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Tetrabutylammonium tribromide impregnated MCM-48 as a heterogeneous catalyst for selective oxidation of sulfides

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General Information All solvents and chemicals were purchased commercially and used without further purification. TBATB and MCM-48 were purchased from sigma aldrich. ^{1}H and ^{13}C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 400 and 100 MHz respectively. All NMR samples were recorded in deuterated chloroform. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Elemental analyses were performed on a Flash 2000 Thermo Scientific instrument at NIT Silchar.The TEM characterization were carried out at model no.CM-12 Philips TEM (IIT Kharagpur).

Typical Procedure

A 50% hydrogen peroxide solution (1.2 equiv.) was added to a solution containing the sulfide **1** (0.5 mmol), TBATB/MCM-48 (2 mol%) and 2 mL EtOH. The reaction mixture was stirred at room temperature until completion of reaction was monitored by GC. After complete conversion of the reactant, the product was extracted with EtOAc and washed with water. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography (eluting with 1:1 hexane/EtOAc).

Preparation of TBATB/MCM-48

TBATB (160 mg, 0.5 mmol), MCM-48 (1.0 g), and DCM (20 mL) were placed in a 50 mL two-neck flask with a magnetic stirring bar. The reaction mixture being stirring for 72 h at 0 ^{o}C under an argon atmosphere. The solution was filtered and washed with DCM, and the obtained solid was dried in vacuo.

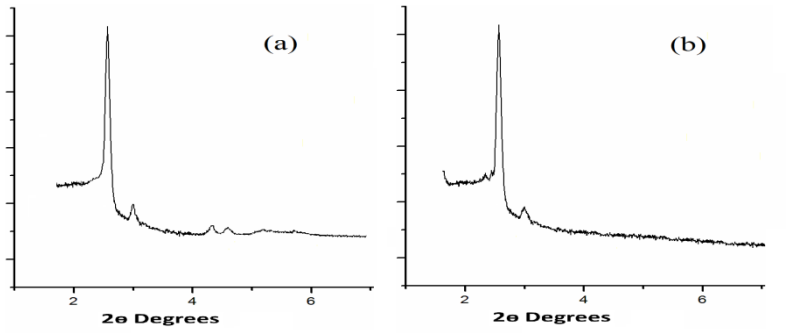


Fig. 1 Low angle XRD patterns of (a) pure silica MCM-48, and (b) impregnation (TBATB/MCM-48)

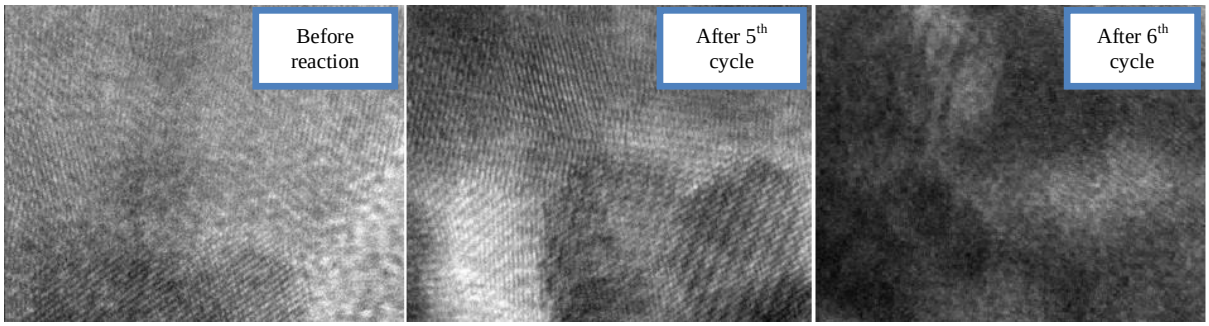


Figure 4.TEM images of TBATB/MCM-48 system at different reaction conditions: scale bar 50 nm

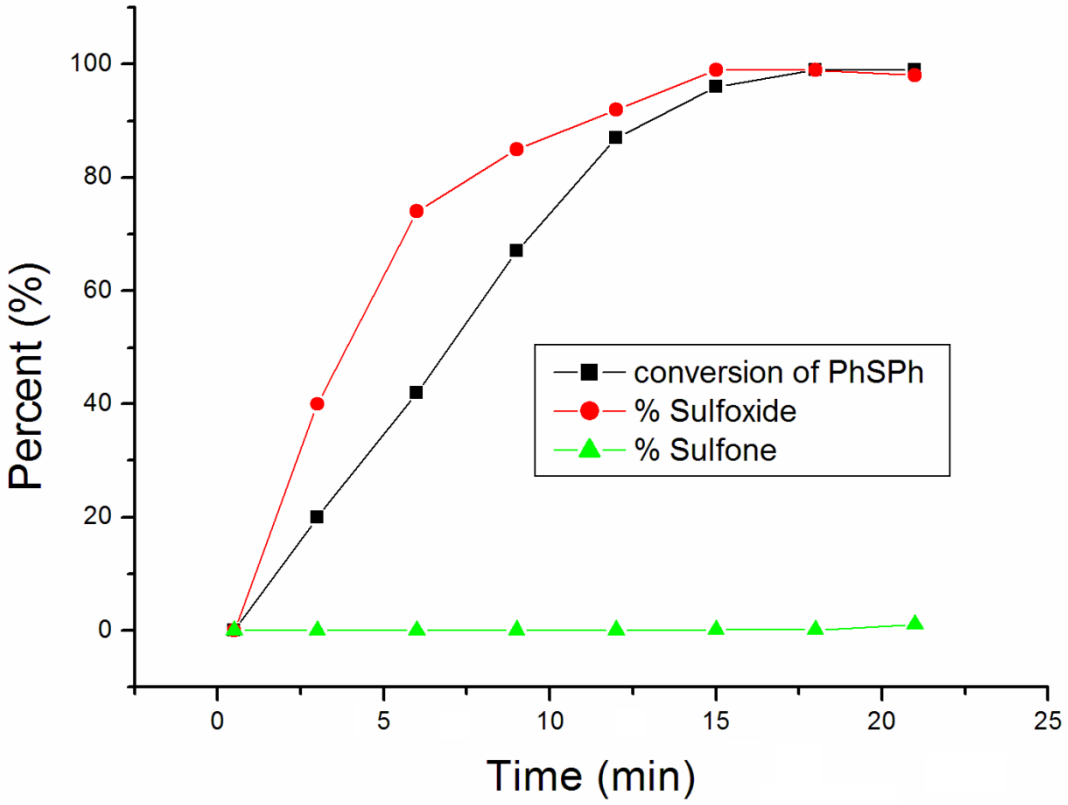


Fig. 5 Progress of reactions at room temperature; reaction condition: substrate 1 (0.5 mmol), 1.2 equiv of H_2O_2, TBATB/MCM-48 (2.0 mol%) in EtOH (2 mL).

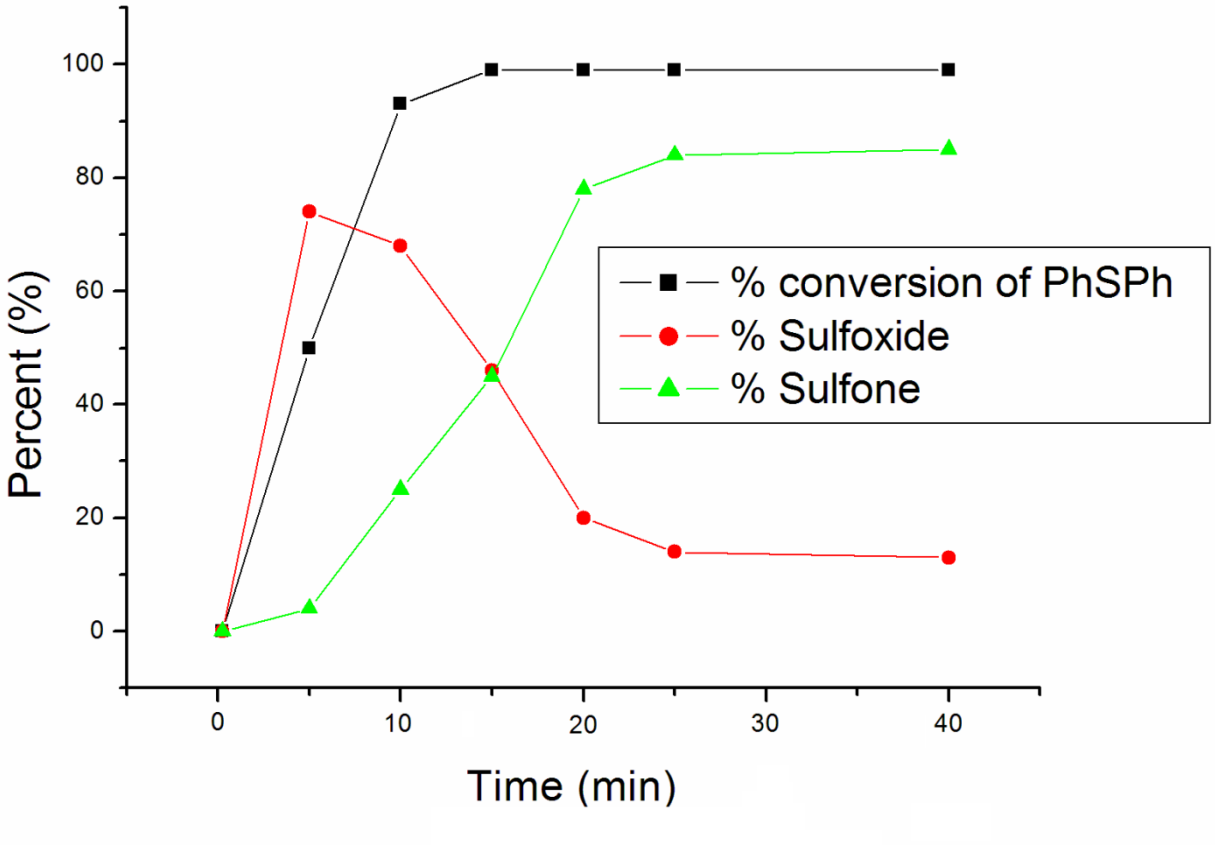


Fig. 6 Progress of reactions at 80 ^{o}C; reaction condition: substrate 1 (0.5 mmol), 1.5 equiv of H_2O_2, TBATB/MCM-48 (2.0 mol%) in EtOH (2 mL).

Dibenzyl sulfoxide (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 10H), 3.90-3.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.3, 130.6, 127.3, 126.7, 57.2; Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 73.04; H, 6.14.

2-Nitrophenyl benzyl sulfoxide (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J*= 9.1 Hz, 1H), 7.95 (d, *J*= 8 Hz, 1H),7.83 (t, *J*= 8.24 Hz, 1H), 7.54 (t, *J*=7.92 Hz, 1H), 7.32-7.21 (m, 5H), 4.11 (d, *J*=12.16 Hz, 1H), 3.88 (d, *J*=12.08 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.7, 134.1, 133.7, 129.3, 129.1, 128.5, 128.2, 127.4, 125.1, 61.4; Anal. Calcd for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.73; H, 4.27; N, 5.22

4- Chlorophenyl benzyl sulfoxide (2c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.40 (m, 7H),6.93-6.87 (m, 1H),4.01 (d,*J*=12.4 Hz, 1H), 3.70 (d, *J*=12.6 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.5, 133.6, 129.2, 128.7, 127.4, 127.0, 124.1, 63.1; Anal. Calcd for $C_{13}H_{11}ClOS$: C, 62.27; H, 4.42. Found: C, 62.30; H, 4.41.

4 Nitrobenzyl phenyl sulfoxide (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J*=8.4 Hz, 2H), 7.56-7.40 (m, 5H),7.07 (d, *J*=8.0 Hz, 2H), 4.25 (d, *J*=11.8 Hz, 1H), 3.97 (d, *J*=12.2 Hz, 1H);Anal. Calcd for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.80; H, 4.21; N, 5.37.

Benzyl p-methoxyphenyl sulfoxide (2e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 7.18-7.09 (m, 4H), 4.06 (d, *J*=12.2 Hz, 1H), 3.96 (d, *J*=12.2 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 141.2, 131.0, 127.8, 127.0, 126.1, 123.6, 115.2, 63.7, 55.1.

4-methoxy benzyl phenyl sulfoxide (2f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 5H), 6.91 (d, *J*= 7.84 Hz, 2H), 6.75 (d, *J*=7.5 Hz, 2H), 4.05 (d, *J*=12.2 Hz, 1H),3.89 (d,*J*=12 Hz, 1H), 3.52 (s, 1H);Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.25; H, 5.79.

Benzyl 4-bromobenzyl sulfoxide (2g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 9H), 3.88-3.80 (m, 4H); Anal. Calcd for $C_{14}H_{13}BrOS$: C, 54.38; H, 4.24. Found: C, 54.40; H, 4.27.

Benzyl 4-methylphenyl sulfoxide (2h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 5H),7.07-6.93 (m, 4H), 4.09-4.01 (m, 2H), 2.31 (s, 3H); Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: : C, 73.11; H, 6.12.

Benzyl 4-nitrophenyl sulfoxide (2i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J*= 8.4 Hz, 2H), 7.97 (d, *J*= 8.0 Hz, 2H), 7.57-7.43 (m, 5H), 3.92-3.82 (m, 2H); Anal. Calcd for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.81; H, 4.20; N, 5.37.

Benzyl phenyl sulfoxide (2j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 10H), 4.02-3.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ138.0, 134.5, 133.2, 130.8, 129.7, 128.8, 127.1, 124.8, 63.2. Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.17; H, 5.60.

Diallyl sulfoxide (2k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23-6.09 (m, 4H), 5.51-5.30 (m, 4H), 3.19 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ125.1, 123.1, 54.6. Anal. Calcd for $C_6H_{10}OS$: C, 55.35; H, 7.74. Found: C, 55.39; H, 7.71.

Allyl phenyl sulfoxide (2l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H),6.23-5.86 (m, 1H), 5.02 (dd, *J*=1.2 Hz, 8.4 Hz, 2H), 3.41 (d, *J*=7.2 Hz, 2H); Anal. Calcd for C_7H_8OS: C, 59.97; H, 5.75. Found: C, 59.94; H, 5.81.

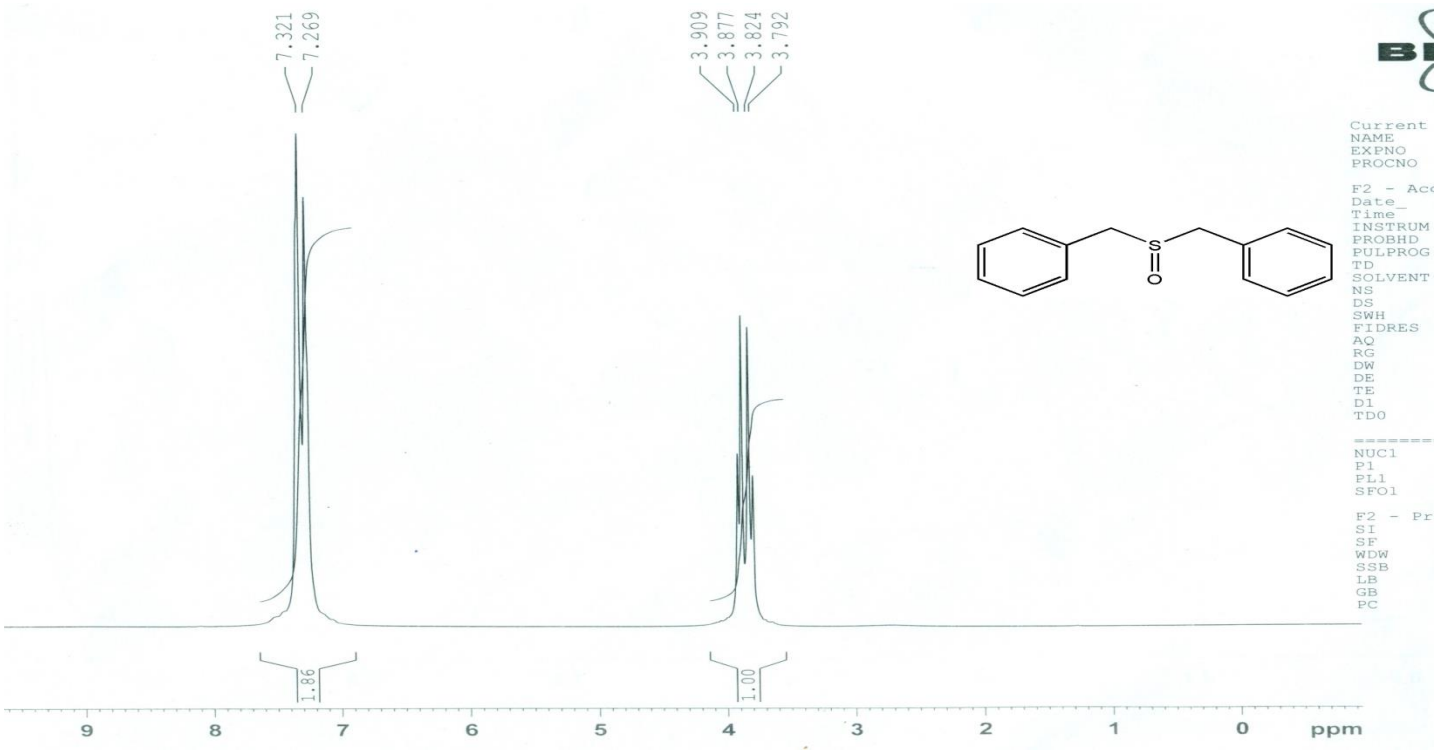
Methyl phenyl sulfoxide (2n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.57 (m, 2H), 7.42-7.33 (m, 3H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ142.4, 131.3, 129.5, 123.3, 43.5.

4-chlorophenyl 4-nitrophenyl sulfoxide (2o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J*=7.2 Hz, 2H), 7.86 (d, *J*=7.5 Hz, 2H), 7.68 (d, *J*=7.8 Hz, 2H), 7.59 (d, *J*=8.5 Hz, 2H);Anal. Calcd for $C_{12}H_8ClNO_3S$: C, 51.16; H, 2.86; N, 4.97. Found: C, 51.11; H, 2.77; N, 4.99.

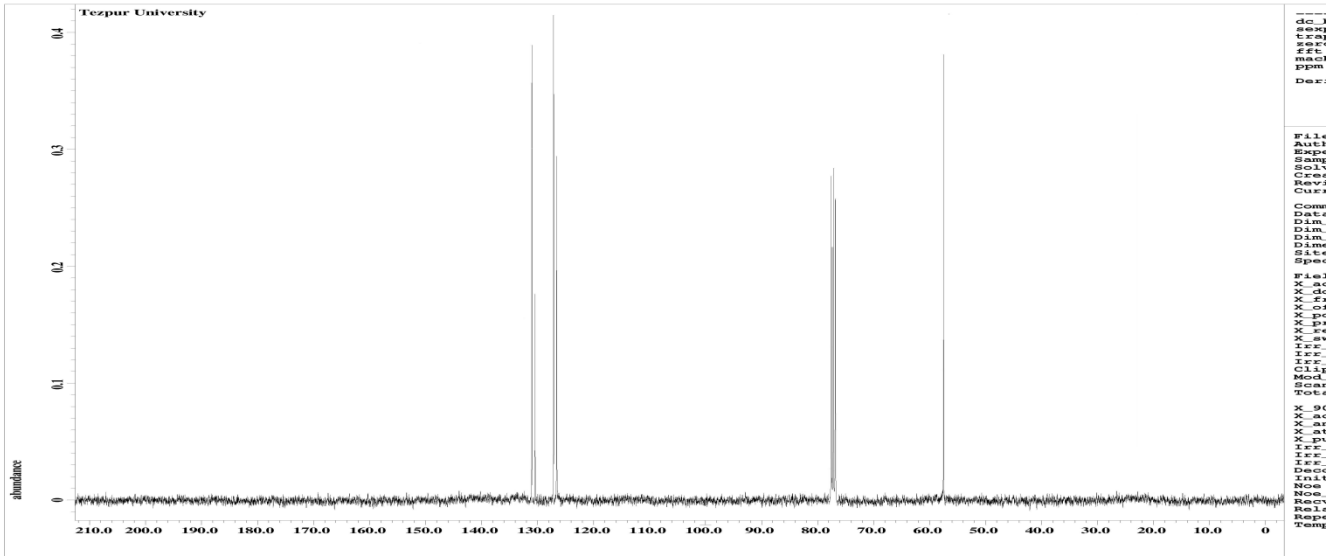
Methyl 4-nitrophenyl sulfoxide (2p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J*=8.0 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ152.6, 150.1, 126.7, 125.8, 43.5. Anal. Calcd for $C_7H_7NO_3S$: C, 45.40; H, 3.81; N, 7.56. Found: C, 45.44; H, 3.82; N, 7.62.

Di t-butyl sulfoxide(2q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ δ56.7, 25.6.

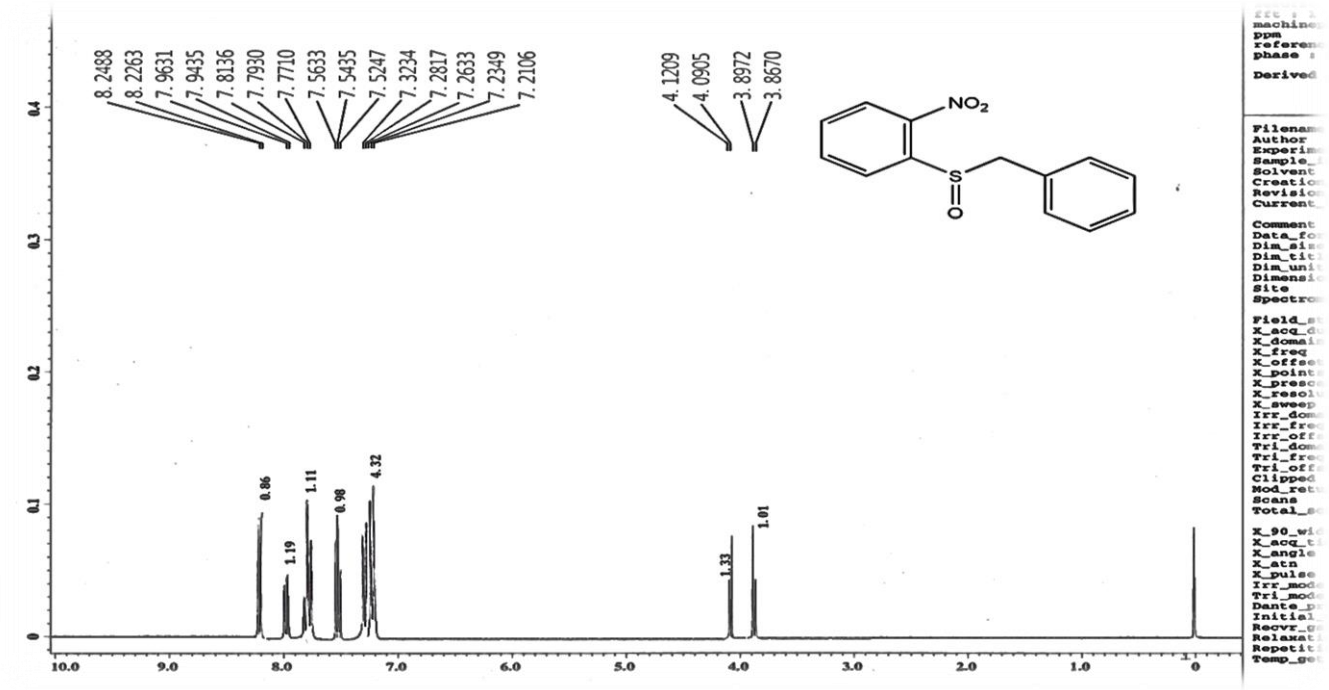
^{1}H NMR of Dibenzyl sulfoxide(2a)



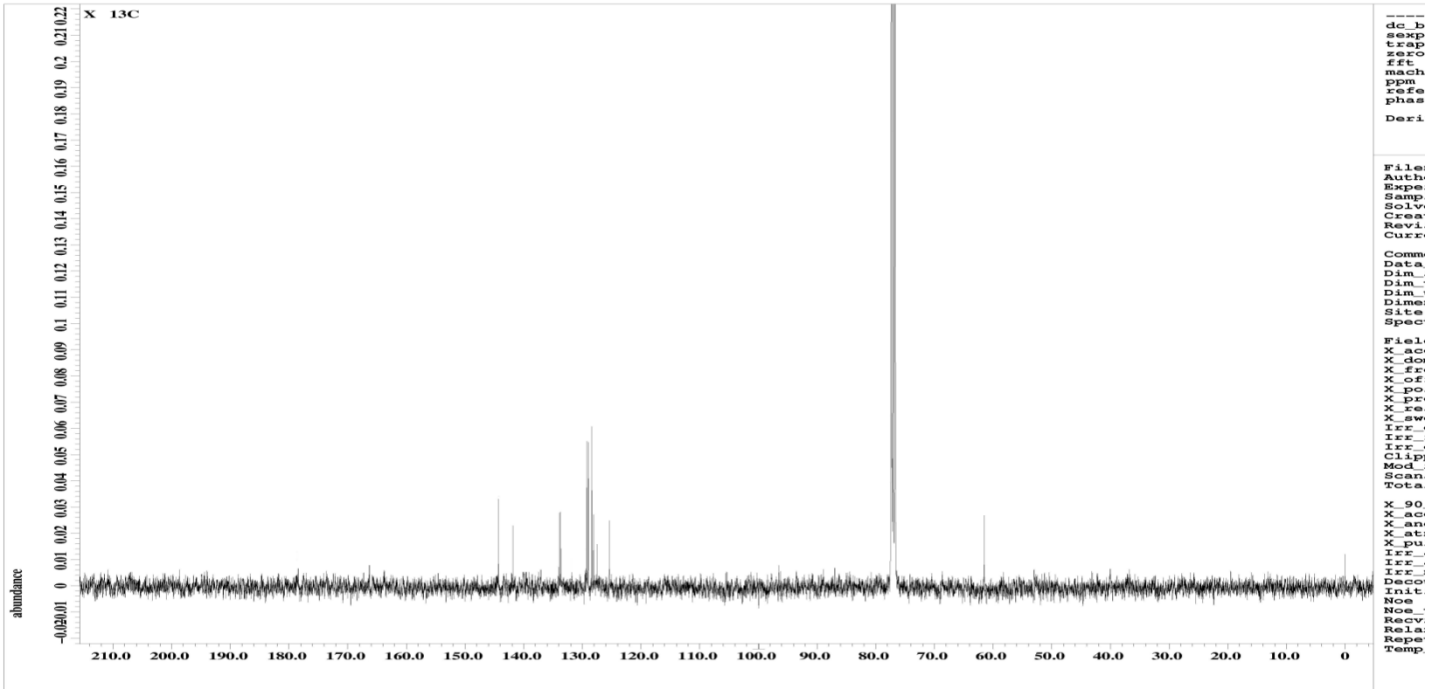
^{13}C NMR of Dibenzyl sulfoxide(2a)



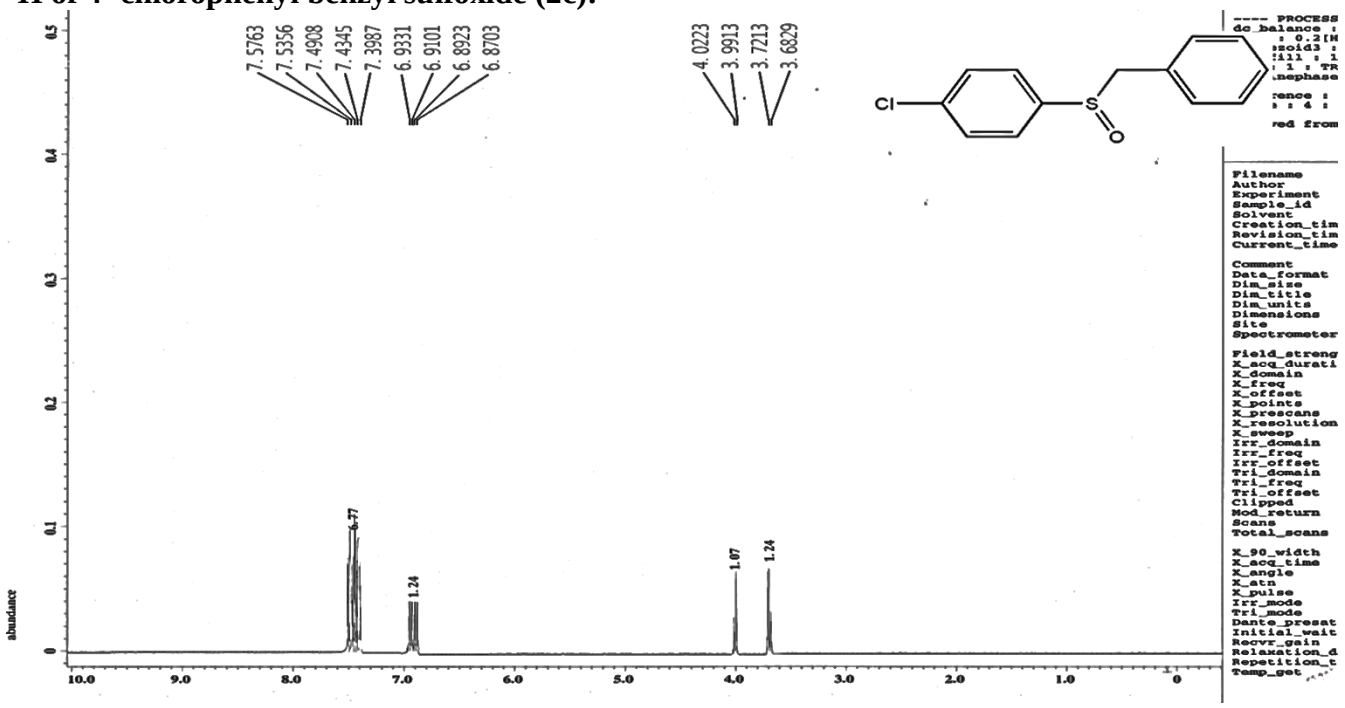
^{1}H NMR of 2-Nitrophenyl benzyl sulfoxide (2b):



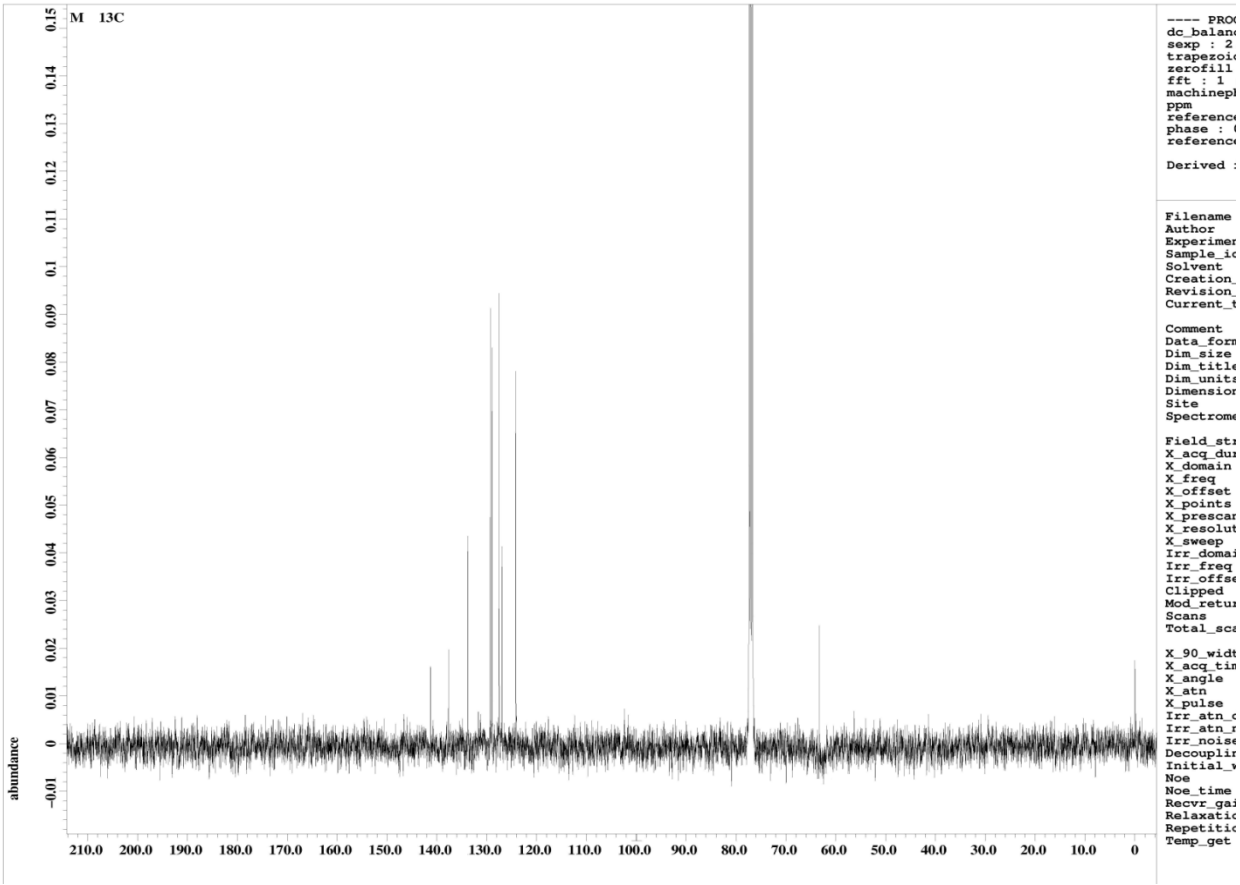
^{13}C NMR of 2-Nitrophenyl benzyl sulfoxide (2b):



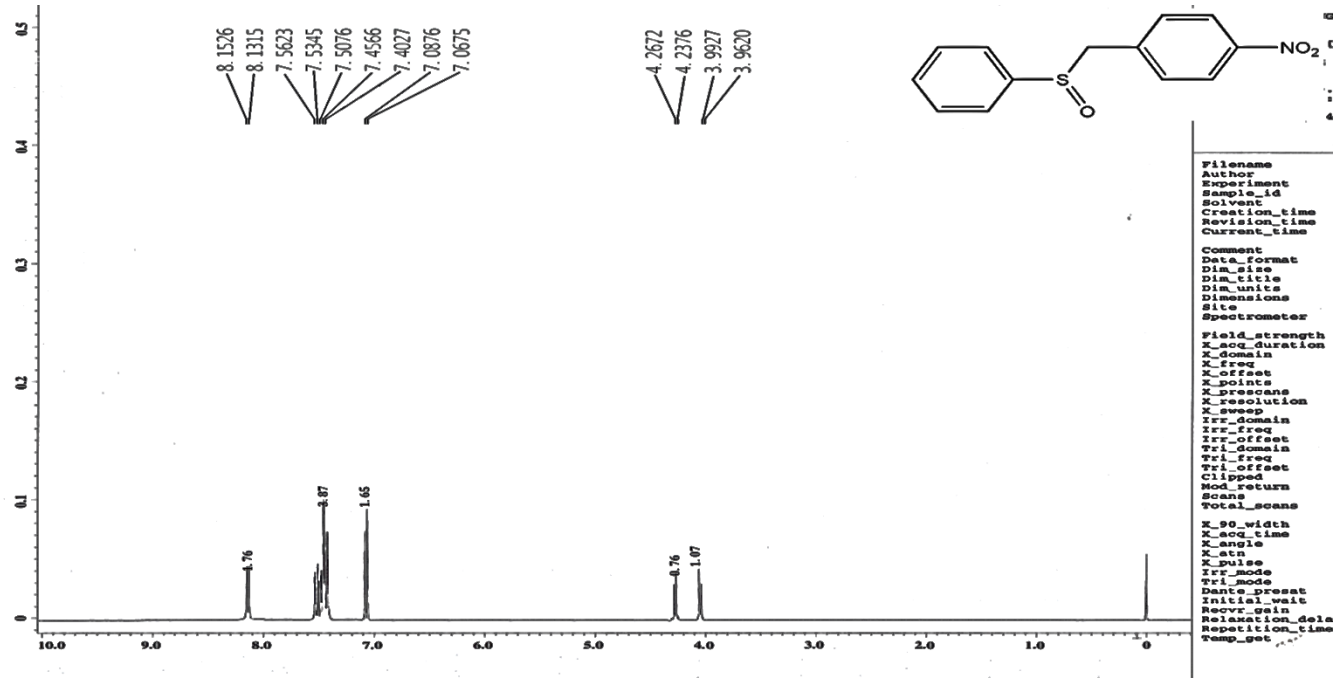
^{1}H of 4- chlorophenyl benzyl sulfoxide (2c):



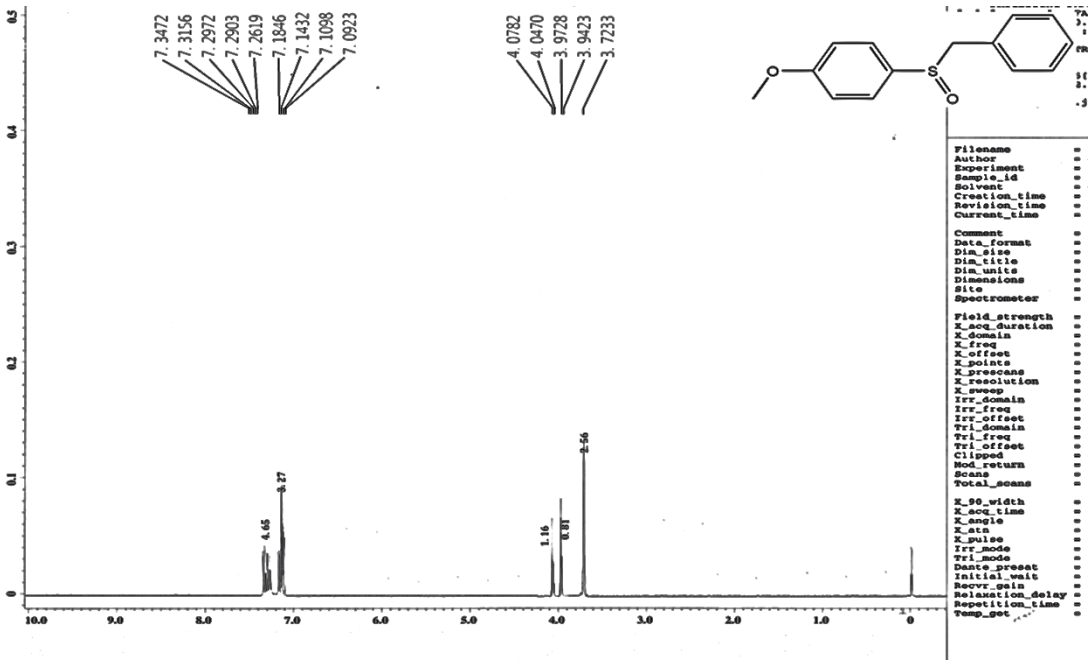
^{13}C NMR of 4- chlorophenyl benzyl sulfoxide (2c):



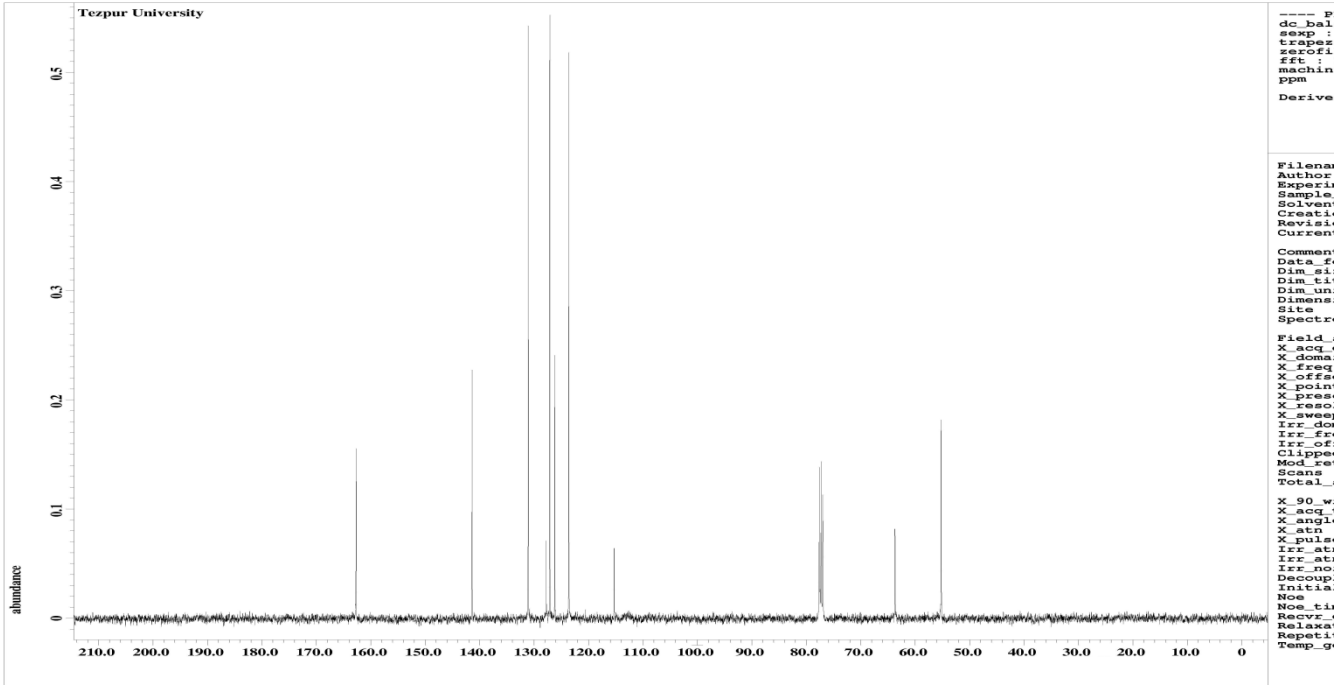
^{1}H NMR of 4 Nitrobenzyl phenyl sulfoxide (2d):



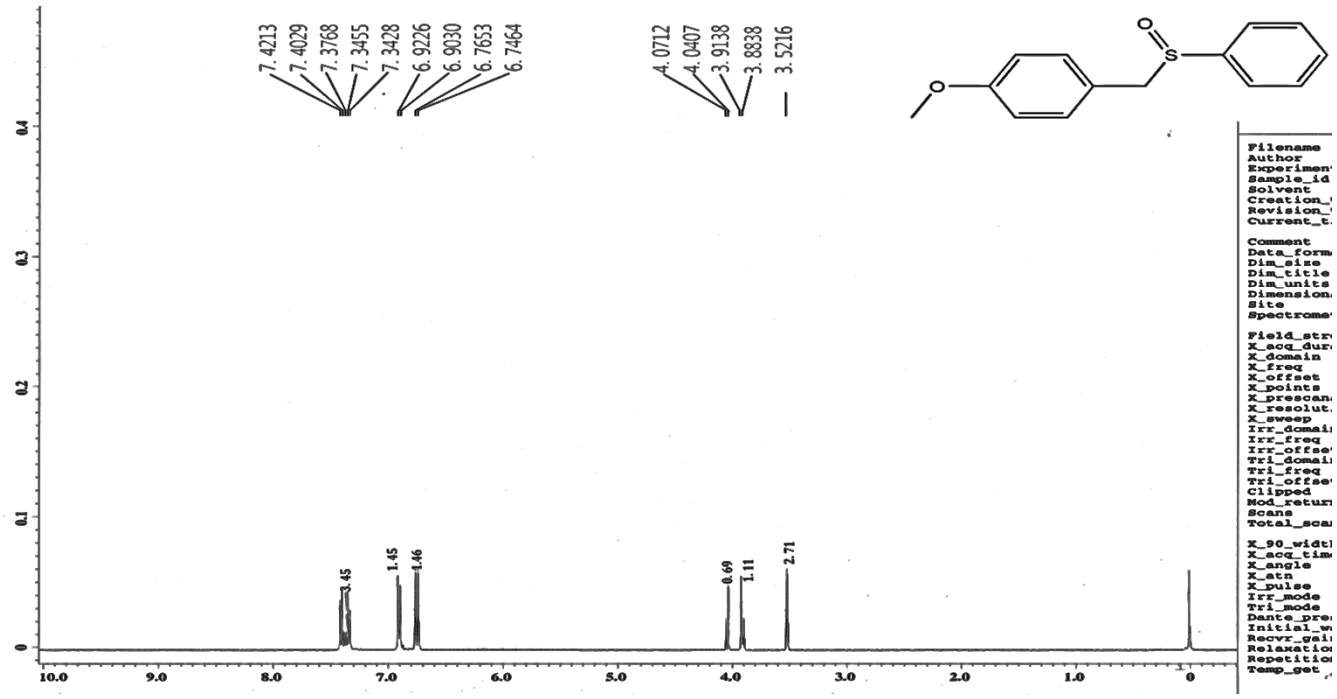
^{1}H NMR of Benzyl p-methoxyphenyl sulfoxide (2e):



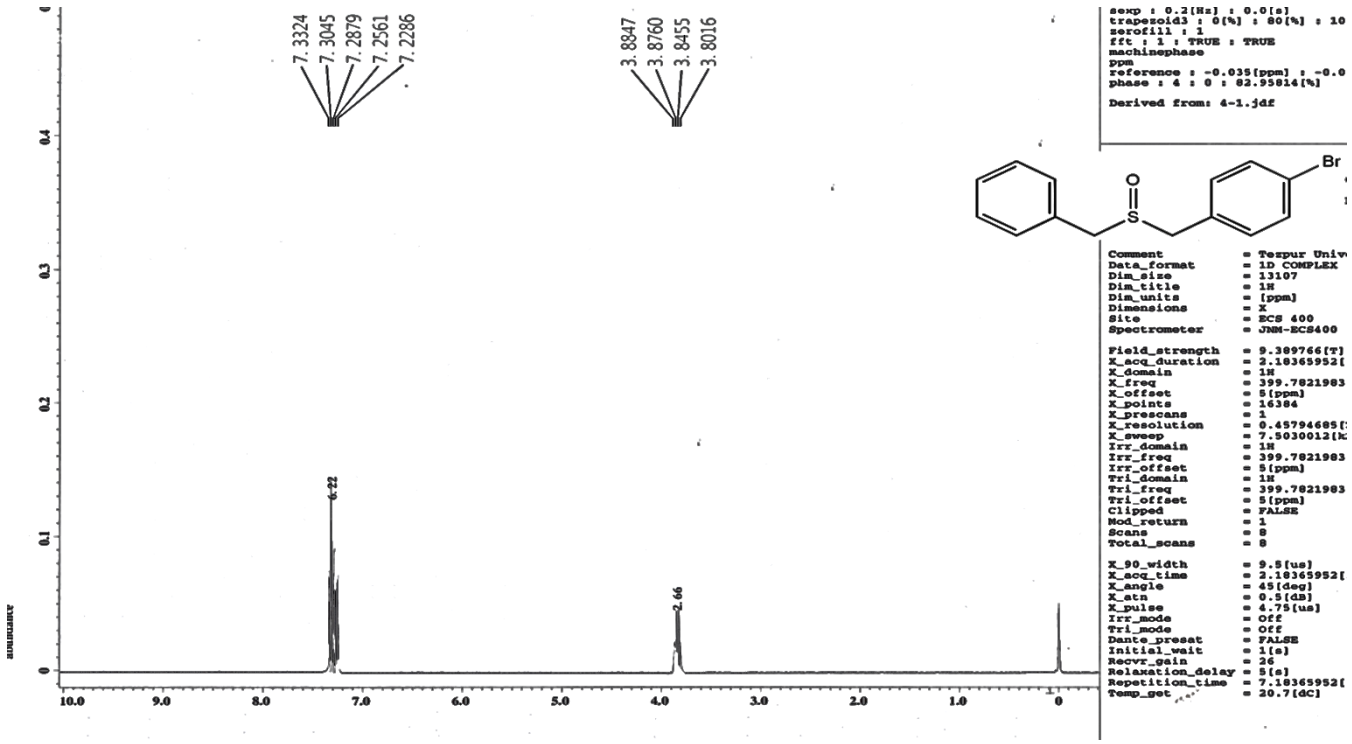
^{13}C NMR of Benzyl p-methoxyphenyl sulfoxide (2e):



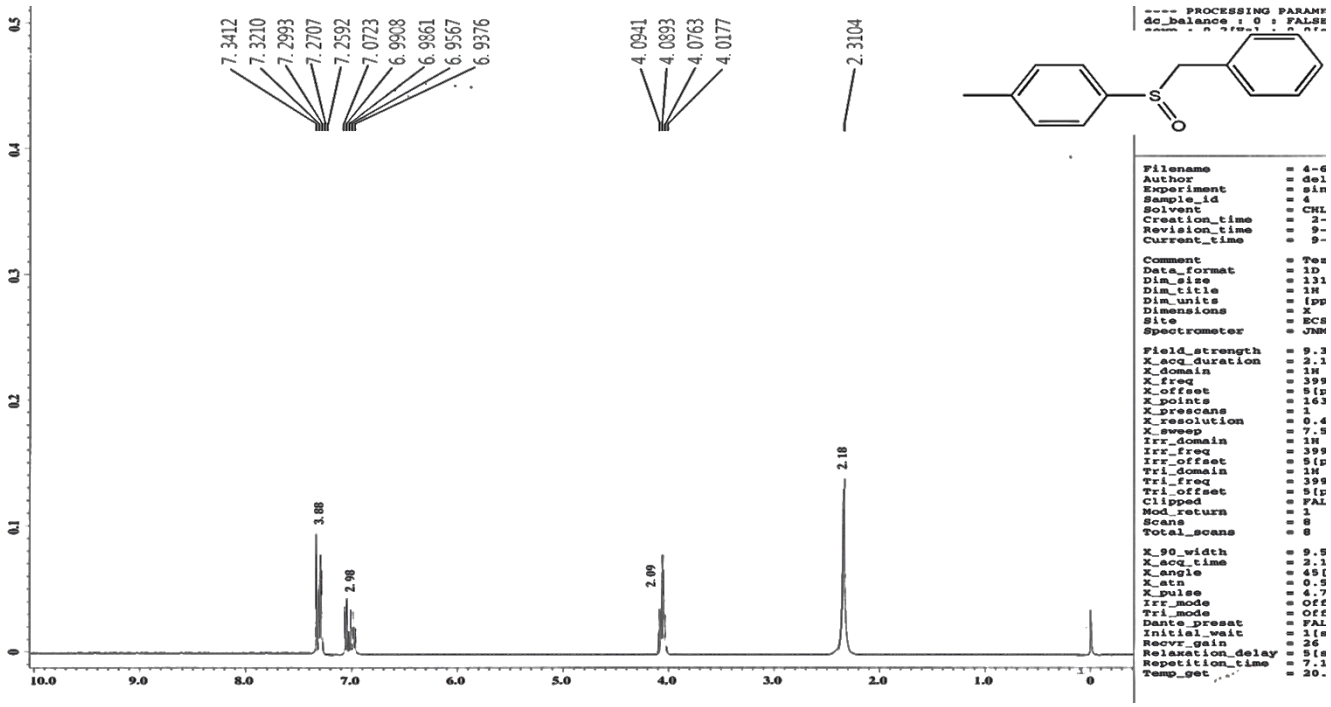
^{1}H NMR of 4-methoxy benzyl phenyl sulfoxide (2f):



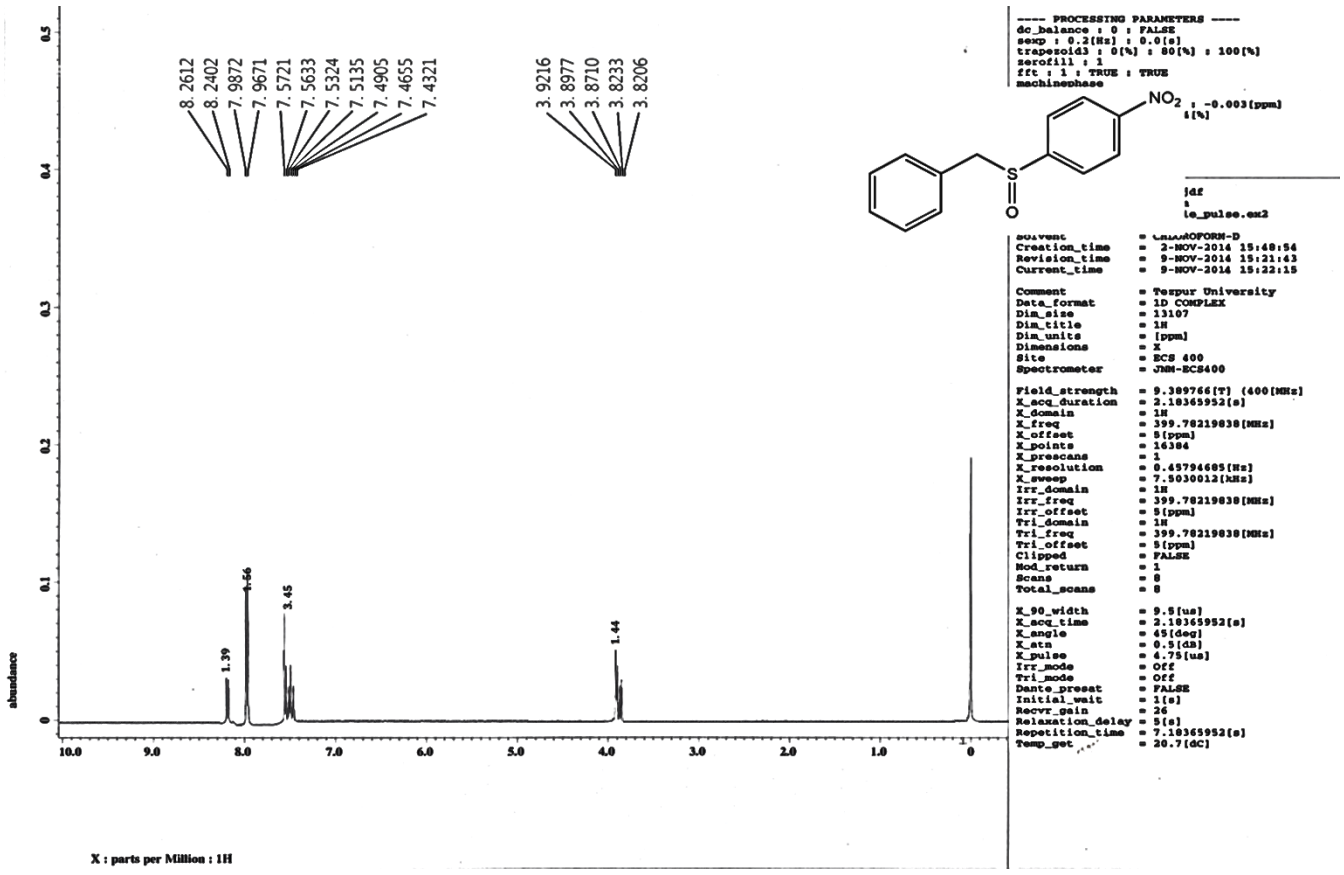
^{1}H NMR of Benzyl 4-bromobenzyl sulfoxide (2g):



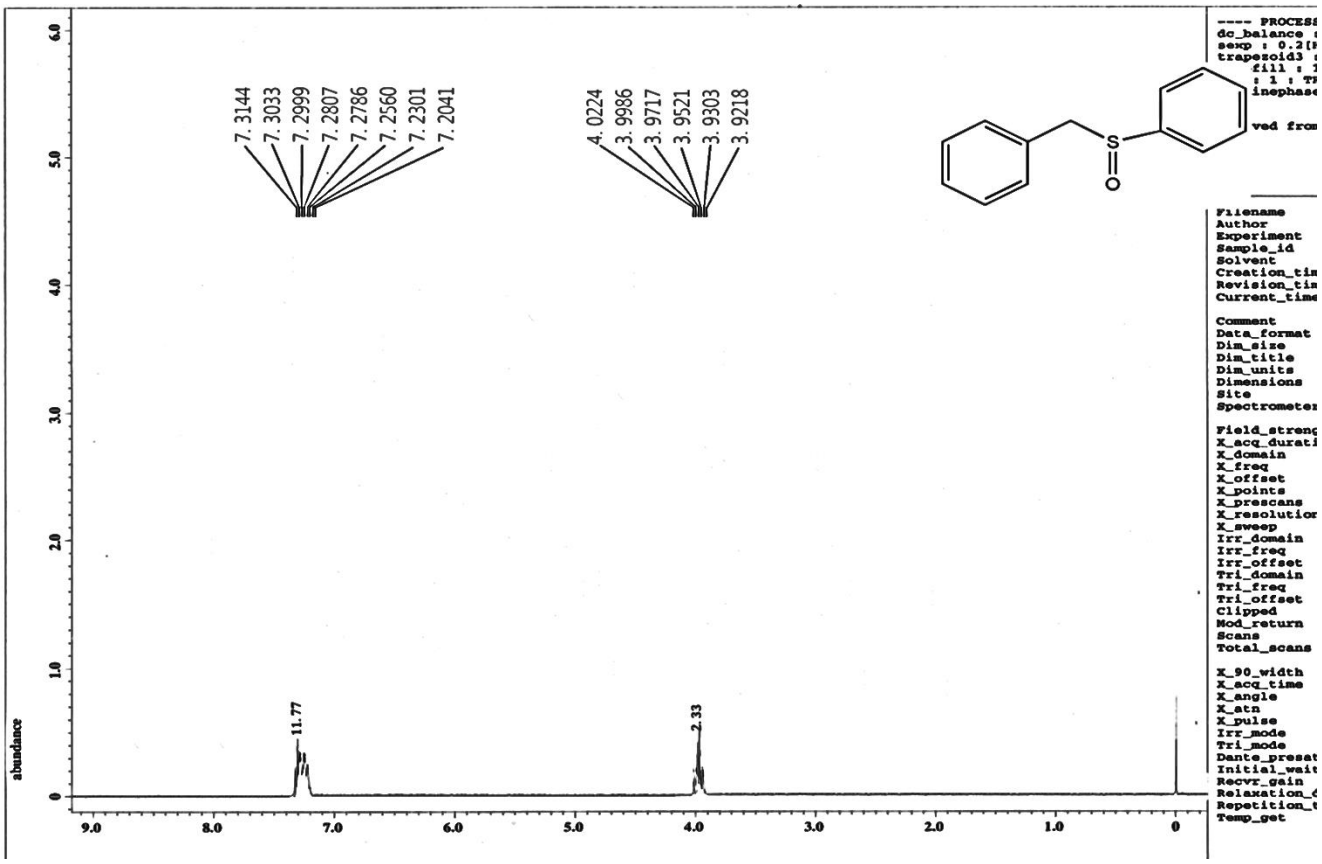
^{1}H NMR of Benzyl 4-methylphenyl sulfoxide (2h):



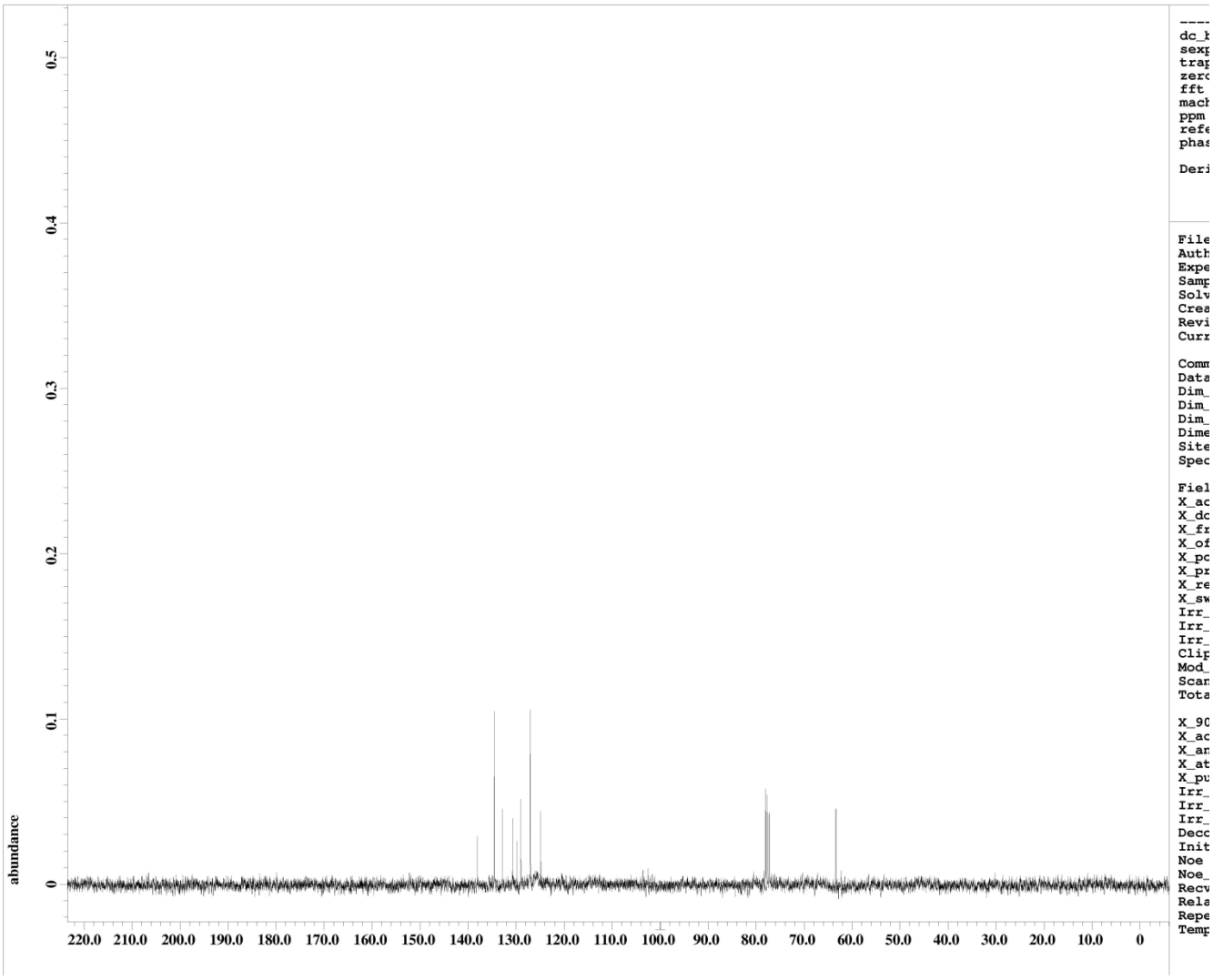
^{1}H NMR of Benzyl 4-nitrophenyl sulfoxide (2i):



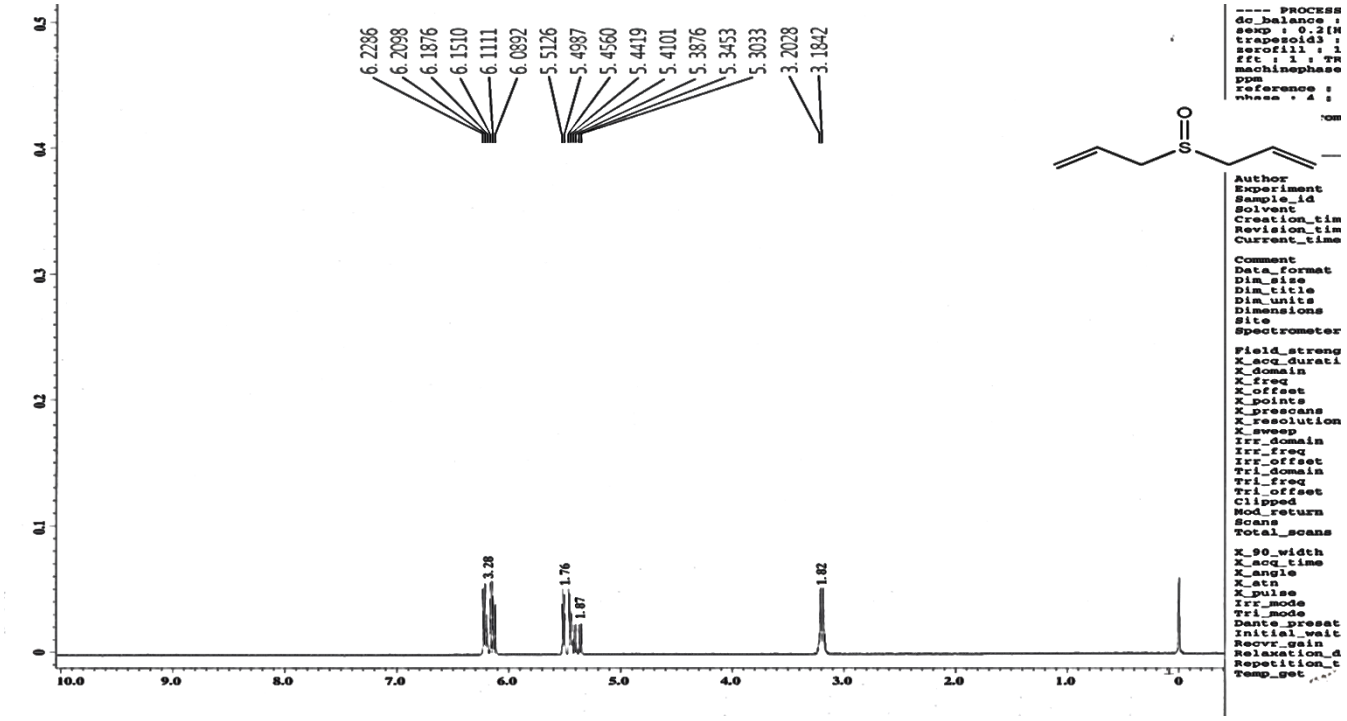
^{1}H NMR of Benzyl phenyl sulfoxide (2j):



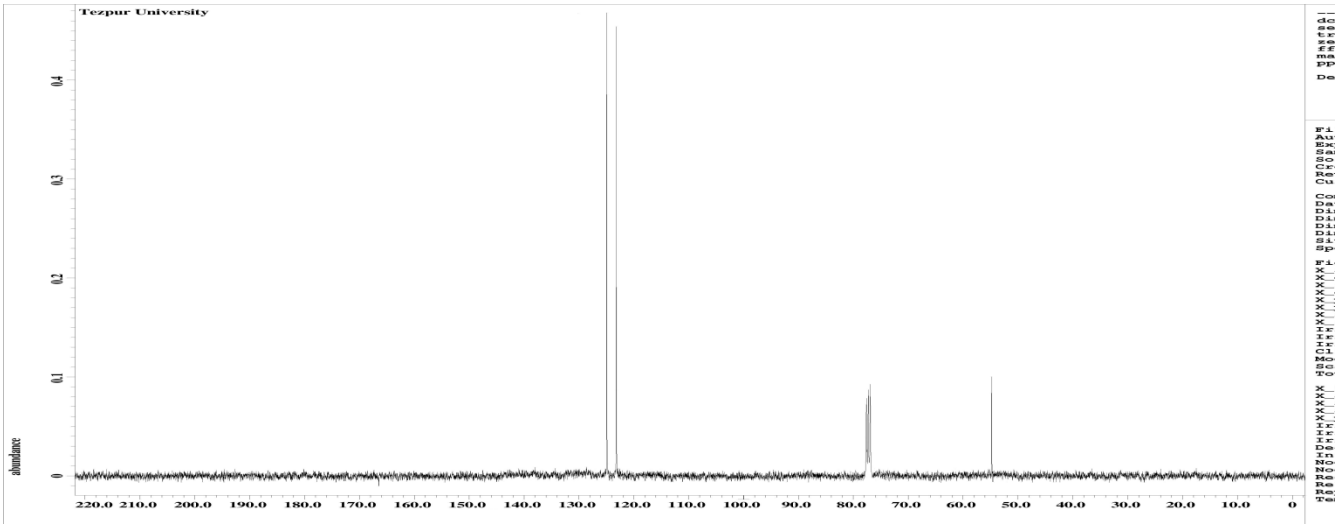
^{13}C NMR of Benzyl phenyl sulfoxide (2j):



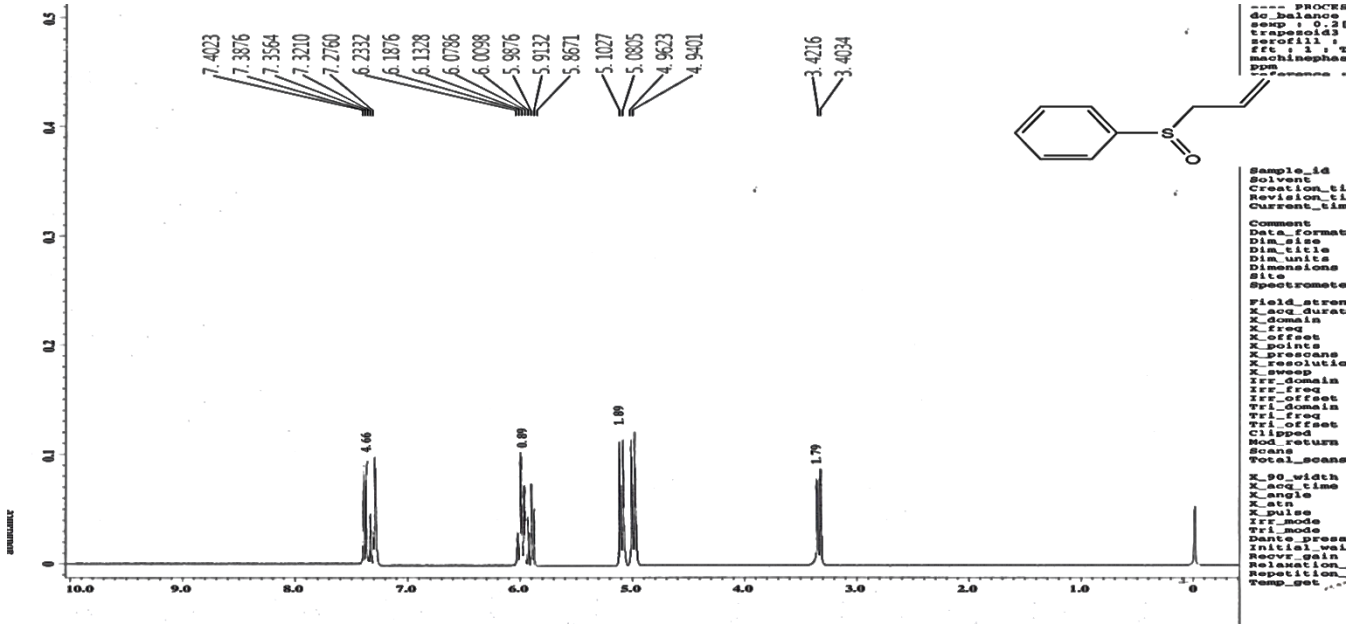
^{1}H NMR of Diallyl sulfoxide (2k):



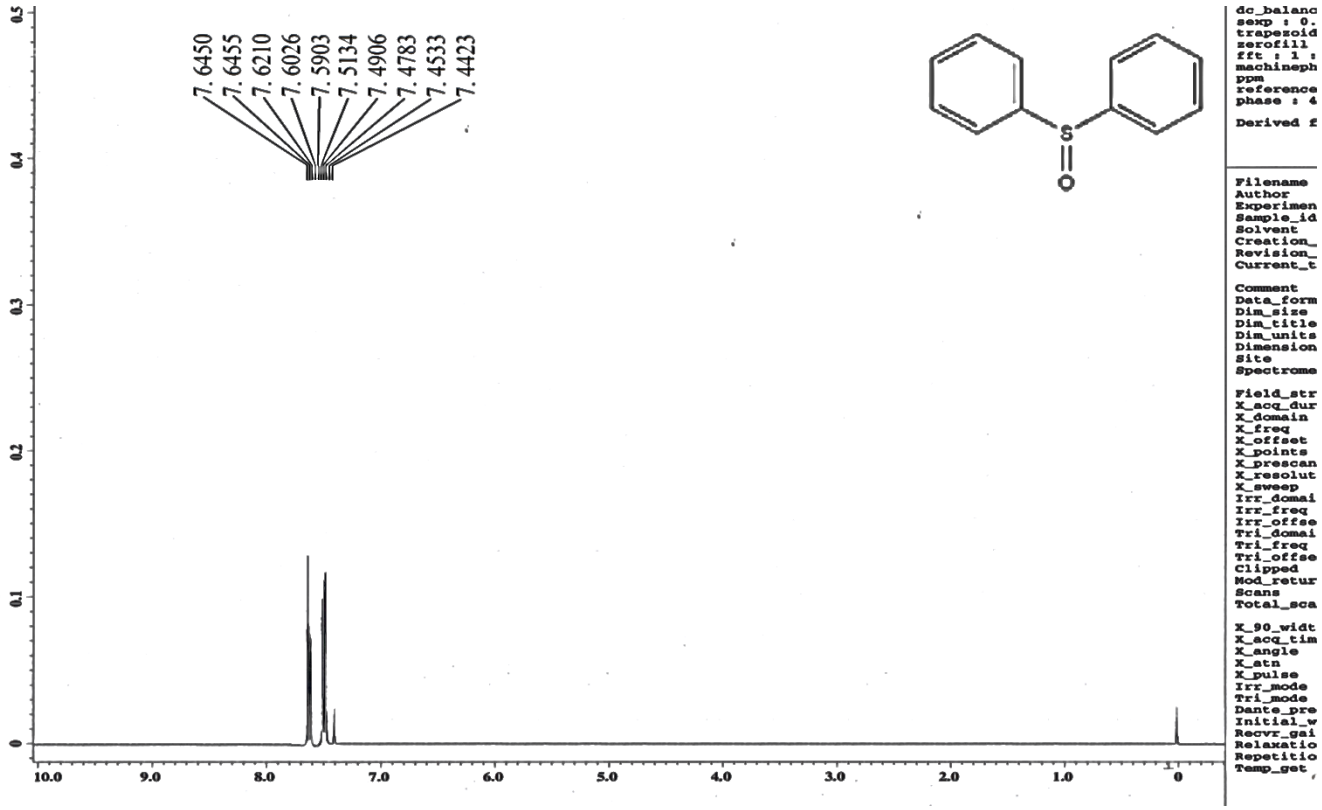
^{13}CNMR of Diallyl sulfoxide (2k):

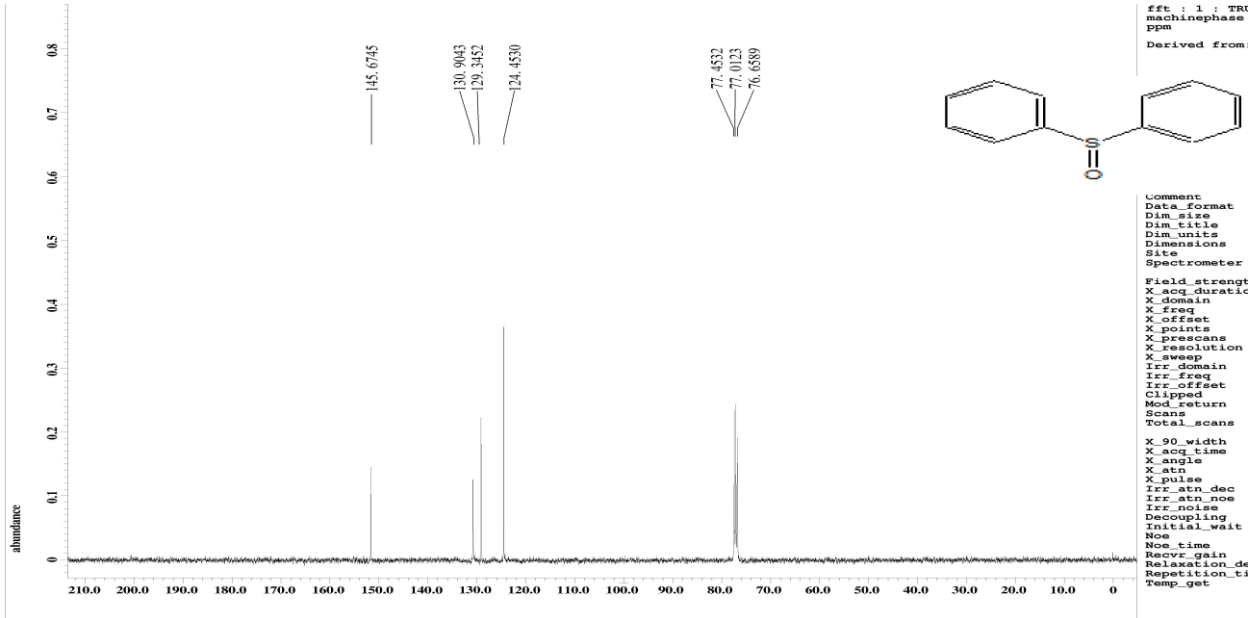


^{1}H NMR of Allyl phenyl sulfoxide (2l):

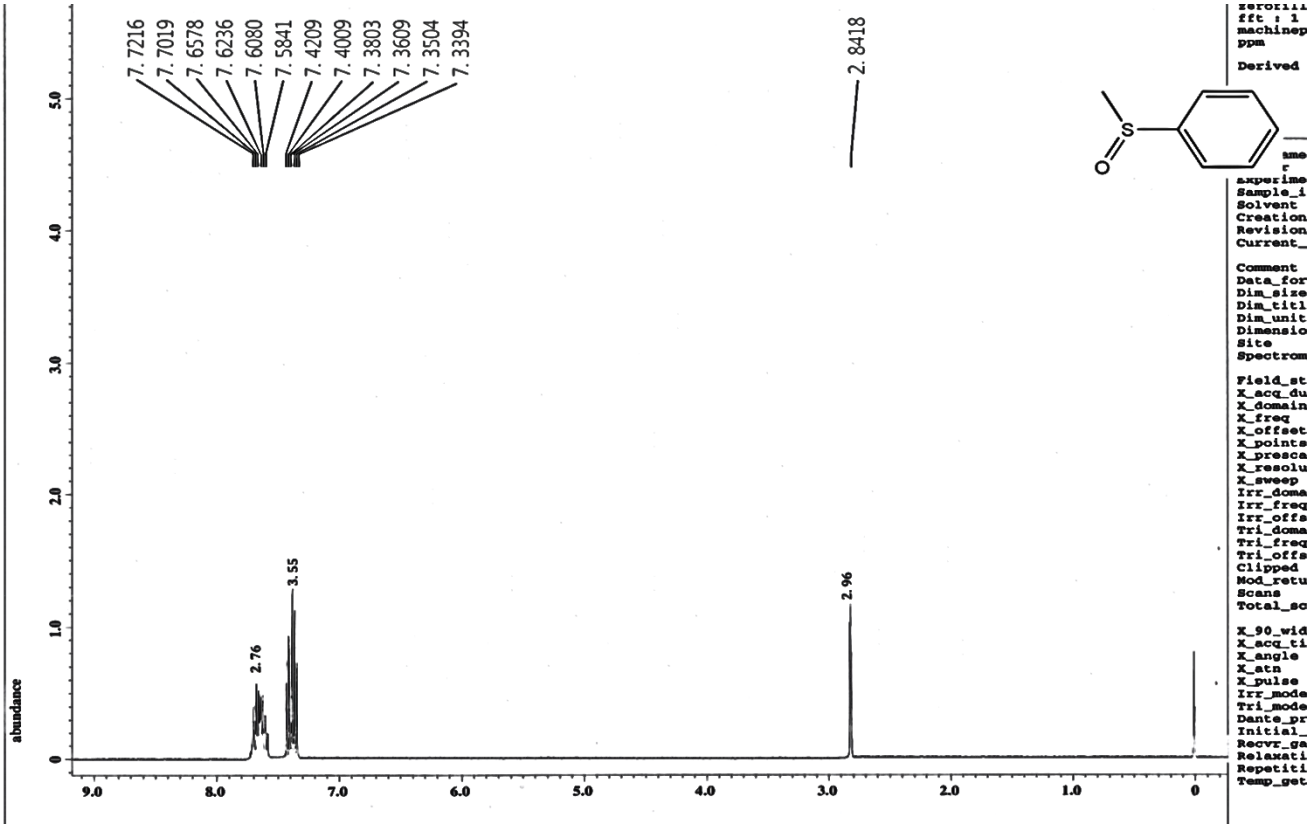


^{1}H NMR of Diphenyl sulfoxide (2m):

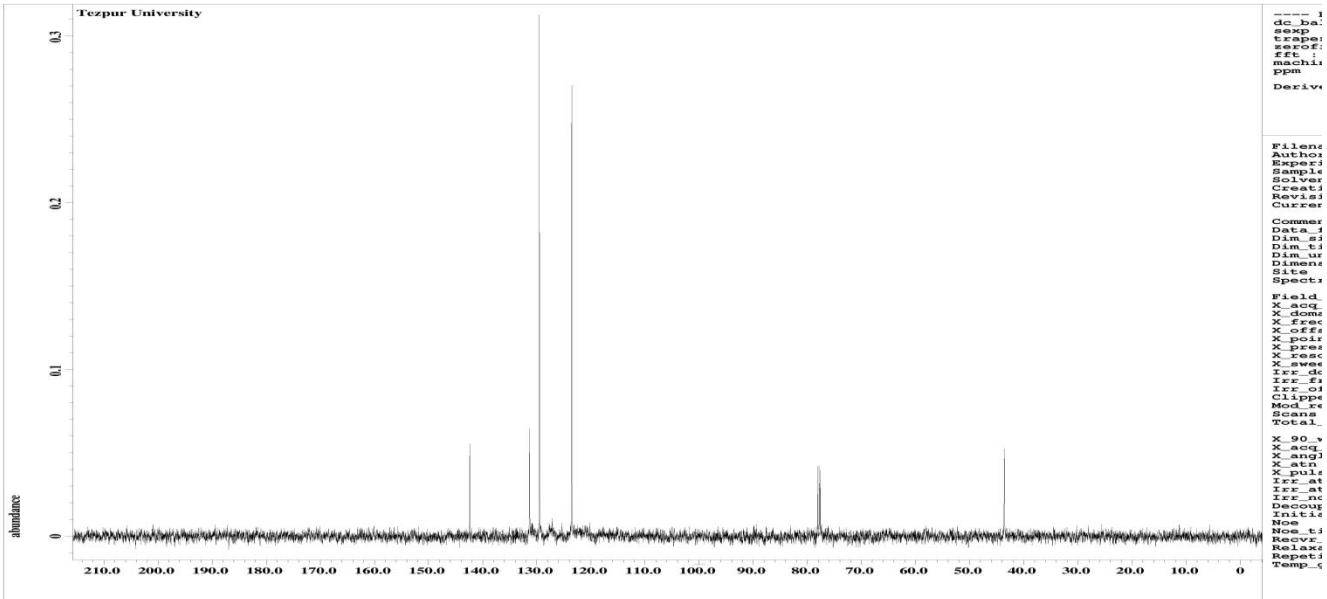




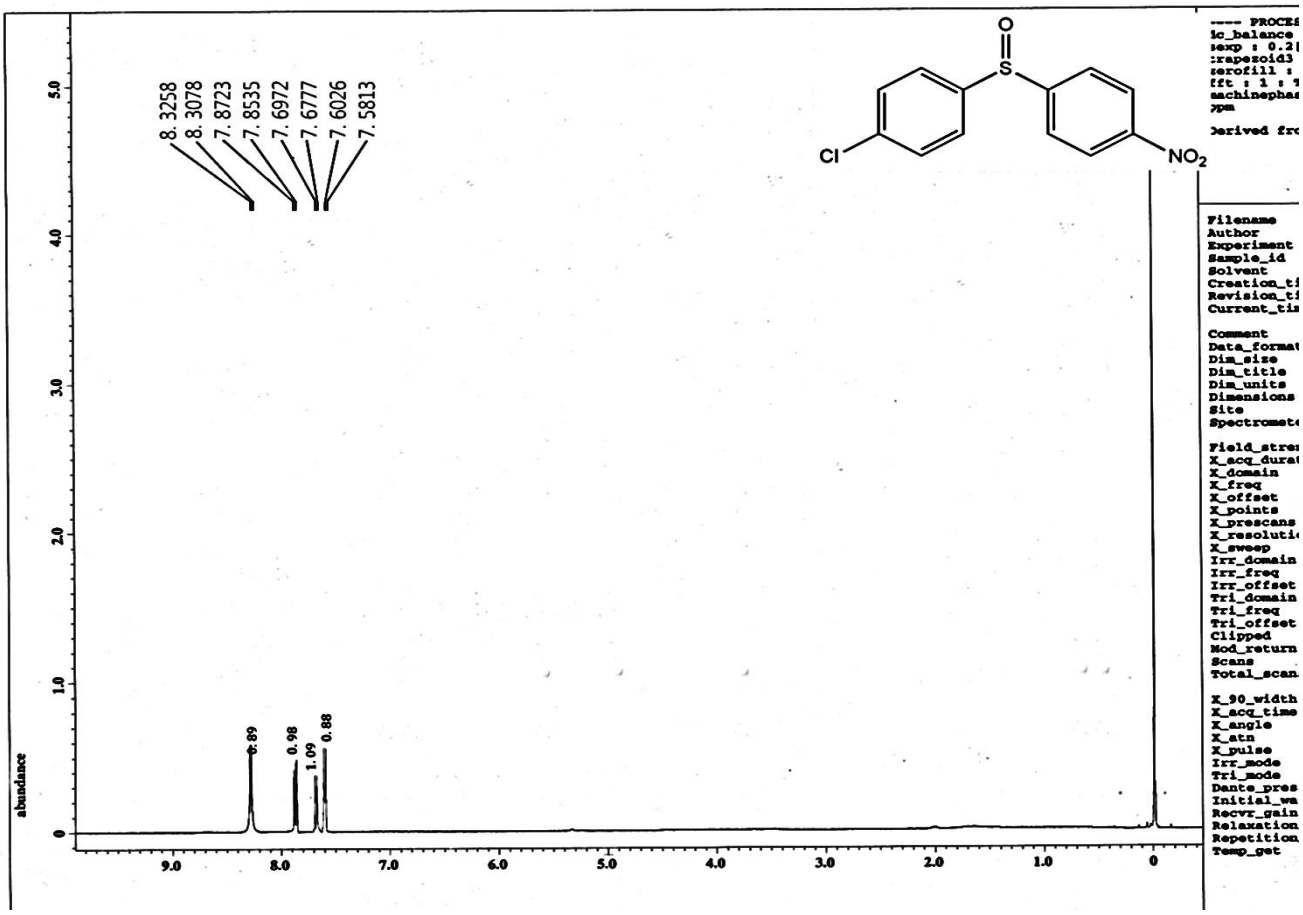
^{1}H NMR of Methyl phenyl sulfoxide (2n):



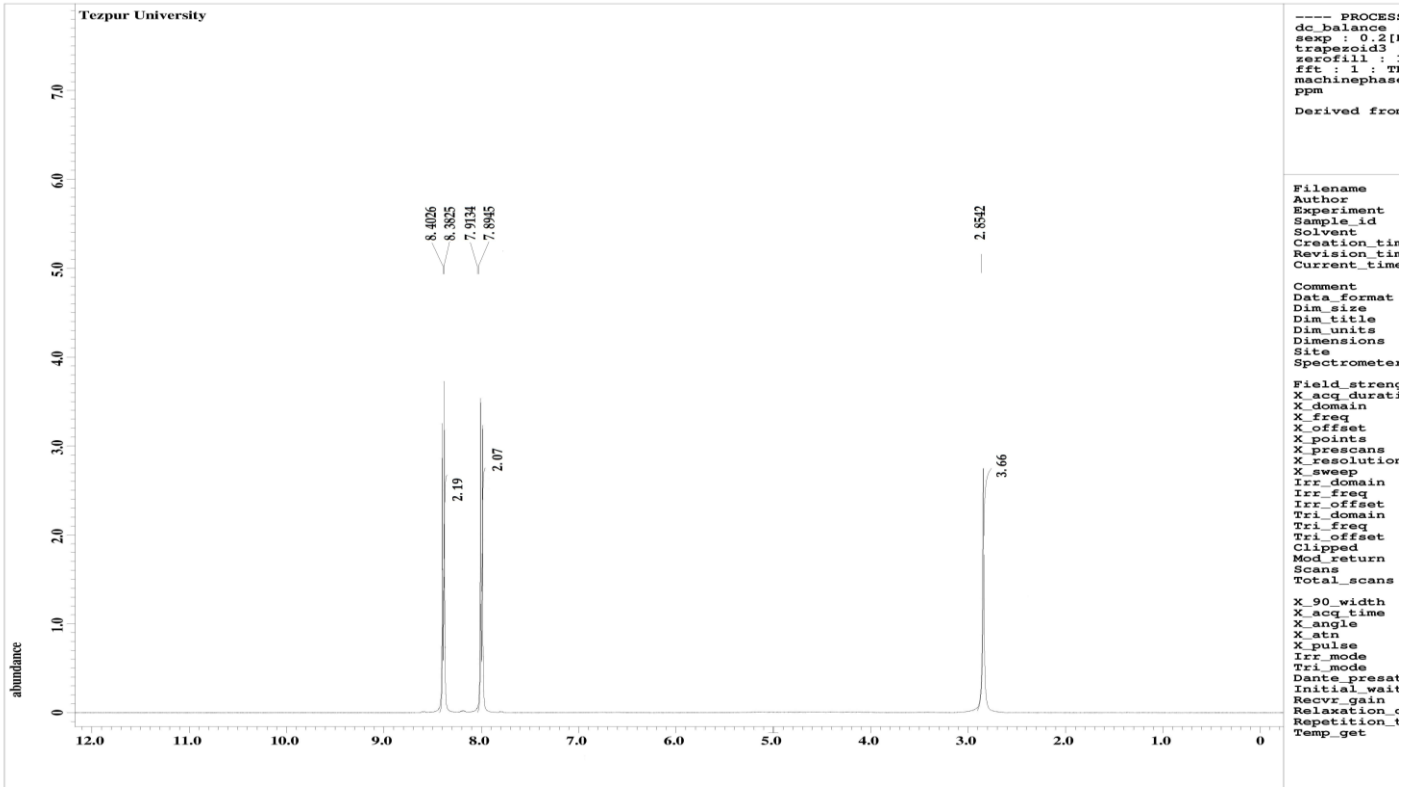
^{13}C NMR of Methyl phenyl sulfoxide (2n):



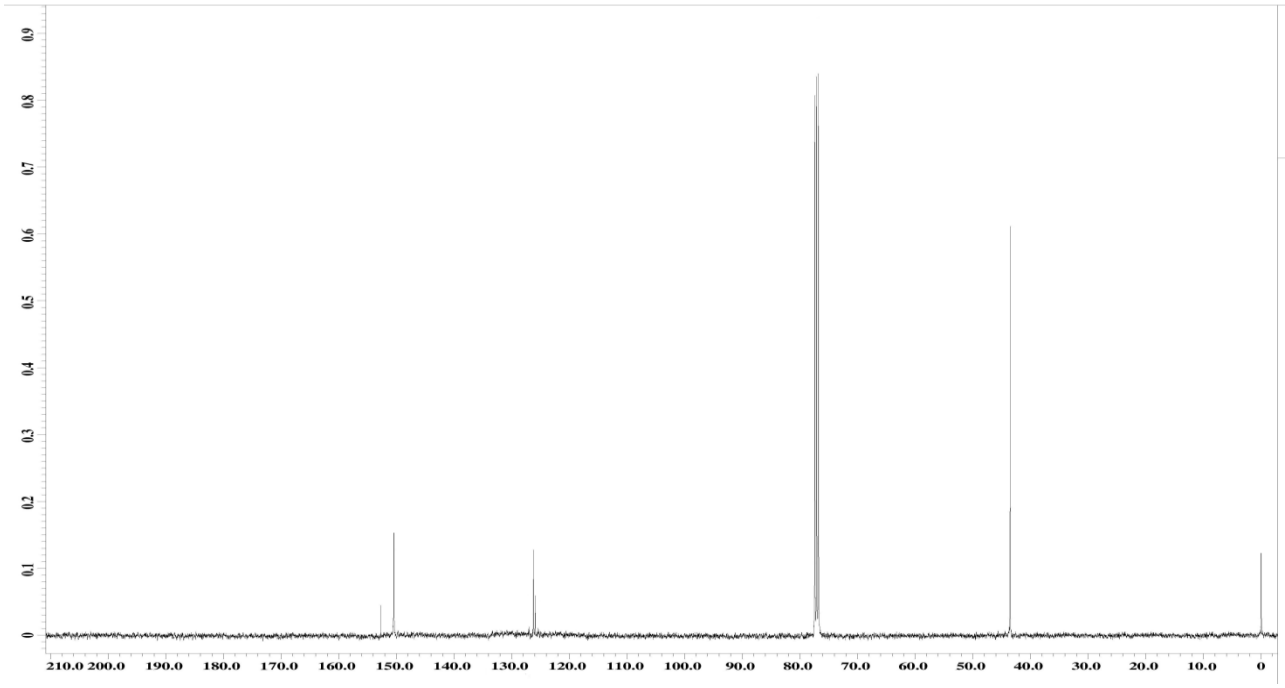
^{1}H NMR of 4-chlorophenyl 4-nitrophenyl sulfoxide (2o):



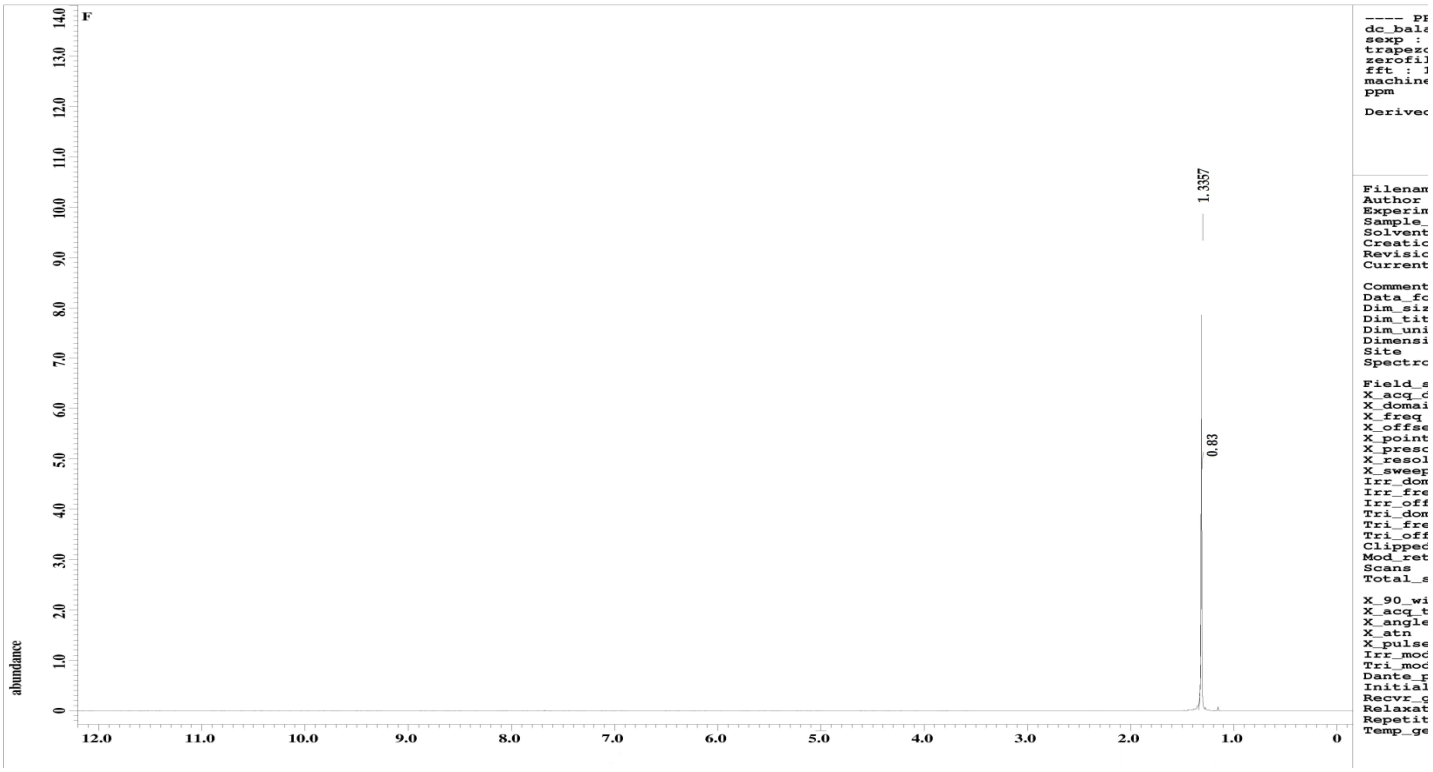
^{1}H NMR of Methyl 4-nitrophenyl sulfoxide (2p):



^{13}C NMR of Methyl 4-nitrophenyl sulfoxide (2p):



^{1}H NMR of Di t-butyl sulfoxide(2q):



^{13}C NMR of Di t-butyl sulfoxide(2q):