CHAPTER 4

Development of a novel reagent Cetyltrimethylammonium Periodate (CTAPI) for selective oxidation of sulfides to sulfoxides

4.1 Abstract

Development of a new oxidant, cetyltrimethylammonium periodate (CTAPI) and its application in selective oxidation of sulfides to corresponding sulfoxides has been described in this chapter. The advantage of CTAPI over existing oxidants has also been discussed.

4.2 Introduction

Development of efficient and milder reaction conditions for various organic transformations is an active ongoing research area. Oxidation is one of the most fundamental reactions among such transformations in organic chemistry. It is essential when functional group is to be oxidized to the level required in the product. There are a number of oxidizing agents employed in organic transformations for same type of transformations with different efficiencies and under different conditions. In organic chemistry, oxidation is defined as the conversion of a functional group in a molecule from one category to higher one. Most oxidation in organic chemistry involves a gain of oxygen and/or loss of hydrogen.[1]

Sulfoxides are one of the most important classes of organosulfur compounds.[2,3] Sulfoxides are useful building blocks especially as chiral auxiliaries in organic synthesis.[4,5] Apart from this various allyl alcohols from aldehyde and ketones and cyclohexane-1,3-diones derivatives are also prepared from sulfoxides.[6,7] Also sulfoxides are used for activation of unreactive substrates for glycosidation.[8] Therefore selective oxidation of sulfides to sulfoxides is an important transformation in synthetic organic chemistry.[9] Sulfoxides are represented by pyramidal rearrangement, two ligands, one oxygen atom and a lone pairs of electrons around sulfur atom (**Figure 4.1**).

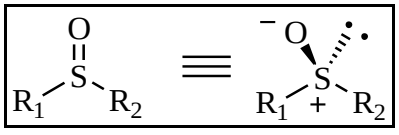


Figure 4.1 Representation of sulfoxide

The synthesis of sulfoxides was reported for the first time by Marcker in 1865[10] and since then a number of methods have been developed for the conversion of sulfides into sulfoxides. However unwanted over-oxidation of sulfides to sulfones are often observed (**Figure 4.2**). Sulfoxide can be obtained selectively from sulfide using mild reaction conditions and using either equimolar or slightly excess of oxidants. A number of oxidizing agents such as hydrogen peroxide (H_2O_2),[11] sodium

metaperiodate ($NaIO_4$),[12,13] *m*-CPBA,[14] ozone,[15] oxygen and *t*-BuOOH[16] have been employed for this purpose.

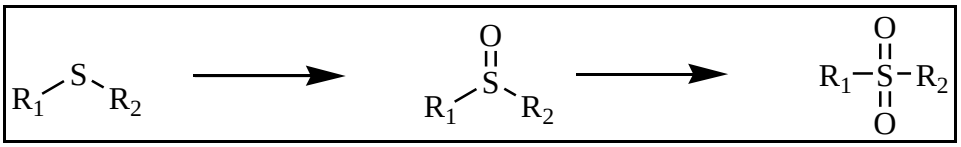
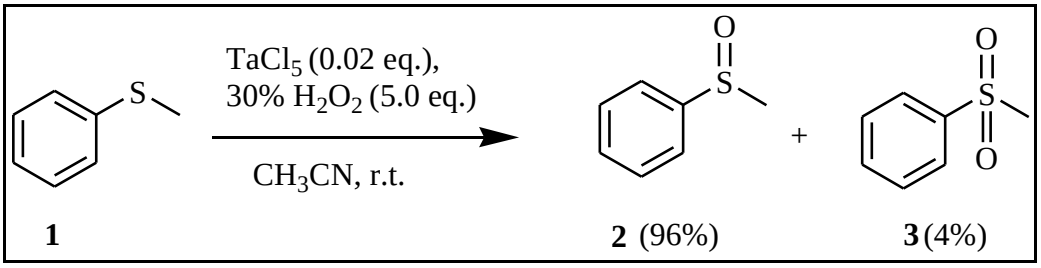


Figure 4.2 Oxidation of sulfide to sulfoxide and sulfone

One of the most commonly employed oxidant for oxidation of sulfide is hydrogen peroxide. Various acid sensitive sulfoxides such as allylic sulfoxides, silyl substituted sulfoxides and thietane sulfoxides can be prepared using this oxidant. Also hydrogen peroxide is environmentally benign, however it generally takes 18 hours or more for the sulfoxidation.[17] Moreover H_2O_2 should be used in controlled manner to avoid over-oxidation. Hydrogen peroxide in the presence of complexes or salts of metals such as tantalum, vanadium, molybdenum, tungsten as catalysts selectively furnishes sulfoxides.[11,18] The main disadvantages in these methods are the over-oxidation to corresponding sulfone as well as use of toxic heavy metals thus detracting their practical application in many cases. **Scheme 4.1** shows oxidation of methyl phenyl sulfide (**1**) to methyl phenyl sulfoxide (**2**) along with 4% of over oxidize product sulfone (**3**) using expensive tantalum (V) chloride as a catalyst.[19]

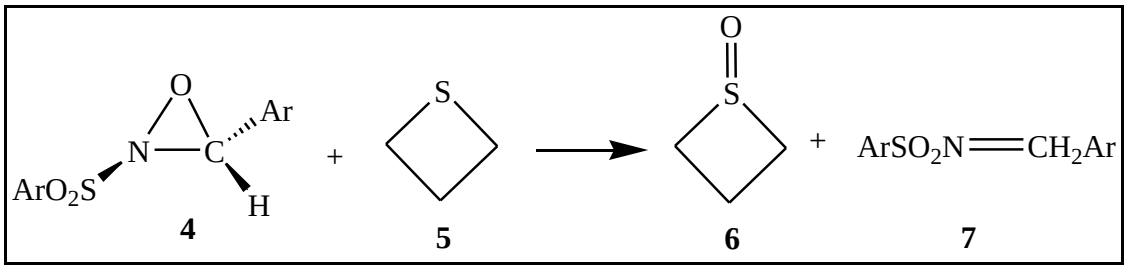


Scheme 4.1 Oxidation of methyl phenyl sulfide (**1**) using tantalum (V) chloride as a catalyst

Organic and inorganic nitrates, nitric acid as well as nitronium salts are also known to oxidize sulfides to sulfoxides. Marcker was the first to use nitric acid for oxidation of dibenzyl sulfide to corresponding sulfoxide.[10] Since then it was used as oxidant for preparation of structurally different sulfoxides.[20] A study showed that higher yields of sulfoxides were obtained by using $FeBr_3$ and the coordination

compound $(FeBr_3)(DMSO)_3$ in catalytic amount during the oxidation of sulfide using nitric acid.[21]

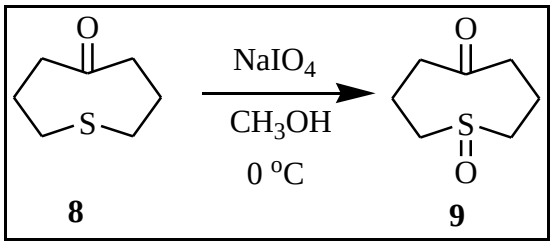
Oxaziridines are also reported for the selective oxidation of sulfides. Sulfoxides are obtained in good yields exceeding 80% at room temperature by using this method. For example 2-arenesulfonyl-3-aryloxaziridines (**4**) oxidizes thietane (**5**) to corresponding sufoxide (**6**) in chloroform solvent at room temperature (**Scheme 4.2**).[22]



Scheme 4.2 Oxidation of sulfides using 2-arenesulfonyl-3-aryloxaziridines (**4**)

However yield of reaction is strongly dependent on the structure of the oxaziridine, stable oxaziridine give low yield (5-7 %) of sulfoxides. Perfluoro-*cis*-2,3-dialkyl oxaziridines are reported to selective oxidize sulfides to sulfoxides at -40 ^oC on increasing the temperature to -20 ^oC over-oxidize product sulfone is formed.[23]

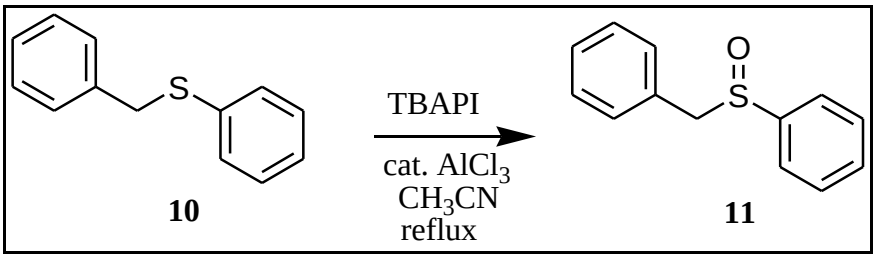
Sodium metaperiodate has been reported by Sykes and Todd in 1940's for oxidation of sulfide functionality of benzyl penicillin methyl ester and related systems to sulfoxide.[24] Leonard and Johnson[12] adopted the procedure of Sykes and Todd for oxidation of 1-thiacyclooctan-5-one (**8**) to corresponding sulfoxides (**9**) in 91 % yield (**Scheme 4.3**). Encouraged by the success of this conversion they provided additional examples of the oxidation using structurally different sulfides to demonstrate the generality and selectivity of the method. It should be noted that although, $NaIO_4$ may be stored and used safely, it requires 12 hours or more for sulfoxidation.[12,13]



Scheme 4.3 Oxidation of 1-thiacyclooctan-5-one (**8**) to corresponding sulfoxides (**9**) using sodium metaperiodate

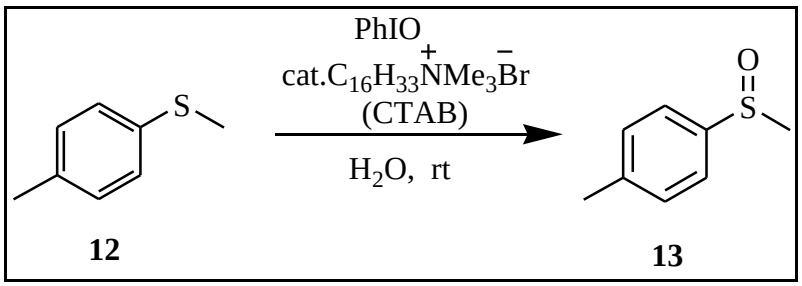
Thus most of the oxidizing agents used for sulfoxidation are either hazardous peroxy acids or involve toxic heavy metals or rare oxidants that are difficult to prepare thus detracting their practical application in many cases. A variety of oxidants in combination with metal Schiff base complexes as catalysts have also been used for this purpose however, this method has low operational stability due to facile oxidative degradation of porphyrin rings, phthalocyanines and salens. [25-29] Thus, many of the reagents and catalysts used suffer from drawbacks such as over-oxidation, long reaction times, low selectivity and low yields.

In continuation of our research in the development of novel anticoagulants we sought an oxidant which could selectively oxidize sulfide (**23**, **scheme 2.2**, chapter 2) to sulfoxide (**25**, **scheme 2.2**, chapter 2). Many of the reagents and catalysts employed for the transformation suffer from drawbacks as discussed above. Therefore, in a search for a novel reagent which can overcome the confines of the existing reagents, we found oxidizing agents based on quaternary ammonium salts exploited in many organic reactions.[30-34] These agents have several characteristics such as solubility in several solvents which provide advantages in terms of mildness, operational simplicity, selectivity, high reaction rates, low reaction temperatures and absence of side-reactions. However, some of them require catalysts for activation. For example, tetrabutylammonium periodate (TBAPI) alone is not able to convert sulfides to sulfoxides. In the presence of a Lewis acid ($AlCl_3$) as catalyst and at reflux temperature, TBAPI oxidizes sulfides to sulfoxides in CH_3CN.[35] **Scheme 4.4** shows the oxidation of benzyl phenyl sulfide (**10**) to benzyl phenyl sulfoxide (**11**) using TBAPI as oxidant, catalytic amount of aluminium chloride in acetonitrile in 75 % yield.



Scheme 4.4 Oxidation of Benzyl phenyl sulfide (**10**) to Benzyl phenyl sulfoxide (**11**) using TBAPI as oxidant

Cetyltrimethylammonium bromide (CTAB) is also reported to catalyze the oxidation of sulfides to sulfoxides using hypervalent iodine reagents. Oxidation reactions of methyl *p*-tolyl sulfide (**12**) to methyl *p*-tolyl sulfoxide (**13**) in water using iodosobenzene (PhIO) in the presence of a catalytic amount of the cationic surfactant, cetyltrimethylammonium bromide (CTAB) is shown in **scheme 4.5**. [36]

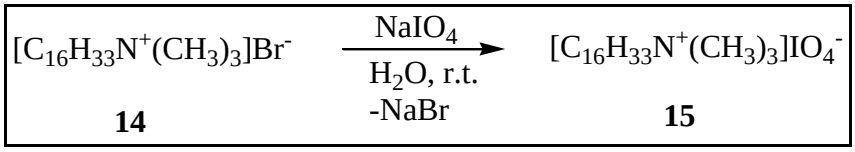


Scheme 4.5 Oxidation of methyl *p*-tolyl sulfide (**12**) to methyl *p*-tolyl sulfoxide (**13**) using iodosobenzene (PhIO) as oxidant in the presence of a catalytic amount of (CTAB)

Our efforts to develop a novel reagent cetyltrimethylammonium periodate (CTAPI) (**15**) and its application for the oxidation of sulfides which was hitherto unknown to the best of our knowledge are presented here.[37]

4.3 Results and Discussion

Cetyltrimethylammonium ion (CTA) is well known for its amphipathicity (ability to make a substance soluble in both aqueous and non-aqueous media). CTA also has relatively small head group and a well-balanced hydrophobic group. Therefore it was thought worthwhile to explore the oxidation of sulfides using cetyltrimethylammonium periodate (CTAPI) (**15**) which can be easily obtained as a white crystalline solid in excellent yield by mixing aqueous solutions of sodium metaperiodate and cetyltrimethylammonium bromide (CTAB) at room temperature (**Scheme 4.6**).



Scheme 4.6 Preparation of Cetyltrimethylammonium periodate (CTAPI) (**15**)

The structure of CTAPI (**15**) was confirmed by its spectral data. The IR spectra of CTAB (**14**) and CTAPI (**15**) show similar absorption bands except for a strong band at 852 cm^{-1} in the spectrum of CTAPI which may be attributed to IO_4^- stretching (**Figure 4.3**).

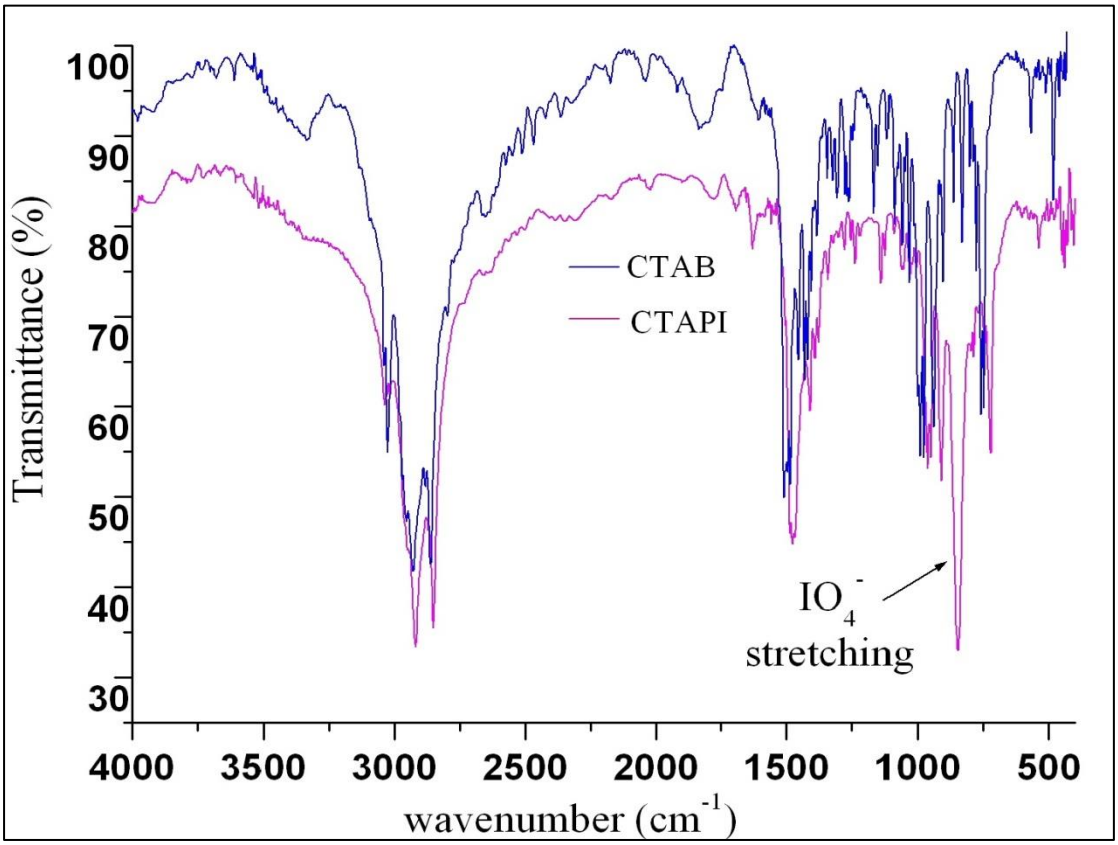
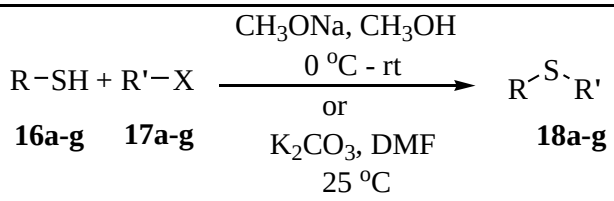


Figure 4.3 FTIR spectra of CTAB (**14**) and CTAPI (**15**)

The proton NMR spectrum of CTAPI (**15**) exhibits a triplet at δ 0.88 for protons of terminal methyl group of cetyl chain, multiplet between δ 1.26-1.37 for protons of twelve methylene groups, multiplet between δ 1.76-1.88 for protons of two methylene groups, a singlet at δ 3.24 for nine protons of three methyl group attached to nitrogen atom, a multiplet between 3.34-3.39 for methylene protons attached to nitrogen. The elemental analysis was in good agreement with the required for $C_{19}H_{42}NIO_4$ it was calculated C, 48.00; H, 8.84; N, 2.94 and found: C, 47.85; H, 8.82; N, 2.88.

In order to explore the application of CTAPI (**15**), various structurally different sulfides **18a-g** were prepared by reported methods in literature[38,39] (**Scheme 4.7**, **Table 4.1**) and **18h** and **18i** were purchased from Sigma Aldrich.



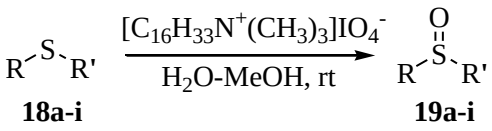
(**a**) R = p-$CH_3COO(C_6H_4)CH_2$, R' = Me; (**b**) R =Ph, R' = $PhCH_2$; (**c**) R = $PhCH_2$, R' = C_2H_5; (**d**) R = R' = $PhCH_2$; (**e**) R = Ph, R' = n-C_4H_9; (**f**) R = Ph, R' = C_2H_5; (**g**) R = $CH_2COOC_2H_5$, R' =C_2H_5.

Scheme 4.7 Preparation of structurally different sulfides **18a-g**

Table 4.1 Preparation of sulfides (R-S-R') **(18a-g)** from corresponding thiols **(16a-g)** and alkyl halide **(17a-g)**.

Entry (**18**)	R	R'	Time (min)	Yield (%)
a	4- $CH_3COO(C_6H_4)CH_2$	Me	90	86
b	Ph	$PhCH_2$	60	74
c	$PhCH_2$	C_2H_5	120	66
d	$PhCH_2$	$PhCH_2$	45	81
e	Ph	C_4H_9	50	89
f	Ph	C_2H_5	60	76
g	$CH_2COOC_2H_5$	C_2H_5	70	67

The oxidizing properties of CTAPI **(15)** were explored for oxidation of methyl 4-[(methylthio)methyl] benzoate **(18a)** in water-methanol, which furnished methyl 4-[(methylsulfoxy)methyl] benzoate **(19a)** in 94% yield. The general reaction is shown in **Scheme 4.8**.



18a-i **19a-i**

(**a**) R = p-$CH_3COO(C_6H_4)CH_2$, R' = Me; (**b**) R =Ph, R' = $PhCH_2$; (**c**) R = $PhCH_2$, R' = C_2H_5; (**d**) R = R' = $PhCH_2$; (**e**) R = Ph, R' = n-C_4H_9; (**f**) R = Ph, R' = C_2H_5; (**g**) R = $CH_2COOC_2H_5$, R' =C_2H_5; (**h**) R = R' = Ph; (**i**) R = R' = n-Bu

Scheme 4.8 Selective oxidation of sulfides **18a-i** to sulfoxides **19a-i** using CTAPI (**15**)

The structures of **19a-i** were confirmed by FTIR, ^{1}H NMR and mass. The FTIR spectrum of **19a** showed a characteristic strong band at 1718 cm^{-1} for the carbonyl group. The ^{1}H NMR spectrum of **19a** displayed a singlet at δ 2.47 for methyl group on sulfur, a singlet at δ 3.93 for methyl group of ester, a doublet of doublet at δ 4.00 and 4.05 for diastereotopic protons of methylene group, two doublets at δ 7.38 and 8.06 for aromatic protons. The structure of **19a** was further confirmed by its mass spectrum which gave a molecular ion peak at 211.99.

In order to optimize the reaction conditions, the oxidation of methyl 4-[(methylthio)methyl]benzoate **(18a)**, as a model substrate, was studied under different reaction conditions as shown in **Table 4.2**.

Table 4.2 Oxidation of Methyl 4-[(Methylthio)methyl] benzoate **(18a)** under different conditions

Entry	Solvent	CTAPI (equi.)	Time (h)	Sulfoxide (R-S(O)-R') **(19a)** yield[b] (%)	Sulfone ($R-S(O)_2-R'$) yield[b] (%)
1	H_2O	3.5	2.75	76	0
2	CH_3OH	3.5	0.75	63.15	31.5
3	H_2O-CH_3OH (8:2)	1.5	12	64[a]	0
4	H_2O-CH_3OH (8:2)	2.5	12	79[a]	0
5	H_2O-CH_3OH (8:2)	3.0	2.5	82	0
6	H_2O-CH_3OH (8:2)	3.5	1	94	0
7	H_2O-CH_3OH (8:2)	4.5	0.25	78	17
8	CH_3CN	3.5	12	33.33 [a]	0
9	CH_2Cl_2	3.5	12	13.8 [a]	0
10	EtOAc	3.5	12	0	0
11	THF	3.5	12	0	0

[a] Yield based on recovery of sulfide. [b] Isolated yields.

The reactions were carried out at room temperature. The oxidation was first investigated by changing the mole proportion of the reagent in H_2O and MeOH separately. The reaction was not found to reach completion with less than 3.5 equivalents of CTAPI in either H_2O or MeOH. The rate of oxidation was slow in H_2O and the yield of sulfoxide was also low (**Table 4.2**, **entry 1**). However in MeOH, the rate of oxidation was found to be quite fast but the over oxidation of sulfide to sulfone

was observed (**Table 4.2**, **entry 2**). Further the oxidation was also investigated using different mole proportions of CTAPI in H_2O-MeOH solvent mixture. In the experiments using 1.5 and 2.5 mole equivalent of CTAPI (**Table 4.2**, **entries 3** and **4**), the reaction was not complete even after 12 h. The oxidation of methyl 4-[(methylthio)methyl] benzoate **(18a)** revealed that the use of 3.5 mole equivalent of CTAPI **(15)** afforded corresponding sulfoxide in 1h in excellent yield without any significant over oxidation (**Table 4.2**, **entry 6**). Based on the results obtained from above stoichiometry study (**Table 4.2**, **entries 3-7**), the best molar ratio of sulfide and CTAPI was found to be 1.0:3.5. Increasing the moles of the reagent beyond this ratio increased the oxidation rate however it was accompanied by the over oxidation of sulfide to sulfone (**Table 4.2**, **entry 7**).

The effect of solvents on the oxidation was also studied using 3.5 mole equivalent of CTAPI (**15**). Among the solvents examined, aqueous organic solvent mixture, H_2O-MeOH, was found to be most effective. In organic solvents the reaction was not complete (**Table 4.2, entry 8 and 9**) and in some cases the reaction did not even proceed (**Table 4.2, entry 10 and 11**).

The oxidant was found to work smoothly with a variety of structurally different sulfides such as alkylaryl sulfide, alkylaralkyl sulfides, diaralkyl sulfides, arylaralkyl sulfides, dialkyl sulfide, and diaryl sulfide under the optimized reaction conditions (**Table 4.3**). The reactions exhibited very high selectivity for sulfoxides in relatively short reaction time. The reactivity and reaction period were found to be dependent on the nature of the substituents. As seen from the **Table 4.3**, the oxidation of the less reactive diphenyl sulfide (**18h**) could also be accomplished using 4.5 mole equivalent of CTAPI which is an exception to the optimized reaction conditions.

Table 4.3 Oxidation of sulfides (R-S-R') **(18a-i)** to sulfoxides (R-S(O)-R') **(19a-i)** using CTAPI (**15**) (3.5 equiv.) in water-methanol.

Entry (**19**)	R	R'	Time (min)	Yield[a] (%)
a	4- $CH_3COO(C_6H_4)CH_2$	Me	60	94
b	Ph	$PhCH_2$	75	92
c	$PhCH_2$	C_2H_5	45	89
d	$PhCH_2$	$PhCH_2$	165	91
e	Ph	C_4H_9	210	90
f	Ph	C_2H_5	225	93
g	$CH_2COOC_2H_5$	C_2H_5	40	92
h[b]	Ph	Ph	150	87
i	n-Bu	n-Bu	40	93

[a] Isolated yields. [b] 4.5 equivalent CTAPI used

4.4 Experimental

Melting points were recorded in open capillary tubes in melting point apparatus and are uncorrected. Infrared (IR) absorption spectra were obtained on a SHIMADZU FTIR-2450 spectrophotometer. ^{1}H NMR spectra were determined on a Bruker-(200/300/400/500) FT-NMR spectrometer in $CDCl_3$ or DMSO-d_6 (TMS as an internal standard). Mass spectra were recorded on a Thermo-Fischer DSQ II GCMS instrument. Thin layer chromatography (TLC) analysis was performed on glass plates using silica gel-G containing 13% calcium sulfate as a binder. Visualization of spots was achieved by exposure to iodine vapor. Column chromatography was carried out on Acme's silica gel (60-120 mesh size) and eluted using light petroleum (60-80) and ethyl acetate mixtures.

General procedure for preparation of sulfides (**18a, 18c, 18d, 18g**).[38,39] To a stirred solution of sodium metal (0.22 g, 0.0096 mol) in methanol (10 ml) at 0 ^{o}C under nitrogen was added mercaptan (0.0081 mol). The reaction was stirred for 30 minutes at 0 ^{o}C after addition of appropriate alkyl halide (0.0088 mol). The mixture was then warmed to room temperature and allowed to stir for appropriate time **(Table 4.1)**. The solvent was removed *in vacuo*, and the residue was extracted with ethyl acetate (4 × 25 ml), washed with water (30 ml) and brine (25 ml) and dried over anhydrous sodium sulfate. Removal of the solvent gave the crude product which on purification by column chromatography, afforded compound.

General procedure for preparation of sulfides (**18b, 18e, 18f**).[40] To a stirred solution of potassium carbonate (0.0161 mol) in DMF (10 ml) at room temperature was added thiol (0.0080 mol) followed by dropwise addition of appropriate alkyl halide (0.0121 mol). After stirring for appropriate time **(Table 4.1)** the reaction mixture was filtered to remove the solid and the solvent was evaporated under reduced pressure. The crude product was purified using column chromatography to afford pure compounds.

Preparation of Cetyltrimethylammonium Periodate (CTAPI) (15).[37] To a stirred solution of cetyltrimethylammonium bromide (10g, 0.027 mol) in water (200 mL) was slowly added a solution of sodium metaperiodate (5.87g, 0.027 mole) in water (110 mL) at room temperature (27 ^{o}C). The reaction mixture was stirred for 15

minutes and the white precipitate obtained was collected, washed with water and dried in hot air oven (60 ^{o}C) for 24 h to give CTAPI (12.7g, 97%) as colorless crystal, mp 126 ^{o}C. IR (KBr) cm^{-1}: 2943, 2918, 2876, 2854, 1485, 1477, 852, 721. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 0.88 (3H, t, *J* = 6.5 Hz), 1.26-1.37 (24H, m), 1.76-1.88 (4H, m), 3.24 (9H, s), 3.34-3.39 (2H, m). *Anal*. Calcd for $C_{19}H_{42}NIO_4$: C, 48.00; H, 8.84; N, 2.94. Found: C, 47.85; H, 8.82; N, 2.88.

General Procedure for the Oxidation of Sulfides (18a-i) to Sulfoxides (19a-i). To a stirred solution of the sulfide (1 mmol) in aqueous methanol (8:2) (5 mL) at room temperature was added CTAPI (1.66g, 3.5 mmol) in portions over a period of 15 minutes; the mixture was then stirred for the appropriate time (**Table 4.3**). After completion of reaction (TLC), the reaction mixture was filtered to remove the iodate salt and the filtrate was extracted with ethyl acetate (4×10 mL). The combined organic extracts were washed successively with water (2×4 mL), brine solution (10 mL) and dried over anhydrous sodium sulfate (Na_2SO_4). Removal of solvent under reduced pressure furnished the crude sulfoxides (**19a-i**), which were chromatographed using mixtures of light petroleum (60-80) and ethyl acetate.

Methyl 4-[(Methylsulfoxy)methyl] benzoate (19a):[41] Colorless crystal; mp 70 ^{o}C. IR (KBr) cm^{-1}: 3020, 2960, 1718, 1467, 1420, 1240, 1090, 743. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.47 (3H, s), 3.93 (3H, s), 4.00 (1H, d, *J* =12.8 Hz), 4.05 (1H, d, *J*=12.8 Hz), 7.38 (2H, d, *J* =8.2 Hz), 8.06 (2H, d, *J* =8.2 Hz). MS m/z 211.99

Benzyl phenyl sulfoxide (19b):[42] Colorless crystal; mp 122 ^{o}C. IR (KBr) cm^{-1}: 3060, 2980, 1535, 1447, 1070, 740, 692. . ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 3.99 (1H, d, *J* =12.6 Hz), 4.10 (1H, d, *J* =12.6 Hz), 6.95-7.00 (2H, m), 7.24-7.29 (3H, m), 7.37-7.45 (5H, m). MS m/z 216.12 (M^+)

Benzyl ethyl sulfoxide (19c):[43] Colorless oil; IR (KBr) cm^{-1}: 3058, 2986, 2944, 1516, 1468, 1057, 738. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.31 (3H, t, *J* =7.5), 2.51-2.67 (2H, m), 3.93 (1H, d, *J* =12.9 Hz), 4.00 (1H, d, *J* =12.9 Hz), 7.28-7.30 (2H, m), 7.32-7.39 (3H, m). MS m/z 168.10 (M^+)

Dibenzyl sulfoxide (19d):[44] Colorless crystal; mp 135 ^{o}C. IR (KBr) cm^{-1}: 3035, 2956, 1605, 1452, 1032, 775, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.87 (2H, d, *J* =13

Hz), 3.92 (2H, d, *J* =13 Hz), 7.25-7.30 (4H, m), 7.33-7.40 (6H, m). MS m/z 230.18 (M^+)

n-Butyl phenyl sulfoxide (19e):[45] Colorless oil; IR (KBr) cm^{-1}: 3075, 2960, 2883, 1450, 1086, 1045, 758. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.92 (3H, t, *J* =7.4 Hz), 1.38-1.78 (4H, m), 2.77-2.84 (2H, m), 7.48-7.54 (3H, m), 7.61-7.65 (2H, m). MS m/z 182.14 (M^+)

Ethyl phenyl sulfoxide (19f):[42] Colorless oil; IR (KBr) cm^{-1}: 3066, 2927, 1489, 1075, 1037, 780, 715. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.20 (3H, t, *J* =7.4 Hz), 2.73-2.95 (2H, m), 7.48-7.55 (3H, m), 7.60-7.62 (2H, m). MS m/z 154.14 (M^+)

Ethyl 2-(ethyl sulfinyl) acetate (19g):[43] Colorless oil; IR (KBr) cm^{-1}: 2982, 2839, 1735, 1263, 1024, 1081, 783. ^1H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.25 (3H, t, *J* =7.4 Hz), 1.27 (3H, t, *J* =7.1 Hz), 2.81-2.98 (2H, m), 3.78 (1H, d, *J* =14.1 Hz), 4.02 (1H, d, *J* =14.1 Hz), 4.21 (2H, q, *J* =7.1 Hz). MS m/z 164.07 (M^+)

Diphenyl sulfoxide (19h):[46] Colorless crystal; mp 72 ^oC. IR (KBr) cm^{-1}: 3068, 1466, 1440, 1082, 1048, 743, 694. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41-7.48 (6H, m), 7.63-7.66 (4H, m). MS m/z 202.10 (M^+)

Di-n-butyl sulfoxide (19i):[47] Colorless oil; IR (KBr) cm^{-1}: 2960, 2874, 1465, 1078, 1026, 742. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.94 (6H, t, *J* =7.4 Hz), 1.39-1.56 (4H, m), 1.69-1.77 (4H, m), 2.58-2.73 (4H, m). MS m/z 162.03 (M^+)

4.5 Conclusion

We have reported a new oxidant cetyltrimethylammonium periodate (CTAPI), which efficiently and selectively oxidizes sulfides to corresponding sulfoxides. The reaction proceeds smoothly with no significant over oxidation to sulfones in aqueous methanol (8:2) at room temperature. CTAPI possesses advantages such as use of mild reaction conditions, convenient and safe to handle, short reaction periods and excellent yields.

4.6 References

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4.7 Spectral data of compounds

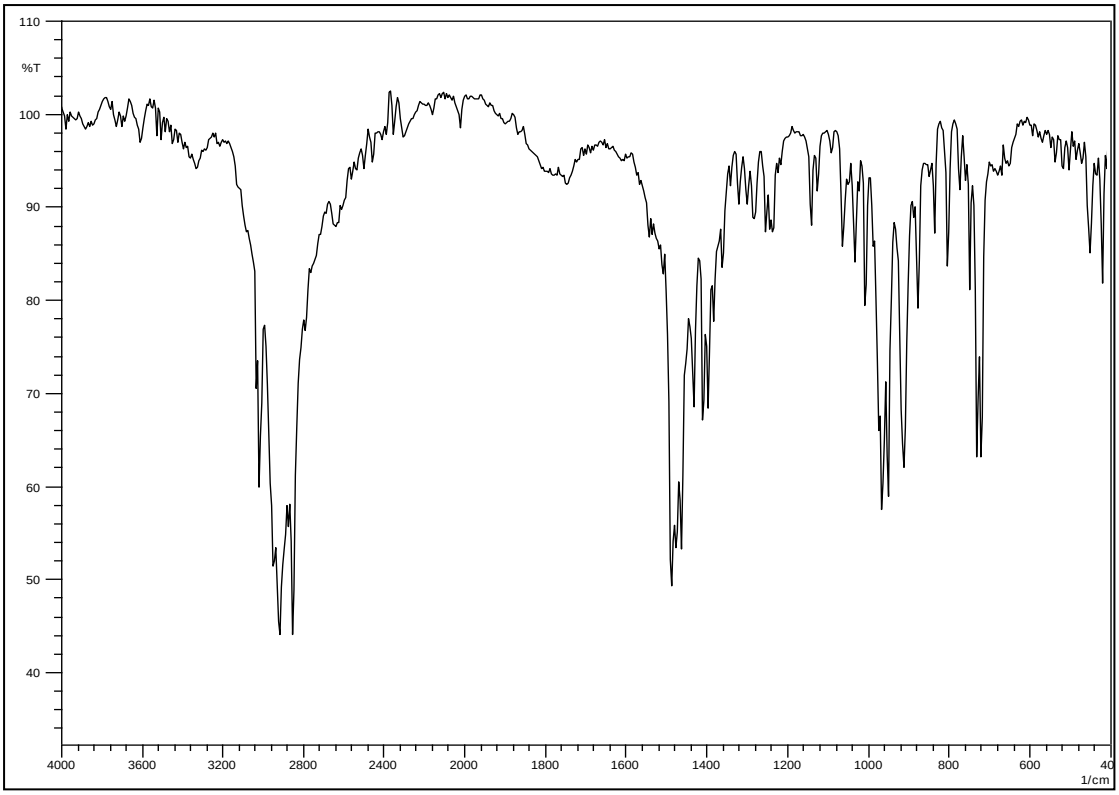

Figure 4.4 FTIR spectrum of Cetyltrimethyl ammonium bromide (CTAB)

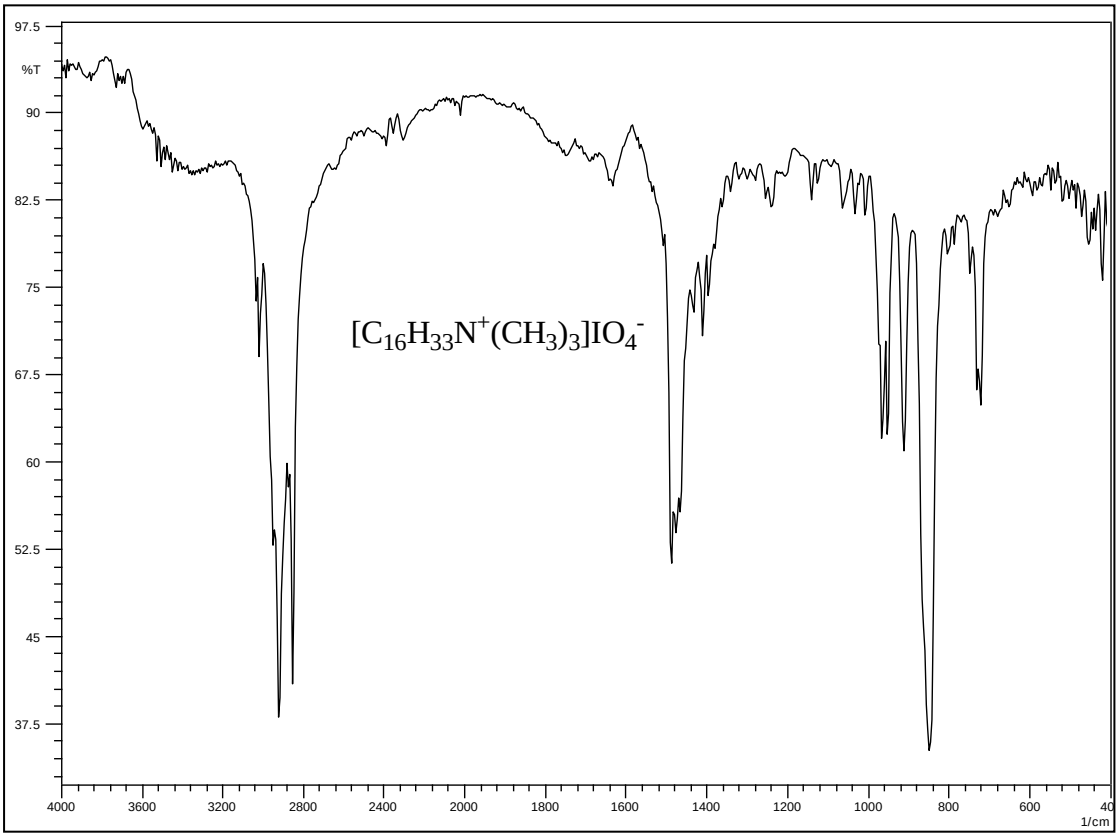

Figure 4.5 FTIR spectrum of Cetyltrimethyl ammonium periodate (CTAPI) (**15)**

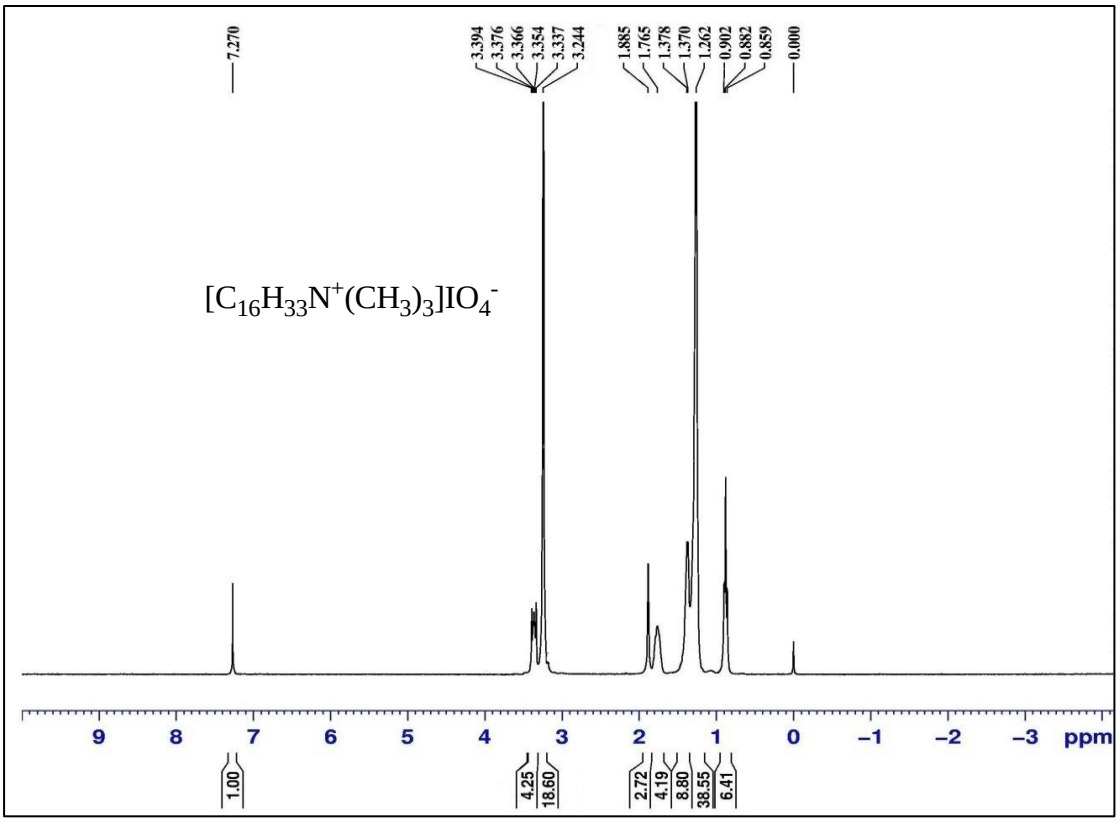

Figure 4.6 ^{1}H NMR spectrum of CTAPI (**15)**

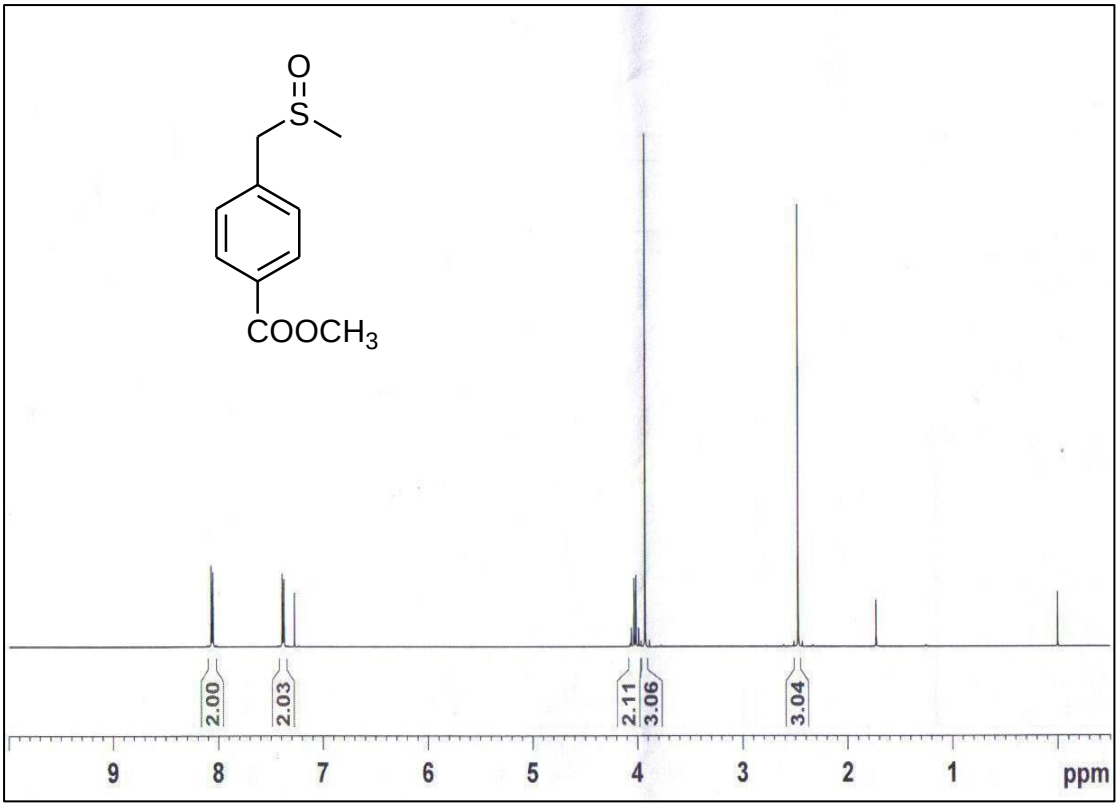

Figure 4.7 ^{1}H NMR spectrum of Methyl 4-[(Methylsulfoxy)methyl] benzoate **(19a)**

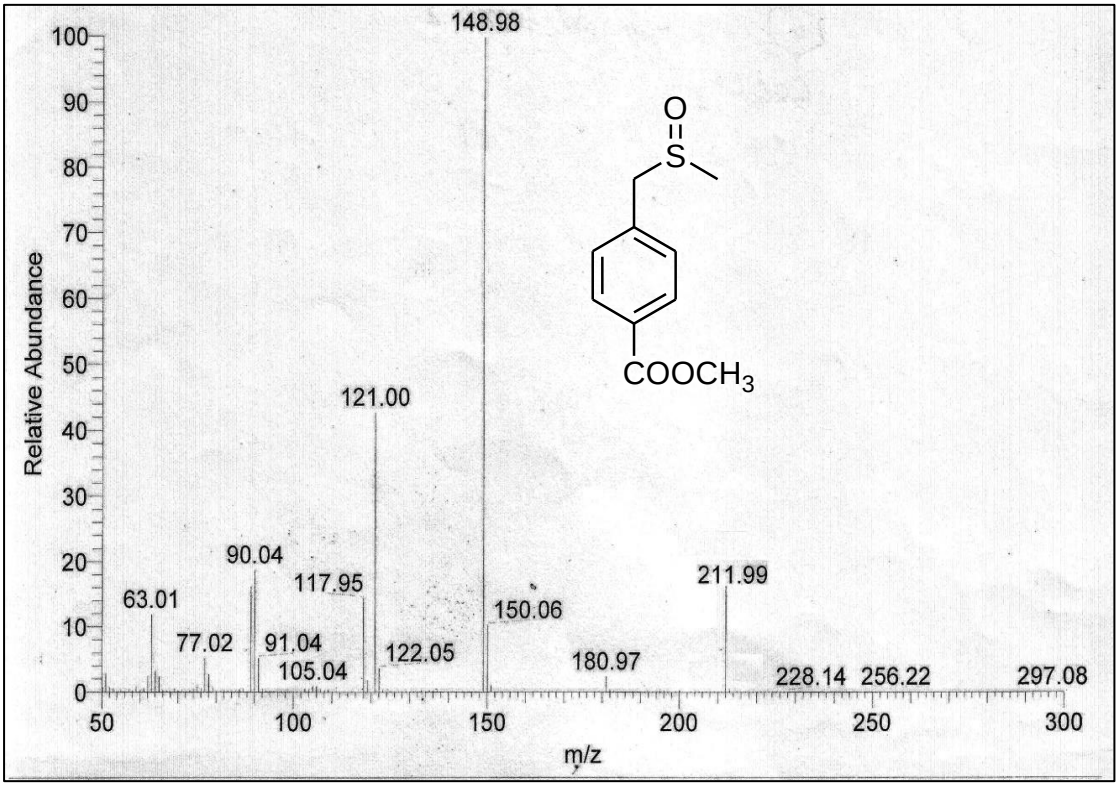

Figure 4.8 Mass spectrum of Methyl 4-[(Methylsulfoxy)methyl] benzoate **(19a)**

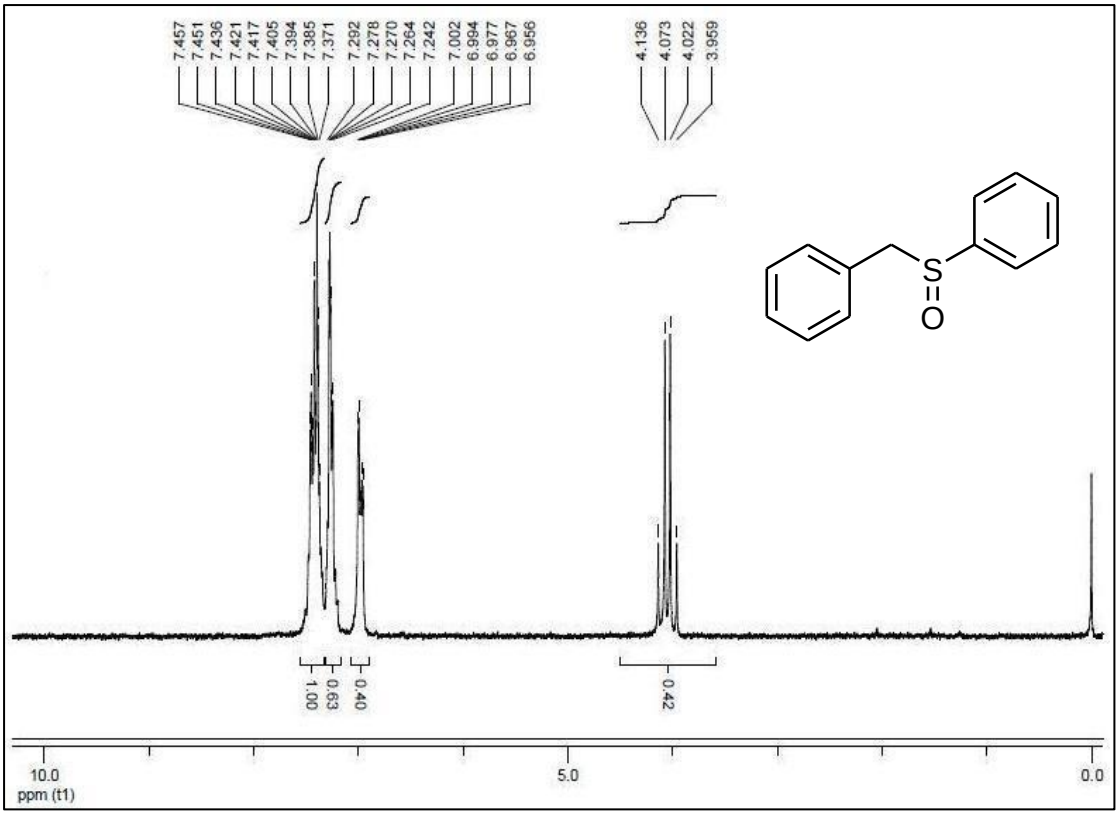

Figure 4.9 ^{1}H NMR spectrum of Benzyl phenyl sulfoxide **(19b)**

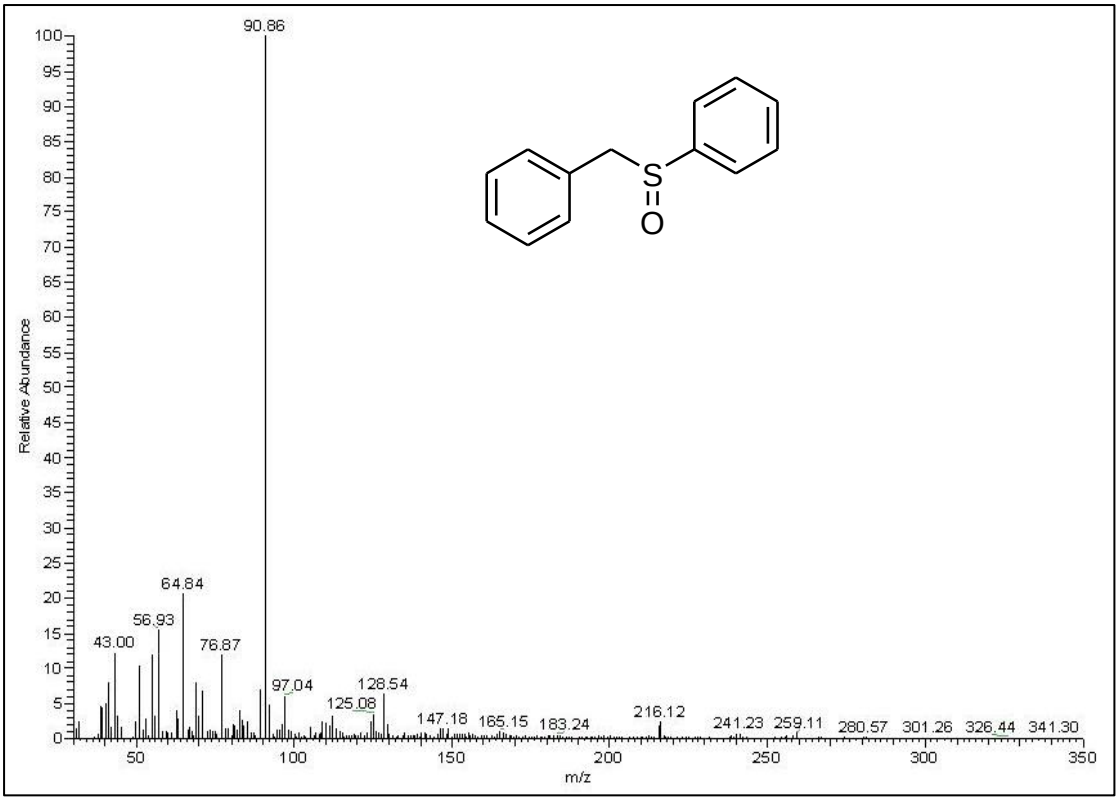

Figure 4.10 Mass spectrum of Benzyl phenyl sulfoxide **(19b)**

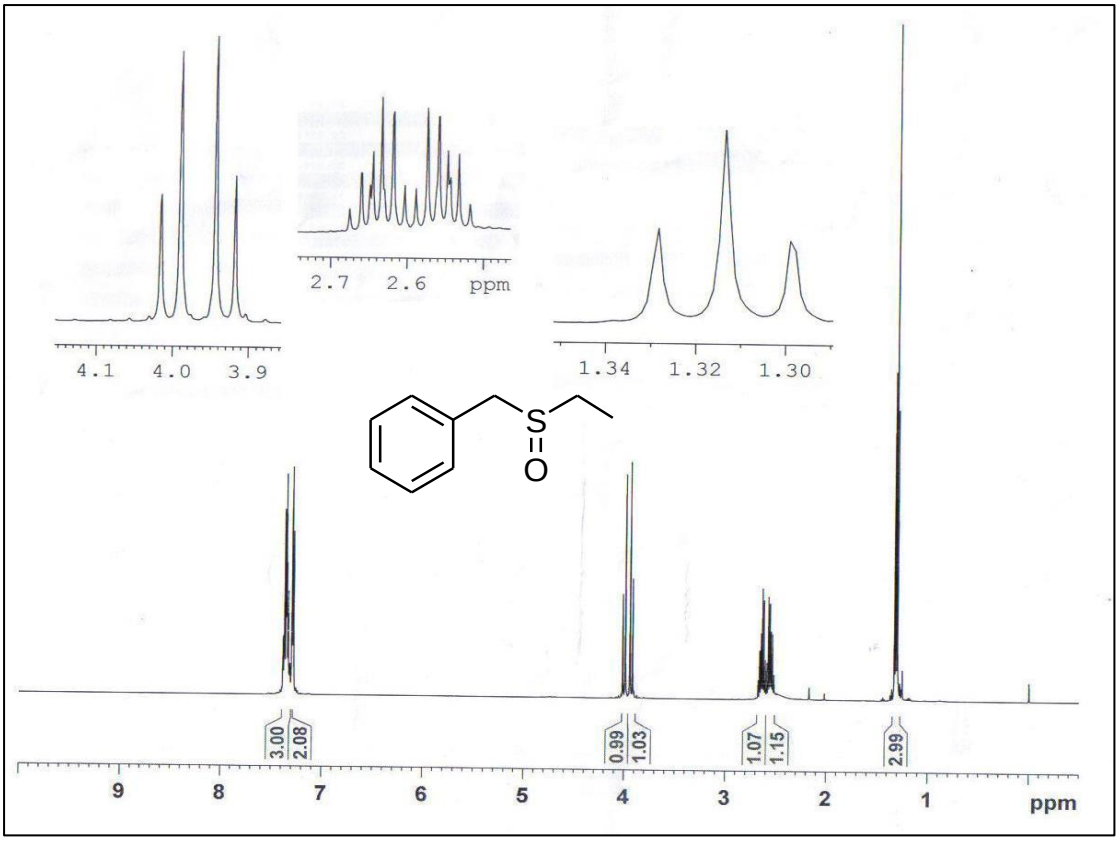

Figure 4.11 ^{1}H NMR spectrum of Benzyl ethyl sulfoxide **(19c)**

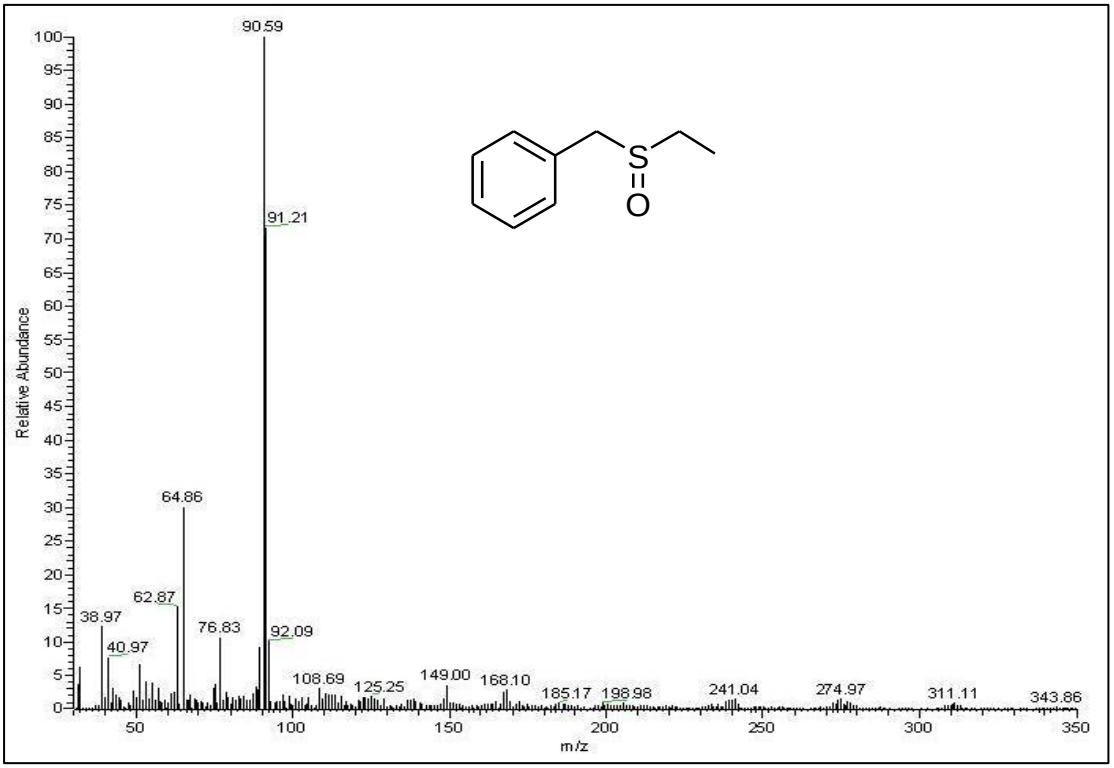

Figure 4.12 Mass spectrum of Benzyl ethyl sulfoxide **(19c)**

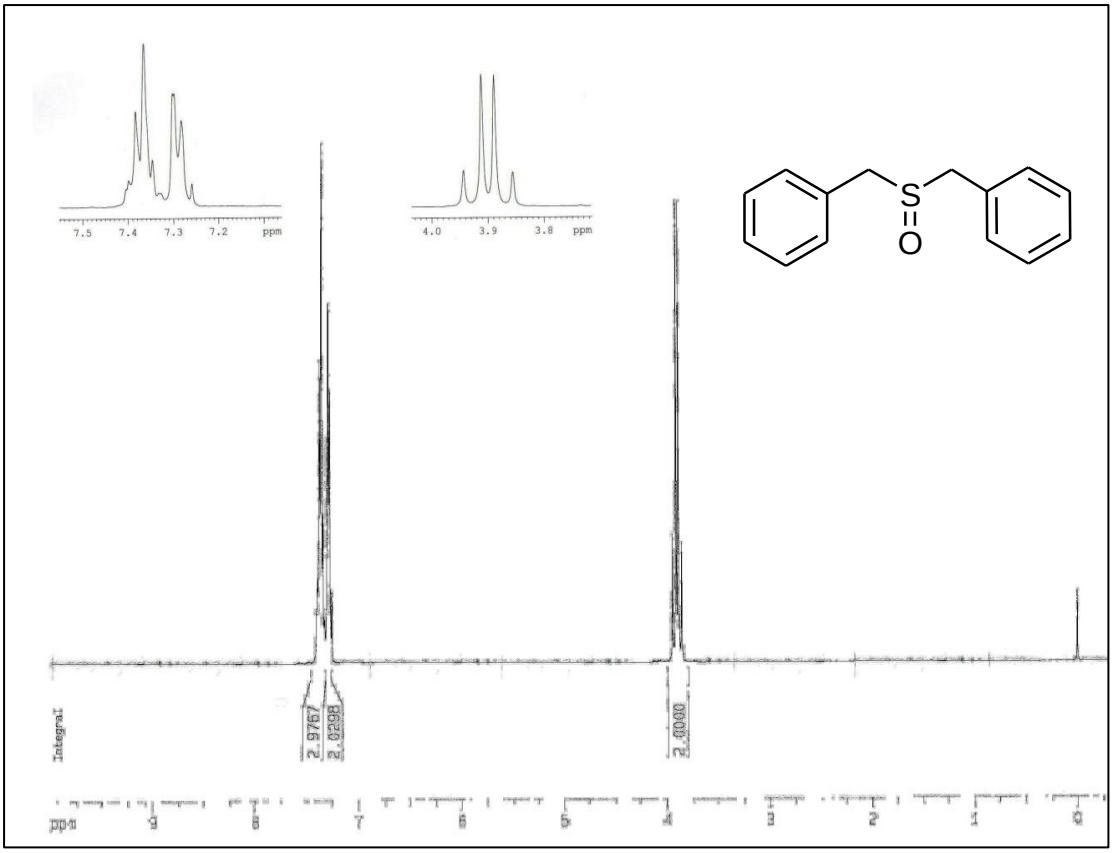

Figure 4.13 ^{1}H NMR spectrum of Dibenzyl sulfoxide **(19d)**

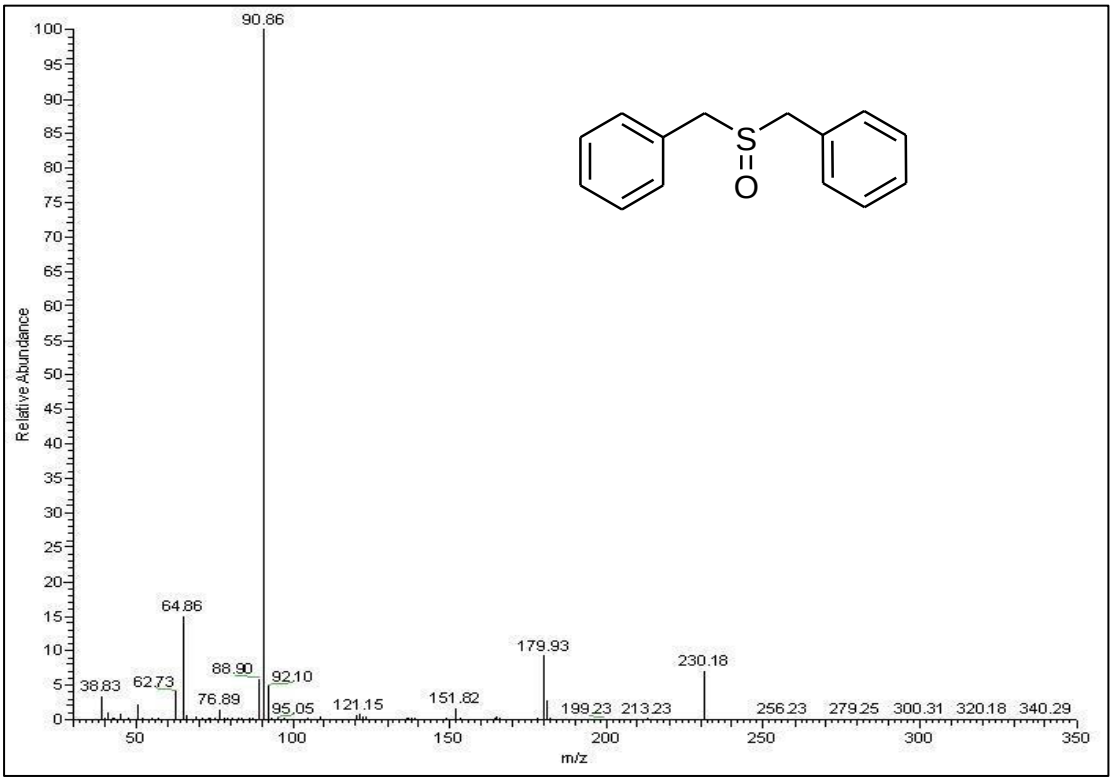

Figure 4.14 Mass spectrum of Dibenzyl sulfoxide **(19d)**

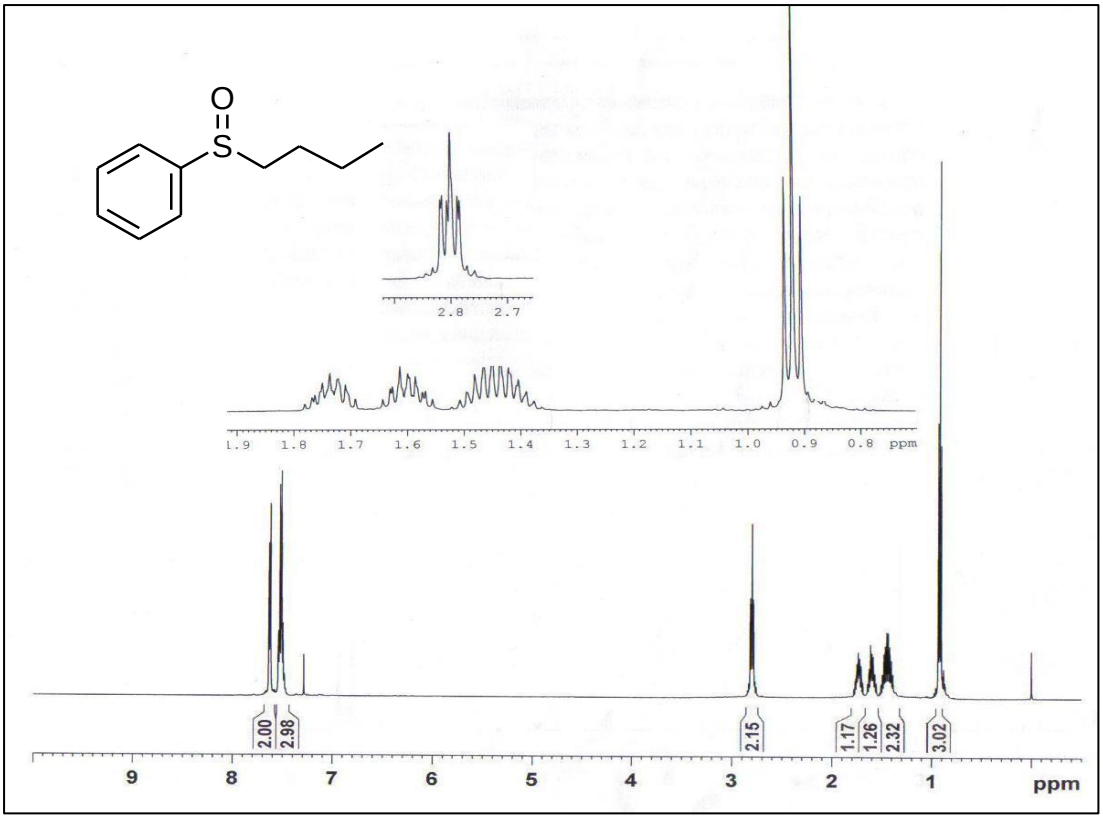

Figure 4.15 ^{1}H NMR spectrum of n-Butyl phenyl sulfoxide **(19e)**

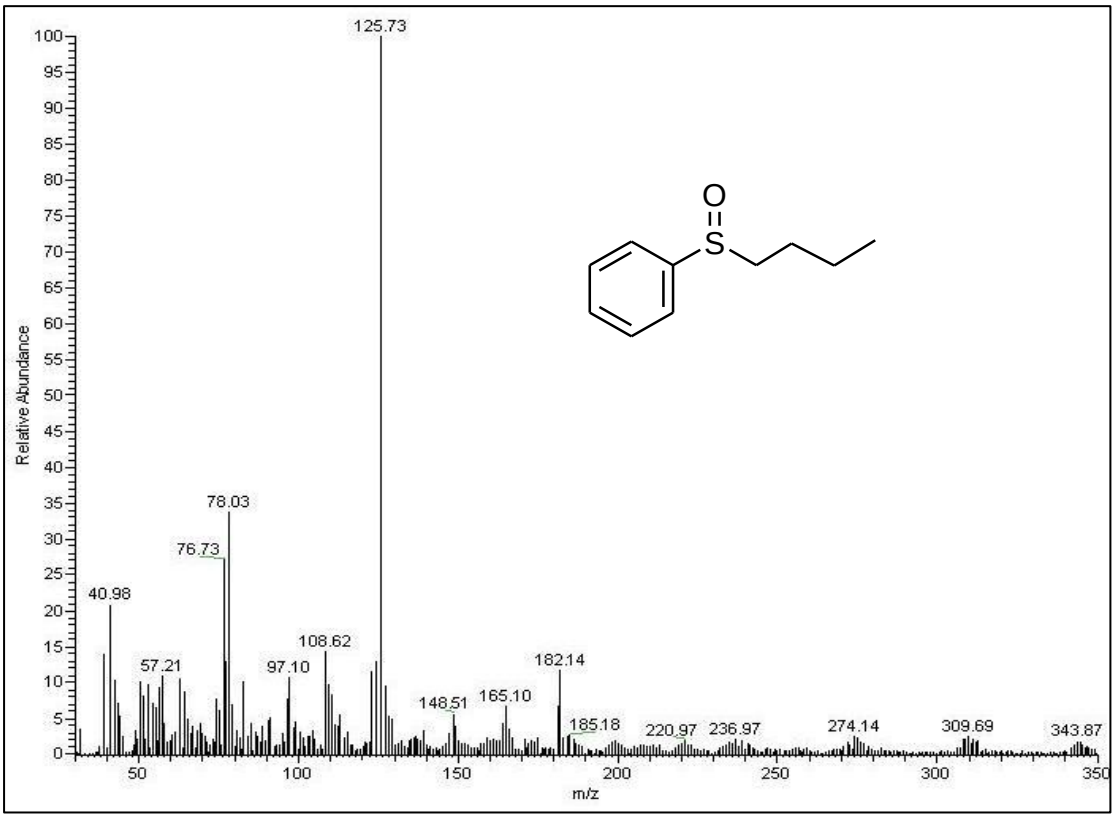

Figure 4.16 Mass spectrum of n-Butyl phenyl sulfoxide **(19e)**

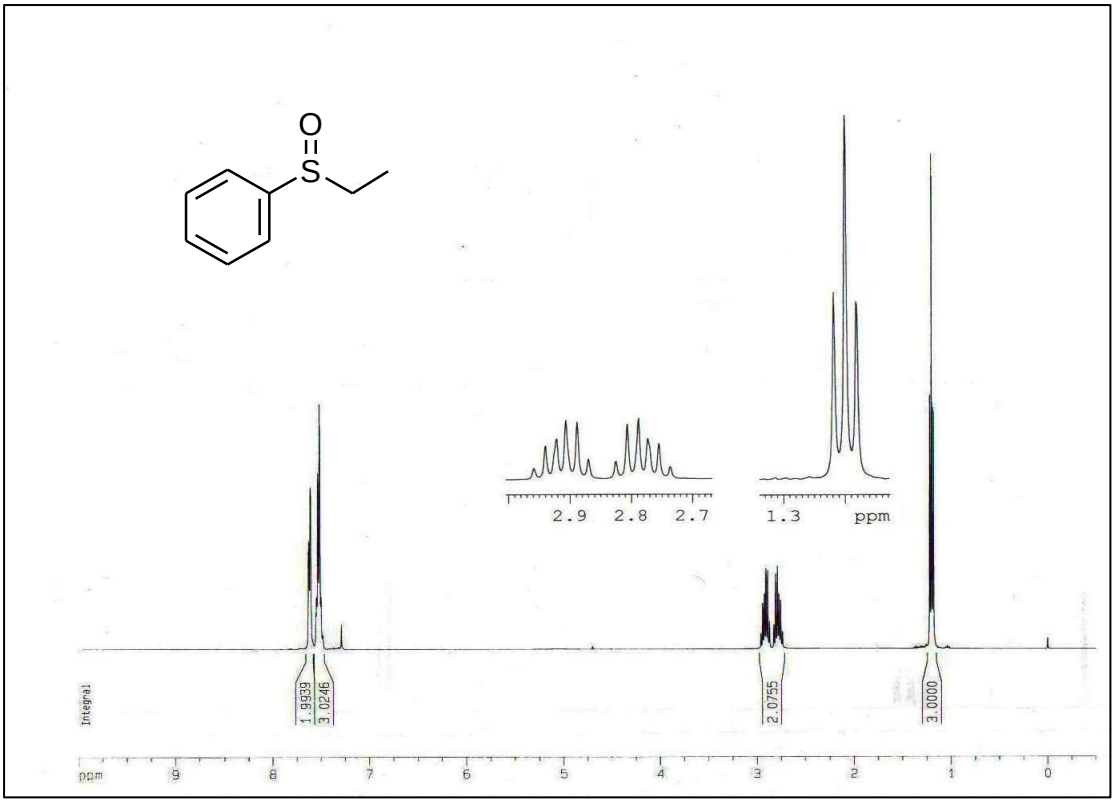

Figure 4.17 ^{1}H NMR spectrum of Ethyl phenyl sulfoxide **(19f)**

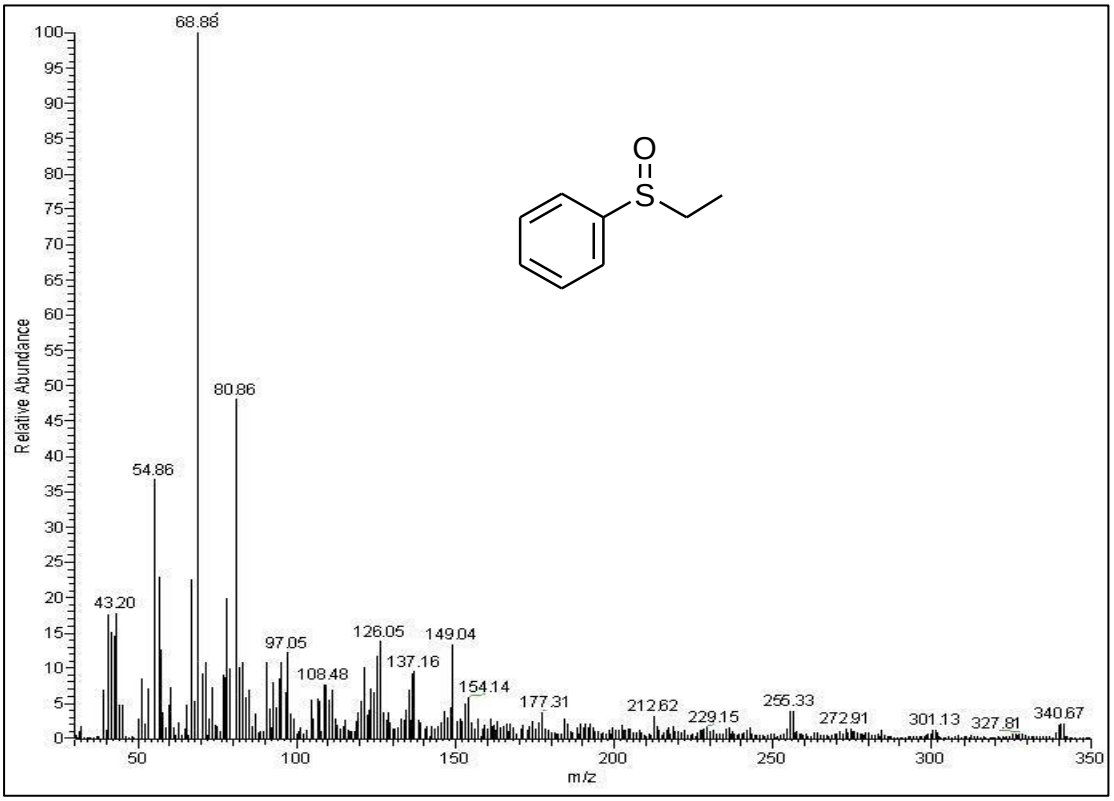

Figure 4.18 Mass spectrum of Ethyl phenyl sulfoxide **(19f)**

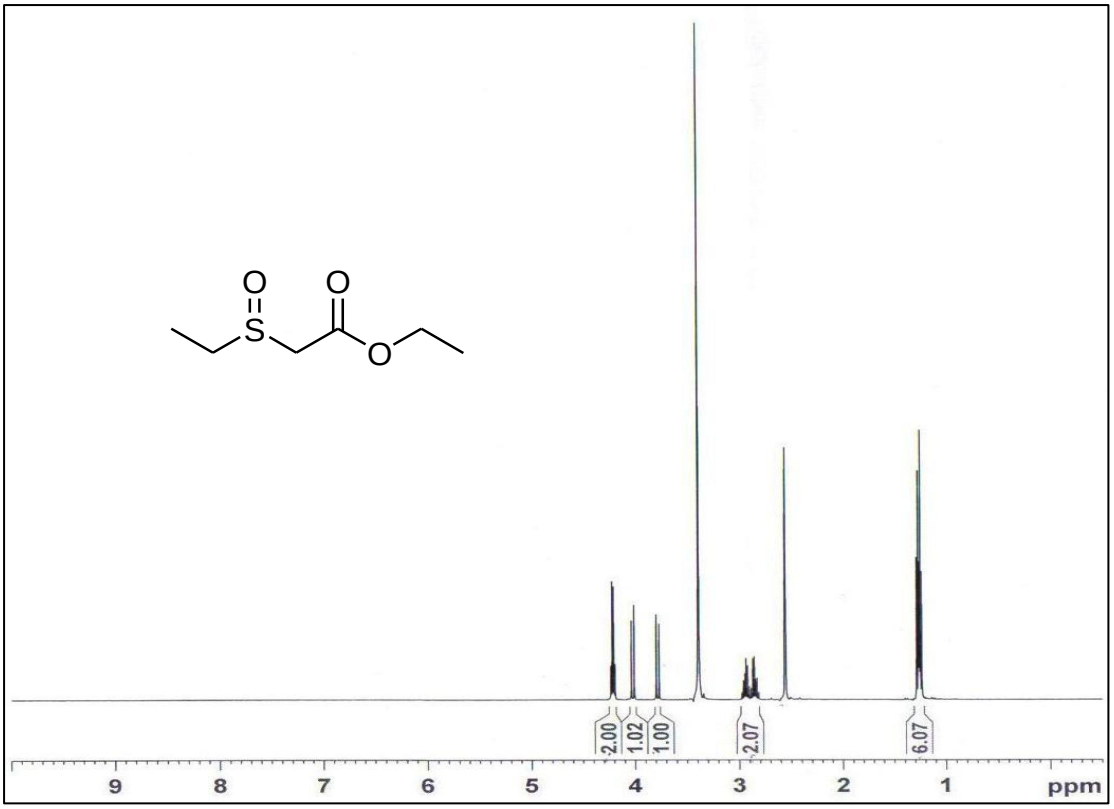

Figure 4.19 ^{1}H NMR spectrum of Ethyl 2-(ethyl sulfinyl) acetate **(19g)**

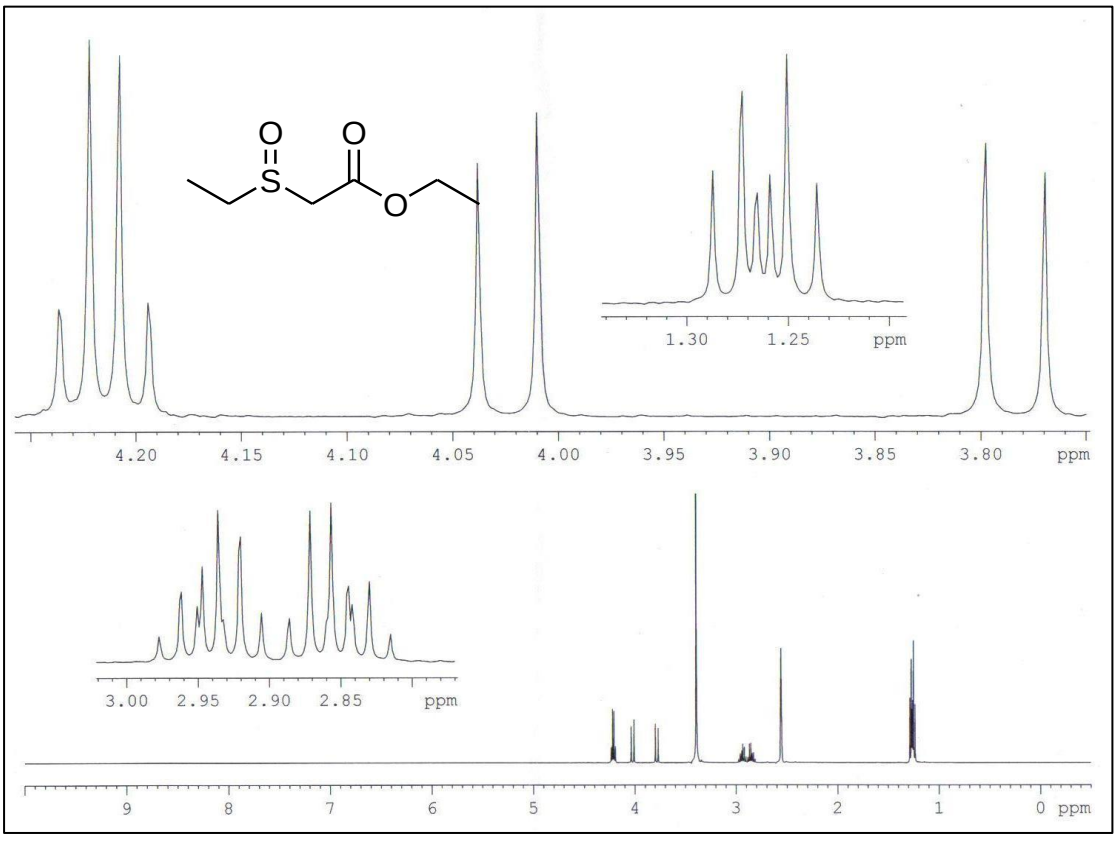

Figure 4.20 Expanded ^{1}H NMR spectrum of Ethyl 2-(ethyl sulfinyl) acetate **(19g)**

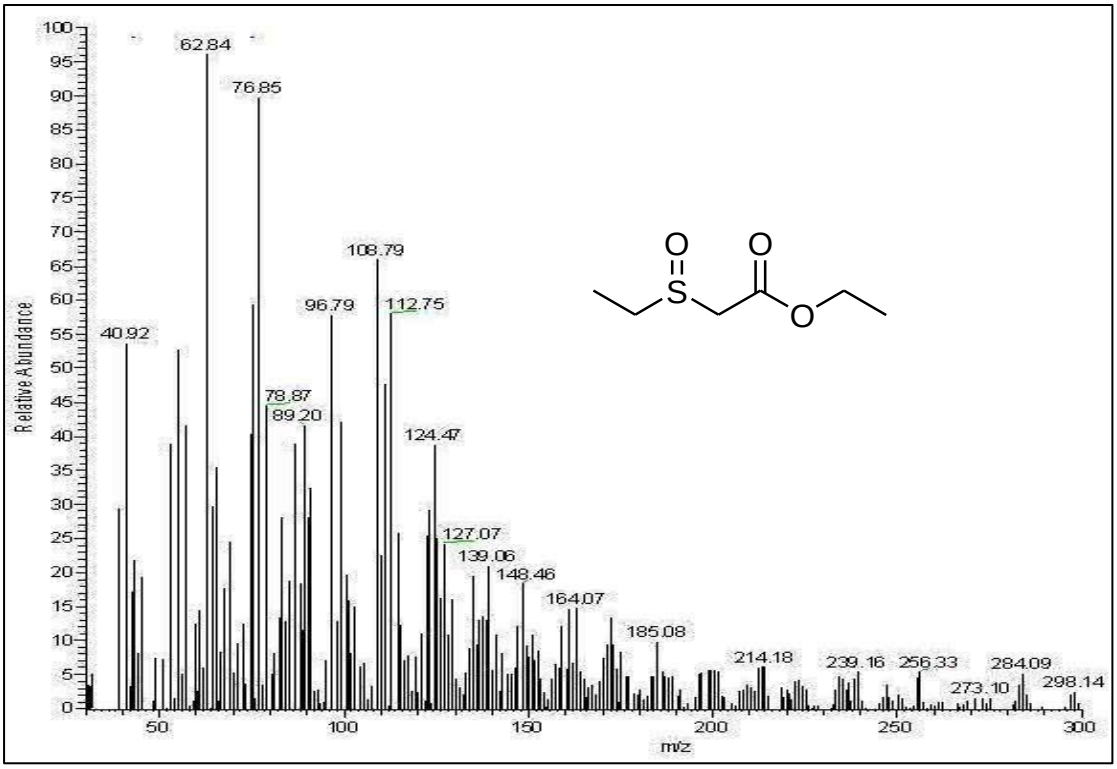

Figure 4.21 Mass spectrum of Ethyl 2-(ethyl sulfinyl) acetate **(19g)**

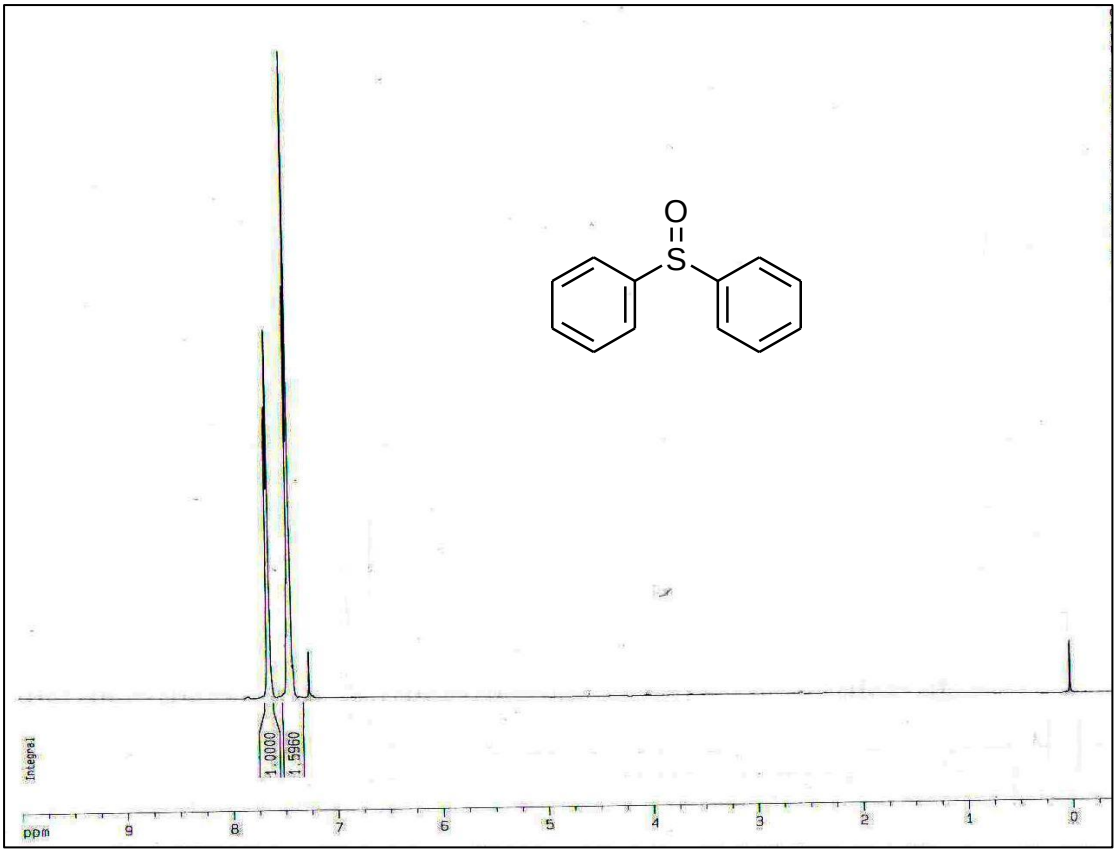

Figure 4.22 ^{1}H NMR spectrum of Diphenyl sulfoxide **(19h)**

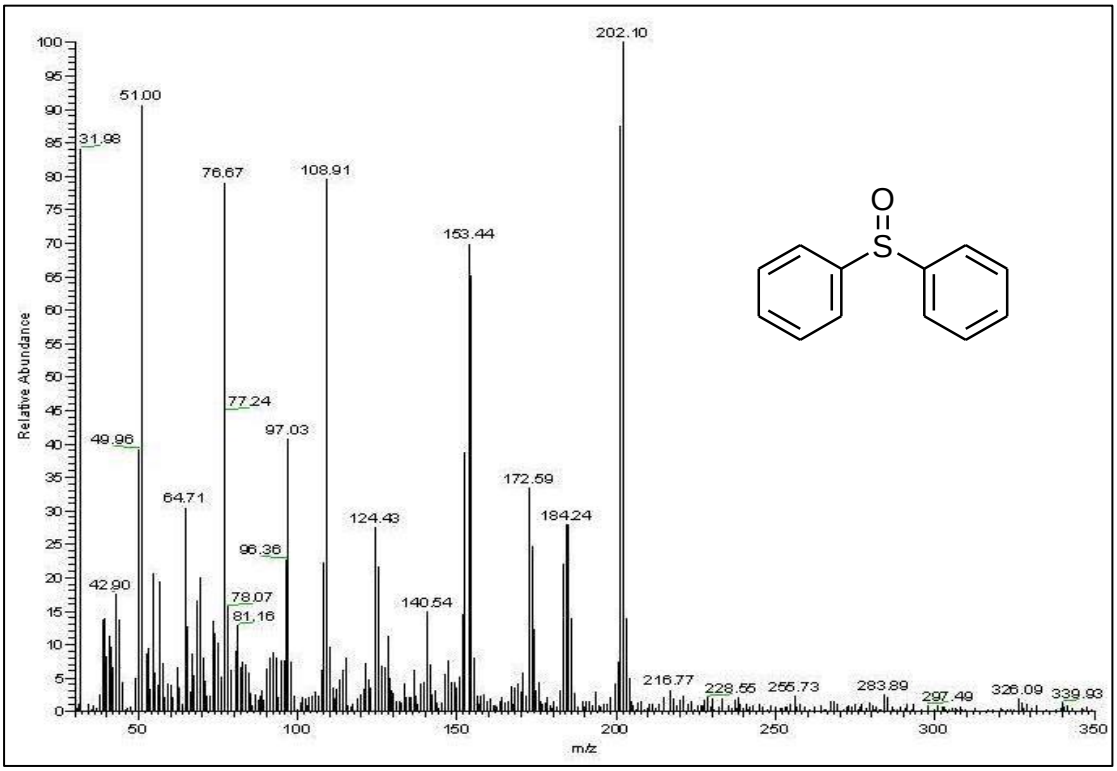

Figure 4.23 Mass spectrum of Diphenyl sulfoxide **(19h)**

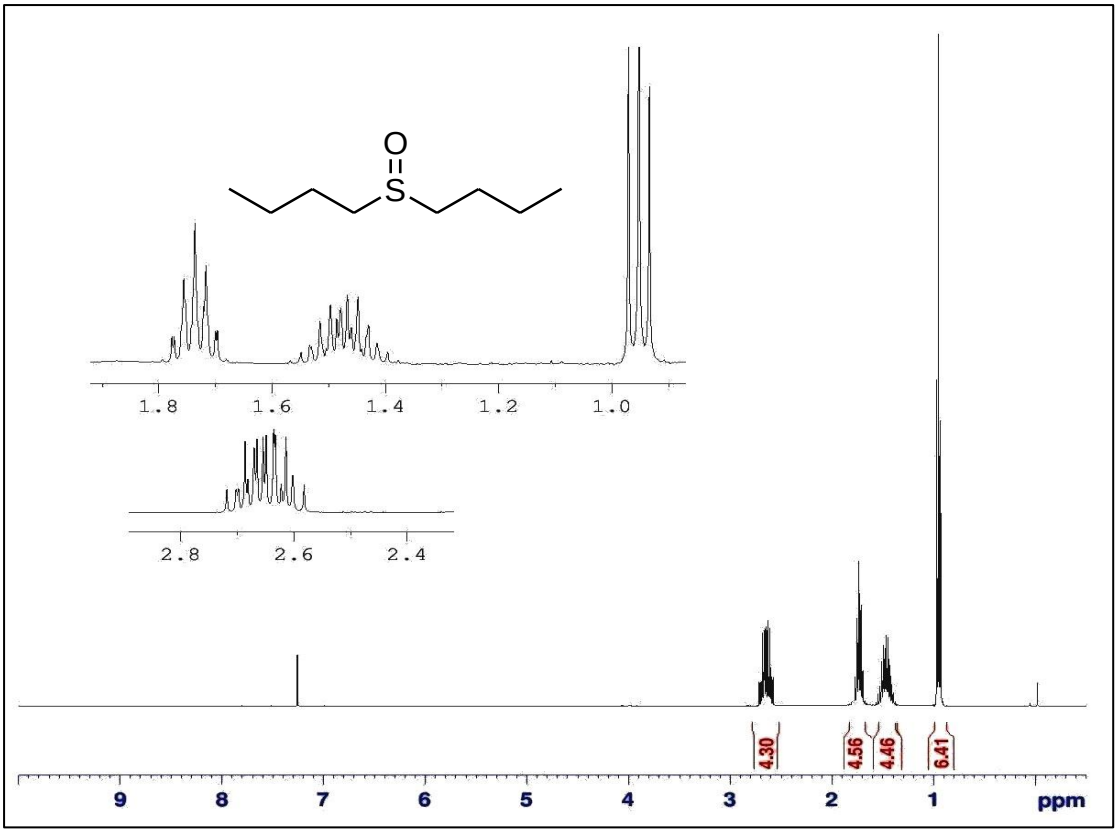

Figure 4.24 ^{1}H NMR spectrum of Di-n-butyl sulfoxide **(19i)**

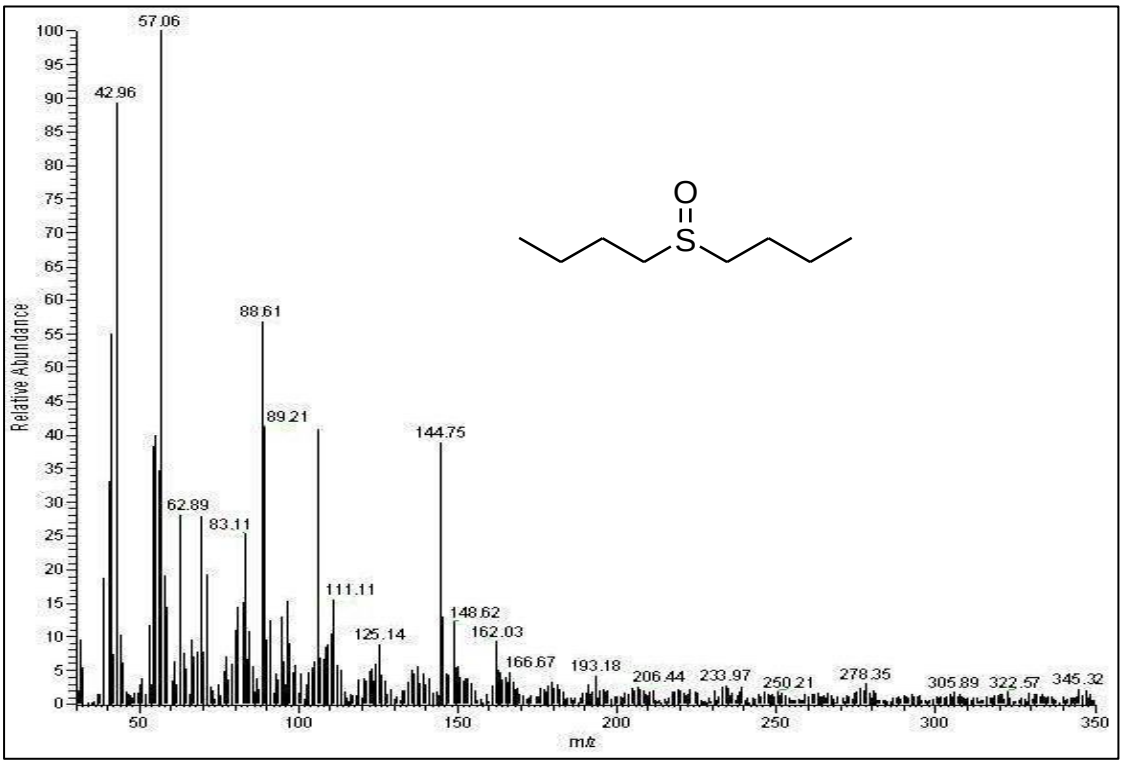

Figure 4.25 Mass spectrum of Di-n-butyl sulfoxide **(19i)**