SUPPORTING INFORMATION

High surface and magnetically recoverable mPANI/pFe_3O_4 nanocomposites for C-S bond formation in water

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General Information:

All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. Purification of products was carried out by column chromatography using commercial column chromatography grade silica gel (60-120 mesh) purchased from s. d. fine-chemicals Ltd. using mixture of ethyl acetate and hexane as eluting agent. All known compounds were characterized and compared with the literature reports. Visualization was accomplished with UV lamp.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-Avance (300 MHz), Varian-Gemini (200 MHz) and Varian-Inova (500 MHz) spectrophotometer, in $CDCl_3$ using TMS as the internal standard, Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. All the chemicals were purchased from Sigma Aldrich, USA. and used without further purification. ^{1}H NMR and ^{13}C NMR of the compounds were proved either by comparison to the known compounds or the synthesized compounds according to the literature.[1-5] General Information: ACME SILICA GEL (100-200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F254 plates.

Procedure for the synthesis of mPANI/pFe_3O_4

[A] Synthesis and chemical modification of porous Fe_3O_4 nanoparticles

The magnetic Fe_3O_4 particles were prepared through a solvothermal reaction. $FeCl_3 \cdot 6H_2O$ (1.35 g) and sodium acetate (3.6 g) were dissolved in ethylene glycol (40 mL) under stirring condition. The homogeneous yellow solution was obtained and then transferred to a teflon-lined stainless-steel autoclave and sealed to heat at 200 °C. After 8 h, the autoclave was cooled to room temperature. The obtained black magnetite particles were washed with ethanol several times and then dried in vacuum at 60 °C for 12 h. Subsequently, the Fe_3O_4 particles were chemically modified by using APTMS. Typically, porous Fe_3O_4 particles (0.1 g) and APTMS (2 mL) were dissolved in anhydrous ethanol (50 mL). The mixture was refluxed for 12 h under dry nitrogen. The resulting modified porous Fe_3O_4 particles were

separated with the help of an external magnet and then washed with ethanol. Finally, the product was dried in vacuum at 60 °C for 24 h to obtain the amine functionalized Fe_3O_4 particles (NH_2-Fe_3O_4).

[B] Synthesis of porous mPANI/pFe_3O_4 nanocomposites

The bifunctional mPANI/pFe_3O_4 nanocomposite was prepared by an in situ surface polymerization method in the presence of PVP and SDBS. In a typical procedure, PVP (0.05 g) and SDBS (0.01 g) were dissolved in 130 mL of deionized water, and then the NH_2-Fe_3O_4 particles (0.015 g) were added. The mixture was then ultrasonically dispersed, and a solution of aniline (20 μL) in HCl (0.1 mL) was added into the mixture under vigorous stirring. Afterwards, the mixture was mechanically stirred for 30 min at 20 °C. Then an aqueous solution (20 mL) of APS (0.2 g) was added into the above mixture instantly to start the oxidative polymerization. The polymerization was performed under mechanical stirring for 5 h (stirring speed 2000 rotation per minute (rpm)). The resulting precipitates were washed with deionized water and ethanol several times. Finally, the solid was dried in vacuum at 60 °C for 24 h to obtain of the desired mPANI/pFe_3O_4 composite as a dark powder.

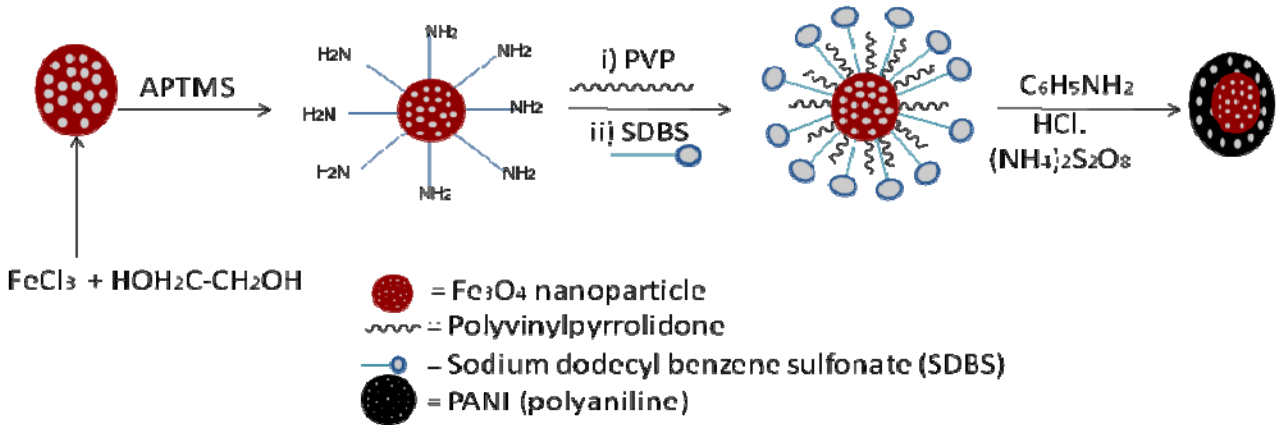


Figure 1. Step-wise preparation of the porous Fe_3O_4 nanoparticles@mesoporous PANI core-shell nanocomposites

XRD analysis:

X-ray diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} torr. The XRD patterns of magnetic Fe_3O_4 nanoparticles reveal that the crystal structure is indexed as face centered cubic (fcc) (JCPDS card No. 19-629).

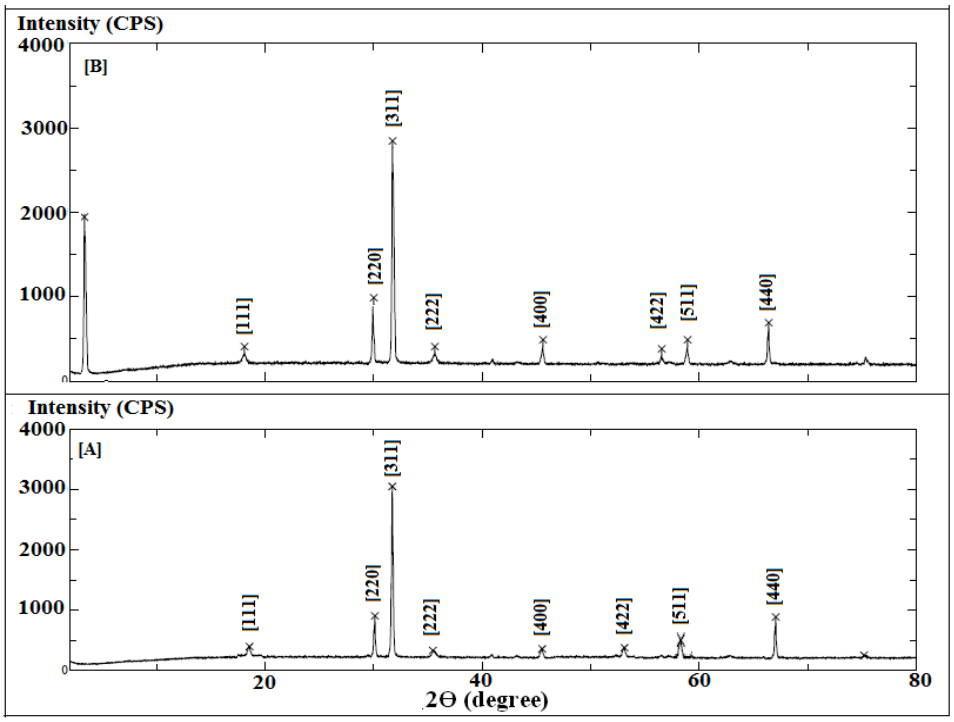


Figure 2. XRD pictures of [A] Fe_3O_4 nanoparticles, and [B] Fe_3O_4 @ mesoporous PANI.

No other characteristic peaks due to the impurities of hematite or hydroxides were detected (Fig 1). It is found that the strong diffraction peaks situated at 2Θ of 18.9^0, 30.22^0, 32.53^0, 43.24^0, 53.97^0, 57.44^0, and 67.94^0, corresponding to the diffractions of [111], [220], [311], [400], [422], [511], and [440] crystal faces of porous Fe_3O_4 structures.

FT-IR analysis:

FT-IR spectra of these samples were recorded on KBr pellets by using a Nicolet NEXUS-FT IR 670 spectrometer (Nicolet Corporation Ltd. USA).

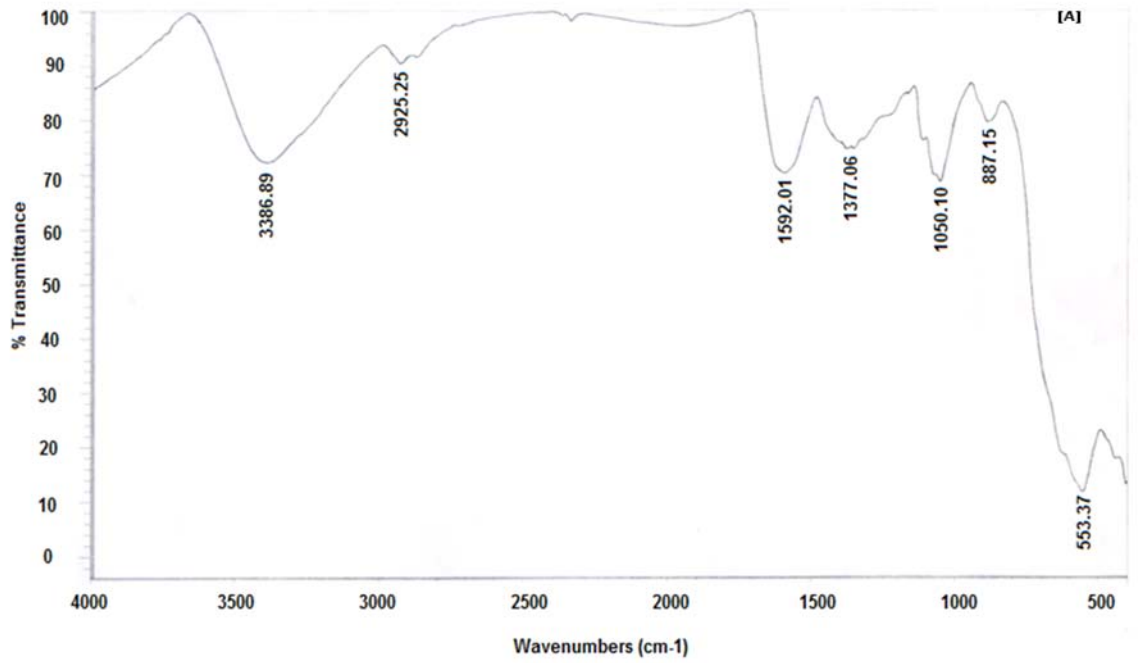


Figure 3. FTIR spectrum of polyaniline

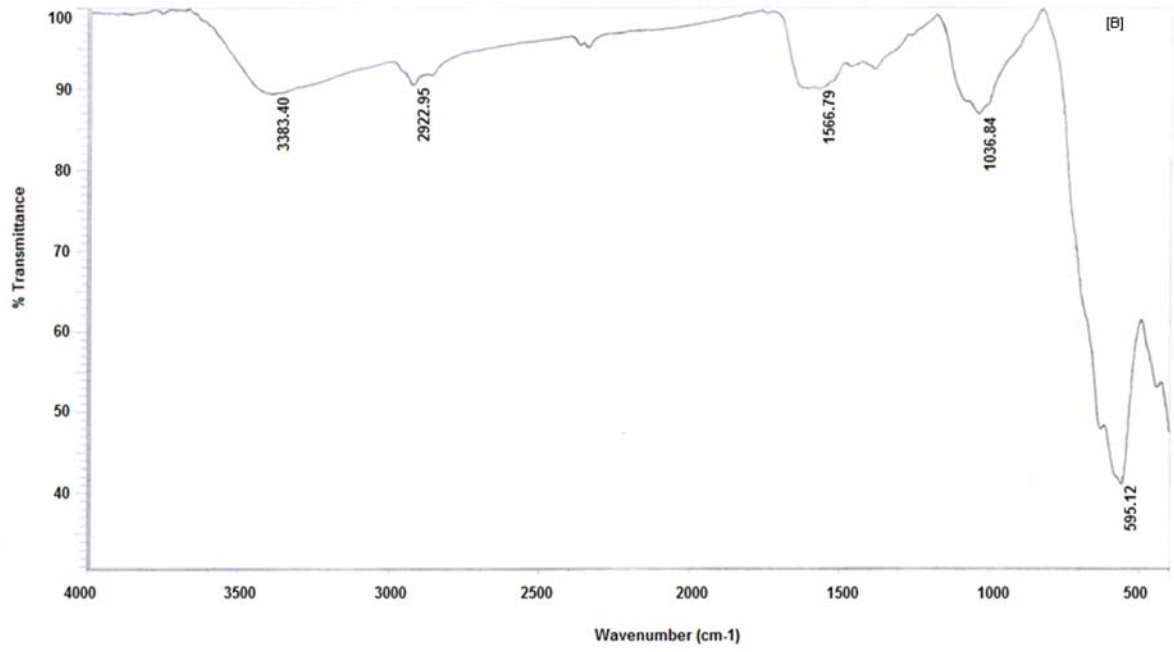


Figure 3. FTIR spectrum of Fe_3O_4 nanoparticles

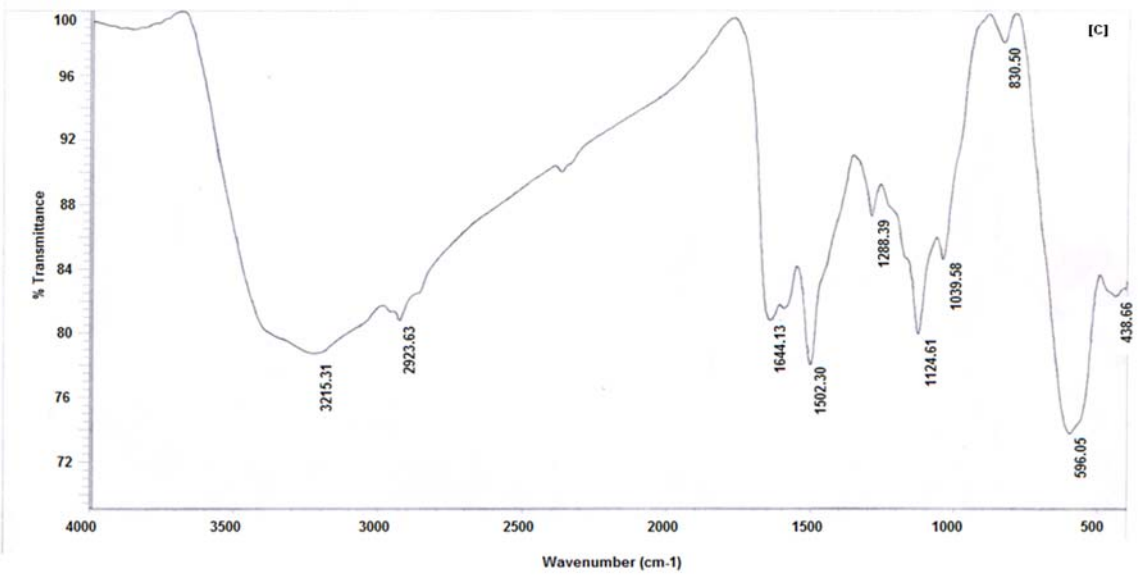
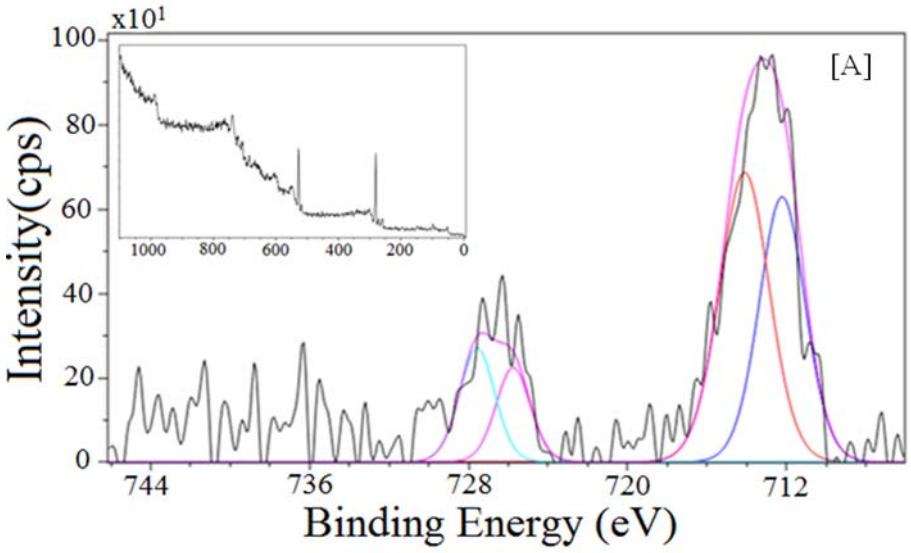


Figure 3. FTIR spectrum of mPANI/pFe_3O_4

XPS analysis:

The XPS of the fresh pFe_3O_4@*m*PANI nano composites are shown in Figure 4. [A]. The XPS of C_{1s}, O_{2p}, N_{1s} and Fe_{2p} level give a proof for approximate chemical structure of mPANI coated pFe_3O_4 nanocomposites. Peaks at 284, 398, 538 eV were ascribed to the carbon, nitrogen and oxygen in polyaniline. The binding energies at 712 and 725 eV the characteristic peaks from $Fe_{2p3/2}$ and $Fe_{2p1/2}$ core level electron.



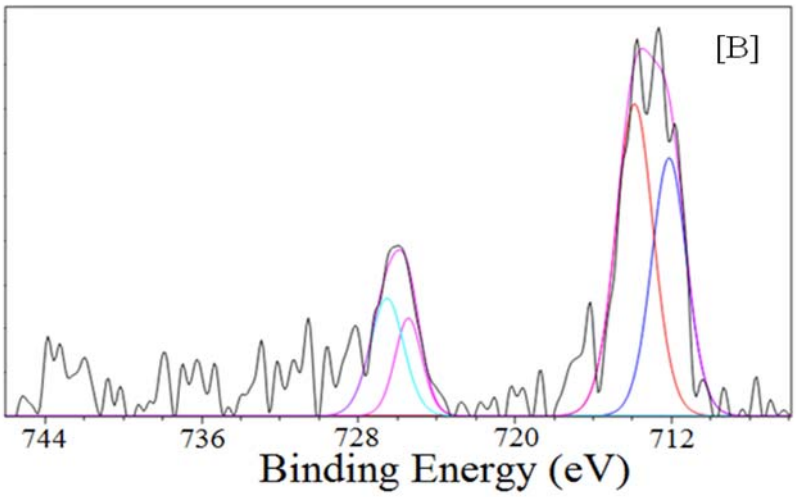


Figure 4. [A] XPS spectrum of the as-synthesized magnetite mPANI/ pFe_3O_4 nano composite. [B] XPS spectrum of the reused mPANI/ pFe_3O_4 nano composite after 5th cycle.

The binding energies for Fe_3O_4 of fresh mPANI/pFe_3O_4 nanocomposites (Figure 4. [A]) and reused mPANI/pFe_3O_4 nanocomposites (Figure 4. [B]) are in good agreement with the values reported for Fe_3O_4 in the literature.[7] indicates that there is no chemical change occurred in $Fe_{2p3/2}$ and $Fe_{2p1/2}$ core level.

TEM analysis:

The TEM image of a Fe_3O_4 [A-C], Fe_3O_4@PVP+SDBS [D-F] and Fe_3O_4@mPANI[G-I] sample synthesized are shown in Figure 5, respectively. The image confirms the formation of low electron density spherical white spots of ~2.0 and ~6.0 nm sizes, corresponding to small to medium size mesopores formation in the bare Fe_3O_4 nanoparticles and mPANI/pFe_3O_4 microspheres. The presence of the pores for both the samples were further confirmed through N_2 adsorption-desorption experiments. Thus from the XRD patterns and the TEM image analysis, we could conclude porous Fe_3O_4 /mPANI nano composite microspheres.

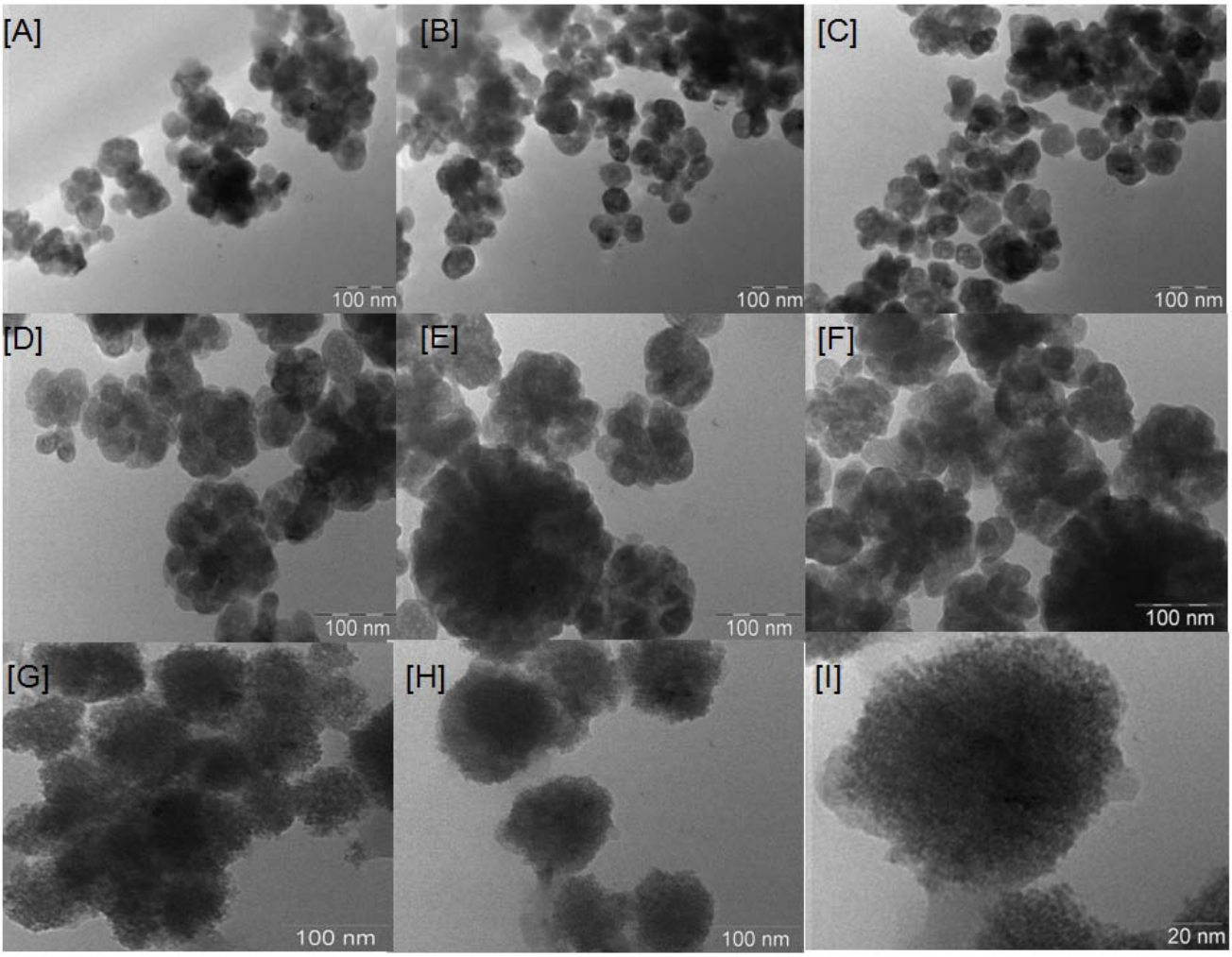


Figure 5. TEM images of bare porous Fe_3O_4 nanoparticles [A-C], Fe_3O_4@PVP+SDBS [D-F] and mPANI/p Fe_3O_4 [G-I].

SEM:

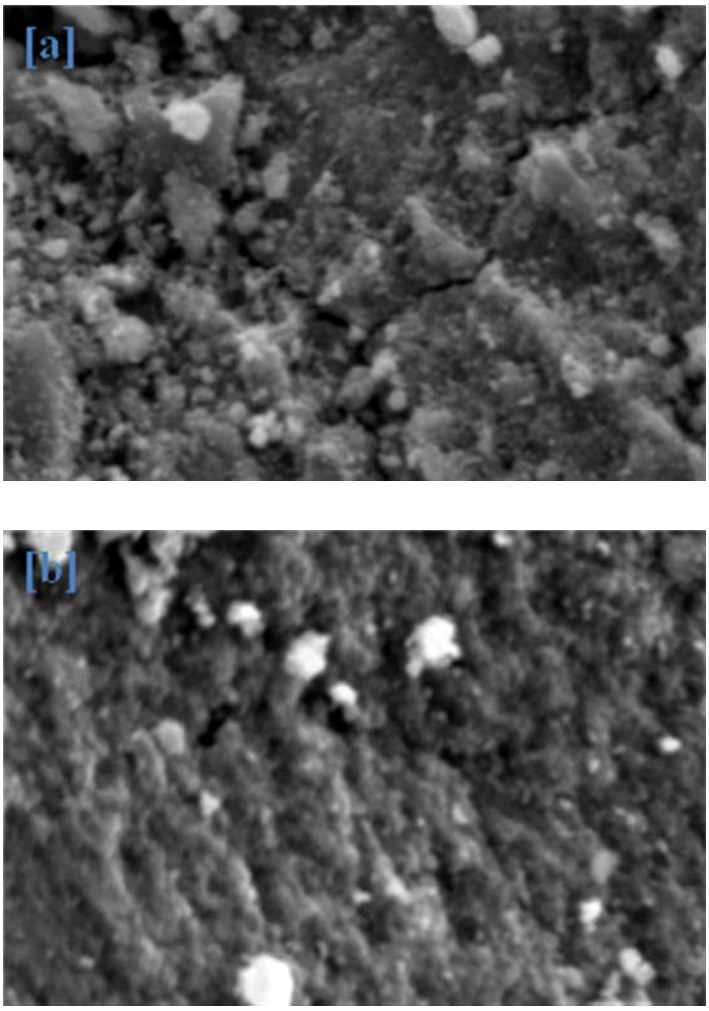


Figure 6. [a] SEM images of the as- prepared magnetite mPANI/pFe_3O_4 nanocomposite. [b] and the mPANI/pFe_3O_4 nanocomposite after 5th cycle.

From the images of Scanning Electron Microscopy of freshly synthesized mPANI/pFe_3O_4 and recycled nano composite after its 5th cycle, we observed that there is no change in morphology of the catalyst before the reaction and after its successive cycles.

[A] General procedure for the synthesis of unsymmetrical diaryl sulfides:

To develop new synthetic methods with inexpensive and efficient heterogeneous catalysts we have recently developed high surface mesoporous polyaniline/porous magnetic Fe_3O_4, mPANI/pFe_3O_4 nanocomposite for the *O*- arylation reaction of aryl chlorides with phenols.[6] In continuation of our work, herein we report C-S cross coupling using mPANI/pFe_3O_4 as a catalyst. The catalyst was used for the S- arylation of thiolphenol with deactivated aryl chlorides also examined for the synthesis of

symmetrical diaryl sulfides from the reaction of aryl iodides with thiourea under mild reaction condition using water as green solvent.

The reaction vessel was charged with aryl chloride (1.0 mmol), thiophenol (1.0 mmol), KOH (1.5 mmol) and the catalyst (mPANI/pFe_3O_4) (25 mg, 5 mol %) in water (3 mL). The reaction mixture was then stirred for 8h at reflux temperature. The progress of the reaction was monitored by TLC. At the end of the reaction, the reaction mixture was allowed to cool to room temperature. Then reaction mixture was treated with excess of cold water, organic phase was extracted by adding ethyl acetate and dried over anhydrous Na_2SO_4. The crude mixture was purified by chromatography on silica gel to afford the coupled product.

[B] General procedure for the synthesis of symmetrical diaryl sulfides:

A mixture of aryl iodide (1.0 mmol), thiourea (0.75 mmol), mPANI/pFe_3O_4 (25 mg, 6.6 mol %), and KOH (1.5 equiv.) was stirred at reflux temperature for 24h in water (3.0 mL) solvent. The progress of the reaction was monitored by TLC. When the reaction was complete, the reaction mixture was allowed to cool, a mixture of ethyl acetate and water (20 mL) were added and the catalyst was separated with the use of an external magnet. The organic solution was washed with brine water and dried with Na_2SO_4. The solvent and volatiles were completely removed under vacuum to give the crude product, which was purified by column chromatography on silica gel to obtain the desired symmetrical diaryl sulfide.

Reusability Study:

For any heterogeneous system, it is important to know its ease of separation and possible reuse. The mPANI/pFe_3O_4 catalyst can easily be separated by an external magnet. The recovered catalyst, after washing with ethyl acetate and acetone followed by drying at 65° C, was used in the next run and consistent activity was observed (for e.g Table 1, entry 1, 1st cycle 88%, 5^{th} cycle 86%). Next to see whether the reaction was occurring mainly due to leached metal or the supported catalyst, a reaction between 4-nitro chlorobenzene and thiophenol was terminated after 20% conversion (80 min) and the

catalyst was separated using an external magnet and the reaction was continued with the filtrate for 12 hours. No change in the conversion of 4-nitro chlorobenzene was observed. These studies clearly prove that the *S*- arylation reaction occurs only heterogeneously.

Table 1. Reusability study of mPANI/pFe_3O_4 catalyst in the *S*-arylation of 4-nitro chlorobenzene with thiophenol [A][a] and in synthesis symmetric diaryl sulfide from thiourea and 4-methoxy iodobenzene [B].[b]

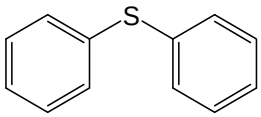
S-arylation	No. of cycles	Fresh	Run 1	Run 2	Run 3	Run 4	Run 5
[A]	Yield [%][c]	88	88	86	87	86	86
[B]	Yield [%][c]	92	90	90	88	85	87

[a] Reaction conditions: 4-nitro chlorobenzene (1.0 mmol), thiophenol (1.0 mmol), catalyst (25 mg, 5 mol%), KOH (1.5 equiv.), water (3.0 mL), reflux temperature for 8 h.

[b] Reaction conditions: 4-methoxy iodobenzene (1.0 mmol), thiourea (0.75 mmol), catalyst (25 mg, 6.6 mol%), KOH (1.5 equiv.) water (3.0 mL), reflux temperature for 24 h.

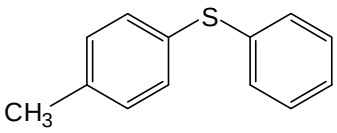
[c] Isolated yields of product.

Spectroscopic data of representative compounds:



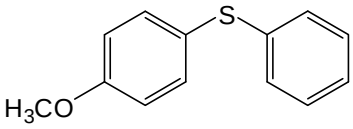
Diphenylsulfane: (Table 2 and 3, entries 1 and 3)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.47 – 7.16 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 137.06, 128.99, 127.50, 127.05. EI-MS (m/z) = 186.



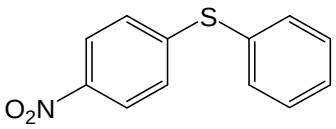
Phenyl(*p*-tolyl)sulfane: (Table 2, entry 2)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.33- 7.23 (m, 4H), 7.20 – 7.15 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 137.58, 137.03, 132.30, 131.30, 129.74, 129.01,126.41, 21.07. EI-MS (m/z) = 200.



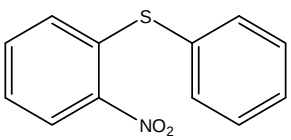
(4-Methoxyphenyl)(phenyl)sulfane: (Table 2, entry 3)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.37 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.10-7.05 (m, 3H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 159.8,138.53, 129.04, 128.04, 128.25, 125.80, 124.16, 114.9, 55.2. EI-MS (m/z) = 216.



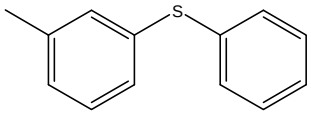
(4-Nitrophenyl)(phenyl)sulfane: (Table 2, entry 4)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.07 (d, *J* = 9.0 Hz, 2H), 7.60–7.36 (m, 5H), 7.18 – 7.14 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 149.2, 146.1, 136.3, 131.5, 130.1, 130.2, 128.2, 125.4. EI-MS (m/z) = 231.



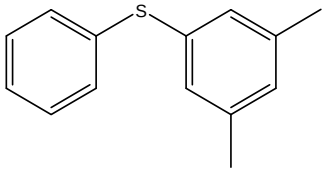
2- nitro diphenyl sulfane (Table 2, entry 5)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.42 (d, J = 7.5, 1H), 7.24-7.01 (m, 6H), 6.73 (d, J = 9.0, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 148.73, 137.49, 131.13, 129.12, 126.5, 125.5, 118.75, 115.38. EI-MS (m/z) = 231.27.



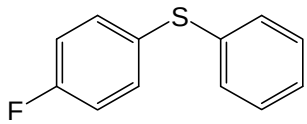
3-methyl diphenyl sulfane (Table 2, entry 6)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.34-7.23 (m, 4H), 7.22-7.10 (m, 4H), 7.02 (d, J = 7.25, 1H) 2.32 (S, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 138.95, 136.06, 135.16, 131.75, 129.03, 128.28, 127.94, 126.75, 21.23. EI-MS (m/z) = 200.



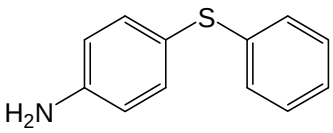
(3,5-dimethylphenyl)(phenyl)sulfane (Table 2, entry 7)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.33-7.16 (m, 5H), 6.97 (s, 2H), 6.86 (s, 1H) 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 138.8, 136.3, 134.7, 130.4, 129.1, 126.6, 21.4. EI-MS (m/z) = 214.



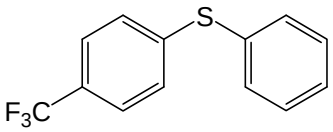
(4-Flurophenyl)(phenyl)sulfane: (Table 2, entry 8)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.36 – 7.30 (m, 2H), 7.26 – 7.13 (m, 5H), 6.99 (t, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ =163.9, 160.6, 136.6, 34.0, 133.9, 130.1, 129.8, 129.1, 126.7, 116.5, 116.2. EI-MS (m/z) = 204.



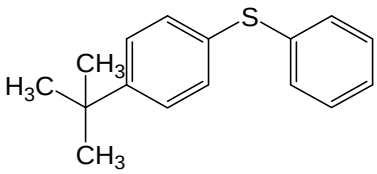
4-(Phenylthio)benzenamine: (Table 2, entry 9)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.30 – 7.23(m, 2H), 7.19 – 7.12 (m, 2H), 7.09 – 7.01 (m, 3H), 6.61 (d, *J* = 8.05 Hz, 2H) 3.67 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 146.6, 139.69, 136.02, 128.80, 127.41, 125.19, 121.02, 116.07. EI-MS (m/z) = 201.



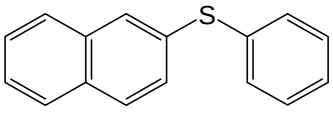
(4-(Trifluoromethyl)phenyl)(phenyl)sulfane: (Table 2, entry 10)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.50 – 7.42 (m, 4H), 7.39 – 7.31 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 142.89, 133.50, 132.71, 129.61, 128.71, 128.28, 127.79, 125.7, 122.28. EI-MS (m/z) = 254.



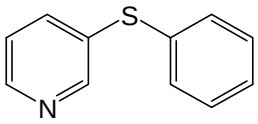
(4-*Tert*-butylphenyl)(phenyl)sulfane: (Table 2, entry 11)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.28 – 7.16 (m, 9H), 1.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 150.43, 136.54, 131.37, 130.14, 128.96, 128.36, 126.54, 126.12, 124.25, 34.55, 31.24. EI-MS (m/z) = 242.



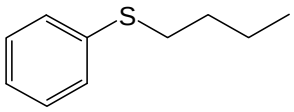
Naphthalen-2-yl(phenyl)sulfane: (Table 2, entry 12)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.85 – 7.71 (m, 4H), 7.46 – 7.18 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 138.6, 135.4, 134.5, 133.3, 131.7, 130.8, 129.9, 129.4, 128.2, 127.8, 127.5, 127.2, 125.8, 127.3. EI-MS (m/z) = 236.



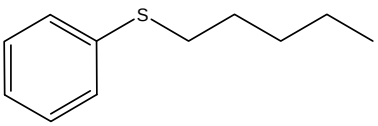
3-(Phenylthio)pyridine: (Table 2, entry 13)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.77 – 8.18 (m, 2H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.05 (m, 5H), 7.19 (dd, *J* = 5.12, 2.93 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 149.6, 137.1, 135.3, 130.2, 129.9, 129.5, 129.2, 125.8, 122.0. EI-MS (m/z) = 187.



Butyl(phenyl)sulfane: (Table 2, entry 14)

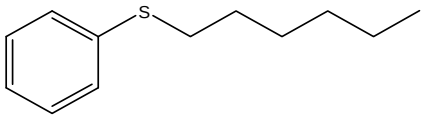
^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.33–7.18 (m, 4H), 7.16–7.04 (m, 1H), 2.90 (t, *J* = 7.5, 6.7 Hz, 2H), 1.59 (m, 2H), 1.50 (m, 2H), 0.95 (t, *J* = 7.5, 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 138.2, 131.3, 130.0, 129.3, 128.1, 125.4, 34.3, 32.1, 22.2, 13.9. EI-MS *m*/*z* = 166.



Pentyl(phenyl)sulfane: (Table 2, entry 15)

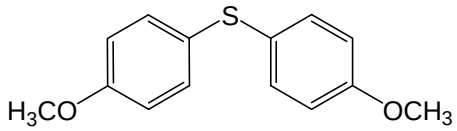
^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.33–7.06 (m, 5H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.63 (p, *J* = 7.5 Hz,

2H), 1.47-1.23 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 136.97, 128.81, 125.63, 33.45, 30.95, 28.80, 22.23, 14.06. EI-MS m/z = 180.



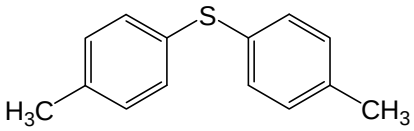
hexyl(phenyl)sulfane (Table 2, entry 16)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.36-7.02 (m, 5H), 2.87 (t, J = 7.54, 2H), 1.69-1.56 (m, 2H) 1.47-1.22 (m, 6H), 0.90 (t, J = 7.54, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 137.1, 128.9, 128.8, 125.6, 33.6, 31.3, 29.1, 28.5, 22.5, 14.0. EI-MS (m/z) = 214.



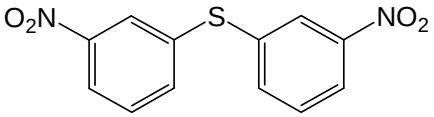
Bis(4-Methoxyphenyl)sulfane: (Table 3, entry 1)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.60-7.43 (m, 4H), 6.97 (d, J = 7.9 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 160.01, 134.26, 128.64, 115.19, 55.33. EI-MS (m/z) = 246.



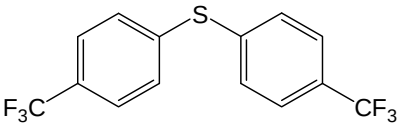
Di-*p*-tolylsulfane: (Table 3, entry 2)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.19 (d, J = 8.1 Hz, 4H), 7.08 (d, J = 7.9 Hz, 4H), 2.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 138.8, 131.84, 130.07, 129.20, 21.37. EI-MS (m/z) = 214.



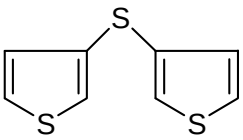
Bis(3-Nitrophenyl)sulfane: (Table 3, entry 4):

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 8.76-8.23 (m, 4H), 7.82 (d, *J* = 7.85 Hz, 2H), 7.31 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ =149.10, 136.82, 131.26, 126.07, 122.47. EI-MS (m/z) = 276.



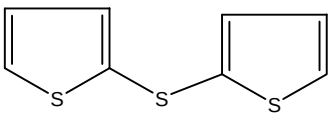
Bis(4-(trifluoromethyl)phenyl)sulfane: (Table 3, entry 5)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.78-7.35 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 140.9, 136.4, 134.2, 129.8, 127.8, 124.4, 121.8. EI-MS (m/z) = 322.



Dithiophen-3-ylsulfane (Table 3, entry6)

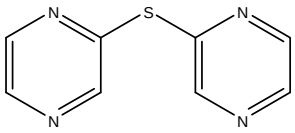
^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.33-7.27 (m, 2H), 7.15-7.10 (m, 2H), 7.0-6.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 130.17, 126.76, 125.00. EI-MS (m/z) = 197.



Dithiophen-2-ylsulfane (Table 3, entry 7)

^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ = 7.74-7.58 (m, 1H), 7.53-7.41 (m, 2H), 7.29-7.15 (m, 3H).

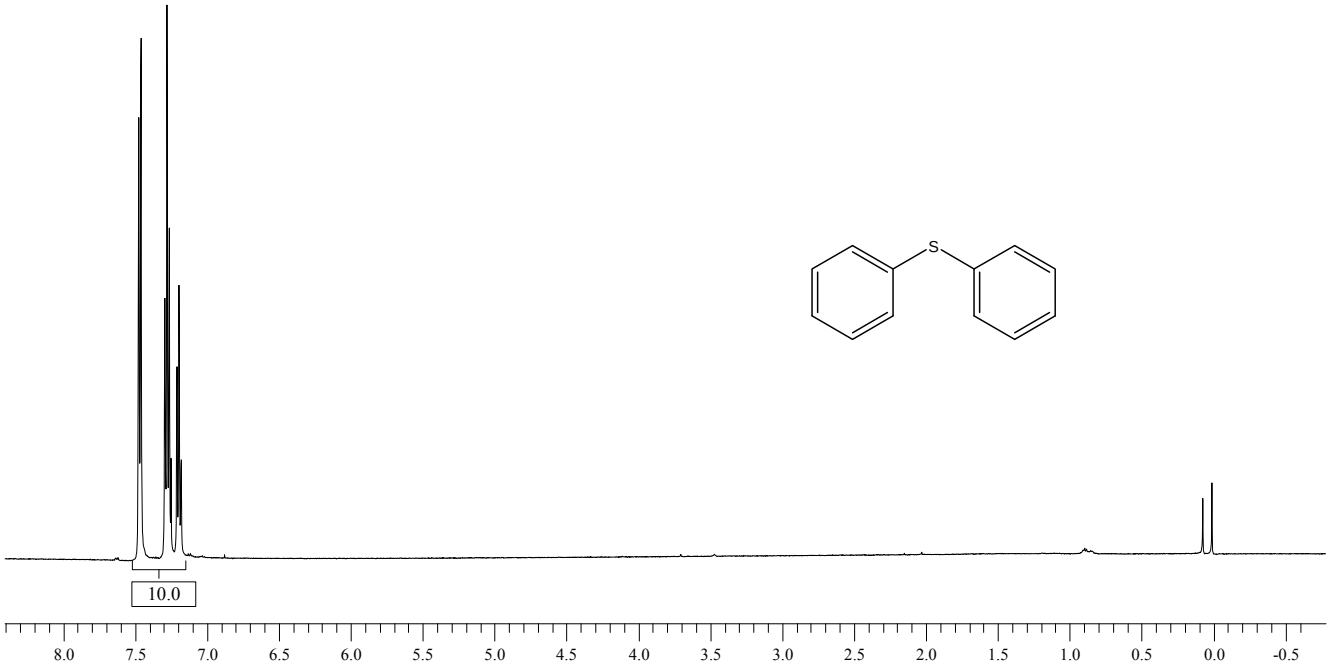
EI-MS (m/z) = 197.

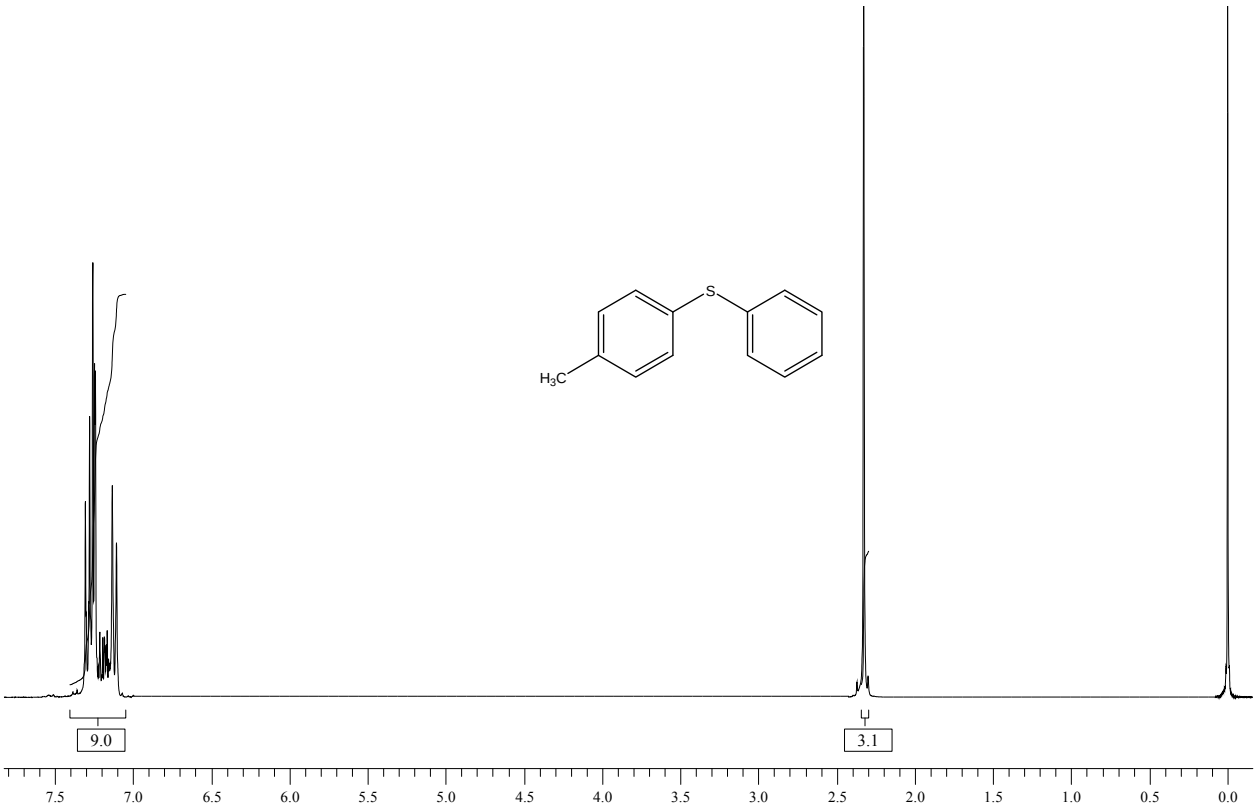


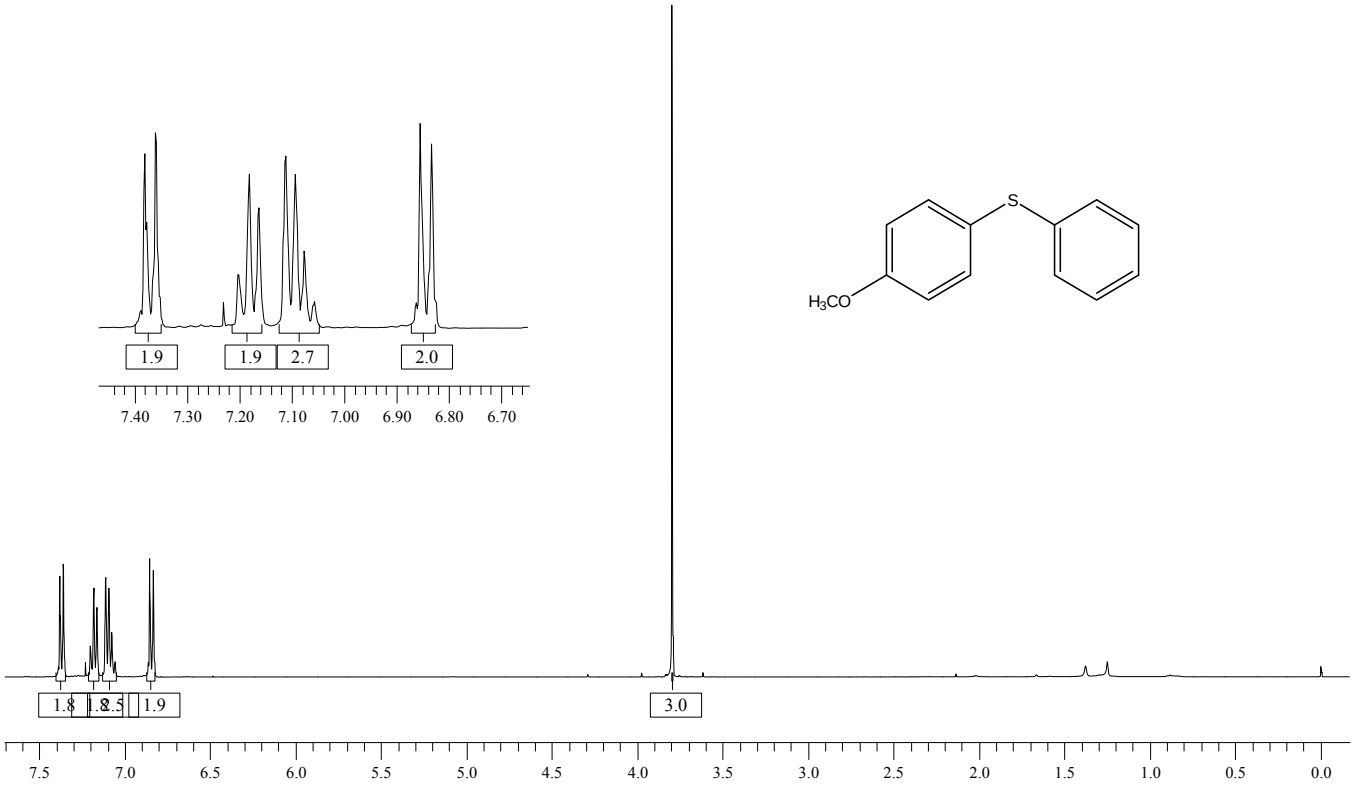
Dipyrazin-2-ylsulfane (Table 3, entry 8)

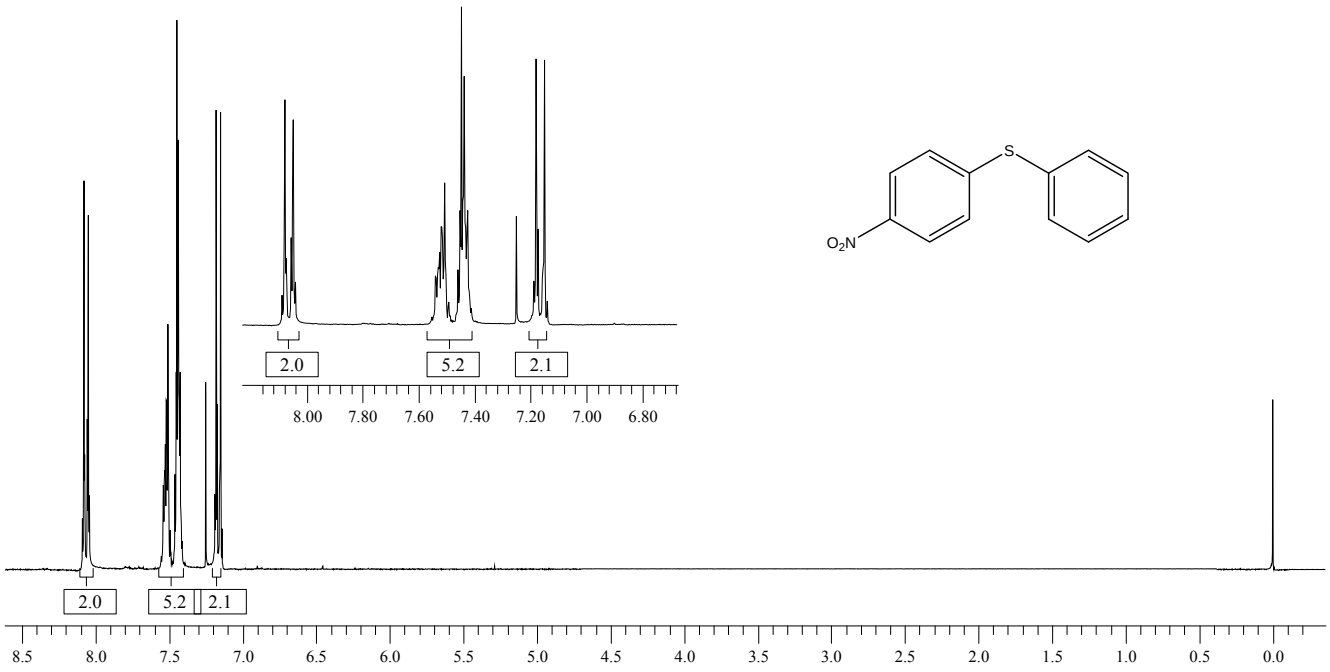
^{1}HNMR (300 MHz, $CDCl_3$, ppm): δ =8.75-8.68 (m, 2H), 8.50-8.38 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 147.12, 145.07, 143.04. EI-MS (m/z) = 190.

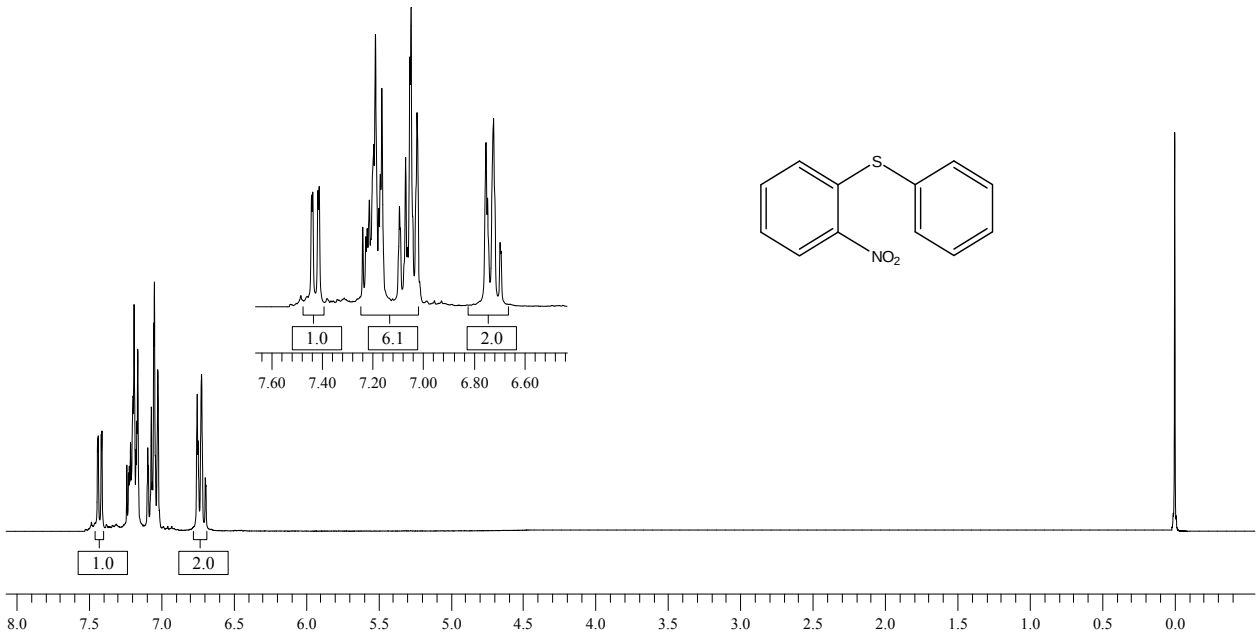
^{1}H NMR spectra of the products:

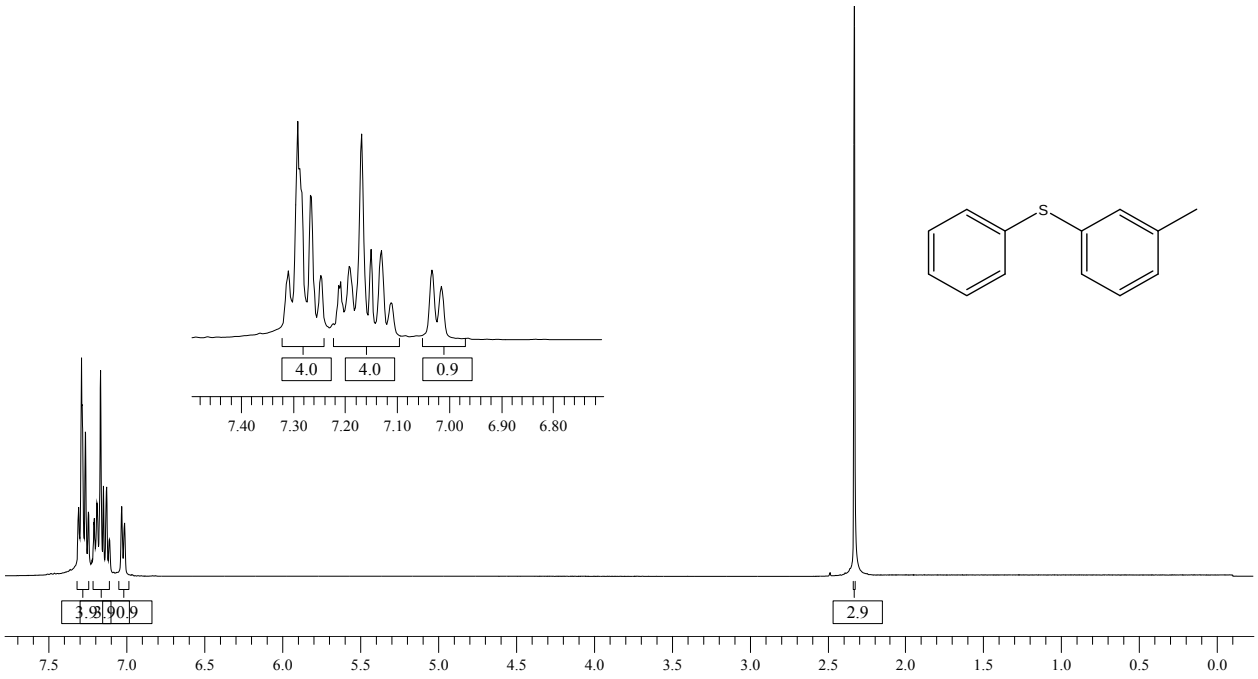


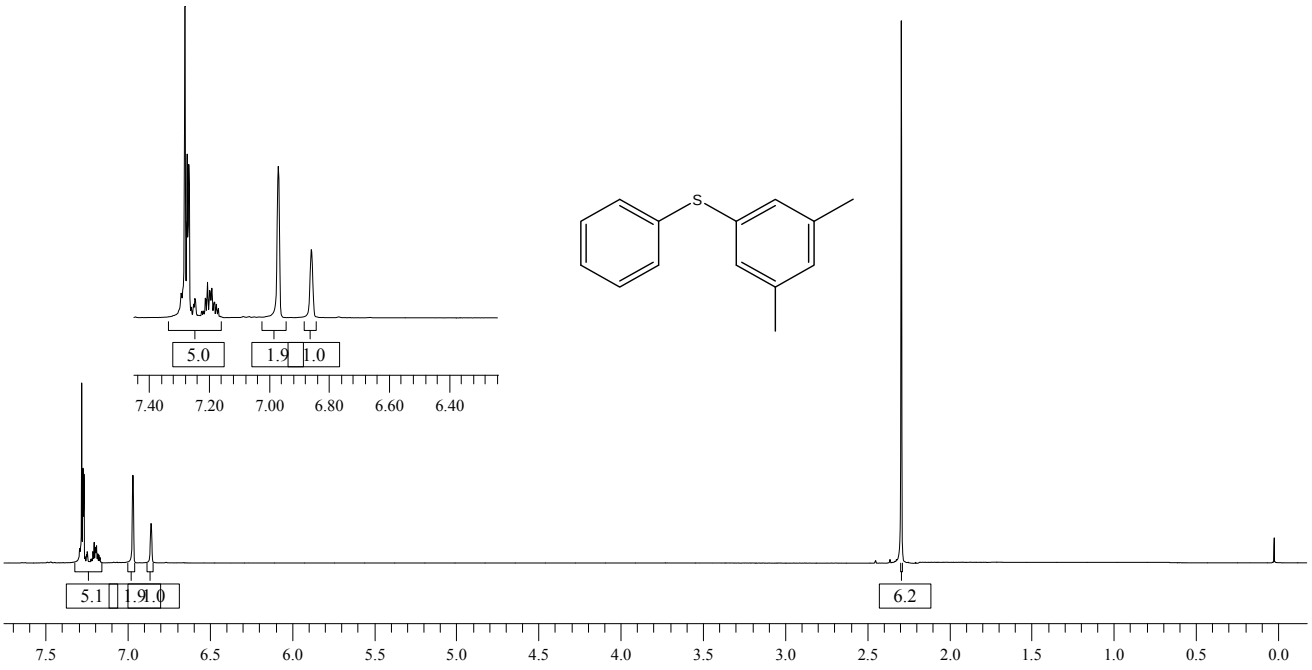


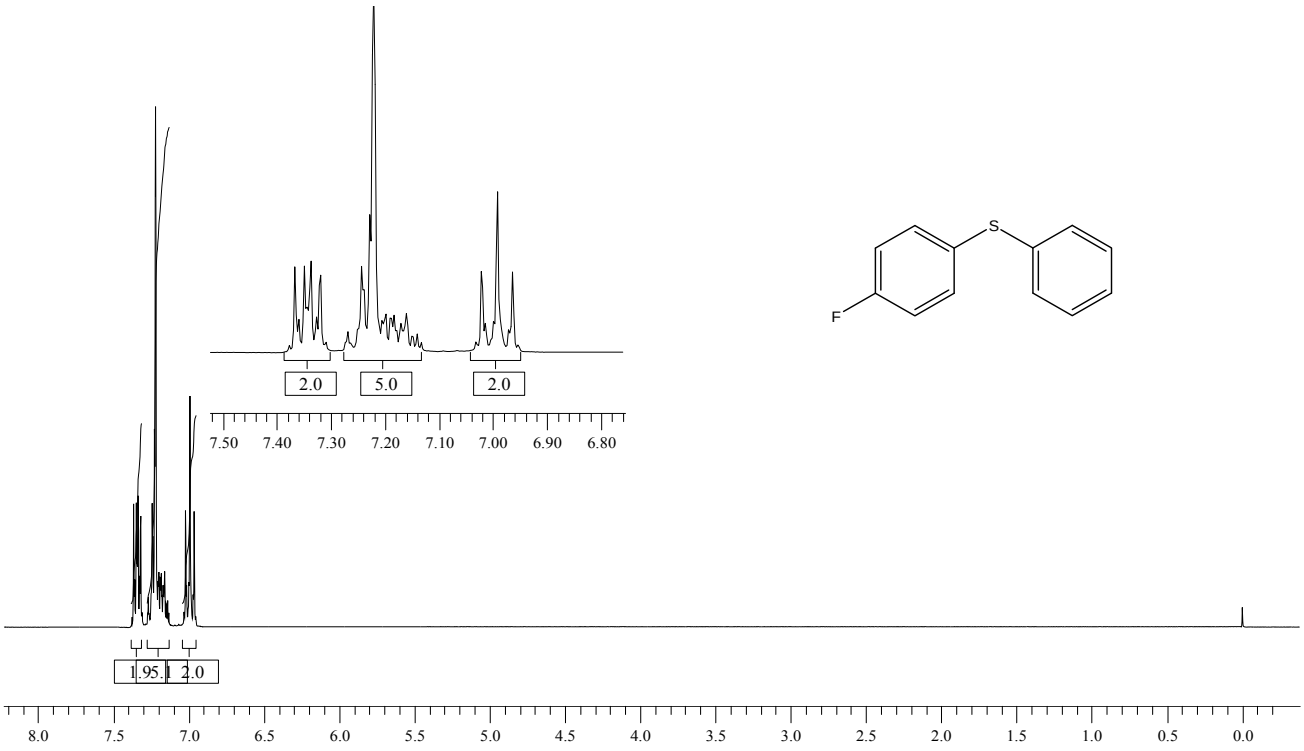


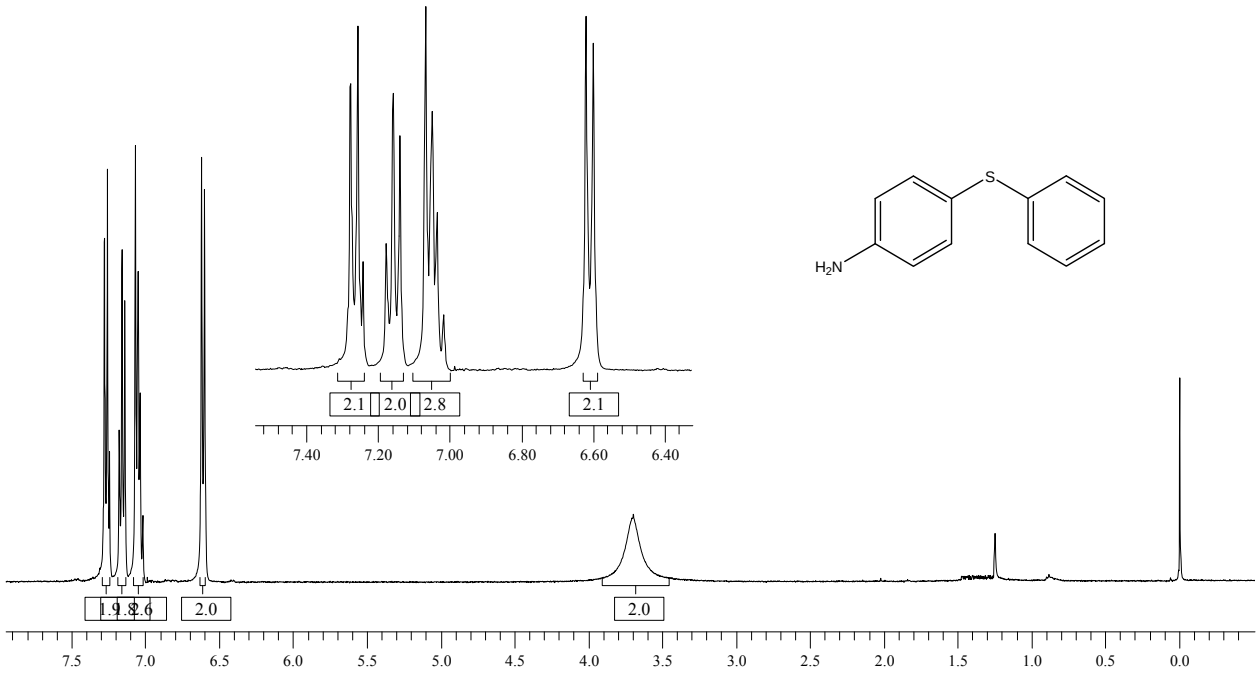


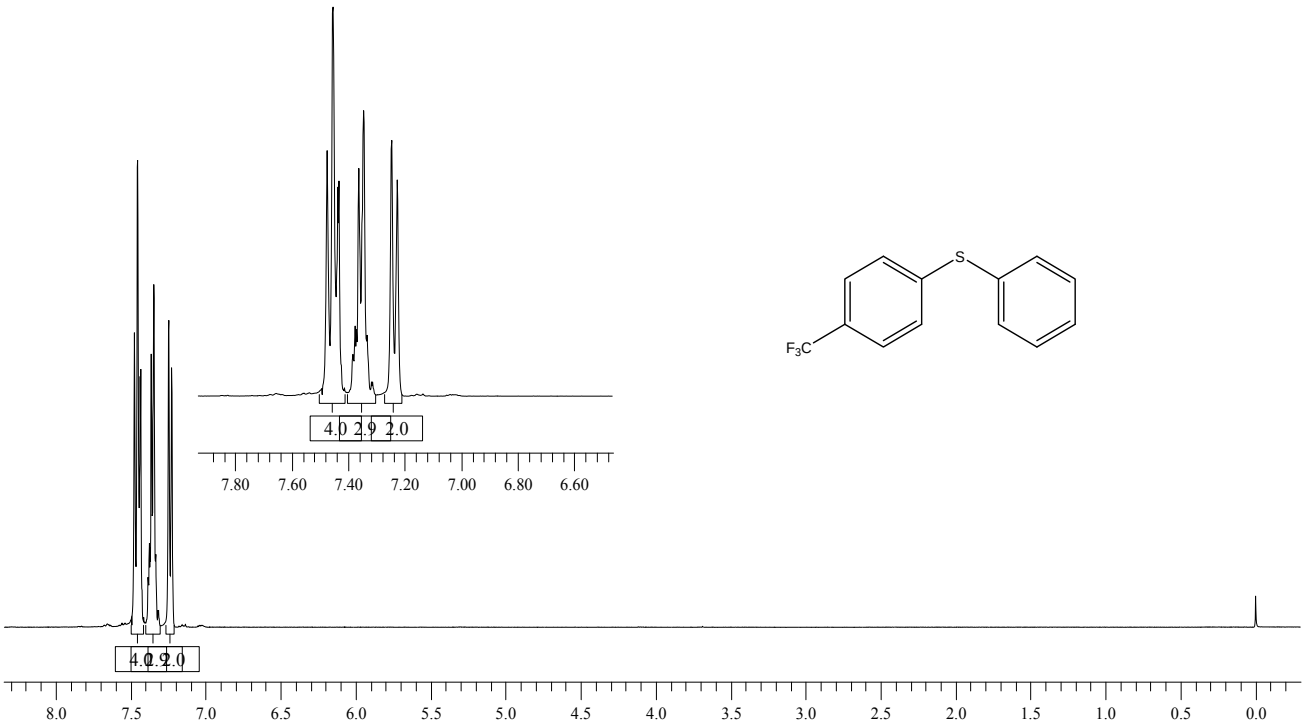


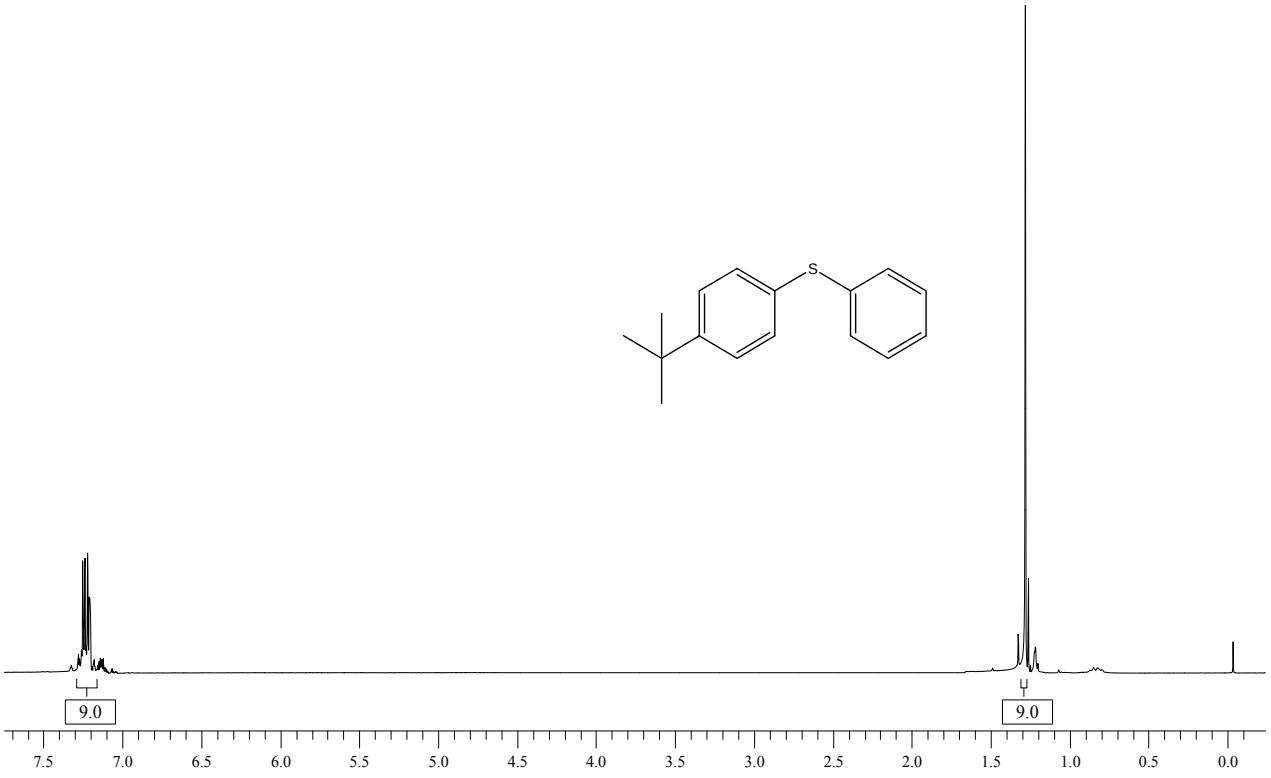


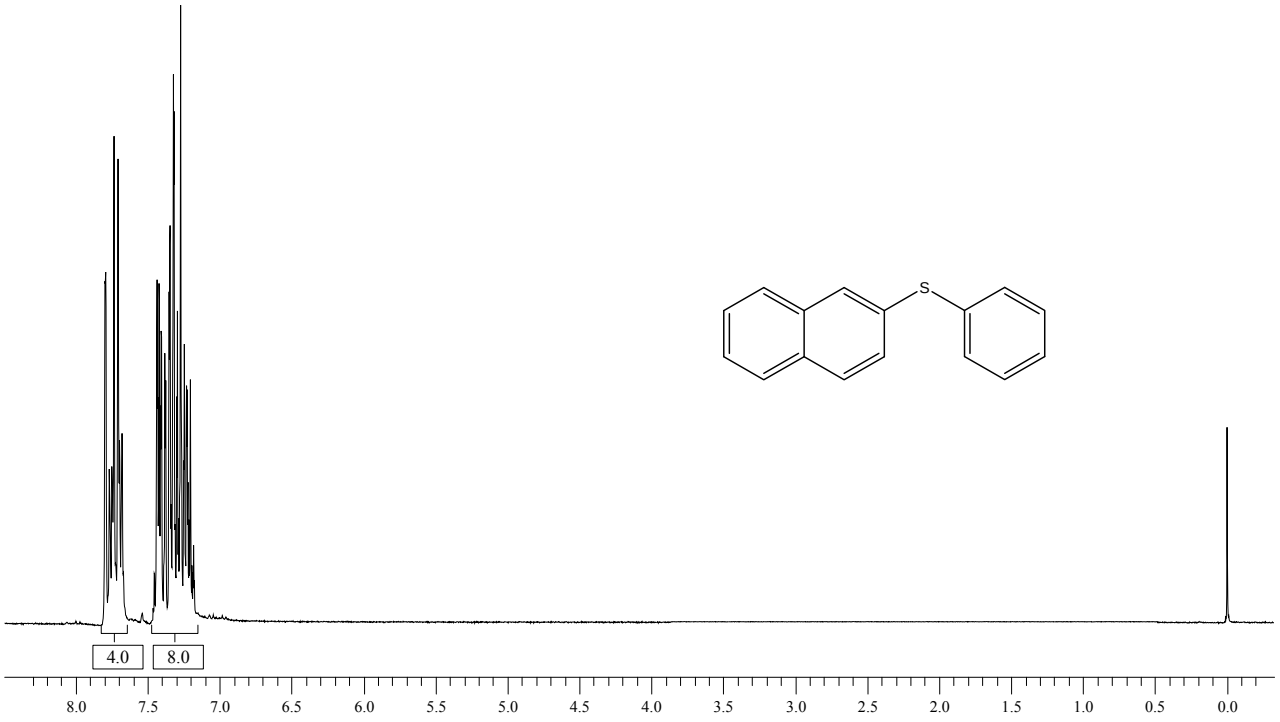


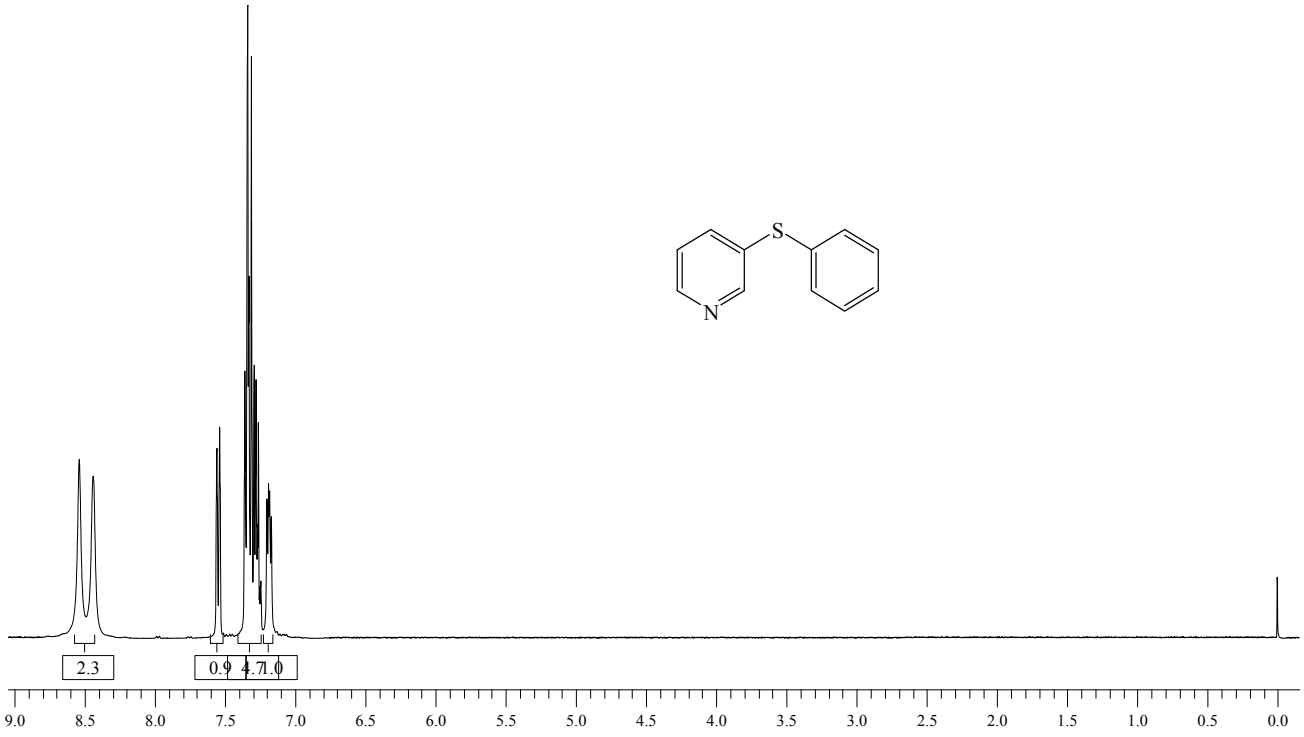


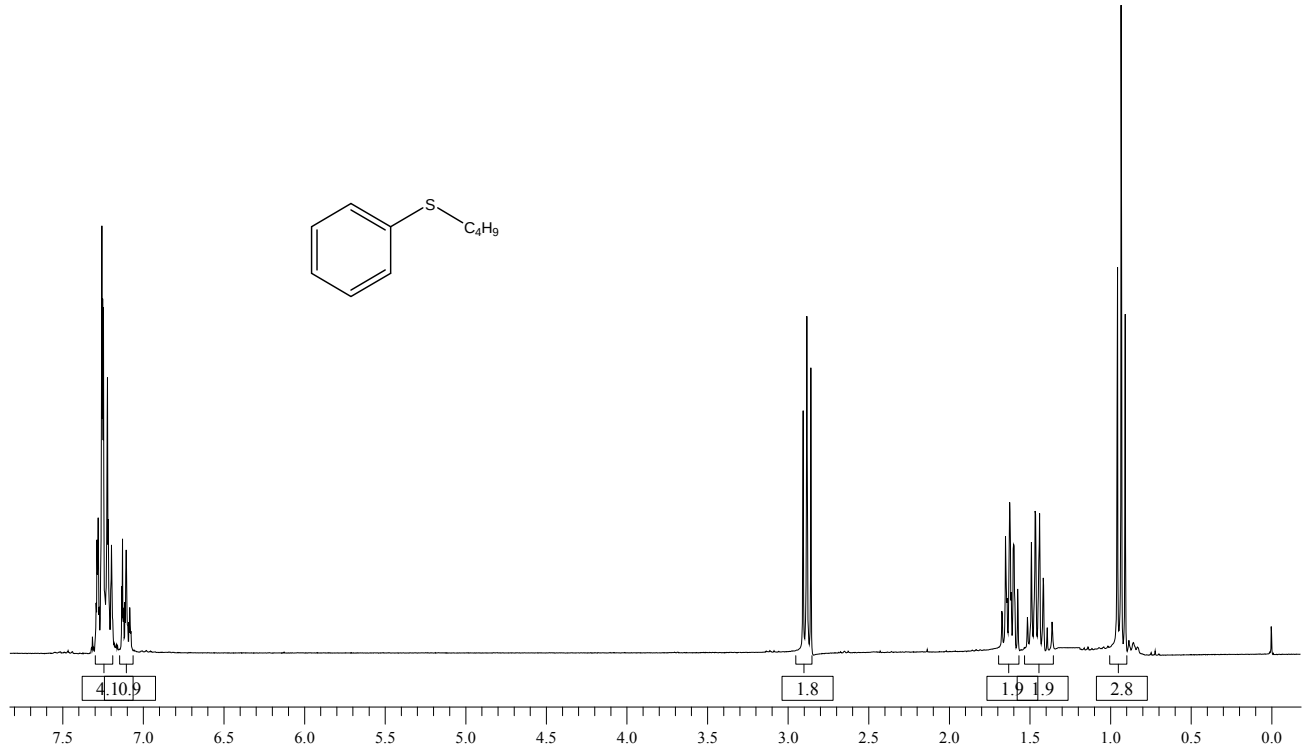


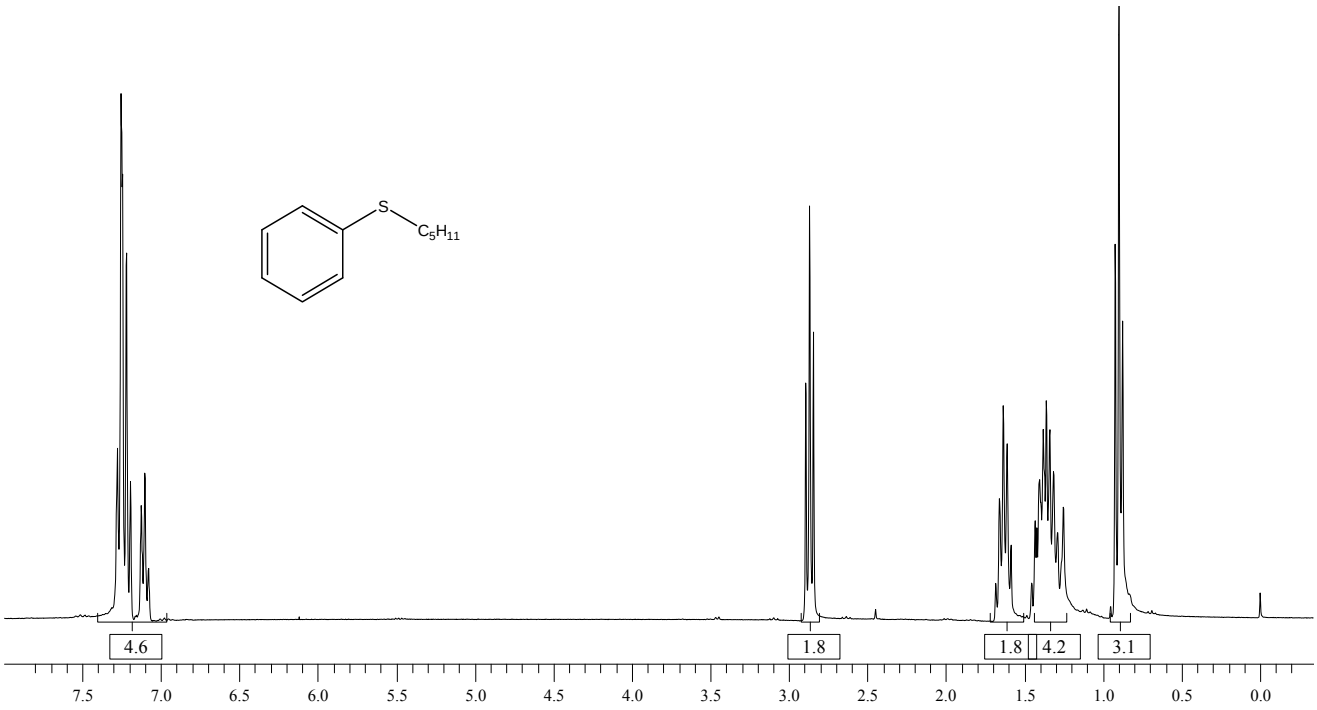


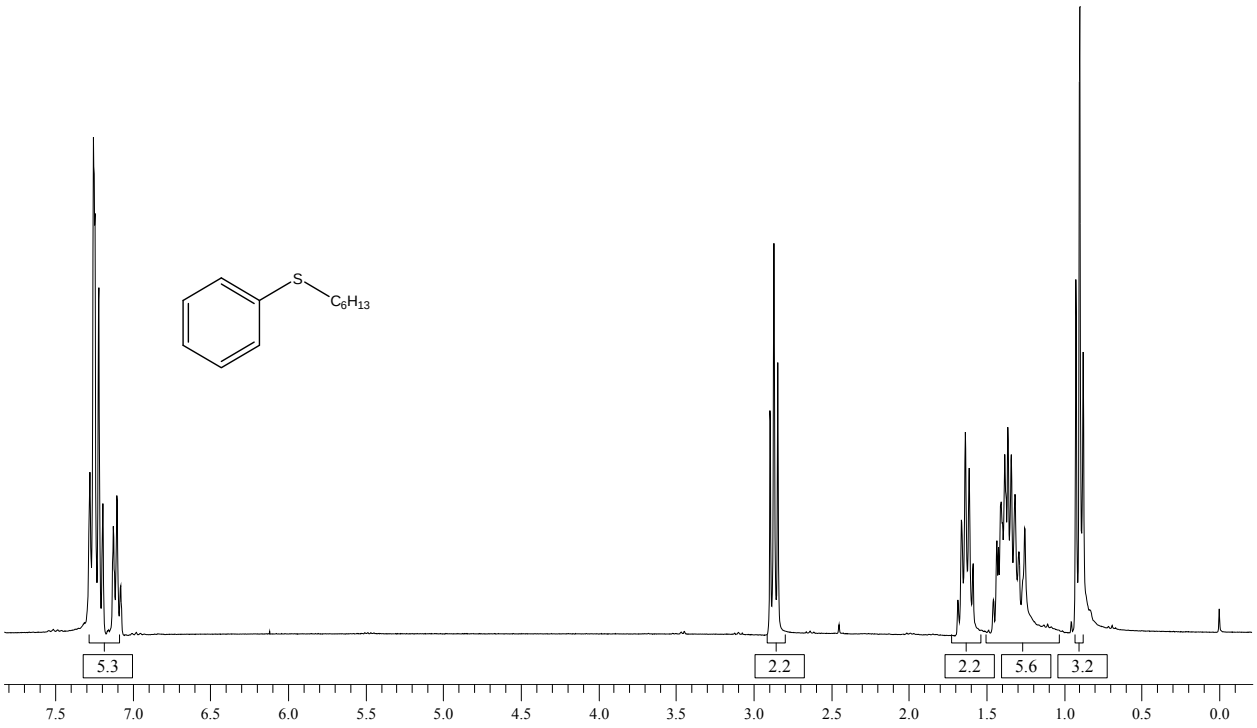


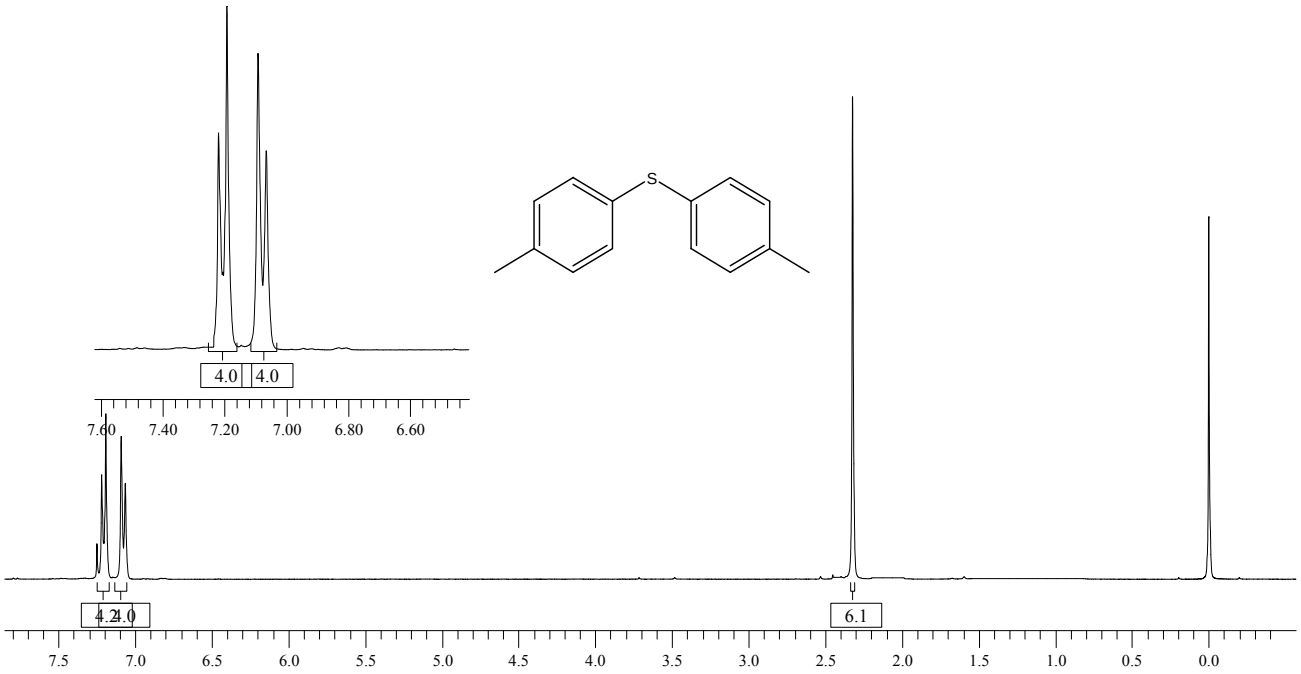


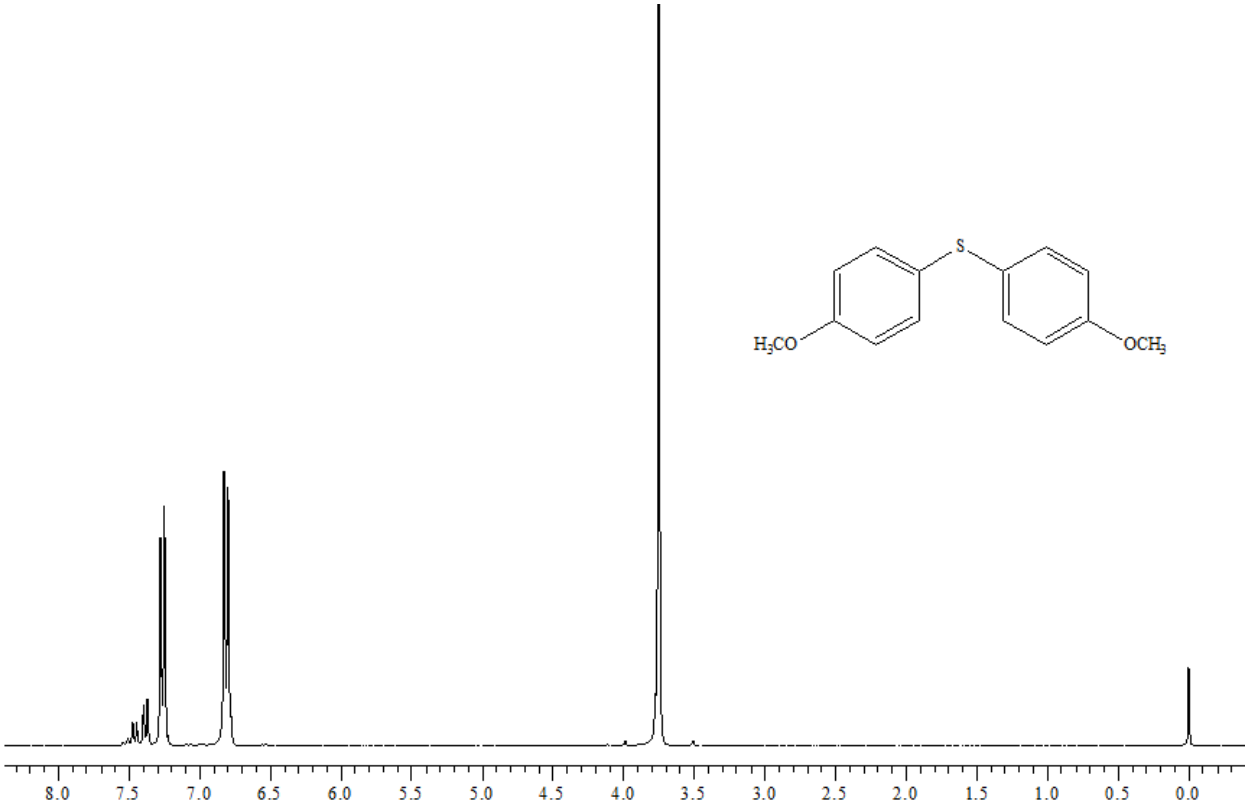


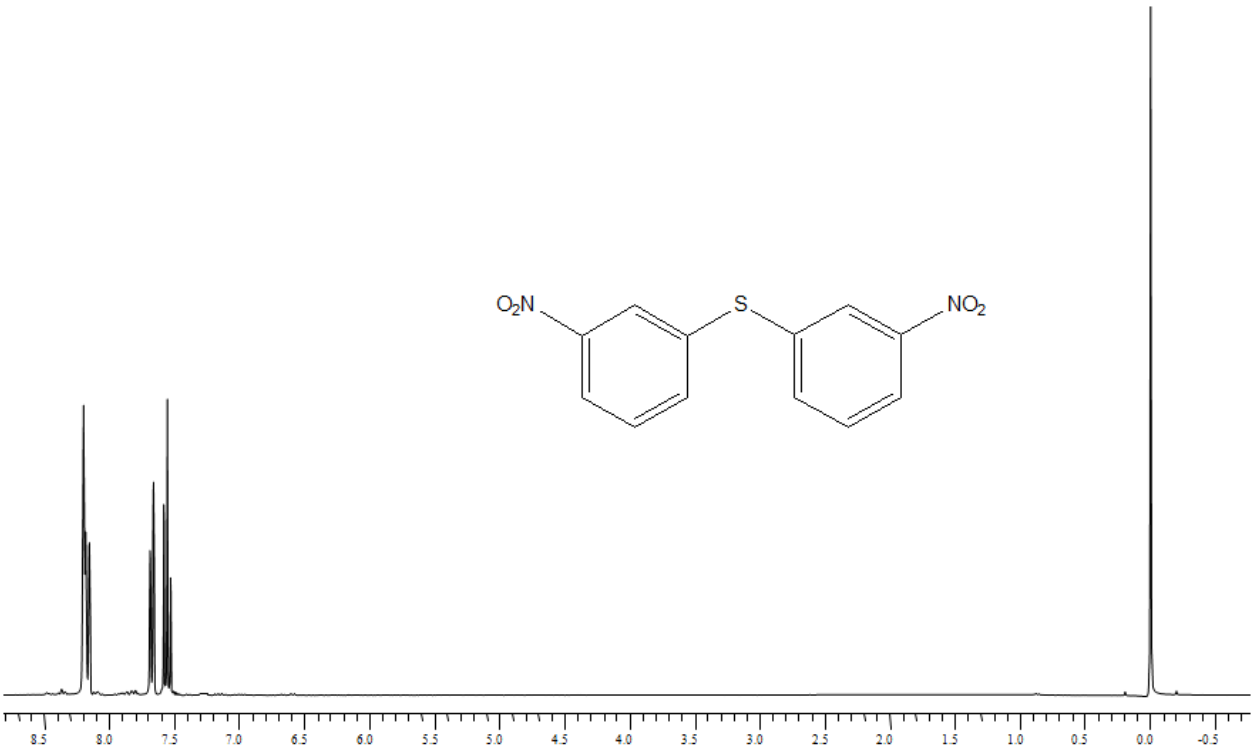


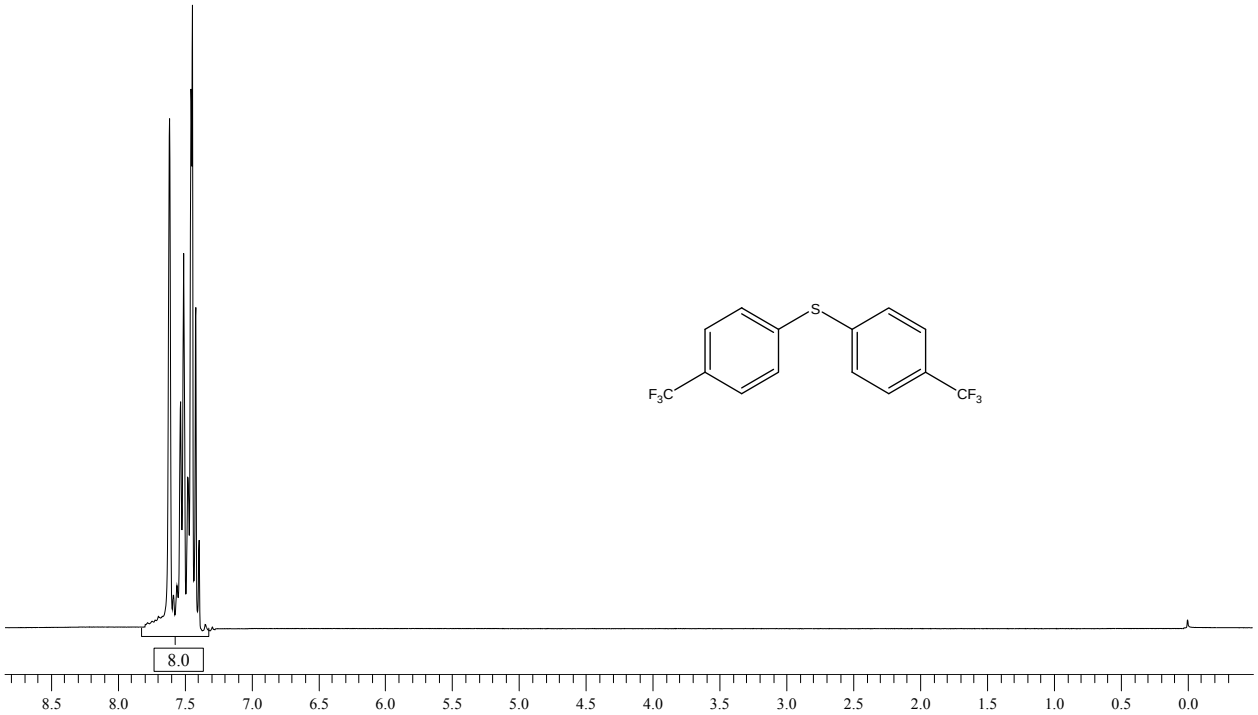


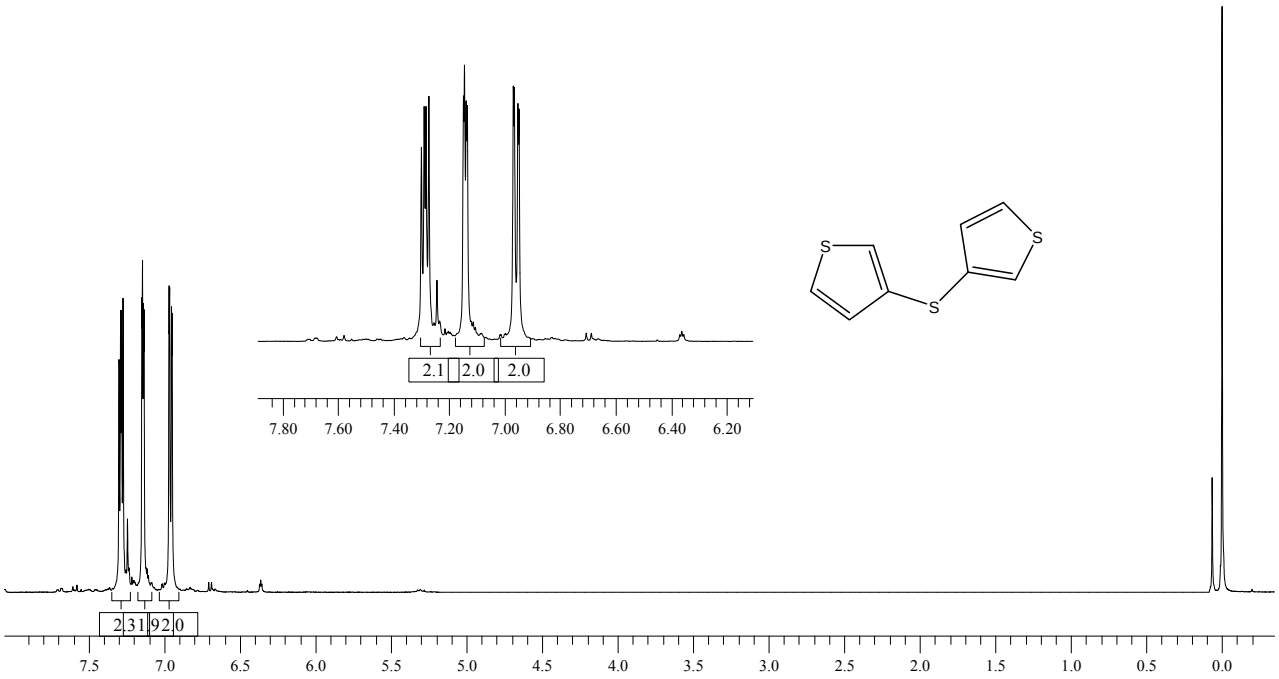


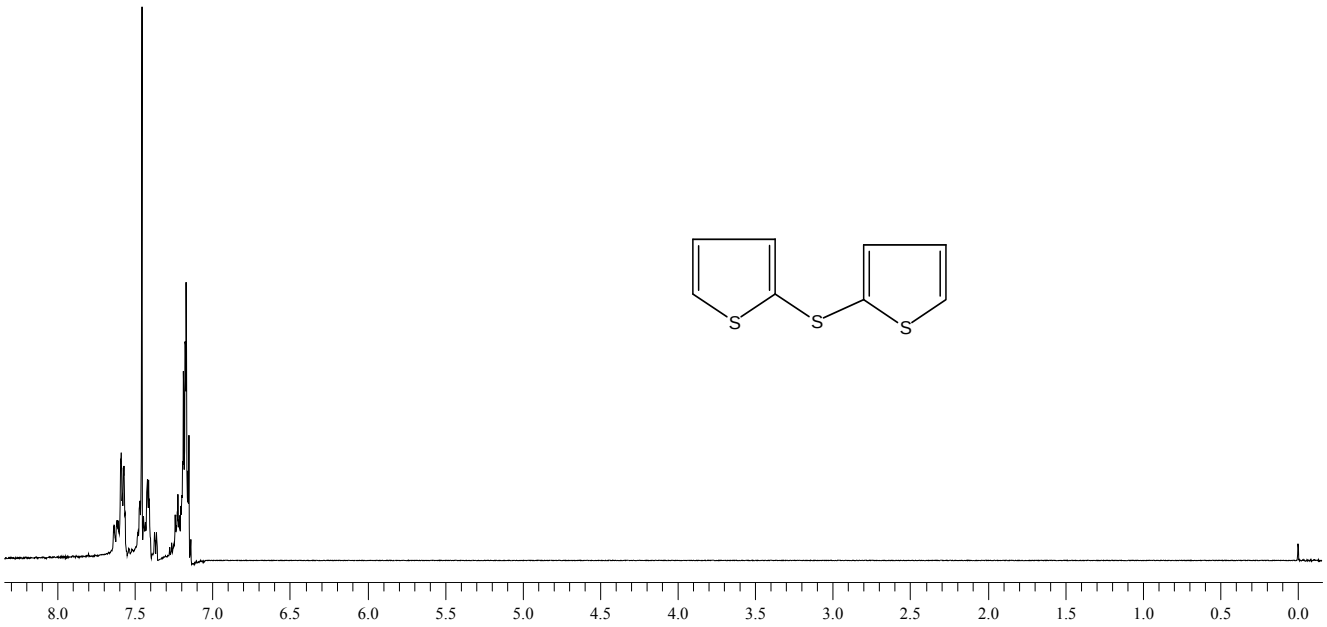


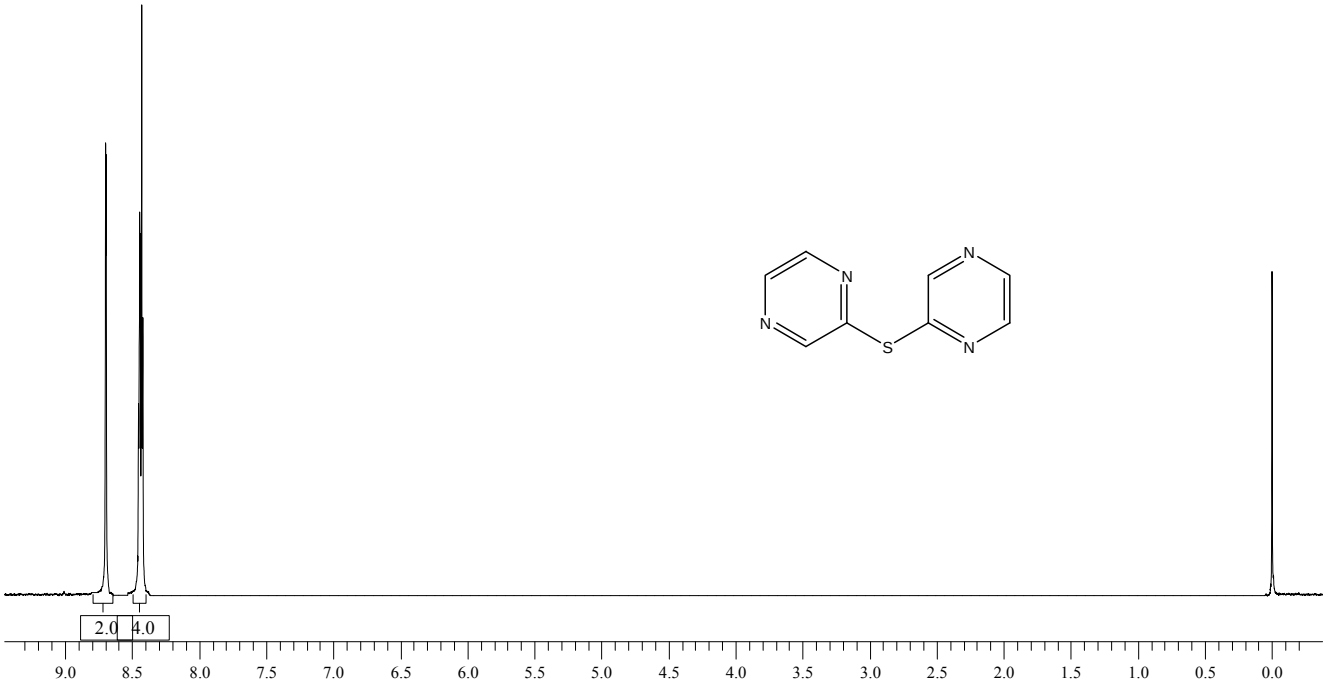




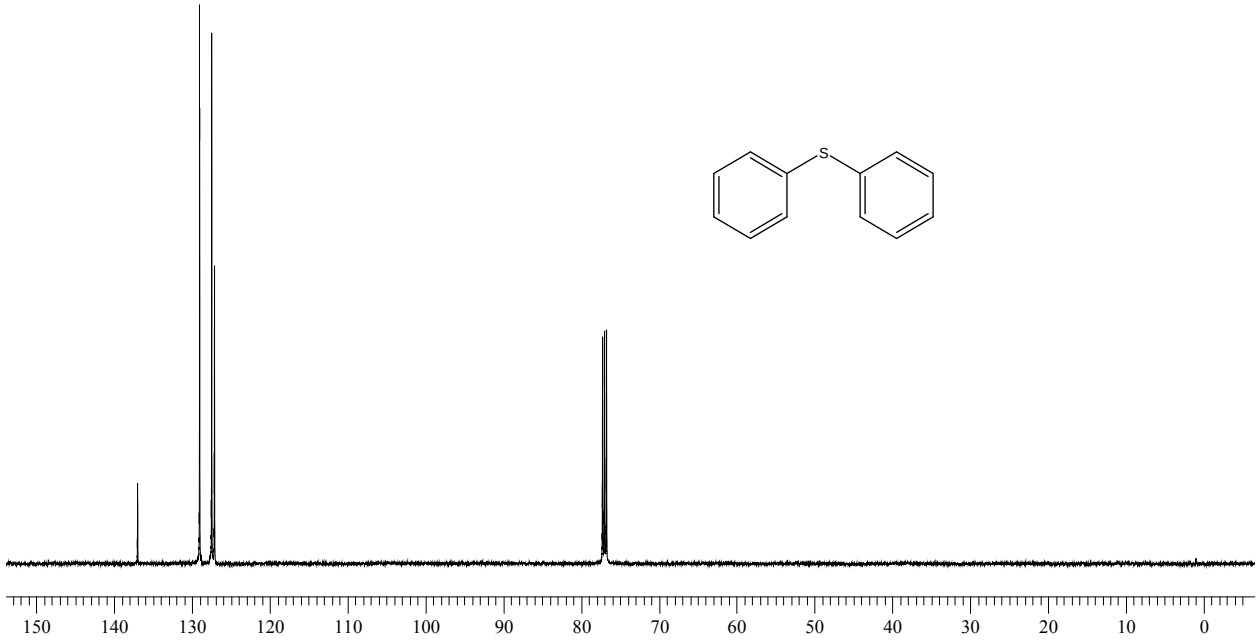


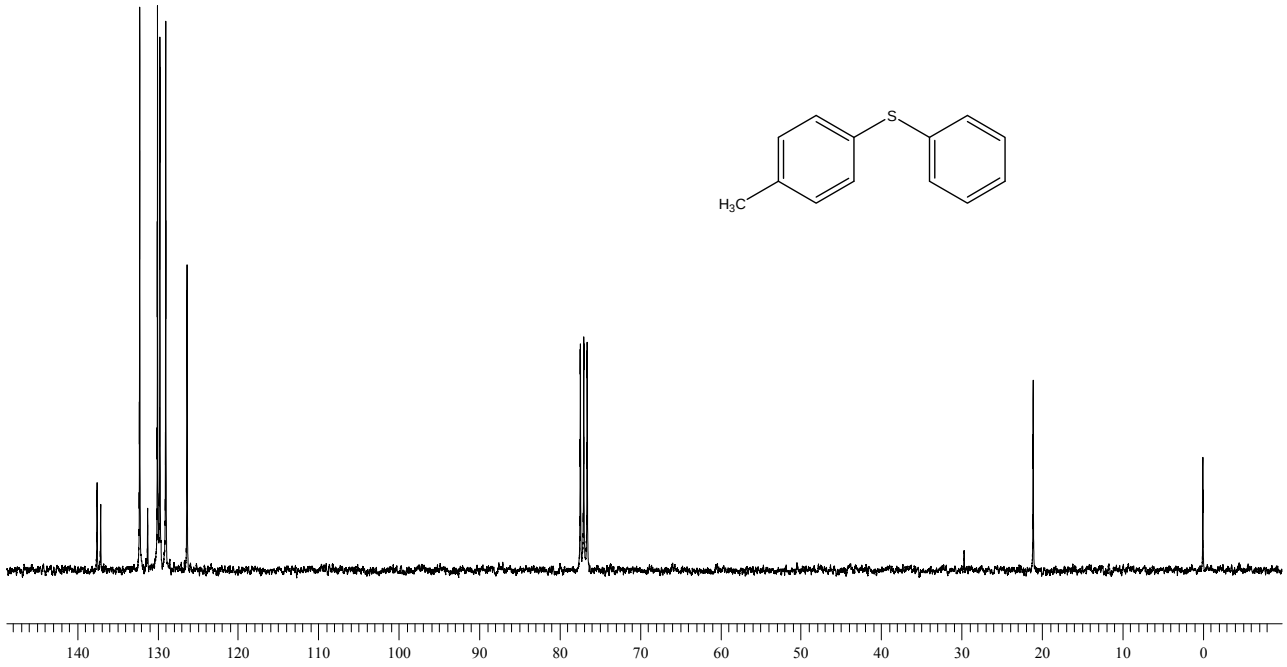


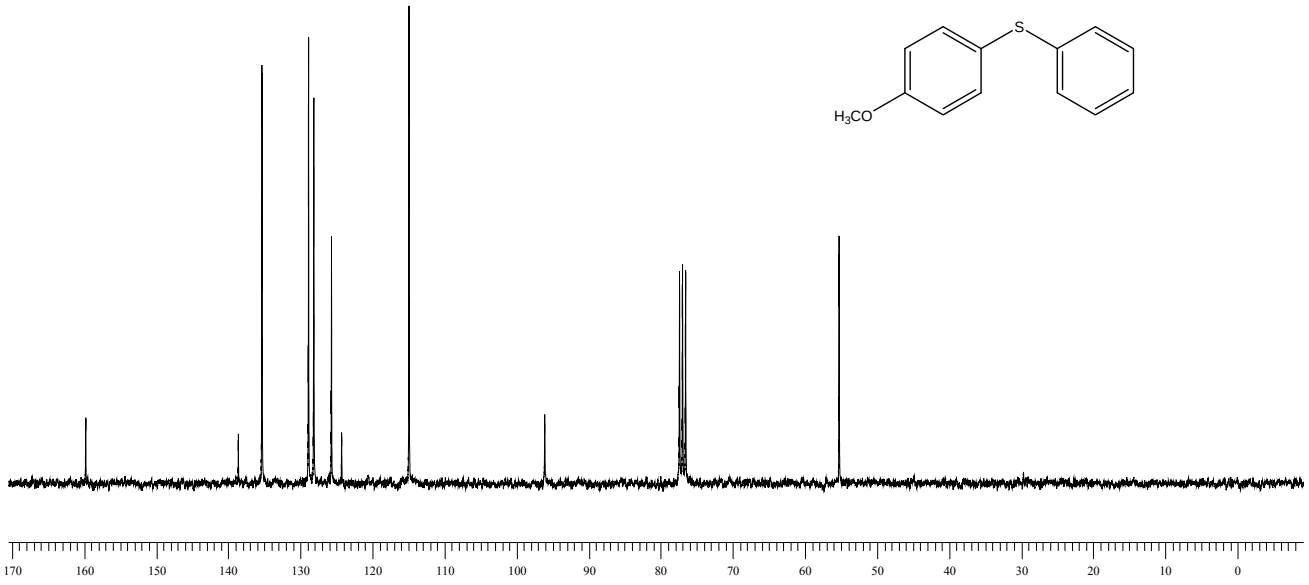


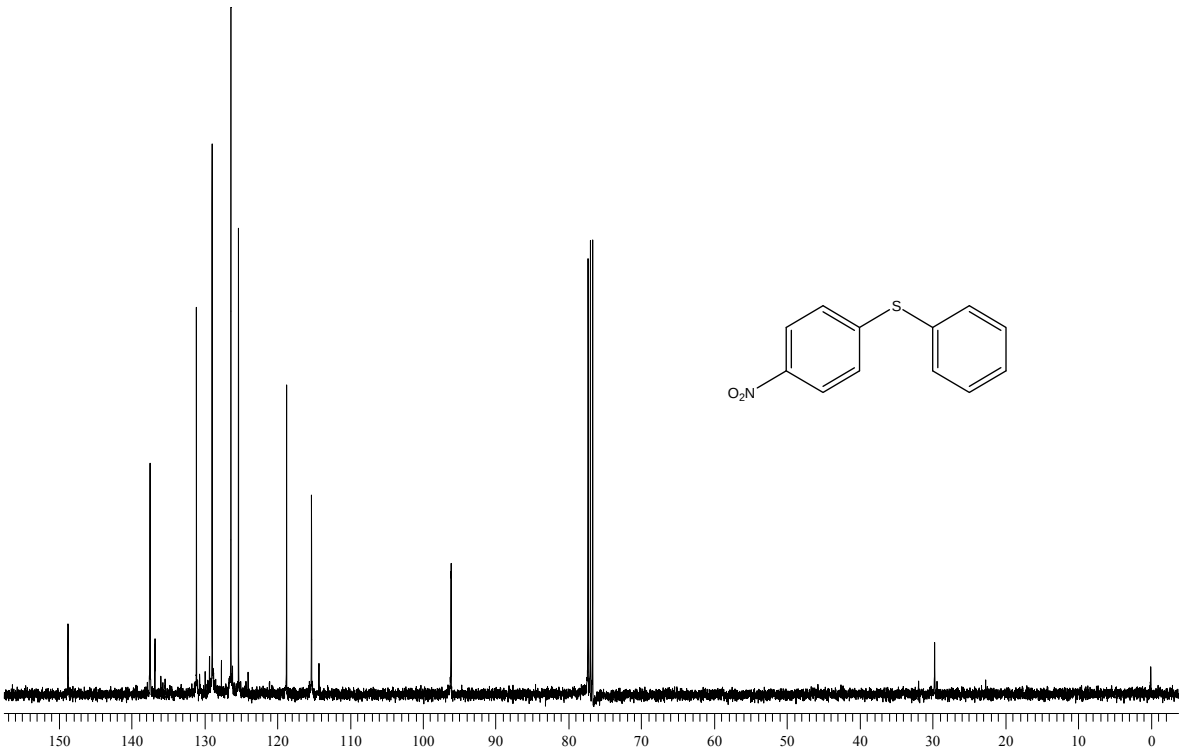


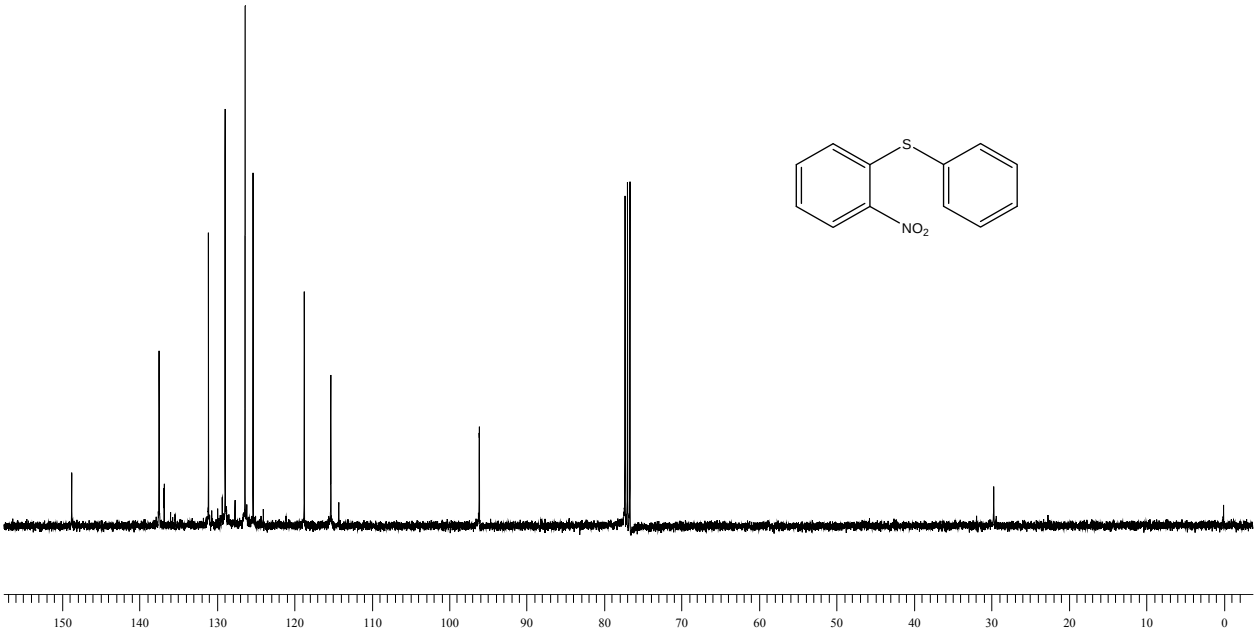
^{13}C NMR spectra of the products:

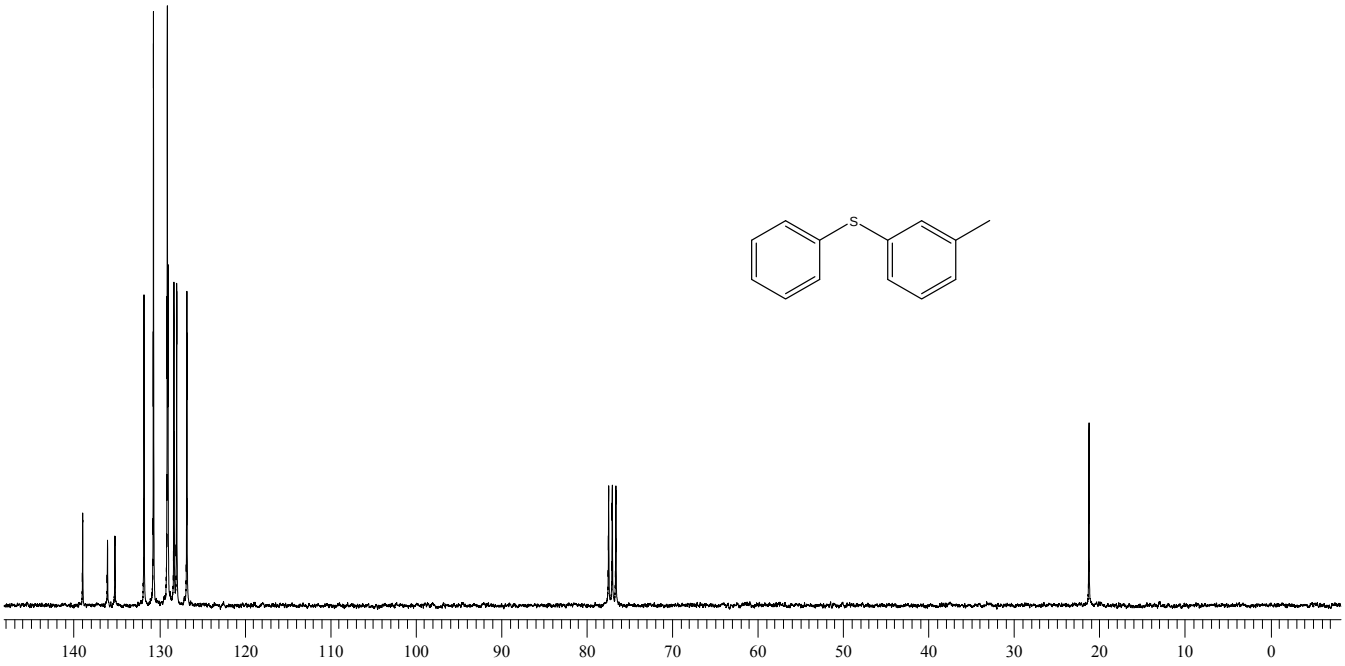


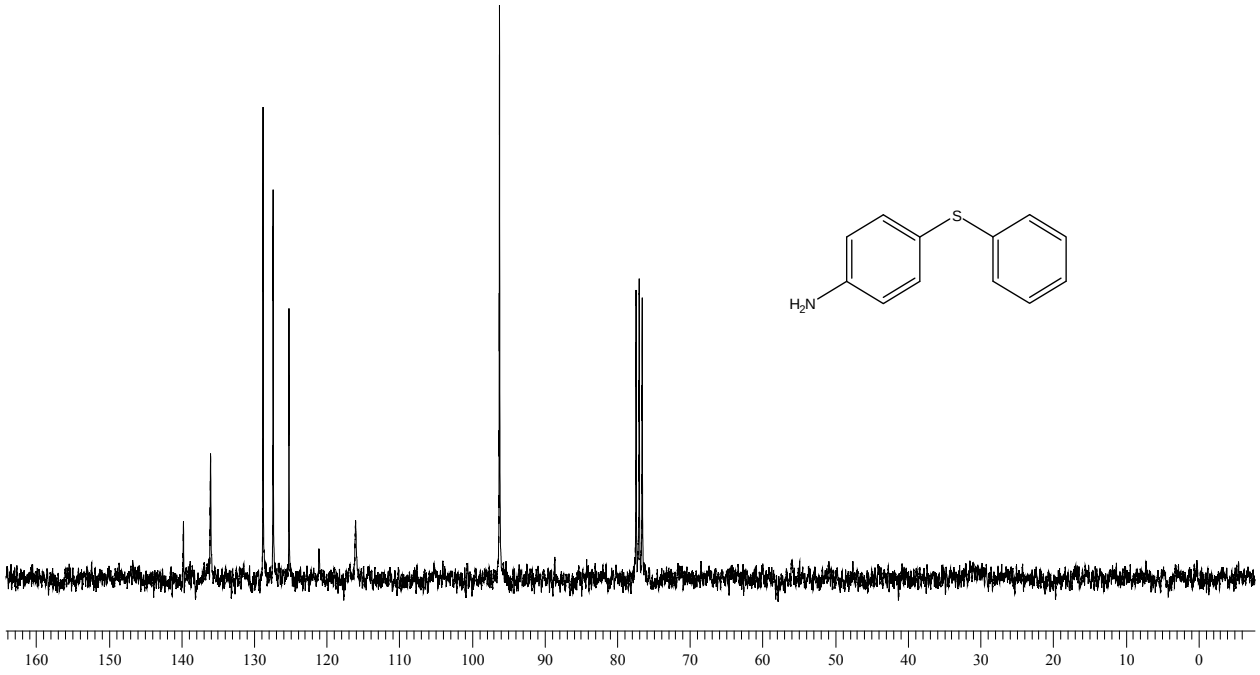


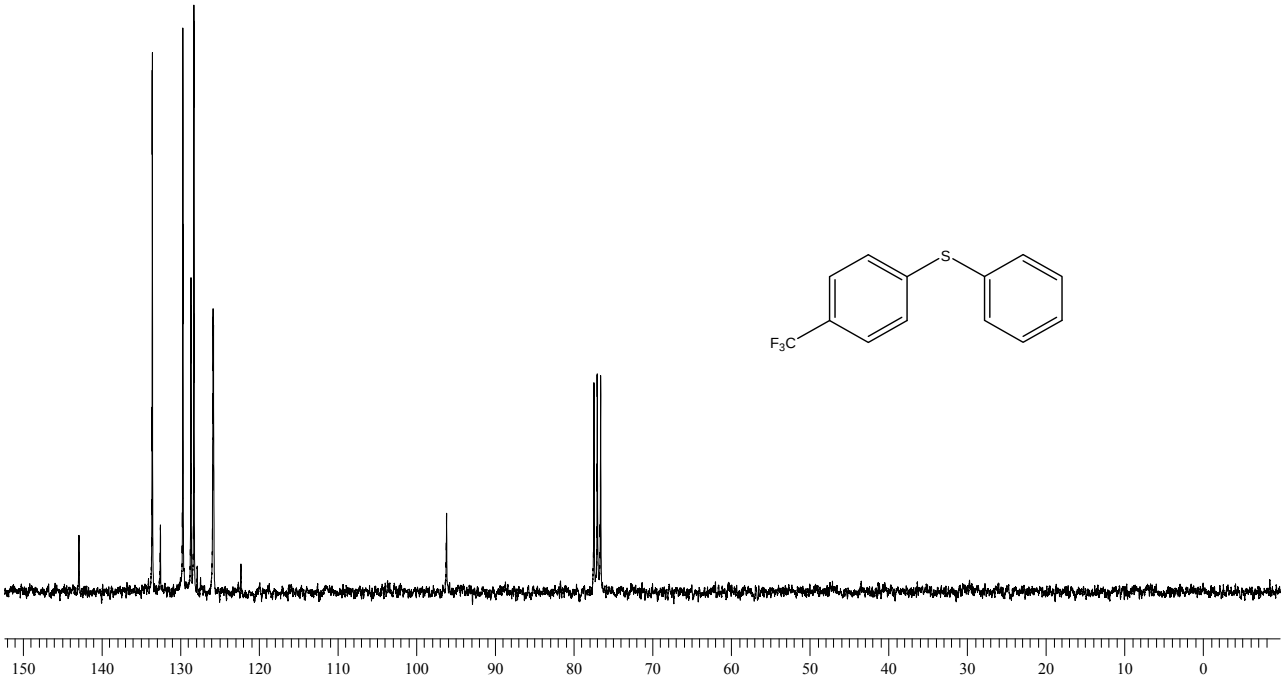


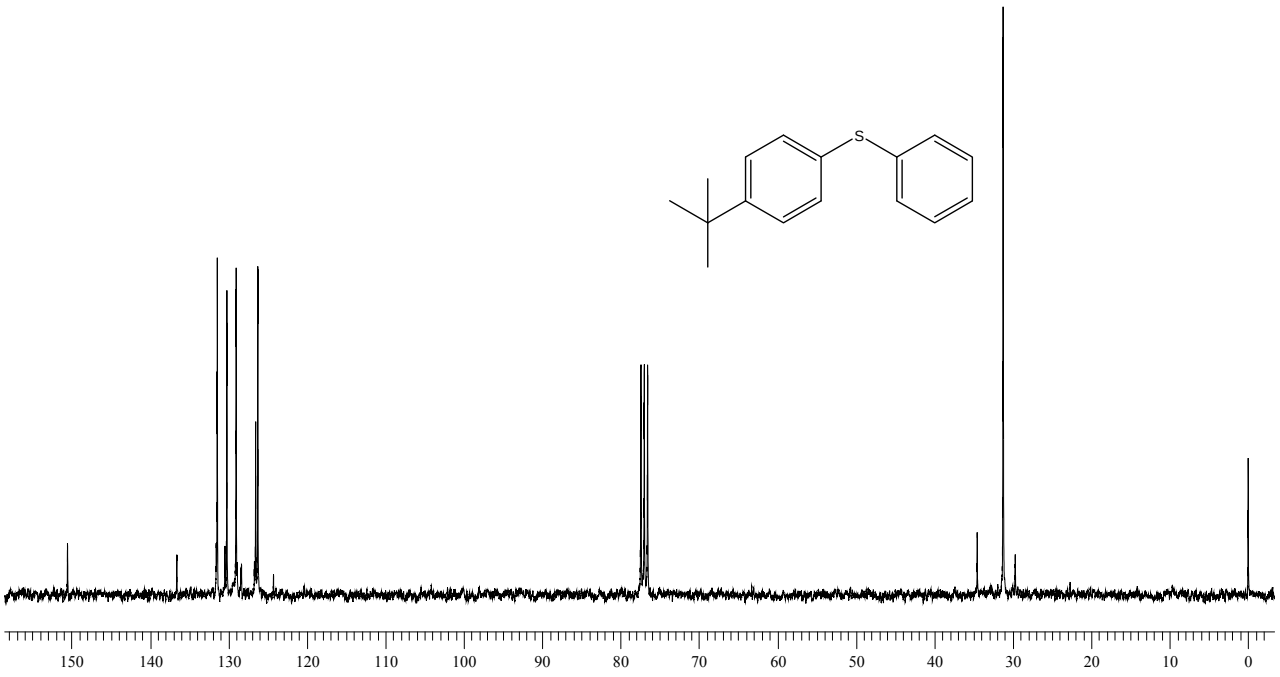


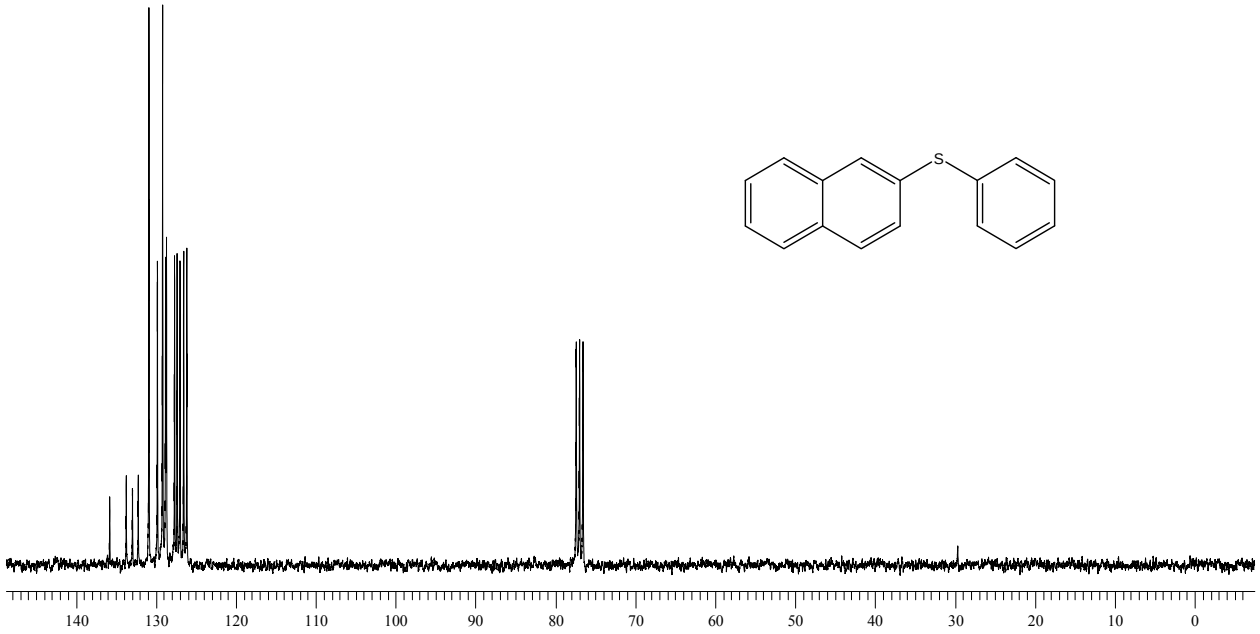


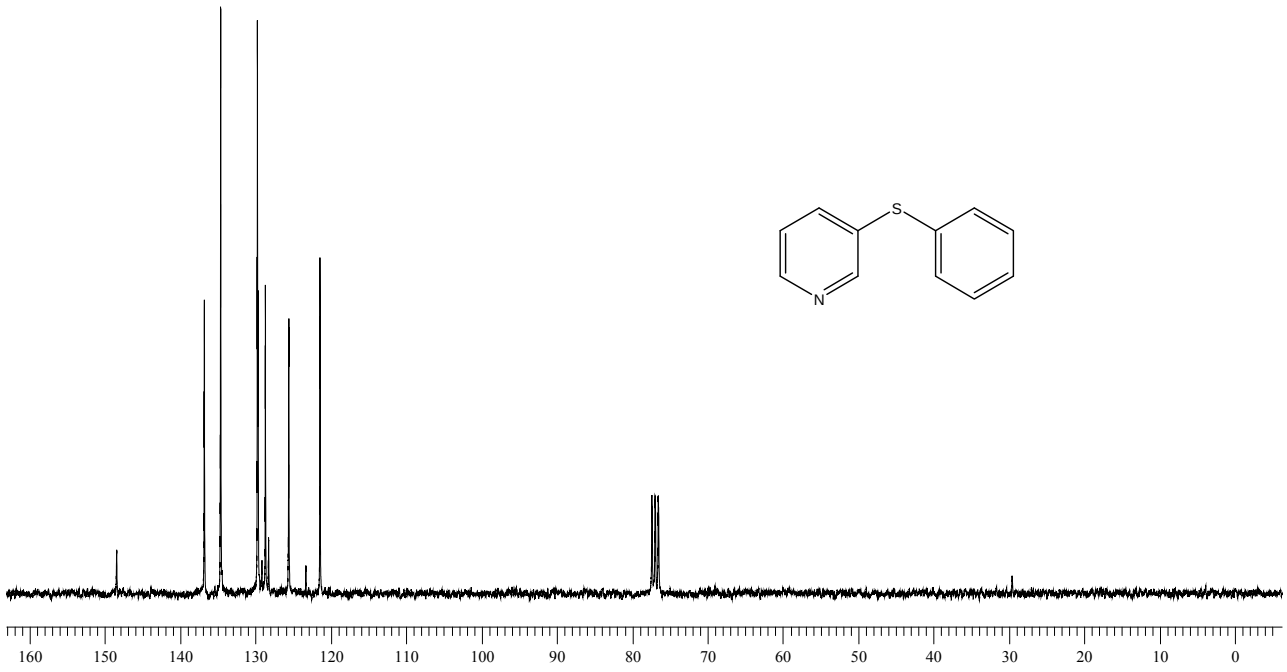


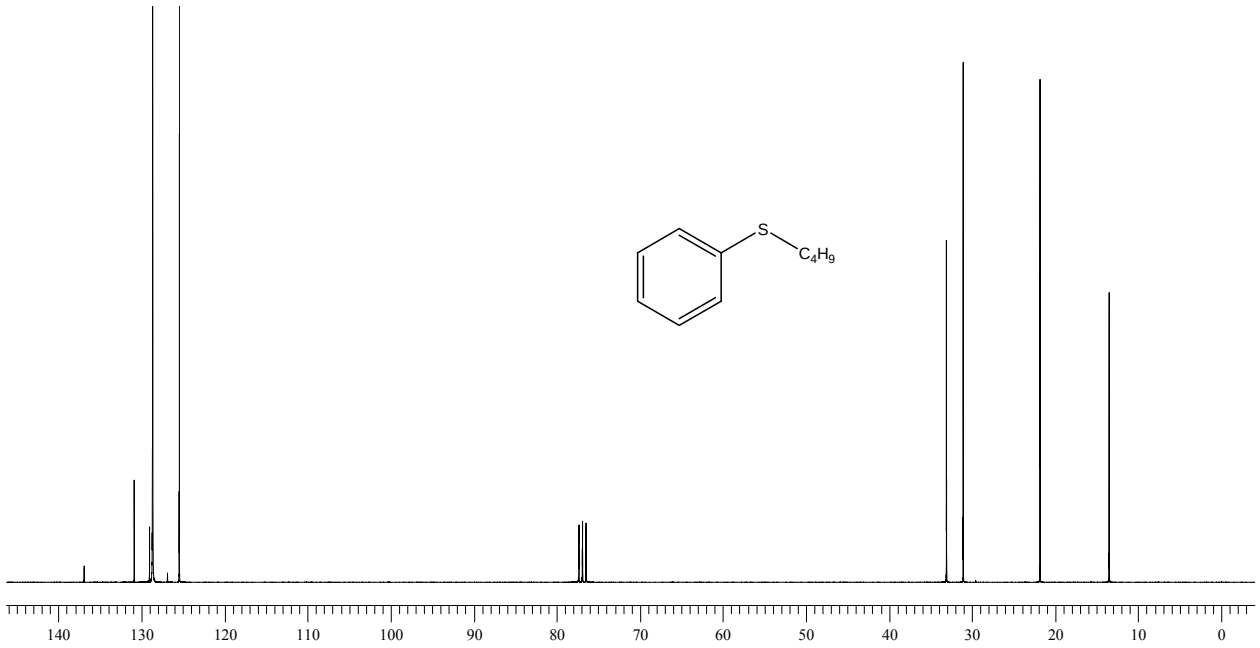


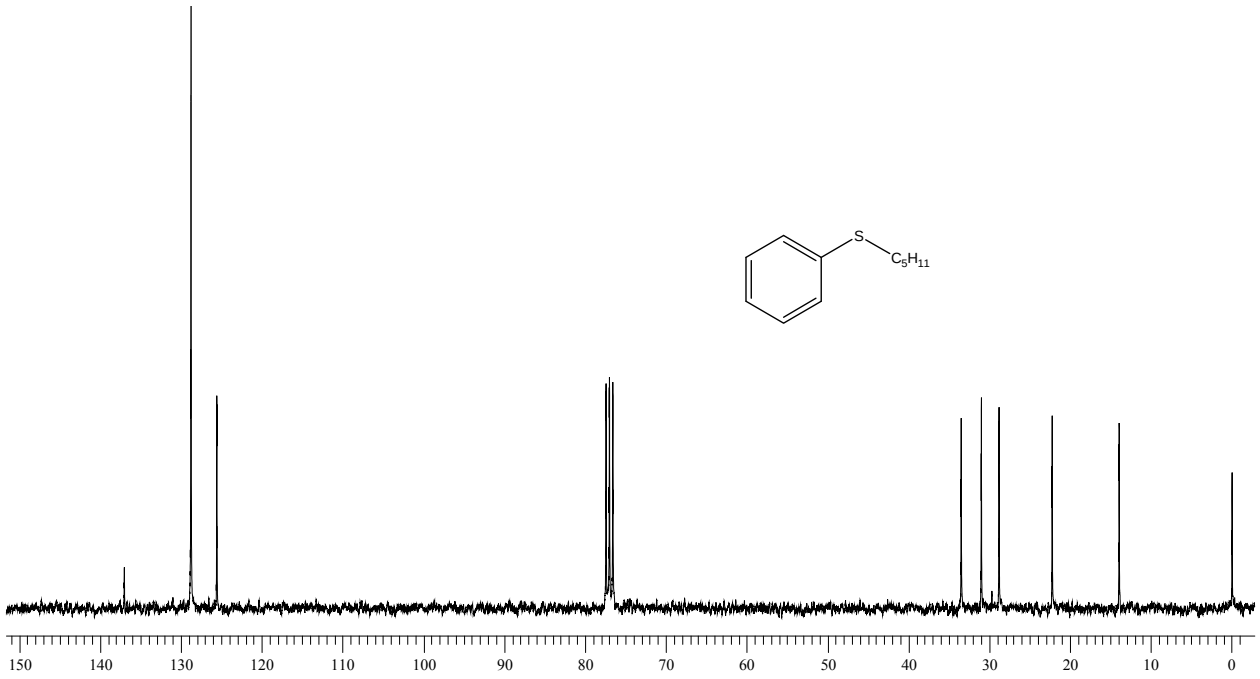


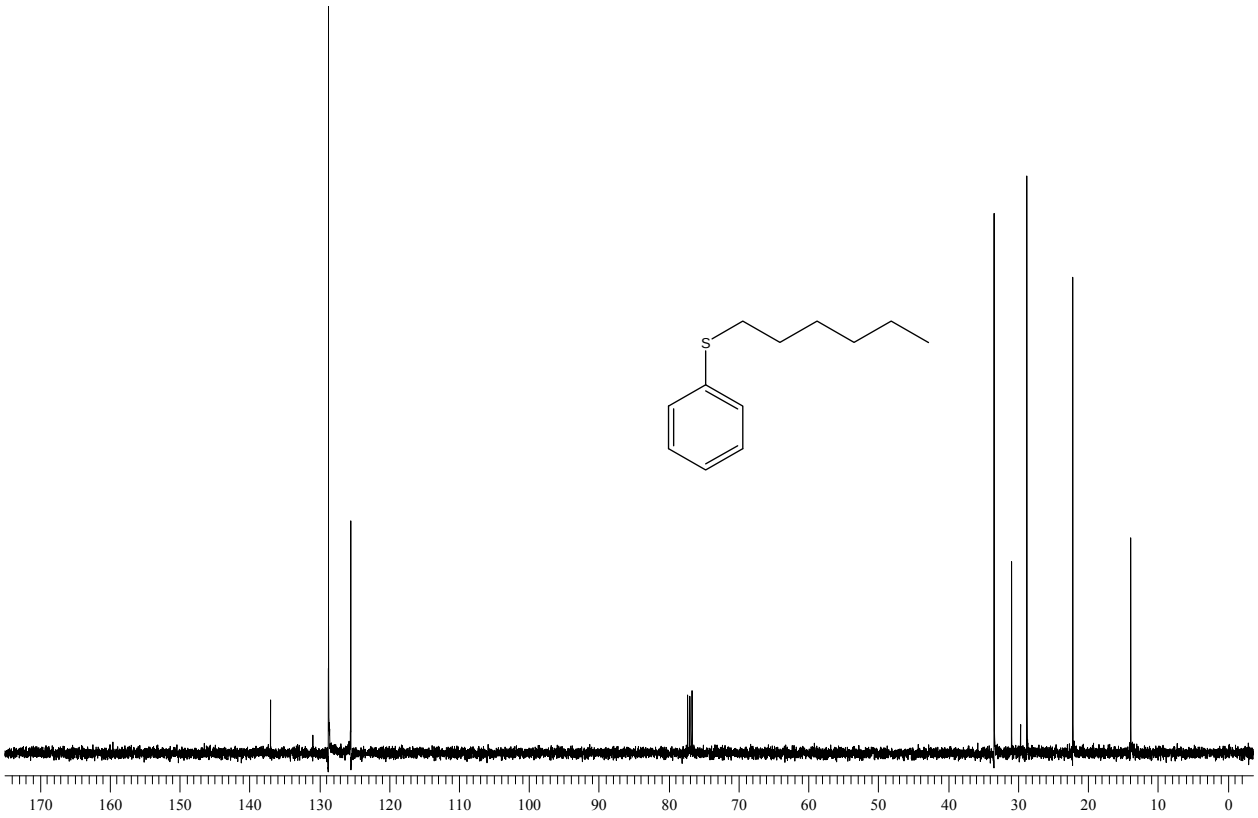


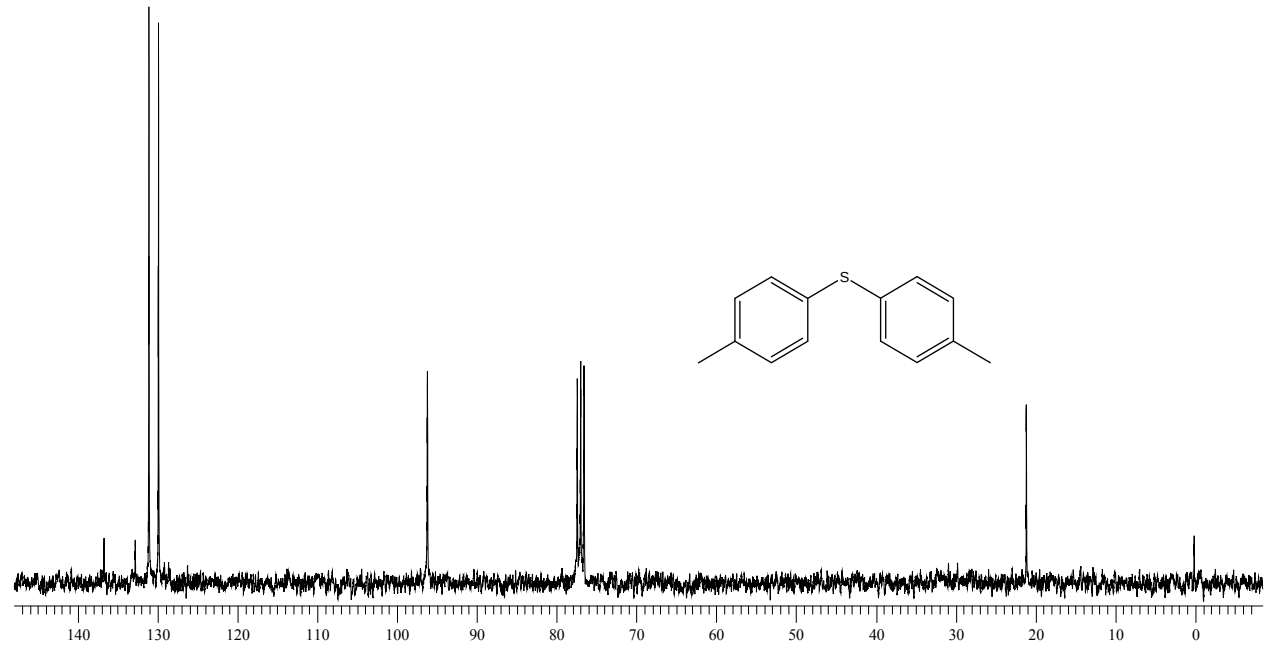


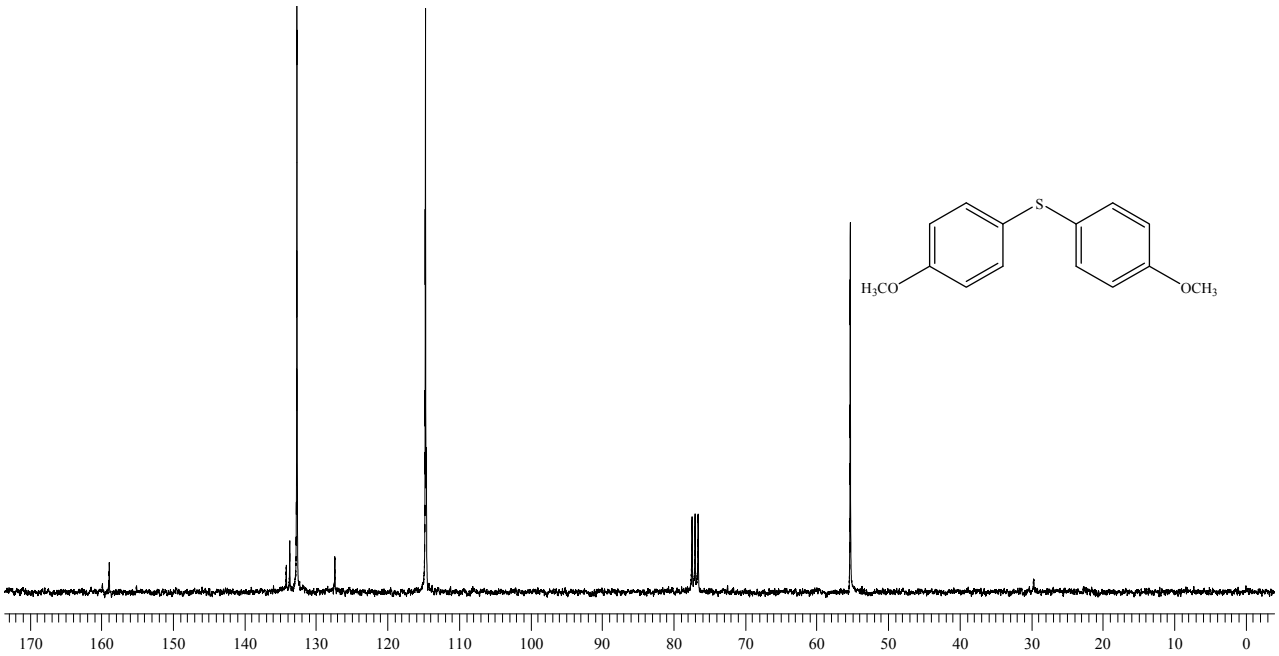


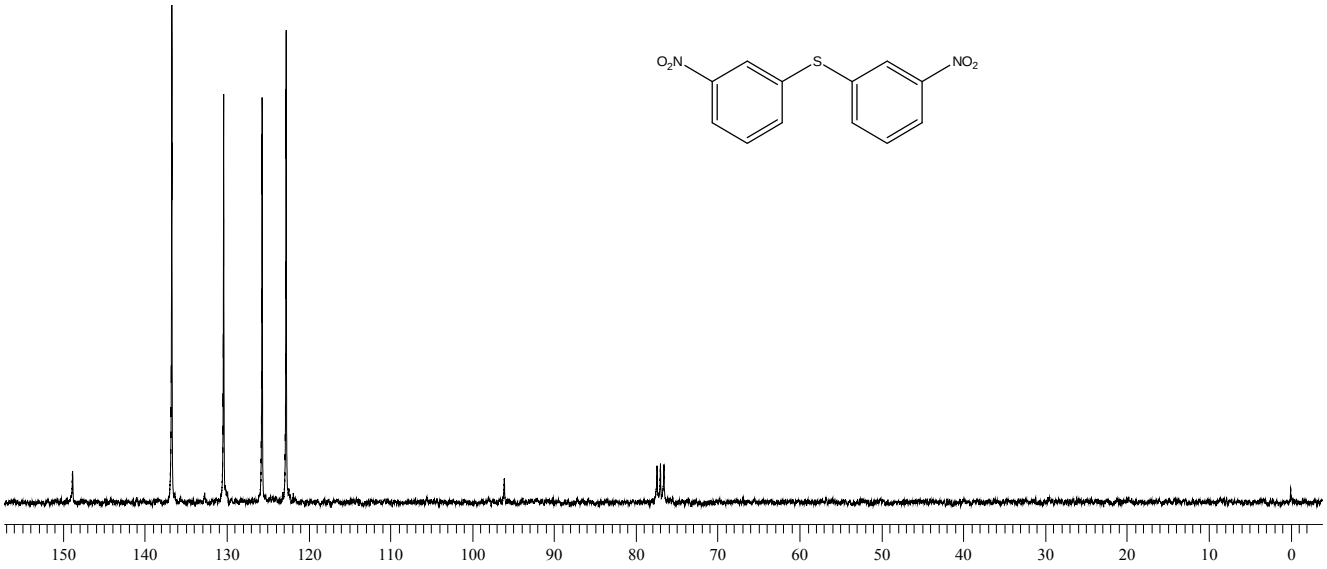


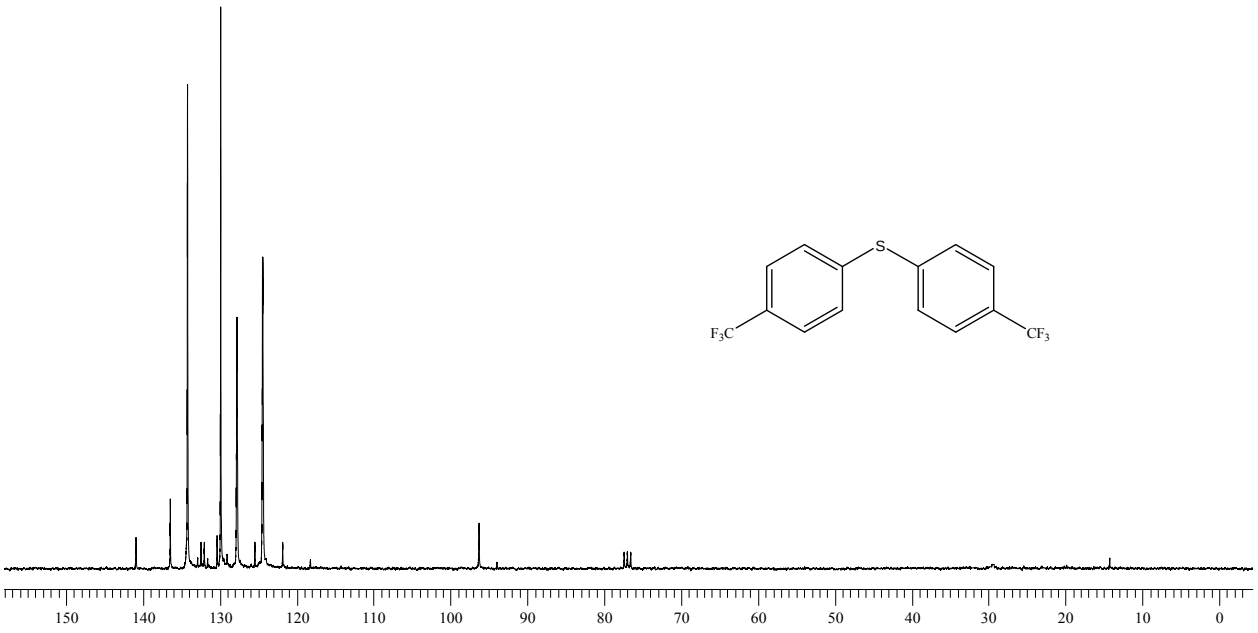


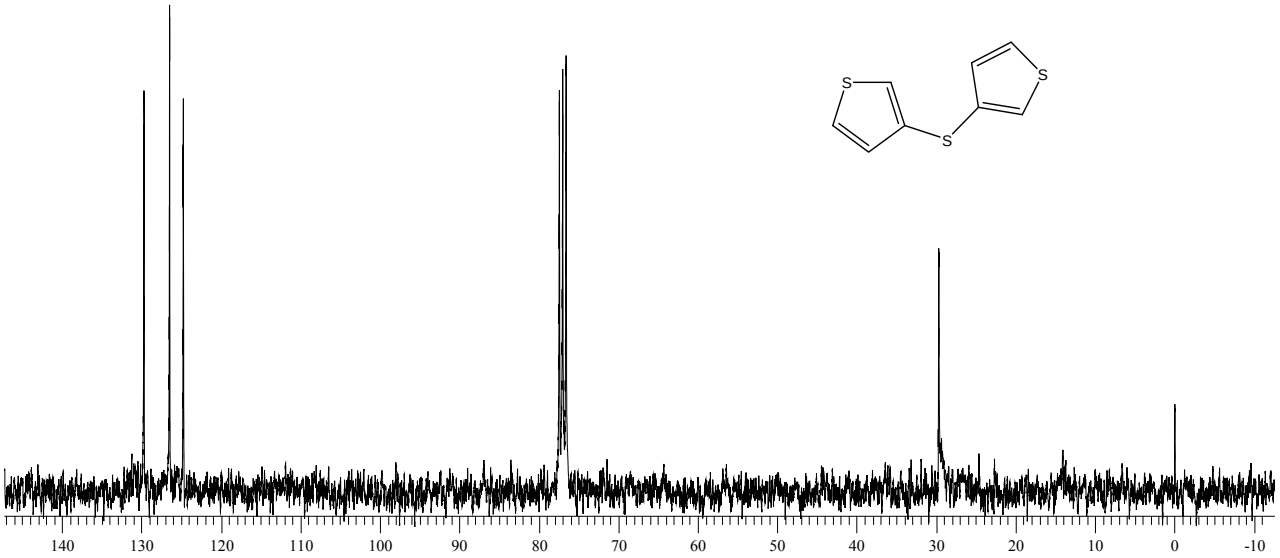


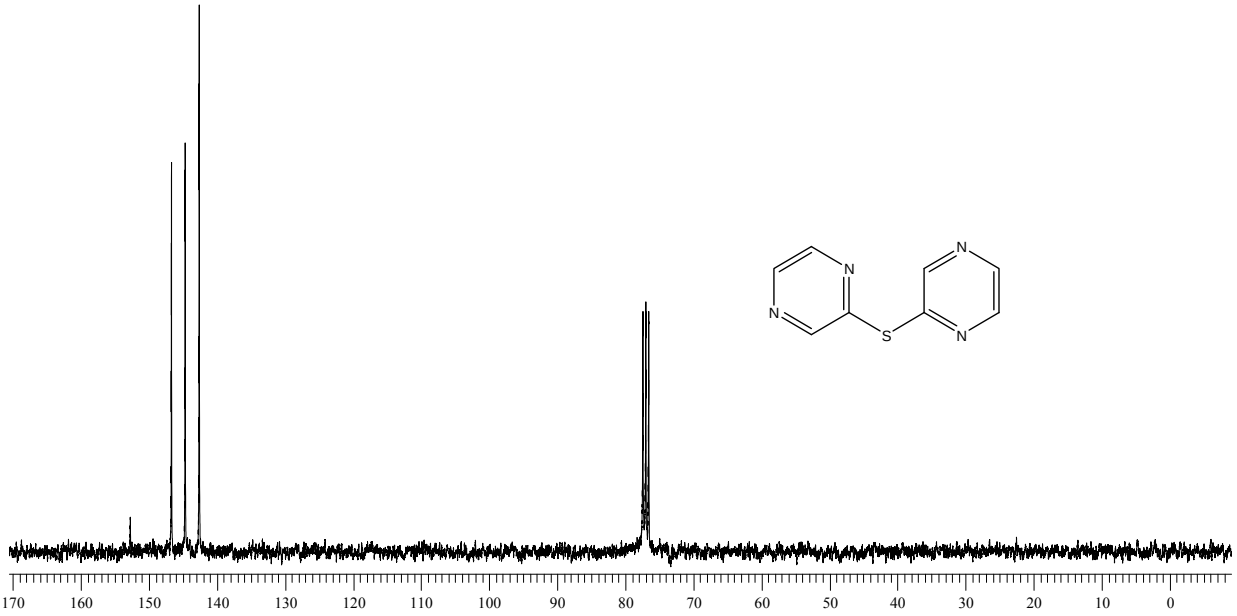












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