Supplementary Information

Amino acid and water-driven tunable green protocol to access S-S/C-S bonds via aerobic oxidative coupling and hydrothiolation

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General Information:

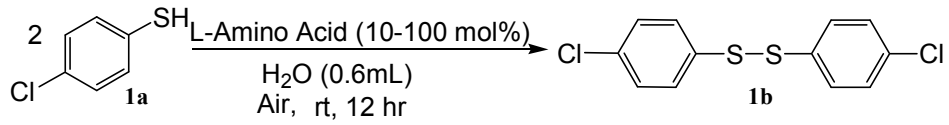
All glassware was dried prior to use. Distilled water was used wherever mentioned. All reactions were carried out in open air or under oxygen/nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on precoated, aluminium-backed silica gel (Merck 60 F254). Visualization of the TLCs of Disulfides or vinyl sulfides was performed by Iodine. Column chromatography was performed using 60-120 mesh silica (Merck). The melting points were determined on a digital Barnsted Electrothermal 9100 apparatus. ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker Avance-300 spectrometer. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet. The ^{13}C NMR spectra are proton decoupled. CEM Discover© focused microwave (2450 MHz, 300W) was used wherever mentioned. The temperature of reactions in MW experiments was measured by an inbuilt infrared temperature probe that determined the temperature on the surface of reaction flask. The sensor is attached in a feedback loop with an on-board microprocessor to control the temperature rise rate. Sonics vibracell ultrasonicator© (20 KHz, 400W) was used with 35% duty, using a microtip wherever mentioned. In case of conventional heating in an oil bath, the temperature of reaction mixture was monitored by an inner thermometer. HRMS-ESI spectra were determined using micromass Q-TOF ultima spectrometer. Absorbance of test solutions for UV titrations was performed using a Shimadzu UV–VIS-3450 spectrophotometer.

Reagents: All the substrates were obtained from commercial sources (Sigma Aldrich or Acros) and were used as such. The thiophenol and phenyl acetylene derivatives were purchased from Sigma Aldrich. L-Arginine and other amino acids were purchased from Sigma Aldrich and Himedia. Distilled water (HPLC grade milipore) was used for carrying out all the reactions. The solvents used for isolation/purification of compound were obtained from commercial sources (Merck) and were used without further purification.

Optimization of Reaction conditions: The reaction conditions for the facile formation of disulfide bond (S-S bond) were thoroughly screened using variable amounts

of L-Arginine, conducting reactions at variable temperatures, use of other solvents and effect of green tools, viz. microwave and ultrasonicator etc. Here we take them into account one by one:

(a) Optimization of the amount of catalyst (L-Arginine) for formation of 1b (Table S1):



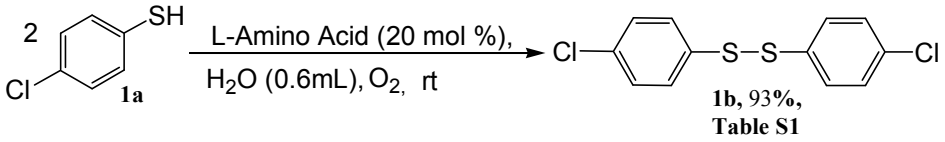
Inspired by amino acid catalyzed disulphide formation (Table 1 of manuscript), we next attempted to optimize the amount of organocatalyst (L- Arginine) and henceforth reaction was conducted at variable concentrations of arginine as shown in **Table S1**. In the beginning, 0.25 mmol of the 4-chlorothiophenol **(1a)** was added to 0.6 mL of distilled water and an amount of 50 mol% of L-Arg was added as the catalyst. After stirring the reaction mixture in open air for 12 h and constant monitoring using TLC revealed the complete consumption of starting material and formation of product **(1b)**. The product upon complete chemical characterization by GC-MS and NMR studies was revealed to be 4,4'-Dichloro diphenyl disulfide **(1b)**. Next we thought of decreasing the catalyst load and an amount of 20 mol% of organocatalyst L-Arg was found to be efficient for promoting the synthesis of **1b** in 12 h in open air.

Table S1: **Optimization of the amount of catalyst for formation of 1b**

S.No	Amount of Organocatalyst (L-Arginine)	% Yield (on GC basis)
1.	50 mol%	92
2.	100 mol%	91
3.	30 mol%	92
4.	**20 mol%**	**93**
5	10 mol%	70

Hence an optimum amount of 20 mol% of L-Arg was selected and kept constant for carrying out oxidative coupling of **1a** to **1b** during adjusting the other parameters.

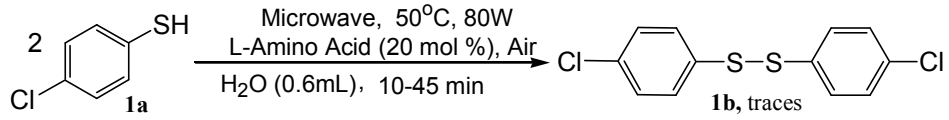
(b) Impact of O_2 towards formation of 1b:



Our next goal was to reduce the reaction time of 12 h (Table S1). To accomplish this, reaction was conducted under oxygen atmosphere (instead of open air) provided **1b** in 93% yield in shorter reaction times (5 h). As expected, oxidative coupling between two molecules of thiols was taking place readily in the presence of O_2. It is to mention that the reaction conducted under O_2 in water without addition of Arg didn't lead to the formation of **1b** thus emphasizing the important role of Arg.

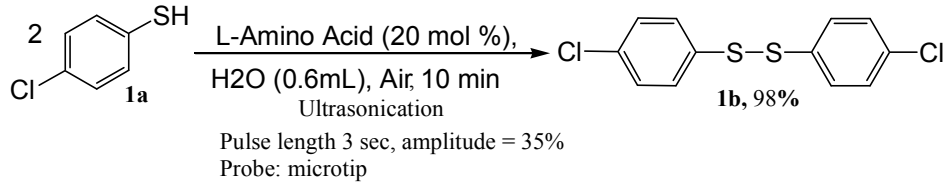
Modern tools of green chemistry (viz. Microwave and ultrasound) also help in reducing the reaction time, hence, were screened for oxidative coupling reaction.

(c) Impact of microwave irradiations (CEM monomode, focused) for reduction in reaction time:



To facilitate the reaction in shorter time, the similar reaction (conversion of 1a into 1b) when conducted under focused microwave (50°C, 80W) under air proved out to be futile even variations in temp and time (up to 45 min) were not helpful. It was possibly because of immediate making and breaking of the hydrogen bonds with the substrates which didn't lead to facile union of two molecules of thiophenols probably because of disruption of hydrogen bonding at higher temperature.

(d) Impact of ultrasonicator for reduction in reaction time:

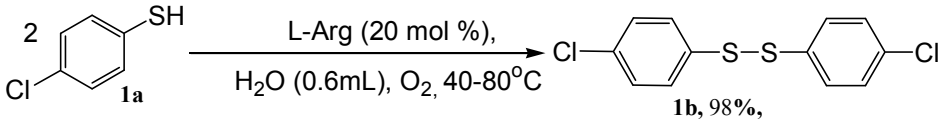


Interestingly, the reaction furnished **1b** in 98% yield in 10 min in open air under ultrasonicator. But because of the malodorous smell of thiols, the reactions were planned to be conducted in well ventilated hoods in closed vessels (i.e. sealed tube with septum). Hence the oxidative coupling reactions were conducted in conventional manner in O_2

atmosphere in well ventilated hoods. Further the parameter of temperature was planned to be screened.

(e) Optimization of the reaction temperature for formation of 1b:

Next we ventured to gauge the specific effect of temperature in accomplishing the reaction and conducted at variable temperatures. It was found that optimum temperature of 50°C using 20 mol% L-Arg in the presence of O_2, the reaction mixture yielded **1b** in 98% yield (on GC basis) in 15 min only **(Table S2)**.



1b, 98**%,**
Table S2, entry 1

Table S2: **Optimization of the reaction temperature for formation of 1b using 20 mol % of L-Arg**

S.No	Temperature in °C	Time	% Yield (on GC basis)
1.	**50**	**15 min**	**98**
2.	40	90 min	90
3	70	20 min	92
4.	80	15 min	80

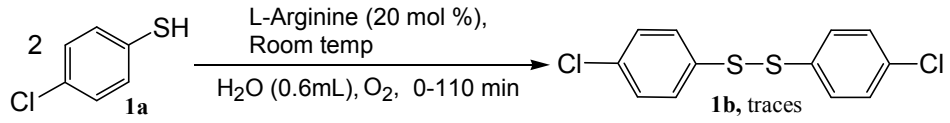
Hence the reaction got completed in 15 min at 50°C using arginine (20 mol %), O_2 and water (0.6 mL) with complete consumption of starting material **1a** (0.25mmol) and providing **1b** in 98% yield (Table S2, entry 1). Now after having the optimized conditions in hand a number of diphenyl disulfides from respective thiols were synthesized in water/arginine at 50°C and the various disulfides were obtained in moderate to excellent yields (55-98% on GC-MS basis) in 15-110 min depending upon the nature of corresponding thiol (Table 2 of manuscript).

Mechanistic studies: Inspired by our previous study in which the ambiphillic character of the ionic liquid [hmim]Br was probed by NMR[1a] titrations, we attempted to establish the mechanistic aspect of our reaction utilizing arginine/water with a co-solvent. Also there are other reports[1b] which demonstrate the role of NMR based studies in establishing the mechanistic pathway of the reaction. But unfortunately our all attempts

to trace the mechanistic pathway by NMR based study failed, due to precipitation or co-precipitation of the Arg or the starting substrates. It is to mention that arginine is soluble in water while 4-chloro thiophenol (**1a**) is soluble in organic solvents. Different combinations of D_2O and D_2O miscible solvents (MeOD, DMSO-d6 etc) were screened for NMR studies to establish the interaction between arginine and 4-chrothiophenol (1a) but to no avail. Moreover, HRMS studies using Q-TOF spectrometer also failed due to the problem in the solubility of the substrates.

Further after going through the literature search, it was found that UV[2-4] based mechanistic studies are helpful in establishing the mechanism of reactions involving amino acids with zwitterionic[5] structures in water, hence the following studies was undertaken:

UV- Visible titrations:



The standard solution of thiophenol (1a) was prepared in optimized solvent mixture of MeOH: H_2O (95:5) in concentration of 1mg/1mL. The solution of Arg in MeOH: H_2O was prepared in same concentration of 1mg/mL. Further, different aliquots from ongoing reaction (i.e. thiophenol + Arg + O_2 + water) in were taken at intervals of 0, 2, 4, 6, 8,10 up to110 min (till product formation).

All the aliquots withdrawn from the reaction mixture were vacuum evaporated to remove the water till the constant weight of sample and repeated this process (taking the aliquots and vacuum drying) according to above time intervals. Now, 1mg each of the samples were weighed and further diluted to same concentration (95:5, MeOH: H_2O) of 1mg/mL. Thereafter, all the solutions of thiophenol, arginine and dilutions were subjected to UV-visible titrations for studying their absorbance profiles. The UV- visible spectras of neat arginine, 4-chlorothiophenol and the standard 4,4'-dichloro disulfide were taken in 95:5 ratio of MeOH: H_2O. The respective UV spectras of these three compounds are shown below. It is important to mention here that the formation of **1b** at 50^{o}C takes place in 15-20 min only and it was difficult to trace the mechanistic pathway at this temperature,

hence the reaction was carried out at room temperature under the influence of O_2. The standard **1b** for our study was prepared using our ionic liquid[1a] ([hmim]Br) mediated disulfide synthesis.

[1] a) R. Kumar, N. Sharma, U. K. Sharma, A. Shard and A. K. Sinha. *Adv. Synth. Catal.*, **2012**, *354*, 2107–2112. b)
A. K. Chakraborti, S. R. Roy, *J. Am. Chem. Soc*. **2009**, *131*, 6902–6903.
[2] G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar, Ray J. Butcher. *J. Am. Chem. Soc.* **2001**, *123,* 839-850.
[3] L. Parimala, J. Santhanalakshmi, *Nanoscience and Nanotechnology: An International Journal* **2013**, *3*, 4-11.
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[5] J. L. Alonso, E. J. Cocinero, A. Lesarri, M. E. Sanz, J. C. Lopez, *Angew. Chem. Int. Ed*. **2006**, *45*, 3471-3474.

UV based mechanistic studies of complexation between 4-chlorothiophenol (1a) and arginine with ultimate formation of 4,4-dichlorodisulfide (1b).

The UV- visible spectras of neat arginine & 4-chlorothiophenol were taken in 95:5 ratio of MeOH: H_2O. The respective UV spectras of two compounds are shown below (fig 1&2).

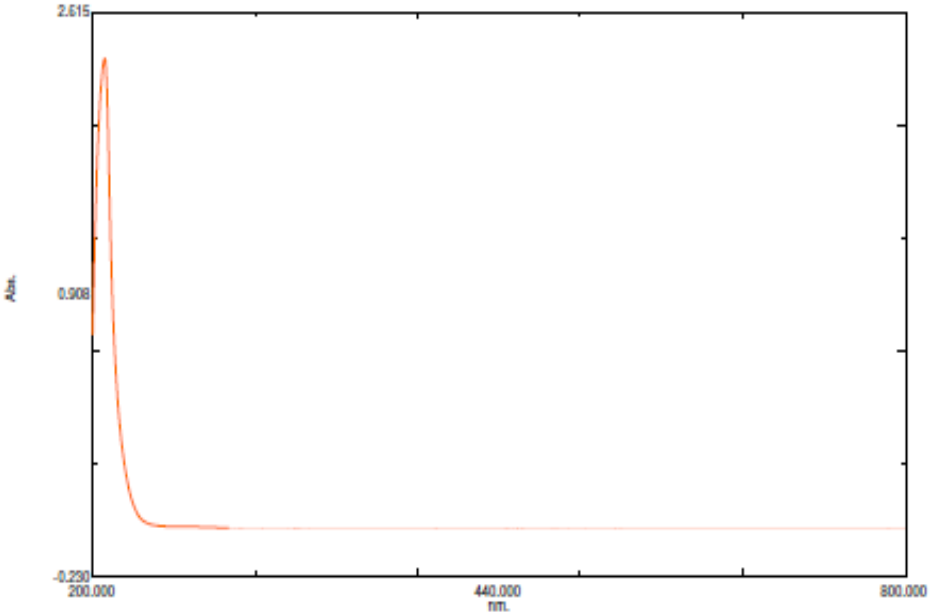


Figure 1: UV spectra of L- Arginine (neat) having a λ_{max} at 207.5 nm

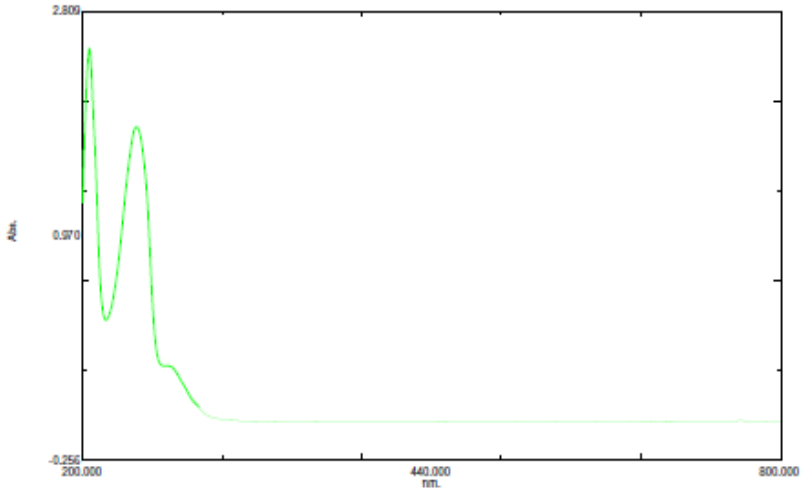
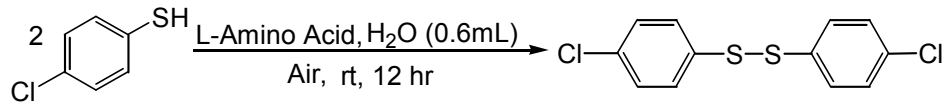


Figure 2: UV spectra of 4-chlorothiophenol (neat) having a λ_{max} at 246.5 nm



Now from the reaction mixture of 4-chlorothiophenol and arginine monitored at room temperature various aliquots of different timings (0 to 110 mins) were withdrawn and respective solutions were subjected to UV studies with concentration of 1mg/1mL in 95:5 methanol:water. Fig.3 shows the bathochromic shift of λ_{max} = 246.5 nm to λ_{max} = 274.5 nm which indicates initiation of complexation between 4-chlorothiophenol and zwitterionic arginine at 0 min of the reaction.

UV-visible spectra's of respective aliquots starting from 0 min of the reaction up to 110 mins are presented below.

UV spectra with complementing bathochromic shift from λ_{max} 246.5-276.5 nm at 0min is shown in Fig 3.

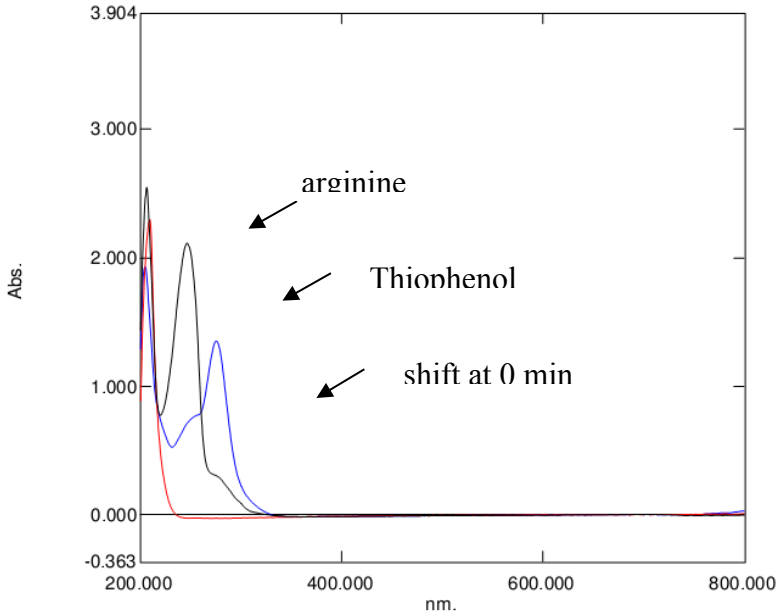


Fig. 3 The initiation of complexation that causes instant shift in λ_{max} of 4-chlorothiophenol from λ_{max} = 246.5 nm to 276.5 nm at 0 min of the reaction along with arginine and 4-chlorothiophenol.

UV spectra showing shift from λ_{max}= 246.5 nm to λ_{max} = 276.5 nm at 0min.

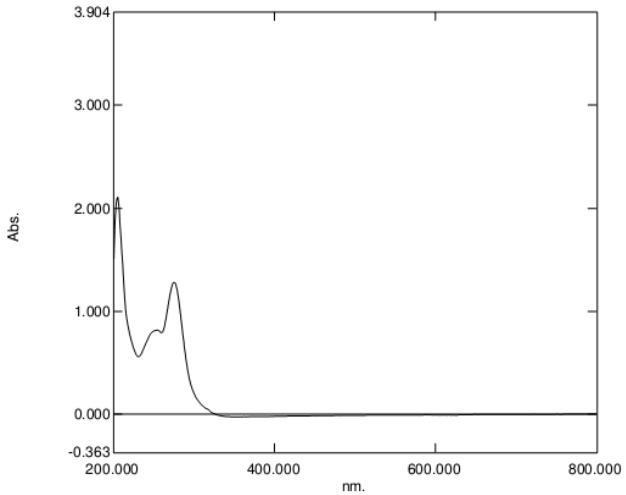


Fig.4: Initiation of complexation at 0 min (neat) of the reaction mixture

Absorption spectras of aliquots at 3 & 6 mins of reaction mixture confirms initiation of complexation as, they overlay with absorption spectra at 0 mins (retains λ_{max} at 276.5 nm fig.4 & 5).

iii) UV overlay spectra of 3 min with 0 min is shown here (Fig 5)

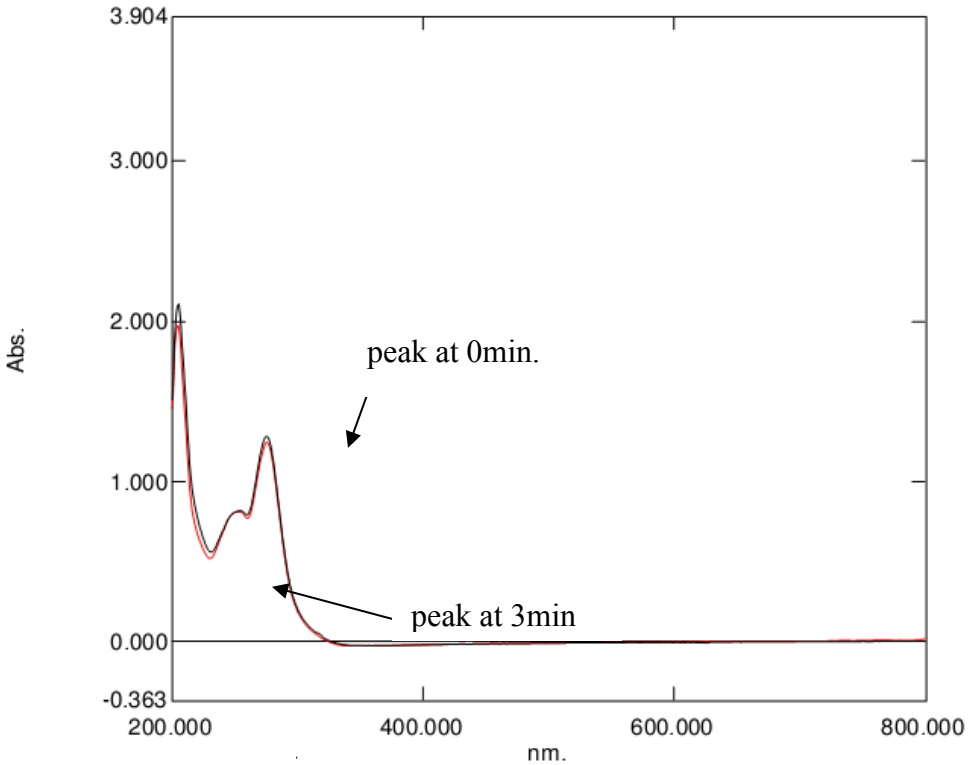


Fig.5: Overlaying of peaks at 0 min and 3min.

iv) UV overlay spectra of aliquot at 6 min with 0 min and 3min spectra.

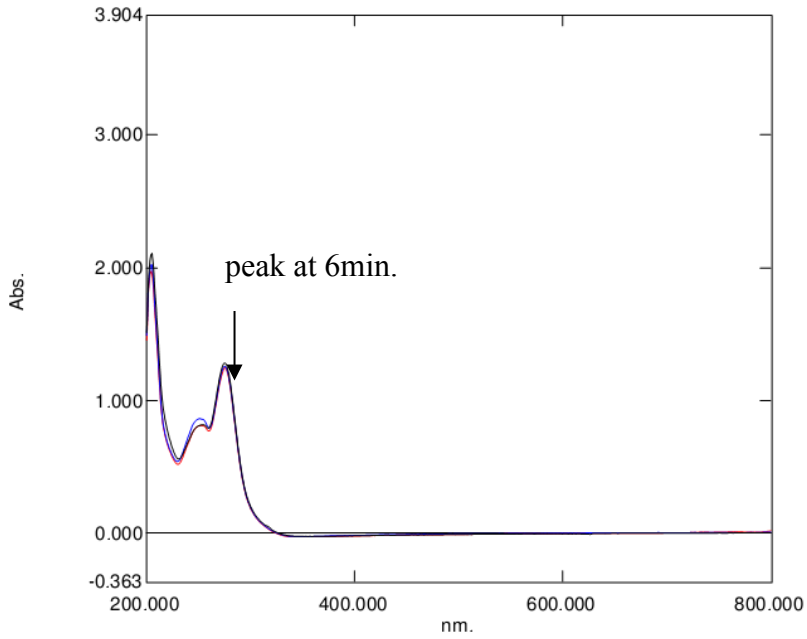


Fig. 6 Absorption spectra of 6 min overlaying with absorption spectra of 0 and 3 min indicating consistency in complex formation.

(v) UV overlay spectra of 9 min. with 6 min.

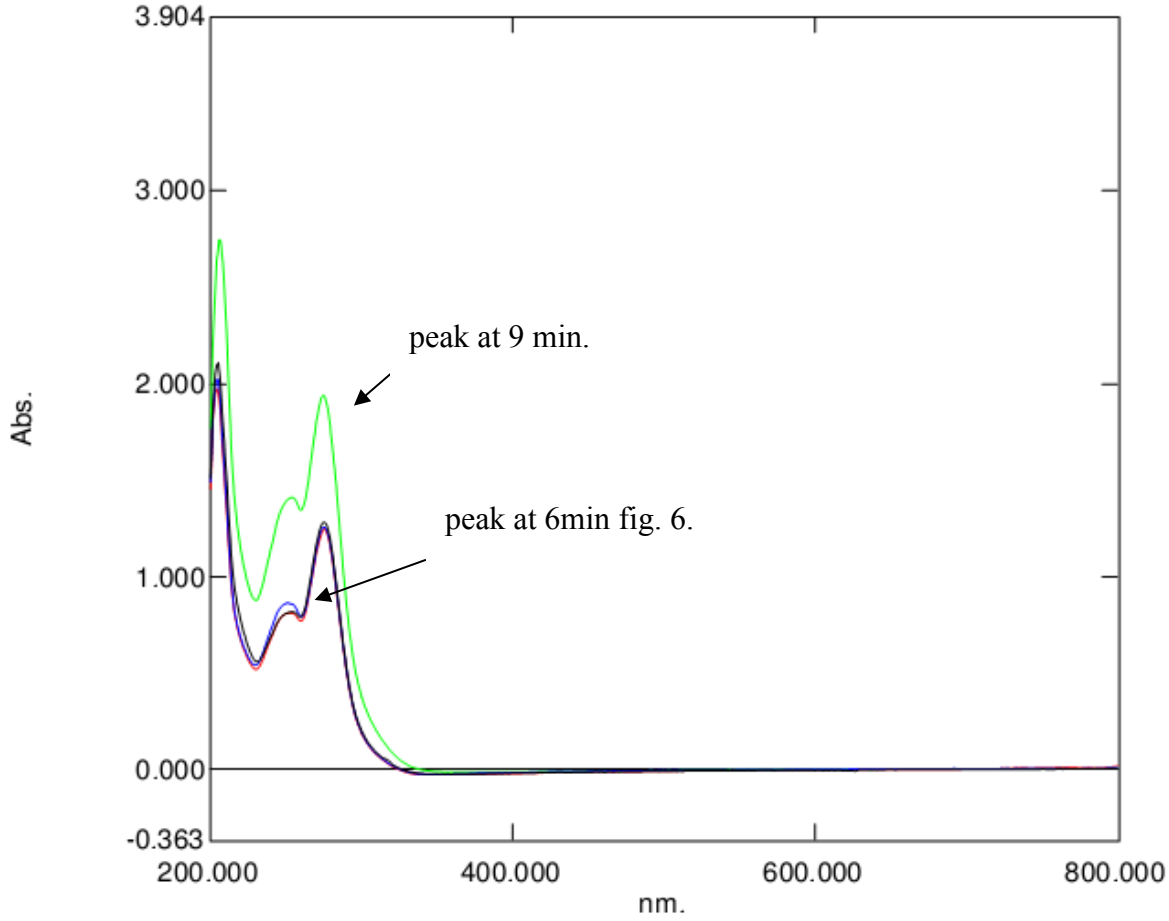


Fig.7: Completion of complex formation at 9 min. of the reaction mixture as there is rise in absorbance from 1.3 to 1.9 indicating maximum complex concentration at 9 min.

Absorption spectra at 9 min have shown exponential increase in peak height which might indicate completion of complex formation.

vi) UV overlay spectra of 12 min.

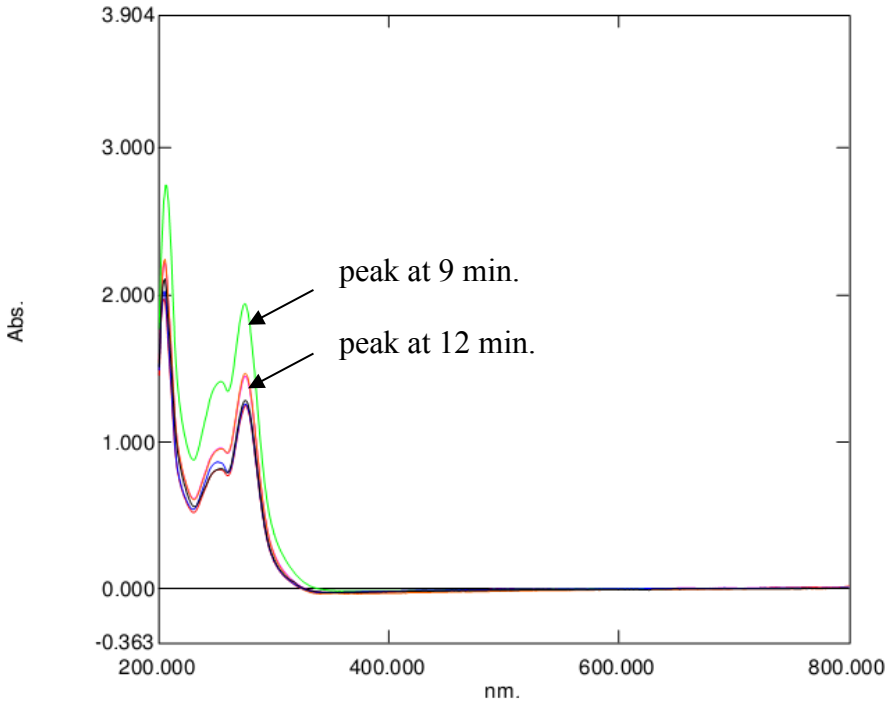


Fig. 8: Initiation of product formation after 12 min.

As seen in Fig. 7, after 12 min decrease in the absorbance from 1.9 to 1.5 (hypochromic shift) of complex indicates that complex starts getting converted into product.

vii) UV overlay spectra at 12 min.

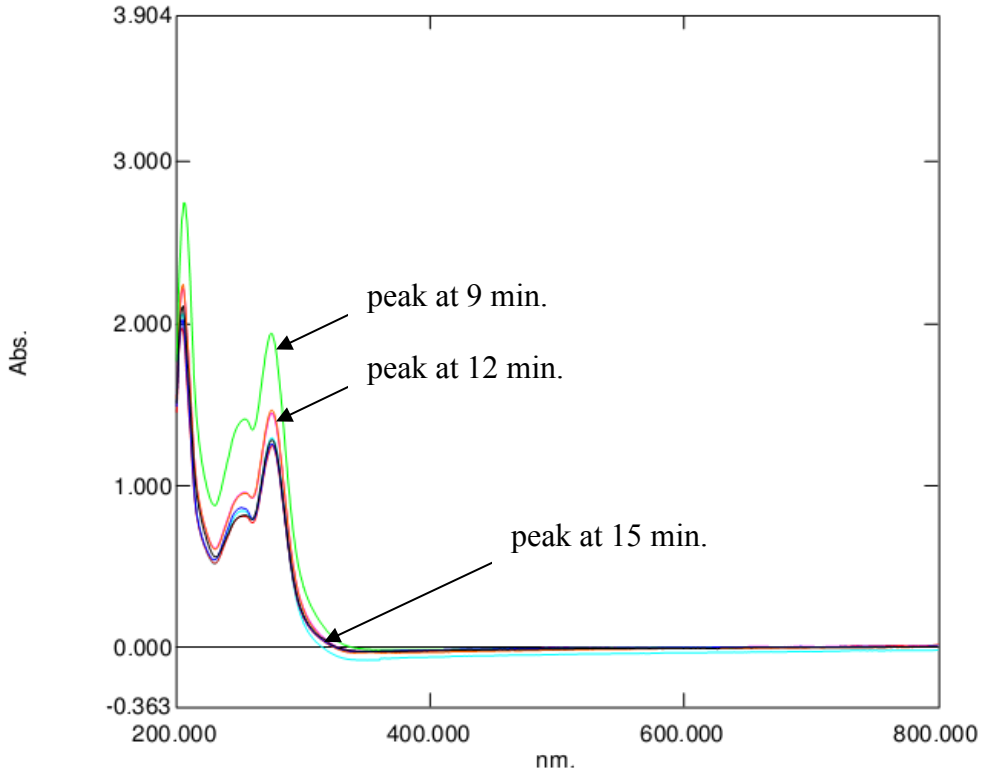


Fig. 9: Decrease in absorbance of aliquot at 15 min indicating consistent conversion of complex into disulfide.

The increase in the concentration of the complex was probably because of interaction of two molecules of thiophenols with the Arg leading to the formation of a cyclic intermediate as shown in manuscript (Fig. 4)

viii) UV overlay spectra at 20 min.

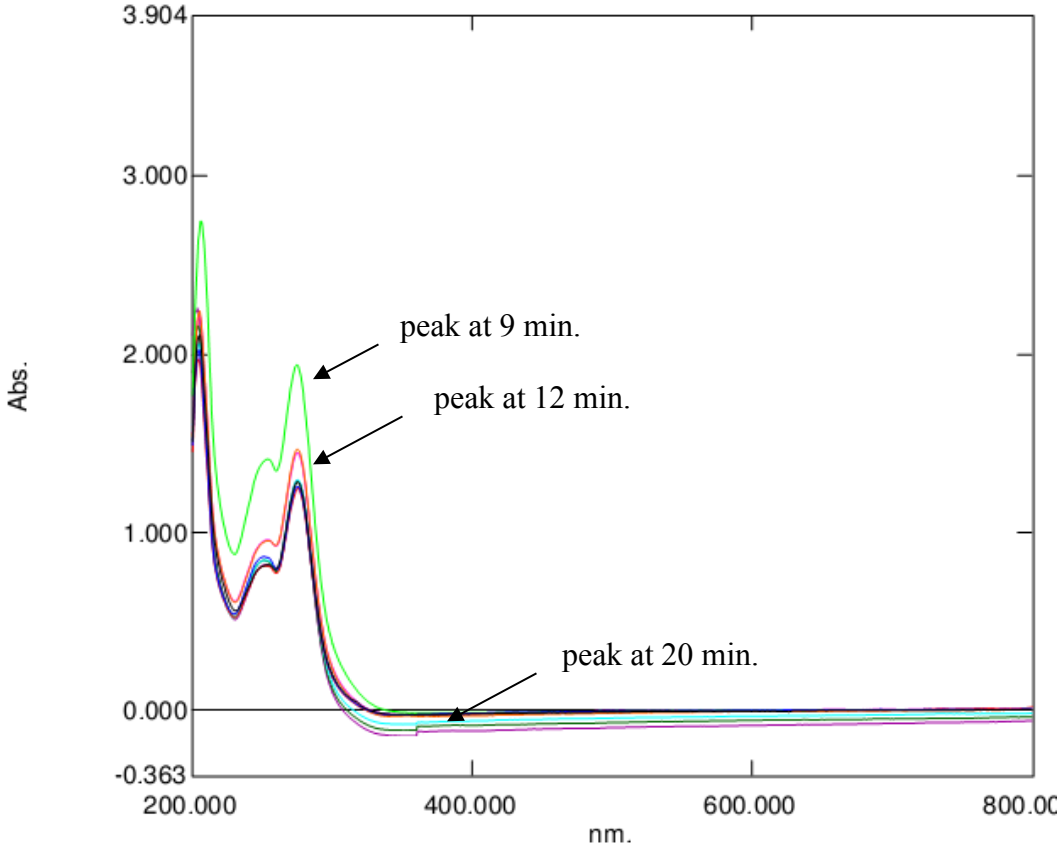


Fig.10: Absorbance at 20 min. of the reaction mixture indicating complete diminution of complex followed by initiation formation of product.

ix) UV spectra of overlaying at 20 min.

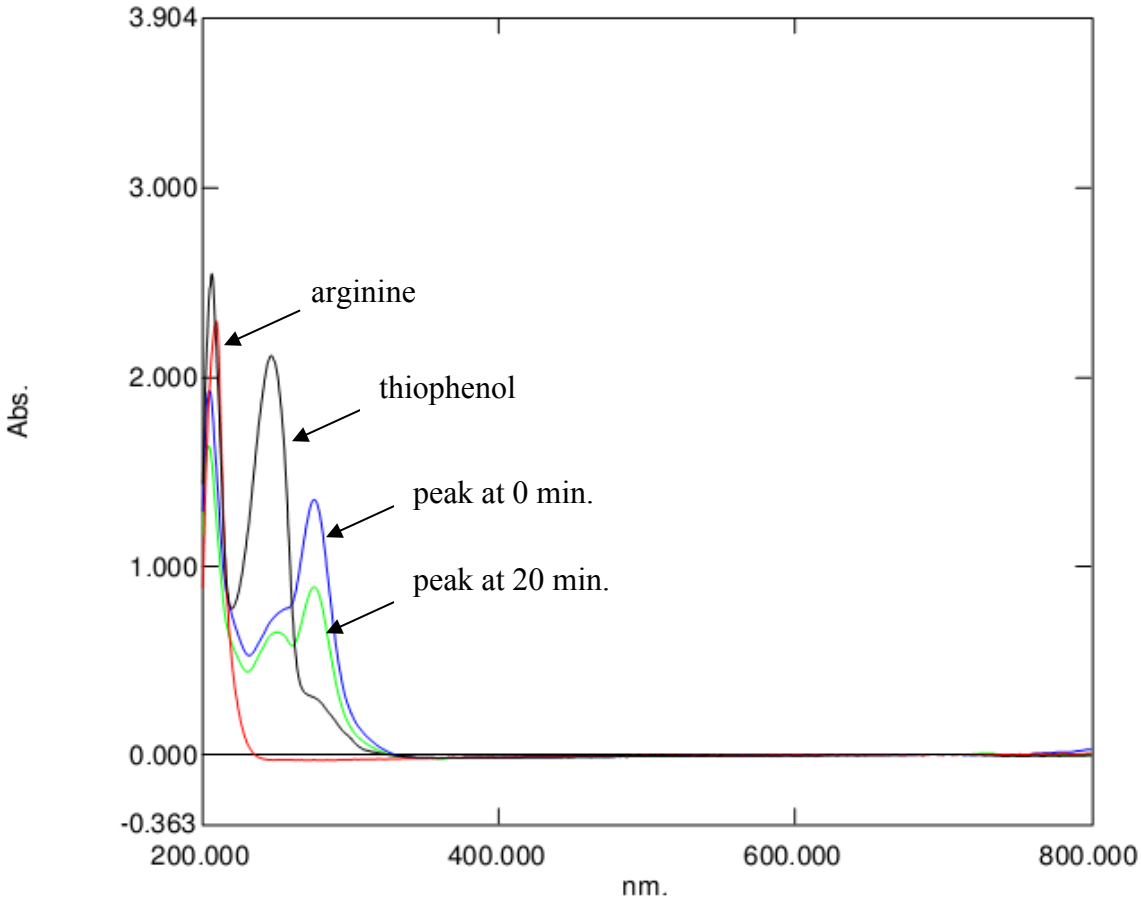


Fig.11: Initiation of product formation at 20 min.

x) UV overlay spectra at 30 min.

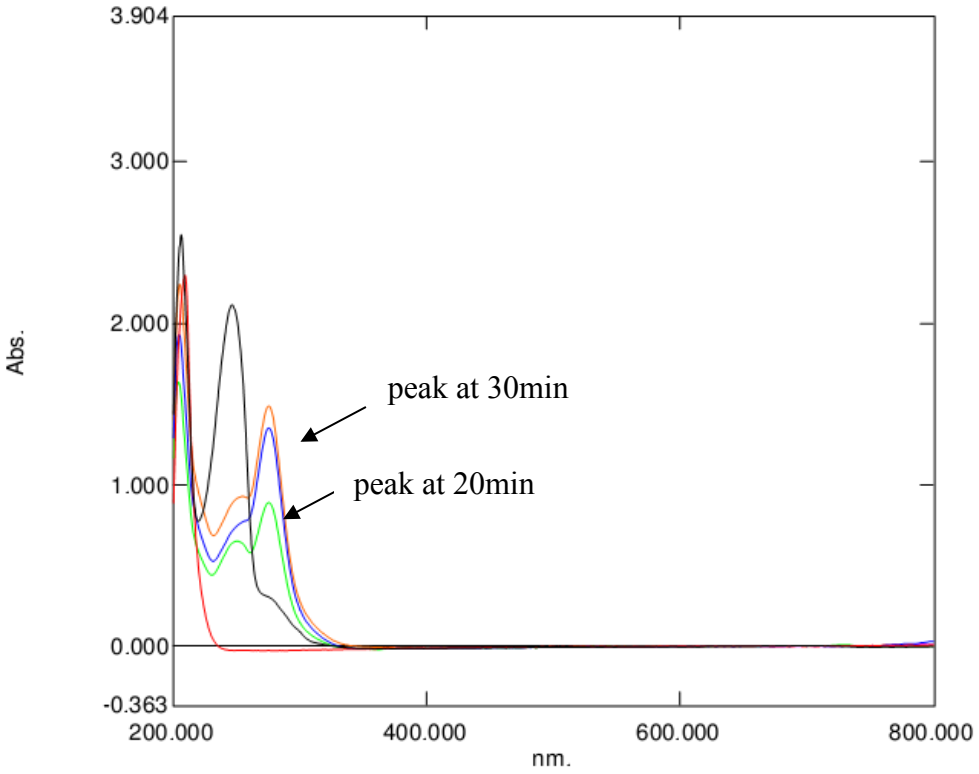


Fig.12: Increase in formation of product at 30 min. with rise in absorbance

xi) UV overlay spectra of 40 and 50 min.

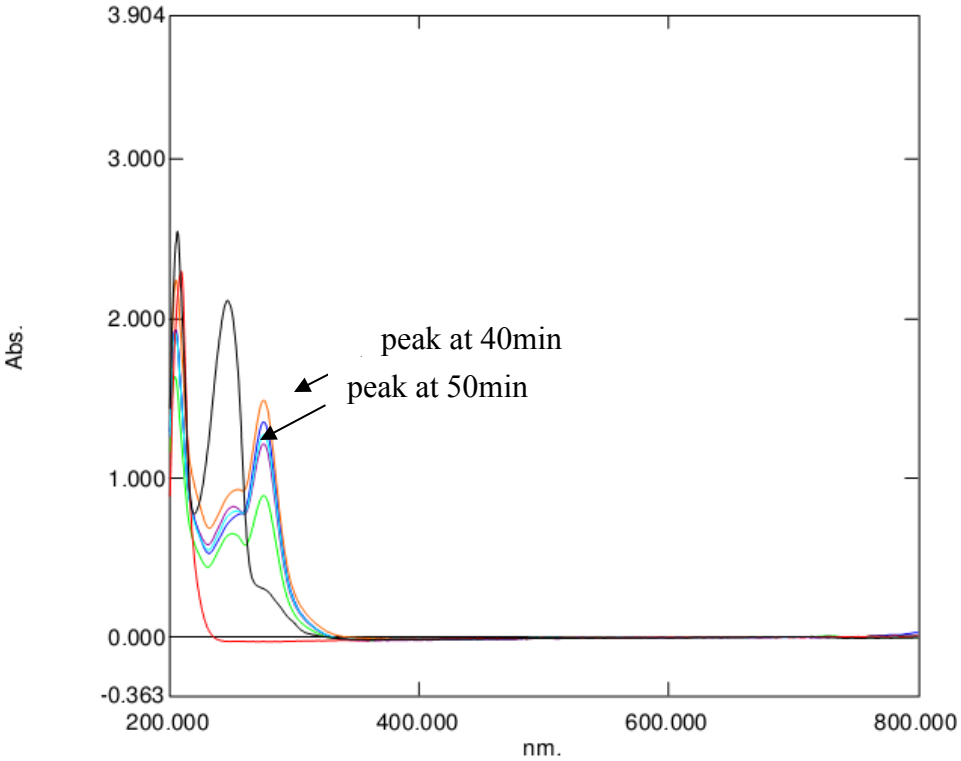


Fig.13: Product formation at 40 and 50 min of the reaction.

xii) UV overlay spectra at 60 min.

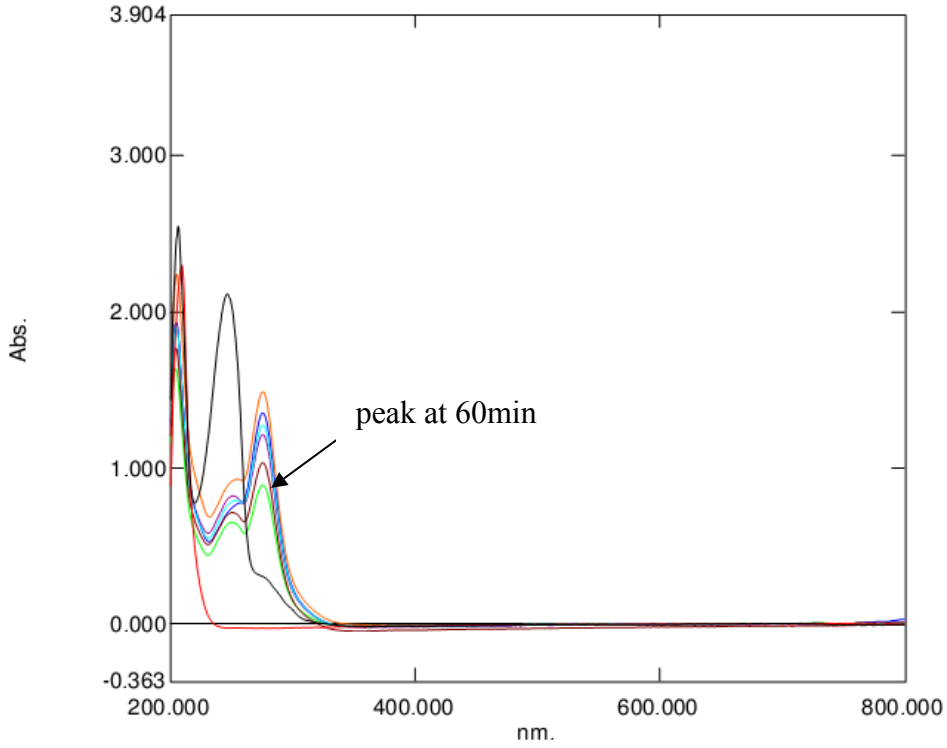


Fig.14: Product formation at 60 min with consequent decrease in absorbance

xiii) UV overlay spectra at 70 min.

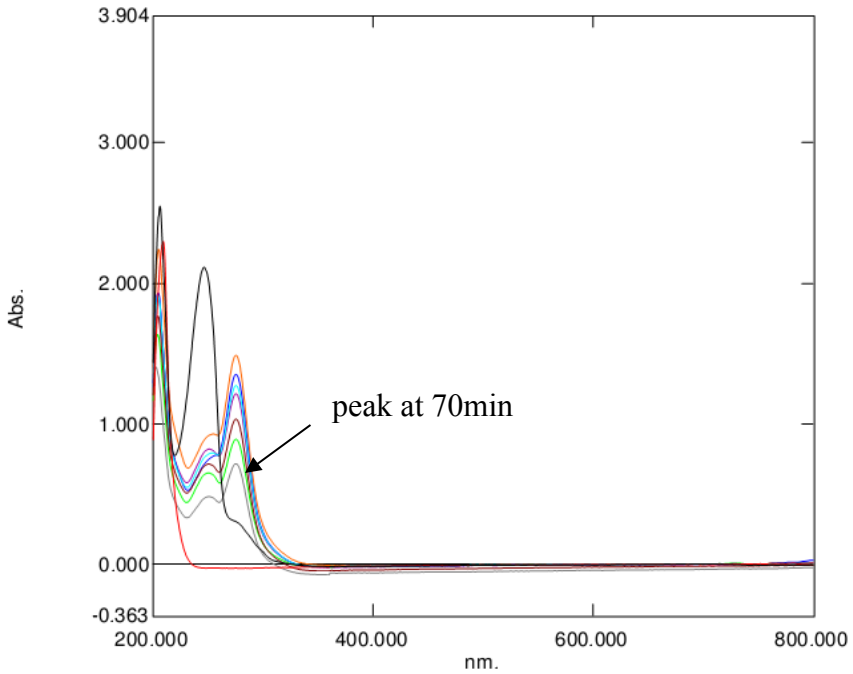


Fig.15: An exponential decrease in absorbance at 70 min which is probably an indication of complete conversion of complex into product.

xiii) UV spectra overlay at 80 min.

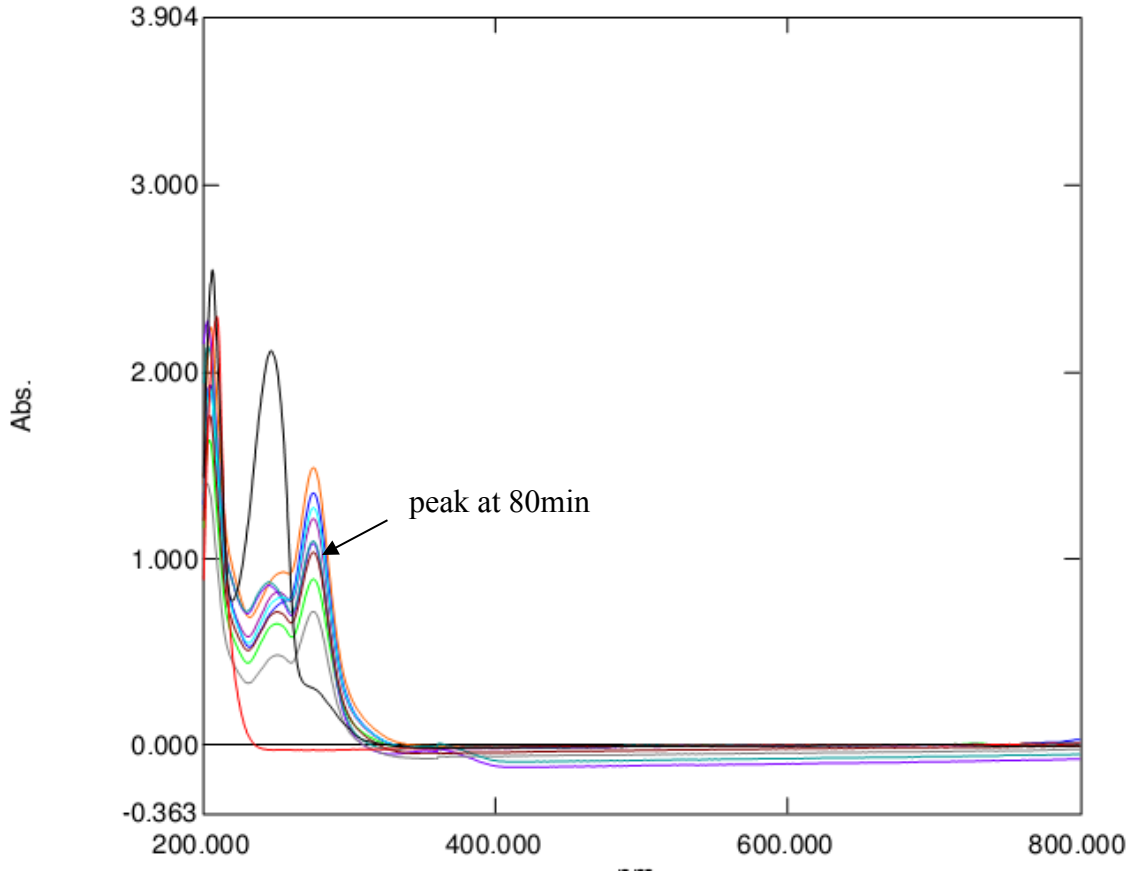


Fig.16: A slight increase in the absorbance of aliquot at 80 min indicates that complex had been transformed into product

After 80 min of the reaction, it was observed that there was neither increase nor decrease in absorbance of the reaction aliquots indicating completion of product (1b) formation.

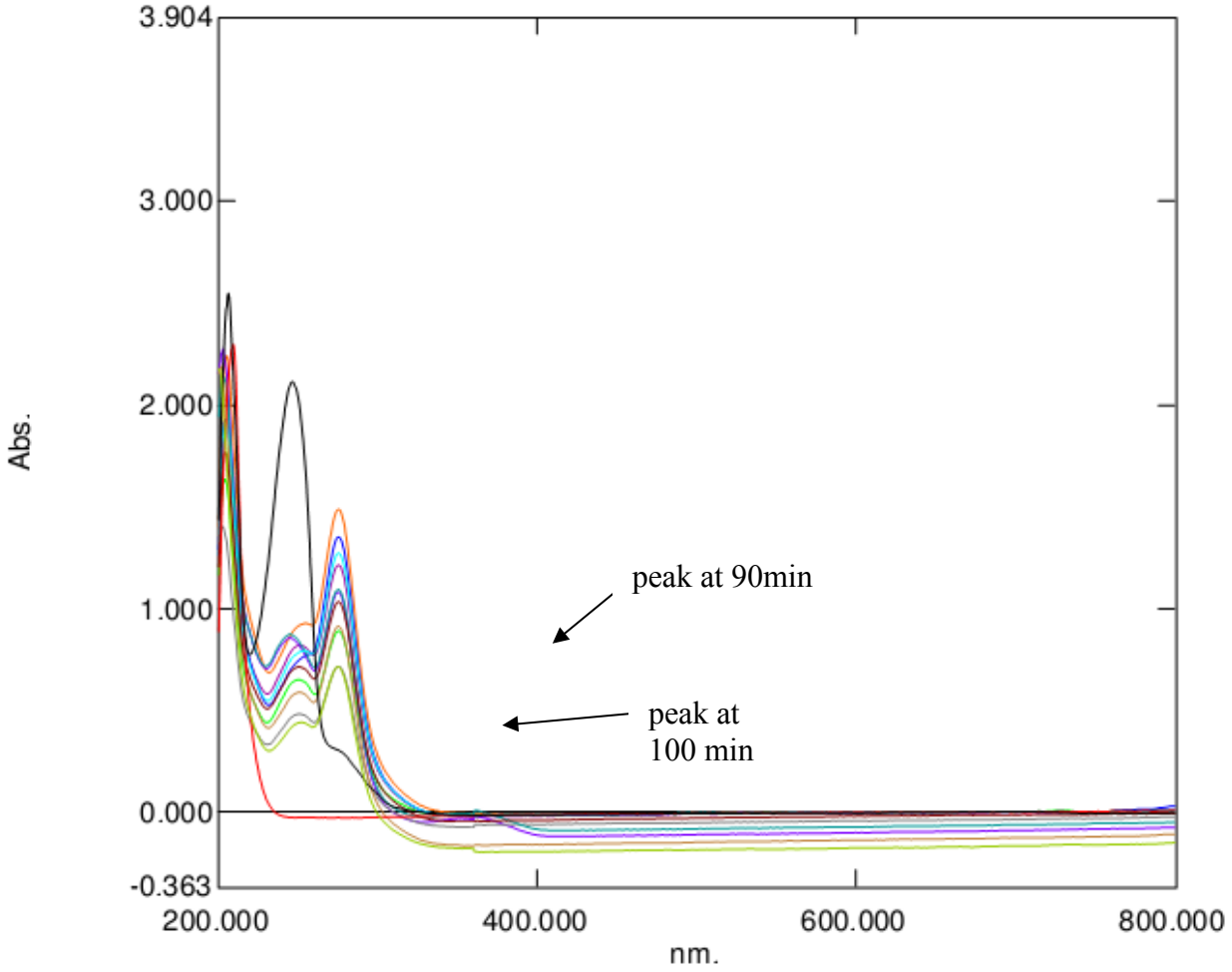


Fig.17: Spectral overlay of absorbance of aliquots at 90 and 100 min of the reaction respectively.

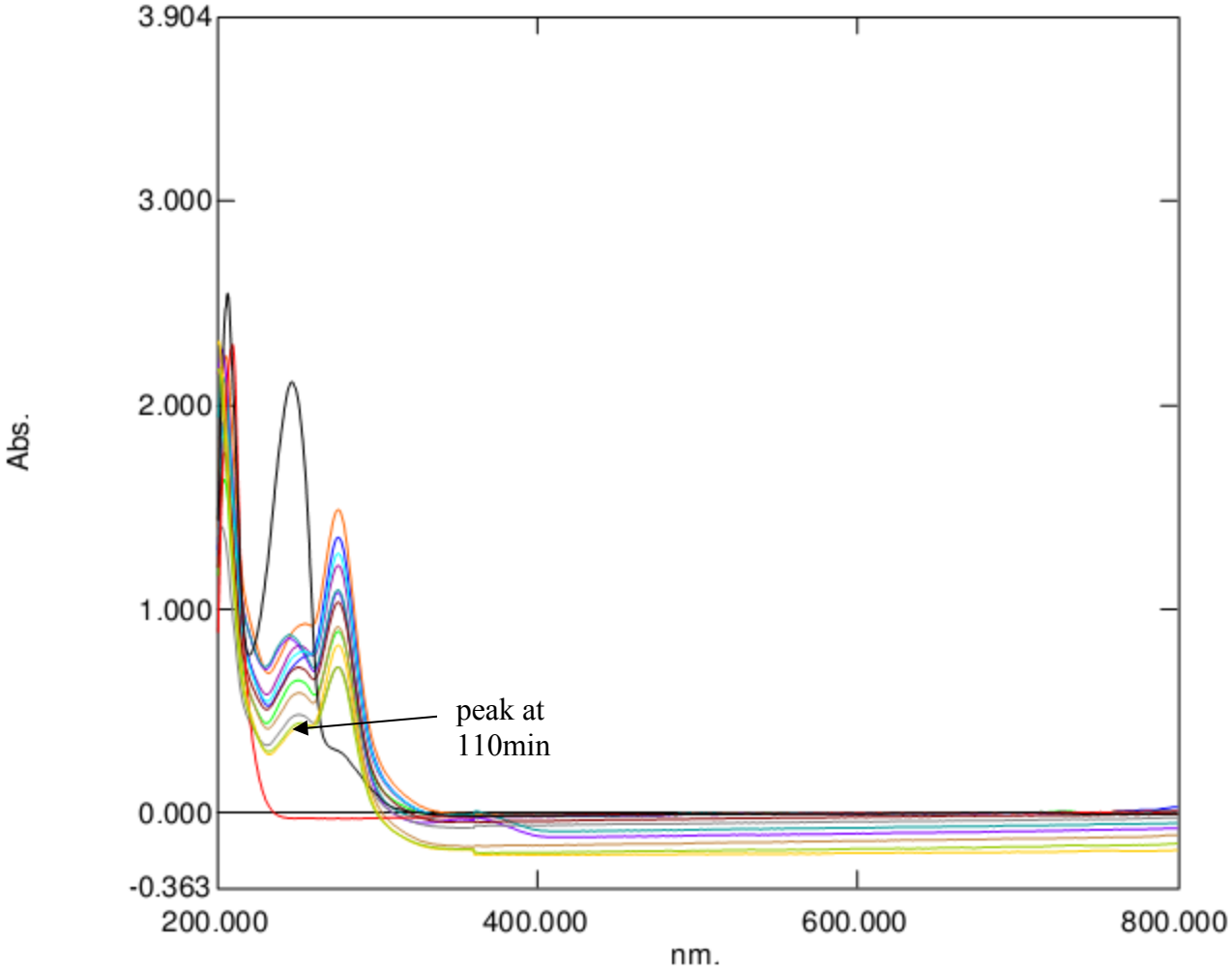


Fig.18: Absorbance of aliquot at 110 min with complete product (1b) formation.

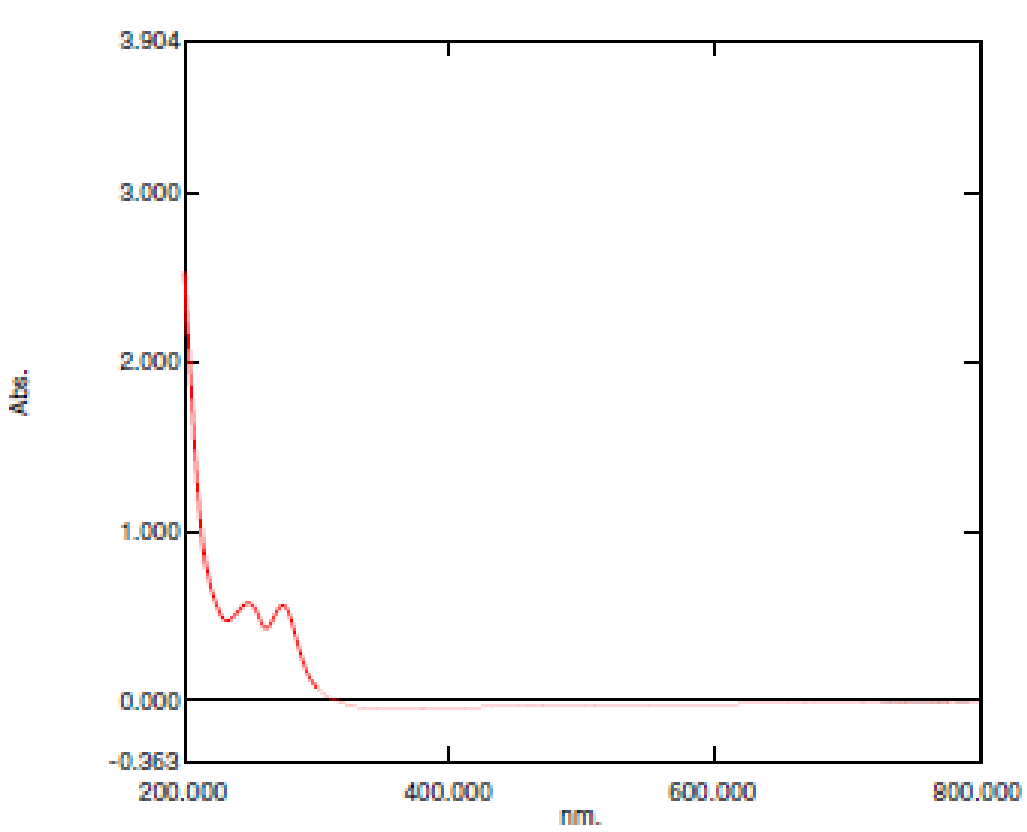


Fig.19: Absorption spectra of product 4,4 Dichloro diphenyldisulfide (standard).

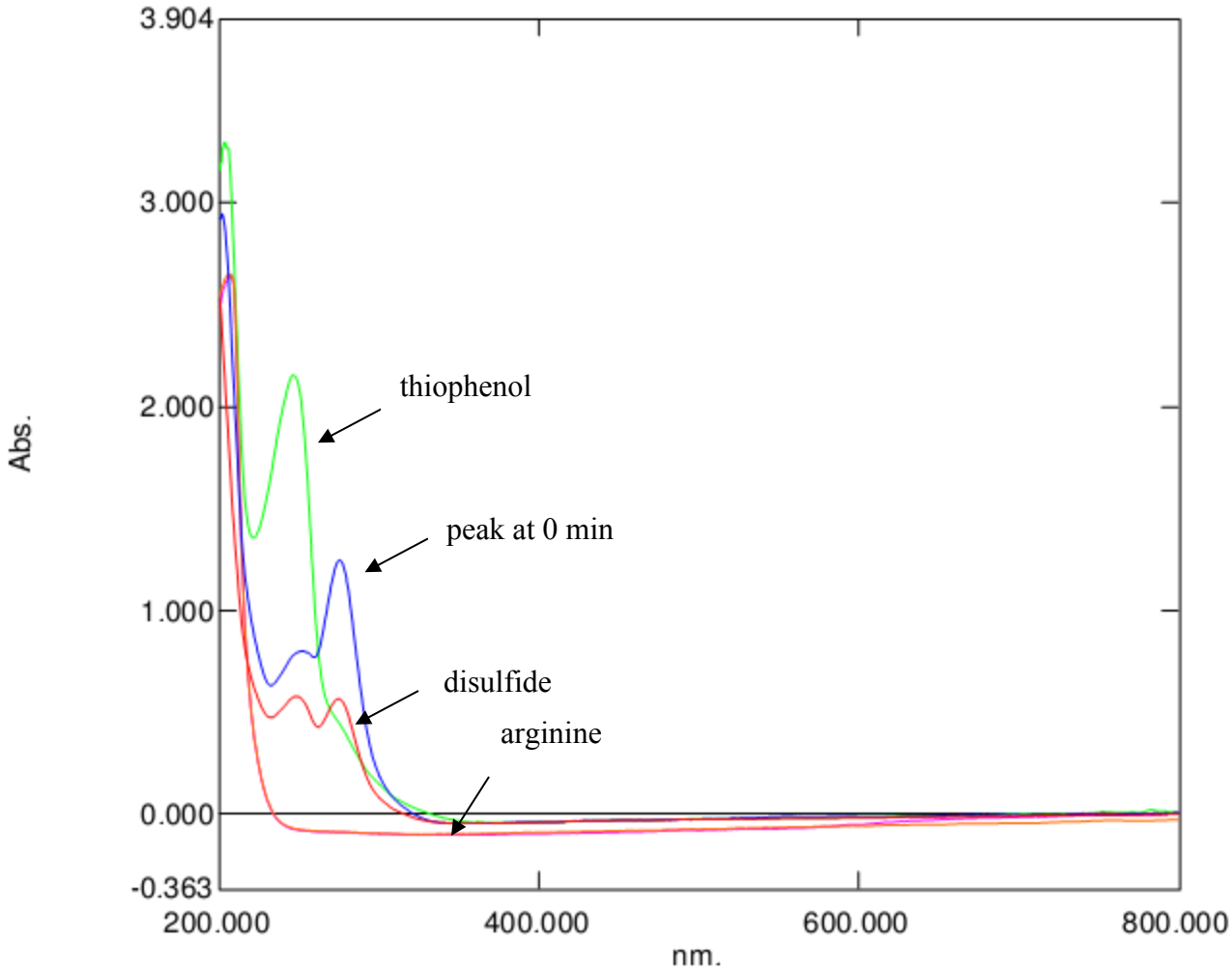


Fig.20: Absorption profiles of thiophenol, arginine, complexation and 4, 4' diphenyl disulfide at 0 min and at the completion of reaction (after 110 min).

Hence it was evident that **1b** was formed completely at room temperature in 110 min (Figure 18) with simultaneous regeneration of Arg. Thus formation of **1b** follows the sequences like initial bathochromic shift, followed by hyperchromic shift and thereafter diminution in the intensity of complex followed by product formation.

In summary, the λ_{max} of 4-chlorothiophenol (**1a**) and Arg appeared at 246.5 nm and 207.5 nm respectively (Figure 1 and 2). However, when the substrates were stirred, the spectral analysis clearly indicated that **1a** and an aqueous solution of zwitterionic Arg led to immediate initiation of complexation evident by bathochromic shift from λ_{max} 246.5 nm to 274.6 nm. It was observed that complexation between iminium-ion of arginine and

the heteroatom (S) of thiophenol exponentially increased up to 9 min leading to a hyperchromic shift which probably is an indicative of increase in concentration of complex "C". Diminution in the absorbance (hypochromic shift) of C appeared after 12 min (Fig 8) with initiation of formation of **1b** which finally completed in 110 min at room temperature.

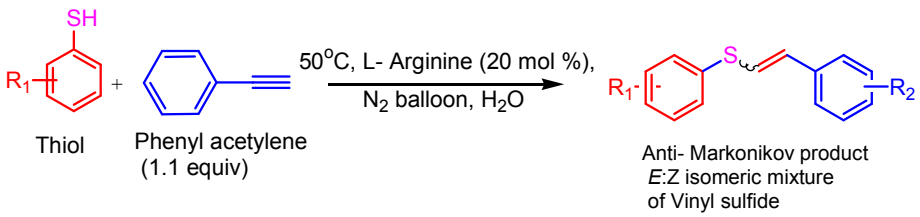
Recyclability experiments:

In this experiment, 0.25 mmol of **1a**, 20 mol % of Arg, O_2 and 0.6 mL of water were heated at 50^{o}C, the resulting product **1b** was formed in 20 min. The aqueous solution containing Arg and **1b** was extracted using ethyl acetate. The ethyl acetate layer was vacuum evaporated to obtain **1b**, whereas the same aqueous solution containing Arg was used repeatedly for carrying out the oxidative coupling for a number of times (Note: aqueous solution containing Arg was concentrated under vacuum to remove the last traces of organic solvent if any before going for next catalytic cycle).

Finally, the recyclability experiments revealed that the catalytic system could time and again be recycled and there was no loss in the catalytic efficiency of the same up to 7 consecutive cycles, after which a slight decline in the yield of the product was observed. The decrease yield of **1b** could be readily compensated by the addition of relatively catalytic amount of arginine (5 mol %). The same catalytic system could be used up to 10 times and enhancement in yield up to 96%.

Optimization of the reaction conditions for the formation of Vinyl sulfides:

To an aqueous charged pool containing Arg (20 mol%), it was observed that if the thiol was added in the beginning and the phenyl acetylene was added at last, it led to formation of undesired diphenyl disulfide. To circumvent the problem, phenyl acetylene was first added to the water containing Arg, and then stirred for few minutes in the presence of nitrogen. Later on, thiophenol was added to the vigorously stirring solution of arginine/Water and stirred at 50^{o}C which upon TLC basis showed the complete consumption of starting material, and upon NMR analysis it was confirmed to be vinyl sulfide (*E:Z* isomeric mixture) (Scheme S1).

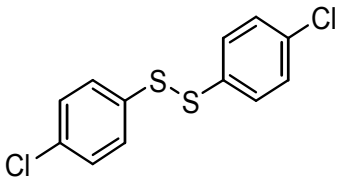


Scheme S1: Optimized conditions for the synthesis of Vinyl sulfides.

The catalytic system comprised of Arg/H_2O/N_2 was also tried for the efficient hydrothiolation of stryrenes towards thiol-ene coupling (TEC), but unfortunately no profound effect of arginine was found on the rate of reaction and yield of product in comparison to the reported protocol.

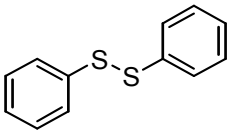
(^{1}H & C^{13}) NMR values of disulphides

Bis(4-chlorophenyl) disulphide[1a] **(1b)**



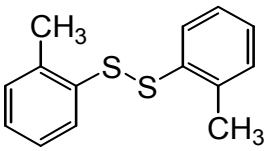
White solid, mp 62-65°C (lit mp 64-66°C) , ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45 (4H, d, J = 8.65 Hz), 7.32 (4H, d, J = 8.65 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 135.6, 134.1, 129.8 and 129.7.

Diphenyl disulphide[1a] **(2b)**



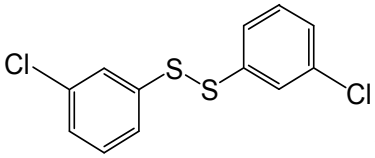
White solid, mp 51-54°C (lit mp 52-54°C), ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.52 (4H, m), 7.36-7.25 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 137.5, 129.5, 128.0 and 127.6.

Bis(2-methylphenyl) disulphide[1a] **(3b)**



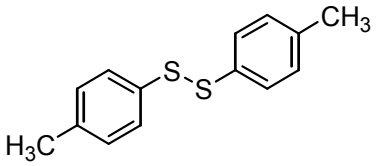
White solid, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43 (4H, d, J = 8.14 Hz), 7.15 (4H, d, J = 8.02 Hz), 2.37 (6H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 137.8, 134.8, 130.2, 129.0 and 21.5.

Bis(3-chlorophenyl) disulphide[1a] **(4b)**



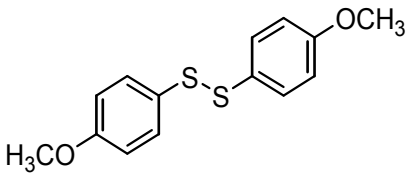
White solid, m.p. 70-72°C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51 (2H, s), 7.39-7.33 (2H, m), 7.26-7.20 (4H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 138.8, 135.6, 130.6, 128.0, 127.4 and 125.8.

Bis(4-methylphenyl) disulphide[1a]**(5b)**



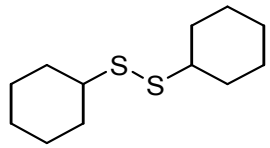
Colorless solid, mp 82-84°C (lit mp 81-83°C), ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (4H, d, J = 8.19 Hz), 7.15 (4H, d, J = 7.97 Hz), 2.35 (6H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 137.9, 134.3, 130.2, 129.0 and 21.5.

Bis(4-methoxyphenyl) disulphide[1a] **(6b)**



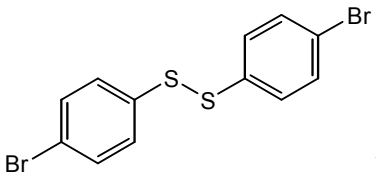
Colorless solid, mp 33-36°C (lit mp 35-37°C), ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (4H, d, J = 8.77 Hz), 6.87 (4H, d, J = 8.75 Hz), 3.83 (6H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 160.3, 133.1, 128.8, 115.0 and 54.4.

Dicyclohexyl disulphide[1a] **(7b)**



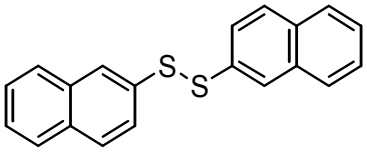
Colorless oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.71-2.64 (2H, m), 2.06-2.04 (4H, m), 1.80-1.79 (4H, m), 1.64-1.61 (2H, m), 1.35-1.26 (10H, m), ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 50.4, 33.2, 26.5 and 26.1.

Bis(4-bromophenyl) disulphide[6a] **(8b)**



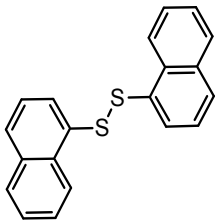
White solid, mp 92-96°C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.42 (4H, m), 7.37-7.33 (4H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 135.1, 132.6, 129.8 and 129.9.

Bis(2-nathphalenyl disulphide) [6a] **(9b)**



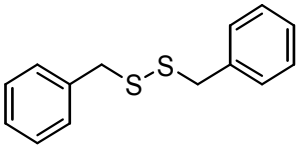
White solid, mp 133-136°C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (2H, s), 7.83-7.75 (6H, m), 7.68 (2H, d, J = 8.63 Hz), 7.52 (4H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 134.7, 133.9, 132.9, 129.4, 128.2, 127.9, 127.2, 127.0, 126.7 and 126.1.

Bis(1-nathphalenyl disulphide[6a] **(10b)**



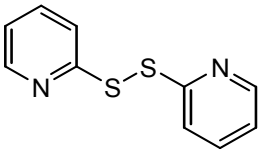
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02-7.56 (4H, m), 7.50-7.10 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 132.9, 130.9, 129.4, 126.2, 124.9, 124.2, and 126.1.

Bis(phenylmethyl) disulphide[1a] **(11b)**



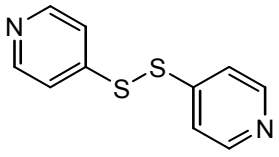
White solid, mp 57-60°C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.26 (10H, m), 3.64 (4H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 137.8, 129.8, 128.9, 127.8 and 43.7.

Bis(2-pyridinyl) disulphide[1a] **(12b)**



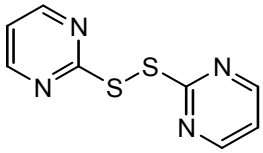
Colorless solid, mp 53-56°C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.52-8.51 (2H, m), 7.67-7.65 (4H, m), 7.12-7.00 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 159.5, 149.9, 137.7, 121.4 and 120.1.

Bis(4-pyridinyl) disulphide[1a] **(13b)**



Colorless solid, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.52-8.51 (2H, m), 7.67-7.65 (4H, m), 7.12-7.00 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 159.5, 149.9, 137.7, 121.4 and 120.1

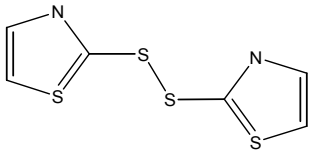
bis(2-pyrimidinyl) disulfide[6c] (14b)



White powder, mp 141-143° (lit mp 140-142°C) ^{1}H NMR ($CDCl_3$, 300 MHz): 7.35 (2H, t, J= 4.2 Hz) and 8.70 (4H, d, J = 4.1 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz); 167.83, 158.53 and

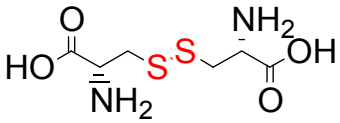
119.11.

bis(2-thiazolyl) disulfide[6c] (15b)



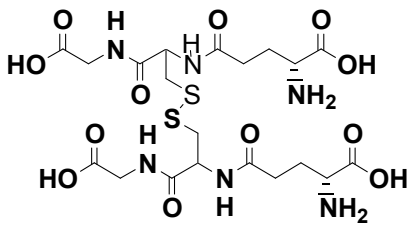
White powder, mp 78-80°C (lit mp 77-78°C) ^{1}H NMR ($CDCl_3$, 300 MHz) 7.37 (2H, d, J = 3.2 Hz), 7.78 (2H, d, J = 3.1 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 160.80, 140.3 and121.4.

L-Cystine[6b] (18b)



Colorless solid, mp 222-225°C, ^{1}HNMR (4% NaOD in D_2O); δ 3.47-3.43 (2H, m), 3.02-2.96 (2H, m), 2.81-2.75 (2H, m); ^{13}C NMR (4% NaOD in D_2O) δ 181.1, 55.4, 44.5.

Glutathione disulfide[6b] (19b)



Colorless solid, mp 176-179°C (lit[7]mp 178-180°C) ^{1}HNMR (4% NaOD in D_2O) δ 3.47-3.42 (m,1H), 3.12-3.10 (m, 3H), 3.03-2.95 (m, 1H), 2.53 (dd, *J* = 7.5, 1H), 1.81-1.57 (m, 8H) ; ^{13}C NMR (4% NaOD in D_2O) δ 183.4, 183.2, 181.2, 128.9, 56.3, 55.3, 44.0, 34.5 and 32.2.

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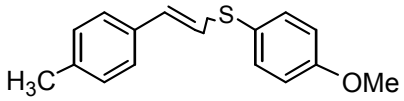
[6] a) Thurow *et al Tet. Lett.* **2011**, 52, 640–643; b) M.Oha, K. Tanaka, K. Nishiyama, W. Ando. *J. Org. Chem*. **2011**, *76*, 4173-4177. c) H. T. Abdel-Mohsen, K. Sudheendran, J. Conrad and U. Beifuss. *Green Chem*., 2013, 15, 1490-95

[7] *Merck Index* **2001**, *13*, 2811.

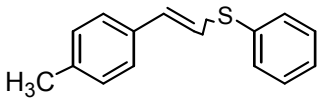
^{1}H & C^{13} NMR values of Vinyl Sulfides[7-9] (Table 3):-

1-methoxy-4-{2-(4-methyl phenyl)ethenyl] sulfanyl benzene[9] (20b)



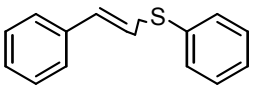
White solid, mp 60-62°C, *E:Z* ratio= 13:87. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47-7.41 (4H, m), 727-7.22 (2H, m), 7.14 (0.05 X 1, d, J = 15.33 Hz), 6.93-6.89 (2H, m), 6.77 (0.05 X 1, d, J = 15.33 Hz), 6.52 (1, d, J = 10.87 Hz), 6.39 (1H, d, J = 10.87 Hz), 3.84 (3H, s), 2.40 (3H, s).^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 159.9, 137.2,134.2, 133.6, 133.2, 129.4, 129.0, 127.5, 127.4, 126.2, 115.2, 55.8, 21.7.

1-methyl-4-[-2-(phenyl sulfanyl)ethenyl]benzene[9] (21b)



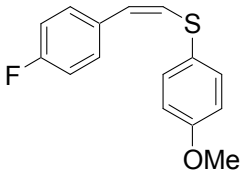
Pale yellow solid, *E:Z* ratio= 93:7. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.41 (4H, m), 727-7.22 (2H, m), 7.19-7.16 (2H, m), 6.91 (1H, d, J = 15.6 Hz), 6.81 (1H, d, J = 15.6 Hz), 6.61 (0.05 X 1, d, J = 10.5 Hz), 6.51 (0.05 X 1, d, J = 10.5 Hz), 2.41 (3H, s). ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 138.0, 136.9, 134.2, 132.9, 129.9, 129.8, 129.5 127.2, 126.4, 122.3, 21.6.

Phenyl sulfanylethenyl benzene (22b)



Viscous colorless oil in 75% yield, E:Z ratio: 40:60. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52–7.21 (m, 10H), 6.91 (d, 0.46 × 1H, J = 15.2 Hz), 6.75 (d, 0.46 × 1H, J = 15.3 Hz), 6.61 (d, 0.51 × 1H, = 10.8 Hz), 6.51 (d, 0.51 × 1H, J = 10.8 Hz). ^{13}C NMR (CDCl3, 75 MHz) δ 136.4, 135.1, 131.7, 129.9, 129.7, 129.0, 128.6, 128.2, 127.5, 127.1, 127.0,126.8, 125.9, 123.3.

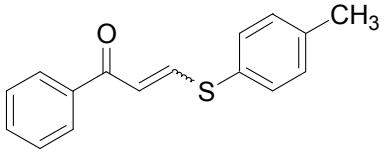
1-{2-(*Z*-4-fluorophenyl) ethenyl]sulfanyl}-4-methoxy benzene[9] (23b)



Off white solid, *E:Z* ratio= 0:100. mp 68-71°C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54-7.50 (2H, m), 7.45-7.41 (2H, m), 7.12-7.07 (2H, m), 6.93 (2H, d, J = 8.75 Hz), 6.49 (1H, d, J = 10.7 Hz),

6.41 (1H, d, J = 10.7 Hz), 3.84 (3H, s). ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 163.5, 160.3, 159.9, 133.3, 130.6, 128.3, 126.8, 125.0, 115.7, 115.4, 55.7.

3-[(4-methylphenyl) sulfanyl]-1-phenylprop-2-en-1-one[10-11] (**24b**)



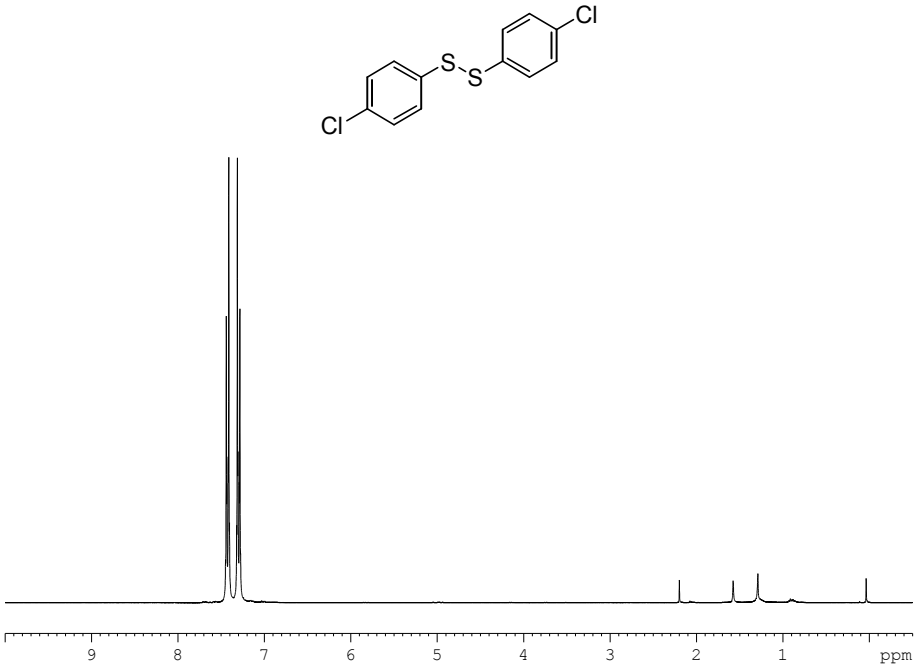
Yellow viscous oil, *E:Z* ratio= 15:85. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04-8.00 (2H, m), 7.86-7.83 (d, 0.2X 1H, J = 8.66 Hz), 7.58-7.42 (m, 6H), 7.28-7.20 (2H, m), 7.16 (1H, d, J = 9.66 Hz), 6.84 (0.09 X 1H, d, J = 14.86 Hz), 2.39 (3H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz); δ 189.4, 153.3, 149.9, 138.9, 138.2, 132.9, 131.4, 130.5, 129.0, 128.4, 116.5 and 30.1.

[8] R. Sarma, N. Rajesh, D. Prajapati, *Chem. Commun*. **2012**, *48*, 4014–4016.

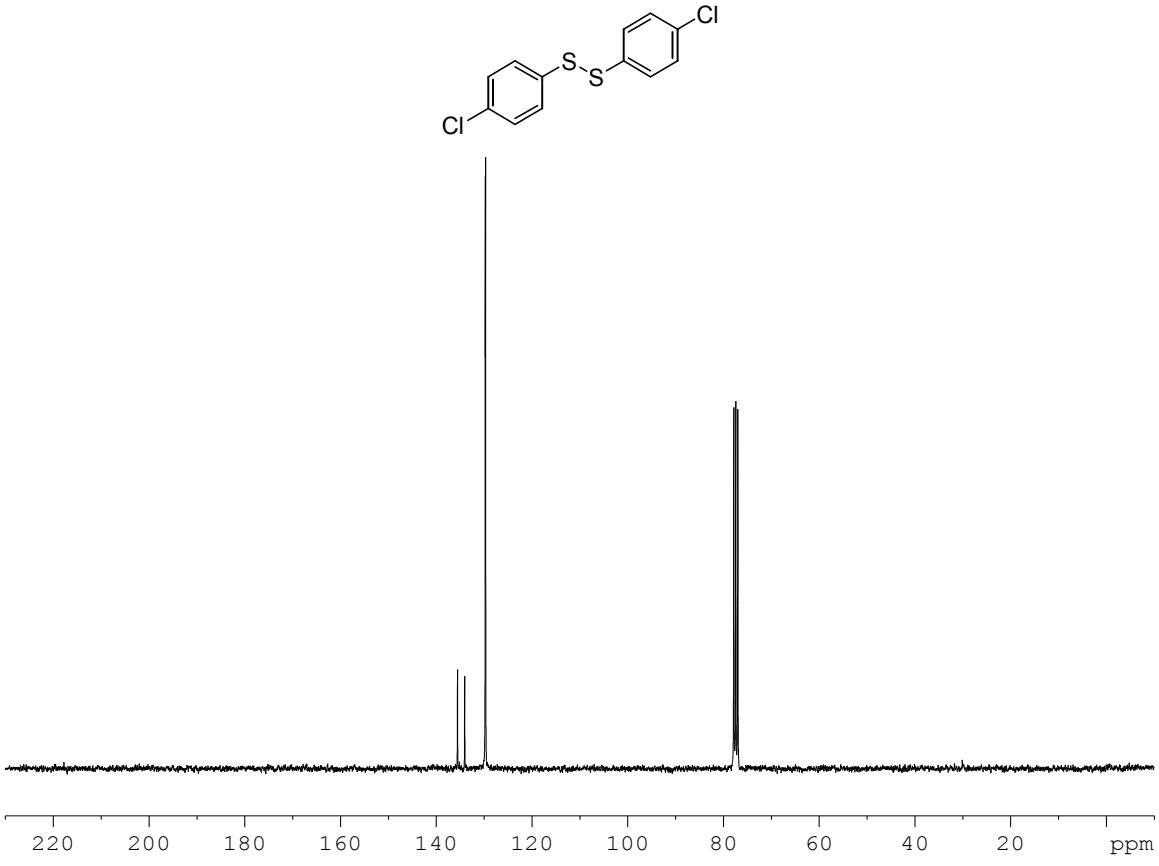
[9] R. Singh, D.S. Raghuvanshi, K. N. Singh. *Org. Lett.*, **2013**, *15*, 4202–4205.

NMR Spectra's of some representative Disulfides

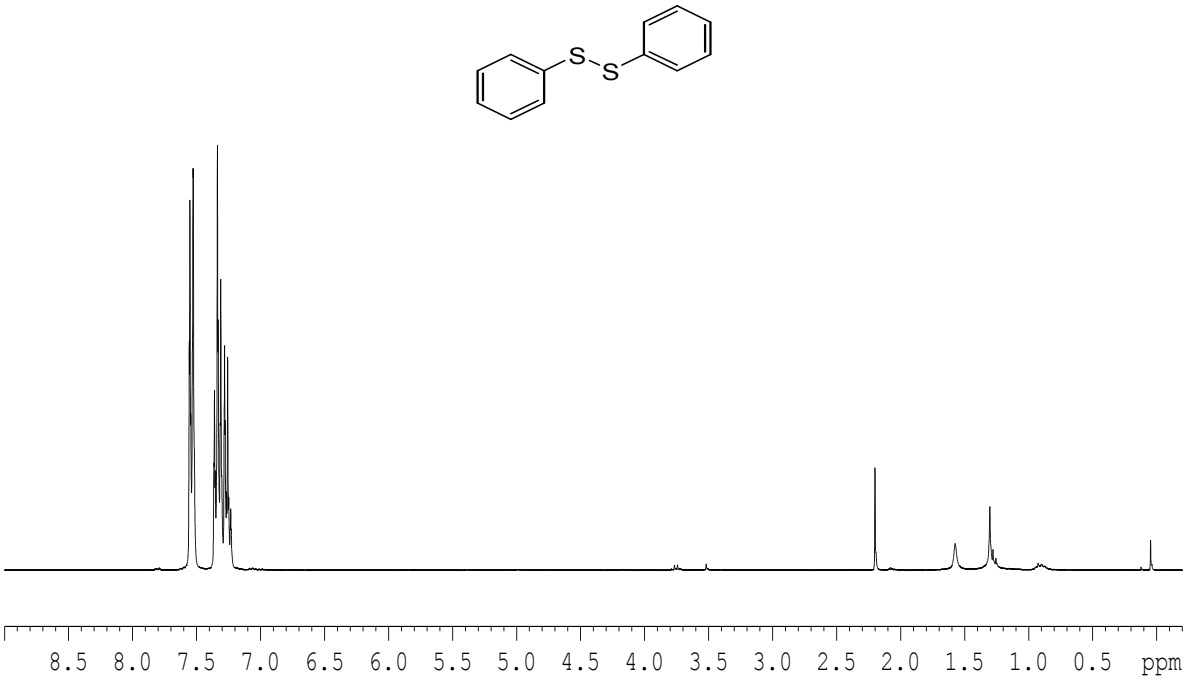
^{1}H NMR (in $CDCl_3$) 1b



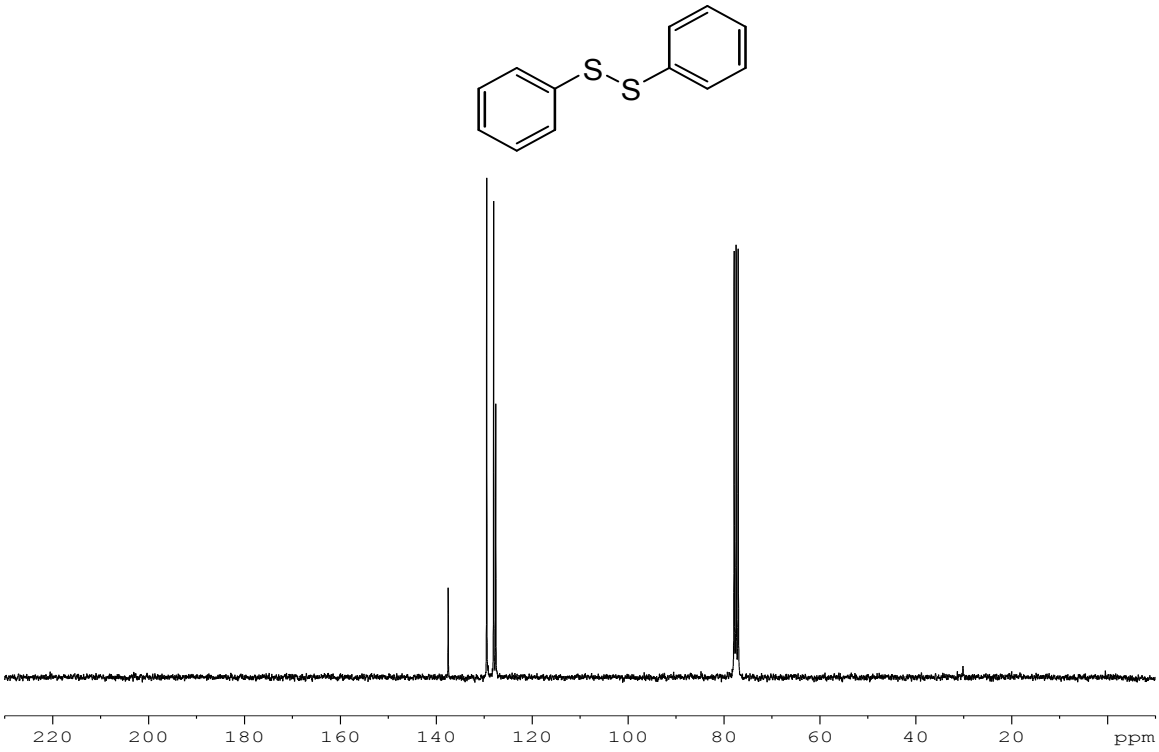
^{13}C NMR (in $CDCl_3$)



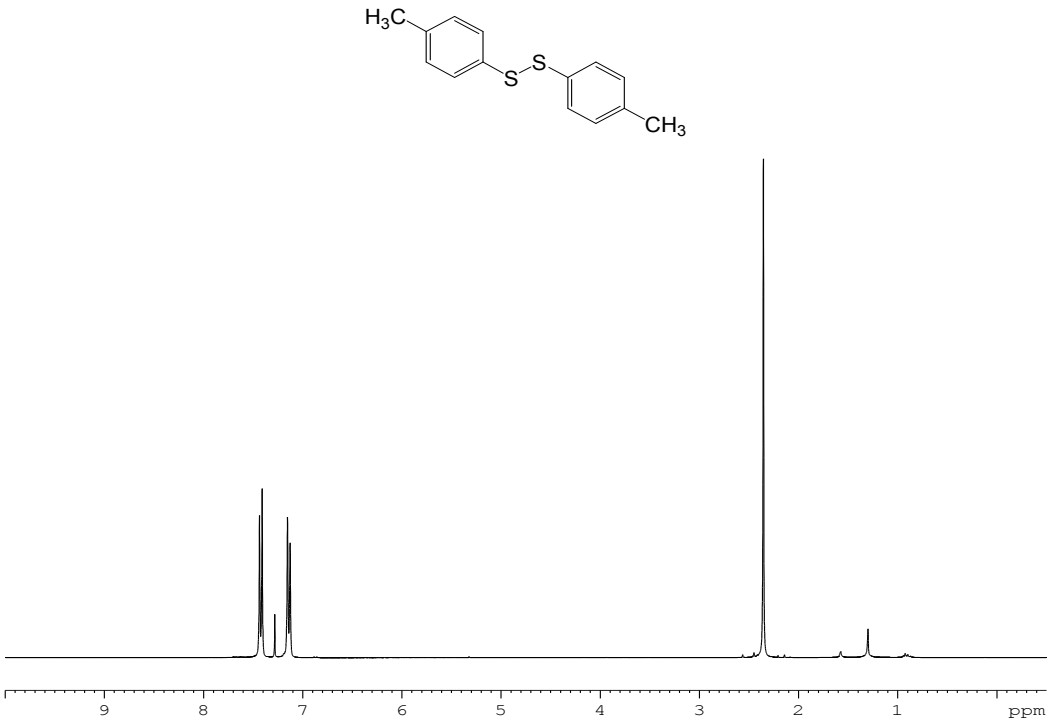
^{1}H NMR (in $CDCl_3$) 2b



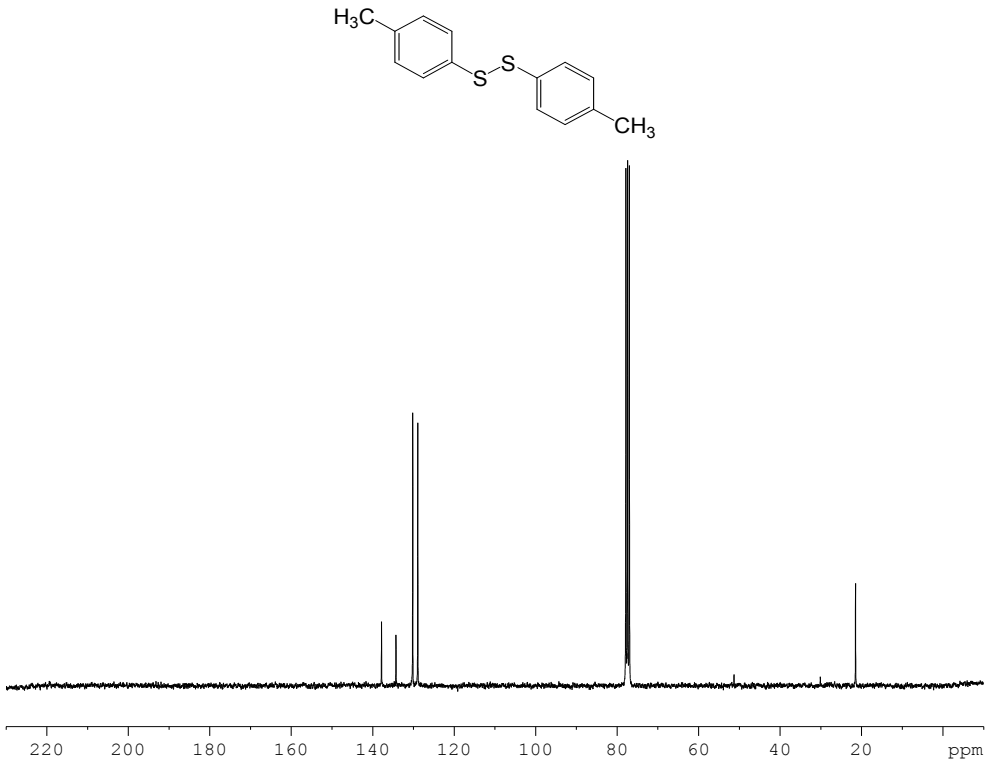
^{13}C NMR (in $CDCl_3$) 2b



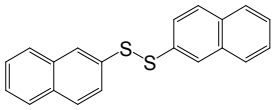
^{1}H NMR (in $CDCl_3$) 5b

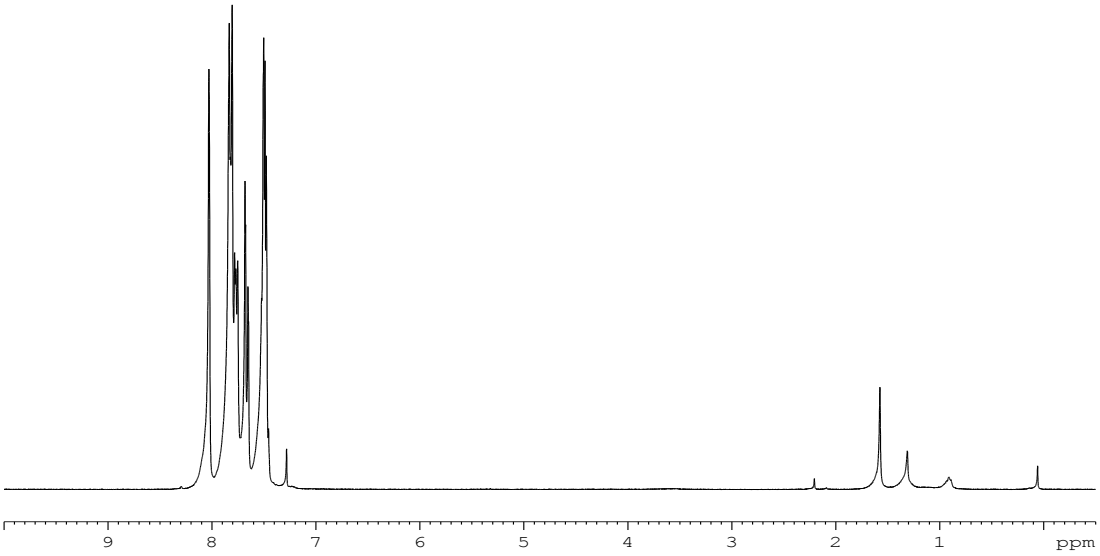


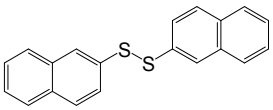
^{13}C NMR (in $CDCl_3$) 5b



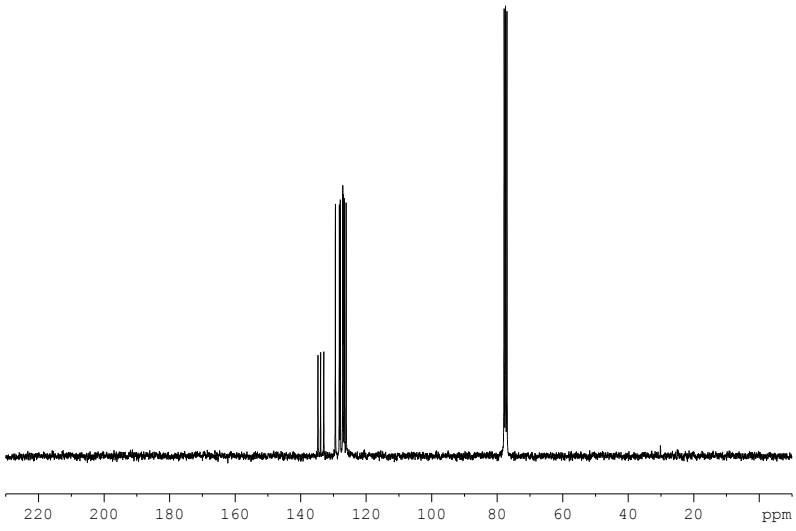
^{1}H NMR (in $CDCl_3$) 9b



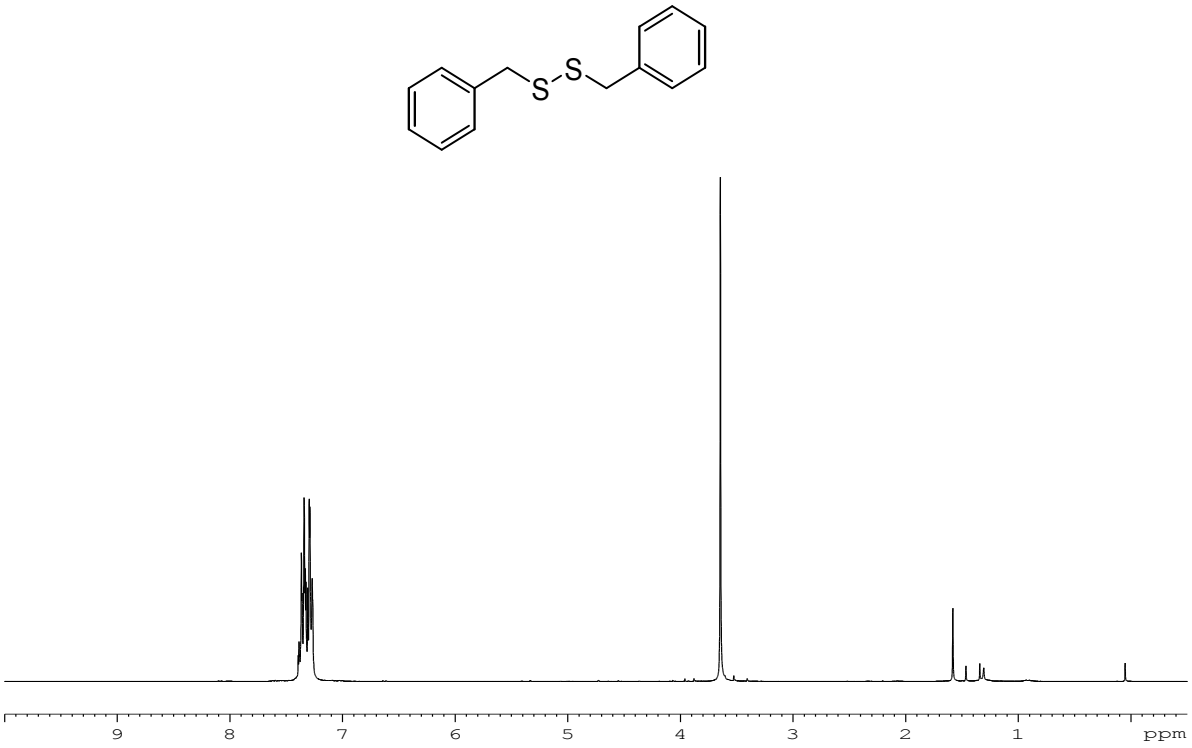




^{13}C NMR (in $CDCl_3$)

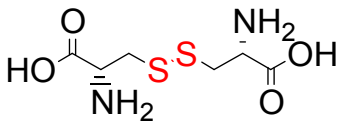


^{1}H NMR (in $CDCl_3$) 11b

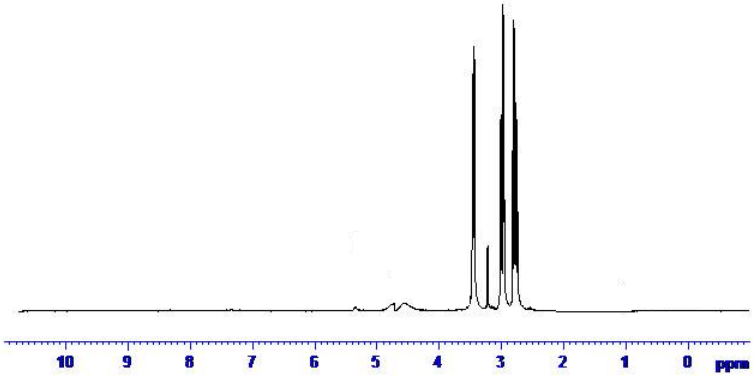


^{13}C NMR (in $CDCl_3$)

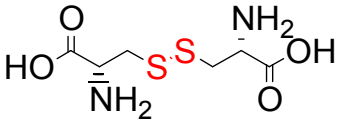
L-Cystine[6] (18b)



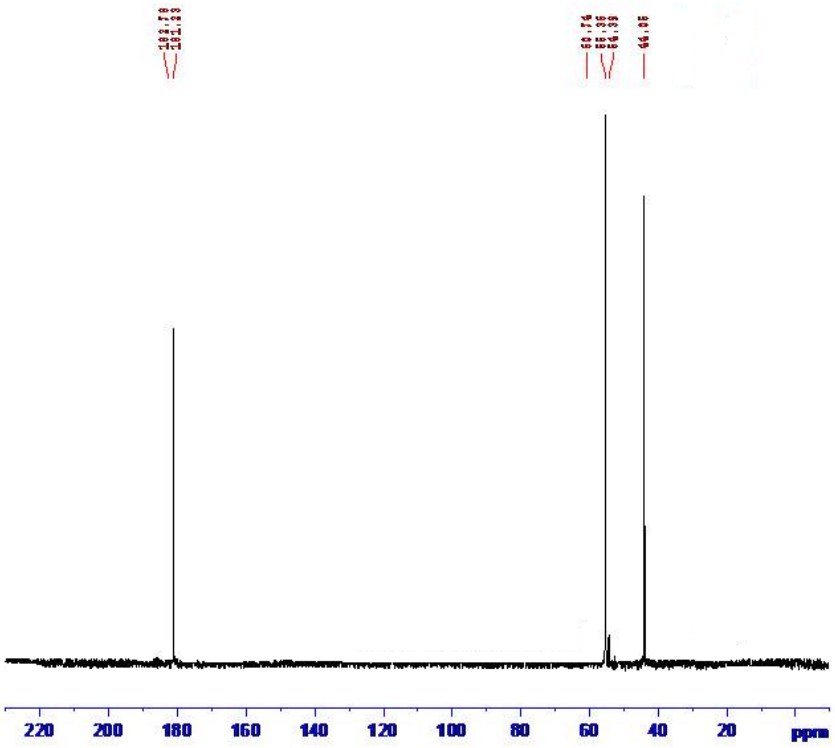
^{1}HNMR (4% NaOD in D_2O, 300Mhz)



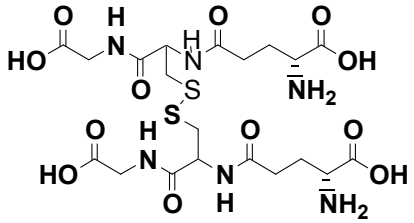
L-Cystine[6] (18b)



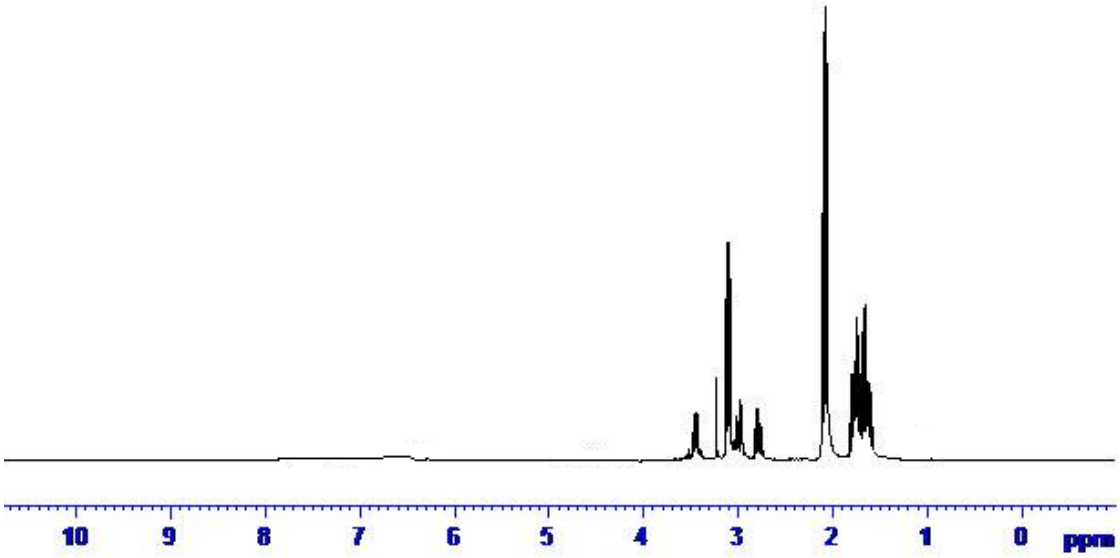
^{13}CNMR (4% NaOD in D_2O, 75.4 MHz)



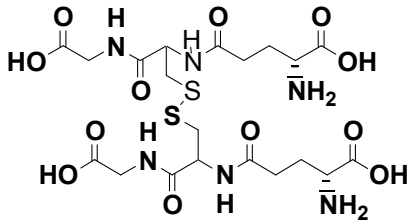
Glutathione disulfide[6] (19b)



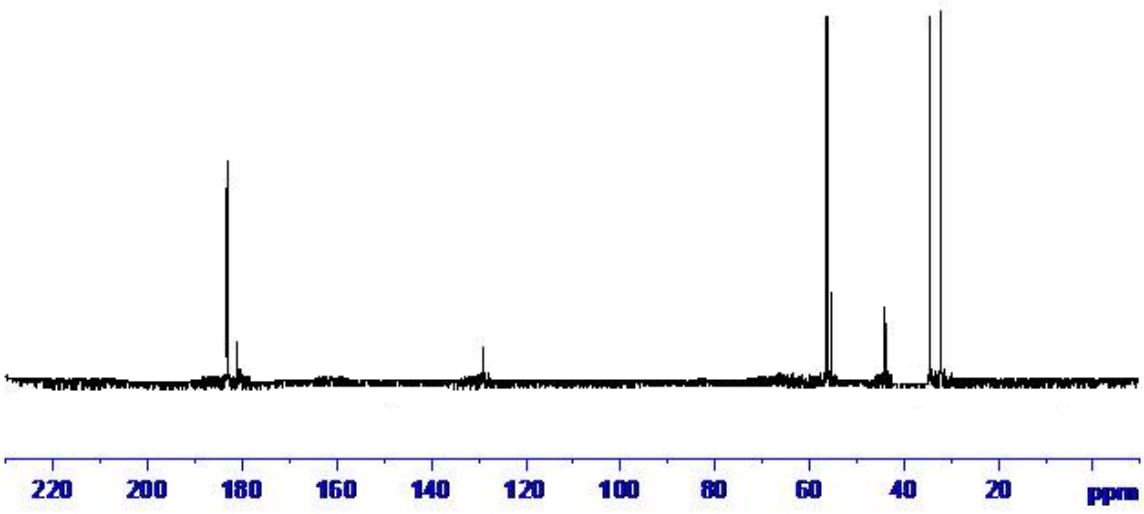
^{1}HNMR (4% NaOD in D_2O, 300Mhz)



Glutathione disulfide[6] (19b)

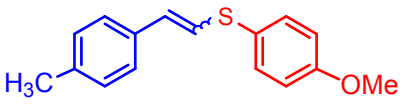


^{13}CNMR (4% NaOD in D_2O, 75.4MHz)

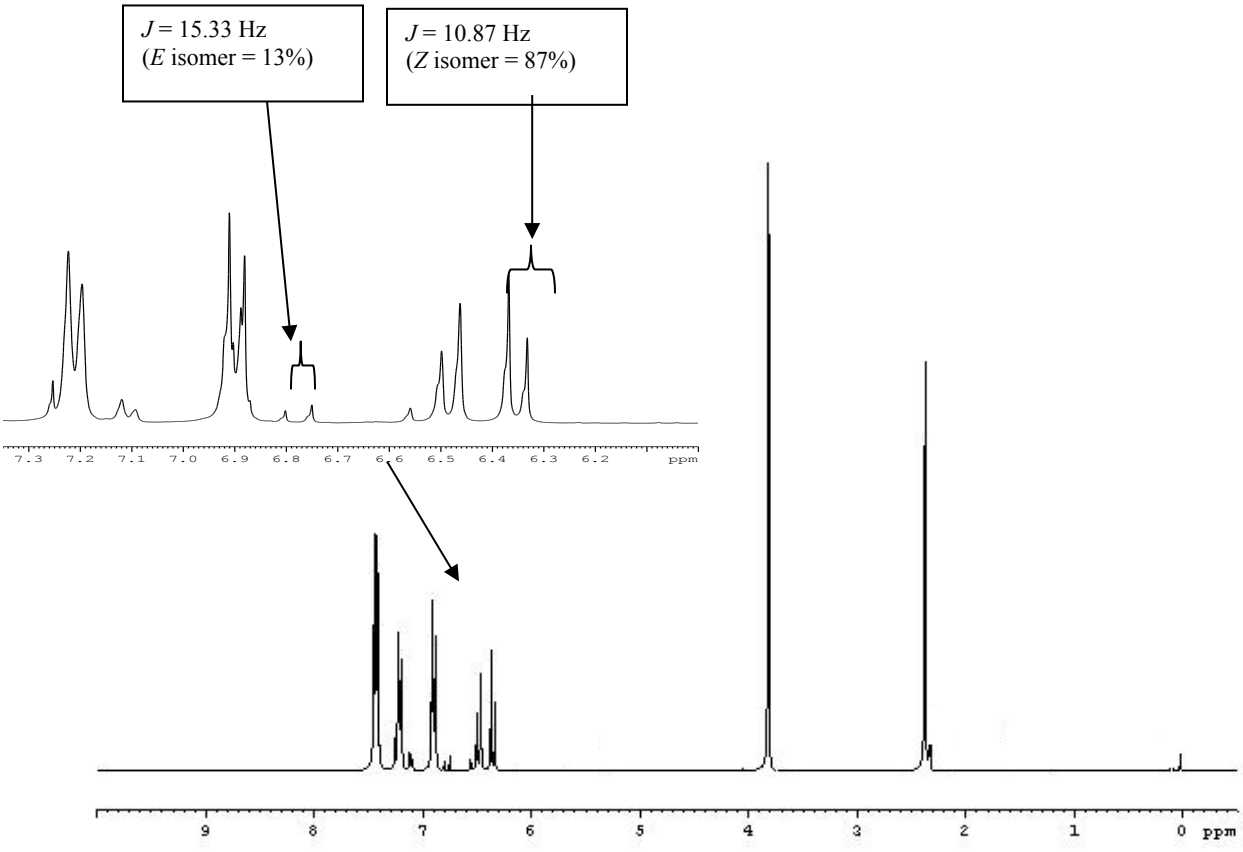


NMR Spectra's of Vinyl Sulfides

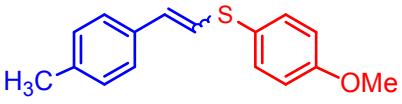
1-methoxy-4-{[(*E*)-2-(4-methyl phenyl)ethenyl] sulfanyl benzene (20b)



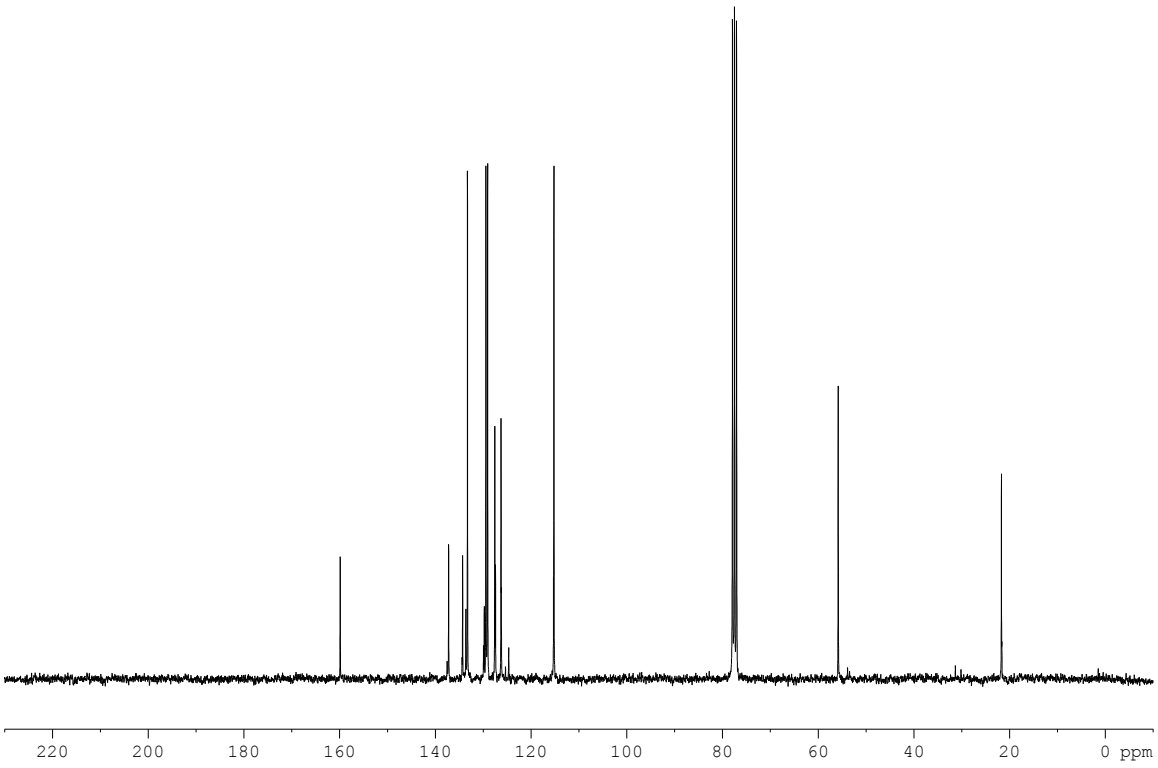
^{1}H NMR ($CDCl_3$, 300 MHz)



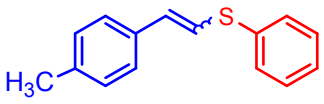
1-methoxy-4-{[2-(4-methyl phenyl)ethenyl] sulfanyl benzene (20b)



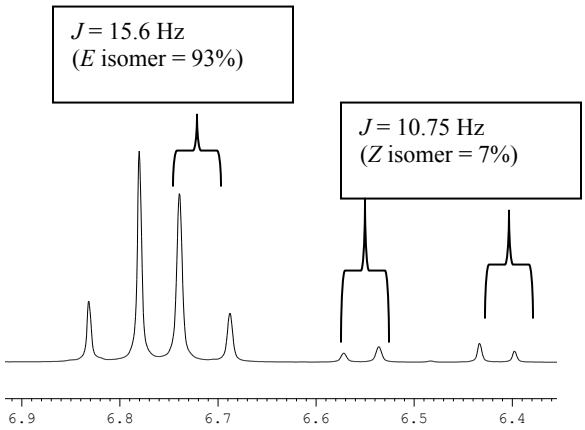
^{13}C NMR ($CDCl_3$, 75.4 MHz)

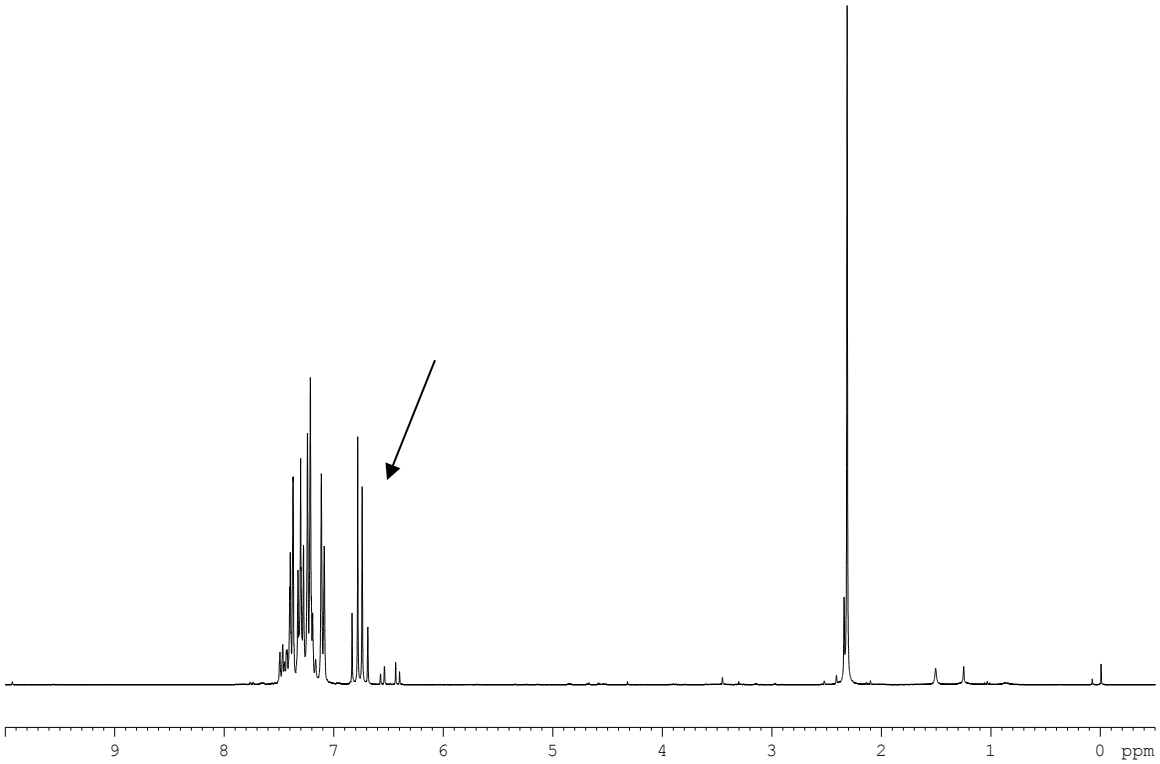


1-methyl-4-[2-(phenyl sulfanyl)ethenyl] benzene (21b)

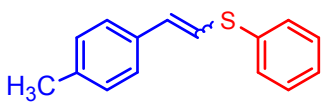


^{1}H NMR ($CDCl_3$, 300 MHz)

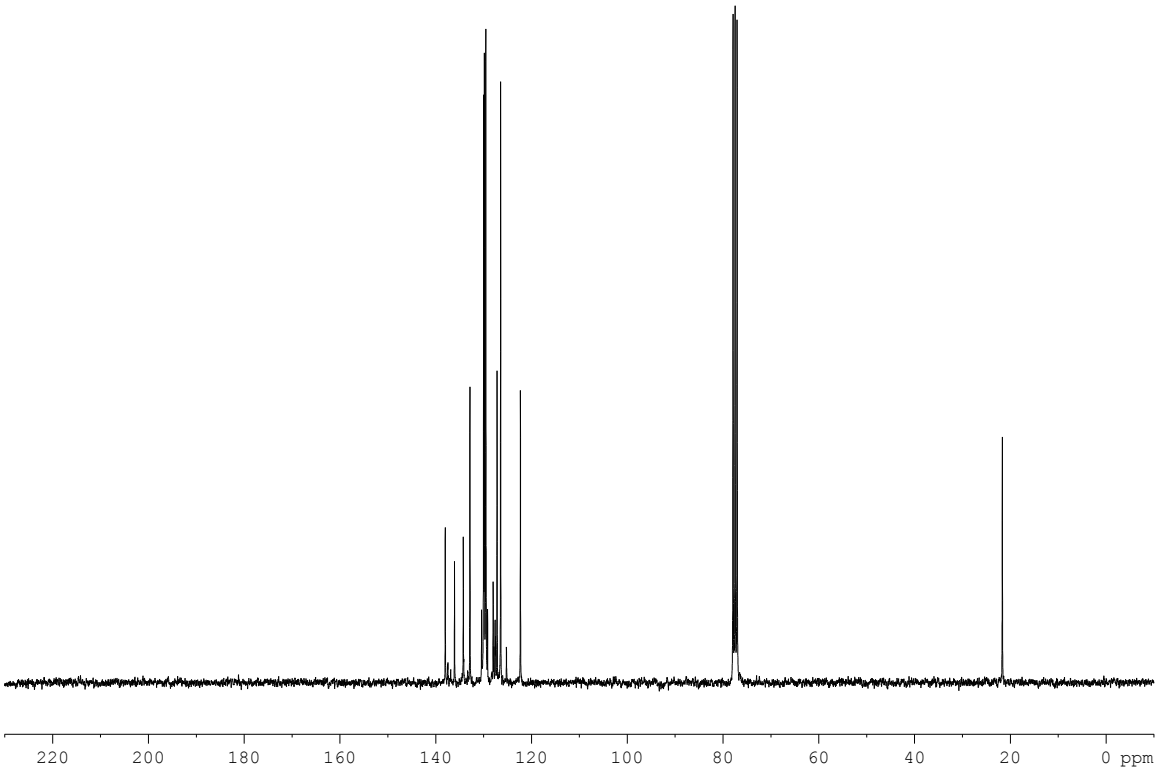




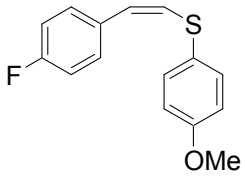
1-methyl-4-[2-(phenyl sulfanyl)ethenyl] benzene (21b)



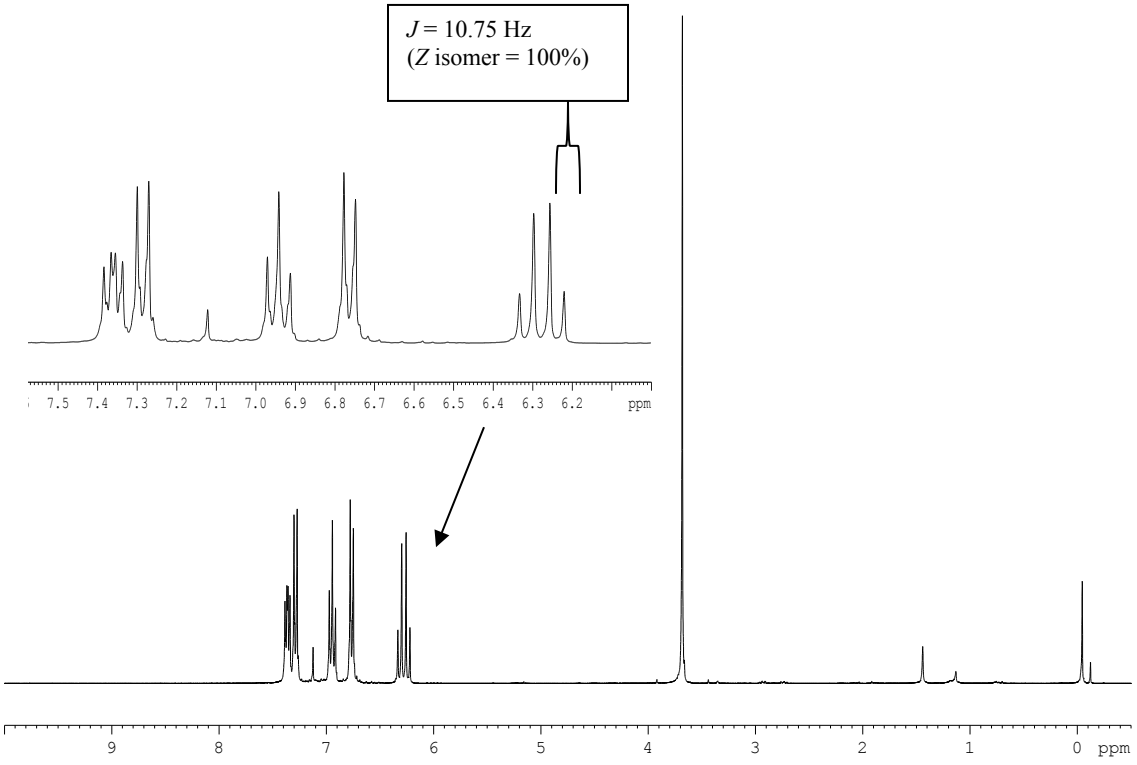
^{13}C NMR ($CDCl_3$, 300 MHz)



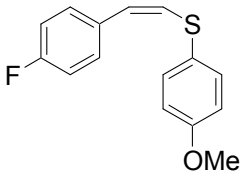
1-{[(*Z*)-2-(4-fluorophenyl) ethenyl]sulfanyl}-4-methoxy benzene (23b)



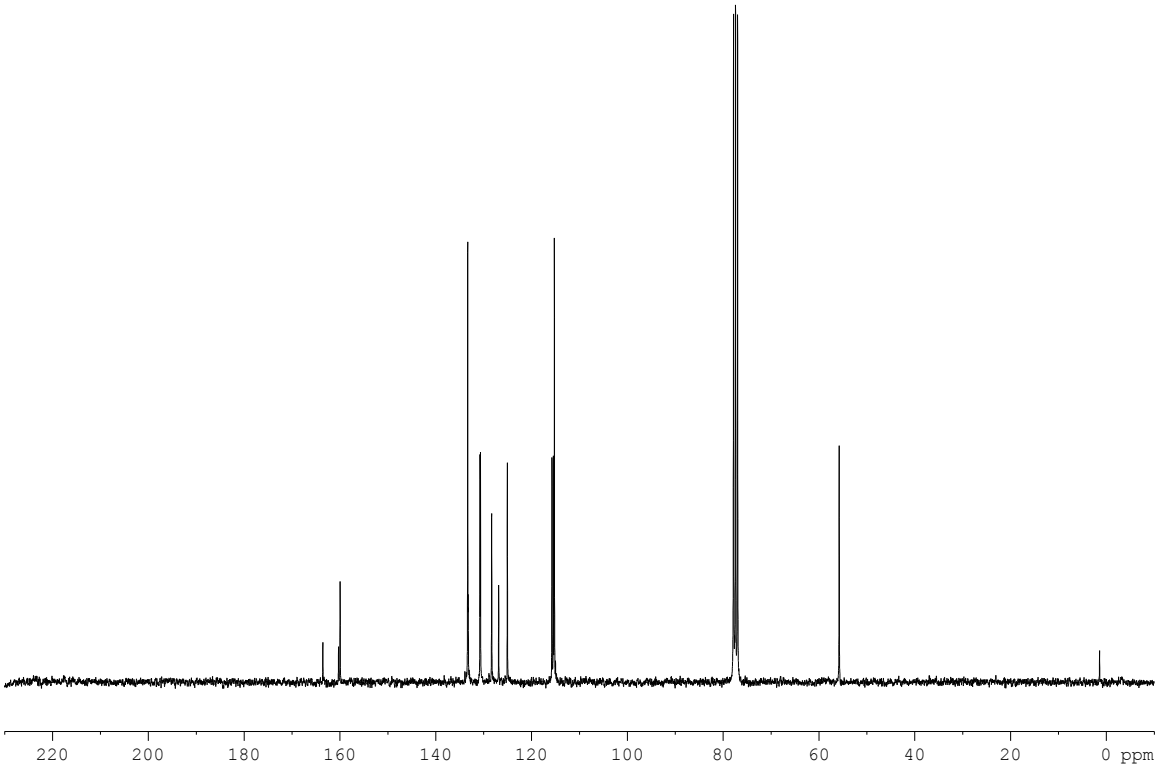
^{1}H NMR ($CDCl_3$, 300 MHz)


J = 10.75 Hz
(Z isomer = 100%)
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 ppm
9 8 7 6 5 4 3 2 1 0 ppm

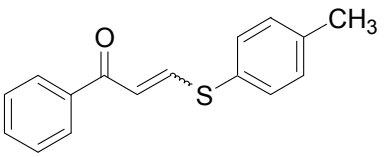
1-{[(*Z*)-2-(4-fluorophenyl) ethenyl]sulfanyl}-4-methoxy benzene (23b)



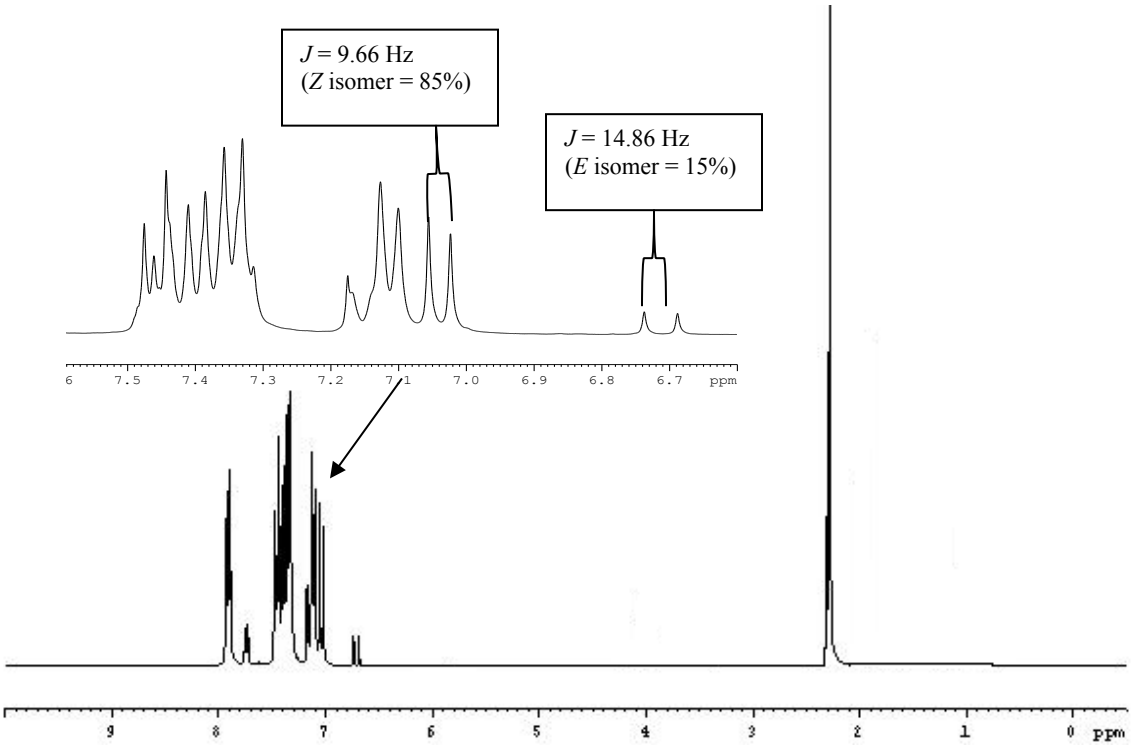
^{13}C NMR ($CDCl_3$, 75.4 MHz)



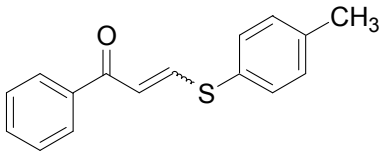
3-[(4-methylphenyl) sulfanyl]-1-phenylprop-2-en-1-one (24b)



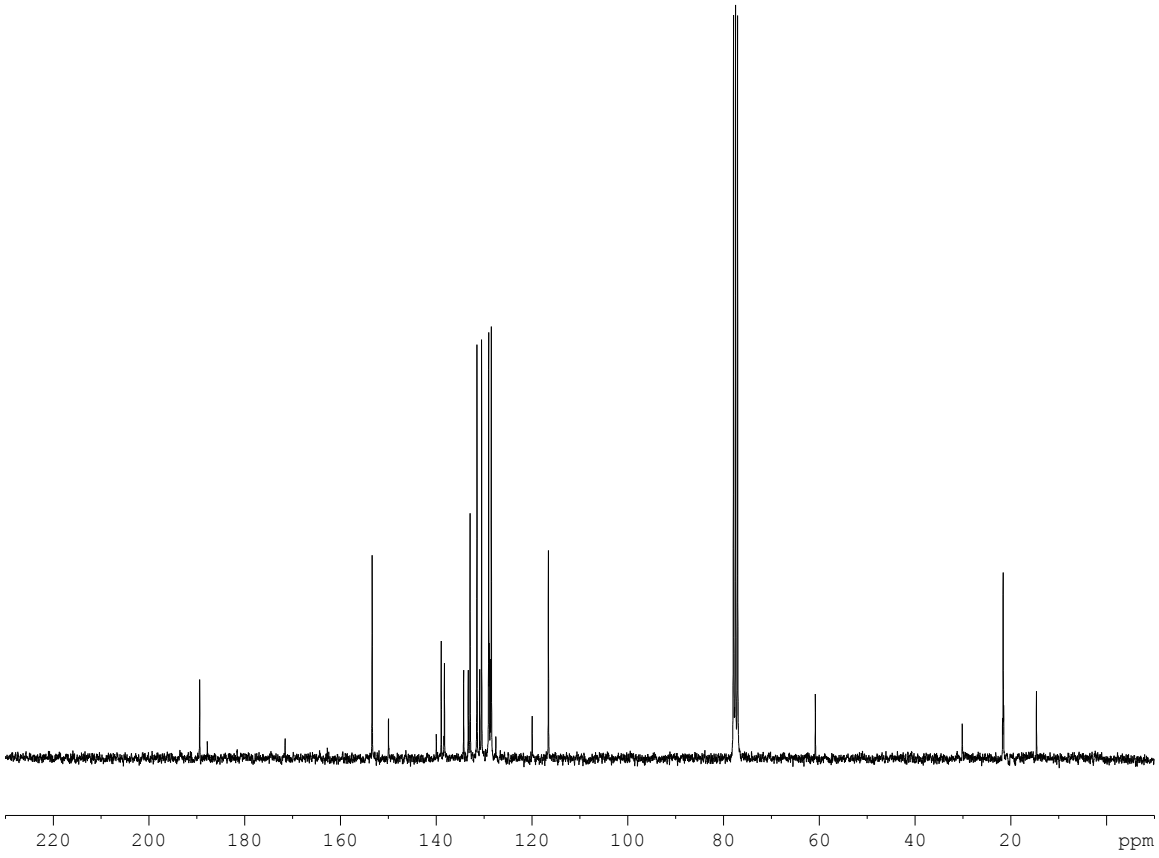
^{1}H NMR ($CDCl_3$, 300 MHz)



3-[(4-methylphenyl) sulfanyl]-1-phenylprop-2-en-1-one (24b)



^{13}C NMR ($CDCl_3$, 75.4 MHz)



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[11] T. Nishio , Y. Omote. *J. Chem. Soc., Perkin Trans. 1: Org. and Bio-Organic Chemistry* **1981**, *1972-1999*, 934-938.