Supporting info

Synthesis of aryl sulfides via visible-light induced solventylation in diarylazo sulfides

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General Information. Anilines, thiols, TEMPO, sodium nitrite, sodium acetate, sodium sulfite and solvents (HPLC grade) were commercially available and used as received. Analytical thin layer chromatography (TLC) plates (silica gel 60 F254) were visualized either with a UV lamp (254 nm), or by submersion in the chosen stain for TLC. Column chromatography was carried out on silica gel (average particle size 60 μm) by using automatic LC system. ^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz and proton-decoupled carbon 13C{1H} NMR spectra were recorded at 75 MHz or Bruker Avance Neo 400 MHz and proton-decoupled carbon 13C{1H} NMR spectra were recorded at 100 MHz. The attributions were made on the basis of ^{1}H and ^{13}C NMR experiments; chemical shifts are reported in parts per million (ppm) downfield from TMS. The following abbreviations are used for the multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). GC/MS analyses were carried out on a Thermo Scientific DSQII single quadrupole GC/MS system (TraceDSQII mass spectrometer, Trace GC Ultra gas chromatograph, TriPlus autosampler - ThermoFisher Scientific, Waltham, MA, USA), available at the Centro Grandi Strumenti (CGS) at the University of Pavia. Chromatography was performed on a Rxi-5ms capillary column (30 m length×0.25 mm ID×0.25 μm film thickness, Restek, Milan, Italy) with Helium (>99.99 %) as carrier gas at a constant flow-rate of 1.0 mL/min. An injection volume of 1 μL was employed. The injector temperature was set at 250 °C and it was operated in split mode, with a split flow of 10 mL/min. The oven temperature was programmed from 80 °C (isothermal for 5 min) to 120 °C at the rate of 3 °C/min, then from 120 °C to 250 °C (isothermal for 5 min) at the rate of 10 °C/min. Mass transfer line temperature was set at 270 °C. Total GC running time was 36 min. All mass spectra were acquired with an electron ionization system (EI, Electron Impact mode) with ionization energy of 70 eV and source temperature of 250 °C, with spectral acquisition in Full Scan mode, positive polarity, over a mass range of 40–600 Da with a scan rate of 750 amu/s. High resolution mass spectra were determined on an X500B QTOF System (SCIEX, Framingham, MA 01701 USA) available at the Centro Grandi Strumenti (CGS) of the University of Pavia, equipped with the Twin Sprayer ESI probe and coupled to an ExionLC™ system (SCIEX). UV–Vis spectra were recorded on a V-550 Jasco spectrophotometer. Photochemical reactions have been carried out with a 427 nm lamp (Kessil PR-160L, 45 W, for emission spectrum: https://kessil.com/products/science_PR160L.php) as the light source and a box equipped with a fan as the cooling system. For *in-vial* test a photobox has been employed while for 5 mL scale solutions the appropriate vessel was directly irradiated by the 427 nm Kessil PR-160L lamp (see Figure S1).
GC/MS analyses were carried out on a Thermo Scientific DSQII single quadrupole GC/MS system (TraceDSQII mass spectrometer, Trace GC Ultra gas chromatograph, TriPlus autosampler - ThermoFisher Scientific, Waltham, MA, USA), available at the Centro Grandi Strumenti (CGS) at

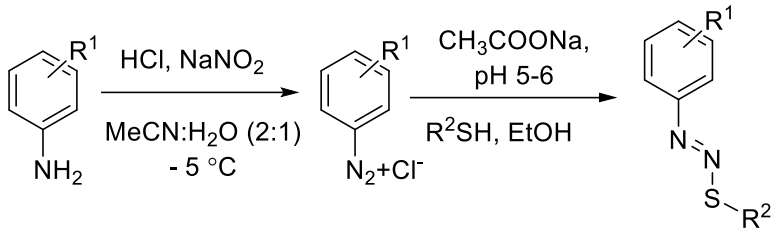
the University of Pavia. Chromatography was performed on a Rxi-5ms capillary column (30 m length×0.25 mm ID×0.25 μm film thickness, Restek, Milan, Italy) with Helium (>99.99 %) as carrier gas at a constant flow-rate of 1.0 mL/min. An injection volume of 1 μL was employed. The injector temperature was set at 250 °C and it was operated in split mode, with a split flow of 10 mL/min. The oven temperature was programmed from 80 °C (isothermal for 5 min) to 120 °C at the rate of 3 °C/min, then from 120 °C to 250 °C (isothermal for 5 min) at the rate of 10 °C/min. Mass transfer line temperature was set at 270 °C. Total GC running time was 36 min. All mass spectra were acquired with an electron ionization system (EI, Electron Impact mode) with ionization energy of 70 eV and source temperature of 250 °C, with spectral acquisition in Full Scan mode, positive polarity, over a mass range of 40–600 Da with a scan rate of 750 amu/s.

The chromatogram acquisition, detection of mass spectral peaks and their waveform processing were performed using Xcalibur MS Software Version 2.1 (Thermo Scientific Inc.). Assignment of chemical structures to chromatographic peaks was based on the comparison with the databases for GC-MS NIST Mass Spectral Library (NIST 08) and Wiley Registry of Mass Spectral Data (8th Edition).

GC-FID analyses were performed using a HP SERIES 5890 II equipped with a fire ion detector (FID, temperature 350 °C). Analytes were separated using a Restek Rtx-5MS (30 m×0.25 mm×0.25 μm) capillary column with nitrogen as a carrier gas at 1 mL min^{-1}. The injector temperature was 250 °C. The GC oven temperature was held at 80 °C for 2 min, increased to 250 °C by a temperature ramp of 10 °C min^{-1}, and held for 10 min. HPLC analyses have been performed by means of a JASCO system (Jasco LC-NET II/ ADC, Japan instrument, JASCO-PU980 pumps and JASCO-UV975 detector) using Thermo Fisher ODS-Hypersyl column C20 HPLC Column (25 cm × 4.6 mm, 5 μm particle size). Solvents used for the elution process was 1,4-Dioxane, and a flow rate of 0.7 mL min^{-1} was adopted. For the injection has been used a 20 μL coil autosampler. The UV detector was set to operate at 270 nm.

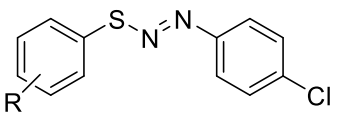
1. Experimental details

1.1 General procedure for the synthesis of diarylazo sulfides (1a-1q):[S1]

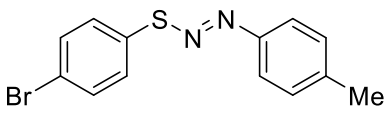


1a-1q

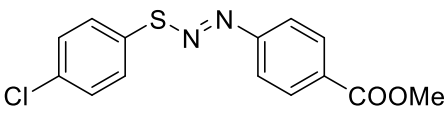
To a 15 mL MeCN/H_2O (2:1) solution of the desired aniline (5.6 mmol), concentrated HCl (1.9 mL) was added slowly at -5 °C. After 15 min, a solution of $NaNO_2$ (8.5 mmol) in 5 mL H_2O was added. Subsequently, a solution of CH_3COONa (2 g in 5 mL H_2O) was added to adjust the pH to 5-6. Finally, a 15 mL EtOH solution of the thiol (6.1 mmol) was added slowly. The mixture was maintained under vigorous stirring at 0 °C for approximately 15 min while protected from light using an aluminum covering. The reaction was then allowed to reach room temperature and monitored by TLC (cyclohexane: EtOAc 95:5). After 1 h, the reaction mixture was filtered using a Büchner funnel. The crude product was purified by dissolution in a minimal volume of ethanol and precipitated upon cooling at 0 °C, yielding diarylazo sulfides as a yellow powder. The purified compounds (see Chart S1) were stored in dark bottles and kept in a refrigerator to prevent any light-induced degradation.



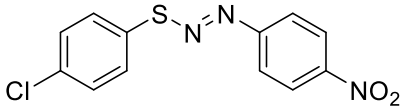
1a, R = 4-OMe; 53%
1b, R = 4-Me; 81%
1c, R = 4-tBu; 62%
1d, R = 4-H; 84%
1e, R = 4-Cl; 89%
1f, R = 4-F; 70%
1g, R = 4-CN; 51%
1h R = 3-Br; 79%
1i, R = 2-OMe; 62%
1j, R = 2-Br; 71%
1k, R = 2,4-Me; 51%
1l, R = 2,5-Cl; 56%



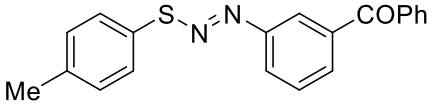
1m; 56%



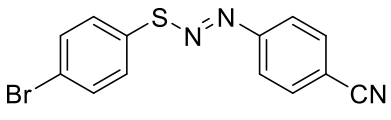
1n; 86%



1o; 97%

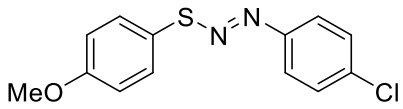


1p; 86%



1q; 79%

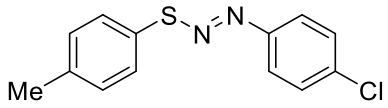
Chart S1. Arylazo sulfides employed in the present work**.**



1-(4-Chlorophenyl)-2-((4-methoxyphenyl)thio)diazene (1a).[S1] Compound **1a** was obtained from 4-chloroaniline (721 mg, 5.6 mmol) and 4-methoxythiophenol (855 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1a** was obtained in 53% yield as a yellow solid (752 mg). m.p. (dec) = 56 °C.

1a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65–7.59 (m, 2H), 7.53–7.46 (m, 2H), 7.42–7.36 (m, 2H), 7.08–7.02 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 161.2, 150.1, 135.6, 135.0, 132.6, 129.1, 123.6, 122.7, 114.7, 114.5, 55.4.

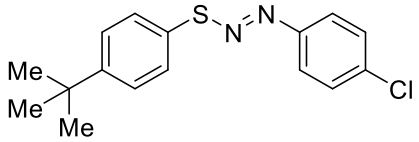
HRMS (ESI) m/z: calcd. for $C_{13}H_{11}ClN_2OS$ $[M+H]^+$: 279.0353, found: 279.0352.



1-(4-chlorophenyl)-2-(*p*-tolylthio)diazene (**1b**). Compound **1b** was obtained from 4-chloroaniline (721 mg, 5.68 mmol) and 4-methylthiophenol (758 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1b** was obtained in 81% yield as a yellow solid (1.2 g). m.p. (dec) = 61 °C.

1b: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 19.6, 8.3 Hz, 4H), 7.36 (dd, *J* = 20.6, 8.3 Hz, 4H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.1, 139.8, 135.7, 131.8, 129.9, 129.1, 122.7, 21.3.

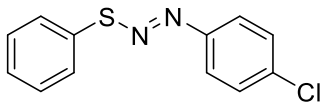
HRMS (ESI) m/z: calcd. for $C_{13}H_{11}ClN_2S$ [M+H]+ : 263.0404, found: 263.0404.



1-((4-(tert-butyl)phenyl)thio)-2-(4-chlorophenyl)diazene (**1c**). Compound **1c** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 4-tert-butylthiophenol (1.02 mL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1c** was obtained in 62% yield as a yellow solid (1.06 g). m.p. (dec) = 41 °C.

1c: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65–7.62 (m, 2H), 7.54 (dd, *J* = 8.6, 2.1 Hz, 4H), 7.43–7.38 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 152.8, 150.2, 135.7, 131.2, 130.2, 129.2, 126.2, 122.8, 34.7, 31.1.

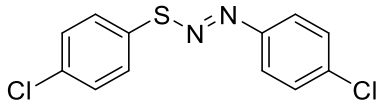
HRMS (ESI) m/z: calcd. for $C_{16}H_{17}ClN_2S$ $[M+H]^+$: 305.0874, found: 305.0869.



1-(4-chlorophenyl)-2-(phenylthio)diazene (**1d**). Compound **1d** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and thiophenol (617 μL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1d** was obtained in 84% yield as a yellow solid (1.18 g). m.p. (dec) = 63 °C.

1d: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.57–7.48 (m, 5H), 7.44–7.40 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.2, 135.9, 133.8, 130.9, 129.2, 129.1, 129.1, 122.8.

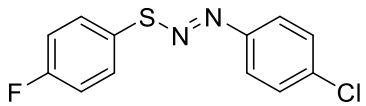
HRMS (ESI) m/z: calcd. for $C_{12}H_9ClN_2S$ $[M+H]^+$: 249.0248, found: 249.0245.



1-(4-Chlorophenyl)-2-((4-chlorophenyl)thio)diazene (**1e**).[S1] Compound **1e** was obtained from 4-chloroaniline (721 mg, 5.6 mmol) and 4-chlorothiophenol (882 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1e** was obtained in 89% yield as a yellow solid (1.42 g). m.p. (dec) = 98 °C.

1e: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.62–7.57 (m, 2H), 7.53–7.44 (m, 4H), 7.42–7.37 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.7, 136.8, 136.2, 132.9, 132.8, 130.0, 129.9, 123.5.

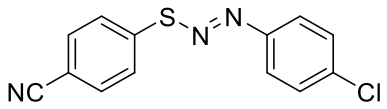
HRMS (ESI) m/z: calcd. for $C_{12}H_8Cl_2N_2S$ $[M+H]^+$: 282.9858, found: 282.9855.



1-(4-Chlorophenyl)-2-((4-fluorophenyl)thio)diazene (**1f**). Compound **1f** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 4-fluorothiophenol (642 μL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1f** was obtained in 70% yield as a yellow solid (1.05 g). m.p. (dec) = 62 °C.

1f: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70–7.64 (m, 2H), 7.53–7.49 (m, 2H), 7.43–7.39 (m, 2H), 7.22 (ddt, *J* = 8.7, 6.6, 2.1 Hz, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.3, 161.9, 150.0, 135.9, 134.3, 134.2, 129.2, 128.5, 128.5, 122.8, 116.5, 116.2.

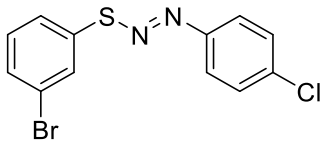
HRMS (ESI) m/z: calcd. for $C_{12}H_8ClFN_2S$ $[M+H]^+$: 267.0154, found: 267.0158.



4-(((4-Chlorophenyl)diazenyl)thio)benzonitrile (**1g**). Compound **1g** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 4-mercaptobenzonitrile (824 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1g** was obtained in 51% yield as a yellow solid (790 mg). m.p. (dec) = 108 °C.

1g: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.81–7.74 (m, 4H), 7.60–7.56 (m, 2H), 7.49–7.44 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.0, 141.1, 136.8, 132.5, 129.4, 128.1, 122.9, 118.2, 111.6.

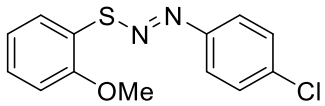
HRMS (ESI) m/z: calcd. for $C_{13}H_8ClN_3S$ $[M+H]^+$: 274.0200, found: 274.0198.



1-((3-Bromophenyl)thio)-2-(4-chlorophenyl)diazene (**1h**). Compound **1h** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 3-bromothiophenol (710 µL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1h** was obtained in 79% yield as a yellow solid (1.4 g). m.p. (dec) = 83 °C.

1h: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.4 Hz, 1H), 7.60–7.53 (m, 4H), 7.43 (dd, *J* = 8.8, 1.0 Hz, 2H), 7.40–7.35 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.0, 136.2, 135.9, 132.7, 131.9, 130.4, 129.3, 128.7, 122.9, 122.9.

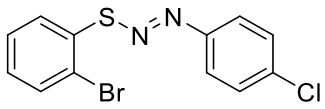
HRMS (ESI) m/z: calcd. for $C_{12}H_8BrClN_2S$ $[M+H]^+$: 326.9353, found: 326.9353.



1-(4-Chlorophenyl)-2-((2-methoxyphenyl)thio)diazene (**1i**). Compound **1i** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 2-methoxythiophenol (731 µL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1i** was obtained in 62% yield as a yellow solid (979 mg). m.p. (dec) = 64 °C.

1i: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.49–7.43 (m, 1H), 7.42–7.38 (m, 2H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.6, 150.3, 135.5, 132.4, 131.1, 129.1, 122.8, 121.6, 121.2, 111.2, 55.9.

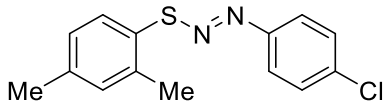
HRMS (ESI) m/z: calcd. for $C_{13}H_{11}ClN_2OS$ $[M+H]^+$: 279.0353, found: 279.0353.



1-((2-Bromophenyl)thio)-2-(4-chlorophenyl)diazene (**1j**). Compound **1j** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 2-bromothiophenol (720 µL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1j** was obtained in 71% yield as a yellow solid (1.31 g). m.p. (dec) = 93 °C.

1j: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.73–7.69 (m, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.49–7.42 (m, 3H), 7.32–7.26 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.2, 136.2, 135.5, 133.1, 130.9, 129.9, 129.3, 127.9, 123.9, 122.9.

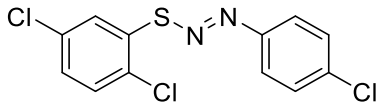
HRMS (ESI) m/z: calcd. for $C_{12}H_8BrClN_2S$ $[M+H]^+$: 326.9353, found: 326.9353.



1-(4-Chlorophenyl)-2-((2,4-dimethylphenyl)thio)diazene (**1k**). Compound **1k** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 2,5-dimethoxythiophenol (828 µL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1k** was obtained in 51% yield as a yellow solid (790 mg). m.p. (dec) = 41 °C.

1k: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54–7.49 (m, 3H), 7.42–7.37 (m, 2H), 7.29–7.20 (m, 2H), 2.40 (s, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.2, 137.4, 136.2, 135.6, 133.5, 131.7, 131.0, 130.4, 129.1, 122.7, 20.8, 19.9.

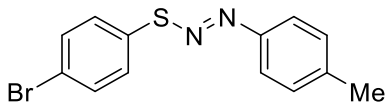
HRMS (ESI) m/z: calcd. for $C_{14}H_{13}ClN_2S$ $[M+H]^+$: 277.0561, found: 277.0559.



1-(4-Chlorophenyl)-2-((2,5-dichlorophenyl)thio)diazene (**1l**). Compound **1l** was synthesized from 4-chloroaniline (721 mg, 5.6 mmol) and 2,5-dichlorothiophenol (758 µL, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1l** was obtained in 56% yield as a yellow solid (997 mg). m.p. (dec) = 94 °C.

1l: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.58–7.51 (m, 3H), 7.45–7.38 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.0, 136.3, 135.7, 135.5, 132.5, 131.5, 129.8, 129.3, 127.7, 122.9.

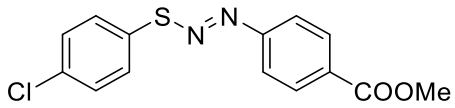
HRMS (ESI) m/z: calcd. for $C_{12}H_7Cl_3N_2S$ $[M+H]^+$: 316.9468, found: 316.9471.



1-((4-Bromophenyl)thio)-2-(*p*-tolyl)diazene (1m).[S1] Compound **1m** was obtained from 4-toluidine (605 mg, 5.6 mmol) and 4-bromothiophenol (1.15 g, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1m** was obtained in 56% yield as a yellow solid (971 mg). m.p. (dec) = 82 °C.

1m: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66–7.60 (m, 2H), 7.59–7.53 (m, 2H), 7.53–7.47 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.6, 141.4, 134.0, 132.8, 132.6, 130.3, 123.8, 122.2, 22.0.

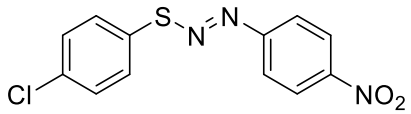
HRMS (ESI) m/z: calcd. for $C_{13}H_{11}BrN_2S$ $[M+H]^+$: 306.9899, found: 306.9898.



Methyl 4-(((4-chlorophenyl)thio)diazenyl)benzoate (**1n**).[S1] Compound **1n** was obtained from methyl 4-aminobenzoate (775 mg, 5.6 mmol) and 4-chlorothiophenol (882 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1n** was obtained in 86% yield as a yellow solid (1.49 g). m.p. (dec) = 91 °C.

1n: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.32–7.23 (m, 4H), 7.15 (d, *J* = 8.5 Hz, 2H), 3.60 (s, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.9, 154.6, 136.4, 133.1, 132.4, 131.7, 131.3, 130.1, 122.1, 52.9.

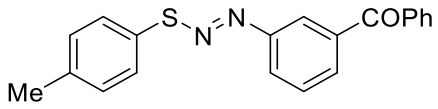
HRMS (ESI) m/z: calcd. for $C_{14}H_{11}ClN_2O_2S$ $[M+H]^+$: 307.0303, found: 307.0298.



1-((4-Chlorophenyl)thio)-2-(4-nitrophenyl)diazene (**1o**).[S1] Compound **1o** was obtained from 4-nitroaniline (780.4 mg, 5.6 mmol) and 4-chlorothiophenol (882 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1o** was obtained in 97% yield as an orange solid (1.61 g). m.p. (dec) = 107 °C.

1o: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.9 Hz, 2H), 7.64 (dd, *J* = 19.6, 8.7 Hz, 4H), 7.50 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 154.6, 148.2, 136.5, 132.9, 131.4, 129.8, 125.0, 122.5.

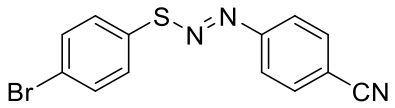
HRMS (ESI) m/z: calcd. for $C_{12}H_8ClN_3O_2S$ $[M+H]^+$: 294.0099, found: 294.0096.



Phenyl(4-((*p*-tolylthio)diazenyl)phenyl)methanone (1p).[S1] Compound 1p was obtained from 3-aminobenzophenone (1.11 g, 5.6 mmol) and 4-methylthiophenol (746 mg, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound 1p was obtained in 86% yield as a yellow solid (1.62 g). m.p. (dec) = 87 °C.

1p: ^{1}H NMR (300 MHz, Chloroform-d) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.82–7.77 (m, 2H), 7.66–7.56 (m, 5H), 7.49 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-d) δ 195.6, 153.5, 139.9, 137.8, 137.1, 132.3, 131.7, 130.8, 129.8, 129.7, 129.6, 128.1, 121.1, 21.1.

HRMS (ESI) m/z: calcd. for C20 H16 N2 OS [M+H]+ : 333.1056, found: 333.1042.



4-(((4-Bromophenyl)thio)diazenyl)benzonitrile (1q).[S1] Compound **1q** was obtained from 4-aminobenzonitrile (668 mg, 5.6 mmol) and 4-bromothiophenol (1.15 g, 6.1 mmol) in 15 mL of MeCN/H_2O 2:1. Compound **1q** was obtained in 79% yield as a yellow solid (1.3 g). m.p. (dec) = 118 °C.

1q: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.76–7.70 (m, 2H), 7.67–7.60 (m, 4H), 7.55–7.50 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 153.4, 133.5, 132.9, 132.7, 132.2, 124.5, 122.4, 118.5, 113.5.

HRMS (ESI) m/z: calcd. for $C_{13}H_8BrN_3S$ $[M+H]^+$: 317.9695, found: 317.9694.

1.2 General procedure for the determination of the quantum yield of decomposition (Φ_{-1}).

Quantum yields of decomposition (Φ_{-1}) were evaluated on the consumption of the chosen arylazo sulfide **1b**, in accordance with the reported literature.[S2] A stock solution was prepared and stored in the dark as much as possible, away from ambient light.

Stock solution: in a volumetric flask diarylazo sulfide **1b** (0.2 mmol) was dissolved in 1,4-dioxane (4 mL). The solution was kept away from the light wrapping the flask with an aluminum foil.

Test set-up: 3 mL of stock solution were placed in quartz vials (2 mm optical path) and purged with nitrogen for 5 min. Once set the right reaction environment, the solution was irradiated for 30 sec using a 427 nm Kessil lamp at 5 cm distance in an optical bench equipped with a photon-counter behind the vial housing. The consumption of **1b** was determined by HPLC technique. This procedure

has been repeated three times from the same stock solution to obtain a consistent set of data and the reported quantum yield resulted in the average value.
Results are summarized below:

Test	Φ_{-1}
1	9.4
2	9.3
3	9.5
Average	9.4

1.3 General procedure for photochemical synthesis of 2a-43a.

In a suitable glass vessel (sealed with a Teflon cap), 0.2 mmol of the selected compound **1** was added to 4 mL of the 1,4-dioxane as a selected solvent. The resulting suspension was purged with nitrogen for 5 min and subsequently irradiated at 427 nm using a Kessil PR-160L lamp (45 W) under continuous stirring for 30 min (Figure S1). A fan was positioned adjacent to the irradiation system to prevent thermal contributions to the reaction.

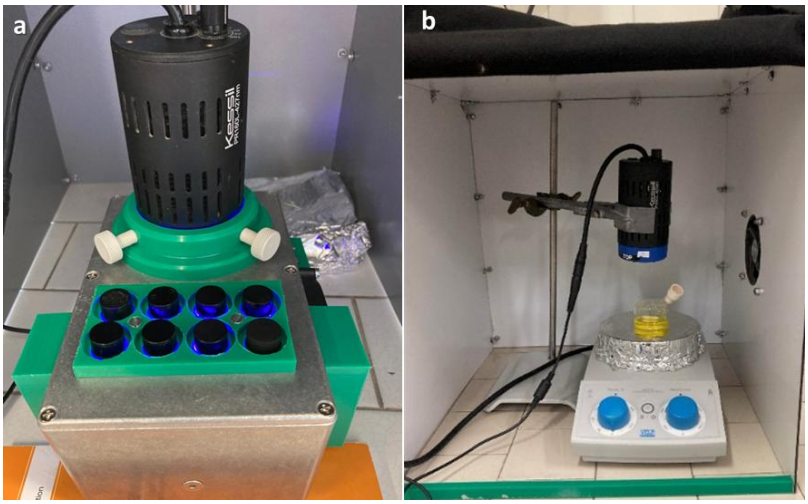
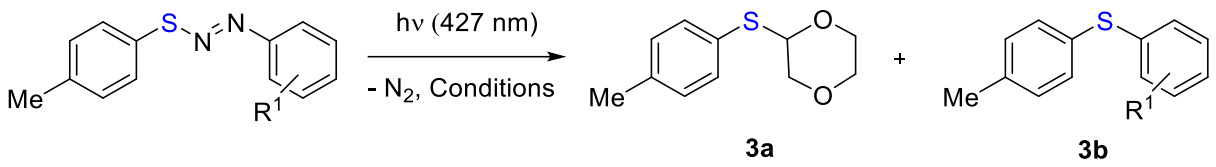


Figure S1. Photochemical set-ups. a) In vials experiments: a fan-cooled photoreactor accommodates a 427 nm Kessil Lamp and vials; the system is placed in a box equipped with a fan to keep reaction temperature equal to ambient. b) Large scale experiments: a fan-cooled photoreactor accommodates a 427 nm Kessil Lamp and vials; the system is placed in a box equipped with a fan to keep reaction temperature equal to ambient.

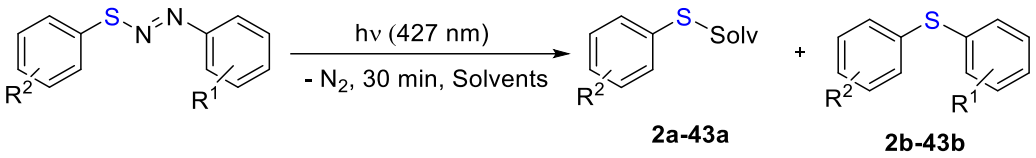
Table S1. Optimization of the reaction conditions

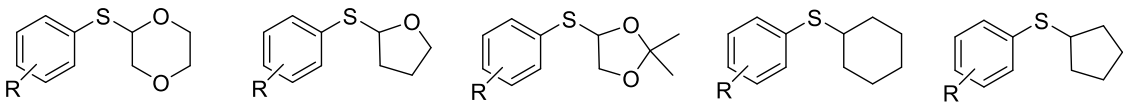


Entry	Arylazo Sulfide	UV Lamp (Wavelength)	Solvent	Conc.	Reaction Time (h)	% Yield (3a)[a]	% Yield (3b)[a]
1	**1b,** R^1 = 4-Cl	427 nm	DMC/1,4-Dioxane 10 equiv.	0.05 M	16 h	11	37
2	**1b,** R^1 = 4-Cl	427 nm	1,4-Dioxane	0.05 M	16 h	64	13
3	**1b,** R^1 = 4- Cl	427 nm	1,4-Dioxane	0.05 M	8 h	73	10
4	**1b, R^1 = 4- Cl**	**427 nm**	**1,4-Dioxane**	**0.05 M**	**30 min**	**82**	**8**
5	**1b,** R^1 = 4- Cl	427 nm	1,4-Dioxane	0.1 M	30 min	74	13
6	**1b,** R^1 = 4- Cl	427 nm	1,4-Dioxane	0.2 M	30 min	53	19
7	**1p,** R^1 = 4-COPh	427 nm	1,4-Dioxane	0.05 M	30 min	39	13
8[b]	**1b,** R^1 = 4-Cl	427 nm	1,4-Dioxane	0.05 M	30 min	-	-

[a]Isolated yield. [b] Vessel covered with an aluminium foil.

Table S2. Scope of the reaction. [a]





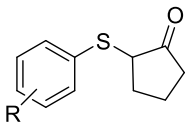
2a, R = 4-OMe
3a, R = 4-Me
4a, R = 4-tBu
5a, R = 4-H
6a, R = 4-Cl
7a, R = 4-Br
8a, R = 4-F
9a, R = 4-CN
10a, R = 3-Br
11a, R = 2-OMe
12a, R = 2-Br
13a, R = 2,4-Me
14a, R = 2,5-Cl

15a, R = 4-OMe
16a, R = 4-Me
17a, R = 4-H
18a, R = 4-Cl
19a, R = 4-Br
20a, R = 4-CN
21a, R = 2-OMe

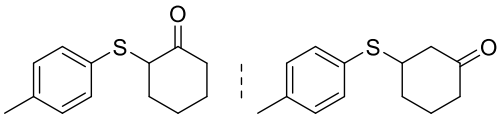
22a, R = 4-OMe
23a, R = 4-Me
24a, R = 4-Cl

25a, R = 4-OMe
26a, R = 4-Me
27a, R = 4-H
28a, R = 4-Cl
29a, R = 4-CN

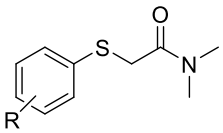
30a, R = 4-OMe
31a, R = 4-Me
32a, R = 4-H
33a, R = 4-Cl
34a, R = 3-Br



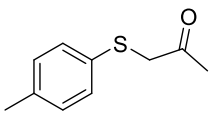
35a, R = 4-OMe
36a, R = 4-Me
37a, R = 4-Cl



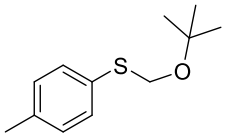
38a **38a'**



39a, R = 4-OMe
40a, R = 4-Cl
41a, R = 4-Br



42a

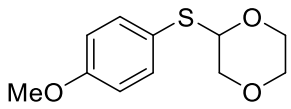


43a

Diarylazo sulfides 1	Medium (Solv-H)	% Yield	% Yield
1a, R^2 = 4-OMe, R^1 = 4-Cl	1,4-Dioxane	**2a**, 86%	**2b**, 12%
1b, R^2 = 4-Me, R^1 = 4-Cl	1,4-Dioxane	**3a**, 82%	**3b**, 8%
1c, R^2 = 4-*t*Bu, R^1 = 4-Cl	1,4-Dioxane	**4a**, 77%	**4b**, 19%
1d, R^2 = 4-H, R^1 = 4-Cl	1,4-Dioxane	**5a**, 80%	**5b**, 11%
1e, R^2 = 4-Cl, R^1 = 4-Cl	1,4-Dioxane	**6a**, 83%	**6b**, 12%
1n, R^2 = 4-Cl, R^1 = 4-CO_2Me	1,4-Dioxane	**6a**, 65%	**6b**, 13%
1o, R^2 = 4-Cl, R^1 = 4-NO_2	1,4-Dioxane	**6a**, 27%	**6b**, 12%
1m, R^2 = 4-Br, R^1 = 4-Me	1,4-Dioxane	**7a**, 77%	**7b**, 13%
1q, R^2 = 4-Br, R^1 = 4-CN	1,4-Dioxane	**7a**, 70%	**7b**, 9%
1f, R^2 = 4-F, R^1 = 4-Cl	1,4-Dioxane	**8a**, 78%	**8b**, 8%
1g, R^2 = 4-CN, R^1 = 4-Cl	1,4-Dioxane	**9a**, 61%	**9b**, 6%
1h, R^2 = 3-Br, R^1 = 4-Cl	1,4-Dioxane	**10a**, 84%	**10b**, 13%
1i, R^2 = 2-OMe, R^1 = 4-Cl	1,4-Dioxane	**11a**, 71%	**11b**, 5%
1j, R^2 = 2-Br, R^1 = 4-Cl	1,4-Dioxane	**12a**, 75%	**12b**, 13%

1k, R^2 = 2,4-Me, R^1 = 4-Cl	1,4-Dioxane	**13a**, 80%	**13b**, 14%
1l, R^2 = 2,5-Cl, R^1 = 4-Cl	1,4-Dioxane	**14a**, 77%	**14b**, 13%
1a, R^2 = 4-OMe, R^1 = 4-Cl	THF	**15a**, 61%	**15b**, 11%
1b, R^2 = 4-Me, R^1 = 4-Cl	THF	**16a**, 51%	**16b**, 9%
1d, R^2 = 4-H, R^1 = 4-Cl	THF	**17a**, 59%	**17b**, 8%
1e, R^2 = 4-Cl, R^1 = 4-Cl	THF	**18a**, 56%	**18b**, 9%
1m, R^2 = 4-Br, R^1 = 4-Me	THF	**19a**, 52%	**19b**, 9%
1g, R^2 = 4-CN, R^1 = 4-Cl	THF	**20a**, 40%	**20b**, 11%
1i, R^2 = 2-OMe, R^1 = 4-Cl	THF	**21a**, 66%	**21b**, 8%
1a, R^2 = 4-OMe, R^1 = 4-Cl	2,2-dimethyl-1,3-dioxolane	**22a**, 83%	**22b**, 11%
1b, R^2 = 4-Me, R^1 = 4-Cl	2,2-dimethyl-1,3-dioxolane	**23a**, 75%	**23b**, 10%
1e, R^2 = 4-Cl, R^1 = 4-Cl	2,2-dimethyl-1,3-dioxolane	**24a**, 73%	**24b**, 10%
1a, R^2 = 4-OMe, R^1 = 4-Cl	Cyclohexane	**25a**, 64%	**25b**, 17%
1b, R^2 = 4-Me, R^1 = 4-Cl	Cyclohexane	**26a**, 47%	**26b**, 9%
1d, R^2 = 4-H, R^1 = 4-Cl	Cyclohexane	**27a**, 68%	**27b**, 11%
1n, R^2 = 4-Cl, R^1 = 4-CO_2Me	Cyclohexane	**28a**, 63%	**28b**, 10%
1g, R^2 = 4-CN, R^1 = 4-Cl	Cyclohexane	**29a**, 41%	**29b**, 12%
1a, R^2 = 4-OMe, R^1 = 4-Cl	Cyclopentane	**30a**, 72%	**30b**, 12%
1b, R^2 = 4-Me, R^1 = 4-Cl	Cyclopentane	**31a**, 61%	**31b**, 9%
1d, R^2 = 4-H, R^1 = 4-Cl	Cyclopentane	**32a**, 61%	**32b**, 7%
1e, R^2 = 4-Cl, R^1 = 4-Cl	Cyclopentane	**33a**, 65%	**33b**, 12%
1h, R^2 = 3-Br, R^1 = 4-Cl	Cyclopentane	**34a**, 63%	**34b**, 10%
1a, R^2 = 4-OMe, R^1 = 4-Cl	Cyclopentanone	**35a**, 68%	**35b**, 13%
1b, R^2 = 4-Me, R^1 = 4-Cl	Cyclopentanone	**36a**, 67%	**36b**, 14%
1e, R^2 = 4-Cl, R^1 = 4-Cl	Cyclopentanone	**37a**, 59%	**37b**, 9%
1b, R^2 = 4-Me, R^1 = 4-Cl	Cyclohexanone	**38a**, 34%; **38a'**, 23%	**38b**, 10%
1a, R^2 = 4-OMe, R^1 = 4-Cl	Cyclopentanone	**35a**, 68%	**35b**, 13%
1a, R^2 = 4-OMe, R^1 = 4-Cl	DMF	**39a**, 35%	**39b**, 14%
1e, R^2 = 4-Cl, R^1 = 4-Cl	DMF	**40a**, 44%	**40b**, 17%
1m, R^2 = 4-Br, R^1 = 4-Me	DMF	**41a**, 31%	**41b**, 13%
1b, R^2 = 4-Me, R^1 = 4-Cl	Acetone	**42a**, 46%	**42b**, 43%
1b, R^2 = 4-Me, R^1 = 4-Cl	*tert*-Butyl methyl ether	**43a**, 32%	**43b**, 36%

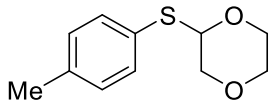
[a] Reaction conditions. A solution of the diarylazo sulfide **1a–1q** (0.05 M), irradiated for 30 min at 427 nm (32 W Kessil lamp) in the chosen medium.



2-((4-Methoxyphenyl)thio)-1,4-dioxane (2a). Compound **2a** was obtained from **1a** (56 mg, 0.2 mmol) in 86% yield (pale yellow liquid, 39.1 mg) along with compound **2b**[S3] (6 mg, 12% yield).

2a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50–7.45 (m, 2H), 6.89–6.85 (m, 2H), 4.94 (dd, *J* = 6.3, 2.9 Hz, 1H), 4.24–4.17 (m, 1H), 3.99–3.94 (m, 1H), 3.82 (s, 3H), 3.72–3.63 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.7, 134.9, 123.4, 114.4, 83.7, 69.7, 66.3, 64.2, 55.2.

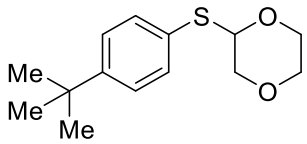
Spectroscopic data of compound **2a** was in accordance with the literature.[S4]



2-(*p*-Tolylthio)-1,4-dioxane (3a). Compound **3a** was obtained from **1b** (52.6 mg, 0.2 mmol) in 82% yield (pale yellow liquid, 34.5 mg) along with compound **3b**[S1] (4 mg, 8% yield).

3a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.45–7.40 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.05 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.23 (ddd, *J* = 10.8, 4.8, 2.4 Hz, 1H), 4.03–3.97 (m, 1H), 3.75–3.67 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.8, 132.5, 130.1, 129.9, 83.6, 70.0, 66.6, 64.2, 21.2.

Spectroscopic data of compound **3a** was in accordance with the literature.[S5]

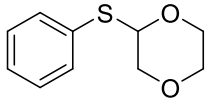


2-((4-(*tert*-Butyl)phenyl)thio)-1,4-dioxane (4a). Compound **4a** was obtained from **1c** (61 mg, 0.2 mmol) in 77% yield (pale yellow liquid, 39 mg) along with compound **4b**[S6] (11 mg, 19% yield).

4a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 5.09 (dd, J = 5.9, 3.0 Hz, 1H), 4.28–4.22 (m, 1H), 4.03–3.98 (m, 1H), 3.76–3.68 (m, 4H), 1.33 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.6, 131.7, 130.1, 125.9, 83.3, 69.8, 66.4, 63.8, 34.4, 31.1.

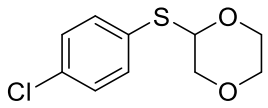
Spectroscopic data of compound **4a** was in accordance with the literature.[S4]



2-(Phenylthio)-1,4-dioxane (5a). Compound **5a** was obtained from **1d** (50 mg, 0.2 mmol) in 80% yield (pale yellow-brown liquid, 31.4 mg) along with compound **5b**[S7] (5 mg, 11% yield).

5a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.36–7.27 (m, 3H), 5.14 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.28–4.22 (m, 1H), 4.04–3.98 (m, 1H), 3.77–3.68 (m, 4H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.1, 131.7, 129.1, 127.5, 83.4, 70.0, 66.6, 63.9.

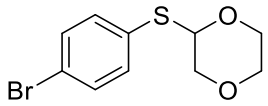
Spectroscopic data of compound **5a** were in accordance with the literature.[S5]



2-((4-Chlorophenyl)thio)-1,4-dioxane (6a). Compound **6a** was obtained from **1e** (52.5 mg, 0.2 mmol) in 83% yield (pale yellow solid, 38.3 mg) along with compound **6b**[S1] (6 mg, 12% yield).

6a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.02 (dd, *J* = 5.4, 3.0 Hz, 1H), 4.20–4.13 (m, 1H), 3.91 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.69–3.57 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 133.5, 132.8, 132.4, 128.9, 83.2, 69.7, 66.4, 63.4.

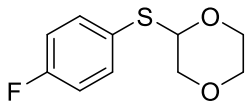
Spectroscopic data of compound **6a** was in accordance with the literature.[S5]



2-((4-Bromophenyl)thio)-1,4-dioxane (7a). Compound **7a** was obtained from **1m** (61.5 mg, 0.2 mmol) in 77% yield (pale yellow solid, 45.5 mg) along with compound **7b**[S1] (7.3 mg, 13% yield).

7a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.48–7.40 (m, 2H), 7.40–7.34 (m, 2H), 5.11 (dd, *J* = 5.3, 3.0 Hz, 1H), 4.29–4.22 (m, 1H), 3.99 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.77–3.66 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 132.9, 132.7, 131.7, 121.2, 82.9, 69.5, 66.2, 63.2, 29.4.

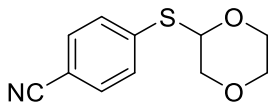
Spectroscopic data of compound **7a** was in accordance with the literature.[S8]



2-((4-Fluorophenyl)thio)-1,4-dioxane (8a). Compound **8a** was obtained from **1f** (61 mg, 0.2 mmol) in 78% yield (pale yellow-brown liquid, 33.4 mg) along with compound **8b**[S9] (4 mg, 8% yield).

8a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.02 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.25 (ddd, *J* = 7.8, 4.7, 2.5 Hz, 1H), 4.02–3.96 (m, 1H), 3.75–3.67 (m, 4H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.4, 134.3, 128.5, 116.1, 115.8, 83.5, 69.7, 66.4, 63.7.

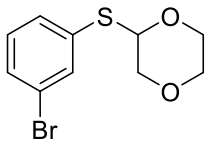
Spectroscopic data of compound **8a** were in accordance with the literature.[S4]



4-((1,4-Dioxan-2-yl)thio)benzonitrile (9a). Compound **9a** was obtained from **1g** (54.7 mg, 0.2 mmol) in 61% yield (pale yellow solid, 27 mg), m.p. (dec) = 76 °C, along with compound **9b**[S10] (3 mg, 6% yield).

9a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.62–7.52 (m, 4H), 5.35 (dd, *J* = 4.1, 3.0 Hz, 1H), 4.34–4.25 (m, 1H), 4.04 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.87–3.78 (m, 3H), 3.74–3.67 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 142.4, 132.2, 129.1, 118.6, 109.6, 82.1, 69.6, 66.6, 62.5.

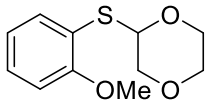
HRMS (ESI) m/z: calcd. for $C_{11}H_{11}NO_2S$ $[M+H]^+$: 222.0583, found: 222.0582.



2-((3-Bromophenyl)thio)-1,4-dioxane (10a). Compound **10a** was obtained from **1h** (66 mg, 0.2 mmol) in 84% yield (pale yellow liquid, 46 mg) along with compound **10b**[S1] (8 mg, 13% yield).

10a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.46–7.36 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 5.18 (dd, *J* = 5.0, 3.0 Hz, 1H), 4.31–4.24 (m, 1H), 4.00 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.80–3.66 (m, 4H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.8, 133.6, 130.3, 130.3, 129.7, 122.8, 83.3, 70.0, 66.7, 63.4.

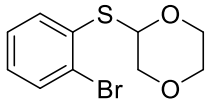
Spectroscopic data of compound **10a** was in accordance with the literature.[S11]



2-((2-Methoxyphenyl)thio)-1,4-dioxane (11a). Compound **11a** was obtained from **1i** (65 mg, 0.2 mmol) in 71% yield (pale yellow-brown solid, 32 mg) along with compound **11b**[S12] (3 mg, 5% yield).

11a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.30–7.24 (m, 1H), 6.98–6.88 (m, 2H), 5.25 (dd, *J* = 5.4, 3.0 Hz, 1H), 4.28–4.21 (m, 1H), 4.03 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.90 (s, 3H), 3.75 (dd, *J* = 4.5, 2.8 Hz, 3H), 3.68–3.62 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.9, 132.6, 128.6, 121.7, 121.1, 110.7, 81.3, 69.8, 66.4, 63.4, 55.7.

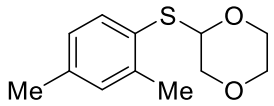
Spectroscopic data of compound **11a** was in accordance with the literature.[S11]



2-((2-Bromophenyl)thio)-1,4-dioxane (12a). Compound **12a** was obtained from **1j** (65.5 mg, 0.2 mmol) in 75% yield (pale yellow liq, 41.3 mg) along with compound **12b**[S1] (8 mg, 13% yield).

12a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 (ddd, *J* = 10.9, 7.9, 1.5 Hz, 2H), 7.32–7.27 (m, 1H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 5.29 (dd, *J* = 4.5, 3.1 Hz, 1H), 4.32 (ddd, *J* = 11.8, 6.5, 3.8 Hz, 1H), 4.06 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.88 (dd, *J* = 11.9, 4.5 Hz, 1H), 3.81–3.77 (m, 2H), 3.68 (ddd, *J* = 11.8, 4.6, 3.1 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.2, 133.2, 131.2, 128.1, 128.0, 125.1, 82.4, 69.9, 66.8, 63.1.

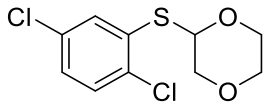
Spectroscopic data of compound **12a** was in accordance with the literature.[S11]



2-((2,4-Dimethylphenyl)thio)-1,4-dioxane (13a). Compound **13a** was obtained from **1k** (55 mg, 0.2 mmol) in 80% yield (pale yellow solid, 35.9 mg), m.p. (dec) = 46 °C, along with compound **13b**[S13] (7 mg, 14% yield).

13a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 1.7 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.8 Hz, 1H), 5.12 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.28–4.21 (m, 1H), 4.05–3.99 (m, 1H), 3.77 (s, 1H), 3.77–3.74 (m, 2H), 3.74–3.66 (m, 1H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.7, 136.6, 133.6, 132.7, 130.6, 128.7, 83.5, 70.8, 67.1, 64.4, 21.5, 20.9.

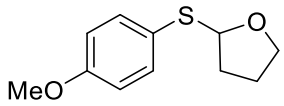
HRMS (ESI) m/z: calcd. for $C_{12}H_{16}O_2S$ $[M+Na]^+$: 247.0763, found: 247.0763.



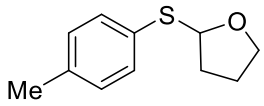
2-((2,5-Dichlorophenyl)thio)-1,4-dioxane (14a). Compound **14a** was obtained from **1l** (63.5 mg, 0.2 mmol) in 77% yield (pale yellow solid, 40.8 mg), m.p. (dec) = 57 °C, along with compound **14b**[S1] (7.7 mg, 13% yield).

14a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.25 (dd, *J* = 4.2, 3.1 Hz, 1H), 4.34–4.27 (m, 1H), 4.05 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.89–3.83 (m, 1H), 3.80–3.76 (m, 2H), 3.70–3.63 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 135.8, 133.4, 132.7, 132.6, 129.7, 127.7, 82.3, 69.9, 66.8, 62.9.

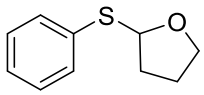
HRMS (ESI) m/z: calcd. for $C_{10}H_{10}Cl_2O_2S$ $[M+Na]^+$: 302.9260, found: 302.9621.



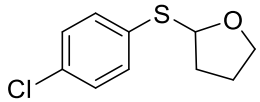
2-((4-Methoxyphenyl)thio)tetrahydrofuran (15a). Compound **15a** was obtained from **1a** (56 mg, 0.2 mmol) in 61% yield (slight yellow liq, 25.7 mg) along with compound **15b**[S3] (6 mg, 12% yield).
15a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.41 (dd, *J* = 7.0, 3.6 Hz, 1H), 3.98–3.82 (m, 2H), 3.73 (s, 3H), 2.31–2.19 (m, 1H), 1.97–1.73 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.6, 134.8, 125.7, 114.6, 88.3, 67.3, 55.5, 32.6, 29.8, 25.0.
Spectroscopic data of compound **15a** was in accordance with the literature.[S5]



2-(*p*-Tolylthio)tetrahydrofuran (16a). Compound **16a** was obtained from **1b** (53 mg, 0.2 mmol) in 51% yield (slight yellow liquid, 19.8 mg) along with compound **16b**[S1] (4 mg, 9% yield).
16a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 5.62–5.58 (m, 1H), 4.07–3.95 (m, 2H), 2.35 (s, 3H), 2.08–1.86 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.9, 131.8, 131.6, 129.5, 87.5, 67.1, 32.5, 24.7, 21.0.
Spectroscopic data of compound **16a** was in accordance with the literature.[S5]

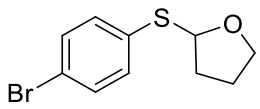


2-(Phenylthio)tetrahydrofuran (17a). Compound **17a** was obtained from **1d** (50 mg, 0.2 mmol) in 59% yield (slight yellow liquid, 21 mg) along with compound **17b**[S7] (3.6 mg, 8% yield).
17a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.57–7.51 (m, 2H), 7.35–7.25 (m, 3H), 5.67 (dd, *J* = 7.1, 3.7 Hz, 1H), 4.10–3.95 (m, 2H), 2.44–2.35 (m, 1H), 2.08–1.87 (m, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 135.6, 130.9, 128.7, 126.7, 87.0, 67.2, 32.5, 24.7.
Spectroscopic data of compound **17a** was in accordance with the literature.[S5]

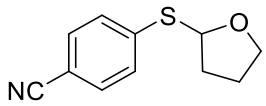


2-((4-Chlorophenyl)thio)tetrahydrofuran (18a). Compound **18a** was obtained from **1e** (57 mg, 0.2 mmol) in 56% yield (slight yellow-brown liquid, 24 mg) along with compound **18b**[S1] (4.6 mg, 9% yield).
18a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40–7.35 (m, 2H), 7.22–7.18 (m, 2H), 5.54 (dd, *J* = 7.2, 3.7 Hz, 1H), 3.98–3.88 (m, 2H), 2.35–2.27 (m, 1H), 1.99–1.79 (m, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.1, 132.9, 132.3, 128.8, 87.1, 67.2, 32.5, 24.7.

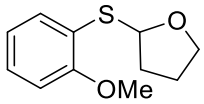
Spectroscopic data of compound **18a** was in accordance with the literature.[S5]



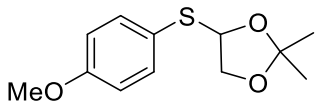
2-((4-Bromophenyl)thio)tetrahydrofuran (19a). Compound **19a** was obtained from **1m** (61.5 mg, 0.2 mmol) in 52% yield (slight yellow liquid, 27 mg) along with compound **19b**[S1] (5 mg, 9% yield).
19a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46–7.37 (m, 4H), 5.63 (dd, *J* = 7.2, 3.8 Hz, 1H), 4.07–3.95 (m, 2H), 2.45–2.32 (m, 1H), 2.09–1.85 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.7, 132.3, 131.6, 120.6, 86.8, 67.0, 32.3, 24.5.
Spectroscopic data of compound **19a** was in accordance with the literature. [S4]



4-((Tetrahydrofuran-2-yl)thio)benzonitrile (20a). Compound **20a** was obtained from **1g** (55 mg, 0.2 mmol) in 40% yield (pale yellow liquid, 16.5 mg) along with compound **20b**[S10] in (6 mg, 11% yield).
20a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56 (s, 4H), 5.80 (dd, *J* = 7.2, 3.8 Hz, 1H), 4.03 (dd, *J* = 7.7, 5.5 Hz, 2H), 2.52–2.41 (m, 1H), 2.14–1.92 (m, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.9, 132.1, 128.7, 118.8, 109.0, 85.6, 67.5, 32.4, 24.7.
Spectroscopic data of compound **20a** was in accordance with the literature.[S14]



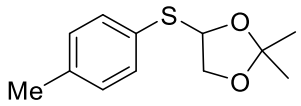
2-((2-Methoxyphenyl)thio)tetrahydrofuran (21a). Compound **21a** was obtained from **1i** (65 mg, 0.2 mmol) in 66% yield (pale yellow liquid, 28 mg) along with compound **21b**[S12] (5 mg, 8% yield).
21a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.28–7.20 (m, 1H), 6.97 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 7.1, 3.5 Hz, 1H), 4.08–3.95 (m, 2H), 3.90 (s, 3H), 2.40 (dt, *J* = 9.7, 7.2 Hz, 1H), 2.12–2.00 (m, 2H), 1.97–1.86 (m, 1H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.3, 131.4, 127.7, 123.8, 121.1, 110.4, 84.9, 67.2, 55.7, 32.5, 24.7.
Spectroscopic data of compound **21a** was in accordance with the literature.[S15]



4-((4-Methoxyphenyl)thio)-2,2-dimethyl-1,3-dioxolane (22a). Compound **22a** was obtained from **1a** (56 mg, 0.2 mmol) in 83% yield (pale yellow liquid, 40 mg) along with compound **22b**[S3] (5.5 mg, 11% yield).

22a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.51–7.48 (m, 1H), 7.44–7.40 (m, 1H), 6.90–6.86 (m, 2H), 5.45–5.38 (m, 1H), 4.32 (dd, *J* = 9.1, 6.3 Hz, 1H), 3.93 (dd, *J* = 9.1, 5.6 Hz, 1H), 3.82 (d, *J* = 1.5 Hz, 3H), 1.51–1.49 (m, 3H), 1.43–1.39 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.8, 159.7, 135.2, 132.6, 123.6, 114.5, 114.4, 111.1, 84.2, 69.3, 55.3, 55.2, 29.6, 26.2, 26.1.

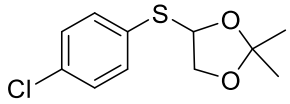
HRMS (ESI) m/z: calcd. for $C_{12}H_{16}O_3S$ [M+Na]$^+$: 263.0712, found: 263.0702.



2,2-Dimethyl-4-(p-tolylthio)-1,3-dioxolane (23a). Compound **23a** was obtained from **1b** (53 mg, 0.2 mmol) in 75% yield (pale yellow liquid, 34 mg) along with compound **23b**[S1] (5 mg, 10% yield).

23a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.51 (t, *J* = 5.9 Hz, 1H), 4.35 (dd, *J* = 9.2, 6.3 Hz, 1H), 3.95 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.36 (s, 3H), 1.52 (s, 3H), 1.42 (s, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.9, 132.7, 130.3, 129.9, 111.5, 84.2, 69.6, 26.4, 21.3.

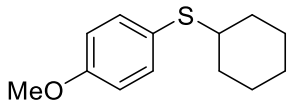
Spectroscopic data of compound **23a** was in accordance with the literature.[S16]



4-((4-Chlorophenyl)thio)-2,2-dimethyl-1,3-dioxolane (24a). Compound **24a** was obtained from **1e** (60 mg, 0.2 mmol) in 73% yield (pale yellow liquid, 36 mg) along with compound **24b**[S1] (6 mg, 10% yield).

24a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.57–5.52 (m, 1H), 4.40–4.34 (m, 1H), 3.96 (dd, *J* = 9.3, 5.4 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 133.6, 133.0, 132.6, 129.0, 111.5, 83.6, 69.3, 26.1.

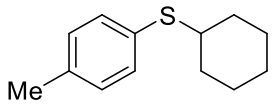
HRMS (ESI) m/z: calcd. for $C_{11}H_{13}ClO_2S$ [M+H]$^+$: 267.0217, found: 267.0233.



Cyclohexyl(4-methoxyphenyl)sulfane (25a). Compound **25a** was obtained from **1a** (56 mg, 0.2 mmol) in 64% yield (pale yellow liquid, 29 mg) along with compound **25b**[S3] (8.7 mg, 17% yield).

25a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 2.93 (dd, *J* = 8.9, 5.1 Hz, 1H), 1.99–1.93 (m, 2H), 1.78 (d, *J* = 5.2 Hz, 2H), 1.65–1.59 (m, 1H), 1.35–1.27 (m, 5H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.2, 135.5, 124.9, 114.2, 55.2, 47.8, 33.3, 26.0, 25.7.

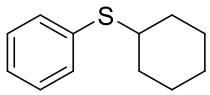
Spectroscopic data of compound **25a** was in accordance with the literature.[S17]



(4-Chlorophenyl)(cyclohexyl)sulfane (26a). Compound **26a** was obtained from **1b** (53 mg, 0.2 mmol) in 47% yield (pale yellow liquid, 19.5 mg) along with compound **26b**[S1] (4.9 mg, 10% yield).

26a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.09–2.99 (m, 1H), 2.35 (s, 3H), 2.03–1.96 (m, 2H), 1.82–1.75 (m, 2H), 1.63 (dd, *J* = 4.7, 2.8 Hz, 1H), 1.40–1.28 (m, 5H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.7, 132.7, 131.1, 129.4, 47.0, 33.3, 26.0, 25.7, 21.0.

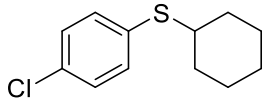
Spectroscopic data of compound **26a** was in accordance with the literature.[S16]



Cyclohexyl(phenyl)sulfane (27a). Compound **27a** was obtained from **1g** (50 mg, 0.2 mmol) in 68% yield (pale yellow liquid, 26 mg) along with compound **27b**[S7] (5 mg, 11% yield).

27a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.44–7.39 (m, 2H), 7.29 (qd, *J* = 7.9, 7.4, 1.6 Hz, 3H), 3.13 (ddd, *J* = 10.3, 6.6, 3.5 Hz, 1H), 2.05–1.97 (m, 2H), 1.83–1.76 (m, 2H), 1.67–1.58 (m, 2H), 1.34 (ddd, *J* = 16.4, 8.6, 4.5 Hz, 4H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 131.6, 128.5, 126.3, 46.31, 33.1, 25.8, 25.5.

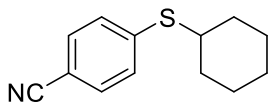
Spectroscopic data of compound **27a** was in accordance with the literature.[S8]



(4-Chlorophenyl)(cyclohexyl)sulfane (28a). Compound **28a** was obtained from **1n** (61 mg, 0.2 mmol) in 63% yield (colorless liquid, 29 mg) along with compound **28b**[S1] (5.8 mg, 10% yield).

28a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28–7.24 (m, 2H), 7.21–7.17 (m, 2H), 3.00 (ddd, *J* = 10.3, 6.5, 3.6 Hz, 1H), 1.94–1.86 (m, 2H), 1.75–1.68 (m, 2H), 1.59–1.51 (m, 1H), 1.33–1.20 (m, 5H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 133.6, 133.1, 132.6, 128.8, 46.8, 33.1, 25.9, 25.6.

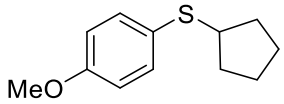
Spectroscopic data of compound **28a** was in accordance with the literature.[S17]



4-(Cyclohexylthio)benzonitrile (29a). Compound **29a** was obtained from **1g** (55 mg, 0.2 mmol) in 41% yield (pale yellow liquid, 19 mg) along with compound **29b**[S10] (6 mg, 12% yield).

29a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56–7.52 (m, 2H), 7.38–7.34 (m, 2H), 3.32 (dd, *J* = 8.8, 5.0 Hz, 1H), 2.09–2.02 (m, 2H), 1.86–1.79 (m, 2H), 1.72–1.64 (m, 1H), 1.48–1.34 (m, 5H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 1439, 132.1, 128.5, 118.8, 108.3, 44.8, 32.8, 25.7, 25.5.

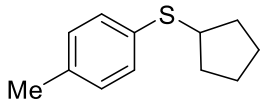
Spectroscopic data of compound **29a** was in accordance with the literature.[S17]



Cyclopentyl(4-methoxyphenyl)sulfane (30a). Compound **30a** was obtained from **1a** (56 mg, 0.2 mmol) in 72% yield (colorless liquid, 30 mg) along with compound **30b**[S3] in (5 mg, 10% yield).

30a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.50–3.39 (m, 1H), 2.03–1.71 (m, 4H), 1.65–1.52 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.1, 134.3, 127.1, 114.5, 55.5, 48.1, 33.5, 24.8.

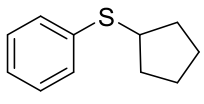
Spectroscopic data of compound **30a** was in accordance with the literature.[S18]



Cyclopentyl(p-tolyl)sulfane (31a). Compound **31a** was obtained from **1b** (53 mg, 0.2 mmol) in 61% yield (colorless liquid, 20.5 mg) along with compound **31b**[S1] (4.4 mg, 9% yield).

31a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.55 (qd, *J* = 7.2, 5.9 Hz, 1H), 2.34 (s, 3H), 2.10–1.98 (m, 2H), 1.80 (dt, *J* = 5.1, 1.8 Hz, 2H), 1.62 (tdd, *J* = 12.6, 7.1, 4.8 Hz, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.0, 133.2, 130.9, 129.4, 46.5, 33.4, 24.6, 20.9.

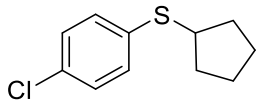
Spectroscopic data of compound **31a** was in accordance with the literature.[S16]



Cyclopentyl(phenyl)sulfane (32a). Compound **32a** was obtained from **1d** (50 mg, 0.2 mmol) in 61% yield (colorless liquid, 23.5 mg) along with compound **32b**[S7] (3.2 mg, 7% yield).

32a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.19 (t, *J* = 3.9 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 3.57–3.49 (m, 1H), 2.03–1.95 (m, 2H), 1.72 (t, *J* = 2.5 Hz, 2H), 1.61–1.51 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.2, 129.9, 128.6, 125.8, 45.8, 33.4, 24.7.

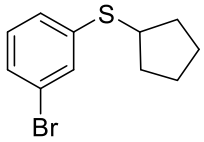
Spectroscopic data of compound **32a** were in accordance with the literature.[S8]



(4-Chlorophenyl)(cyclopentyl)sulfane (33a). Compound **33a** was obtained from **1e** (56.6 mg, 0.2 mmol) in 65% yield (pale yellow liquid, 28 mg) along with compound **33b**[S1] (6 mg, 12% yield).

33a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33–7.24 (m, 4H), 3.65–3.52 (m, 1H), 2.13–2.00 (m, 2H), 1.87–1.55 (m, 6H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.0, 132.5, 132.0, 131.4, 129.6, 129.0, 46.3, 33.6, 24.9.

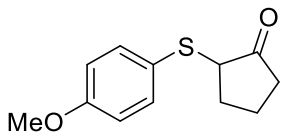
Spectroscopic data of compound **33a** was in accordance with the literature.[S18]



(3-Bromophenyl)(cyclopentyl)sulfane (34a). Compound **34a** was obtained from **1h** (66 mg, 0.2 mmol) in 63% yield (colorless liquid, 34 mg) along with compound **34b**[S1] (5.8 mg, 10% yield).

34a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 1.9 Hz, 1H), 7.33–7.25 (m, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 3.68–3.58 (m, 1H), 2.10 (qd, *J* = 6.2, 5.4, 2.3 Hz, 2H), 1.86–1.57 (m, 6H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 139.7, 132.9, 131.5, 129.7, 129.4, 128.4, 127.6, 122.4, 45.3, 33.2, 24.5.

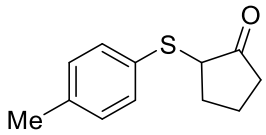
Spectroscopic data of compound **34a** was in accordance with the literature.[S18]



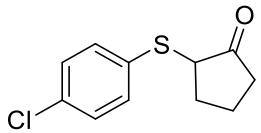
2-((4-Methoxyphenyl)thio)cyclopentan-1-one (35a). Compound **35a** was obtained from **1a** (56 mg, 0.2 mmol) in 68% yield (colorless liquid, 30 mg) along with compound **35b**[S3] (6.7 mg, 13% yield).

35a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47–7.41 (m, 2H), 6.88–6.83 (m, 2H), 3.82 (s, 3H), 3.45–3.39 (m, 1H), 2.32–2.23 (m, 3H), 2.08–1.85 (m, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 213.8, 160.0, 136.1, 135.6, 123.0, 114.6, 114.5, 55.2, 53.2, 45.0, 44.6, 36.7, 36.5, 30.1, 29.2, 20.1.

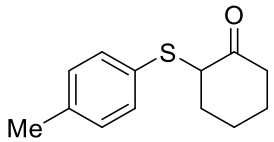
HRMS (ESI) m/z: calcd. for $C_{12}H_{14}O_2S$ $[M+H]^+$: 223.0787, found: 223.0787.



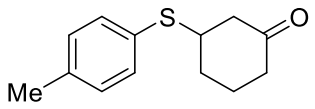
2-((3-Chlorophenyl)thio)cyclopentan-1-one (36a). Compound **36a** was obtained from **1b** (53 mg, 0.2 mmol) in 67% yield (pale yellow liquid, 28 mg) along with compound **36b**[S1] (6.7 mg, 14% yield).
36a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 3.52 (dd, *J* = 7.4, 6.1 Hz, 1H), 2.35 (s, 3H), 2.31–2.26 (m, 2H), 2.12–1.85 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 213.7, 138.1, 133.3, 129.7, 129.3, 52.6, 36.5, 30.4, 21.0, 20.2.
Spectroscopic data of compound **36a** was in accordance with the literature.[S16]



2-((4-Chlorophenyl)thio)cyclopentan-1-one (37a). Compound **37a** was obtained from **1e** (60 mg, 0.2 mmol) in 59% yield (pale yellow-brown liquid, 27 mg) along with compound **37b**[S1] (5.5 mg, 9% yield).
37a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 3.58–3.52 (m, 1H), 2.40–2.29 (m, 3H), 2.14–2.06 (m, 1H), 1.95 (ddd, *J* = 10.1, 6.7, 3.3 Hz, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 213.2, 133.7, 133.6, 131.6, 128.9, 52.0, 36.2, 30.2, 20.0.
Spectroscopic data of compound **37a** was in accordance with the literature.[S16]



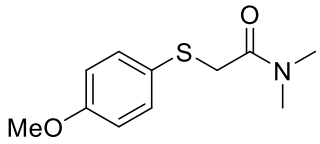
2-(*p*-Tolylthio)cyclohexan-1-one (38a). Compound **38a** was obtained from **1b** (53 mg, 0.2 mmol) in 34% yield (pale yellow solid, 15 mg). along with compound **38b**[S1] (5 mg, 10% yield).
38a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.77 (ddd, J = 6.5, 5.2, 1.5 Hz, 1H), 2.99–2.89 (m, 1H), 2.34 (s, 3H), 2.21 (d, *J* = 5.7 Hz, 1H), 2.11 (dd, *J* = 3.4, 1.7 Hz, 1H), 2.00–1.66 (m, 5H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 207.6, 137.7, 132.6, 129.8, 129.7, 56.9, 38.8, 33.7, 27.2, 22.4, 21.0.
Spectroscopic data of compound **38a** was in accordance with the literature.[S19]



3-(*p*-Tolylthio)cyclohexan-1-one (38a'). Compound **38a'** was obtained from **1b** (53 mg, 0.2 mmol) in 23% yield (pale yellow liquid, 10 mg).

38a': ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 3.36 (ddt, *J* = 9.0, 5.9, 3.3 Hz, 1H), 2.73–2.64 (m, 1H), 2.41–2.33 (m, 6H), 2.21–2.12 (m, 2H), 1.72 (ddd, *J* = 9.0, 6.1, 4.2 Hz, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 208.8, 138.1, 133.9, 129.7, 129.0, 47.7, 46.4, 40.8, 31.2, 23.9, 21.0.

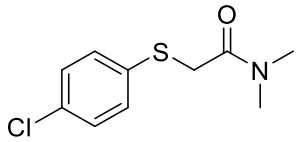
Spectroscopic data of compound **38a'** were in accordance with the literature.[S19]



***S*-(4-methoxyphenyl) dimethylcarbamothioate (39a).** Compound **39a** was obtained from **1a** (56 mg, 0.2 mmol) in 35% yield (pale yellow-brown solid, 18 mg) along with compound **39b**[S3] (7 mg, 14% yield).

39a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36–7.31 (m, 2H), 6.88–6.83 (m, 2H), 3.75 (s, 3H), 2.99 (s, 6H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.4, 160.3, 137.1, 119.1, 114.3, 55.1, 36.6.

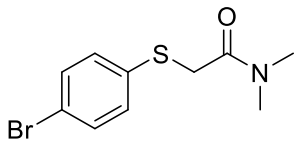
Spectroscopic data of compound **39a** was in accordance with the literature.[S20]



***S*-(4-Chlorophenyl) dimethylcarbamothioate (40a).** Compound **40a** was obtained from **1e** (56 mg, 0.2 mmol) in 44% yield (pale yellow liquid, 19 mg) along with compound **40b**[S1] (8.7 mg, 17% yield).

40a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47–7.40 (m, 2H), 7.40–7.35 (m, 2H), 3.08 (s, 6H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.0, 136.6, 135.3, 128.8, 127.0, 29.4.

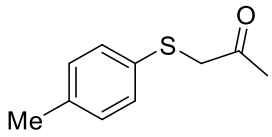
Spectroscopic data of compound **40a** was in accordance with the literature.[S20]



***S*-(4-Bromophenyl) dimethylcarbamothioate (41a).** Compound **41a** was obtained from **1m** (61.5 mg, 0.2 mmol) in 31% yield (pale yellow solid, 16 mg) along with compound **41b**[S1] (7.3 mg, 13% yield).

41a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 3.08 (s, 6H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.9, 136.8, 131.8, 127.7, 123.6.

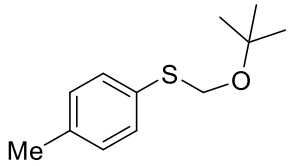
Spectroscopic data of compound **41a** was in accordance with the literature.[S20]



1-(*p*-Tolylthio)propan-2-one (42a). Compound **42a** was obtained from **1b** (53 mg, 0.2 mmol) in 46% yield (pale yellow liquid, 16 mg) along with compound **42b**[S1] (20 mg, 43% yield).

42a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.63 (s, 2H), 2.33 (s, 3H), 2.28 (s, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) δ 203.5, 137.2, 130.7, 130.4, 129.9, 45.3, 27.9, 20.9.

Spectroscopic data of compound **42a** was in accordance with the literature.[S21]



(*tert*-Butoxymethyl)(*p*-tolyl)sulfane (43a). Compound **43a** was obtained from **1b** (53 mg, 0.2 mmol) in 32% yield (pale yellow liquid, 14 mg) along with compound **43b**[S1] (17 mg, 36% yield).

43a: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.15–7.10 (m, 2H), 4.88 (s, 2H), 2.34 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.5, 132.7, 130.6, 129.4, 75.1, 68.7, 27.7, 20.9.

Spectroscopic data of compound **43a** was in accordance with the literature.[S22]

1.4 General procedure for the photochemical synthesis of 9a under solar light simulated conditions.

In a suitable glass vessel sealed with a Teflon cap, **1g** (1 mmol, 274 mg) was dissolved in 20 mL of 1,4-dioxane. The resulting solution was purged with nitrogen for 10 min. and subsequently irradiated by using a Solar Box 1500E under continuous stirring for 90 min (Figure S2). After completion of the reaction, the mixture was concentrated and purified to afford 133 mg of **9a** (60% yield, pale yellow solid), along with 15 mg of **9b** (6% yield).

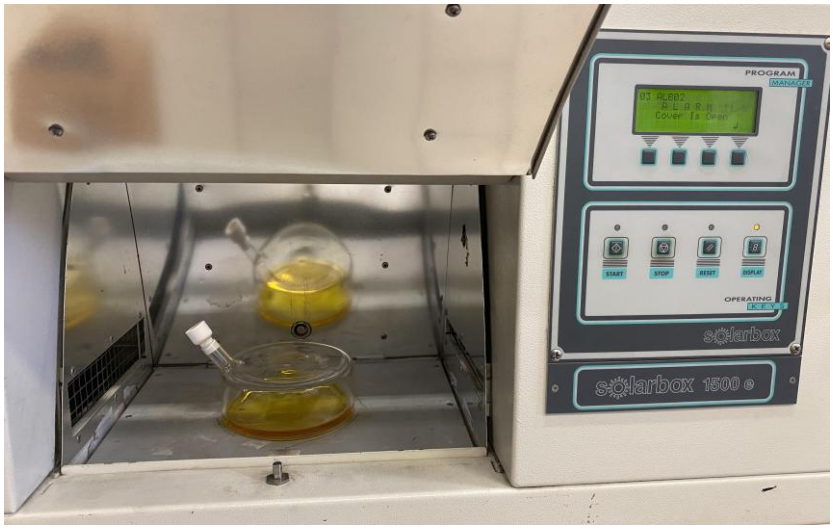


Figure S2. Photochemical setup (large-scale experiment) using a Solar Box.

1.5 Trapping experiment with 2,2,6,6-Tetramethyl-1-piperidinyloxy radical (TEMPO)

In a *vial*, 16 mg of arylazo sulfide **1q** (0.05 mmol) and 15.6 mg of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 10 equiv.) were dissolved in cyclohexane/DMC 5:1 (1.0 mL). The solution was purged with nitrogen for 10 min, capped and irradiated with a 427 nm Kessil lamp for 30 min. After total consumption of arylazo sulfide, GC-FID analysis of the crude mixture has been performed. GC-MS analyses pointed out the presence of 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine **44** (retention time: 18.07 min) as the main product along with a minor amount of diaryl sulfide **7b** (retention time: 24.75 min, Figure S3).

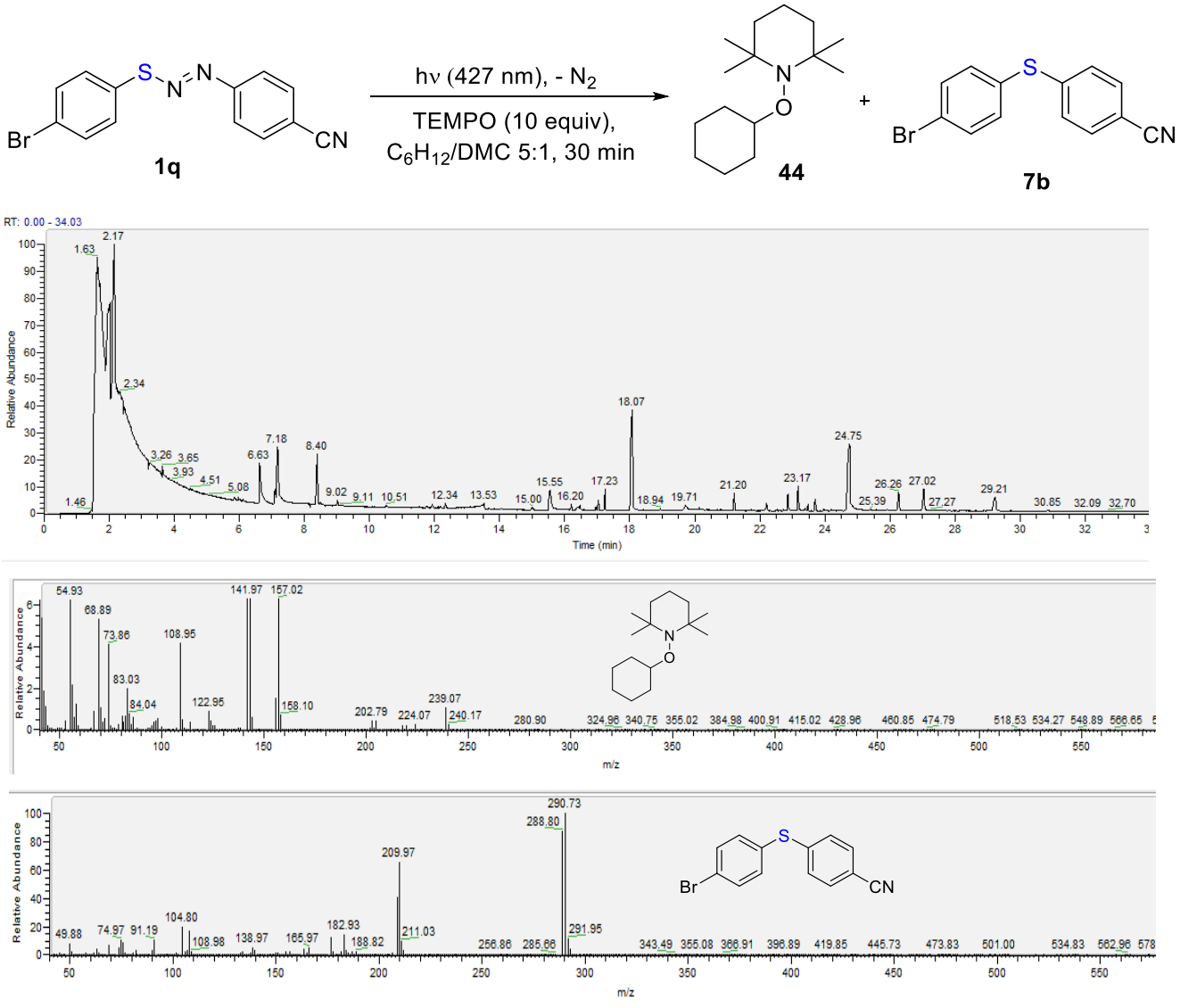


Figure S3. GC-MS analysis of a solution of **1q** (0.05 M) and TEMPO (10 equiv.) in cyclohexane/DMC 5:1 irradiated for 30 min.

2. References.

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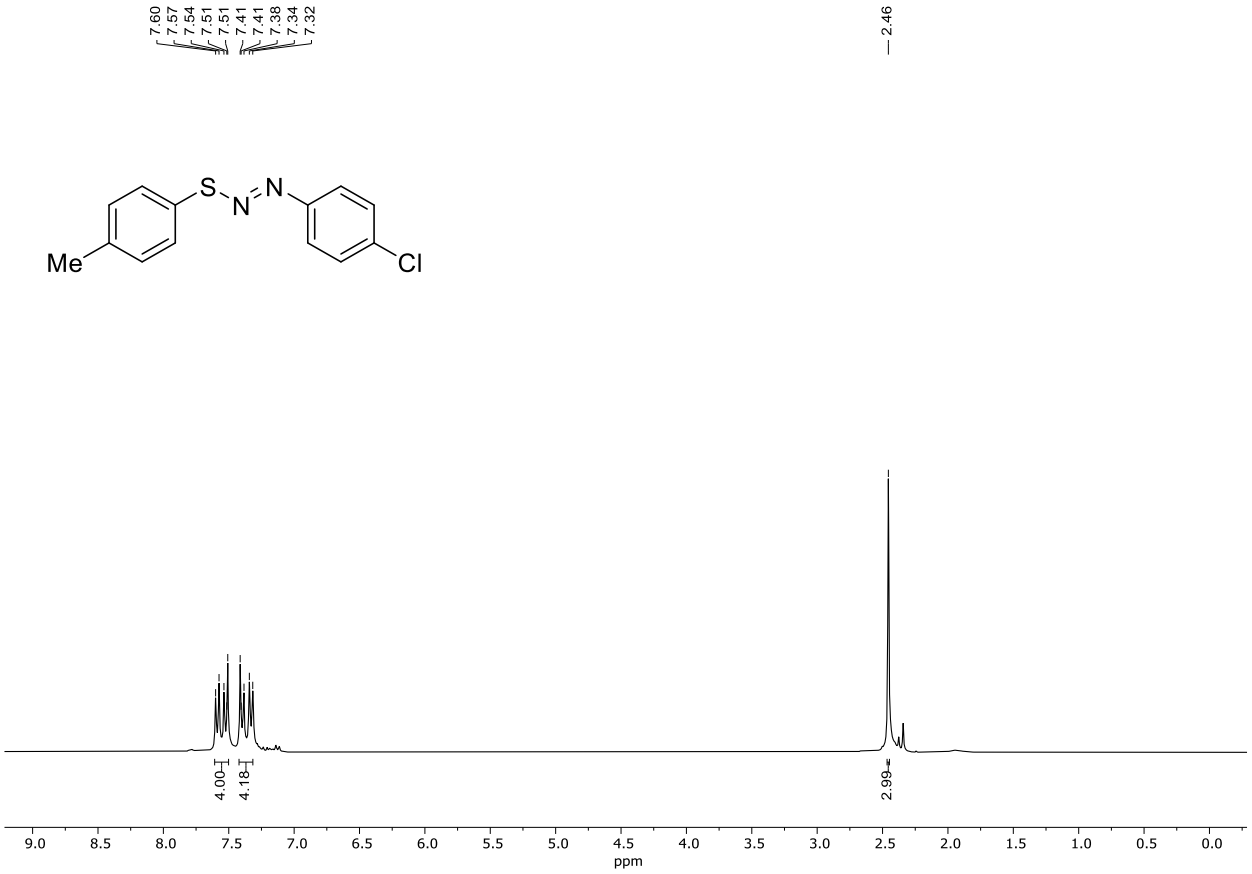
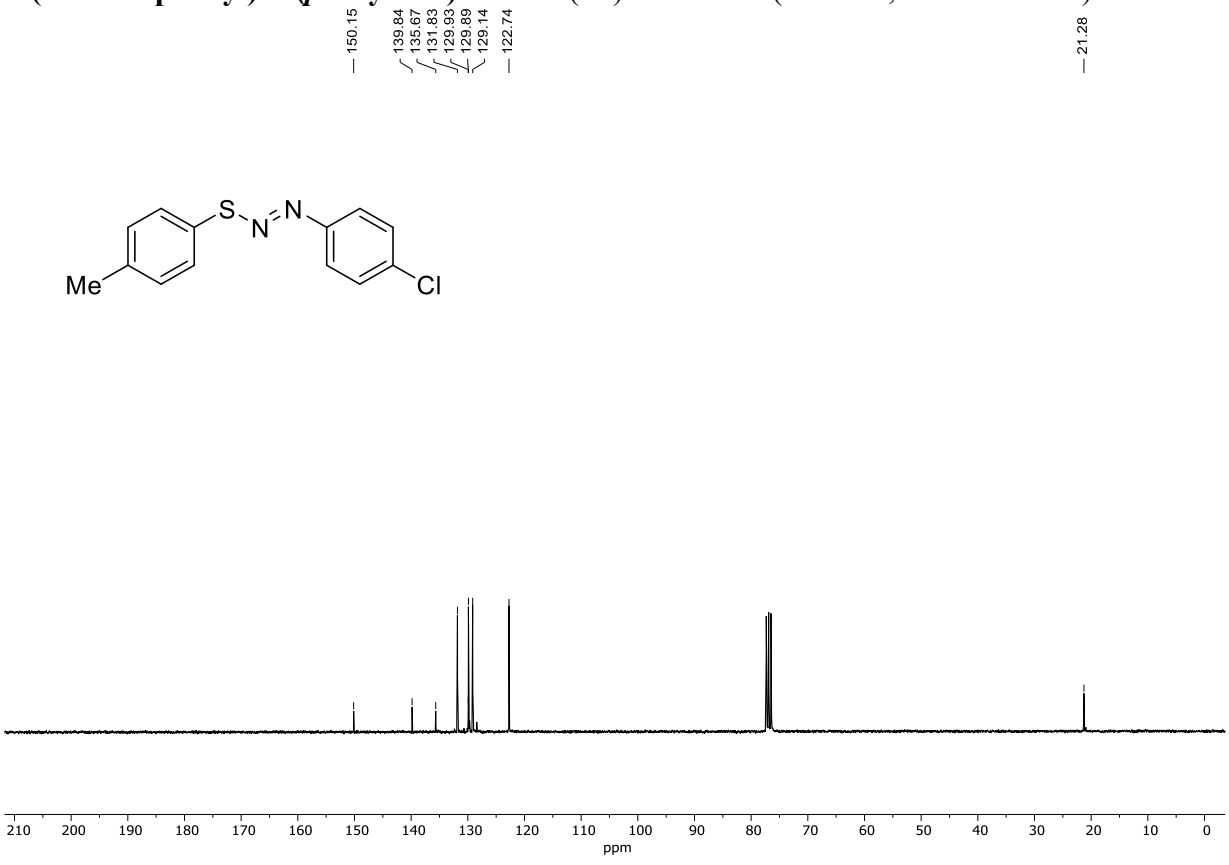
3. Copy of the NMR spectra.

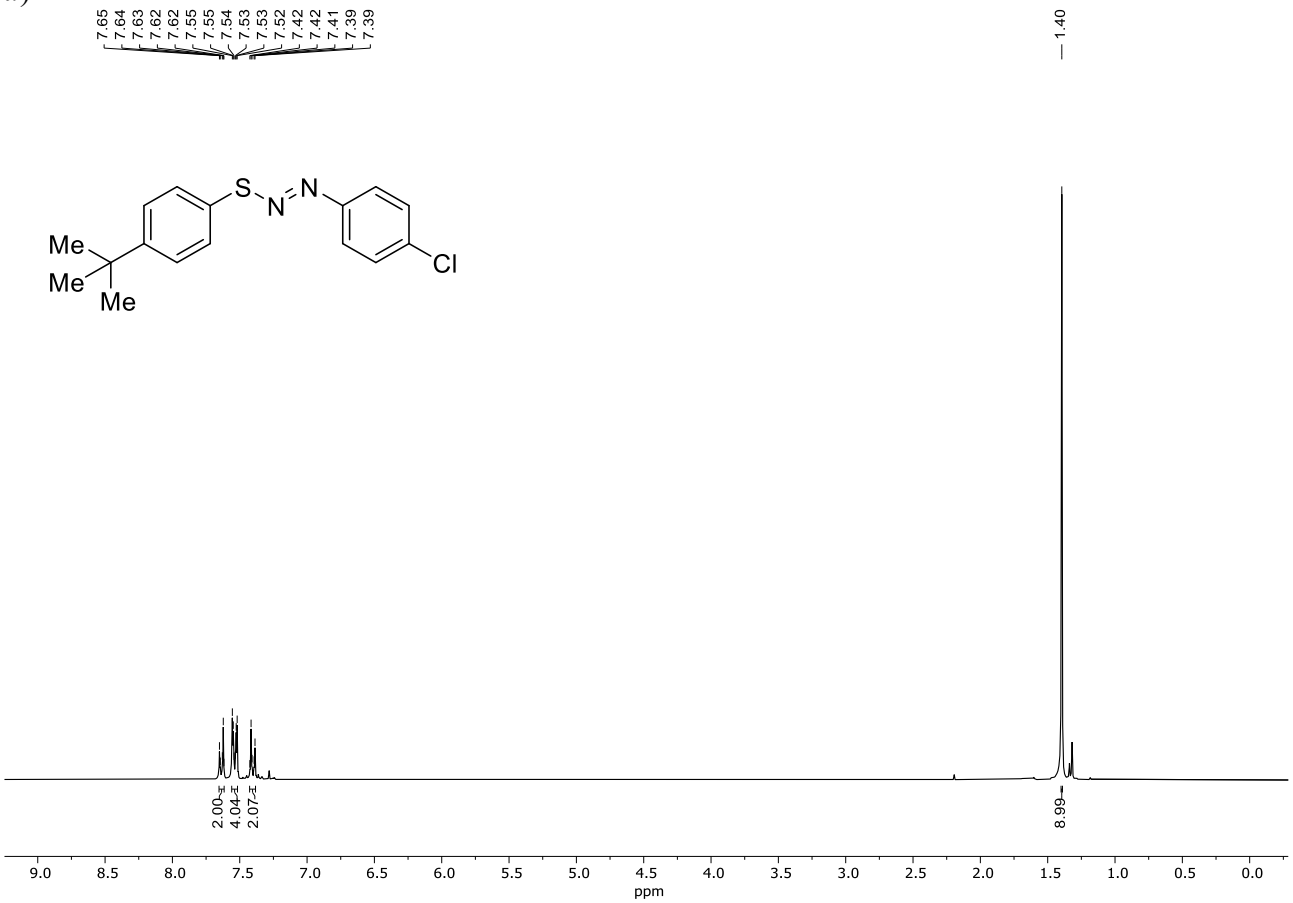
1-(4-chlorophenyl)-2-(*p*-tolylthio)diazene (1b) . ^{1}H NMR (300 MHz, Chloroform- *d*)



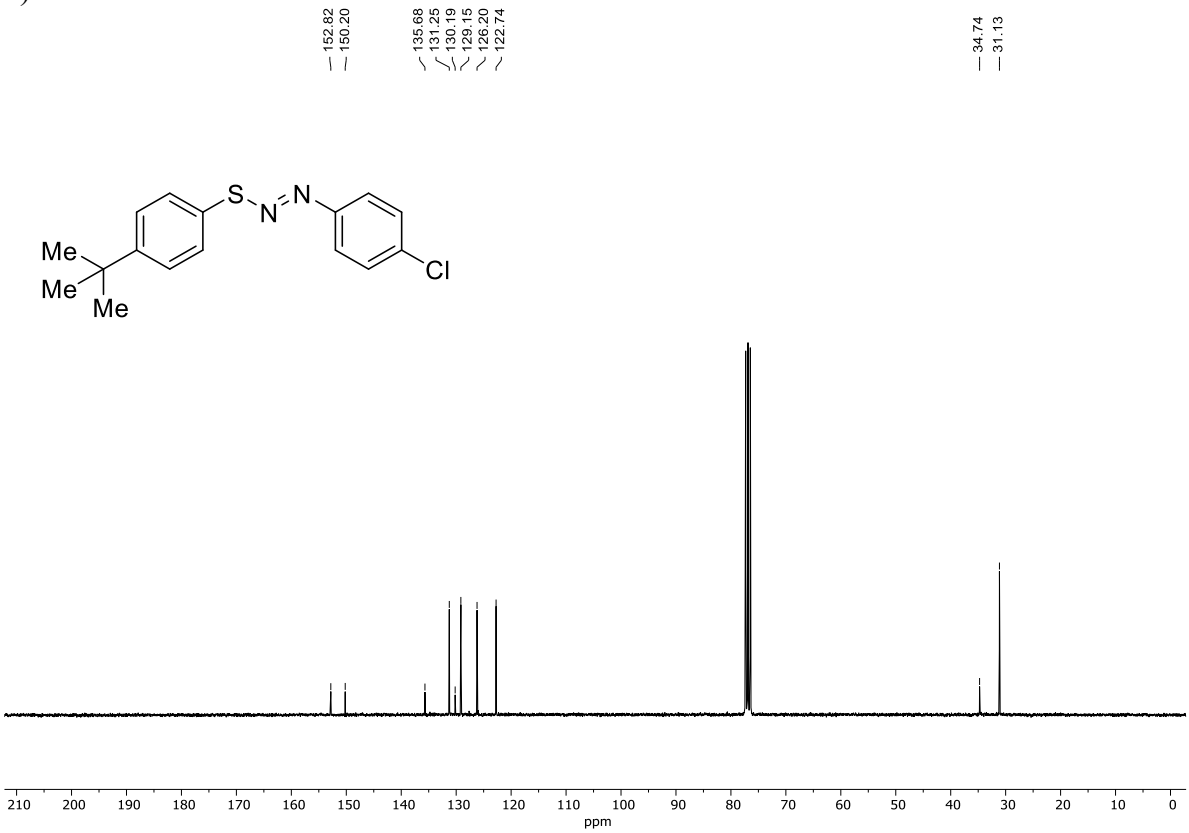
1-(4-chlorophenyl)-2-(*p*-tolylthio)diazene (1b). ^{13}C NMR (75 MHz, Chloroform-*d*)



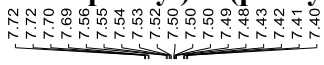
1-((4-(tert-butyl)phenyl)thio)-2-(4-chlorophenyl)diazene (1c). ^{1}H NMR (300 MHz, Chloroform-*d*)

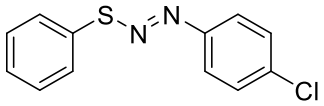


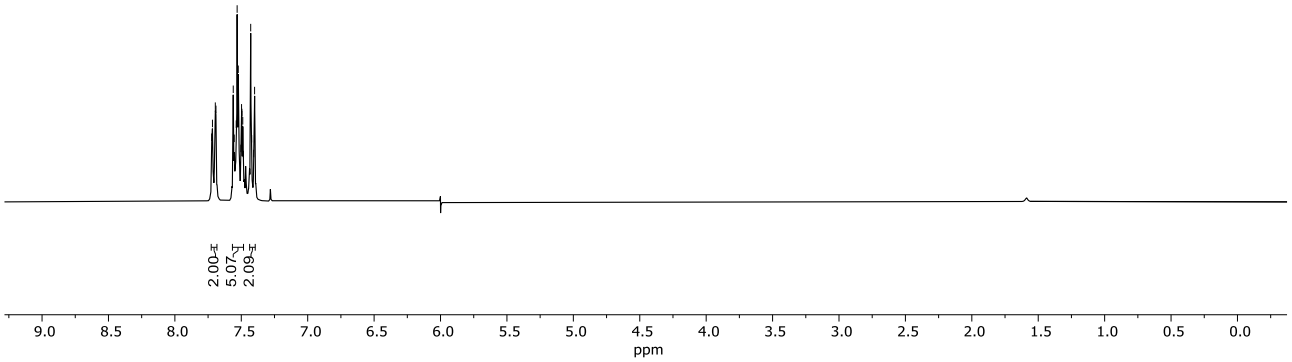
1-((4-(tert-butyl)phenyl)thio)-2-(4-chlorophenyl)diazene (1c). ^{13}C NMR (75 MHz, Chloroform-*d*)



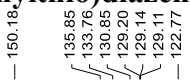
1-(4-chlorophenyl)-2-(phenylthio)diazene (**1d**). ^{1}H NMR (300 MHz, Chloroform-*d*).

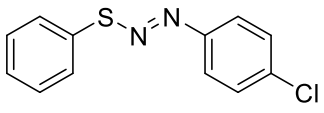


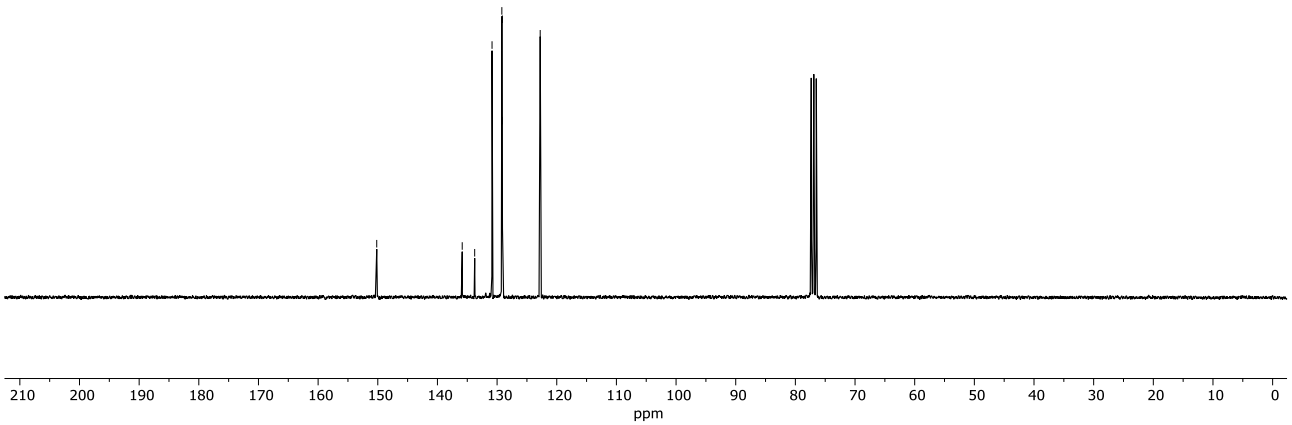




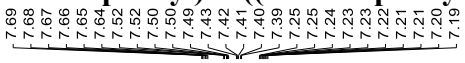
1-(4-chlorophenyl)-2-(phenylthio)diazene (**1d**). ^{13}C NMR (75 MHz, Chloroform-*d*)

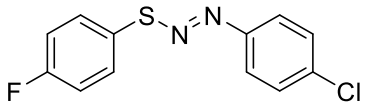


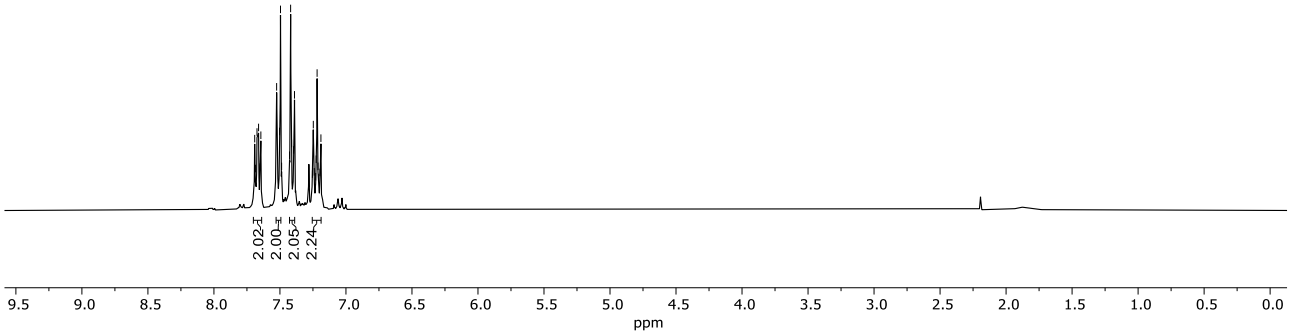




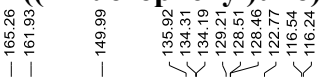
1-(4-chlorophenyl)-2-((4-fluorophenyl)thio)diazene (**1f**). ^{1}H NMR (300 MHz, Chloroform-*d*).

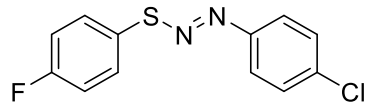


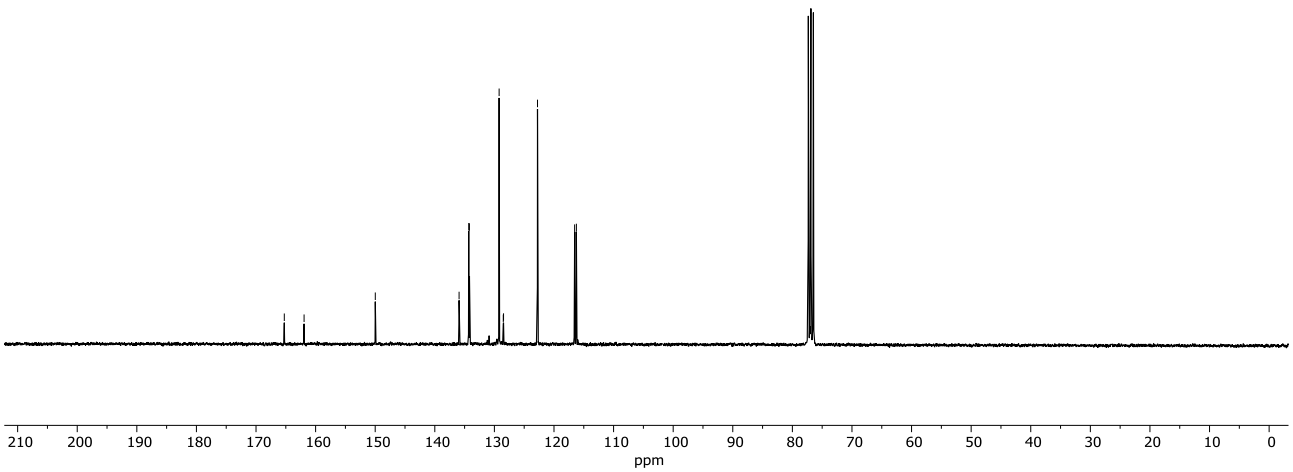




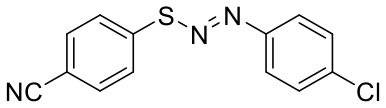
1-(4-chlorophenyl)-2-((4-fluorophenyl)thio)diazene (**1f**). ^{13}C NMR (75 MHz, Chloroform-*d*)

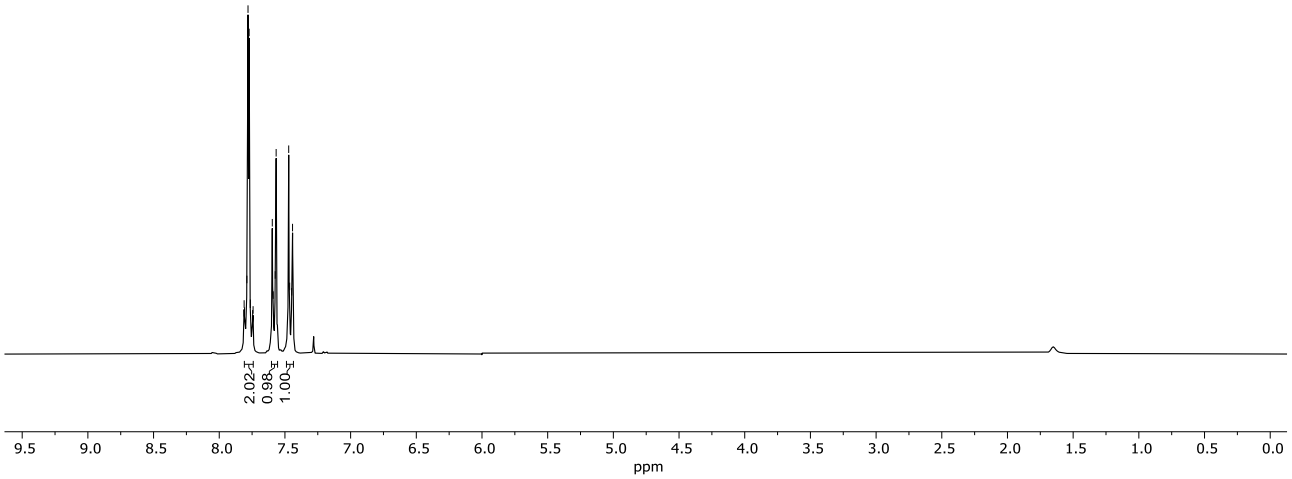




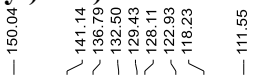


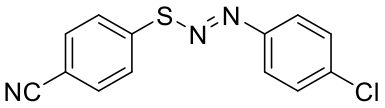
4-(((4-chlorophenyl)diazenyl)thio)benzonitrile (**1g**). ^{1}H NMR (300 MHz, Chloroform-*d*).

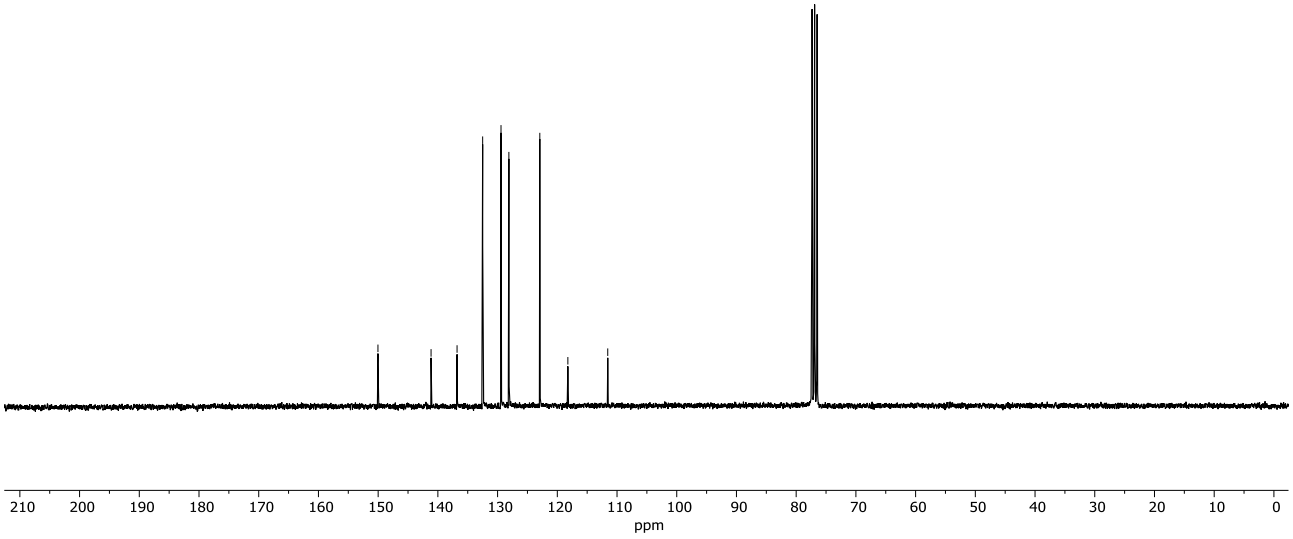




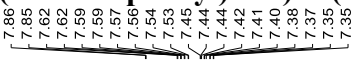
4-(((4-chlorophenyl)diazenyl)thio)benzonitrile (**1g**). ^{13}C NMR (75 MHz, Chloroform-*d*)

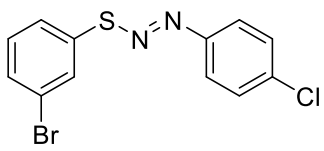


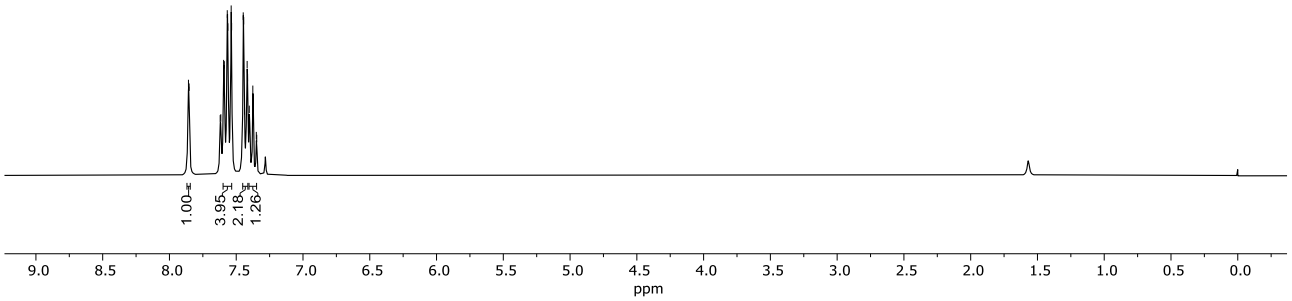




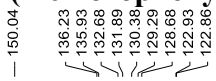
1-((3-bromophenyl)thio)-2-(4-chlorophenyl)diazene (**1h**). ^{1}H NMR (300 MHz, Chloroform-*d*).

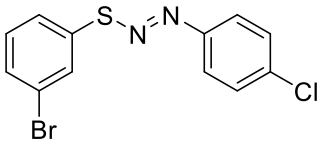


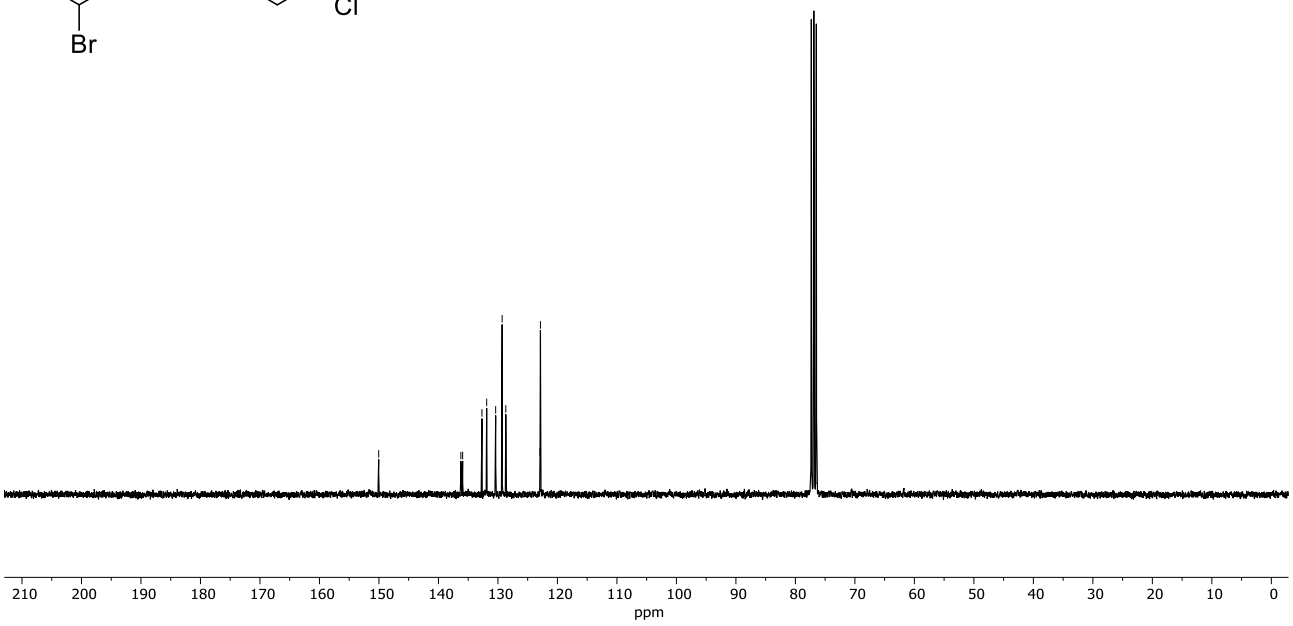




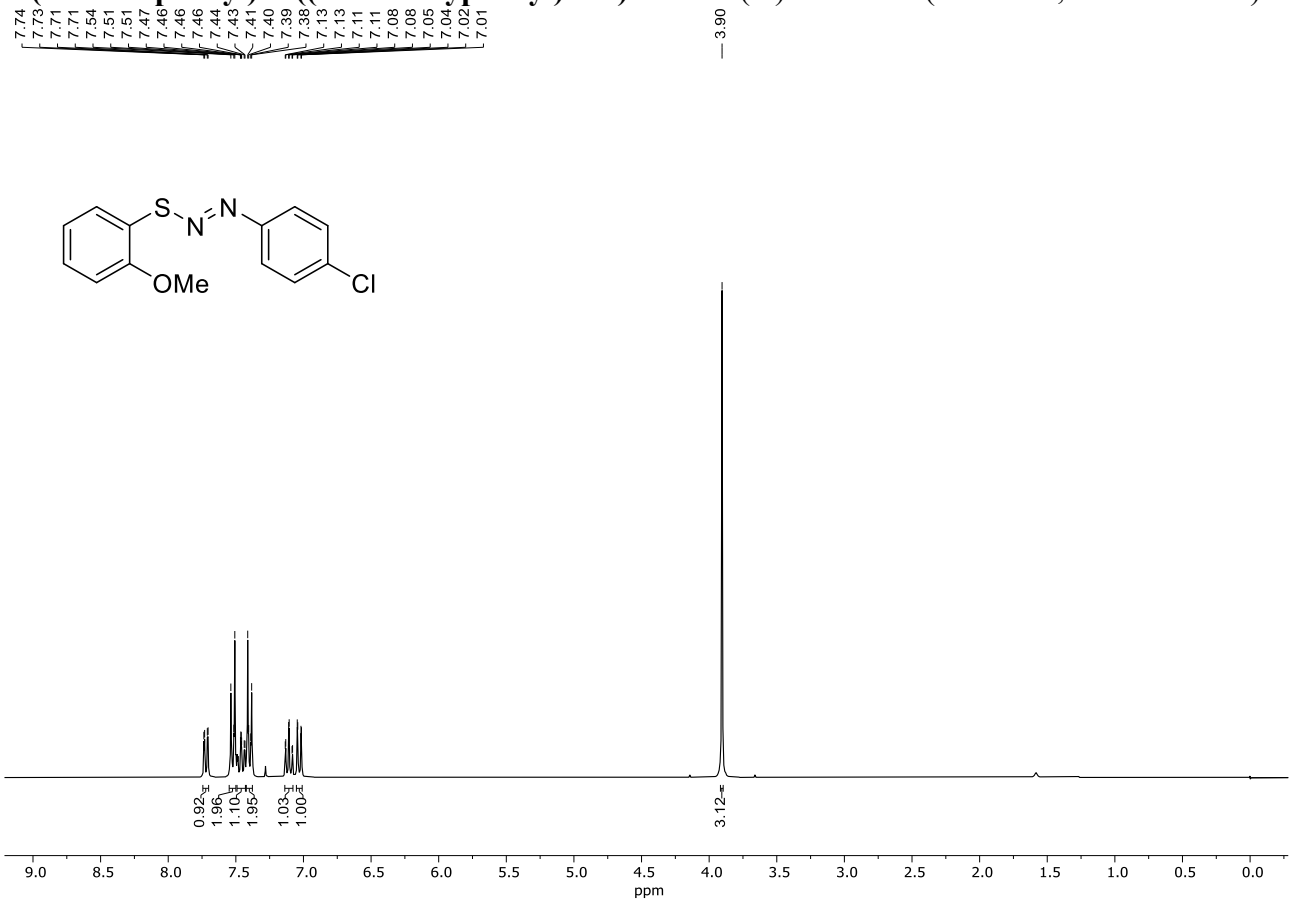
1-((3-bromophenyl)thio)-2-(4-chlorophenyl)diazene (**1h**). ^{13}C NMR (75 MHz, Chloroform-*d*)



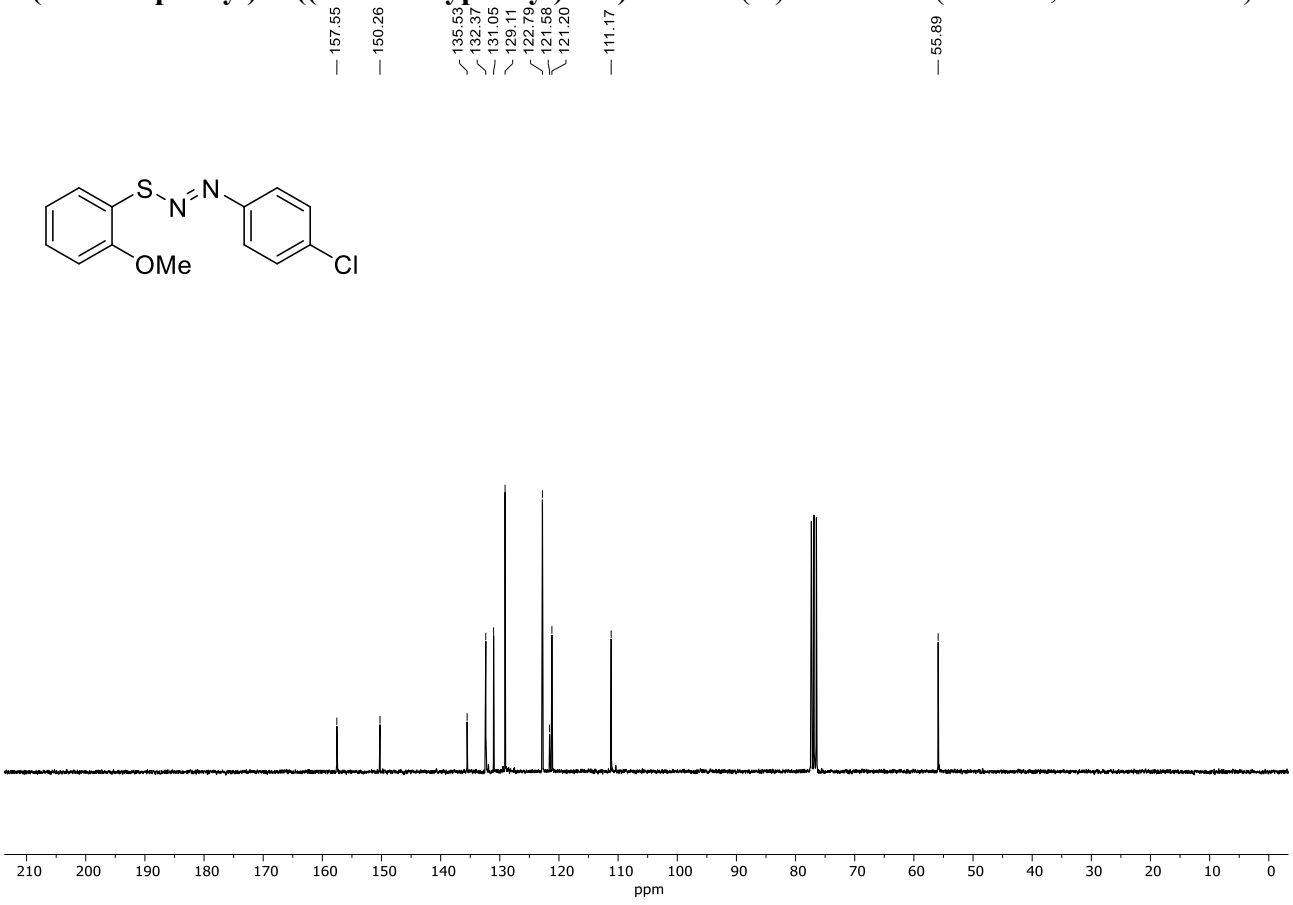




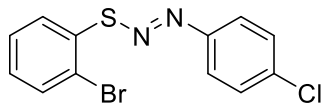
1-(4-chlorophenyl)-2-((2-methoxyphenyl)thio)diazene (**1i**). ^{1}H NMR (300 MHz, Chloroform-*d*).

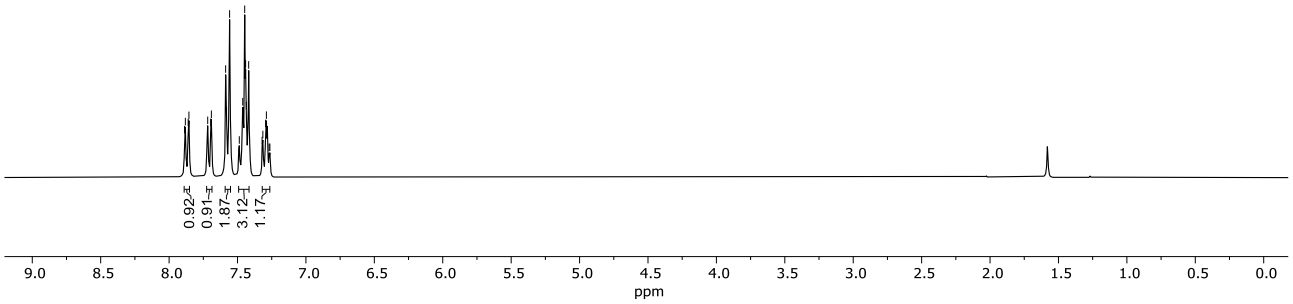


1-(4-chlorophenyl)-2-((2-methoxyphenyl)thio)diazene (**1i**). ^{13}C NMR (75 MHz, Chloroform-*d*)

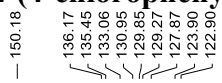


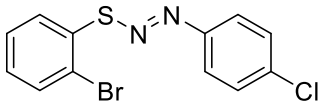
1-((2-bromophenyl)thio)-2-(4-chlorophenyl)diazene (**1j**). ^{1}H NMR (300 MHz, Chloroform-*d*).

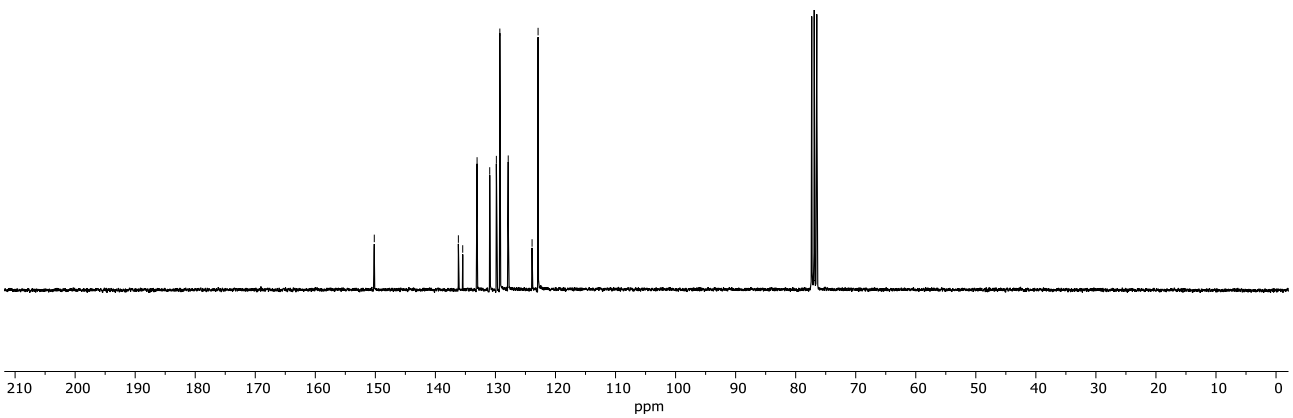




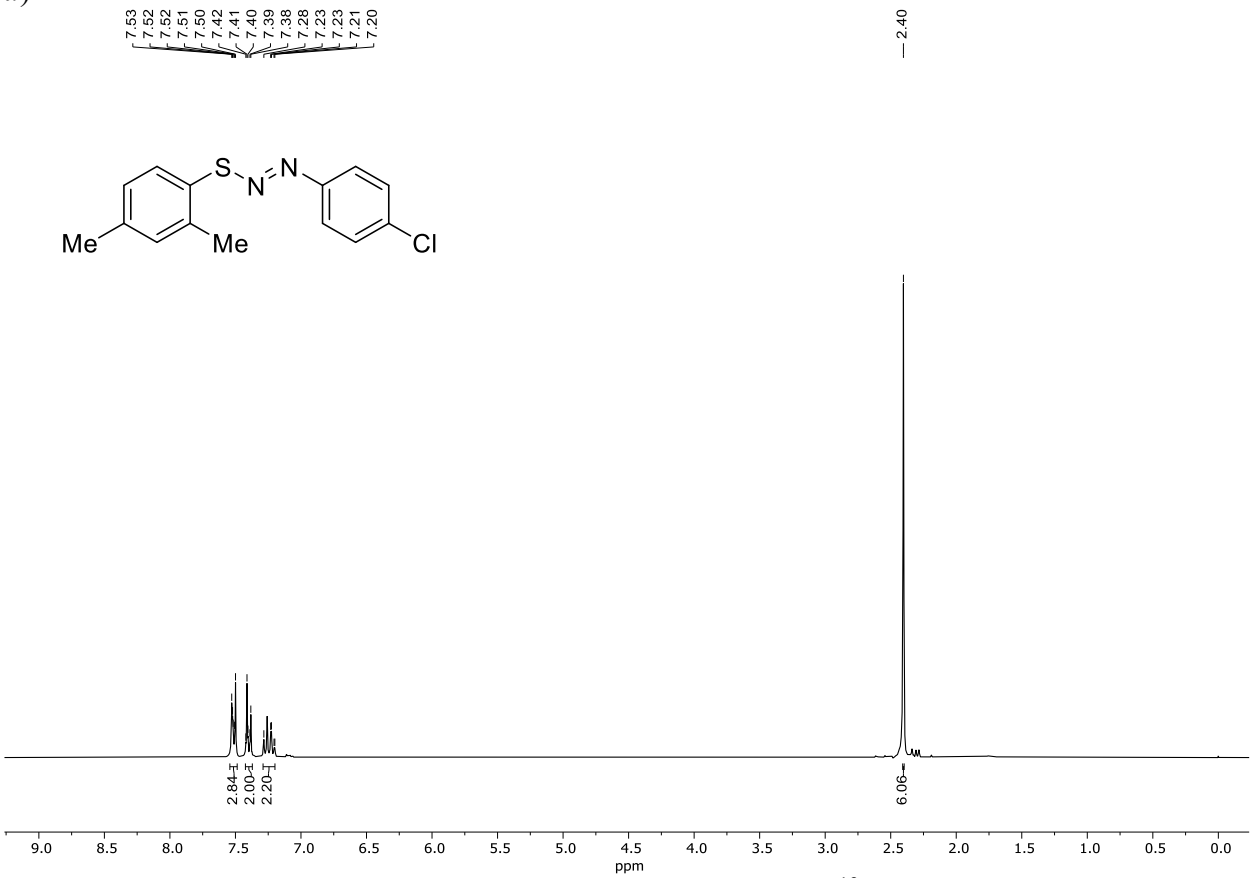
1-((2-bromophenyl)thio)-2-(4-chlorophenyl)diazene (**1j**). ^{13}C NMR (75 MHz, Chloroform-*d*)



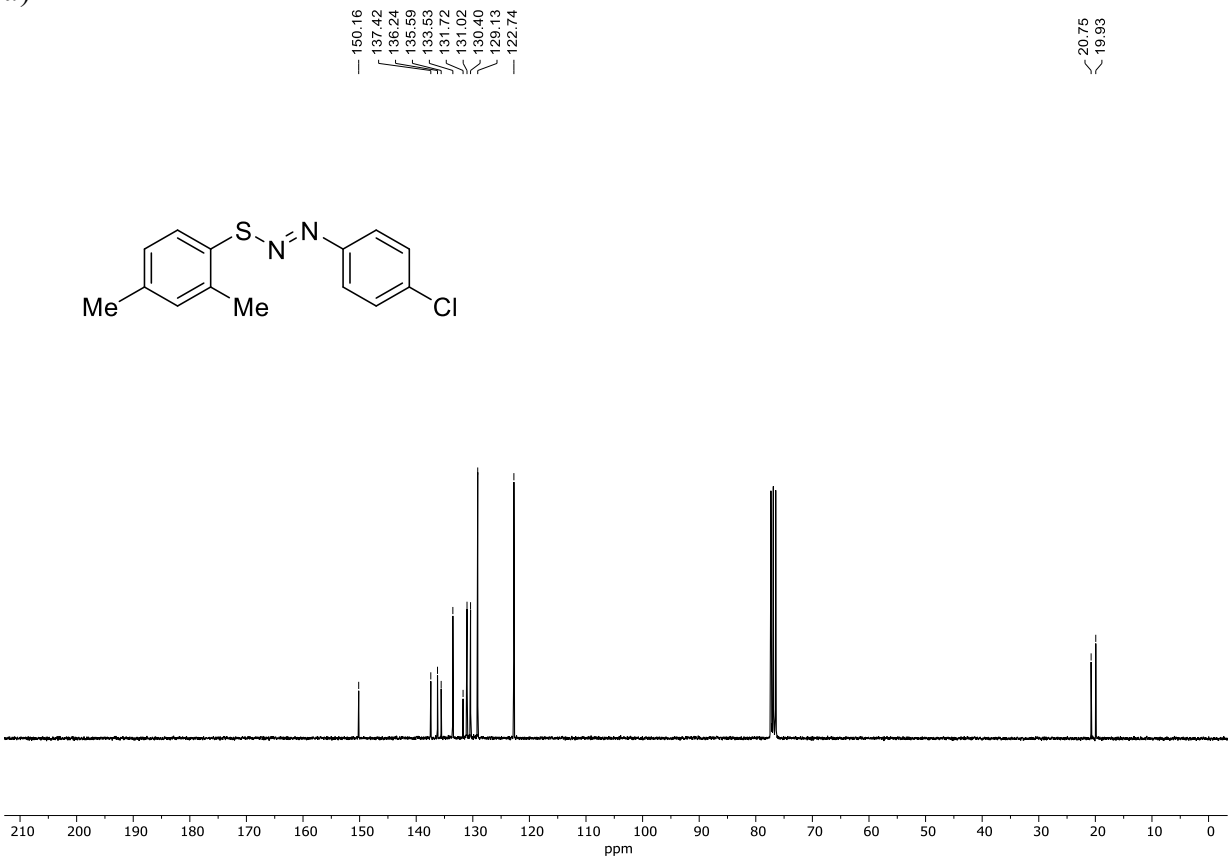




1-(4-chlorophenyl)-2-((2,4-dimethylphenyl)thio)diazene (**1k**). ^{1}H NMR (300 MHz, Chloroform-*d*).



1-(4-chlorophenyl)-2-((2,4-dimethylphenyl)thio)diazene (**1k**). ^{13}C NMR (75 MHz, Chloroform-*d*)



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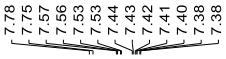
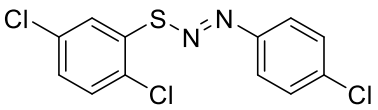
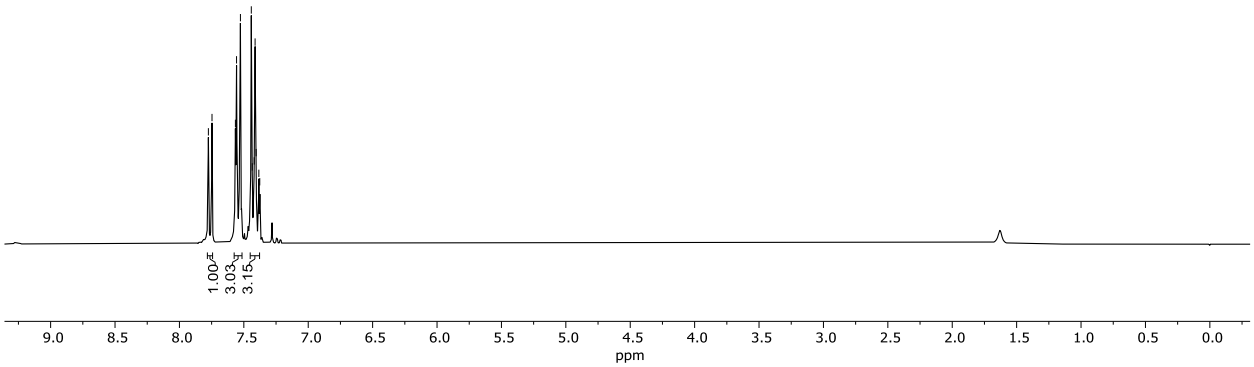
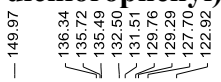
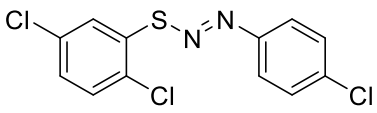


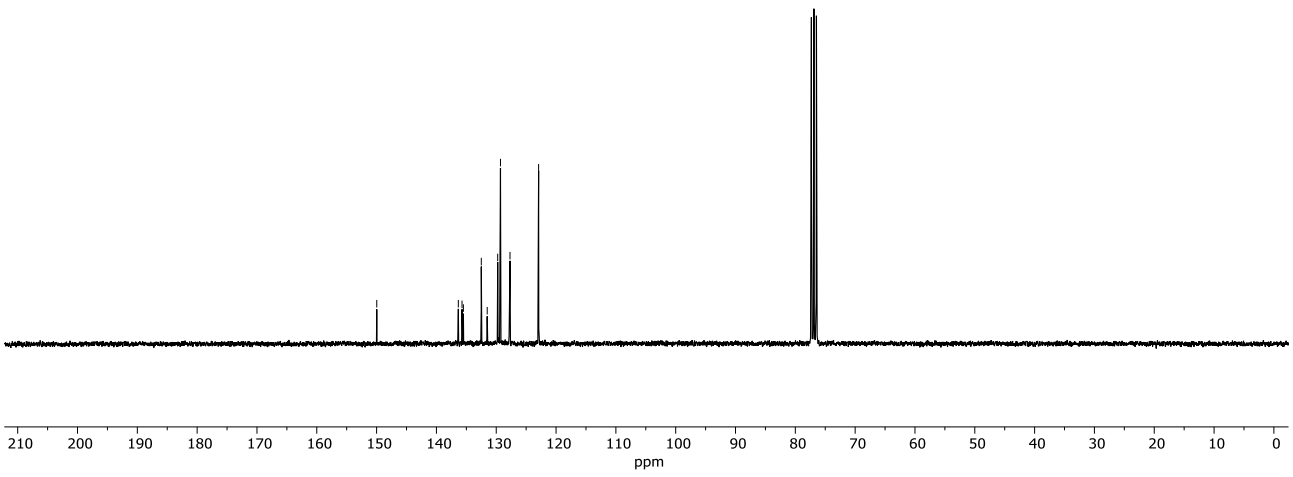




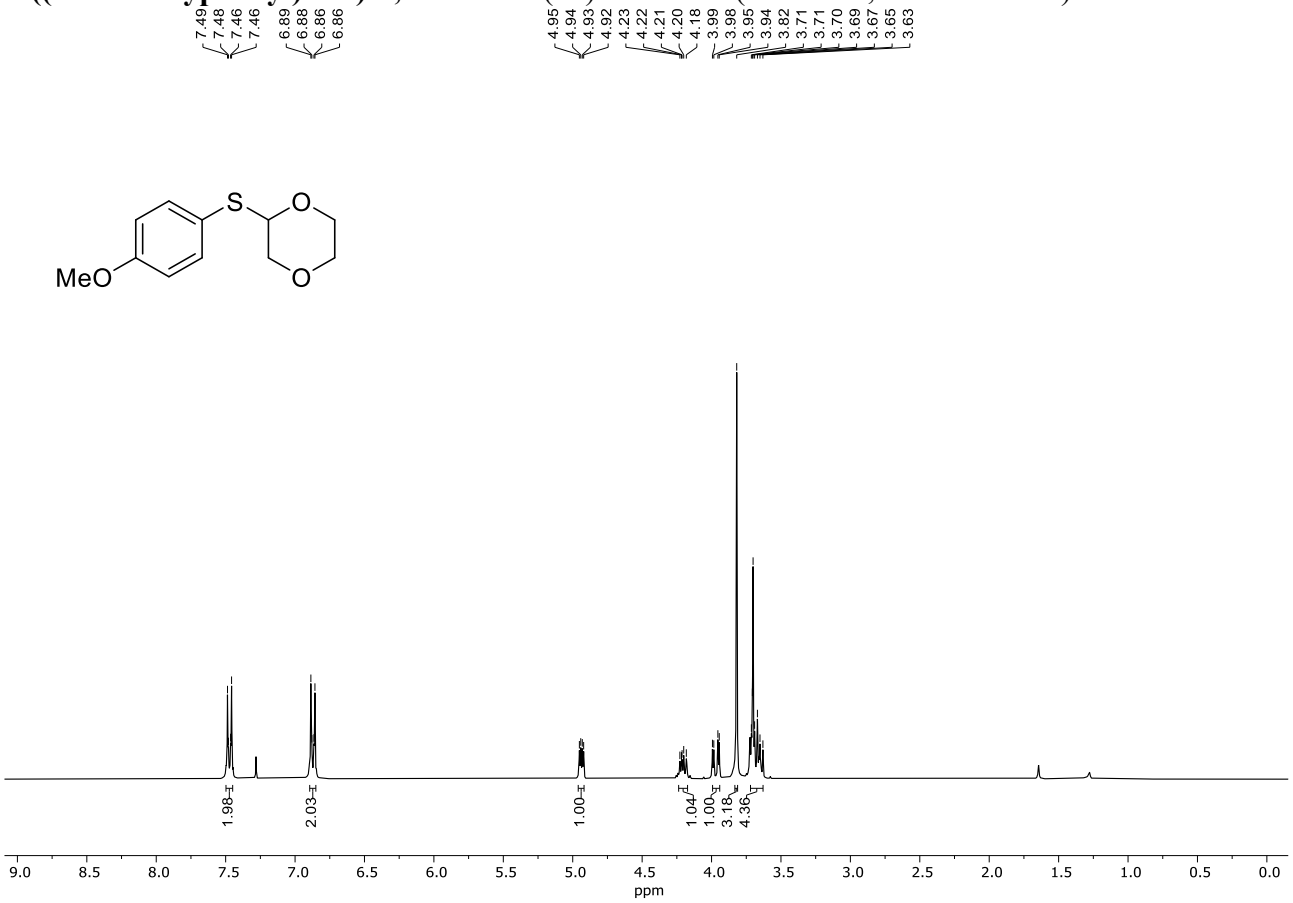
1-(4-chlorophenyl)-2-((2,5-dichlorophenyl)thio)diazene (**1l**). ^{13}C NMR (75 MHz, Chloroform-*d*)



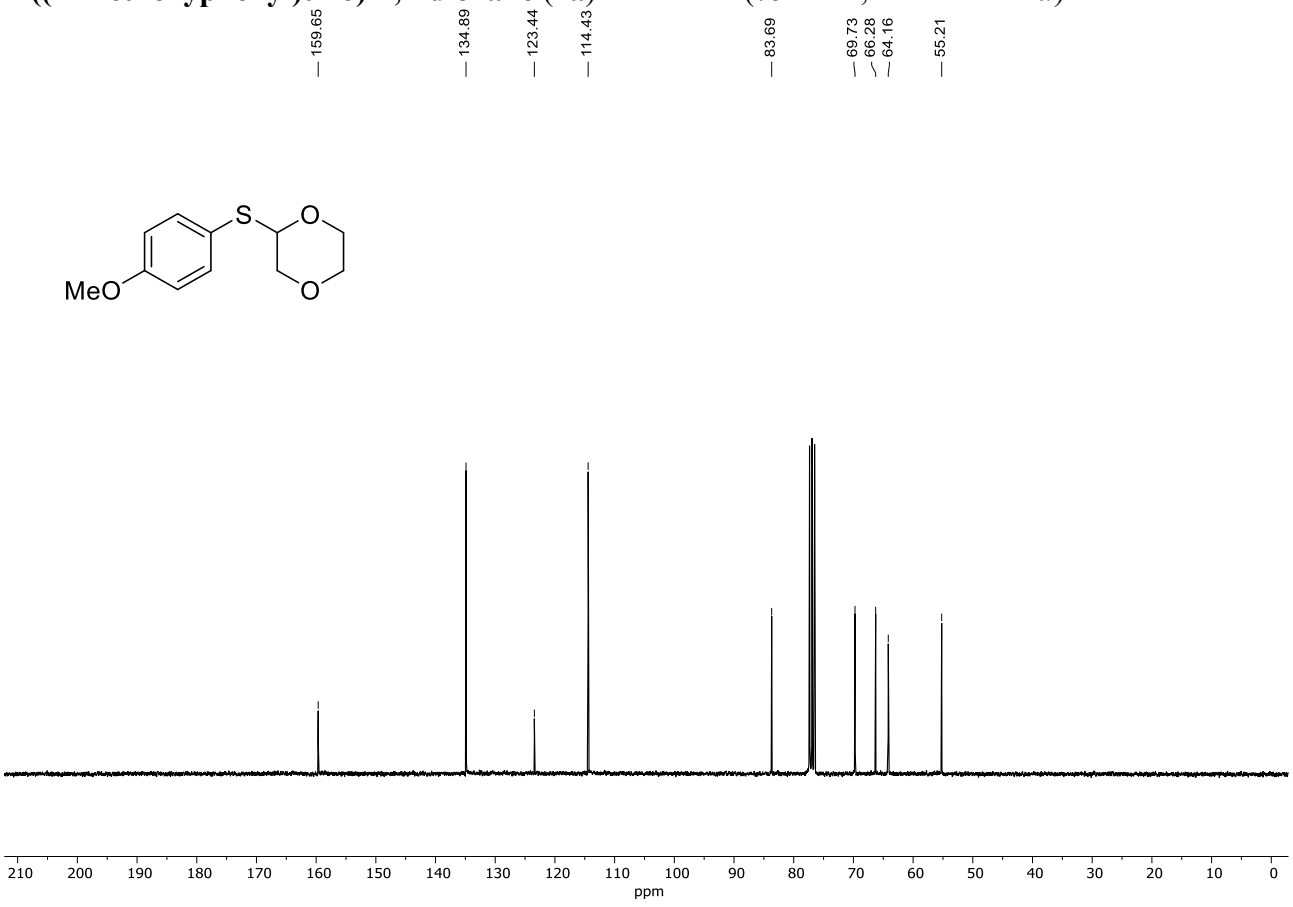




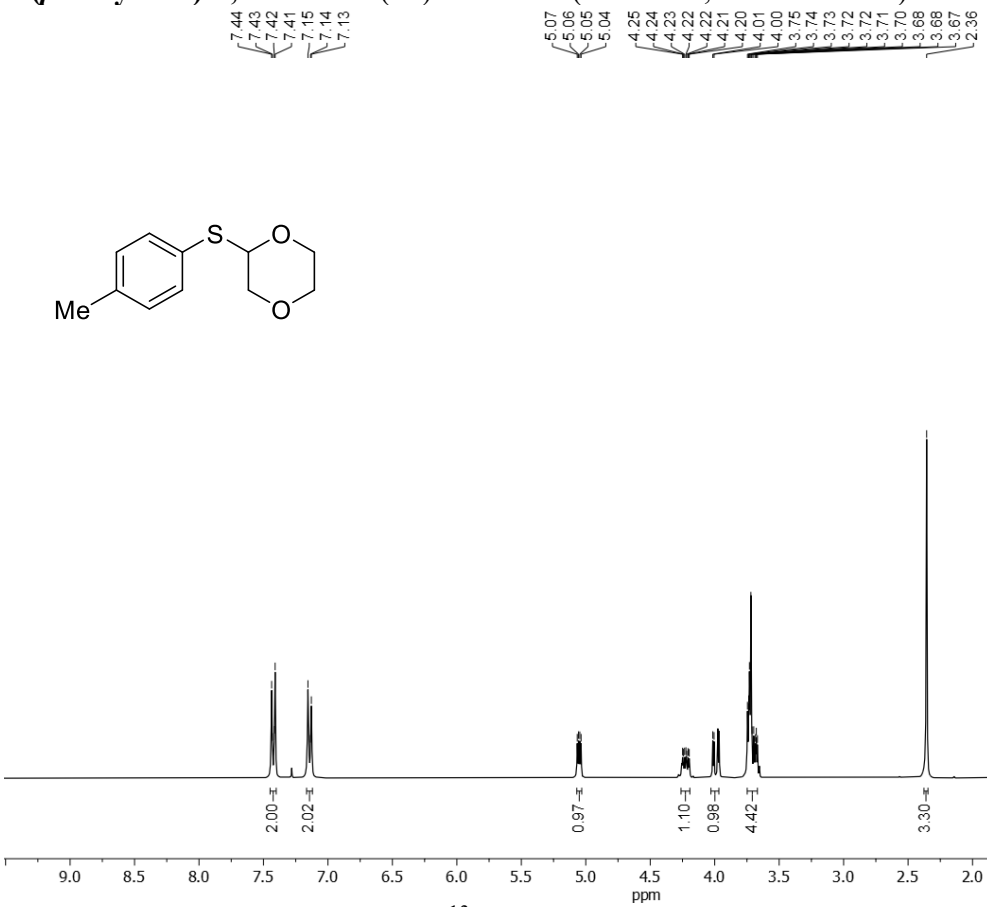
2-((4-Methoxyphenyl)thio)-1,4-dioxane (**2a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



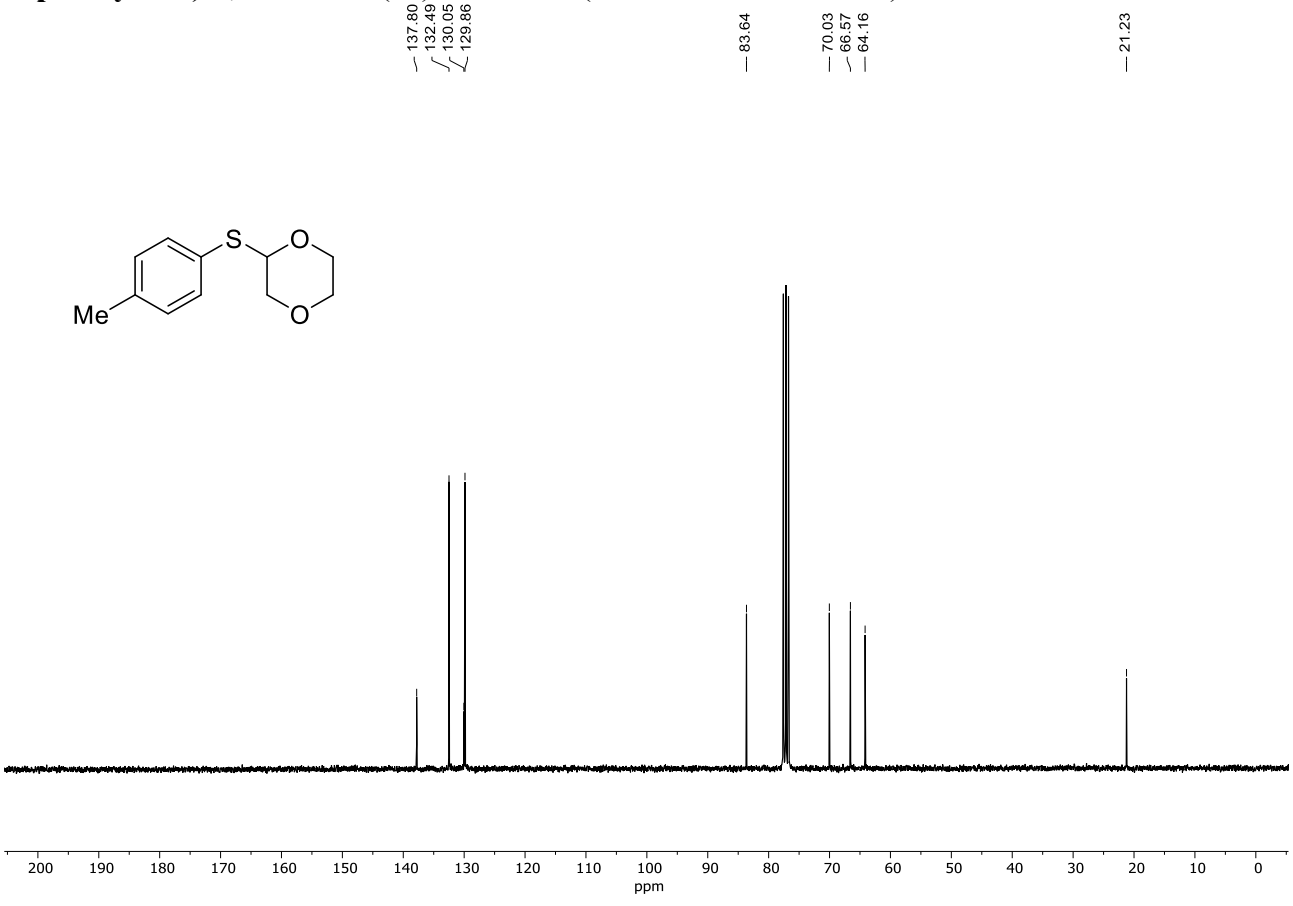
2-((4-Methoxyphenyl)thio)-1,4-dioxane (**2a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



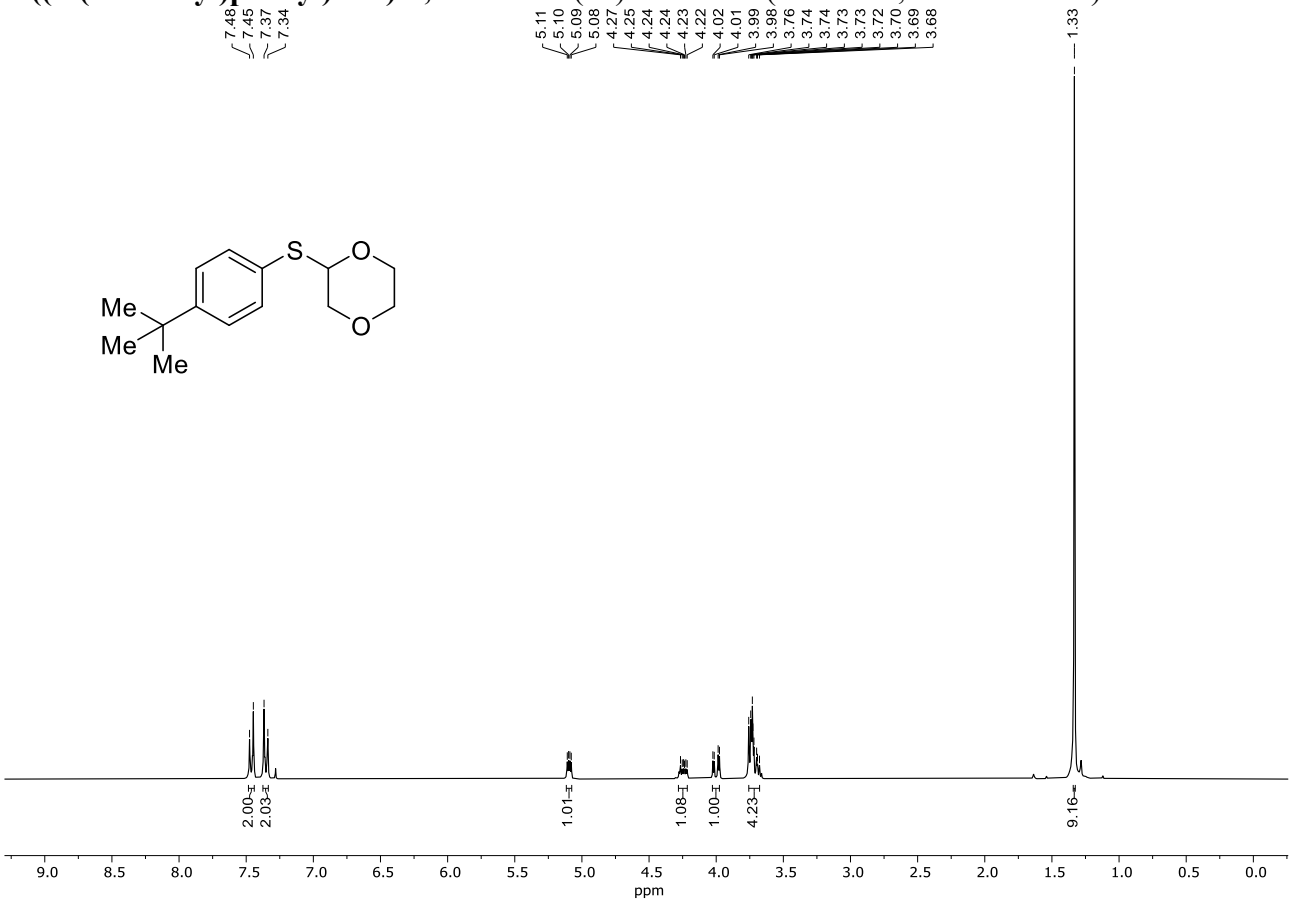
2-(*p*-Tolylthio)-1,4-dioxane (3a). ^{1}H NMR (300 MHz, Chloroform-*d*).



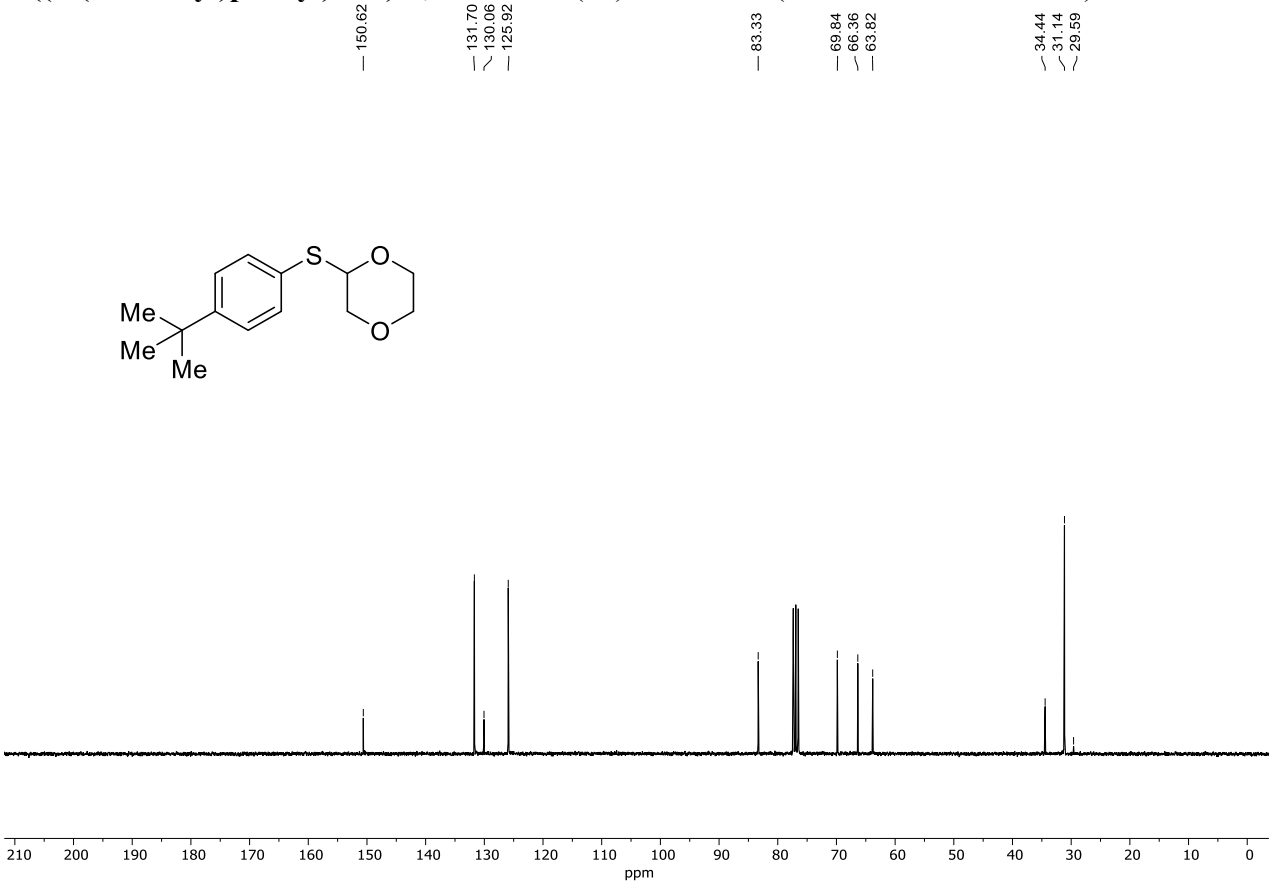
2-(*p*-Tolylthio)-1,4-dioxane (3a). ^{13}C NMR (75 MHz, Chloroform-*d*)



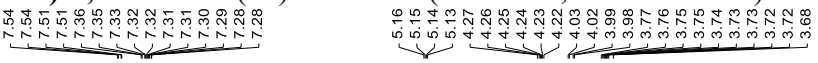
2-((4-(*tert*-Butyl)phenyl)thio)-1,4-dioxane (**4a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

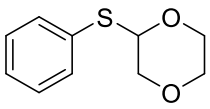


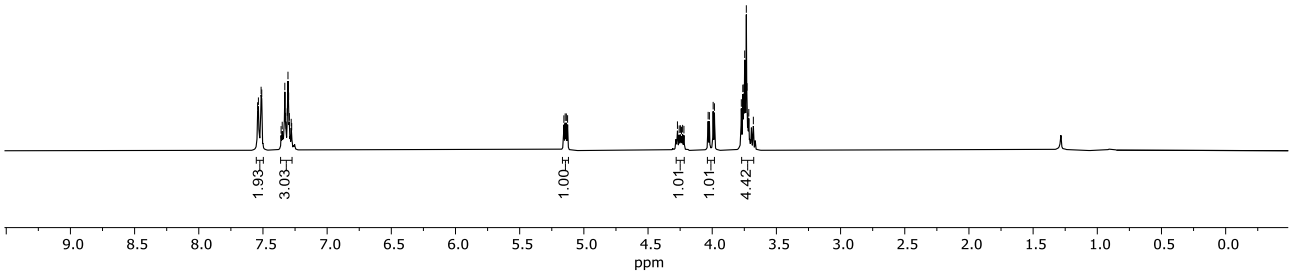
2-((4-(*tert*-Butyl)phenyl)thio)-1,4-dioxane (**4a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



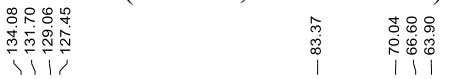
2-(Phenylthio)-1,4-dioxane (**5a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

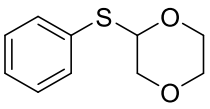


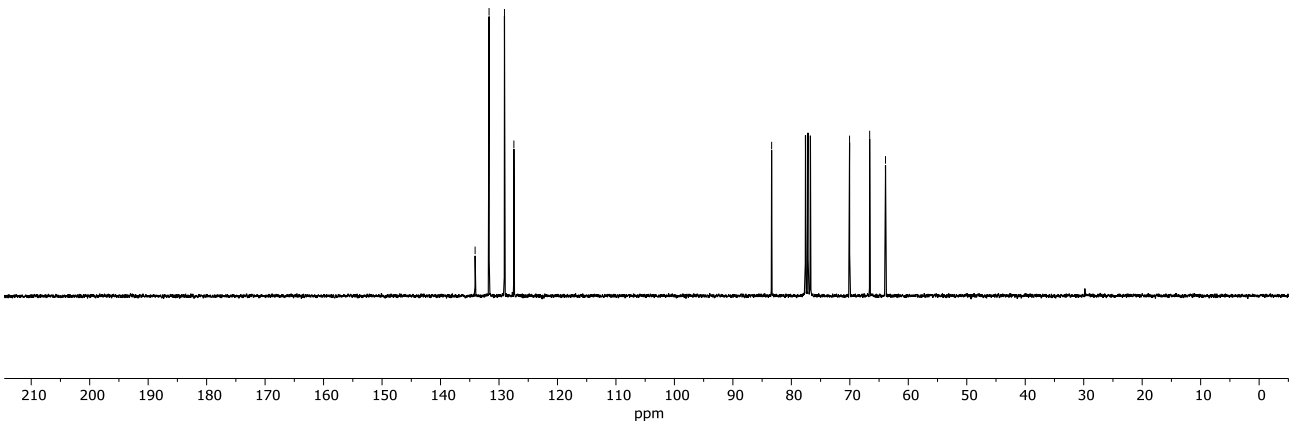




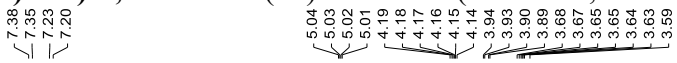
2-(Phenylthio)-1,4-dioxane (**5a**). ^{13}C NMR (75 MHz, Chloroform-*d*)

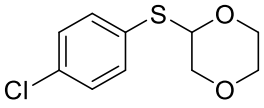


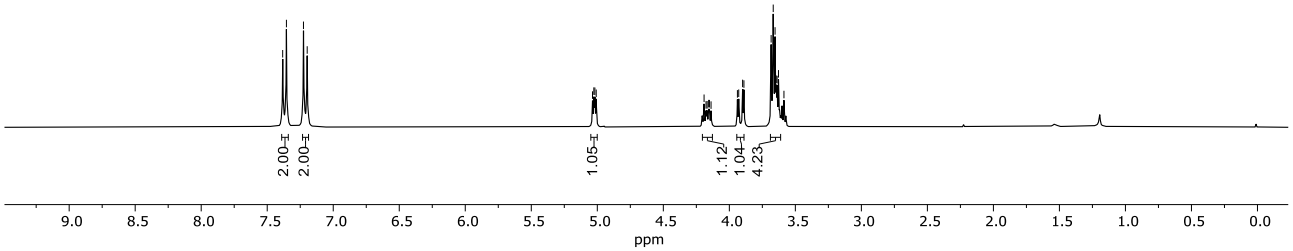




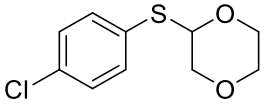
2-((4-Chlorophenyl)thio)-1,4-dioxane (**6a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

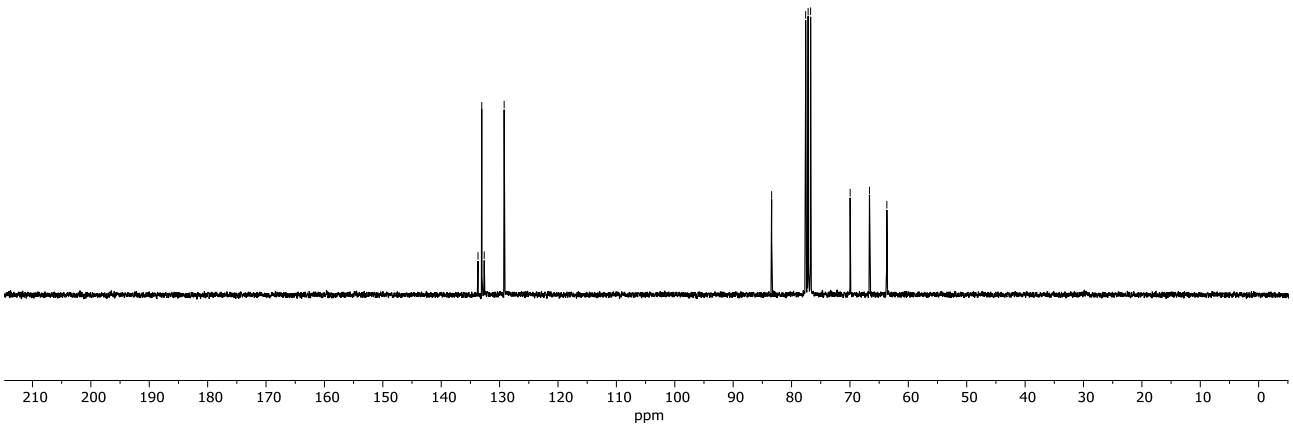




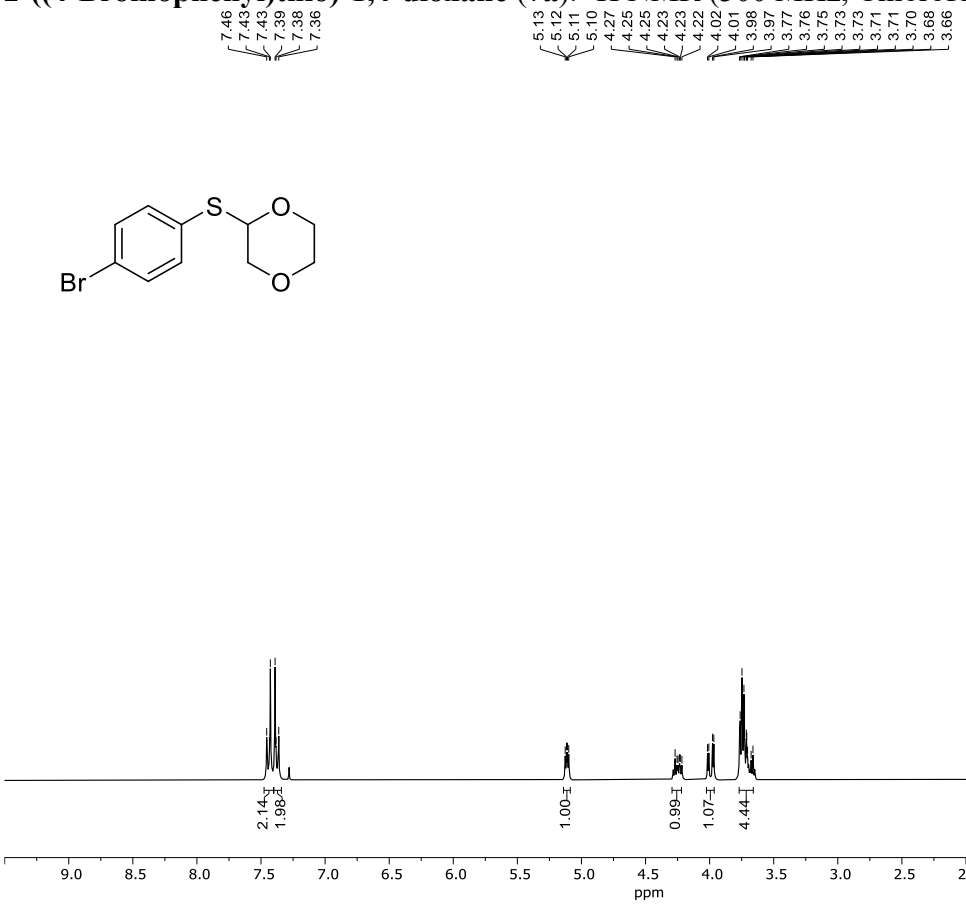


2-((4-Chlorophenyl)thio)-1,4-dioxane (**6a**). ^{13}C NMR (75 MHz, Chloroform-*d*)

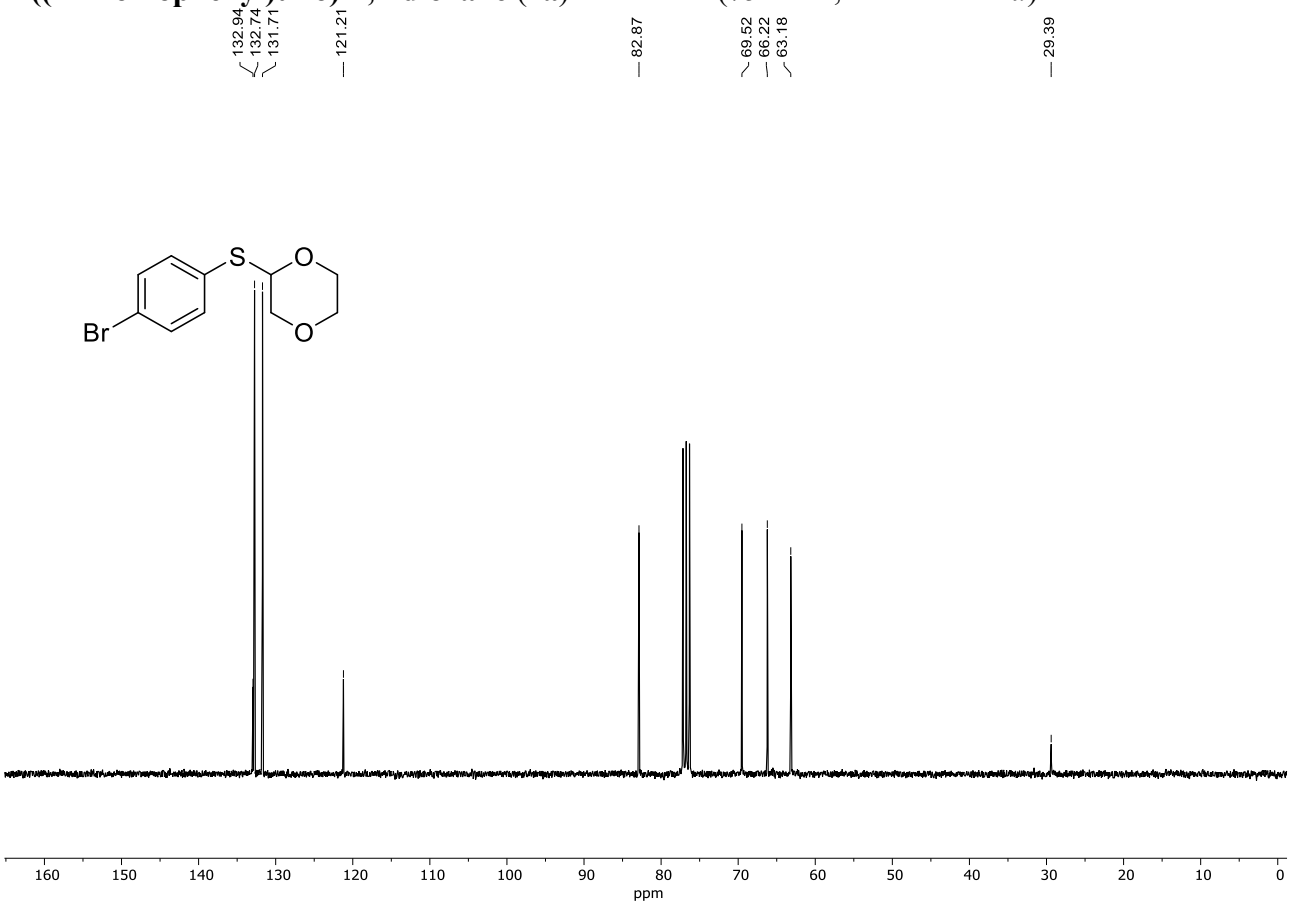




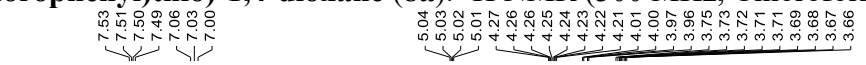
2-((4-Bromophenyl)thio)-1,4-dioxane (**7a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

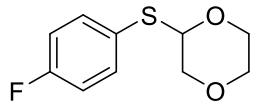


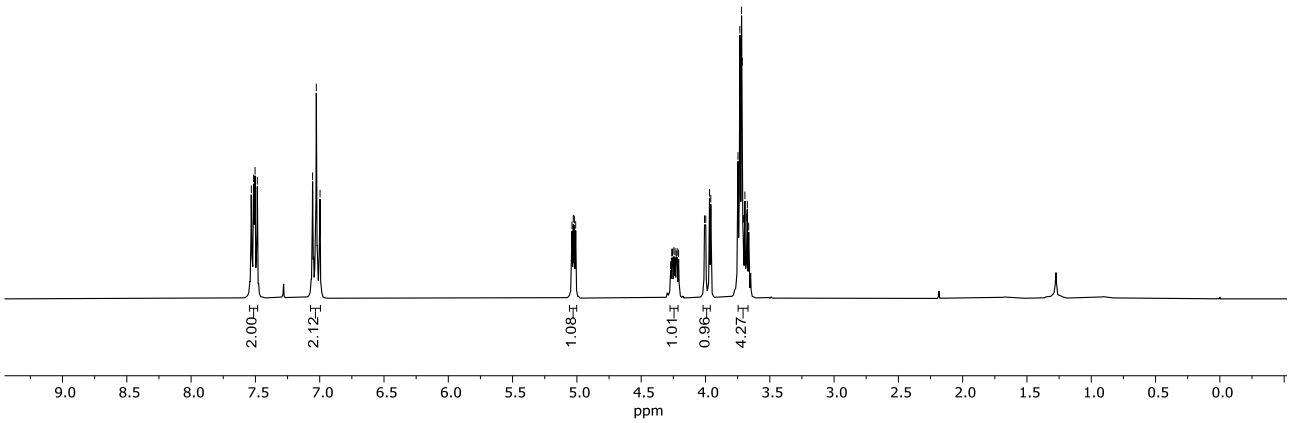
2-((4-Bromophenyl)thio)-1,4-dioxane (**7a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



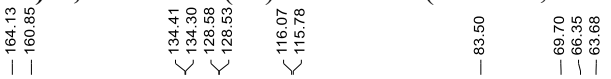
2-((4-Fluorophenyl)thio)-1,4-dioxane (**8a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

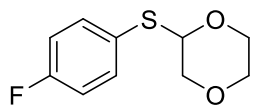


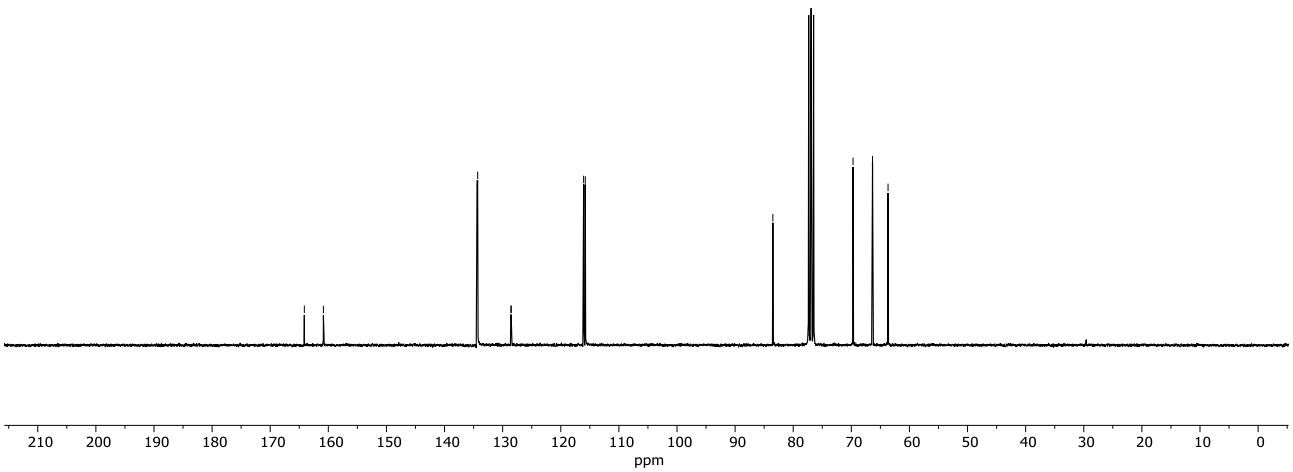




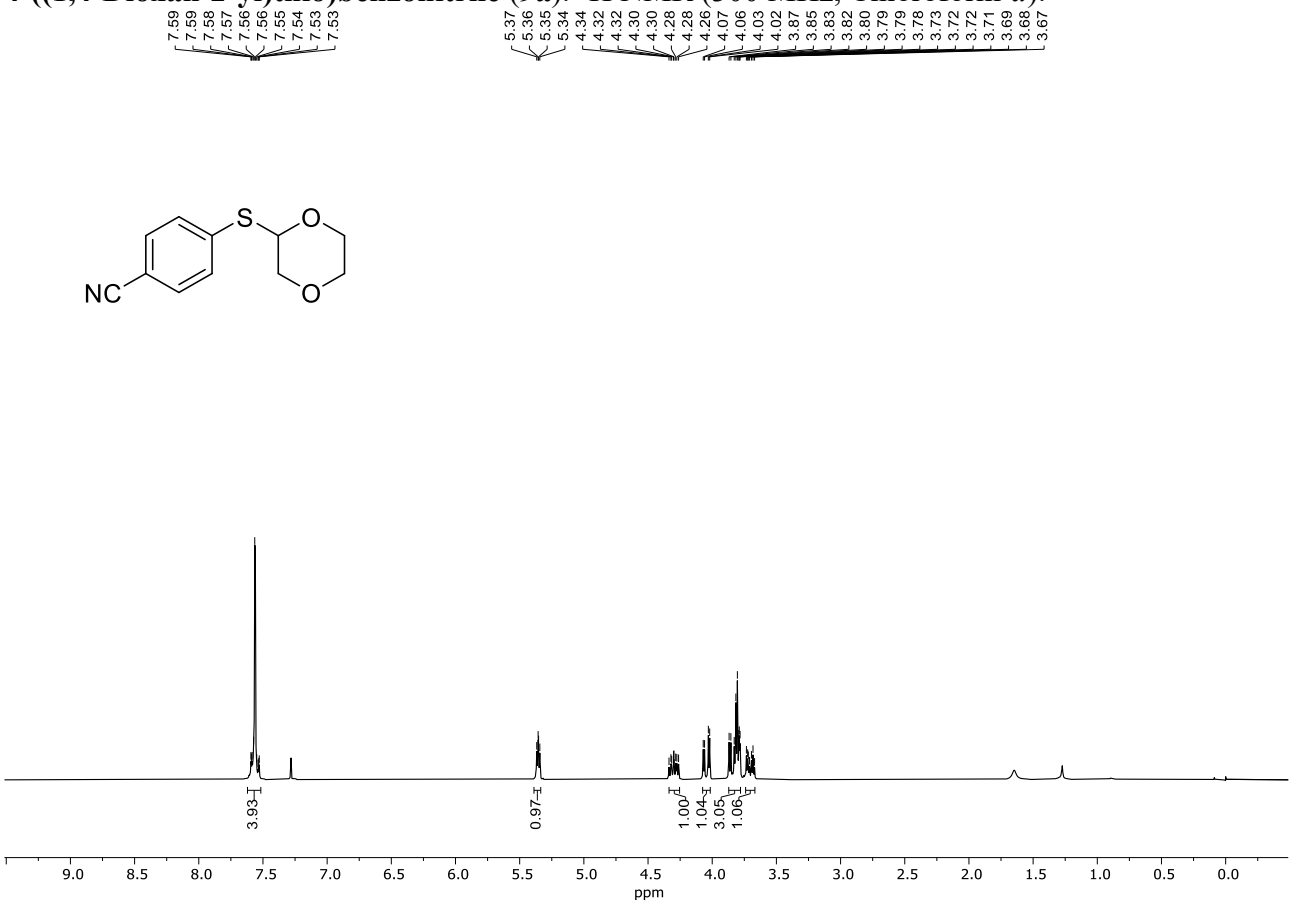
2-((4-Fluorophenyl)thio)-1,4-dioxane (**8a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



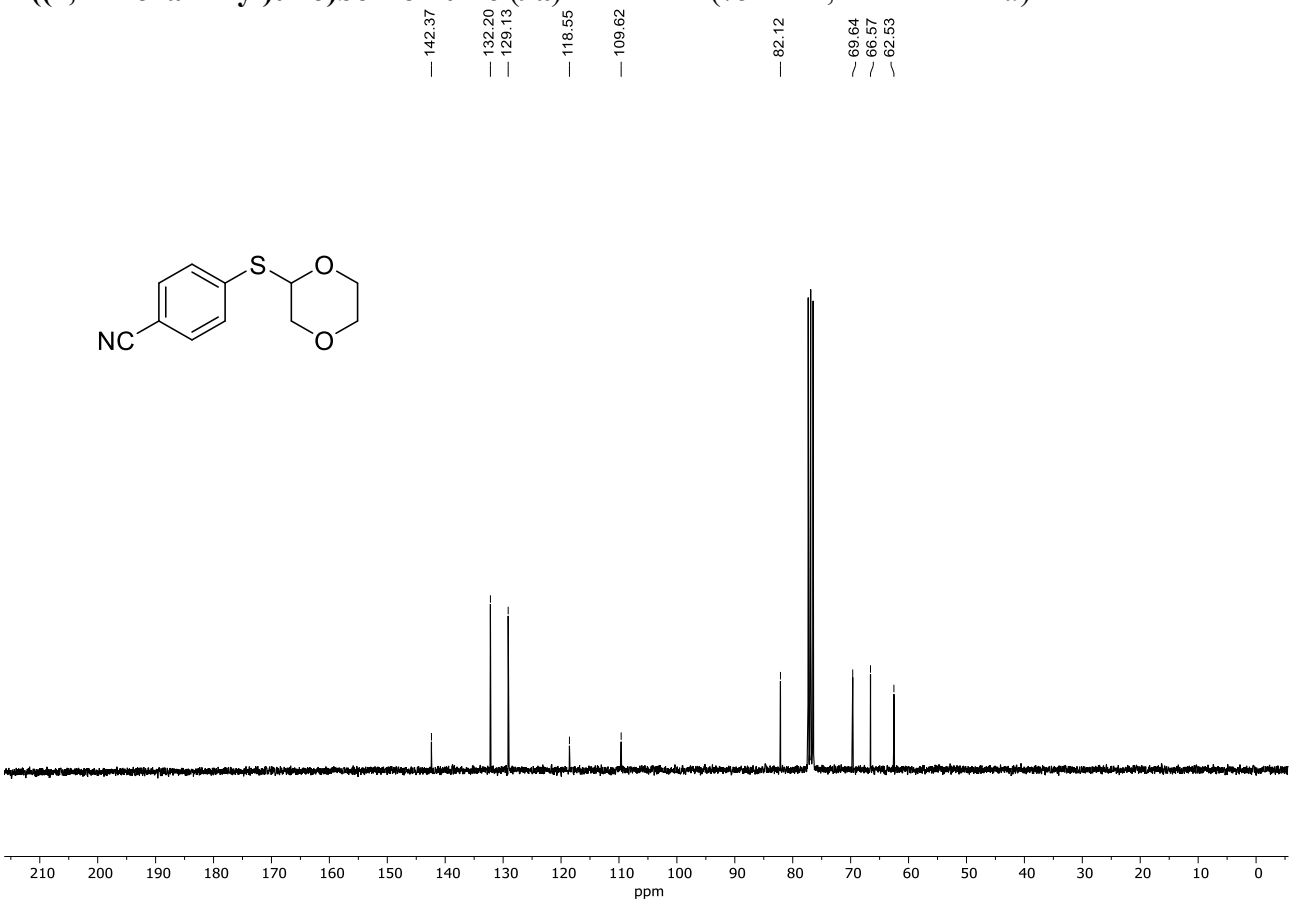




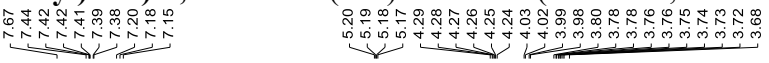
4-((1,4-Dioxan-2-yl)thio)benzonitrile (**9a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

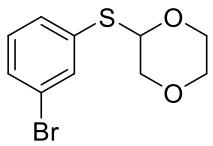


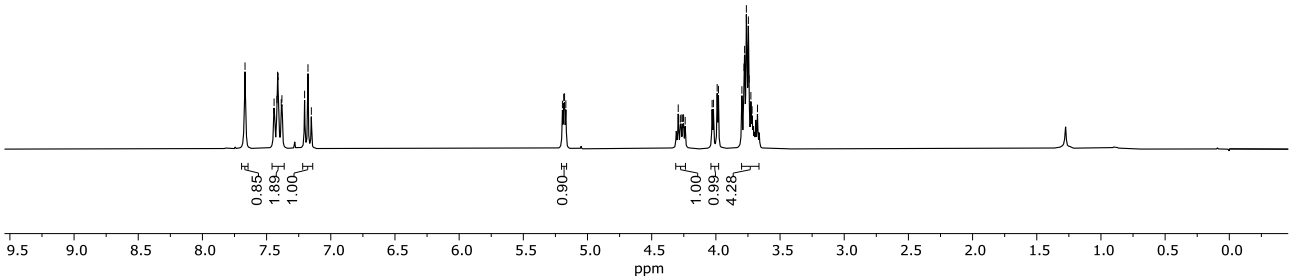
4-((1,4-Dioxan-2-yl)thio)benzonitrile (**9a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



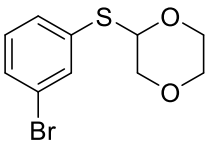
2-((3-Bromophenyl)thio)-1,4-dioxane (**10a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

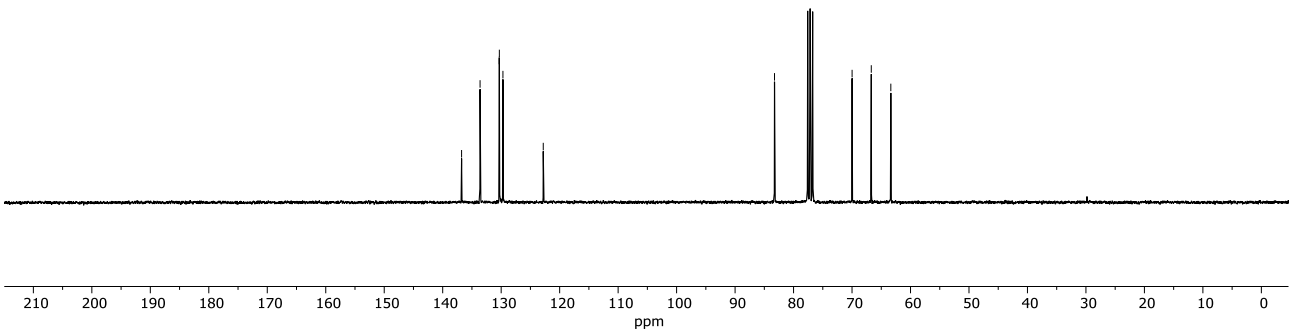




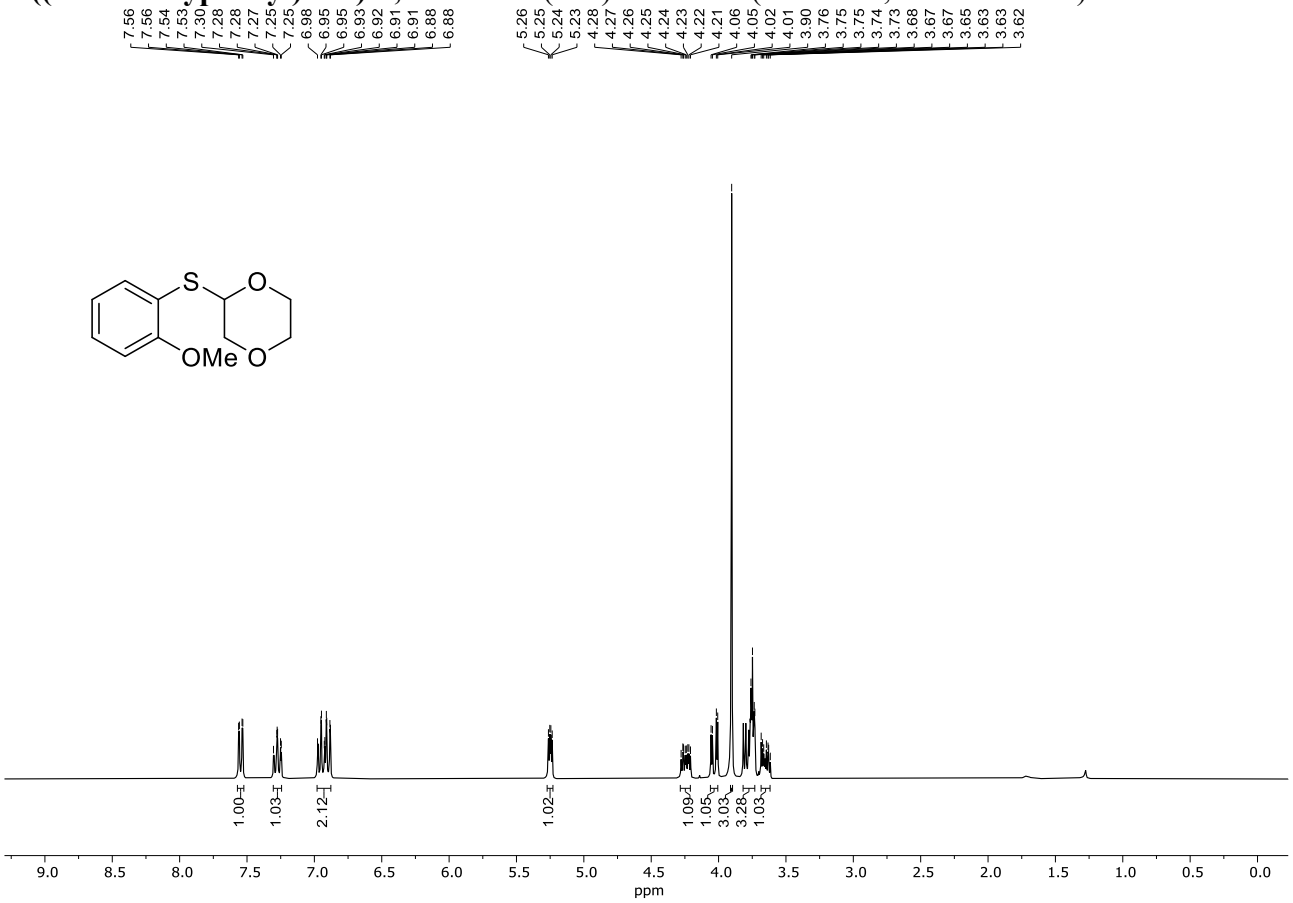


2-((3-Bromophenyl)thio)-1,4-dioxane (**10a**). ^{13}C NMR (75 MHz, Chloroform-*d*)

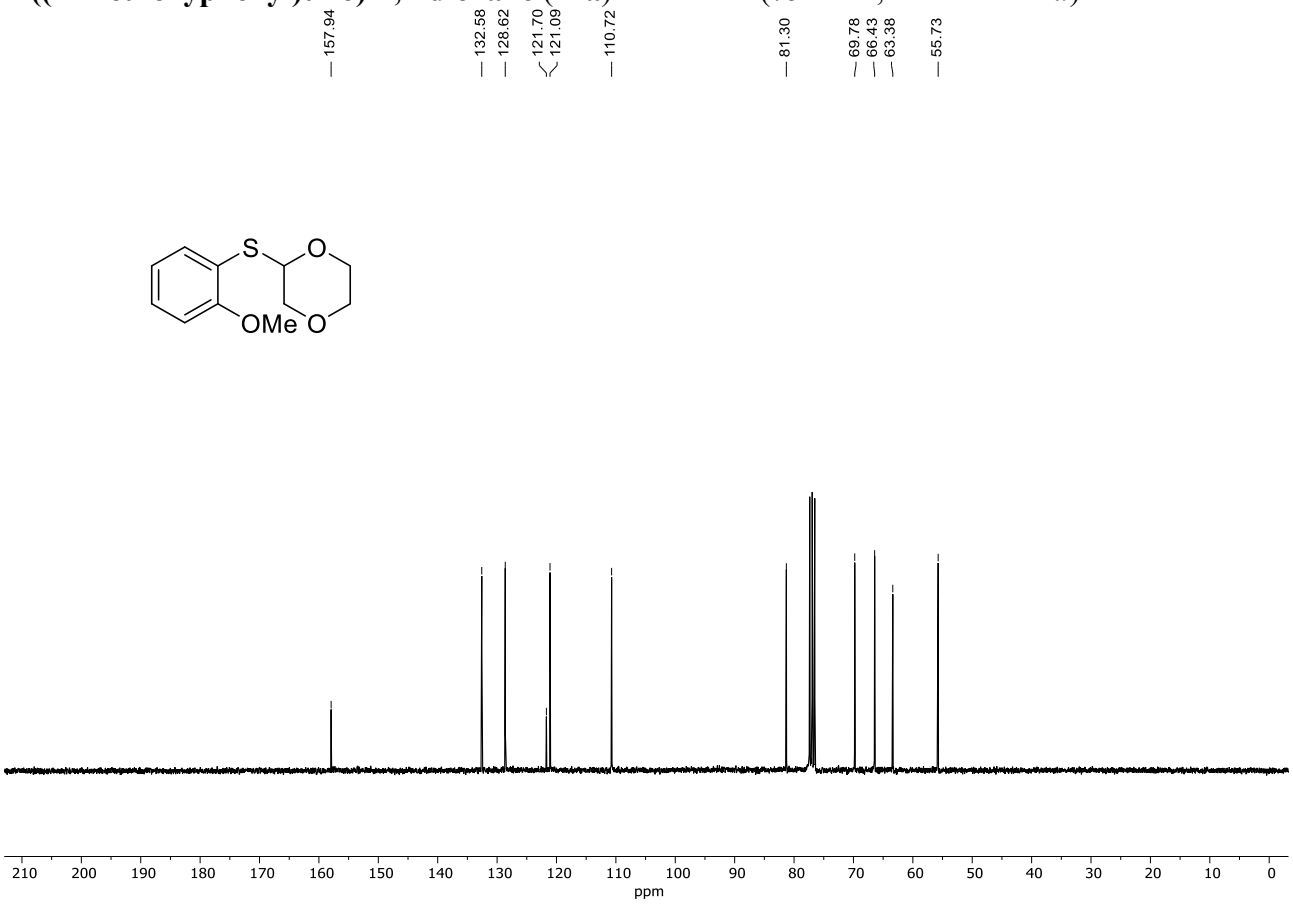




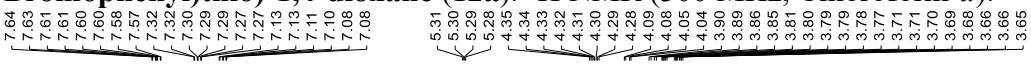
2-((2-Methoxyphenyl)thio)-1,4-dioxane (**11a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

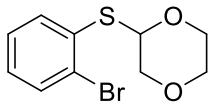


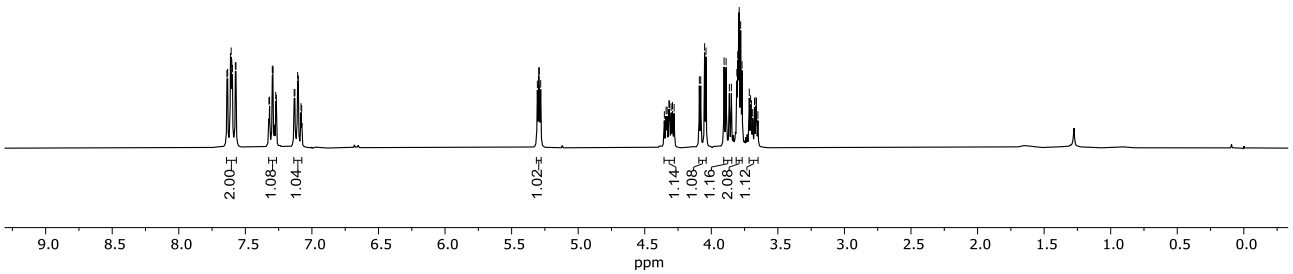
2-((2-Methoxyphenyl)thio)-1,4-dioxane (**11a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



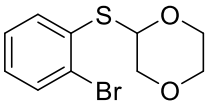
2-((2-Bromophenyl)thio)-1,4-dioxane (**12a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

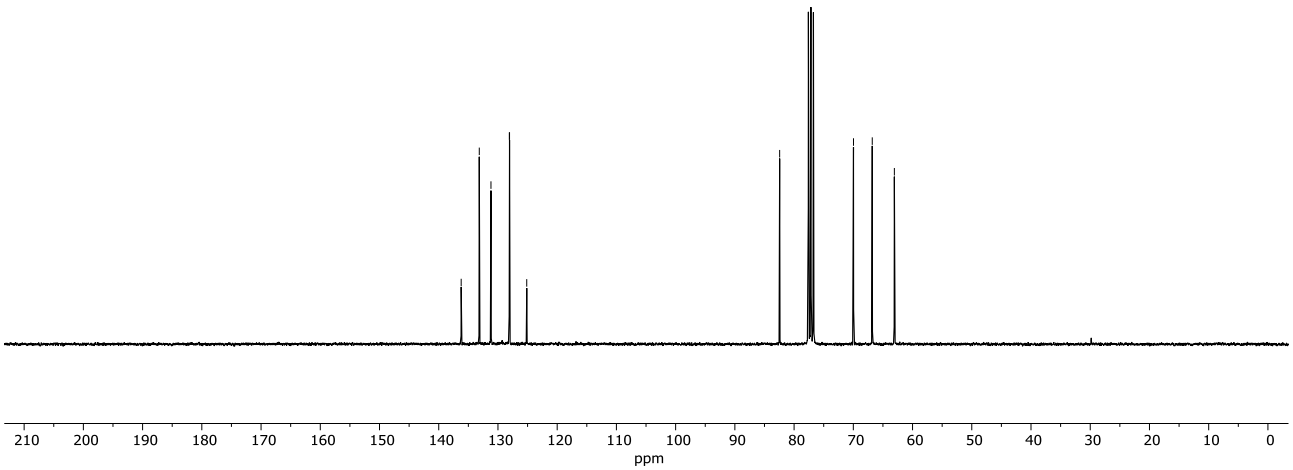




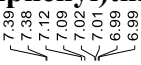


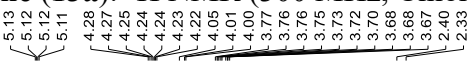
2-((2-Bromophenyl)thio)-1,4-dioxane (**12a**). ^{13}C NMR (75 MHz, Chloroform-*d*)

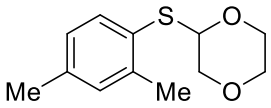


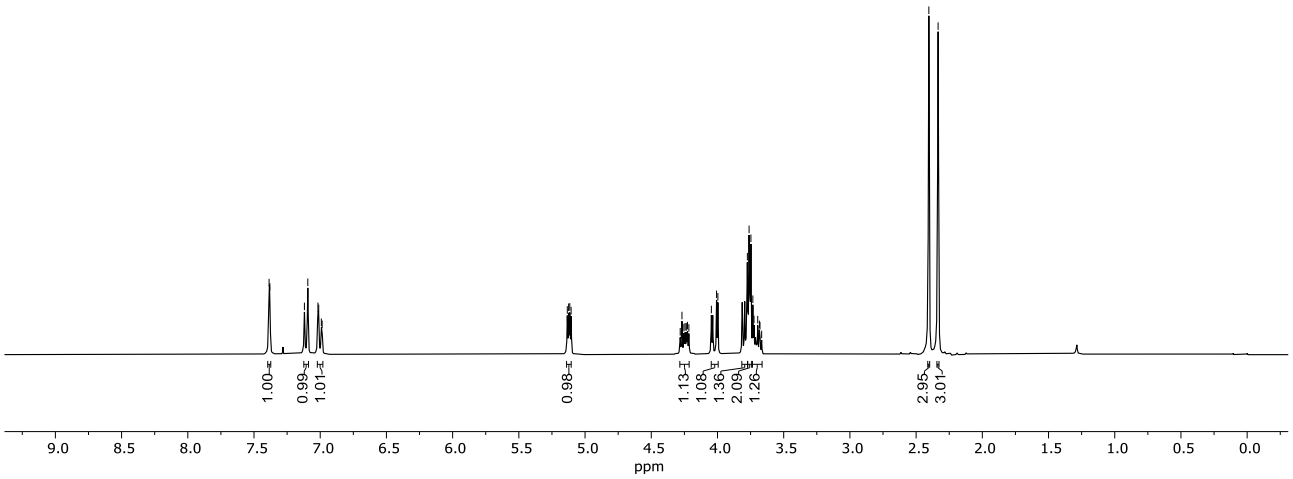


2-((2,4-Dimethylphenyl)thio)-1,4-dioxane (**13a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

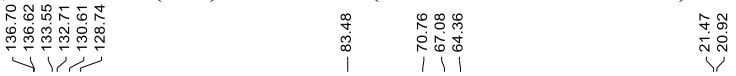


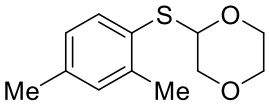


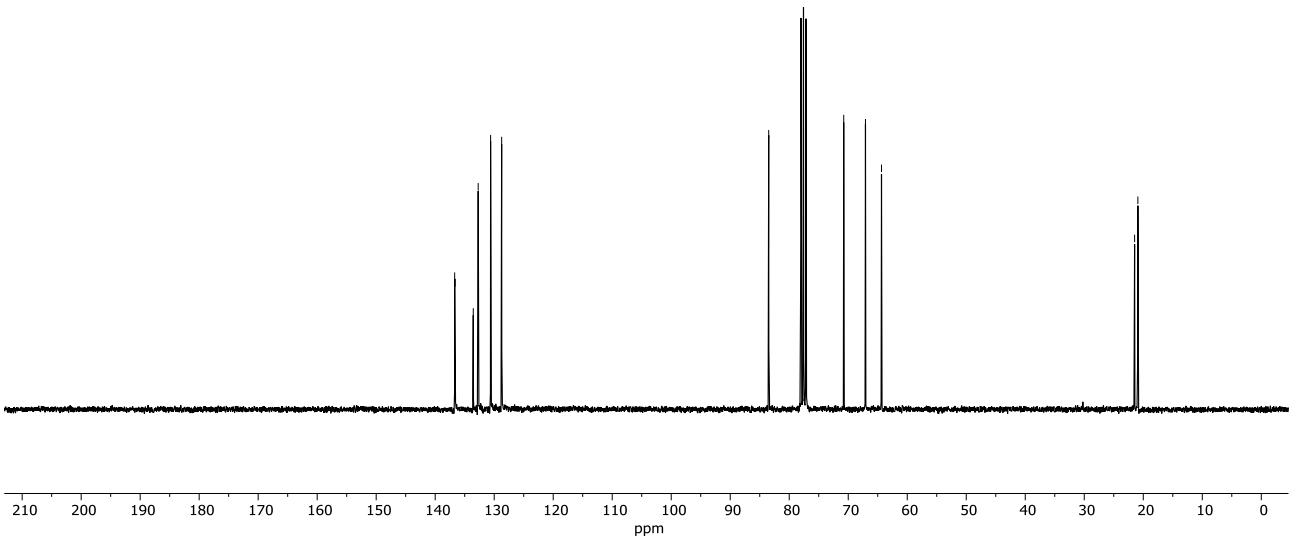




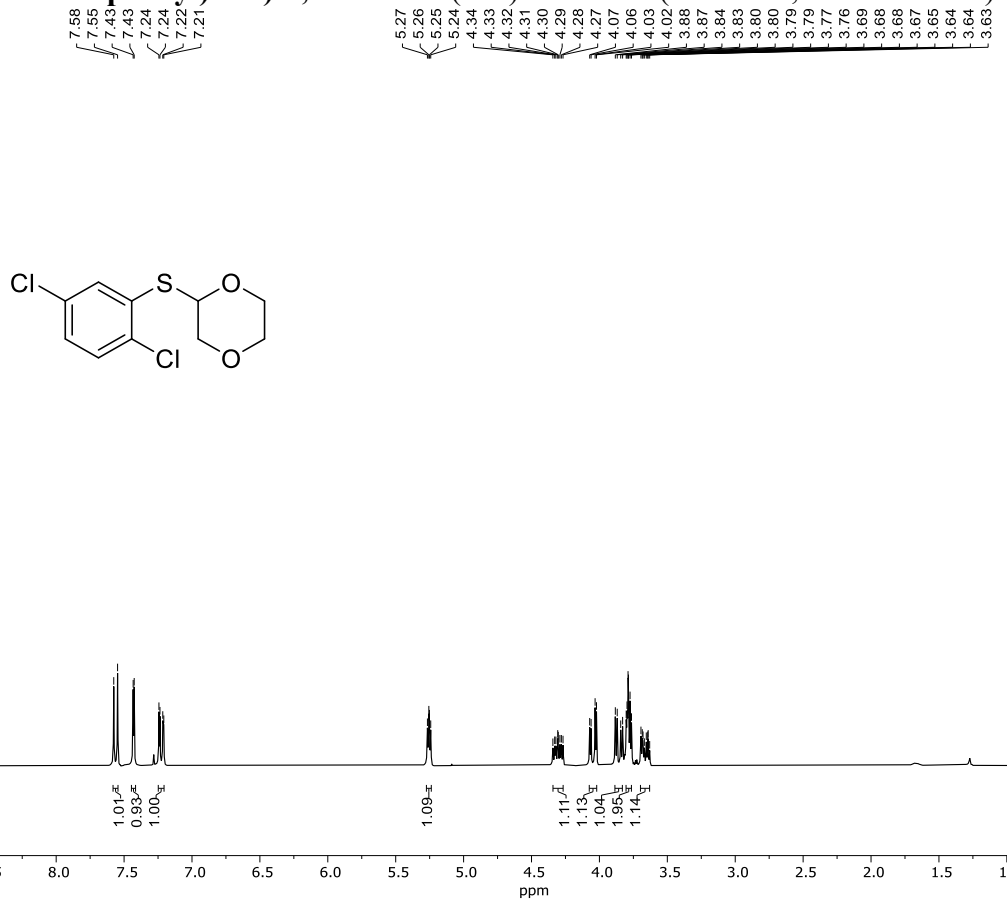
2-((2,4-Dimethylphenyl)thio)-1,4-dioxane (**13a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



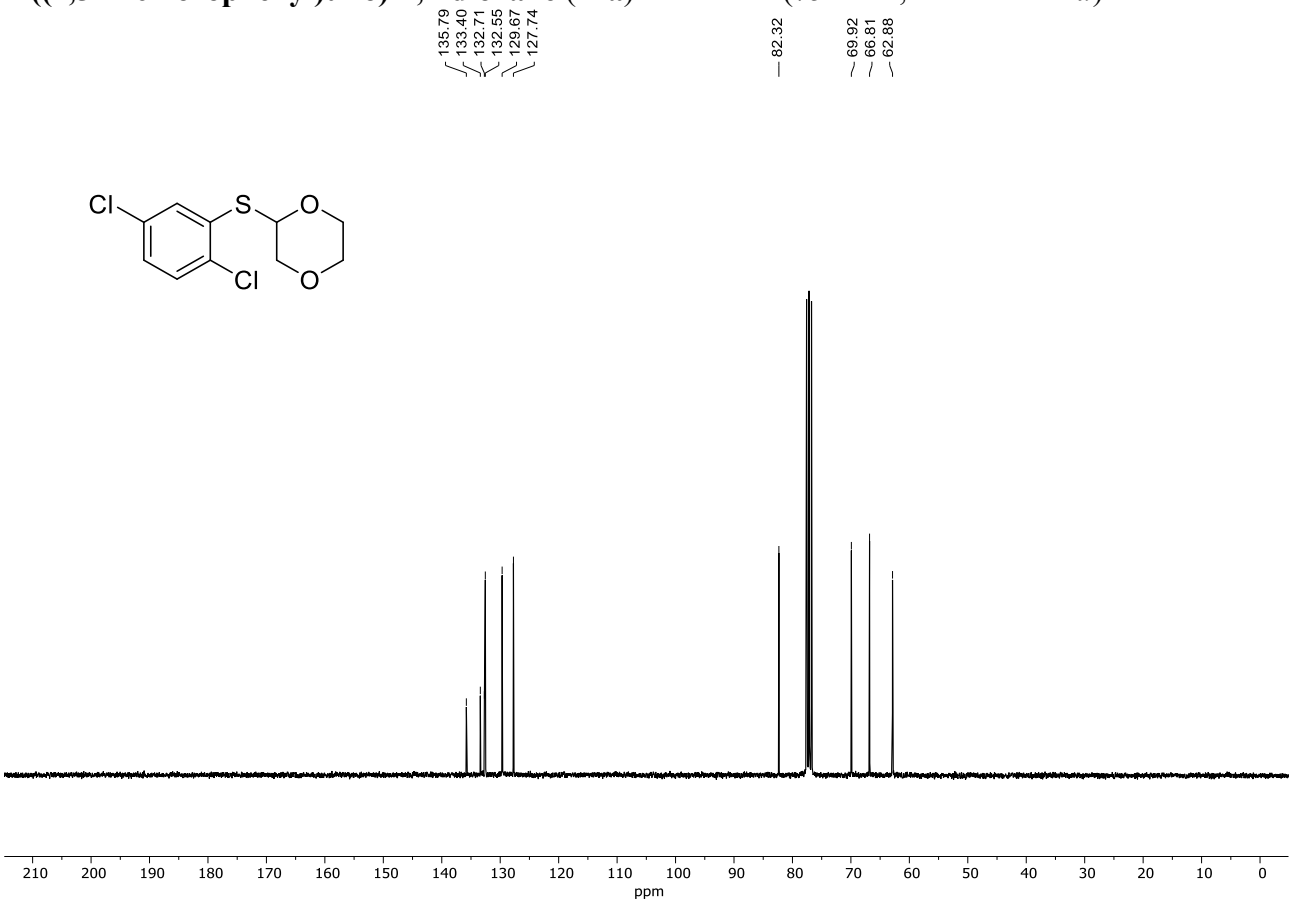




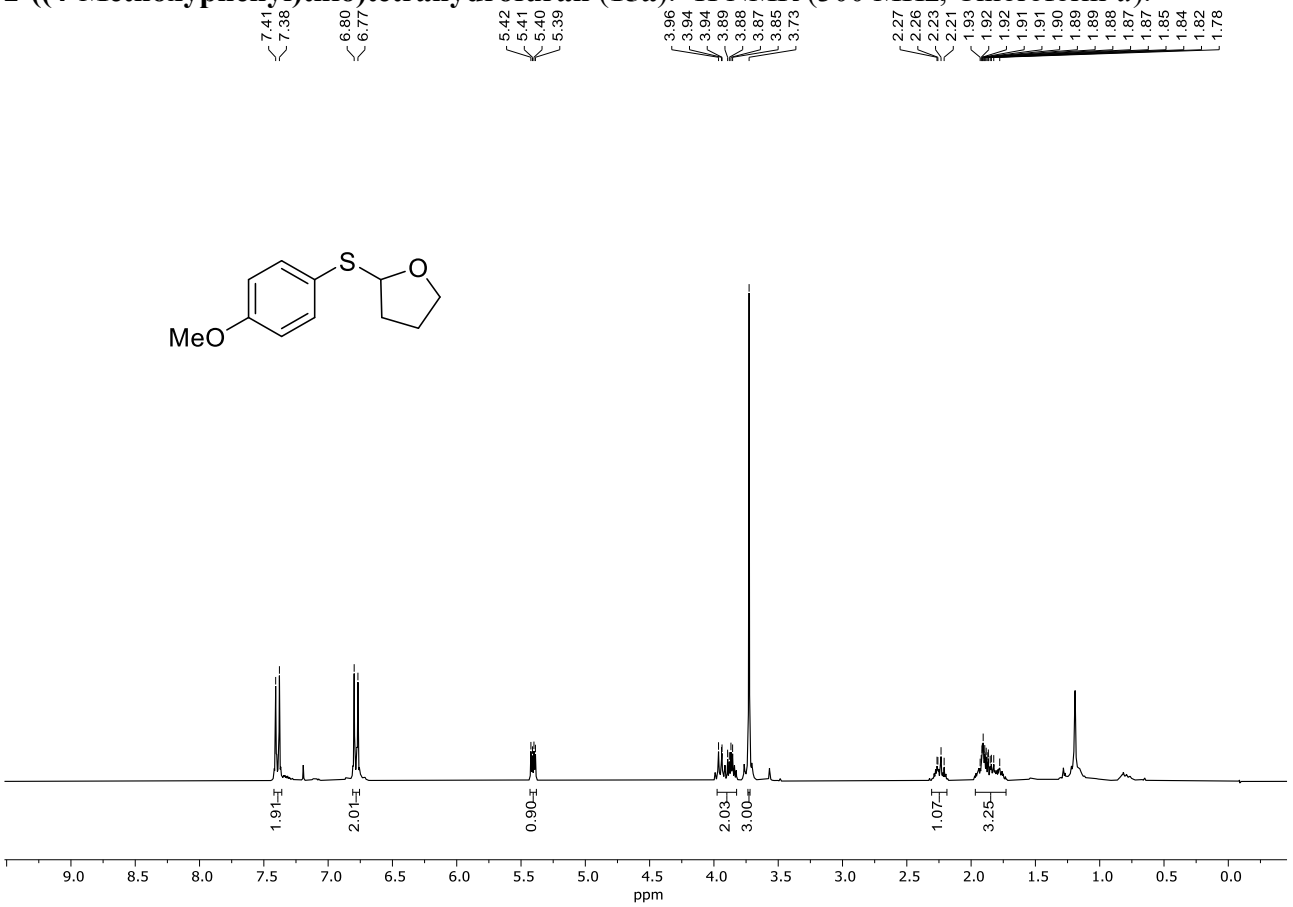
2-((2,5-Dichlorophenyl)thio)-1,4-dioxane (14a). ^{1}H NMR (300 MHz, Chloroform-*d*).



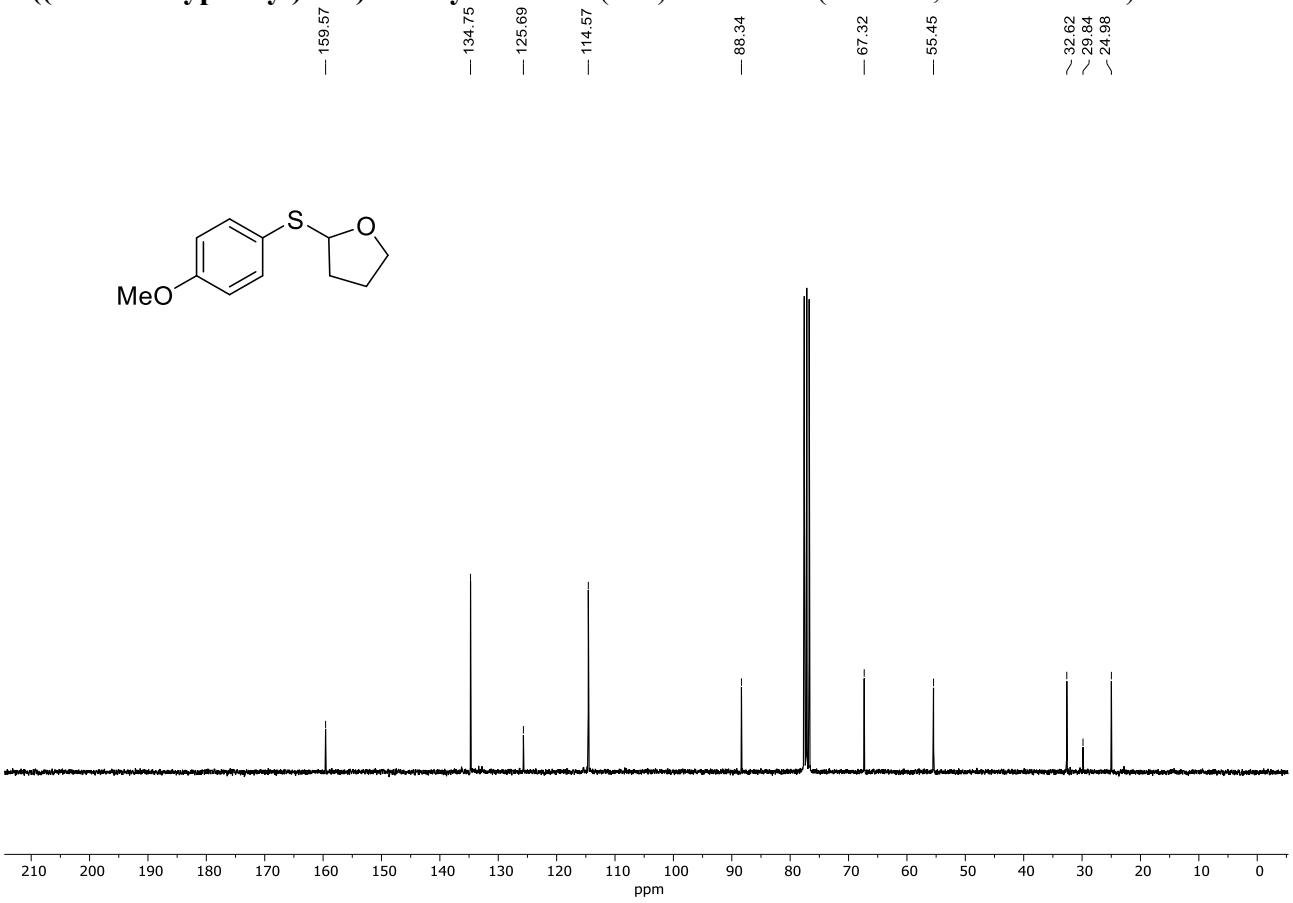
2-((2,5-Dichlorophenyl)thio)-1,4-dioxane (14a). ^{13}C NMR (75 MHz, Chloroform-*d*)



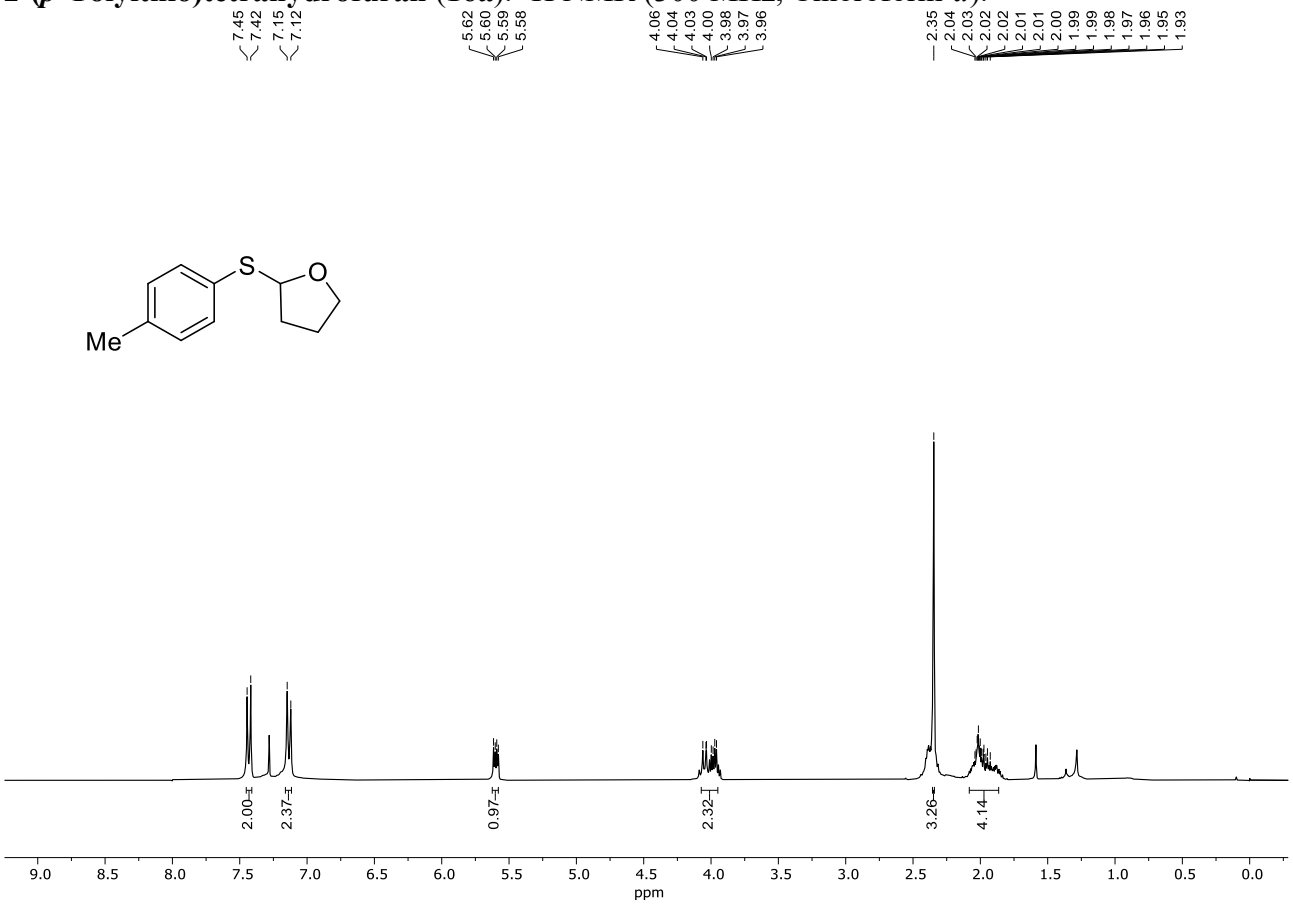
2-((4-Methoxyphenyl)thio)tetrahydrofuran (**15a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



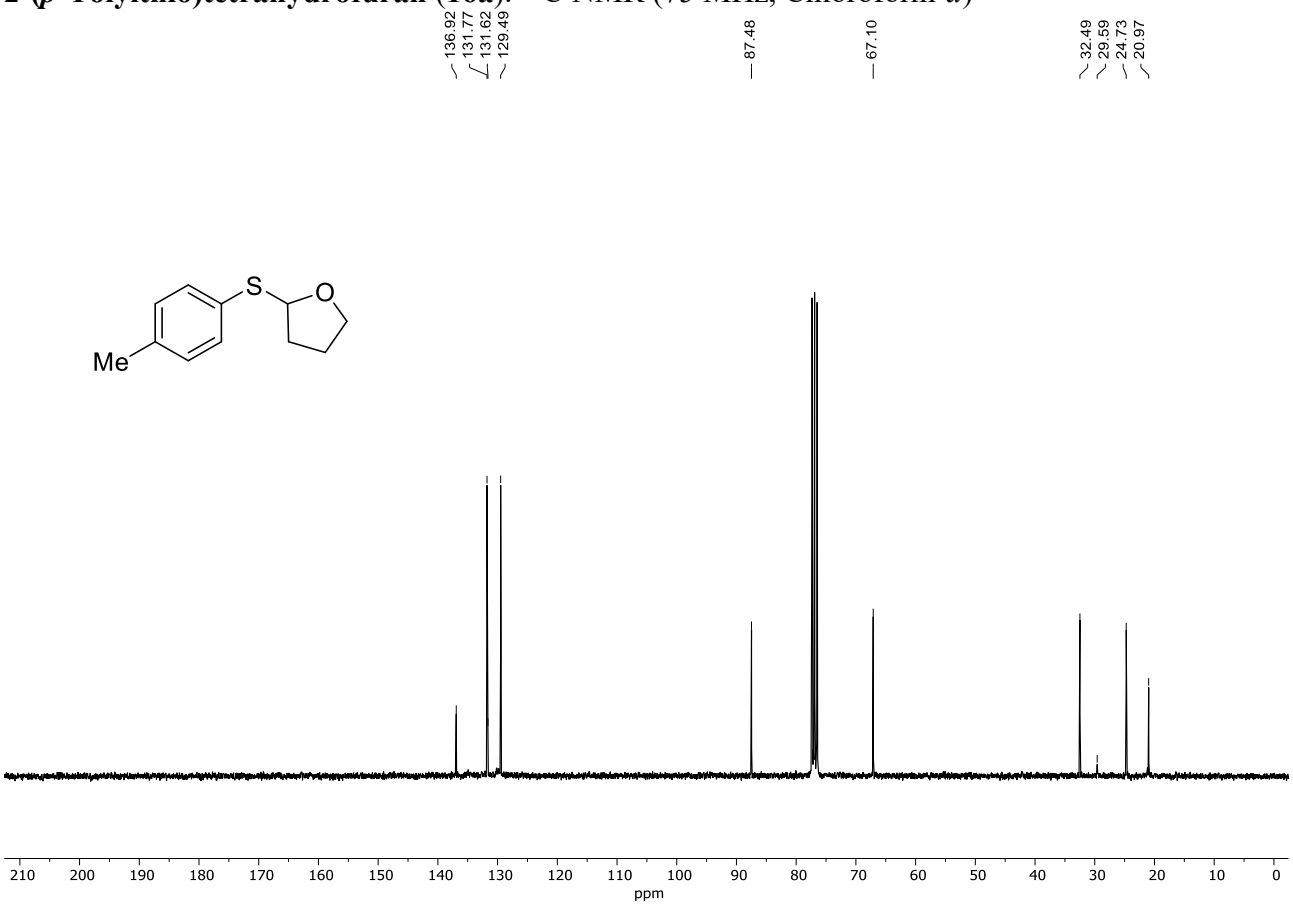
2-((4-Methoxyphenyl)thio)tetrahydrofuran (**15a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



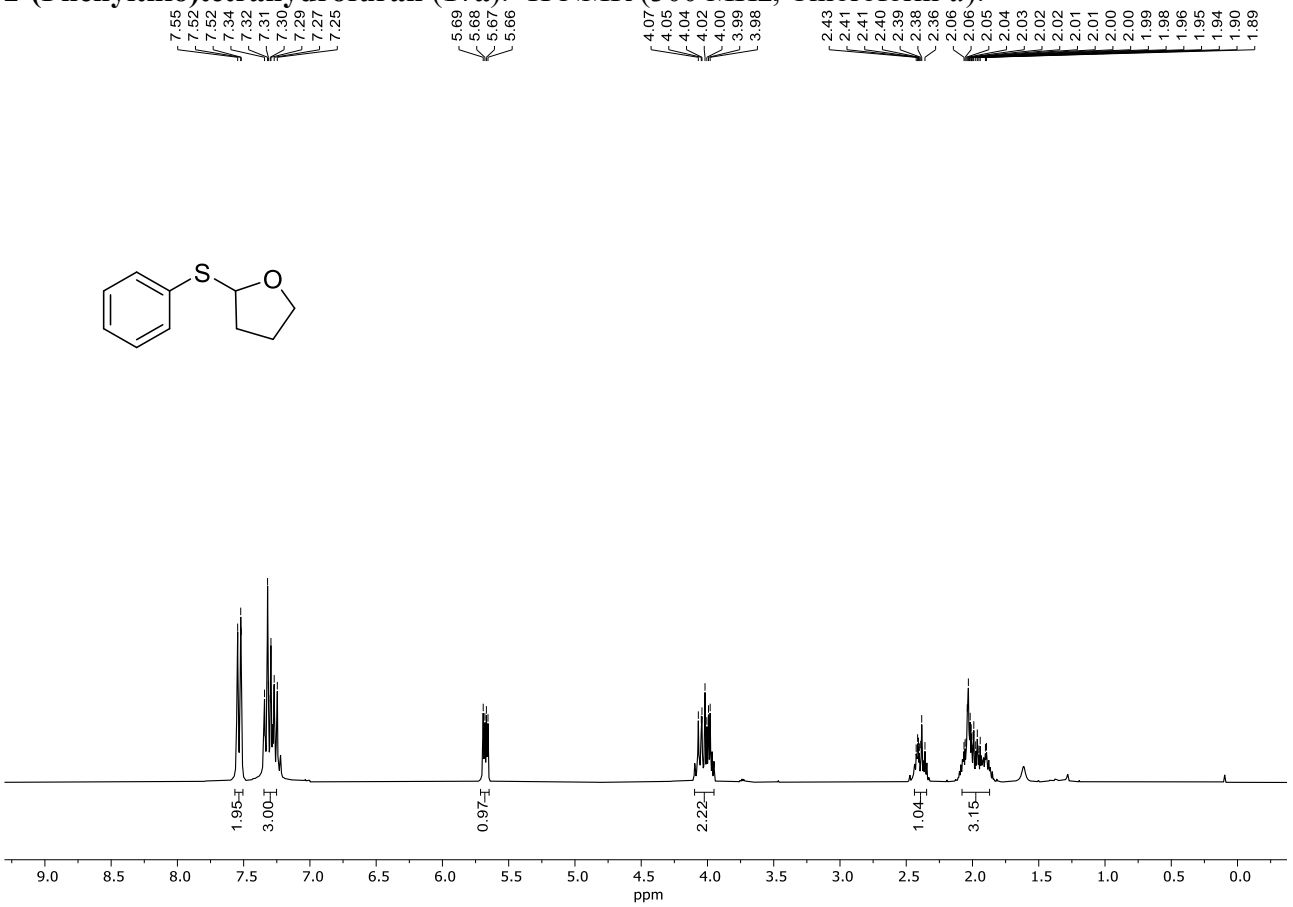
2-(*p*-Tolylthio)tetrahydrofuran (16a). ^{1}H NMR (300 MHz, Chloroform-*d*).



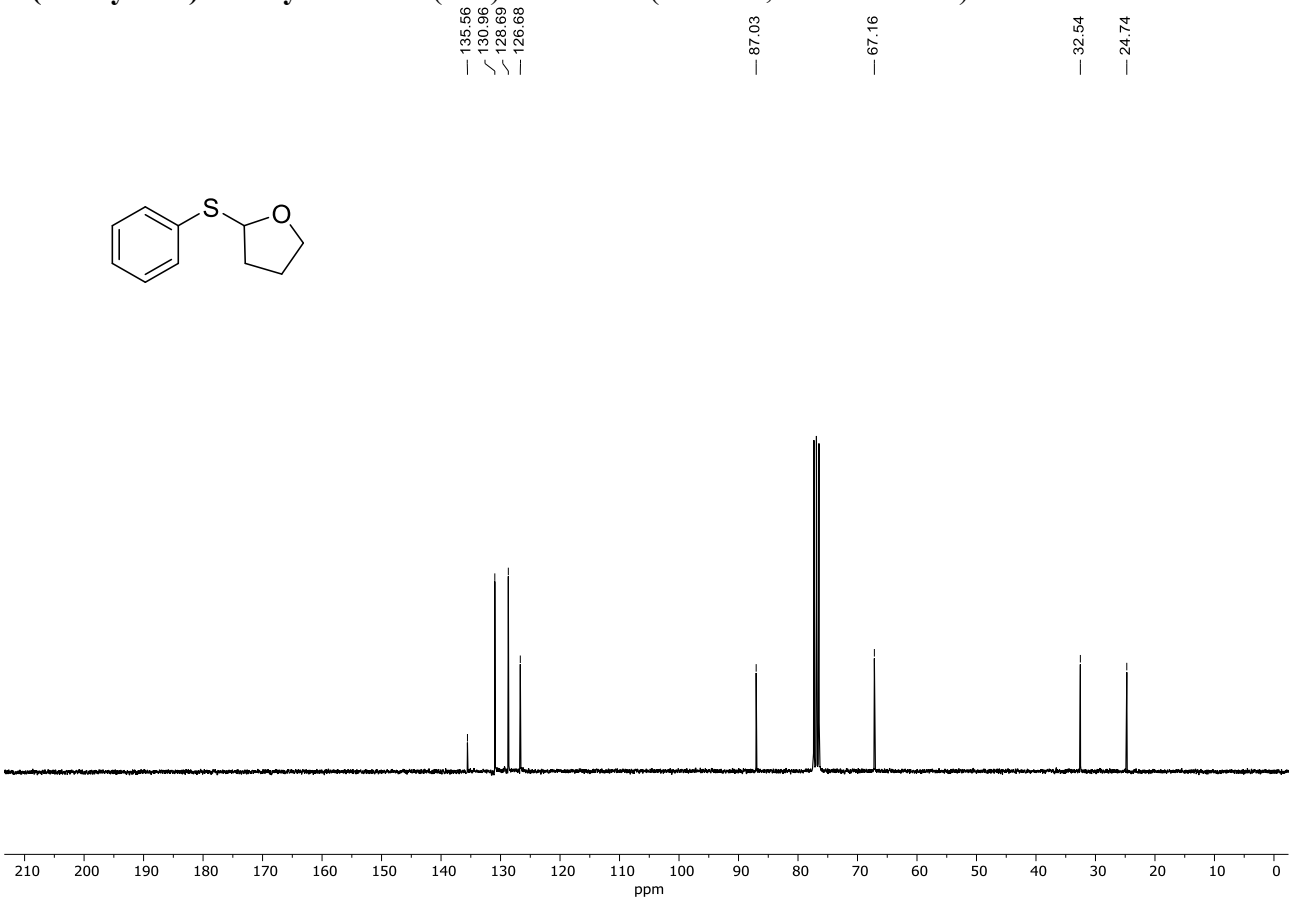
2-(*p*-Tolylthio)tetrahydrofuran (16a). ^{13}C NMR (75 MHz, Chloroform-*d*)



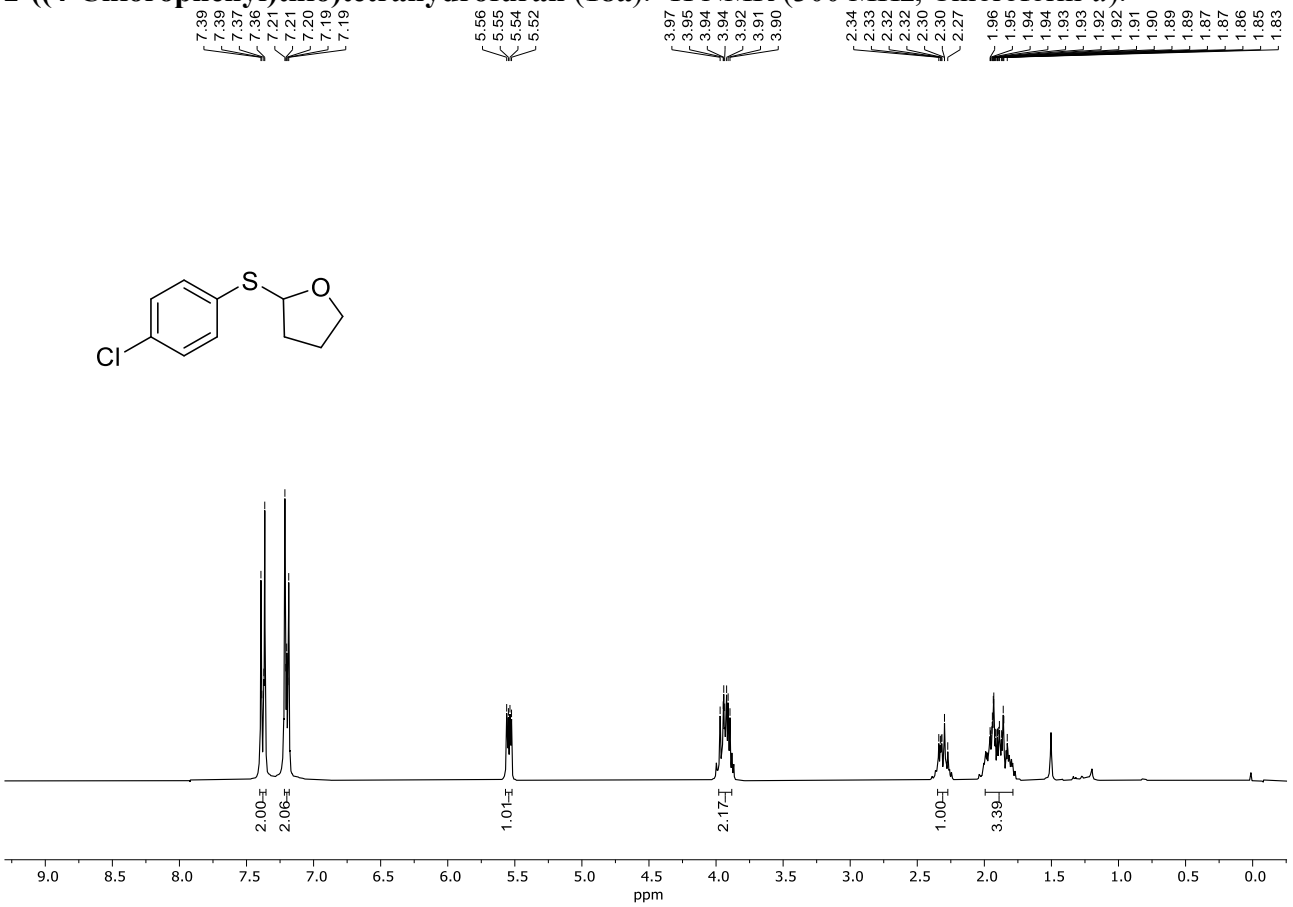
2-(Phenylthio)tetrahydrofuran (**17a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



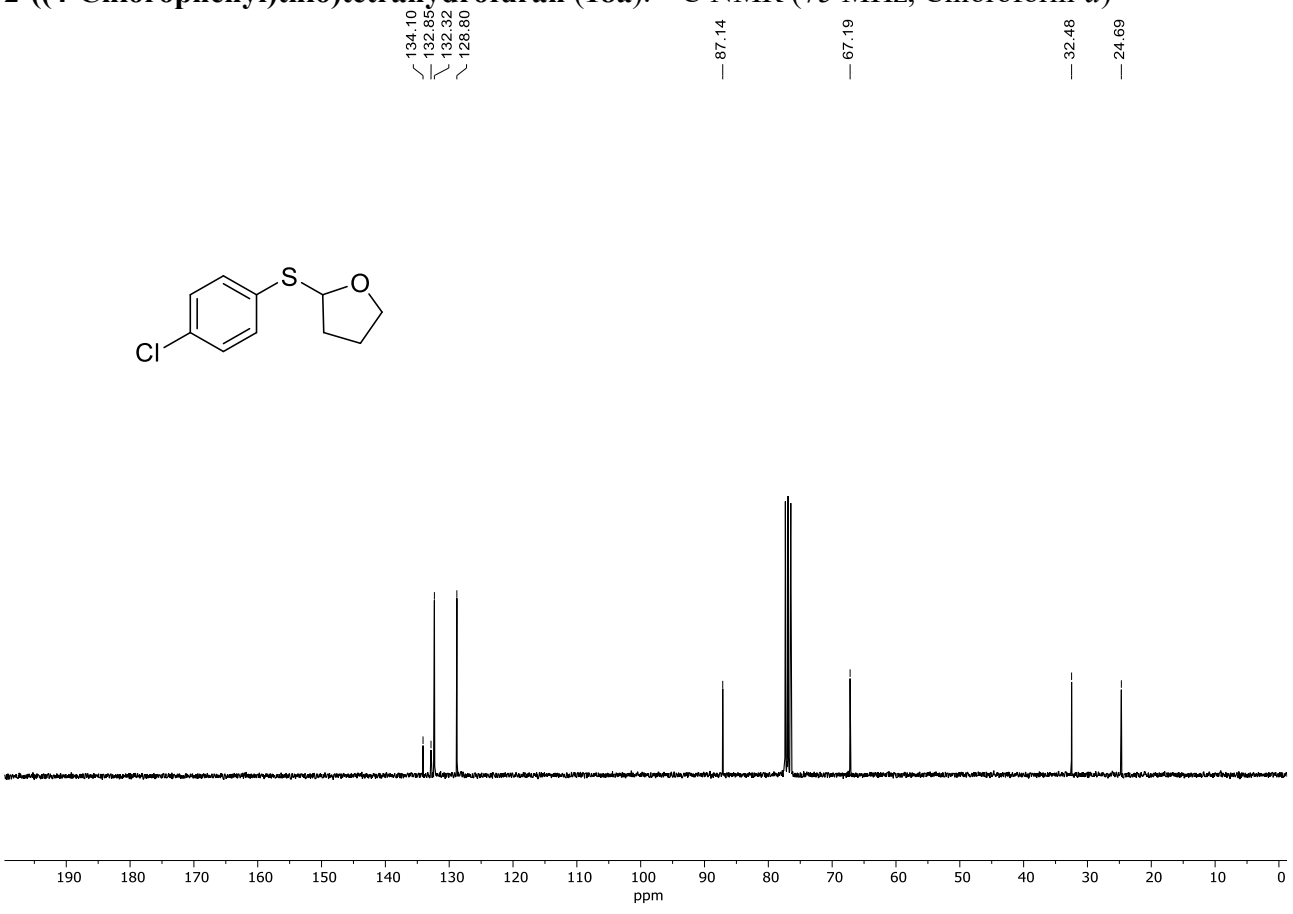
2-(Phenylthio)tetrahydrofuran (**17a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



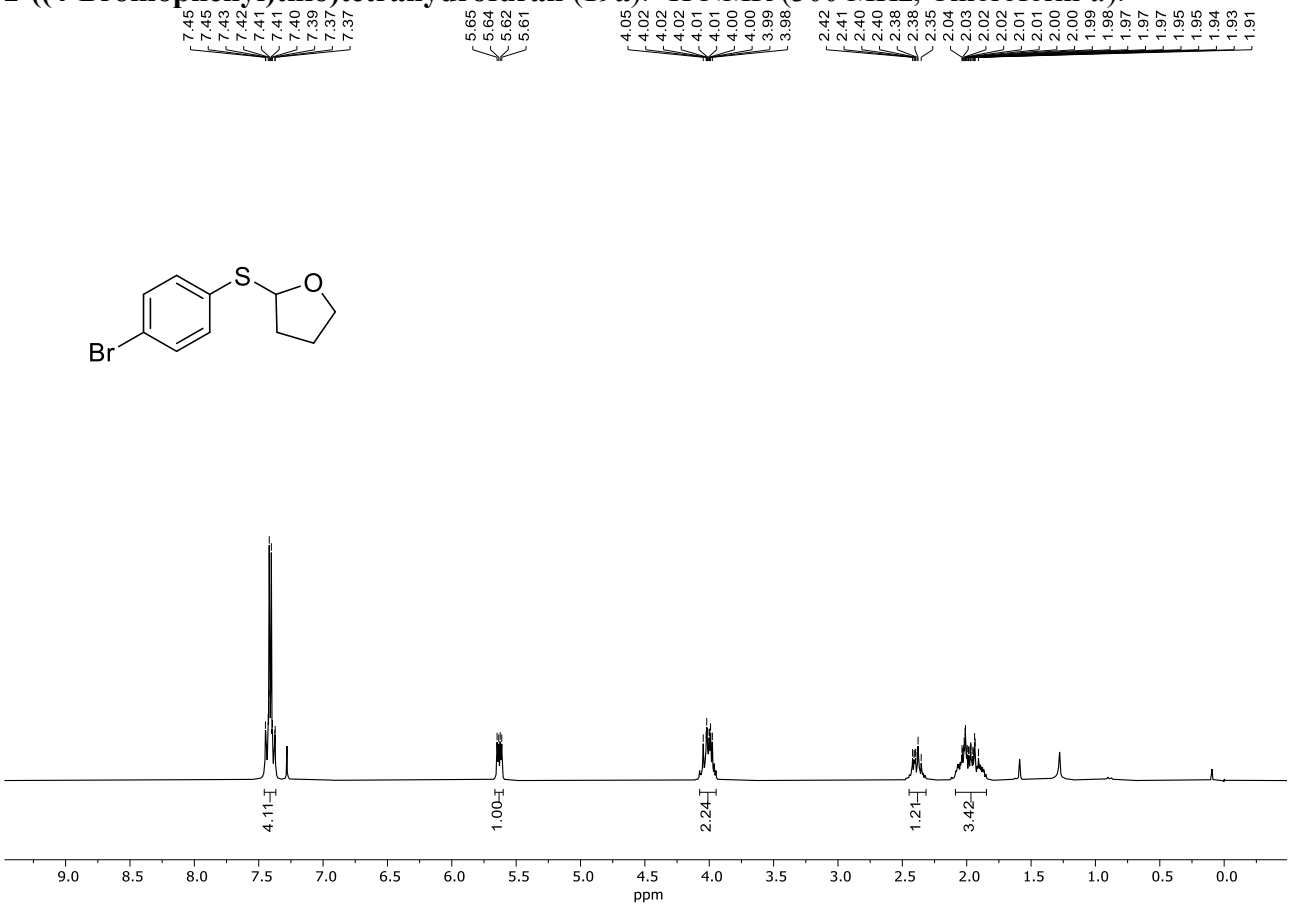
2-((4-Chlorophenyl)thio)tetrahydrofuran (**18a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



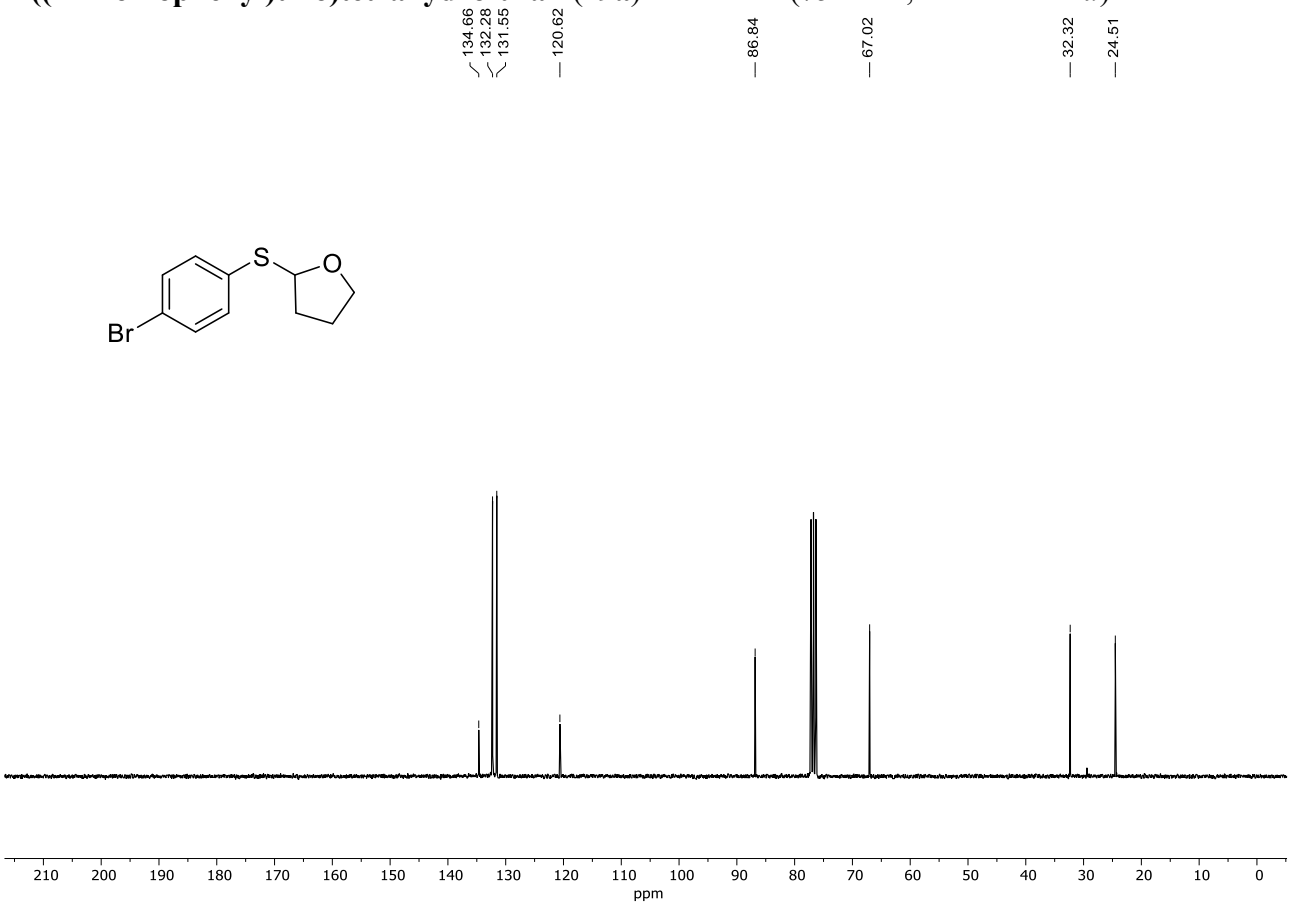
2-((4-Chlorophenyl)thio)tetrahydrofuran (**18a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



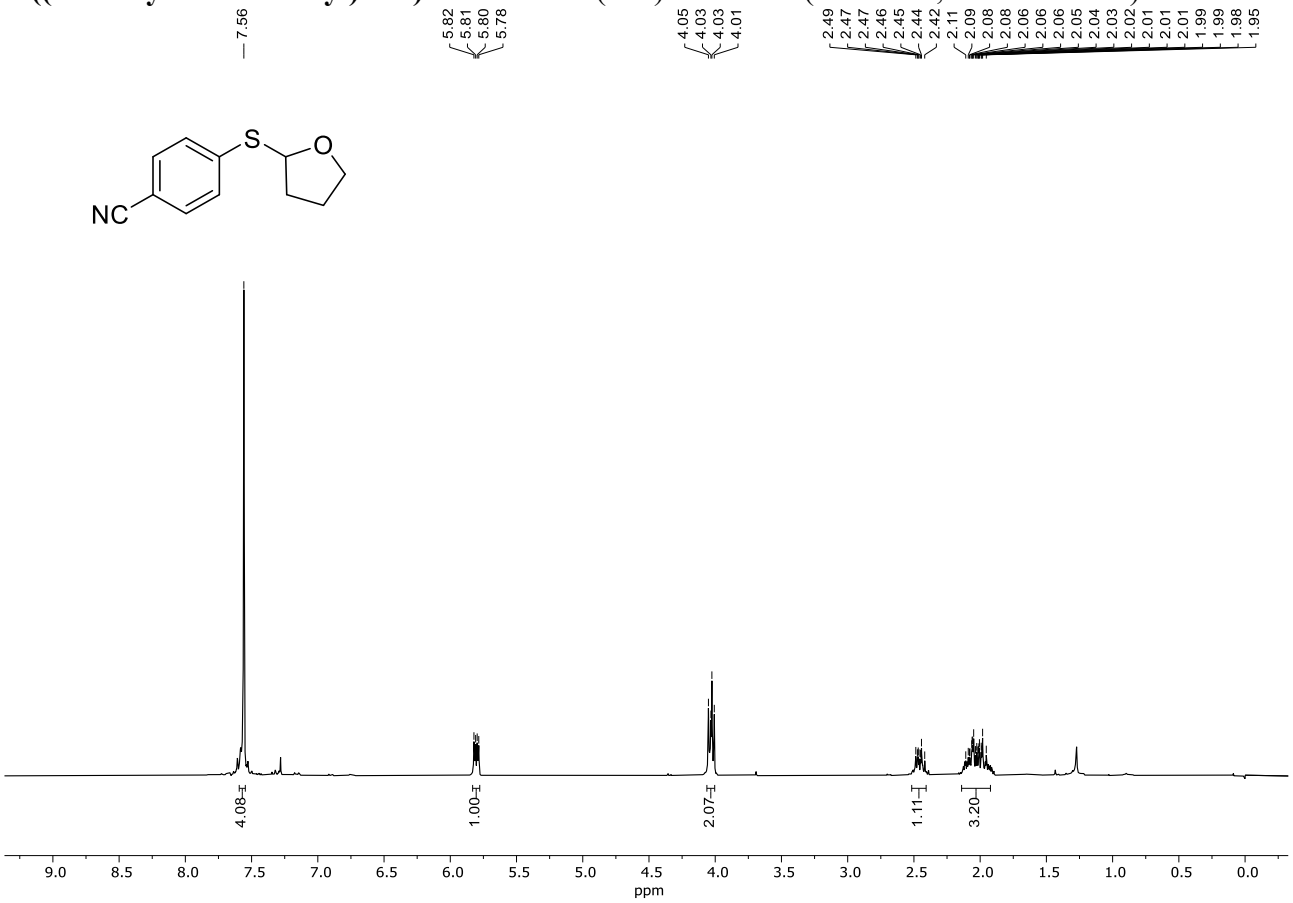
2-((4-Bromophenyl)thio)tetrahydrofuran (**19a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



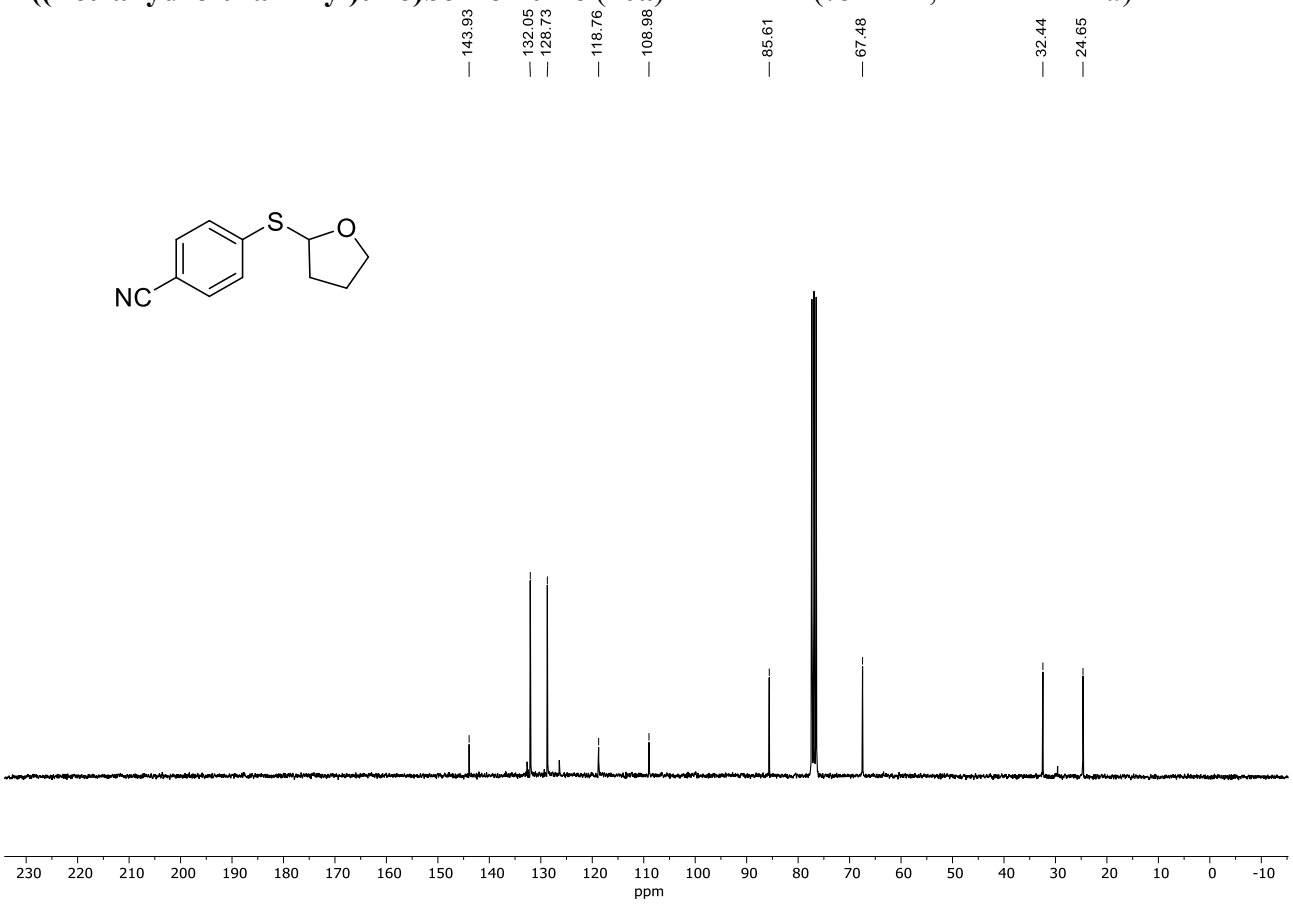
2-((4-Bromophenyl)thio)tetrahydrofuran (**19a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



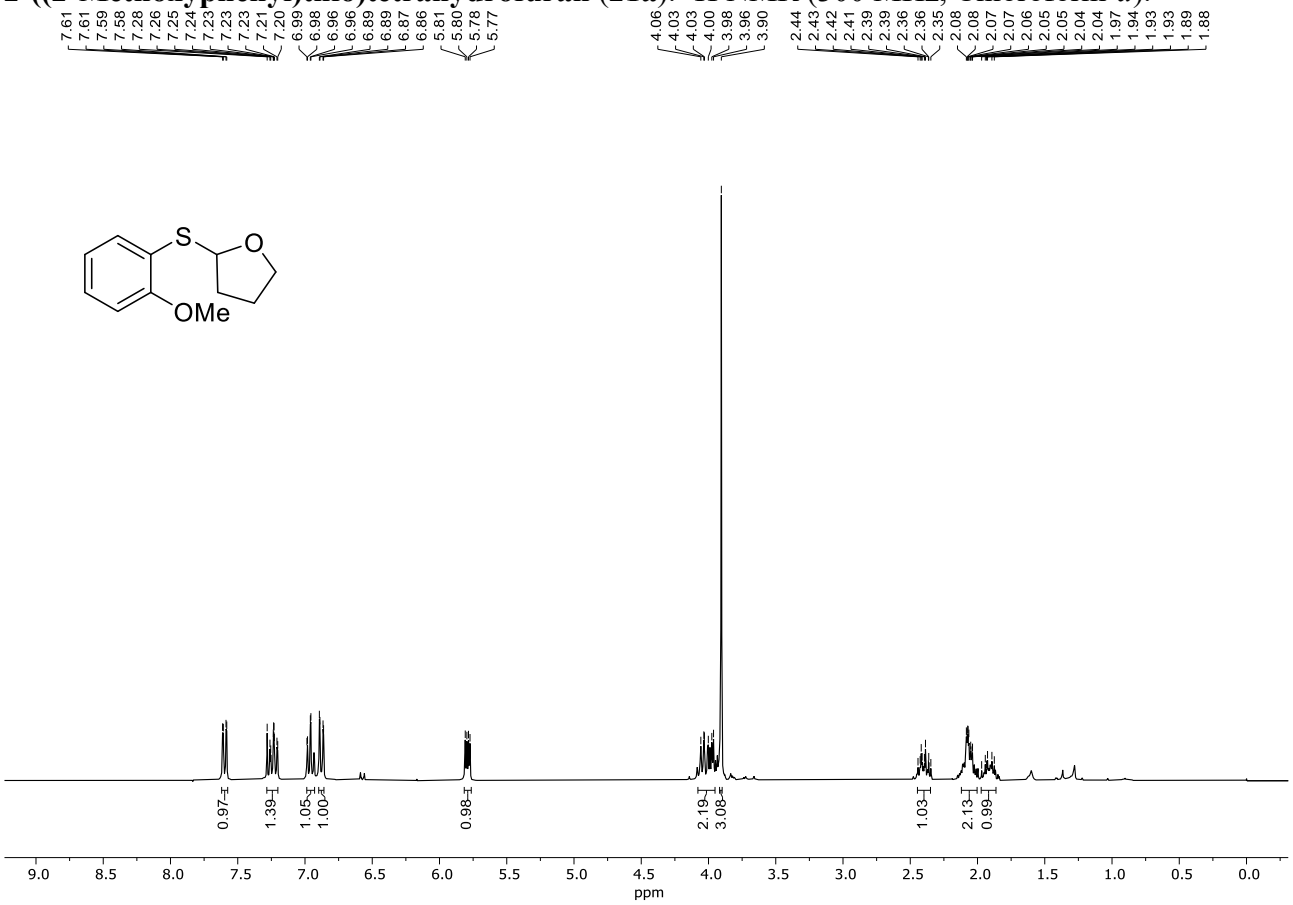
4-((Tetrahydrofuran-2-yl)thio)benzonitrile (20a). ^{1}H NMR (300 MHz, Chloroform-*d*).



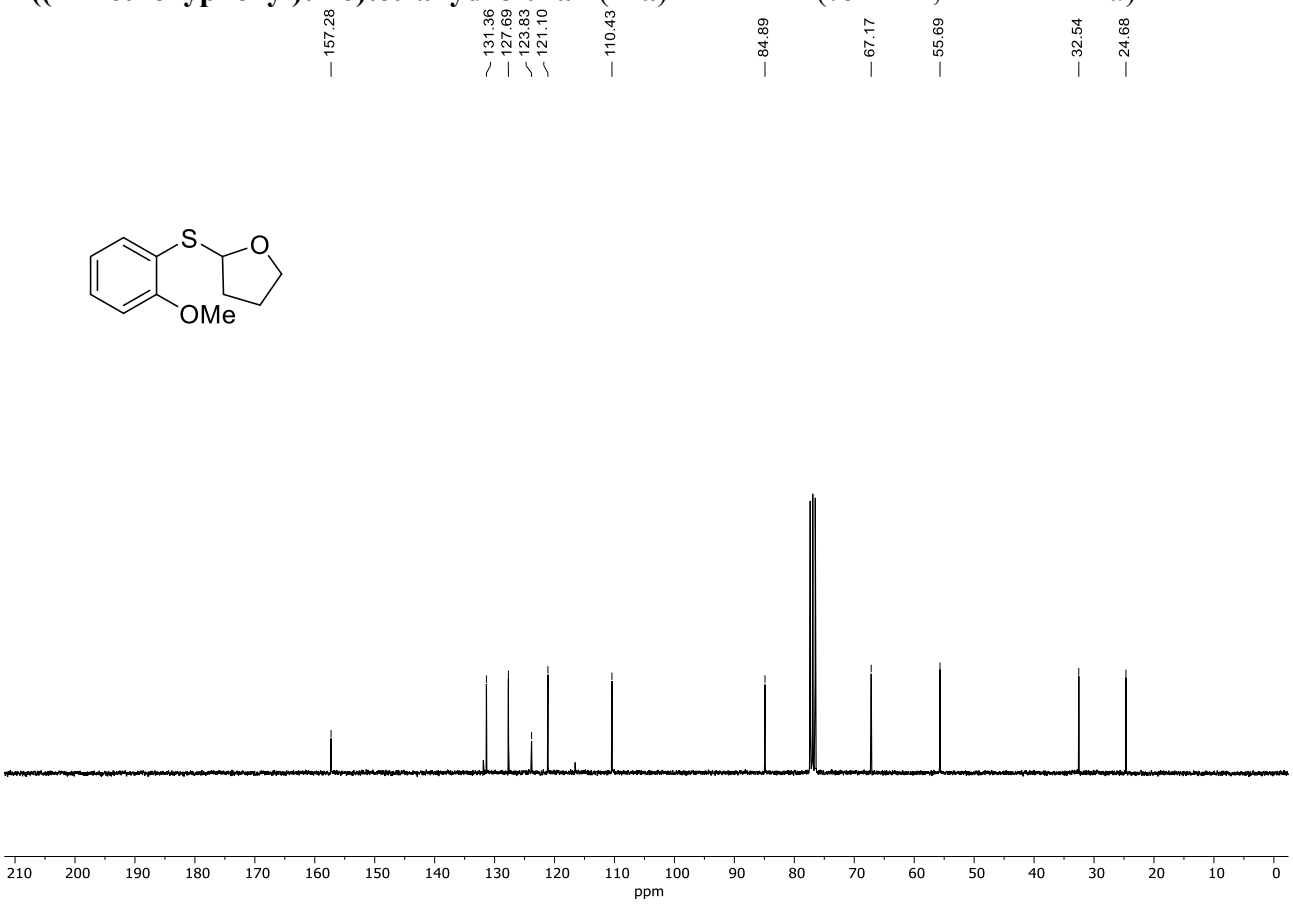
4-((Tetrahydrofuran-2-yl)thio)benzonitrile (20a). ^{13}C NMR (75 MHz, Chloroform-*d*)



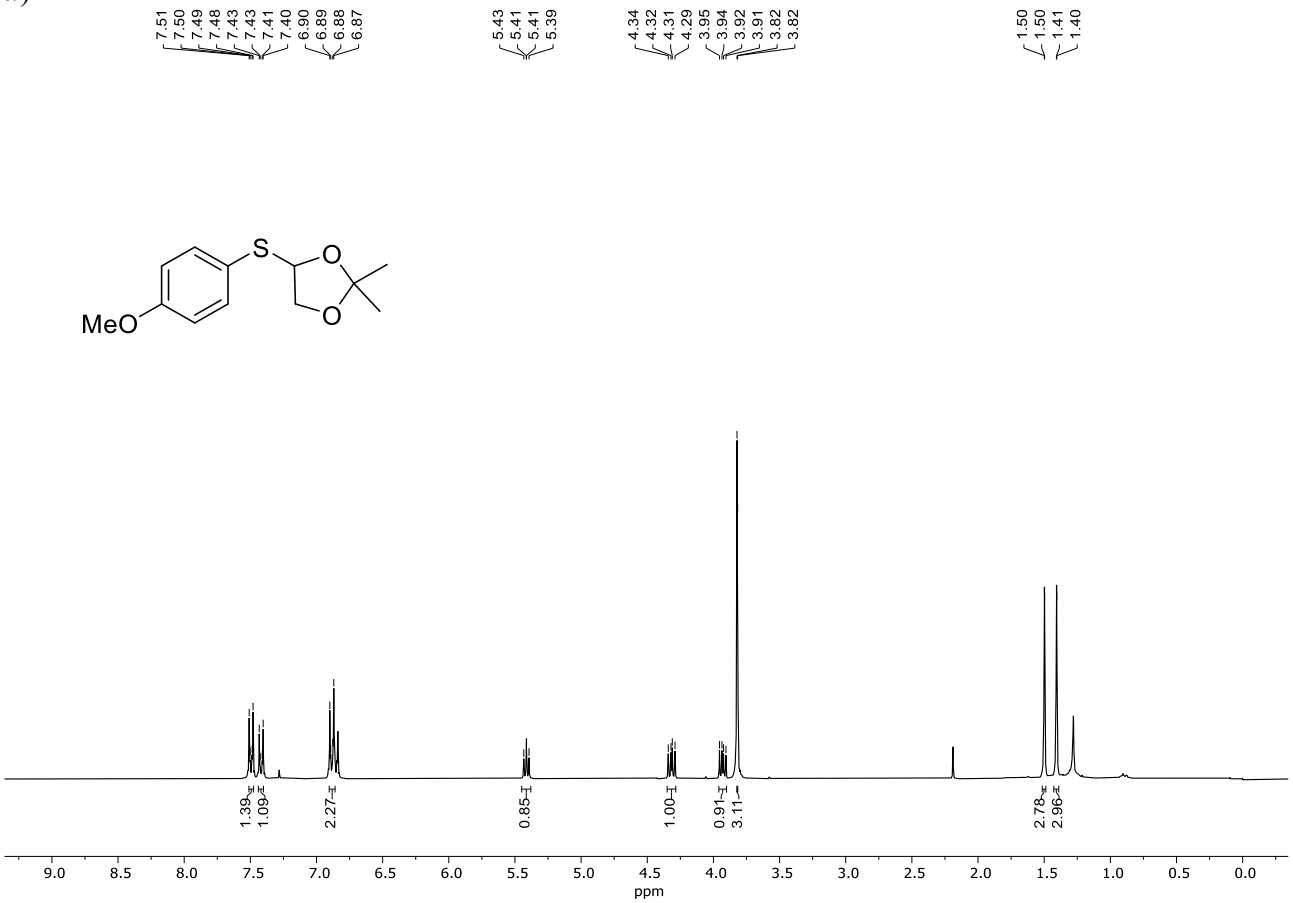
2-((2-Methoxyphenyl)thio)tetrahydrofuran (**21a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



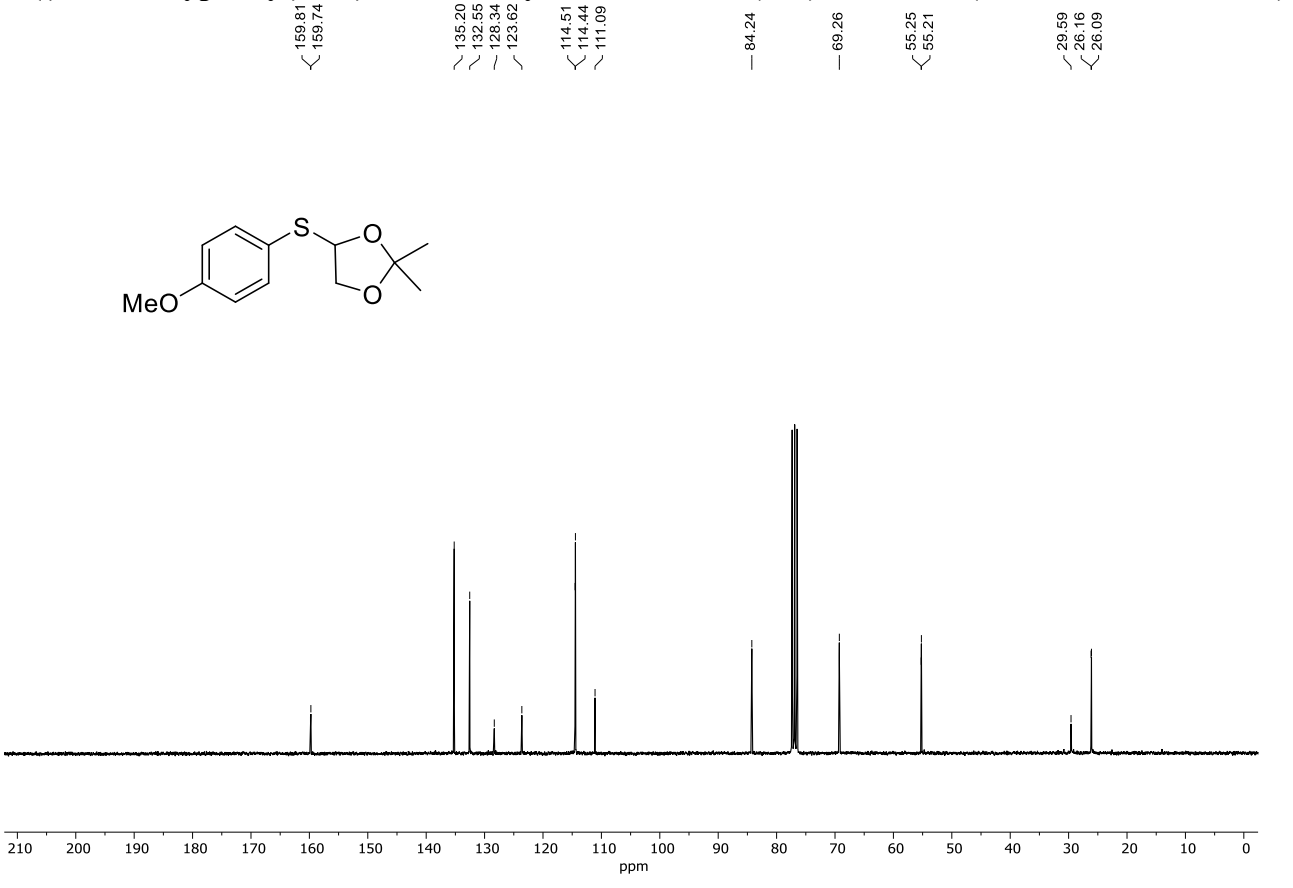
2-((2-Methoxyphenyl)thio)tetrahydrofuran (**21a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



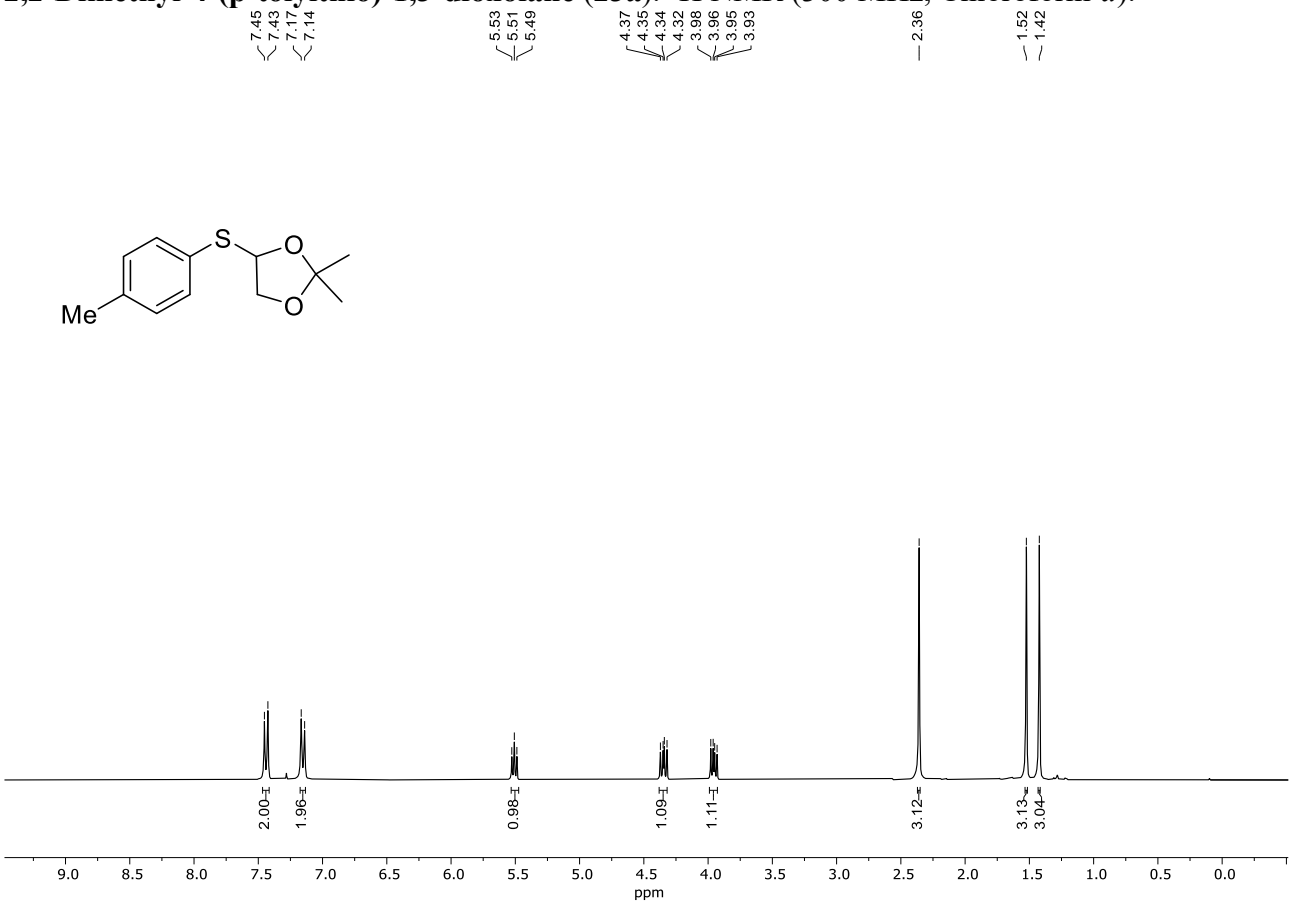
4-((4-Methoxyphenyl)thio)-2,2-dimethyl-1,3-dioxolane (**22a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



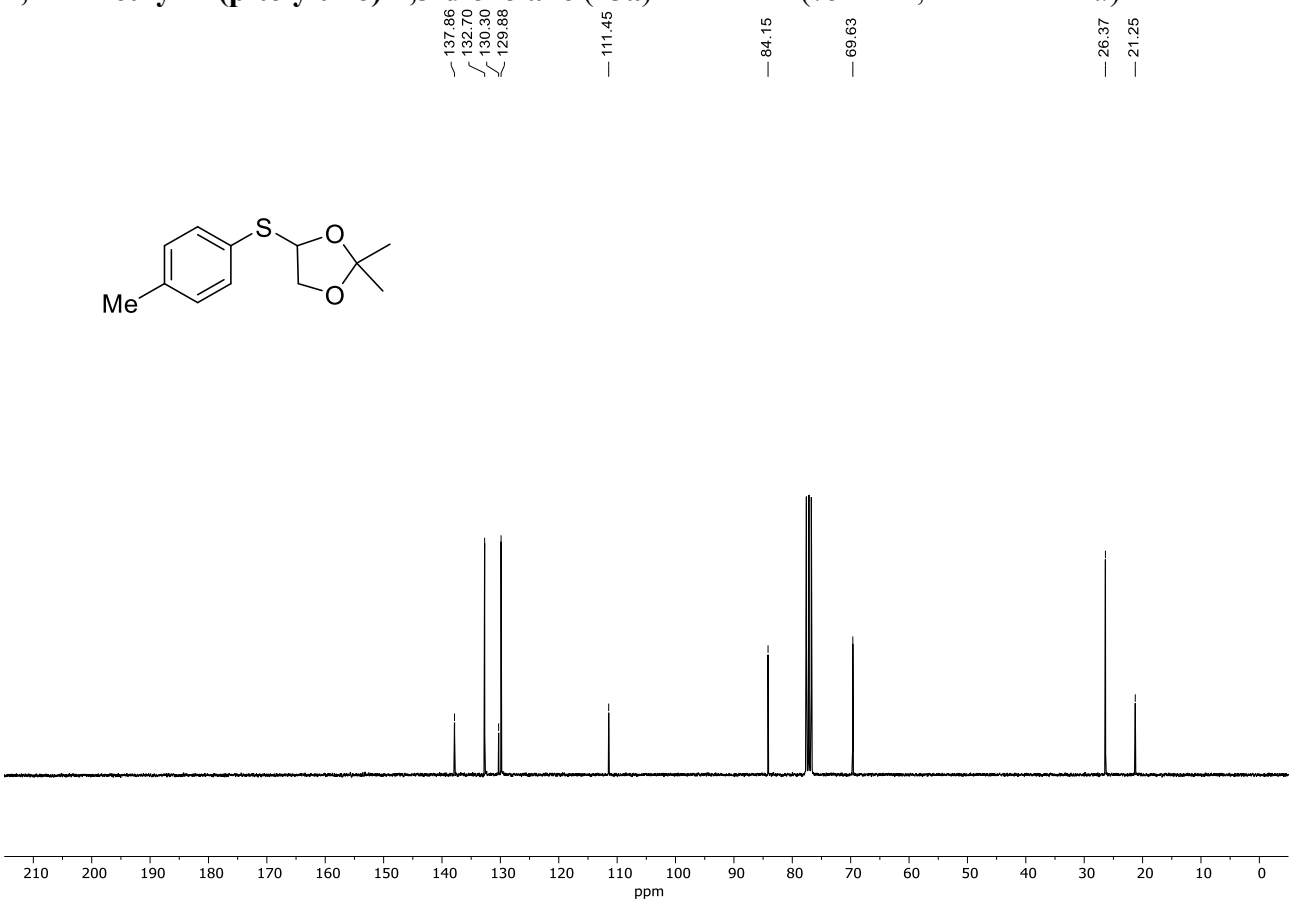
4-((4-Methoxyphenyl)thio)-2,2-dimethyl-1,3-dioxolane (**22a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



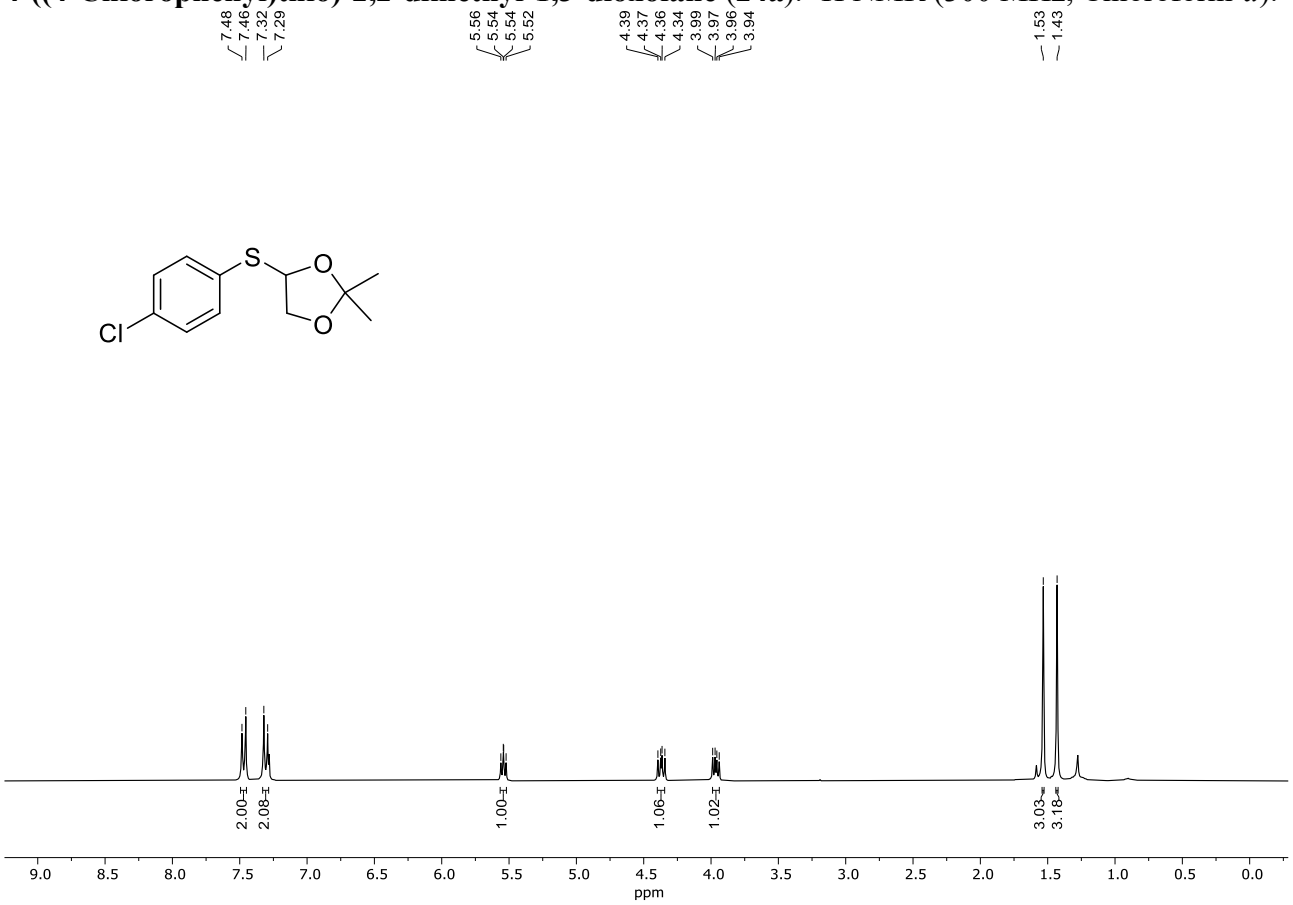
2,2-Dimethyl-4-(p-tolylthio)-1,3-dioxolane (**23a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



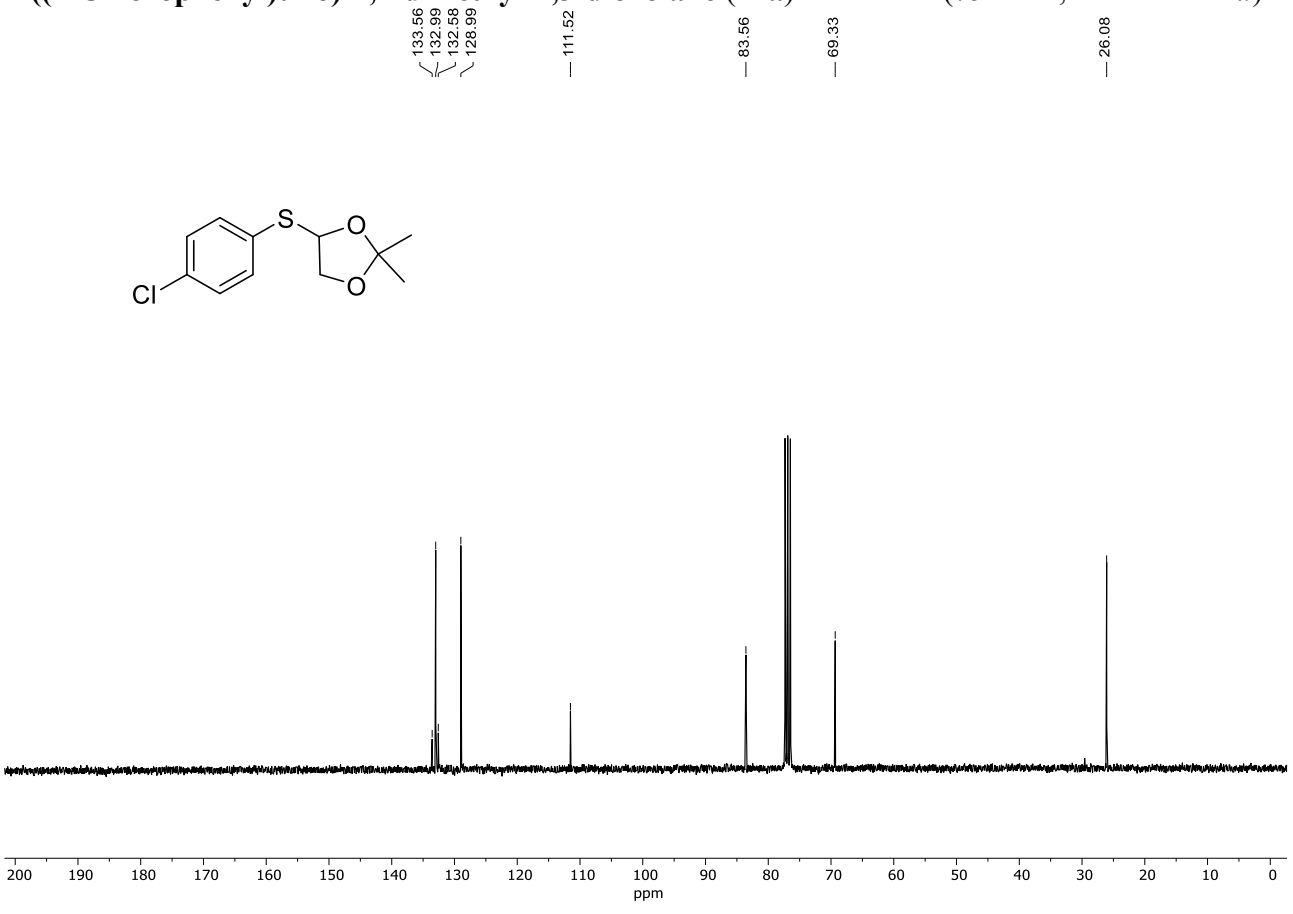
2,2-Dimethyl-4-(p-tolylthio)-1,3-dioxolane (**23a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



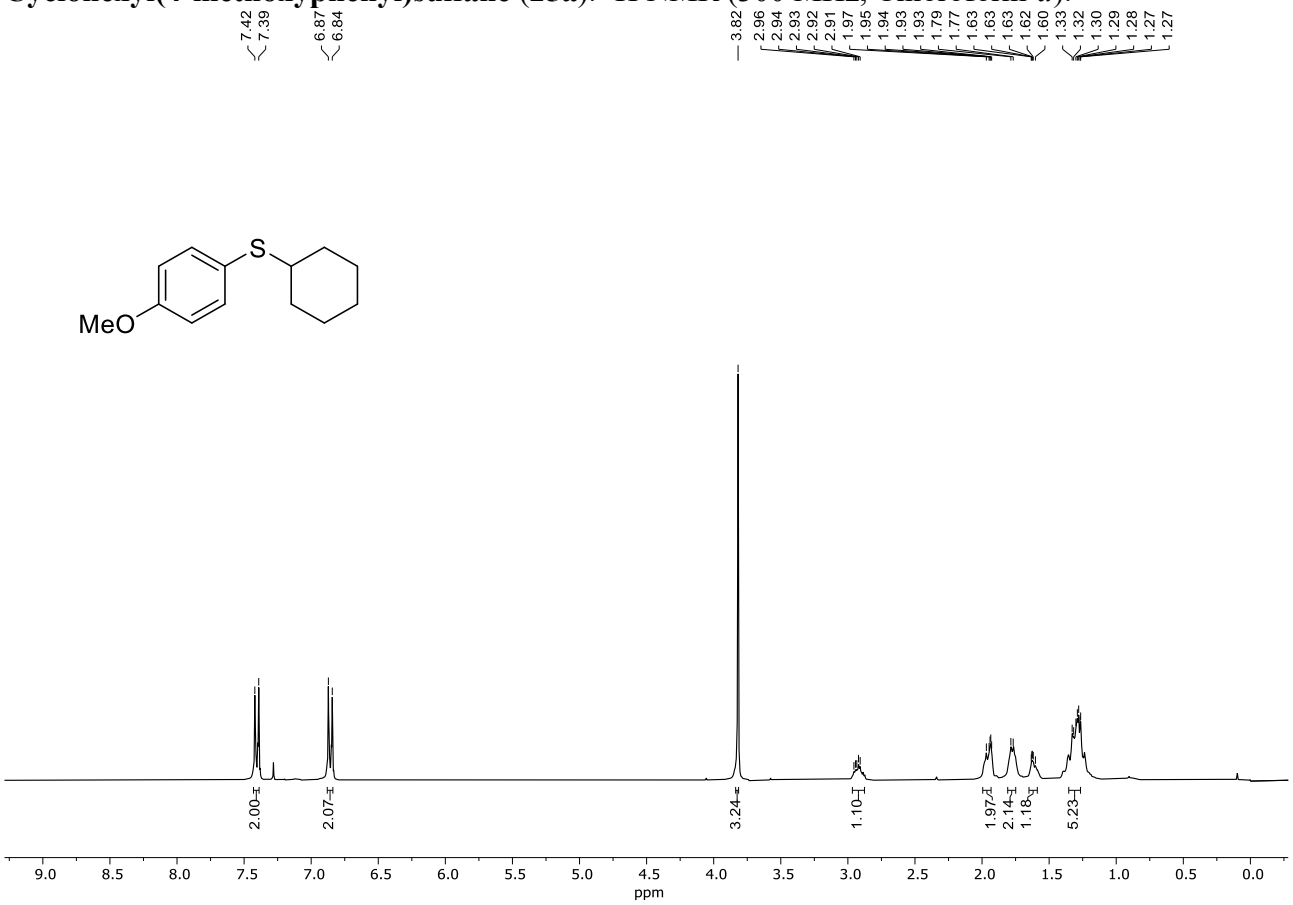
4-((4-Chlorophenyl)thio)-2,2-dimethyl-1,3-dioxolane (**24a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



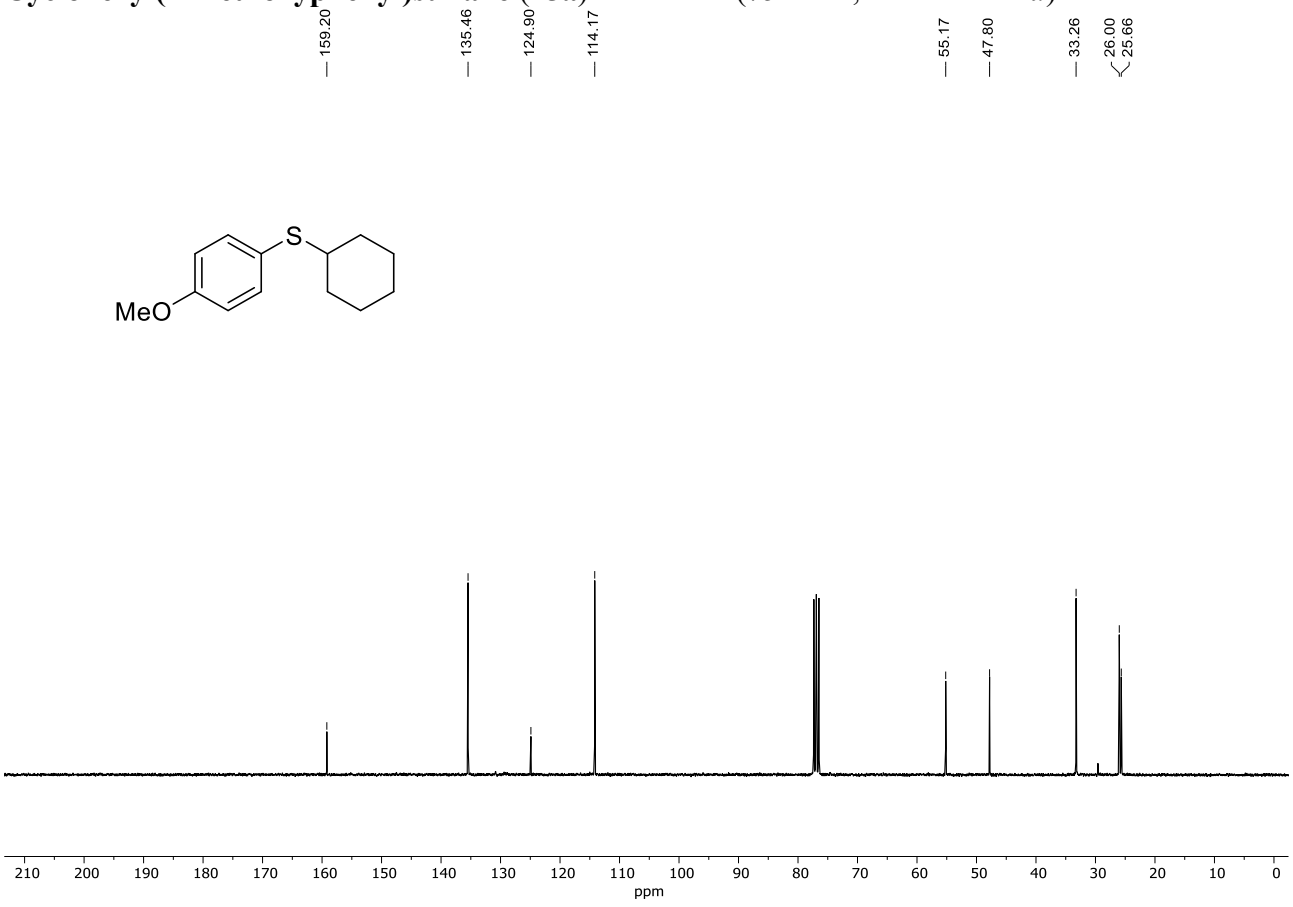
4-((4-Chlorophenyl)thio)-2,2-dimethyl-1,3-dioxolane (**24a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



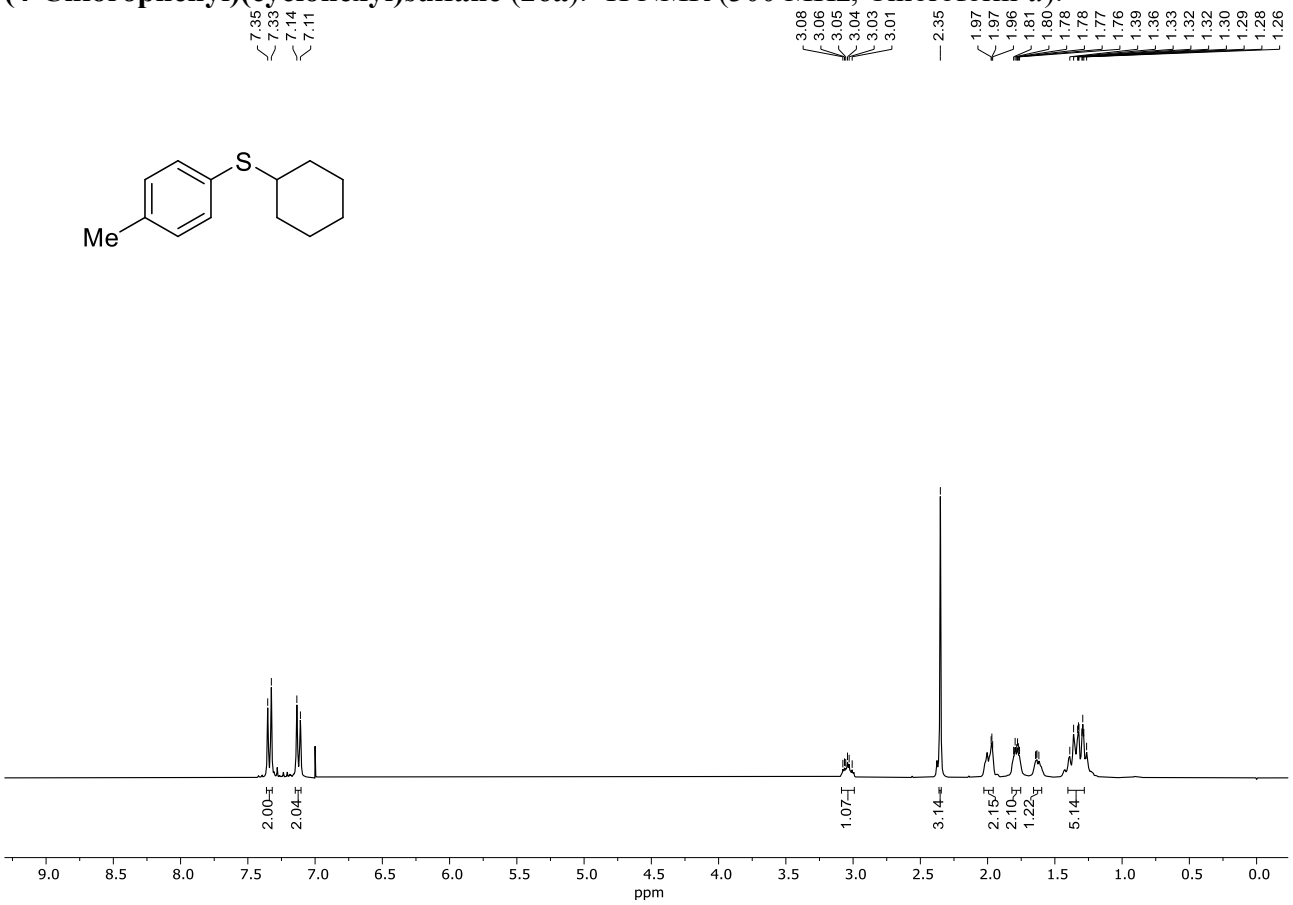
Cyclohexyl(4-methoxyphenyl)sulfane (**25a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



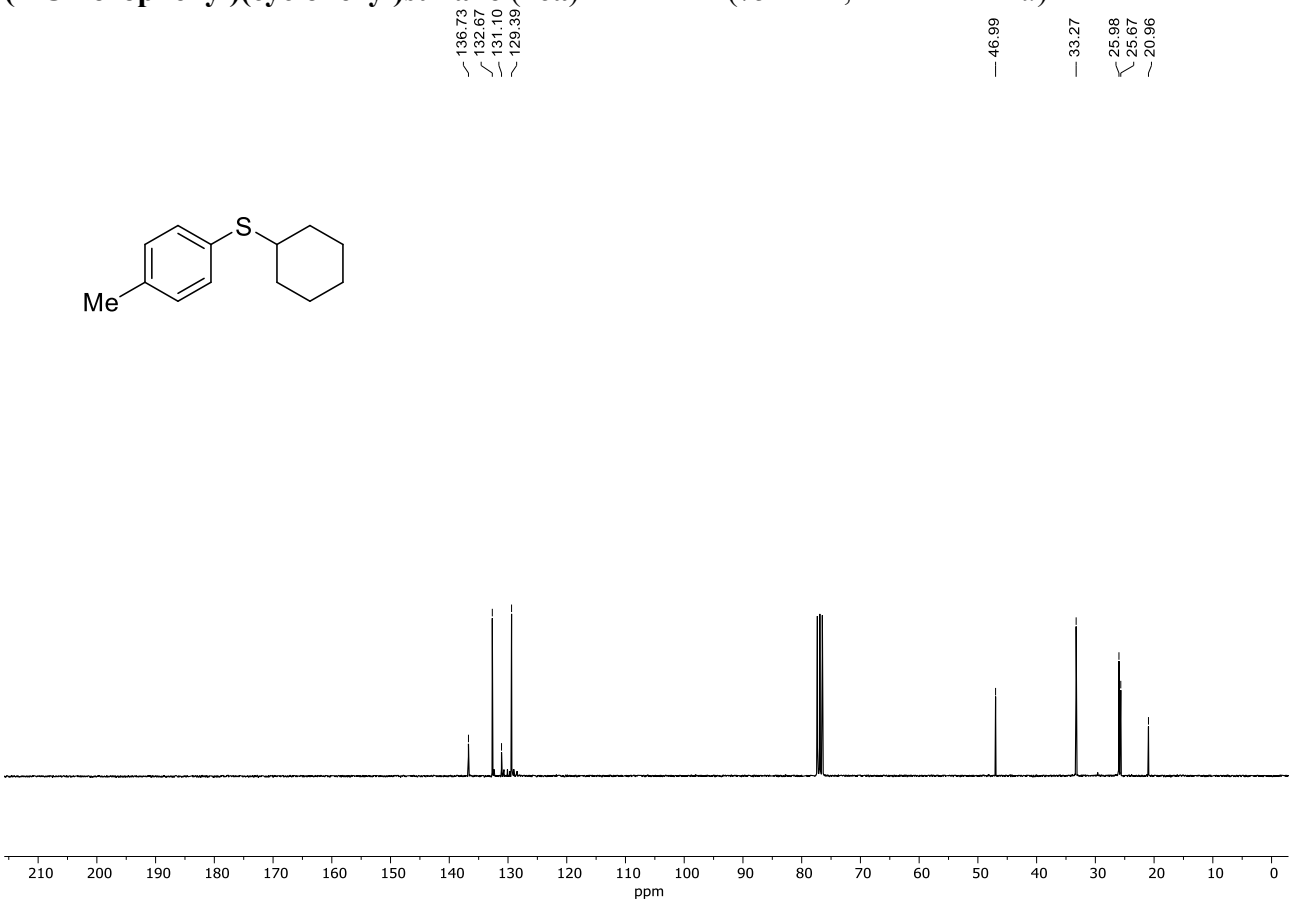
Cyclohexyl(4-methoxyphenyl)sulfane (**25a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



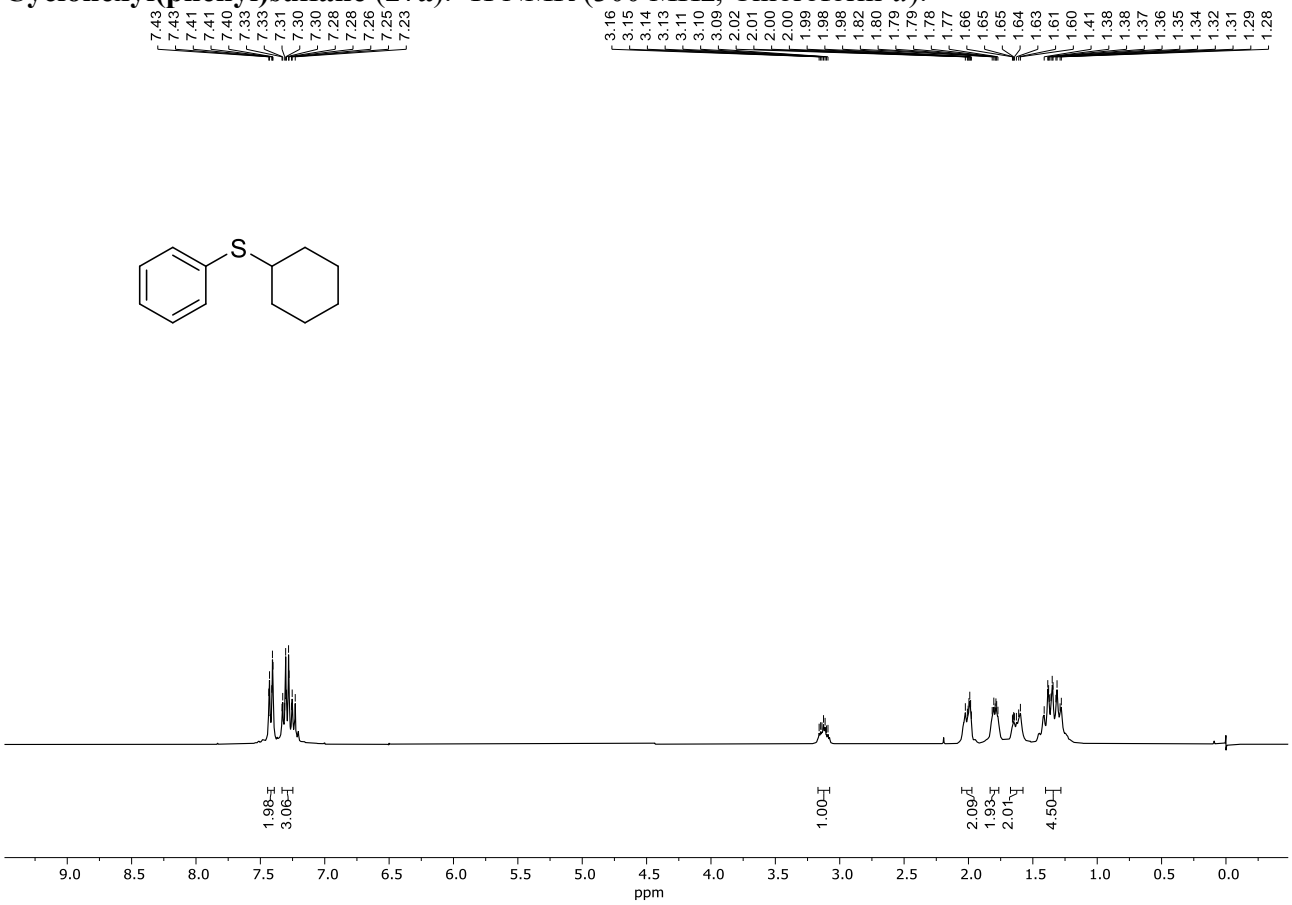
(4-Chlorophenyl)(cyclohexyl)sulfane (**26a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



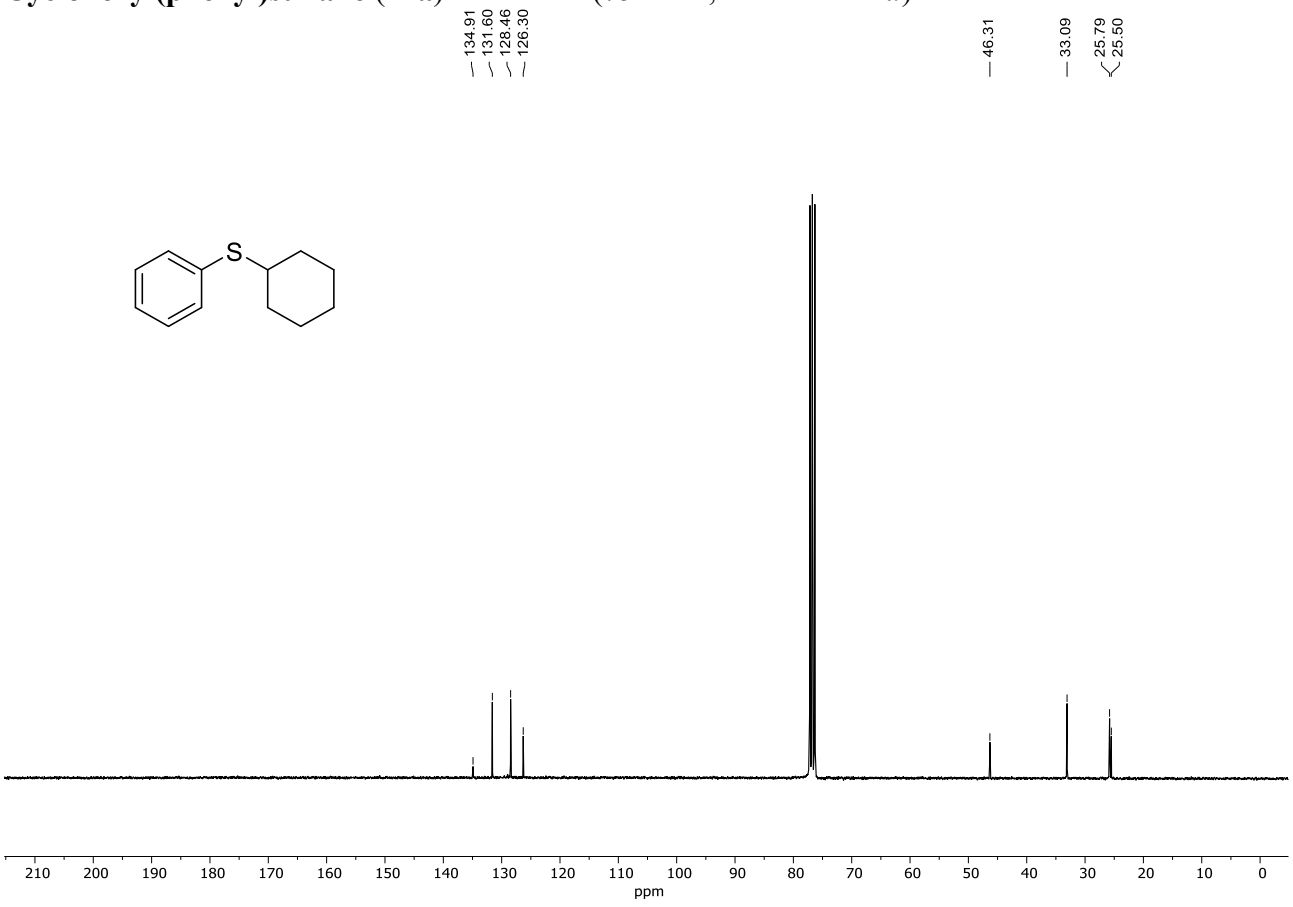
(4-Chlorophenyl)(cyclohexyl)sulfane (**26a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



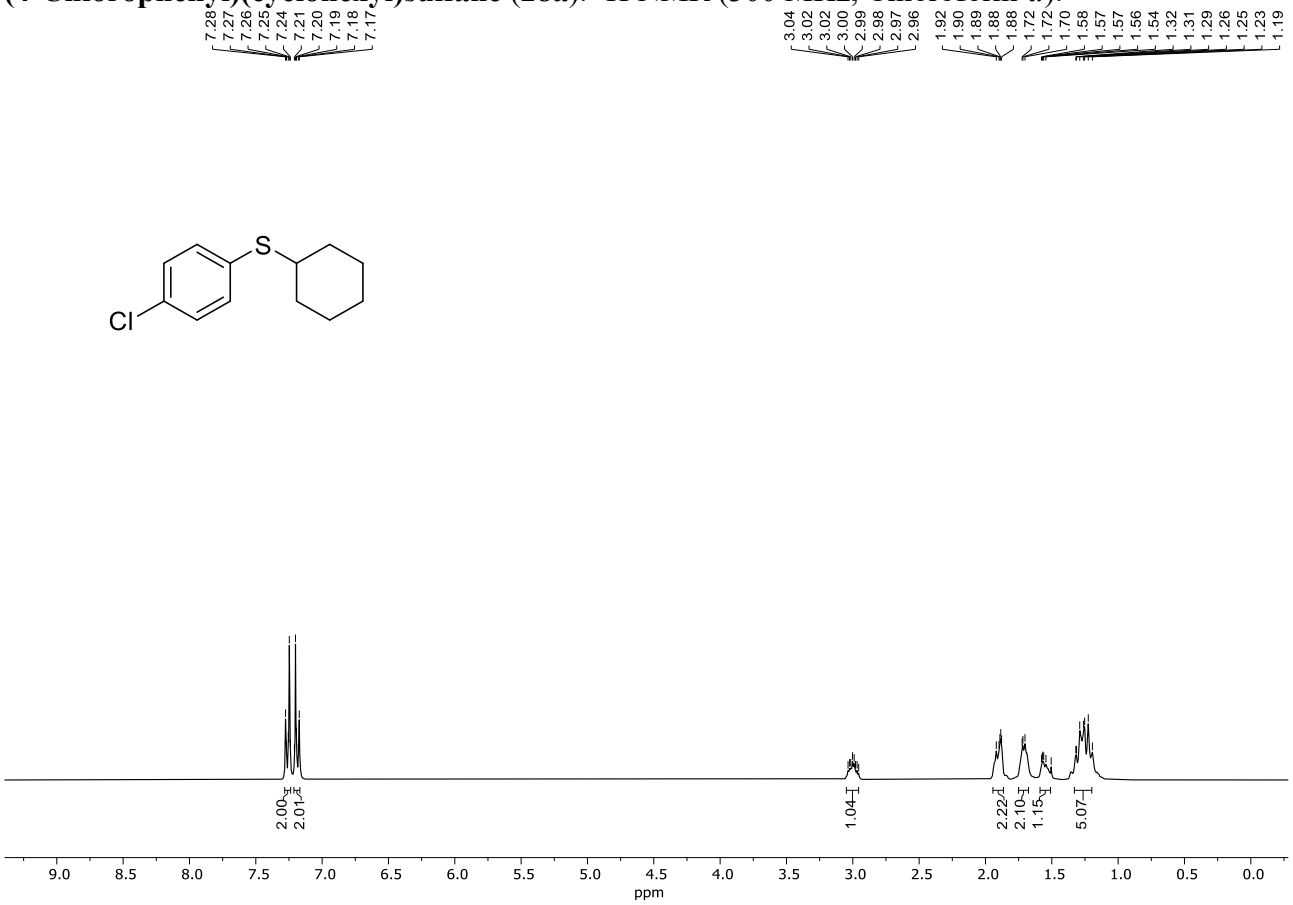
Cyclohexyl(phenyl)sulfane (**27a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



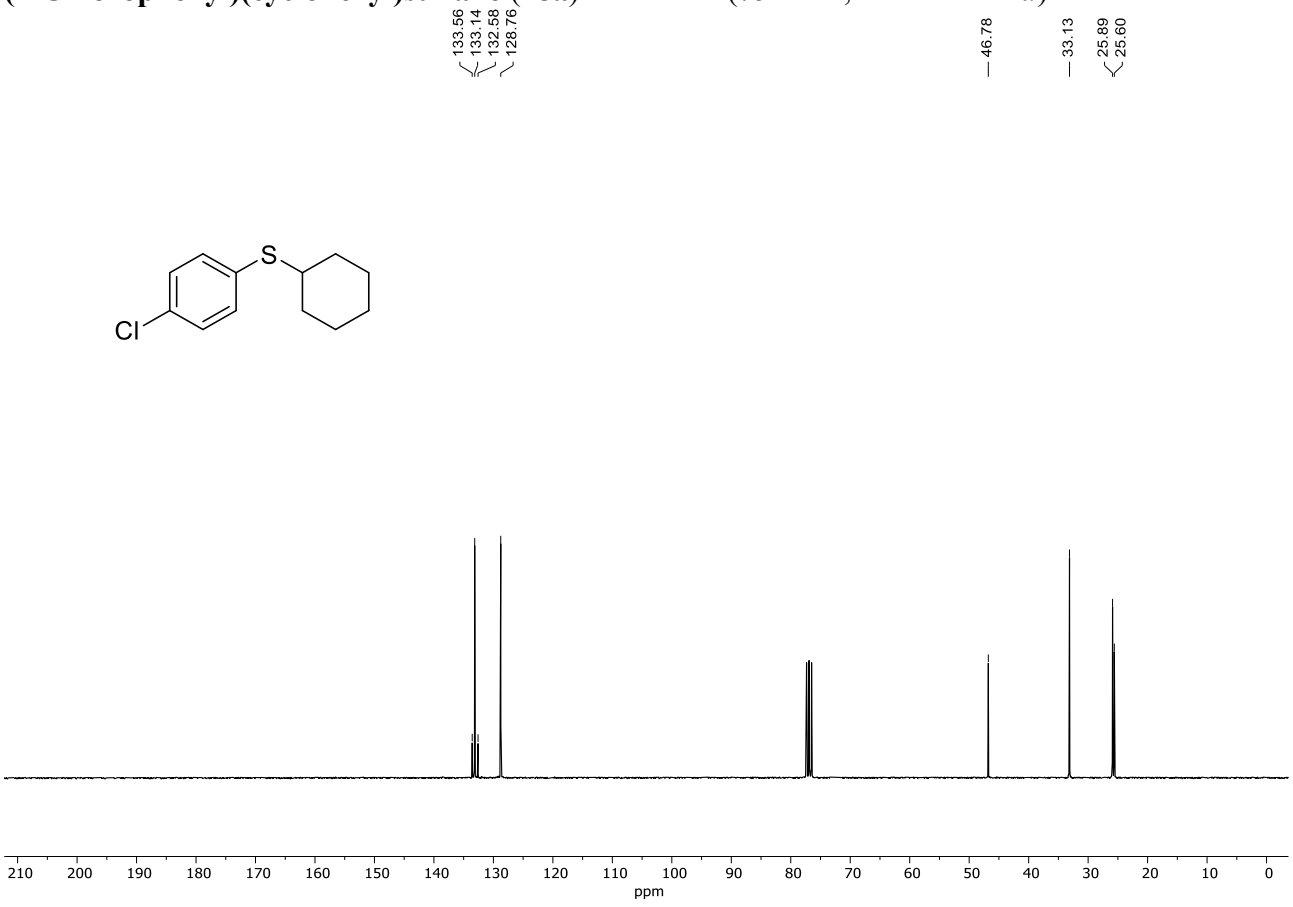
Cyclohexyl(phenyl)sulfane (**27a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



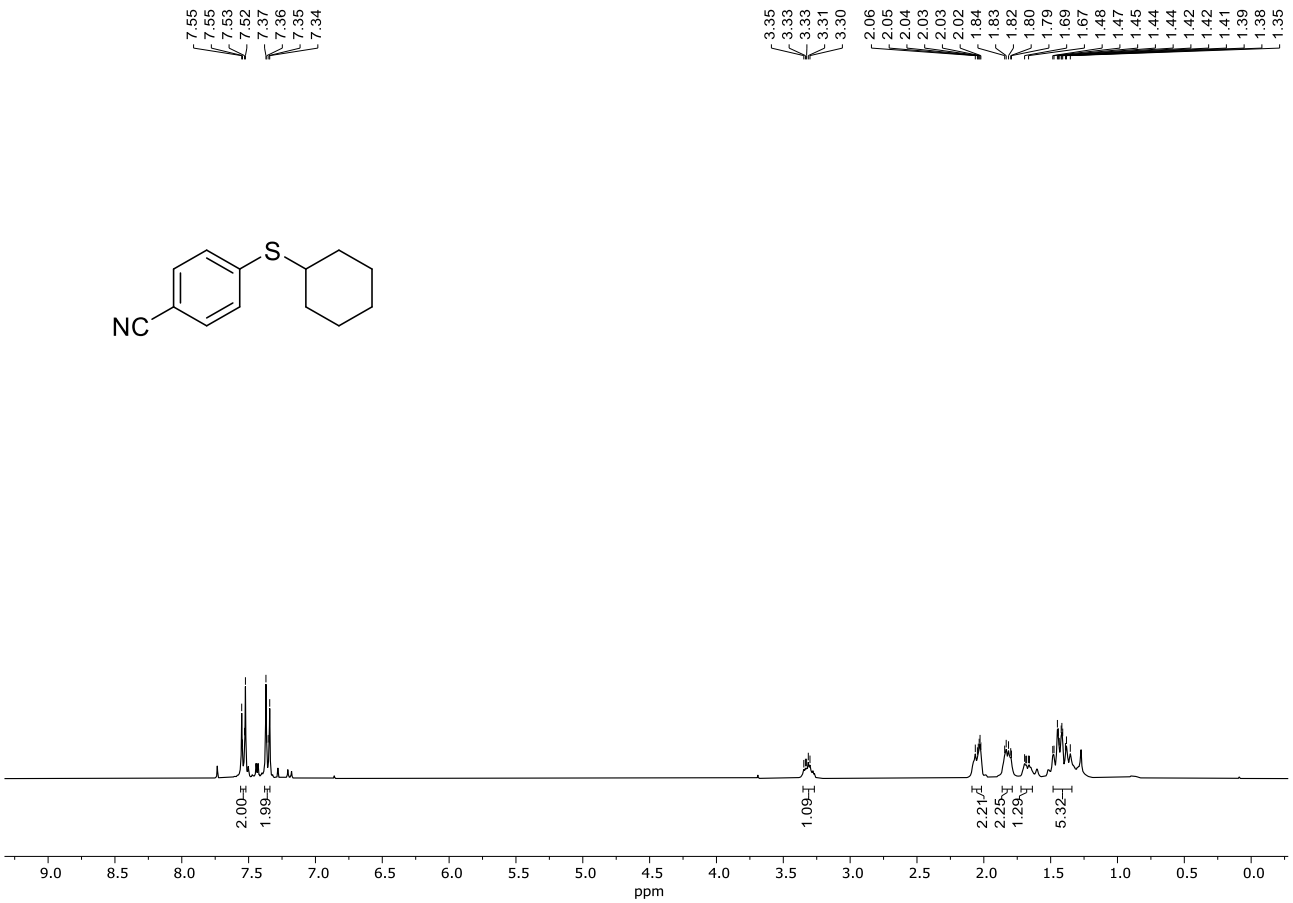
(4-Chlorophenyl)(cyclohexyl)sulfane (**28a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



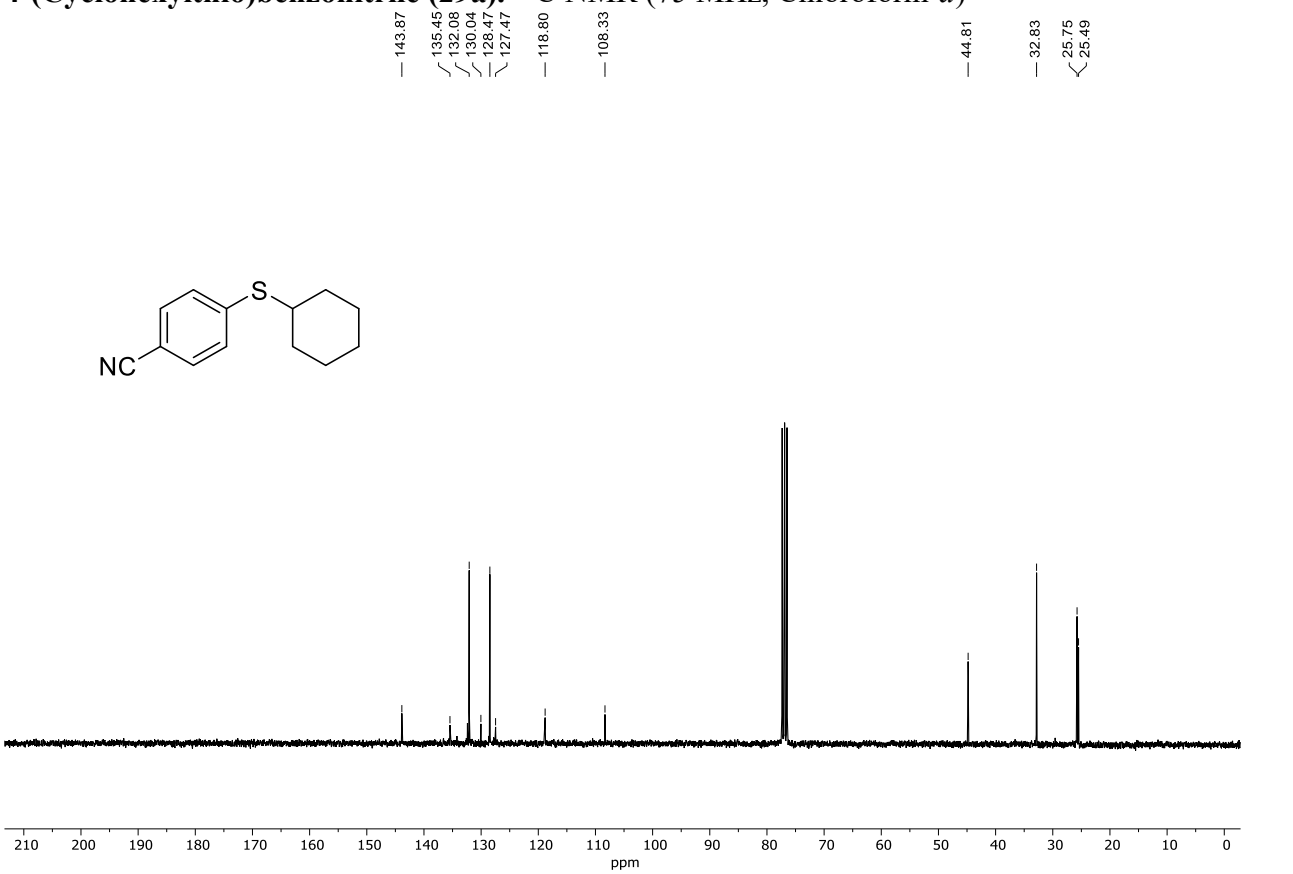
(4-Chlorophenyl)(cyclohexyl)sulfane (**28a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



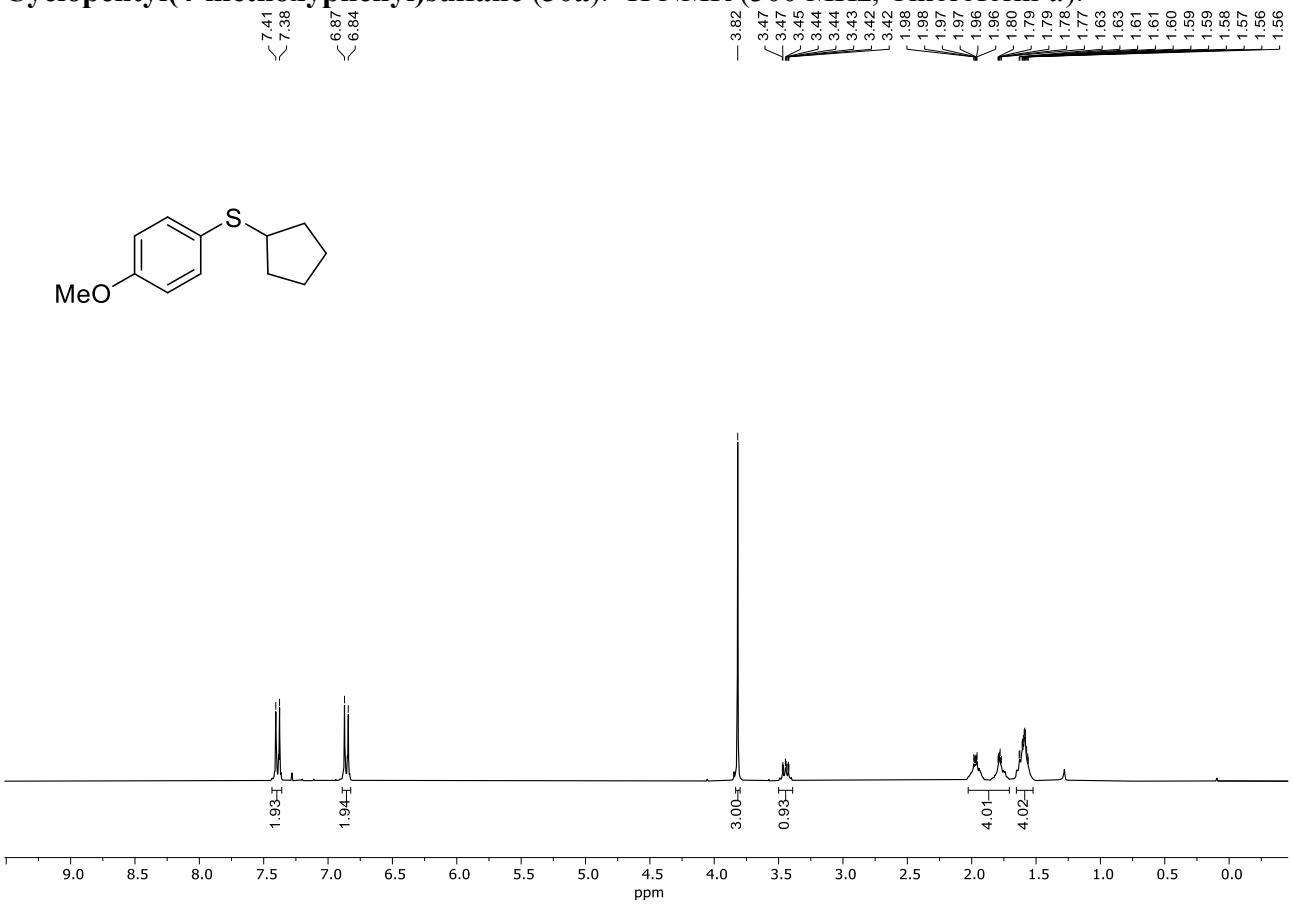
4-(Cyclohexylthio)benzonitrile (29a). ^{1}H NMR (300 MHz, Chloroform-*d*).



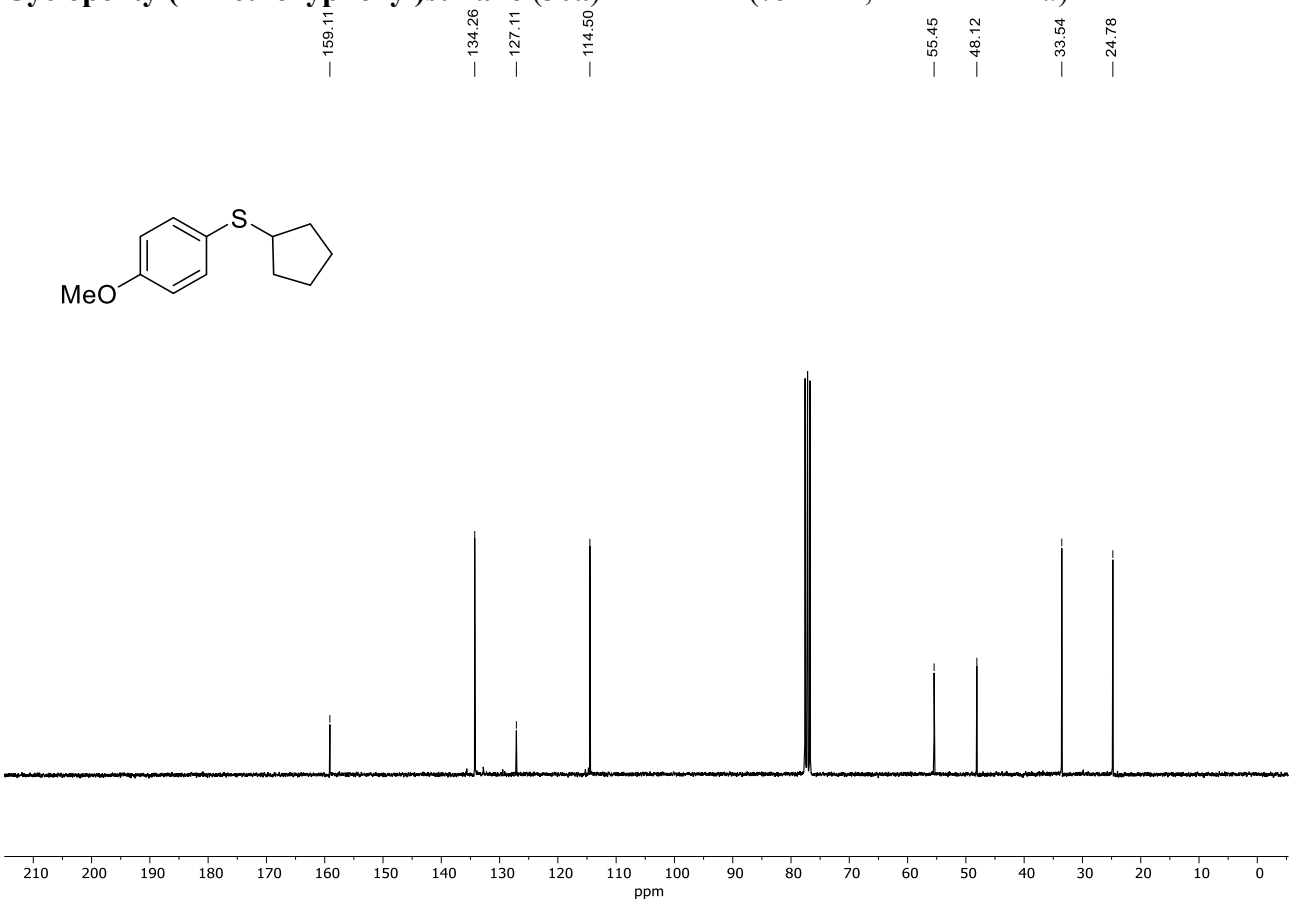
4-(Cyclohexylthio)benzonitrile (29a). ^{13}C NMR (75 MHz, Chloroform-*d*)



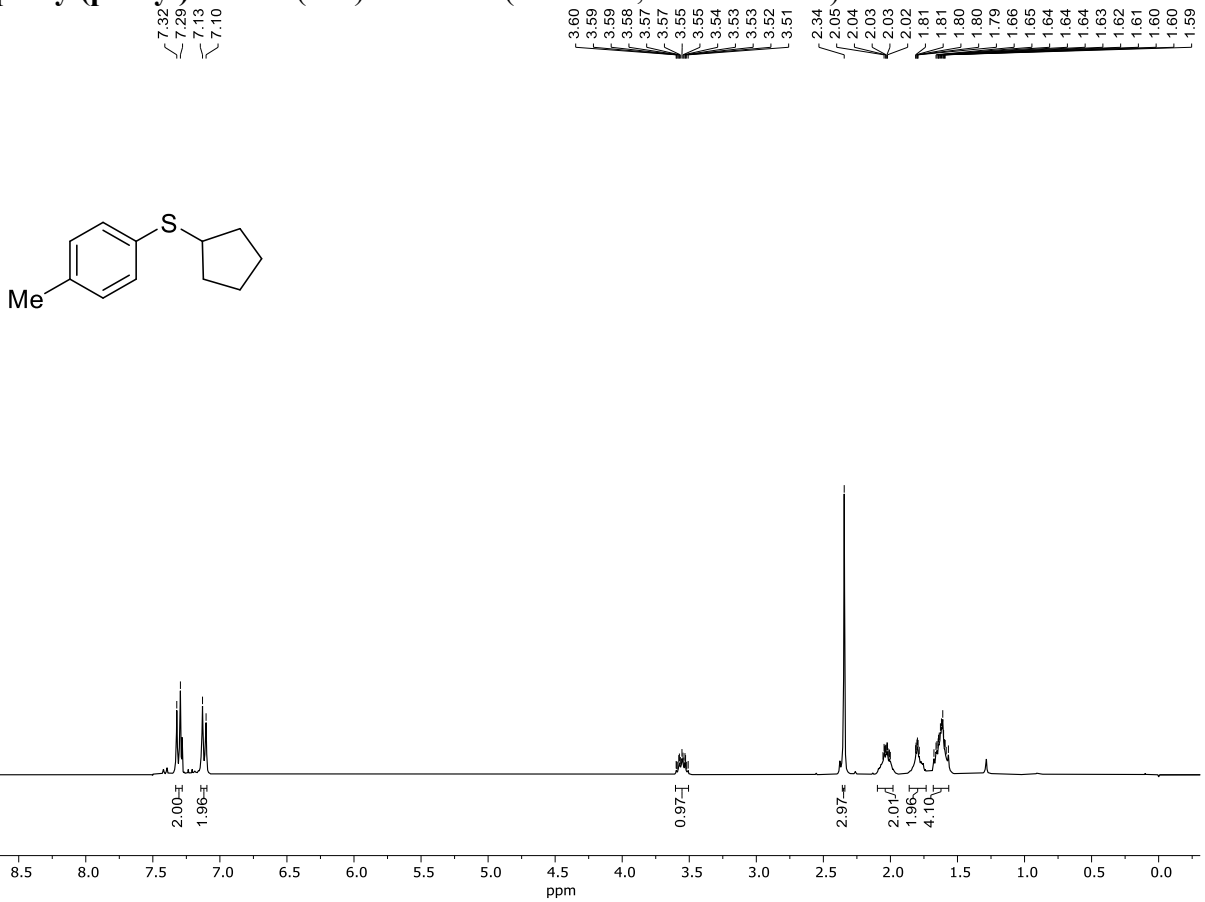
Cyclopentyl(4-methoxyphenyl)sulfane (**30a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



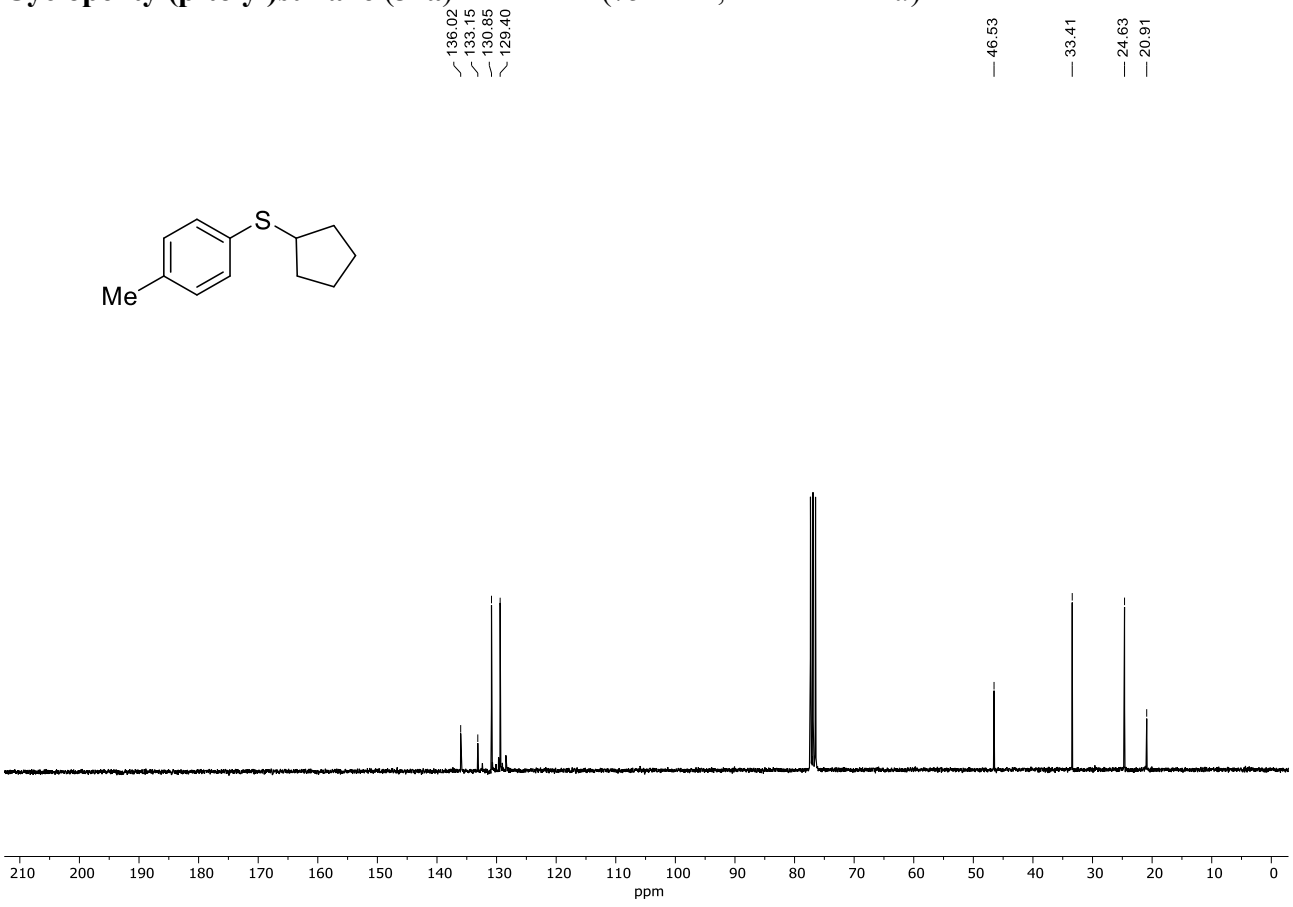
Cyclopentyl(4-methoxyphenyl)sulfane (**30a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



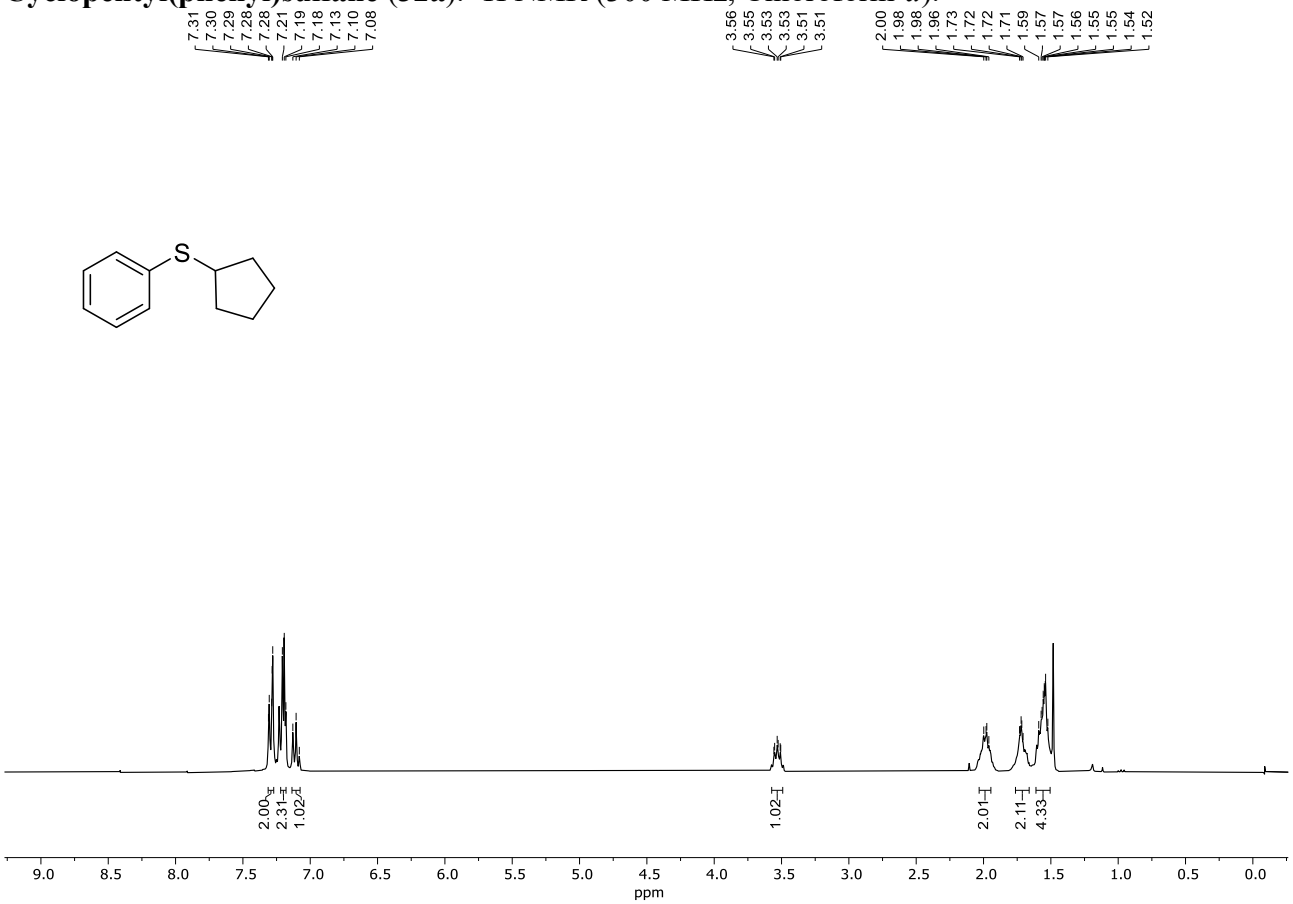
Cyclopentyl(p-tolyl)sulfane (**31a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



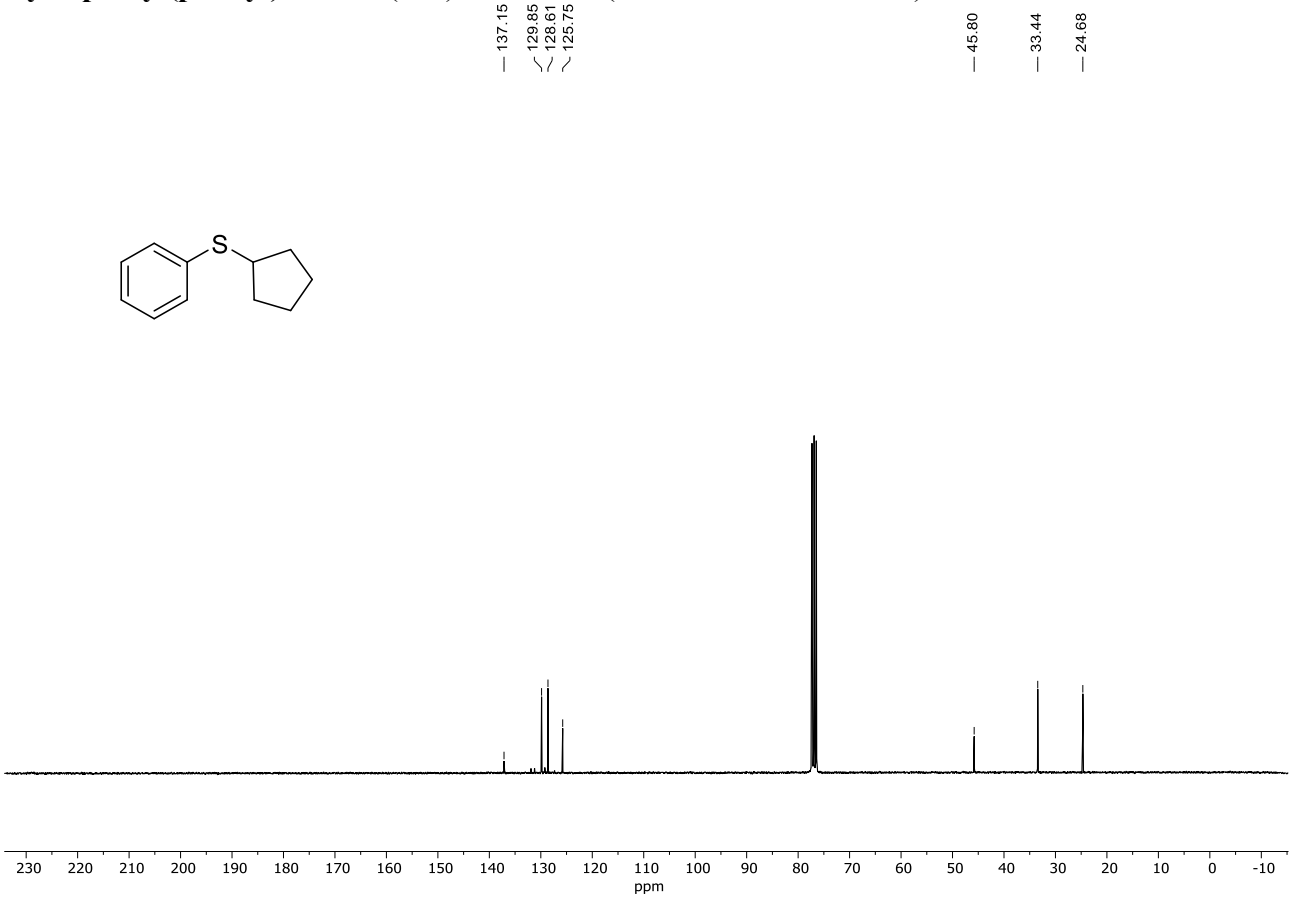
Cyclopentyl(p-tolyl)sulfane (**31a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



Cyclopentyl(phenyl)sulfane (**32a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

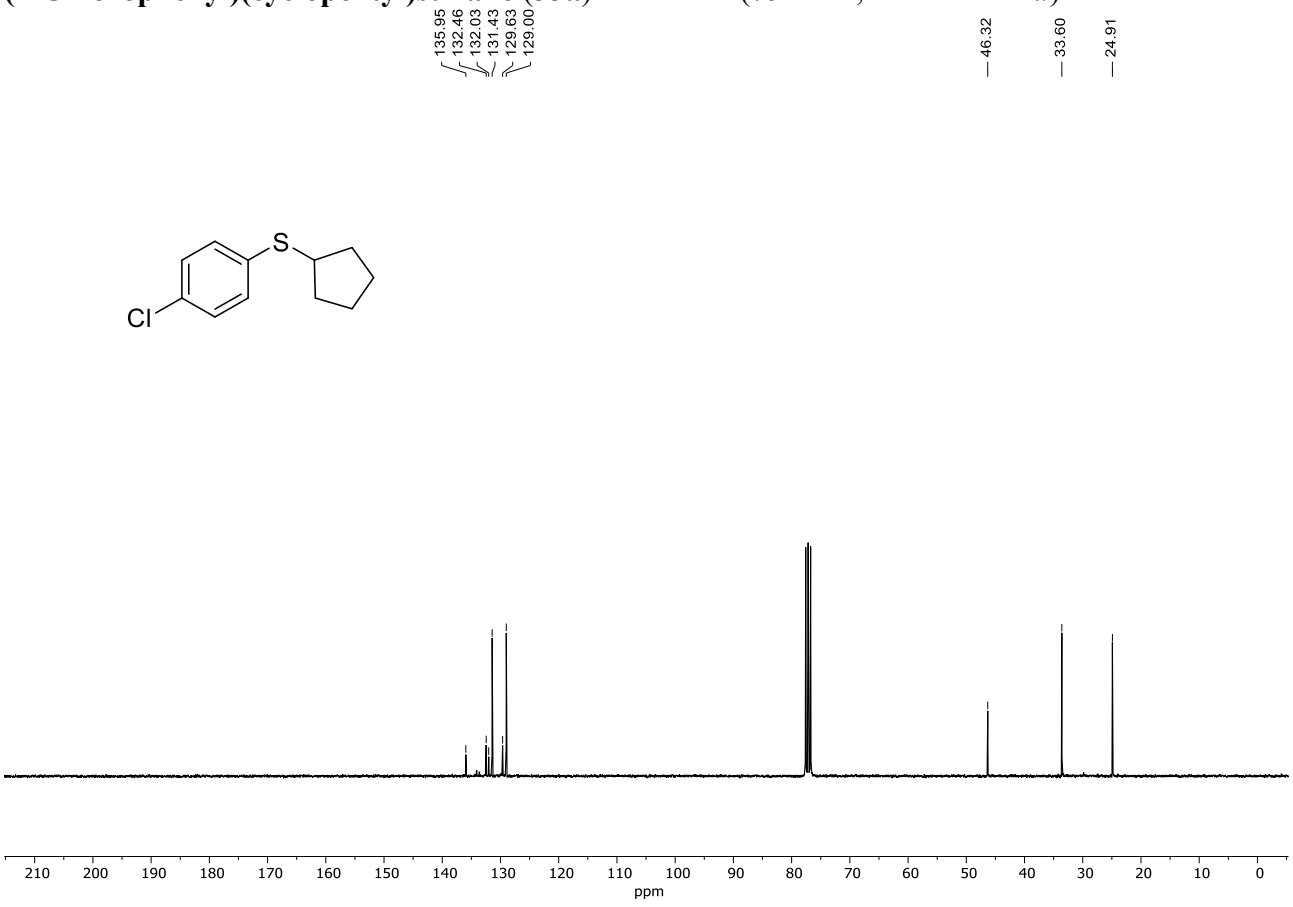


Cyclopentyl(phenyl)sulfane (**32a**). ^{13}C NMR (75 MHz, Chloroform-*d*)

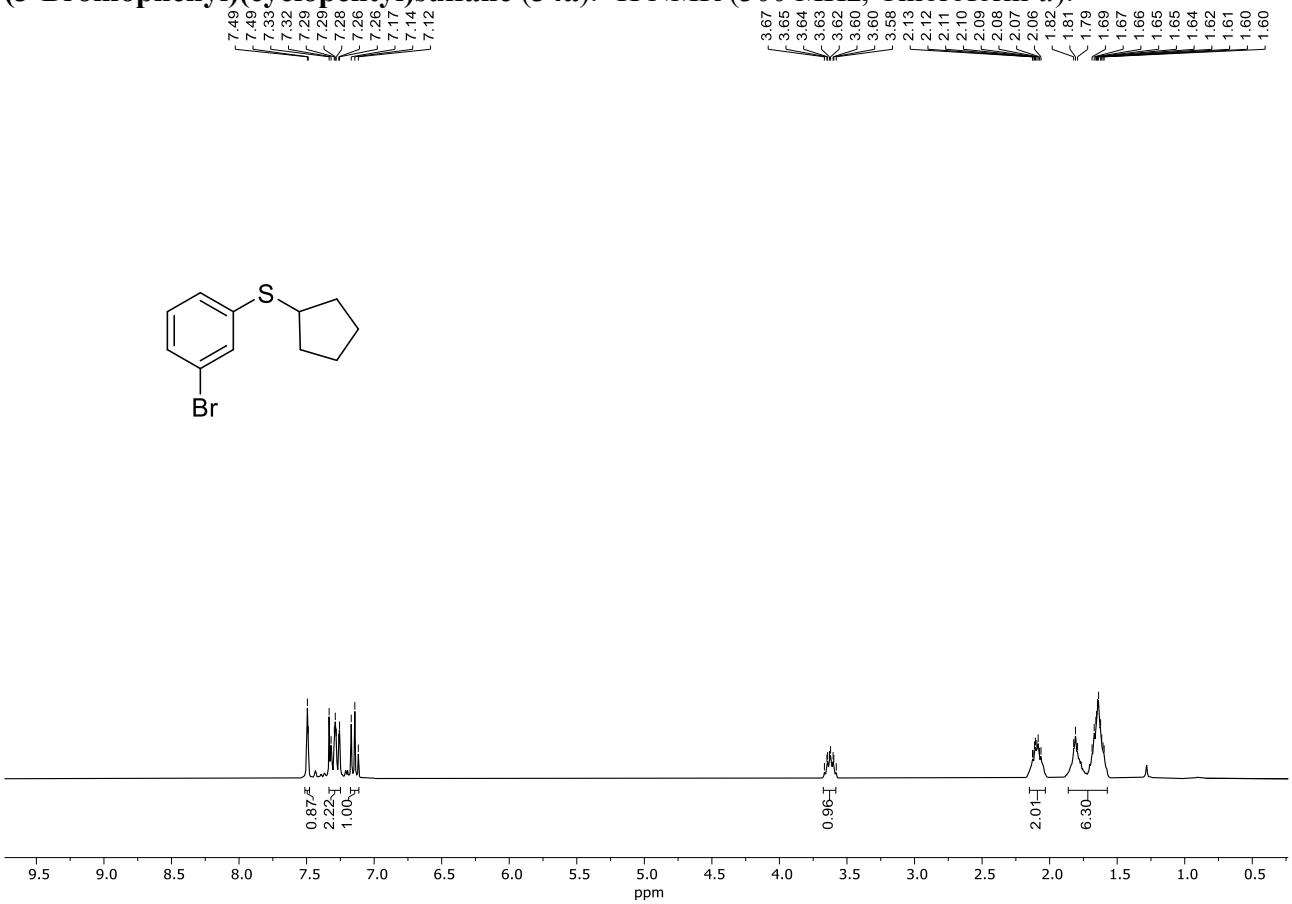


(4-Chlorophenyl)(cyclopentyl)sulfane (**33a**). ^{1}H NMR (300 MHz, Chloroform-*d*).

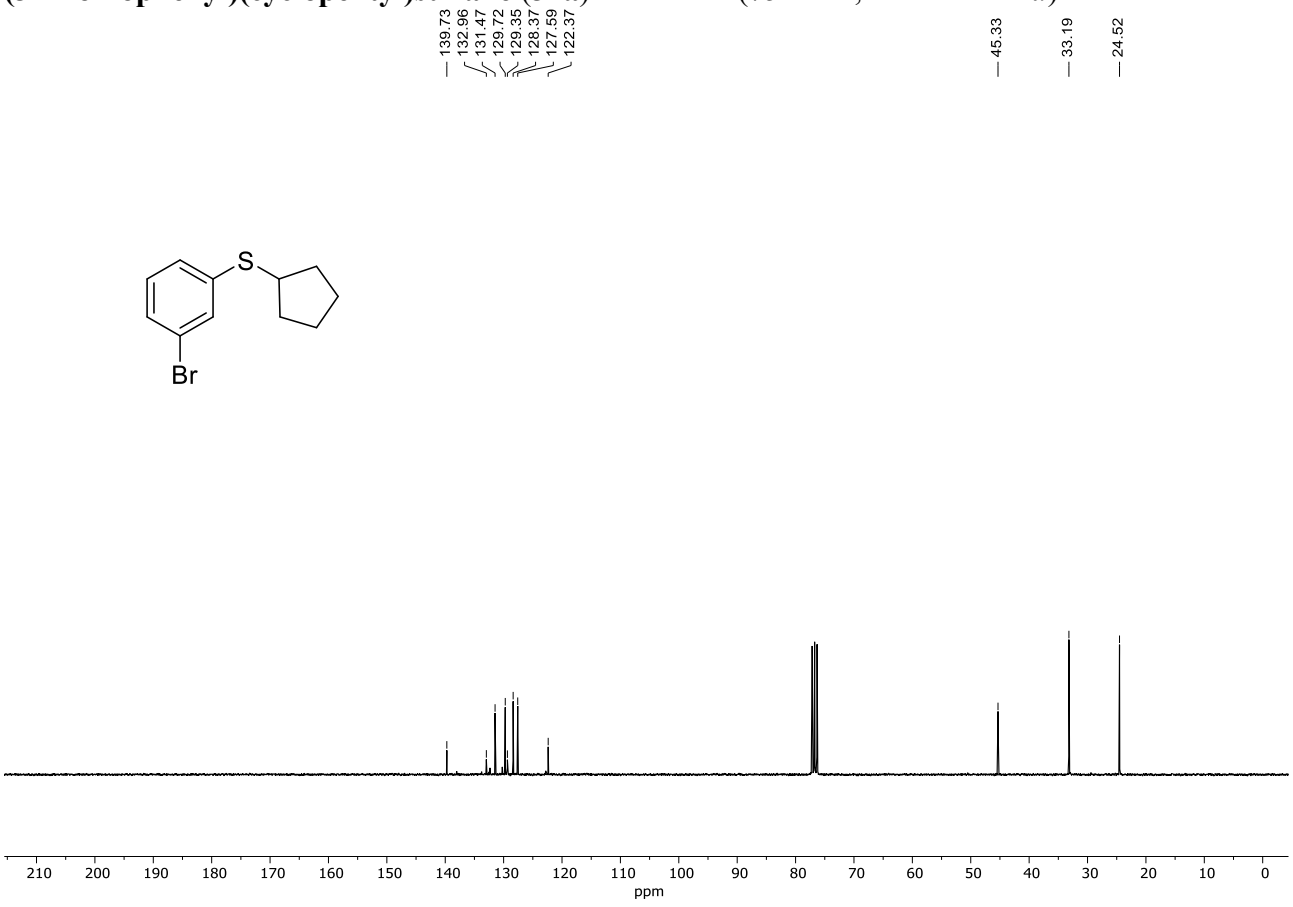
(4-Chlorophenyl)(cyclopentyl)sulfane (**33a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



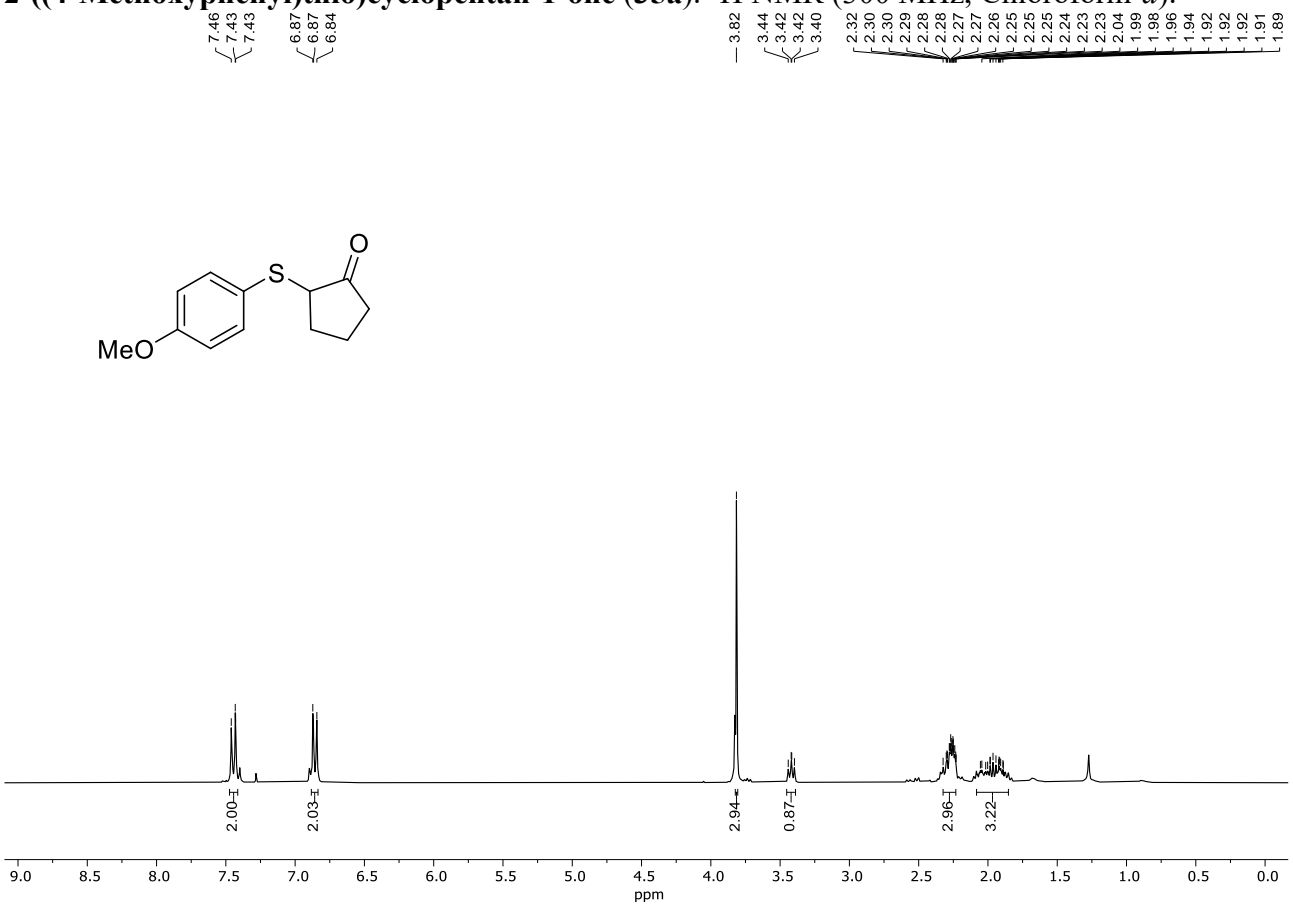
(3-Bromophenyl)(cyclopentyl)sulfane (**34a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



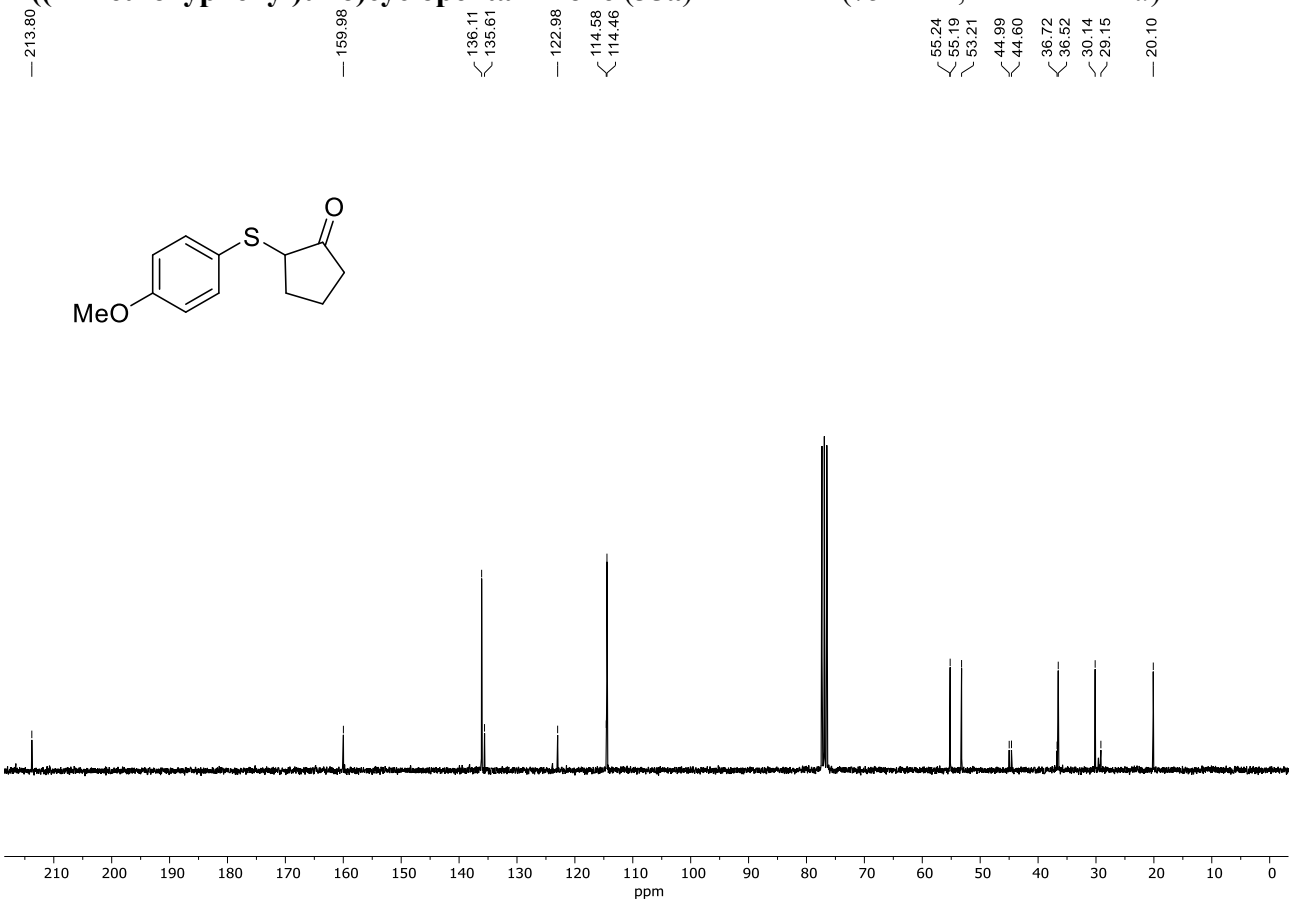
(3-Bromophenyl)(cyclopentyl)sulfane (**34a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



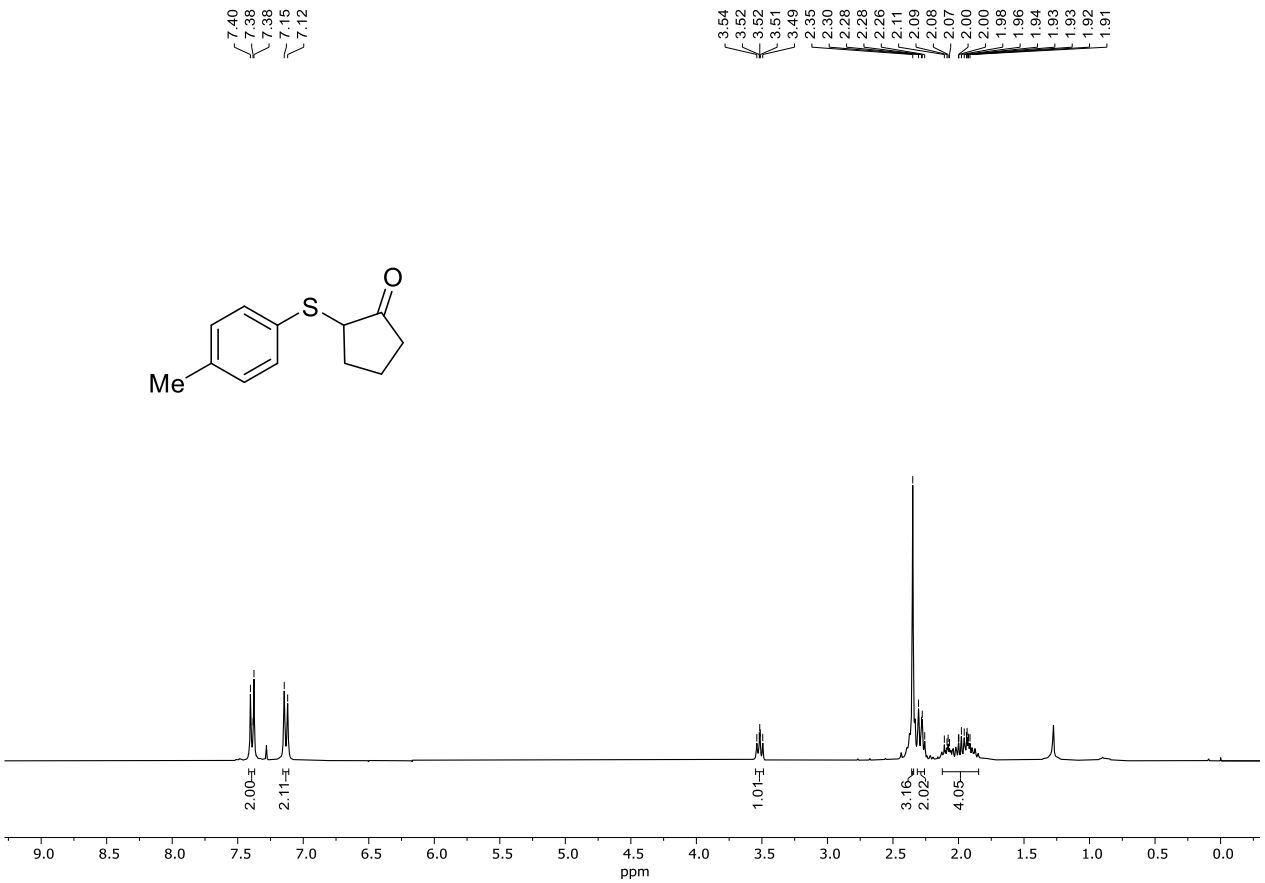
2-((4-Methoxyphenyl)thio)cyclopentan-1-one (**35a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



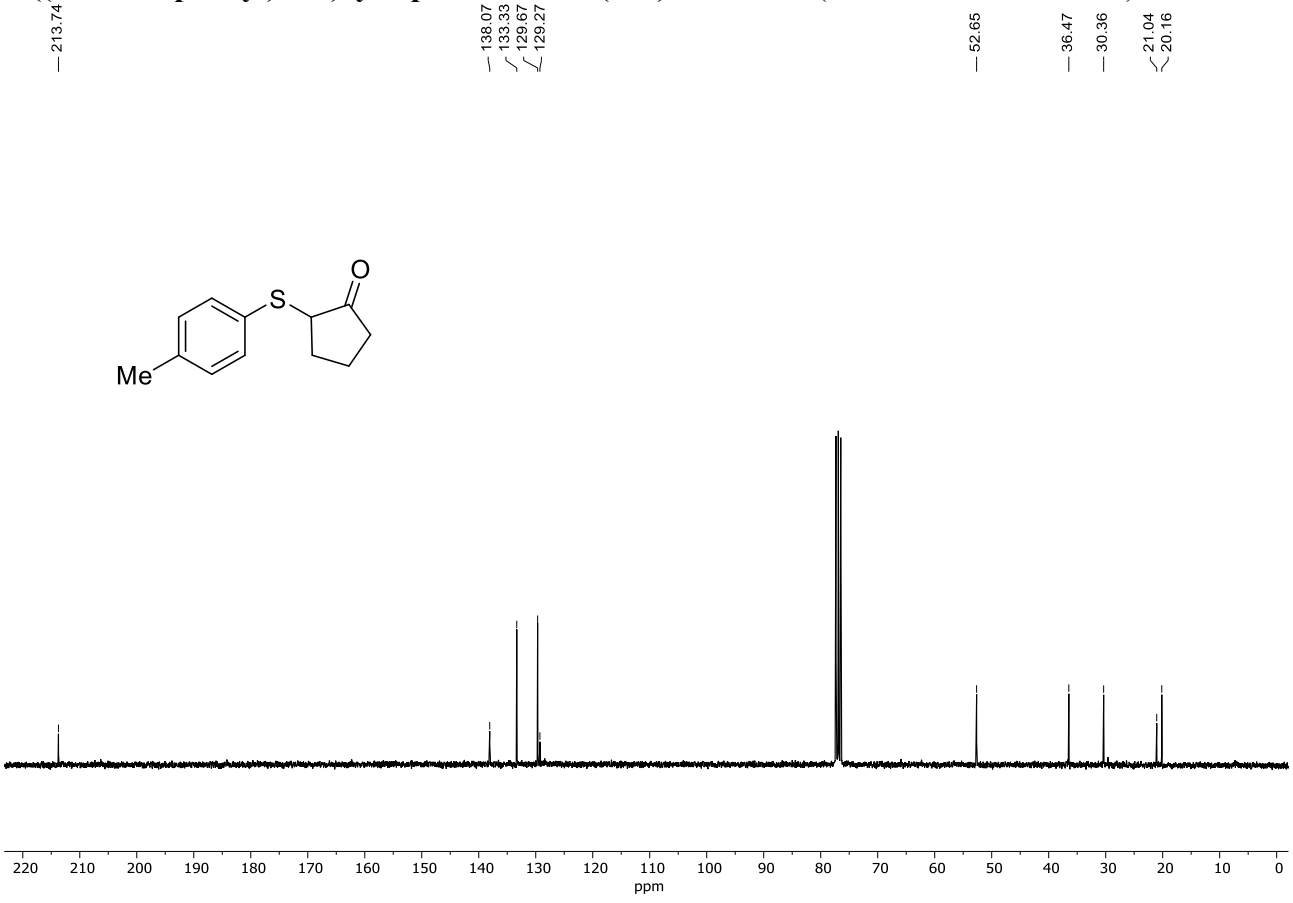
2-((4-Methoxyphenyl)thio)cyclopentan-1-one (**35a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



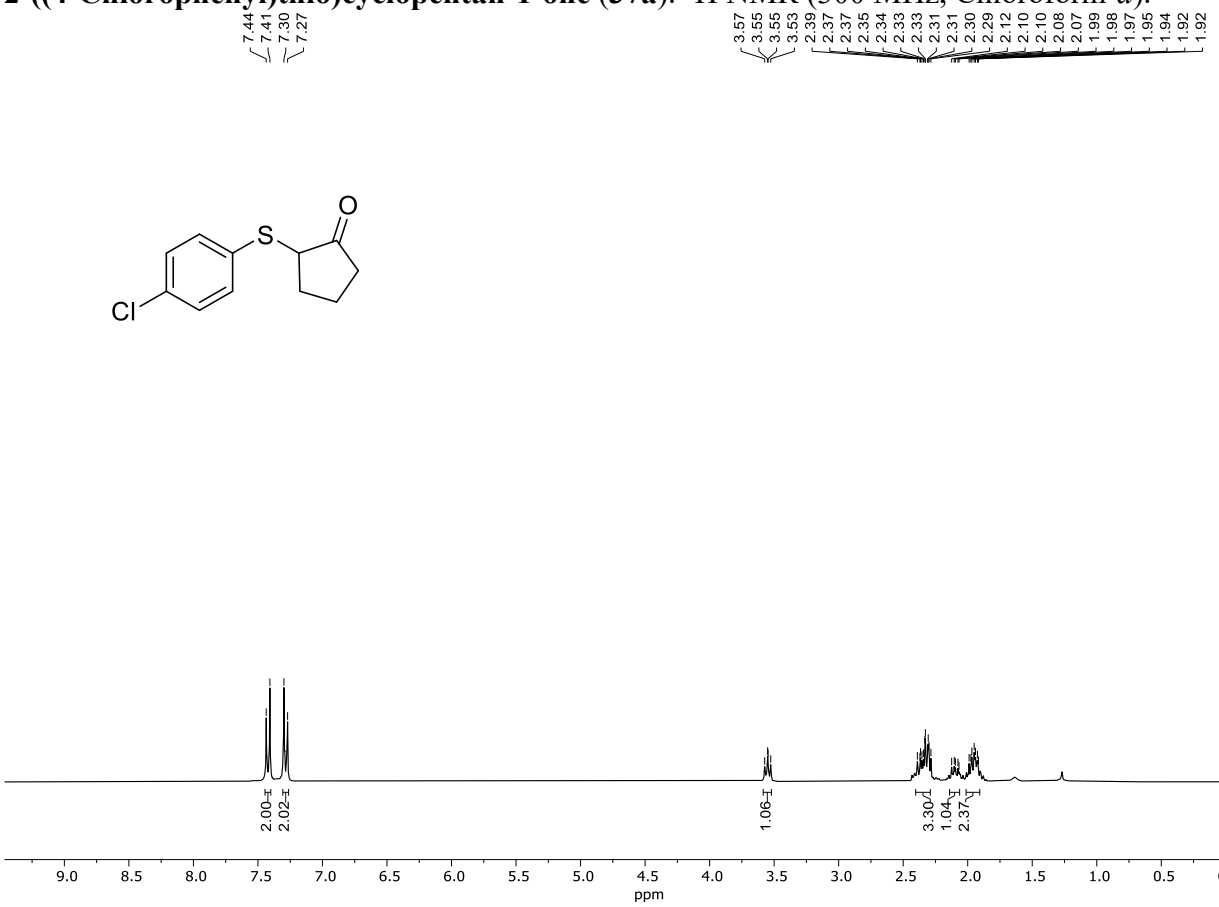
2-((3-Chlorophenyl)thio)cyclopentan-1-one (36a). ^{1}H NMR (300 MHz, Chloroform-*d*).



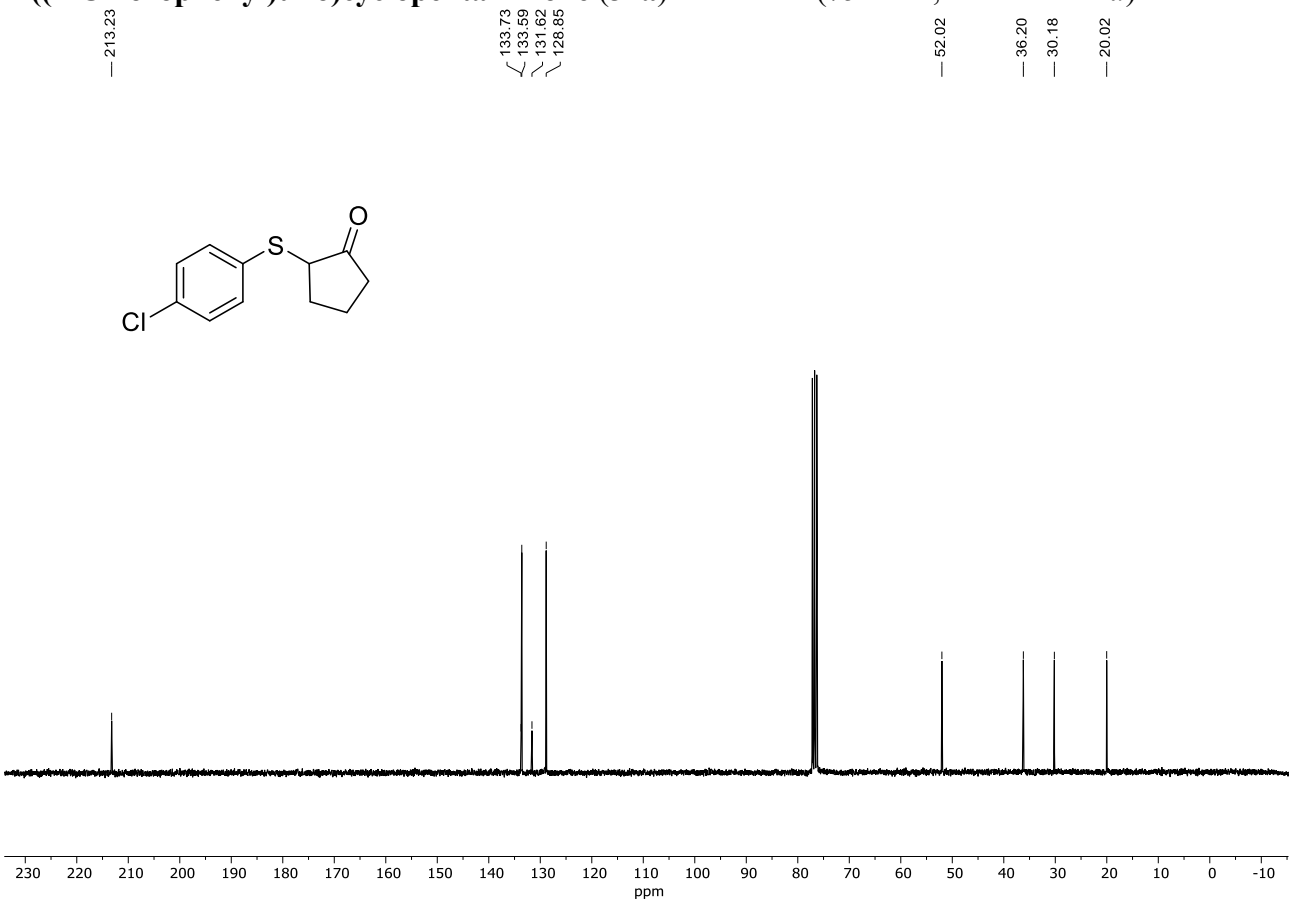
2-((3-Chlorophenyl)thio)cyclopentan-1-one (36a). ^{13}C NMR (75 MHz, Chloroform-*d*)



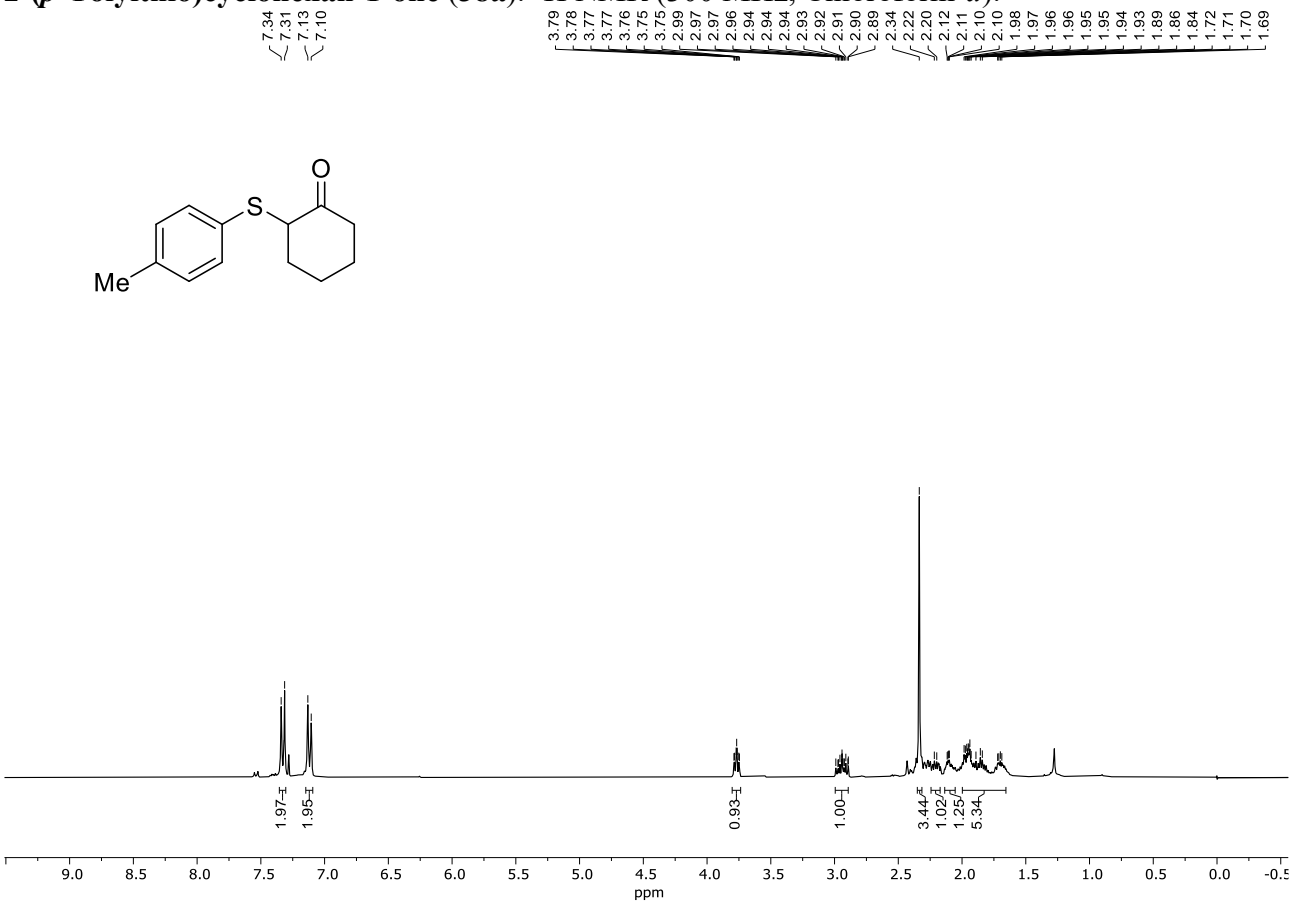
2-((4-Chlorophenyl)thio)cyclopentan-1-one (**37a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



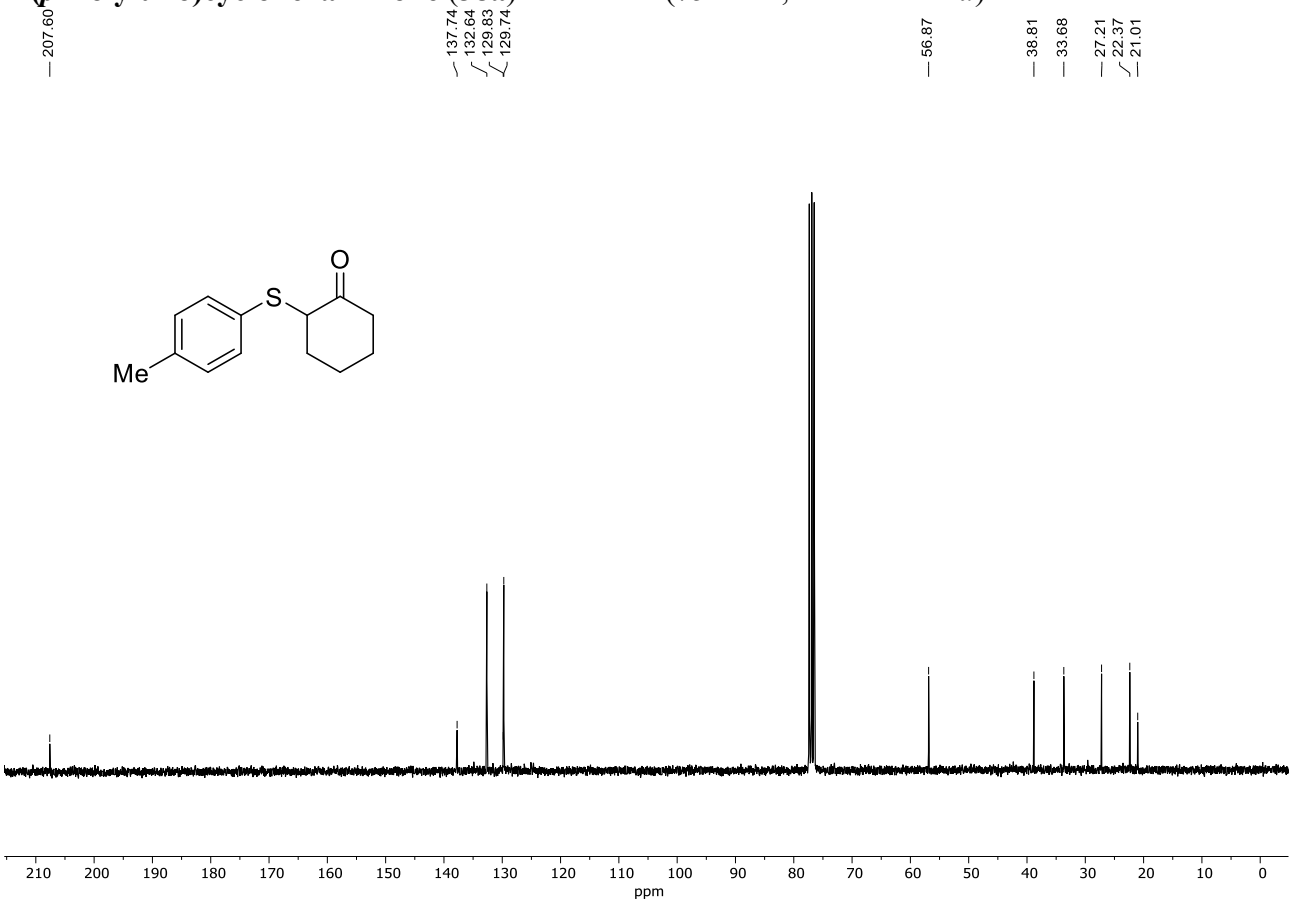
2-((4-Chlorophenyl)thio)cyclopentan-1-one (**37a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



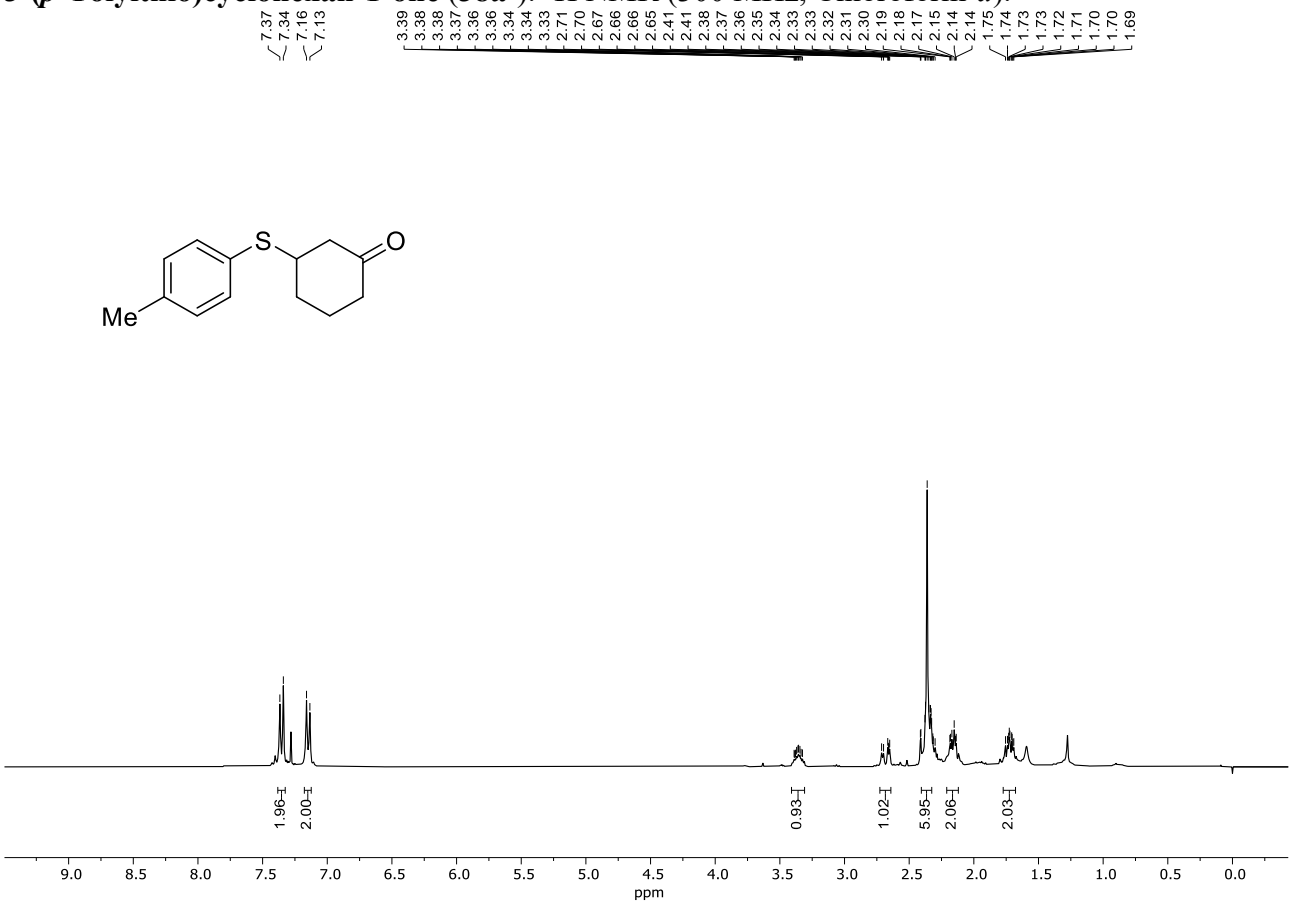
2-(*p*-Tolylthio)cyclohexan-1-one (38a). ^{1}H NMR (300 MHz, Chloroform-*d*).



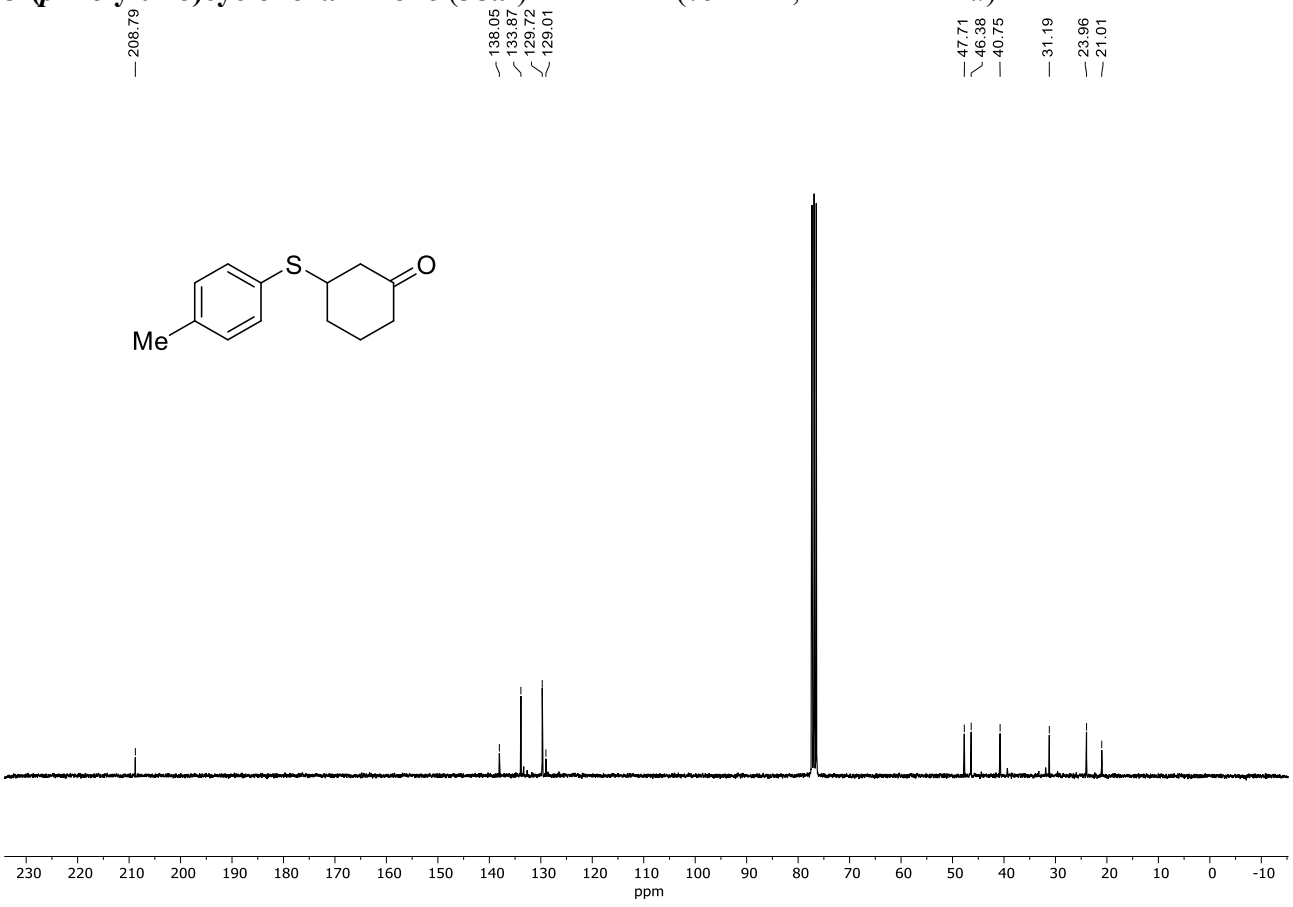
2-(*p*-Tolylthio)cyclohexan-1-one (38a). ^{13}C NMR (75 MHz, Chloroform-*d*)



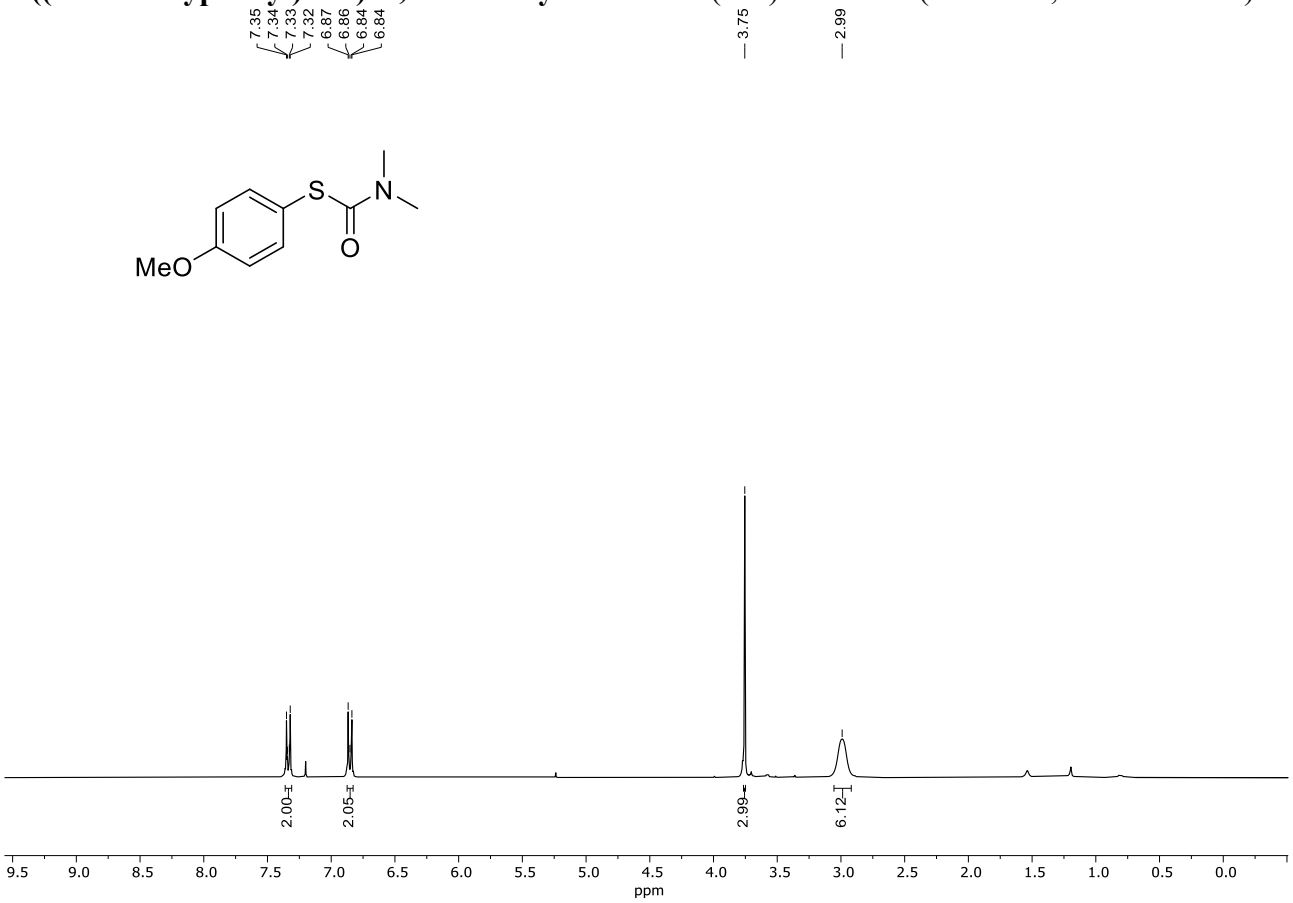
3-(*p*-Tolylthio)cyclohexan-1-one (38a'). ^{1}H NMR (300 MHz, Chloroform-*d*).



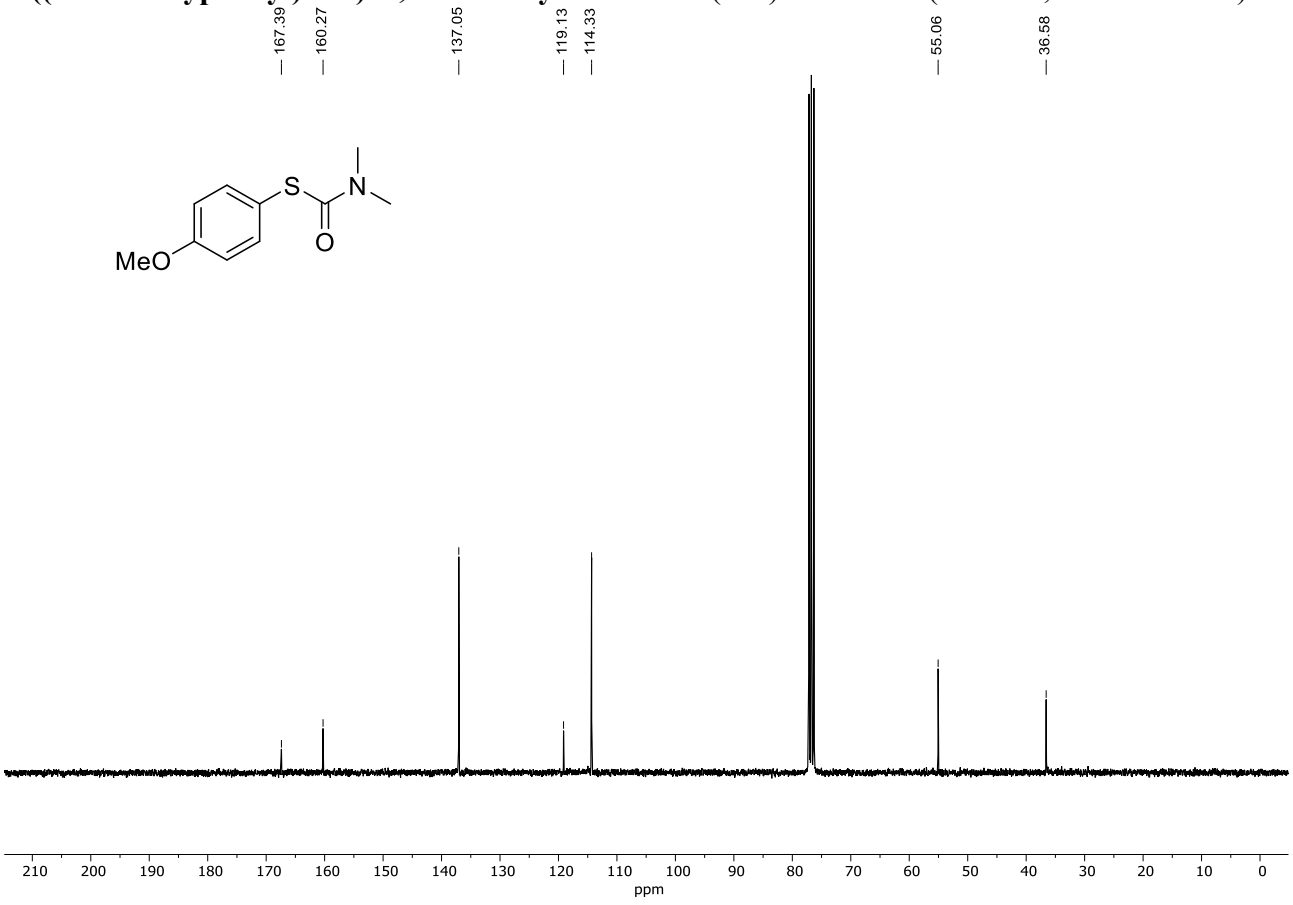
3-(*p*-Tolylthio)cyclohexan-1-one (38a'). ^{13}C NMR (75 MHz, Chloroform-*d*)



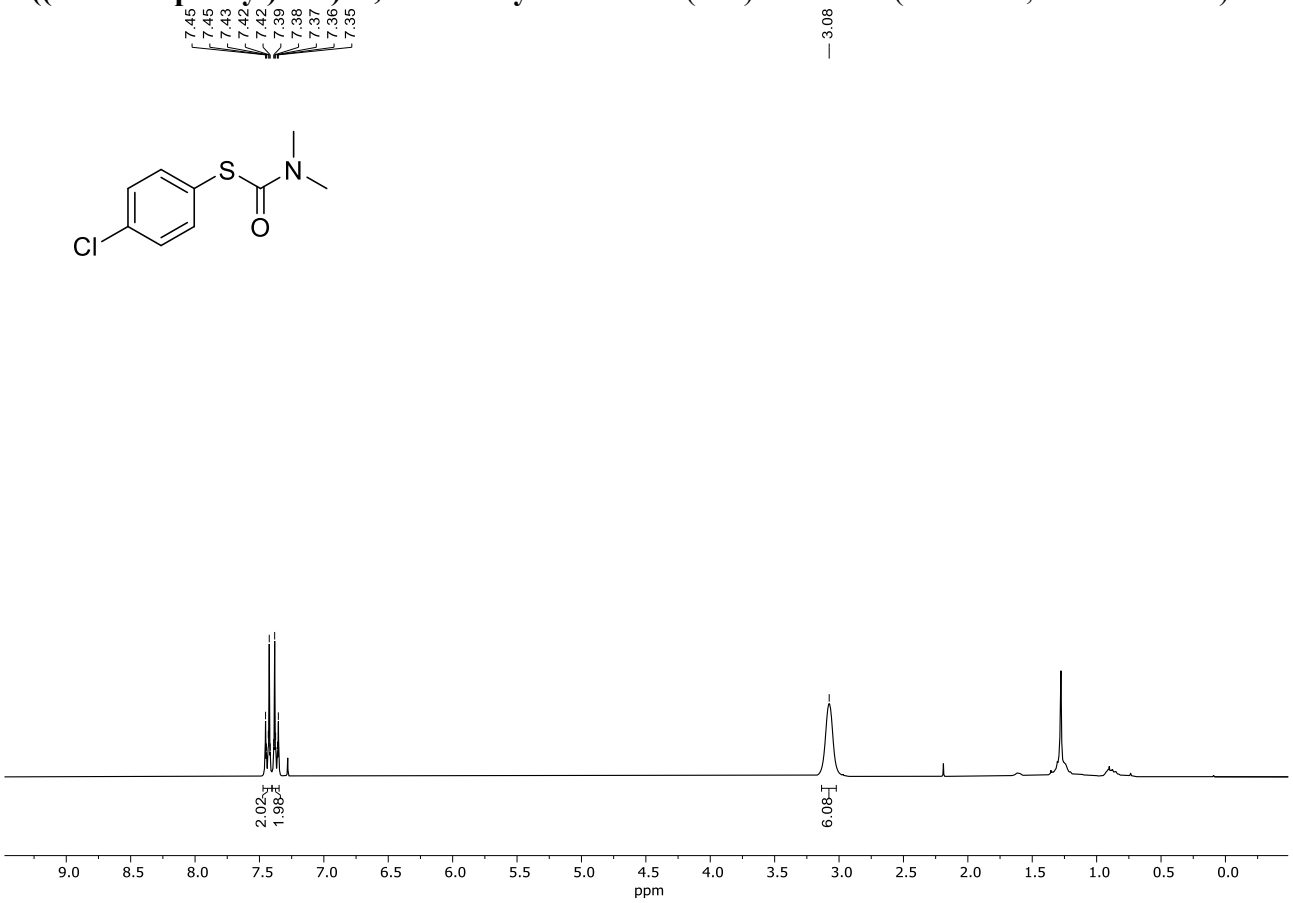
2-((4-Methoxyphenyl)thio)-*N*,*N*-dimethylacetamide (**39a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



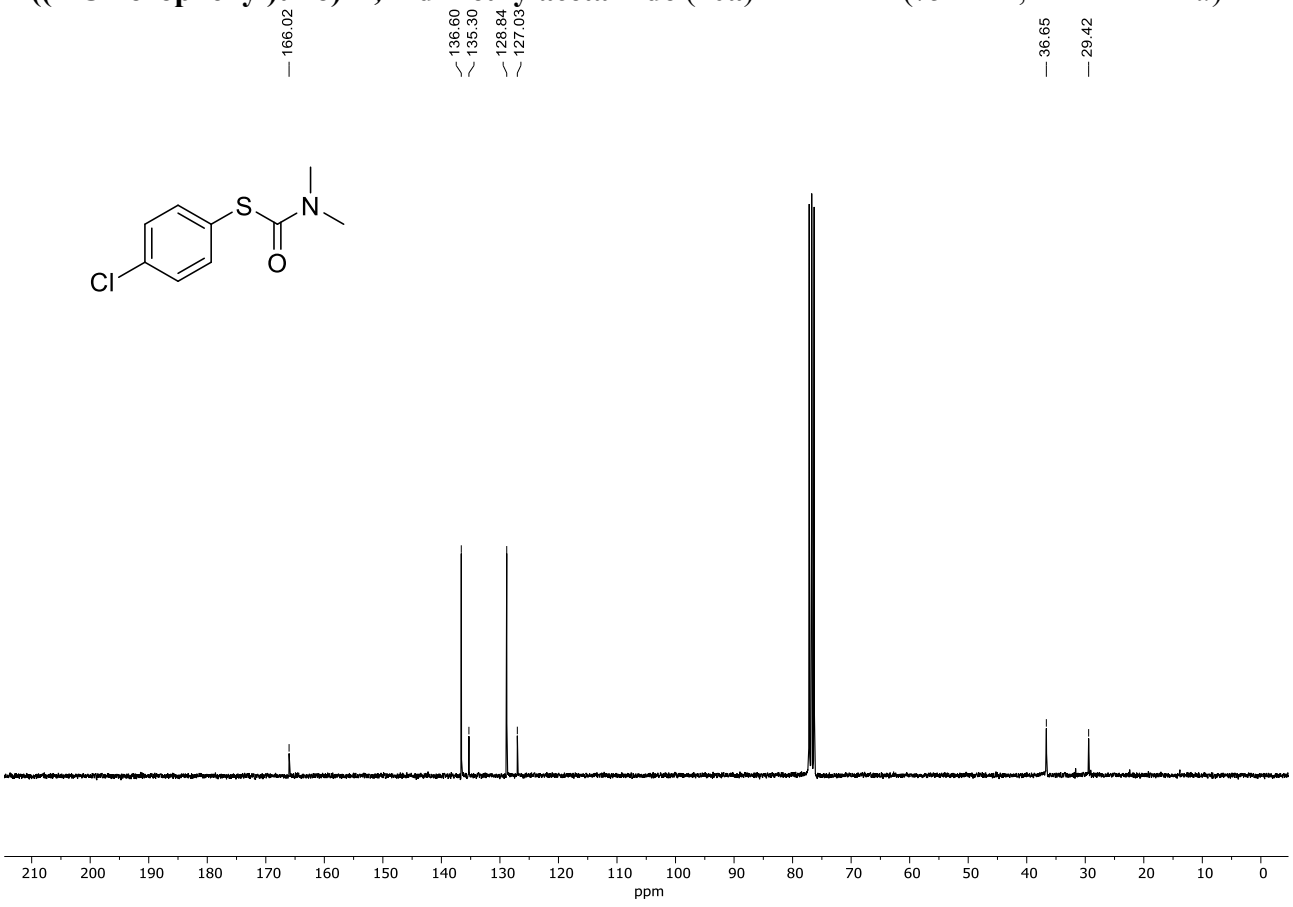
2-((4-Methoxyphenyl)thio)-*N*,*N*-dimethylacetamide (**39a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



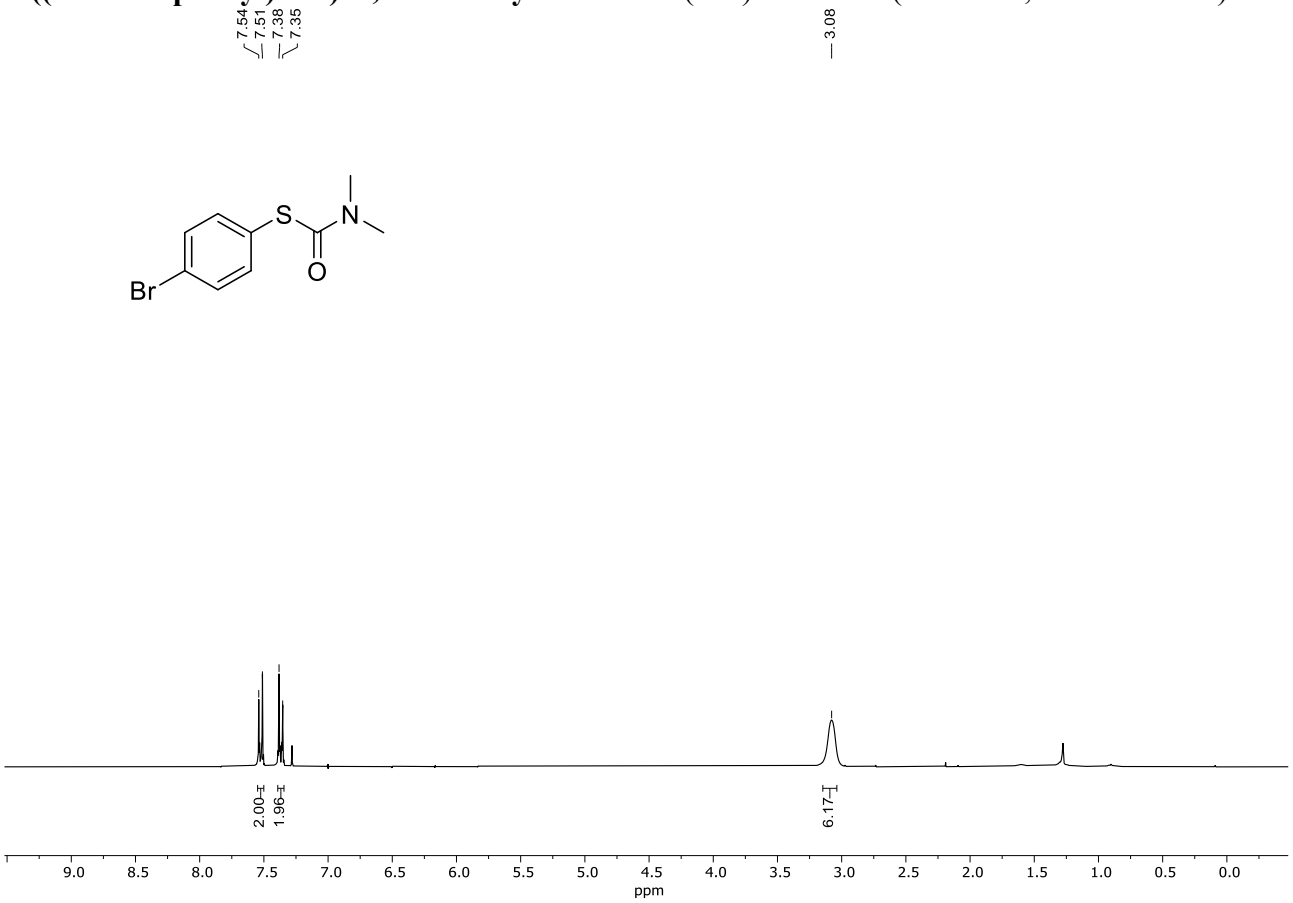
2-((4-Chlorophenyl)thio)-*N*,*N*-dimethylacetamide (**40a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



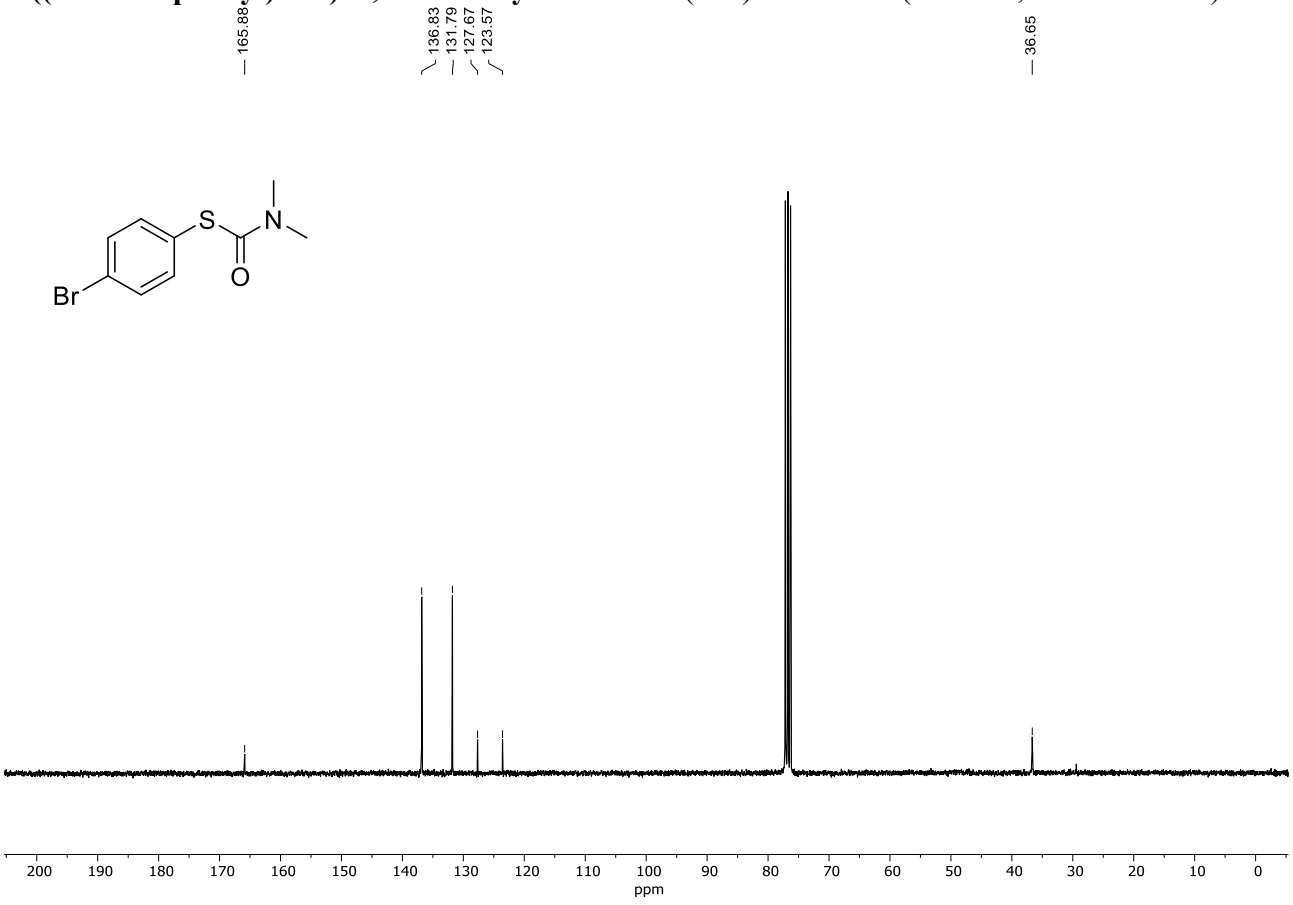
2-((4-Chlorophenyl)thio)-*N*,*N*-dimethylacetamide (**40a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



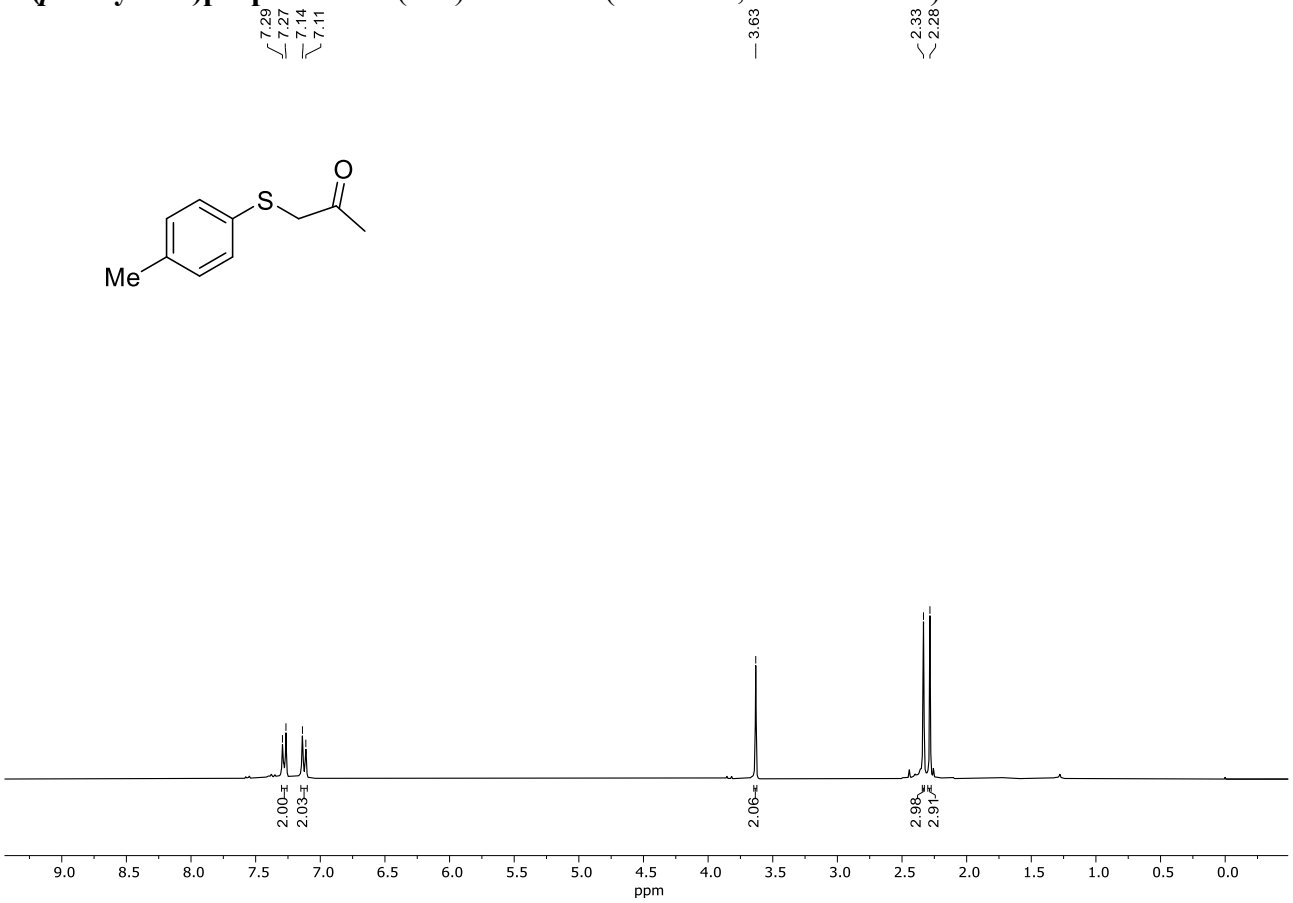
2-((4-Bromophenyl)thio)-*N*,*N*-dimethylacetamide (**41a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



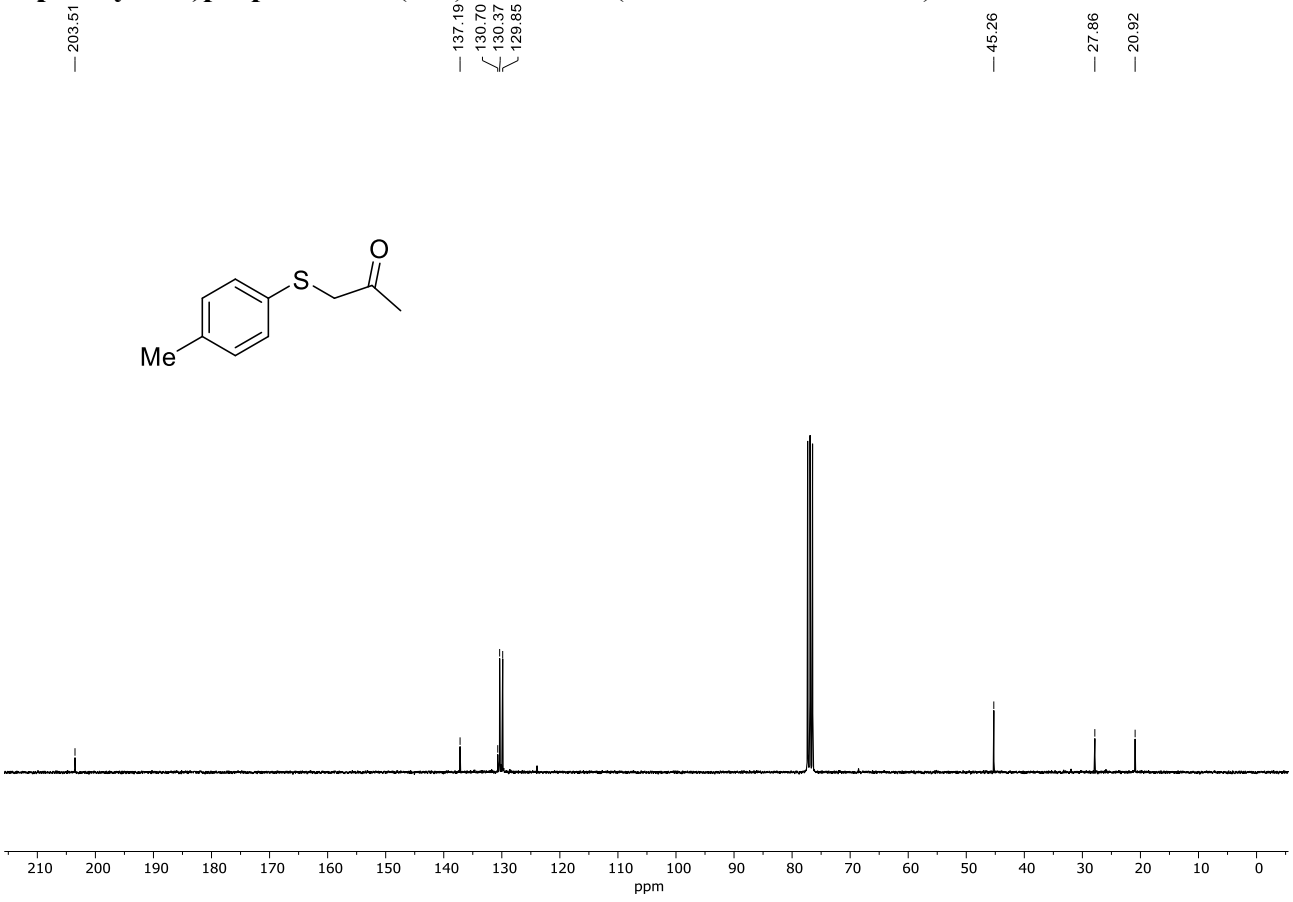
2-((4-Bromophenyl)thio)-*N*,*N*-dimethylacetamide (**41a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



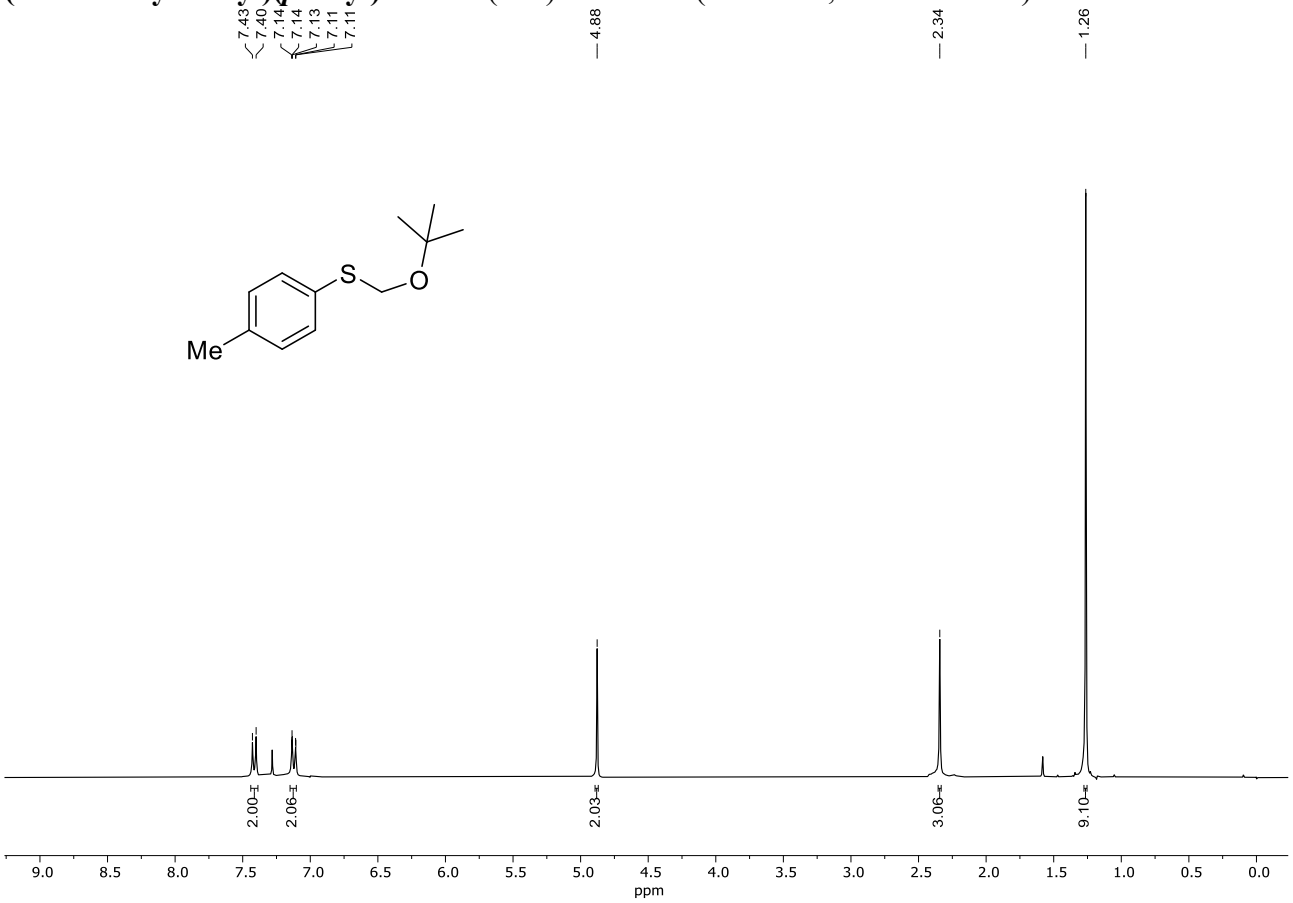
1-(*p*-Tolylthio)propan-2-one (**42a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



1-(*p*-Tolylthio)propan-2-one (**42a**). ^{13}C NMR (75 MHz, Chloroform-*d*)



(*tert*-Butoxymethyl)(*p*-tolyl)sulfane (**43a**). ^{1}H NMR (300 MHz, Chloroform-*d*).



(*tert*-Butoxymethyl)(*p*-tolyl)sulfane (**43a**). ^{13}C NMR (75 MHz, Chloroform-*d*)