# Supporting Information

## Metal-free trifunctionalization of phenylacetylenes: An efficient one-pot two-step synthesis of *gem*-bis(dithiocarbamates)

Manas Mondal,[a] Debajyoti Saha,[b,*] and Amit Saha[a,*]

[a]Department of Chemistry, Jadavpur University, Kolkata 700032, India

[b]Department of Chemistry, Krishnagar Govt. College, Krishnagar, West Bengal, India

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## A. General Information:

All chemicals were purchased and used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (Merck silica gel, $f_{24}$). In column-chromatographic purification process, silica gel 60-120 mesh has been used. The $^{1}H$ spectra of synthesized products were recorded in $CDCl_3$ on Brucker Spectrometer at 300, 400 MHz. The $^{19}F$ spectra of synthesized fluorinated productswere recorded in $CDCl_3$ on Brucker Spectrometer, 300 MHz. The $^{13}C$ spectra of synthesized products were recorded in $CDCl_3$ on Brucker Spectrometer at 75, 100 MHz. In all NMR experiments, $CDCl_3$ were used as solvent and TMS as internal standard. Chemical shifts were reported in ppm referenced to 0.00 ppm for TMS. HRMS were measured in methanol solvent on a Waters Micromass Q-tof Micromassspectrometer.

## B. General experimental procedure:

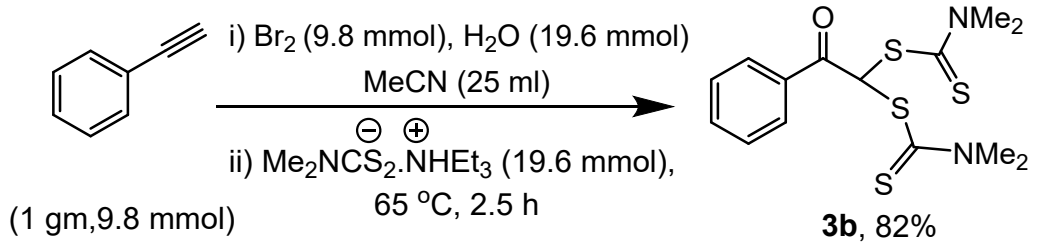
### Preparation of dithiocarbamates salts:

$CS_2$ (0.2 mL, 3 mmol) was added dropwise to a solution of secondary amine (2 mmol) and $Et_3N$ (0.28 mL, 2 mmol) in acetonitrile (2 mL) at 5 $^{o}$C. The resulting solution was stirred at room temperature for 5 min.

### Preparation of *gem*-bis(dithiocarbamates):

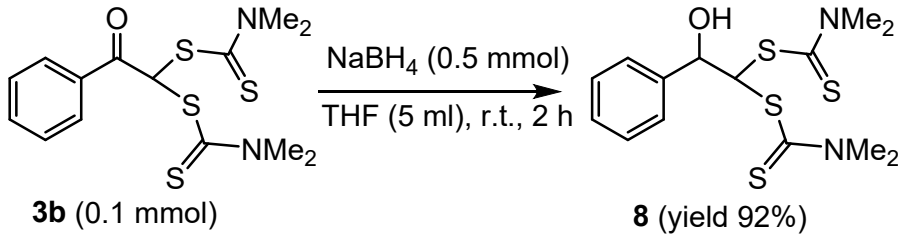
$Br_2$ (0.05 mL, 1 mmol) in MeCN (1 mL) was added dropwise to the solution of aromatic acetylene (1 mmol) in MeCN (2 mL) containing 0.04 mL of water at 5 $^{o}$C. After complete addition, the reaction mixture was allowed to stir for 30 min at room temperature. Then the freshly prepared dithiocarbamate salt (2 mmol) was added to the reaction mixture and was stirred at 65 $^{o}$C for a certain reaction time period. After completion of the reaction (checked by TLC), the solvent was evaporated under reduced pressure. The crude product was extracted with ethyl acetate and purified by column chromatography to obtain the desired product.

### C. Gram-scale Experiment (9.8 mmol scale)




$Br_2$ (0.49 mL, 9.8 mmol) in MeCN (5 mL) was added dropwise to the solution of phenylacetylene (1.08 ml, 9.8mmol) in MeCN (10 mL) containing 0.4 mL of water at 5 °C. After complete addition, the reaction mixture was allowed to stir for 30 min at room temperature. Then the freshly prepared dithiocarbamate salt ($Me_2NCS_2.NHEt_3$, 19.6 mmol) was added to the reaction mixture and was stirred at 65 °C for 2h. After completion of the reaction (checked by TLC), the solvent was evaporated under reduced pressure. The crude product was extracted with ethyl acetate and purified by column chromatography to obtain the desired product.

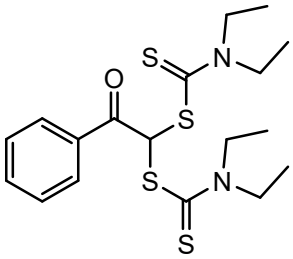
## D. Post functionalization




To a solution of compound **3b** (35.8 mg, 0.1 mmol) in THF (5 ml) at 0 °C, was added THF solution of $NaBH_4$ (19 mg, 0.5 mmol) for a period of 30 min duration. Then the reaction mixture was stirred at room temperature for 2 h. It was quenched with saturated $NH_4Cl$ aqueous solution and the aqueous phase was extracted three times with ethyl acetate. The combined organic phase was dried over sodium sulphate. Then, the crude compound was purified by column chromatography to obtain the desired product.

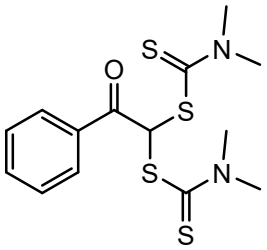
## E. Characterization Data of Synthesized Compounds:

**1.** 2-oxo-2-phenylethane-1,1-diylbis(diethylcarbamodithioate) **(3a)**[1]: White solid,



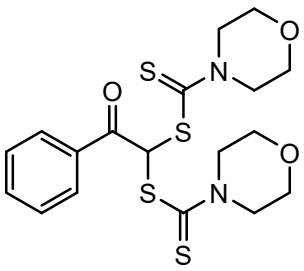
$^1$H NMR(400 MHz, $CDCl_3$) δ: 1.25-1.32(m, 12H), 3.66-3.74(m, 4H), 3.90-4.02(m, 4H), 7.43-7.49(m, 2H), 7.52-7.57(m, 1H), 7.78(s, 1H), 8.16-8.20(m, 2H), $^{13}$C NMR (100MHz,$CDCl_3$) δ: 10.52, 11.74, 46.25, 48.96, 60.92, 127.50 (2C), 128.24 (2C), 132.08, 134.37, 189.98, 190.76 (2C).

**2.** 2-oxo-2-phenylethane-1,1-diylbis(dimethylcarbamodithioate) **(3b)**: Yellow



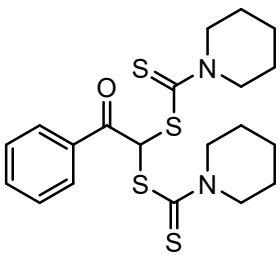
solid,$^1$H NMR (400 MHz, $CDCl_3$) δ: 3.35 (s, 6H), 3.50 (s, 6H), 7.43-7.49 (m, 2H), 7.53-7.59(m, 1H) 7.73 (s, 1H), 8.14-8.17 (m, 2H), $^{13}$C NMR (100MHz, $CDCl_3$) δ: 41.72, 45.77, 62.90, 128.63(2C), 129.22(2C), 133.34, 135.14, 190.51, 193.04, HRMS (ESI) m/z calcd for $C_{14}H_{18}N_2OS_4$ $[M + H]^+$, 358.0302, found 359.0526.

**3.** 2-oxo-2-phenylethane-1,1-diylbis(morpholine-4-carbamodithioate) **(3c)**: White



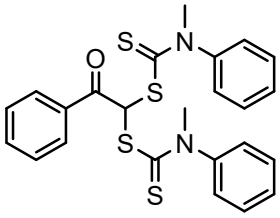
solid,$^1$H NMR (400 MHz, $CDCl_3$) δ: 3.75(s, 8H), 3.88 (broad, 4H), 4.25 (broad, 4H), 7.45-7.51 (m, 2H), 7.59-7.61(m, 1H), 7.89 (s, 1H), 8.14-8.17 (m, 2H), $^{13}$C NMR (100 MHz,$CDCl_3$) δ: 50.80, 51.71, 61.55, 66.13(2C), 128.73(2C), 129.23(2C), 133.55, 134.91, 190.45, 193.16(2C). HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_3S_4$ $[M + H]^+$, 442.0513, found 443.0593.

**4.** 2-oxo-2-phenylethane-1,1-diylbis(piperidine-1-carbamodithioate) **(3d)**: Light



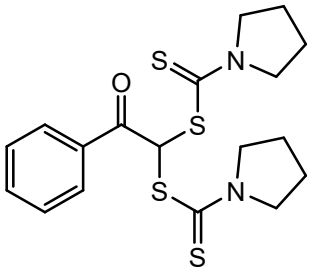
yellow solid,$^1$H NMR (400 MHz, $CDCl_3$) δ: 1.69(s, 12H), 3.84(broad, 4H), 4.19-4.23(broad, 4H), 7.45-7.49(m, 2H ), 7.54-7.59(m, 1H), 7.88(s, 1H) , 8.18-8.20(m, 2H), $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 24.05, 25.32, 26.07, 51.89, 53.38, 61.85, 128.58(2C), 129.27(2C), 133.22, 135.24, 190.97, 191.57(2C), HRMS (ESI) m/z calcd for $C_{20}H_{26}N_2OS_4$ $[M + H]^+$, 438.0928, found 439.0497.

**5.** 2-oxo-2-phenylethane-1,1-diylbis(methyl(phenyl)carbamodithioate) **(3e)**: Light



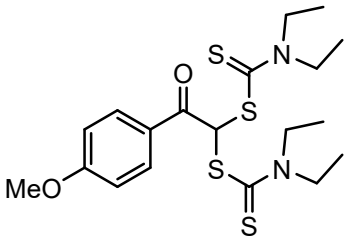
yellow solid, $^{1}$H NMR(400 MHz, $CDCl_3$) δ: 3.71(s, 6H), 7.20-7.22(m, 4H), 7.37-7.48(m, 8H), 7.54-7.60(m, 2H), 8.11-8.13(m, 2H), $^{13}$C NMR(100 MHz, $CDCl_3$) δ: 46.53, 63.27, 126.91, 128.54, 129.14, 129.28, 129.87, 133.16, 135.35, 143.96, 190.96, 195.36(2C), HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2OS_4$ $[M + H]^+$, 482.061, found 483.108.

**6.** 2-oxo-2-phenylethane-1,1-diylbis(pyrrolidine-1-carbamodithioate) **(3f):** White



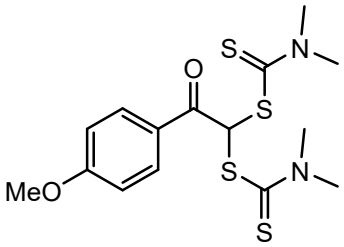
solid, $^{1}$HNMR (300 MHz, $CDCl_3$) δ: 1.95-2.10(m, 8H), 3.64(t, J=6.9 Hz, 4H), 3.87(t, J=6.9 Hz ,4H), 7.43-7.58(m, 3H), 7.83(s, 1H), 8.17-8.20(m, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 24.30, 26.12, 50.73, 51.43, 60.87, 128.60(2C), 129.30(2C), 133.30, 135.12, 186.60, 190.97(2C), HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2OS_4$ $[M + H]^+$, 410.0615, found 411.0692.

**7.** 2-(4-methoxyphenyl)-2-oxoethane-1,1-diyl bis(diethylcarbamodithioate) **(3g):**



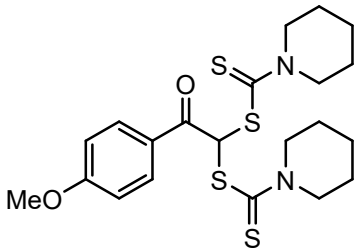
Light yellow solid, $^{1}$HNMR (300 MHz, $CDCl_3$) δ: 1.22-1.31(m, 12H), 3.67-3.74(m, 4H), 3.86(s, 3H), 3.92-4.01(m, 4H), 6.94(d, J= 8.7 Hz, 2H), 7.74(s, 1H), 8.18(d, J= 9 Hz, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ:10.51, 11.72, 46.17, 54.44, 60.67, 112.79(2C), 127.19, 130.63(2C), 162.64, 188.70, 190.81(2C), HRMS (ESI) m/z calcd for $C_{19}H_{28}N_2O_2S_4$ $[M + Na]^+$, 467.0931, found 467.0988.

**8.** 2-(4-methoxyphenyl)-2-oxoethane-1,1-diyl bis(dimethylcarbamodithioate) **(3h):**



Light yellow solid, $^{1}$H NMR (300MHz, $CDCl_3$) δ: 3.35(s, 6H), 3.50(s, 3H), 3.86(s, 3H), 6.94(d, J= 9 Hz, 2H), 7.69(s, 1H), 8.16(d, J= 9 Hz, 2H), $^{13}$C NMR (75MHz, $CDCl_3$) δ: 41.67, 45.71, 55.49, 62.73, 113.89(2C), 128.08, 131.62(2C), 189.42, 193.22(2C), HRMS (ESI) m/z calcd for $C_{15}H_{20}N_2O_2S_4$ $[M]^+$, 388.04, found 388.21.

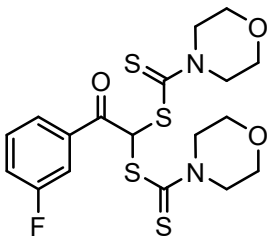
**9.** 2-(4-methoxyphenyl)-2-oxoethane-1,1-diyl bis(piperidine-1-carbamodithioate)



**(3i):** White solid, $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 1.67(s, 12H), 3.82(broad, 4H), 3.86(s, 3H), 4.19(broad, 4H), 6.94(d, J= 9.2 Hz, 2H), 7.81(s, 1H), 8.18(d, J= 8.8 Hz,

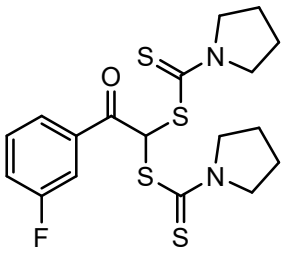
2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 24.08, 25.31, 26.05, 51.81, 53.81, 55.51, 61.73, 113.85(2C), 128.16, 131.67(2C), 163.70, 189.64, 191.76(2C), HRMS (ESI) m/z calcd for $C_{21}H_{28}N_2O_2S_4$ $[M + Na]^+$, 491.0931, found 491.0933.

**10.** 2-(3-fluorophenyl)-2-oxoethane-1,1-diyl bis(morpholine-4-carbamodithioate)



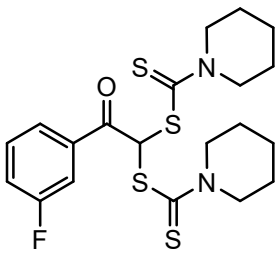
**(3j):** White solid, $^1$H NMR (300 MHz, $CDCl_3$) δ: 3.75(s, 8H), 3.88(broad, 4H), 4.25(broad, 4H), 7.24-7.31(m, 1H), 7.42-7.49(m, 1H), 7.80-7.84(m, 2H), 7.95-7.97(m, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 50.94, 51.76, 61.46, 66.17(2C), 115.92(J=22.8 Hz), 120.52(J=21.37 Hz), 124.93(J=3.07 Hz), 130.36(J=7.42 Hz), 137.05(J=6.6 Hz), 162.78(J=246 Hz), 189.41(J=2.17 Hz), 192.93(2C), HRMS (ESI) m/z calcd for $C_{18}H_{21}FN_2O_3S_4$ $[M + H]^+$, 460.0419, found 461.0156.

**11.** 2-(3-fluorophenyl)-2-oxoethane-1,1-diyl bis(pyrrolidine-1-carbamodithioate)



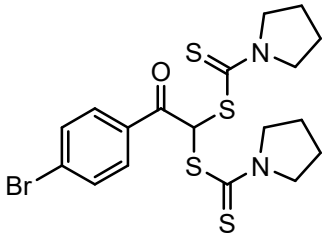
**(3k):** Light yellow solid, $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.95-2.15(m, 8H), 3.67(t, J=6.9 Hz, 4H), 3.91(t, J=6.9 Hz, 4H), 7.28-7.31(m, 1H), 7.44-7.51(m, 1H), 7.81(s, 1H), 7.87-7.90(m, 1H), 8.03-8.05(m, 1H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 24.30, 26.23, 50.78, 55.50, 60.80, 115.93(J=23.25 Hz), 120.27(J=21 Hz), 125.03(J=3 Hz), 130.25(J=7.5 Hz), 137.27(J=6.75 Hz), 162.75(J=246 Hz), 188.33(2C), 189.91(J=2.25 Hz), HRMS (ESI) m/z calcd for $C_{18}H_{21}FN_2OS_4$ $[M + H]^+$, 428.0521, found 429.0115.

**12.** 2-(3-fluorophenyl)-2-oxoethane-1,1-diyl bis(piperidine-1-carbamodithioate)



**(3l):** Light yellow solid, $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.72(s,12H), 3.86(broad,4H), 4.23(broad,4H), 7.28-7.31(m,1H), 7.44-7.51(m,2H), 7.86-7.91(m,2H), 8.02-8.05(m,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 24.04, 25.32, 26.07, 51.93, 53.46, 61.78, 115.93(J=22.5 Hz),120.16(J=21 Hz) , 125.01(J=3 Hz), 130.20(J=8.25 Hz), 137.41(J=6.75 Hz), 162.76(J=246 Hz), 189.91(J=2.25 Hz), 191.35(2C), HRMS (ESI) m/z calcd for $C_{20}H_{25}FN_2OS_4$ $[M + H]^+$, 456.0834, found 457.0468.

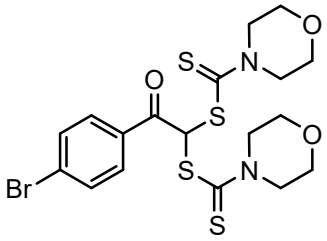
**13.** 2-(4-bromophenyl)-2-oxoethane-1,1-diyl bis(pyrrolidine-1-carbamodithioate)



**(3m):** White solid, $^1$H NMR (400 MHz, $CDCl_3$) δ: 1.93-2.00(m, 4H), 2.04-2.11(m, 4H), 3.64(t, J=6.8 Hz , 4H), 3.88(t, J=7.2 Hz , 4H), 7.59-7.62(m, 2H), 7.79(s, 1H), 8.05-

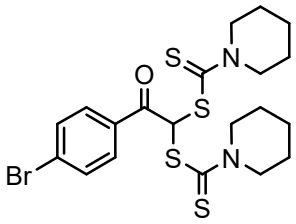
8.08(m, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 24.30, 26.22, 50.77, 55.51, 60.67, 128.46**,** 130.82(2C), 131.92(2C), 133.96, 188.40, 190.19(2C), HRMS (ESI) m/z calcd for $C_{18}H_{21}BrN_2OS_4$ $[M + H]^+$, 489.5361, found 490.9411.

**14.** 2-(4-bromophenyl)-2-oxoethane-1,1-diyl bis(morpholine-4-carbamodithioate)



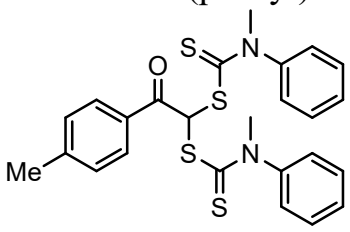
**(3n):** White solid, $^1$H NMR (300 MHz, $CDCl_3$) δ: 3.74(s, 8H), 3.88(broad, 4H), 4.24(broad, 4H), 7.61(d, J=8.4 Hz, 2H), 7.85(s, 1H), 8.02(d, J=8.7 Hz, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 50.85, 51.74, 61.30, 66.17(2C), 128.75,130.73(2C), 132.05(2C), 133.73, 189.66, 192.94(2C). HRMS (ESI) m/z calcd for $C_{18}H_{21}BrN_2O_3S_4$ $[M + H]^+$, 519.9618, found 520.9148.

**15.** 2-(4-bromophenyl)-2-oxoethane-1,1-diyl bis(piperidine-1-carbamodithioate)



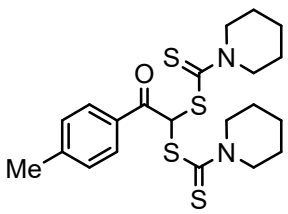
**(3o):** Light yellow solid, $^1$H NMR (300 MHz, $CDCl_3$) δ: 1.50(s, 12H), 3.76(broad, 4H), 4.13(broad, 4H), 7.52-7.55(m, 2H), 7.76(s, 1H), 7.98-8.00(m, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 24.02, 25.30, 26.04, 51.90, 53.45, 61.67, 128.32, 130.81(2C), 131.88(2C), 134.14, 190.13, 191.44(2C), HRMS(ESI) m/z calcd for $C_{20}H_{25}BrN_2OS_4$ $[M + H]^+$, 516.0033, found 517.0233.

**16.** 2-oxo-2-(p-tolyl)ethane-1,1-diyl bis(methyl(phenyl)carbamodithioate) **(3p):**



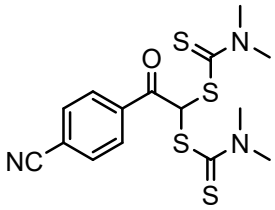
White solid,$^1$HNMR (400 MHz, $CDCl_3$) δ: 2.41(s, 3H), 3.70(s, 6H), 7.20-7.27(m, 6H), 7.37-7.41(m, 6H), 7.56(s, 1H), 8.01-8.03(m. 2H),$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 21.79, 46.48, 63.24, 126.93, 129.28, 129.85, 132.81, 144.03, 190.61, 195.45(2C). ), HRMS (ESI) m/z calcd for $C_{25}H_{24}N_2OS_4$ $[M + H]^+$, 496.077, found 497.0989.

**17.** 2-oxo-2-(p-tolyl)ethane-1,1-diyl bis(piperidine-1-carbamodithioate) **(3q):**



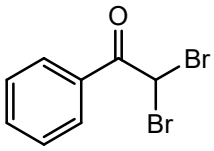
White solid, $^1$H NMR (300 MHz, $CDCl_3$) δ : 1.69(s, 12H), 2.41(s, 3H), 3.83(broad, 4H), 4.20(broad, 4H), 7.28(broad, 1H),7.84(s, 1H) , 8.09(d, J=8.1 Hz, 2H), $^{13}$C NMR(75 MHz, $CDCl_3$) δ: 21.78, 24.07, 25.32, 26.04, 51.84, 53.31, 61.82, 129.33(2C), 129.44(2C), 132.68, 144.09, 190.63, 191.74(2C), HRMS(ESI) m/z calcd for $C_{21}H_{28}N_2OS_4$ $[M + H]^+$, 452.108, found 453.629.

**18.** 2-(4-cyanophenyl)-2-oxoethane-1,1-diylbis(dimethylcarbamodithioate) **(3r):**

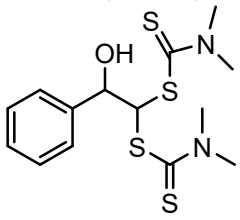


White solid, $^{1}$H NMR (400 MHz, $CDCl_3$) δ : 3.36(s, 6H), 3.51(s, 6H), 7.75-7.77(m, 3H), 8.23-8.26(m, 2H), $^{13}$C NMR(100 MHz, $CDCl_3$) δ: 40.78, 44.92, 61.62, 115.19, 117.14, 128.79(2C), 131.44(2C), 137.50, 188.51, 191.52, HRMS (ESI) m/z calcd for $C_{15}H_{17}N_3NaOS_4$ [M + Na]$^+$, 406.0152, found 406.0144.

**19.** 2,2-dibromo-1-phenylethan-1-one **(4):** Yellow liquid, $^{1}$H NMR (300 MHz, $CDCl_3$) δ : 6.71(s, 1H), 7.49-7.54(m, 2H), 7.62-7.67(m, 1H), 8.07-8.10(m, 2H), $^{13}$C NMR (75MHz,$CDCl_3$) δ: 39.69, 128.96(2C), 129.73(2C), 130.87, 134.47, 185.99

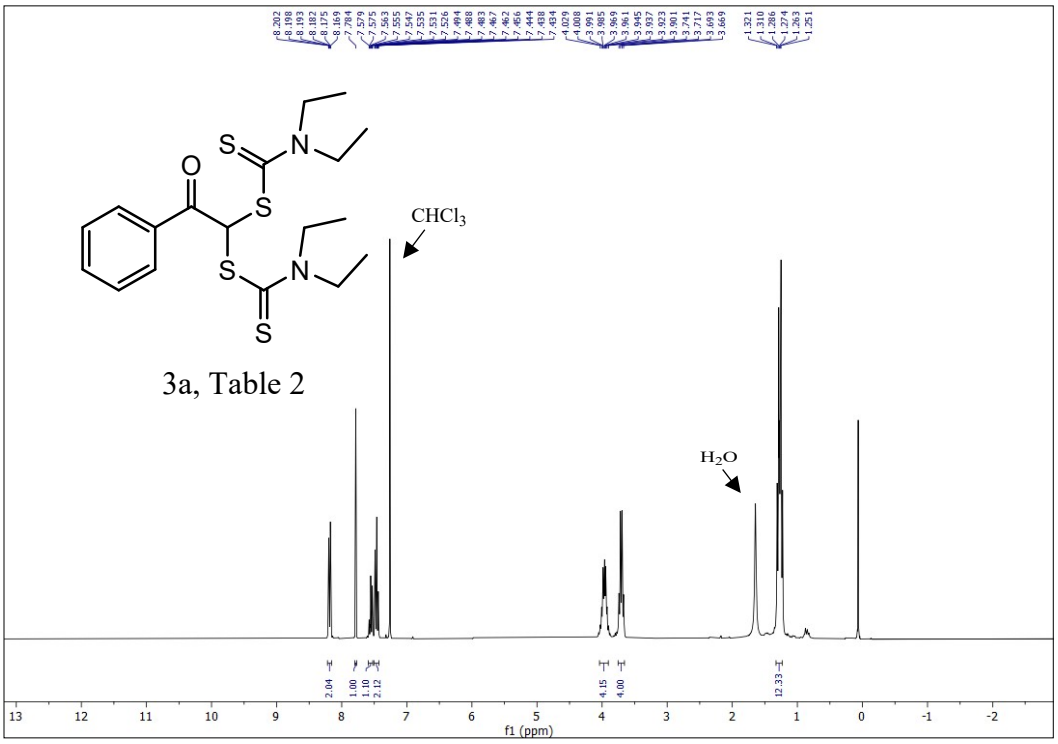


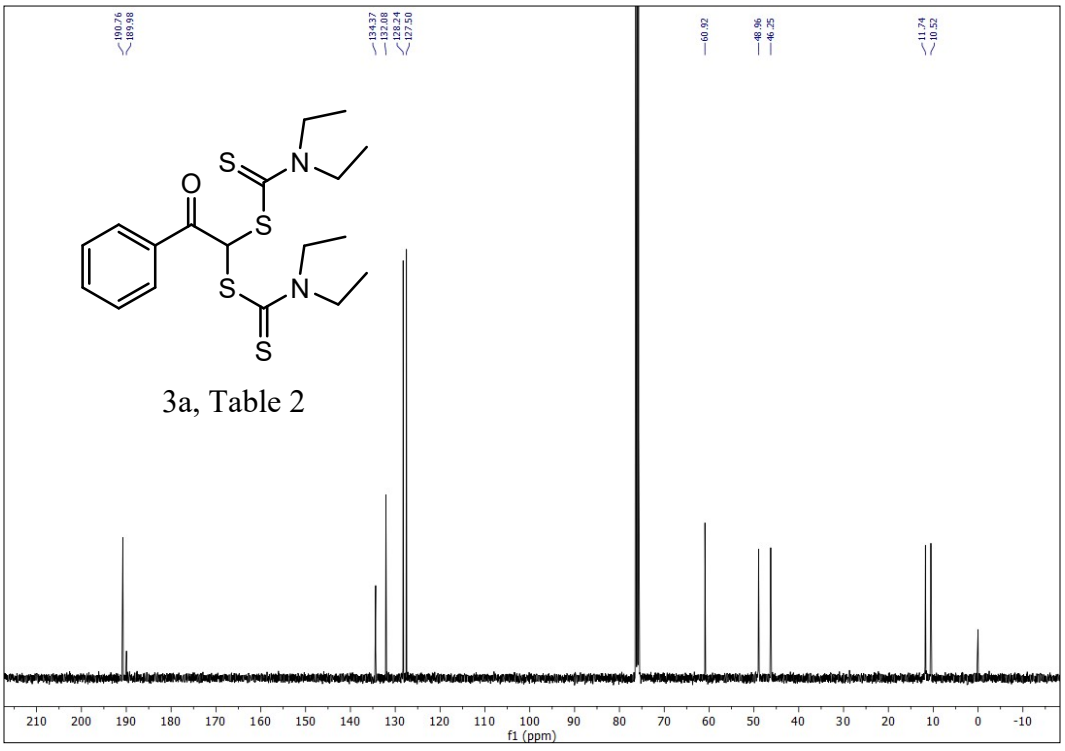
**20.** 2-hydroxy-2-phenylethane-1,1-diyl bis(dimethylcarbamodithioate) **(8):** White solid, $^{1}$H NMR (300 MHz, $CDCl_3$) δ : 3.33-3.37(m, 6H), 3.50-3.55(m, 7H), 5.66-5.67(broad, 1H), 6.64(m, 1H), 7.28-7.39(m, 3H), 7.66-7.68(m, 2H), $^{13}$C NMR (75MHz,$CDCl_3$) δ: 41.64, 41.73, 45.16, 45.72, 69.24, 75.15, 126.77(2C), 127.84, 128.06(2C), 140.42, 194.19, 195.20.



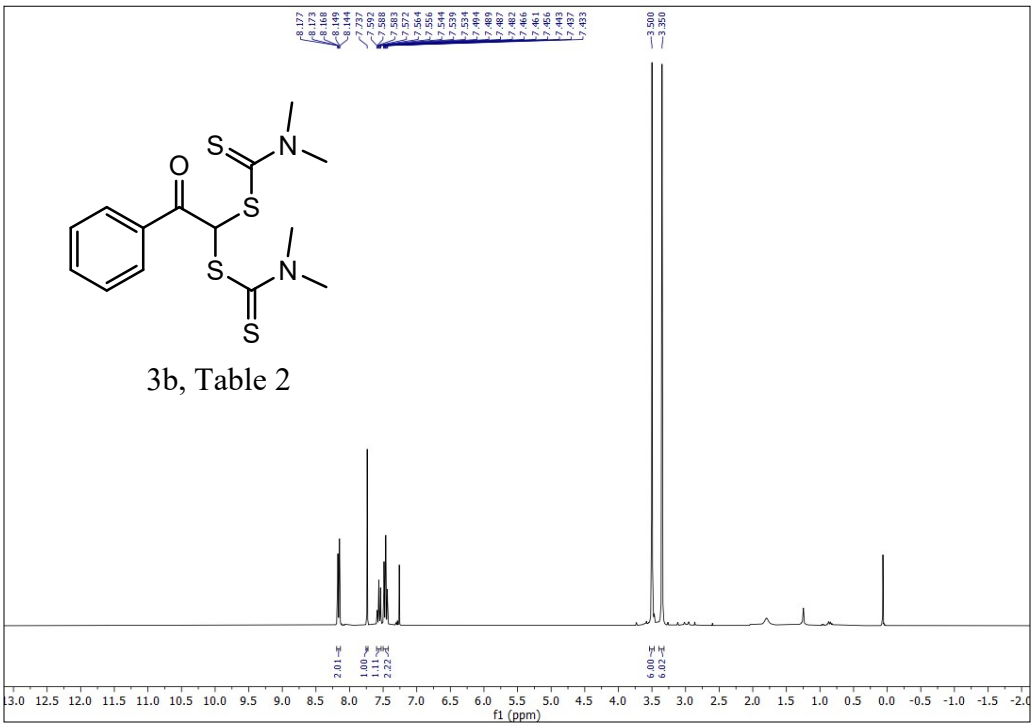
## F. $^{1}H$ and $^{13}C$ Spectra of synthesized compounds:

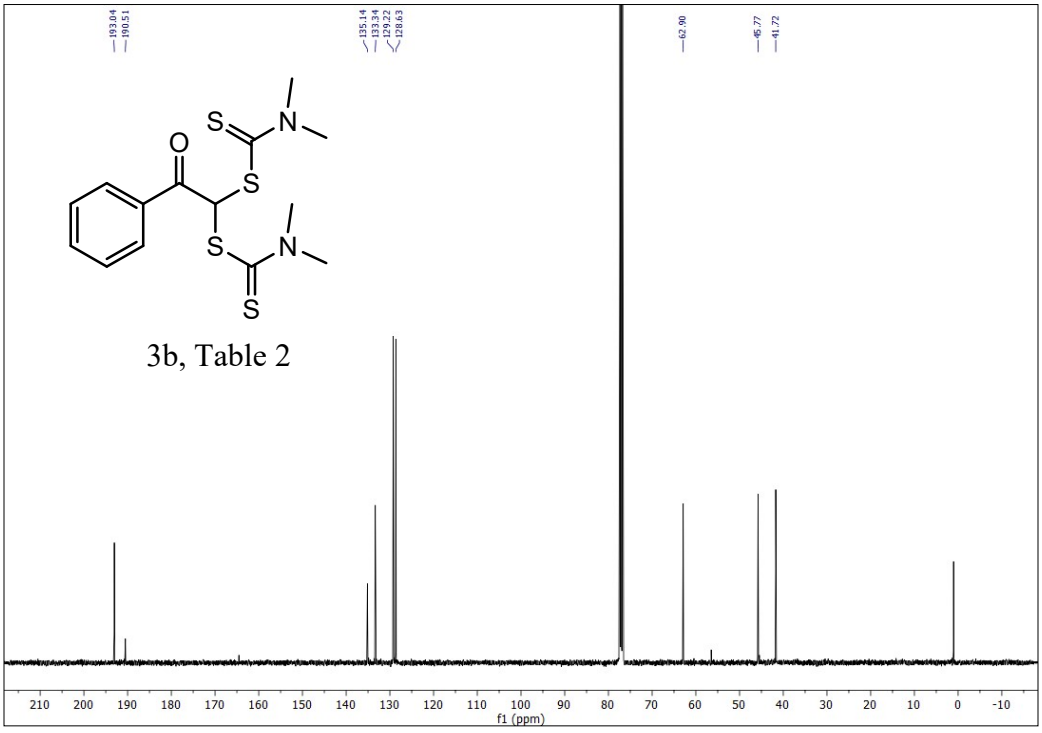
**1.** $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of **3a**



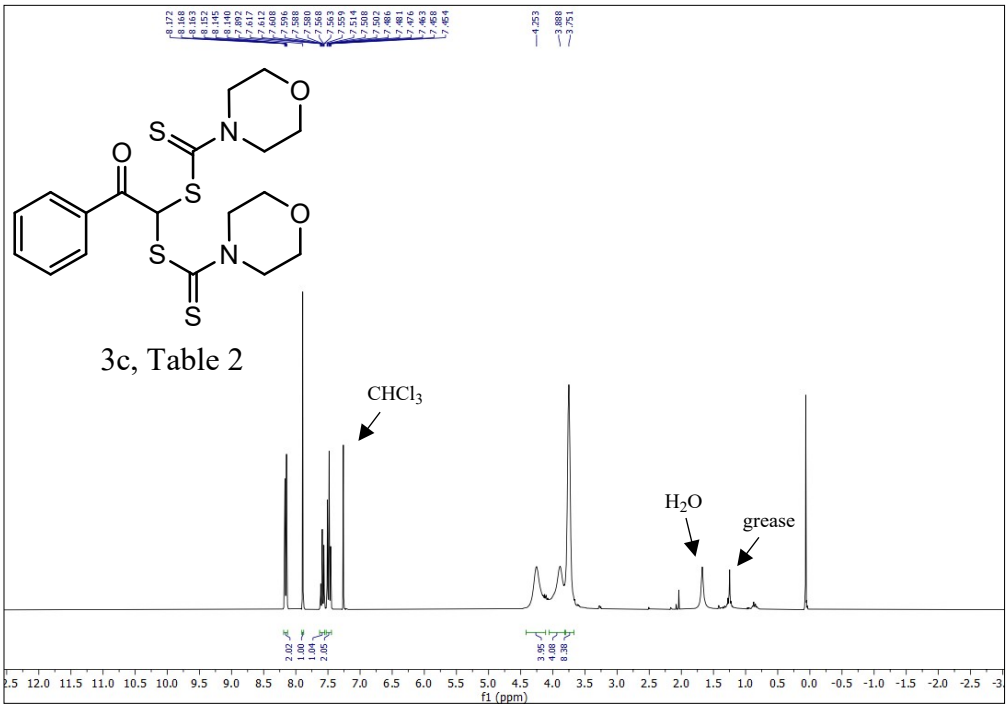



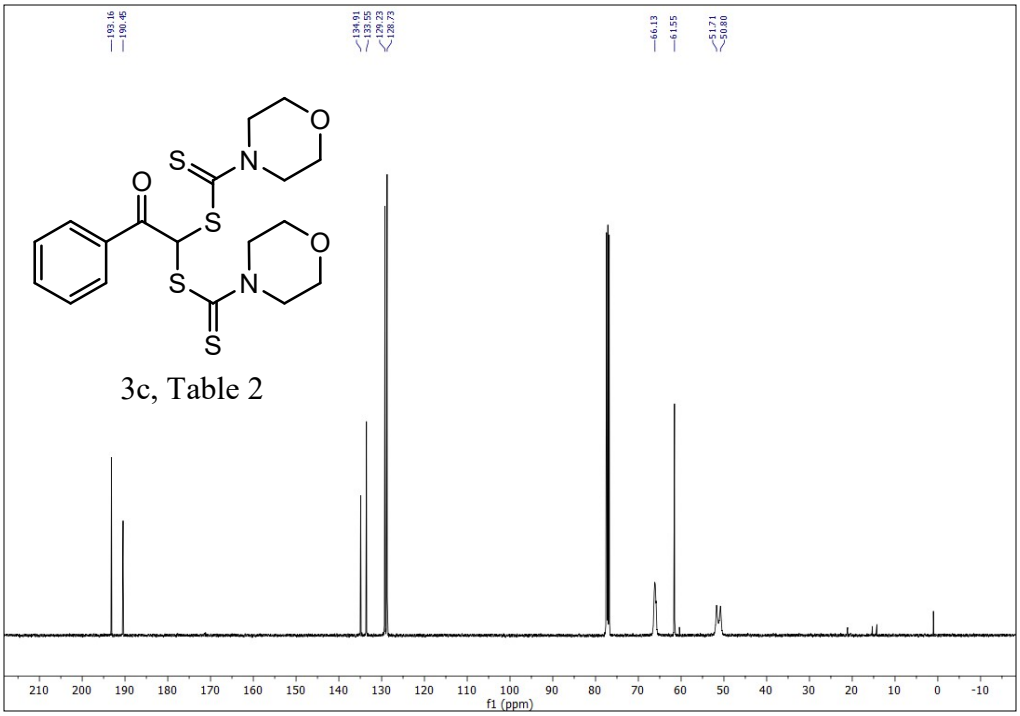
**2.** $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of **3b**



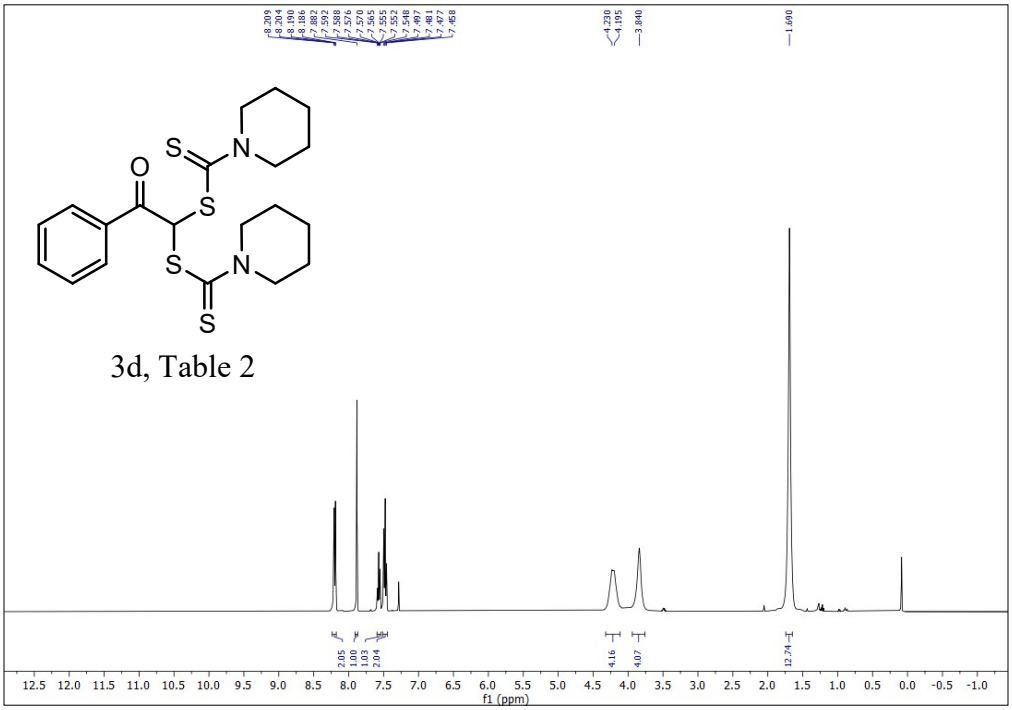



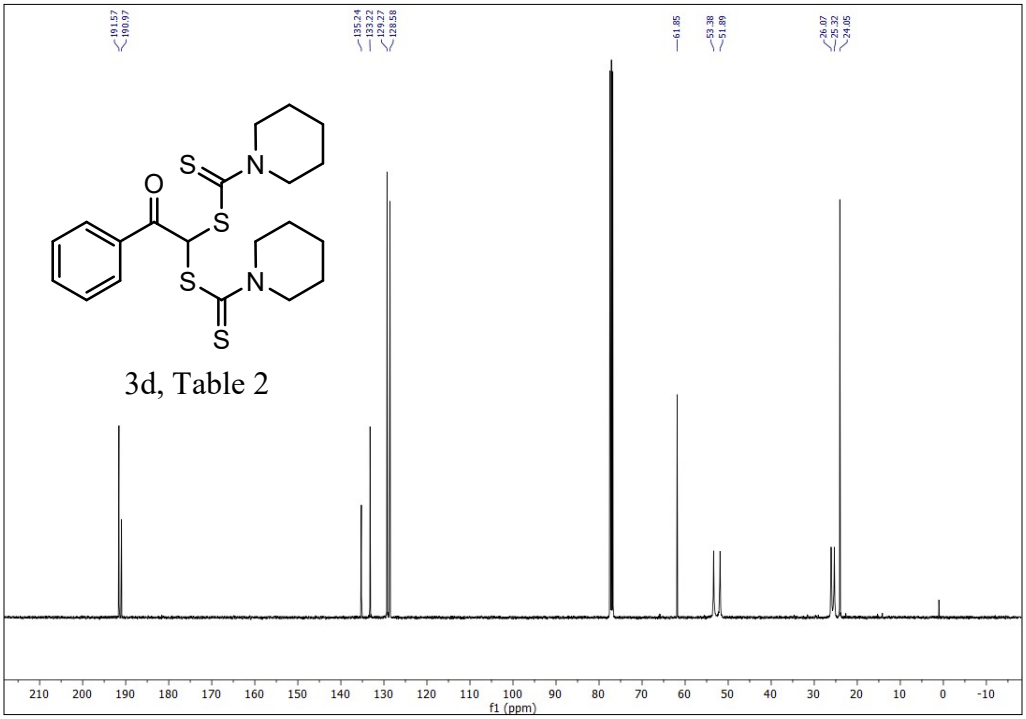
**3.** $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of **3c**



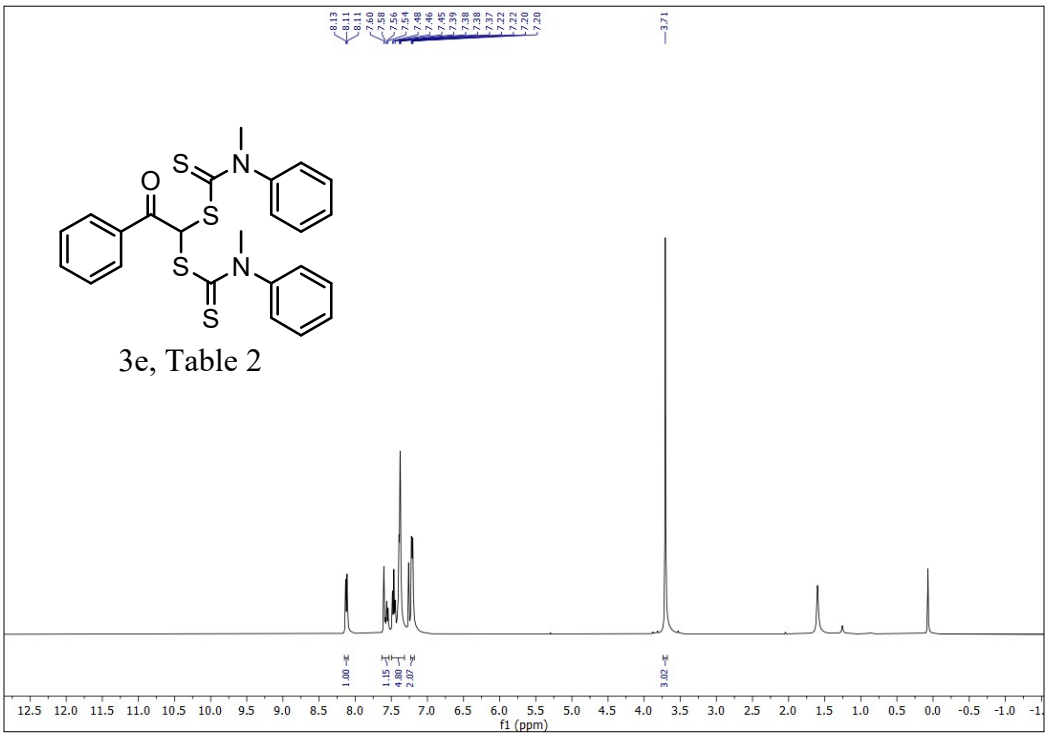



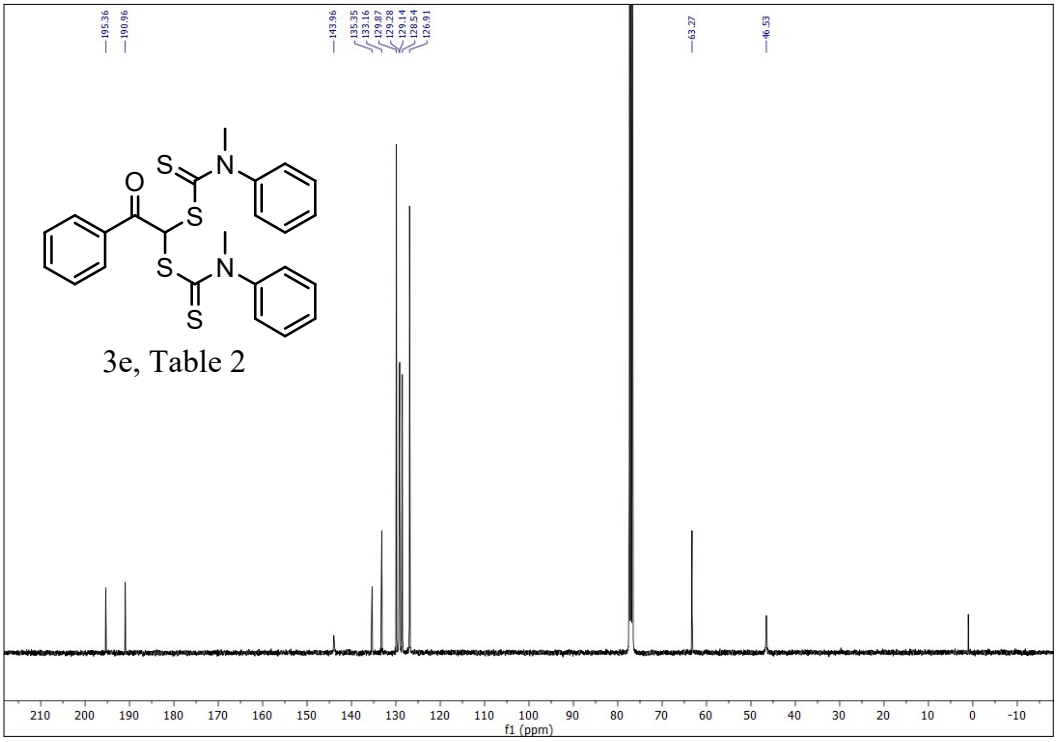
**4.** $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of **3d**



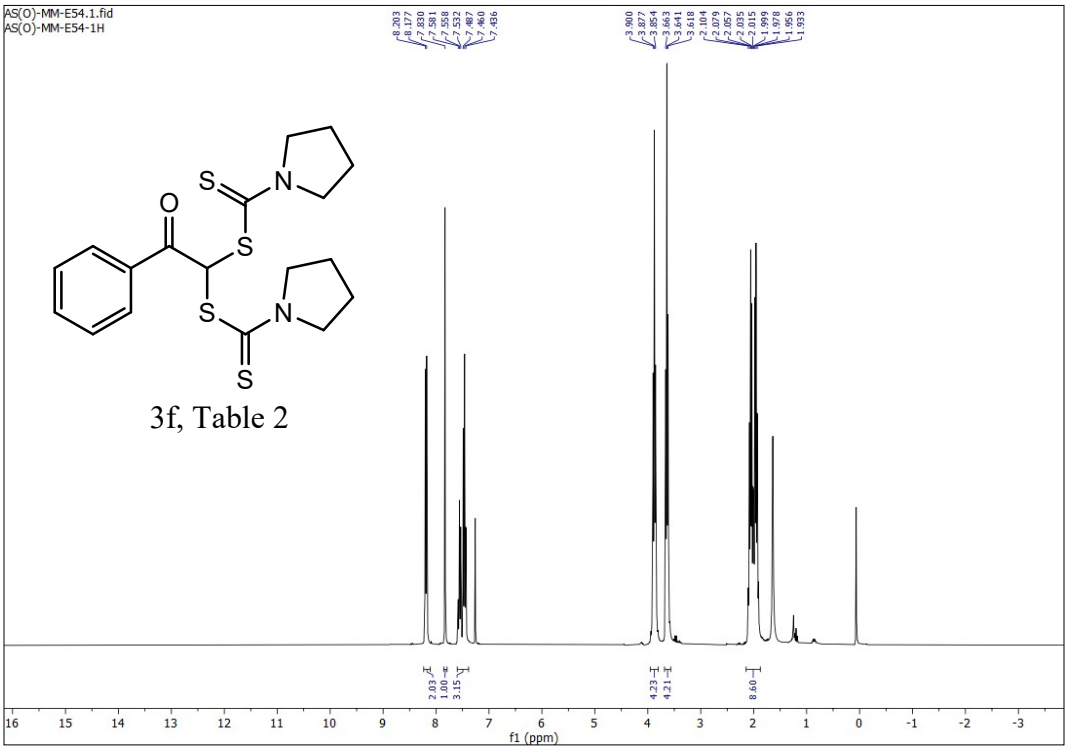



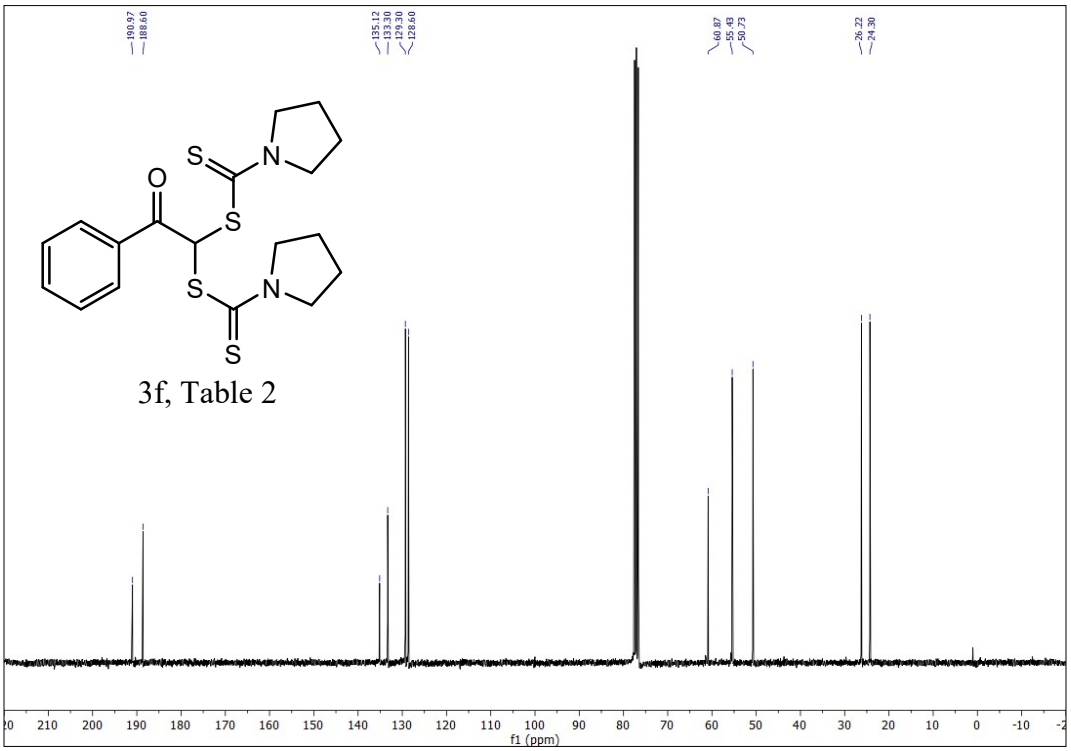
**5.** $^{1}$H NMR (400 MHz, $CDCl_3$) and $^{13}$C NMR (100 MHz, $CDCl_3$) spectra of **3e**



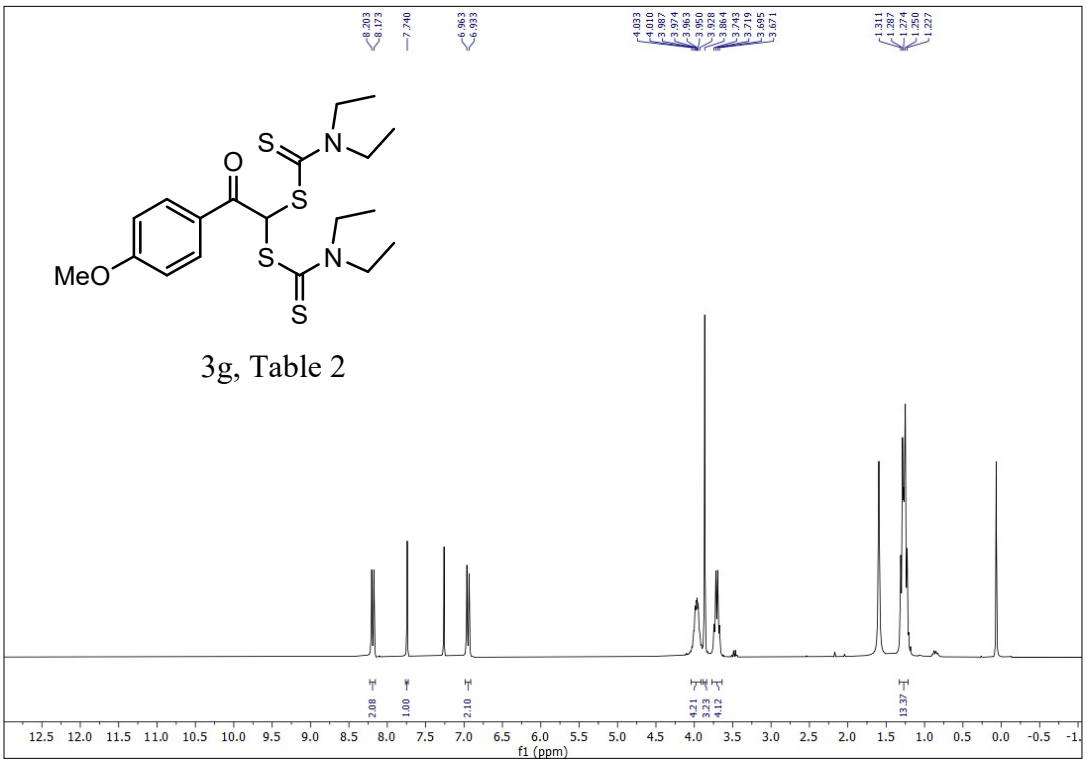



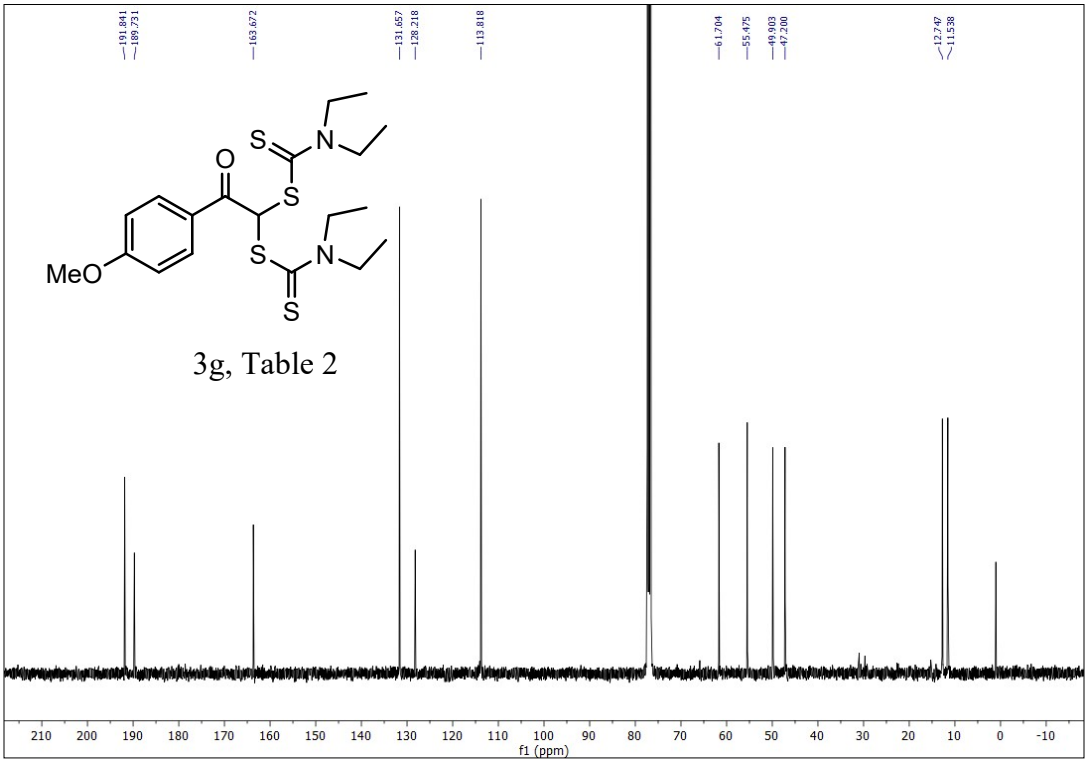
**6.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3f**



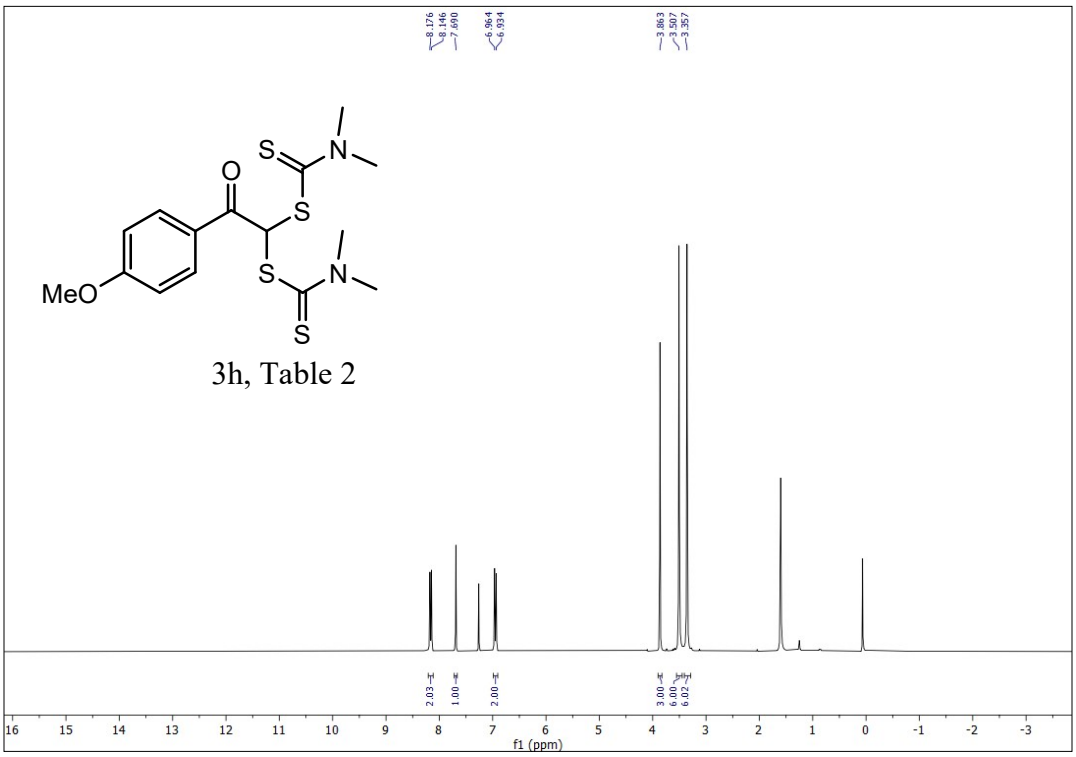



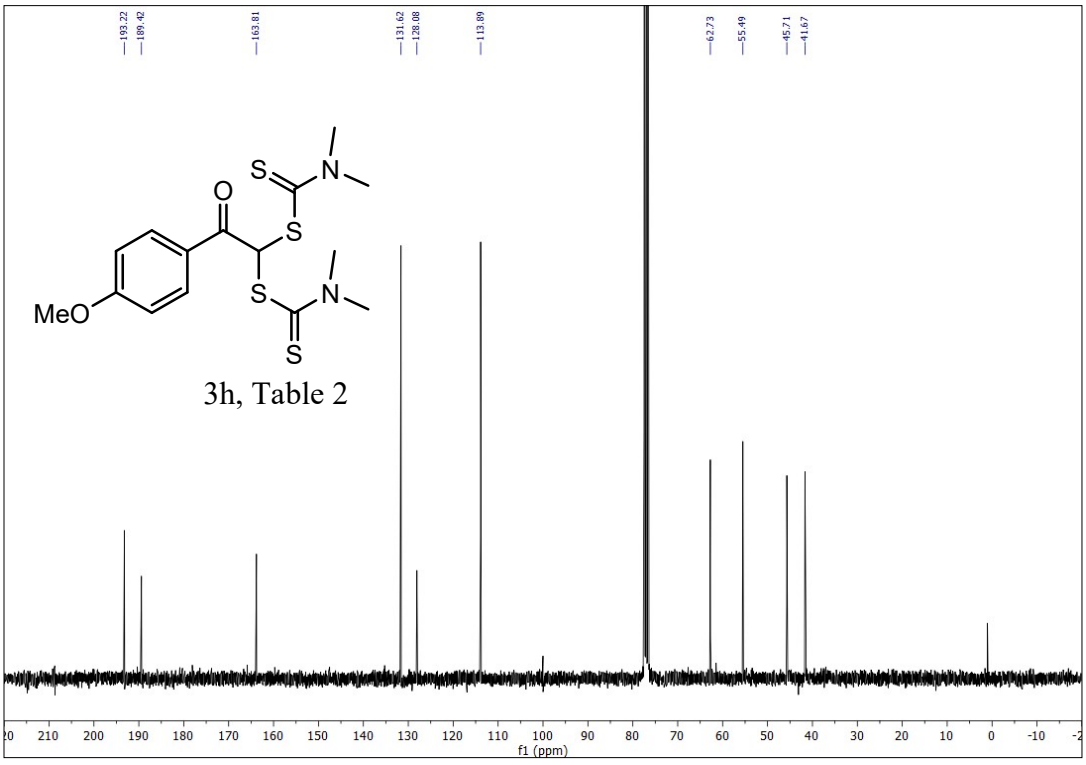
**7.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3g**



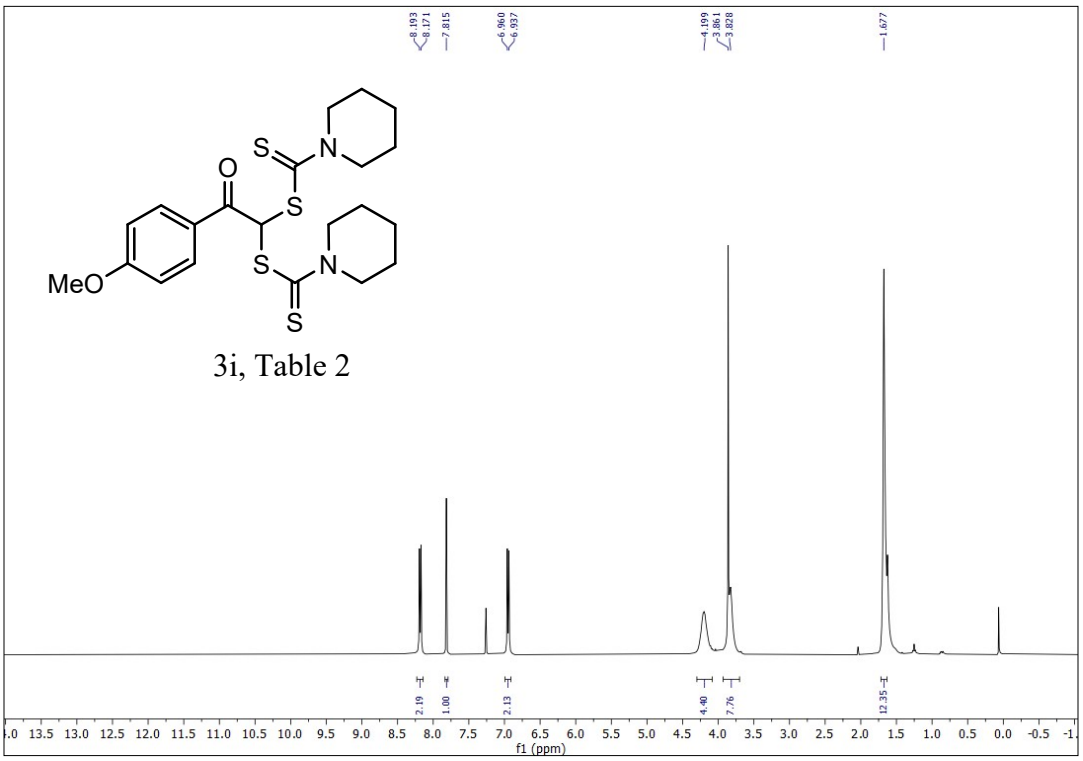



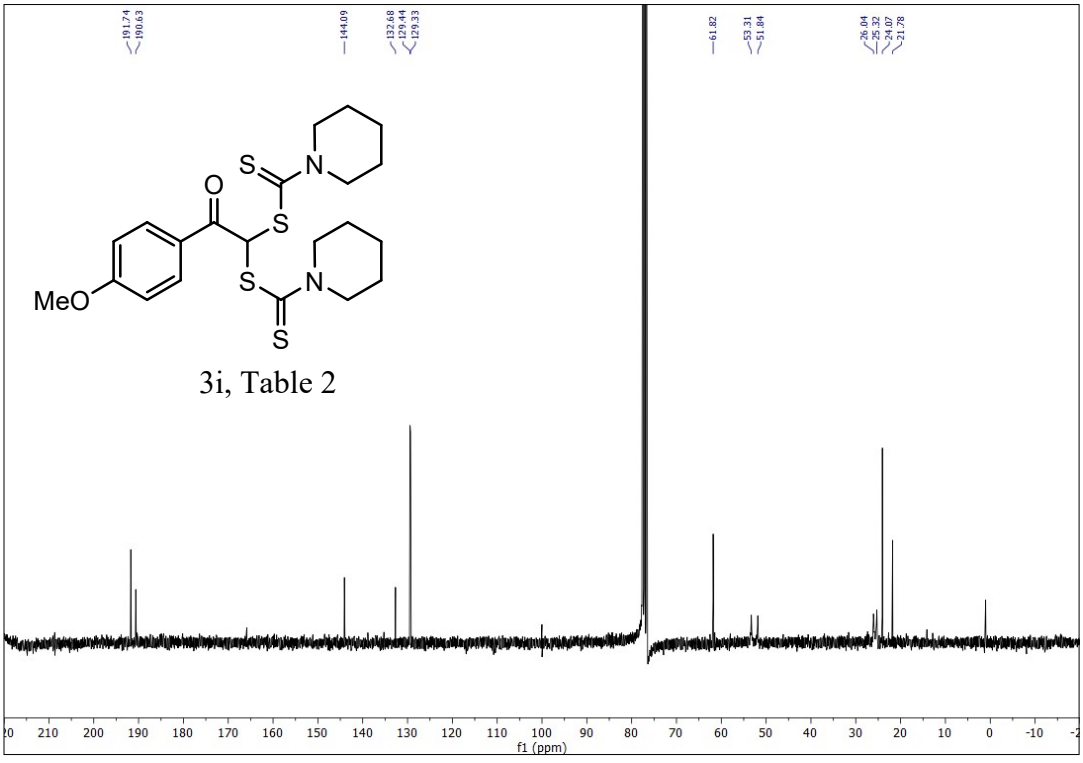
**8.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3h**



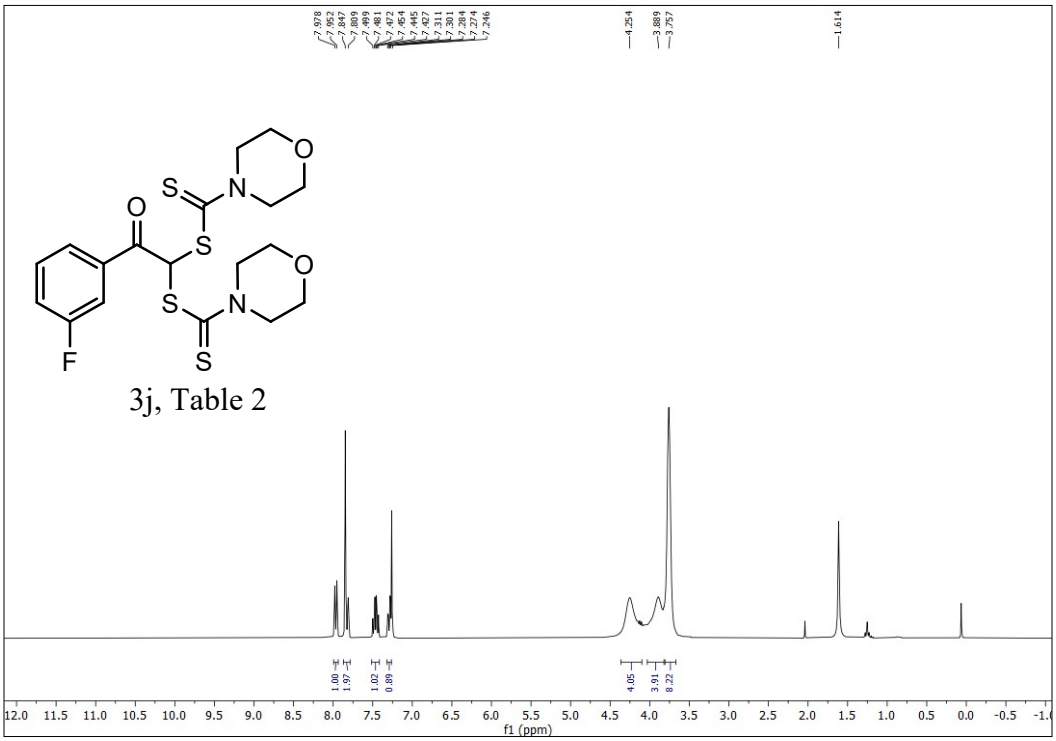



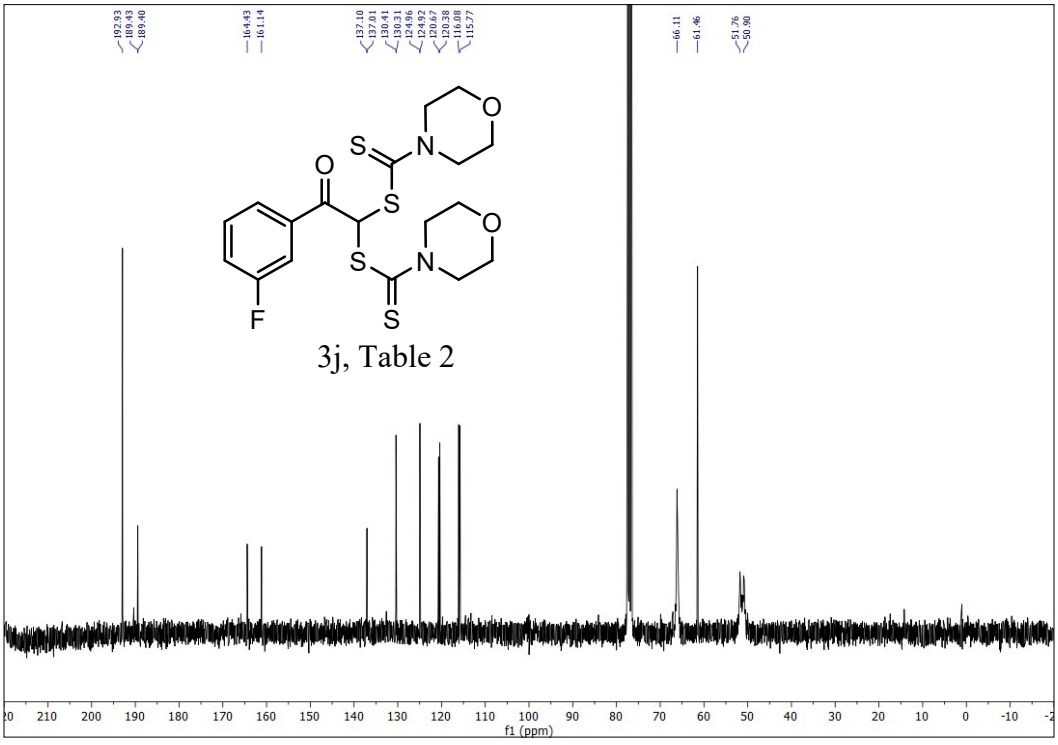
**9.** $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of **3i**



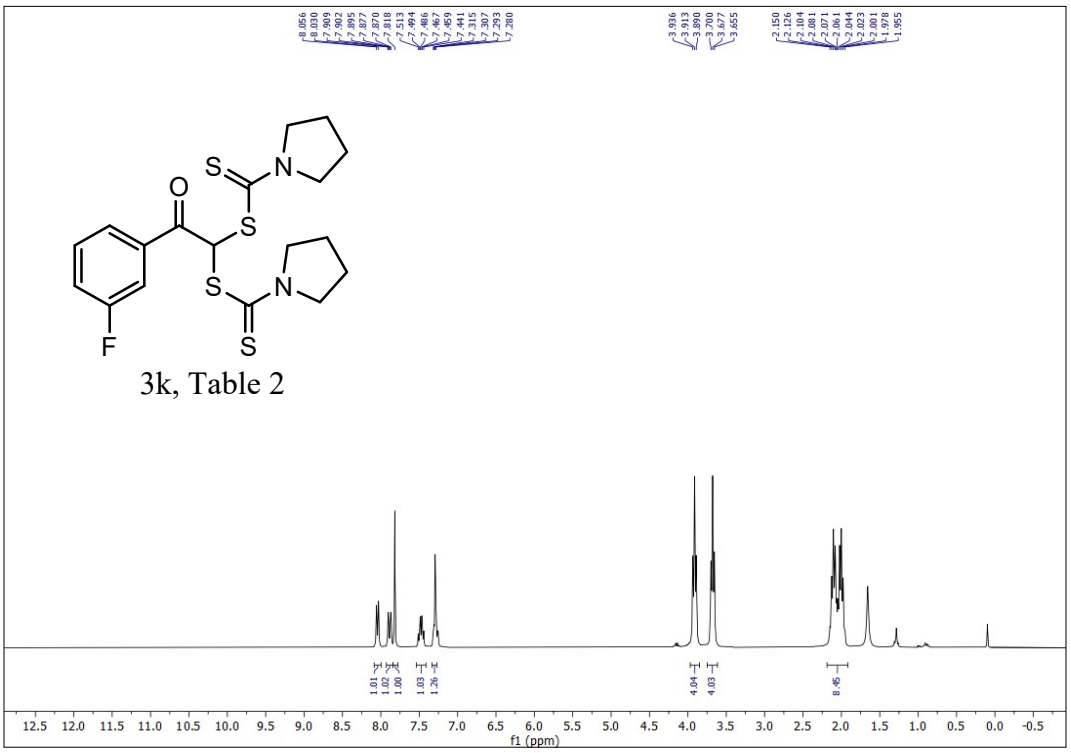



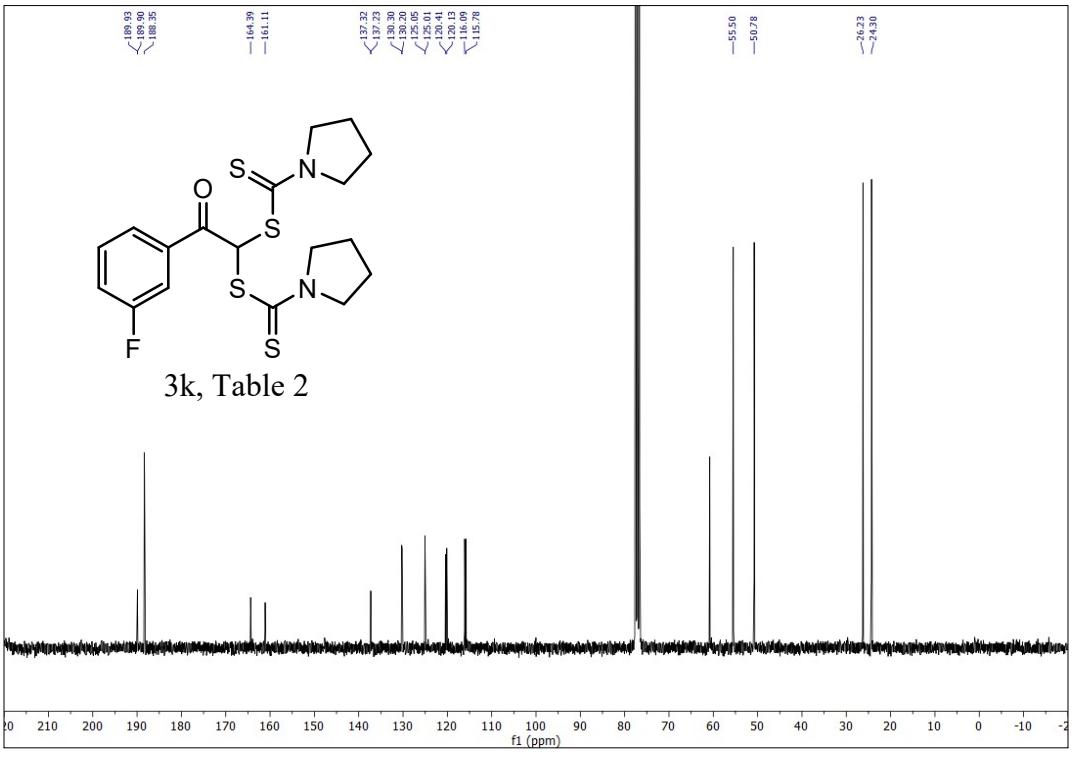
**10.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3j**



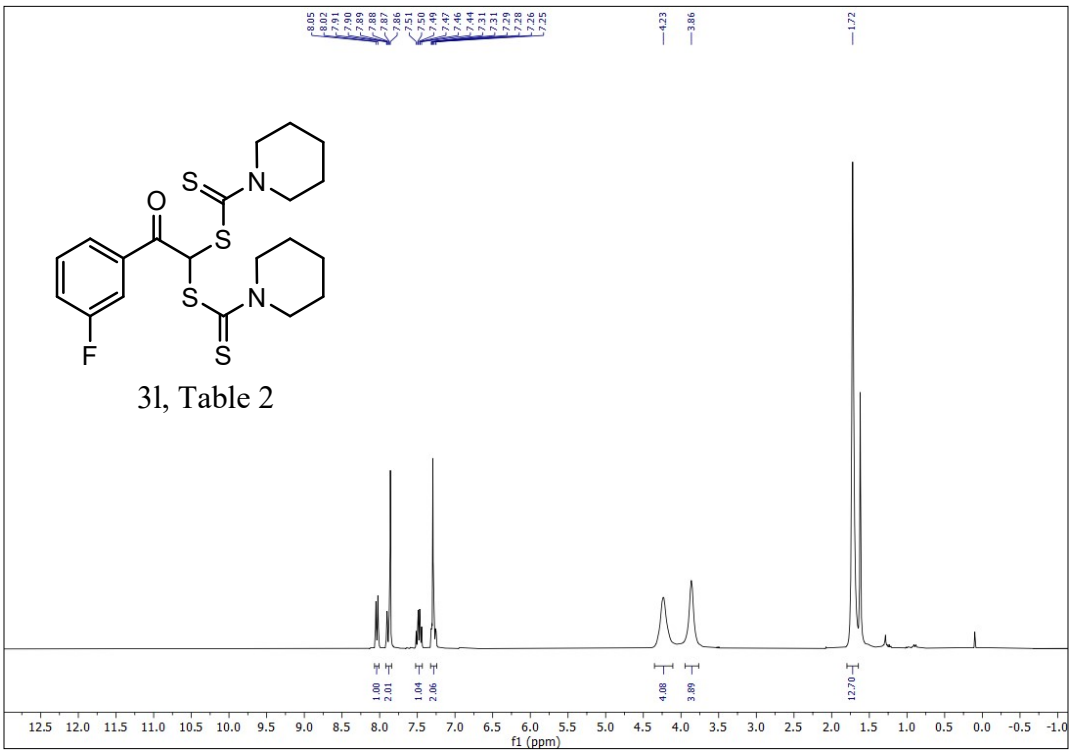



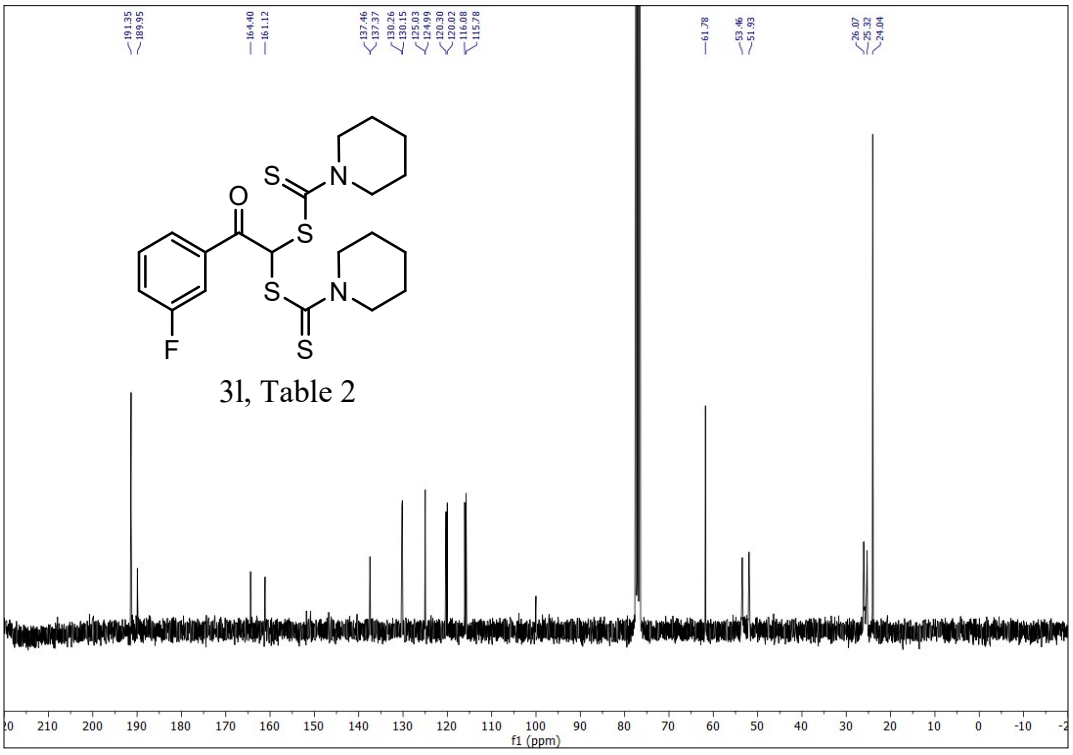
**11.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3k**



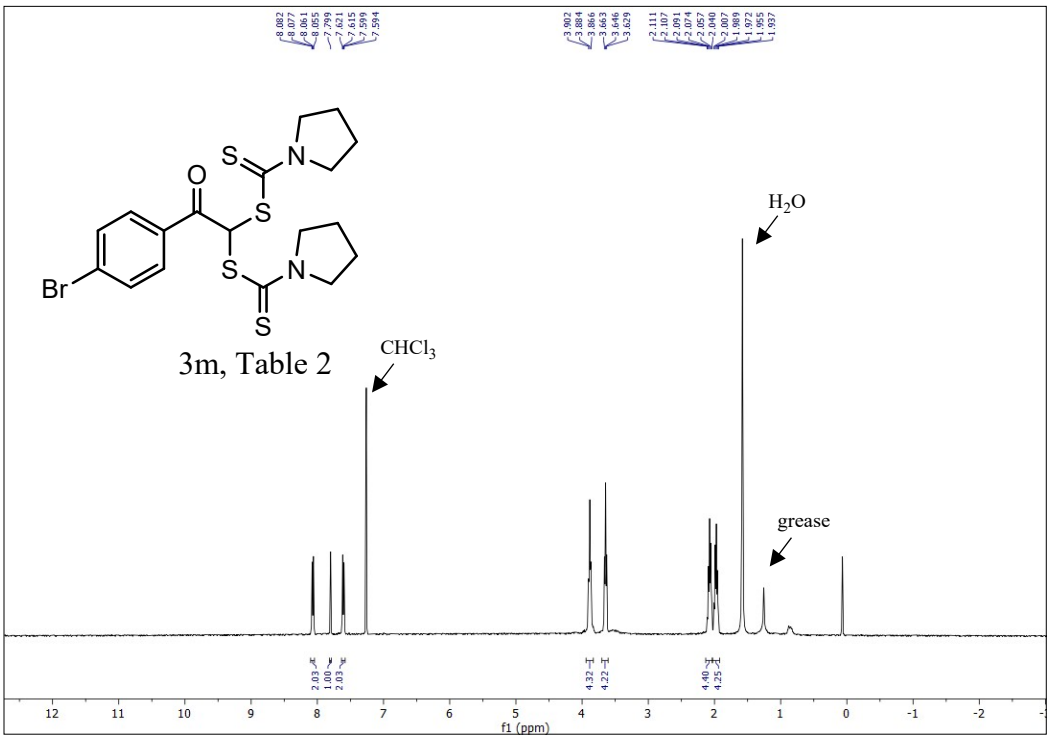



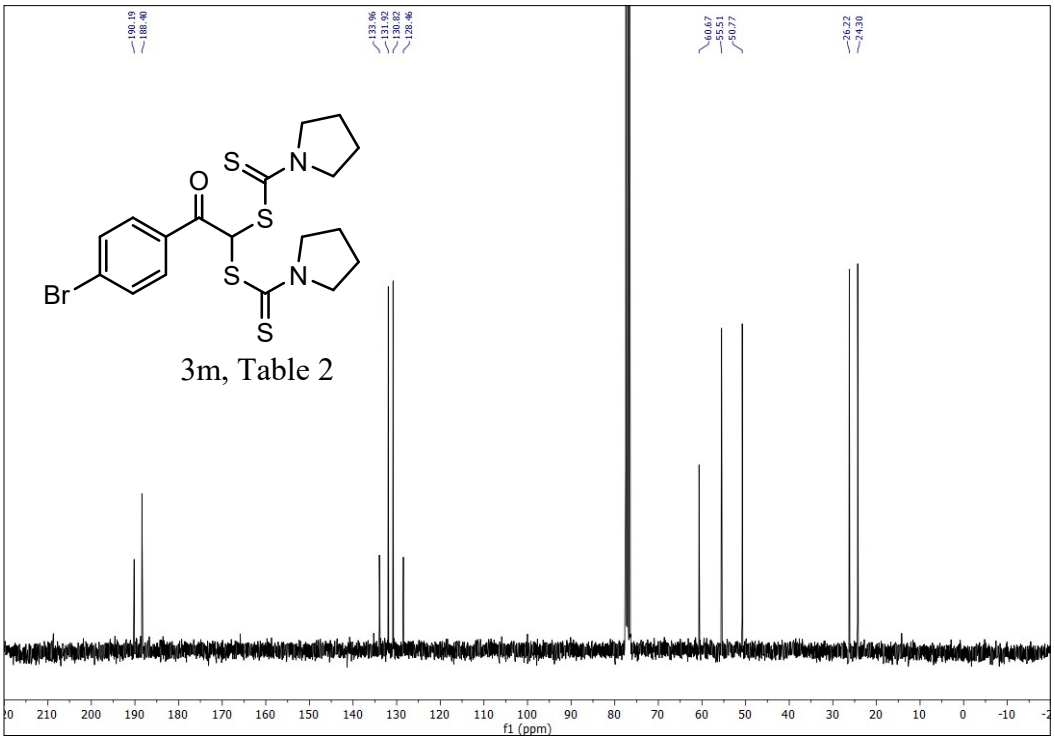
**12.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3l**



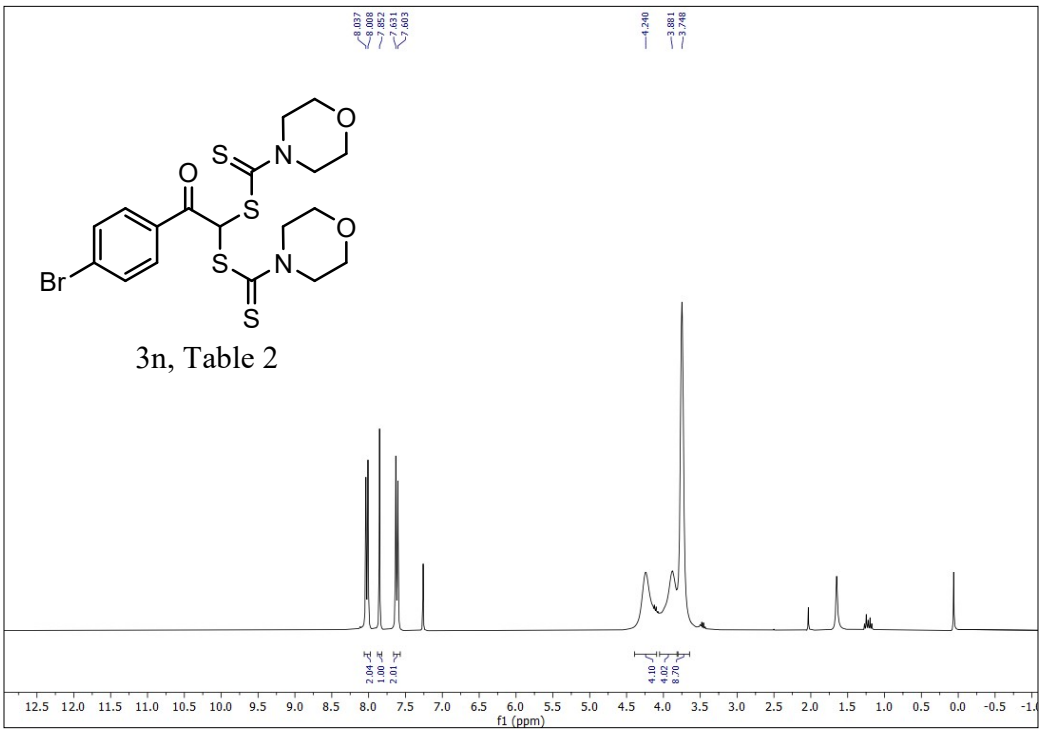



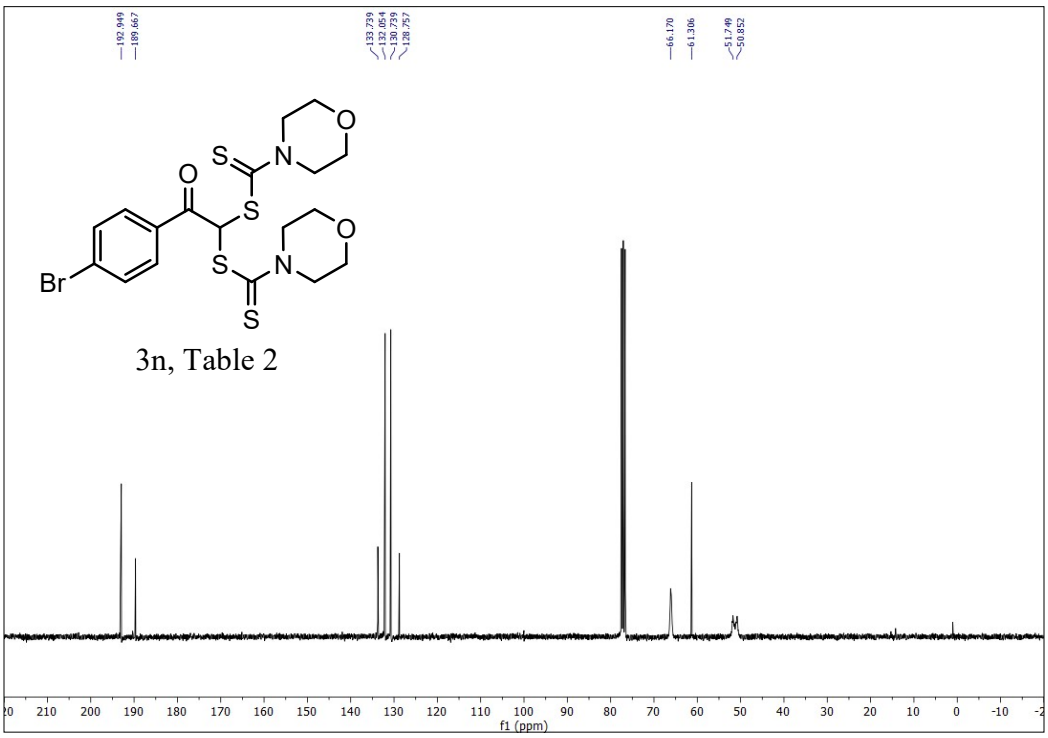
**13.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3m**



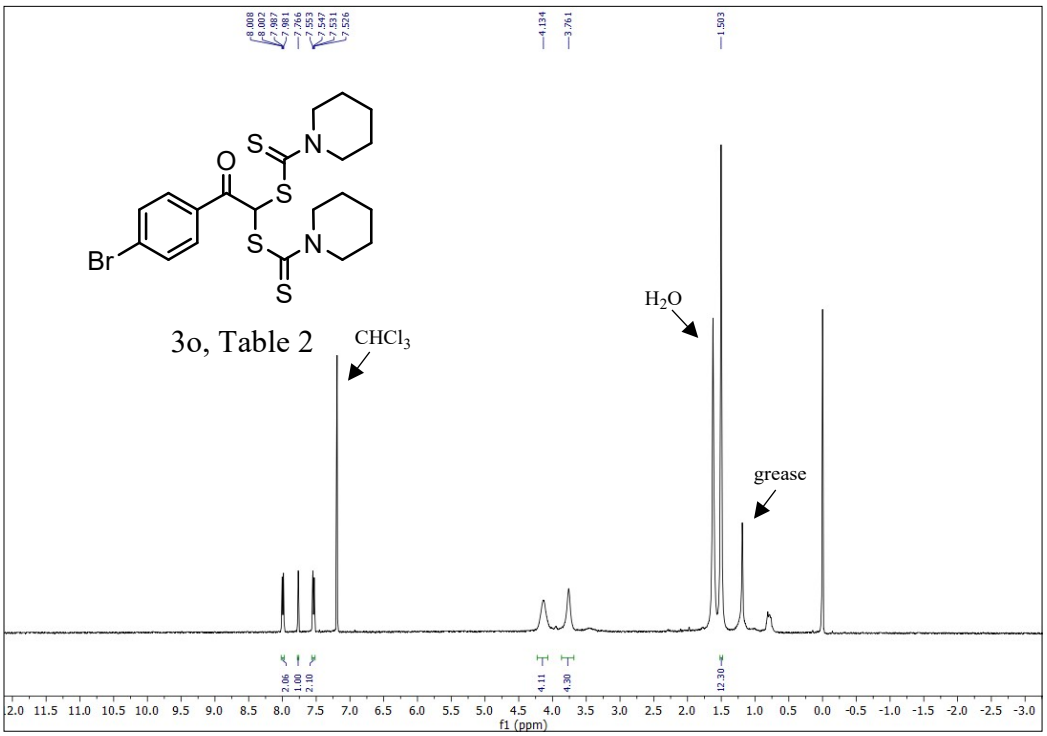



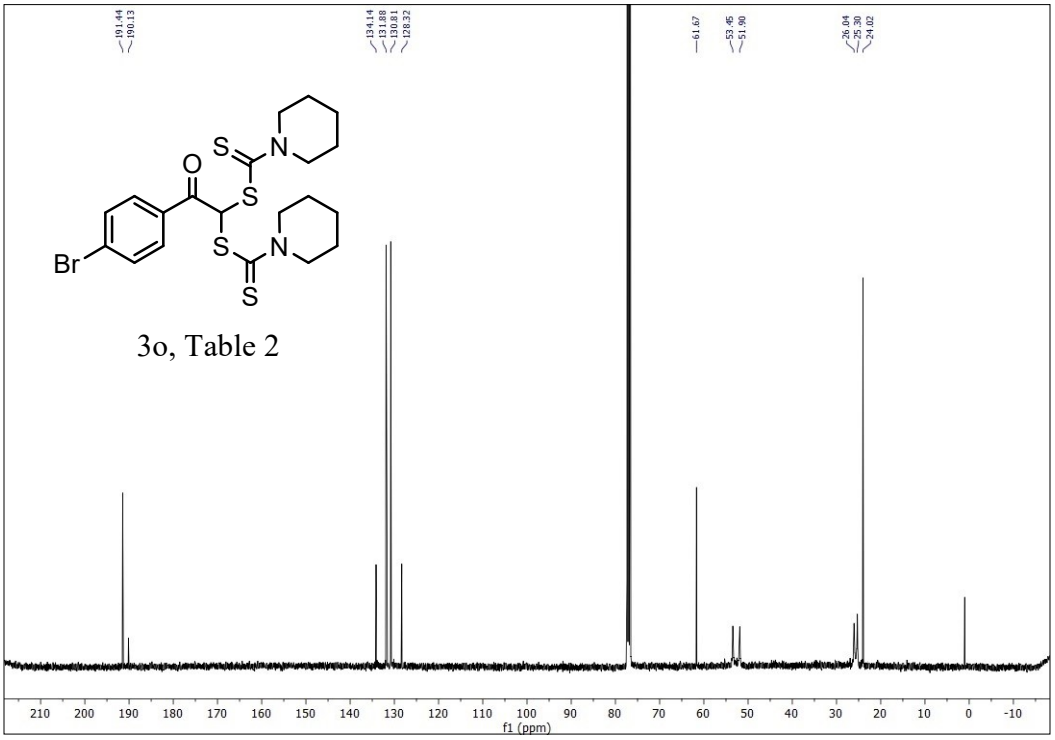
**14.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3n**



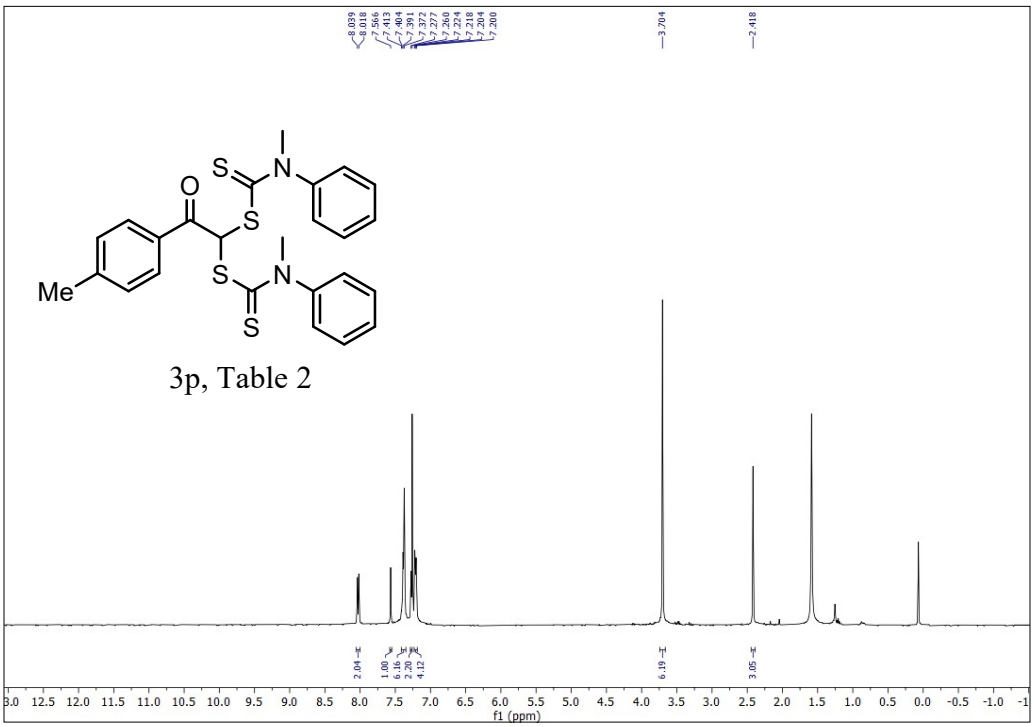



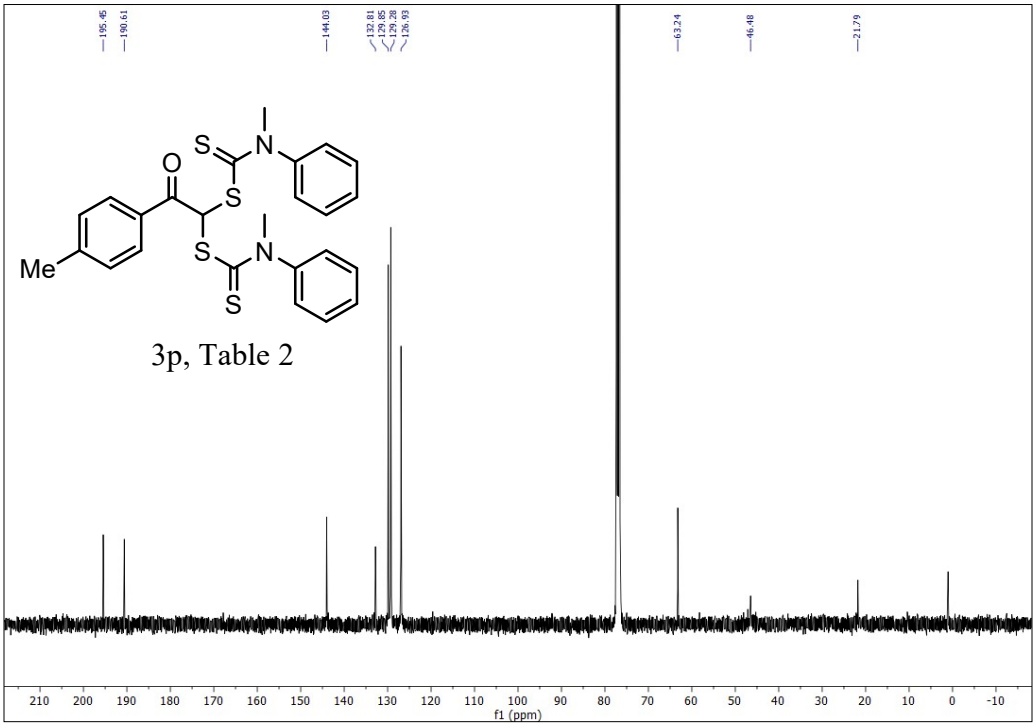
**15.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3o**



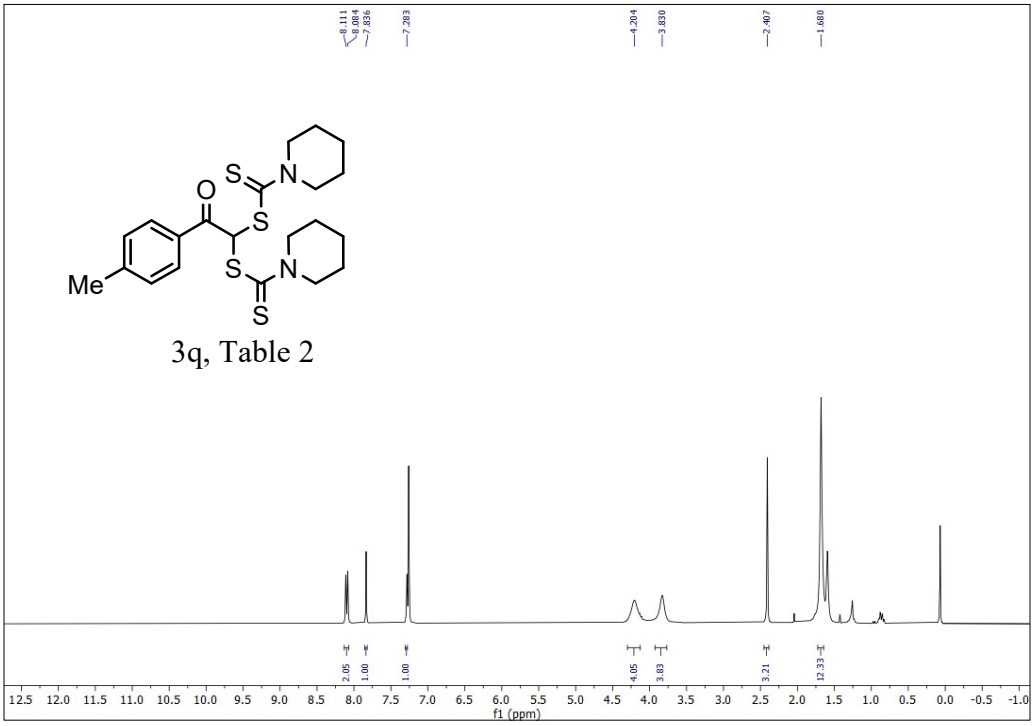



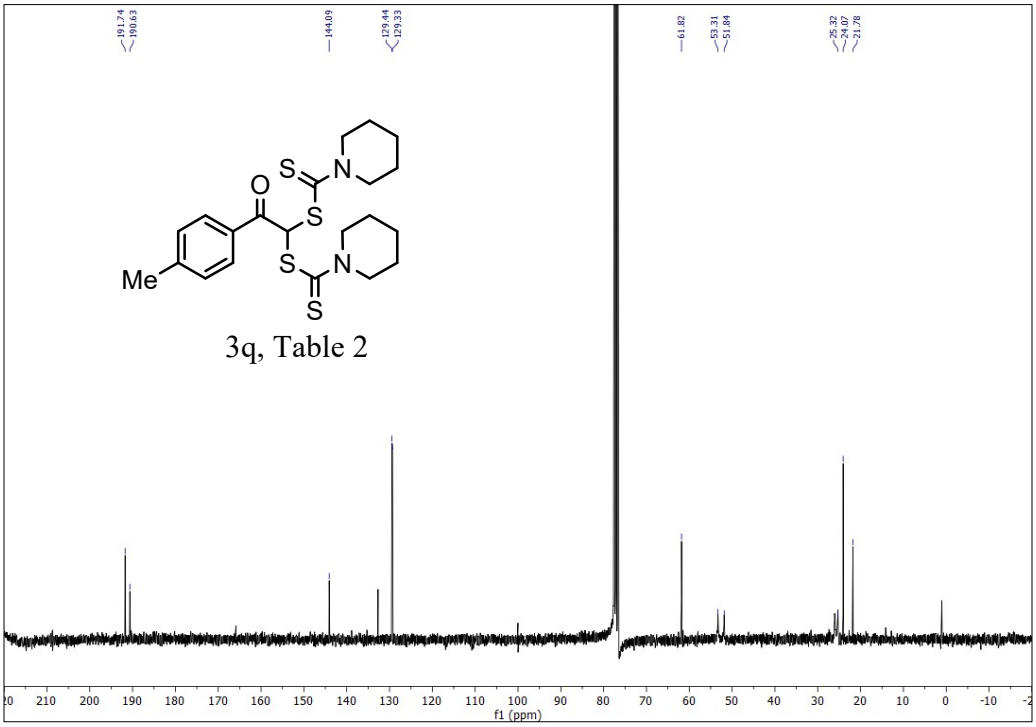
**16.** $^{1}H$ NMR (400 MHz, $CDCl_3$) and $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of **3p**



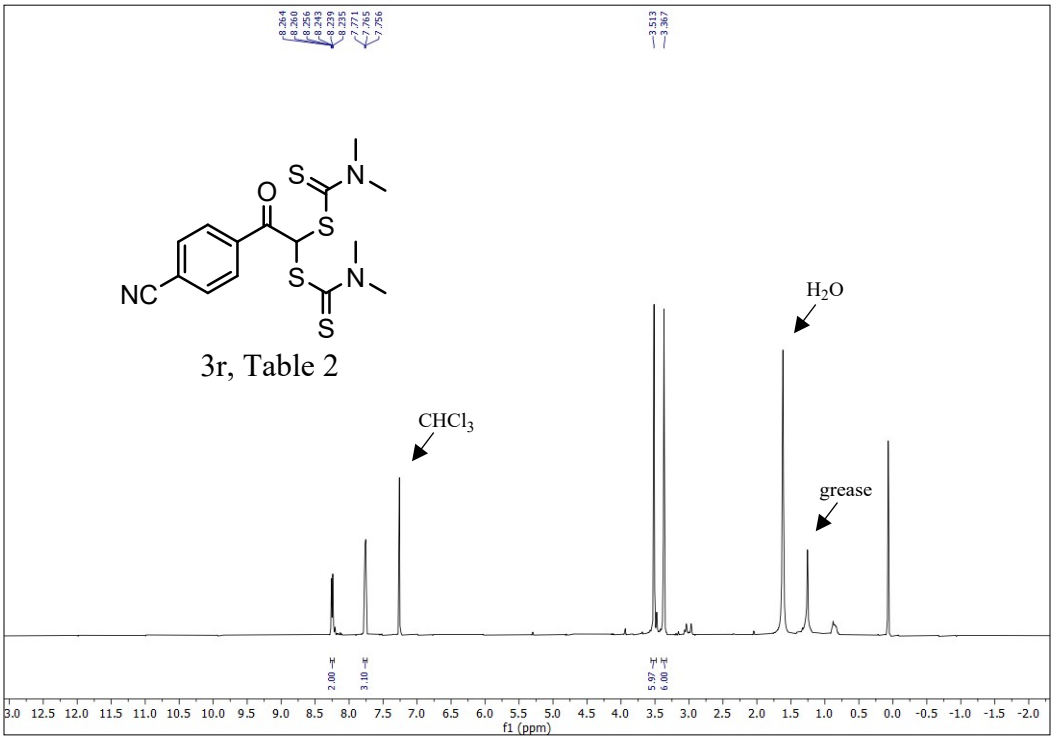



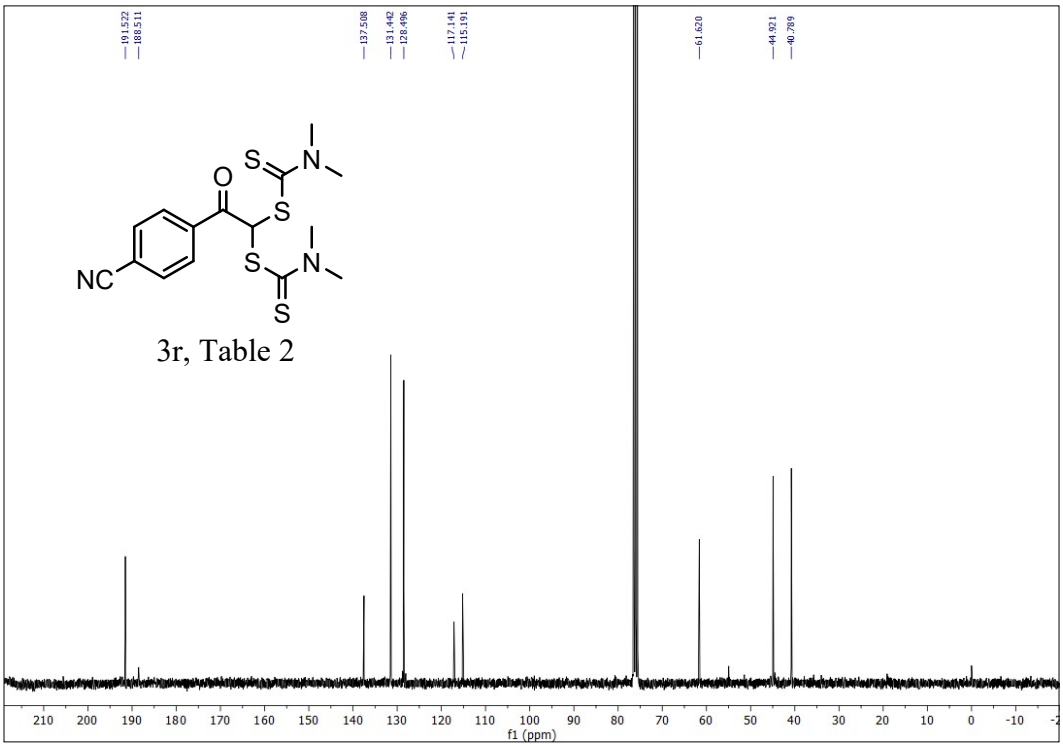
**17.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3q**



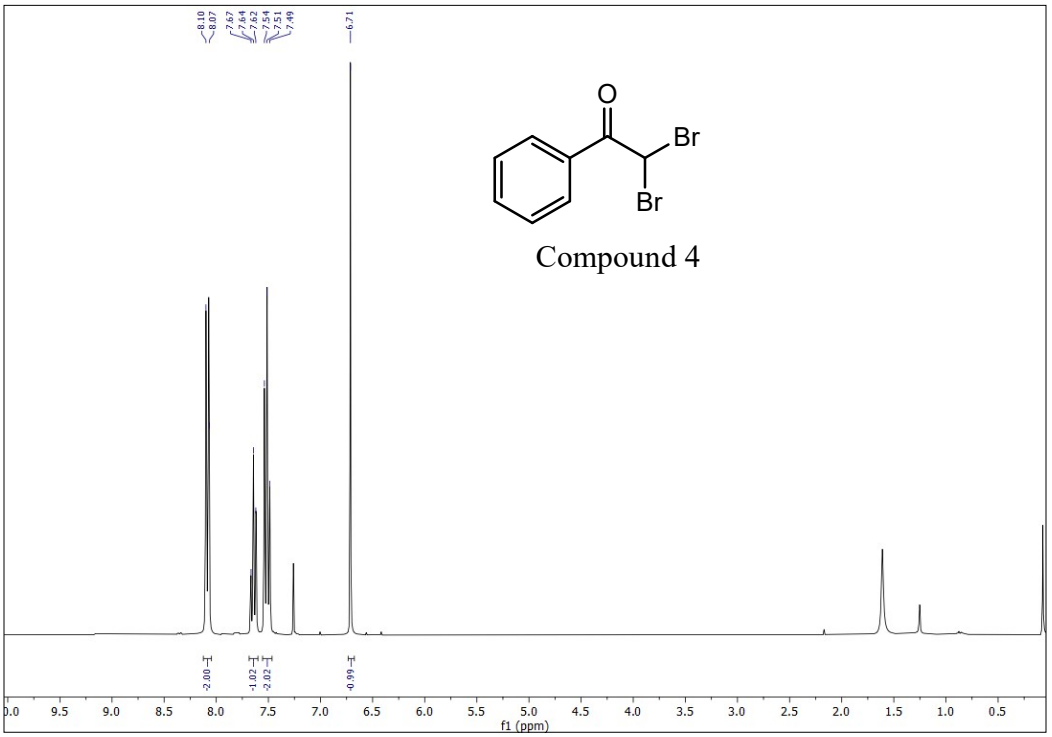



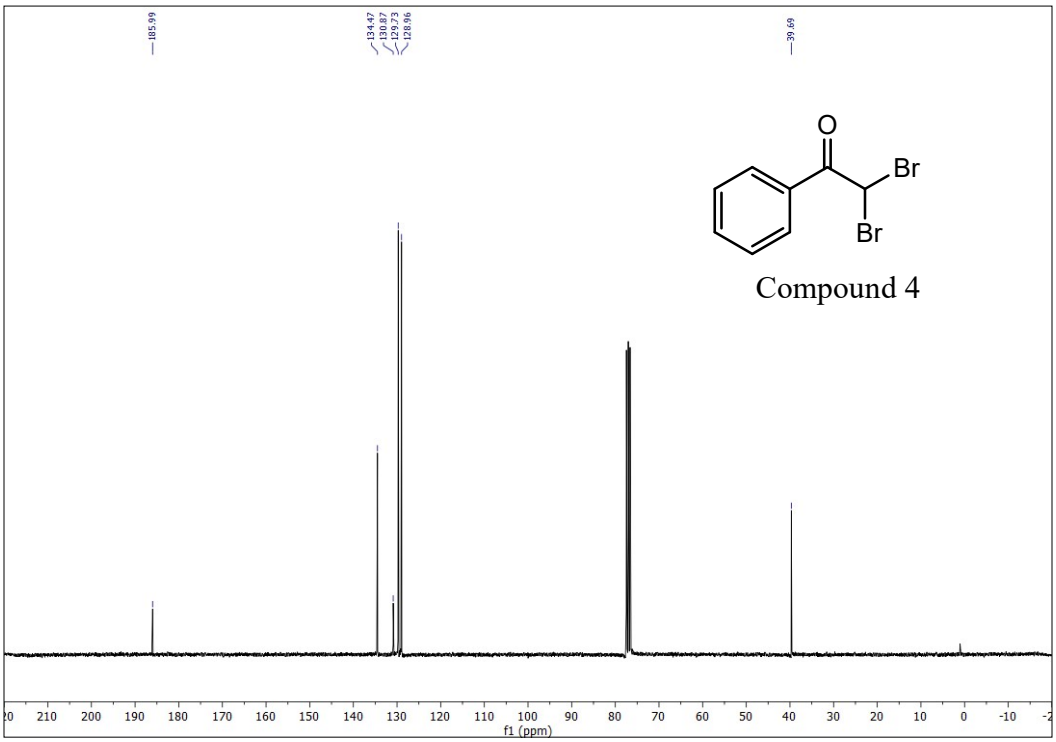
**18.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **3r**



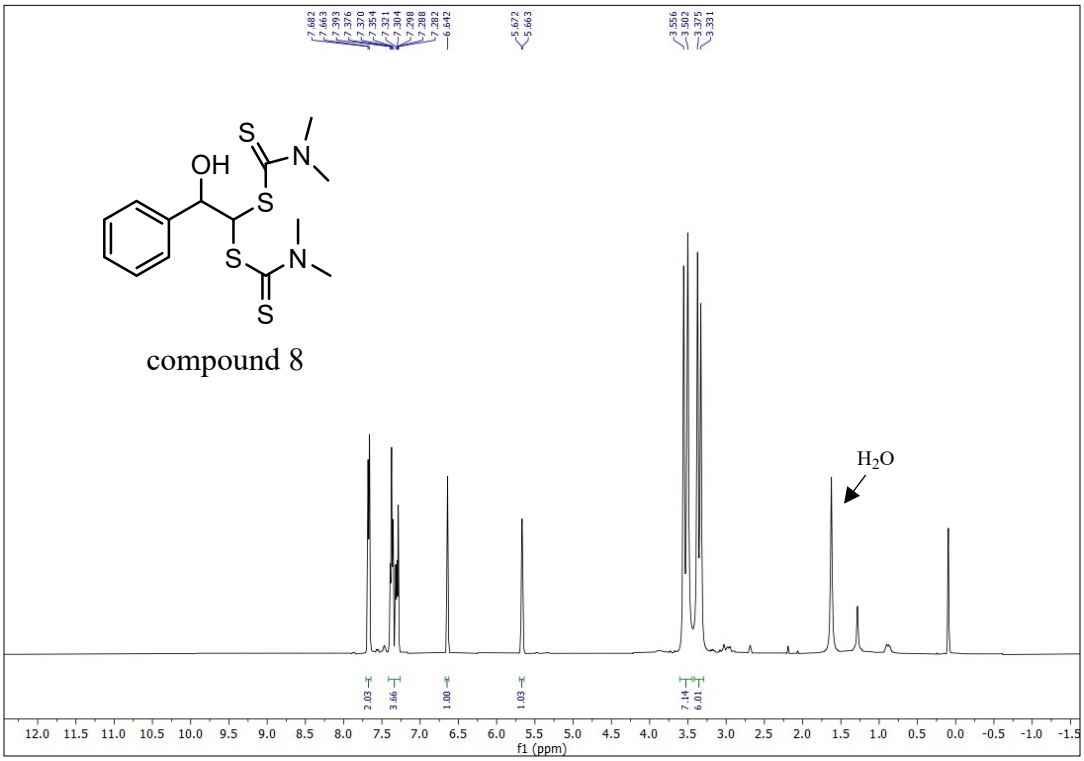



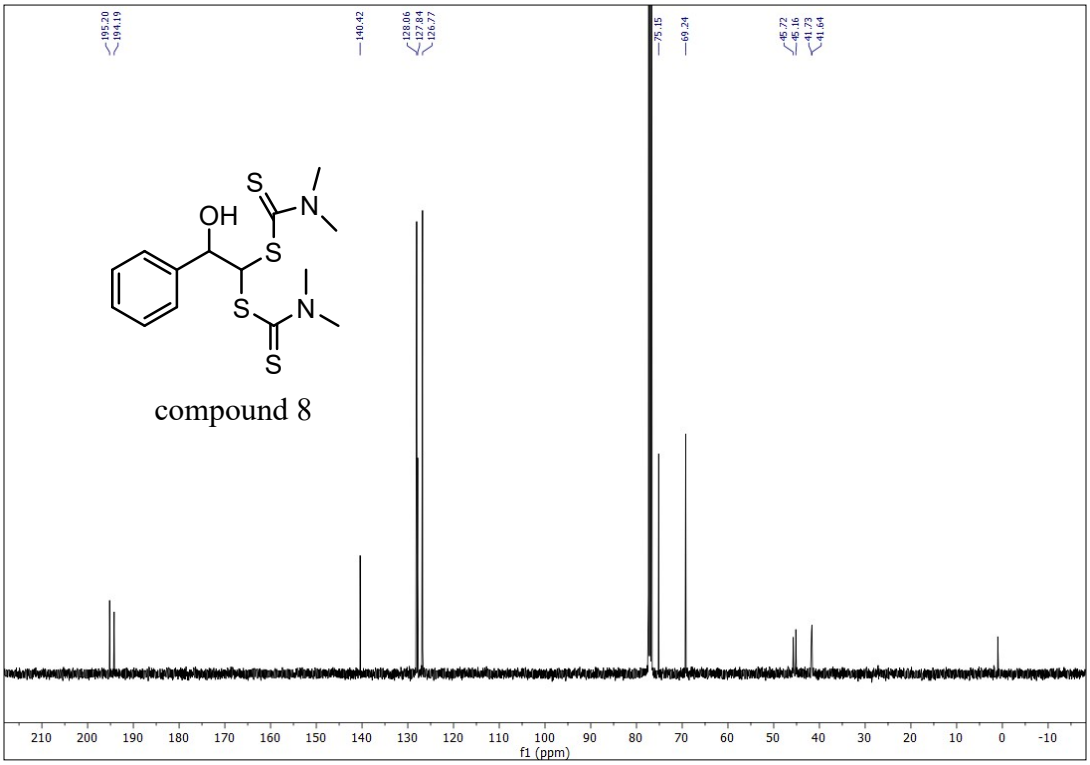
**19.** $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **compound 4**



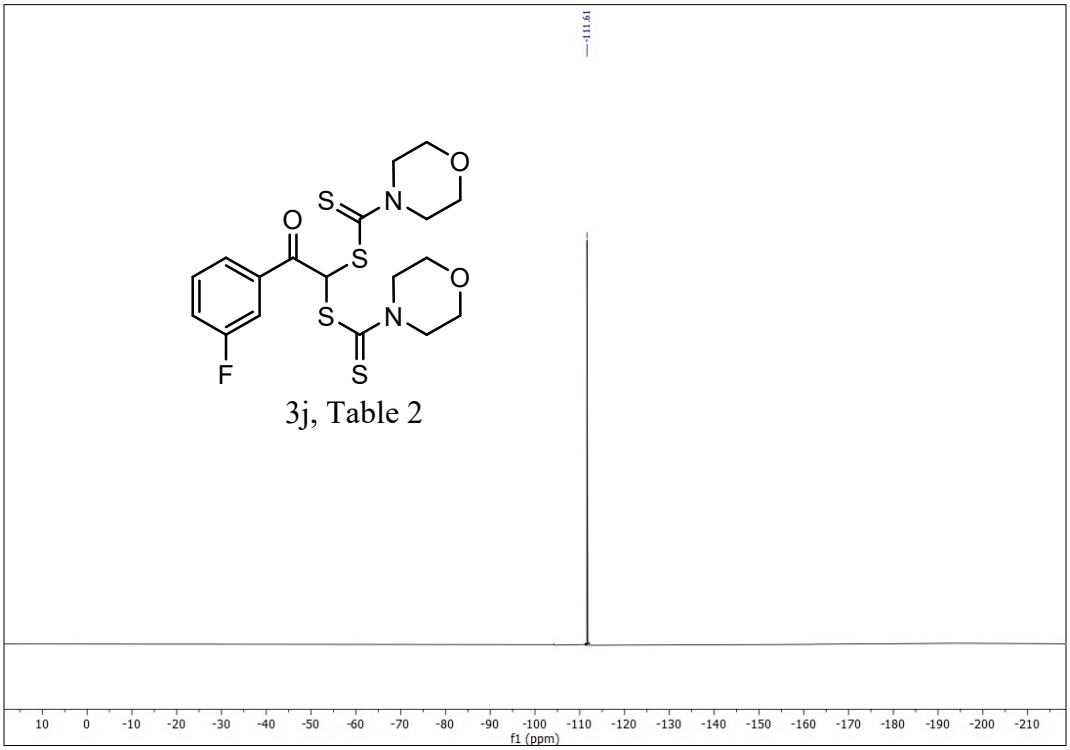



20. $^{1}H$ NMR (300 MHz, $CDCl_3$) and $^{13}C$ NMR (75 MHz, $CDCl_3$) spectra of **compound 8**

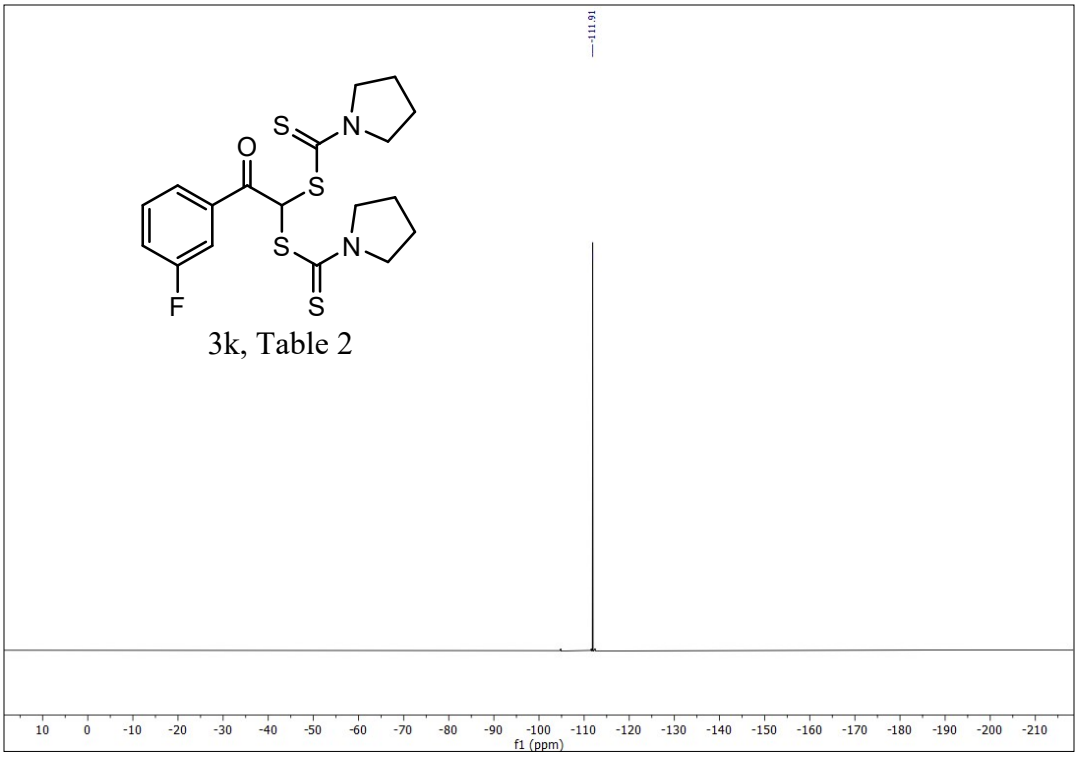


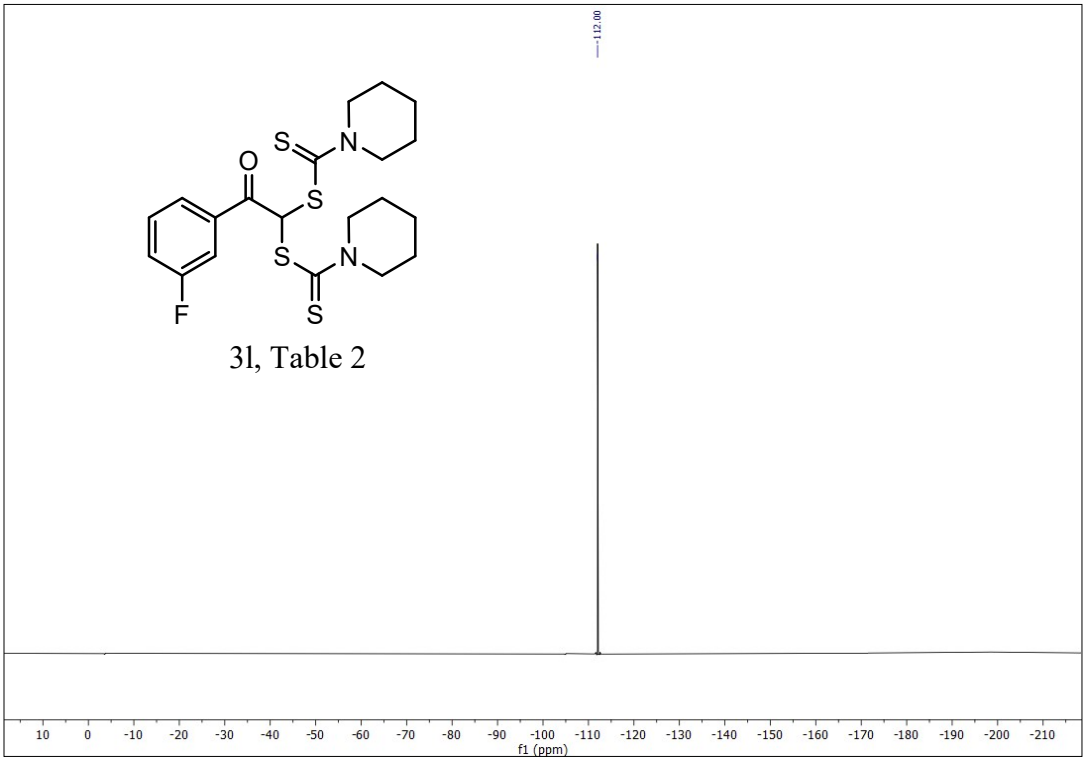
## G. $^{19}$F NMR spectra of fluorinated products (3j, 3k, 3l):




3j, Table 2

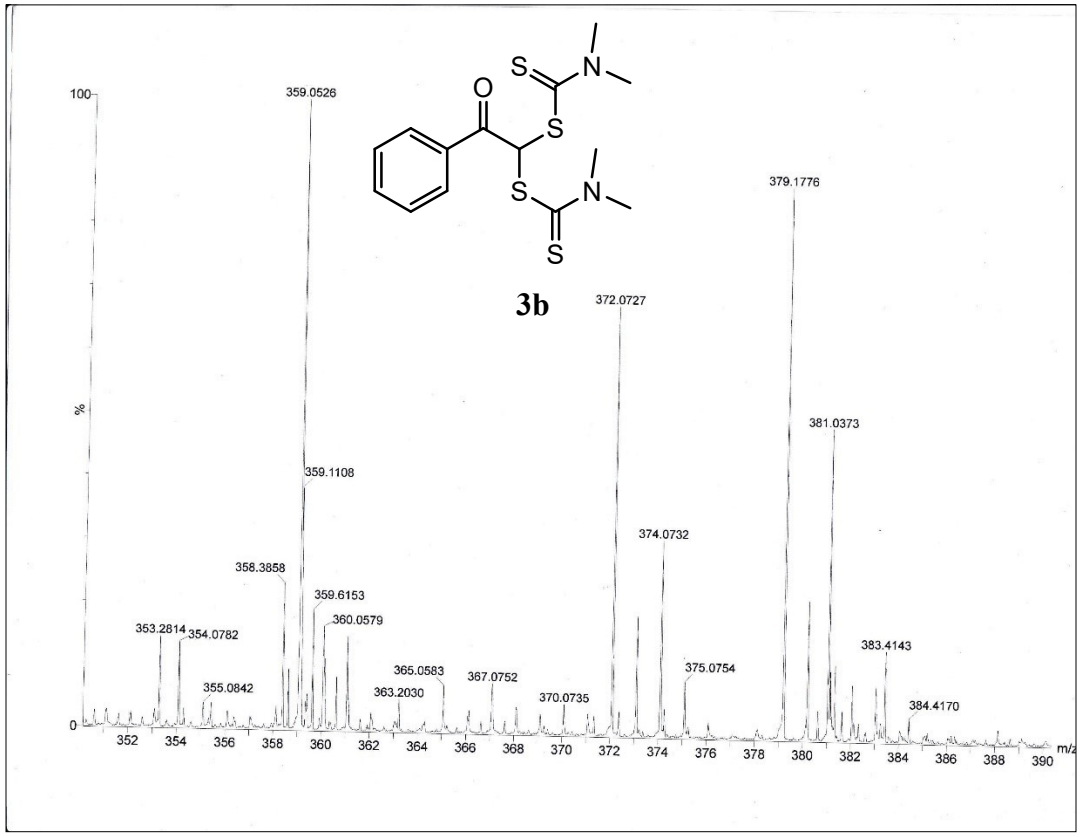



3k, Table 2

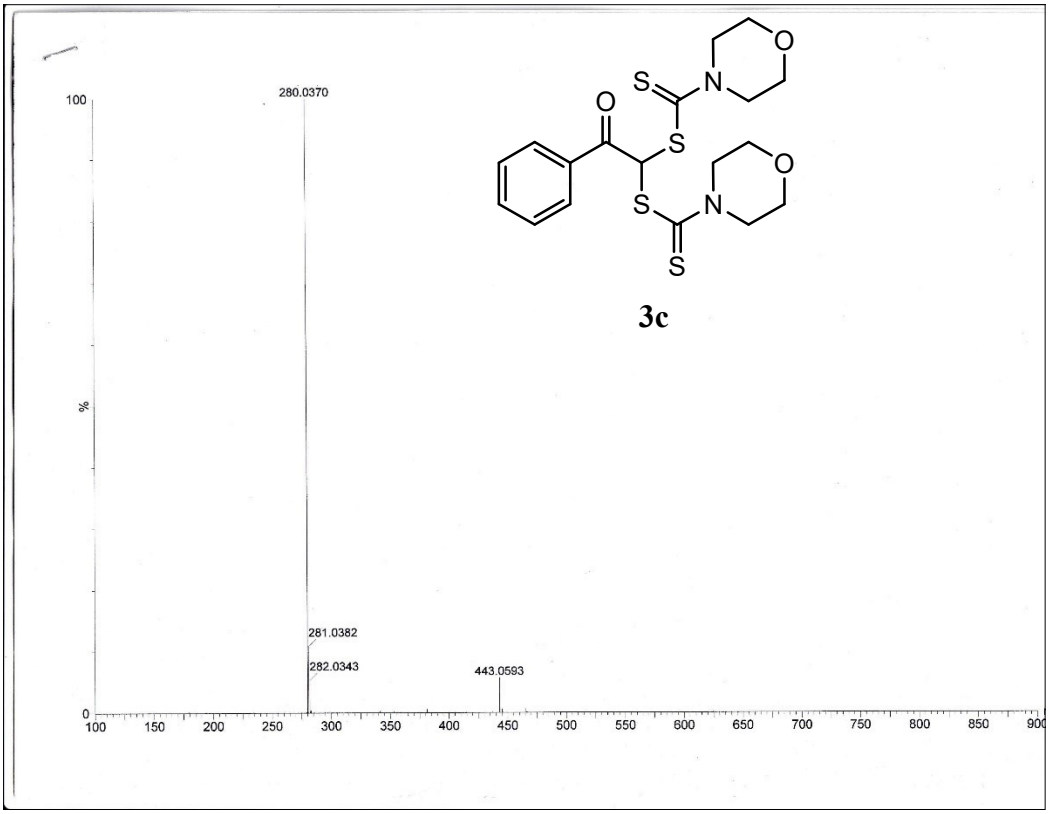



3l, Table 2

## H. HRMS spectra of few selected products (3b, 3c, 3d, 3e, 3f, 3h, 3k, 3l, 3n, 3p, 3r):




**3b**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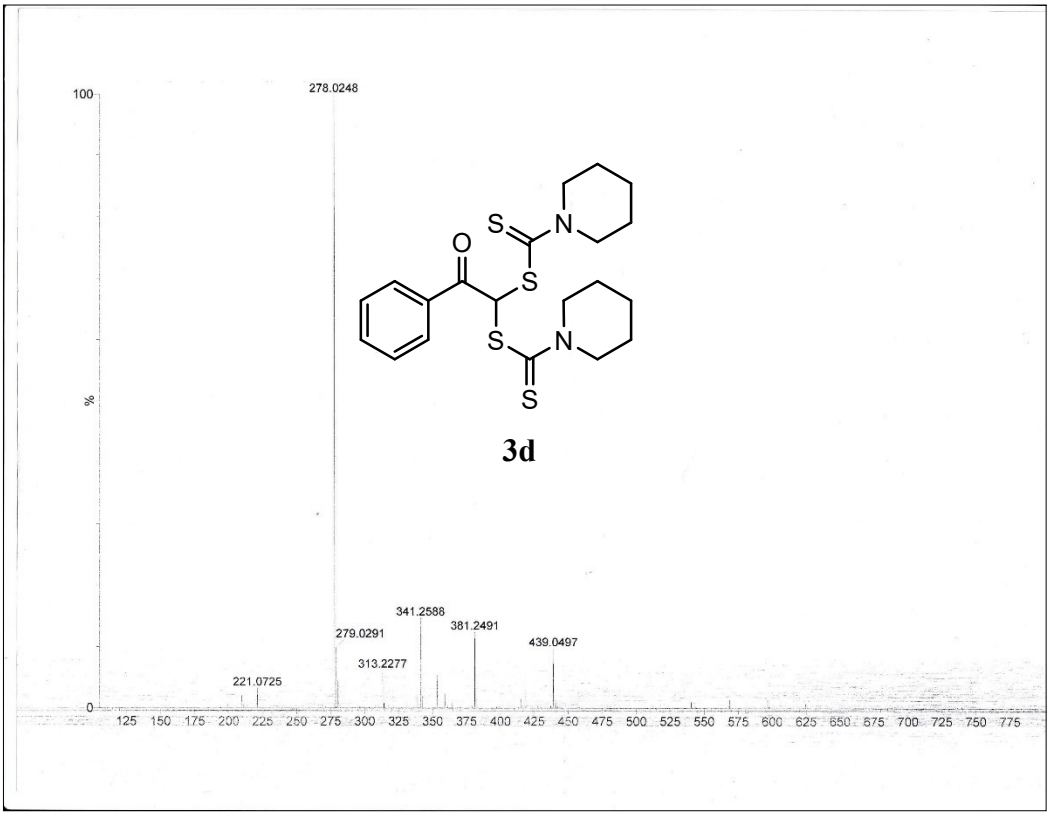
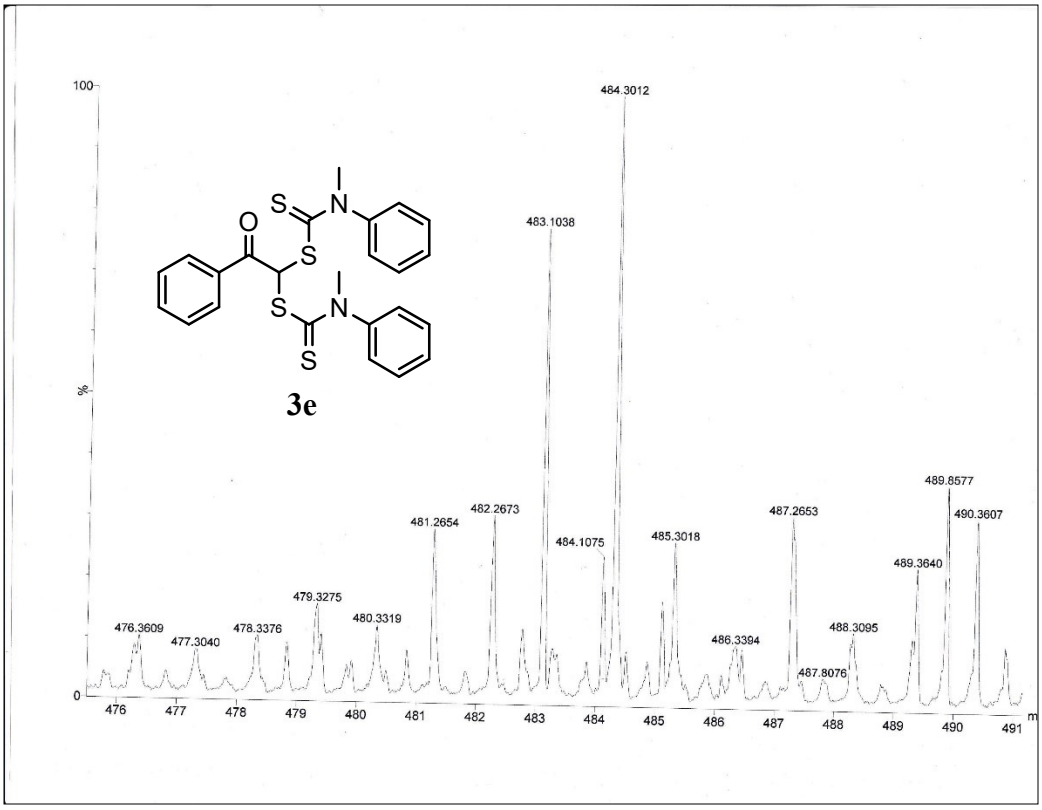
281.0382
282.0343
443.0593
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
O
S
N
O
S
S
O
S
N
S

**3c**


100
%
0
278.0248
341.2588
279.0291
381.2491
439.0497
313.2277
221.0725
125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675 700 725 750 775
O
S
N
S
S
N
S

**3d**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%
0
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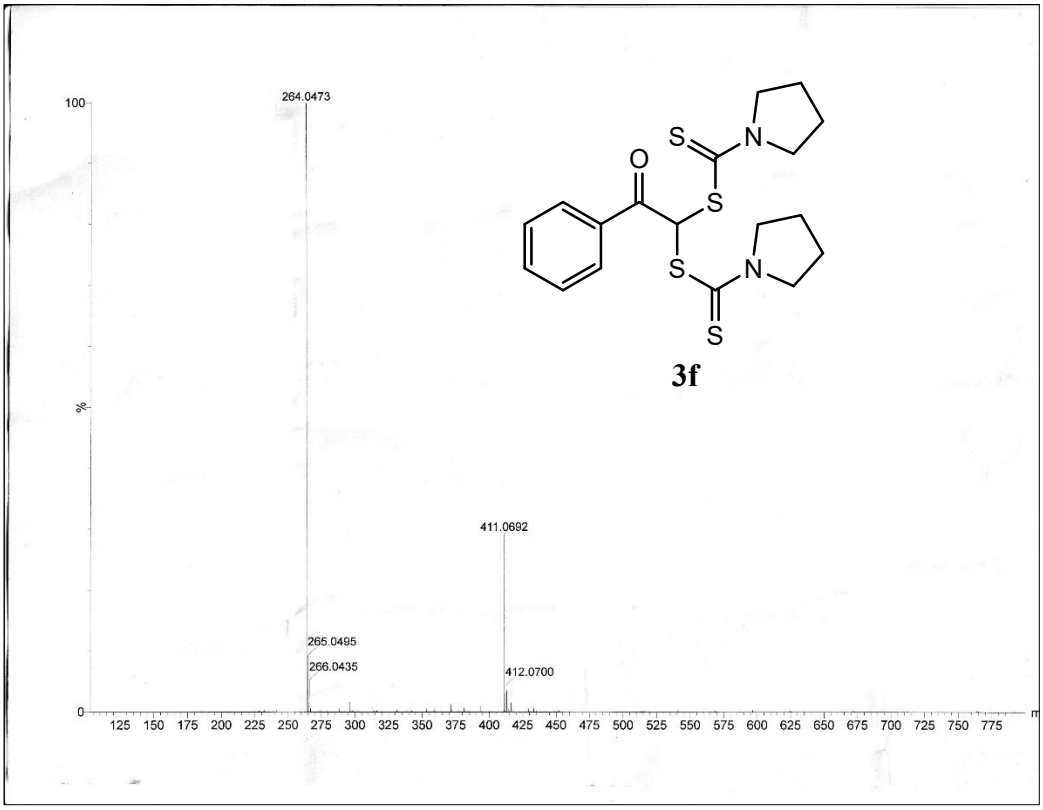
483.1038
482.2673
481.2654
485.3018
484.1075
489.8577
490.3607
487.2653
489.3640
479.3275
480.3319
476.3609
477.3040
478.3376
486.3394
488.3095
487.8076
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
m

**3e**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%
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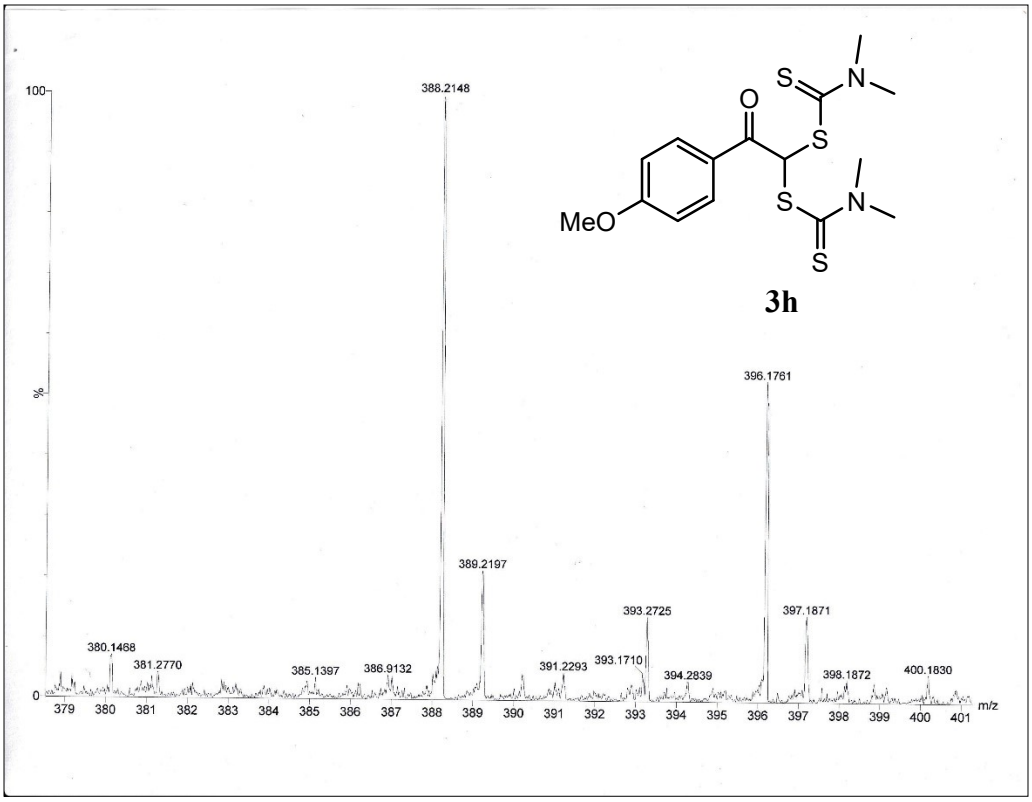
411.0692
265.0495
266.0435
412.0700
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
575
600
625
650
675
700
725
750
775
m

**3f**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%
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396.1761
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393.2725
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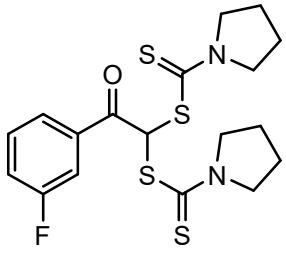
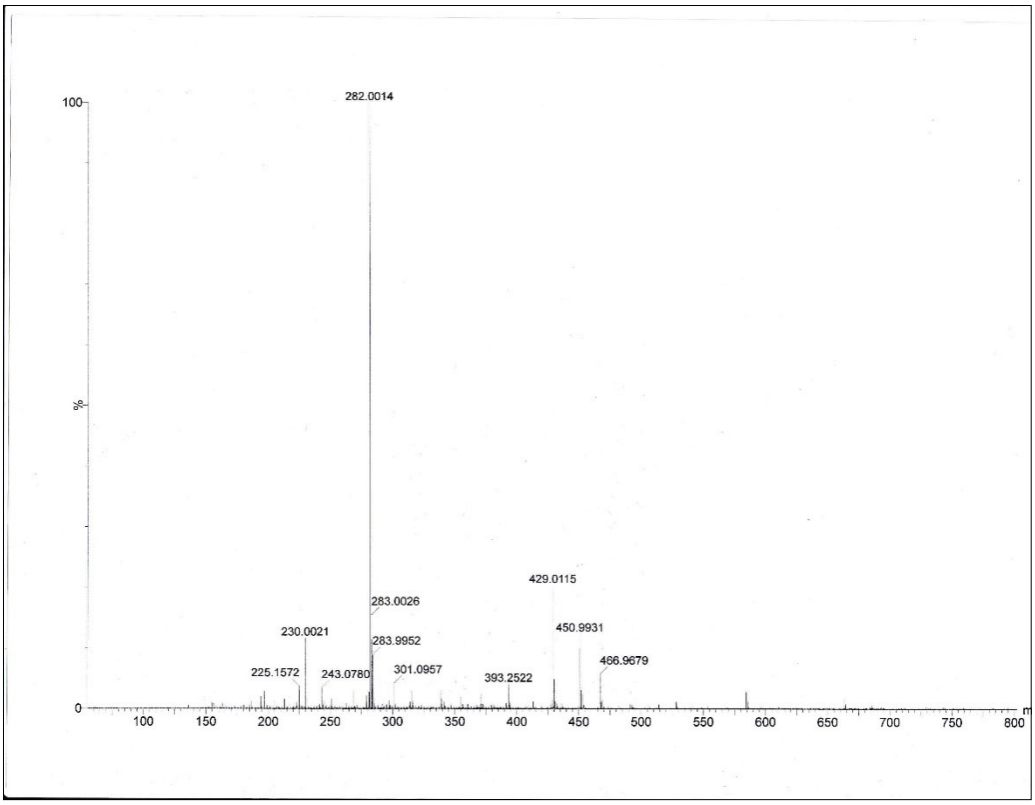
386.9132
391.2293
393.1710
394.2839
398.1872
400.1830
379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401
m/z
MeO
O
S
N
S
S
N
S

**3h**


O
S
N
S
S
N
S
F

**3k**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%
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283.9952
230.0021
225.1572
243.0780
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100
150
200
250
300
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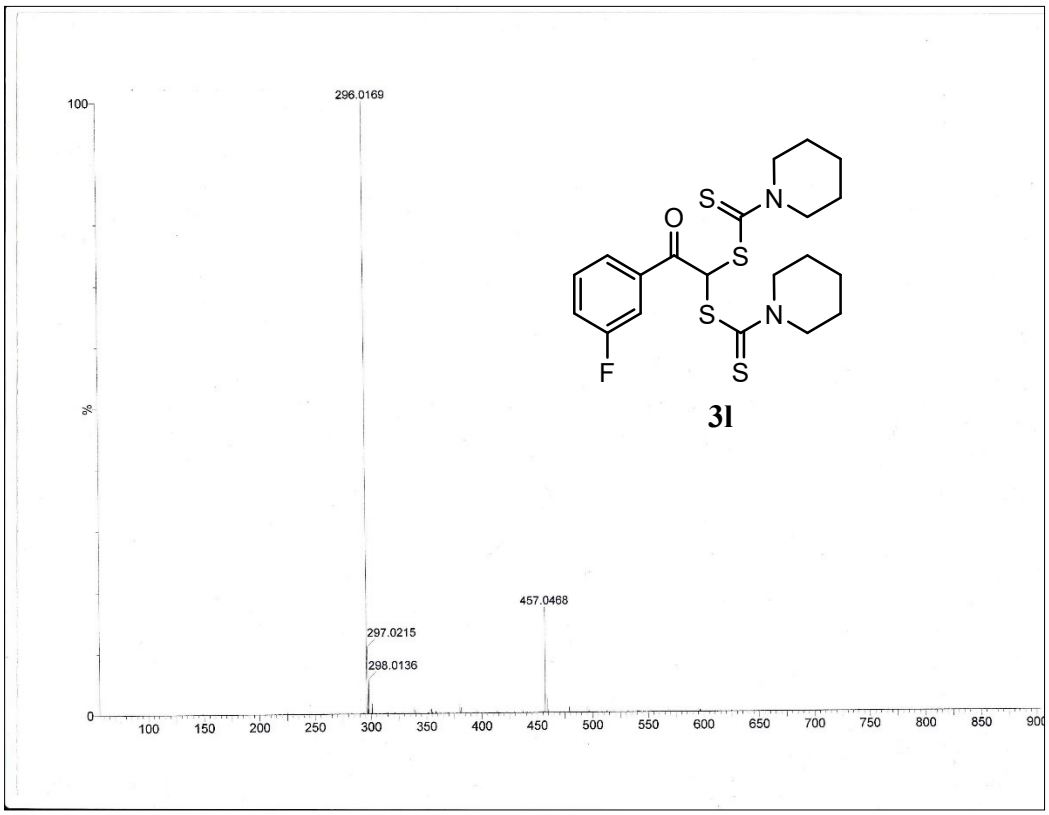
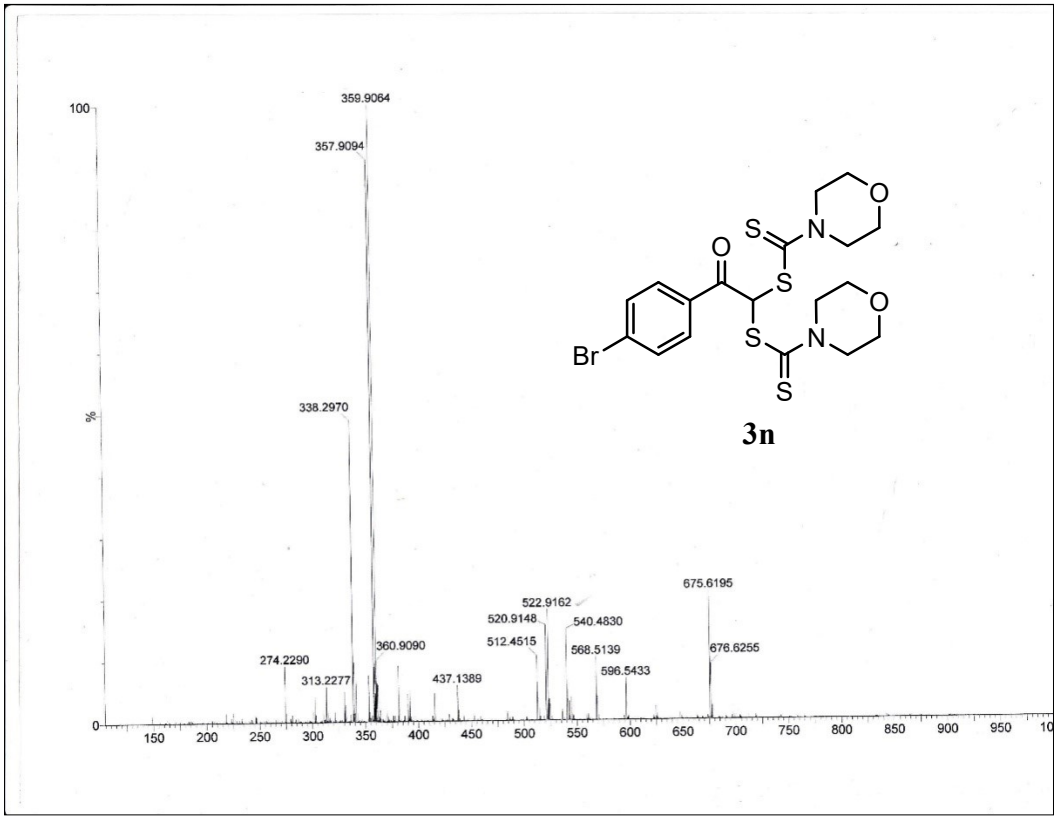
450
500
550
600
650
700
750
800


296.0169
100
%
0
457.0468
297.0215
298.0136
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
O
S
N
S
S
N
F
S

**3l**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%
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357.9094
338.2970
274.2290
313.2277
360.9090
437.1389
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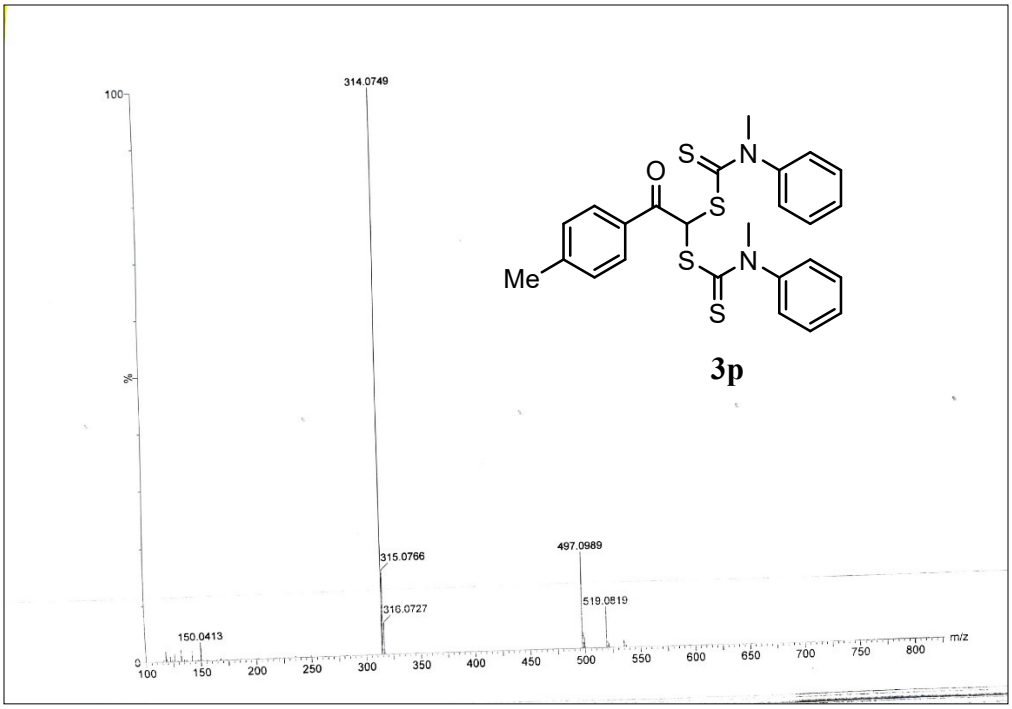
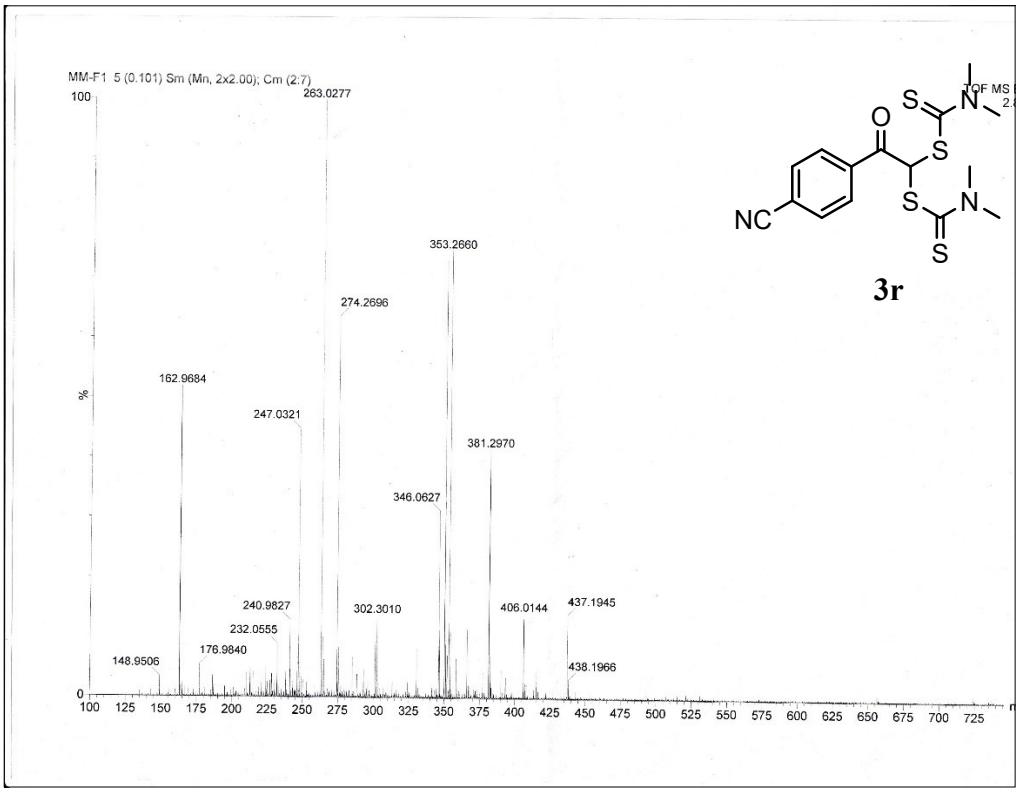
520.9148
522.9162
540.4830
568.5139
596.5433
675.6195
676.6255
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
Br
O
S
N
O
S
S
N
O
S

**3n**

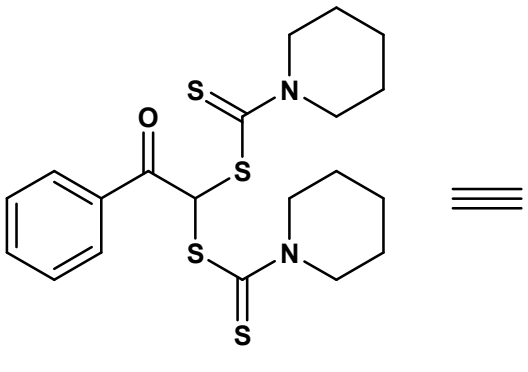

314.0749
100
%
315.0766
316.0727
497.0989
519.0819
150.0413
0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z
S
N
O
S
S
N
S
Me

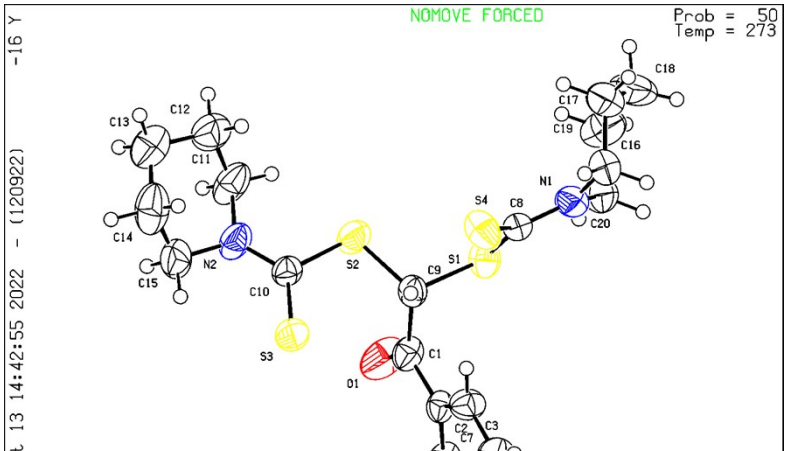
**3p**




# I. X-ray Crystallography Data:

**Fig. 1.** ORTEP diagram of the crystal structure of **3d** at 50% probability level



Details of the crystal structure investigation can be obtained from the Cambridge crystallographic data centre, 12 Union Road, Cambridge, CB2 1EZ, UK (3d: CCDC deposition no 2246557)

## Crystallographic data and structural refinement parameters for 3d

| | | | |
|---|---|---|---|
| Bondprecision: | C-C=0.0154A | Wavelength=0.71073 | |
| Cell: | a=16.9533(15) | b=7.7548(6) | c=17.8906(15) |
| | alpha=90 | beta=110.685(2) | gamma=90 |
| Temperature: | 273K | | |
| | Calculated | Reported | |
| Volume | 2200.5(3) | 2200.4(3) | |
| Spacegroup | P21/n | P21/n | |

| | | |
|---|---|---|
| Hallgroup | -P2yn | -P2yn |
| MoietyformulaC20H26N2OS4 | | ? |
| Sumformula | C20H26N2OS4 | C20H26N2OS4 |
| Mr | 438.67 | 438.67 |
| Dx,gcm-3 | 1.324 | 1.324 |
| Z | 4 | 4 |
| Mu(mm-1) | 0.445 | 0.445 |
| F000 | 928.0 | 928.0 |
| F000’ | 930.23 | |
| h,k,lmax | 22,10,23 | 22,10,23 |
| Nref | 5062 | 4977 |
| Tmin, Tmax | | |
| Tmin | | |
| Correctionmethod=Notgiven | | |
| Datacompleteness=0.983 | Theta(max)=27.532 | |
| R(reflections)=0.1652(3887) | WR2 (reflections) = 0.2800 (4977) | |
| S=1.562 | | Npar=248 |

## J. Gas chromatograms:

GC-MS data were collected from PerkinElmer Clarus SQ 8 C Mass spectrometer. Column specification (COL-Elite-5mS-30).

**Experimental procedure of the preparation of GC-MS sample:**

$Br_2$ (0.05 mL, 1 mmol) in MeCN (1 mL) was added drop-wise to the solution of phenylacetylene (0.1 ml, 1 mmol) in MeCN (2 mL) containing 0.04 mL of water at 5 $^oC$. After complete addition, the reaction mixture was allowed to stir for 15 min at room temperature. Then, two drop of reaction mixture was taken in a vial and diluted with 2 ml acetonitrile solvent. This dilute reaction mixture was used for GC-MS analysis.

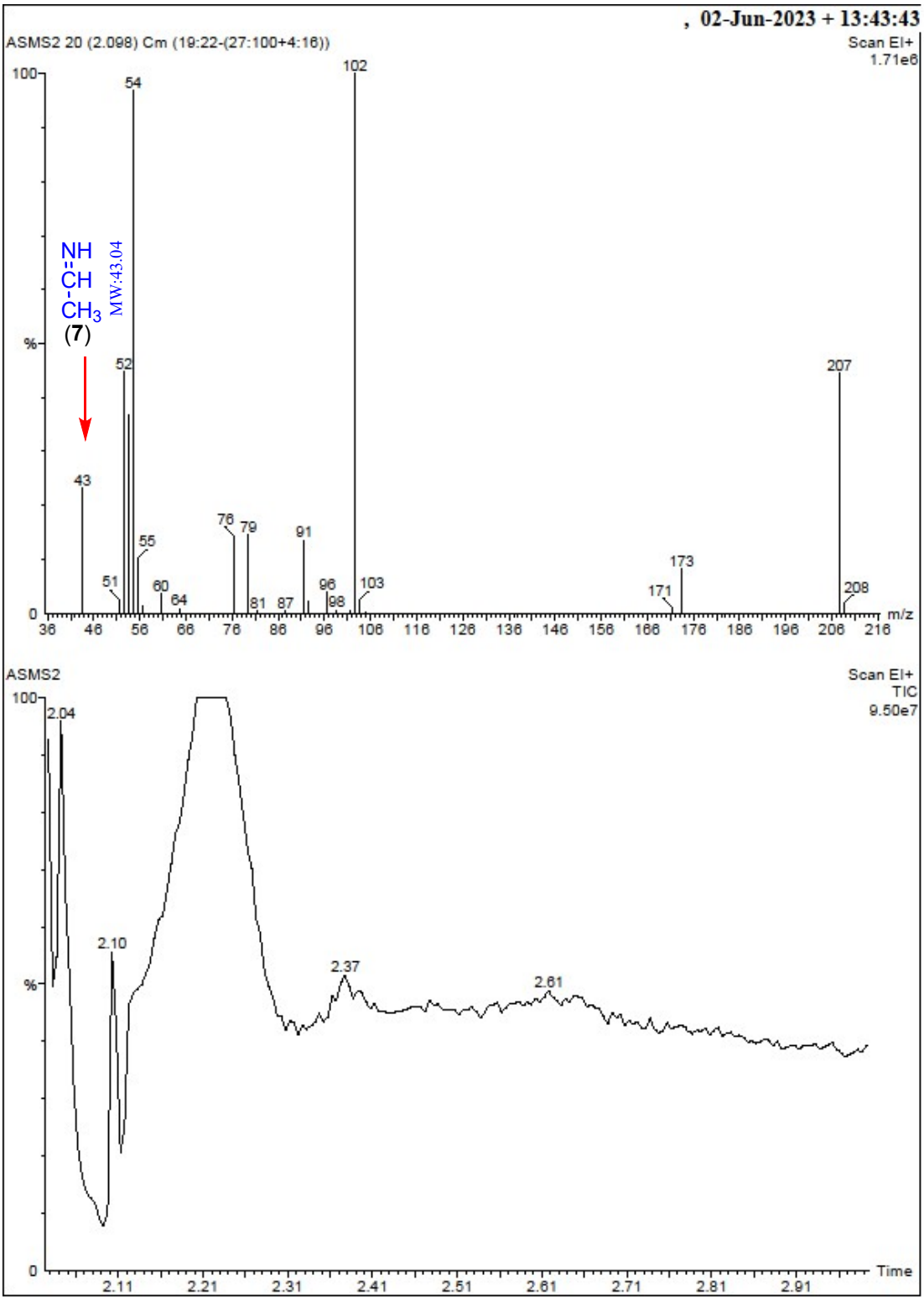



**Fig. 2.** GC spectrum of the reaction mixture described in Scheme 3a.

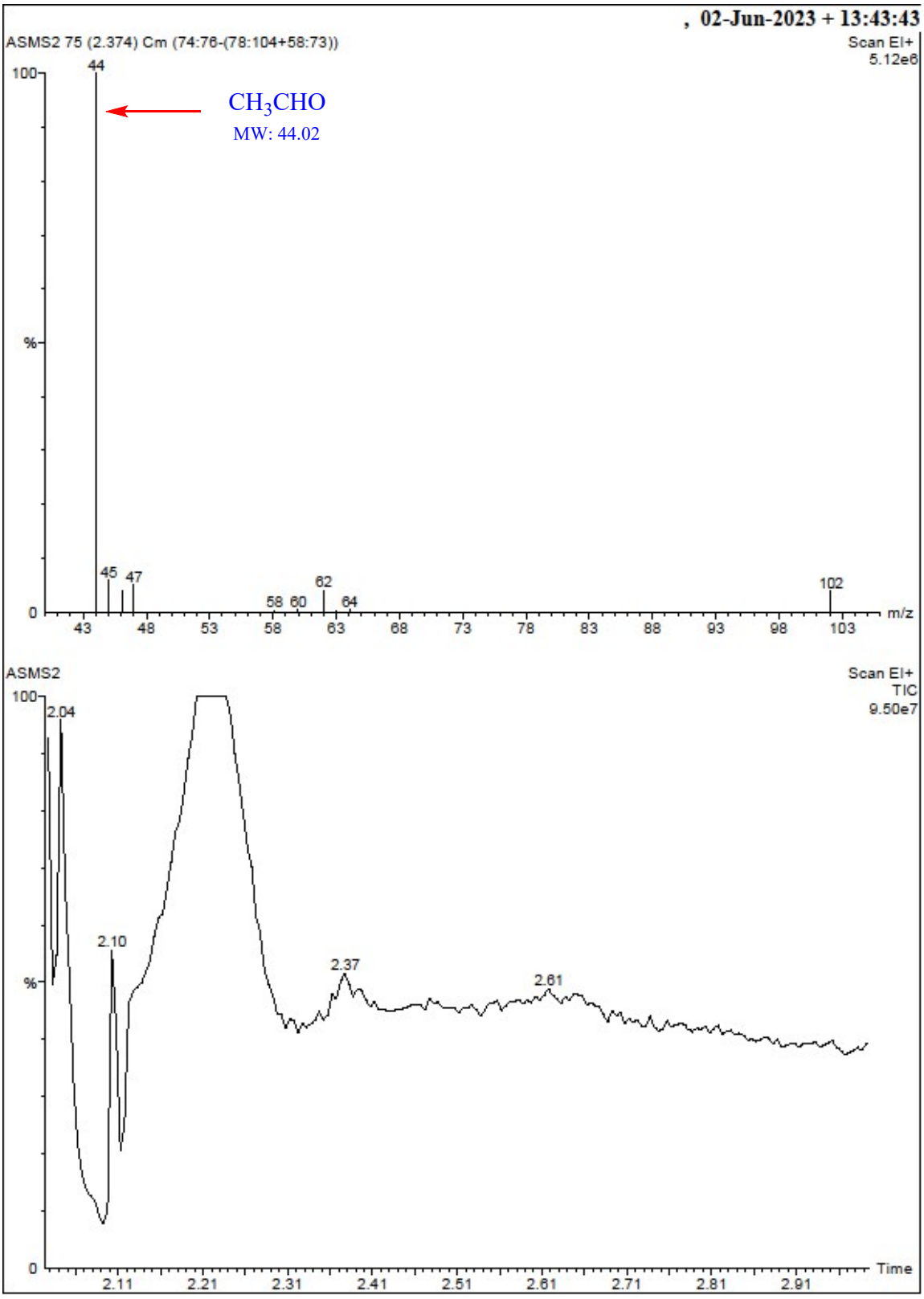



**Fig. 3.** GC spectrum of the reaction mixture described in Scheme 3a.

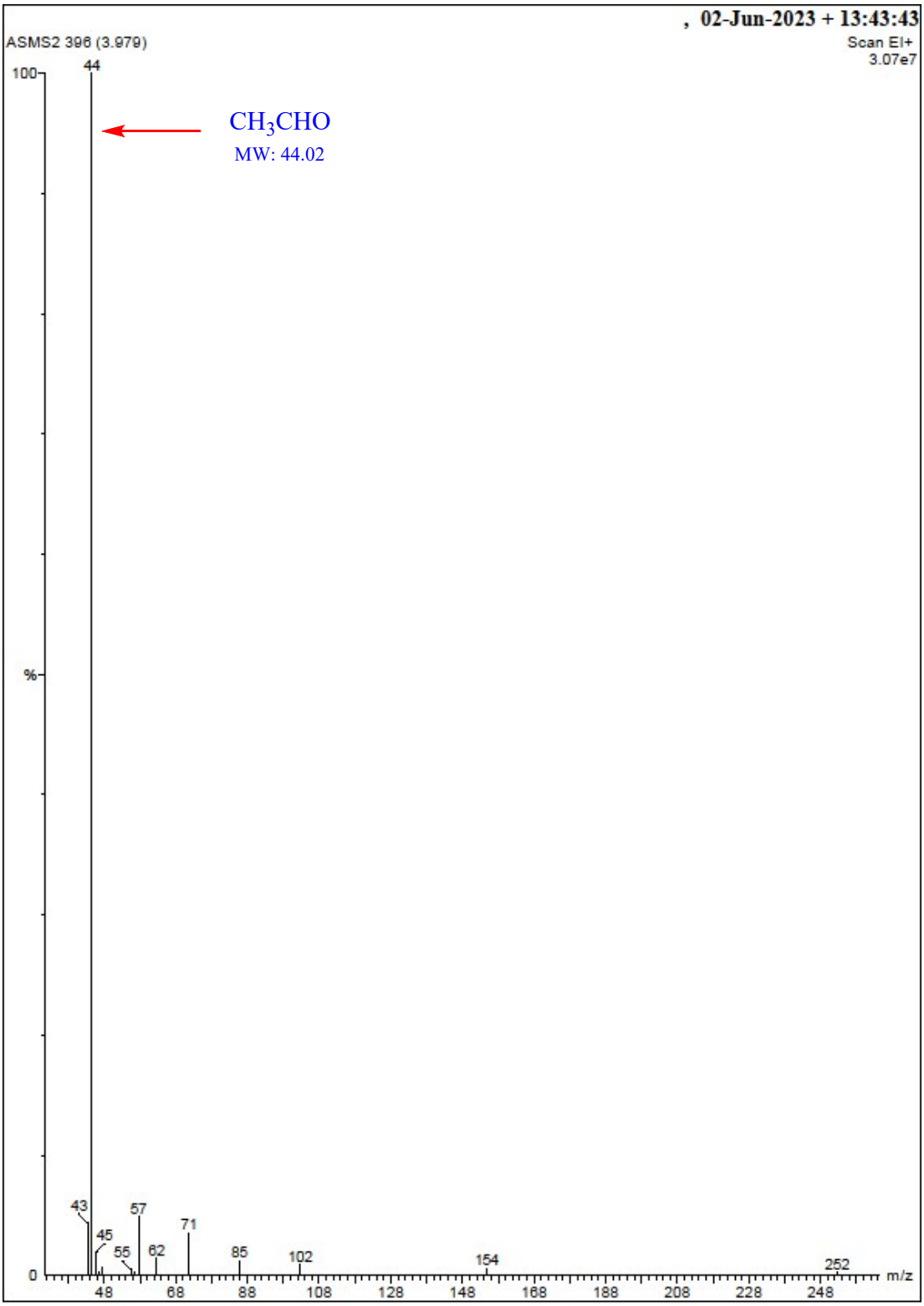



**Fig. 4.** GC spectrum of the reaction mixture described in Scheme 3a.

**K. Reference:**

1. B. Duan, H. Li, Y. Chen, C. Xu, G. Yin, *Tetrahedron Lett.,* 2022, **94**, 153697.