Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2021

SUPPORTING INFORMATION

Modulating catalytic activity of a modified flavin analogue via judicially positioned metal ion toward aerobic sulphoxidation

M. Vinod Mouli and Ashutosh Kumar Mishra*

Department of Chemistry, IIT Hyderabad, 502285, India

Table of contents

1. Materials and Physical Measurements…….....…2
2. Synthetic Procedure……..….3
3. Photophysical studies.……..….9
4. SC-XRD analysis of **Flc-Cd**…….…….……10
5. Plausible mechanism for catalysis……...17
6. References…….…..……18
7. List of NMR…….……19

1. Materials and Physical Measurements.

All chemicals and reagents are purchased from commercial sources Sigma Aldrich, SRL, Alfa Aesar and TCI chemicals and used without purification. Nuclear magnetic resonance spectra were collected using a Bruker DRX-400 spectrometer. ^{13}C NMR spectra were collected at 100 MHz, and ^{1}H NMR spectra were collected at 400 MHz. Resonances are reported in parts per million (ppm) and coupling constants, J, are reported in hertz (Hz). High resolution mass spectra was obtained by Electron Spray Ionization method (ESI) using Agilent QTOF 6538. UV-Visible spectral measurements were obtained from JASCO Spectrophotometer V730 and Fluorescence measurements were taken from JASCO Spectrofluorometer FP-8300. For diffraction measurements, a crystal of **Flc-Cd** with suitable dimensions was mounted on a nylon Loop with a layer of paraben oil. Diffraction measurements were recorded using Bruker APEX (II) CCD monochromatic Mo-Kα (0.71073 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S1. The structures were solved by direct methods and refined on F2 by full-matrix least-squares methods; using SHELXL-97.[1] The crystal data of Flc-Cd has been treated by the PLATON SQUEEZE to remove disordered solvent molecules. Yields of catalytic reaction were determined using HPLC (Shimadzu-UFLC) by eluting with Acetonitrile water mixture.

2. Synthetic Procedure

Synthesis of 1

To 4-Chloro-3-nitro benzoic acid (5g, 24.8 mmol) taken in 100 ml RB flask added 25ml methanol and kept for stirring in ice for 15 minutes. Then added 6 ml concentrated Sulphuric acid dropwise followed by stirring in ice bath for 10 minutes. The reaction was then refluxed for 24 hours. Added water to reaction mixture to get white precipitate which is filtered using suction filtration, washed the white solid with 50 ml water followed by hexane to get pure white solid 2, yield 94%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, 1H, *J* = 2 Hz), 8.17 (dd, 1H, *J* = 8.4, 2 Hz), 7.66 (d, 1H, *J* = 8.4 Hz), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.22, 147.9, 133.59, 132.2, 131.68, 130.06, 126.61, 52.94.

Synthesis of 2

1 (3g, 13.92 mmol) was taken in 100ml 2 neck RB flask and to it added 30ml Acetonitrile and water mixture (3:1). To the contents added sodium acetate (2.28g, 27.8 mmol) followed by followed by addition of n-propylamine (1.23g, 20.88 mmol) dropwise. Reaction mixture was then kept for reflux for 12 hours. After completion of reaction, RB flask is cooled, filtered and washed with cold water to obtain nitroamine 2 as yellow solid, yield 94%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, 1H, *J* = 2.1 Hz), 8.37 (s, 1H), 8.03 (ddd, 1H, *J* = 9.1, 2.1, 0.6 Hz), 6.86 (d, 1H, *J* = 9.1 Hz), 3.9 (s, 3H), 3.33 (td, 2H, *J* = 7.1, 5.3 Hz), 1.83-1.74 (m, 2H), 1.07 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.65, 147.8, 136.27, 131.12, 129.54, 116.95, 113.53, 52.06, 44.95, 22.14, 11.5.

Synthesis of 3

Nitro group of nitroaniline was reduced by addition of 2 (1g, 4.18 mmol) to RB flask containing methanol. Pd/C (50 mg) is added followed by addition of sodium borohydride (636 mg, 16.7 mmol) in 3 parts and kept the reaction stirring at room temperature for 2 hours. Upon completion monitored by TLC, solvent extraction was done using chloroform (100 ml) and water (50 ml), concentrated

organic layer and subsequently used the yellow oil obtained for next reaction without any further purification.

Alloxan monohydrate (0.67 g, 4.18 mmol) and boric acid (0.26g, 4.18 mmol) was dissolved in methanol (5 mL). 3 in acetic acid (15 mL) was added dropwise to reaction mixture for 30 minutes. Continued stirring at room temperature under nitrogen for 12 h. To yellow precipitate obtained was added diethyl ether (10 mL) followed by stirring for 30 minutes. Filtered under suction and yellow solid precipitated was washed with diethyl ether (10 mL) followed with water (10 mL). Dried the yellow solid and silica gel column chromatography was done using gradient elution with $CHCl_3$ and MeOH to give pure flavin 3, yield 78%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.5 (d, 1H, *J* = 2 Hz), 8.32 (dd, 1H, *J* = 9, 2 Hz), 8.07 (d, 1H, *J* = 9.1 Hz), 4.54-4.5 (m, 2H), 3.94 (s, 3H), 1.76-1.72 (m, 2H), 1.04 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.85, 159.39, 155.6, 150.82, 140.04, 135.55, 134.02, 133.8, 132.57, 126.47, 117.09, 52.66, 45.8, 19.74, 10.96. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{14}N_4O_4$: 315.1088 Found 315.1108.

Synthesis of 4

Flavin 3 (0.5g, 1.6 mmol) was added to 25 ml RB flask, to it added 10 ml DMF followed by addition of potassium carbonate (0.44g, 3.18 mmol) and Methyl iodide (1.13 g, 7.96 mmol). Reaction was kept at 80 ^{o}C for 6 hours. After completion of reaction, it is then cooled and filtered the precipitate through suction filtration followed by washing with 20 ml water and 20 ml diethyl ether. Flavin 5 obtained is then dried to give yellow solid, yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, 1H, *J* = 1.9 Hz), 8.45 (dd, 1H, *J* = 9, 1.9 Hz), 7.65 (d, 1H, *J* = 9 Hz), 4.65 (t, 2H, *J* = 7.76 Hz), 3.98 (s, 3H), 3.49 (s, 3H), 1.92-1.87 (m, 2H), 1.11 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.94, 159.26, 155.65, 149.04, 137.86, 135.52, 135.34, 135.06, 135.01, 128.05, 115.41, 52.85, 46.46, 28.84, 20.48, 11.2. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{16}H_{17}N_4O_4$: 351.1064 Found 351.1077.

Synthesis of Flc

To flavin 5 (0.5 g, 1.51 mmol) in 25 ml RB flask added 5 ml concentrated HCl. Kept the reaction for heating at 90 ^{o}C for 3 hours. Cooled the contents and added water and suction filtered to get Flc as yellow solid, yield 97%.

^{1}H NMR (400 MHz, Trifluoroacetic acid-d) δ 9.11 (d, 1H, *J* = 1.8 Hz), 8.88 (dd, 1H, *J* = 9.2, 1.9 Hz), 8.29 (d, 1H, *J* = 9.3 Hz), 4.79-4.83 (m, 2H), 3.56 (s, 3H), 2.03-1.97 (m, 2H), 1.18 (t, 3H, *J* = 7.3 Hz). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.5 (s, 1H), 8.5 (s, 1H), 8.35 (d, 1H, *J* = 8.8 Hz), 8.11 (d, 1H, *J* = 9 Hz), 4.58-4.55 (m, 2H), 3.3 (s, 3H), 1.8-1.74 (m, 2H), 1.04 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, Trifluoroacetic acid-d) δ 168.18, 158.41, 149.71, 140.99, 139.72, 139.48, 136, 133.32, 133.28, 132.35, 117.72, 51.49, 28.5, 20.59, 8.41. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{15}N_4O_4$: 337.0907 Found 337.0923.

Synthesis of Flc-Cd

Complex preparation was done by addition of Flc (0.33 mmol) to 10 ml RB flack followed by addition of respective metal acetate (0.33 mmol) and refluxing in 5 ml methanol for 4 hours. The reaction mixture was then filtered and washed with methanol and dried to give metal complexes as orange solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (d, 1H, *J* = 1.9 Hz), 8.46 (dd, 1H, *J* = 8.9, 1.9 Hz), 8.06 (d, 1H, *J* = 9.1 Hz), 4.56-4.6 (m, 2H), 3.29 (s, 3H), 1.81-1.75 (m, 2H), 1.05 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.66, 159.97, 155.75, 149.62, 138.74, 136.06, 135.03, 134.35, 133.23, 133.03, 116.64, 28.51, 20.38, 11.47. HRMS (ESI) *m*/*z*: $[FLC\text{-}Cd^+]$ calcd: 426.9965 Found 426.9988.

Catalytic studies

Flc (0.0387 mmol) was taken in a glass vial, to it added 1 ml TFE solvent followed by addition of $Cd(OAc)_2.2H_2O$ (0.0194 mmol). The vial is heated until the solution becomes clear orangish indicating the complex formation. To it added L-Ascorbic (0.194 mmol) acid followed by addition of 0.5 ml water. Sulphide (0.194 mmol) is then added to the glass vial and kept for stirring under oxygen atmosphere. After 24 hours the reaction was stopped and the yield of sulphoxide is determined by using HPLC.

Methyl phenyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, 2H, *J* = 7.7, 1.7 Hz), 7.56-7.5 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.65, 131.07, 129.38, 123.5, 43.97.

Methyl p-tolyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, *J* = 8 Hz), 7.33 (d, 2H, *J* = 7.9 Hz), 2.71 (d, 2H, *J* = 0.5 Hz), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.44, 141.52, 130.04, 123.54, 43.99, 21.41.

4-Methoxyphenyl methyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (d, 2H, *J* = 8.8 Hz), 7.03 (d, 2H, *J* = 8.8 Hz), 3.86 (s, 3H), 2.7 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.96, 136.56, 125.46, 114.85, 55.54, 44.02.

4-Chlorophenyl methyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.57 (m, 2H), 7.56-7.48 (m, 2H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.19, 137.27, 129.68, 124.99, 44.06.

4-Hydroxyphenyl methyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.56-7.44 (m, 2H), 7.03-6.92 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 133.13, 126.16, 116.84, 43.02.

Allylphenyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.41 (m, 5H), 5.62-5.51 (m, 1H), 5.25 (dd, 1H, *J* = 10.2, 0.6 Hz), 5.12 (dd, 1H, *J* = 17, 1.1 Hz), 3.53-3.4 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.82, 131.13, 129.06, 125.21, 124.33, 123.94, 60.81.

4-Acetylphenyl methyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.03 (m, 2H), 7.84-7.68 (m, 2H), 2.77 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.08, 150.91, 139.10, 129.18, 123.77, 43.83, 26.82.

4-Cyanophenyl methyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, *J* = 8.2 Hz), 7.75 (d, 2H, *J* = 8.1 Hz), 2.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.42, 133.03, 124.34, 117.76, 114.78, 43.81.

4-Nitrophenyl methyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, 2H, *J* = 8.8 Hz), 7.78 (d, 2H, *J* = 8.9 Hz), 2.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.21, 149.51, 124.69, 124.52, 43.88.

Diphenyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.42-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.55, 131.1, 129.36, 124.82.

Phenothiazine-5-oxide. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.91 (dd, 2H, *J* = 7.8, 1.4 Hz), 7.62 (ddd, 2H, *J* = 8.5, 7.2, 1.5 Hz), .7.4 (dd, 2H, *J* = 8.3, 0.8 Hz), 7.22-7.2 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.32, 133.19, 131.62, 121.67, 121.33, 117.27.

Dibenzyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.03 (m, 2H), 7.18-7.32 (m, 10H), 3.81 (q, 4H, *J* = 13 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.17, 130.14, 128.99, 128.40, 57.27.

Difurfuryl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) 7.47-7.46 (m, 1H), 6.47 (d, 1H, *J* = 3.3 Hz), 6.42-6.4 (m, 1H), 4.02 (dd, 2H, *J* = 50, 14.1 Hz). δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.75, 143.71, 111.81, 111.26, 49.46.

Tetrahydrothiophene-1-oxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96-2.82 (m, 4H), 2.5-2.41 (m, 2H), 2.08-1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.44, 25.53.

Butyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67-2.53 (m, 2H), 1.72-1.64 (m, 2H), 1.51-1.34 (m, 2H), 0.9 (t, 3H, *J* = 7.3 Hz). 52.07, 24.57, 22.04, 13.67.

Allyl sulphoxide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88-5.78 (m, 1H), 5.41-5.31 (m, 2H), 3.47 (dd, 1H, *J* = 13, 7.3 Hz), 3.34 (dd, 1H, *J* = 13, 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.67, 123.74, 54.14.

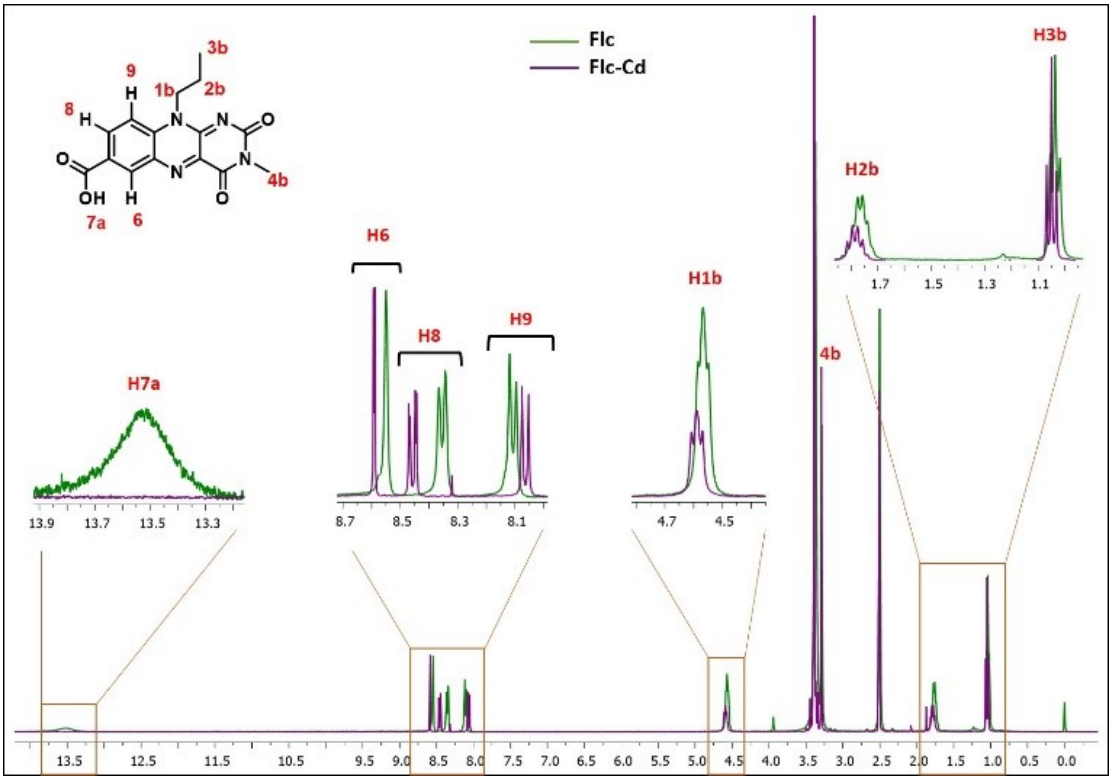


Fig. S1 NMR spectra as recorded for **Flc** and **Flc-Cd** in DMSO-d_6

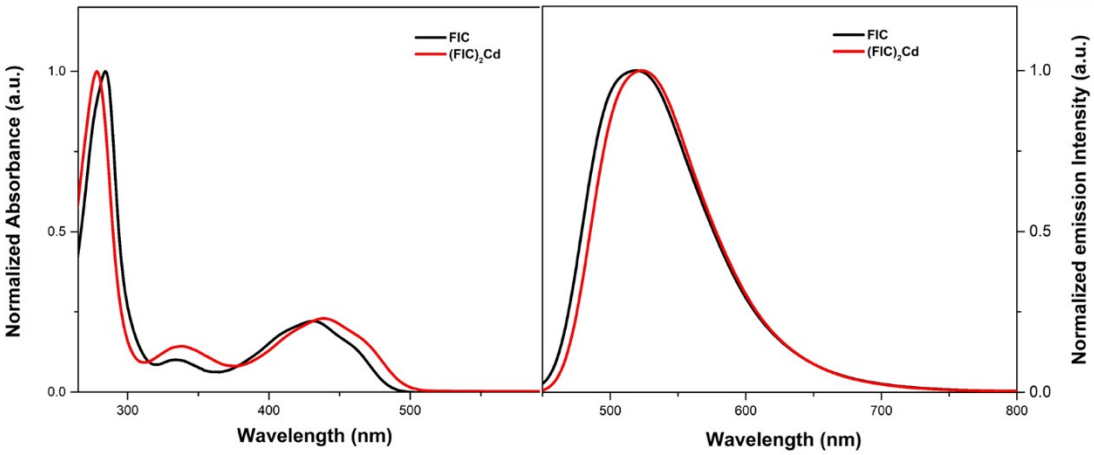


Fig. S2 Absorption and emission spectra of **Flc** and **Flc-Cd** as recorded in DMSO.

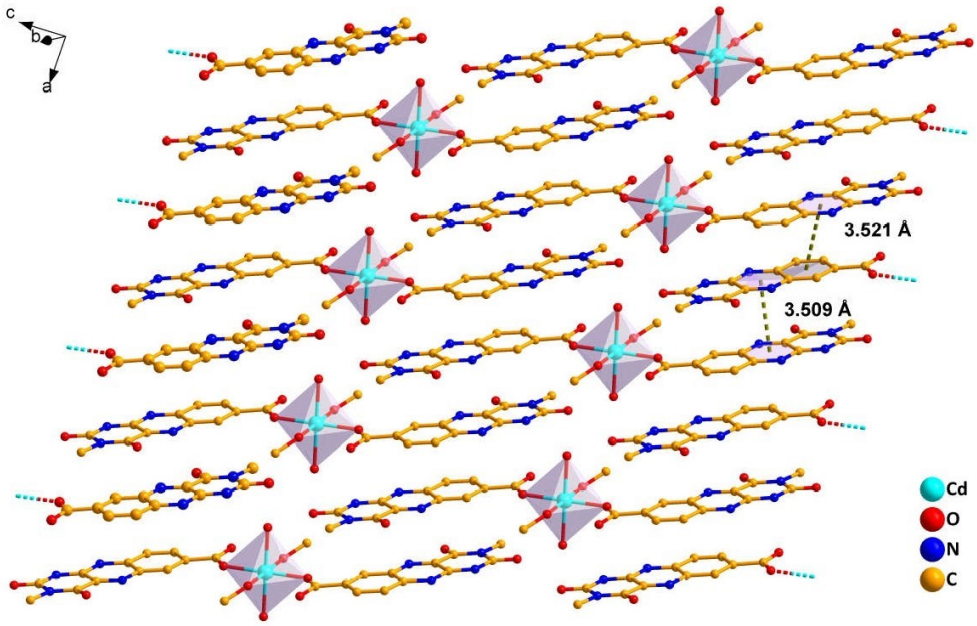


Fig. S3 Representative picture of arrangement of **Flc-Cd** in crystal lattice

Compound Reference	**Flc-Cd**
empirical formula	$C_{32}H_{32}N_8O_{12}Cd$
formula weight	833.05
crystal colour	Yellow
crystal system	Triclinic
space group	P -1
a/Å	7.6046(12)
b/Å	10.4682(16)
c/Å	12.881(2)
α/deg	75.411(4)
β/deg	86.794(5)
γ/deg	79.566(5)
volume/Å^3	975.9(3)
D_{calcd} (g/cm^3)	1.417
temp/K	298
Z	1
μ (mm^{-1})	0.627
F(000)	424
Reflections total	11510
Reflections observed	2587
Rint	0.0718
No. of param	244
final R1 values (all data)	0.0604
final wR(F2) values(all data)	0.1513
GOF	0.978

Table S1. Crystallographic and Refinement Data of FlC complexes synthesized

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) Flc-Cd

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: Flc-Cd

Bond precision: C-C = 0.0069 A Wavelength=0.71073

Cell: a=7.6046(12) b=10.4682(16) c=12.881(2)
alpha=75.411(4) beta=86.794(5) gamma=79.566(5)
Temperature: 298 K

	Calculated	Reported
Volume	975.9(3)	975.9(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C32 H32 Cd N8 O12 [+ solvent]	C32 H32 Cd N8 O12
Sum formula	C32 H32 Cd N8 O12 [+ solvent]	C32 H32 Cd N8 O12
Mr	833.07	833.05
Dx,g cm-3	1.418	1.417
Z	1	1
Mu (mm-1)	0.627	0.627
F000	424.0	424.0
F000’	423.40	
h,k,lmax	9,13,16	9,13,16
Nref	4344	4270
Tmin,Tmax	0.945,0.957	
Tmin’	0.945	

Correction method= Not given

Data completeness= 0.983 Theta(max)= 27.187

R(reflections)= 0.0604(2587) wR2(reflections)=

0.1513(4270)

S = 0.978 Npar= 244

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT230_ALERT_2_B Hirshfeld Test Diff for  N10  --C1B  .  10.2 s.u.
```

Author response
This alert concerns with vibration of flexible propyl chain.

```
PLAT230_ALERT_2_B Hirshfeld Test Diff for  C1B  --C2B  .  7.3 s.u.
```

Author response
This alert concerns with vibration of flexible propyl chain.

```
PLAT430_ALERT_2_B Short Inter D...A Contact  O1  ..O6  .  2.76 Ang.
                                              1+x,y,1+z  =      1_656 Check
```

Author response
O6 is the oxygen atom of water molecule coordinated to Cd(II). This is concerned with short distance between Flc-O2 of one molecule and O6 of another molecule.

Alert level C

```
PLAT213_ALERT_2_C Atom C3B             has ADP max/min Ratio .....        3.3 prolat
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        4.2 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        4.7 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C2B      --C3B      .       0.18 Ang.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        Cd1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C2B Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.5 Note
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C1B      - C2B      .       1.39 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         14 Report
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  1.02A   From O6             0.51 eA-3
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  0.78A   From O6             0.42 eA-3
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  0.93A   From O6             0.42 eA-3
```

Alert level G

```
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure         59 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         13 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cd1       (II)      .       2.20 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         59 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        2.7 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

```
 0 ALERT level A = Most likely a serious problem - resolve or explain
 3 ALERT level B = A potentially serious problem, consider carefully
12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 8 ALERT level G = General information/check it is not something unexpected

 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
13 ALERT type 2 Indicator that the structure model may be wrong or deficient
 4 ALERT type 3 Indicator that the structure quality may be low
 4 ALERT type 4 Improvement, methodology, query or suggestion
 1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

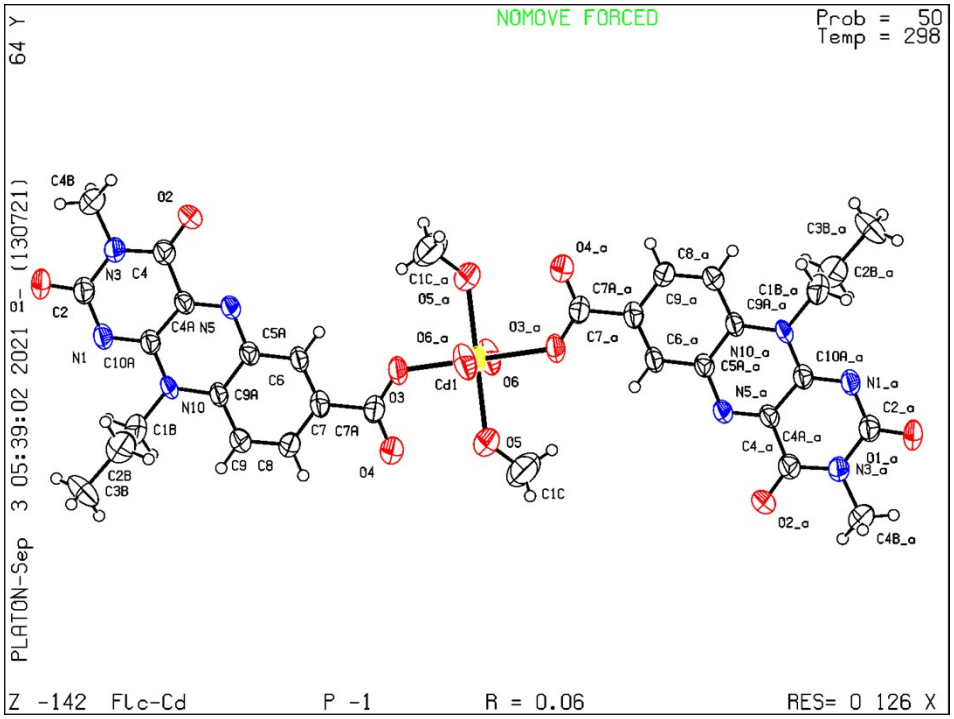
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

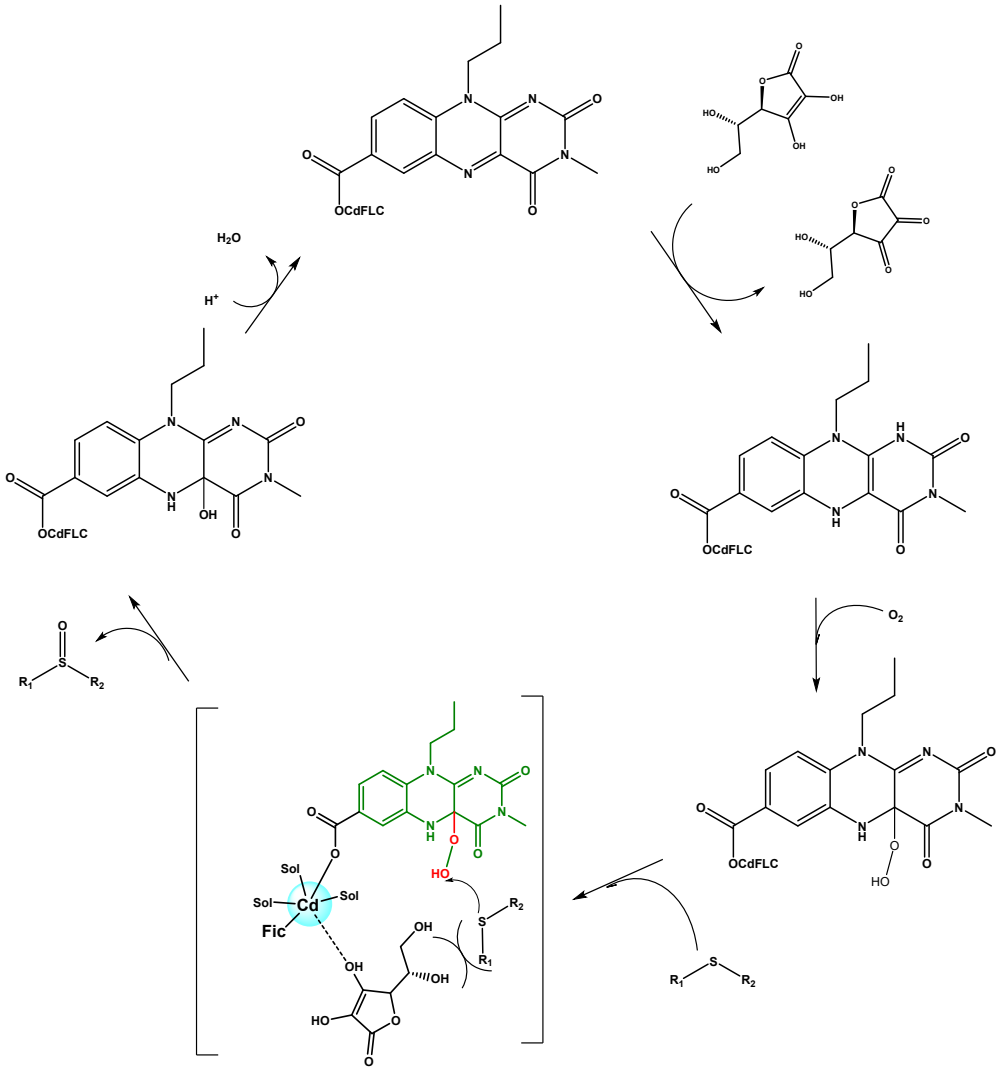
PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock Flc-Cd - ellipsoid plot



3. Plausible Mechanism for catalysis

Based on our understanding from the previous literature reports, a plausible mechanism for the aerobic oxidation reaction discussed in the manuscript is given below as scheme S1.[2] The first step involves reduction of the oxidized flavin gets reduce in the presence of L-Ascorbic acid to form dihydroflavin, which is then activated by molecular oxygen to give hydroperoxyflavin (Fl-OOH). Attack of sulphide substrate at the activated catalyst to abstract the oxygen results in formation of corresponding sulphoxide product and hydroxyflavin intermediate which then get hydrolysed to form the oxidised flavin catalyst.



Scheme S1. Plausible mechanism for the catalytic reaction.[2]

References

1. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2. *J. Appl. Crys.* 2009, **42**, 339-341.
2. Y. Imada, T. Kitagawa, H.-K. Wang, N. Komiya and T. Naota, *Tetrahedron Lett.,* 2013, **54**, 7, 621-624.

List of NMR Spectra

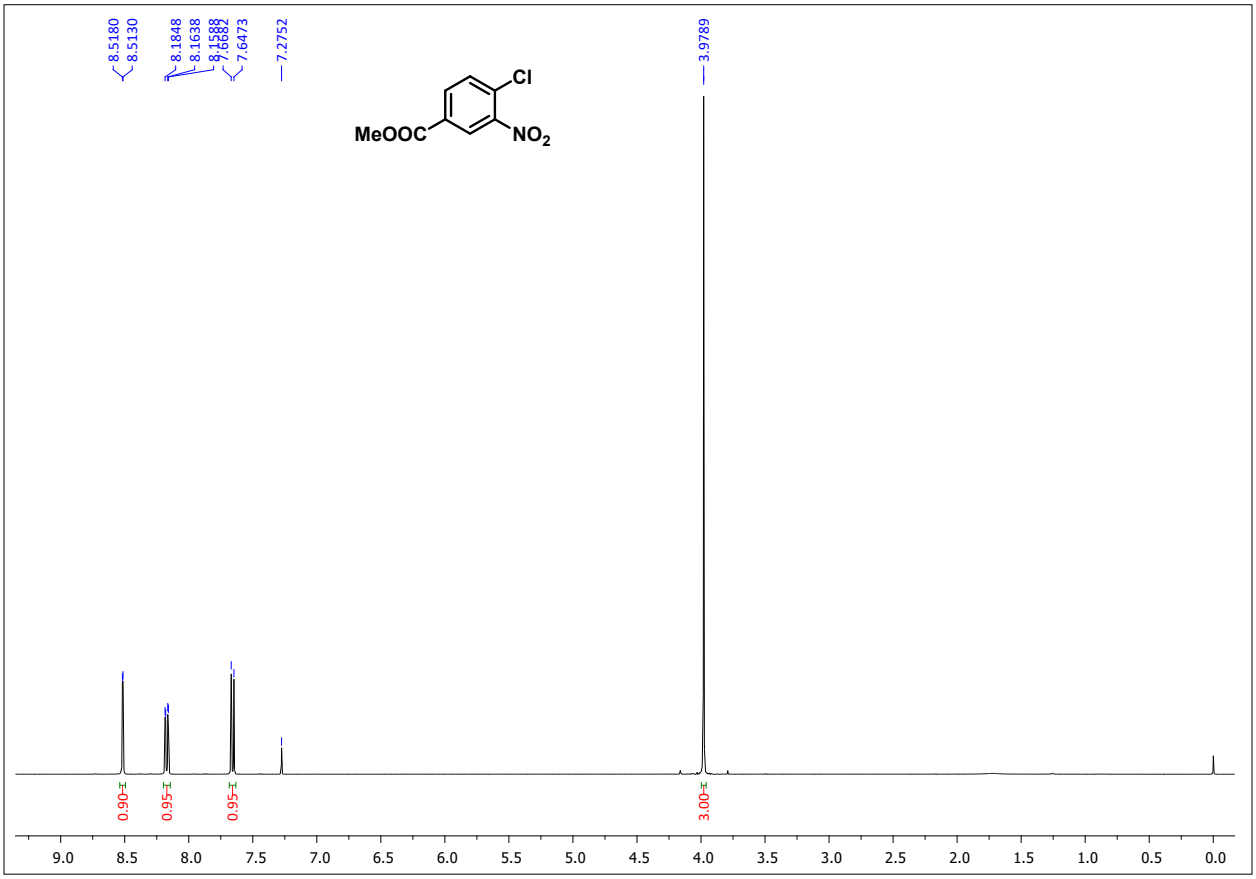


Figure S4. ^{1}H NMR of **1** in $CDCl_3$

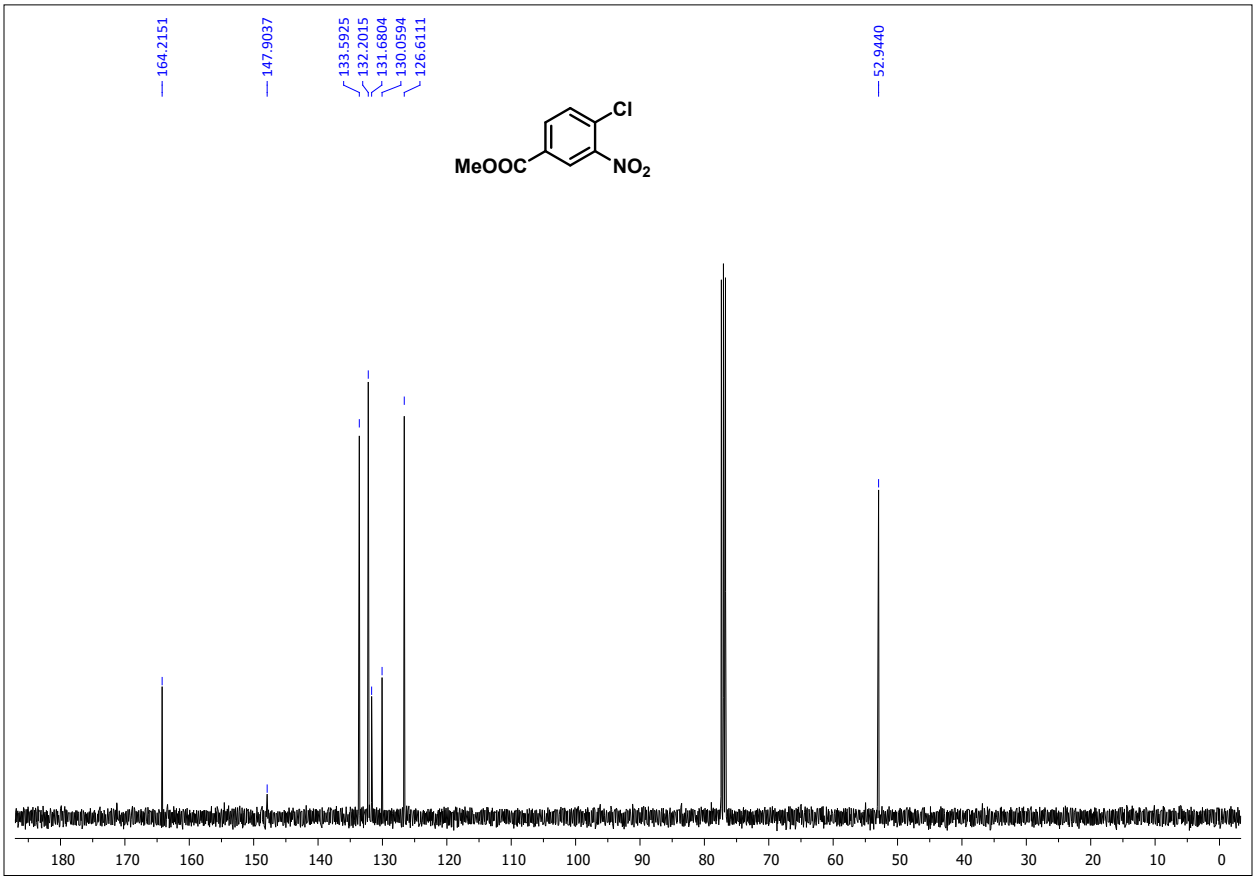


Figure S5. ^{13}C NMR of **1** in $CDCl_3$

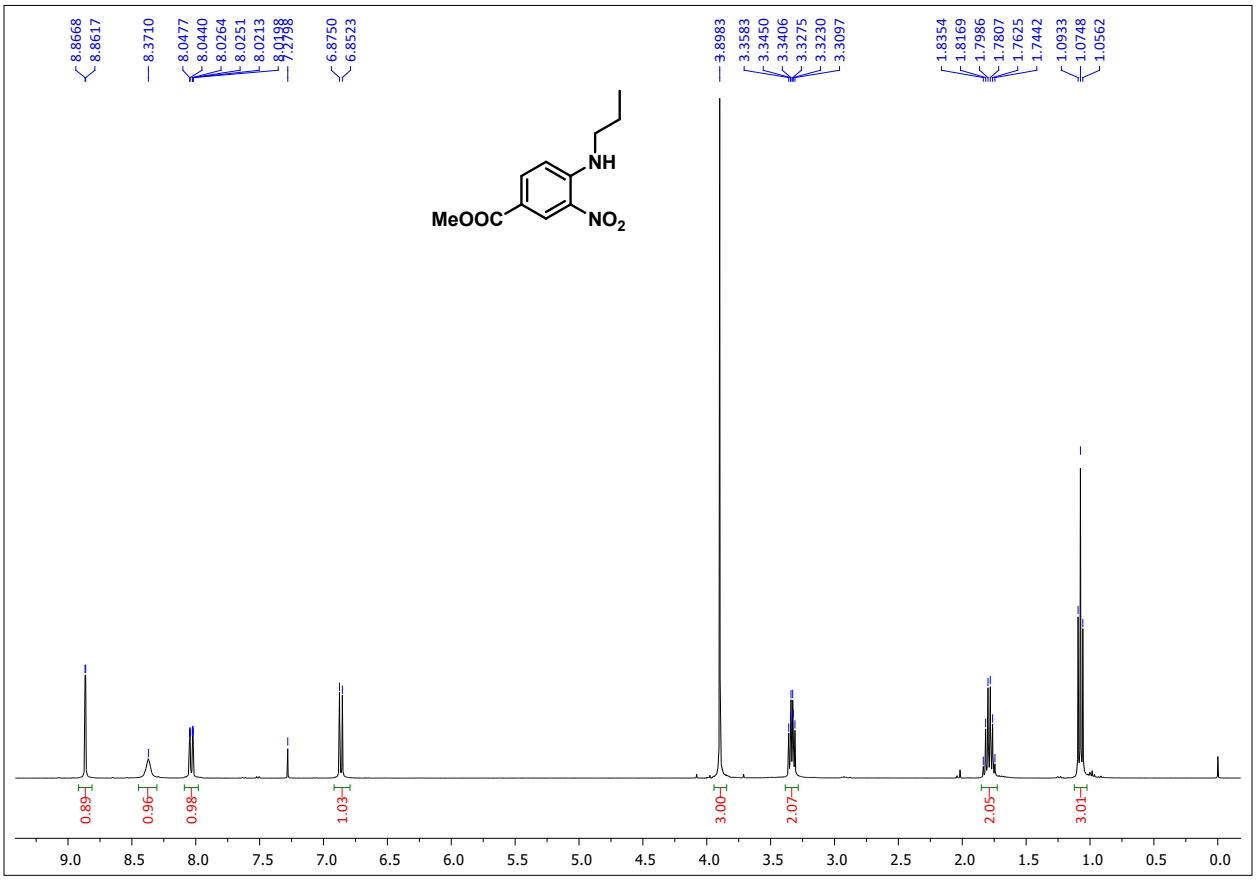


Figure S6. ^{1}H NMR of **2** in $CDCl_3$

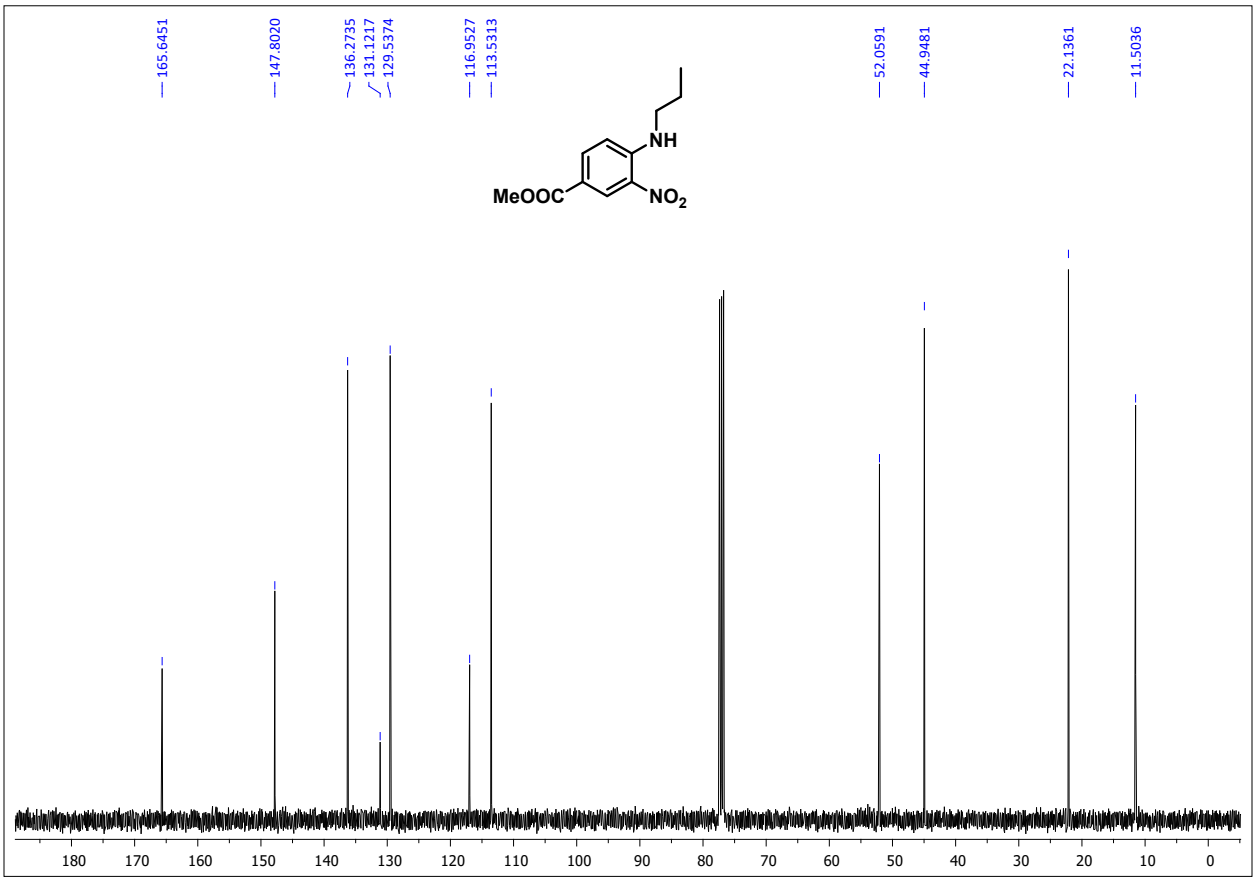


Figure S7. ^{13}C NMR of **2** in $CDCl_3$

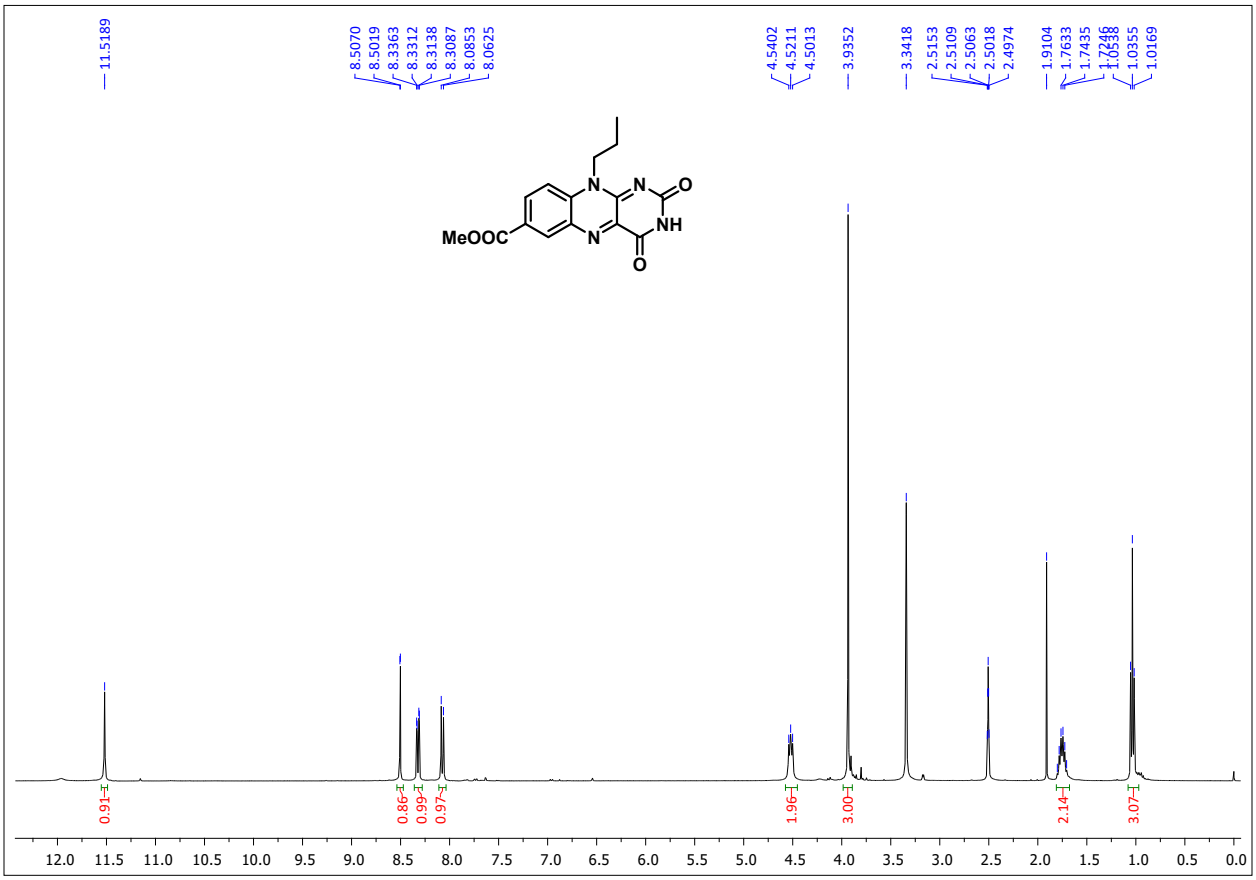


Figure S8. ^{1}H NMR of **3** in DMSO-d_6

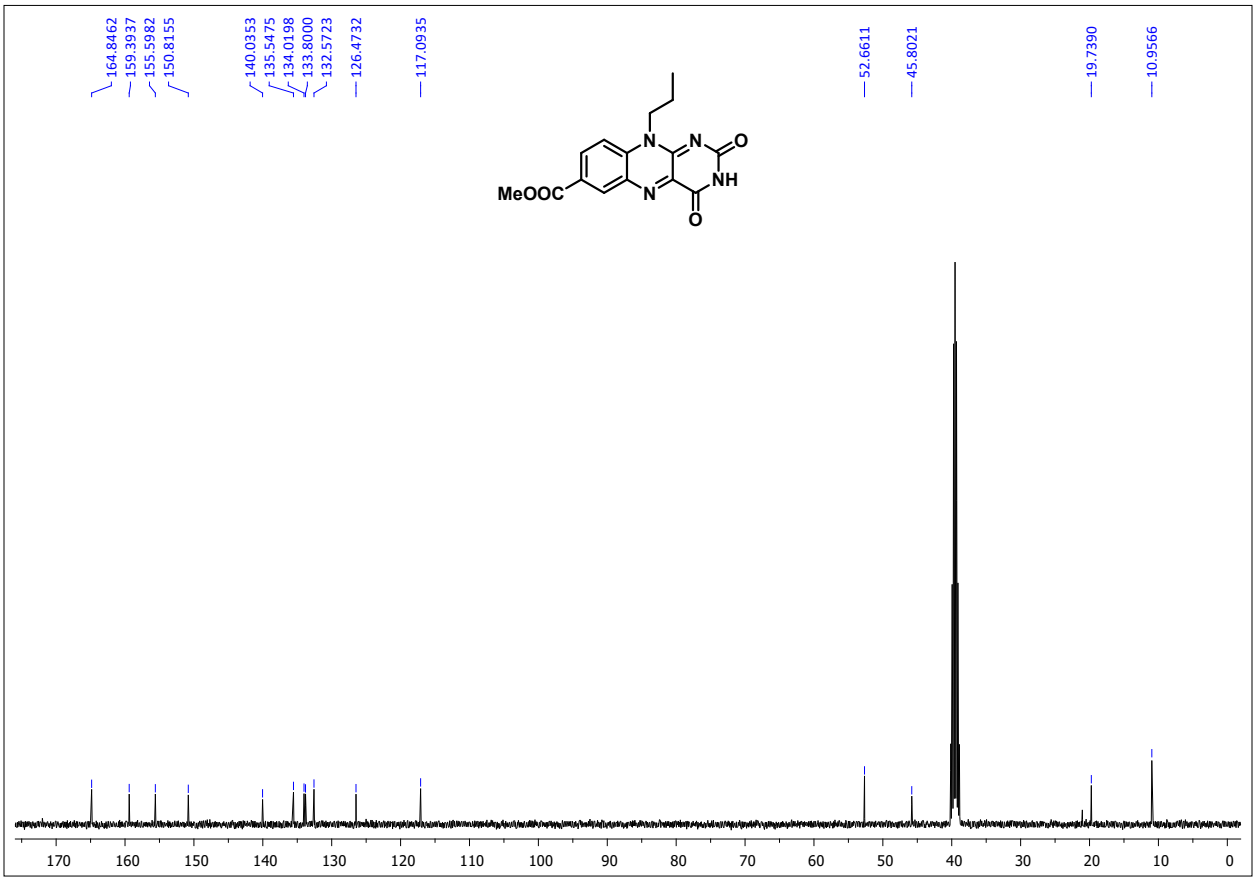


Figure S9. ^{13}C NMR of **3** in DMSO-d_6

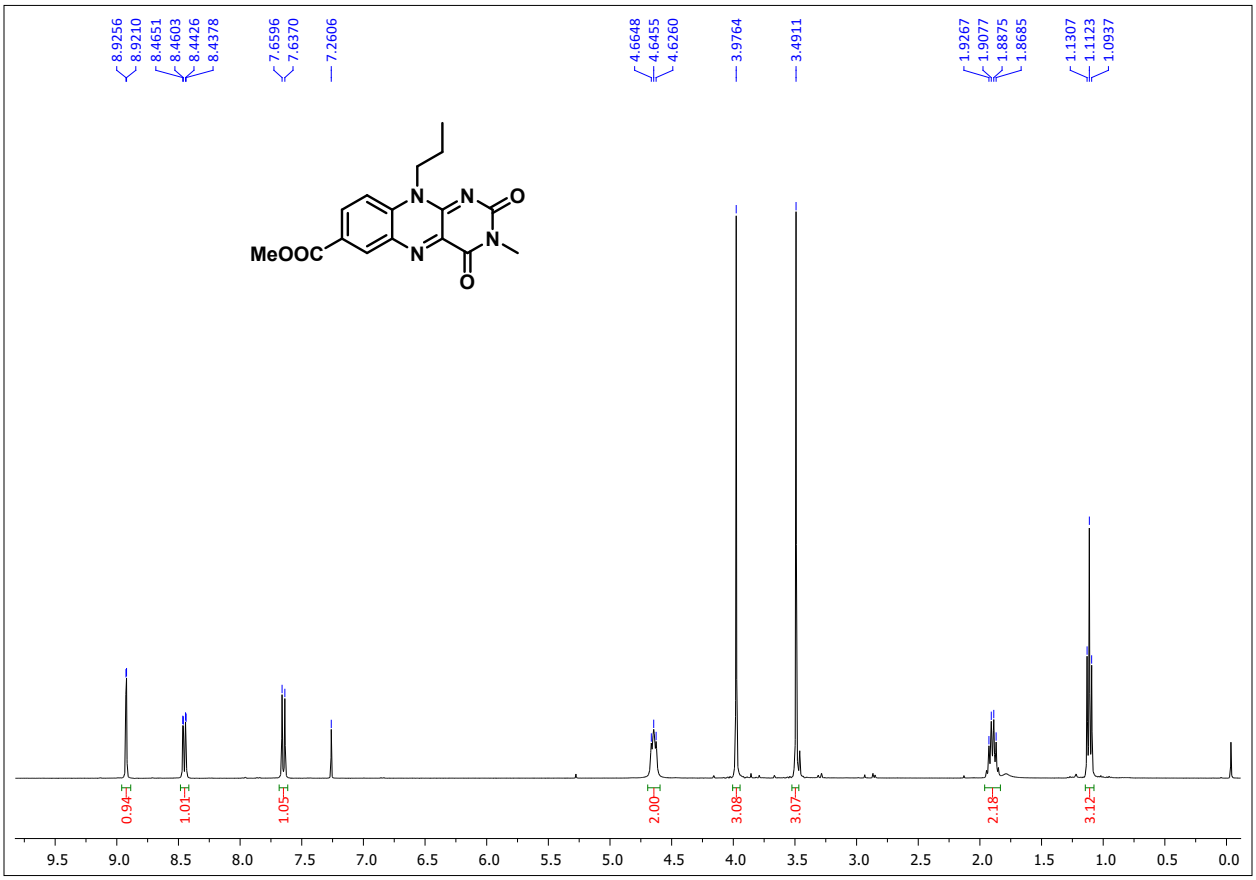


Figure S10. ^{1}H NMR of **4** in $CDCl_3$

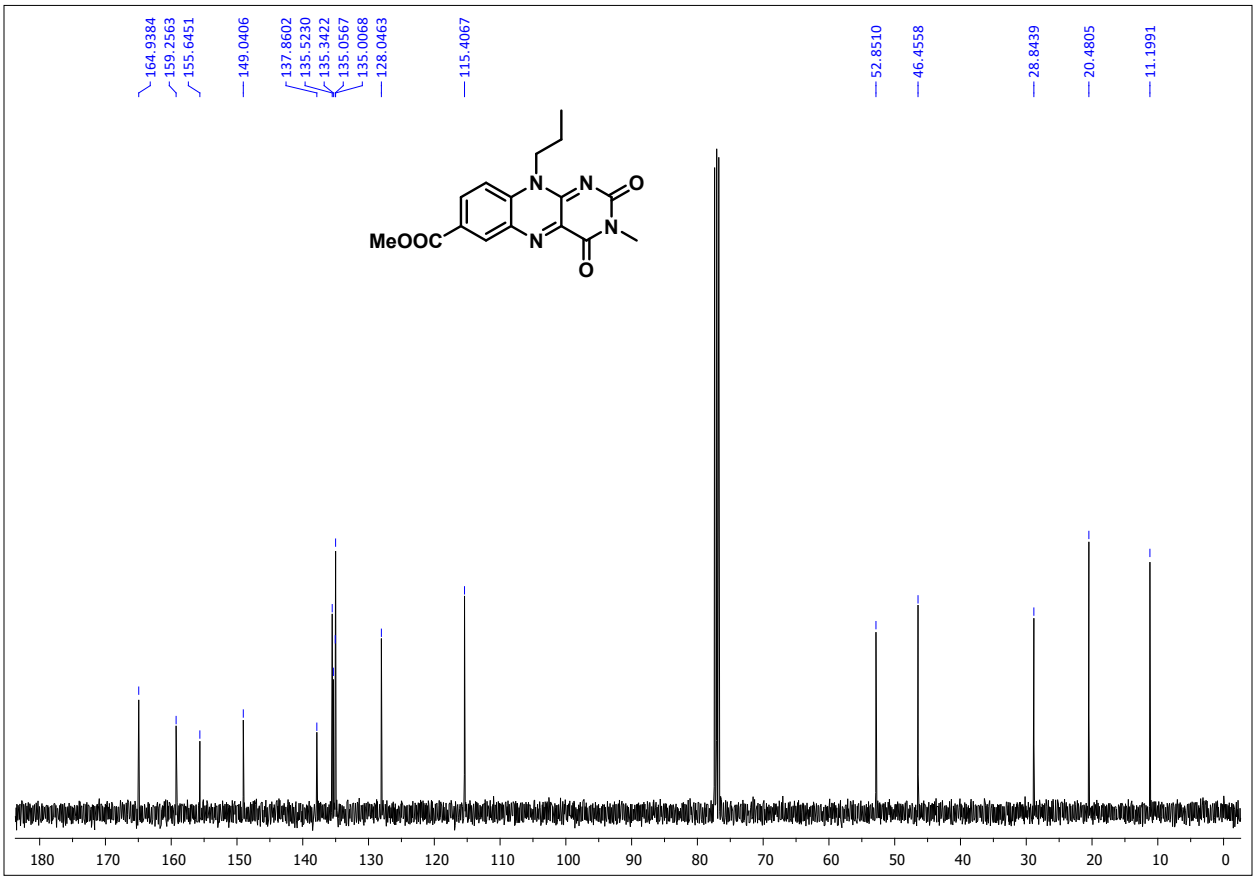


Figure S11. ^{13}C NMR of **4** in $CDCl_3$

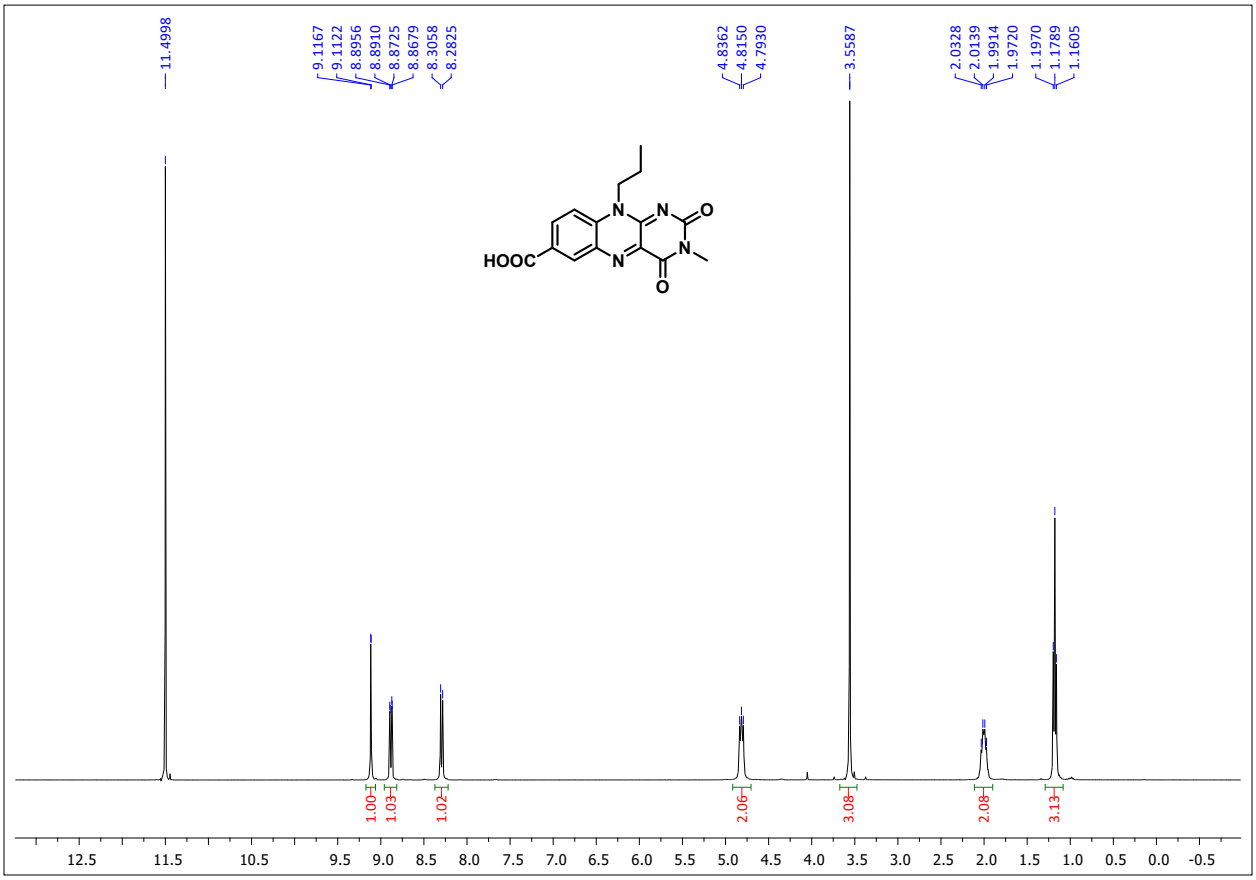


Figure S12. ^{1}H NMR of **Flc** in Trifluoroaceticacid-d

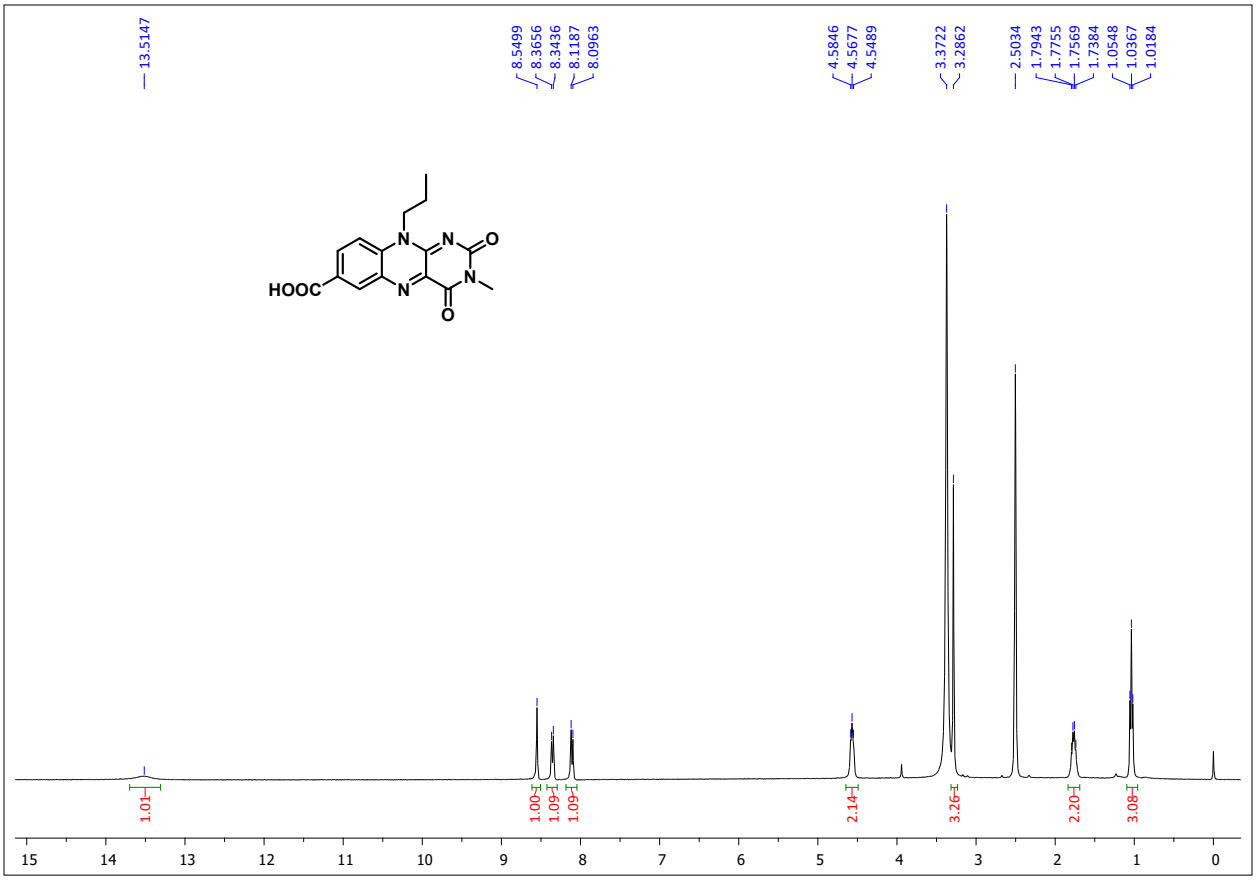


Figure S13. ^{1}H NMR of **Flc** in DMSO-d_6

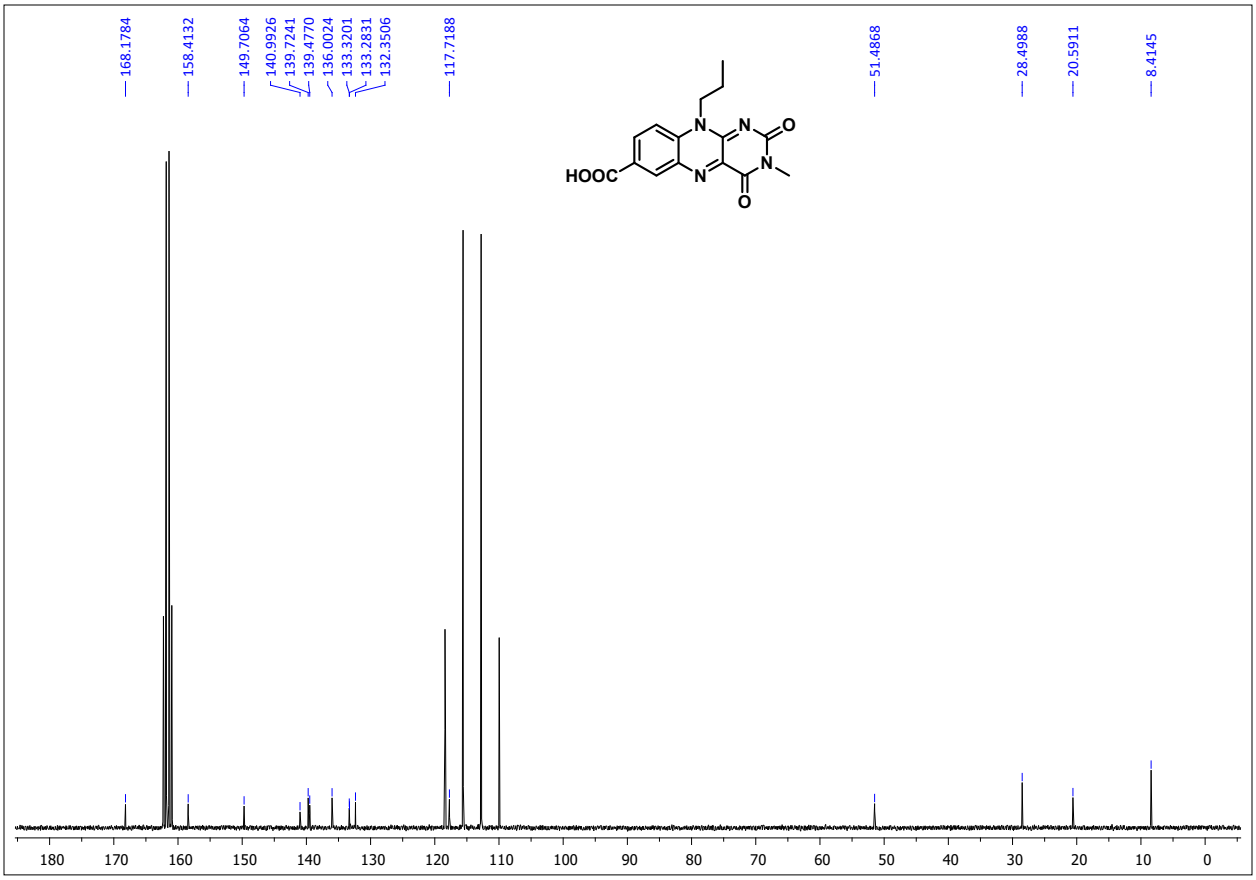


Figure S14. ^{13}C NMR of **Flc** in Trifluoroaceticacid-d

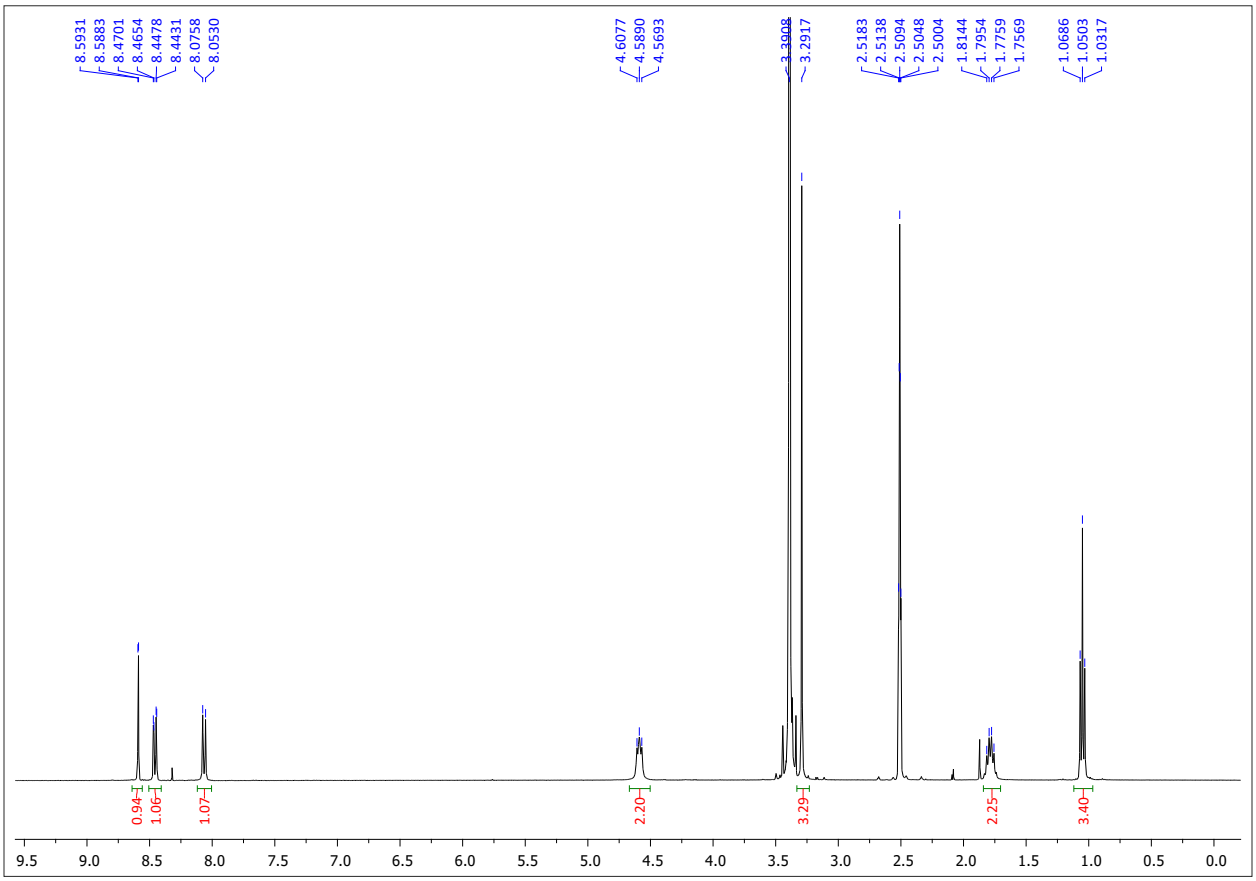


Figure S15. ^{1}H NMR of **Flc-Cd** in DMSO-d_6

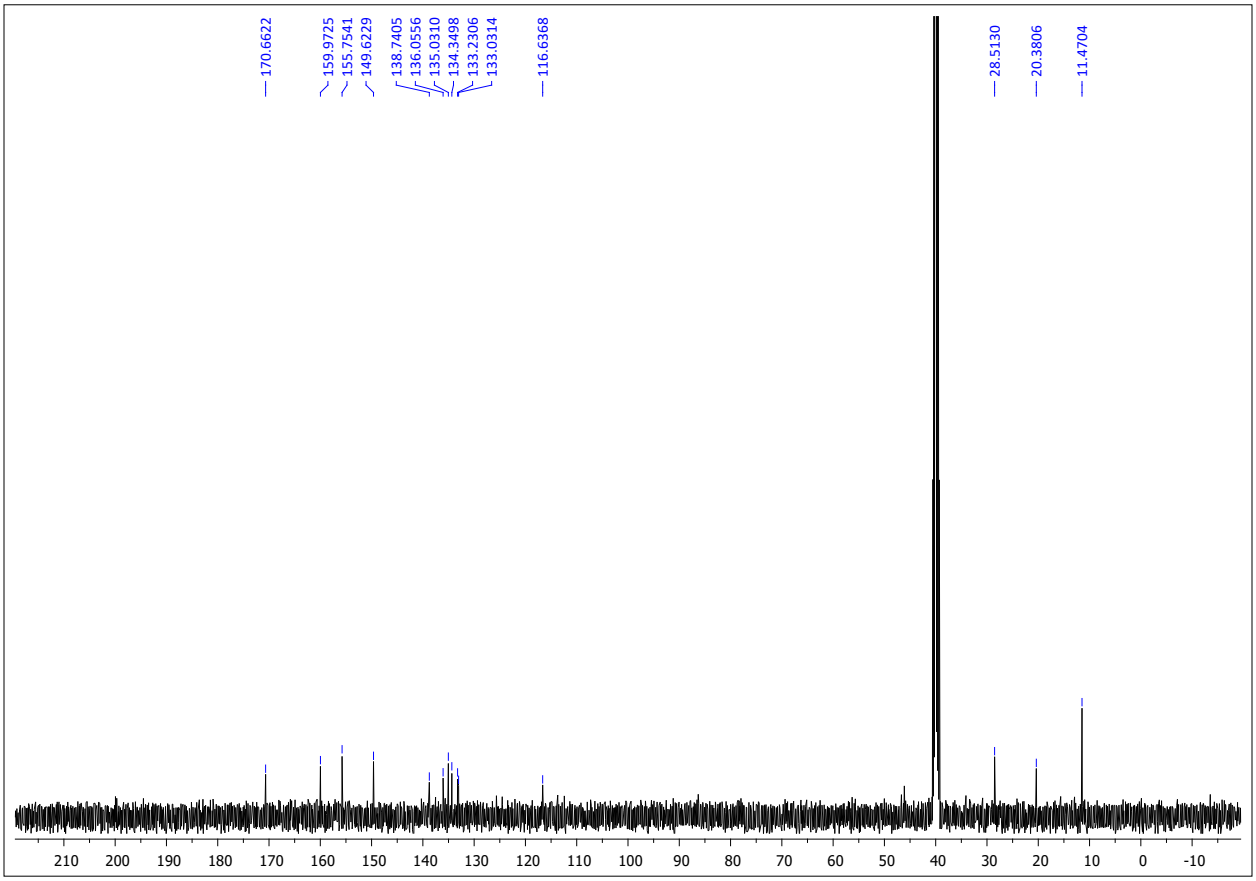


Figure S16. ^{13}C NMR of **Flc-Cd** in DMSO-d_6

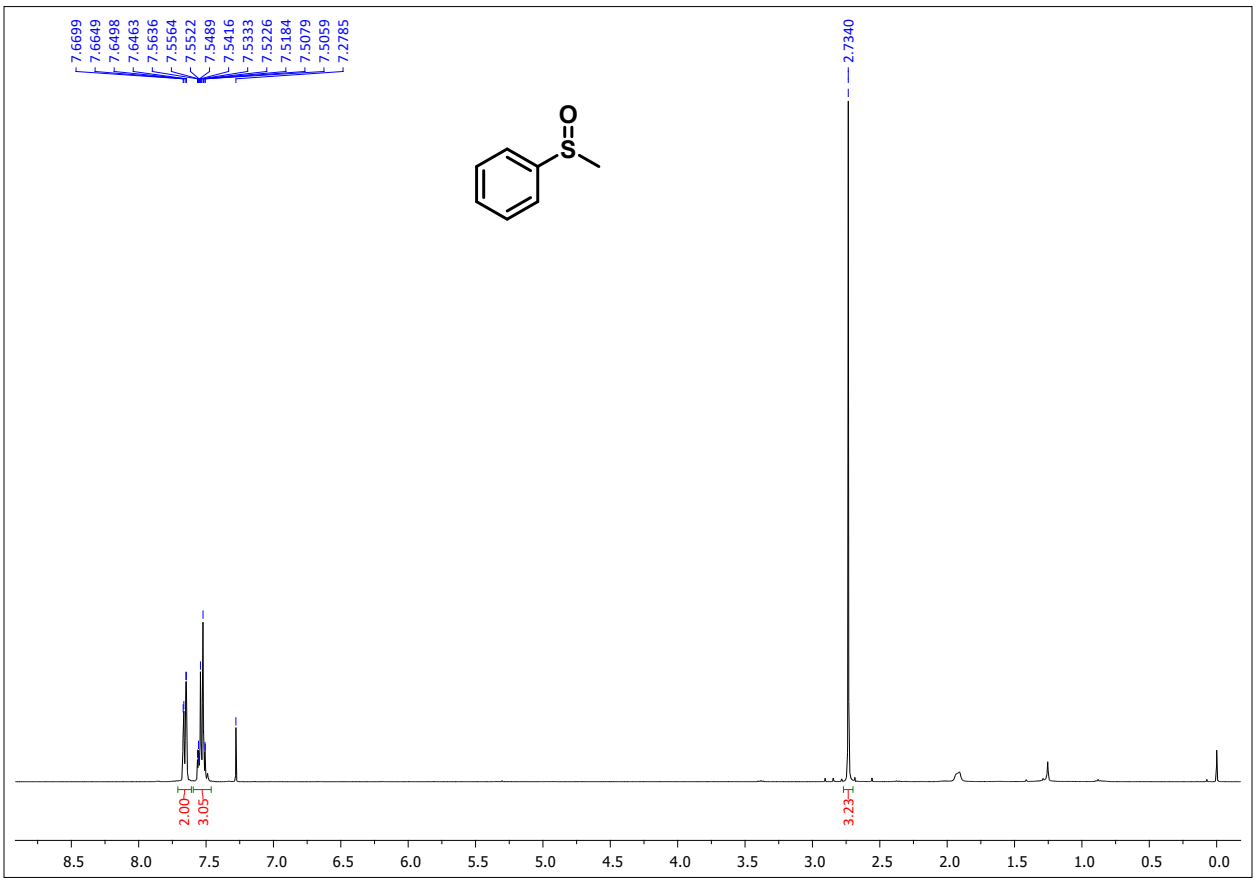


Figure S17. ^{1}H NMR of Methyl phenyl sulphoxide in $CDCl_3$

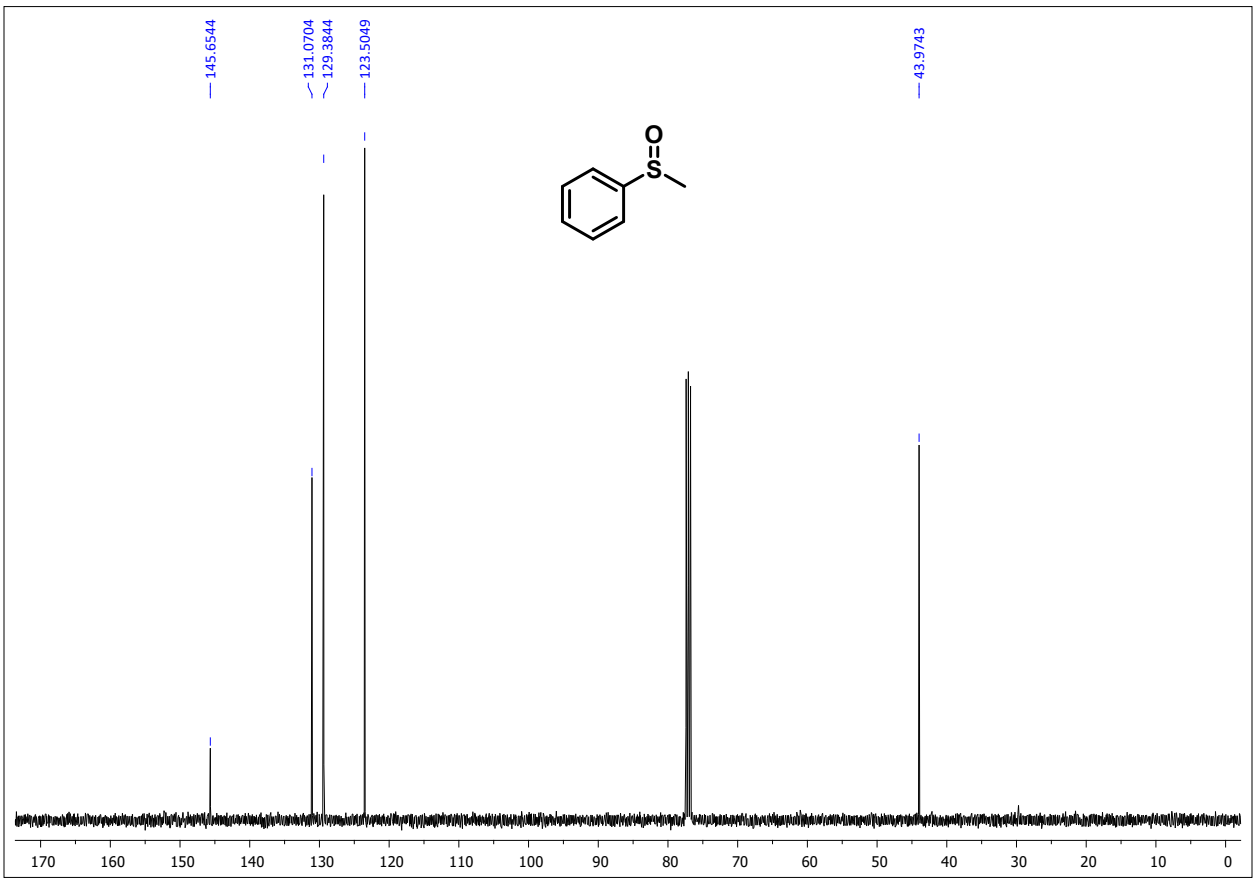


Figure S18. ^{13}C NMR of Methyl phenyl sulphoxide in $CDCl_3$

Figure S19. ^{1}H NMR of Methyl p-tolyl sulphoxide in $CDCl_3$

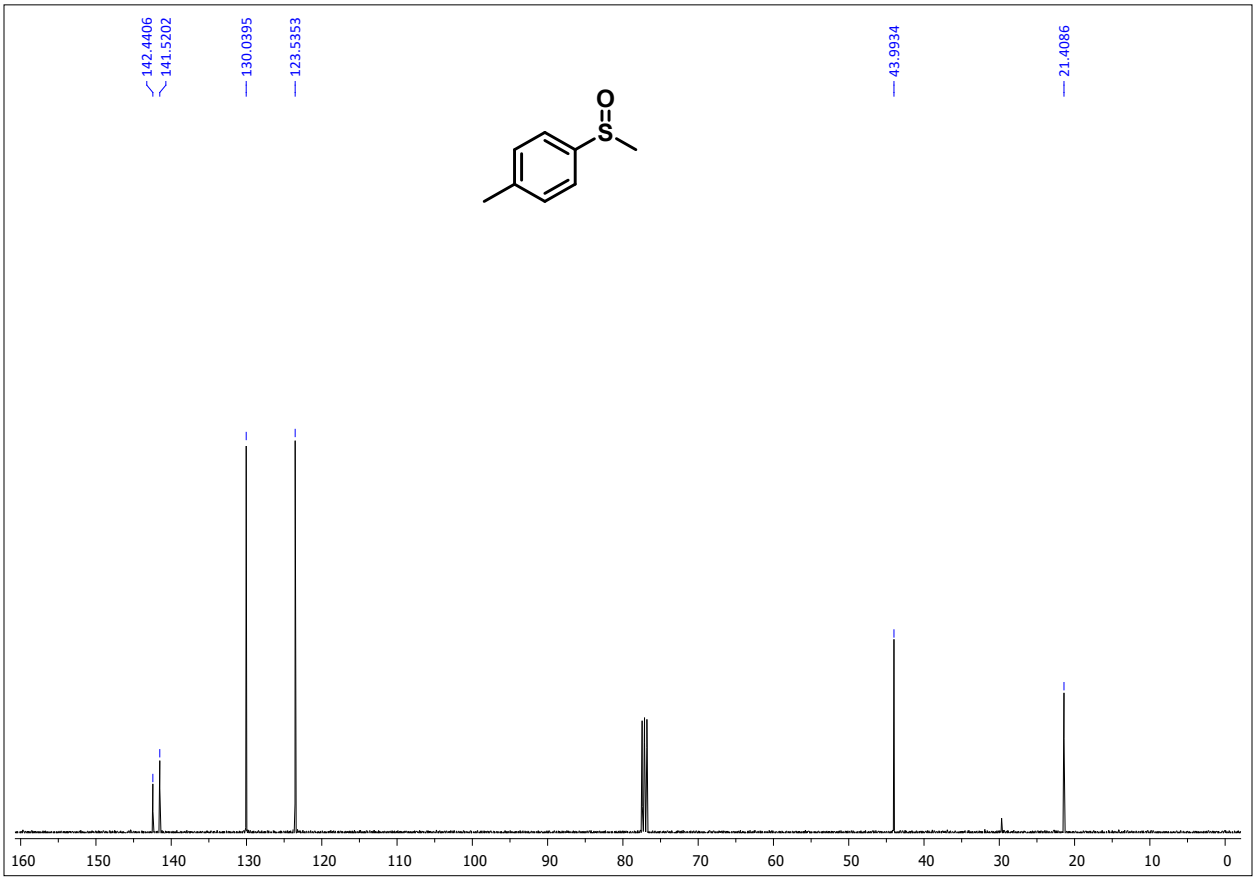


Figure S20. ^{13}C NMR of Methyl p-tolyl sulphoxide in $CDCl_3$

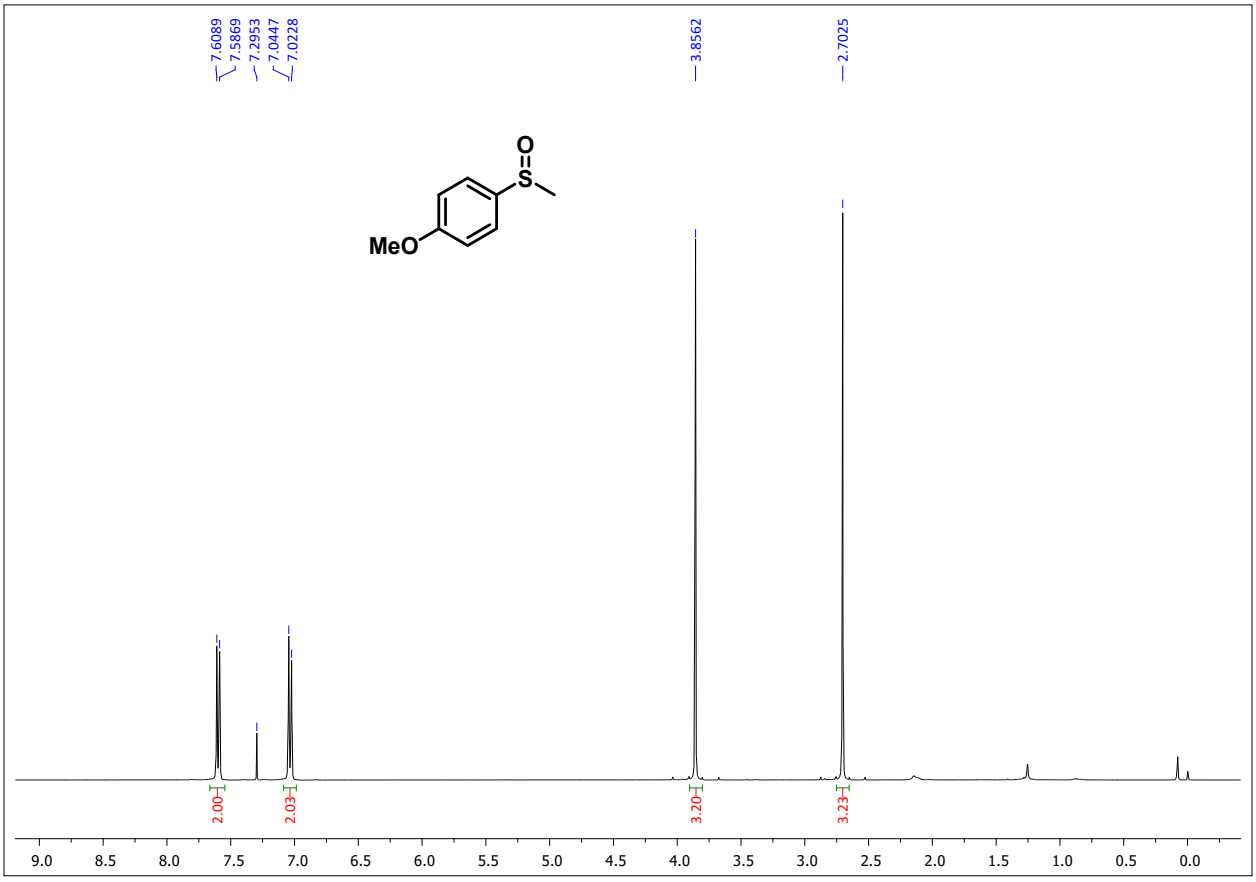


Figure S21. ^{1}H NMR of 4-Methoxyphenyl methyl sulphoxide in $CDCl_3$

\

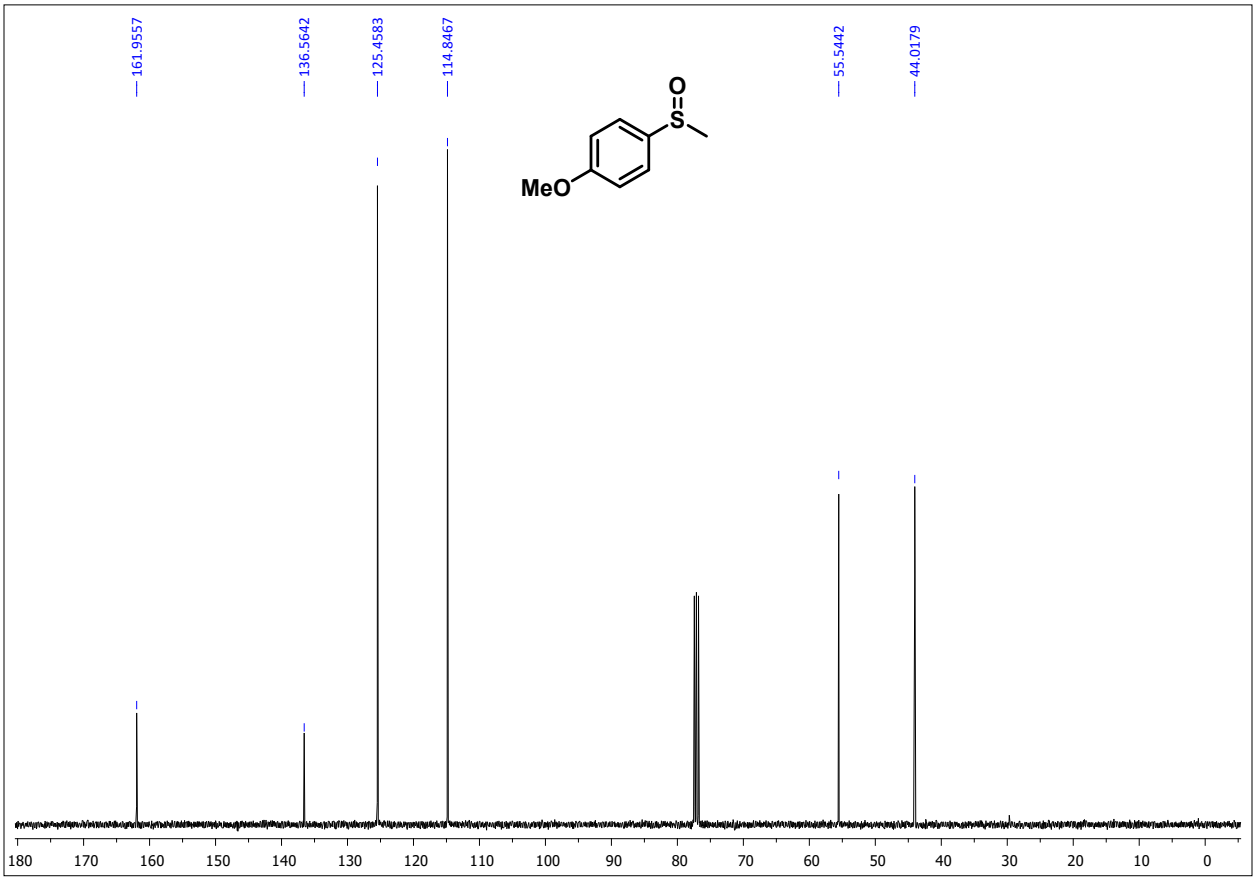


Figure S22. ^{13}C NMR of 4-Methoxyphenyl methyl sulphoxide in $CDCl_3$

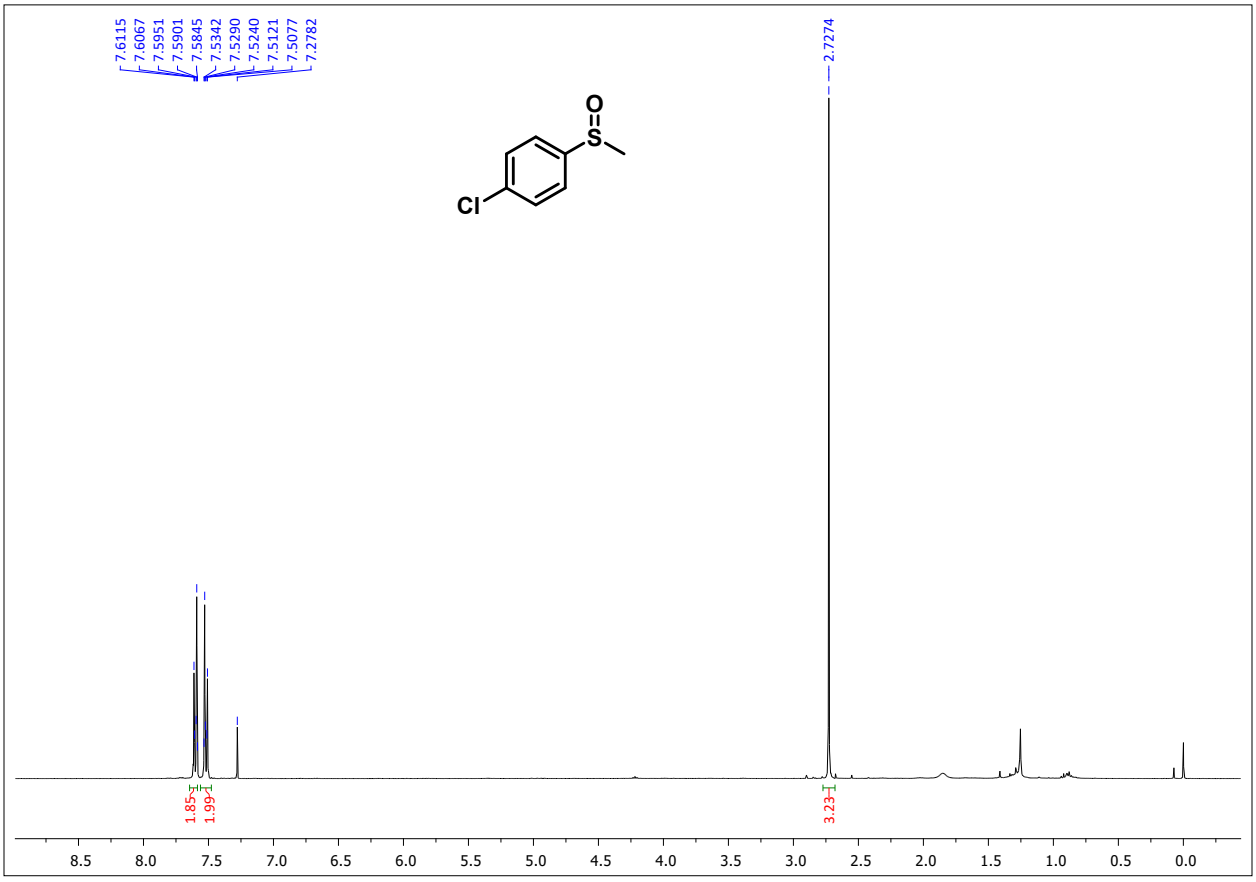


Figure S23. ^{1}H NMR of 4-Chlorophenyl methyl sulphoxide in $CDCl_3$

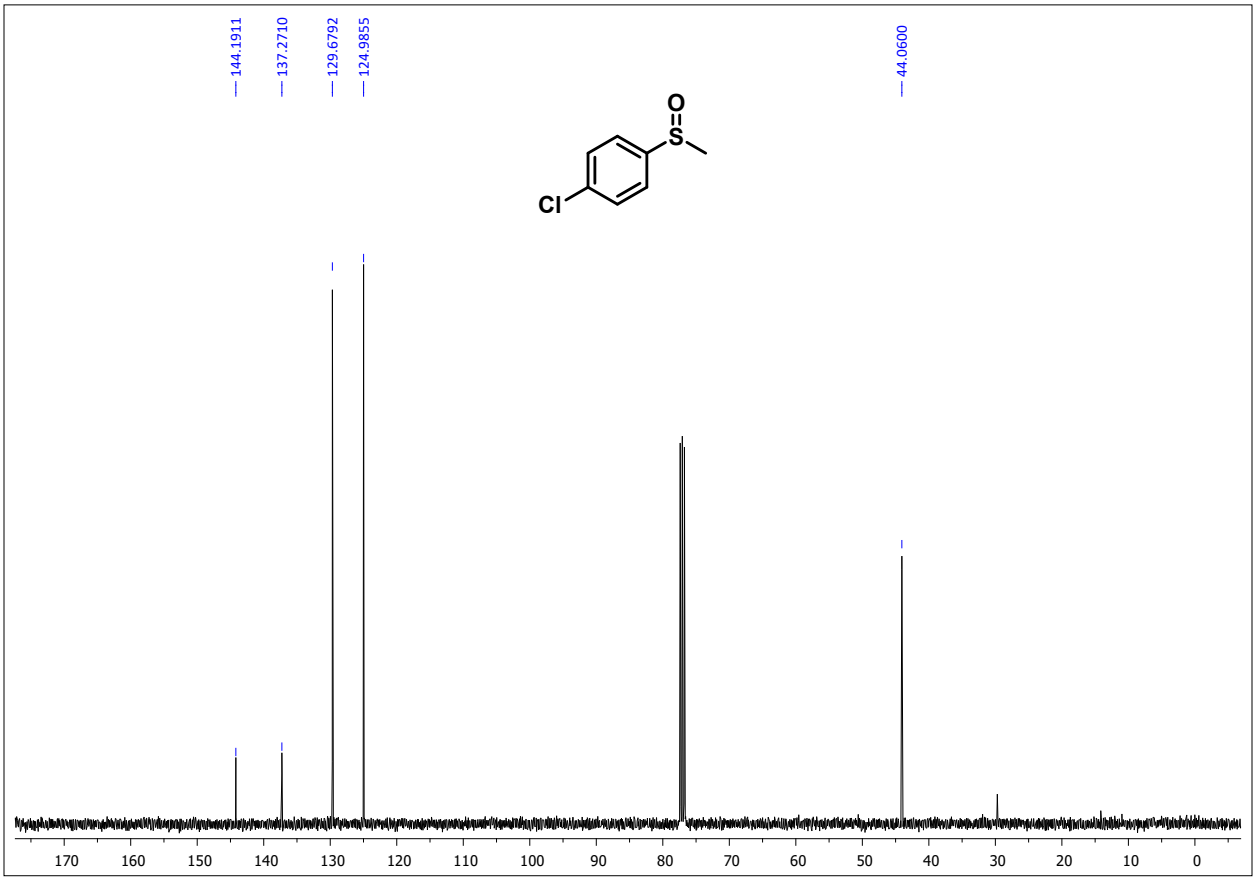


Figure S24. ^{13}C NMR of 4-Chlorophenyl methyl sulphoxide in $CDCl_3$

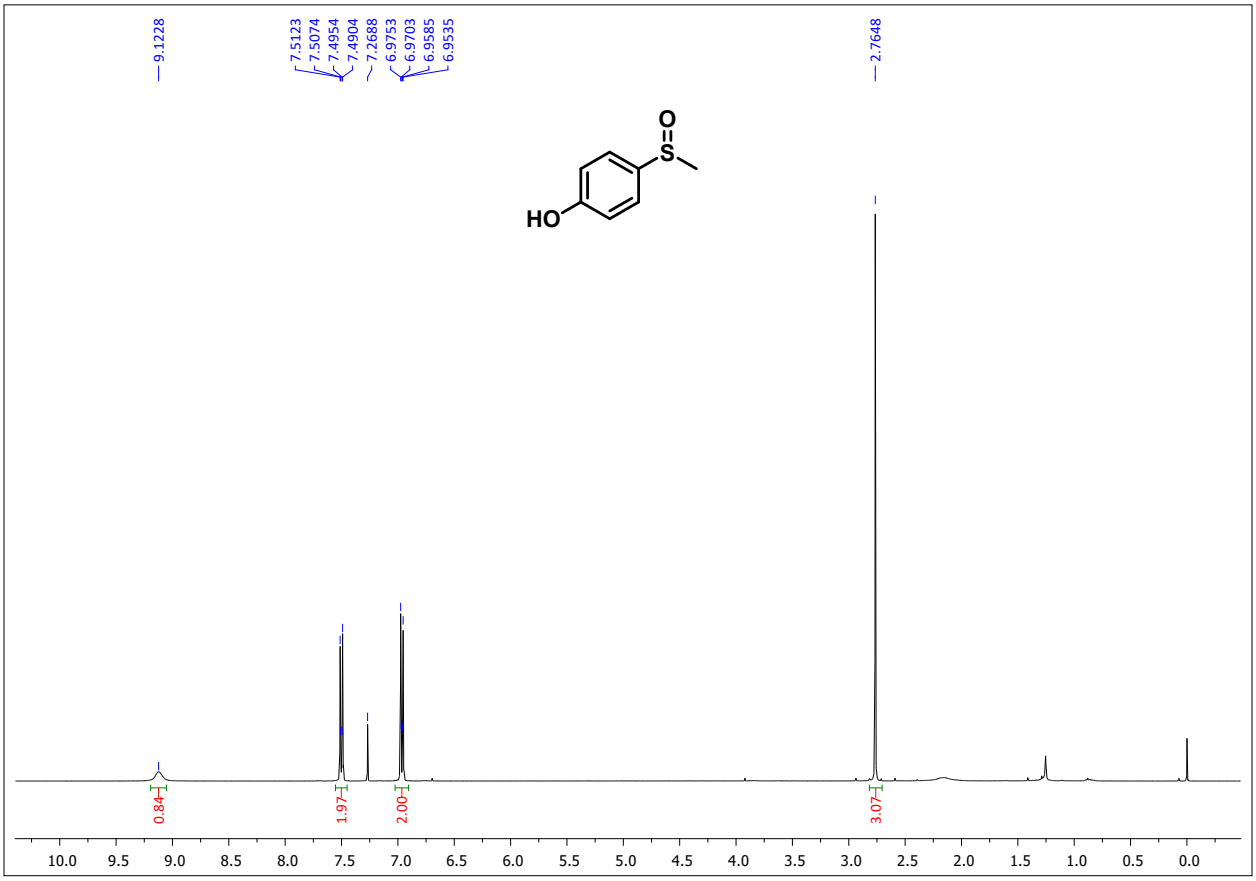


Figure S25. ^{1}H NMR of 4-Hydroxyphenyl methyl sulphoxide in $CDCl_3$

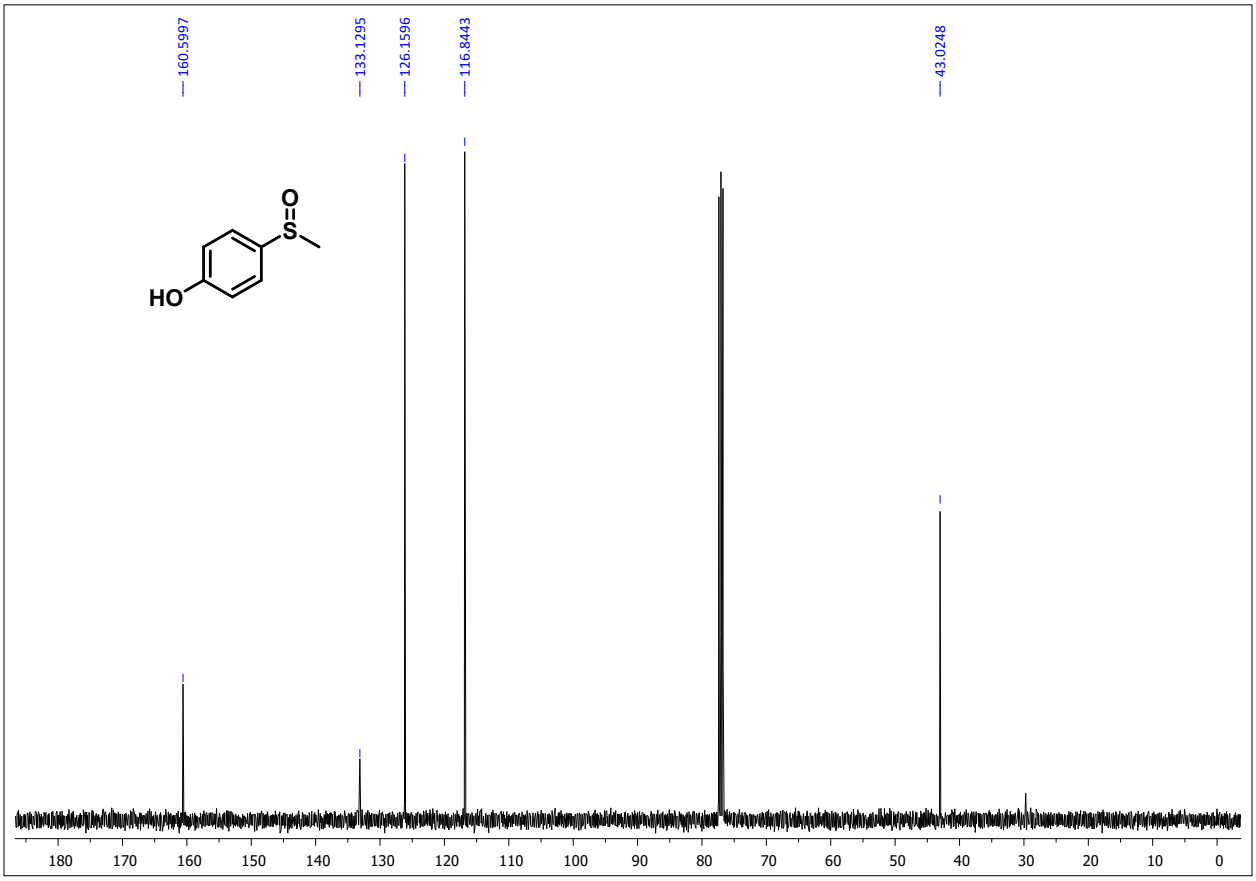


Figure S26. ^{13}C NMR of 4-Hydroxyphenyl methyl sulphoxide in $CDCl_3$

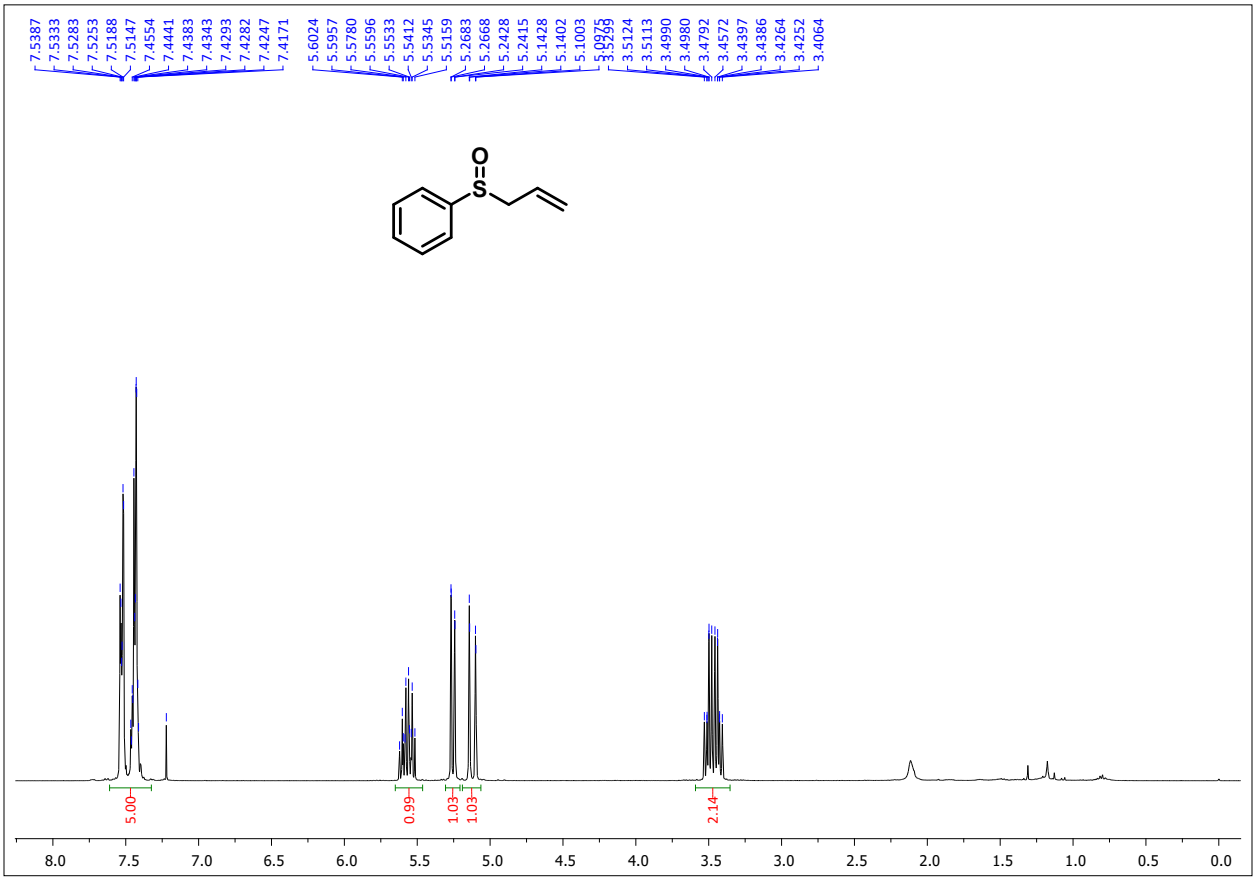


Figure S27. ^{1}H NMR of Allylphenyl sulphoxide in $CDCl_3$

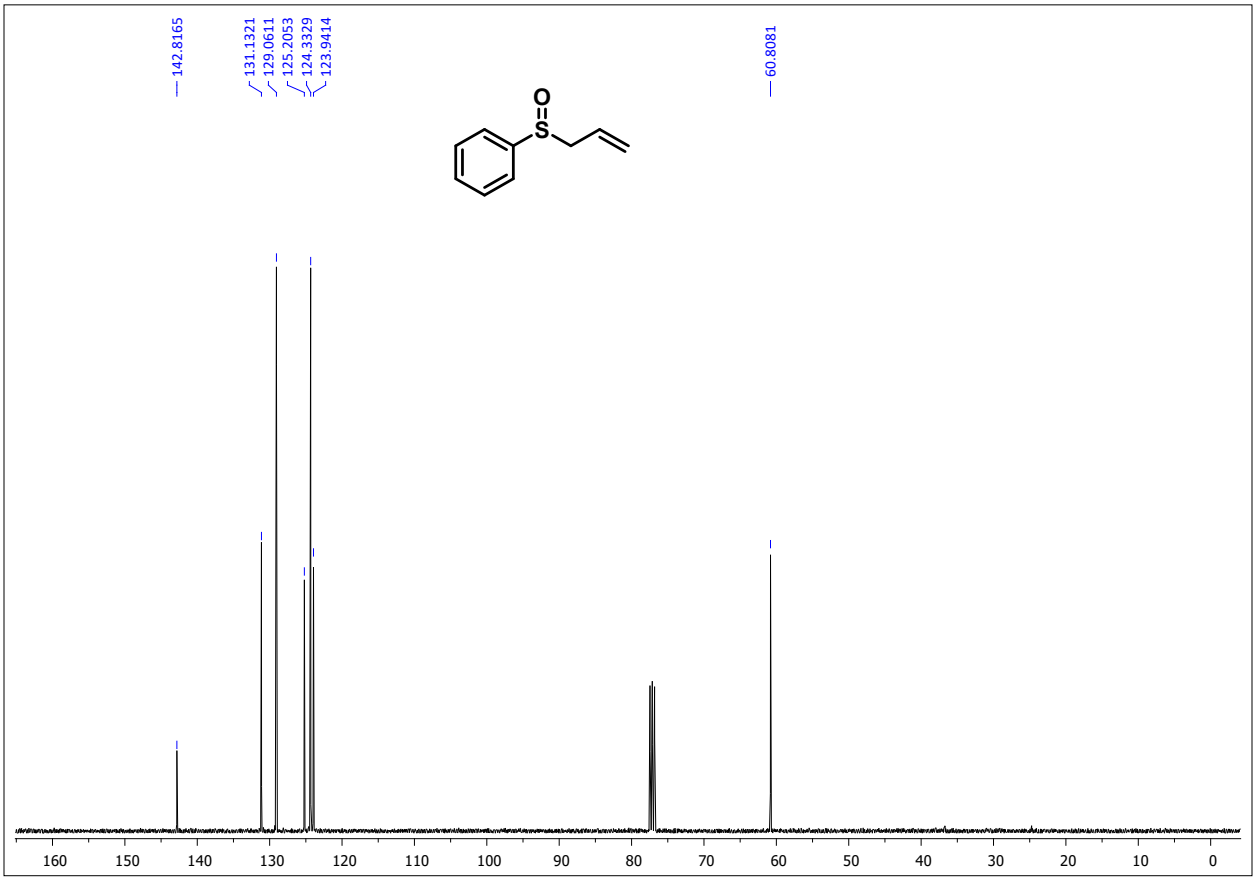


Figure S28. ^{13}C NMR of Allylphenyl sulphoxide in $CDCl_3$

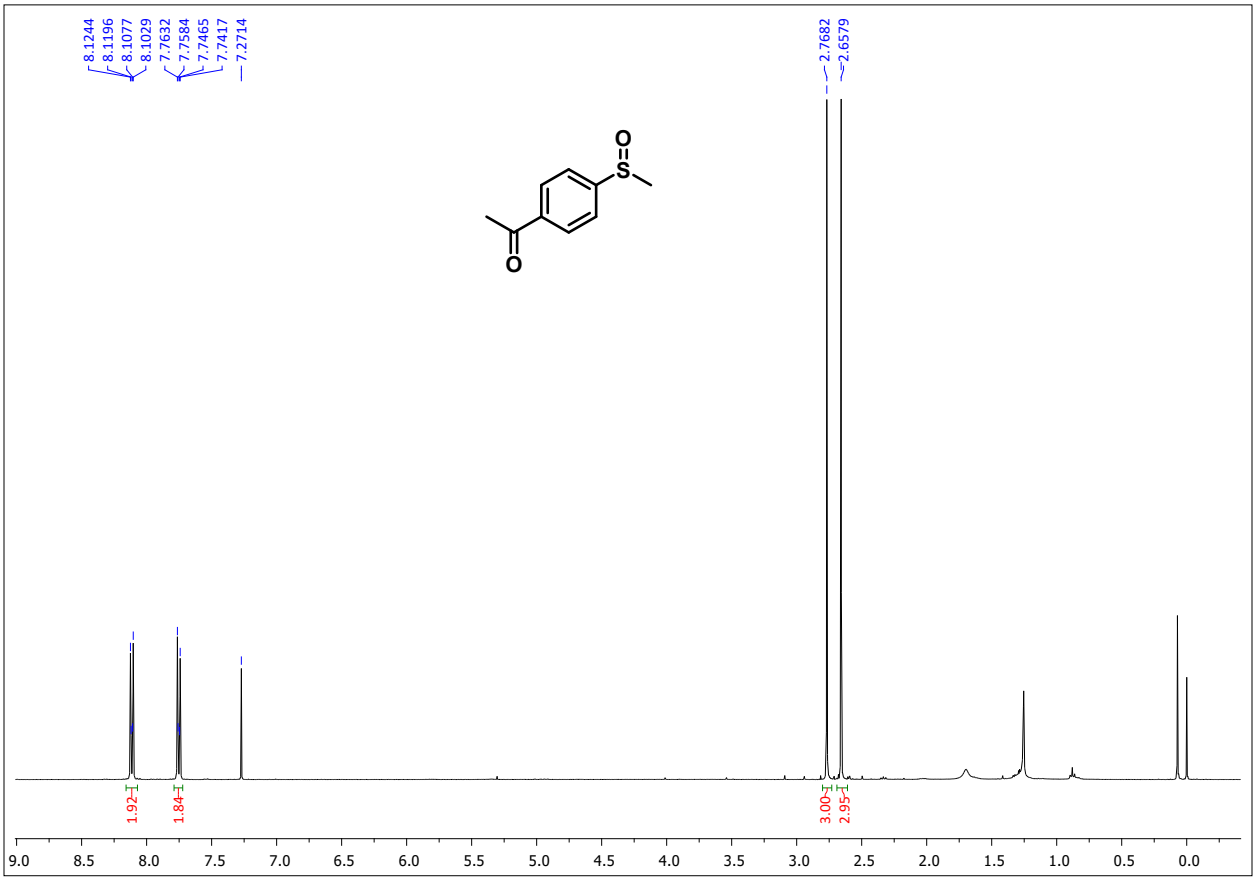


Figure S29. ^{1}H NMR of 4-Acetylphenyl methyl sulphoxide in $CDCl_3$

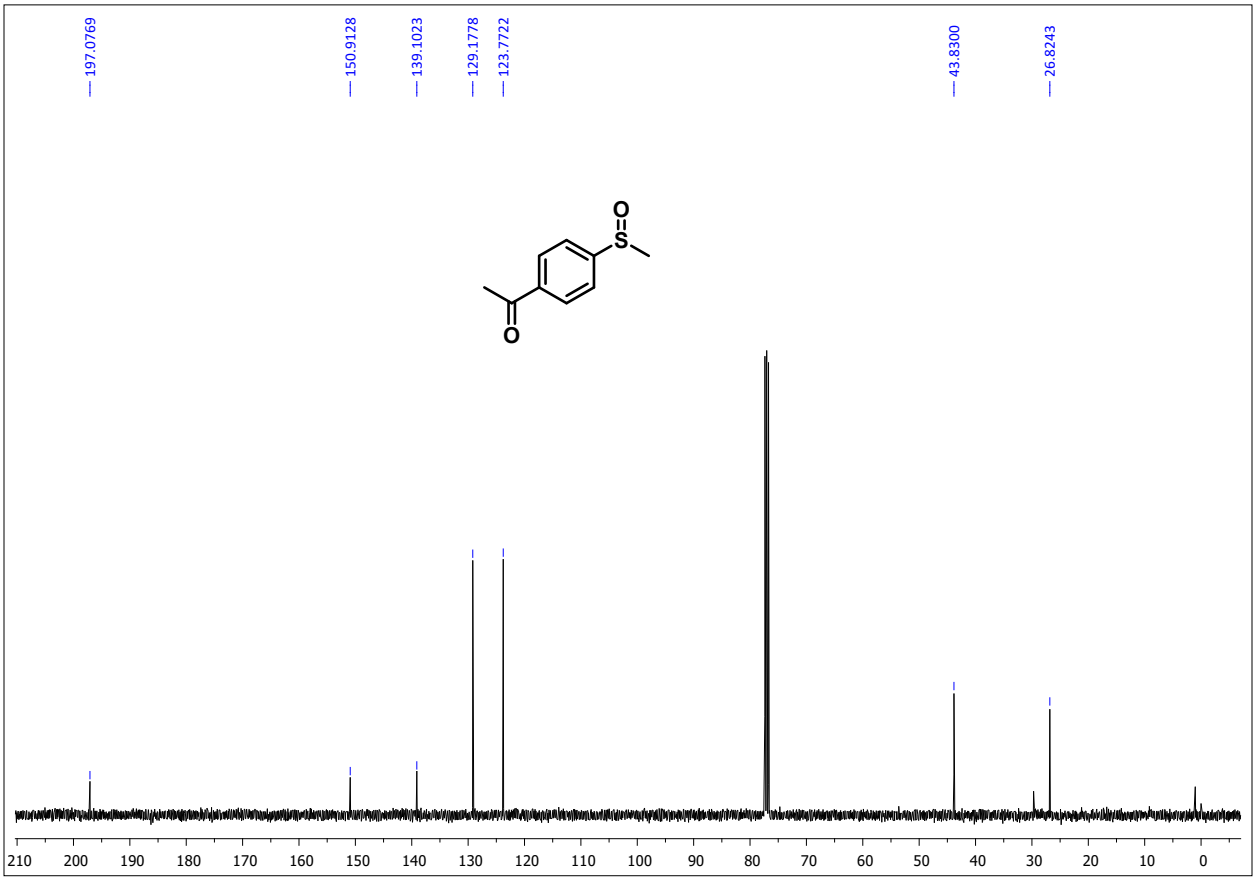


Figure S30. ^{13}C NMR of 4-Acetylphenyl methyl sulphoxide in $CDCl_3$

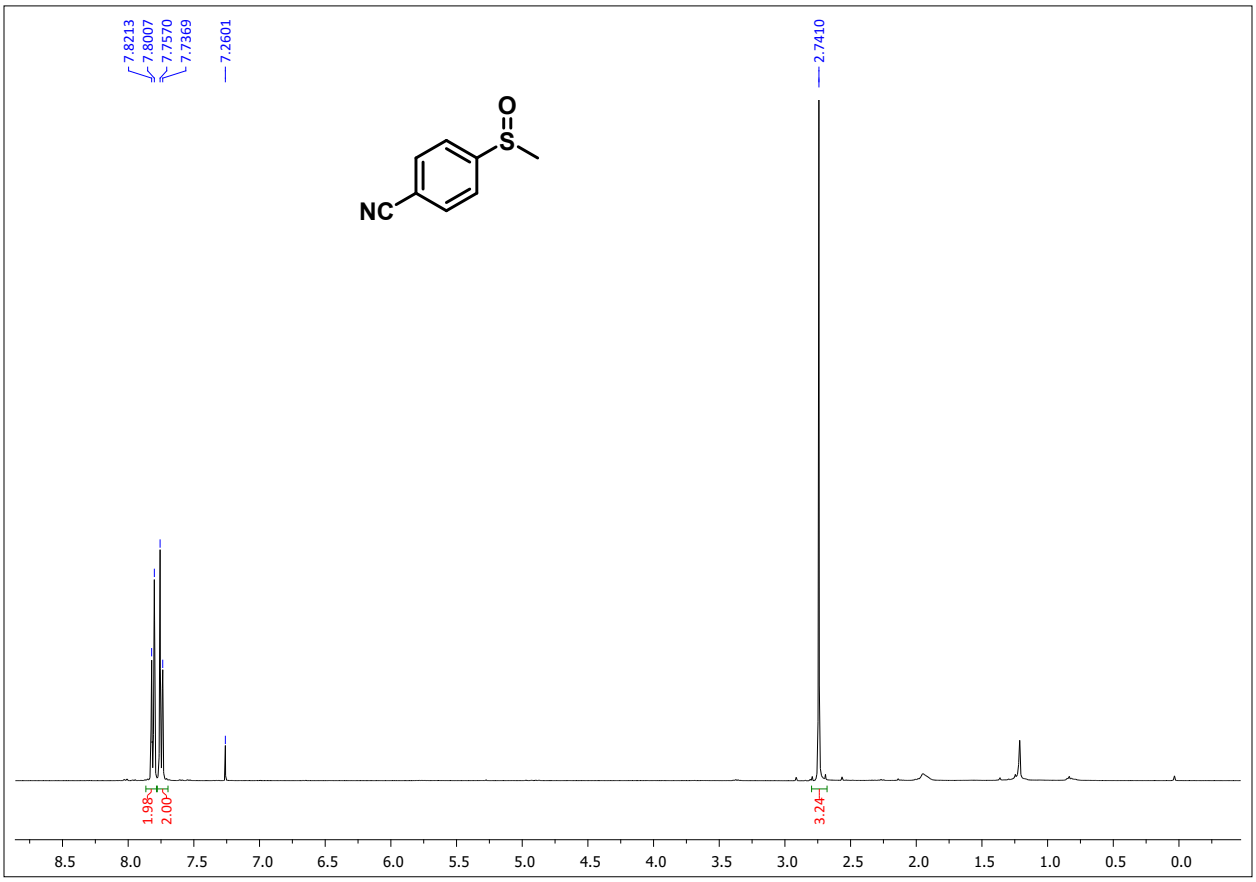


Figure S31. ^{1}H NMR of 4-Cyanophenyl methyl sulphoxide in $CDCl_3$

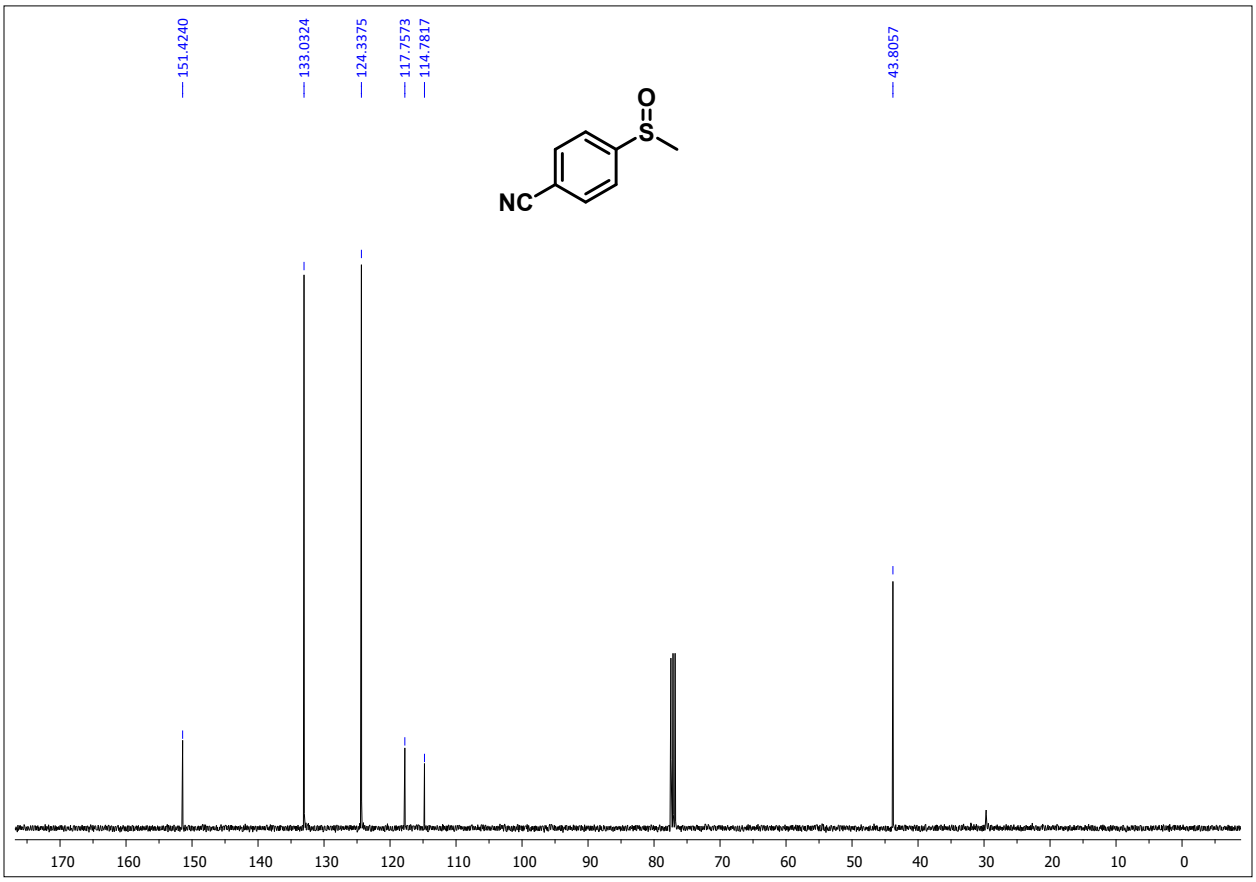


Figure S32. ^{13}C NMR of 4-Cyanophenyl methyl sulphoxide in $CDCl_3$

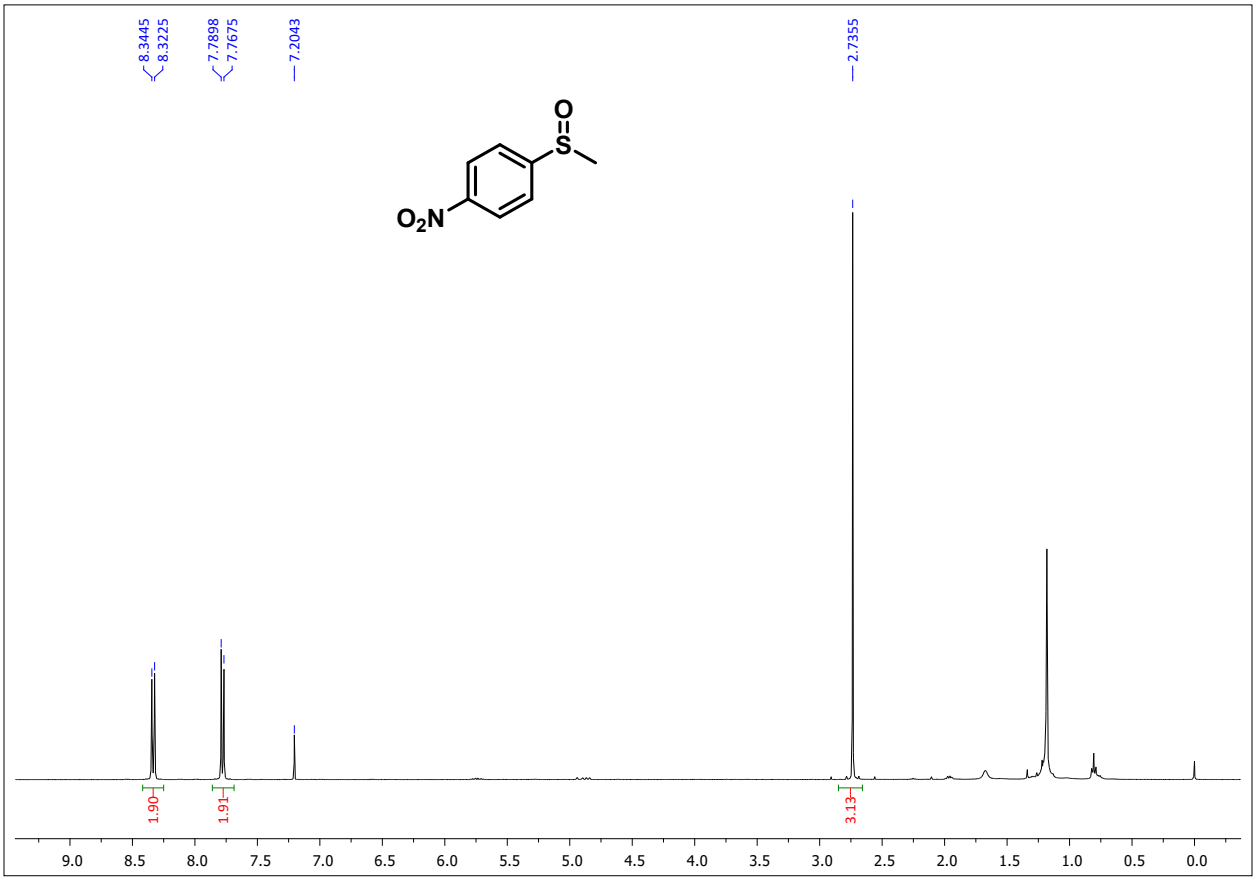


Figure S33. ^{1}H NMR of 4-Nitrophenyl methyl sulphoxide in $CDCl_3$

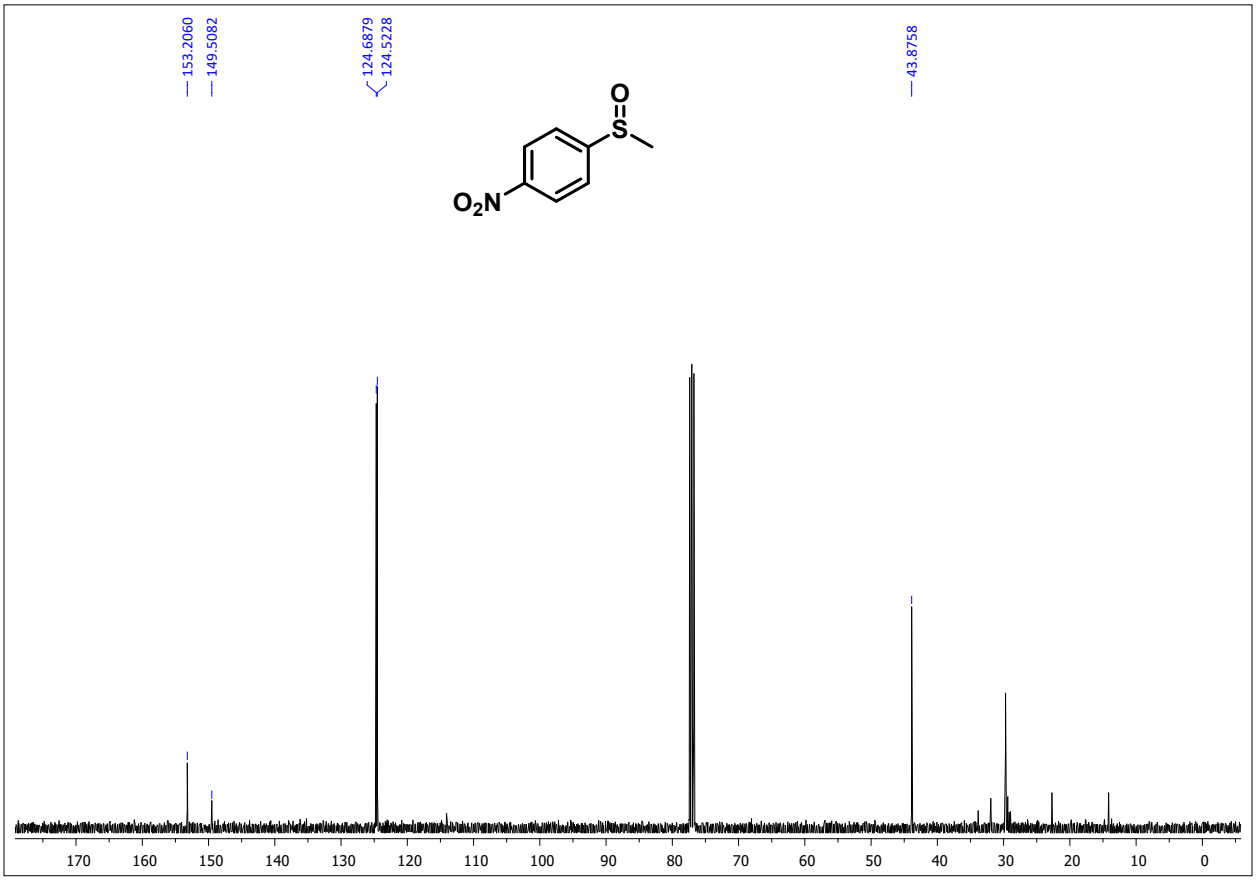


Figure S34. ^{13}C NMR of 4-Nitrophenyl methyl sulphoxide in $CDCl_3$

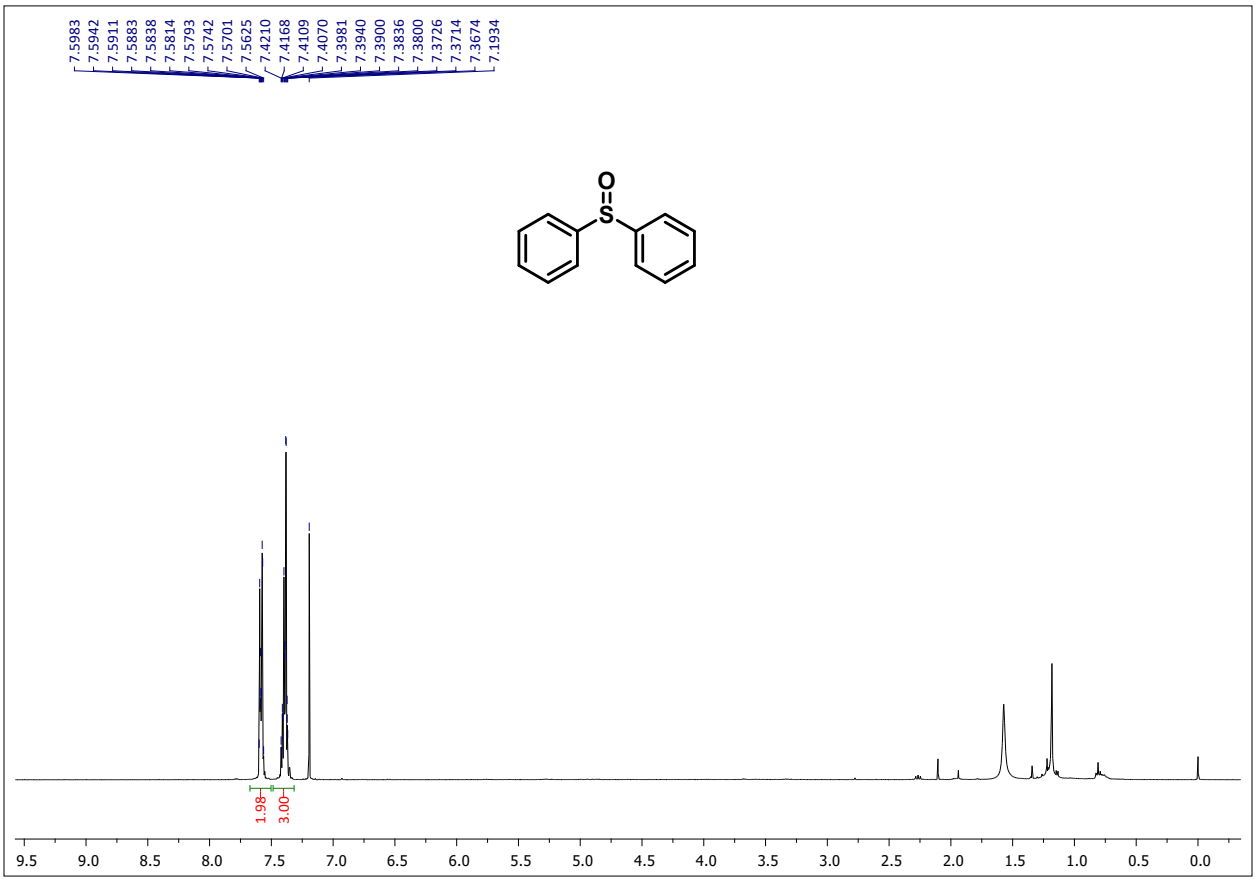


Figure S35. ^{1}H NMR of Diphenyl sulphoxide in $CDCl_3$

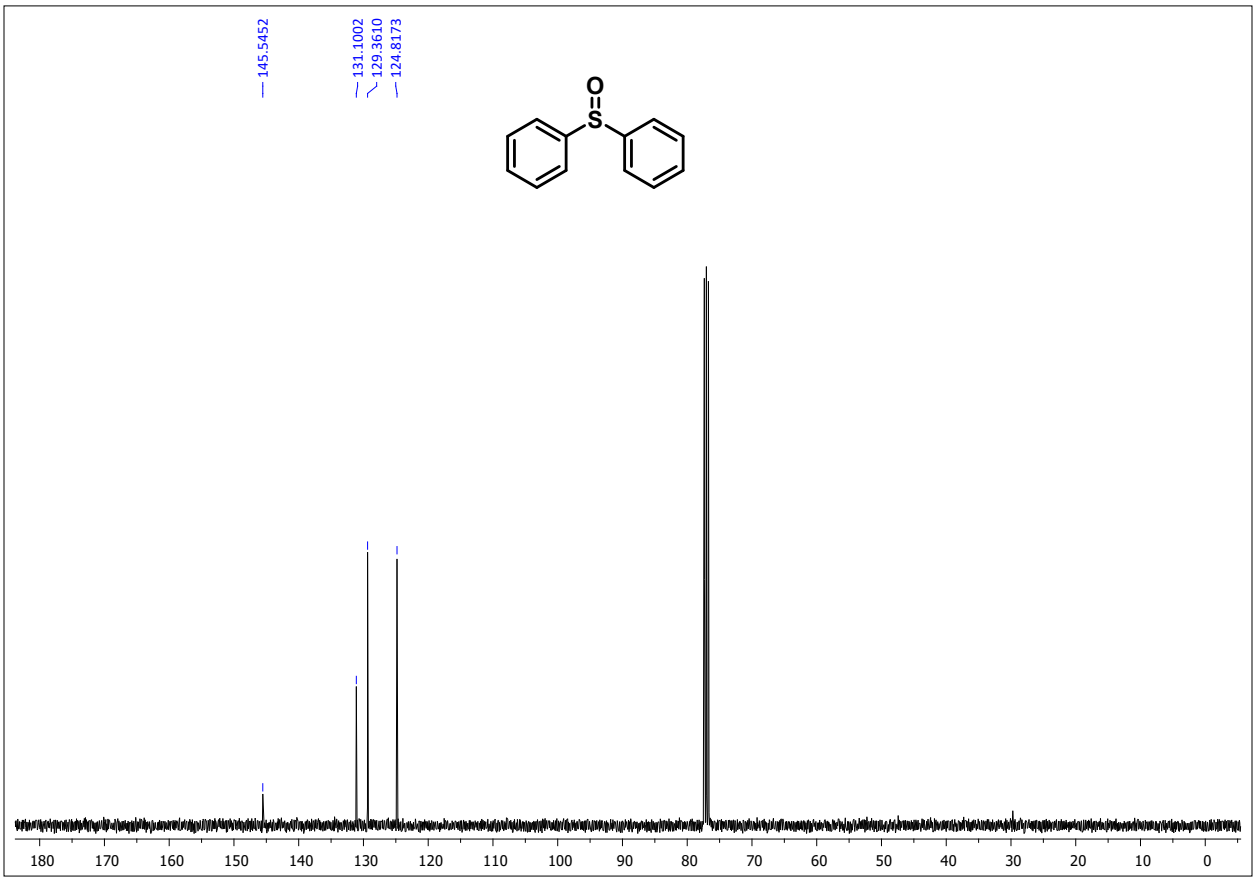


Figure S36. ^{13}C NMR of Diphenyl sulphoxide in $CDCl_3$

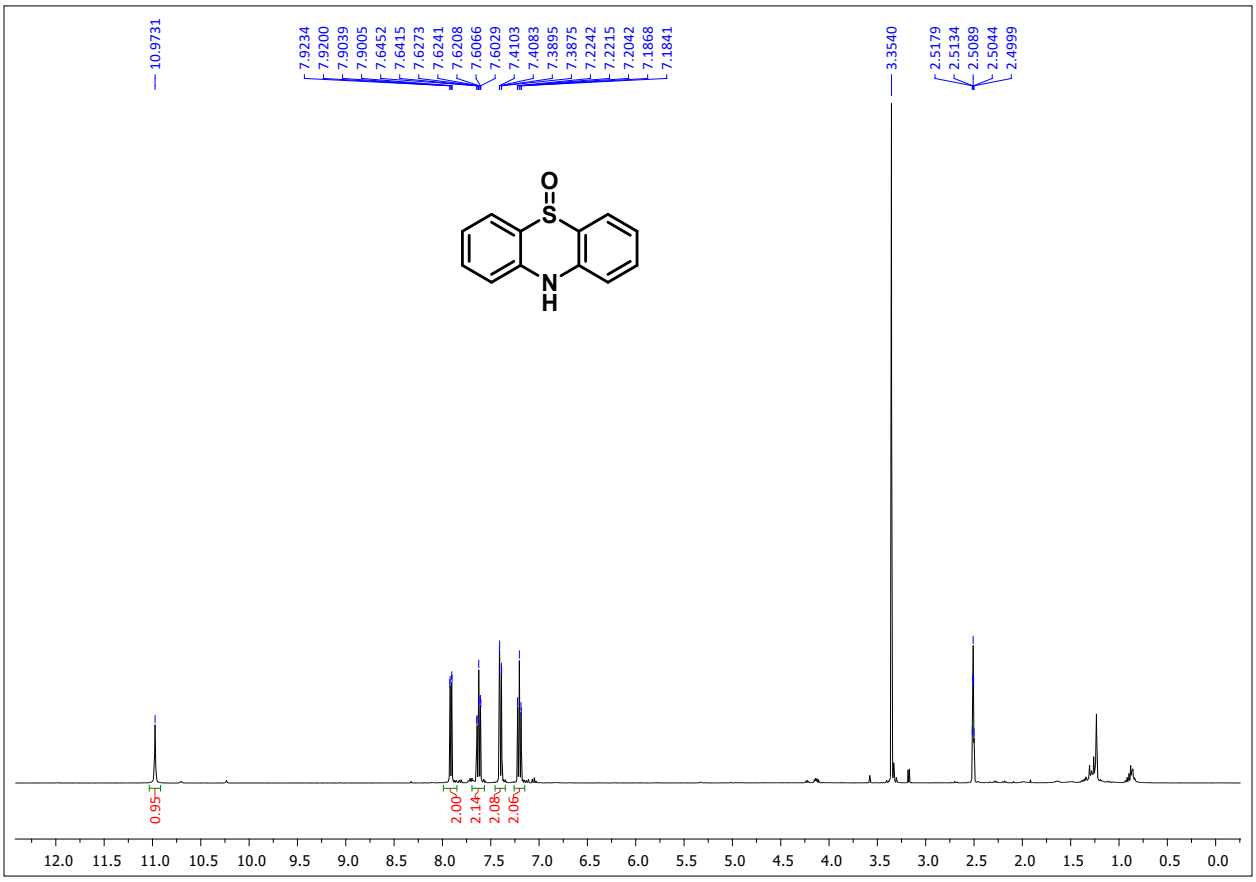


Figure S37. ^{1}H NMR of Phenothiazine-5-oxide in DMSO-d_6

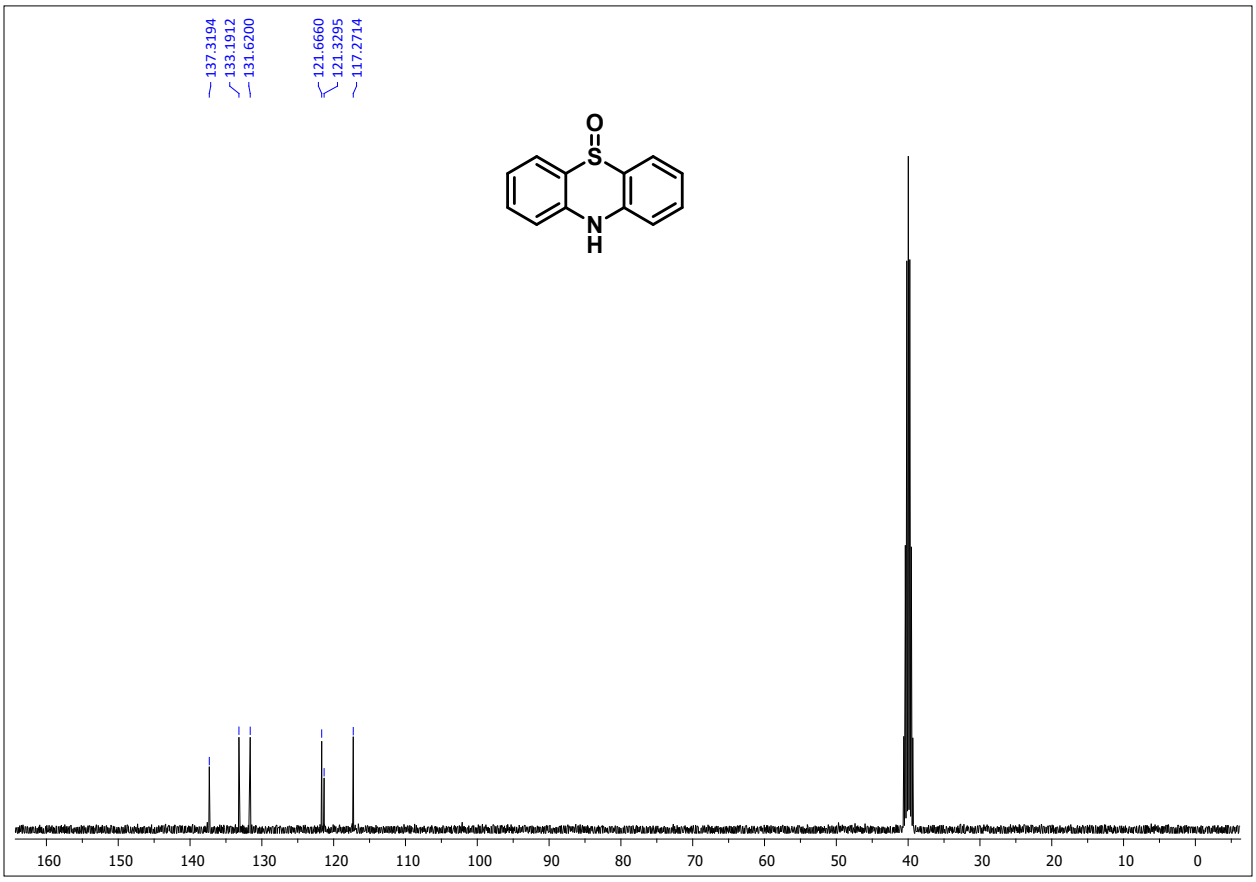


Figure S38. ^{13}C NMR of Phenothiazine-5-oxide in DMSO-d_6

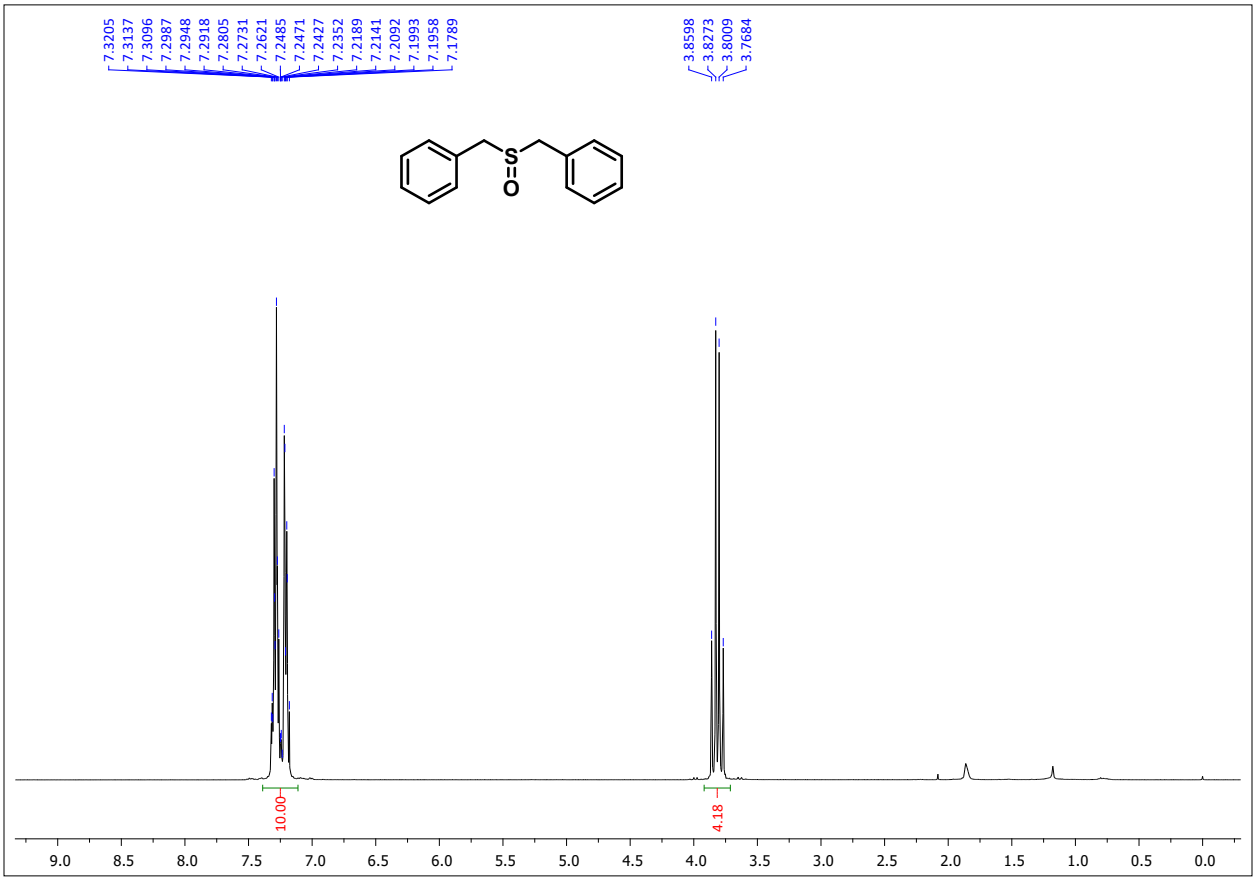


Figure S39. ^{1}H NMR of Dibenzyl sulphoxide in $CDCl_3$

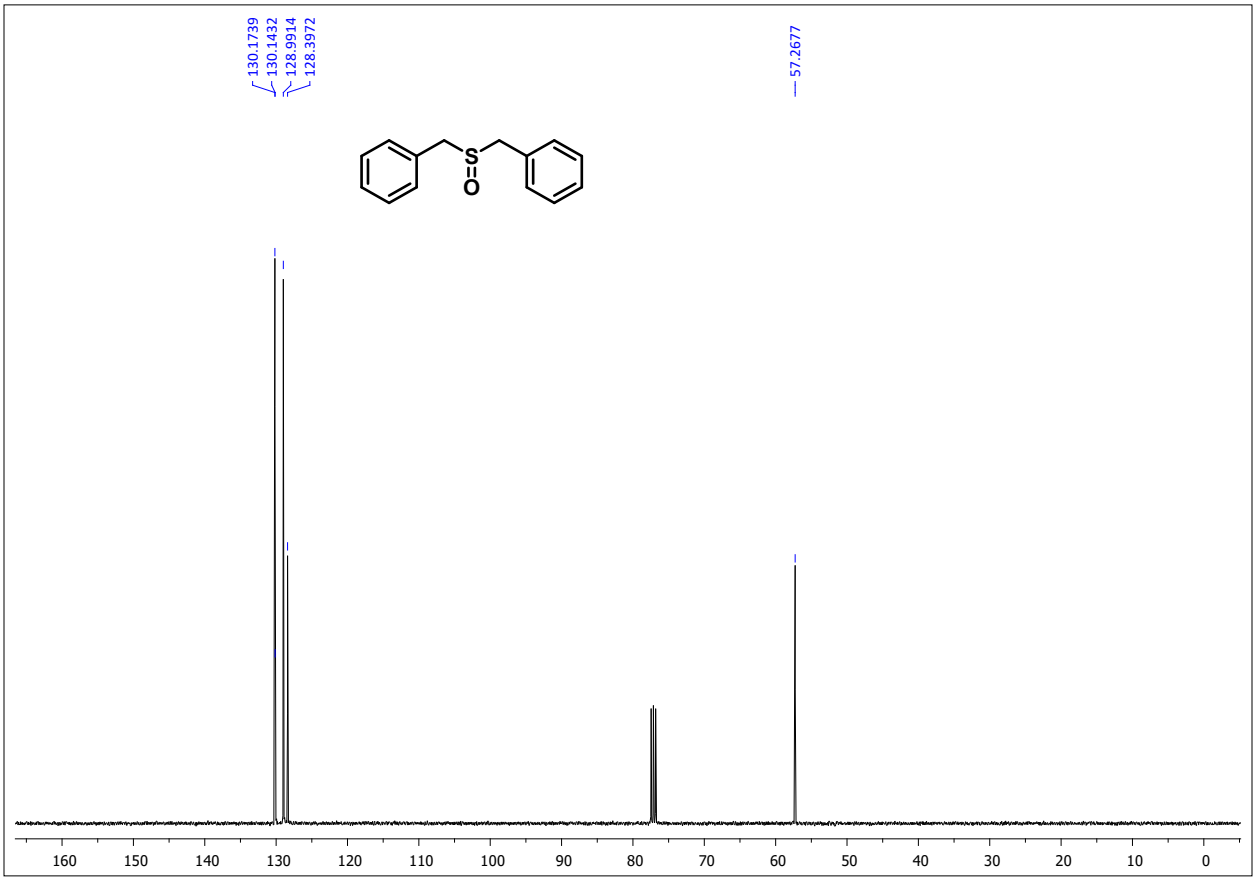


Figure S40. ^{13}C NMR of Dibenzyl sulphoxide in $CDCl_3$

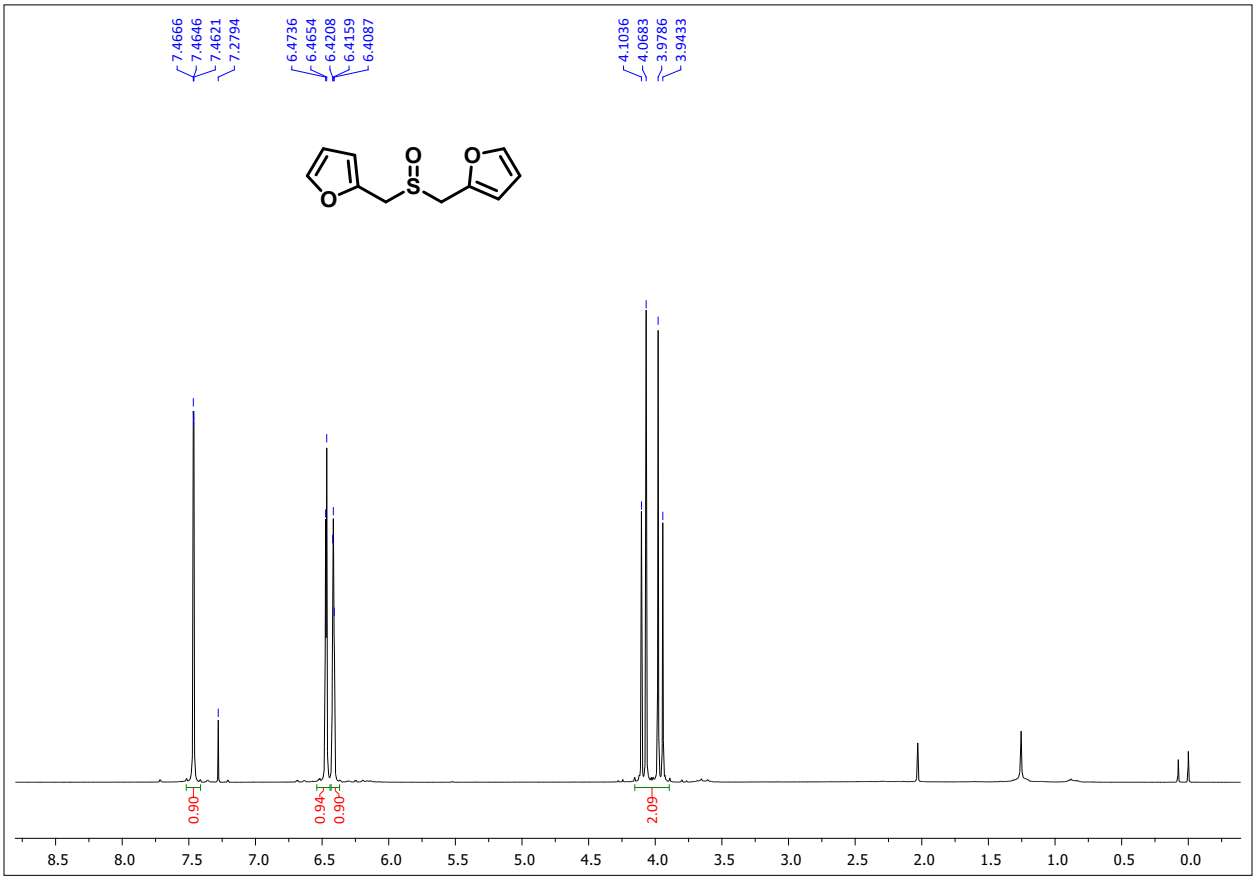


Figure S41. ^{1}H NMR of Difurfuryl sulphoxide in $CDCl_3$

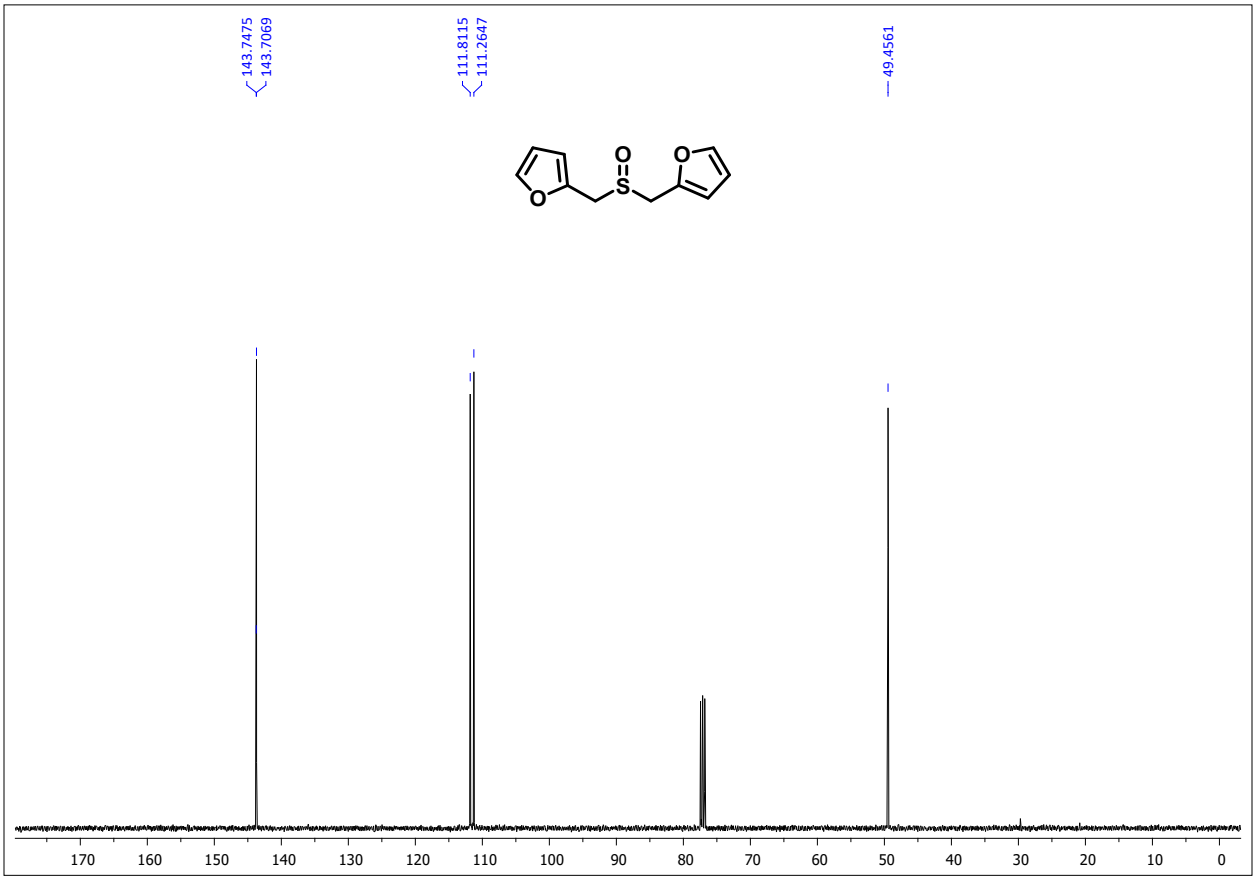


Figure S42. ^{13}C NMR of Difurfuryl sulphoxide in $CDCl_3$

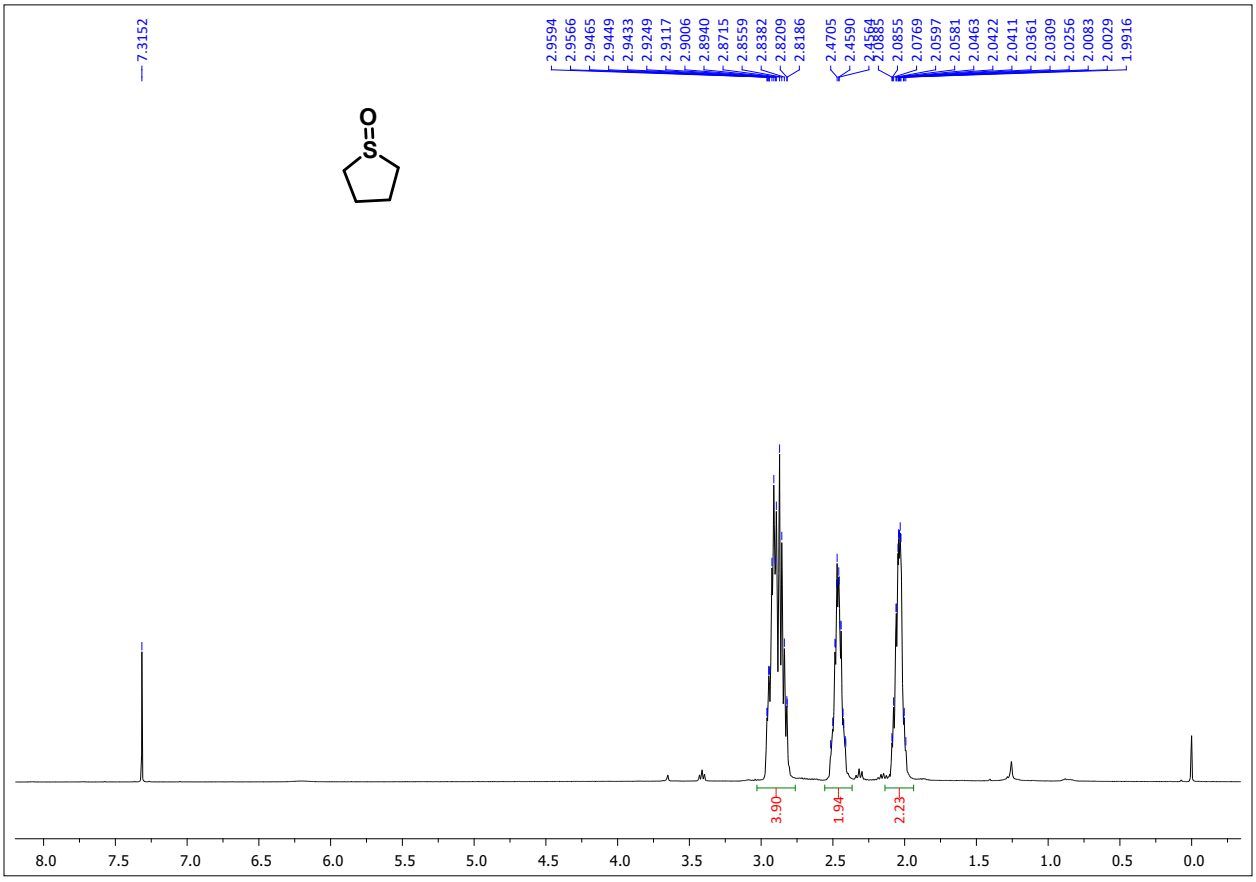


Figure S43. ^{1}H NMR of Tetrahydrothiophene-1-oxide in $CDCl_3$

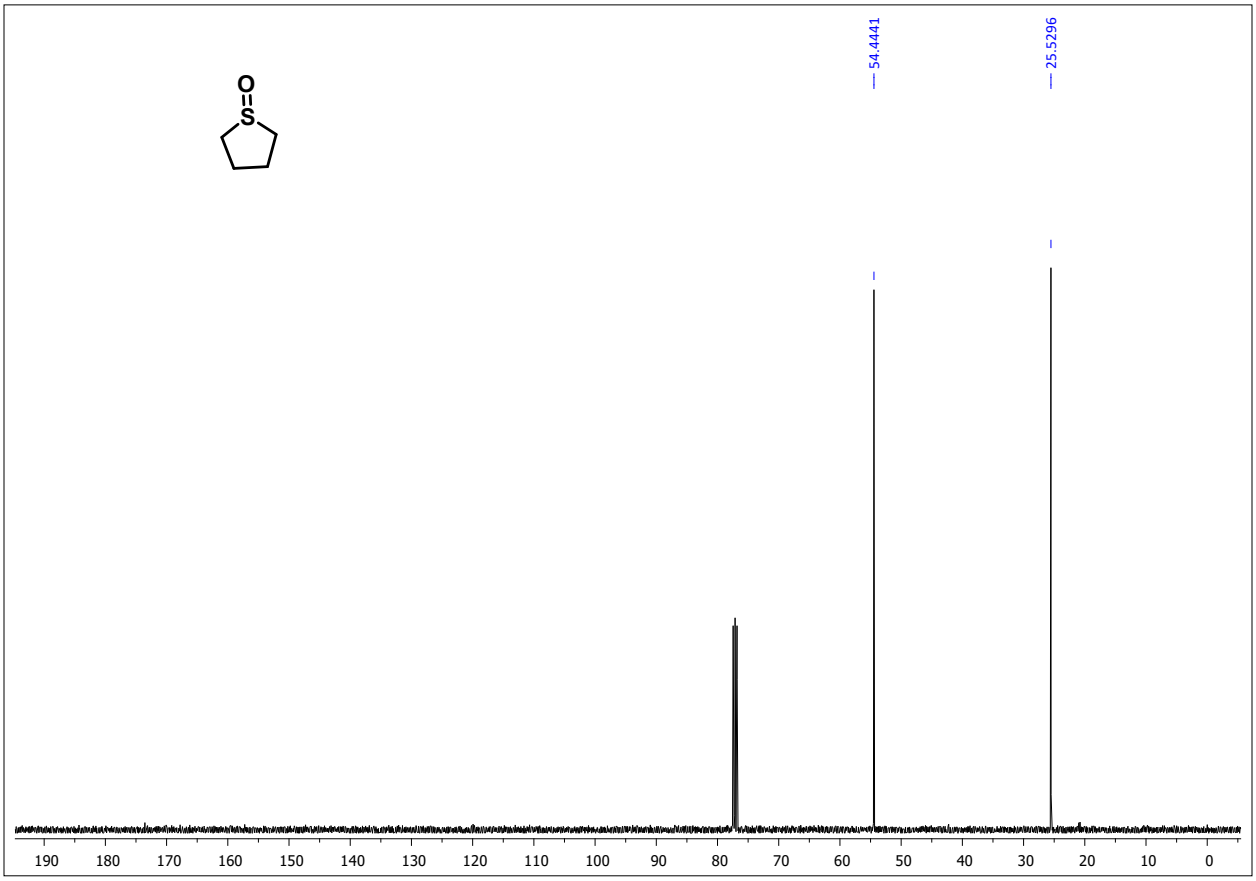


Figure S44. ^{13}C NMR of Tetrahydrothiophene-1-oxide in $CDCl_3$

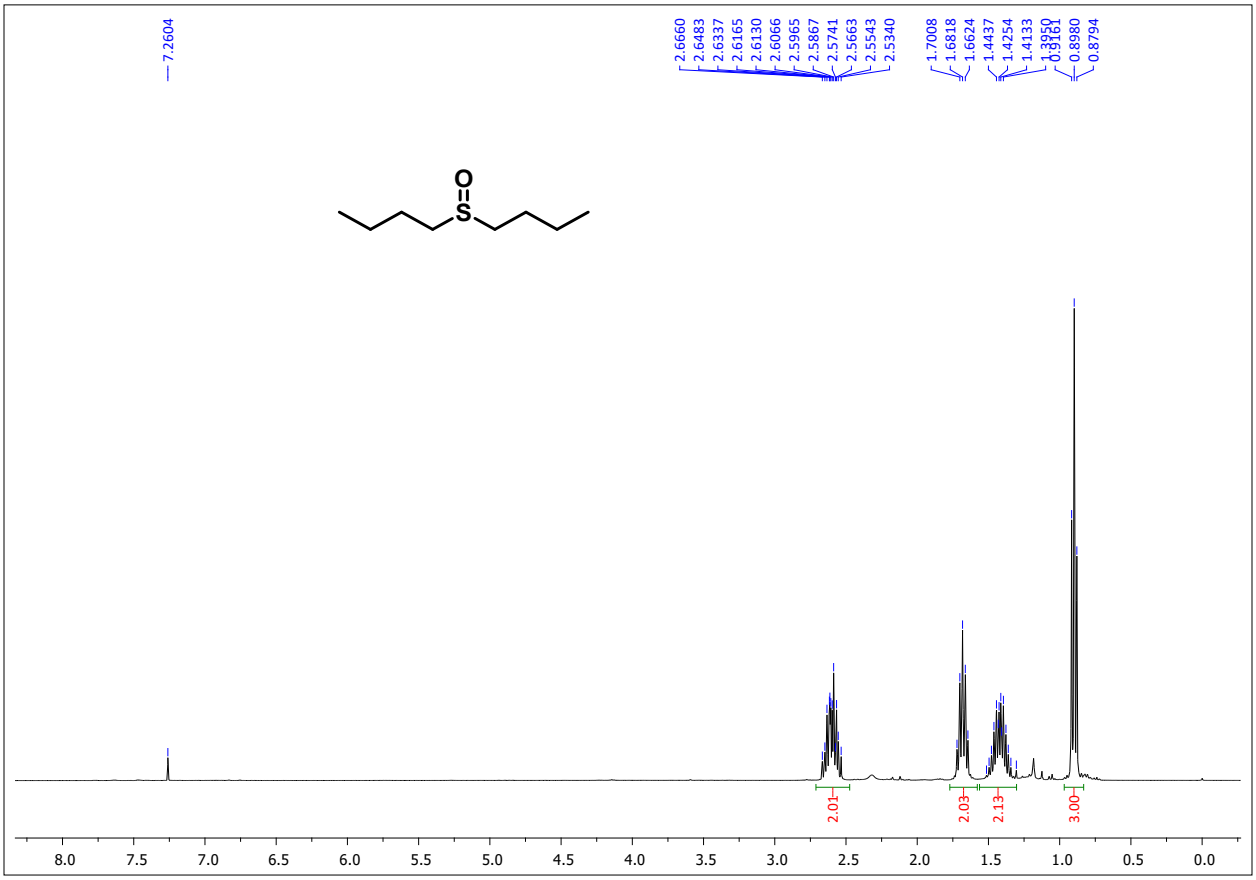


Figure S45. ^{1}H NMR of Butyl sulphoxide in $CDCl_3$

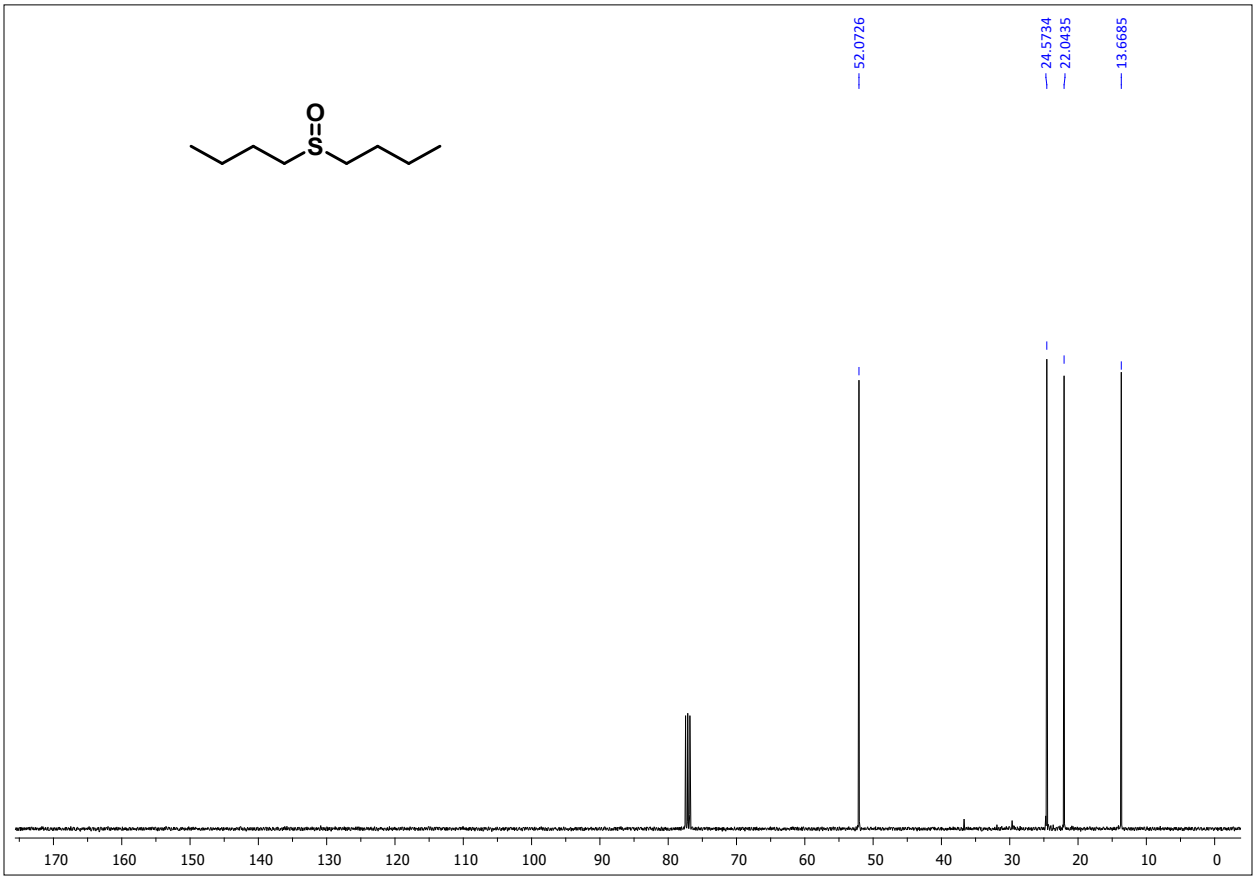


Figure S46. ^{13}C NMR of Butyl sulphoxide in $CDCl_3$

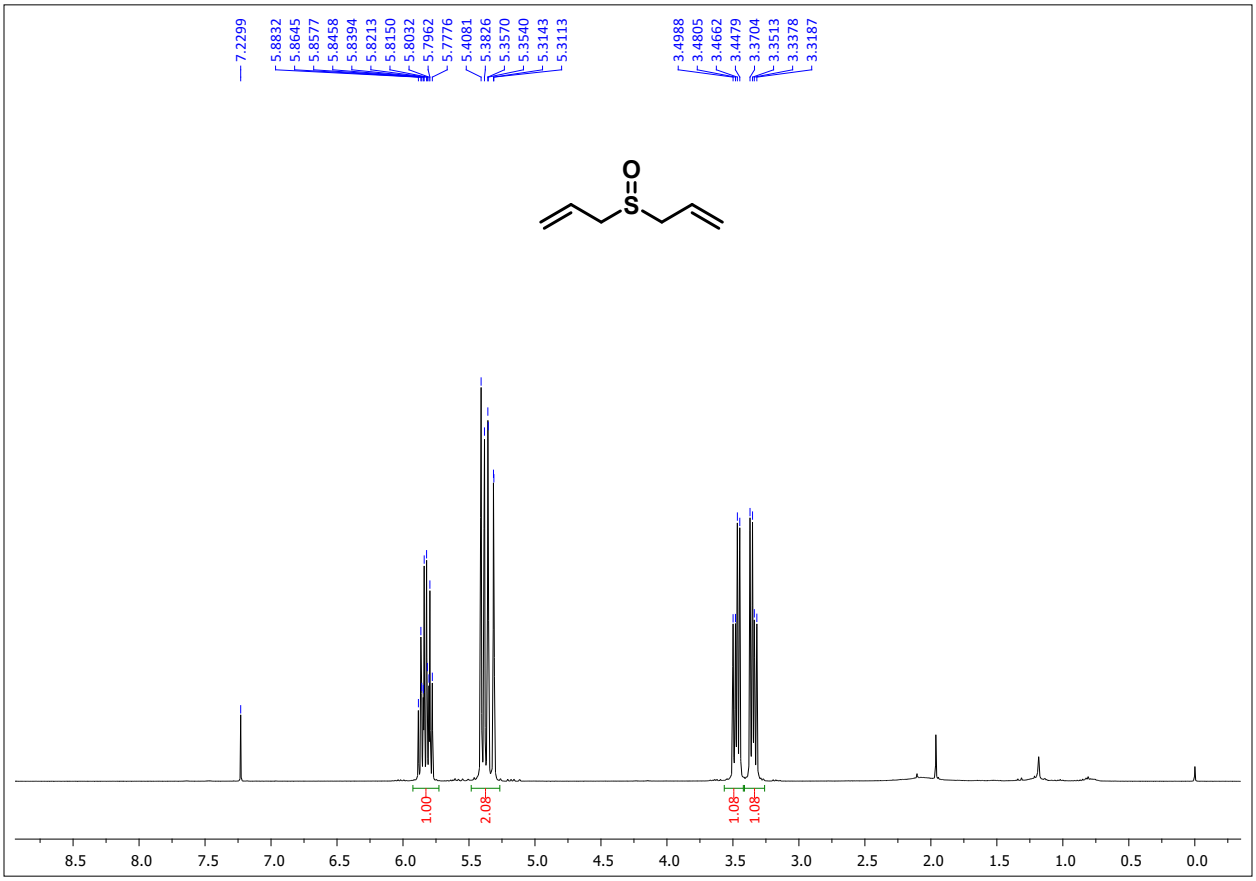


Figure S47. ^{1}H NMR of Allyl sulphoxide in $CDCl_3$

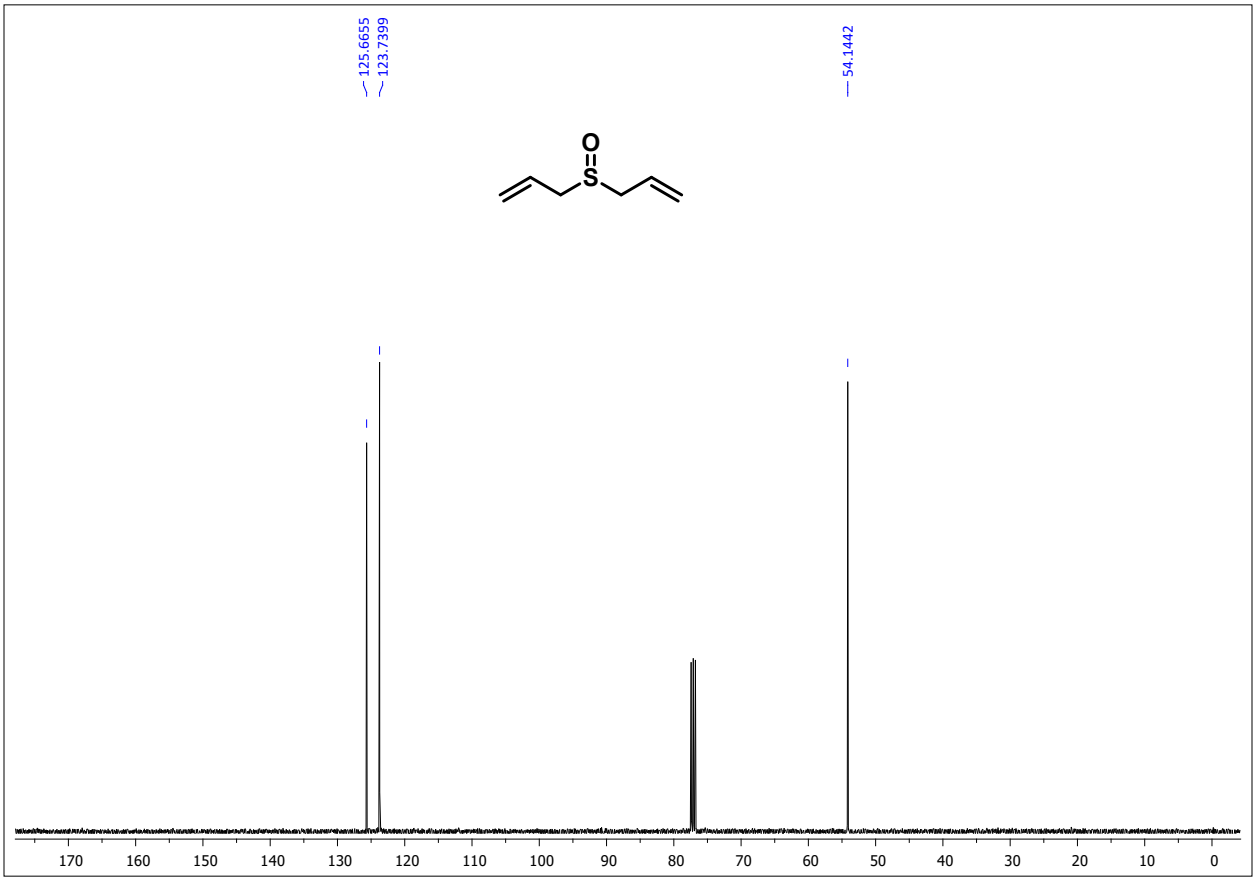


Figure S48. ^{13}C NMR of Allyl sulphoxide in $CDCl_3$