Supporting Information for

Aerobic Copper-Catalyzed Decarboxylative Thiolation

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I. General Considerations

^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra were recorded on an Agilent 400 MHz spectrometer or a Varian INOVA 600 MHz spectrometer. Chemical shifts are given in parts per million and referenced to the residual solvent signal;[1] all coupling constants are reported in Hz. High resolution mass spectra were obtained on a Thermo Finnigan Linear Trapping Quadrupole mass spectrometer. IR spectra were recorded on a PerkinElmer (Spectrum 100) FT-IR spectrometer. Melting points were taken on a Mel-Temp melting point apparatus. Column chromatography was performed using Silicycle Silia Flash P60 silica gel. All chemicals, except 1-tosyl-1*H*-indole-2-carboxylic acid, were purchased from commercial sources and used without further purification. Anhydrous DMSO was dried by refluxing over CaH_2 and subsequent distillation. *p*-Xylene and anisole were freshly distilled over Na and benzophenone. DMF was taken from a solvent system which passes the solvent through a column of activated molecular sieves. NMP was purchased from Alfa as super-dry solvent.

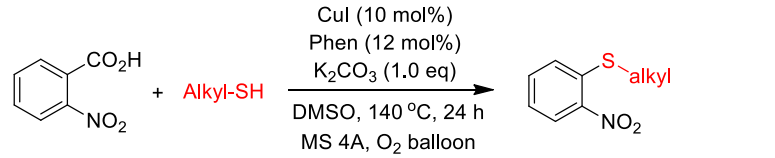
II. General Method for Screening of Reaction Conditions

CuI (5.7 mg, 0.03 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), 2-nitrobenzoic acid (50.1 mg, 0.3 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which thiophenol (61 μL, 0.6 mmol) and dry DMSO (5.0 mL) were added *via* syringe. The reaction mixture was fitted with an O_2 balloon attached to a needle inserted through the septum and stirred at 140 ^{o}C for 24 h. Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated (by rotary evaporation). Then 1,3,5-trimethoxylbenzene (5.0 mg) was added to the residue and the crude mixture was dissolved in $CDCl_3$ for ^{1}H NMR analysis.

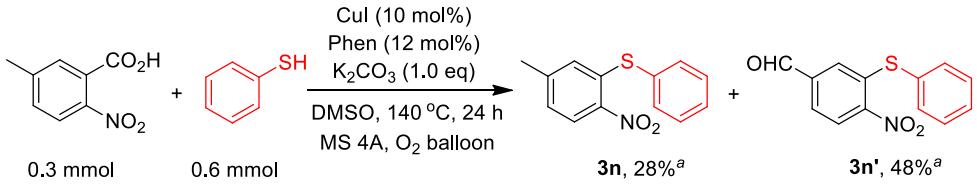
(1) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* 1997, **62**, 7512.

III. Challenging Substrates Under the Standard Reaction Conditions

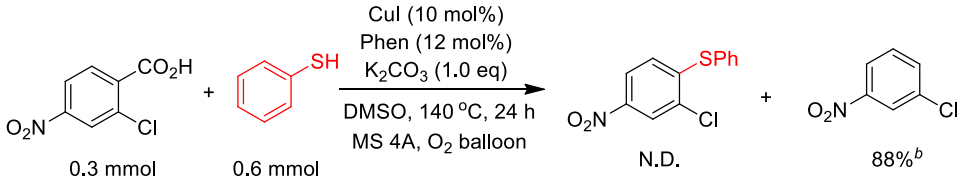
(a) The Reaction Results of alkyl thiols



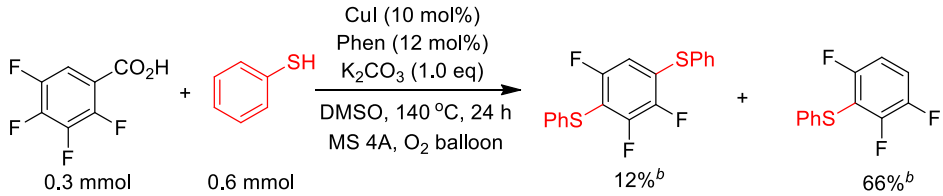
(b) The Reaction Result of 5-Methyl-2-nitrobenzoic Acid



(c) The Reaction Result of 4-Nitro-2-chlorobenzoic Acid



(d) The Reaction Result of 2,3,4,5-tetrafluorobenzoic Acid



[a] isolated yield. [b] NMR yield with 1,3,5-trimethoxylbenzene as internal standard

Scheme S1. Challenging substrates under the standard conditions.

IV. Synthesis and Characterization of N-Tosylindole-2-carboxylic acid

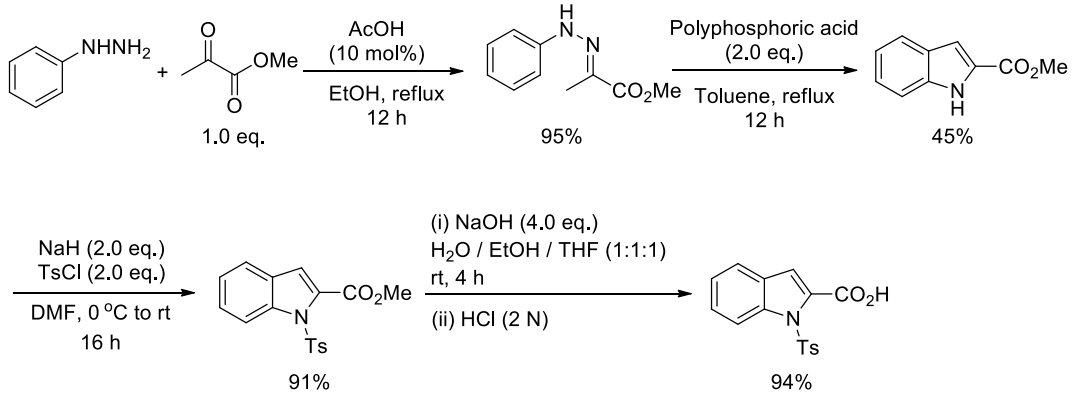
The 1-tosyl-1*H*-indole-2-carboxylic acid was prepared according to literature procedure with slight modifications, from phenylhydrazine through Fischer indole synthesis,[2] N-protection[3] and hydrolysis of the ester[4] (Scheme S2). Acetic acid (5 mmol, 286 μL, 0.1 equiv.) was added to a solution of the phenylhydrazine (50 mmol, 4.9 mL, 1.0 equiv) and methyl pyruvate (50 mmol, 4.5 mL, 1.0 equiv) in ethanol (100 mL). The reaction mixture was heated at reflux for 12 h followed by evaporation to yield phenylhydrazone as a yellow solid. Without purification the phenylhydrazone was directly mixed with polyphosphoric acid (2.0

(2) L. Zhao, Z.-Y. Li, L. Chang, J.-Y. Xu, H.-Q. Yao, X.-M. Wu, *Org. Lett.,* 2012, **14**, 2066.
(3) A. Karadeolian, M. Kerr, *J. Org. Chem.,* 2010, **75**, 6830.
(4) R. Silvestri, G. Martino, G. Regina, M. Artico, S. Massa, L. Vargiu, M. Mura, A. Loi, T. Marceddu, P. Colla, *J. Med. Chem.,* 2003, **46**, 2482.

equiv.) in toluene (50 mL) and heated at reflux for 24 h. After reaction, the mixture was quenched with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica column chromatography (hexane/ethyl acetate = 4/1) to afford methyl-1*H*-indole-2-carboxylate in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.35 (m, 1H), 7.31 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.21 (dd, *J* = 2.1, 0.9 Hz, 1H), 7.18 – 7.06 (m, 1H), 3.99 – 3.89 (m, 3H). The spectral data are consistent with those reported in the literature.[2]

Then, the N-H indole (1.0 equiv.) was added in portions to a solution of NaH (2.0 equiv.) in DMF at 0°C (ice and water). After the release of H_2 gas ceased, a solution of TsCl (2.0 equiv.) in DMF was added dropwise. The mixture was stirred at 0°C for 0.5 h, then at room temperature for 16 h. The reaction mixture was then quenched with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica column chromatography (hexane/ethyl acetate = 10/1) to afford methyl N-tosylindole-2-carboxylate in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 – 8.05 (m, 1H), 7.97 – 7.84 (m, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.41 (ddd, *J* = 8.5, 7.4, 1.2 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.14 (s, 1H), 3.92 (s, 3H), 2.33 (s, 3H). The spectral data are consistent with those reported in the literature.[3]

The N-tosylindole-2-carboxylate (1.0 equiv.) was added to a KOH (4.0 eq., 2 N) solution in H_2O / EtOH / THF (1:1:1) and stirred for 4 h at room temperature. The solution was then cooled to 0°C (ice and water) and acidified by HCl aq. (2 N) to pH = 2. The solution was extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4, filtered and evaporated to furnish the title compound as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.59 (s, 1H), 8.00 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.45 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.26 (m, 2H), 2.34 (s, 3H). The spectral data are consistent with those reported in the literature.[4]



Scheme S2. Preparation of 1-tosyl-1*H*-indole-2-carboxylic acid.

V. Representative Procedure for the Decarboxylative Thiolation of Benzoic Acids with Thiophenols (Products in Table 2)

CuI (5.7 mg, 0.030 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), 2-nitrobenzoic acid (50.1 mg, 0.30 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which thiophenol (61 μL, 0.60 mmol) and dry DMSO (5.0 mL) were added *via* syringe. The reaction tube was fitted with an O_2 balloon attached to a needle inserted through the septum and stirred at 140°C for 24 h. Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated (by rotary evaporation). The residue was purified by flash chromatography (SiO_2, hexane to hexane/ethyl acetate = 20/1 gradient elution), yielding the (2-nitrophenyl)(phenyl)sulfane **3a** (R_f = 0.42 in hexane/ethyl acetate = 8/1) in 85% yield (59.0 mg, 0.255 mmol). The 10 mmol reaction was conducted in a 100 mL round bottom flask under identical conditions. Similar compounds were prepared following the standard procedure unless otherwise noted in the main manuscript.

VI. Representative Procedure for the Decarboxylative Thiolation of Heteroaromatic Acids with Thiophenols (Products in Table 3)

CuI (5.7 mg, 0.030 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), 4-methyl-2-phenyloxazole-5-carboxylic acid (61.0 mg, 0.30 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which thiophenol (91 μL, 0.90 mmol) and dry DMSO (5.0 mL) were added *via* syringe. The reaction mixture was connected an O_2 balloon and stirred at 160°C for 24 h. Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted by ethyl acetate (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated (by rotary evaporation). The residue was purified by flash chromatography (SiO_2, hexane / ethyl acetate gradient), yielding the 4-methyl-2-phenyl-5-(phenylthio)oxazole **4a** in 59% yield (47.3 mg, 0.177 mmol). Similar compounds were prepared following the standard procedure unless otherwise noted in the main manuscript.

VII. Procedure for the Decarboxylative Selenation of 2-Nitrobenzoic Acids (Scheme 3)

CuI (5.7 mg, 0.030 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), 2-nitrobenzoic acid (50.1 mg, 0.30 mmol), 1,2-diphenyldiselenide (140.5 mg, 0.45 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which a dry DMSO (5.0 mL) was added *via* syringe. The reaction mixture was fitted with an O_2 balloon attached to a needle inserted through the septum and stirred at 140°C for

24 h. Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated ((by rotary evaporation). The residue was purified by flash chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution), yielding the (2-nitrophenyl)(phenyl)selane **5** (R_f = 0.40 in hexane/ethyl acetate = 8/1) in 53% yield (44.2 mg, 0.159 mmol).

VIII. Procedures for the Control Experiments for the formation and Reaction of Disulfide (Eq. 1 & 2)

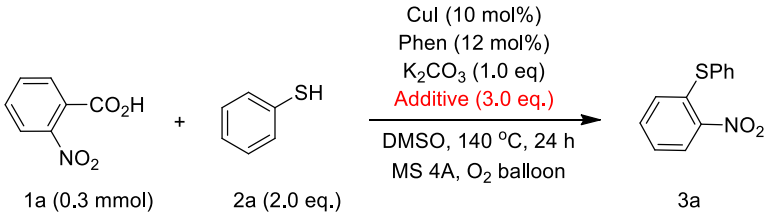
CuI (5.7 mg, 0.030 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which thiophenol (61 μL, 0.60 mmol) and dry DMSO (5.0 mL) were added *via* syringe. The reaction mixture was fitted with an O_2 balloon attached to a needle inserted through the septum and stirred at 140°C for 24 h. Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated (by rotary evaporation). The residue was purified by flash chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution), yielding the diphenyl disulfide (R_f = 0.60 in hexane/ethyl acetate = 8/1) in 93% yield (60.9 mg, 0.279 mmol).

CuI (5.7 mg, 0.030 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), 2-nitrobenzoic acid (50.1 mg, 0.30 mmol), diphenyldisulfide (65.5 mg, 0.30 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which a dry DMSO (5.0 mL) was added *via* syringe. The reaction mixture was fitted with an O_2 balloon attached to a needle inserted through the septum and stirred at 140°C for 24 h. Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated (by rotary evaporation). The residue was purified by flash chromatography (SiO_2, hexane to hexane/ethyl acetate = 20/1 gradient elution), yielding the (2-nitrophenyl)(phenyl)sulfane **3a** (R_f = 0.42 in hexane/ethyl acetate = 8/1) in 82% yield (56.8 mg, 0.246 mmol).

IX. Procedure and Results for the Decarboxylative Thiolation of 2-Nitrobenzoic Acid with Thiolphenol in the Presence of Radical Scavengers

CuI (5.7 mg, 0.030 mmol), 1,10-phenanthroline (6.5 mg, 0.036 mmol), 2-nitrobenzoic acid (50.1 mg, 0.30 mmol), 1,2-diphenyldiselane (140.5 mg, 0.45 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), TEMPO (140.6 mg, 0.90 mmol) or 9.10-dihydroanthracene (162.2 mg, 0.90 mmol) and 4Å molecular sieves (500 mg) were combined in a dried 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with O_2 three times after which dry DMSO (5.0 mL) was added *via* syringe. The reaction mixture was fitted with an O_2 balloon attached to a needle inserted through the septum and stirred at 140°C for 24 h.

Upon completion, the mixture was cooled to room temperature and filtered through celite. The solution was diluted with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated (by rotary evaporation). Then 1,3,5-trimethoxylbenzene (5.0 mg) was added to the residue and the crude mixture was dissolved in $CDCl_3$ for ^1H NMR analysis.



1a (0.3 mmol) 2a (2.0 eq.) 3a

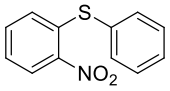
Additive	yield of 3a[a]
—	88%
TEMPO	75%
9,10-dihydroanthracene	83%

[a]: 1H NMR yield with 1,3,5-trimethoxylbenzene as internal standard.

Table S1. The comparison of reaction results with and without radical scavengers.

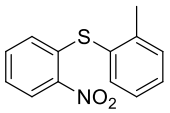
X. Characterization of Decarboxylative Thiolation Products (3a-3r)

(2-Nitrophenyl)(phenyl)sulfane (3a)



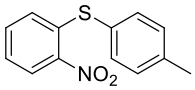
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.42 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 80 – 82°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.53 – 7.44 (m, 3H), 7.36 – 7.30 (m, 1H), 7.21 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0, 139.4, 135.9, 133.4, 131.0, 130.1, 123.0, 128.3, 125.7, 124.9. The spectral data are consistent with those reported in the literature.[5]

(2-Nitrophenyl)(*o*-tolyl)sulfane (3b)



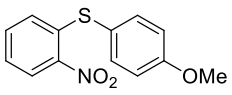
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.50 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 85 – 87°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.32 (ddd, *J* = 7.2, 4.7, 1.5 Hz, 2H), 7.20 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 6.70 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.9, 143.3, 138.8, 137.2, 133.5, 131.3, 130.7, 129.8, 127.5, 127.3, 126.0, 124.7, 20.5. The spectral data are consistent with those reported in the literature.[5]

(2-Nitrophenyl)(*p*-tolyl)sulfane (3c)



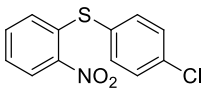
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.48 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 88 – 90°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.35 – 7.26 (m, 3H), 7.19 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.8, 140.4, 140.0, 135.9, 133.3, 130.9, 128.1, 127.2, 125.7, 124.7, 21.4. The spectral data are consistent with those reported in the literature.[5]

(4-Methoxyphenyl)(2-nitrophenyl)sulfane (3d)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 10/1 gradient elution) to yield the title compound (R_f = 0.23 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 95 – 97°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.35 – 7.29 (m, 1H), 7.18 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.1, 144.5, 140.6, 137.6, 133.3, 127.8, 125.7, 124.6, 121.1, 115.6, 55.4. The spectral data are consistent with those reported in the literature.[5]

(4-Chlorophenyl)(2-nitrophenyl)sulfane (3e)

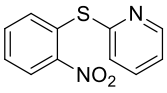


The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.38 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 94 –

(5)Z. Duan, S. Ranjit, P. Zhang, X. Liu, *Chem. Eur. J.* 2009, **15**, 3666.

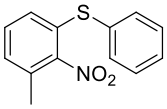
96°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 1H), 7.26 (ddd, *J* = 8.4, 4.6, 1.0 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.1, 138.7, 137.1, 136.5, 133.5, 130.3, 129.6, 128.2, 125.8, 125.2. The spectral data are consistent with those reported in the literature.[6]

2-((2-Nitrophenyl)thio)pyridine (3f)



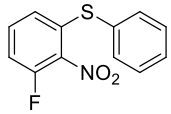
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 10/1 gradient elution) to yield the title compound (R_f = 0.30 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 72 – 74°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (ddd, *J* = 4.8, 1.9, 0.8 Hz, 1H), 8.09 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.67 (td, *J* = 7.7, 1.9 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 7.28 – 7.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.5, 150.8, 147.7, 137.6, 133.3, 133.1, 131.7, 127.6, 126.9, 125.4, 122.8. The spectral data are consistent with those reported in the literature.[7]

(3-Methyl-2-nitrophenyl)(phenyl)sulfane (3g)



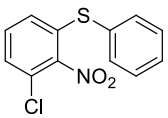
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.42 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.38 (m, 2H), 7.38 – 7.29 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.15 (ddd, *J* = 7.6, 1.3, 0.6 Hz, 1H), 7.07 (dd, *J* = 7.8, 0.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.5, 133.2, 132.8, 131.0, 130.4, 130.3, 130.1, 129.8, 129.5, 128.4, 17.9. FTIR (ATR, cm^{-1}): 2971, 1537, 1375, 1253, 1056, 1010, 801, 723, 685; HRMS m/z (ESI) calcd for $C_{13}H_{12}NO_2S$ $[M + H]^+$ 246.0589 found 246.0588.

(3-Fluoro-2-nitrophenyl)(phenyl)sulfane (3h)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.35 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.29 (m, 5H), 7.29 – 7.20 (m, 1H), 7.09 – 6.96 (m, 1H), 6.81 (ddd, *J* = 9.4, 8.2, 4.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.8 (d, $^1J_{C\text{-}F}$ = 263 Hz), 136.2 (d, $^3J_{C\text{-}F}$ = 7 Hz), 134.5, 132.1 (d, $^2J_{C\text{-}F}$ = 22 Hz), 131.9 (d, $^3J_{C\text{-}F}$ = 9 Hz), 131.1, 129.9, 129.6, 125.5 (d, $^4J_{C\text{-}F}$ = 4 Hz), 114.1 (d, $^2J_{C\text{-}F}$ = 20 Hz); FTIR (ATR, cm^{-1}): 2981, 1580, 1529, 1457, 1351, 1261, 904, 848, 783, 752, 690; ^{19}F NMR (376 MHz, $CDCl_3$): δ = 120.8 (dd, $^3J_{F\text{-}H}$ = 9 Hz, $^4J_{F\text{-}H}$ = 5 Hz). HRMS m/z (ESI) calcd for $C_{12}H_9FNO_2S$ $[M + H]^+$ 250.0338 found 250.0314.

(3-Chloro-2-nitrophenyl)(phenyl)sulfane (3i)

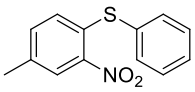


The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.38 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 – 7.43 (m, 2H), 7.40 – 7.36 (m, 3H), 7.34 (dd, J = 8.1, 1.2 Hz,

(6) C.-M. Tan, G.-S. Chen, C.-S. Chen, J.-W. Chern, *J. Chin. Chem. Soc. (Taipei, Taiwan)*, 2011, **58**, 94.
(7) Y. Goriya, C. V. Ramana, *Tetrahedron,* 2010, **66**, 7642.

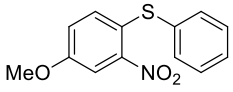
1H), 7.24 (d, J = 8.1 Hz, 1H), 7.10 (dd, J = 8.0, 1.2 Hz, 1H); FTIR (ATR, cm^{-1}): 2926, 1576, 1549, 1477, 1441, 1363, 850, 779, 749, 689; ^{13}C NMR (151 MHz, CDCl3) δ 149.3, 133.5, 132.7, 131.8, 130.8, 130.3, 129.7, 129.1, 128.5, 125.9; HRMS m/z (ESI) calcd for $C_{12}H_9{}^{35}ClNO_2S$ $[M + H]^+$ 266.0043 found 266.0033.

(4-Methyl-2-nitrophenyl)(phenyl)sulfane (3j)



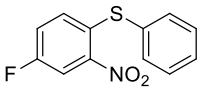
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.42 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 1.0 Hz, 1H), 7.56 (ddd, *J* = 3.7, 3.1, 1.4 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.15 (ddd, *J* = 8.3, 2.0, 0.6 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0, 135.7, 135.6, 135.5, 134.5, 131.5, 129.9, 129.7, 128.4, 125.7, 20.39; The spectral data are consistent with those reported in the literature.[8]

(4-Methoxy-2-nitrophenyl)(phenyl)sulfane (3k)



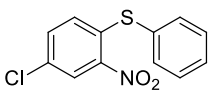
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.40 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 2.8 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.46 – 7.39 (m, 3H), 6.95 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 3.84 (s, 3H); FTIR (ATR, cm^{-1}): 3072, 2930, 2838, 1610, 1560, 1514, 1473, 1438, 1328, 1293, 1277, 1221, 1022, 800, 750, 691; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.2, 146.0, 141.8, 135.0, 132.0, 130.0, 129.8, 129.4, 121.5, 108.9, 55.8; HRMS m/z (ESI) calcd for $C_{13}H_{12}NO_3S$ $[M + H]^+$ 262.0538 found 262.0523.

(4-Fluoro-2-nitrophenyl)(phenyl)sulfane (3l)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.54 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.51 – 7.45 (m, 3H), 7.11 (ddd, *J* = 9.1, 7.2, 2.8 Hz, 1H), 6.86 (dd, *J* = 9.1, 5.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.3 (d, $^1J_{C\text{-}F}$ = 249 Hz), 145.1 (d, $^3J_{C\text{-}F}$ = 8 Hz), 135.7, 134.8 (d, $^4J_{C\text{-}F}$ = 3 Hz), 130.8, 130.2, 130.1, 130.0 (d, $^3J_{C\text{-}F}$ = 7 Hz), 121.3 (d, $^2J_{C\text{-}F}$ = 22 Hz), 112.6 (d, $^2J_{C\text{-}F}$ = 27 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7 (ddd, $^3J_{F\text{-}H}$ = 7, $^3J_{F\text{-}H}$ = 5, $^4J_{F\text{-}H}$ = 3 Hz). The spectral data are consistent with those reported in the literature.[9]

(4-Chloro-2-nitrophenyl)(phenyl)sulfane (3m)

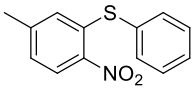


The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.50 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 82 – 84°C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 2.3 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.52 – 7.46 (m, 3H), 7.28 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (101 MHz,

(8) K. Su, Y. Qiu, Y. Yao, D. Zhang, S. Jiang, *Synlett*, 2012, **23**, 2853.
(9) J. Braun, M. M. Moeckel, T. Strittmatter, A. Marx, U. Groth, T. U. Mayer, *ACS Chem. Biol.* 2015, **10**, 554.

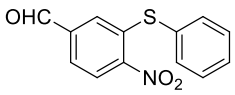
$CDCl_3$): δ = 144.9, 138.1, 135.7, 133.4, 130.6, 130.3, 130.2, 130.2, 129.3, 125.4. The spectral data are consistent with those reported in the literature.[10]

(5-Methyl-2-nitrophenyl)(phenyl)sulfane (3n)



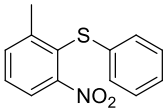
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 50/1 gradient elution) to yield the title compound (R_f = 0.60 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 88 – 90°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.4 Hz, 1H), 7.58 (ddd, *J* = 5.1, 4.0, 2.1 Hz, 2H), 7.53 – 7.43 (m, 3H), 6.99 (ddd, *J* = 8.4, 1.8, 0.6 Hz, 1H), 6.62 (d, *J* = 0.9 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.7, 142.3, 139.3, 135.8, 131.1, 130.0, 129.9, 128.3, 125.9, 125.7, 21.6. The spectral data are consistent with those reported in the literature.[7]

4-Nitro-3-(phenylthio)benzaldehyde (3n')



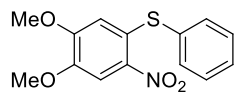
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 4/1 gradient elution) to yield the title compound (R_f = 0.15 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 114 – 116°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.58 – 7.49 (m, 3H), 7.33 (d, *J* = 1.6 Hz, 1H); FTIR (ATR, cm^{-1}): 3098, 2929, 2851, 1702, 1592, 1572, 1506, 1475, 1440, 1331, 1305, 1189, 1027, 832, 690; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.0, 147.6, 140.9, 138.6, 135.8, 130.5, 130.4, 130.2, 129.9, 126.4, 124.5; HRMS m/z (ESI) calcd for $C_{13}H_{10}NO_3S$ $[M + H]^+$ 260.0381 found 260.0379.

(2-Methyl-6-nitrophenyl)(phenyl)sulfane (3o)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.42 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 70 – 72°C;^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.14 (m, 1H), 7.11 – 7.06 (m, 2H), 2.37 (s, 3H); FTIR (ATR, cm^{-1}): 2922, 2852, 1532, 1475, 1456, 1440, 1371, 1260, 1022, 911, 736, 684; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.4, 135.3, 133.6, 132.2, 129.4, 129.1, 128.0, 126.3, 125.3, 121.0, 21.4; HRMS m/z (ESI) calcd for $C_{13}H_{12}NO_2S$ $[M + H]^+$ 246.0589 found 246.0594.

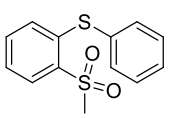
(4,5-Dimethoxy-2-nitrophenyl)(phenyl)sulfane (3p)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.30 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 110 – 112°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.64 – 7.56 (m, 2H), 7.48 (dd, *J* = 4.2, 2.4 Hz, 3H), 6.18 (s, 1H), 3.91 (s, 3H), 3.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.5, 146.3, 137.3, 135.9, 134.2, 131.5, 130.0, 129.9, 109.2, 107.8, 56.3, 55.7; FTIR (ATR, cm^{-1}): 2928, 1500, 1463, 1437, 1344, 1315, 1213, 1186, 1118, 1041, 1024, 850, 750; HRMS m/z (ESI) calcd for $C_{14}H_{14}NO_4S$ $[M + H]^+$ 292.0644 found 292.0614.

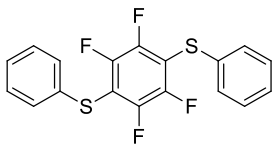
(10) B. Stump, M. Kaiser, R. Brun, R. L. Krauth-Siegel, F. Diederich, *ChemMedChem* 2007, **2**, 1708.

(2-(methylsulfonyl)phenyl)(phenyl)sulfane (3q)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 4/1 gradient elution) to yield the title compound (R_f = 0.15 in hexane/ethyl acetate = 4/1) as a white solid, m.p. = 67 – 69 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.08 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.51 (ddd, *J* = 4.4, 2.4, 1.4 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.40 – 7.35 (m, 1H), 7.33 – 7.28 (m, 1H), 7.04 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 139.5, 137.5, 134.3, 133.6, 131.9, 130.1, 129.9, 129.8, 129.2, 125.8, 41.9; FTIR (ATR, cm^{-1}): 2925, 1577, 1475, 1446, 1431, 1305, 1148, 1130, 1041, 953, 910, 777, 747, 690; HRMS m/z (ESI) calcd for $C_{13}H_{13}O_2S_2$ $[M + H]^+$ 265.0357 found 265.0354.

(Perfluoro-1,4-phenylene)bis(phenylsulfane) (3r)

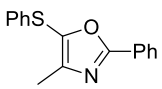


The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.50 in hexane/ethyl acetate = 8/1) as a white solid, m.p. = 109 – 111°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.38 (m, 4H), 7.35 – 7.28 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.3-148.0 (m), 145.8-145.5 (m), 132.5, 130.9, 129.3, 128.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -132.05. The spectral data are consistent with those reported in the literature.[11]

(11) C. Yu, C. Zhang, X. Shi, *Eur. J. Org. Chem.* 2012, 1953.

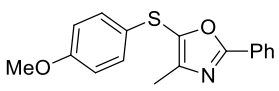
XI. Characterization of Heteroaromatic Acid Decarboxylative Coupling Products (4a-4j)

4-Methyl-2-phenyl-5-(phenylthio)oxazole (4a)



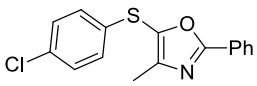
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.33 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 63 – 65°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 – 8.01 (m, 2H), 7.48 – 7.39 (m, 3H), 7.30 – 7.23 (m, 2H), 7.23 – 7.14 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.5, 145.9, 136.8, 135.3, 130.8, 129.2, 128.7, 127.4, 127.0, 126.5, 126.5, 12.3. The spectral data are consistent with those reported in the literature.[12]

5-((4-Methoxyphenyl)thio)-4-methyl-2-phenyloxazole (4b)



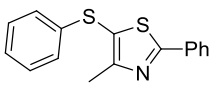
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 10/1 gradient elution) to yield the title compound (R_f = 0.25 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 – 7.99 (m, 2H), 7.44 (ddd, J = 3.6, 2.4, 1.2 Hz, 3H), 7.34 – 7.23 (m, 2H), 6.88 – 6.80 (m, 2H), 3.76 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.0, 159.1, 144.4, 138.5, 130.9, 130.6, 128.7, 127.1, 126.4, 125.3, 114.8, 55.3, 12.3; FTIR (ATR, cm^{-1}): 2956, 2835, 1738, 1589, 1542, 1492, 1448, 1376, 1287, 1250, 1172, 1122, 1027, 822, 713, 689; HRMS m/z (ESI) calcd for $C_{17}H_{16}NO_2S$ $[M + H]^+$ 298.0902 found 298.0883.

5-((4-Chlorophenyl)thio)-4-methyl-2-phenyloxazole (4c)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.32 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 86 – 88°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 – 7.97 (m, 2H), 7.54 – 7.40 (m, 3H), 7.29 – 7.21 (m, 2H), 7.19 – 7.10 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.7, 146.1, 136.3, 133.8, 132.7, 130.9, 129.3, 128.8, 128.7, 126.9, 126.5, 12.2; FTIR (ATR, cm^{-1}): 3061, 2970, 1738, 1474, 1377, 1337, 1217, 1125, 1088, 1069, 1012, 815, 712, 685; HRMS m/z (ESI) calcd for $C_{16}H_{13}{}^{35}ClNOS$ $[M + H]^+$ 302.0406 found 302.0405.

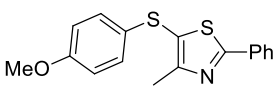
4-Methyl-2-phenyl-5-(phenylthio)thiazole (4d)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.31 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.88 (m, 2H), 7.46 – 7.40 (m, 3H), 7.31 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 159.9, 137.2, 133.3, 130.4, 129.1, 128.9, 126.9, 126.4, 126.1, 120.2, 15.7; FTIR (ATR, cm^{-1}): 3059, 2922, 1737, 1581, 1477, 1454, 1438, 1370, 1230, 1061, 1023, 1000, 984, 761, 736, 686; HRMS m/z (ESI) calcd for $C_{16}H_{14}NS_2$ $[M + H]^+$ 284.0568 found 284.0559.

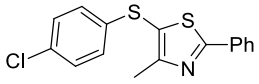
5-((4-Methoxyphenyl)thio)-4-methyl-2-phenylthiazole (4e)

(12) J. D. Kreisberg, P. Magnus, S. Shinde, *Tetrahedron Lett.*, 2002, **43**, 7393.



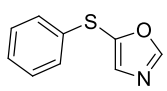
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 10/1 gradient elution) to yield the title compound (R_f = 0.22 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.83 (m, 2H), 7.47 – 7.35 (m, 3H), 7.29 – 7.20 (m, 2H), 6.89 – 6.80 (m, 2H), 3.78 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 158.9, 158.1, 133.4, 130.6, 130.2, 128.8, 127.4, 126.3, 123.0, 114.8, 55.3, 15.7; FTIR (ATR, cm^{-1}): 3062, 2999, 2938, 1737, 1591, 1491, 1454, 1287, 1242, 1172, 1029, 821, 760, 687; HRMS m/z (ESI) calcd for $C_{17}H_{16}NOS_2$ $[M + H]^+$ 314.0673 found 314.0673.

5-((4-Chlorophenyl)thio)-4-methyl-2-phenylthiazole (4f)



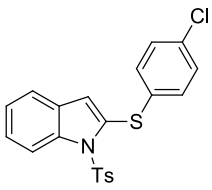
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.30 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 – 7.88 (m, 2H), 7.45 (ddt, *J* = 4.4, 2.2, 1.2 Hz, 3H), 7.25 (dt, *J* = 4.8, 2.8 Hz, 3H), 7.15 – 7.08 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.3, 160.1, 135.7, 133.2, 132.2, 130.5, 129.2, 129.0, 128.1, 126.4, 119.6, 15.7; FTIR (ATR, cm^{-1}): 3063, 2923, 2854, 1738, 1474, 1370, 1230, 1090, 1010, 811, 760, 687; HRMS m/z (ESI) calcd for $C_{16}H_{13}{}^{35}ClNS_2$ $[M + H]^+$ 318.0178 found 318.0173.

5-(Phenylthio)oxazole (4g)



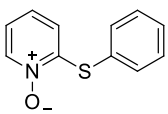
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 10/1 gradient elution) to yield the title compound (R_f = 0.20 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.37 (s, 1H), 7.33 – 7.22 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.3, 133.7, 133.0, 129.3, 128.9, 127.3; FTIR (ATR, cm^{-1}): 3016, 2970, 1738, 1472, 1365, 1228, 1217, 1099, 1066, 943, 910, 843, 740, 688; HRMS m/z (ESI) calcd for C_9H_8NOS $[M + H]^+$ 178.0327 found 178.0443.

2-((4-Chlorophenyl)thio)-N-tosylindole (4h)



The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.35 in hexane/ethyl acetate = 8/1) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.38 – 7.32 (m, 1H), 7.29 – 7.13 (m, 7H), 6.50 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0, 138.2, 135.5, 133.7, 133.1, 131.7, 131.6, 129.6, 129.3, 129.1, 127.0, 125.1, 123.7, 120.2, 116.9, 114.9, 21.5; FTIR (ATR, cm^{-1}): 3063, 2970, 1596, 1474, 1439, 1370, 1224, 1171, 1123, 1086, 1011, 809, 744, 675; HRMS m/z (ESI) calcd for $C_{21}H_{17}{}^{35}ClNO_2S_2$ $[M + H]^+$ 414.0389 found 414.0392.

2-(Phenylthio)pyridine 1-oxide (4i)

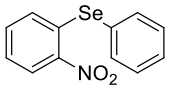


The crude mixture was purified by silica column chromatography (ethyl acetate/methanol = 20/1) to yield the title compound (R_f = 0.25 in dichloromethane/methanol = 10/1) as a lemon-yellow solid, m.p. = 110 – 112^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (dd, *J* = 6.2, 1.3 Hz, 1H), 7.60

(ddd, J = 5.5, 4.5, 2.6 Hz, 2H), 7.54 – 7.41 (m, 3H), 7.00 (pd, J = 7.5, 1.8 Hz, 2H), 6.50 (dd, J = 7.9, 2.2 Hz, 1H); FTIR (ATR, cm^{-1}): 3099, 2923, 1463, 1443, 1412, 1265, 1249, 1224, 1139, 1083, 1024, 941, 838, 751, 687; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.0, 138.2, 136.0, 130.3, 130.1, 128.4, 125.6, 121.9, 120.5; HRMS m/z (ESI) calcd for $C_{11}H_{10}NOS$ $[M + 2H]^{2+}$ 205.0561 found 205.0517.

XII. Characterization of Selenide Coupling Product

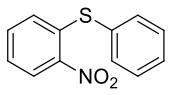
(2-Nitrophenyl)(phenyl)selane (5)



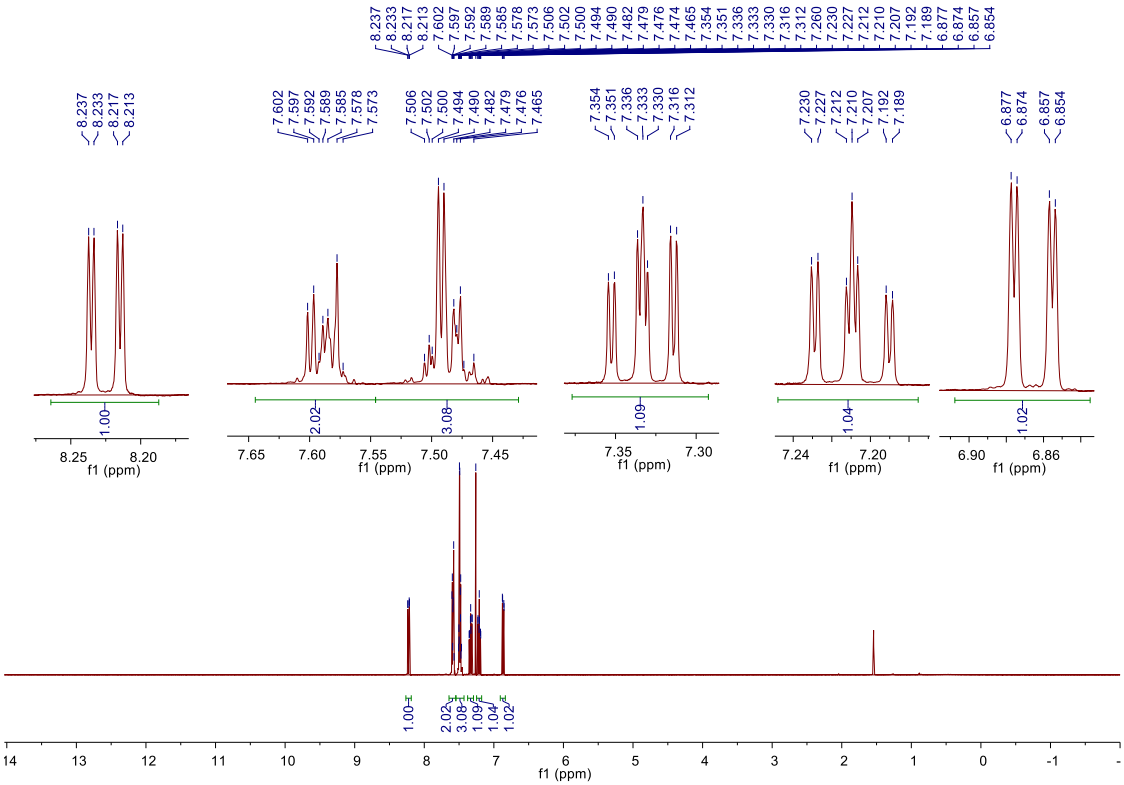
The crude mixture was purified by silica column chromatography (hexane to hexane/ethyl acetate = 20/1 gradient elution) to yield the title compound (R_f = 0.40 in hexane/ethyl acetate = 8/1) as a yellow solid, m.p. = 90 – 92°C; (600 MHz, $CDCl_3$) δ = 8.30 (dd, J = 8.1, 1.6 Hz, 1H), 7.70 (dt, J = 8.2, 1.7 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.47 – 7.42 (m, 2H), 7.27 (dddd, J = 9.5, 7.1, 5.1, 1.5 Hz, 2H), 6.99 (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.5, 137.3, 135.8, 133.6, 130.2, 130.0, 129.8, 128.1, 126.0, 125.7. The spectral data are consistent with those reported in the literature.[13]

(13) J.-M. Becht, C. Drian, *J. Org. Chem.,* 2011, **76**, 6327.

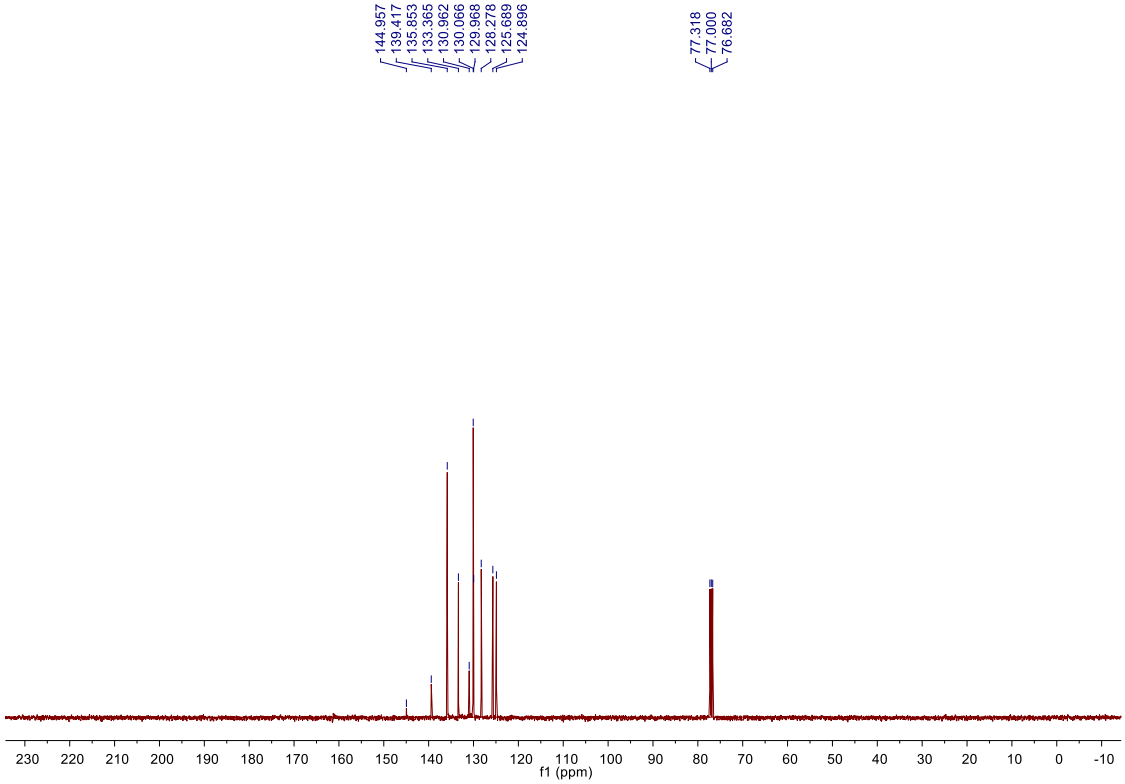
XIII. ^{1}H and ^{13}C NMR Spectra of Coupling Products (3, 4, and 5).



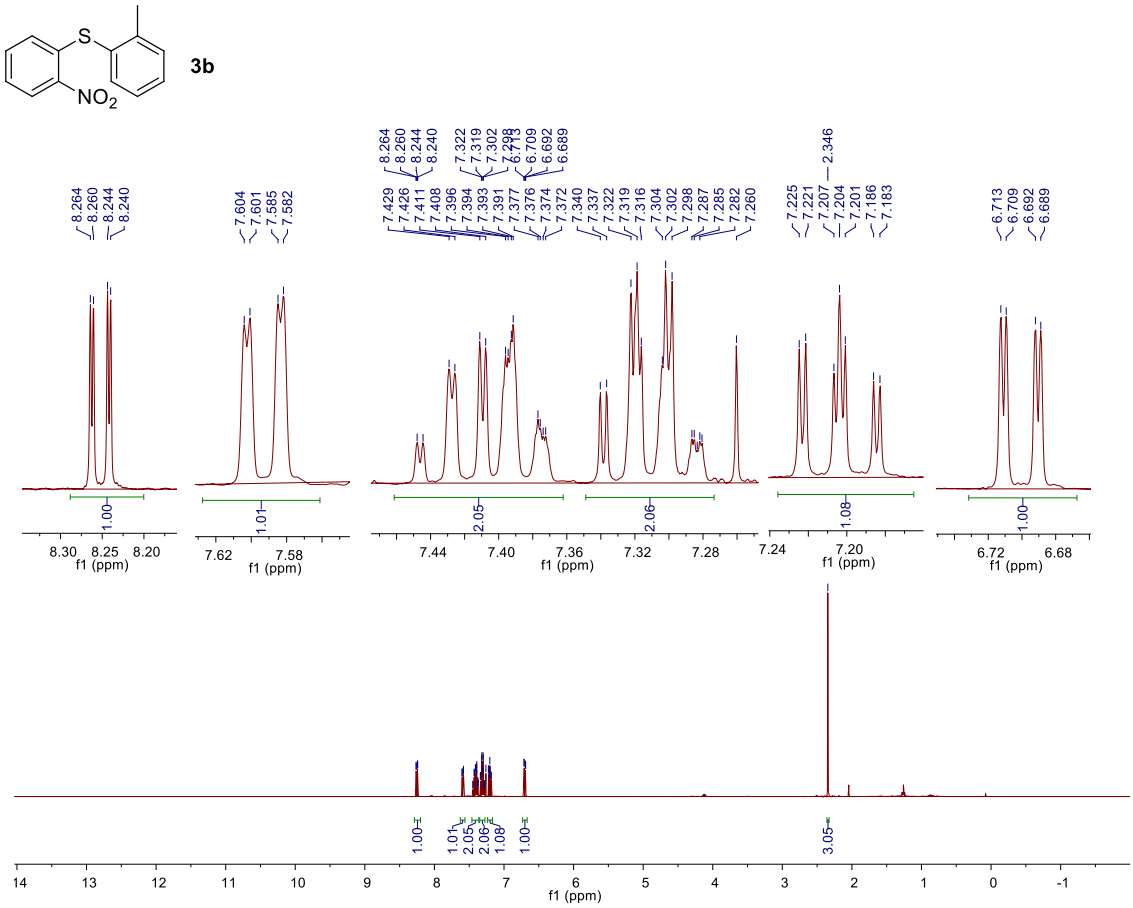
3a



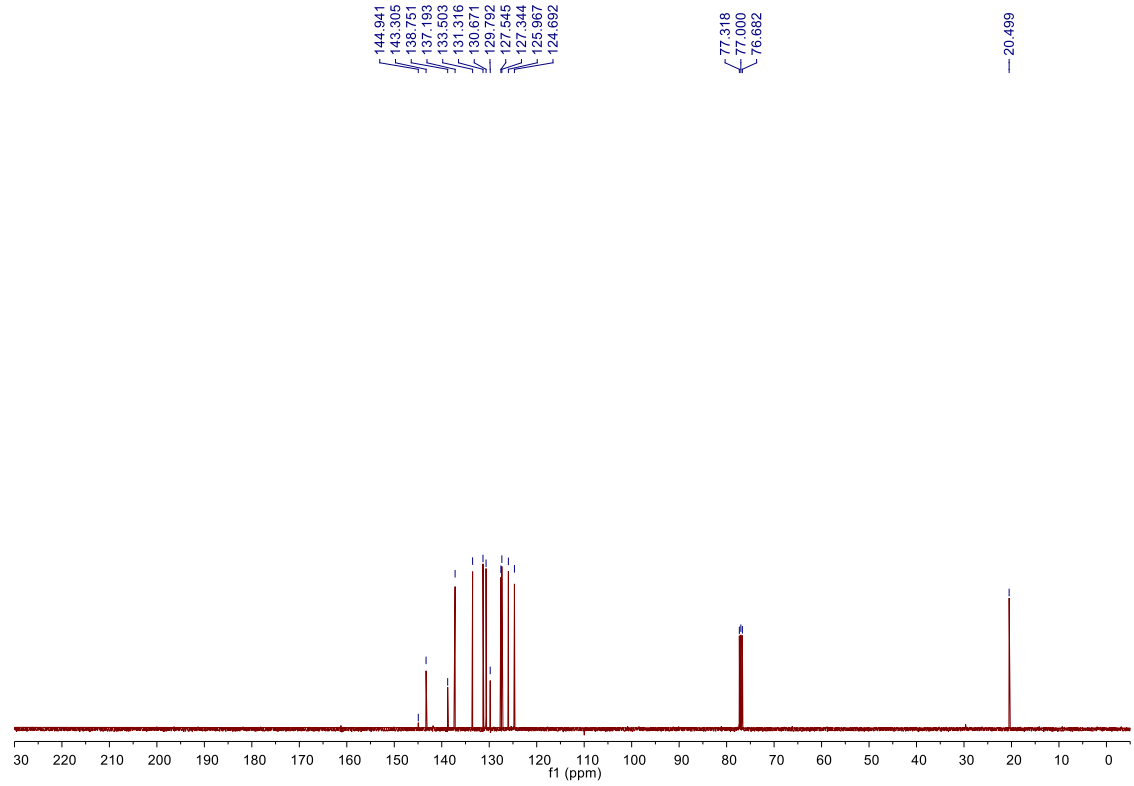
^{1}H NMR spectrum of **(2-nitrophenyl)(phenyl)sulfane** (**3a**) in $CDCl_3$ at 400 MHz.



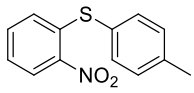
^{13}C NMR spectrum of **(2-nitrophenyl)(phenyl)sulfane** (**3a**) in $CDCl_3$ at 101 MHz.



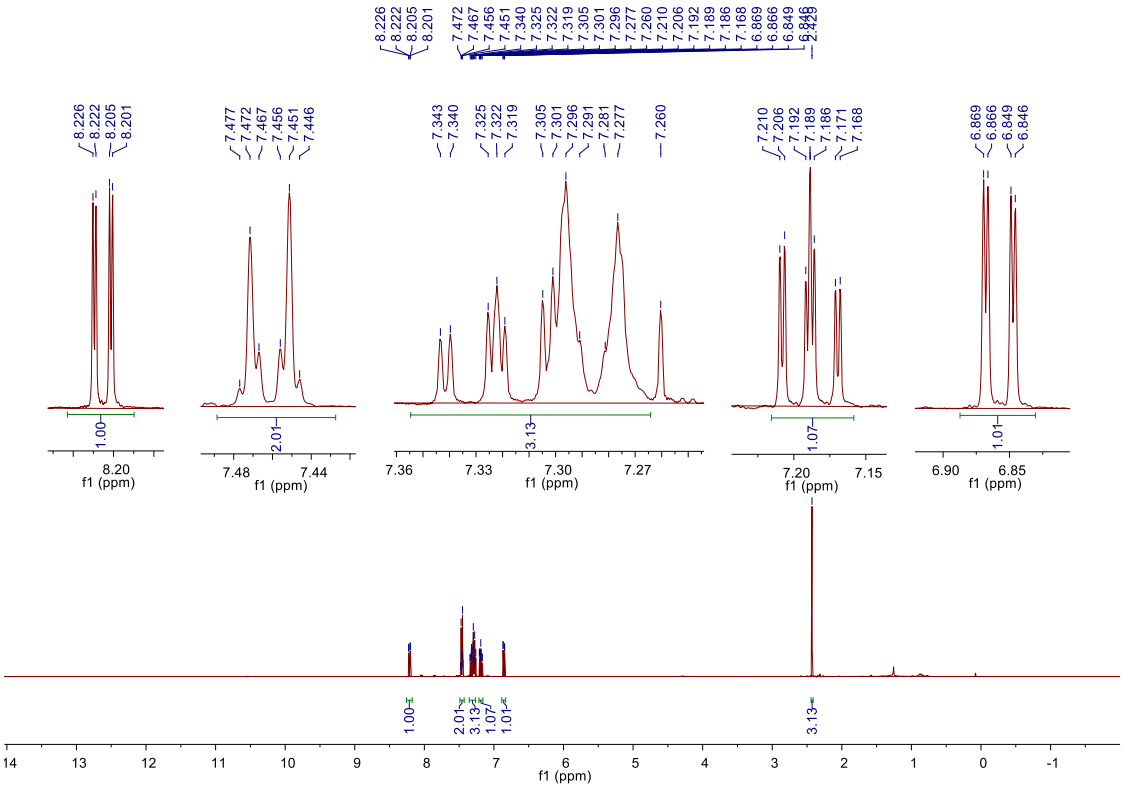
^{1}H NMR spectrum of **(2-nitrophenyl)(p-tolyl)sulfane (3b)** in $CDCl_3$ at 400 MHz.



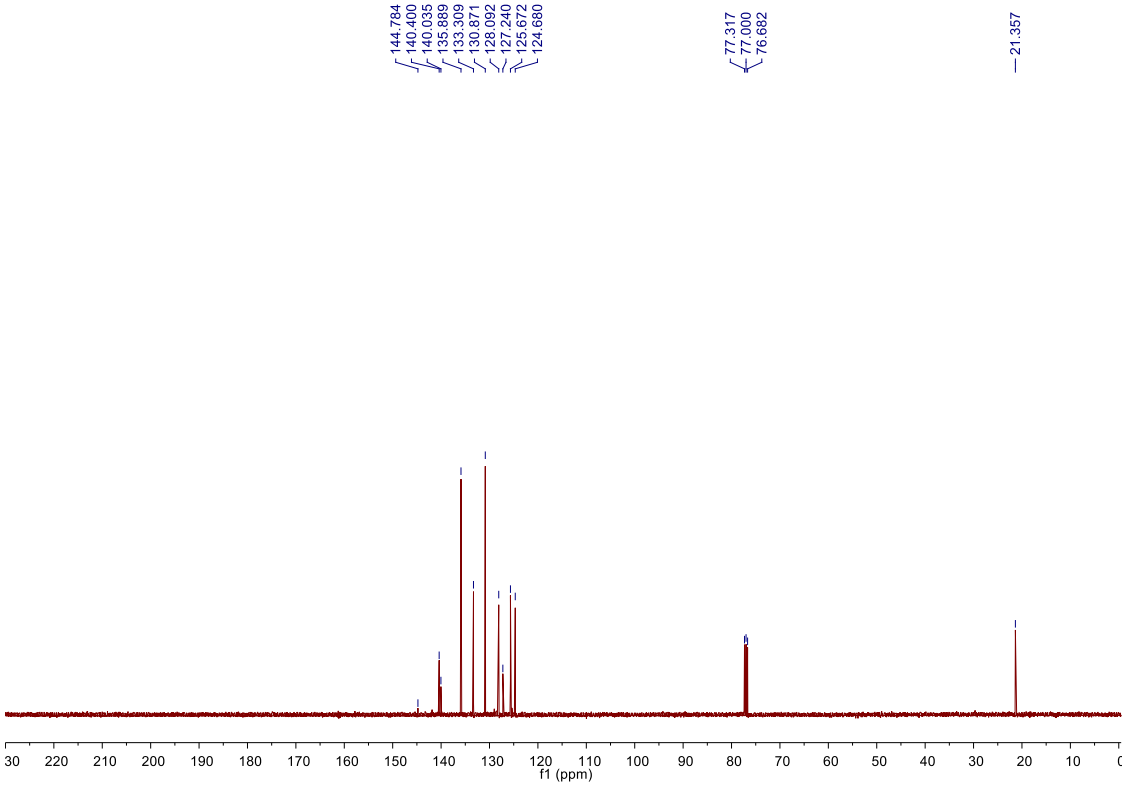
^{13}C NMR spectrum of **(2-nitrophenyl)(p-tolyl)sulfane (3b)** in $CDCl_3$ at 101 MHz.



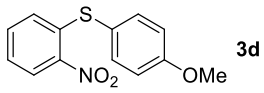
3c



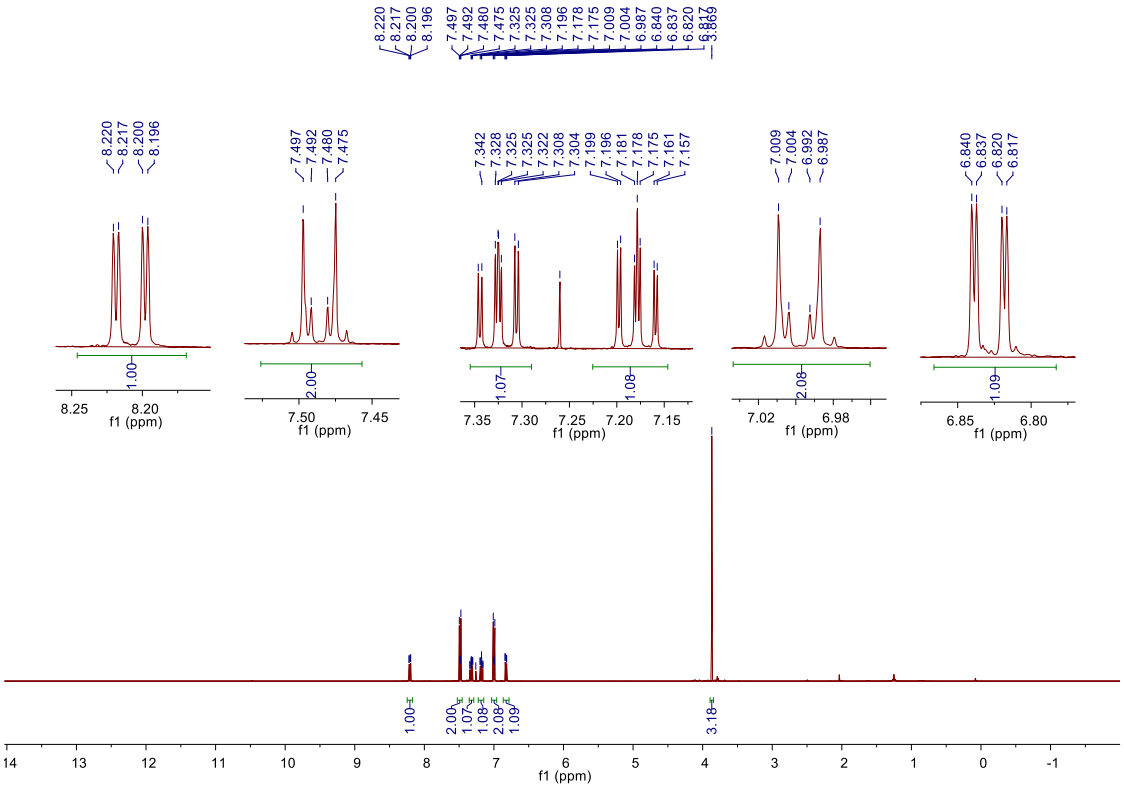
^{1}H NMR spectrum of **(2-nitrophenyl)(p-tolyl)sulfane (3c)** in $CDCl_3$ at 400 MHz.



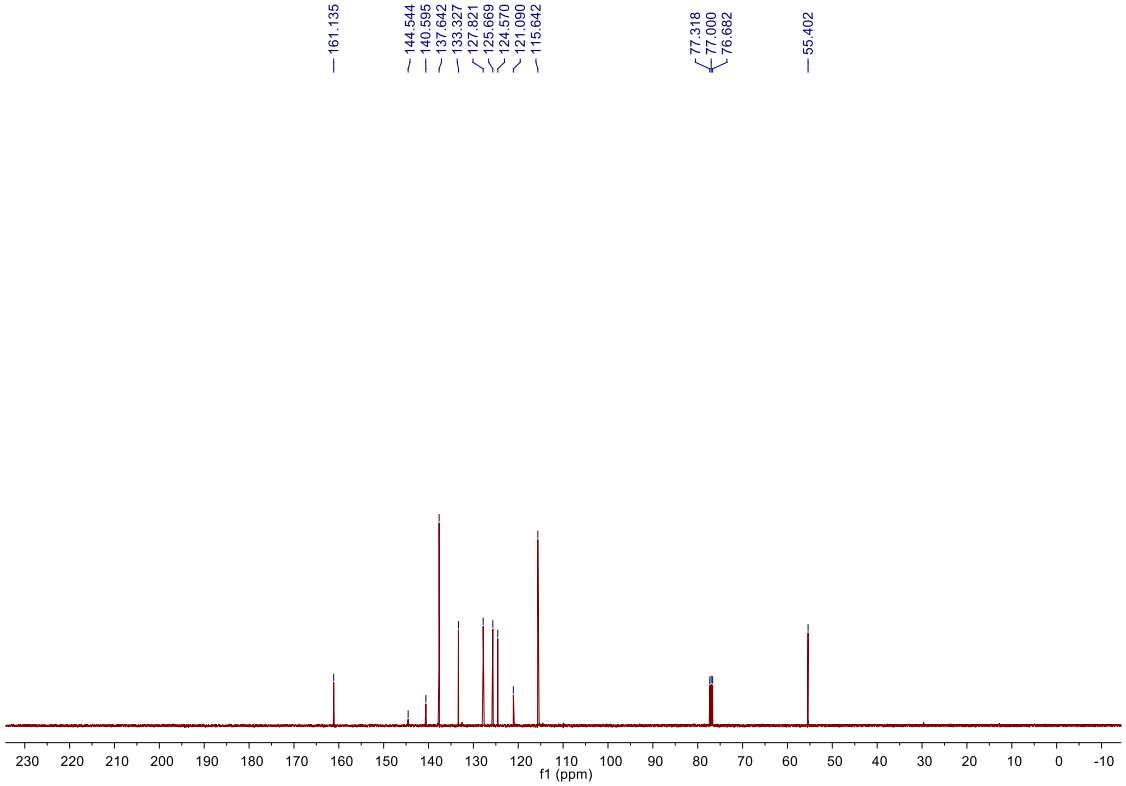
^{13}C NMR spectrum of **(2-nitrophenyl)(p-tolyl)sulfane (3c)** in $CDCl_3$ at 101 MHz.



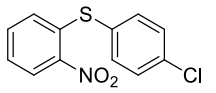
3d



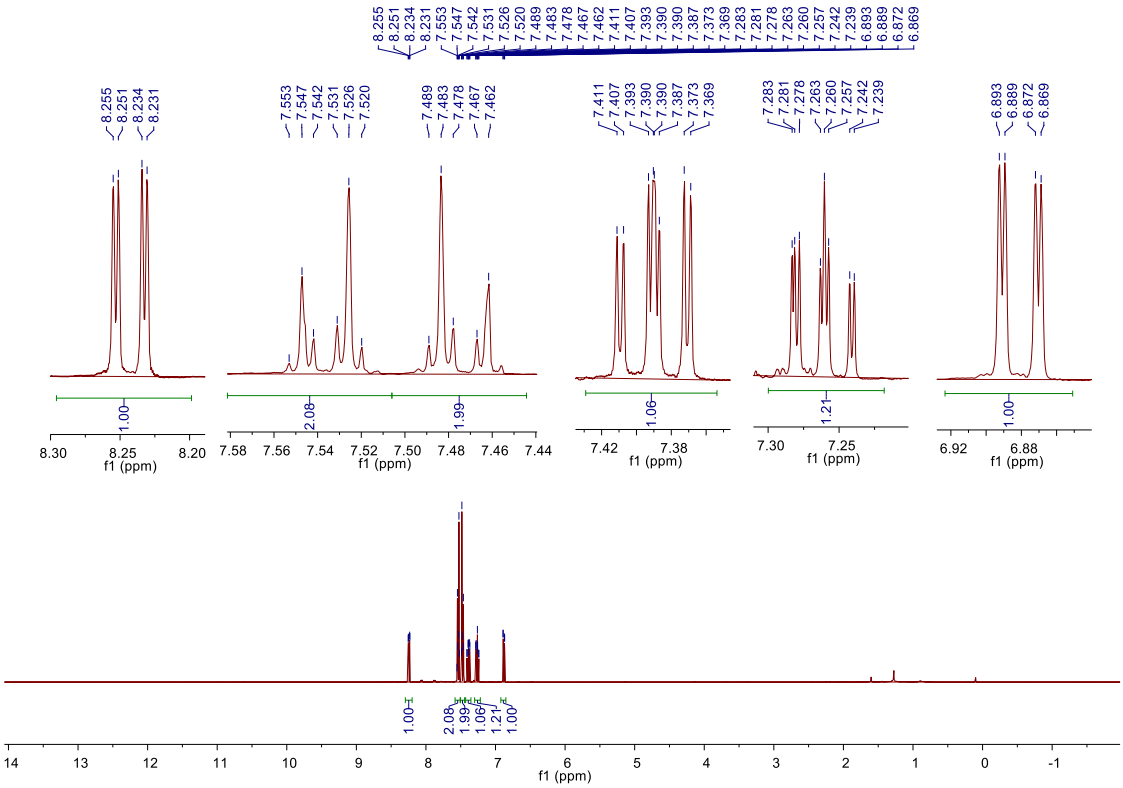
^{1}H NMR spectrum of **(4-methoxyphenyl)(2-nitrophenyl)sulfane (3d)** in $CDCl_3$ at 400 MHz.



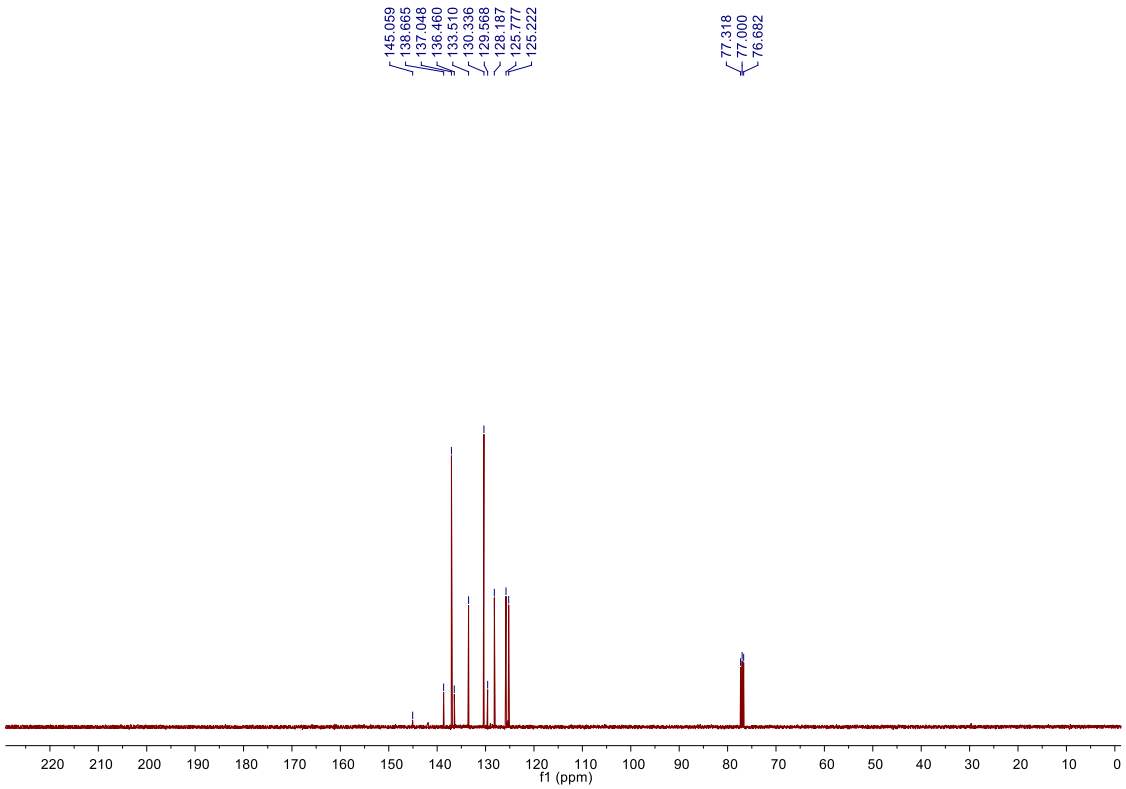
^{13}C NMR spectrum of **(4-methoxyphenyl)(2-nitrophenyl)sulfane (3d)** in $CDCl_3$ at 101 MHz.



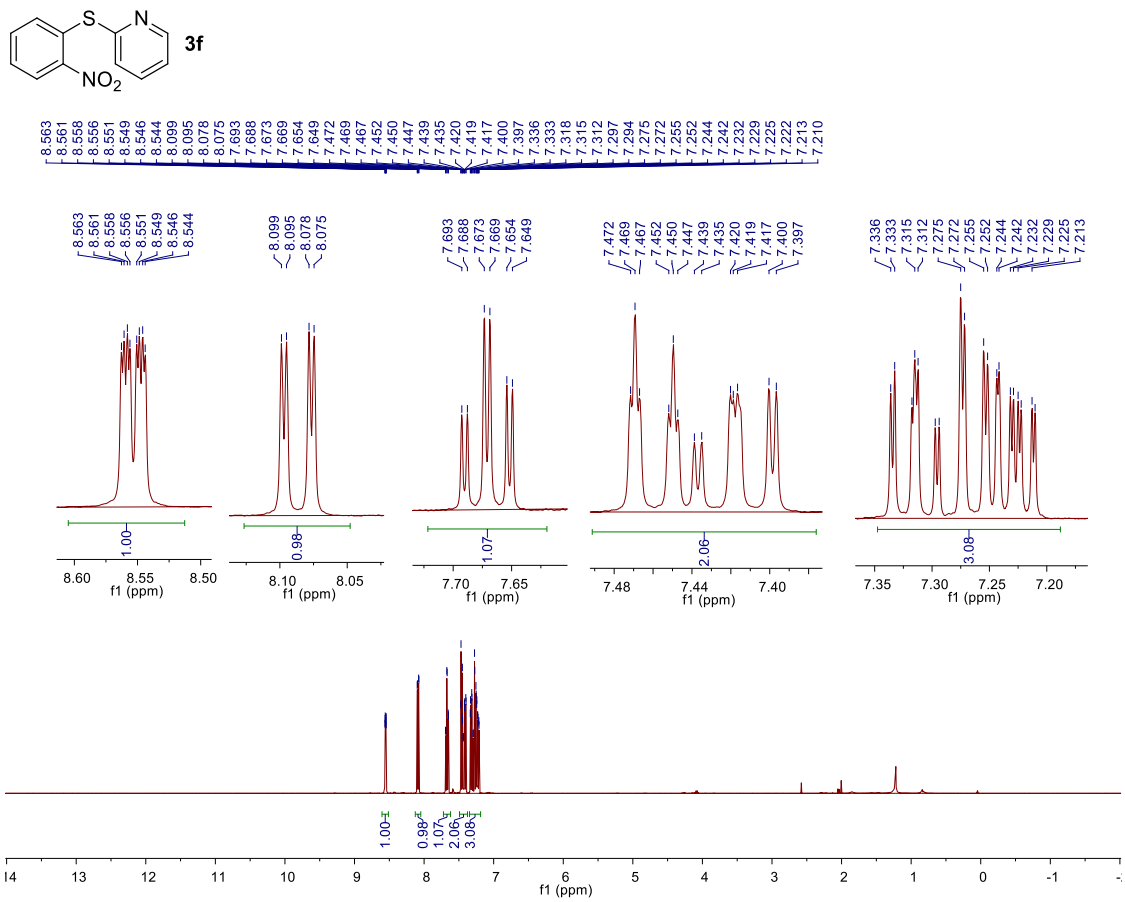
3e



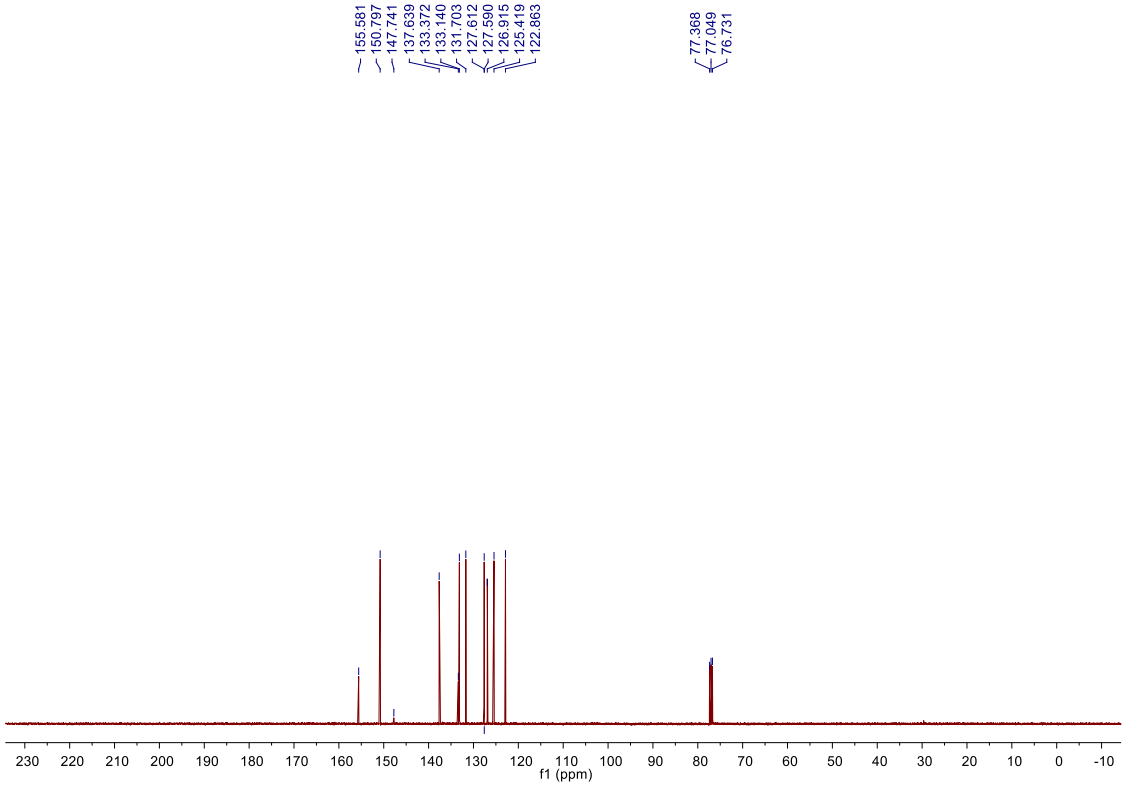
^{1}H NMR spectrum of **(4-chlorophenyl)(2-nitrophenyl)sulfane (3e)** in $CDCl_3$ at 400 MHz.



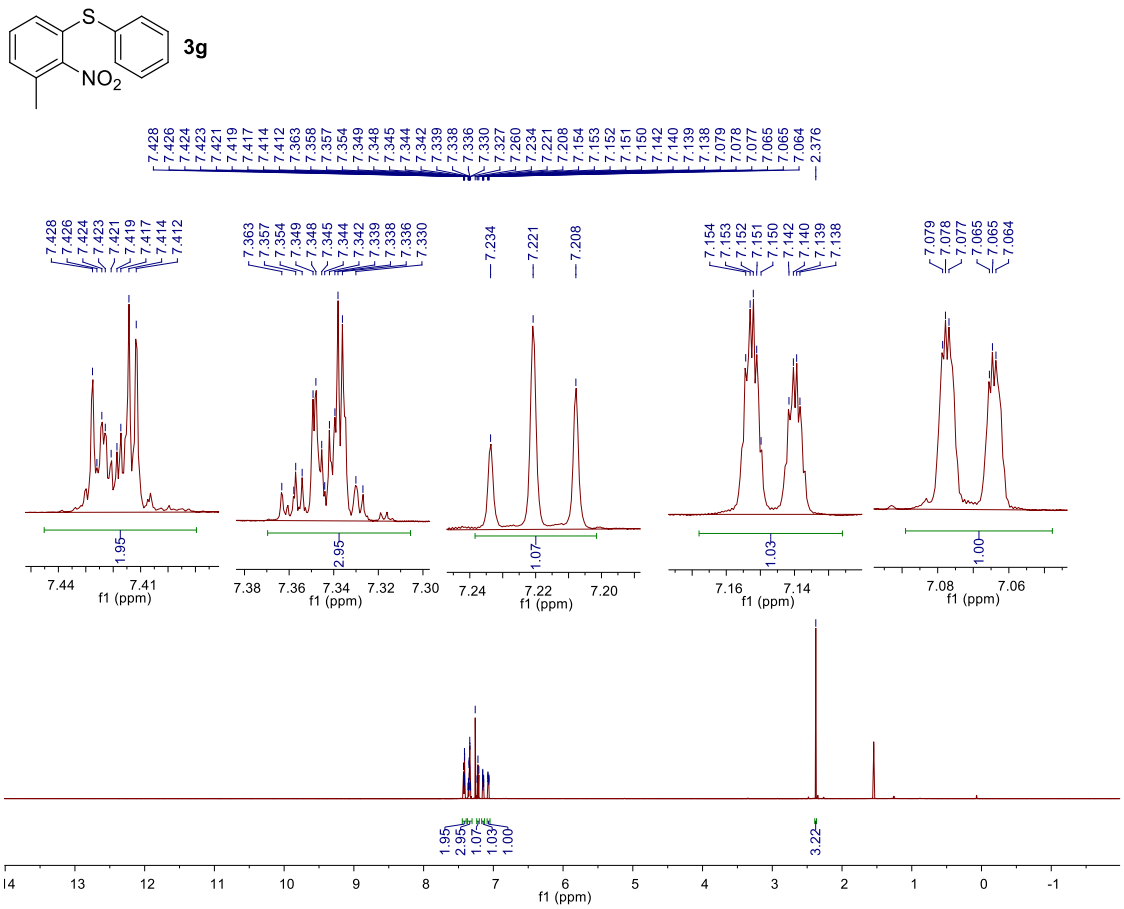
^{13}C NMR spectrum of **(4-chlorophenyl)(2-nitrophenyl)sulfane (3e)** in $CDCl_3$ at 101 MHz.



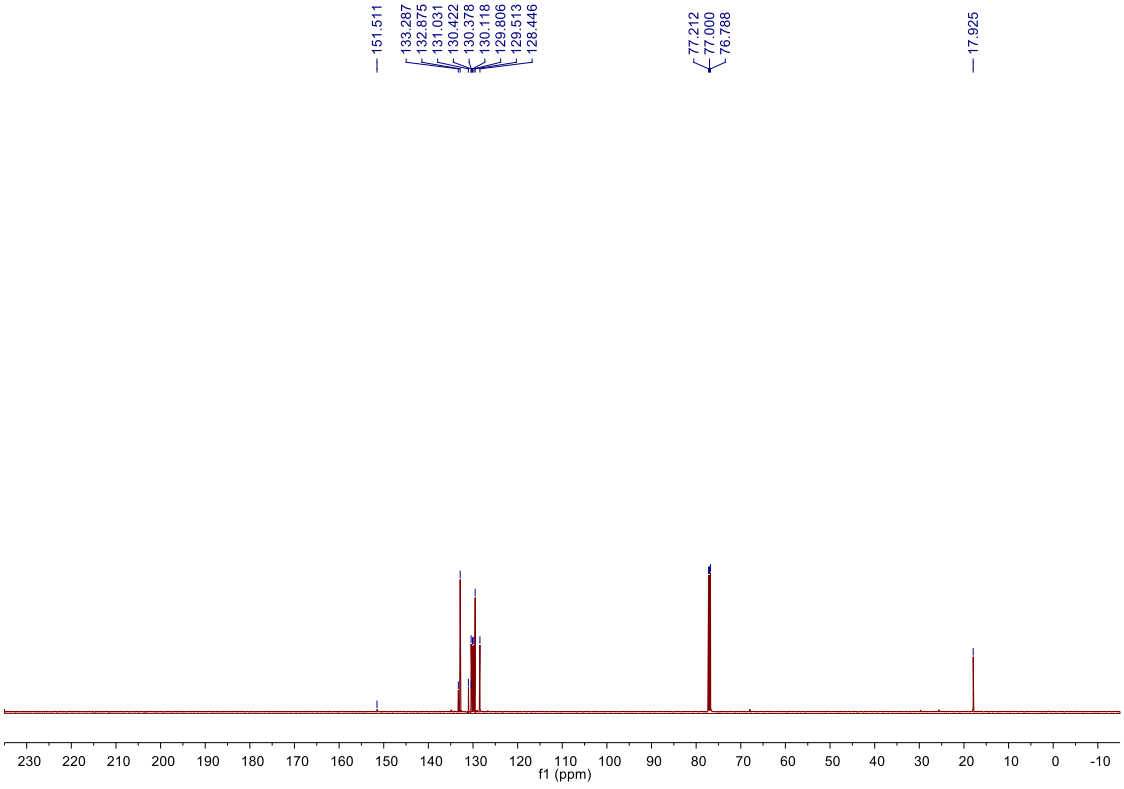
^{1}H NMR spectrum of **2-((2-nitrophenyl)thio)pyridine (3f)** in $CDCl_3$ at 400 MHz.



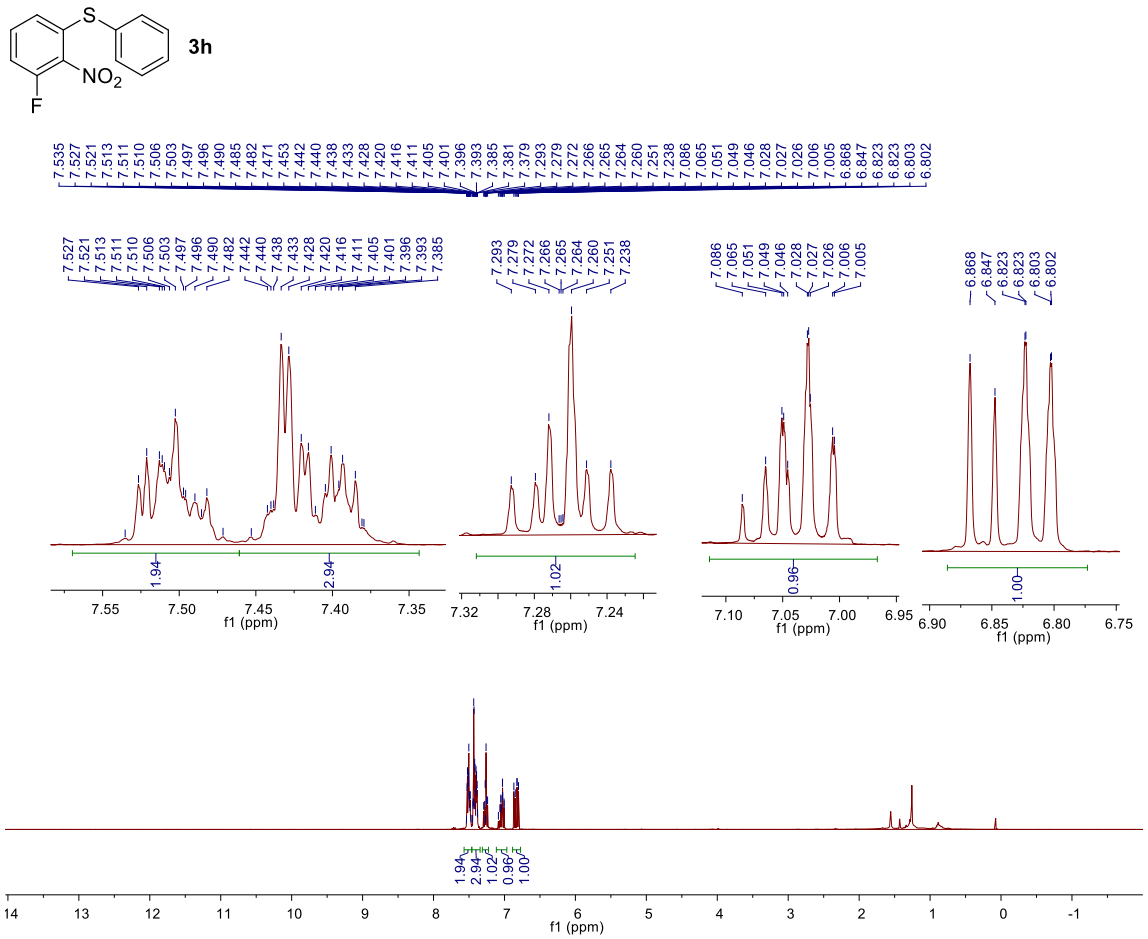
^{13}C NMR spectrum of **2-((2-nitrophenyl)thio)pyridine (3f)** in $CDCl_3$ at 101 MHz



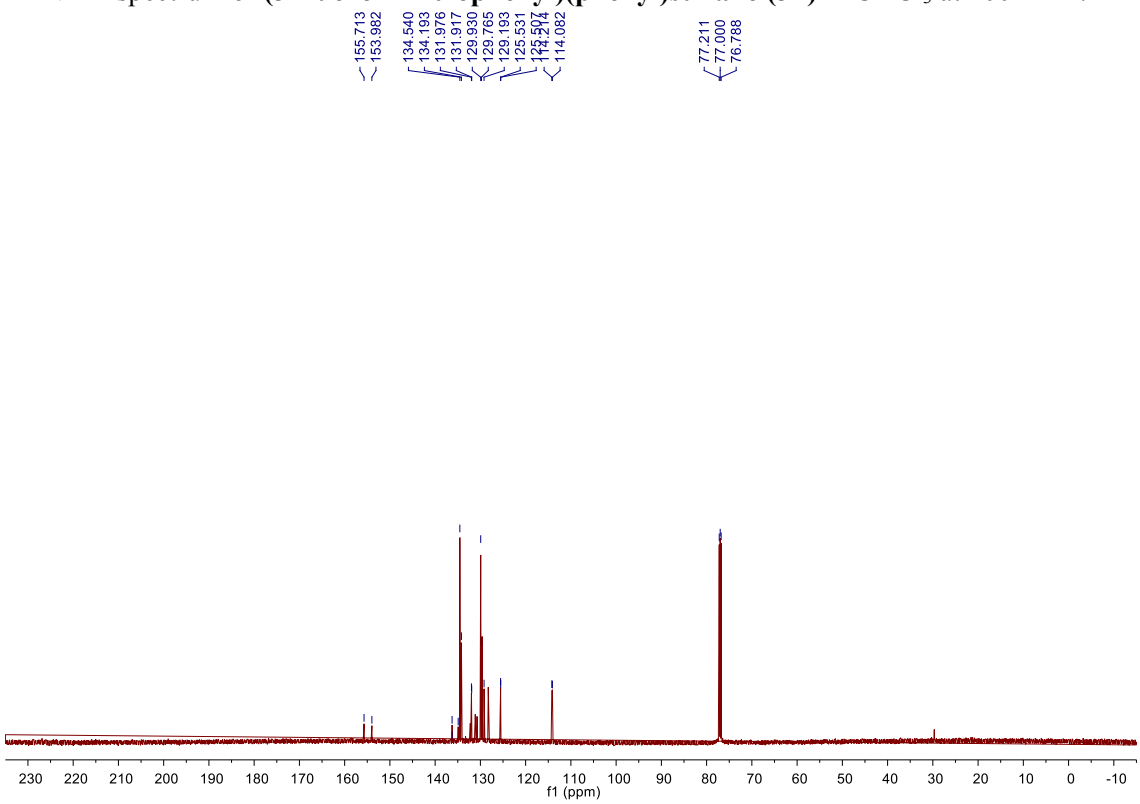
^{1}H NMR spectrum of **(3-methyl-2-nitrophenyl)(phenyl)sulfane (3g)** in $CDCl_3$ at 600 MHz.



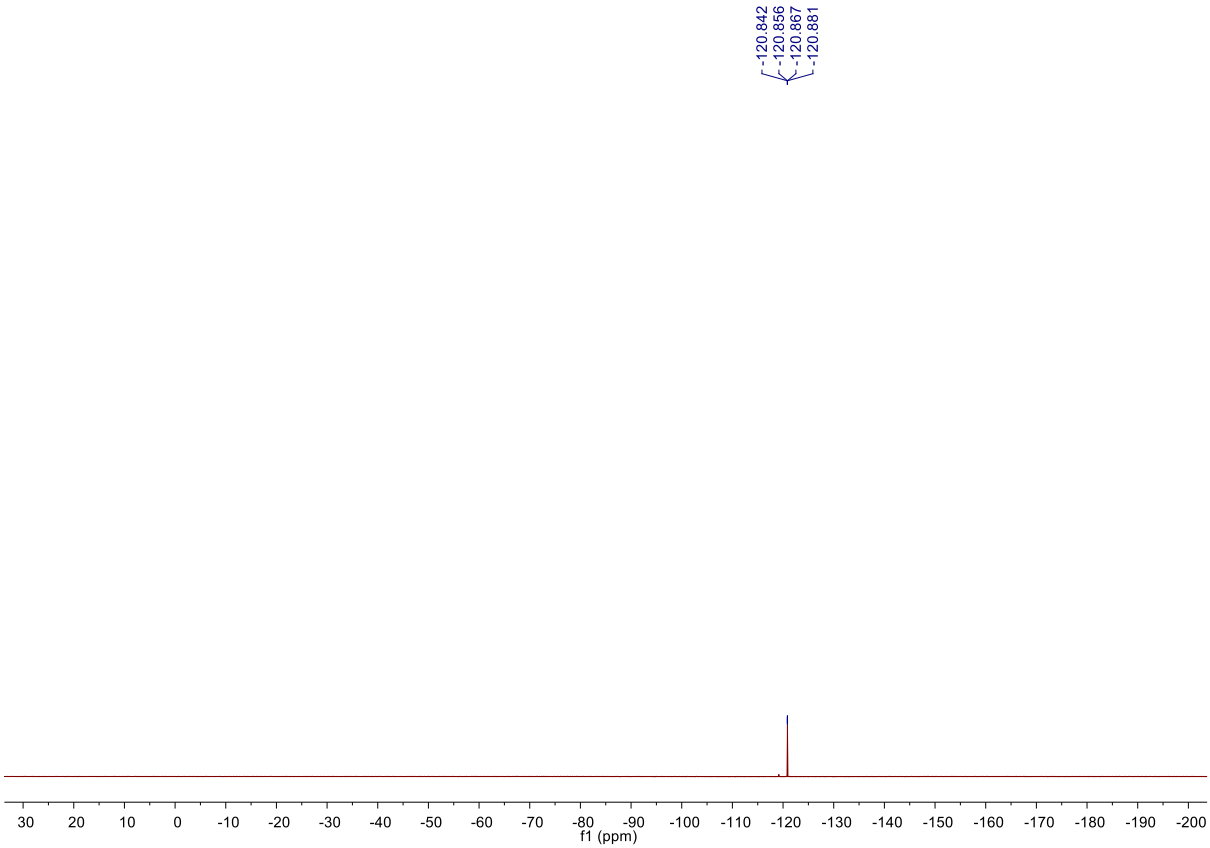
^{13}C NMR spectrum of **(3-methyl-2-nitrophenyl)(phenyl)sulfane (3g)** in $CDCl_3$ at 151 MHz.



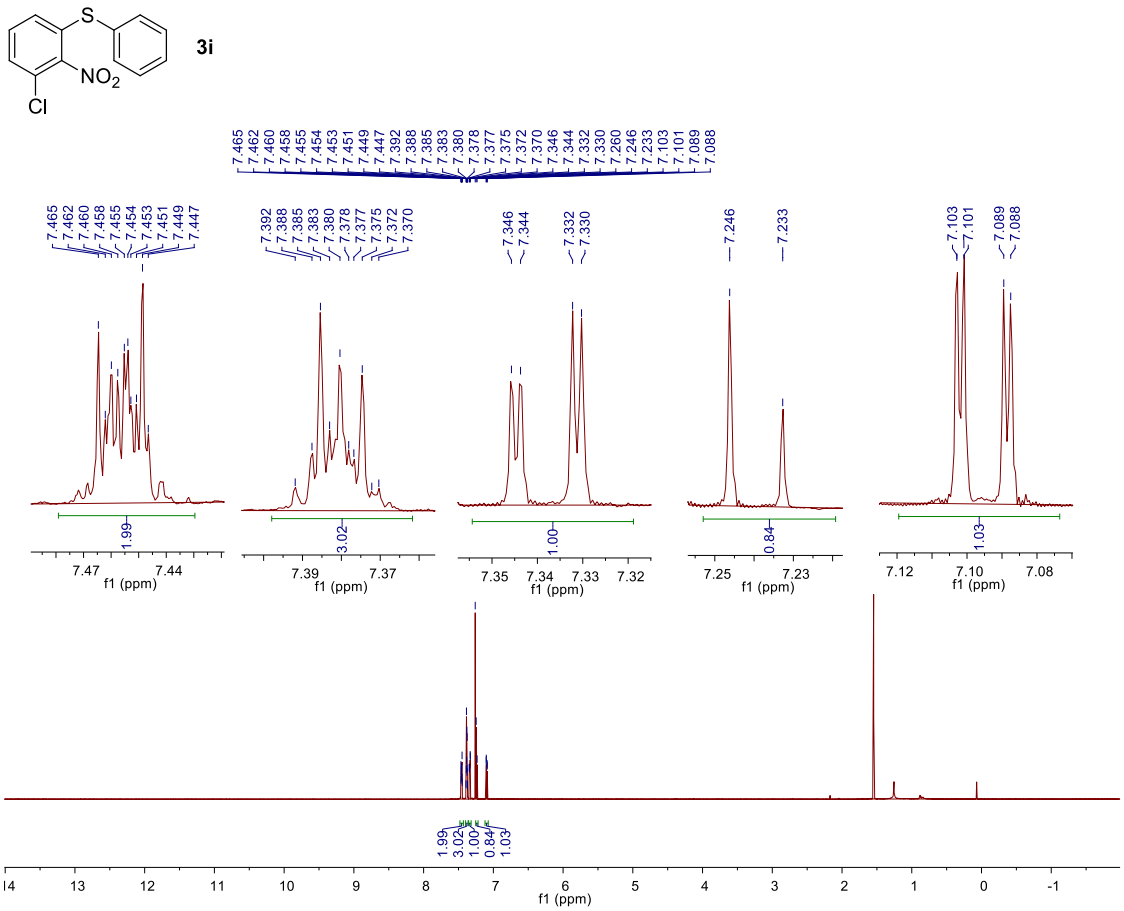
^{1}H NMR spectrum of **(3-fluoro-2-nitrophenyl)(phenyl)sulfane (3h)** in $CDCl_3$ at 400 MHz.



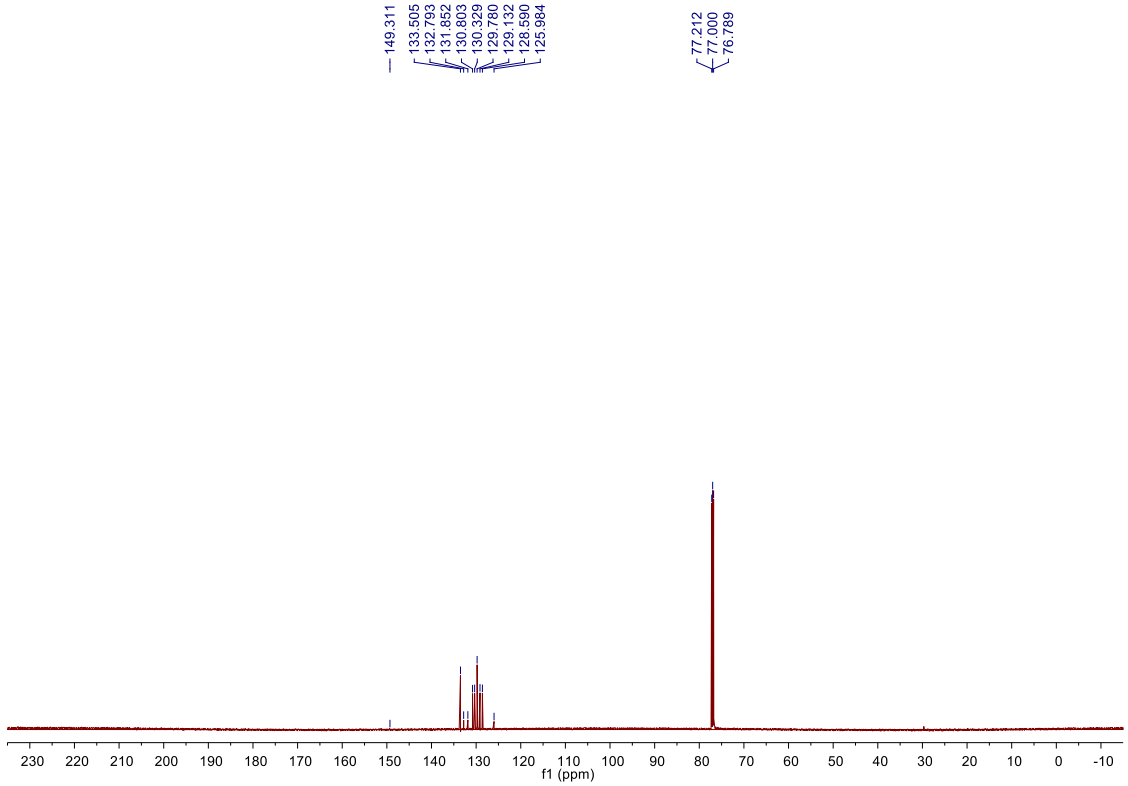
^{13}C NMR spectrum of **(3-fluoro-2-nitrophenyl)(phenyl)sulfane (3h)** in $CDCl_3$ at 101 MHz.



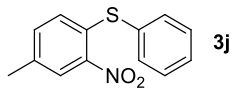
^{19}F NMR spectrum of **(3-fluoro-2-nitrophenyl)(phenyl)sulfane (3h)** in $CDCl_3$ at 376 MHz.



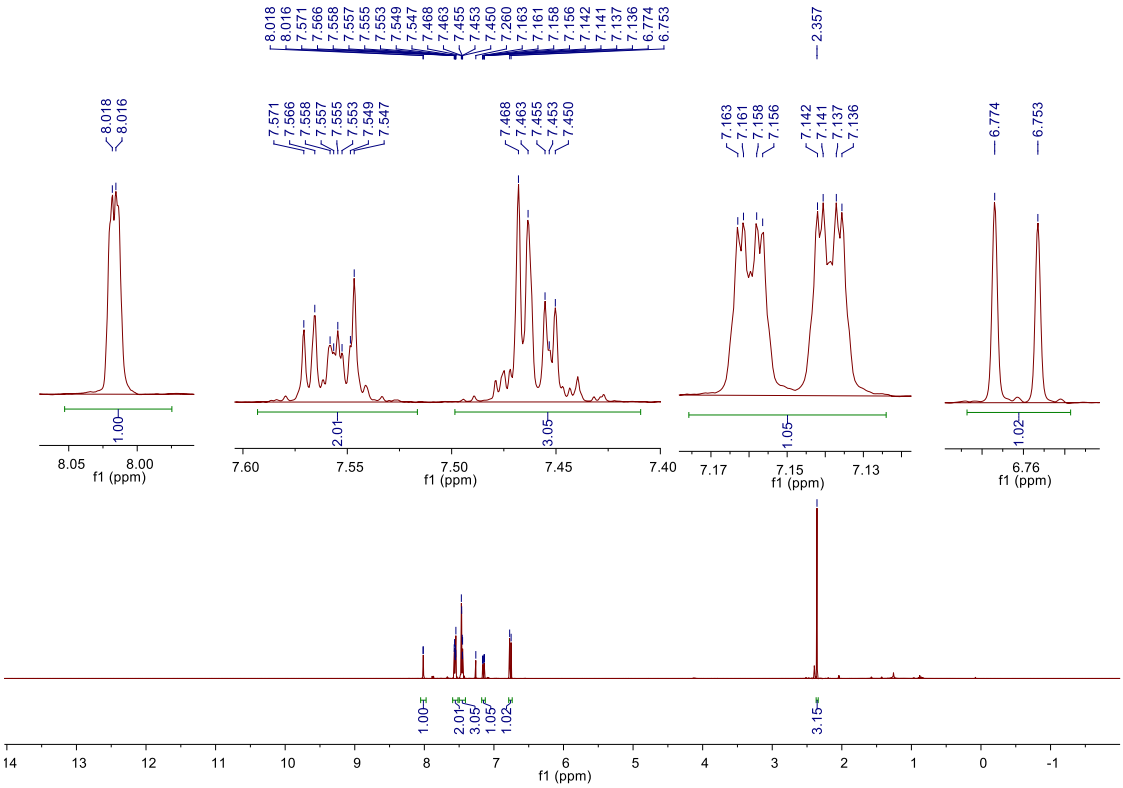
^{1}H NMR spectrum of **(3-chloro-2-nitrophenyl)(phenyl)sulfane (3i)** in $CDCl_3$ at 600 MHz.



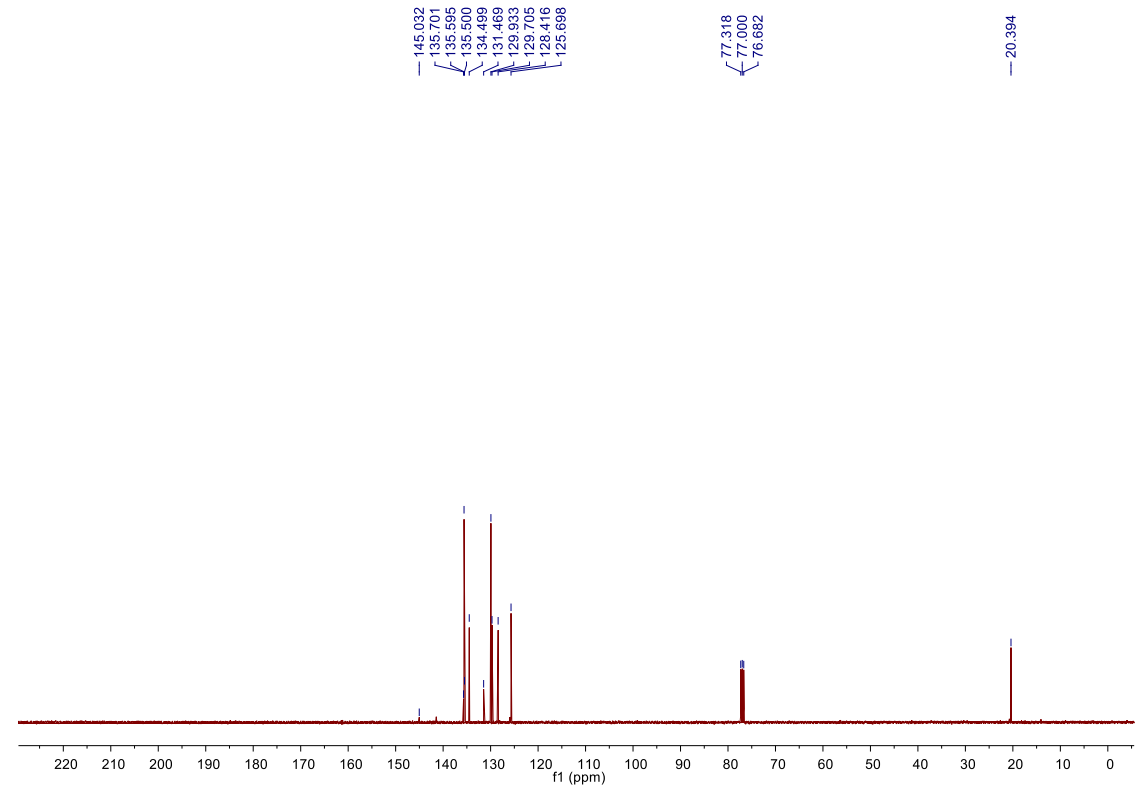
^{13}C NMR spectrum of **(3-chloro-2-nitrophenyl)(phenyl)sulfane (3i)** in $CDCl_3$ at 151 MHz.



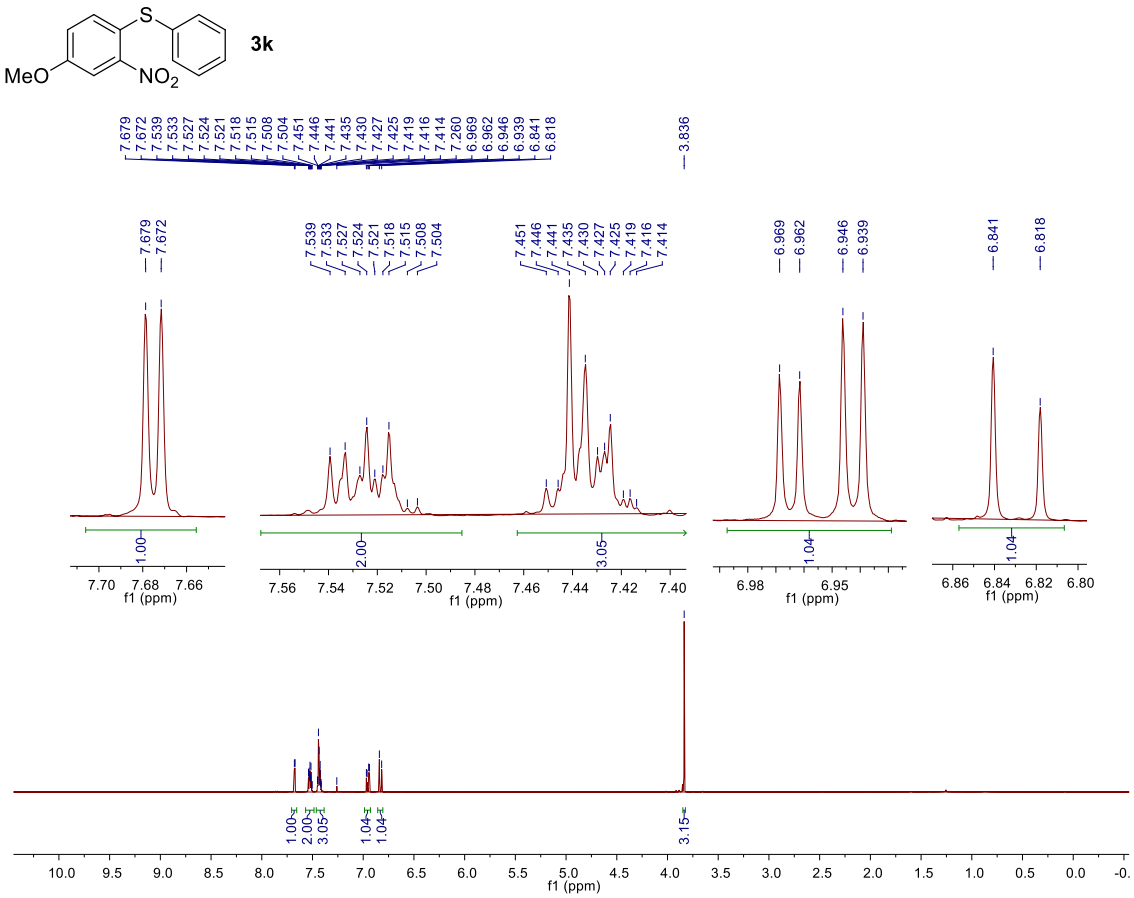
3j



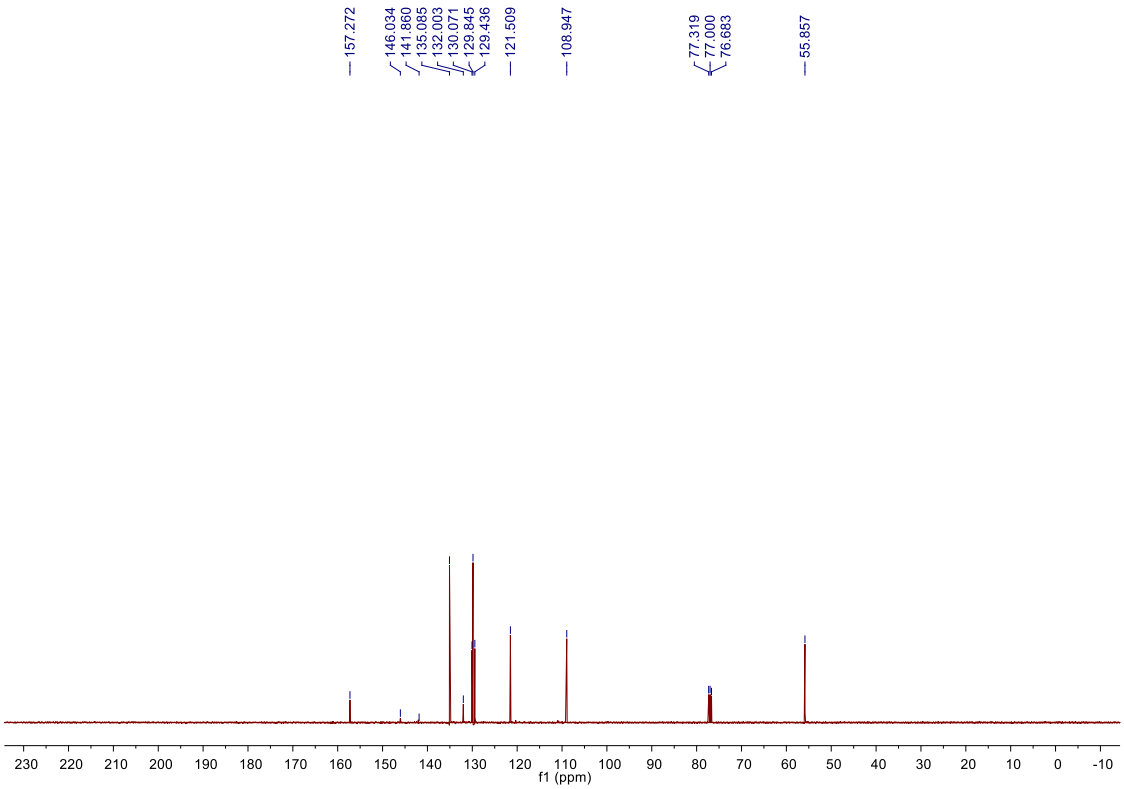
^{1}H NMR spectrum of **(4-methyl-2-nitrophenyl)(phenyl)sulfane (3j)** in $CDCl_3$ at 400 MHz.



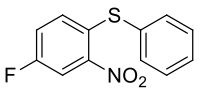
^{13}C NMR spectrum of **(4-methyl-2-nitrophenyl)(phenyl)sulfane (3j)** in $CDCl_3$ at 101 MHz.



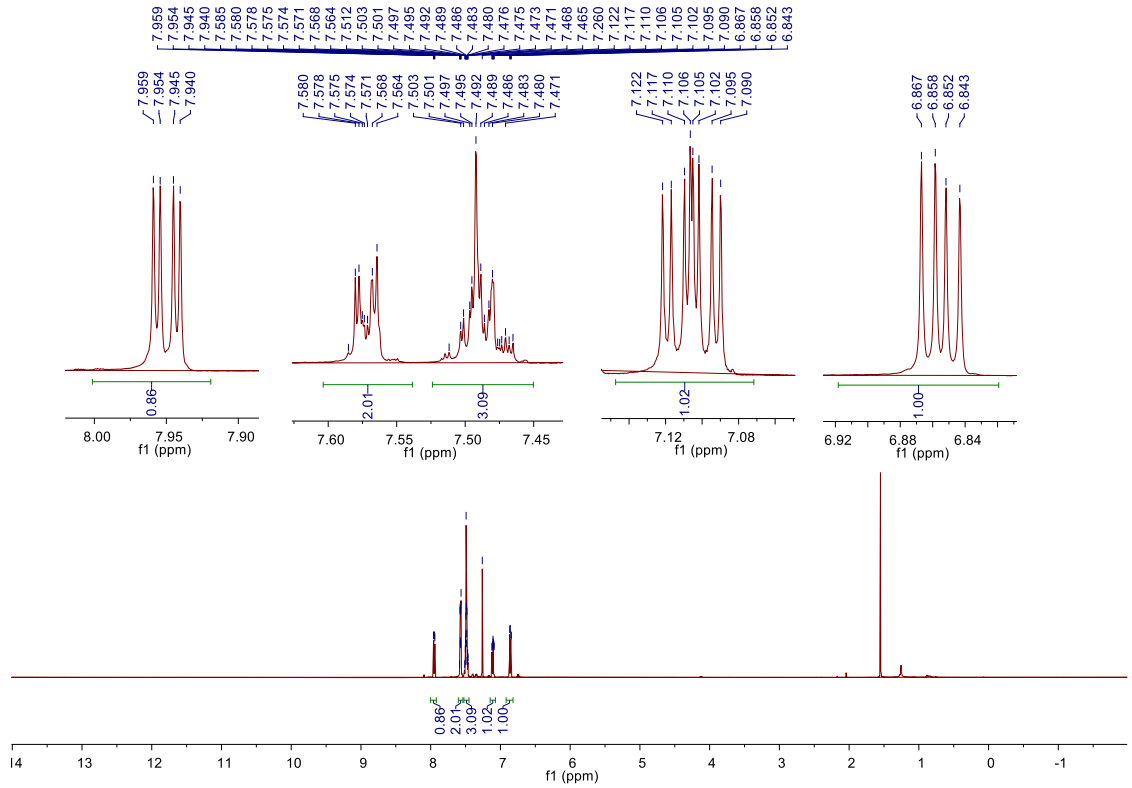
^{1}H NMR spectrum of **(4-methoxy-2-nitrophenyl)(phenyl)sulfane (3k)** in $CDCl_3$ at 400 MHz.



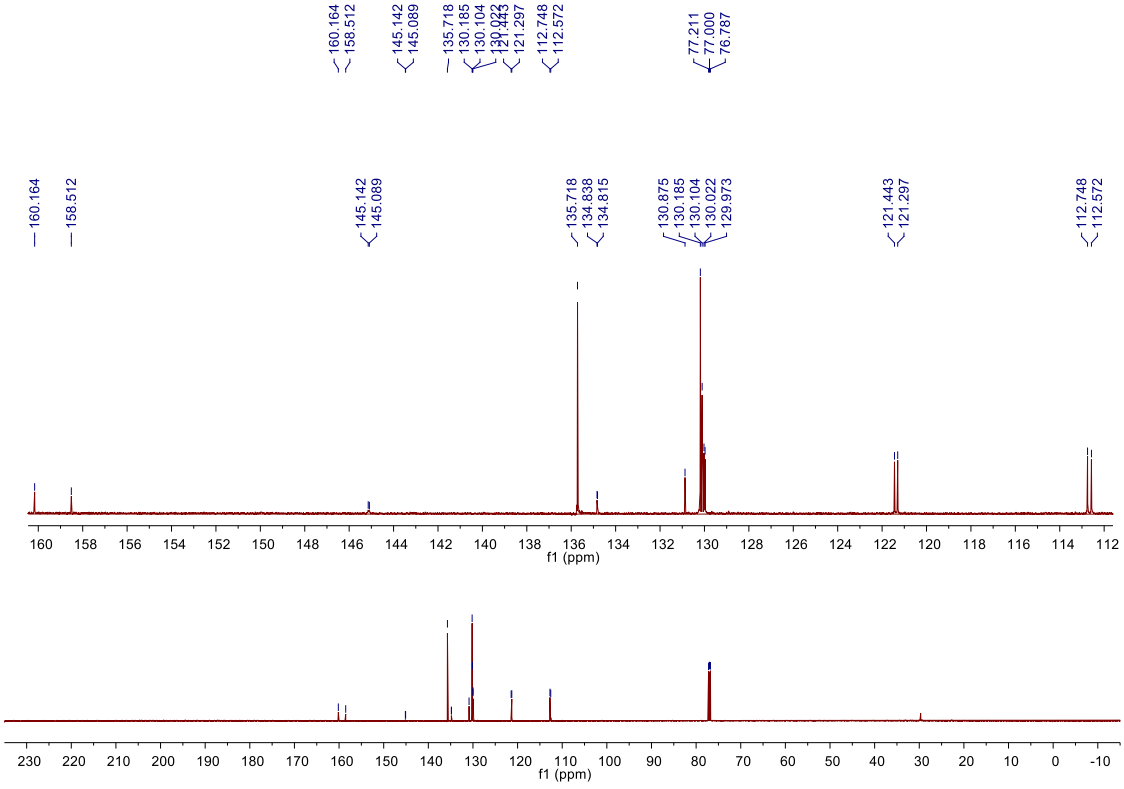
^{13}C NMR spectrum of **(4-methoxy-2-nitrophenyl)(phenyl)sulfane (3k)** in $CDCl_3$ at 101 MHz.



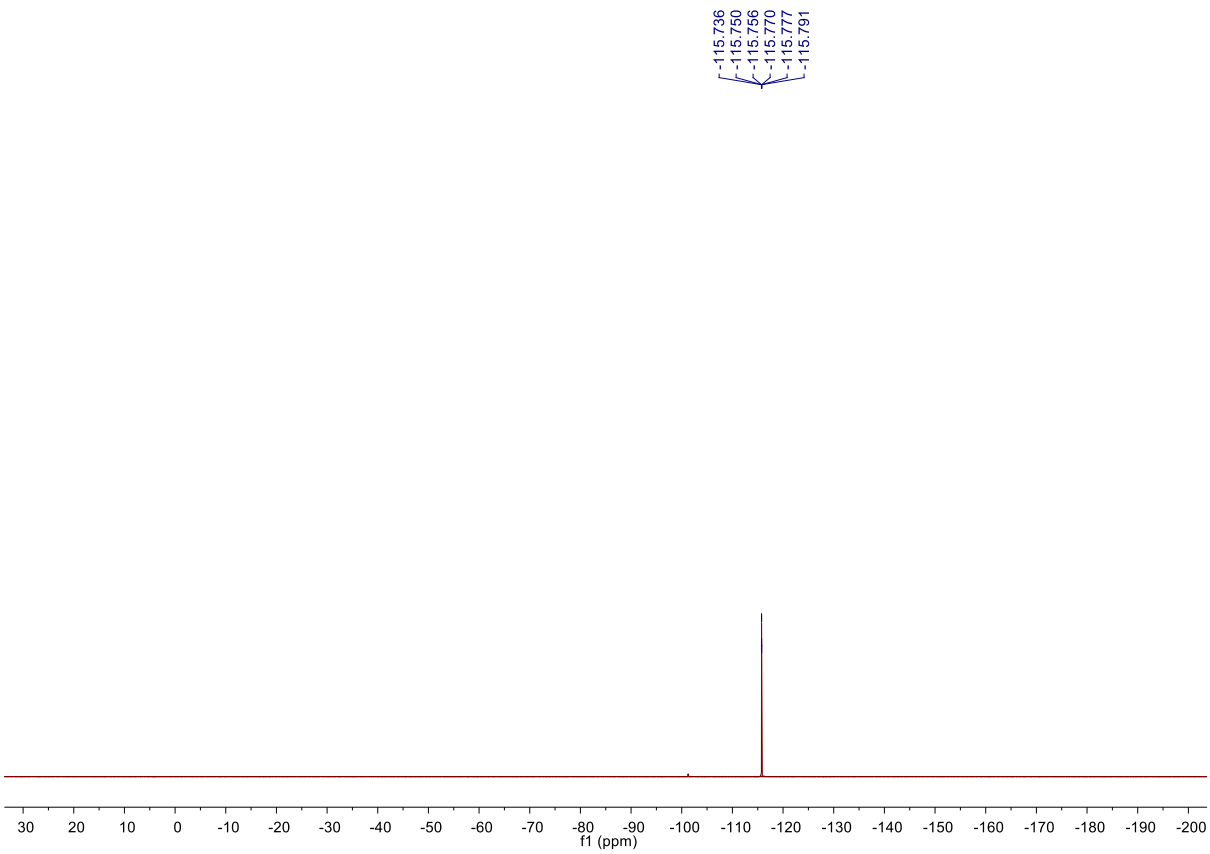
3l



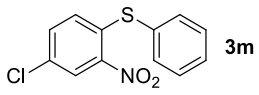
^{1}H NMR spectrum of **(4-fluoro-2-nitrophenyl)(phenyl)sulfane (3l)** in $CDCl_3$ at 600 MHz.

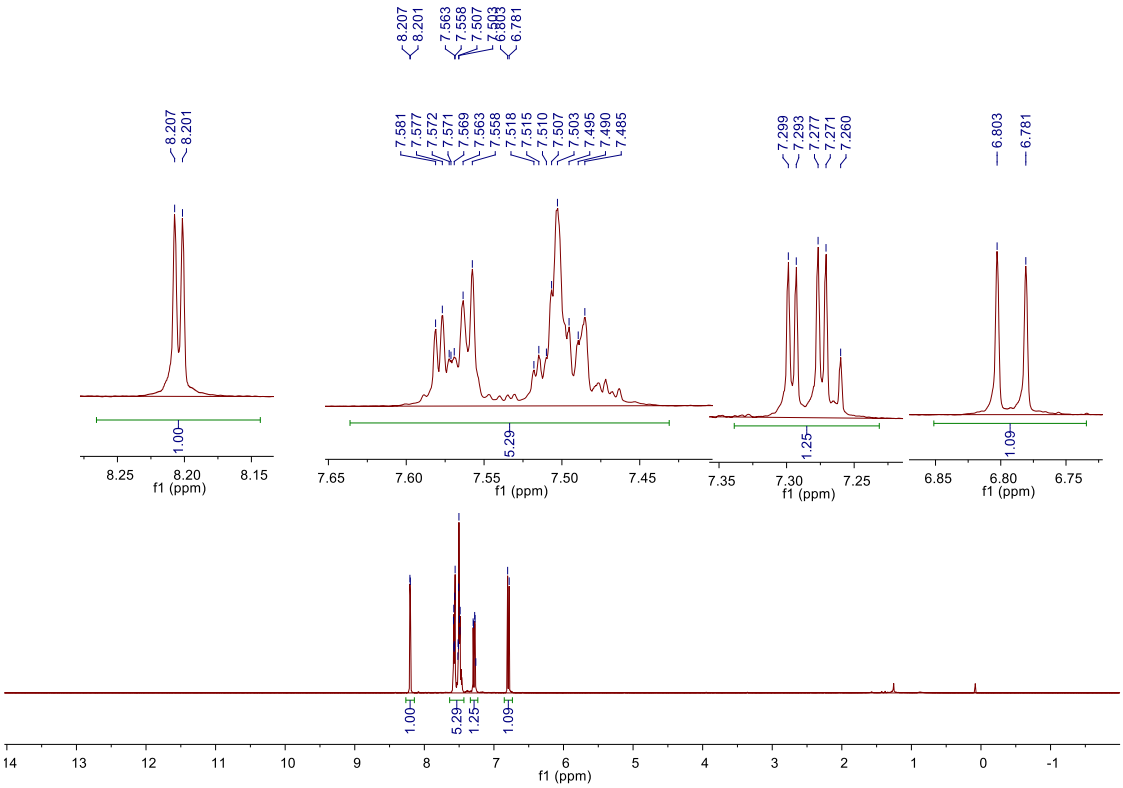


^{13}C NMR spectrum of **(4-fluoro-2-nitrophenyl)(phenyl)sulfane (3l)** in $CDCl_3$ at 151 MHz.

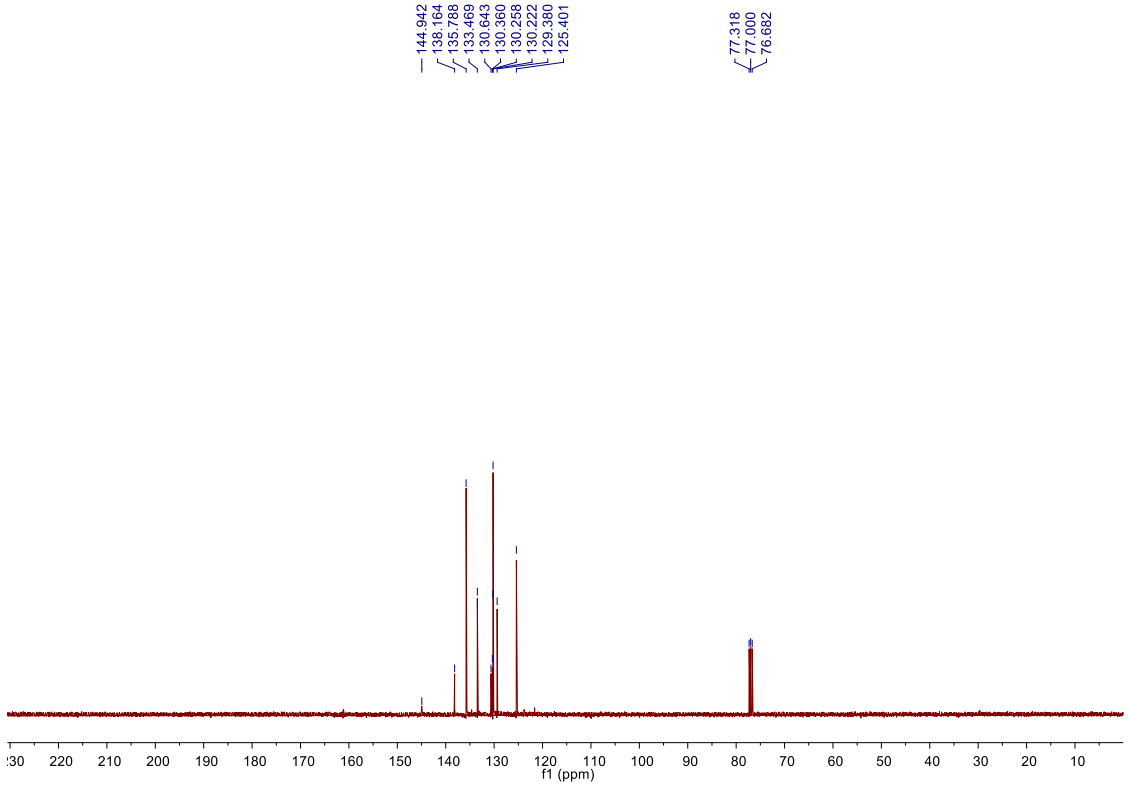


^{19}F NMR spectrum of **(4-fluoro-2-nitrophenyl)(phenyl)sulfane (3l)** in $CDCl_3$ at 376 MHz.

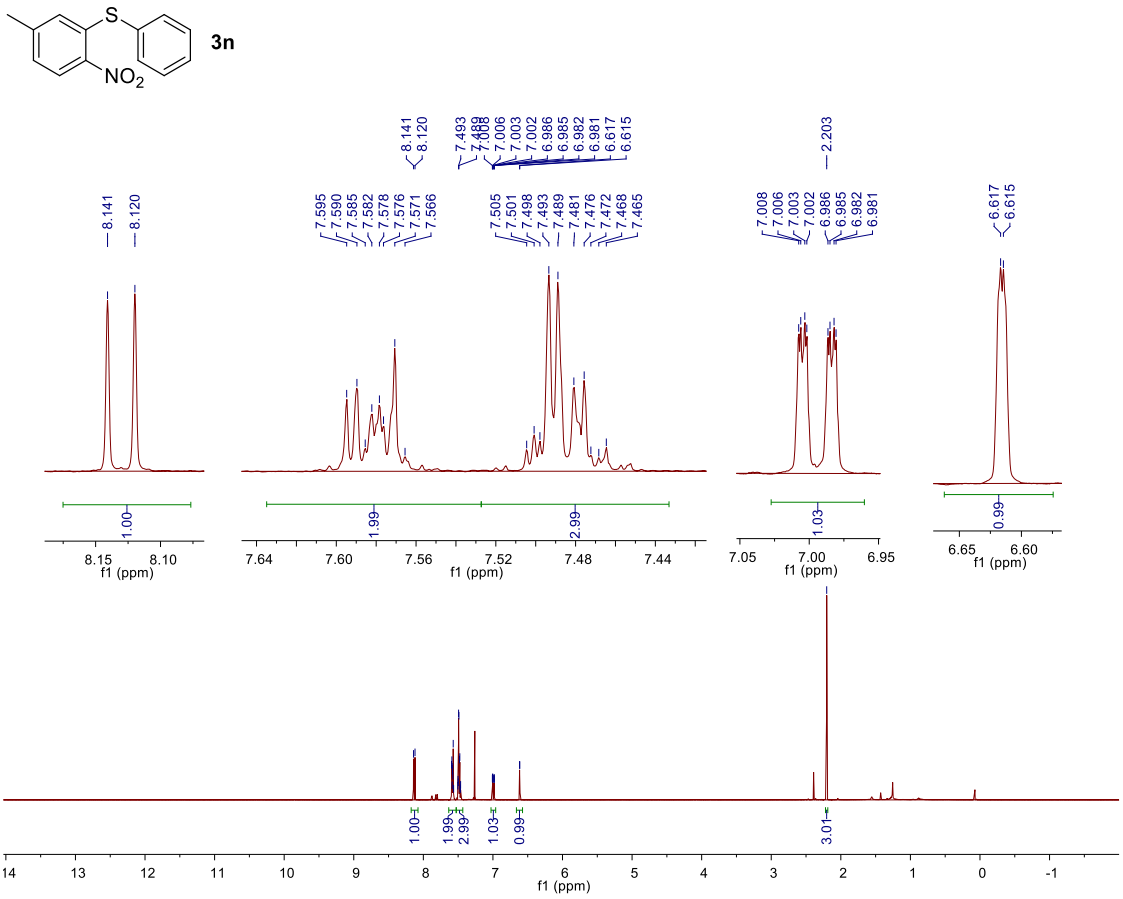




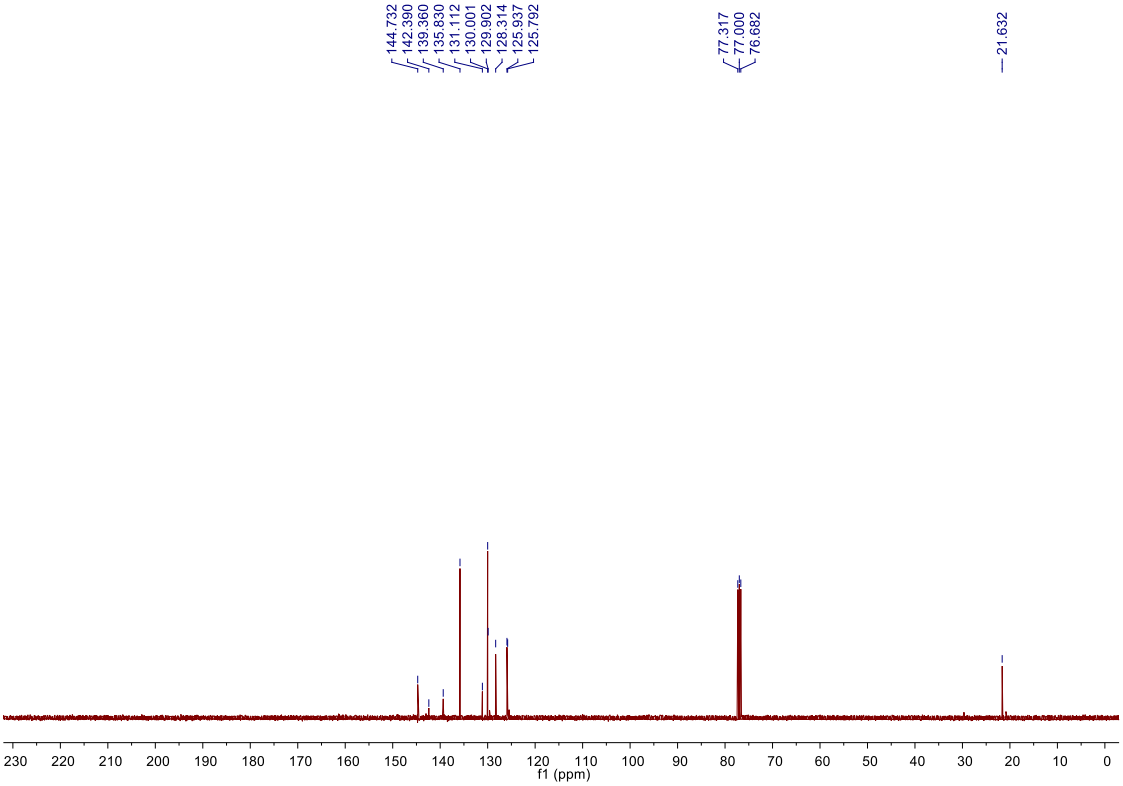
^{1}H NMR spectrum of **(4-chloro-2-nitrophenyl)(phenyl)sulfane (3m)** in $CDCl_3$ at 400 MHz.



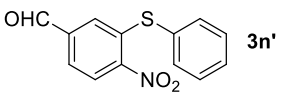
^{13}C NMR spectrum of **(4-chloro-2-nitrophenyl)(phenyl)sulfane (3m)** in $CDCl_3$ at 101 MHz.



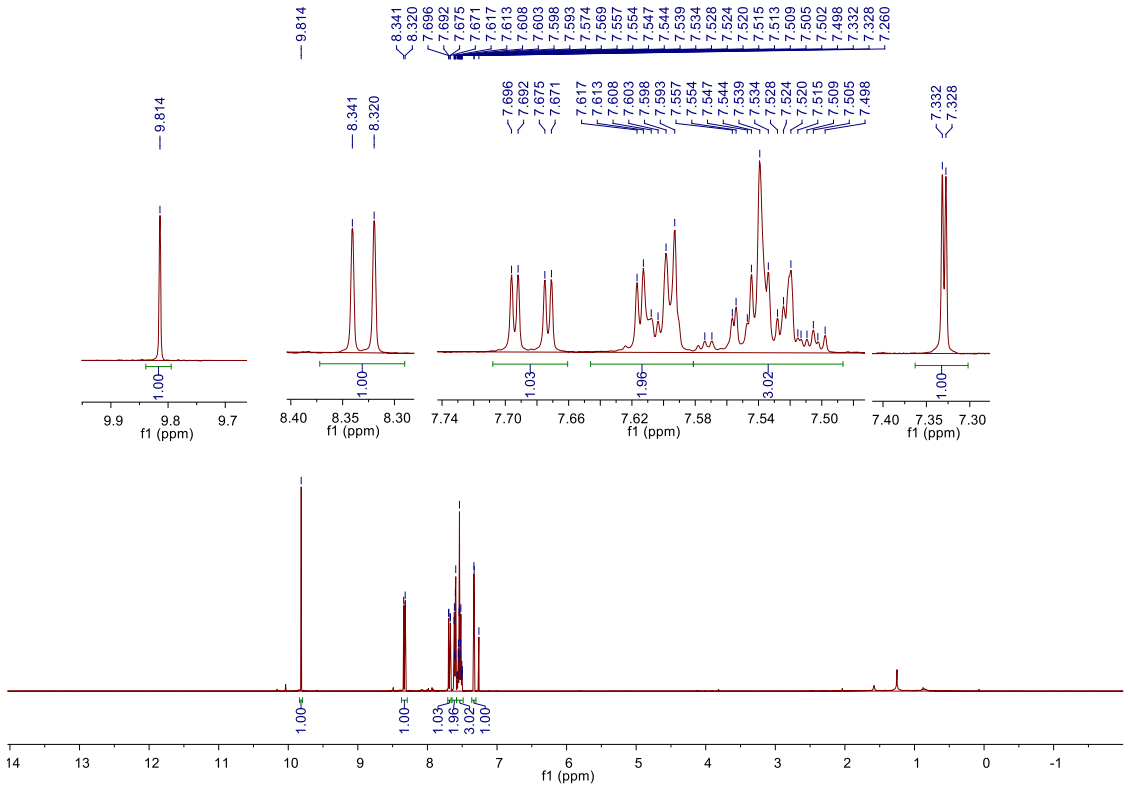
^{1}H NMR spectrum of **(5-methyl-2-nitrophenyl)(phenyl)sulfane (3n)** in $CDCl_3$ at 400 MHz.



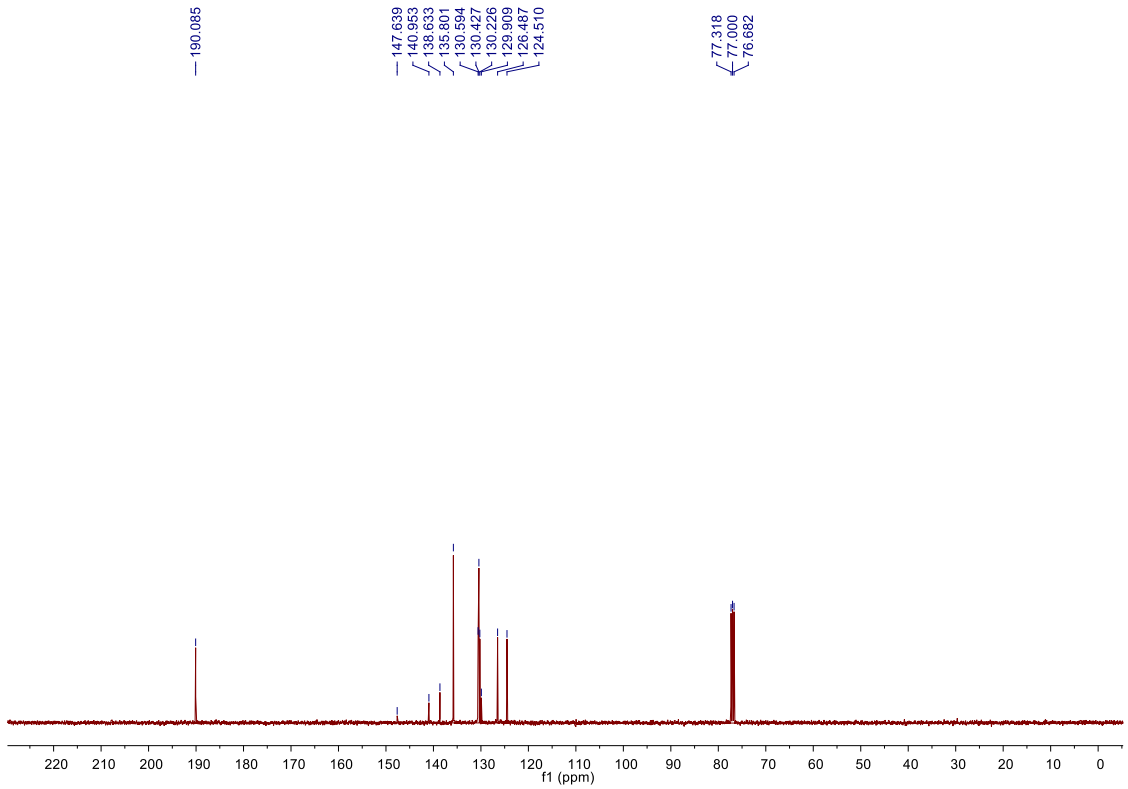
^{13}C NMR spectrum of **(5-methyl-2-nitrophenyl)(phenyl)sulfane (3n)** in $CDCl_3$ at 101 MHz.



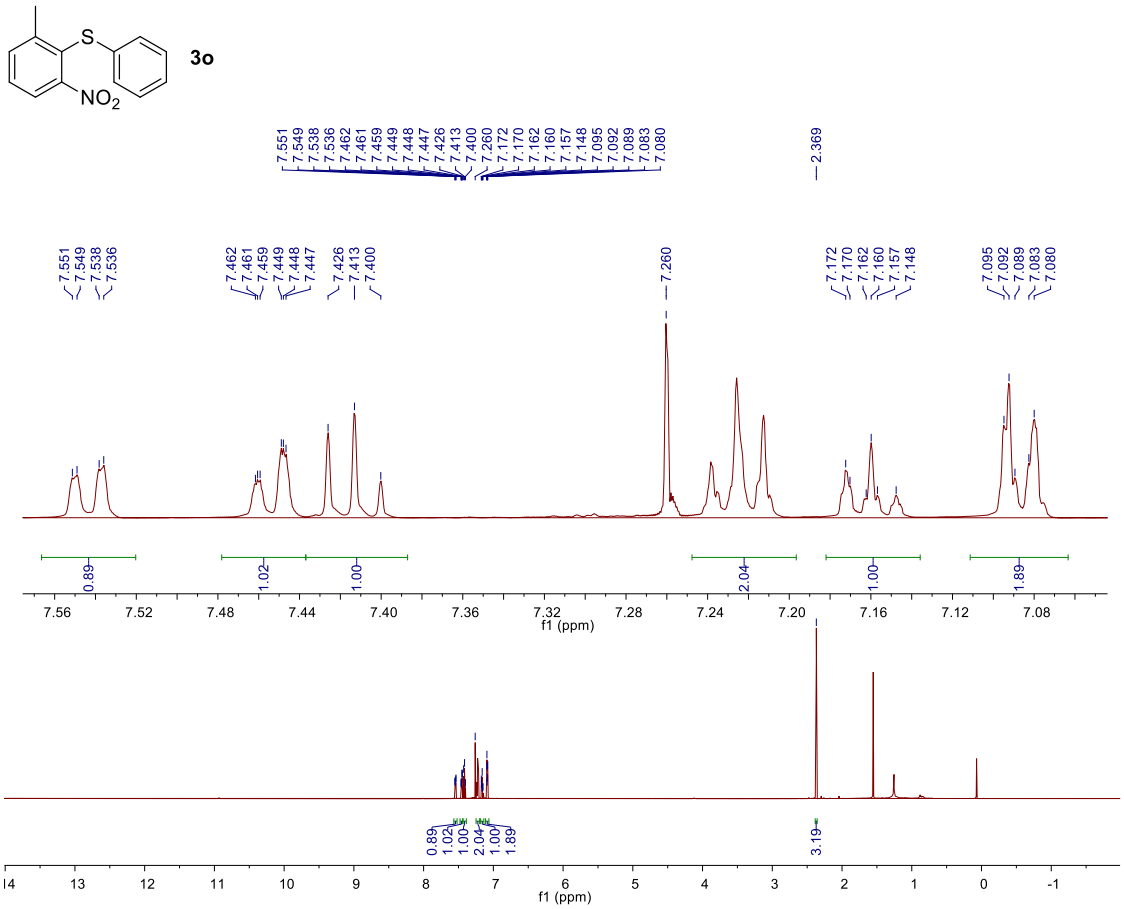
3n'



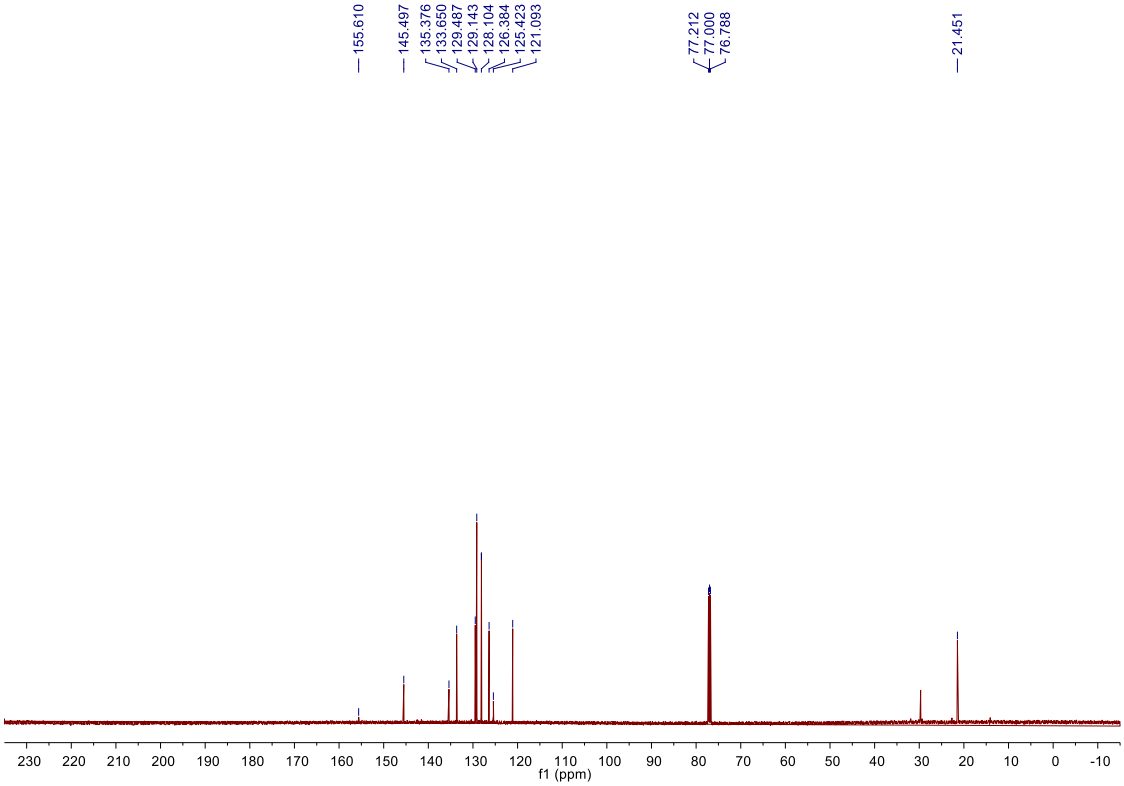
^{1}H NMR spectrum of **4-nitro-3-(phenylthio)benzaldehyde (3n')** in $CDCl_3$ at 400 MHz.



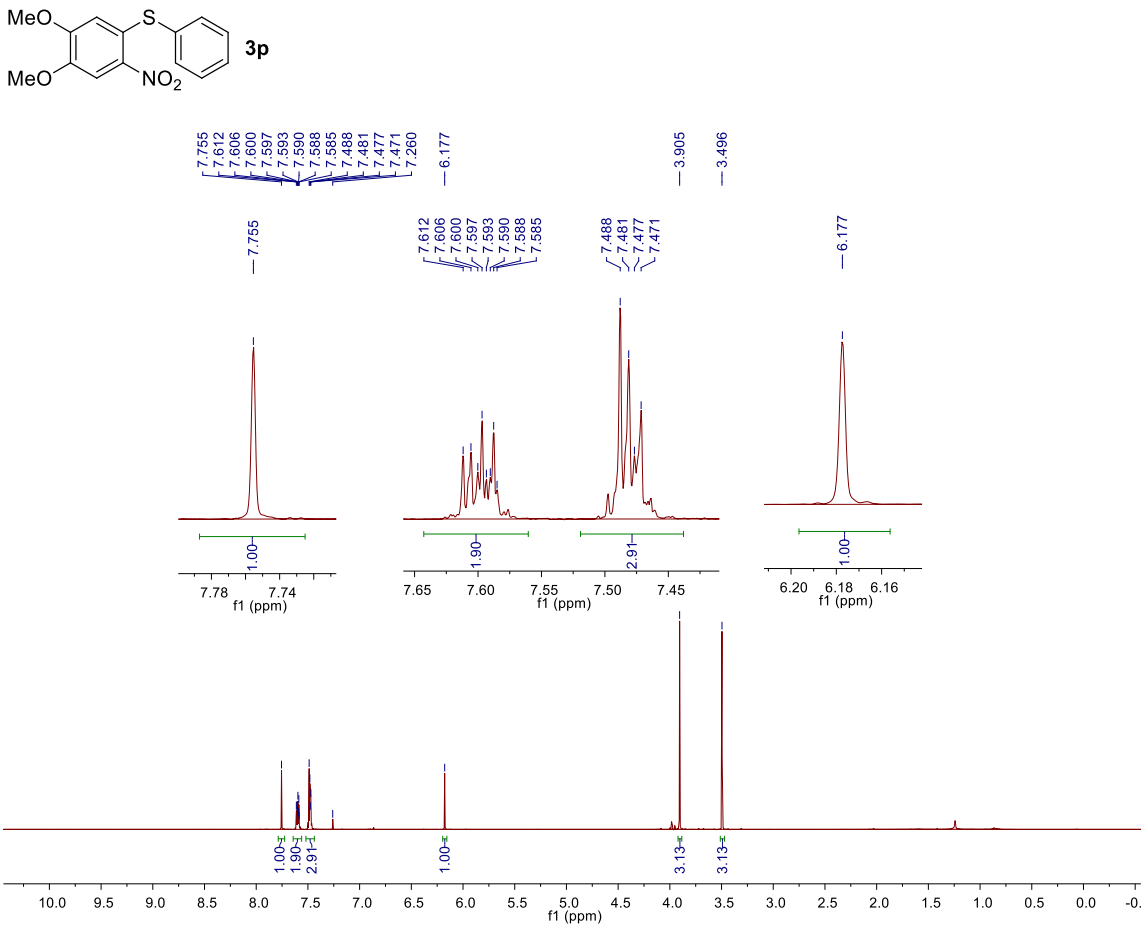
^{13}C NMR spectrum of **4-nitro-3-(phenylthio)benzaldehyde (3n')** in $CDCl_3$ at 101 MHz.



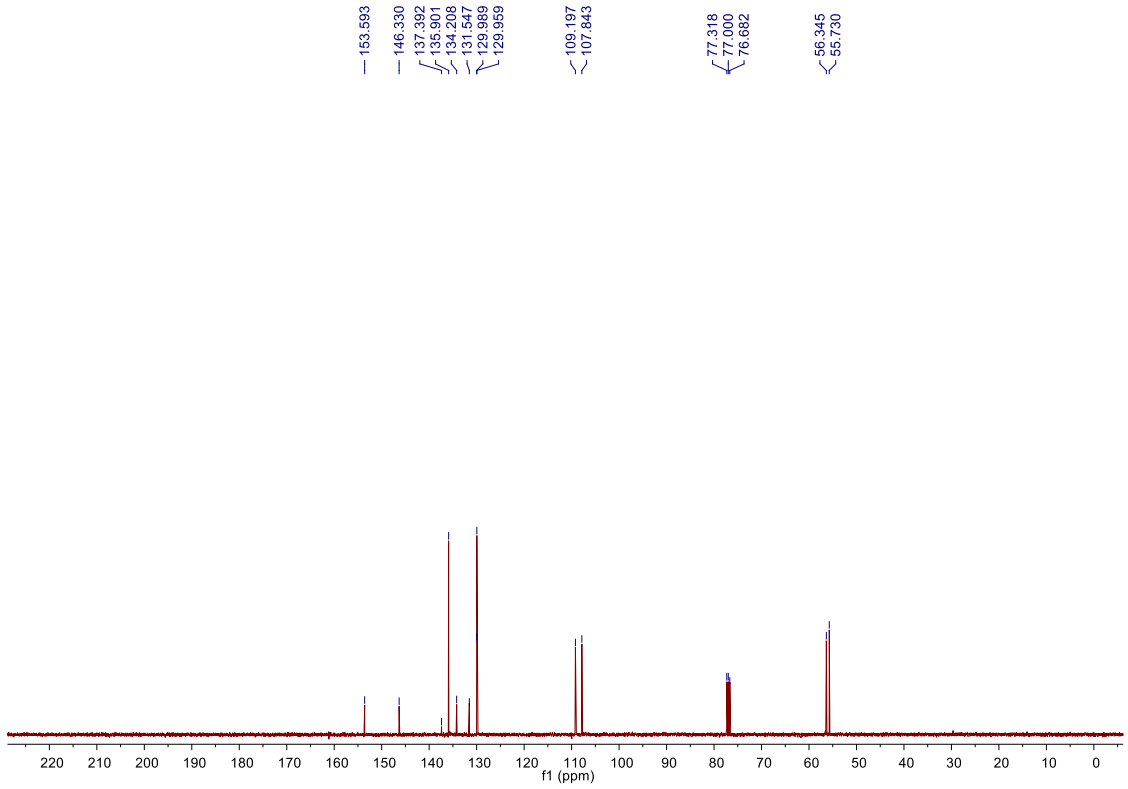
^{1}H NMR spectrum of **(2-methyl-6-nitrophenyl)(phenyl)sulfane (3o)** in $CDCl_3$ at 600 MHz.



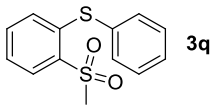
^{13}C NMR spectrum of **(2-methyl-6-nitrophenyl)(phenyl)sulfane (3o)** in $CDCl_3$ at 151 MHz.

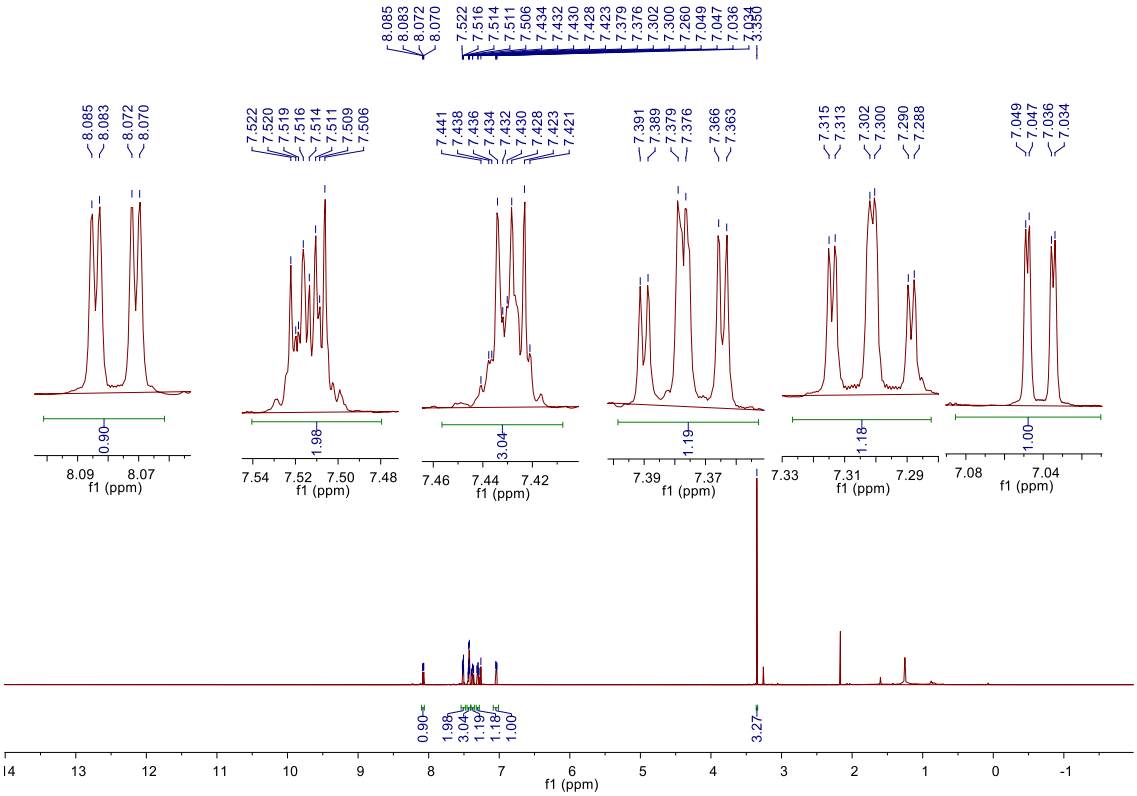


^{1}H NMR spectrum of **(4,5-dimethoxy-2-nitrophenyl)(phenyl)sulfane (3p)** in $CDCl_3$ at 400 MHz.

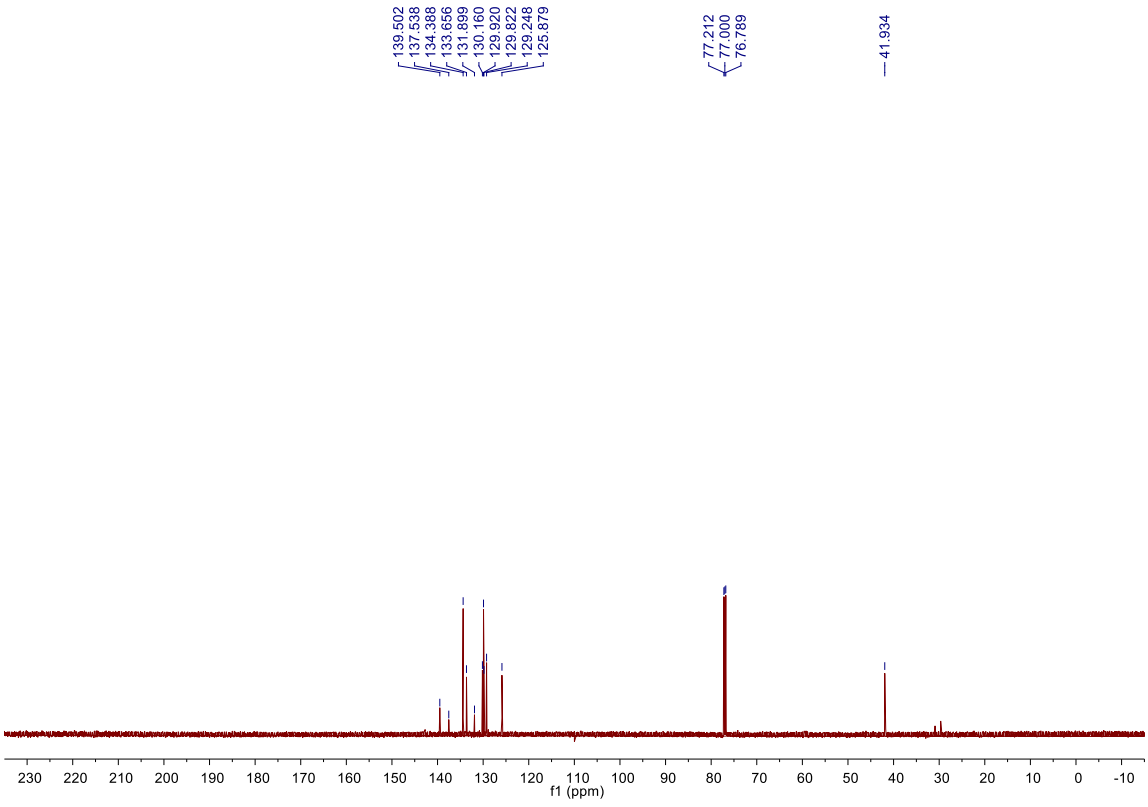


^{13}C NMR spectrum of **(4,5-dimethoxy-2-nitrophenyl)(phenyl)sulfane (3p)** in $CDCl_3$ at 101 MHz.

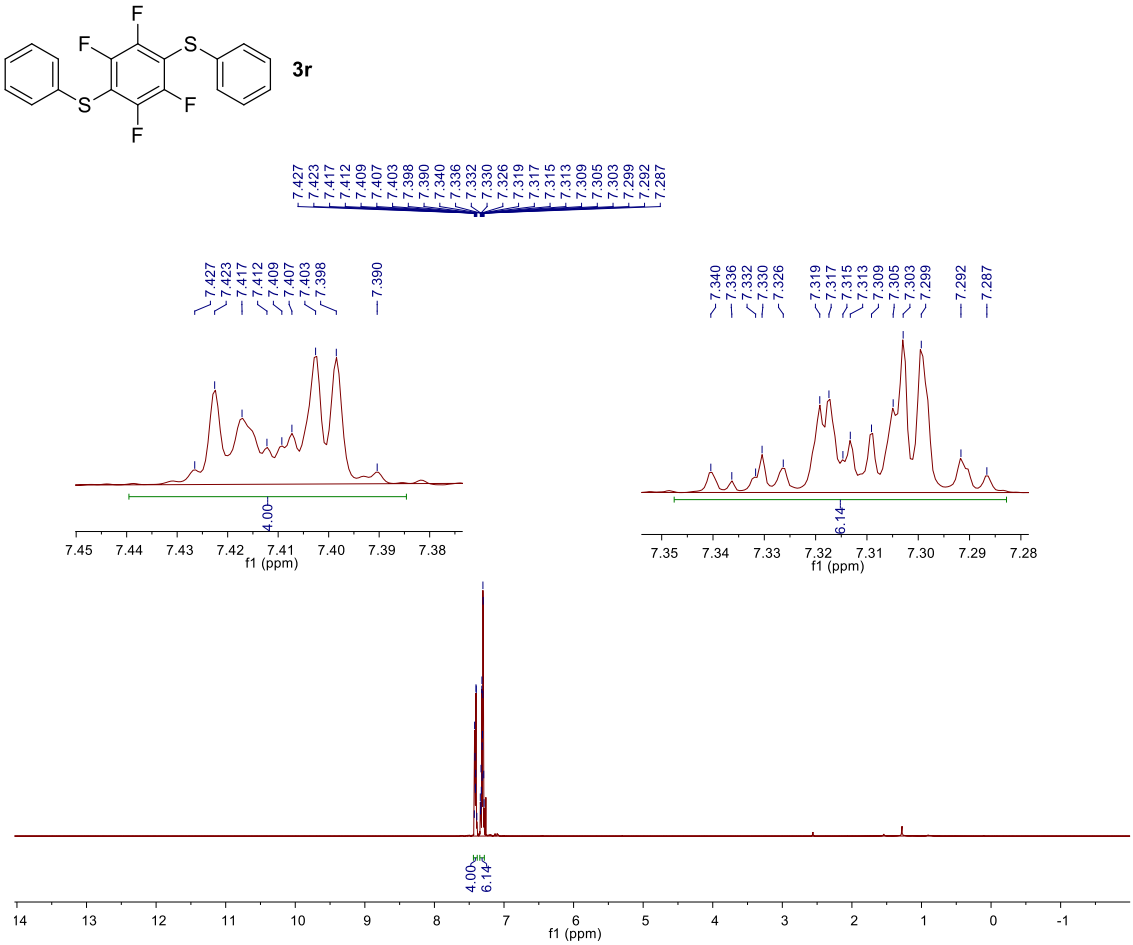




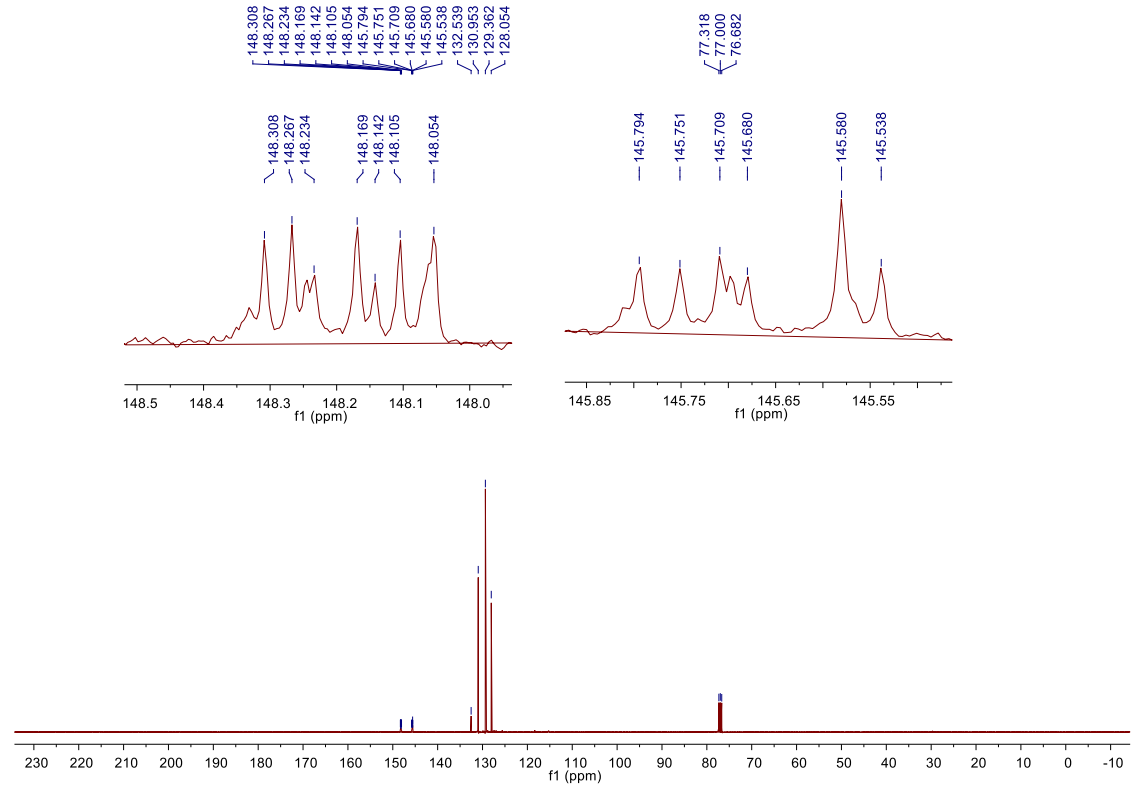
^{1}H NMR spectrum of **(2-(methylsulfonyl)phenyl)(phenyl)sulfane (3q)** in $CDCl_3$ at 600 MHz.



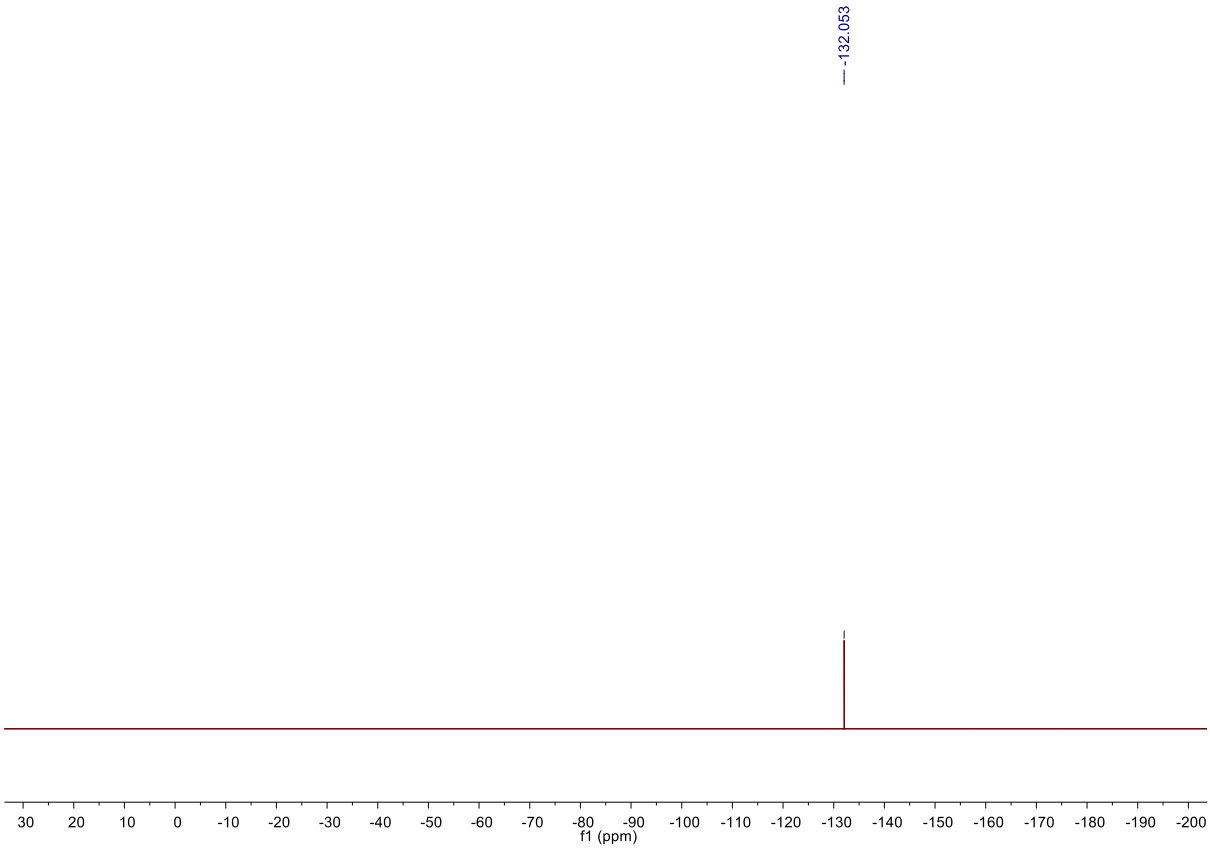
^{13}C NMR spectrum of **(2-(methylsulfonyl)phenyl)(phenyl)sulfane (3q)** in $CDCl_3$ at 151 MHz.



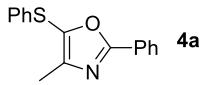
^{1}H NMR spectrum of **(perfluoro-1,4-phenylene)bis(phenylsulfane) (3r)** in $CDCl_3$ at 400 MHz.



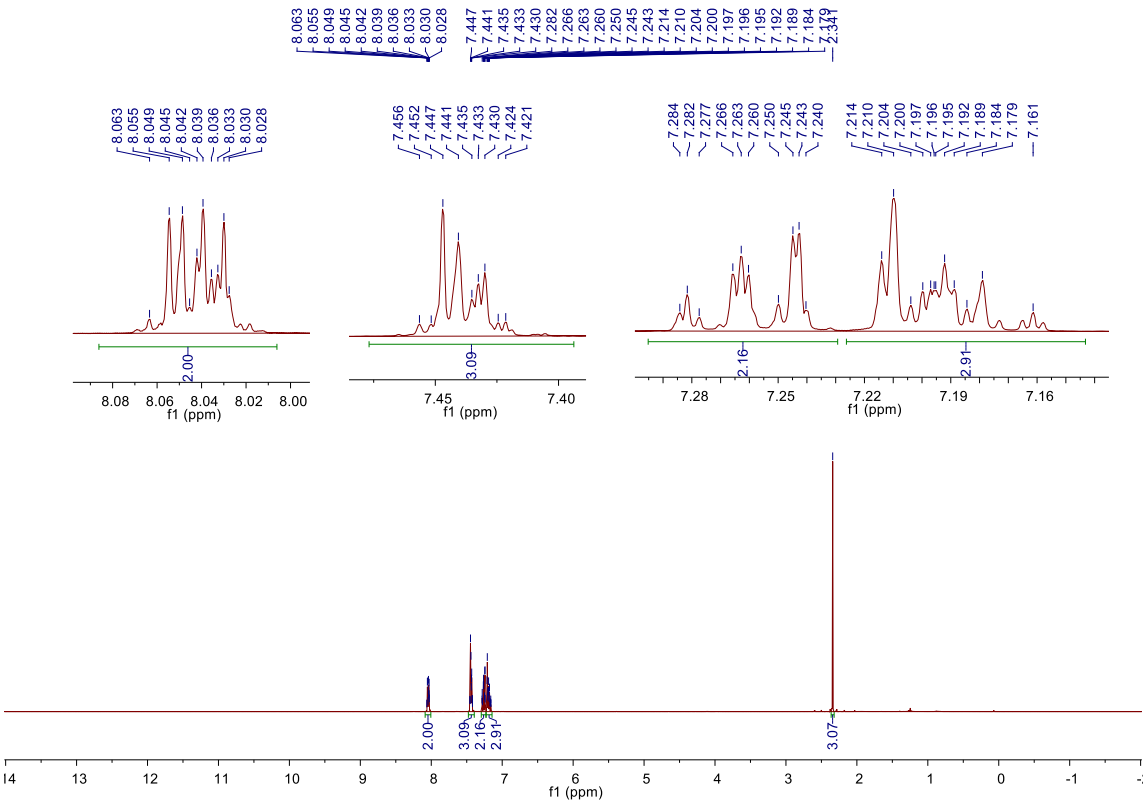
^{13}C NMR spectrum of **(perfluoro-1,4-phenylene)bis(phenylsulfane) (3r)** in $CDCl_3$ at 101 MHz.



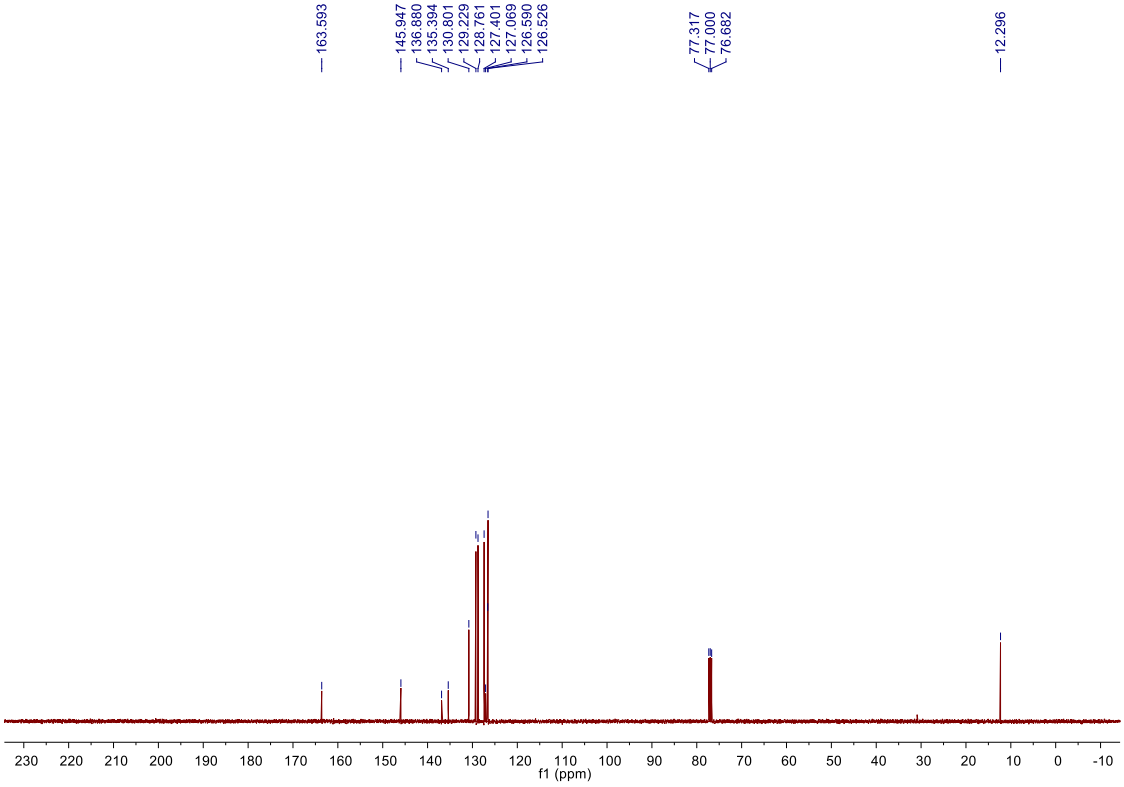
^{19}F NMR spectrum of **(perfluoro-1,4-phenylene)bis(phenylsulfane) (3r)** in $CDCl_3$ at 376 MHz.



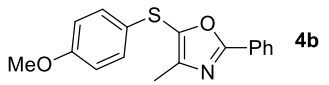
4a



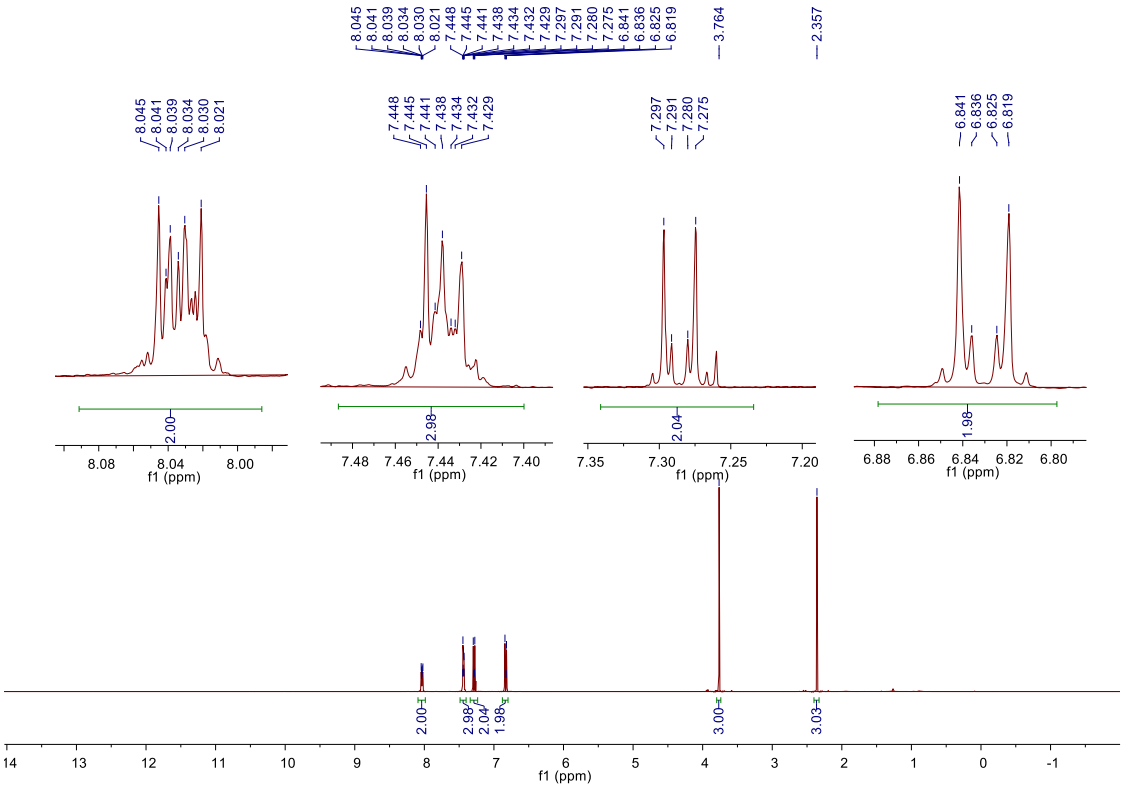
^{1}H NMR spectrum of **4-methyl-2-phenyl-5-(phenylthio)oxazole (4a)** in $CDCl_3$ at 400 MHz.



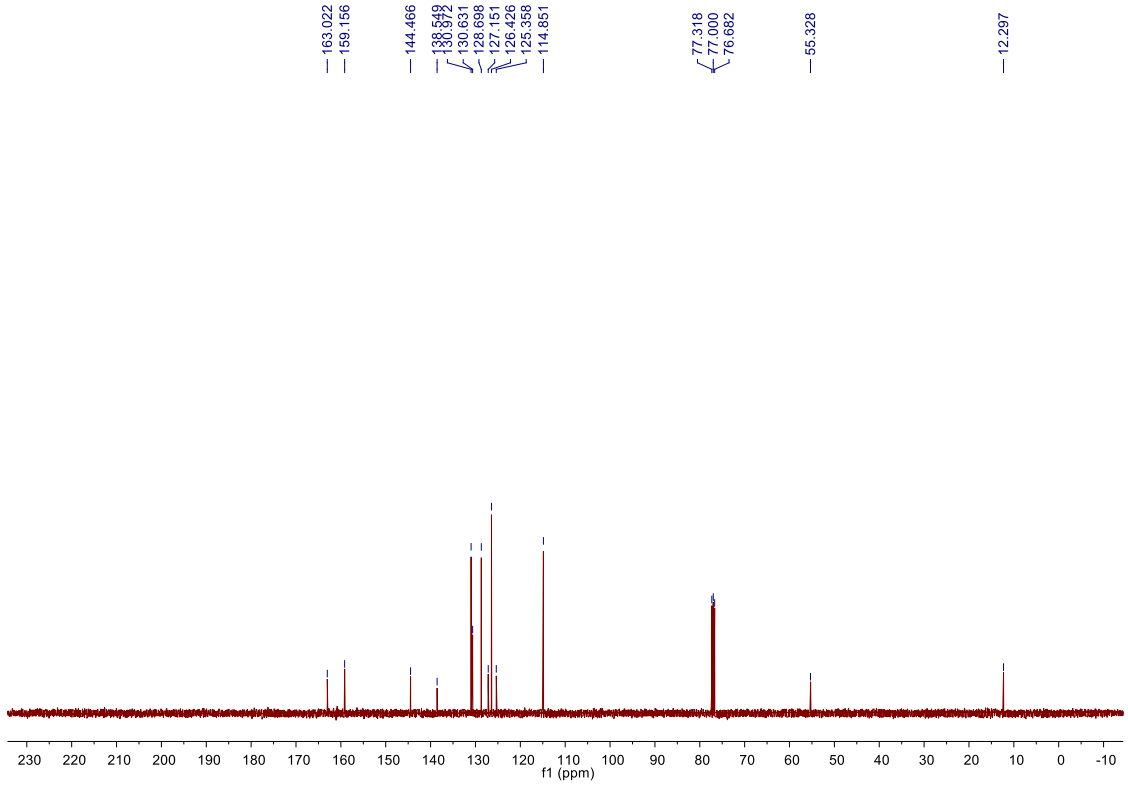
^{13}C NMR spectrum of **4-methyl-2-phenyl-5-(phenylthio)oxazole (4a)** in $CDCl_3$ at 101 MHz.



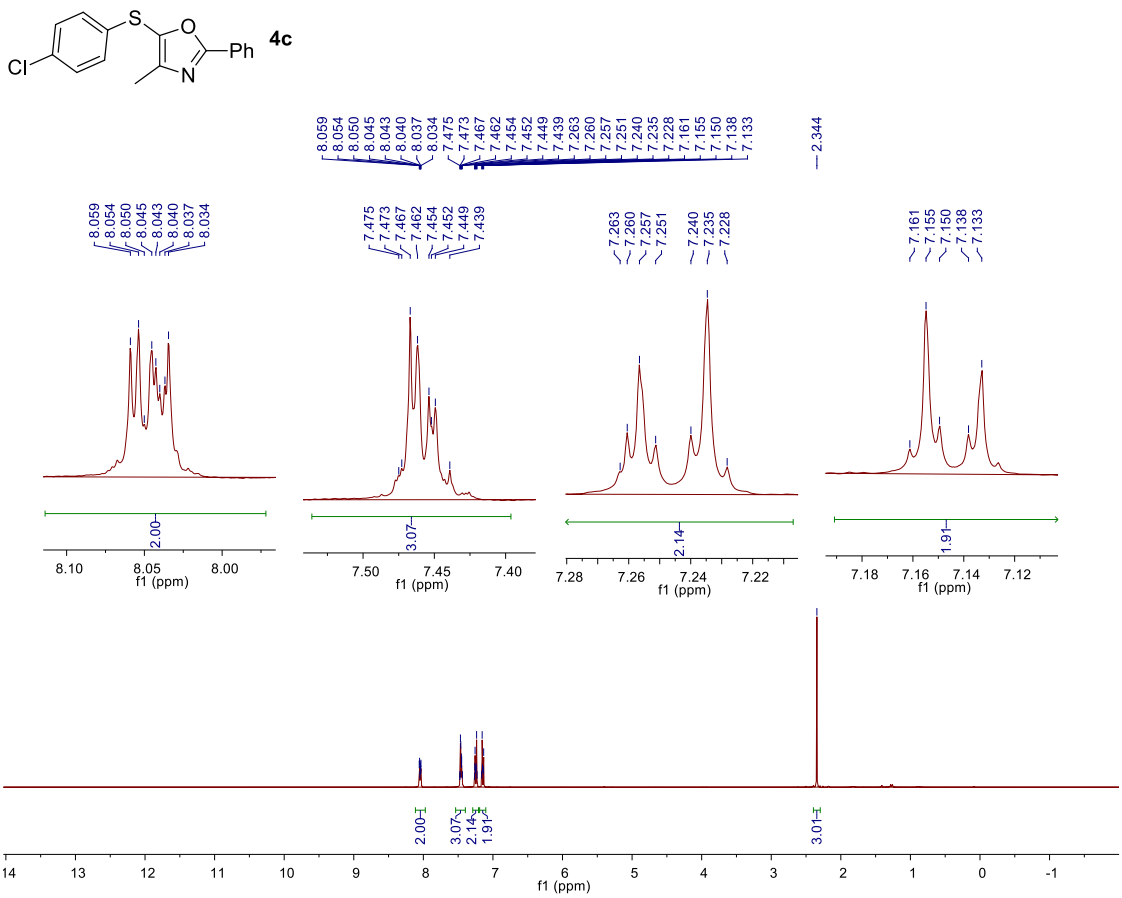
4b



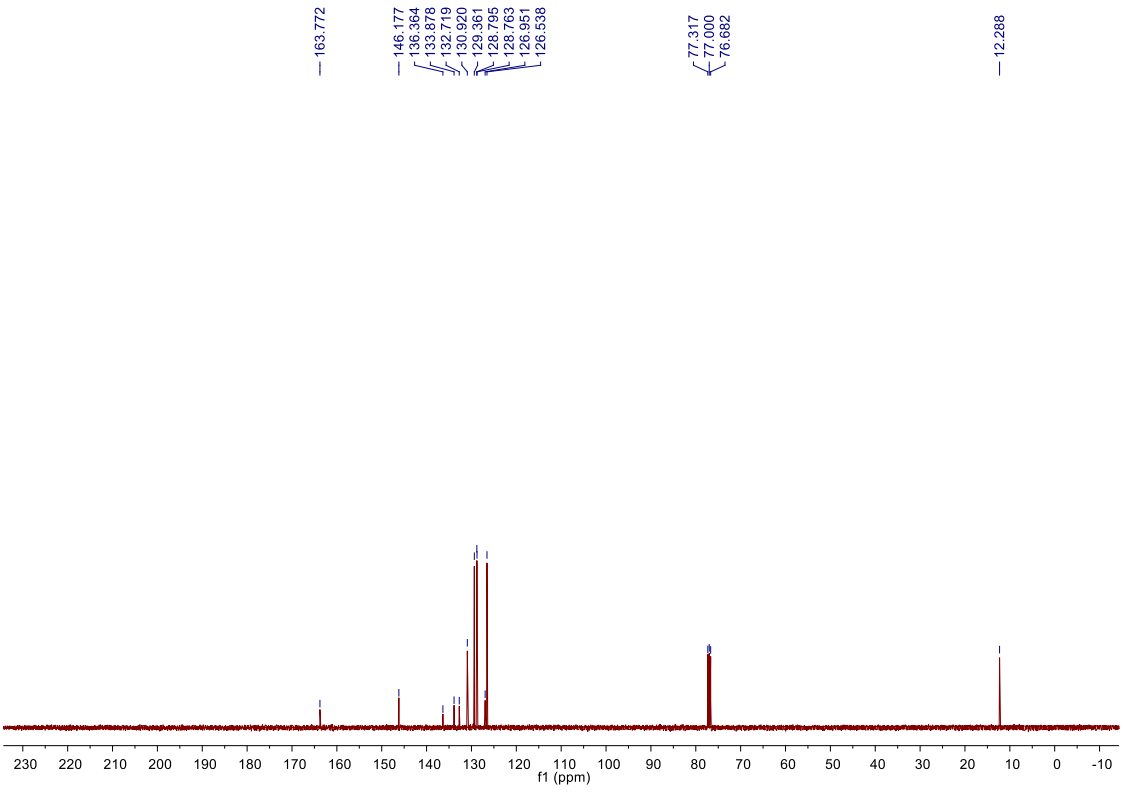
^{1}H NMR spectrum of **5-((4-methoxyphenyl)thio)-4-methyl-2-phenyloxazole (4b)** in $CDCl_3$ at 400 MHz.



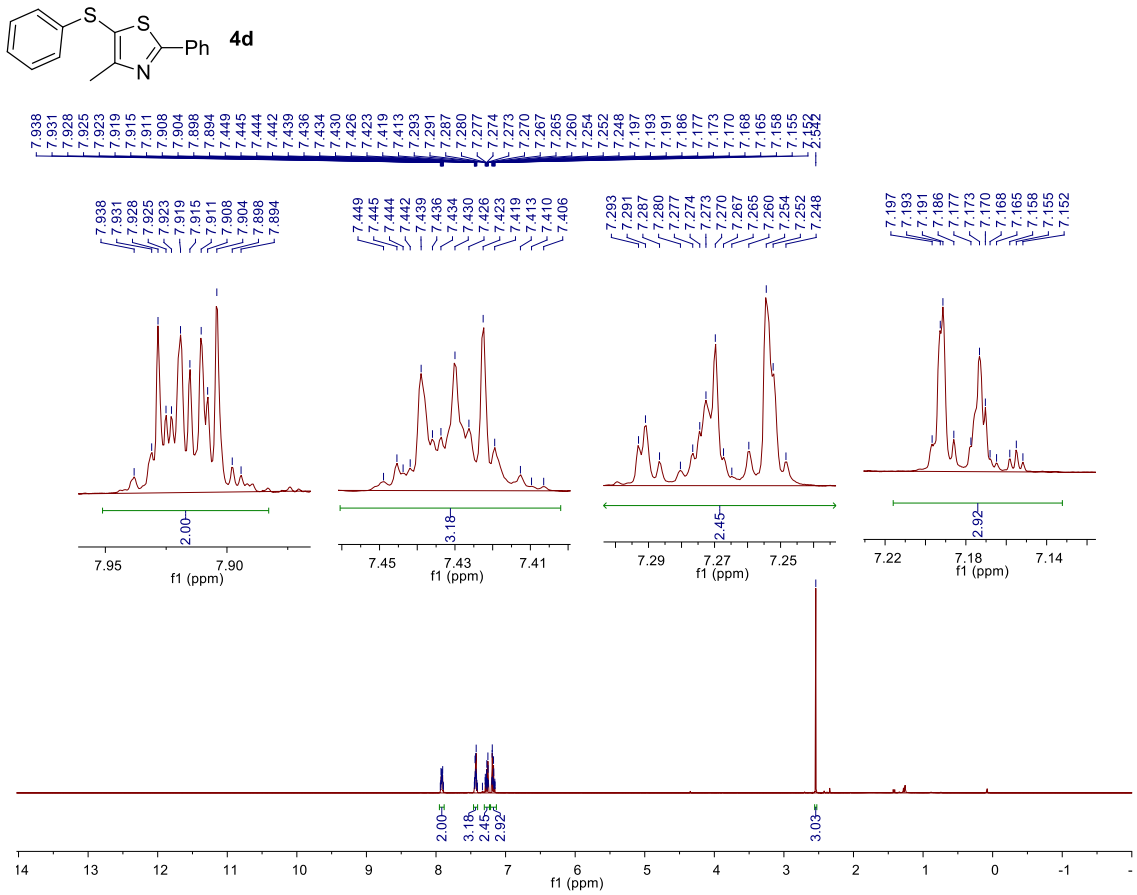
^{13}C NMR spectrum of **5-((4-methoxyphenyl)thio)-4-methyl-2-phenyloxazole (4b)** in $CDCl_3$ at 101 MHz.



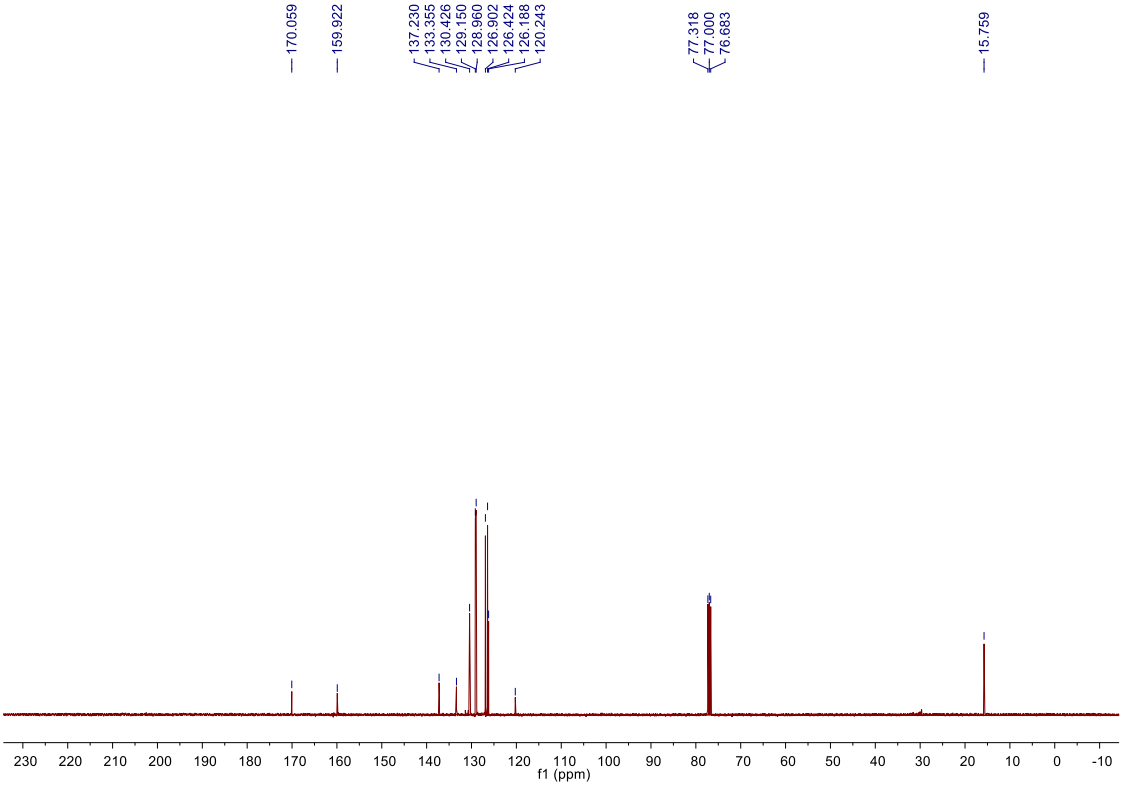
^{1}H NMR spectrum of **5-((4-chlorophenyl)thio)-4-methyl-2-phenyloxazole (4c)** in $CDCl_3$ at 400 MHz.



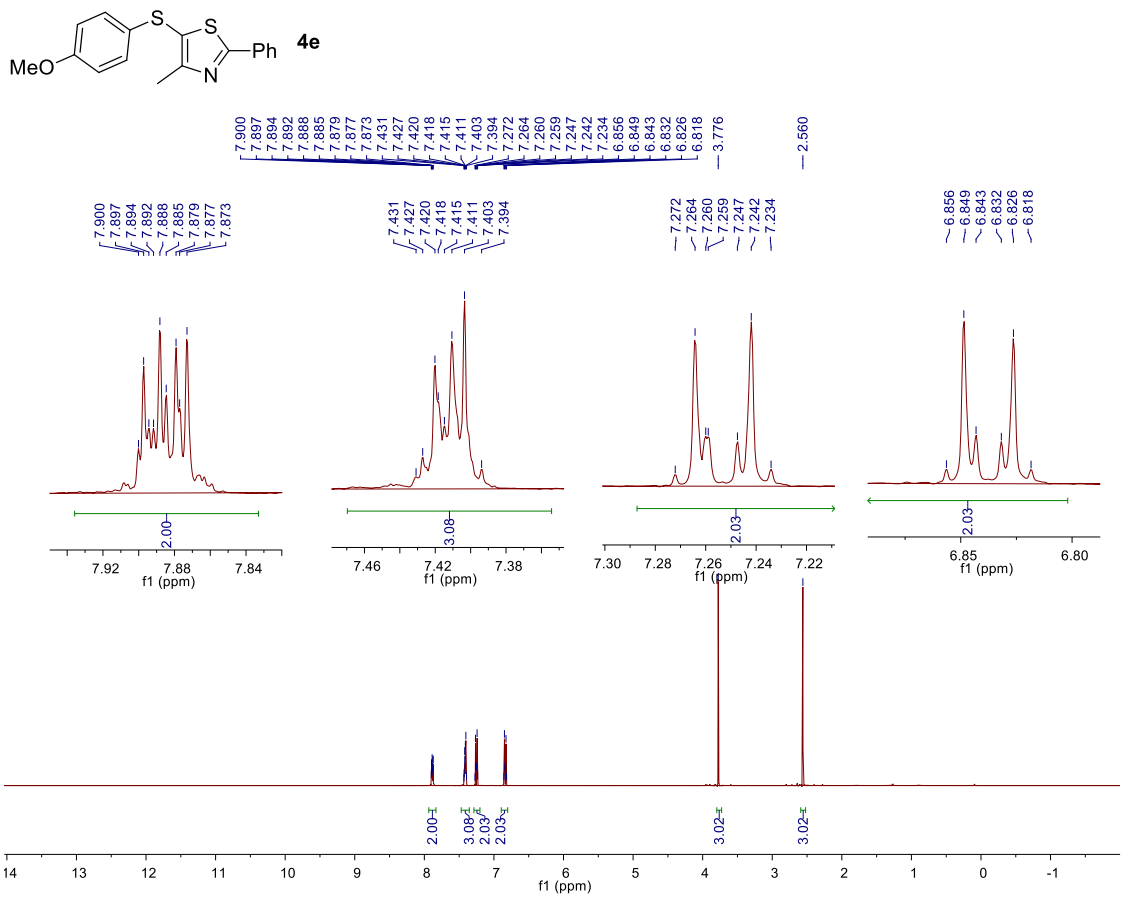
^{13}C NMR spectrum of **5-((4-chlorophenyl)thio)-4-methyl-2-phenyloxazole (4c)** in $CDCl_3$ at 101 MHz.



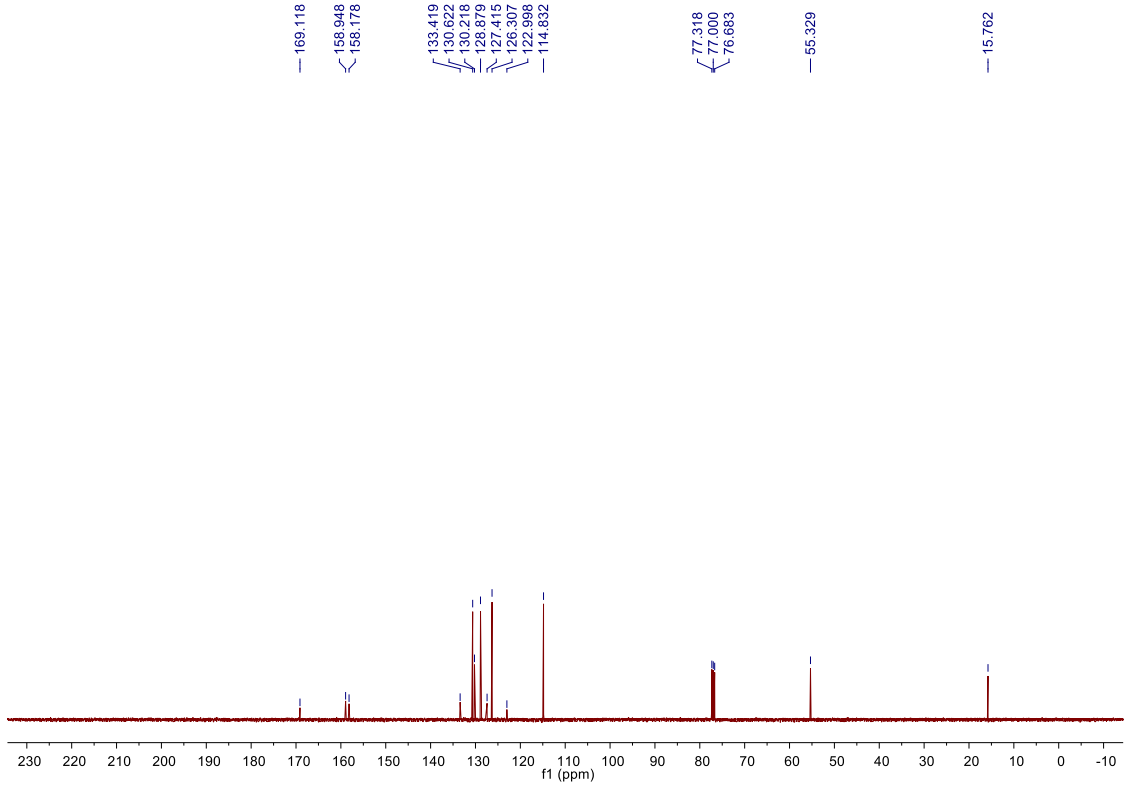
^{1}H NMR spectrum of **4-methyl-2-phenyl-5-(phenylthio)thiazole (4d)** in $CDCl_3$ at 400 MHz.



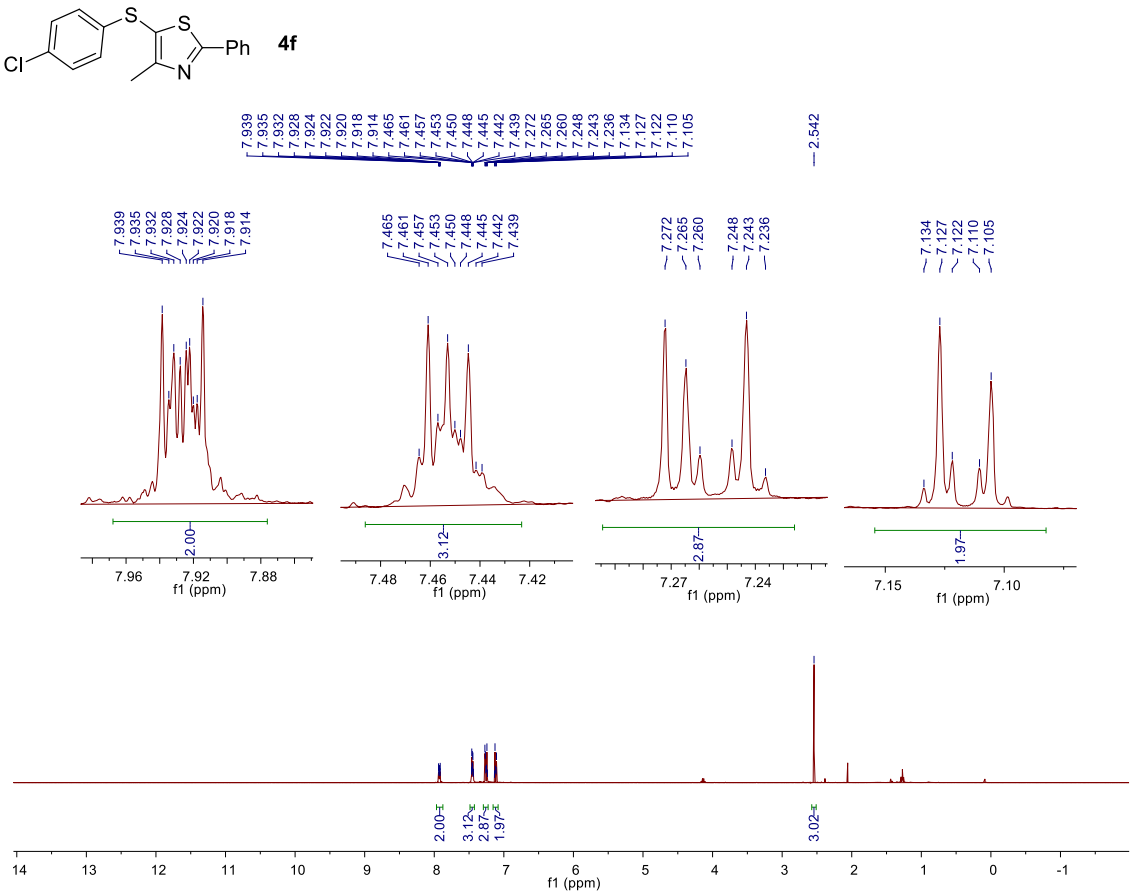
^{13}C NMR spectrum of **4-methyl-2-phenyl-5-(phenylthio)thiazole (4d)** in $CDCl_3$ at 101 MHz.



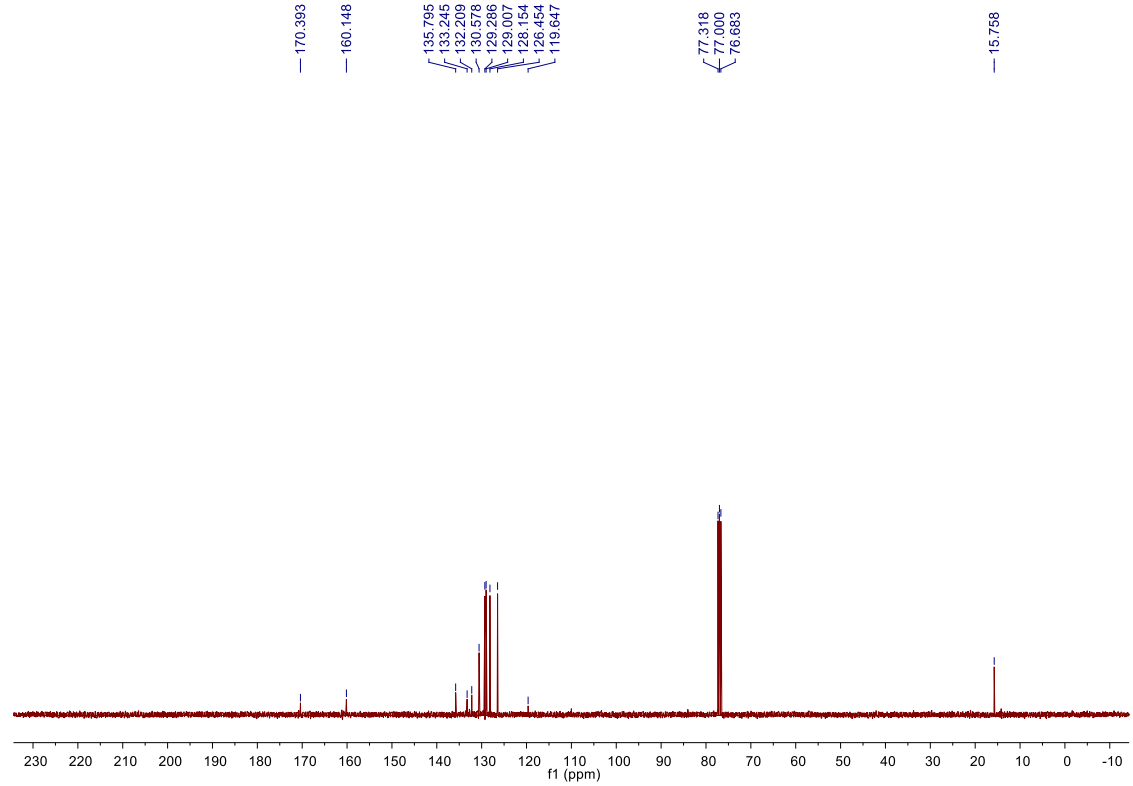
^{1}H NMR spectrum of **5-((4-methoxyphenyl)thio)-4-methyl-2-phenylthiazole (4e)** in $CDCl_3$ at 400 MHz.



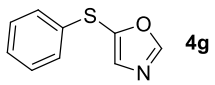
^{13}C NMR spectrum of **5-((4-methoxyphenyl)thio)-4-methyl-2-phenylthiazole (4e)** in $CDCl_3$ at 101 MHz



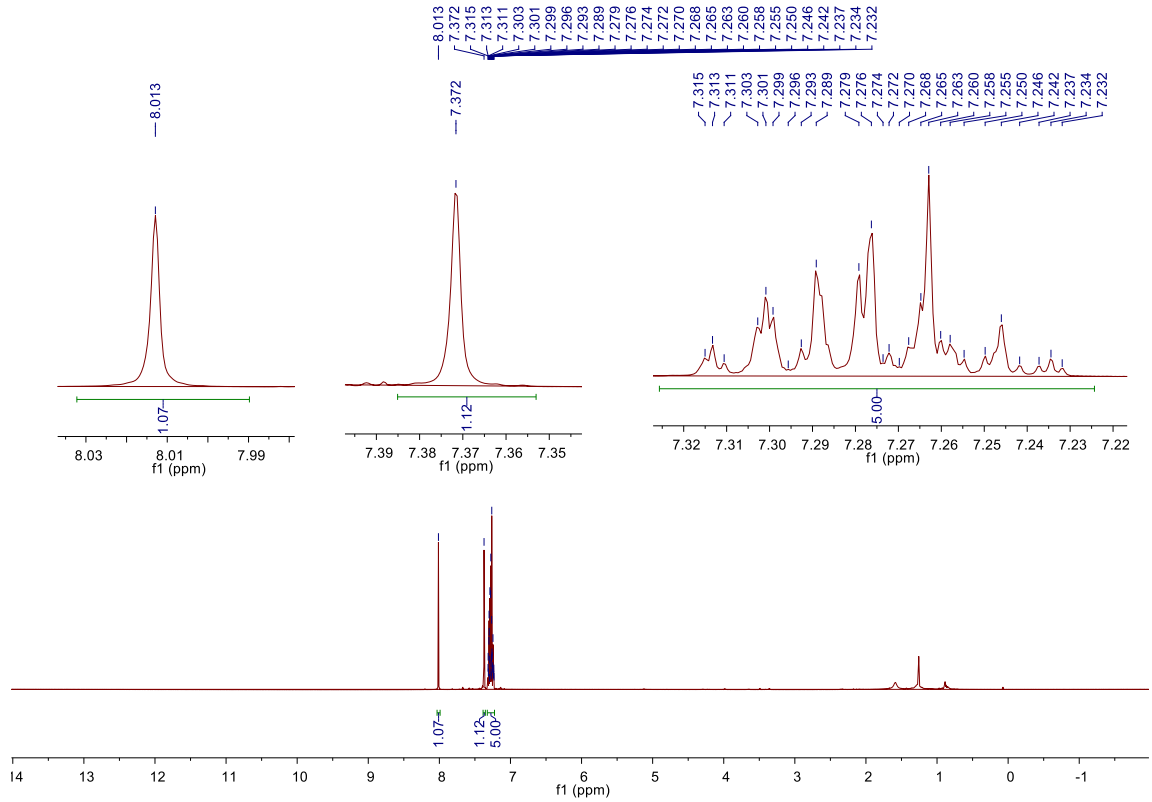
^{1}H NMR spectrum of **5-((4-chlorophenyl)thio)-4-methyl-2-phenylthiazole (4f)** in $CDCl_3$ at 400 MHz.



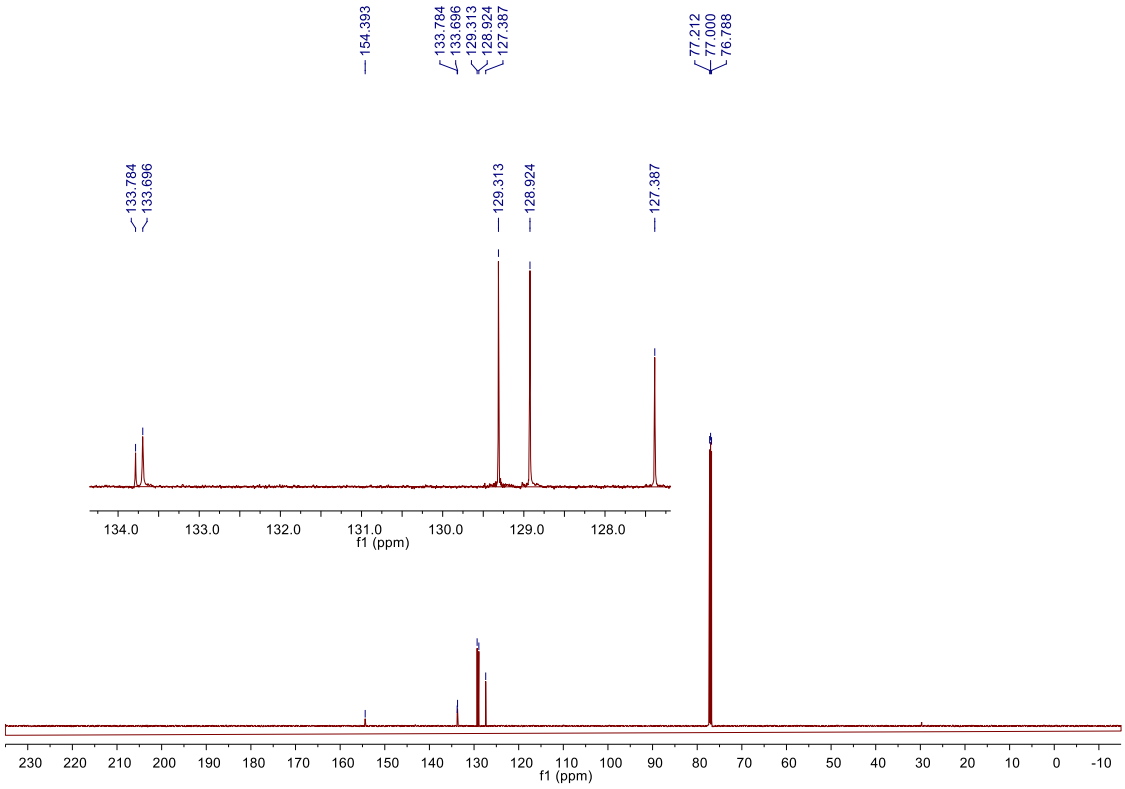
^{13}C NMR spectrum of **5-((4-chlorophenyl)thio)-4-methyl-2-phenylthiazole (4f)** in $CDCl_3$ at 101 MHz.



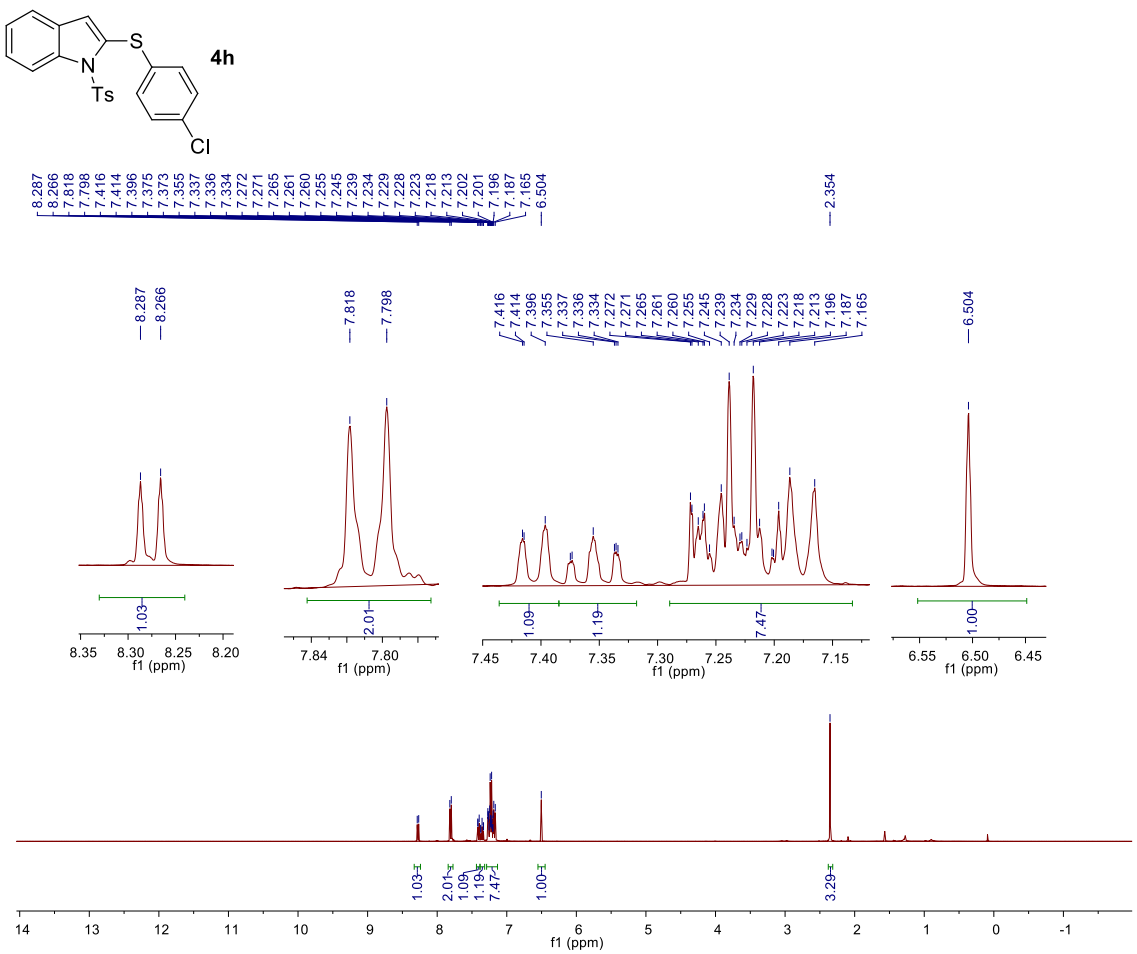
4g



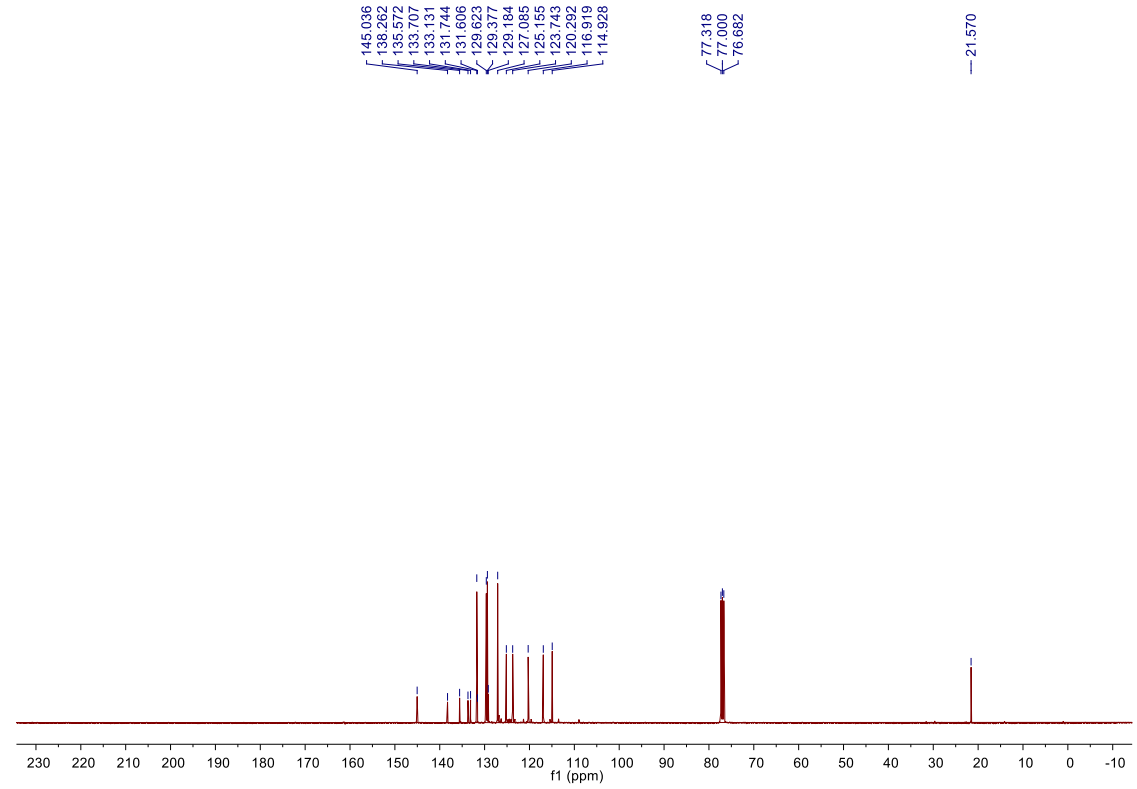
^{1}H NMR spectrum of **5-(phenylthio)oxazole (4g)** in $CDCl_3$ at 400 MHz.



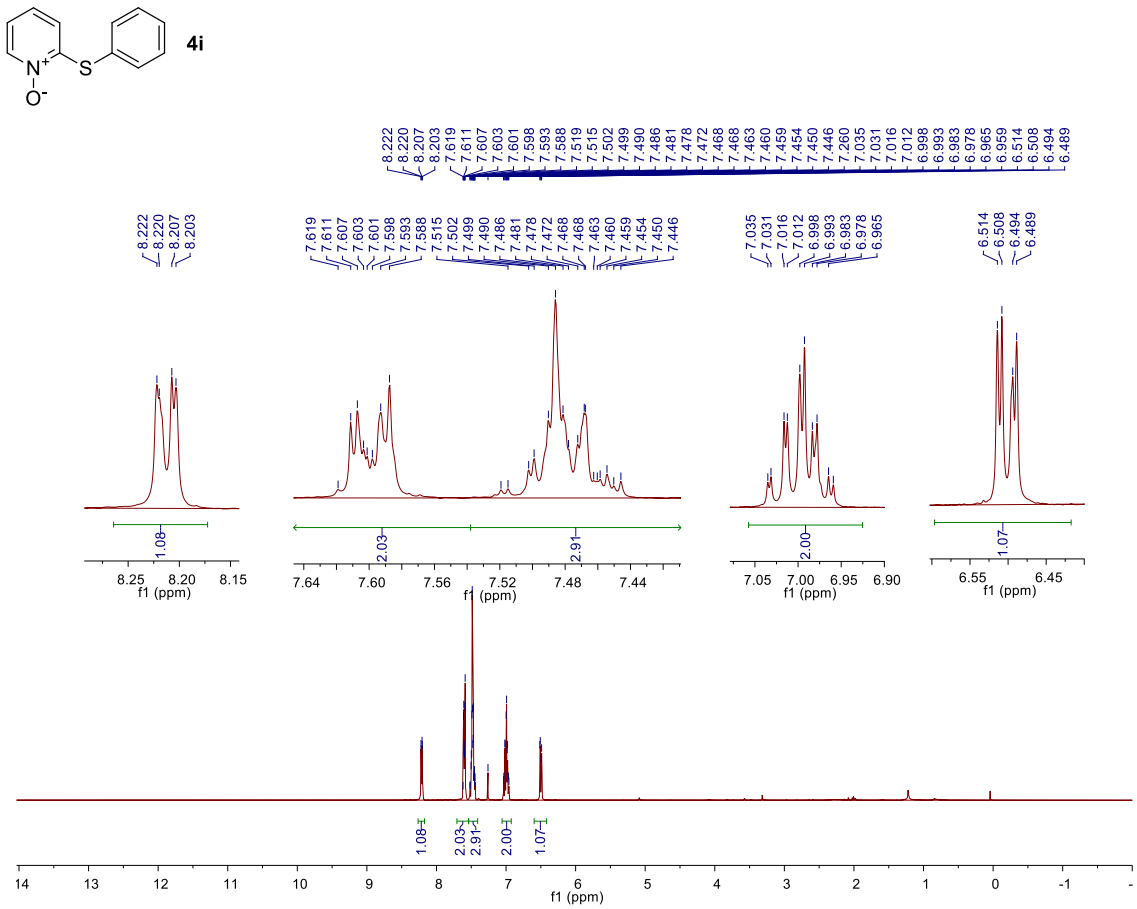
^{13}C NMR spectrum of **5-(phenylthio)oxazole (4g)** in $CDCl_3$ at 101 MHz.



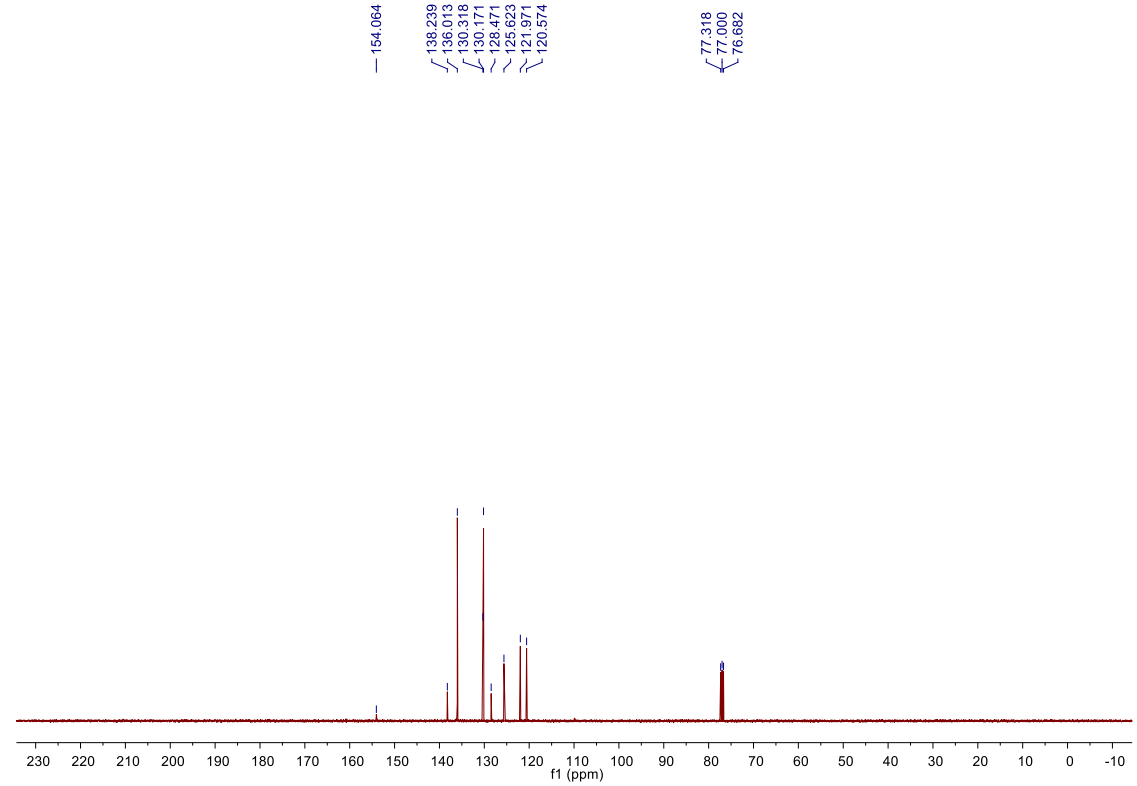
^{1}H NMR spectrum of **2-((4-chlorophenyl)thio)-N-tosylindole (4h)** in $CDCl_3$ at 400 MHz.



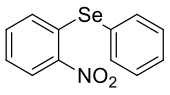
^{13}C NMR spectrum of **2-((4-chlorophenyl)thio)-N-tosyl-indole (4h)** in $CDCl_3$ at 101 MHz.



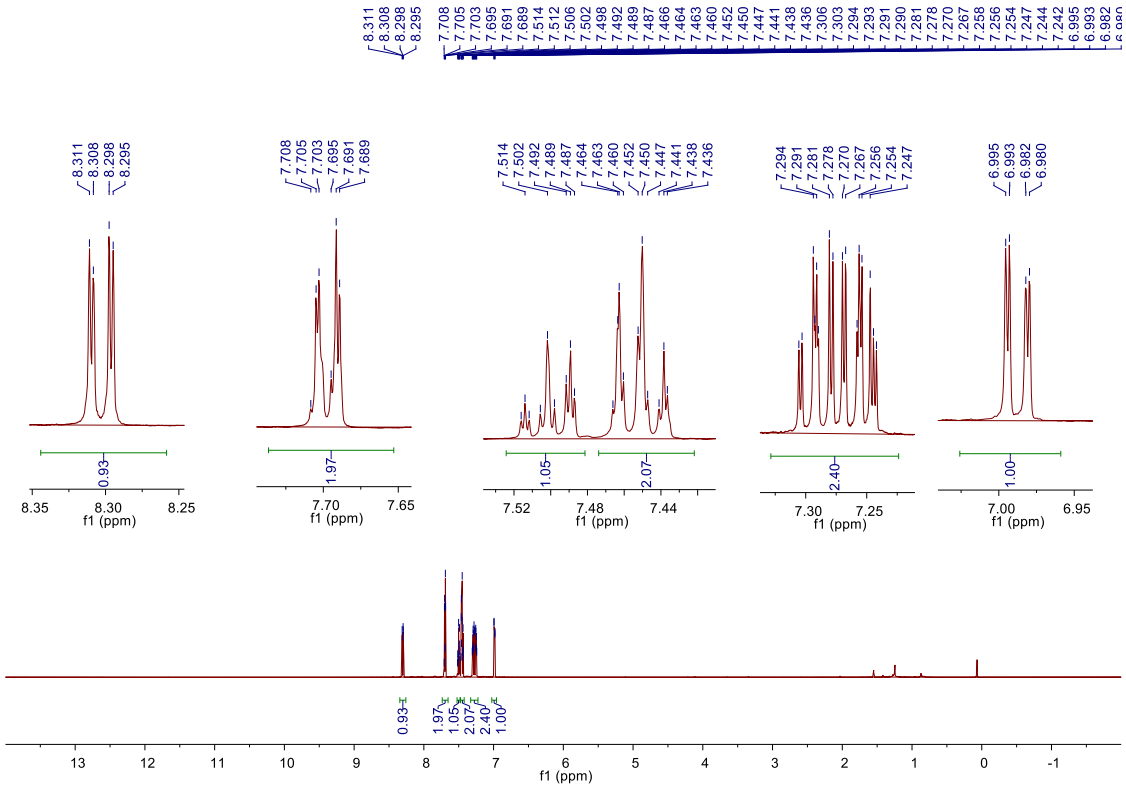
^{1}H NMR spectrum of **2-(phenylthio)pyridine-1-oxide (4i)** in $CDCl_3$ at 400 MHz.



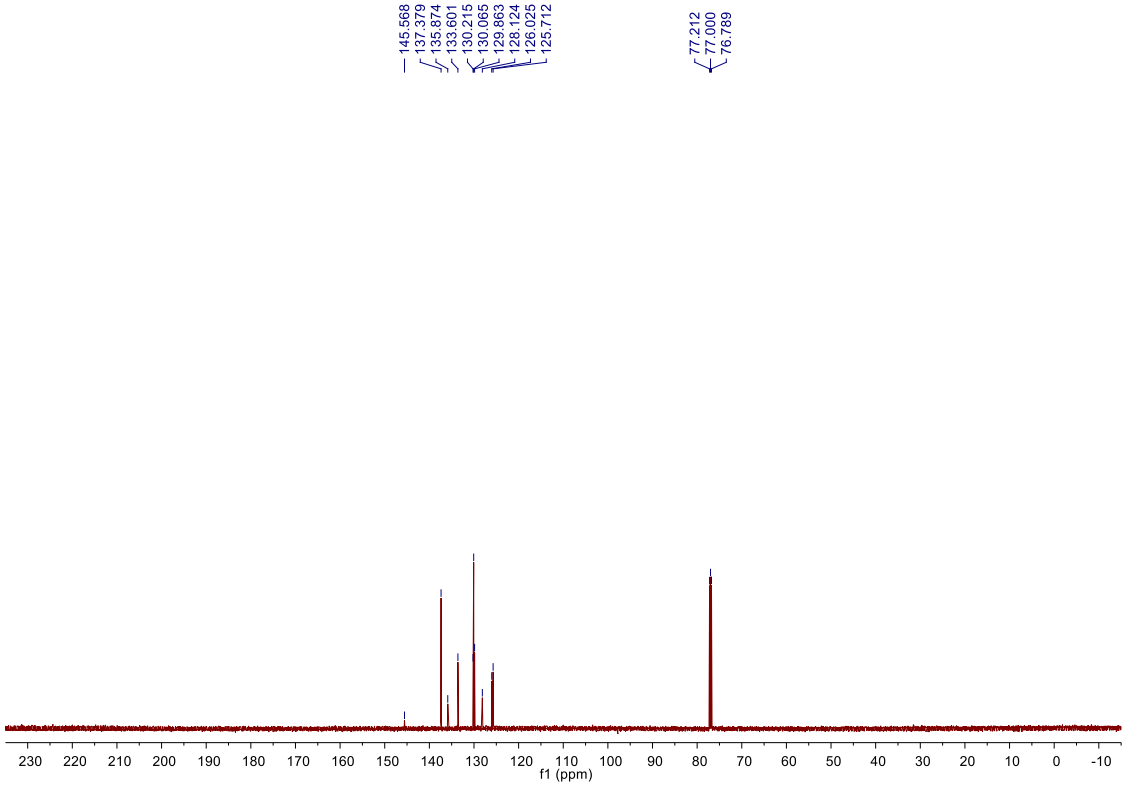
^{13}C NMR spectrum of **2-(phenylthio)pyridine-1-oxide (4i)** in $CDCl_3$ at 101 MHz.



5



^{1}H NMR spectrum of **(2-nitrophenyl)(phenyl)selane (5)** in $CDCl_3$ at 600 MHz.



^{13}C NMR spectrum of **(2-nitrophenyl)(phenyl)selane (5)** in $CDCl_3$ at 151 MHz.