Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Cerium catalyst promoted C-S cross-coupling: Synthesis of thioethers, Dapsone and RN-18 precursors

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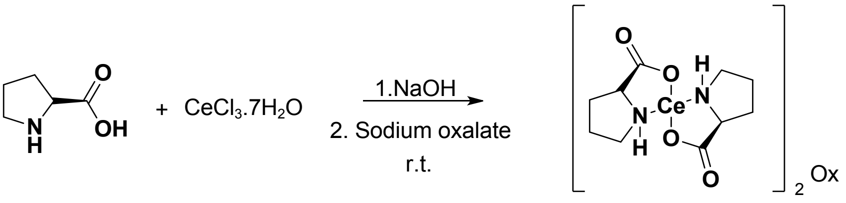
1. General Procedure

All chemical reagents and solvents were used without any specific treatment. The respective reactions were monitored by Thin Layer Chromatography (TLC)

MACHEREY-NAGEL (SIL G / UV_{254}). The purification of the compounds was performed by column chromatography on silica gel using appropriated quantities of hexane and acetyl acetate. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO on Bruker (300 MHz and 75 MHz respectively) spectrometer. ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q =quartet, m = multiplet), coupling constants (*J*) and assignment. The infrared spectra were recorded on FT/IR 4100 type A spectrometer of Jasco. The qualitative chemical analysis of hybrid materials were obtained by the Dispersive Energy Spectroscopy (EDS) and scanning electron microscopy (SEM), were done by a Quanta 250 FEI and AZTec software, with an enlargement of 20 to 305,070 times, resolution ≤ 35 nm, MAG camera with a zoom of 20 to 489 times.

2. Experimental Procedure

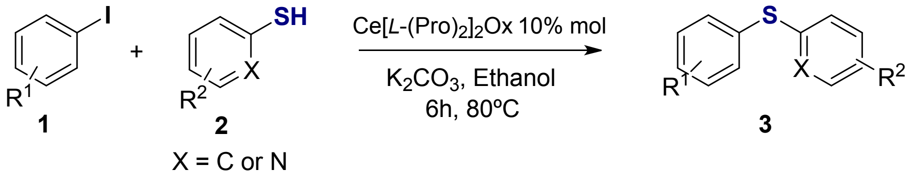
2.1. Catalyst - Procedure of [Ce(*L*-Pro)$_2$]$_2$Ox



[Ce(*L*-Pro)$_2$]$_2$Ox was obtain using proline (5.0 mmol) in methanol (15 mL) and aqueous sodium hydroxide solution (5.0 mmol in 3mL) at room temperature for 10 minutes. After that, it was added $CeCl_3.7H_2O$ (2.5 mmol in 1mL), the reaction was stirred overnight and it was added few drops of sodium oxalate solution (0.1g/mL) as precipitate agent. The solid was filtrated, washed with methanol and dried (92%).

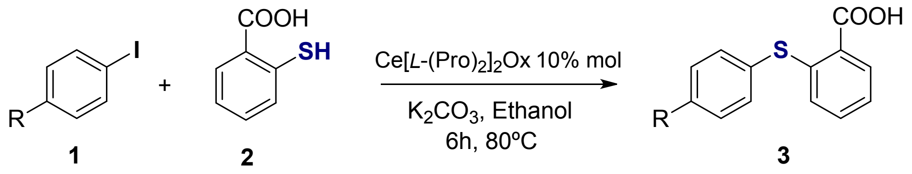
Reference: Silva, C. D. G., Oliveira, A. R., Rocha, M. P. D., Katla, R. Botero, E. R., Silva, E. C., Domingues, N. L. C. *RCS Adv.*, 2016, 6, n. 32, 27213.

2.2. General procedure for the C-S cross coupling to thiols with aryl halides



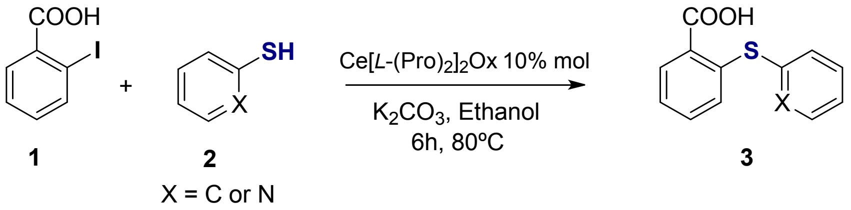
In a tube was added aryl halide (0.5 mmol) and thiol (1.0 mmol) in ethanol (4 mL), K_2CO_3 (2.5 mmol) in the presence of 10% mol of cerium catalyst, and the mixture was heated at 80°C during 6 hours. TLC monitored the progress of reaction. After the reaction was complete, the catalyst was centrifuged and the solvent was removed under vacuum. The residue was extract with chloroform (2x20 mL) and drying over $MgSO_4$. The solvent was removed under vacuum to give the crude products, which were purified by column chromatography on silica gel using appropriated quantities of hexane and acetyl acetate.

2.3. C-S cross coupling to thiosalicylic acid with aryl halides (entry 15 and 16)



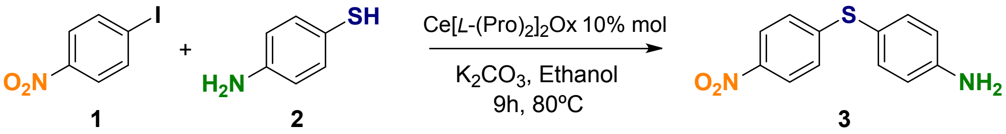
In a tube was added 10 mol% of cerium catalyst, aryl halide (0.5 mmol) and thiosalicylic acid (1.0 mmol), K_2CO_3 (2.5 mmol) in ethanol (4 mL) and the mixture was heated at 80°C during 6 hours. The progress of reaction was monitored by TLC (EtOAc: hexane, 1:1). After the reaction was complete, the catalyst was filtered, the solvent was removed under vacuum and then ice water was added to the reaction mixture, ruling by acidification using 5N HCl leading to the precipitation of crude product. The solid was filtered and washed several times with petroleum ether and recrystallized using ethanol affords the products.

2.4. C-S cross coupling to thiols with 2-iodobenzoic acid (entry 17 and 18)



In a tube was added 10 mol% of cerium catalyst, 2-iodobenzoic acid (0.5 mmol) and benzenethiol (1.0 mmol), K_2CO_3 (2.5 mmol) in ethanol (4 mL) and the mixture was heated at 80°C during 6 hours. The progress of reaction was monitored by TLC (EtOAc: hexane, 1:1). After the reaction was complete, the catalyst was filtered, the solvent was removed under vacuum and then ice water was added to the reaction mixture, ruling by acidification using 5N HCl leading to the precipitation of crude product. The solid was filtered and washed several times with petroleum ether and recrystallized using ethanol affords the products.

2.5. General procedure for the synthesis of Dapsone-precursor



Specially Dapsone-precursor was carried out in gram-scale, the reaction was performed using 1-iodo-4-nitrobenzene (5 mmol) and 4-aminothiophenol (10 mmol) in ethanol (4 mL), K_2CO_3 (25 mmol) in the presence of 10% mol of cerium catalyst, and the mixture was heated at 80°C during 9 hours. TLC monitored the progress of reaction. After the reaction was complete, the catalyst was filtered and the solvent was removed under vacuum. The residue was extract with chloroform (2x20 mL) and drying over $MgSO_4$. The solvent was removed under vacuum to give the crude products, which were purified by column chromatography on silica gel using appropriated quantities of hexane and acetyl acetate (83% of yield, 1.02g).

3. Characterization of [Ce(*L*-Pro)$_2$]$_2$Ox before and after reaction

The catalyst [Ce(*L*-Pro)$_2$]$_2$Ox was characterized by Scanning Electron Microscopy (SEM) and Dispersive Energy Spectroscopy (EDS), were done by a Quanta 250 FEI and AZTec software in gold, aluminum base metallization and without metallization, with an enlargement of 20 to 305,070 times, resolution ≤ 35 nm, MAG camera with a zoom of 20 to 489 times.

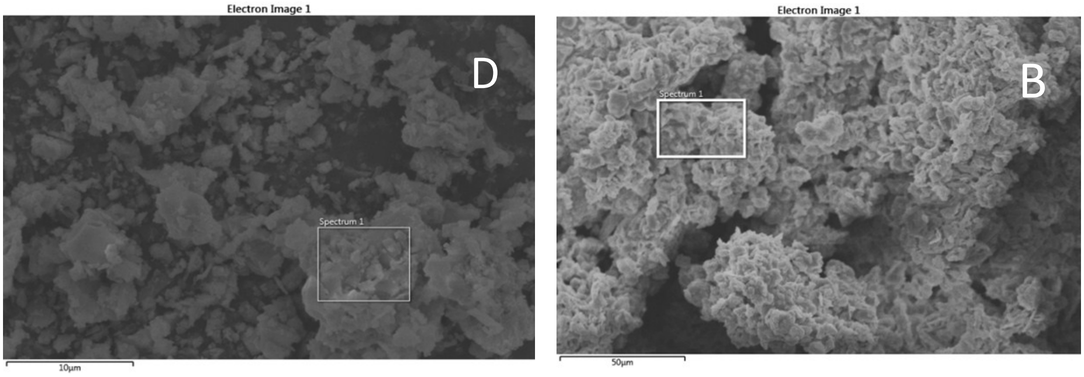
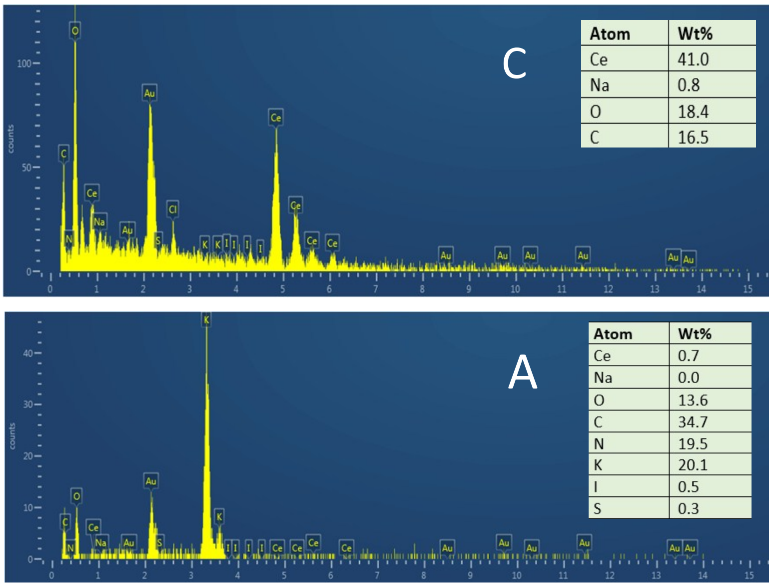


Figure 1. SEM for [Ce(*L*-Pro)$_2$]$_2$Ox before (A) the reaction and after five cycles (B) by gold based metallization

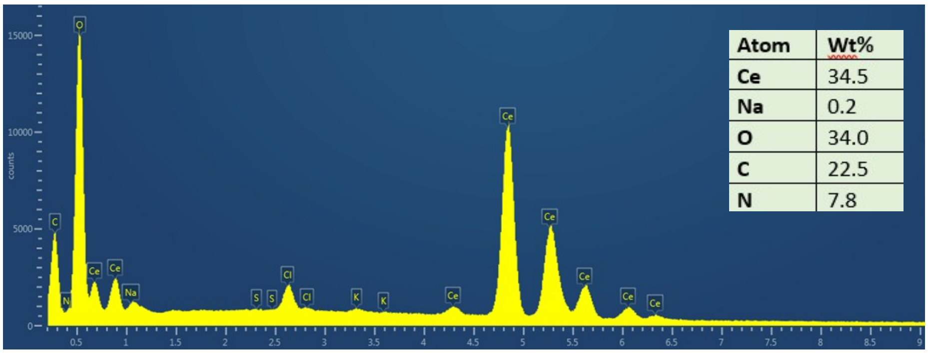


Atom	Wt%
Ce	41.0
Na	0.8
O	18.4
C	16.5

Atom	Wt%
Ce	0.7
Na	0.0
O	13.6
C	34.7
N	19.5
K	20.1
I	0.5
S	0.3

Figure 2. EDS for [Ce(*L*-Pro)$_2$]$_2$Ox before (C) the reaction and after five cycles (D) by gold based metallization

In order to make evident the catalysis for C-S cross coupling promoted by cerium catalyst we performed de SEM and EDS analysis without gold metallization before reaction using aluminum base (Figure 3 & 4).



Atom	Wt%
Ce	34.5
Na	0.2
O	34.0
C	22.5
N	7.8

Figure 3. SEM for [Ce(*L*-Pro)$_2$]$_2$Ox before the reaction by aluminum base metallization.

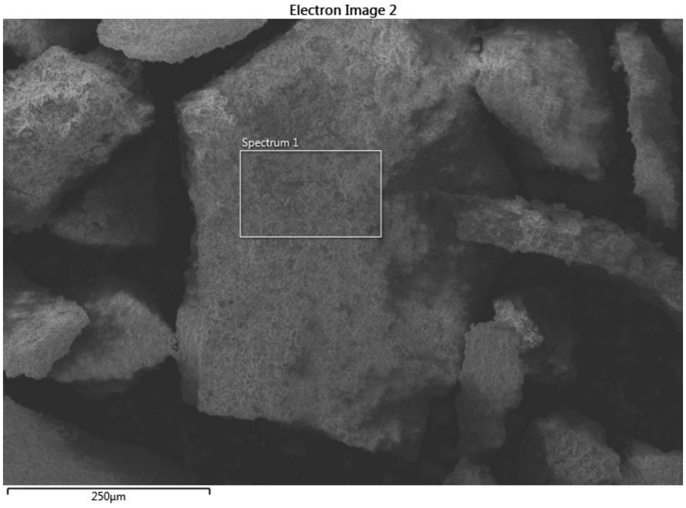


Figure 4. EDS for [Ce(*L*-Pro)$_2$]$_2$Ox before the reaction by aluminum base metallization

In addition, we performed de SEM and EDS analysis of cerium catalysis before reaction using carbon coating (Figure 5 & 6).

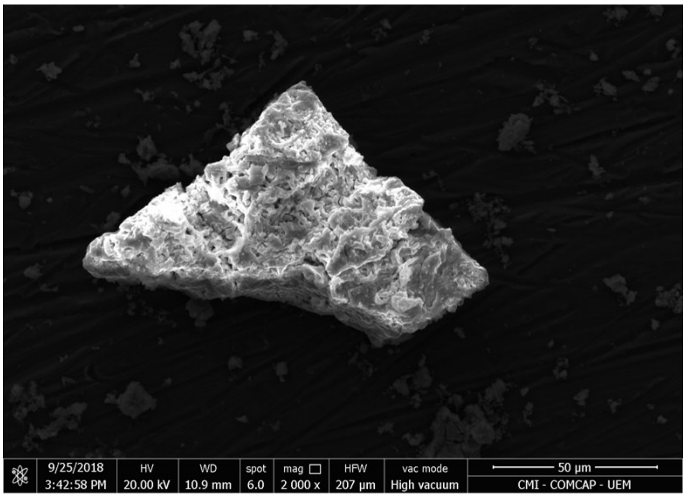
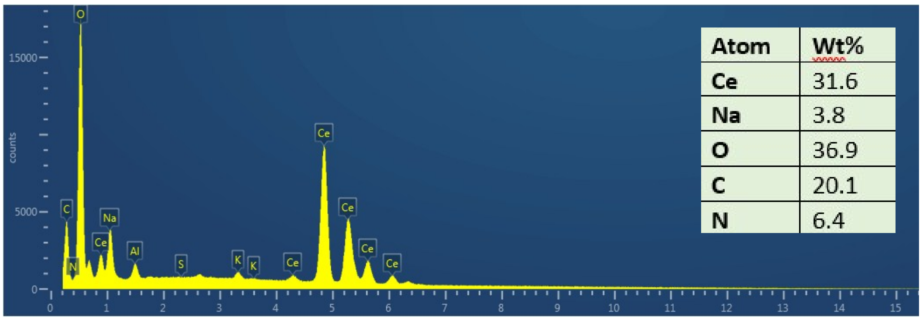


Figure 5. SEM for $[Ce(L\text{-}Pro)_2]_2Ox$ before the reaction using carbon coating.

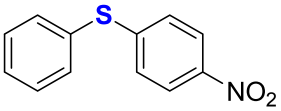


Atom	Wt%
Ce	31.6
Na	3.8
O	36.9
C	20.1
N	6.4

Figure 6. EDS for $[Ce(L\text{-}Pro)_2]_2Ox$ before the reaction by carbon coating

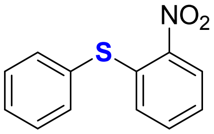
3. ^{1}H AND ^{13}C NMR SPECTRA ANALYSIS:

(4-nitrophenyl)(phenyl)sulfane (entry 1):



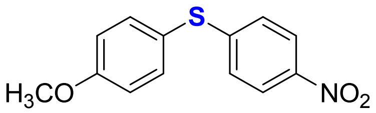
Yellow solid. MW: 231.27 g/mol. $C_{12}H_9NO_2S$. **IR (KBr):** υcm^{-1} 1572, 1504, 1337, 1083, 851, 745, 688. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 8.04-8.07 (d, *J*= 8.06 Hz, 2H), 7.53-7.56 (m, 2H), 7.44-7.48 (m, 3H), 7.16-7.19 (d, *J*= 7.17 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ ppm 124.06, 126.71, 127.52, 129.71, 130.07, 130.47, 134.77, 145.37, 148.53.

(4-nitrophenyl)(phenyl)sulfane (entry 2):



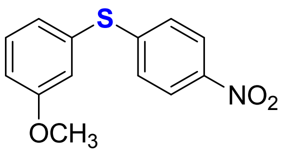
Yellow solid. MW: 231.27 g/mol. $C_{12}H_9NO_2S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 6.86-6.88 (d, *J*= 6.87 Hz, 2H), 7.48-7.50 (m, 3H), 7.57-7.60 (m, 2H), 8.21-8.23 (d, *J*= 8 Hz, 2 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 124.97, 125.74, 128.33, 130.04, 130.13, 130.99, 133.45, 135.91, 139.47, 144.99.

(4-methoxyphenyl)(4-nitrophenyl)sulfane (entry 3):



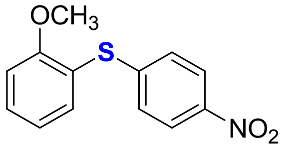
Yellow oil. MW: 291.39 g/mol. $C_{13}H_{11}NO_3S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 3.86 (s, 3H), 7.07-7.10 (d, *J*= 7.08 Hz, 2H) 7.38-7.41 (d, *J*= 7.39 Hz, 2 H), 7.47-7.50 (d, *J*= 7.48 Hz, 2H), 8.01-8.04 (d, *J*= 8.02 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ ppm 55.48, 114.63, 115.68, 123.96, 125.57, 132.67, 137.17, 145.01, 150.09, 159.93.

(3-methoxyphenyl)(4-nitrophenyl)sulfane (entry 4):



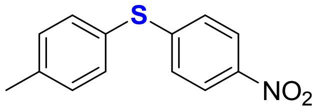
Yellow oil. MW: 291.39 g/mol. $C_{13}H_{11}NO_3S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm. 3.82 (s, 3H), 6.98-7.01 (ddd, *J*= 6.99 Hz, 1H), 7.06-7.08 (m, *J*= 7.07 Hz, 1H), 7.11-7.14 (m, *J*= 7.12 Hz, 1H), 7.18-7.23 (m, *J*=7.20 Hz, 2H), 7.34-7.40 (m, *J*= 7.37 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 55.69, 115.79, 119.85, 124.27, 126.96, 127.03, 131.05, 131.16, 145.58, 148.53, 160.74.

(2-methoxyphenyl)(4-nitrophenyl)sulfane (entry 5):



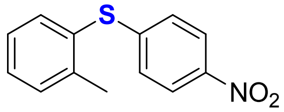
Yellow oil. MW: 291.39 g/mol. $C_{13}H_{11}NO_3S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 3.83 (s, 3H), 7.01-7.04 (d, *J*= 7 Hz), 7.12-7.15 (d, *J*= 7.13, 2H), 7.47-7.54 (dd, *J*= 7.5 Hz, 2H), 8.03-8.06 (d, *J*= 8 Hz) Elemental analysis theoretical C, 59.76; H, 4.24; N, 5.36; O, 18.37; S, 12.27; experimental C, 59.72; H, 4.27; N, 5.39.

(*p*-tolyl)(4-nitrophenyl)sulfane (entry 6):



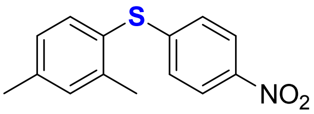
Yellow solid. MW: 245.30 g/mol. $C_{13}H_{11}NO_2S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 2.42 (s, 3H), 7.12-7.15 (d, *J*= 7 Hz, 2H), 7.25-7.28 (d, *J*= 7.27, 2H), 7.42-7.45 (d, *J*= 7.5 Hz, 2H), 8.03-8.06 (d, *J*= 8 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 21.35, 123.98, 126.14, 130.87, 135.09, 138.68, 140.25, 145.15,149.35.

(*o*-tolyl)(4-nitrophenyl)sulfane (entry 7):



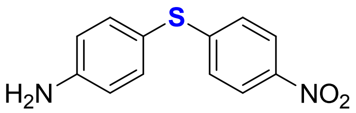
Yellow solid. MW: 245.30 g/mol. $C_{13}H_{11}NO_2S$ **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 2.38 (s, 3H), 7.04-7.09 (m, *J*= 7.07 Hz, 2H), 7.29-7.32 (m, *J*= 7.30 Hz, 1H), 7.38-7.26 (m, *J*= 7.42 Hz, 2H), 7.55-7.58 (m, *J*= 7.57 Hz, 1H), 8.03-8.08 (m, *J*= 8.06 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 20.88, 124.3, 126.02, 127.69, 129.18, 130.73, 131.61, 136.75, 142.92, 145.3, 148.54.

(2,4-dimethylphenyl)(4-nitrophenyl)sulfane (entry 8):



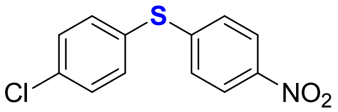
Yellow solid. MW: 259,32 g/mol. $C_{14}H_{13}NO_2S$ **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 2.33 (s, 3H), 2.39 (s, 3H), 7.01-7.05 (m, *J*= 7.04 Hz, 2H), 7.09-7.12 (ddd, *J*= 7.10 Hz, 1H), 7.21 (m, 1H), 8.02-8.05 (m, *J*= 8.04 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 20.77, 21.49, 124.24, 125.43, 125.63, 128.51, 132.47, 136.9, 141.18, 142.85, 145.13. 149.2;

4-((4-nitrophenyl)thio)aniline (entry 9):



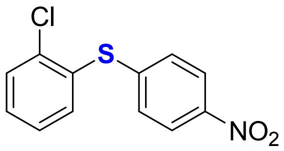
Yellow solid. MW: 246.28 g/mol. $C_{12}H_{10}N_2O_2S$. **IR (KBr):** υcm^{-1} 3466 (N-**H**), 3379 (N-**H**), 1619, 1576, 1492, 1322, 1183, 1077, 825, 742, 516. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ ppm 6.73-6.76 (d, *J*= 6.75 Hz, 2H), 7.07-7.10 (d, *J*= 7 Hz, 2H), 7.32-7.35 (d, *J*= 7.35, 2H), 8.01-8.04 (d, *J*= 8 Hz, 2H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ ppm 116.36, 116.59, 124.10, 125.44, 137.45, 145.00, 148.59, 151.28.

(4-chlorophenyl)(4-nitrophenyl)sulfane (entry 10):



Yellow solid. MW: 265.72 g/mol. C12H_8ClNO_2S. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ ppm 7.17-7.20 (d, *J*= 7 Hz, 2H), 7.41-7.49 (m, 4H), 8.06-8.10 (d, *J*= 8 Hz, 2H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ ppm 124.17, 124.86, 126.97, 129.17, 130.29,135.85, 138.68, 145.62, 147.61.

(2-chlorophenyl)(4-nitrophenyl)sulfane (entry 11):



Yellow solid. MW: 265.72 g/mol. $C_{12}H_8ClNO_2S$. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ ppm 7.19-7.22 (d, *J*= 7.20 Hz, 2H), 7.31-7.44 (m, 2H), 7.55-7.60 (m, 2H), 8.09-8.12 (d, *J*= 8 Hz, 2H). ^{13}**C NMR** (75 MHz, DMSO) δ ppm 125.66, 126.66, 128.74, 132.26, 133.96, 139.57, 168.28; Elemental analysis theoretical C, 54.24; H, 3.03; Cl, 13.34; N, 5.27; O, 12.04; S, 12.07; experimental C, 54.27; H, 3.05; N, 5.26.

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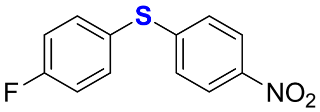
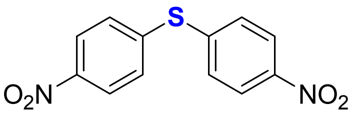
(4-fluorophenyl)(4-nitrophenyl)sulfane (entry 12):



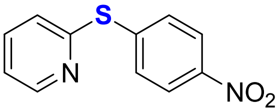
Yellow solid. MW: 249.26 g/mol. $C_{12}H_8FNO_2S$. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ ppm 7.12-7.19 (m, 4H), 7.52-7.57 (m, 2H), 8.05-8.08 (d, *J*= 8 Hz, 4H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 117.29, 117.47, 124.10, 126.29, 137.28, 145.40, 148.50, 162.71, 164.71.

bis(4-nitrophenyl)sulfane (entry 13):



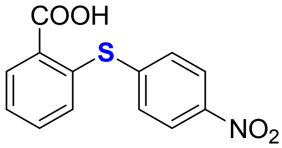
Yellow solid. MW: 276,27 g/mol. $C_{12}H_8N_2O_4S$. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ ppm 7.69-7.72 (d, *J*= 7.70 Hz, 2H), 7.81-7.84 (d, J= 7.80 Hz, 2H), 8.38-8.43 (m, 4H).

2-((4-nitrophenyl)thio)pyridine (entry 14):



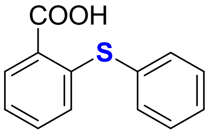
Yellow solid MW: 232.26 g/mol. $C_{11}H_8N_2O_2S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.19-7.21 (ddd, *J*= 7,19 Hz, 1H), 7.29-7.32 (m, *J*= 7.3 Hz, 1H), 7.57-7.67 (m, *J*=7.51 Hz, 3H), 8.16-8.20 (m, *J*= 8.18 Hz, 2H), 8.50-8.53 (ddd, J= 8.52 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 122.26, 124.37, 125.13, 132.04, 137.68, 142.63, 147.11, 150.67, 156.72.

2-((4-nitrophenyl)thio)benzoic acid (entry 15):



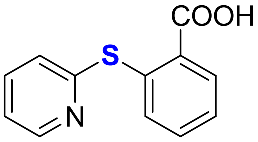
Yellow solid MW: 275.28g/mol. $C_{13}H_9NO_4S$. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.16-7.18 (dd, *J*= 8.0 Hz, 1H), 7.36-7.39 (t, 1H), 7.44-7.47 (t, 1H), 7.57-7.59 (d, *J*= 9.0 Hz, 2H), 8.13-8.14 (dd, *J*= 8.0 Hz, 1H), 8.22-8.24 (d, *J*= 9.0 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO): δ ppm 124.96, 126.46, 127.90, 131.14, 131.68, 132.34, 133.05, 133.74, 135.67, 139.39, 146.90, 168.08.

2-(phenylthio)benzoic acid (entry 16 and 17):



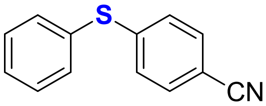
White solid. MW: 230.28 g/mol. $C_{13}H_{10}O_2S$. **^{1}H NMR** (300 MHz, DMSO) δ ppm 7.15-7.20 (t, 2H), 7.30-7.40 (m, 2H), 7.49-7.62 (m, 3H), 7.89-7.91 (d, *J*= 7.9 Hz, 1 H), 8.00-8.03 (d, *J*= 8 Hz, 1H). **^{13}C NMR** (75 MHz, DMSO) δ ppm 124.99, 126.47, 128.54, 131.37, 131.84, 132.06, 132.86, 133.76, 138.75, 139.40, 168.09.

2-(pyridin-2-ylthio)benzoic acid (entry 18):



White solid. MW: 231,27 g/mol. $C_{12}H_9NO_2S$. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.19 (d, 1H), 7.21-7.22 (d, 1H), 7.24 (d, 1H), 7.43-7.49 (td, *J*= 7.46 Hz, 2H), 8.02 (d, 1H), 8.05-8.06 (m, 2H), 8.08-8.09 (d, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 94.96, 128.26, 132.31, 133.32, 133.79, 142.19, 171.25; Elemental analysis theoretical C, 62.32; H, 3.92; N, 6.06; O, 13.84; S, 13.86; experimental C, 62.33; H, 3.95; N, 6.07.

4-(phenylthio)benzonitrile (entry 19):



Colourless oil. MW: 211.28 g/mol. $C_{13}H_9NS$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.15-7.18 (d, J= 7.17 Hz, 1H), 7.35-7.38 (d, J= 7.37 Hz, 2H), 7.42-7.47 (m, 2H), 7.49-7.54 (m, 2 H), 7.84-7.87 (d, *J*= 7.85 Hz, 2H).

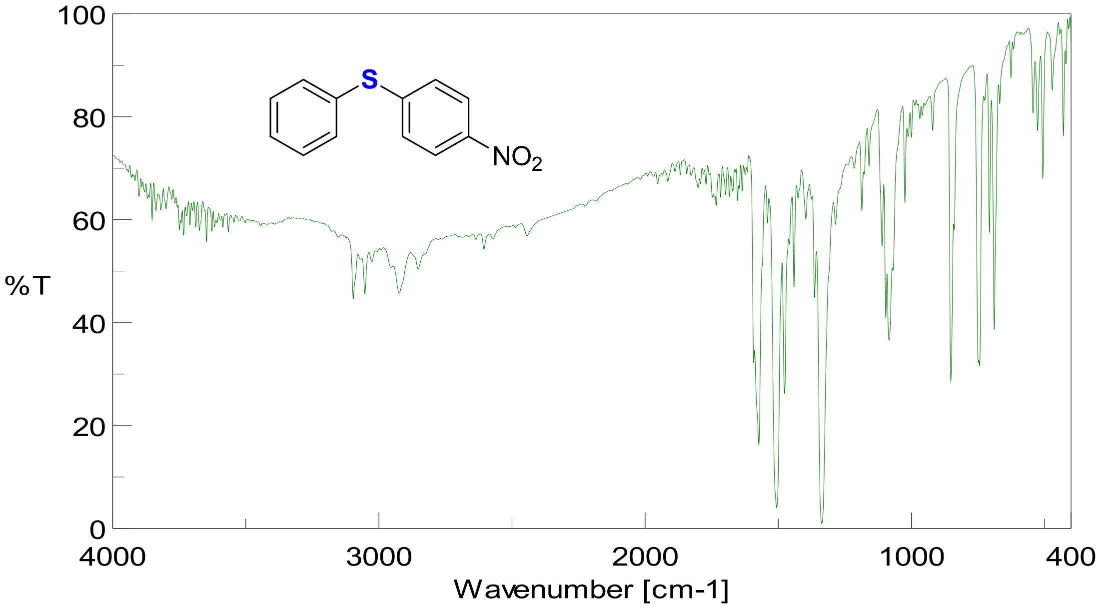


Figure 7. FTIR for the (4-nitrophenyl)(phenyl)sulfane (entry 1)

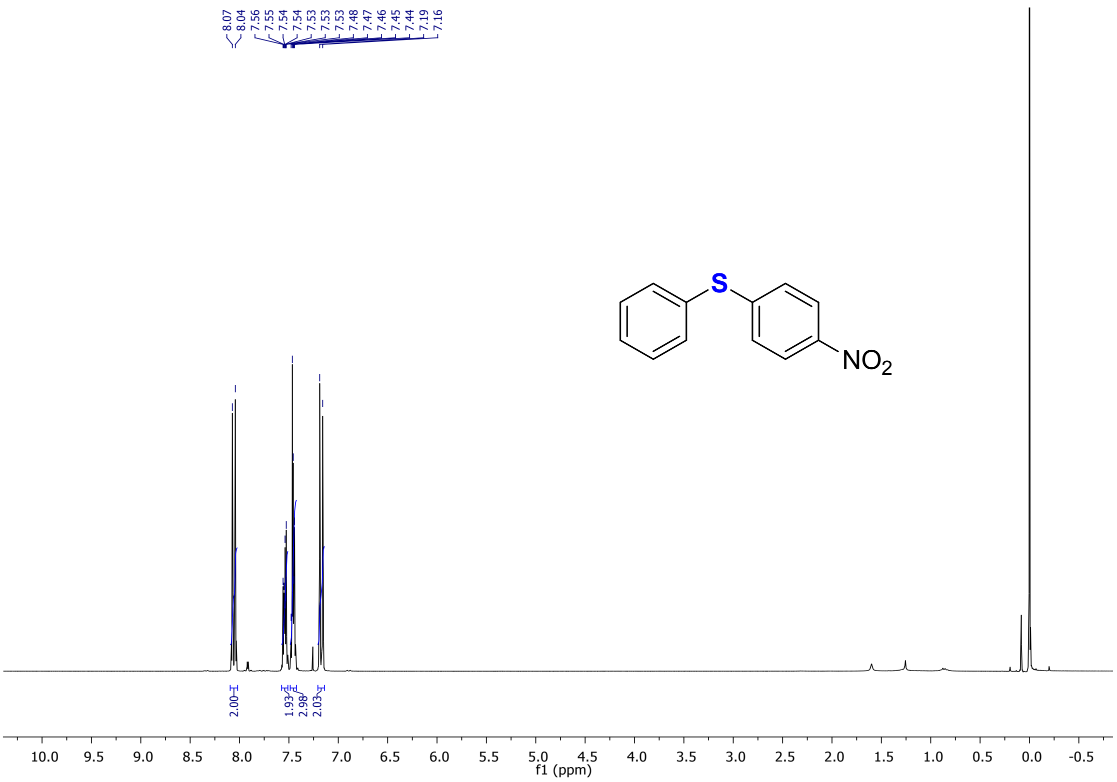


Figure 8. ^{1}H NMR spectra for the (4-nitrophenyl)(phenyl)sulfane (entry 1)

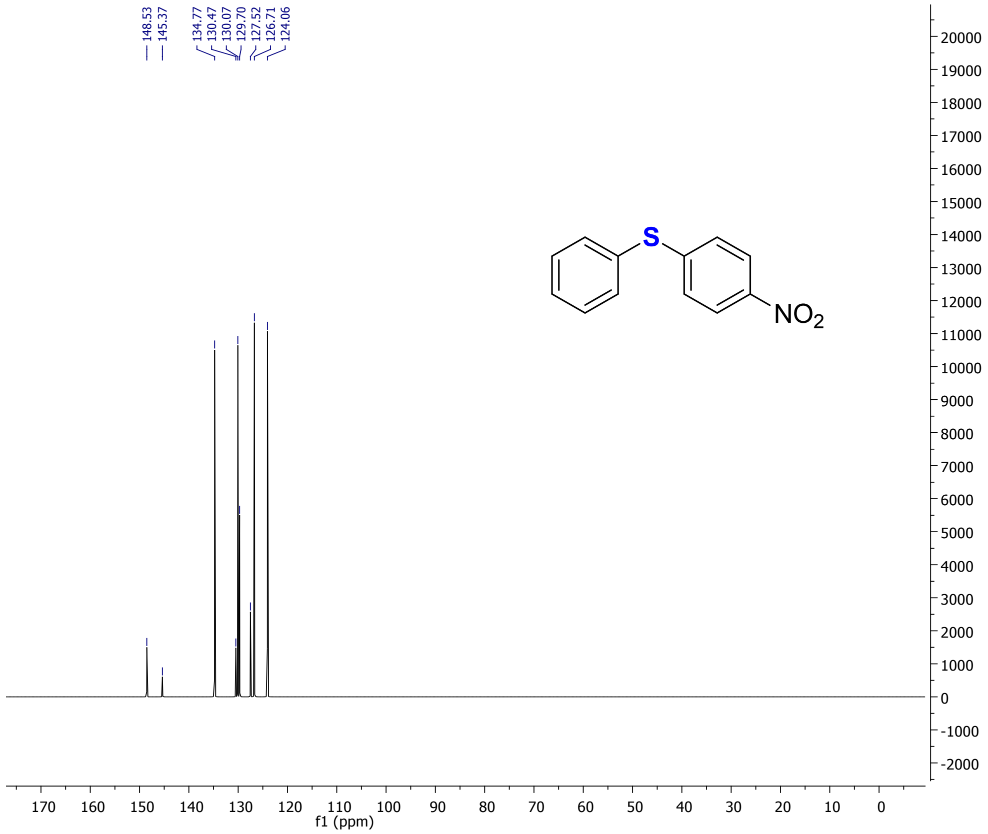


Figure 9. ^{13}C NMR spectra for the (4-nitrophenyl)(phenyl)sulfane (entry 1)

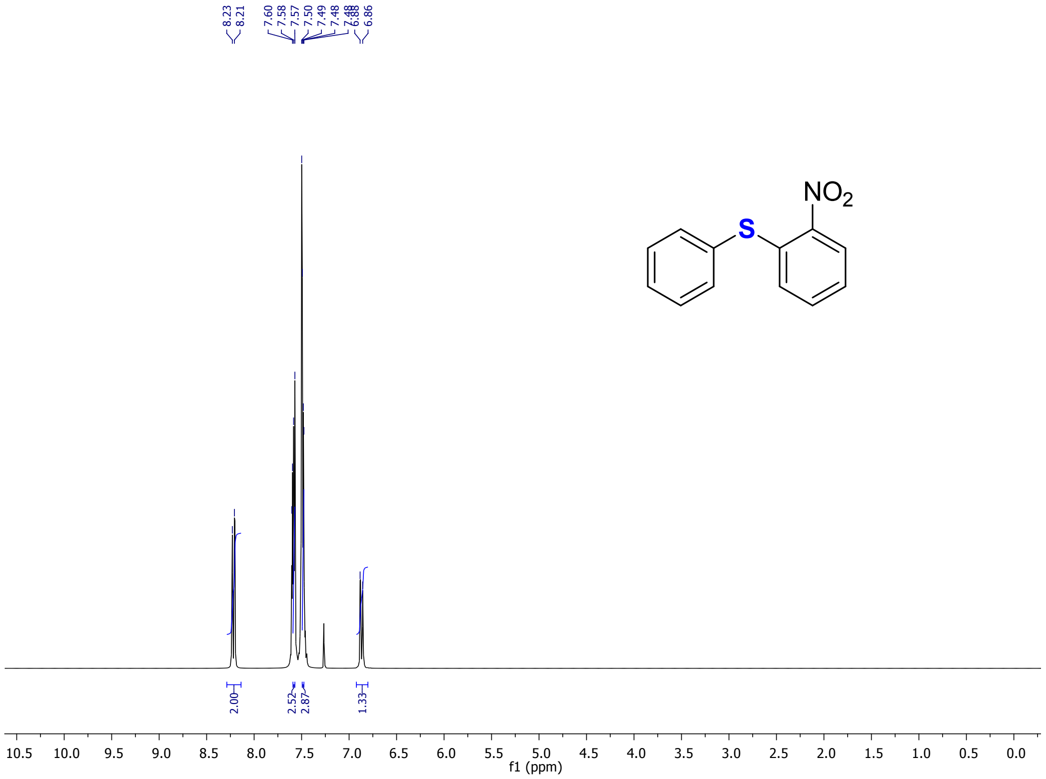


Figure 10. ^{1}H NMR spectra for the (2-nitrophenyl)(phenyl)sulfane (entry 2)

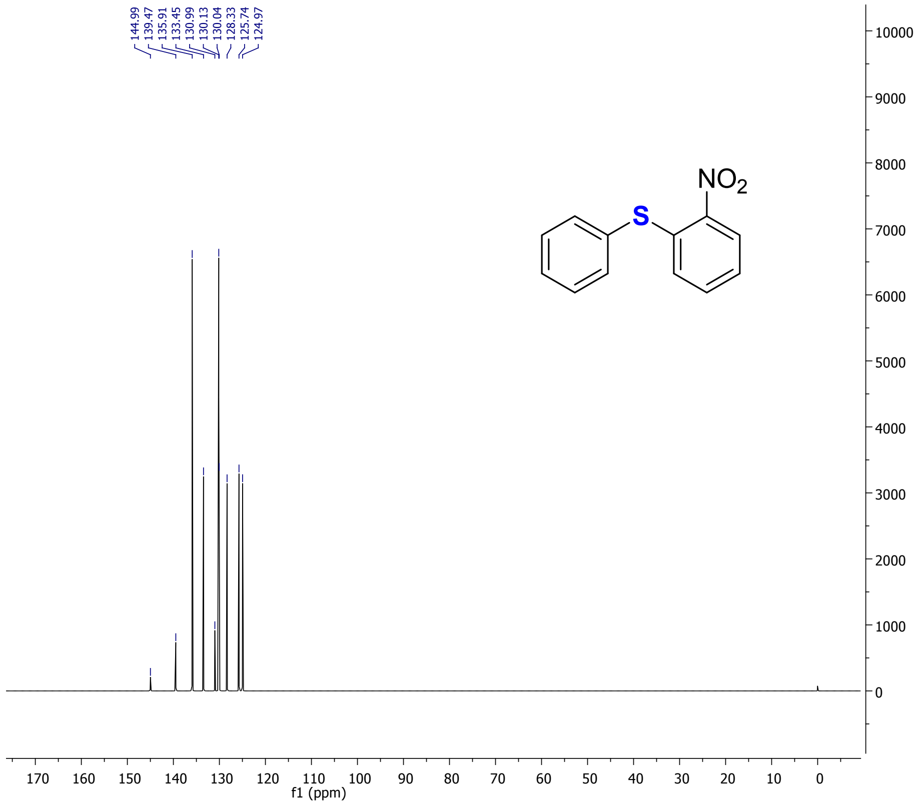


Figure 11. ^{13}C NMR spectra for the (2-nitrophenyl)(phenyl)sulfane (entry 2)

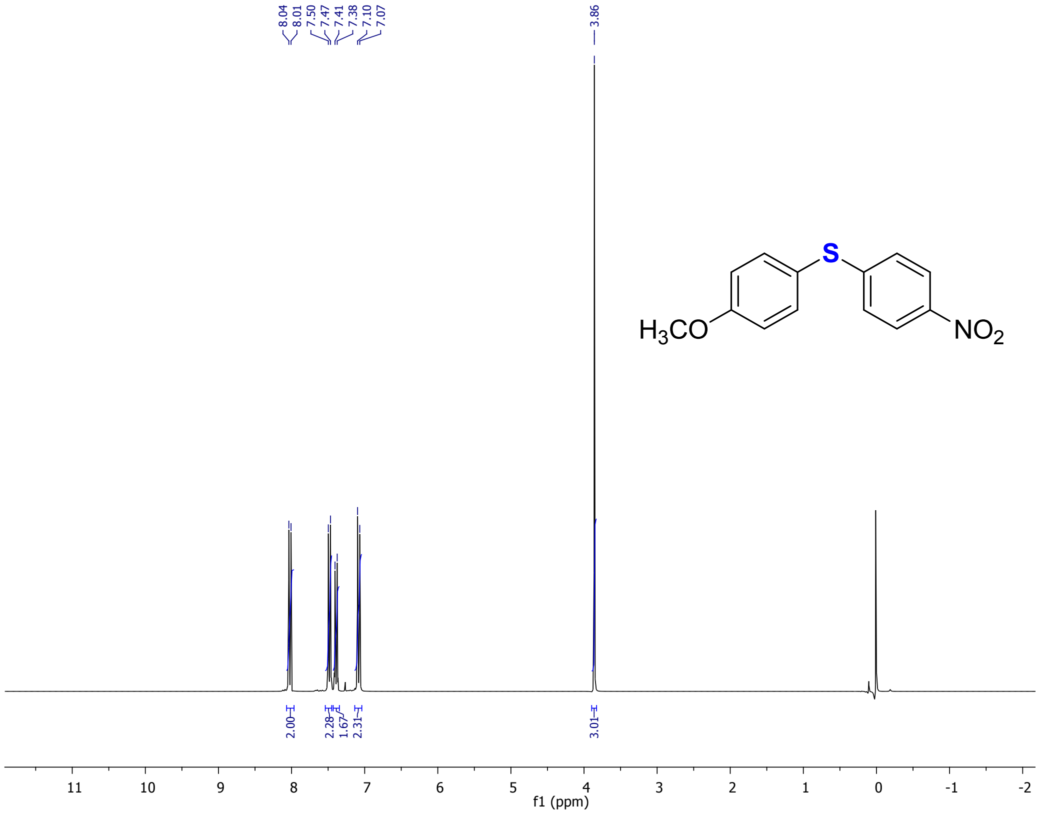


Figure 12. ^{1}H NMR spectra for the (4-methoxyphenyl)(4-nitrophenyl)sulfane (entry 3)

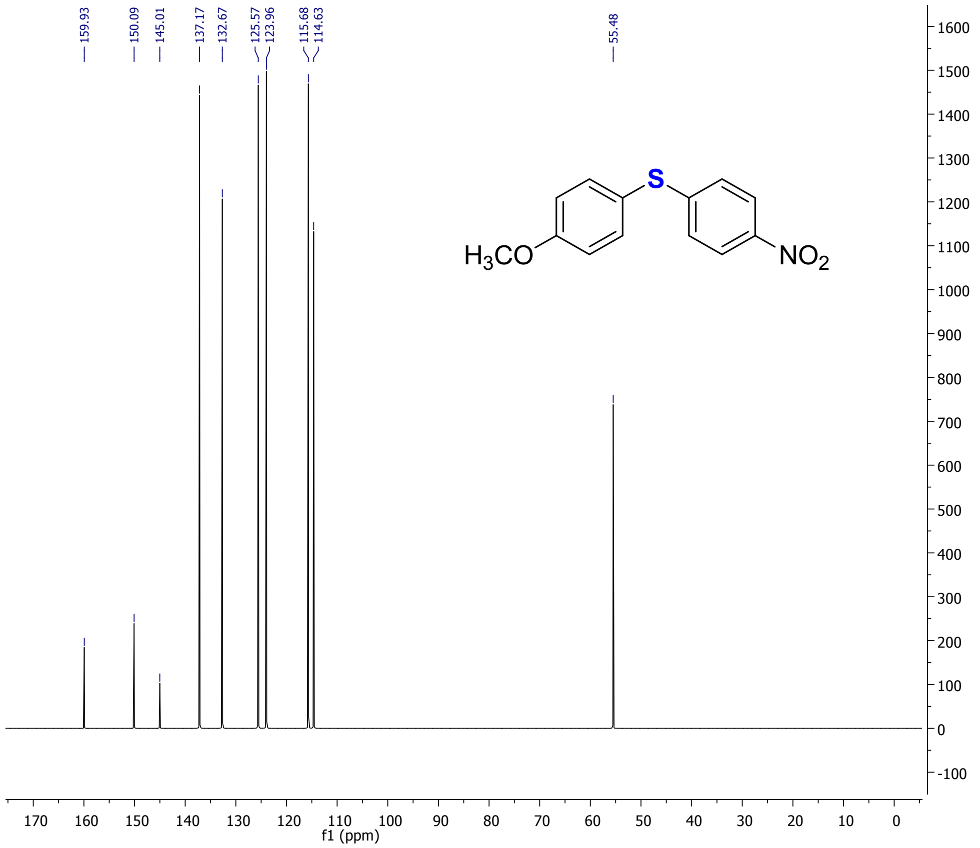


Figure 13. ^{13}C NMR spectra for the (4-methoxyphenyl)(4-nitrophenyl)sulfane (entry 3)

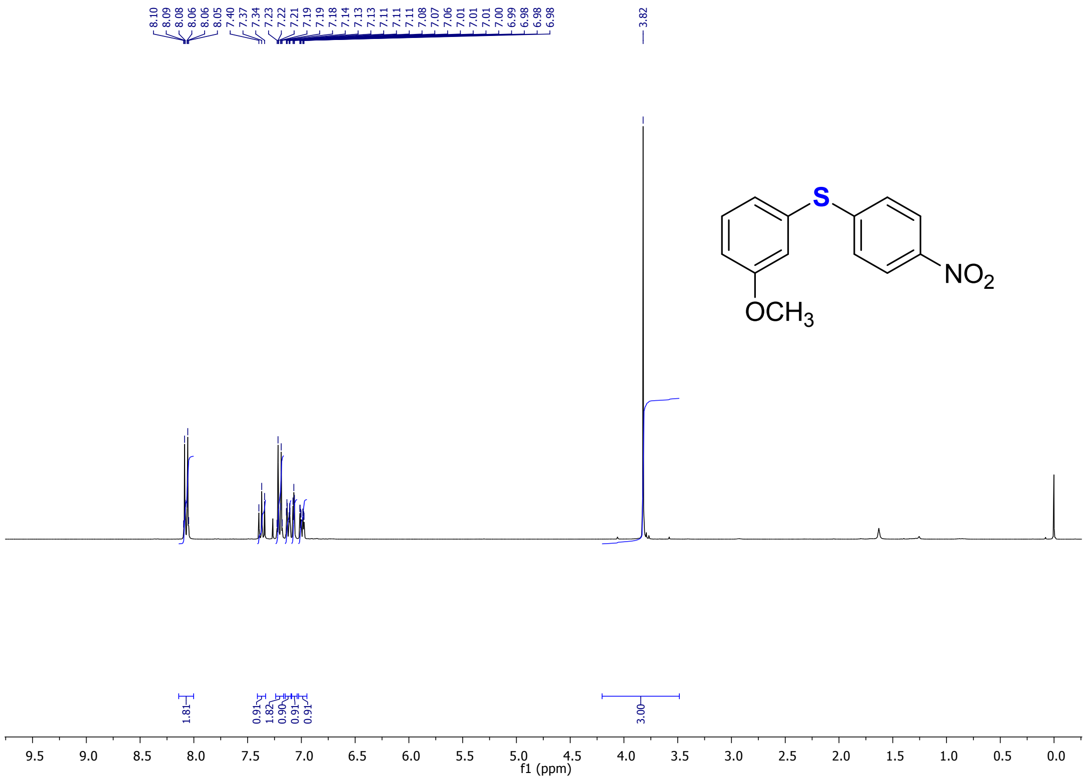


Figure 14. ^{1}H NMR spectra for the (3-methoxyphenyl)(4-nitrophenyl)sulfane (entry 4)

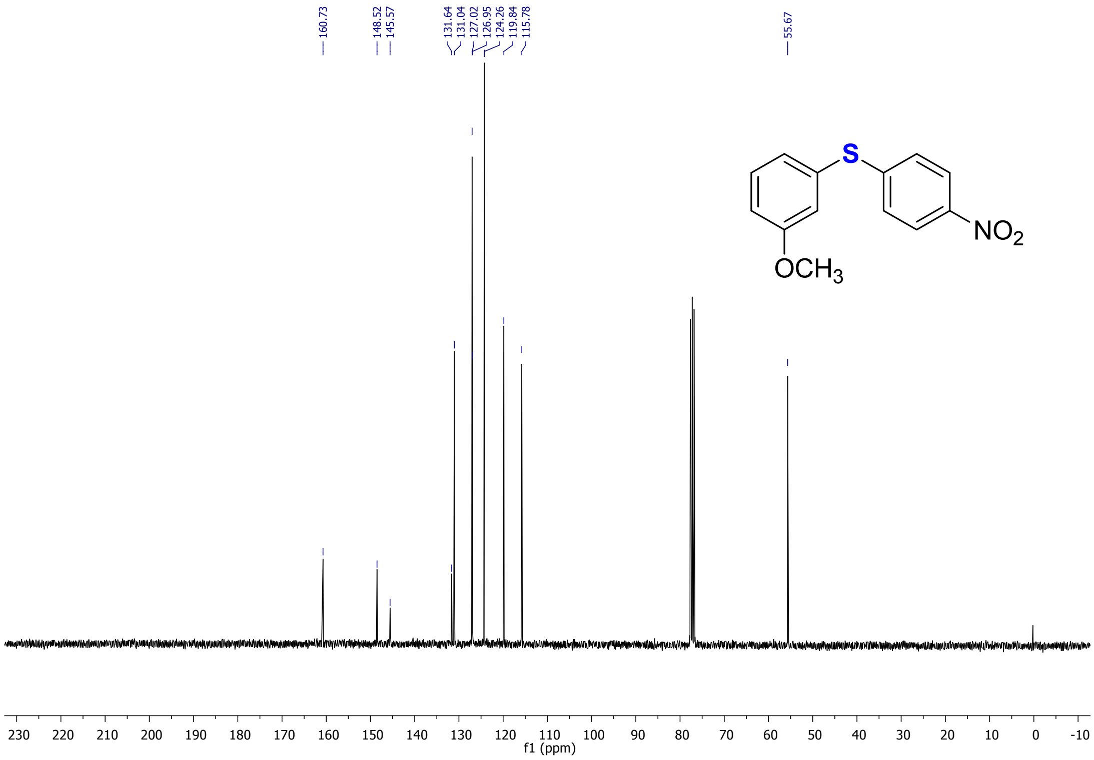


Figure 15. ^{13}C NMR spectra for the (3-methoxyphenyl)(4-nitrophenyl)sulfane (entry 4)

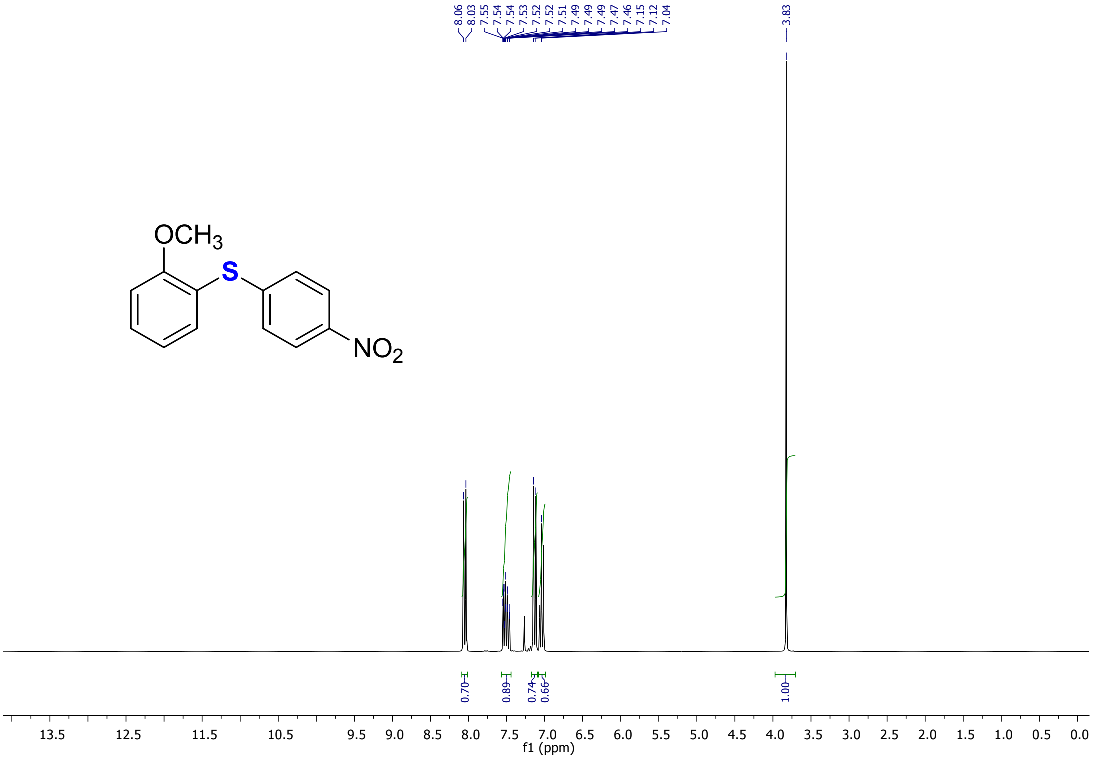


Figure 16. ^{1}H NMR spectra for the (2-methoxyphenyl)(4-nitrophenyl)sulfane (entry 5)

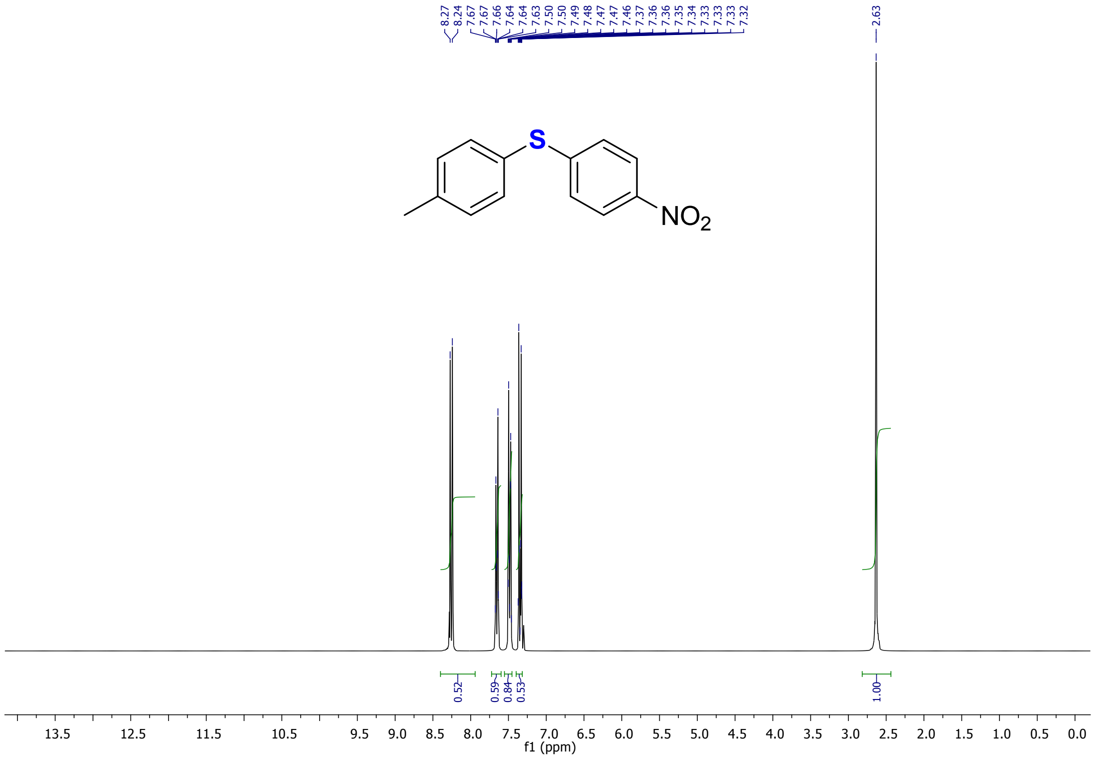


Figure 17. ^{1}H NMR spectra for the (*p*-tolyl)(4-nitrophenyl)sulfane (entry 6)

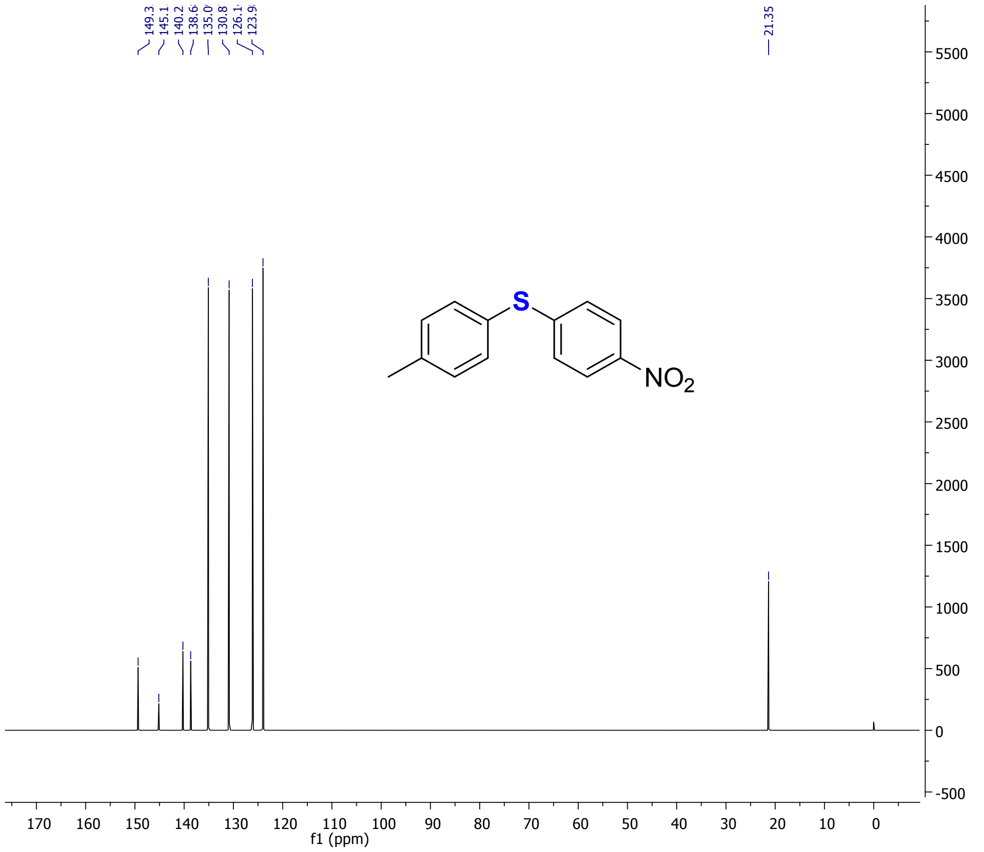


Figure 18. ^{13}C NMR spectra for the (*p*-tolyl)(4-nitrophenyl)sulfane (entry 6)

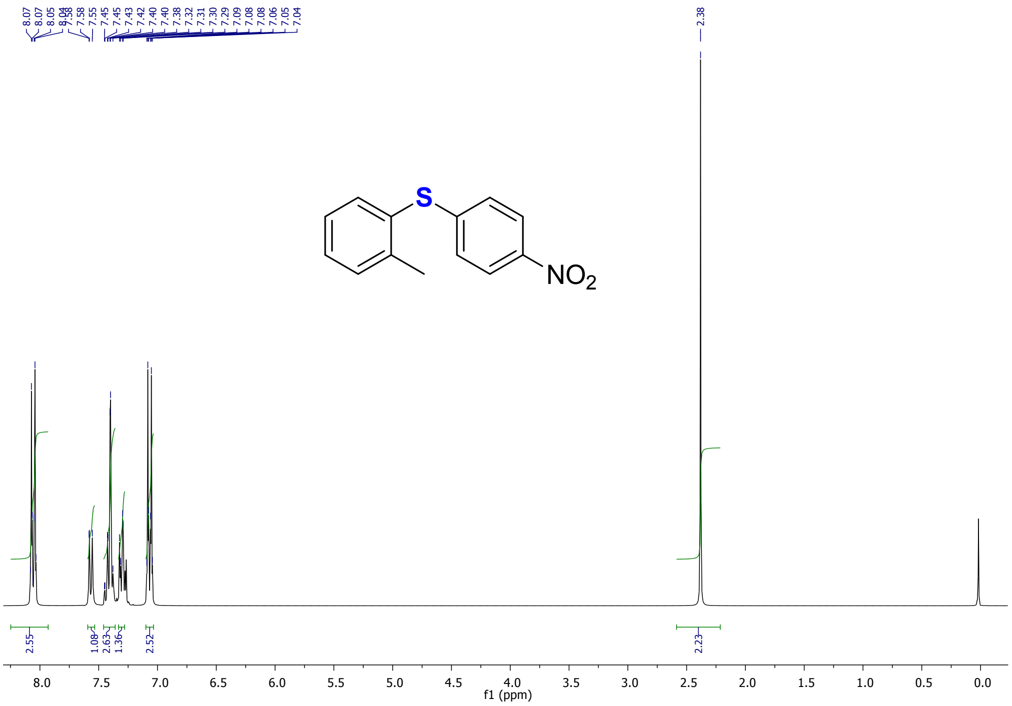


Figure 19. ^{1}H NMR spectra for the (*o*-tolyl)(4-nitrophenyl)sulfane (entry 7)

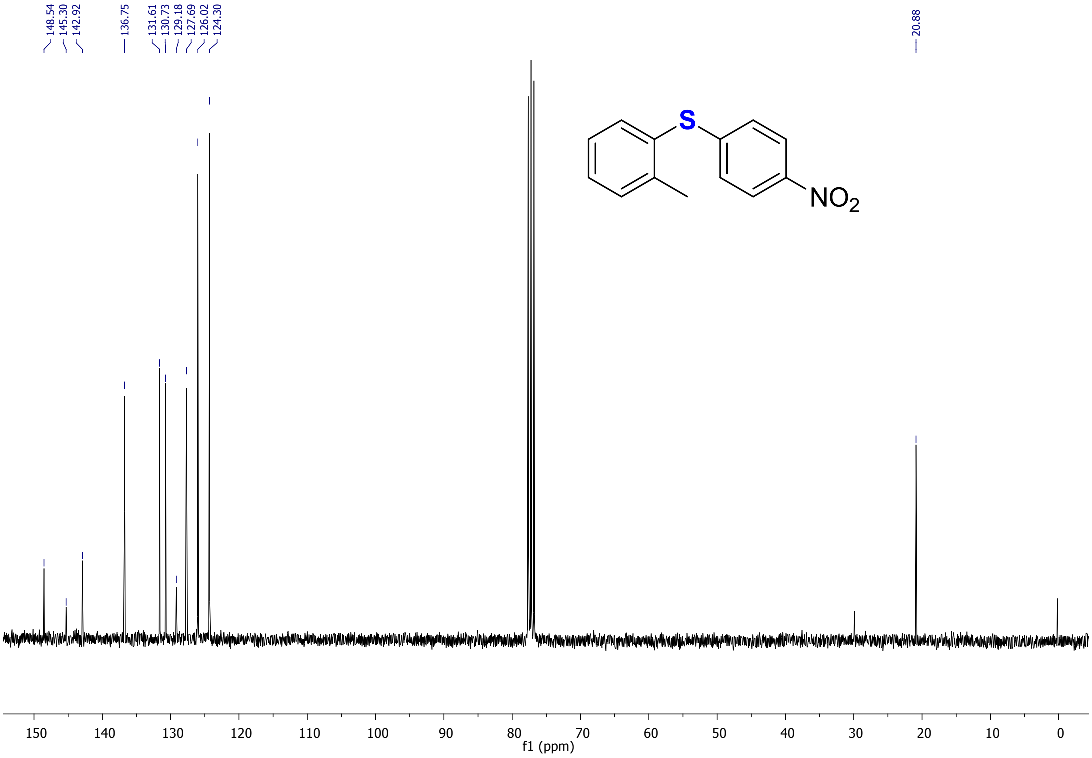


Figure 20. ^{13}C NMR spectra for the (*o*-tolyl)(4-nitrophenyl)sulfane (entry 7)

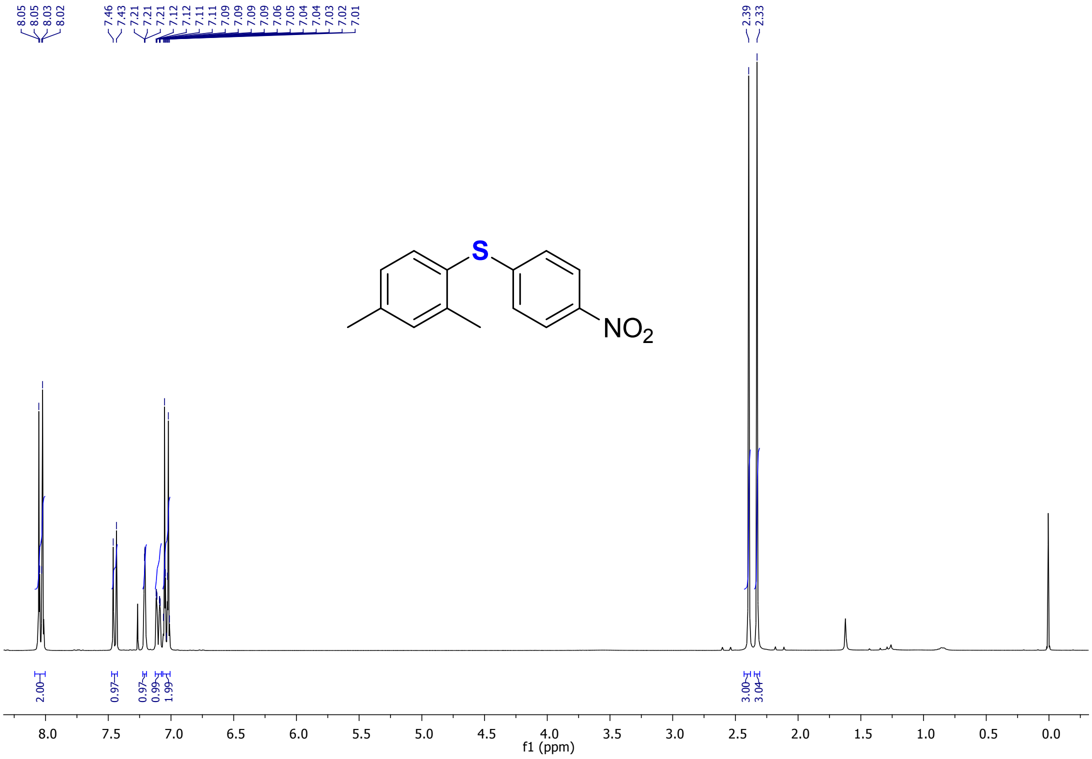


Figure 21. ^{1}H NMR spectra for the (2,4-dimethylphenyl)(4-nitrophenyl)sulfane (entry 8)

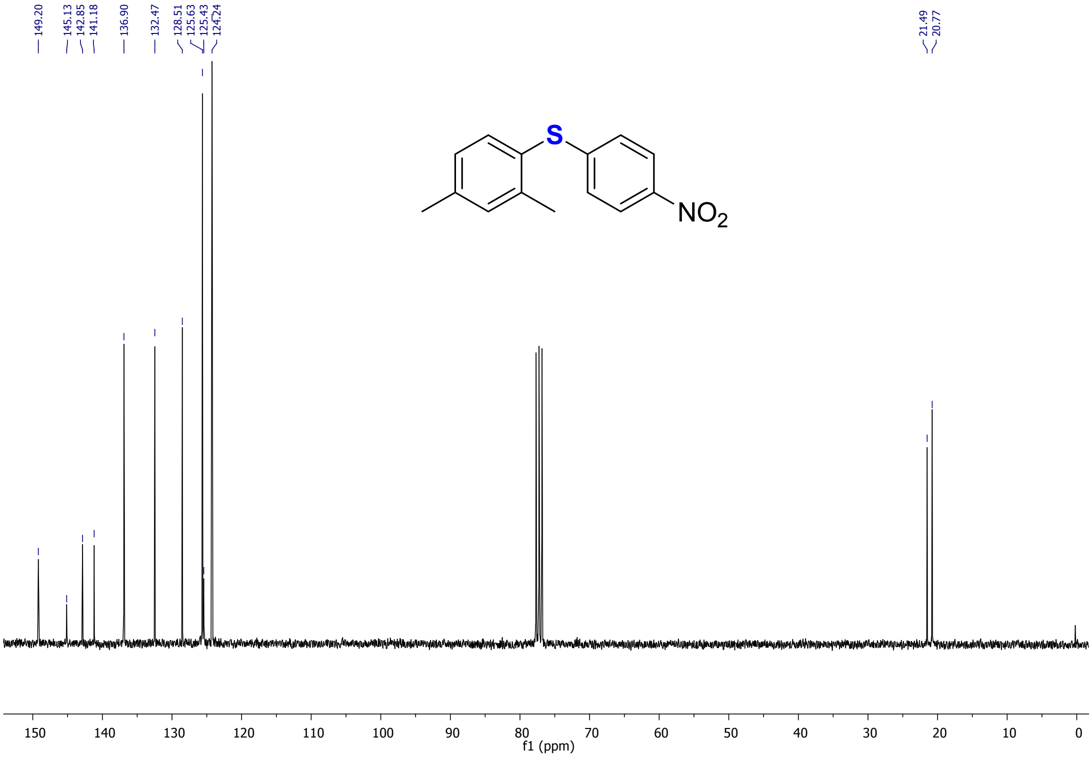


Figure 22. ^{13}C NMR spectra for the (2,4-dimethylphenyl)(4-nitrophenyl)sulfane (entry 8)

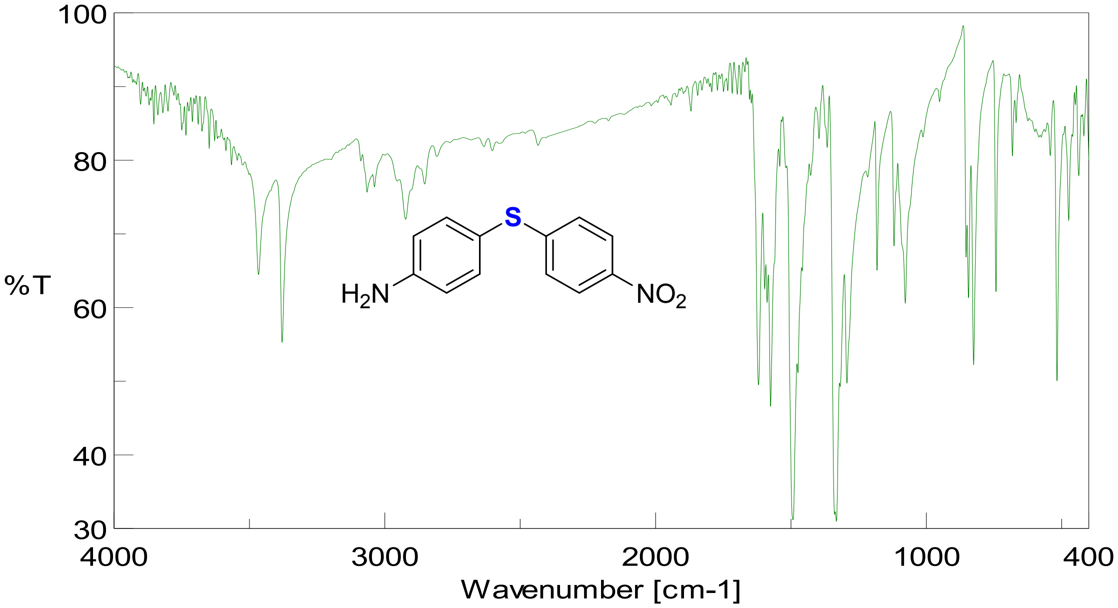


Figure 23. FTIR for the 4-((4-nitrophenyl)thio)aniline (entry 9)

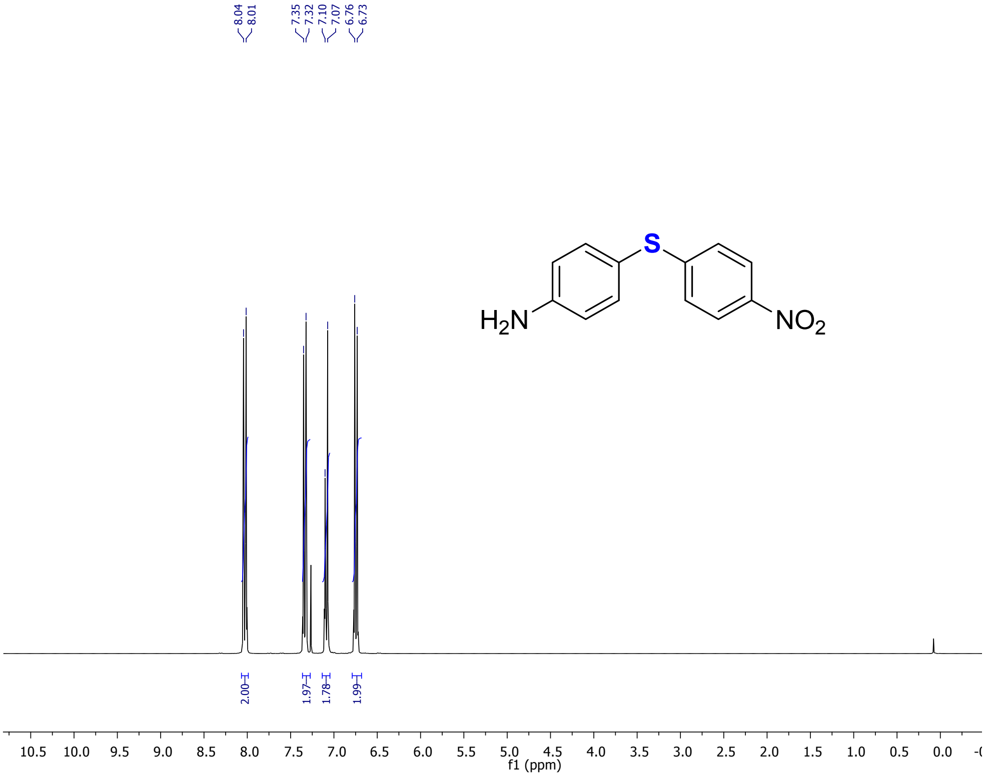


Figure 24. ^{1}H NMR spectra for the 4-((4-nitrophenyl)thio)aniline (entry 9)

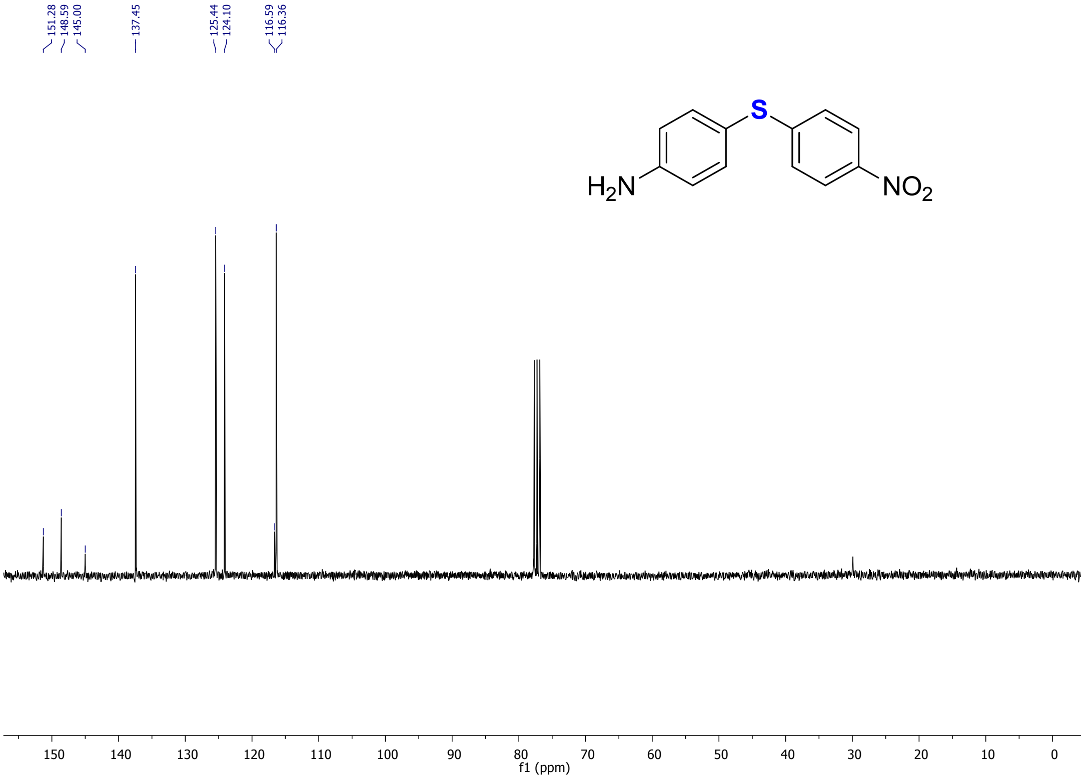


Figure 25. ^{13}C NMR spectra for the 4-((4-nitrophenyl)thio)aniline (entry 9)

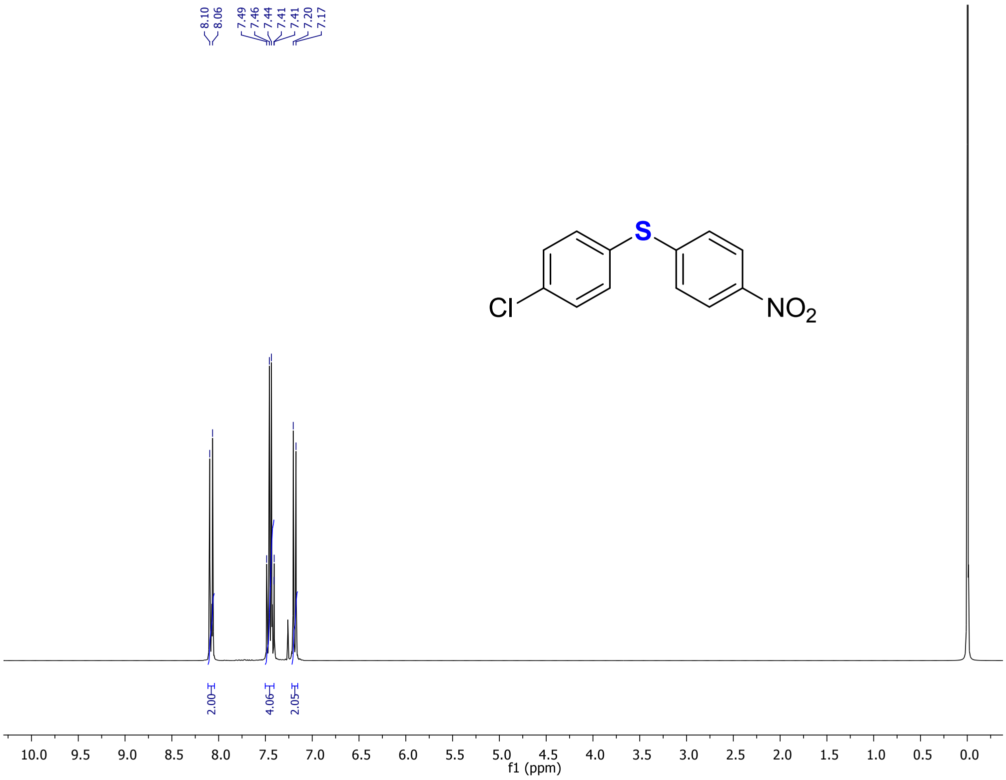


Figure 26. ^{1}H NMR spectra for the (4-chlorophenyl)(4-nitrophenyl)sulfane (entry 10)

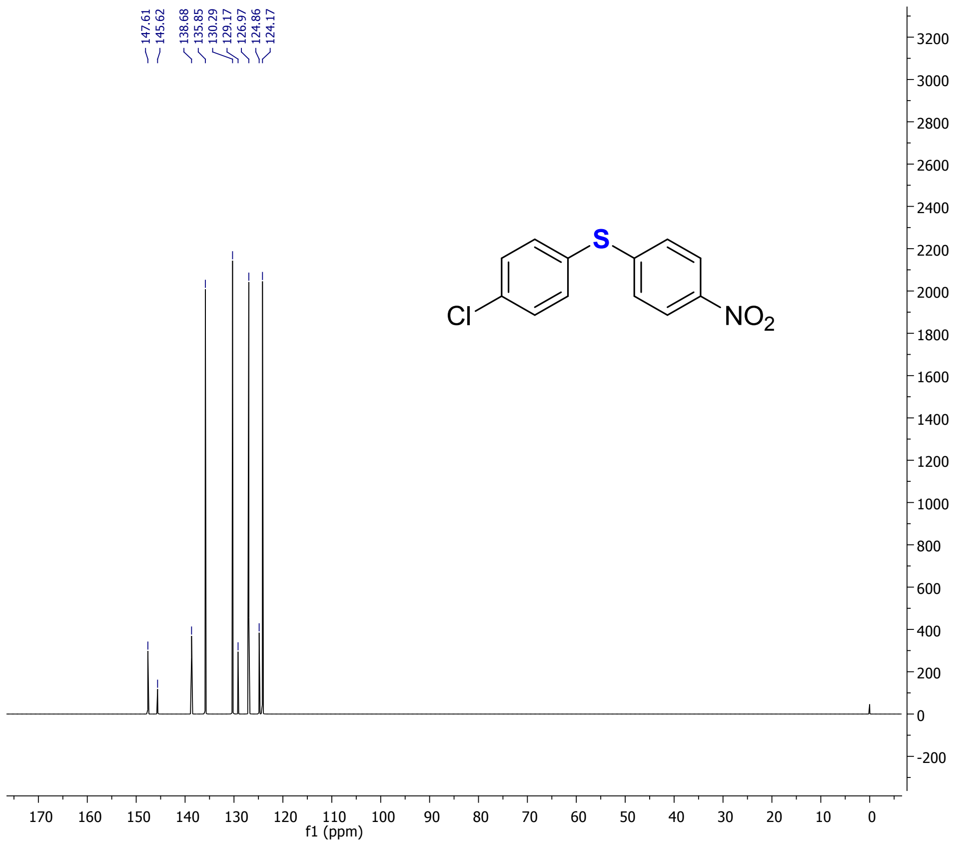


Figure 27. ^{13}C NMR spectra for the (4-chlorophenyl)(4-nitrophenyl)sulfane (entry 10)

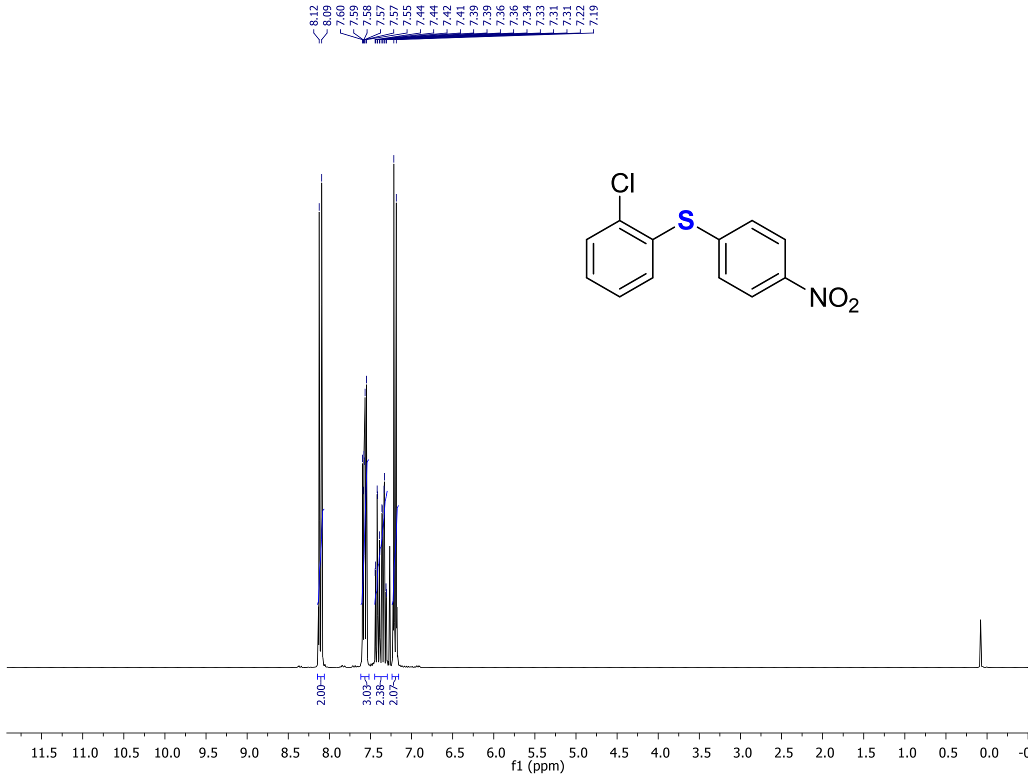


Figure 28. ^{1}H NMR spectra for the (2-chlorophenyl)(4-nitrophenyl)sulfane (entry 11)

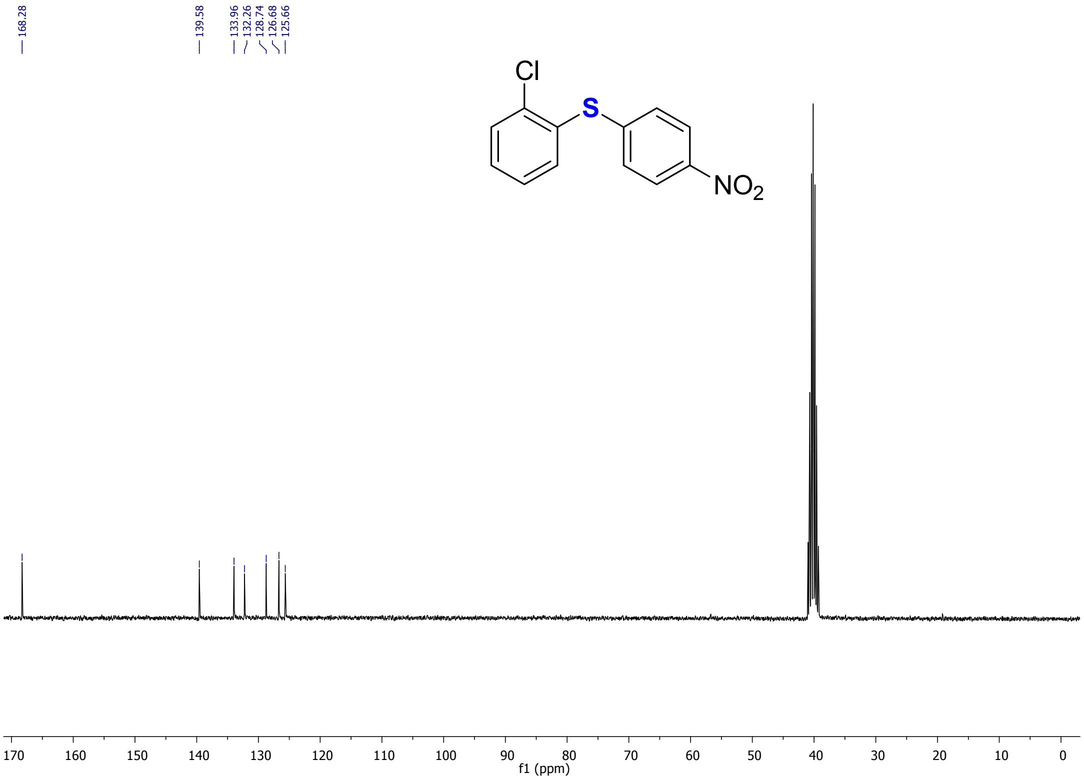


Figure 29. ^{13}C NMR spectra for the (2-chlorophenyl)(4-nitrophenyl)sulfane (entry 11)

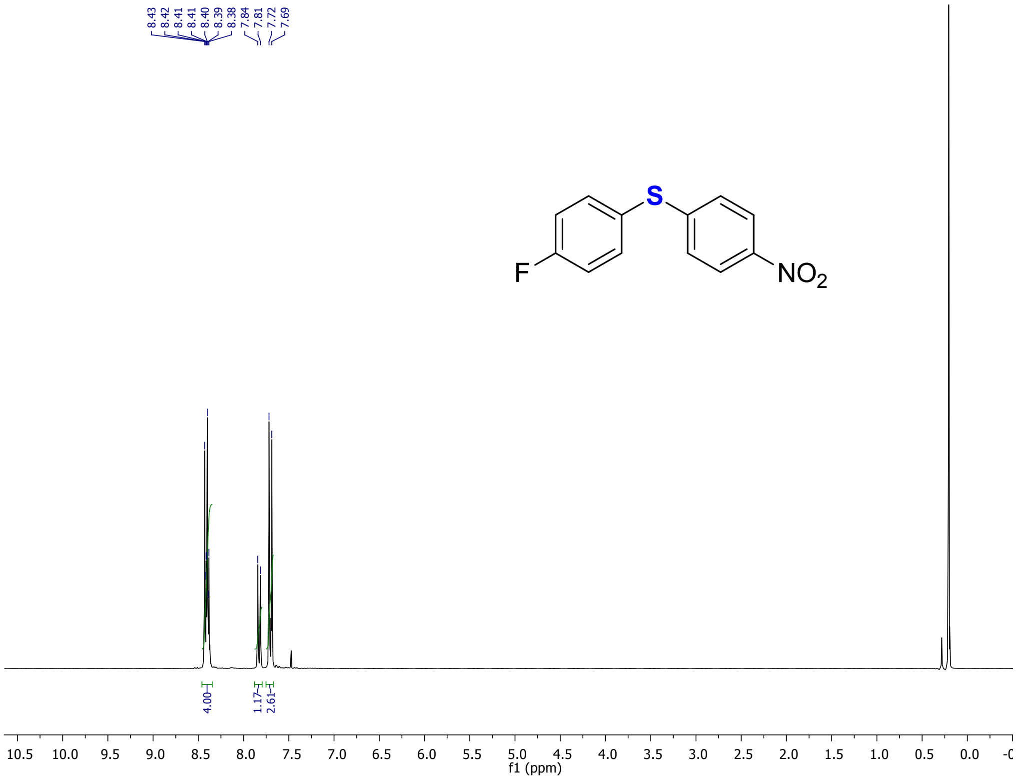


Figure 30. ^{1}H NMR spectra for the (4-fluorophenyl)(4-nitrophenyl)sulfane (entry 12)

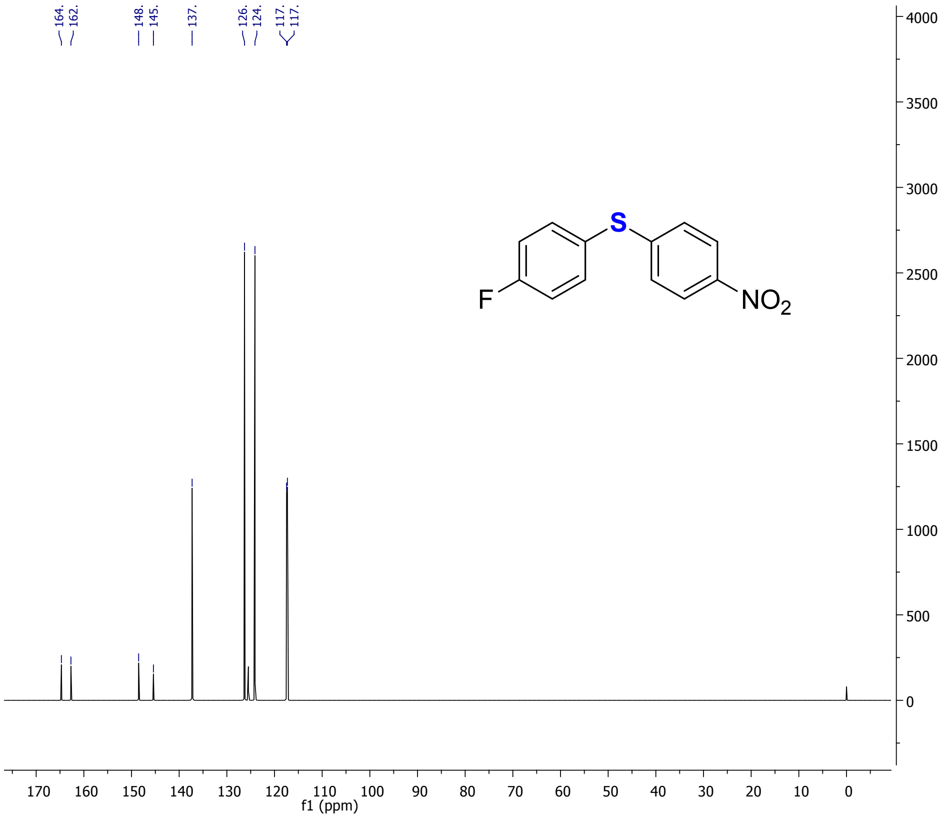


Figure 31. ${}^{13}C$ NMR spectra for the (4-fluorophenyl)(4-nitrophenyl)sulfane (entry 12)

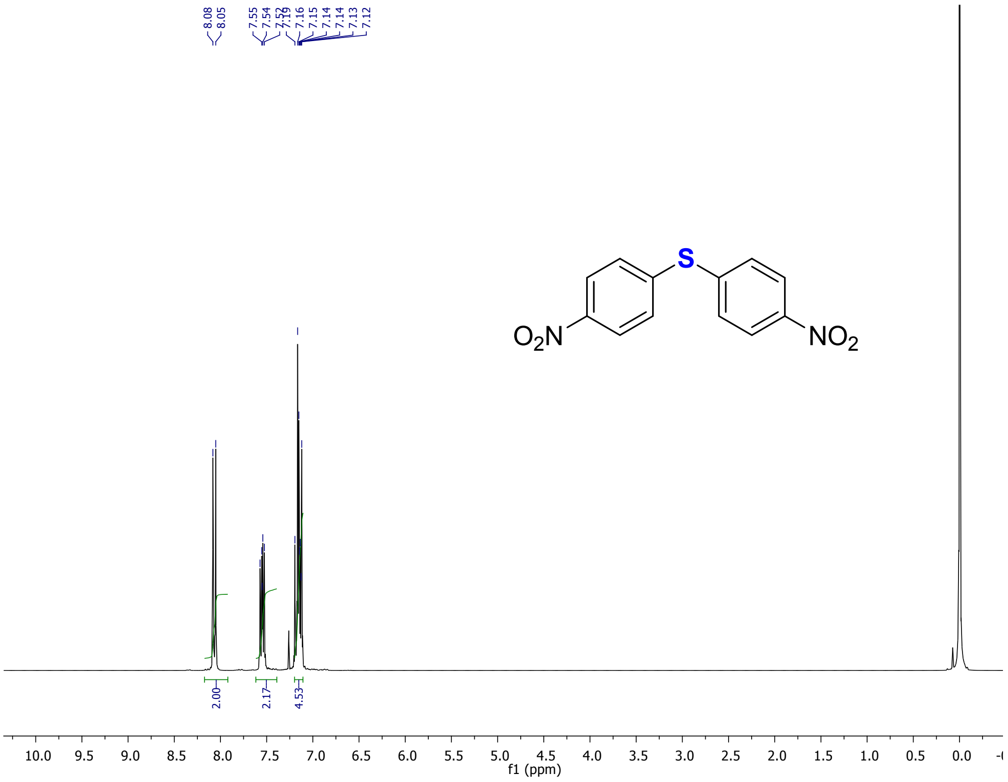


Figure 32. ${}^{1}H$ NMR spectra for the bis(4-nitrophenyl)sulfane (entry 13)

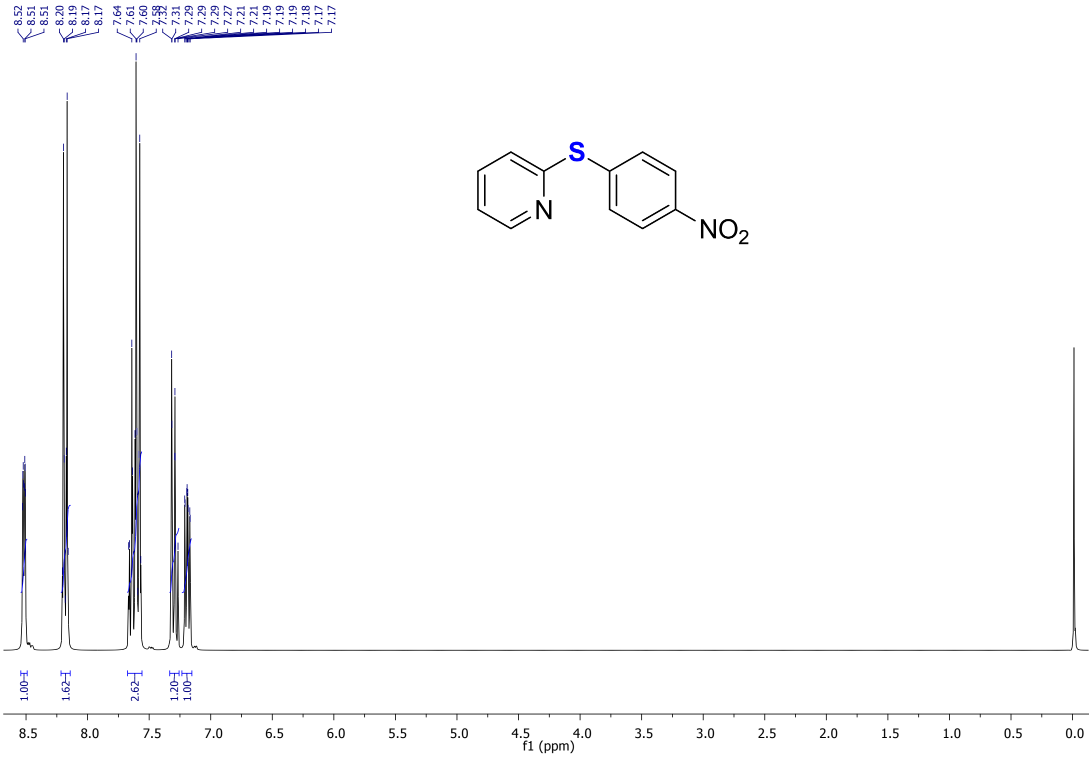


Figure 33. ^{1}H NMR spectra for the 2-((4-nitrophenyl)thio)pyridine (entry 14)

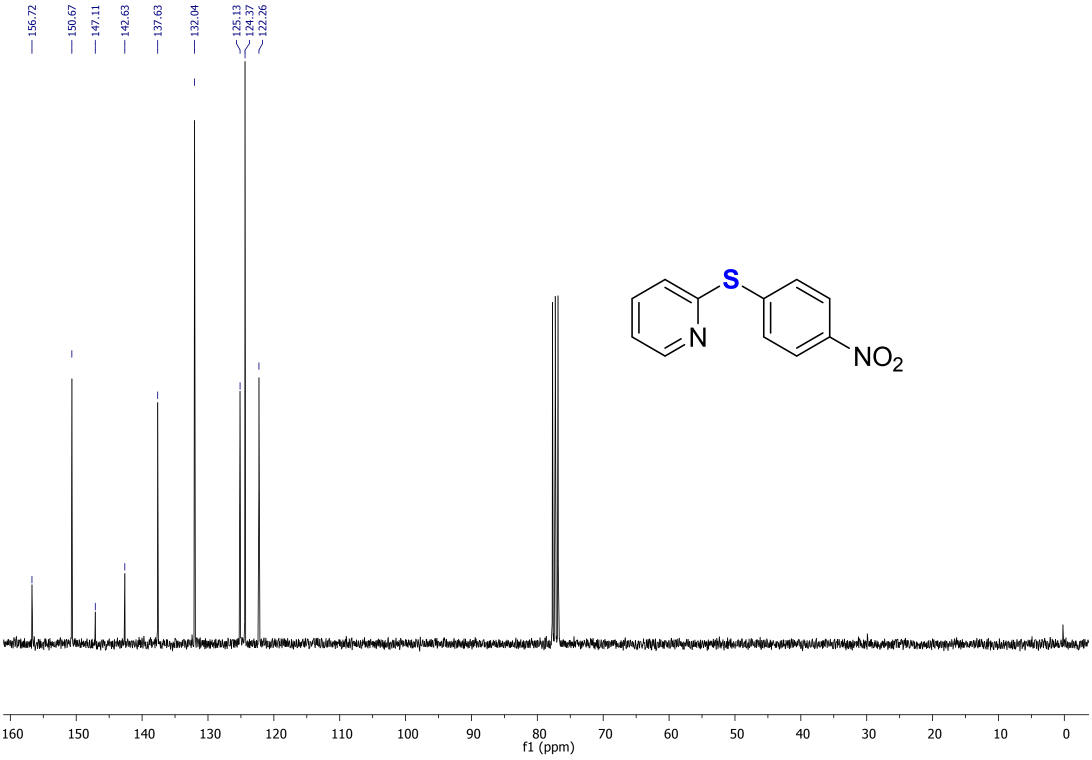


Figure 34. ^{13}C NMR spectra for the 2-((4-nitrophenyl)thio)pyridine (entry 14)

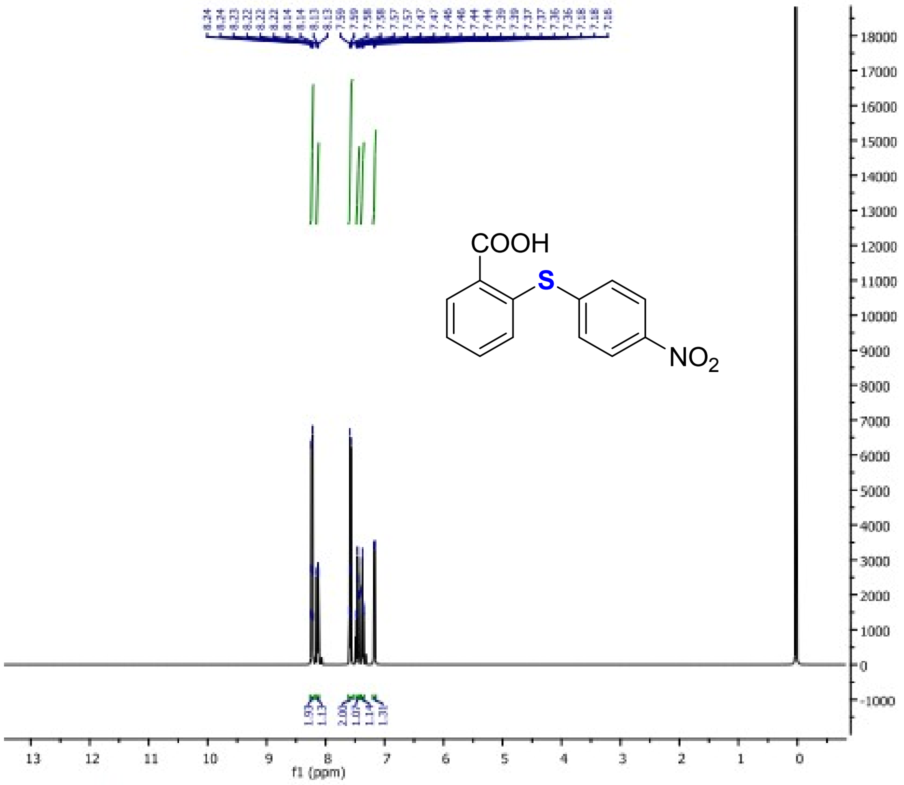


Figure 35. ^{1}H NMR spectra for the 2-((4-nitrophenyl)thio)benzoic acid (entry 15)

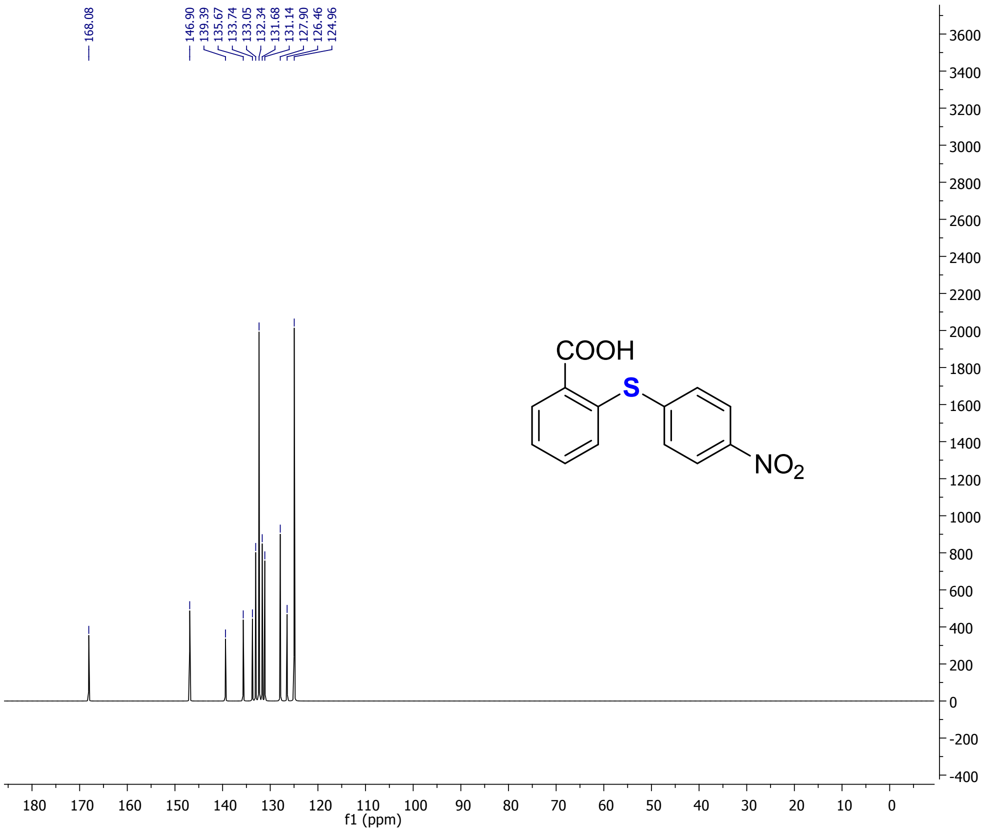


Figure 36. ^{13}C NMR spectra for the 2-((4-nitrophenyl)thio)benzoic acid (entry 15)

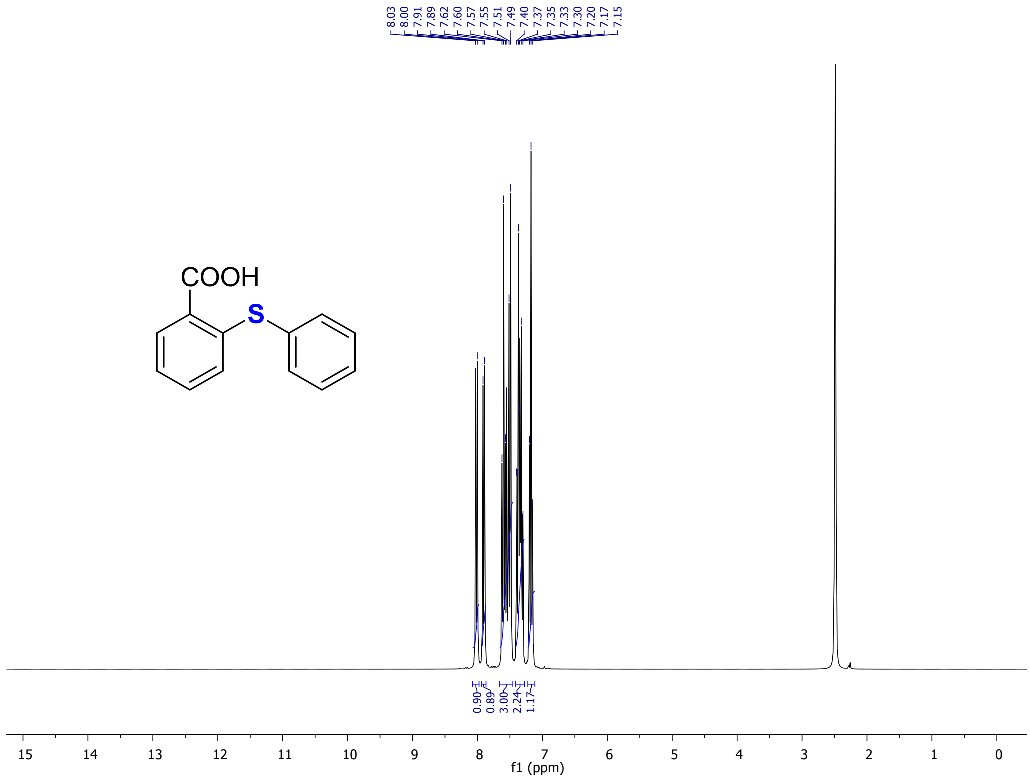


Figure 37. ^{1}H NMR spectra for the 2-(phenylthio)benzoic acid (entry 16 and 17)

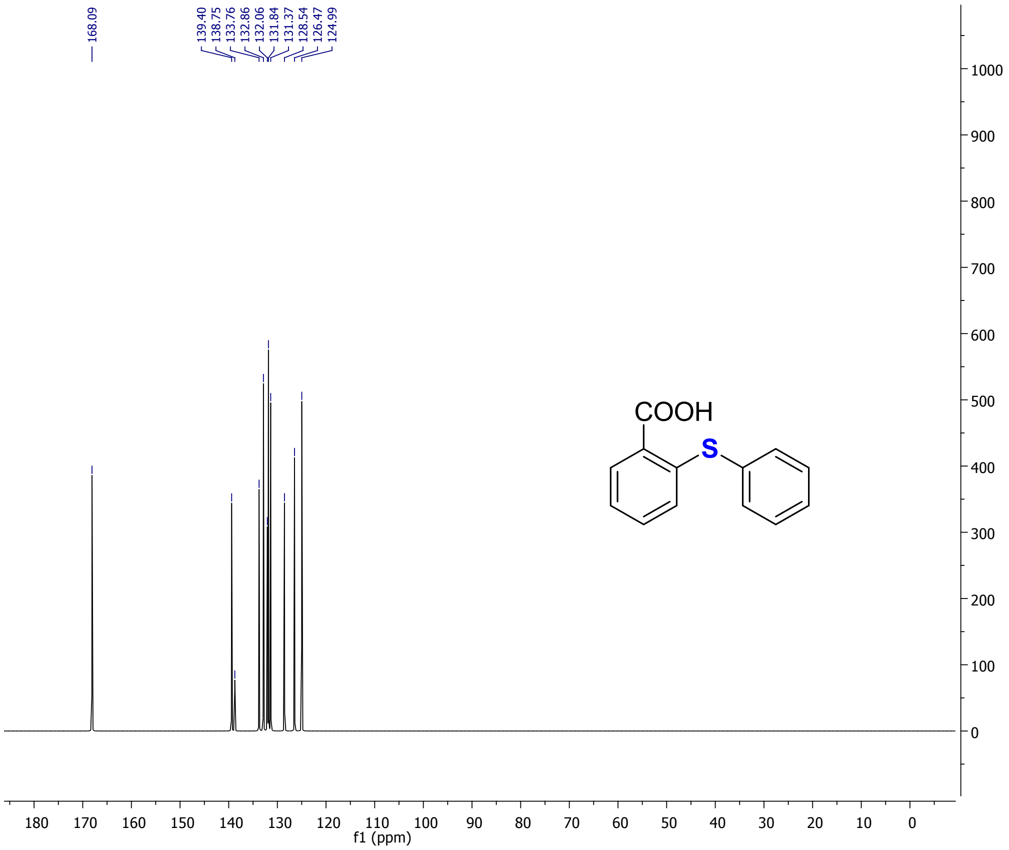


Figure 38. ^{13}C NMR spectra for the 2-(phenylthio)benzoic acid (entry 16 and 17)

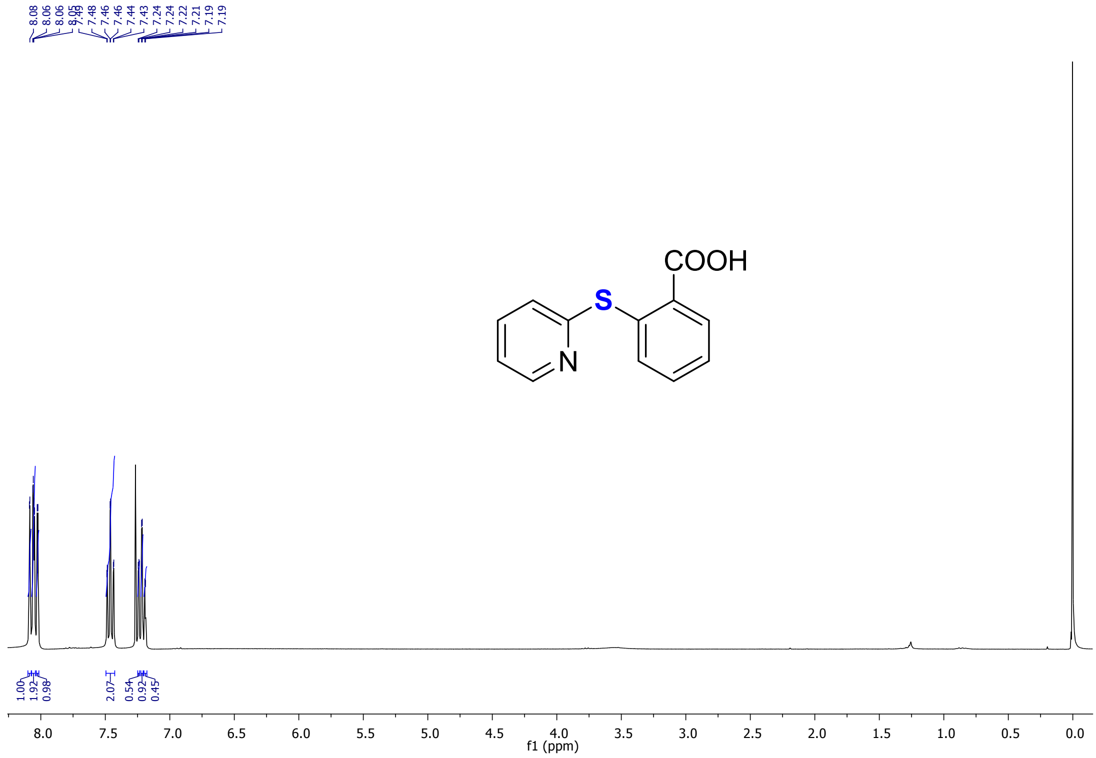


Figure 39. ^{1}H NMR spectra for the 2-(phenylthio)benzoic acid (entry 18)

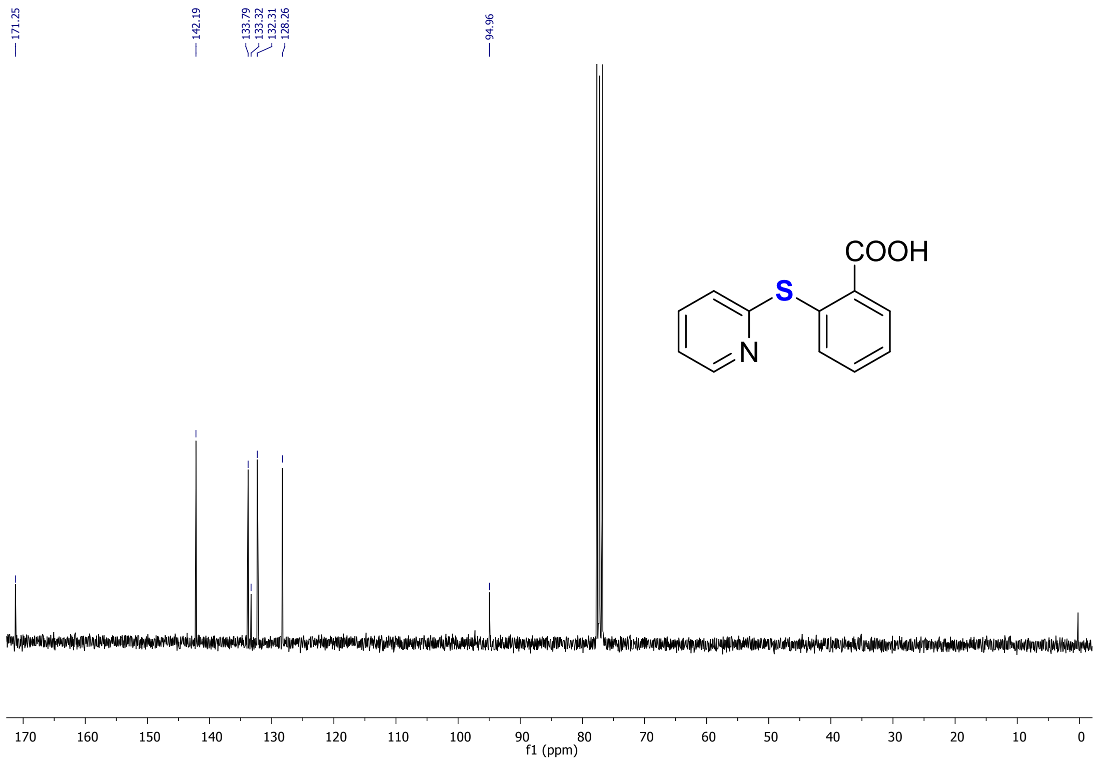


Figure 40. ^{13}C NMR spectra for the 2-(phenylthio)benzoic acid (entry 18)

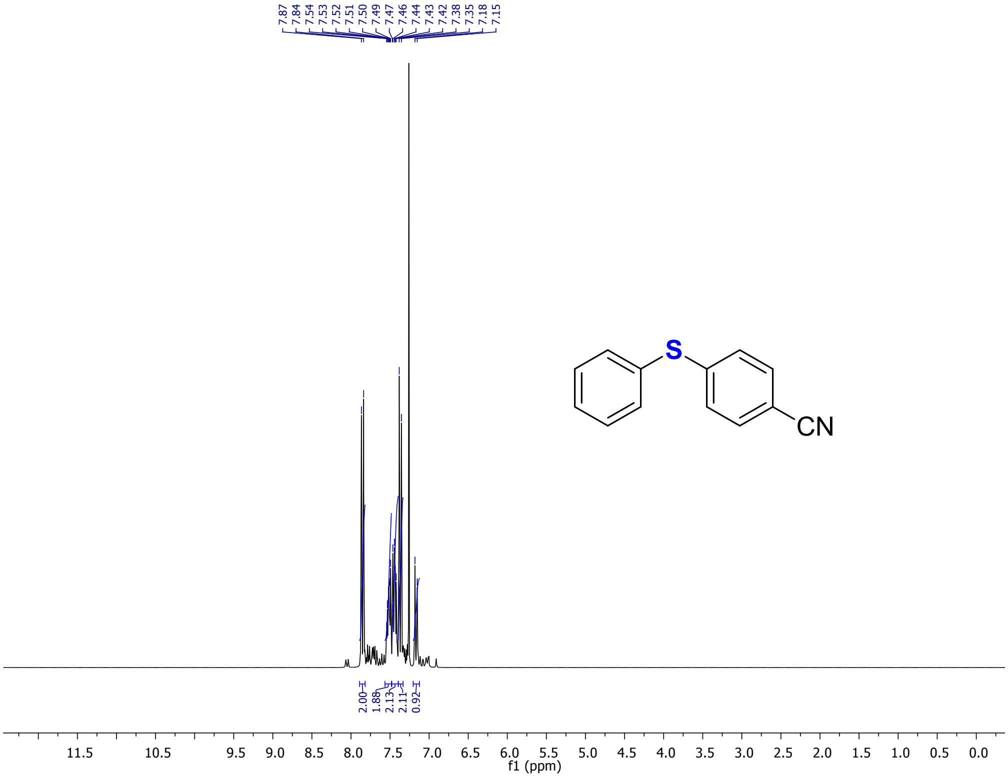


Figure 41. ^{1}H NMR spectra for the 4-(phenylthio)benzonitrile (entry 19)