Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

One-pot synthesis of *S*-alkyl dithiocarbamates via the reaction of *N*-Tosylhydrazones, Carbon Disulfide and Amines

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CONTENTS

Ⅰ.General Information and Materials

All solvents and chemicals (AR grade) were obtained from commercial sources and were used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60–90 ℃ range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on Silicycle silica gel (200–300 mesh). Melting Experimental Section points were obtained using a Yamato melting point apparatus Model MP-21 and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DRX 500 (500 MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. Ms spectra were recorded using a Thermo Scientific TSQ Quantum analyzer. Elemental analyses of new compounds were recorded using a Perkin-Elmer C, H, N analyzer. The known compounds were identified by comparison of their physical and spectral data with those reported in the literature.

Ⅱ.Typical Procedure

General procedure for the three-component reaction of *N*-Tosylhydrazone (1a) with CS_2 and morpholine (2a).

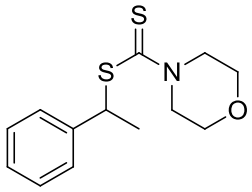
A Schlenk tube with a magnetic stir bar charged with tosylhydrazone **1a** (86.4 mg, 0.3 mmol), CS_2 (45.6 mg, 0.6 mmol), morpholine (52.0 mg, 0.6 mmol), K_2CO_3 (124.0 mg, 0.9 mmol) and dioxane (3 mL). The system was heated at 110 ℃ with stirring for 4 h, The reaction mixture was then allowed to cool to ambient temperature. After concentrated in vacuo, the crude product was purified by column chromatography.

General procedure for the reaction of carbonyl compounds with CS_2 and morpholine in the presence of $TsNHNH_2$.

A Schlenk tube with a magnetic stir bar charged with acetophenone (36.0 mg, 0.3 mmol), 4-methylbenzenesulfonohydrazide (56.0 mg, 0.3 mmol), and dioxane (3 mL). The system was heated at 80 ℃ with stirring for 1.5 h, then K_2CO_3 (124.0 mg, 0.9 mmol), CS_2 (45.6 mg, 0.3 mmol) and morpholine (52.0 mg, 0.6 mmol) were added, the mixture was heated at 110 ℃ with stirring for 5 h. The reaction mixture was then allowed to cool to ambient temperature. After concentrated in vacuo, the crude product was purified by column chromatography.

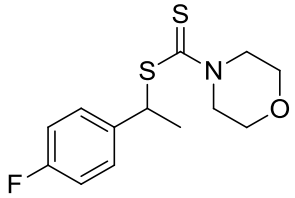
Ⅲ.Spectroscopic Data of Products

1-phenylethyl morpholine-4-carbodithioate (3a)



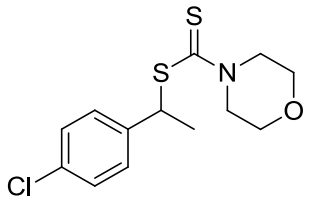
Light yellow liquid; yield: 72.1 mg (90%); R_f = 0.25 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.27-7.25 (m, 1H), 5.31 (q, *J* = 7 Hz, 1H), 4.32 (br, 2H), 3.91 (br, 2H), 3.73 (br, 4H), 1.79 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.62, 141.92, 128.60, 127.87, 127.56, 66.25, 50.92, 22.06.
GC-MS (EI, 70 eV): *m/z* = 267.
Anal. Calcd for $C_{13}H_{17}NOS_2$: C, 58.39; H, 6.41; N, 5.24. Found: C, 58.43; H, 6.45; N, 5.20.

1-(4-fluorophenyl)ethyl morpholine-4-carbodithioate (3b)



Yellow solid; yield: 61.6 mg (72%); mp 93-94 ^{o}C; R_f = 0.22 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.36 (m, 2H), 7.01-6.97 (m, 2H), 5.28 (q, *J* = 6.5 Hz, 1H), 4.28 (br, 2H), 3.90 (br, 2H), 3.71 (br, 4H), 1.75 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.24, 162.01 (*J* = 245 Hz), 137.90, 129.47 (*J* = 8 Hz), 115.39 (*J* = 21 Hz), 66.22, 50.68, 50.08, 22.16.
GC-MS (EI, 70 eV): *m/z* = 285.
Anal. Calcd for $C_{13}H_{16}FNOS_2$: C, 54.71; H, 5.65; N, 4.91. Found: C, 54.60; H, 6.69; N, 4.98.

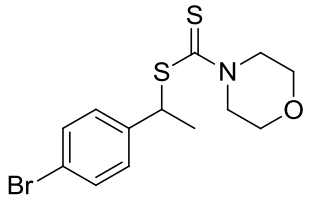
1-(4-chlorophenyl)ethyl morpholine-4-carbodithioate (3c)



Yellow solid; yield: 56.9 mg (63%); mp 90-91 ^{o}C; R_f = 0.25 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 5.28 (q, *J* = 7 Hz, 1H), 4.30 (br, 2H), 3.89 (br, 2H), 3.73 (br, 4H), 1.75 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.06, 140.76, 133.19, 129.24, 128.68, 66.21,

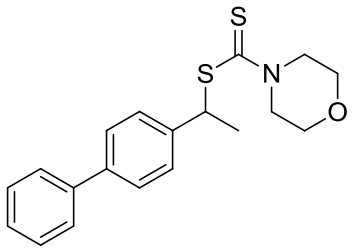
50.75, 50.08, 21.97.
GC-MS (EI, 70 eV): *m/z* = 301.
Anal. Calcd for $C_{13}H_{16}ClNOS_2$: C, 51.73; H, 5.34; N, 4.64. Found: C, 51.64; H, 5.39; N, 4.68.

1-(4-bromophenyl)ethyl morpholine-4-carbodithioate (3d)



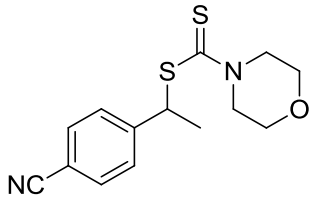
Yellow solid; yield: 69.1 mg (67%); mp 61-62 ^{o}C; R_f = 0.23 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 5.26 (q, *J* = 7 Hz, 1H), 4.30 (br, 2H), 3.89 (br, 2H), 3.73 (br, 4H), 1.74 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.02, 141.32, 131.63, 129.59, 121.32, 66.15, 51.04, 50.12, 21.92.
GC-MS (EI, 70 eV): *m/z* = 345.
Anal. Calcd for $C_{13}H_{16}BrNOS_2$: C, 45.09; H, 4.66; N, 4.04. Found: C, 45.14; H, 4.69; N, 4.01.

1-([1,1'-biphenyl]-4-yl)ethyl morpholine-4-carbodithioate (3e)



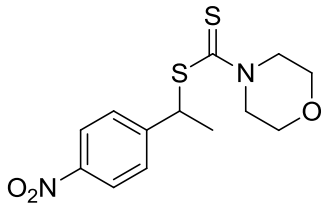
Yellow solid; yield: 55.6 mg (54%); mp 117-118 ^{o}C; R_f = 0.19 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60-7.56 (m, 4H), 7.51 (d, *J* = 8 Hz, 2H), 7.46-7.43 (m, 2H), 7.37-7.34 (m, 1H), 5.38 (q, *J* = 7 Hz, 1H), 4.34 (br, 2H), 3.93 (br, 2H), 3.75 (br, 4H), 1.84 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.53, 141.00, 140.71, 140.48, 128.82, 128.31, 127.34, 127.11, 66.31, 50.65, 22.04.
GC-MS (EI, 70 eV): *m/z* = 343.
Anal. Calcd for $C_{19}H_{21}NOS_2$: C, 66.43; H, 6.16; N, 4.08. Found: C, 66.51; H, 6.19; N, 4.00.

1-(4-cyanophenyl)ethyl morpholine-4-carbodithioate (3f)



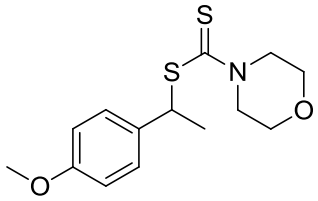
Yellow solid; yield: 70.1 mg (80%); mp 99-100 ^{o}C; R_f = 0.06 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H), 5.34 (q, *J* = 7.5 Hz, 1H), 4.27 (br, 2H), 3.89 (br, 2H), 3.73 (br, 4H), 1.73 (d, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.25, 148.16, 132.30, 128.68, 118.76, 111.10, 66.20, 51.10, 50.07, 21.67.
GC-MS (EI, 70 eV): *m/z* = 292.
Anal. Calcd for $C_{14}H_{16}N_2OS_2$: C, 57.50; H, 5.52; N, 9.58. Found: C, 57.52; H, 5.55; N, 9.53.

1-(4-nitrophenyl)ethyl morpholine-4-carbodithioate (3g)



Light yellow liquid; yield: 76.8 mg (82%); R_f = 0.08 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8 Hz, 2H), 7.59 (d, *J* = 8 Hz, 2H), 5.39 (q, *J* = 7 Hz, 1H), 4.29 (br, 2H), 3.90 (br, 2H), 3.73 (br, 4H), 1.76 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.07, 150.35, 147.02, 128.78, 123.73, 66.24, 51.25, 49.78, 21.73.
GC-MS (EI, 70 eV): *m/z* = 312.
Anal. Calcd for $C_{13}H_{16}N_2O_3S_2$: C, 49.98; H, 5.16; N, 8.97. Found: C, 49.91; H, 5.15; N, 9.03.

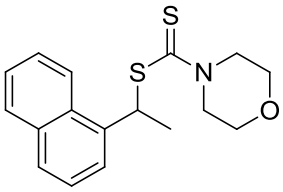
1-(4-methoxyphenyl)ethyl morpholine-4-carbodithioate (3h)



Light yellow liquid; yield: 84.6 mg (95%); R_f = 0.14 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.26 (q, *J* = 7 Hz, 1H), 4.31 (br, 2H), 3.79 (br, 2H), 3.79 (s, 3H), 3.73 (br, 4H), 1.77 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.78, 158.95, 133.79, 128.99, 113.95, 66.28, 55.31, 50.50, 22.11.

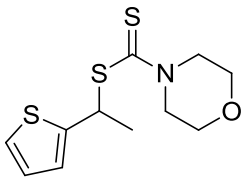
GC-MS (EI, 70 eV): *m/z* = 297.
Anal. Calcd for $C_{14}H_{19}NO_2S_2$: C, 56.53; H, 6.44; N, 4.71. Found: C, 56.45; H, 6.49; N, 4.73.

1-(naphthalen-1-yl)ethyl morpholine-4-carbodithioate (3i)



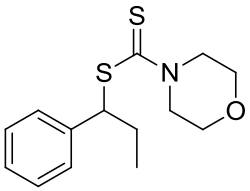
Light yellow liquid; yield: 61.8 mg (65%); R_f = 0.30 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7 Hz, 2H), 7.61-7.58 (m, 1H), 7.54-7.51 (m, 1H), 7.48-7.45 (m, 1H), 6.10 (q, *J* = 7 Hz, 1H), 4.39 (br, 2H), 3.76 (br, 6H), 1.98 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.91, 136.53, 133.98, 131.05, 128.92, 128.62, 126.69, 126.02, 125.23, 125.13, 123.87, 66.25, 66.11, 51.12, 46.95, 21.25.
GC-MS (EI, 70 eV): *m/z* = 317.
Anal. Calcd for $C_{17}H_{19}NOS_2$: C, 64.32; H, 6.03; N, 4.41. Found: C, 64.35; H, 6.09; N, 4.36.

1-(thiophen-2-yl)ethyl morpholine-4-carbodithioate (3j)



Brown liquid; yield: 22.1 mg (27%); R_f = 0.31 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 5 Hz, 1 Hz, 1H), 7.08 (d, *J* = 3.5 Hz, 1H), 6.95-6.93 (m, 1H), 5.60 (q, *J* = 7 Hz, 1H), 4.33 (br, 2H), 3.89 (br, 2H), 3.74 (br, 4H), 1.87 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.03, 145.43, 126.72, 125.32, 124.85, 66.28, 50.59, 46.52, 23.06.
GC-MS (EI, 70 eV): *m/z* = 273.
Anal. Calcd for $C_{11}H_{15}NOS_3$: C, 48.32; H, 5.53; N, 5.12. Found: C, 48.30; H, 5.59; N, 5.16.

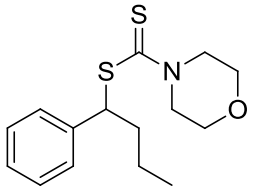
1-phenylpropyl morpholine-4-carbodithioate (3k)



Light yellow liquid; yield: 53.1 mg (63%); R_f = 0.34 (PE-EtOAc, 10:1).

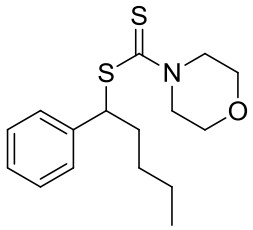
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7 Hz, 2H), 7.35-7.31 (m, 2H), 7.27-7.24 (m, 2H), 5.10 (dd, *J* = 9 Hz, 5.5 Hz, 1H), 4.30 (br, 2H), 3.94 (br, 2H), 3.72 (br, 4H), 2.27-2.20 (m, 1H), 2.06-2.00 (m, 1H), 0.94 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.73, 140.73, 128.54, 128.42, 127.47, 66.27, 57.45, 50.72, 29.51, 12.27.
GC-MS (EI, 70 eV): *m/z* = 281.
Anal. Calcd for $C_{14}H_{19}NOS_2$: C, 59.75; H, 6.80; N, 4.98. Found: C, 59.71; H, 6.83; N, 4.96.

1-phenylbutyl morpholine-4-carbodithioate (3l)



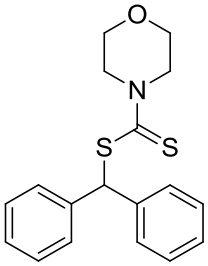
Light yellow liquid; yield: 54.0 mg (61%); R_f = 0.32 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.26-7.24 (m, 1H), 5.21 (dd, *J* = 9.5 Hz, 6 Hz, 1H), 4.29 (br, 2H), 3.93 (br, 2H), 3.71 (br, 4H), 2.21-2.14 (m, 1H), 2.03-1.95 (m, 1H), 1.42-1.26 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.70, 141.11, 128.54, 128.34, 127.43, 66.30, 55.69, 50.76, 38.37, 20.81, 13.80.
GC-MS (EI, 70 eV): *m/z* = 295.
Anal. Calcd for $C_{15}H_{21}NOS_2$: C, 60.98; H, 7.16; N, 4.74. Found: C, 60.91; H, 7.13; N, 4.76.

1-phenylpentyl morpholine-4-carbodithioate (3m)



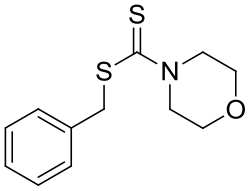
Light yellow liquid; yield: 60.3 mg (65%); R_f = 0.32 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.5 Hz, 2H), 7.35-7.31 (m, 2H), 7.27-7.24 (m, 2H), 5.17 (dd, *J* = 9 Hz, 6 Hz, 1H), 4.24 (br, 2H), 3.94 (br, 2H), 3.72 (br, 4H), 2.23-2.16 (m, 1H), 2.03-1.96 (m, 1H), 1.37-1.22 (m, 4H), 0.87 (t, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.74, 141.09, 128.54, 128.53, 128.34, 127.42, 66.28, 55.94, 50.67, 36.00, 29.73, 22.41, 13.99.
GC-MS (EI, 70 eV): *m/z* = 309.
Anal. Calcd for $C_{16}H_{23}NOS_2$: C, 62.09; H, 7.49; N, 4.53. Found: C, 62.01; H, 7.53; N, 4.56.

benzhydryl morpholine-4-carbodithioate (3n)



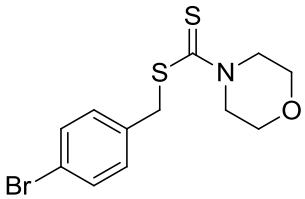
Yellow solid; yield: 59.2 mg (60%); mp 135-137 ^{o}C; R_f = 0.21 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42-7.40 (m, 4H), 7.34-7.31 (m, 4H), 7.27-7.24 (m, 2H), 6.64 (s, 1H), 4.27 (br, 2H), 4.01 (br, 2H), 3.74 (br, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.81, 140.42, 128.93, 128.52, 127.34, 66.27, 59.83, 51.23.
GC-MS (EI, 70 eV): *m/z* = 329.
Anal. Calcd for $C_{18}H_{19}NOS_2$: C, 65.62; H, 5.81; N, 4.25. Found: C, 65.61; H, 5.83; N, 4.26.

benzyl morpholine-4-carbodithioate (3o)



Yellow solid; yield: 69.8 mg (92%); mp 59-60 ^{o}C; R_f = 0.19 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7 Hz, 2H), 7.34-7.27 (m, 2H), 7.27-7.26 (m, 1H), 4.59 (s, 2H), 4.33 (br, 2H), 3.94 (br, 2H), 3.75 (br, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.19, 135.77, 129.43, 128.67, 127.66, 66.31, 50.68, 42.04.
GC-MS (EI, 70 eV): *m/z* = 253.
Anal. Calcd for $C_{12}H_{15}NOS_2$: C, 56.88; H, 5.97; N, 5.53. Found: C, 56.81; H, 6.03; N, 5.56.

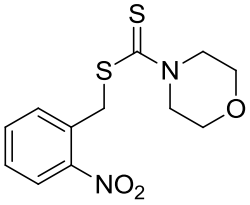
4-bromobenzyl morpholine-4-carbodithioate (3p)



Yellow solid; yield: 85.4 mg (86%); mp 90-91 ^{o}C; R_f = 0.15 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.54 (s, 2H), 4.33 (br, 2H), 3.92 (br, 2H), 3.75 (br, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.60, 135.24, 131.72, 131.07, 121.54, 66.22, 50.43, 41.00.
GC-MS (EI, 70 eV): *m/z* = 331.0.

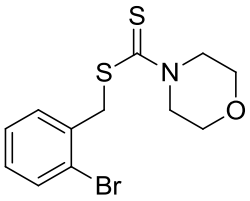
Anal. Calcd for $C_{12}H_{14}BrNOS_2$: C, 43.38; H, 4.25; N, 4.22. Found: C, 43.35; H, 4.23; N, 4.26.

2-nitrobenzyl morpholine-4-carbodithioate (3q)



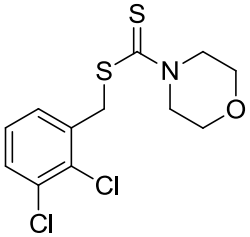
Yellow solid; yield: 67.9 mg (76%); mp 105-107 ^oC; R_f = 0.08 (PE-EtOAc, 10:1).
^1H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.45-7.42 (m, 1H), 5.02 (s, 2H), 4.31 (br, 2H), 3.93 (br, 2H), 3.74 (br, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.47, 148.51, 133.46, 133.07, 132.97, 128.67, 125.09, 66.24, 50.67, 38.29.
GC-MS (EI, 70 eV): *m/z* = 298.
Anal. Calcd for $C_{12}H_{14}N_2O_3S_2$: C, 48.30; H, 4.73; N, 9.39. Found: C, 48.34; H, 4.73; N, 9.36.

2-bromobenzyl morpholine-4-carbodithioate (3r)



Yellow solid; yield: 84.4 mg (85%); mp 100-101 ^oC; R_f = 0.19 (PE-EtOAc, 10:1).
^1H NMR (500 MHz, $CDCl_3$): δ = 7.58-7.55 (m, 2H), 7.28-7.25 (dm, 1H), 7.16-7.12 (m, 1H), 4.75 (s, 2H), 4.33 (br, 2H), 3.96 (br, 2H), 3.75 (br, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.86, 135.91, 132.95, 131.65, 129.34, 127.65, 125.05, 66.26, 50.84, 42.09.
GC-MS (EI, 70 eV): *m/z* = 331.
Anal. Calcd for $C_{12}H_{14}BrNOS_2$: C, 43.38; H, 4.25; N, 4.22. Found: C, 43.34; H, 4.23; N, 4.26.

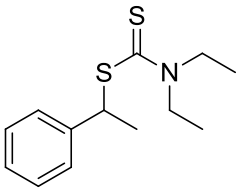
2,3-dichlorobenzyl morpholine-4-carbodithioate (3s)



Yellow solid; yield: 89.6 mg (93%); mp 135-137 ^oC; R_f = 0.27 (PE-EtOAc, 10:1).
^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8 Hz, 1H), 7.17-7.13 (m, 1H), 4.77 (s, 2H), 4.32 (br, 2H), 3.94 (br, 2H), 3.75 (br, 4H).

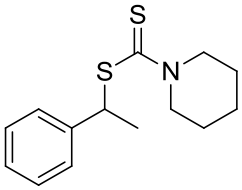
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.50, 136.77, 133.35, 132.89, 129.82, 129.64, 127.29, 66.28, 50.67, 40.00.
GC-MS (EI, 70 eV): *m/z* = 321.
Anal. Calcd for $C_{12}H_{13}Cl_2NOS_2$: C, 44.72; H, 4.07; N, 4.35. Found: C, 44.74; H, 4.03; N, 4.36.

1-phenylethyl diethylcarbamodithioate (3t)



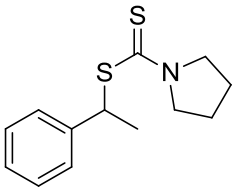
Light yellow liquid; yield: 66.0 mg (87%); R_f = 0.60 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.5 Hz, 2H), 7.36-7.33 (m, 2H), 7.28-7.25 (m, 1H), 5.30 (q, *J* = 7 Hz, 1H), 4.03 (q, *J* = 7 Hz, 2H), 3.70 (q, *J* = 7 Hz, 2H), 1.81 (d, *J* = 7 Hz, 3H), 1.29 (t, *J* = 7 Hz, 3H), 1.26 (t, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.64, 142.30, 128.57, 127.95, 127.40, 50.88, 49.33, 46.71, 22.20, 12.60, 11.73.
GC-MS (EI, 70 eV): *m/z* = 253.
Anal. Calcd for $C_{13}H_{19}NS_2$: C, 61.61; H, 7.56; N, 5.53. Found: C, 61.64; H, 7.53; N, 5.56.

1-phenylethyl piperidine-1-carbodithioate (3u)



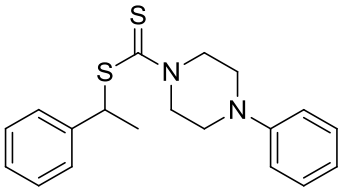
Light yellow liquid; yield: 70.0 mg (88%); R_f = 0.60 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.5 Hz, 2H), 7.35-7.32 (m, 2H), 7.27-7.24 (m, 1H), 5.30 (q, *J* = 7.5 Hz, 1H), 4.27 (br, 2H), 3.84 (br, 2H), 1.79 (d, *J* = 7Hz, 3H), 1.69 (m, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.62, 142.25, 128.56, 127.93, 127.42, 52.70, 51.28, 50.95, 26.08, 25.50, 24.36, 22.20.
GC-MS (EI, 70 eV): *m/z* = 265.
Anal. Calcd for $C_{14}H_{19}NS_2$: C, 63.35; H, 7.21; N, 5.28. Found: C, 63.31; H, 7.23; N, 5.26.

1-phenylethyl pyrrolidine-1-carbodithioate (3v)



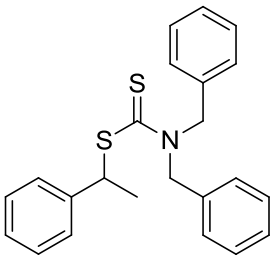
Light yellow liquid; yield: 64.0 mg (85%); R_f = 0.47 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45-7.43 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.23 (m, 1H), 5.32 (q, *J* = 7 Hz, 1H), 3.94-3.91 (m, 2H), 3.62-3.54 (m, 2H), 2.05-2.00 (m, 2H), 1.97-1.93 (m, 2H), 1.79 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.83, 142.32, 128.57, 127.81, 127.39, 54.87, 50.57, 50.10, 26.07, 24.27, 22.18.
GC-MS (EI, 70 eV): *m/z* = 251.
Anal. Calcd for $C_{13}H_{17}NS_2$: C, 62.11; H, 6.82; N, 5.57. Found: C, 62.21; H, 7.73; N, 5.56.

1-phenylethyl 4-phenylpiperazine-1-carbodithioate (3w)



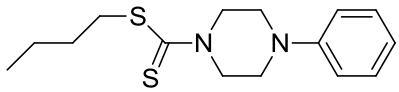
Light yellow liquid; yield: 80.0 mg (78%); R_f = 0.44 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.5 Hz, 2H), 7.38-7.35 (m, 2H), 7.33-7.27 (m, 3H), 6.95-6.92 (m, 3H), 5.35 (q, *J* = 7.5 Hz, 1H), 4.51 (br, 2H), 4.07 (br, 2H), 3.28 (br, 4H), 1.83 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.20, 150.28, 142.00, 129.39, 128.65, 127.94, 127.59, 120.61, 116.35, 51.07, 48.77, 22.13.
GC-MS (EI, 70 eV): *m/z* = 342.
Anal. Calcd for $C_{19}H_{22}N_2S_2$: C, 66.62; H, 6.47; N, 8.18. Found: C, 66.61; H, 6.43; N, 8.16.

1-phenylethyl dibenzylcarbamodithioate (3x)



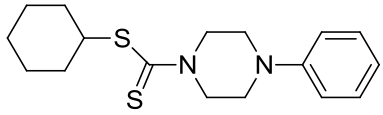
Light yellow liquid; yield: 81.4 mg (72%); R_f = 0.54 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 2H), 7.37-7.20 (m, 13H), 5.41-5.30 (m, 3H), 4.91 (s, 2H), 1.87 (d, *J* = 7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.70, 142.03, 135.65, 134.74, 128.98, 128.84, 128.61, 128.02, 127.80, 127.70, 127.54, 127.25, 55.78, 53.98, 52.05, 22.22.
GC-MS (EI, 70 eV): *m/z* = 377.
Anal. Calcd for $C_{23}H_{23}NS_2$: C, 73.17; H, 6.14; N, 3.71. Found: C, 73.11; H, 6.13; N, 3.76.

butyl 4-phenylpiperazine-1-carbodithioate (3y)



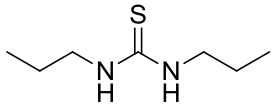
Yellow solid; yield: 66.2 mg (75%); mp: 60-61 ^{o}C; R_f = 0.54 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32-7.28 (m, 2H), 6.94-6.91 (m, 3H), 4.50 (br, 2H), 4.13 (br, 2H), 3.36-3.29 (m, 6H), 1.75-1.69 (m, 2H), 1.49-1.45 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.77, 150.32, 129.37, 120.58, 116.34, 48.79, 37.05, 30.72, 22.22, 13.78.
GC-MS (EI, 70 eV): *m/z* = 294.
Anal. Calcd for $C_{15}H_{22}N_2S_2$: C, 61.18; H, 7.53; N, 9.51. Found: C, 61.11; H, 7.51; N, 9.59.

cyclohexyl 4-phenylpiperazine-1-carbodithioate (3z)



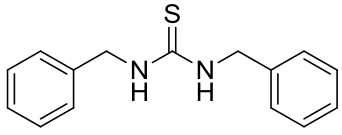
Yellow solid; yield: 60.5 mg (63%); mp: 126-128 ^{o}C; R_f = 0.54 (PE-EtOAc, 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 2H), 6.94-6.92 (m, 3H), 4.50 (br, 2H), 4.11 (br, 2H), 4.00 (m, 1H), 3.30 (s, 4H), 2.16-2.15 (m, 2H), 1.76-1.74 (m, 2H), 1.53-1.48 (m, 4H), 1.29-1.26 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.97, 129.36, 120.59, 116.34, 50.42, 48.80, 32.93, 29.74, 26.24, 25.68.
GC-MS (EI, 70 eV): *m/z* = 320.
Anal. Calcd for $C_{17}H_{24}N_2S_2$: C, 63.70; H, 7.55; N, 8.74. Found: C, 63.61; H, 7.51; N, 8.78.

1,3-dipropylthiourea (4a)[1]



^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.12 (s, 2H), 3.36 (m, 4H), 1.60-1.56 (m, 4H), 0.93-0.90 (m, 6H).

1,3-dibenzylthiourea (4b)[2]



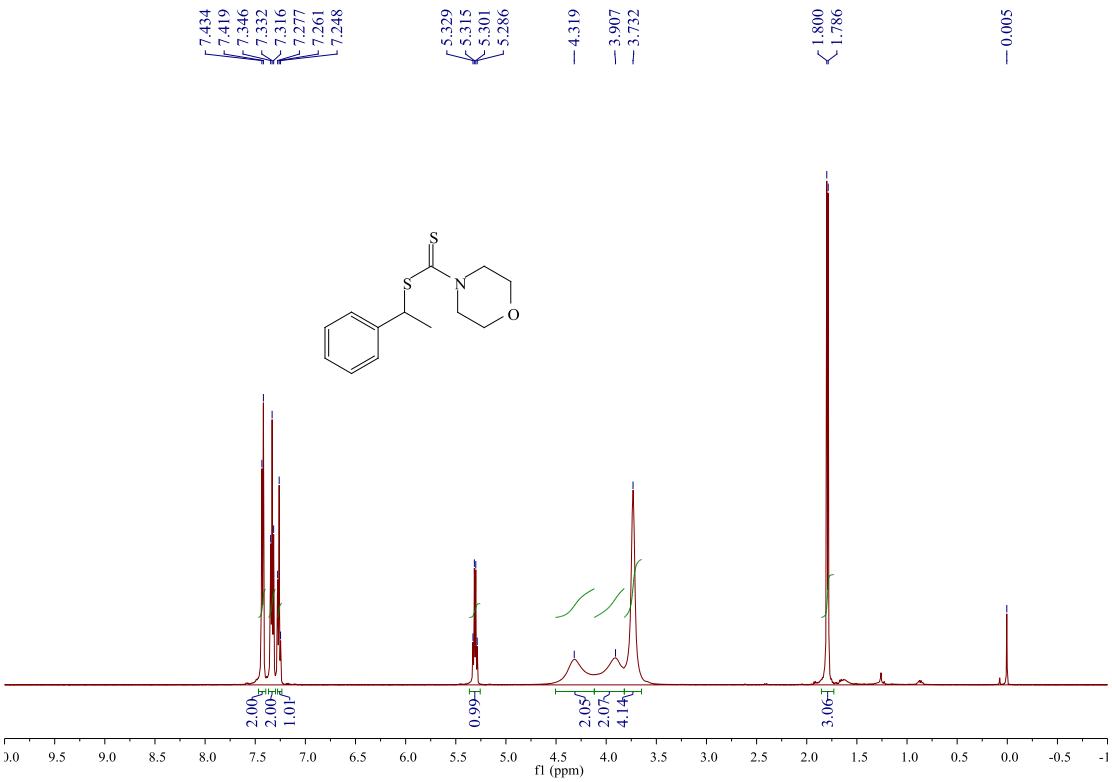
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32-7.22 (m, 10H), 6.00 (s, 2H), 4.61 (s, 2H).

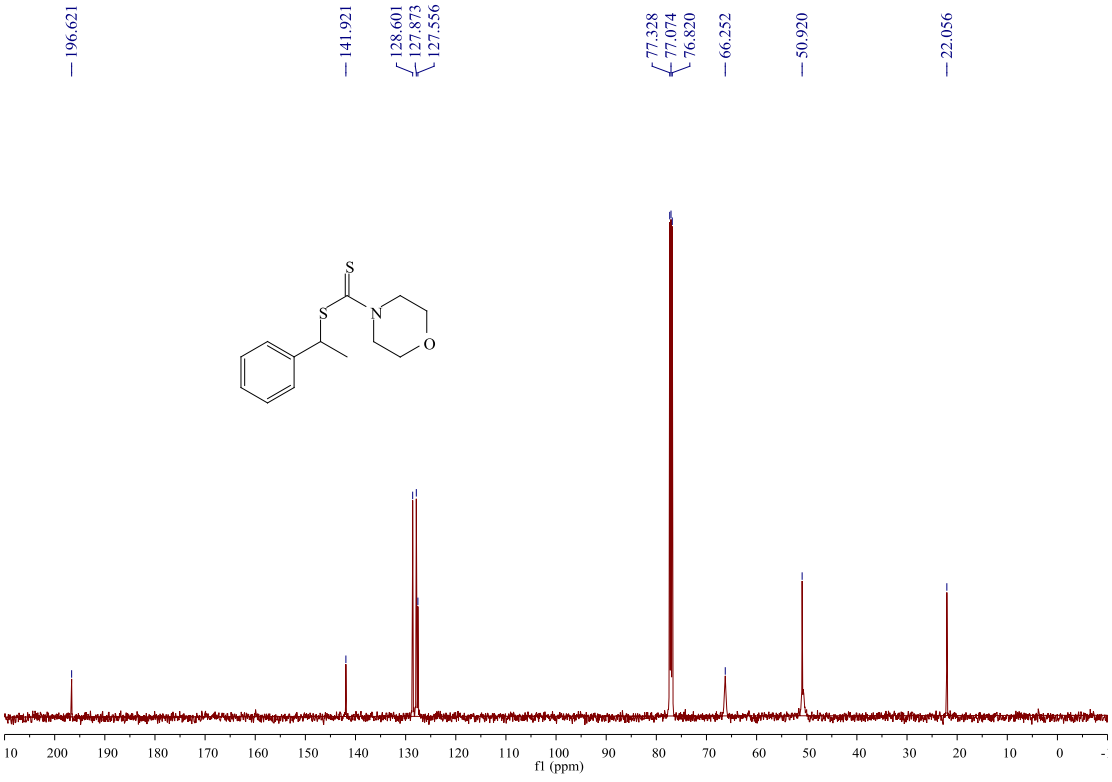
References

1. Y. Takikaw, N. Inoue, R. Sato and S. Takizawa, *Chem. Lett.*, 1982, 641-642.
2. S. Perveen, S. M. Abdul Hai and R. A. Khan, *Synthetic Commun.*, 2005, **35**, 1663-1674.

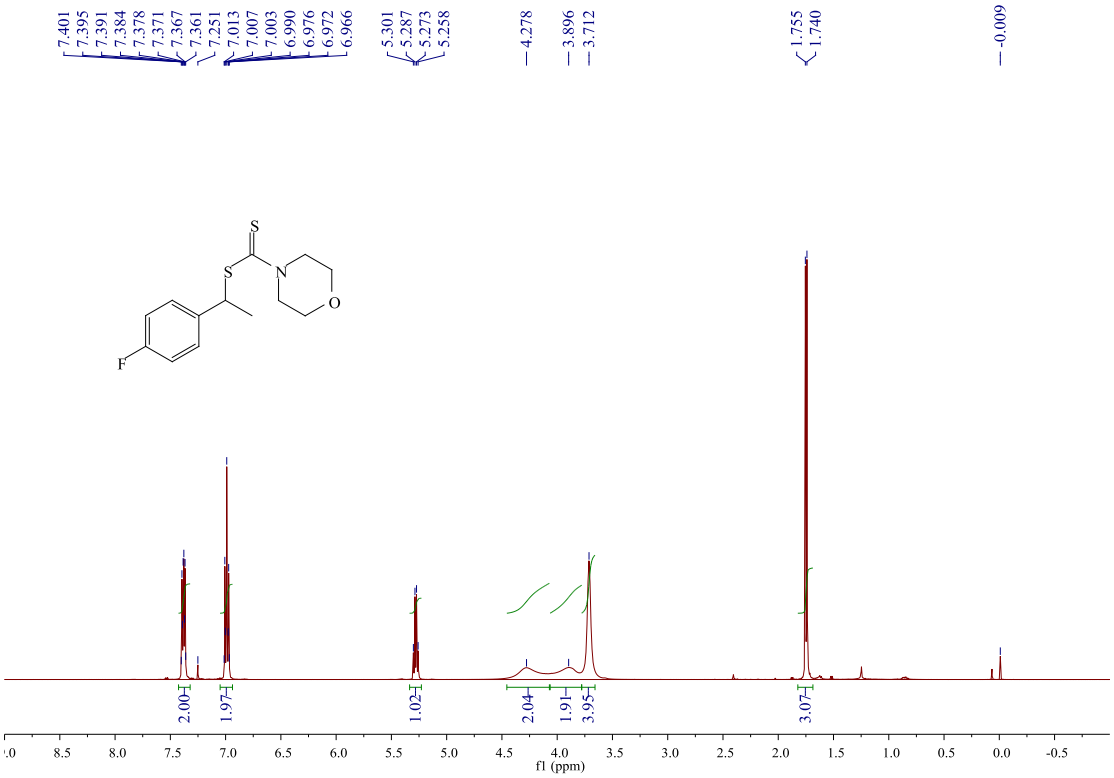
Ⅳ.Copies of ^{1}H and ^{13}C NMR Spectra

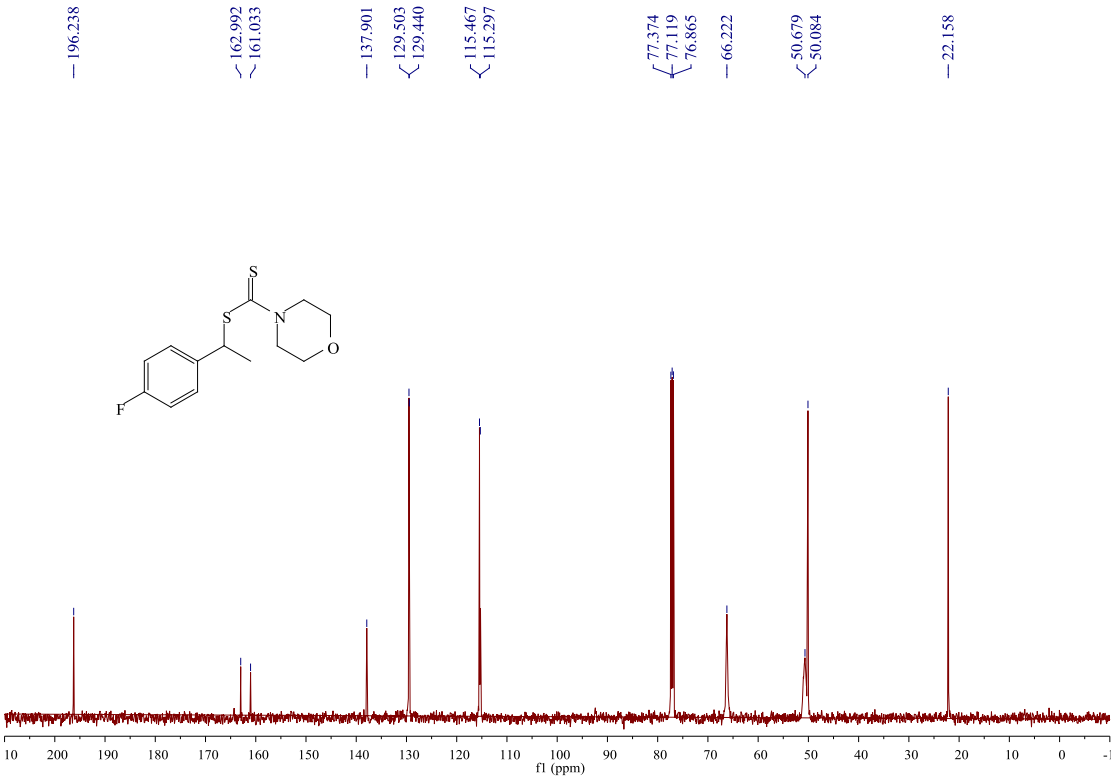
1-phenylethyl morpholine-4-carbodithioate (3a)



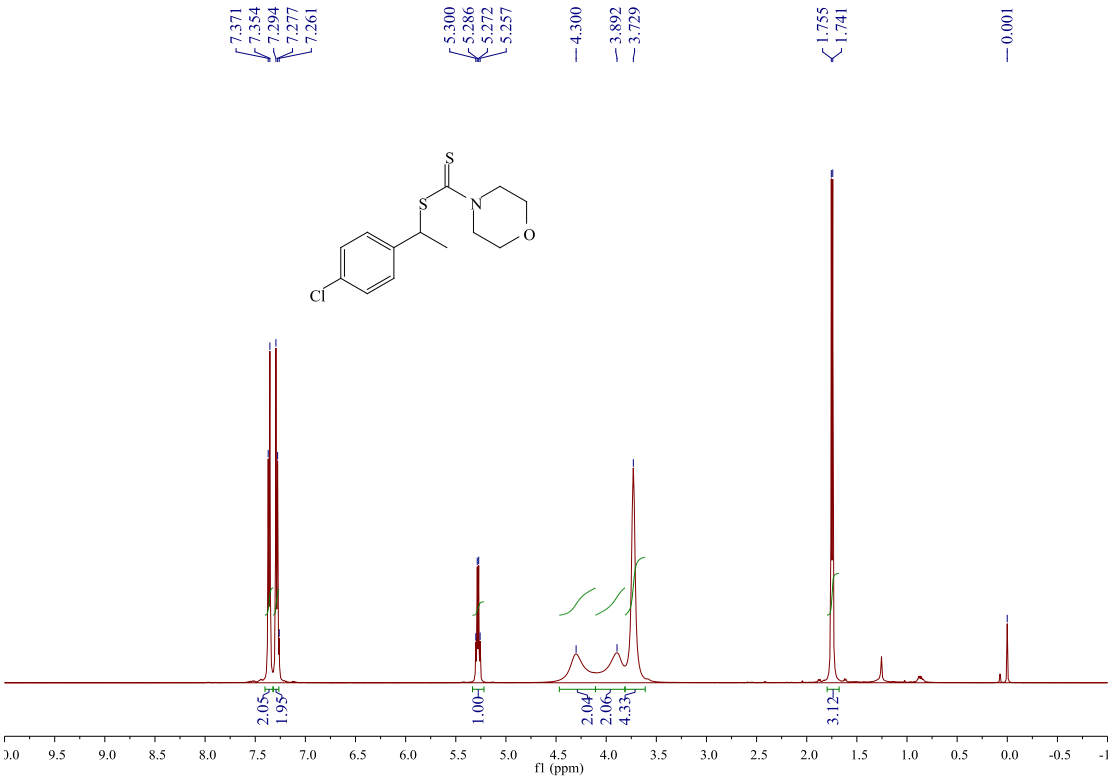


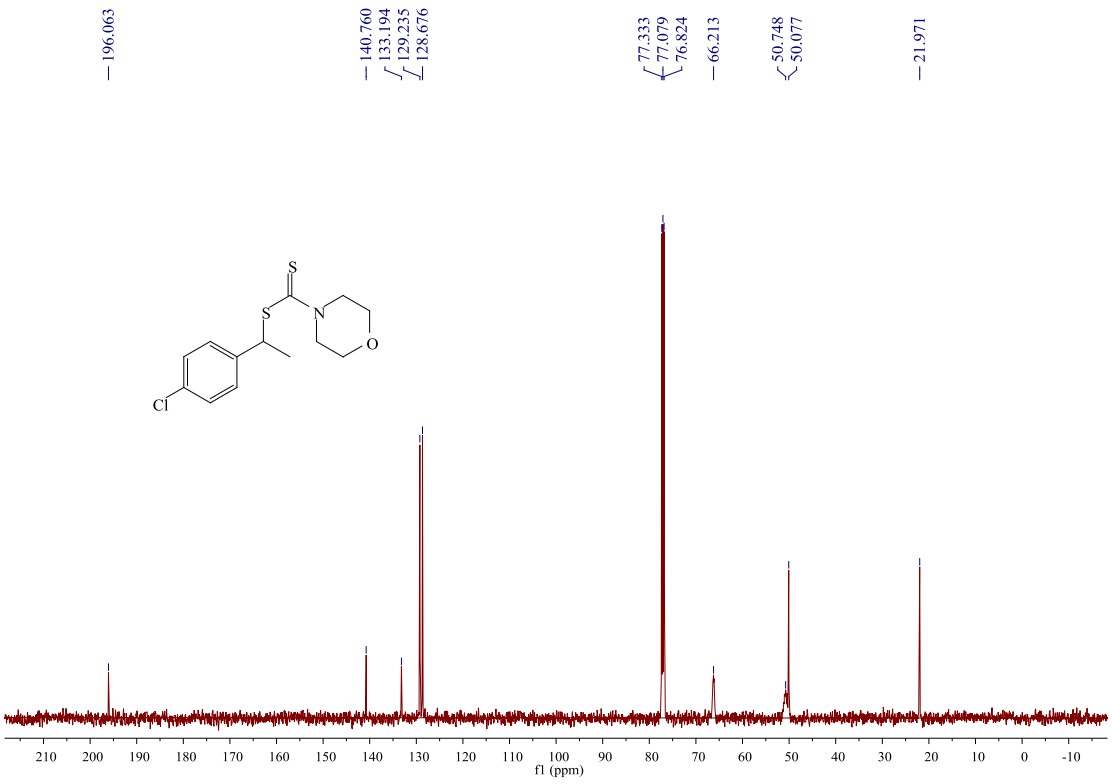
1-(4-fluorophenyl)ethyl morpholine-4-carbodithioate (3b)



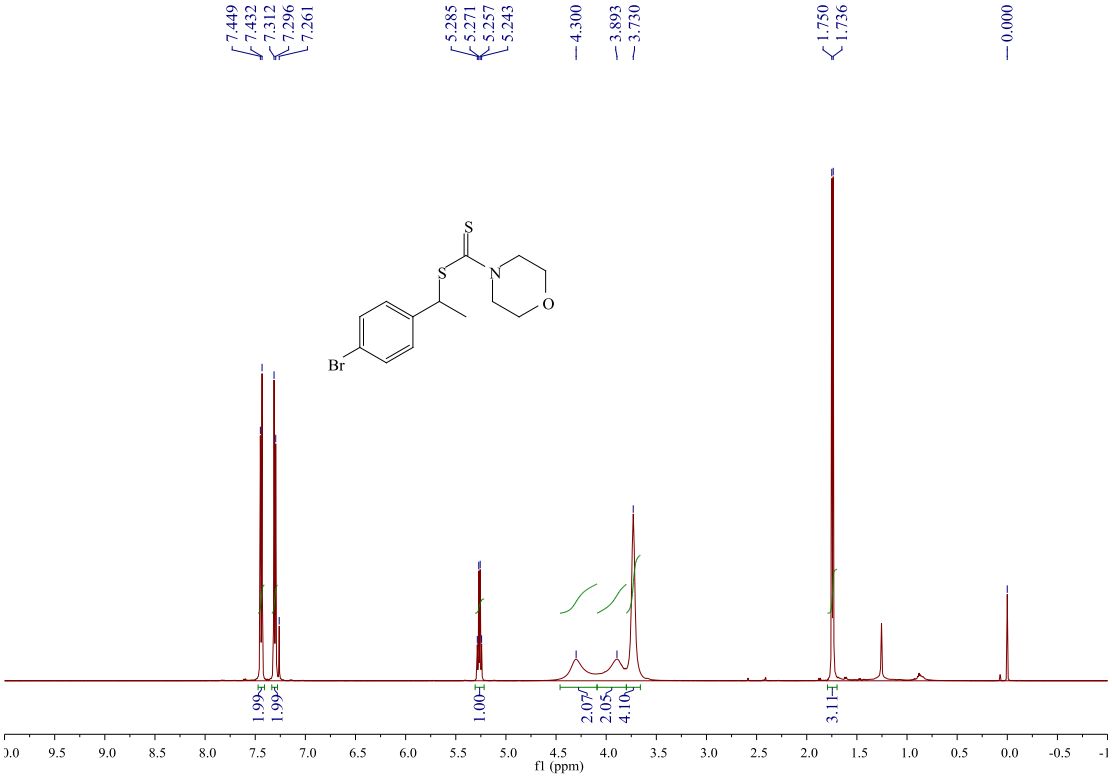


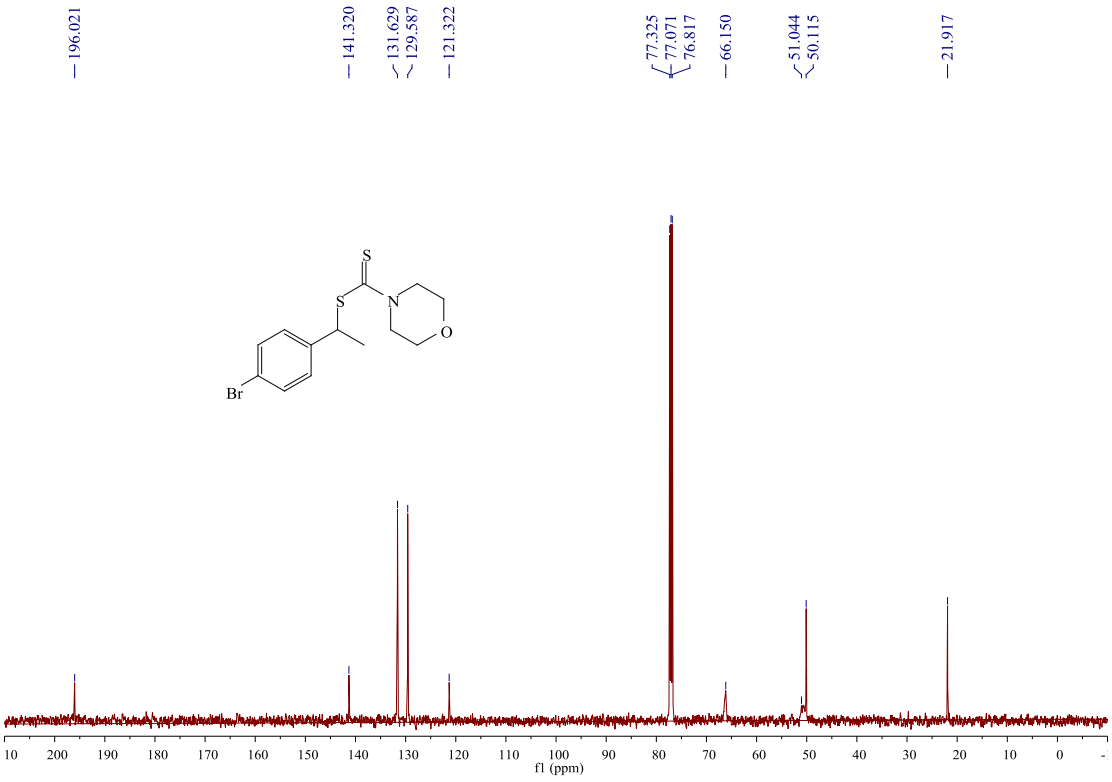
1-(4-chlorophenyl)ethyl morpholine-4-carbodithioate (3c)



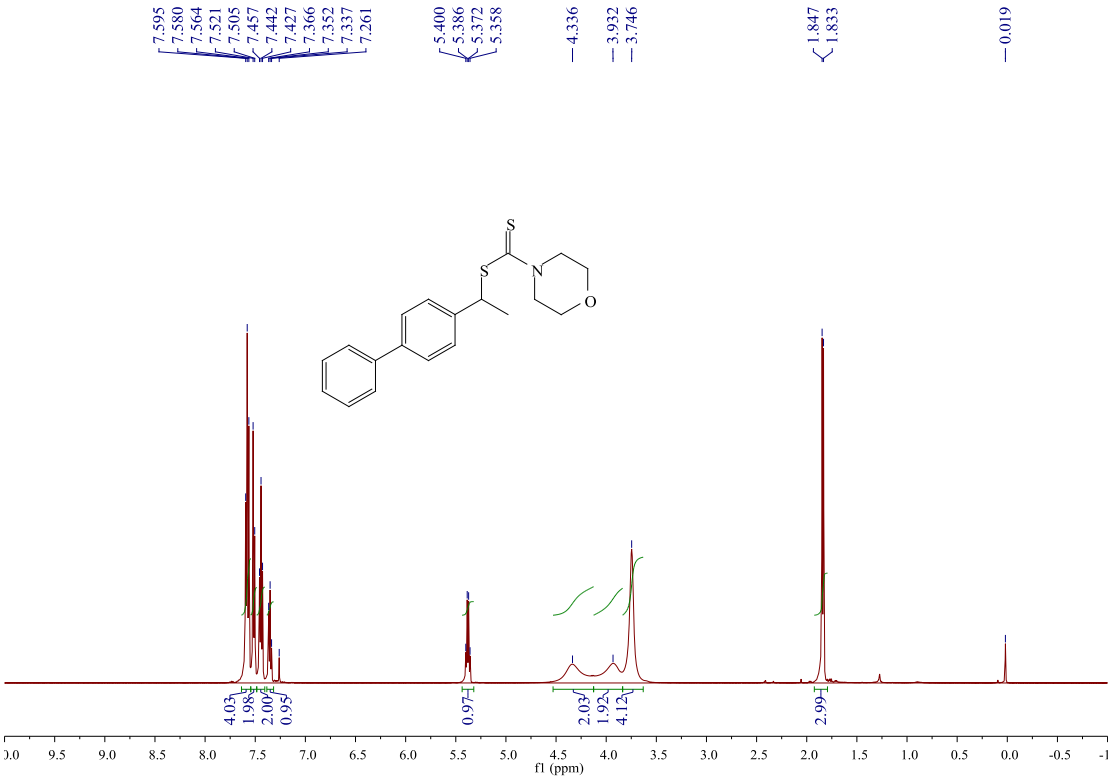


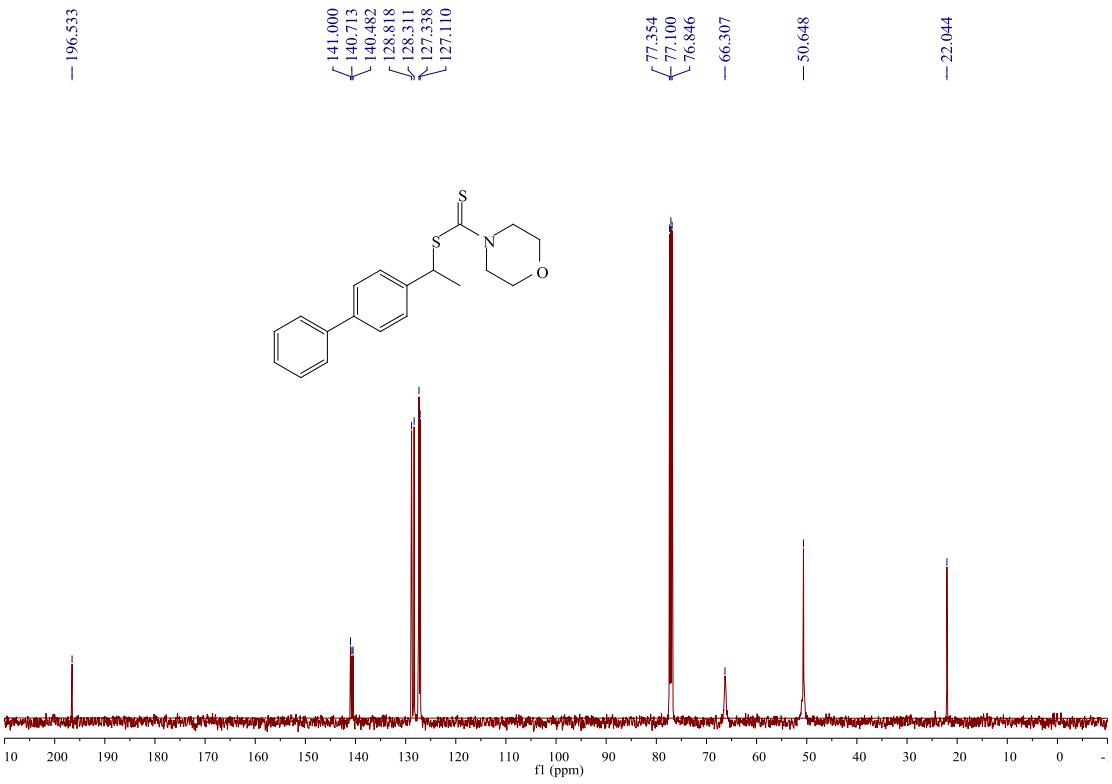
1-(4-bromophenyl)ethyl morpholine-4-carbodithioate (3d)



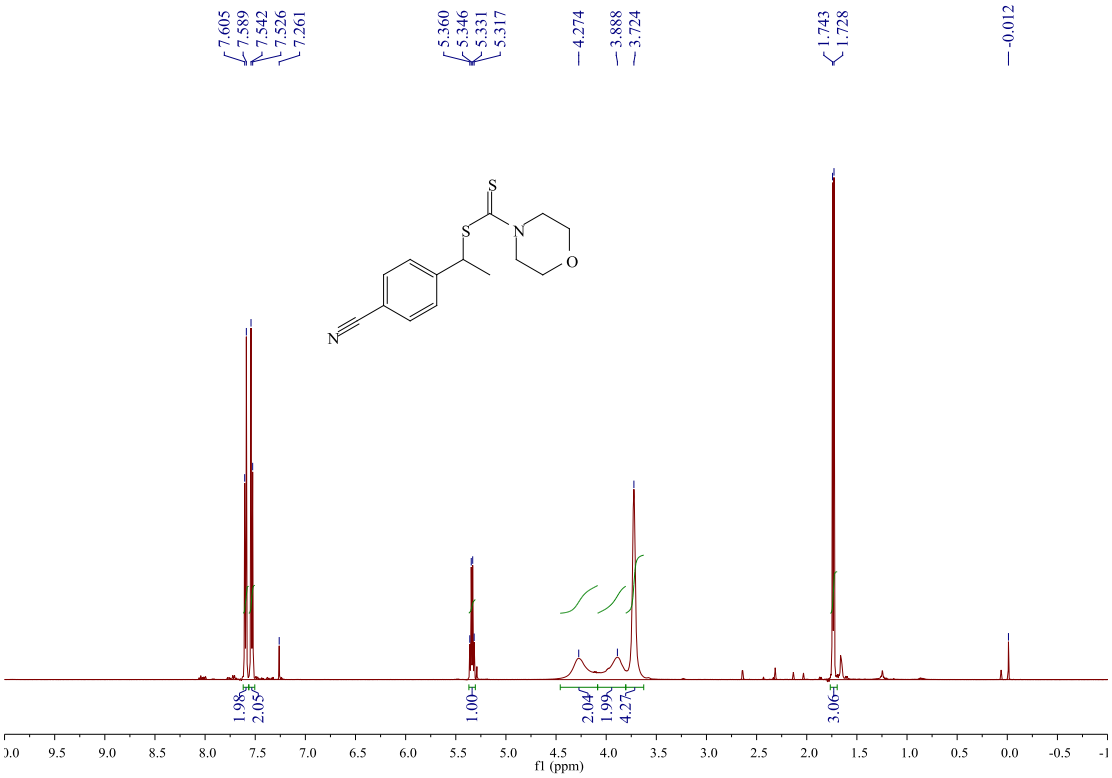


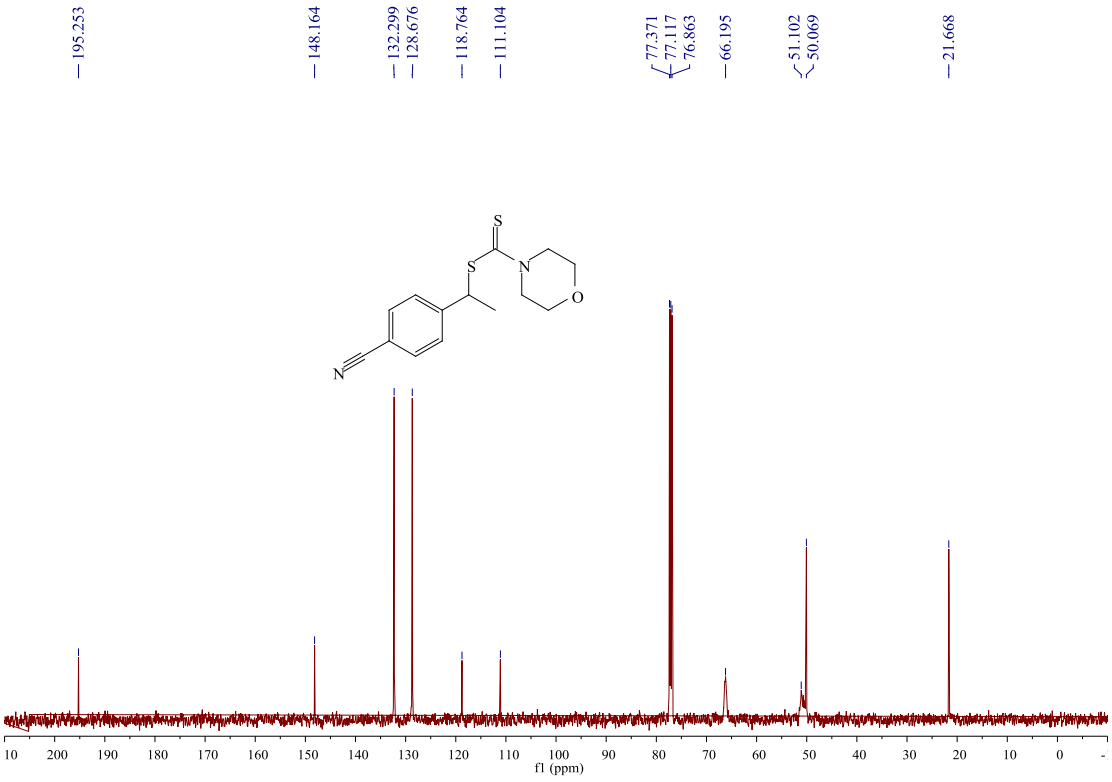
1-([1,1'-biphenyl]-4-yl)ethyl morpholine-4-carbodithioate (3e)



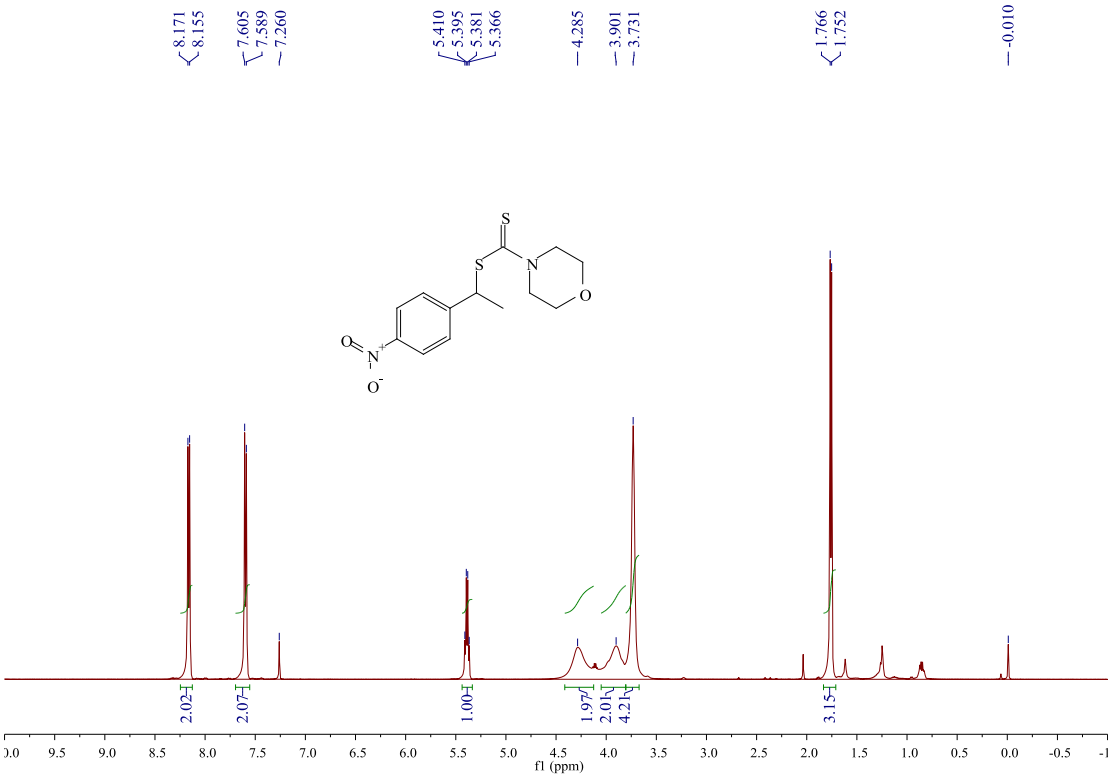


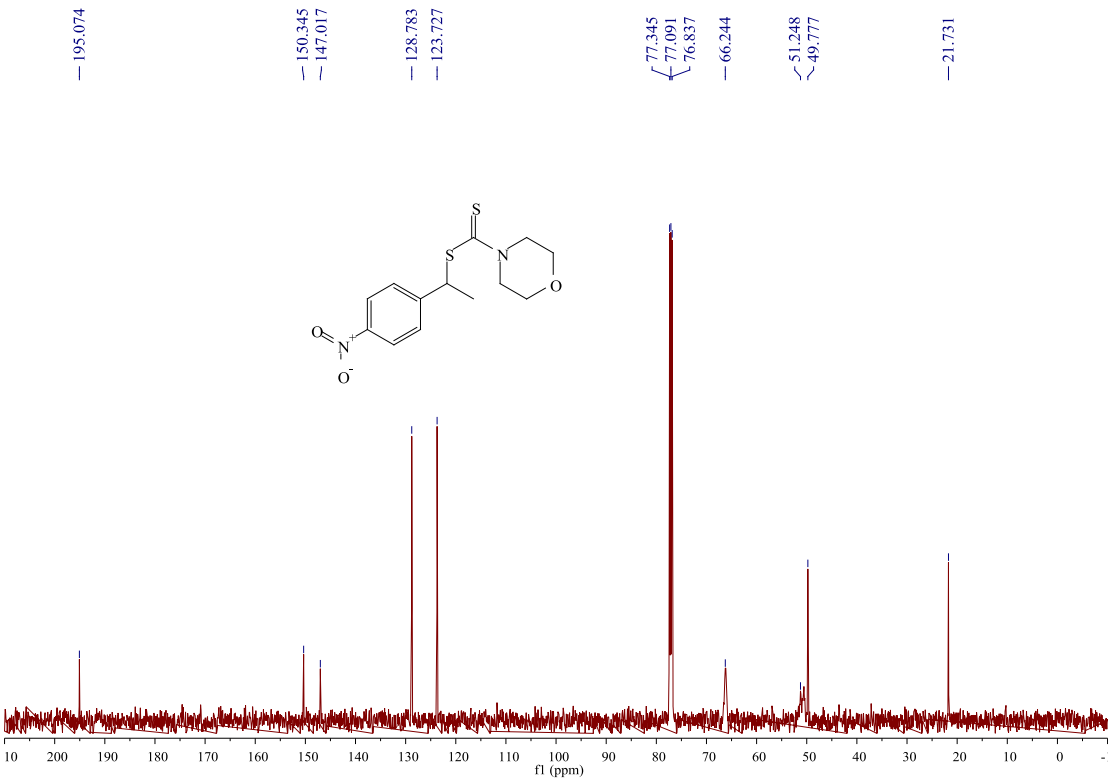
1-(4-cyanophenyl)ethyl morpholine-4-carbodithioate (3f)



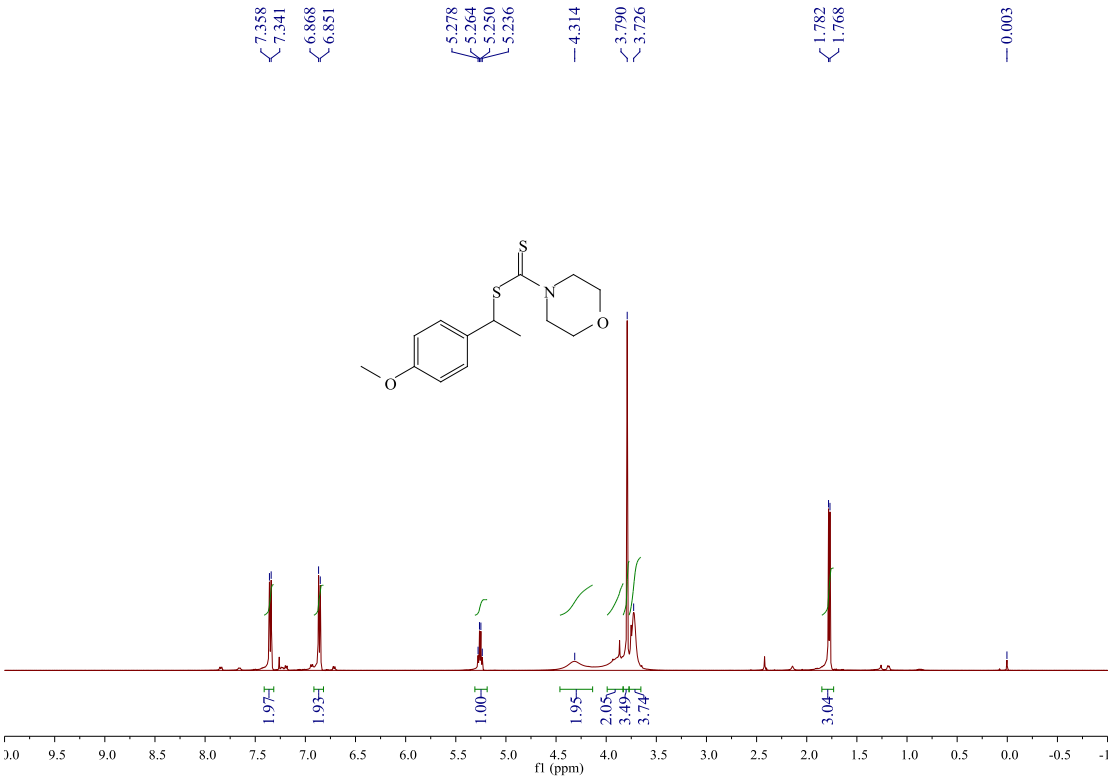


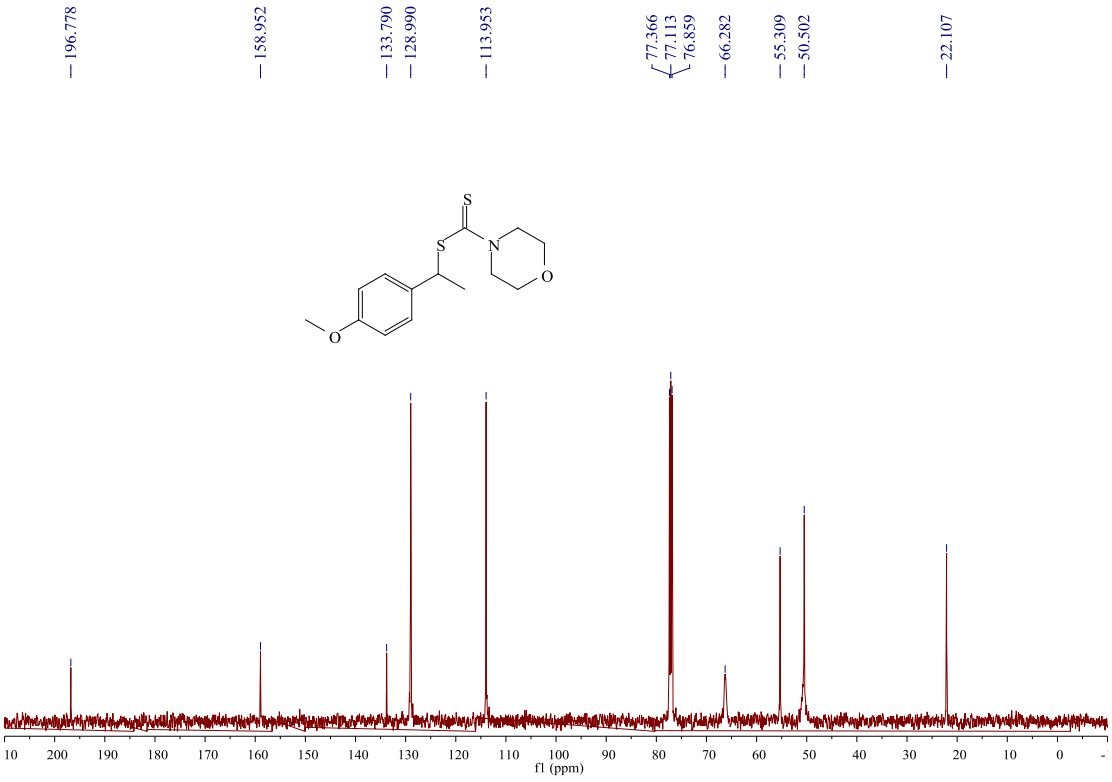
1-(4-nitrophenyl)ethyl morpholine-4-carbodithioate (3g)



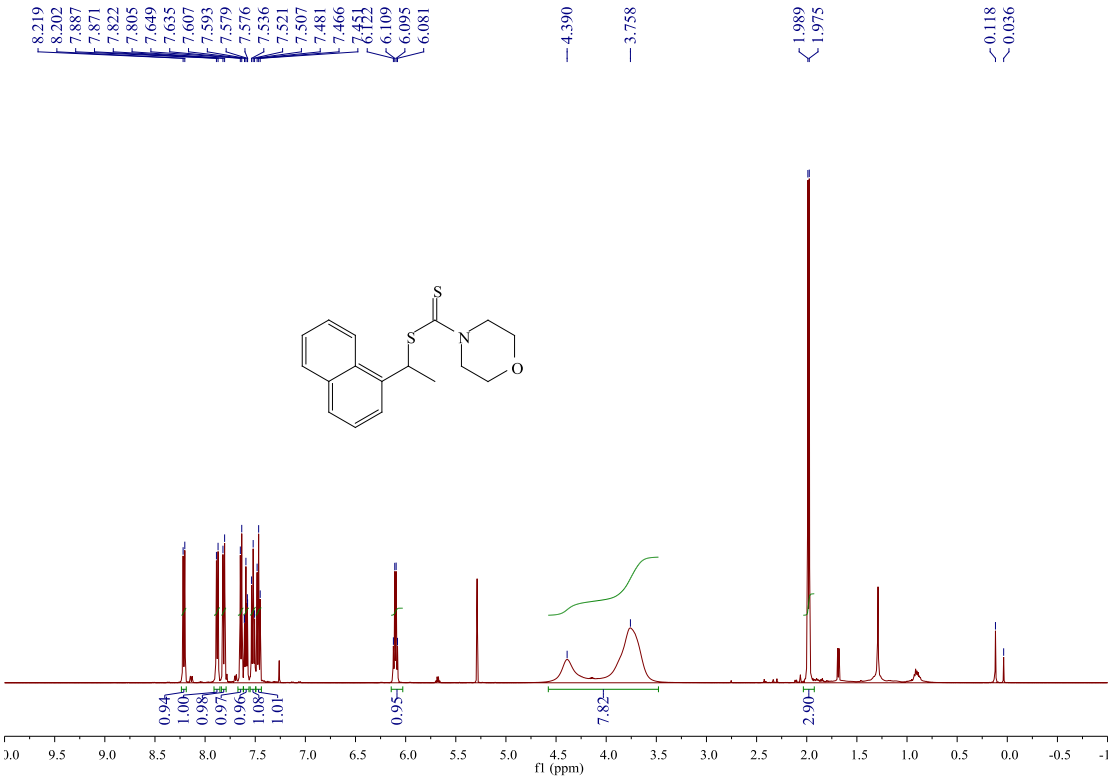


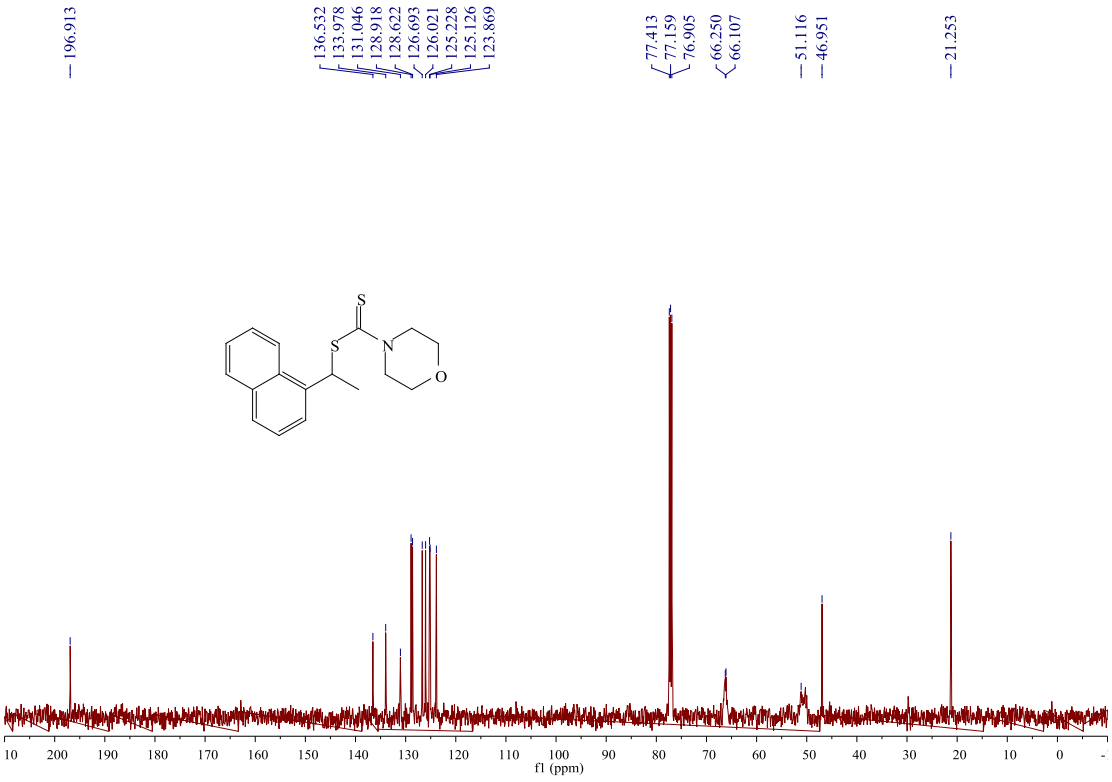
1-(4-methoxyphenyl)ethyl morpholine-4-carbodithioate (3h)



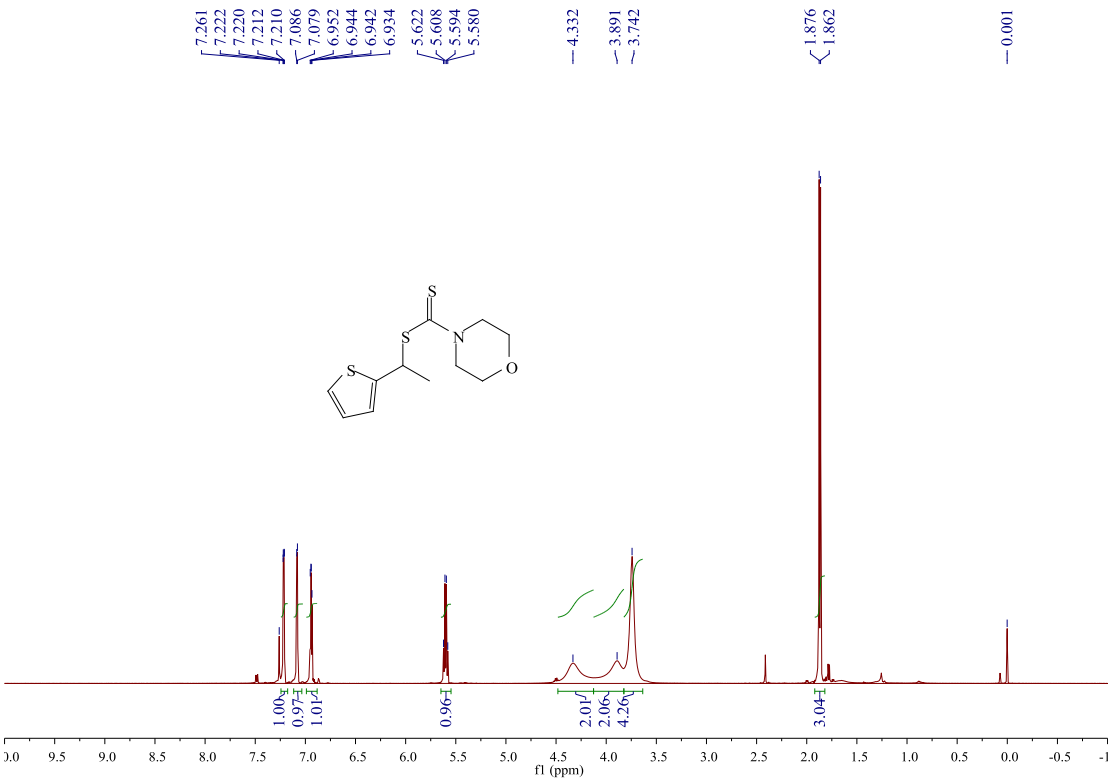


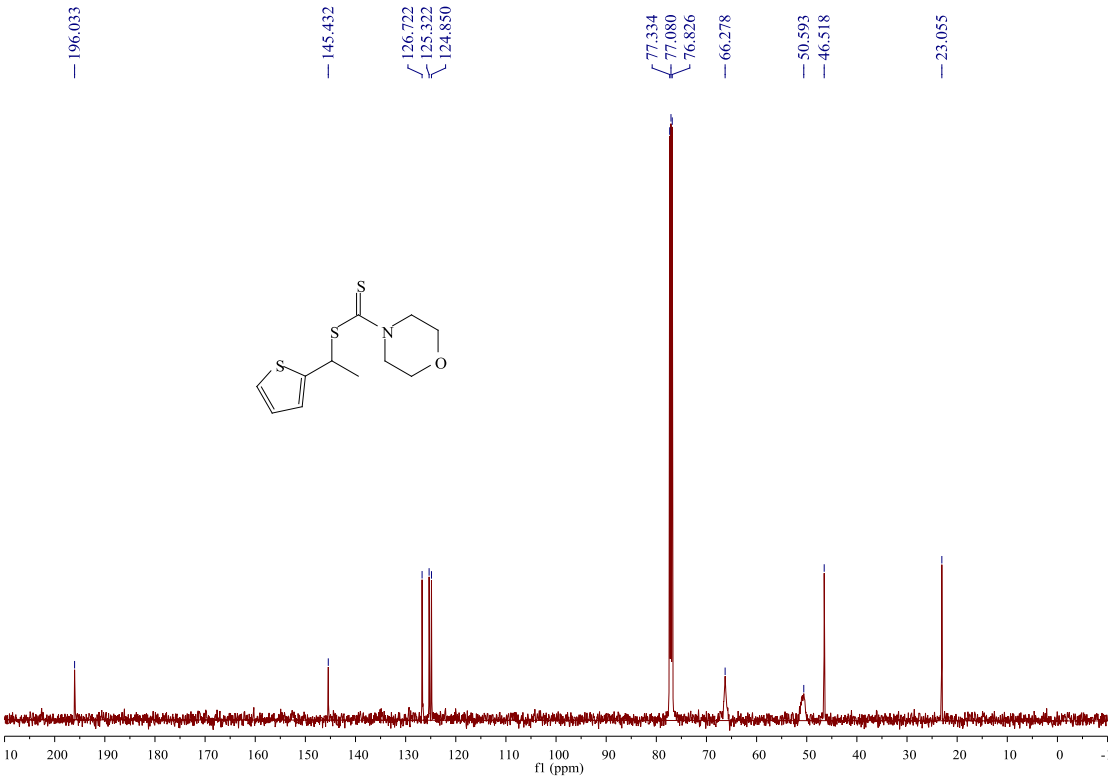
1-(naphthalen-1-yl)ethyl morpholine-4-carbodithioate (3i)



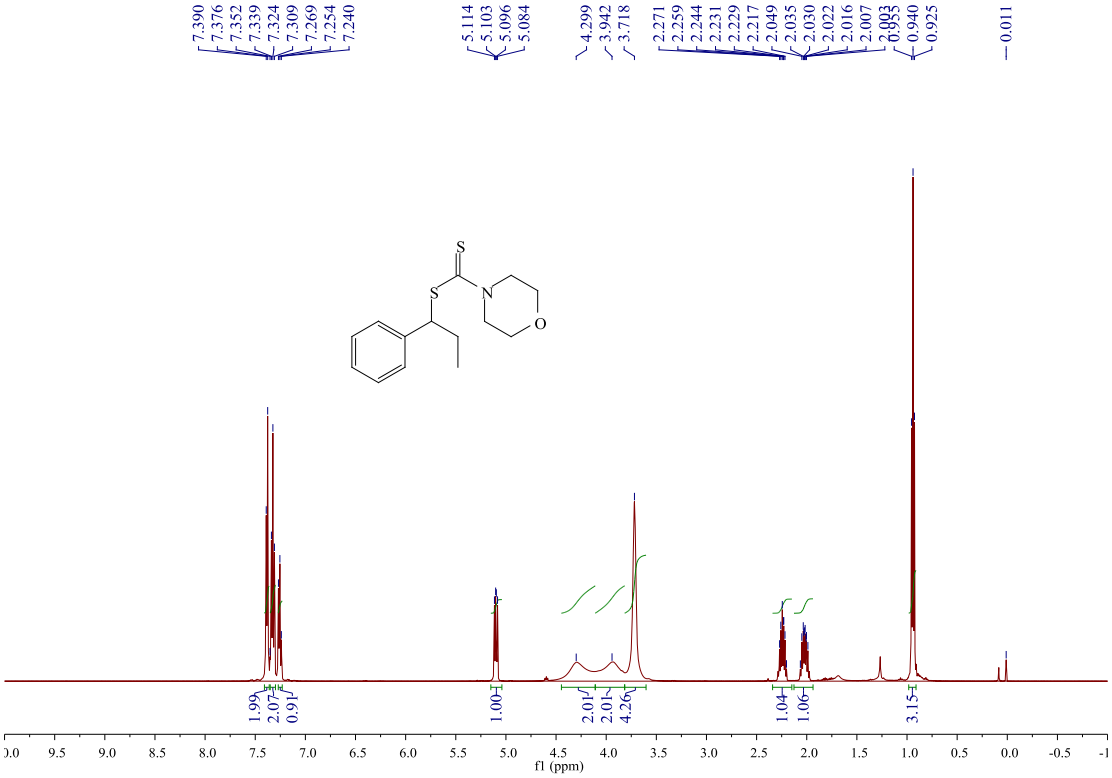


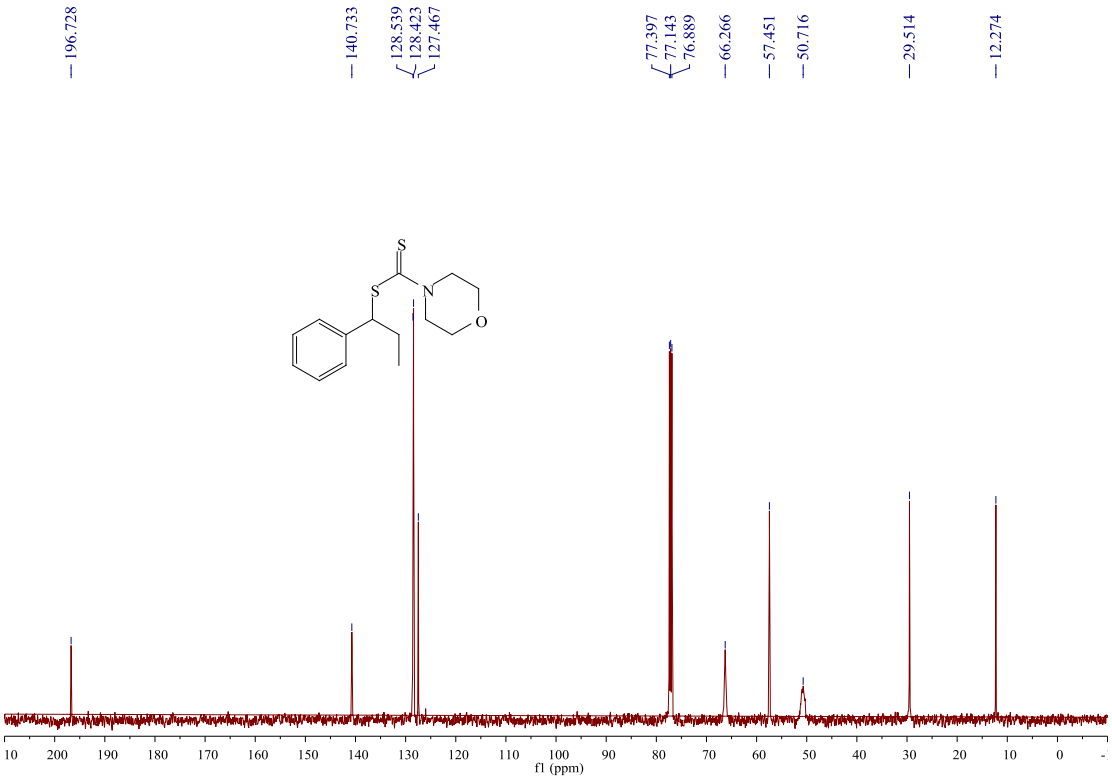
1-(thiophen-2-yl)ethyl morpholine-4-carbodithioate (3j)



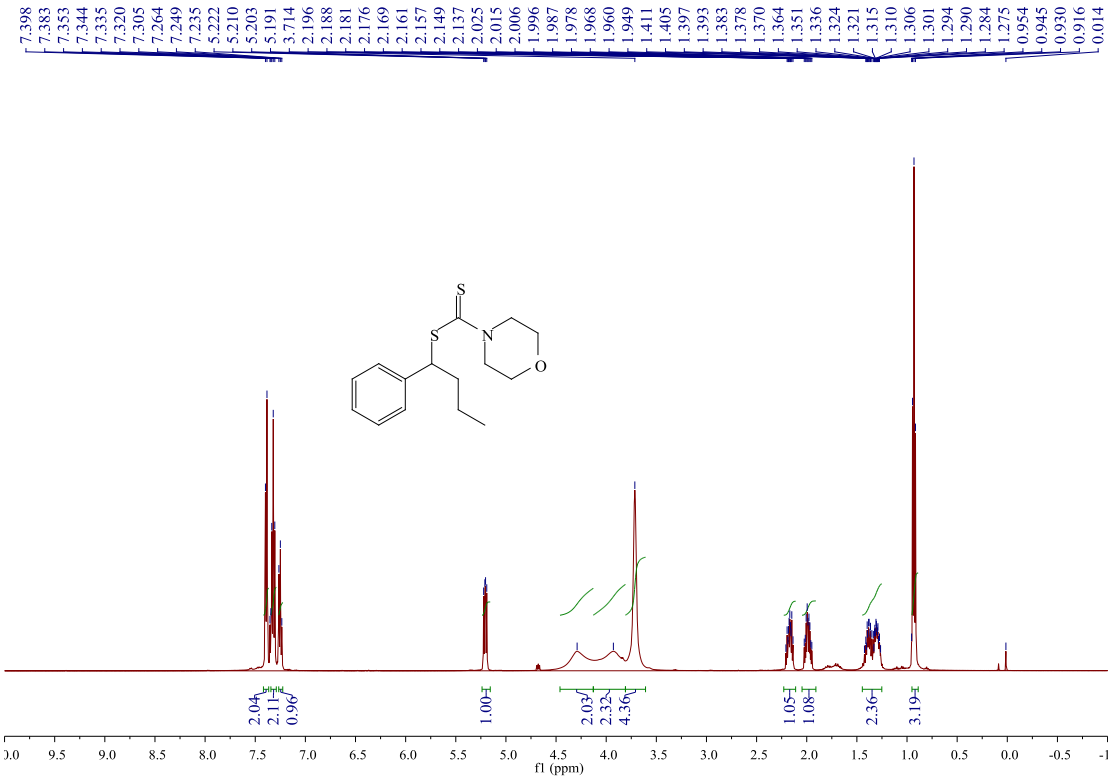


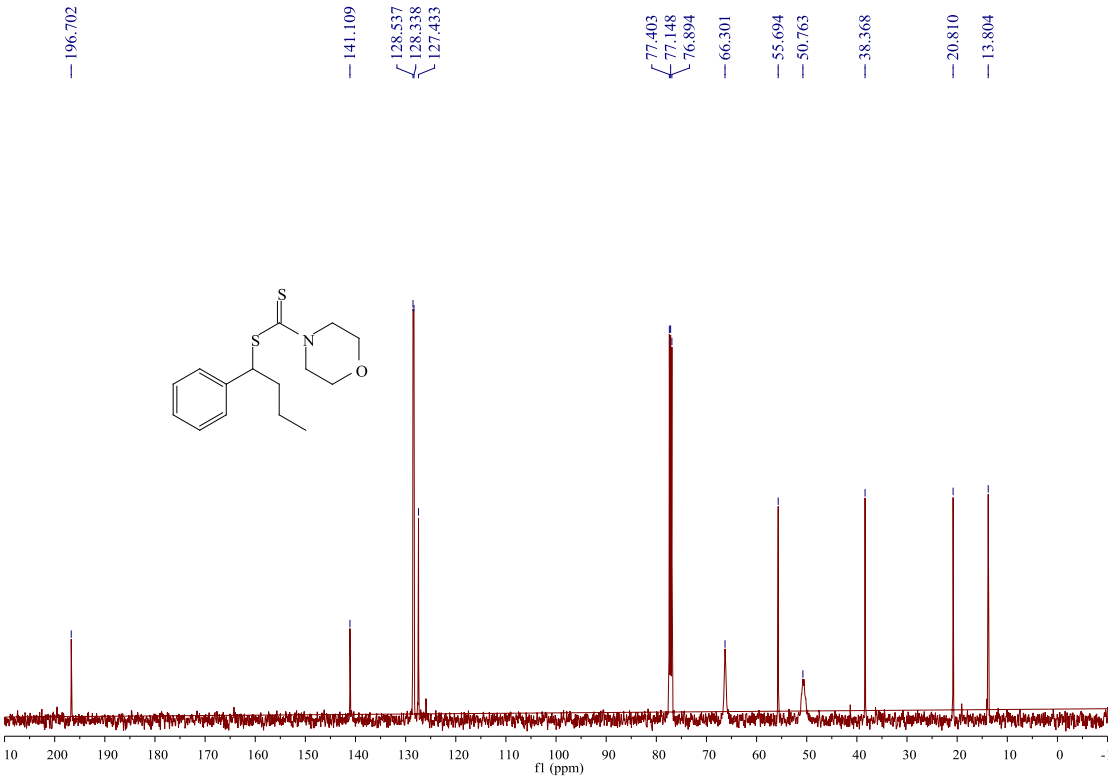
1-phenylpropyl morpholine-4-carbodithioate (3k)



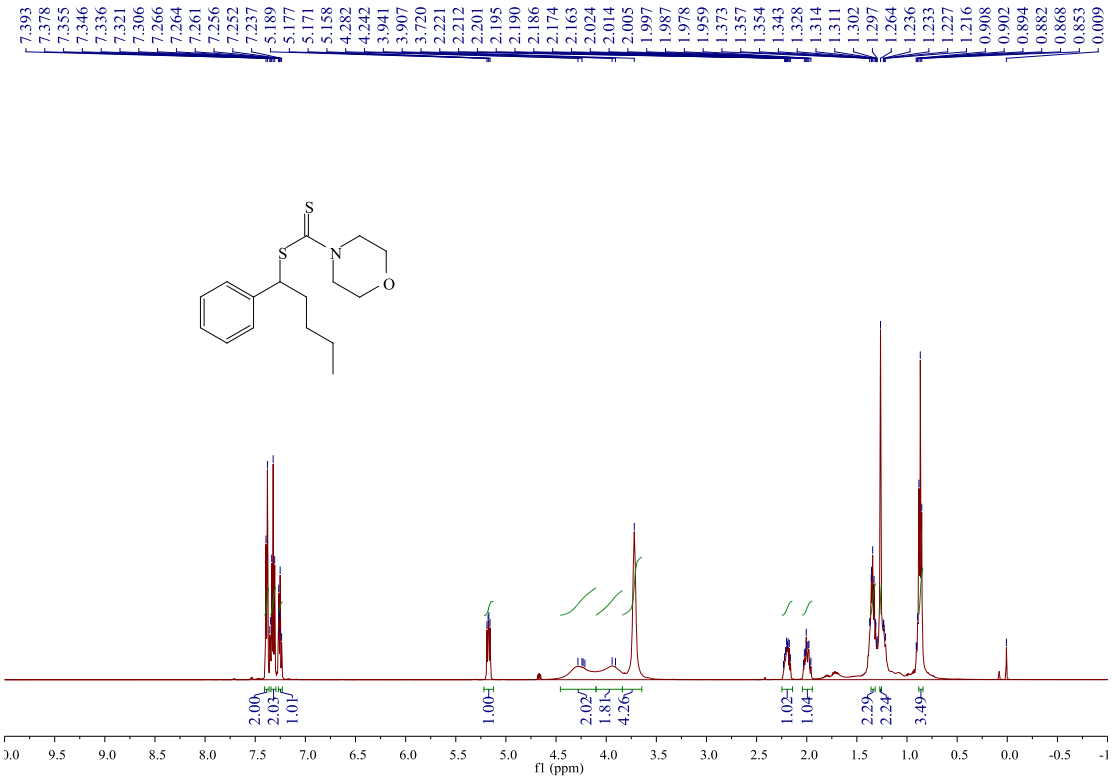


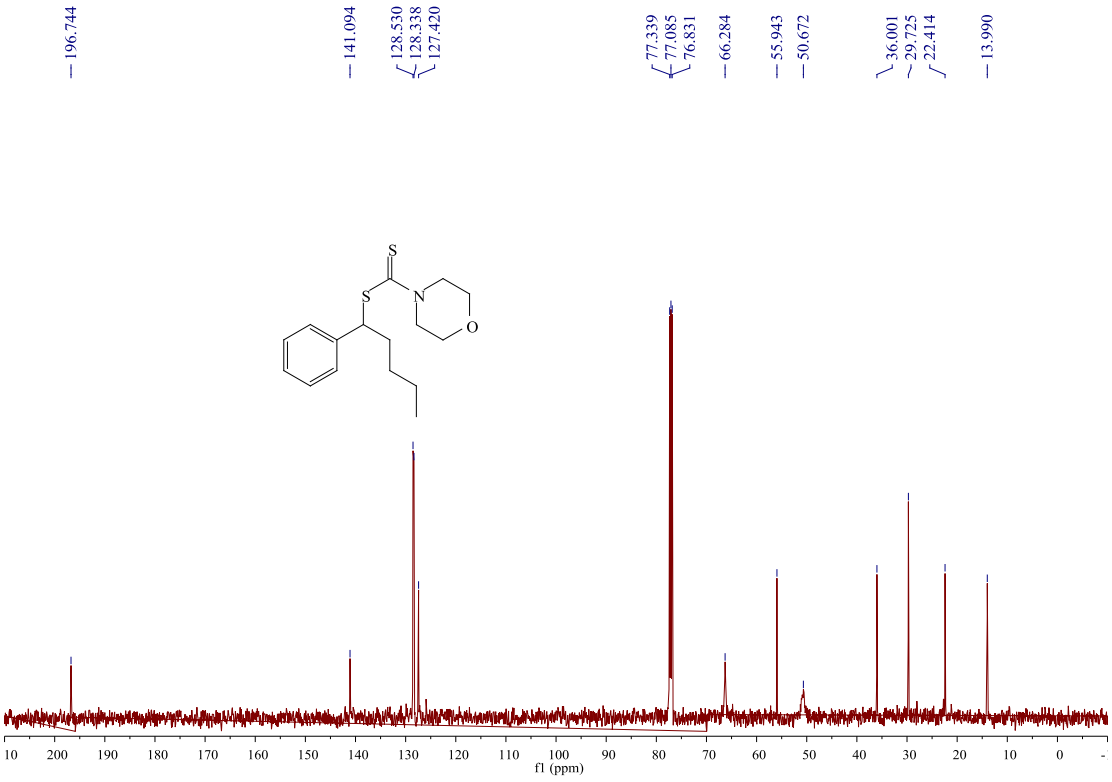
1-phenylbutyl morpholine-4-carbodithioate (3l)



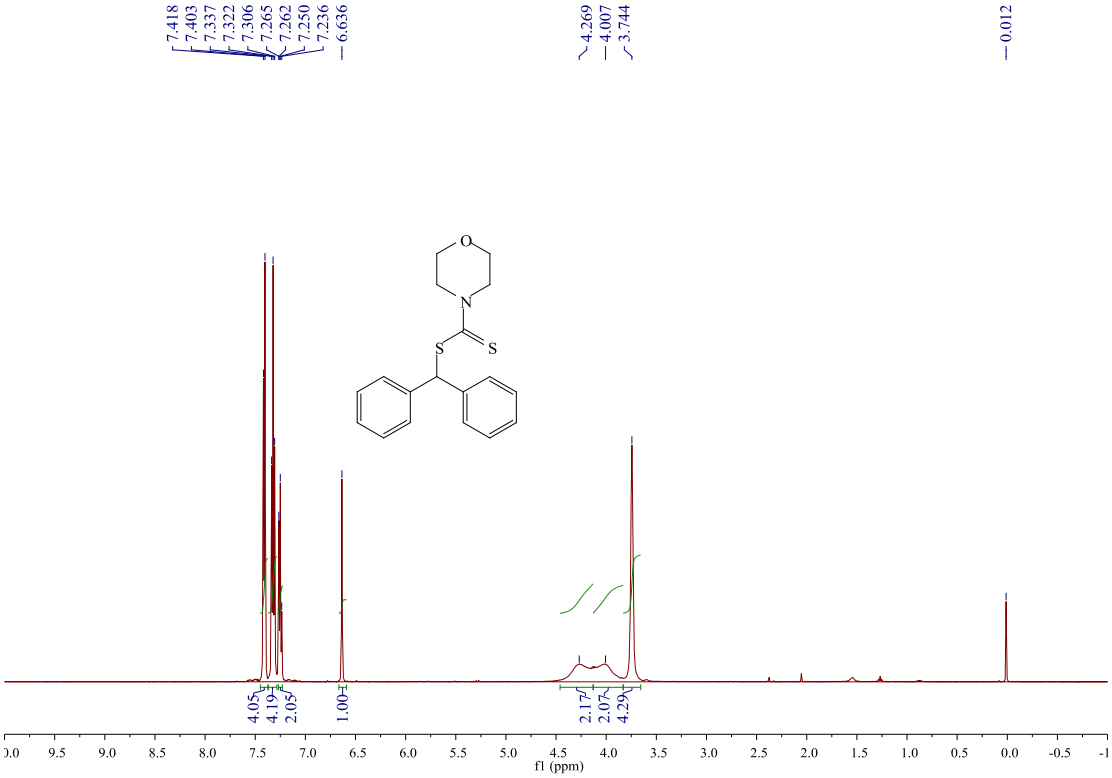


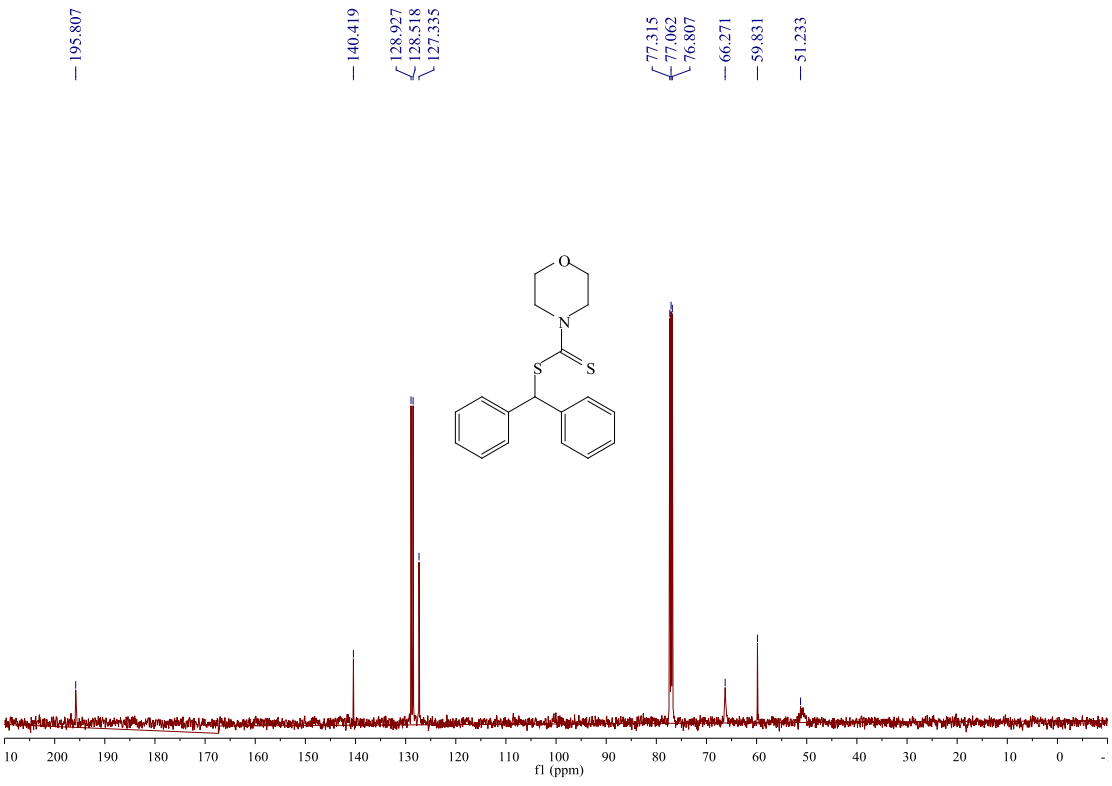
1-phenylpentyl morpholine-4-carbodithioate (3m)



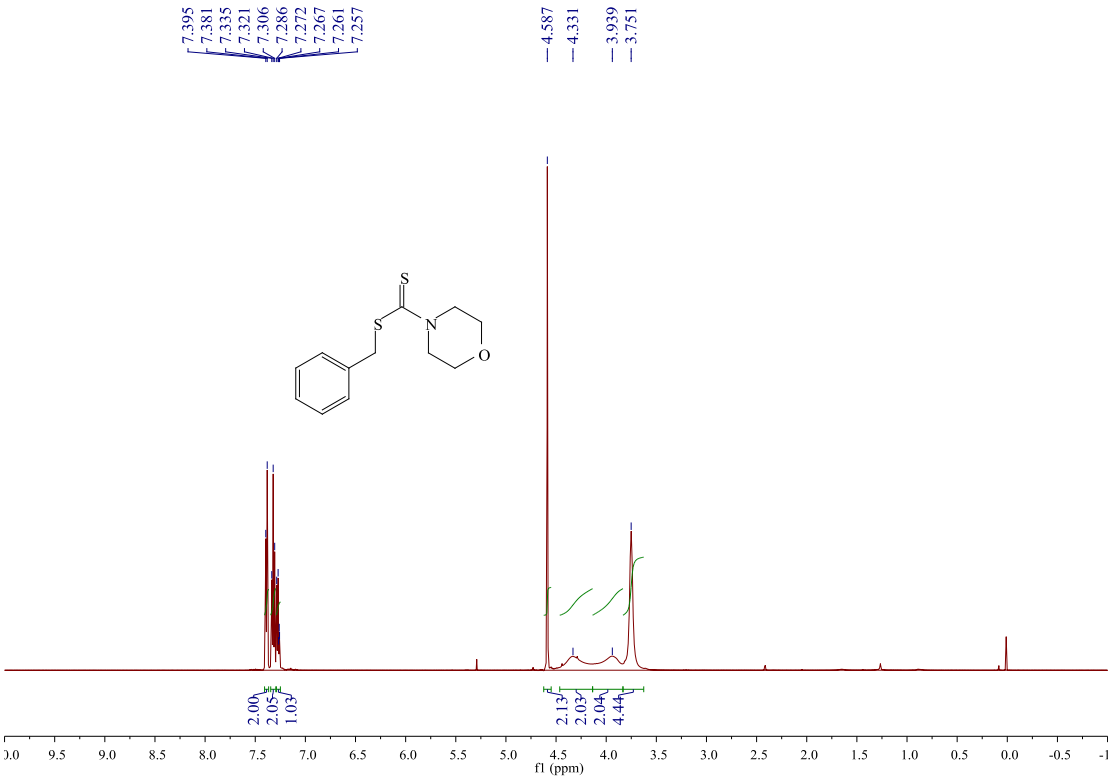


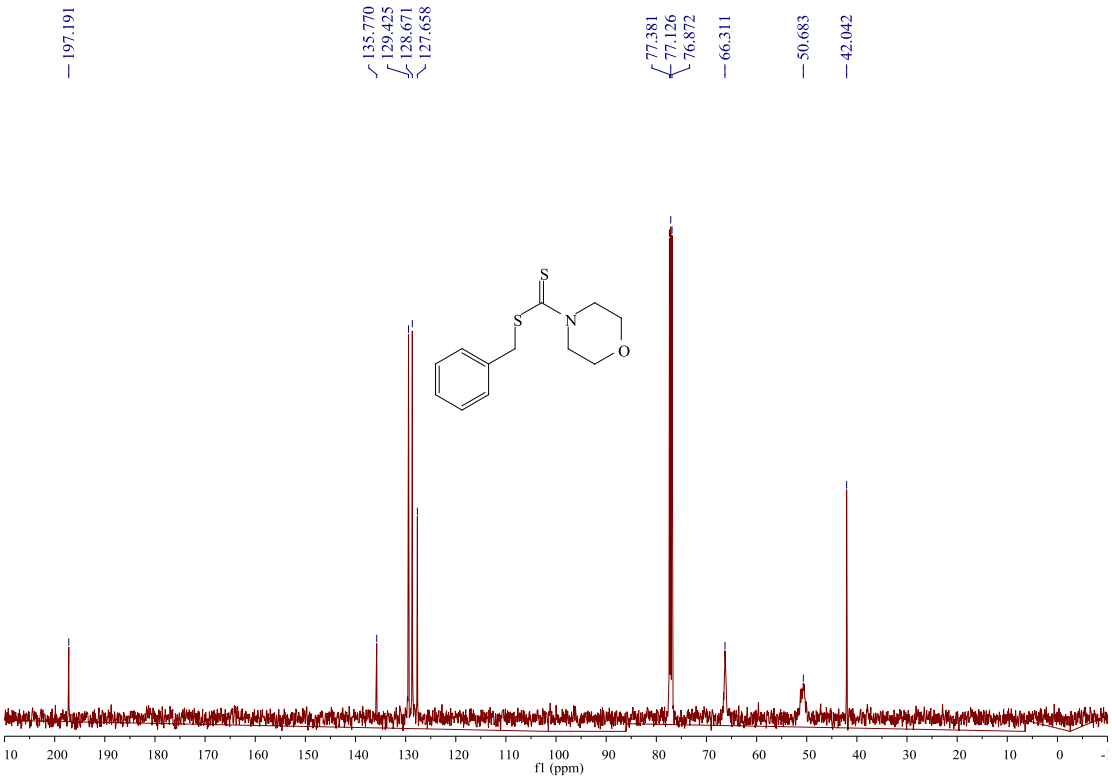
benzhydryl morpholine-4-carbodithioate (3n)



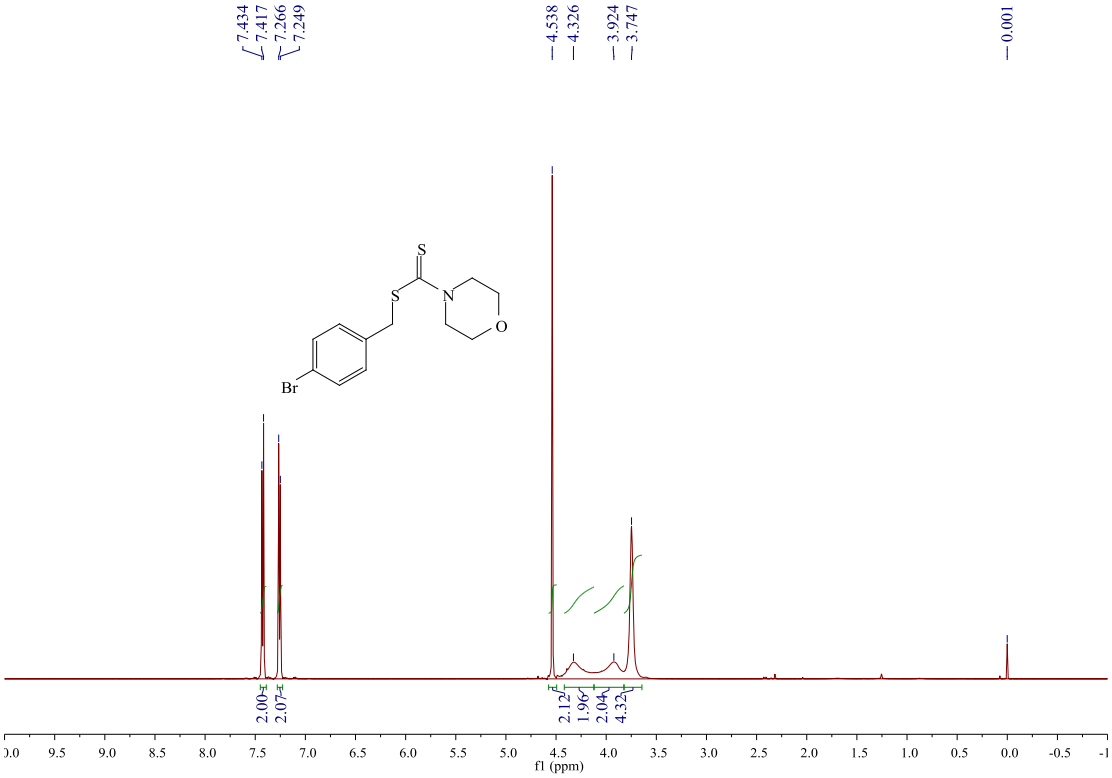


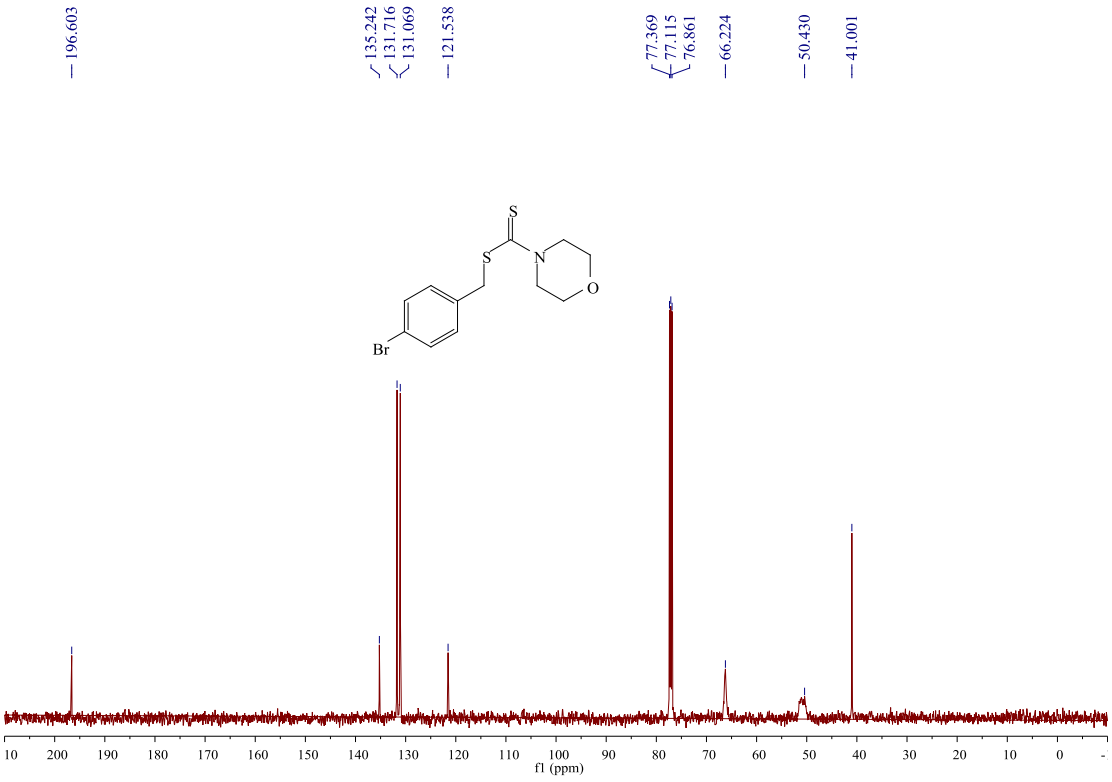
benzyl morpholine-4-carbodithioate (3o)



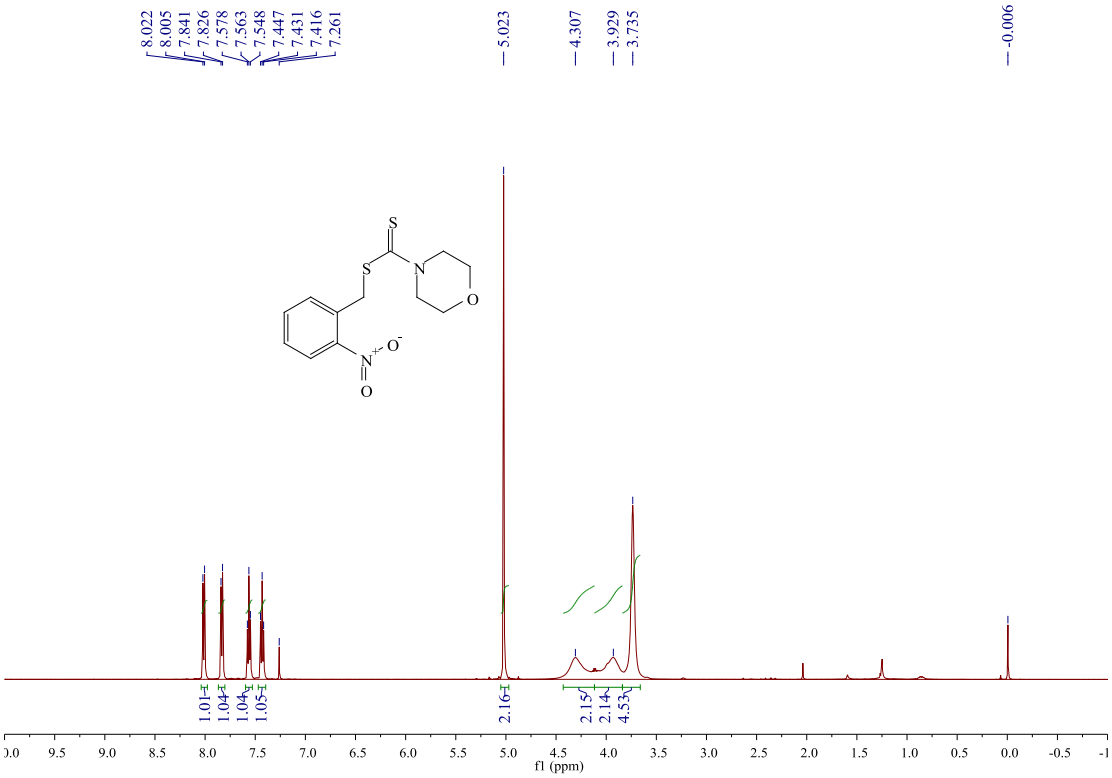


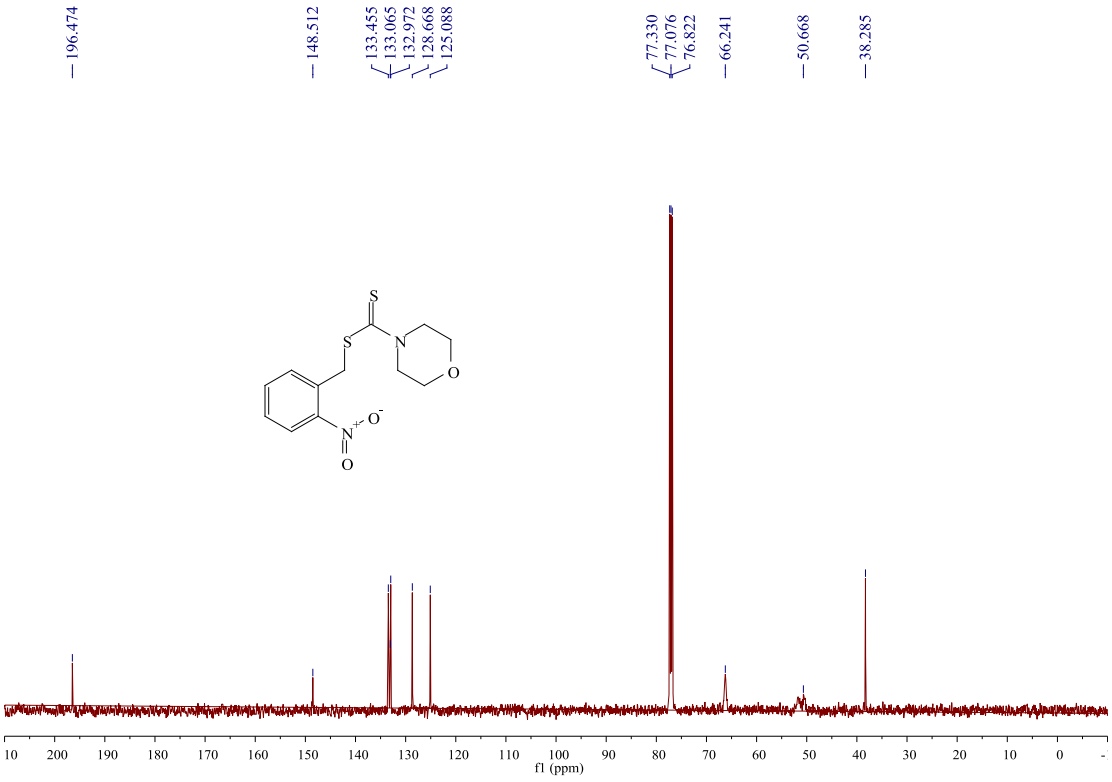
4-bromobenzyl morpholine-4-carbodithioate (3p)



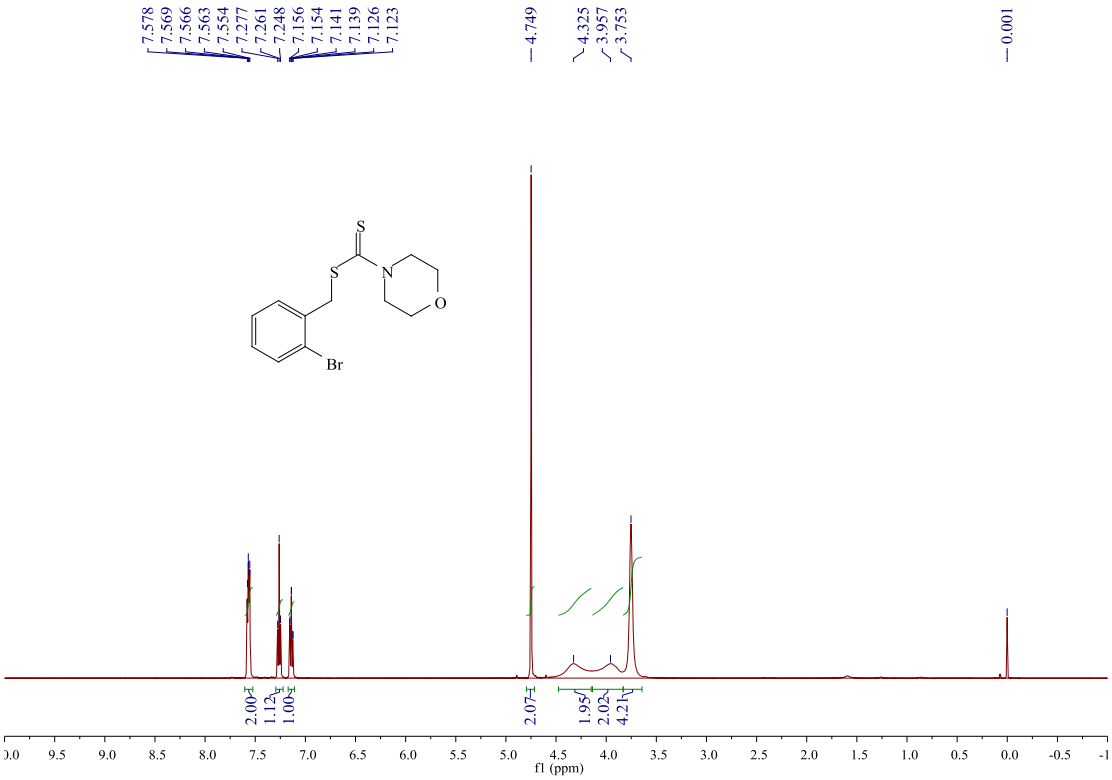


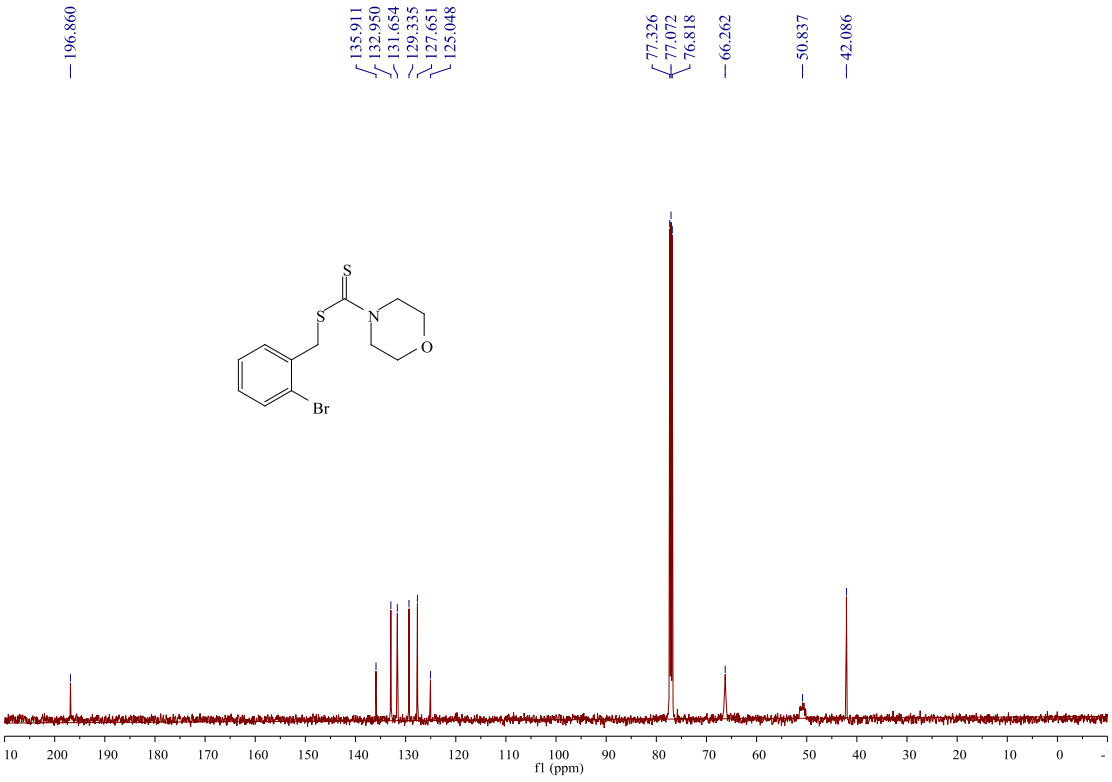
2-nitrobenzyl morpholine-4-carbodithioate (3q)



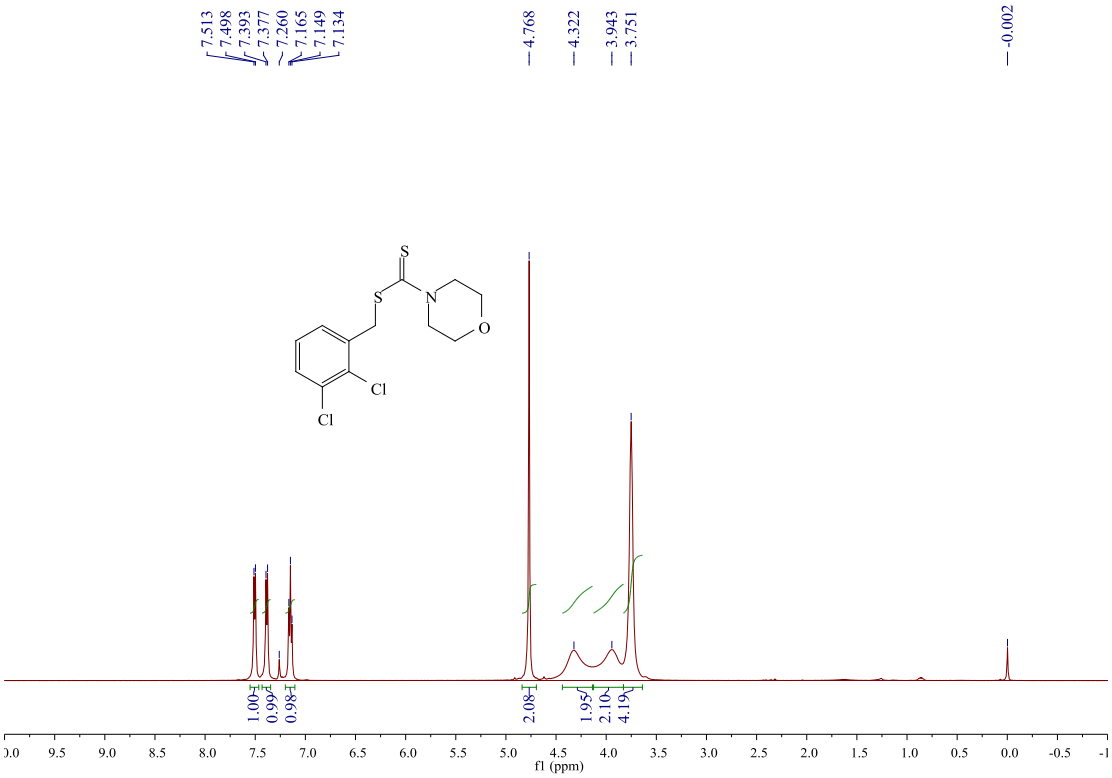


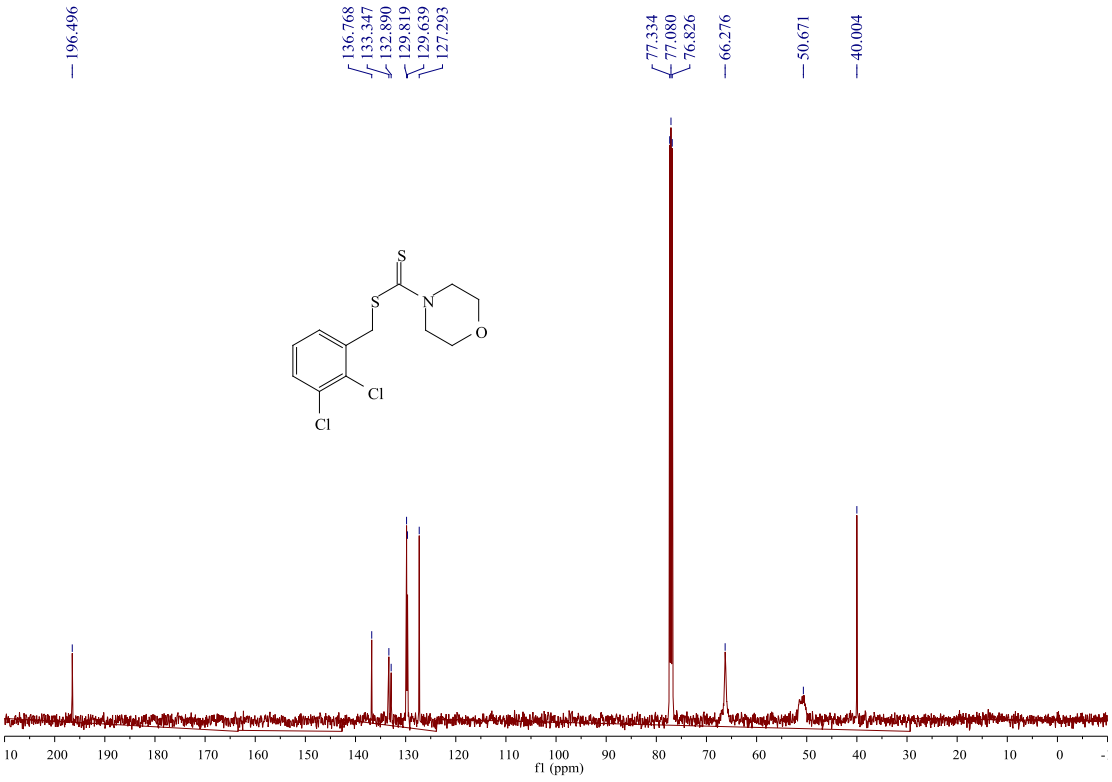
2-bromobenzyl morpholine-4-carbodithioate (3r)



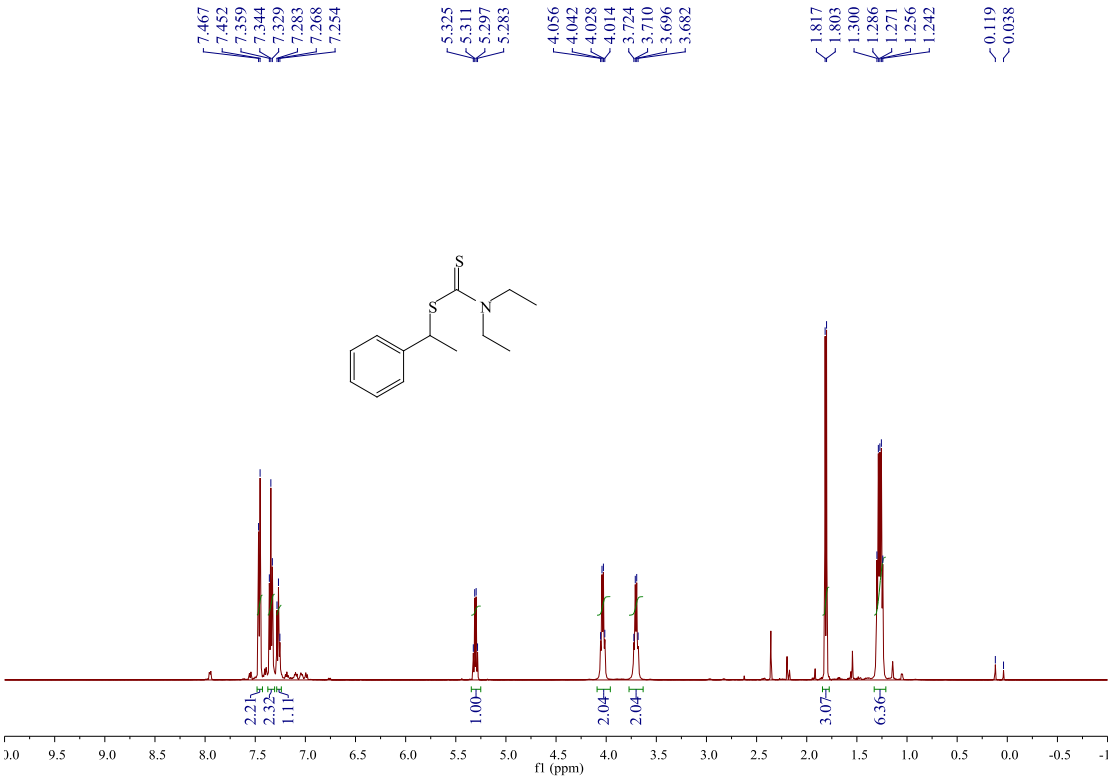


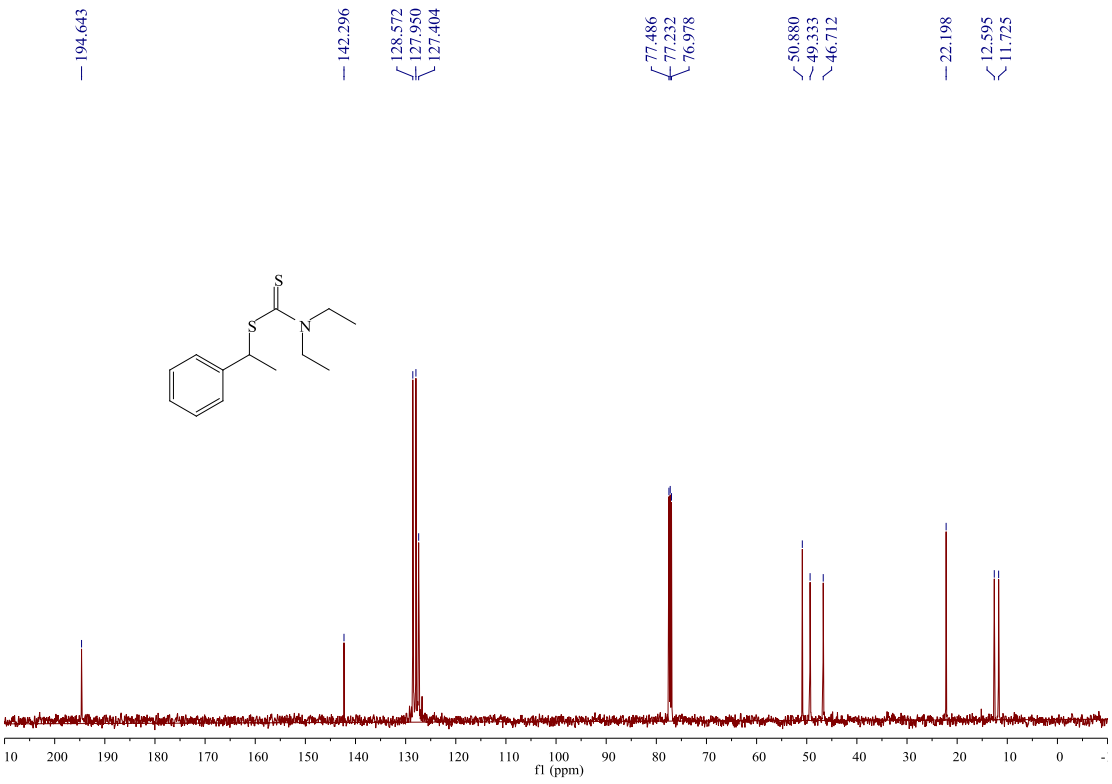
2,3-dichlorobenzyl morpholine-4-carbodithioate (3s)



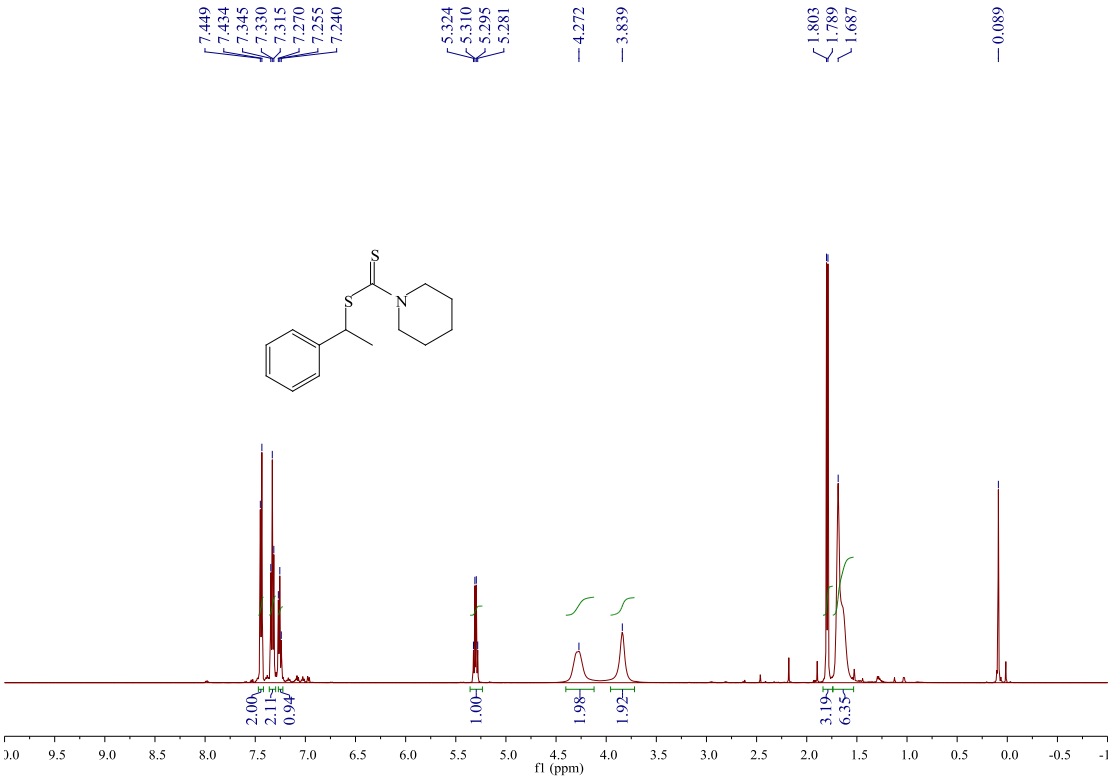


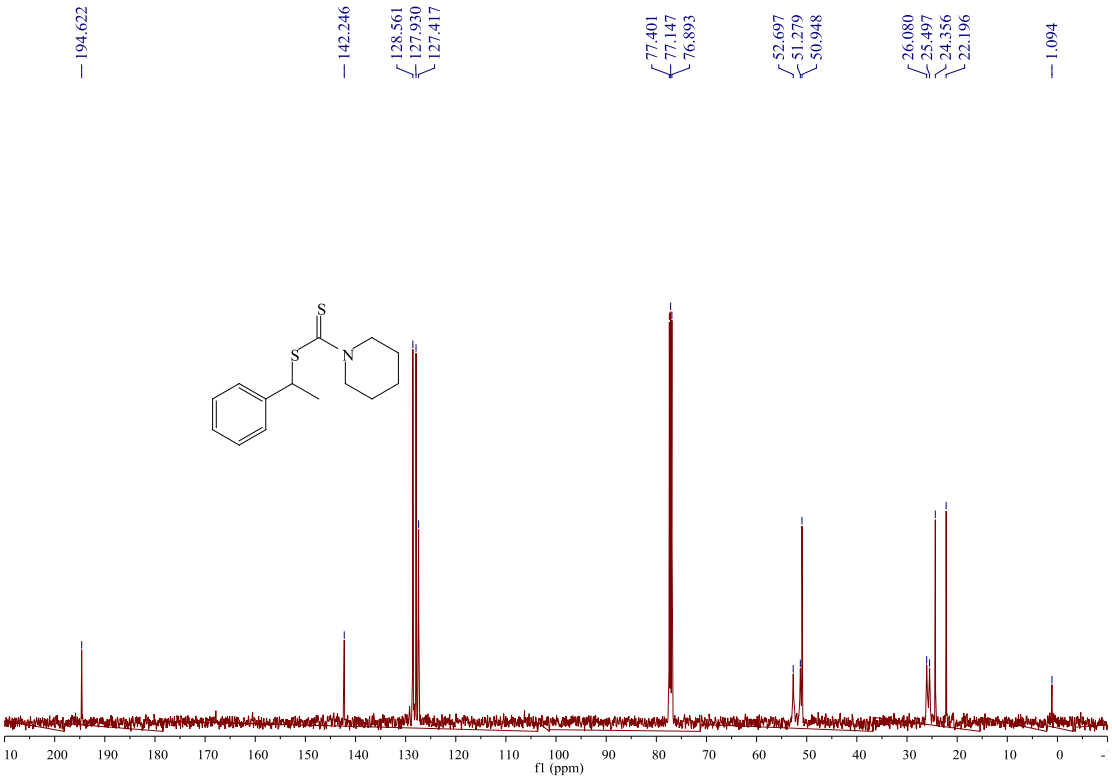
1-phenylethyl diethylcarbamodithioate (3t)



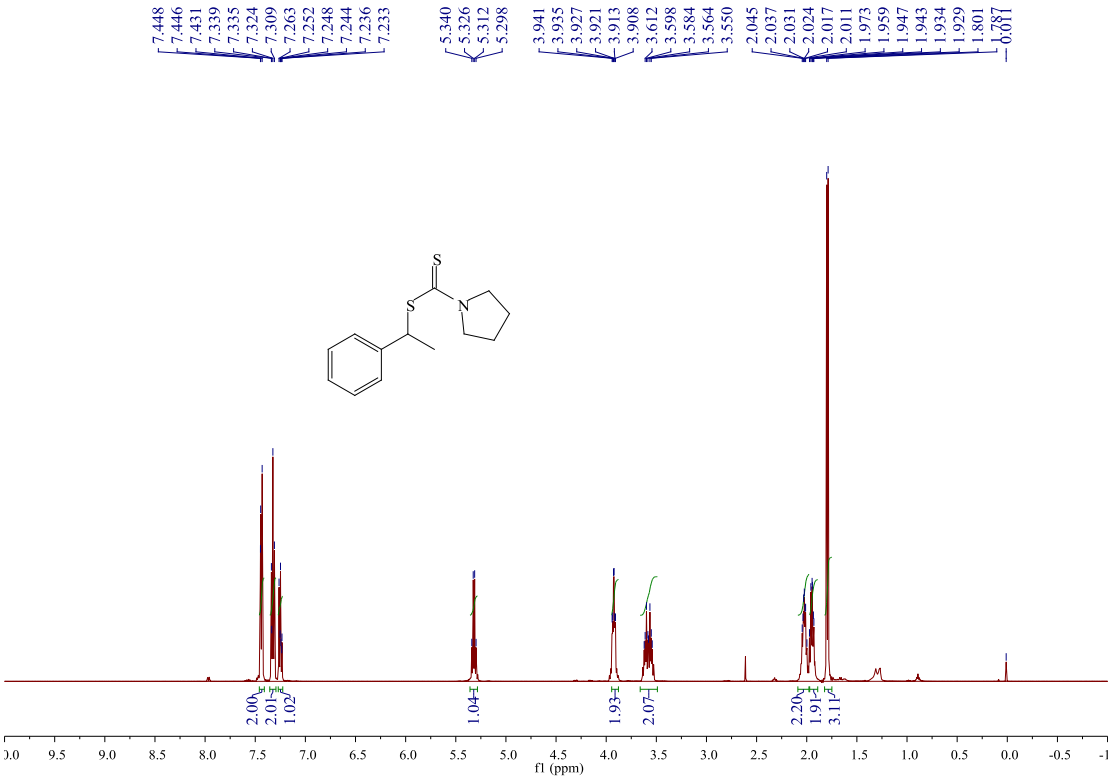


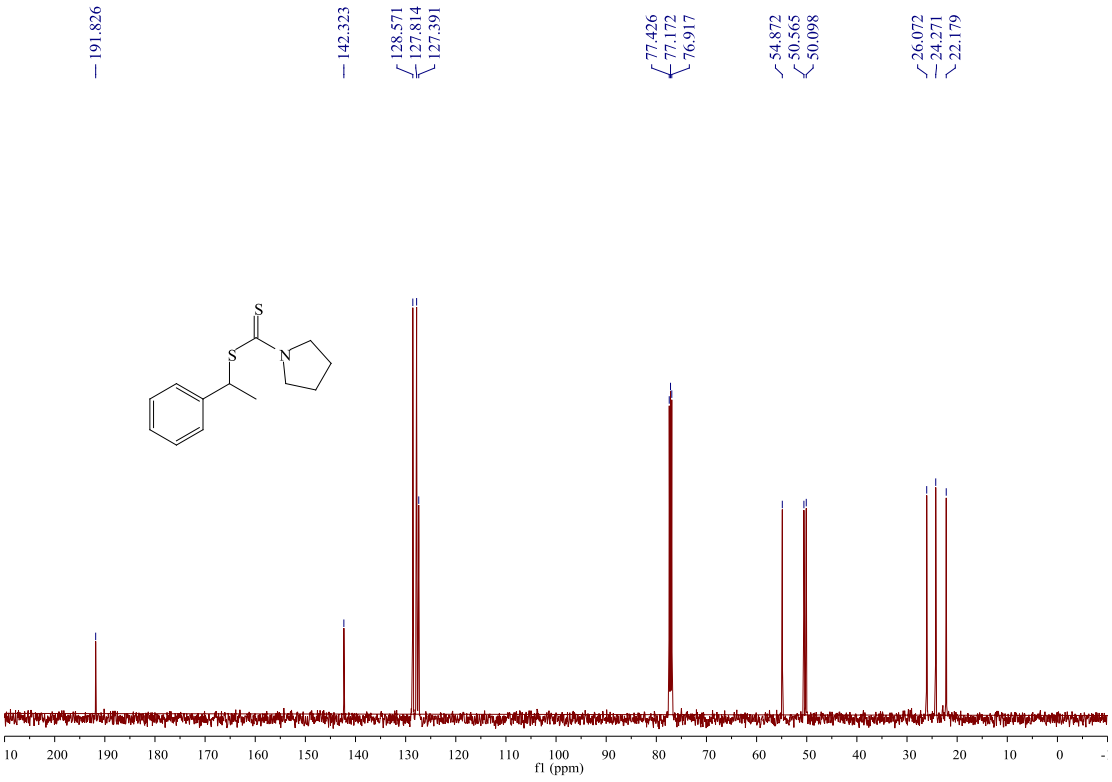
1-phenylethyl piperidine-1-carbodithioate (3u)



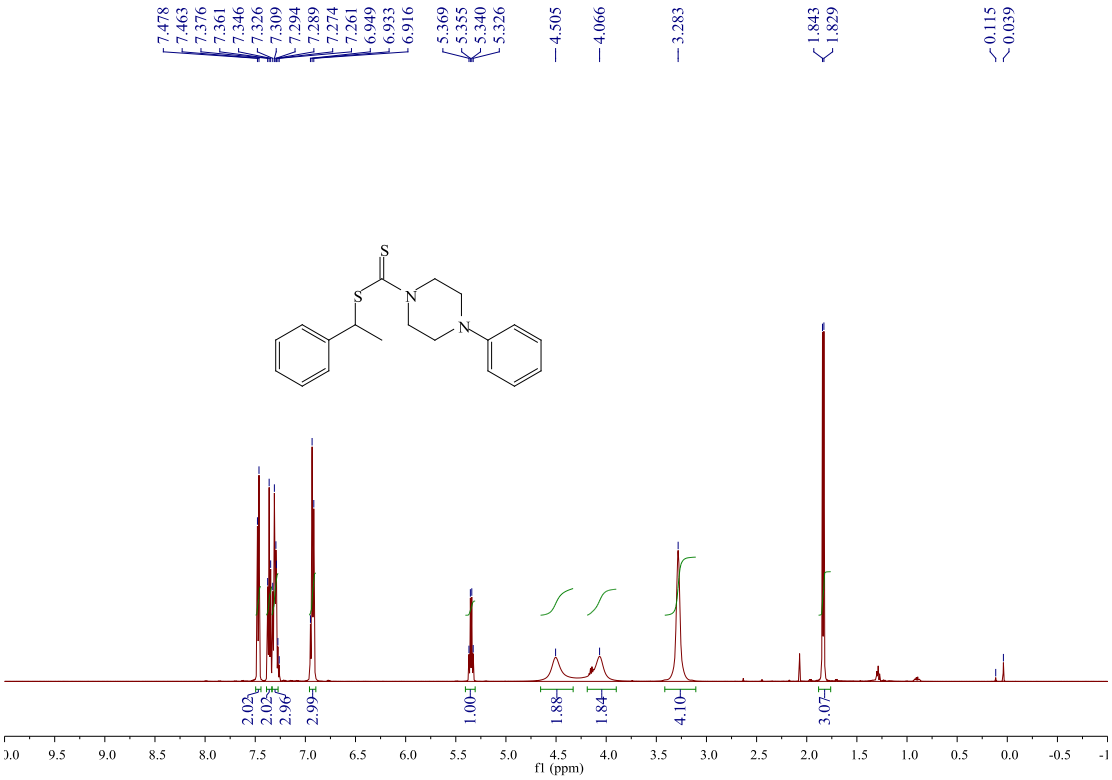


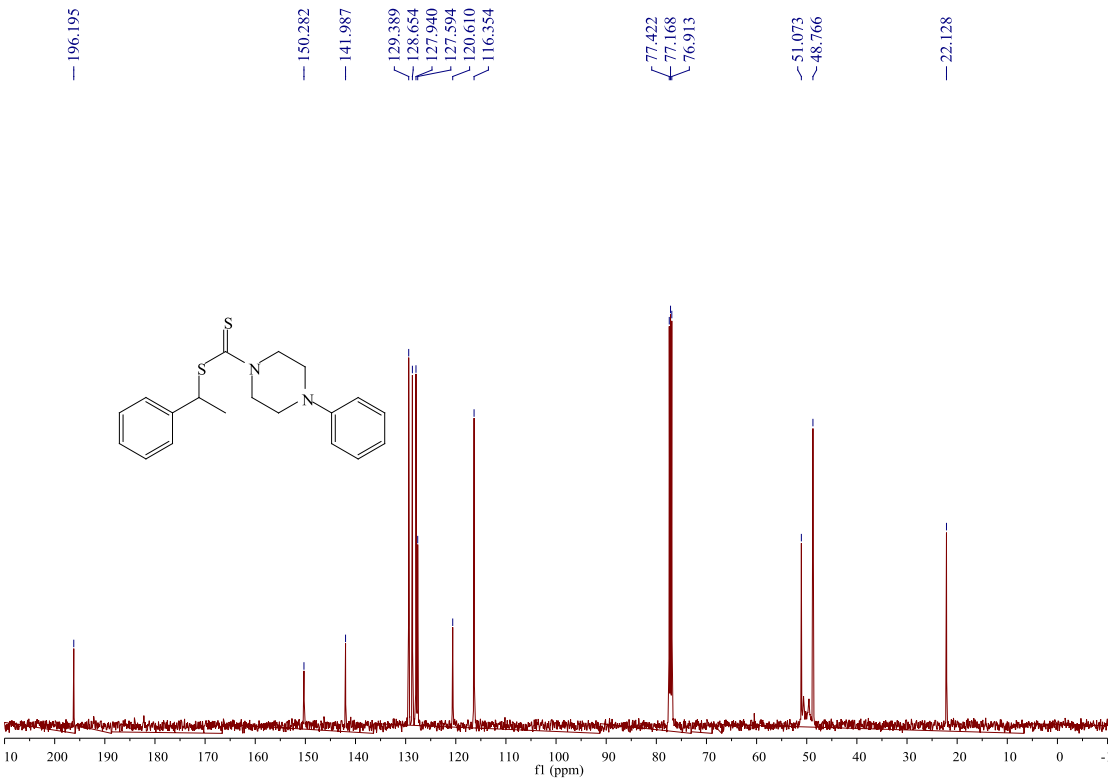
1-phenylethyl pyrrolidine-1-carbodithioate (3v)



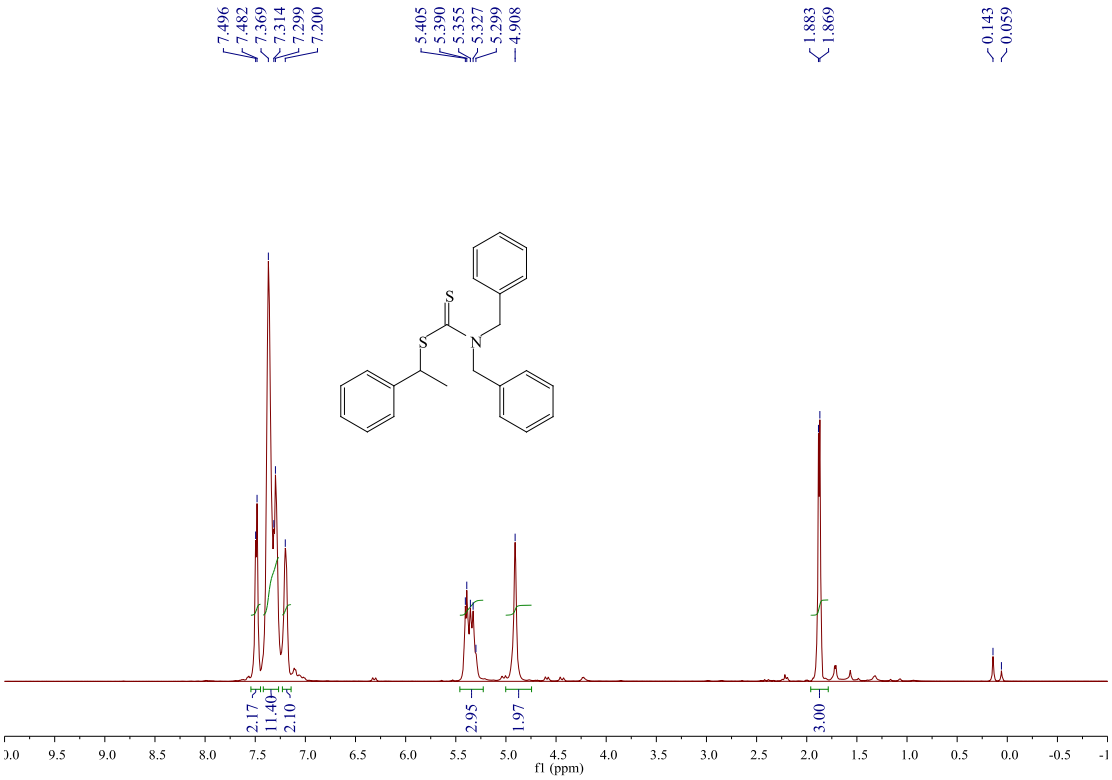


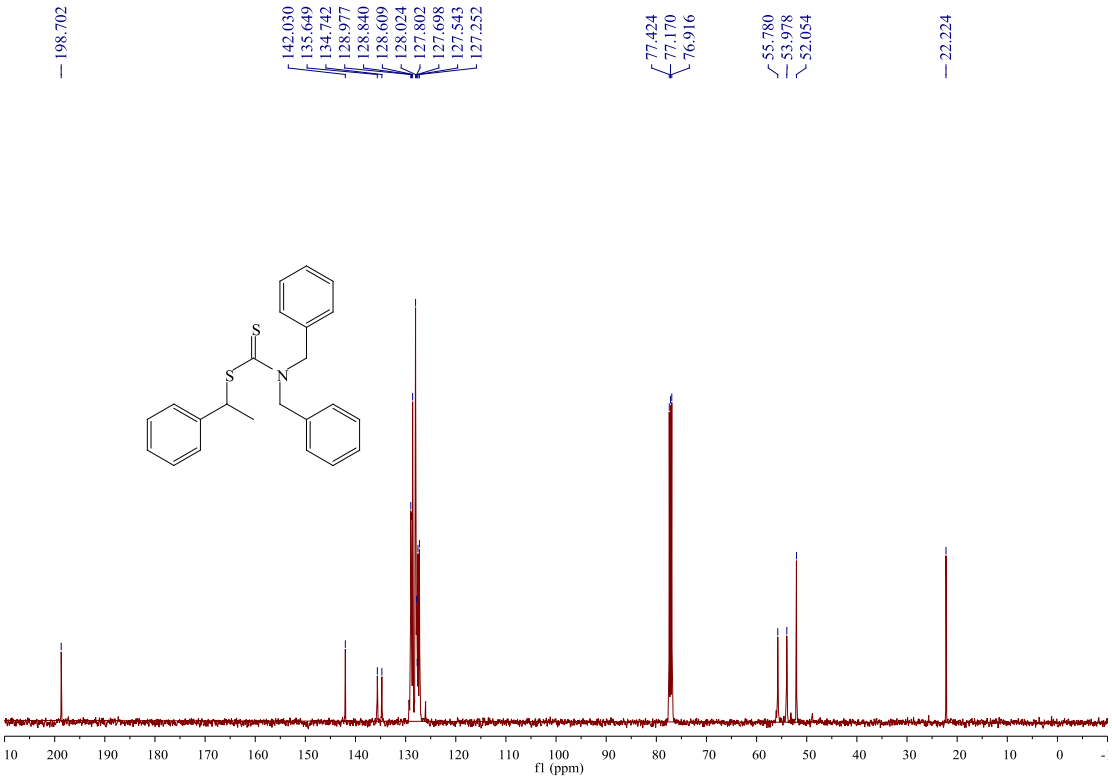
1-phenylethyl 4-phenylpiperazine-1-carbodithioate (3w)



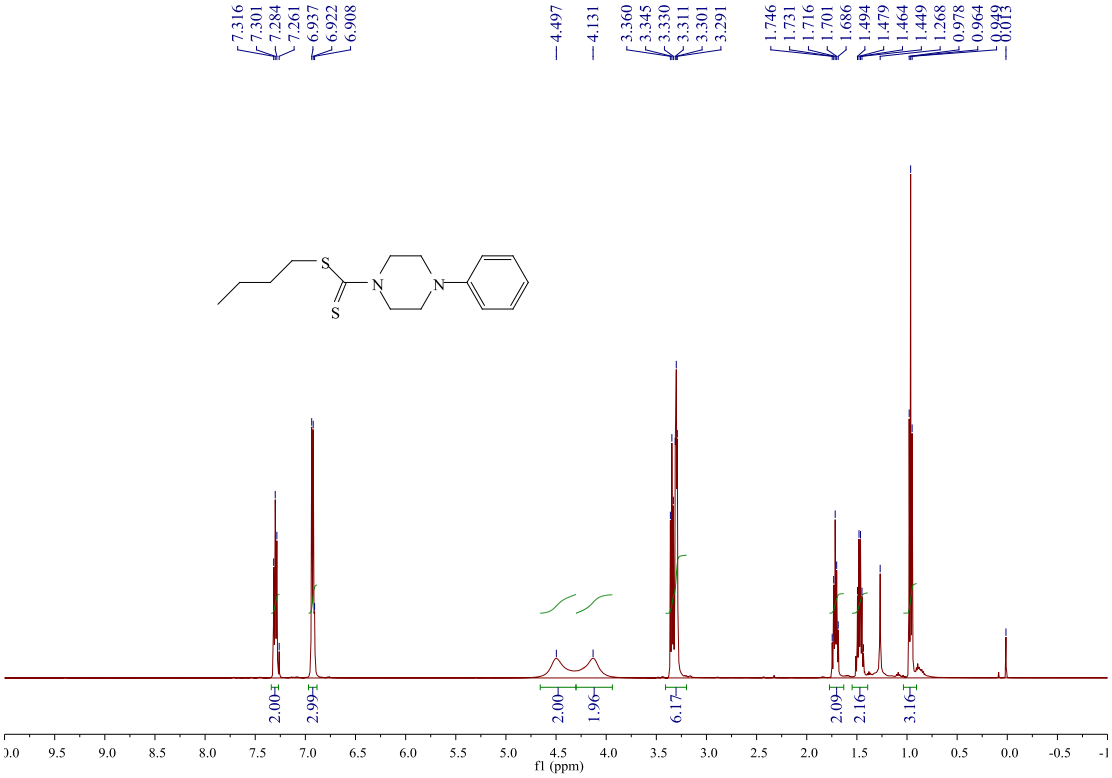


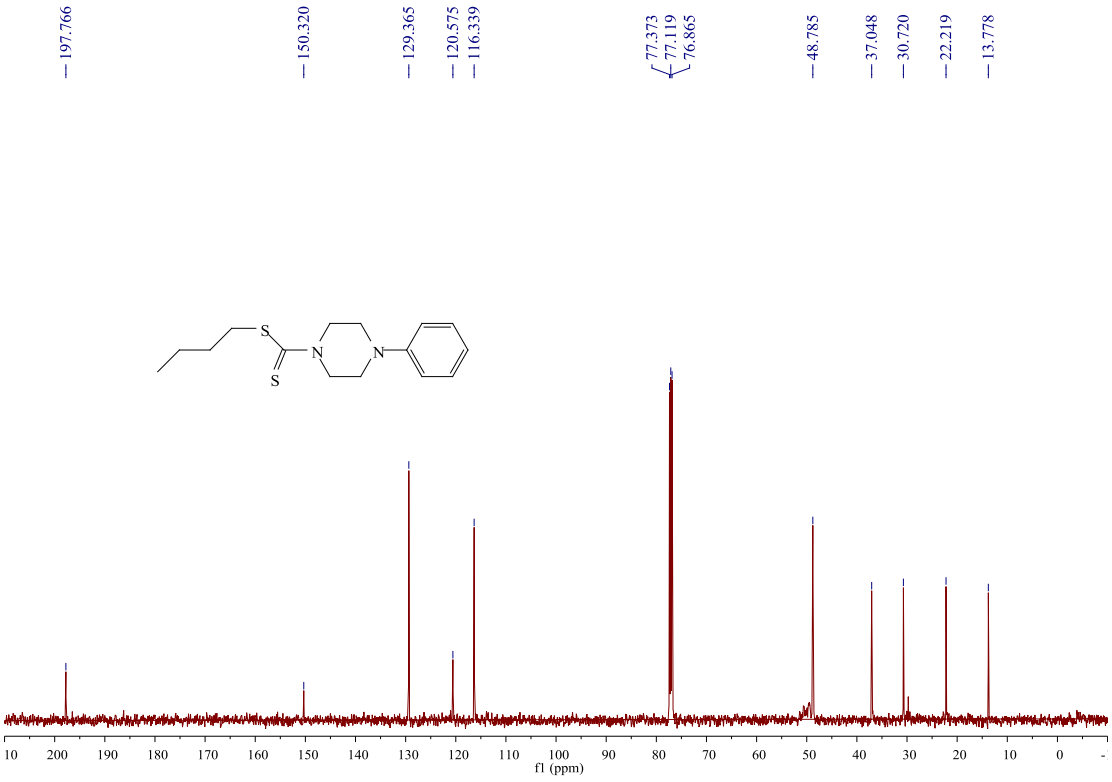
1-phenylethyl dibenzylcarbamodithioate (3x)



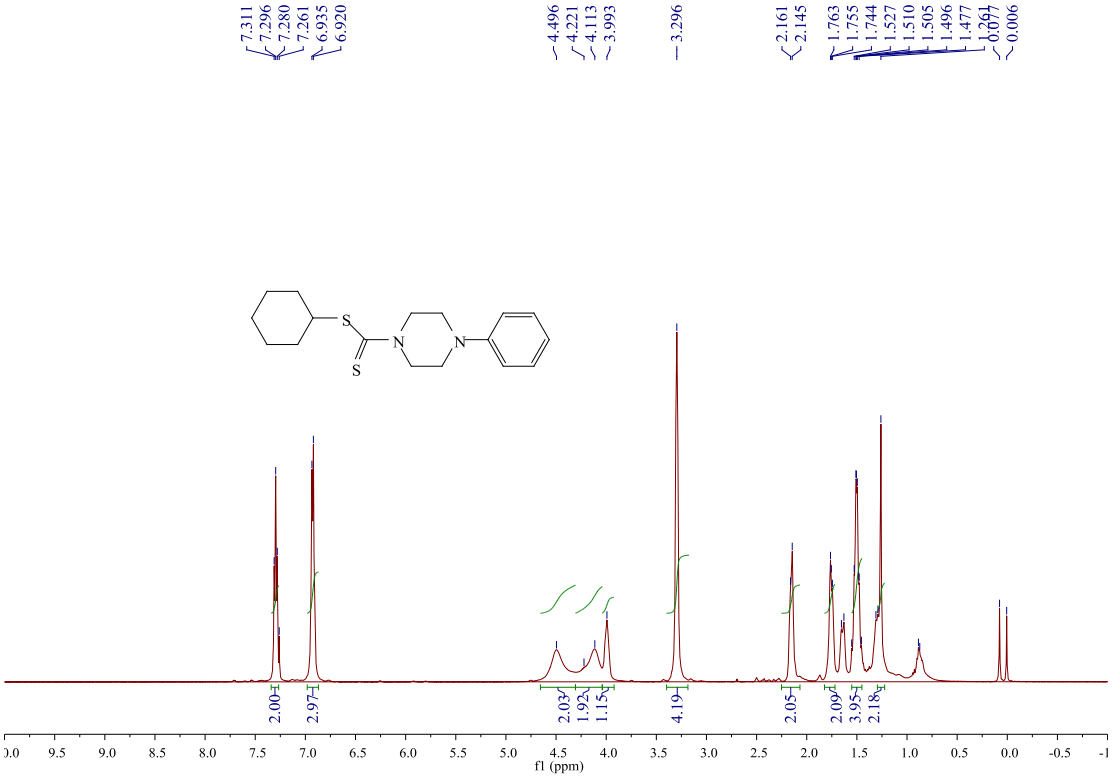


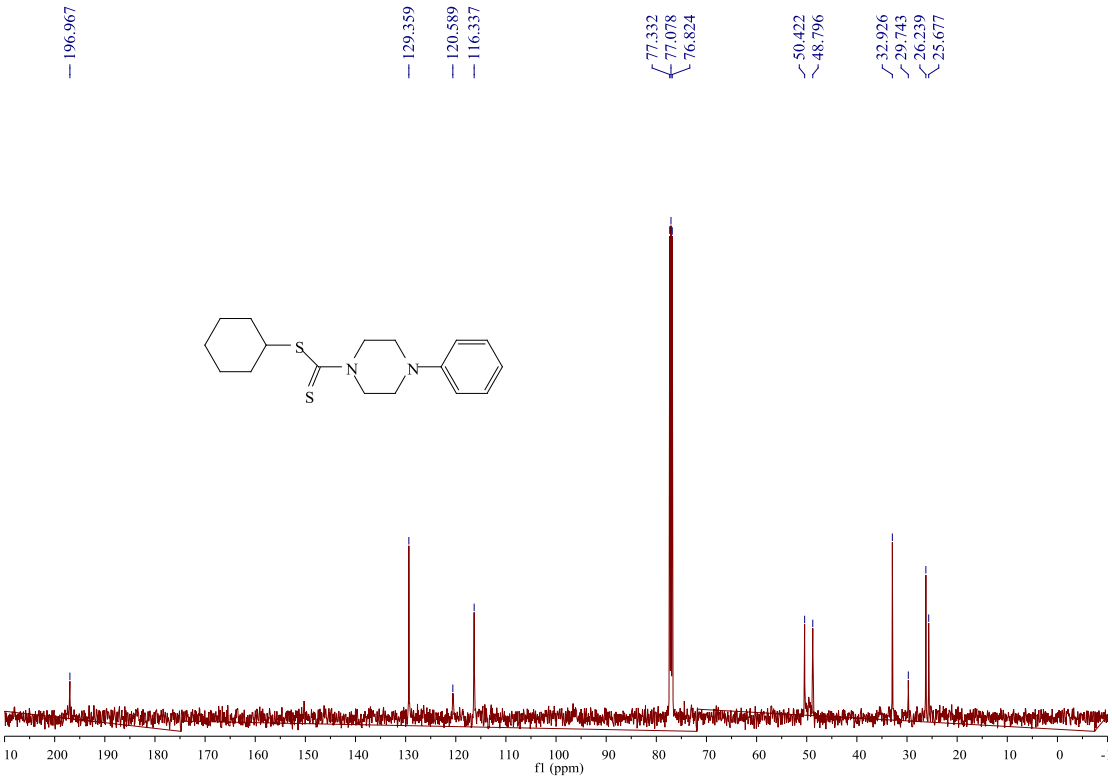
butyl 4-phenylpiperazine-1-carbodithioate (3y)



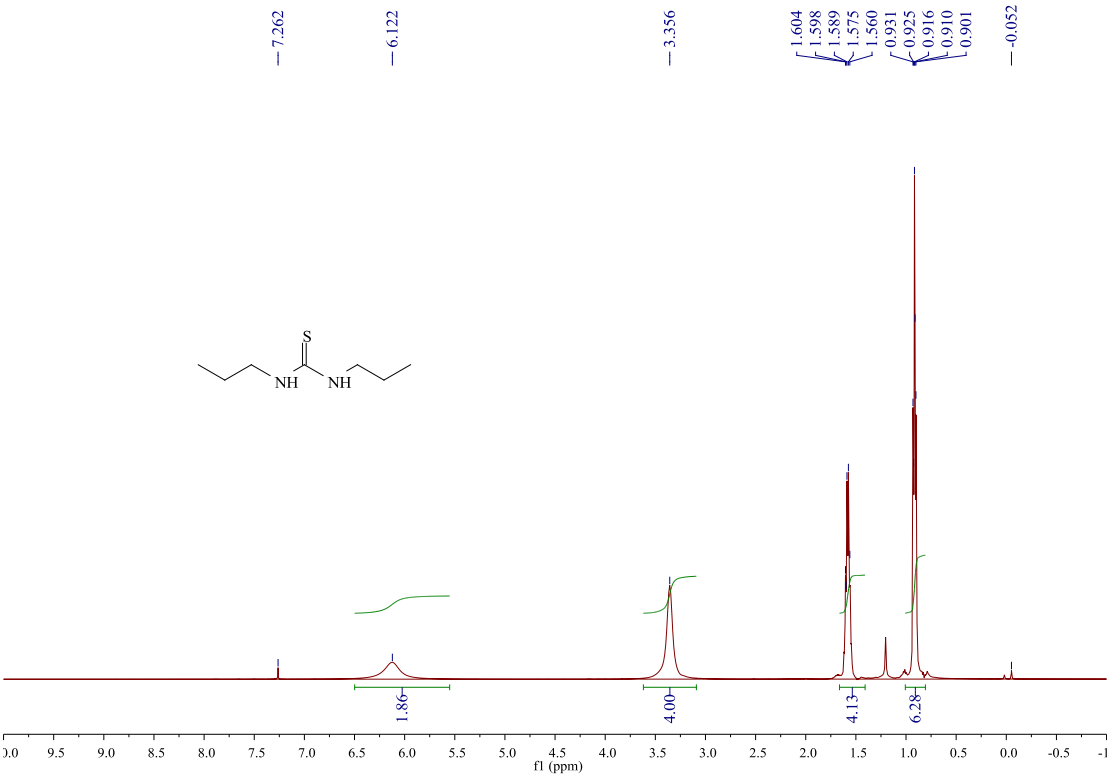


cyclohexyl 4-phenylpiperazine-1-carbodithioate (3z)





1,3-dipropylthiourea (4a)



1,3-dibenzylthiourea (4b)