SUPPLEMENTARY INFORMATION

Visible-Light-Induced Photocatalytic Synthesis of β -Keto Dithiocarbamates via Difunctionalization of Styrenes

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1. General Information:

^{1}H, ^{13}C and ^{19}F Spectra were recorded on a JEOL ECZ 500R FT NMR spectrometer (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz & ^{19}F NMR at 471 MHz). Chemical shifts for protons and carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the residual deuterium in the solvent (^{1}H NMR: $CDCl_3$ at 7.26 ppm) and carbon of the solvent peak (^{13}C NMR: $CDCl_3$ at 77.160 ppm) respectively. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, brs = broad singlet, and m = multiplet), coupling constant (*J*) (Hz), and integration. Mass spectra were recorded on a SCIEX X500R QTOF mass spectrometer. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 GF 254 plates (thickness 0.25 mm). Visualization of TLC was performed with a 254 nm UV lamp, and by staining in I_2 chamber. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Purification of the crude products was done by column chromatography using silica gel 100–200 mesh. All the reactions were carried out in oven-dried open glass vessels. Yield refers to the isolated analytically pure material.

2. Materials:

All the reagents and solvents were purchased from Sigma-Aldrich, Merck and TCI Chemicals. The chemicals were used as such without any further purification, whereas the solvents were purified by standard methods.

3. General Experimental Procedure:

A mixture of amine (**3**, 1.2 mmol), carbon disulfide (**2**, 2.4 mmol) and DMF (2 mL), contained in a 25-mL borosilicate RB flask, was stirred at room temperature for 5 minutes followed by the addition of styrene (**1**, 1 mmol), rhodamine B base (3 mol%) and aq. TBHP (2 equiv.). The contents were stirred and irradiated by Luxeon rebel blue LED (470 nm) under ambient conditions for 36 h. The distance from the light source to the irradiation vessel was approximately 2 cm and no filters were used. After completion of the reaction (monitored through TLC), a cold brine solution (10 mL) was added to the mixture, and then extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated using rotary vacuum evaporator. The residue was purified by column chromatography using ethyl acetate/n-hexane as eluent to afford the pure product **4** and **5**.

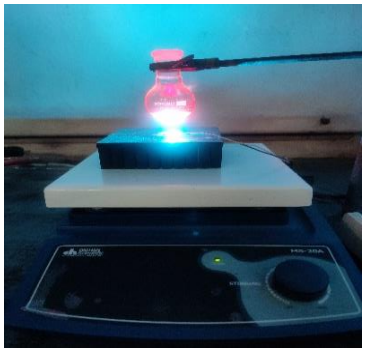
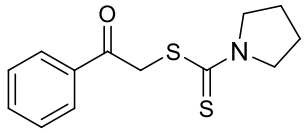


Figure S1. A picture of the LED set up.

4. Physical and Spectral Data:

2-Oxo-2-phenylethyl pyrrolidine-1-carbodithioate (4a):[1]



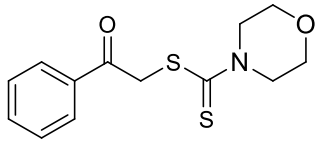
Light yellow solid (207 mg, 78% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 4.92 (s, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.77 (t, *J* = 7.0 Hz, 2H), 2.13–2.08 (m, 2H), 2.02–1.96 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 191.2, 136.2, 133.6, 128.8, 128.7, 55.6, 50.9, 44.6, 26.3, 24.5.

HRMS Calcd for $C_{13}H_{16}NOS_2^+$ $(M+H)^+$ 266.0668; Found 266.0676.

2-Oxo-2-phenylethyl morpholine-4-carbodithioate (4b):[1]

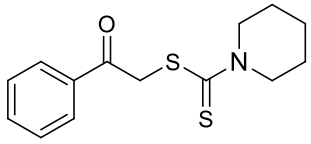


Light yellow solid (155 mg, 55% yield) Purification by column chromatography (ethyl acetate/hexane, v/v = 2:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 4.88 (s, 2H), 4.25–3.99 (m, 4H), 3.74 (t, *J* = 4.5 Hz, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 192.9, 136.0, 133.5, 128.7, 128.5, 66.1 (2C), 51.7, 50.6, 44.7.

2-Oxo-2-phenylethyl piperidine-1-carbodithioate (4c):



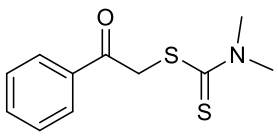
White solid (204 mg, 73% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:20)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 4.91 (s, 2H), 4.26 (brs, 2H), 3.96 (brs, 2H), 1.71 (brs, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 193.6, 136.3, 133.6, 128.8, 128.7, 53.7, 51.8, 45.1, 26.2, 25.5, 24.3.

HRMS Calcd for $C_{14}H_{18}NOS_2^+$ $(M+H)^+$ 280.0824; Found 280.0827.

2-Oxo-2-phenylethyl dimethylcarbamodithioate (4d):



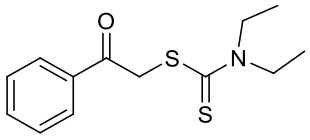
White solid (179 mg, 75% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 4.89 (s, 2H), 3.55 (s, 3H), 3.46 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 193.4, 136.3, 133.6, 128.8, 128.7, 46.0, 45.6, 41.8.

HRMS Calcd for $C_{11}H_{14}NOS_2^+$ $(M+H)^+$ 240.0512; Found 240.0503.

2-Oxo-2-phenylethyl diethylcarbamodithioate (4e):[1]

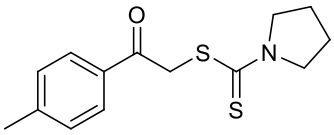


Light yellow solid (198 mg, 74% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:20)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 4.90 (s, 2H), 4.04–4.00 (m, 2H), 3.85–3.81 (m, 2H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 193.7, 136.3, 133.6, 128.8, 128.7, 50.2, 47.2, 45.2, 12.7, 11.7.

2-Oxo-2-(*p*-tolyl)ethyl pyrrolidine-1-carbodithioate (4f):



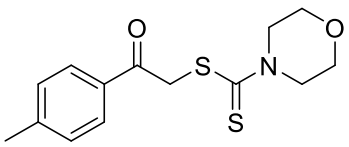
Light yellow solid (212 mg, 76% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 4.90 (s, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.77 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.13–2.07 (m, 2H), 2.01–1.96 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 191.3, 144.6, 133.7, 129.5, 128.8, 55.6, 50.9, 44.6, 26.3, 24.5, 21.9.

HRMS Calcd for $C_{14}H_{18}NOS_2^+$ $(M+H)^+$ 280.0824; Found 280.0820.

2-Oxo-2-(*p*-tolyl)ethyl morpholine-4-carbodithioate (4g):



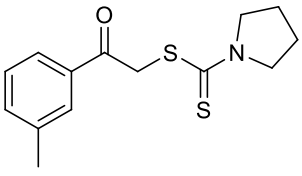
Light yellow solid (186 mg, 63% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 2:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.89 (s, 2H), 4.29–4.04 (m, 4H), 3.78 (t, *J* = 4.5 Hz, 4H), 2.42 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 192.7, 144.6, 133.7, 129.5, 128.8, 66.3 (2C), 52.0, 50.8, 44.9, 21.8.

HRMS Calcd for $C_{14}H_{18}NO_2S_2^+$ $(M+H)^+$ 296.0773; Found 296.0773.

2-Oxo-2-(*m*-tolyl)ethyl pyrrolidine-1-carbodithioate (4h):



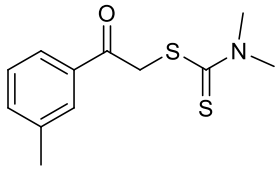
Light yellow solid (201 mg, 72% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (brs, 2H), 7.41–7.36 (m, 2H), 4.91 (s, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.14–2.08 (m, 2H), 2.02–1.97 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 191.2, 138.7, 136.2, 134.5, 129.2, 128.7, 125.9, 55.6, 50.9, 44.7, 26.3, 24.5, 21.5.

HRMS Calcd for $C_{14}H_{18}NOS_2^+$ $(M+H)^+$ 280.0824; Found 280.0824.

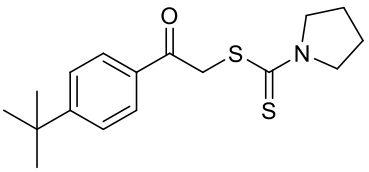
2-Oxo-2-(*m*-tolyl)ethyl dimethylcarbamodithioate (4i):



White solid (177 mg, 70% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (brs, 2H), 7.42–7.36(m, 2H), 4.88 (s, 2H), 3.55 (s, 3H), 3.46 (s, 3H), 2.43 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 193.6, 138.7, 136.3, 134.5, 129.1, 128.7, 125.9, 46.0, 45.7, 41.8, 21.5.
HRMS Calcd for $C_{12}H_{16}NOS_2^+$ $(M+H)^+$ 254.0668; Found 254.0666.

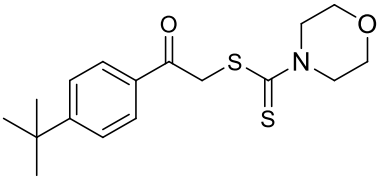
2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4j):



Light yellow solid (257 mg, 80% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 4.91 (s, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.77 (t, *J* = 7.0 Hz, 2H), 2.13–2.08 (m, 2H), 2.02–1.96 (m, 2H), 1.34 (s, 9H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 191.3, 157.5, 133.6, 128.7, 125.8, 55.6, 50.9, 44.6, 35.3, 31.2, 26.3, 24.5.
HRMS Calcd for $C_{17}H_{24}NOS_2^+$ $(M+H)^+$ 322.1294; Found 322.1294.

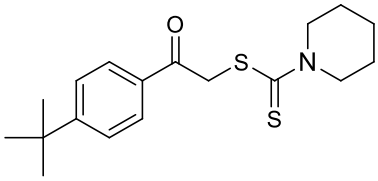
2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl morpholine-4-carbodithioate (4k):



Light yellow solid (202 mg, 60% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 4.91 (s, 2H), 4.29–4.06 (m, 4H), 3.79 (t, *J* = 5.0 Hz, 4H), 1.35 (s, 9H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 192.8, 157.6, 133.6, 128.7, 125.9, 66.3 (2C), 51.6, 50.8, 44.9, 35.4, 31.2.
HRMS Calcd for $C_{17}H_{24}NO_2S_2^+$ $(M+H)^+$ 338.1243; Found 338.1238.

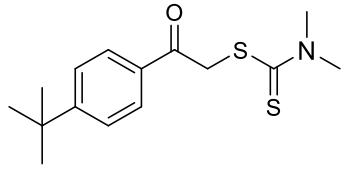
2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl piperidine-1-carbodithioate (4l):



Light yellow solid (241 mg, 72% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:20)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.90 (s, 2H), 4.27 (brs, 2H), 3.97 (brs, 2H), 1.72 (brs, 6H), 1.35 (s, 9H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 193.2, 157.4, 133.7, 128.7, 125.8, 53.7, 51.8, 45.1, 35.3, 31.2, 26.2, 25.5, 24.3.
HRMS Calcd for $C_{18}H_{26}NOS_2^+$ $(M+H)^+$ 336.1450; Found 336.1460.

2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl dimethylcarbamodithioate (4m):



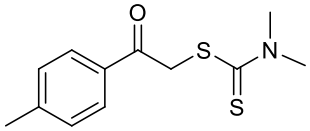
White solid (230 mg, 78% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 4.88 (s, 2H), 3.55 (s, 3H), 3.46 (s, 3H), 1.35 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 193.0, 157.4, 133.6, 128.7, 125.8, 46.0, 45.6, 41.8, 35.3, 31.2.

HRMS Calcd for $C_{15}H_{22}NOS_2^+$ $(M+H)^+$ 296.1137; Found 296.1142.

2-Oxo-2-(*p*-tolyl)ethyl dimethylcarbamodithioate (4n):



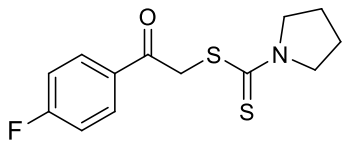
White solid (192 mg, 76% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.86 (s, 2H), 3.54 (s, 3H), 3.45 (s, 3H), 2.42 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 193.0, 144.5, 133.7, 129.5, 128.8, 45.9, 45.6, 41.8, 21.8.

HRMS Calcd for $C_{12}H_{16}NOS_2^+$ $(M+H)^+$ 254.0668; Found 254.0663.

2-(4-Fluorophenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4o):



Light yellow solid (176 mg, 62% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

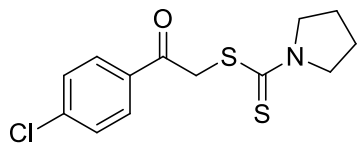
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14–8.11 (m, 2H), 7.18–7.14 (m, 2H), 4.88 (s, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.77 (t, *J* = 7.0 Hz, 2H), 2.14–2.09 (m, 2H), 2.03–1.97 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 191.0, 167.2 (d, *J* = 256.3 Hz), 132.7, 131.5 (d, *J* = 9.5 Hz), 116.1, 115.9, 55.7, 50.9, 44.3, 26.3, 24.5.

HRMS Calcd for $C_{13}H_{15}FNOS_2^+$ $(M+H)^+$ 284.0574; Found 284.0581;

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.24.

2-(4-Chlorophenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4p):



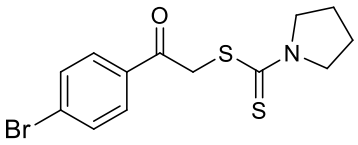
Light yellow solid (203 mg, 68% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.85 (s, 2H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.76 (t, *J* = 7.0 Hz, 2H), 2.13–2.08 (m, 2H), 2.02–1.96 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6, 190.9, 140.1, 134.5, 130.1, 129.1, 55.7, 50.9, 44.2, 26.3, 24.5.

HRMS Calcd for $C_{13}H_{15}ClNOS_2^+$ $(M+H)^+$ 300.0278; Found 300.0254.

2-(4-Bromophenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4q):



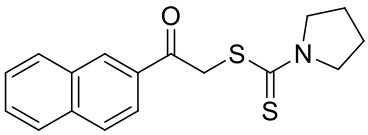
Light yellow solid (223 mg, 65% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.76 (t, *J* = 7.0 Hz, 2H), 2.13–2.08 (m, 2H), 2.02–1.96 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 190.9, 135.0, 132.1, 130.2, 128.9, 55.7, 50.9, 44.2, 26.3, 24.5.

HRMS Calcd for $C_{13}H_{15}BrNOS_2^+$ $(M+H)^+$ 343.9773; Found 343.9771.

2-(Naphthalen-2-yl)-2-oxoethyl pyrrolidine-1-carbodithioate (4r):



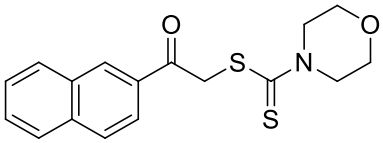
Light yellow solid (243 mg, 77% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.11 (d, *J* = 9.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.92–7.88 (m, 2H), 7.63–7.55 (m, 2H), 5.05 (s, 2H), 3.95 (t, *J* = 7.0 Hz, 2H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.14–2.08 (m, 2H), 2.02–1.97 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 191.2, 135.9, 133.5, 132.6, 130.6, 129.9, 128.8, 128.7, 127.9, 127.0, 124.3, 55.6, 50.9, 44.6, 26.3, 24.5.

HRMS Calcd for $C_{17}H_{18}NOS_2^+$ $(M+H)^+$ 316.0824; Found 316.0796.

2-(Naphthalen-2-yl)-2-oxoethyl morpholine-4-carbodithioate (4s):



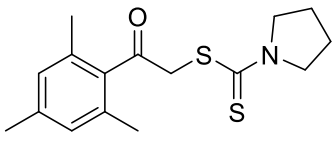
Light yellow solid (235 mg, 71% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 2:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.11–8.09 (m, 1 H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.93–7.88 (m, 2H), 7.64–7.56 (m, 2H), 5.06 (s, 2H), 4.33–4.06 (m, 4H), 3.80 (t, *J* = 5.0 Hz, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 193.2, 136.0, 133.5, 132.6, 130.6, 129.9, 128.9, 128.8, 128.0, 127.1, 124.2, 66.4(2C), 51.9, 50.8, 44.9.

HRMS Calcd for $C_{17}H_{18}NO_2S_2^+$ $(M+H)^+$ 332.0773; Found 332.0783.

2-Mesityl-2-oxoethyl pyrrolidine-1-carbodithioate (4t):



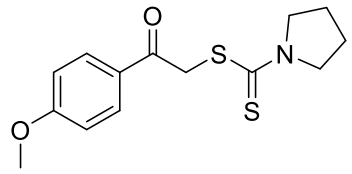
White solid (200 mg, 65% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.82 (s, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.79 (t, *J* = 6.5 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 6H), 2.14–2.08 (m, 2H), 2.03–1.97 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 191.0, 139.2, 137.7, 133.5, 128.8, 55.8, 50.9, 49.4, 26.2, 24.5, 21.2, 19.6.

HRMS Calcd for $C_{16}H_{22}NOS_2^+$ $(M+H)^+$ 308.1138; Found 308.1141.

2-(4-Methoxyphenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4u):



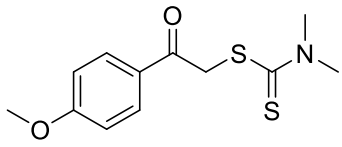
White solid (218 mg, 74% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:7)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 4.88 (s, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 3.77 (t, *J* = 7.0 Hz, 2H), 2.13–2. 07 (m, 2H), 2.02–1.96 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 191.4, 164.0, 131.1, 129.2, 114.0, 55.7, 50.9, 44.4, 26.3, 24.5.

HRMS Calcd for $C_{14}H_{18}NO_2S_2^+$ $(M+H)^+$ 296.0774; Found 296.0769.

2-(4-Methoxyphenyl)-2-oxoethyl dimethylcarbamodithioate (4v):



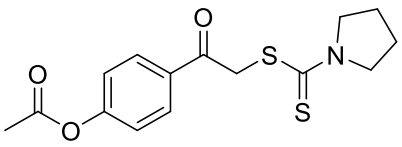
White solid (191 mg, 71% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:7)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.86 (s, 2H), 3.88 (s, 3H), 3.55 (s, 3H), 3.46 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9, 192.0, 164.0, 131.1, 129.3, 114.0, 55.7, 46.0, 45.5, 41.8.

HRMS Calcd for $C_{12}H_{16}NO_2S_2^+$ $(M+H)^+$ 270.0617; Found 270.0613.

4-(2-((Pyrrolidine-1-carbonothioyl)thio)acetyl)phenyl acetate (4w):



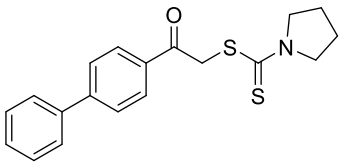
White solid (233 mg, 72% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:6)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.87 (s, 2H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.75 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 2.12–2.07 (m, 2H), 2.01–1.95 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4, 190.9, 168.9, 154.7, 133.7, 130.4, 122.0, 55.6, 50.9, 44.3, 26.2, 24.4, 21.3.

HRMS Calcd for $C_{15}H_{18}NO_3S_2^+$ $(M+H)^+$ 324.0723; Found 324.0715.

2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl pyrrolidine-1-carbodithioate (4x):



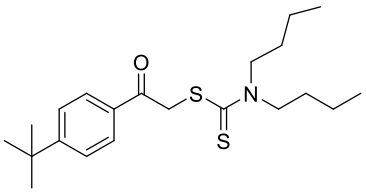
White solid (249 mg, 73% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.95 (s, 2H), 3.95 (t, *J* = 7.0 Hz, 2H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.14–2.09 (m, 2H), 2.03–1.97 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 191.2, 146.3, 140.0, 134.9, 129.3, 129.1, 128.4, 127.5, 127.4, 55.6, 50.9, 44.6, 26.3, 24.5.

HRMS Calcd for $C_{19}H_{20}NOS_2^+$ $(M+H)^+$ 342.0981; Found 342.0975.

2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl dibutylcarbamodithioate (4y) :



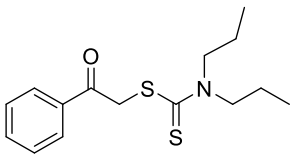
Colourless liquid (186 mg, 49% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:40)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 4.88 (s, 2H), 3.95 (t, *J* = 8.0 Hz, 2H), 3.75 (t, *J* = 7.5 Hz, 2H), 1.77–1.69 (m, 4H), 1.41–1.37 (m, 4H), 1.35 (s, 9H), 0.99–0.93 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 193.3, 157.4, 133.7, 128.7, 125.8, 55.8, 53.0, 45.2, 35.3, 31.2, 29.5, 28.5, 20.2, 14.0, 13.9.

HRMS Calcd for $C_{21}H_{34}NOS_2^+$ $(M+H)^+$ 380.2077; Found 380.2079.

2-Oxo-2-phenylethyl dipropylcarbamodithioate (4z):



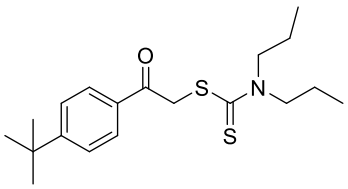
Colourless liquid (136 mg, 46% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:40)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 4.87 (s, 2H), 3.89 (t, *J* = 7.5 Hz, 2H), 3.69 (t, *J* = 7.5 Hz, 2H), 1.80–1.70 (m, 4H), 0.96–0.88 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 193.5, 136.1, 133.4, 128.6, 128.5, 57.4, 54.6, 45.0, 20.8, 19.6, 11.2.

HRMS Calcd for $C_{15}H_{22}NOS_2^+$ $(M+H)^+$ 296.1138; Found 296.1149.

2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl dipropylcarbamodithioate (4aa) :



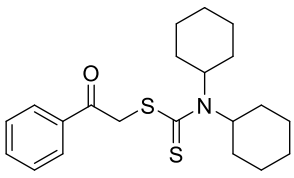
Colourless liquid (176 mg, 50% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:40)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 4.89 (s, 2H), 3.92 (t, *J* = 7.5 Hz, 2H), 3.72 (t, *J* = 8.0 Hz, 2H), 1.82–1.73 (m, 4H), 1.35 (s, 9H), 0.98–0.93 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 193.3, 157.4, 133.7, 128.7, 125.8, 57.5, 54.8, 45.3, 35.3, 31.2, 20.9, 19.8, 11.4.

HRMS Calcd for $C_{19}H_{30}NOS_2^+$ $(M+H)^+$ 352.1764; Found 352.1780.

2-Oxo-2-phenylethyl dicyclohexylcarbamodithioate (4ab):



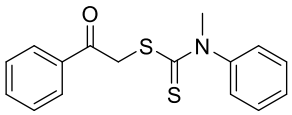
Colourless liquid (169 mg, 45% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:40)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 4.82 (s, 2H), 3.46–2.81 (m, 2H), 1.90–1.16 (m, 20H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 136.5, 133.3, 128.6, 128.6, 64.8, 44.9, 43.8, 30.1, 26.7, 25.8, 25.3.

HRMS Calcd for $C_{21}H_{30}NOS_2^+$ $(M+H)^+$ 376.1764; Found 376.1738.

2-Oxo-2-phenylethyl methyl(phenyl)carbamodithioate (4ac):



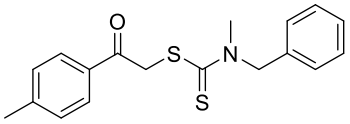
White solid (226 mg, 75% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:50)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.49–7.42 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 2H), 3.78 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 193.5, 136.4, 133.6, 130.0, 129.4, 128.8, 128.6, 127.1, 46.7, 45.8.

HRMS Calcd for $C_{16}H_{16}NOS_2^+$ $(M+H)^+$ 302.0668; Found 302.0666.

2-Oxo-2-(*p*-tolyl)ethyl benzyl(methyl)carbamodithioate (4ad):



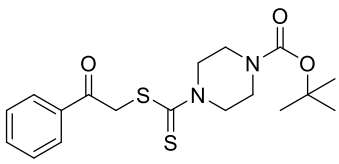
White solid (230 mg, 70% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:7)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (t, *J* = 7.5 Hz, 2H), 7.38–7.29 (m, 7H), 5.36 (s, 1H), 5.09 (s, 1H), 4.94 (brs, 2H), 3.47–3.35 (m, 3H), 2.43 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 193.0, 144.6, 133.8, 129.6, 129.1, 128.9, 128.8, 127.9, 127.4, 60.2, 58.2, 45.9, 45.6, 39.2, 21.9.

HRMS Calcd for $C_{18}H_{20}NOS_2^+$ $(M+H)^+$ 330.0981; Found 330.0963.

***tert*-Butyl 4-(((2-oxo-2-phenylethyl)thio)carbonothioyl)piperazine-1-carboxylate (4ae):**



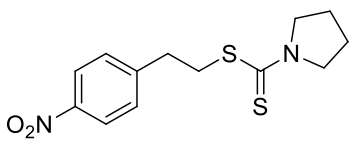
White solid (137 mg, 36% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 2:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 4.91 (s, 2H), 4.27 (brs, 2H), 4.05 (brs, 2H), 3.58 (t, *J* = 4.5 Hz, 4H), 1.48 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 193.1, 154.5, 136.2, 133.7, 128.9, 128.7, 80.8, 51.2, 50.2, 45.0, 43.0, 28.5.

HRMS Calcd for $C_{18}H_{25}N_2O_3S_2^+$ $(M+H)^+$ 381.1301; Found 381.1290.

4-Nitrophenethyl pyrrolidine-1-carbodithioate (5a):



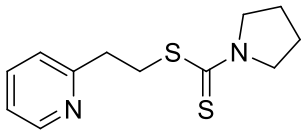
Yellow solid (284 mg, 96% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:4)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 3.60 (t, *J* = 6.5 Hz, 2H), 3.52 (t, *J* = 7.5 Hz, 2H),3.09 (t, *J* = 8.0 Hz, 2H),2.07–2.02 (m, 2H), 1.97–1.92 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 147.9, 146.9, 129.6, 123.6, 55.0, 50.6, 36.5, 35.3, 26.0, 24.2.

HRMS Calcd for $C_{13}H_{17}N_2O_2S_2^+$ $(M+H)^+$ 297.0726; Found 297.0720.

2-(Pyridin-2-yl)ethyl pyrrolidine-1-carbodithioate (5b):



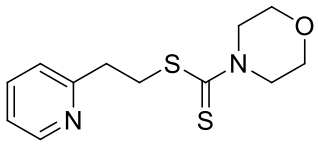
Light yellow solid (234 mg, 93% yield); Purification by column chromatography (ethyl acetate/hexane, v/v =1:4)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.5 Hz, 1H),7.63 (t, *J* = 7.0 Hz, 1H), 7.29–7.27 (m, 1H), 7.15–7.14 (m, 1H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.72 (t, *J* = 7.5 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.23 (t, *J* = 8.0 Hz, 2H), 2.09–2.04 (m, 2H), 2.00–1.95 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 159.9, 149.4, 136.5, 123.4, 121.6, 55.0, 50.6, 37.6, 35.6, 26.1, 24.3.

HRMS Calcd for $C_{12}H_{17}N_2S_2^+$ $(M+H)^+$ 253.0828; Found 253.0827.

2-(Pyridin-2-yl)ethyl morpholine-4-carbodithioate (5c):



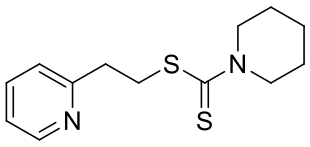
Light yellow solid (255 mg, 95% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.0 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.07–7.04 (m, 1H), 4.21 (brs, 2H), 3.86 (brs, 2H), 3.68–3.65 (m, 6H), 3.15 (t, *J* = 7.5 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3 159.5, 149.2, 136.3, 123.2, 121.5, 66.1, 50.5, 37.1, 35.9.

HRMS Calcd for $C_{12}H_{17}N_2OS_2^+$$(M+H)^+$ 269.0777; Found 269.0772.

2-(Pyridin-2-yl)ethyl piperidine-1-carbodithioate (5d):

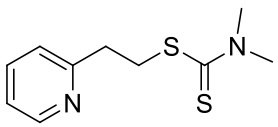


Yellow solid (253 mg, 95% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 1:4)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.0 Hz, 1H),7.57 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5Hz, 1H), 7.09 (t, *J* = 6.0 Hz, 1H), 4.24 (brs, 2H), 3.81 (brs, 2H), 3.67 (t, *J* = 7.5 Hz, 2H),3.17–3.14 (m, 2H), 1.69–1.61 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 159.8, 149.2, 136.4, 123.3, 121.5, 52.8, 51.2, 37.4, 36.2, 25.9, 25.4, 24.2. HRMS Calcd for $C_{13}H_{19}N_2S_2^+$ $(M+H)^+$ 267.0984; Found 267.0982.

2-(Pyridin-2-yl)ethyl dimethylcarbamodithioate (5e):



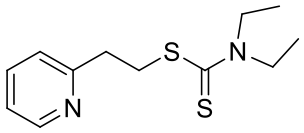
Light yellow solid (247 mg, 98% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 2:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44–8.42 (m, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 4.5 Hz, 1H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.43 (s, 3H), 3.23 (s, 3H), 3.11 (t, *J* = 7.0 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$)δ 196.8, 159.5, 149.1, 136.3, 123.2, 121.4, 45.1, 41.3, 37.1, 36.5.

HRMS Calcd for $C_{10}H_{15}N_2S_2^+$ $(M+H)^+$ 227.0671; Found 227.0671.

2-(Pyridin-2-yl)ethyl diethylcarbamodithioate (5f):



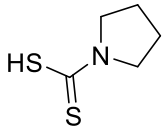
Yellow liquid (247 mg, 97% yield) Purification by column chromatography (ethyl acetate/hexane, v/v = 2:9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 5.5 Hz, 1H), 4.05 (d, *J* = 6.5 Hz, 2H), 3.72–3.68 (m, 4H), 3.23 (t, *J* = 7.5 Hz, 2H), 1.27 (brs, 6H);

^{13}C NMR (126 MHz, $CDCl_3$)δ 195.6, 160.0, 149.4, 136.5, 123.5, 121.6, 49.5, 46.8, 37.6, 36.4, 12.6, 11.7.

HRMS Calcd for $C_{12}H_{19}N_2S_2^+$ $(M+H)^+$ 255.0984; Found 255.0985.

Pyrrolidine-1-carbodithioic acid (I):



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 3.88 (t, *J* = 6.5 Hz, 2H), 3.47 (t, *J* = 7.0 Hz, 2H), 2.00–1.96 (m, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 53.8, 45.1, 26.0, 24.4.

HRMS Calcd for $C_5H_{10}NS_2^+$ $(M+H)^+$ 148.0249; Found 148.0256.

5. Reference

1. Khalilzadeh, M. A.; Hossaini, Z.; Baradarani, M. M.; Hasannia, A. *Tetrahedron* **2010**, *66*, 8464 – 8467.

6. Cyclic Voltammogram of Pyrrolidine-1-carbodithioic acid (I):

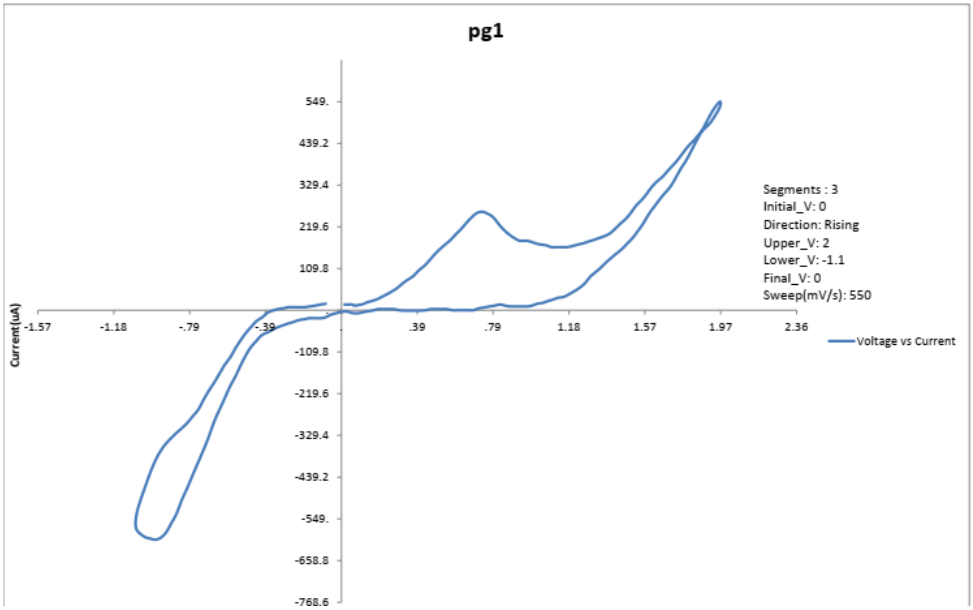
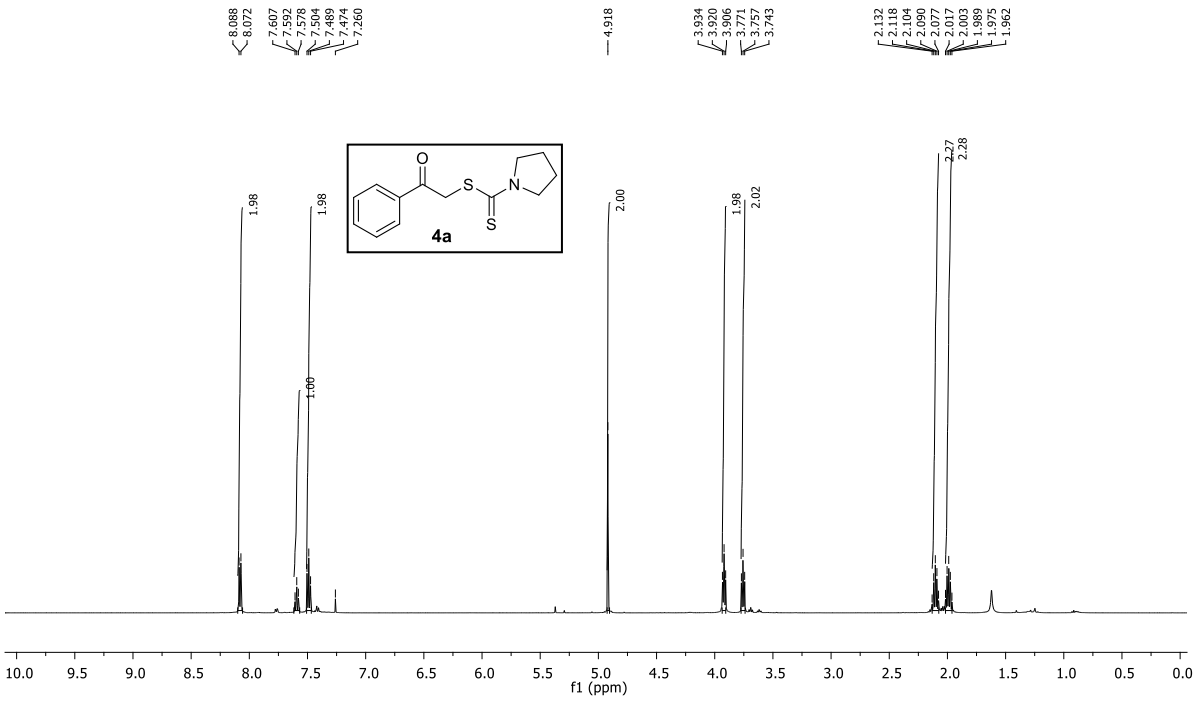


Figure S2. Cyclic voltammogram of **I** recorded in 0.1 M CH_3CN/TBAP at scan rate of 550 mVs-1. Working electrode: Glassy carbon electrode; Counter electrode: Platinum wire; Reference electrode: Ag/AgCl.

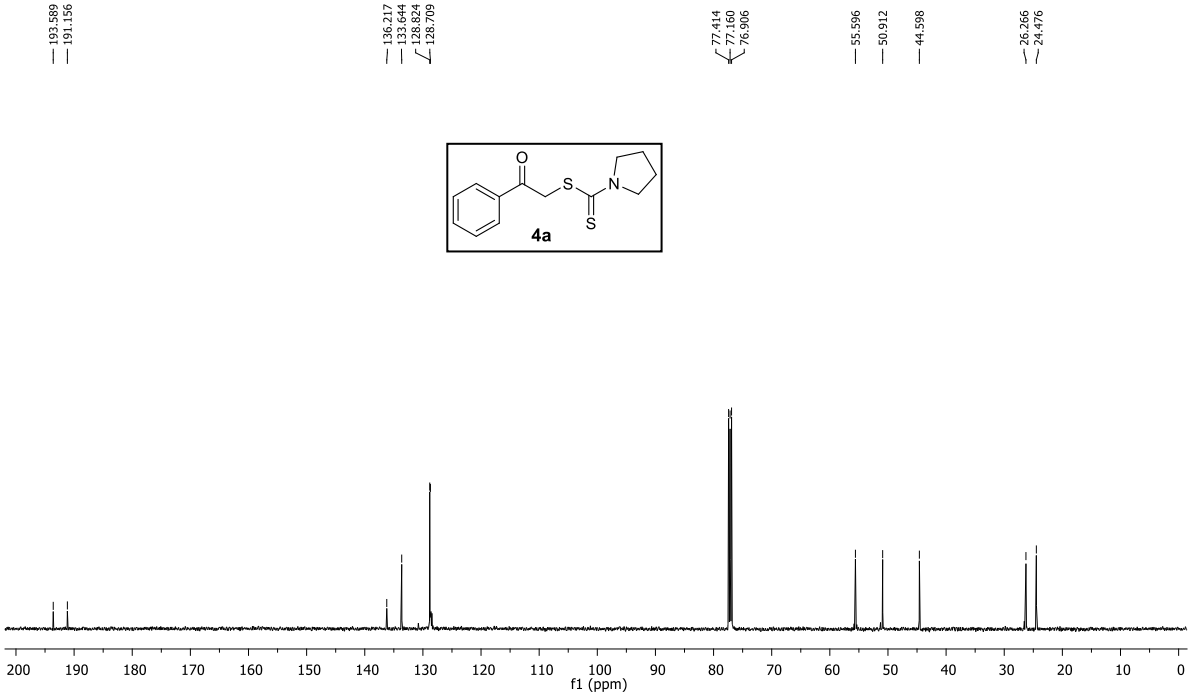
7. Copies of ^{1}H and ^{13}C and ^{19}F Spectra.

2-Oxo-2-phenylethyl pyrrolidine-1-carbodithioate (4a):[1]

^{1}H NMR, $CDCl_3$, 500 MHz

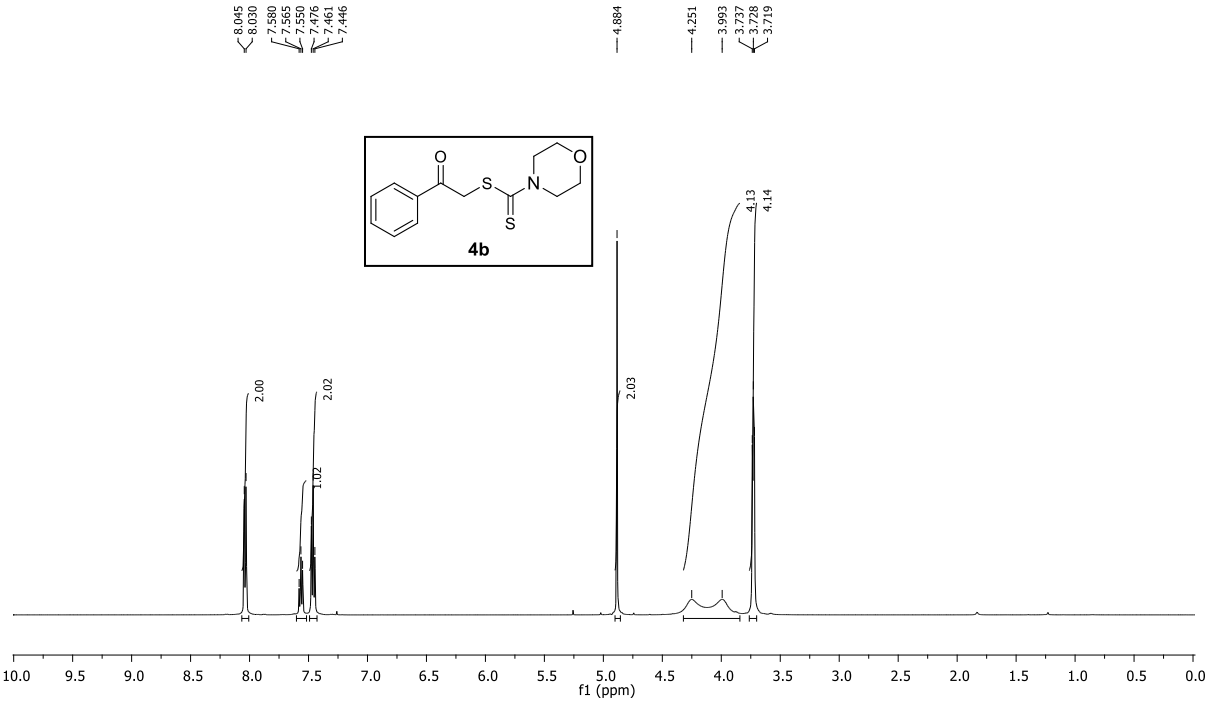


^{13}C NMR, $CDCl_3$, 126 MHz

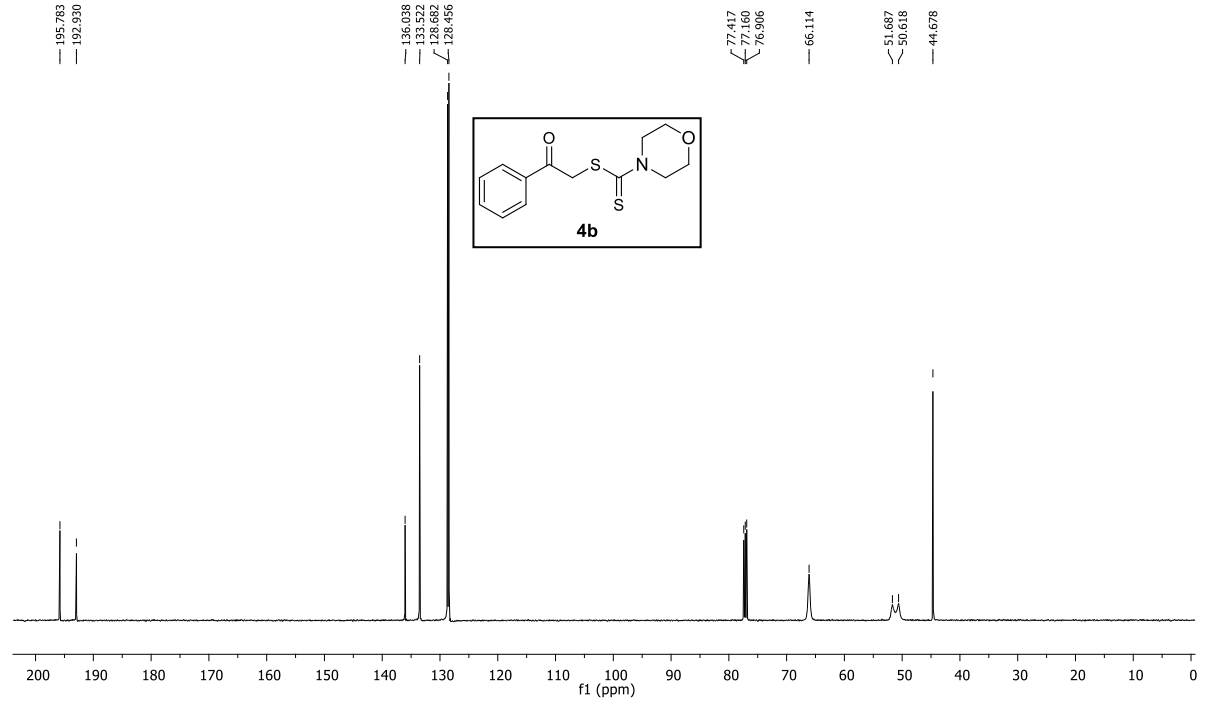


2-Oxo-2-phenylethyl morpholine-4-carbodithioate (4b):[1]

^{1}H NMR, $CDCl_3$, 500 MHz

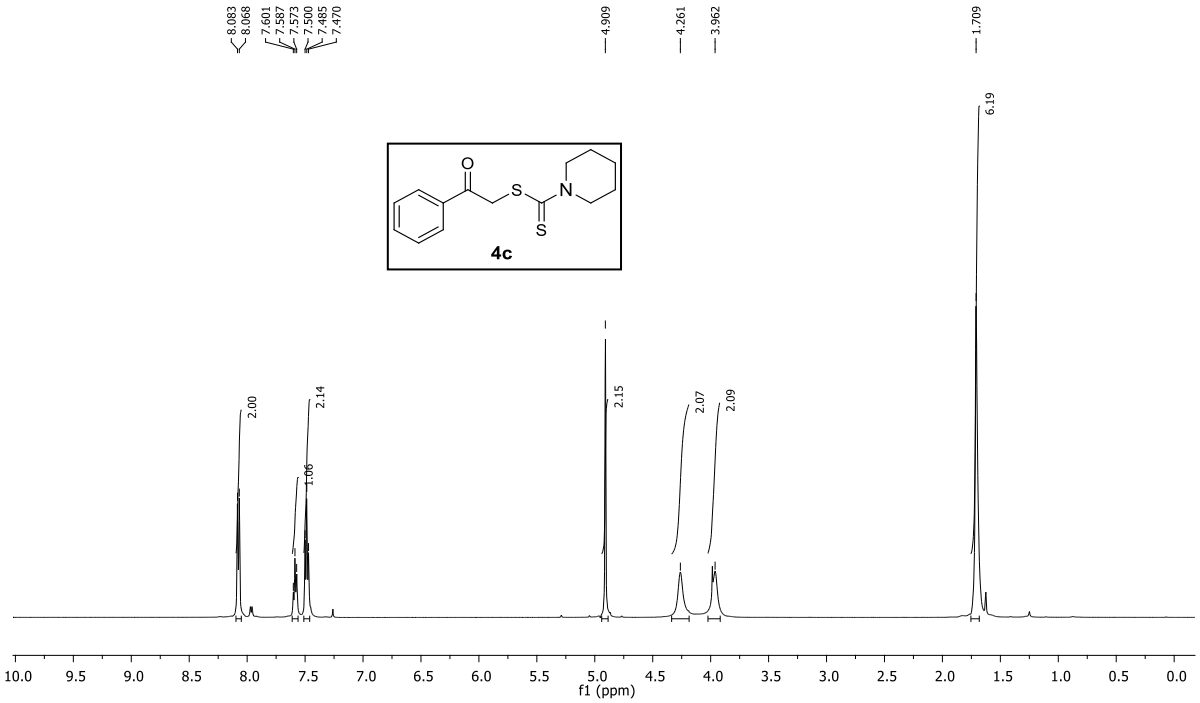


^{13}C NMR, $CDCl_3$, 126 MHz

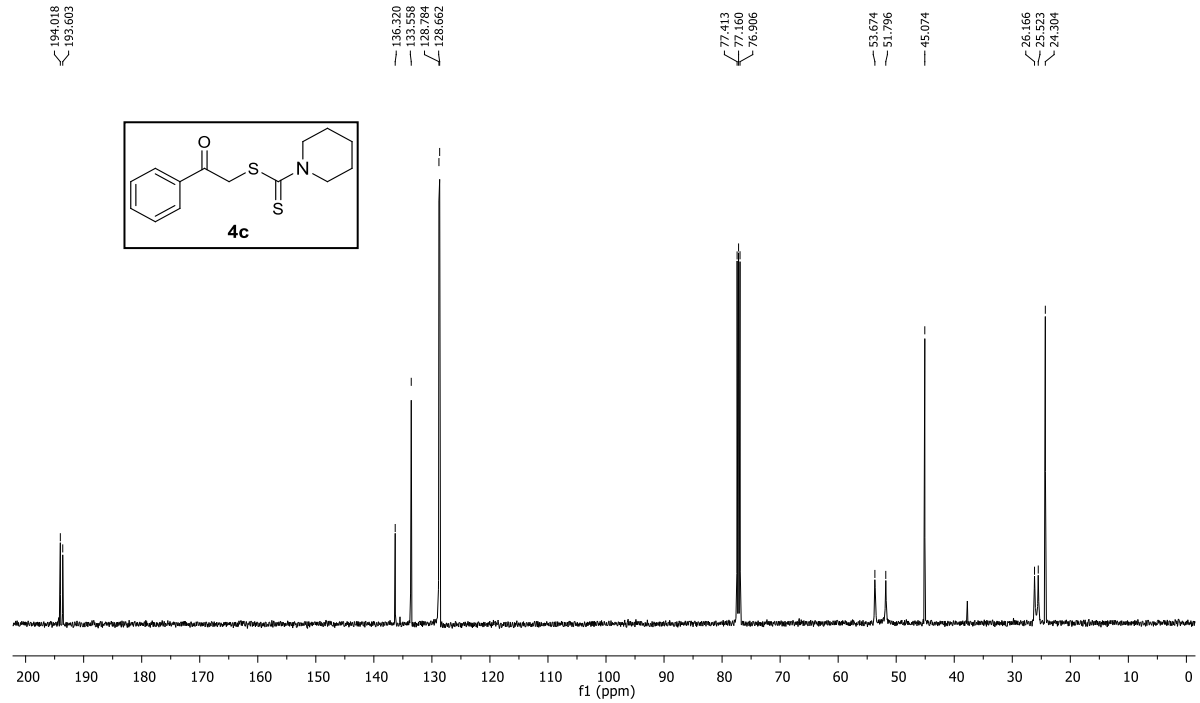


2-Oxo-2-phenylethyl piperidine-1-carbodithioate (4c):

^{1}H NMR, $CDCl_3$, 500 MHz

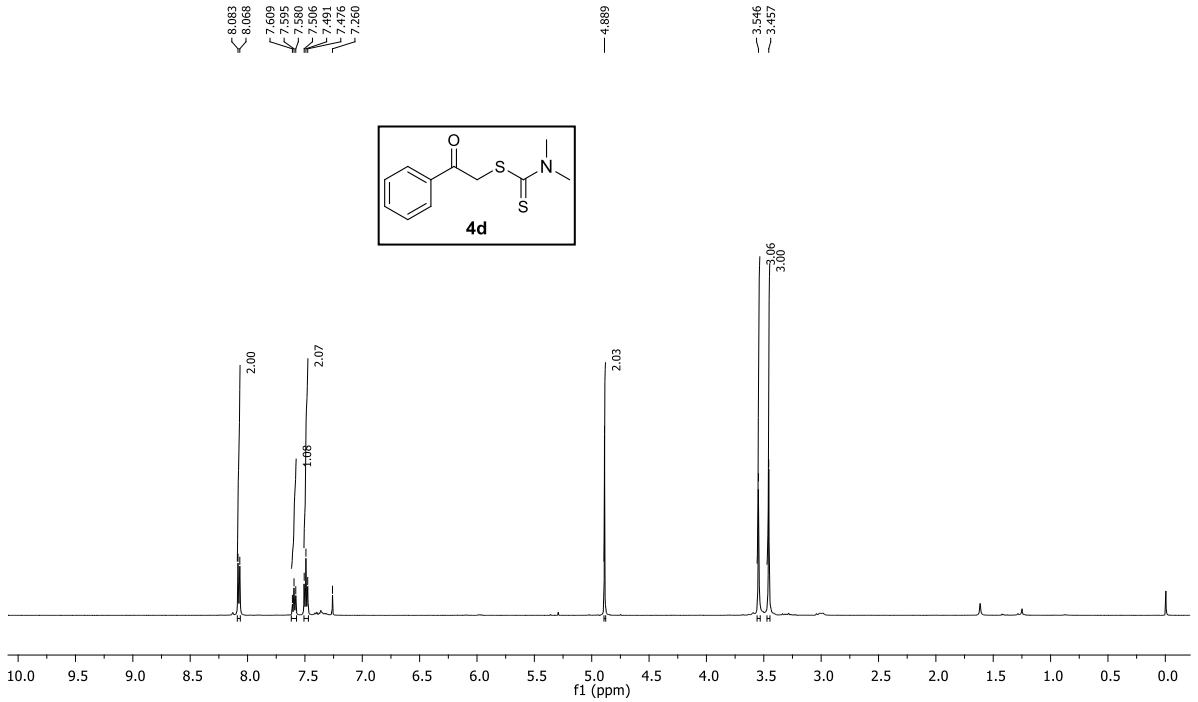


^{13}C NMR, $CDCl_3$, 126 MHz

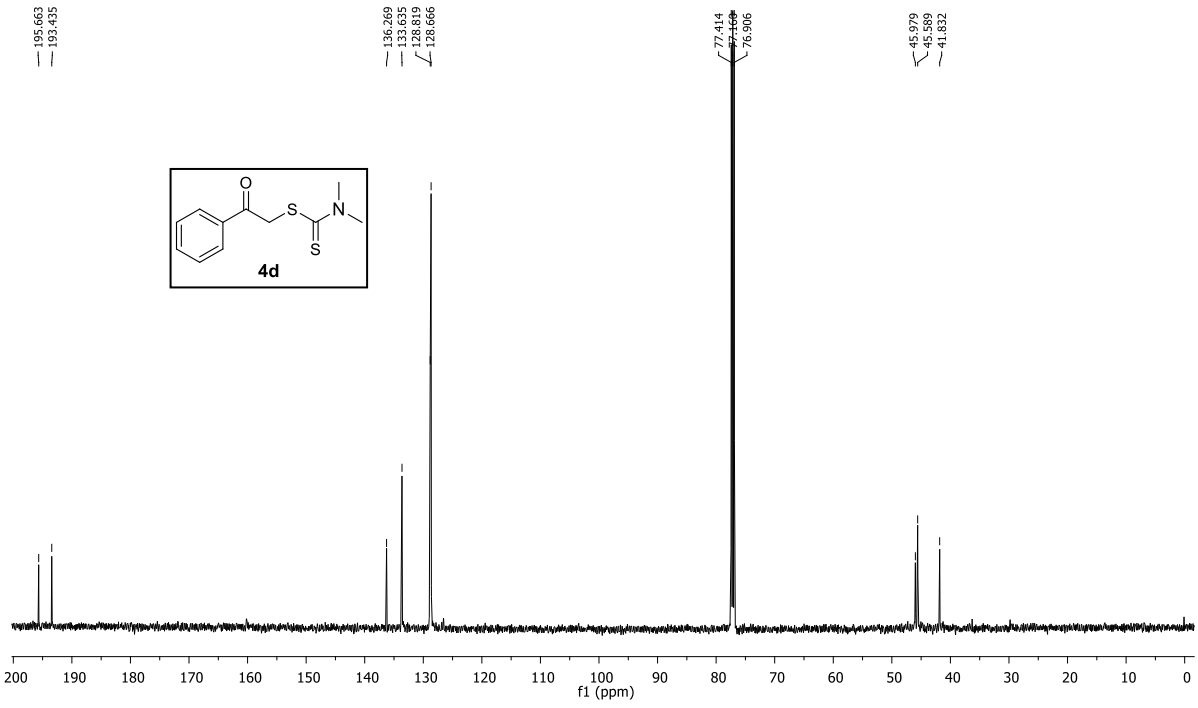


2-Oxo-2-phenylethyl dimethylcarbamodithioate (4d):

^{1}H NMR, $CDCl_3$, 500 MHz

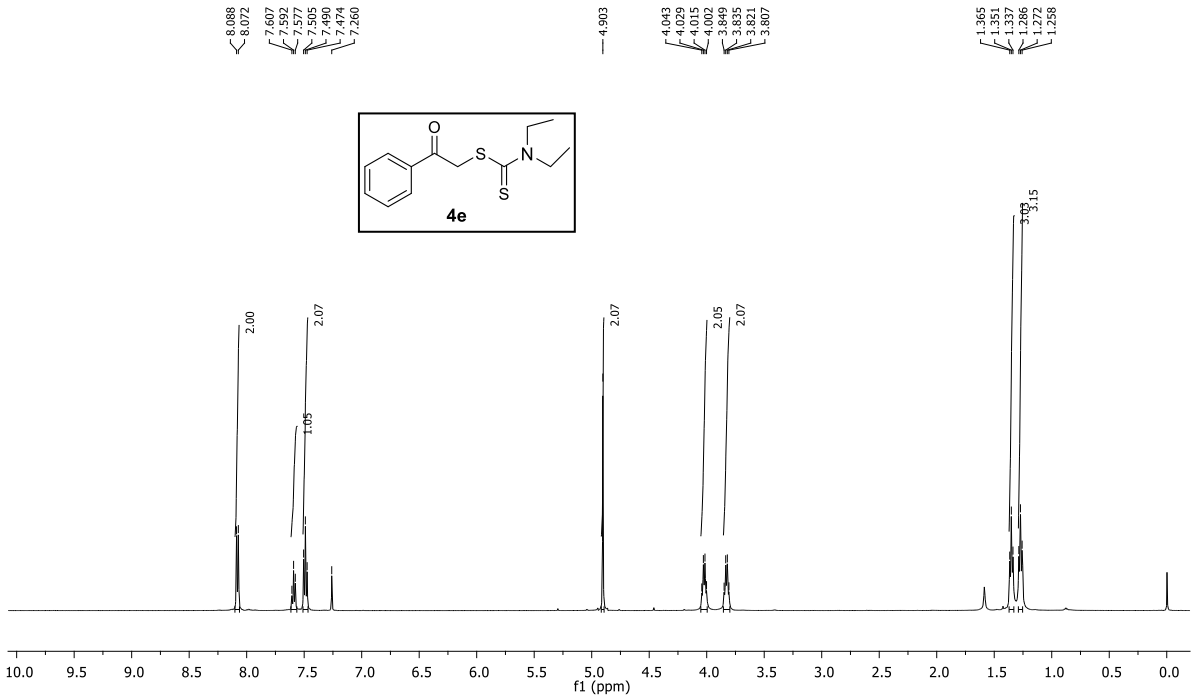


^{13}C NMR, $CDCl_3$, 126 MHz

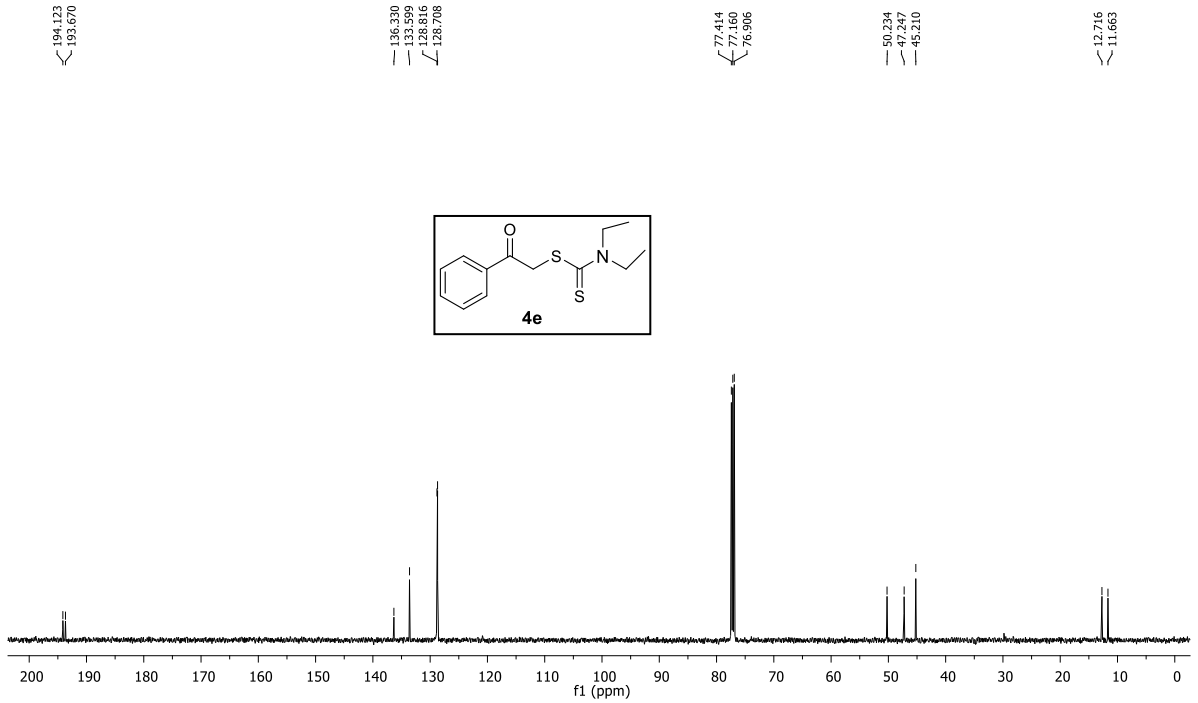


2-Oxo-2-phenylethyl diethylcarbamodithioate (4e):[1]

^{1}H NMR, $CDCl_3$, 500 MHz

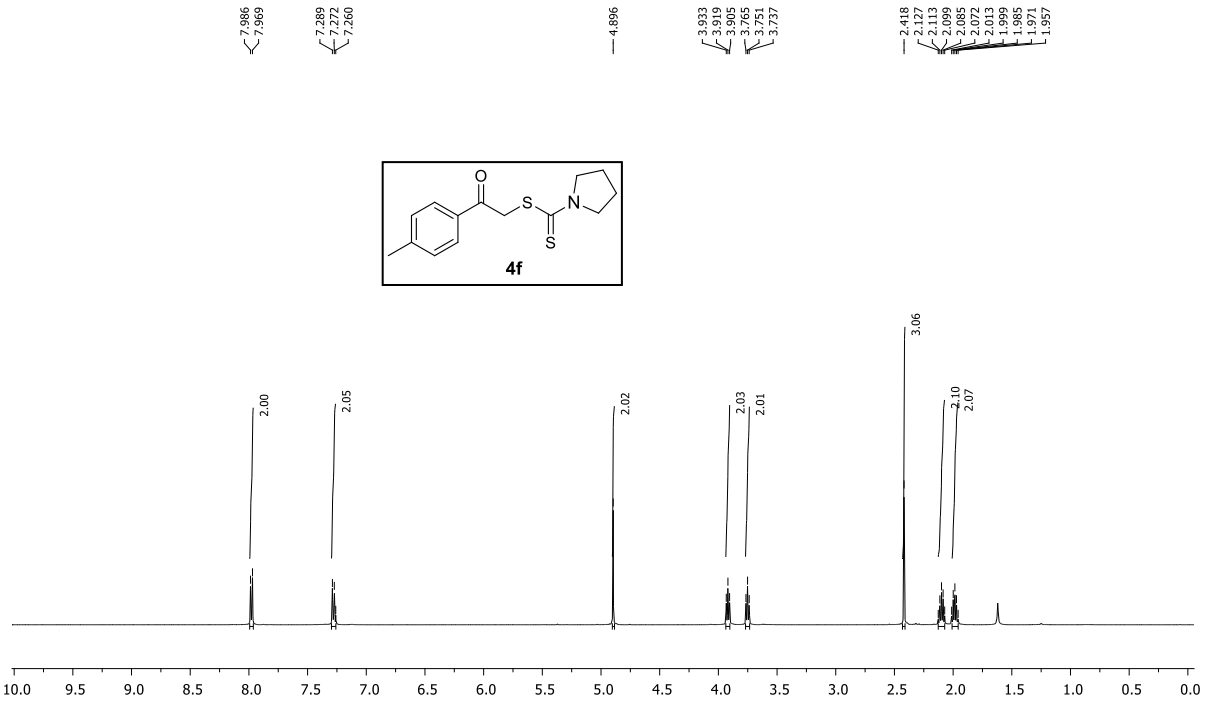


^{13}C NMR, $CDCl_3$, 126 MHz

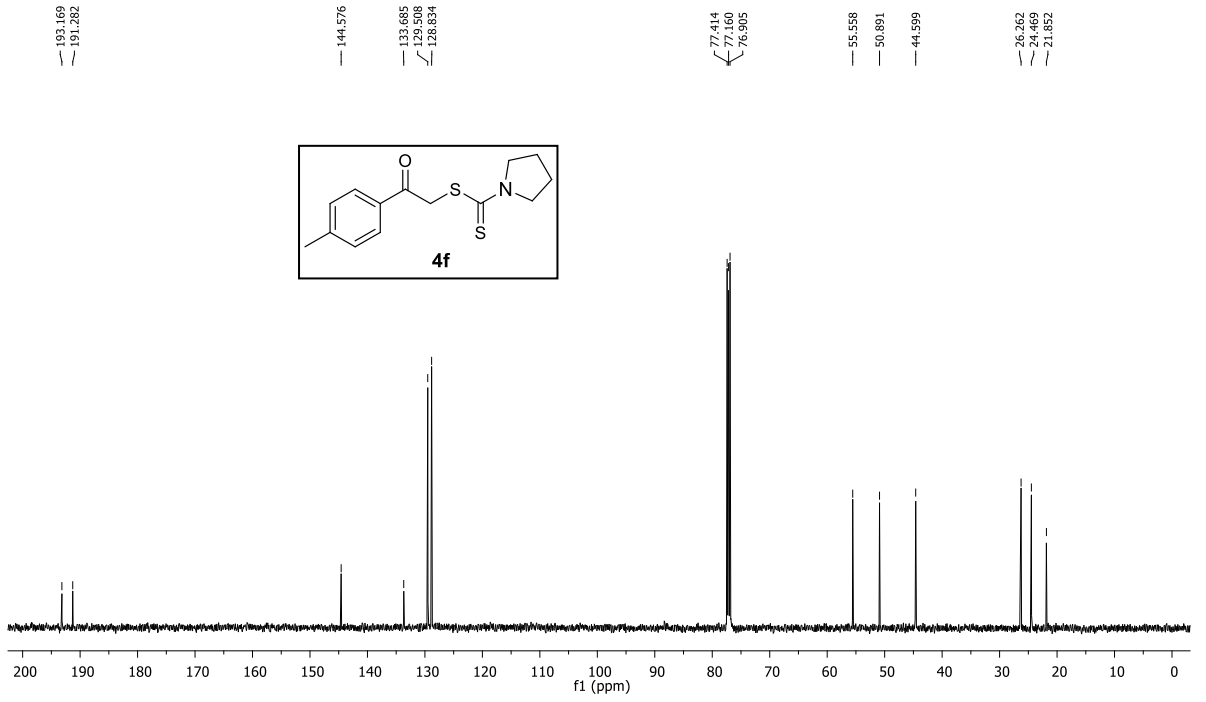


2-Oxo-2-(*p*-tolyl) ethyl pyrrolidine-1-carbodithioate (4f):

^{1}H NMR, $CDCl_3$, 500 MHz

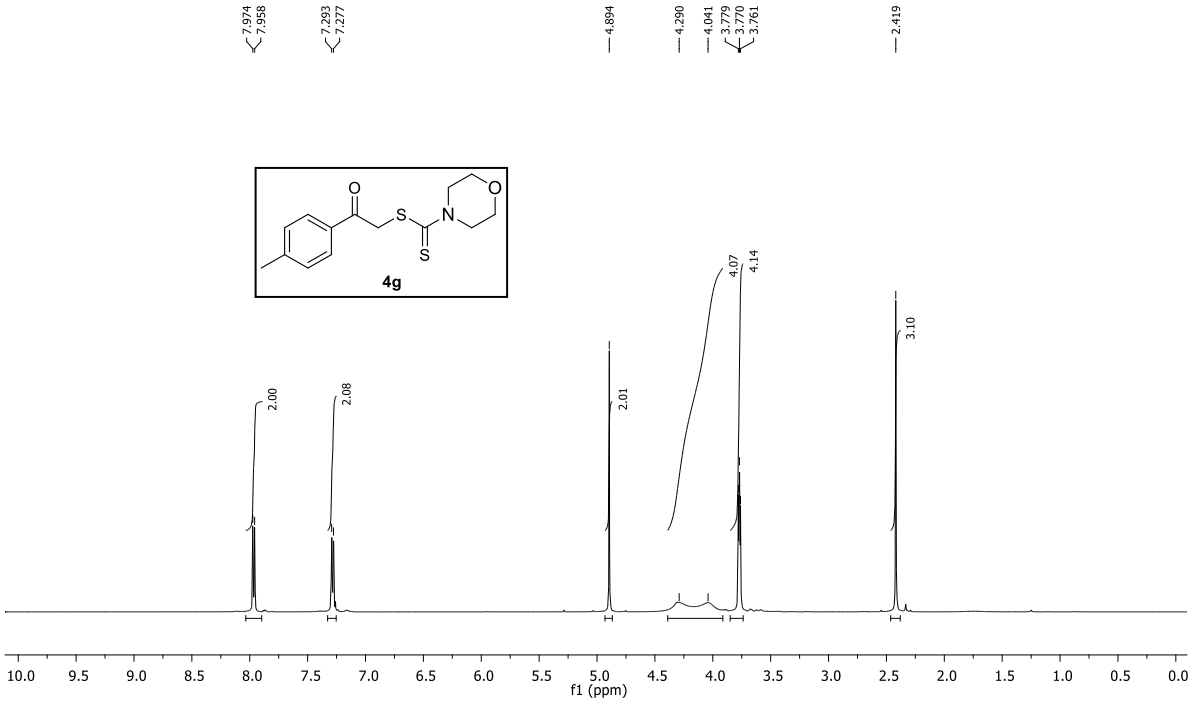


^{13}C NMR, $CDCl_3$, 126 MHz

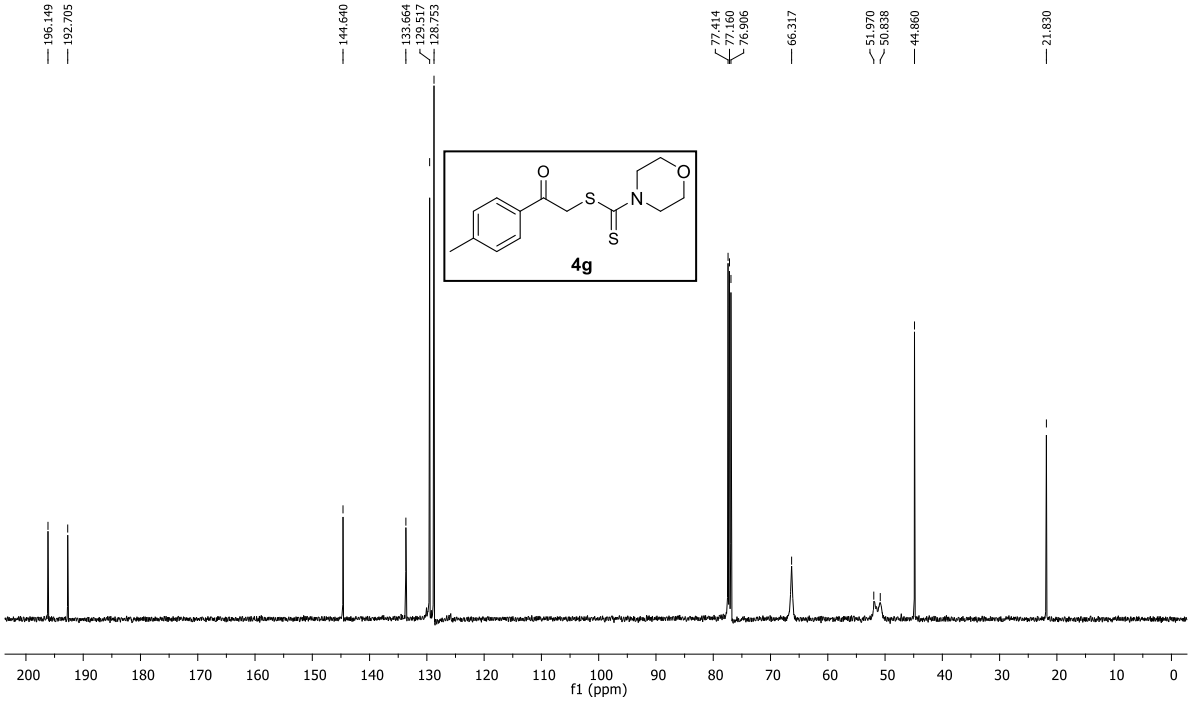


2-Oxo-2-(*p*-tolyl)ethyl morpholine-4-carbodithioate (4g):

^{1}H NMR, $CDCl_3$, 500 MHz

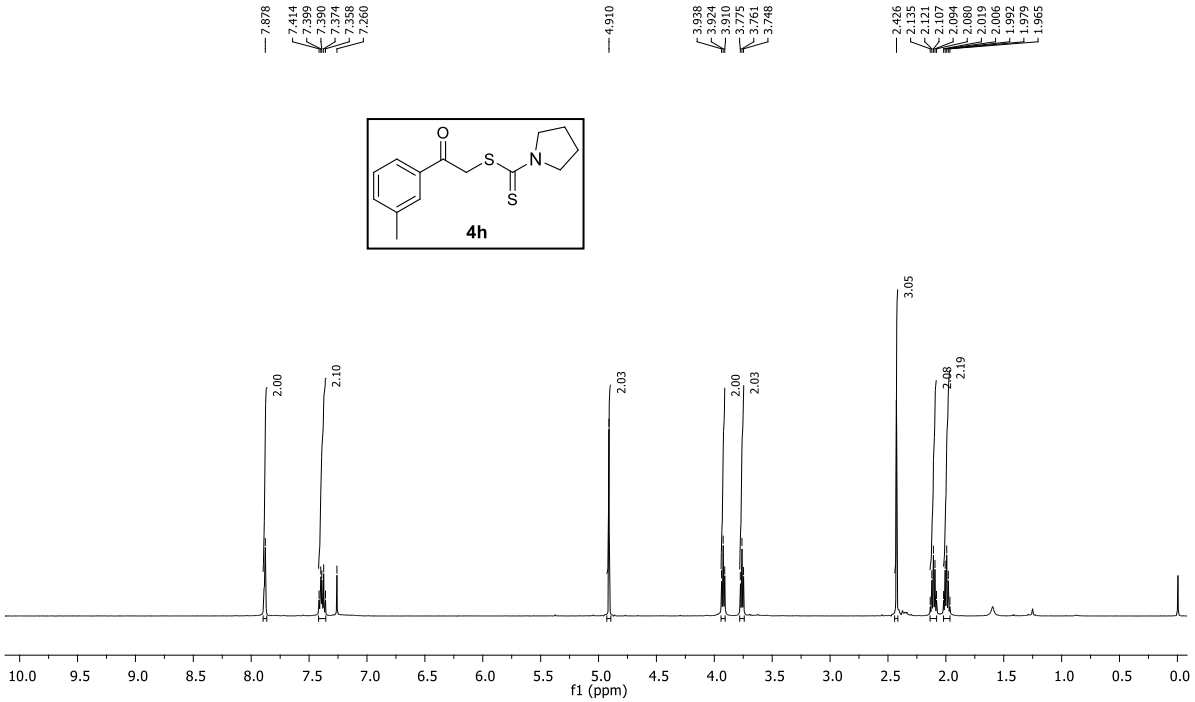


^{13}C NMR, $CDCl_3$, 126 MHz

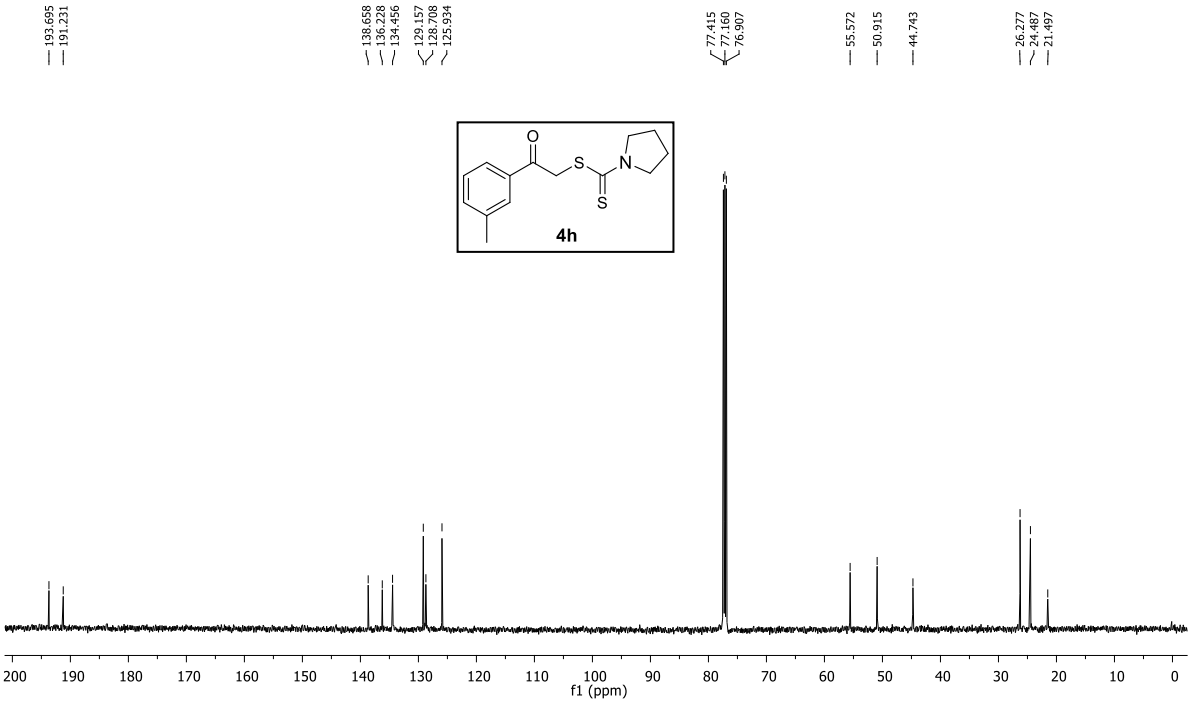


2-Oxo-2-(*m*-tolyl)ethyl pyrrolidine-1-carbodithioate (4h):

^{1}H NMR, $CDCl_3$, 500 MHz

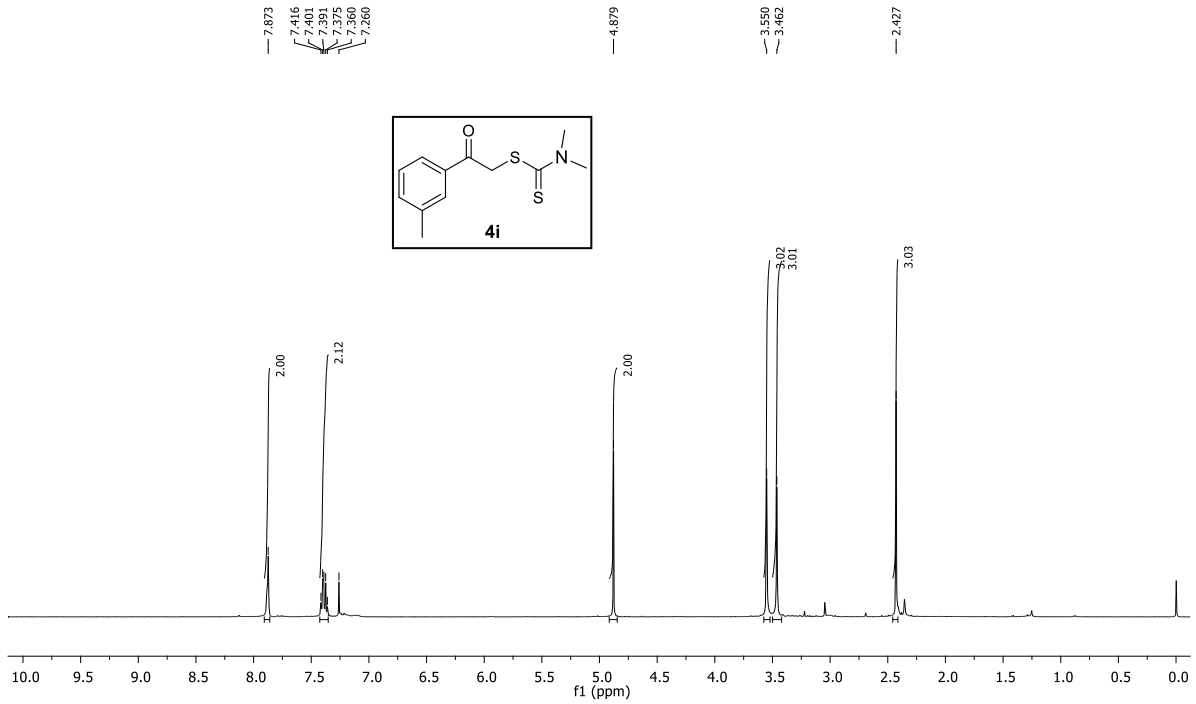


^{13}C NMR, $CDCl_3$, 126 MHz

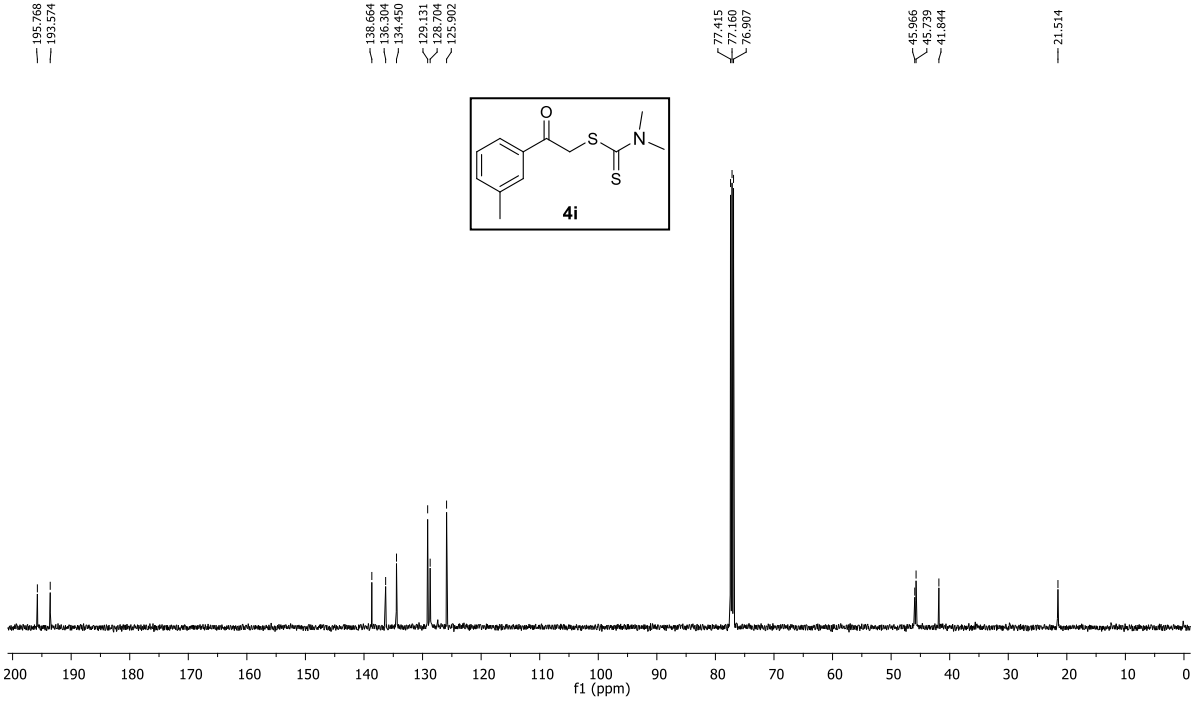


2-Oxo-2-(*m*-tolyl) ethyl dimethylcarbamodithioate (4i):

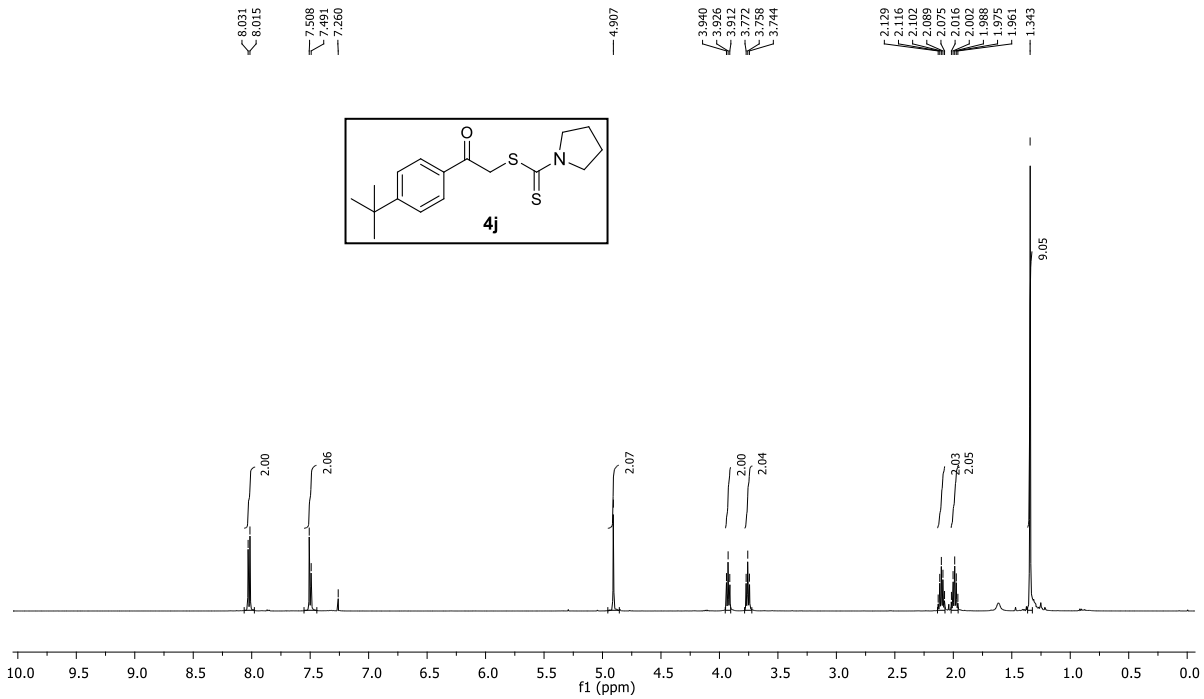
^{1}H NMR, $CDCl_3$, 500 MHz



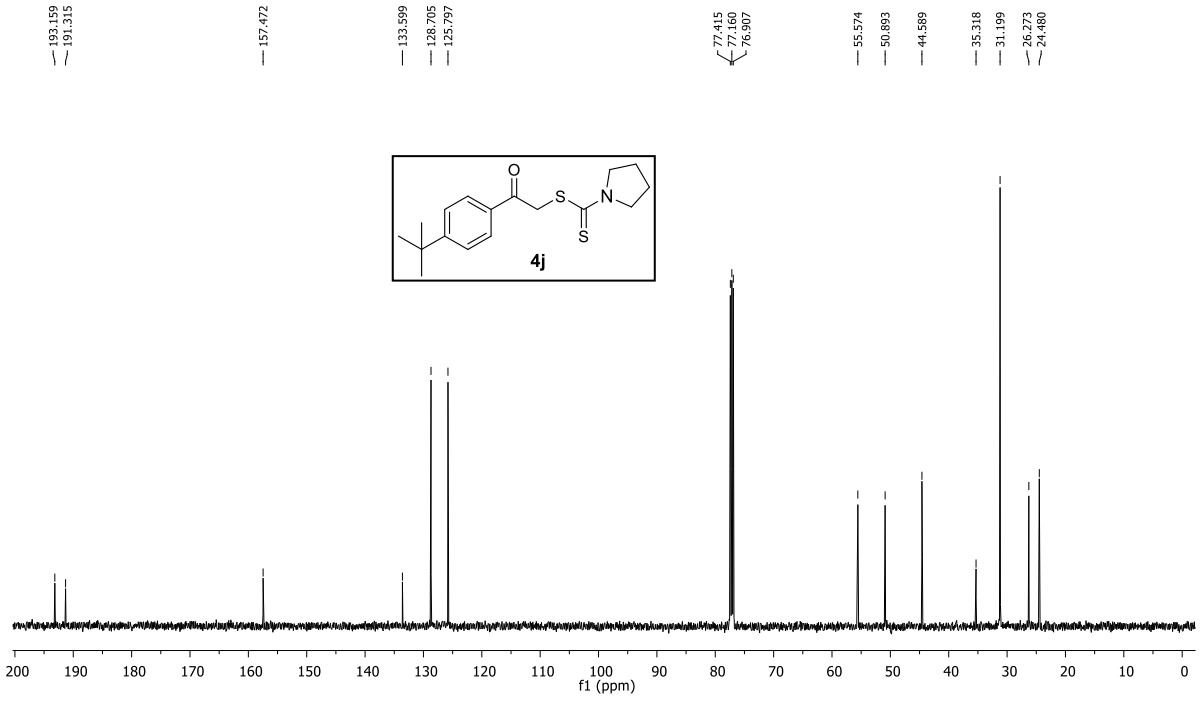
^{13}C NMR, $CDCl_3$, 126 MHz



2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4j):
^{1}H NMR, $CDCl_3$, 500 MHz

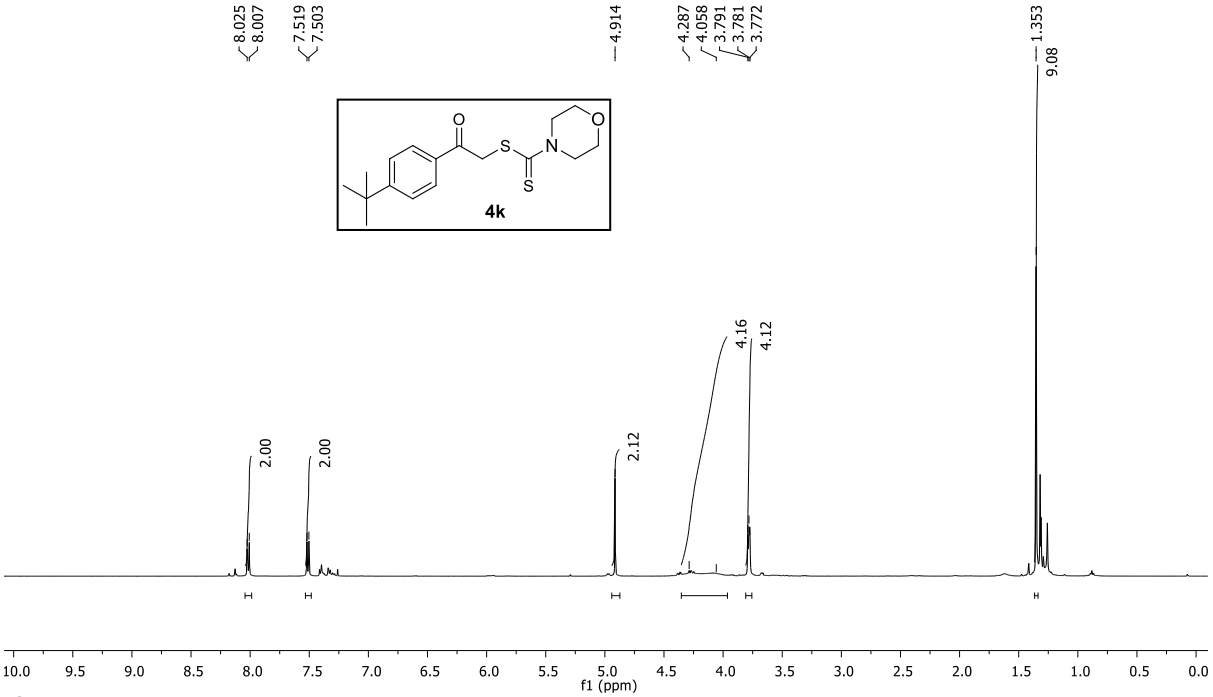


^{13}C NMR, $CDCl_3$, 126 MHz

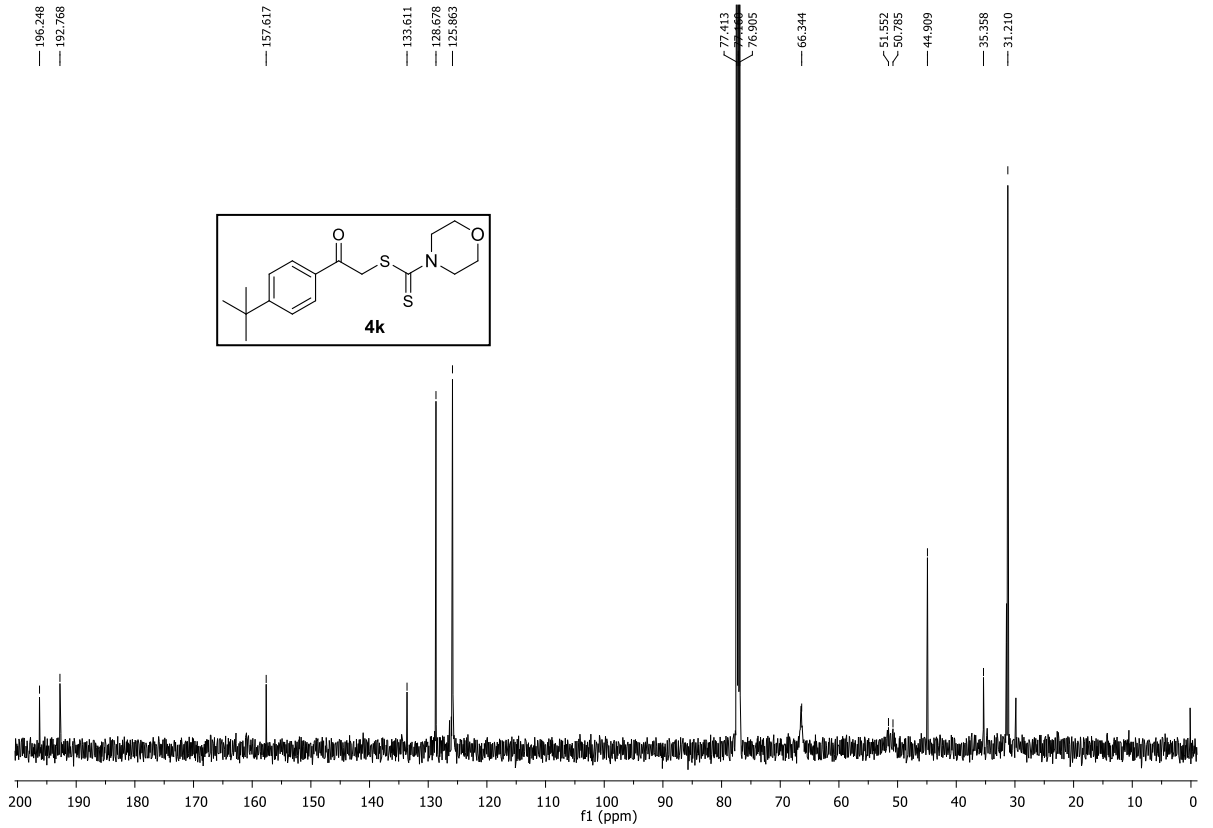


2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl morpholine-4-carbodithioate (4k):

^{1}H NMR, $CDCl_3$, 500 MHz

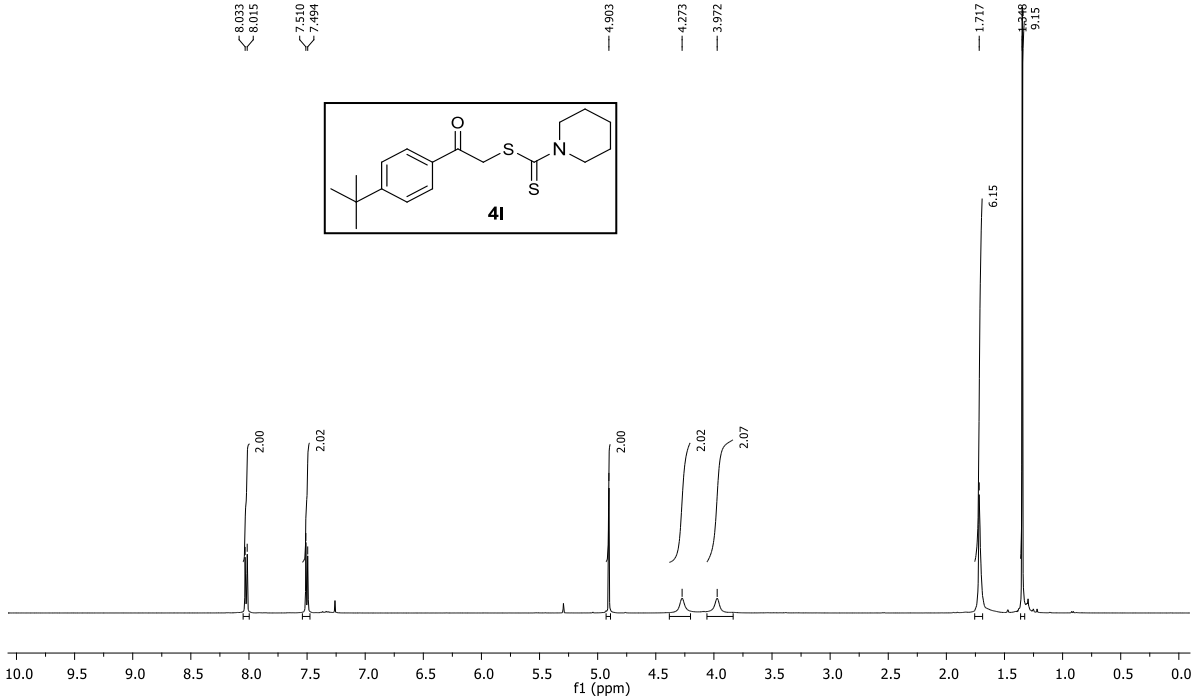


^{13}C NMR, $CDCl_3$, 126 MHz

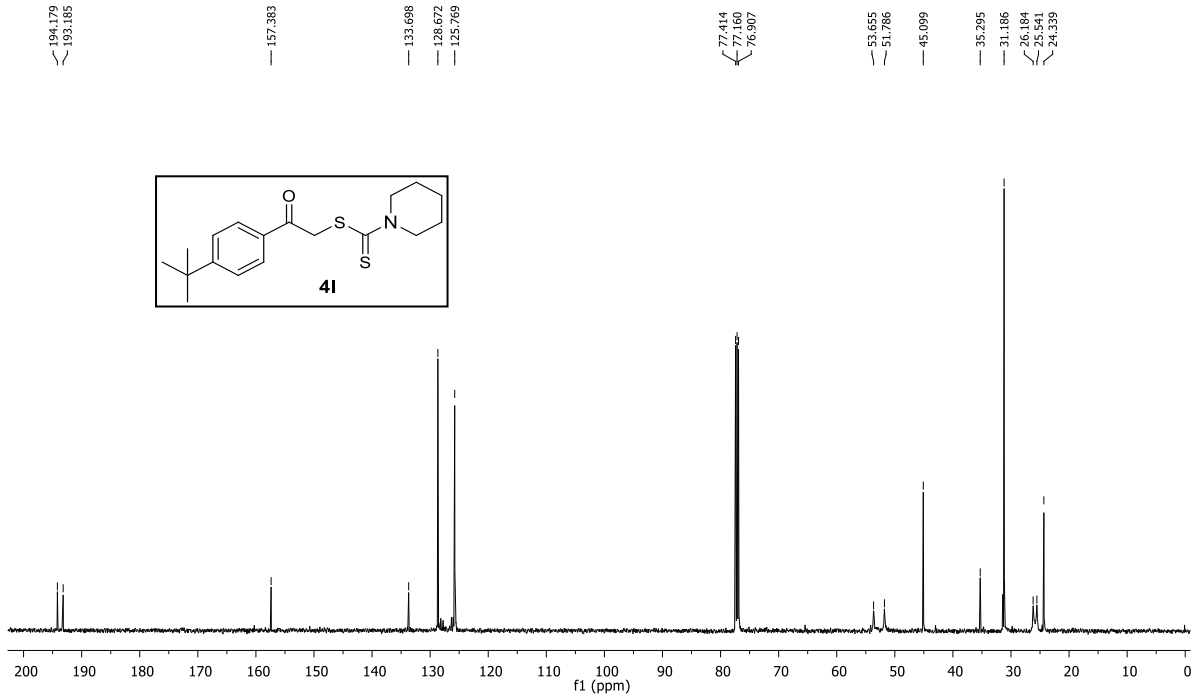


2-(4-(*tert*-Butyl) phenyl)-2-oxoethyl piperidine-1-carbodithioate (4l):

^{1}H NMR, $CDCl_3$, 500 MHz

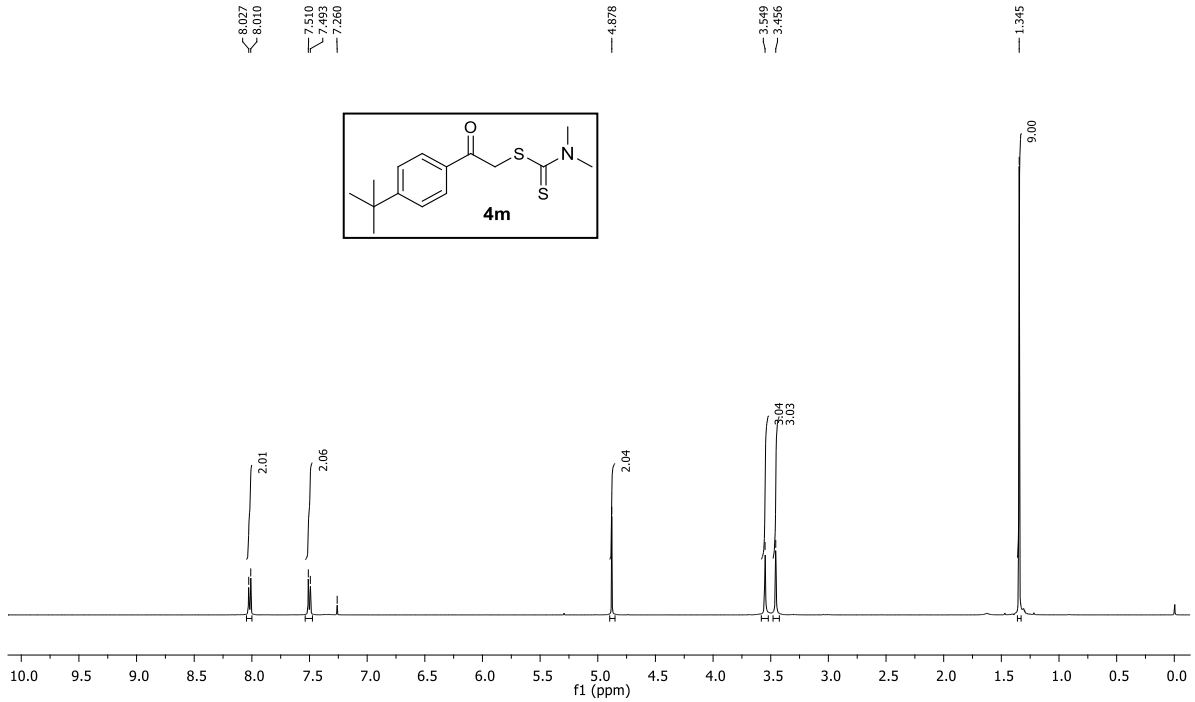


^{13}C NMR, $CDCl_3$, 126 MHz

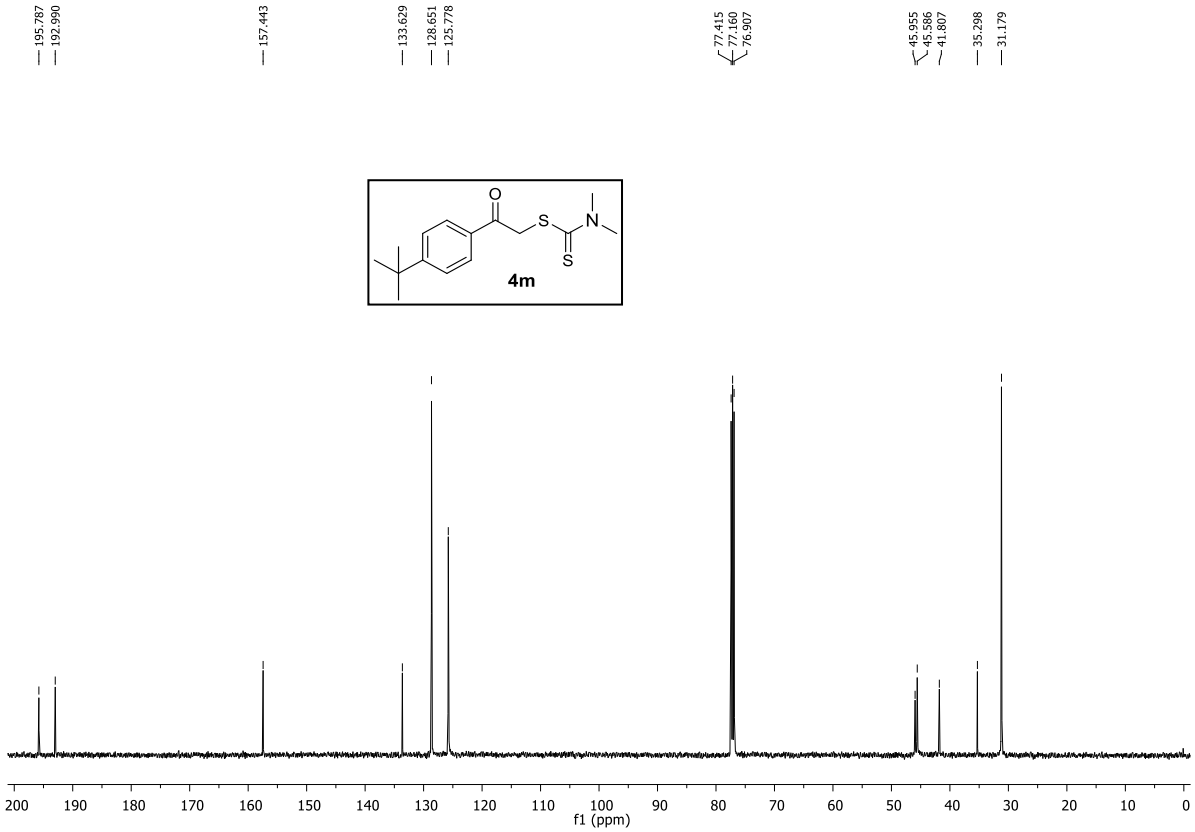


2-(4-(*tert*-Butyl) phenyl)-2-oxoethyl dimethylcarbamodithioate (4m):

^{1}H NMR, $CDCl_3$, 500 MHz

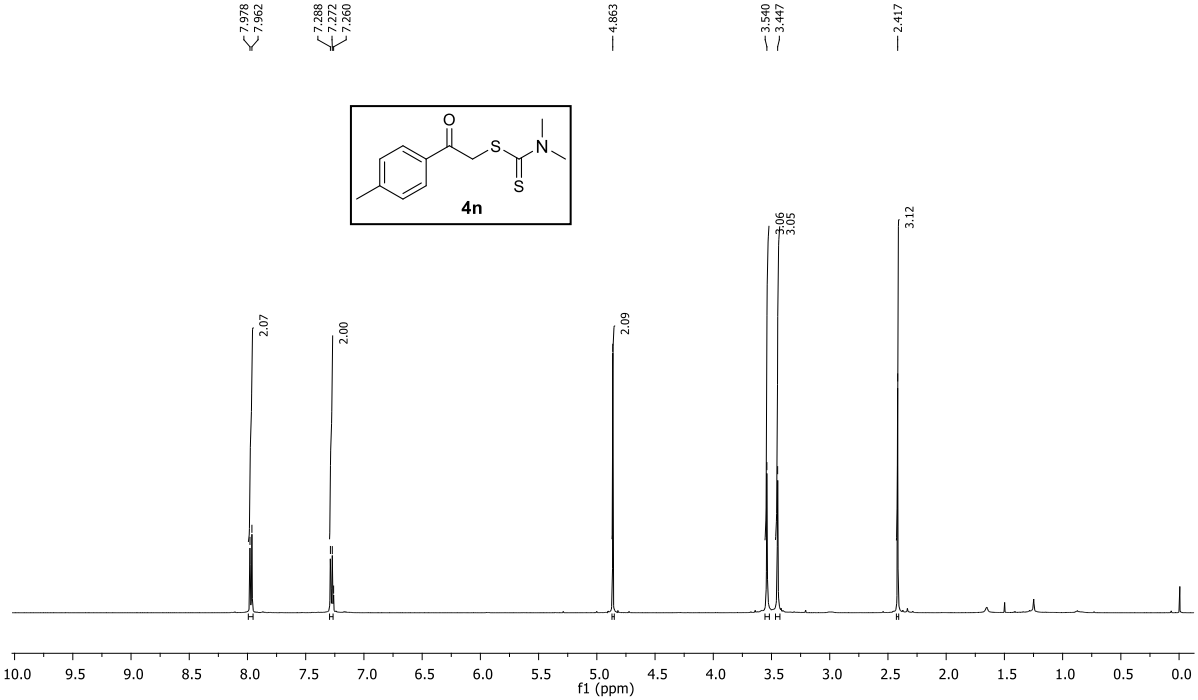


^{13}C NMR, $CDCl_3$, 126 MHz

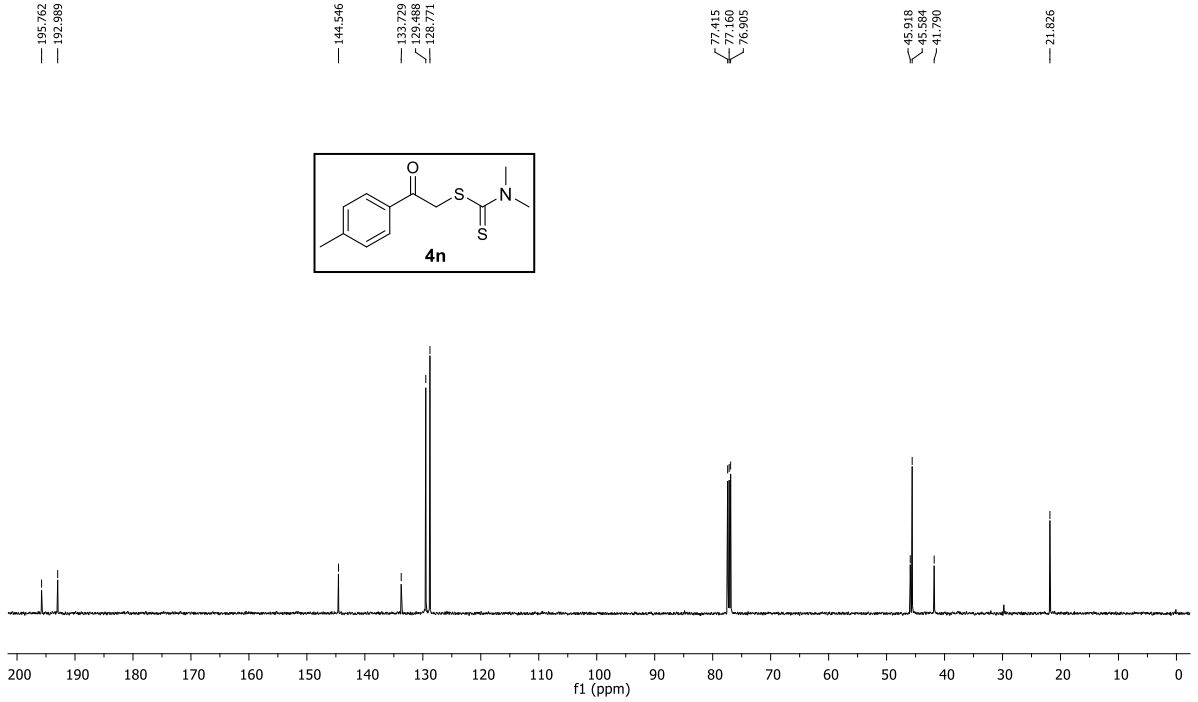


2-Oxo-2-(*p*-tolyl) ethyl dimethylcarbamodithioate (4n):

^{1}H NMR, $CDCl_3$, 500 MHz

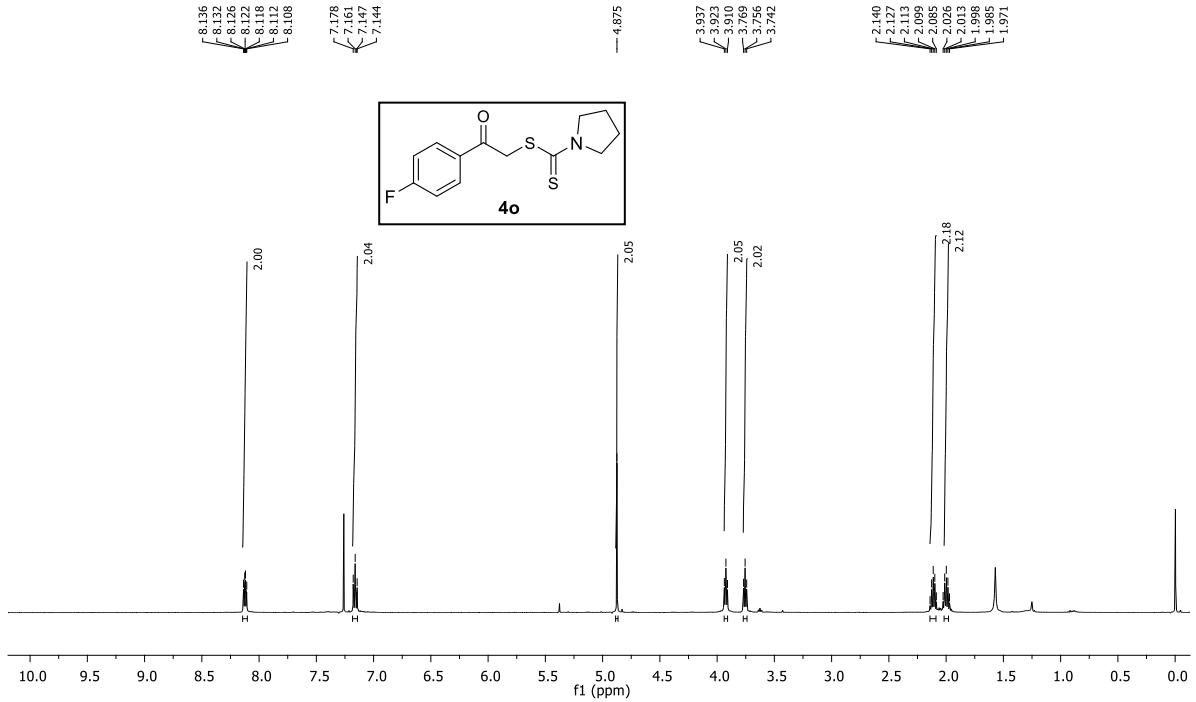


^{13}C NMR, $CDCl_3$, 126 MHz

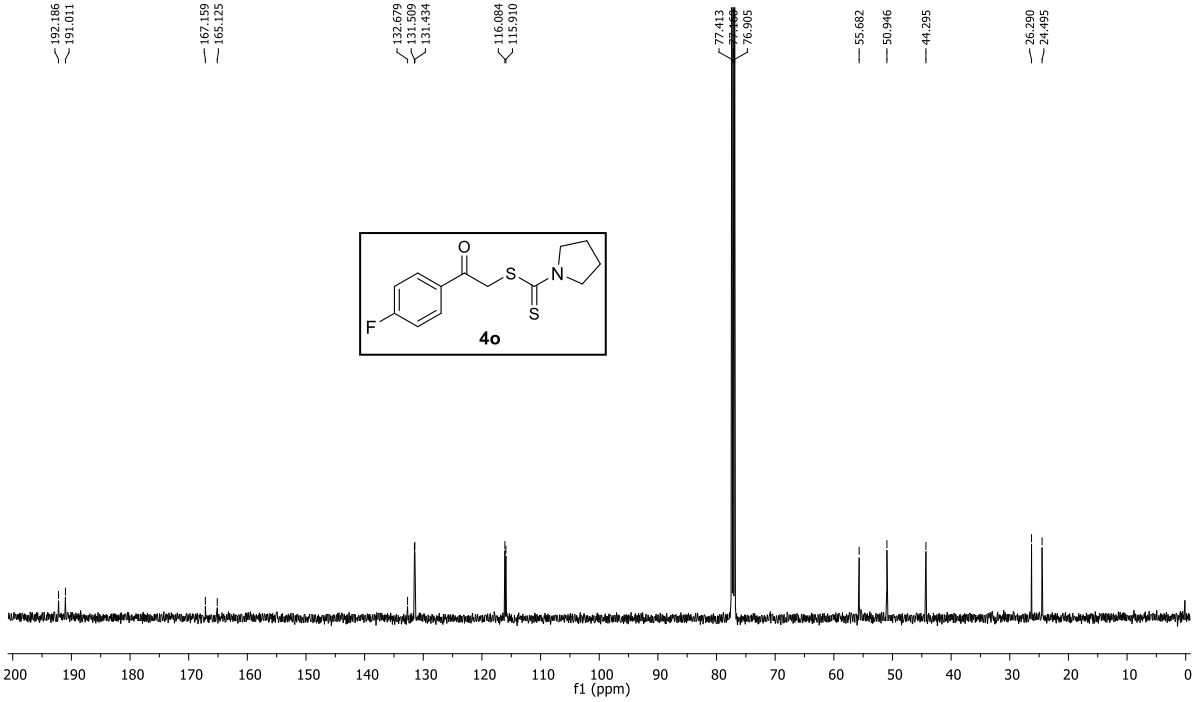


2-(4-Fluorophenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4o):

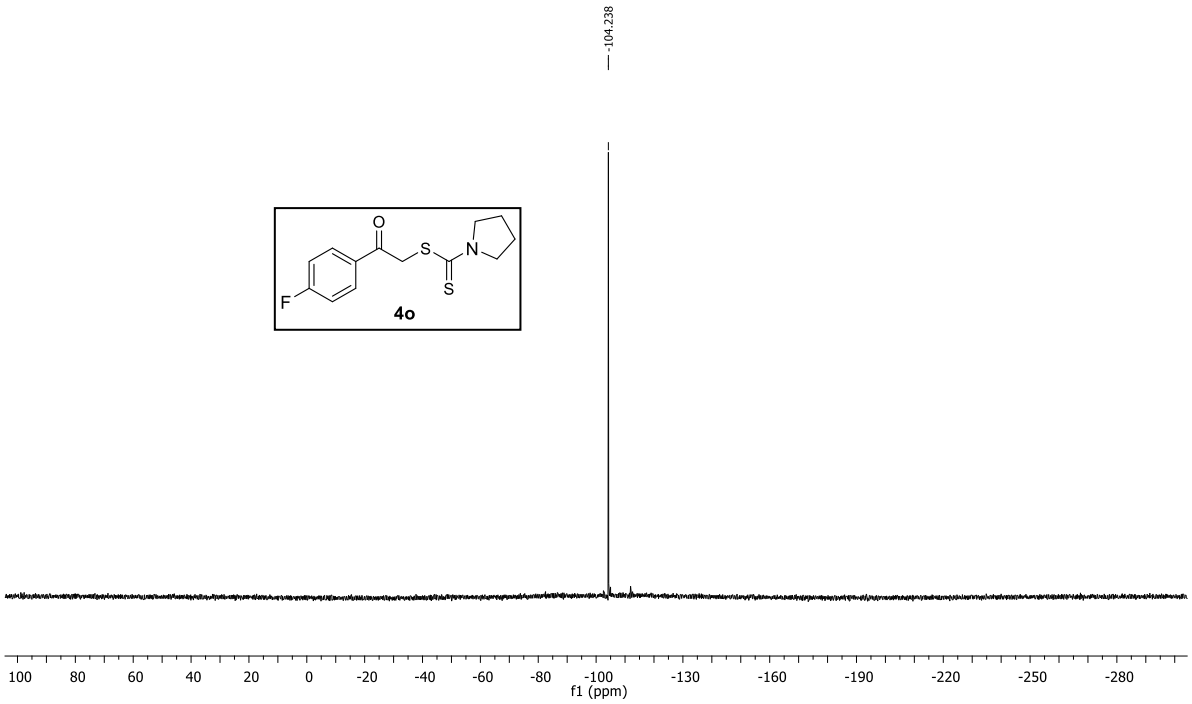
^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

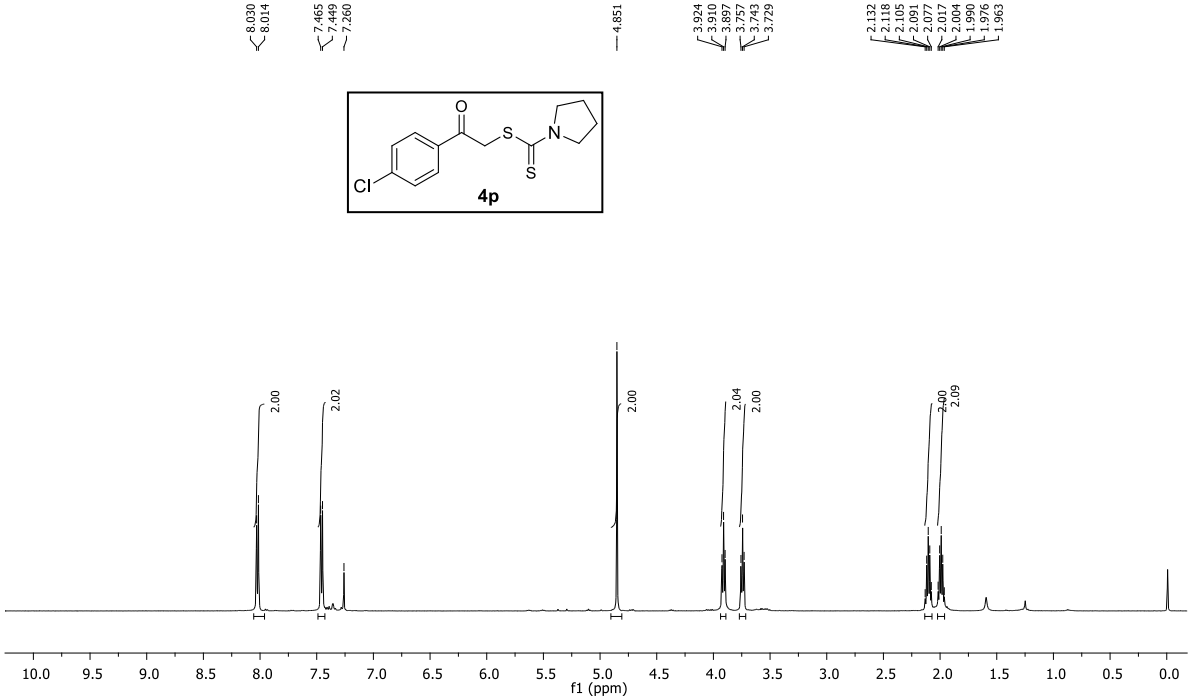


^{19}F NMR, $CDCl_3$, 471 MHz

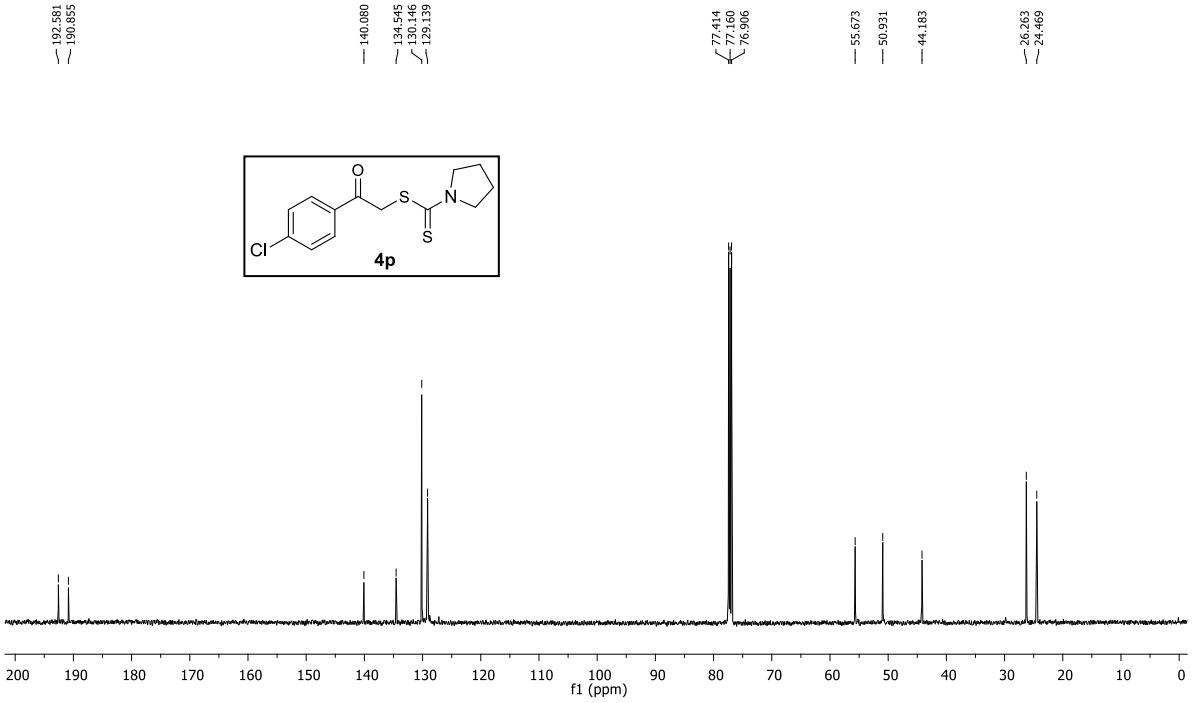


2-(4-Chlorophenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4p):

^{1}H NMR, $CDCl_3$, 500 MHz

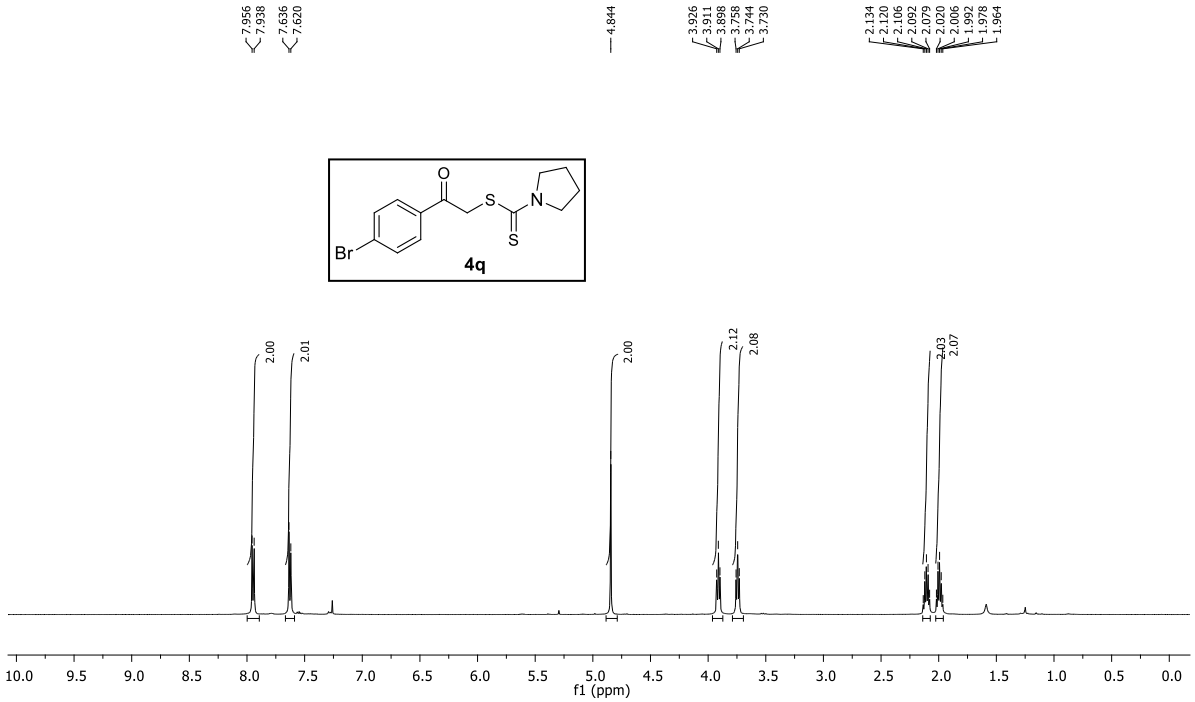


^{13}C NMR, $CDCl_3$, 126 MHz

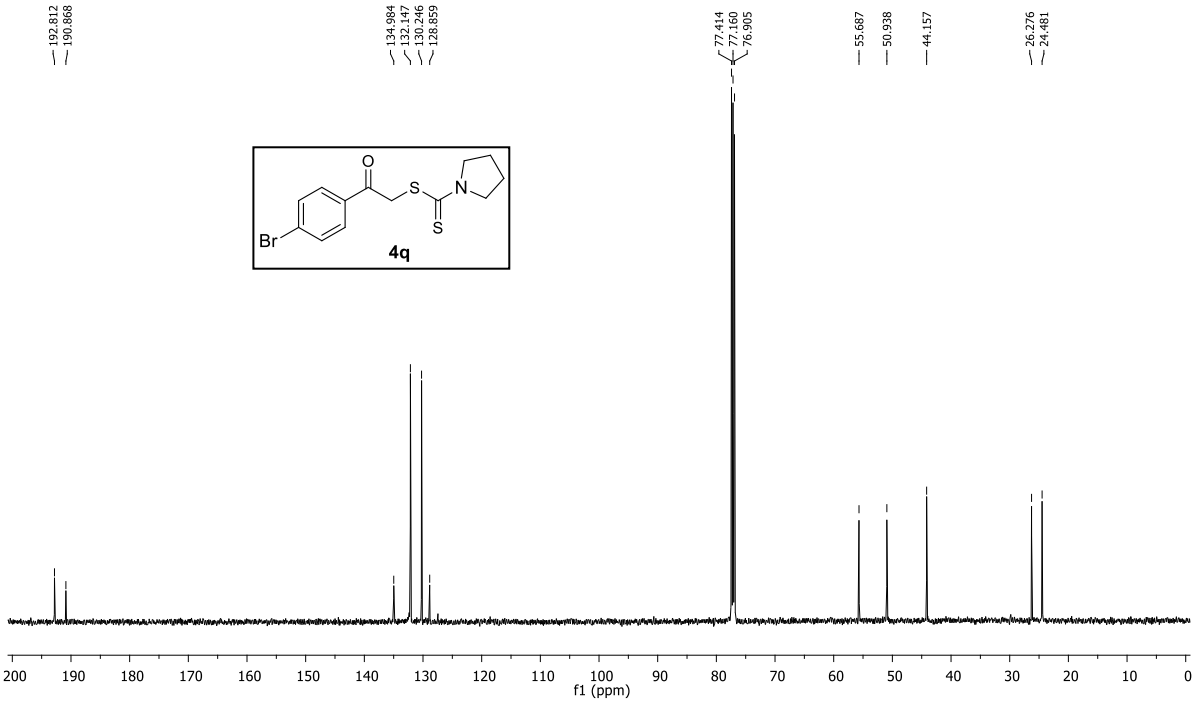


2-(4-Bromophenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4q):

^{1}H NMR, $CDCl_3$, 500 MHz

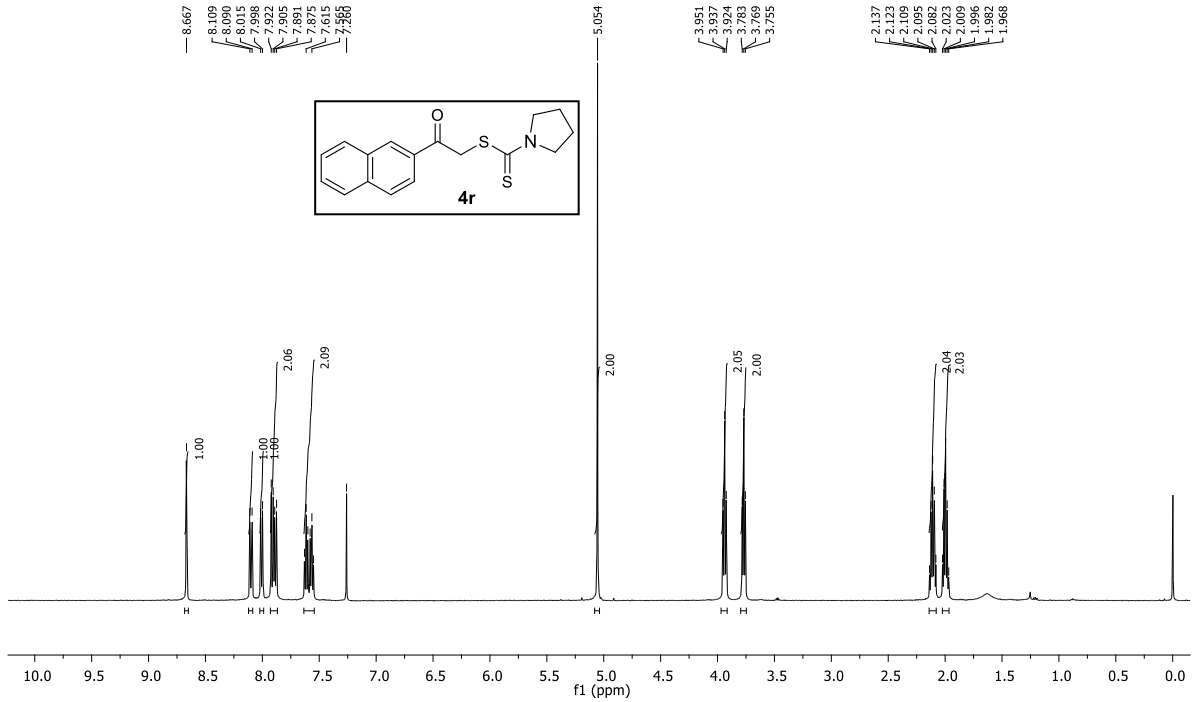


^{13}C NMR, $CDCl_3$, 126 MHz

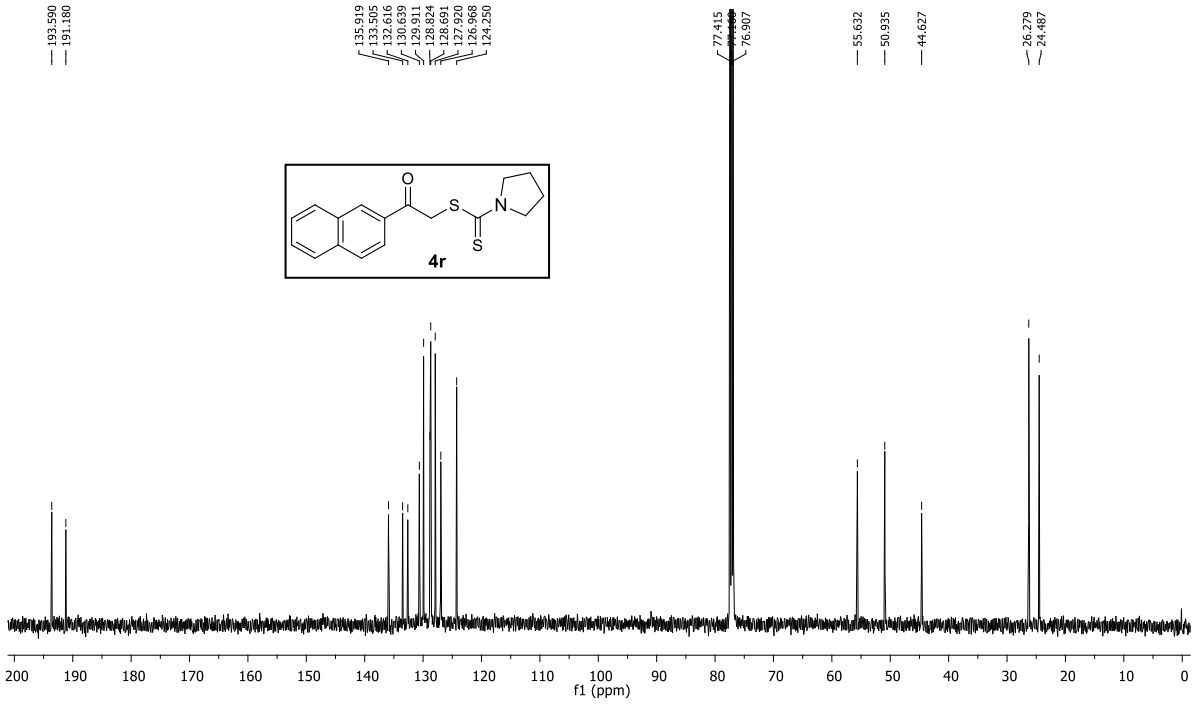


2-(Naphthalen-2-yl)-2-oxoethyl pyrrolidine-1-carbodithioate (4r):

^{1}H NMR, $CDCl_3$, 500 MHz

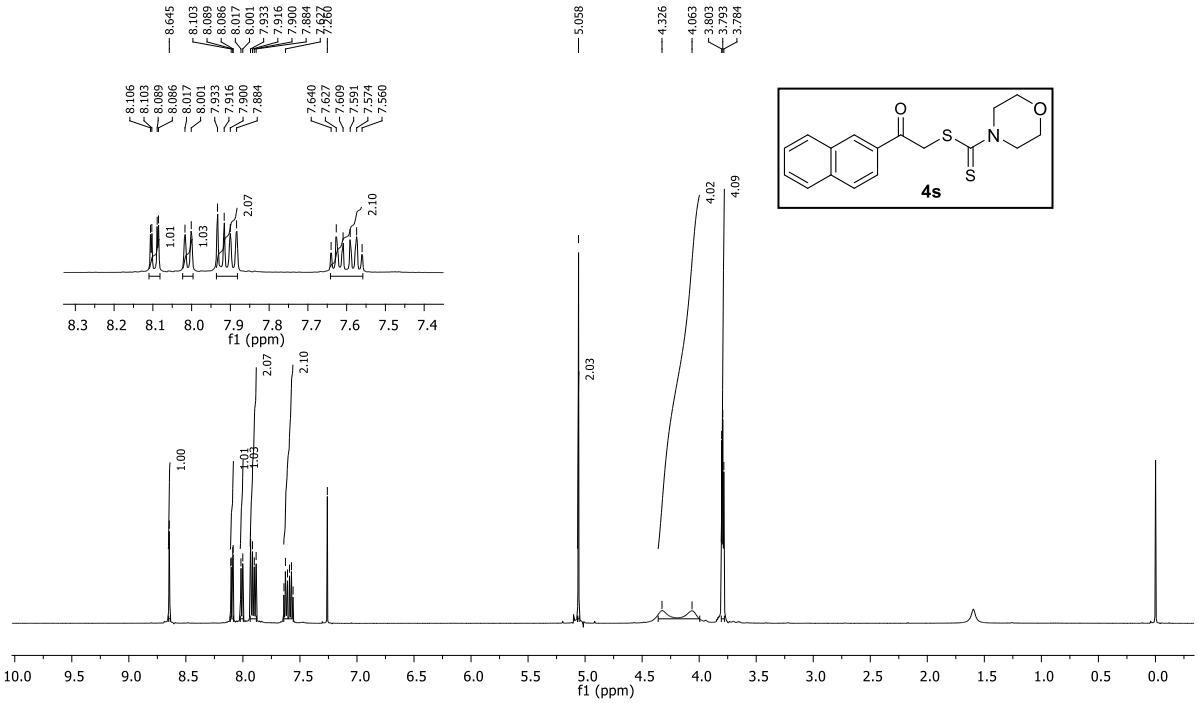


^{13}C NMR, $CDCl_3$, 126 MHz

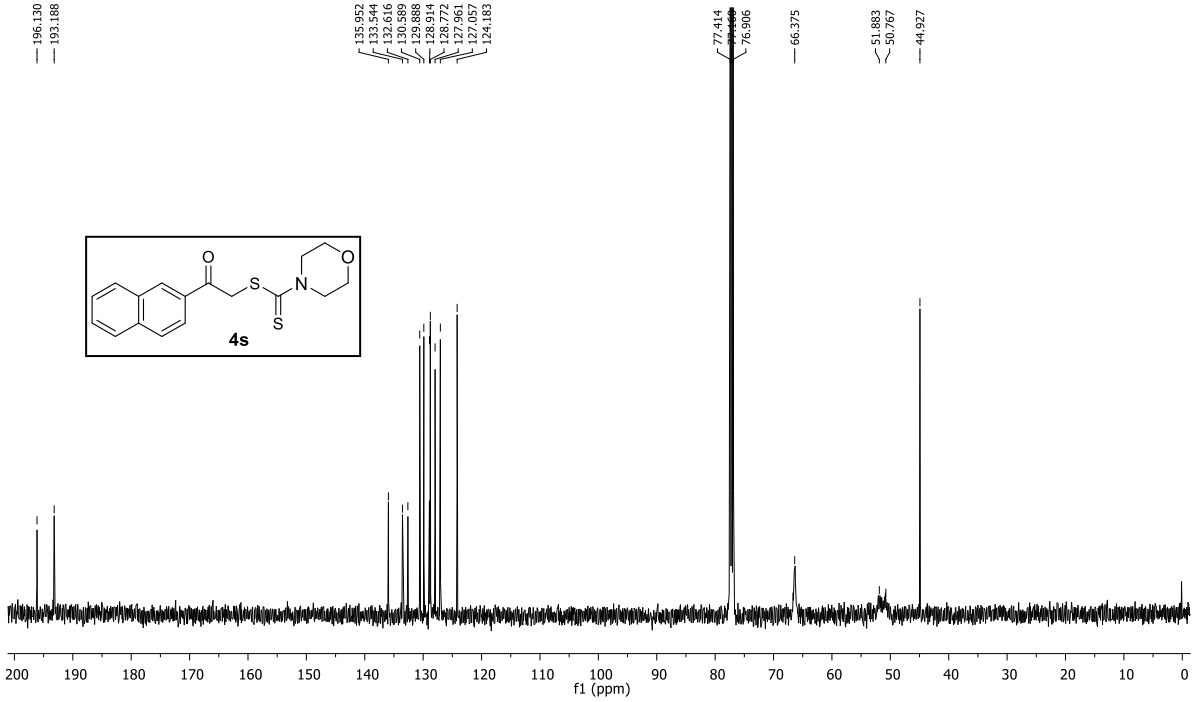


2-(Naphthalen-2-yl)-2-oxoethyl morpholine-4-carbodithioate (4s):

^{1}H NMR, $CDCl_3$, 500 MHz

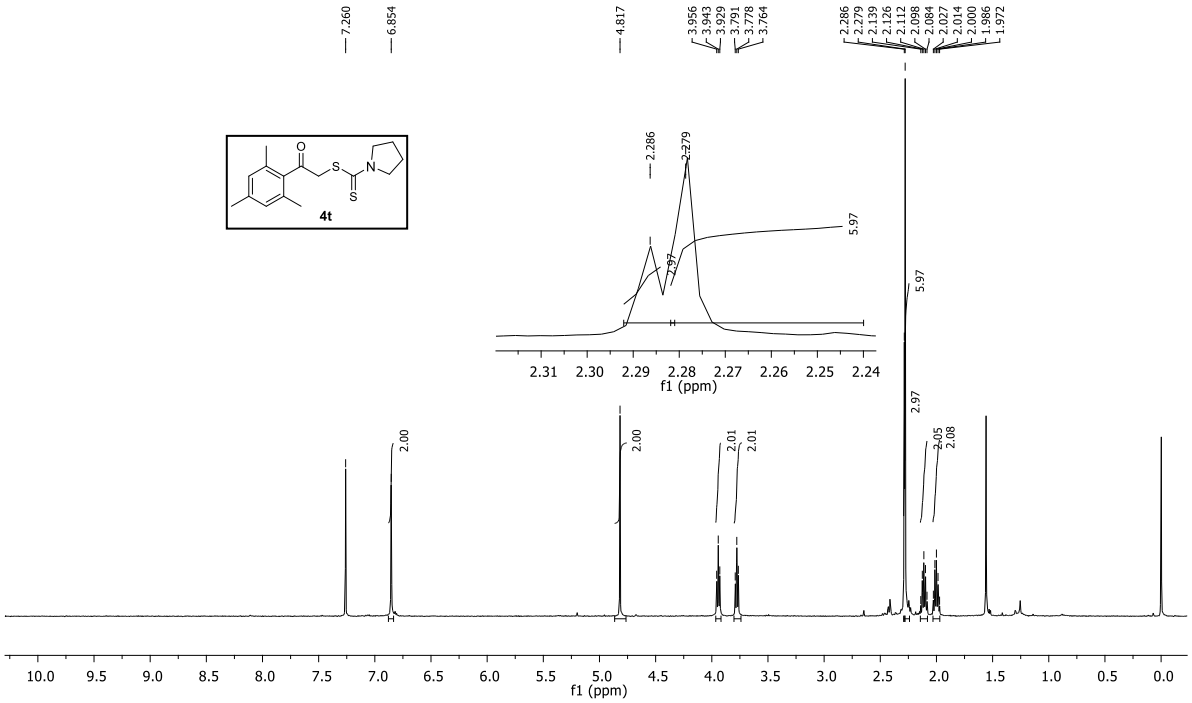


^{13}C NMR, $CDCl_3$, 126 MHz

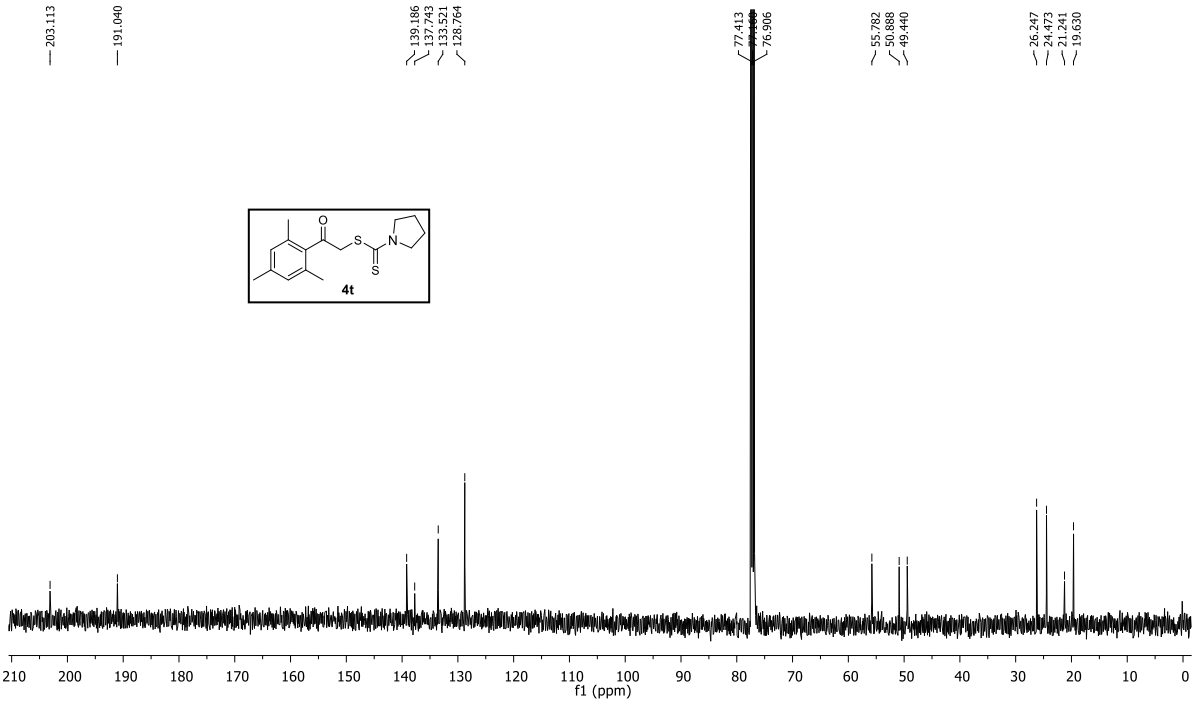


2-Mesityl-2-oxoethyl pyrrolidine-1-carbodithioate (4t):

^{1}H NMR, $CDCl_3$, 500 MHz

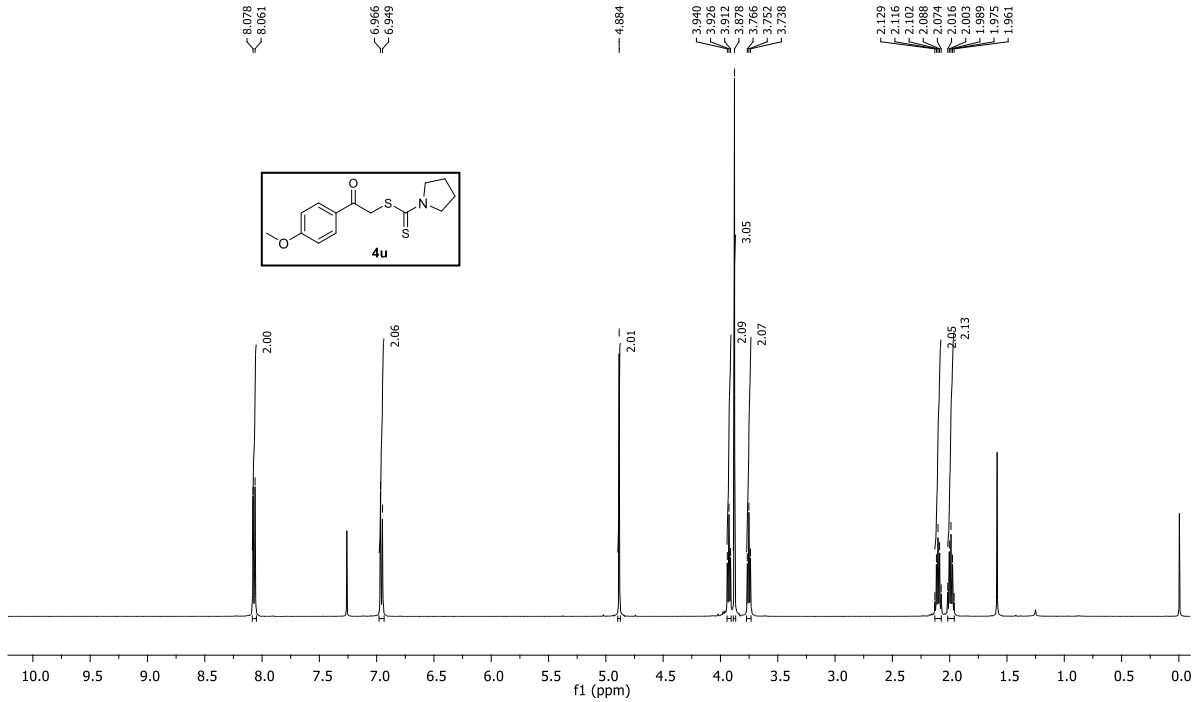


^{13}C NMR, $CDCl_3$, 126 MHz

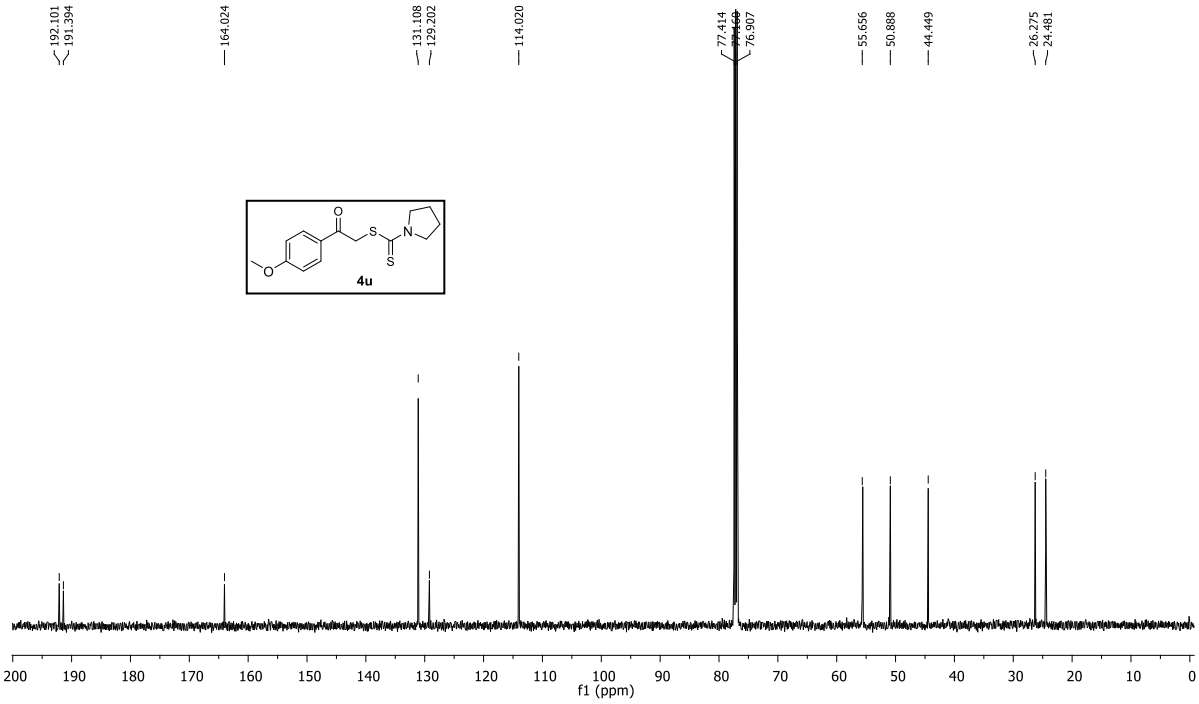


2-(4-Methoxyphenyl)-2-oxoethyl pyrrolidine-1-carbodithioate (4u):

^{1}H NMR, $CDCl_3$, 500 MHz

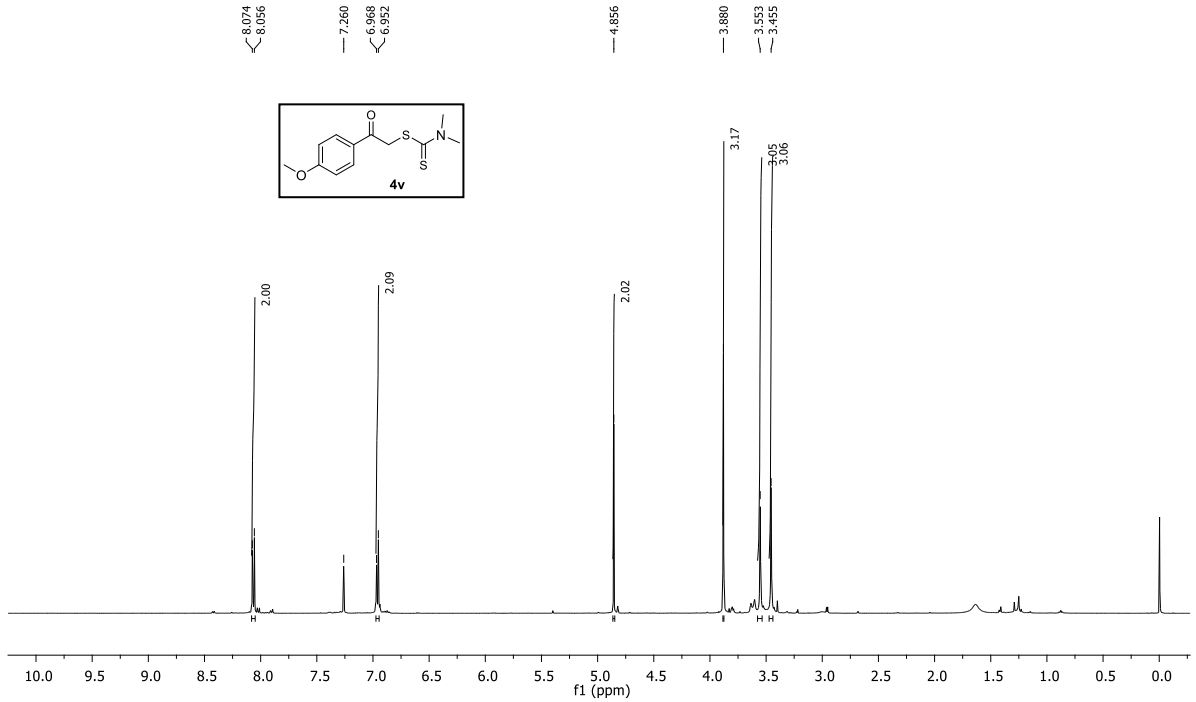


^{13}C NMR, $CDCl_3$, 126 MHz

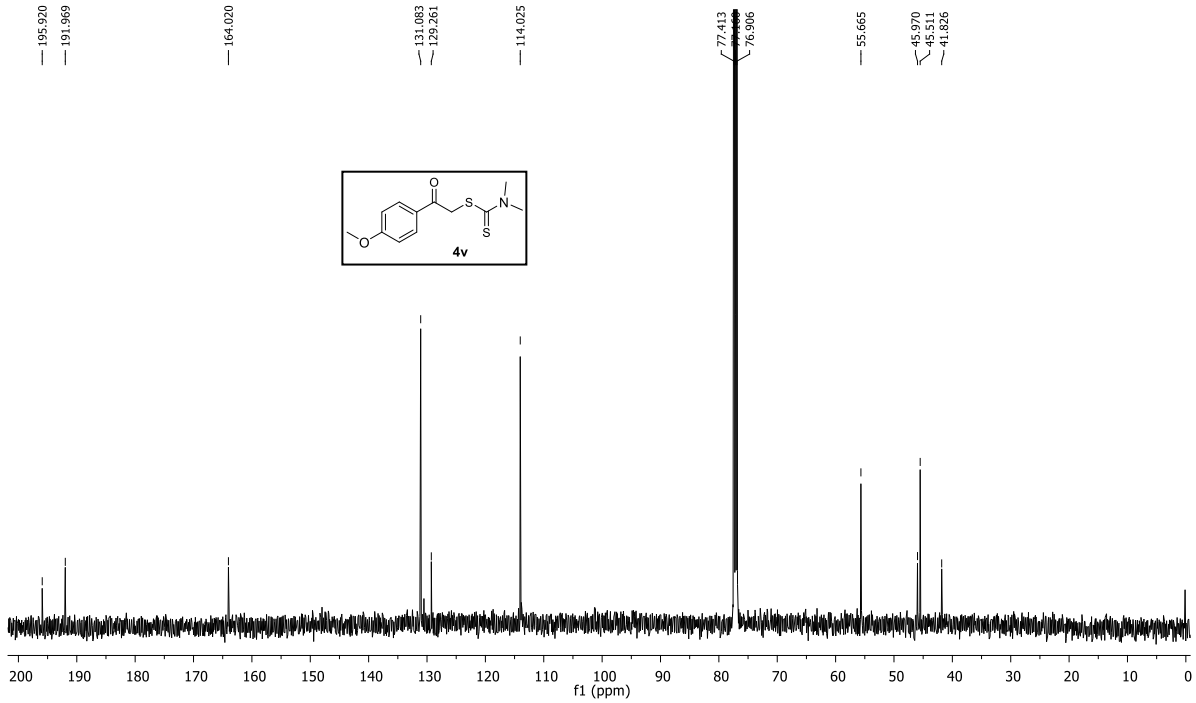


2-(4-Methoxyphenyl)-2-oxoethyl dimethylcarbamodithioate (4v):

^{1}H NMR, $CDCl_3$, 500 MHz

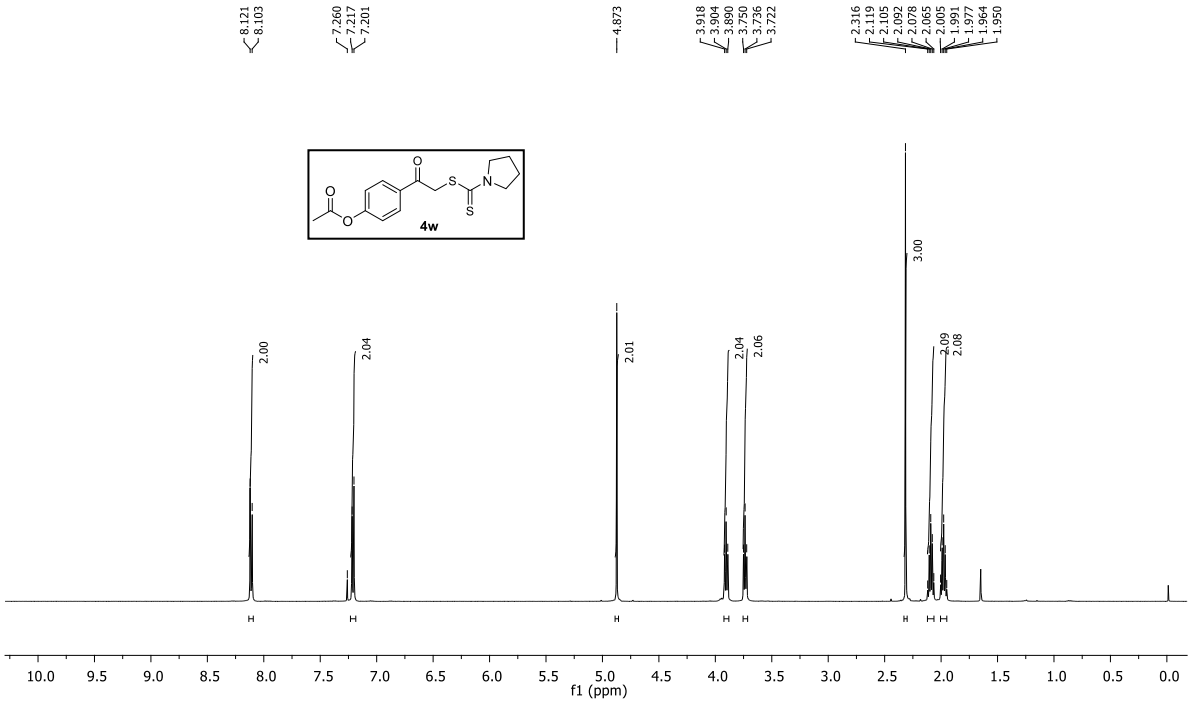


^{13}C NMR, $CDCl_3$, 126 MHz

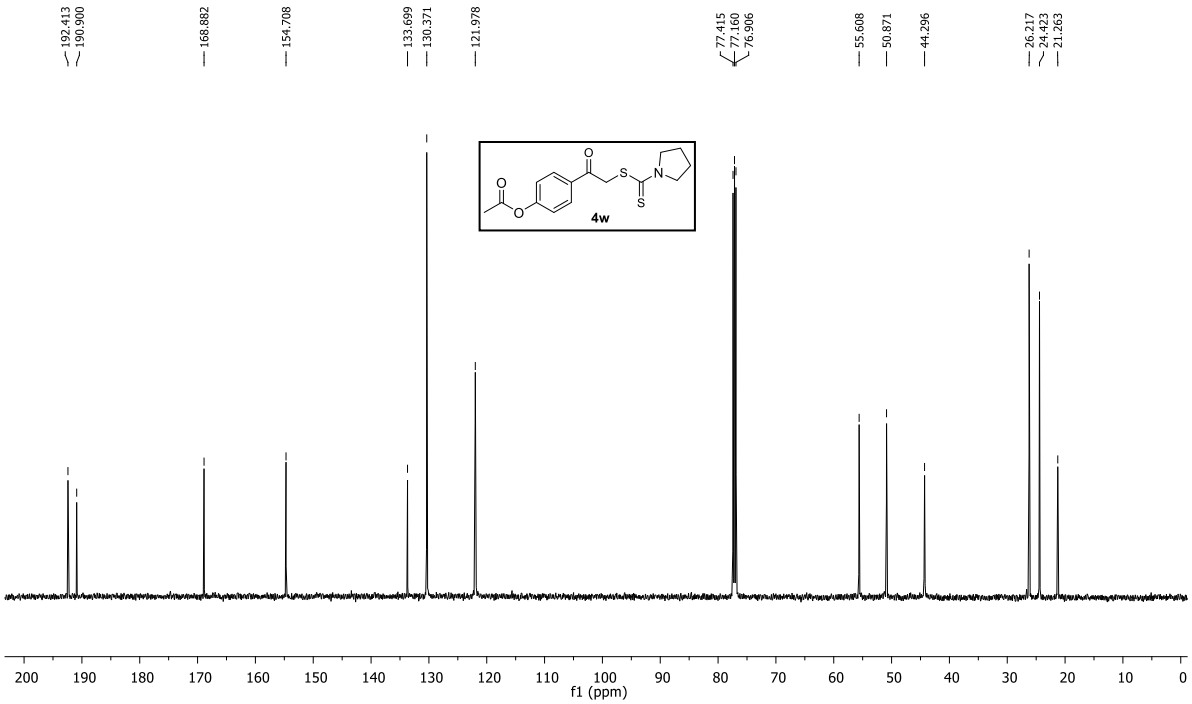


4-(2-((Pyrrolidine-1-carbonothioyl)thio)acetyl)phenyl acetate (4w):

^{1}H NMR, $CDCl_3$, 500 MHz

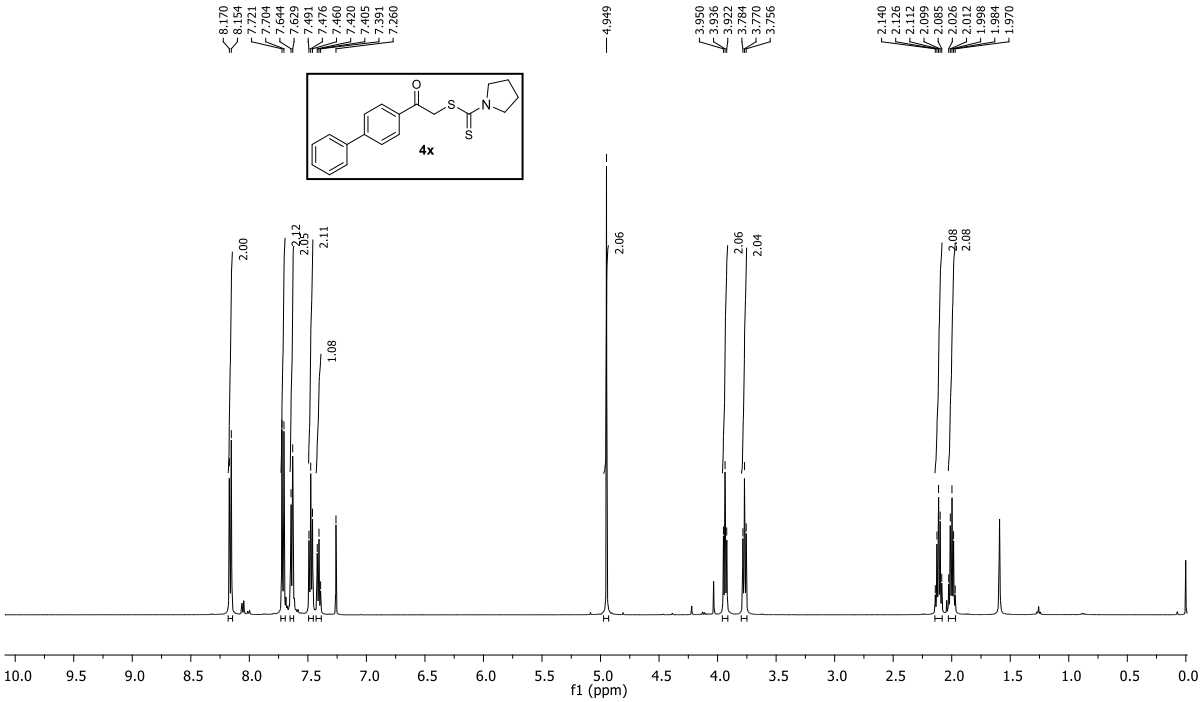


^{13}C NMR, $CDCl_3$, 126 MHz

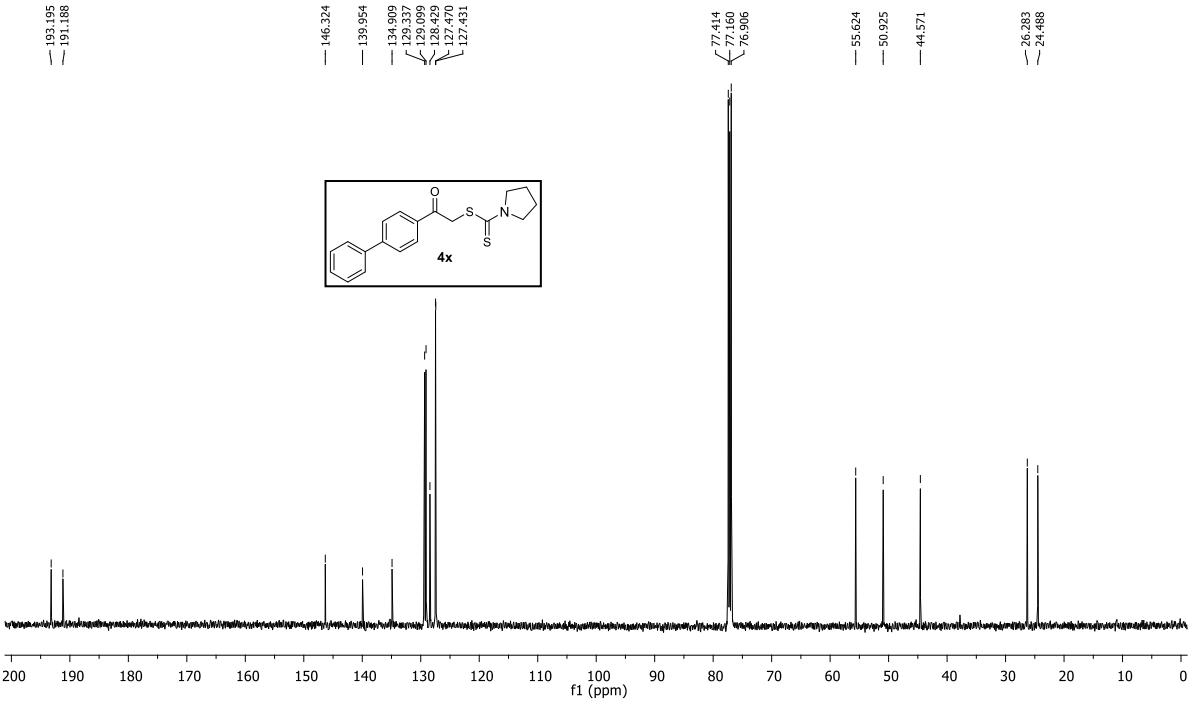


2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl pyrrolidine-1-carbodithioate (4x):

^{1}H NMR, $CDCl_3$, 500 MHz

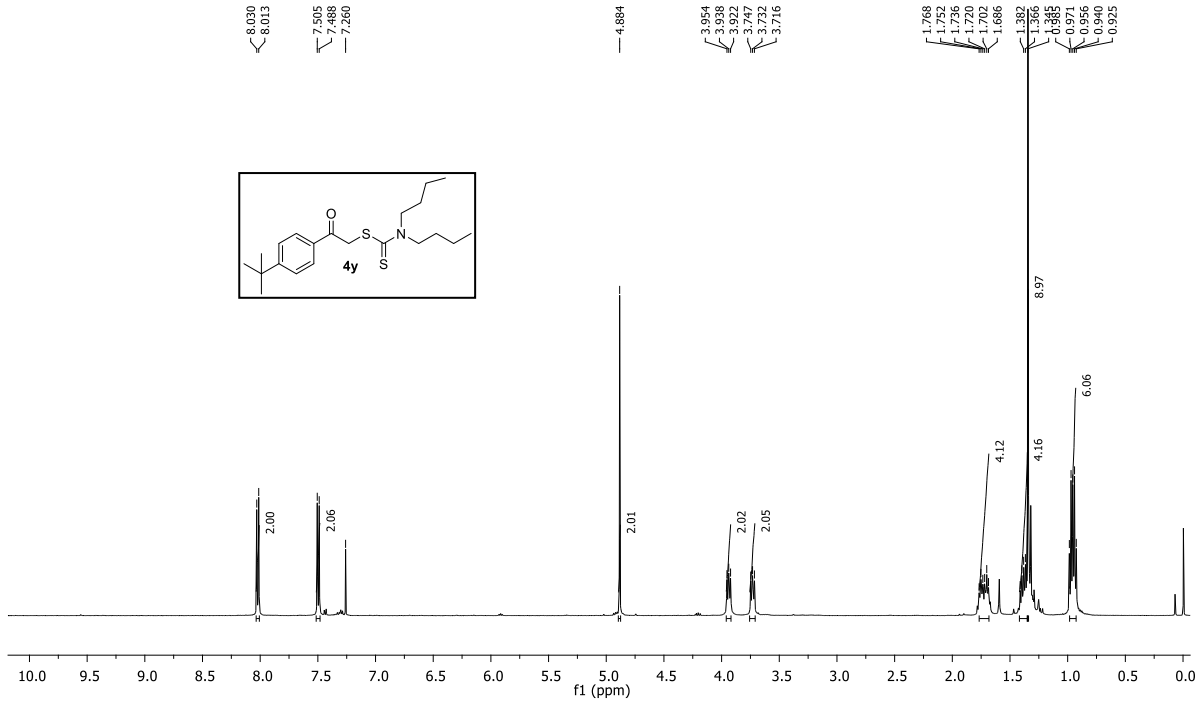


^{13}C NMR, $CDCl_3$, 126 MHz

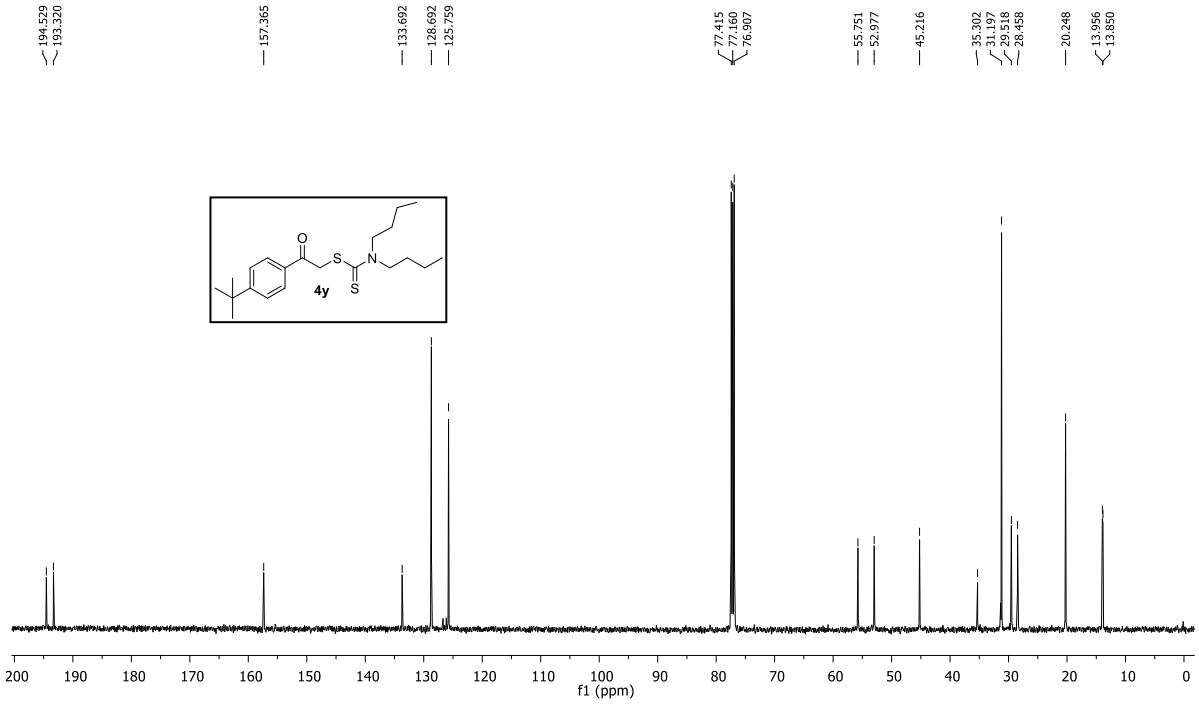


2-(4-(*tert*-Butyl) phenyl)-2-oxoethyl dibutylcarbamodithioate (4y):

^{1}H NMR, $CDCl_3$, 500 MHz

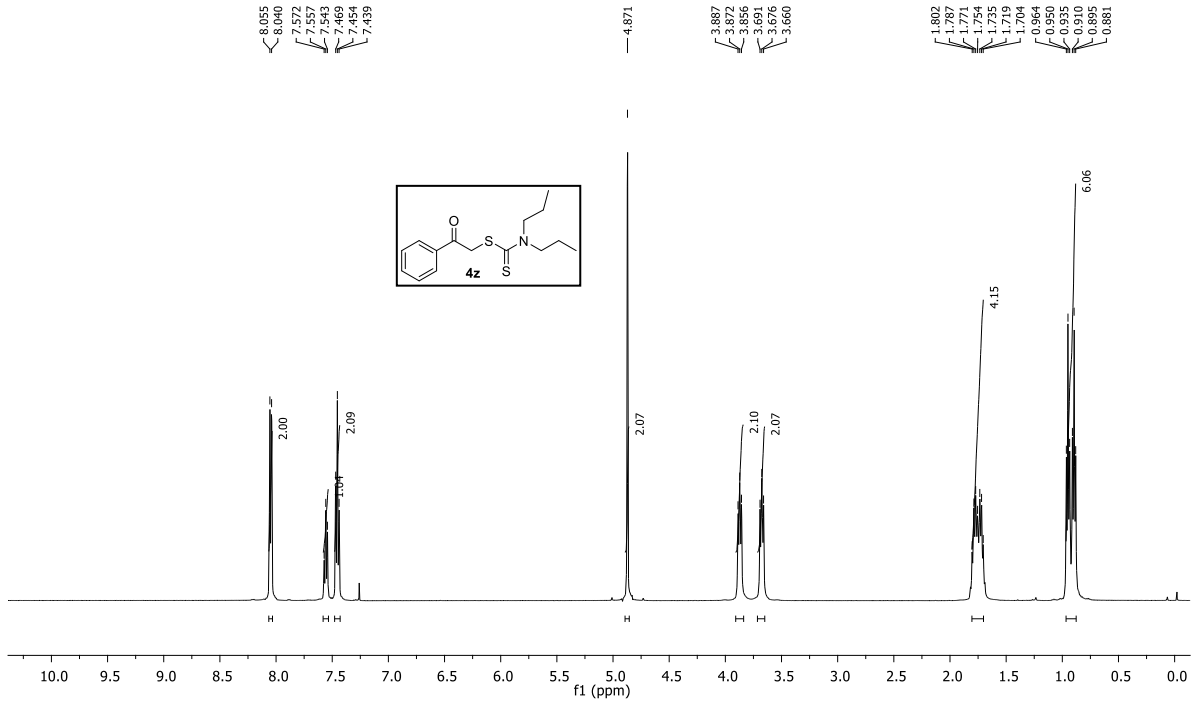


^{13}C NMR, $CDCl_3$, 126 MHz

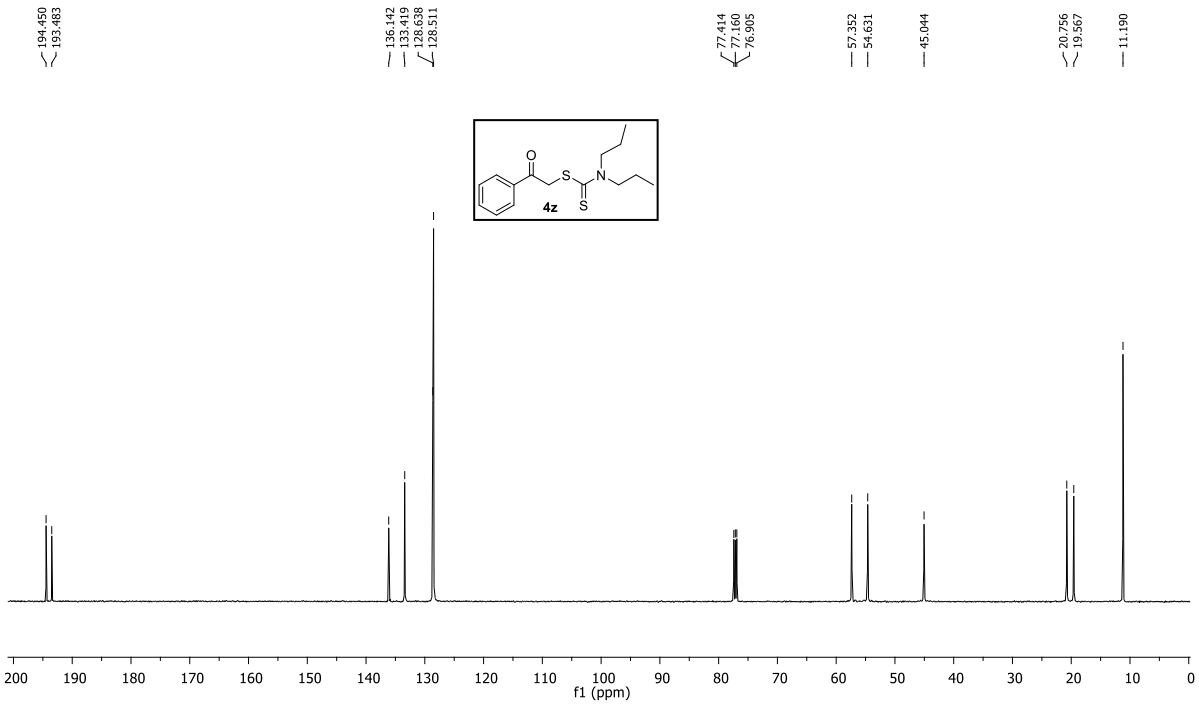


2-Oxo-2-phenylethyl dipropylcarbamodithioate (4z):

^{1}H NMR, $CDCl_3$, 500 MHz

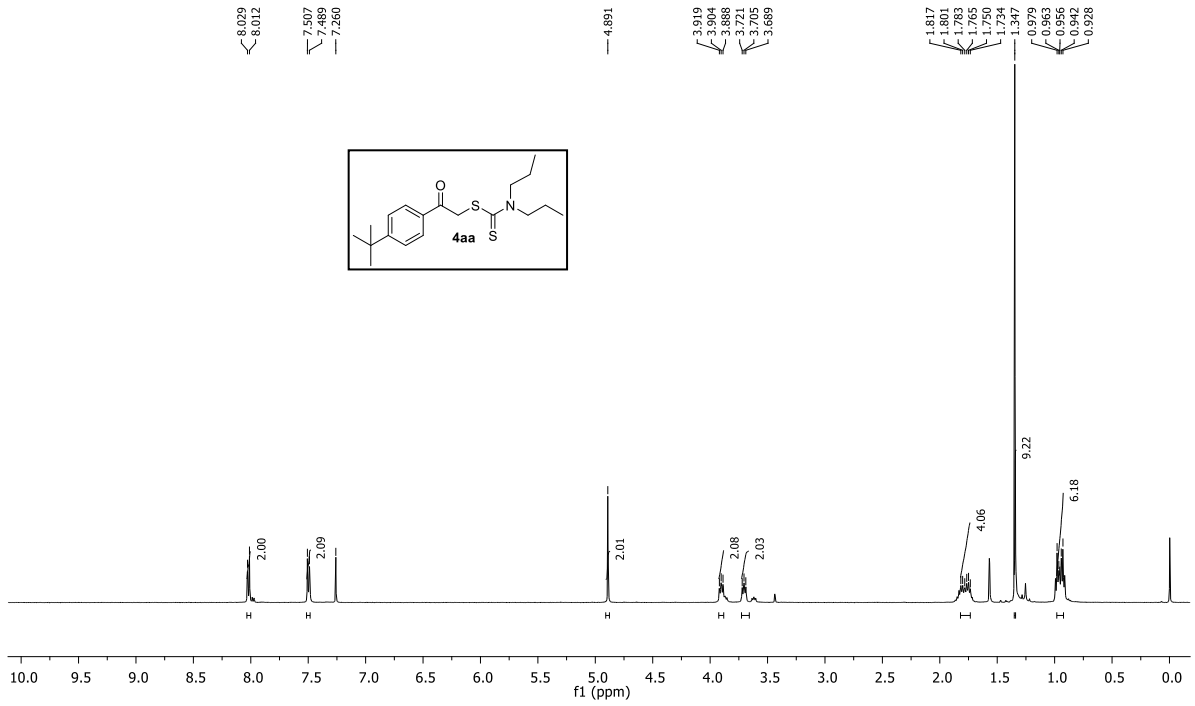


^{13}C NMR, $CDCl_3$, 126 MHz

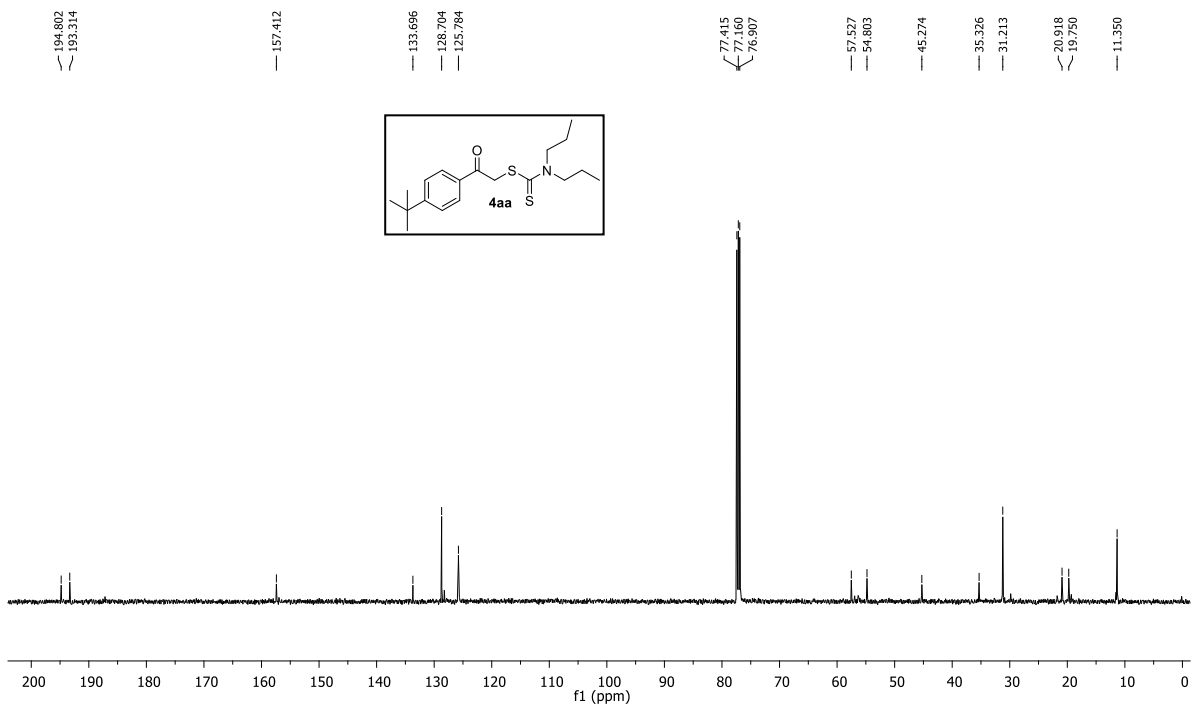


2-(4-(*tert*-Butyl) phenyl)-2-oxoethyl dipropylcarbamodithioate (4aa):

^{1}H NMR, $CDCl_3$, 500 MHz

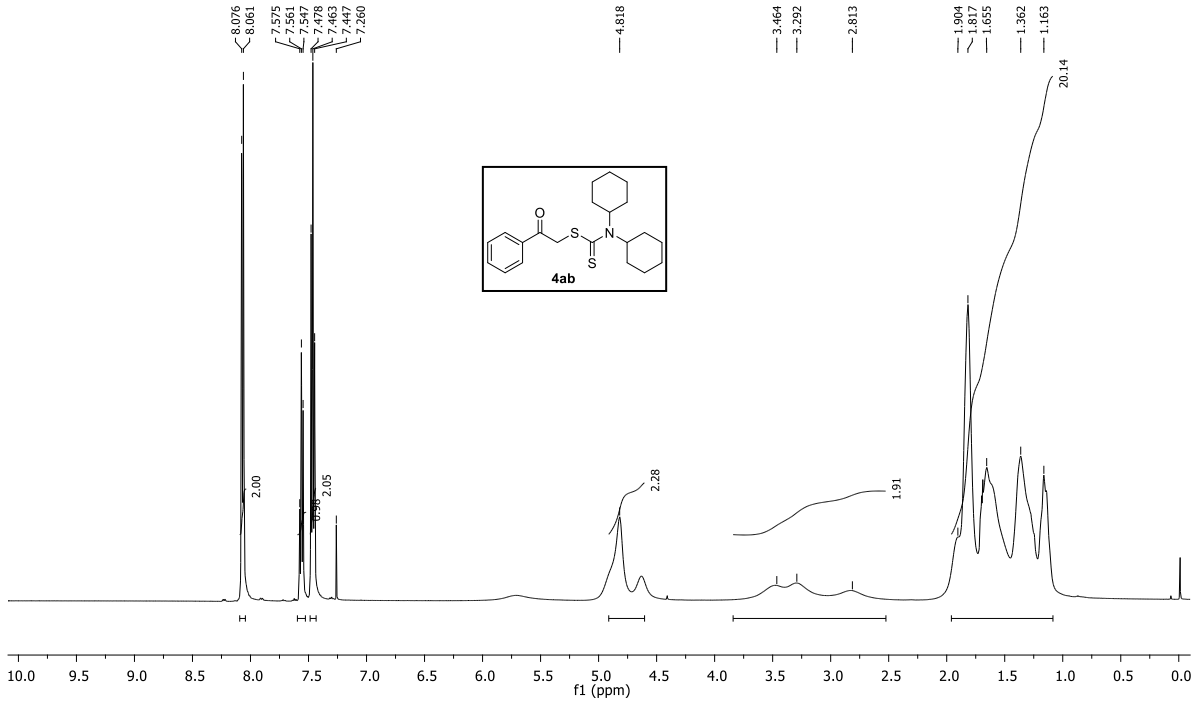


^{13}C NMR, $CDCl_3$, 126 MHz

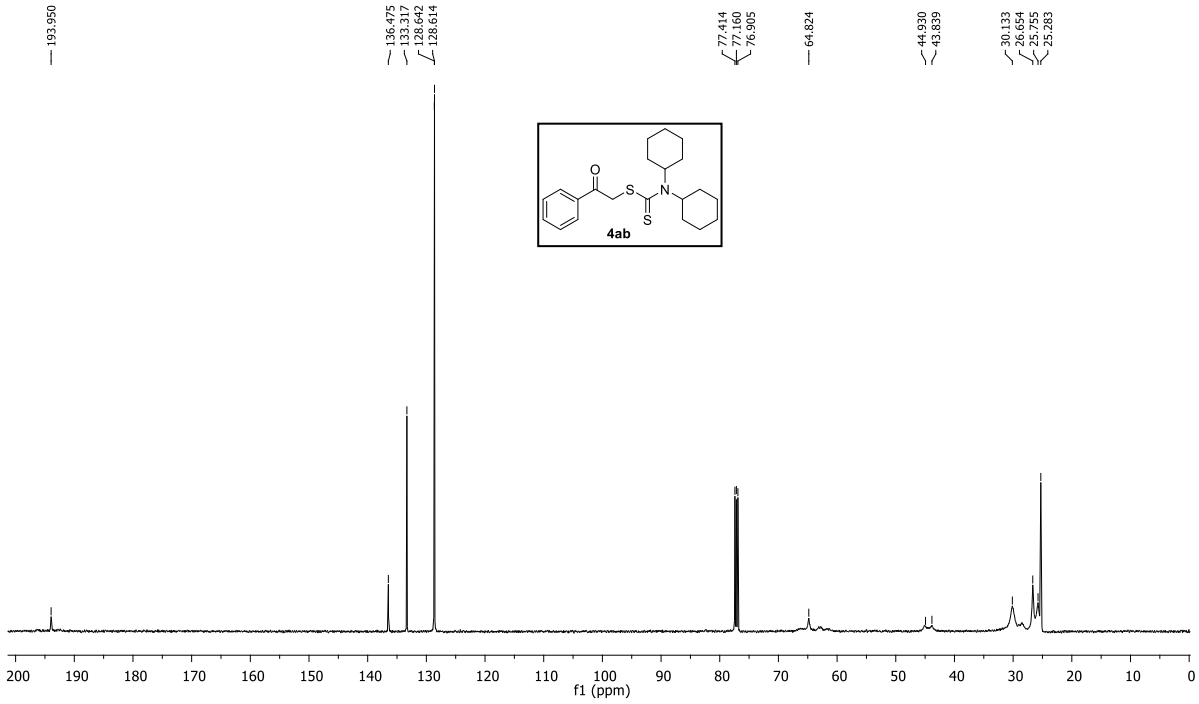


2-Oxo-2-phenylethyl dicyclohexylcarbamodithioate (4ab):

^{1}H NMR, $CDCl_3$, 500 MHz

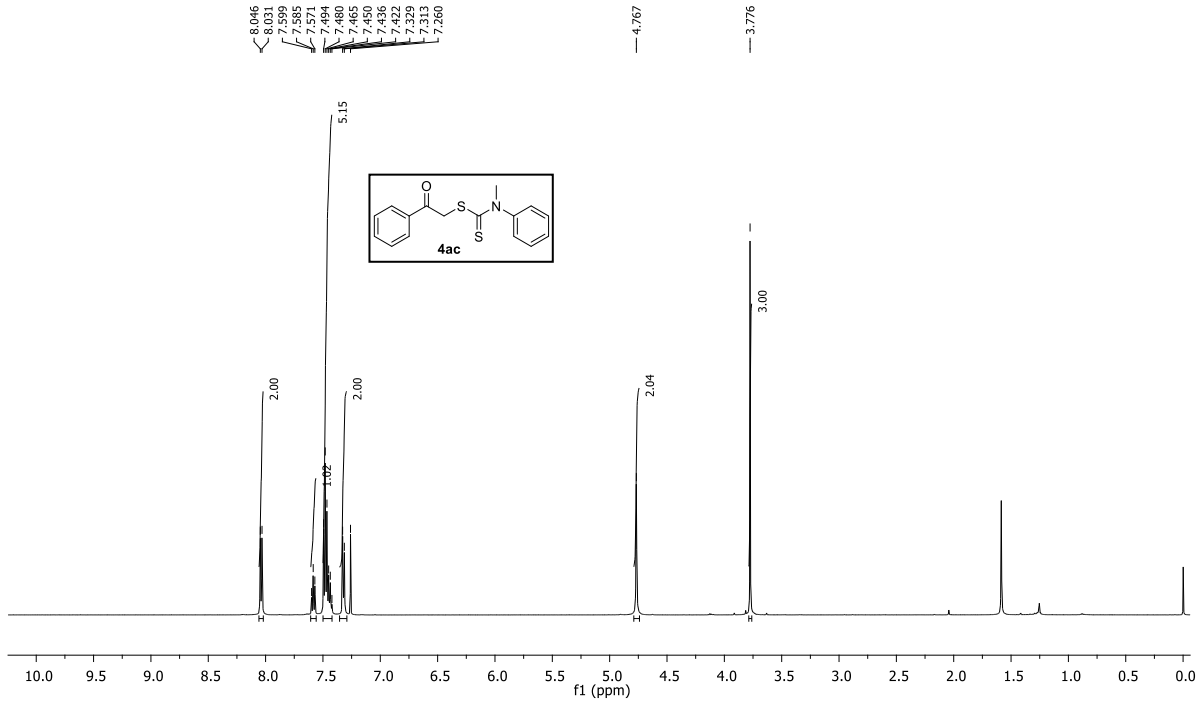


^{13}C NMR, $CDCl_3$, 126 MHz

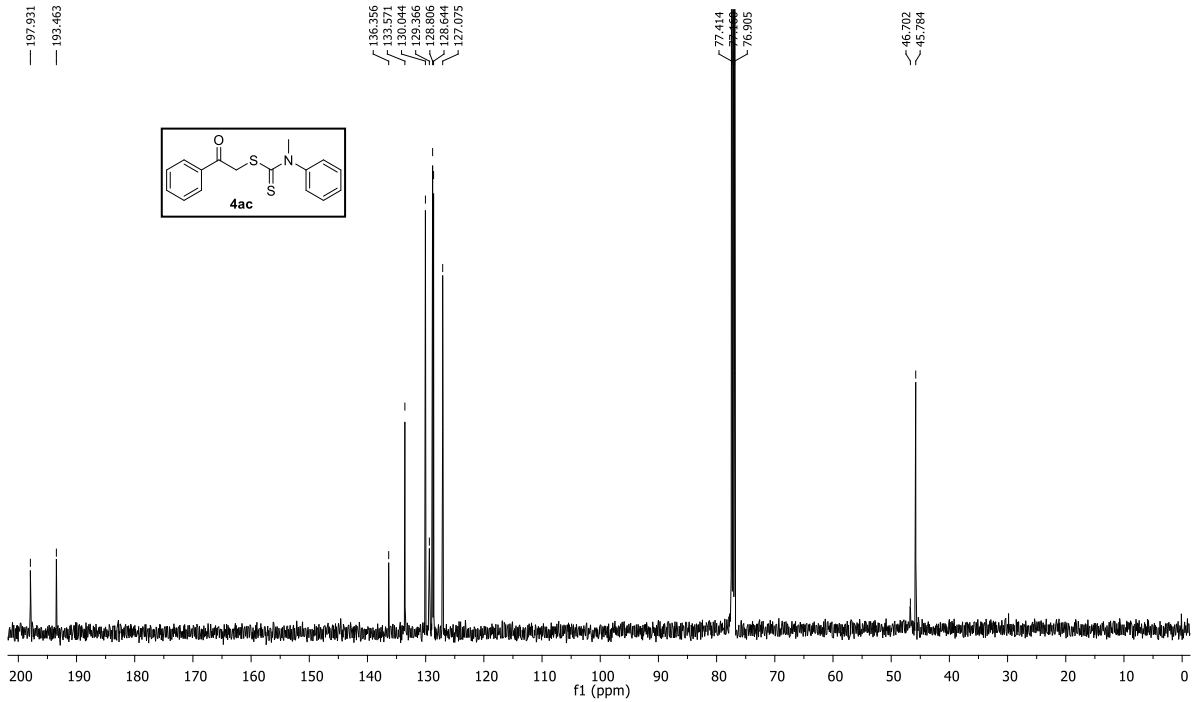


2-Oxo-2-phenylethyl methyl(phenyl)carbamodithioate (4ac):

^{1}H NMR, $CDCl_3$, 500 MHz

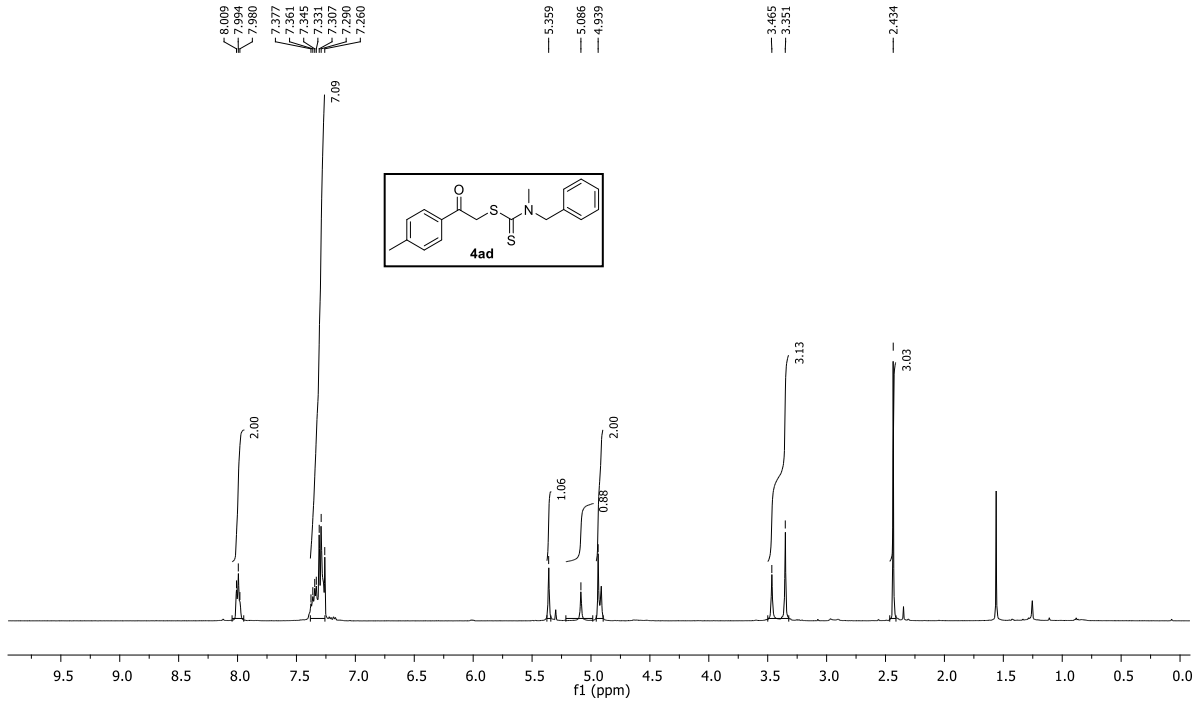


^{13}C NMR, $CDCl_3$, 126 MHz

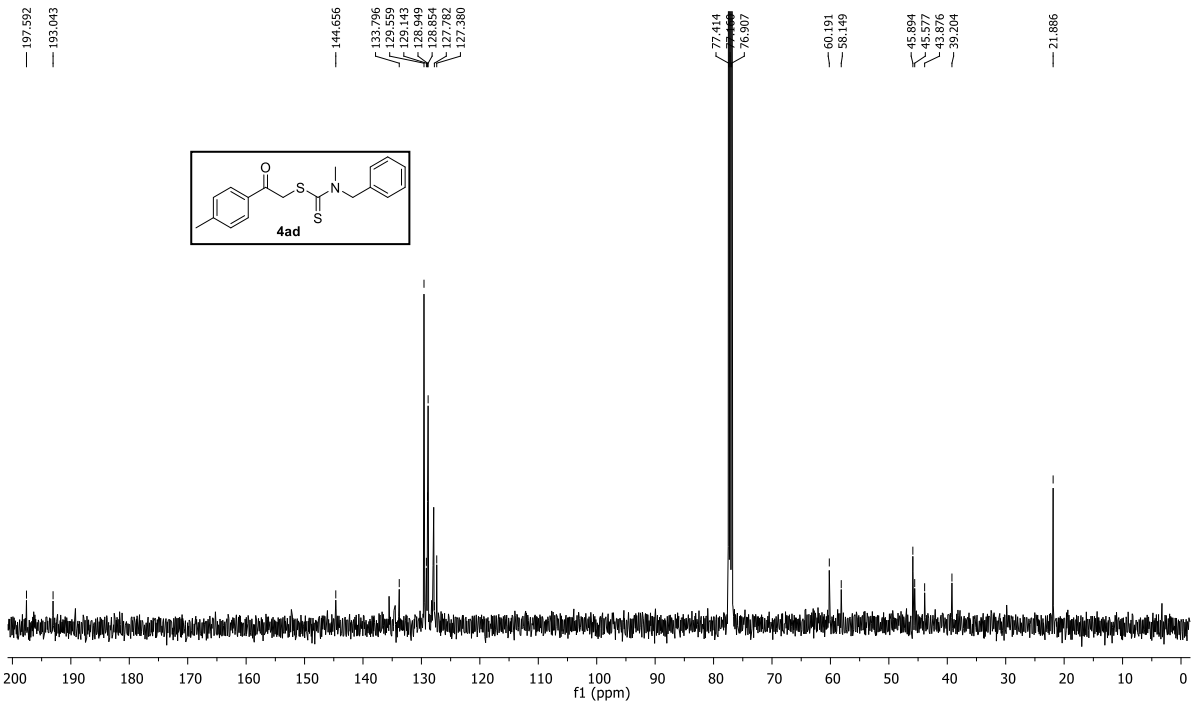


2-Oxo-2-(*p*-tolyl) ethyl benzyl(methyl)carbamodithioate (4ad):

^{1}H NMR, $CDCl_3$, 500 MHz

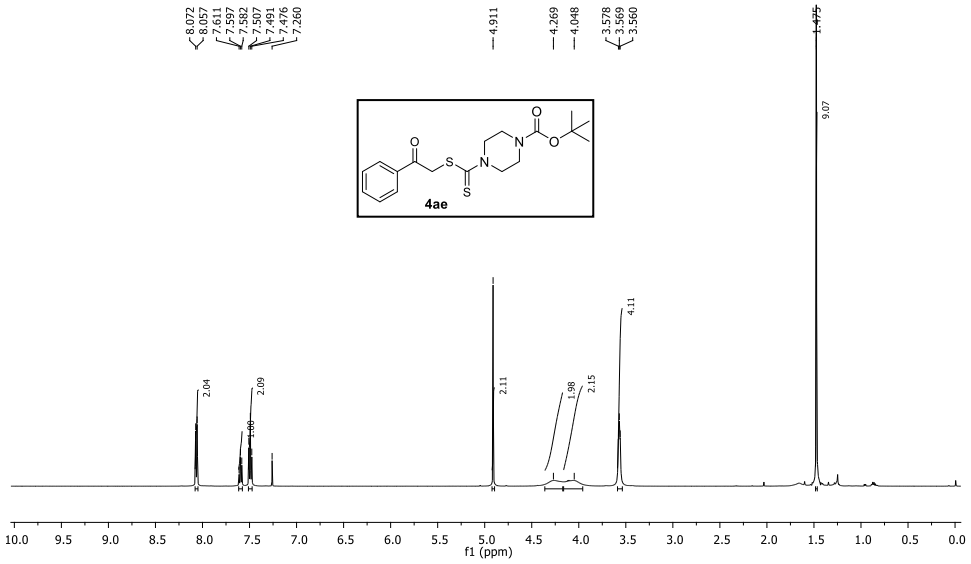


^{13}C NMR, $CDCl_3$, 126 MHz

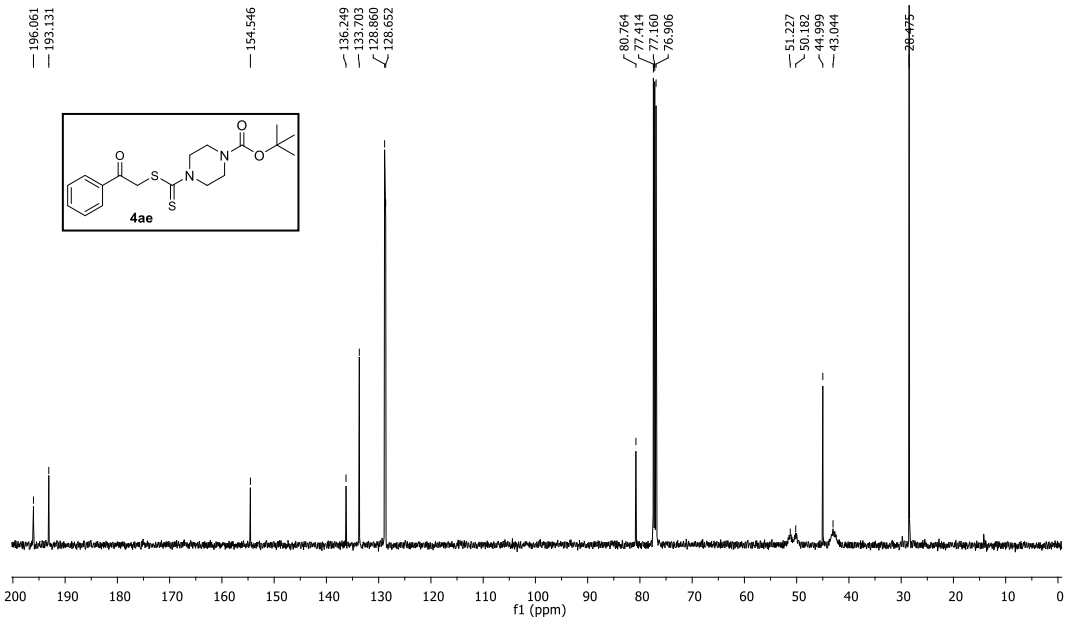


***tert*-Butyl 4-(((2-oxo-2-phenylethyl)thio) carbonothioyl)piperazine-1-carboxylate (4ae):**

^{1}H NMR, $CDCl_3$, 500 MHz

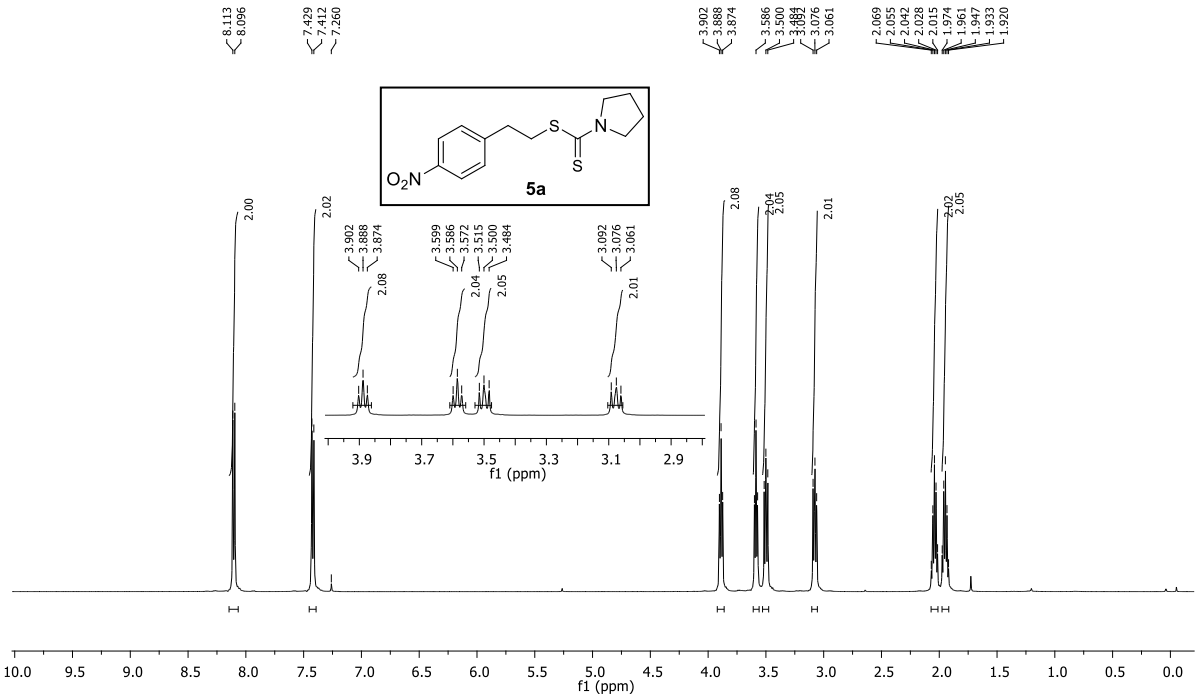


^{13}C NMR, $CDCl_3$, 126 MHz

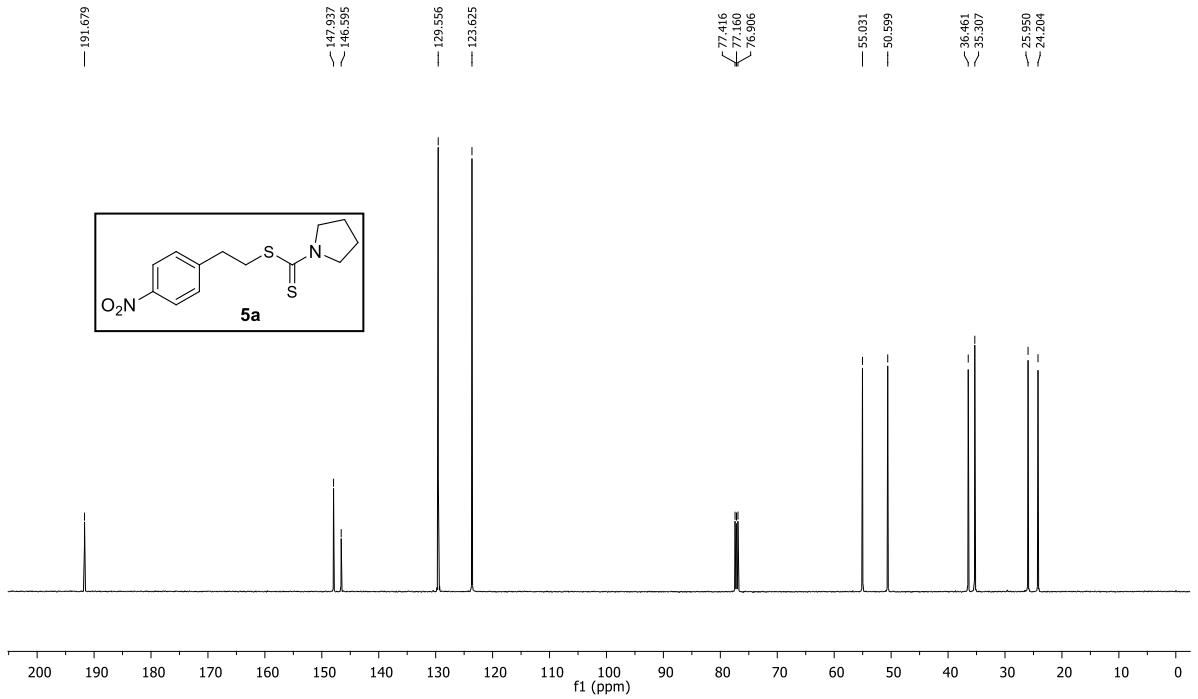


4-Nitrophenethyl pyrrolidine-1-carbodithioate (5a):

^{1}H NMR, $CDCl_3$, 500 MHz

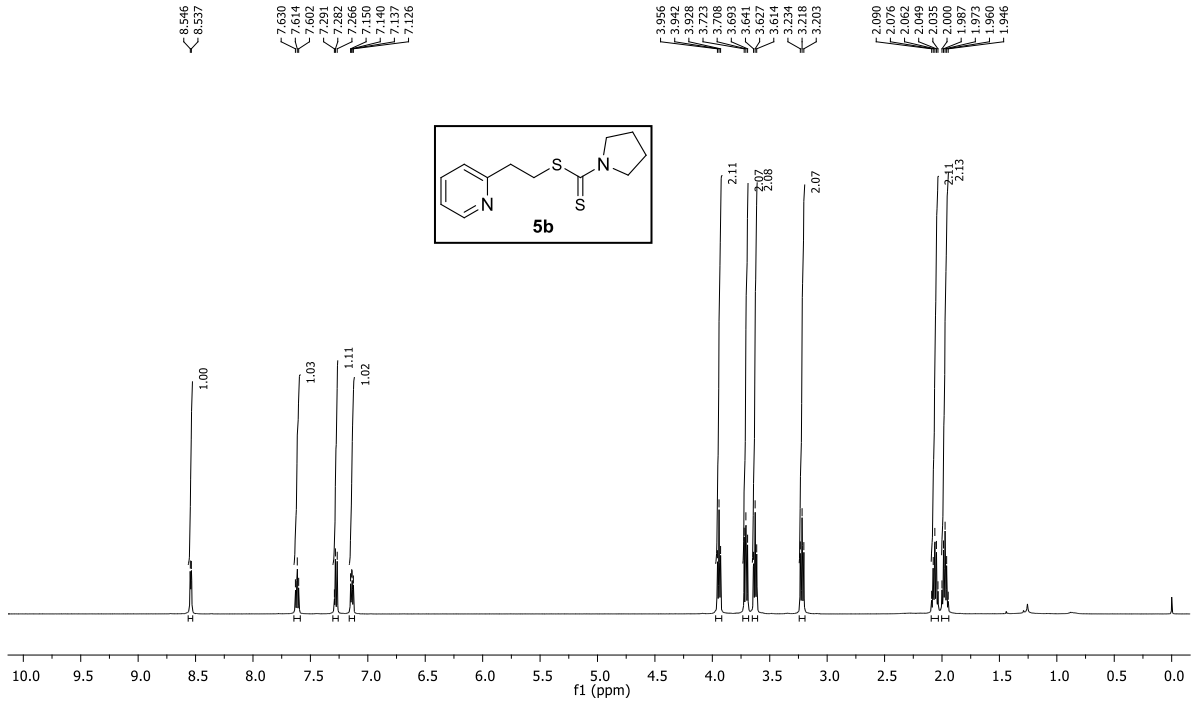


^{13}C NMR, $CDCl_3$, 126 MHz

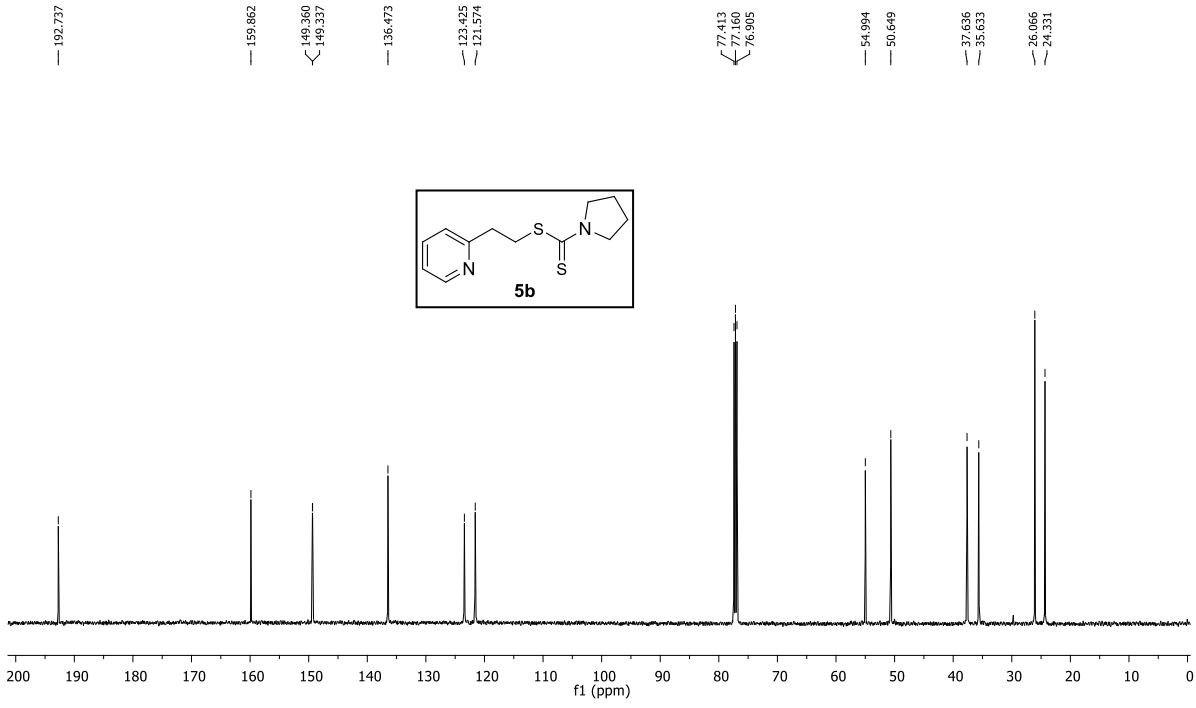


2-(Pyridin-2-yl) ethyl pyrrolidine-1-carbodithioate (5b):

^{1}H NMR, $CDCl_3$, 500 MHz

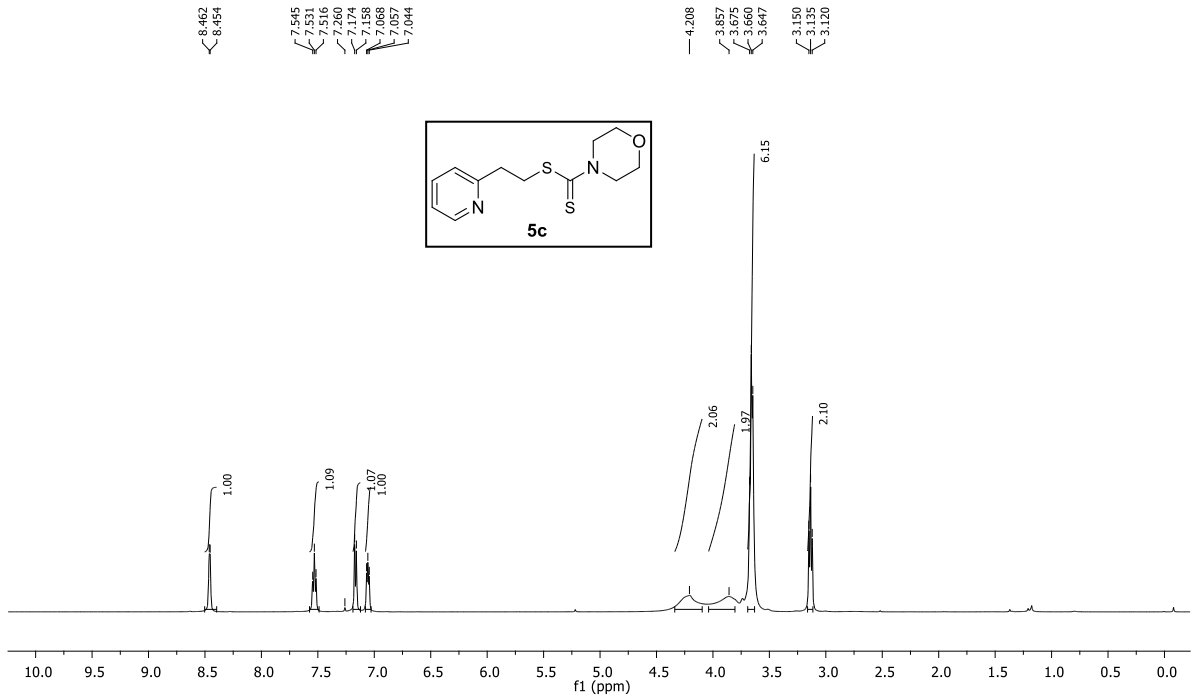


^{13}C NMR, $CDCl_3$, 126 MHz

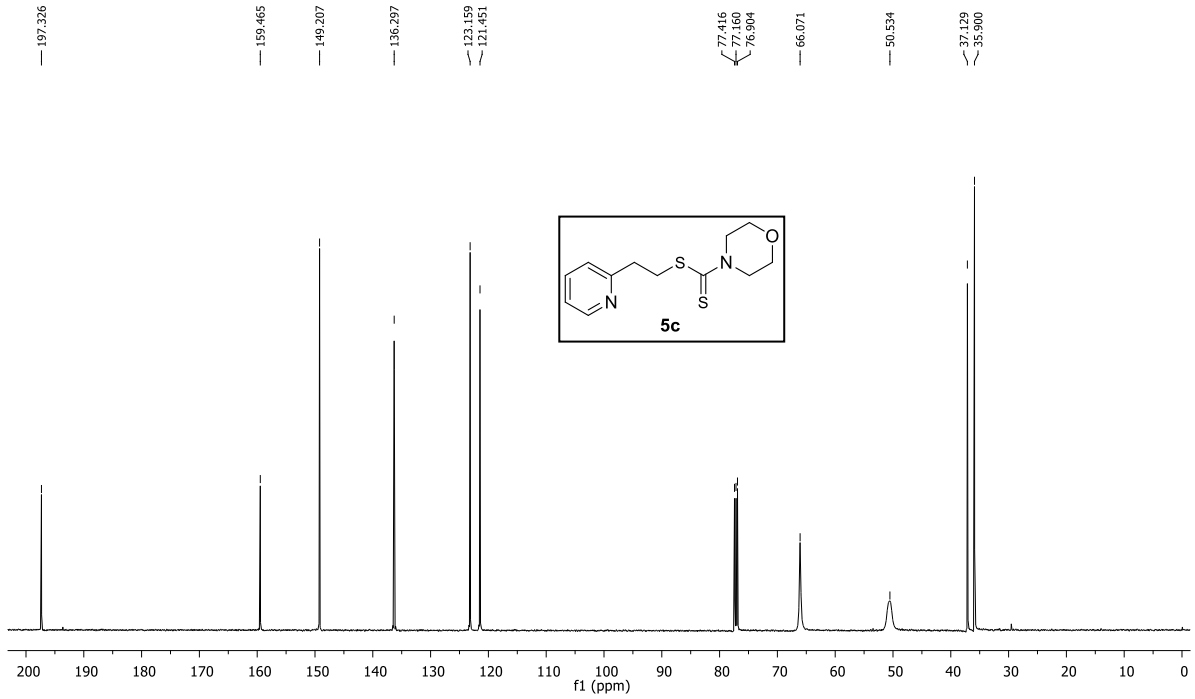


2-(Pyridin-2-yl) ethyl morpholine-4-carbodithioate (5c):

^{1}H NMR, $CDCl_3$, 500 MHz

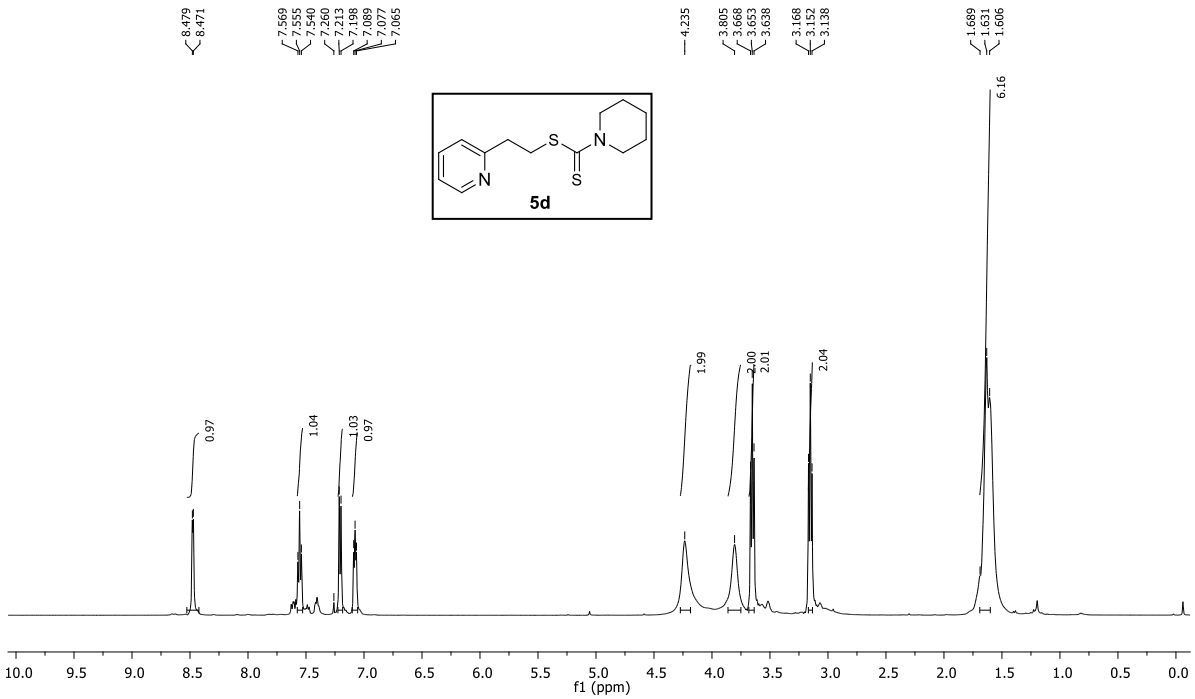


^{13}C NMR, $CDCl_3$, 126 MHz

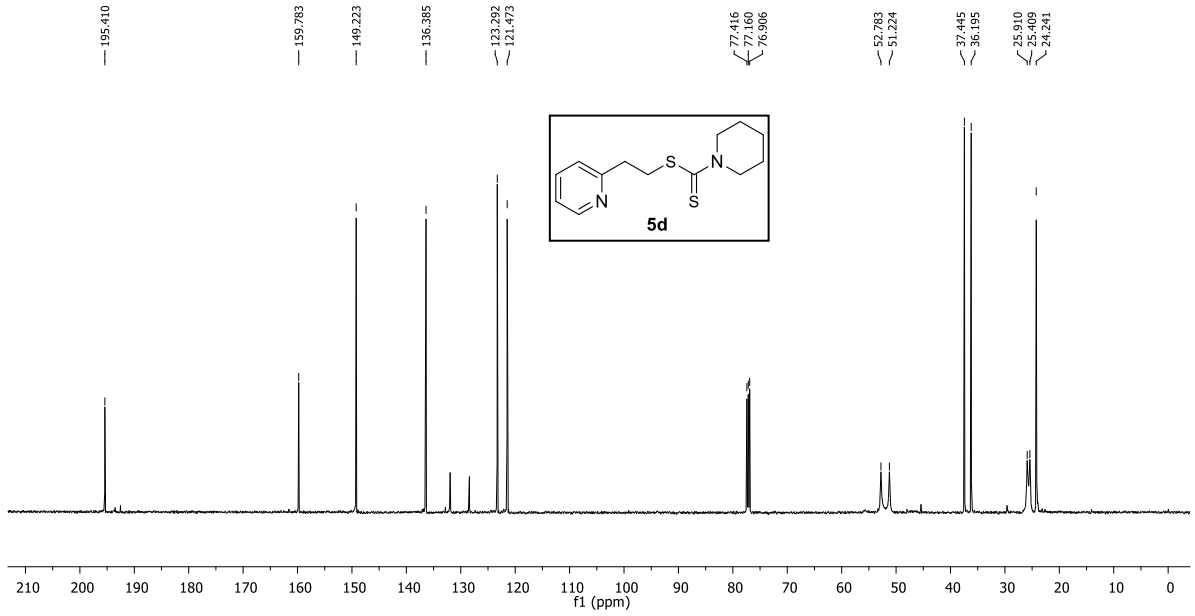


2-(Pyridin-2-yl) ethyl piperidine-1-carbodithioate (5d):

^{1}H NMR, $CDCl_3$, 500 MHz

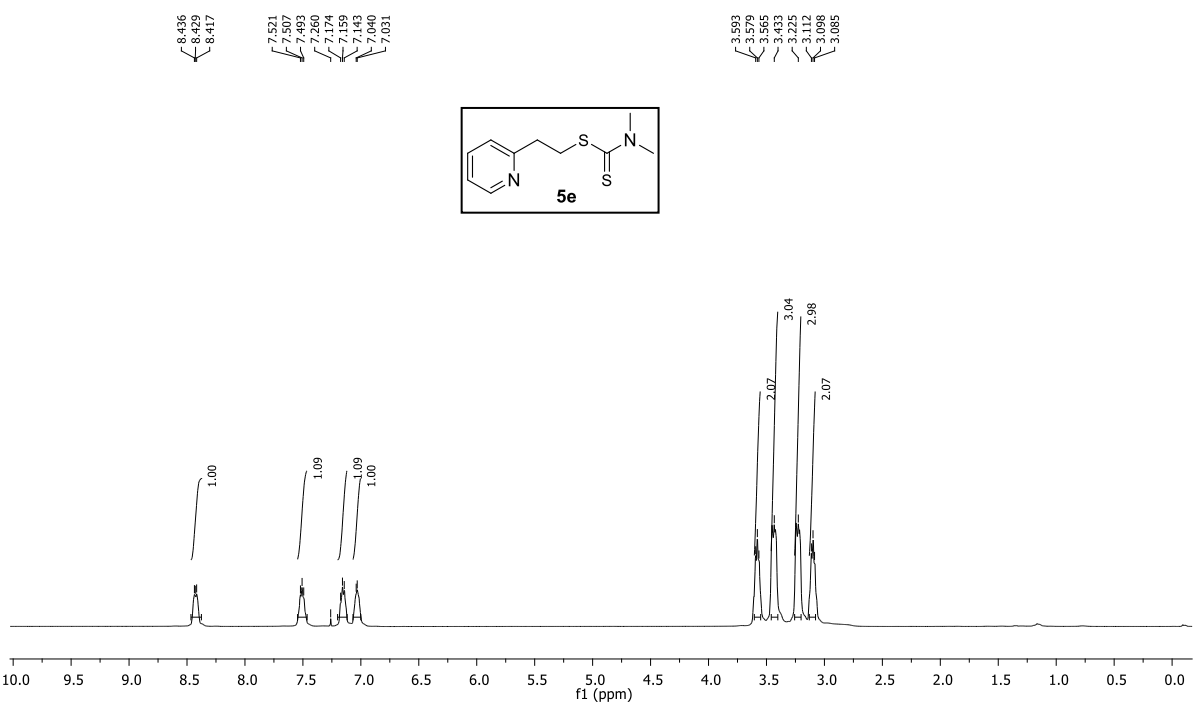


^{13}C NMR, $CDCl_3$, 126 MHz

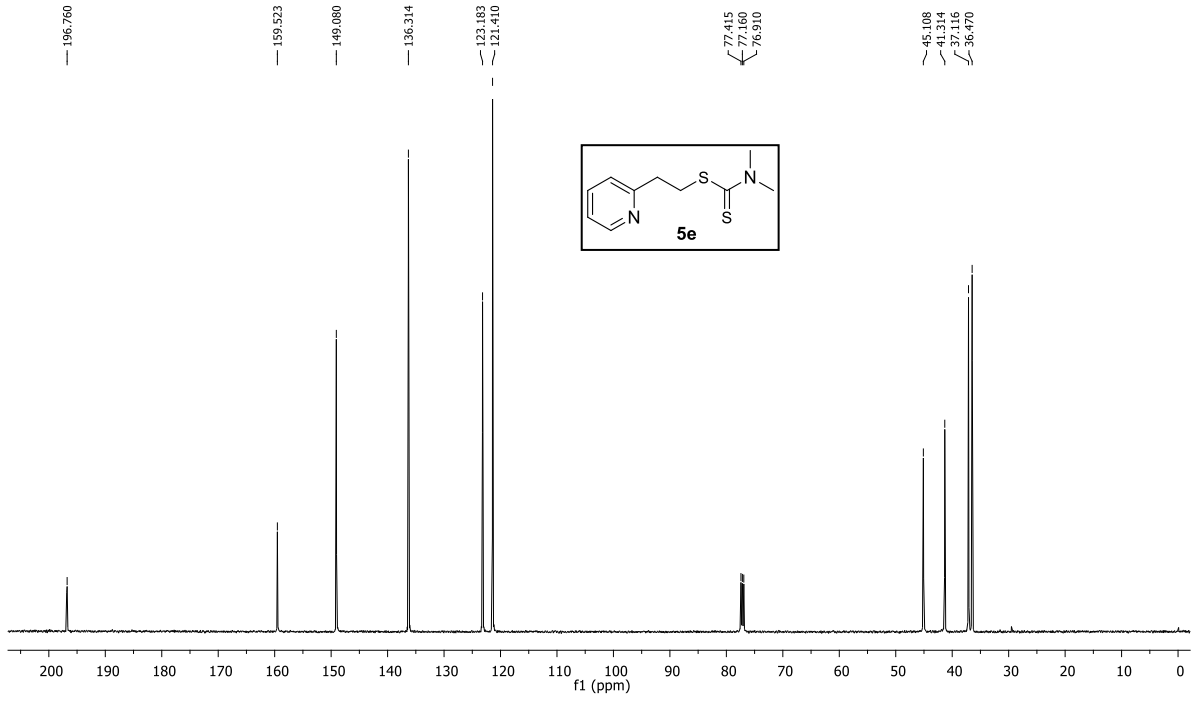


2-(Pyridin-2-yl) ethyl dimethylcarbamodithioate (5e):

^{1}H NMR, $CDCl_3$, 500 MHz

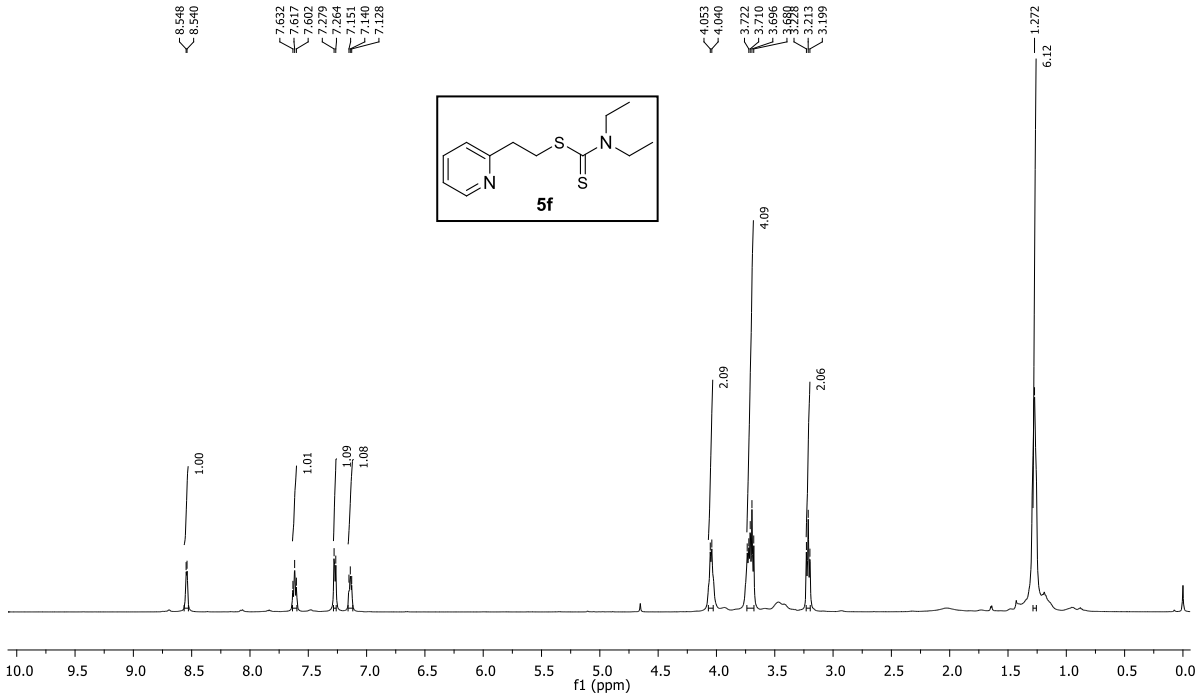


^{13}C NMR, $CDCl_3$, 126 MHz

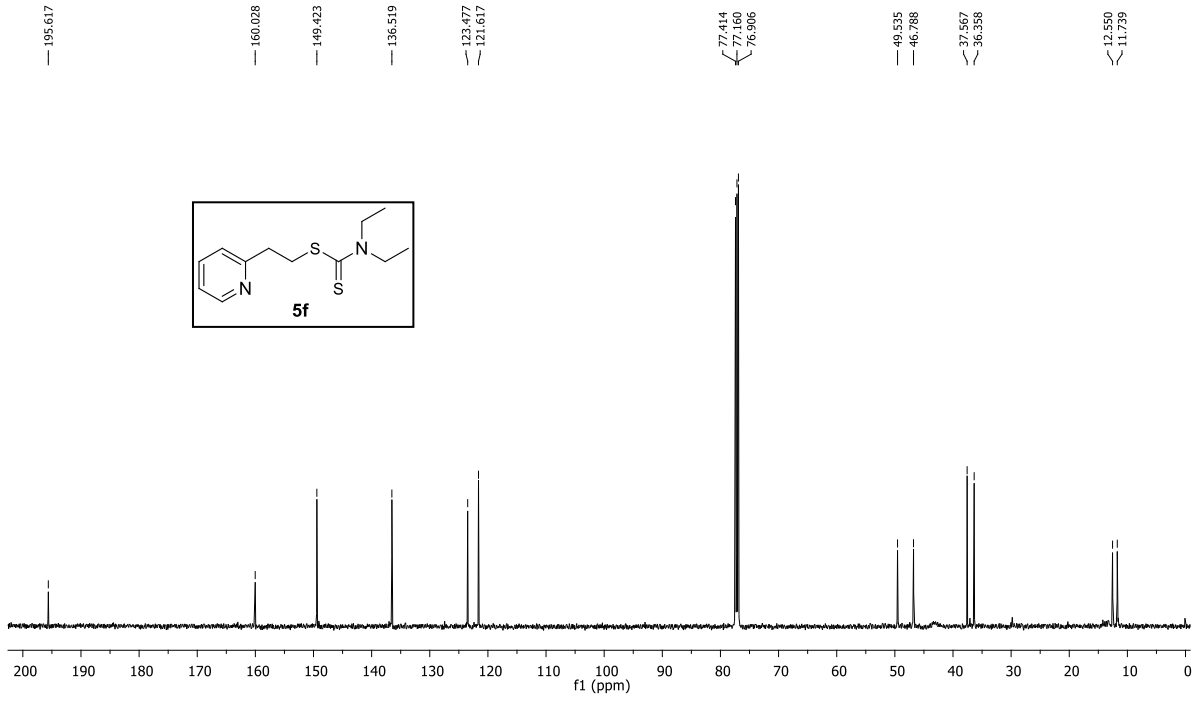


2-(Pyridin-2-yl) ethyl diethylcarbamodithioate (5f):

^{1}H NMR, $CDCl_3$, 500 MHz

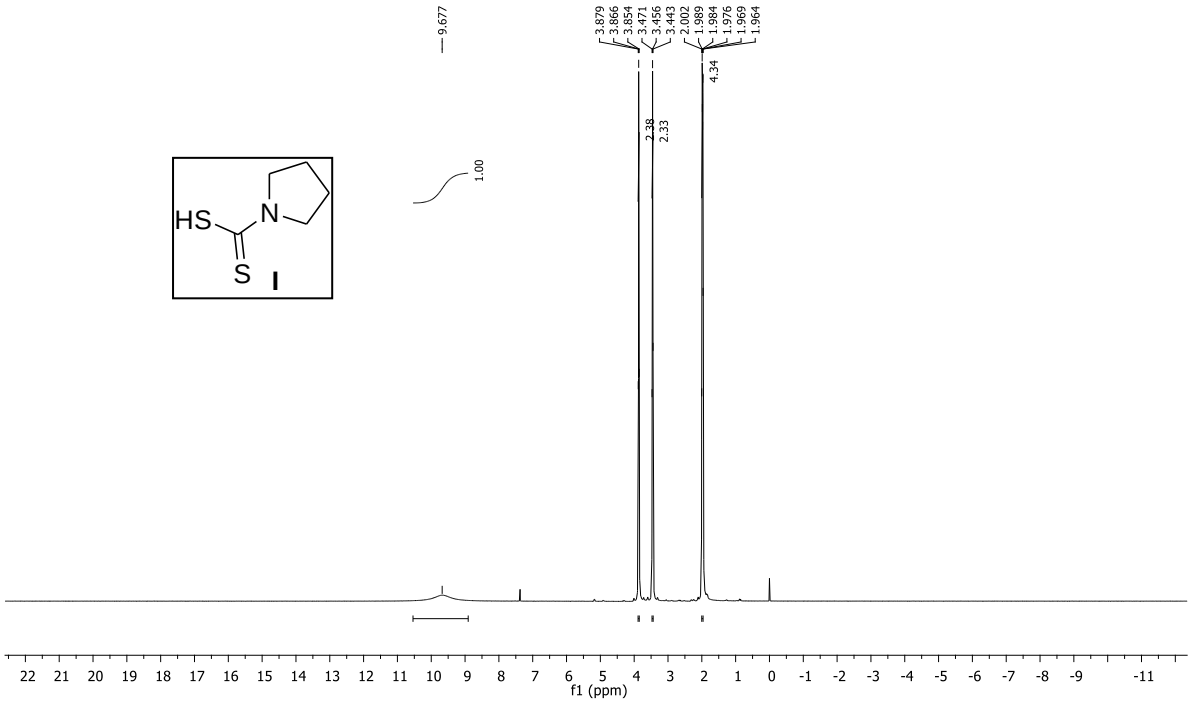


^{13}C NMR, $CDCl_3$, 126 MHz

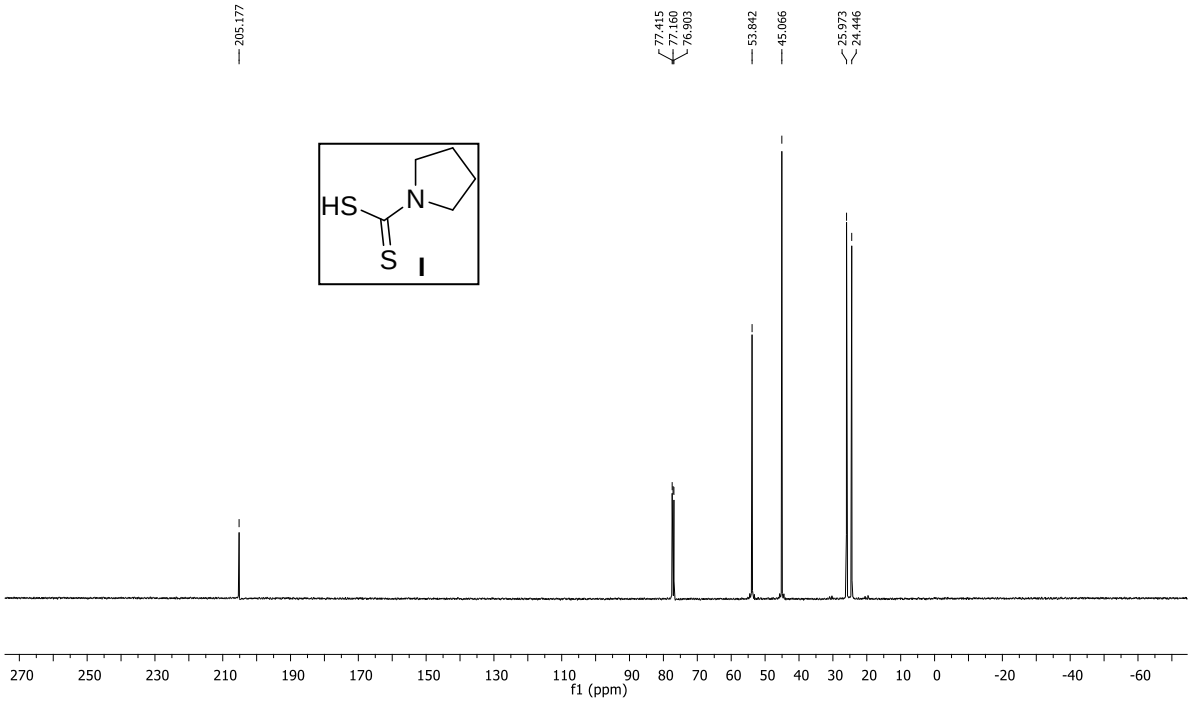


Pyrrolidine-1-carbodithioic acid (I):

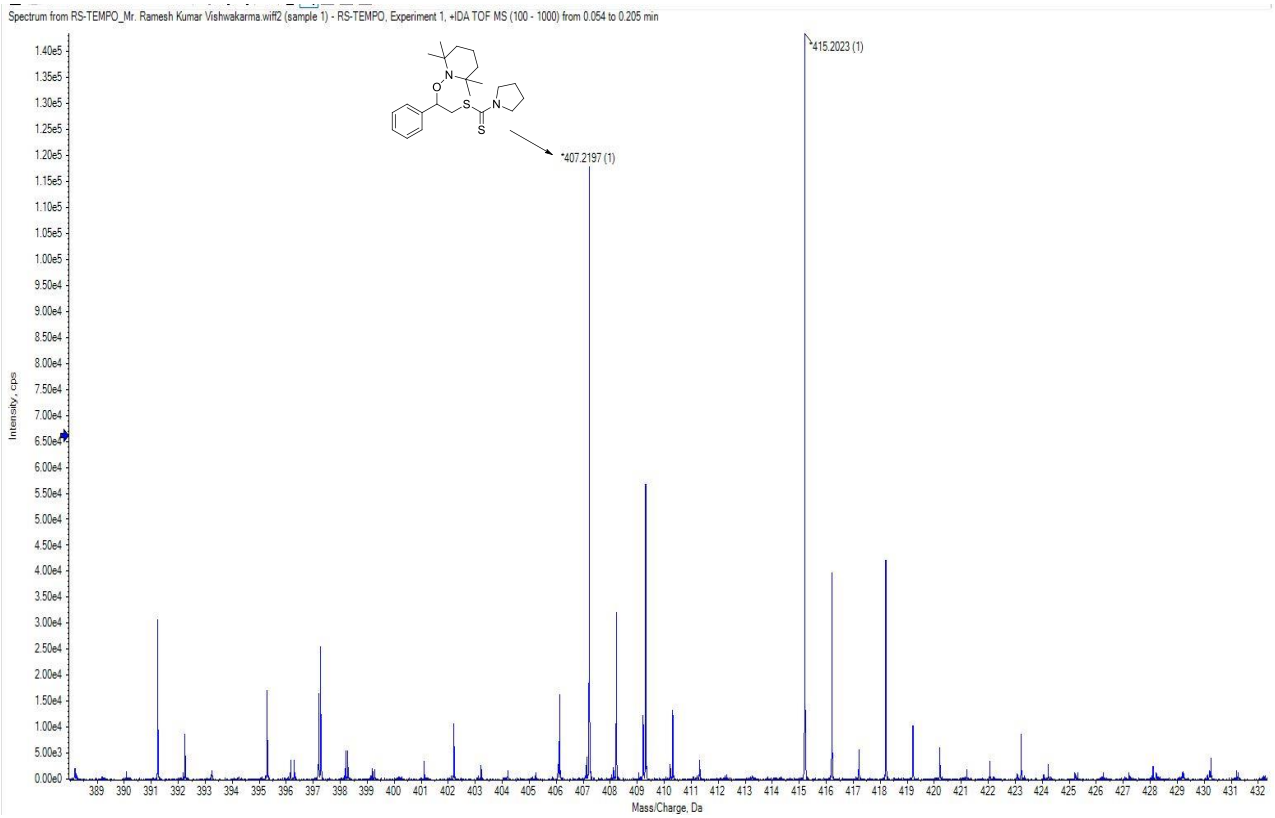
^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



8. HRMS of TEMPO adduct:

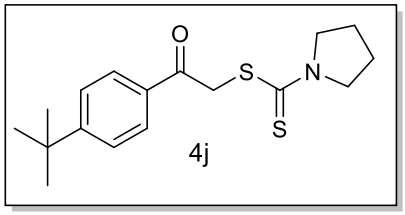


9. Crystallographic Data:

Crystal of compound **4j** was grown by slow evaporation of a solution of the compound in $CDCl_3/CH_2Cl_2$.

All the measurements were obtained on a BRUKER Single Crystal X-Ray Diffractometer, Germany (model of the instrument – AXS D8 Quest System).

Specification: D8 QUEST, Horizontal Goniometer, Fixed Chi stage, Goniometer head manual, Photon 100 CMOS Detector, two pinhole collimator (0.3/17 mrad, 0.6/17 mrad), Ceramic Tube KFF Mo-2K-90c, Head turned by 90^0, Video microscope SCD, APEX2 w. SHELXTL S/W, Cryostream-700plus extended range low Temperature.



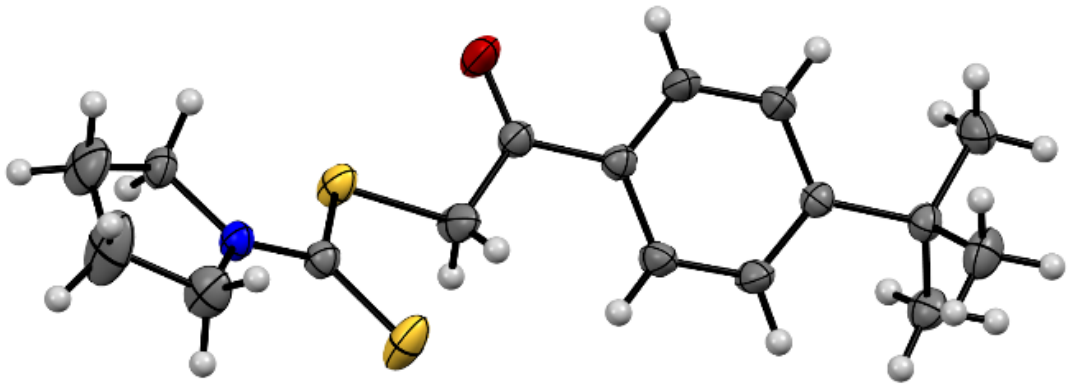


Figure S3. View of the molecular structure of **4j**. Displacement ellipsoids are drawn at the 50% probability level.

Table T1. Crystallographic data for compound **4j**.

Crystallized from	$CDCl_3/CH_2Cl_2$
Empirical formula	$C_{17}H_{23}NOS_2$
Formula weight [g mol^{-1}]	321.48
Crystal colour, habit	Pale yellow, block
Crystal dimensions (mm)	0.25 × 0.22 × 0.18
Temperature [K]	273(2)
Crystal system	triclinic
Space group	*P-1*
a/Å	7.922(3)
b/Å	10.486(4)
c/Å	11.678(4)
α/°	110.375(9)
β/°	104.172(8)
γ/°	96.339(9)
V[$Å^3$]	861.0(5)
Z	2
Dx [g/cm^3]	1.240
μ (MoKα) [mm^{-1}]	0.308
F(000)	344.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.132 to 50.204
Index ranges	$-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	13698
Independent reflections	3066 [R_{int} = 0.0283, R_{sigma} = 0.0216]
Data/restraints/parameters	3066/0/194
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.1092
Final R indexes [all data]	R_1 = 0.0538, wR_2 = 0.1172
Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.35