New nanoparticles of $Nife_2O_4@SiO_2$ based tungstate interphase: a highly efficient and selective catalyst for the oxidation of sulfides to sulfoxides

Mohammad Reza Mohammad Shafiee,*[a] Mahnaz Mirheidari, Arshia Eilbeigi

Experimental

General

The chemical compounds including $FeCl_3.6H_2O$, $Si(OEt)_4$, $FeCl_2.4H_2O$, and organic material were purchased from Merck and Aldrich company.The following instruments were used for the catalyst characterization and organic materials analysis: The X-ray diffraction pattern (XRD) was recorded by X-ray diffractometer (Philips, D5000, Cu-Kα irradiation). The Field emission-scanning electron microscopy (FE-SEM) were obtained by Hitachi S-4160. TGA-DTA analysis was carried out by TA (Q600) instrument. The FT-IR spectra were recorded as KBr disks using Thermo (AVATAR) instrument. ^{1}HNMR spectra were recorded on Bruker Avance DPX 400 MHz spectrometer in $CDCl_3$ as solvent relative to TMS (0.00 pm).

Preparation of $NiFe_2O_4$

$NiCl_2.6H_2O$ (0.02 mol) and $FeCl_3.6H_2O$ (0.04 mol) were dissolved in 100 ml deionized water in a 250-ml beaker under a magnetic stirring. The dilute solution of NH_4OH was added to the mixture dropwise until the mixture get PH=10. The obtained solid was washed with deionized water two times and then was calcined at 700 °C.

Preparation of $NiFe_2O_4@SiO_2$

$NiFe_2O_4$ nanoparticles (3 g) were dispersed in 150 ml ethanol and then tetraethyl orthosilicate

(7 ml) was added and mixed for 1h under mechanical stirring. Then, the PH for solution was adjusted to 8.5 by using NH_4OH (20% solution in water) and stirred at room temperature for 48 h. At the end, the magnetic solid ($NiFe_2O_4@SiO_2$) was separated by a magnet and washed thoroughly with water and dried at 100 °C in the air atmosphere.

Preparation of $Nife_2O_4@SiO_2@WO_4^{2-}$

To functionalize the solid support, $NiFe_2O_4@SiO_2$ (5 g) and N-(2-aminoethyl)-N'- (3-(trimethoxysilyl)propyl)ethane-1,2-diamine (2.5 mmol) were mixed together in a 250 ml balloon equipped with a condenser and refluxed for 24h. The obtained solid was separated and washed with toluene and dried at 70 °C. In the next step, the functionalized $Nife_2O_4@SiO_2$ (5g) was disperse in 100 ml CH_3Cl and then drop by drop mixed with trifluorosulfulnic acid and stirred for 10 h. Afterward, the solvent of the product was evaporated and the obtained solid was washed with deionized water and combined with sodium tungstate (10 M, 50 ml). At the end, the resulted solid was separated and washed with ethanol and dried.

Measuring acidity using $BaWO_4$ test

The prepared catalyst (1g) was dispersed in 100 ml deionized water and mixed with barium chloride (1M). The sample was placed at room temperature for precipitation of $BaWO_4$. After completion of precipitation, the collected solid was precisely measured and used for estimating the quantity of tungstate. The value of tungstate for the catalyst was 1.14 mmol/g. According to this, the capacity of positive hydrogen ion (H^+) in the sample was measured 2.28 mmol H^+/g.

The general procedure for oxidation

The prepared catalyst (0.025 g) was added to the mixture of sulfide (2 mmol) and H_2O_2 (30%, 6 eq) in 10 ml ethanol and mixed together by mechanical stirring at room temperature until the completion of the reaction (monitored by TLC). After the reaction progress finished, the catalyst was separated by an external magnetic. Then, the solvent under reduced pressure was removed and the products were purified by silica gel column chromatography.

Spectral data

Methyl phenyl sulfoxide (a_1): white solid; ^{1}HNMR (500 MHz, $CDCl_3$): δ= 2.72 (s, 3H, CH_3), 7.44-7.53 (m, 3H), 7.19 (d, *J*= 7.8 Hz, 2H).

(4-Methoxyphenyl)(methyl) sulfoxide (a_2): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.75 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.97 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H) ppm

Benzyl phenyl sulfoxide (a_3): white solid; m.p.: 127-129 °C, ^{1}HNMR (500 MHz, $CDCl_3$): δ= 4.03 (d, *J*= 12.8 Hz, 1H), 4.16 (d, *J*= 12.8 Hz, 1H), 6.98 (t, *J*= 8.0 Hz, 2H), 7.19 (t, *J*= 8.0 Hz, 1H), 7.27-7.50 (m, 7H).

Benzyl p-tolyl sulfoxide (a_4): white solid; m.p.: 139-141 °C; ^{1}HNMR (500 MHz, $CDCl_3$): δ= 2.41 (s, 3H), 3.96 (d, *J*= 12.4 Hz, 1H), 4.07 (t, *J*= 12.4 Hz, 1H), 6.98 (d, *J*= 7.8 Hz, 2H), 7.18-7.40 (m, 7H).

4-methoxybenzyl p-tolyl sulfoxide (a_5): white solid; m.p.:123-125 °C; ^{1}HNMR (500 MHz, $CDCl_3$): δ= 2.38 (s, 3H), 3.83 (s, 3H), 3.92 (d, *J*= 12.6 Hz, 1H), 4.01 (t, *J*= 12.6 Hz, 1H), 6.78 (d, *J*= 7.8 Hz, 2H), 6.99 (d, *J*=7.8 Hz, 2H), 7.19 (d, *J*=7.6 Hz, 2H), 7.28 (d, *J*=7.6 Hz, 2H).

Benzyl 2-methoxyphenyl sulfoxide (a_6): Oil; ^{1}HNMR (500 MHz, $CDCl_3$): δ= 3.86 (s, 3H), 3.95 (d, *J*=12.6 Hz, 1H), 6.92 (d, *J*=7.8 Hz, 1H), 6.97 (d, *J*=7.8Hz, 1H), 7.03 (t, *J*=7.6 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 7.17-7.31 (m, 3H), 7.43 (d, *J*=7.6 Hz, 2H).

Benzyl 3-methoxyphenyl sulfoxide (a_7): Oil; ^{1}HNMR (500 MHz, $CDCl_3$): δ= 3.74 (s, 3H), 3.97 (d, *J*=12.6 Hz, 1H), 4.11 (d, *J*=12.6 Hz, 1H), 6.88-7.33 (m, 7H), 7.45 (d, *J*=7.6 Hz, 2H).

Diphenyl sulfoxide (a_8): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 7.44 (t, *J* = 7.6 Hz, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 4H) ppm

Dibenzo[b,d]thiophene 5-oxide (a_9): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 7.49 (t, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 8.0 (d, *J* = 8.0 Hz, 2H) ppm

(4-Nitrophenyl)(methyl) sulfoxide (a_{10}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 3.11 (s, 3H, CH_3), 7.97 (d, *J* = 7.8 Hz, 2H), 8.46 (d, *J* = 7.8 Hz, 2H) ppm

(Ethyl)(phenyl) sulfoxide (a_{11}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 1.54 (t, *J* = 6.8 Hz, 3H), 2.76 (q, *J* = 6.8 Hz, 2H), 7.47-7.64 (m, 5H) ppm

Tetrahydrothiophene 1-oxide (a_{12}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 1.21-1.26 (m, 4H), 2.61-2.66 (m,4H) ppm

1-(Propylsulfinyl)propane (a_{13}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.93 (t, *J* = 6.7 Hz, 4H), 1.84-1.88 (m, 4H), 1.57 (t, *J* = 6.7 Hz, 6H) ppm

(4-Chlorophenyl)(methyl) sulfoxide (a_{14}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.79 (s, 3H, CH_3), 7.67 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H) ppm

(2-Cloro-4-Nitrophenyl)(methyl) sulfoxide (a_{15}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 3.15 (s, 3H, CH_3), 8.25 (d, *J* = 8.2 Hz, 1H), 8.40-8.42 (m, 2H) ppm

(2-Clorophenyl)(methyl) sulfoxide (a_{16}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.82 (s, 3H, CH_3), 7.55-7.67 (m, 3H), 7.83 (d, *J* = 8.0 Hz, 1H) ppm

(4-Bromophenyl)(methyl) sulfoxide (a_{17}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.86 (s, 3H, CH_3), 7.71 (d, *J*= 7.8 Hz, 2H), 7.83 (d, *J*= 7.8 Hz, 2H) ppm

2-(Methylsulfinyl)naphthalene (a_{18}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.83 (s, 3H, CH_3), 7.19-7.28 (m, 2H), 7.43 (d, *J*= 8.4 Hz, 1H), 7.77 (d, *J*= 8.6 Hz, 1H), 7.83-7.93 (m, 3H) ppm.

Tetrahydro-2H-thiopyran 1-oxide (a_{19}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 1.58-1.69 (m, 4H), 2.09-2.15 (m, 2H), 2.79-2.94 (m, 4H) ppm.

(Benzylsulfinyl)benzene (a_{20}): ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.03 (d, *J* = 10.8 Hz, 1H), 4.13 (d, *J* = 10.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 2H), 7.27-7.47 (m, 8H) ppm

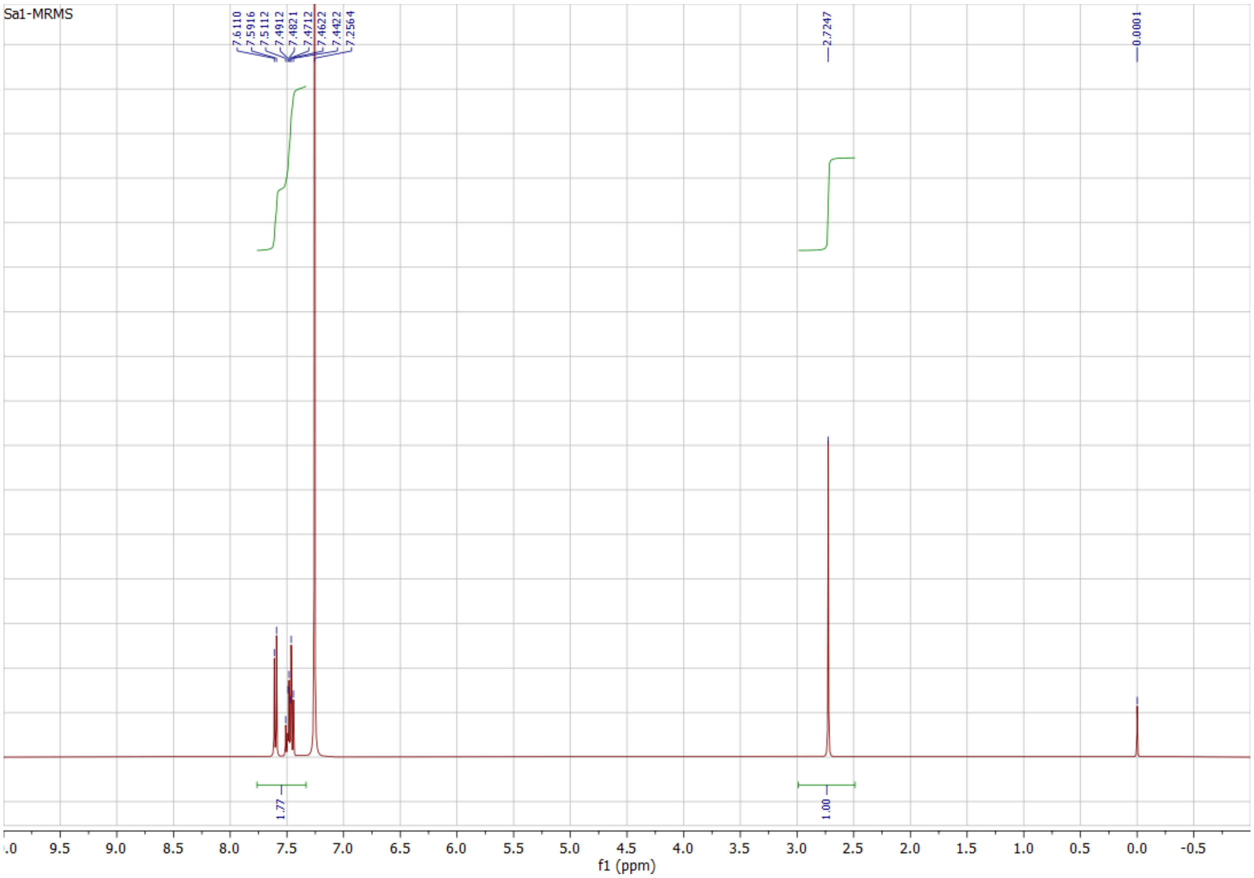

Figure S1: 1H-NMR spectrum of methyl phenyl sulfoxide (a_1)

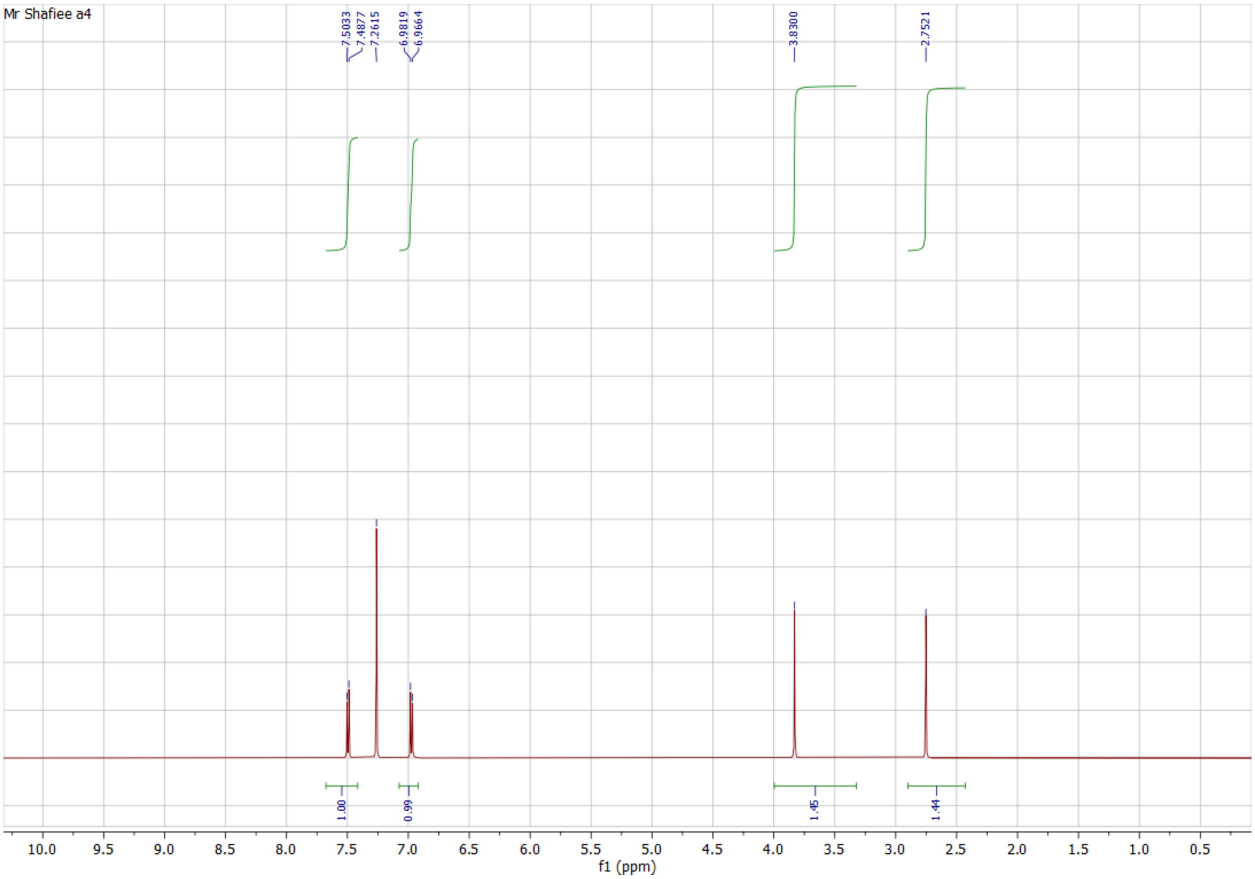

Figure S$_2$: ^{1}H-NMR spectrum of (4-methoxyphenyl)(methyl) sulfoxide (a$_2$)

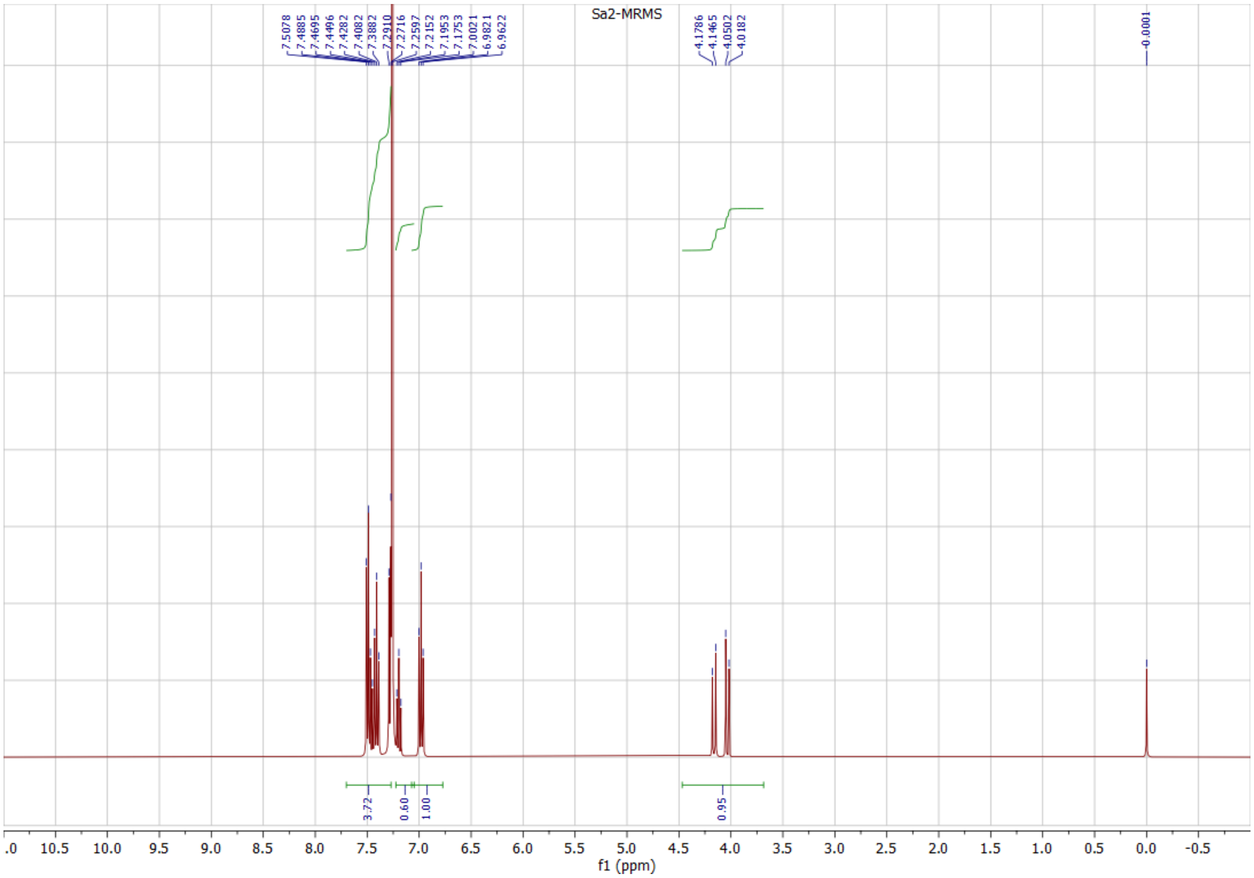

Figure S3: 1H-NMR spectrum of benzyl phenyl sulfoxide (a3):

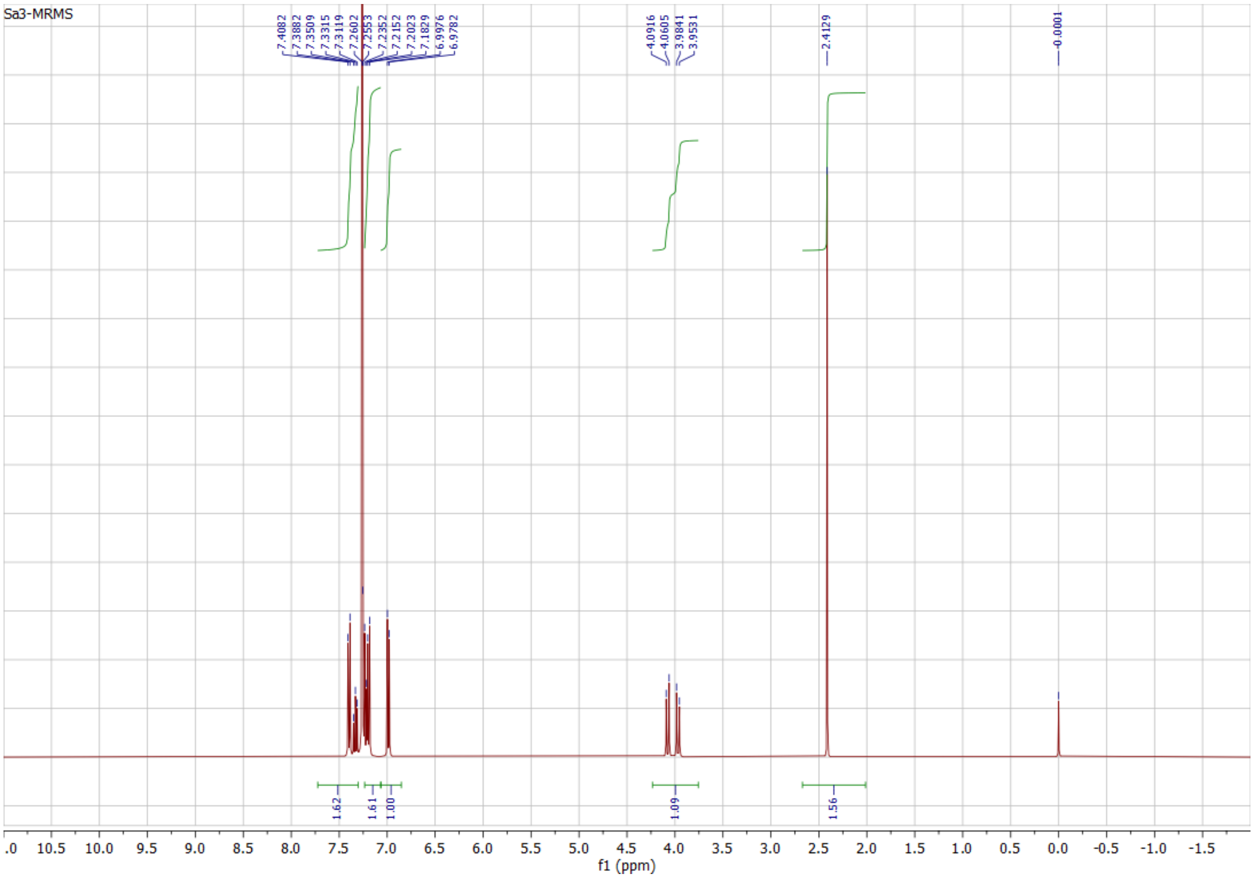

Figure S4: 1H-NMR spectrum of benzyl p-tolyl sulfoxide (a4)

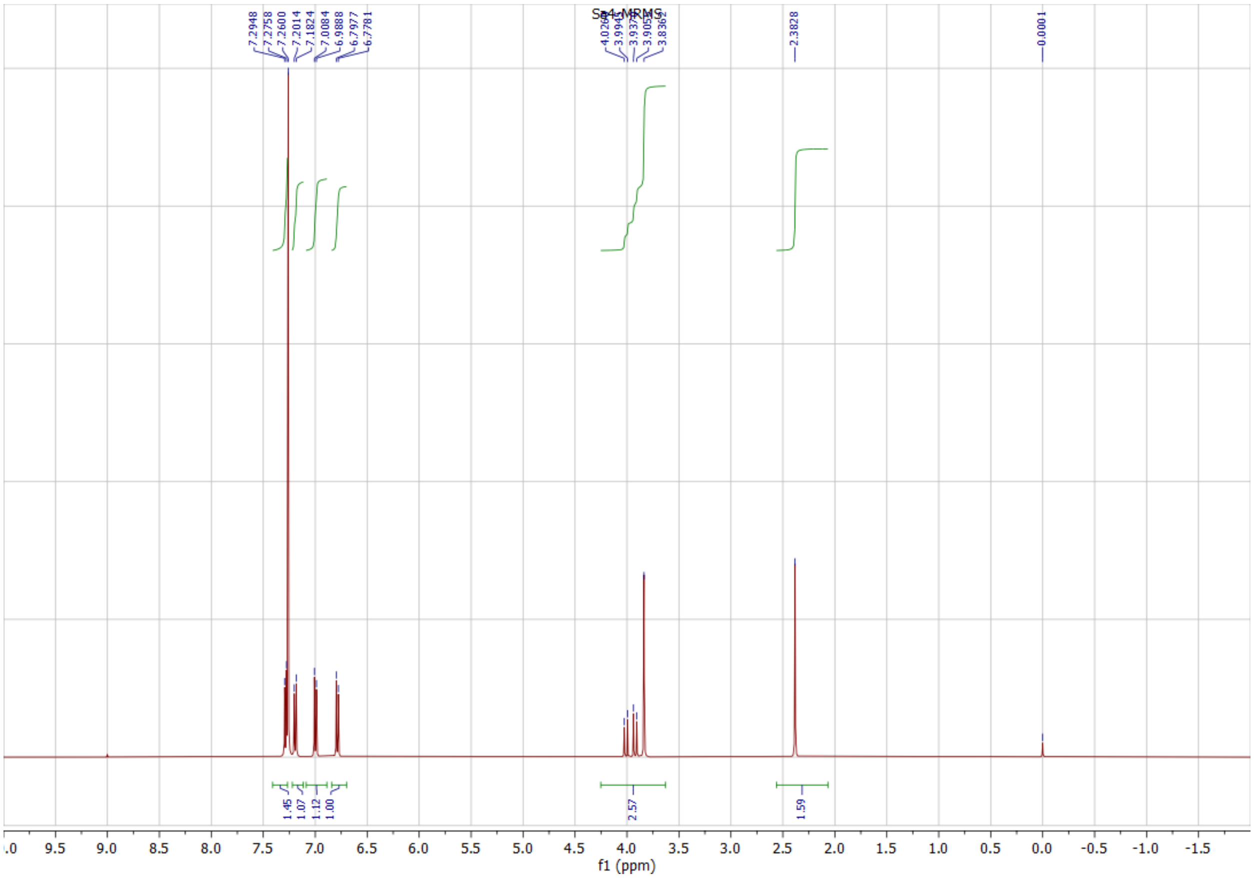

Figure S5: 1H-NMR spectrum of 4-methoxybenzyl p-tolyl sulfoxide (a5)

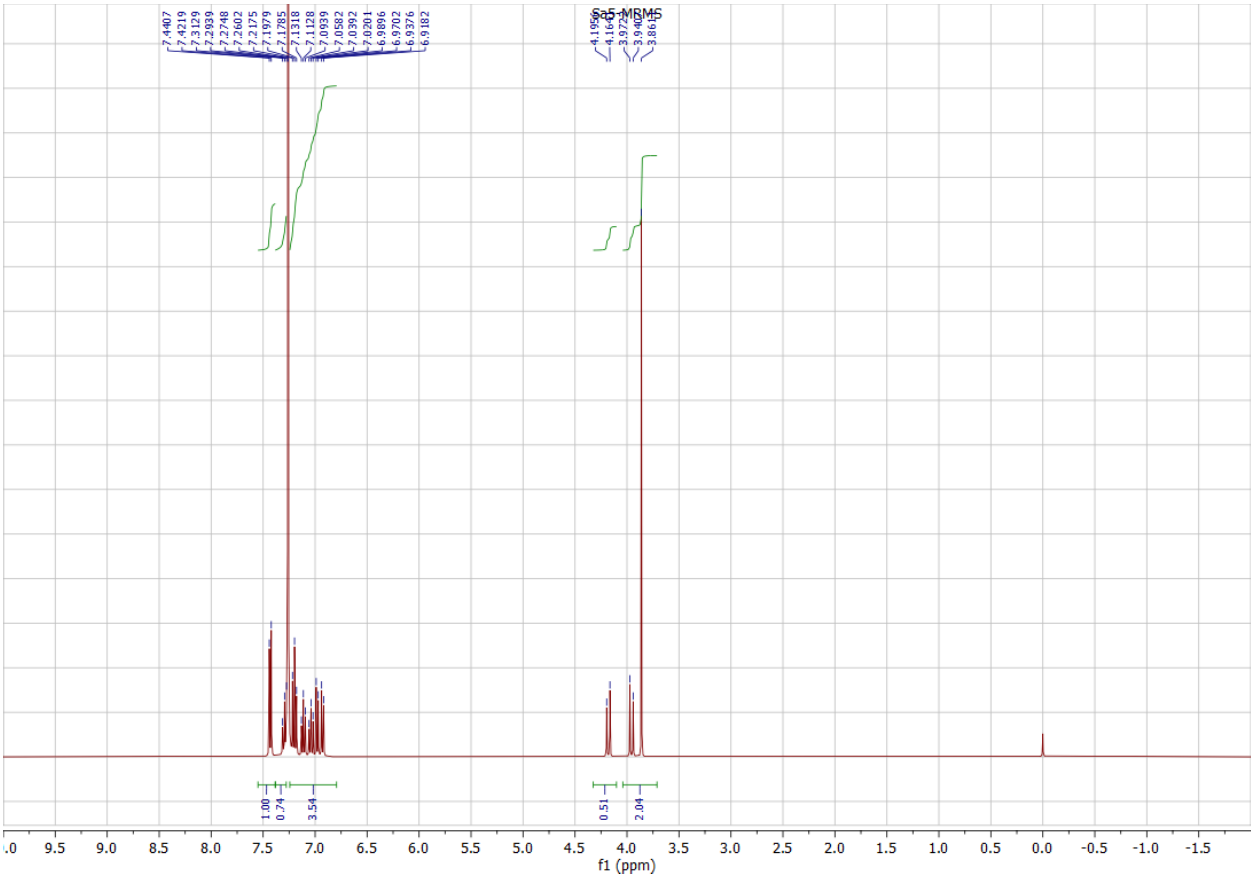

Figure S_6: 1H-NMR spectrum of benzyl 2-methoxyphenyl sulfoxide (a_6)

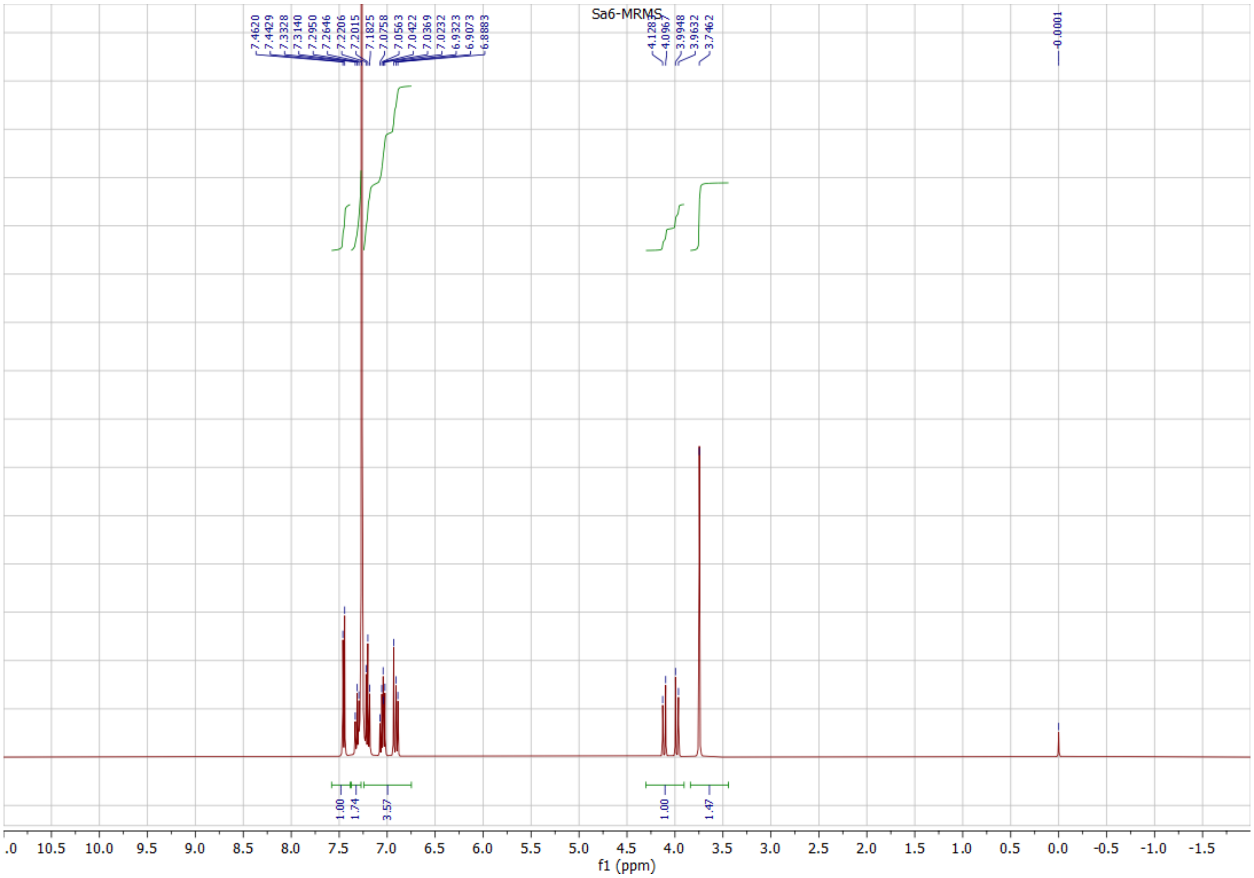

Figure S7: 1H-NMR spectrum of benzyl 3-methoxyphenyl sulfoxide (a7)

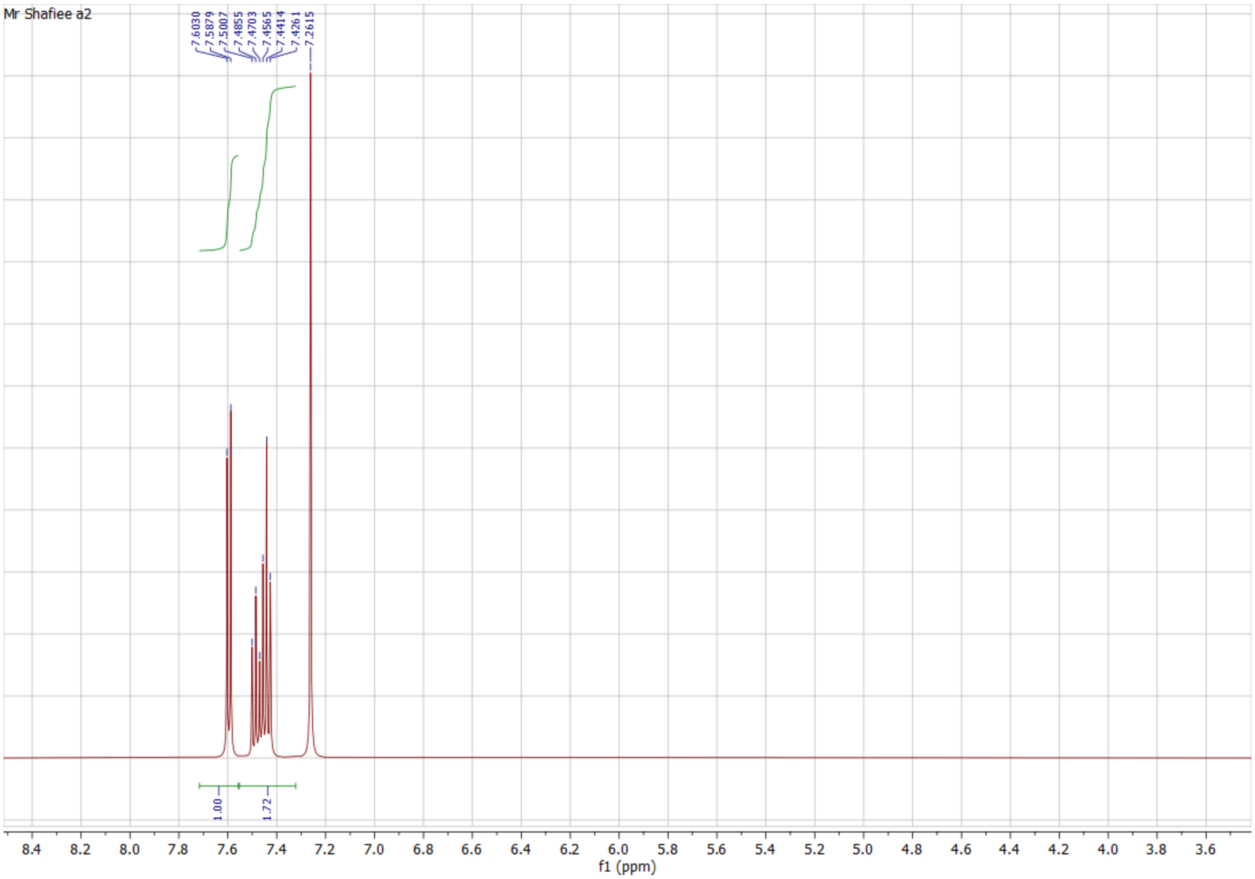

Figure S_8: ^{1}H-NMR spectrum of diphenyl sulfoxide (a_8)

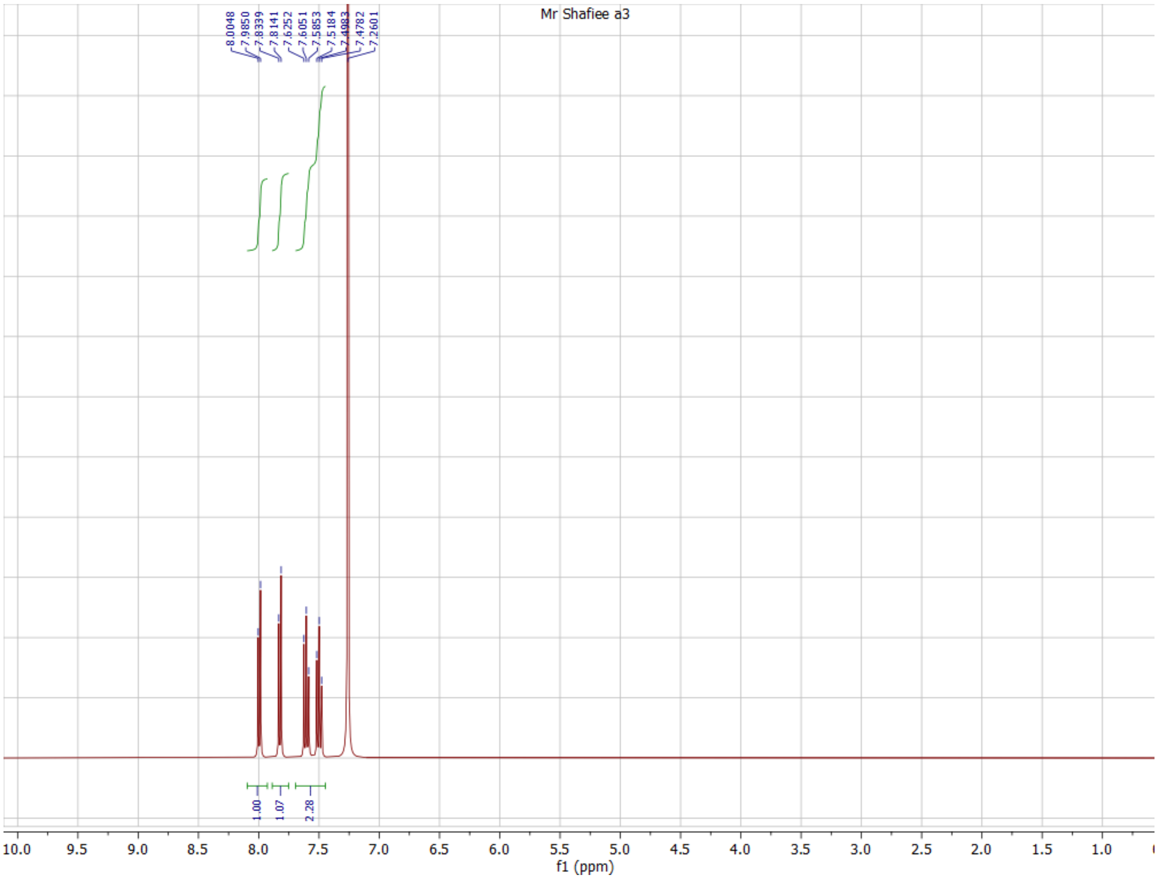

Figure S9: ^{1}H-NMR spectrum of dibenzo[b,d]thiophene 5-oxide (a_9)

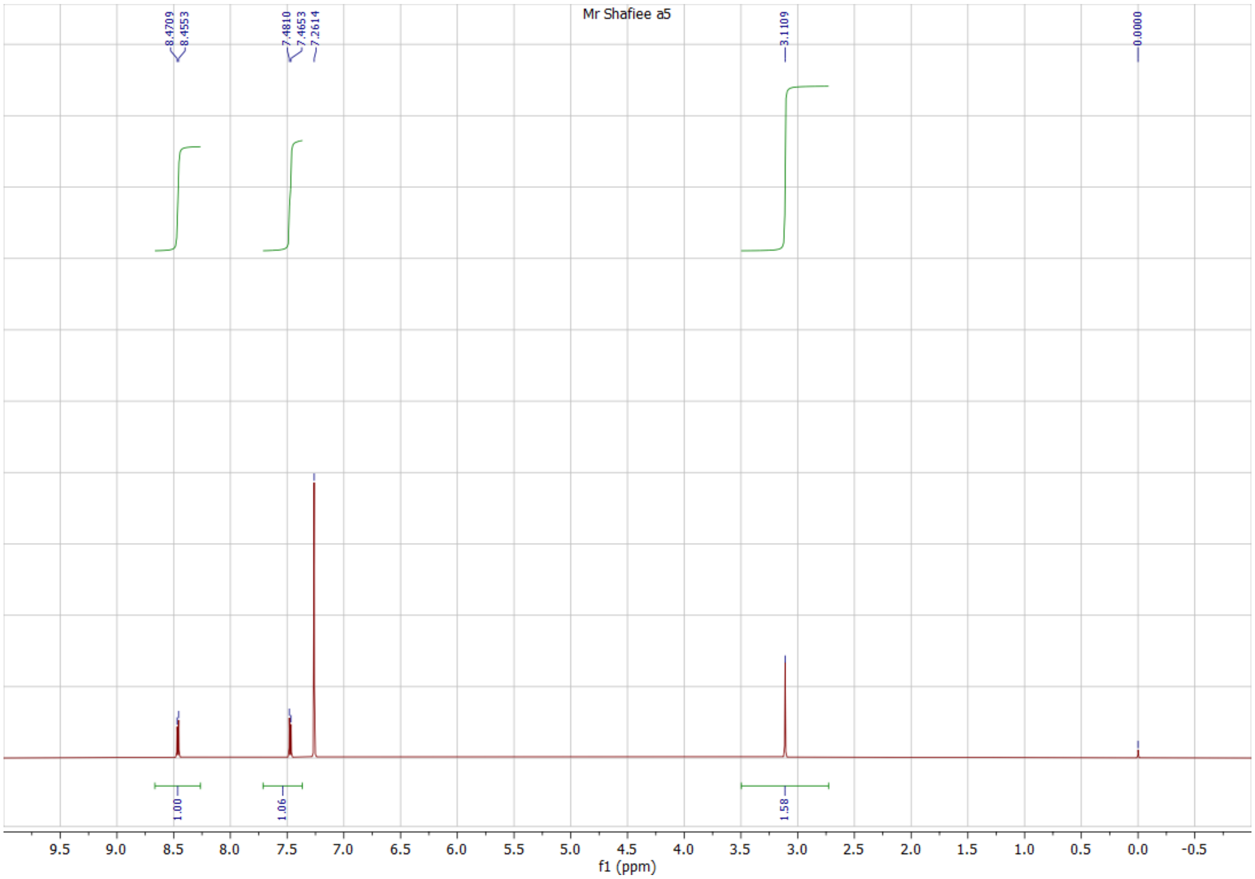

Figure S$_{10}$: ^{1}H-NMR spectrum of (4-Nitrophenyl)(methyl) sulfoxide (a$_{10}$)

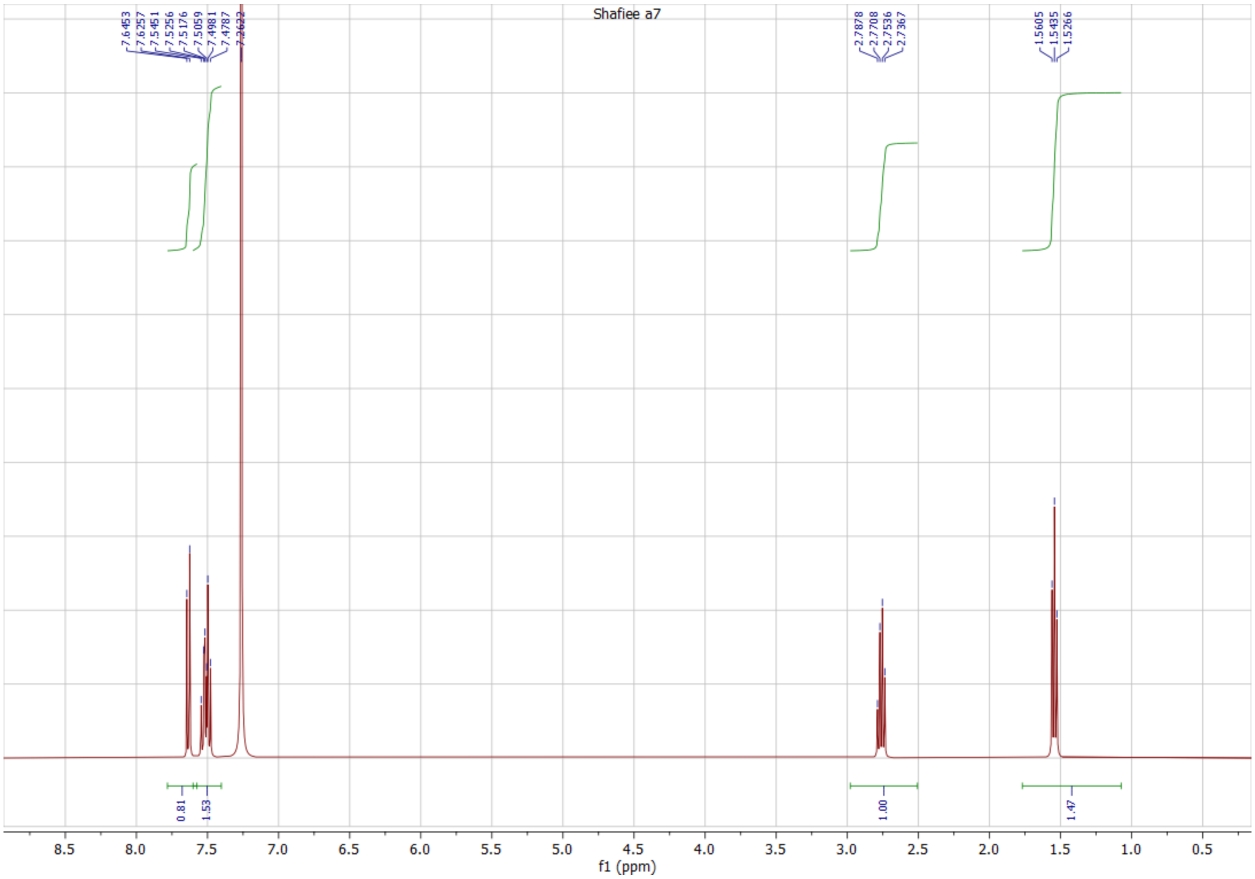

Figure S_{11}: ^{1}H-NMR spectrum of (ethyl)(phenyl) sulfoxide (a_{11})

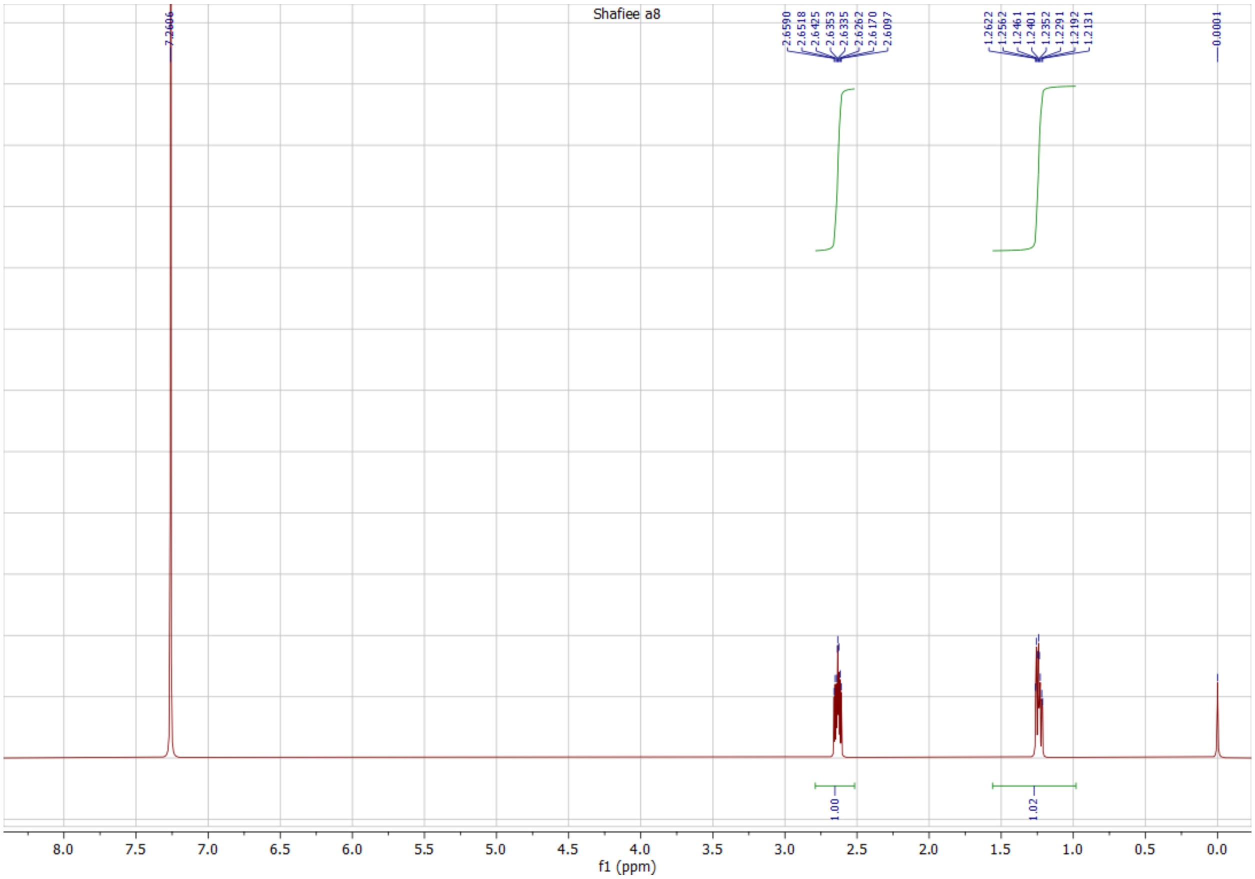

Figure S_{12}: ^{1}H-NMR spectrum of tetrahydrothiophene 1-oxide (a_{12})

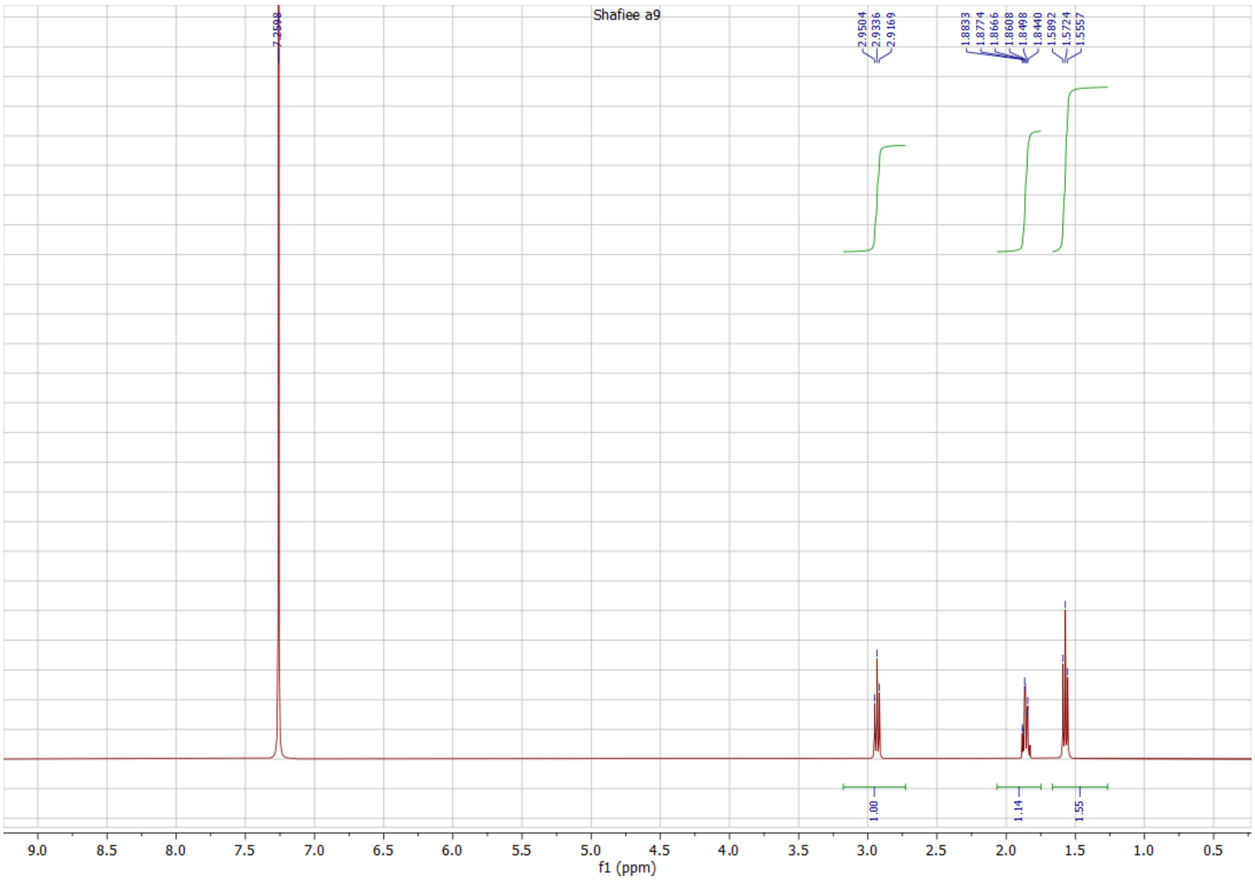

Figure S_{13}: ^{1}H-NMR spectrum of 1-(propylsulfinyl)propane (a_{13})

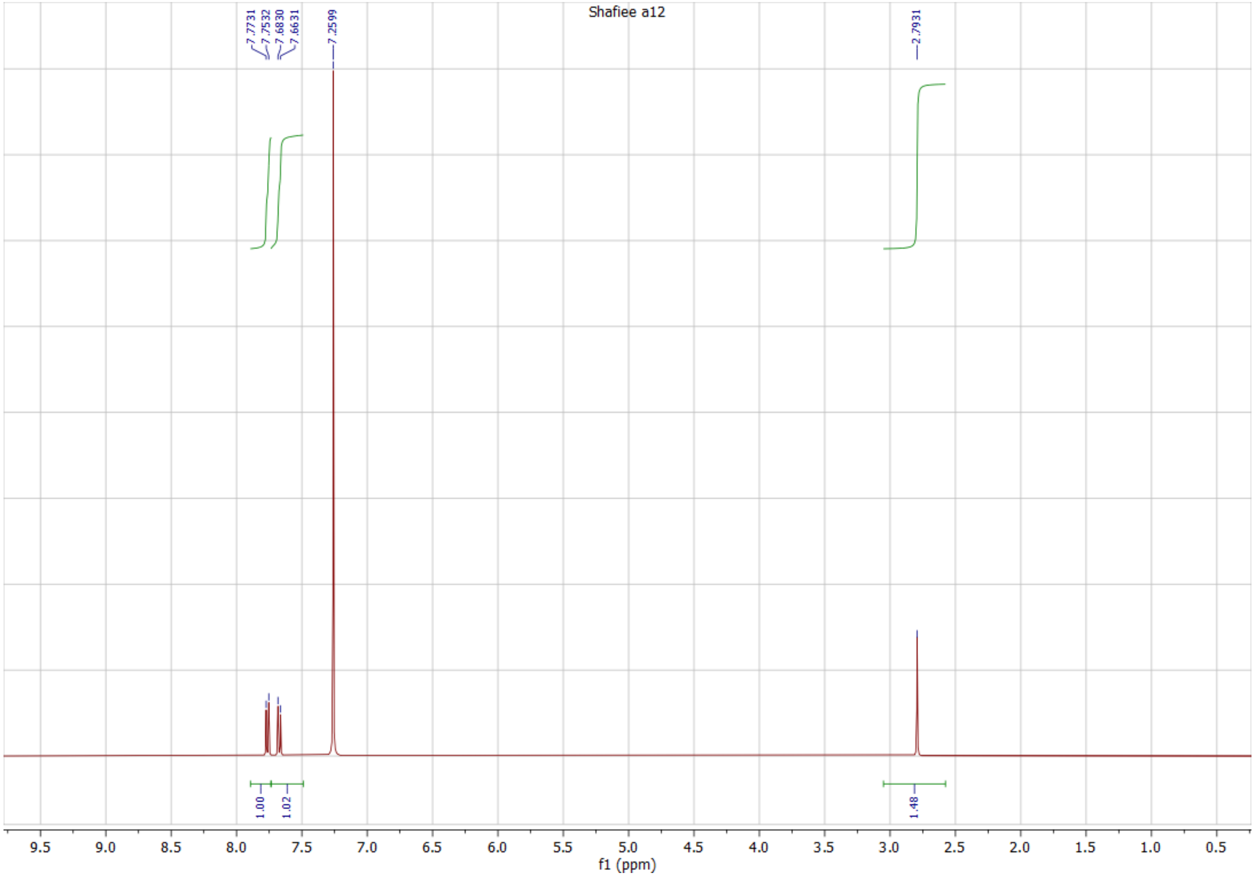

Figure S14: : ^{1}H-NMR spectrum of (4-Chlorophenyl)(methyl) sulfoxide (a_{14})

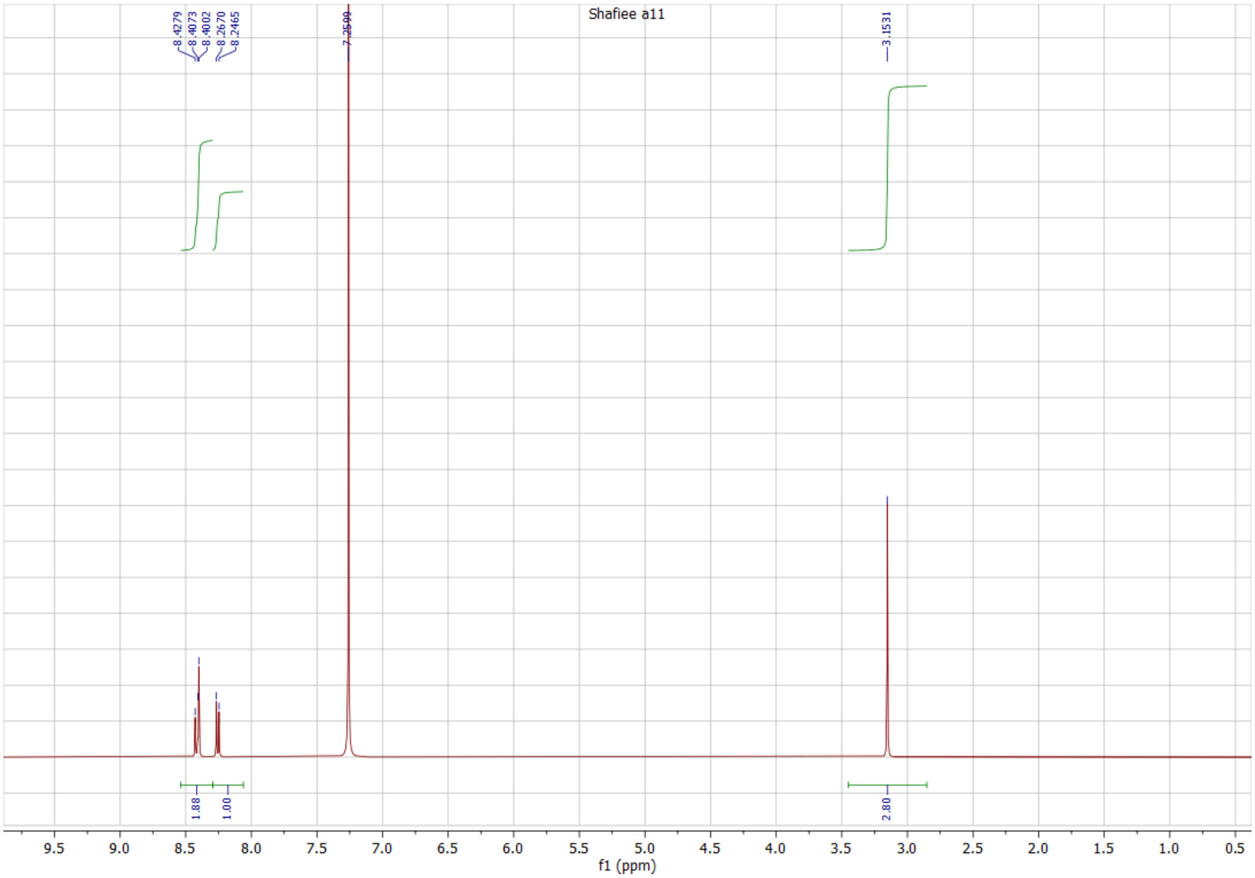

Figure S$_{15}$: ^{1}H-NMR spectrum of (2-Chloro-4-nitrophenyl)(methyl) sulfoxide (a$_{15}$)

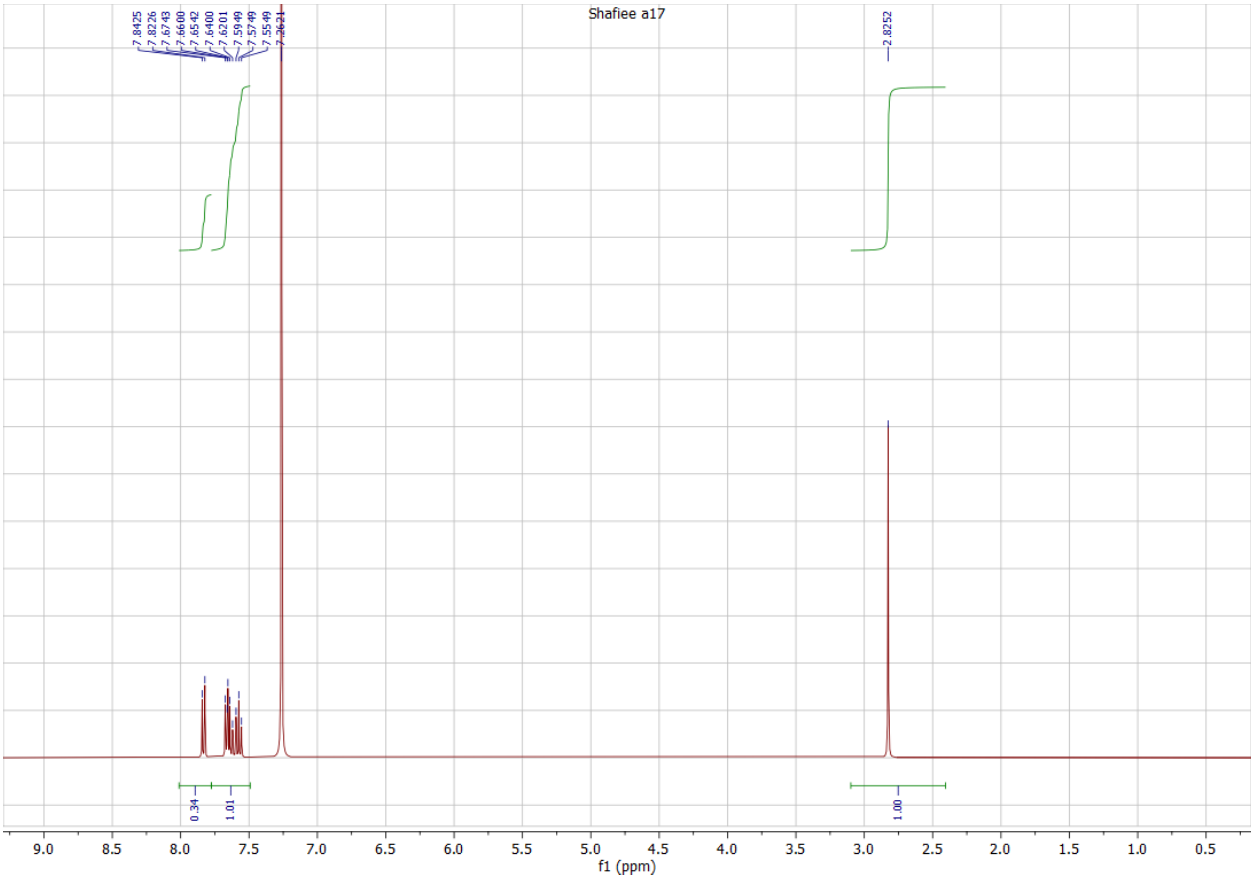

Figure S16: ^{1}H-NMR spectrum of (2-Chlorophenyl)(methyl) sulfoxide (a$_{16}$)

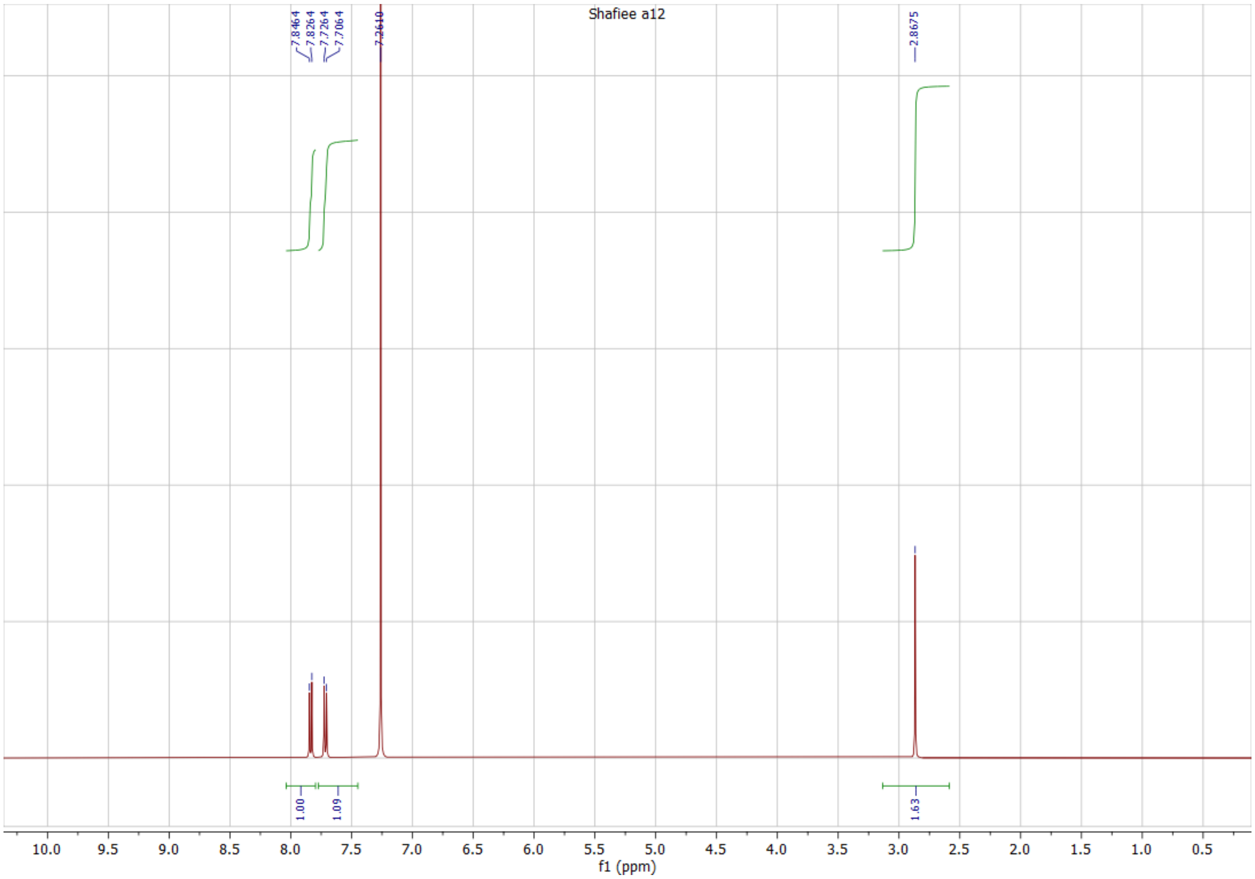

Figure S$_{17}$: ^{1}H-NMR spectrum of (4-Bromophenyl)(methyl) sulfoxide (a$_{17}$)

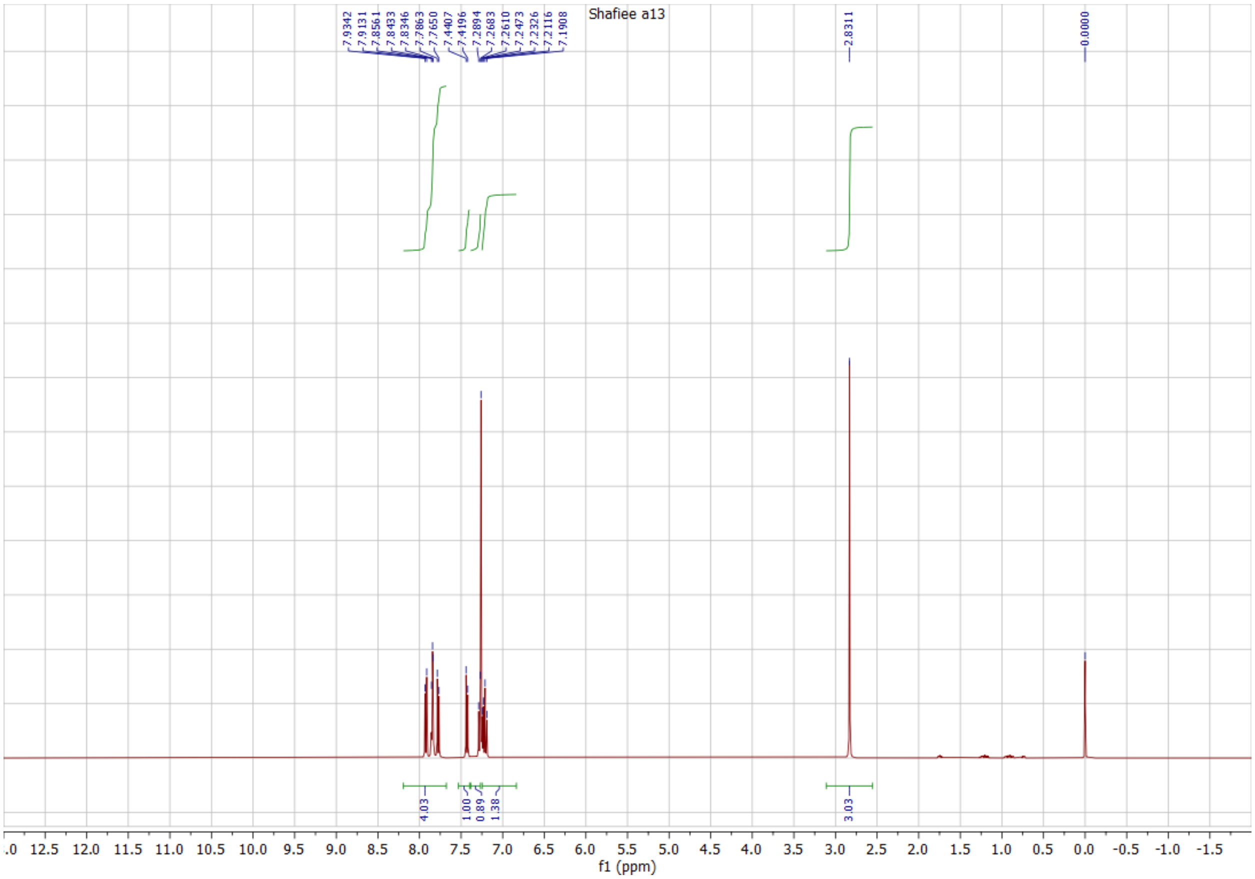

Figure S18: ^{1}H-NMR spectrum of 2-(methylsulfinyl)naphthalene (a_{18})

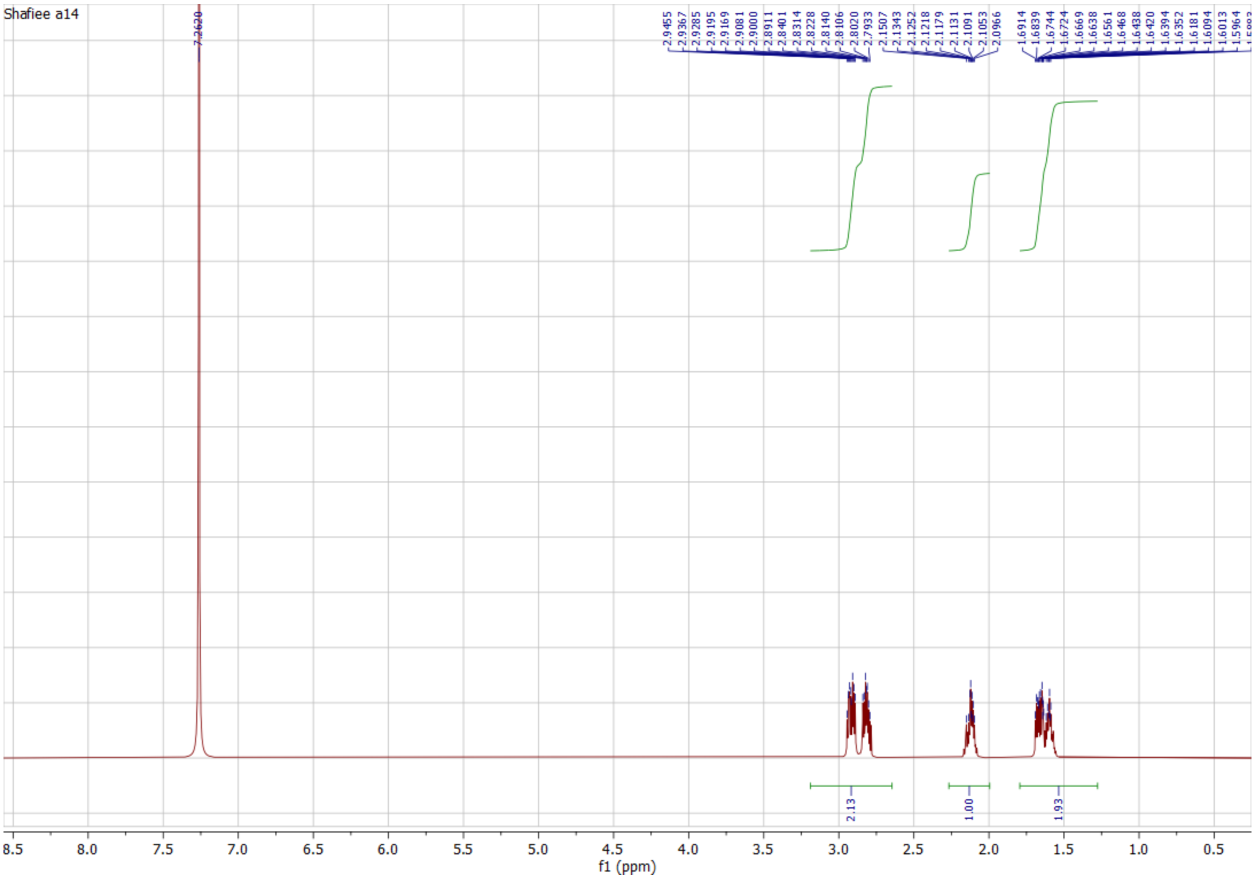

Figure S19: ^{1}H-NMR spectrum of tetrahydro-2H-thiopyran 1-oxide (a19)

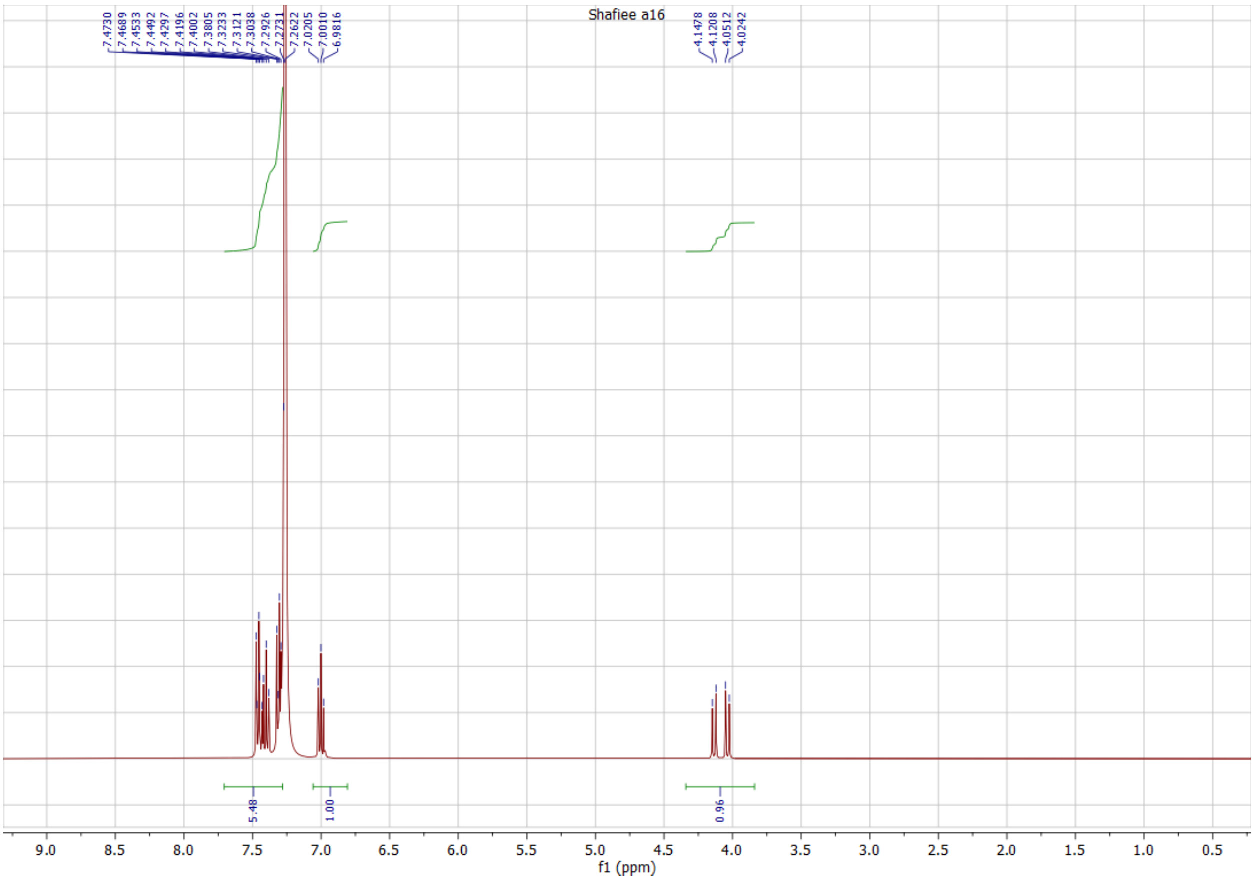

Figure S20: ^{1}H-NMR spectrum of (benzylsulfinyl)benzene (a_{20})