

Supporting Information

One-Pot Two-Step Dithiocarbamylation of Styrenes: Metal free Stereoselective Synthesis of Styrenyl Dithiocarbamates

Manas Mondal and Amit Saha*

Department of Chemistry, Jadavpur University, Kolkata 700032, India

List of Contents

A. General Information.....	2
B. General Experimental Procedure.....	2-3
C. Characterization Data of Synthesized Compounds.....	3-9
D. ¹ H and ¹³ C Spectra of All Compounds.....	10-28
E. ¹⁹ F NMR spectra of fluorinated products.....	29-30
F. Mass Spectra of Some Compounds.....	31-36
G. References.....	37

A. General Information:

All chemicals were used without further purification. All the reactions were checked by using TLC on silica gel plates (Merck silica gel, f_{24}). All synthesized products were purified by column chromatography on 100-200 mesh silica gel. The ^1H spectra of synthesized products were recorded in CDCl_3 on Bruker Spectrometer at 300, 400 MHz. The ^{19}F spectra of synthesized fluorinated products were recorded in CDCl_3 on Bruker Spectrometer, 300 MHz. The ^{13}C spectra of synthesized products were recorded in CDCl_3 on Bruker Spectrometer at 75, 100 MHz. Chemical shifts were reported in ppm referenced to 0.00 ppm for TMS. The coupling constant (J) values are shown in hertz, and splitting patterns of the proton are described as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet). HRMS were measured in methanol solvent on a Waters Micromass Q-tofMicromass spectrometer.

B. General experimental procedure:

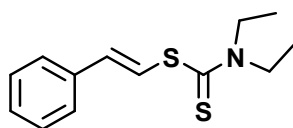
Preparation of dithiocarbamate anion: CS_2 (0.1 mL, 1.5 mmol) was added drop wise to a solution of secondary amine (1 mmol) and Et_3N (0.28 mL, 2 mmol) in acetonitrile (1 mL) at 5 °C. The resulting solution was stirred at room temperature for 5 min.

Synthesis of styrenyldithiocarbamate: Br₂ (0.05 mL, 1 mmol) in MeCN (1 mL) was added drop wise to the styrene (1 mmol) solution in MeCN (2 mL) at 5 °C. After complete addition, the reaction mixture was allowed to stir for 30 min at room temperature. Then the solution of freshly prepared dithiocarbamate anion (1 mmol) containing Et₃N (0.28 mL, 2 mmol) was added slowly into the brominated reaction mixture. The reaction mixture was allowed to stir at 65 °C for a certain reaction time period. After completion of 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.

All the styrenyldithiocarbamate products (**3a-3p**) were characterized by ¹H and ¹³C NMR spectroscopy. HRMS was recorded for the all unknown compounds.

C. Characterization Data of Synthesized Compounds

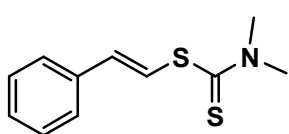
Styryldiethylcarbamoedithioate (**3a**): White solid, ¹H NMR (300 MHz, CDCl₃) δ:



1.26-1.34(m, 6H), 3.74-3.77(m, 2H), 4.04-4.06(m, 2H),
6.75(d, J=15.9 Hz, 1H), 7.28-7.51(m, 6 Hz), ¹³C NMR (75
MHz, CDCl₃) δ: 11.69, 12.74, 47.11, 49.42, 122.92,

126.68(2C), 128.13, 128.74(2C), 132.28, 136.43, 193.31, . HRMS (ESI) m/z calcd for C₁₃H₁₇NS₂ [M + H]⁺ , 252.0802, found 252.0194.

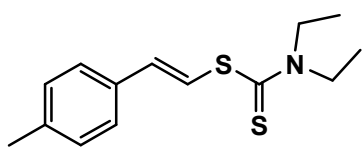
Styryldimethylcarbamdithioate (**3b**).¹White solid, ¹H NMR (300 MHz, CDCl₃) δ:



3.43(s, 3H), 3.60(s, 3H), 6.79(d, J=15.9 Hz, 1H), 7.28-7.39(m, 3H), 7.43-7.52(m, 3H), ¹³C NMR (75 MHz,

CDCl₃) δ: 41.61, 45.09, 123.06, 126.63(2C), 128.15, 128.69(2C), 132.37, 136.25, 194.84.

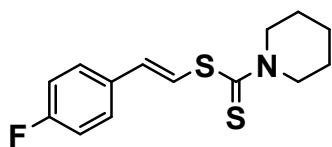
Diethyl-1-carbodithioic acid(4-methyl-phenyl-vinyl ester) (**3c**): Light yellow solid,



¹H NMR (300 MHz, CDCl₃) δ: 1.30-1.39(m, 6H), 2.37(s, 3H), 3.72-3.79(m, 2H), 4.04-4.11(m, 2H), 6.75(d, J=15.9 Hz, 1H), 7.17(d, J=8.1 Hz, 1H), 7.37-

7.44(m, 3H), ¹³C NMR (75 MHz, CDCl₃) δ: 11.62, 12.66, 21.30, 47.02, 49.31, 121.50, 126.55(2C), 129.38(2C), 132.49, 133.63, 138.05, 193.53, . HRMS (ESI) m/z calcd for C₁₄H₁₉NS₂ [M + H]⁺, 265.1039, found 265.8385.

Piperidine-1-carbodithioic acid(4-fluoro-phenyl-vinyl ester) (**3d**): Yellow solid, ¹H



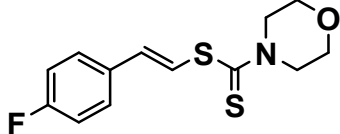
NMR (300 MHz, CDCl₃) δ: 1.73(s, 6H), 3.88(broad, 2H), 4.29(broad, 2H), 6.70(d, J=15.9 Hz, 1H), 7.00-7.06(m, 2H), 7.36-7.45(m, 3H), ¹³C NMR (75 MHz, CDCl₃) δ:

24.33, 25.59, 26.22, 51.85, 52.76, 115.77(d, J_{C-F} = 21.75 Hz, 2C), 122.48(d, J_{C-F} = 2.25 Hz), 128.33(d, J_{C-F} = 8.25 Hz, 2C), 131.44, 132.70(d, J_{C-F} = 3.75

Hz), 162.71(d, J_{C-F} = 246.75 Hz), 193.27, ¹⁹F NMR(300 MHz, CDCl₃) δ: -113.40

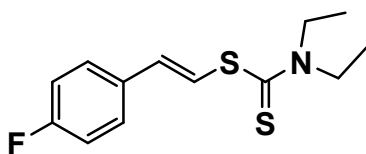
HRMS (ESI) m/z calcd for C₁₄H₁₆NFS₂ [M + H]⁺, 282.0788, found 282.0788.

Morpholine-1-carbodithioic acid(4-fluoro-phenyl-vinyl ester) (**3e**): Yellow solid,



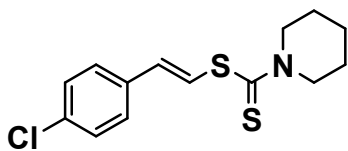
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 3.75-3.81(m, 4H), 4.06-4.24(m, 4H), 6.73(d, $J=15.9$ Hz, 1H), 7.00-7.06(m, 2H), 7.34(d, $J=15.9$ Hz, 1H), 7.40-7.45(m, 2H), $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 50.96(d, $J_{\text{C-F}} = 13.5$ Hz, 2C), 66.29(2C), 26.22, 115.74(d, $J_{\text{C-F}} = 21.75$ Hz, 2C), 121.34(d, $J_{\text{C-F}} = 2.25$ Hz), 128.31(d, $J_{\text{C-F}} = 8.25$ Hz, 2C), 132.30, 132.36(d, $J_{\text{C-F}} = 3$ Hz), 162.73(d, $J_{\text{C-F}} = 246.75$ Hz), 195.16, $^{19}\text{F NMR}$ (300 MHz, CDCl_3) δ : -112.97, HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{NFOS}_2$ $[\text{M} + \text{H}]^+$, 284.0581, found 284.0100.

Diethyl-1-carbodithioic acid(4-fluoro phenyl-vinyl ester) (**3f**): Yellow oil, $^1\text{H NMR}$



(300 MHz, CDCl_3) δ : 1.26-1.37(m, 6H), 3.72-3.79(m, 2H), 4.01-4.08(m, 2H), 6.71(d, $J=15.9$, 1H), 7.00-7.06(m, 2H), 7.36-7.45(m, 3H), $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 11.70, 12.76, 47.14, 49.44, 122.95, 126.69(2C), 128.22, 128.77(2C), 132.27, 136.44, 193.28, $^{19}\text{F NMR}$ (300 MHz, CDCl_3) δ : -113.44, HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NFS}_2$ $[\text{M} + \text{H}]^+$, 270.0788, found 270.0788.

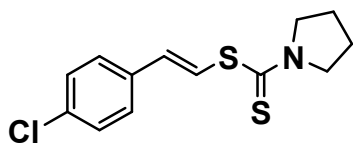
Piperidine-1-carbodithioic acid(4-chloro-phenyl-vinyl ester) (**3g**).¹ Yellow solid,



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.73(s, 6H), 3.88(broad, 2H), 4.30(broad, 2H), 6.69(d, $J=15.9$ Hz, 1H), 7.30(d, $J=8.4$ Hz, 2H), 7.38(d, $J=8.7$ Hz, 2H), 7.50(d, $J=15.9$

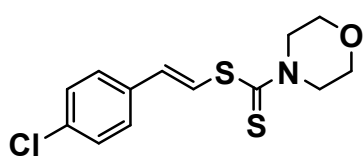
Hz, 1H), ^{13}C NMR (75 MHz, CDCl_3) δ : 24.23, 25.46, 26.05, 51.80, 52.71, 123.69, 127.76(2C), 128.87(2C), 130.83, 133.73, 134.87, 192.84.

Pyrrolidine-1-carbodithioic acid(4-chloro-phenyl-vinyl ester) (**3h**).¹ Yellow solid,



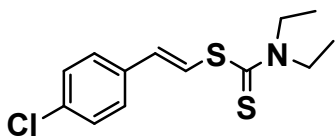
^1H NMR (300 MHz, CDCl_3) δ : 1.96-2.16(m, 4H), 3.68(t, $J=6.9$ Hz, 2H), 3.96(t, $J=6.9$ Hz, 2H), 6.70(d, $J=16.2$ Hz, 1H), 7.28-7.39(m, 4H), 7.58(d, $J=16.2$ Hz, 1H) ^{13}C NMR (75 MHz, CDCl_3) δ : 24.36, 26.19, 50.85, 54.96, 123.78, 127.79(2C), 128.93(2C), 130.25, 133.76, 134.88, 189.84.

Morpholine-1-carbodithioic acid(4-chloro-phenyl-vinyl ester) (**3i**): Yellow solid,



^1H NMR (300 MHz, CDCl_3) δ : 3.77-3.80(m, 4H), 4.10(broad, 4H), 6.71(d, $J=16.2$ Hz, 1H), 7.29-7.40(m, 4H), 7.44(d, $J=15.9$ Hz, 1H), ^{13}C NMR (75 MHz, CDCl_3) δ : 50.85(2C), 66.18(2C), 122.59, 127.81(2C), 128.92(2C), 131.79, 133.99, 134.60, 194.79, HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{NClOS}_2$ [$\text{M} + \text{H}$]⁺, 300.0285 found 300.0286.

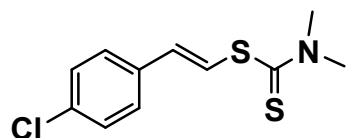
Diethyl-1-carbodithioic acid(4-chloro-phenyl-vinyl ester) (**3j**): Yellow solid, ^1H



NMR (400 MHz, CDCl_3) δ : 1.27-1.35(m, 2H), 3.71-3.77(m, 2H), 4.01-4.06(m, 2H), 6.69(d, $J=16$ Hz, 1H), 7.28-7.31(m, 2H), 7.36-7.38(m, 2H), 7.49(d, $J=16$ Hz,

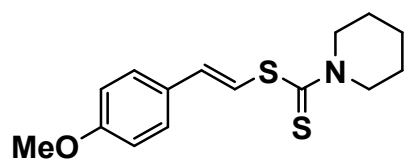
1H), ^{13}C NMR (100 MHz, CDCl_3) δ : 11.46, 12.74, 47.15, 49.44, 123.95, 127.82(2C), 128.93(2C), 130.59, 133.76, 134.95, 192.83, HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NCIS}_2$ $[\text{M} + \text{H}]^+$, 285.0413, found 286.0493.

Dimethyl-1-carbodithioic acid(4-chloro-phenyl-vinyl ester) (**3k**).² Light yellow



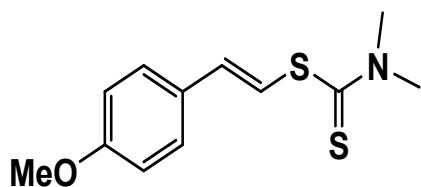
solid, ^1H NMR (300 MHz, CDCl_3) δ : 3.43(s, 3H), 3.60(s, 3H), 6.73(d, $J=15.9$ Hz, 1H), 7.33(d, $J=8.4$ Hz, 2H), 7.41(d, $J=8.1$ Hz, 2H), 7.50(d, $J=16.2$ Hz, 1H), ^{13}C NMR (75 MHz, CDCl_3) δ : 41.61, 45.13, 124.03, 127.77, 128.88, 130.74, 133.80, 134.77, 194.42.

Piperidine-1-carbodithioic acid(4-methoxy-phenyl-vinyl ester) (**3l**).¹ White solid,



^1H NMR (300 MHz, CDCl_3) δ : 1.74(s, 6H), 3.84(s, 3H), 3.90(broad, 2H), 4.31(broad, 2H), 6.72(d, $J=16.5$ Hz, 1H), 6.89(d, $J=7.2$ Hz, 2H), 7.27(d, $J=12.9$ Hz, 1H), 7.43(d, $J=6.6$ Hz, 2H), ^{13}C NMR (75 MHz, CDCl_3) δ : 24.31, 25.52, 26.01, 51.72, 52.50, 55.42, 114.09(2C), 119.77, 127.97(2C), 129.37, 132.88, 159.73, 193.90.

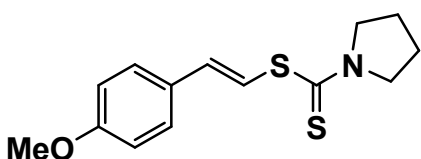
Dimethyl-1-carbodithioic acid(4-methoxy-phenyl-vinyl ester) (**3m**).¹ Yellow solid,



^1H NMR (300 MHz, CDCl_3) δ : 3.38(s, 3H), 3.55(s, 3H), 3.81(s, 3H), 6.70(d, $J=15.9$ Hz, 1H), 7.28-7.39(m, 4H) 7.58(d, $J=16.2$ Hz, 1H), ^{13}C NMR (75

MHz, CDCl₃) δ : 41.60, 45.05, 55.35, 114.12(2C), 120.06, 127.97(2C), 129.13, 132.65, 159.71, 195.38.

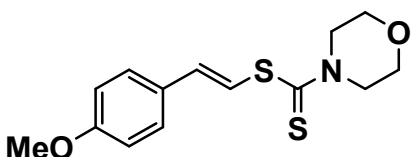
Pyrolidine-1-carbodithioic acid(4-methoxy-phenyl-vinyl ester) (**3n**): Yellow solid,



¹H NMR (300 MHz, CDCl₃) δ : 1.98-2.07(m, 2H), 2.09-2.18(m, 2H), 3.70(t, J=6.6 Hz, 2H), 3.84(s, 3H), 3.98(t, J=6.9 Hz, 2H), 6.73(d, J=15.9 Hz, 1H),

6.93(d, J=8.7 Hz, 2H), 7.33-7.43(m, 3H), ¹³C NMR (75 MHz, CDCl₃) δ : 24.32, 26.15, 50.72, 54.77, 55.34, 114.10(2C), 119.70, 127.93(2C), 129.19, 132.19, 159.66, 190.81, HRMS (ESI) m/z calcd for C₁₄H₁₇NOS₂ [M + H]⁺, 279.0752, found 279.0913.

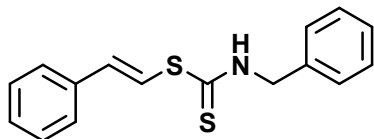
Morpholine-1-carbodithioic acid(4-methoxy-phenyl-vinyl ester) (**3o**): White solid,



¹H NMR (300 MHz, CDCl₃) δ : 3.79-3.82(m, 4H), 3.84(s, 3H), 4.0-4.50(m, 4H), 6.74(d, J=15.9 Hz, 1H), 6.90(d, J=8.7 Hz, 1H), 7.22(d, J=15.6 Hz, 1H),

7.42(d, J=8.7 Hz, 2H), ¹³C NMR (75 MHz, CDCl₃) δ : 50.79, 51.06, 55.35, 66.28(2C), 114.15(2C), 118.65, 128.06(2C), 129.01, 133.76, 159.85, 195.89, HRMS (ESI) m/z calcd for C₁₄H₁₇NO₂S₂ [M + H]⁺, 296.0701, found 296.0780.

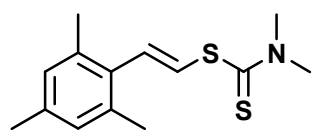
Styrylbenzylcarbamdithioate (**3p**): yellow solid, ¹H NMR (300 MHz, CDCl₃) δ :



5.43(s, 2H), 6.51(s, 1H), 6.94-6.95(m, 2H), 7.11(d,

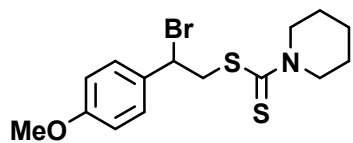
$J=7.2$ Hz, 2H), 7.21-7.23(m, 3H), 7.42-7.44(m, 5H), ^{13}C NMR (75 MHz, CDCl_3)
 δ : 50.87, 108.95, 127.06(2C), 127.57, 128.49(2C), 128.68(2C), 129.49(2C),
 129.89, 130.61, 135.33, 144.85, 189.08, HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{NS}_2$ [$\text{M} + \text{H}$] $^+$, 286.0646, found 286.0726.

Dimethyl-1-carbodithioic acid(2,4,6-trimethyl-phenyl-vinyl ester) (**3q**): White



solid, ^1H NMR (300 MHz, CDCl_3) δ : 2.29(s, 3H), 2.38(s, 3H), 3.41(s, 3H), 3.57(s, 3H), 6.82(d, $J=16.2$ Hz, 1H), 6.90(s, 2H), 6.97(d, $J=16.5$ Hz, 1H), ^{13}C NMR (75 MHz, CDCl_3) δ : 21.03, 21.29(2C), 41.68, 45.01, 126.49, 128.84(2C), 131.30, 132.58, 136.20(2C), 136.93, 195.37, HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{NS}_2$ [$\text{M} + \text{H}$] $^+$, 266.0959, found 266.1044.

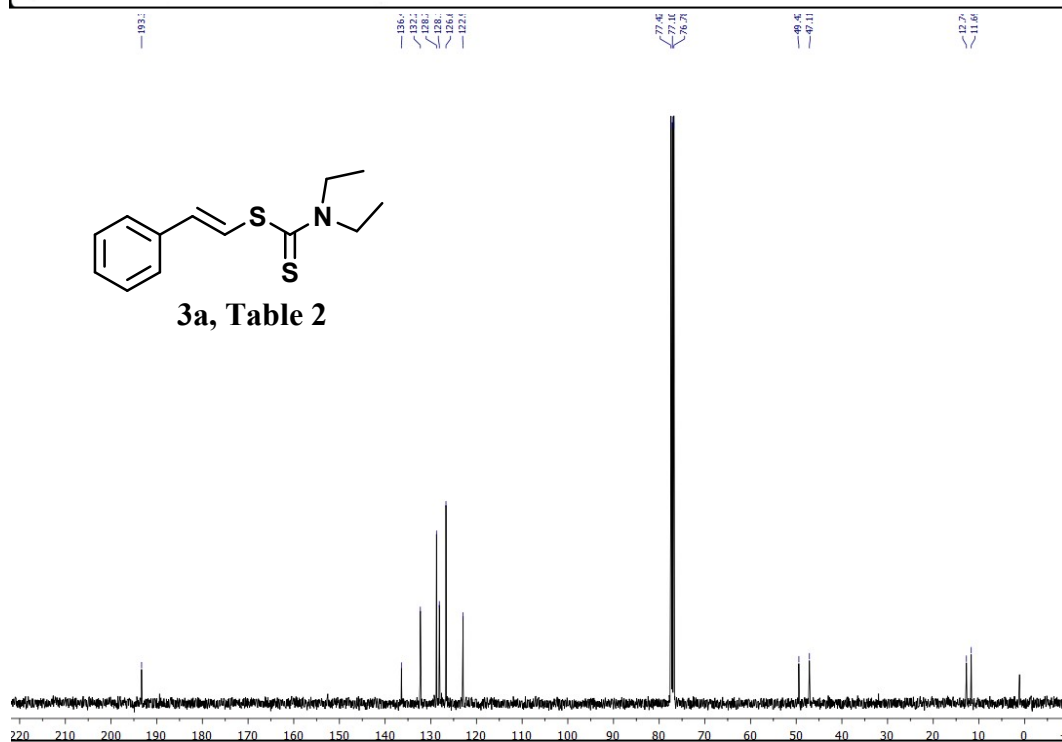
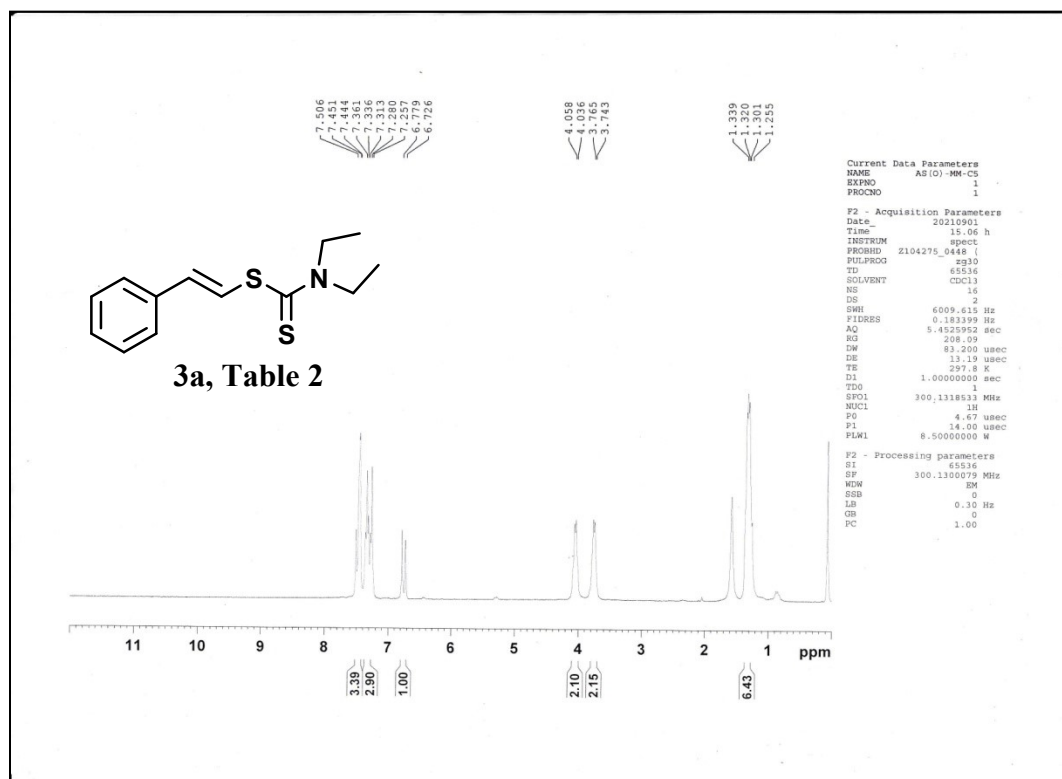
2-bromo-2-(4-methoxyphenyl)ethyl piperidine-1-carbodithioate (**5**) Yellow liquid,



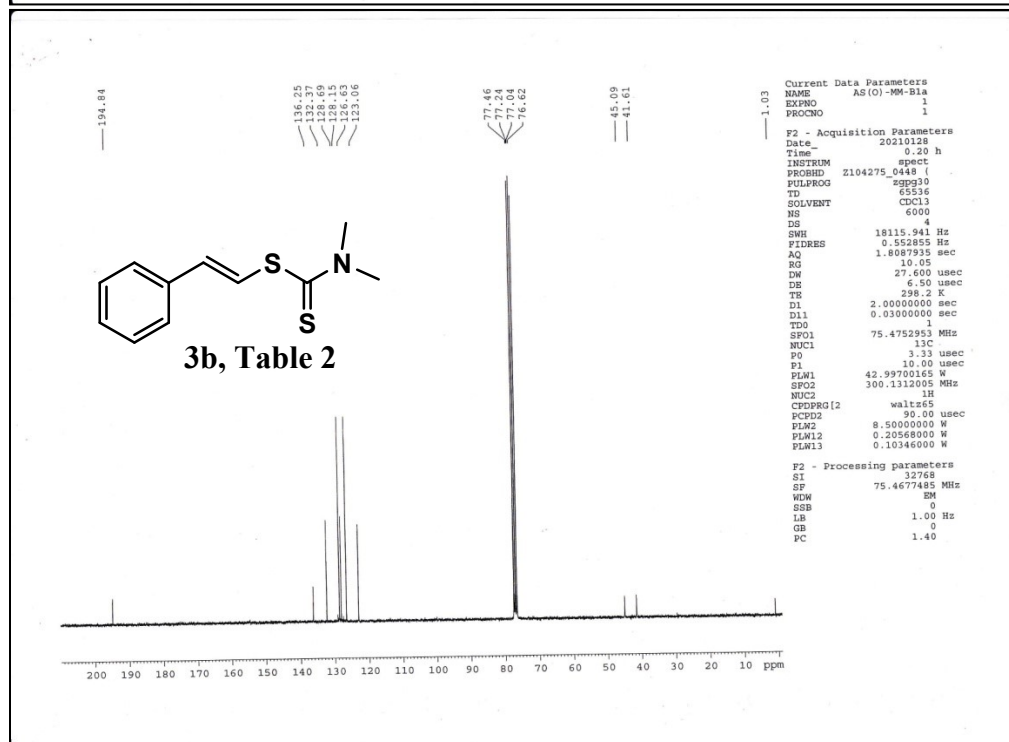
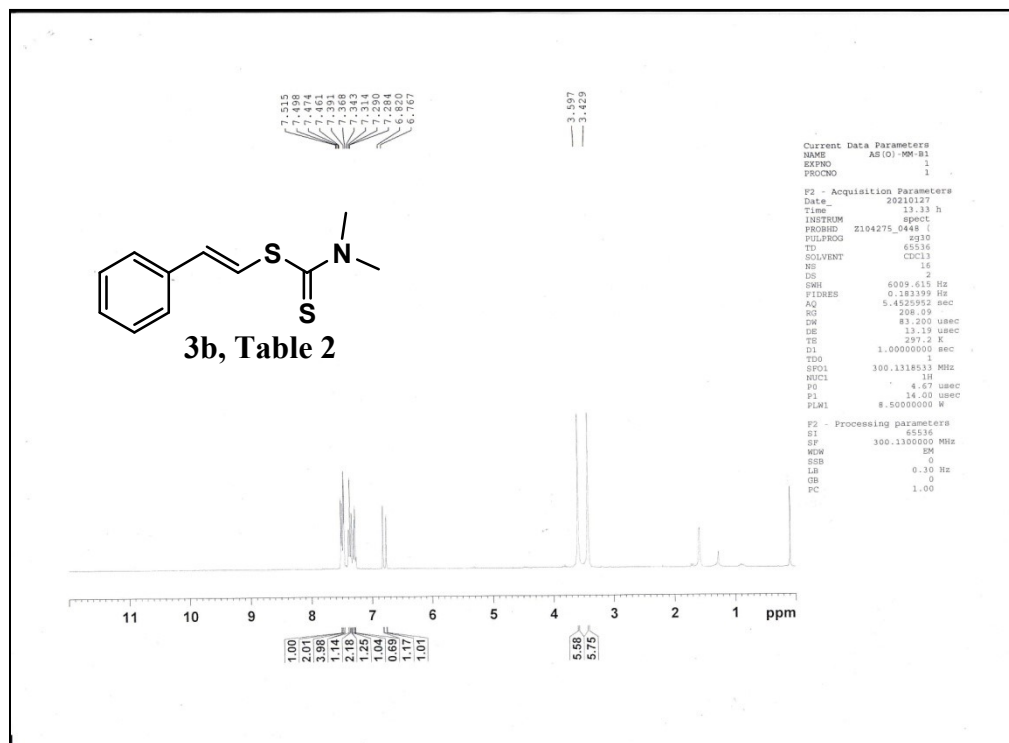
^1H NMR (300 MHz, CDCl_3) δ : 1.67(s, 6H), 1.75(s, 1H), 1.78(s, 1H), 3.79(s, 3H), 3.81(broad, 2H), 4.26(broad, 2H), 5.20-5.27(m, 1H), 6.83-6.87(m, 2H), 7.33-7.38(m, 2H), ^{13}C NMR (75 MHz, CDCl_3) δ : 21.90, 24.25, 25.34, 26.16, 50.42, 51.16, 52.42, 55.21, 113.81(2C), 128.87(2C), 134.09, 158.67, 194.74

D.¹H and ¹³C NMR spectra of products

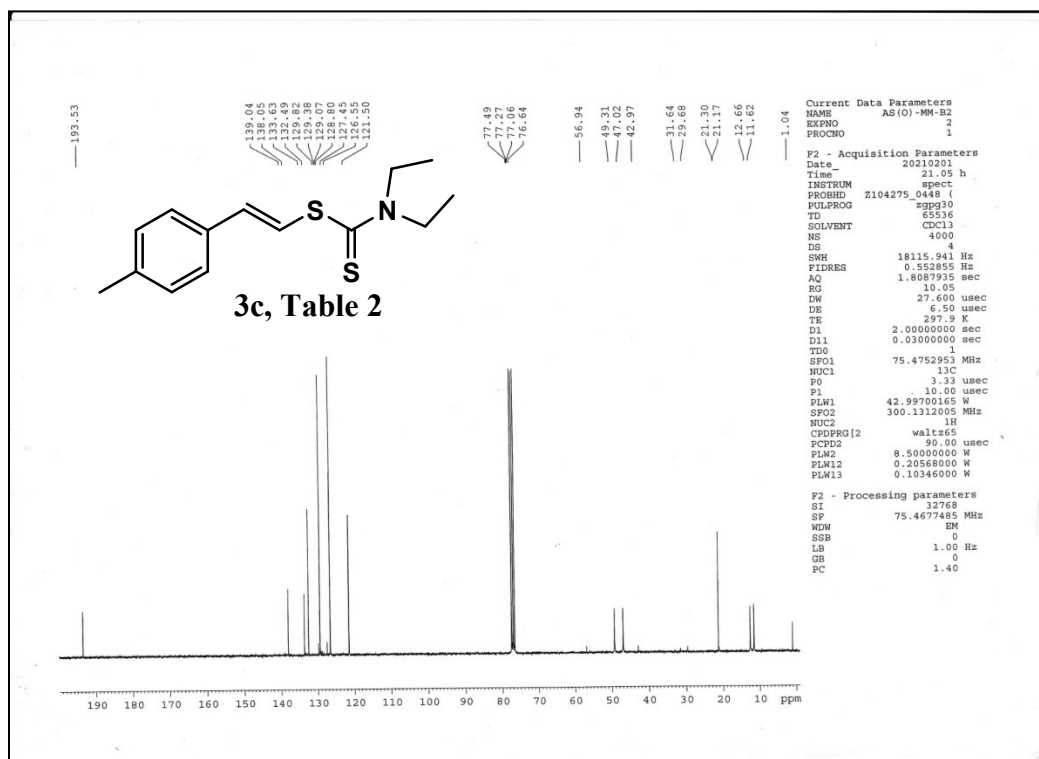
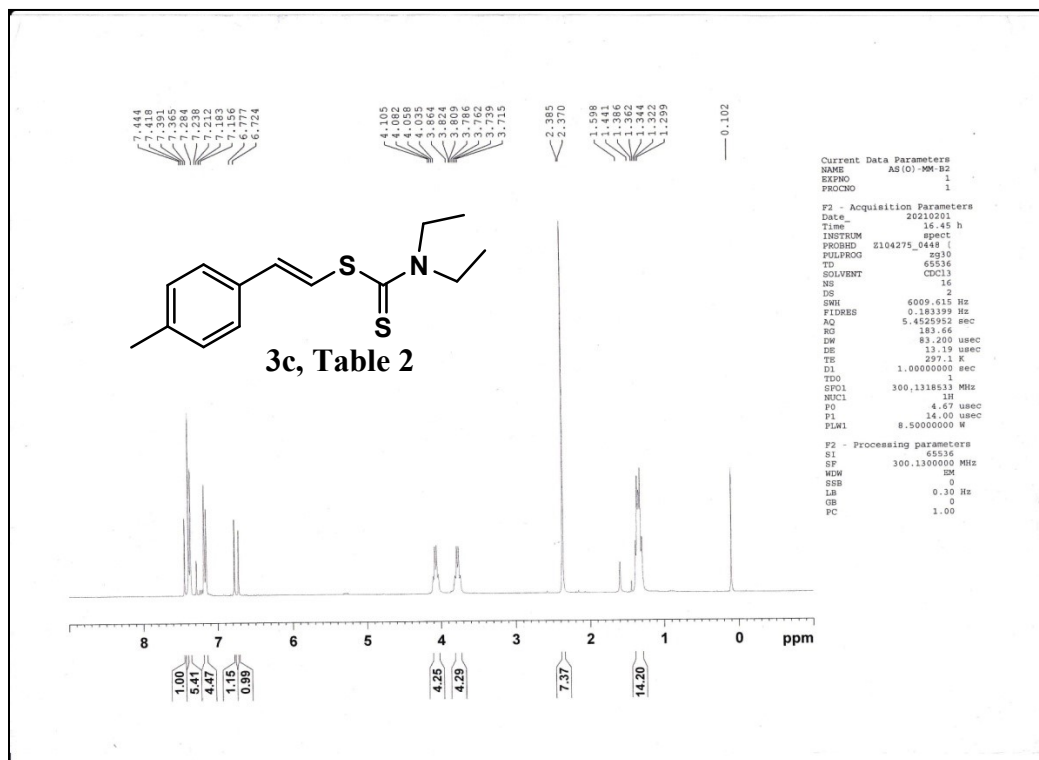
1. ¹H NMR (300 MHz, CDCl₃) spectrum of 3a



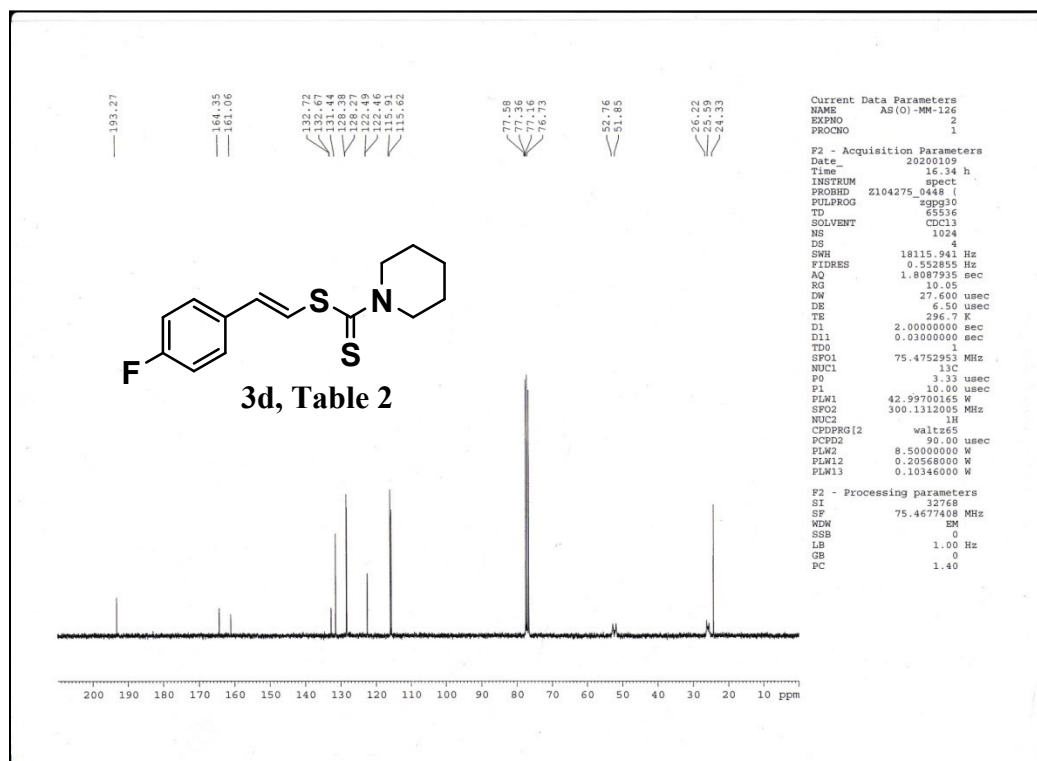
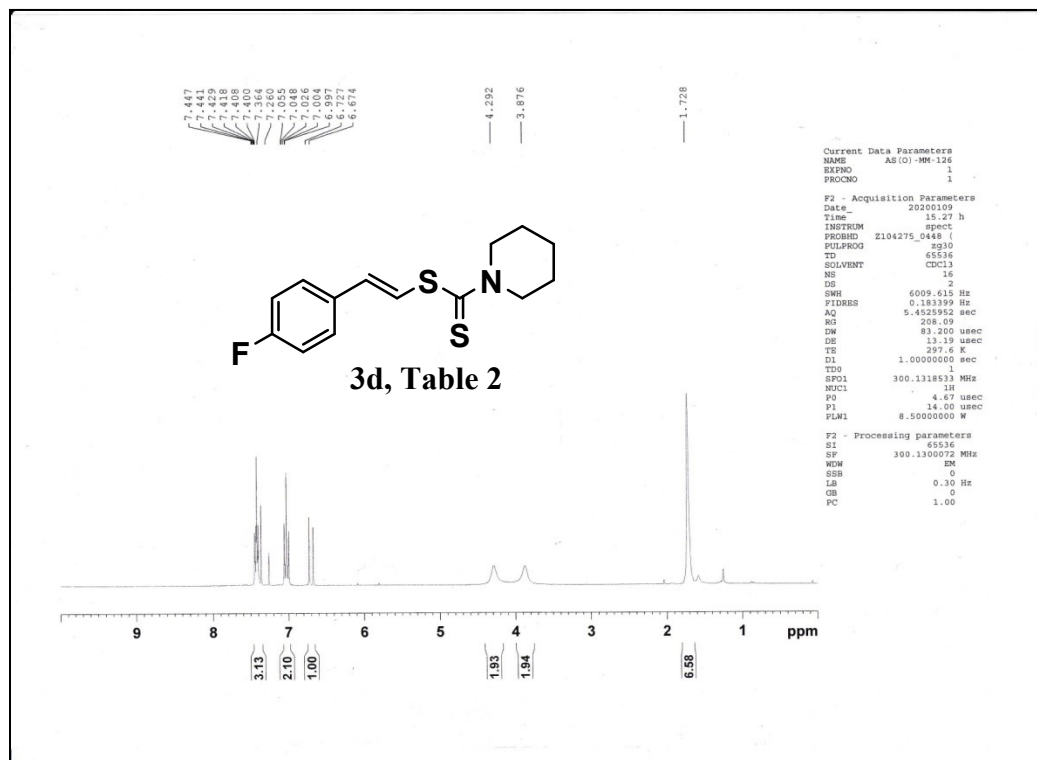
2.¹H NMR (300 MHz, CDCl₃) and ¹³C NMR(75 MHz, CDCl₃) spectrum of 3b



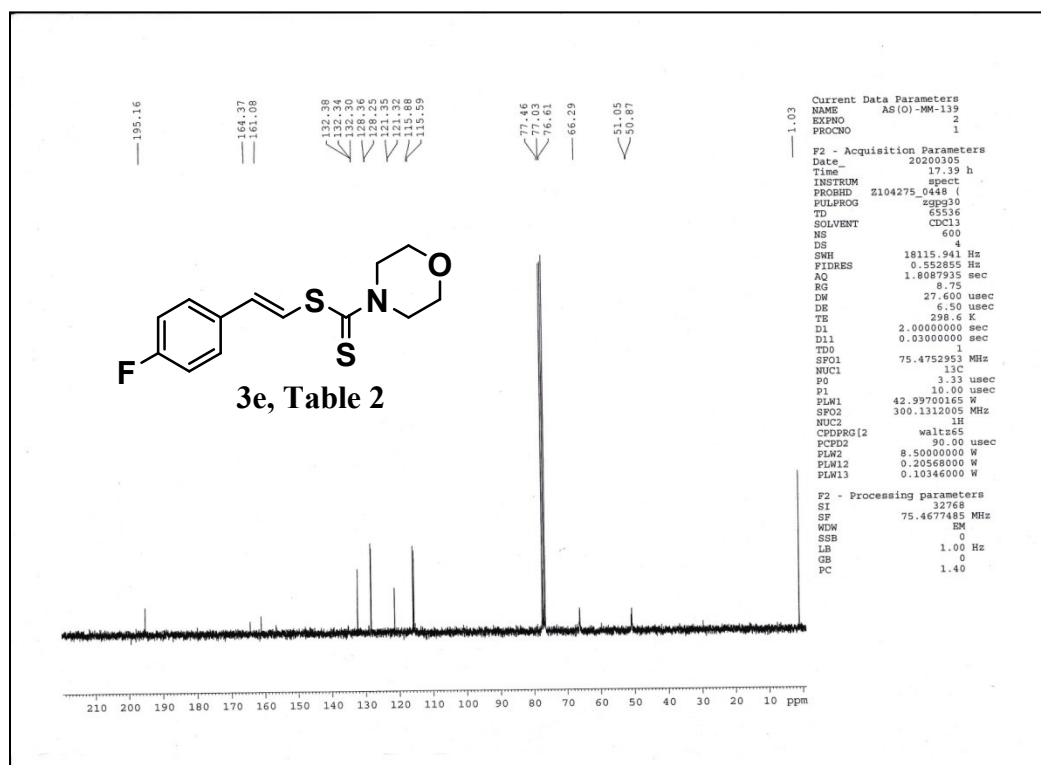
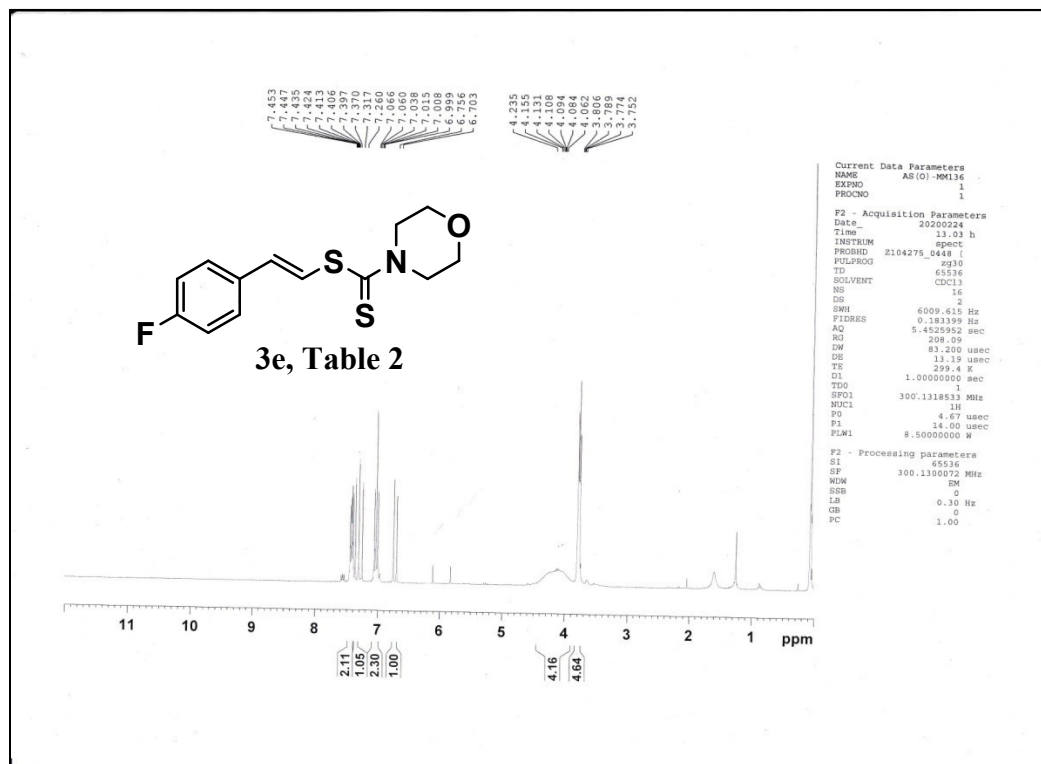
3. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3c



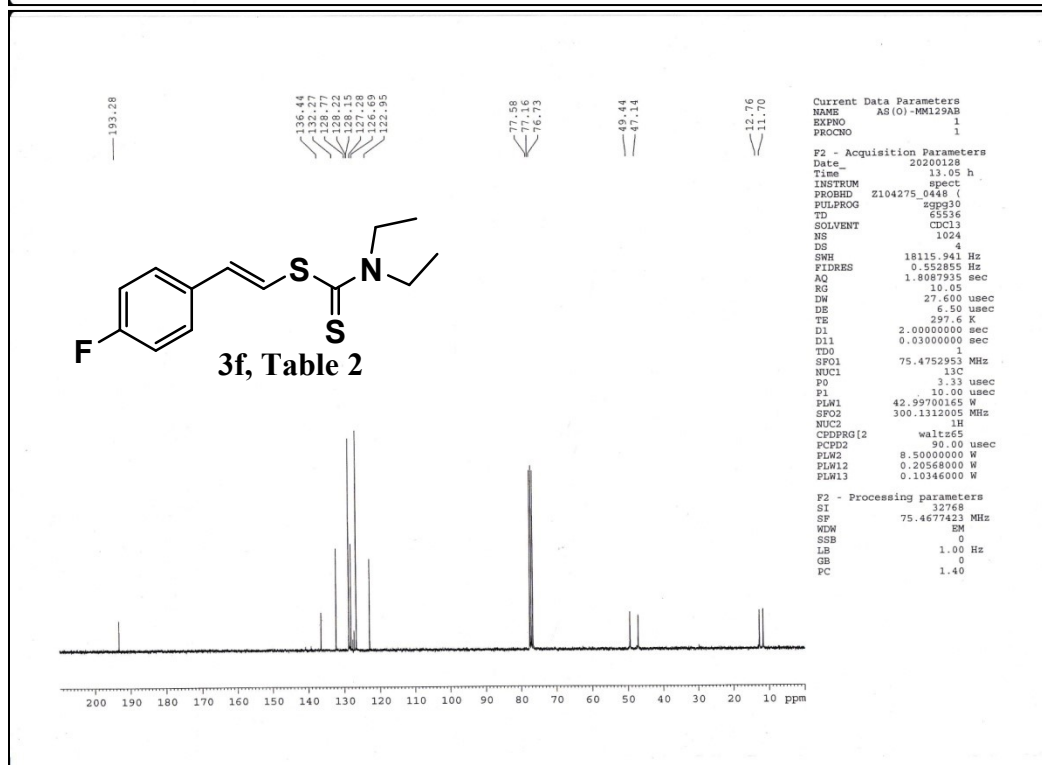
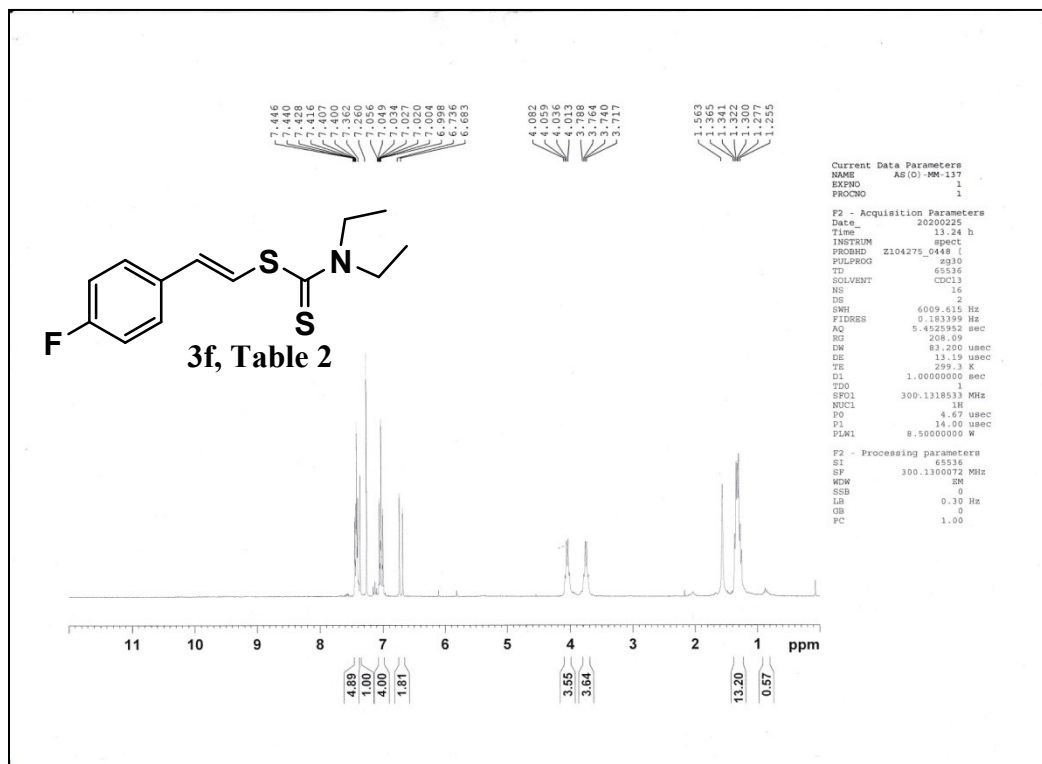
4. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3d



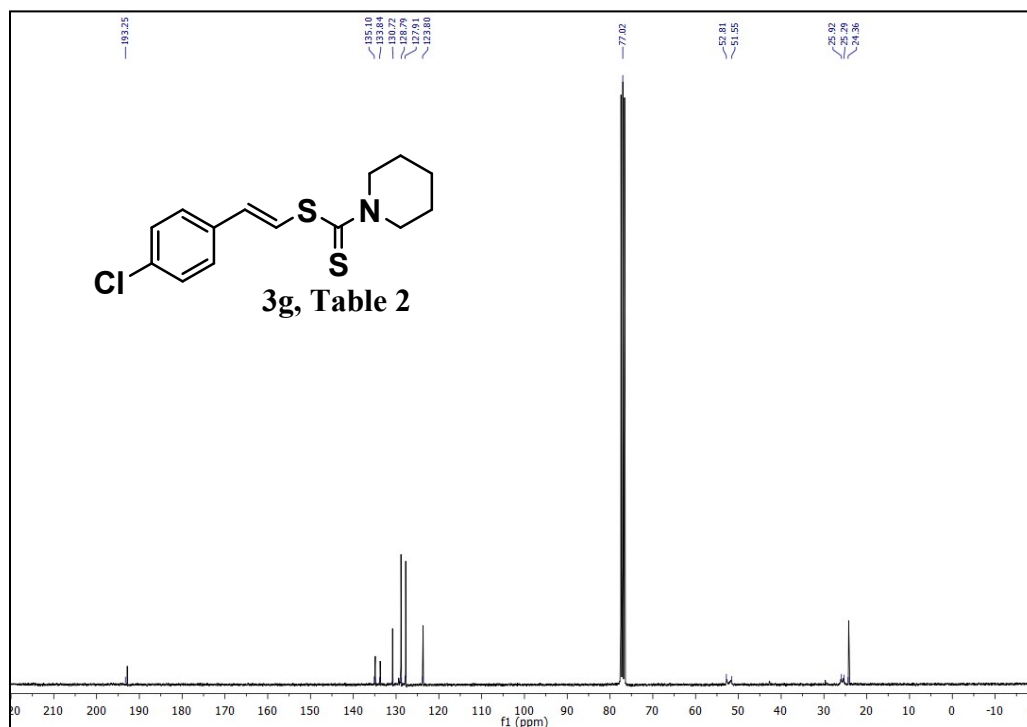
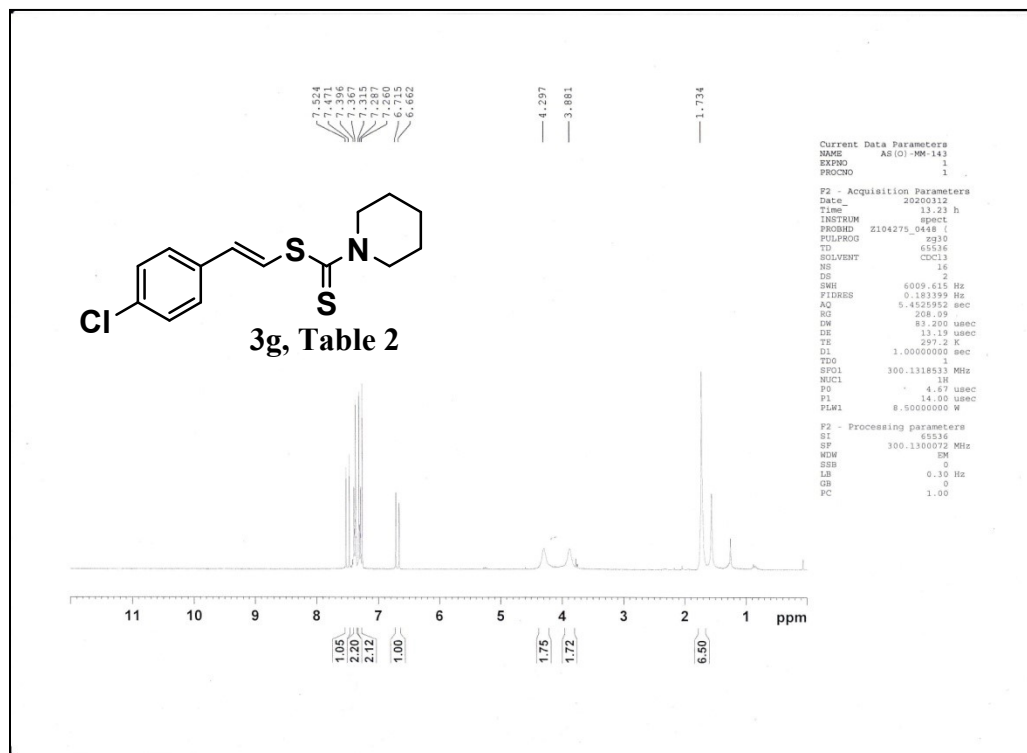
5.¹H NMR (300 MHz, CDCl₃) and ¹³C NMR(75 MHz, CDCl₃) spectrum of 3e



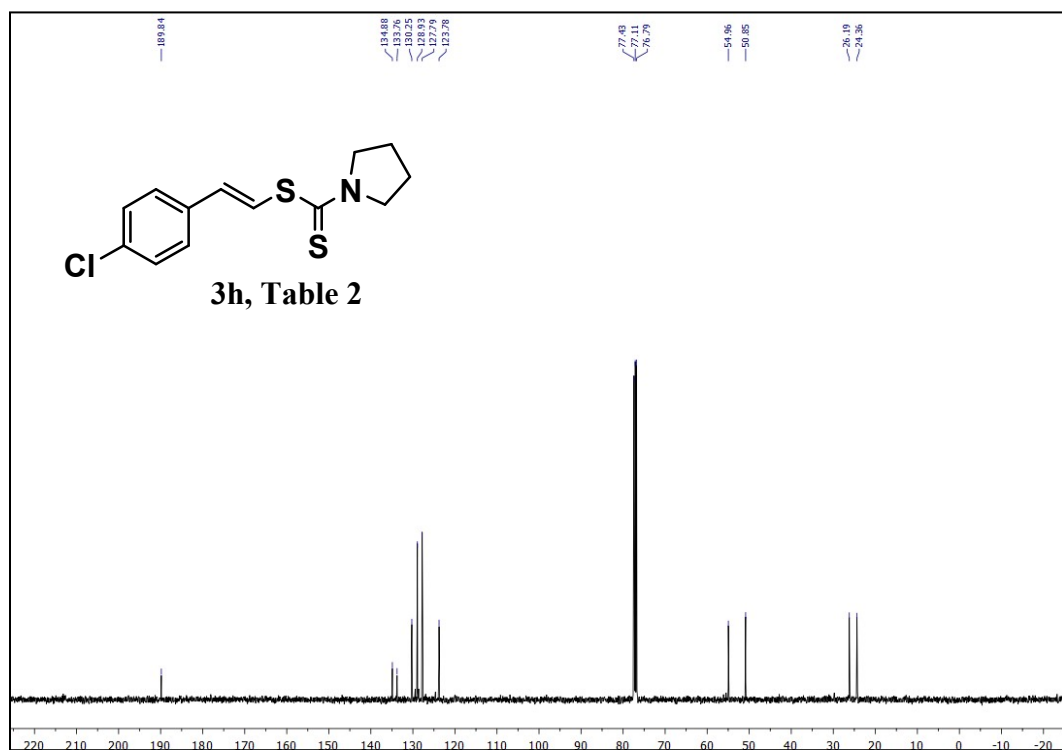
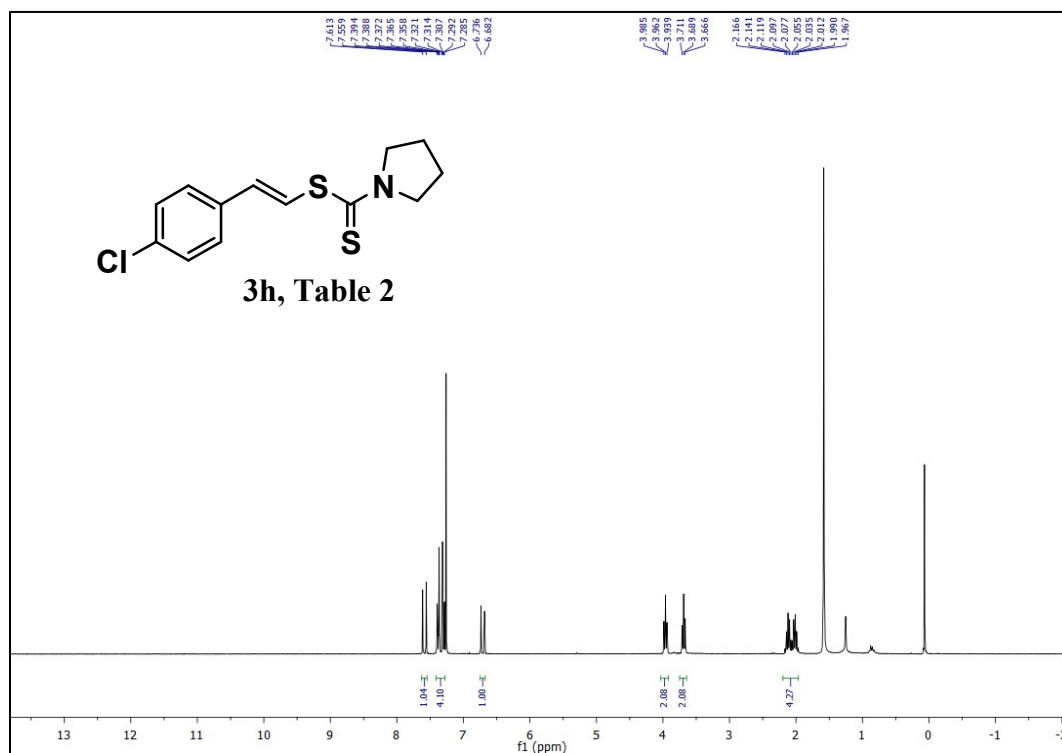
6. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3f



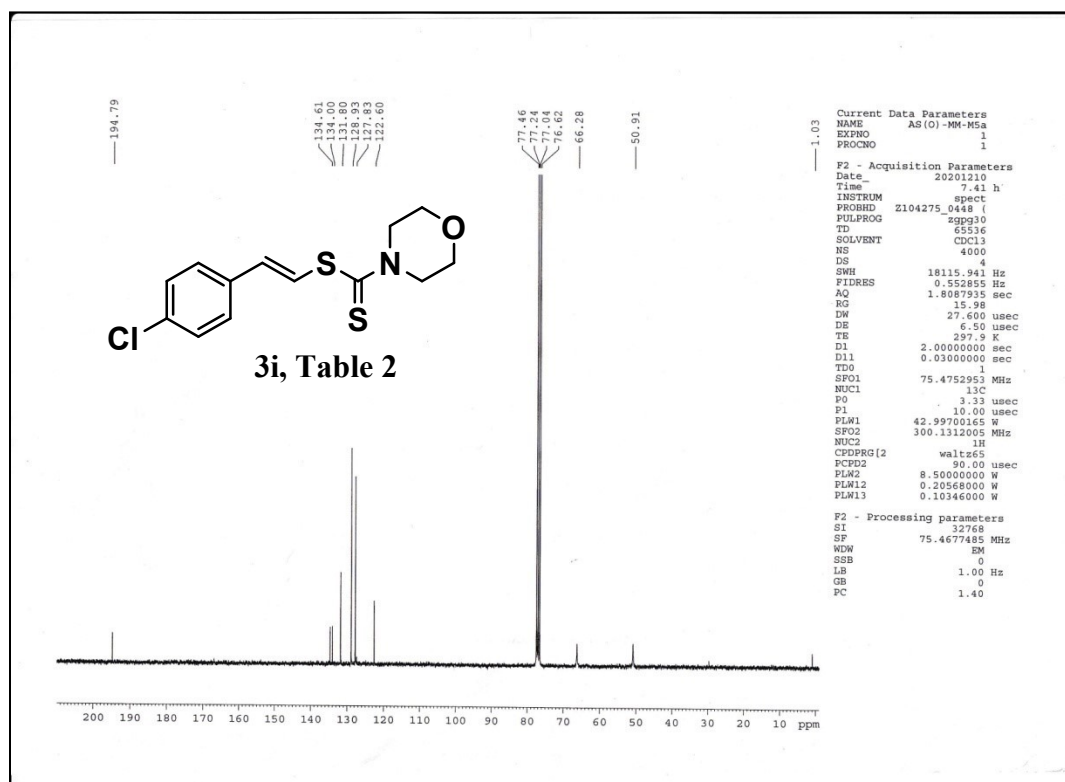
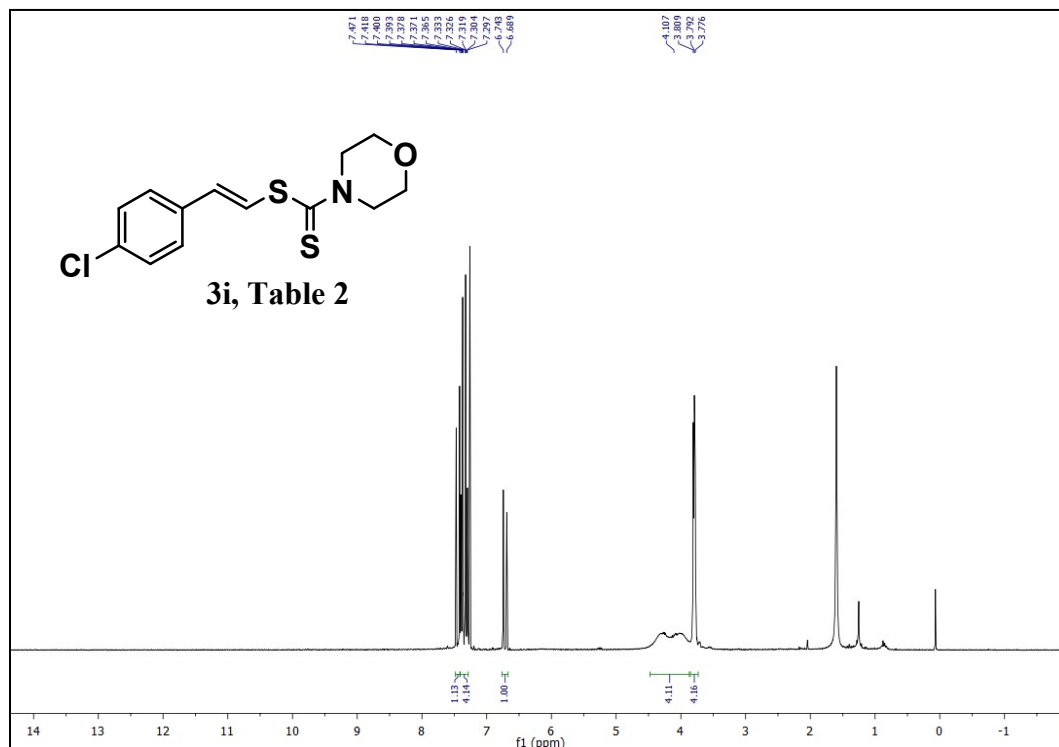
7.¹H NMR (300 MHz, CDCl₃) and ¹³C NMR(75 MHz, CDCl₃) spectrum of 3g



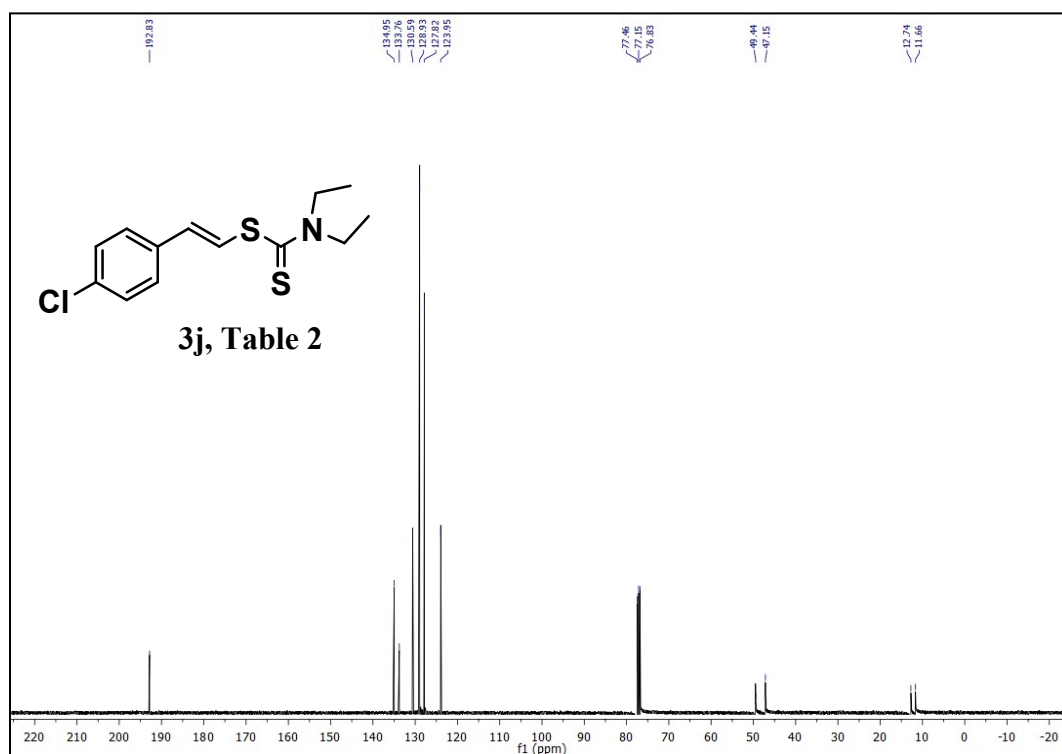
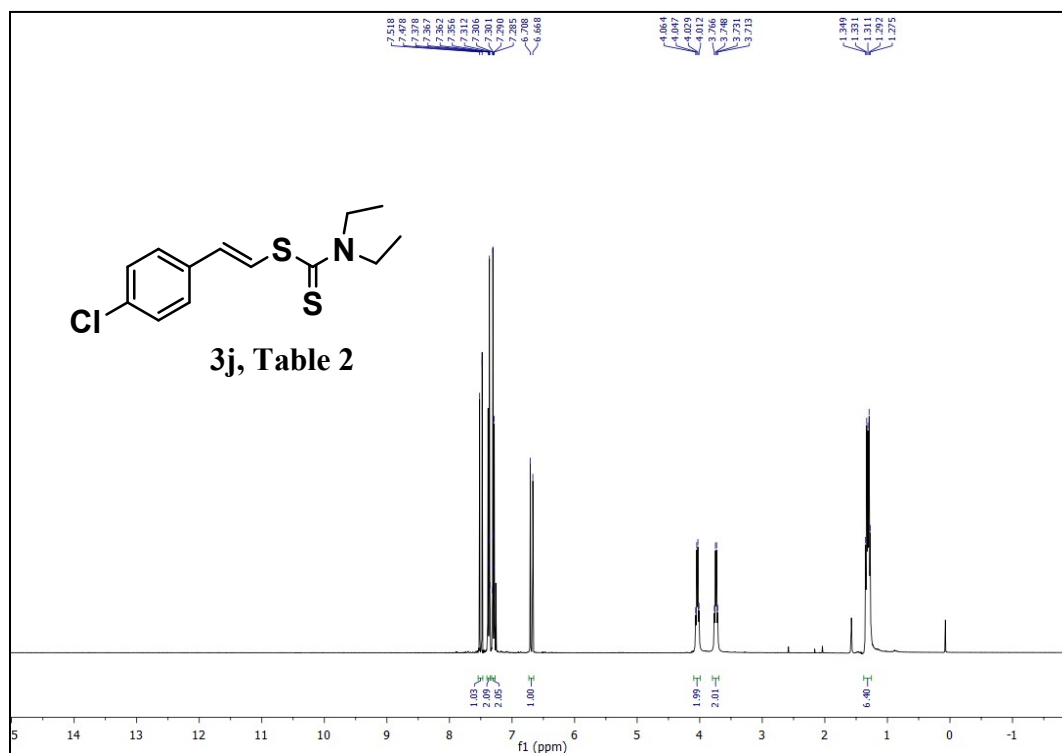
8. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3h



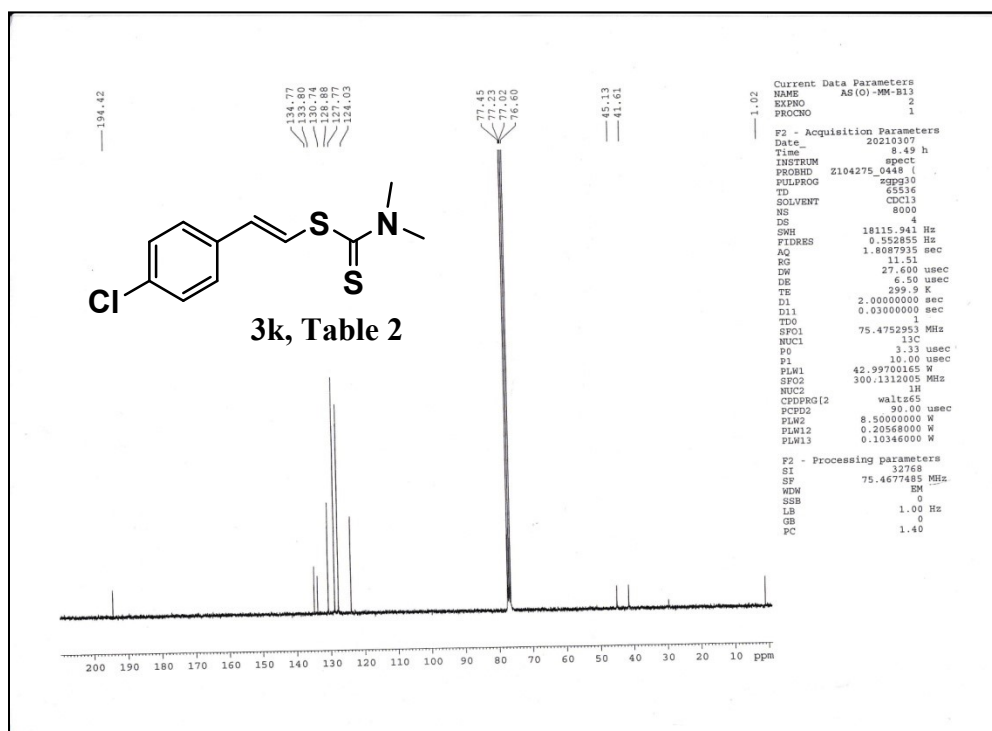
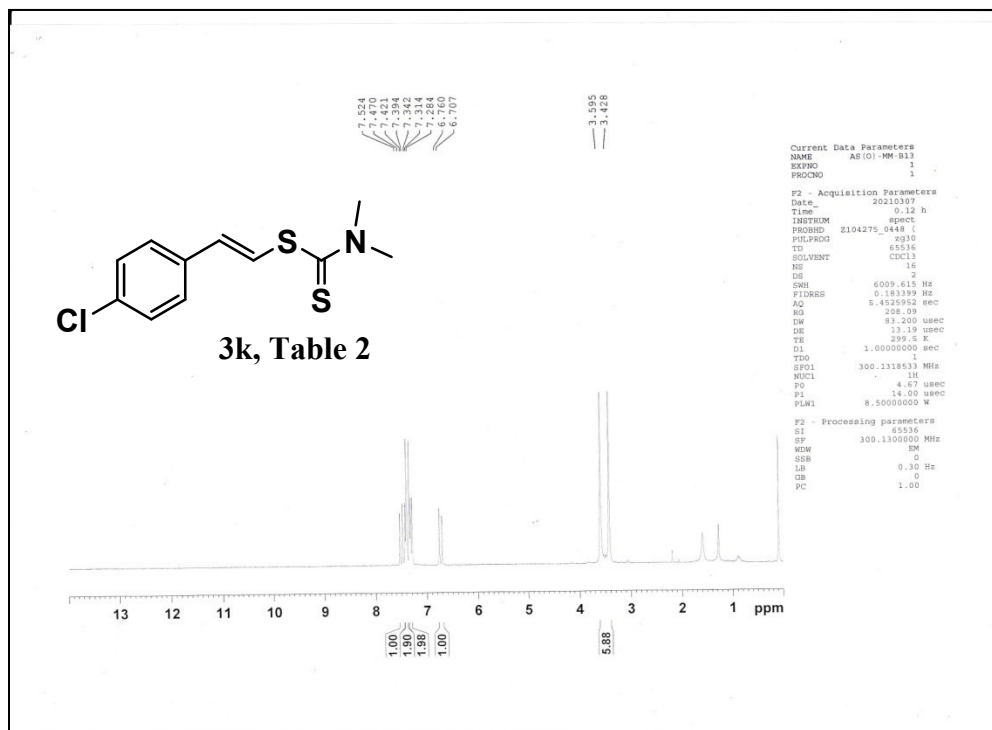
9.¹H NMR (300 MHz, CDCl₃) and ¹³C NMR(75 MHz, CDCl₃) spectrum of 3i



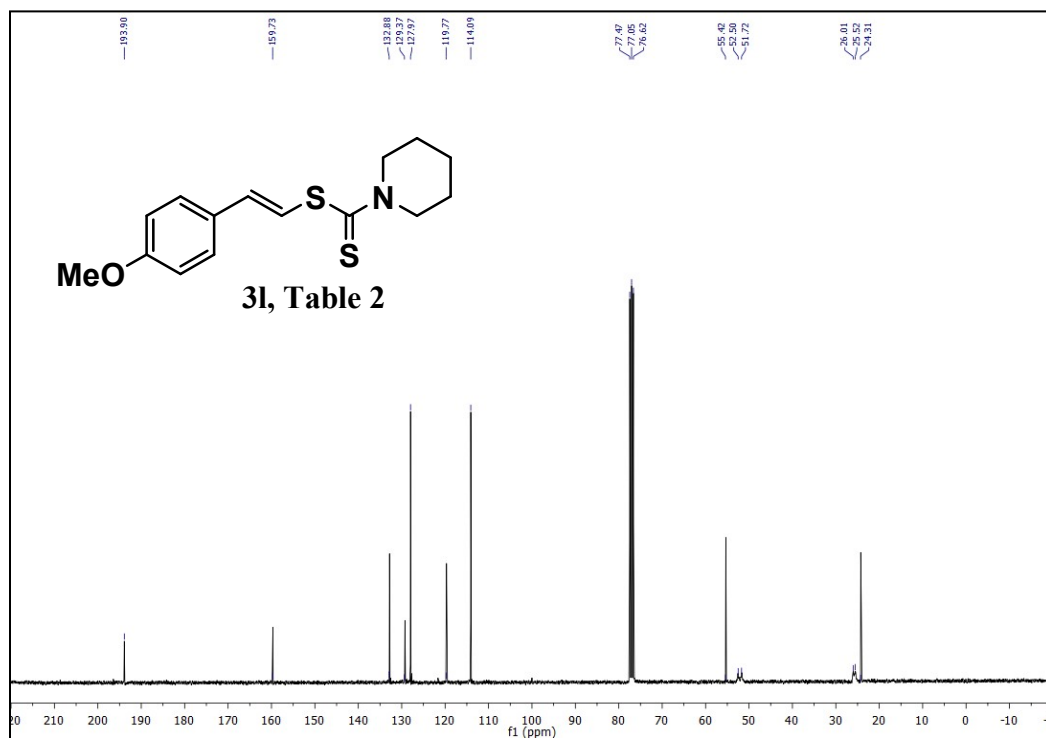
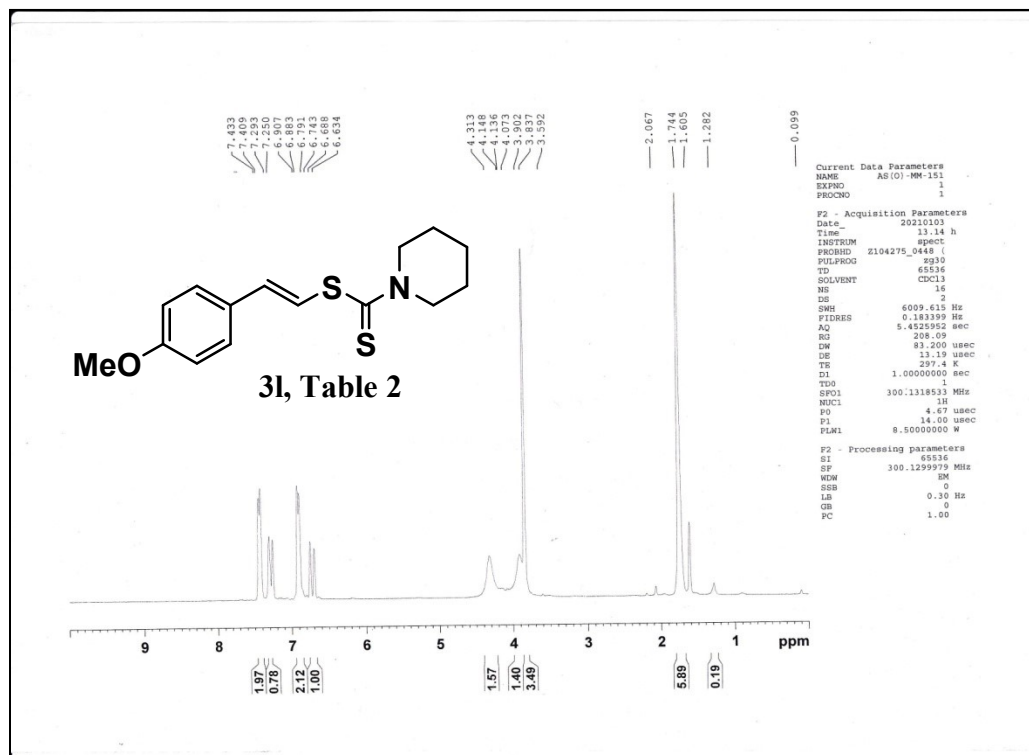
10. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3j



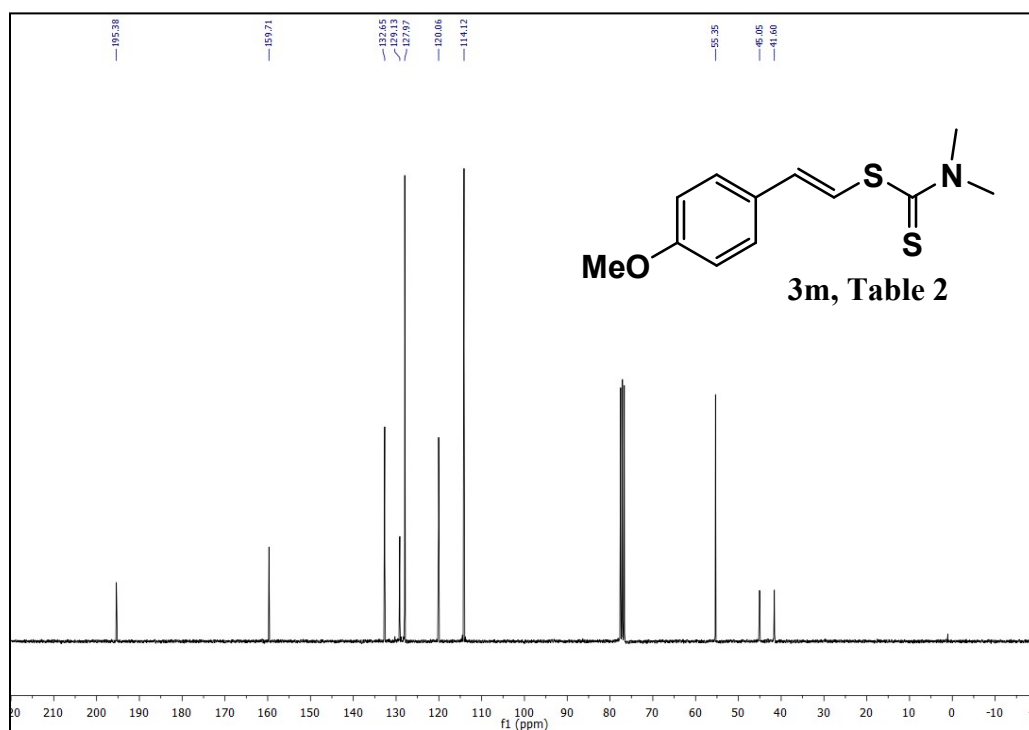
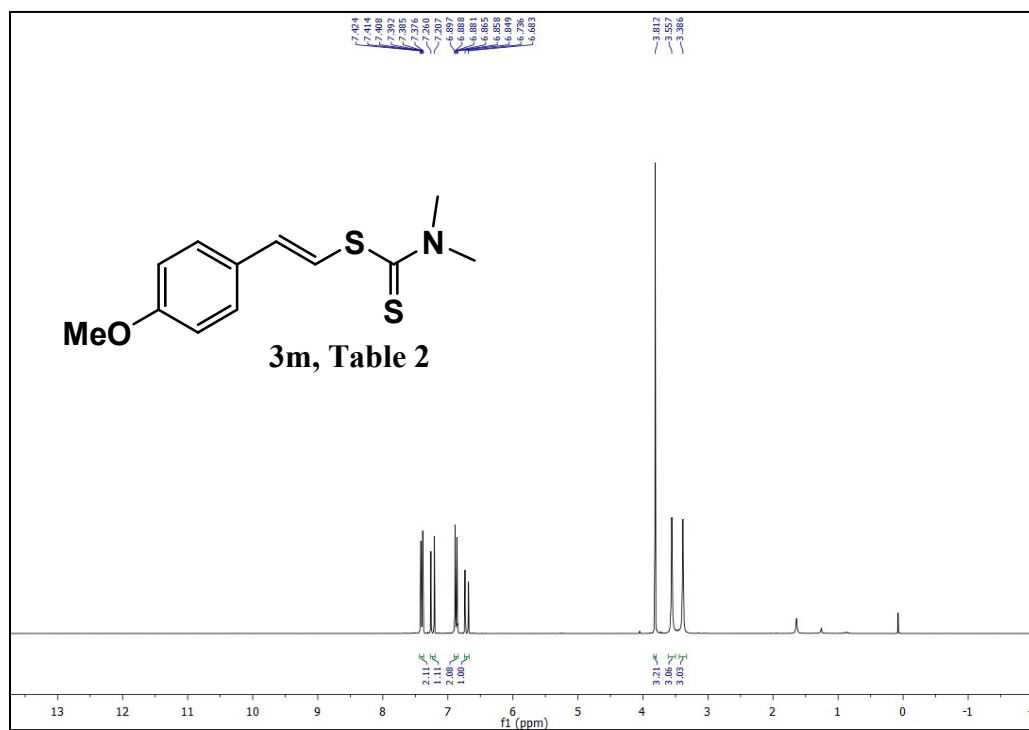
11. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR(75 MHz, CDCl_3) spectrum of 3k



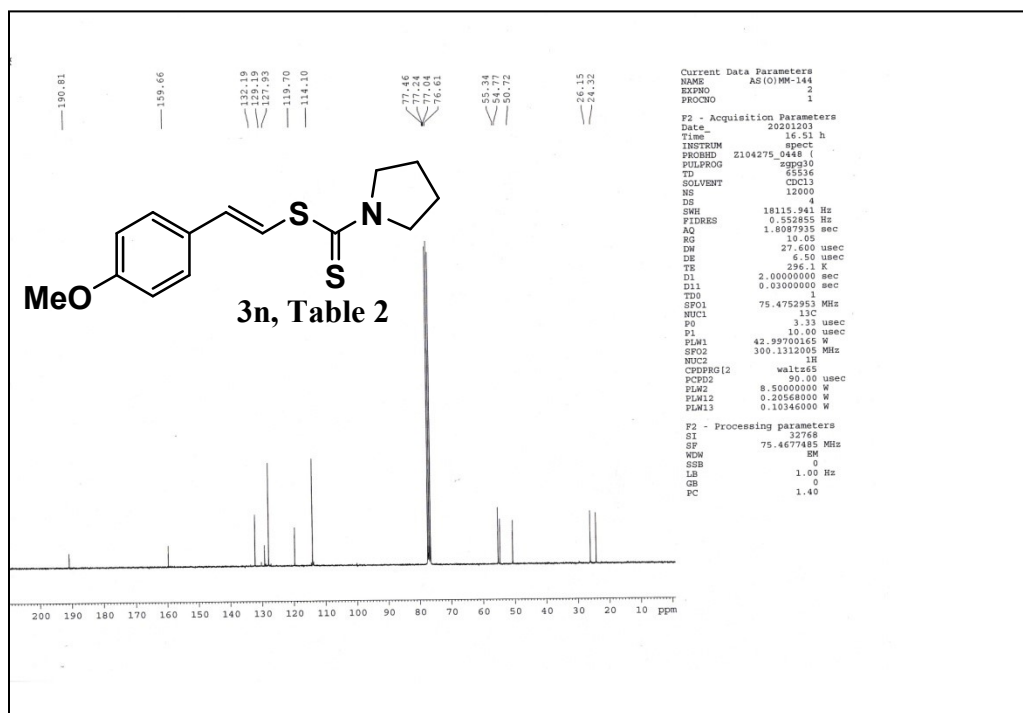
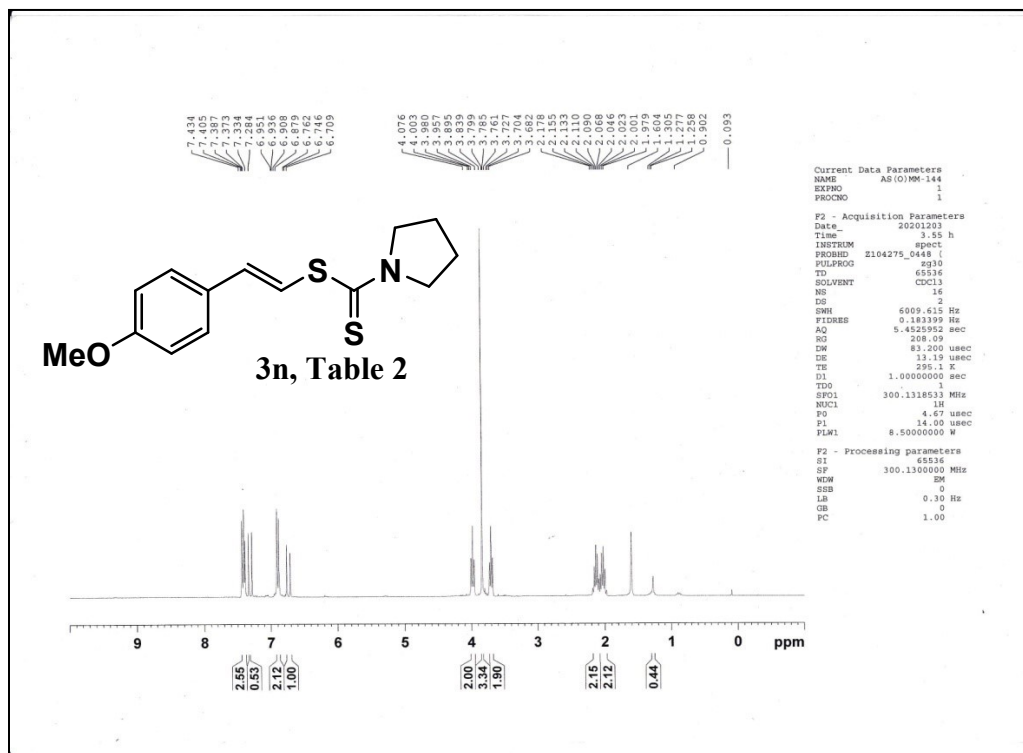
12. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3l



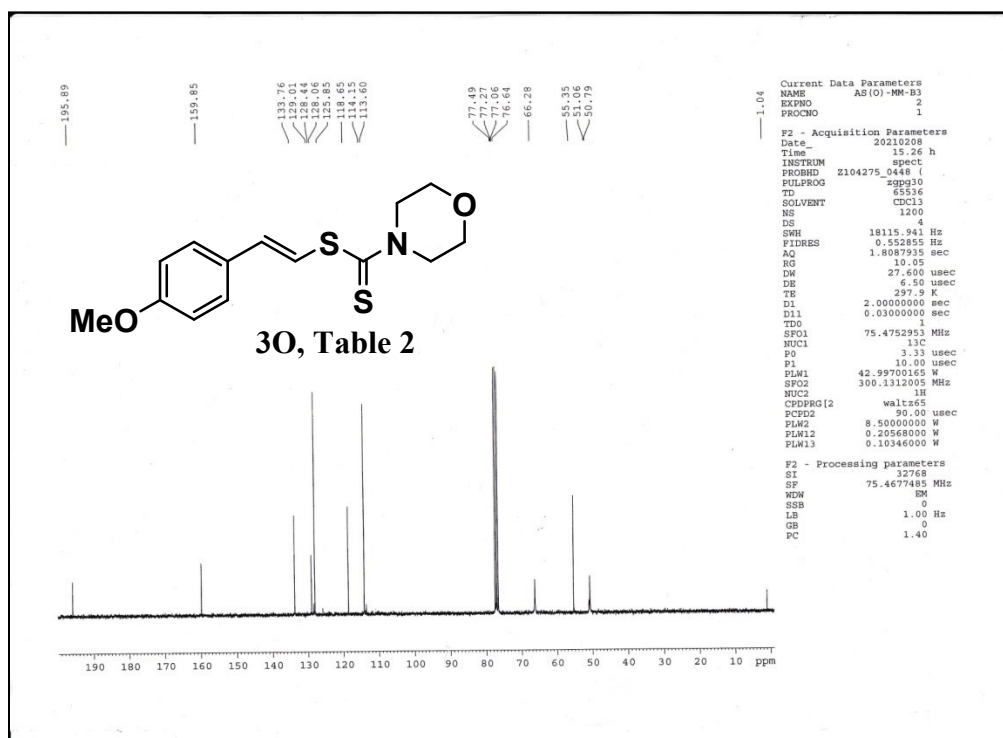
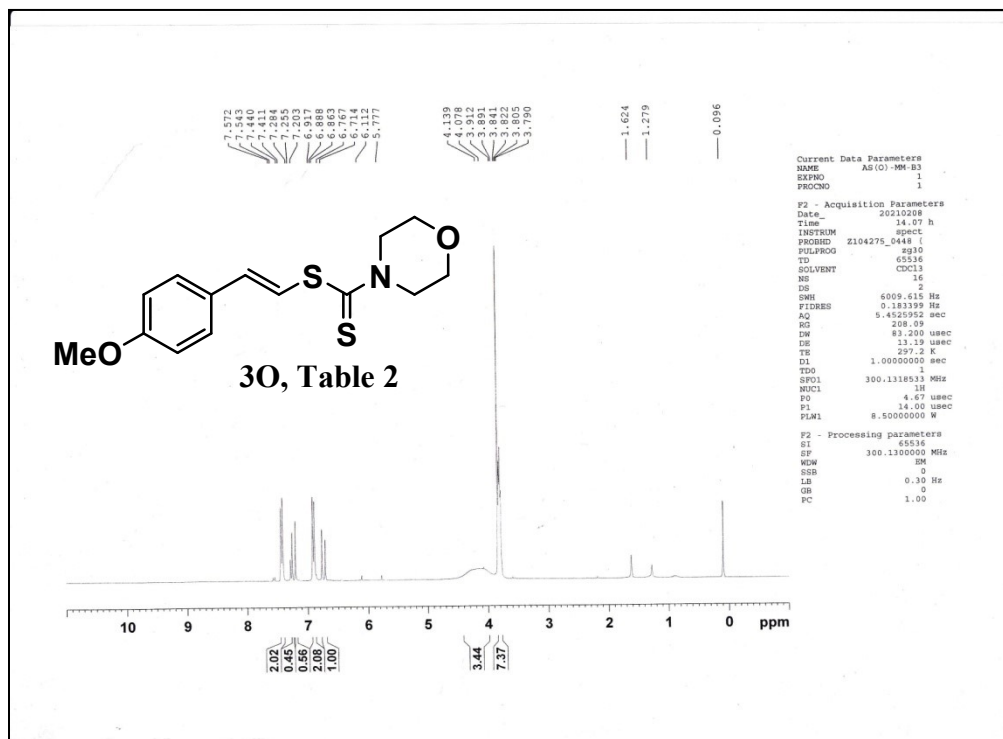
13.¹H NMR (300 MHz, CDCl₃) and ¹³C NMR(75 MHz, CDCl₃) spectrum of 3m



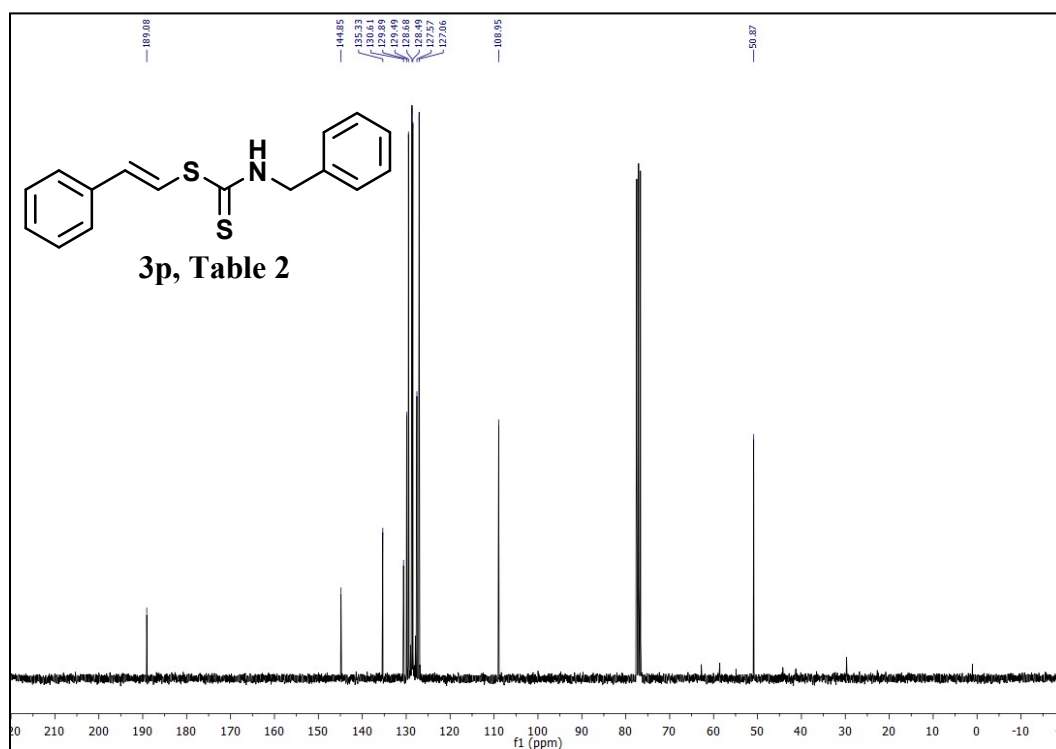
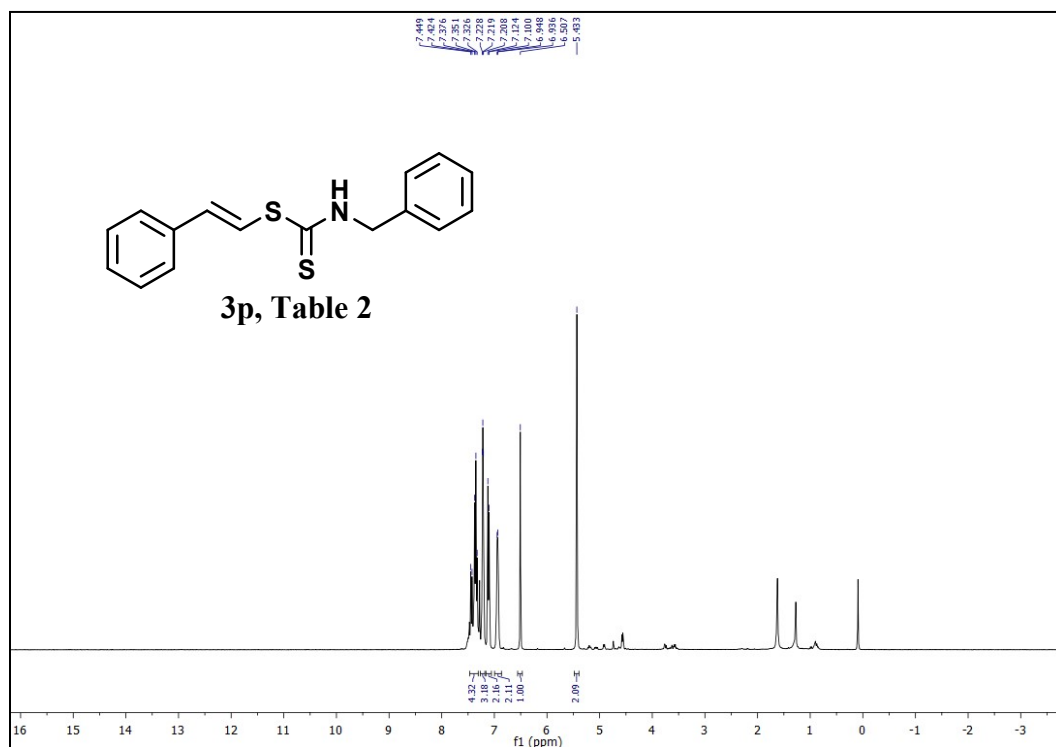
14. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3n



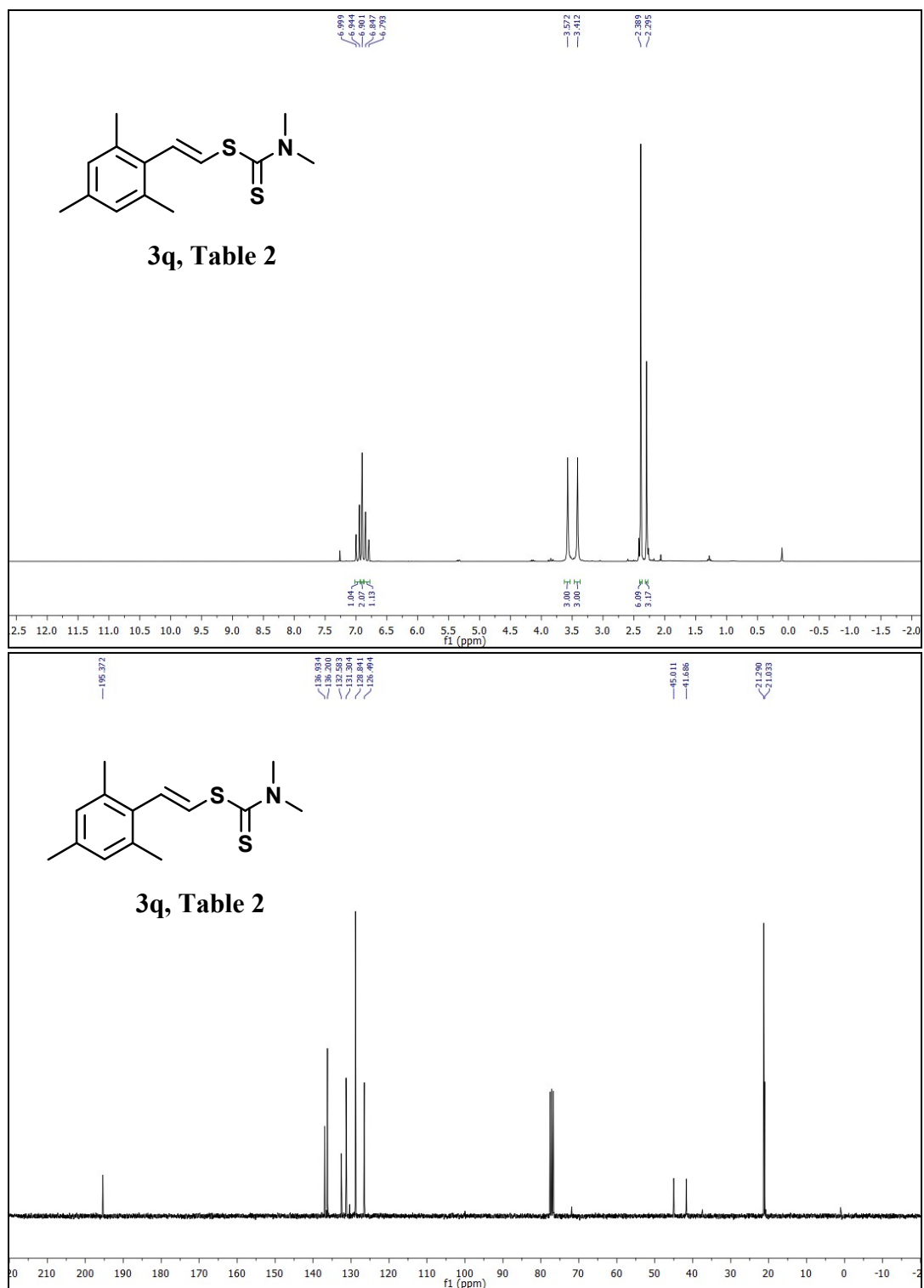
15. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 30



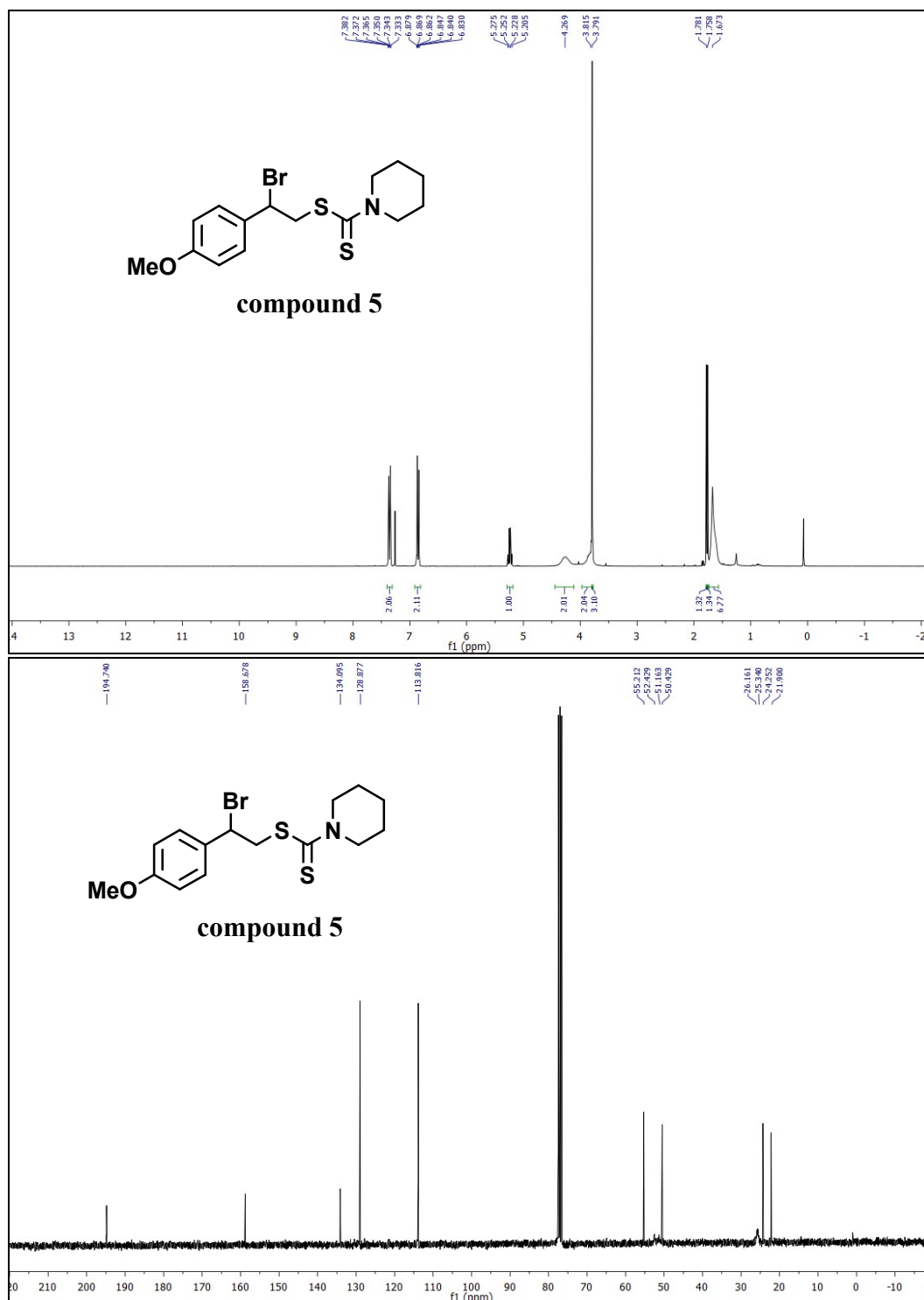
16. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3p

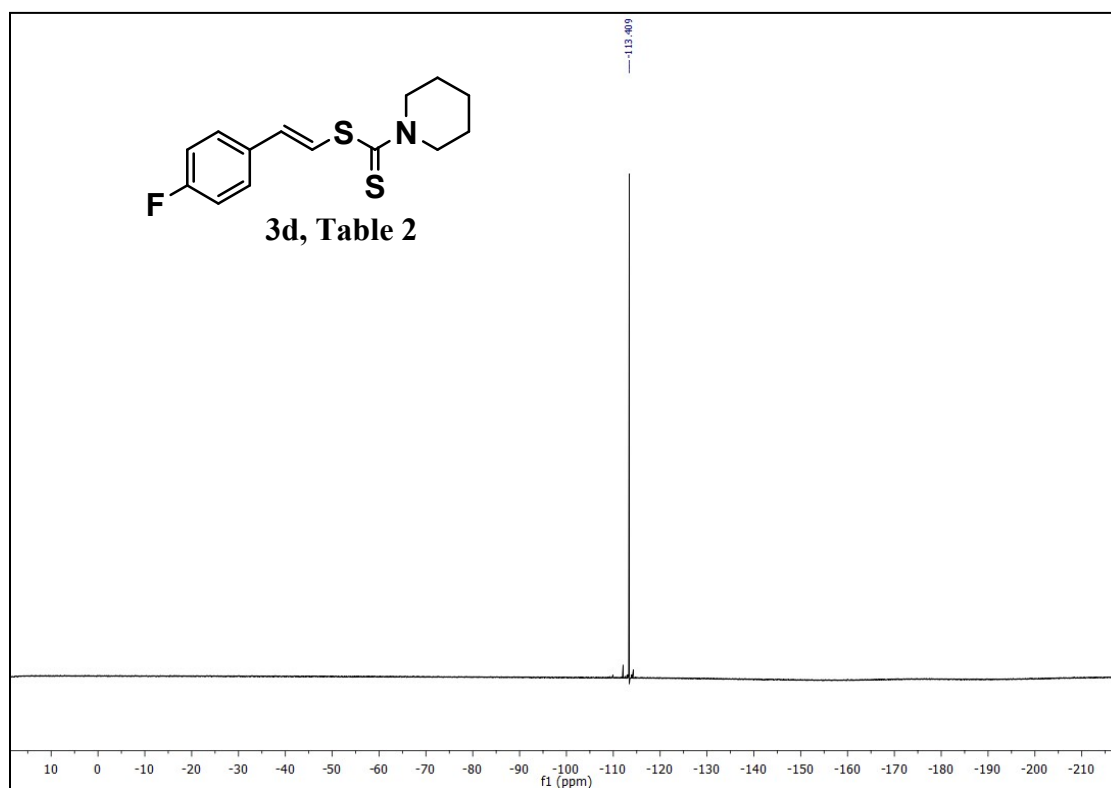


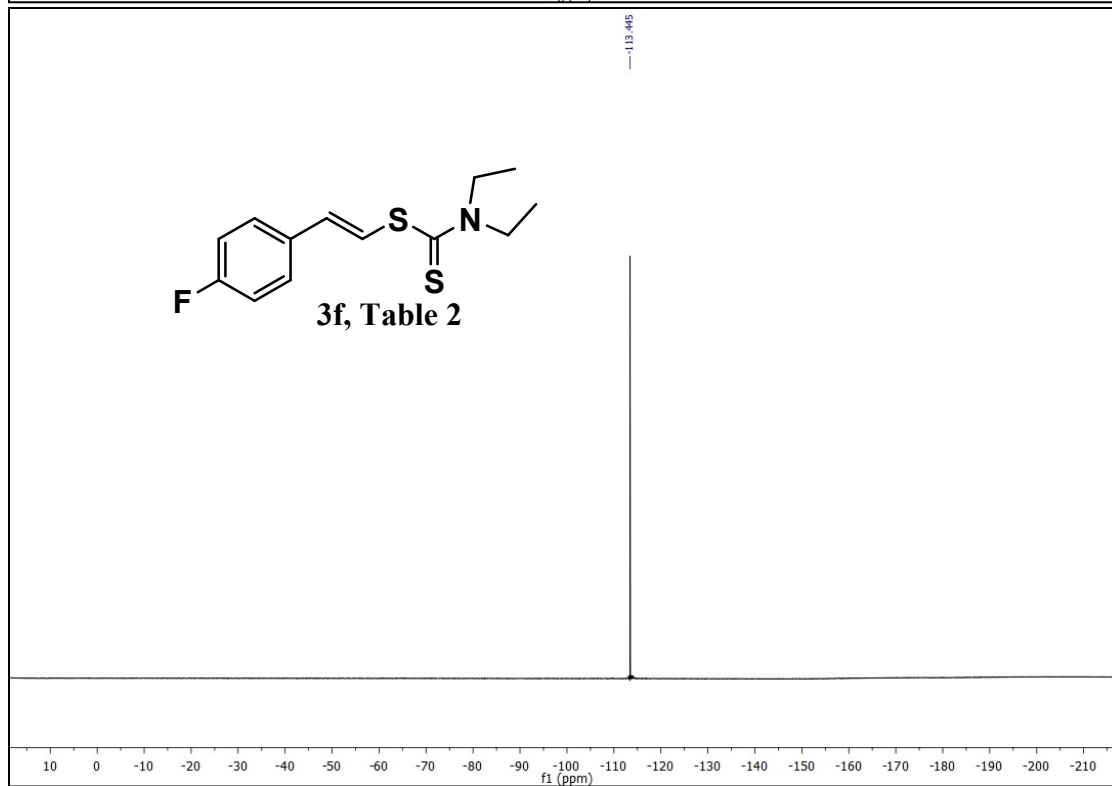
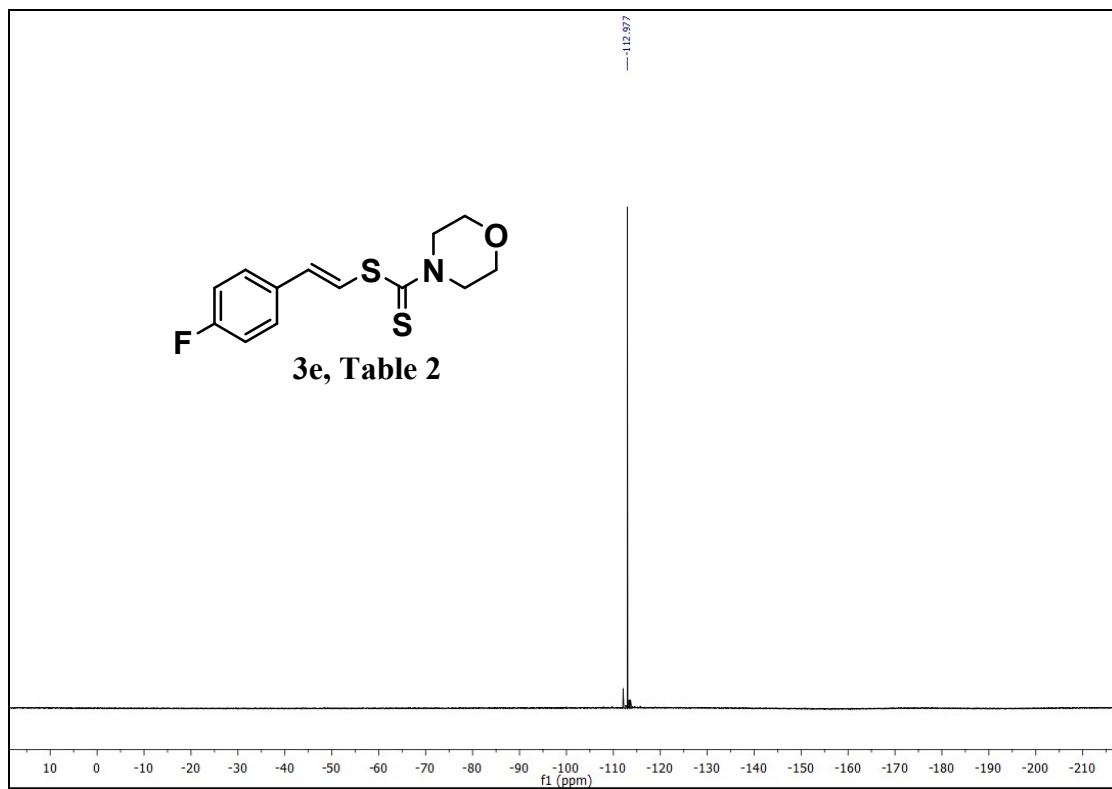
17. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3q



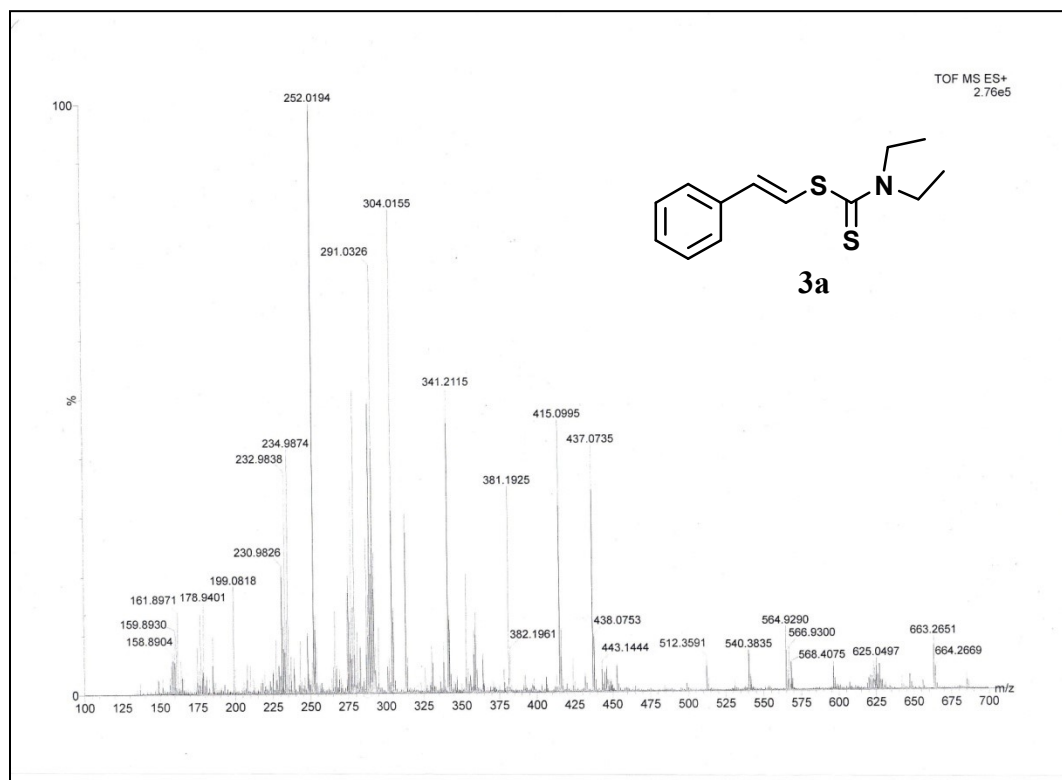
19. ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectrum of compound 5

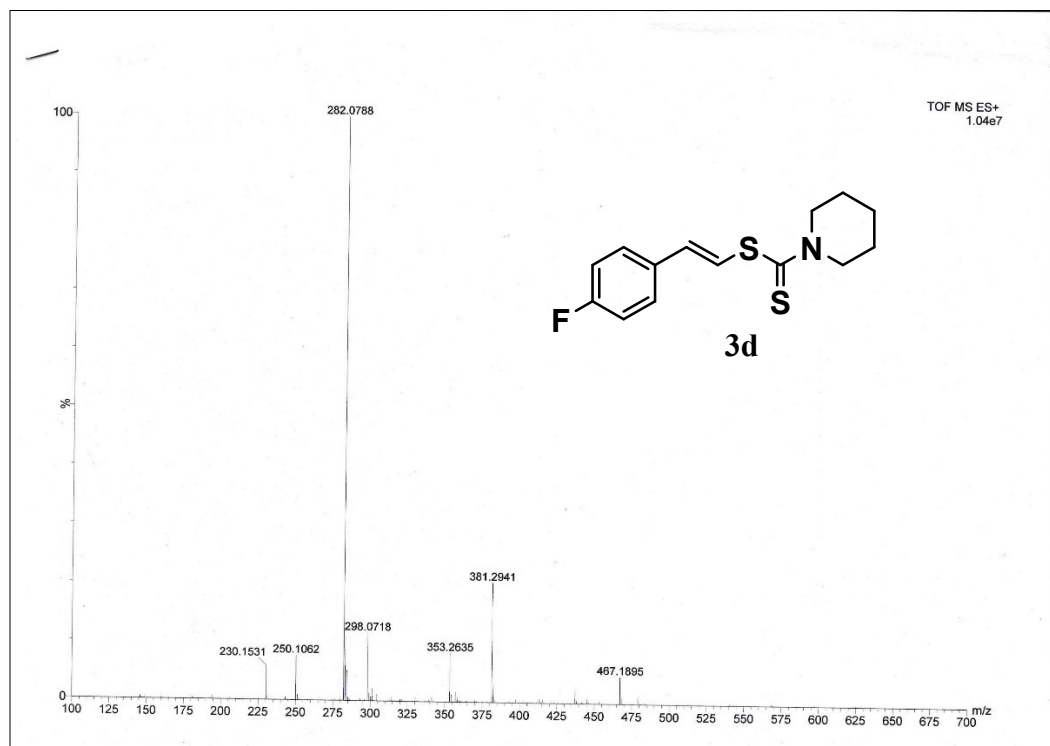
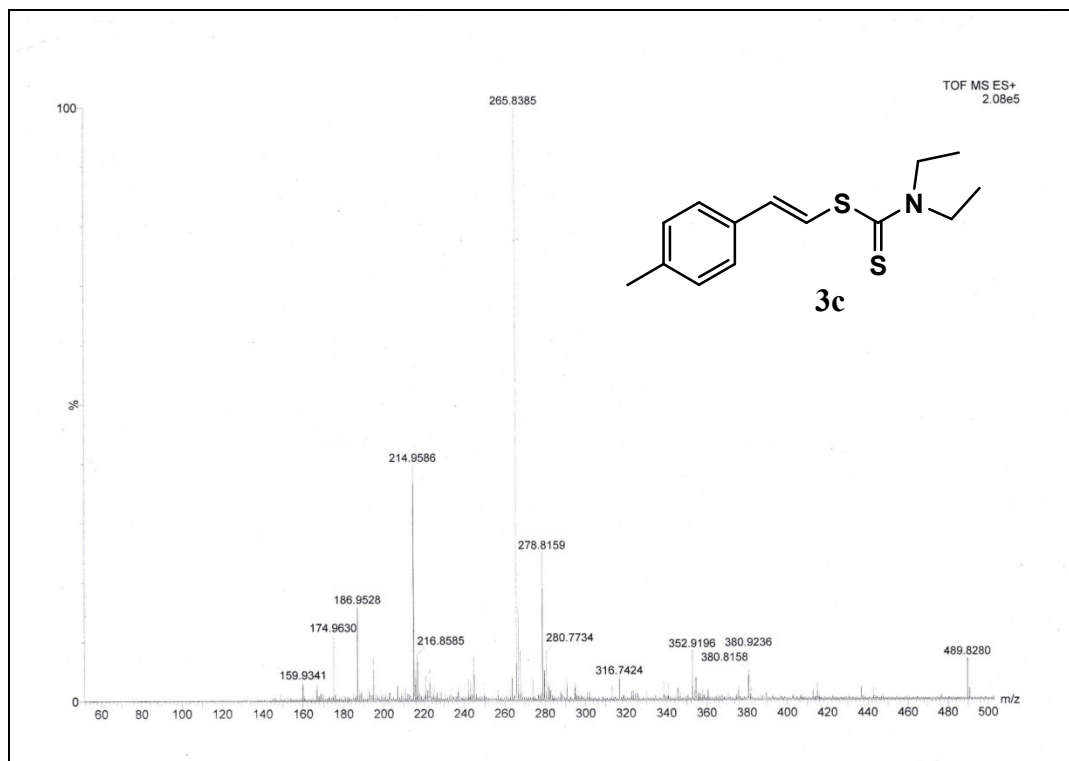


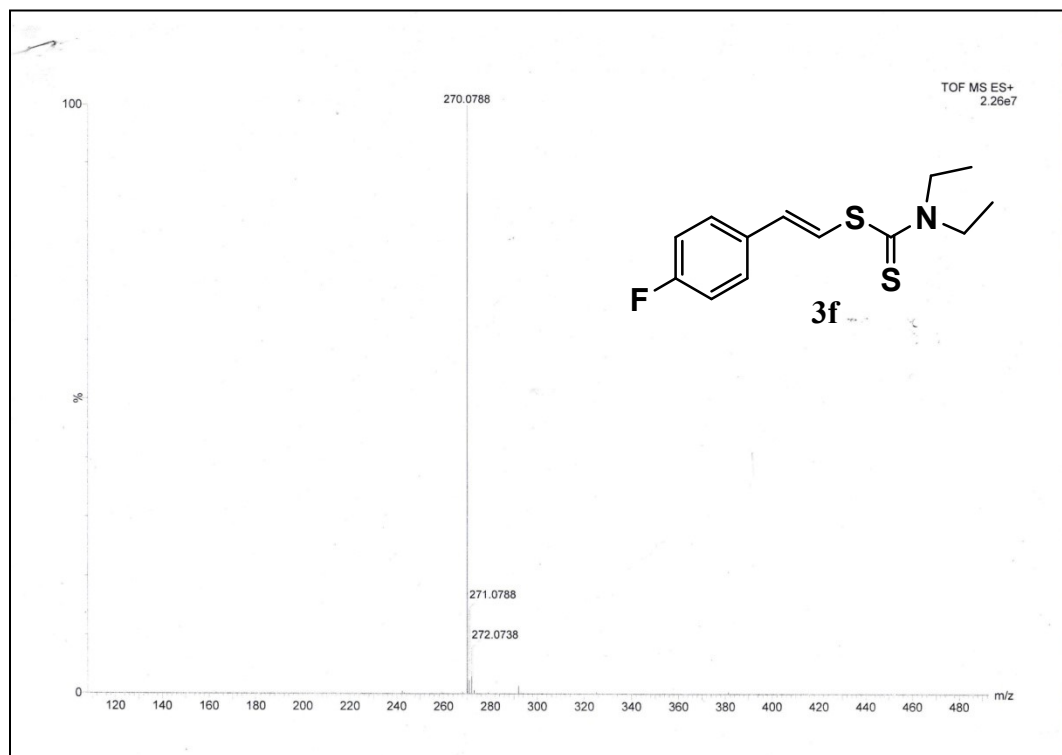
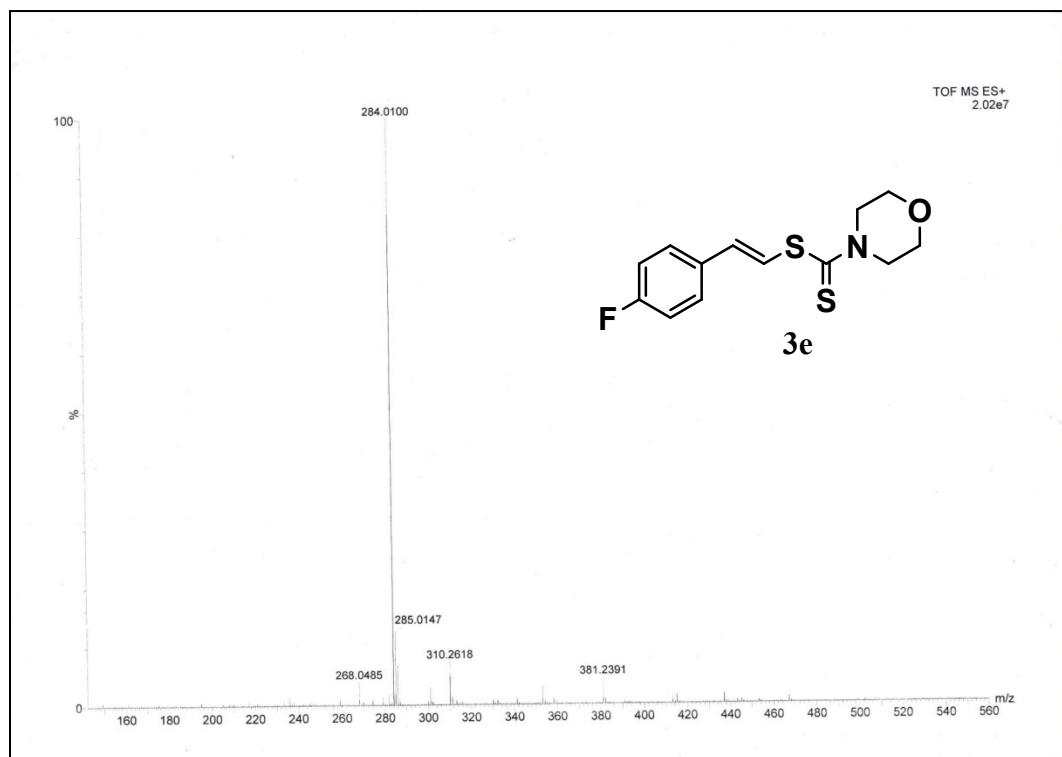
E. ^{19}F NMR spectra of fluorinated products

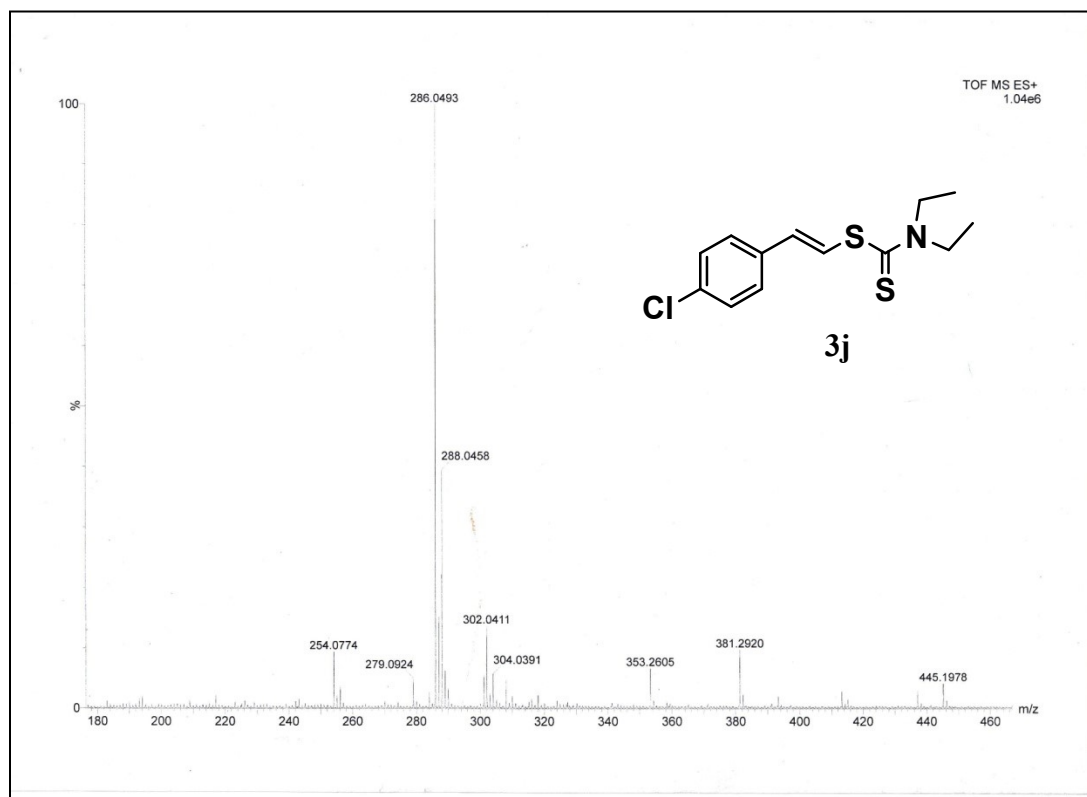
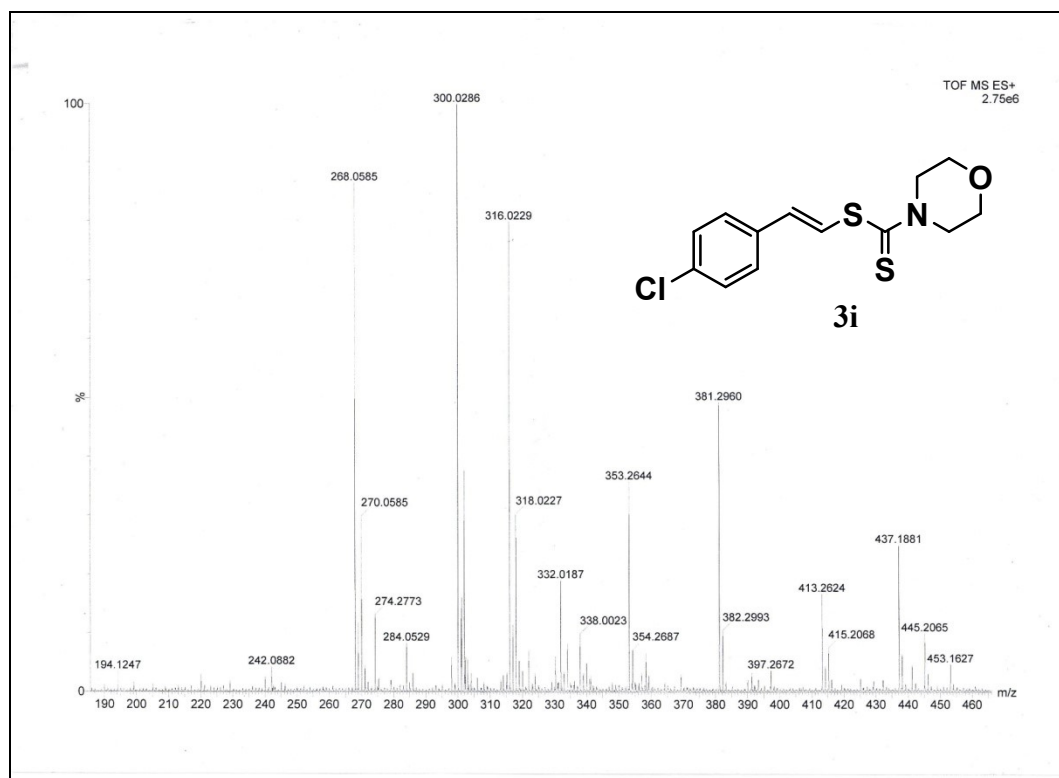


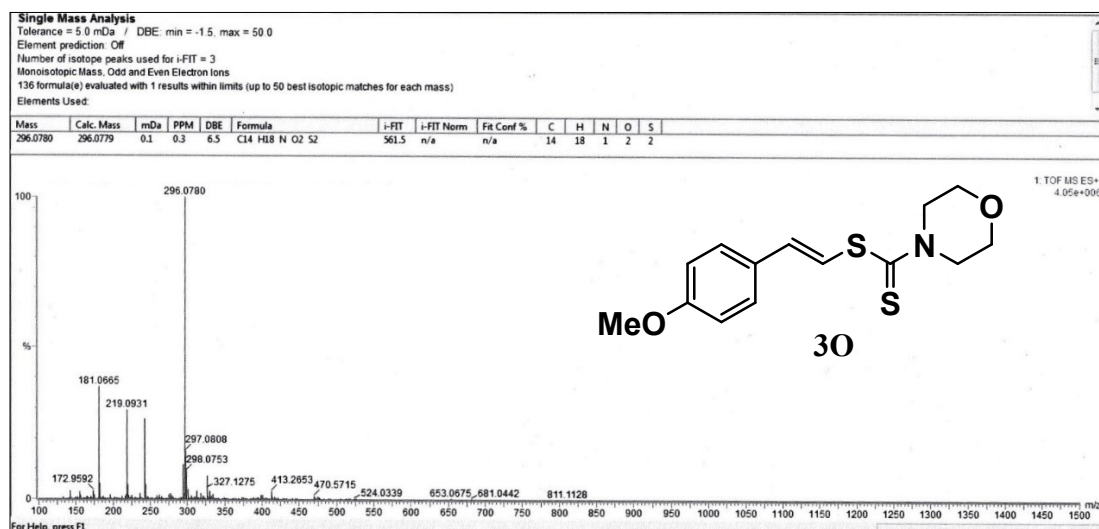
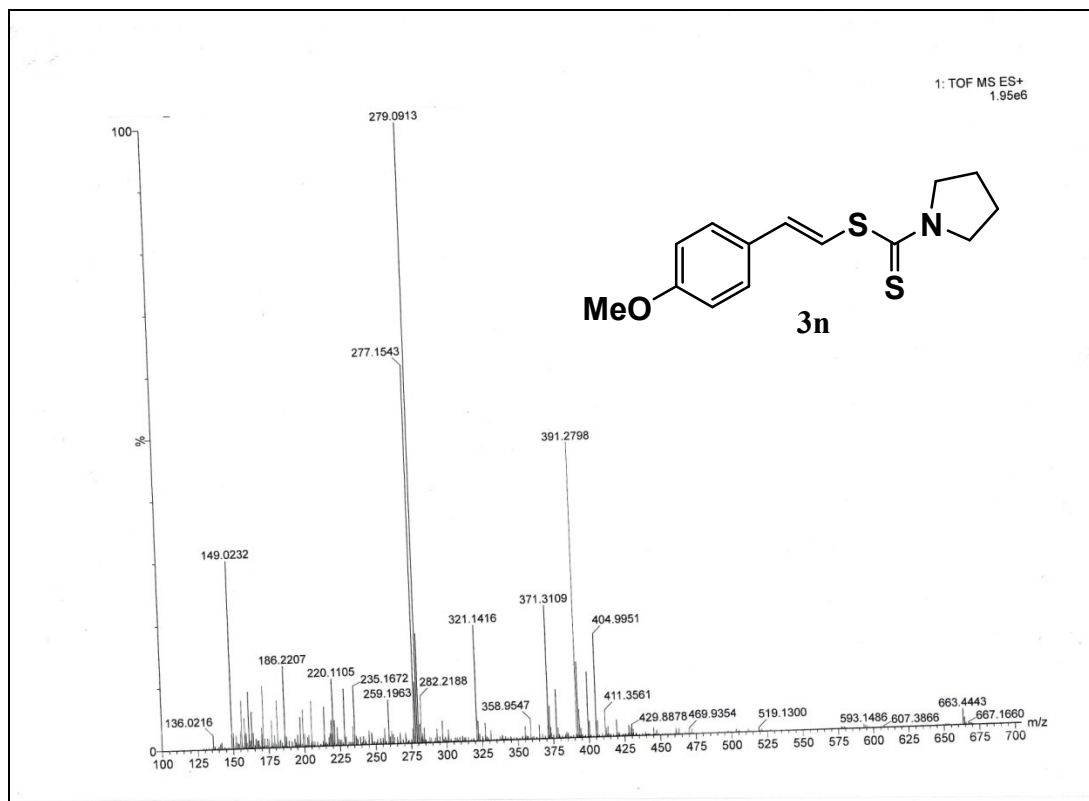
Mass spectra of products(3a, 3c, 3d,3e, 3f, 3i, 3j, 3n, 3o, 3p,3q)

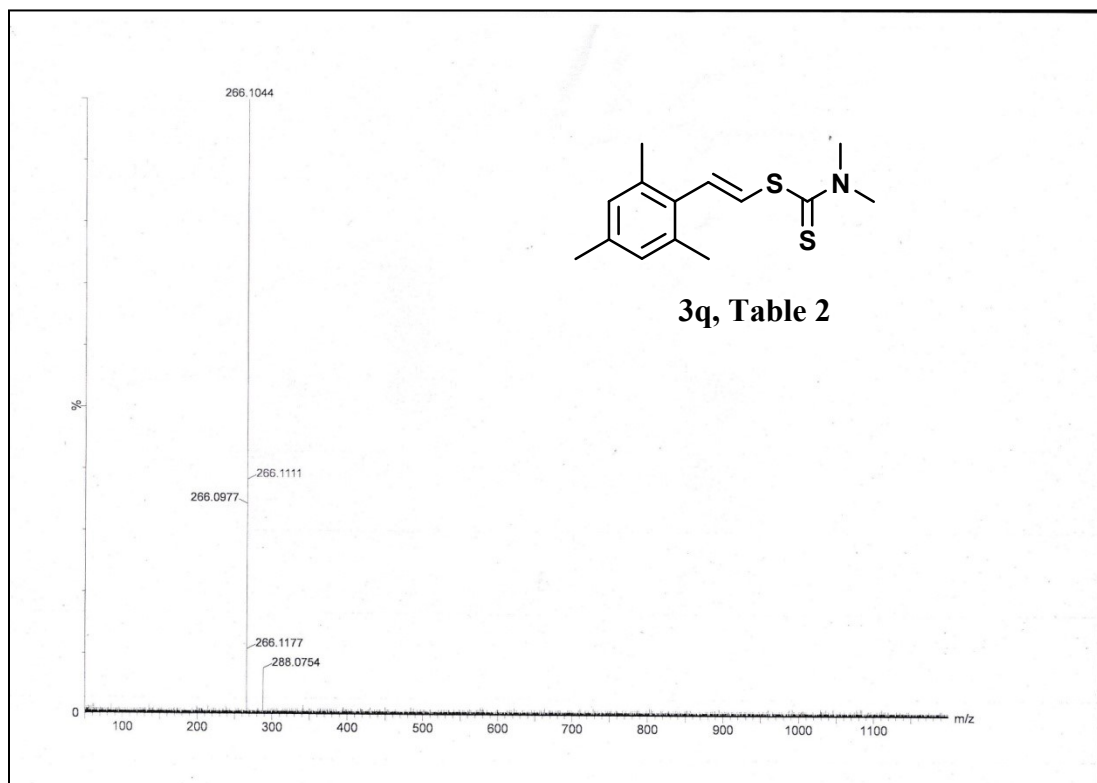
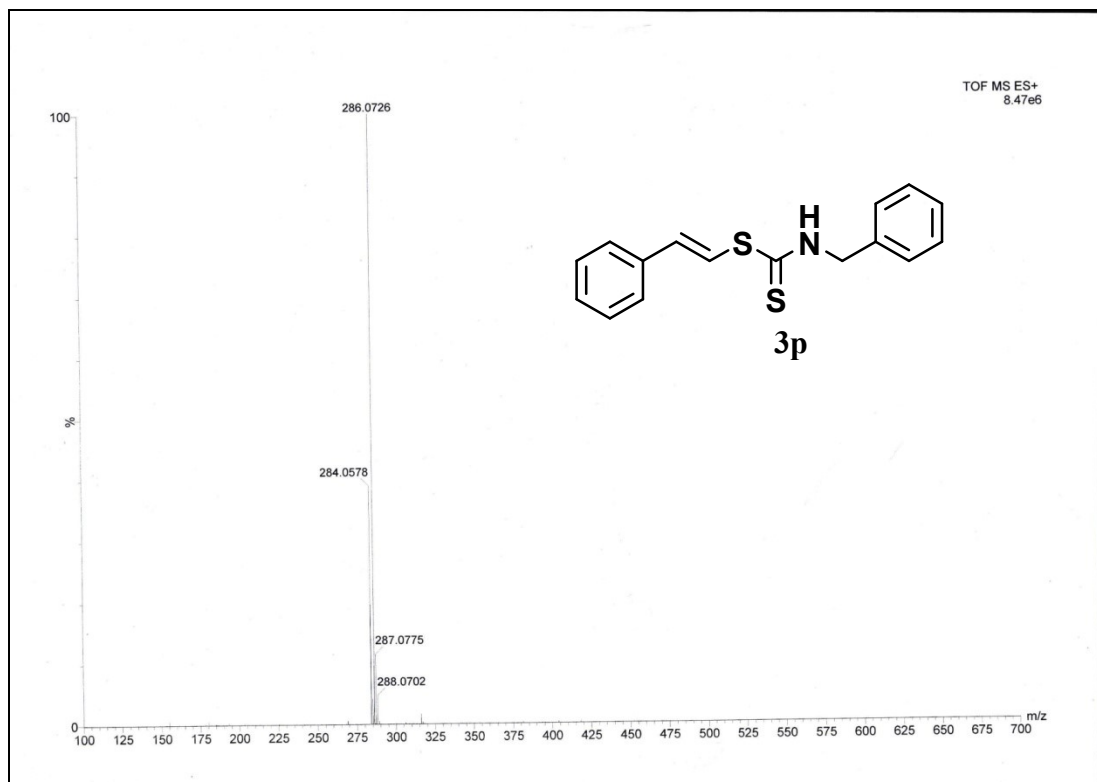












References:

1. S.Bhadra, A.Saha and B. C.Ranu, *Green Chem.*,2008, **10**, 1224–1230.
2. W.Xu, F.Gao and Z. B.Dong, *Eur. J. Org. Chem.*,2018, 821–828.