Chapter III

Environmentally benign approach towards C-S cross coupling reaction by organo-copper(II) complex

III.A. Introduction

Now a day, carbon-hetero bond is the most important in organic synthesis. It has widely used as a precursor or as an intermediate in the formation of basis or vital infrastructure in the organic synthesis.[1] Carbon-sulphur bond is one of them. Over the last decades, organosulfur or sulphur containing compounds draws significant attention towards the extraordinary applications in the frontiers of modern organic synthetic chemistry like material science and biochemistry and it also widely used in the field of medicine and modern chemical.[2,3] C-S cross coupling reaction is one of fascinating approach for the synthesis of pharmaceutically as well as industrially important compounds.[4-7] Furthermore, aryl-sulfide functional group containing derivatives have been widely used in a number of drugs such as Parkinson's, diabetes, Alzheimer's, cancer, HIV diseases, Leprosy, Tuberculosis.[8-10]

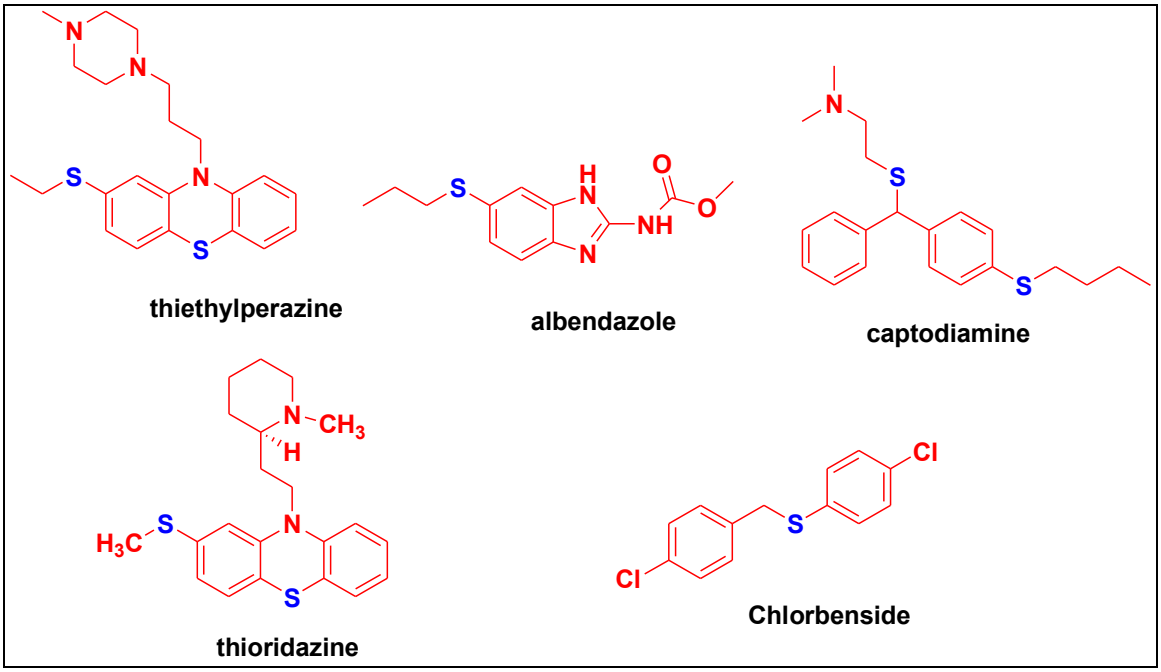
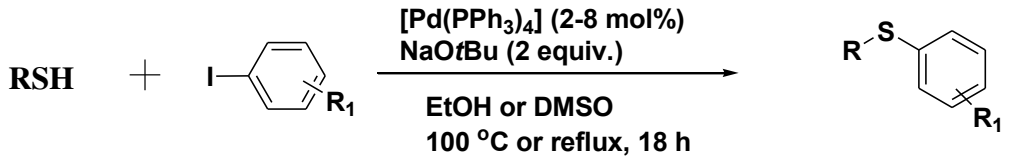


Figure III.1. Some important examples of pharmaceutically and biologically active molecules with aryl alkyl and diaryl sulphide skeleton

III.B. Backgrounds and Objectives

III.B.1. Modern methods for the C-S cross coupling

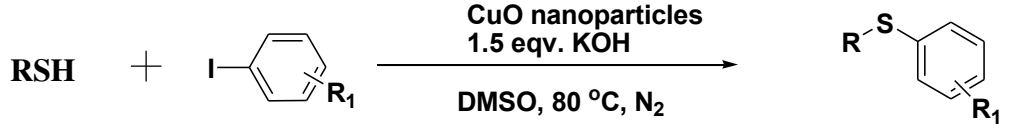
C-S cross-coupling was first reported by Migita *et al.*[11] in 1980, which was involving cross coupling between aryl halides and thiols by using the $Pd(PPh_3)_4$. They investigated various transition metal catalytic systems (Scheme III.1).[12-16]



Scheme III.1. T. Migita proposed first palladium-catalysed C-S coupling reaction

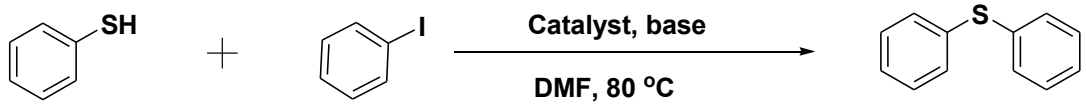
But this protocol has several limitations like use of cost material, long reaction time, use of toxic substances and low turnover numbers. Despite of the several drawbacks mentioned, there is required an alternative simple and efficient synthetic strategies for the formation of carbone-sulphur bond through the C-S cross coupling reaction. A number of methods have been proposed for the C-S coupling reaction.

In the year of 2007, Punniyamurthy *et al.* reported the first time C-S cross coupling reaction of aromatic and aliphatic thiols with iodobenzene by using the easy recyclable CuO nanoparticle as a catalyst with KOH base in DMSO solvent at 80 ^{o}C. This protocol was efficient to give good yield of the desired product (Scheme III.2).[17]



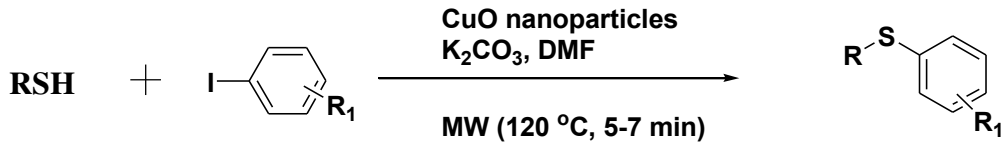
Scheme III.2. CuO nanoparticles catalysed C–S cross-coupling

R. Gupta *et al.*[18] in 2012 published a nickel-based coordination polymers based on metalloligands catalysed C-S cross coupling reaction with the substituted aromatic halides to that of thiophenol as well as cyclohexane thiol and ethane thiol (Scheme III.3).



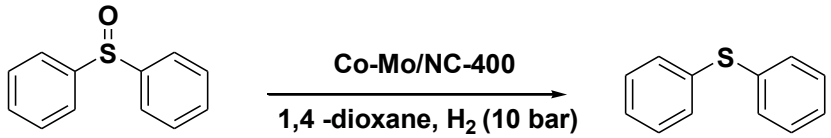
Scheme III.3. Nickel-based coordination polymers based on metalloligands catalysed synthesis of diaryl sulfide

In 2007, Ranu *et al.*[19] have been proposed ligand free microwave irradiation copper nanoparticles catalysed C-S cross coupling reaction of aryl iodides with a series of thiophenols and alkanethiols by using K_2CO_3 as base in DMF solvent at 120 ^{o}C temperature (Scheme III.4).



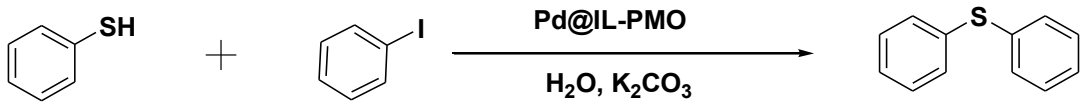
Scheme III.4. Cu-nanoparticles catalysed cross-coupling reaction

K. Yao *et al.* successfully reported an efficient nitrogen-doped carbon-supported heterogeneous cobalt–molybdenum catalysed hydrodeoxygenation of sulfoxides into sulfides under mild conditions at 25-80 ^{o}C (Scheme III.4).[20]



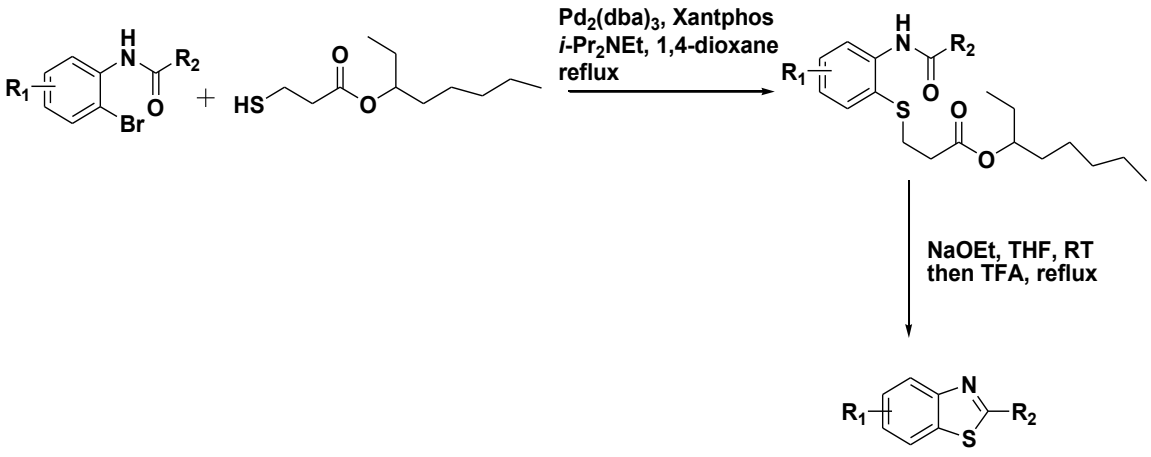
Scheme III.5. Cobalt–molybdenum bimetallic catalysed hydrodeoxygenation of sulfoxides into sulfides

S. Rostamnia *et al.* in 2016, were able to developed an efficient and green method for the C-S coupling by using their synthesised palladium ions supported inside periodic mesoporous organosilica with ionic liquid framework as a catalyst (Pd@IL-PMO) with K_2CO_3 base in water medium (Scheme III.6).[21]



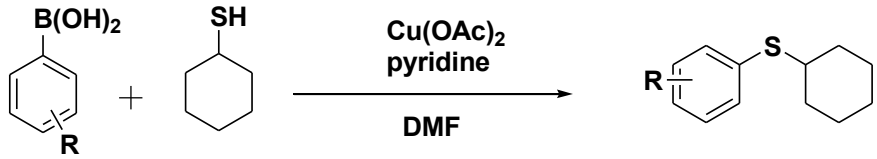
Scheme III.6. Pd@IL-PMO catalysed C-S coupling reaction

In 2007, T. Itoh *et al.* reported the Pd catalysed synthesis of substituted benzothiazoles through the intermolecular C-S bond formation. They carried out the reaction between 2-bromoanilides and 2-ethylhexyl 3-mercaptopropionate with Pd catalyst in 1,4-dioxane and then afforded the corresponding benzothiazoles (Scheme III.7).[22]



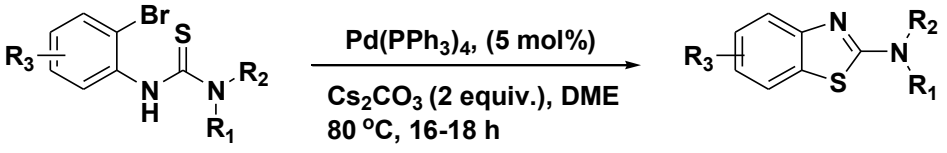
Scheme III.7. Synthesis of substituted benzothiazoles via the C-S bond formation

R. K. Guy *et al.*[23] in the year of 2000, developed a copper(II) acetate catalysed cross-coupling reaction of aryl boronic acids and alkane thiols, mediated by pyridine in anhydrous dimethylformamide affords the corresponding aryl alkyl sulfides in good yield. This protocol covers a wide variety of substituted aryl boronic acids and by this method they were also able to synthesis of aryl sulfides of cysteine (Scheme III.8).



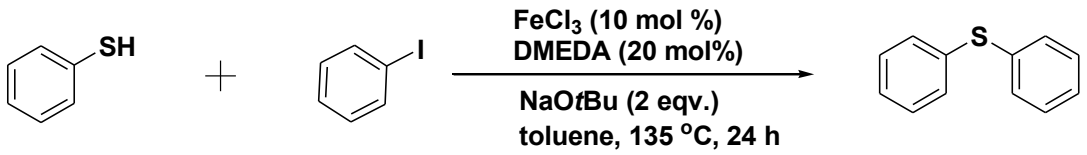
Scheme III.8. Copper-mediated cross-coupling of aryl boronic acids and alkyl thiols

In 2004, R. A. Batey *et al.*[24] developed an interesting copper or palladium-catalysed intramolecular C-S coupling reaction protocol for the synthesis of 2-aminobenzothiazoles from aryl halide and a thiourea derivative. They were found that the catalysis of copper was superior over palladium-catalyst (Scheme III.9).



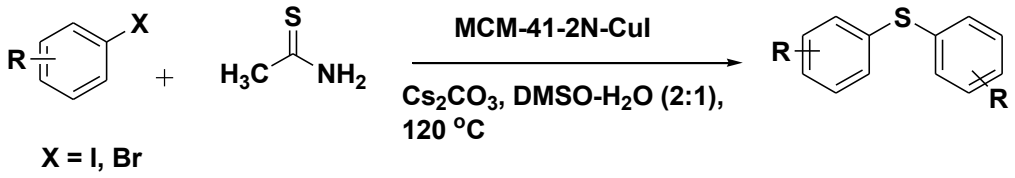
Scheme III.9. Copper or palladium-catalysed synthesis of 2-aminobenzothiazoles through the C-S bond formation

C. Bolm *et al.* in 2008, have successfully reported the first iron-catalysed C-S cross-coupling reaction of aryl iodides with aryl thiols by using the *N,N*-dimethylethylenediamine (DMEDA) (Scheme III.10).[25]



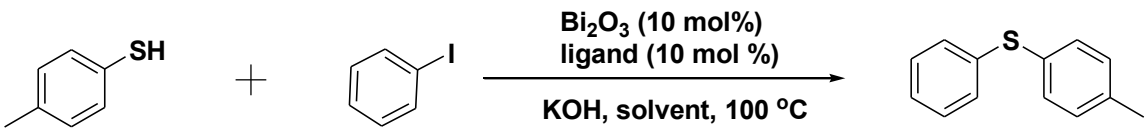
Scheme III.10. Iron-catalysed C-S cross-coupling reaction

In 2014, H. Zhao *et al.* published a simple and efficient heterogeneous catalysed carbon-sulphur coupling reaction of aryl halides with thioacetamide. They carried out the reaction by the treatment of heterogeneous MCM-41-immobilized bidentate nitrogen copper(I) complex [MCM-41-2N-CuI] as catalyst with aryl halides with thioacetamide and yielded the diaryl sulfides product moderate to high (Scheme III.11).[26]



Scheme III.11. MCM-41-2N-CuI catalysed C-S coupling reaction of aryl halides with thioacetamide

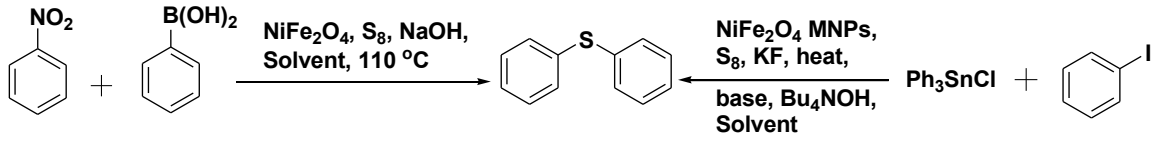
D. Chakraborty *et al.*[27] proposed a simple, efficient and multi-functional groups tolerance Bi_2O_3 catalysed synthetic route for the coupling of aryl halides with thiophenols in water medium and yielded the product moderate to high (Scheme III.12).



Scheme III.12. Bi_2O_3 catalysed C-S coupling reaction

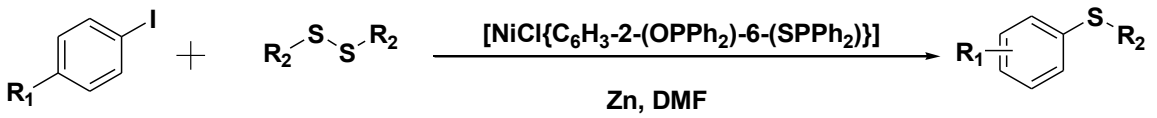
In 2017, S. Farzin *et al.*[28] have been reported an efficient one-pot methodologies for the synthesis of unsymmetrical diaryl sulfides by using of arylboronic acid/S_8 or triphenyltin chloride/S_8 as a thiolating agents with aryl halides or nitroarenes. The reaction was carried

out by $NiFe_2O_4$ magnetic nanoparticles (MNPs) in the presence of K_2CO_3 or NaOH in water at 80-110 ^oC. The reaction method was green and eco-friendly (Scheme III.13).



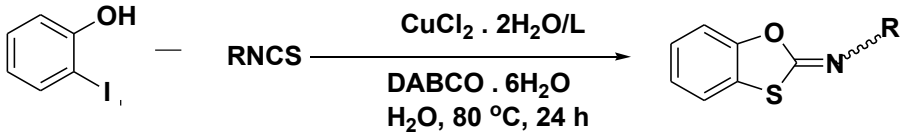
Scheme III.13. $NiFe_2O_4$ magnetic nanoparticles (MNPs) catalysed C-S coupling reaction

D. Morales-Morales *et al.*[29] reported the C-S cross-coupling reaction of disulfides with iodobenzenes by using their own synthesised non-symmetric phosphinito-thiophosphinito PSCOP-Ni(II) pincer complex as a catalyst in DMF solvent at 130 ^oC (Scheme III.14).



Scheme III.14. Nickel catalysed C-S coupling of disulfides with iodobenzenes

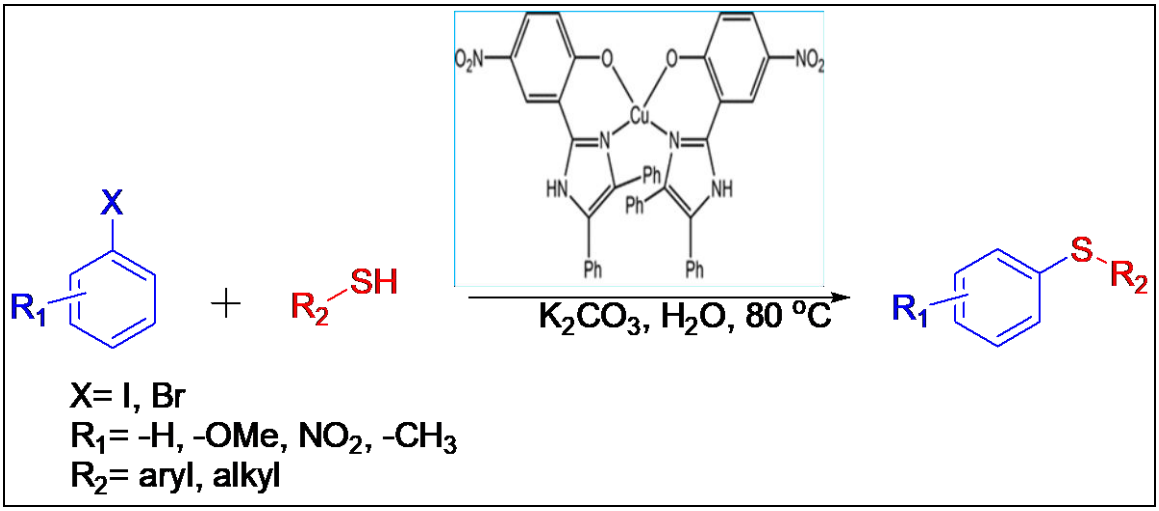
In 2011, Q. Ding *et al.*[30] published a water mediated environmentally benign $CuCl_2.H_2O$ catalysed tandem C-S cross-coupling reaction of 2-iodophenol with isothiocyanate (Scheme III.15).



Scheme III.15. $CuCl_2.H_2O$ catalysed tandem C-S cross-coupling reaction of 2-iodophenol with isothiocyanate

III.C. Present Work

Here we report the water mediated C-S cross coupling reaction by using newly developed bis[2-(4,5-diphenyl-1*H*-imidazol-2-yl)-4-nitrophenolato]copper(II)-dehydrate complex as catalyst. In this method the desired product was obtained in good yields.



Scheme III.16. C-S cross coupling reaction

III.C.1. Result and discussion

In order to explore the catalytic activity of the newly synthesize copper catalyst, we begun C-S cross-coupling as a model reaction by the conventional method. The results of the optimization studies are summarized in table III.1.

Table III.1. Optimization of reaction parameters for the C-S coupling reaction[a]

Entry[a]	Catalyst (mg)	Time (h)	Solvent	Base	Temperature (^oC)	Yield[b] (%)
1	12	10	DMF	K_2CO_3	80	90
2	12	10	DMSO	K_2CO_3	80	87
3	12	10	CH_3CN	K_2CO_3	80	90
4	12	10	Toluene	K_2CO_3	80	92
5	12	10	Ethanol	K_2CO_3	80	91
6	**12**	**10**	**Water**	**K_2CO_3**	**80**	**96**
7	12	10	Water	K_2CO_3	100	97
8	12	10	water	K_2CO_3	60	40
9	12	10	Water	K_2CO_3	RT	Nil
10	Nil	24	Water	K_2CO_3	80	Nil
11	12	10	Water	Cs_2CO_3	80	97
12	12	10	Water	KO^tBu	80	60
13	12	10	Water	Et_3N	80	62
14	12	10	Water	KOH	80	70

[a]Reactions carried out with 10 mg synthesised copper catalyst, 4-iodo anisole (1 mmol), thiophenol (1 mmol), K_2CO_3 (1.2 mmol), [b] Yield based on column chromatography, [c]Reaction carried out without catalyst

Initially, a mixture of 4-iodoanisole (1 mmol), thiophenol (1 mmol), K_2CO_3 (1.2 mmol) and 12 mg of synthesised catalyst were taken in water as solvent and heated in a round bottom flask under reflux condition for 10 h. We observed that the reaction was completed with a 96 % yield of the desired C-S coupled product (Table III.1, entry 6). However, the same reaction when carried out under similar condition but in the absence of catalyst we did not get the desired product. Therefore, we concluded that the reaction does not proceed in the absence of catalyst (Table III.1, entry 10). Hence, to explore the role of catalyst we repeated the model reaction with varying amount of catalyst (Table III.2) and out of all attempt we established that 12 mg of the synthesised catalyst yielded the best result (Table III.2, Entry 5). Further increase in the amount of catalyst the yield of the product did not increase considerably. We also examined the protocol using various solvents, such as DMF, DMSO, CH_3CN, toluene, ethanol, but none of them could able to beat the efficiency of water as a solvent. Keeping this observation in mind water was chosen as the optimal medium of the reaction. Further, in order to optimize the reaction temperature, the model reaction was carried out at 60, 80 and 100 ^oC. Among them 80 ^oC was found to yield the best result (Table III.1, entry 6). We also studied the reaction by using various bases (Table III.1) and among them K_2CO_3 and Cs_2CO_3 were found to produce the best yield of the desired product. However, considering the cost of Cs_2CO_3 and as the product yield is not considerably greater than K_2CO_3, the latter was chosen as the optimized base of the reaction. With this optimized greener reaction condition we performed the reaction with various substituents (Table III.3).

Table III.2. Optimization of catalyst loading

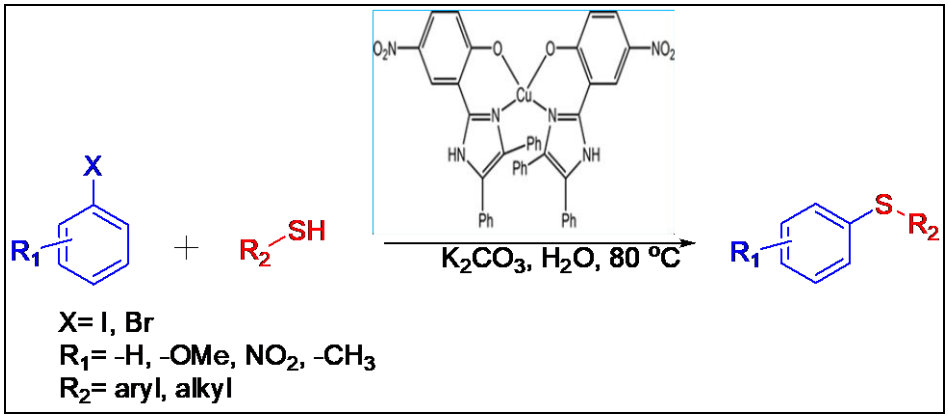
Entry	Catalyst (mg)	Yield (%)
1	4	30
2	6	45
3	8	72
4	10	85
5	**12**	**96**
6	14	97

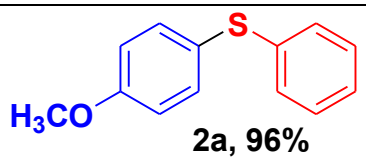
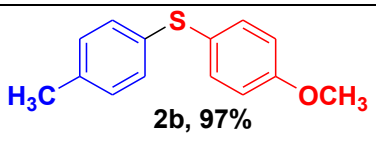
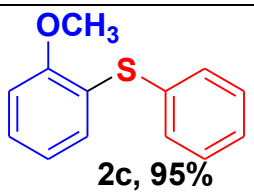
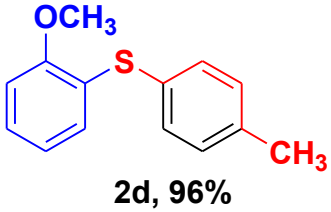
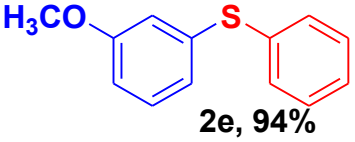
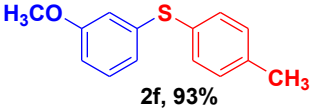
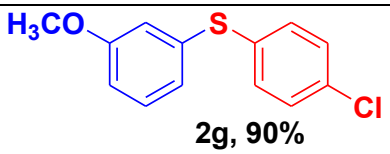
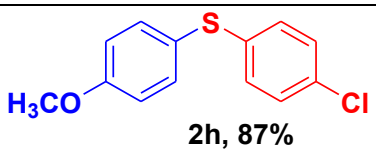
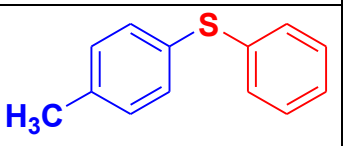
Reaction conditions: 4-iodoanisole (1 mmol), thiophenol (1 mmol), K_2CO_3 (1.2 mmol), water solvent and 12 mg catalyst at 80 ^oC.

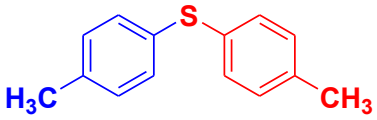
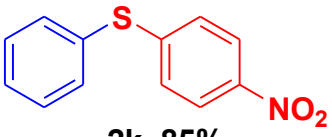
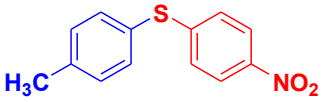
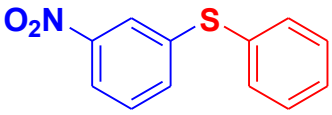
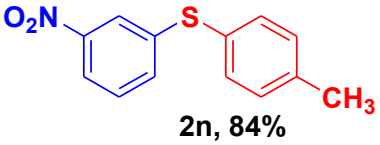
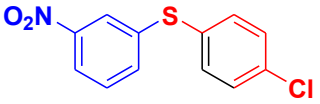
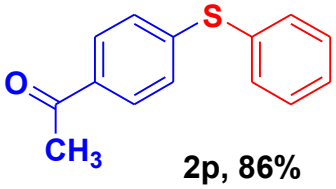
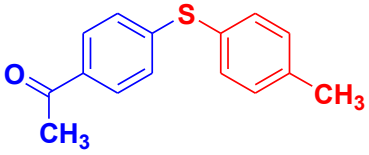
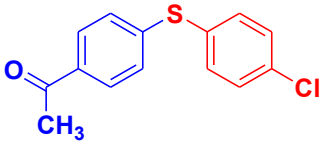
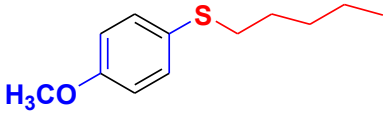
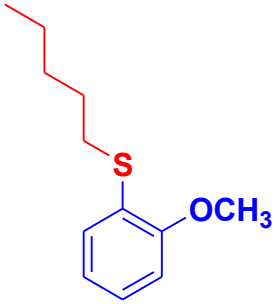
To investigate the catalytic activity of the synthesized catalyst and to cheek the generality of the C-S coupling reaction, we carried out the reaction with a variety of halo arenes and aliphatic as well as aromatic thiols. Both the electron donating/electron withdrawing groups

of the haloarenes were employed with the thiols. Haloarenes with electron donating groups afforded the desired product with good yields which might be due to the increase the electron density towards the nucleus of the haloarenes and thereby facilitating the reaction faster (Table III.3). Bromo and iodobenzene were tried which afforded the product with excellent yields and the order of reactivity of the haloarenes are I>Br (Table III.3). Haloarenes with electron withdrawing group such as -NO_2 needed more time for completion but gave good yield (Table III.3, entry 2k, 2l, 2m, 2n, 2o) of the product. On the other hand, aromatic thiols with electron donating group also produce better result (Table III.3). The reaction was also examined with the aliphatic thiol which also gave the corresponding product and in good yield (Table III.3, 2s, 2t). Thus, it appeared that the newly developed catalyst might direct the C-S coupling reaction with a wide range of substrates(Table III.3).

Table III.3. Synthesized copper catalysed C-S cross-coupling of aryl halides and aryl thiols[a]



 2a, 96%	 2b, 97%	 2c, 95%
 2d, 96%	 2e, 94%	 2f, 93%
 2g, 90%	 2h, 87%	 2i, 90%

 2j, 95%	 2k, 85%	 2l, 86%
 2m, 93%	 2n, 84%	 2o, 80%
 2p, 86%	 2q, 87%	 2r, 84%
 2s, 80%	 2t, 79%	

[a] Reactions carried out with 10 mg synthesised copper catalyst, 4-iodo anisole (1 mmol), thiophenol (1 mmol), K_2CO_3 (1.2 mmol) in water medium at 80 ^oC, [b] Yield based on column chromatography

III.D. Conclusion

We investigate the catalytic activity of our synthesized copper(II) catalyst in the C-S cross coupling reaction of haloarene and thiols in water medium and obtained the expected product in good yield. The recyclability of the synthesized catalyst was found to be capable up to fifth run without significant loss of the yield of the product. The catalyst was also easily recovered after completion of the reaction.

III.E. Experimental

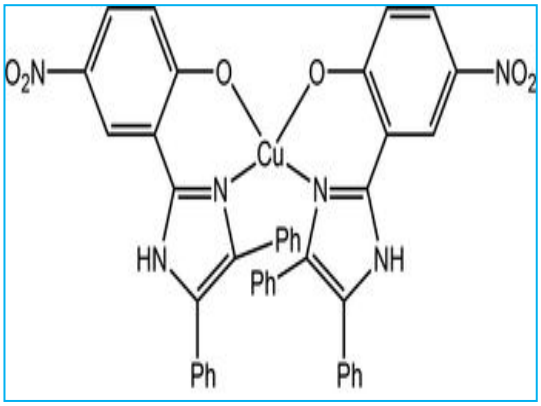
III.E.1. Material Apparatus

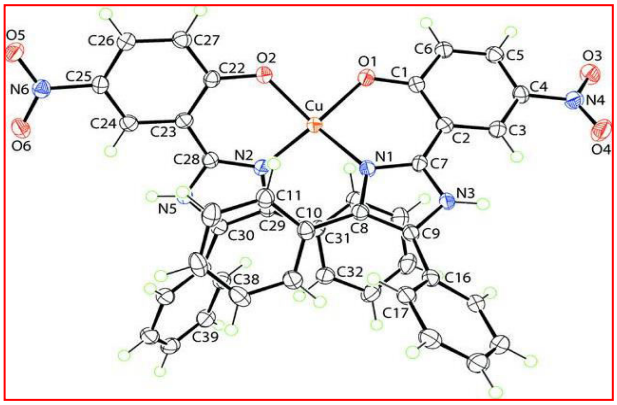
All the synthesized products were purified by column chromatography on 60-120 mesh silica gel (SRL, India). For TLC, Merck plates coated with silica gel 60, F254 were used. IR spectra were recorded on KBr disc in the range 4000-400 cm^{-1} on Shimadzu FT-IR 8300 Spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on 400 MHz and 300 MHz Bruker Avance NMR Spectrometer using TMS as internal standard.

III.E.2. Preparation and characterization of catalyst

The Cu (II) catalyst has been prepared by the reported procedure. [31] In a multi-component template synthesis of tri-aryl imidazole, the titled copper complex was obtained when 2-hydroxy 5-nitro benzaldehyde (1 mmol), benzil (1 mmol) and ammonium acetate (2.5 mmol) was allowed to react in the presence of CuB_4O_7 (1 mmol) at a temperature 130 ºC in the presence of silica gel as a solid support. After completion of the reaction, blue coloured crystal was obtained and the product was washed with methanol followed by diethyl ether to afford the pure complex. Melting point >300 ºC, IR (KBr, cm^{-1}): 3430 (O-H stretching of H_2O), 3065 (N-H Stretching), 2926 (Aromatic C-H Stretching), 1578 (C=N Stretching), 1487, 1135 (C-H stretching), 466 (Cu-N stretching).

The molecular structure and the packing of the crystal are given below:





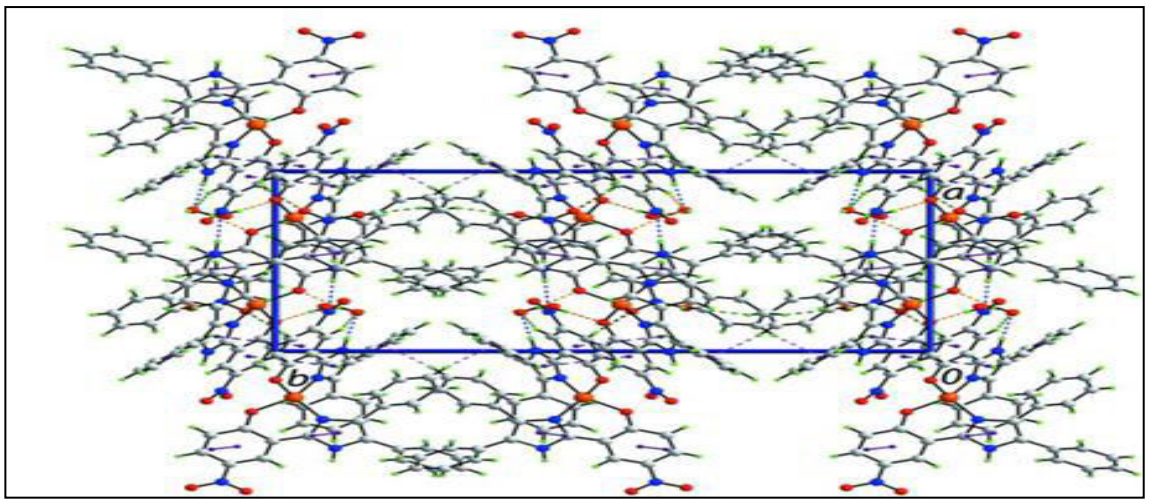


Figure III.2. The molecular packing of the crystal

The molecular packing in the crystal of Cu (II) complex, isolated as $[Cu(C_{21}H_{14}N_3O_3)_2]\cdot 2H_2O$

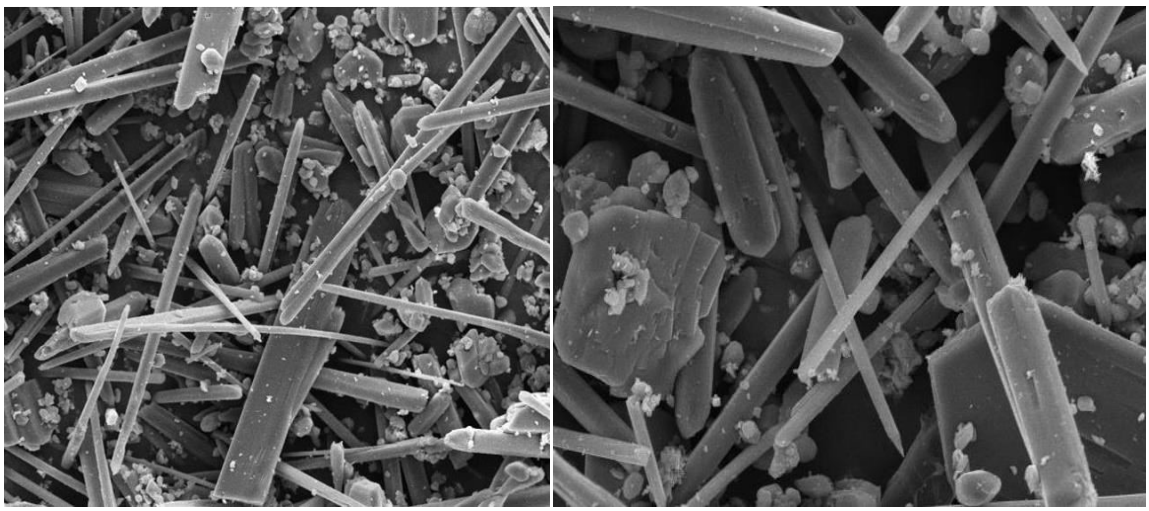


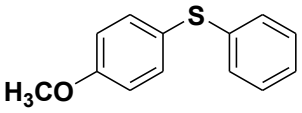
Figure III.3. SEM image of the synthesized catalyst

III.E.3. General procedure for the synthesis of the C-S cross-coupled compounds

A 25 mL round-bottom flask was charged with a mixture of 4-iodoanisole (1 mmol), thiophenol (1 mmol), K_2CO_3 (1.2 mmol) and 12 mg of synthesised catalyst were taken in water, as the solvent and heated under reflux condition. The reaction mixture was stirred under reflux condition until consumption of the reactants indicated by TLC. After completion of the reaction the reaction mixture was partitioned between ethyl acetate and water. And the catalyst was separated by simple filtration. The combined organic layer was dried over anhydrous sodium sulphate and concentrated under water bath. After that the products were purified by column chromatography on 60-120 mesh silica gel.

III.E.4. Physical properties and spectroscopy data of synthesized C-S coupled compounds

(4-Methoxyphenyl)(phenyl)sulfane (2a)



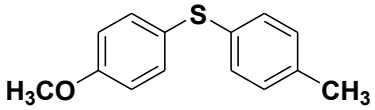
Slightly yellow liquid

IR (neat, $\nu_{máx}$, cm^{-1}): 690, 2802, 2919, 2942, 3042, 3085.

^{1}H NMR (300MHz, $CDCl_3$) δ ppm: 3.80 (s, 3H), 6.87-6.90 (m, 2H), 7.09-7.25 (m, 4H), 7.39-7.43 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 55.38, 115.02, 124.30, 125.78, 128.21, 128.96, 135.41, 138.64, 159.85.

(4-Methoxyphenyl)(*p*-tolyl)sulfane (2b)



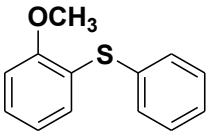
White solid, m.p. 46 °C.

IR (KBr, $\nu_{máx}$, cm^{-1}): 635, 822, 2846, 2925.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.22 (s, 3H), 3.73 (s, 3H), 6.77-6.81(m, 2H), 6.97-7.06 (m, 4H), 7.27-7.30 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 20.99, 55.36, 114.85, 125.59, 129.34, 129.77, 134.37, 136.12, 159.44.

(2-Methoxyphenyl)(phenyl)sulfane (2c)



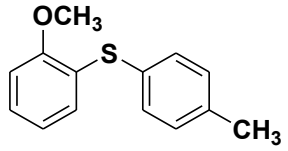
Colourless oil

IR (neat, $\nu_{max,}$ cm^{-1}): 690, 753, 2837, 2974.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.72 (s, 3H), 6.74-6.78 (m, 2H), 6.96-6.99 (m, 1H), 7.11-7.25 (m, 6 H).

^{13}C N MR (75 MHz, $CDCl_3$) δ ppm: 54.75, 109.73, 120.14, 122.89, 125.98, 127.26, 128.06, 130.34, 130.48, 133.35, 156.16.

(2-Methoxyphenyl)(*p*-tolyl)sulfan (2d)



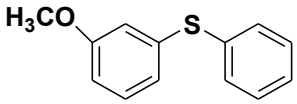
Colourless liquid

IR (neat, $\nu_{max,}$ cm^{-1}): 681, 743, 1272, 1473, 1576, 2835, 2934, 3005.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.34 (s, 3H), 3.87 (s, 3H), 6.79-6.94 (m, 3H), 7.12-7.23 (m, 3H), 7.30-7.32 (d, *J* = 6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 21.23, 55.89, 110.59, 121.23, 125.72, 127.44, 129.73, 129.83, 130.15, 133.04, 137.80, 156.48.

(3-Methoxyphenyl)(phenyl)sulfane (2e)



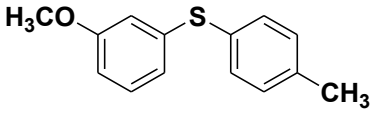
Slightly yellow liquid

IR (neat, $\nu_{max,}$ cm^{-1}): 691, 2806, 2932, 2954, 3026, 3078.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.73 (s, 3H), 6.74-6.77 (m, 1H), 6.86-6.91 (m, 2H), 7.16-7.37 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 55.30, 112.81, 115.93, 122.98, 127.30, 129.27, 130.00, 131.46, 135.29, 137.26, 160.07.

(3-Methoxyphenyl)(*p*-tolyl)sulfane (2f)



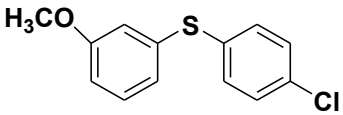
Yellow oil

IR (neat, $\nu_{max,}$ cm^{-1}): 692, 1247, 1478, 1574,1591.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.31 (d, *J* = 8.1, 2H), 7.12-7.19 (m, 3H), 6.78-6.83 (m, 2H), 6.70-6.73 (m, 1H), 3.72 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 21.19, 55.26, 112.05, 114.77, 121.73, 130.12, 130.72, 132.66, 137.86, 138.64, 159.98, 162.33.

(4-Chlorophenyl)(3-methoxyphenyl)sulfane (2g)



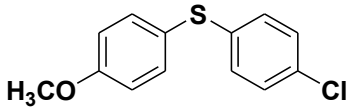
Yellow oil

IR (neat, $\nu_{máx,}$ cm^{-1}): 680, 741, 1272, 1475, 1576, 2930, 2957.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.15 (s, 3H), 6.26 (d, *J* = 7.5 Hz, 3H), 6.65-6.69 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 54.71, 112.50, 115.63, 122.60, 128.73, 129.49, 131.75, 132.61, 133.55, 135.88, 159.50.

(4-Chlorophenyl)(4-methoxyphenyl)sulfane (2h)



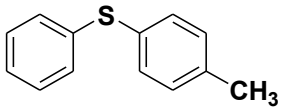
Colourless oil

IR (neat, $\nu_{máx,}$ cm^{-1}): 685, 741, 1276, 1470, 1578, 2935, 2960.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.82 (s, 3H), 6.89-6.92 (m, 2H), 7.04-7.08 (m, 2H), 7.17-7.25 (m, 2H), 7.38-7.44 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 55.40, 115.12, 129.01, 129.26, 131.55, 132.19, 135.54, 135.93, 137.37.

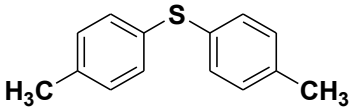
Phenyl(*p*-tolyl)sulfane (2i)



^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.33 (s, 3H), 7.11-7.21 (m, 2H), 7.25-7.41 (m, 6H), 7.45-7.50 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 21.17, 126.42, 127.49, 129.07, 130.10, 131.25, 132.32, 137.14, 137.64.

Di-*p*-tolylsulfane (2j)



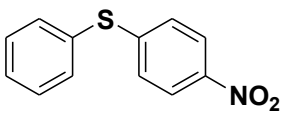
Slightly yellow oil

IR (neat, $\nu_{max,}$ cm^{-1}): 690, 743, 810, 1020, 1093, 1442, 1482, 1490, 1591, 2930, 3051.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.31 (s, 6H), 6.97-7.10 (m, 4H), 7.21-7.23 (m, 3H), 7.36-7.39 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 21.13, 128.55, 129.96, 131.09, 132.67, 136.94.

(4-Nitrophenyl)(phenyl)sulfane (2k)



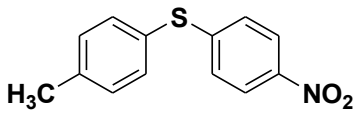
Yellow solid m.p.: 54 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 514, 691, 741, 851, 1082, 1430, 1475, 1515, 1577, 3065.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.15-7.17 (m, 2H), 7.44-7.52 (m, 5H) , 8.04 (d, *J* = 6.6, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 124.05, 126.71, 129.70, 130.07, 130.48, 134.77, 145.38, 148.53.

(4-Nitrophenyl)(*p*-tolyl)sulfane (2l)



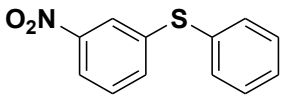
Yellow solid, m.p.: 87 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 686, 1338, 1506, 1570.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.40 (s, 3H), 7.12 (d, *J* = 7. 5, 2H), 7.42 (d, *J* = 6.9, 2H), 8.02 (d, *J* = 7.2, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 21.36, 123.98, 124.54, 126.14, 126.51, 130.88, 135.09, 140.25, 145.15, 149.36.

(3-Nitrophenyl)(phenyl)sulfane (2m)



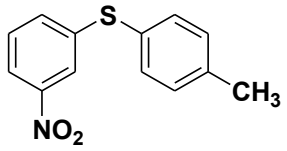
Yellow oil

IR (neat, $\nu_{máx,}$ cm^{-1}): 656, 782, 998, 1056, 1453, 1472, 1565, 3098.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.94-8.00 (m, 2H), 7.36-7.72 (m, 3H), 7.09-7.26 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 120.93, 123.10, 128.99, 129.76, 129.91, 132.14, 133.45, 134.27, 140.58, 148.67.

(3-Nitrophenyl)(*p*-tolyl)sulfane (2n)



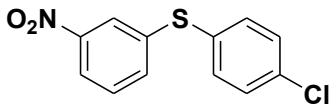
Yellow solid, m.p.: 61 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 680, 1573, 1338, 1507.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.39 (m, 3H), 7.22-7.26 (m, 2H), 7.35-7.45 (m, 4H), 7.95-7.96 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 120.44, 122.19, 127.82, 129.54, 130.73, 133.32, 134.20, 139.60, 141.65, 148.67.

(4-Chlorophenyl)(3-nitrophenyl)sulfane (2o)



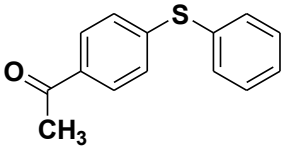
Yellow solid, m.p. 58 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 688, 1338, 1506, 1572.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.37-7.50 (m, 6H), 8.03 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 121.34, 123.47, 129.90, 130.06, 130.95, 134.45, 134.57, 135.17, 139.76, 148.72.

1-(4-(Phenylthio)phenyl)ethanone (2p)



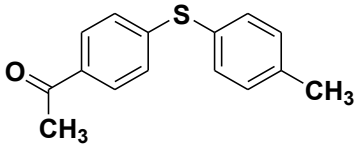
White solid. m.p.: 67 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 680, 1680, 2821, 2942, 2910, 3012, 3060.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.47 (s, 3H), 7.19-7.26 (m, 1H), 7.39-7.50 (m, 6H), 7.81 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 26.50, 127.45, 128.82, 128.91, 129.70, 132.07, 133.90, 134.46, 144.96, 197.19,

1-(4-(*p*-Tolylthio)phenyl)ethanone (2q)



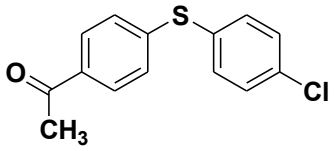
White solid, m.p.: 92 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 680, 1685, 2821, 2915, 2943, 3009, 3059.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.39 (s, 3H), 2.54 (s, 3H), 7.15 (d , *J* = 8.4, 2H), 7.21-7.26 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.78-7.81 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 21.30, 26.47, 126.63, 127.86, 128.84, 130.55, 134.10, 134.52, 139.37, 145.98, 197.22.

1-(4-(4-Chlorophenylthio)phenyl)ethanone (2r)



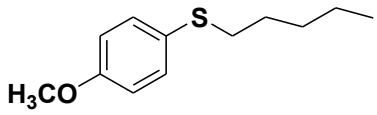
White solid, m.p.: 42 °C.

IR (KBr, $\nu_{máx,}$ cm^{-1}): 685, 1687, 2822, 2916, 2943, 3010, 3060.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.55 (s, 3H), 7.21 (d, *J* = 6.6 Hz, 2H), 7.38 (d, *J* = 6 Hz, 4H), 7.83 (d, *J* = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 26.37, 29.63, 126.16, 127.84, 128.94, 129.81, 130.97, 134.75, 143.90, 196.95.

(4-Methoxyphenyl)(pentyl)sulfane (2s)



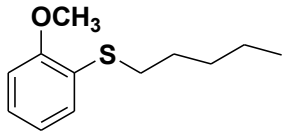
Colourless oil

IR (neat, $\nu_{máx,}$ cm^{-1}): 683, 1024, 1270, 1470, 1577, 2929, 2959.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.81(t, *J* = 6.9 Hz, 3H), 1.01-134 (m, 4H), 1.45-1.53 (m, 2H), 2.71-2.75 (m, 2H), 3.71 (s, 3H), 6.75-6.776 (m, 2H), 7.18-7.34 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 14.00, 22.27, 29.04, 30.90, 35.80, 55.33, 114.47, 126.92, 132.90, 158.69.

(2-Methoxyphenyl)(pentyl)sulfane(2t)



Colourless oil

IR (neat, $\nu_{máx,}$ cm^{-1}): 683, 741, 1270, 1475, 1576, 2928, 2954.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.91 (t, 3H), 1.29-1.45 (m, 4H), 1.59-1.68 (m, 2H), 2.85-2.90 (m, 2H), 3.88 (s, 3H), 6.82-6.94 (m, 2H), 7.13-7.25 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.99, 22.30, 28.60, 31.15, 31.80, 56.76, 110.29, 121.02, 125.26, 126.56, 128.53, 156.97.

III.E.5. Scanned copies of ^{1}H and ^{13}C NMR spectra of various synthesized C-S coupled compounds

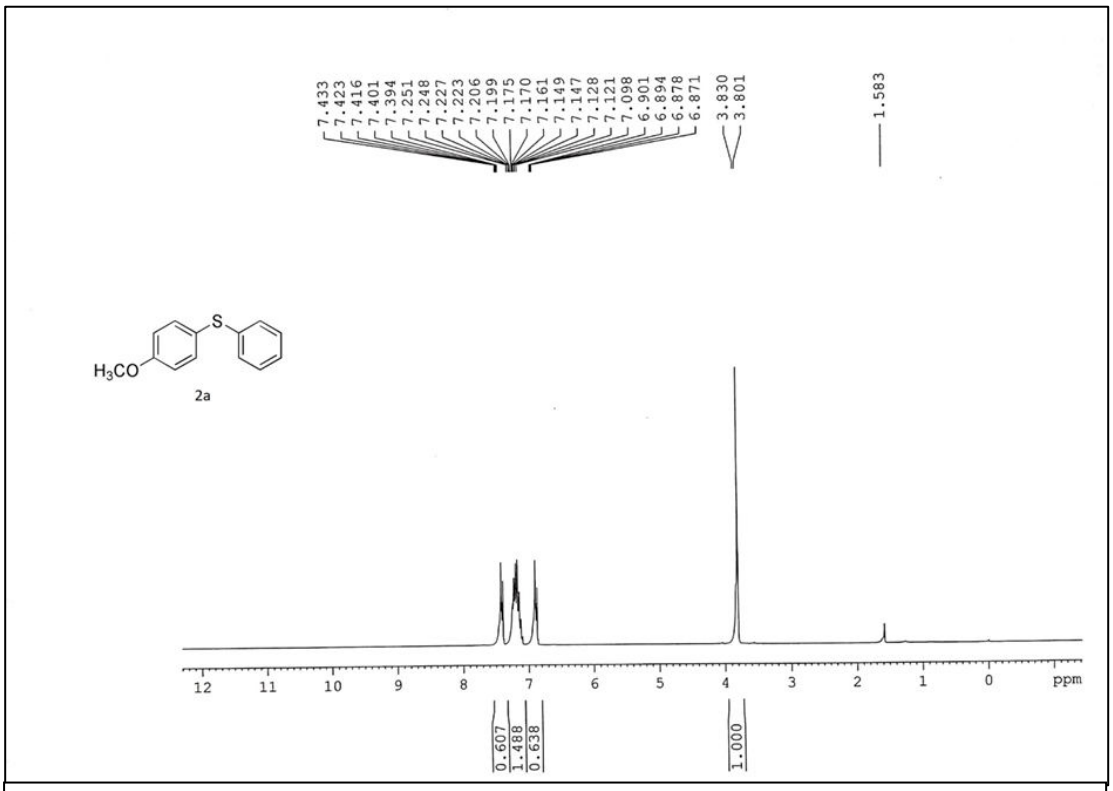


Figure III.4. ^{1}H NMR scanned copy of (4-methoxyphenyl)(phenyl)sulfane (2a)

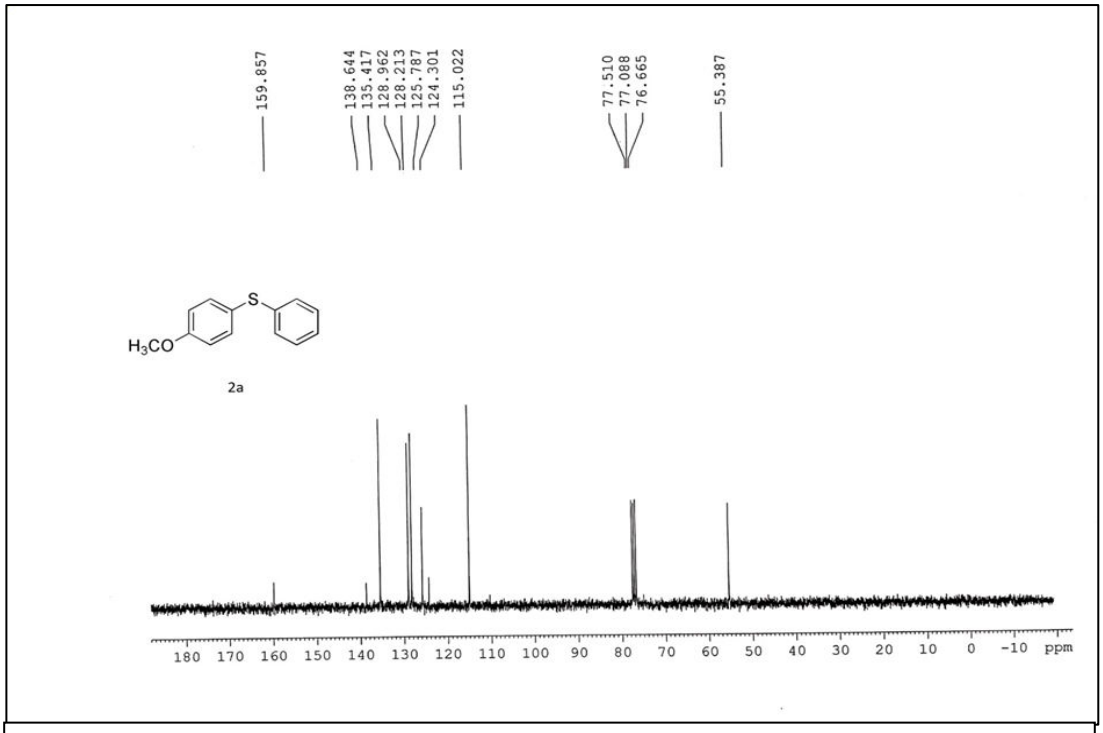


Figure III.5. ^{13}C NMR scanned copy of (4-methoxyphenyl)(phenyl)sulfane (2a)

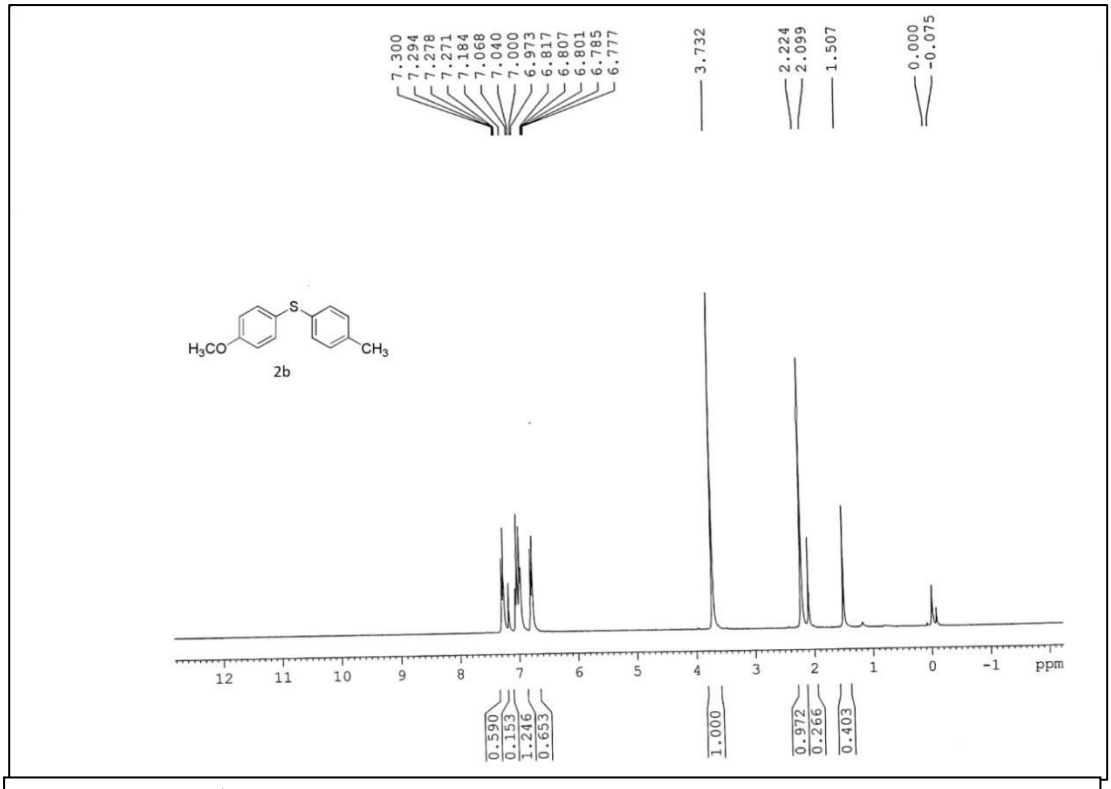


Figure III.6. ^{1}H NMR scanned copy of (4-methoxyphenyl)(*p*-tolyl)sulfane (2b)

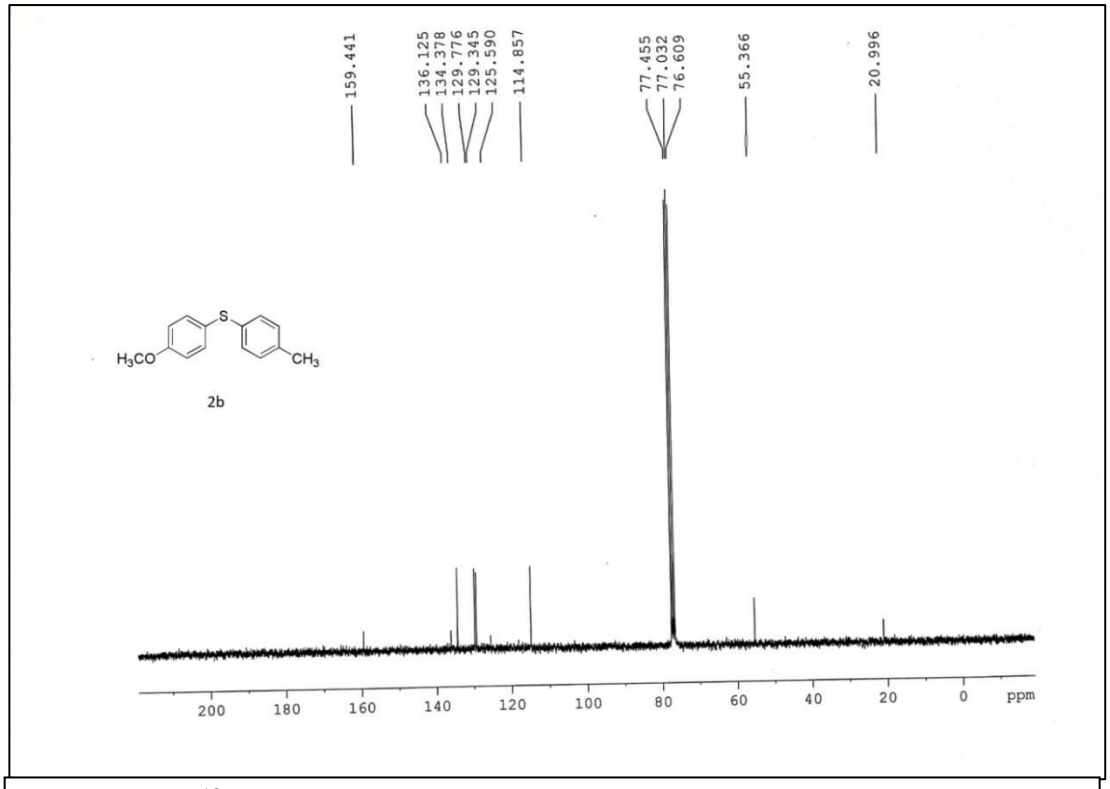


Figure III.7. ^{13}C NMR scanned copy of (4-methoxyphenyl)(*p*-tolyl)sulfane (2b)

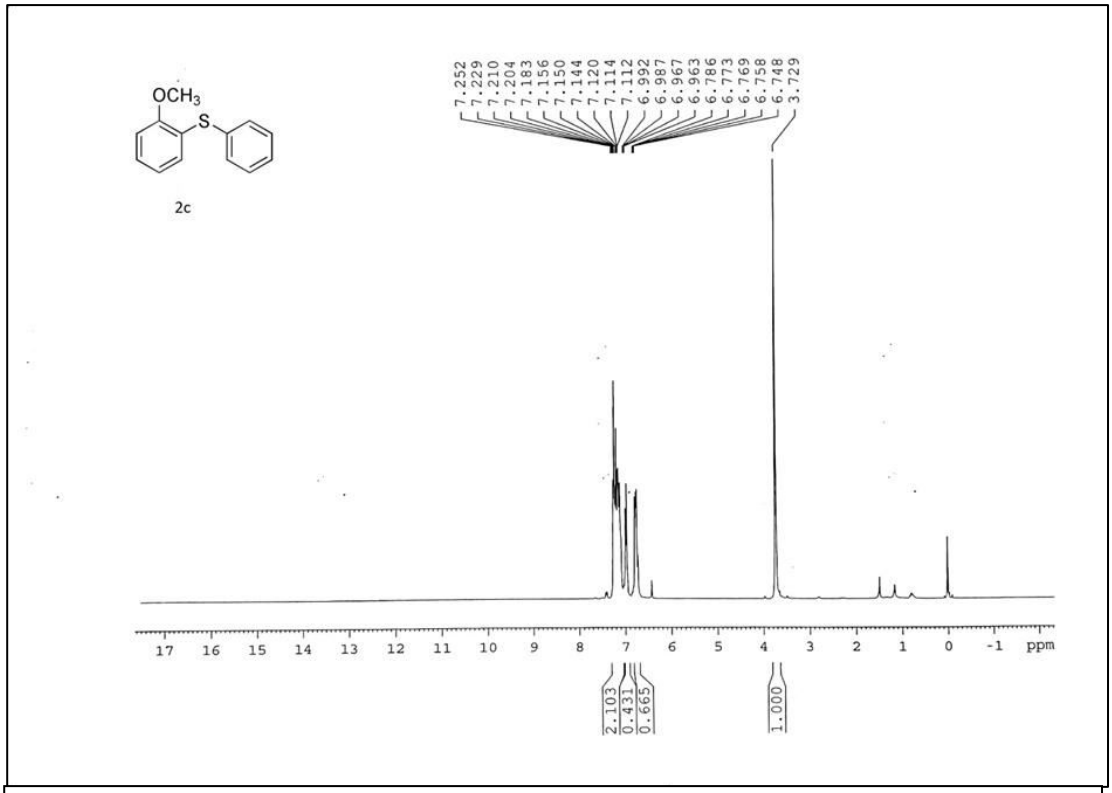


Figure III.8. ^{1}H NMR scanned copy of (2-methoxyphenyl)(phenyl)sulfane (2c)

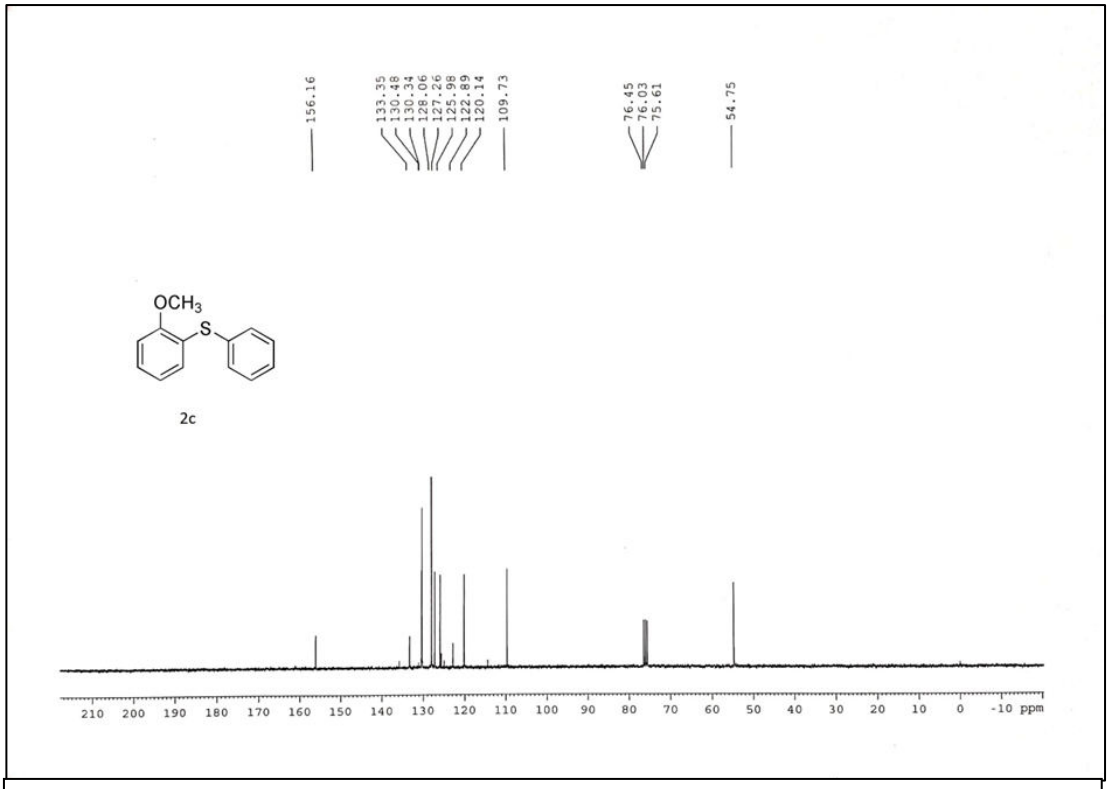


Figure III.9. ^{13}C NMR scanned copy of (2-methoxyphenyl)(phenyl)sulfane (2c)

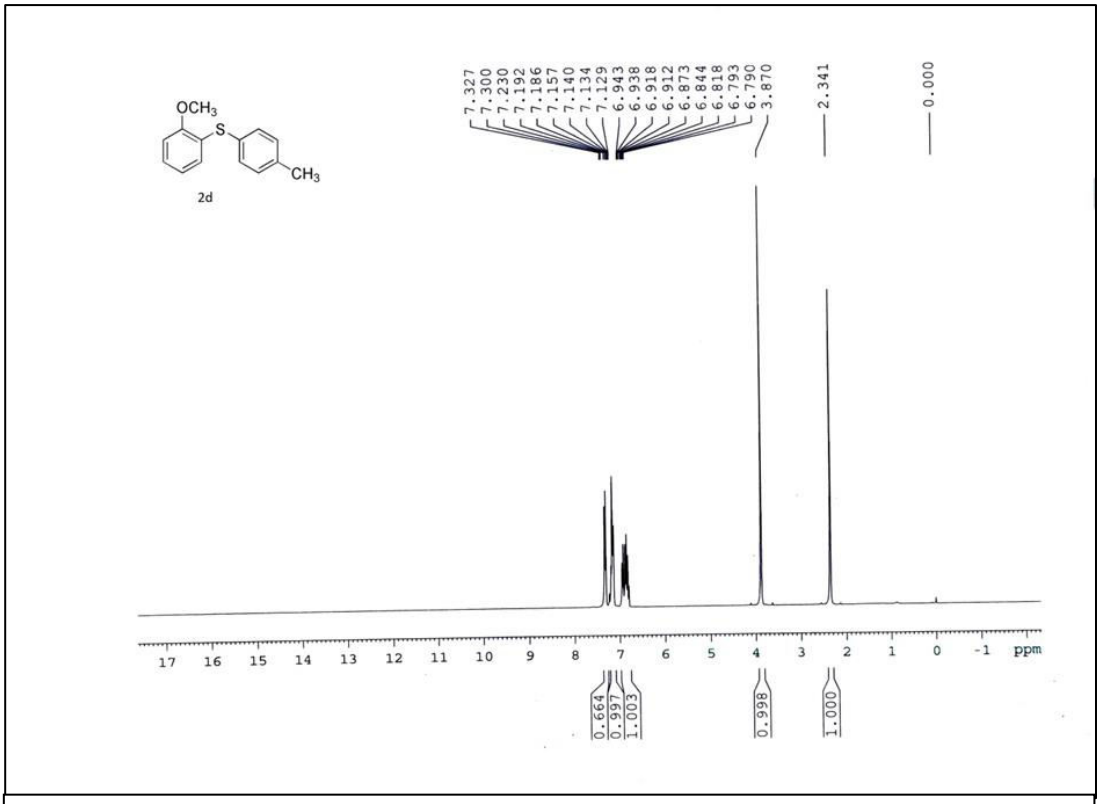


Figure III.10. ^{1}H NMR scanned copy of (2-methoxyphenyl)(*p*-tolyl)sulfan (2d)

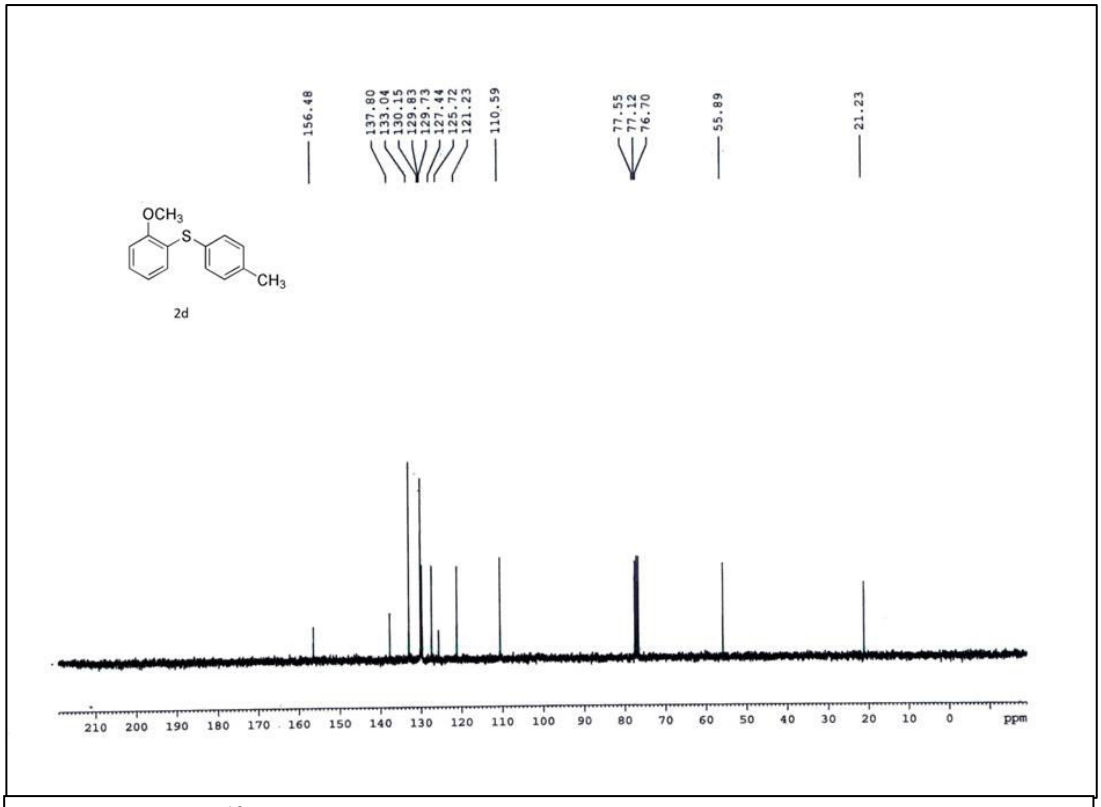


Figure III.11. ^{13}C NMR scanned copy of (2-methoxyphenyl)(*p*-tolyl)sulfan (2d)

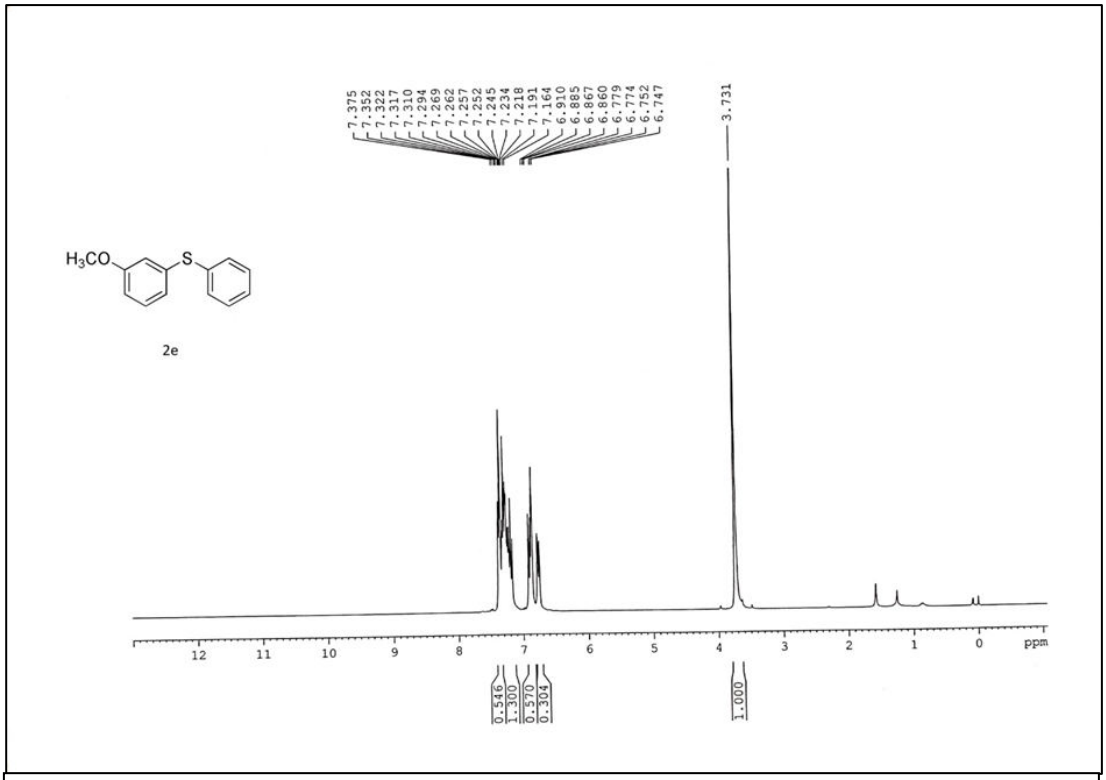


Figure III.12. ^{1}H NMR scanned copy of (3-methoxyphenyl)(phenyl)sulfane (2e)

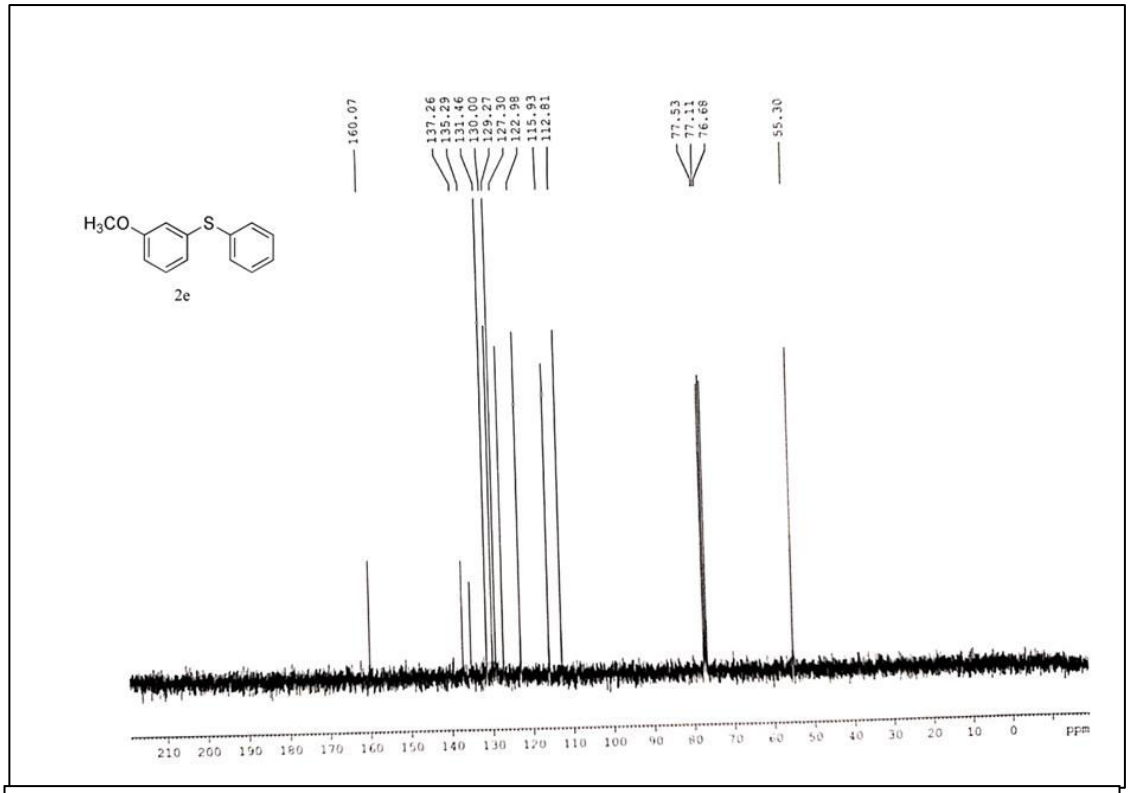


Figure III.13. ^{13}C NMR scanned copy of (3-methoxyphenyl)(phenyl)sulfane (2e)

III.F. References

References are given in BIBLIOGRAPHY under Chapter III.