Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Visible-Light-mediated C(sp^3)–H functionalization of Alkyl Arylacetates: An Easy Approach to *S*-Benzyl Dithiocarbamate Acetates

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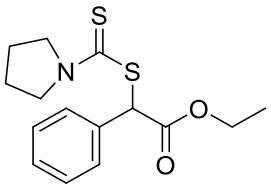
1. General Information:

All the reagents were purchased from Sigma-Aldrich, Alfa Aesar, and E. Merck, and were used as received. ^{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 125 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, dd = double doublet, brs = broad singlet, and m = multiplet), coupling constant (J) (Hz), and integration. Mass spectra were recorded on a SCIEX X500R QTOF mass spectrometer. IR spectra were recorded on Perkin Elmer FT-IR 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.

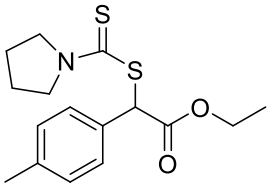
2. General Procedure for the Synthesis of Products 4a-4t:

A mixture of amine (**3**, 1.2 mmol), carbon disulfide (**2**, 2.5 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 alkyl arylacetates (**1**, 1 mmol), Eosin Y (5 mol%), iodine (20 mol %) and K_2CO_3 (2 equiv.). The contents were stirred and irradiated by white LED (400-800 nm) under ambient conditions for 20 h. After completion of the reaction (monitored through TLC), the reaction was quenched with a sodium thiosulphate pentahydrate aqueous solution (10 mL), and then extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over anhydrous 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**.

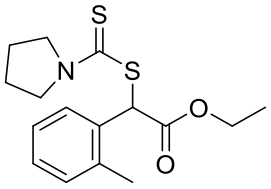
3. Physical and Spectral Data of the Products 4a-4t.



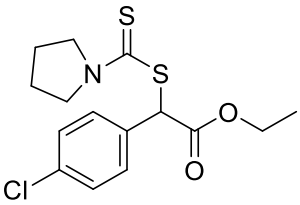
Ethyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4a):[1] White solid (72 %), m.p. 114-115˚C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.36-7.30 (m, 3H), 5.84 (s, 1H), 4.32-4.25 (m, 1H), 4.19-4.13 (m, 1H), 3.92 (q, *J* = 6.5 Hz, 2H), 3.74-3.69 (m, 1H), 3.60-3.55 (m,1H), 2.10-2.03 (m, 2H), 1.99-1.94 (m, 2H), 1.27 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.6, 170.3, 134.3, 129.0, 128.9, 128.6, 62.2, 58.5, 55.1, 50.7, 26.3, 24.4, 14.2.



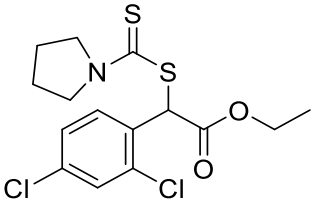
Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(p-tolyl)acetate (4b):[1] White solid (71 %), m.p. 116-117˚C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.78 (s, 1H), 4.30-4.25 (m, 1H), 4.17-4.11 (m, 1H), 3.91 (q, *J* = 6.5 Hz, 2H), 3.73-3.68 (m, 1H), 3.59-3.54 (m, 1H), 2.33 (s, 3H), 2.07-2.02 (m, 2H), 1.98-1.94 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.8, 170.4, 138.6, 131.2, 129.8, 128.8, 62.2, 58.2, 55.0, 50.7, 26.3, 24.4, 21.3, 14.2.



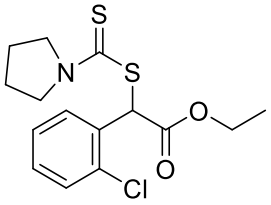
Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(o-tolyl)acetate (4c): Brown liquid (68 %), IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2967, 2925, 2872, 1739, 1463, 1435, 1250, 1161, 1095, 1028, 1009, 957; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, 1H, *J* = 7.5 Hz), 7.22 (d, 2H, *J* = 4.0 Hz), 7.18-7.15 (m, 1H), 6.01 (s, 1H), 4.32-4.26 (m, 1H), 4.18-4.15 (m, 1H), 3.92 (q, *J* = 6.5 Hz, 2H), 3.75-3.72 (m, 1H), 3.59-3.54 (m, 1H), 2.48 (s, 3H), 2.08-2.04 (m, 2H), 2.0-1.96 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 191.0, 170.6, 137.2, 132.4, 131.1, 128.6, 128.5, 126.5, 62.2, 55.7, 55.1, 50.7, 26.3, 24.4, 19.9, 14.2. HRMS (TOF-MS) for $C_{16}H_{22}NO_2S_2$ m/z $[M + H]^+$ calcd: 324.1086, found: 324.1083



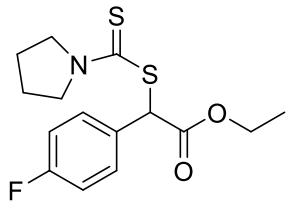
Ethyl 2-(4-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4d)[1]: Yellow liquid (70 %), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.87 (s, 1H), 4.28-4.25 (m, 1H), 4.19-4.14 (m, 1H), 3.90 (q, *J* = 6.5 Hz, 2H), 3.72-3.66 (m, 1H), 3.61- 3.56 (m, 1H), 2.08-2.05 (m, 2H), 1.99-1.95 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.0, 170.0, 134.56, 133.4, 130.3, 129.2, 62.4, 57.7, 55.2, 50.8, 26.3, 24.4, 14.2.



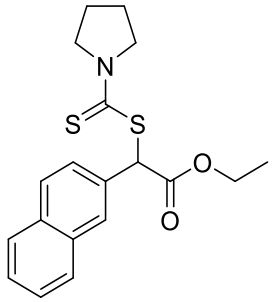
Ethyl 2-(2,4-dichlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4e): Light yellow solid (66 %), m.p. 77-78˚C, IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2967, 2926, 2871, 1738, 1439, 1162, 1100, 1028, 799; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 9.5 Hz, 1H), 7.23-7.21 (m, 1H), 6.45 (s, 1H), 4.27-4.22 (m, 2H), 3.92 (q, *J* = 6.5 Hz, 2H), 3.73-3.70 (m, 1H), 3.62-3.59 (m, 1H), 2.09-2.05 (m, 2H), 1.99-1.95 (m, 2H), 1.26-1.23 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.0, 169.3, 135.2, 135.0, 132.5, 131.4, 130.0, 127.5, 62.6, 55.7, 55.5, 50.7, 26.3, 24.4, 14.2. HRMS (TOF-MS) for $C_{15}H_{18}NCl_2O_2S_2$ m/z $[M + H]^+$ calcd: 378.0151, found: 378.0154



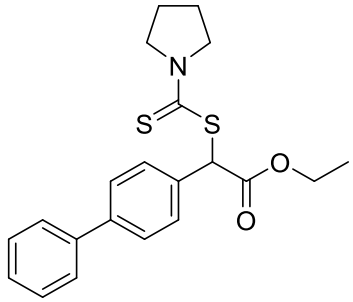
Ethyl 2-(2-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4f): Sticky solid (69 %), IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2976, 2871, 1738, 1463, 1436, 1250, 1219, 1160, 1028, 1008, 956; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52-7.51 (m, 1H), 7.43 (d, 1H, *J* = 8.5 Hz), 7.28-7.23 (m, 2H), 6.46 (s, 1H), 4.27-4.20 (m, 2H), 3.94 (q, *J* = 6.0 Hz, 2H), 3.77-3.72 (m, 1H), 3.63-3.58 (m, 1H), 2.09-2.06 (m, 2H), 2.0-1.96 (m, 2H), 1.27-1.24 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.4, 169.7, 134.4, 133.3, 130.5, 130.1, 129.7, 127.2, 62.4, 56.1, 55.4, 50.7, 26.2, 24.4, 14.2. HRMS (TOF-MS) for $C_{15}H_{19}ClNO_2S_2$ m/z $[M + H]^+$ calcd: 344.0540, found: 344.0546.



Ethyl 2-(4-fluorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4g): Sticky solid ; (65 %), IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2977, 2926, 2873, 1737, 1603, 1508, 1463, 1436, 1223, 1160, 1010, 1027, 957; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.42 (m, 2H), 7.04 (t, *J* = 8.0 Hz, 2H), 5.85 (s, 1H), 4.29-4.25 (m, 1H), 4.19-4.14 (m, 1H), 3.91 (q, *J* = 6.5 Hz, 2H), 3.71-3.68 (m, 1H), 3.62-3.57 (m, 1H), 2.08-2.05 (m, 2H), 1.98-1.95 (m, 2H), 1.27-1.24 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.2, 170.2, 163.8, 161.9, 130.8, 130.7, 116.1, 115.9, 115.5, 115.3, 62.3, 57.6, 55.1, 50.8, 26.3, 24.4, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.1. HRMS (TOF-MS) for $C_{15}H_{19}FNO_2S_2$ m/z $[M + H]^+$ calcd: 328.0836, found: 328.0831.

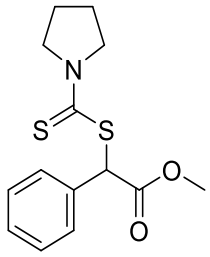


Ethyl 2-(naphthalen-2-yl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4h): Colourless solid (73 %), m.p. 149-150˚C, IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2980, 2948, 1741, 1598, 1510, 1434, 1331, 1260, 1217, 1185, 1162, 1031, 1008, 954. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 10.5 Hz, *J* = 8.0 Hz, 2H), 7.59-7.57 (m, 2H), 7.53-7.50 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.7 (s, 1H), 4.35-4.28 (m, 1H), 4.22-4.17 (m, 1H), 3.97-3.92 (q, *J* = 10.5 Hz, 2H), 3.76-3.71 (m, 1H), 3.54-3.49 (m, 1H), 2.07-1.95 (m, 4H), 1.24 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 191.0, 170.6, 137.2, 132.4, 131.1, 128.6, 128.5, 126.5, 62.2, 55.7, 55.1, 50.7, 26.3, 24.4, 19.9, 14.2. HRMS (TOF-MS) for $C_{19}H_{22}NO_2S_2$ m/z $[M + H]^+$ calcd: 360.1086, found: 360.1093.

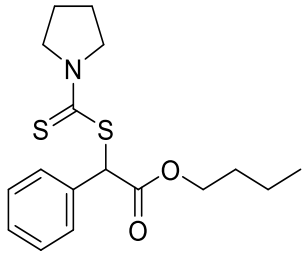


Ethyl 2-([1,1'-biphenyl]-4-yl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4i): White solid (70 %), m.p. 148-149˚C, IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2978, 1731, 1464, 1445, 1282, 1184, 1167, 1103, 1007, 956, 784, 734, 702; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (dd, *J* = 8.0 Hz, 6.5 Hz, 6H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.36-7.34 (m, 1H), 5.91 (s, 1H),

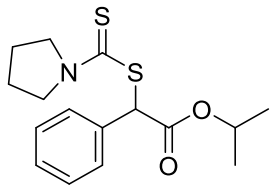
4.35-4.28 (m,1H), 4.22-4.15 (m, 1H), 3.92 (brs, 2H), 3.73 (m, 2H), 2.10-2.04 (m, 2H), 2.0 (q, *J* = 7.0 Hz, 2H), 1.30-1.27 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.4, 170.2, 141.6, 140.5, 133.5, 129.3, 128.9, 127.7, 127.2, 62.3, 58.2, 55.1, 50.7, 26.3, 24.4, 14.2. HRMS (TOF-MS) for $C_{21}H_{24}NO_2S_2$ m/z $[M + H]^+$ calcd: 386.1243, found: 386.1247.



Methyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4j)[2]: White solid (70 %), m.p. 114-115˚C (lit. 112-113˚C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.44 (m, 2H), 7.37-7.33 (m, 3H), 5.87 (s, 1H), 3.92 (q, *J* = 6.5 Hz, 2H), 3.76 (s, 3H), 3.73-3.69 (m, 1H), 3.60-3.56 (m, 1H), 2.08-2.05 (m, 2H), 2.0-1.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.5, 170.8, 134.2, 129.1, 129.0, 128.7, 58.3, 55.1, 53.2, 50.8, 26.3, 24.4.

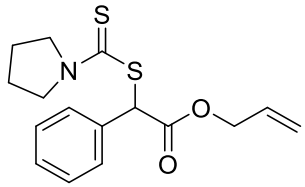


Butyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4k): White solid (68 %), m.p. 96-97˚C, IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2959, 2872, 1738, 1435, 1261, 1160, 1010, 957; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.36-7.31 (m, 3H), 5.84 (s, 1H), 4.24-4.19 (m, 1H), 4.13-4.08 (m, 1H), 3.93-3.87 (m, 2H), 3.74-3.69 (m, 1H), 3.61-3.56 (m, 1H), 2.09-2.03 (m, 2H), 1.99 (q, *J* = 7.0 Hz, 2H), 1.63-1.59 (m, 2H), 1.34-1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.6, 170.4, 134.5, 129.0, 129.0, 128.6, 66.1, 58.6, 55.1, 50.7, 30.6, 26.3, 24.4, 19.1, 13.8. HRMS (ESI) for $C_{17}H_{24}NO_2S_2$ m/z $[M + H]^+$ calcd: 338.1243, found: 338.1249.

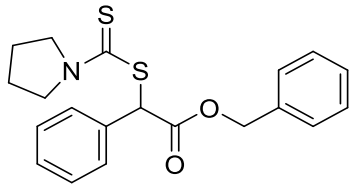


Isopropyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4l)[2]: White solid (72%), m.p. 146-147˚C (lit. 145-146˚C), IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2967, 2924, 2866, 1731, 1464, 1445, 1282, 1184, 1167, 1103. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.45 (d, *J* = 7.0 Hz, 2H), 7.35-7.30 (m, 3H), 5.80 (s, 1H), 3.91-3.88 (m, 2H), 3.74-3.69 (m, 1H), 3.60-3.55 (m, 1H), 2.08-2.04 (m, 2H), 1.99-1.95 (m, 2H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.15 (d, *J* = 6.5 Hz, 3H).

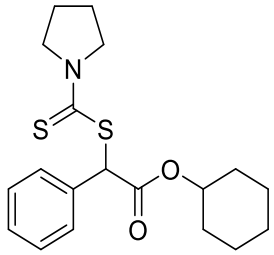
^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.7, 169.7, 134.6, 129.0, 128.9, 128.5, 69.8, 58.7, 55.0, 50.7, 26.3, 24.4, 21.8, 21.6.



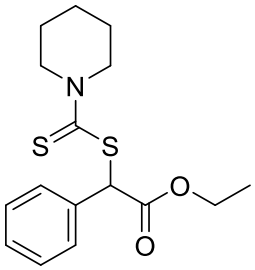
Allyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4m)[2]: White solid (68%), m.p. 104-105˚C (lit. 102-103˚C), IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2956, 2869, 1737, 1463, 1436, 1326, 1300, 1283, 1167, 1145, 1014, 984. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 3H), 5.91-5.85 (m, 2H), 5.27-5.24 (m, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 4.72-4.69 (m, 1H), 4.63-4.60 (m, 1H), 3.92 (q, *J* = 6.5 Hz, 2H), 3.74-3.69 (m, 1H), 3.60-3.55 (m, 1H), 2.08-2.05 (m, 2H), 1.99-1.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.5, 170.0, 134.2, 131.9, 129.0, 129.0, 128.7, 118.5, 66.6, 58.5, 55.1, 50.7, 26.3, 24.4.



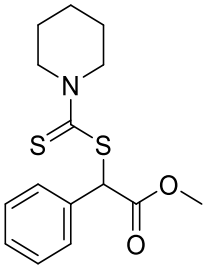
Benzyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4n)[2]: Yellow oil (67%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.41 (m, 2H), 7.32-7.29 (m, 8H), 5.90 (s, 1H), 5.27-5.24 (m, 1H), 5.15-5.12 (m, 1H), 3.91 (q, *J* = 6.5 Hz, 2H), 3.73-3.68 (m, 1H), 3.60-3.55 (m, 1H), 2.08-2.05 (m, 2H), 2.0-1.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.5, 170.2, 135.7, 134.0, 129.0, 129.0, 128.7, 128.5, 128.2, 128.2, 67.7, 58.5, 55.1, 50.7, 26.3, 24.4.



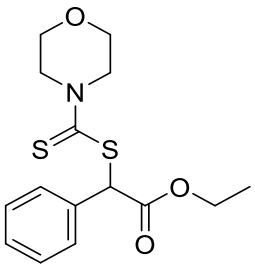
Cyclohexyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4o): White solid (65 %), m.p. 123-124˚C; IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2933, 2856, 1733, 1435, 1261, 1165, 1012, 799; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 3H), 5.82 (s, 1H), 4.86-4.81 (m, 1H), 3.91-3.88 (m, 2H), 3.74-3.69 (m, 1H), 3.60-3.55 (m, 1H), 2.08-2.04 (m, 2H), 1.99-1.94 (m, 2H), 1.74-1.68 (m, 2H), 1.54-1.48 (m, 2H), 1.36-1.25 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.7, 169.6, 134.7, 128.8, 128.7, 128.5, 74.5, 58.8, 55.0, 50.7, 31.5, 31.2, 26.3, 25.5, 24.4, 23.7, 23.6. HRMS (ESI) for $C_{19}H_{26}NO_2S_2$ m/z $[M + H]^+$ calcd: 364.1399 , found: 364.1401.



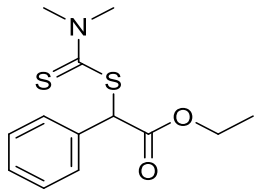
Ethyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (4p)[1]**:** White solid (65 %), m.p. 69-70˚C, IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2925, 2853, 1739, 1479, 1454, 1432, 1365, 1301, 1279, 1240, 1156, 1110, 1030, 1003, 977.^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.35-7.31 (m, 3H), 5.79 (s, 1H), 4.32-4.25 (m, 2H), 4.18-4.13 (m, 2H), 3.89-3.81 (m, 2H), 1.69 (s, 6H), 1.27 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.5, 170.3, 134.1, 129.4, 129.0, 128.7, 62.2, 59.2, 52.9, 24.3, 14.2.



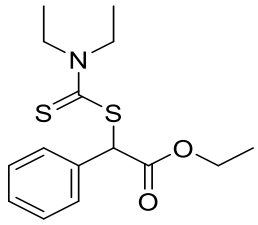
Methyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (4q)[2]**:** White solid (65 %), m.p. 70-71˚C (lit. 71-72˚C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 6.0 Hz, 3H), 5.80 (s, 1H), 4.36 (brs, 1H), 4.24 (brs, 1H), 4.11 (brs, 1H), 3.90 (s, 1H), 3.82 (s, 1H), 3.76 (s, 3H), 1.69 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.3, 170.8, 133.8, 129.0, 128.9, 128.7, 58.9, 53.1, 52.9, 51.7, 26.1, 25.4, 24.2.



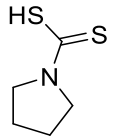
Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4r)[1]**:** White solid (66 %), m.p. 100-101˚C, IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2959, 2923, 2853,1739, 1455, 1422, 1332, 1305, 1269, 1160, 1105, 1027, 876. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.43 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 3H), 5.78 (s, 1H), 4.30-4.26 (m, 2H), 4.19-4.12 (m, 2H), 3.90 (m, 1H), 3.75 (brs, 4H), 3.65-3.61 (m, 1H), 1.27-1.25 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 195.4, 170.0, 133.8, 129.1, 129.0, 128.7, 66.4, 62.3, 59.0, 50.9, 14.2.



Ethyl 2-((dimethylcarbamothioyl)thio)-2-phenylacetate (4s): Yellow liquid (62 %), IR (KBr, 4000-600 cm^{-1}): ν_{max} = 2961, 2922, 2851, 1738, 1497, 1378, 1260, 1155, 1094, 1025, 802; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 6.0 Hz, 2H), 7.37-7.32 (m, 3H), 5.74 (s, 1H), 4.32-4.26 (m, 1H), 4.17-4.14 (m, 1H), 3.52 (s, 3H), 3.37 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 195.1, 170.2, 134.0, 129.1, 129.0, 128.7, 62.2, 59.7, 45.3, 41.7, 14.2. HRMS (ESI) for $C_{13}H_{22}NO_2S_2$ m/z $[M + H]^+$ calcd: 280.0773 , found: 280.0774.



Ethyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate (4t)[1]: Yellow liquid (62 %), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 6.0 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 3H), 5.77 (s, 1H), 4.29-4.26 (m, 1H), 3.99 (d, *J* = 7.0 Hz, 2H), 3.79 (m, 1H), 3.70-3.65 (m, 1H), 1.29 (d, *J* = 6.5 Hz, 3H), 1.26 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.9, 170.3, 134.2, 129.1, 129.0, 128.7, 62.1, 59.1, 49.5, 47.1, 14.2, 12.7, 11.7.



Pyrrolidine-1-carbodithioic acid (A)[3]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.72 (brs, 1H), 3.83-3.78 (m, 2H), 3.42-3.37 (m, 2H), 1.91 (brs, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 205.3, 54.0, 45.2, 26.1, 24.6.

4. References.

1. N. Kumar, R. Venkatesh, and J. Kandasamy, *Org. Biomol. Chem*.**, 2022**, 20, 6766.

2. Y. Lv, R. Liu, H. Ding, W. Wei, X. Zhao, and L. He, *Org. Chem. Front*.**, 2022**, 9, 3486.

3. R. K. Vishwakarma, S. Kumar and K. N. Singh, *Org. Lett.*, 2021, **23**, 4147.

5. Crystallographic Data for the Product 4h.

Datablock: mr-24_auto

Bond precision: C-C = 0.0039 A**, Wavelength**=1.54184

Cell: a= 15.3229(3), **b=** 8.7687(2), **c=**13.8326(3)

alpha= 90, **beta=** 104.502(2), **gamma=** 90

Temperature: 293 K

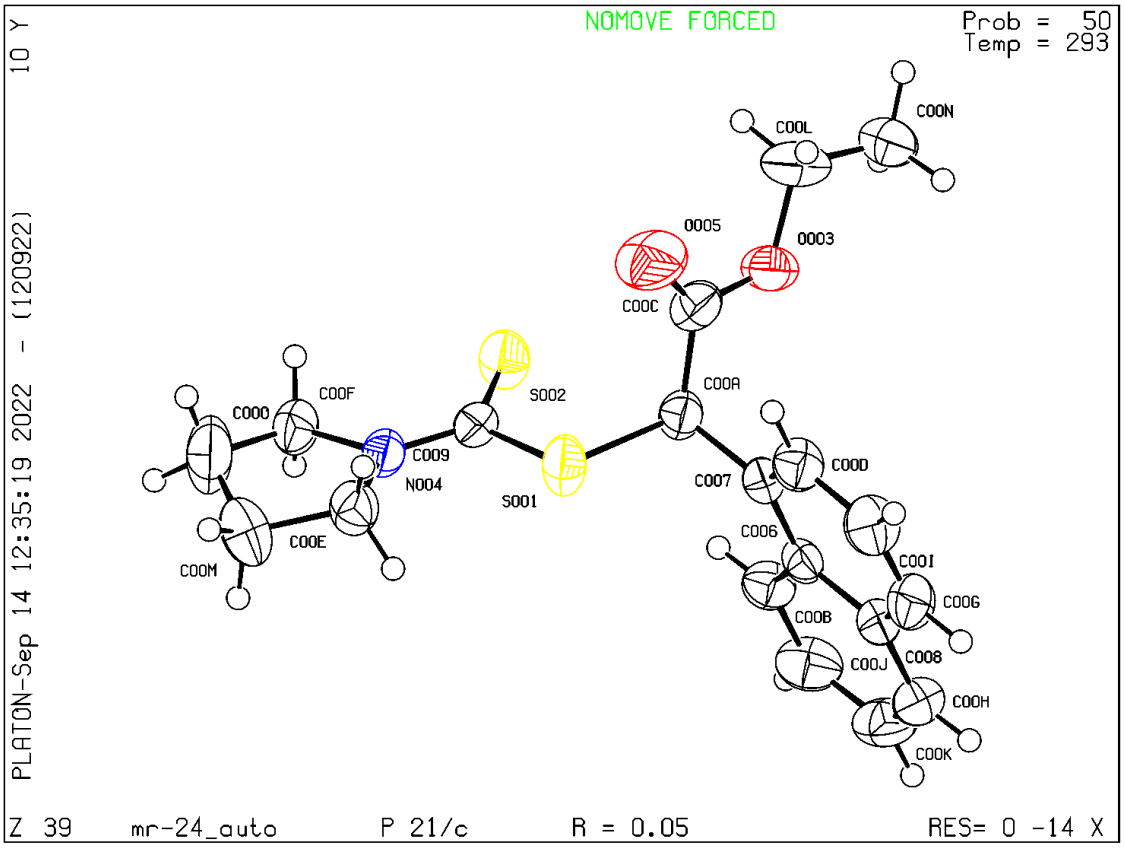
	Calculated	Reported
Volume	1799.36(7)	1799.36(7)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H21 N O2 S2	?
Sum formula	C19 H21 N O2 S2	C19 H21 N O2 S2
Mr	359.49	359.49
Dx,g cm-3	1.327	1.327
Z	4	4
Mu (mm-1)	2.766	2.766
F000	760.0	760.0
F000'	764.49	
h,k,lmax	18,10,16	18,10,16
Nref	3292	3262
Tmin,Tmax	0.506,0.575	
Tmin'	0.393	

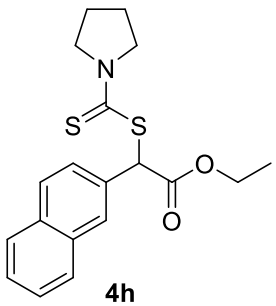
Correction method= Not given

Data completeness= 0.991, **Theta(max)=** 68.125

R(reflections)= 0.0481(2985), **wR2(reflections)=** 0.1350 (3262)

S = 1.009**, Npar=** 218

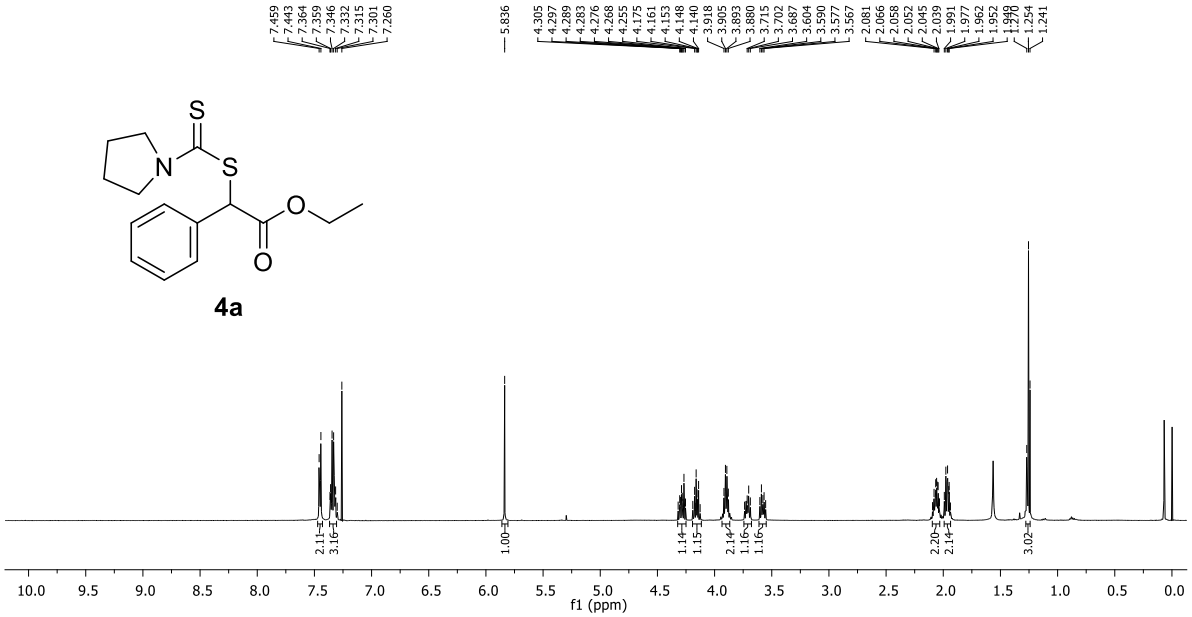

NOMOVE FORCED
Prob = 50
Temp = 293
10 Y
PLATON-Sep 14 12:35:19 2022 - (120922)
COOL
COON
O005
O003
COOC
COOA
SO02
SO01
COOF
COOO
CO09
NO04
COOE
COOM
COO7
COOD
COO6
COOI
COOG
COOB
COOJ
CO08
COOH
COOK
Z 39
mr-24_auto
P 21/c
R = 0.05
RES= 0 -14 X


N
S
S
O
O

4h

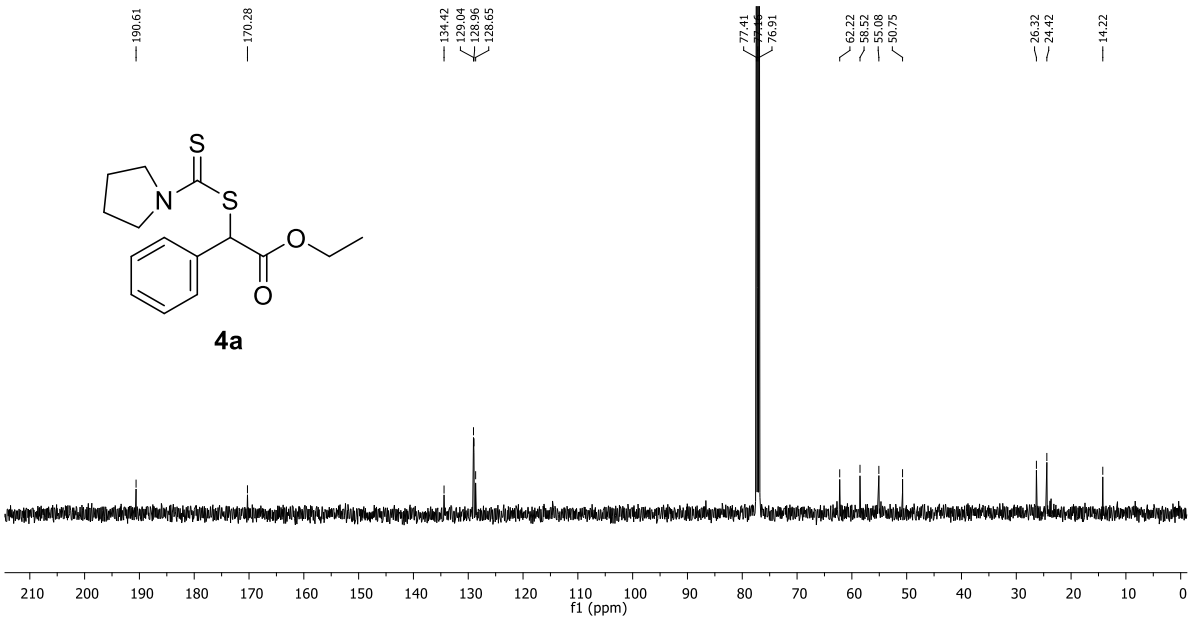
6. Copies of ^{1}H, ^{13}C and ^{19}F Spectra of the Product 4a-4t.

^{1}H NMR of Ethyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4a):

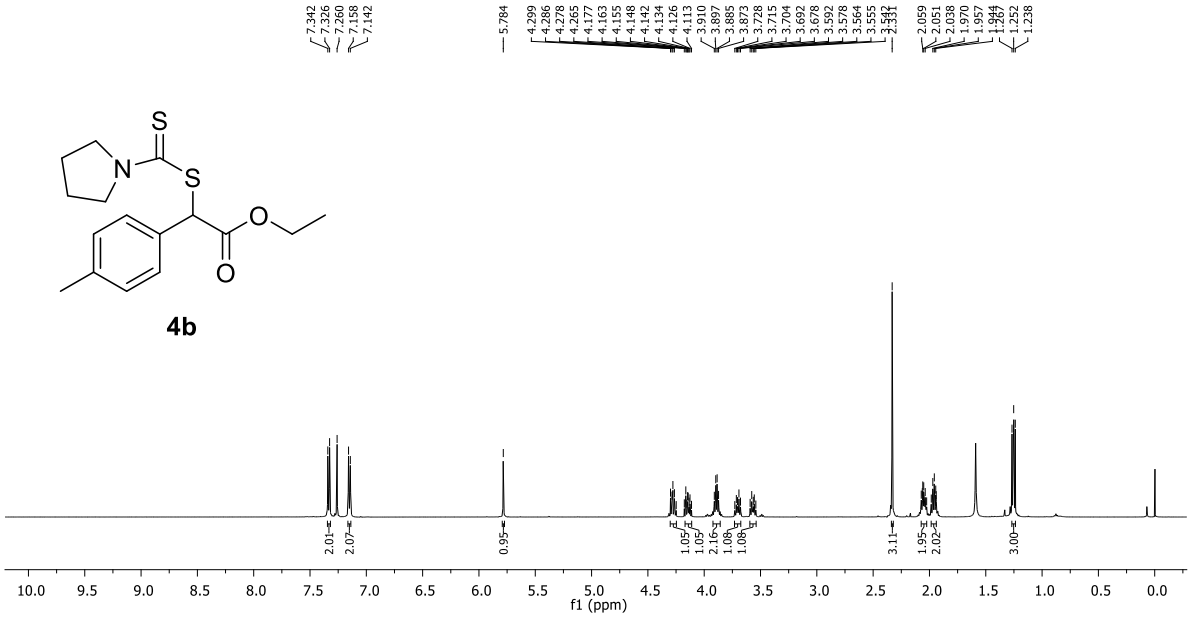


4a (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4a):

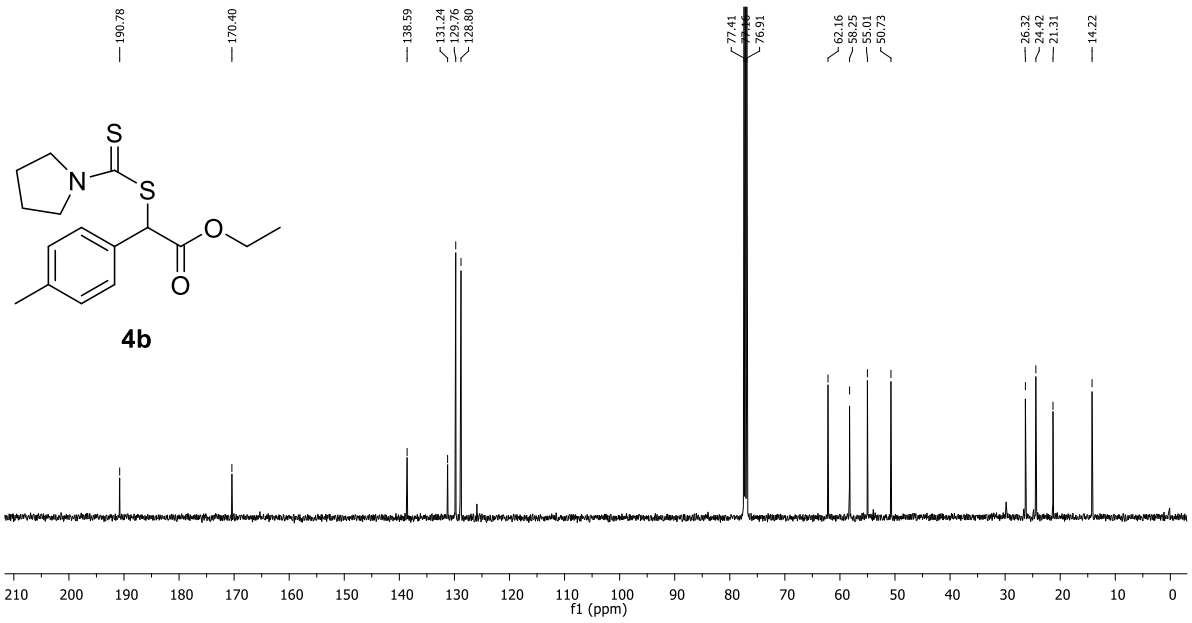


^{1}H NMR of Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(p-tolyl)acetate (4b):

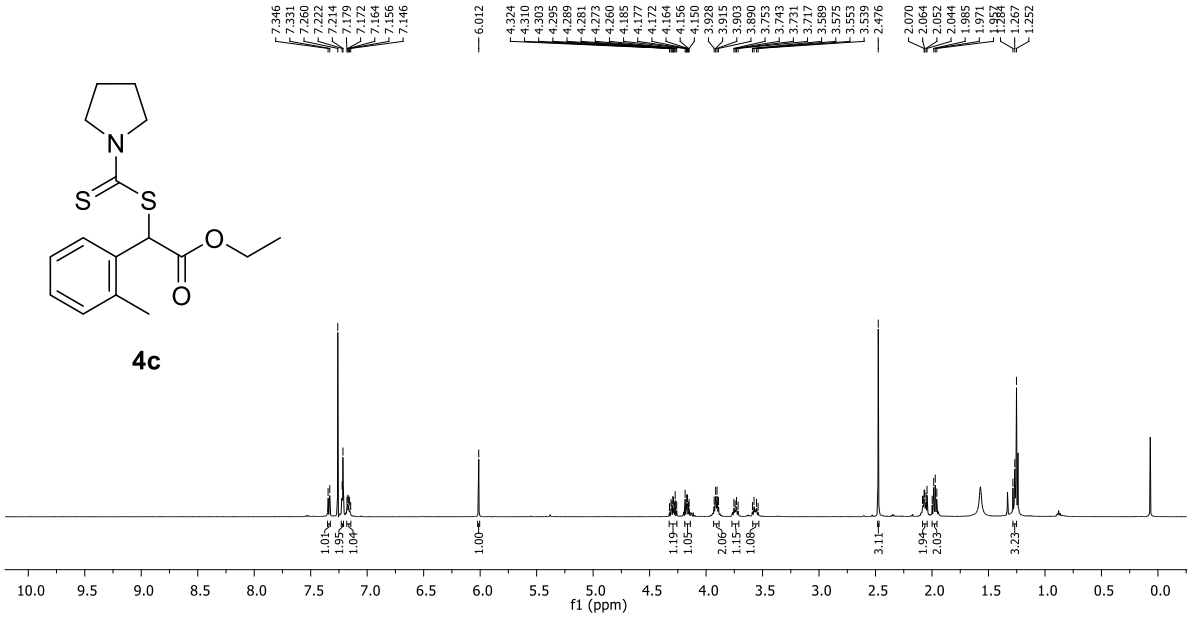


4b (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(p-tolyl)acetate (4b):

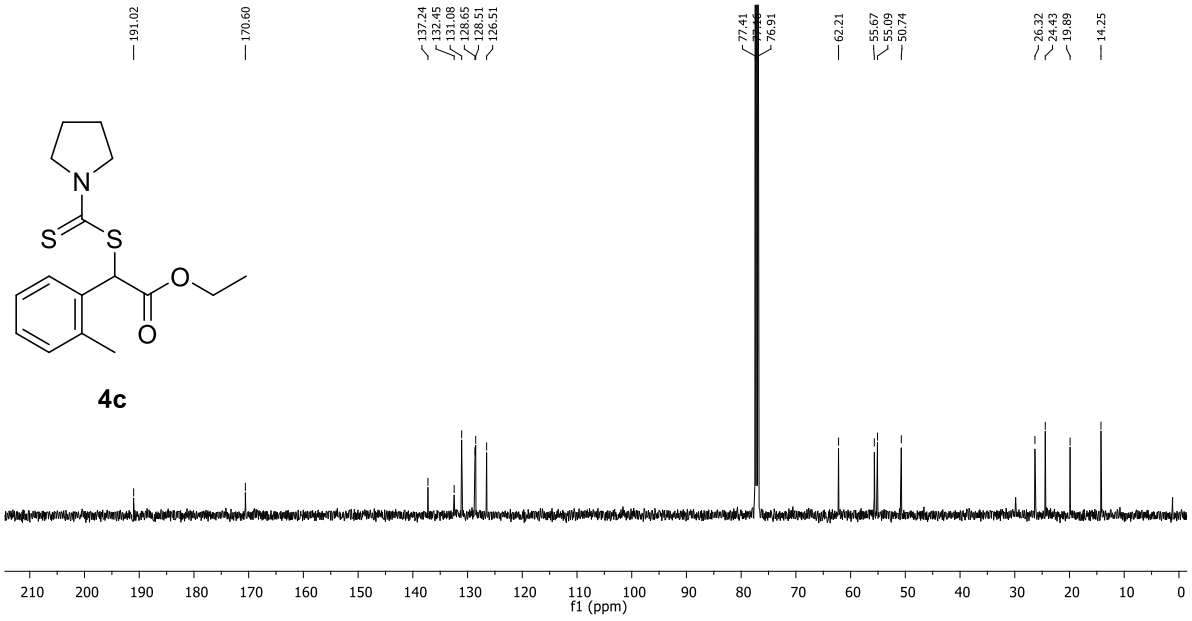


^{1}H NMR of Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(o-tolyl)acetate (4c):

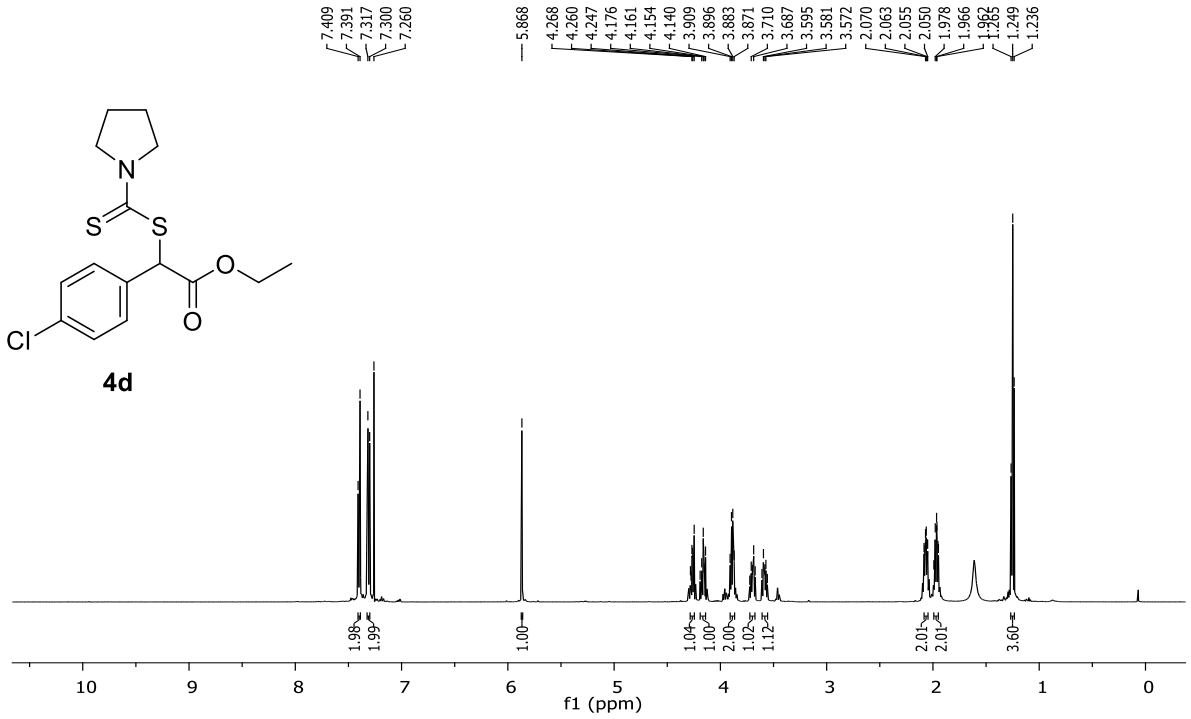


4c (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(o-tolyl)acetate (4c):

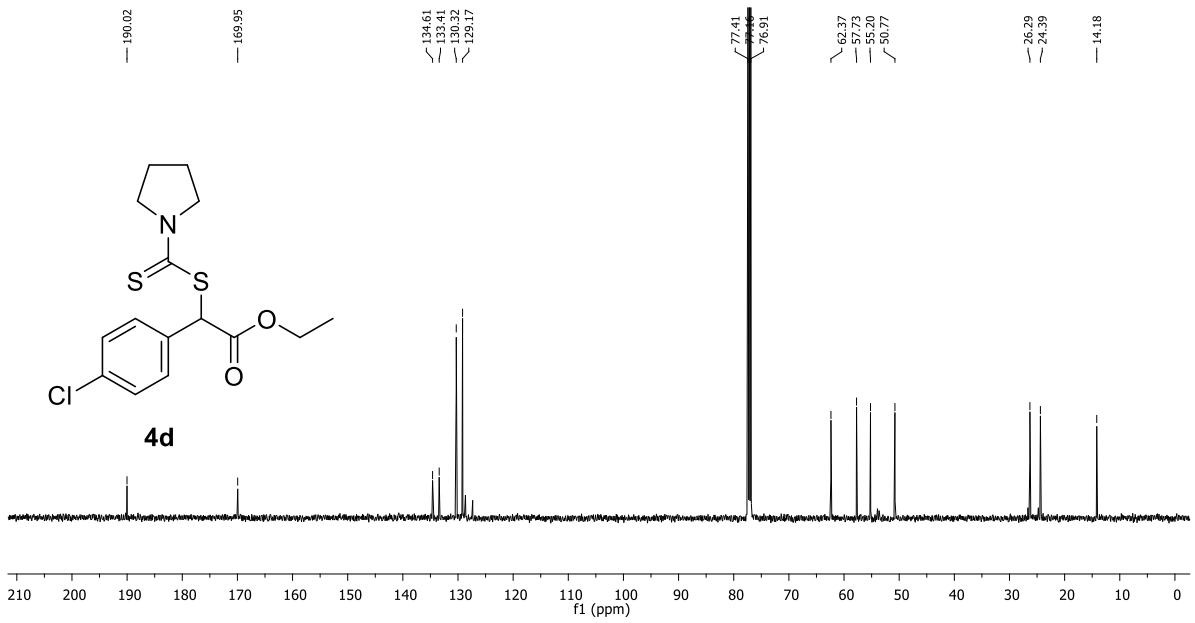


^{1}H NMR of Ethyl 2-(4-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4d):

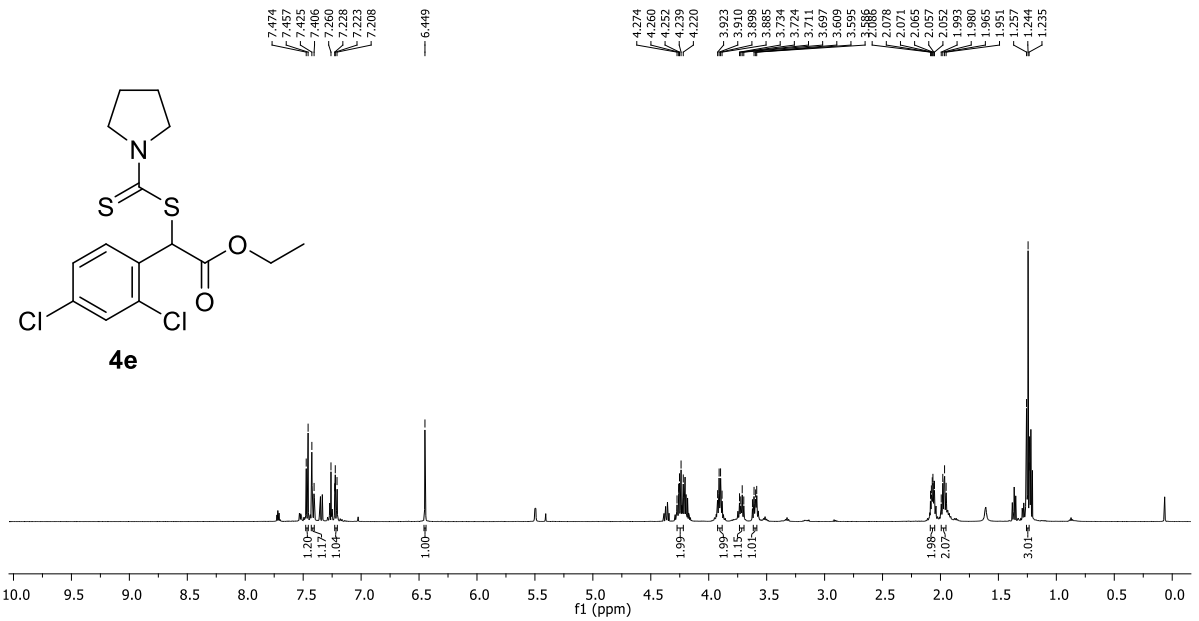


4d (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-(4-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4d):

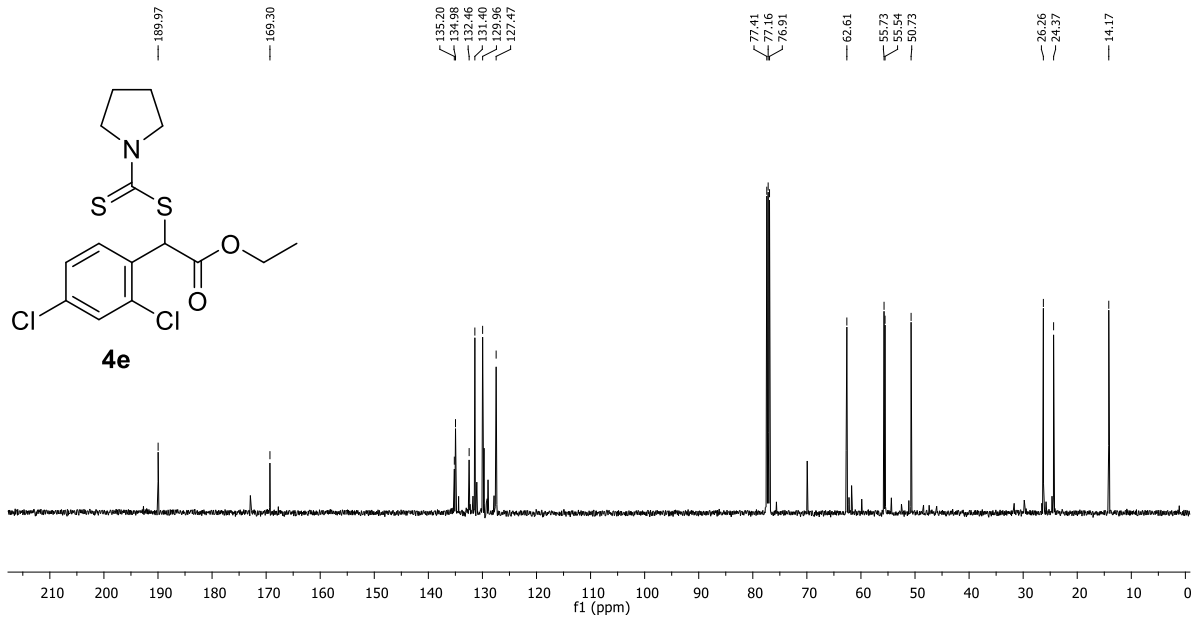


^{1}H NMR of Ethyl 2-(2,4-dichlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4e):

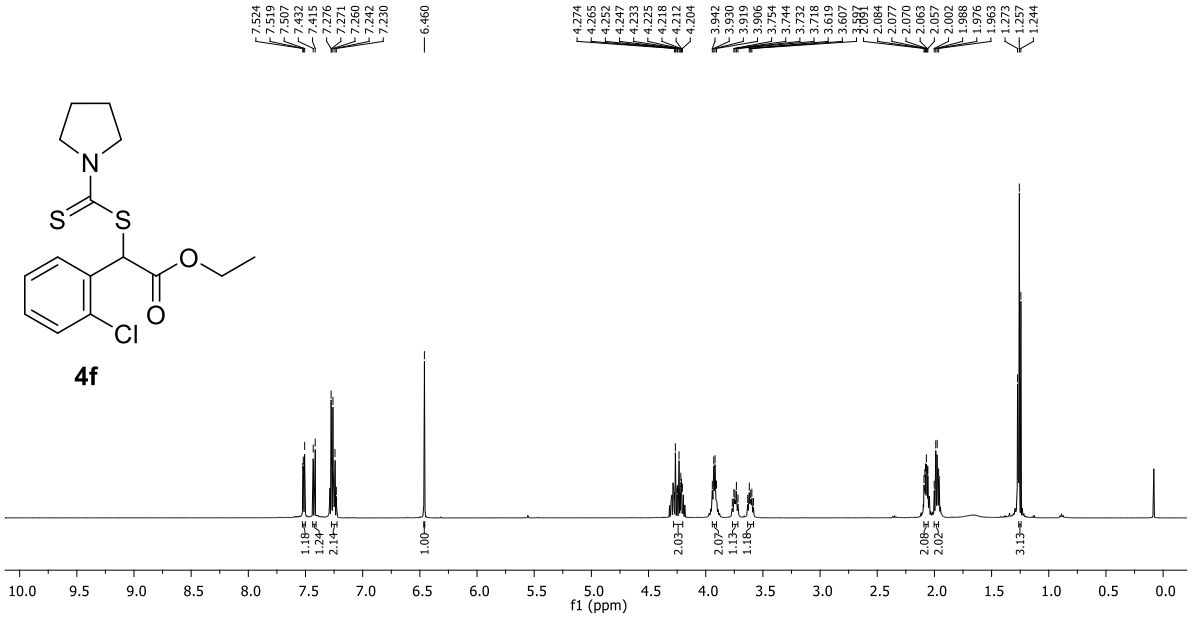


4e (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-(2,4-dichlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4e):



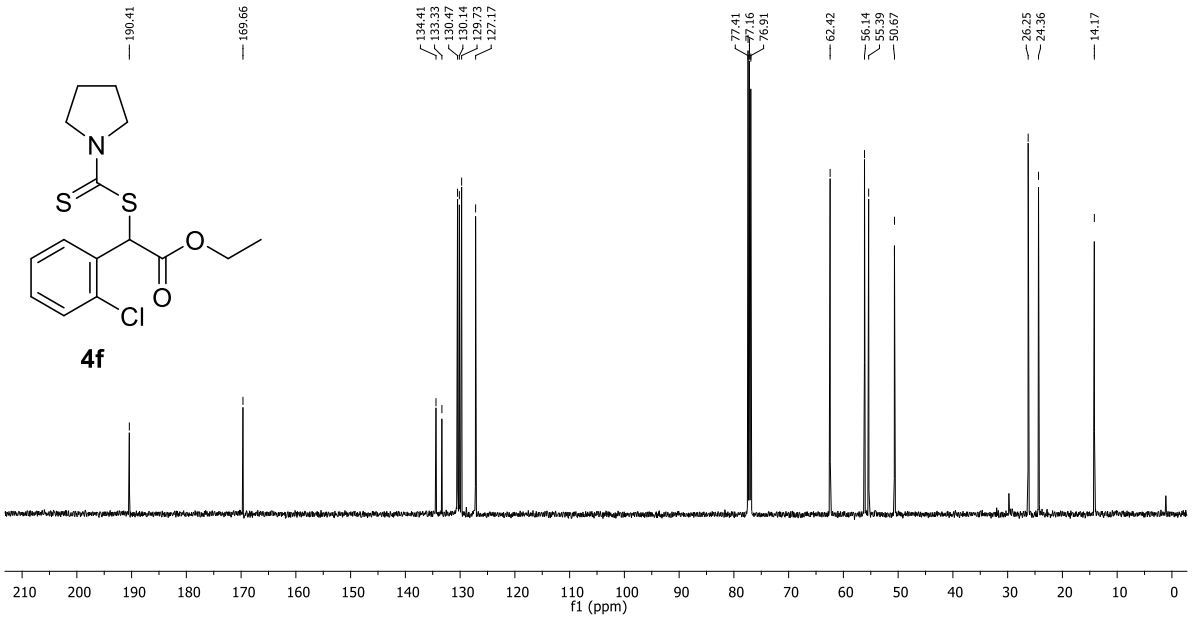
^{1}H NMR of Ethyl 2-(2-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4f):



4f

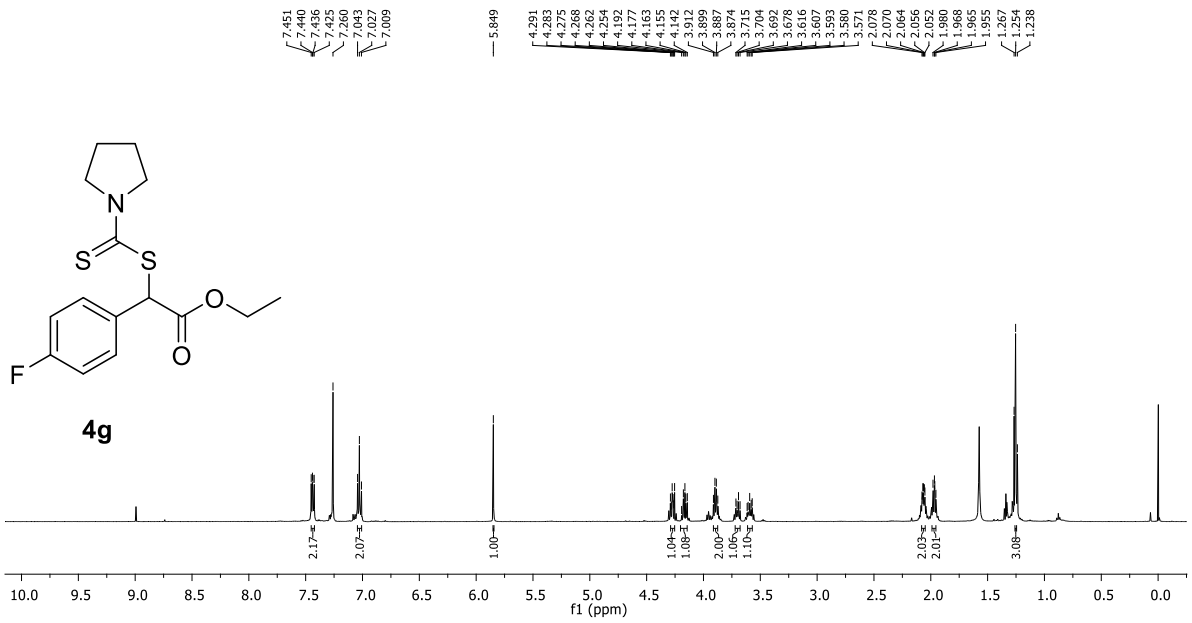
4f (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-(2-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4f):



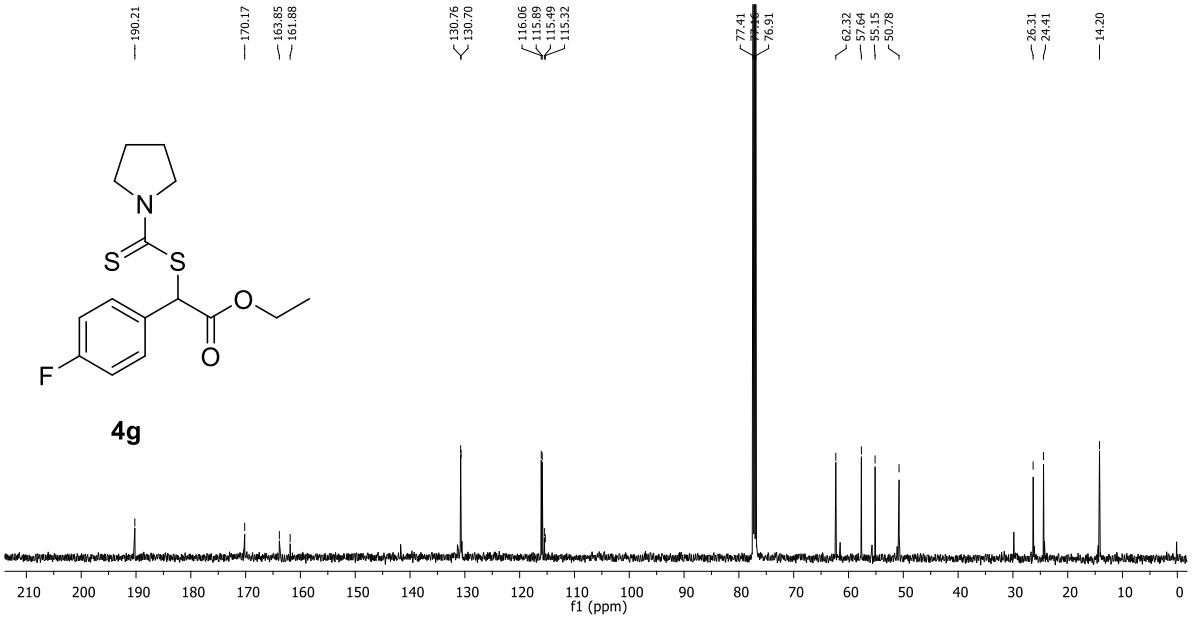
4f

^{1}H NMR of Ethyl 2-(4-fluorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4g):



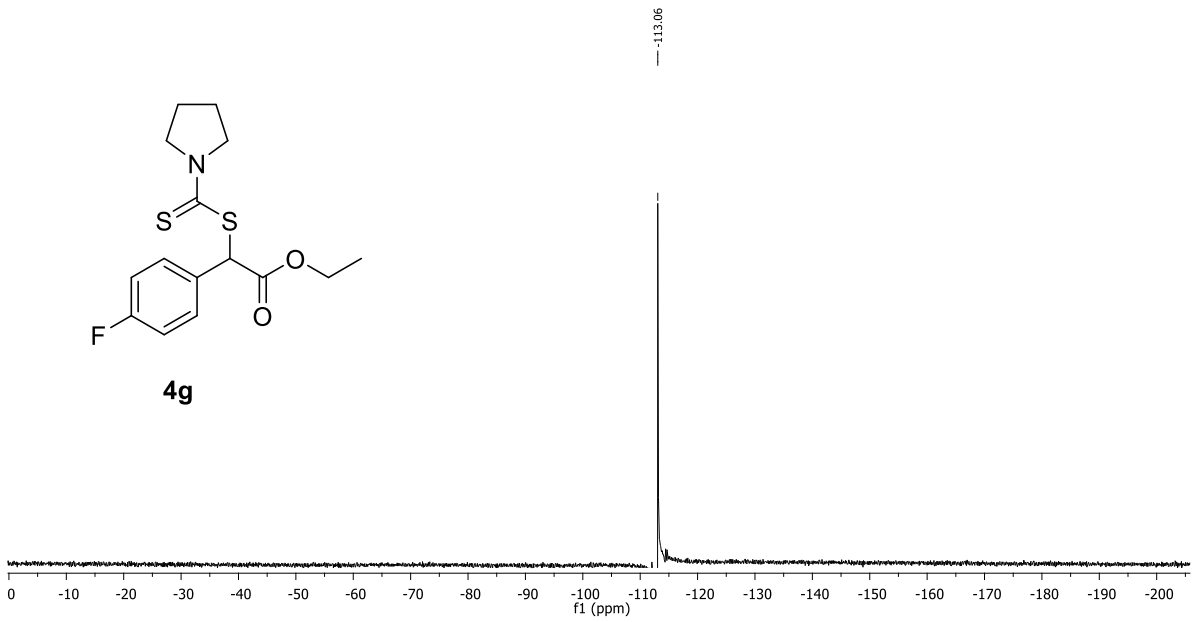
4g (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-(4-fluorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4g):

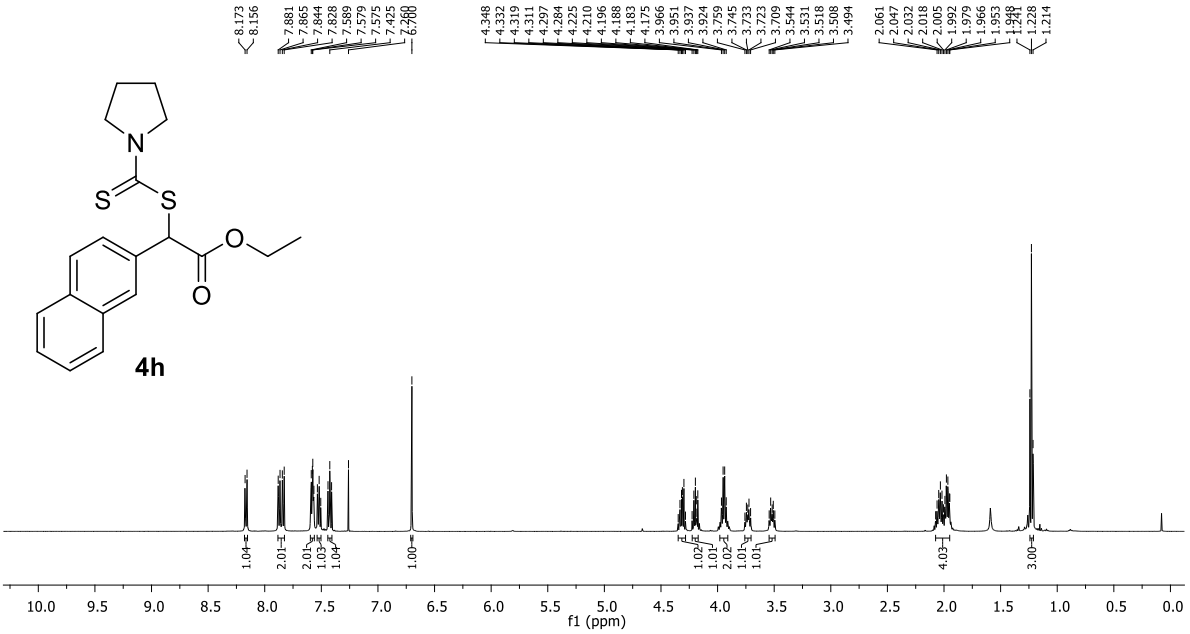


^{19}F NMR of Ethyl 2-(4-fluorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4g):

4g (471 MHz, NMR, $CDCl_3$)

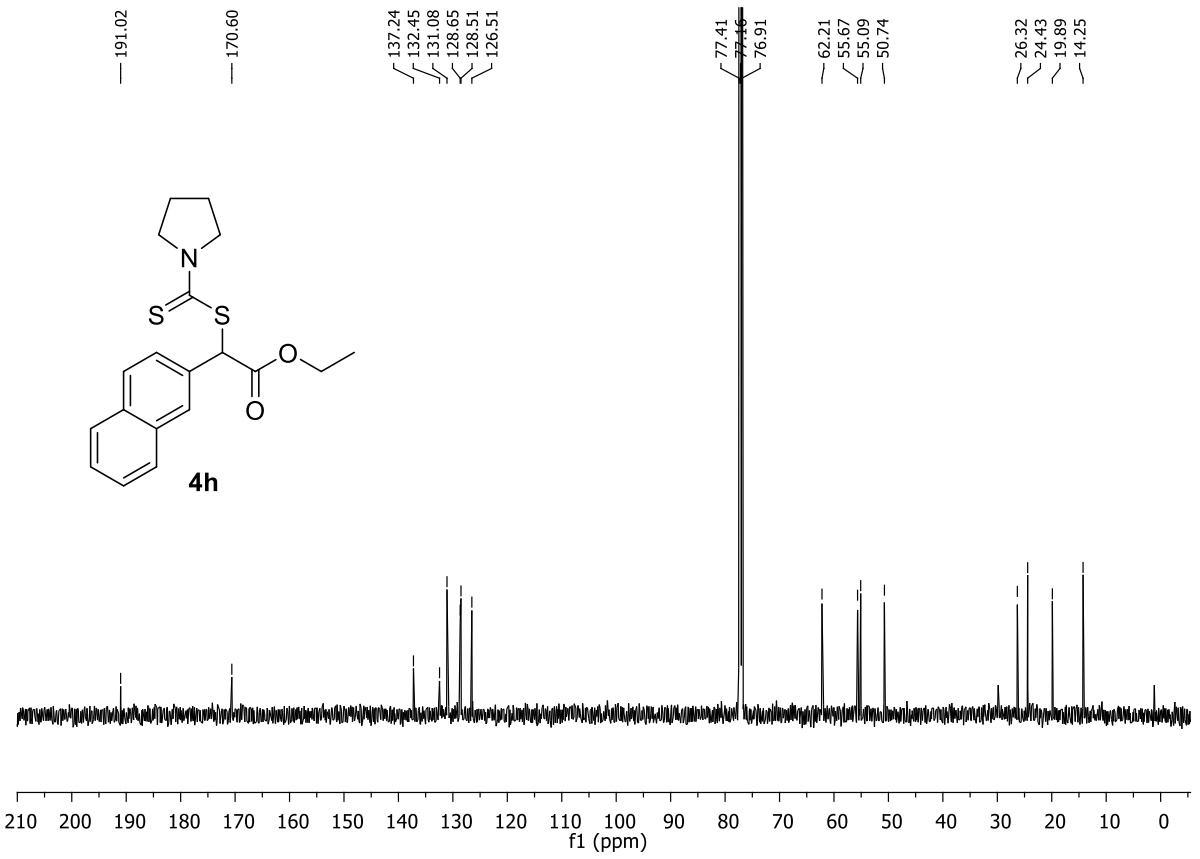


^{1}H NMR of Ethyl 2-(naphthalen-2-yl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4h):

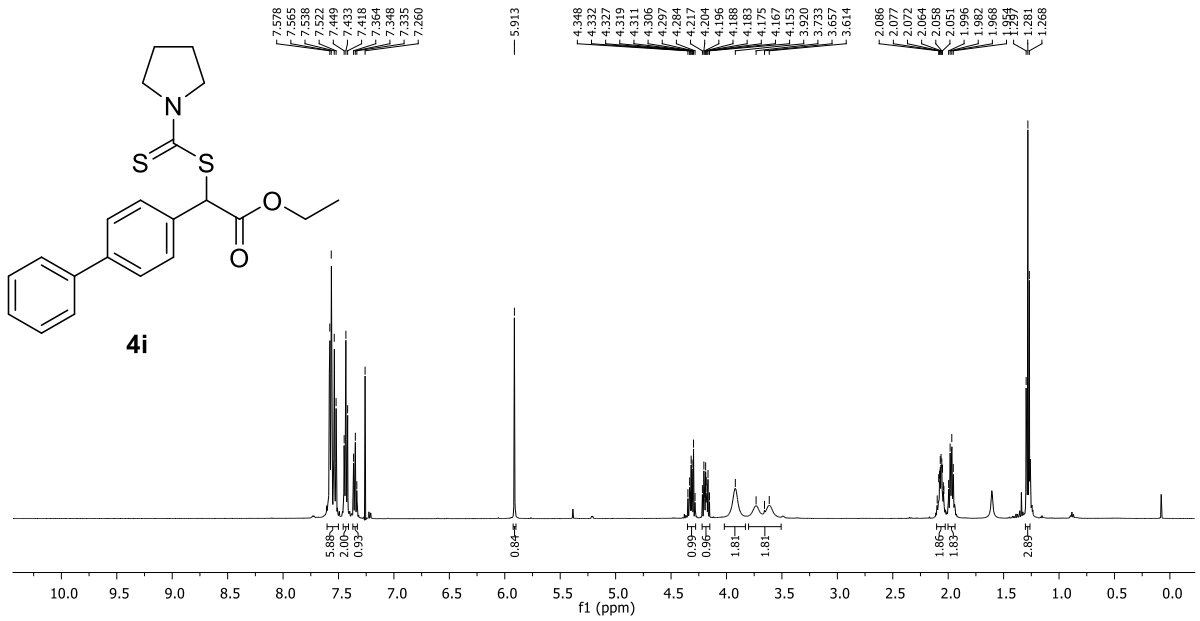


4h (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-(naphthalen-2-yl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4h):

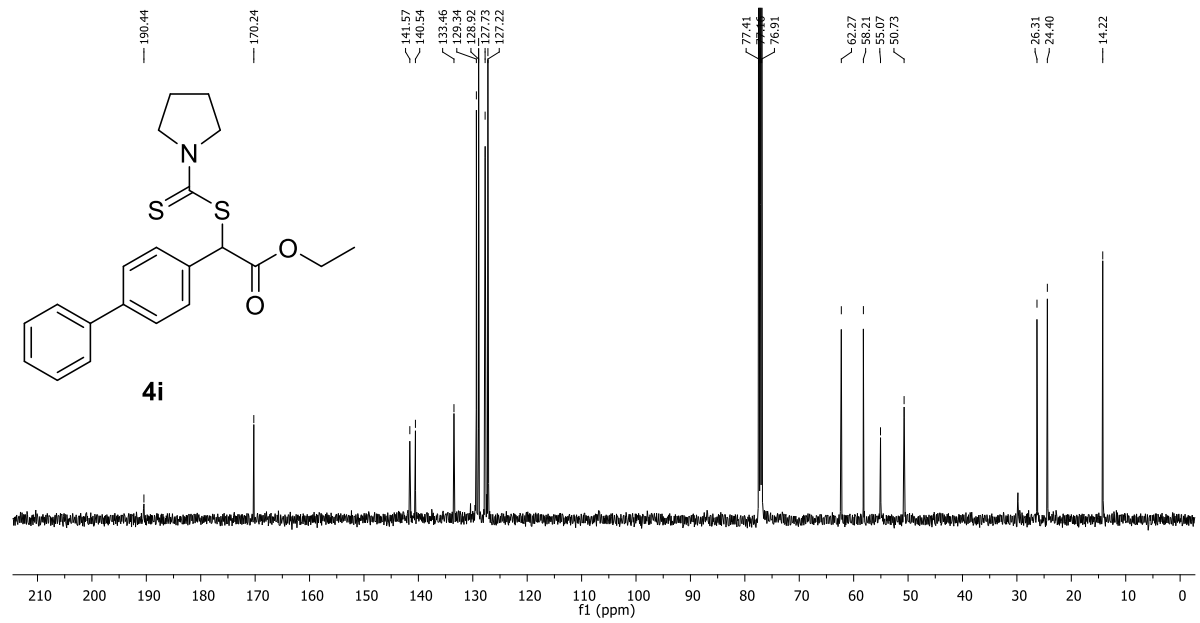


^{1}H NMR of Ethyl 2-([1,1'-biphenyl]-4-yl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4i):

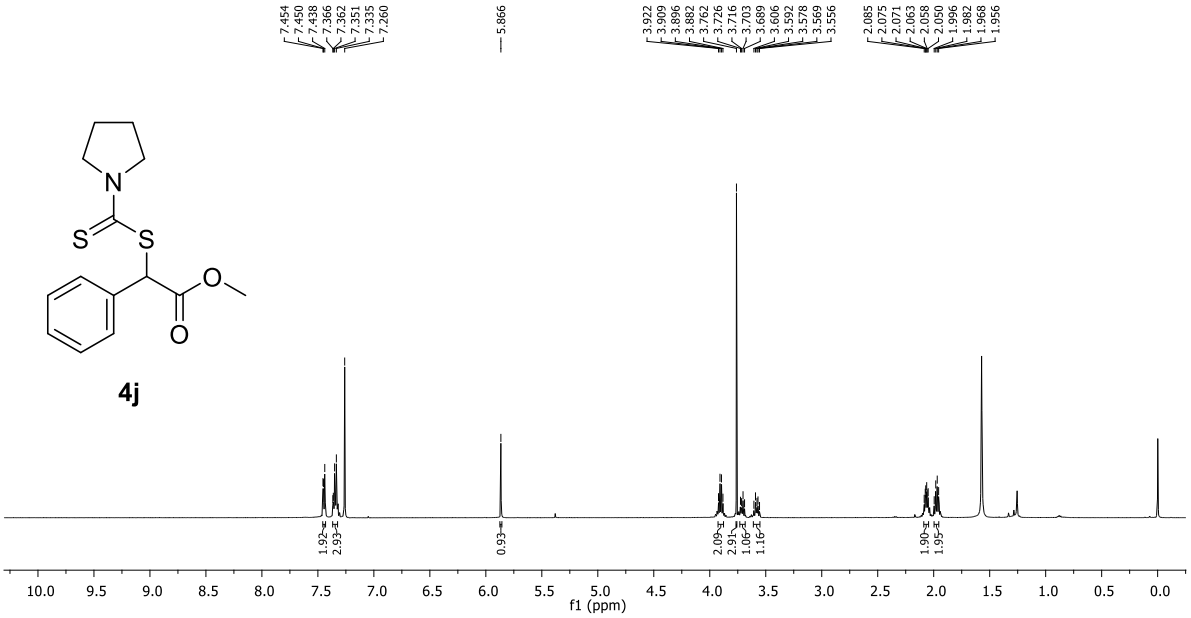


4i (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-([1,1'-biphenyl]-4-yl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4i):

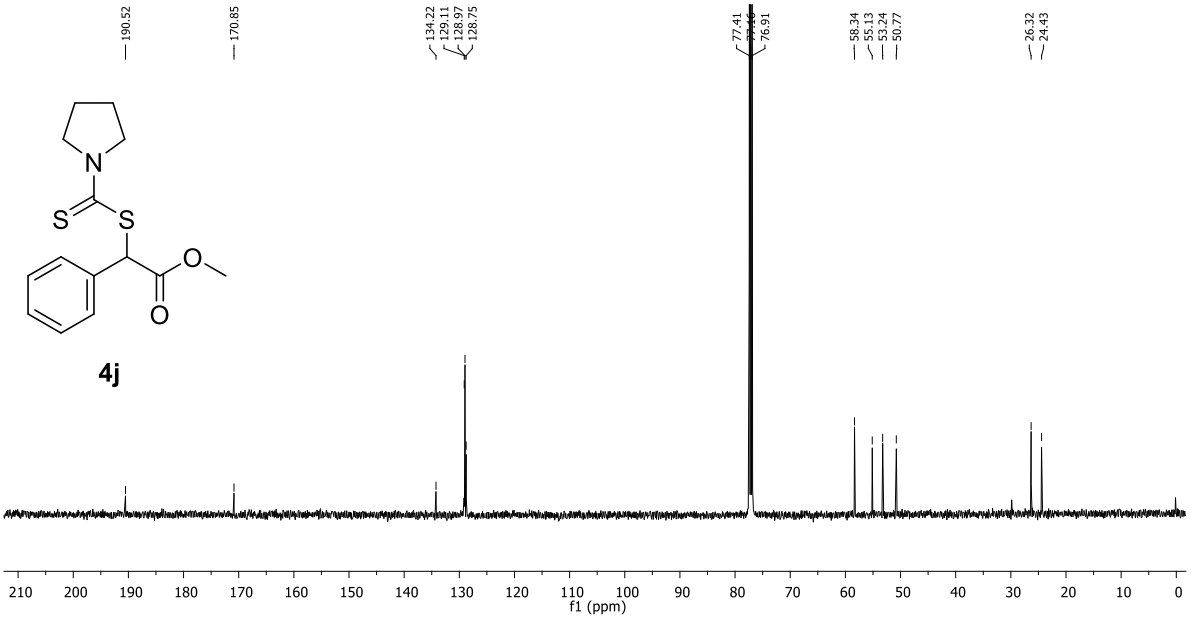


^{1}H NMR of Methyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4j):

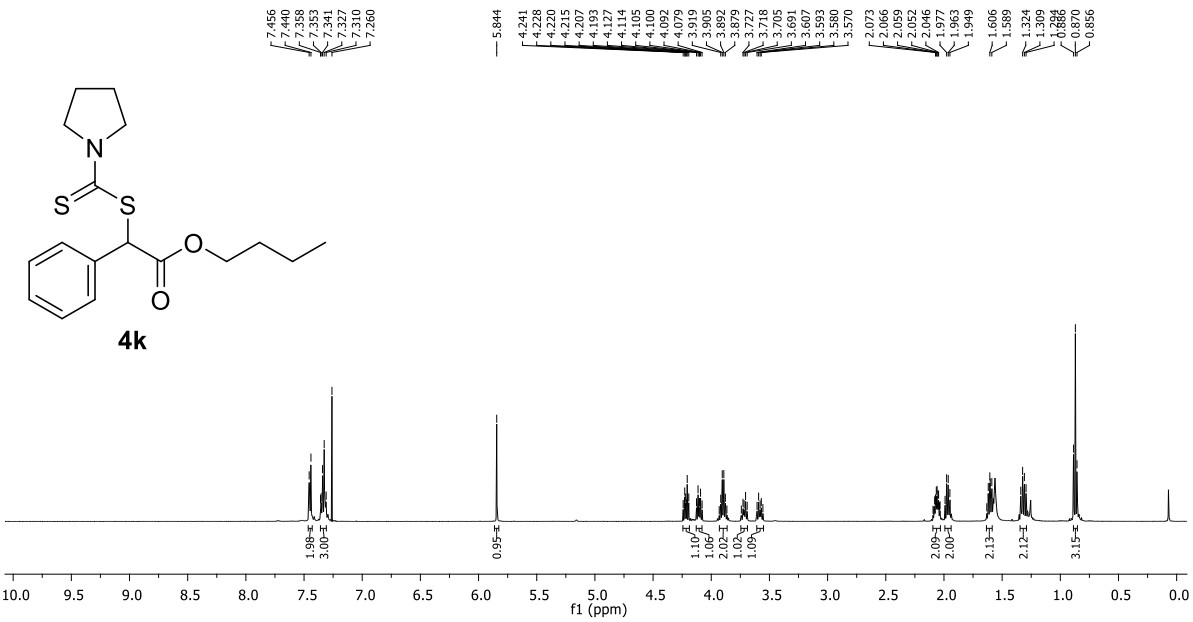


4j (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Methyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4j):

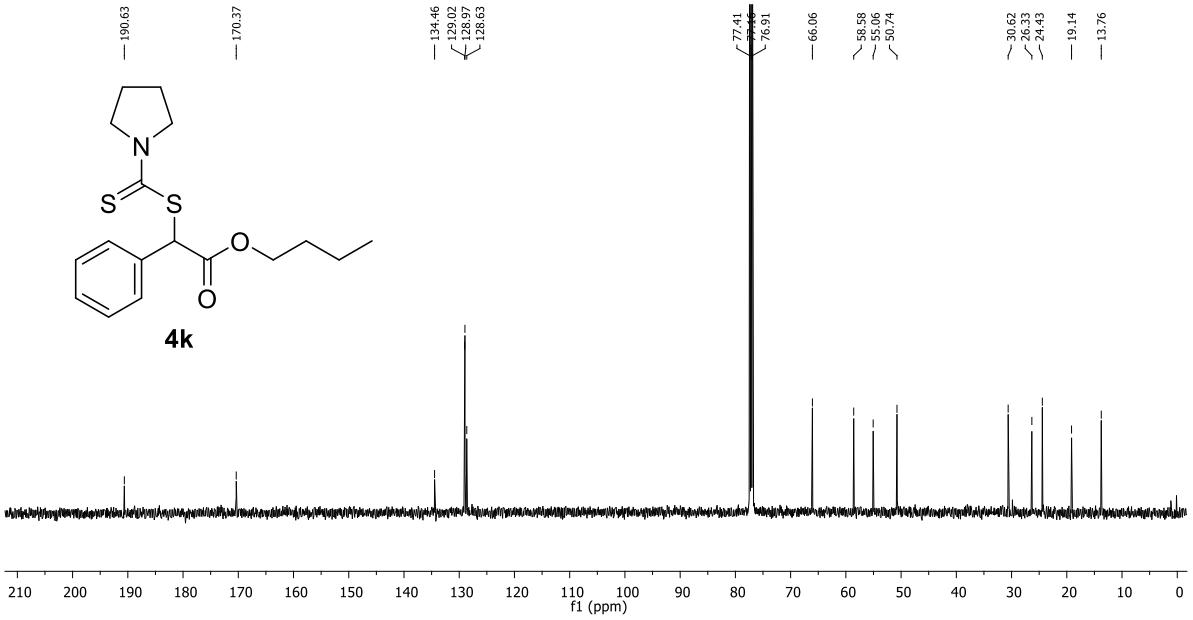


^{1}H NMR of Butyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4k):

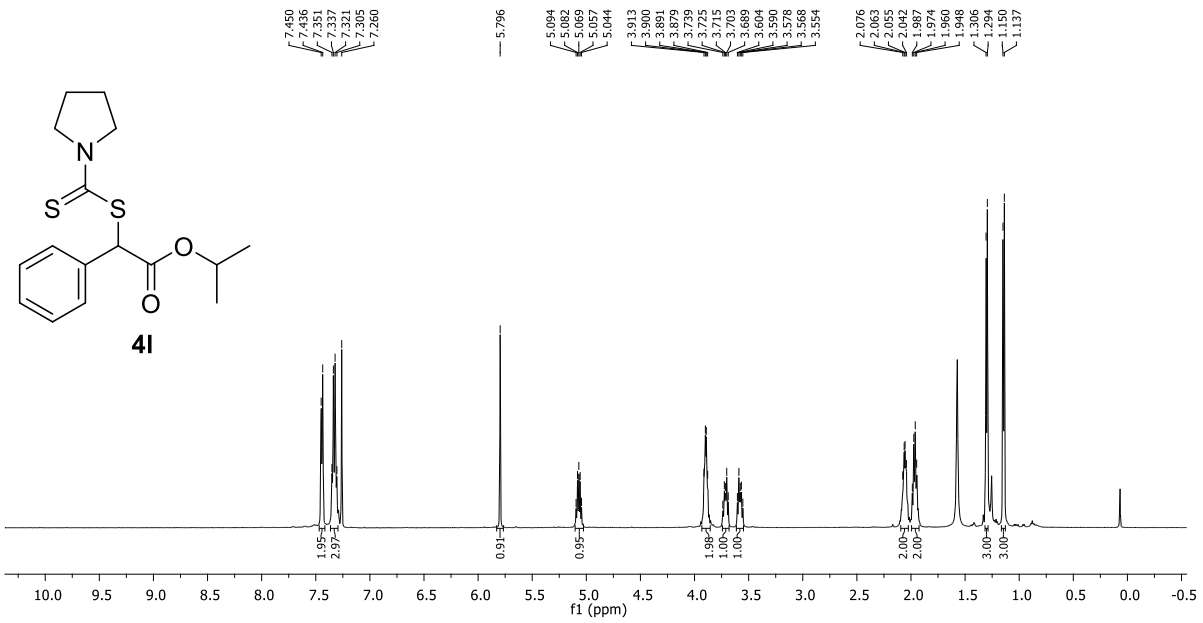


4k (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Butyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4k):

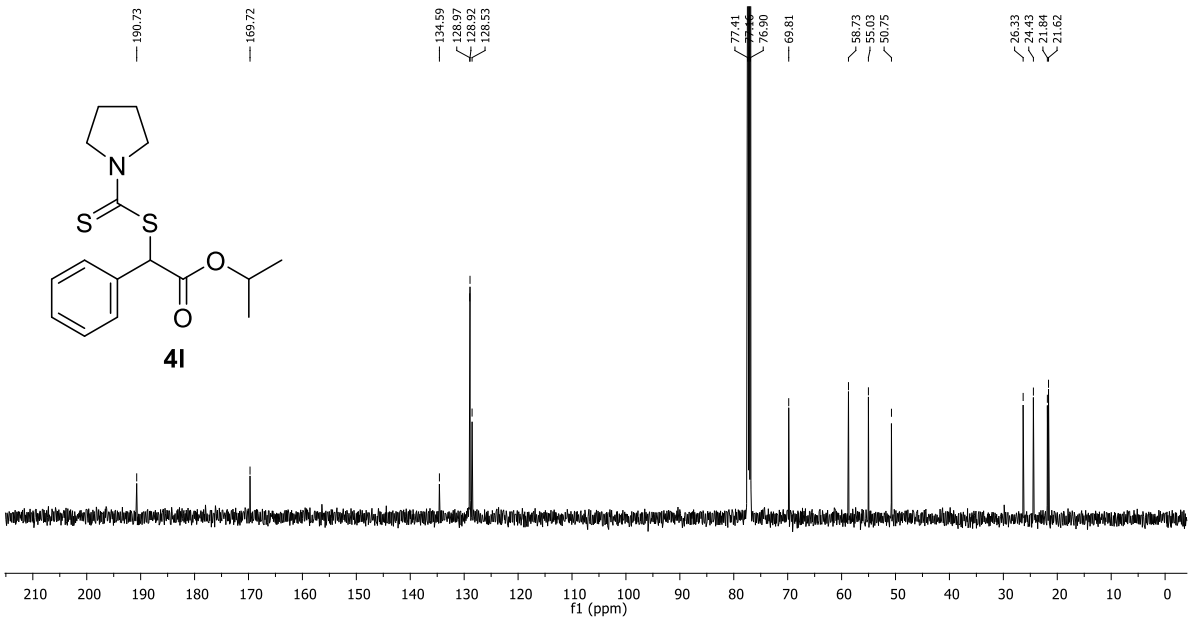


^{1}H NMR of Isopropyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4l):

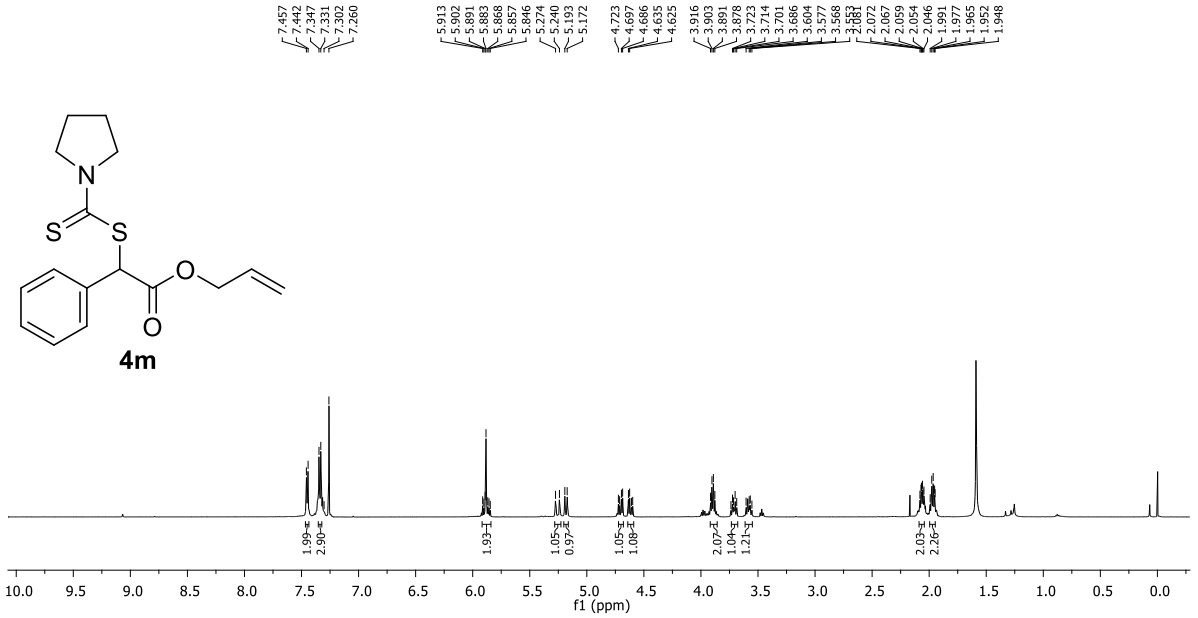


4l (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Isopropyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4l):

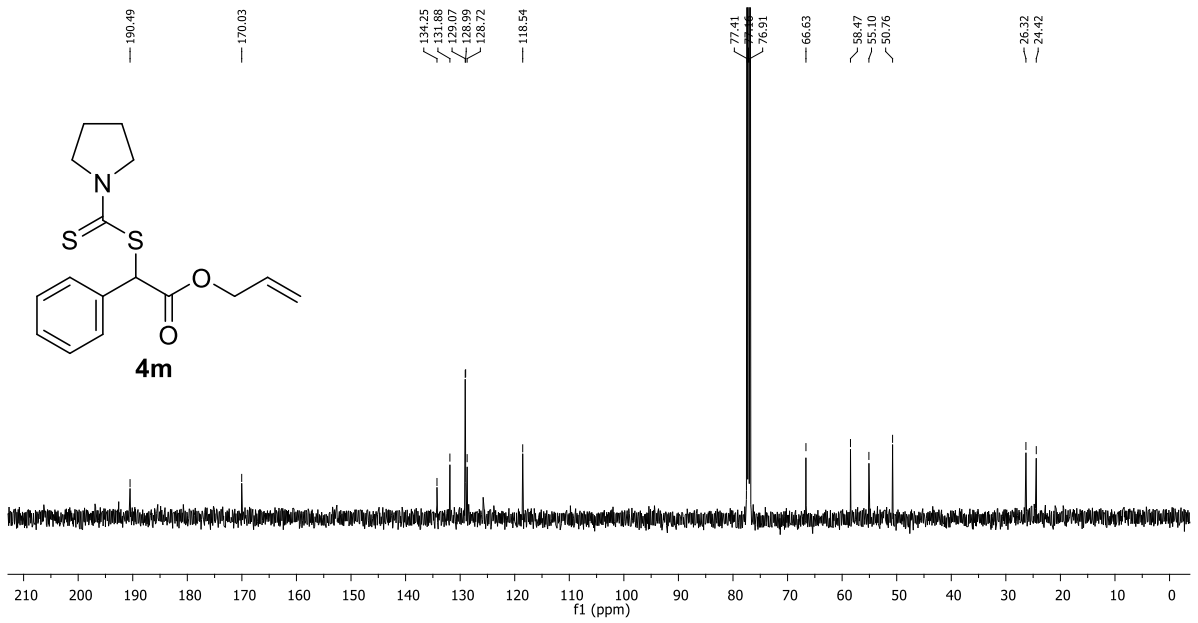


^{1}H NMR of Allyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4m):

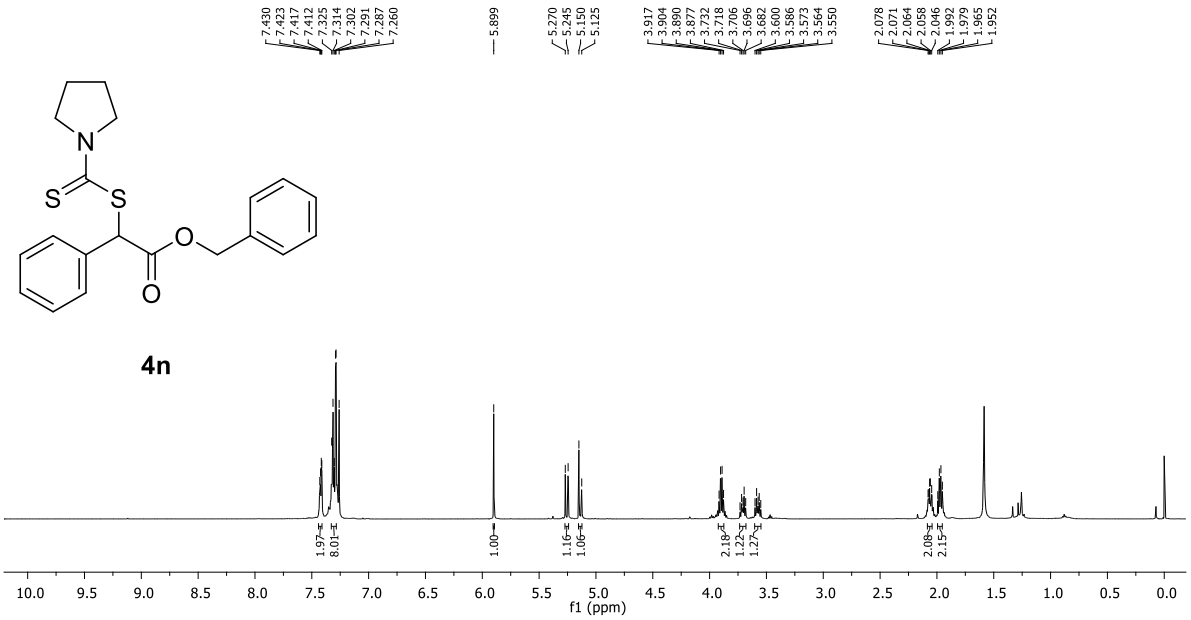


4m (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Allyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4m):

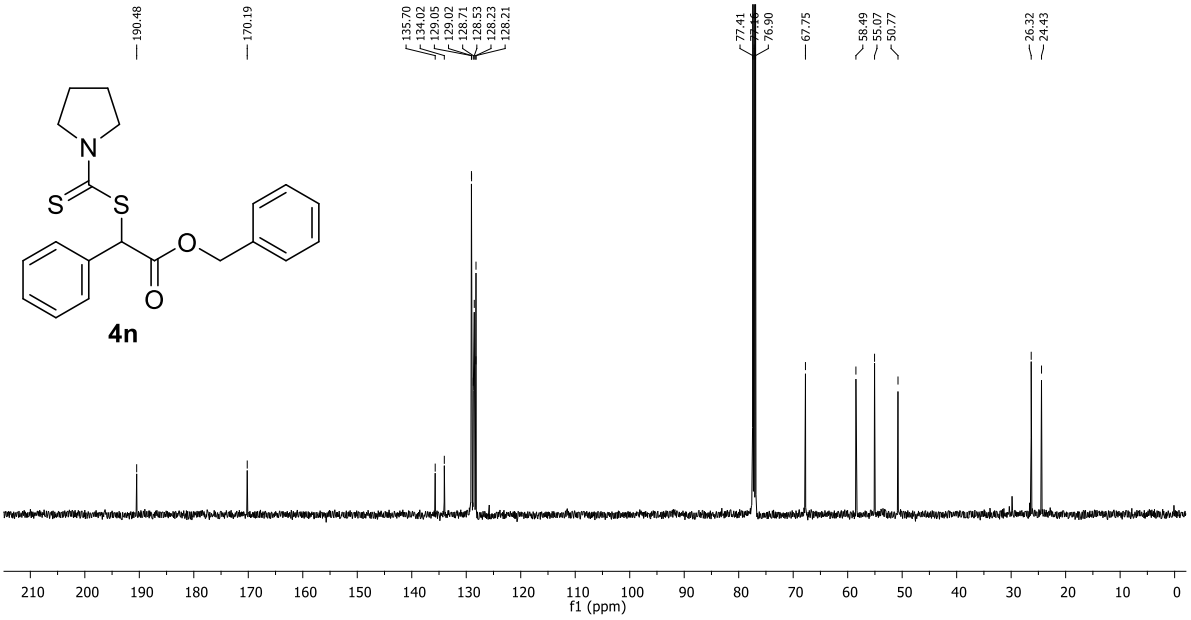


^{1}H NMR of Benzyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4n):

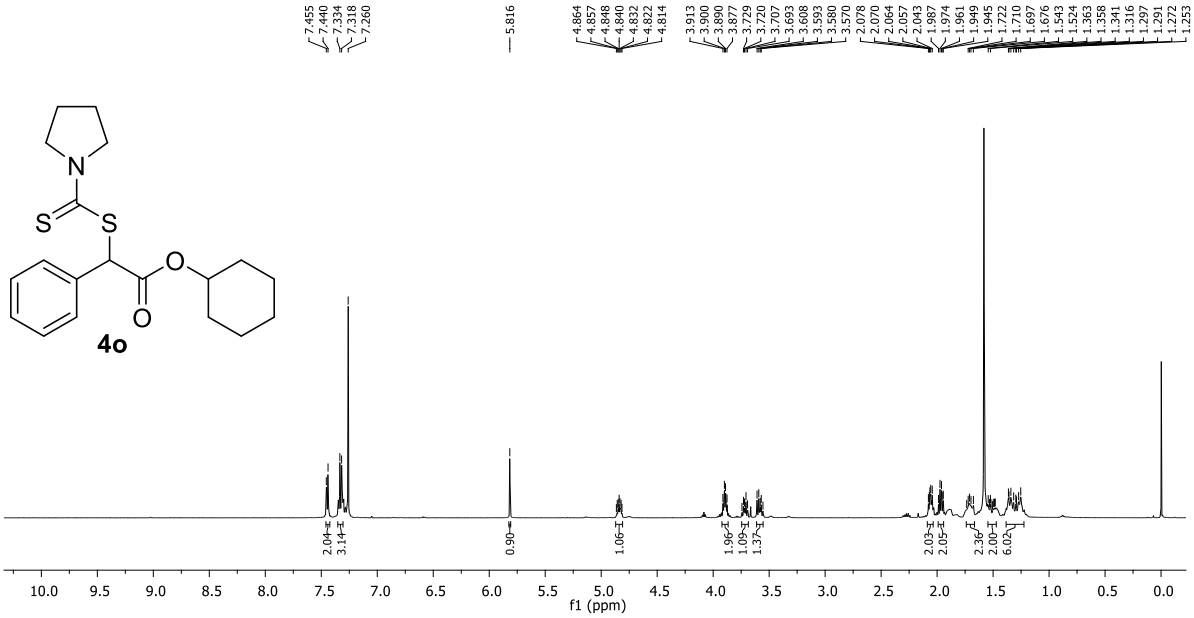


4n (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Benzyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4n):

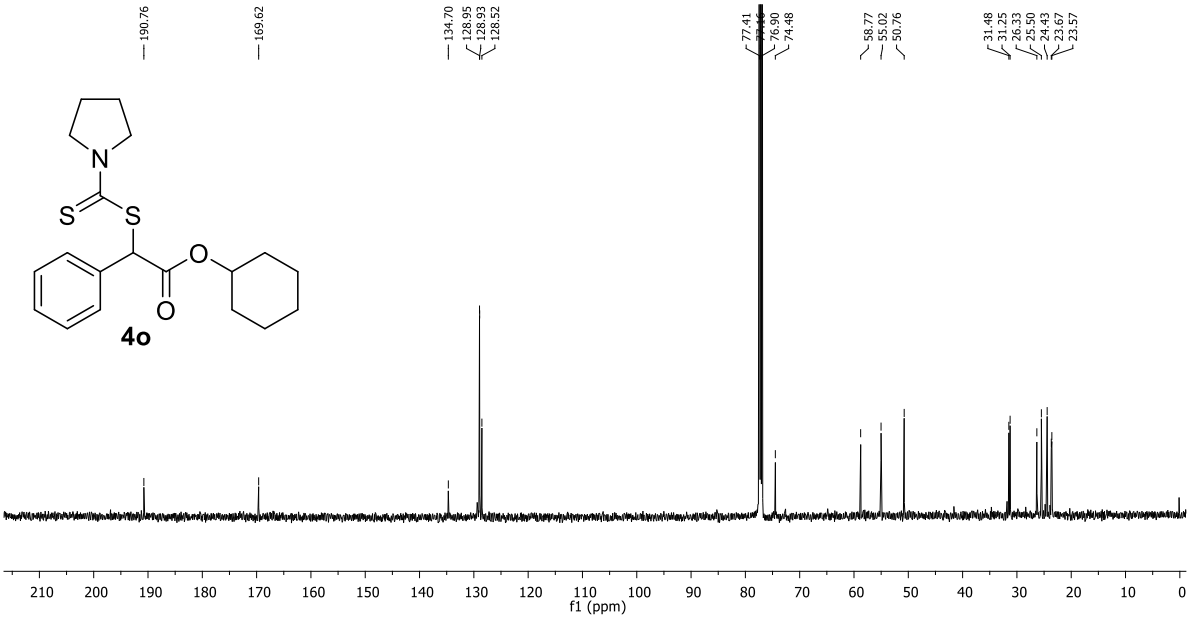


^{1}H NMR of Cyclohexyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4o):

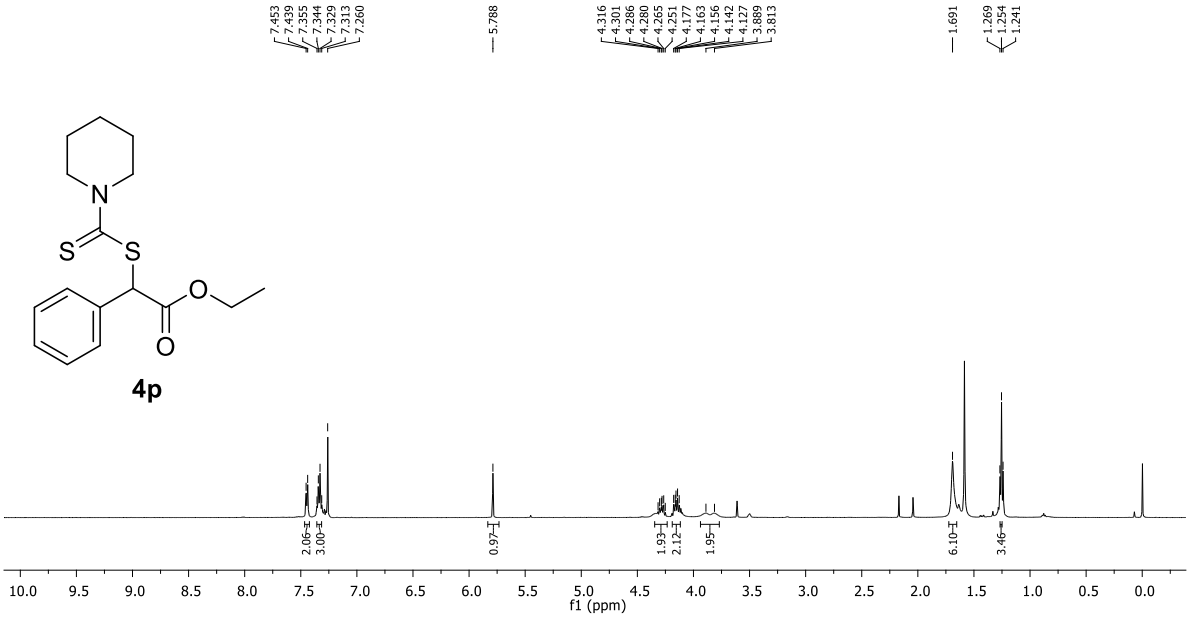


4o (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Cyclohexyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (4o):

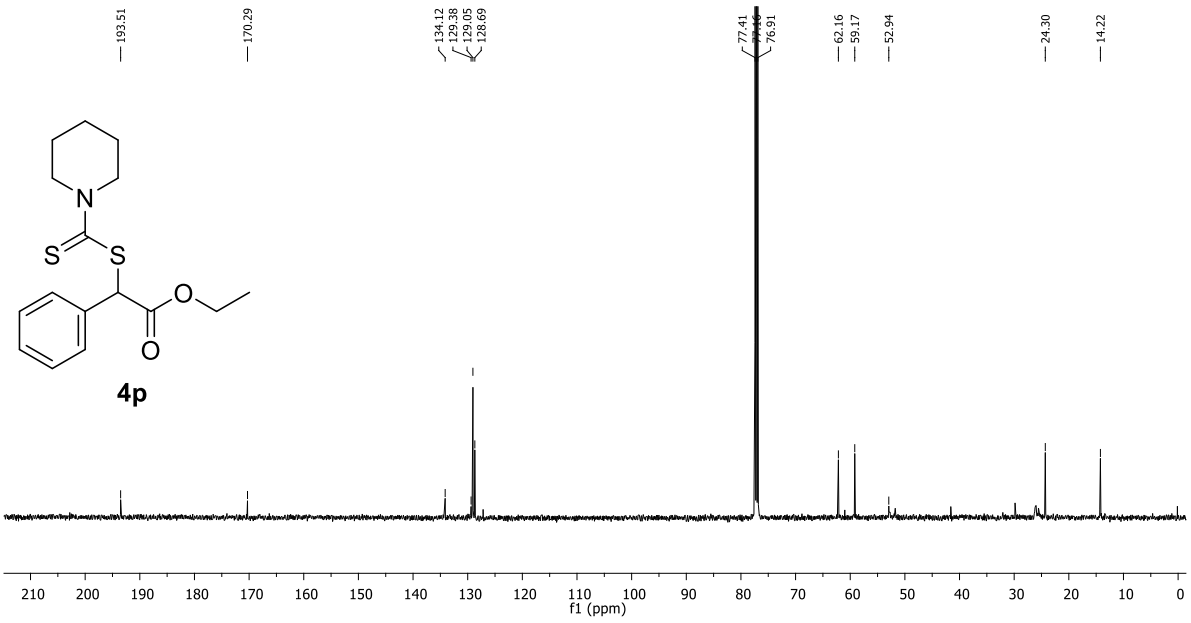


^{1}H NMR of Ethyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (4p):

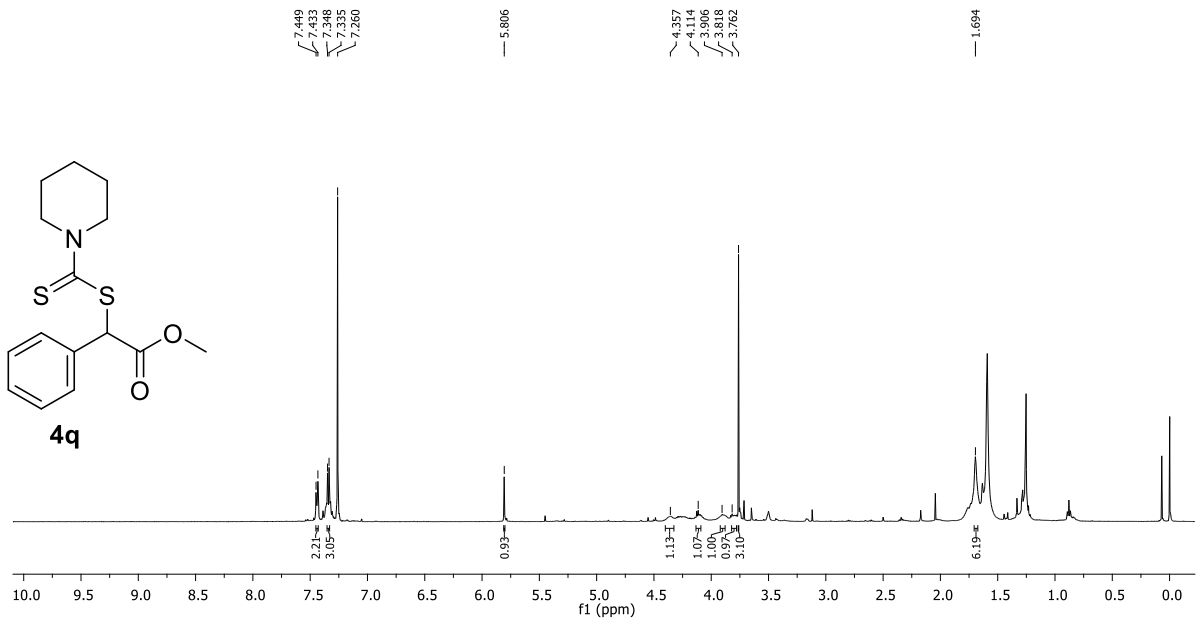


4p (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (4p):

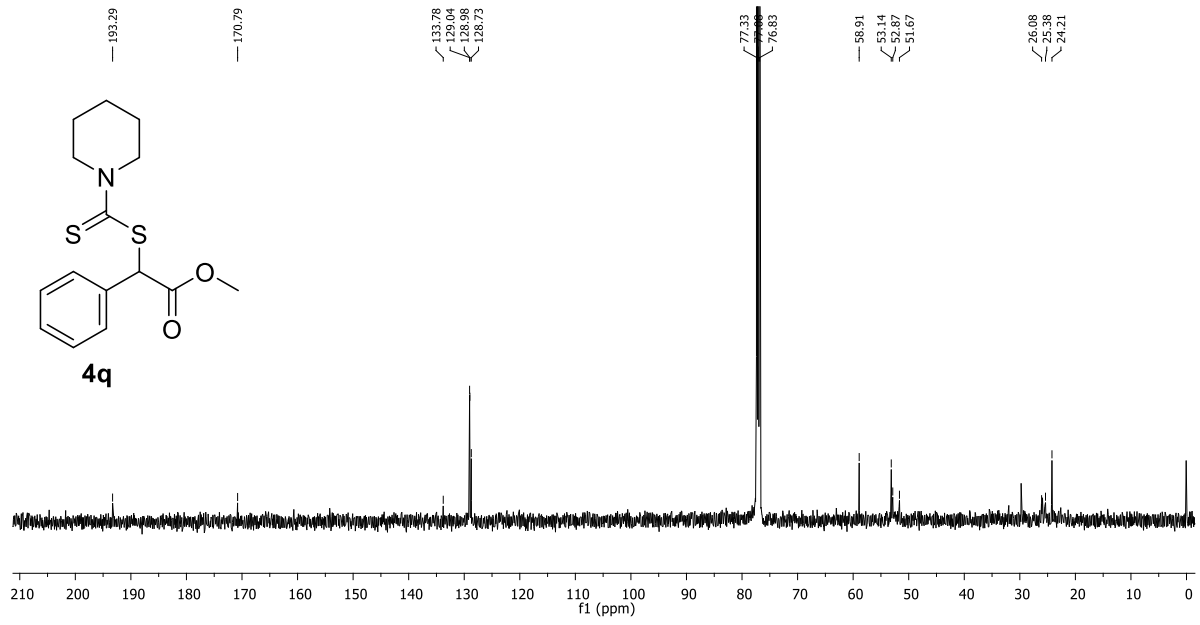


^{1}H NMR of Methyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (4q):

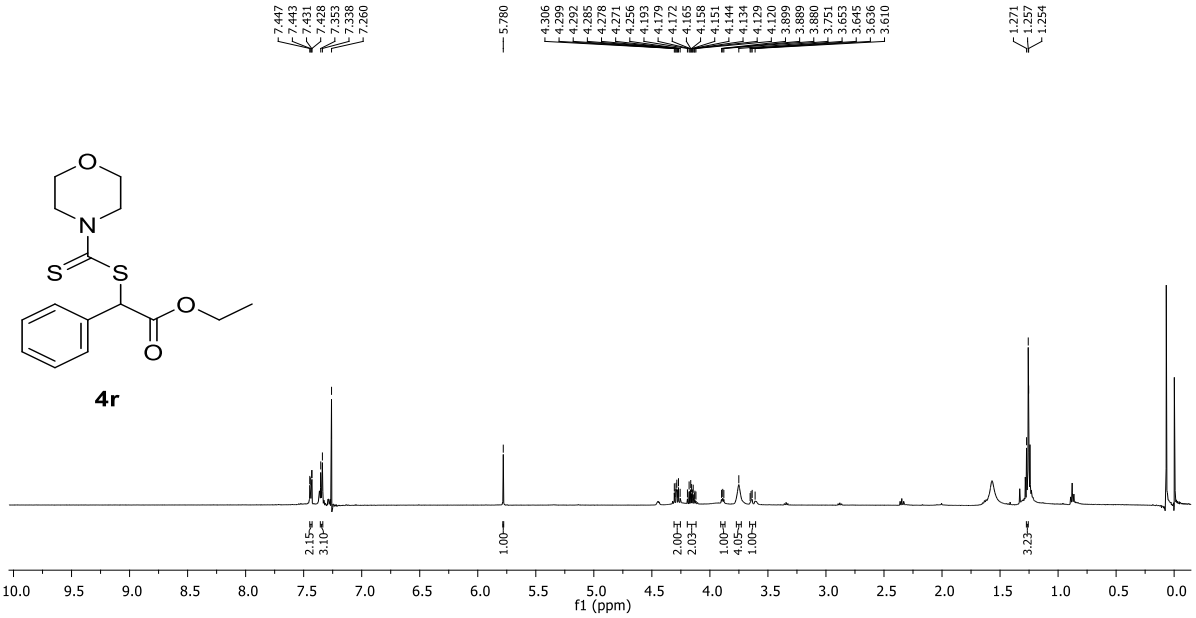


4q (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Methyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (4q):

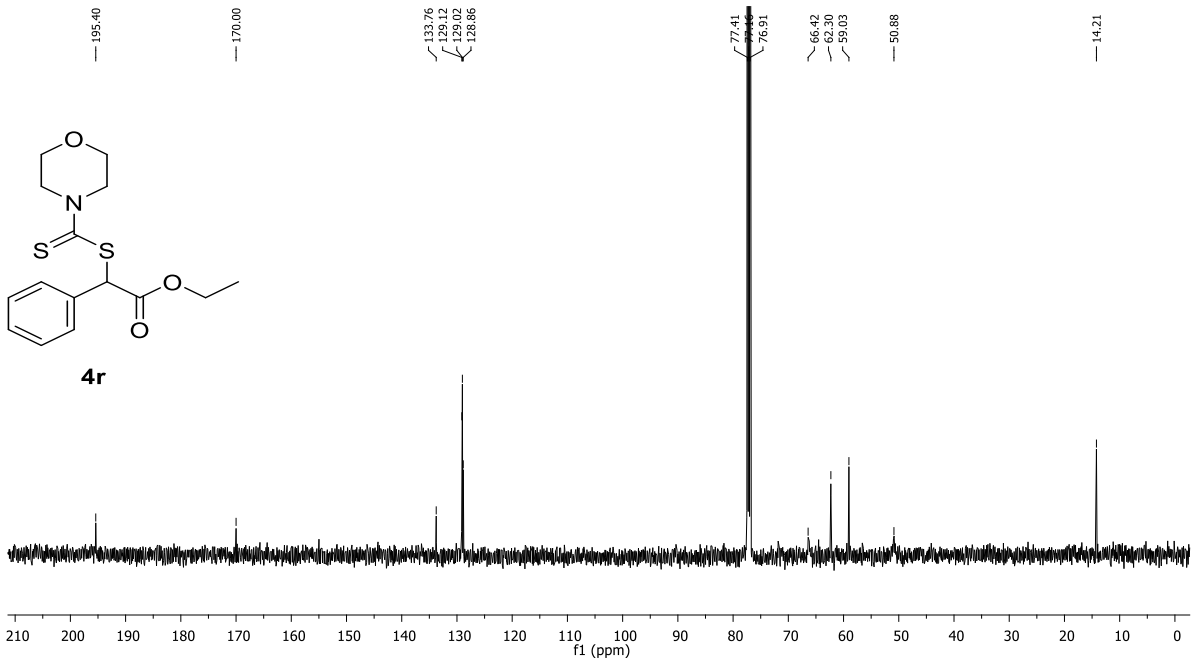


^{1}H NMR of Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4r):

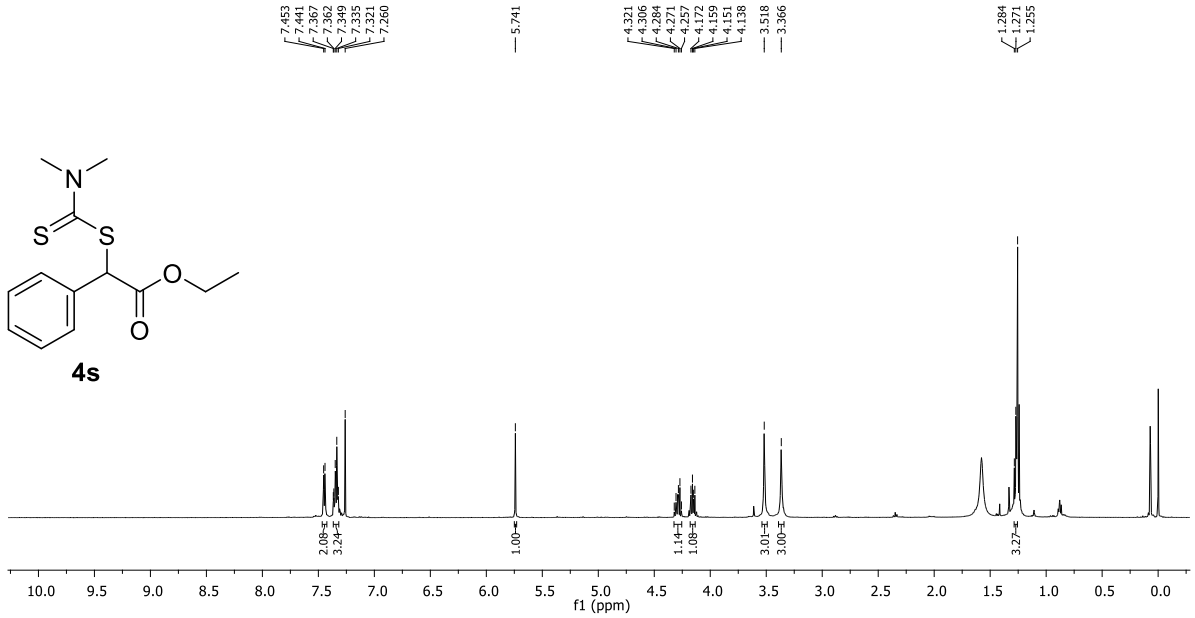


4r (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4r):

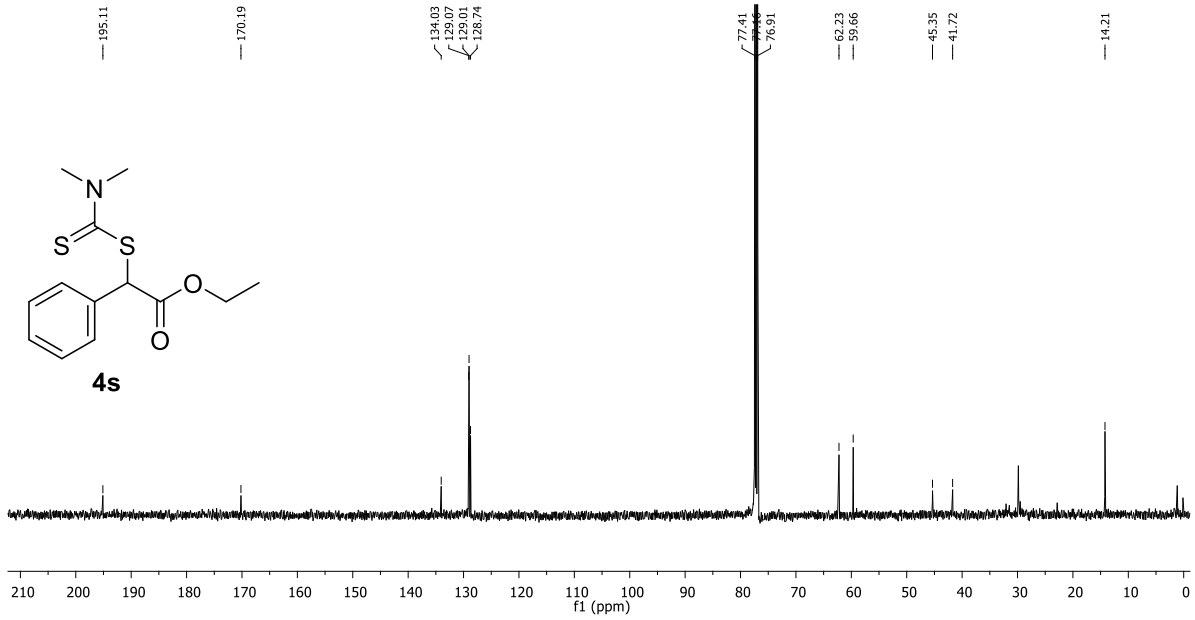


^{1}H NMR of Ethyl 2-((dimethylcarbamothioyl)thio)-2-phenylacetate (4s):

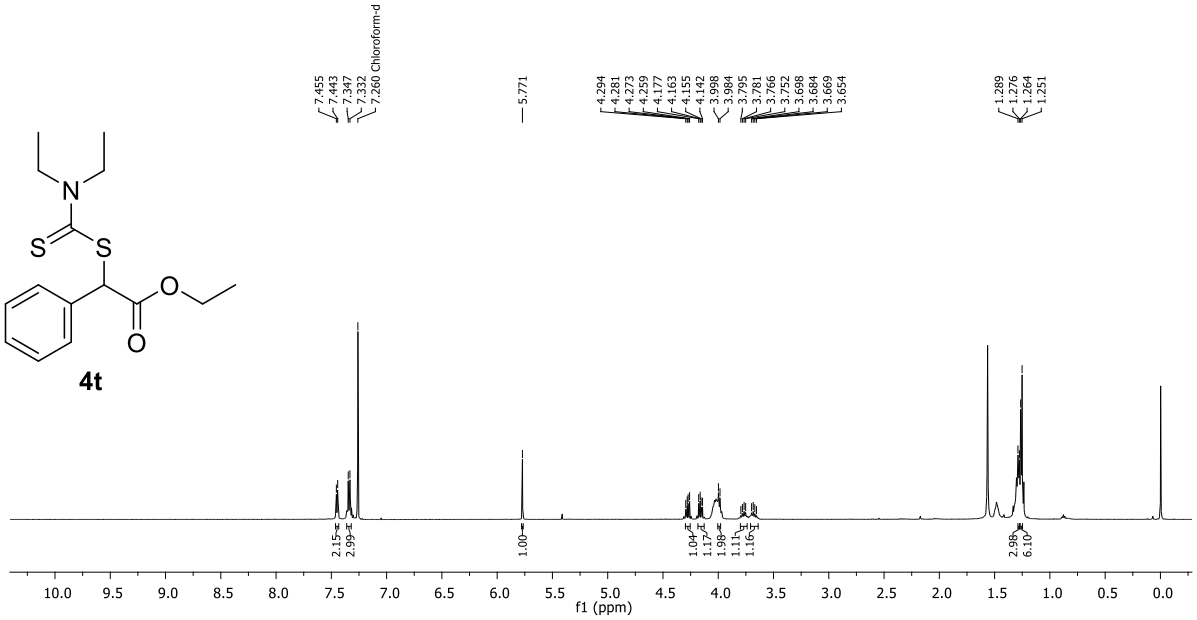


4s (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-((dimethylcarbamothioyl)thio)-2-phenylacetate (4s):

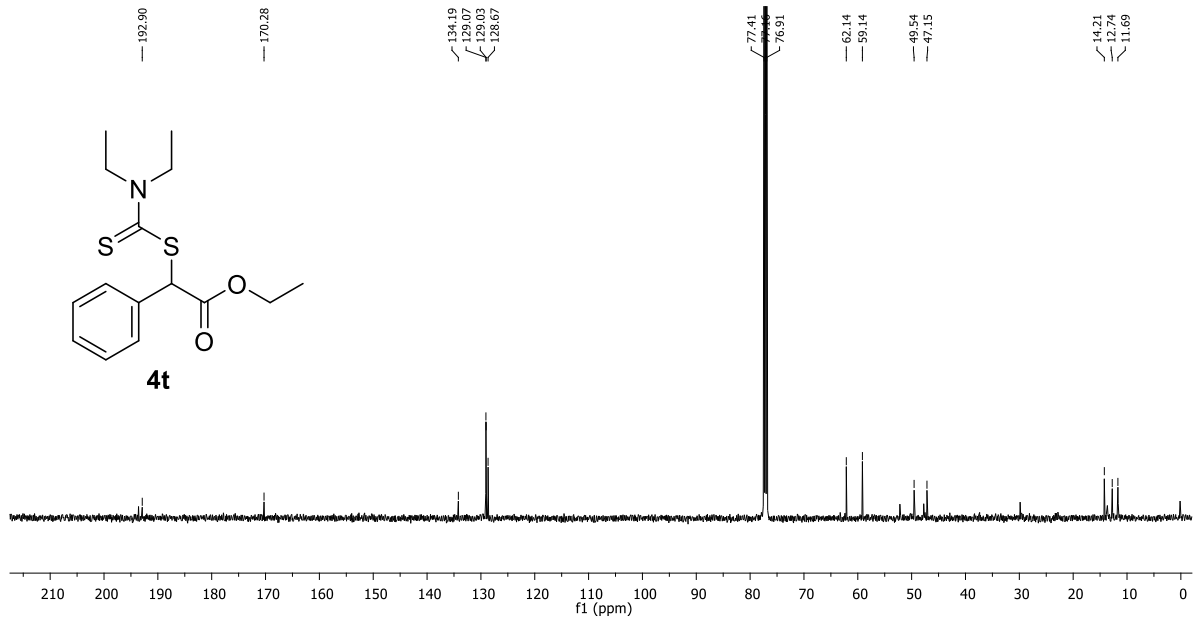


^{1}H NMR of Ethyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate (4t):

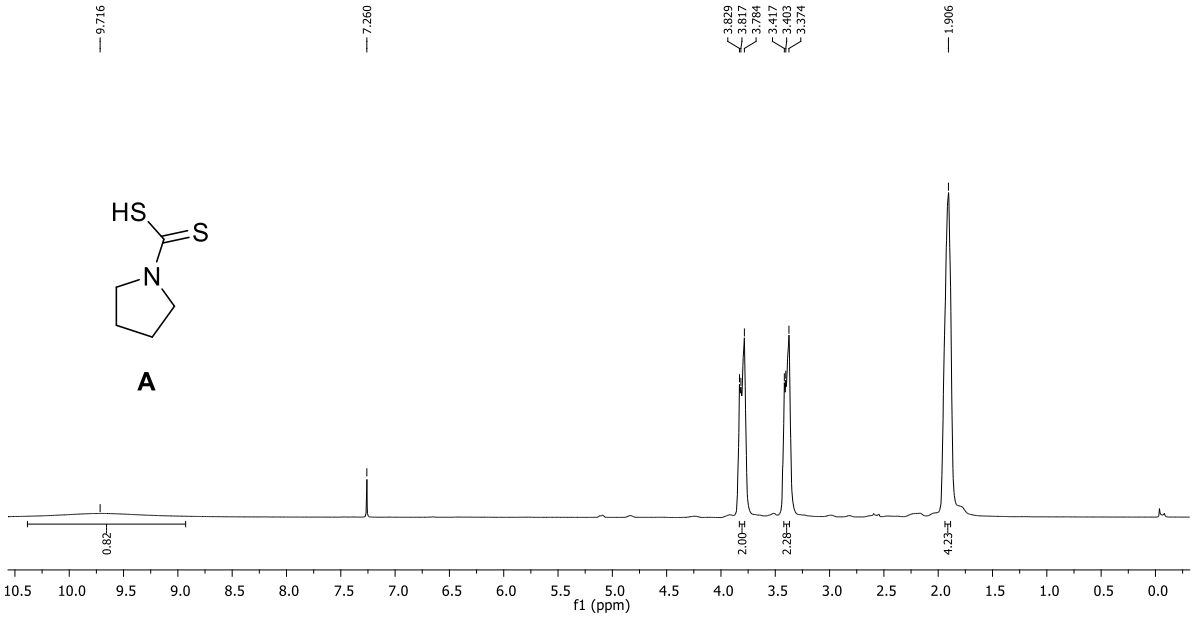


4t (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Ethyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate (4t):

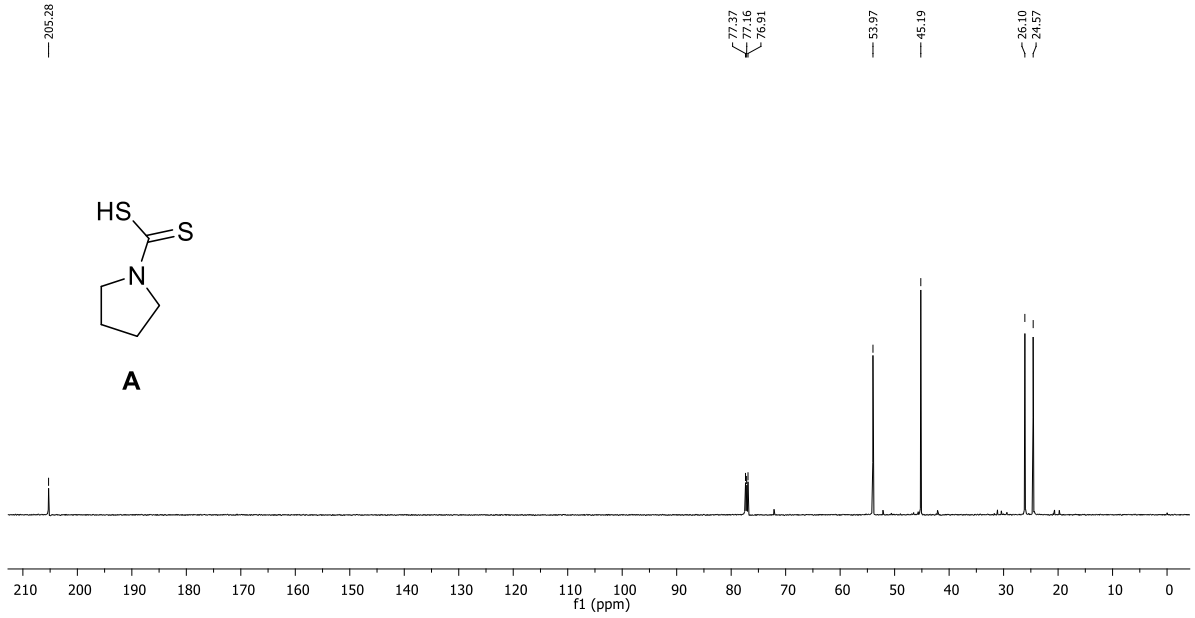


^{1}H NMR of Pyrrolidine-1-carbodithioic acid (A):



A (500 MHz, NMR, $CDCl_3$)

^{13}C NMR of Pyrrolidine-1-carbodithioic acid (A):



7. **HRMS of Pyrrolidine-1-carbodithioic acid (A) and pyrrolidine-1-carbothioic dithioperoxyanhydride (B):** HRMS (TOF-MS) for $C_5H_9NS_2$ m/z $[M + K]^+$ = 185.1119 and $C_{10}H_{16}N_2S_4$ m/z $[M + K]^+$ = 330.9828.