Supporting Information

For

First Enantioselective Iron-Porphyrin-Catalyzed Sulfide Oxidation with Aqueous Hydrogen Peroxide

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A. General Experiments

All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate drying agent prior to use: MeOH from turning Mg. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck pre-coated aluminium foil sheets (Silica gel 60 with fluorescent indicator UV_{254}). Compounds were visualized with UV light at 254 nm. Column chromatographies were carried out using silica gel from Merck (0.063-0.200 mm).. UV-visible spectra were recorded on a UVIKON XL from Biotech. Gas chromatography analysis were performed on a Varian CP- 3380 gas chromatography equipped with a CP-1177 injector The enantiomeric excess of the sulfoxides was determined on a Varian Prostar 218 system equipped with Chiralcel columns. The optical rotations were determined on a Perkin Elmer 341 polarimeter.

The porphyrins were synthesised by literature methods. The corresponding iron porphyrins were prepared as previously reported.[28]

Catalytic Oxidation Procedures

Fer porphyrin complex **1** (1.8mg, 1 µmol) was placed in a test tube under argon. Then, 1 ml of distilled methanol was added, followed by sulfide (100 µmol) and 35 % H_2O_2 (11.6 mg, 120 µmol) in one portion. After 1 hour, the mixture was analysed by GC for yield. Then, the reaction was quenched by addition of water and the sulfoxides were extracted with CH_2Cl_2. The ees of the sulfoxides were determined by chiral HPLC.

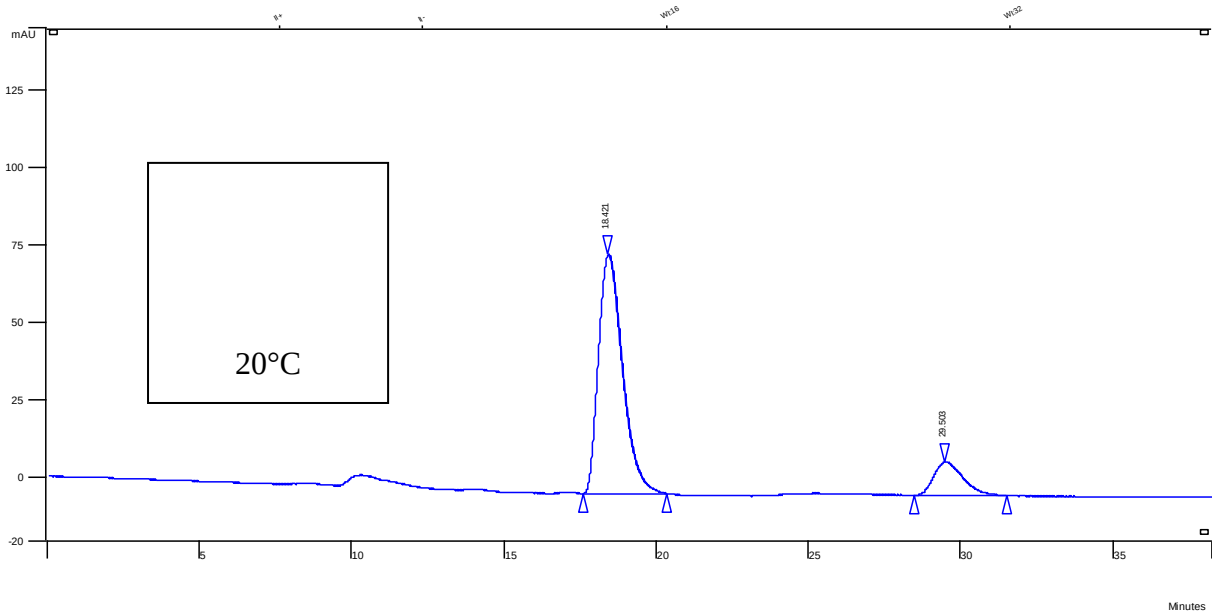

Figure S1 : HPLC of methyl phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 70/30, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	18.421	85.4720	
2	29.503	14.5280	70.944

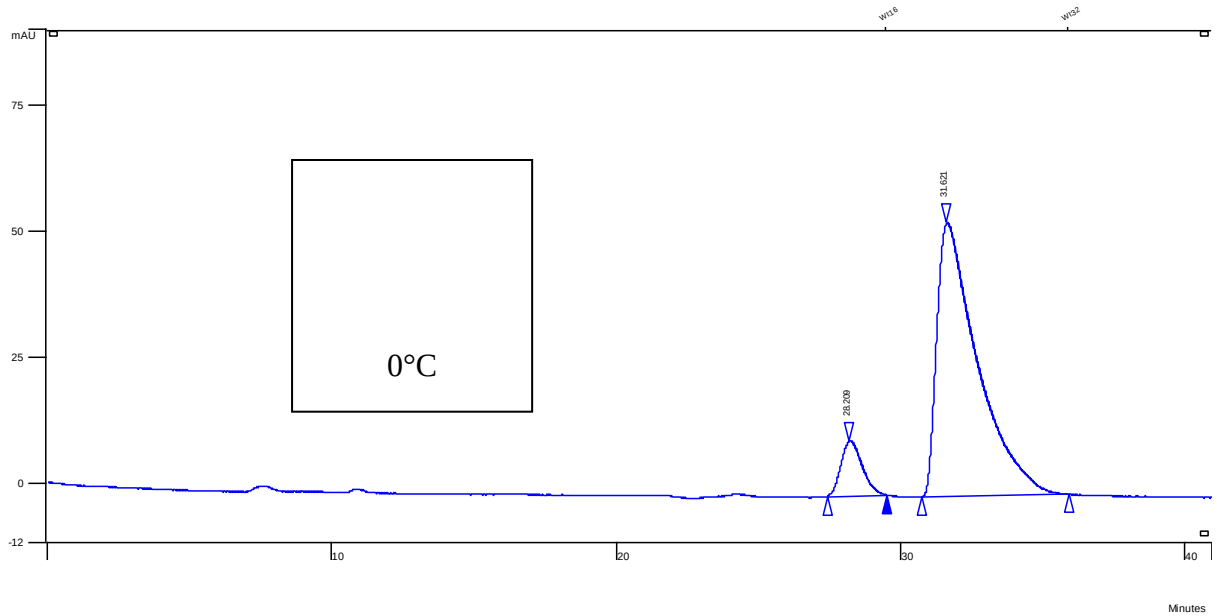

Figure S2 : HPLC of methyl phenyl sulfoxide with a chiralcel OD-H column: n-hexane/isopropanol = 90/10, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	28.209	9.5111	
2	31.621	90.4889	80.9778

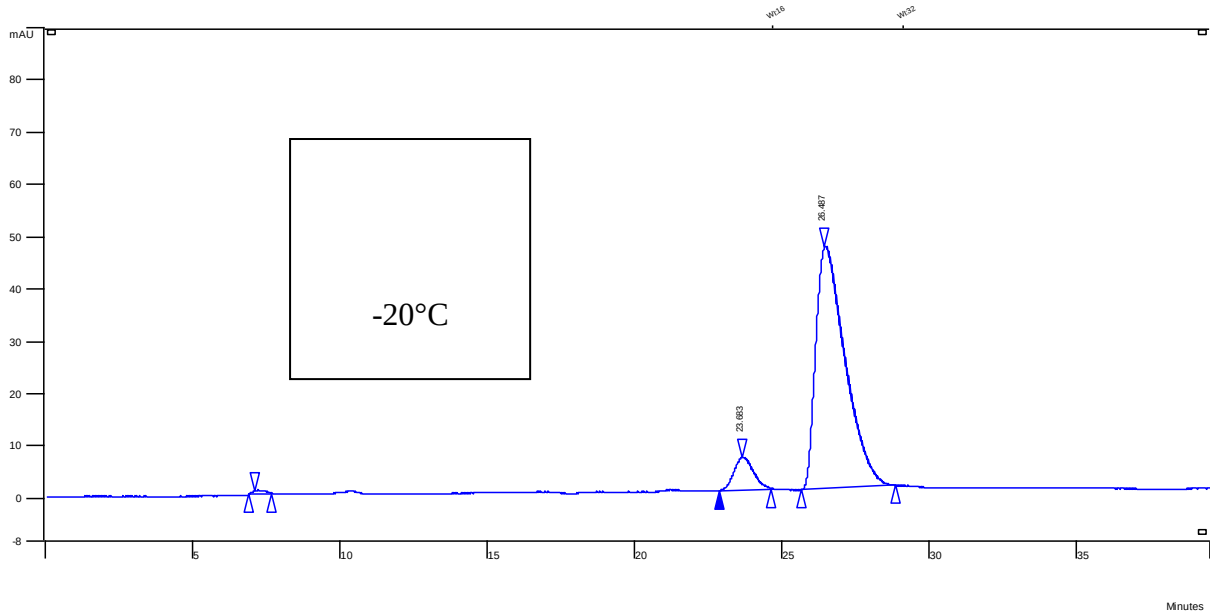

Figure S3: HPLC of methyl phenyl sulfoxide with a chiralcel OD-H column: n-hexane/isopropanol = 90/10, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	23.683	8.0443	
2	26.487	91.9557	83.9114

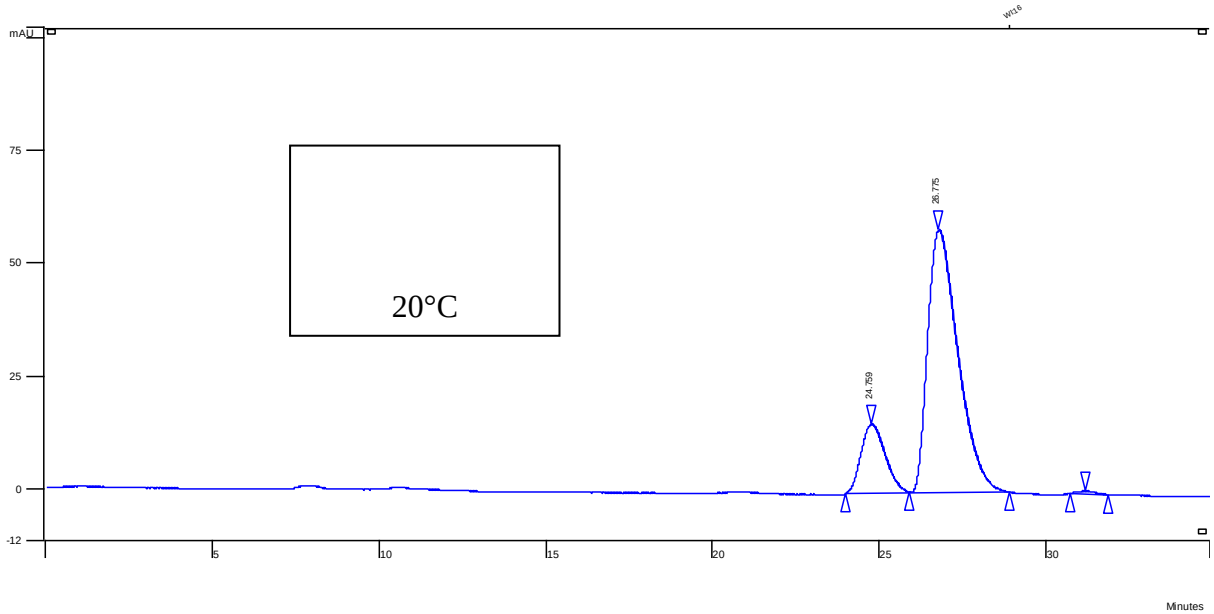

Figure S4: HPLC of methyl tolyl sulfoxide with a chiralcel OD-H column: n-hexane/isopropanol = 90/10, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	24.759	17.5130	
2	26.775	82.4870	64.974

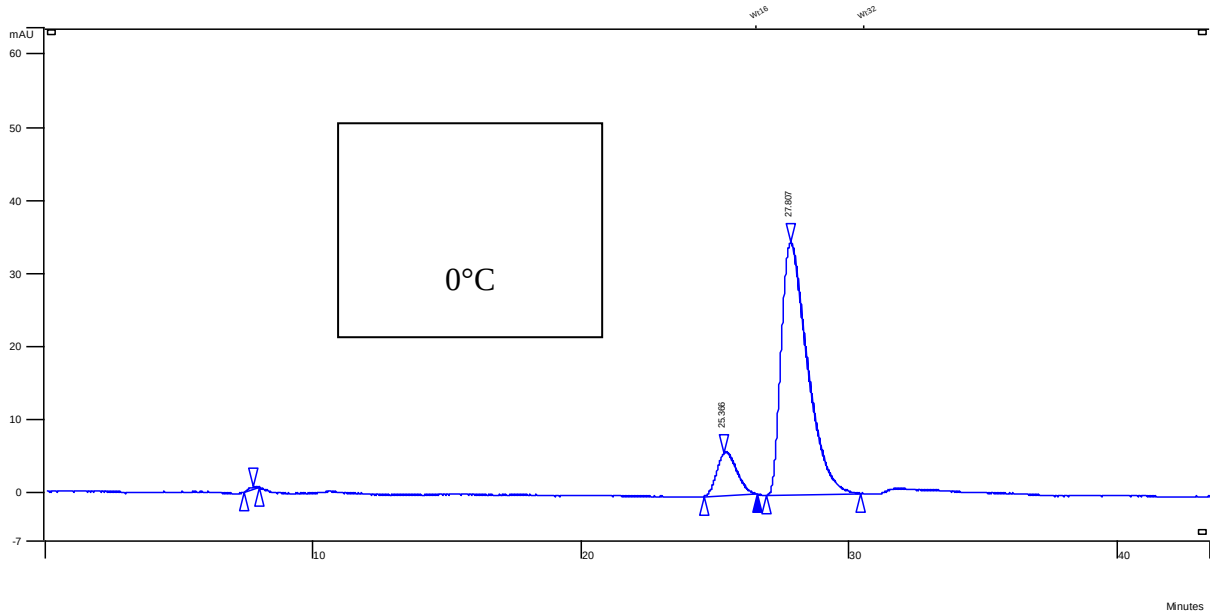

Figure S5: HPLC of methyl tolyl sulfoxide with a chiralcel OD-H column: n-hexane/isopropanol = 90/10, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	25.366	11.6868	
2	27.807	88.3132	76.6264

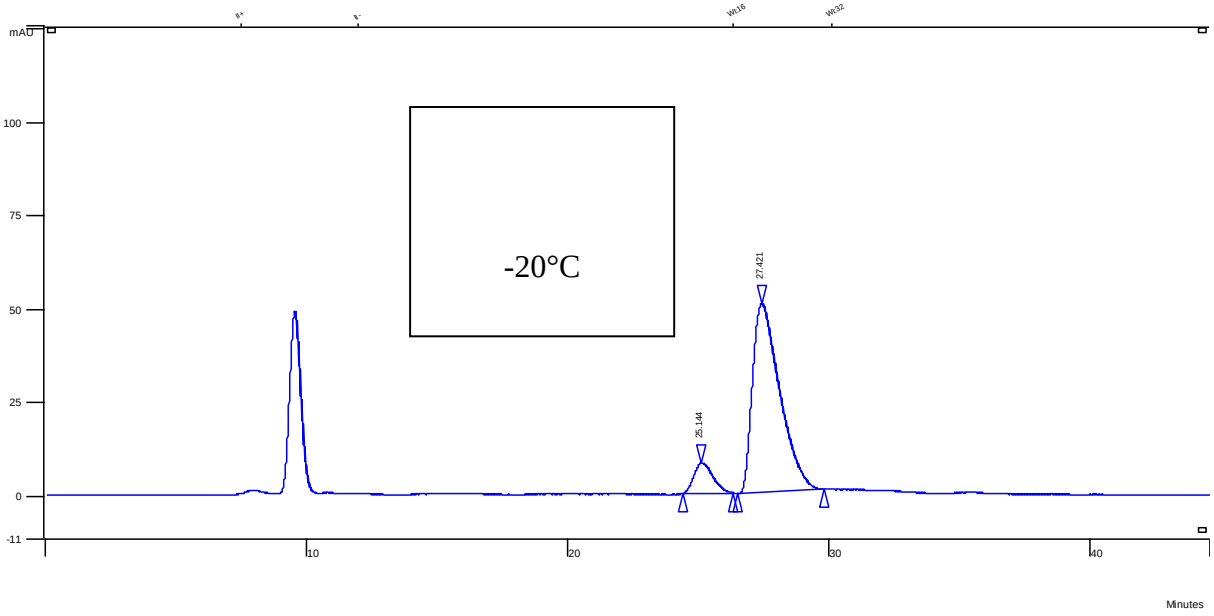

Figure S6: HPLC of methyl tolyl sulfoxide with a chiralcel OD-H column: n-hexane/isopropanol = 90/10, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	25.137	10.5337	
2	27.421	89.4662	78.9325

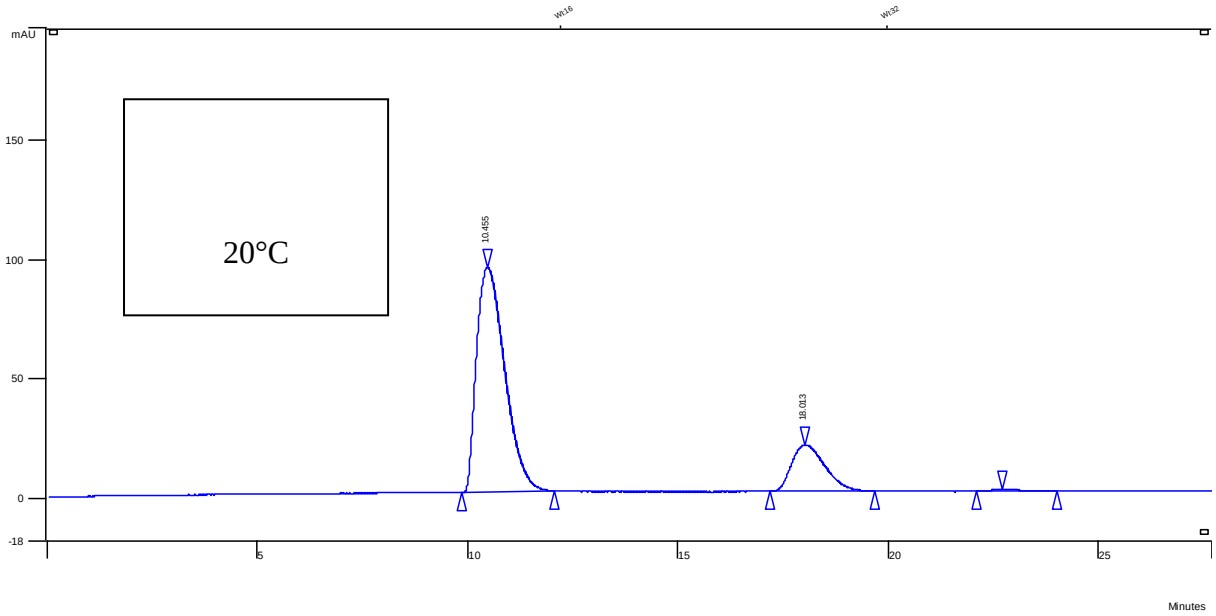

Figure S7: HPLC of methyl p-methoxy phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	10.455	80.3742	
2	18.013	19.6258	67.7484

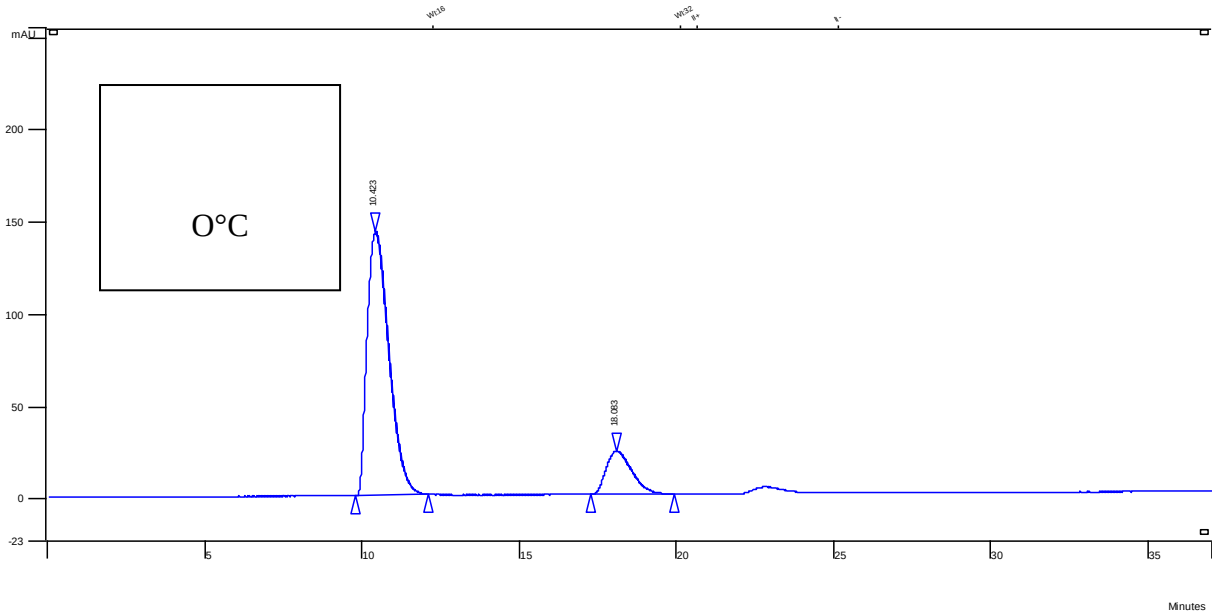

Figure S8: HPLC of methyl p-methoxy phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	10.423	83.9410	
2	18.083	16.0589	67.8821

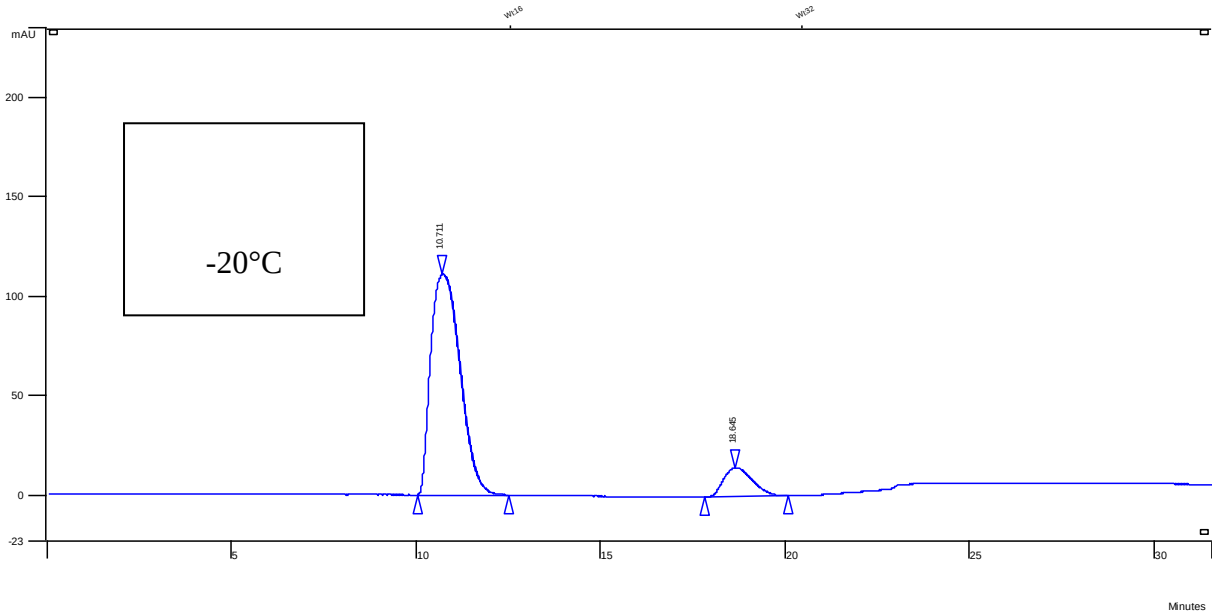

Figure S9: HPLC of methyl p-methoxy phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	10.711	88.3163	
2	18.645	11.6837	76.6326

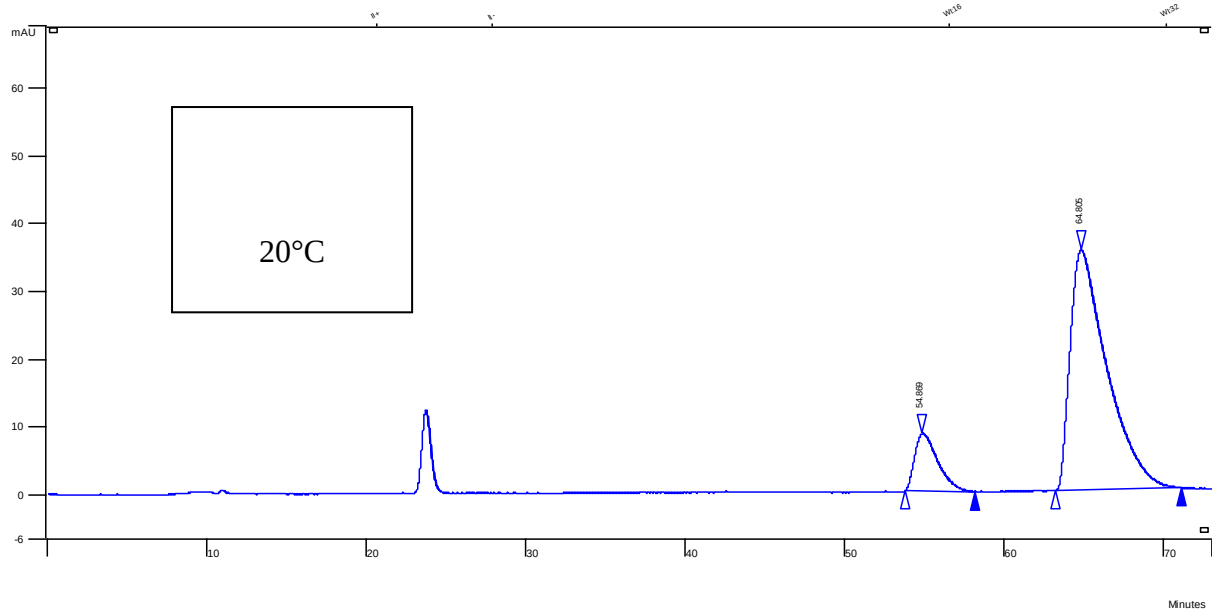

Figure S10: HPLC of methyl p-nitro phenyl sulfoxide with a chiralcel OJ-H column: n-hexane/isopropanol = 80/20, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	54.885	12.8524	
2	64.813	87.1475	74.2951

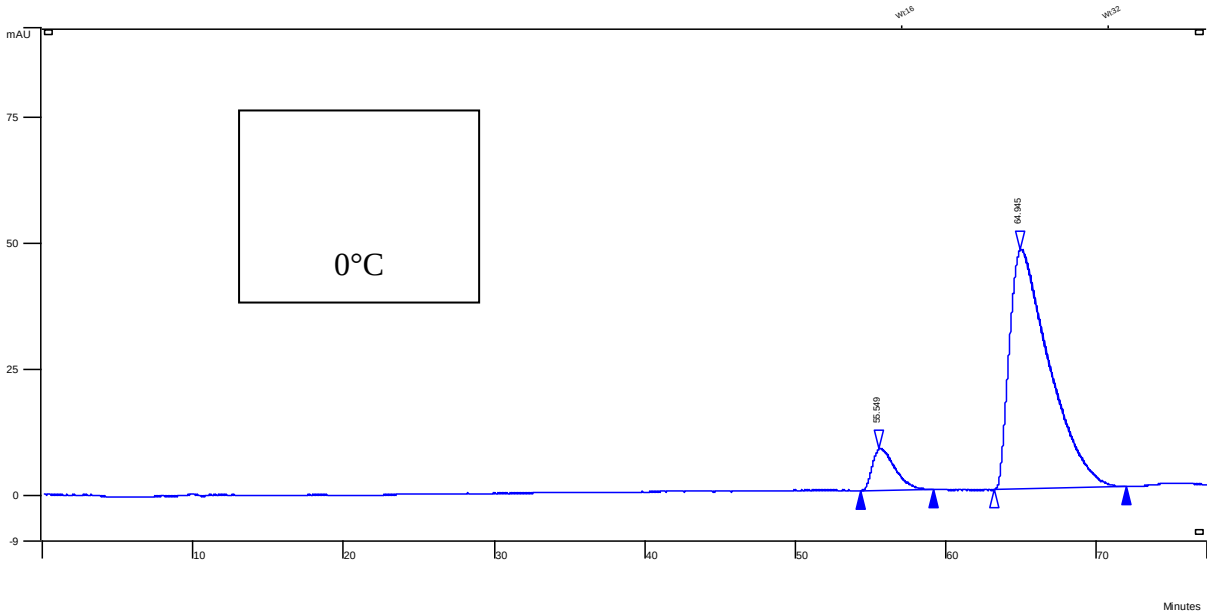

Figure S11: HPLC of methyl p-nitro phenyl sulfoxide with a chiralcel OJ-H column: n-hexane/isopropanol = 80/20, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	55.549	8.8198	
2	64.945	91.1802	82.3604

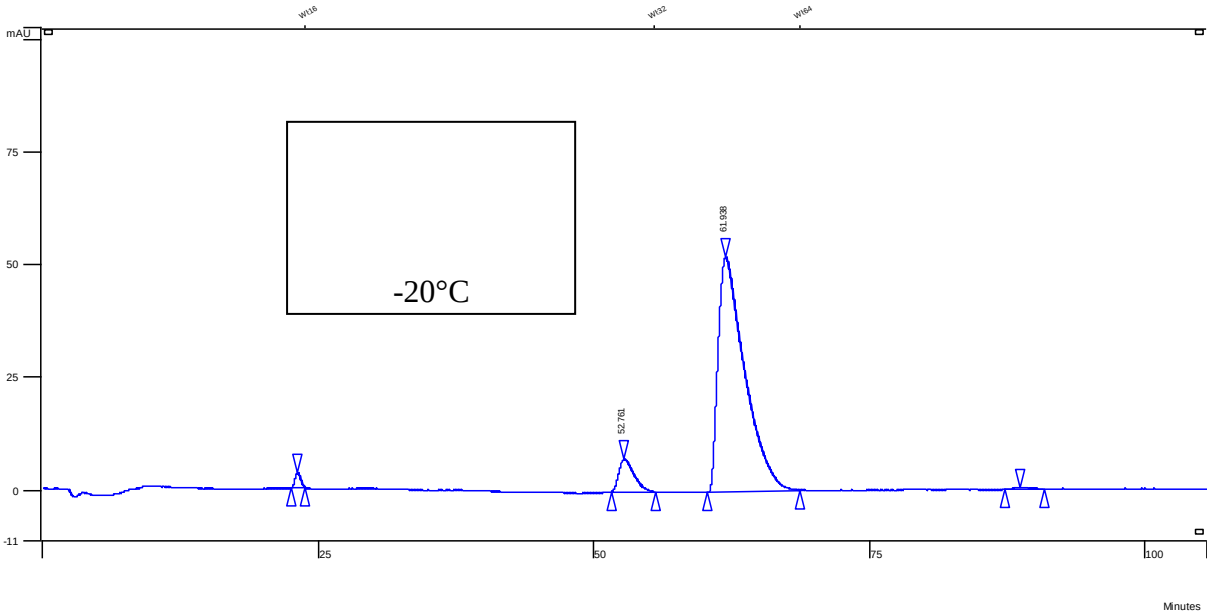

Figure S12: HPLC of methyl p-nitro phenyl sulfoxide with a chiralcel OJ-H column: n-hexane/isopropanol = 80/20, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	52.761	7.3998	
2	61.938	92.6002	85.2004

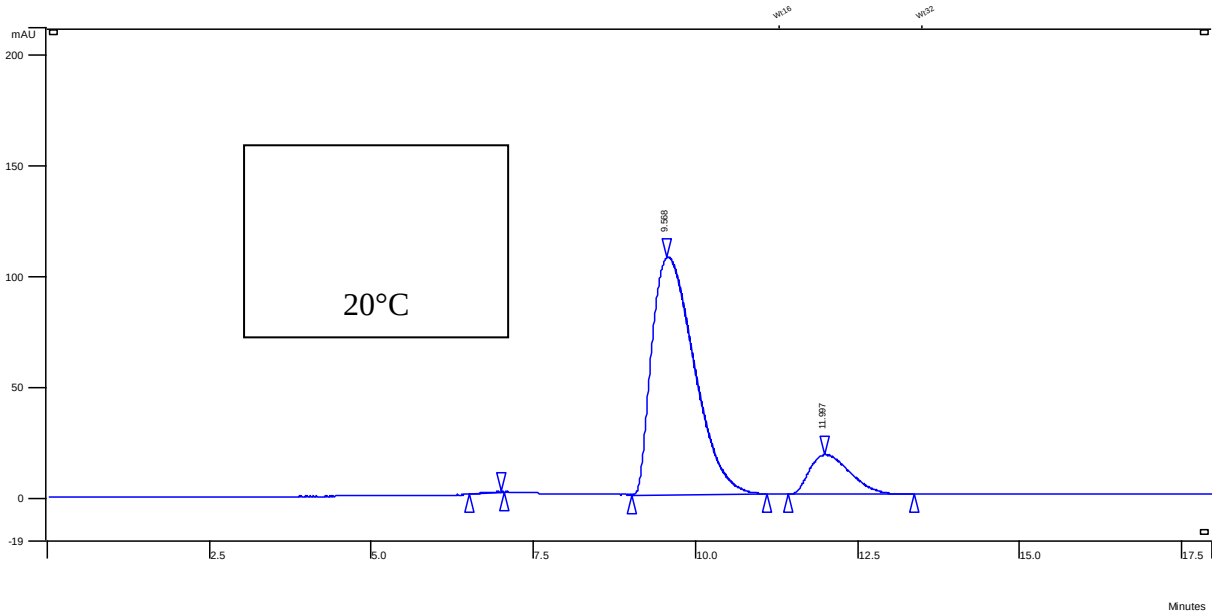

Figure S13: HPLC of methyl p-bromo phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	9.568	86.1846	
2	11.997	13.8153	72.3693

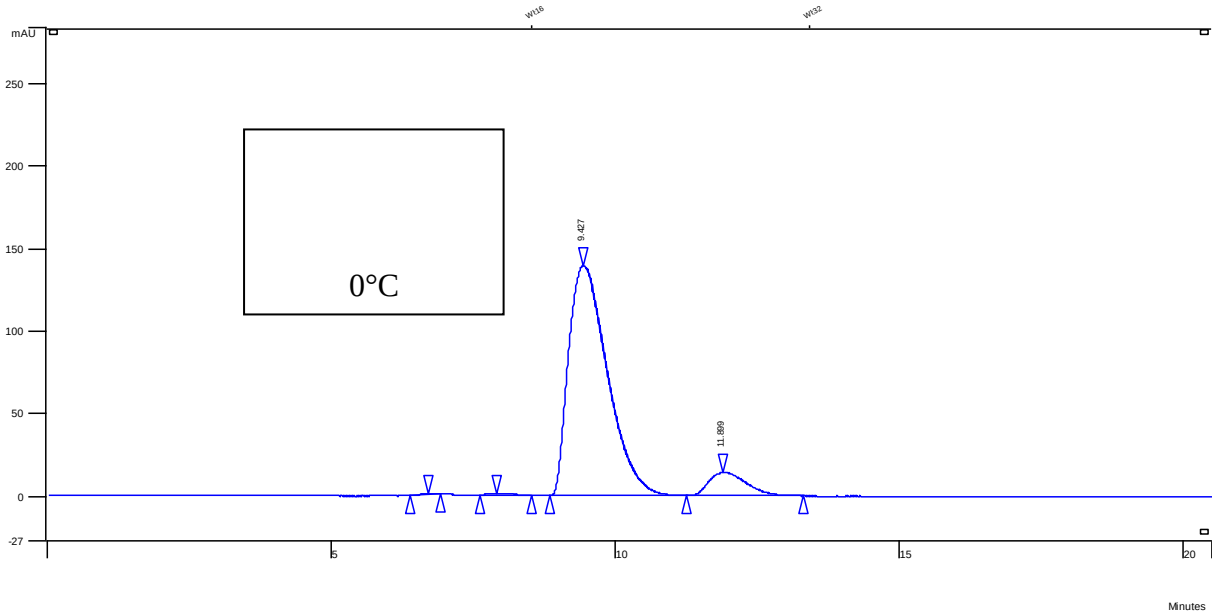

Figure S14: HPLC of methyl p-bromo phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	9.427	91.0857	
2	11.899	8.9143	82.1714

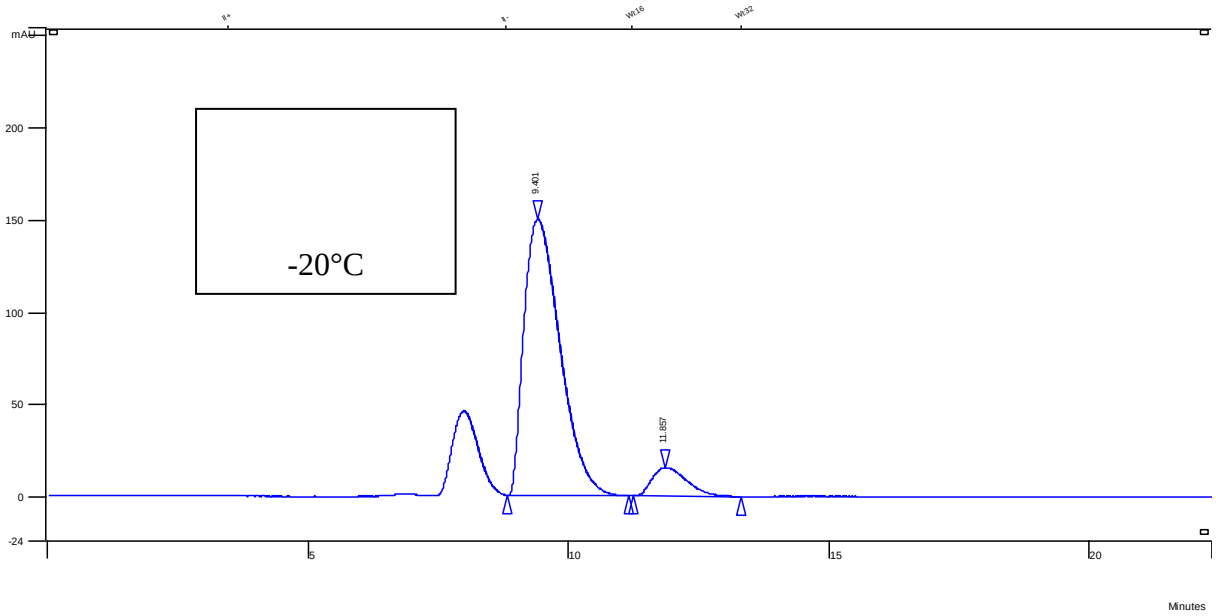

Figure S15: HPLC of methyl p-bromo phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	9.401	91.0708	
2	11.857	8.9291	82.1417

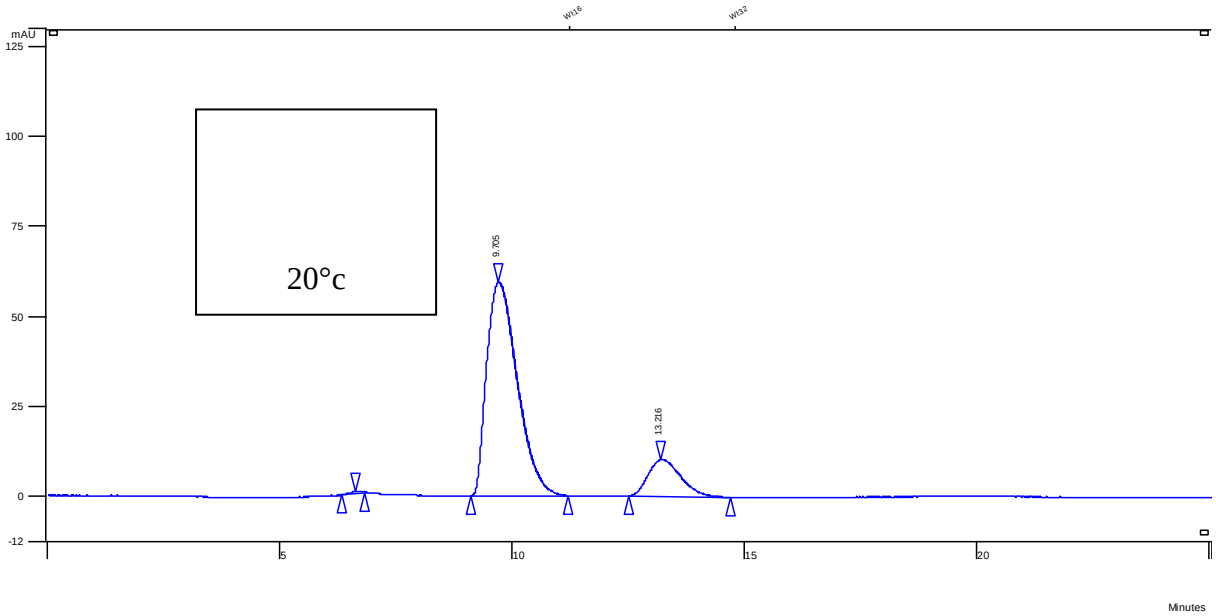

Figure S16: HPLC of methyl o-bromo phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	9.705	84.5615	
2	13.216	15.4385	69.1230

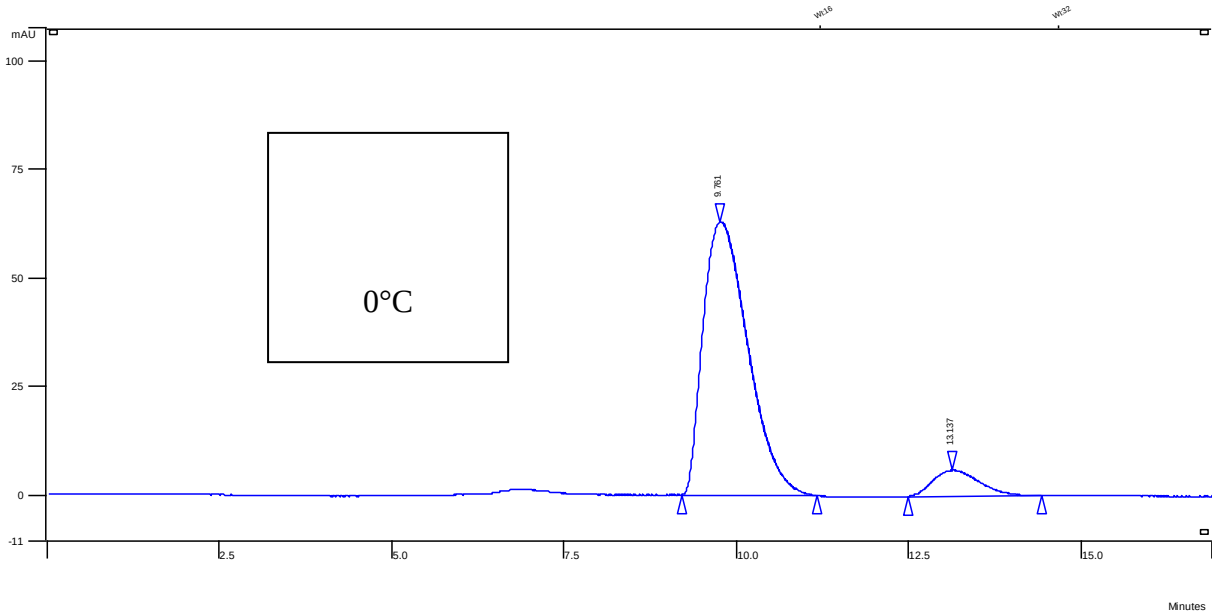

Figure S17: HPLC of methyl o-bromo phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	9.761	90.9667	
2	13.137	9.0333	81.9334

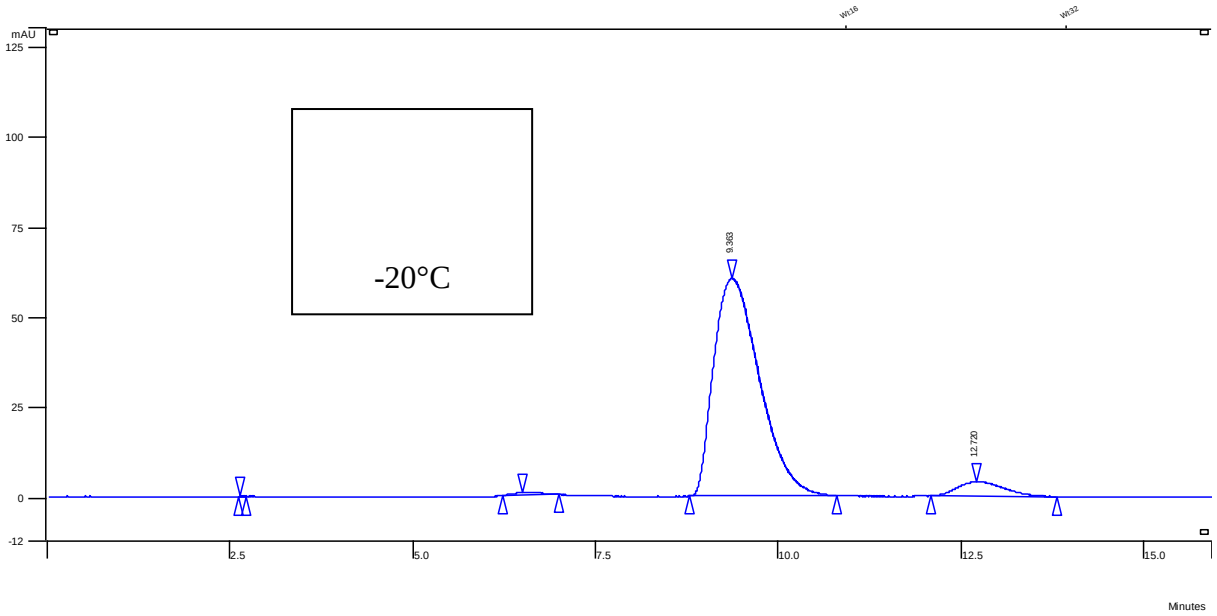

Figure S18: HPLC of methyl o-bromo phenyl sulfoxide with a chiralcel OB-H column: n-hexane/isopropanol = 50/50, flow rate = 0.5ml/mn, wavelength = 220 nm.

Peak	Ret. Time (min)	% Area	EE (%)
1	9.363	93.6558	
2	12.720	6.3442	87.3116

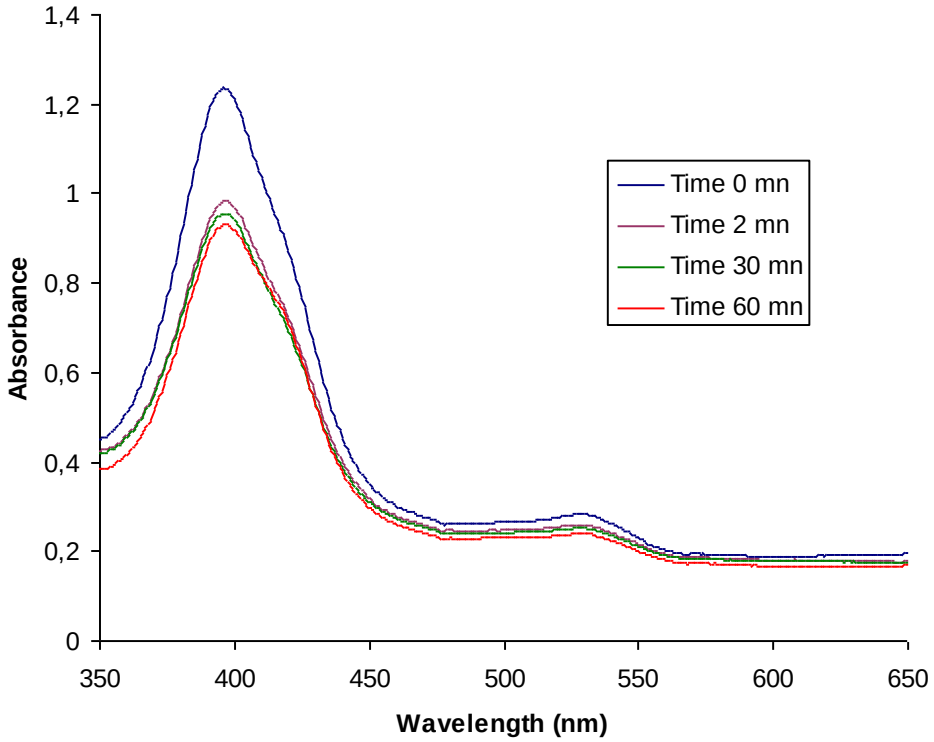

Figure S19. Visible spectral changes observed after addition of H_2O_2 to a solution of **1** in MeOH at ambient temperature

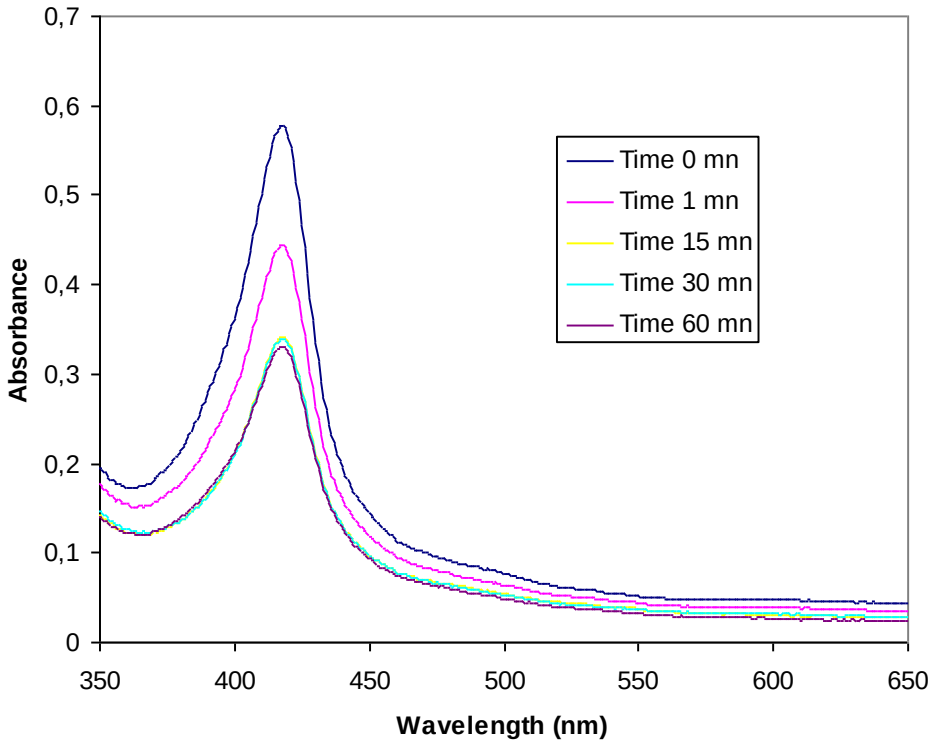

Figure S20. Visible spectral changes observed after addition of H_2O_2 to a solution of **1** + 2-Me Imidazole (10 eq.) in MeOH at ambient temperature