Carbon Nitride Creates Thioamides in High Yields by Photocatalytic Kindler Reaction

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Supporting information

General information

^{1}H and ^{13}C NMR spectra were recorded on Agilent 400 MHz (at 400 MHz for Protons and 101 MHz for Carbon-13). Chemical shifts are reported in ppm downfield from TMS (^{1}H, ^{13}C) as an internal standard.

High-resolution mass spectral data were obtained using Waters XEVO G2-XS QTOF with Aquity H-Class (HPLC).

Size exclusion chromatography (SEC) was conducted in N,N-dimethyl formamide (DMF, Sigma Aldrich, GC grade) with 0.05 mol·L^{-1} LiBr and BSME as internal standard using a column system by PSS GRAM 100/1000 column (8 × 300 mm, 7 μm particle size) with a PSS GRAM precolumn (8 × 50 mm) and a Shodex RI-71 detector and a calibration with PS standards from PSS. Samples were sonicated until they are dissolved in DMF and injected to a column system through a syringe equipped with VWR PTFE microfilter in order to prevent the entrance of undissolved macromolecules.

Fourier transform infrared (FT-IR) spectra were recorded on Thermo Scientific Nicolet iD5 spectrometer.

Irradiance of the LED modules was measured using PM400 Optical Power and Energy Meter equipped with integrating sphere S142C.

Powder X-Ray diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuKα radiation (λ = 0.15418 nm) applying 2θ step size of 0.05° and counting time of 3s per step.

Nitrogen adsorption/desorption measurements were performed after degassing the samples at 150 °C for 20 hours using a Quantachrome Quadrasorb SI-MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) model to adsorption isotherms for $0.05 < p/p0 < 0.3$ using the QuadraWin 5.11 software package.

Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW Class WA hemispherical electron analyzer. A dual anode Al Kα X-ray source (1486.6 eV) was used as incident radiation. Survey and high resolution spectra were recorded in constant pass energy mode (44 and 22 eV, respectively). During the UPS (He I excitation energy $h\nu$=21.23 eV) measurements a bias of 15.32 V was applied to the sample, in order to avoid interference of the spectrometer threshold in the UP spectra. The values of the valence band maximum (VBM) are determined by fitting a straight line into the leading edge.

Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere.

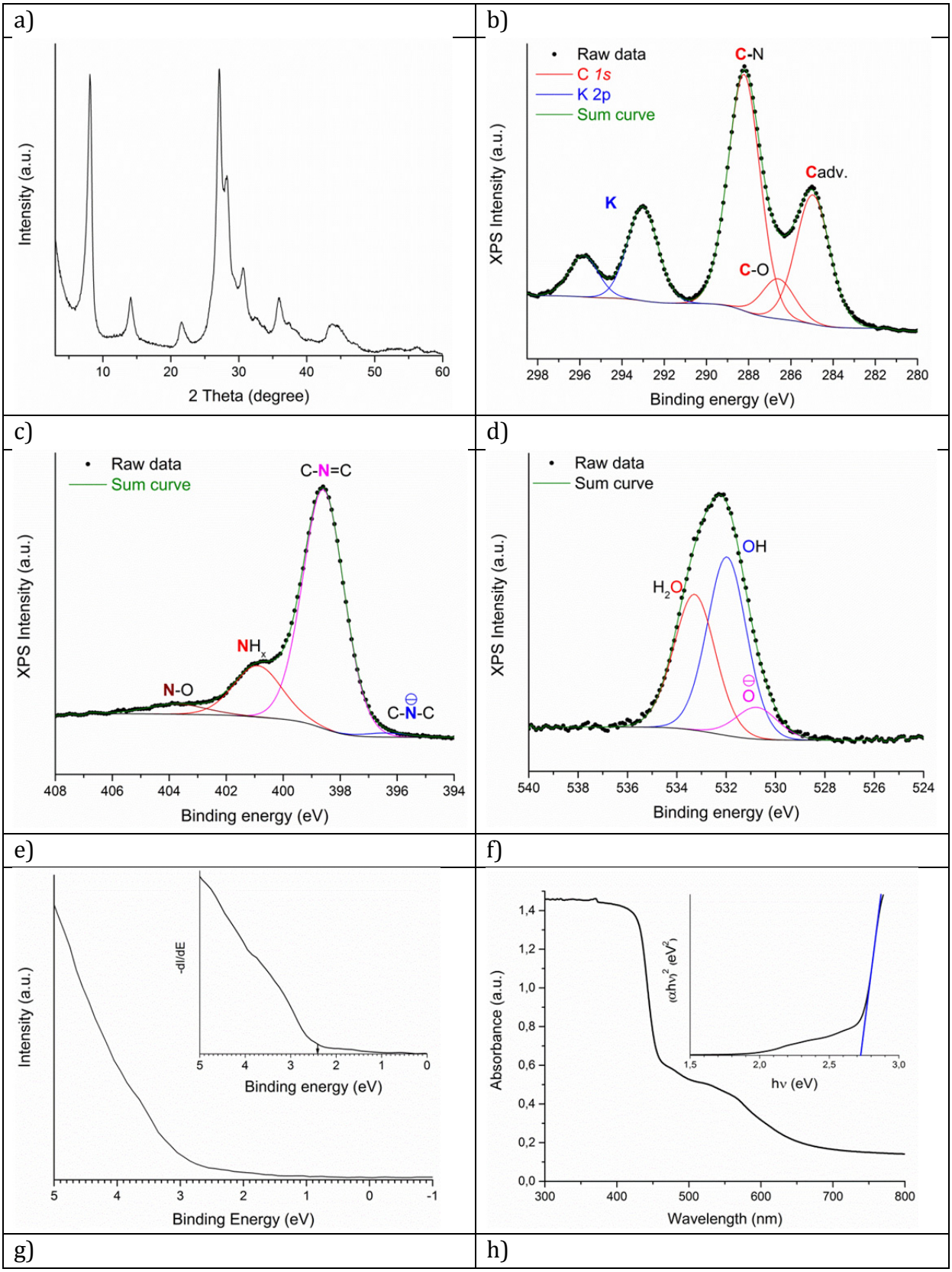
Emission spectra were recorded on Jasco FP-8300 instrument. The excitation wavelength was 360 nm.

The TEM measurements were acquired using a double-corrected Jeol ARM200F, equipped with a cold field emission gun and a Gatan GIF Quantum. The used acceleration voltage was 200kV and the emission was set to 10μA in order to reduce beam damage. An objective aperture with a diameter of 60μm was introduced into the beam to improve the contrast while still allowing for atomic resolution.

Experimental part

1. Preparation procedure and characterization of K-PHI

Potassium poly(heptazine imide) was synthesized according to the previously described procedure.[1] Mixture of lithium chloride (3.71 g), potassium chloride (4.54 g) and 5-aminotetrazole (1.65 g) was grinded in ball mill for 5 min at the shaking rate 25 s^{-1}. Reaction mixtures were transferred into porcelain crucibles and covered with lids. Crucibles were placed in the oven and heated under constant nitrogen flow (15 $L \cdot min^{-1}$) and atmospheric pressure at a following temperature regime: heating from room temperature to 550 °C for 4 hours, annealing at 550 °C for 4 hours. After completion of the heating program, the crucibles were allowed to cool slowly to room temperature under nitrogen flow. The crude products were removed from the crucibles, washed with deionized water (100 mL) for 3 hours in order to remove salts, then filtered, extensively washed with deionized water and dried in a vacuum oven (20 mbar) at 50 °C for 15 h.


a)
Intensity (a.u.)
10
20
30
40
50
60
2 Theta (degree)
b)
Raw data
C 1s
K 2p
Sum curve
C-N
Cadv.
K
C-O
XPS Intensity (a.u.)
298
296
294
292
290
288
286
284
282
280
Binding energy (eV)
c)
Raw data
Sum curve
C-N=C
NHx
N-O
C-N-C
XPS Intensity (a.u.)
408
406
404
402
400
398
396
394
Binding energy (eV)
d)
Raw data
Sum curve
OH
H2O
O
XPS Intensity (a.u.)
540
538
536
534
532
530
528
526
524
Binding energy (eV)
e)
Intensity (a.u.)
-dI/dE
5
4
3
2
1
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5
4
3
2
1
0
-1
Binding Energy (eV)
f)
Absorbance (a.u.)
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0,4
0,2
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(αhν)2 (eV2)
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hν (eV)
300
400
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700
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Wavelength (nm)
g)
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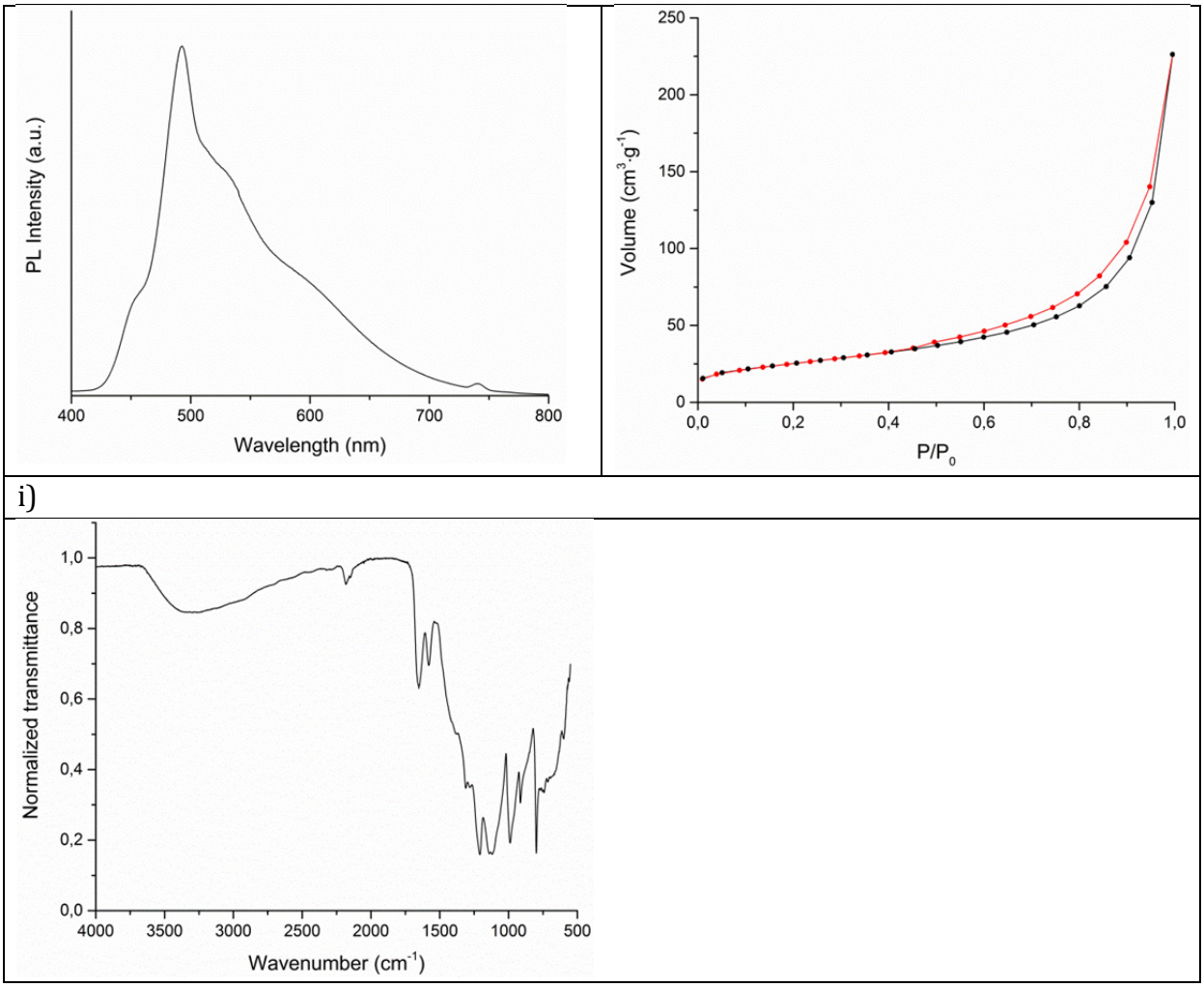


Figure S1. a) PXRD pattern of K-PHI; b) XPS C 1s and K 2p spectra of K-PHI; c) XPS N 1s spectrum of K-PHI; d) XPS O 1s spectrum of K-PHI; e) UPS spectrum of K-PHI; f) UV-vis absorption spectrum of K-PHI with Tauc plot as inset assuming that K-PHI is a direct semiconductor; g) room temperature PL spectrum of K-PHI obtained upon excitation with 350 nm wavelength; h) N_2 sorption isotherm measured at 77 K; i) FT-IR spectrum of K-PHI.

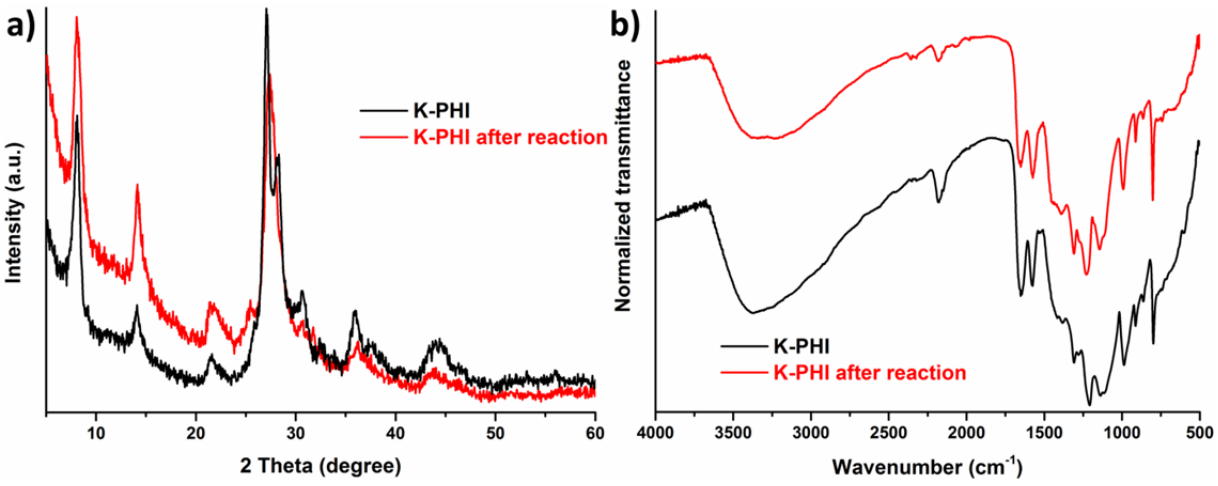
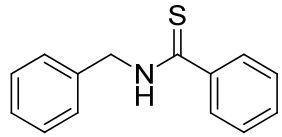


Figure S2. PXRD patterns (a) and FT-IR spectra (b) of K-PHI before and after photocatalytic experiments.

2. General method of thioamide preparation from single amine.

Glass Tube with Rubber-Lined Cap was evacuated and filled with argon three times. To this tube amine (0.5 mmol), sulphur (1.5 mmol), K-PHI (10 mg) and corresponding solvent (2 mL) were added (Scheme 4). Resulting mixture was stirred at temperature listed at Scheme 4 under irradiation of Blue LED (461 nm, 79 mW·cm^{-2}) for time listed at Scheme 4. Then reaction mixture was cooled to room temperature and centrifuged, clear solution was separated and solid residue was washed with dioxane (2 mL) and centrifuged again. Organic solutions were combined and evaporated to dryness. Thioamides **2b**, **2c**, **2d**, **2f**, **2g**, **2i** were obtained by recrystallization of crude residue after evaporation in mixture ethyl acetate/hexane (1:4) and thioamides **2a**, **2e**, **2h**, **2j**, **2k** were purified by flash silica gel column chromatography using mixture of diethyl ether/dichloromethane (1:2) as an eluent.

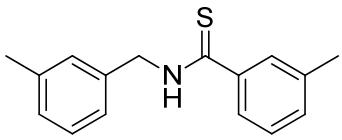


*N-Benzylbenzothioamide **(2a)***.

Yellowish solid (yield 90%), m.p. 84-85°C (Lit.[2] m.p. 85 °C)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.75 (s, 1H), 7.75 (d, J = 7.0 Hz, 2H), 7.46 (m, 1H), 7.40 (m, 2H), 7.36 – 7.28 (m, 4H), 7.24 (m, 1H), 4.95 (d, J = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 141.6, 136.2, 131.2, 129.0, 128.5, 128.4, 128.2, 126.7, 51.0.

HRMS m/z (EI, $[M+H]^+$): $C_{14}H_{14}NS^+$ calcd 228.0847, found 228.0852.

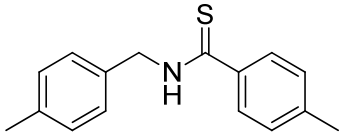


*3-Methyl-N-(3-methylbenzyl)benzothioamide **(2b)***.

Yellowish solid (yield 92%), m.p. 84-86°C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (br s, 1H), 7.59 (s, 1H), 7.50 (m, 1H), 7.30 – 7.12 (m, 6H), 4.93 (d, J = 5.0 Hz, 2H), 2.36 (br s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 141.6, 138.8, 138.4, 136.1, 131.9, 129.2, 128.9, 128.4, 127.7, 125.4, 123.4, 51.1, 21.4, 21.4.

HRMS m/z (EI, $[M+H]^+$): $C_{16}H_{18}NS^+$ calcd 256.1160, found 256.1168.

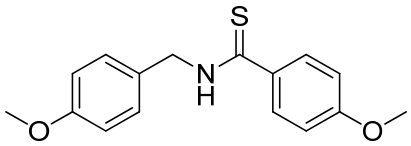


*4-Methyl-N-(4-methylbenzyl)benzothioamide **(2c)***.

Yellowish solid (yield 90%), m.p. 75-76°C (Lit.[3] m.p. 72-74 °C)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.60 (s, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.20 (m, 4H), 7.11 (d, J = 7.9 Hz, 2H), 4.89 (d, J = 5.9 Hz, 2H), 2.30 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.6, 141.2, 138.7, 136.6, 134.9, 129.3, 128.9, 128.0, 127.8, 49.1, 21.3, 21.1.

HRMS m/z (EI, $[M+H]^+$): $C_{16}H_{18}NS^+$ calcd 256.1160, found 256.1154.

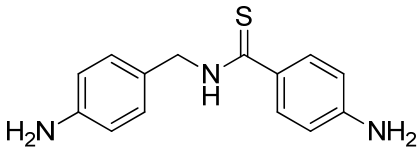


4-Methoxy-N-(4-methoxybenzyl)benzothioamide ***(2d)****.*

Yellowish solid (yield 91%), m.p. 92-94°C (Lit.[3] m.p. 91-94 °C)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.49 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.86 (d, *J* = 5.8 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.5, 161.9, 158.8, 133.5, 130.0, 129.7, 129.5, 114.1, 113.6, 55.9, 55.5, 48.9.

HRMS m/z (EI, $[M+H]^+$): $C_{16}H_{18}NO_2S^+$ calcd 288.1058, found 288.1051.

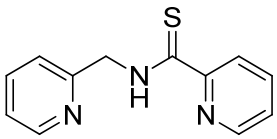


4-Amino-N-(4-aminobenzyl)benzothioamide ***(2e).***

Yellowish solid (yield 82%), m.p. 79-81°C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.39 (br s, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.82 (d, *J* = 4.7 Hz, 2H), 3.94 (br s, 2H), 3.71 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 149.6, 146.4, 129.8, 128.6, 128.2, 126.2, 115.3, 113.9, 50.9.

HRMS m/z (EI, $[M+Na]^+$): $C_{14}H_{15}N_3SNa^+$ calcd 280.0884, found 280.0878.

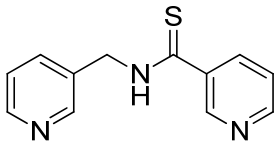


N-(pyridin-2-ylmethyl)pyridine-2-carbothioamide ***(2f)****.*

Yellowish solid (yield 88%), m.p. 91-92°C (Lit.[4] m.p. 93-94 °C)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.38 (s, 1H), 8.64 (d, *J* = 5.5 Hz, 1H), 8.54 (d, *J* = 5.4 Hz, 1H), 8.50 (d, *J* = 7.9 Hz, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.62 (dd, *J* = 7.4, 4.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 5.05 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 155.0, 151.3, 149.4, 147.3, 137.1, 136.8, 126.0, 124.8, 122.6, 122.2, 50.5.

HRMS m/z (EI, $[M+H]^+$): $C_{12}H_{12}N_3S^+$ calcd 230.0752, found 230.0754.

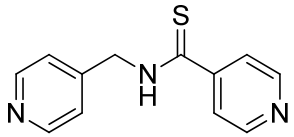


N-(pyridin-3-ylmethyl)pyridine-3-carbothioamide ***(2g)****.*

Yellowish solid (yield 89%), m.p. 88-90°C

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (s, 1H), 8.93 – 8.81 (m, 1H), 8.66 – 8.52 (m, 2H), 8.46 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.13 – 8.04 (m, 1H), 7.77 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.35 (dd, *J* = 7.5, 5.1 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.8, 151.8, 149.7, 148.9, 148.0, 136.9, 136.0, 135.4, 133.1, 124.0, 123.5, 47.3.

HRMS m/z (EI, [M+H]$^+$): $C_{12}H_{12}N_3S^+$ calcd 230.0752, found 230.0760.

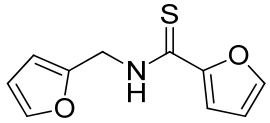


N-(pyridin-4-ylmethyl)pyridine-4-carbothioamide ***(2h)****.*

Yellowish solid (yield 68%), m.p. 109-110°C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 6.1 Hz, 2H), 8.61 (d, *J* = 6.0 Hz, 2H), 7.96 (s, 1H), 7.58 (d, *J* = 6.1 Hz, 2H), 7.28 (d, *J* = 5.9 Hz, 2H), 5.06 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.63, 150.34, 150.22, 147.77, 144.84, 122.65, 120.52, 49.02.

MS (EI): 229 (M^+). HRMS m/z (EI, [M-HS]$^+$): $C_{12}H_{10}N_3^+$ calcd 196.0874, found 196.0862.

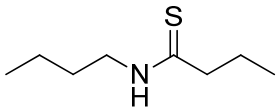


N-(Furan-2-ylmethyl)furan-2-carbothioamide ***(2i)****.*

Brown solid (yield 85%), m.p. 103-104°C

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 7.87 (m, 1H), 7.56 (m, 1H), 7.22 (d, *J* = 3.5 Hz, 1H), 6.60 (m, *J* = 3.5, 1.7 Hz, 1H), 6.39 – 6.36 (m, 1H), 6.30 (d, *J* = 3.1 Hz, 1H), 4.87 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.1, 152.3, 150.7, 145.9, 142.7, 117.0, 113.3, 111.0, 108.5, 41.2.

HRMS m/z (EI, [M+H]$^+$): $C_{10}H_{10}NO_2S^+$ calcd 208.0432, found 208.0439.

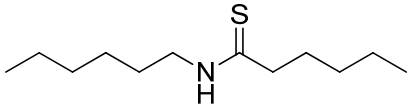


N-butylbutanethioamide ***(2j).***

Orange oil (yield 72%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 3.69 – 3.61 (m, 2H), 2.63 – 2.55 (m, 2H), 1.79 (m, 2H), 1.62 (m, 2H), 1.38 (m, 7.4 Hz, 2H), 0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3, 49.3, 45.8, 30.1, 22.7, 20.2, 13.7, 13.3.

HRMS m/z (EI, $[M+H]^+$): $C_8H_{18}NS^+$ calcd 160.1160, found 160.1172.



N-hexylhexanethioamide ***(2k).***

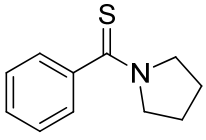
Brown oil (yield 78%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 3.70 – 3.57 (m, 2H), 2.67 – 2.56 (m, 2H), 1.75 (m, 2H), 1.63 (m, 2H), 1.30 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5, 47.4, 46.1, 31.4, 31.1, 29.1, 28.0, 26.6, 22.5, 22.4, 14.0, 13.9.

MS (EI): 215 (M^+). HRMS m/z (EI, $[M-HS]^+$): $C_{12}H_{24}N^+$ calcd 182.1908, found 182.1890.

3. General method of thioamide preparation from two different amines.

Glass Tube with Rubber-Lined Cap was evacuated and filled with argon three times. To this tube benzylamine (0.5 mmol), corresponding secondary amine (1.5 mmol), sulfur (3 mmol), K-PHI (10 mg) and dioxane (4 mL) were added. Resulting mixture was stirred at 70 °C under irradiation with Blue LED (461 nm, 79 mW·cm^{-2}) for 20 hours. Then reaction mixture was cooled to room temperature and centrifuged, clear solution was separated and solid residue was washed with dioxane (2x2 mL) and centrifuged again. Organic solutions were combined, evaporated to dryness, dissolved in dichlormethane (3 mL) and washed with distilled water (2x2 mL). Organic layer was dried over Na_2SO_4 and evaporated to dryness. Thioamides were obtained after flash silica gel column chromatography by using mixtures of ethyl acetate/hexane (1:4) for **2m,n** and diethyl ether/dichlormethan (1:2) for **2o** as eluents.

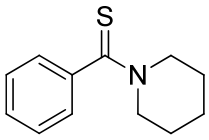


1-Thiobenzoyl pyrrolidine ***(2m).***

Pale yellow solid (yield 83%), m.p. 68-71°C (Lit.[5] mp 73 °C)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 3.97 (t, *J* = 7.1 Hz, 2H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.07 (p, *J* = 6.8 Hz, 2H), 1.95 (p, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 144.0, 128.7, 128.3., 125.6, 53.8, 53.4, 26.5, 24.6.

HRMS m/z (EI, $[M+H]^+$): $C_{11}H_{14}NS^+$ calcd 192.0847, found 192.0859.

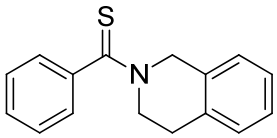


1-Thiobenzoyl piperidine ***(2n).***

Pale yellow solid (yield 72%), mp. 63-64°C (Lit.[6] m.p. 64-65 °C)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 4.43 – 4.26 (m, 2H), 3.54 – 3.45 (m, 2H), 1.81 (m, 2H), 1.73 (m, 2H), 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 143.4, 128.4, 128.3, 125.4, 53.1, 50.6, 26.9, 25.5, 24.2.

HRMS m/z (EI, $[M+H]^+$): $C_{12}H_{16}NS^+$ calcd 206.1003, found 206.1015.



(3,4-Dihydroisoquinolin-2(1H)-yl)(phenyl)methanethione ***(2o).***

Yellow solid (yield 76%), mp. 77-78°C

^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers)[7] δ 7.40 – 7.12 (m, 8H), 6.87 (d, *J* = 7.7 Hz, 1H), 5.38 (s, 1H), 4.67 (s, 1H), 4.49 (t, *J* = 6.2 Hz, 1H), 3.81 – 3.71 (m, 1H), 3.12 (t, *J* = 6.2 Hz, 1H), 2.89 (t, *J* = 5.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 200.1, 143.2, 134.9, 133.4, 132.3, 128.8, 128.7, 128.5, 128.5, 128.4, 128.3, 127.5, 127.0, 126.9, 126.9, 126.6, 126.0, 125.7, 53.9, 52.1, 49.9, 48.4, 29.8, 28.0.

HRMS m/z (EI, $[M+H]^+$): $C_{16}H_{16}NS^+$ calcd 254.1003, found 254.1009.

4. **General method of thioamide preparation from p- and m-xylylenediamine.**

Glass tube with rubber-lined cap was evacuated and filled with argon three times. To this tube p-xylylenediamine (m-xylylenediamine) (68.1mg, 0.5mmol), sulphur (48mg, 1.5 mmol), PHIK (10mg) and 4ml of N,N-dimethylformamide (DMF) were added. Resulting mixture was stirred at 70ºC under irradiation of Blue LED (461 nm, 79 mW/cm^2) for 20 hours. Then reaction mixture was centrifuged, clear solution was separated and solid residue was washed with 1 ml of DMF and centrifuged again. DMF solutions were combined and added dropwise into 20ml of diethyl ether. Obtained yellowish precipitate was separated by filtration and washed twice with 20ml of diethyl ether, then dried in vacuum at 50ºC.

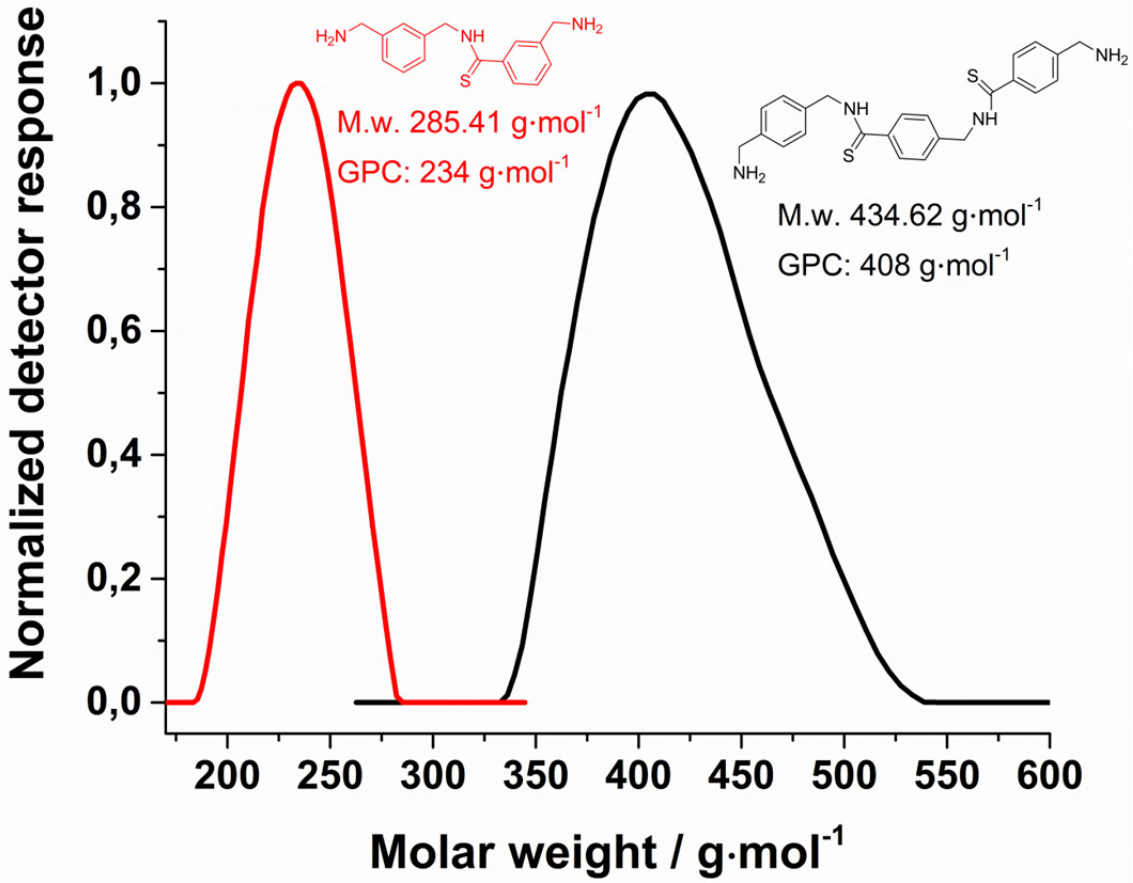
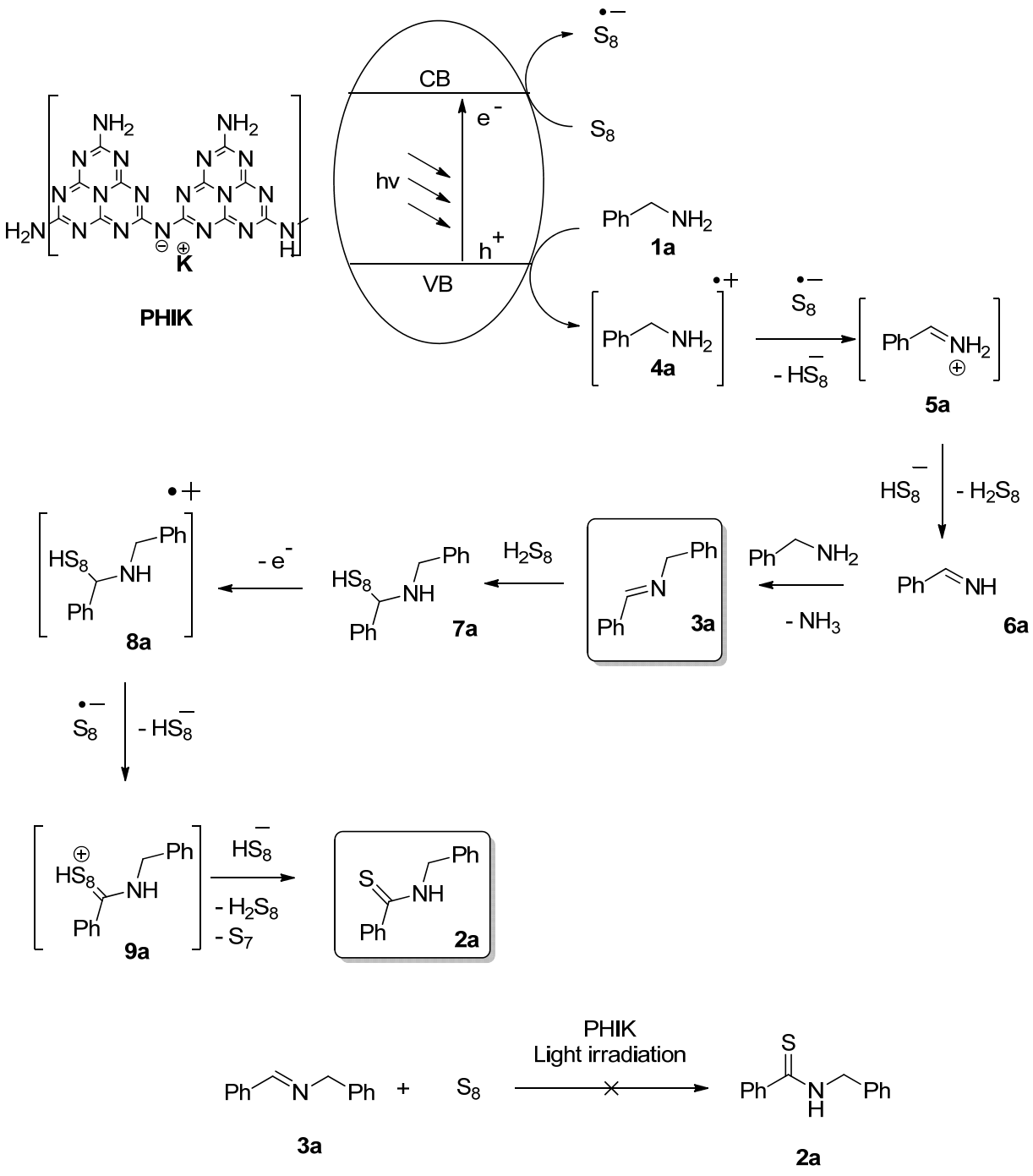


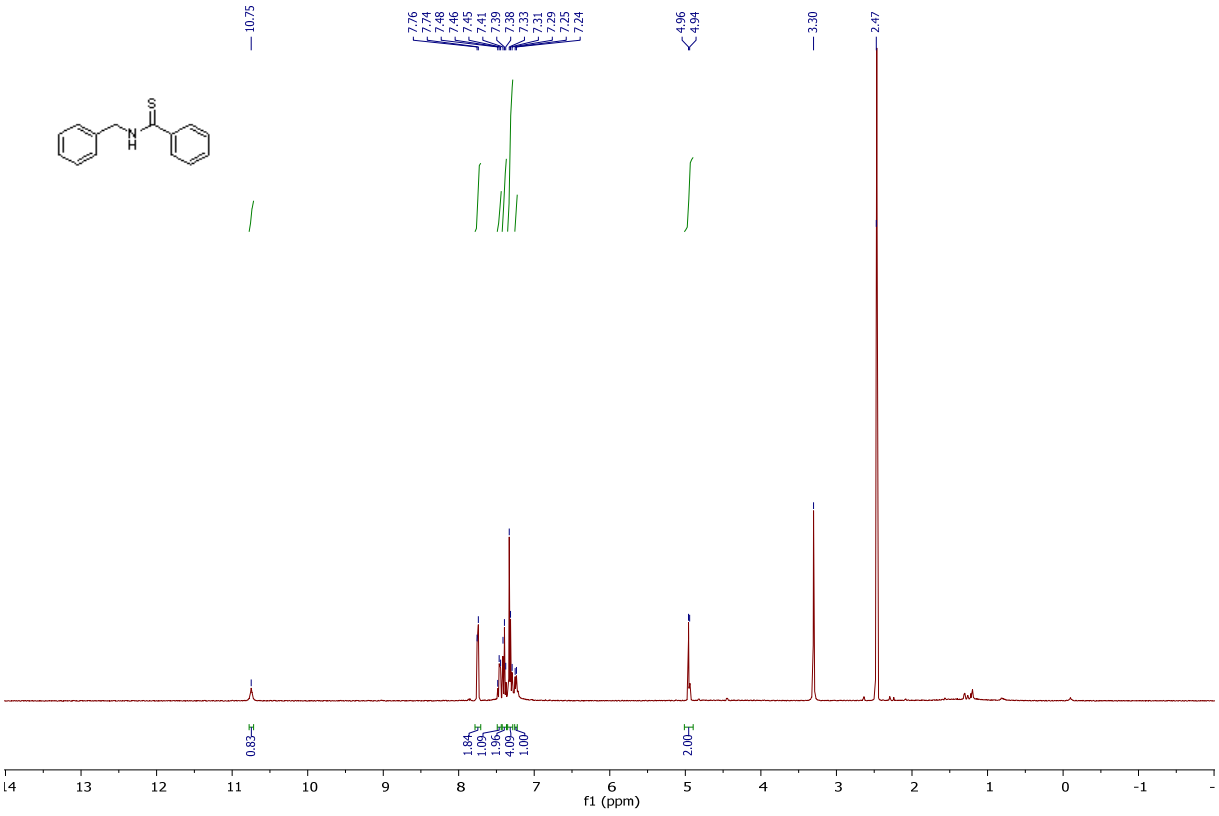
Figure S3. p-xylylenediamine and m-xylylenediamine polymerization experiments. GPC data.



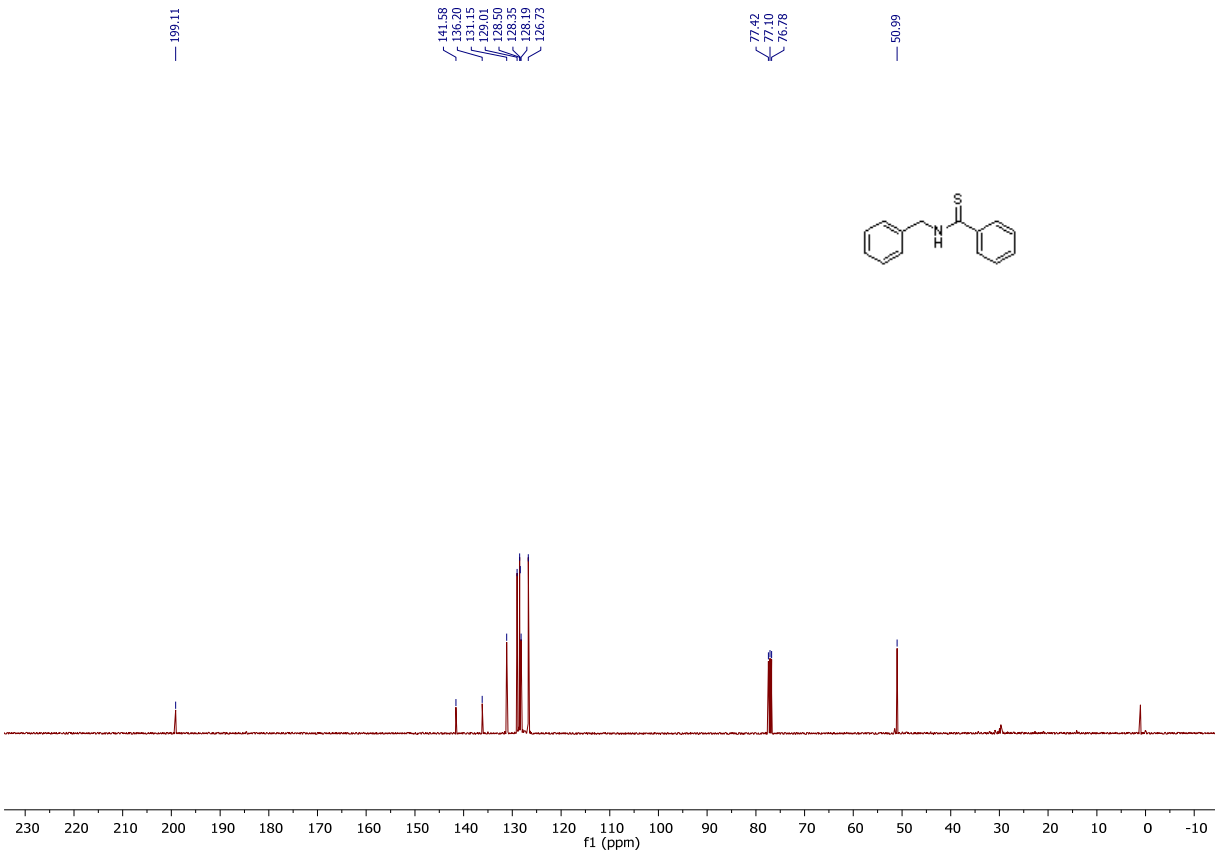
Scheme S4. The expanded mechanism of thioamide synthesis.

^{1}H and ^{13}C NMR spectra of thioamides

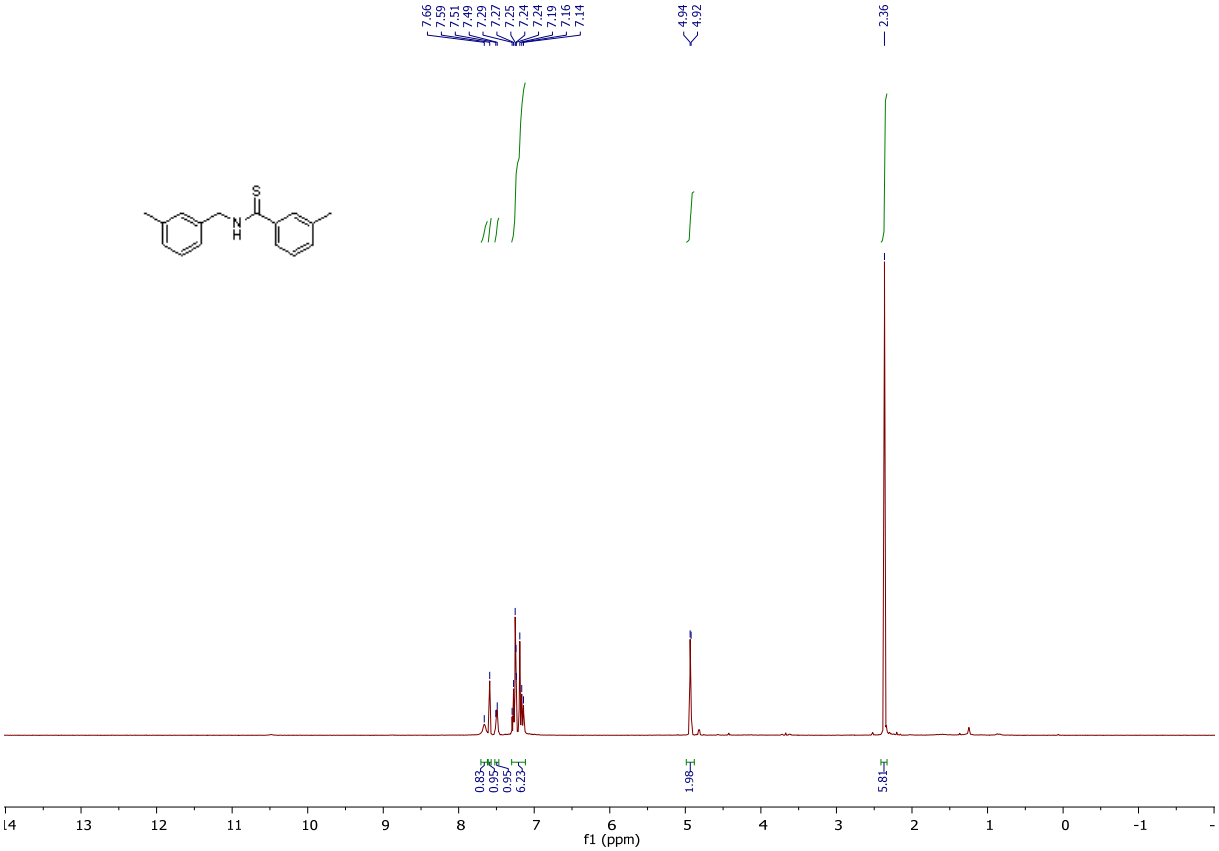
N-Benzylbenzothioamide (2a). ^{1}H NMR



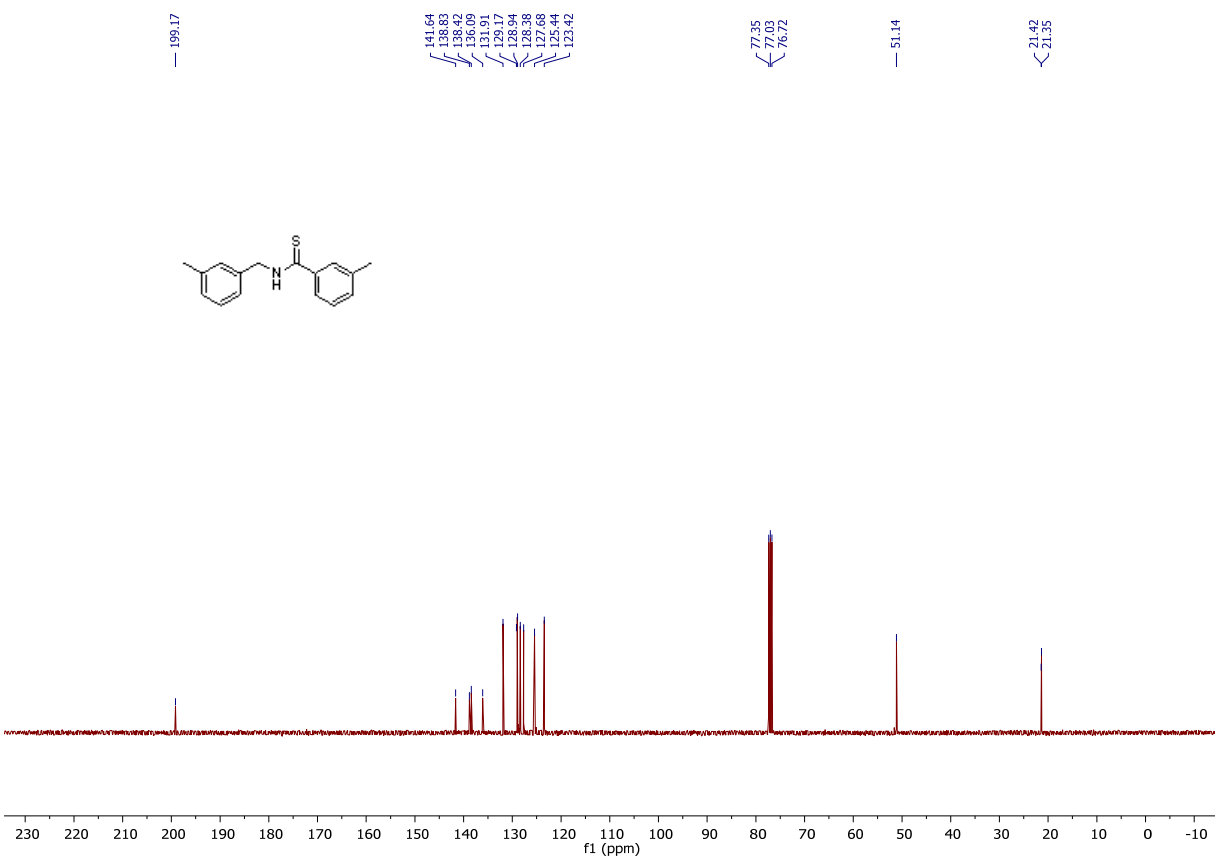
^{13}C NMR



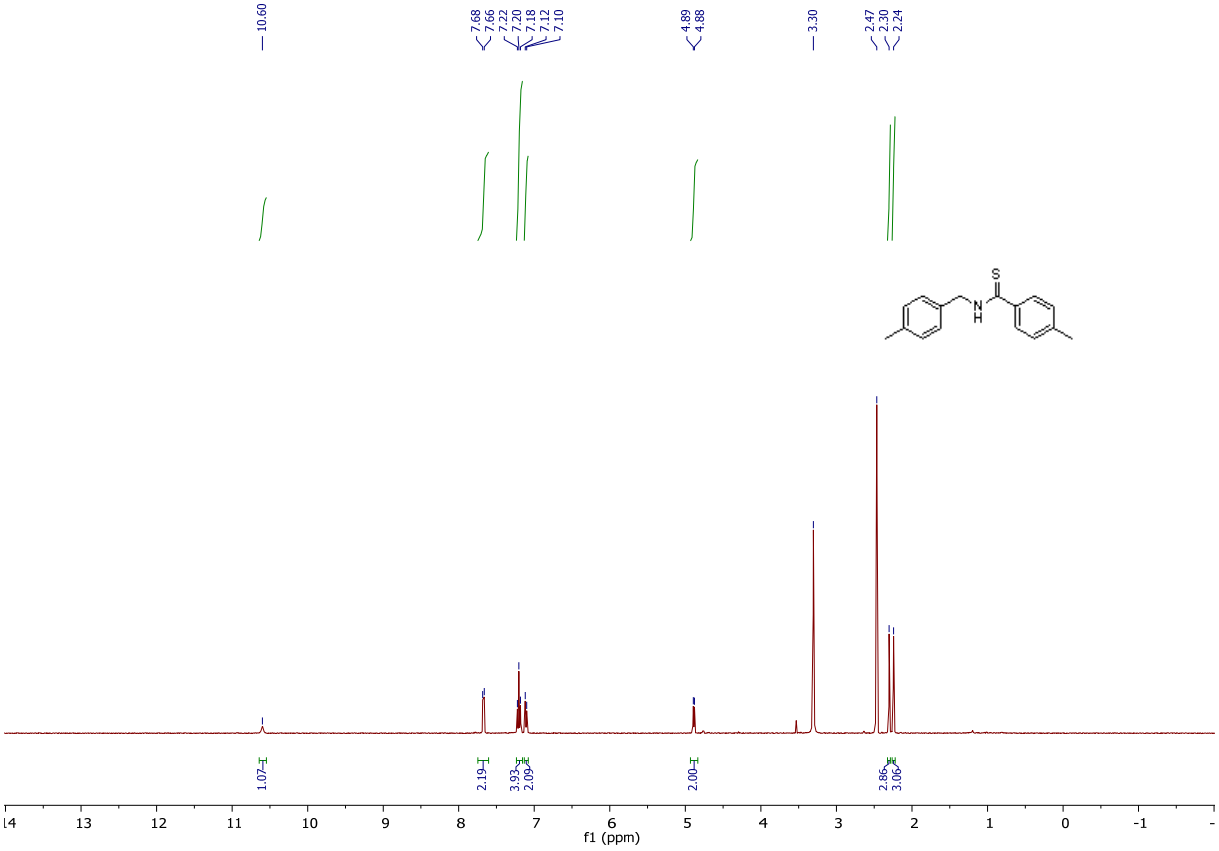
3-Methyl-N-(3-methylbenzyl)benzothioamide (2b). ^{1}H NMR



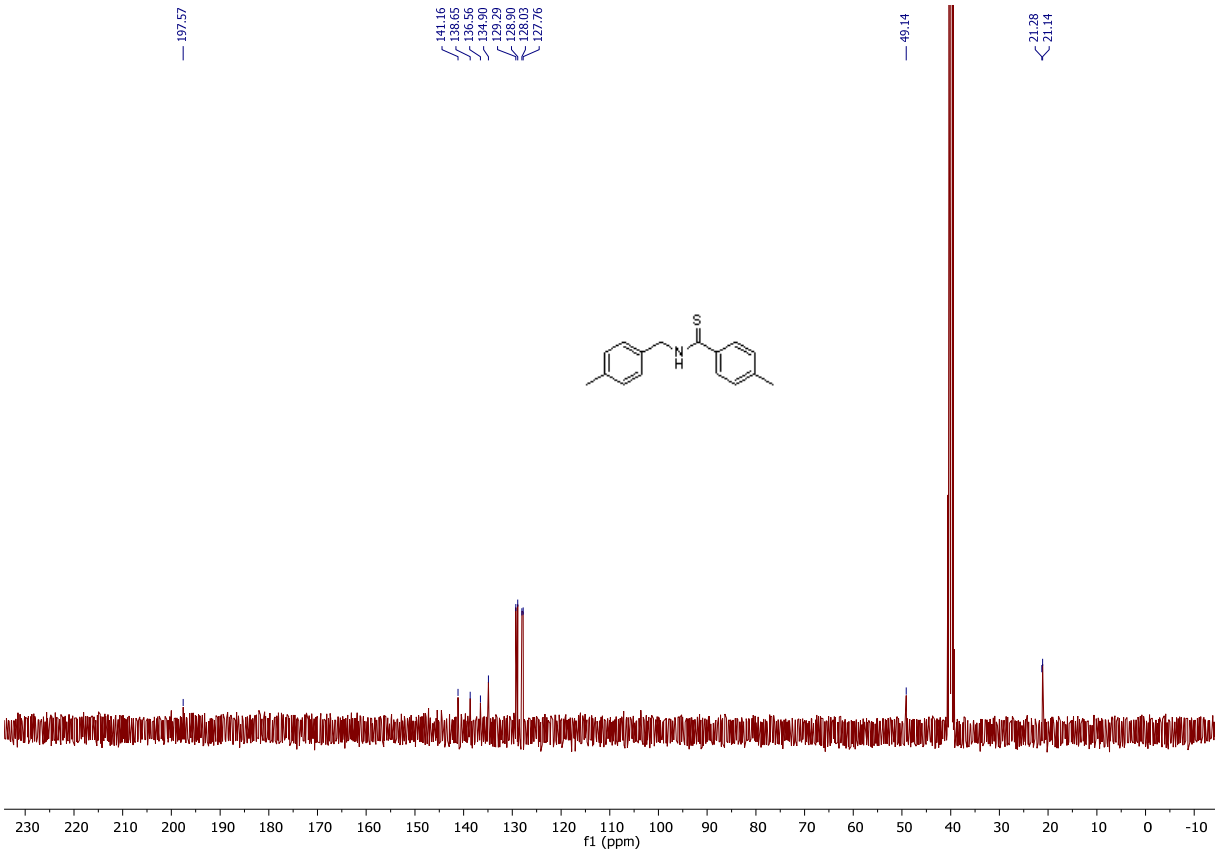
^{13}C NMR



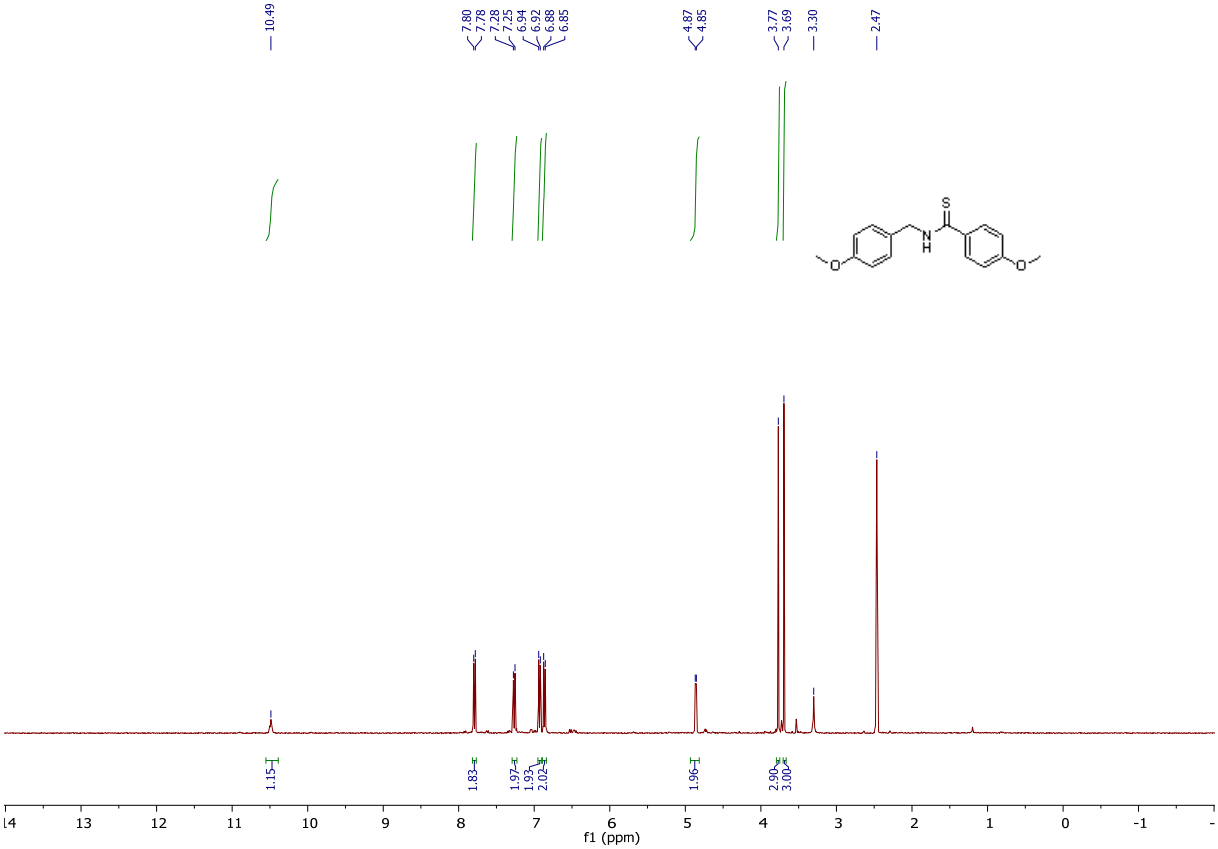
4-Methyl-N-(4-methylbenzyl)benzothioamide (2c). ^{1}H NMR



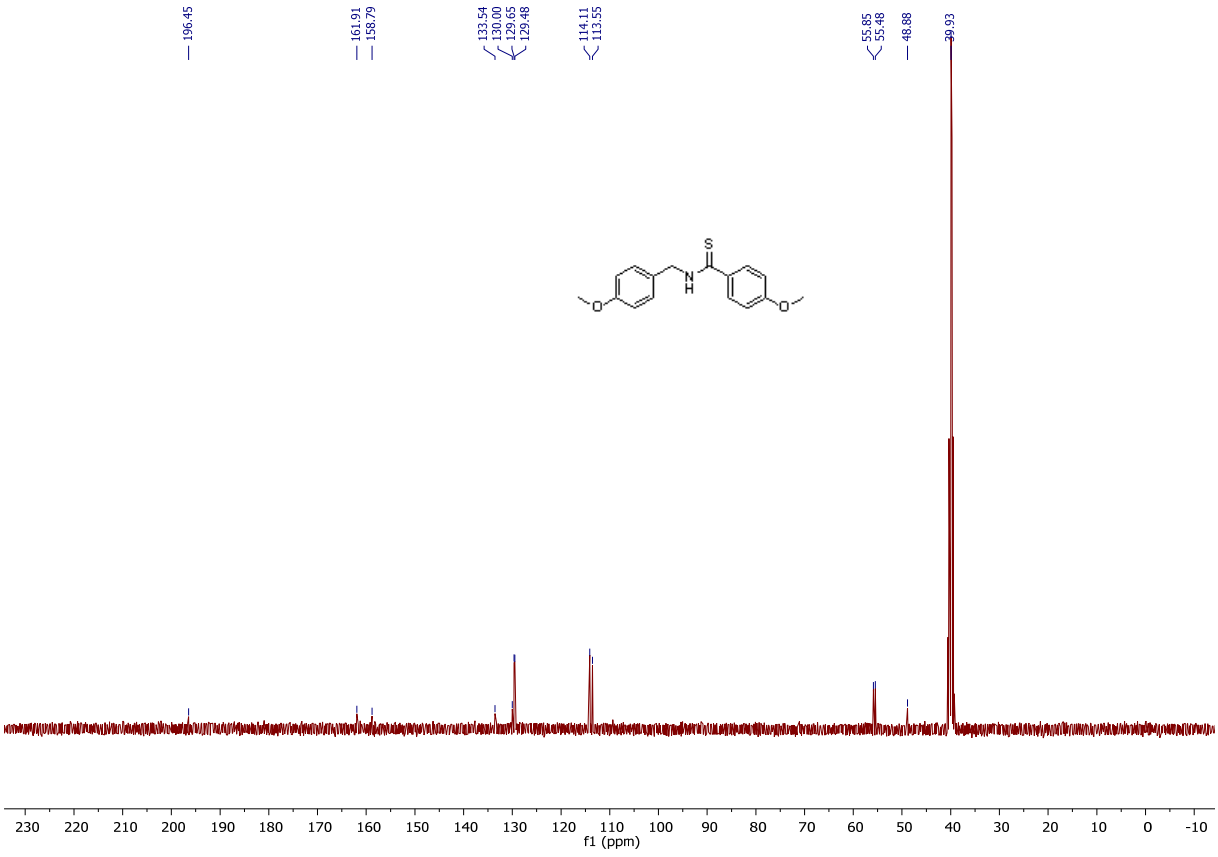
^{13}C NMR



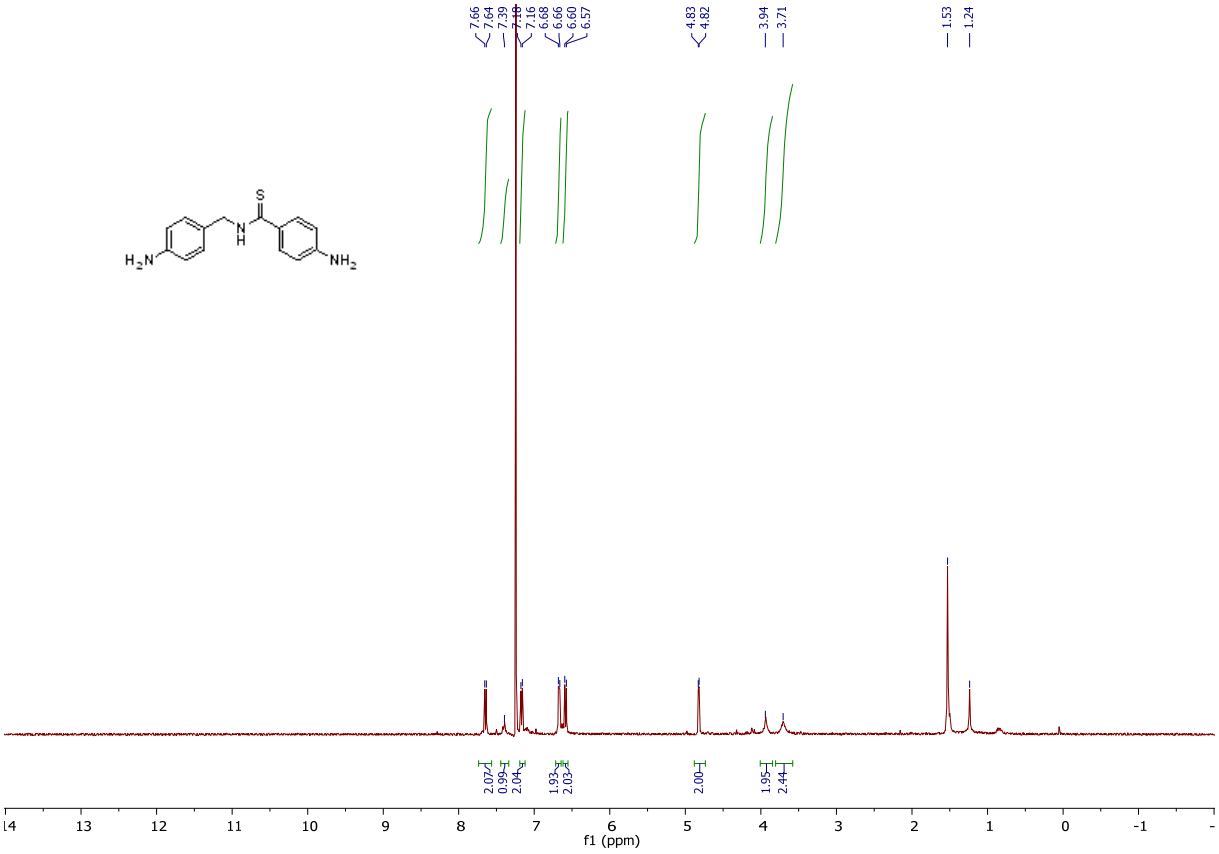
4-Methoxy-N-(4-methoxybenzyl)benzothioamide (2d). ^{1}H NMR



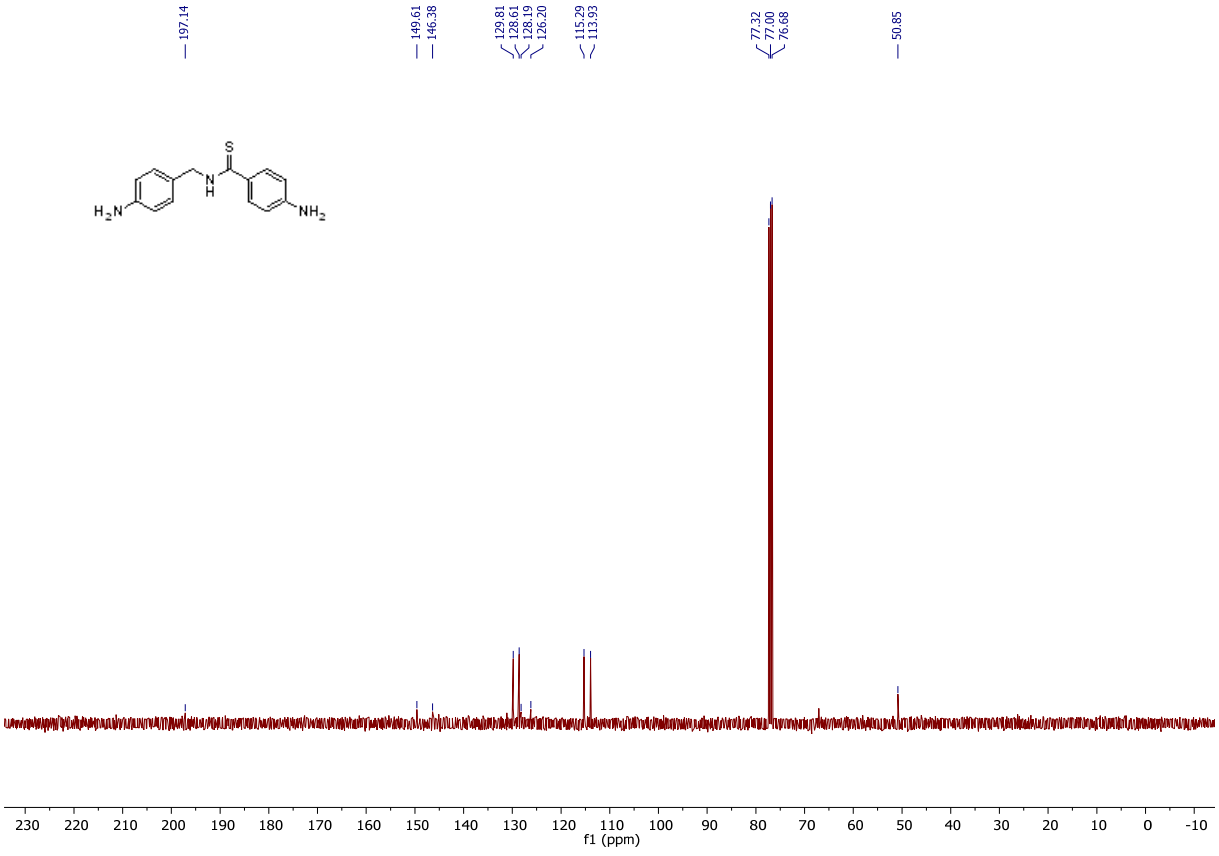
^{13}C NMR



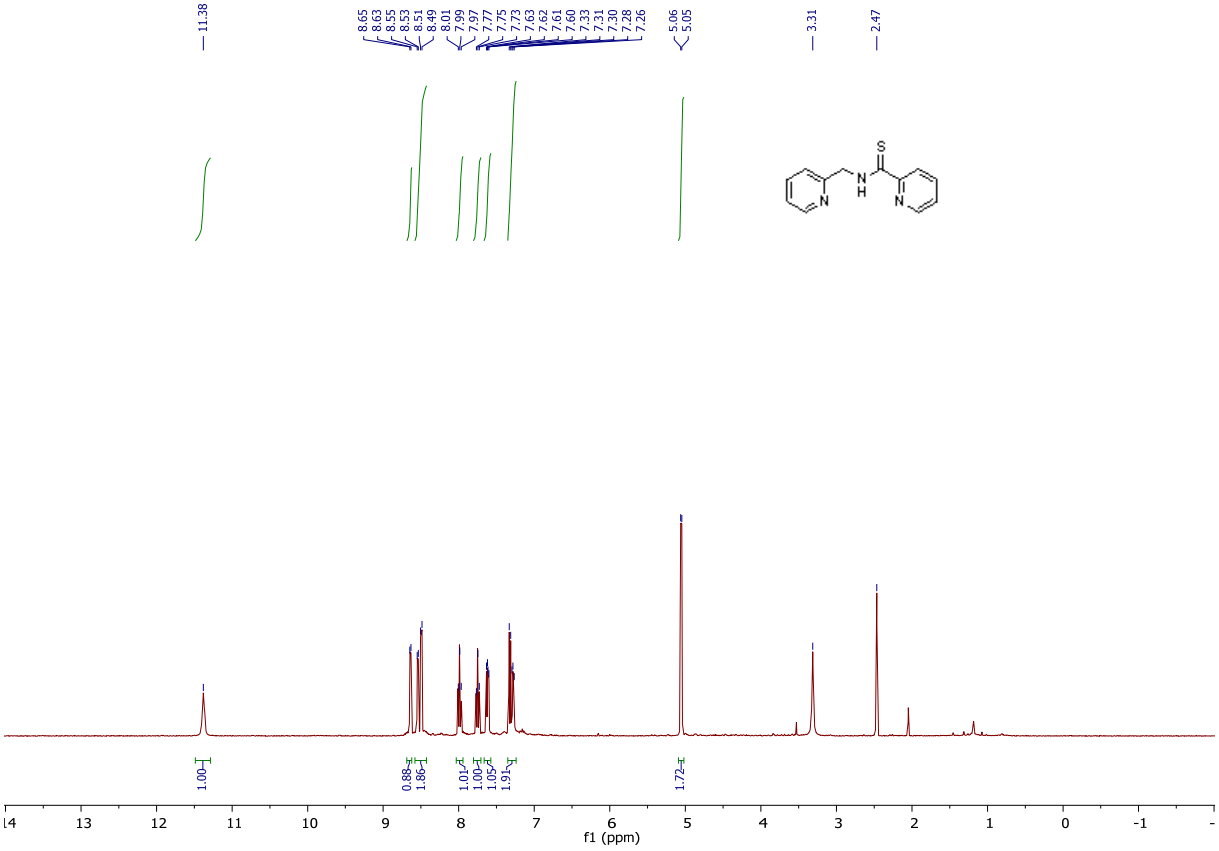
4-Amino-N-(4-aminobenzyl)benzothioamide (2e). ^{1}H NMR



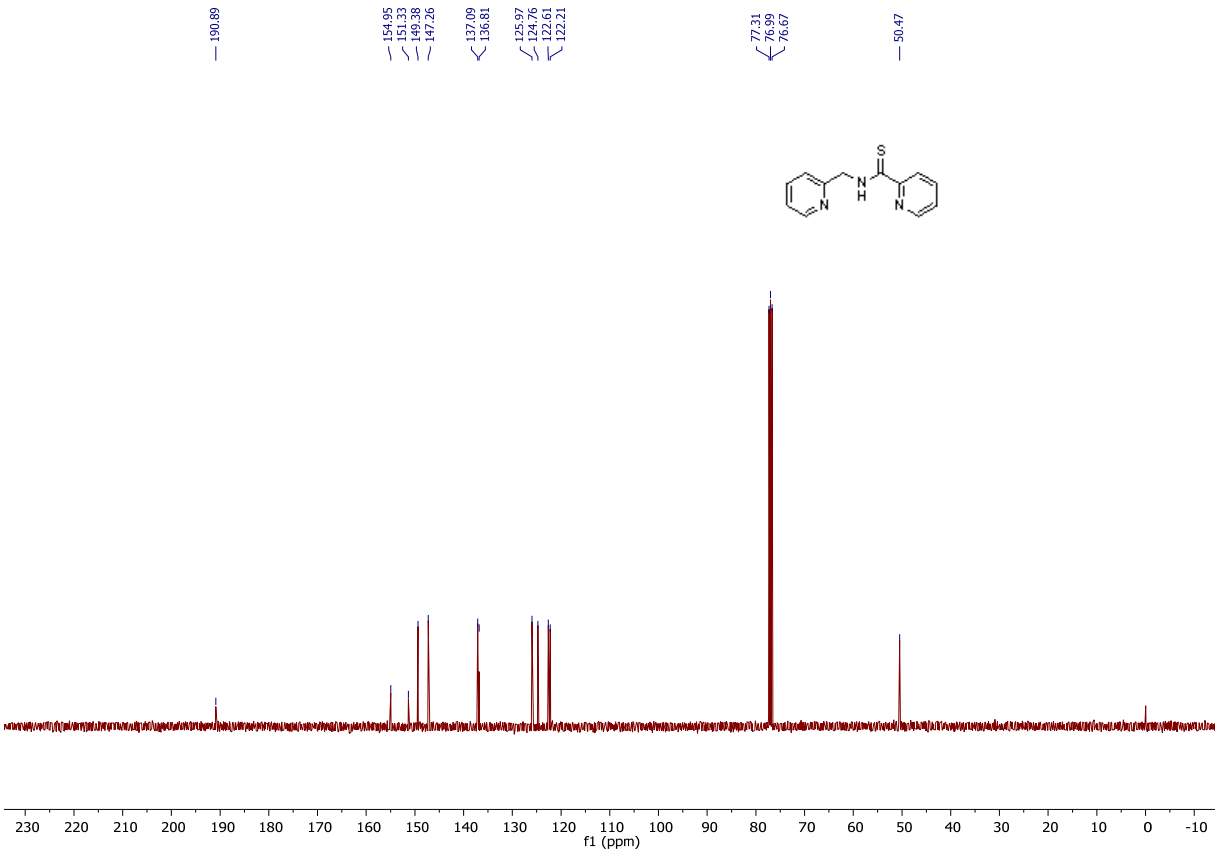
^{13}C NMR



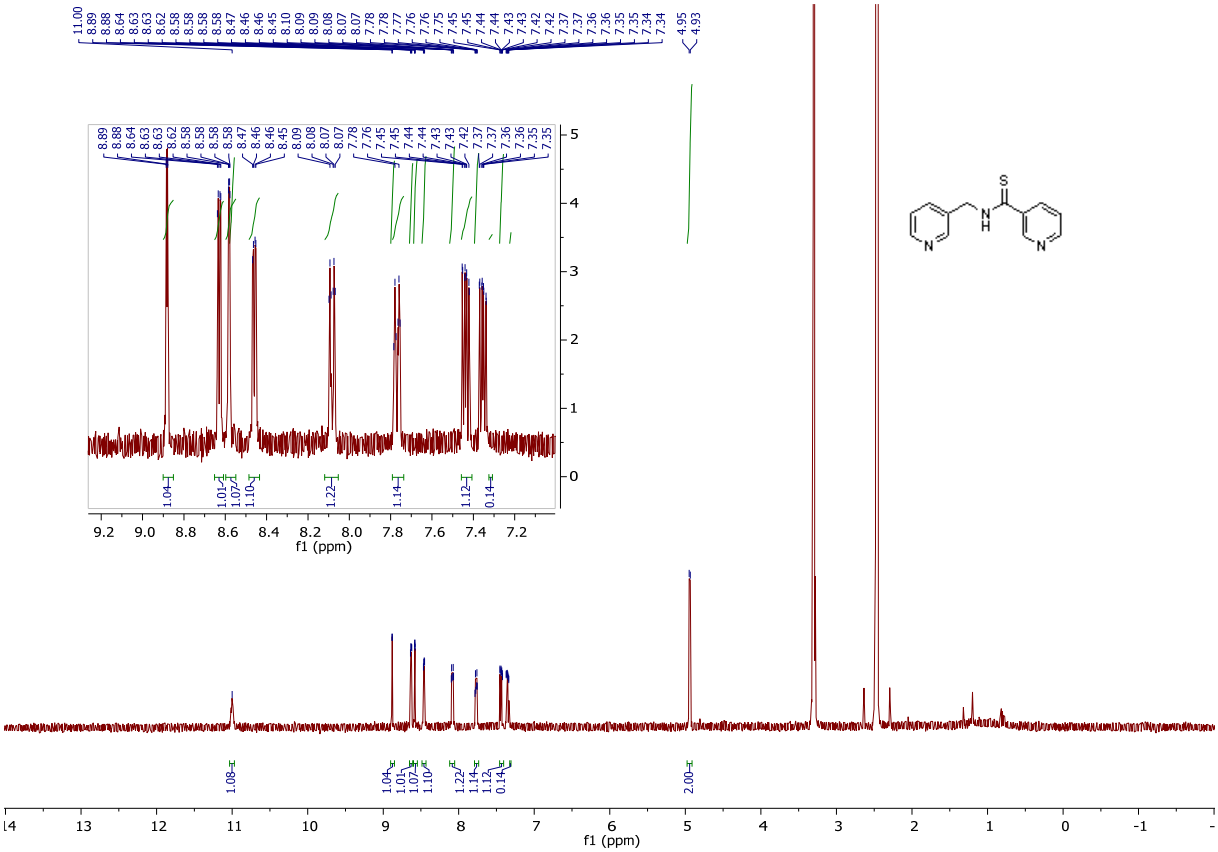
N-(pyridin-2-ylmethyl)pyridine-2-carbothioamide (2f). ^{1}H NMR



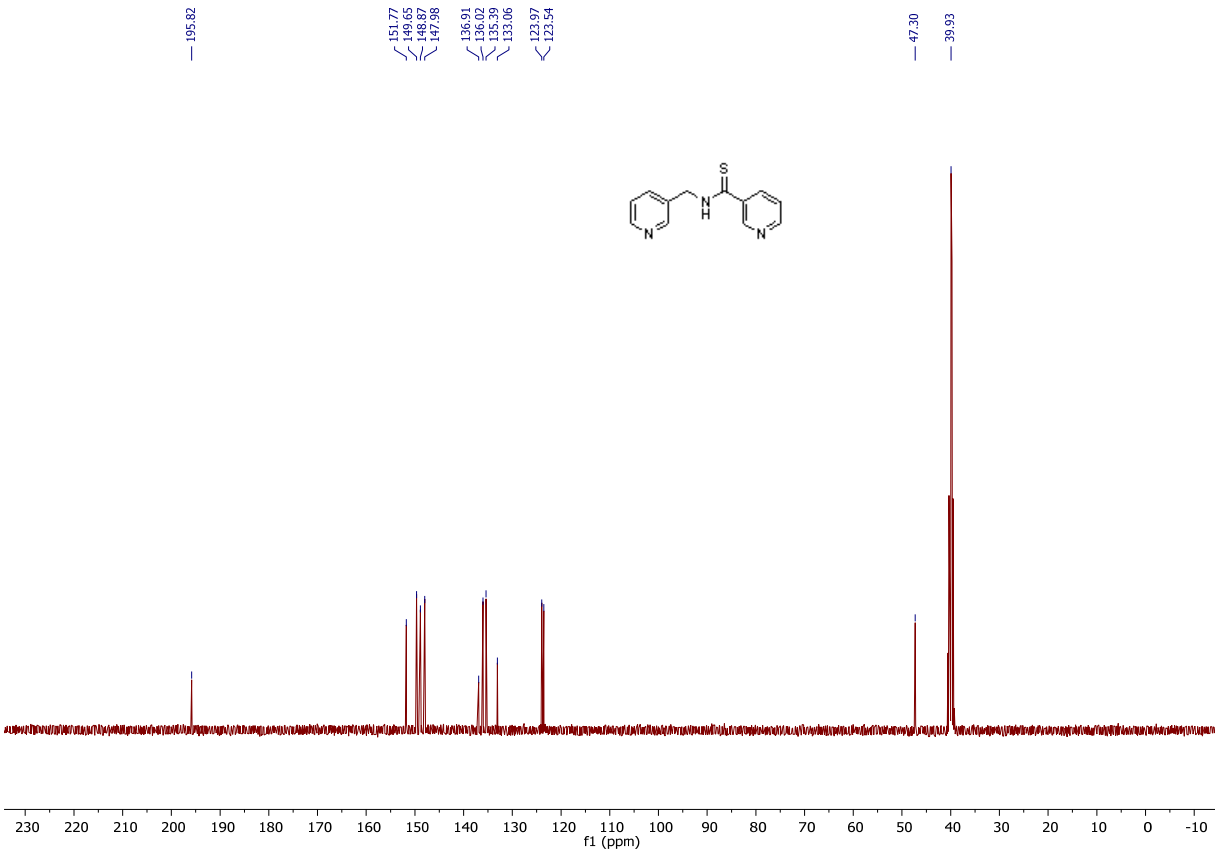
^{13}C NMR



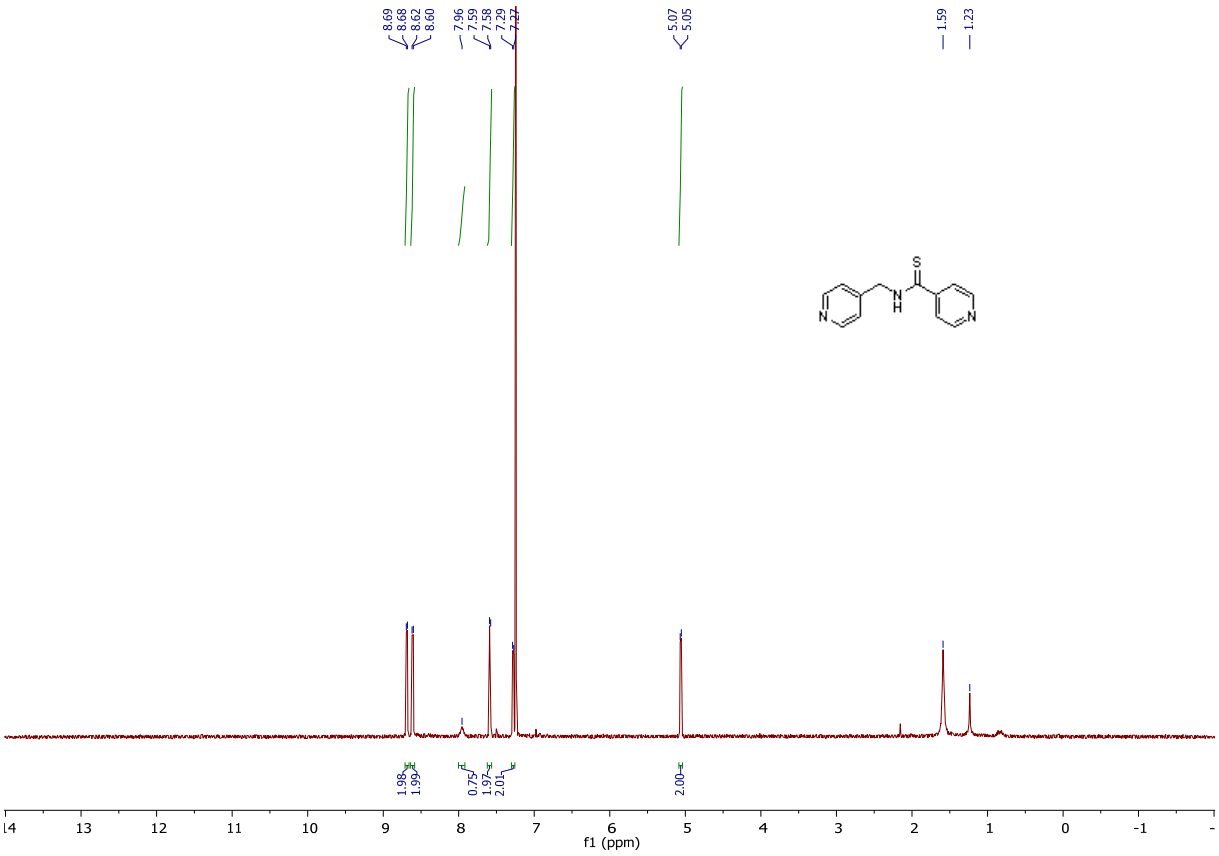
N-(pyridin-3-ylmethyl)pyridine-3-carbothioamide (2g). ^{1}H NMR



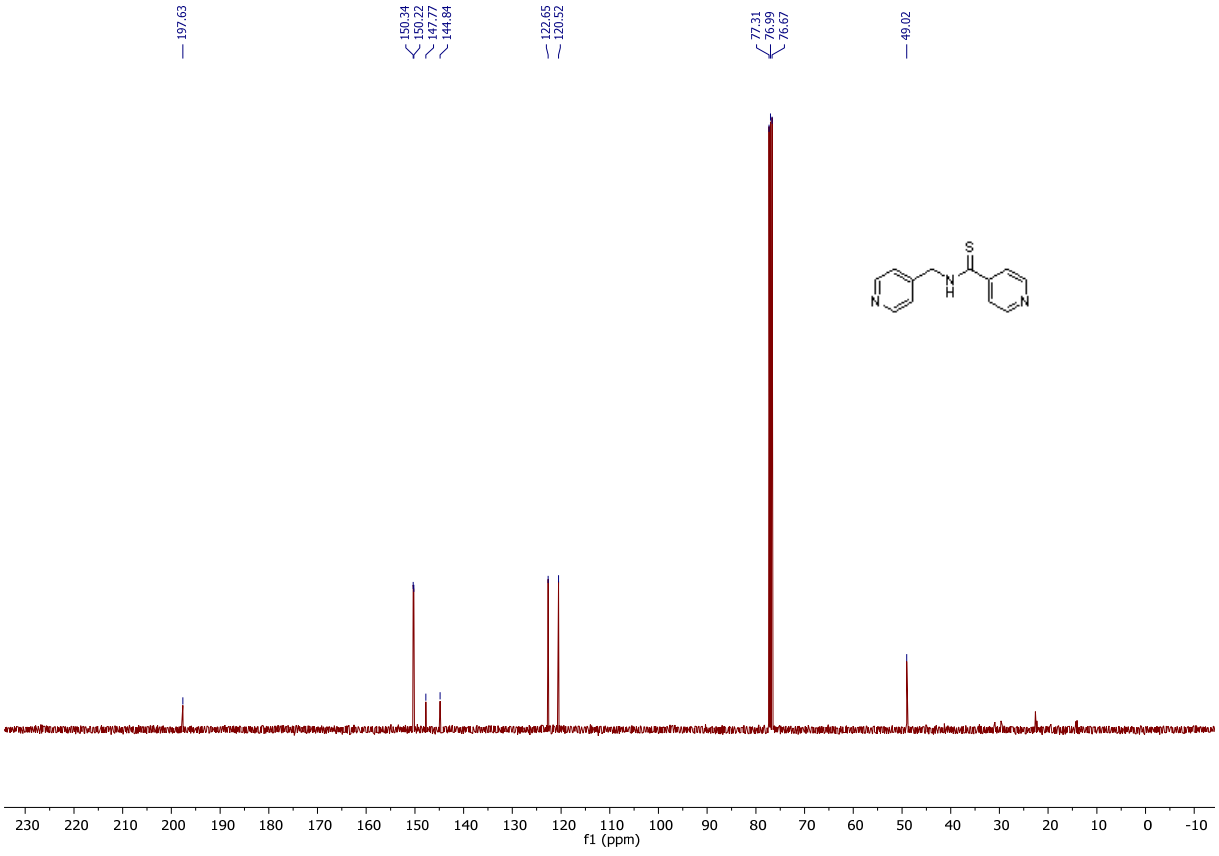
^{13}C NMR



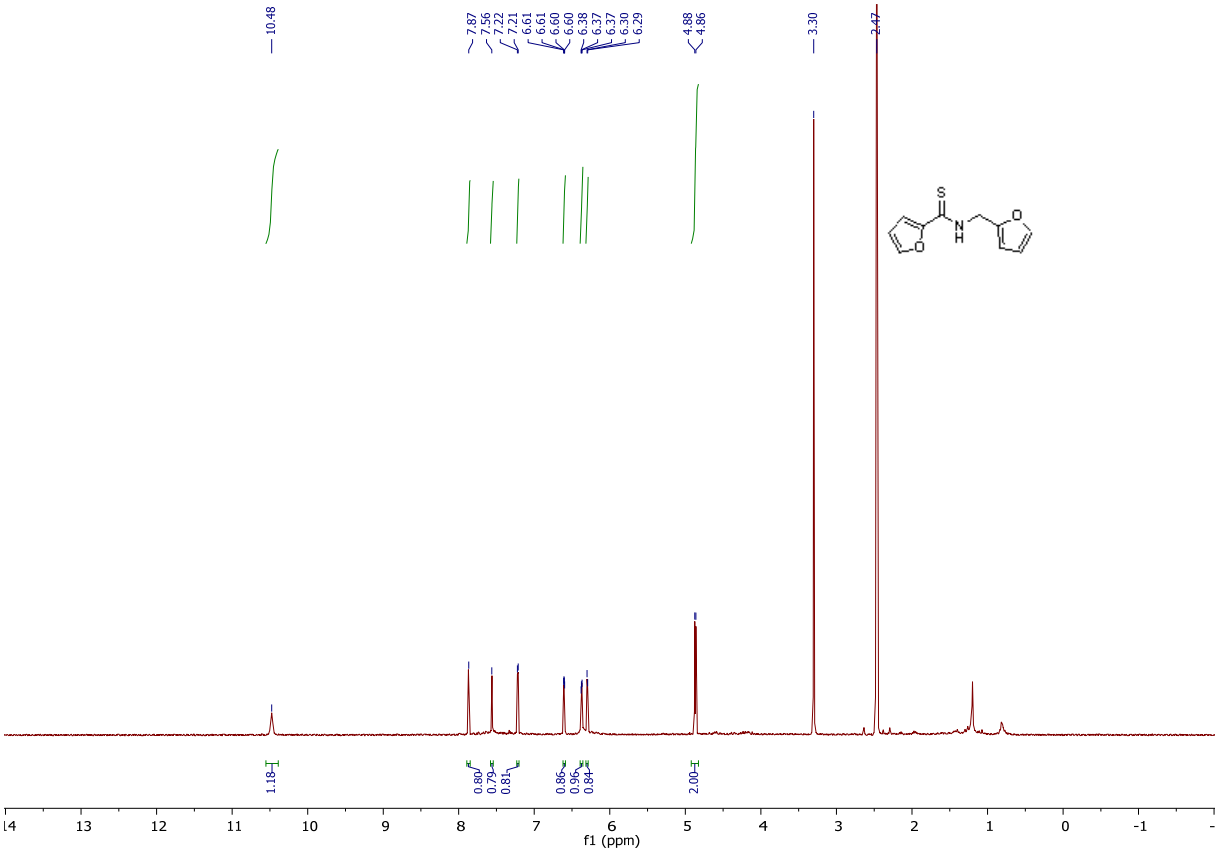
N-(pyridin-4-ylmethyl)pyridine-4-carbothioamide (2h). ^{1}H NMR



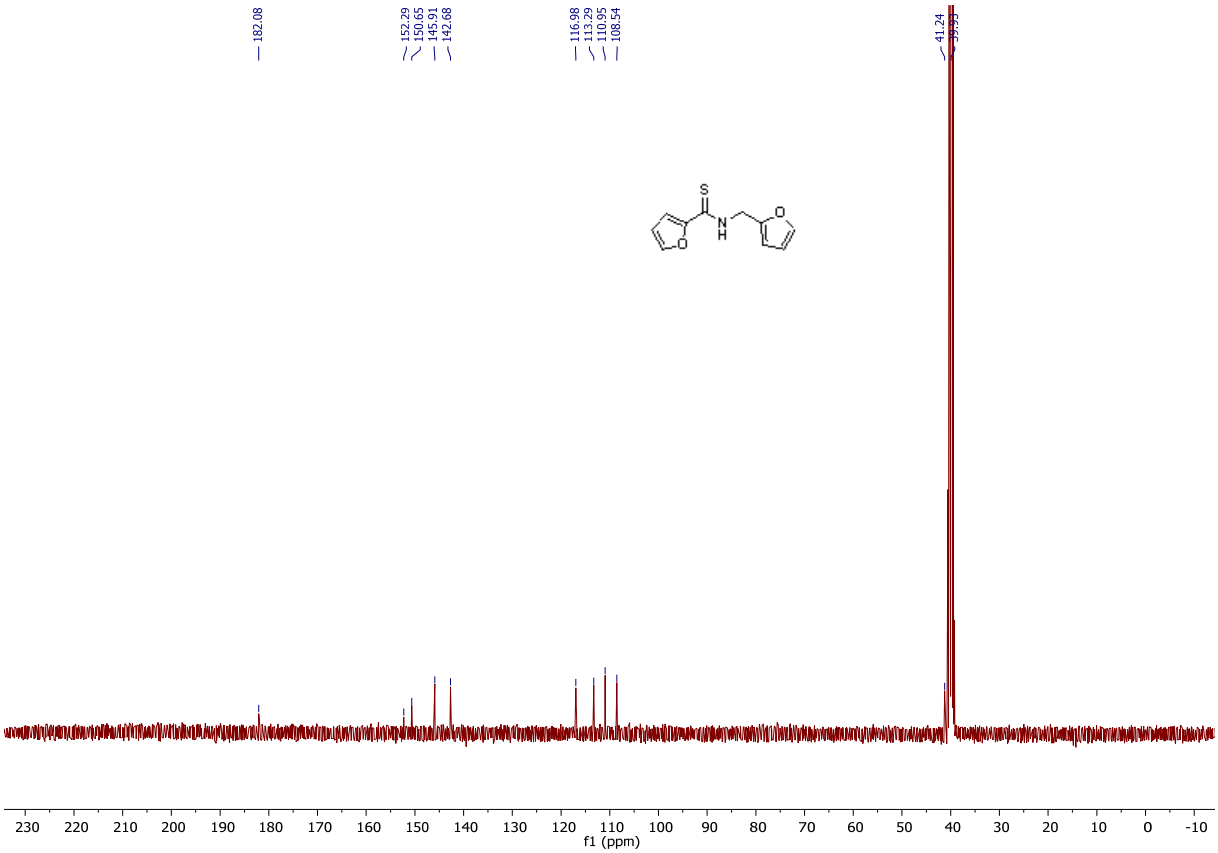
^{13}C NMR



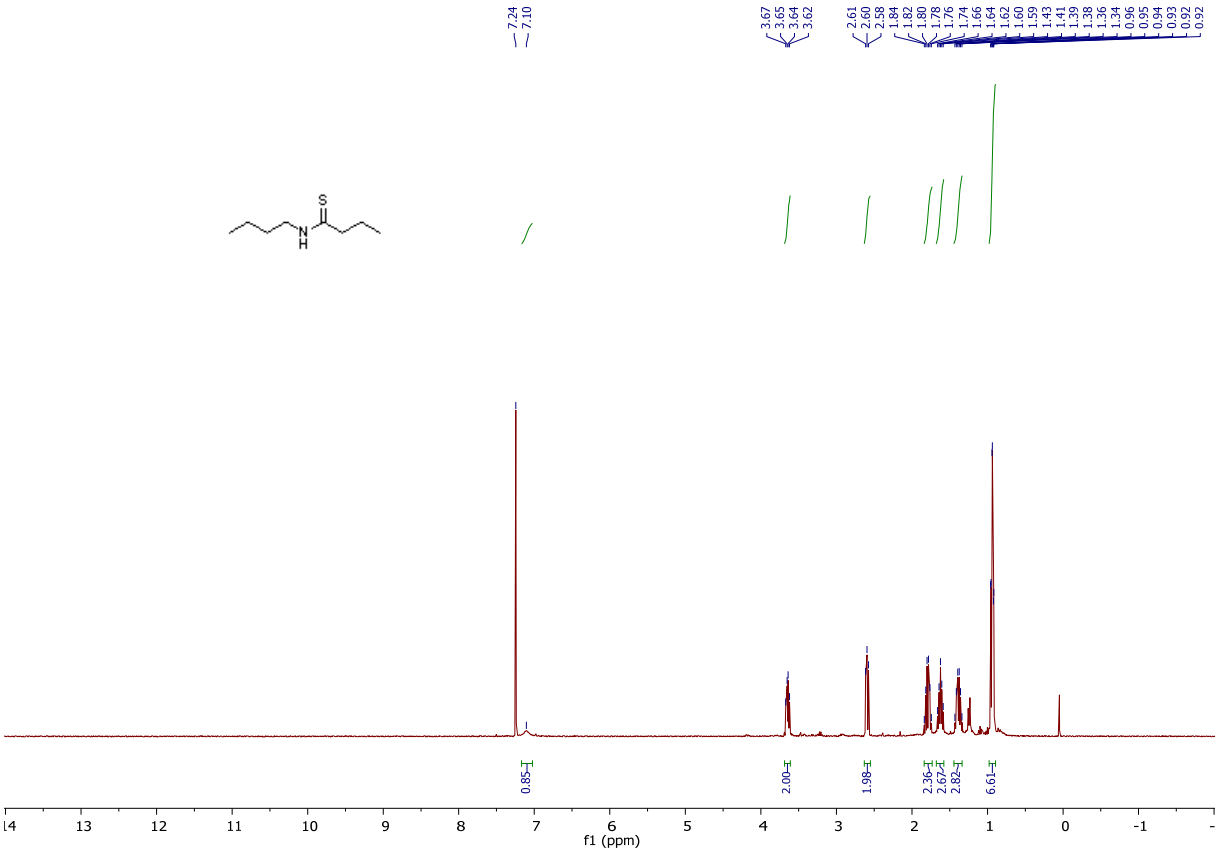
N-(Furan-2-ylmethyl)furan-2-carbothioamide (2i). ^{1}H NMR



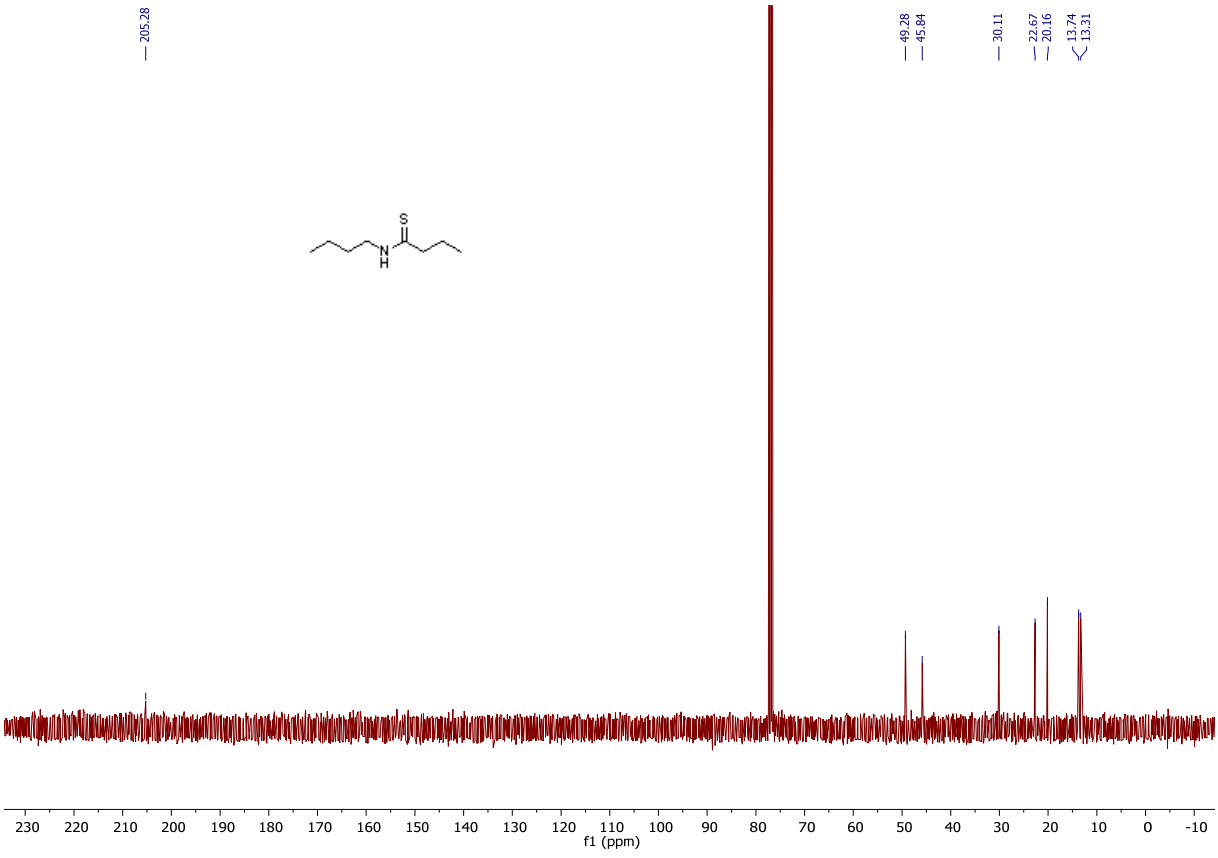
^{13}C NMR



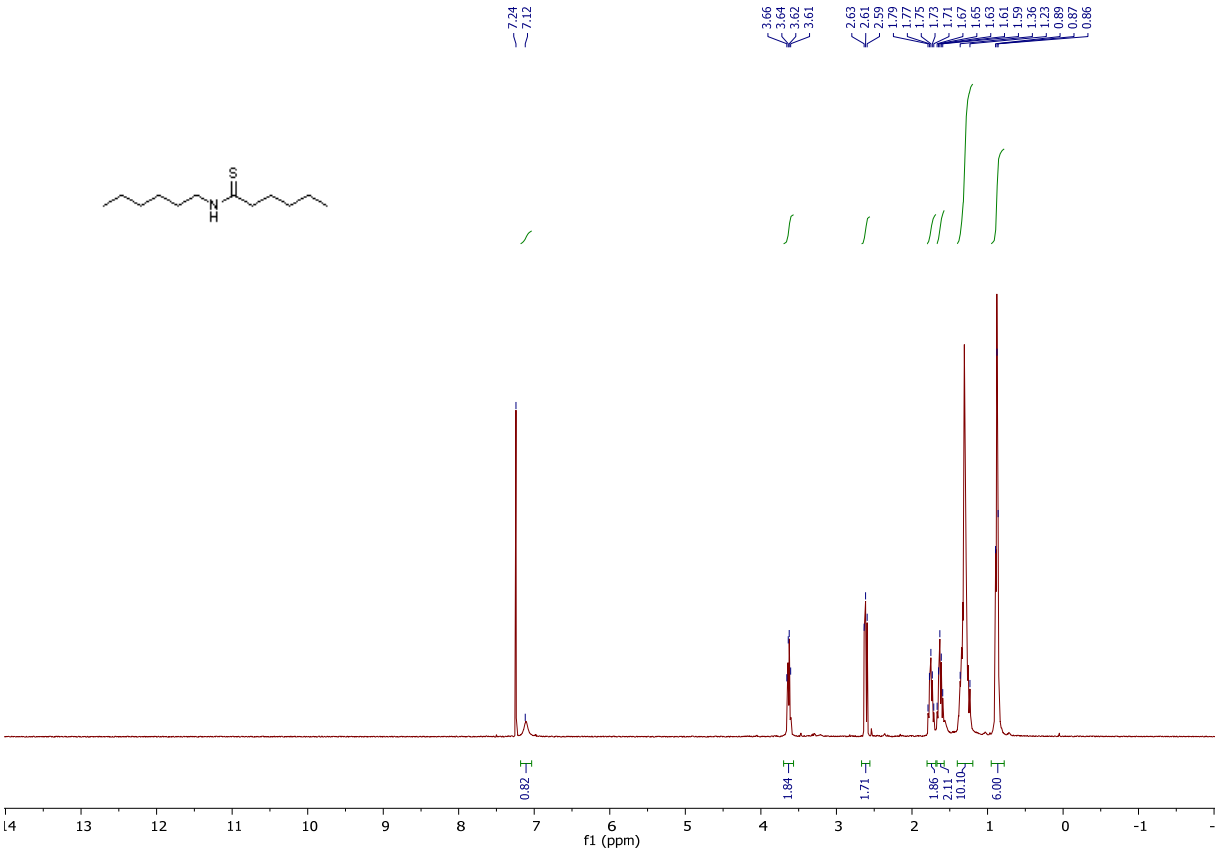
N-butylbutanethioamide (2j).^{1}H NMR



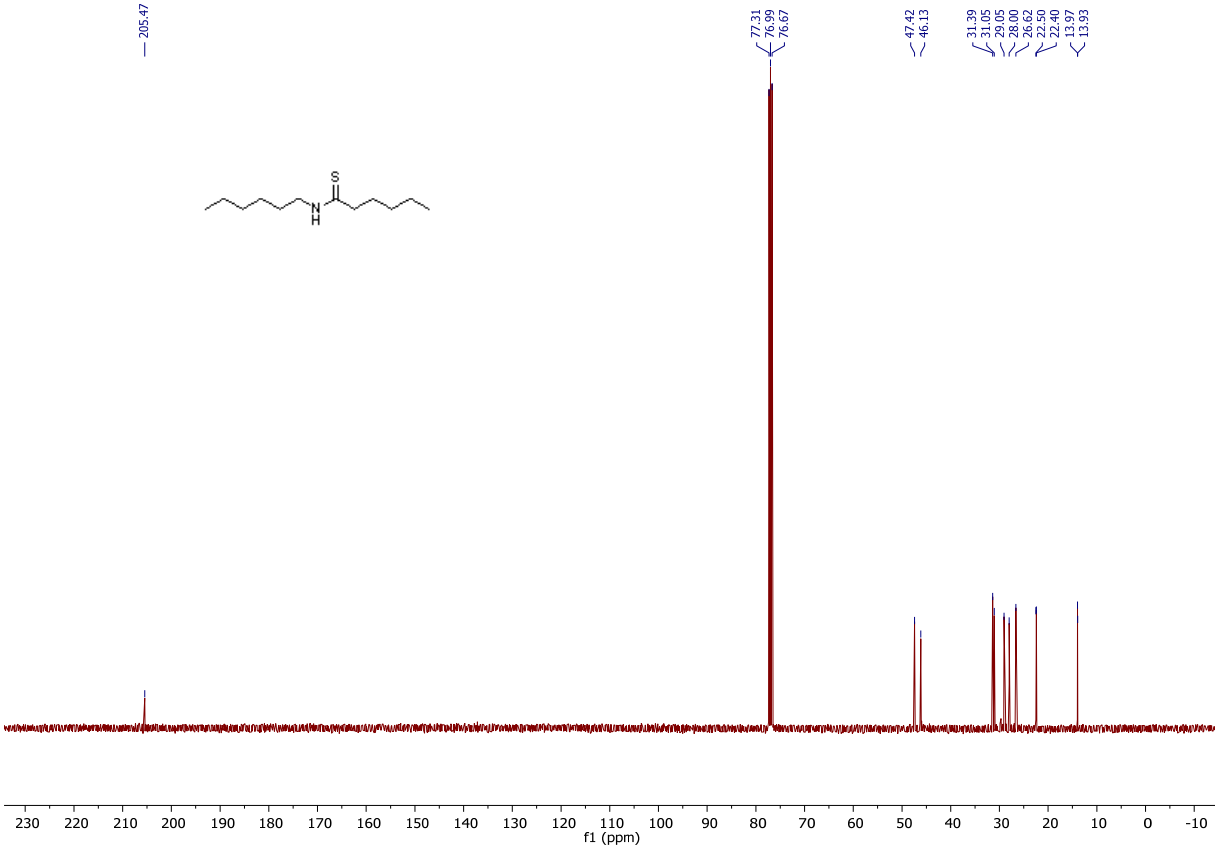
^{13}C NMR



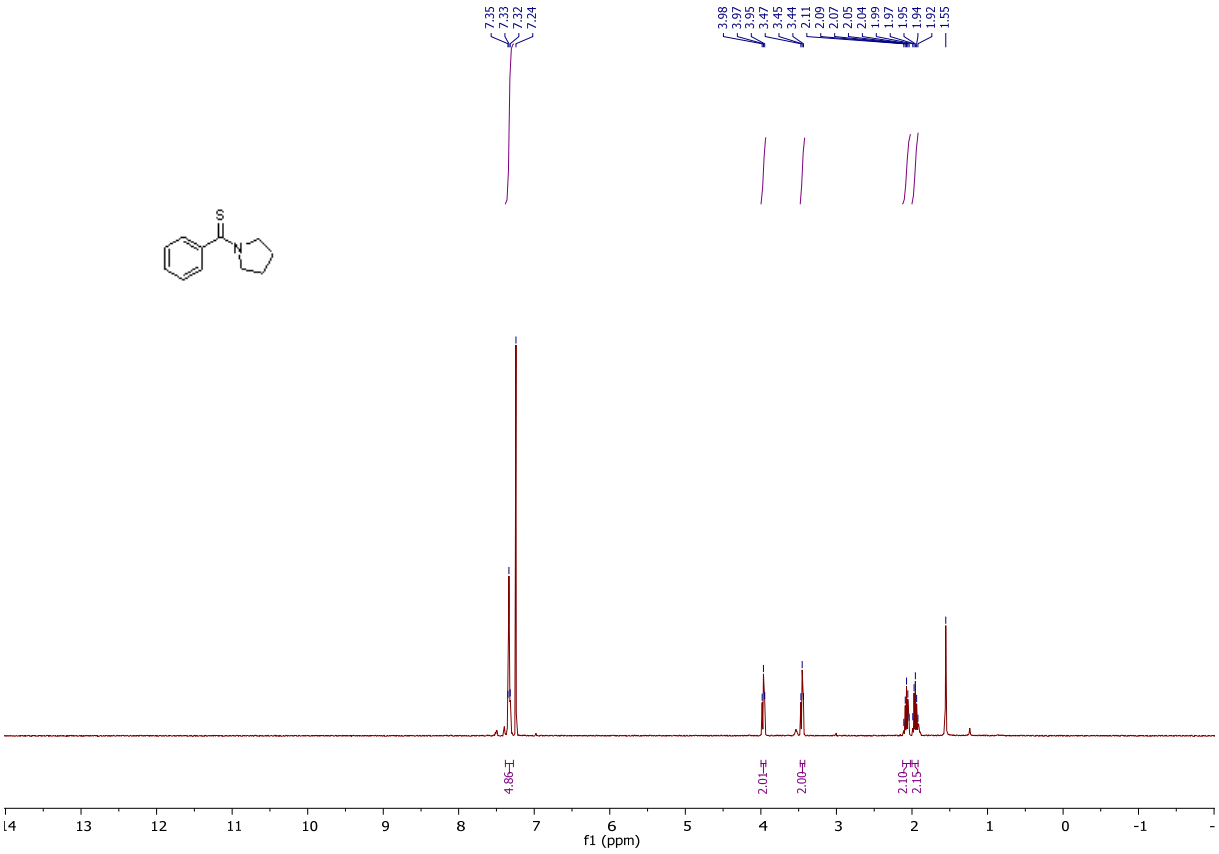
N-hexylhexanethioamide (2k). ^{1}H NMR



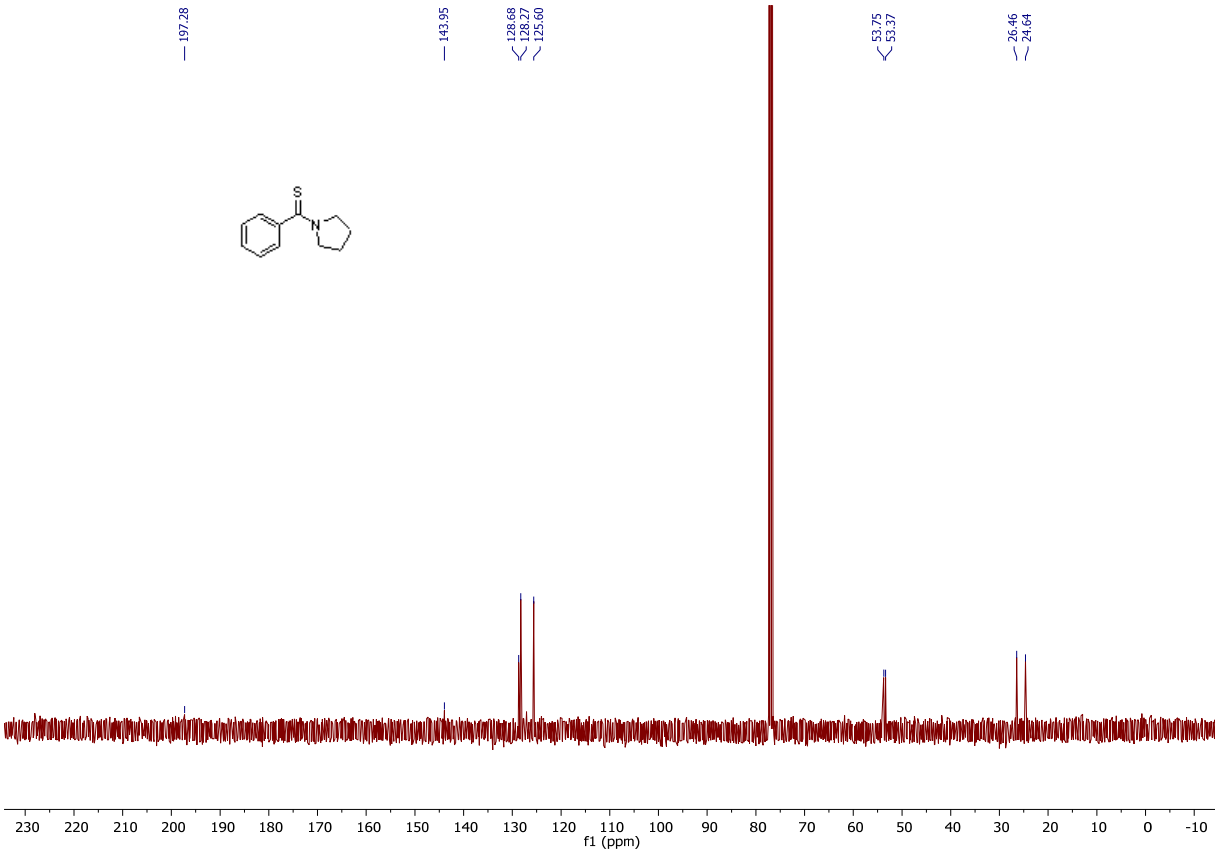
^{13}C NMR



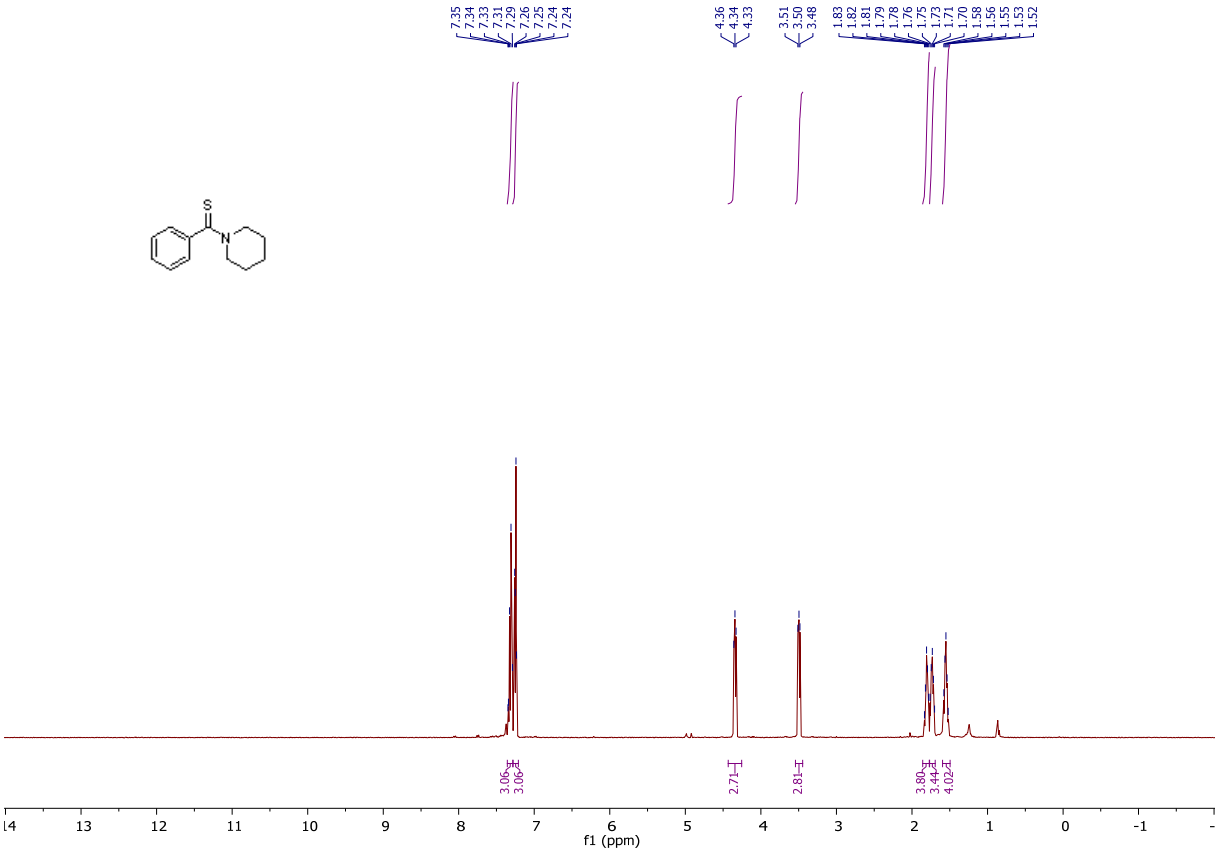
1-Thiobenzoyl pyrrolidine (2m). ^{1}H NMR



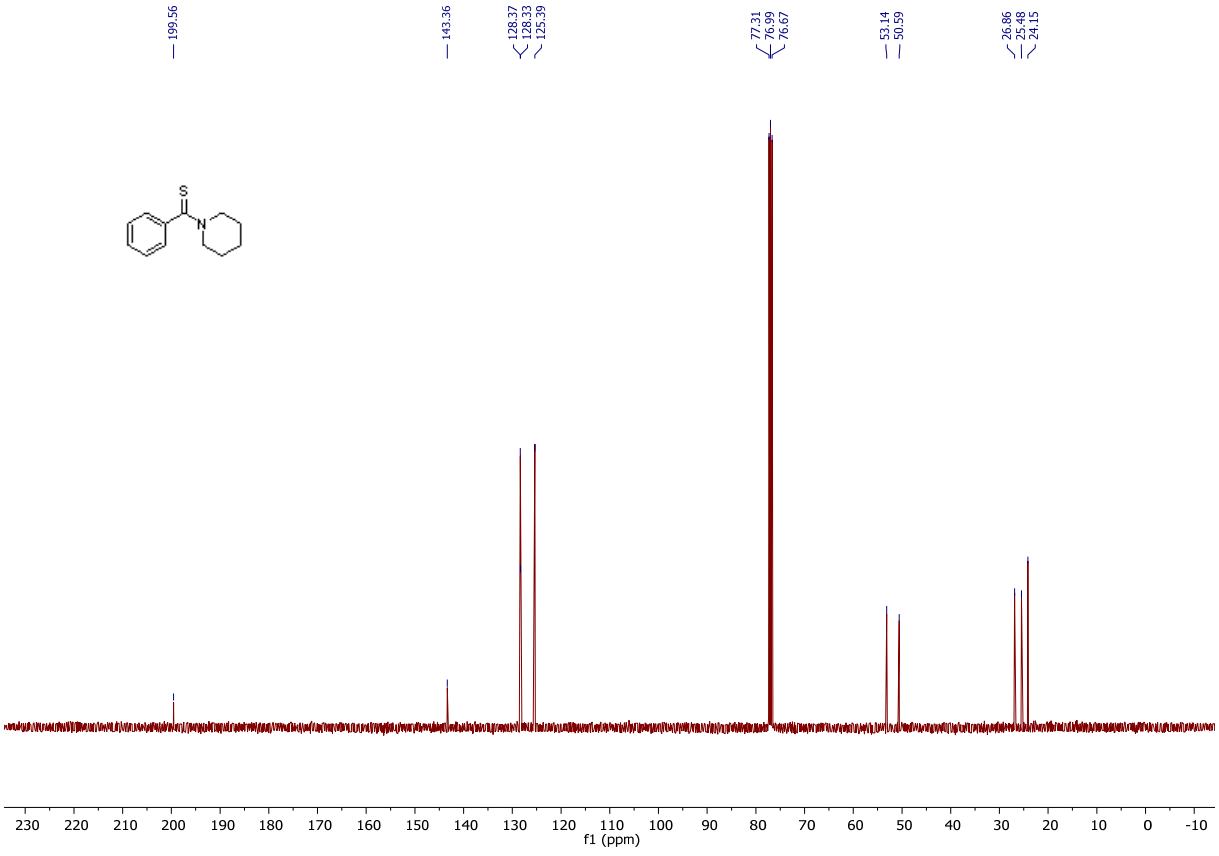
^{13}C NMR



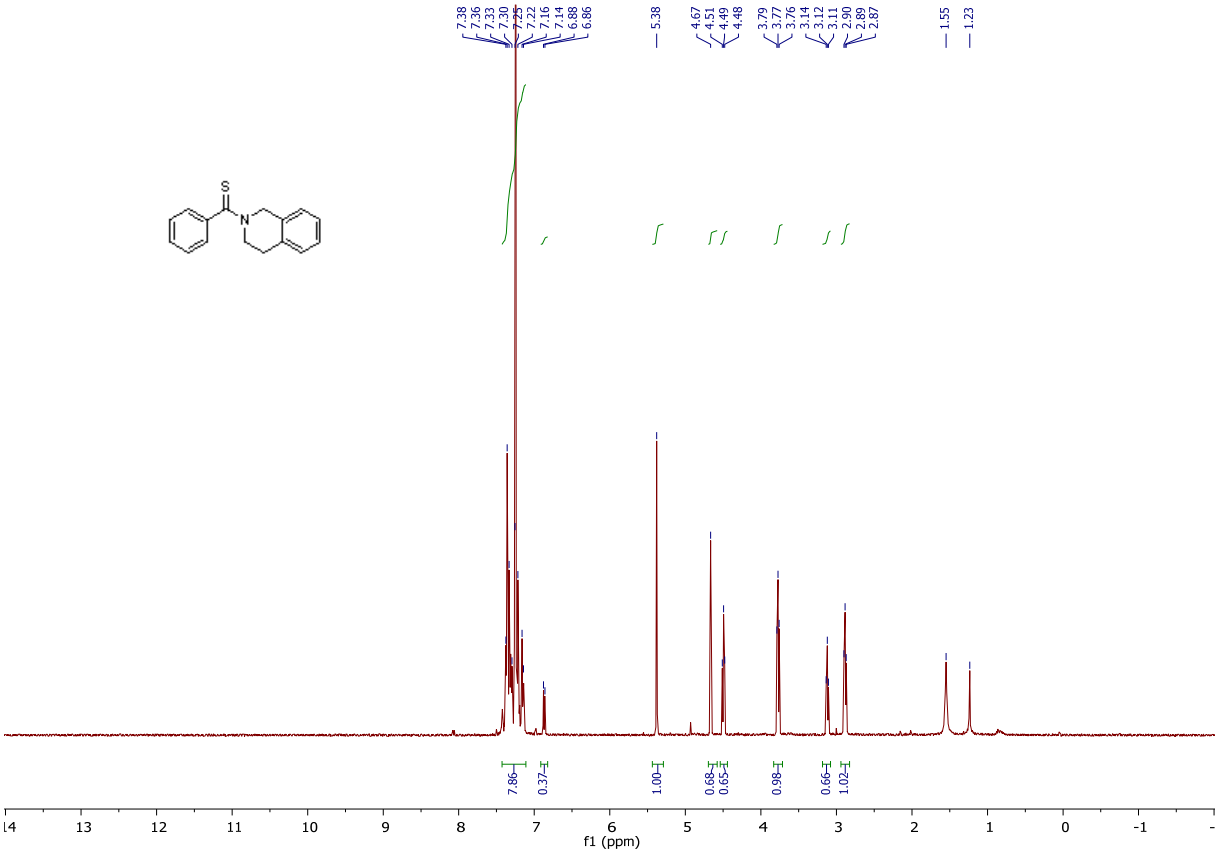
1-Thiobenzoyl piperidine (2n). ^{1}H NMR



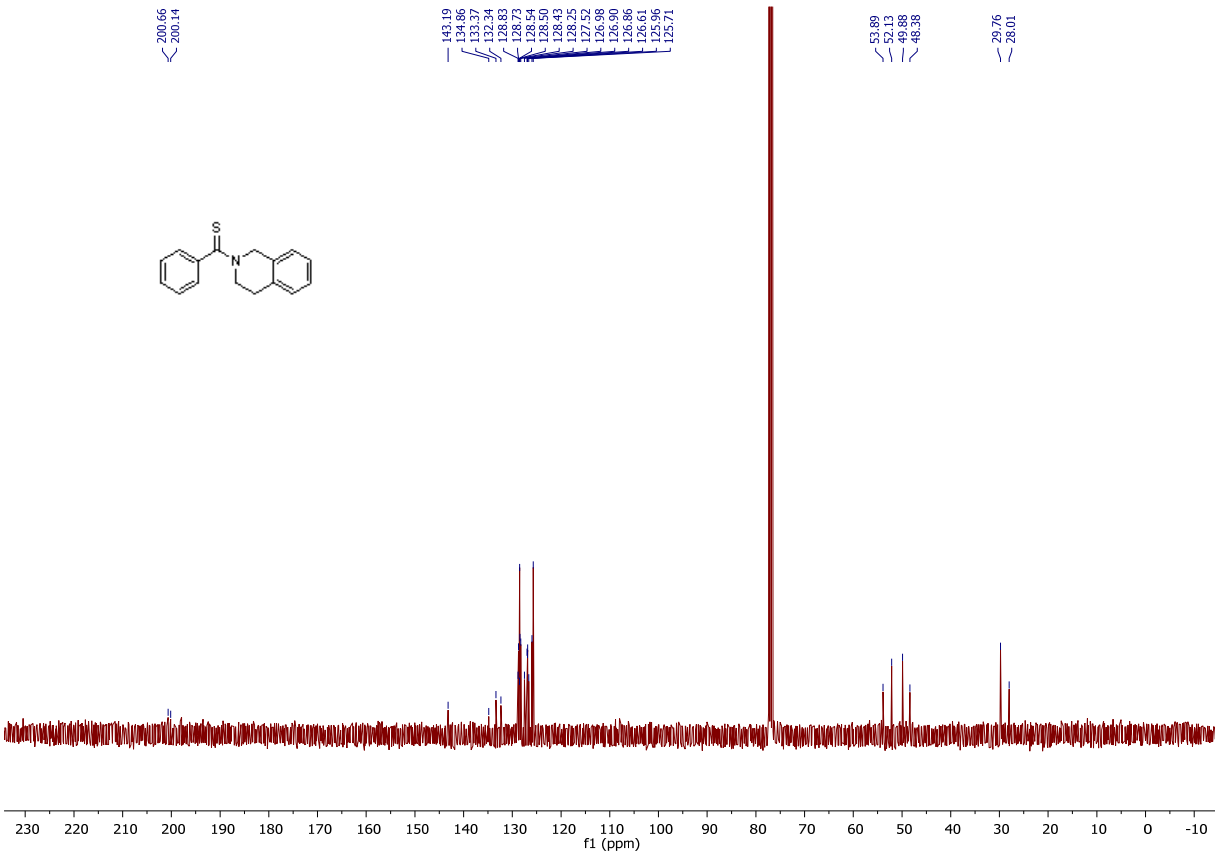
^{13}C NMR



(3,4-Dihydroisoquinolin-2(1H)-yl)(phenyl)methanethione (2o). ^{1}H NMR



^{13}C NMR



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