Supporting information

Enzymatic Kinetic Resolution of Chiral Sulfoxides - An Enantiocomplementary Approach

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1. General

All starting reagents were commercially available and of analytical purity, which were used without further treatment unless otherwise stated. Racemic sulfoxides were prepared according to the literature procedures[1–4] unless otherwise stated. Solvents were dried according to standard methods. ^{1}H NMR spectra were obtained at 400 MHz. ^{13}C NMR spectra were obtained at 100 MHz and were ^{1}H decoupled. Chemical shifts (δ) are reported in ppm relative to solvent ($(CH_3)_2SO$: δ_C = 40.2 ppm) or residual solvent peak ($(CH_3)_2SO$: δ_H = 2.50 ppm). Accurate mass measurements (HRMS) were obtained by ESI on an Agilent 6530 Q-TOF MS spectrometer. Analytical HPLC was performed under the following conditions: Agilent Eclipse plus C18 column (3.5 µL, 4.6×100 mm); UV/Vis detection at λ_{obs} = 254 nm, 220 nm or 300 nm; flow rate 0.4 mL/min; gradient elution method (0.1% aqueous formic acid – CH_3CN from 95:5 to 0:100 in 13 min. Analytical TLC was performed using a precoated silica gel 60 Å F_{254} plates (0.2 mm thickness) and visualized by irradiation with UV light at 254 nm or by dipping in stain solution ($KMnO_4$, CAM) followed by heating. Preparative column chromatography was carried out using silica gel 60 Å (particle size 0.063–0.200mm). Enantiomeric excesses were determined by chiral HPLC analysis using Daicel Chiralpak (IA, IC) and Chiralcel OD-H columns and a mixture of *n*-heptane/propan-2-ol as the eluent. The detailed conditions are given at the characterization part of the products. The absolute configurations of the products were determined by the comparison of chiral HPLC retention times and optical rotation values with the literature. Selectivity factor *s* was calculated according to formula $s = \ln[(1-c)(1-ee)]/\ln[(1-c)(1+ee)]$.[5] Optical rotations were measured on an automatic polarimeter Autopol III. Infrared spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrophotometer. Purifications by HPLC were performed under the following conditions: Agilent ZORBAX SBC18 column (5 µL, 9.4x150 mm); UV/Vis detection at λ_{obs} = 254 and 300 nm; flow rate 4 mL/min; gradient elution methods (method 0.1% ammonium formate in H_2O – CH_3CN from 50:50 to 0:100 in 20 min.

2. Preparation of Methionine Sulfoxide Reductases B (*H. sapiens* (CBS-1),[6] *N. gonorrhoeae* (pilB),[7] *T. kodakarensis* (MsrB)[8] and *A. thaliana* (MsrB2)[9])

Genes of MsrB domains (*H. sapiens* (CBS-1), *N. gonorrhoeae* (pilB), *T. kodakarensis* (MsrB)) in pET16b vectors from Genescript and MsrB2 (*A. thaliana*) in pQE30 vector[9] were transformed into chemically competent *E. coli* BL21(DE3) cells (Agilent) according to the manufactures protocol and an aliquot was plated on LB agar with ampicillin (100 mg/L) and grew overnight at 37 °C. One colony of *E. coli* BL21(DE3) with the corresponding MsrB was used for overnight preculture, then the preculture (0.4 mL) was used to inoculate 100 ml of LB medium with ampicillin (100 mg/L). The bacterial culture was incubated at 37 °C, 200 rpm until OD_{600} ~ 0.4 was reached. Then the production of MsrB was induced either with 0.2 mM IPTG (MsrB2 from *A. thaliana*) or 0.5 mM IPTG (all other MsrBs) and the culture was incubated either at 22 °C (MsrB2 from *A. thaliana*) or at 37 °C (all other MsrBs), 200 rpm overnight. Cells were harvested by centrifugation (4000 × g for 30 min at 4 °C). The cell pellet was resuspended in LEW buffer (50 mM NaH_2PO_4, 300 mM NaCl, pH 8) and lysed by ultrasound. Cell debris was removed by centrifugation (10 000 × g for 30 min at 4 °C), the soluble fraction was loaded onto Protino Ni-IDA resin column (Macherey-Nagel) and purified by gravity flow at ambient temperature. The column was washed with 2 × 8 mL of LEW buffer and finally the protein was eluted with 2 × 2 mL of elution buffer (50 mM NaH_2PO_4, 300 mM NaCl, 250 mM imidazole, pH 8). Purity was determined via SDS-PAGE. Elution buffer was exchanged to storage buffer (20 mM Tris-HCl buffer, 1 mM DTT, 10% glycerol, 0.1 M NaCl, pH 8.0) with Amicon Ultra-4 centrifugal filter (3000 MWCO) and yielded approximately 10 mg of protein. Purification of CBS-1 reductase provided only a very low yield of the desired product and thus this reductase was not used in further experiments. Protein concentration was determined from the absorbance at 280 nm (using calculated extinction coefficient).

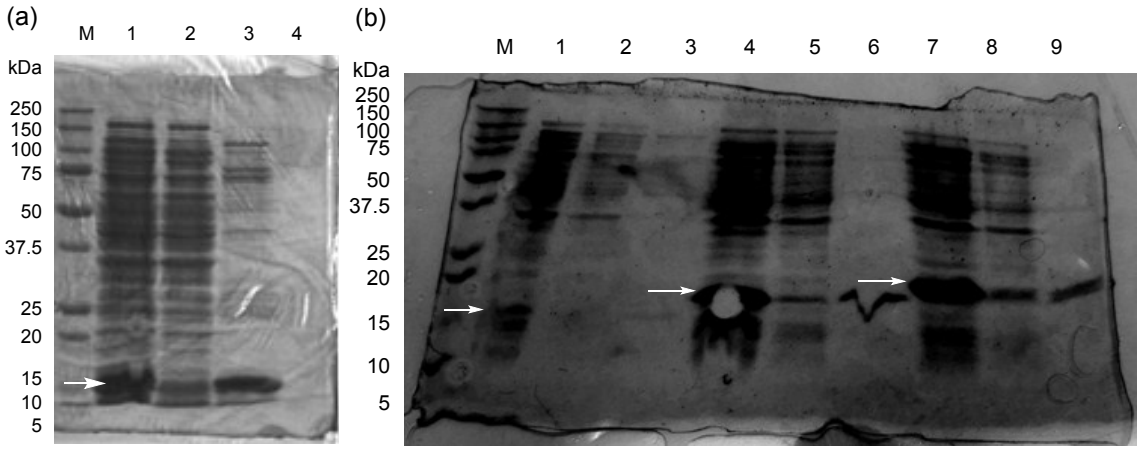
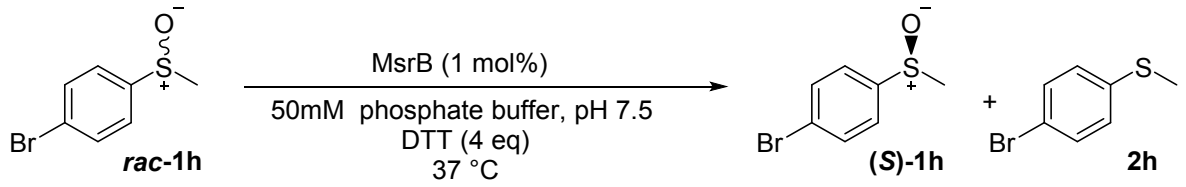


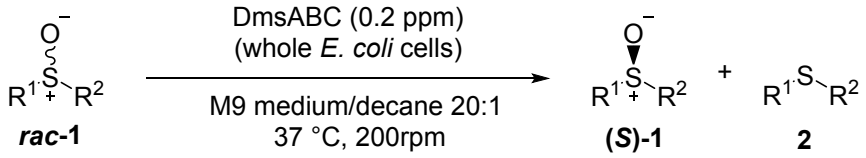
Fig. S1: (a) SDS-PAGE MsrB2 (*A. thaliana*): (M)-protein mass marker, (1)-lysate, (2)-flow through, (3)-elution; (b): SDS-PAGE MsrBs: (M)-protein mass marker; CBS-1 (*H. sapiens*): (1)-lysate, (2)- flow through, (3)- elution; PilB (*N. gonorrhoeae*): (4)-lysate, (5)- flow through, (6)- elution; MsrB (*T. kodakarensis*): (7)-lysate, (8)- flow through, (9)- elution.

3. Procedure for the Kinetic Resolution of Racemic Sulfoxides with Isolated Enzymes MsrBs (*N. gonorrhoeae* (pilB), *T. kodakarensis* (MsrB) and *A. thaliana* (MsrB2))



A 1.5 mL Eppendorf vial was charged with individual solutions of DTT (1440 µL of 27 mM, 4 equivs., 26 mM final concentration) in phosphate buffer (50 mM Na_2HPO_4, 50 mM NaH_2PO_4, 50 mM NaCl, pH 7.5) and a racemic sulfoxide (30 µL of 324 mM, 9.7 µmol, 6.5 mM final concentration) in CH_3CN. The resulting mixture was gently mixed and the reaction was initiated by the addition of the corresponding MsrB (1 mol%, 65 µM final concentration) in a storage buffer. The reaction mixture was incubated at 37 °C at 250 rpm. The course of the reaction was monitored by analytical HPLC. After 44 h the reaction with the highest conversion of 44% (MsrB2 *A. thaliana*) was selected for further analysis (the conversion of the reactions with the other MsrBs was below 10%). The reaction mixture was extracted with toluene (2 × 4 mL), washed with H_2O (2 mL), brine (2 mL), dried under $MgSO_4$ and concentrated by rotary evaporation under reduced pressure. The enantiomeric excess of the crude product was determined by chiral HPLC (ee = 63%) providing s = 17.

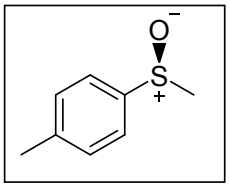
4. General Procedure for the Kinetic Resolution of Racemic Sulfoxides with DmsABC reductase



A 2 mL preculture of *E. coli* (*msrA* knock out - KEIO collection ID JW4178)[10] was used to inoculate 400 mL LB medium with kanamycin (50 mg/L). The bacterial culture was incubated at 37 °C, 200 rpm until OD_{600} of 3 was reached. Then, 47 mL aliquot of the bacterial culture was withdrawn, and cells were harvested by centrifugation (4200 × g, 30 min, 4 °C). The cell pellet was washed with M9 minimal medium (48 mM Na_2HPO_4, 22 mM KH_2PO_4, 8.6 mM NaCl, 18.7 mM NH_4Cl, 2 mM $MgSO_4$, 0.1 mM $CaCl_2$, 0.4% glycerol, pH 7.0) and centrifuged (4200 × g, 30 min, 4 °C). Cells resuspended in M9 minimal medium (2 mL) were added to a mixture of racemic sulfoxide (0.065 mmol) in M9 minimal medium (8 mL) in 100mL Erlenmeyer flask and then decane (0.5 mL) was added. The final OD_{600} in the reaction mixture was 14 (0.2 ppm of DmsABC) unless otherwise stated. The reaction mixture was incubated at 37 °C, 200 rpm. The conversion of the reaction was determined by analytical HPLC. Then, the reaction mixture was centrifuged (16900 × g, 2 min, 4 °C). The supernatant was extracted with EtOAc (4 ml), the organic phase was washed with H_2O (1 mL) and brine (1 ml), dried over $MgSO_4$, and concentrated by rotary evaporation under reduced pressure. The enantiomeric excess was determined by chiral HPLC. The absolute configuration of the sulfoxides was determined by comparison of the HPLC retention times and the optical rotation with the reported data.[1]

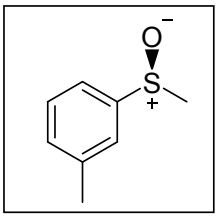
A modified protocol was utilized for substrates **1n**-**1p**. Due to low solubility and acidic instability of the substrates,[11] pH of M9 minimal buffer was adjusted to 9.0 and methanol (2 %) was added to the reaction. Decane as co-solvent was omitted in these experiments. Also, reactions were carried out at 14.5 μmol scale.

(*S*)-1-Methyl-4-(methylsulfinyl)benzene (1a)[1]



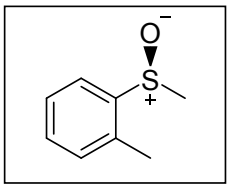
$C_8H_{10}OS$ (154.23 g/mol), conversion 50% in 2 h, $s > 100$. The enantiomeric excess (ee > 99%) was determined by HPLC (ODH chiralcel: heptane/propan-2-ol (98:2); flow rate 1mL/min; 25 °C; 254 nm; t_r= 32.1 and 35.7 min).

(*S*)-1-Methyl-3-(methylsulfinyl)benzene (1b)[1]



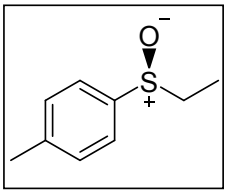
$C_8H_{10}OS$ (154.23 g/mol), conversion 50% in 1 h, $s > 100$. The enantiomeric excess (ee > 99%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (80:20); flow rate 1mL/min; 25 °C; 254 nm; t_r= 24.4 and 29.9 min).

(S)-1-Methyl-2-(methylsulfinyl)benzene (1c)[1]



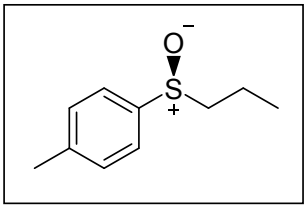
$C_8H_{10}OS$ (154.23 g/mol), final OD_{600} = 28 (0.4 ppm of DmsABC), conversion 50 % in 2 h, $s > 100$. The enantiomeric excess (ee = 98%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (80:20); flow rate 1mL/min; 25 °C, 254 nm, t_r= 23.2 and 24.8 min)

(*S*)-1-(Ethylsulfinyl)-4-methylbenzene (1d)[1]



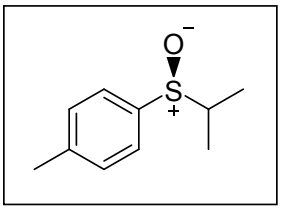
$C_9H_{12}OS$ (168.25 g/mol), final OD_{600} = 28 (0.4 ppm of DmsABC), conversion 52 % in 2 h, $s > 100$. The enantiomeric excess (ee = 99 %) was determined by HPLC (IA chiralpak: heptane/propan-2-ol (95:5); flow rate 0.5 mL/min; 25 °C; 254 nm; t_r= 27.4 and 29.2 min).

(*S*)-1-(Propylsulfinyl)-4-methylbenzene (1e)[12]



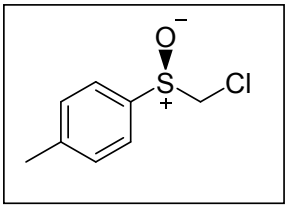
$C_{10}H_{14}OS$ (182,28 g/mol), final OD_{600} = 28 (0.4 ppm of DmsABC), conversion 39 % in 2 h, s = 3. The enantiomeric excess (ee = 26 %) was determined by HPLC (IA chiralpak: heptane/propan-2-ol (95:5); flow rate 1 mL/min; 25 °C; 254 nm; t_r= 12.9 and 13.7 min).

1-(Isopropylsulfinyl)-4-methylbenzene (1f)[13]



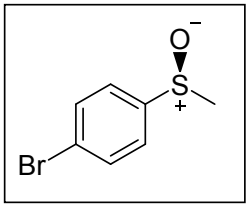
$C_{10}H_{14}OS$ (182,28 g/mol), final OD_{600} = 28 (0.4 ppm of DmsABC), conversion 9 % in 2 h, s = 0. The enantiomeric excess (ee = 0 %) was determined by HPLC (IA chiralpak: heptane/propan-2-ol (95:5); flow rate 1 mL/min; 25 °C; 254 nm; t_r= 12.0 and 12.8 min).

(*R*)-1-((chloromethyl)sulfinyl)-4-methylbenzene (1g)[2]



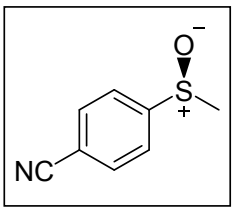
C_8H_9ClOS (188,67 g/mol), final OD_{600} = 28 (0.4 ppm of DmsABC), conversion 52 % in 2 h, *s* > 100. The enantiomeric excess (ee = 99 %) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (80:20); flow rate 1 mL/min; 25 °C; 254 nm; t_r= 17.8.7 and 19.4 min). ; $[\alpha]_D^{25}$ – 139.0 (c = 0.5, $CHCl_3$), lit:$[\alpha]_D^{25}$ +136 (c = 1.0, $CHCl_3$) for (*S*), ee = 95 %)[2]

(*S*)-1-Bromo-4-(methylsulfinyl)benzene (1h)[1]



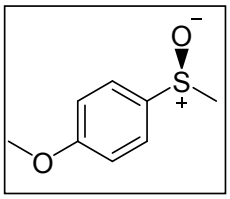
C_7H_7BrOS (219.10 g/mol), conversion 51 % in 1 h, *s* > 100. The enantiomeric excess (ee > 99%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (80:20); flow rate 1mL/min; 25 °C; 254 nm; t_r= 18.6 and 20.2 min).

(*S*)-4-(Methylsulfinyl)benzonitrile (1i)[1]



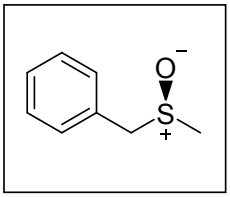
C_8H_7NOS (165.21 g/mol), conversion 52 % in 1 h, *s* > 100. The enantiomeric excess (ee = 99 %) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (80:20); flow rate 1mL/min; 25 °C; 254 nm; t_r= 47.0 and 51.3 min).

(*S*)-1-Methoxy-4-(methylsulfinyl)benzene (1j)[1]



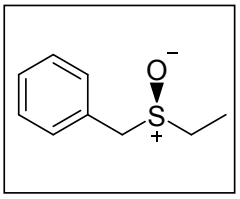
$C_8H_{10}O_2S$ (170.23 g/mol), conversion 48% in 1 h, *s* > 100. The enantiomeric excess (ee = 98%) was determined by HPLC (ODH chiralcel: heptane/propan-2-ol (90:10); flow rate 1mL/min; 25 °C; 254 nm; t_r= 17.0 and 18.1 min).

(*S*)-((Methylsulfinyl)methyl)benzene (1k)[1]



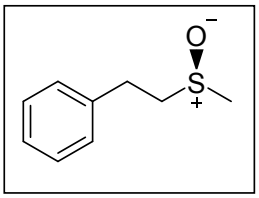
$C_8H_{10}OS$ (154.23 g/mol), conversion 48% in 1 h, *s* > 100. The enantiomeric excess (ee = 99%) was determined by HPLC (IA chiralpak: heptane/propan-2-ol (95:5); flow rate 1mL/min; 25 °C; 25 °C; 220 nm; t_r= 21.9 and 24.0 min).

(*S*)- ((Ethylsulfinyl)methyl)benzene (1l)[1]



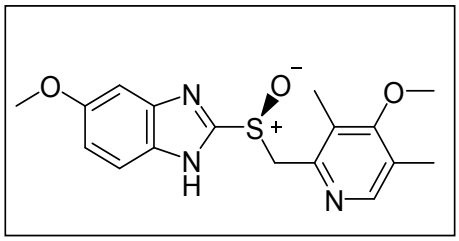
$C_9H_{12}OS$ (168.25 g/mol), conversion 49% in 1 h, s > 100. The enantiomeric excess (ee = 99%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (80:20); flow rate 1mL/min; 25 °C; 220 nm; t_r= 24.0 and 26.5 min).

(*S*)- (2-(Methylsulfinyl)ethyl)benzene (1m)[1]



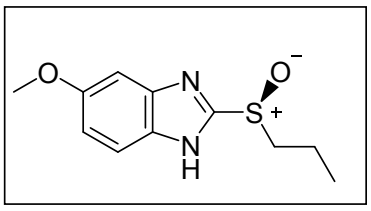
$C_9H_{12}OS$ (168.25 g/mol), conversion 51% in 1 h, s > 100. The enantiomeric excess (ee = 99%) was determined by HPLC (IA chiralpak: heptane/propan-2-ol (95:5); 1mL/min; 25 °C; 220 nm; t_r= 23.1 and 25.2 min).

Esomeprazole (1n)[11]



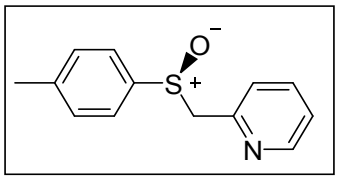
$C_{17}H_{19}N_3O_3S$ (345,42 g/mol), 14.5 µmol scale, final OD_{600} = 40 (2.0 ppm of DmsABC), conversion 29% in 2 h, s > 100. The enantiomeric excess (ee = 40%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (60:40); 1mL/min; 25 °C; 300 nm; t_r= 20.4 and 33.3 min).

5-methoxy-2-(propylsulfinyl)-1H-benzo[d]imidazole (1o)



$C_{11}H_{14}N_2O_2S$ (238.31 g/mol), 14.5 µmol scale, final OD_{600} = 40 (2.0 ppm of DmsABC), conversion 42% in 2 h, s = 3. The enantiomeric excess (ee = 28%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (60:40); 1mL/min; 25 °C; 300 nm; t_r= 6.3 and 7.7 min).

2-((p-Tolylsulfinyl)methyl)pyridine (1p)[4]



$C_{13}H_{13}NOS$ (231.31 g/mol), 14.5 µmol scale, final OD_{600} = 40 (2.0 ppm of DmsABC), conversion 20% in 2 h, s = 3. The enantiomeric excess (ee = 11%) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (60:40); 1mL/min; 25 °C; 254 nm; t_r= 21.5 and 29.4 min).

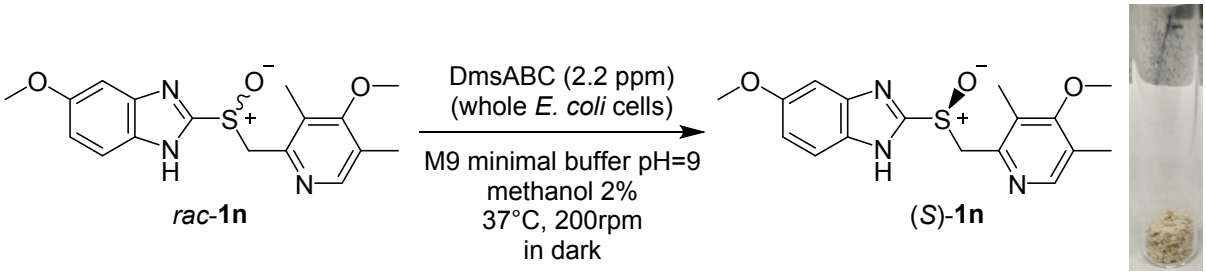
5. Proteomic Analysis

Cell pellets in 100 mM triethylammonium bicarbonate (TEAB) buffer containing 1% sodium deoxycholate (SDC) were boiled at 95°C for 5 min. Protein concentration was determined using BCA protein assay kit (Thermo) and 20 µg of protein per sample was used for MS sample preparation. Cysteines were reduced with 5 mM final concentration of tris(2-carboxyethyl)phosphine (TCEP) at 60 °C for 60 min, and blocked with 10 mM S-methyl methanethiosulfonate (MMTS) for 10 min at room temperature. Samples were digested with trypsin (trypsin/protein ratio of 1/20) at 37 °C overnight. After digestion samples were acidified with trifluoroacetic acid (TFA) to 1% final concentration. SDC was removed by extraction to ethylacetate and peptides were desalted on Michrom C18 column.[14]

Nano reversed phase column (EASY-Spray column, 50 cm × 75 µm ID, PepMap C18, 2 µm particles, 100 Å pore size) was used for LC/MS analysis. Mobile phase buffer A was composed of water and 0.1% formic acid. Mobile phase B was composed of acetonitrile and 0.1% formic acid. Samples were loaded onto the trap column (Acclaim PepMap300, C18, 5 µm, 300 Å Wide Pore, 300 µm × 5 mm) at a flow rate of 15 µL/min. Loading buffer was composed of water, 2% acetonitrile and 0.1% TFA. Peptides were eluted with gradient of B from 4% to 35% over 60 min at a flow rate of 300 nL/min. Eluting peptide cations were converted to gas-phase ions by electrospray ionization and analyzed on a Thermo Orbitrap Fusion (Q-OT- qIT, Thermo). Survey scans of peptide precursors from 400 to 1600 m/z were performed at 120K resolution (at 200 m/z) with a 5×10^5 ion count target. Tandem MS was performed by isolation at 1.5 Da with the quadrupole, HCD fragmentation with normalized collision energy of 30, and rapid scan MS analysis in the ion trap. The MS2 ion count target was set to 10^4, and the max injection time was 35 ms. Only those precursors with charge state 2–6 were sampled for MS2. The dynamic exclusion duration was set to 45 s with a 10 ppm tolerance around the selected precursor and its isotopes. Monoisotopic precursor selection was turned on. The instrument was run in top speed mode with 2 s cycles.

All data were analyzed and quantified with the MaxQuant software (version 1.5.3.8)[15] The false discovery rate (FDR) was set to 1% for both proteins and peptides and we specified a minimum length of seven amino acids. The Andromeda search engine was used for the MS/MS spectra search against the *Escherichia coli* database (downloaded from Uniprot on November 2016, containing 6 072 entries). Enzyme specificity was set as C-terminal to Arg and Lys, also allowing cleavage at proline bonds and a maximum of two missed cleavages. Dithiomethylation of cysteine was selected as fixed modification and N-terminal protein acetylation and methionine oxidation as variable modifications. The "match between runs" feature of MaxQuant was used to transfer identifications to other LC-MS/MS runs based on their masses and retention times (maximum deviation 0.7 min) and this was also used in quantification experiments. Quantifications were performed with the label-free algorithms described recently.[16] Data analysis was performed using Perseus 1.5.2.4 software.[17]

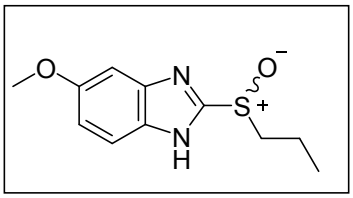
5. Procedure for Kinetic Resolution of Omeprazole



2.5 mL preculture of *E. coli* (*msrA* knock out - KEIO collection ID JW4178)[10] was used to inoculate each of three 500 mL LB media with kanamycin (50 mg/L) in three 2 L Erlenmeyer flask. The bacterial cultures were incubated at 37 °C, 200 rpm until OD_{600} of 3 was reached (6 hours). Then, cells were harvested by centrifugation (4200 × g, 30 min, 4 °C). Resuspended cells in M9 minimal medium (10 mL, pH 9) were added to a solution of racemic omeprazole (50 mg, 0.145 mmol, final concentration 0.5 mg/mL) in M9 minimal medium (88 mL, pH 9) and methanol (2 mL) in 1 L Erlenmeyer flask. The reaction mixture was incubated at 37 °C, 200 rpm in the dark. The conversion of the reaction was determined by analytical HPLC. After 3 h (conversion = 56 %), the reaction mixture was centrifuged (4200 × g, 20 min, 4 °C) and the supernatant was extracted with diethyl ether (4 × 200 mL), the organic phase was washed with H_2O (40 mL) and brine (40 ml), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation under reduced pressure. Purification of the crude product by HPLC afforded **1n** in 36% yield (18 mg) as an off-white solid; $[\alpha]_D^{25} = -147°$ (c = 0.2, $CHCl_3$); lit: $[\alpha]_D^{25} = -157°$ (c 0.5, $CHCl_3$) for (*S*)-omeprazole sodium salt, ee > 99%).[18] **^{1}H NMR** (400 MHz, CD_3OD) δ 8.13 (s, 1H), 7.54 (d, J = 8.9 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.00 (dd, J = 8.9, 2.4 Hz, 1H), 4.80 (d, J = 13.2 Hz, 1H), 4.73 (d, J = 13.2 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 2.26 (s, 3H), 2.18 (s, 3H). The spectrum is in agreement with the reported data.[11] Enantiomeric excess (ee = 98 %) was determined by HPLC (IC chiralpak: heptane/propan-2-ol (60:40); 1mL/min; 25 °C; 300 nm; t_r= 18.1 and 29.4 min).

6. Preparation of Racemic Sulfoxide **1o**

rac-5-methoxy-2-(propylsulfinyl)-1H-benzo[d]imidazole (1o)



Compound **1o** was prepared according to modified protocols[19,20]

To a solution of 5-methoxybenzimidazole-2-thiol (360 mg, 2 mmol) in ethanol (10 mL), water (2 mL) and sodium hydroxide (160 mg, 4 mmol), propyl 4-tolylsulfonate (419 mg, 2 mmol) was added portionwise and the reaction mixture was stirred first at room temperature for 2 h and then at 70 °C overnight. Then, reaction mixture was extracted with dichloromethane (3 × 40 mL) and the organic phase was washed with water (10 mL) and brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation under reduced pressure to provide crude sulfide, which was used in the next step without further purification. To a stirred solution of a crude sulfide in dichloromethane (20 mL) and methanol (1 mL), solution of *m*-chloroperoxybenzoic acid (≤77%, 450 mg, 2 mmol) in dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred at –30 °C for 1 h. Reaction mixture was diluted with dichloromethane (70 mL), washed with saturated $NaHCO_3$ (20 mL), 10% solution of NaS_2O_3 (10 mL), water (10 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated by rotary evaporation under reduced pressure. Purification of the crude product by column chromatography on silica gel (dichlormethane/methanol 10/1 then 5/1) afforded **1o** in 47 % yield (222 mg) as a viscous oil. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): 13.42 (bs, 1H), 7.53 (d, J = 8.9 Hz, 1H), 7.08 (s, 1H), 6.91 (d, J = 8.9 Hz, 1H), 3.80 (s, 3H), 3.26-3.13 (m, 2H), 1.80-1.67 (m, 1H), 1.60-1,47 (m, 1H), 0.98 (t, 3H). **^{13}C NMR** (101 MHz, $(CD_3)_2SO$): 156.9, 153.4, 137.4, 119.2, 113.7 (2 C), 97.8, 55.9, 55.6, 15.5, 13.3. **HRMS (ESI)**: *m*/*z* $[M+H]^+$ calcd for $C_{11}H_{15}N_2O_2S^+$ 239.0849; found: 239.0849. **IR(KBr + acetone)**: 3070, 1625, 1413, 1305, 1272, 1204, 1156, 1024.

7. References

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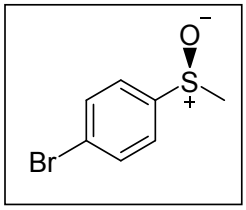
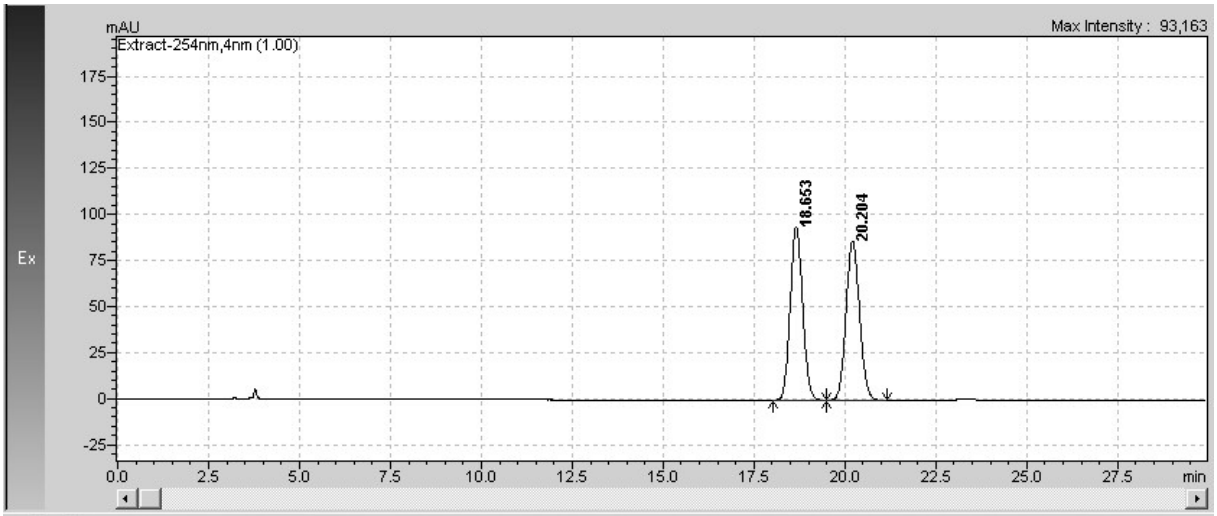
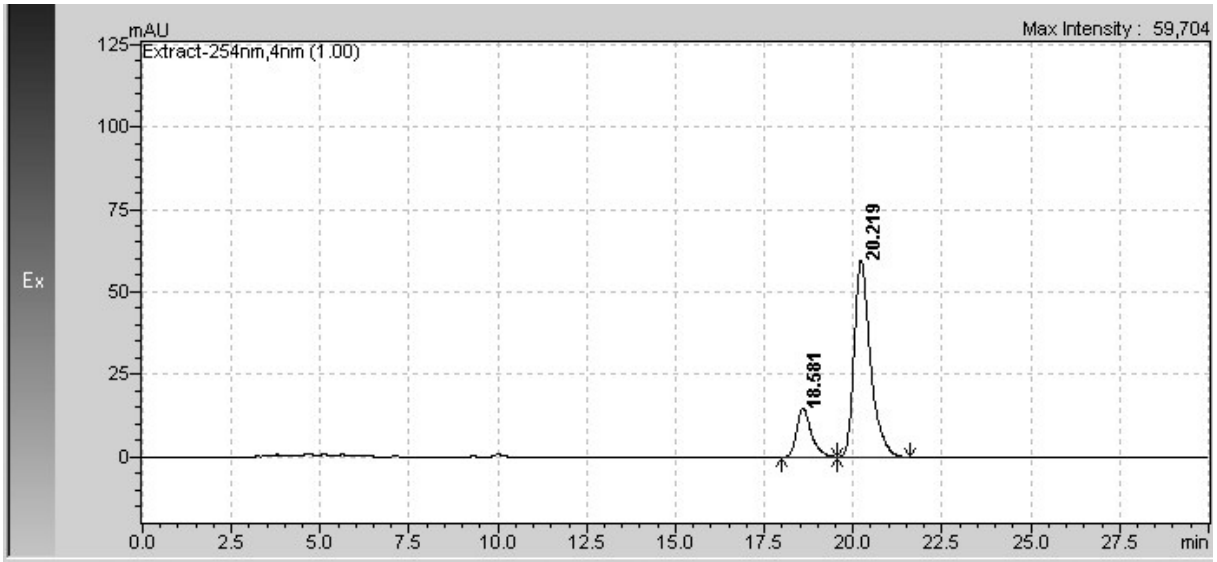
8. HPLC Traces: Kinetic Resolution with Isolated Enzyme MsrB (*A. thaliana*)





Peak Table

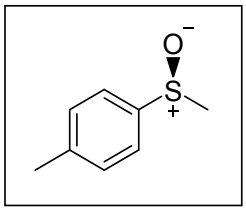
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		18.653	49.99205	2242286	94050	18.037	19.499	49.9920
2		20.204	50.00795	2243000	86376	19.499	21.152	50.0080

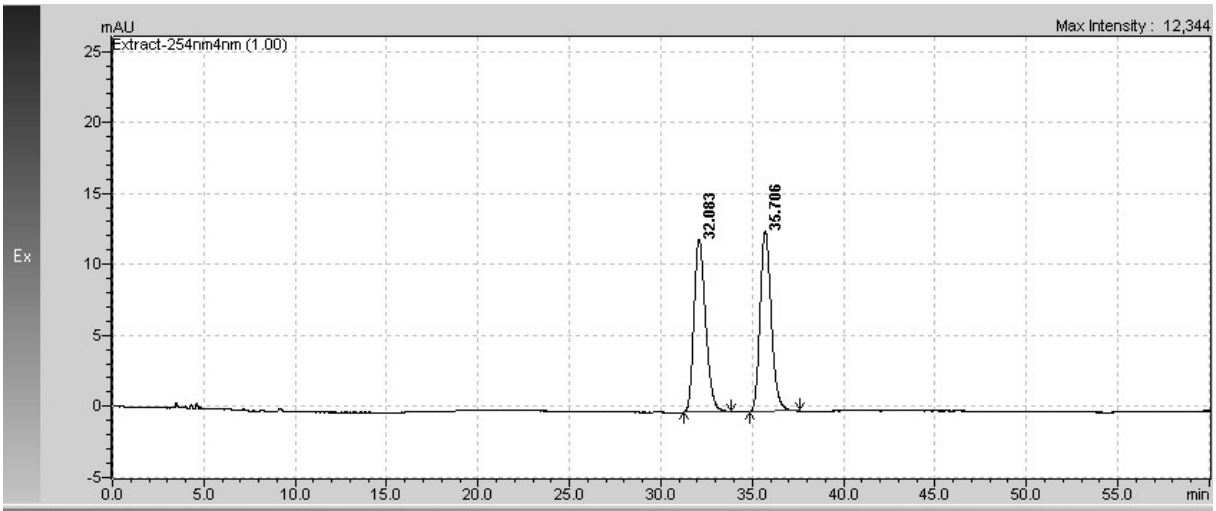


Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		18.581	18.34778	429135	14825	17.984	19.552	18.3478
2		20.219	81.65222	1909760	59805	19.552	21.589	81.6522

9. HPLC Traces: Kinetic Resolution with DmsABC (whole *E. coli* cells)





Peak Table

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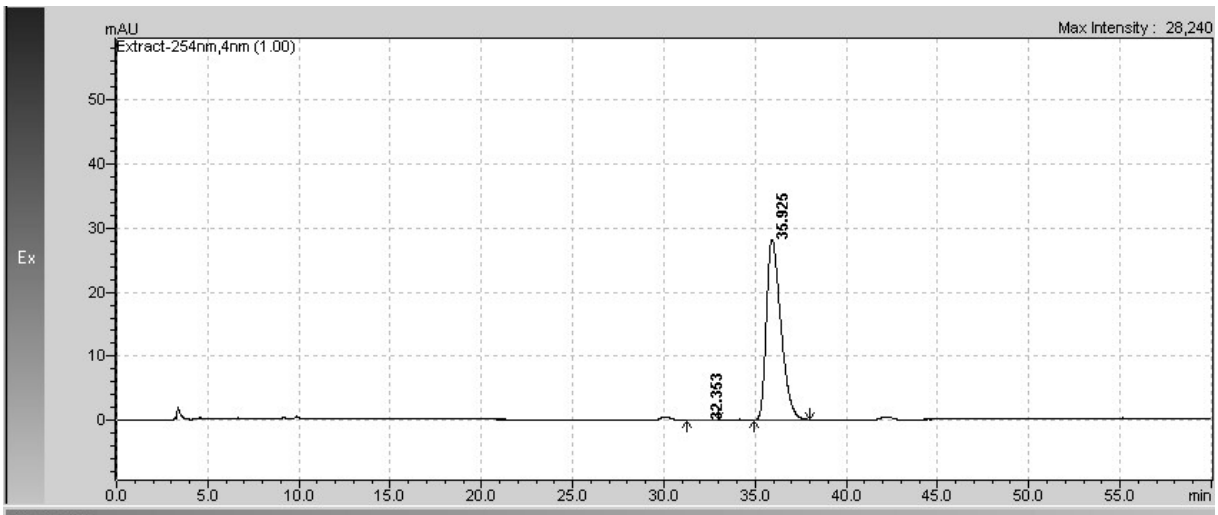
1		32.083	50.01244	541045	12129	31.253	33.845	50.0124
2		35.706	49.98756	540776	12705	34.848	37.600	49.9876



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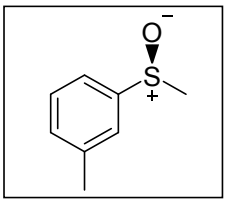
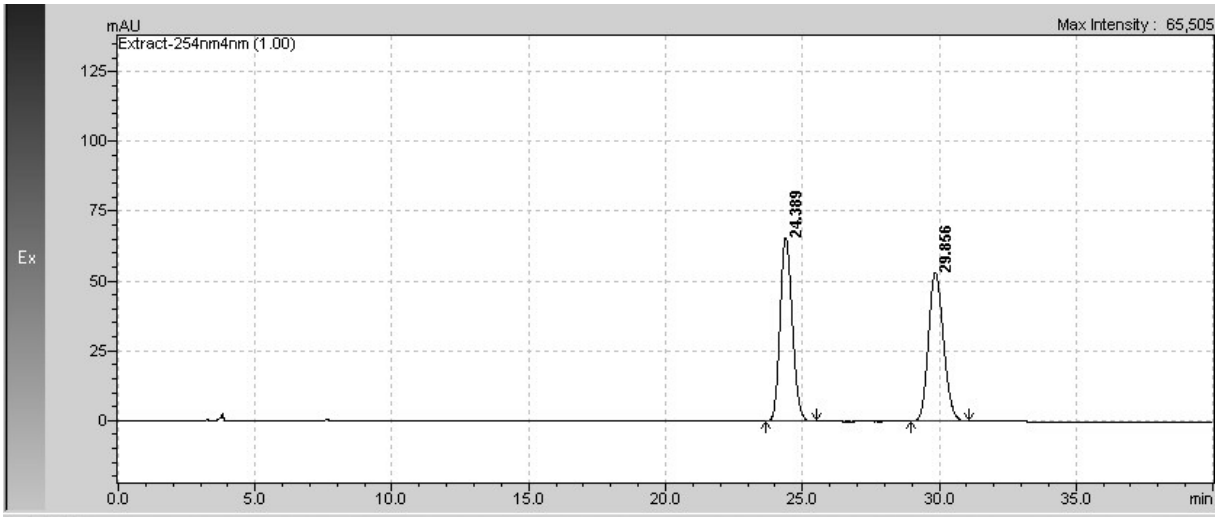
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		32.353	0.15516	2412	65	31.264	33.003	0.1552
2		35.925	99.84484	1552155	28176	34.965	37.995	99.8448





Peak Table

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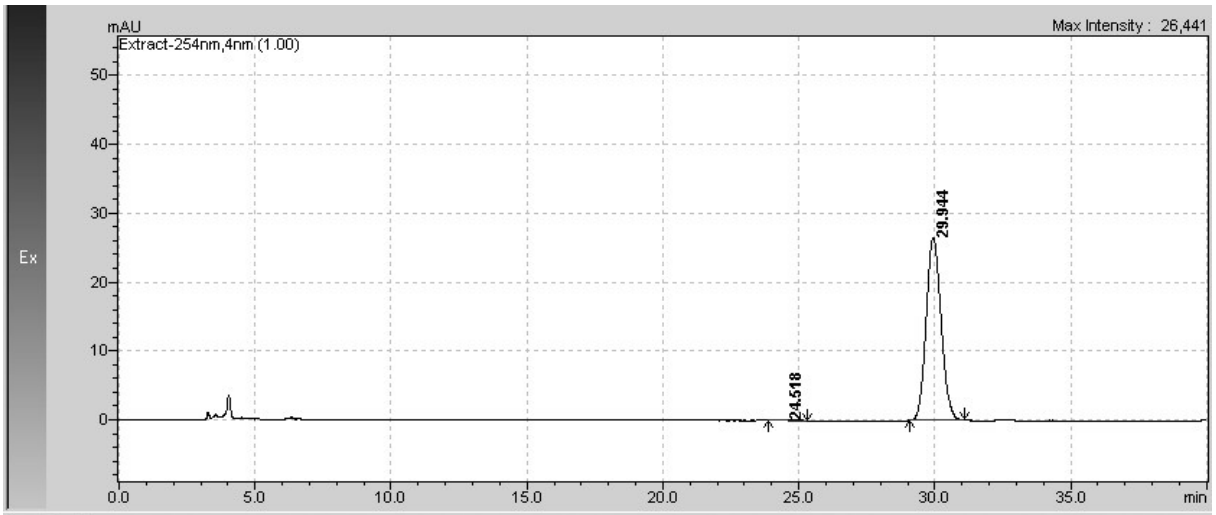
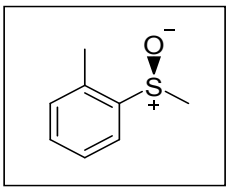
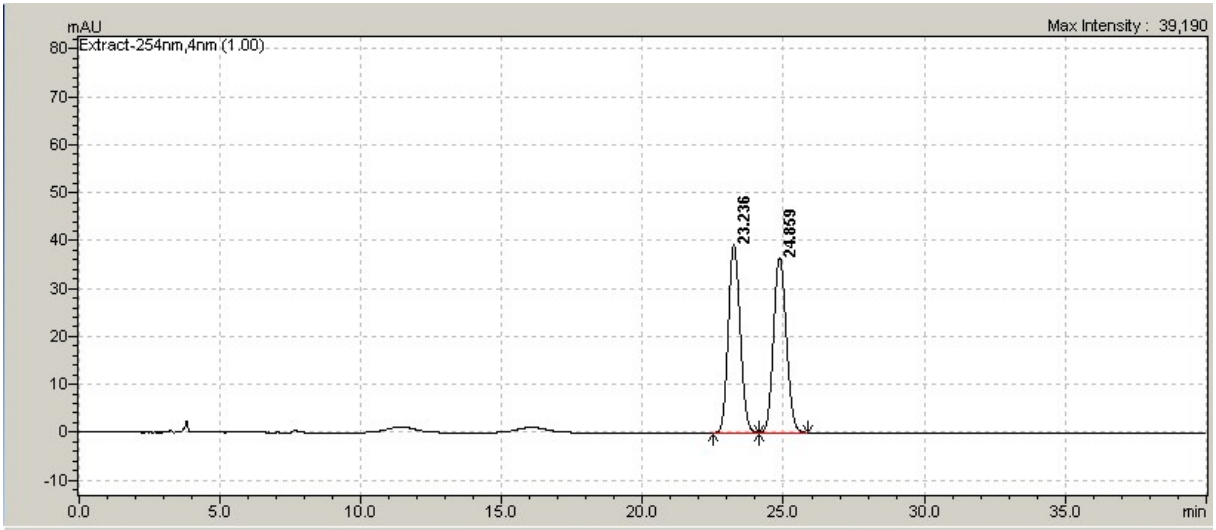
1		24.389	50.08914	2056267	65793	23.637	25.515	50.0891
2		29.856	49.91086	2048948	53233	28.960	31.061	49.9109



Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		24.518	0.33491	3417	97	23.872	25.312	0.3349
2		29.944	99.66509	1016936	26525	29.077	31.083	99.6651





Peak Table

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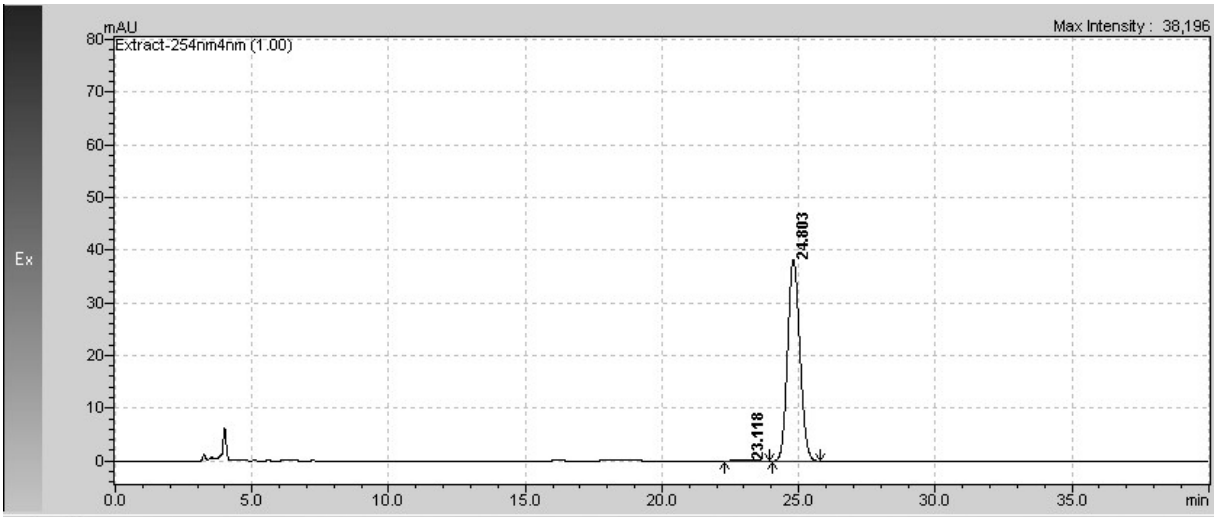

Peak Table

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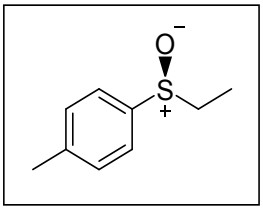
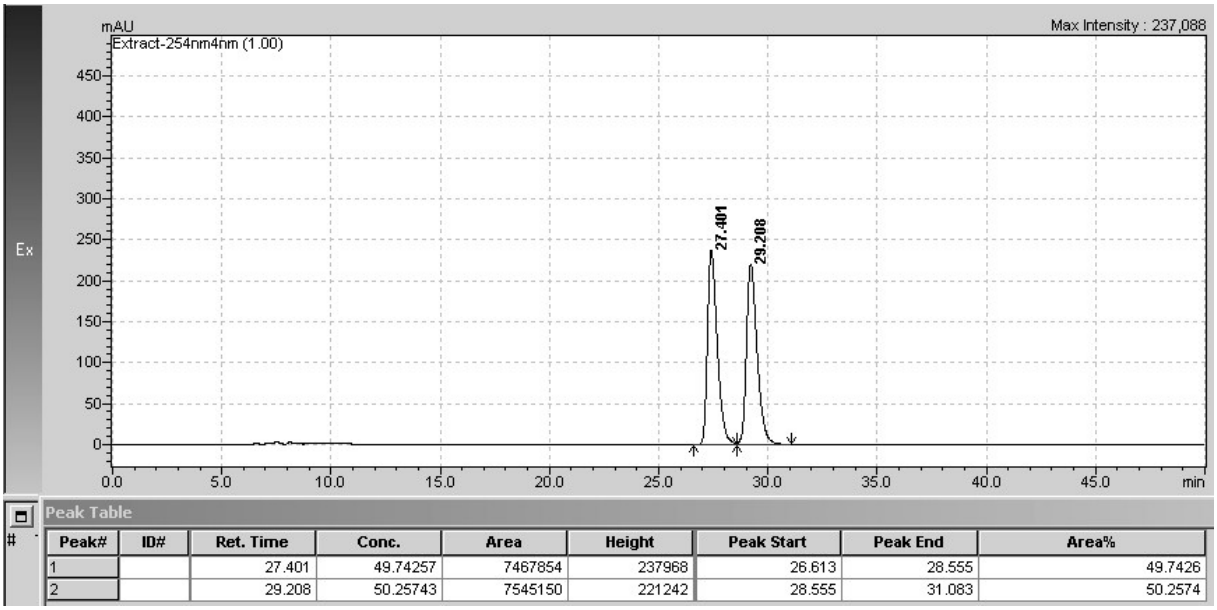
1		23.118	0.85236	10331	221	22.293	23.925	0.8524
2		24.803	99.14764	1201682	38253	24.043	25.813	99.1476





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1		27.401	49.74257	7467854	237968	26.613	28.555	49.7426
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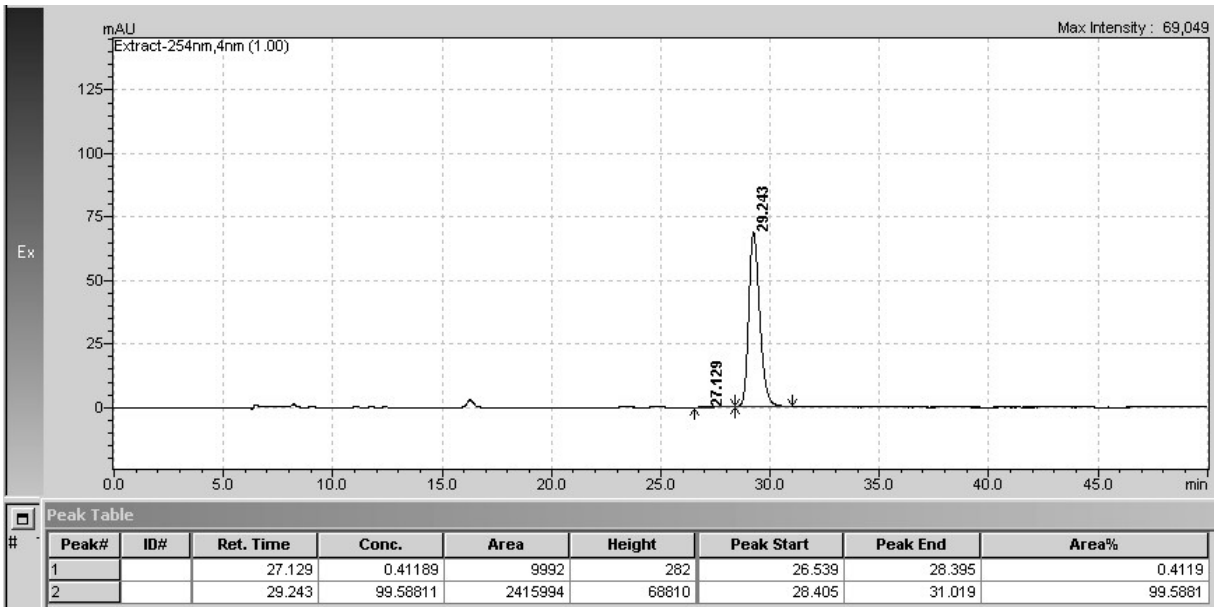

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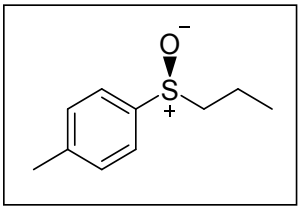
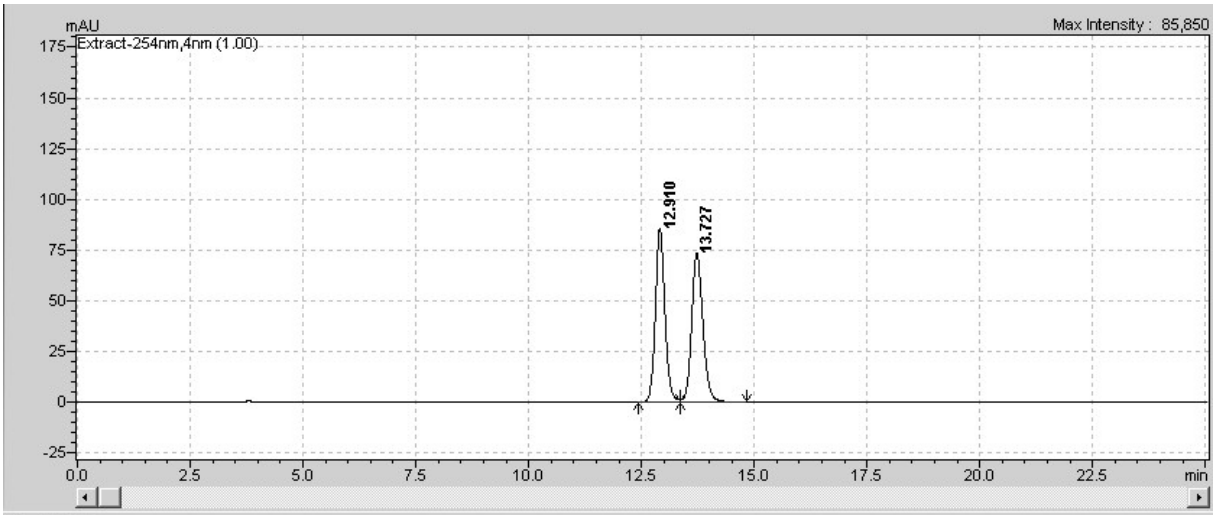
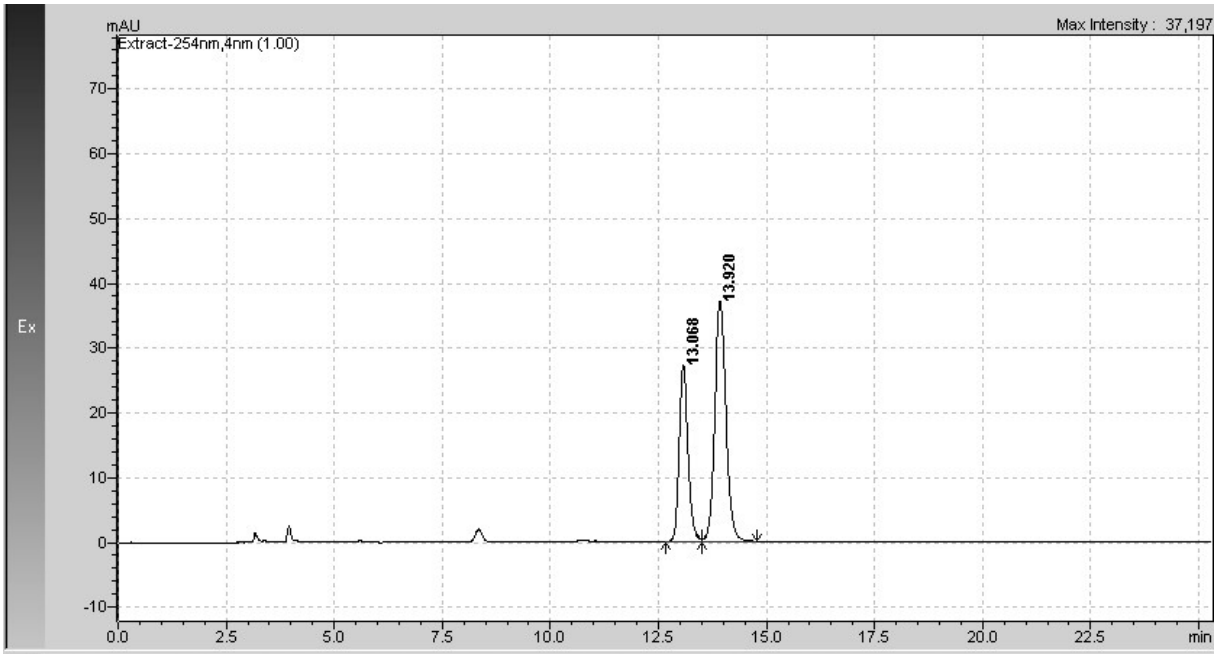
1		27.129	0.41189	9992	282	26.539	28.395	0.4119
2		29.243	99.58811	2415994	68810	28.405	31.019	99.5881





Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		12.910	49.60811	1259108	85749	12.427	13.355	49.6081
2		13.727	50.39189	1279002	73204	13.355	14.827	50.3919



Peak Table

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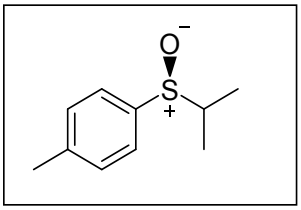
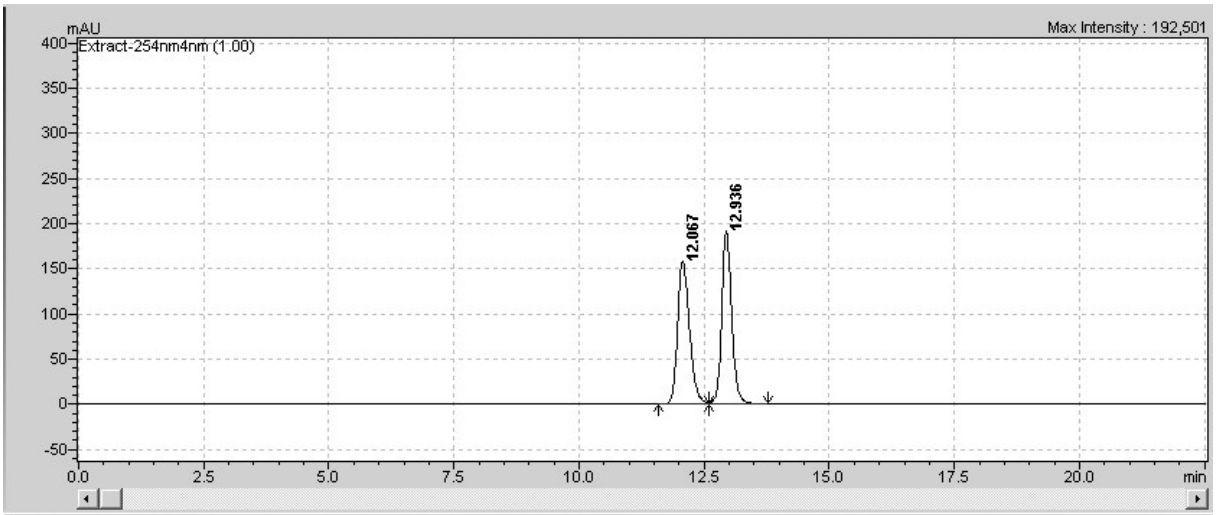
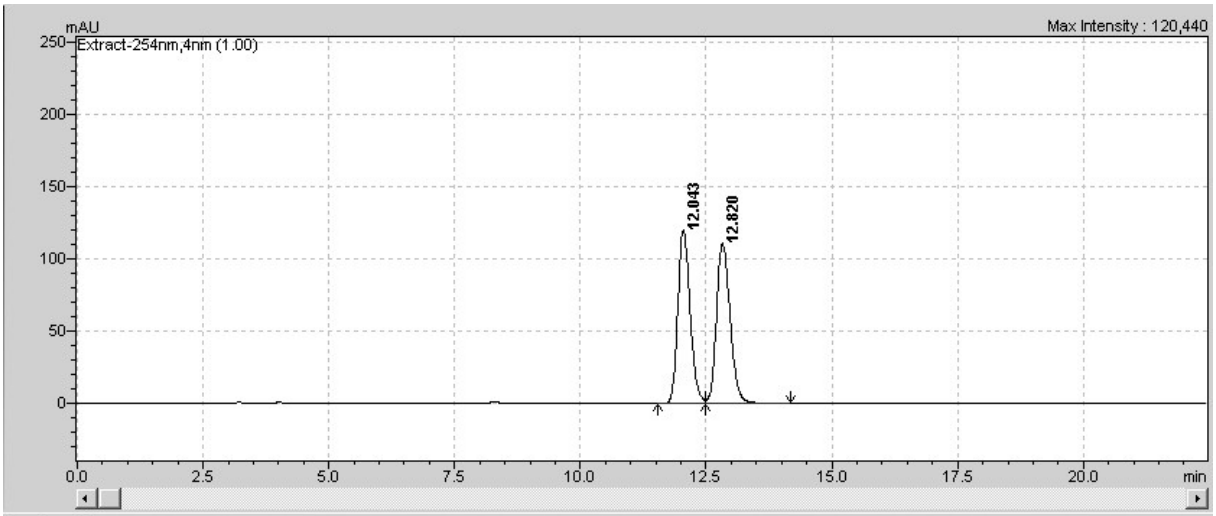
1		13.068	36.59434	384646	27254	0.0000	12.683	13.515	36.5943
2		13.920	63.40566	666462	37019	0.0000	13.515	14.795	63.4057





Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		12.067	49.66676	2627426	158354	11.573	12.587	49.6668
2		12.936	50.33324	2662684	192061	12.587	13.771	50.3332



Peak Table

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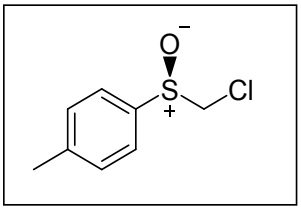

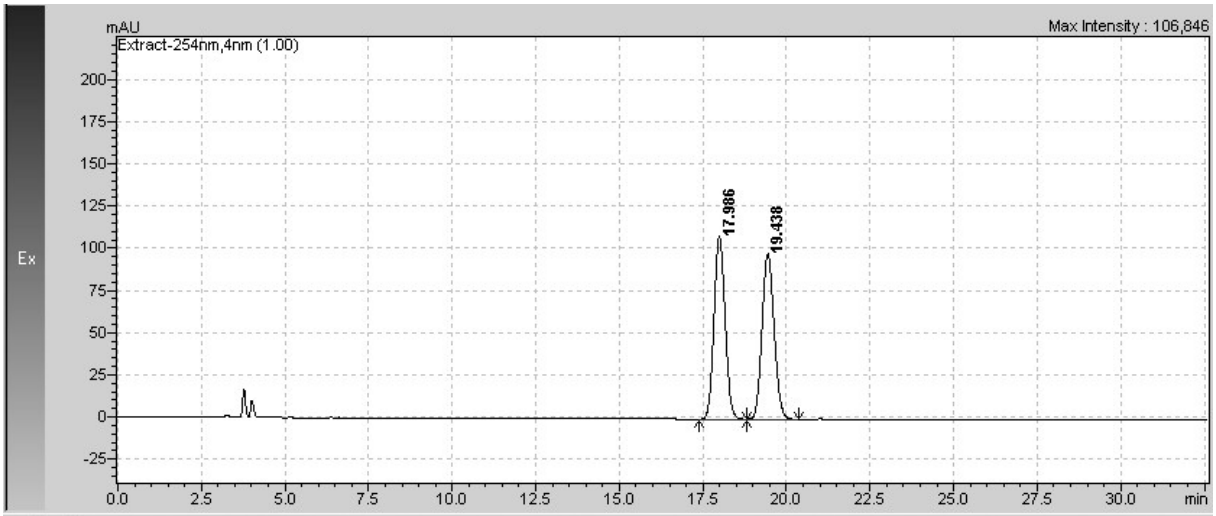

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1		17.986	50.39607	2480591	108191	17.376	18.805	50.3961
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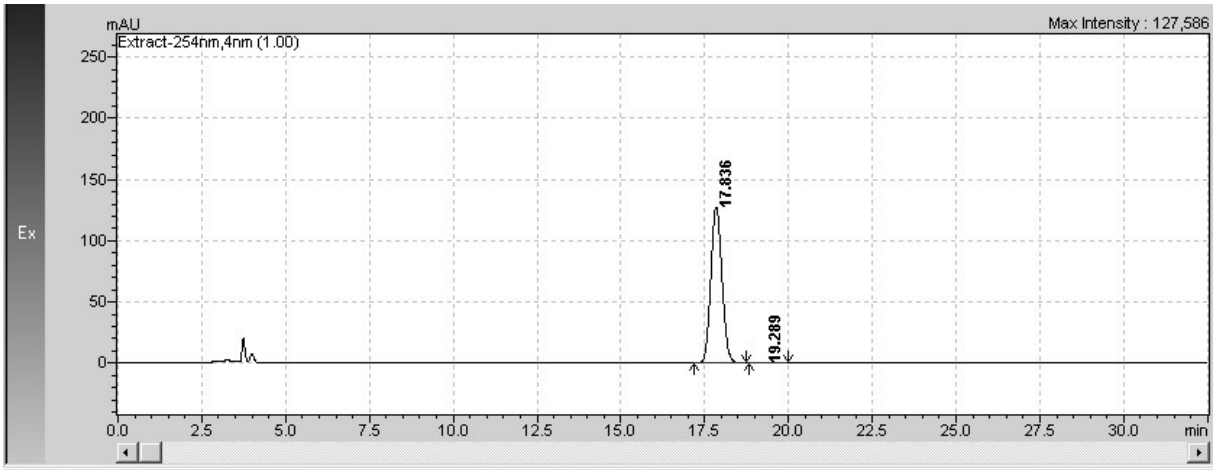

Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Simila	Peak Start	Peak End	Area%
1		17.836	99.95888	2940440	127608	0.0000	17.195	18.731	99.9589
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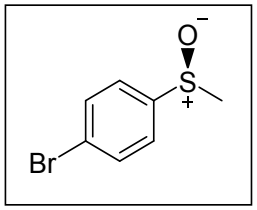

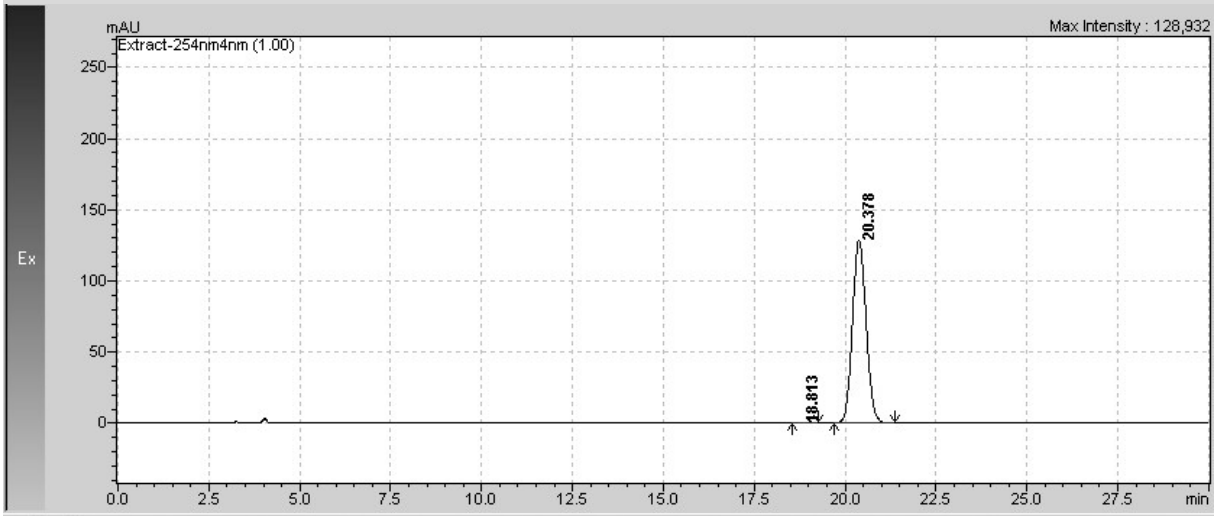

Peak Table

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1		18.813	0.14345	4831	225	18.528	19.253	0.1434
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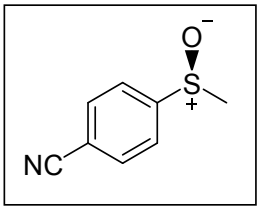
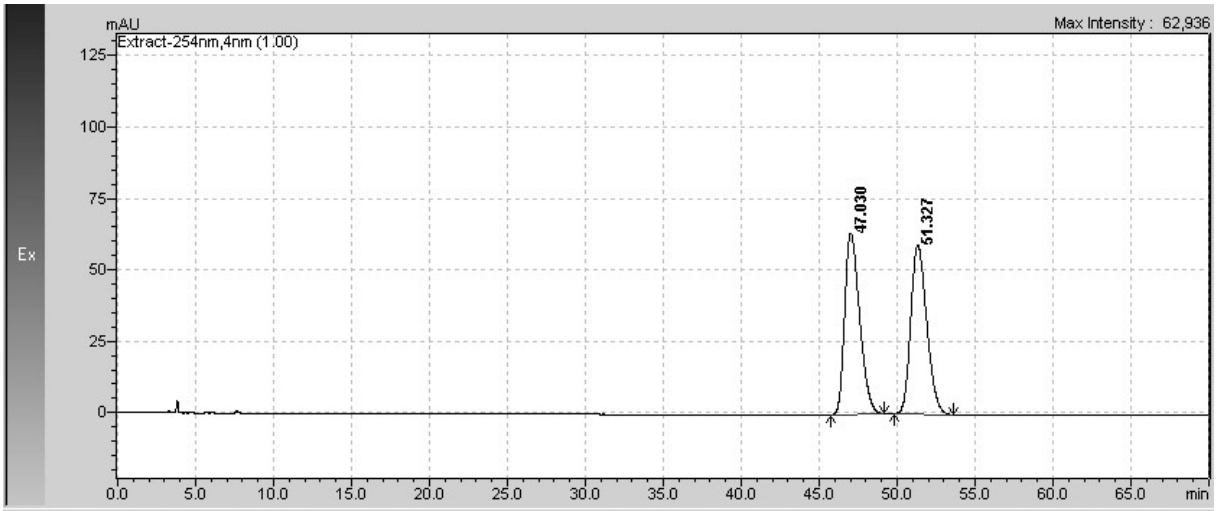
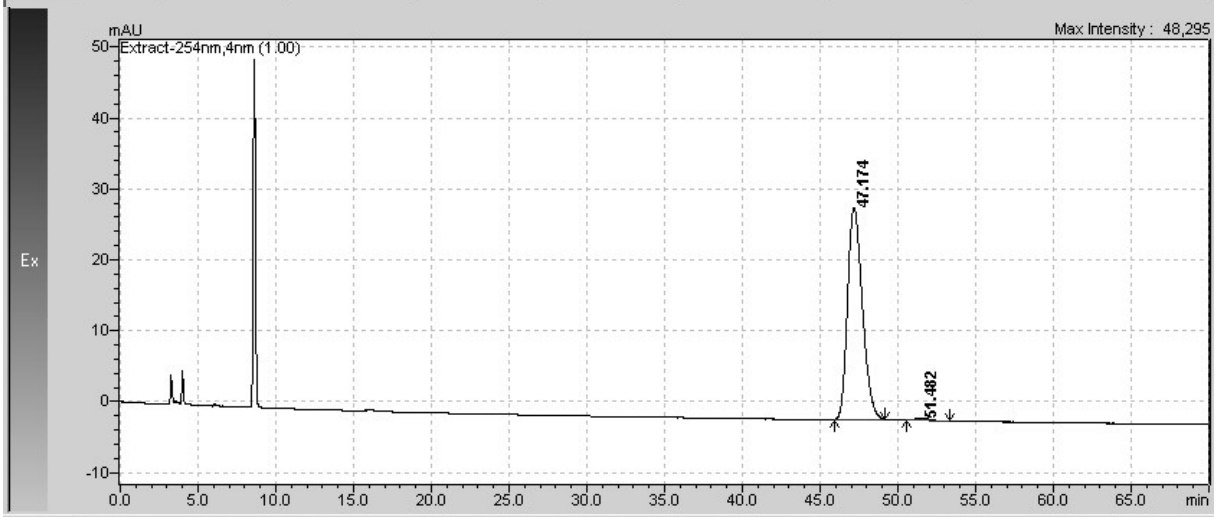




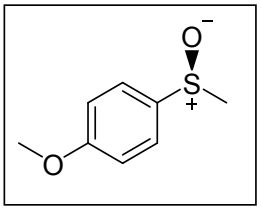
Peak Table

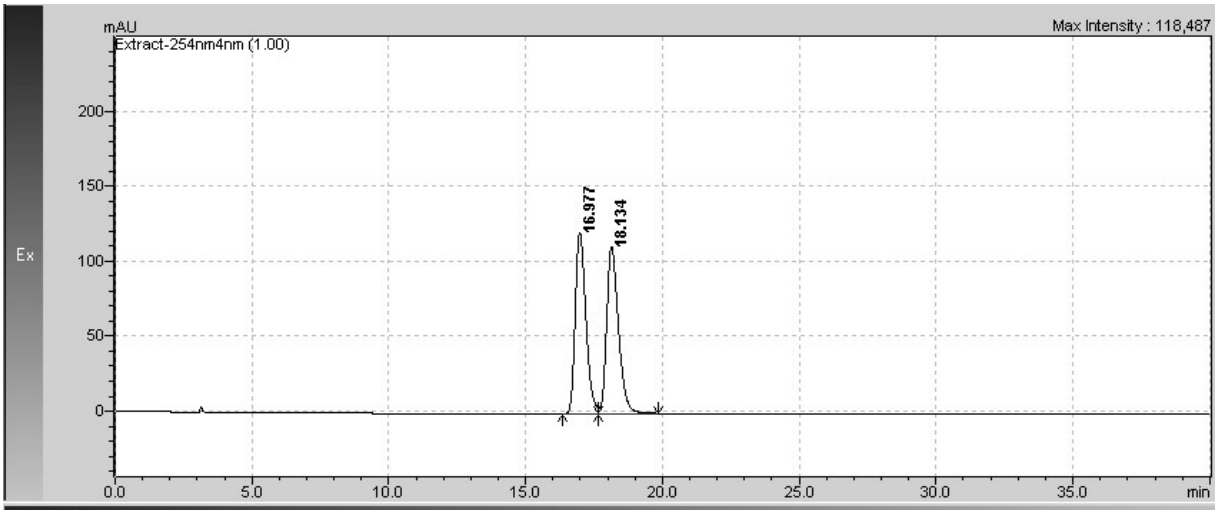
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		47.030	50.04075	4235095	63579	45.760	49.216	50.0408
2		51.327	49.95925	4228197	59125	49.856	53.589	49.9592



Peak Table

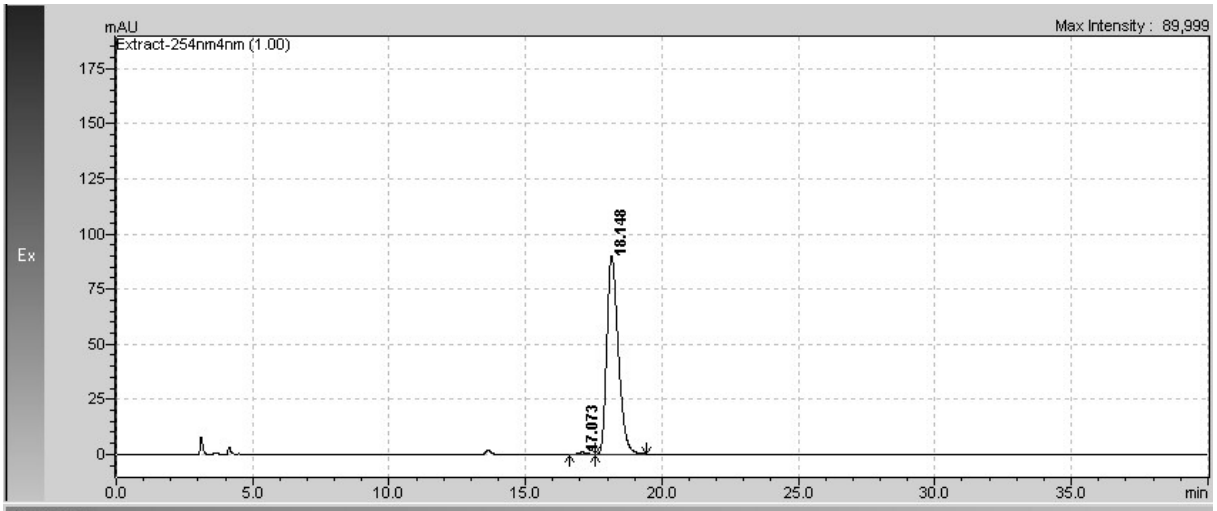
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		47.174	99.24373	1976196	29899	45.909	49.184	99.2437
2		51.482	0.75627	15059	253	50.560	53.312	0.7563





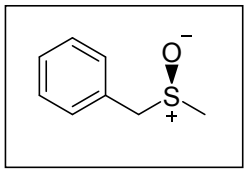
Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		16.977	49.39902	3243797	120161	16.352	17.675	49.3990
2		18.134	50.60098	3322723	111294	17.675	19.851	50.6010



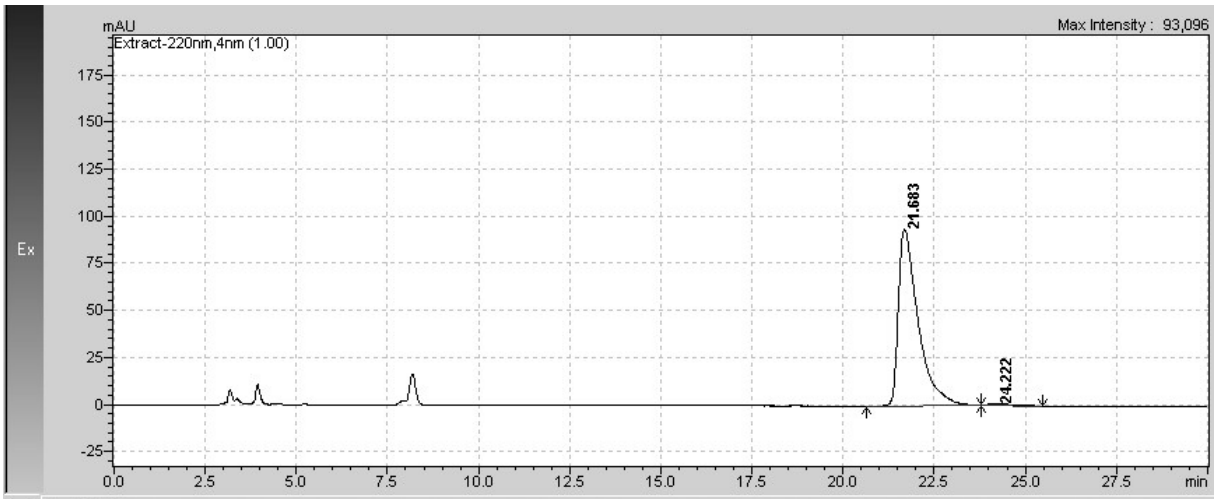
Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		17.073	1.09229	29117	1163	16.608	17.557	1.0923
2		18.148	98.90771	2636554	89993	17.557	19.445	98.9077



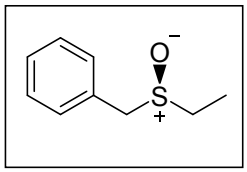
Peak Table

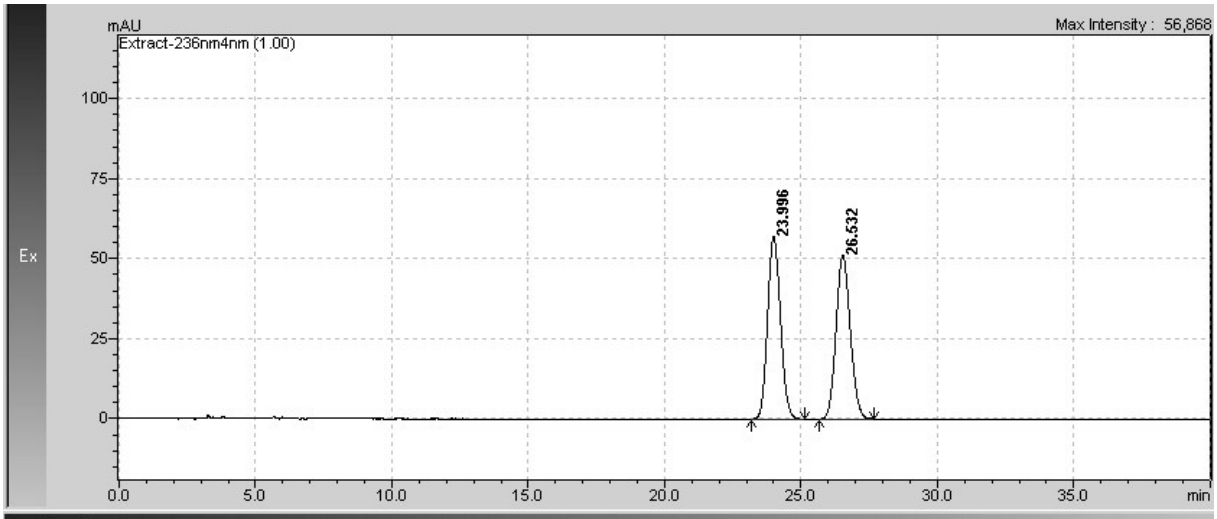
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		21.892	49.62415	3561050	98637	21.248	23.403	49.6242
2		23.967	50.37585	3614992	87413	23.403	26.741	50.3758



Peak Table

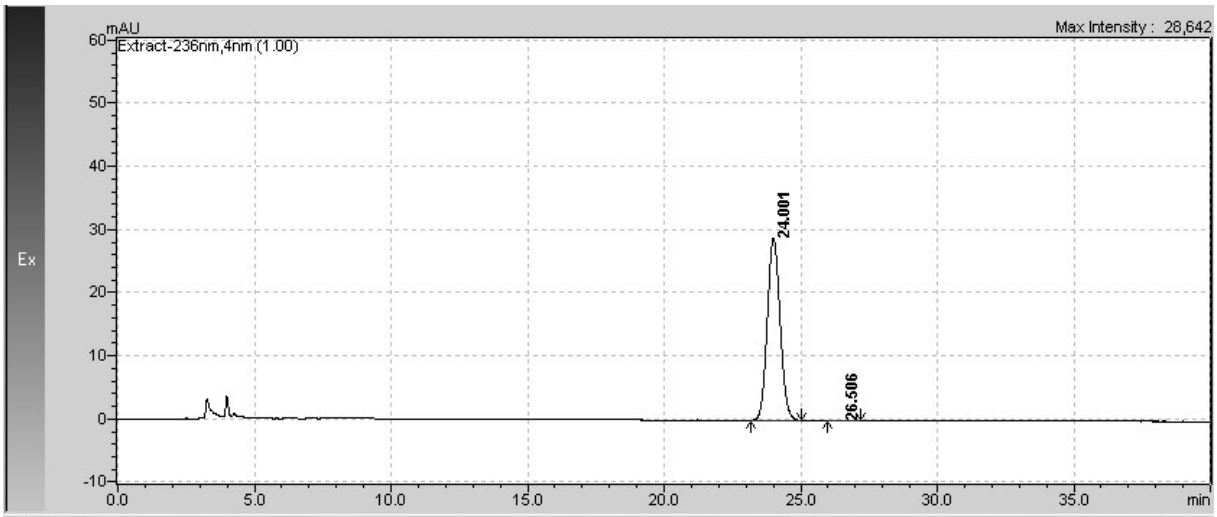
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		21.683	99.26179	3511009	93701	20.640	23.787	99.2618
2		24.222	0.73821	26111	819	23.787	25.483	0.7382





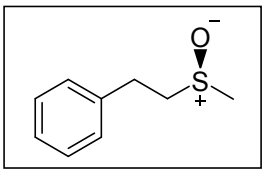
Peak Table

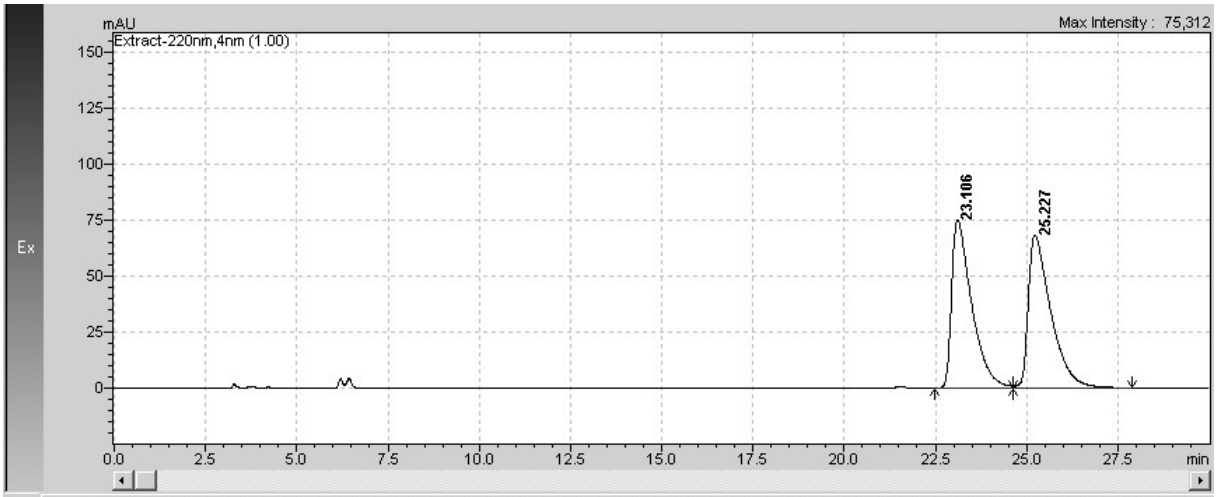
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		23.996	50.06152	1865426	56997	23.168	25.120	50.0615
2		26.532	49.93848	1860841	51153	25.653	27.669	49.9385



Peak Table

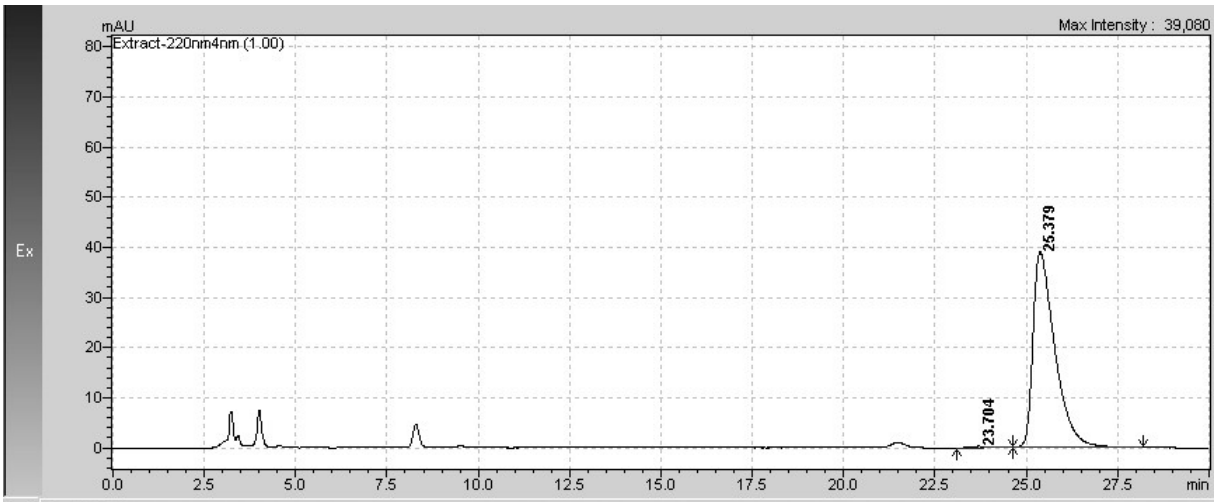
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		24.001	99.62846	946681	28864	23.200	25.045	99.6285
2		26.506	0.37154	3530	99	25.984	27.200	0.3715





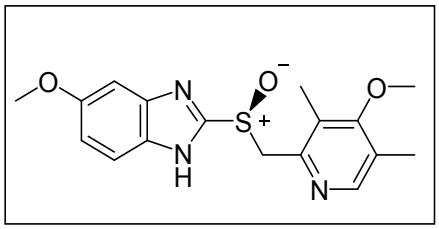
Peak Table

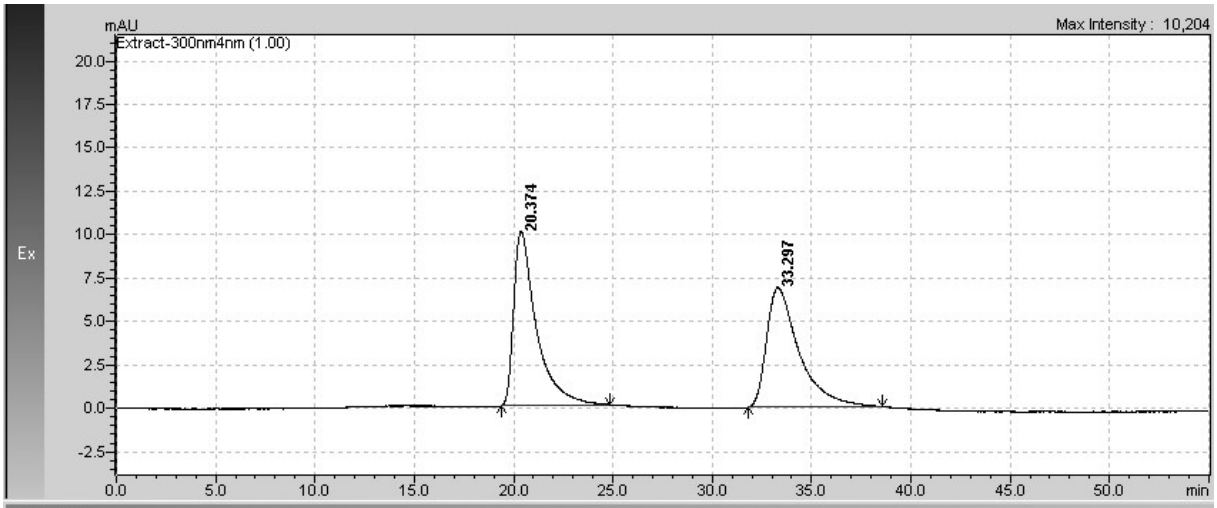
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		23.106	49.53740	2886575	75253	22.475	24.640	49.5374
2		25.227	50.46260	2940487	68248	24.640	27.904	50.4626



Peak Table

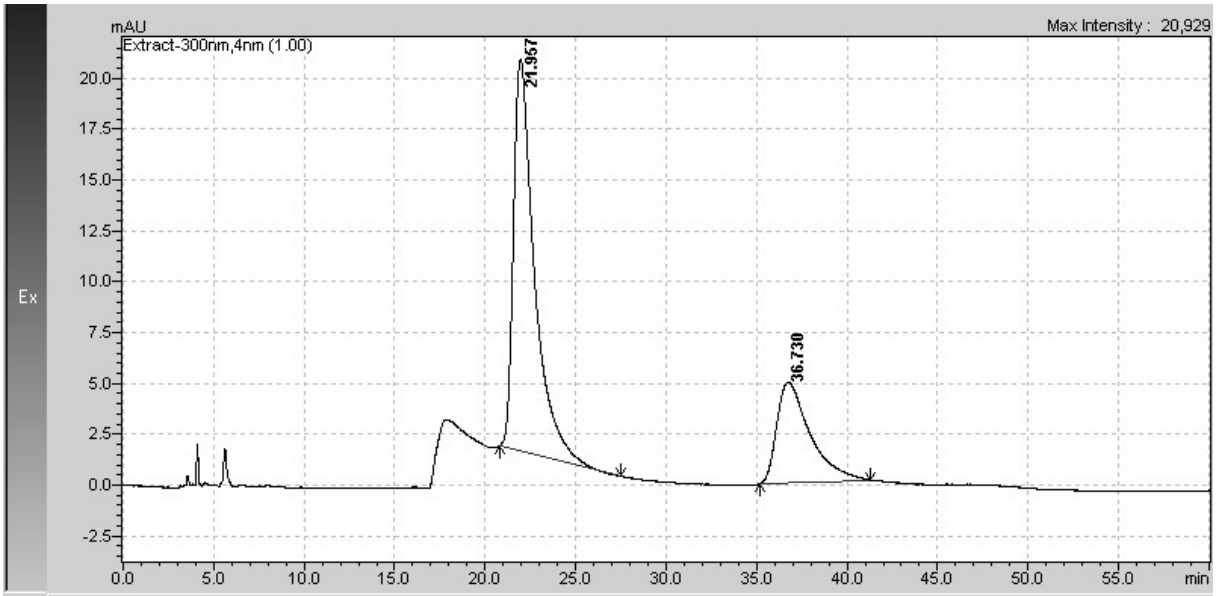
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		23.704	0.67226	11052	307	23.093	24.619	0.6723
2		25.379	99.32774	1633016	39030	24.619	28.203	99.3277





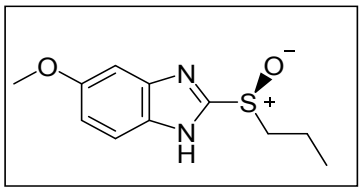
Peak Table

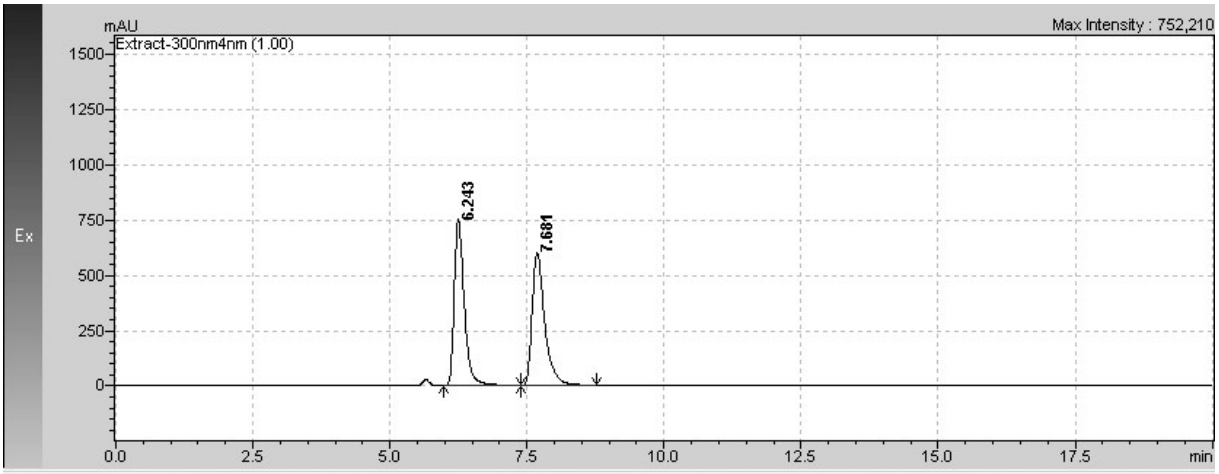
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		20.374	50.32145	793763	10042	19.381	24.843	50.3215
2		33.297	49.67855	783622	6902	31.829	38.560	49.6785



Peak Table

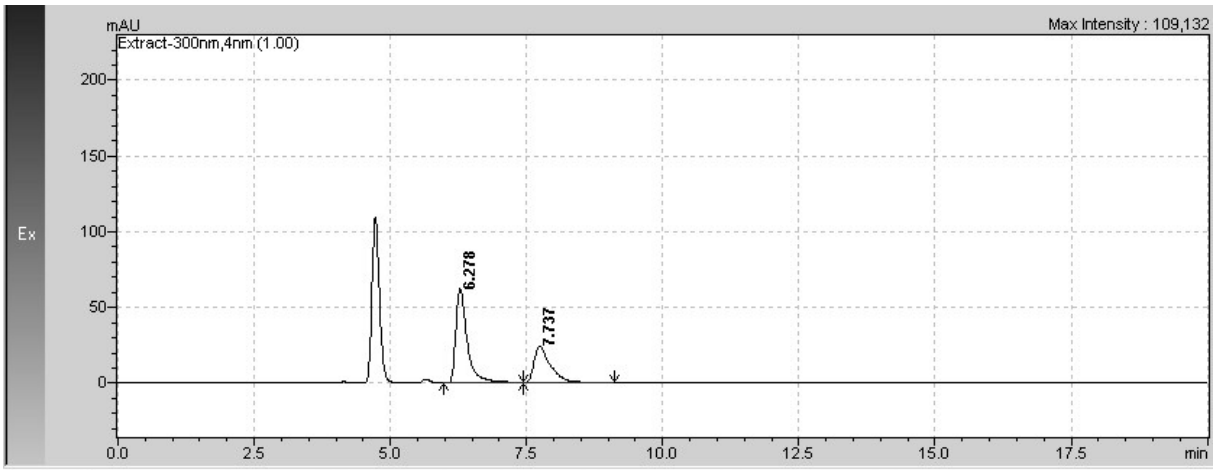
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Si	Peak Start	Peak End	Area%
1			21.957	71.22617	1560191	19271	0.0	20.789	27.467	71.2262
2			36.730	28.77383	630283	4955	0.0	35.221	41.280	28.7738





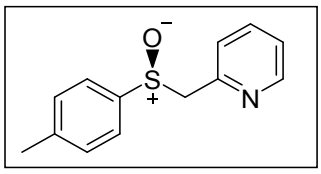
Peak Table

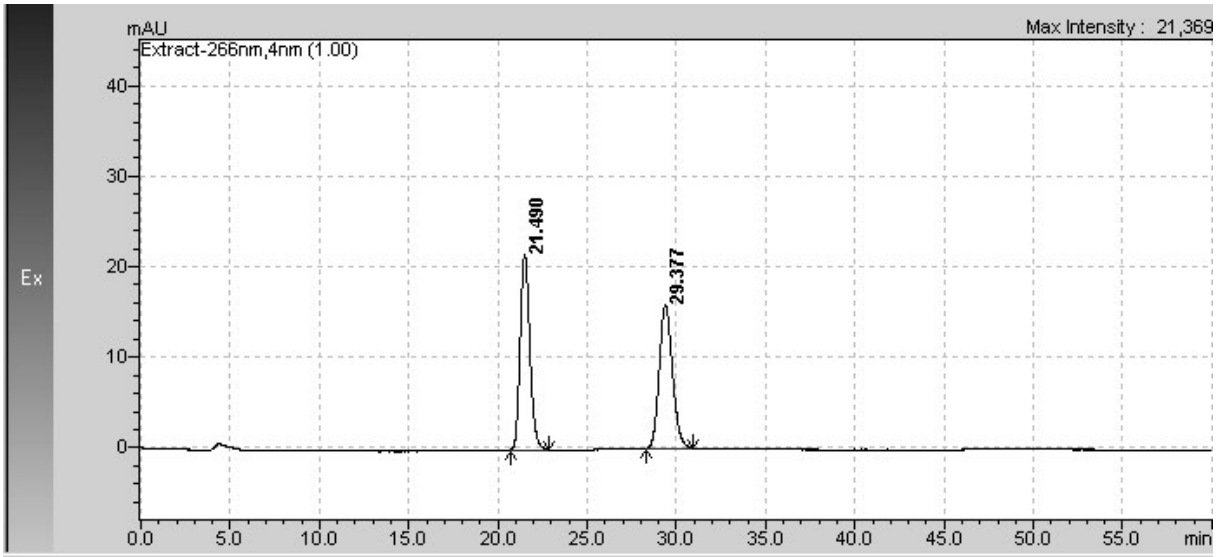
Peak#	ID#	Ret. Time	Conc.	Area	Height	Simila	Peak Start	Peak End	Area%
1		6.243	49.98166	9731591	751749	0.0000	5.973	7.381	49.9817
2		7.681	50.01834	9738734	601074	0.0000	7.381	8.768	50.0183



Peak Table

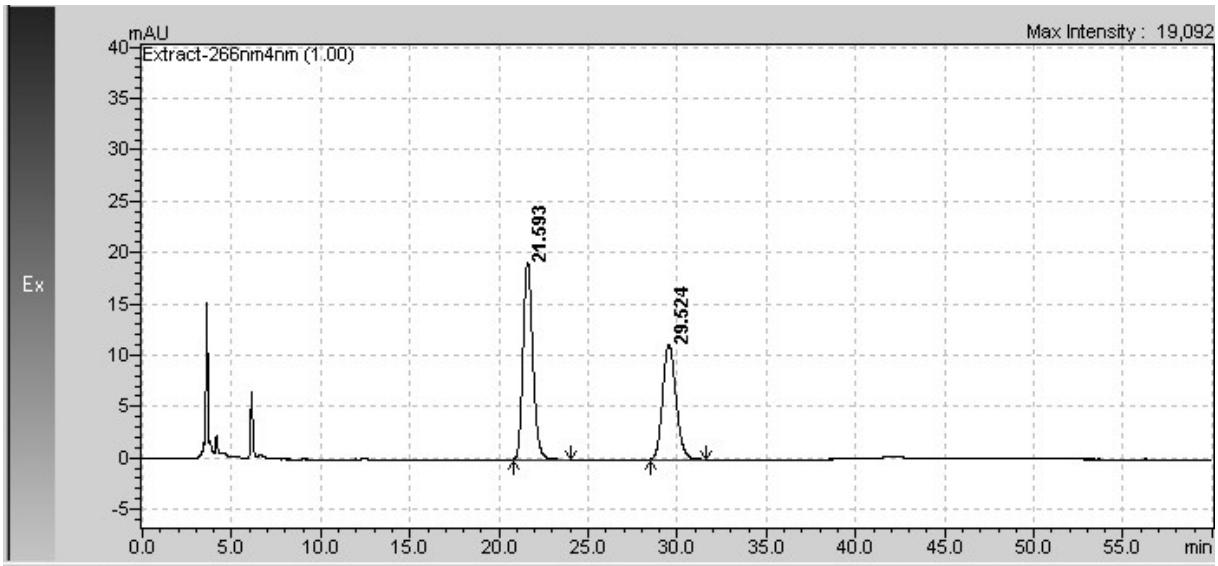
Peak#	ID#	Ret. Time	Conc.	Area	Height	Simila	Peak Start	Peak End	Area%
1		6.278	64.03012	925784	62250	0.0000	5.984	7.435	64.0301
2		7.737	35.96988	520073	24510	0.0000	7.435	9.120	35.9699





Peak Table

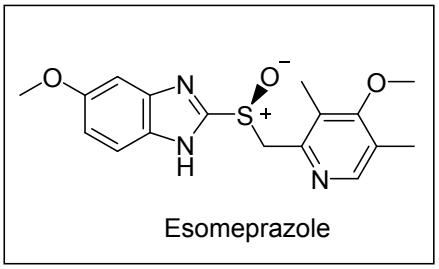
Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		21.490	50.11292	817426	21615	20.672	22.901	50.1129
2		29.377	49.88708	813742	15779	28.331	30.901	49.8871



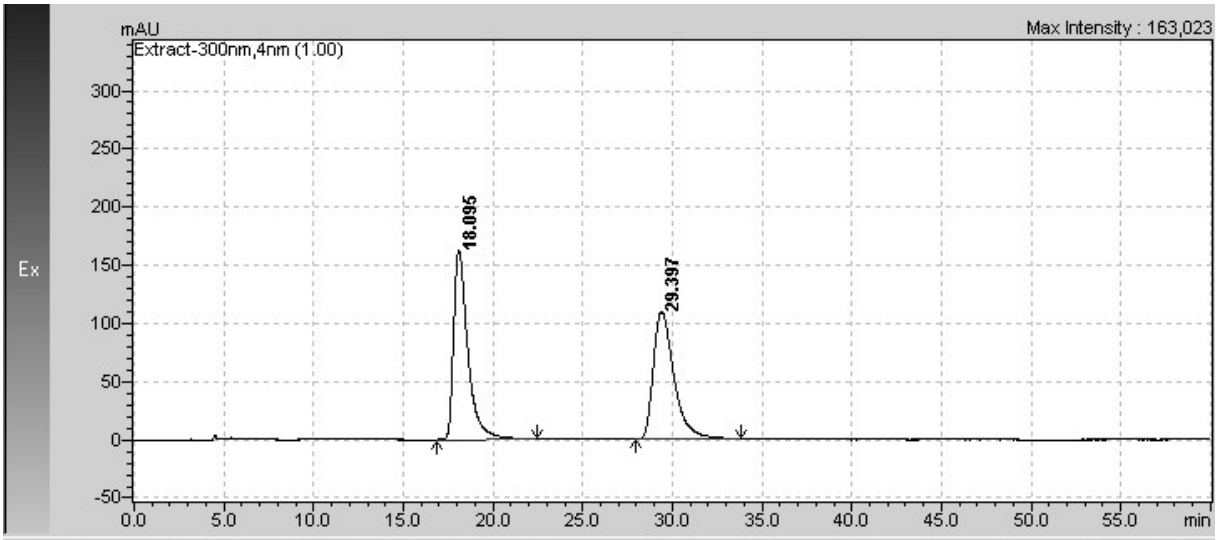
Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		21.593	55.65715	735374	19268	20.768	24.021	55.6572
2		29.524	44.34285	585883	11222	28.469	31.605	44.3428

10. HPLC Traces: Preparative Kinetic Resolution of Omeprazole

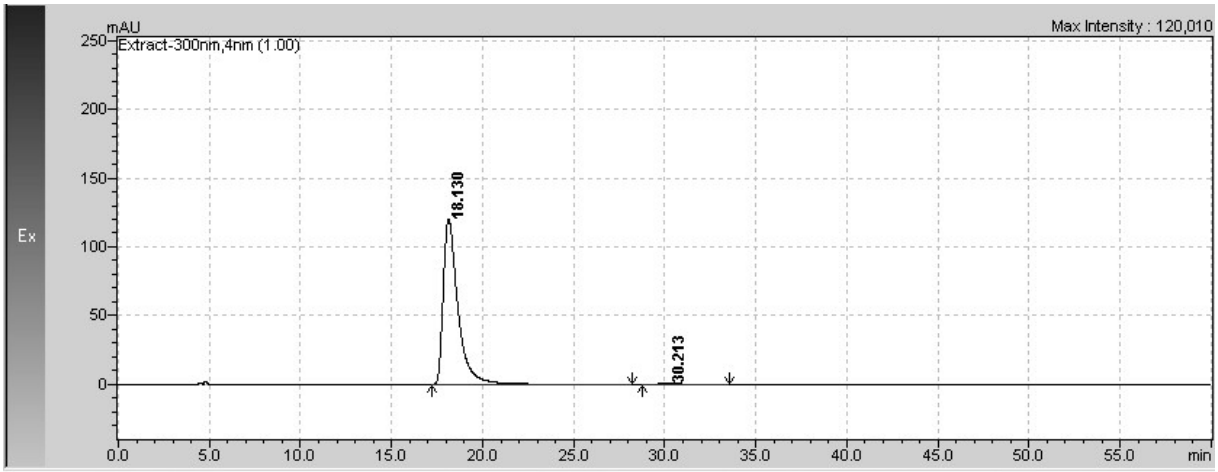


Esomeprazole



Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Peak Start	Peak End	Area%
1		18.095	50.44296	8976828	162728	16.907	22.421	50.4430
2		29.397	49.55704	8819168	110169	27.947	33.856	49.5570

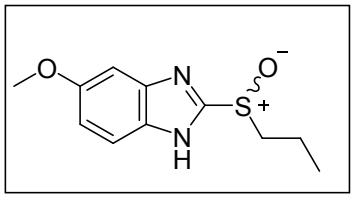


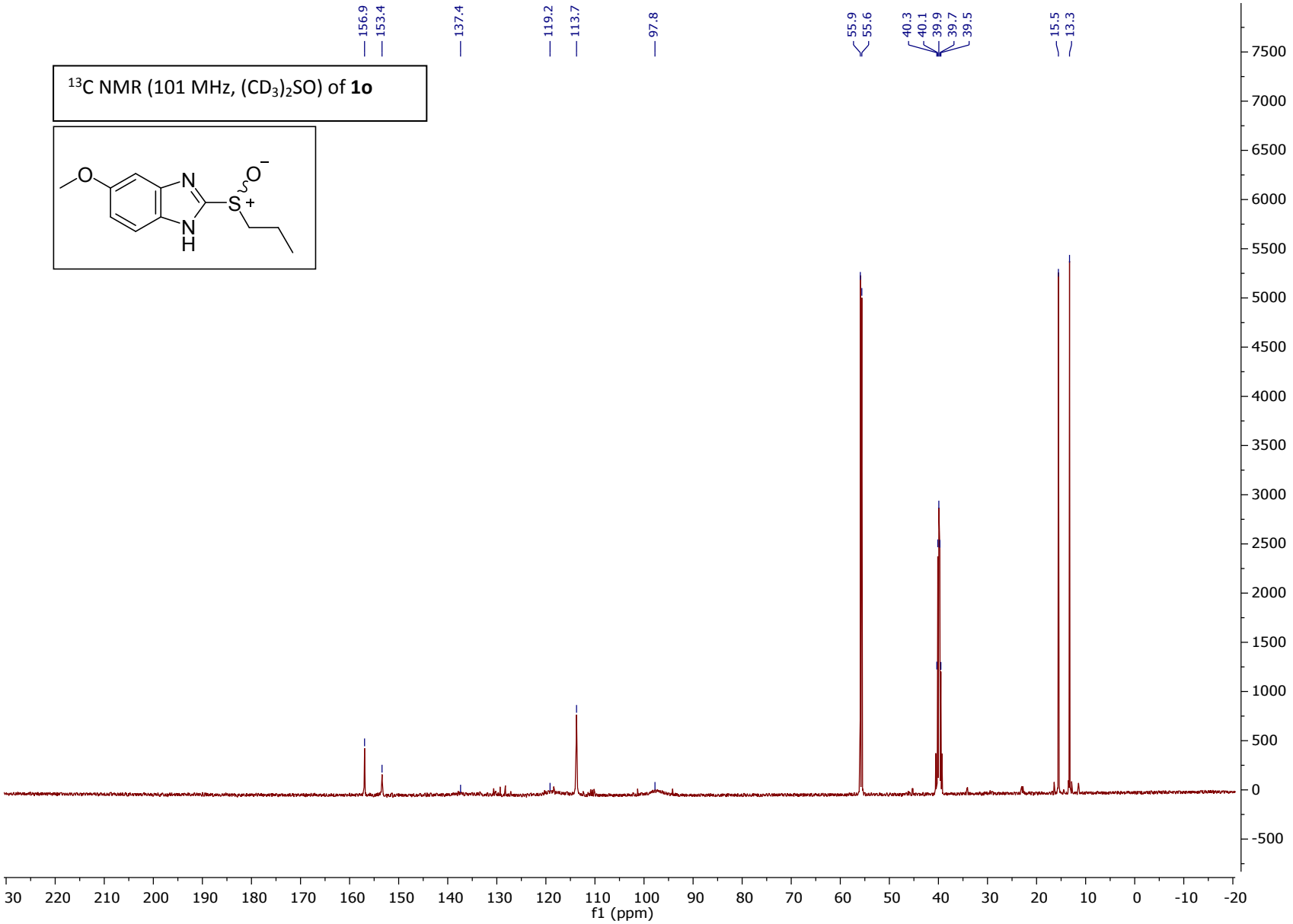
Peak Table

Peak#	ID#	Ret. Time	Conc.	Area	Height	Simila	Peak Start	Peak End	Area%
1		18.130	98.92774	6855017	120400	0.0000	17.205	28.181	98.9277
2		30.213	1.07226	74300	701	0.0000	28.800	33.568	1.0723

11. NMR Spectra

^{1}H NMR (400 MHz, $(CD_3)_2SO$) of ***rac*-1o**




156.9
153.4
137.4
119.2
113.7
97.8
55.9
55.6
40.3
40.1
39.9
39.7
39.5
15.5
13.3
^{13}C NMR (101 MHz, $(CD_3)_2SO$) of **1o**
O
N
O
S
N
H
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)