1,2-Disulfoxides as products in the thermolysis of sulfinimines

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Supplementary Information

1. General remarks

Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. The sulfinimines were synthesised following previously described procedures and their spectroscopy data compared to values reported in literature. Compound **5** was synthesised following a reported procedure and its spectroscopy data matches those previously described.All reactions were carried out in flame-dried glassware under Ar atmosphere. THF was distilled from Na/benzophenone immediately prior to use. DCM was dried over 4Å molecular sieves prior to use. Column chromatography was carried on silica gel Fluka 60 using petroleum ether (40-60°C)/ethyl acetate as eluent, whilst monitoring by UV (254 nm) and thin layer chromatography (PMA stain). All NMR spectra were obtained in CDCl3 at room temperature using Bruker® DPX300, Bruker® AV400 spectrometers for which chemical shifts are expressed in ppm relative to the solvent and coupling constants are expressed in Hz. Infrared spectroscopic data were recorded using a Bruker® Tensor27 FTIR spectrometer. Mass spectral data (and HRMS) were obtained using a Bruker® MicroTOF spectrometer. Melting points were measured on a Gallenkamp® apparatus.

2. Screening of solvents

Entry	Conditions	**4a** [%][a]	**3a** [%][a]
1	**1aa**, **2** (0.07M in benzene), 100ºC, 20h	57	40
2	**1aa** (0.07M in benzene), 100ºC, 20h	60	40
3	**1aa** (0.07M in dichloroethane), 100ºC, 20h	50	36
4	**1aa** (0.07M in dioxane), 100ºC, 20h	43	33
5	**1aa** (0.07M in toluene), 100ºC, 20h	25	35
6	**1aa** (0.07M in heptane), 100ºC, 20h	20	46
7	**1aa** (0.14M in benzene), 100ºC, 20h	41	52
8	**1aa** (0.03M in benzene), 100ºC, 20h	52	33
9	**1aa** (0.07M in benzene), 100ºC, 20h[b]	40	52
10	**1aa** (0.07M in benzene), 100ºC, O_2 (1atm), 20h[b]	53	46

[a] GC yields. [b] Reaction mixture was previously degassed.

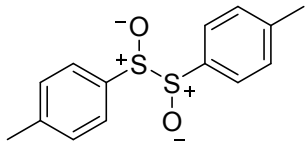
3. Procedures for the synthesis of vicinal disulfoxides.

2.1 General procedure for the synthesis of vicinal disulfoxide 4: A solution of the corresponding sulfinimine **1** (0.48 mmol) in benzene (7 mL) was stirred at 100 ºC (unless otherwise stated). After 15 h (unless otherwise stated) the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (silicagel, petrol ether/EtOAc 10%) to afford the desired vicinal disulfoxide and the corresponding disulfide.

2.2 Experiment with radical inhibitors: A solution of (*E*)-*N*-benzyliden-4-methylbenzenesulfinamide **1aa** (0.01 g, 0.041 mmol) in benzene (0.7 mL) was stirred at 100 ºC in the presence of butylated hydroxytoluene (BHT) (0.018 g, 0.082 mmol). After 15 h the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (silicagel, petrol ether/EtOAc 10%) to afford 4 mg of the vicinal disulfoxide (52%) and the corresponding disulfide.

3. Characterisation of vicinal disulfoxides 4a and 4b, disulfides 3a and 3b, thiolsulfinate 5 and 2-naphthalene nitrile..

4-Methyl-phenyl-disulfoxide 4a.



Synthesized according to the general procedure described above. Isolated as a white solid.

m.p. = 72-75 °C.

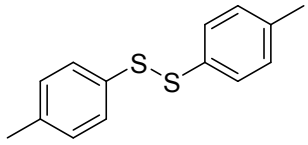
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.4 Hz, 2H), 7.29-7.16 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 144.6 (s), 142.0 (s), 140.5 (s), 136.5 (s), 130.2 (d), 129.4 (d), 127.6 (d), 124.6 (s), 21.7 (q), 21.5 (q).

IR ν(cm^{-1}): 3012, 2926, 1596, 1491, 1453, 1401, 1328, 1305, 1144, 1079, 1018.

HRMS (ESI-MS): calcd. for $C_{14}H_{14}NaO_2S_2$: 301.0327, found: 301.0323.

4-Methyl-phenyl-disulfide 3a.



Synthesized according to the general procedure described above. Isolated as a white solid.

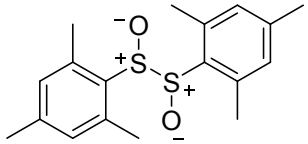
m.p. = 43-45 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.2 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 2.32 (s, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 137.4 (s), 133.9 (s), 129.8 (s), 128.5 (s), 21.0 (q).

IR ν(**cm^{-1}**): 3011, 2925, 2867, 1490, 1452, 1398, 1262, 1079, 1016

2,4,6-Trismethyl-phenyl-disulfoxide 4b.



Synthesized according to the general procedure described above. Isolated as a white solid.

m.p. = 79-81 °C

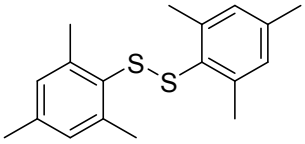
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.01 (s, 2H), 6.91 (s, 2H), 2.66 (bs, 6H), 2.56 (s, 6H), 2.33 (s, 3H), 2.32 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 144.6 (s), 141.7 (s), 140.7 (s), 137.7 (s), 131.9 (d), 130.6 (bs), 129.5 (d), 23.5 (q), 21.5 (q), 21.4 (q), 19.1 (q).

IR ν(cm^{-1}): 3012, 2925, 1596, 1490, 1453, 1402, 1328, 1304, 1144, 1079, 1017.

HRMS (ESI-MS): calcd. for $C_{18}H_{22}NaO_2S_2$: 357.0959, found: 357.0953.

1,2-dimesityldisulfane 3b



Synthesized according to the general procedure described above. Isolated as a white solid.

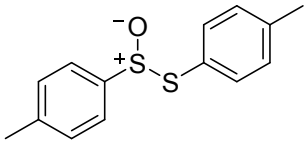
m.p. = 50-52 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.84 (s, 4H), 2.25 (s, 6H), 2.21 (s, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.2 (s), 139.2 (s), 128.9 (d), 131.6 (s), 21.4 (q), 21.1(q).

IR ν(cm^{-1}): 3013, 2927, 2860, 1493, 1398, 1260, 1080, 1011.

(*p*-tolyl) 4-methylbenzenesulfinothioate 5

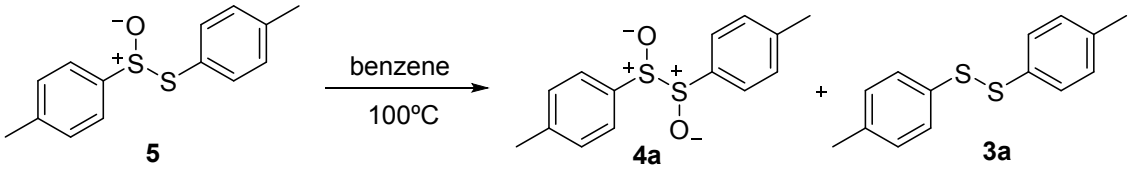


To a cold solution (-40ºC) of disulfide **3a** (0.06 g, 0.2 mmol) in DCM (2 mL) was added mCPBA (0.035 g, 0.2 mmol) and the mixture was stirred at -40ºC for 1h. After that time an aqueous saturated solution of $NaHCO_3$ was added and the aqueous phase extracted with DCM (3x). Combined organic layers were dried (Na_2SO_4), filtered and solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (silicagel, petrol ether/EtOAc 10%) to afford 30 mg (57%) of a white

solid identified (*p*-tolyl) 4-methylbenzenesulfinothioate **5**. Due to previously described instability the compound was immediately submitted to the disproportionation reaction described below.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).

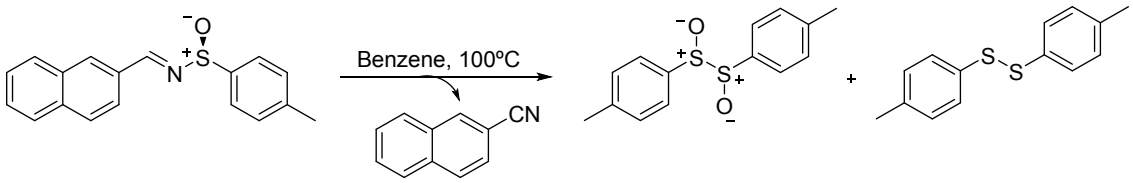
HRMS (ESI-MS): calcd. for $C_{14}H_{15}OS_2$: 263.0564, found: 263.0548.



5 **4a** **3a**

A solution of the thiolsulfinate **5** (0.01g, 0.038 mmol) in benzene (0.7 mL) was stirred at 100ºC for 15 h. Then solvent was removed and the crude reaction analysed by ^{1}H-NMR to observe a clean transformation to the depicted disulfoxide **4a** and disulfide **3a** in a ratio **4a**:**3a** 1:1.2. Disulfoxide **4a** was isolated in 43% yield after purification by column chromatography.

2-naphthalene nitrile.



A solution of the sulfinimine **1ae** (0.14g, 0.48 mmol) in benzene (7 mL) was stirred at 100ºC. After 20 h the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (silicagel, petrol ether/EtOAc 5%) to afford 30 mg of a white solid identified as 2-naphthalene nitrile (40% yield) together with the desired vicinal disulfoxide and disulfide.

m.p. = 64-67 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.95-7.91 (m, 3H), 7.68-7.62 (m, 3H).

HRMS (ESI-MS): calcd. for $C_{11}H_7NNa$: 153.0578, found: 153.0582.

4. X-Ray analytical data of vicinal disulfoxides 4a and 4b and disulfide 3a.

4.1 General procedure for the crystallisation of compounds 4a, 3a and 4b.

The compound was dissolved in a mixture of chloroform and dichloromethane and it was recrystallised by slow evaporation at 0ºC.

4.2 X-Ray analytical data for compound 4a.

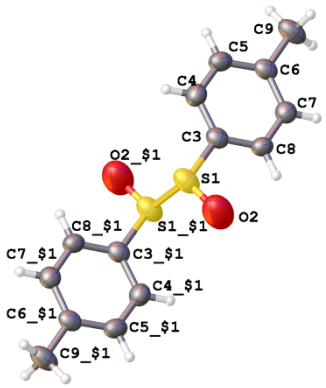


Table 1 Crystal data and structure refinement for 4a

Identification code	4a
Empirical formula	$C_{14}H_{14}O_2S_2$
Formula weight	278.37
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.7235(12)
b/Å	7.5497(11)
c/Å	15.671(2)
α/°	90
β/°	97.432(15)
γ/°	90
Volume/Å^3	671.45(19)
Z	2
ρ_{calc}mg/mm^3	1.377
m/mm^{-1}	3.519
F(000)	292.0
Crystal size/mm^3	0.612 × 0.2273 × 0.046
2Θ range for data collection	13.038 to 149.622°
Index ranges	$-7 \le h \le 6$, $-9 \le k \le 9$, $-19 \le l \le 19$
Reflections collected	2646
Independent reflections	1306[R(int) = 0.0257]
Data/restraints/parameters	1306/0/95
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	$R_1 = 0.0517$, $wR_2 = 0.1339$
Final R indexes [all data]	$R_1 = 0.0617$, $wR_2 = 0.1443$

Largest diff. peak/hole / e Å^{-3} 0.37/-0.36

Table 2 Bond Lengths for 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	S1[1]	2.1096(15)	C4	C5	1.381(4)
S1	O2	1.379(6)	C5	C6	1.395(4)
S1	O2A	1.261(7)	C6	C7	1.386(4)
S1	C3	1.778(3)	C6	C9	1.505(4)
C3	C4	1.391(4)	C7	C8	1.382(4)
C3	C8	1.388(4)			

[1]1-X,1-Y,1-Z

Table 3 Bond Angles for 4a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	S1[1]	111.9(3)	C5	C4	C3	119.1(2)
O2	S1	C3	108.9(3)	C4	C5	C6	121.4(2)
O2A	S1	S1[1]	113.0(4)	C5	C6	C9	120.3(3)
O2A	S1	C3	109.2(4)	C7	C6	C5	118.3(2)
C3	S1	S1[1]	96.50(9)	C7	C6	C9	121.3(3)
C4	C3	S1	119.2(2)	C8	C7	C6	121.3(2)
C8	C3	S1	120.4(2)	C7	C8	C3	119.5(2)
C8	C3	C4	120.4(2)				

[1]1-X,1-Y,1-Z

Table 4 Torsion Angles for 4a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1[1]	S1	C3	C4	85.1(2)	C3	C4	C5	C6	-0.3(4)
S1[1]	S1	C3	C8	-95.8(2)	C4	C3	C8	C7	1.2(4)
S1	C3	C4	C5	178.3(2)	C4	C5	C6	C7	0.9(4)
S1	C3	C8	C7	-177.79(19)	C4	C5	C6	C9	-178.4(3)
O2	S1	C3	C4	-159.0(4)	C5	C6	C7	C8	-0.4(4)
O2	S1	C3	C8	20.0(4)	C6	C7	C8	C3	-0.6(4)
O2A	S1	C3	C4	-32.0(5)	C8	C3	C4	C5	-0.8(4)
O2A	S1	C3	C8	147.0(5)	C9	C6	C7	C8	178.9(3)

[1]1-X,1-Y,1-Z

3.2.2 X-Ray analytical data for compound 4b.

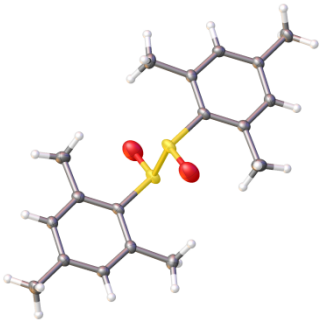


Table 1 Crystal data and structure refinement for 4b

Identification code	4b
Empirical formula	$C_{18}H_{22}O_2S_2$
Formula weight	334.47
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.5624(11)
b/Å	8.0233(11)
c/Å	8.1209(9)
α/°	84.776(10)
β/°	69.822(12)
γ/°	61.946(15)
Volume/Å^3	406.64(11)
Z	1
ρ_{calc}mg/mm^3	1.366
m/mm^{-1}	2.995
F(000)	178.0
Crystal size/mm^3	0.4824 × 0.1558 × 0.1068
2Θ range for data collection	11.652 to 155.654°
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $-10 \le l \le 10$
Reflections collected	7093
Independent reflections	1709[R(int) = 0.0342]
Data/restraints/parameters	1709/0/113
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1733
Final R indexes [all data]	R_1 = 0.0584, wR_2 = 0.1748
Largest diff. peak/hole / e Å^{-3}	0.69/-0.45

Table 2 Bond Lengths for 4b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	S1[1]	2.1282(12)	C4	C9	1.510(3)
S1	O2	1.468(5)	C5	C6	1.393(4)
S1	O2A	1.392(6)	C6	C7	1.396(3)
S1	C3	1.784(2)	C6	C10	1.505(3)
C3	C4	1.408(3)	C7	C8	1.393(3)
C3	C8	1.405(4)	C8	C11	1.508(3)
C4	C5	1.393(3)			

[1]1-X,-Y,1-Z

Table 3 Bond Angles for 4b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	S1[1]	112.7(2)	C5	C4	C9	118.9(2)
O2	S1	C3	109.8(2)	C6	C5	C4	122.0(2)
O2A	S1	S1[1]	112.4(3)	C5	C6	C7	118.4(2)
O2A	S1	C3	114.1(3)	C5	C6	C10	121.4(2)
C3	S1	S1[1]	96.16(8)	C7	C6	C10	120.2(2)
C4	C3	S1	119.73(19)	C8	C7	C6	121.9(2)
C8	C3	S1	118.87(19)	C3	C8	C11	123.1(2)
C8	C3	C4	121.4(2)	C7	C8	C3	118.2(2)
C3	C4	C9	123.1(2)	C7	C8	C11	118.7(2)
C5	C4	C3	118.0(2)				

[1]1-X,-Y,1-Z

3.2.3 X-Ray analytical data for compound 3a.

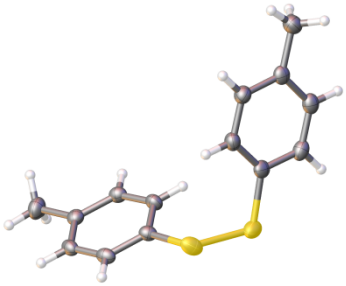


Table 1 Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{14}H_{14}S_2$
Formula weight	246.37
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.5701(7)
b/Å	5.7018(6)
c/Å	14.6979(13)
α/°	90
β/°	94.682(8)
γ/°	90
Volume/Å^3	632.29(10)
Z	2
ρ_{calc}mg/mm^3	1.294
m/mm^{-1}	3.545
F(000)	260.0
Crystal size/mm^3	0.5996 × 0.2451 × 0.0366
2Θ range for data collection	6.034 to 153.092°
Index ranges	$-9 \le h \le 9$, $-6 \le k \le 7$, $-14 \le l \le 18$
Reflections collected	4647
Independent reflections	2393[R(int) = 0.0298]
Data/restraints/parameters	2393/1/147
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0787
Final R indexes [all data]	R_1 = 0.0329, wR_2 = 0.0819
Largest diff. peak/hole / e Å^{-3}	0.25/-0.21
Flack parameter	0.132(15)

Table 2 Bond Lengths for 3a.

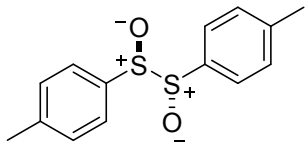
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	S2	2.0255(13)	C7	C8	1.389(4)
S1	C3	1.790(3)	C10	C11	1.386(4)
S2	C10	1.786(3)	C10	C15	1.385(5)
C3	C4	1.391(4)	C11	C12	1.394(4)
C3	C8	1.387(4)	C12	C13	1.389(5)
C4	C5	1.383(4)	C13	C14	1.394(5)
C5	C6	1.391(4)	C13	C16	1.504(4)

C6	C7	1.393(4)	C14	C15	1.384(5)
C6	C9	1.512(4)			

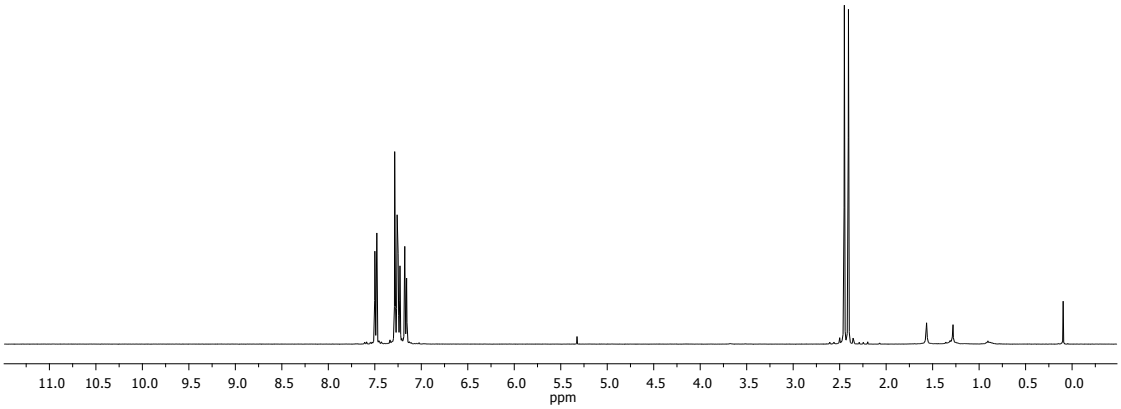
Table 3 Bond Angles for 3a.

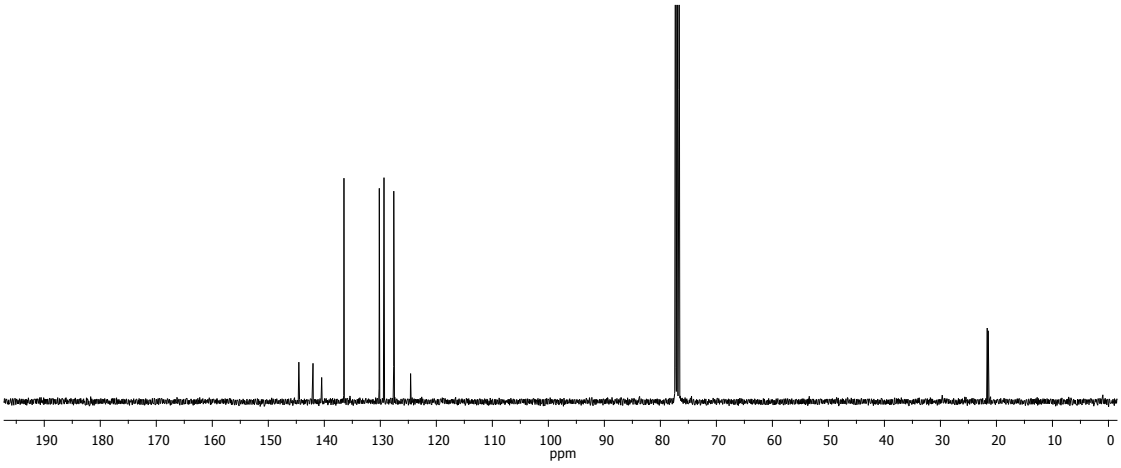
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S1	S2	105.50(11)	C3	C8	C7	119.2(3)
C10	S2	S1	106.55(12)	C11	C10	S2	124.3(2)
C4	C3	S1	115.9(2)	C15	C10	S2	115.6(2)
C8	C3	S1	123.7(2)	C15	C10	C11	120.1(3)
C8	C3	C4	120.4(3)	C10	C11	C12	119.5(3)
C5	C4	C3	119.5(3)	C13	C12	C11	121.3(3)
C4	C5	C6	121.2(3)	C12	C13	C14	118.0(3)
C5	C6	C7	118.4(3)	C12	C13	C16	121.7(3)
C5	C6	C9	121.5(3)	C14	C13	C16	120.3(3)
C7	C6	C9	120.1(3)	C15	C14	C13	121.3(3)
C8	C7	C6	121.3(3)	C14	C15	C10	119.9(3)

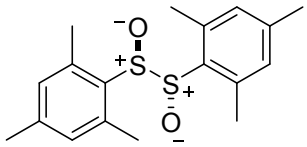
4. Spectral characterisation of vicinal disulfoxides 4a and 4b, disulfides 3a and 3b, thiosulfinate 5 and 2-naphthalene nitrile.



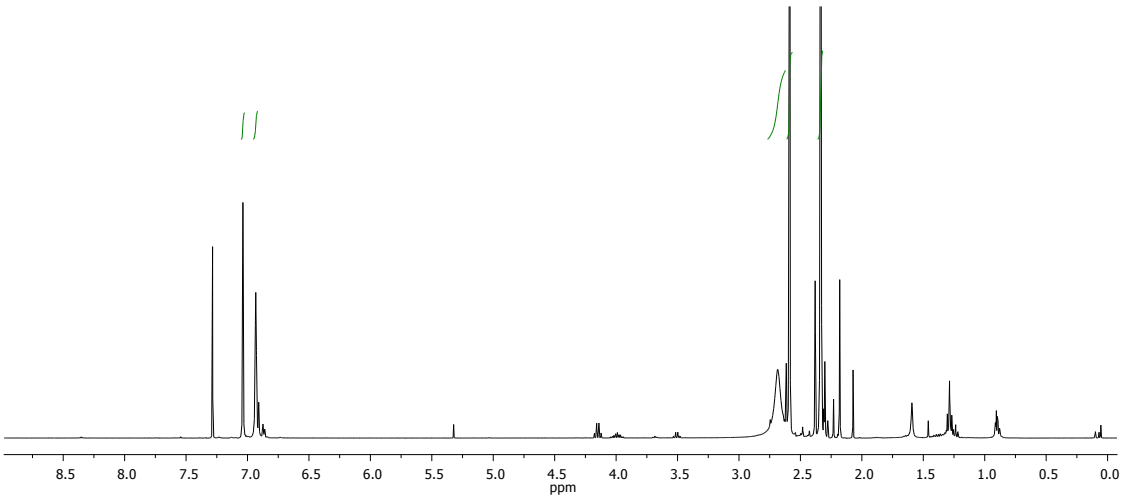
4a

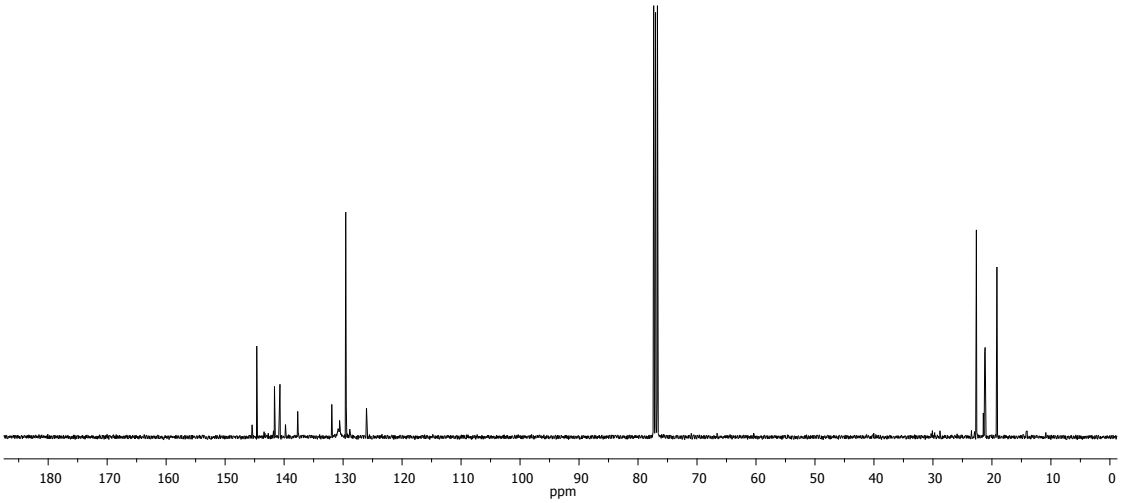


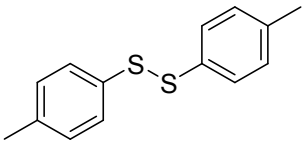




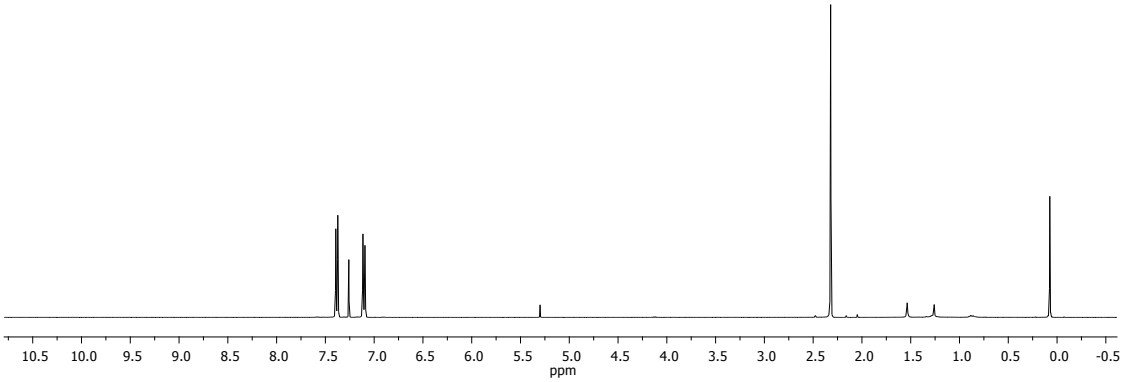
4b

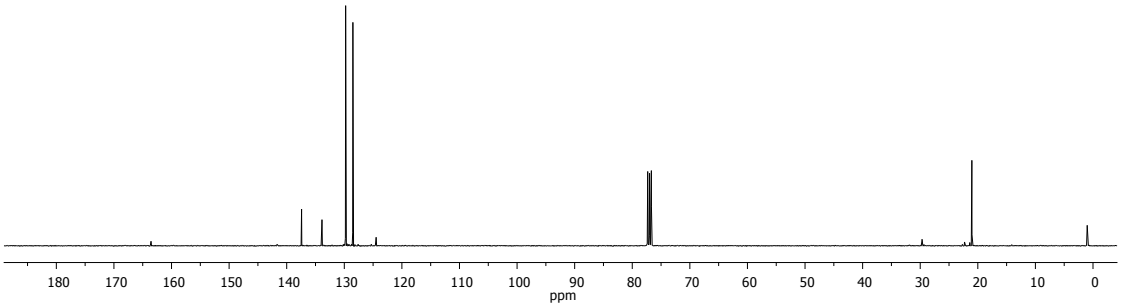

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

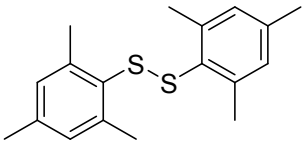

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



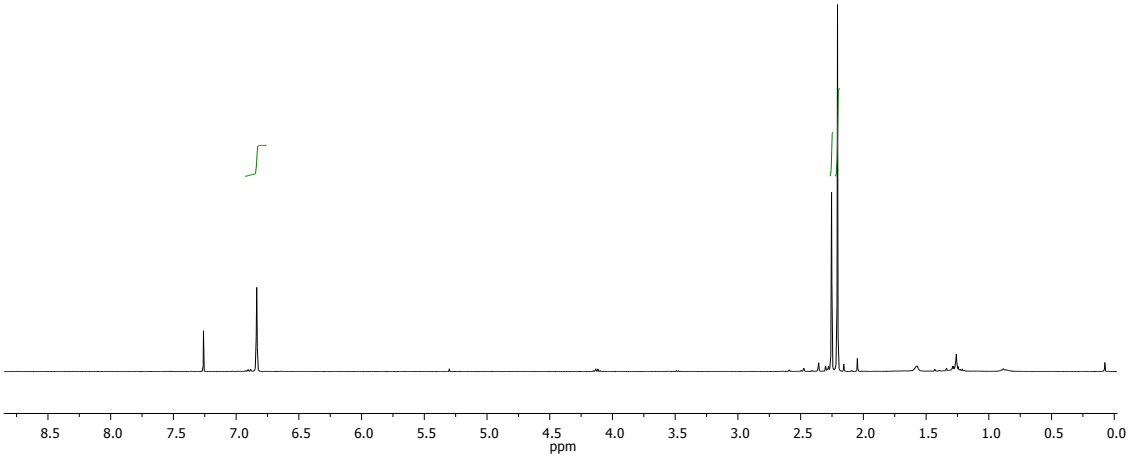
3a

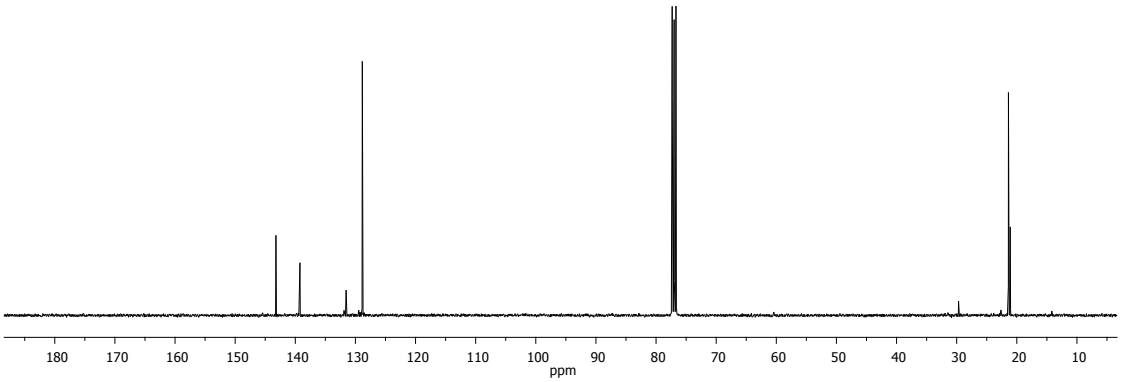

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

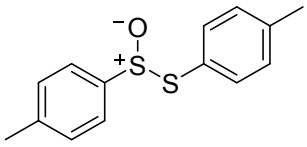

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



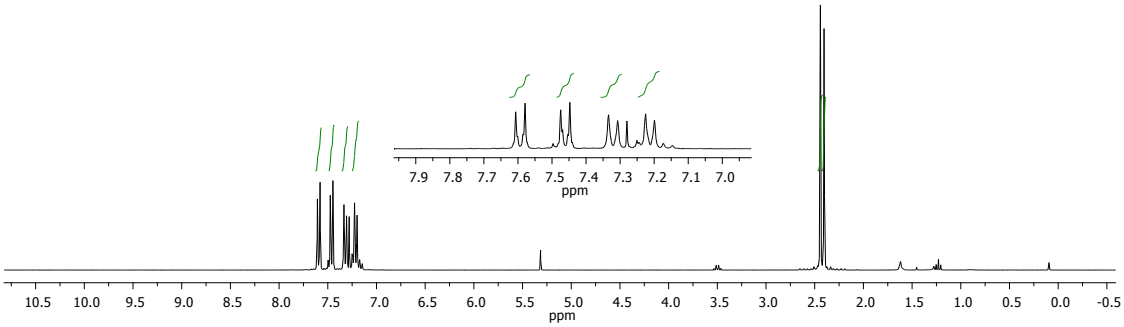
3b

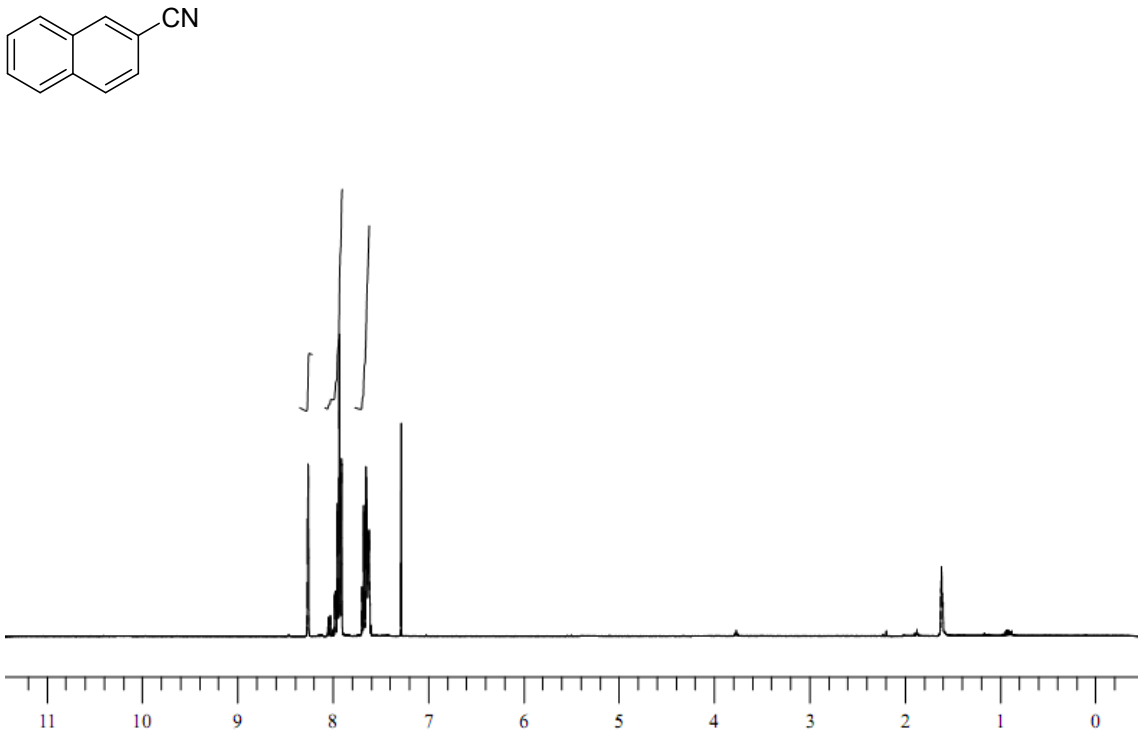

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

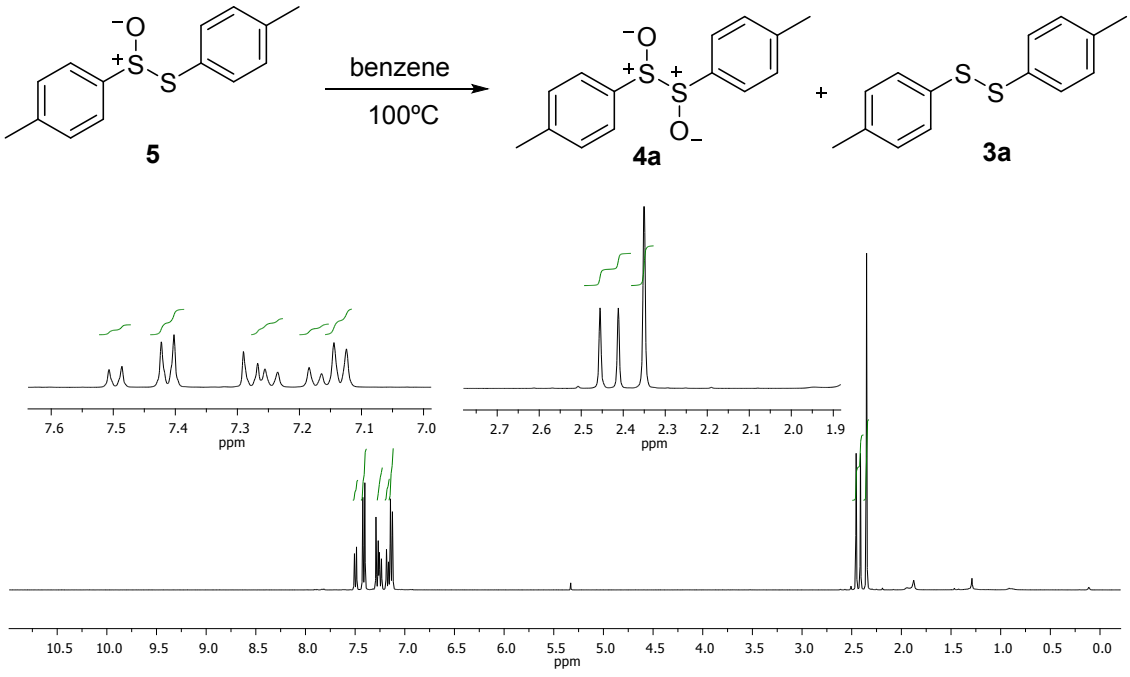

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



5


7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
ppm
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


CN
11
10
9
8
7
6
5
4
3
2
1
0


benzene
100ºC
5
4a
3a
7.6 7.5 7.4 7.3 7.2 7.1 7.0
ppm
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
ppm
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm