Selective hydrogen peroxide oxidation of sulfides to sulfoxides or sulfones with MWW-type titanosilicate zeolite catalyst under organic solvent-free conditions

Yoshihiro Kon, Dr. Toshiyuki Yokoi, Masato Yoshioka, Shinji Tanaka, Yumiko Uesaka, Takehisa Mochizuki, Kazuhiko Sato, Takashi Tatsumi

PII: S0040-4020(14)01134-X
DOI: 10.1016/j.tet.2014.07.091
Reference: TET 25885

To appear in: *Tetrahedron*

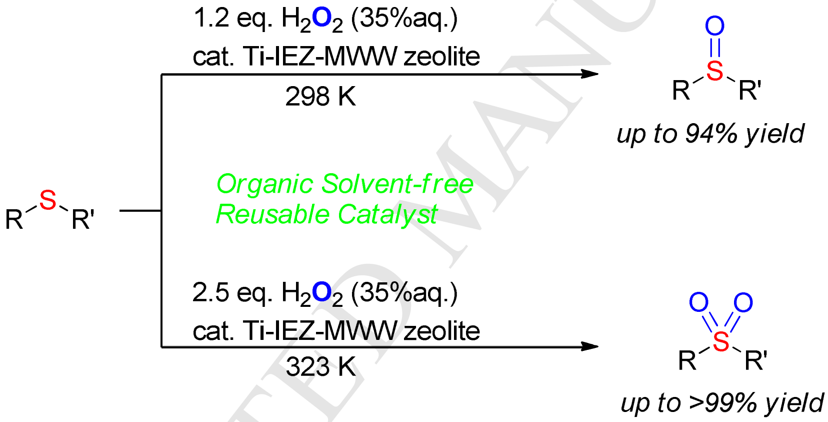
Received Date: 14 April 2014
Revised Date: 24 July 2014
Accepted Date: 25 July 2014

Please cite this article as: Kon Y, Yokoi T, Yoshioka M, Tanaka S, Uesaka Y, Mochizuki T, Sato K, Tatsumi T, Selective hydrogen peroxide oxidation of sulfides to sulfoxides or sulfones with MWW-type titanosilicate zeolite catalyst under organic solvent-free conditions, *Tetrahedron* (2014), doi: 10.1016/j.tet.2014.07.091.

Graphical Abstract

Selective hydrogen peroxide oxidation of sulfides to sulfoxides or sulfones with MWW-type titanosilicate zeolite catalyst under organic solvent-free conditions

Yoshihiro Kon1), Toshiyuki Yokoi2), Masato Yoshioka2), Shinji Tanaka1), Yumiko Uesaka1), Takehisa Mochizuki1), Kazuhiko Sato1)*, Takashi Tatsumi2)*



Title

Selective hydrogen peroxide oxidation of sulfides to sulfoxides or sulfones with MWW-type titanosilicate zeolite catalyst under organic solvent-free conditions

Authors

Yoshihiro Kon1), Toshiyuki Yokoi2), Masato Yoshioka2), Shinji Tanaka1), Yumiko Uesaka1), Takehisa Mochizuki 1), Kazuhiko Sato1)*, Takashi Tatsumi2)*

Affiliation

1) *National Institute of Advanced Industrial Science and Technology (AIST), Central5 Higashi 1-1-1, Tsukuba 305-8565, Japan*

2) *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

---

* Corresponding author. Tel.: +81-29-861-4511; fax: +81-29-861-4511; e-mail: k.sato@aist.go.jp

* Corresponding author. Tel.: +81-45-924-5238; fax: +81-45-924-5282; e-mail: ttatsumi@cat.res.titech.ac.jp

Contact address:

Dr. Yoshihiro Kon

National Institute of Advanced Industrial Science and Technology (AIST)

Address: Central 5 Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan.

Fax: +81-29-861-4511

Tel: +81-29-861-4425

E-mail:y-kon@aist.go.jp

Abstract

Selective oxidation of sulfides to sulfoxides and sulfones with hydrogen peroxide under organic solvent-free conditions was demonstrated by the **MWW**-type titanosilicate zeolite catalyst. Sulfides were oxidized smoothly to give sulfoxides with good selectivities at ambient temperature using 1.0-1.2 equivalent of hydrogen peroxide with the **MWW**-type titanosilicate zeolite catalyst. Especially, the Ti-MWW with an interlayer-expanded structure (Ti-IEZ-MWW) catalyst showed high activity with good chemoselectivity for the oxidation of various sulfides. The catalyst is recyclable for at least five cycles, and the only byproduct is water. Sulfides were directly oxidized to give sulfones in high yields by 2.5 equivalent of hydrogen peroxide with the **MWW**-type titanosilicate zeolite catalyst under organic solvent-free conditions.

Keywords

oxidation; green chemistry; hydrogen peroxide; titanosilicate zeolite catalyst; sulfide

1. **Introduction**

The selective oxidation of sulfides to sulfoxides or sulfones is a useful transformation in organic chemistry.[1] Sulfoxides and sulfones are known as valuable intermediates or building blocks of pharmaceuticals such as antifungal and antihypertensive agents. [1a,c, 2] And many kinds of oxidants such as nitric acid, organic peroxides, and heavy metal oxidants have been employed as effective oxidants to form sulfoxides and/or sulfones in high yields. [1] Among various kinds of oxidants, hydrogen peroxide (H_2O_2) is one of the most straightforward, clean, and versatile oxidant[3] from both an environmental and economic perspective because H_2O_2 has a high content of active oxygen and its byproduct is water.[4]

There are numerous methods for oxidation of sulfides using aqueous H_2O_2 as an oxidant.[1,5-14] And it is well known that sulfides are oxidized to generate sulfoxides and sulfones by H_2O_2 at elevated temperature and/or with a long reaction time without a metal catalyst.[5] However, highly selective oxidation of sulfides under mild reaction conditions is achieved by the application of optimized catalysts and/or reaction systems.[6-10] For example, application of a micro-reactor,[6] an acid- or substrate-catalyzed reaction,[7] and homogeneous catalysts are well known as effective converting methods.[8-10] These reactions, however, require large amounts of hazardous organic solvent and/or high temperature. When a homogeneous catalyst is used, it is also difficult to separate and reuse it after the reaction. On the other hand, solid catalysts are more easily removed and reused after the reaction.[11-18] The use of titanosilicate zeolite catalysts such as TS-1 and Ti-MWW as a solid catalyst is one of the simplest and most effective choices for achieving high-yield syntheses of various sulfoxides and sulfones. There are several reports on the synthesis of sulfoxides and sulfones by titanosilicate zeolite catalysts in the presence of H_2O_2.[12, 13] However, the reactions require large amounts of organic solvents such as haloalkanes, alcohols, and MeCN. The removal of organic solvents in these oxidation processes would be required to create environmentally friendly chemical processes. Recently, we reported on effective methods of the synthesis using an interlayer expanded titanosilicate zeolite with the MWW-type structure catalyst (Ti-IEZ-MWW) to give bulky diphenyl sulfoxide under organic solvent-free reaction conditions.[14] A high-yield synthesis of sulfoxide was achieved by optimization of the zeolite structure to overcome the disadvantage of organic solvent-free conditions.

We report herein a detailed study on high-yield syntheses of various sulfoxides using 1.0-1.2 equivalent of 30-35% H_2O_2 aqueous solution with well-designed titanosilicate zeolite catalysts including Ti-MWW and Ti-IEZ-MWW under organic solvent-free conditions. An effective oxidation of sulfides to give sulfones by 2.5 equivalent of 35% H_2O_2 aqueous solution with the **MWW**-type titanosilicate zeolite catalyst was also shown.

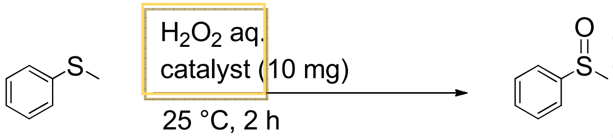
2. **Results and Discussion**

2.1. H_2O_2 oxidation of sulfides to sulfoxides using titanosilicate zeolite catalysts

Three types of titanosilicate zeolite catalysts (TS-1, Ti-MWW, and Ti-IEZ-MWW) were prepared to construct an optimized oxidation system. TS-1 was employed as a standard titanosilicate zeolite catalyst having an **MFI**-type structure with three-dimensional 10-membered-ring (3D 10-MR) pores.[15] Ti-MWW was prepared as an **MWW**-type structure which had 12-MR with a system of independent 10-MR channels.[16] Ti-IEZ-MWW was prepared as an interlayer-expanded MWW zeolite by the silylation of the layered precursor of the **MWW**-type titanosilicate (Ti-MWW(P)) with diethoxydimethylsilane (DEDMS) under acidic conditions followed by calcination.[17] The atomic ratio of Si/Ti in titanosilicate zeolite catalyst was estimated by ICP analysis; the ratios were 72, 57, and 86 for TS-1, Ti-MWW, and Ti-IEZ-MWW, respectively (Table 1). BET (Brunauer-Emmett-Teller) surface area in titanosilicate zeolite catalyst was calculated from the amount of absorbed N_2 on the surface; the values were 471, 499, and 521 for TS-1, Ti-MWW, and Ti-IEZ-MWW, respectively (Table 1).

Thioanisole was selected as a screening substrate to estimate the catalytic activities of titanosilicate zeolite catalysts. The reaction was conducted with 30-35% H_2O_2 (1.0-1.2 equivalent to thioanisole) and titanosilicate zeolite catalyst (10 mg) in open air at 25 °C for 2 h with vigorous stirring, and the results are summarized in Table 1.

Table 1. The oxidation of thioanisole with TS-1, Ti-MWW, and Ti-IEZ-MWW catalysts using aqueous H_2O_2[a]



Entry	Catalyst	Si /Ti ratio[b]	BET surface area[c]	Conv. (%)[d]	Yield (%)[d]		Selectivity (%)[e]	TON[f]
					sulfoxide	sulfone		
1	None	-	-	19	18	0	95	-
2	TS-1	72	471	65	53	8	82	230
3	Ti-MWW	57	499	>99	89	10	89	310
4	Ti-IEZ-MWW	86	521	79	70	6	89	370
5[g]	Ti-IEZ-MWW	86	521	>99	94	6	94	490

[a] Reaction conditions: thioanisole (1.0 mmol), 30% H_2O_2 (1.0 mmol), titanosilicate zeolite catalyst (10 mg), 25 °C, 1000 rpm, 2 h.

[b] The atomic ratio of Si/Ti in titanosilicate zeolite catalyst was estimated by ICP analysis.

[c] The BET surface area in titanosilicate zeolite catalyst was calculated from the amount of adsorbed N_2 on the surface.

[d] Yield and conversion on the basis of thioanisole, determined by GC analysis with biphenyl as an internal standard.

[e] Yield/conversion x 100

[f] moles of product per a mole of Ti atom

[g] Reaction conditions: thioanisole (1.0 mmol), 35% H_2O_2 (1.2 mmol), pretreated Ti-IEZ-MWW (10 mg), 25 °C, 1000 rpm, 2 h.

It is well known that the thioanisole is easily oxidized to give methyl phenyl sulfoxide without a catalyst at higher temperatures and/or longer reaction times.[5, 7b, 9l] The reaction at lower temperature (25 °C) without organic solvent reaction conditions for 2 h resulted in lower levels of sulfoxidation (18% yield, Table 1, entry 1). TS-1 is known as a common titanosilicate zeolite catalyst that showed a good reactivity for H_2O_2 oxidation of sulfides by an optimized organic solvent.[12, 13] However, TS-1 did not show a high activity under organic solvent-free conditions; it gave methyl phenyl sulfoxide in 53% yield with methyl phenyl sulfone in 8% yield (Table 1, entry 2). Ti-MWW showed high activity levels even under organic solvent-free conditions; it catalyzed the sulfoxidation of thioanisole to give the corresponding sulfoxide in high yield (89%, Table 1, entry 3). Ti-MWW having a 10-MR interlayer pore has proved to be much more active than TS-1 in the epoxidation of linear alkenes with H_2O_2.[18] Ti-IEZ-MWW catalyst also showed high activity to give methyl phenyl sulfoxide in 70% yield with 89% selectivity (Table 1, entry 4). The optimization of the amount of H_2O_2 about the reaction using Ti-IEZ-MWW was carried out. The yields of methyl phenyl sulfoxide using 1.0 eq. of 30% H_2O_2, 1.2 eq. of 30% H_2O_2, 1.0 eq. of 35% H_2O_2, and 1.2 eq. of 35% H_2O_2 were 70% (Table 1, entry 4), 86%, 79%, and 91%, respectively. In addition, calcination of Ti-IEZ-MWW at 550 °C for 5 h just before the reaction improved the activity of Ti-IEZ-MWW toward the oxidation of thioanisole using 1.2 eq. of 35% H_2O_2 (conversion, >99%; yields, 94%; selectivity, 94%; Table 1, entry 5). On the other hand, the same treatment had almost no effect on the reactions using TS-1 and Ti-MWW catalysts. Although Ti-IEZ-MWW seems to show the high activity derived from 12-MR interlayer pore in addition to **MWW**-type structure, it also tends to adsorb water and/or organic compounds and to diminish the activity. Calcination of Ti-IEZ-MWW just before the reaction and the use of 1.2 eq. of 35%H_2O_2 aq. would be effective for recovering the original activity of Ti-IEZ-MWW. The turnover numbers (TONs) in TS-1, Ti-MWW, Ti-IEZ-MWW, and Ti-IEZ-MWW (calcined) were found to be 230, 310, 370, and 490, respectively. The calculated turn over frequencies (TOFs) in Ti-MWW and Ti-IEZ-MWW at the oxidation of thioanisole were on the same levels (1900 and 2000 h^{-1} for Ti-MWW and Ti-IEZ-MWW, respectively).

Thioanisole was converted to the corresponding sulfoxide in high yield with good selectivity in the presence of the Ti-IEZ-MWW catalyst. On the other hand, small amounts of sulfone (6% yield) were observed. This trend was also observed by the X_{SO} experiment (Figure 1).[19] The X_{SO} value reflected the extent of oxidation at the SO site in thianthrene 5-oxide (SSO). The oxidation of SSO using the Ti-IEZ-MWW catalyst was carried out at 40 °C for 18 hours. And the generated oxidized products were detected by NMR analysis. The yields of products were as follows; 1.1% yield for thianthrene 5,5-dioxide (SSO_2), 54.2% yield for thianthrene 5,10-dioxide (*cis*- and *trans*-mixture, SOSO), 6.7% yield for thianthrene 5,5,10-trioxide ($SOSO_2$). The X_{SO} value of Ti-IEZ-MWW was calculated to be 0.11. This X_{SO} value was in a similar range to those of Ti-beta (0.07 and 0.19), which has the ***BEA**-type structure with three-dimensional 12 MR pores.[19d]

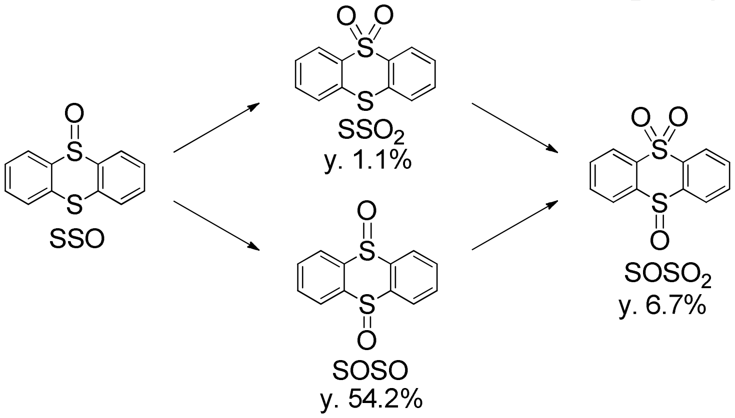


Figure 1. Oxidation of thianthrene 5-oxide (SSO) by Ti-IEZ-MWW catalyst

Competitive experiments using a 1:1 mixture of thioanisole and *para* substituted thioanisole showed the Hammett linear free-energy relationship; σ+ correlated well with ρ = -0.41 (Table 2 and Figure 2). The negative ρ value suggests the electrophilic nature of Ti active species generated in Ti-IEZ-MWW. This tendency is consistent with previously reported sulfide oxidation with H_2O_2.[9a, 20]

Table 2. Competitive oxidation of *para* substituted thioanisoles[a]

Entry	*para* substituents(X)	Conv. of *para* X(%) [b]	Conv. of H (%)[b]
1	Me	7.60	6.03
2	Cl	7.29	8.60
3	OMe	5.46	2.73
4	H	-	-

[a]Reaction was run using a 1:1 mixture of thioanisole and *para* substituted thioanisole (2.0 mmol), 35% H_2O_2 aq. (1.4 mmol), and Ti-IEZ-MWW (10 mg) at 25 ˚C for 5 min.

[b]Determined by GC analysis.

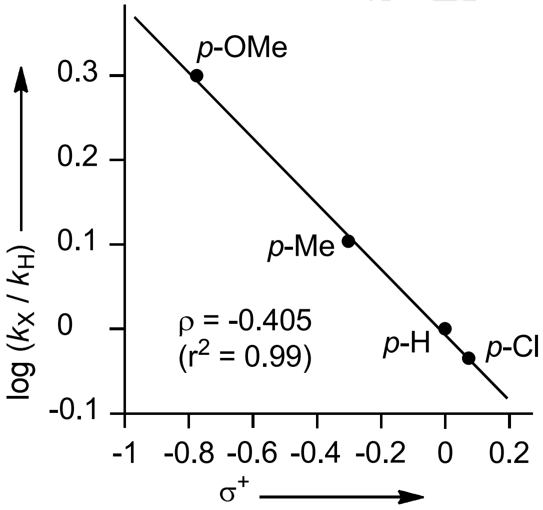


Figure 2. Hammett plots for the competitive oxidation of thioanisole and *para* substituted thioanisole. Slope = -0.41 (r^2 = 0.99).

The application of TS-1−, Ti-MWW−, and Ti-IEZ-MWW−catalyzed H_2O_2 oxidation to various sulfides is shown in Table 3. In the case of the TS-1 catalyst, methyl 4-methylphenyl, 4-chlorophenyl methyl, and 4-bromophenyl methyl sulfoxides were given in 21%, 14%, and 14% yields, respectively (Table 3, entries 2-4). Ti-MWW and

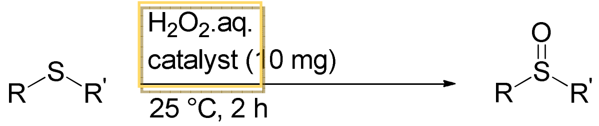
Ti-IEZ-MWW catalysts gave methyl *para* substituted phenyl sulfoxides in high yields (76-93% for Ti-MWW and 75-92% for Ti-IEZ-MWW; Table 3, entries 2-4). These results showed that Ti-MWW, which has a 10-MR interlayer pore, is much more active than TS-1 for the sulfoxidation of *para* substituted thioanisoles under organic solvent-free conditions. The reaction of 2-methyl sulfanyl pyridine, which includes a nitrogen atom as well as a sulfur atom as a reactive site, gave the corresponding sulfoxide in moderate to good yields using TS-1, Ti-MWW, and Ti-IEZ-MWW catalysts (62% yield for TS-1, 79% yield for Ti-MWW, and 79% yield for Ti-IEZ-MWW, respectively; Table 3, entry 5). In these reactions, *N*-oxide of 2-methyl sulfanyl pyridine was not observed. Chemoselectivity of this catalytic system was also checked by the reactions of allyl phenyl sulfide and 2-phenylthioethanol. Allyl phenyl sulfide and 2-phenylthioethanol were oxidized by Ti-IEZ-MWW to give the corresponding sulfoxides in 72% and 95% yields, respectively (Table 3, entries 6 and 7). In these oxidations, epoxidation nor carbonyl compounds were not observed.

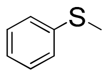
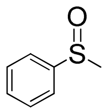
The significance of Ti-IEZ-MWW was exerted in the case of sulfides having bulky substituents such as diphenyl sulfide.[21] Oxidation of diphenyl sulfide gave the corresponding sulfoxide in good yield by the Ti-IEZ-MWW catalyst (50% yield; Table 3, entry 8). In contrast, the reactions of diphenyl sulfide using the TS-1 or Ti-MWW catalyst gave the corresponding sulfoxide in low yields (8% and 29% yields for TS-1 and Ti-MWW, respectively; Table 3, entry 8). The calculated TOFs were 15 for Ti-MWW and 41 for Ti-IEZ-MWW. Ti-IEZ-MWW showed a higher catalytic activity for sulfoxidation of diphenyl sulfide than did Ti-MWW. The BET surface area of the titanosilicate zeolite catalysts was almost within the same range, and thus the reactivity of the catalysts showed a direct correlation with the relative ease with which sulfides contact to the Ti active sites of the zeolites similar to the case of Ti-beta.[13b] Although the potential advantages of the **MWW**-type materials are expected from their supercages and side pockets, access to the supercages is seriously restricted by the openings of the elliptical 10-MR pores. Because Ti-IEZ-MWW has a 12-MR interlayer pore, bulkier aryl sulfides can access the Ti active site of Ti-IEZ-MWW. TS-1 and Ti-MWW do not have a 12-MR interlayer pore, and it is hard for bulkier aryl sulfides to come into contact with the Ti active sites of TS-1 and Ti-MWW. Similar results were observed from the reactions of the dialkyl sulfides. Di-*n*-butyl sulfide was sulfoxidized effectively to give di-*n*-butyl sulfoxide in this order: Ti-MWW (80% yield) > Ti-IEZ-MWW (62% yield) > TS-1 (27% yield). Ti-MWW and Ti-IEZ-MWW showed a higher activity than TS-1. The activities of titanosilicate zeolite catalysts for the sulfoxidation of di-*n*-octyl sulfide were directly linked to their interlayer pore size: Ti-IEZ-MWW (29% yield) >

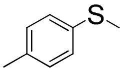
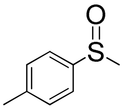
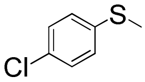
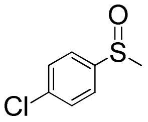
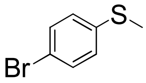
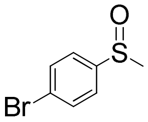
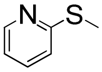
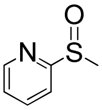
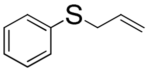
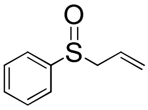
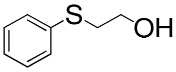
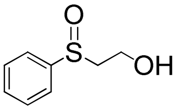
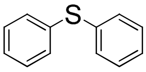
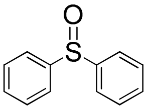
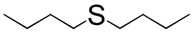
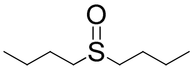
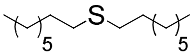
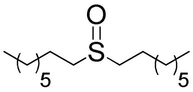
Ti-MWW (12% yield) > TS-1 (7% yield). Elongation of the interlayer would also be effective for the sulfoxidation of bulky alkyl sulfides (Table 3, entries 9 and 10).

In the reaction of diphenyl sulfide using the Ti-IEZ-MWW catalyst, the removal of the catalyst in the middle of the reaction stopped the sulfoxidation. Ti in the filtrate of diphenyl sulfide oxidation was not detected by ICP analysis. These results clearly showed that the sulfoxidation was catalyzed at the Ti active sites on solid Ti-IEZ-MWW. The Ti-IEZ-MWW catalyst could easily be reused in the next reaction. In the sulfoxidation of thioanisole, no decrease in yields was detected after five cycles to give the corresponding sulfoxide in 85-94% yields (Table 4). The Ti-IEZ-MWW catalyst was removed from the product after the reaction, washed by water and acetone, and then calcinated at 550 °C for 5 h for use in the next reaction.

Table 3. The oxidation of various sulfides to sulfoxides with TS-1, Ti-MWW, and Ti-IEZ-MWW catalysts using aqueous H_2O_2[a]



Entry	Substrate	Product	Conv. (%) [b]	Yield (%) [b]	Selectivity (%) [c]
1			19[d]	18[d]	95[d]
			65[e]	53[e]	82[e]
			>99[f]	89[f] (85)[h]	89[f]
			>99[g]	94[g] (83)[h]	94[g]

2			10[d] 27[e] 95[f] >99[g]	8[d] 21[e] 88[f] 92[g] (84)[i]	80[d] 78[e] 93[f] 92[g]
3			1[d] 16[e] 98[f] 97[g]	1[d] 14[e] 93[f] 87[g] (82)[i]	>99[d] 88[e] 95[f] 90[g]
4			1[d] 18[e] 84[f] 98[g]	1[d] 14[e] 76[f] 75[g] (77)[i]	>99[d] 78[e] 90[f] 77[g]
5			12[d] 68[e] 82[f] 82[g]	12[d] 62[e] 79[f] 79[g] (84)[j]	>99[d] 91[e] 96[f] 96[g]
6			2[d] 3[e] 86[f] 90[g]	1[d] 2[e] 72[f] 72[g] (84)[j]	50[d] 67[e] 84[f] 80[g]
7			85[d] 85[e] 97[f] 95[g]	85[d] 85[e] 97[f] 95[g] (84)[j]	>99[d] >99[e] >99[f] >99[g]
8[k]			11[d] 16[e] 36[f] 64[g]	5[d] 8[e] 29[f] 50[g] (47)[i]	45[d] 50[e] 81[f] 78[g]
9[l]			26[d] 32[e] 96[f] 90[g]	25[d] 27[e] 80[f] 82[g] (79)[i]	96[d] 84[e] 83[f] 91[g]
10[l]			6[d] 8[e] 12[f] 30[g]	6[d] 7[e] 12[f] 29[g] (32)[j]	>99[d] 88[e] >99[f] 97[g]

[a] Reaction conditions: for no-catalyst, TS-1, and Ti-MWW: sulfide (1.0 mmol), 30% H_2O_2 (1.0 mmol), catalyst (10 mg), 25 °C, 1000 rpm, 2 h, unless otherwise stated; for Ti-IEZ-MWW: sulfide (1.0 mmol), 35% H_2O_2 (1.2 mmol), Ti-IEZ-MWW (10 mg), 25 °C, 1000 rpm, 2 h, unless otherwise stated.

[b] Yield and conversion on the basis of sulfide, determined by GC analysis with biphenyl

or *n*-decane as an internal standard.

[c] Yield/conversion x 100.

[d] no catalyst.

[e] using TS-1 catalyst.

[f] using Ti-MWW catalyst.

[g] using Ti-IEZ-MWW catalyst.

[h] isolated yield (10 mmol scale).

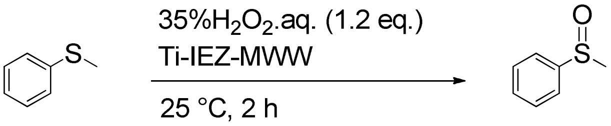
[i] isolated yield (3 mmol scale).

[j] mixture of sulfoxide and sulfone was obtained, the yield was calculated by ^{1}H NMR (3 mmol scale).

[k] 40 °C, 1000 rpm, 18 h.

[l] 25 °C, 1000 rpm, 4 h.

Table 4. Oxidation of thioanisole to methyl phenyl sulfoxide with Ti-IEZ-MWW catalyst using 35% aqueous H_2O_2, and recycling of catalyst[a]



Number of reuses	1	2	3	4	5
Yield of methyl phenyl sulfoxide (%)[b]	85	90	91	89	94

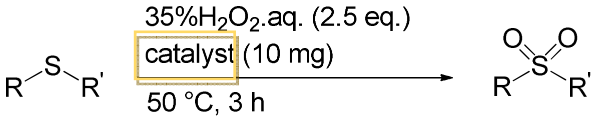
[a] Substrate: catalyst ratio (wt%); thioanisole: Ti-IEZ-MWW = 1 : 0.08, 35% H_2O_2 (1.2 eq.) was used. 25 °C, 1000 rpm, 2 h.

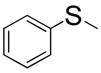
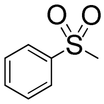
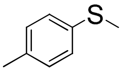
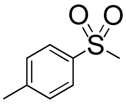
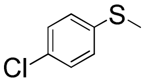
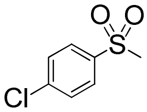
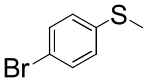
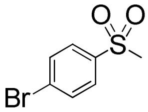
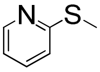
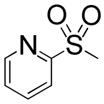
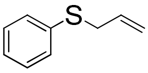
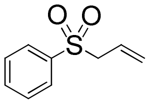
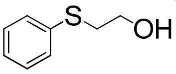
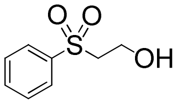
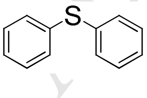
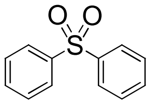
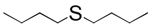
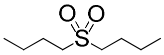
[b] Yield on the basis of thioanisole, determined by GC analysis with biphenyl as an internal standard.

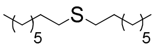
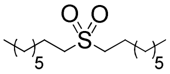
2.2. H_2O_2 oxidation of sulfides to sulfones using titanosilicate zeolite catalyst

Oxidation of sulfides to sulfones was attempted using 2.5 eq. of 35% H_2O_2 aq. with Ti-zeolite catalyst at 50 °C for 3 h (Table 5). Thioanisole was oxidized under catalyst-free conditions to give methyl phenyl sulfoxide in 92% yield, although the desired sulfone was generated only in 8% yield (Table 5, entry 1). TS-1 catalyst gave sulfone in 55% yield, while Ti-MWW and Ti-IEZ-MWW catalysts gave methyl phenyl sulfone quantitatively (Table 5, entry 1). Thioanisole derivatives such as 4-methyl, 4-chloro, and 4-bromo thioanisole were effectively catalyzed by Ti-IEZ-MWW to give the corresponding sulfones in high yields (87%, 97%, and 94%, respectively; Table 5, entries 2-4). TS-1 and Ti-MWW catalyzed the oxidation of *para* substituted thioanisoles, producing the corresponding sulfones in 28-35% and 76-94% yields, respectively (Table 5, entries 2-4). Nitrogen-containing sulfide was effectively oxidized to give methyl pyridyl sulfone in 67%, 58%, and 78% yields for TS-1, Ti-MWW, and Ti-IEZ-MWW catalysts, respectively (Table 5, entry 5). Allyl phenyl sulfide was oxidized to give allyl phenyl sulfone in 62% and 61% yields for Ti-MWW and Ti-IEZ-MWW catalysts, respectively (Table 5, entry 6). The reaction of 2-phenylthioethanol using Ti-MWW and Ti-IEZ-MWW gave 2-phenylsulfonylethanol in moderate yields (48% and 55% yields, respectively, Table 5, entries 6 and 7). Diphenyl sulfone was not observed (0% yields) and diphenyl sulfoxide was the only product from the oxidation using 2.5 eq. of 35% H_2O_2 aq. with TS-1, Ti-MWW, and Ti-IEZ-MWW catalysts at 50 °C for 18 h under organic solvent-free conditions because the generated sulfoxide is solid and not to make sufficient contact with H_2O_2 aq. and titanosilicate zeolite catalyst. The oxidation of diphenyl sulfide under catalyst-free conditions or with TS-1 and Ti-MWW catalysts gave no sulfone under toluene solution (Table 5, entry 8). Ti-IEZ-MWW showed an activity for diphenyl sulfide, producing the corresponding sulfone in 38% yield with 93% selectivity under toluene solution (Table 5, entry 8). The larger interlayer pore size of Ti-IEZ-MWW compared to those of TS-1 and Ti-MWW would be effective to proceed the oxidation of bulky sulfides. Oxidation of alkyl sulfides such as di-*n*-butyl sulfide and di-*n*-octyl sulfide also led to the production of their sulfones in good yields (65-88% yields) by Ti-MWW or Ti-IEZ-MWW (Table 5, entries 9 and 10). On the other hand, di-*n*-butyl and di-*n*-octyl sulfoxides were mainly given in the case of using TS-1 or catalyst-free conditions (63-97% yields), and the corresponding sulfones were formed in low yields (8-35% yields; Table 5, entries 9 and 10).

Table 5. The oxidation of various sulfides to sulfones with TS-1, Ti-MWW, and Ti-IEZ-MWW catalysts using 35% aqueous H_2O_2[a]



Entry	Substrate	Product	Conv. (%) [b]	Yield (%) [b]		Selectivity (%) [c]
				Sulfoxide	Sulfone	
1			>99[d]	92[d]	8[d]	8[d]
			>99[e]	44[e]	55[e]	55[e]
			>99[f]	0[f]	>99[f]	>99[f]
			>99[g]	0[g]	>99[g](99)[h]	>99[g]
2			99[d]	91[d]	8[d]	8[d]
			99[e]	64[e]	35[e]	35[e]
			>99[f]	24[f]	76[f]	76[f]
			>99[g]	13[g]	87[g](83)[h]	87[g]
3			98[d]	95[d]	3[d]	3[d]
			98[e]	70[e]	28[e]	29[e]
			>99[f]	12[f]	88[f]	88[f]
			>99[g]	3[g]	97[g](84)[h]	97[g]
4			95[d]	94[d]	0[d]	0[d]
			99[e]	70[e]	29[e]	29[e]
			>99[f]	5[f]	94[f]	94[f]
			>99[g]	5[g]	94[g](92)[h]	94[g]
5			99[d]	79[d]	2[d]	2[d]
			>99[e]	25[e]	67[e]	67[e]
			>99[f]	31[f]	58[f]	58[f]
			>99[g]	13[g]	78[g](85)[h]	78[g]
6			99[d]	82[d]	9[d]	9[d]
			98[e]	68[e]	18[e]	18[e]
			>99[f]	27[f]	62[f]	62[f]
			>99[g]	27[g]	61[g](61)[h]	62[g]
7			>99[d]	96[d]	3[d]	3[d]
			>99[e]	51[e]	48[e]	48[e]
			>99[f]	51[f]	48[f]	48[f]
			>99[g]	44[g]	55[g](50)[h]	55[g]
8[i]			0[d]	0[d]	0[d]	0[d]
			2[e]	2[e]	0[e]	0[e]
			3[f]	3[f]	0[f]	0[f]
			41[g]	2[g]	38[g](23)[h]	93[g]
9[j]			98[d]	90[d]	8[d]	8[d]
			98[e]	63[e]	35[e]	36[e]
			>99[f]	35[f]	65[f]	65[f]
			>99[g]	12[g]	88[g](88)[h]	88[g]

10[j]			>99[d]	97[d]	3[d]	3[d]
			99[e]	75[e]	25[e]	25[e]
			>99[f]	17[f]	83[f]	83[f]
			>99[g]	30[g]	70[g](37)[h]	70[g]

[a] Reaction conditions: sulfide (1.0 mmol), 35% H_2O_2 (2.5 mmol), Ti zeolite catalyst (10 mg), 50 °C, 1000 rpm, 3 h, unless otherwise stated.

[b] Yield and conversion on the basis of sulfide, determined by GC analysis with biphenyl as an internal standard.

[c] Yield/conversion x 100

[d] no catalyst

[e] using TS-1 catalyst

[f] using Ti-MWW catalyst

[g] using Ti-IEZ-MWW catalyst

[h] isolated yield (3 mmol scale)

[i] Reaction under toluene solution, 18 h

[j] Reaction for 4 h

2.3. The reaction mechanism about the H_2O_2 oxidation of sulfide by titanosilicate zeolite catalyst

The reaction mechanisms underlying oxidation of sulfides catalyzed by titanosilicate zeolite have been investigated.[12-14] The reaction of the titanosilicate zeolite catalyst with H_2O_2 gives ≡Ti-OOH active species with desorption of silanol. In the presence of water, the coordination of an H_2O molecule to the ≡Ti-OOH active species forms a cyclic structure. On the basis of previous reports, [12-14] the X_{SO} experiment, and Hammett plots, the reaction mechanism was determined as follows (Figure 3). The nucleophilic attack of the sulfur atom to an oxygen atom of the ≡Ti-OOH active site leads to sulfoxide formation. Deoxygenated ≡Ti-OH was stabilized by the coordination with water and reoxidized by the next H_2O_2 to reproduce ≡Ti-OOH active species. The formation of sulfone is also explained by this mechanism; that is, the nucleophilic attack of the sulfur atom of sulfoxide is a key step. Sulfoxides are generated in good selectivity at 25 °C because the nucleophilic attack by sulfide is far superior to that by sulfoxide. The reactivity can be linked to the topology of the titanosilicate zeolite catalysts due to the relative ease of accessibility of the nucleophilic S atom on the sulfide to the O atom on the ≡Ti-OOH active site.

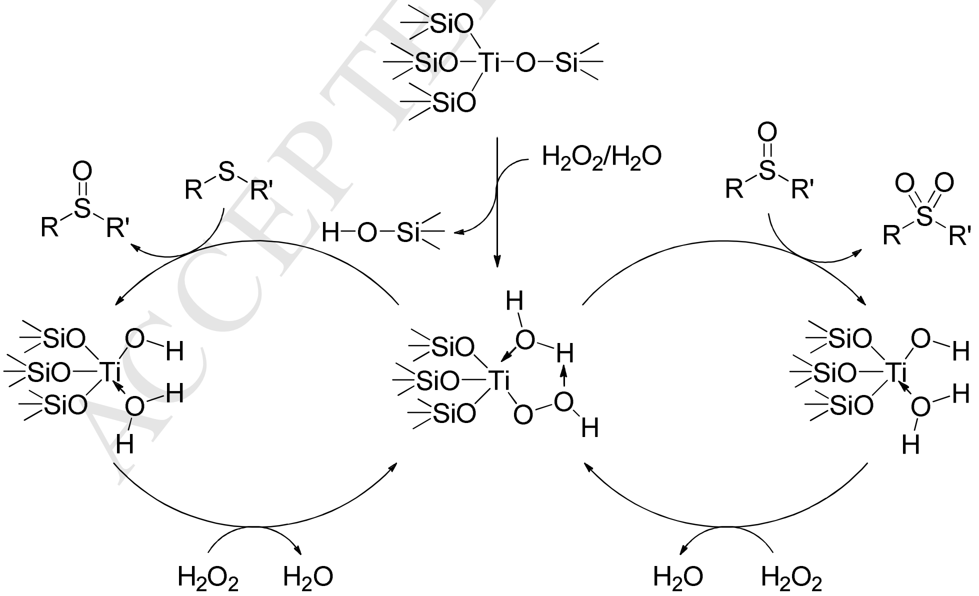


Figure 3. Plausible mechanism for the oxidation of sulfides to sulfoxides and sulfones.

3. Conclusions

Sulfides were oxidized to sulfoxides and sulfones using H_2O_2 aqueous solution with titanosilicate zeolite catalysts. This reaction can be considered a green sustainable process using the titanosilicate zeolite catalyst in the presence of H_2O_2 under organic solvent-free conditions. Thioanisoles were effectively oxidized by titanosilicate zeolite having an **MWW** structure to produce the corresponding sulfoxides in good yields with good selectivities. Interlayer-expanded **MWW**-type titanosilicate (Ti-IEZ-MWW) zeolite was applicable to the oxidation to give sulfoxides and sulfones with bulky structures, such as diphenyl sulfide. The Ti-IEZ-MWW catalyst can be reused to produce thioanisole oxidation in good yields for at least five cycles.

4. Experimental section

4.1. General

Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 using an INERT CAP column (0.25 mm x 30 m, GL Sciences Inc.). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL ECX-400P spectrometer at 298 K. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to residual $CHCl_3$ at 77.0 ppm for ^{13}C unless otherwise noted. UV-vis. diffuse reflectance spectra were recorded on a JASCO V-650DS spectrometer. The diffuse reflectance spectra were converted into the absorption spectra by using the Kubelka-Munk function. Elemental analyses of the samples (Si/Ti ratio) were performed on a Shimadzu ICPE-9000 inductively coupled plasma-atomic emission spectrometer (ICP-AES). N_2 adsorption-desorption measurements were conducted at 77 K on a Quantachrome Autosorb-1 to obtain information on the micro- and meso-porosities. The BET surface area was calculated from the adsorption data in the relative pressure ranging from 0.04 to 0.2. Prior to each adsorption measurement, the sample was evacuated at 200 ºC for 6 h.

4.2. Materials

Methyl phenyl sulfone, methyl phenyl sulfoxide, di-*n*-butyl sulfone, di-*n*-butyl sulfoxide, di-*n*-butyl sulfide, di-*n*-octyl sulfone, di-*n*-octyl sulfoxide, di-*n*-octyl sulfide, 4-bromophenyl methyl sulfone, 4-bromothioanisole, 4-chlorophenyl methyl sulfone, 4-methylthiotoluene, methyl 4-methylphenyl sulfone, diphenyl sulfone, diphenyl sulfide, 4-methoxyphenyl methyl sulfide, 2-methylthiopyridine, thianthrene, decane, biphenyl, diphenyl sulfoxide, Allyl phenyl sulfide, allyl phenyl sulfone and 2-phenylthioethanol were obtained from Tokyo Chemical Industry Co., Ltd. Thioanisole, 4-chlorothioanisole, methanol, 2-phenylsulfonyl ethanol, H_2SO_4, ethanol, dichloromethane and $CDCl_3$ were obtained from Wako Pure Chemical Industries, Ltd. Thirty-five-percent aqueous hydrogen peroxide was obtained from Kanto Chemical Co., Inc. Methyl 4-methylphenyl sulfoxide was obtained from Sigma-Aldrich Corporation. Toluene was obtained from Junsei Chemical Co., Ltd. 4-Chlorophenyl methyl sulfoxide, 4-bromophenyl methyl sulfoxide, methyl 2-pyridyl sulfoxide, methyl 2-pyridyl sulfone, allyl phenyl sulfoxide and 2-phenylsulfinyl ethanol were generated according to the procedure described in the literature.[9j,22,24,26,27] TS-1, Ti-MWW, and Ti-IEZ-MWW were generated according to the procedure described in the literature.[15, 16, 21] All materials were used as received.

4.3. Preparation of titanosilicate zeolite catalysts

Titanosilicate zeolites including TS-1, Ti-MWW, and Ti-IEZ-MWW were prepared and used as oxidation catalysts. $Si(OEt)_4$ (TEOS) and $Ti(OBu\text{-}n)_4$ (TBOT) were used as silica and Ti sources, respectively. The layered precursor of the **MWW** titanosilicate, Ti-MWW(P), was hydrothermally synthesized by a previously reported procedure.[16] Ti-MWW was obtained by the calcination of Ti-MWW(P).[16] Ti-IEZ-MWW was prepared by a silylation of Ti-MWW(P) with DEDMS under acidic conditions.[21] To prepare TS-1, a mother gel containing TEOS, TBOT, $(n\text{-}Pr)_4NOH$ (TPAOH), H_2O_2 aq., and water was prepared based on the procedure reported[15] and hydrothermally treated. After the hydrothermal treatment, the obtained precipitate was centrifuged, washed thoroughly with propanol, and dried at 100 ºC overnight. Acid treatment was conducted to remove extra-framework Ti species; the as-synthesized sample was treated with an acid solution (liquid-to-solid ratio, 50 ml/g) under a stirring condition at room temperature. After the treatment, the sample was filtered, washed with deionized water, and calcined at 550 ºC.

The Ti environment in the titanosilicates was evaluated by the UV-vis spectroscopy technique. The band at around 220 nm, resulting from the charge transfer from O^{2-} to Ti^{4+}, is attributed to the tetrahedrally-coordinated Ti species (framework Ti), and the 260 and 330 nm bands are assigned to the octahedrally-coordinated Ti species (extra-framework Ti) and the anatase-like phase, respectively. The UV-vis spectra indicated that all titanosilicates mainly have tetrahedrally coordinated Ti species, which are the active species for oxidation with H_2O_2. The atomic ratio of Si/Ti in titanosilicate zeolite was estimated by ICP analysis; the ratios were 72, 57, and 86 for TS-1, Ti-MWW, and Ti-IEZ-MWW, respectively. The BET surface area in titanosilicate zeolite was calculated from the amount of adsorbed N_2 on the surface; the values were 471, 499, and 521 for TS-1, Ti-MWW, and Ti-IEZ-MWW, respectively.

4.4. Procedure for the oxidation of thioanisole to give methyl phenyl sulfoxide

A test tube equipped with a magnetic stirring bar was charged with thioanisole (126.5 mg, 1.0 mmol), aqueous 35% H_2O_2 (121 mg, 1.20 mmol), and Ti-IEZ-MWW (9.9 mg). The mixture was stirred at 25 ˚C for 2 h. The conversion and yield were determined by GC analysis of the toluene solution with biphenyl as an internal standard. The yield of methyl phenyl sulfoxide was 94%, conversion of thioanisole was >99%, selectivity (yield/conversion) was 94%, and the yield of methyl phenyl sulfone was 6%.

4.5. Calculation of X_{SO} value

A test tube equipped with a magnetic stirring bar was charged with SSO (50.0 mg, 0.2 mmol), aqueous 35% H_2O_2 (25.6 mg, 0.18 mmol), and Ti-IEZ-MWW (20 mg). The mixture was stirred at 40 ˚C for 18 h under $CDCl_3$ solution (3 ml). After the reaction, *n*-decane (13.7 mg, 0.096 mmol) was added to the extracted $CDCl_3$ solution as an internal standard and ^{1}H NMR was measured. ^{1}H NMR signals in the area between δ 7.70 – 8.25 were assigned as follows in comparison with the ^{1}H NMR data of SSO, SSO_2, SOSO, and $SOSO_2$ which were previously reported[9l, 25] and the products of the oxidation were analyzed quantitatively; $SOSO_2$ δ 7.70 – 7.82 (4H), SSO δ 7.90 – 7.97 (2H), *cis*-, *trans*-SOSO and $SOSO_2$ δ 8.04 – 8.20 (4H), SSO_2 δ 8.20 – 8.25 (4H). The yields of SOSO, SSO_2, and $SOSO_2$ were calculated in 54.2%, 1.1%, and 6.7%, respectively. The X_{SO} value was calculated according to: X_{SO} = (nucleophilic oxidation) / (total oxidation) = (SSO_2 + $SOSO_2$) / (SSO_2 + SOSO + $2SOSO_2$), where X_{SO} = (1.1 + 6.7) / (1.1 + 54.2 + 2 x 6.7) = ca 0.11.

4.6. Hammett plots using *para* substituted thioanisoles

A test tube equipped with a magnetic stirring bar and a reflux condenser was charged with 1.0 mmol of *para* substituted thioanisole, 1.0 mmol of thioanisole, 1.4 mmol of aqueous 35% H_2O_2, and 10 mg of Ti-IEZ-MWW. After the mixture was vigorously stirred at 25 ˚C for 5 min, and Ti-IEZ-MWW was then separated by filtration. The disappearance of the substrates was monitored by GC analysis with an internal standard, biphenyl. The initial relative rates ($\log(k_X/k_H)$) thus determined were 0.301 (OMe), 0.100 (Me), 0 (H), and -0.0718 (Cl), respectively.

4.7. Gram-scale oxidation of thioanisole using Ti-IEZ-MWW catalyst (as a

typical procedure for isolation)

A test tube equipped with a magnetic stirring bar was charged with thioanisole (1.24 g, 10.0 mmol), aqueous 35% H_2O_2 (1.16 g, 12.0 mmol), and Ti-IEZ-MWW (100.2 mg). The mixture was vigorously stirred at 25 ˚C for 2 h. The organic phase was separated and then washed with saturated aqueous $Na_2S_2O_3$ (10 mL). The organic phase was purified by column chromatography on silica gel using 5:1 hexane / ethyl acetate as an eluent to give methyl phenyl sulfoxide as colorless crystals; yield: 1.33 g (83%).

4.7.1. *Methyl phenyl sulfoxide*[23]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (s, 3H), 7.49–7.55 (m, 3H), 7.63–7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.0, 123.5, 129.4, 131.1, 145.7.

4.7.2. *Methyl 4-methylphenyl sulfoxide*[9j]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.70 (s, 3H), 7.33 (d, 2H, J = 8.0 Hz), 7.54 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 43.7, 123.4, 129.9, 141.3, 142.2.

4.7.3. *4-Chlorophenyl methyl sulfoxide*[9j]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (s, 3H), 7.51 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.8, 124.9, 129.5, 137.0, 144.1.

4.7.4. *4-Bromophenyl methyl sulfoxide*[22]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71 (s, 3H), 7.52 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$):

δ 44.1, 125.2, 125.5, 132.7, 145.0.

4.7.5. *2-Methylsulfinyl pyridine* (including 7wt% of sulfone)[24]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (s, 3H), 7.36–7.40 (m, 1H), 7.95 (t, 1H, J = 8.0 Hz), 8.03 (d, 1H, J = 8.0 Hz), 8.62 (d, 1H, J = 8.0 Hz).

4.7.6. *Allyl phenyl sulfoxide*[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.44–3.57 (m, 2H), 5.16 (dt, 1H, J = 4.0, 16.0 Hz), 5.29 (d, 1H, J = 8.0 Hz), 5.56–5.66 (m, 1H), 7.44–7.50 (m, 2H), 7.55–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 123.9, 124.3, 125.3, 129.1, 131.1, 143.0.

4.7.7. *2-Phenylsulfinyl ethanol*[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84–2.89 (m, 1H), 3.17–3.23 (m, 2H), 4.01–4.07 (m, 1H), 4.13–4.19 (m, 1H), 7.52–7.51 (m, 3H), 7.63–7.66 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.3, 59.1, 123.9, 129.3, 131.1, 142.9.

4.7.8. *Diphenyl sulfoxide*[28]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.49 (m, 6H), 7.64–7.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.9, 129.4, 131.2, 145.7.

4.7.9. *Di-n-butyl sulfoxide*[29]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, 6H, J = 8.0 Hz), 1.40–1.55 (m, 4H), 1.67–1.81 (m, 4H), 2.58–2.72 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 22.0, 24.6, 52.1.

4.7.10. *Di-n-octyl sulfoxide* (including 3wt% of sulfone)[30]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 6H, J = 8.0 Hz), 1.28–1.32 (m, 16H), 1.38–1.50 (m, 4H), 1.72–1.80 (m, 4H), 2.58–2.72 (m, 4H,).

4.8. Calculation of TOF by the oxidation of thioanisole using Ti-MWW and Ti-IEZ-MWW

A test tube equipped with a magnetic stirring bar was charged with thioanisole (129.2 mg, 1.0 mmol), aqueous 35% H_2O_2 (120.6 mg, 1.2 mmol), and titanosilicate zeolite catalyst (2.99 mg). The mixture was vigorously stirred at 25 ˚C for 15 min. After the reaction, biphenyl (35.29 mg, 0.23 mmol) was added to the extracted toluene solution as an internal standard and GC was measured. At the case of using Ti-MWW catalyst, the yields of methyl phenyl sulfoxide and sulfone were calculated in 40% and 1%, respectively. The conversion was 43%. And the calculated TOF from the yield of methyl phenyl sulfoxide was 1900 (per Ti atom per hour). At the case of using Ti-IEZ-MWW catalyst, the yields of methyl phenyl sulfoxide and sulfone were calculated in 28% and 0%, respectively. The conversion was 33%. And the calculated TOF from the yield of methyl phenyl sulfoxide was 2000 (per Ti atom per hour).

4.9. Calculation of TOF by the oxidation of diphenyl sulfide using Ti-MWW and Ti-IEZ-MWW

A test tube equipped with a magnetic stirring bar was charged with diphenyl sulfide (189.1 mg, 1.0 mmol), aqueous 35% H_2O_2 (118.1 mg, 1.2 mmol), and titanosilicate zeolite catalyst (10.0 mg). The mixture was vigorously stirred at 40 ˚C for 4 h. After the reaction, biphenyl (34.57 mg, 0.22 mmol) was added to the extracted toluene solution as an internal standard and GC was measured. At the case of using Ti-MWW catalyst, the yields of diphenyl sulfoxide and sulfone were calculated in 17% and 2%, respectively. The conversion was 30%. And the calculated TOF from the yield of diphenyl sulfoxide was 15. At the case of using Ti-IEZ-MWW catalyst, the yields of diphenyl sulfoxide and sulfone were calculated in 31% and 3%, respectively. The conversion was 34%. And the calculated TOF from the yield of diphenyl sulfoxide was 41.

4.10. Procedure for the oxidation of thioanisole to give methyl phenyl sulfone

A test tube equipped with a magnetic stirring bar was charged with thioanisole (130.3 mg, 1.0 mmol), aqueous 35% H_2O_2 (247.7 mg, 2.5 mmol), and Ti-IEZ-MWW (9.9 mg). The mixture was stirred at 50 ˚C for 3 h. The conversion and yield were determined by GC analysis of the toluene solution with biphenyl as an internal standard. The yield of methyl phenyl sulfone was >99%, conversion of thioanisole was >99%, and selectivity (yield/conversion) was >99%.

4.11. A 3.0 mmol-scale oxidation of thioanisole to methyl phenyl sulfone using Ti-IEZ-MWW catalyst (as a typical procedure for isolation)

A test tube equipped with a magnetic stirring bar was charged with thioanisole (383.8 mg, 3.0 mmol), aqueous 35% H_2O_2 (754.7 mg, 7.5 mmol), and Ti-IEZ-MWW (30.02 mg). The mixture was vigorously stirred at 50 ˚C for 3 h. The organic phase was separated and purified by column chromatography on silica gel using 5:1 hexane / ethyl acetate as an eluent to give methyl phenyl sulfone as colorless crystals; yield: 468.0 mg (>99%).

4.11.1. *Methyl phenyl sulfone*[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (s, 3H), 7.58 (t, 2H, J = 8.0 Hz), 7.67 (t, 1H, J = 8.0 Hz), 7.96 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.6, 127.4, 129.5, 133.8, 140.7.

4.11.2. *Methyl 4-methylphenyl sulfone*[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 3.03 (s, 3H), 7.37 (d, 2H, J = 8.0 Hz), 7.83 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 44.7, 127.5, 130.1, 137.9, 144.8.

4.11.3. *4-Chlorophenyl methyl sulfone*[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (s, 3H), 7.56 (d, 2H, J = 8.0 Hz), 7.89 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.6, 129.0, 129.8, 139.1, 140.5.

4.11.4. *4-Bromophenyl methyl sulfone*[11p]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (s, 3H), 7.80–7.83 (m, 2H), 7.82 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.6, 129.1, 132.8, 139.7.

4.11.5. *2-(Methylsulfonyl)pyridine*[26]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.24 (s, 3H), 7.55–7.58 (m, 1H), 7.98 (dt, 1H, J = 4.0, 8.0 Hz), 8.10 (d, 1H, J = 8.0 Hz), 8.74 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.0, 121.0, 127.5, 138.4, 150.0, 157.6.

4.11.6. *Allyl phenyl sulfone*[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (d, 2H, J = 800 Hz), 5.10 (d, 1H, J = 16.0 Hz), 5.27 (d, 1H, J = 8.0 Hz), 5.68–5.78 (m, 1H), 7.50 (t, 2H, J = 8.0 Hz), 7.59 (t, 1H, J = 8.0 Hz), 7.82 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.8, 124.5, 128.4, 129.0, 133.7, 138.2.

4.11.7. *2-Phenylsulfonyl ethanol*[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (t, 1H, J = 8.0 Hz), 3.34–3.37 (m, 2H), 4.00 (dd, 2H, J = 8.0, 12.0 Hz), 7.60 (t, 2H, J = 8.0 Hz), 7.69 (t, 1H, J = 8.0 Hz), 7.93–7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.0, 58.2, 127.9, 129.4, 134.0, 139.0.

4.11.8. *Diphenyl sulfone*[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.59 (m, 6H), 7.94–7.97 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.8, 129.4, 133.3, 141.8.

4.11.9. *Di-n-butyl sulfone*[11p]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, 6H, J = 8.0 Hz), 1.44–1.53 (m, 4H), 1.78–1.86 (m, 4H), 2.95 (t, 4H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 21.9, 24.1, 52.6.

4.11.10. *Di-n-octyl sulfone*[32]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 1H, J = 8.0 Hz), 1.24–1.35 (m, 16H), 1.40–1.45 (m, 4H), 1.79–1.87 (m, 4H), 2.91–2.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.1, 22.7, 28.7, 29.1, 29.2, 31.8, 52.9.

5. Acknowledgment

This work was partially supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan and the Cooperative Research Program of “Network Joint Research Center for Materials and Devices”, Japan.

6. References and notes

1) (a) Madesclaire, M. *Tetrahedron* **1986**, *42*, 5459-5495; (b) Smith, M. B.; March, J. *March’s Advanced Organic Chemistry*, 6th ed.; Wiley: New York, **2007**, pp. 1780–1783; (c) Bäckvall, J.-E. *Modern Oxidation Methods*; Wiley-VCH: Weinheim, 2004, pp. 193–211.

2) Trost, B. M. *Bull Chem. Soc. Jpn*. **1988**, *61*, 107-124.

3) (a) Trost, B. M. *Science*, **1991**, *254*, 1471-1477; (b) Sheldon, R. A. *Chem. Ind.* **1992**, 903-906.

4) (a) Strukul, G. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer: Dordrecht, 1992; (b) Sheldon, R. A.; Dakka, J. *Catal. Today* **1994**, *19*, 215-246; (c) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977-1986.

5) Jereb, M. *Green. Chem*. **2012**, *14*, 3047-3052.

6) Maggi, R.; Chitsaz, S.; Loebbecke, S.; Piscopo, C. G.; Sartori, G.; Schwarzer, M. *Green. Chem*. **2011**, *13*, 1121-1123.

7) (a) Kaczorowska, K.; Kolarska, Z.; Mitka, K.; Kowalski, P. *Tetrahedron*, **2005**, *61*, 8315-8327; (b) Shi, F.; Tse, M. K.; Kaiser, H. M.; Beller, M. *Adv. Synth. Catal*. **2007**, *349*, 2425-2430.

8) For recent reviews, see: (a) Kholdeeva, O. A. *Top Catal*. **2006**, *40*, 229-243; (b) Kholdeeva, O. A.; Maksimovskaya, R. I. *J. Mol. Catal. A: Chem*. **2007**, *262*, 7-24.

9) (a) Yamaura, T.; Kamata, K.; Yamaguchi, K.; Mizuno, N., *Catal. Today*, **2013**, *203*, 76-80; (b) Hussain, S.; Bharadwaj, S. K.; Pandey, R.; Chaudhuri, M. K. *Eur. J. Org. Chem*. **2009**, 3319-3322; (c) Rostami, A.; Akradi, J. *Tetrahedron Lett*. **2010**, *51*, 3501-3503; (d) Bahrami, K. *Tetrahedron Lett*. **2006**, *47*, 2009-2012; (e) Kirihara,

M.; Yamamoto, J.; Noguchi, T.; Itou, A.; Naito, S.; Hirai, Y. *Tetrahedron* **2009**, *65*, 10477-10484; (f) Alonso, D. A.; Nájera, C.; Varea, M. *Tetrahedron Lett*. **2002**, *43*, 3459-3461; (g) Jeyakumar, K.; Chand, D. K. *Tetrahedron Lett*. **2006**, *47*, 4573-4576; (h) Gamelas, C. A.; Lourenço, T.; da Costa, A. P.; Simplício, A. L.; Royo, B.; Romão, C. C. *Tetrahedron Lett*. **2008**, *49*, 4708-4712; (i) Yang, C.; Jin, Q.; Zhang, H.; Liao, J.; Zhu, J.; Yu, B.; Deng, J. *Green Chem*. **2009**, *11*, 1401-1405; (j) Tundo, P.; Romanelli, G. P.; Vázquez, P. G.; Aricò, F. *Catal. Commun*. **2010**, *11*, 1181-1184; (k) Yamazaki, S. *Bull. Chem. Soc. Jpn*. **1996**, *69*, 2955-2959; (l) Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X.-Q.; Noyori, R. *Tetrahedron* **2001**, *57*, 2469-2476; (m) Lindén, A. A.; Krüger, L.; Bäckvall, J.-E. *J. Org. Chem.* **2003**, *68*, 5890-5896 and references cited herein.

10) Enantioselective sulfoxidation; see (a) Fernandez, I.; Khiar, N. *Chem. Rev*. **2003**, *103*, 3651-3705; (b) O'Mahony, G. E.; Ford, A.; Maguire, A. R. *J. Org. Chem.* **2012**, *77*, 3288-3296; (c) H. Egami, T. Katsuki, *J. Am. Chem. Soc.*, **2007**, *129*, 8940; (d) Di, F. F.; Modena, G.; Seraglia, R. *Synthesis* **1984**, 325; (e) Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc*. **1984**, *106*, 8188; (f) Bolm, C.; Bienewald, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *34*, 2640 and references cited herein.

11) Recent examples of highly effective oxidation of sulfides by solid catalyst; see (a) Bigi, F.; Corradini, A.; Quarantelli, C.; Sartori, G. *J. Cat*. **2007**, *250*, 222-230; (b) Sreedhar, B.; Radhika, P.; Neelima, B.; Hebalkar, N.; Mishra, A. K. *Catal. Commun*. **2008**, *10*, 39-44; (c) Reddy, R. S.; Reddy, J. S.; Kumar, P. J. *J. Chem. Soc., Chem. Commun.*, **1992**, 84-85; (d) Bharadwaj, S. K.; Sharma, S. N.; Hussain, S.; Chaudhuri, M. K. *Tetrahedron Lett*. **2009**, *50*, 3767-3771; (e) Iwamoto, M.; Tanaka, Y.; Hirosumi, J.; Kita, N. *Chem. Lett*. **2001**, 226-227; (f) Iwamoto, M.; Tanaka, Y.; Hirosumi, J.; Kita, N.; Triwahyono, S. *Microporous Mesoporous Mater.* **2001**, *48*, 271-277; (g) Jin, C. K.; Yamada, Y. M. A.; Uozumi, Y., *Bull. Kor. Chem. Soc*., **2010**, *31*, 547-548; (h) Shi, X.; Han, X.; Ma, W.; Wei, J.; Li, J.; Zhang, Q.; Chen, Z., *J. Mol. Catal. A: Chem*. **2011**, *341*, 57-62; (i) Das, S.P.; Boruah, J. J.; Sharma, N.; Islam, N. S., *J. Mol. Catal. A: Chem*. **2012**, *356*, 36-45; (j) Fazaeli, R.; Aliyan, H.; Moghadam, M.; Masoudinia, M. *J. Mol. Catal. A: Chem*. **2013**, *374-375*, 46-52; (k) Rahimizadeh, M.; Rajabzadeh, G.; Khatami, S.-M.; Eshghi, H.; Shiri, A. *J. Mol. Catal. A: Chem*. **2010**, *323*, 59-64; (l) Miyamura, H.; Akiyama, R.; Ishida, T.; Matsubara, R.; Takeuchi, M.; Kobayashi, S. *Tetrahedron* **2005**, *61*, 12177-12185; (m) Koo, D. H.; Kim, M.; Chang, S. *Org. Lett*. **2005**, *7*, 5015-5018; (n) Nuzhdin, A. L.; Dybtsev, D. N.; Fedin, V. P.; Bukhtiyarova, G. A. *Dalton Trans*.

2009, 10481-10485; (o) Yamada, Y. M. A.; Tabata, H.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Tetrahedron*, **2004**, *60*, 4087-4096; (p) Zhang, B.; Li, S.; Yue, S.; Cokoja, M.; Zhou, M.-D.; Zang, S.-L.; Kühn, F. E. *J. Organomet. Chem*. **2013**, *744*, 108-112; (q) Fazaeli, R.; Aliyan, H.; Ahmadi, M. A.; Hashemian, S. *Catal. Commun*. 2012, *29*, 48-52; (r) Boruah, J. J.; Das, S. P.; Ankireddy, S. R.; Gogoi, S. R.; Islam, N. S. *Green Chem*. **2013**, *15*, 2944-2959; (s) Shokrolahi, A.; Zali, A.; Keshavarz, M. H. *Chinese J. Catal*. **2010**, *31*, 1427-1432 and references cited therein.

12) Reviews about zeolite catalyzed reactions; see (a) Notari, B. *Adv. in Cat*., **1996**, *41*, 253-334; (b) Tatsumi, T. *Curr. Opin. Solid St. M*., **1997**, *2*, 76-83.

13) (a) Corma, A.; Iglesias, M.; Sánchez, F. *Cat. Lett*. **1996**, *39*, 153-156; (b) Hulea, V.; Moreau, P.; Di Renzo, F. *J. Mol. Catal. A: Chem*. **1996**, *111*, 325-332; (c) Robinson, D. J.; Davies, L.; McGuire, N.; Lee, D. F.; McMorn, P.; Willock, D. J.; Watson, G. W.; Bulman Page, P. C.; Bethell, D.; Hutchings, G. J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1523-1529; (d) Moreau, P.; Hulea, V.; Gomez, S.; Brunel, D.; Renzo, F. D. *Appl. Catal. A: Gen*. **1997**, *155*, 253-263; (e) Hulea, V.; Fajula, F.; Bousquet, J. *J. Catal*. **2001**, *198*, 179-186.

14) Kon, Y.; Yokoi, T.; Yoshioka, M.; Uesaka, U.; Kujira, H.; Sato, K.; Tatsumi, T.

Tetrahedron Lett. **2013**, *54*, 4918-4921.

15) Fan, W.; Duan, R.-G.; Yokoi, T.; Wu, P.; Kubota, Y.; Tatsumi, T. *J. Am. Chem. Soc*. **2008**, *130*, 10150-10164

16) Wu, P.; Tatsumi, T.; Komatsu, T.; Yashima, T. *Chem. Lett*. **2000**, 774-775.

17) Wu, P.; Ruan, J.; Wang, L.; Wu, L.; Wang, Y.; Liu, Y.; Fan, W.; He, M.; Terasaki, O.; Tatsumi, T. *J. Am. Chem. Soc.* **2008**, *130*, 8178-8187.

18) (a) Wu, P.; Tatsumi, T. *J. Phys. Chem. B*, **2002**, *106*, 748-753; (b) Wu, P.; Tatsumi, T.; Komatsu, T.; Yashima, T.; *J. Catal*., **2001**, *202*, 245-255.

19) (a) Adam, W.; Golsch, D. *Chem. Ber*. **1994**, *127*, 1111–1113; (b) Adam, W.; Golsch, D.; Görth, F. C. *Chem. Eur. J.* **1996**, *2*, 255-258; (c) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc*. **1984**, *106*, 5020-5022; (d) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R.; Selvam, T.; Weichold, O. *J. Mol. Cat. A: Chem*. **2000**, *154*, 251-255.

20) Kamata, K.; Hirano, T.; Ishimoto, R.; Mizuno, N. *Dalton Trans*. **2010**, *39*, 5509-5518.

21) Ti-IEZ-MWW catalysts also showed a much higher conversion and specific activity than those of Ti-MWW in cyclohexene oxidation with H_2O_2: Wang, L.; Wang, Y.; Liu, Y.; Wu, H.; Li, X.; He, M.; Wu, P.; *J. Mater. Chem*. **2009**, *19*,

8594-8602.

22) Batigalhia, F.; Zaldini-Hernandes, M.; Fereira, A. G.; Malvestiti, I.; Cass, Q. B. *Tetrahedron* **2001**, *57,* 9669-9676.

23) Moorthy, J. N.; Scnapati, K.; Parida, K. N. *J. Org. Chem.* **2010**, *75*, 8416–8421.

24) Furukawa, N.; Ogawa, S.; Kawai, T.; Oae S. *J. Chem. Soc.*, *Perkin Trans. 1* **1984**, 1839–1845.

25) Kropp, P. J.; Breton, G. W.; Fields, J. D.; Tung, J. C.; Loomis, B. R. *J. Am. Chem. Soc.* **2000**, 122, 4280–4285.

26) Llamas, T.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2007**, 46, 3329–3332.

27) Boruah, J. J.; Das, S. P.; Ankireddy, S. R.; Gogoi, S. R.; Islam, N. S. *Green Chem.* **2013**, 15, 2944–2959.

28) Fukuda, N.; Ikemoto, T. *J. Org. Chem.* **2010**, *75*, 4629–4631.

29) Raju, B. R.; Sarkar, S.; Reddy, U. C.; Saikia, A. K. *J. Mol. Catal. A: Chem.* **2009**, *308*, 169–173.

30) Latassa, D.; Enger, O.; Thilgen, C.; Habicher, T.; Offermanns, H.; Diederich, F. *J. Mater. Chem.* **2002**, *12*, 1993–1995.

31) Yu, B.; Liu, A.-H.; He, L.-N.; Li, B.; Diao, Z.-F.; Li, Y.-N. *Green Chem.* **2012**,

14, 957–962.

32) Katritzky, A. R.; Takahashi, I.; Marson, C. M. *J. Org. Chem.* **1986**, 51, 4914–4920.

Supporting Information

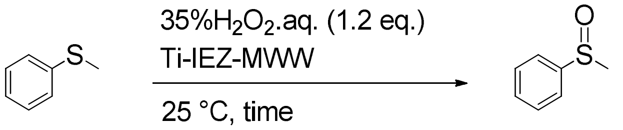
Selective hydrogen peroxide oxidation of sulfides to sulfoxides or sulfones with MWW-type titanosilicate zeolite catalyst under organic solvent-free conditions

Yoshihiro Kon, Toshiyuki Yokoi, Masato Yoshioka, Shinji Tanaka, Yumiko Uesaka,

Takehisa Mochizuki, Kazuhiko Sato , Takashi Tatsumi**

Contents

1. Oxidation of thioanisole using Ti-IEZ-MWW[a]



Reaction time (min.)	15	30	60	120
Conversion (%)	69	90	>99	>99
Yield of methyl phenyl sulfoxide (%)[b]	66	86	94	94
Yield of methyl phenyl sulfone (%)[b]	3	4	6	6

[a] Reaction conditions: thioanisole (1.0 mmol), 35% H_2O_2 (1.2 mmol), Ti-IEZ-MWW (10 mg), 25 °C, 1000 rpm.

[b] Yield and conversion on the basis of thioanisole, determined by GC analysis with biphenyl as an internal standard.

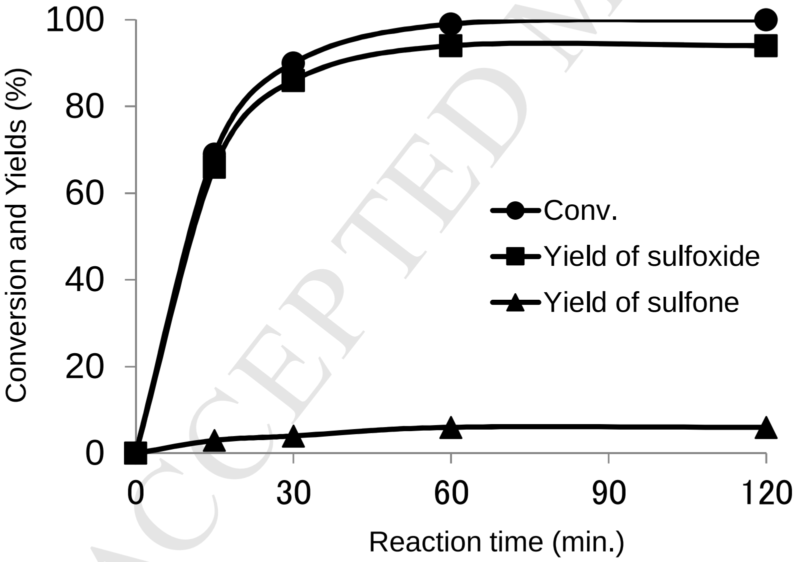
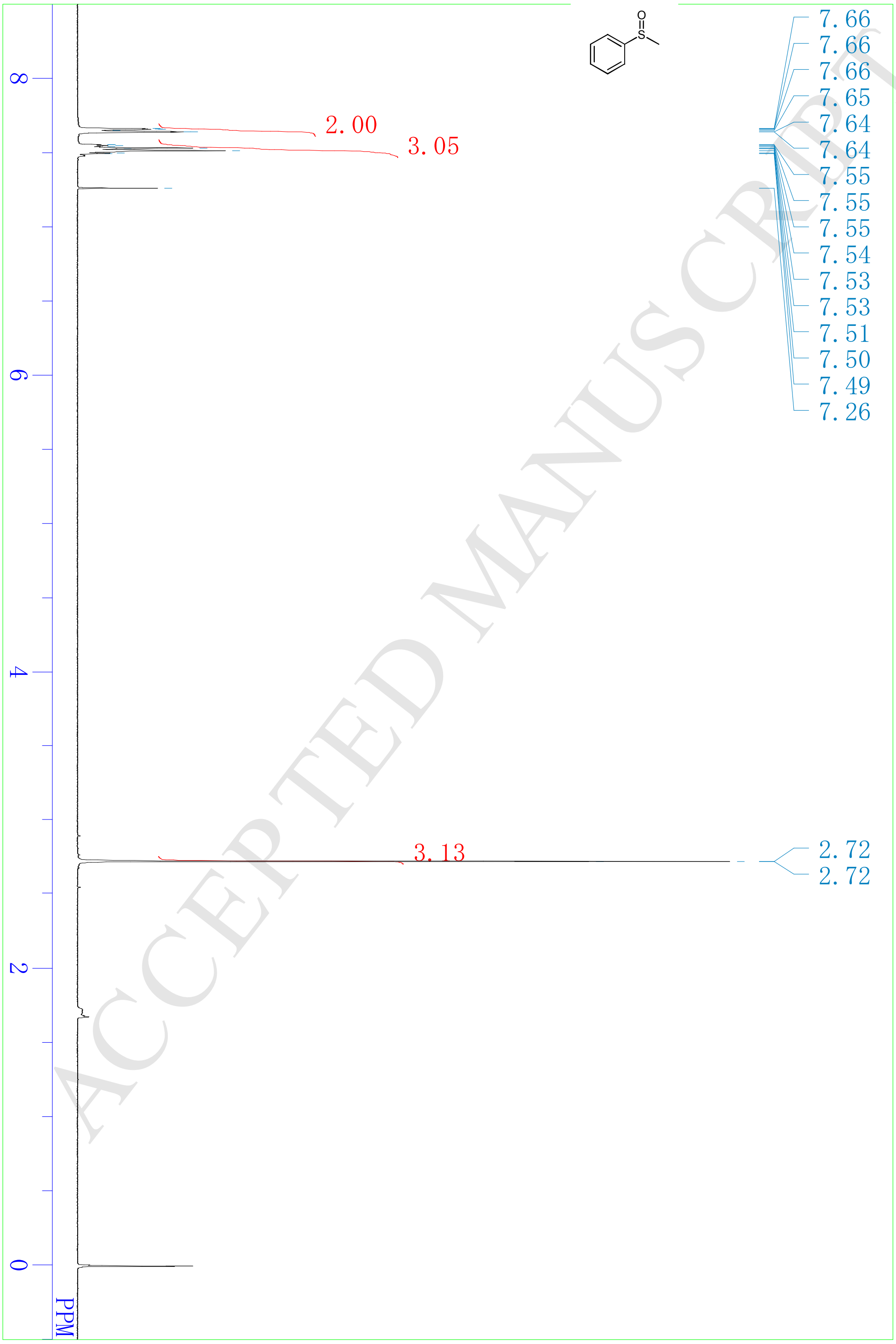


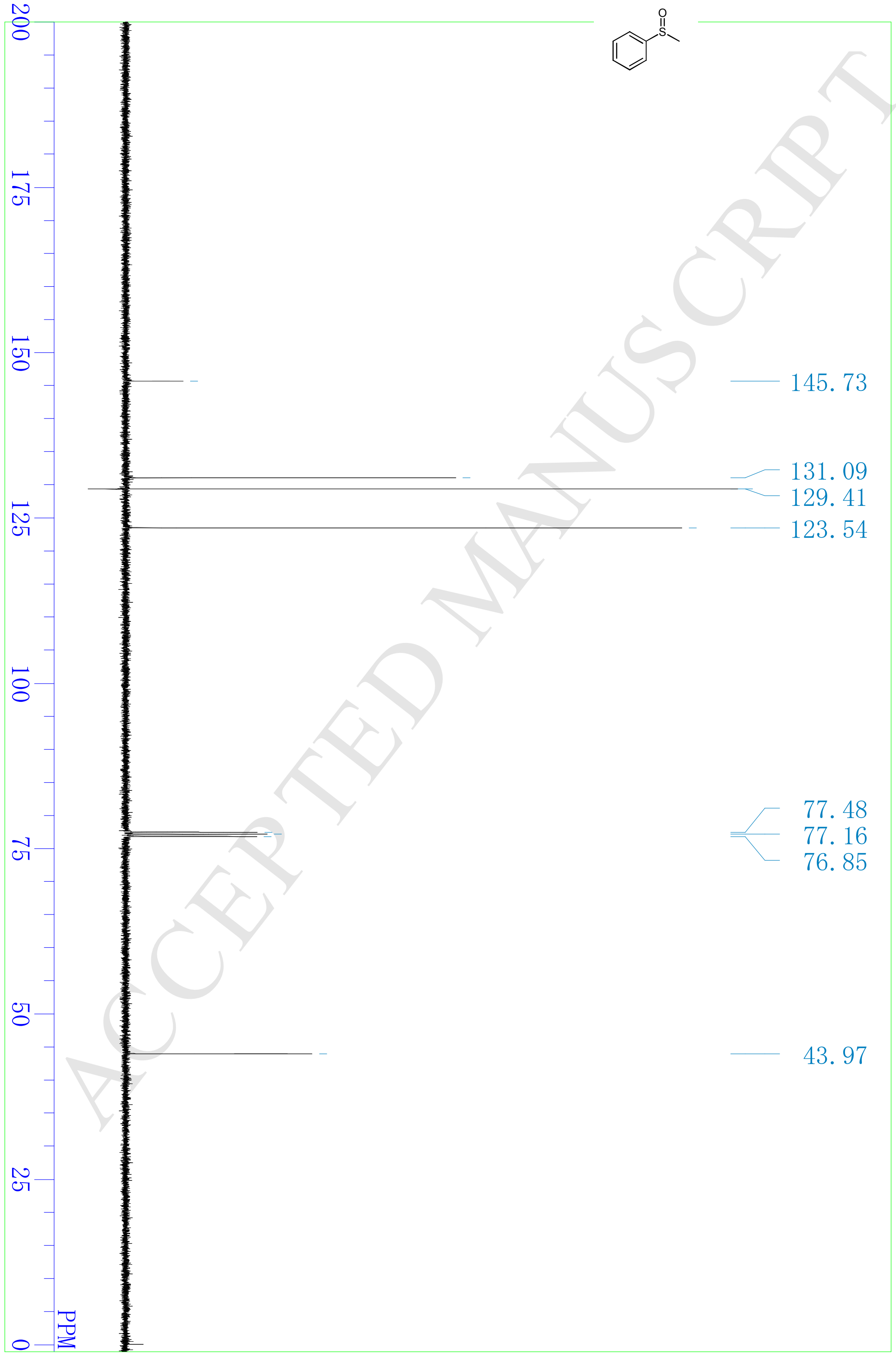
Figure S1. Oxidation of thioanisole using Ti-IEZ-MWW. Conversion (●), yield of methyl phenyl sulfoxide (■), yield of methyl phenyl sulfone (▲). Reaction conditions: thioanisole (1.0 mmol), 35% H_2O_2 (1.2 mmol), Ti-IEZ-MWW (10 mg), 25 °C, 1000 rpm.

2. ^{1}H and ^{13}C NMR Spectra:

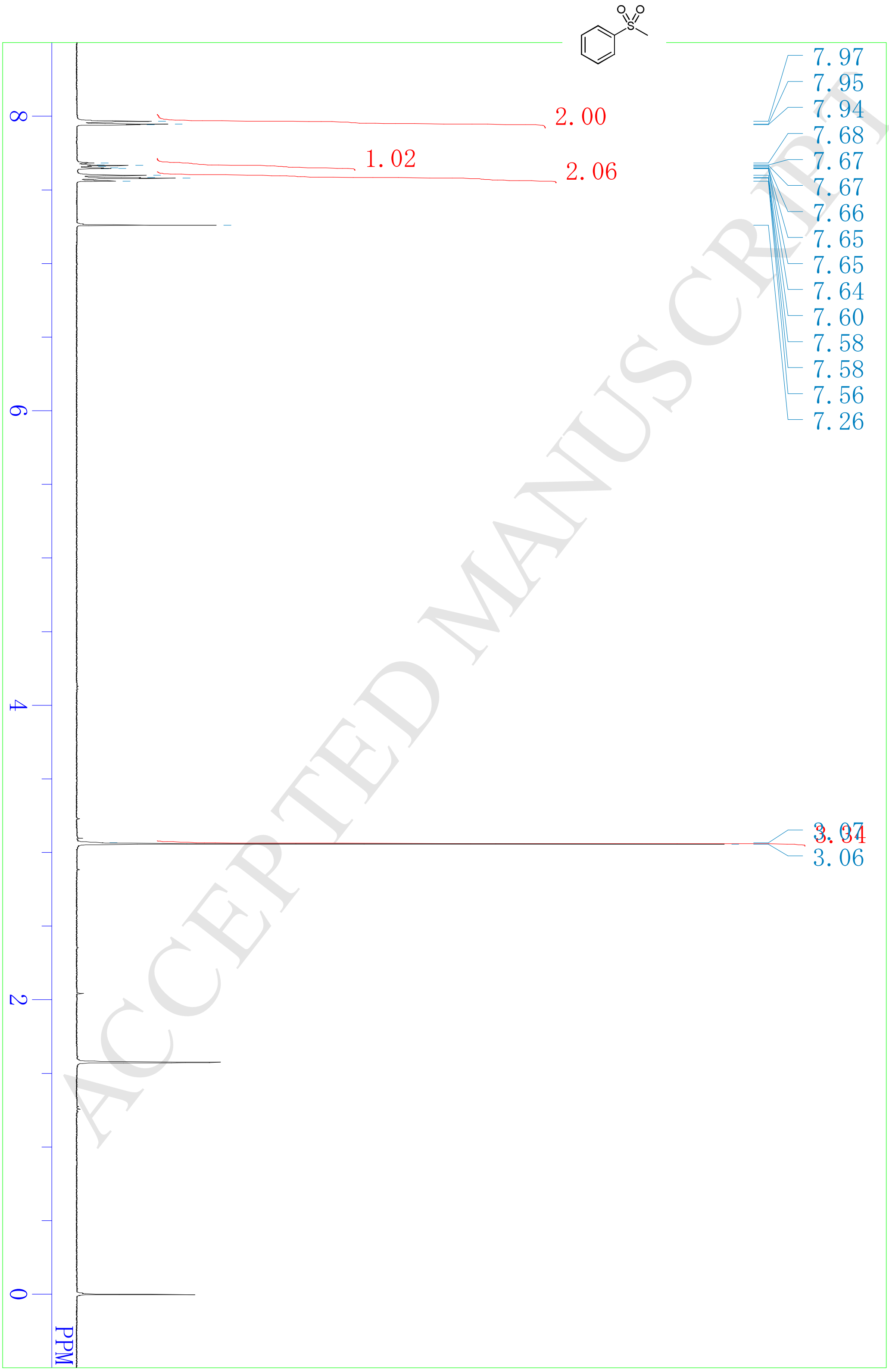
Methyl Phenyl Sulfoxide ^{1}H NMR (400MHz, $CDCl_3$)[1]



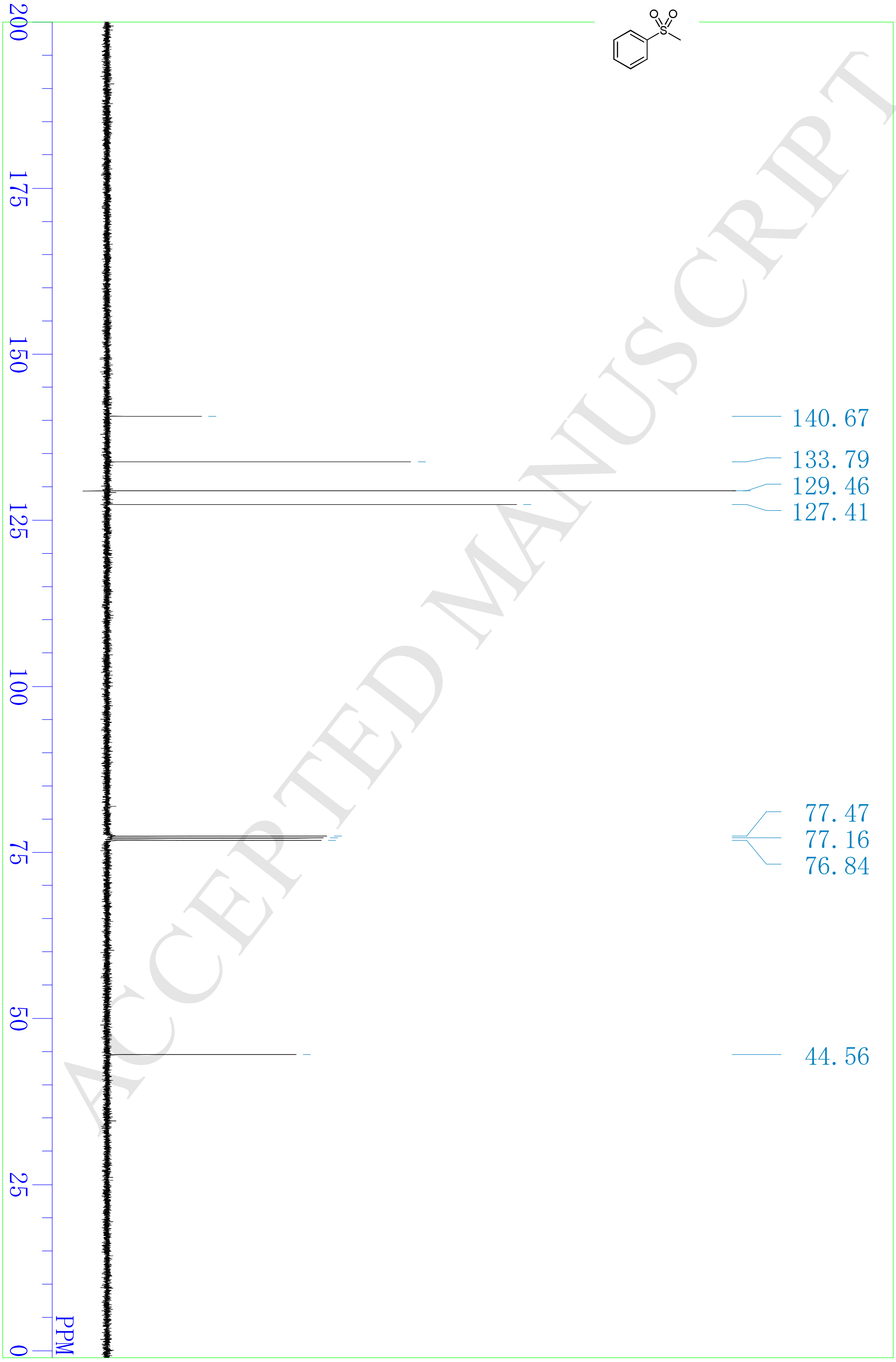
Methyl Phenyl Sulfoxide ^{13}C NMR (100MHz, CDCl$_3$) [1]



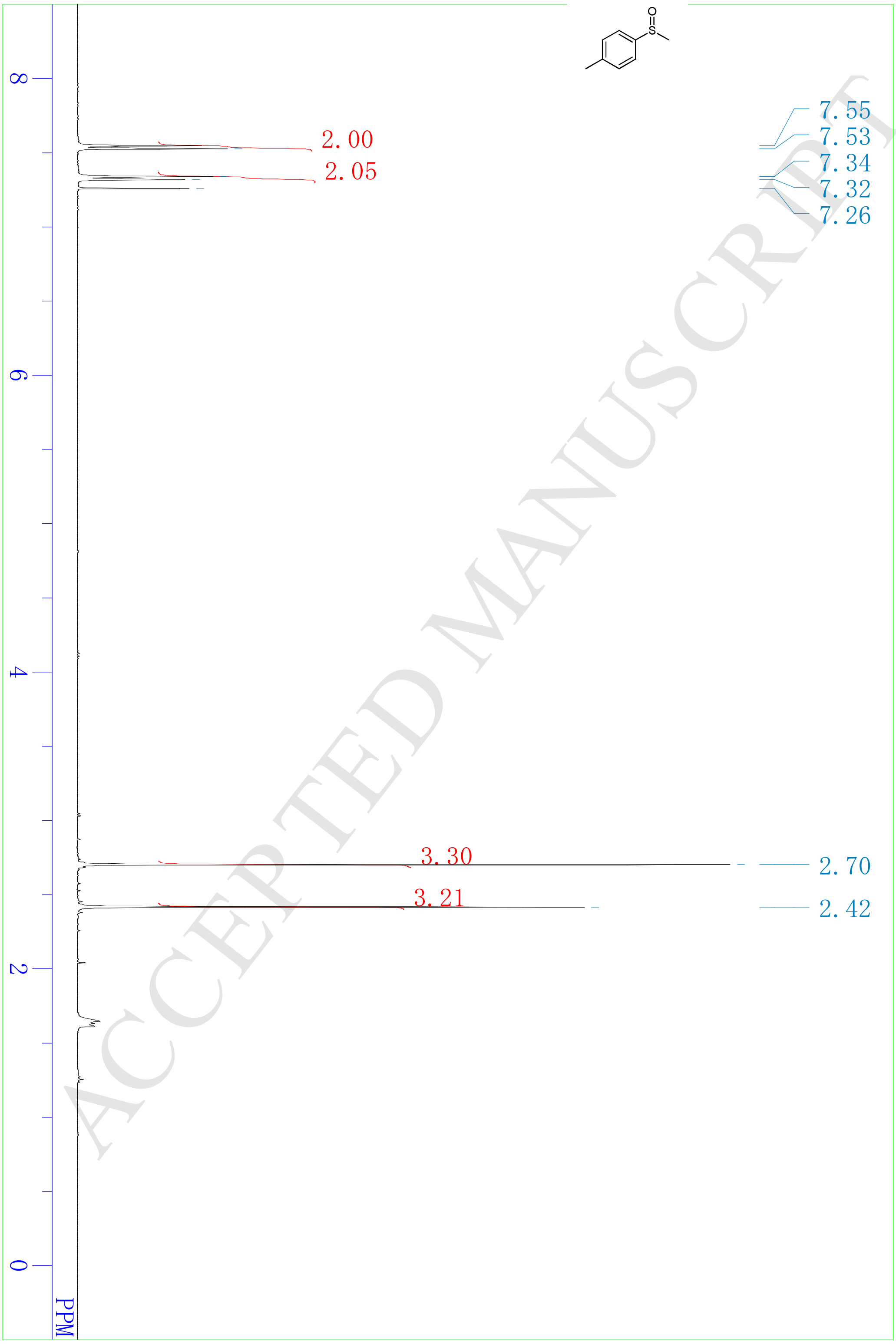
Methyl Phenyl Sulfone ^{1}H NMR (400MHz, $CDCl_3$)[2]



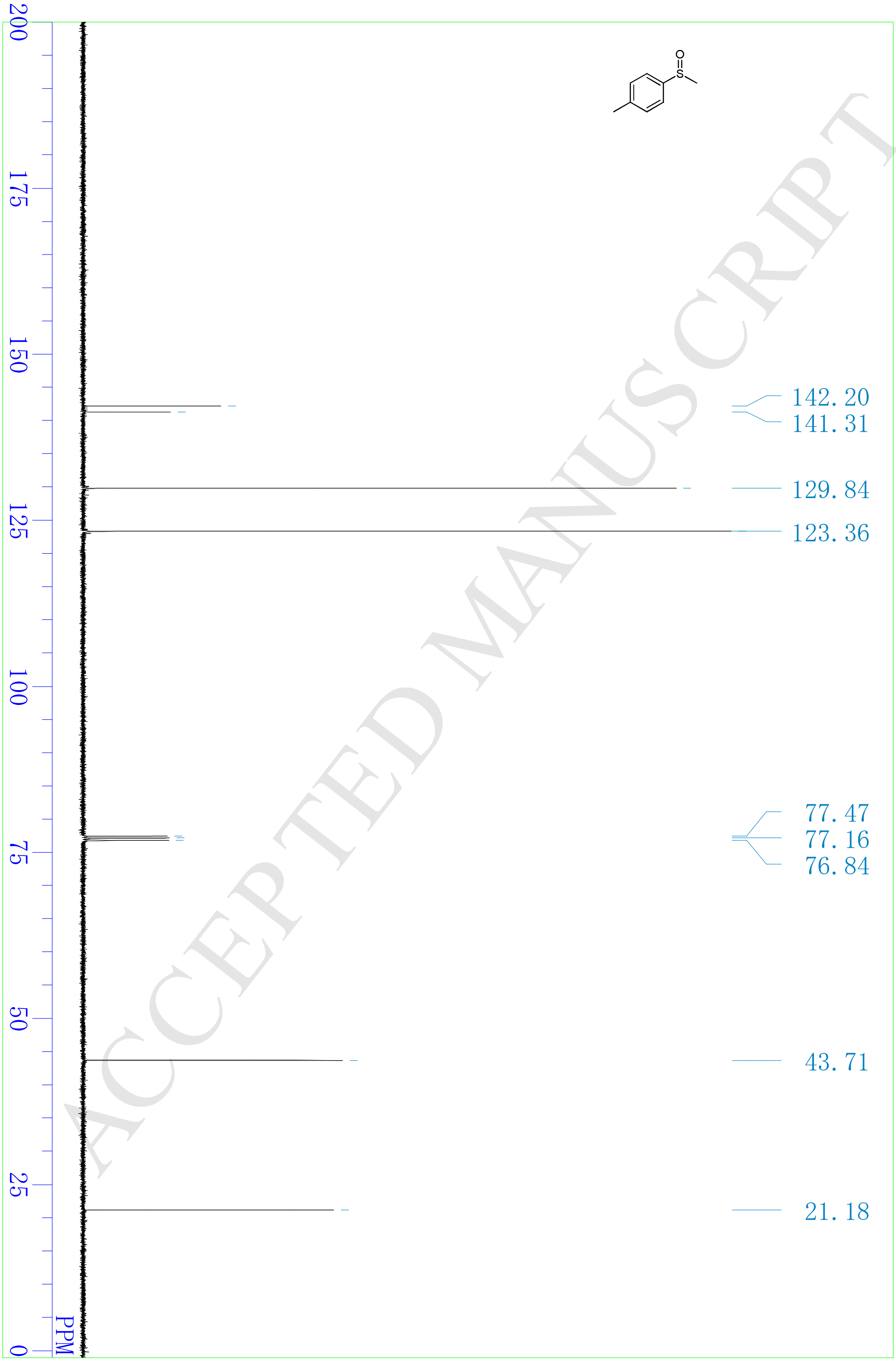
Methyl Phenyl Sulfone ^{13}C NMR (100MHz, $CDCl_3$)^{2}



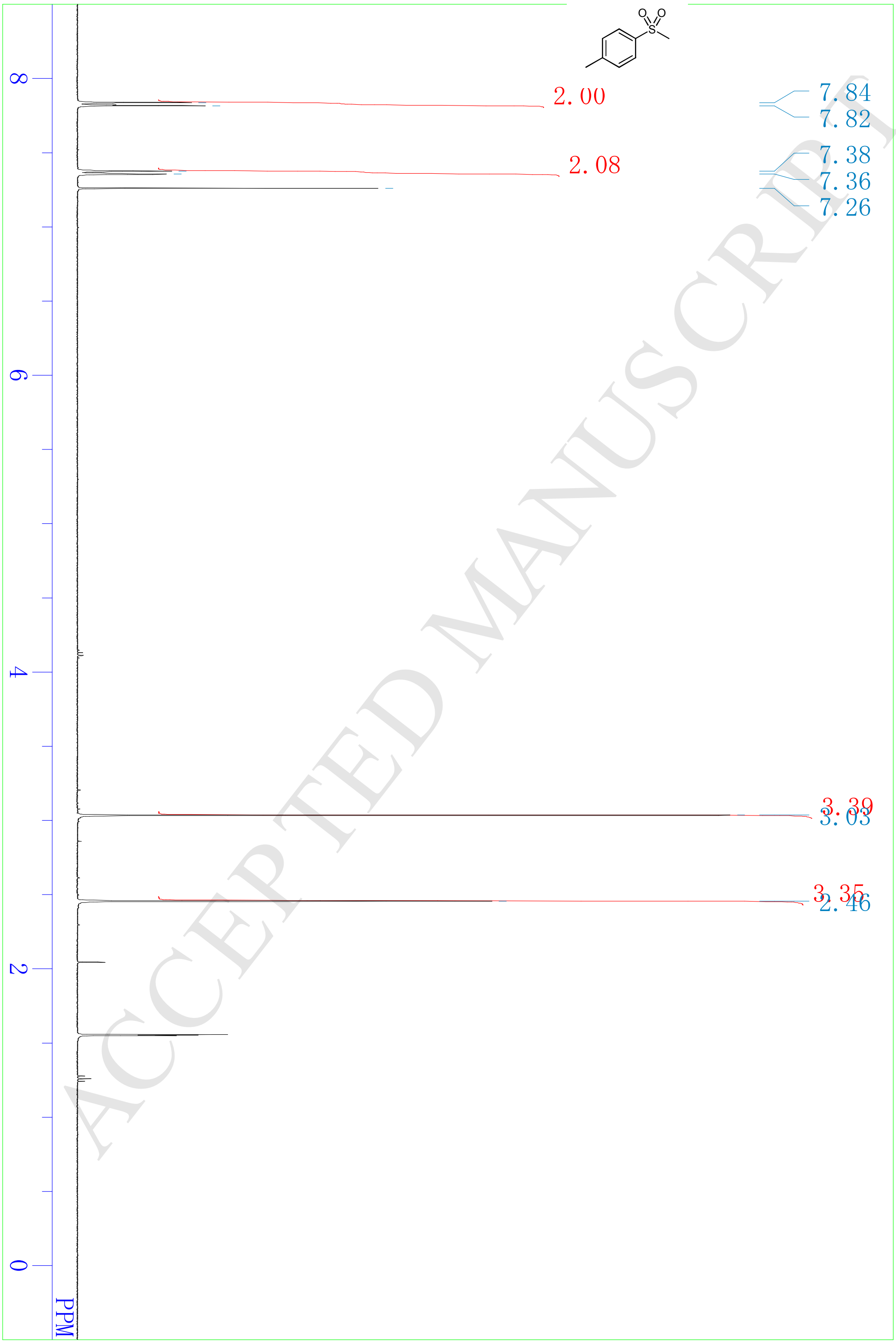
Methyl *p*-Tolyl Sulfoxide ^{1}H NMR (400MHz, $CDCl_3$)[3]



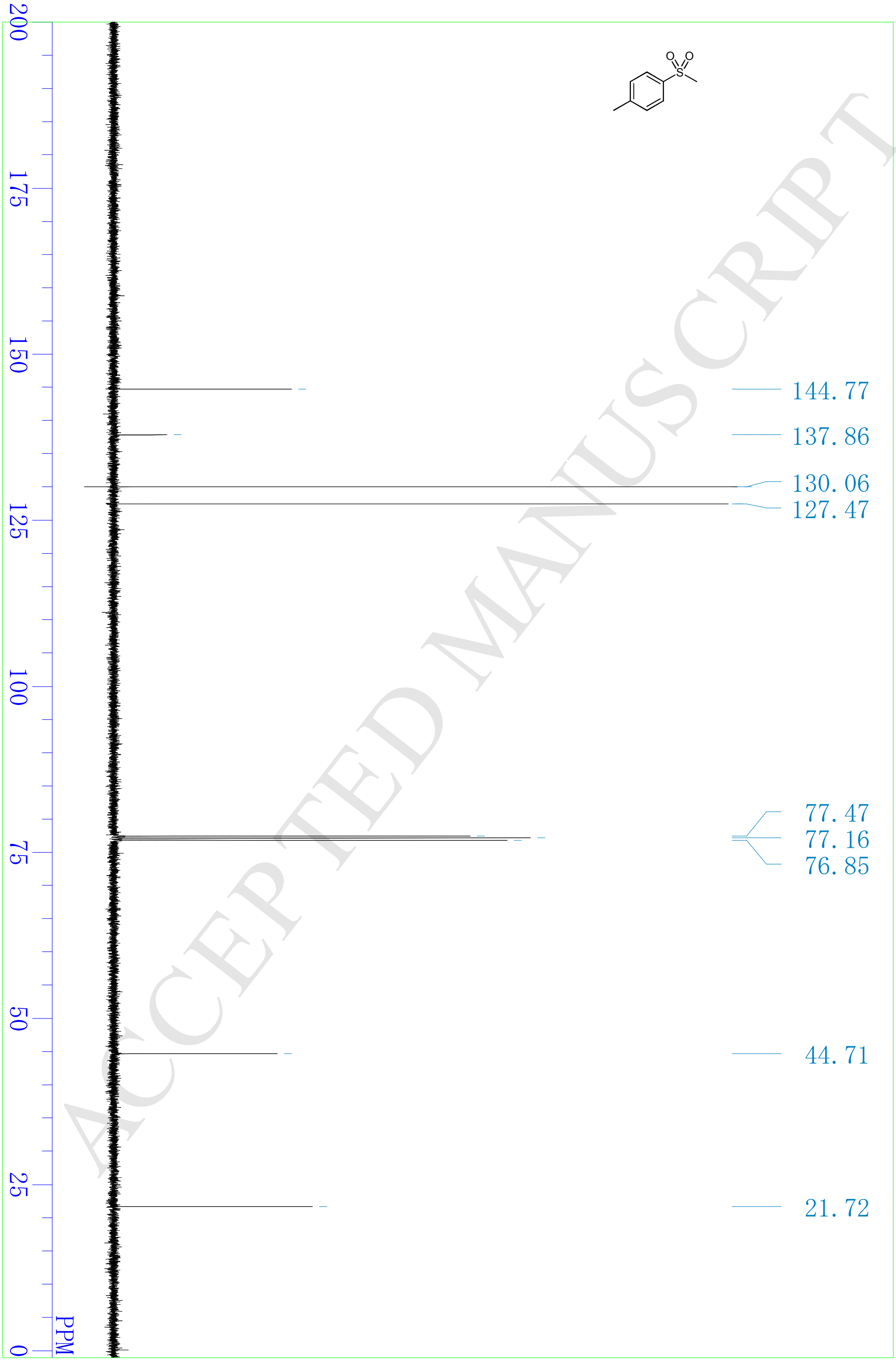
Methyl *p*-Tolyl Sulfoxide ^{13}C NMR (100MHz, CDCl$_3$)^{3}



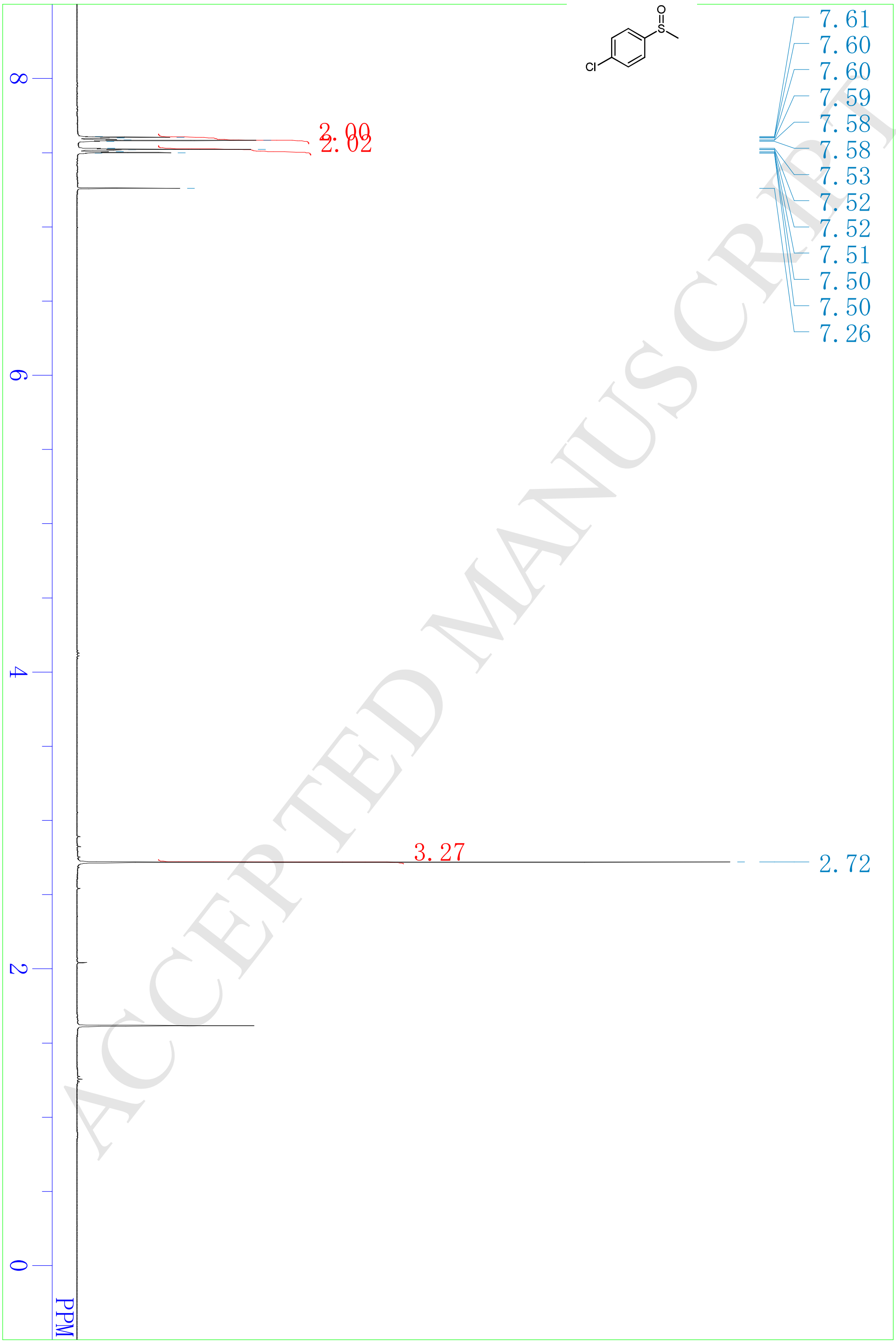
Methyl *p*-Tolyl Sulfone ^{1}H NMR (400MHz, CDCl$_3$)^2



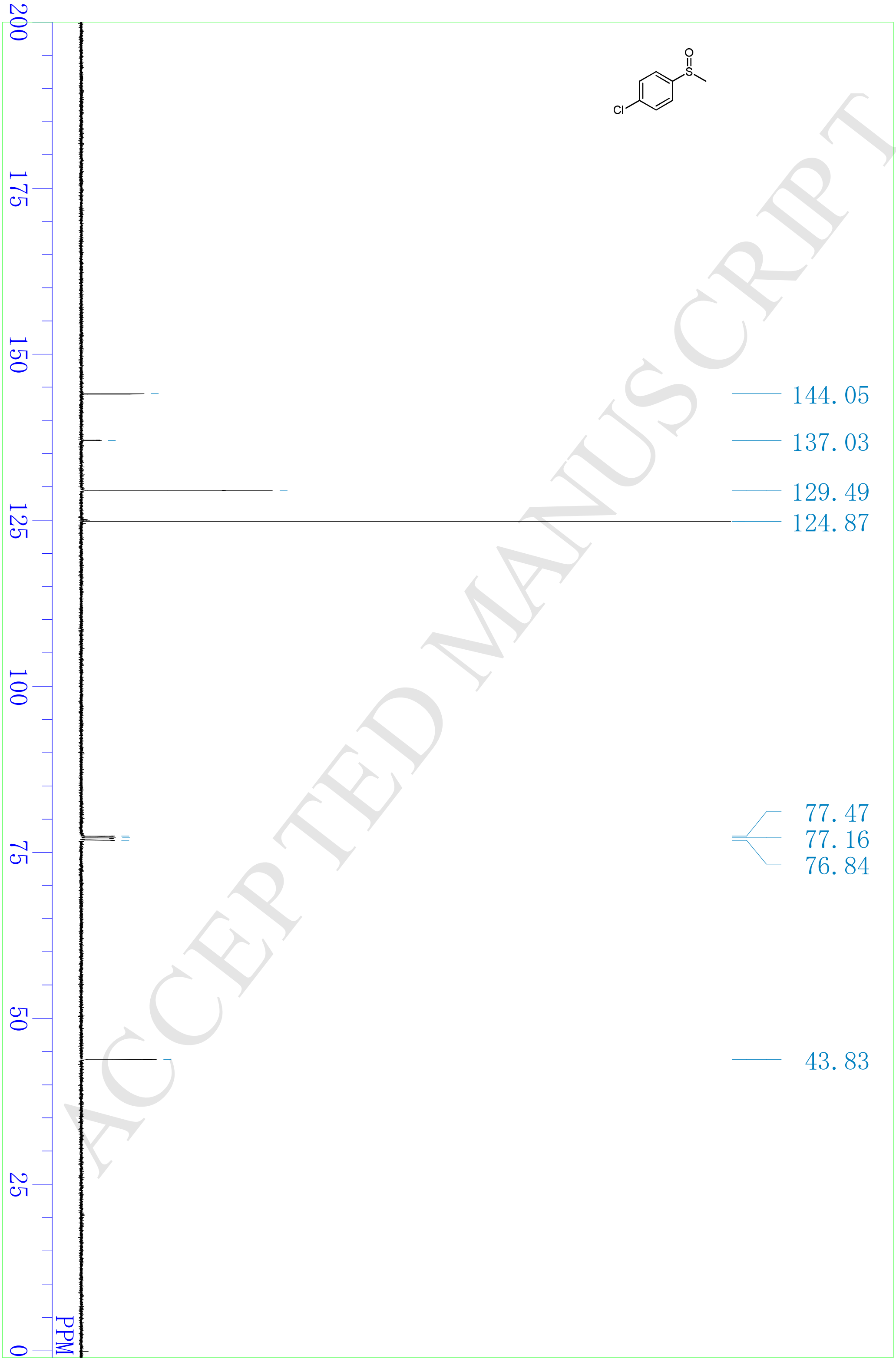
Methyl *p*-Tolyl Sulfone ^{13}C NMR (100MHz, $CDCl_3$)[2]



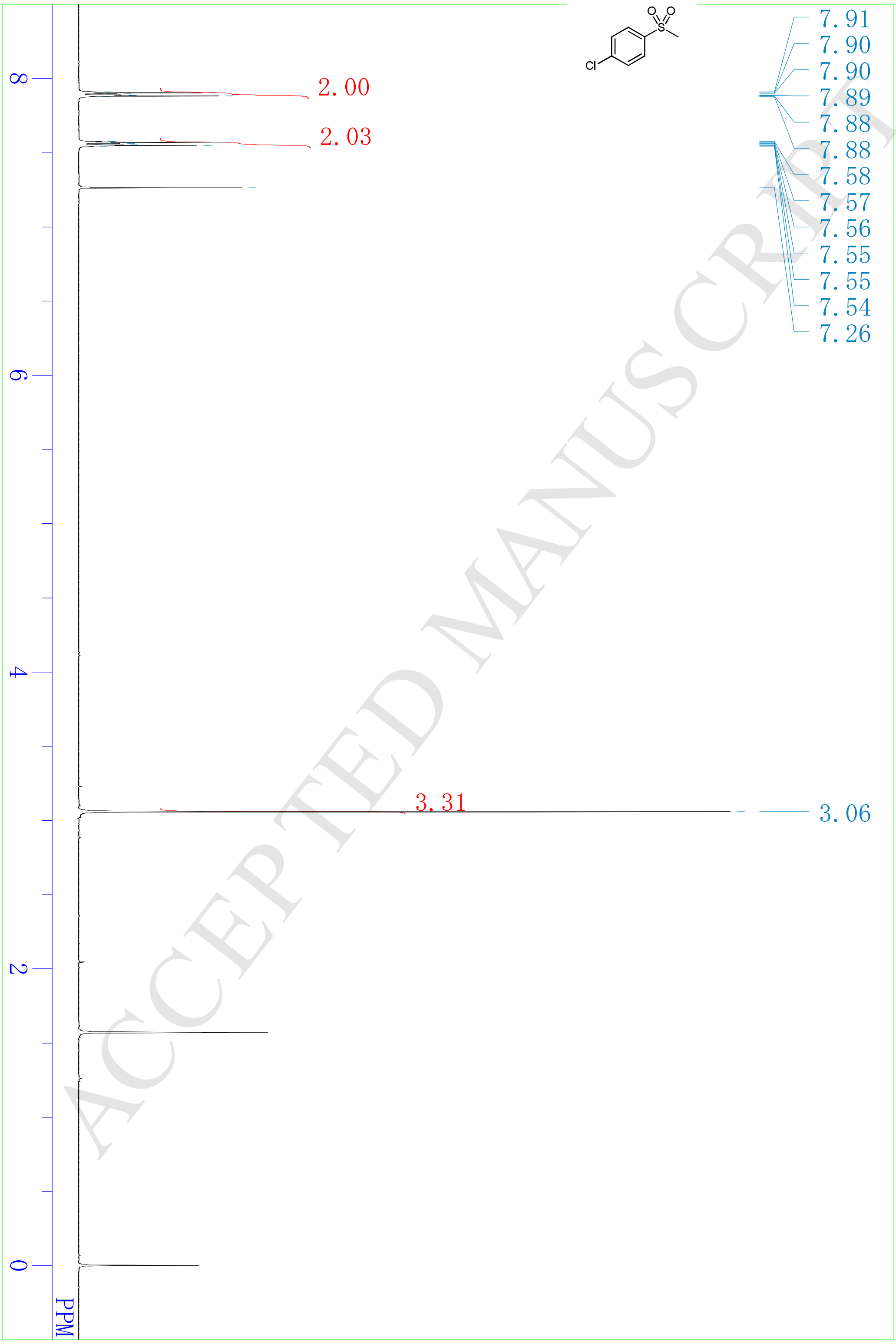
***p*-Chlorophenyl Methyl Sulfoxide** ^{1}H NMR (400MHz, $CDCl_3$)[3]



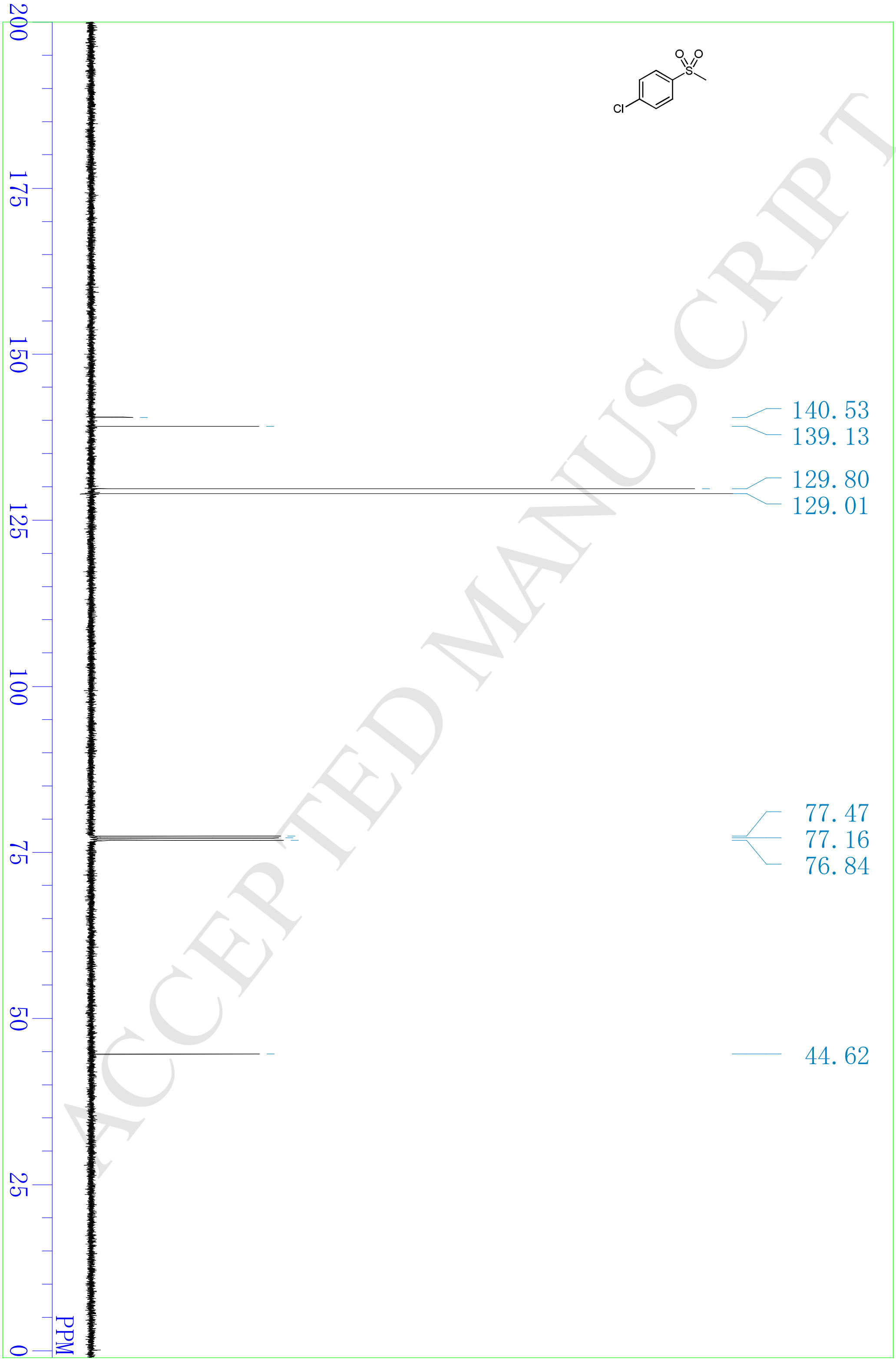
***p*-Chlorophenyl Methyl Sulfoxide** ^{13}C NMR (100MHz, CDCl$_3$) [3]



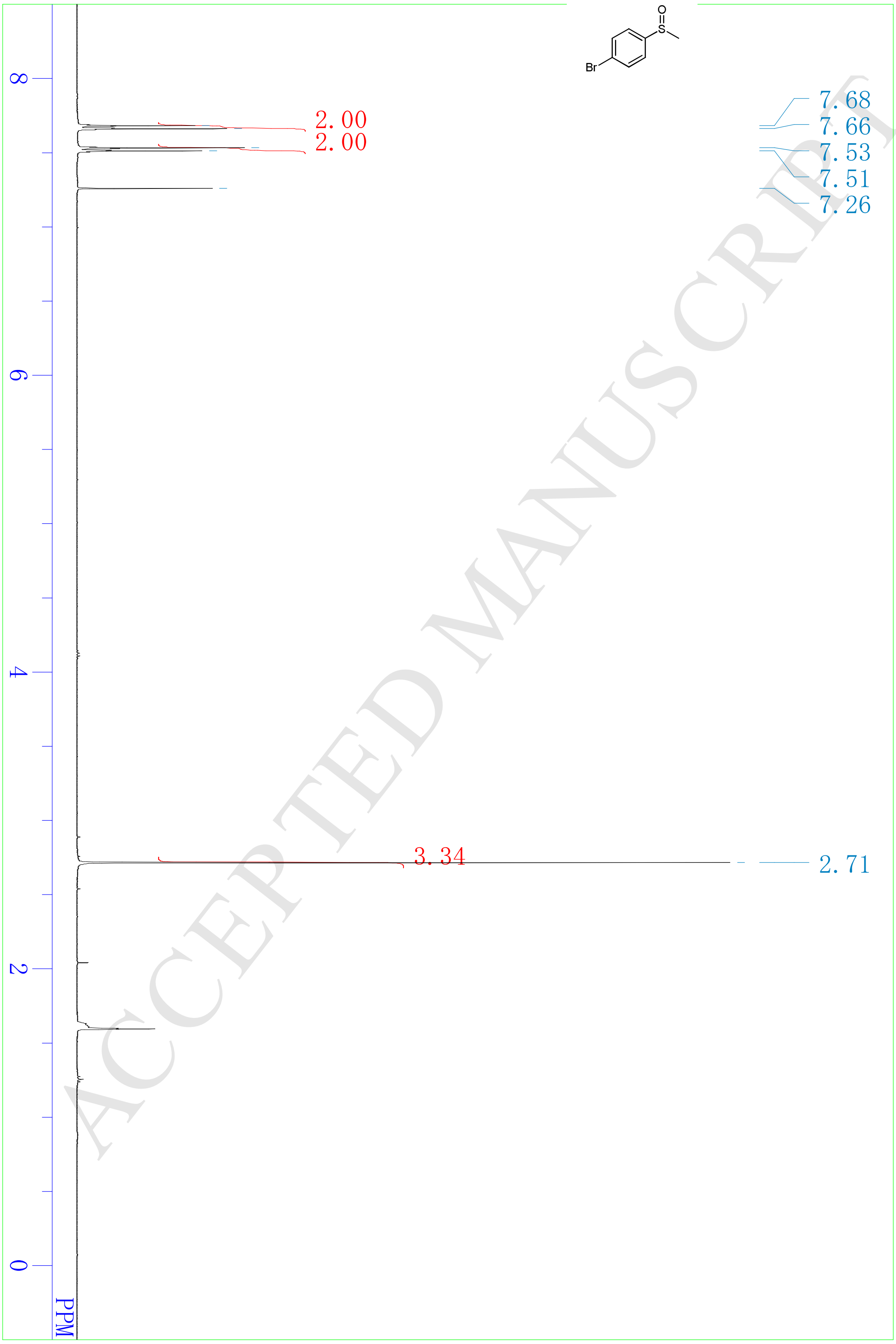
***p*-Chlorophenyl Methyl Sulfone** ^{1}H NMR (400MHz, $CDCl_3$)[2]



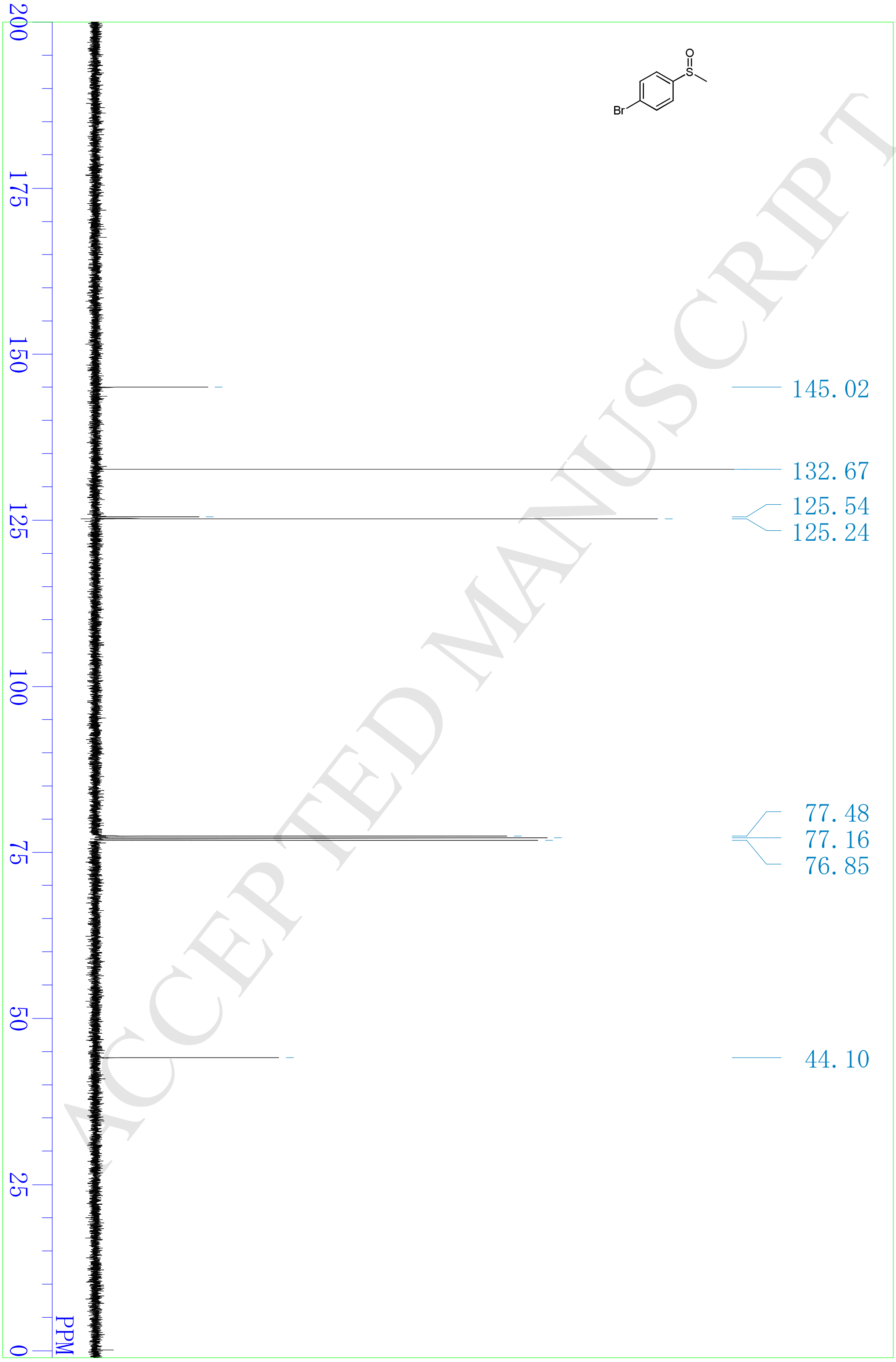
p-Chlorophenyl Methyl Sulfone ^{13}C NMR (100MHz, $CDCl_3$)[2]



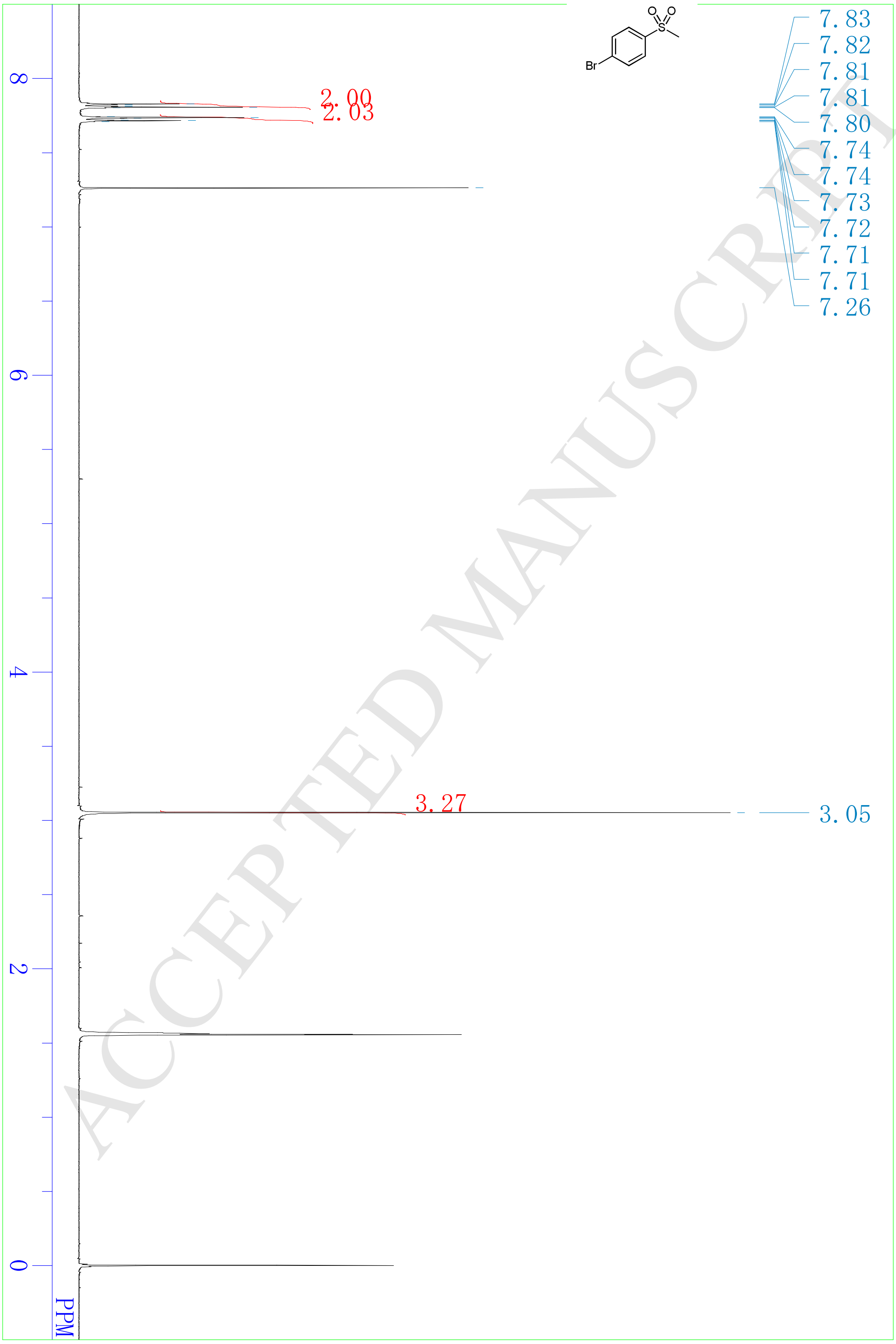
p-Bromophenyl Methyl Sulfoxide ^{1}H NMR (400MHz, $CDCl_3$)[4]



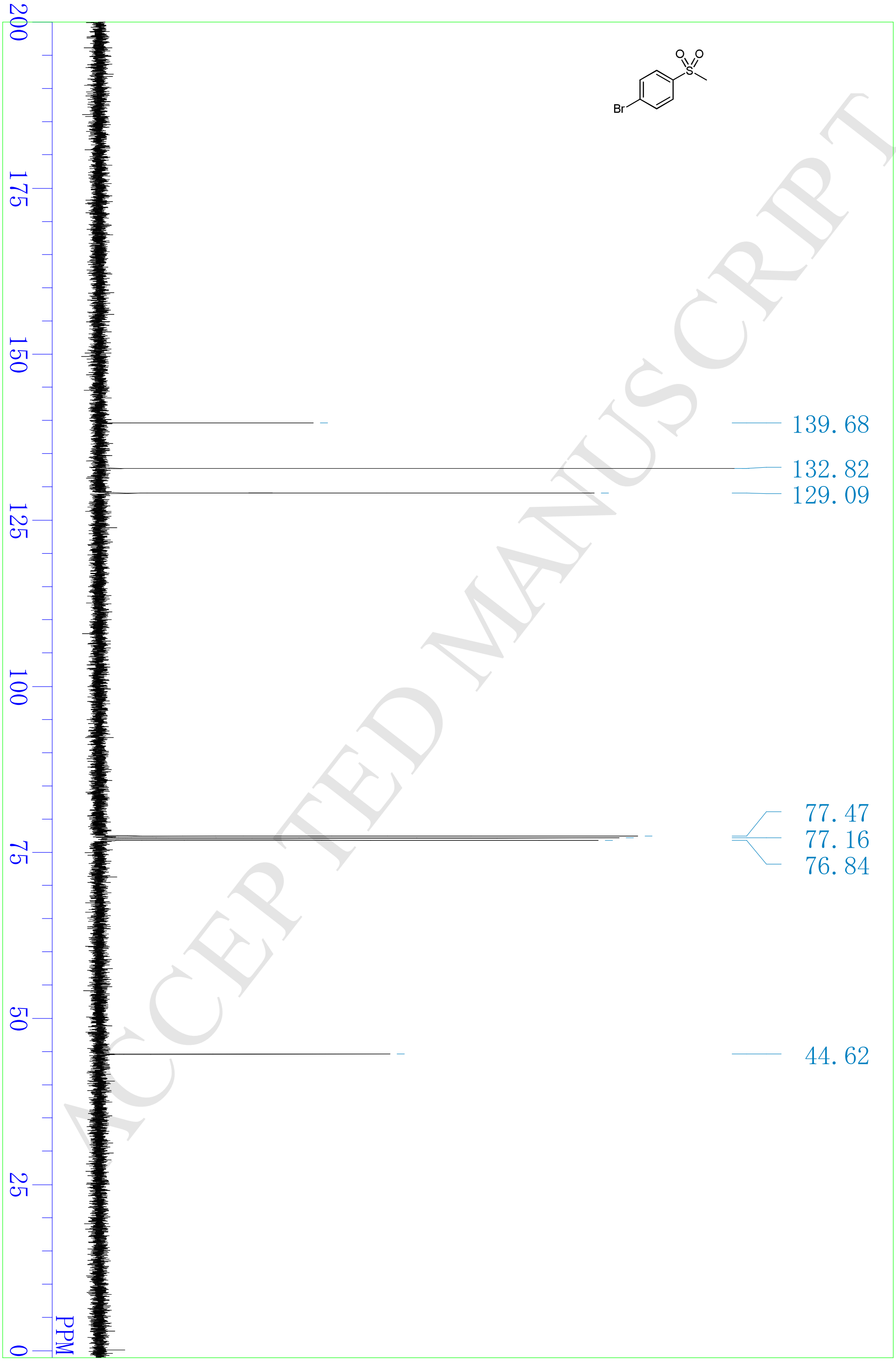
p-Bromophenyl Methyl Sulfoxide ^{13}C NMR (100MHz, $CDCl_3$)[4]



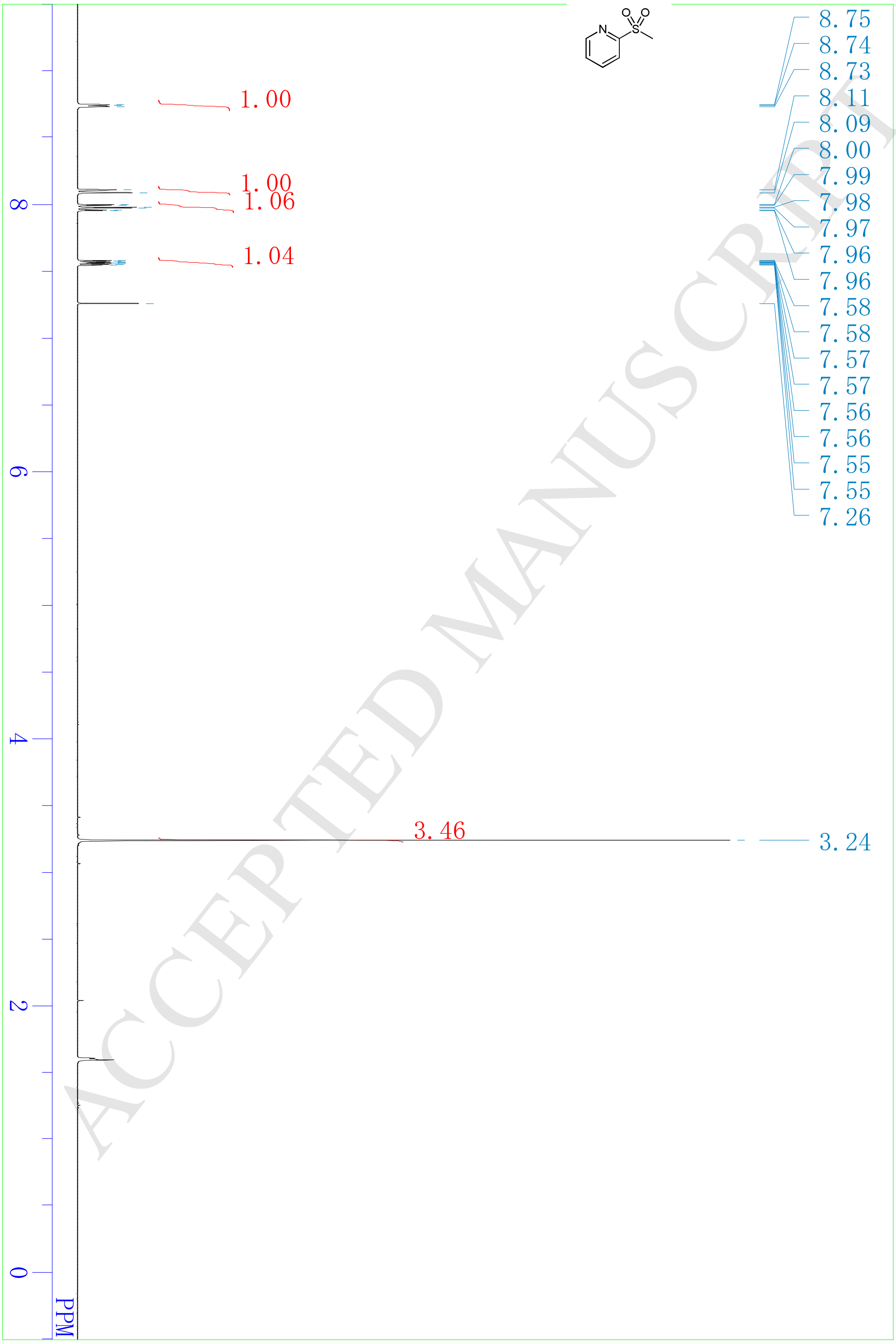
p-Bromophenyl Methyl Sulfone ^{1}H NMR (400MHz, $CDCl_3$)[5]



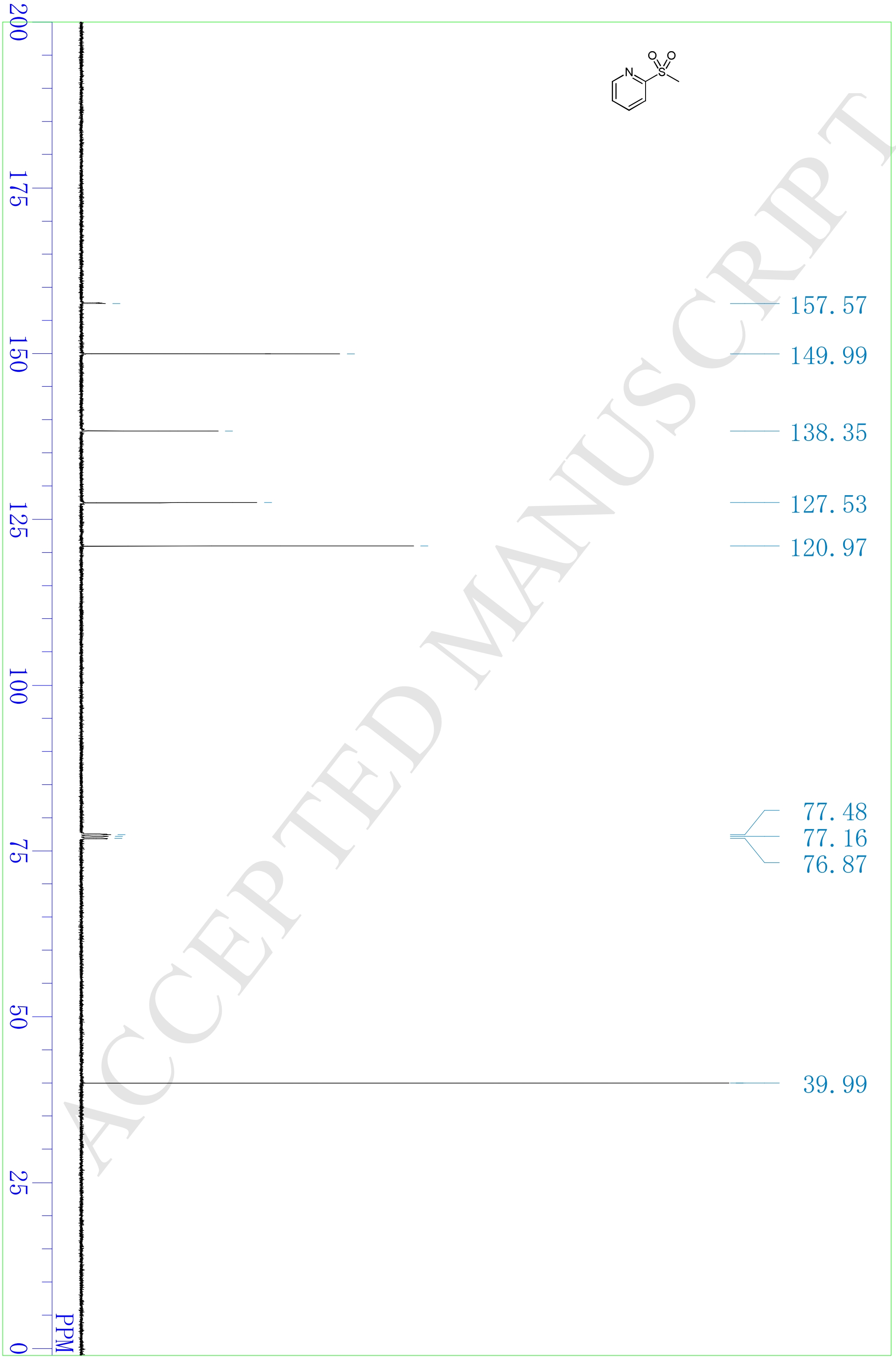
p-Bromophenyl Methyl Sulfone ^{13}C NMR (100MHz, CDCl$_3$) [5]



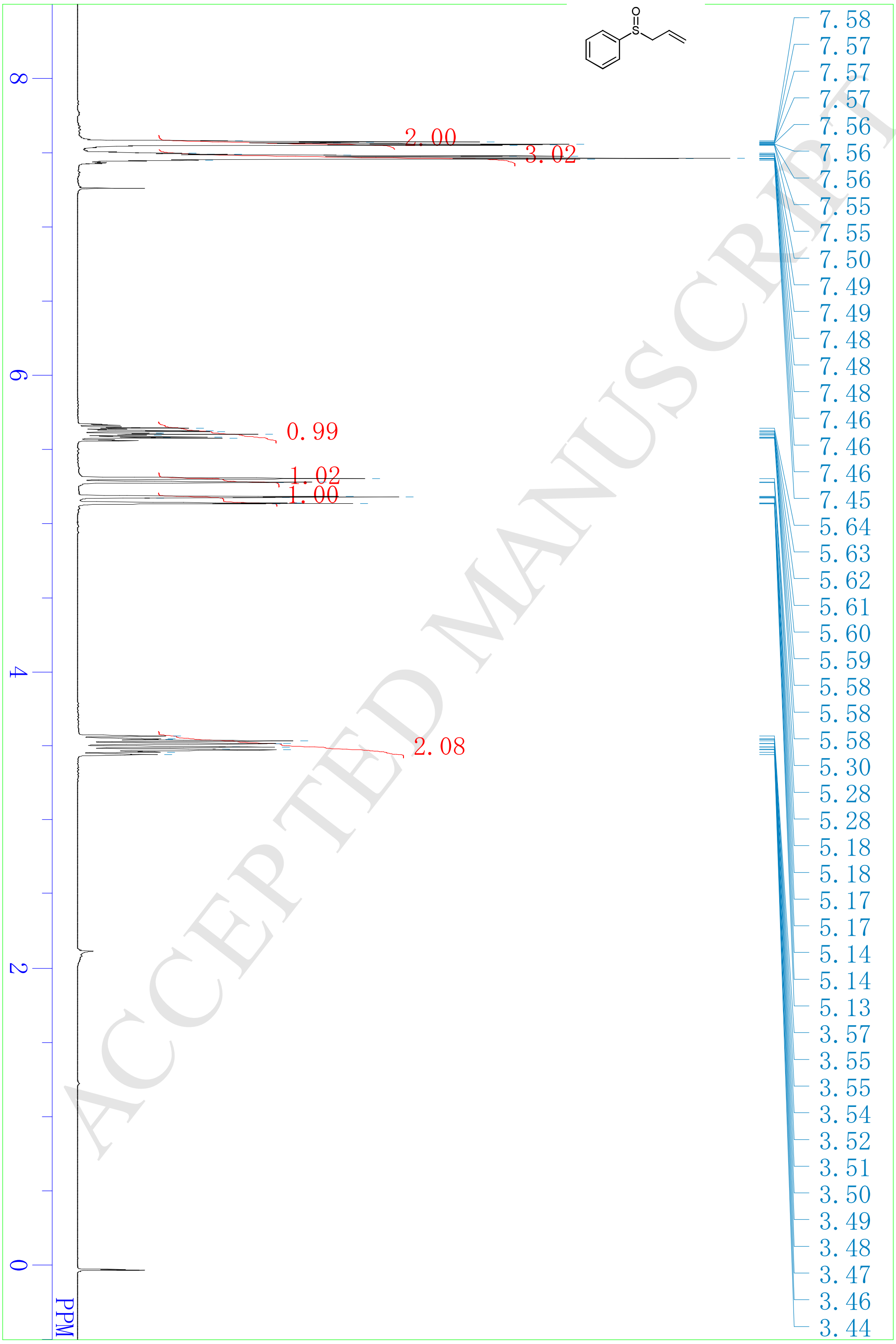
2-Methyl Sulfonyl Pyridine ^{1}H NMR (400MHz, $CDCl_3$)[6]



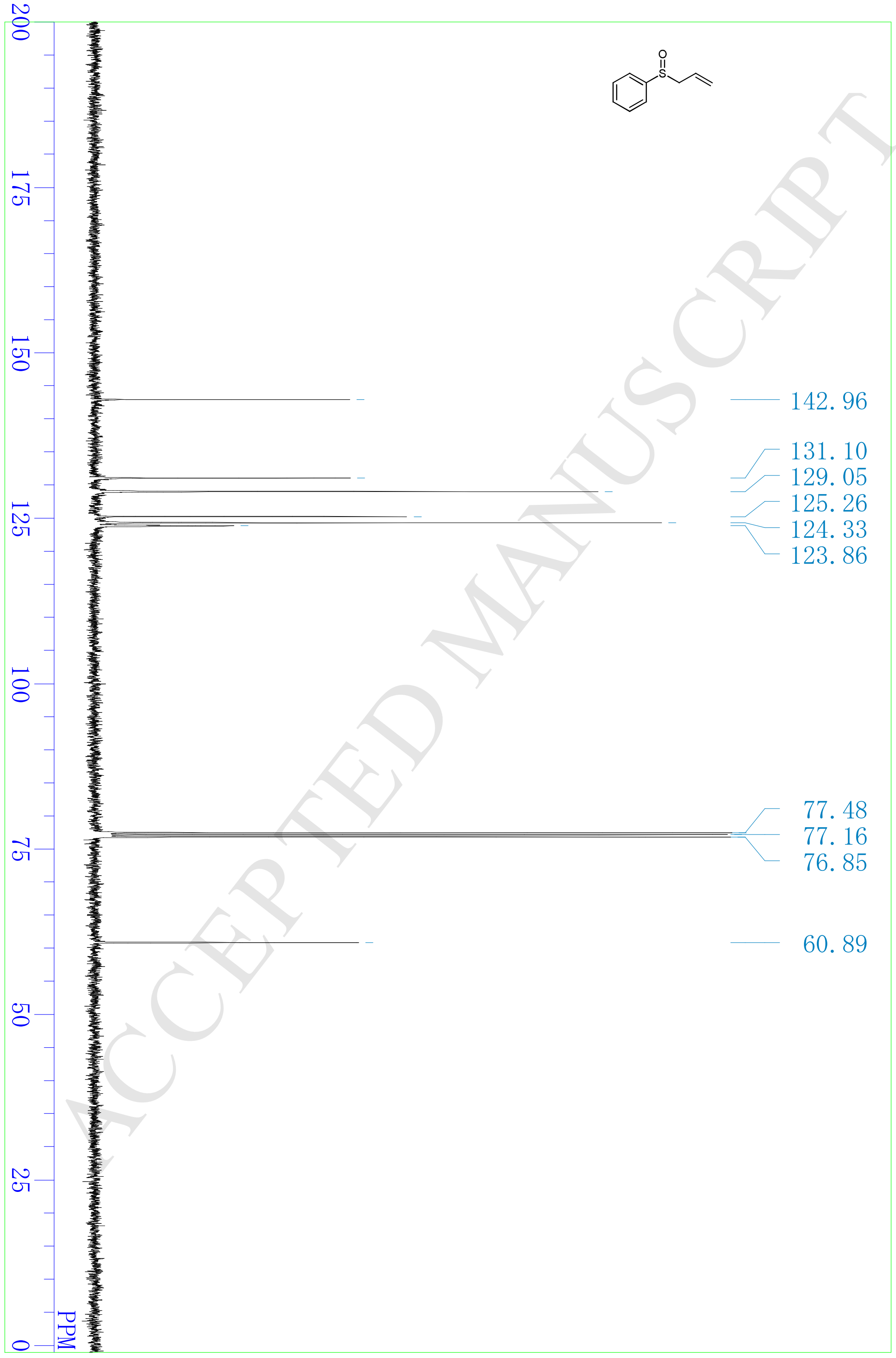
2-Methyl Sulfonyl Pyridine ^{13}C NMR (100MHz, $CDCl_3$) [6]



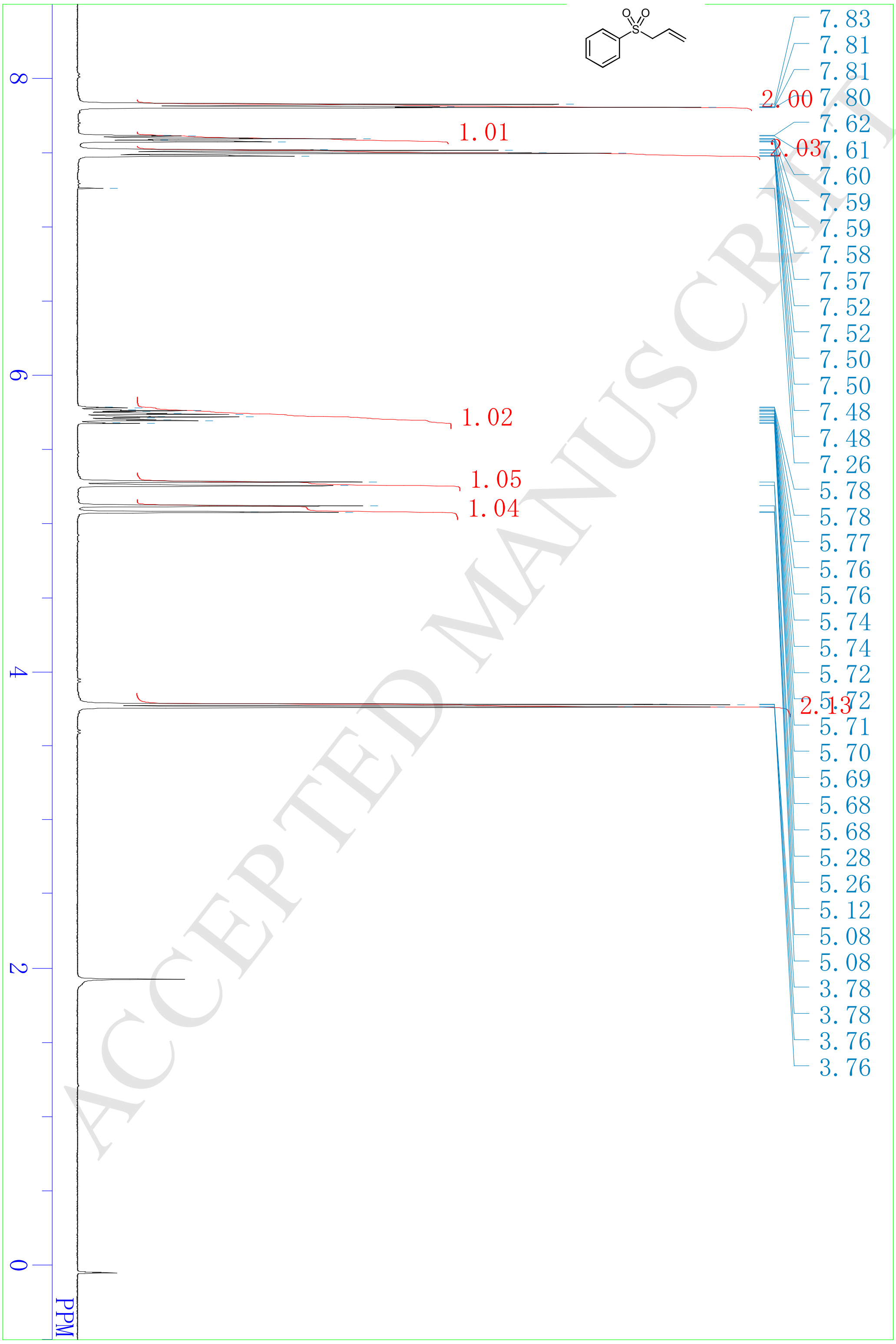
Allyl Phenyl Sulfoxide ^{1}H NMR (400MHz, $CDCl_3$)[7]



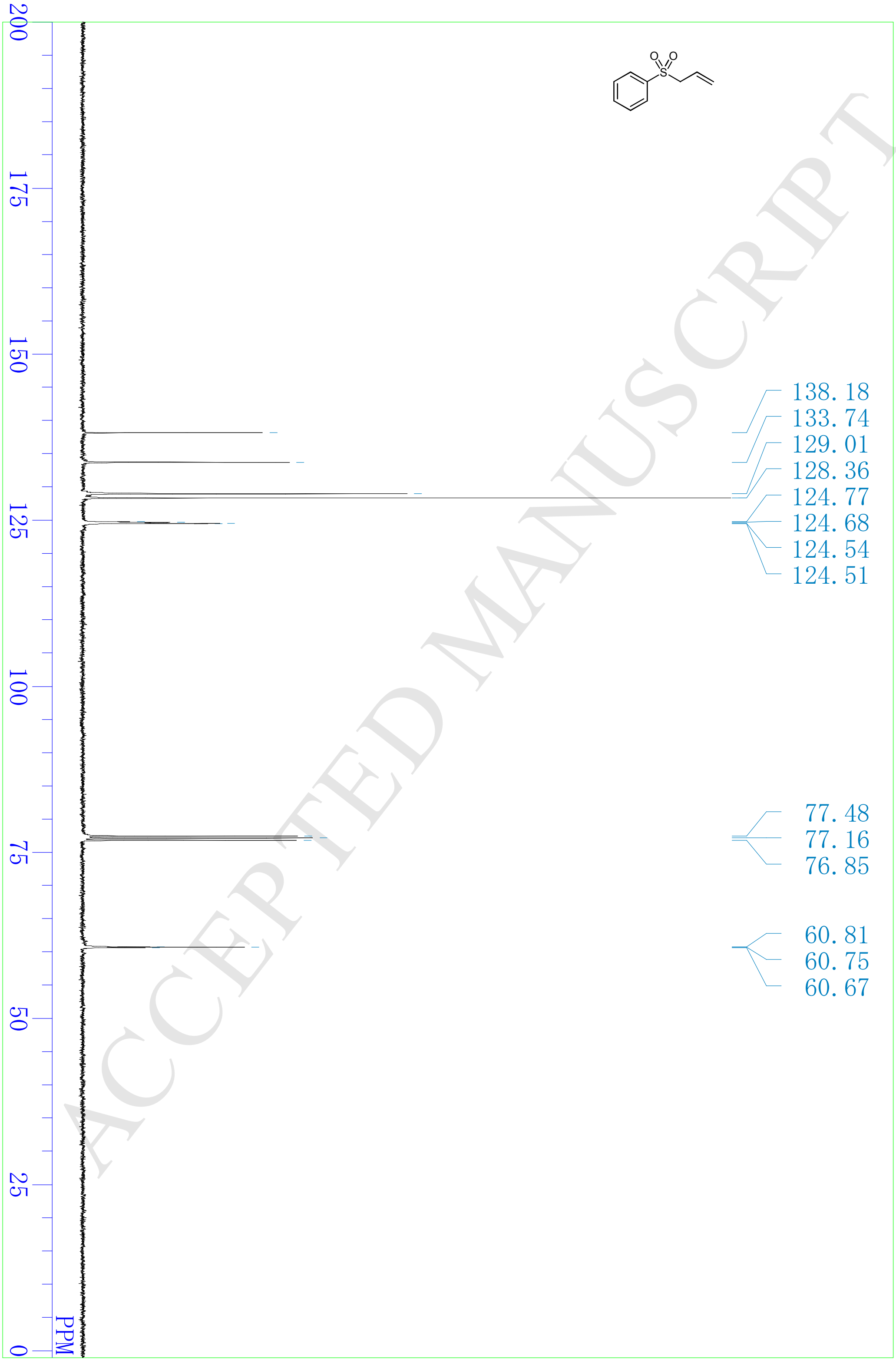
Allyl Phenyl Sulfoxide ^{13}C NMR (100MHz, CDCl$_3$) [7]



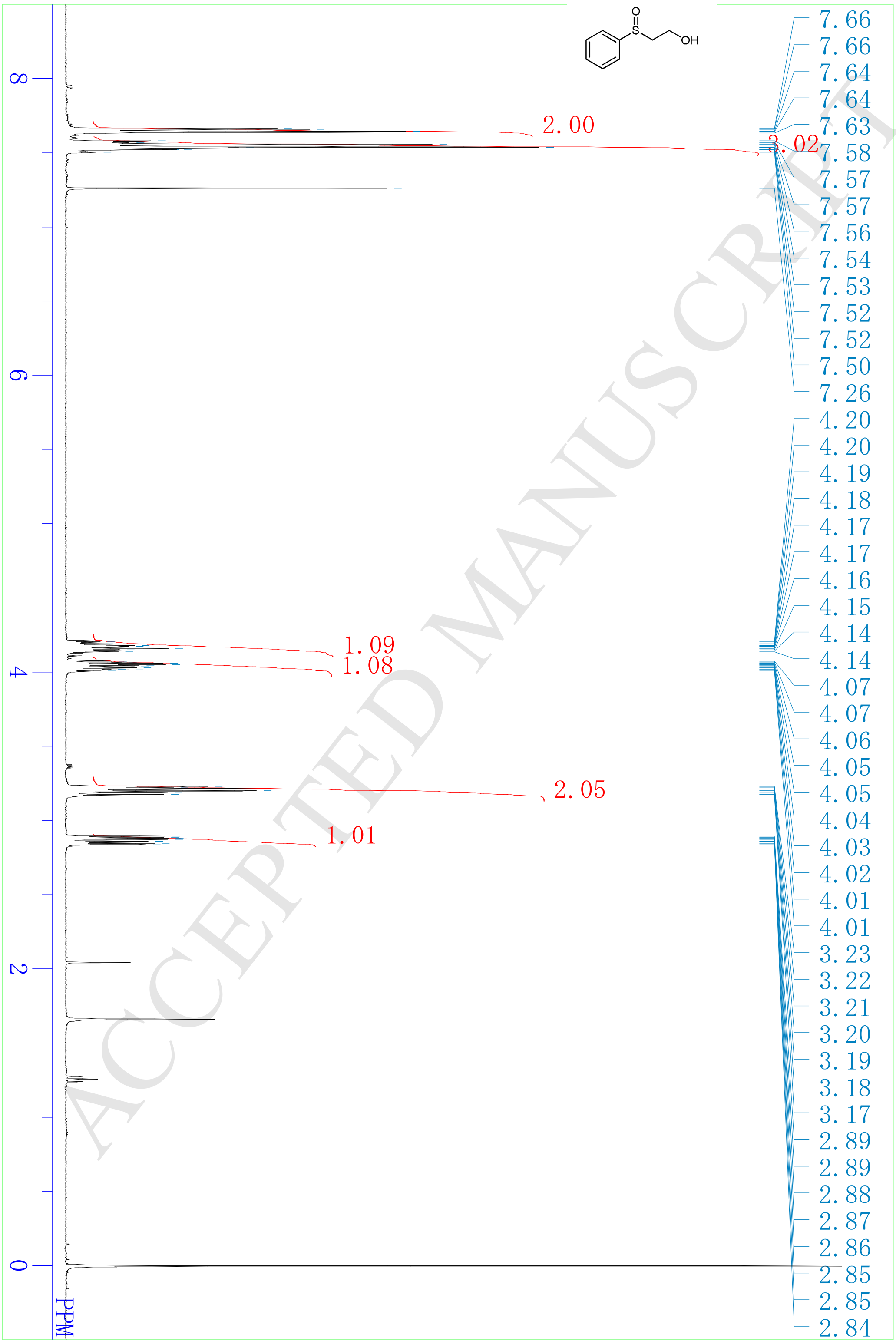
Allyl Phenyl Sulfone ^{1}H NMR (400MHz, CDCl$_3$)[7]



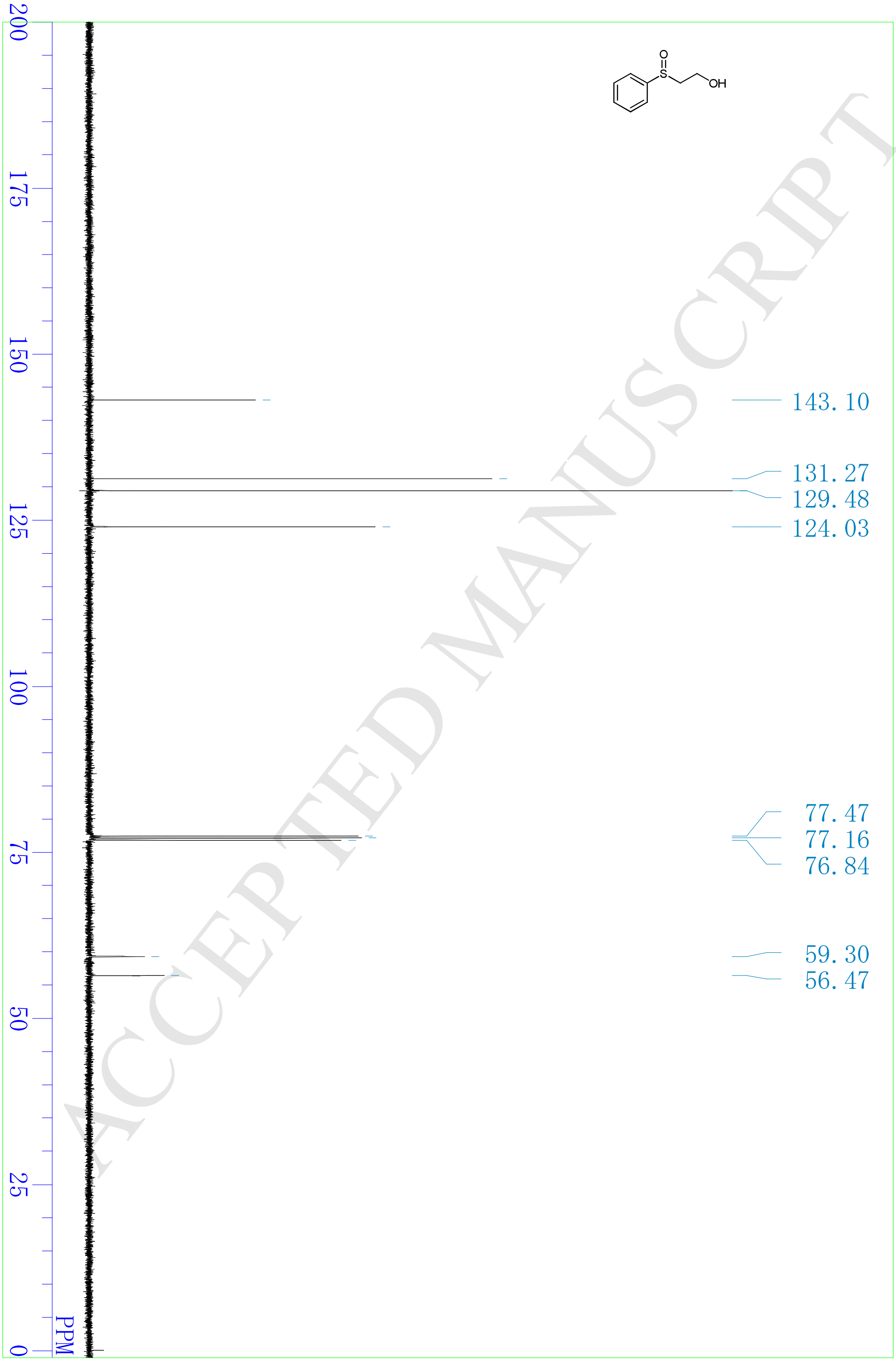
Allyl Phenyl Sulfone ^{13}C NMR (100MHz, CDCl$_3$)[7]



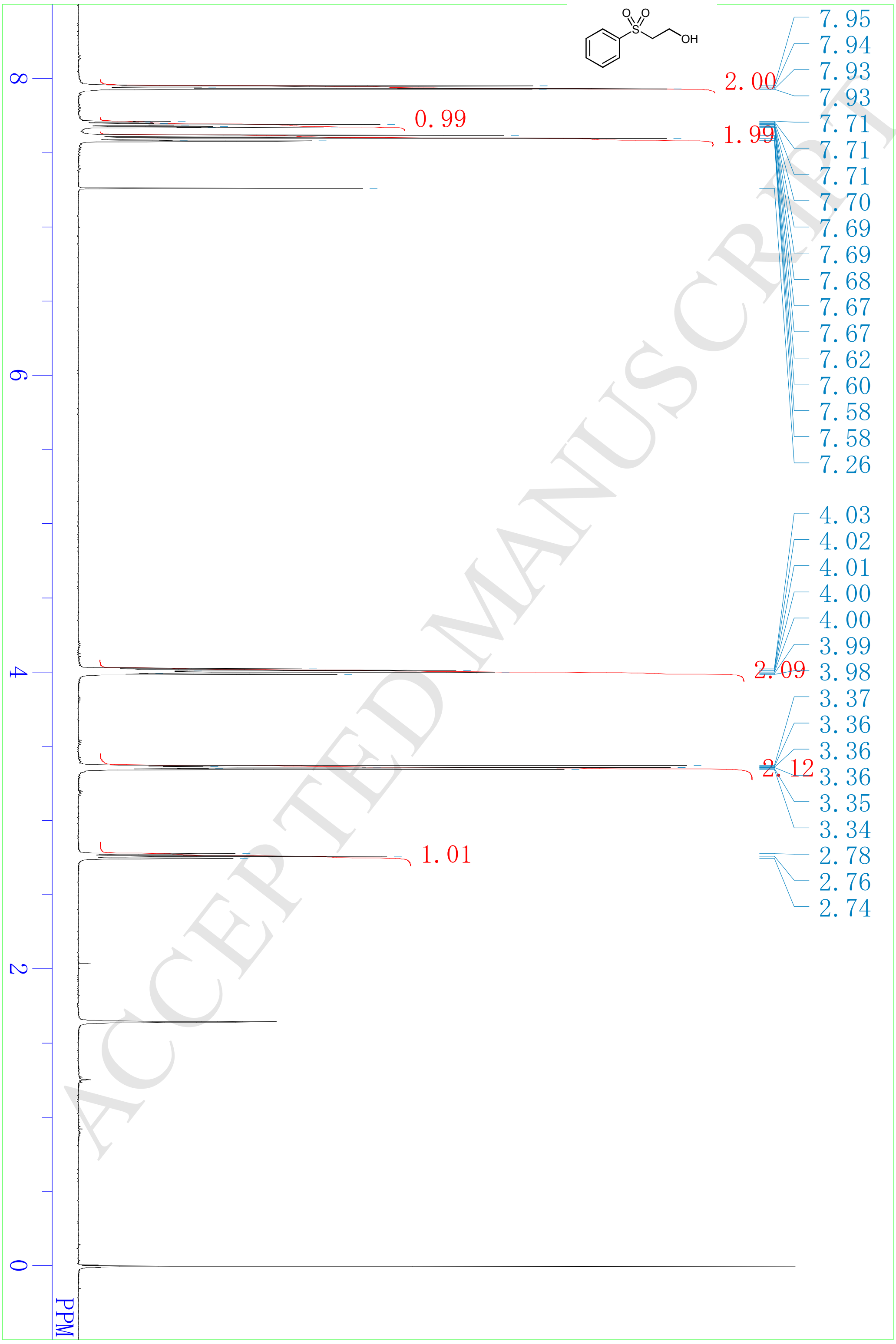
(Phenyl Sulfinyl) Ethanol ^{1}H NMR (400MHz, $CDCl_3$)[7]



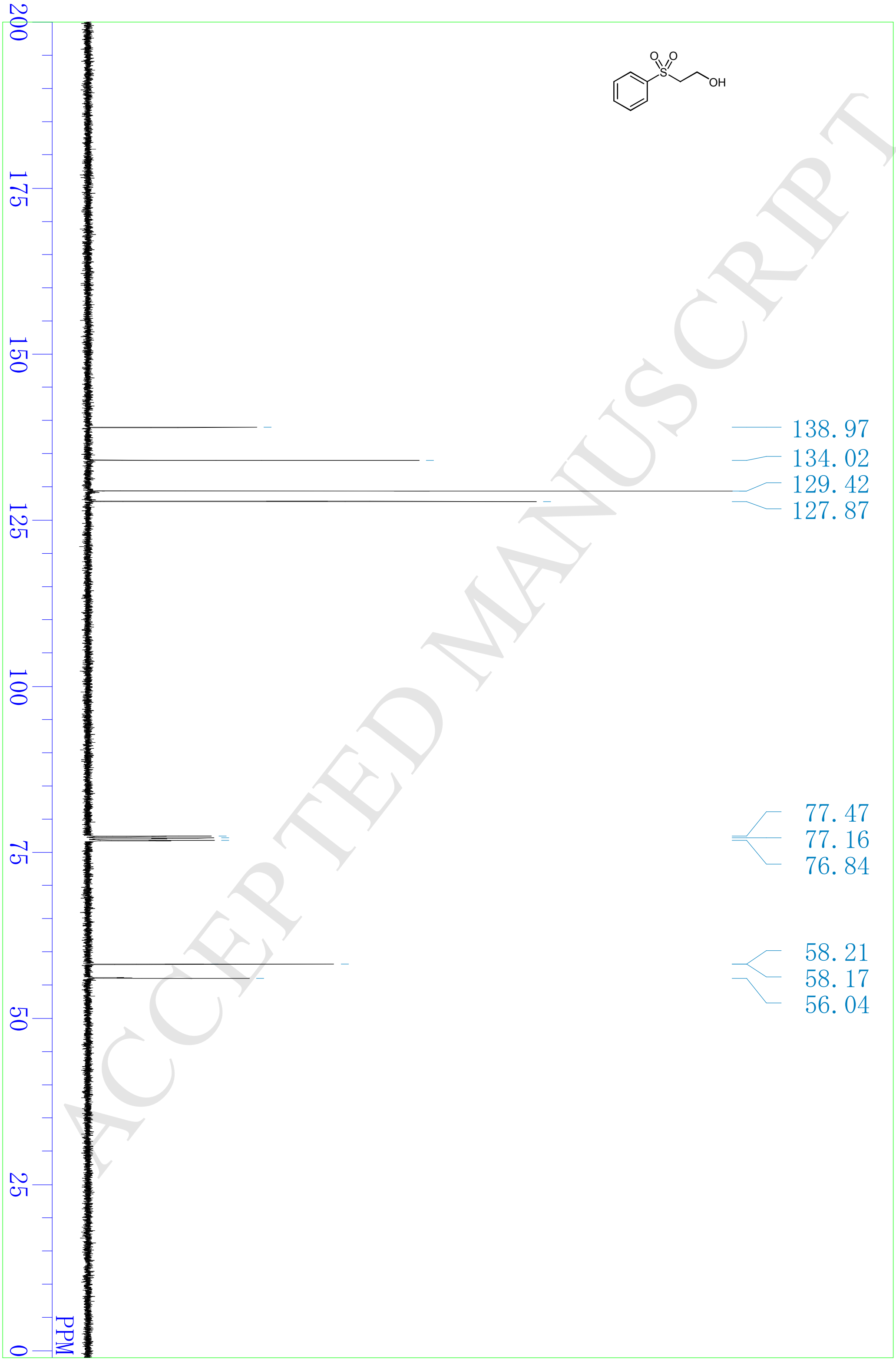
(Phenyl Sulfinyl) Ethanol ^{13}C NMR (100MHz, CDCl$_3$)[7]



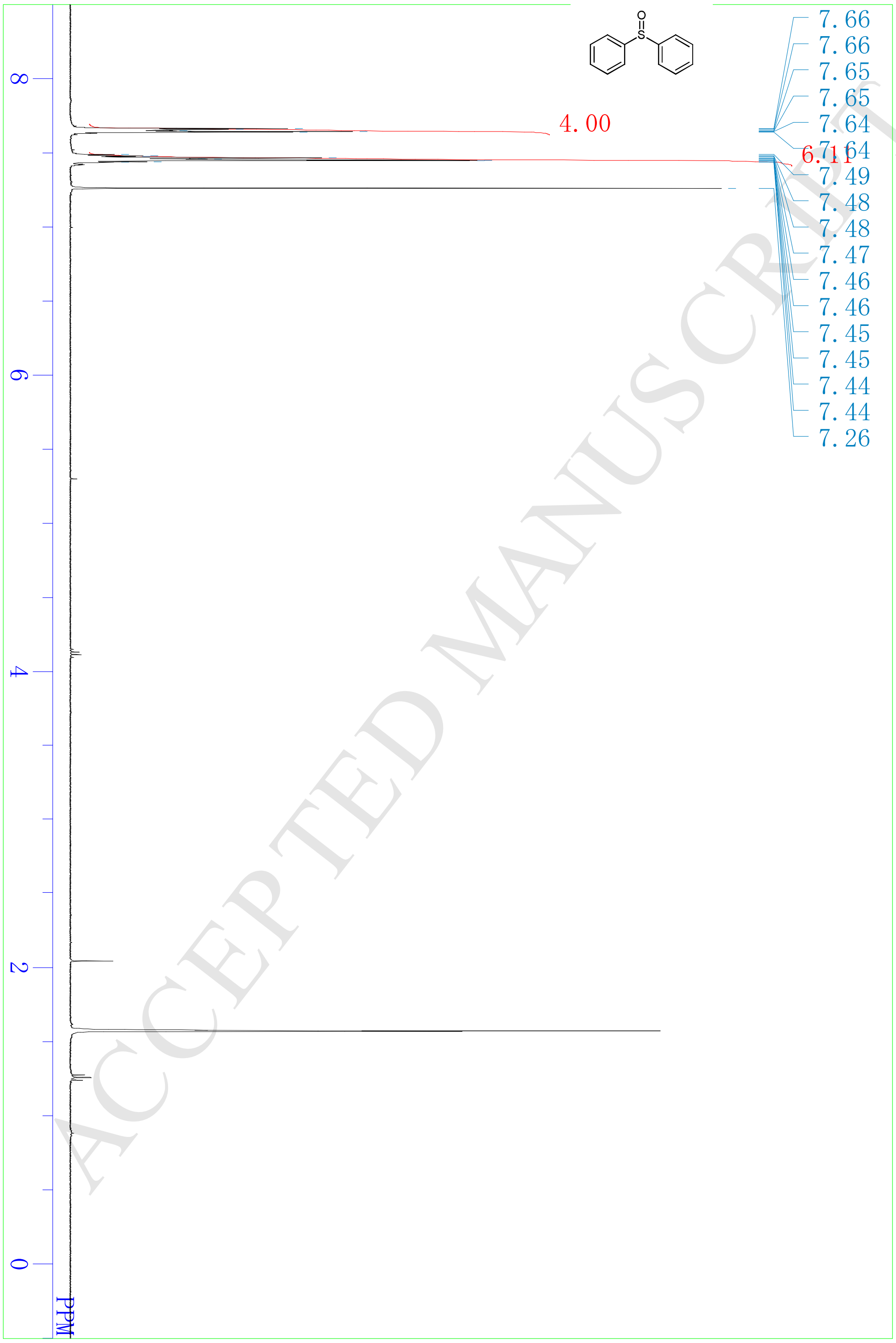
(Phenyl Sulfonyl) Ethanol ^{1}H NMR (400MHz, CDCl$_3$)[7]



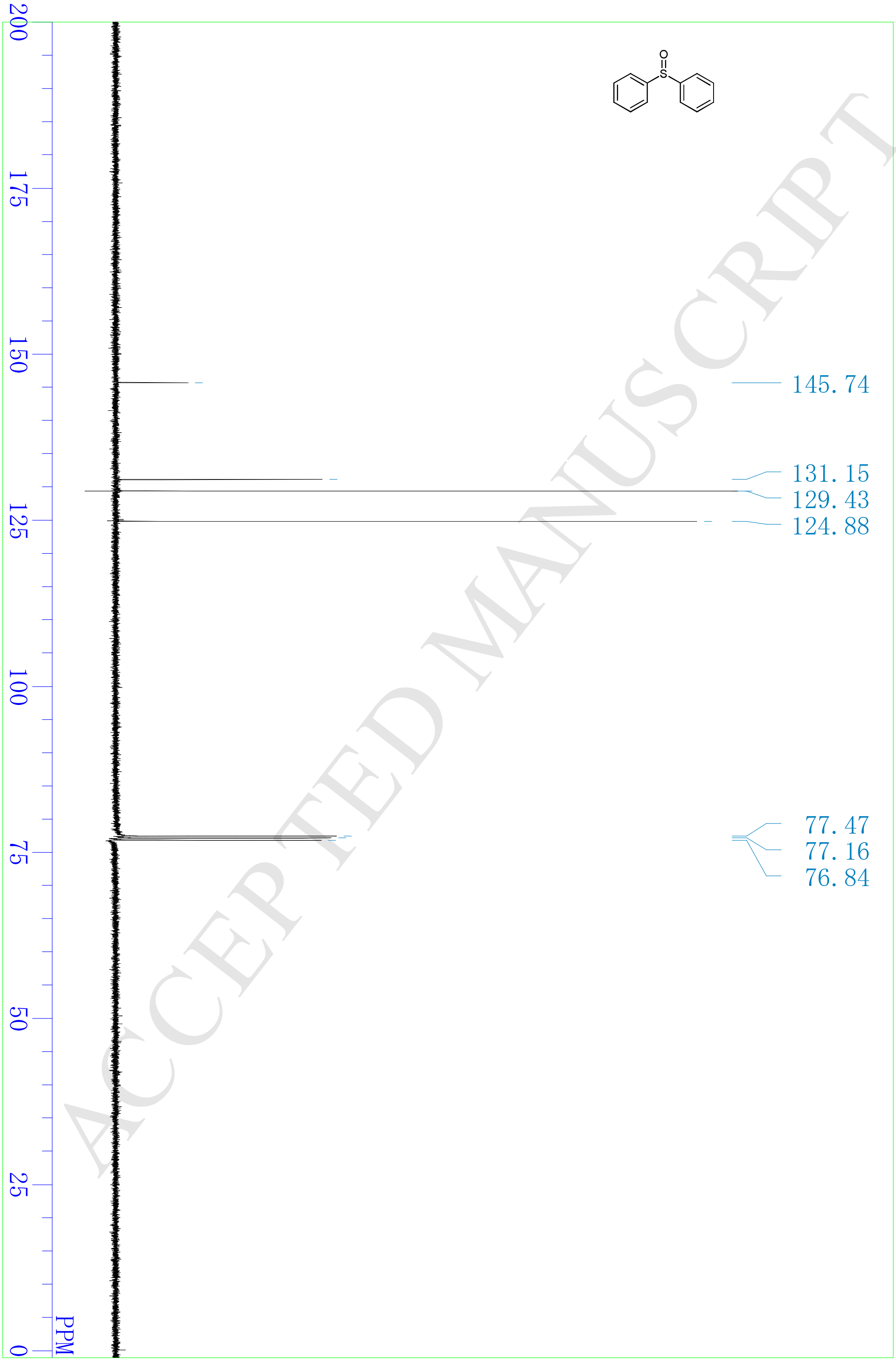
(Phenyl Sulfonyl) Ethanol ^{13}C NMR (100MHz, CDCl$_3$)^{7}



Phenyl Sulfoxide ^{1}H NMR (400MHz, $CDCl_3$)[8]

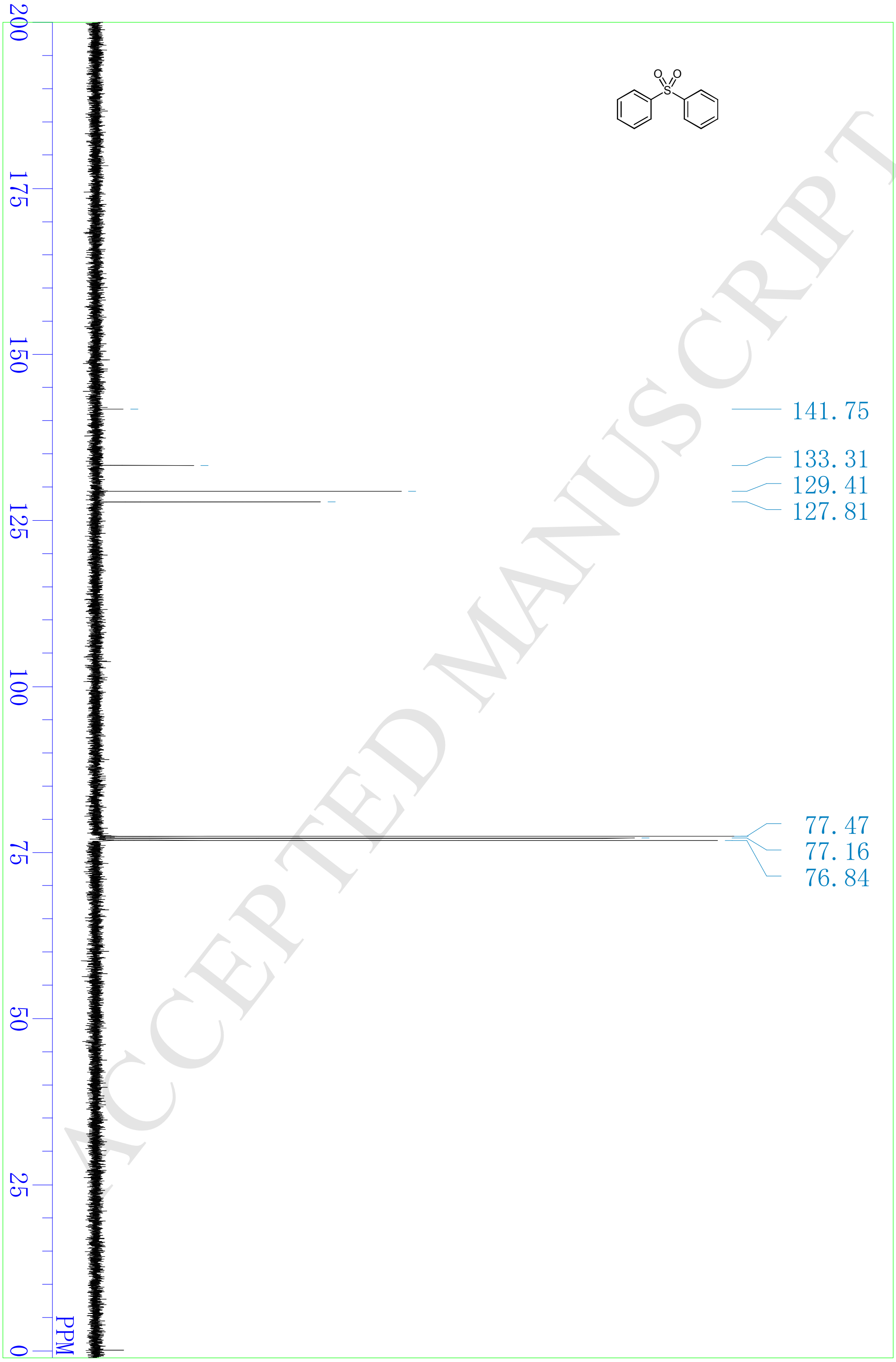


Phenyl Sulfoxide ^{13}C NMR (100MHz, CDCl$_3$) [8]

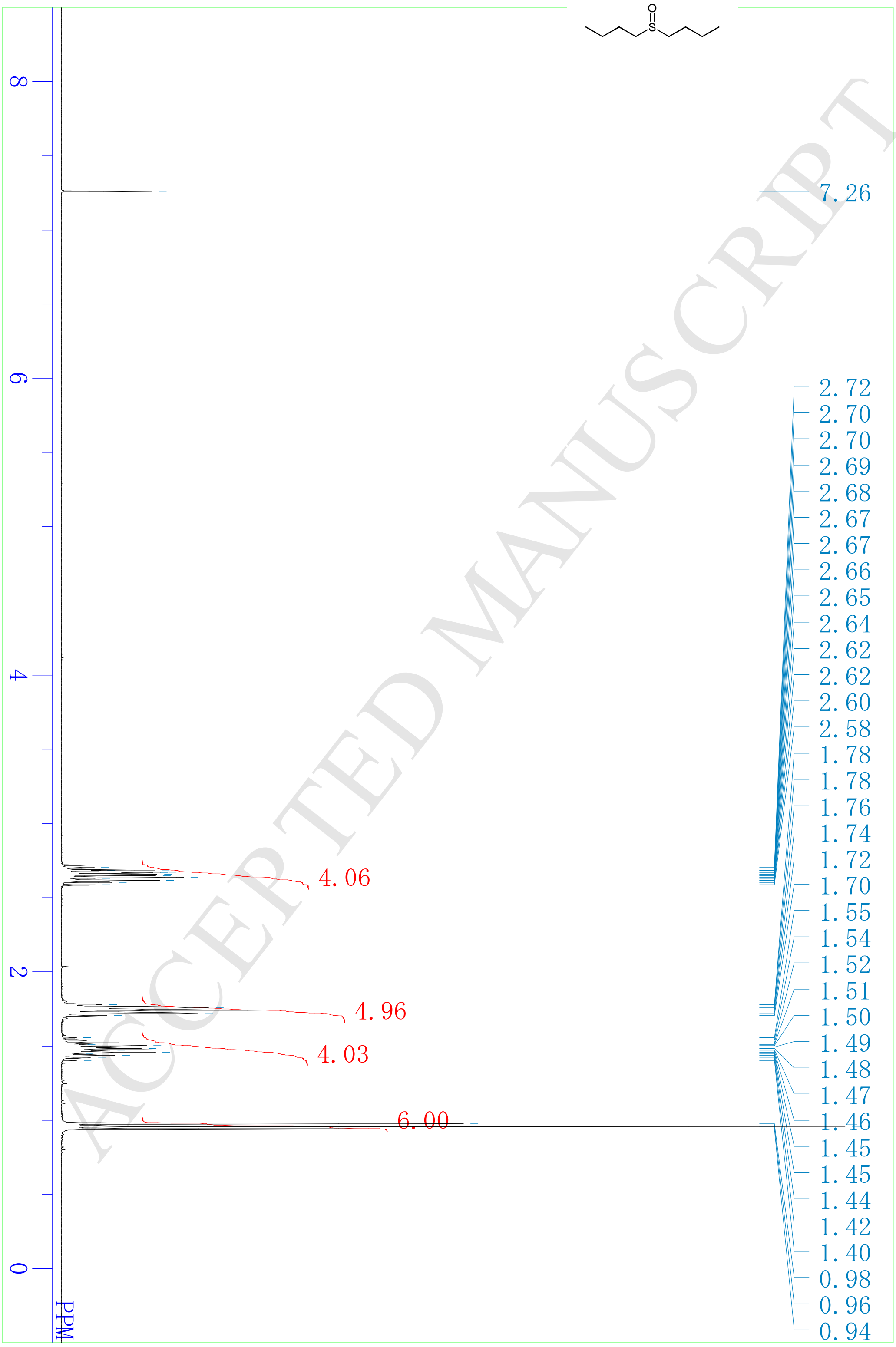


Phenyl Sulfone ^{1}H NMR (400MHz, $CDCl_3$)[2]

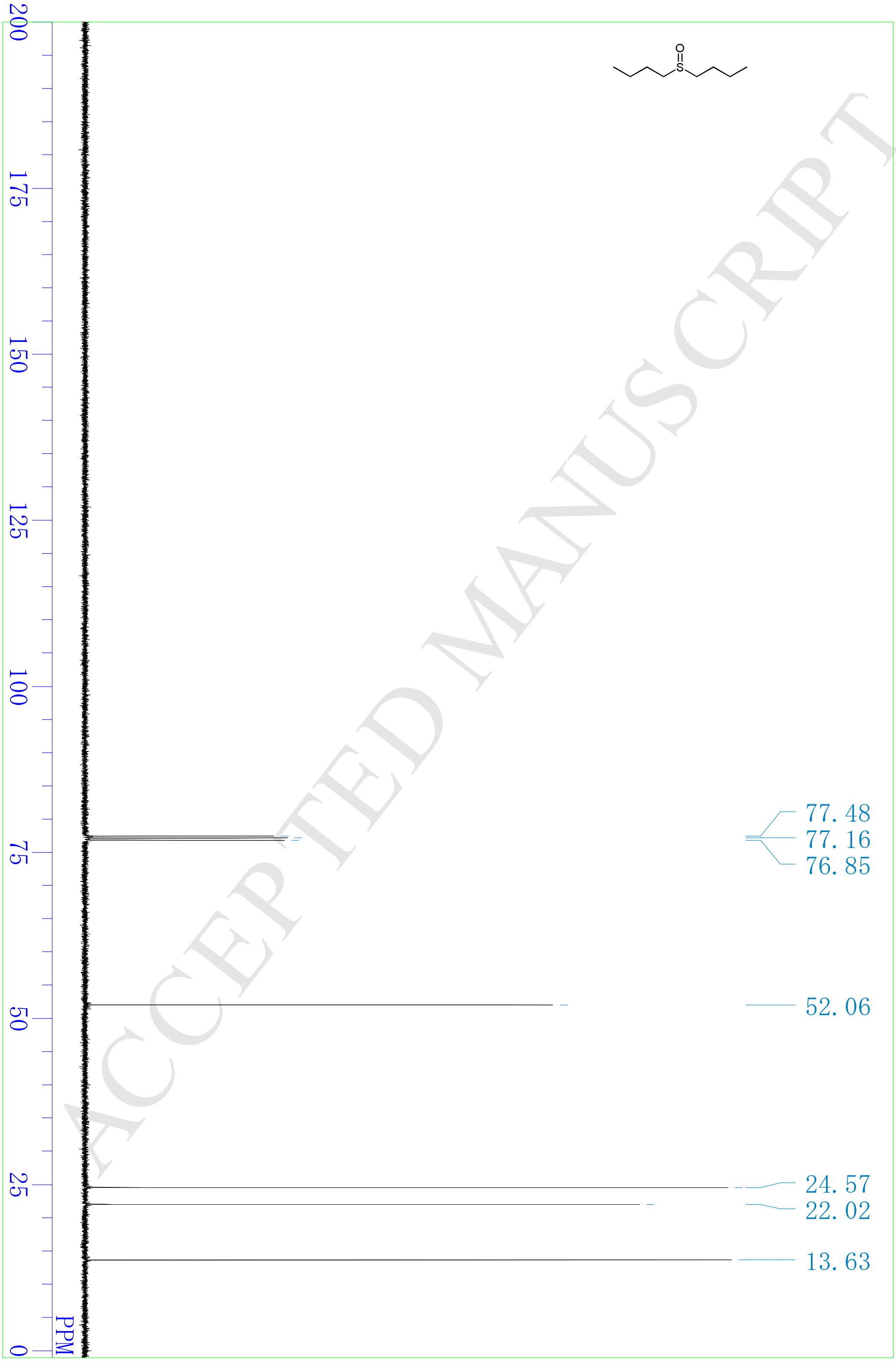
Phenyl Sulfone ^{13}C NMR (100MHz, CDCl$_3$)^{2}



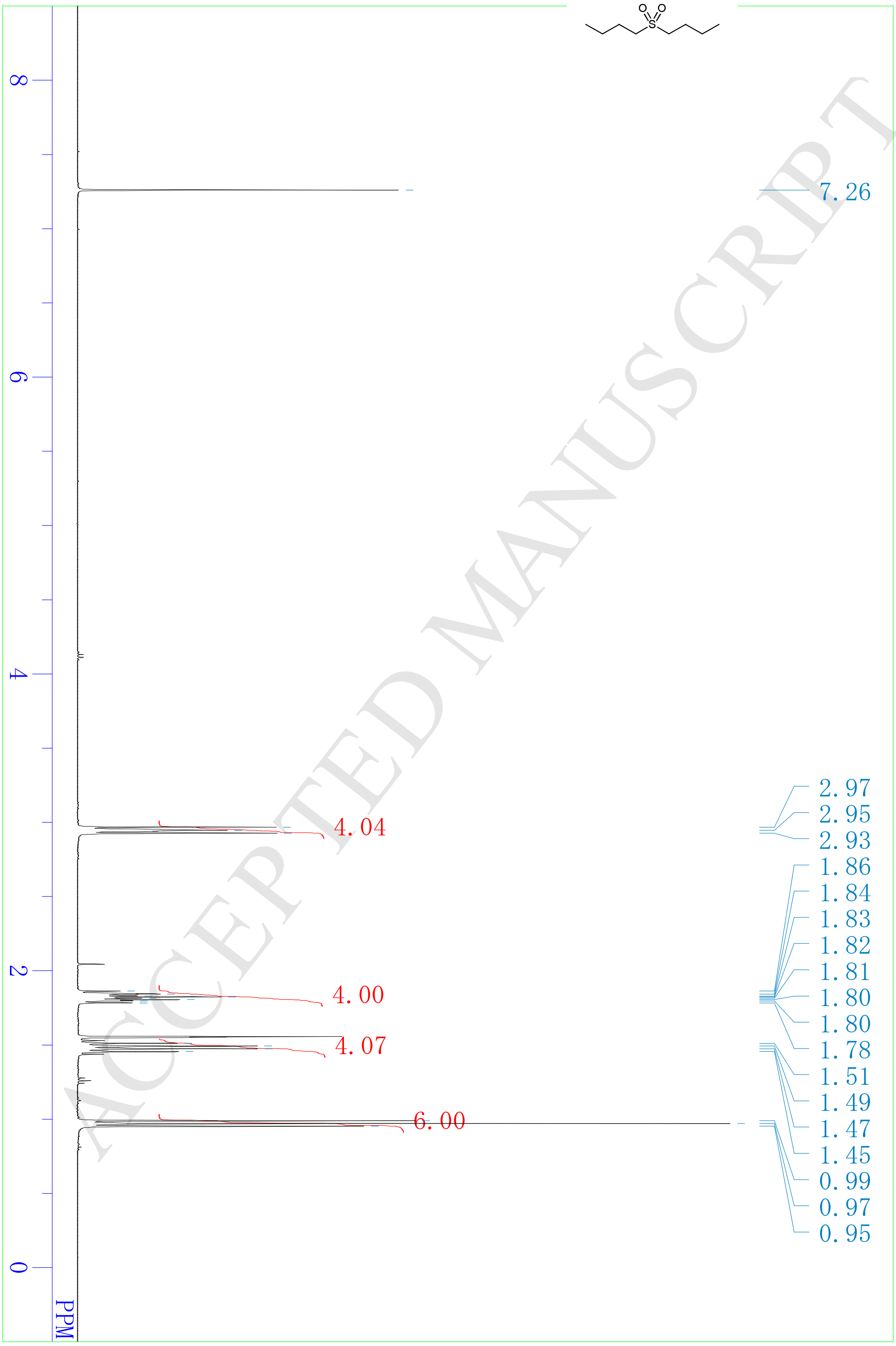
Dibutyl Sulfoxide ^{1}H NMR (400MHz, $CDCl_3$)[9]



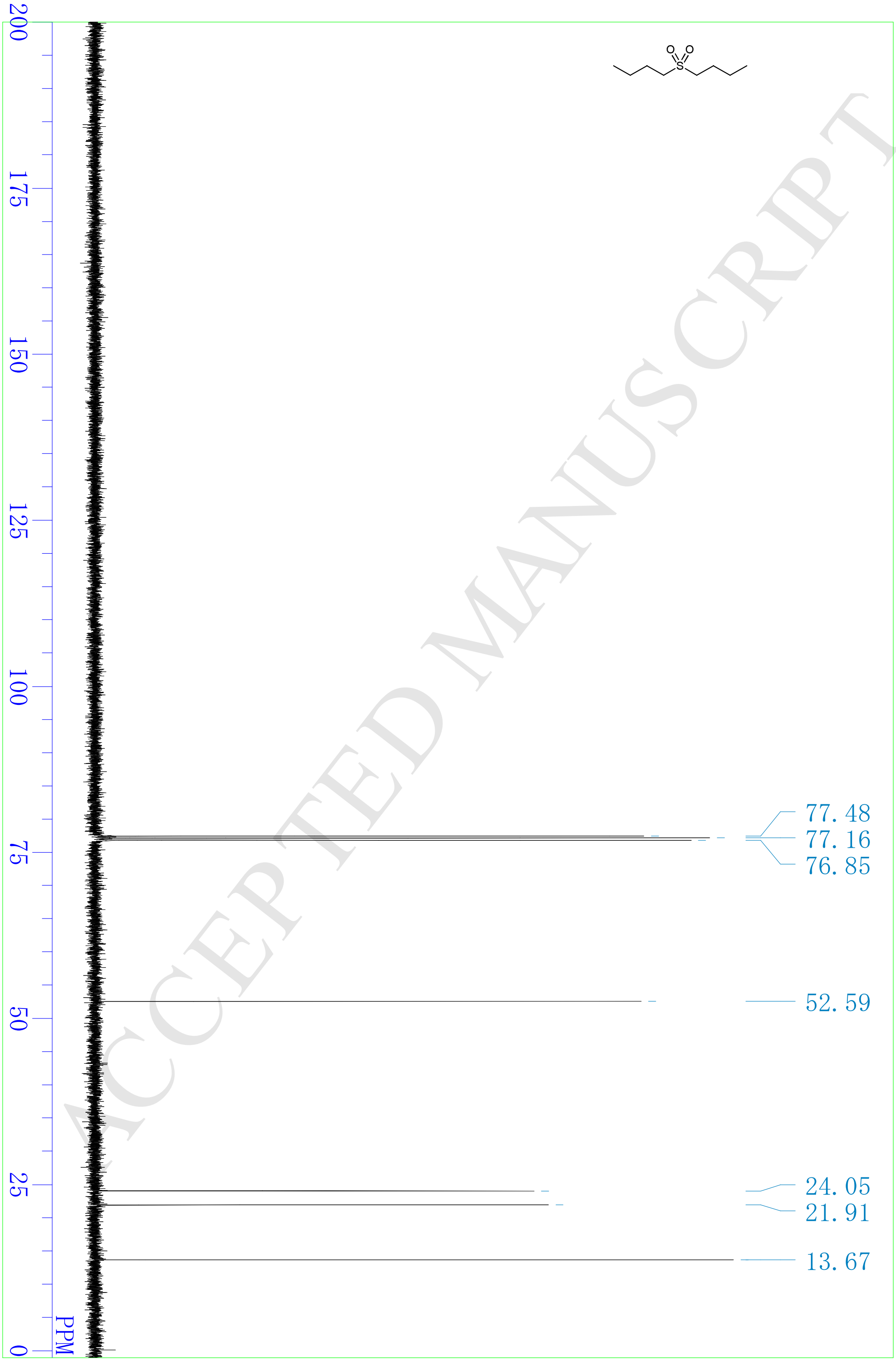
Dibutyl Sulfoxide ^{13}C NMR (100MHz, CDCl$_3$)[9]



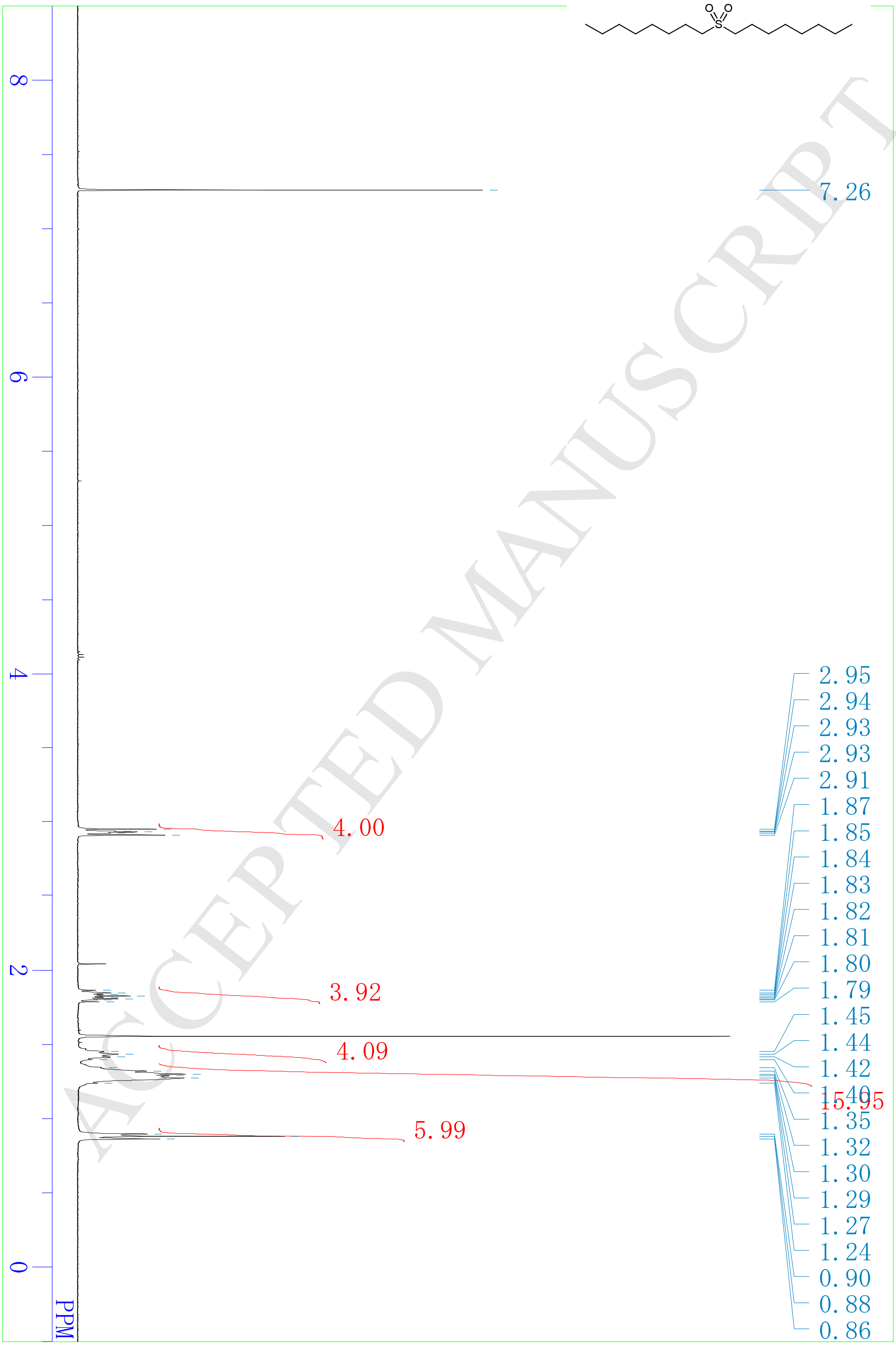
Dibutyl Sulfone ^{1}H NMR (400MHz, CDCl$_3$)^5



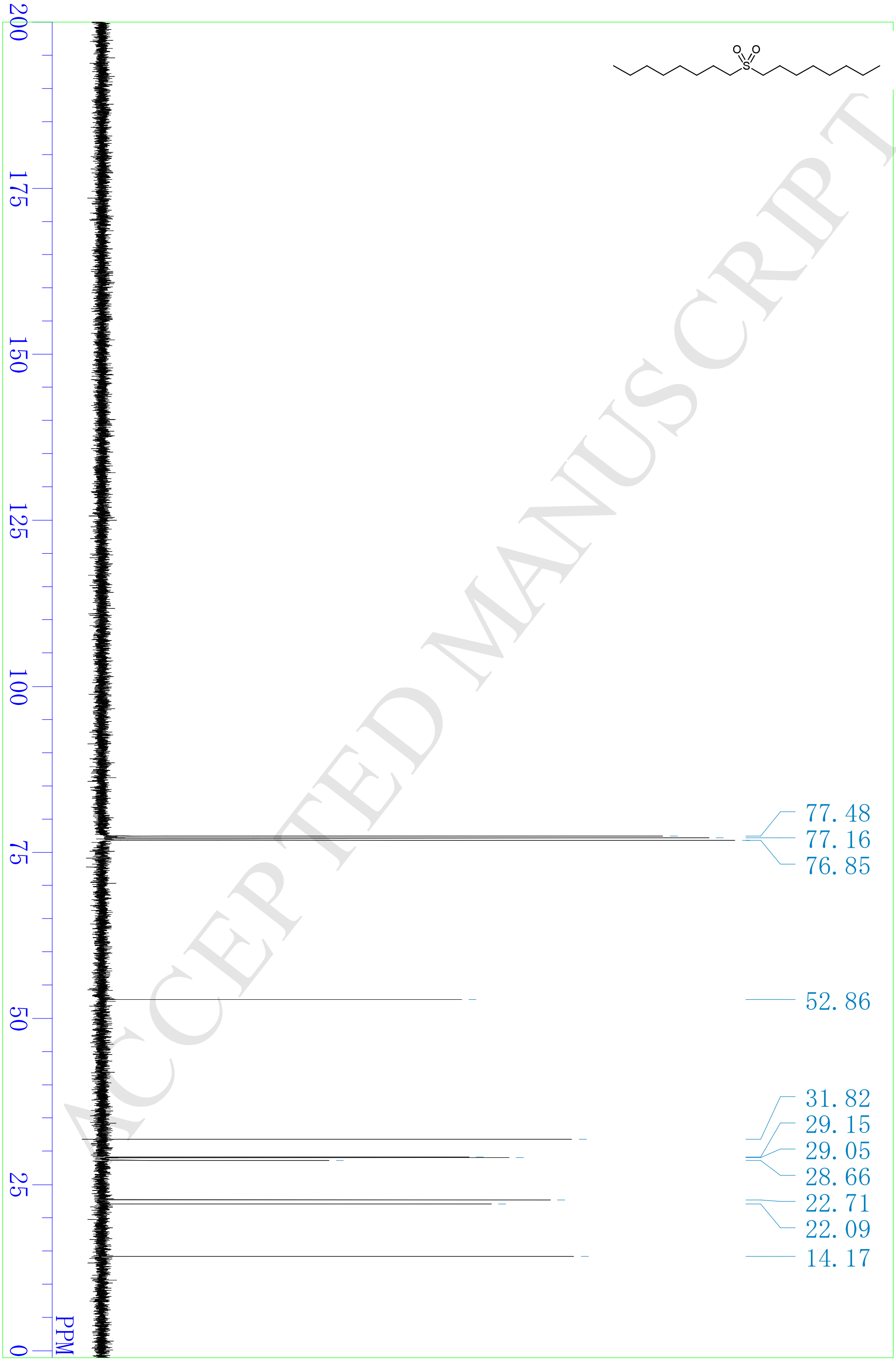
Dibutyl Sulfone ^{13}C NMR (100MHz, $CDCl_3$) [5]



Dioctyl Sulfone ^{1}H NMR (400MHz, $CDCl_3$)[10]



Dioctyl Sulfone ^{13}C NMR (100MHz, CDCl$_3$) [10]



3. References:

1) Moorthy, J. N.; Scnapati, K.; Parida, K. N. *J. Org. Chem.* **2010**, *75*, 8416–8421.

2) Yu, B.; Liu, A.-H.; He, L.-N.; Li, B.; Diao, Z.-F.; Li, Y.-N. *Green Chem.* **2012**, *14*, 957–962.

3) Tundo, P.; Romanelli, G. P.; Vázquez, P. G.; Aricò, F. *Catal. Commun*. **2010**, *11*, 1181-1184.

4) Batigalhia, F.; Zaldini-Hernandes, M.; Fereira, A. G.; Malvestiti, I.; Cass, Q. B. *Tetrahedron* **2001**, *57*, 9669-9676.

5) Zhang, B.; Li, S.; Yue, S.; Cokoja, M.; Zhou, M.-D.; Zang, S.-L.; Kühn, F. E. *J. Organomet. Chem*. **2013**, *744*, 108-112.

6) Llamas, T.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2007**, *46*, 3329–3332.

7) Boruah, J. J.; Das, S. P.; Ankireddy, S. R.; Gogoi, S. R.; Islam, N. S. *Green Chem.* **2013**, *15*, 2944–2959.

8) Fukuda, N.; Ikemoto, T. *J. Org. Chem.* **2010**, *75*, 4629–4631.

9) Raju, B. R.; Sarkar, S.; Reddy, U. C.; Saikia, A. K. *J. Mol. Catal. A: Chem.* **2009**, *308*, 169–173.

10) Katritzky, A. R.; Takahashi, I.; Marson, C. M. *J. Org. Chem.* **1986**, *51*, 4914–4920.