Electronic Supplementary Material (ESI) for Green Chemistry.


# Supplementary Information

## CuI-anchored onto mesoporous SBA-16 functionalized by aminated 3-glycidyloxypropyltrimethoxysilane with thiosemicarbazide (SBA-16/ GPTMS-TSC-CuI): a heterogeneous mesostructured catalyst for S-arylation reaction under solvent-free conditions

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**Experimental**

***General***

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products and the progress of the reactions were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The NMR spectra were recorded on Brucker Avance 400 MHz instruments in $CDCl_3$ and DMSO-$d_6$ as solvent. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in m/z (rel %). All the yields refer to isolated products after purification by thin layer chromatography or recrystallization from ethanol. In addition, the structures of all of prepared products were well corroborated by surveying their high-field $^{1}H$ NMR and $^{13}C$ NMR spectral data and comparison of their melting points with known compounds.

**Diphenyl sulfide[1] (1S)**

Diphenyl sulfide from thiourea (0.176 g, 95%) and $S_8$ (0.182 g, 98%). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.34-7.31 (m, 5H), 7.29-7.25 (m, 3H), 7.23-7.19 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 135.9, 131.2, 129.4, 127.2; MS (70 eV, EI), *m/z* (%): 186 ($M^+$, 12 %), 184 (M-2, 100%), 108 ($C_6H_4S$, 90%), 76 ($C_6H_4$, 42%), 65 ($C_5H_5$, 40%), 51 ($C_4H_3$, 28%).

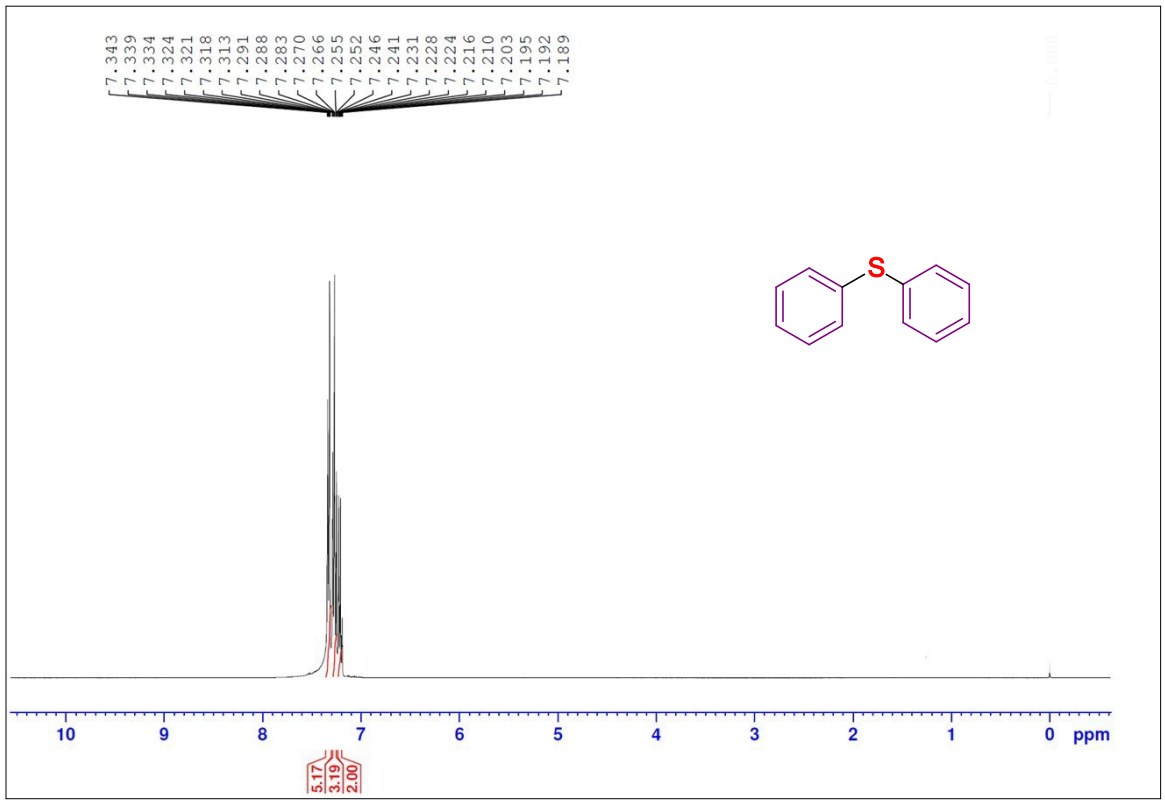


**Figure 1**: $^1$H NMR (400 MHz, $CDCl_3$) of Diphenyl sulfide (**1S**).

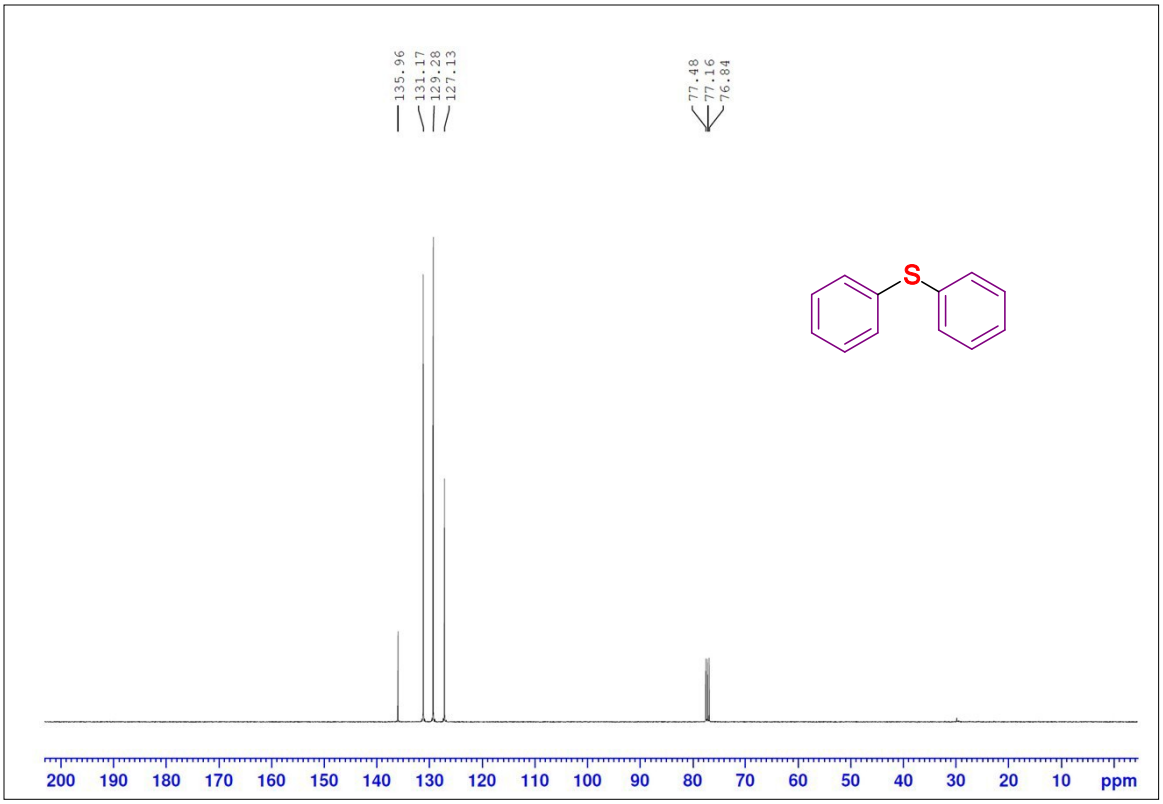


**Figure 2**: $^{13}C$ NMR (100 MHz, $CDCl_3$) of Diphenyl sulfide (**1S**).

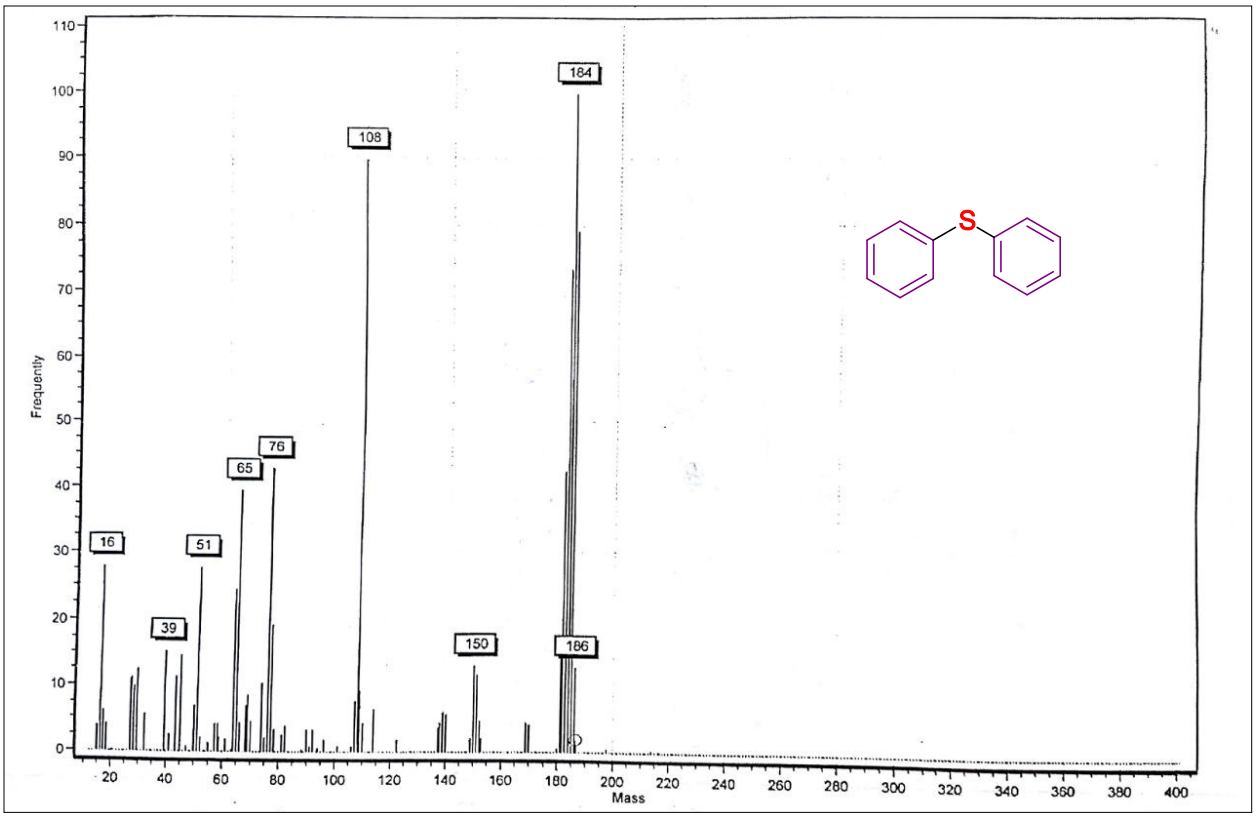


**Figure 3**: Mass spectrum of Diphenyl sulfide (**1S**).

**Bis(4-methoxyphenyl)sulfane[1] (2S)**

Bis(4-methoxyphenyl)sulfane from thiourea (0.172g, 70%) and $S_8$ (0.201 g, 82%). Yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.27 (d, *J* = 8.8 Hz, 4 H, Ar-H), 6.83 (d, *J* = 8.8 Hz, 4 H, Ar-H), 3.78 (s, 6 H, $OCH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 159.1, 132.9, 127.6, 114.9, 55.5; MS (70 eV, EI), *m/z* (%): 246 ($M^+$, 5 %), 243 (M-2, 65%), 140 ($C_7H_7OS$, 23 %), 77 ($C_6H_5$, 80).

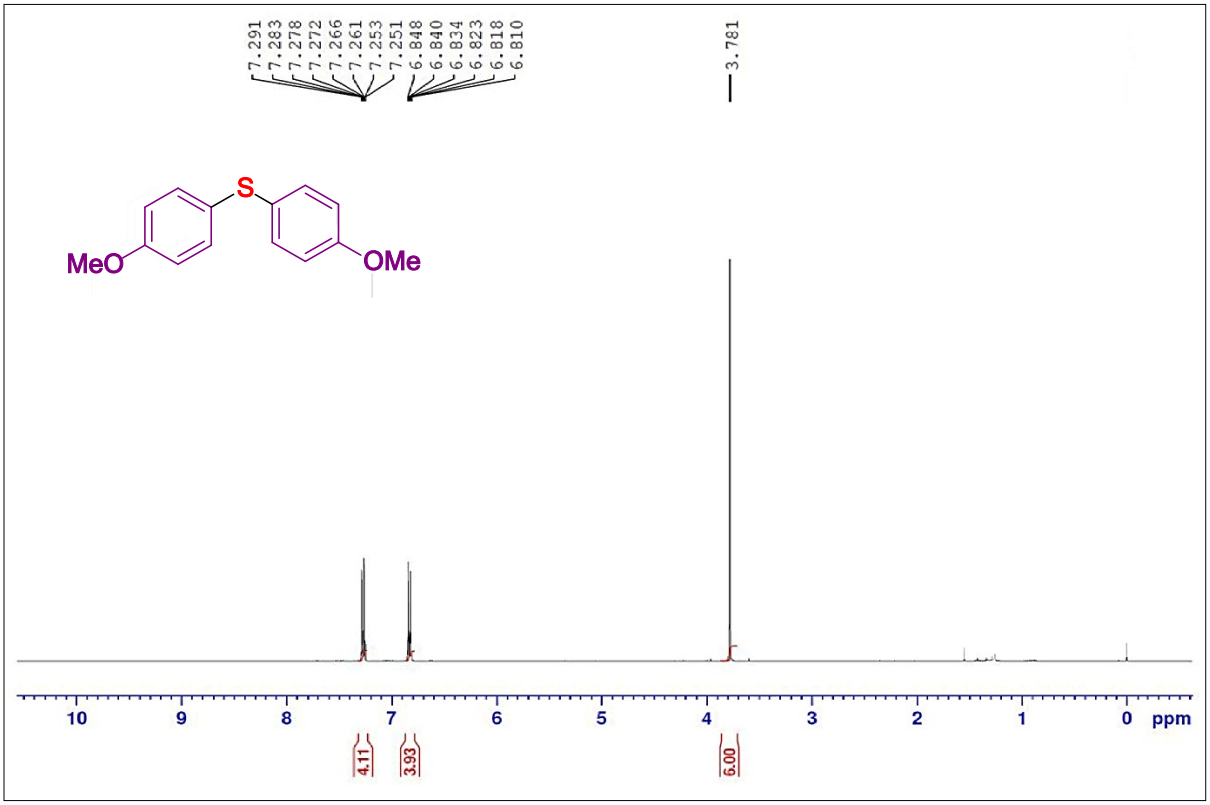


**Figure 4**: $^1$H NMR (400 MHz, $CDCl_3$) of Bis(4-methoxyphenyl)sulfane (**2S**).

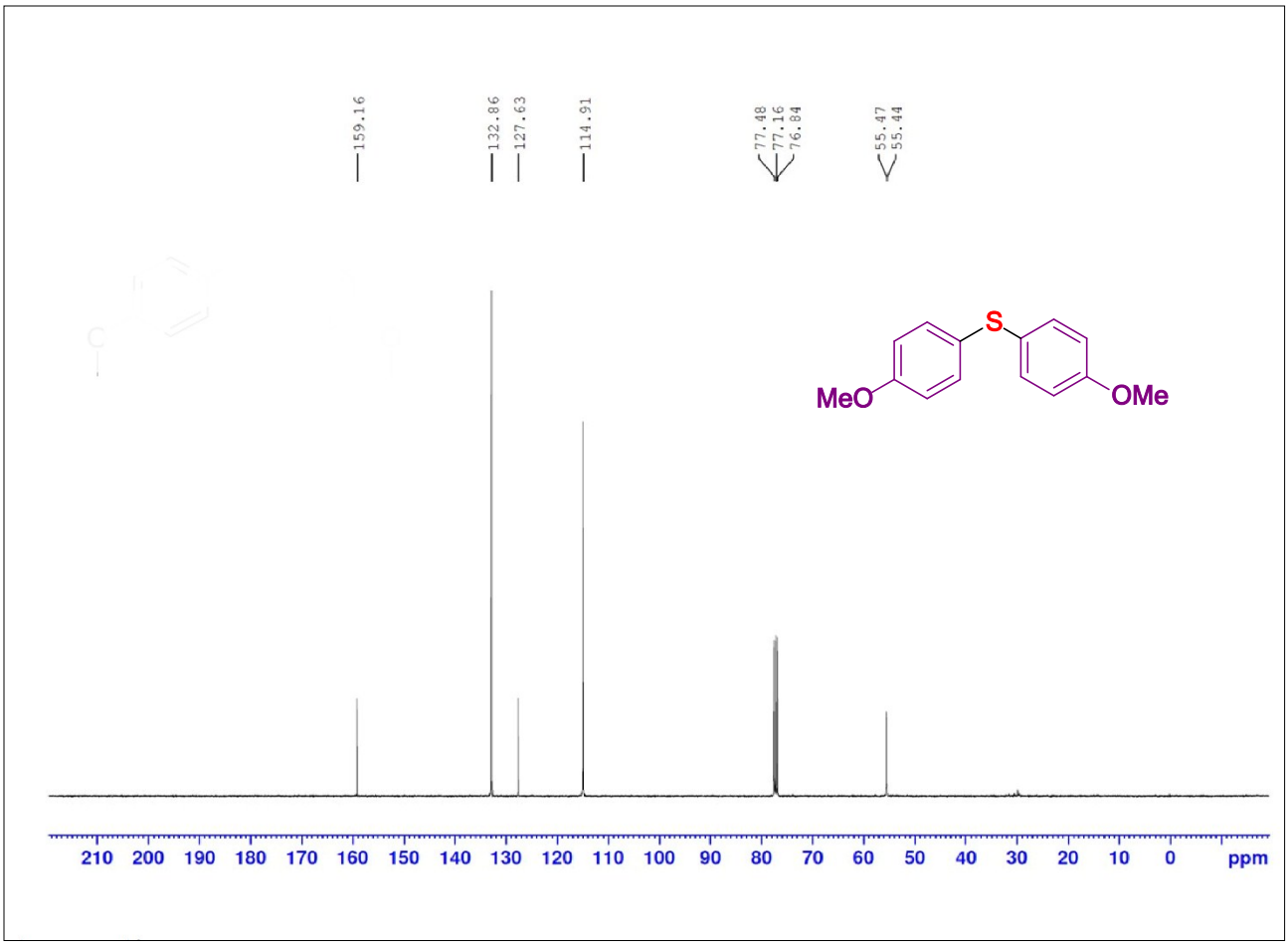


**Figure 5**: $^{13}C$ NMR (100 MHz, $CDCl_3$) of Bis(4-methoxyphenyl)sulfane (**2S**).

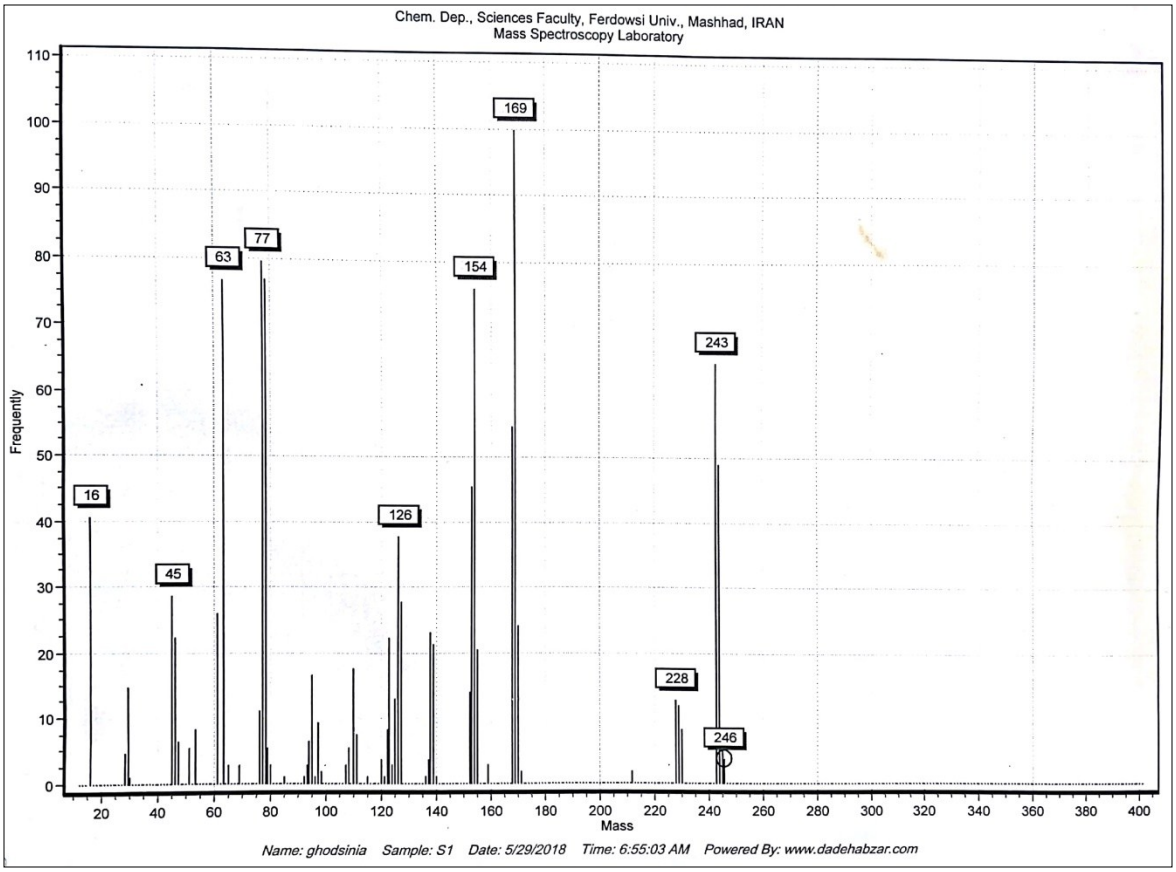


**Figure 6**: Mass spectrum of Bis(4-methoxyphenyl)sulfane (**2S**).

**Di-(*p*-tolyl) sulfane[2] (3S)**

Di-(*p*-tolyl) sulfane from thiourea (0.158 g, 74%) and $S_8$ (0.182 g, 85%). Colorless oil; (Lit. 43–46 °C); $^1$H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.23 d, *J* = 8.4 Hz, 4 H, Ar-H), 7.10 (d, *J* = 7.6 Hz, 4H, ArH), 2.32 (s, 6H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 137.1, 132.8, 131.2, 130.1, 21.3); MS (70 eV, EI), *m/z* (%): 214 ($M^+$, 7%), 212 ( M-2, 50%), 123 ( $C_7H_7S$, 15 %), 91 ($C_7H_7$, 67%).

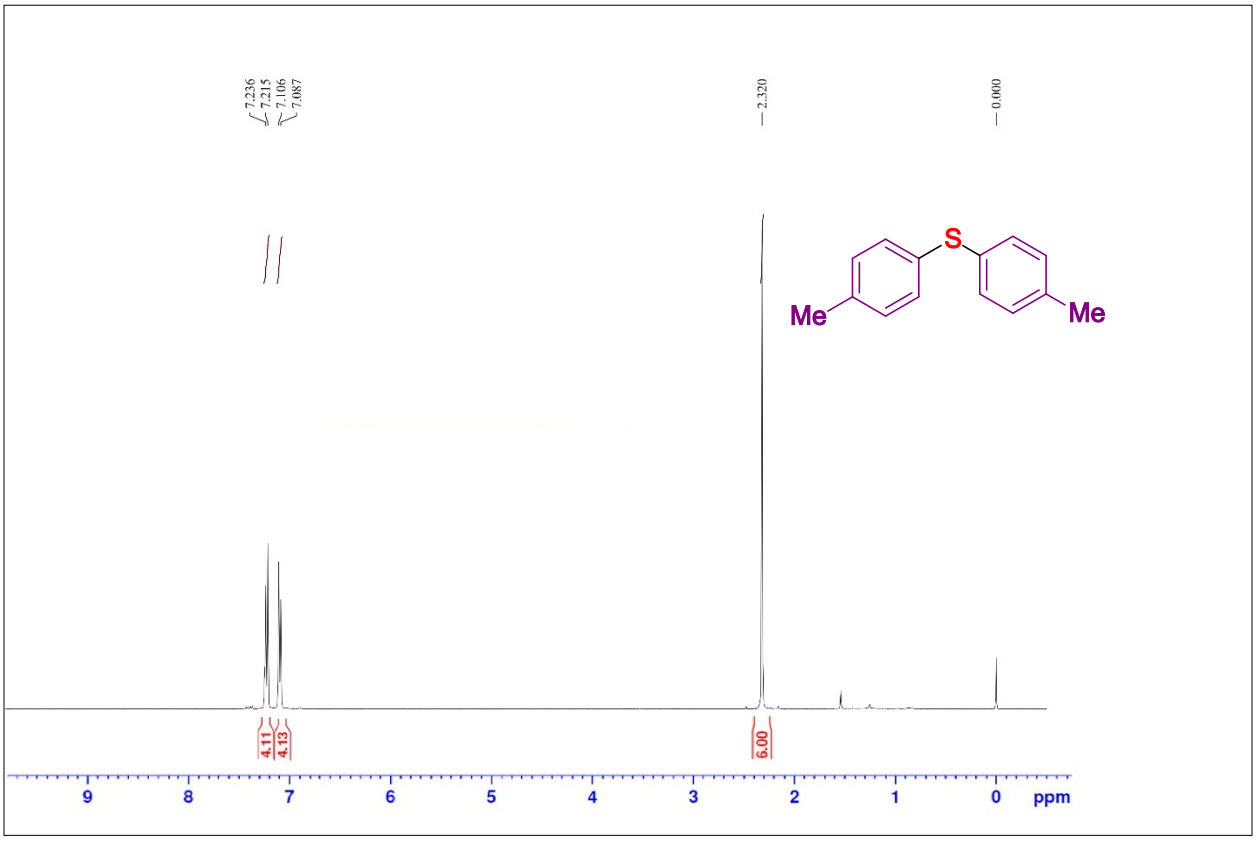


**Figure 7**: $^1$H NMR (400 MHz, $CDCl_3$) of Di-(*p*-tolyl) sulfane (**3S**).

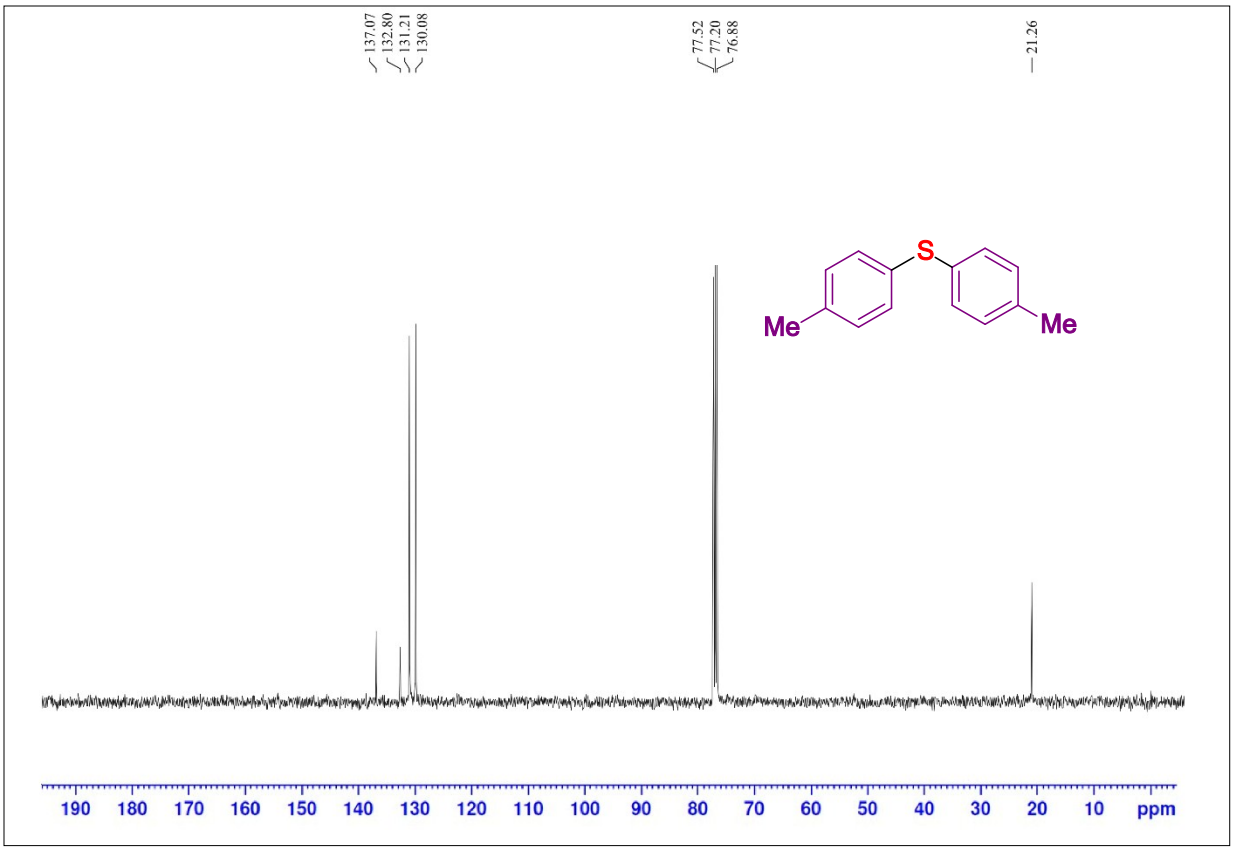


**Figure 8**: $^{13}$CNMR (100 MHz, $CDCl_3$) of Di-(*p*-tolyl) sulfane (**3S**).

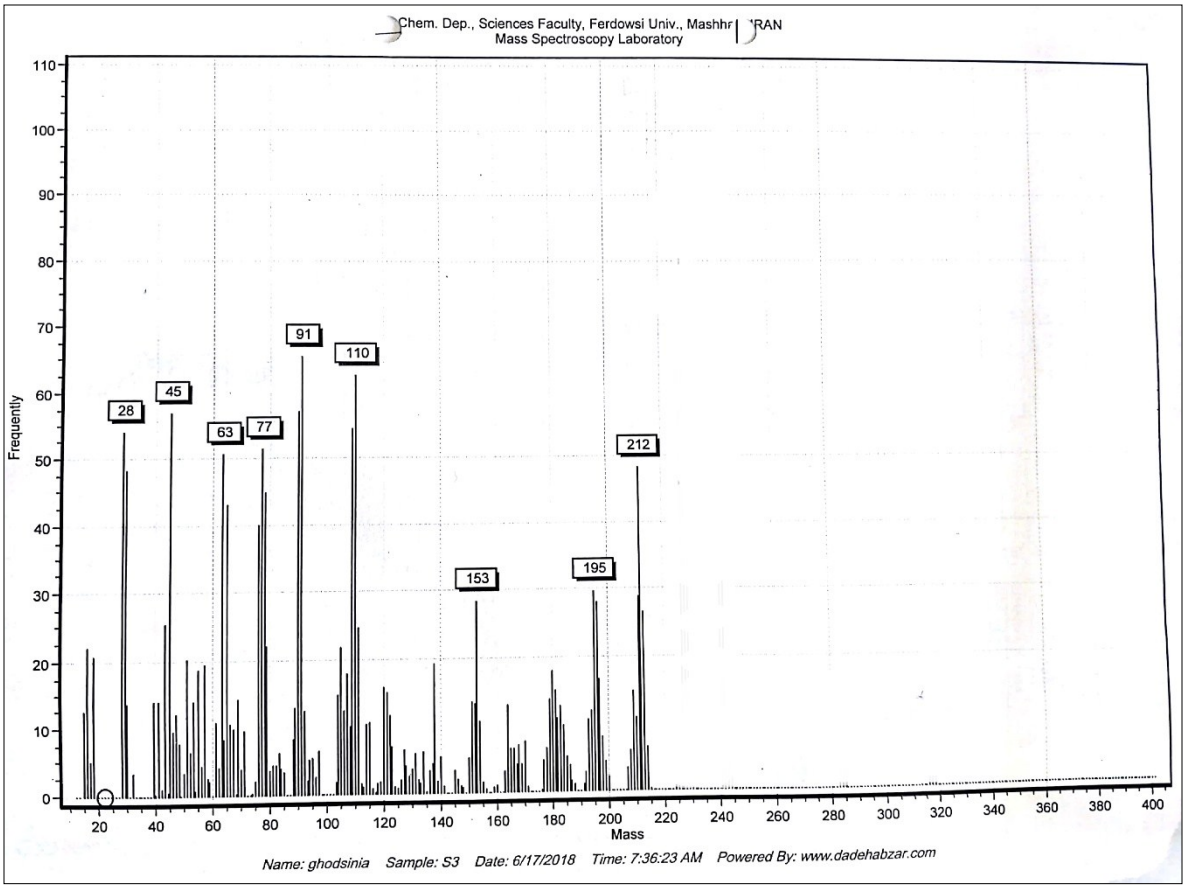


**Figure 9**: Mass spectrum of Di-(*p*-tolyl) sulfane (**3S**).

**4,4'-Thiodibenzonitrile[3] (4S)**

4,4'-Thiodibenzonitrile from thiourea (0.198 g, 84%) and $S_8$ (0.217 g, 91%). Yellow solid; mp 134-135 °C (Lit. 134 – 135 °C); $^1$H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.43 (d, *J* = 8.8 Hz, 4 H, Ar-H), 7.19 (d, *J* = 8.4 Hz, 4 H, Ar-H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 140.6, 133.0, 131.2, 118.2, 111.4.

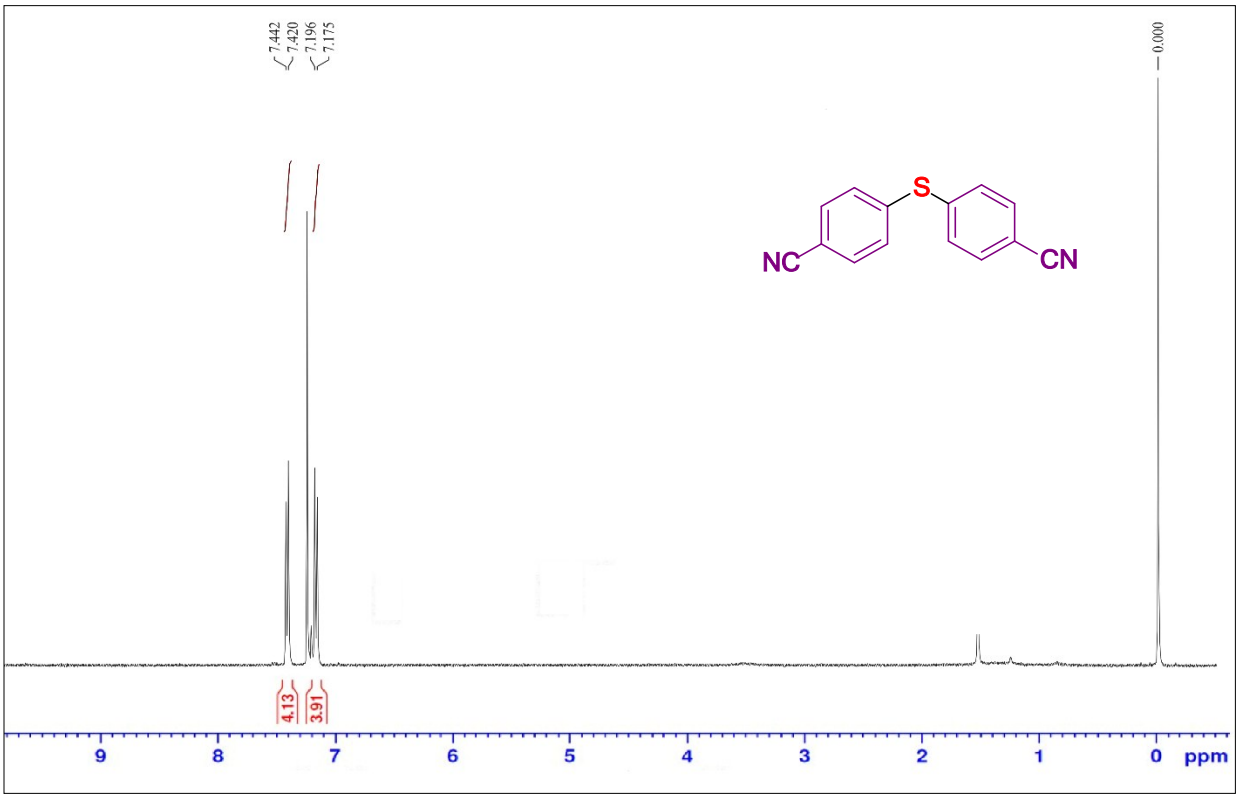


**Figure 10**: $^1$H NMR (400 MHz, $CDCl_3$) of 4,4'-Thiodibenzonitrile (**4S**).

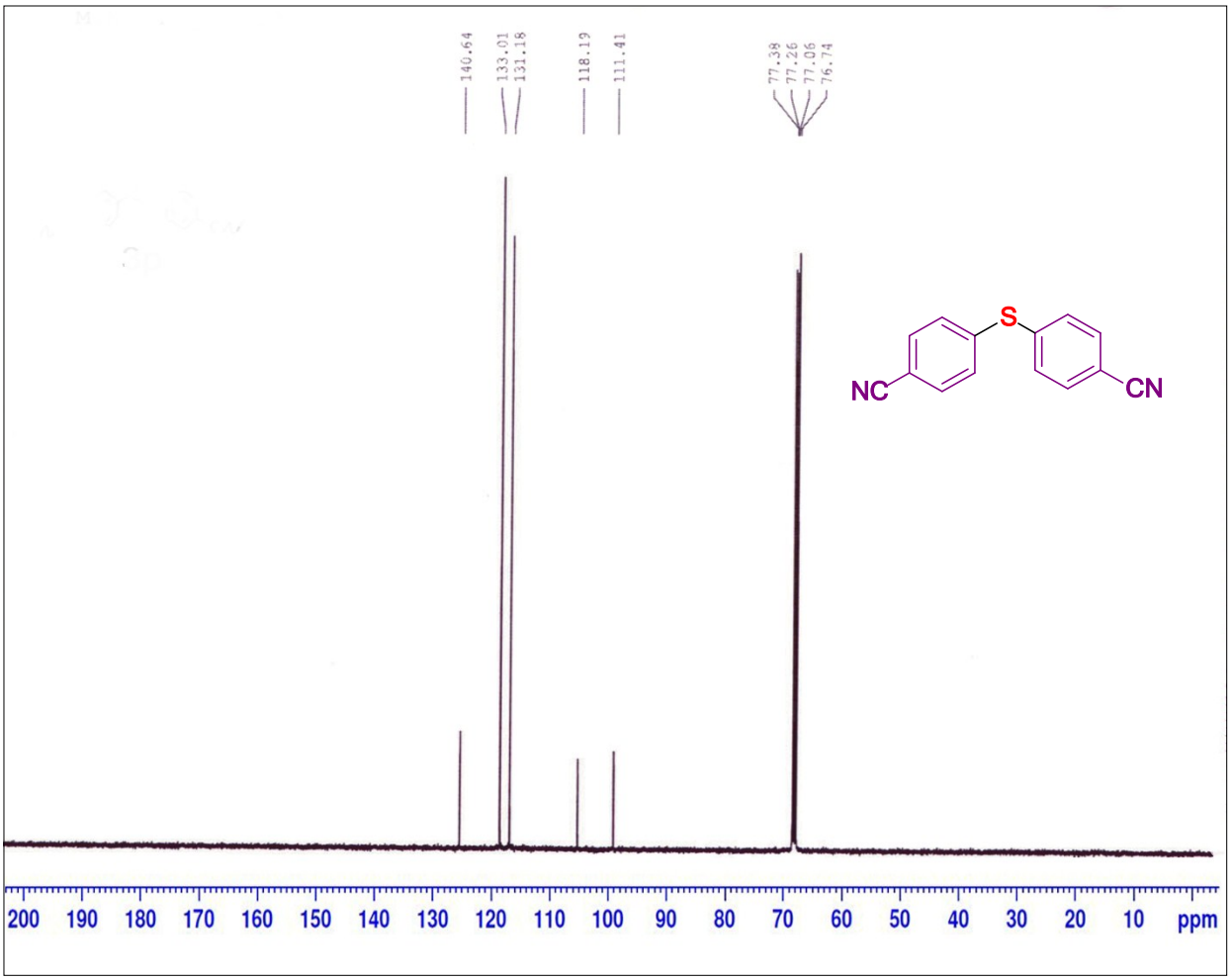


**Figure 11**: $^{13}C$ NMR (100 MHz, $CDCl_3$) of 4,4'-Thiodibenzonitrile (**4S**).

**Bis (4-nitrophenyl) sulfane[4] (5S)**

Bis (4-nitrophenyl) sulfane from thiourea (0.231g, 84%) and $S_8$ (0.245 g, 89%). Yellow solid; mp 149-150 °C (Lit. 149-150 °C); $^1$H NMR (400 MHz, DMSO-$d_6$): δ [ppm] = 7 δ 8.25 (dd, $J$ = 8.4, 1.6 Hz, 4H), 7.64 (dd, $J$ = 8.4, 2.0 Hz, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ [ppm] = 146.7, 142.2, 131.3, 124.8; MS (70 eV, EI), *m/z* (%): 276 ($M^+$, 20%), 275 (M-1, 40%), 155 ($C_6H_5NO_2S$, 65%), 123 ($C_6H_5NO_2$, 90%).

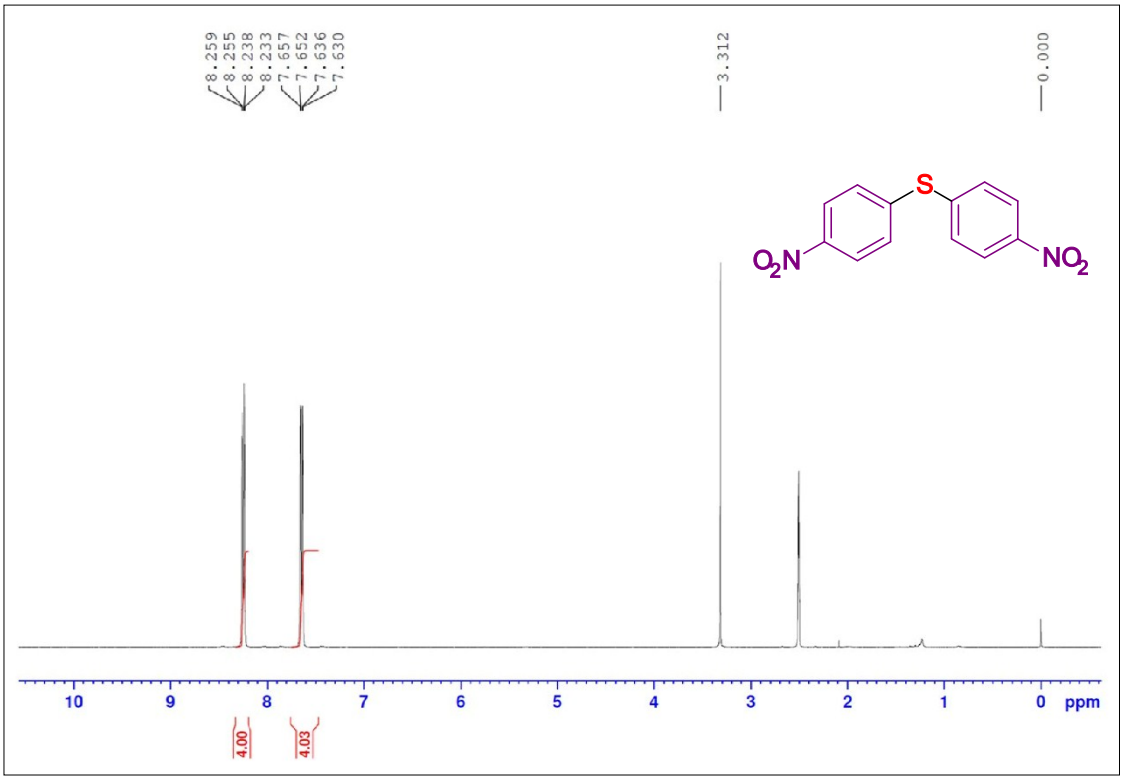


**Figure 12**: $^1$H NMR (400 MHz, DMSO-$d_6$) of Bis (4-nitrophenyl) sulfane (**5S**).

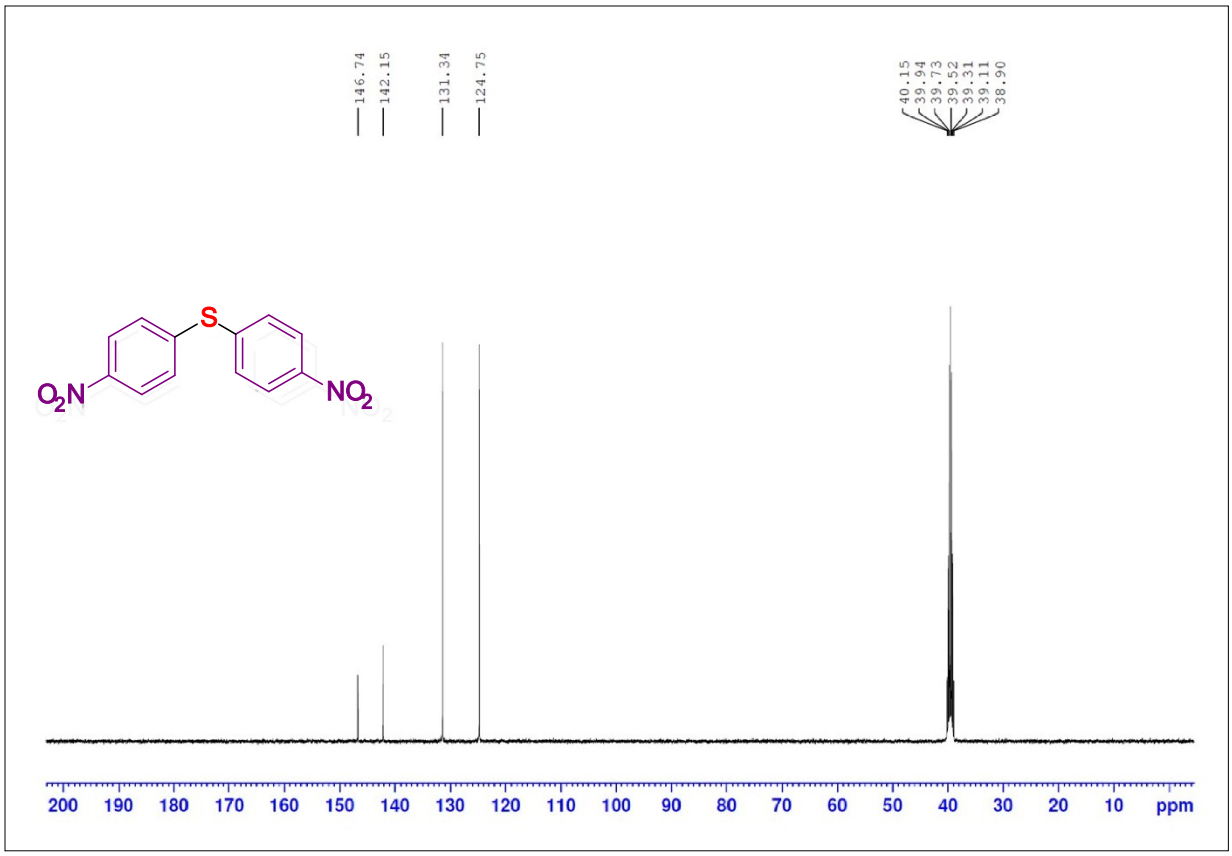


**Figure 13**: $^{13}C$ NMR (100 MHz, DMSO-$d_6$) of Bis (4-nitrophenyl) sulfane (**5S**).

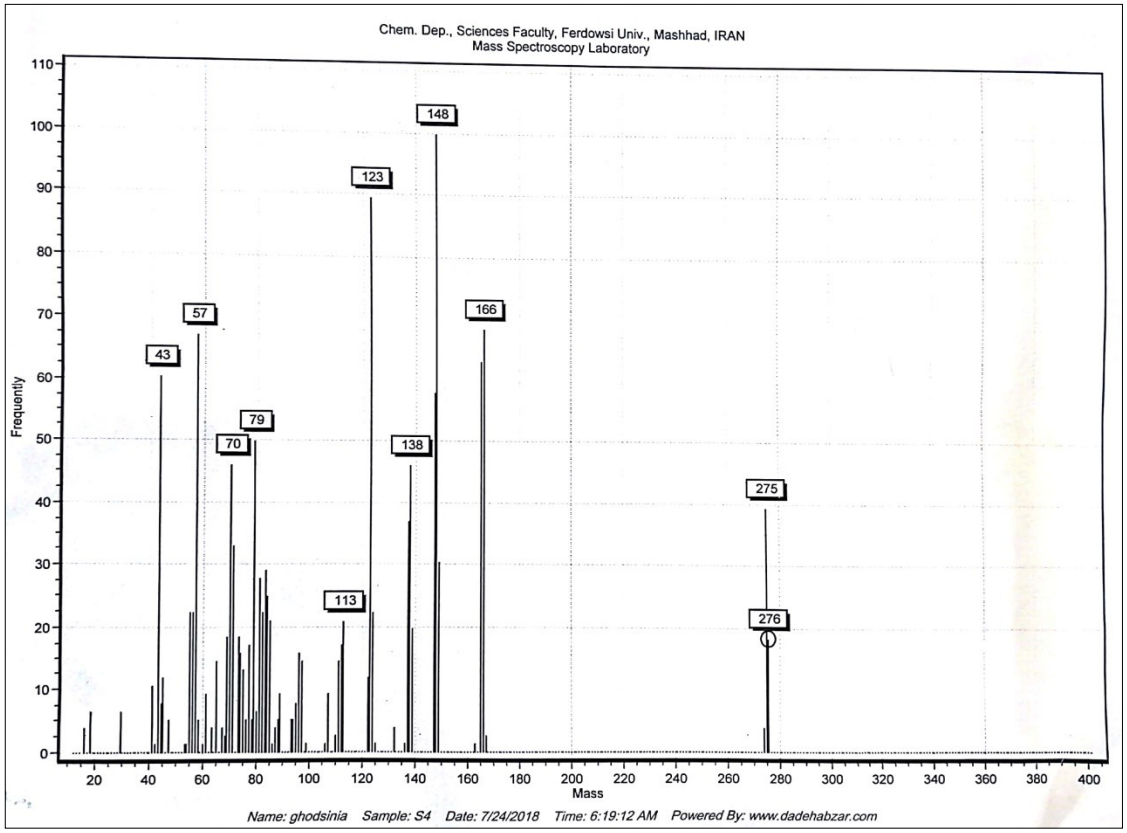


**Figure 14**: Mass spectrum of Bis(4-nitrophenyl) sulfane (**5S**).

**4,4'-Thiodianiline[5] (6S)**

4,4'-Thiodianiline from thiourea (0.177 g, 82%) and $S_8$ (0.185 g, 86%). Brown solid, mp 107-108 °C (Lit. 107-108 °C); $^1$H NMR (400 MHz, $CDCl_3$): δ [ppm] 7.15 (d, $J$ = 8.0 Hz, 4 H, Ar-H), 6.60 (d, $J$ = 8.0 Hz, 4 H, Ar-H), 3.67 (s, 4 H, $NH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 145.8, 132.9, 125.2, 115.9.

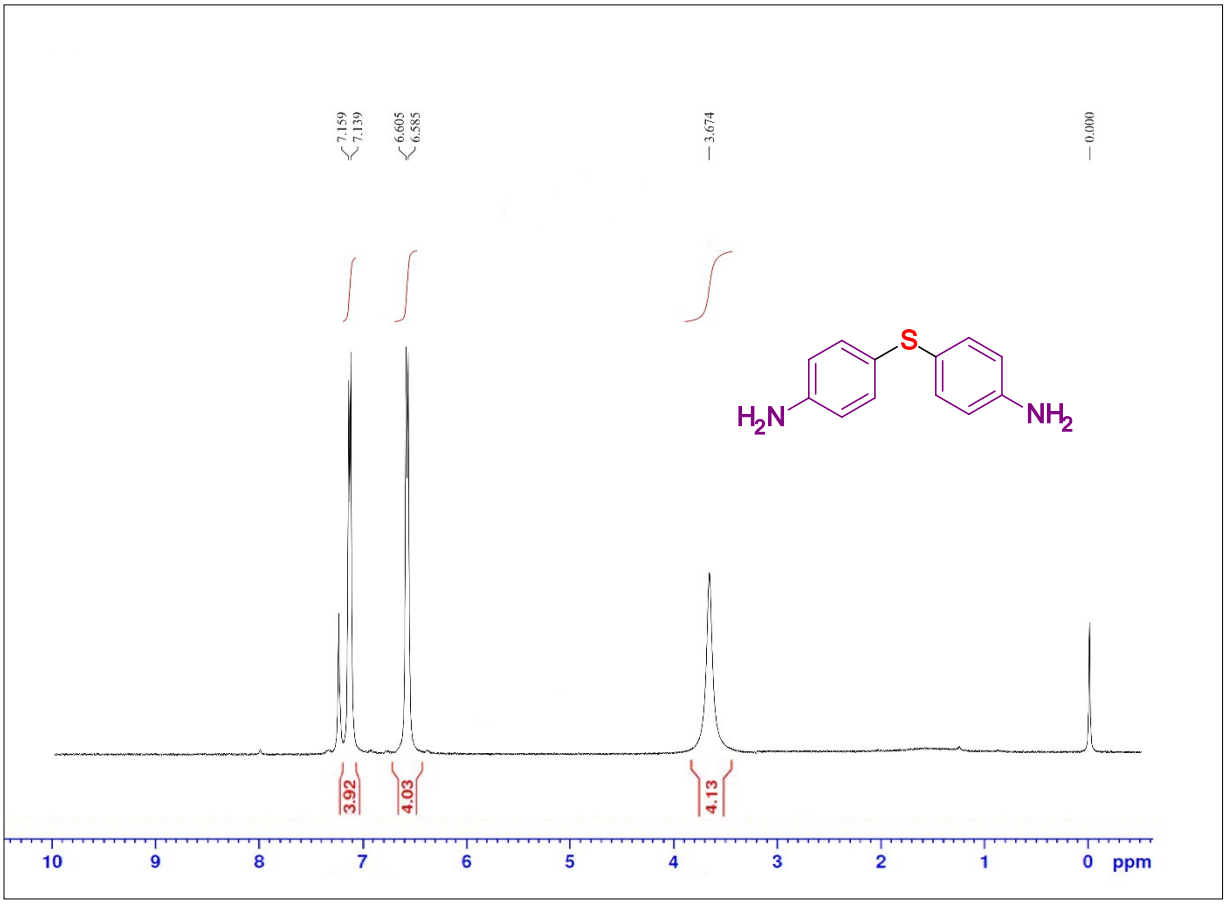

**Figure 15**: $^{1}H$ NMR (400 MHz, $CDCl_3$) of 4,4'-Thiodianiline **(7S)**.

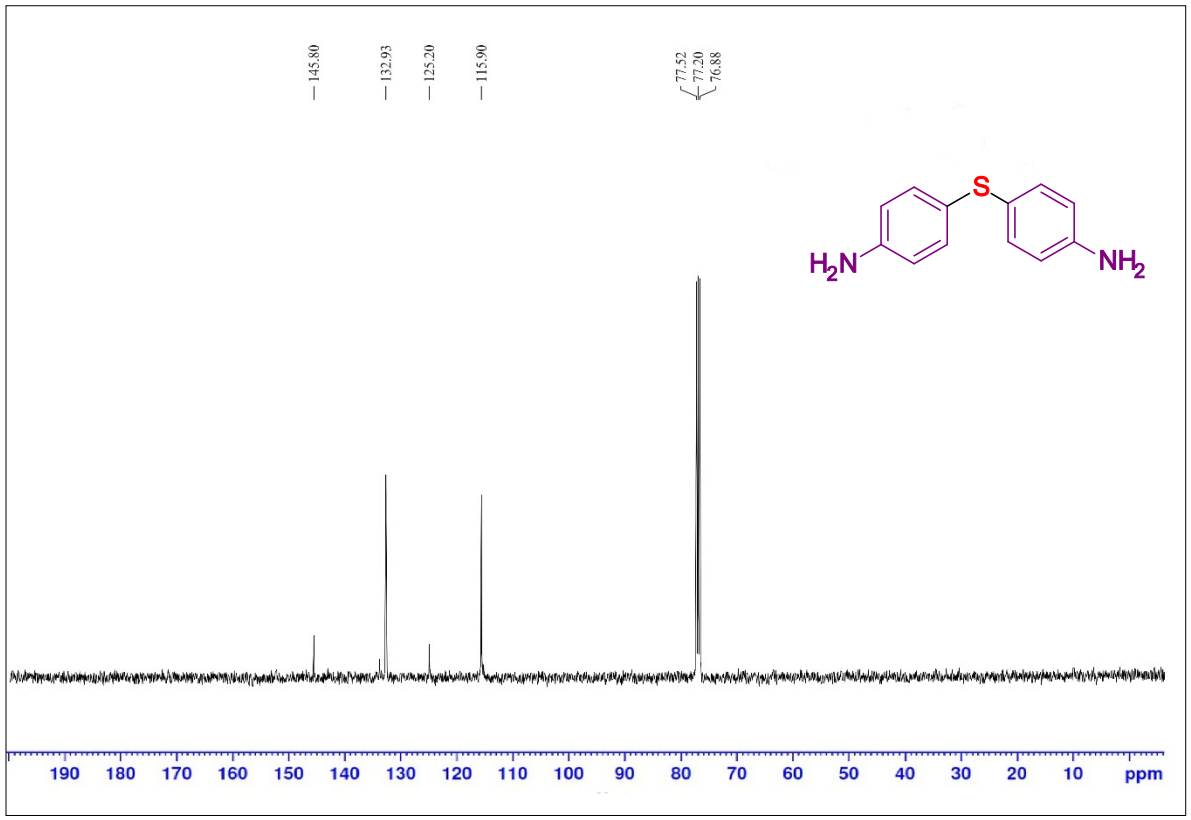


**Figure 16**: $^{13}C$ NMR (100 MHz, $CDCl_3$) of 4,4'-Thiodianiline (**7S**).

**4,4'-Thiodiphenol[6] (7S)**

4,4'-Thiodiphenol from thiourea (0.137 g, 63%) and $S_8$ (0.148 g, 68%). White solid; mp 151-153 °C (Lit. 150-153 °C); $^1$H NMR (400 MHz, (400 MHz, DMSO-$d_6$): δ [ppm] = 9.62 (s, 2H), 7.14 (d, $J$ = 8.4 Hz, 4H), 6.73 (d, $J$ = 8.4 Hz, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ [ppm] = 157.0, 132.7, 124.7, 116.3.

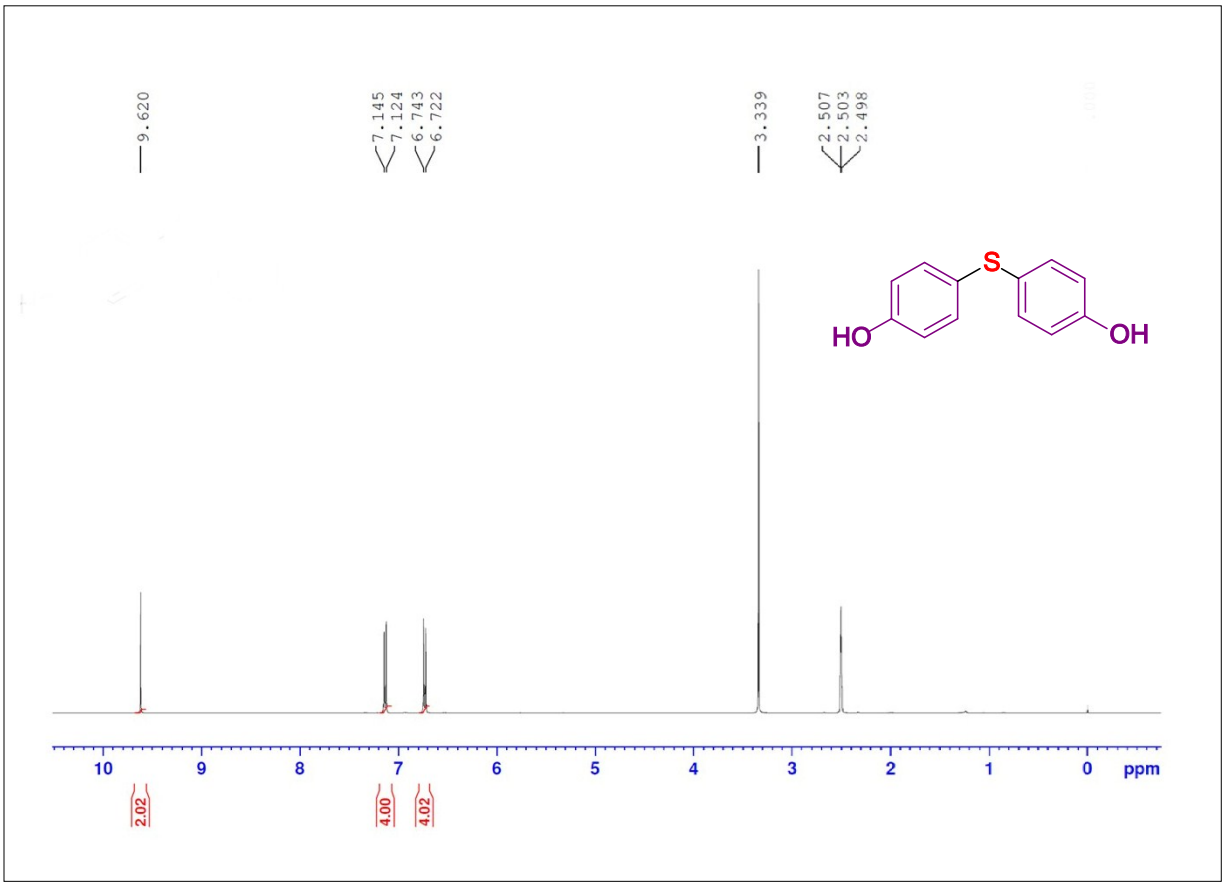


**Figure 17**: $^1$H NMR (400 MHz, DMSO-$d_6$) of 4,4'-Thiodiphenol (**7S)**.

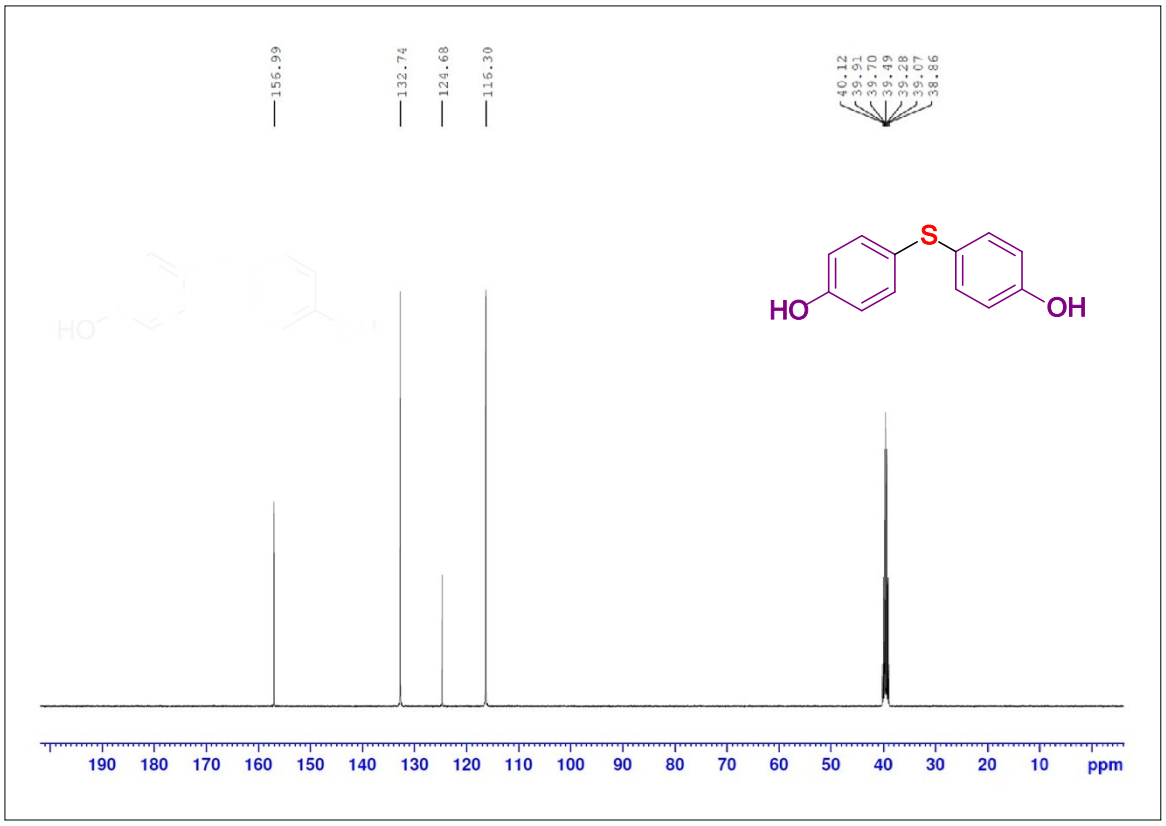


**Figure 18**: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 4,4'-Thiodiphenol (**7S**).

**Di (thiophen-2-yl) sulfane[7] (8S)**

Di (thiophen-2-yl) sulfane from thiourea (0.146 g, 74%) and $S_8$ (0.168 g, 85%). Yellow liquid. $^1H$ NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.63–7.53 (m, 2H), 7.45–7.34 (m, 2H), 7.27–7.11 (m, 2H); $^{13}C$ NMR (100MHz, $CDCl_3$): δ [ppm] = 135.5, 132.7, 129.6, 137.47.

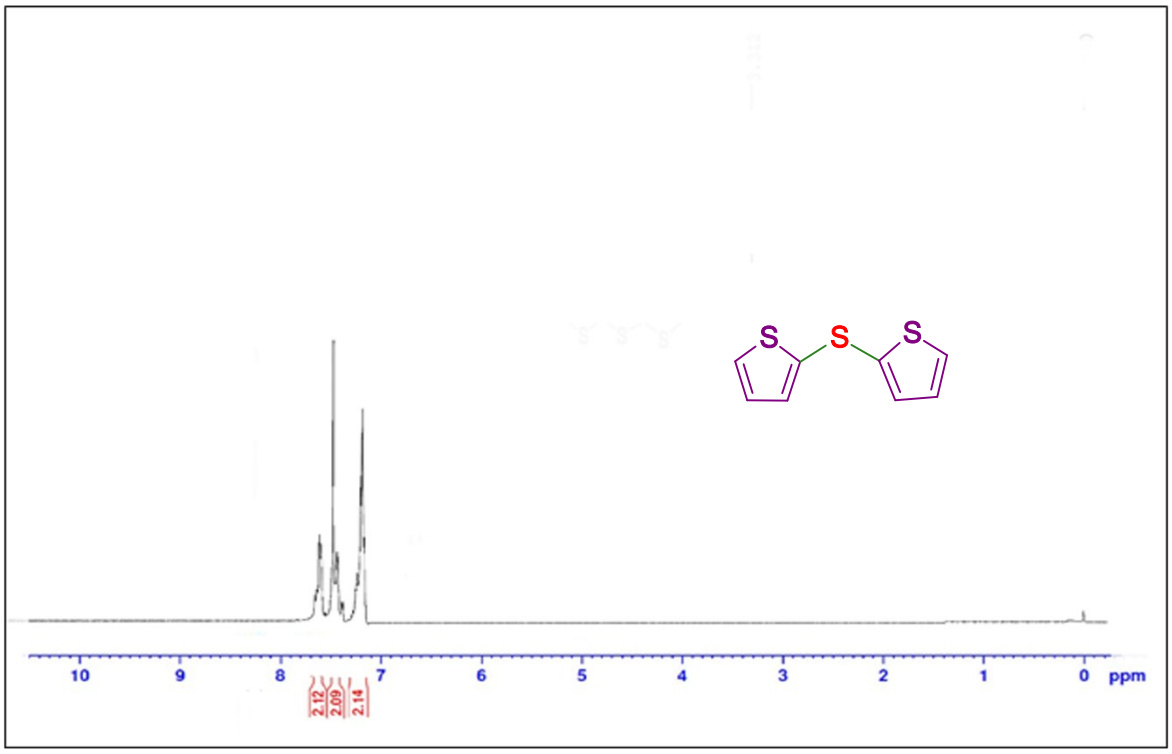


**Figure 19**: $^1H$ NMR (400 MHz, $CDCl_3$) of Di (thiophen-2-yl) sulfane (**8S**).

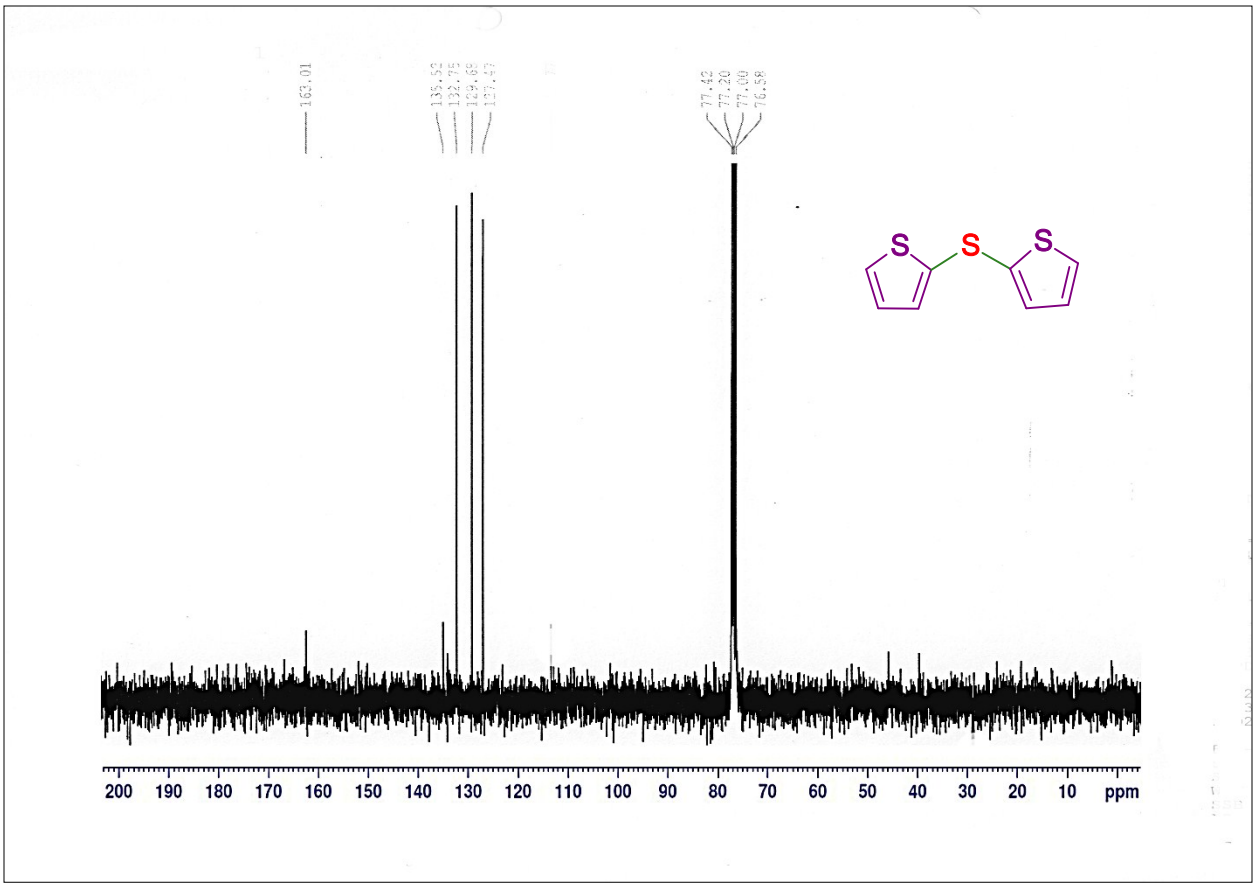


**Figure 20**: $^{13}C$ NMR (100 MHz, $CDCl_3$) of Di (thiophen-2-yl) sulfane (**8S**).

**Di(naphthalen-1-yl)sulfane[8] (9S)**

Di(naphthalen-1-yl)sulfane from thiourea (0.214 g, 75%) and $S_8$ (0.206 g,72%). White solid. mp 156-157 °C (Lit. 156-158 °C), $^1$H NMR (400 MHz, (400 MHz, $CDCl_3$): δ [ppm] = 8.43–8.40 (m, 2 H, Ar-H), 7.89–7.87 (m, 2 H, Ar-H), 7.78–7.76 (m, 2 H, Ar-H), 7.55–7.51 (m, 4 H, Ar-H), 7.32–7.30 (m, 4 H, Ar-H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 134.3, 132.8, 132.6, 130.1, 128.8, 128.2, 126.9, 126.6, 126.0, 125.3; MS (70 eV, EI), *m/z* (%): 286 ($M^+$, 8%), 285 (M-1, 52%), 282 (M-4, 90%), 160 ($C_{10}H_8S$, 70%), 127 ($C_{10}H_7$, 60%).

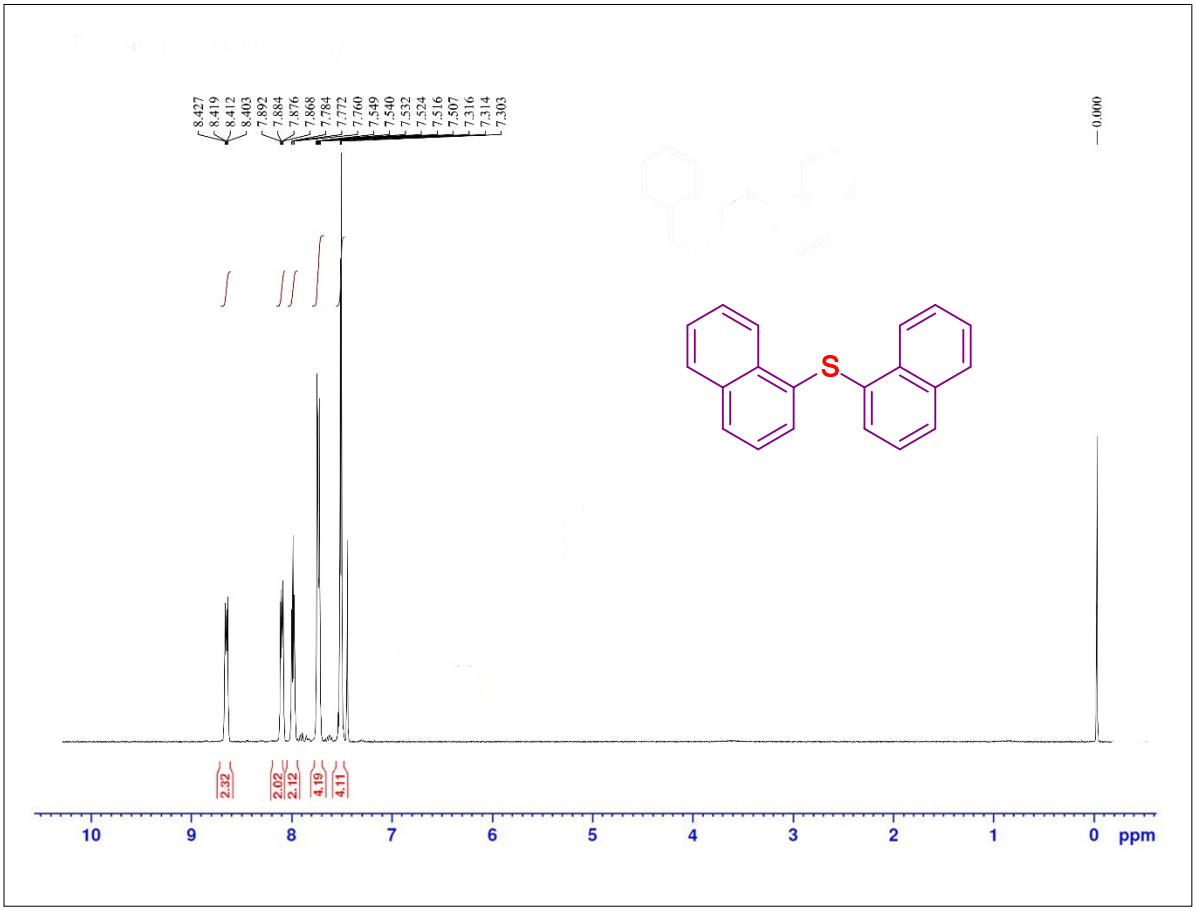


**Figure 21**: $^1$H NMR (400 MHz, $CDCl_3$) of Di(naphthalen-1-yl)sulfane (**9S**).

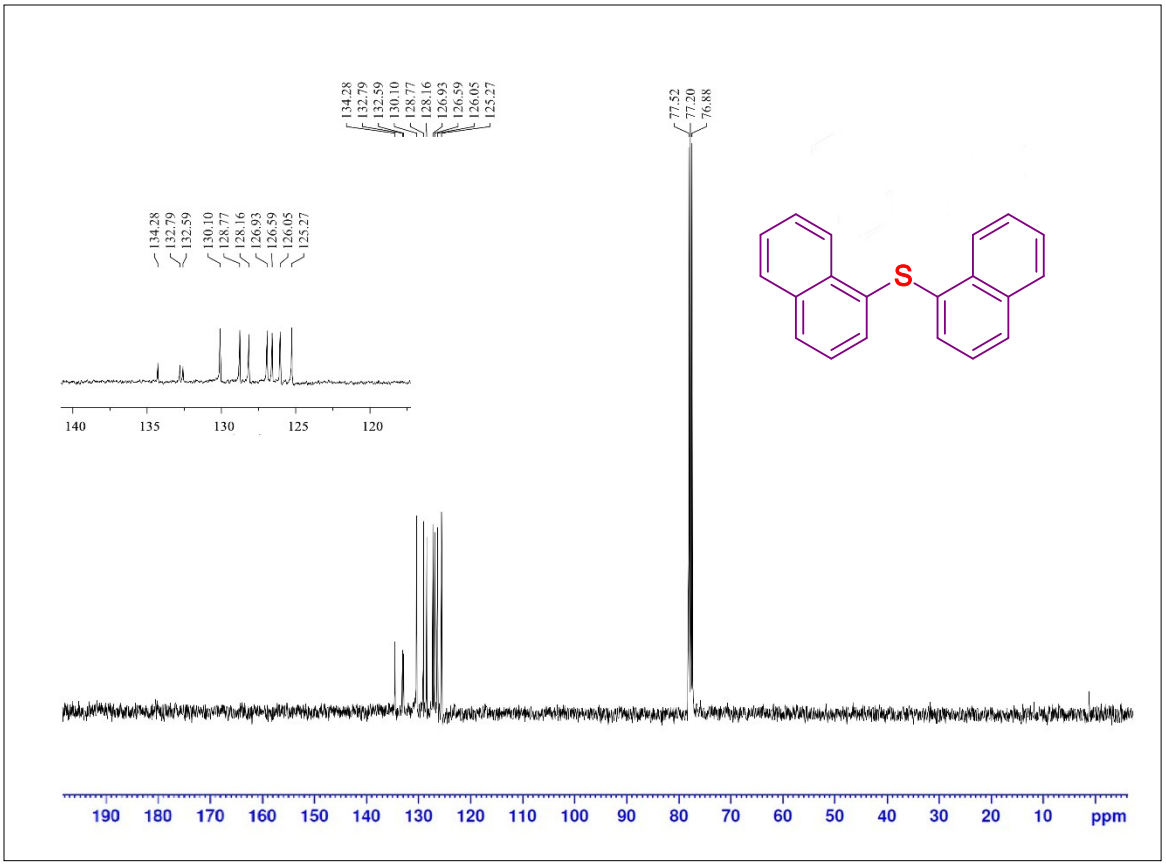


**Figure 22**: $^{13}C$ NMR (100 MHz, $CDCl_3$) of Di(naphthalen-1-yl)sulfane (**9S**).

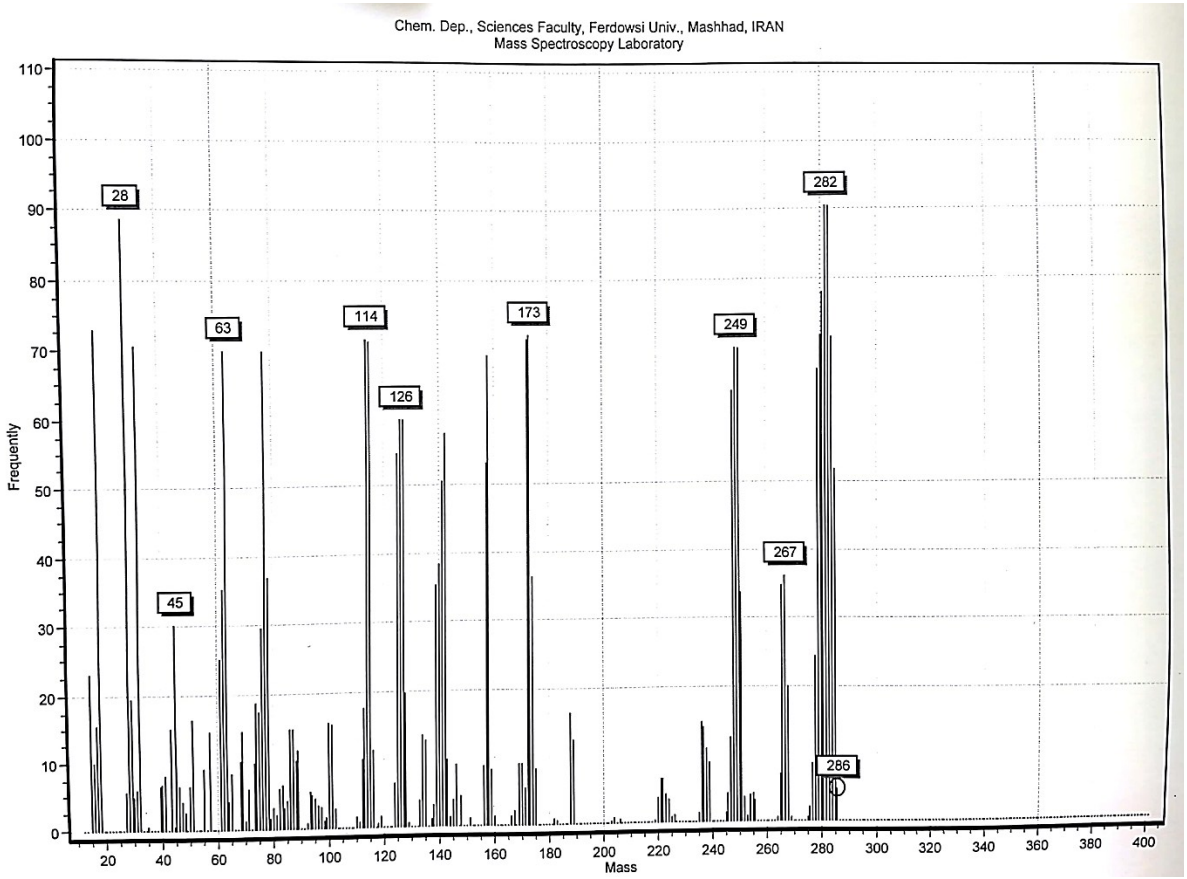


**Figure 23**: Mass spectrum of Di(naphthalen-1-yl)sulfane (**9S**).

## References


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