Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Aryl diazonium salt and thioacetamide: A catalyst free, efficient blend of inexpensive arylating agent with "S" surrogate for sulphides synthesis

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Experimental Section

General

All chemicals were purchased from Loba chemicals, S.D Fine Chemical, Avra, Spectrochem Ltd, commercial suppliers and used without further purifications. The reaction was monitored by TLC and GC analysis performed on PerkinElmer Clarus 480. GC equipped with flame ionized detector with capillary column (Elite- 1701, 30m X 0.32 X 0.25). The product mass conformed by GC–MS-QP 2010 instrument (Rtx-17, 30 m_25 mm ID, film thickness 0.25 µm, column flow: 2 mLmin–1, 80 to 240 °C at 10 °C/ min rise). The products were purified by column chromatography using (60-120 mesh) silica gel with pet ether: Ethyl acetate (90:10) as eluent. The pure product ^{1}H NMR Spectroscopic data of compounds was recorded on a Varian Mercury plus- 400 spectrometer using $CDCl_3$ as a solvent and TMS as internal standard. Aryl diazonium tetraboroflourate are synthesis by known method[1].

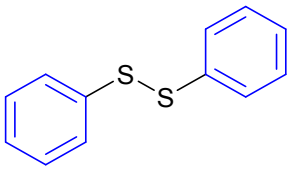
General procedure for synthesis of diaryl disulphide with aryl diazonium salt and thioacetamide

To an oven-dried 25 ml schlenk tube equipped with a magnetic stirring bar was charged with arenediazonium salt (1mmol), thioacetamide (2mmol), anhydrous DMSO (2ml), Reaction mixture was stirred at room temperature for 2 h. The reaction was monitored by GC and TLC. After completion of the reaction, the reaction mixture was diluted with water and reaction extracted in ethyl acetate. The resulting ethyl acetate layer was washed with water and 20% brine solutions. The organic layer was dried over anhydrous sodium sulphate. The solvent was removed under vacuum to get the crude product, which was purified by column chromatography on silica gel eluting with the Pet ether: Ethyl acetate (90:10) mixture to afford the pure product. The purity and identity of known products are conformed by ^{1}H NMR, LCMS and GC-MS Spectroscopic techniques.

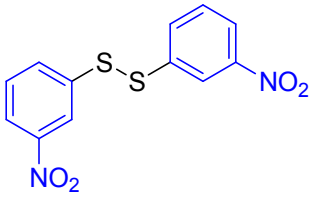
General procedure for synthesis of diaryl disulphide with aryl diazonium salt and thioacetamide

To an oven-dried 25 ml schlenk tube equipped with a magnetic stirring bar was charged with thioacetamide (1 mmol), arenediazonium salt (4 mmol), anhydrous DMSO (2 ml), Reaction mixture was stirred at room temperature for 2 h. The reaction was monitored by GC and TLC. After completion of the reaction, the reaction mixture was diluted with water and reaction extracted in ethyl acetate. The resulting ethyl acetate layer was washed with water and 20% brine solutions. The organic layer was dried over anhydrous sodium sulphate. The solvent was removed under vacuum to get the crude product, which was purified by column chromatography on silica gel eluting with the Pet ether: Ethyl acetate (90:10) mixture to afford the pure product. The purity and identity of known products are conformed by ^{1}H NMR and GC-MS Spectroscopic techniques.

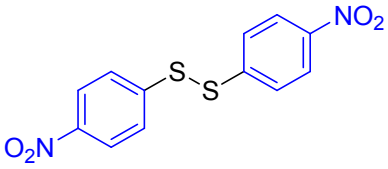
Spectroscopic data:



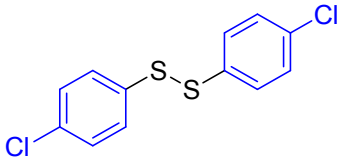
1, 2-diphenyl disulfide (2a)[46]: White solid; yield: 0.097 g (90%); mp 52-57°C; ^{1}H NMR: (400 MHz, $cdcl_3$) δ 7.48 (d, *J* = 7.4 Hz, 4H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.25 – 7.20 (m, 2H); GC-MS m/z (% relative intensity): 154(M+, 30), 152 (100), 77(60).



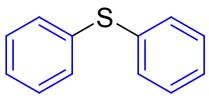
1,2- bis(3-nitrophenyl) disulfide (2e)[27]: Yellow solid; yield: 0.102 g (67%) mp 80-81°C; ^{1}H NMR: (400 MHz, $cdcl_3$) δ 8.36 – 8.31 (m, 2H), 8.07 (d, *J* = 7.2, 5.1 Hz, 2H), 7.85 – 7.76 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H); LC-MS m/z (% relative intensity): 308.



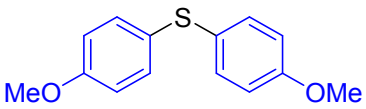
1,2-bis(4-nitrophenyl) disulfide (2f)[47]: Yellow solid; yield: 0.104 g (68%); mp 171-174°C; ^{1}H NMR: (400 MHz, cdcl$_3$) δ 7.46 – 7.35 (m, 4H), 7.26 (d, *J* = 7.3 Hz, 4H); LC-MS m/z (% relative intensity): 308.



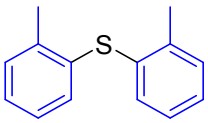
1, 2-bis (4-chlorophenyl) disulfide (2h)[46]: White solid; yield: 0.106 g (74%); mp 69-72°C; ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.46 – 7.35 (m, 4H), 7.26 (d, *J* = 7.3 Hz, 4H); GC-MS m/z (% relative intensity 286(M+, 65), 143(100), 251(5), 222(6), 108(62).



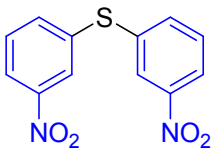
Diphenyl sulphide (3a)[32]: Yellow liquid; yield: 0.137 g (75%); ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.36-7.22 (m, *J* = 7.6 Hz, 10H); GC-MS m/z (% relative intensity): 186(M+, 100), 152 (8), 77(10).



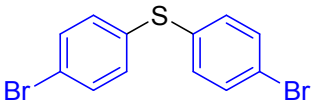
Bis(4-methoxyphenyl) sulphide (3c)[32]: Yellow solid; yield: 0.177 g (72%); mp 46-47°C; ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.25 (d, *J* = 8.8 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 4H), 3.77 (s, 6H); GC-MS m/z (% relative intensity): 246(M+, 100), 231 (40), 128(7), 203(11).



Bis(2-methylphenyl) sulphide (3d)[11]: White solid; yield: 0.142 g (68%); mp 63-65°C; ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.25 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 6H); GC-MS m/z (% relative intensity): 214(M+, 100), 199(11), 184(6), 153(2),122(33), 105(10), 91(13).



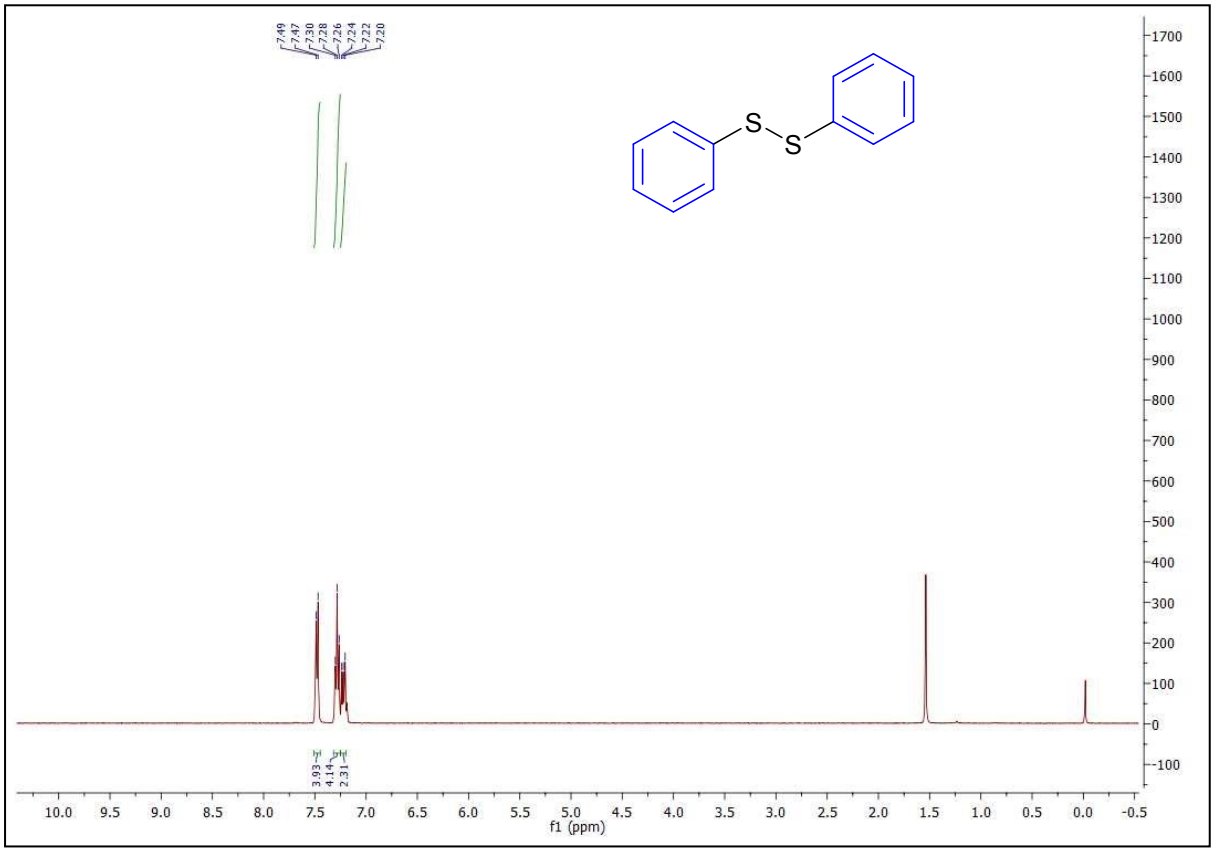
Bis(3-nitrophenyl) sulphide (3e)[32]: Yellow solid; yield: 0.174 g (63%); mp 57-60°C; ^{1}H NMR : (400 MHz, cdcl$_3$) δ 8.18 (s, 2H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 2H).

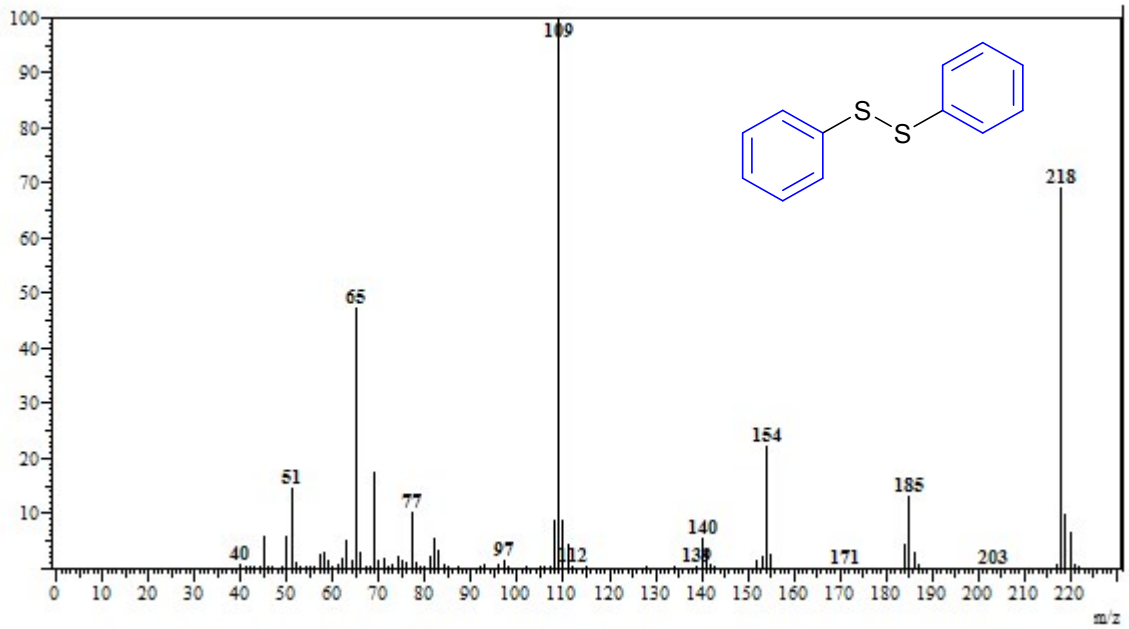


Bis(4-bromophenyl) sulphide (3i)[32]: White solid; yield: 0.24 g (71%); mp 112-114°C; ^{1}H NMR: (400 MHz, cdcl$_3$) δ 7.41 (d, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 8.5 Hz, 4H); GC-MS m/z (% relative intensity): 344(M+, 100), 342(35), 267(33), 183(14), 155(20), 77(20).

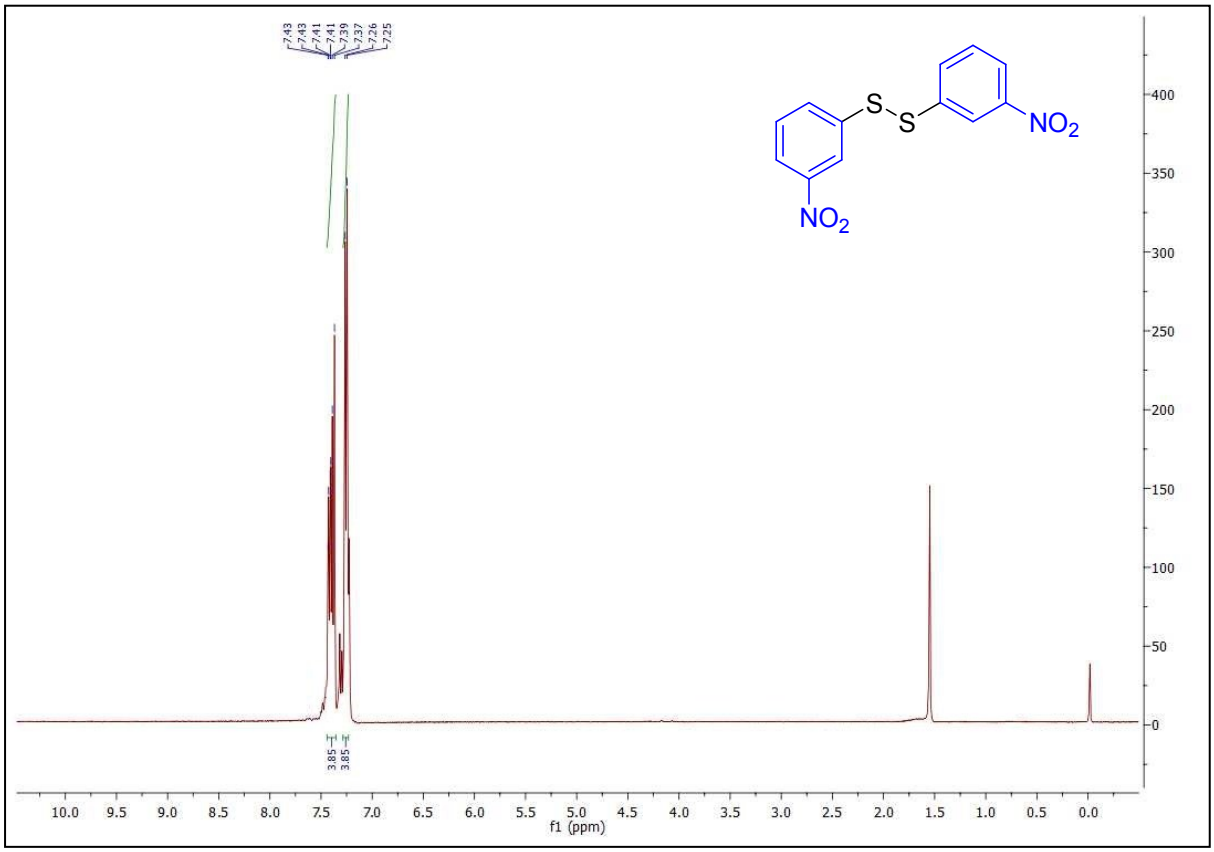
^{1}H NMR and GC-MS data of the product:

1, 2-diphenyl disulfide (2a):

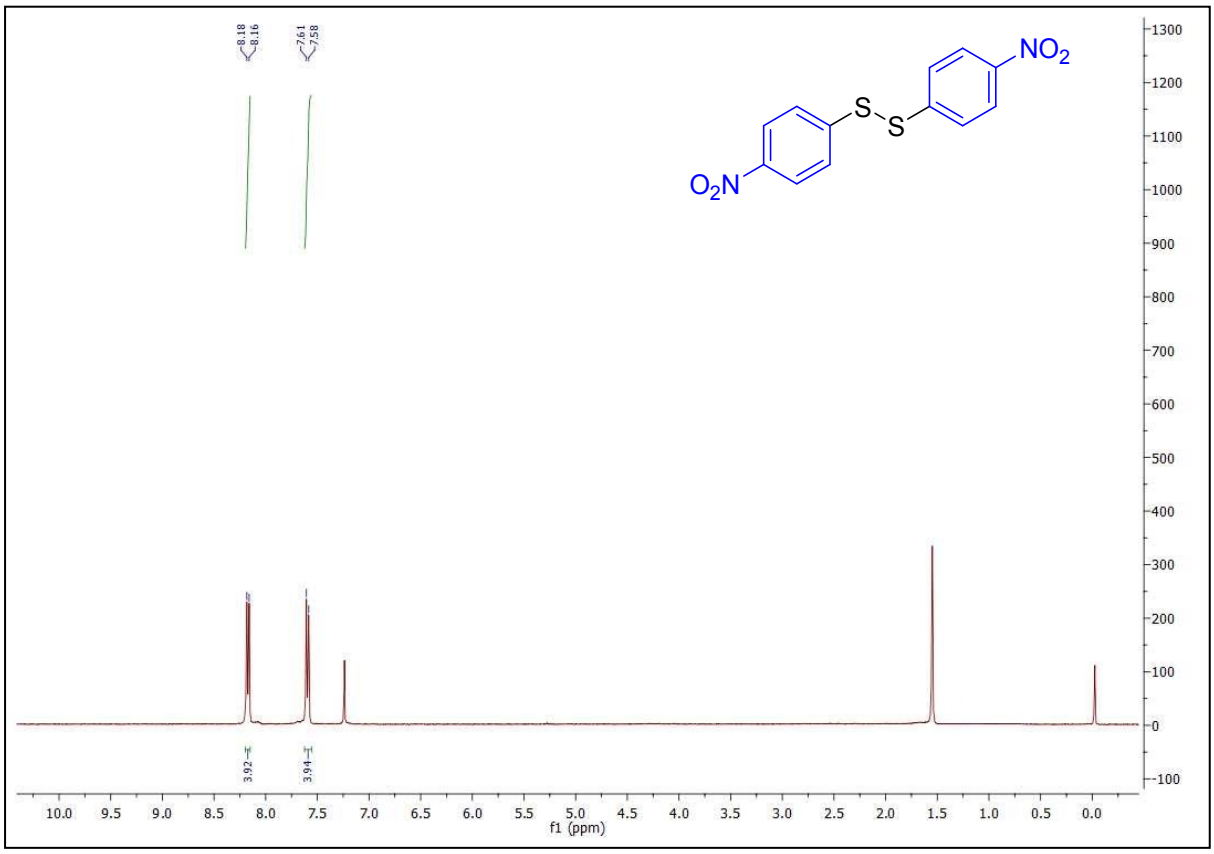




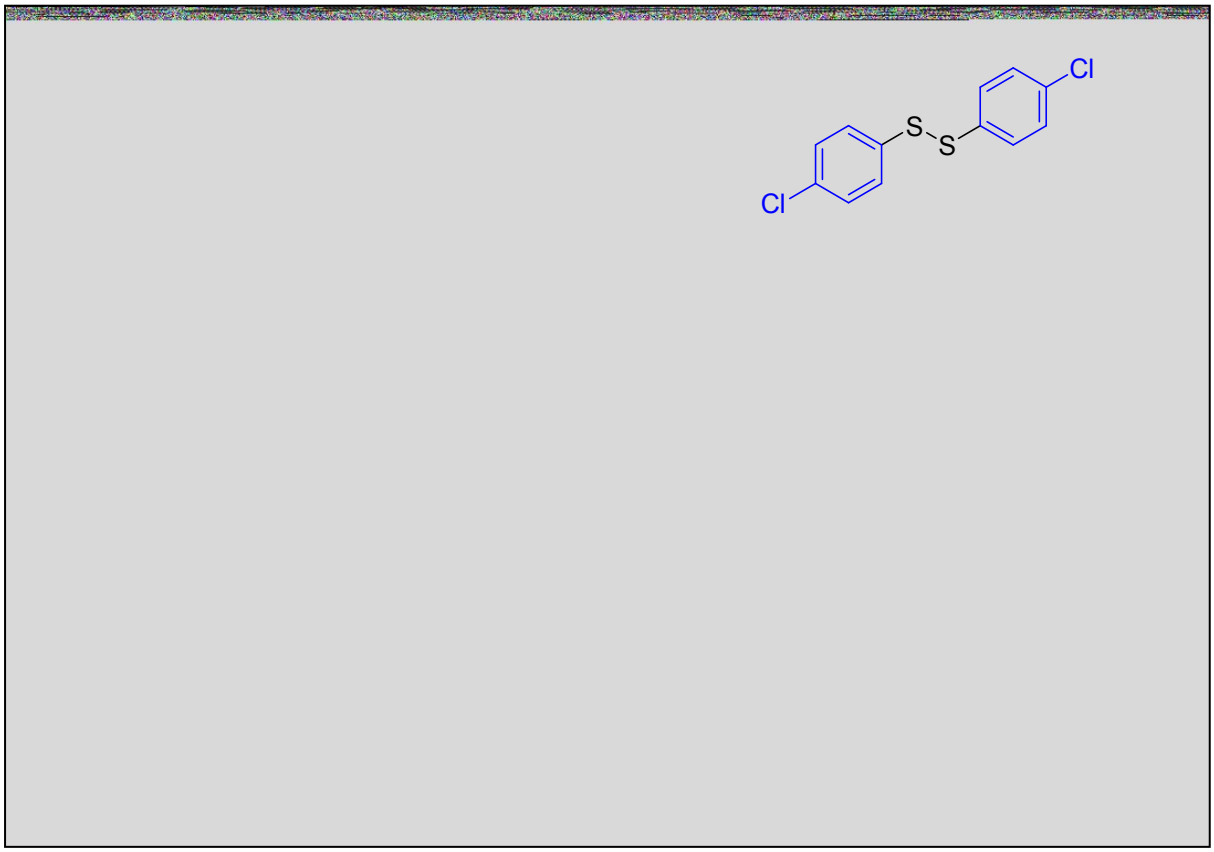
1,2- bis(3-nitrophenyl) disulfide (2e):

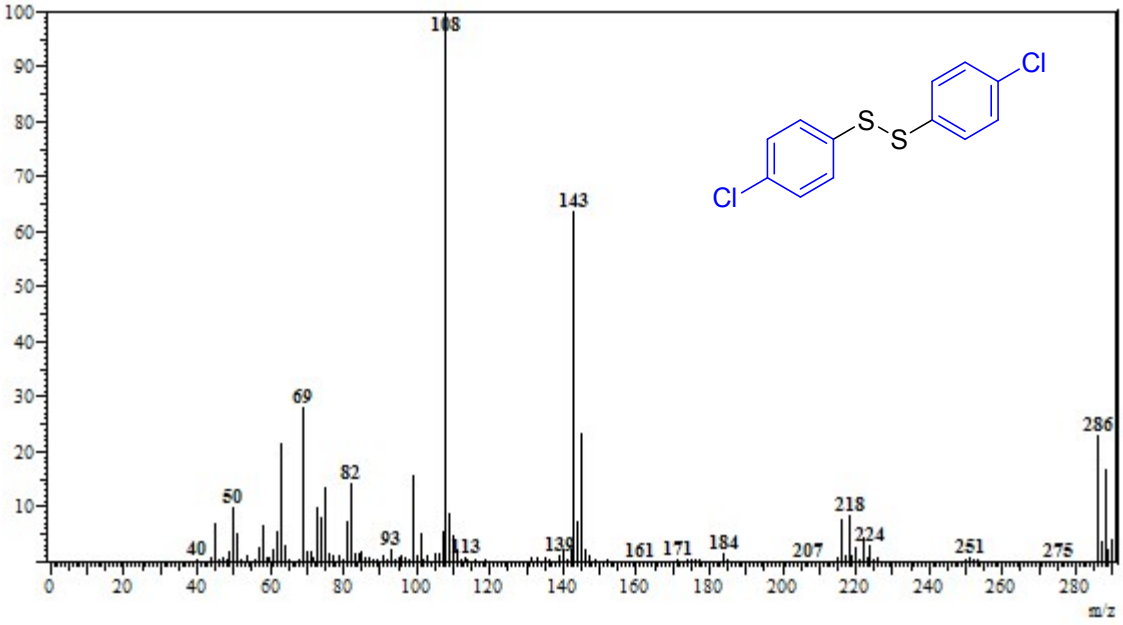


1,2 - bis(4-nitrophenyl) disulfide (2f):

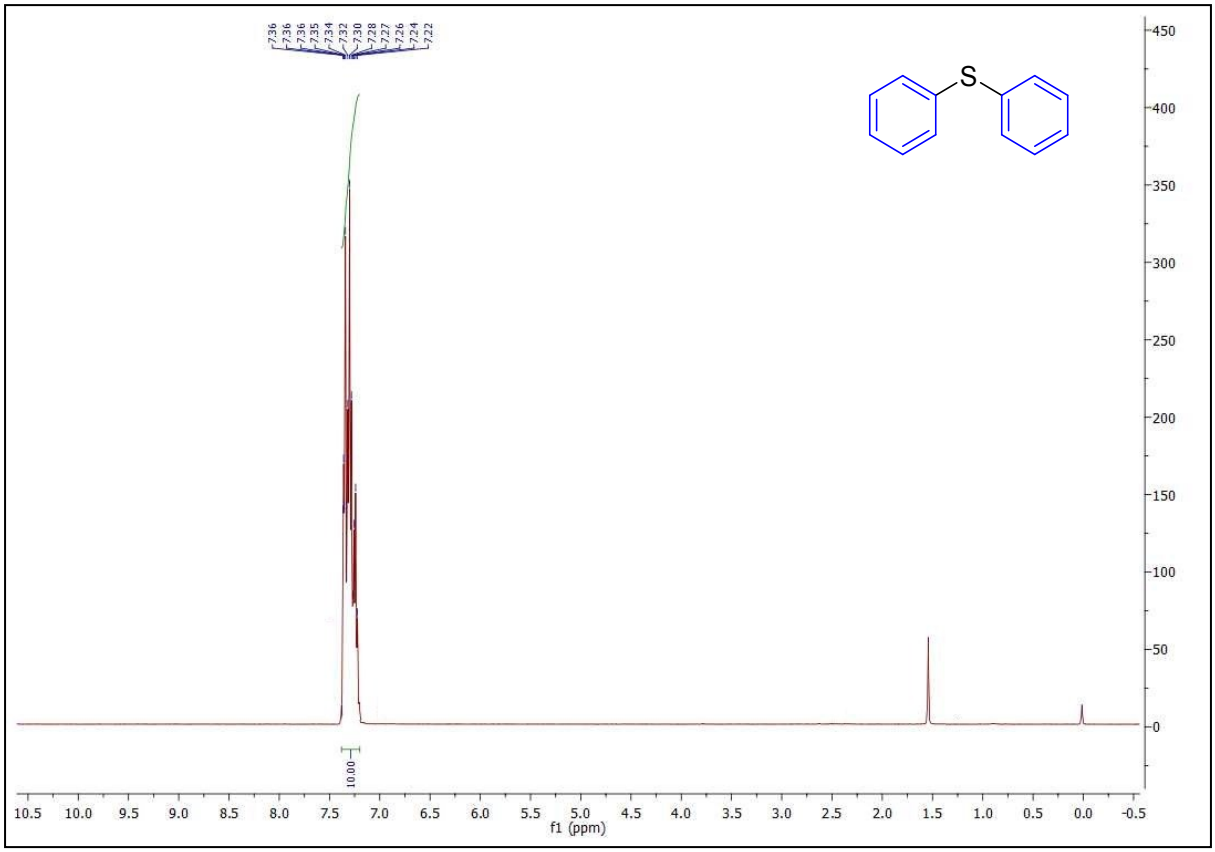


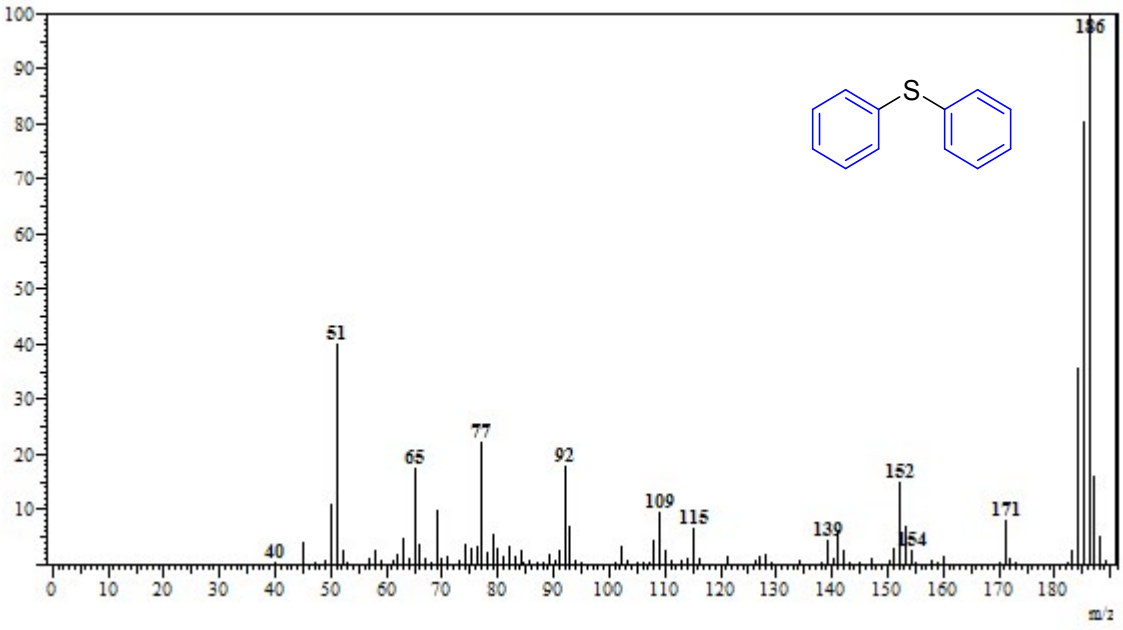
1, 2-bis (4-chlorophenyl) disulfide (2h)



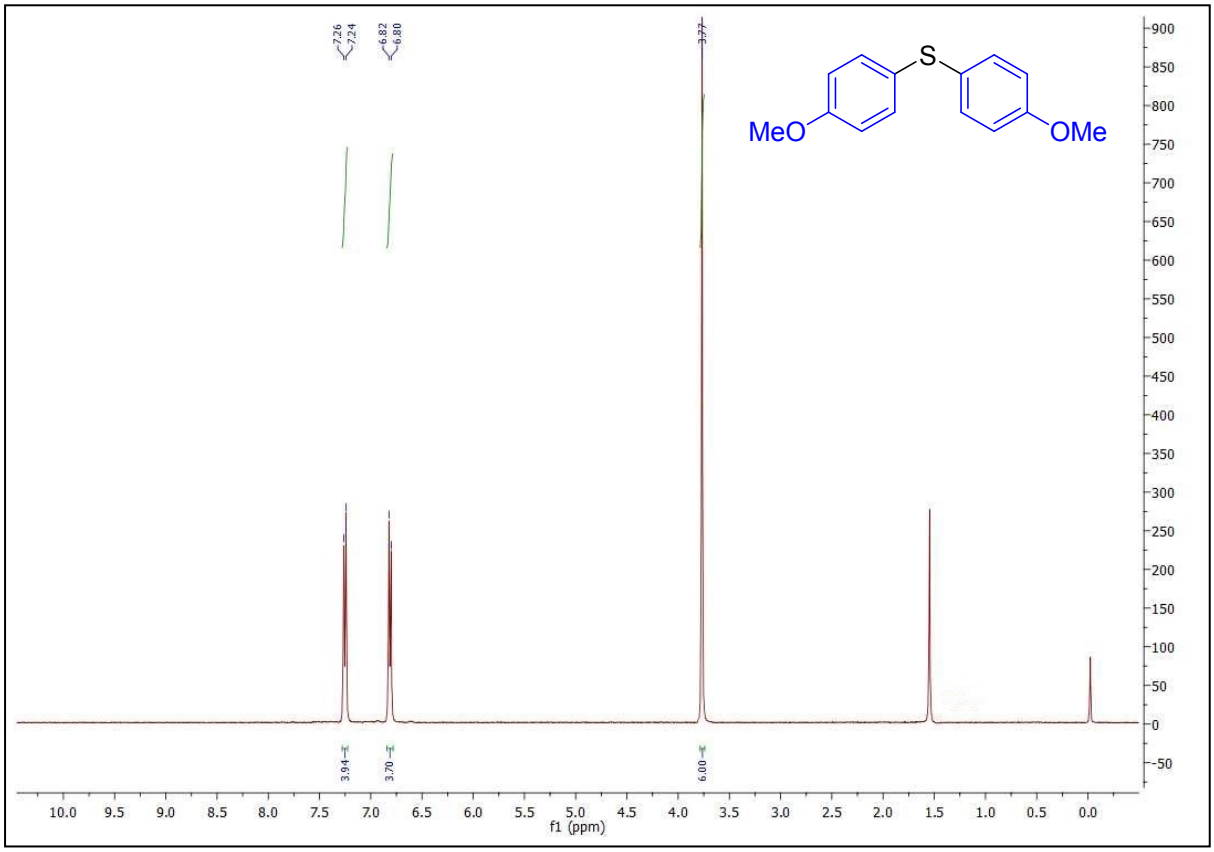


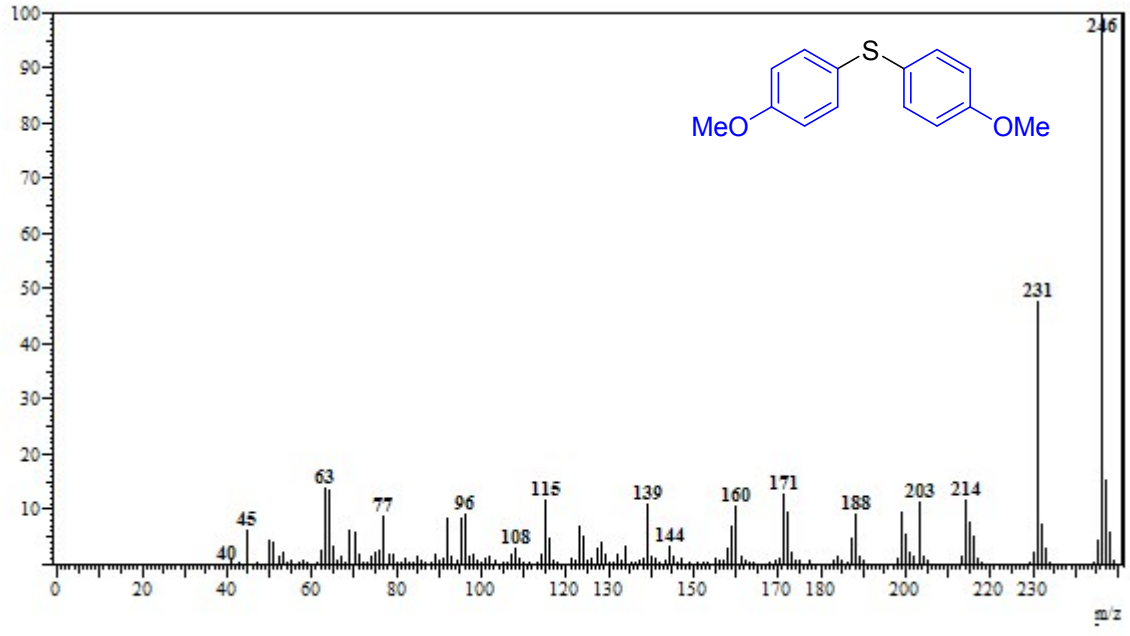
Diphenyl sulphide (3a):



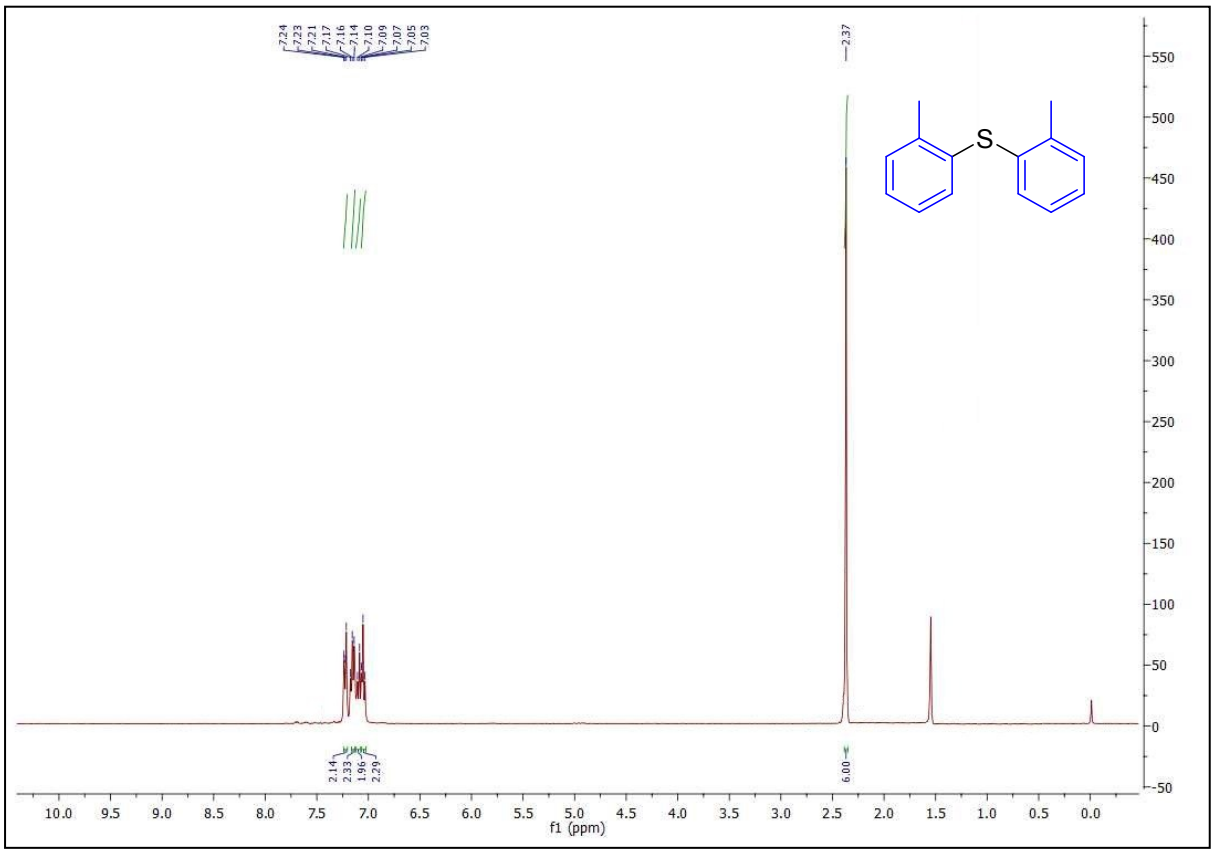


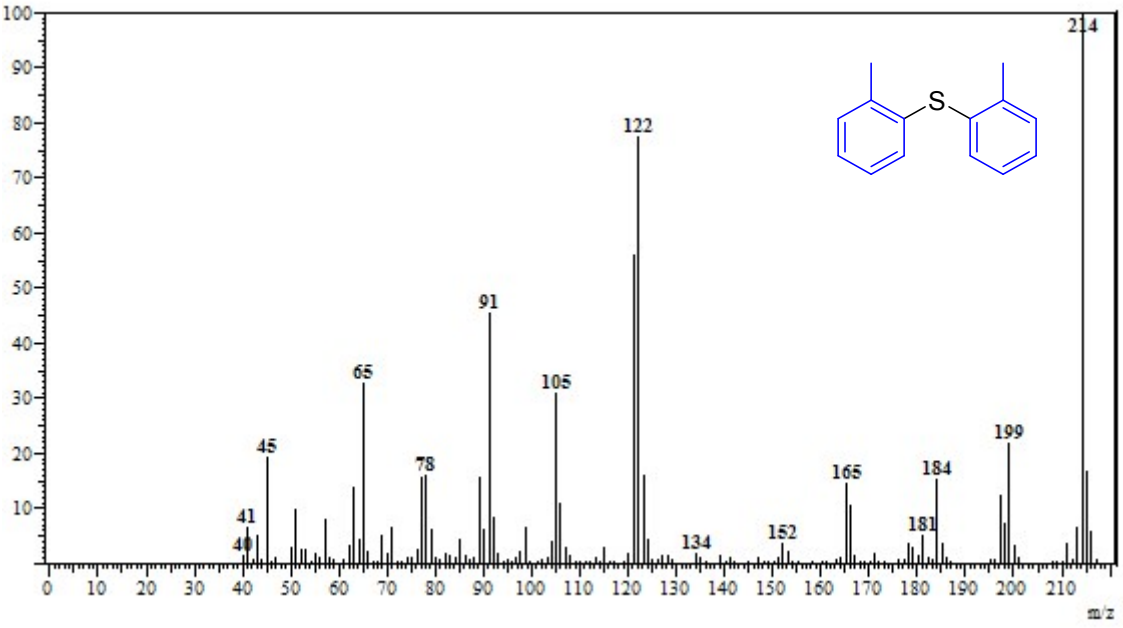
bis (4-methoxyphenyl) sulphide (3c)



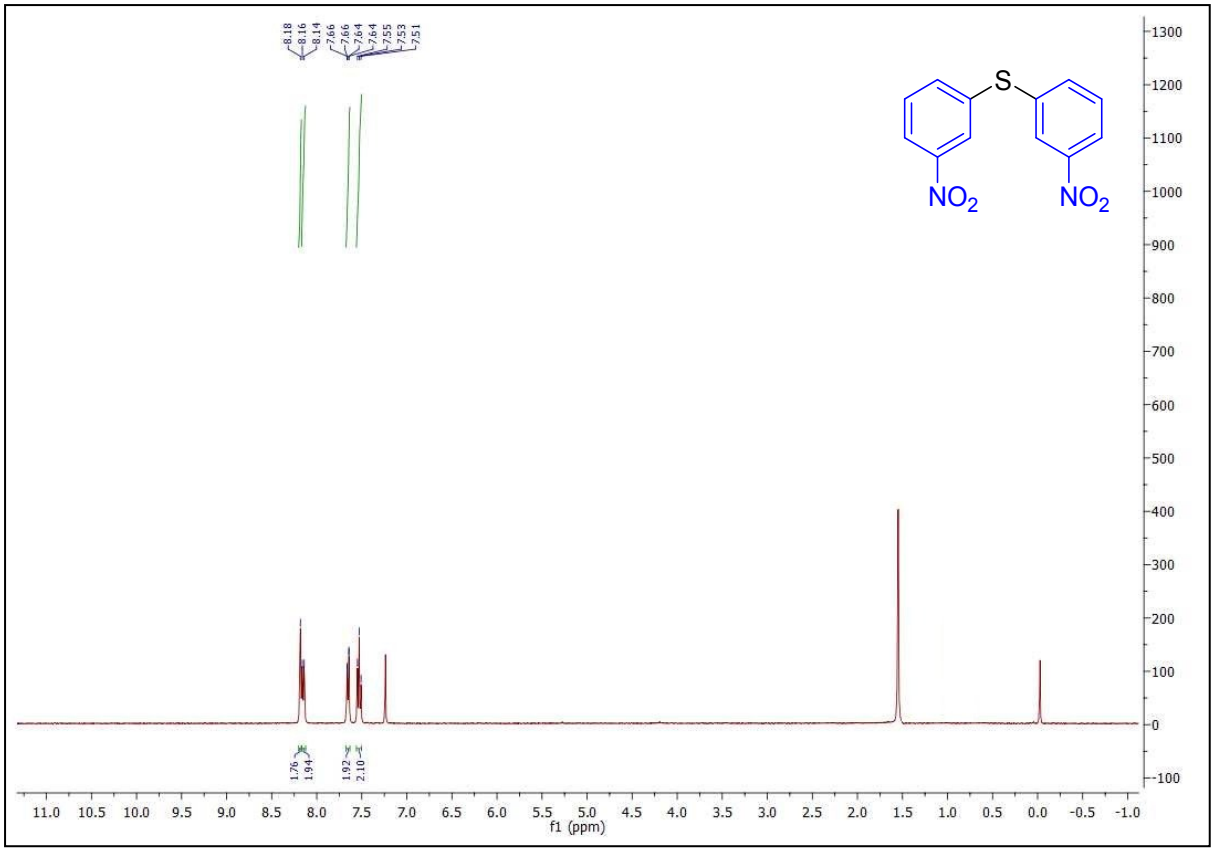


bis (2-methylphenyl) sulphide (3d)

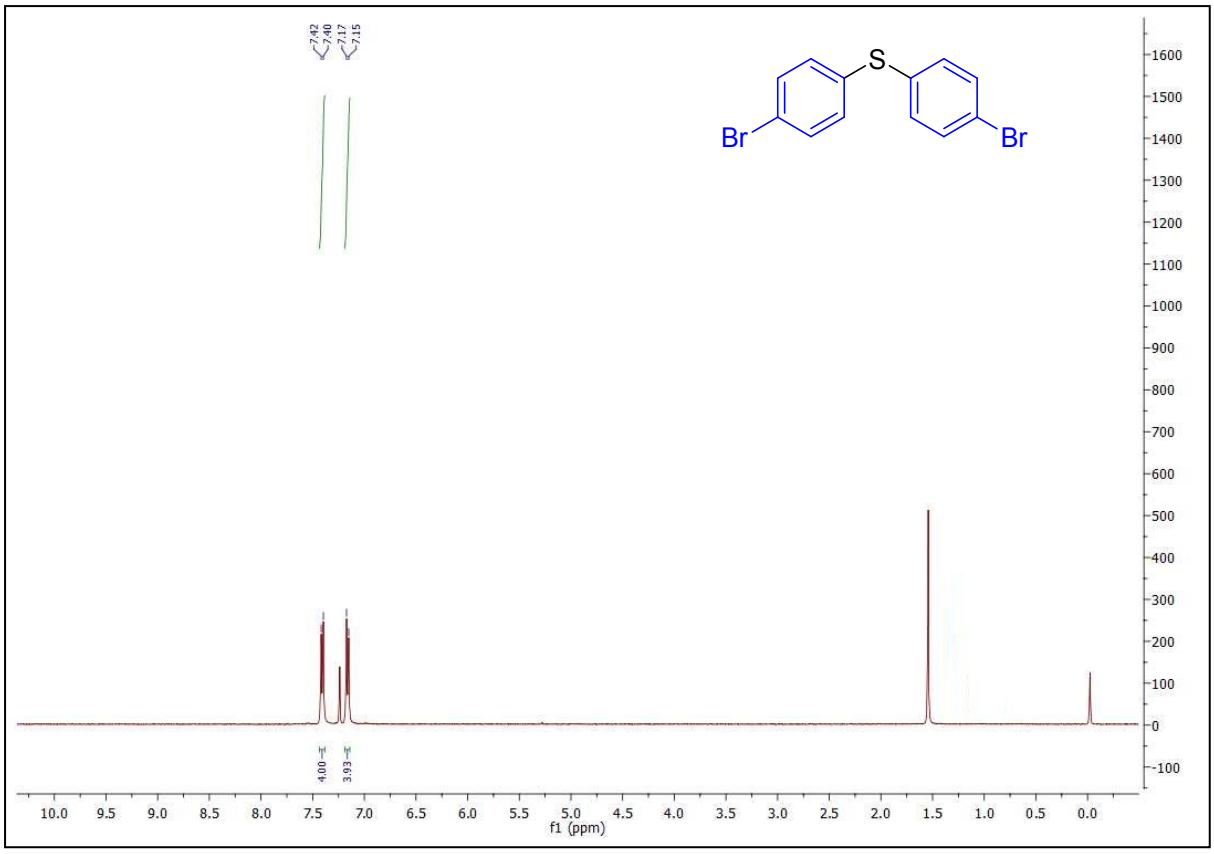


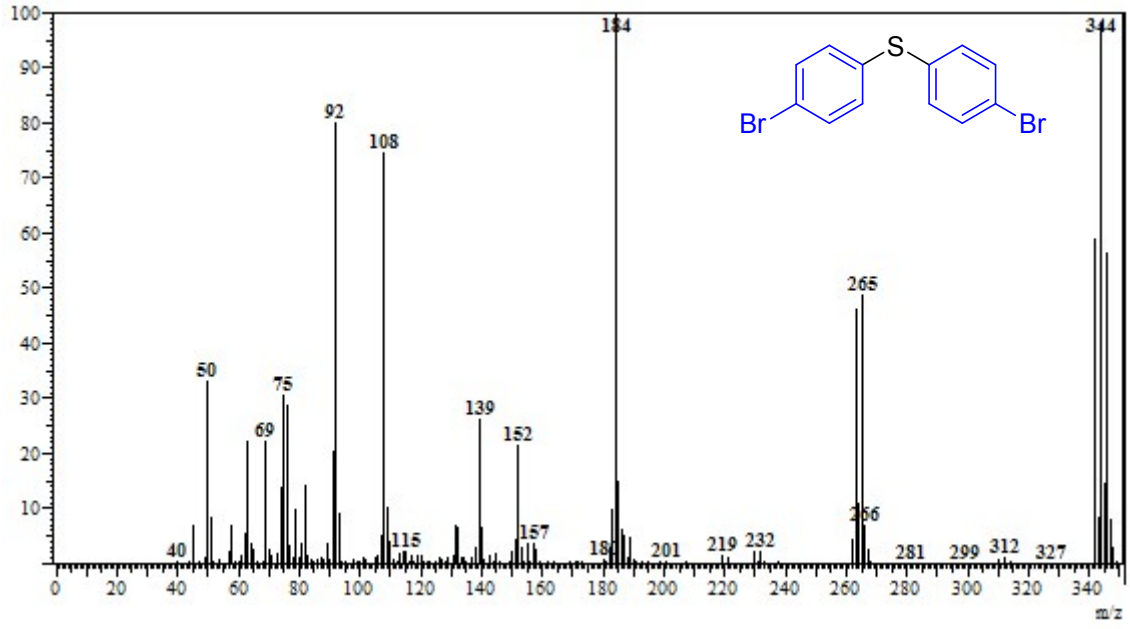


bis (3-nitrophenyl) sulphide (3e)


8.18
8.16
8.14
7.66
7.66
7.64
7.64
7.55
7.53
7.51
S
NO2
NO2
1.76
1.94
1.92
2.10
f1 (ppm)

bis (4-bromophenyl) sulphide (3i)





Reference

1) K. Cheng, C. Wang, Y. Ding, Q. Song, C. Qi, X. M. Zhang, *J. Org. Chem.* ,2011, **76**, 9261