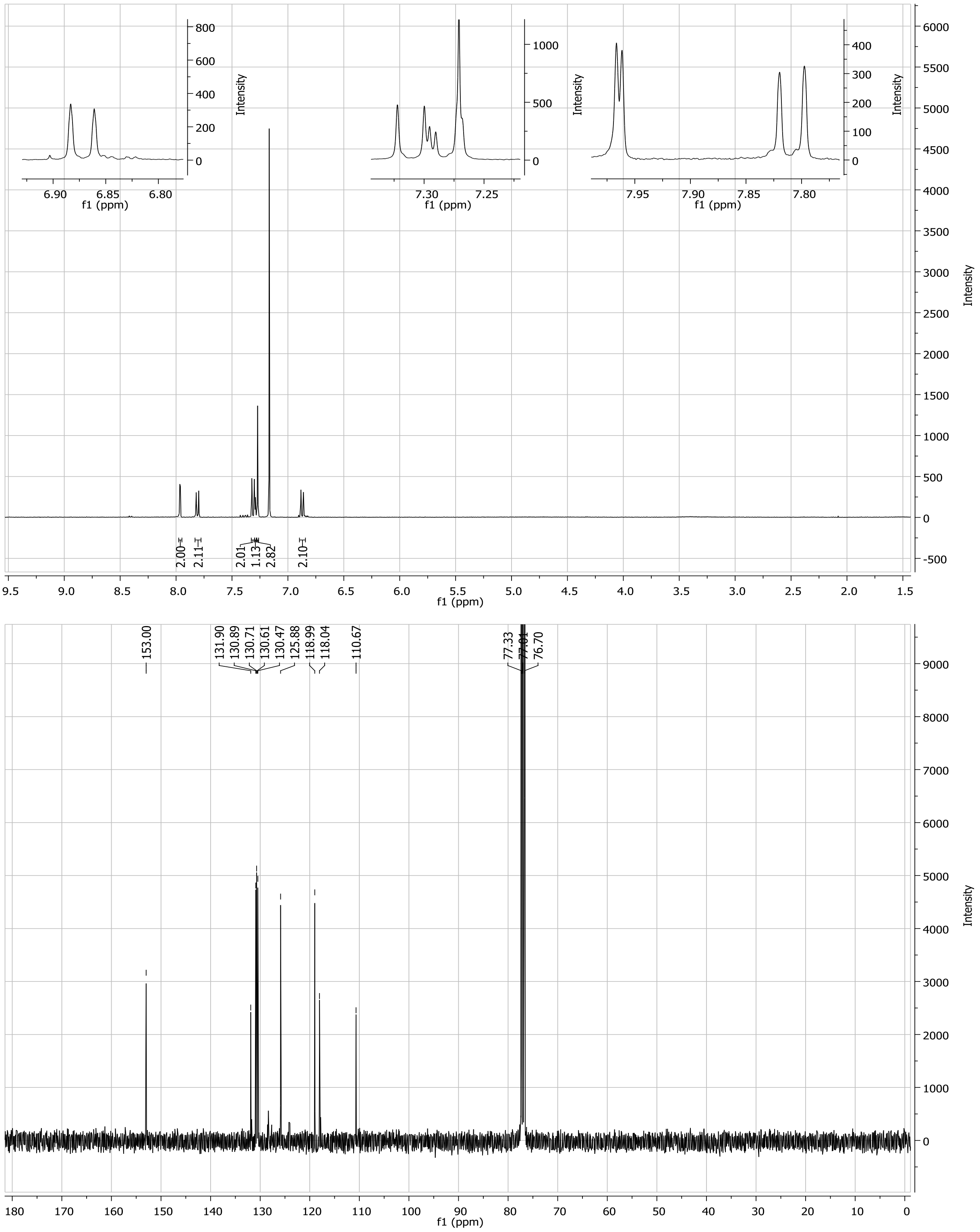
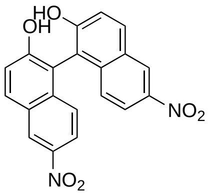


Figure ES7. ^{1}H NMR and ^{13}C NMR spectra of **6b.**

6,6’-dinitro-2,2’-dihidroxy-1,1’-bi-naphthol (6c)[4]



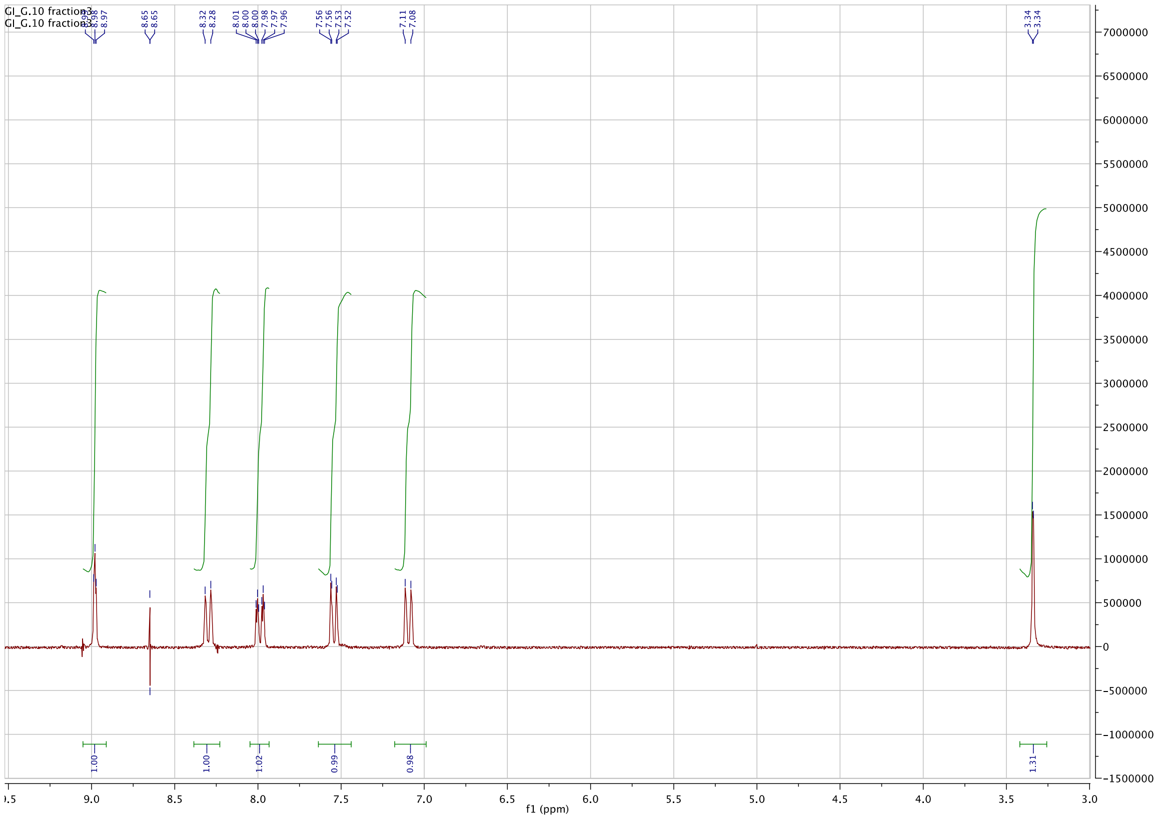
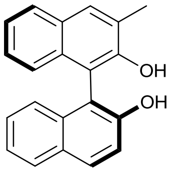
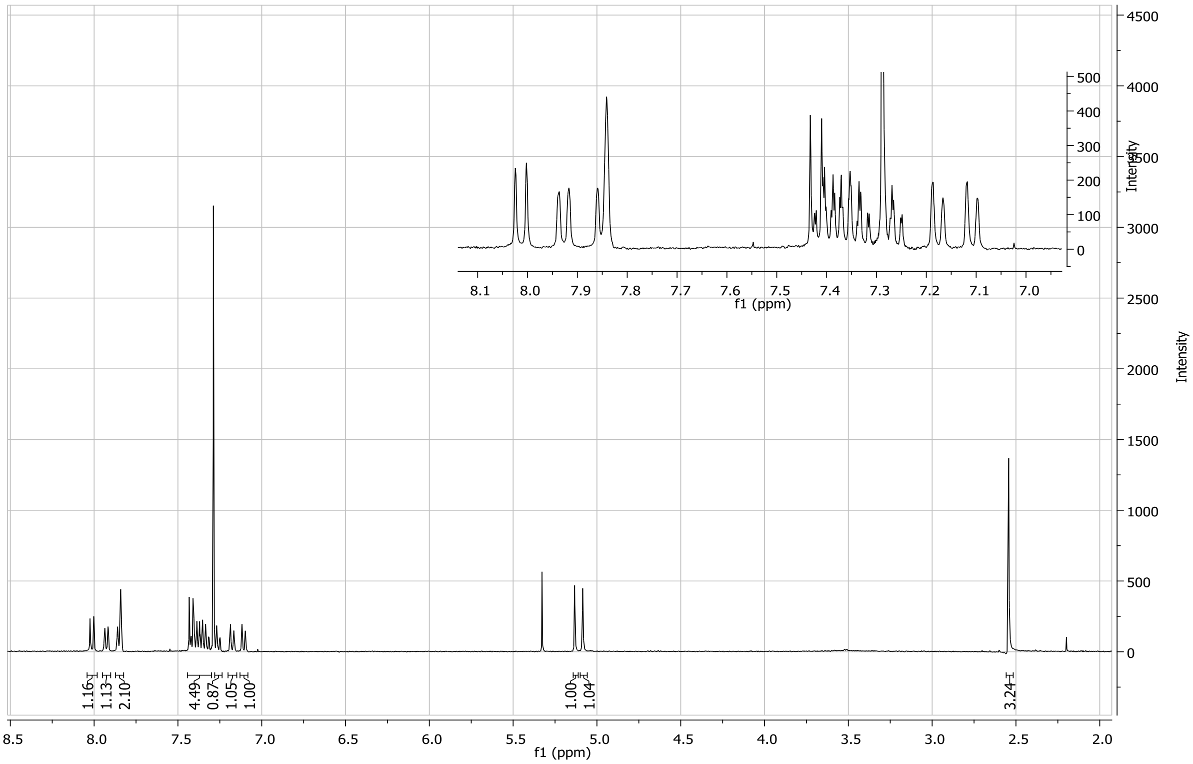


Figure ES8. ^{1}H NMR spectrum of **6c**.

(*S*)-3-Methyl-1,1'-binaphthyl-2,2'-diol ((*S*)-7a)[5]





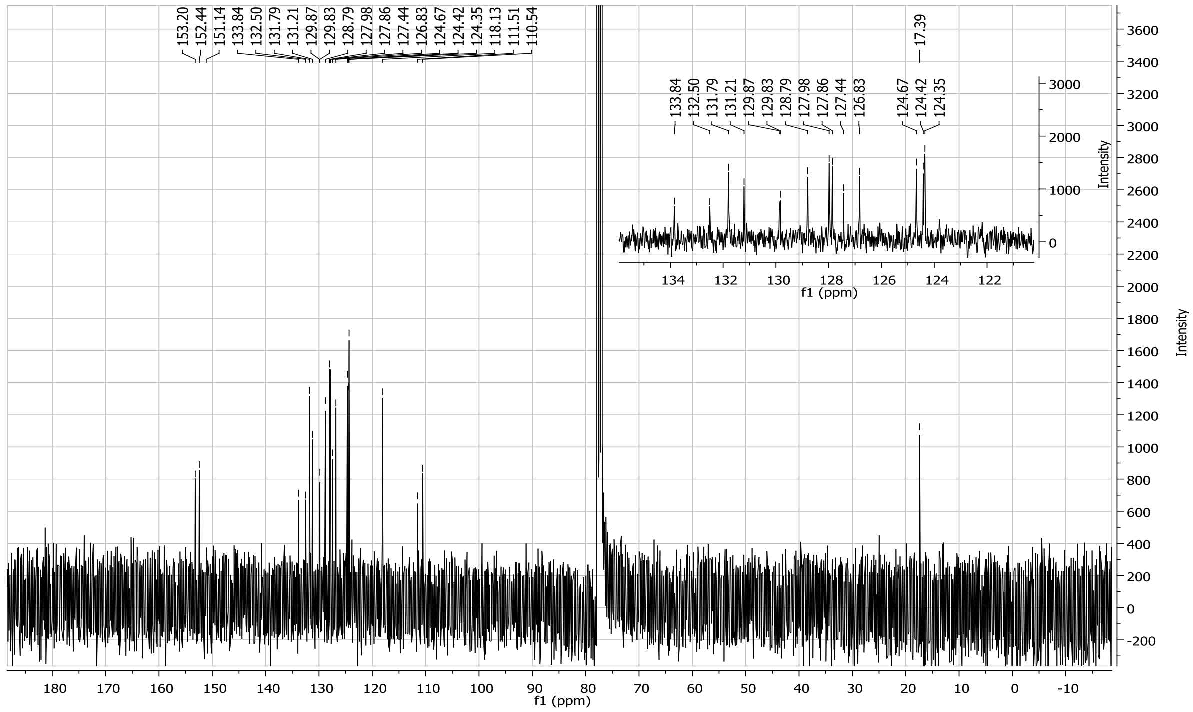
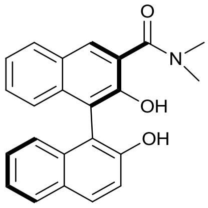


Figure ES9. ^{1}H NMR and ^{13}C NMR spectra of **7a.**

(*R*)-2,2'-Dihydroxy-N,N-dimethyl-1,1'-binaphthyl-3-carboxamide ((*R*)-7b)[5]



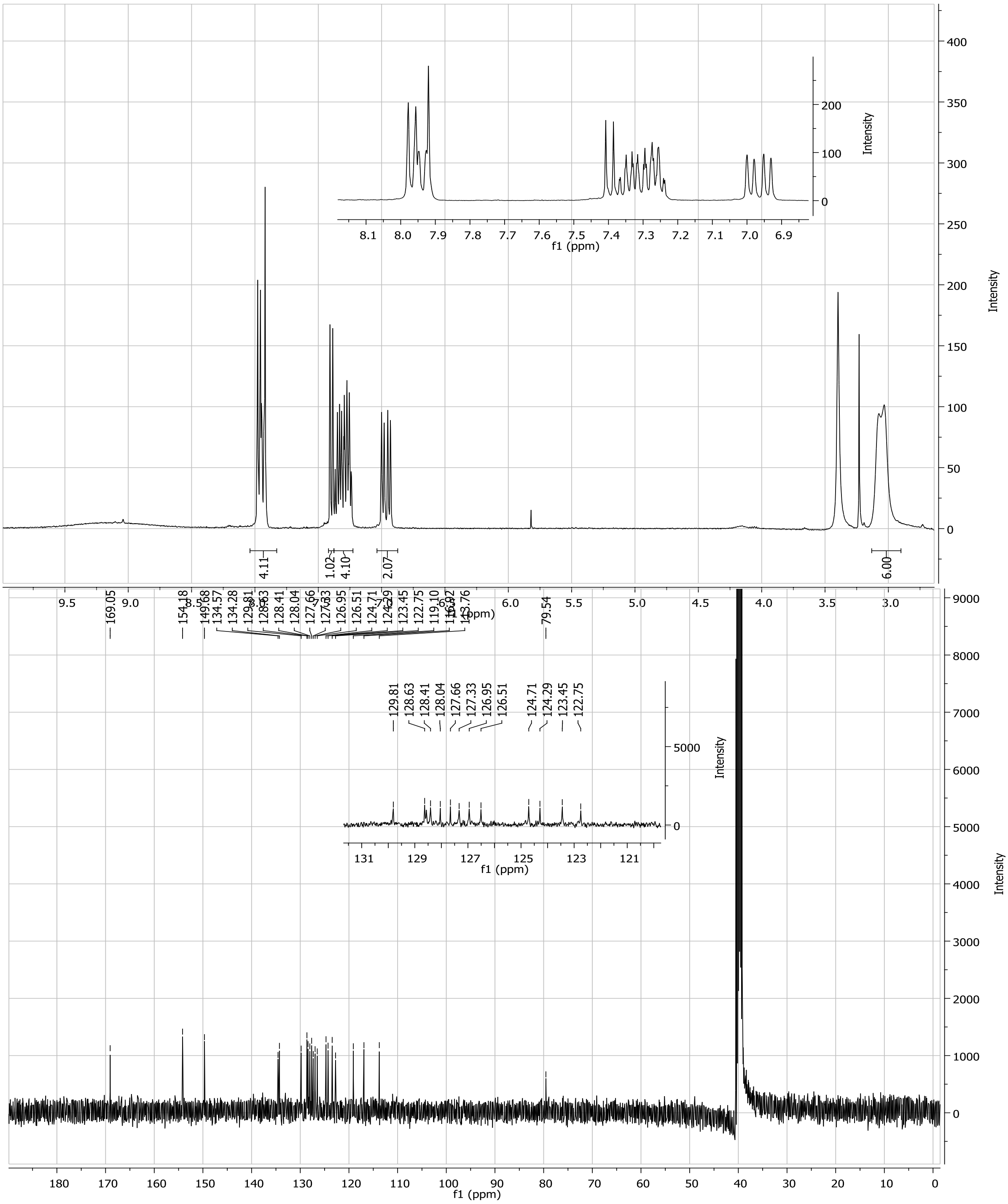
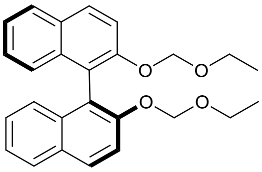


Figure ES10. ^{1}H NMR and ^{13}C NMR spectra of **7b**.

(*S*)-2,2'-Bis(ethoxymethoxy)-1,1'-binaphthyl ((*S*)-7c)[5]



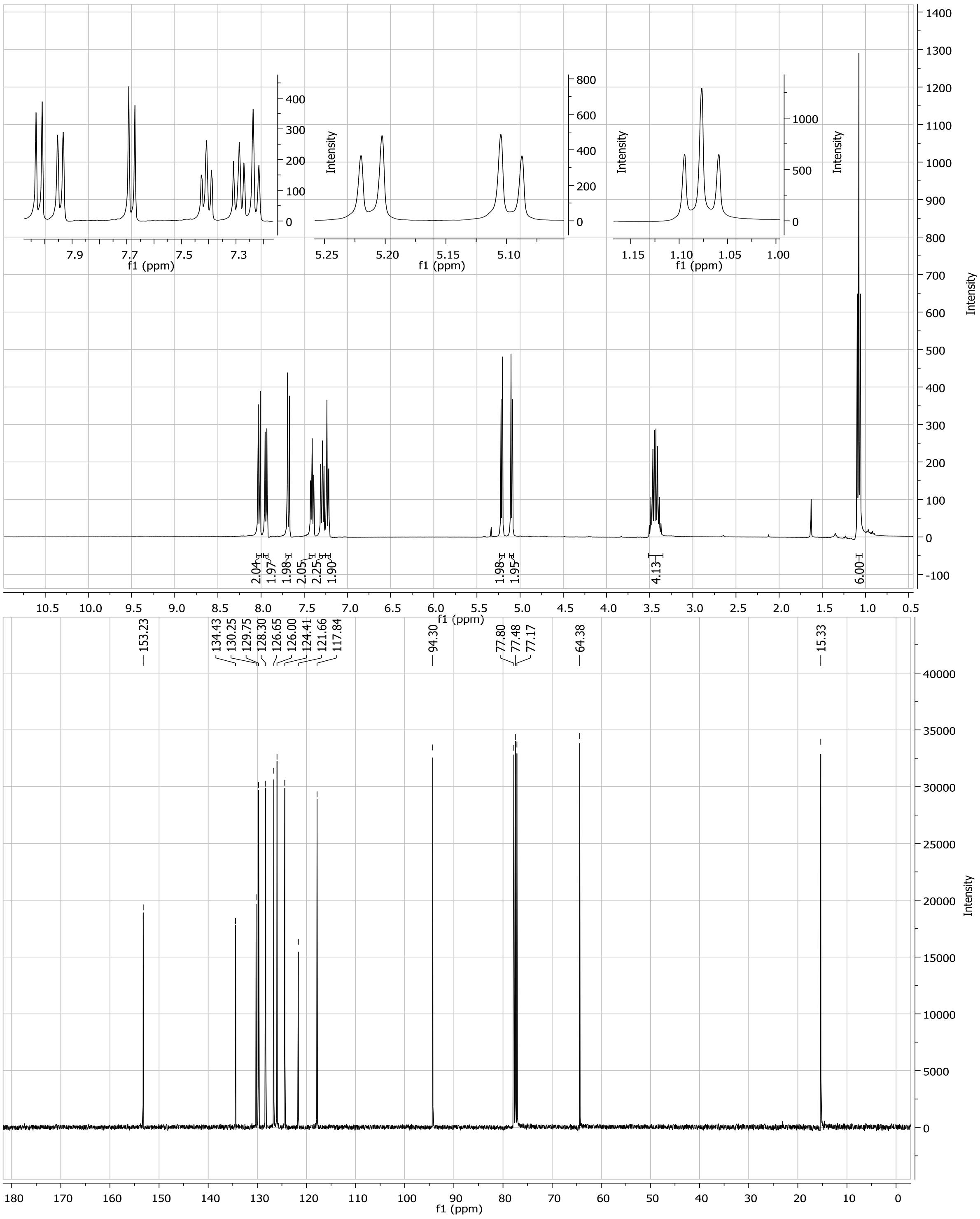


Figure ES11. ^{1}H NMR and ^{13}C NMR spectra of **7c**.

4-Nitrilestyrene[6]

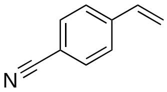
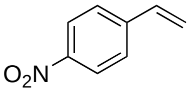


Figure ES12. ^{1}H NMR spectrum of 4-nitrilestyrene.

4-Nitrostyrene[6]



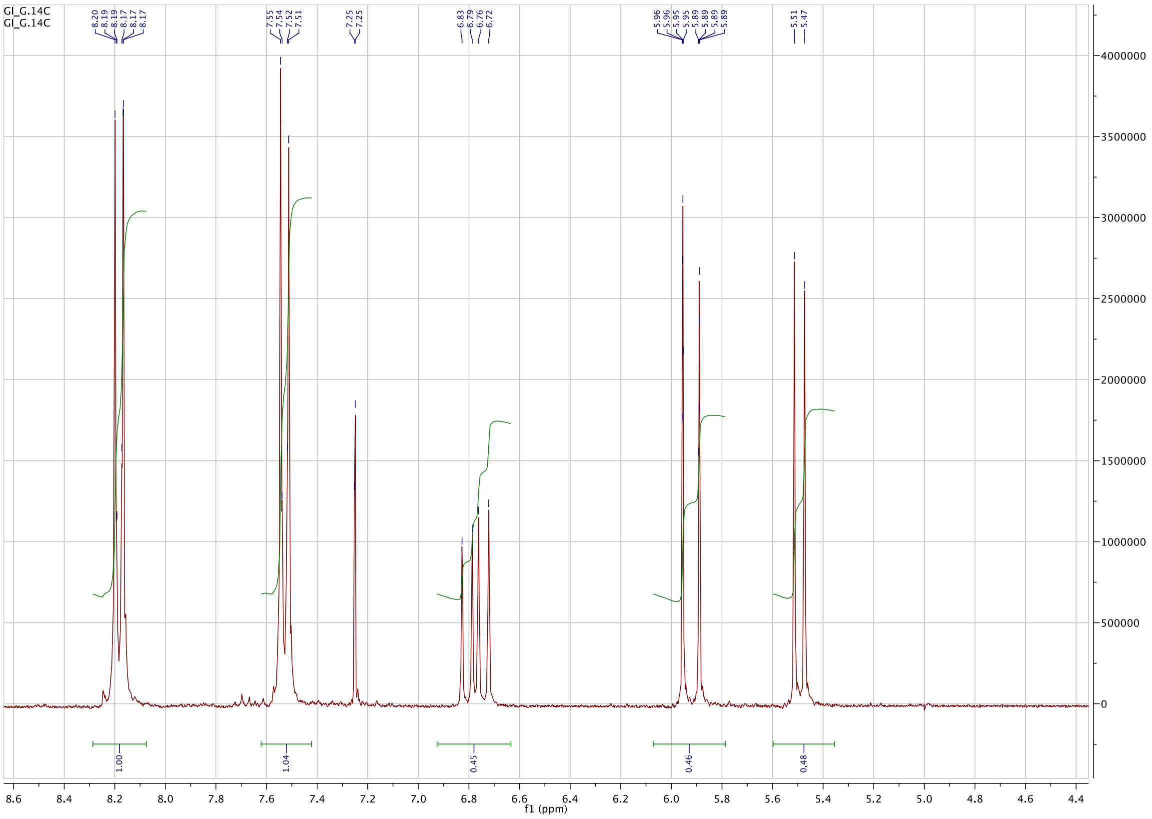


Figure ES13. ^{1}H NMR spectrum of 4-nitrostyrene.

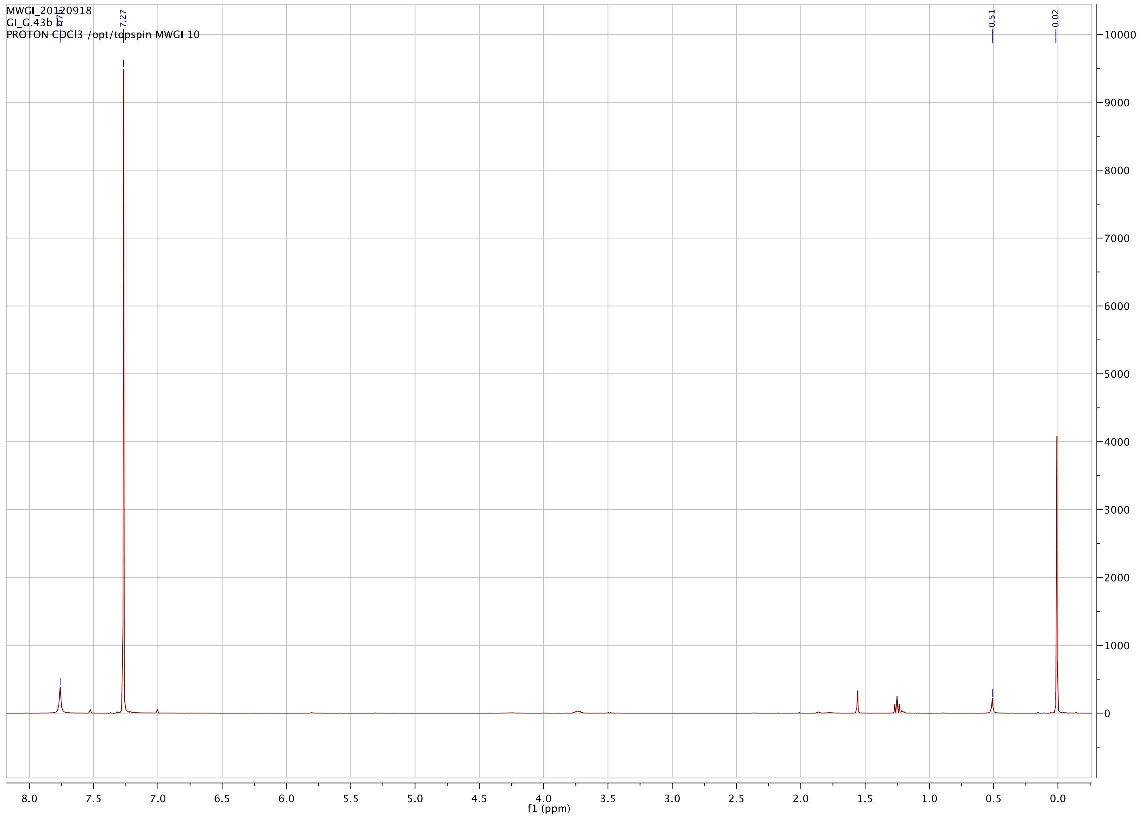


Figure ESI14 1H NMR spectrum used to calculate magnetic moment of complex *9*[7]

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