Supporting Information

Transition metal-free α-Csp3-H oxidative sulfuration of benzyl thiosulfates with anilines to form N-aryl thioamides

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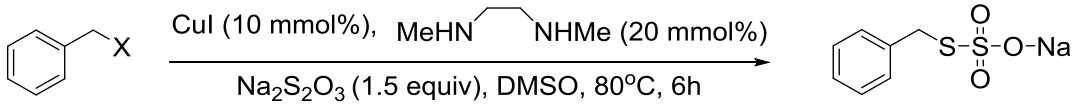
1. General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded in $CDCl_3$ or DMSO-d6 at room temperature on the Bruker DPX-400 spectrometer (400 MHz, 100 MHz and 377 MHz). The chemical-shifts scale is based on internal TMS. For spectra, chemical shifts were reported in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on a MALDI-FTMS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature.

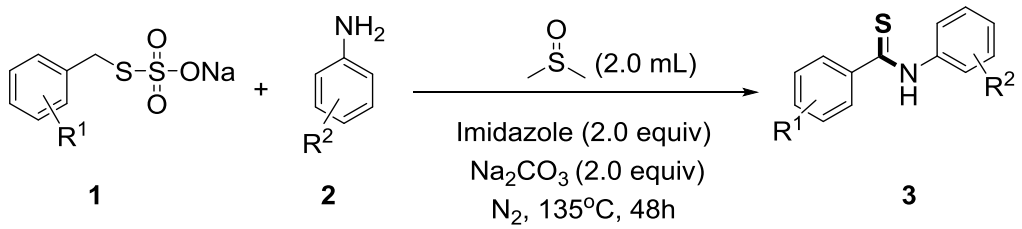
All reactions were monitored and post-processing by TLC with Qingdao GF254 silica gel coated plates. Most reagents were obtained from commercial suppliers such as J&K Scientific and used without further purification unless otherwise noted.

2. General procedure for Bunte salts synthesis

A flask was charged with aryl halides (21.2 mmol, 1.0 eq), anhydrate sodium thiosulfate (31.8 mmol, 1.5 eq) and CuI (2.12 mmol, 10 mmol%). The flask was evacuated and filled with nitrogen. DMSO (21 mL) was charged via syringe followed by DMEDA (0.46 mL, 4.24 mmol, 20 mmol%). The mixture was heated at 80 ^{o}C for 3 h. Then the reaction mixture was cooled to room temperature which followed by crystallization on addition of saturate aqueous NaCl (60 mL). The mixture was filtered and the solid was washed with saturate aqueous NaCl and hexanes. The solid was dissolved in 50 mL MeOH and stirred for 1 h at room temperaturre. The mixture was filtered and the filtrate was concentrated on arotovap at 40-45 ^{o}C. The resulted solid was dried under vacuum[1].



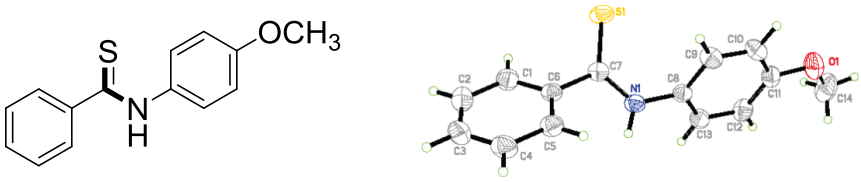
3. General procedure for N-aryl aryl thioamides synthesis



To a solution of the Bunte salts (0.75 mmol) in Dimethyl sulfoxide (2.0 mL) was added aniline (0.25 mmol), imidazole (34 mg, 0.5 mmol), and Na_2CO_3 (53 mg, 0.50 mmol) under nitrogen atmosphere in a screw-cap Schlenk test tube. The reaction mixture was stirred at 135 ℃ for 48 h. After the reaction was finished, the reaction mixture was cooled to room temperature and quenched with water. The mixture was extracted with dichloromethane (3.0 mL ×3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the corresponding products （Petroleum ether / dichloromethane = 3:2-1:1; Petroleum ether / ethyl acetate = 4:1-7:1）(42%-99 %).

4. The Single Crystal X-ray Diffraction Study of 3af, 3ea and intermediate VI

4.1 The Single Crystal X-ray Diffraction Study of 3af

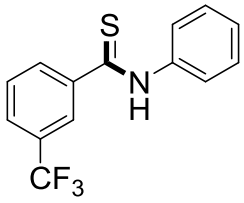


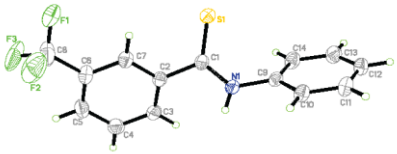
CCDC 1838715 (**3af**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

Identification code	201711223_twin1_hklf4
Empirical formula	$C_{14}H_{13}NOS$
Formula weight	243.31
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.4136(14)
b/Å	12.9765(11)
c/Å	8.1286(6)
α/ °	90
β/°	107.035(10)
γ/°	90
Volume/$Å^3$	1251.9(2)
Z	4
$\rho_{calc}g/cm^3$	1.291
μ/mm^{-1}	2.145
F(000)	512.0

Crystal size/mm^3	0.28 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.448 to 134.312
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -6 ≤ l ≤ 9
Reflections collected	3928
Independent reflections	3928 [R_{int} = ?, R_{sigma} = 0.0428]
Data/restraints/parameters	3928/0/156
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.1015
Largest diff. peak/hole / e Å^{-3}	0.29/-0.15

4.2 The Single Crystal X-ray Diffraction Study of 3ea



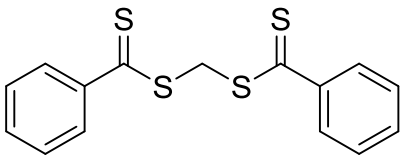


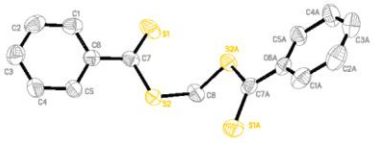
CCDC 1838811 (**3ea**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

Identification code	201803177
Empirical formula	$C_{14}H_{10}F_3NS$
Formula weight	281.29
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.5721(6)
b/Å	12.8938(8)
c/Å	7.9189(4)
α/°	90
β/°	106.101(5)
γ/°	90
Volume/Å^3	1331.42(13)
Z	4
ρ_{calc}g/cm^3	1.403
μ/mm^{-1}	2.374
F(000)	576.0
Crystal size/mm^3	0.19 × 0.13 × 0.07

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.778 to 134.15
Index ranges	$-16 \leq h \leq 10$, $-12 \leq k \leq 15$, $-8 \leq l \leq 9$
Reflections collected	4928
Independent reflections	2380 [R_{int}= 0.0290, R_{sigma} = 0.0392]
Data/restraints/parameters	2380/42/186
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1697
Final R indexes [all data]	R_1 = 0.0764, wR_2 = 0.1865
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.28

4.3 The Single Crystal X-ray Diffraction Study of intermediate VI



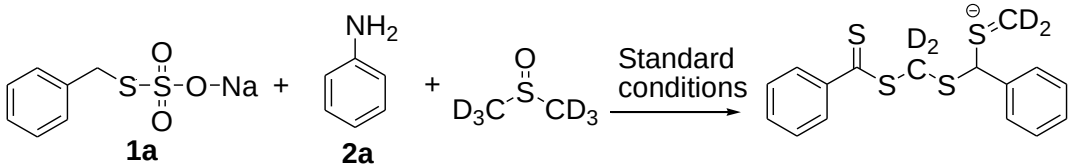


CCDC 1865343(**VI**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

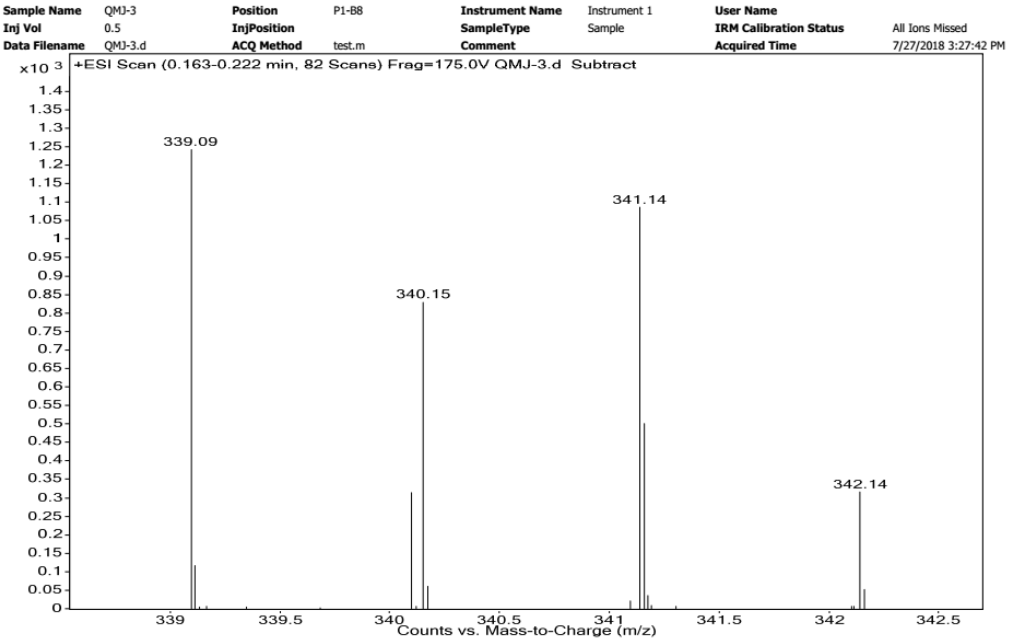
Identification code	201806280
Empirical formula	$C_{15}H_{12}S_4$
Formula weight	320.49
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	14.6712(15)
b/Å	11.6039(10)
c/Å	4.3268(5)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	736.61(13)
Z	2
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	5.766
F(000)	332.0
Crystal size/mm^3	0.25 × 0.15 × 0.13
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.718 to 134.006
Index ranges	-14 ≤ h ≤ 17, -12 ≤ k ≤ 13, -2 ≤ l ≤ 5
Reflections collected	1698
Independent reflections	1136 [R_{int} = 0.0322, R_{sigma} = 0.0489]
Data/restraints/parameters	1136/0/75
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0569, wR_2 = 0.1594
Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.1709
Largest diff. peak/hole / e Å^{-3}	0.32/-0.34
Flack parameter	0.00(5)

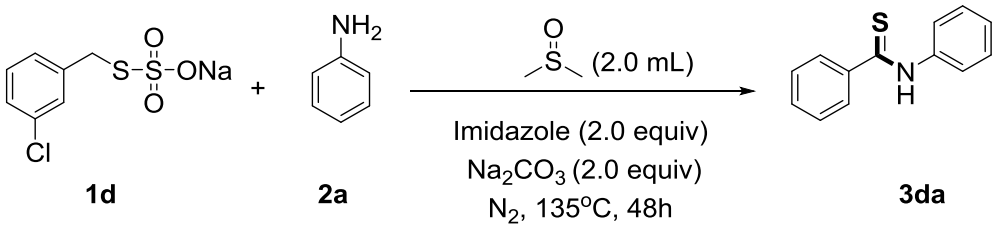
5. The experiment of trapping the intermediate V'



V' , detected by MS(ESI$^+$)
[M+H]$^+$: Calctd. 340.04
Found: 340.15



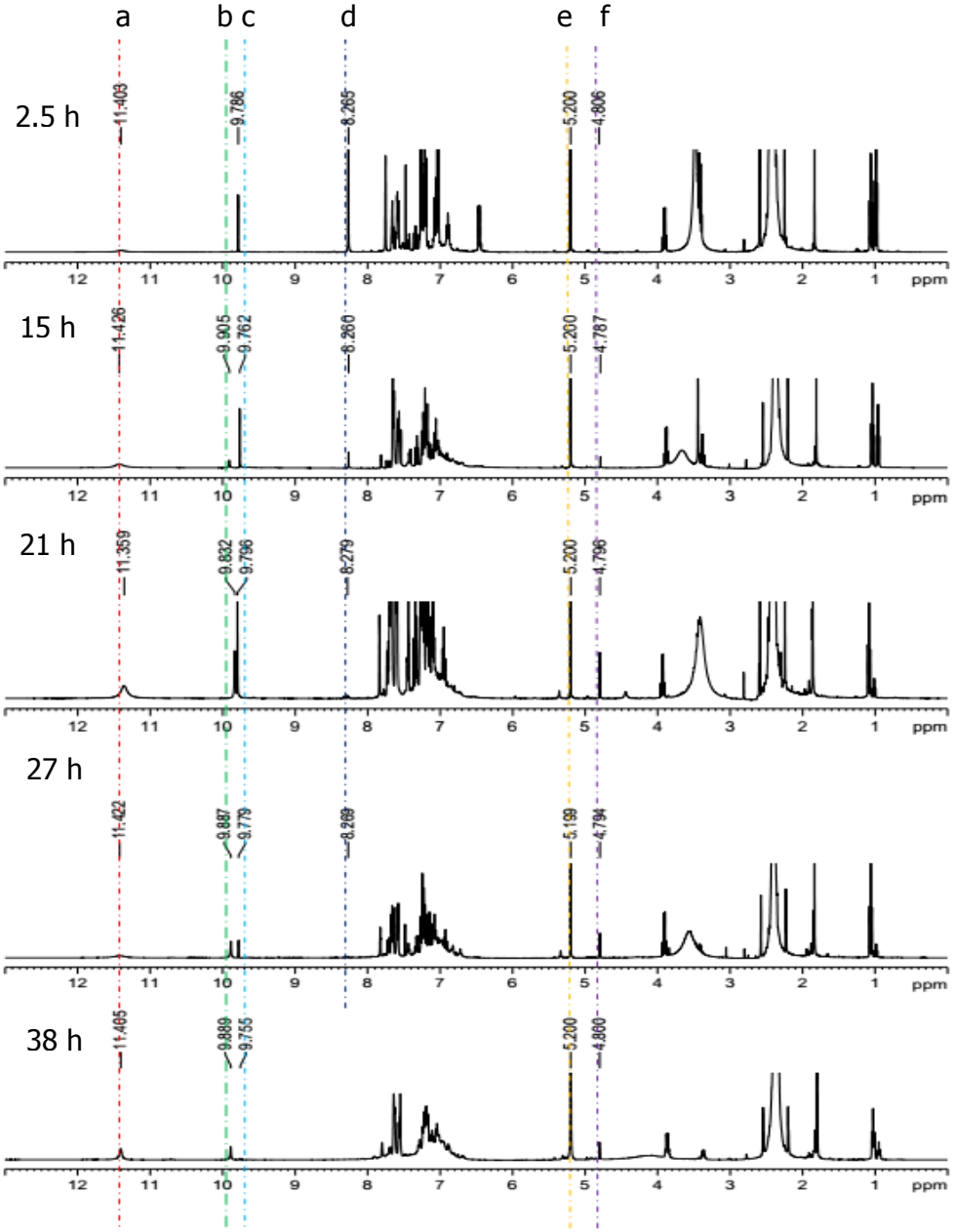
6. Exploring the mechanism by tracking experiments



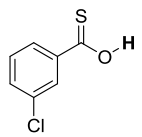
1d **2a** **3da**

To a solution of the Bunte salts **1d** (0.75 mmol) in Dimethyl sulfoxide (2.0 mL) was added aniline **2a** (0.25 mmol), imidazole (34 mg, 0.5 mmol), and Na_2CO_3 (53 mg, 0.50 mmol) under nitrogen atmosphere in five screw-cap Schlenk test tube. The reaction mixture was stirred at 135 ℃, The reaction in sequence for 2.5h, 15h, 21h, 27h and 38h. After the reaction was finished, the reaction mixture was cooled to room temperature. The mixture was extracted with dichloromethane (3.0 mL × 3), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The processed samples were separately passed through mass spectrometry and nuclear magnetic detection. The test results are as follows.

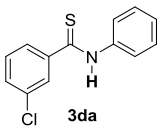
6.1 Nuclear magnetic tracking results



a :

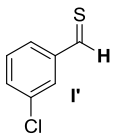


b :



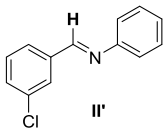
3da

c :



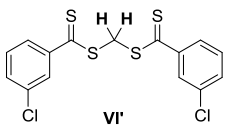
I'

d :



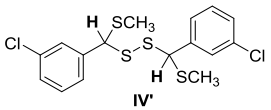
II'

e :



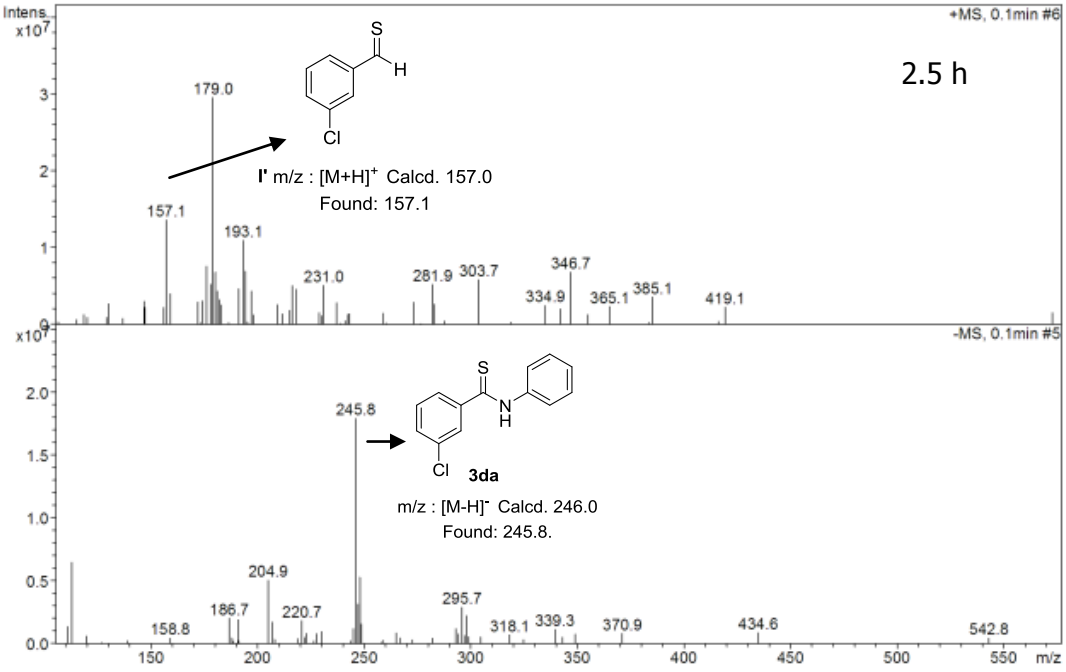
VI'

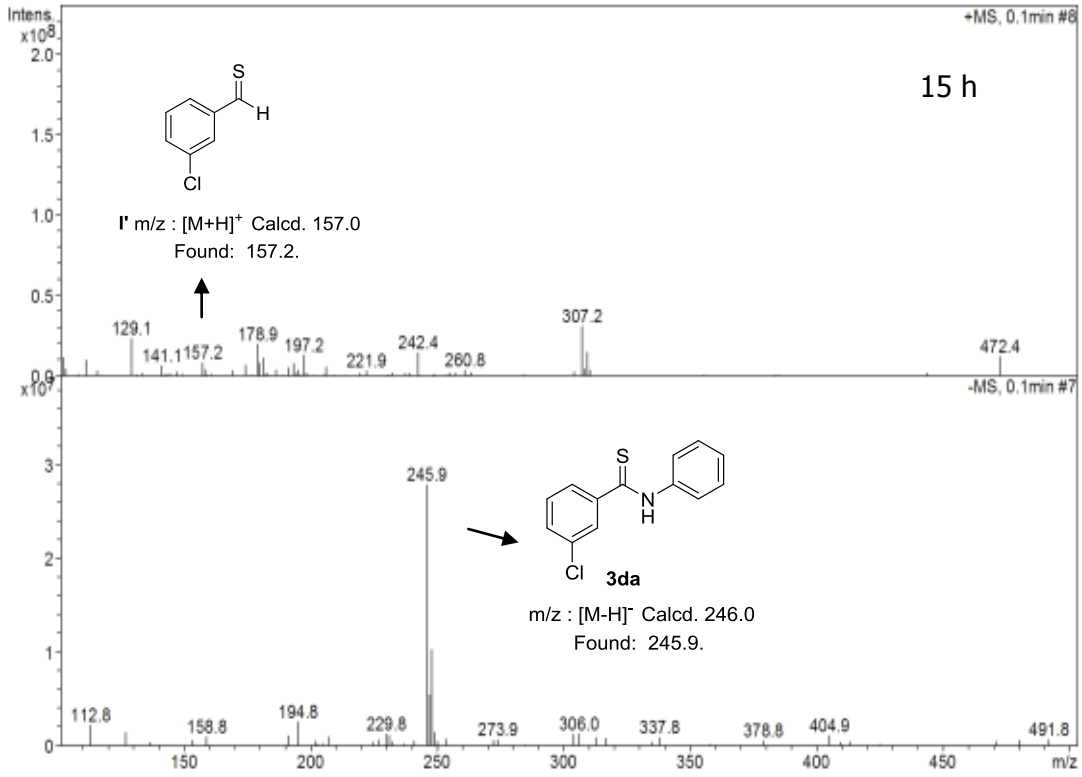
f :

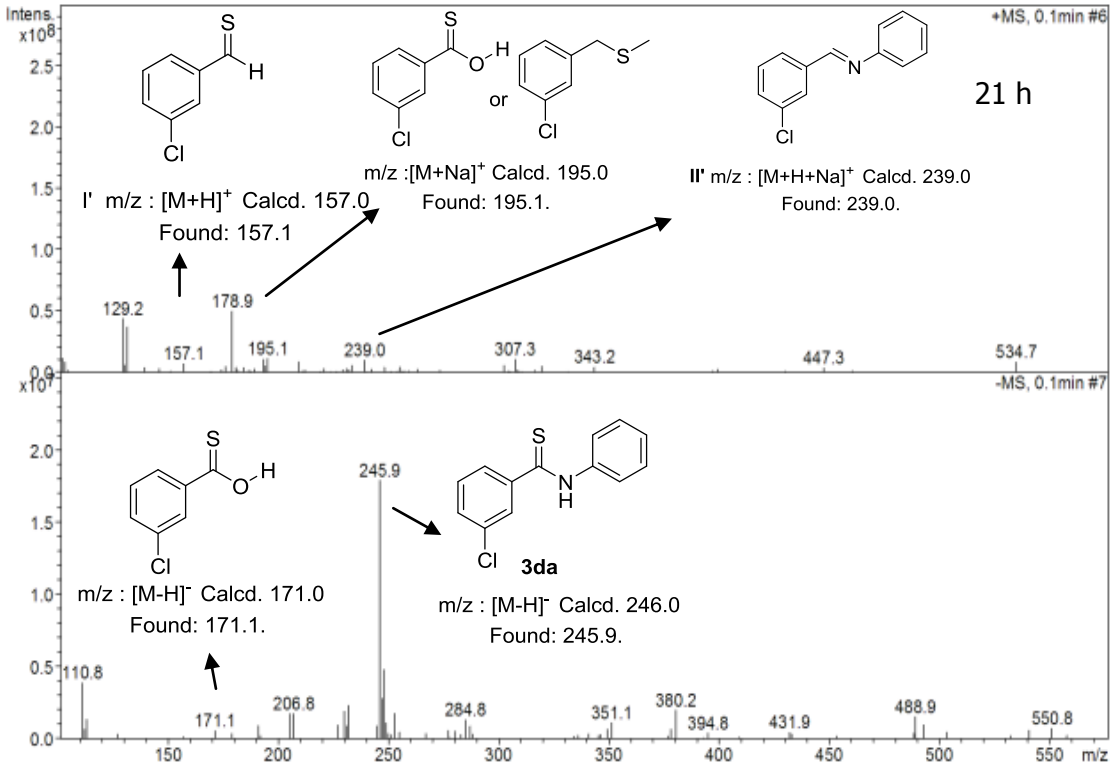


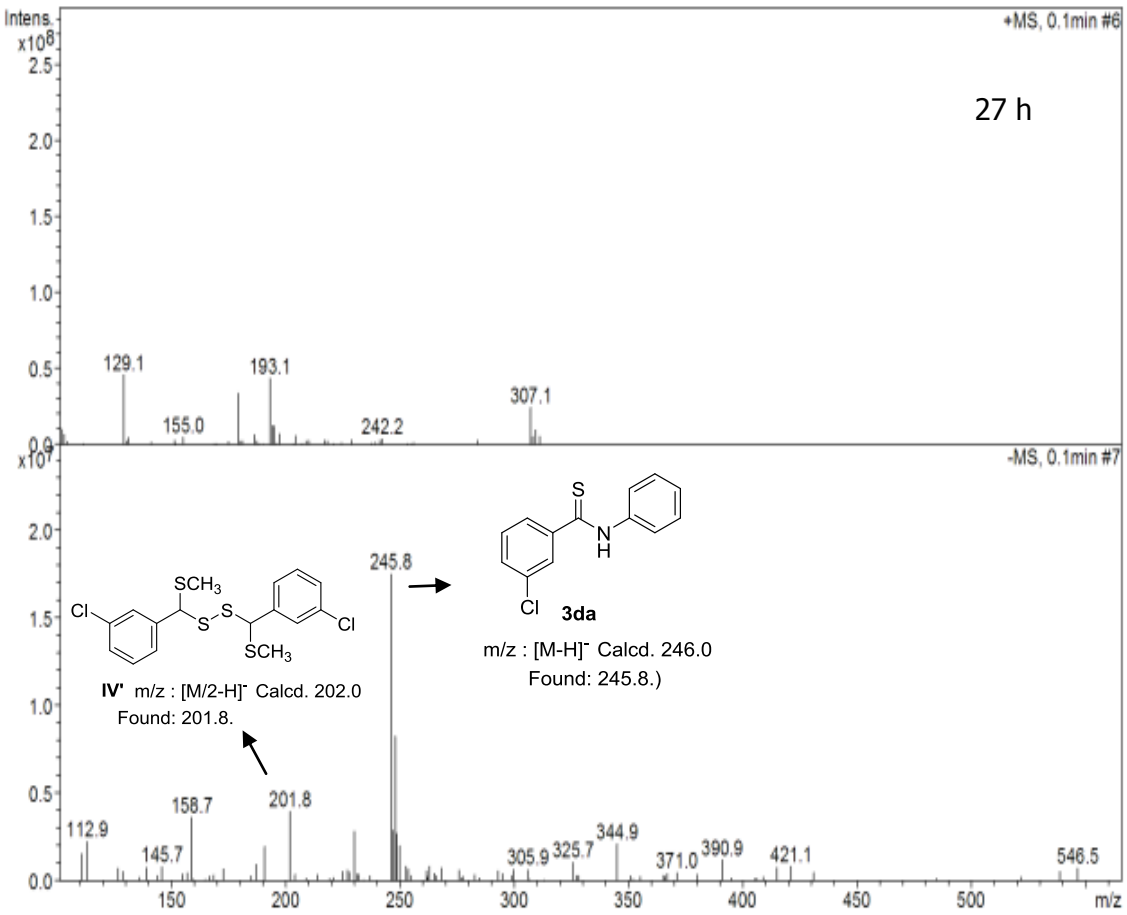
IV'

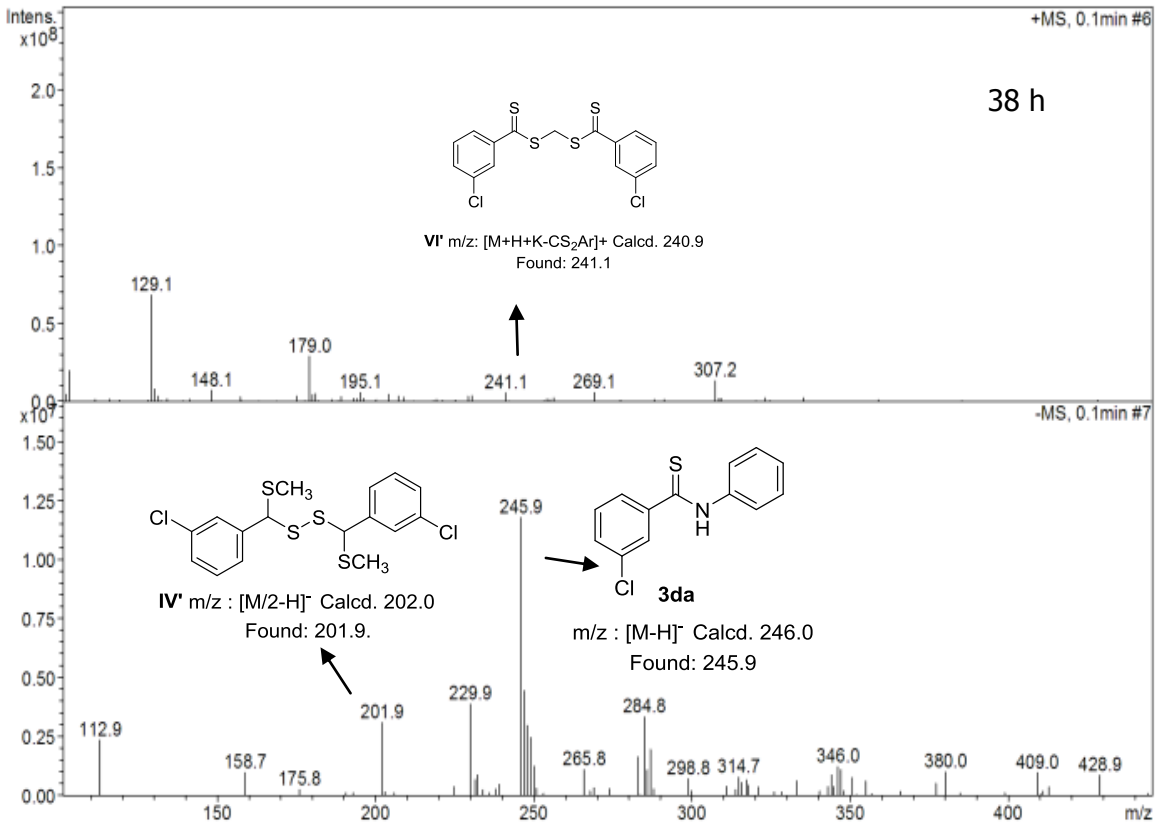
6.2 Mass spectrometry tracking results



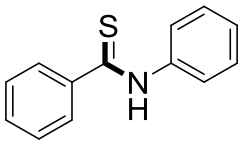



+MS, 0.1min #6
21 h
I' m/z : [M+H]+ Calcd. 157.0
Found: 157.1
m/z :[M+Na]+ Calcd. 195.0
Found: 195.1.
II' m/z : [M+H+Na]+ Calcd. 239.0
Found: 239.0.
-MS, 0.1min #7
m/z : [M-H]- Calcd. 171.0
Found: 171.1.
3da
m/z : [M-H]- Calcd. 246.0
Found: 245.9.
m/z

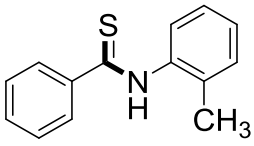

+MS, 0.1min #6
27 h
-MS, 0.1min #7
IV' m/z : [M/2-H]- Calcd. 202.0
Found: 201.8.
3da
m/z : [M-H]- Calcd. 246.0
Found: 245.8.)
m/z



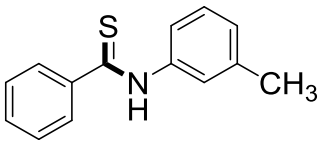
7. Characterization data of products



N-phenylbenzothioamide (**3aa**)**.** Prepared according to the general procedure to afford a yellow solid in 98% yield; **^{1}H NMR** (CDCl3, 400 M Hz) δ 9.12 (s, 1H), 7.77 (d, J = 7.40 Hz, 2H), 7.67 (d, J = 7.68 Hz, 2H), 7.46 (q, J = 8.19 Hz, 1H), 7.37 (d, J = 6.4 Hz, 4H), 7.26 (d, J = 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.41, 142.87, 138.91, 131.25, 128.94, 128.53, 126.95, 126.73, 123.81. The analytical data correspond with those reported in the literature[2].

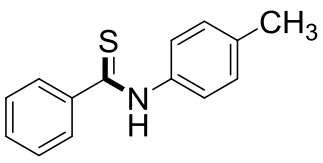


N-(m-tolyl)benzothioamide (**3ab**)**.** Prepared according to the general procedure to afford a yellow solid in 91% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.90 (s, 1H), 7.86 (d, J = 7.4 Hz, 2H), 7.52-7.45 (m, 2H), 7.41 (t, J = 7.52 Hz, 2H), 7.27 (t, J = 4.58 Hz, 3H), 2.29 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 199.62, 142.06, 137.56, 134.34, 131.49, 131.07, 128.69, 128.24, 126.89, 126.83, 126.81, 18.01. The analytical data correspond with those reported in the literature[3].

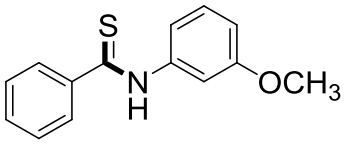


N-(m-tolyl)benzothioamide (**3ac**)**.** Prepared according to the general procedure to afford a yellow solid in 87% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 7.80 (d, J = 7.28 Hz, 2H), 7.53 (d, J = 8.16 Hz, 2H), 7.48 (t, J = 7.74 Hz, 1H), 7.40 (t, J = 7.18 Hz, 2H), 7.30 (t, J = 7.48

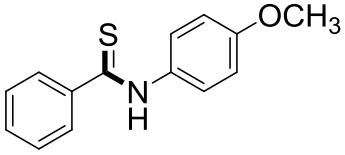
Hz, 1H), 7.09 (d, J = 7.2 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.41, 143.15, 139.10, 138.95, 131.28, 128.88, 128.65, 127.89, 126.76, 124.36, 120.97, 21.48. The analytical data correspond with those reported in the literature[4].



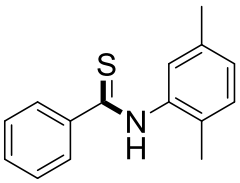
N-(p-tolyl)benzothioamide (**3ad**). Prepared according to the general procedure to afford a yellow solid in 78% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.98 (s, 1H), 7.84 (d, J = 7.48 Hz, 2H), 7.61 (d, J = 8.08 Hz, 2H), 7.50 (t, J = 6.86 Hz, 1H), 7.43 (t, J = 7.44 Hz, 2H), 7.24 (t, J = 7.32 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.37, 143.10, 137.05, 136.48, 131.23, 129.63, 128.64, 126.68, 123.84, 21.19. The analytical data correspond with those reported in the literature[2].



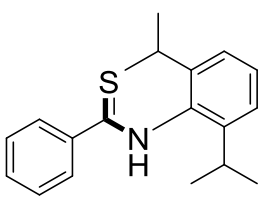
N-(3-methoxyphenyl)benzothioamide (**3ae**). Prepared according to the general procedure to afford a yellow solid in 82% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.05 (s, 1H), 7.81 (d, J = 6.92 Hz, 2H), 7.59 (s, 1H), 7.48 (d, J = 6.84 Hz, 1H), 7.42 (d, J = 7.04 Hz, 2H), 7.31 (t, J = 7.84 Hz, 1H), 7.20 (d, J = 7.08 Hz, 1H), 6.83 (d, J = 7.44 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.30, 159.99, 143.30, 140.13, 131.32, 129.80, 128.68, 126.73, 115.71, 112.83, 109.09, 55.49. The analytical data correspond with those reported in the literature[3].



N-(4-methoxyphenyl)benzothioamide (**3af**). Prepared according to the general procedure to afford a yellow solid in 53% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 7.81 (t, J = 7.88 Hz, 2H), 7.58 (d, J = 8.92 Hz, 2H), 7.46 (t, J = 7.34 Hz, 1H), 7.40 (t, J = 7.48 Hz, 2H), 6.93 (d, J = 8.92 Hz, 2H), 3.81 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.38, 158.23, 142.81, 132.02, 131.28, 128.64, 126.79, 125.73, 114.18, 55.54. The analytical data correspond with those reported in the literature[2].

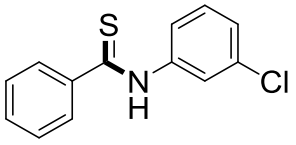


N-(2,5-dimethylphenyl)benzothioamide (**3ag**). Prepared according to the general procedure to afford a yellow solid in 70% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.80 (s, 1H), 7.89 (d, J = 7.44 Hz, 2H), 7.52 (t, J = 7.22 Hz, 1H), 7.44（t, J = 7.44 Hz, 2H, 7.34 (s, 1H), 7.20 (d, J = 7.72 Hz, 1H), 7.10 (d, J = 7.56 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.45, 141.18, 136.24, 135.62, 130.35, 130.05, 129.82, 128.01, 127.63, 126.03, 125.75, 19.94, 16.50. The analytical data correspond with those reported in the literature[5].

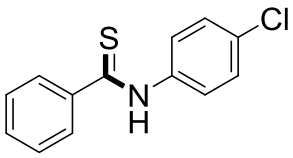


N-(2,6-diisopropylphenyl)benzothioamide (**3ah**)**.** Prepared according to the general procedure to afford a yellow solid in 72% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.63 (s, 1H), 7.93 (s, 1H), 7.91 (d, J = 1.4 Hz, 1H), 7.56-7.50 (m, 1H), 7.48-7.38 (m, 3H), 7.27 (d, J = 7.72 Hz, 2H), 3.07 (m, 2H), 1.28 (d, J = 6.84 Hz, 6H), 1.20 (d, J = 6.92 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100

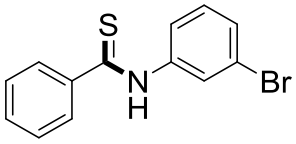
MHz) δ 200.93, 145.88, 141.70, 133.91, 131.50, 129.40, 128.80, 126.75, 124.03, 28.94, 23.96 (d, J = 26.10 Hz). The analytical data correspond with those reported in the literature[6].



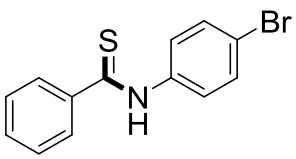
N-(3-chlorophenyl)benzothioamide (**3ai**)**.** Prepared according to the general procedure to afford a yellow solid in 83% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.03 (s, 1H), 7.86 (s, 1H), 7.79 (s, 2H), 7.60 (s, 1H), 7.50 (t, J = 6.90 Hz, 1H), 7.41 (t, J = 7.34 Hz, 2H), 7.34 (t, J = 7.78 Hz, 1H), 7.24 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.81, 142.85, 139.98, 134.56, 131.48, 129.00, 128.68, 126.96, 126.70, 123.70, 121.81. The analytical data correspond with those reported in the literature[2].



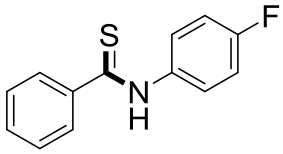
N-(4-chlorophenyl)benzothioamide (**3aj**). Prepared according to the general procedure to afford a yellow solid in 92% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.94 (s, 1H), 7.74 (d, J = 6.99 Hz, 2H), 7.62 (d, J = 7.68 Hz, 2H), 7.42 (d, J = 6.96 Hz, 1H), 7.33 (q, J = 8.77 Hz, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 197.65, 141.80, 136.42, 131.08, 130.45, 128.13, 127.65, 125.66, 124.04. The analytical data correspond with those reported in the literature[2].



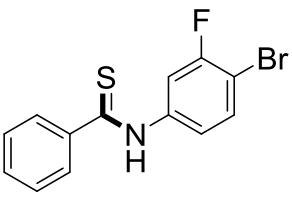
N-(3-bromophenyl)benzothioamide (**3ak**)**.** Prepared according to the general procedure to afford a yellow solid in 52% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.00 (s, 1H), 7.99 (s, 1H), 7.80 (s, 2H), 7.68 (d, J = 4.00 Hz, 1H), 7.50 (t, 6.86 Hz, 1H), 7.42 (t, J = 7.34 Hz, 3H), 7.29 (d, J = 7.12 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.79, 142.84, 140.06, 131.50, 130.27, 129.88, 128.69, 126.68, 126.52, 122.39, 122.30. The analytical data correspond with those reported in the literature[3].



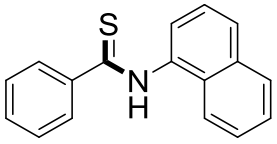
N-(4-bromophenyl)benzothioamide (**3al**). Prepared according to the general procedure to afford a yellow solid in 69% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.99 (s, 1H), 7.81 (d, J = 6.28 Hz, 2H), 7.66 (d, J = 7.28 Hz, 2H), 7.56-7.47 (m, 3H), 7.43 (d, J = 6.96 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.60, 142.89, 137.96, 132.12, 131.47, 128.69, 126.67, 125.25, 119.93. The analytical data correspond with those reported in the literature[3].



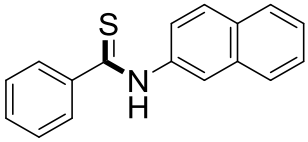
N-(4-fluorophenyl)benzothioamide (**3am**). Prepared according to the general procedure to afford a yellow solid in 98% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.06 (s, 1H), 7.79 (d, J = 7.44 Hz, 2H), 7.63 (q, J = 4.51 Hz, 2H), 7.49 (t, J = 7.34 Hz, 1H), 7.40 (t, 7.56 Hz, 2H), 7.08 (t, 8.54 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.88, 160.88 (d, J_{C-F} = 246.01 Hz), 142.60, 134.94 (d, J_{C-F} = 2.75 Hz), 131.51, 128.69, 126.79, 126.18 (d, J_{C-F} = 8.29 Hz), 115.92 (d, J_{C-F} = 22.64 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.59. The analytical data correspond with those reported in the literature[2].



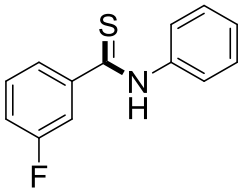
N-(4-bromo-3-fluorophenyl)benzothioamide (**3an**)**.** Prepared according to the general procedure to afford a yellow solid in 62% yield; mp 140 ^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 7.94 (s, 1H), 7.79 (d, J = 5.52 Hz, 2H), 7.59-7.49 (m, 2H), 7.43 (t, J = 7.52 Hz, 2H), 7.33 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.91, 158.85 (d, J_{C-F} = 246.11 Hz), 139.48 (d, J_{C-F} = 9.30 Hz), 133.50, 131.62, 128.77, 126.67, 120.00 (d, J_{C-F} = 3.57 Hz), 111.79, 111.52, 106.30 (d, J_{C-F} = 20.60Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.27; **HR-MS** (ESI^+): calcd. for $C_{13}H_9BrFNS$ $[M+H]^+$: 309.9696, Found: 309.9697.



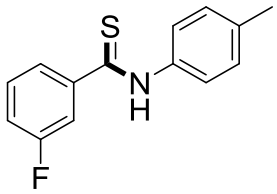
N-(3-bromophenyl)benzothioamide (**3ao**)**.** Prepared according to the general procedure to afford a yellow solid in 35% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.20 (s, 1H), 7.99 (d, J = 7.56 Hz, 2H), 7.94-7.84 (m, 3H), 7.75 (d, J = 7.12 Hz, 1H), 7.57-7.43 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 200.58, 142.04, 134.90, 134.28, 131.57, 128.78, 128.72, 128.56, 126.94, 126.88, 126.50, 125.45, 124.76, 121.86. The analytical data correspond with those reported in the literature[7].



N-(naphthalen-2-yl)benzothioamide (**3ap**). Prepared according to the general procedure to afford a yellow solid in 47% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.18 (s, 1H), 8.39 (s, 1H), 7.87 (d, J = 7.80 Hz, 2H), 7.83 (t, J = 3.66 Hz, 2H), 7.71 (d, J = 8.12 Hz, 1H), 7.50 (q, J = 3.03 Hz, 3H), 7.45 (d, J = 7.36Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.42, 143.12, 136.45, 133.34, 131.99, 131.35, 128.81, 128.69, 127.99, 127.73, 126.70, 126.28, 122.66, 121.24. The analytical data correspond with those reported in the literature[8].

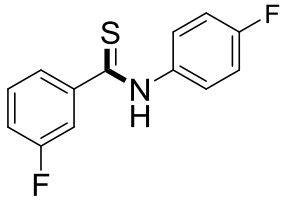


3-fluoro-N-phenylbenzothioamide (**3ba**). Prepared according to the general procedure to afford a yellow solid in 92% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 7.74 (d, J = 7.76 Hz, 2H), 7.58 (d, J = 7.92 Hz, 2H), 7.48-7.38 (m, 3H), 7.31 (t, J = 7.26 Hz, 1H), 7.20 (t, J = 7.94 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.57, 161.50 (d, J_{C-F} = 246.84 Hz), 144.11, 137.74, 129.24 (d, J_{C-F} = 7.87 Hz), 128.10, 126.18, 122.67, 120.80, 117.10 (d, J_{C-F} = 21.18 Hz), 113.50 (d, J_{C-F} = 23.31 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.50. The analytical data correspond with those reported in the literature[10].

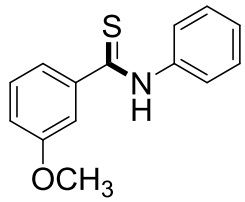


3-fluoro-N-(p-tolyl)benzothioamide (**3bd**). Prepared according to the general procedure to afford a yellow solid in 83% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.97 (s, 1H), 7.59 (t, J = 7.56 Hz, 4H), 7.39 (q, J = 7.16 Hz, 1H), 7.24 (d, J = 7.00 Hz, 2H), 7.18 (dq, J = 9.48 Hz, 2.24 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.45, 161.50 (d, J_{C-F} = 246.81 Hz), 144.01 (d, J_{C-F} = 6.72 Hz), 136.25, 135.22, 129.21 (d, J_{C-F} = 8.18 Hz),

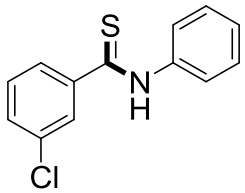
128.66, 122.76, 120.79 (d, J_{C-F} = 2.57 Hz), 117.04 (d, J_{C-F} = 21.28 Hz), 113.49 (d, J_{C-F} = 23.52 Hz), 20.17; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.59. The analytical data correspond with those reported in the literature[10].



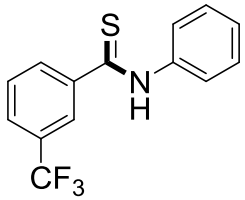
3-fluoro-N-(4-fluorophenyl)benzothioamide (**3bm**)**.** Prepared according to the general procedure to afford a yellow solid in 64% yield, mp 110 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.98 (s, 1H), 7.67 (q, J = 4,49 Hz, 2H), 7.57 (d, J = 7.64 Hz, 2H), 7.40 (q, J = 7.17 Hz, 1H), 7.20 (q, J = 7.36 Hz, 1H), 7.13 (t, J = 8.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 197.08, 162.51 (d, J_{C-F} = 246.55 Hz), 160.94 (d, J_{C-F} = 246.33 Hz), 144.62 (d, J_{C-F} = 7.06 Hz), 134.67, 130.31 (d, J_{C-F} = 8.09 Hz), 126.03 (d, J_{C-F} = 8.31 Hz), 121.81 (d, J_{C-F} = 2.52 Hz), 118.30 (d, J_{C-F} = 21.27 Hz), 116.04 (d, J_{C-F} = 22.74 Hz), 114.52 (d, J_{C-F} = 23.55 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.42, -113.27; **HR-MS** (ESI^+): calcd. for $C_{13}H_9F_2NS$ $[M+H]^+$: 250.0497, Found: 250.0496.



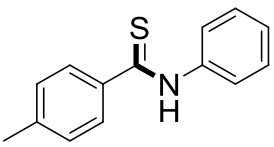
N-(3-bromophenyl)benzothioamide (**3ca**)**.** Prepared according to the general procedure to afford a yellow solid in 65% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 7.77 (d, J = 7.84 Hz, 2H), 7.45 (t, J = 7.04 Hz, 3H), 7.33 (m, 3H), 7.04 (d, J = 7.36 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.12, 159.66, 144.62, 138.90, 129.68, 129.08, 127.03, 123.66, 118.07, 117.40, 112.61, 55.51. The analytical data correspond with those reported in the literature[3].



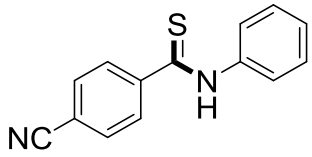
3-chloro-N-phenylbenzothioamide (**3da**). Prepared according to the general procedure to afford a yellow solid in 81% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.90 (s, 1H), 7.83 (s, 1H), 7.75 (d, J = 7.20 Hz, 2H), 7.70 (d, J = 7.36 Hz, 1H), 7.44 (d, J = 7.88 Hz, 3H), 7.37 (t, J = 7.92 Hz, 1H), 7.31 (t, J = 7.06 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.52, 143.70, 137.71, 133.70, 130.10, 128.89, 128.12, 126.20, 125.96, 123.71, 122.64. The analytical data correspond with those reported in the literature[5].



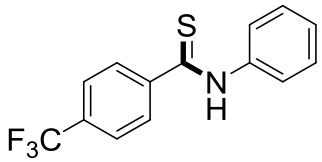
N-phenyl-3-(trifluoromethyl)benzothioamide (**3ea**). Prepared according to the general procedure to afford a yellow solid in 77% yield, mp 130°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.03 (s, 1H), 8.08 (s, 1H), 8.02 (d, J = 7.48 Hz, 1H), 7.75 (d, J = 7.48 Hz, 3H), 7.57 (t, J = 7.56 Hz, 1H), 7.46 (t, J = 7.42 Hz, 2H), 7.33 (t, J = 7.06 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.61, 143.72, 138.64, 131.09 (q, J = 32.72 Hz), 130.02, 129.31, 129.18, 127.67, 127.36, 123.75, 123.60 (q, J = 271.32 Hz), 123.52 (q, J = 3.83 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.65; **HR-MS** (ESI^+): calcd. for $C_{14}H_{10}F_3NS$ $[M+H]^+$: 282.0559, Found: 282.0558.



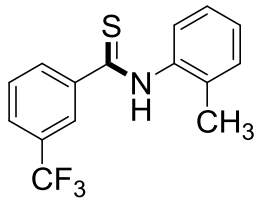
4-methyl-N-phenylbenzothioamide (**3fa**). Prepared according to the general procedure to afford a yellow solid in 44% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.98 (s, 1H), 7.77 (s, 4H), 7.44 (s, 2H), 7.29 (s, 1H), 7.23 (s, 2H), 2.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.28, 141.95, 140.41, 139.11, 129.27, 129.06, 126.91, 126.70, 123.77, 21.40. The analytical data correspond with those reported in the literature[9].



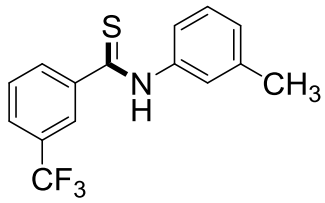
4-cyano-N-phenylbenzothioamide (**3ga**). Prepared according to the general procedure to afford a yellow solid in 87% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.11 (s, 1H), 7.90 (d, J = 8.12 Hz, 2H), 7.76 (d, J = 7.84 Hz, 2H), 7.70 (d, J = 8.16 Hz, 2H), 7.47 (t, J = 7.70 Hz, 2H), 7.34 (t, J = 6.86 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.89, 146.62, 138.52, 132.46, 129.20, 127.46, 127.37, 123.53, 118.10, 114.31. The analytical data correspond with those reported in the literature[3].



N-phenyl-4-(trifluoromethyl)benzothioamide (**3ha**). Prepared according to the general procedure to afford a yellow solid in 99% yield , mp 190 ^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.95 (s, 1H), 7.86 (d, J = 7.44 Hz, 2H), 7.70 (d, J = 7.32 Hz, 2H), 7.63 (d, J = 7.48 Hz, 2H), 7.40 (t, J = 6.98 Hz, 2H), 7.26 (t, J = 6.98 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.70, 145.20, 137.62, 131.73 (q, J = 34.76 Hz), 128.17, 126.33, 126.03, 124,70 (q, J = 3.83 Hz), 122.62 (q, J = 270.60 Hz), 122.57; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.89; **HR-MS** (ESI^+): calcd. for $C_{14}H_{10}F_3NS$ $[M+H]^+$: 282.0559, Found: 282.0557.

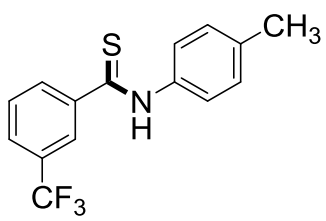


N-(m-tolyl)-3-(trifluoromethyl)benzothioamide (**3eb**). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 82^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.88 (s, 1H), 8.12 (s, 1H), 8.05 (d, J = 7.68 Hz, 1H), 7.76 (d, J = 7.64 Hz, 1H), 7.57 (t, J = 7.76 Hz, 3H), 7.49 (t, J = 4.12 Hz, 1H), 7.30 (d, J = 9.24 Hz, 3H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.76, 141.60, 136.13, 133.25, 130.11, 130.05 (q, J = 32.64 Hz), 128.96, 128.26, 127.45, 126.80 (q, J = 6.90 Hz), 125.88, 125.62, 122.71 (q, J = 3.80 Hz), 122.58 (q, J = 270.80 Hz), 16.91; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.61; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NS$ $[M+H]^+$: 296.0715, Found: 296.0716.

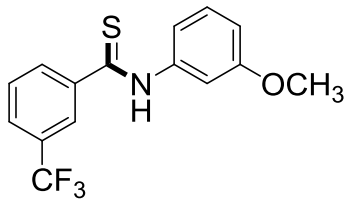


N-(m-tolyl)-3-(trifluoromethyl)benzothioamide (**3ec**). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 126^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.03 (s, 1H), 8.05 (s, 1H), 7.98 (d, J = 7.64 Hz, 1H), 7.73 (d, J = 7.59 Hz, 1H), 7.54 (t, J = 7.44 Hz,

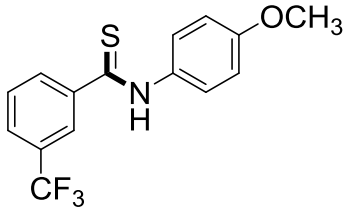
3H), 7.32 (t, J = 7.58 Hz, 1H), 7.12 (d, J = 7.44 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.50, 143.70, 139.23, 138.58, 131.03 (q, J_{C-F} = 32.49 Hz), 130.00, 129.26, 128.96, 128.18, 124.29, 123.60 (q, J_{C-F} = 270.90 Hz), 123.57, 123.54，120.90, 21.41; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.61; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NS$ $[M+H]^+$: 196.0715, Found: 296.0720.



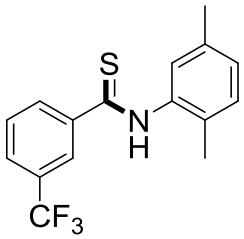
N-(p-tolyl)-3-(trifluoromethyl)benzothioamide (**3ed**). Prepared according to the general procedure to afford a yellow solid in 72% yield, mp 128°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.03 (s, 1H), 8.06 (s, 1H), 8.00 (d, J = 7.80 Hz, 1H), 7.73 (d, J = 7.72 Hz, 1H), 7.56 (q, J = 8.60 Hz, 4H), 7.23 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.49, 143.59, 137.43, 136.13, 131.02 (q, J_{C-F} = 32.78 Hz), 130.02, 129.72, 129.24, 127.53 (q, J_{C-F} = 3.38 Hz), 123.85, 123.67 (q, J_{C-F} = 275.68 Hz), 123.57 (q, J_{C-F} = 3.76 Hz), 21.21; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.62; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NS$ $[M+H]^+$: 296.0715, Found: 296.0715.



N-(3-methoxyphenyl)-3-(trifluoromethyl)benzothioamide (**3ee**)**.** Prepared according to the general procedure to afford a yellow solid in 57% yield, mp 102-103°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.05 (s, 1H), 8.05 (s, 1H), 7.99 (d, J = 6.44 Hz, 1H), 7.74 (d, J = 7.36 Hz, 1H), 7.56 (s, 2H), 7.34 (t, J = 8.34 Hz, 1H), 7.20 (t, J = 6.90 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.39, 160.05, 143.85, 139.77, 131.06 (q, J_{C-F} = 33.76 Hz), 129.98, 129.89, 129.29, 127.65, 123.64 (q, J_{C-F} = 276.00 Hz), 123.54, 115.67, 113.06, 109.13, 55.47; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.61; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NOS$ $[M+H]^+$: 312.0664, Found: 312.0663.

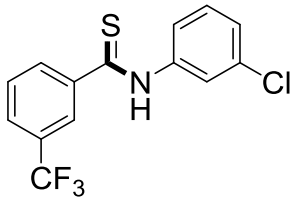


N-(4-methoxyphenyl)-3-(trifluoromethyl)benzothioamide (**3ef**)**.** Prepared according to the general procedure to afford a yellow solid in 83% yield, mp 121°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.04 (s, 1H), 8.05(s, 1H), 7.99 (d, J = 7.84 Hz, 1H), 7.73 (d, 7.76 Hz, 1H), 7.61-7.52 (m, 3H), 6.96-6.93 (m, 2H), 3.83 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.48, 158.42, 143.40, 131.64, 130.99 (q, J_{C-F} = 32.60 Hz), 130.05, 129.23, 127.60 (q, J_{C-F} = 36.53 Hz), 125.63, 123.64 (q, J_{C-F} = 270.96 Hz), 123.58 (q, J_{C-F} = 3.87 Hz), 114.24, 55.50; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.60; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NOS$ $[M+H]^+$: 312.0664, Found: 312.0661.

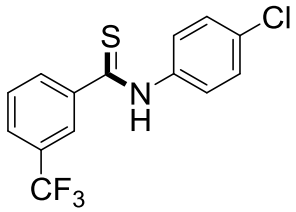


N-(2,5-dimethylphenyl)-3-(trifluoromethyl)benzothioamide (**3eg**). Prepared according to the general procedure to afford a

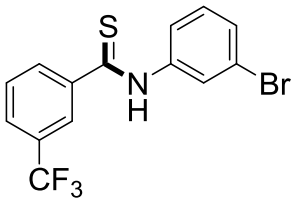
yellow solid in 94% yield, mp 101 ^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.80 (s, 1H), 8.04 (s, 1H), 7.95 (d, J = 7.68 Hz, 1H), 7.67 (d, J = 7.64 Hz, 1H), 7.48 (t, J = 7.76 Hz, 1H), 7.20 (s, 1H), 7.11 (d, J = 7.72 Hz, 1H), 7.02 (d, J = 7.56 Hz, 1H), 2.27 (s, 3H), 2,19 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.66, 141.68, 135.94, 135.72, 130.99 (q, J_{C-F} = 25.76 Hz), 130.20, 130.10, 129.90, 128.94, 128.24 (d, J_{C-F} = 4.93 Hz), 126.71 (q, J_{C-F} = 3.63 Hz), 125.96, 122.72 (q, J_{C-F} = 4.04 Hz), 122.58 (q, J_{C-F} = 267.37 Hz), 19.91, 16.47; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.62; **HR-MS** (ESI^+): calcd. for $C_{16}H_{14}F_3NS$ $[M+H]^+$: 310.0872, Found: 310.0878.



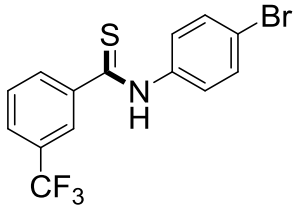
N-(3-chlorophenyl)-3-(trifluoromethyl)benzothioamide (**3ei).** Prepared according to the general procedure to afford a yellow solid in 86% yield, mp 125 ^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 8.04 (s, 1H), 7.98 (s, 1H), 7.86 (s, 1H), 7.75 (d, J = 7.44 Hz, 1H), 7.61 (s, 1H), 7.56 (t, J = 7.30 Hz, 1H), 7.37 (t, J = 7.36 Hz, 1H), 7.28 (d, J = 7.60 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.91, 142.41, 138.66, 133.69, 130.09 (q, J = 32.70 Hz), 129.11, 129.04, 128.31, 126.81, 126.30, 122.74, 122.54 (q, J = 271.03 Hz), 122.50, 120.02; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.65; **HR-MS** (ESI^+): calcd. for $C_{14}H_9ClF_3NS$ $[M+H]^+$: 316.0169, Found: 316.0172.



N-(4-chlorophenyl)-3-(trifluoromethyl)benzothioamide (**3ej**). Prepared according to the general procedure to afford a yellow solid in 66% yield, mp 102^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.02 (s, 1H), 8.04 (s, 1H), 7.99 (d, J = 7.44 Hz, 1H), 7.75 (d, 7.40 Hz, 1H), 7.69 (d, J = 8.12 Hz, 2H), 7.56 (t, J = 7.56 Hz, 1H), 7.40 (d, J = 8.24 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.78, 142.33, 136.07, 131.48, 130.07 (q, J = 32.37 Hz), 129.02, 128.31, 128.25, 126.84, 124.08, 122.55 (q, J = 270.97 Hz), 122.47; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.63; **HR-MS** (ESI^+): calcd. for $C_{14}H_9ClF_3NS$ $[M+H]^+$: 316.0169, Found: 316.0171.

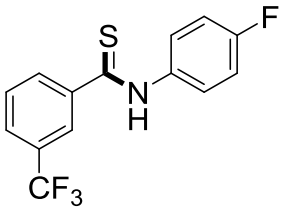


N-(3-bromophenyl)-3-(trifluoromethyl)benzothioamide (**3ek**)**.** Prepared according to the general procedure to afford a yellow solid in 62% yield, mp 103 ^{o}C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.03 (s, 1H), 8.03 (s, 1H), 7.97 (s, 1H), 7.75 (d, J = 7.44 Hz, 1H), 7.67 (s, 1H), 7.56 (t, J = 7.40 Hz, 1H), 7.43 (d, J = 7.64 Hz, 1H), 7.30 (t, J = 7.44 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.93, 143.38, 139.76, 131.13 (q, J_{C-F} = 32.78 Hz), 130.40, 130.25, 130.03, 129.35, 127.86, 126.64, 123.56 (q, J_{C-F} = 270.76 Hz), 123.54, 122.51, 122.37; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.64; **HR-MS** (ESI+): calcd. for $C_{14}H_9BrF_3NS$ $[M+H]^+$: 359.9664, Found: 359.9689.

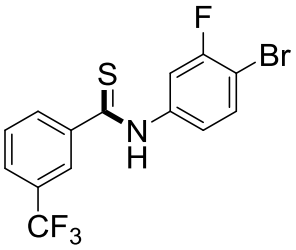


N-(4-bromophenyl)-3-(trifluoromethyl)benzothioamide

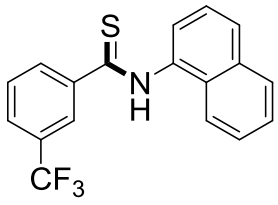
(**3el**). Prepared according to the general procedure to afford a yellow solid in 42% yield, mp 100°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.00 (s, 1H), 8.05 (s, 1H), 8.01 (d, J = 7.44 Hz, 1H), 7.76 (d, 7.32 Hz, 1H), 7.66 (d, J = 8.04 Hz, 2H), 7.56 (t, J = 7.80 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.71, 142.42, 136.63, 131.22, 130.05 (q, J = 32.69 Hz), 129.07, 128.31, 126.82, 124.27, 122.53 (q, J = 270.93 Hz), 122.45, 119.31; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.63; **HR-MS** (ESI^+): calcd. for $C_{14}H_9BrF_3NS$ $[M+H]^+$: 359.9664, Found: 359.9660.



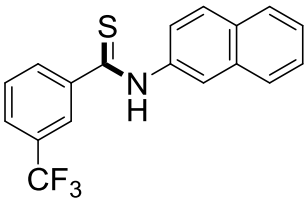
N-(4-fluorophenyl)-3-(trifluoromethyl)benzothioamide (**3em**). Prepared according to the general procedure to afford a yellow solid in 93% yield, mp 89°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.06 (s, 1H), 8.05 (s, 1H), 7.99 (d, J = 7.80 Hz, 1H), 7.74 (d, 7.68 Hz, 1H), 7.66 (m, 2H), 7.56 (t, J = 7.78 Hz, 1H), 7.13 (t, J = 8.52 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 197.10, 161.04 (d, J_{C-F} = 246.61 Hz), 143.31, 134.68 (d, J_{C-F} = 2.98 Hz), 131.10 (q, J_{C-F} = 32.75Hz), 130.12, 129.32, 127.79 (q, J_{C-F} = 3.56 Hz), 126.10 (d, 8.02 Hz), 123.61 (q, J_{C-F} = 270.90 Hz), 123.51 (d, J_{C-F} = 3.63 Hz), 116.06 (d, J_{C-F} = 22.60 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.62, -113.09; **HR-MS** (ESI^+): calcd. for $C_{14}H_9F_4NS$ $[M+H]^+$: 300.0465, Found: 300.0467.



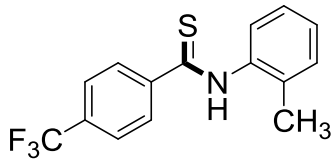
N-(4-bromo-3-fluorophenyl)-3-(trifluoromethyl)benzo-thioamide (**3en**). Prepared according to the general procedure to afford a yellow solid in 42% yield, mp 70 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.97 (s, 1H), 7.96 (s, 1H), 7.91 (d, J = 5.32 Hz, 1H), 7.85 (s, 1H), 7.69 (d, J = 7.68 Hz, 1H), 7.51 (q, J = 8.51 Hz, 2H), 7.28 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.80, 157.89 (d, J_{C-F} = 246.45 Hz), 142.38, 138.13 (d, J_{C-F} = 9.23 Hz), 132.64, 130.20 (q, J_{C-F} = 32.75 Hz), 129.01, 128.39, 126.93 (q, J_{C-F} = 3.47 Hz), 122.51 (q, J_{C-F} = 271.06 Hz), 122.46, 119.04 (d, J_{C-F} = 3.57 Hz), 110.73 (d, J_{C-F} = 26.47 Hz), 105.76 (d, J_{C-F} = 21.14 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.68, 103.99; **HR-MS** (ESI^+): calcd. for $C_{14}H_8BrF_4NS$ $[M+H]^+$: 377.9570, Found: 377.9567.



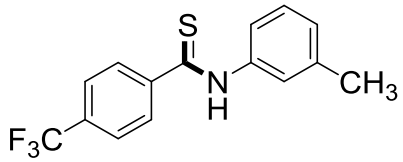
N-(naphthalen-1-yl)benzothioamide(**3eo**)**.** Prepared according to the general procedure to afford a yellow solid in 98% yield, mp 120°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.23 (s, 1H), 8.25 (s, 1H), 8.17 (d, J = 7.64 Hz, 1H), 7.95-7.89 (m, 2H), 7.86 (q, J = 2.97 Hz, 1H), 7.80 (d, J = 7.84 Hz, 1H), 7.76 (d, J = 7.28 Hz, 1H), 7.62 (t, J = 7.86 Hz, 1H), 7.59-7.53 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.76, 142.69, 134.61, 134.33, 131.21 (q, J_{C-F} = 32.72 Hz), 130.07, 129.37, 128.88, 128.73, 127.94, 127.10, 125.63, 125.46, 124.79, 123.82, 123.67 (q, J_{C-F} = 273.57 Hz), 121.70, 105.32; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.56; **HR-MS** (ESI^+): calcd. for $C_{18}H_{12}F_3NS$ $[M+H]^+$: 332.0715, Found: 332.0715.



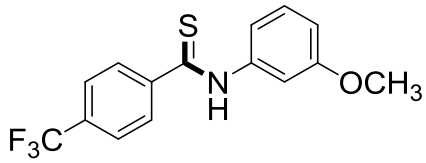
N-(naphthalen-2-yl)-3-(trifluoromethyl)benzothioamide (**3ep**). Prepared according to the general procedure to afford a yellow solid in 49% yield, mp 106°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.14 (s, 1H), 8.29 (s, 1H), 8.03 (s, 1H), 7.96 (d, J = 7.52 Hz, 1H), 7.81 (d, J = 8.80 Hz, 1H), 7.76 (d, J = 2.36 Hz, 2H), 7.68 (d, J = 7.48 Hz, 1H), 7.62 (d, J = 8.40 Hz, 2H), 7.49 (t, J = 7.72 Hz, 1H), 7.43 (q, J = 3.11 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.52, 142.62, 135.10, 132.27, 131.09, 130.05 (q, J_{C-F} = 32.82 Hz), 129.05, 128.27, 127.93, 126.99, 126.75, 126.67, 125.80, 125.47, 122.60 (q, J_{C-F} = 271.06 Hz), 122.57, 121.47, 120.42; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.56; **HR-MS** (ESI^+): calcd. for $C_{18}H_{12}F_3NS$ $[M+H]^+$: 332.0715, Found: 332.0718.



N-(o-tolyl)-4-(trifluoromethyl)benzothioamide (**3hb**)**.** Prepared according to the general procedure to afford a yellow solid in 99% yield , mp 124 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.81 (s, 1H), 7.88 (d, J = 7.84 Hz, 2H), 7.61 (d, J = 8.00 Hz, 2H), 7.44 (s, 1H), 7.23 (d, J = 3.16 Hz, 3H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.92, 144.06, 136.11, 133.14, 131.79 (q, J = 32.63 Hz), 130.12, 127.43, 126.16, 126.87, 125.56, 124.64 (q, J = 3.65Hz), 122.65 (q, J = 270.56 Hz), 16.86; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.88; **HR-MS** (ESI^+): calcd. for $C_{15}H_{11}F_3NS$ $[M+H]^+$: 296.0715, Found: 296.0719.

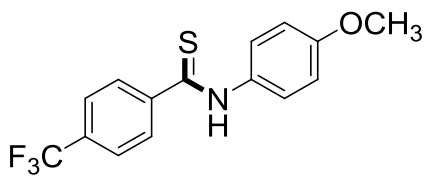


N-(m-tolyl)-4-(trifluoromethyl)benzothioamide (**3hc**). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 129 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.99 (s, 1H), 7.91 (d, J = 7.84 Hz, 2H), 7.68 (d, J = 7.72 Hz, 2H), 7.56 (s, 2H), 7.34 (t, J = 7.62 Hz, 1H), 7.13 (d, J = 7.52 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.61, 146.18, 139.26, 138.54, 132.67 (q, J = 30.58 Hz), 128.99, 128.19, 127.05, 125.69 (q, J = 3.77 Hz), 124.14, 123.65 (q, J = 270.75 Hz), 120.74, 21.44; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.86; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NS$ $[M+H]^+$: 296.0715, Found: 296.0717.

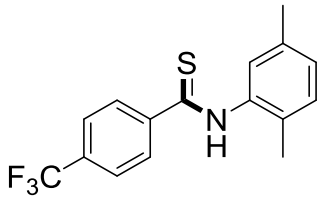


N-(3-methoxyphenyl)-4-(trifluoromethyl)benzo-thioamide (**3hd**). Prepared according to the general procedure to afford a yellow solid in 48% yield, mp 122 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.98 (s, 1H), 7.81 (d, J = 7.20 Hz, 2H), 7.59 (d, J = 7.40 Hz, 2H), 7.51 (s, 1H), 7.26 (t, J = 7.76 Hz, 1H), 7.13 (d, J = 7.48 Hz, 1H), 6.78 (d, J = 7.40 Hz, 1H), 3.75 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.48, 159.06, 145.28, 138.78, 131.65 (q, J_{C-F} = 32.78 Hz), 128.87, 126.04, 124.66, 122.64 (q, J_{C-F} = 271.09 Hz), 114.51, 112.00, 108.01, 54.46; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.88; **HR-MS** (ESI^+): calcd. for

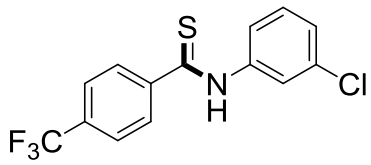
$C_{15}H_{12}F_3NOS$ $[M+H]^+$: 312.0664, Found: 312.0662.



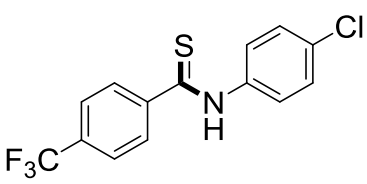
N-(4-methoxyphenyl)-4-(trifluoromethyl)benzothioamide (**3he**). Prepared according to the general procedure to afford a yellow solid in 61% yield, mp 125 ^oC; **^{1}H NMR** (DMSO-d6, 400 MHz) δ 11.89 (s, 1H), 7.97 (d, J = 8.12 Hz, 2H), 7.83 (d, J = 8.24 Hz, 2H), 7.79 - 7.74 (m, 2H), 7.03 - 6.99 (m, 2H), 3.79 (s, 3H); **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 195.20, 157.63, 146.45, 132.96, 130.43C (q, J = 31.74 Hz), 128.34, 125.59, 125.26 (q, J = 3.68 Hz), 124.25 (q, J = 271.98 Hz), 113.87, 55.51; **^{19}F NMR** (377 MHz, DMSO-d6) δ -61.23; **HR-MS** (ESI^+): calcd. for $C_{15}H_{12}F_3NOS$ $[M+H]^+$: 312.0664, Found: 312.0666.



N-(2,5-dimethylphenyl)-4-(trifluoromethyl)benzothioamide (**3hf**)**.** Prepared according to the general procedure to afford a yellow solid in 94% yield, mp 95 ^oC; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.76 (s, 1H), 7.89 (d, J = 7.92 Hz, 2H), 7.62 (d, J = 8.04 Hz, 2H), 7.25 (s, 1H), 7.13 (d, J = 7.76 Hz, 1H), 7.04 (d, J = 7.60 Hz, 1H), 2.29 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.80, 144.18, 135.88, 131.78 (q, J_{C-F} = 32.74 Hz), 129.96, 129.93, 128.27, 126.13, 125.87, 124.66 (q, J_{C-F} = 3.70 Hz), 122.65 (q, J_{C-F} = 270.73 Hz), 19.92, 16.45; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.89; **HR-MS** (ESI^+): calcd. for $C_{16}H_{14}F_3NS$ $[M+H]^+$: 310.0872, Found: 310.0877.

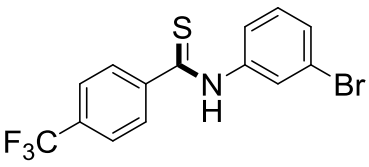


N-(3-chlorophenyl)-4-(trifluoromethyl)benzothioamide (**3hi**). Prepared according to the general procedure to afford a yellow solid in 90% yield, mp 113^oC; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.01 (s, 1H), 7.87 (s, 3H), 7.67 (d, J = 7.20 Hz, 2H), 7.61 (d, J = 5.20 Hz, 1H), 7.35 (d, J = 6.84 Hz, 1H), 7.28 (d, J = 7.44Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 197.04, 145.86, 139.61, 134.74, 132.90 (q, J_{C-F} = 32.66 Hz). 130.17, 127.35, 127.07, 125.75, 123.63, 123.59 (q, J_{C-F} = 270.96 Hz), 121.72; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.90; **HR-MS** (ESI^+): calcd. for $C_{14}H_9ClF_3NS$ $[M+H]^+$: 316.0169, Found: 316.0167.

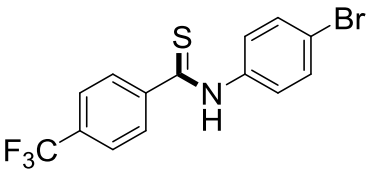


N-(4-chlorophenyl)-4-(trifluoromethyl)benzo thioamide (**3hj**). Prepared according to the general procedure to afford a yellow solid in 71% yield, mp 173^oC; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.99 (s, 1H), 7.92 (d, J = 7.88 Hz, 2H), 7.72 (dq, J = 8.68 Hz, J = 4.92 Hz, 4H), 7.43 (d, J = 8.40 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.89, 144.89, 136.09, 131.87 (q, J = 35.84 Hz), 131.45, 128.28, 126.05, 124.73, 123.89, 122.56 (q, J = 271.56 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.88; **HR-MS** (ESI^+):

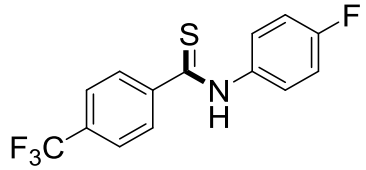
calcd. for $C_{14}H_9ClF_3NS$ $[M+H]^+$: 316.0169, Found: 316.0173.



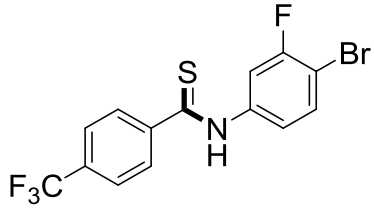
N-(3-bromophenyl)-4-(trifluoromethyl)benzothioamide (**3hk**). Prepared according to the general procedure to afford a yellow solid in 50% yield, mp 98°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.05 (s, 1H), 7.99 (s, 1H), 7.88 (d, J = 6.60 Hz, 2H), 7.67 (d, J = 7.00 Hz, 3H), 7.43 (d, J = 7.60 Hz, 1H), 7.30 (t, J = 7.34 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.03, 144.77, 138.72, 131.85 (q, J = 32.12 Hz). 129.37, 129.22, 126.06, 125.47, 124.70 (q, J = 3.92 Hz), 122.58 (q, J = 270.96 Hz), 121.50, 121.23; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.88; **HR-MS** (ESI^+): calcd. for $C_{14}H_9BrF_3NS$ $[M+H]^+$: 359.9664, Found: 359.9666.



N-(4-bromophenyl)-4-(trifluoromethyl)benzothioamide (**3hl**). Prepared according to the general procedure to afford a yellow solid in 74% yield, mp 126-127°C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.98 (s, 1H), 7.91 (d, J = 7.68 Hz, 2H), 7.69 (t, J = 6.70 Hz, 4H), 7.57 (d, J = 8.32 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.82, 144.93, 136.62, 131.88 (q， J = 30.19 Hz), 131.24, 126.03, 124.73 (q, J = 3.59 Hz), 124.10, 121.51 (q, J = 270.83 Hz), 119.28; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.89; **HR-MS** (ESI^+): calcd. for $C_{14}H_9BrF_3NS$ $[M+H]^+$: 359.9664, Found: 359.9662.

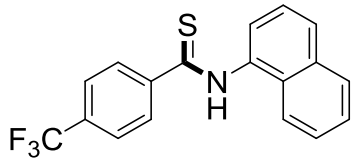


N-(4-fluorophenyl)-4-(trifluoromethyl)benzothioamide (**3hm**). Prepared according to the general procedure to afford a yellow solid in 98% yield, mp 180 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.91 (s, 1H), 7.85 (d, J = 7.80 Hz, 2H), 7.62 (t, J = 7.32 Hz, 4H), 7.08 (t, J = 8.24 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.17, 159.99 (d, J = 246.61 Hz), 144.76, 133.57 (d, J = 2.85 Hz), 131.84 (q, J = 32.60 Hz), 126.05, 124.92 (d, J = 8.24 Hz), 124.73 (d, J = 3.55 Hz), 122.59 (q, J = 270.90 Hz), 115.06 (d, J = 22.71 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.91, -113.02; **HR-MS** (ESI^+): calcd. for $C_{14}H_9F_4NS$ $[M+H]^+$: 300.0465, Found: 300.0459.

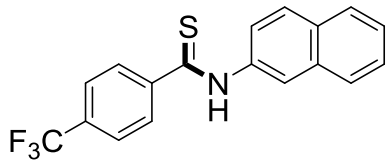


N-(4-bromo-3-fluorophenyl)-4-(trifluoromethyl)-benzothioamide (**3hm**)**.** Prepared according to the general procedure to afford a yellow solid in 86% yield, mp 146 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.01 (s, 1H), 7.88 (d, J = 4.8 Hz, 3H), 7.68 (d, J = 7.88 Hz, 2H), 7.59 (t, J = 7.66 Hz, 1H), 7.35 (d, J = 12.60 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.96, 158.90 (d, J_{C-F} = 246.61 Hz), 139.08 (d, J_{C-F} = 9.71 Hz), 133.67, 133.00 (q, J_{C-F} = 32.94 Hz), 127.06, 125.81 (d, J_{C-F} = 3.59 Hz), 123.56 (q, J_{C-F} = 270.97 Hz), 119.94 (d, J_{C-F} = 3.59 Hz),

111.74, 111.47, 106.77 (d, J_{C-F} = 21.11 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.93, -103.92; **HR-MS** (ESI^+): calcd. for $C_{14}H_8BrF_4NS$ $[M+H]^+$: 377.9570, Found: 377.9577.



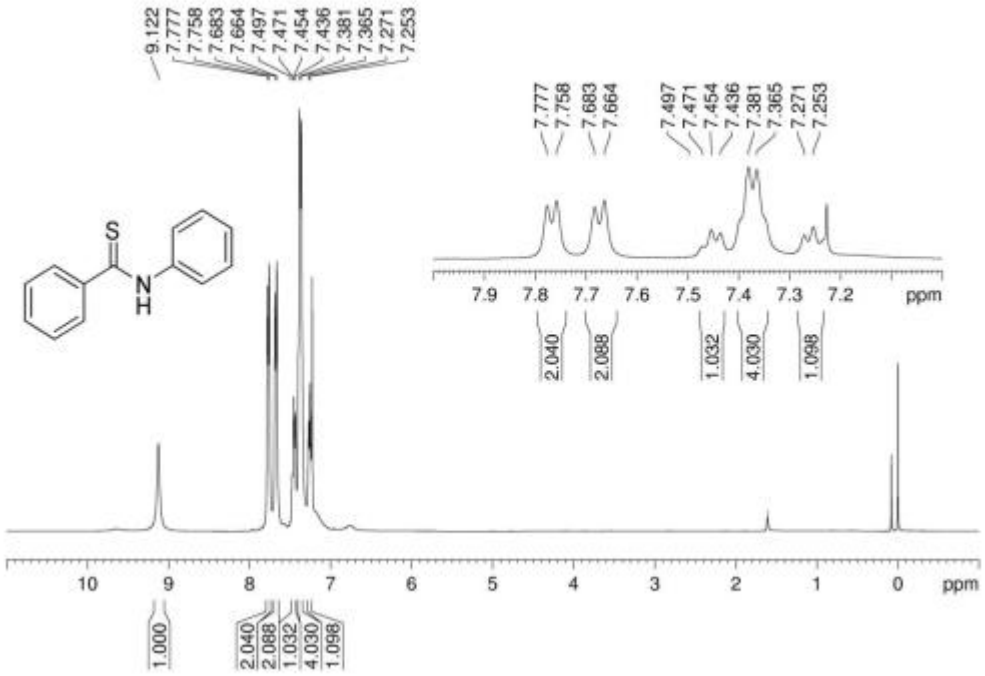
N-(naphthalen-1-yl)-4-(trifluoromethyl)benzothioamide (**3ho**). Prepared according to the general procedure to afford a yellow solid in 52% yield, mp 150 ^oC; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.25 (s, 1H), 8.06 (d, J = 8.00 Hz, 2H), 7.95 - 7.88 (m, 2H), 7.84 (t, J = 4.50 Hz, 1H), 7.76 (d, J = 7.28 Hz, 1H), 7.72 (d, J = 8.08 Hz, 2H), 7.55 (t, J = 7.84 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.89, 145.07, 134.53, 134.33, 132.94 (q, J_{C-F} = 32.20 Hz), 128.91, 128.84, 128.66 , 127.26, 127.09, 126.63, 125.75 (q, J_{C-F} = 3.66 Hz), 125.45, 124.71, 123.68 (q, J_{C-F} = 271.04 Hz), 121.63; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.84; **HR-MS** (ESI^+): calcd. for $C_{18}H_{12}F_3NS$ $[M+H]^+$: 332.0715, Found: 332.0720.

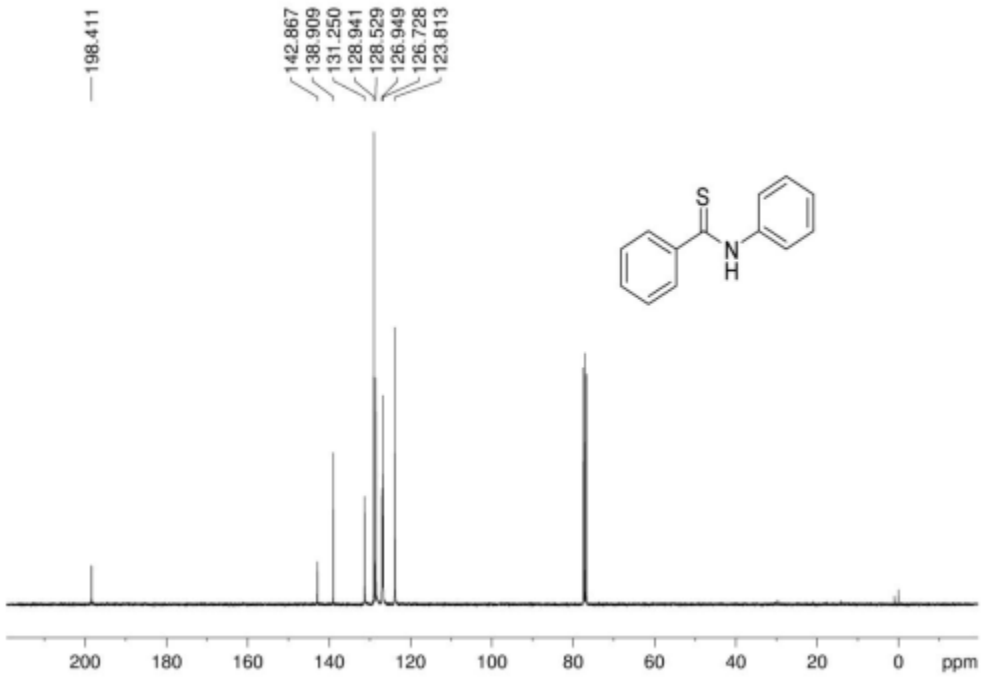


N-(naphthalen-1-yl)-4-(trifluoromethyl)benzothioamide (**3hp**). Prepared according to the general procedure to afford a yellow solid in 58% yield, mp 185 ^oC; **^{1}H NMR** (DMSO-d6, 400 MHz) δ 12.21 (s, 1H), 8.56 (d, J = 1.84 Hz, 2H), 7.99 (d, J = 8.88 Hz, 1H), 7.94 (q, J = 2.57 Hz, 2H), 7.87 (dd, J = 1.72 Hz, J = 8.60 Hz, 3H), 7.56-7.53 (m, 2H); **^{13}C NMR** ($DMSO-d_6$, 100 MHz) δ 196.61, 146.65, 137.86, 133.25, 131.88, 130.88 (q, J_{C-F} = 31.79 Hz), 129.29 (d, J_{C-F} = 12.41 Hz), 128.69, 128.62, 128.31, 128.07, 127.06, 126.65, 125.60 (q, J_{C-F} = 3.72 Hz), 124.49, 123.90; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.21; **HR-MS** (ESI^+): calcd. for $C_{18}H_{12}F_3NS$ $[M+H]^+$: 332.0715, Found: 322.0716.

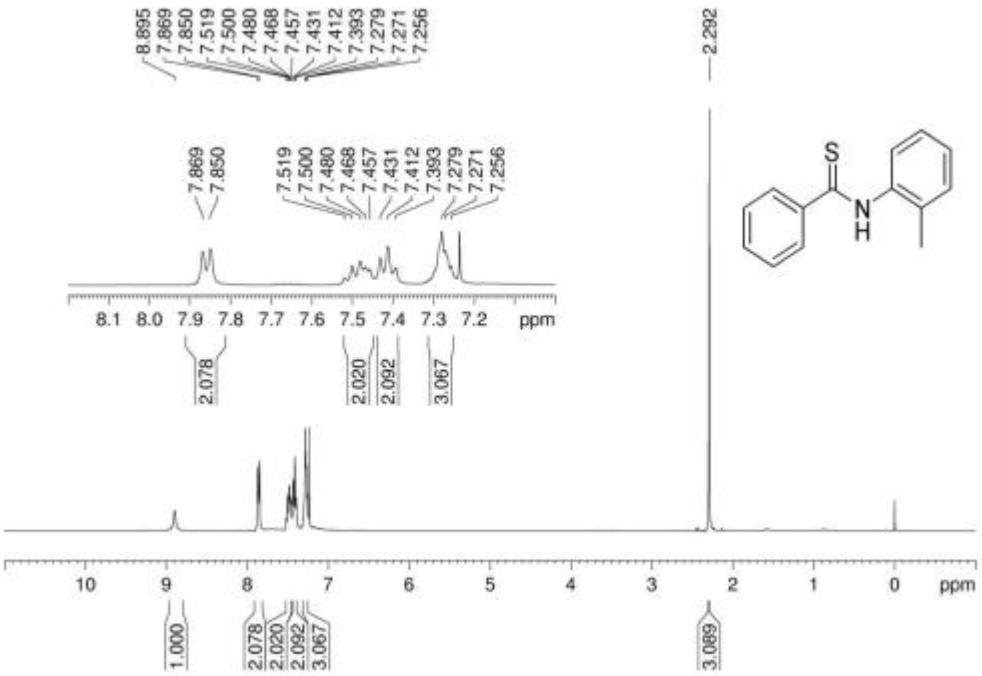
8. NMR spectra

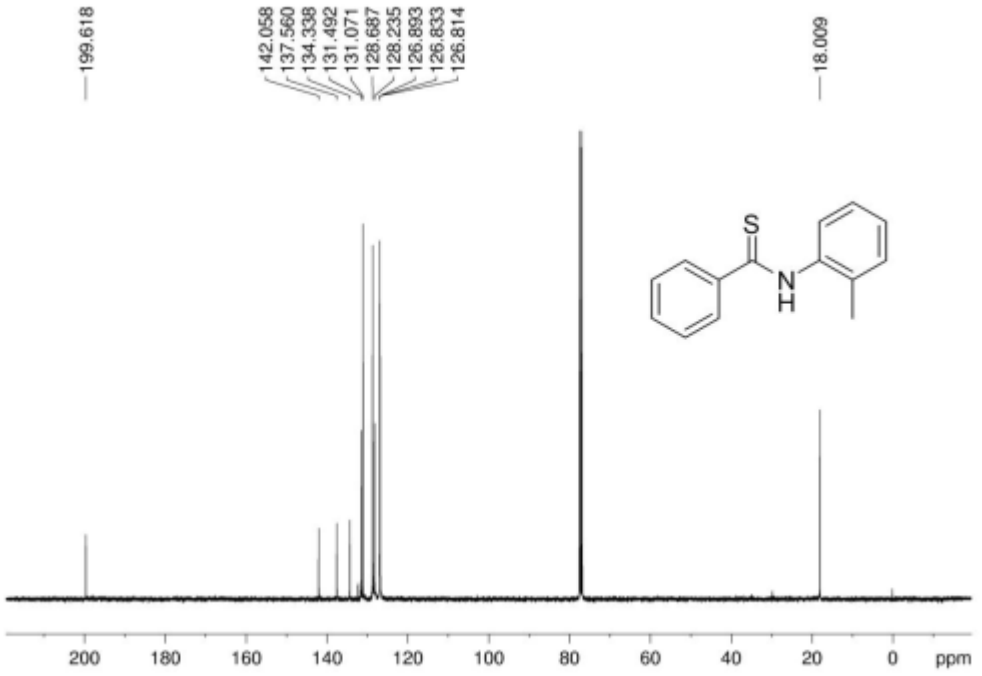
Compound 3aa





Compound 3ab





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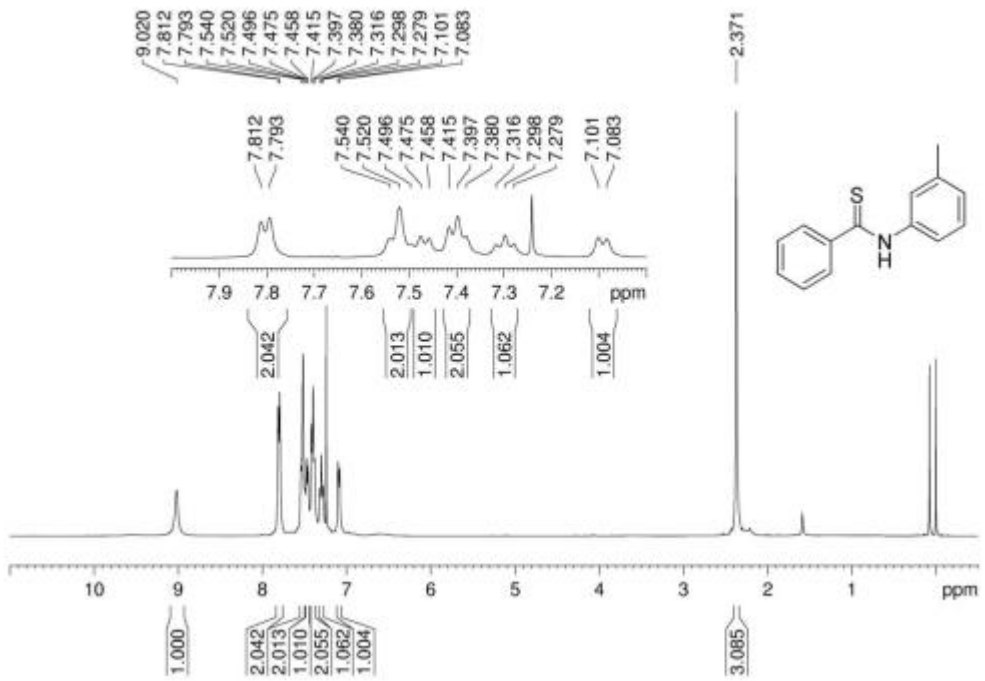
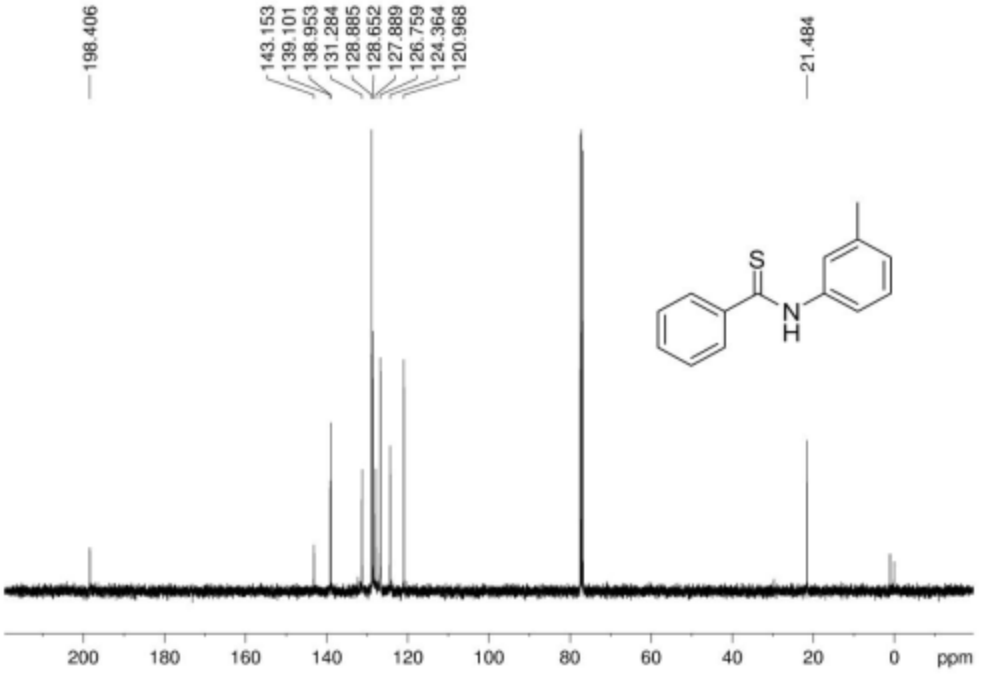
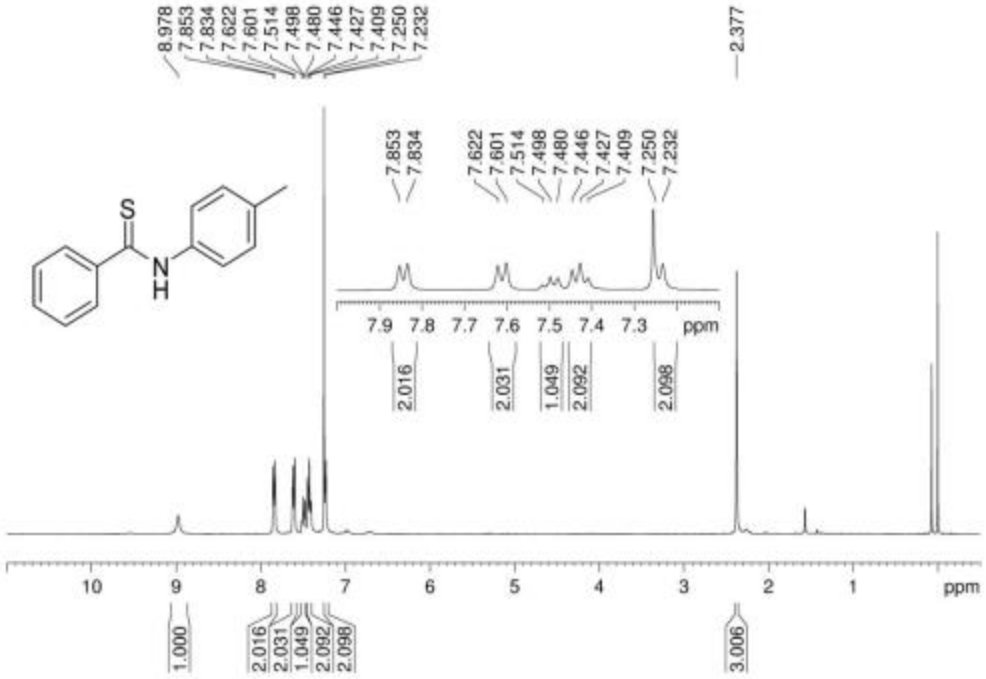
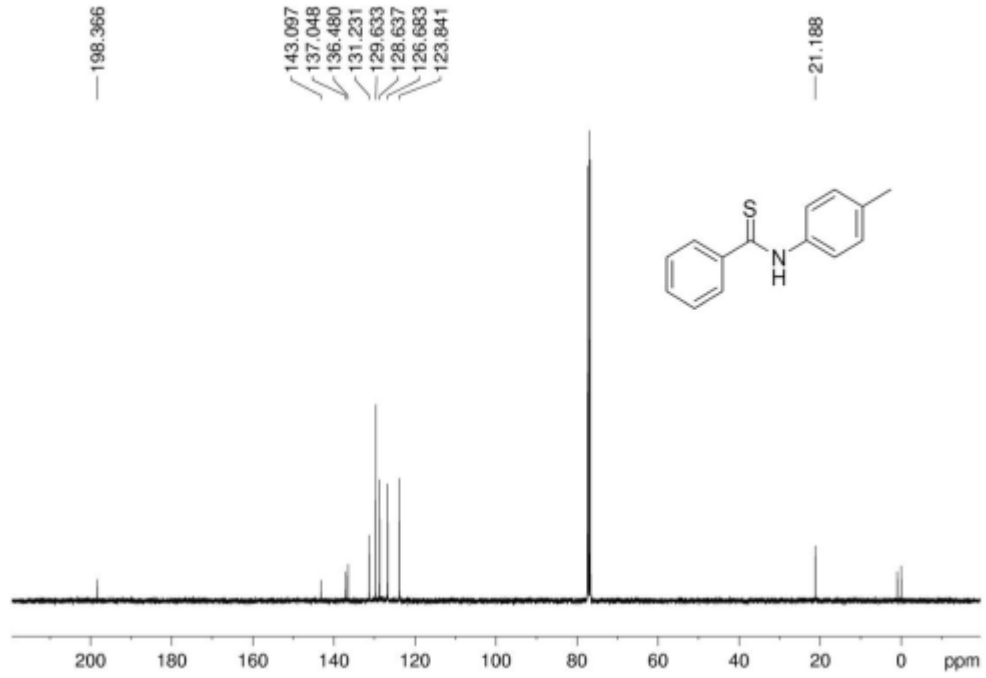


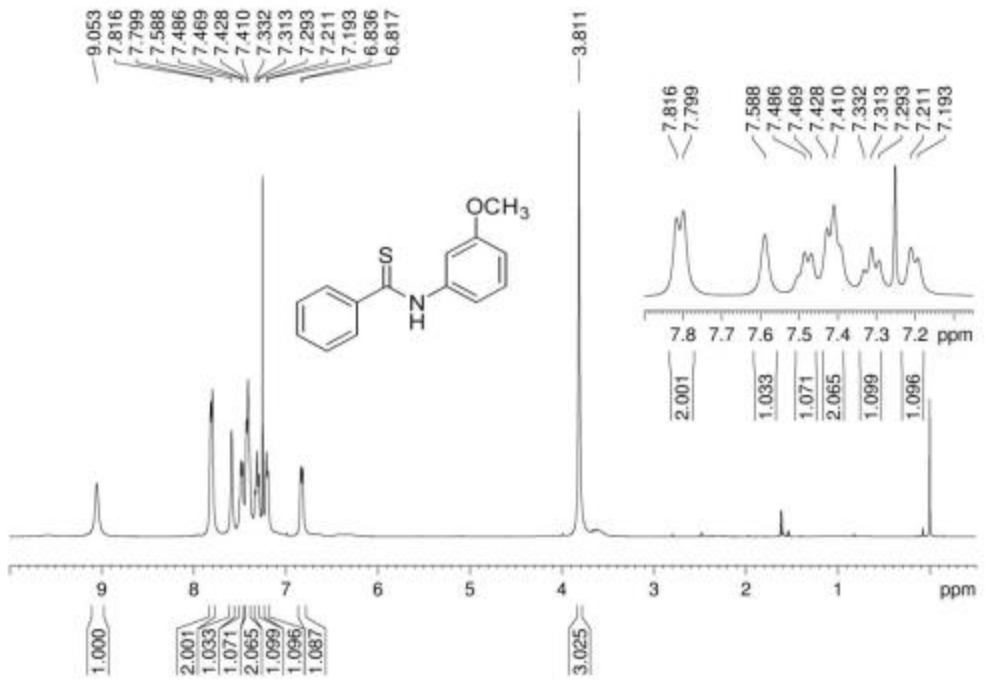


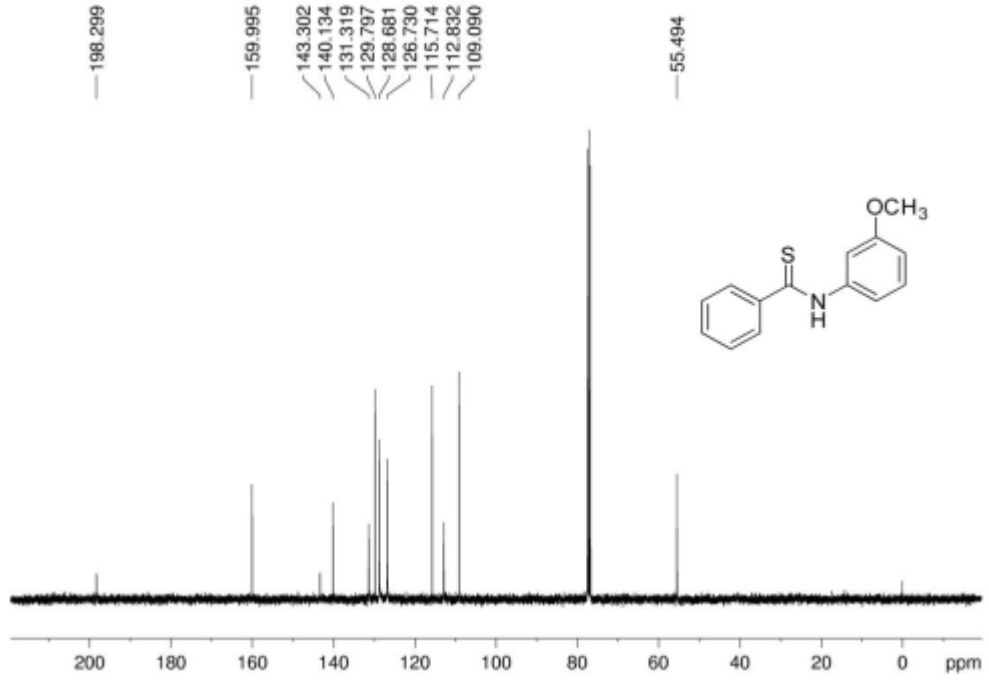
Compound 3ad



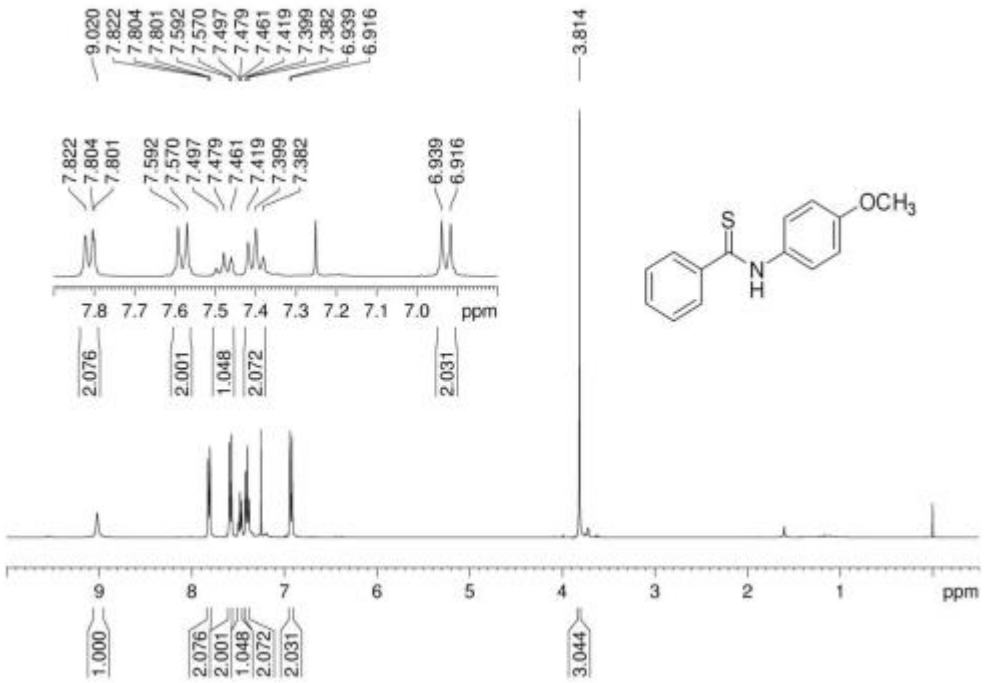


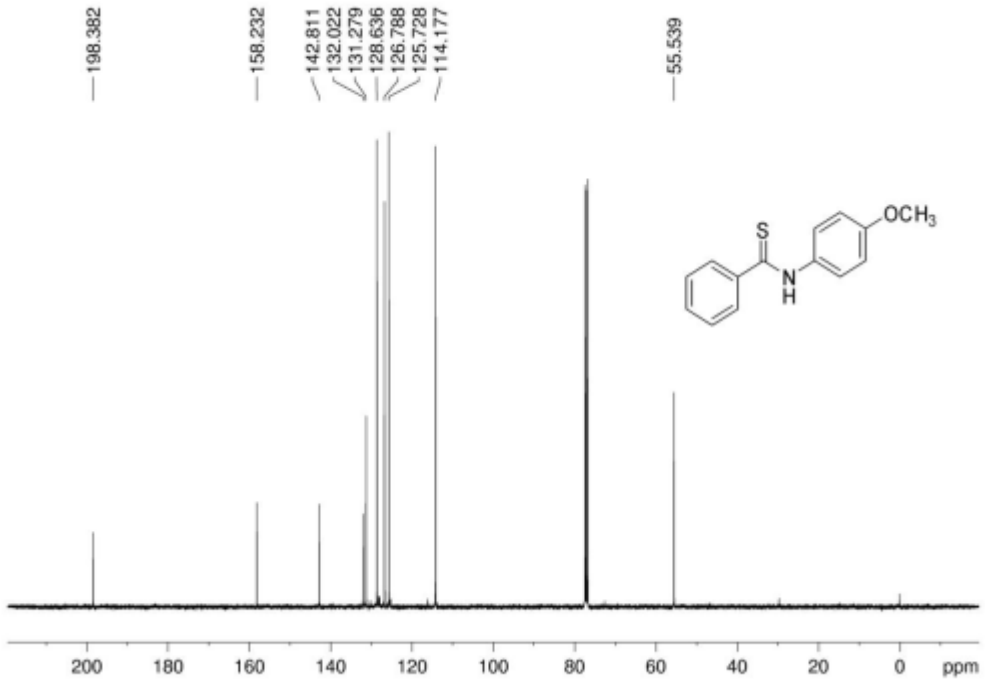
Compound 3ae



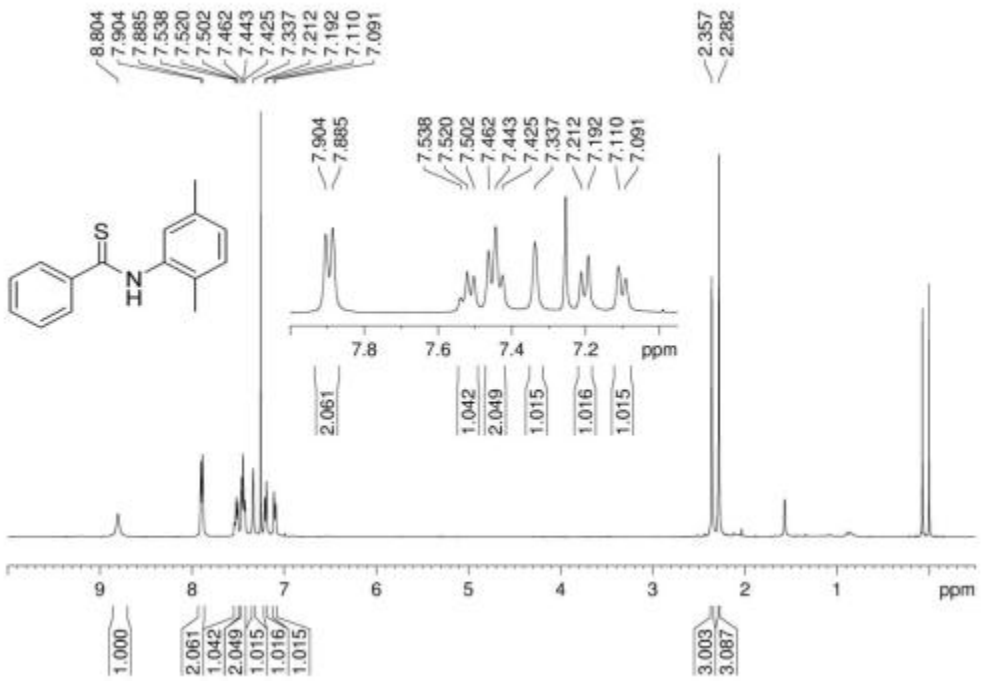


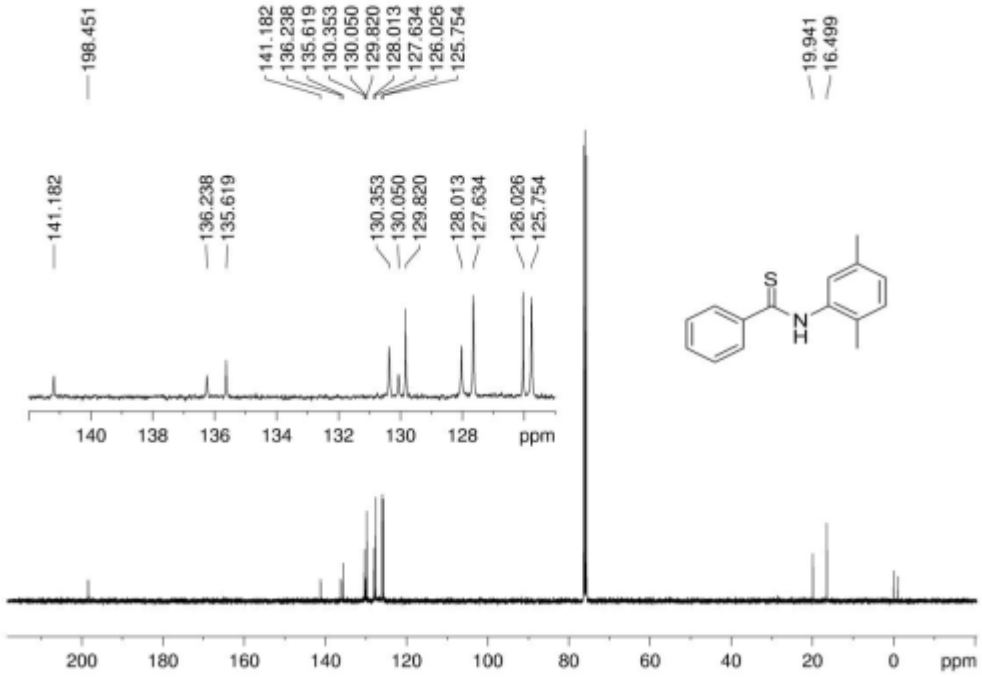
Compound 3af



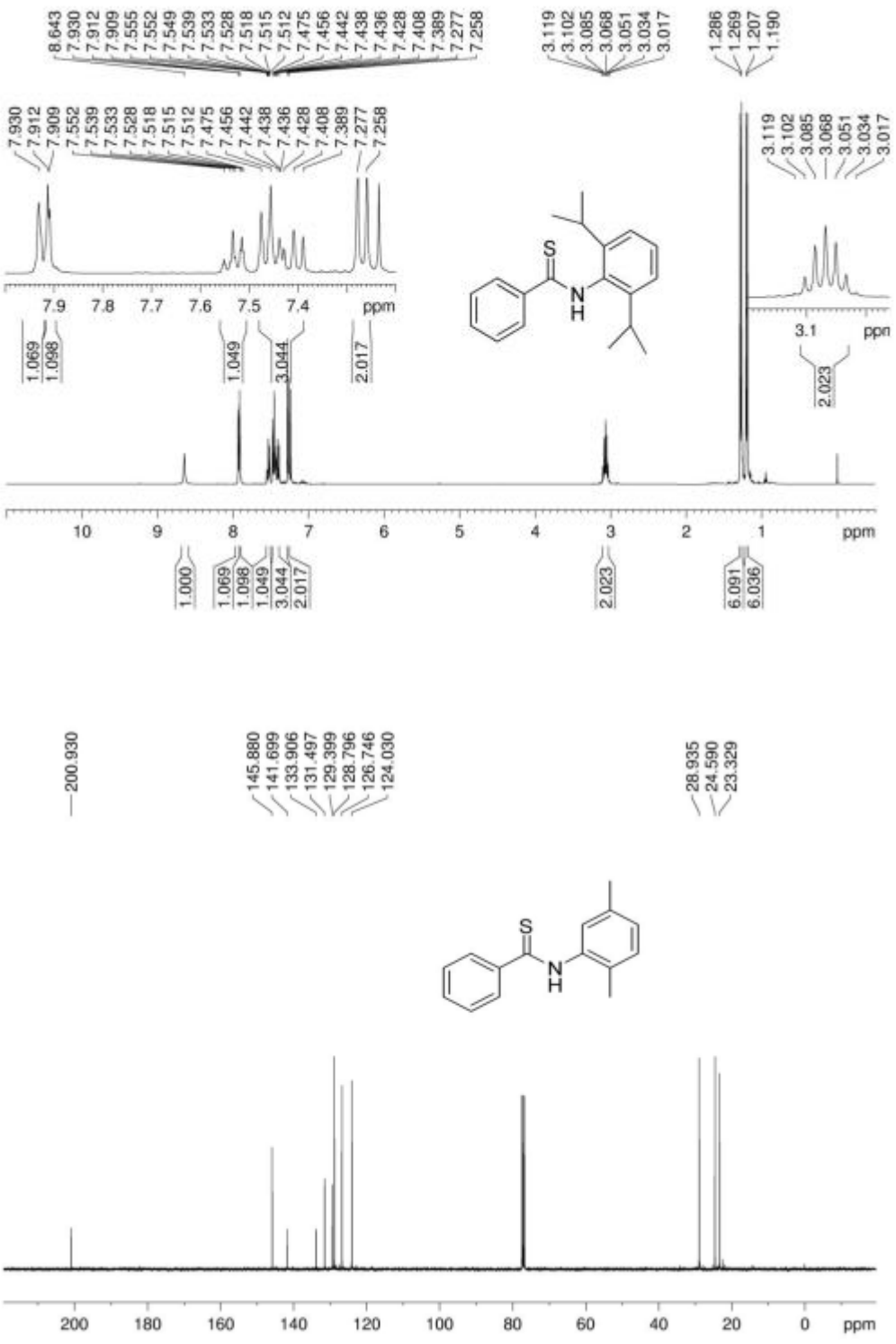


Compound 3ag

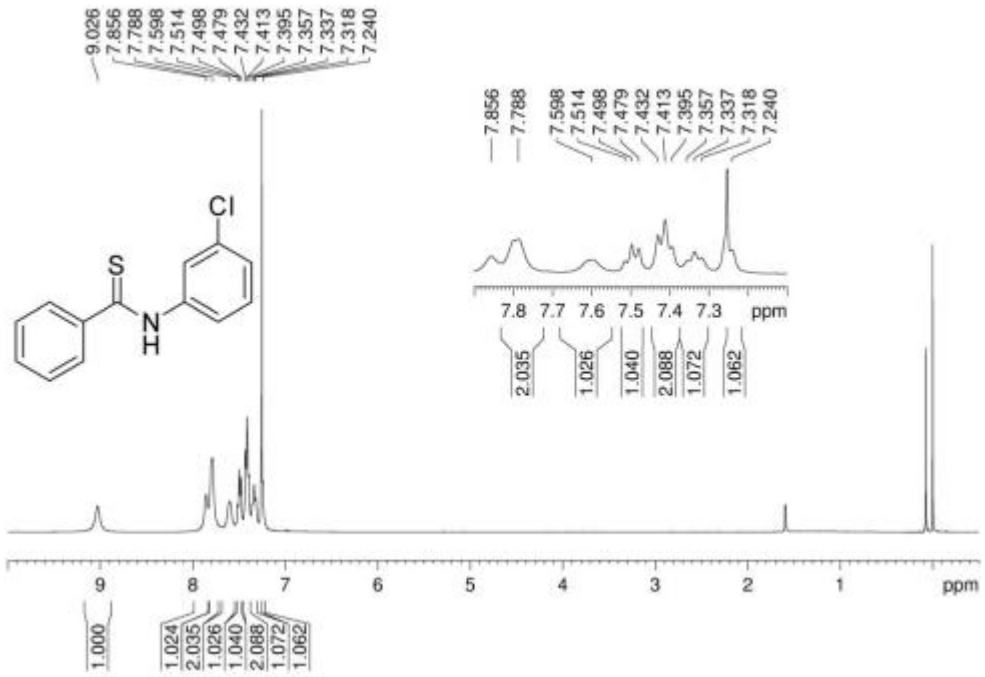


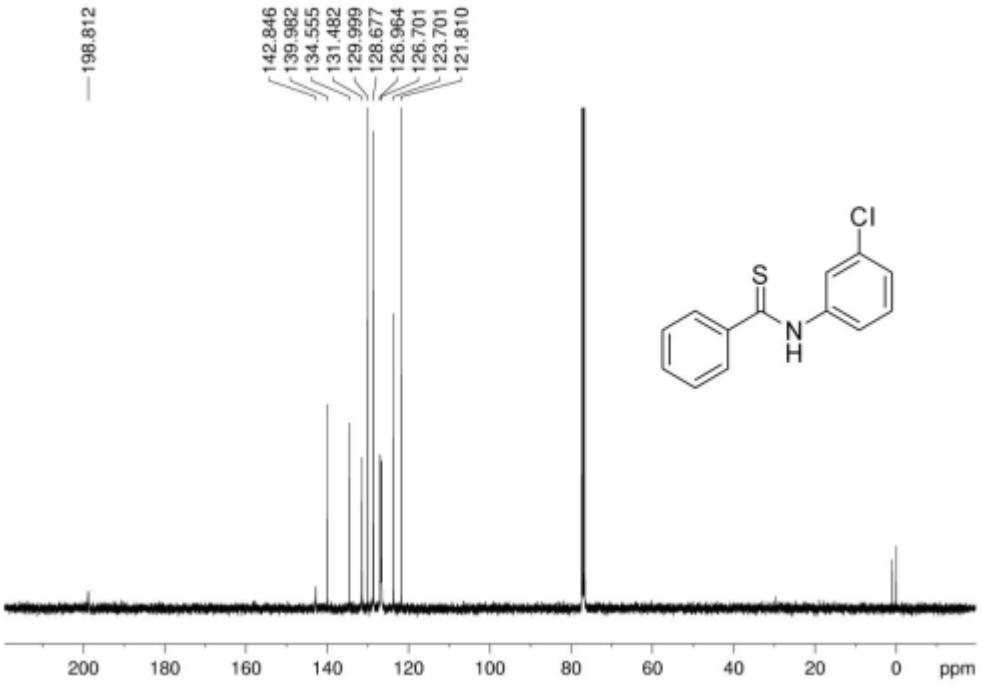


Compound 3ah

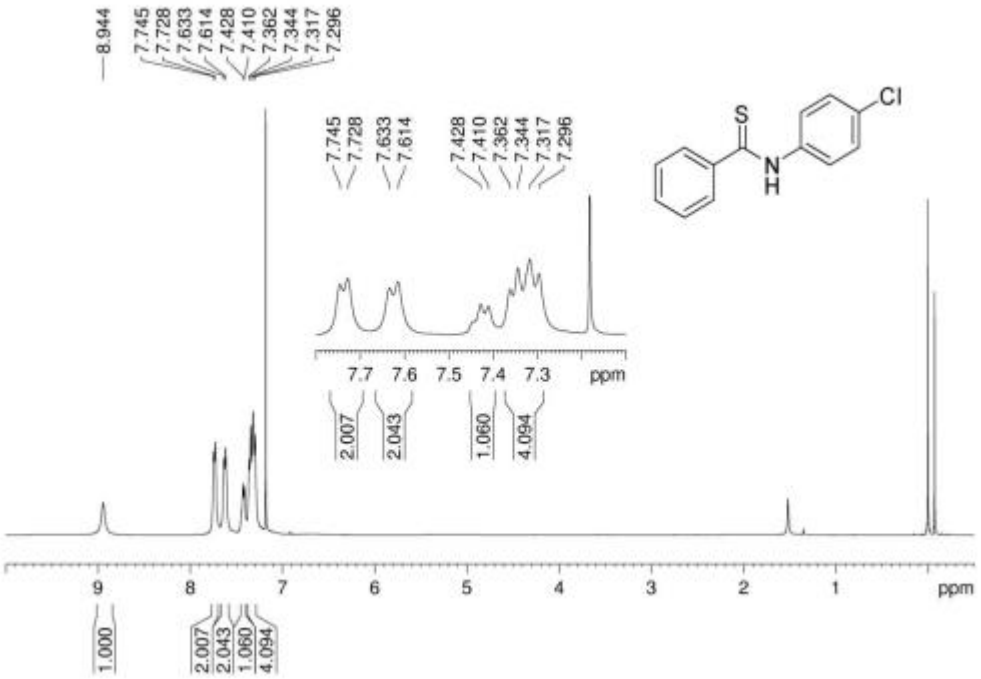


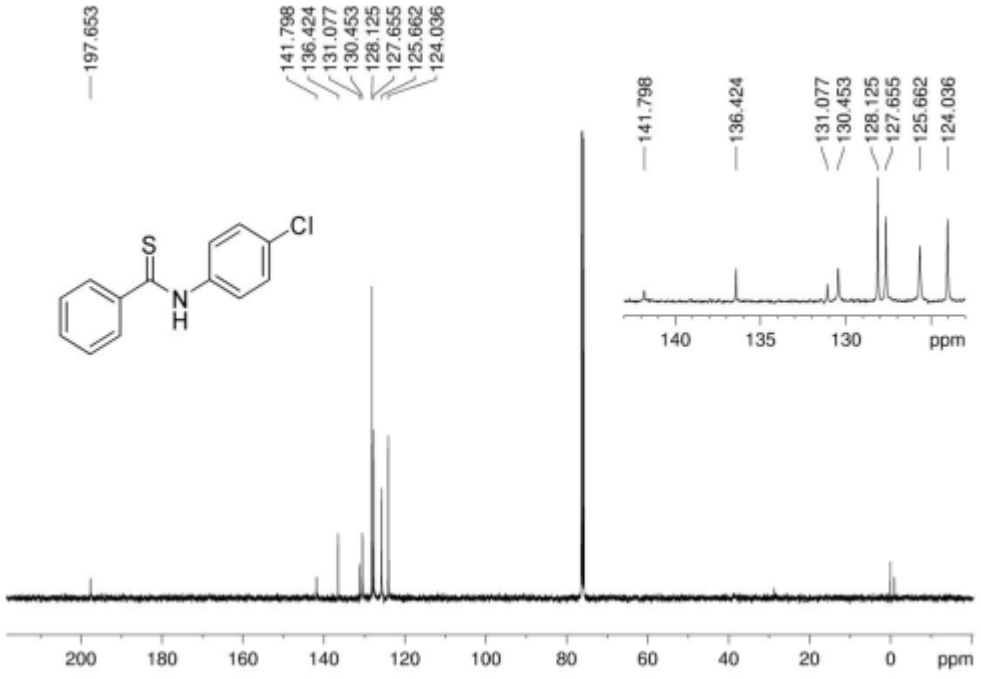
Compound 3ai



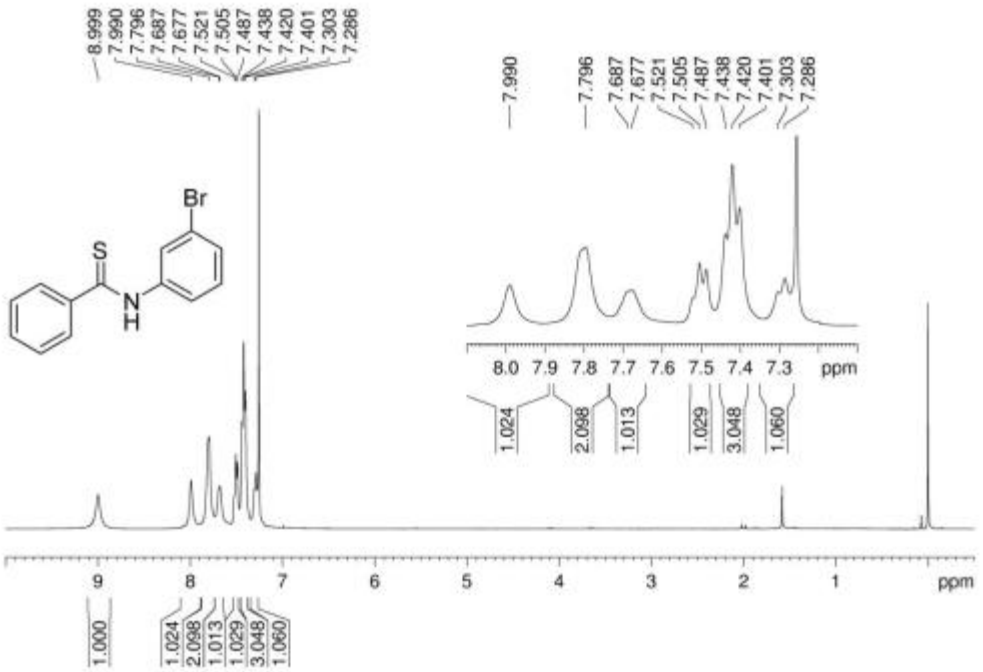


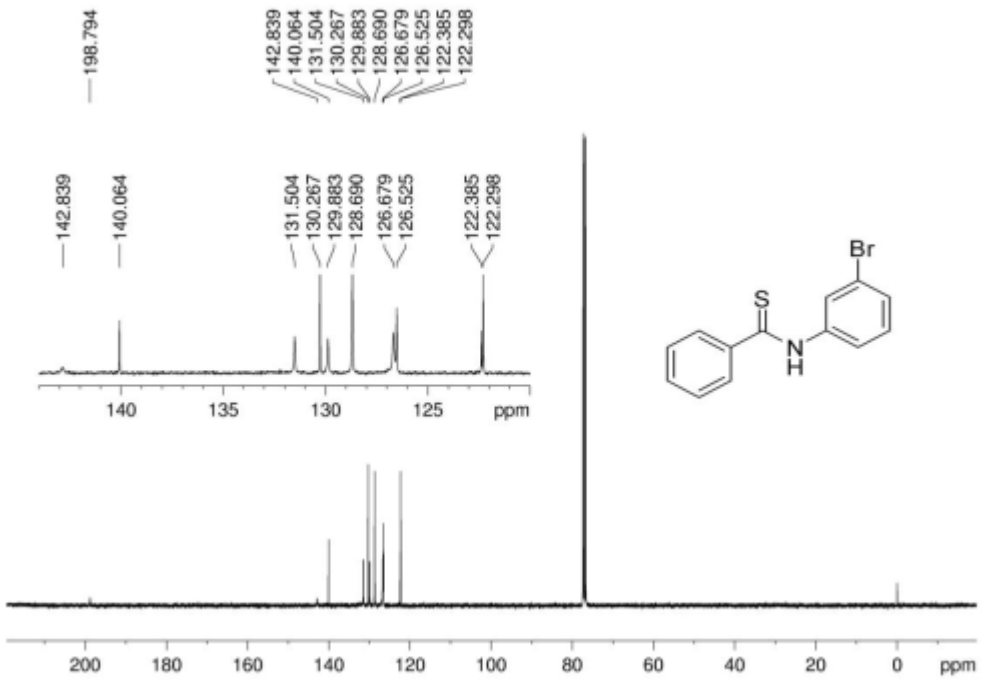
Compound 3aj



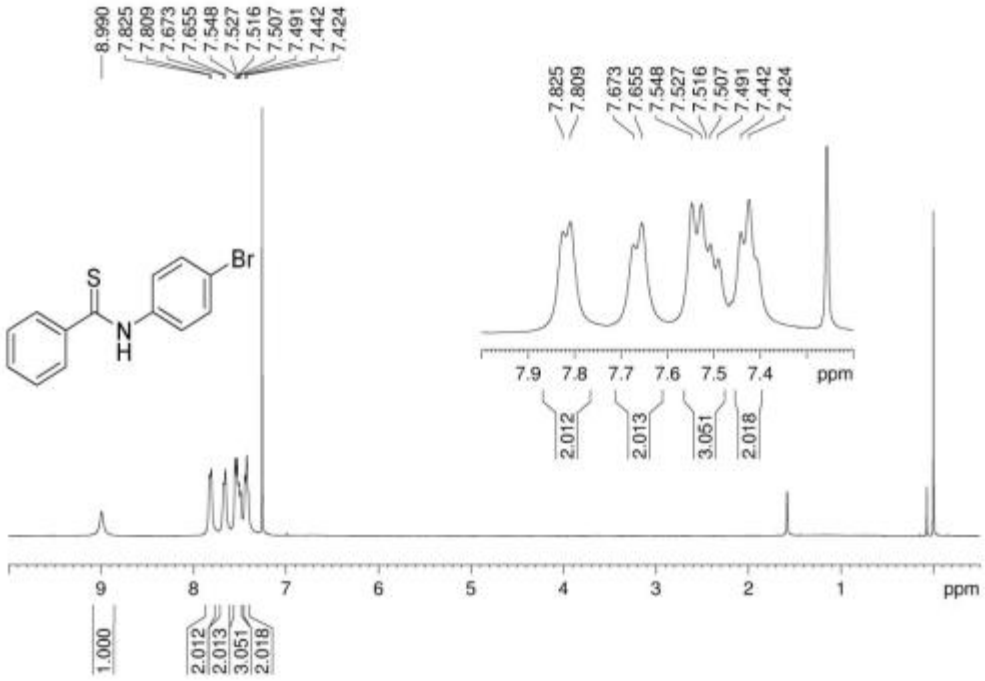


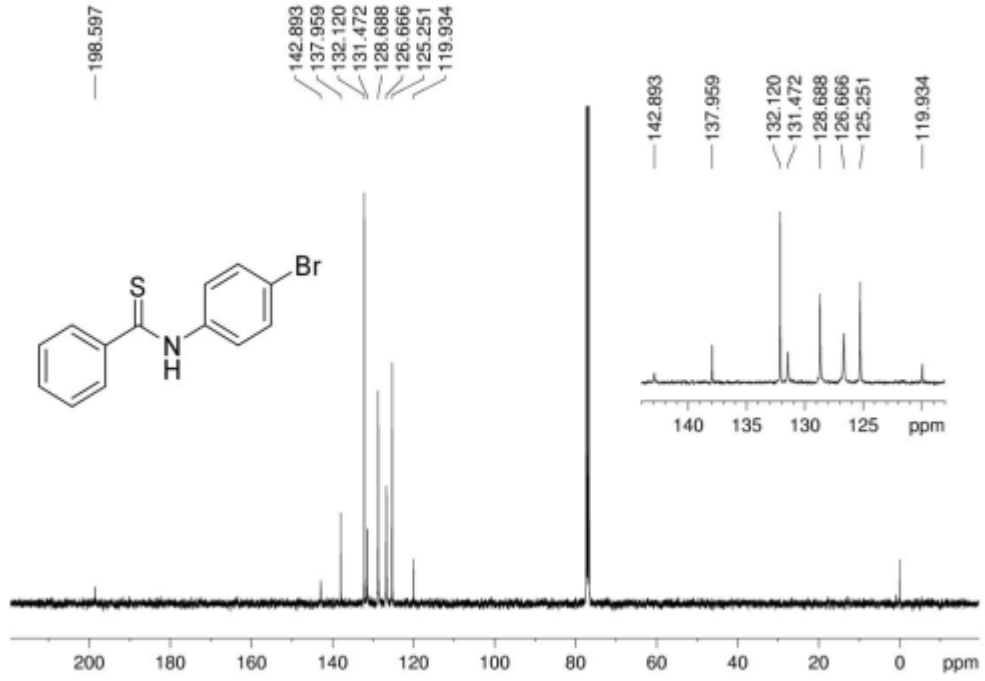
Compound 3ak



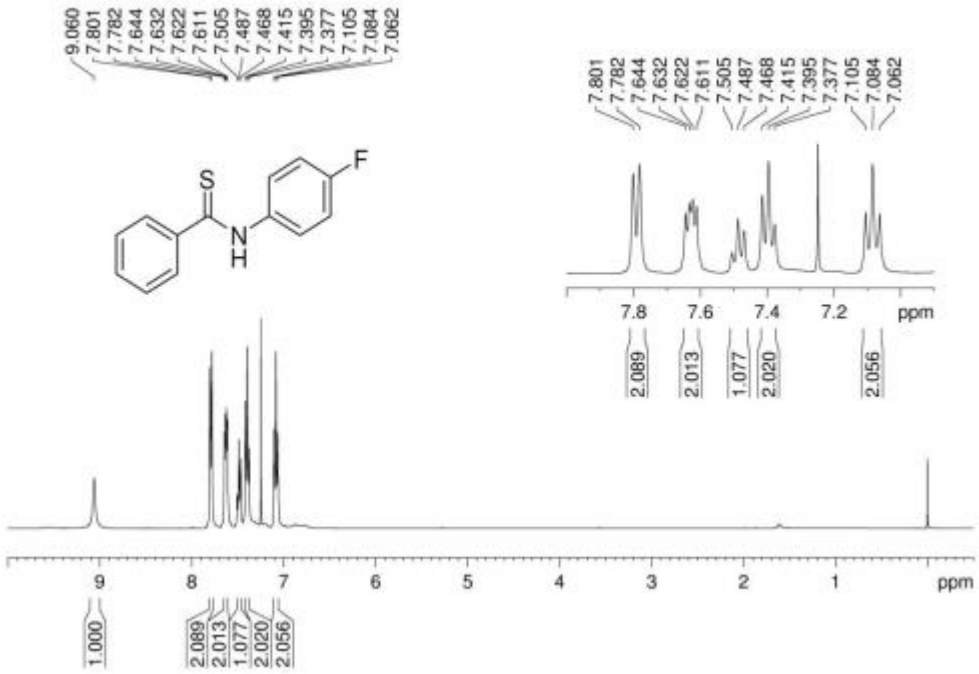


Compound 3al





Compound 3am


9.060
7.801
7.782
7.644
7.632
7.622
7.611
7.505
7.487
7.468
7.415
7.395
7.377
7.105
7.084
7.062
S
N
H
F
7.8
7.6
7.4
7.2
ppm
2.089
2.013
1.077
2.020
2.056
9
8
7
6
5
4
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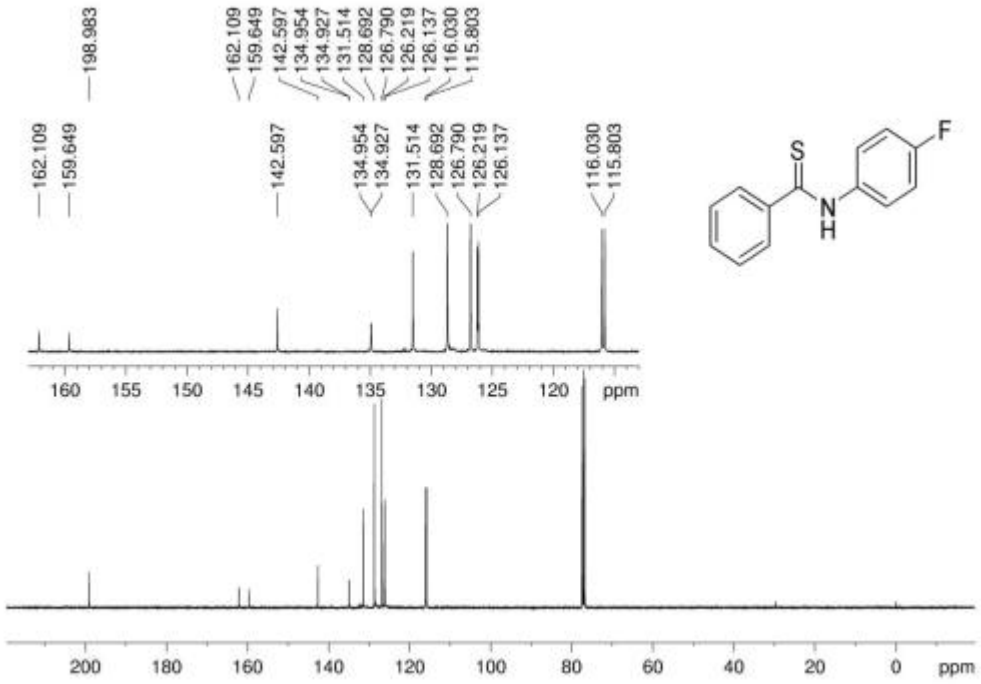
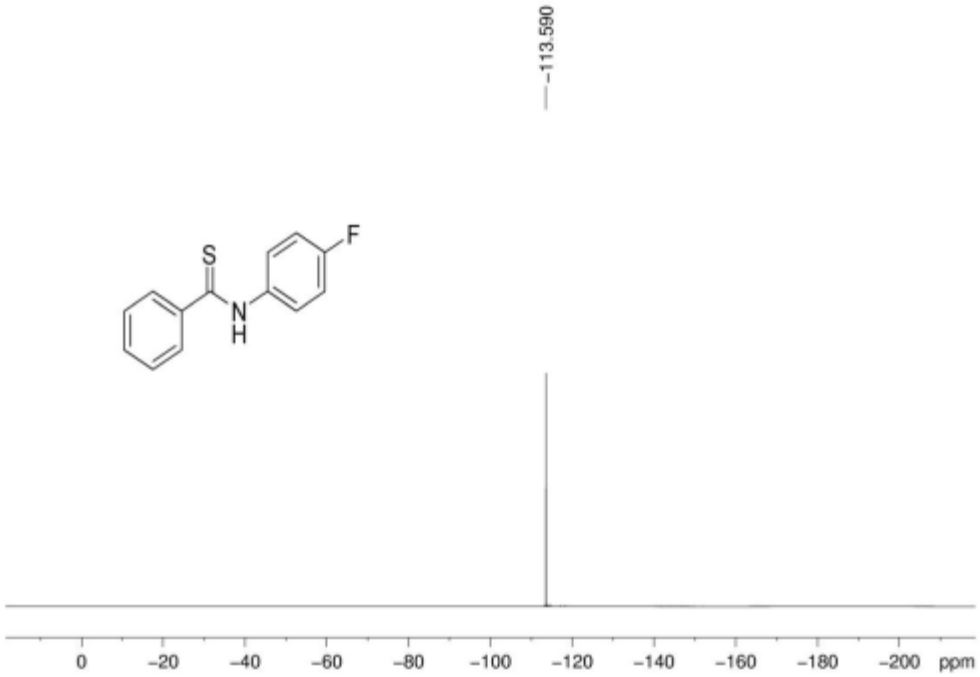
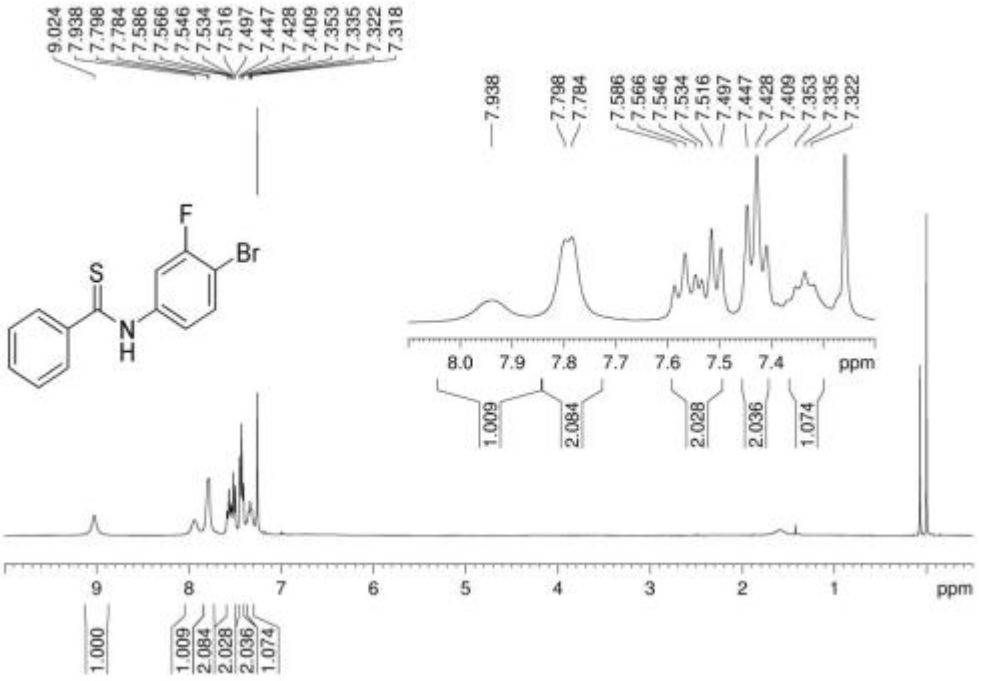
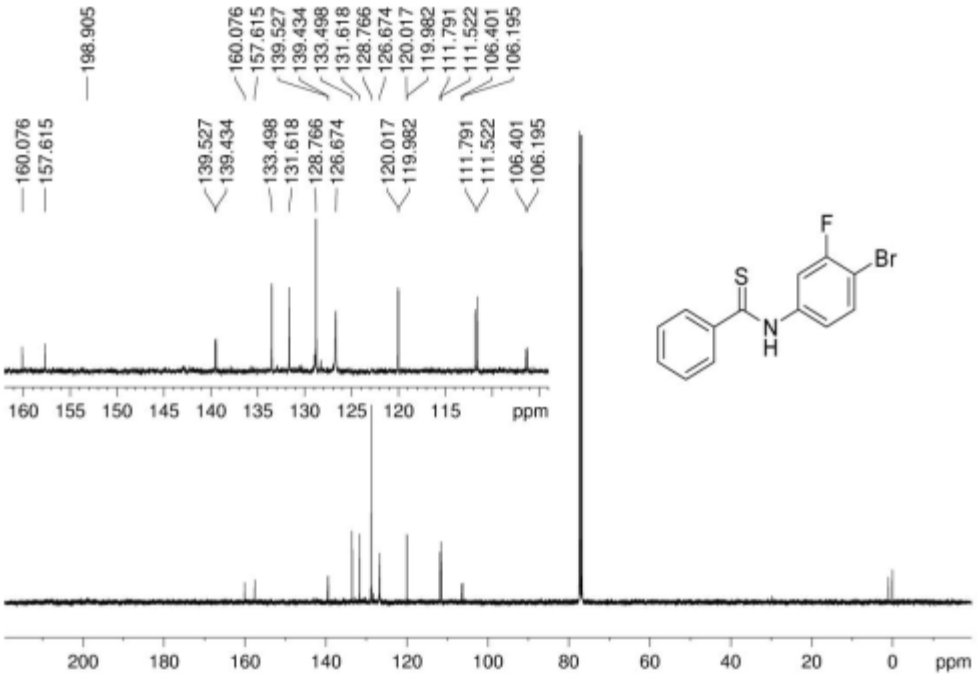
1.000
2.089
2.013
1.077
2.020
2.056

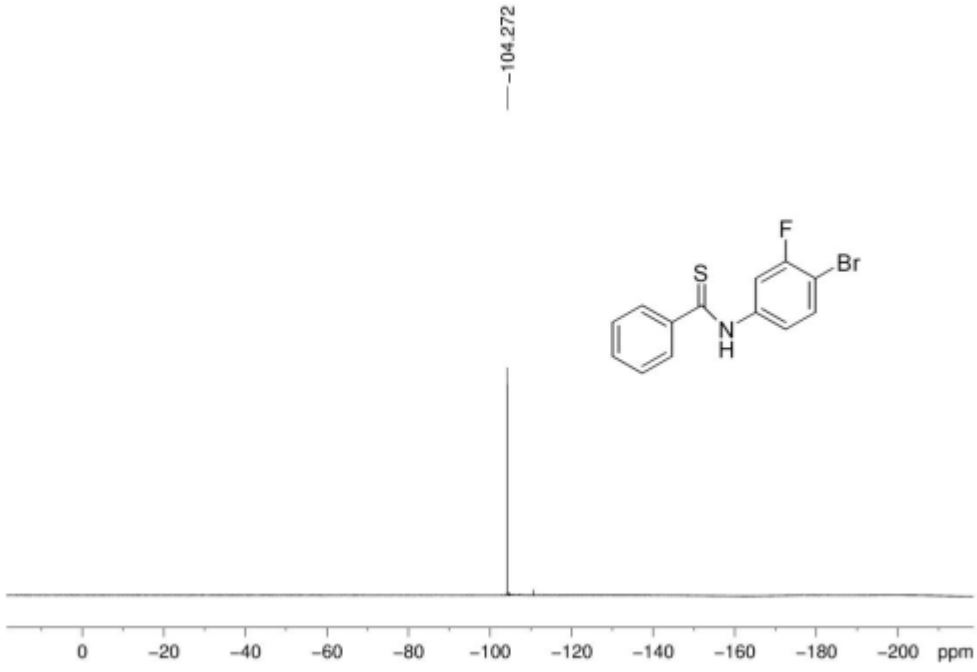

198.983
162.109
159.649
142.597
134.954
134.927
131.514
128.692
126.790
126.219
126.137
116.030
115.803
S
N
H
F
160
155
150
145
140
135
130
125
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



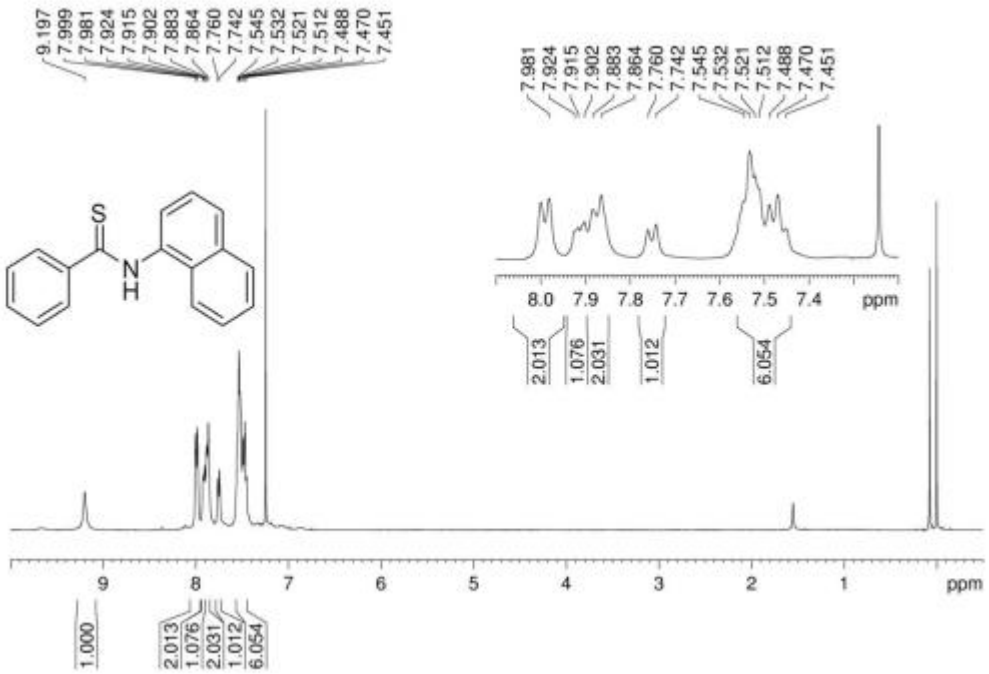
Compound 3an

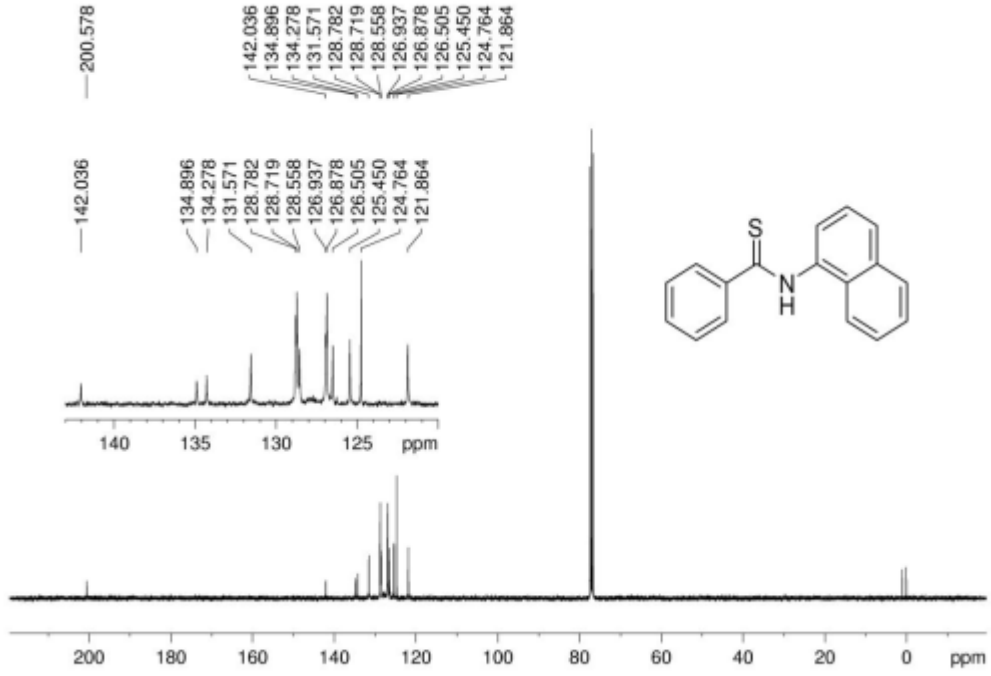




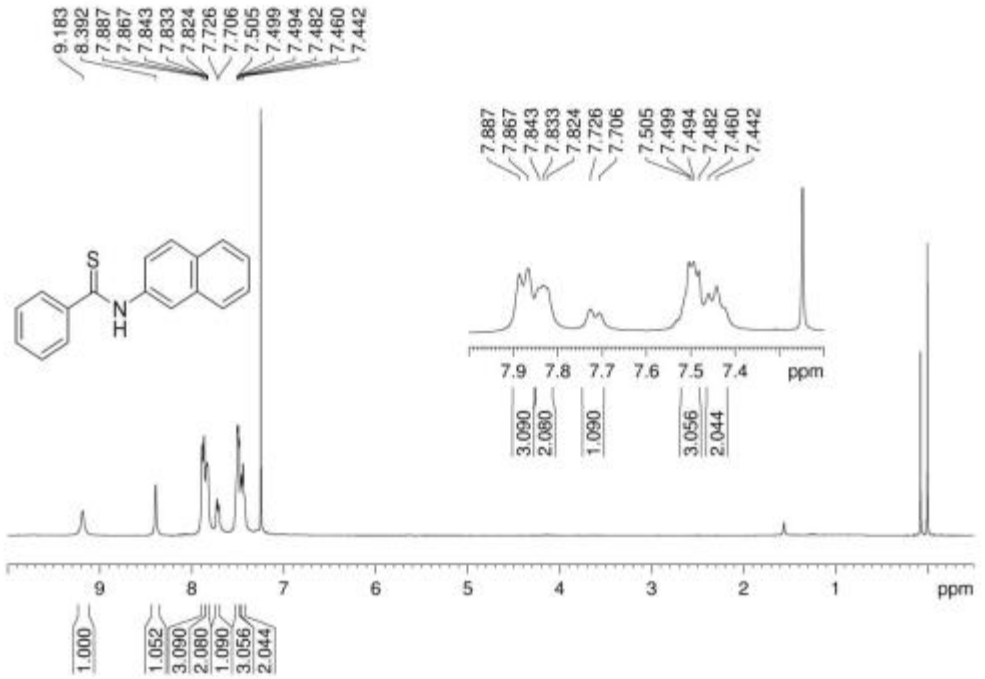


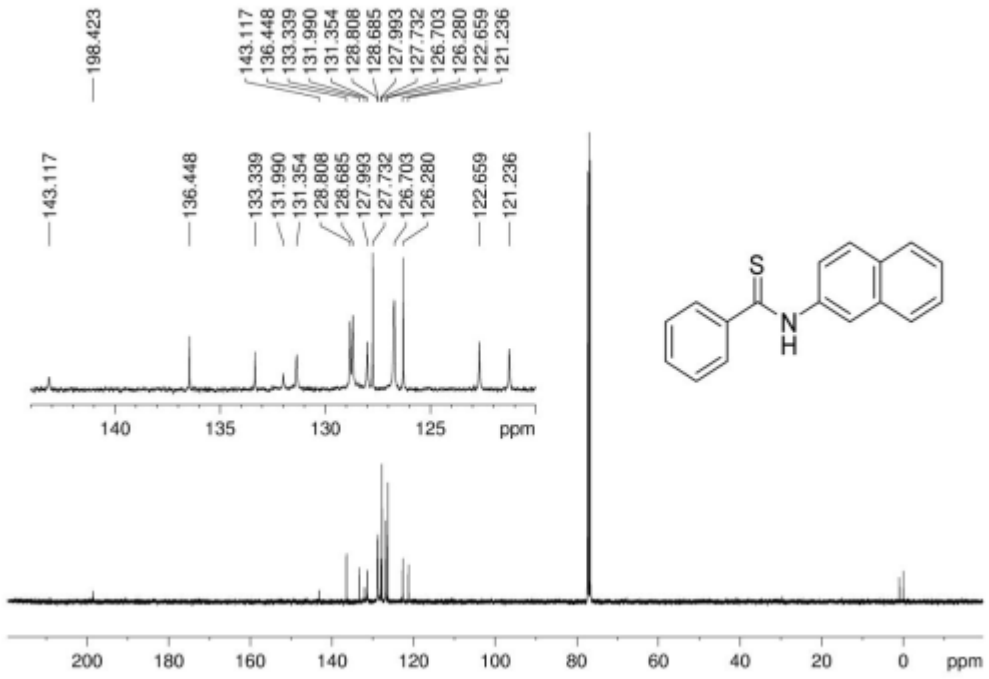
Compound 3ao



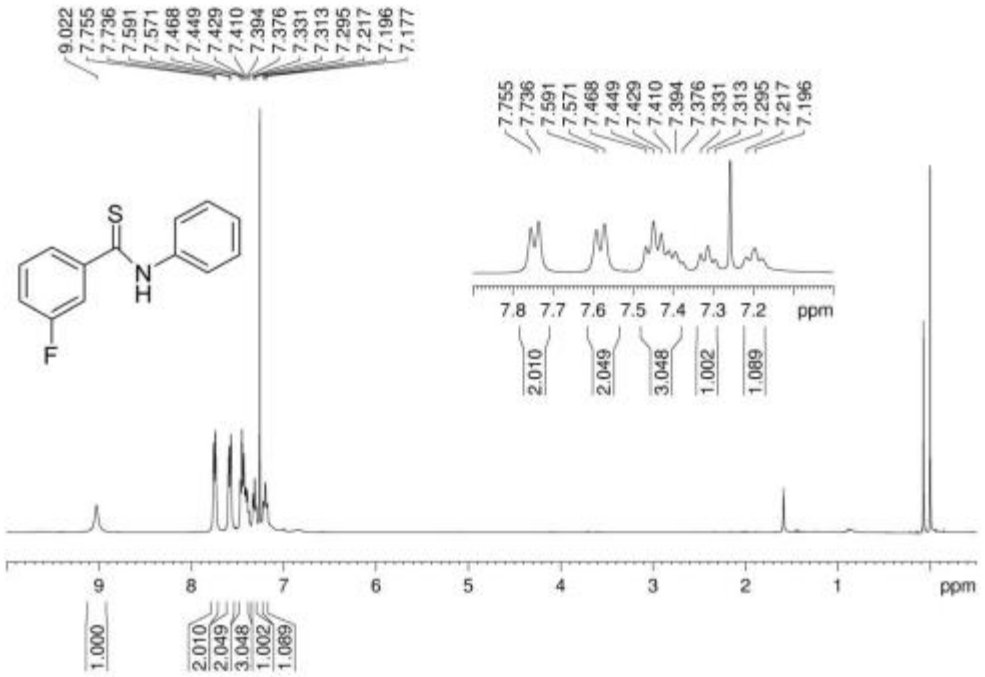


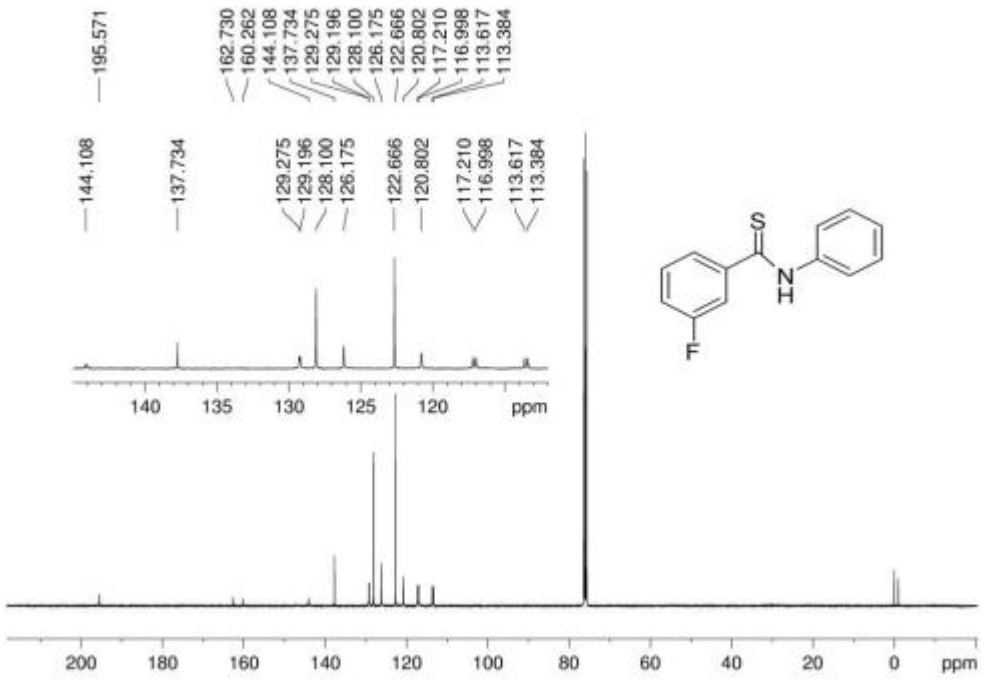
Compound 3ap

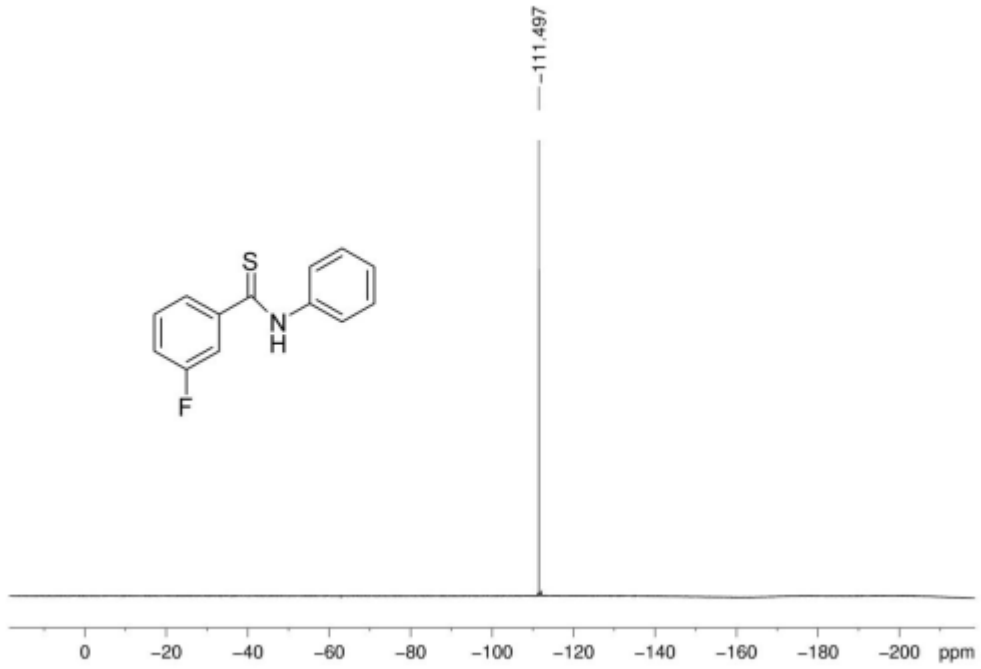




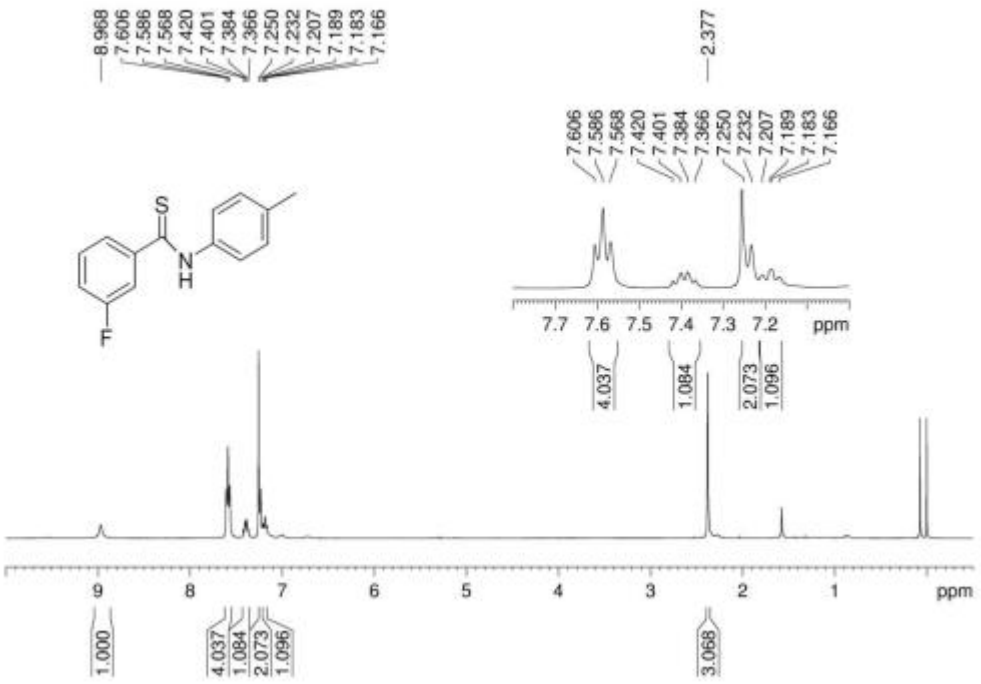
Compound 3ba

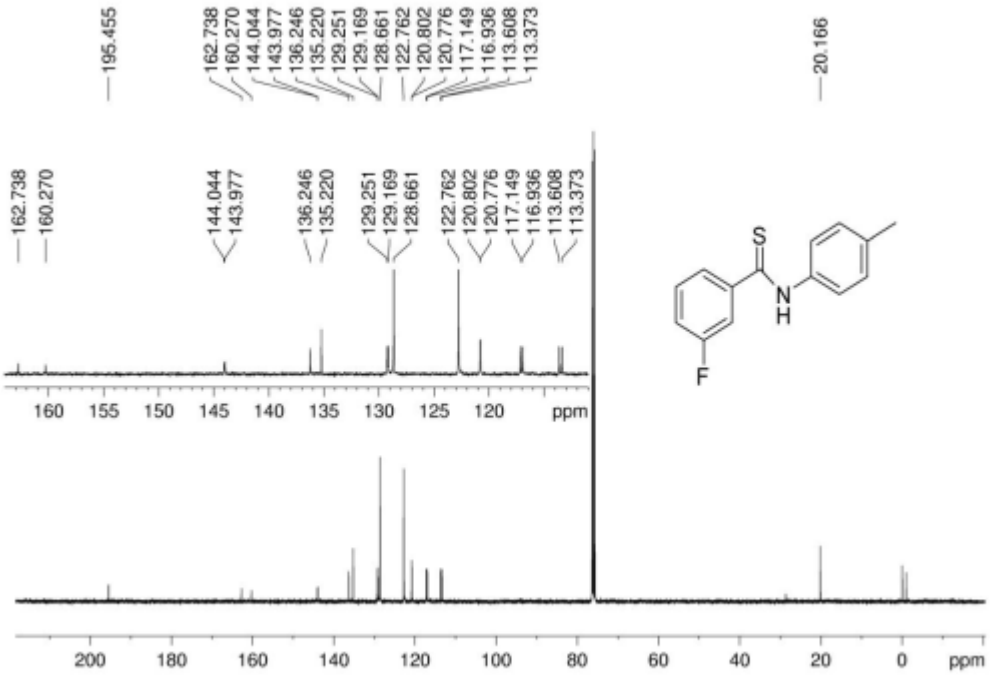

9.022
7.755
7.736
7.591
7.571
7.468
7.449
7.429
7.410
7.394
7.376
7.331
7.313
7.295
7.217
7.196
7.177
S
N
H
F
7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
2.010
2.049
3.048
1.002
1.089
9 8 7 6 5 4 3 2 1 ppm
1.000
2.010
2.049
3.048
1.002
1.089

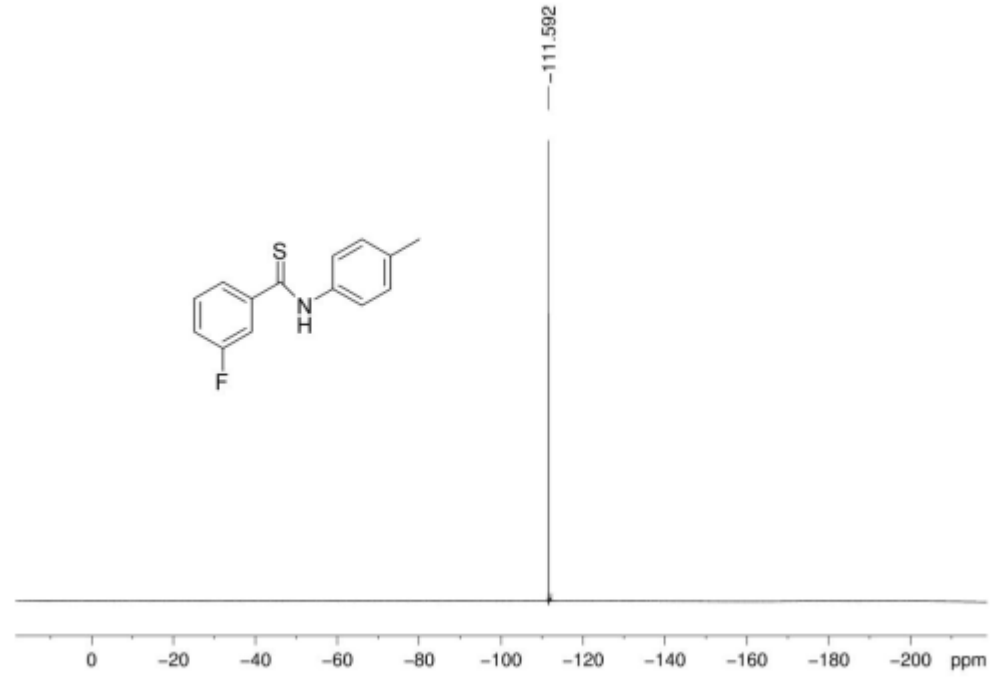

195.571
162.730
160.262
144.108
137.734
129.275
129.196
128.100
126.175
122.666
120.802
117.210
116.998
113.617
113.384
S
N
H
F
140 135 130 125 120 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm



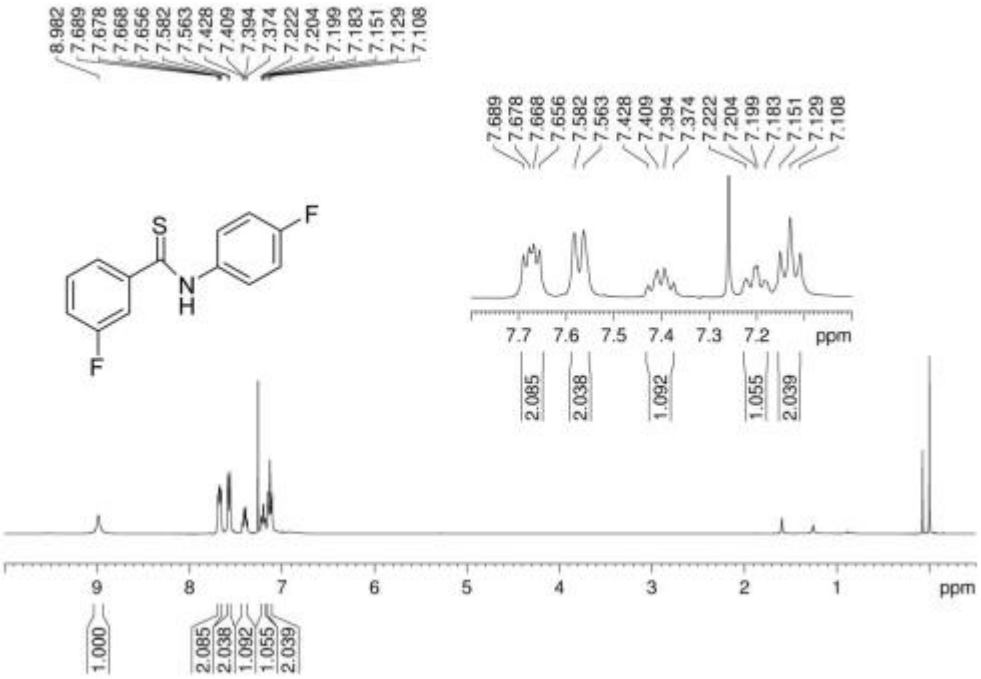
Compound 3bd







Compound 3bm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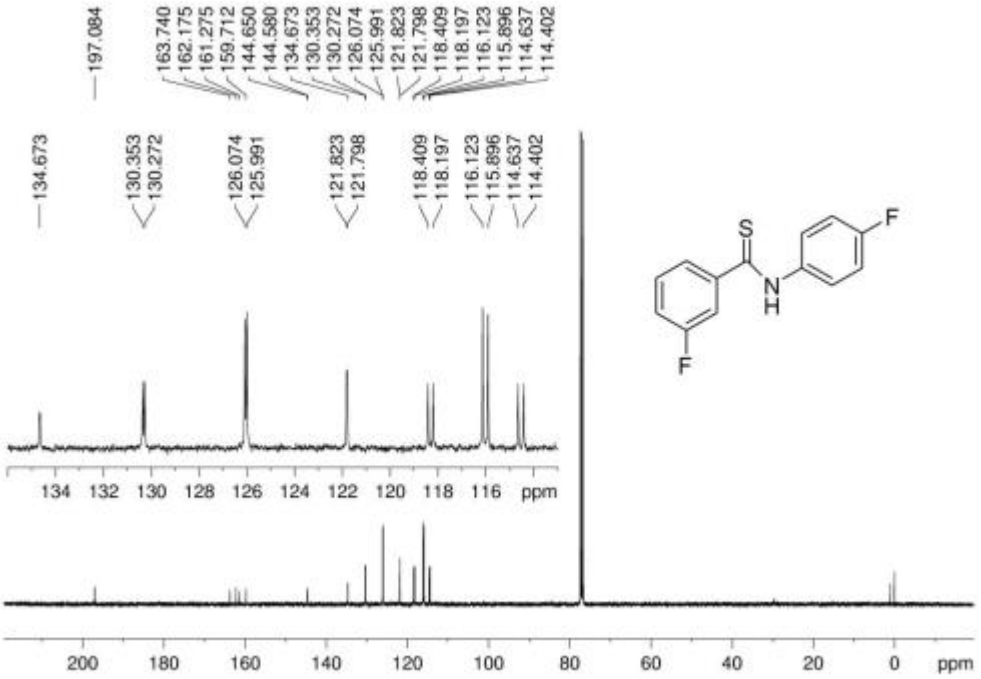
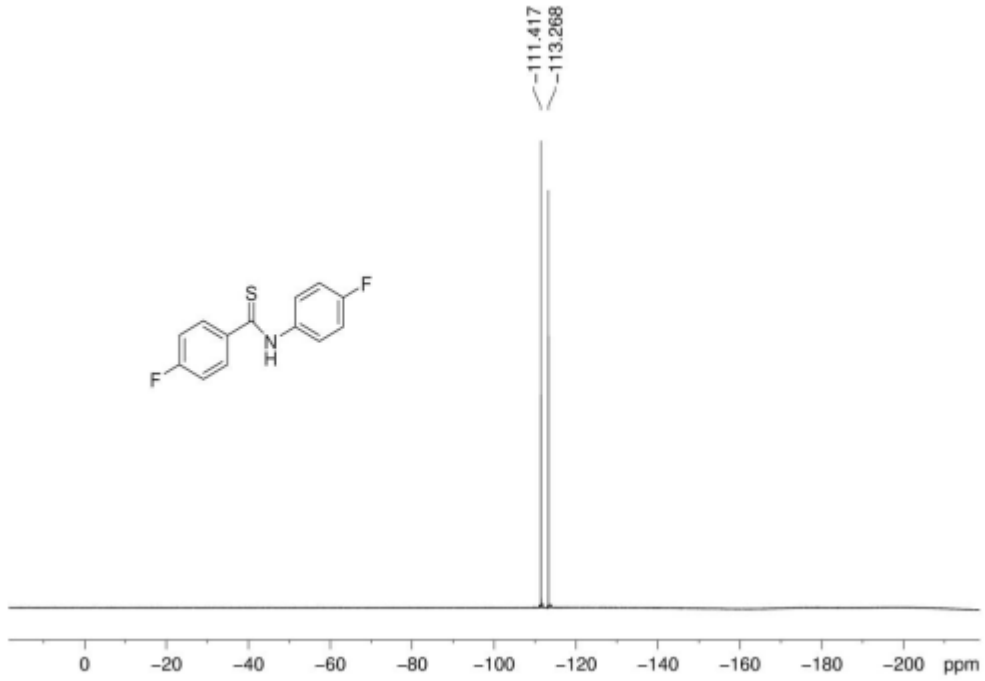
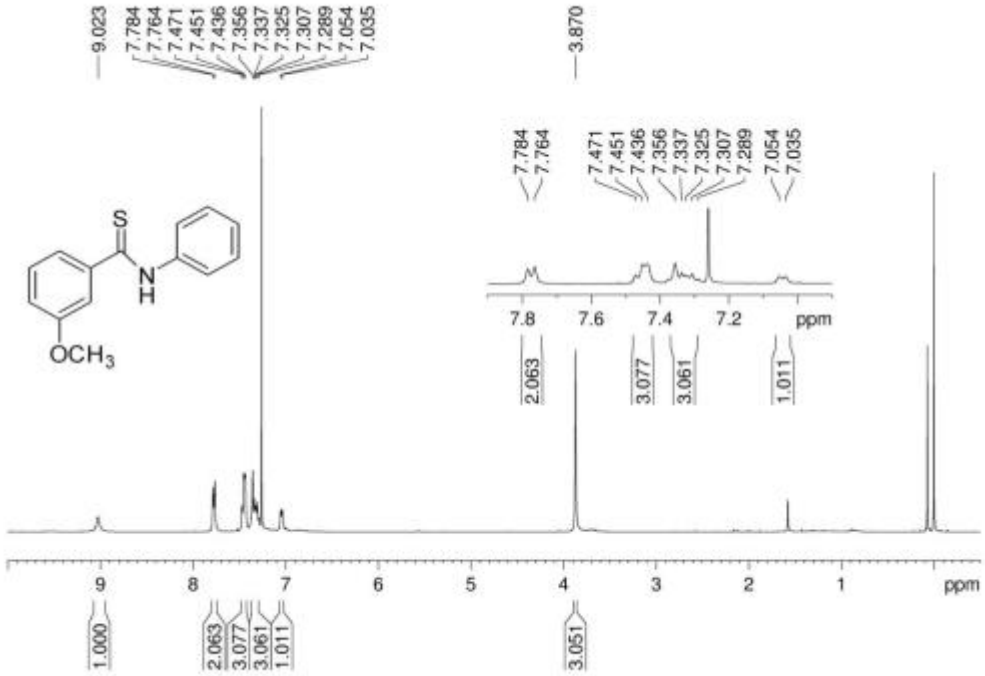
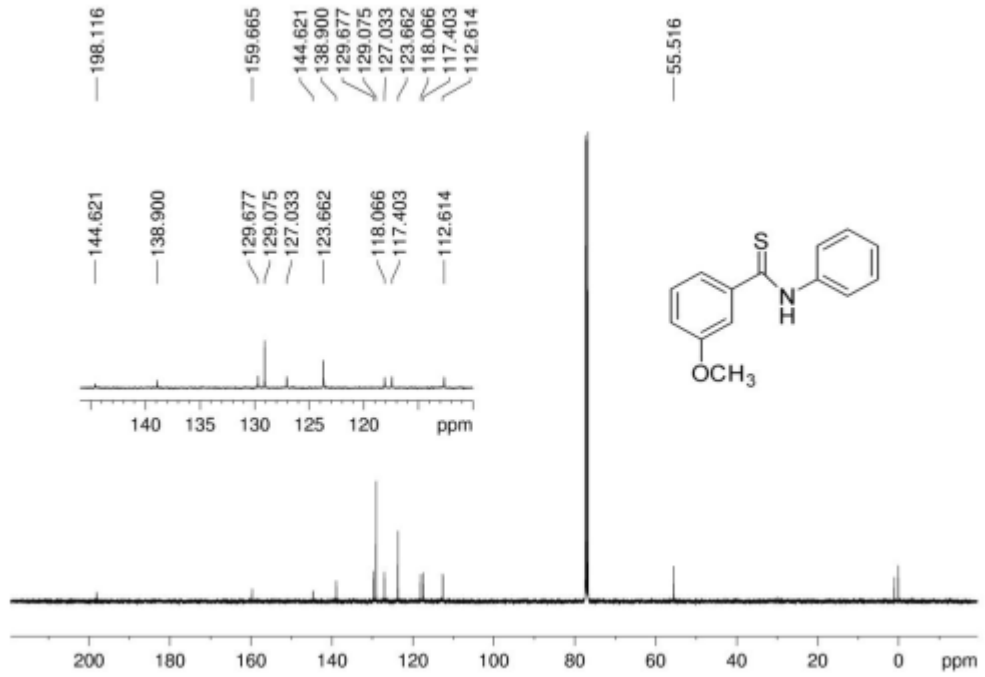
7.689
7.678
7.668
7.656
7.582
7.563
7.428
7.409
7.394
7.374
7.222
7.204
7.199
7.183
7.151
7.129
7.108
S
N
H
F
F
7.7
7.6
7.5
7.4
7.3
7.2
ppm
2.085
2.038
1.092
1.055
2.039
9
8
7
6
5
4
3
2
1
ppm
1.000
2.085
2.038
1.092
1.055
2.039


197.084
163.740
162.175
161.275
159.712
144.650
144.580
134.673
130.353
130.272
126.074
125.991
121.823
121.798
118.409
118.197
116.123
115.896
114.637
114.402
134.673
130.353
130.272
126.074
125.991
121.823
121.798
118.409
118.197
116.123
115.896
114.637
114.402
S
N
H
F
F
134
132
130
128
126
124
122
120
118
116
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

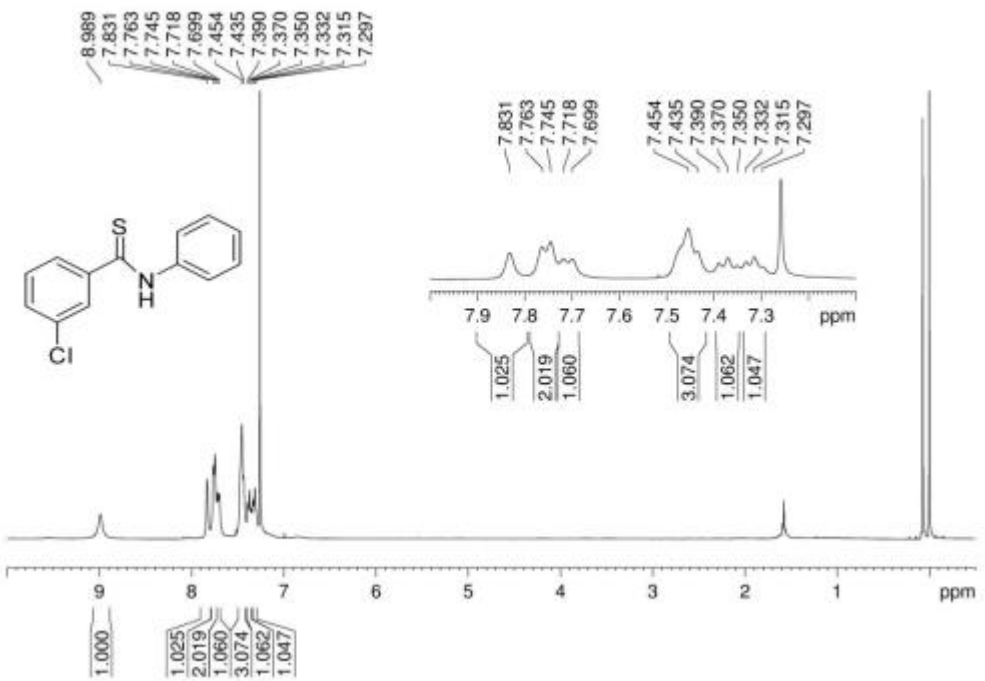


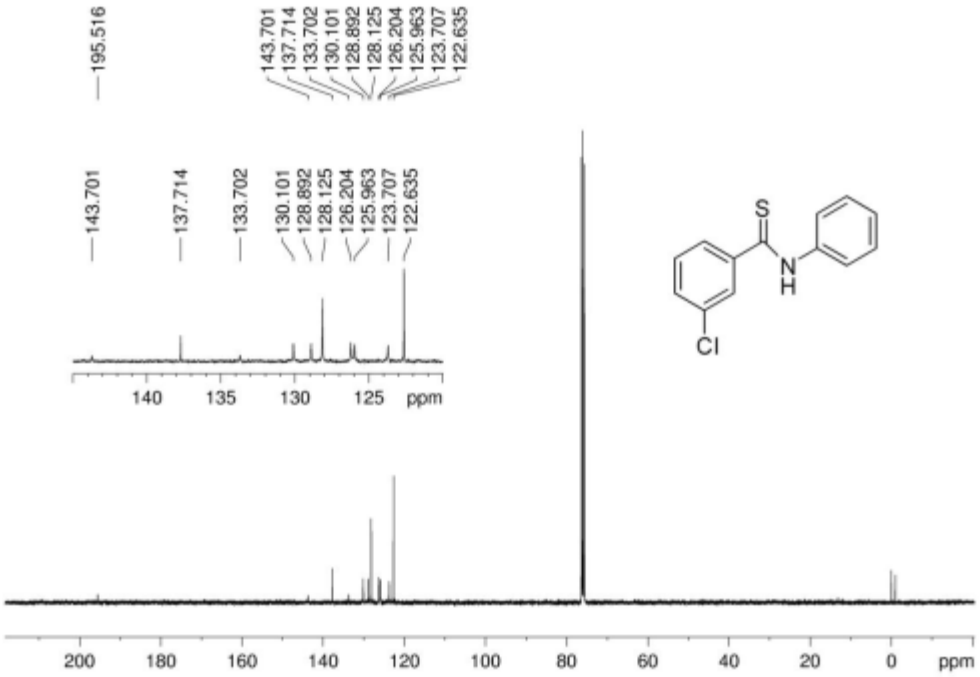
Compound 3ca



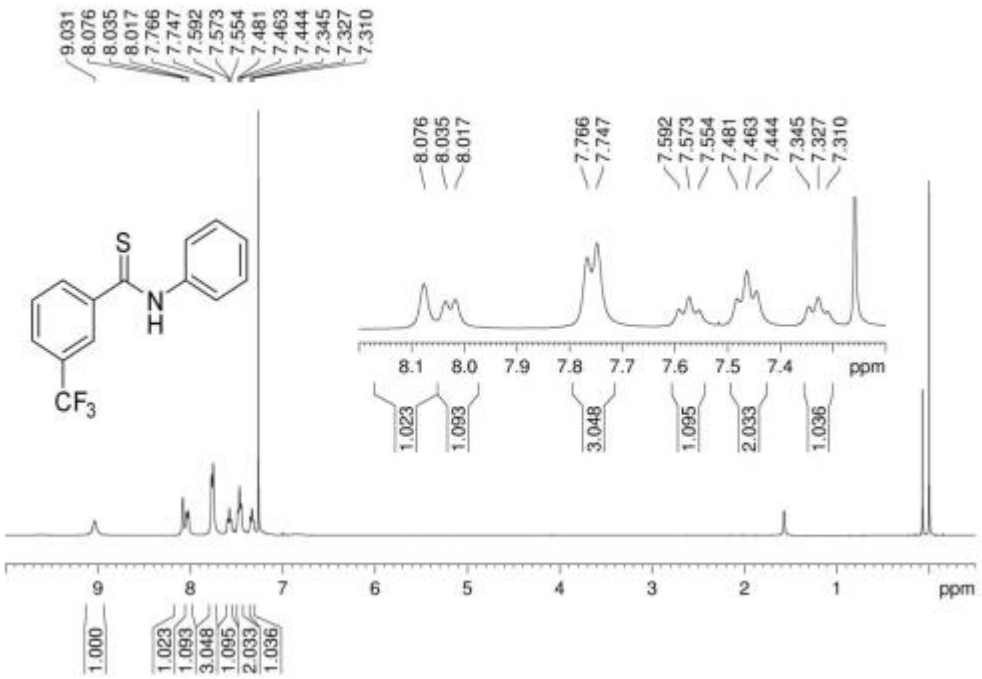


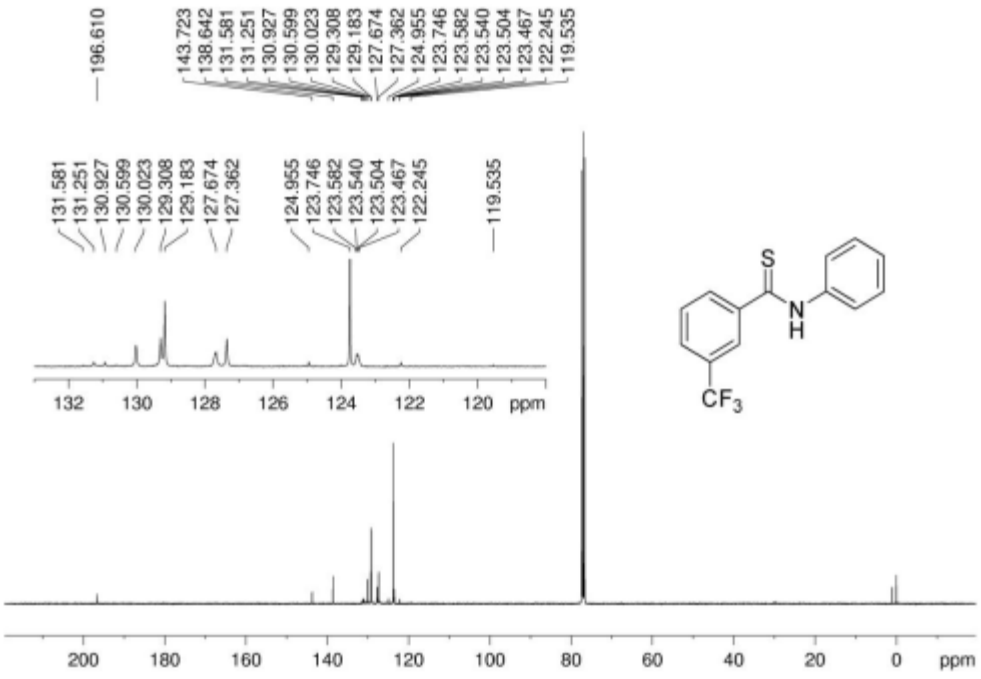
Compound 3da

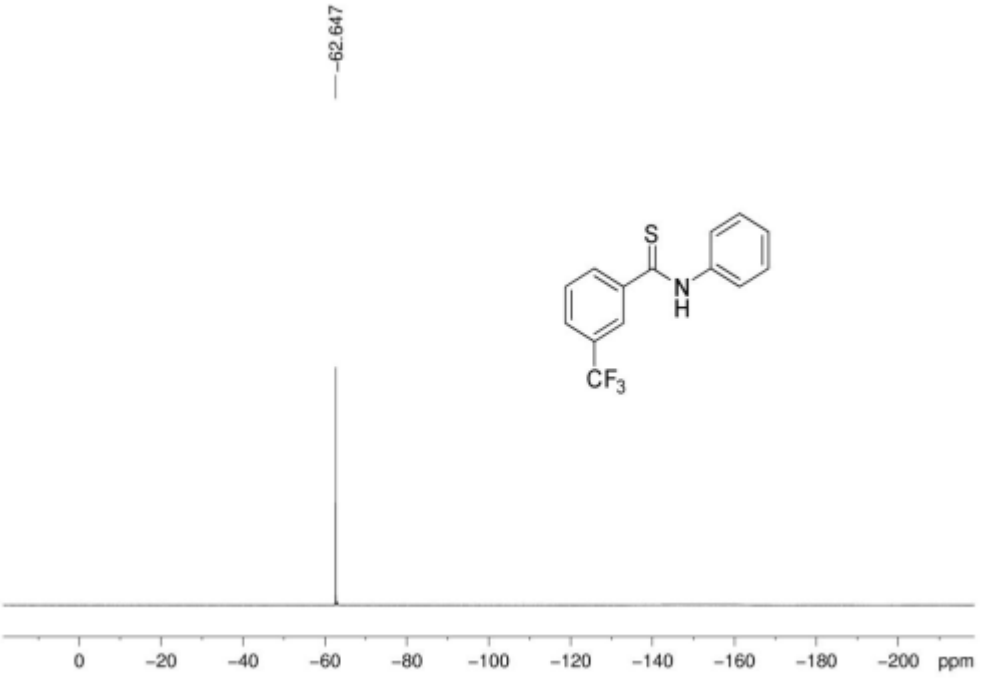




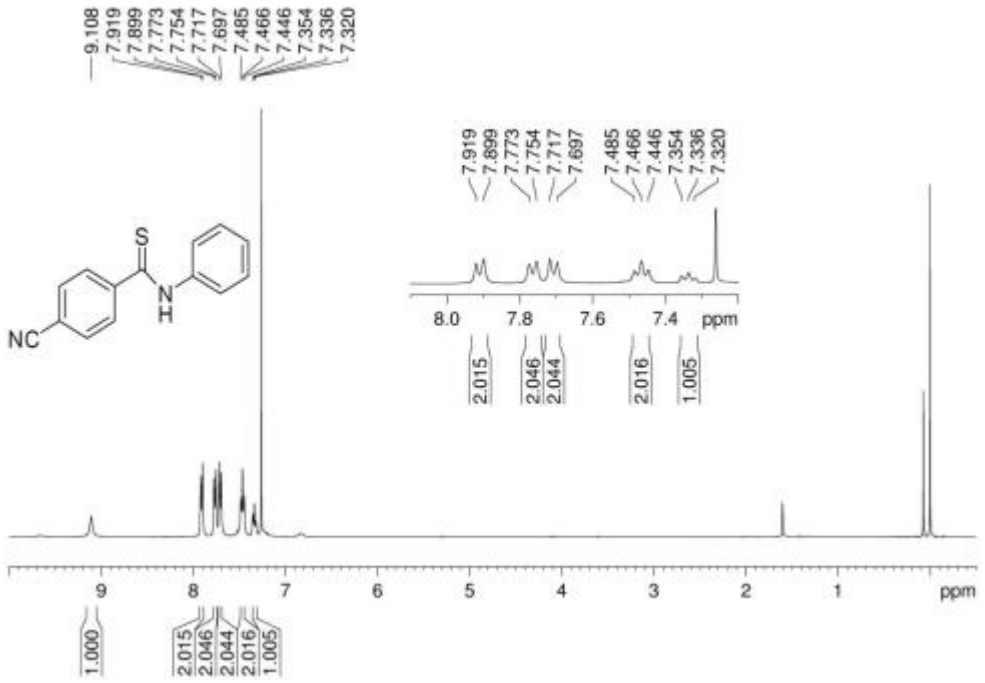
Compound 3ea

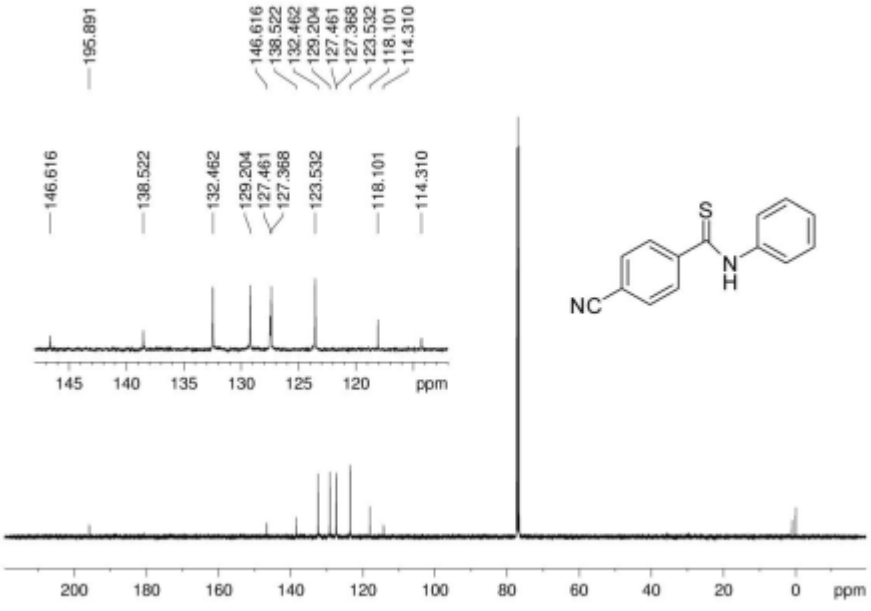




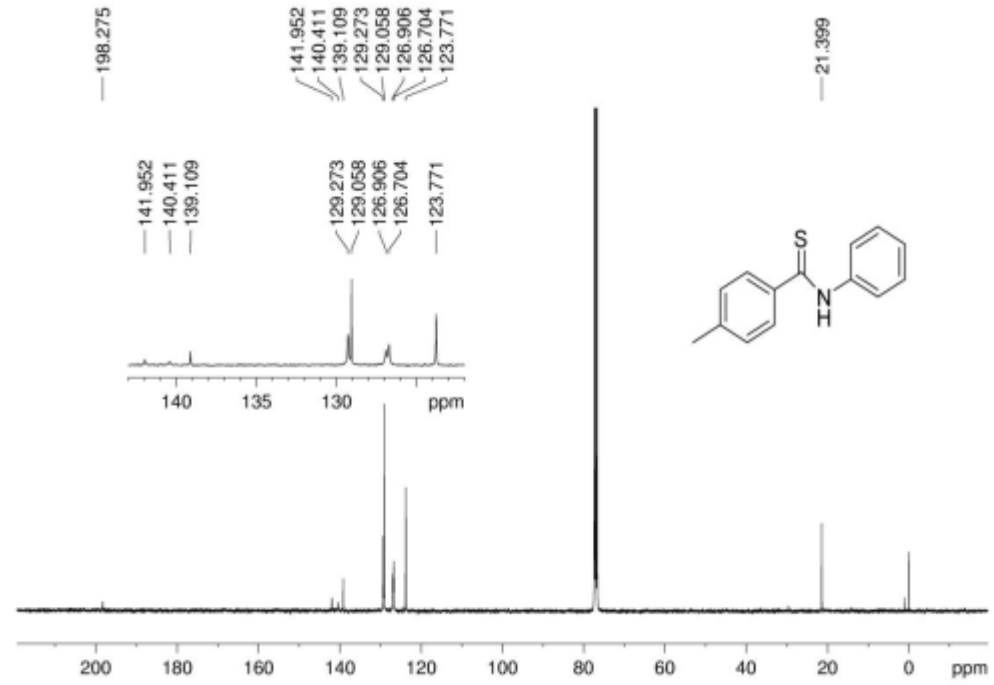


Compound 3fa

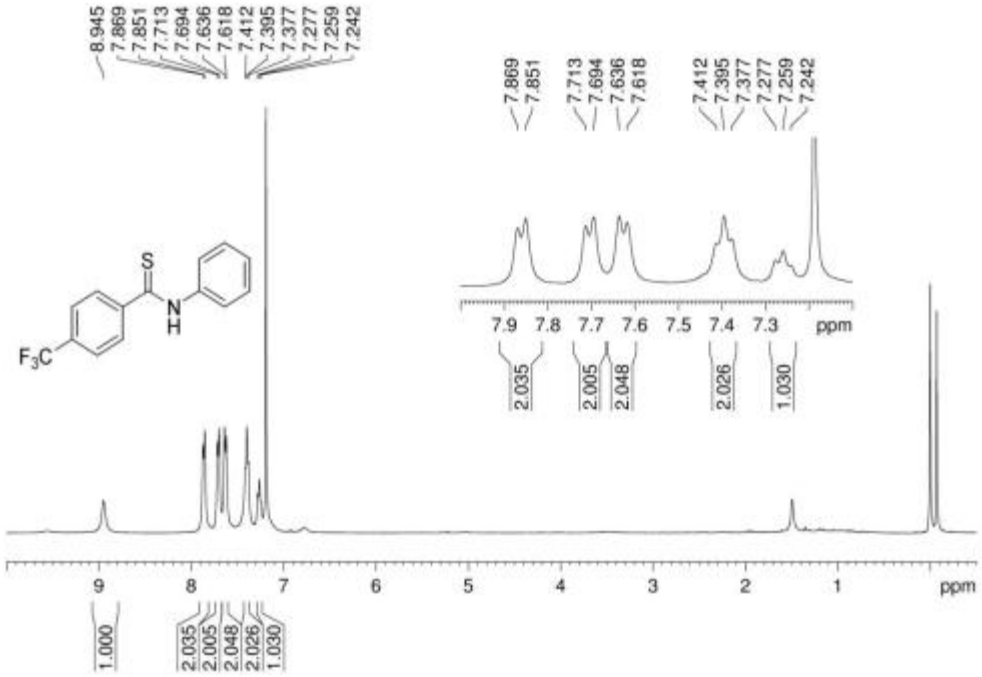


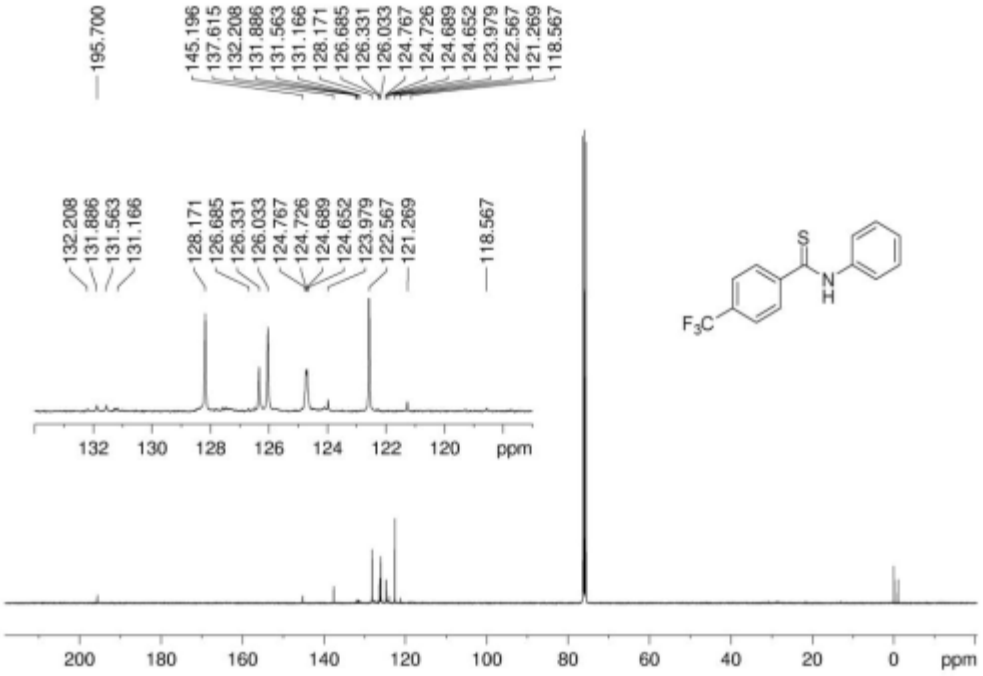


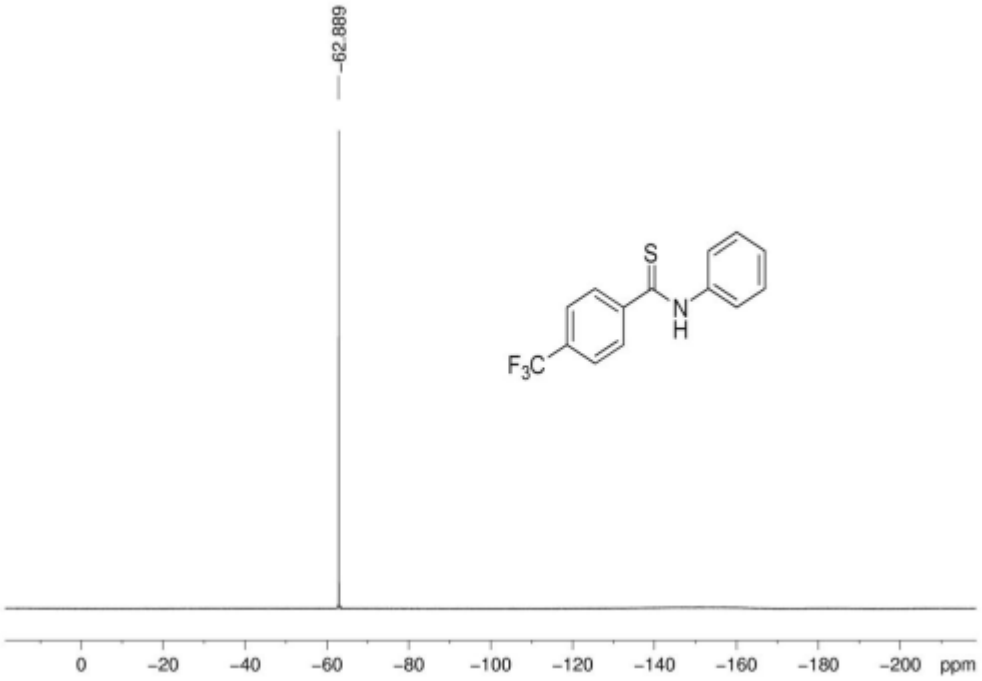
Compound 3ga



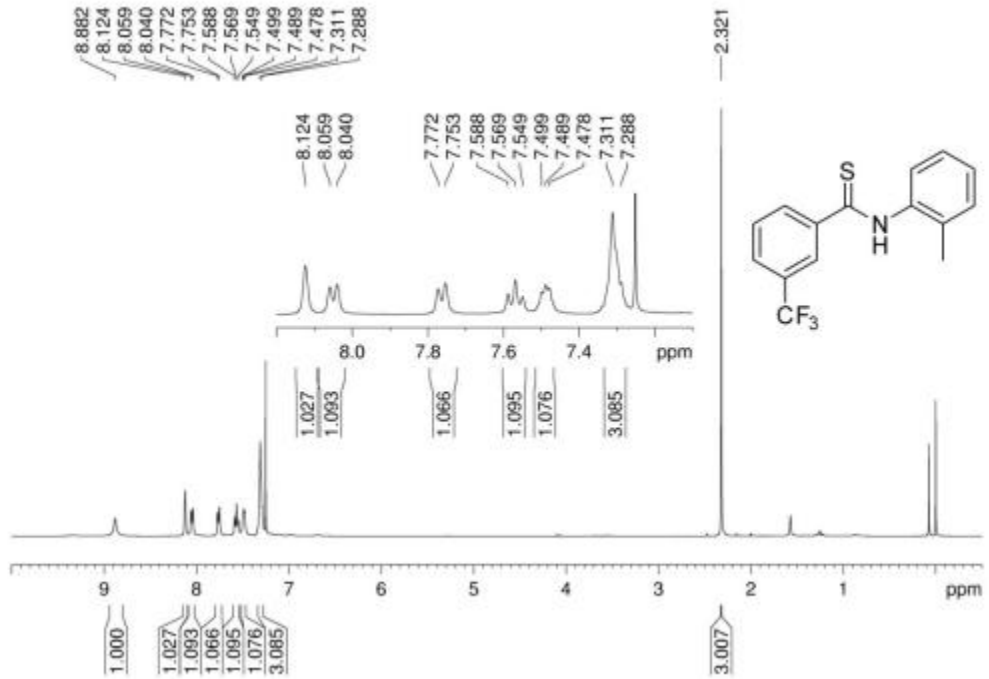
Compound 3ha

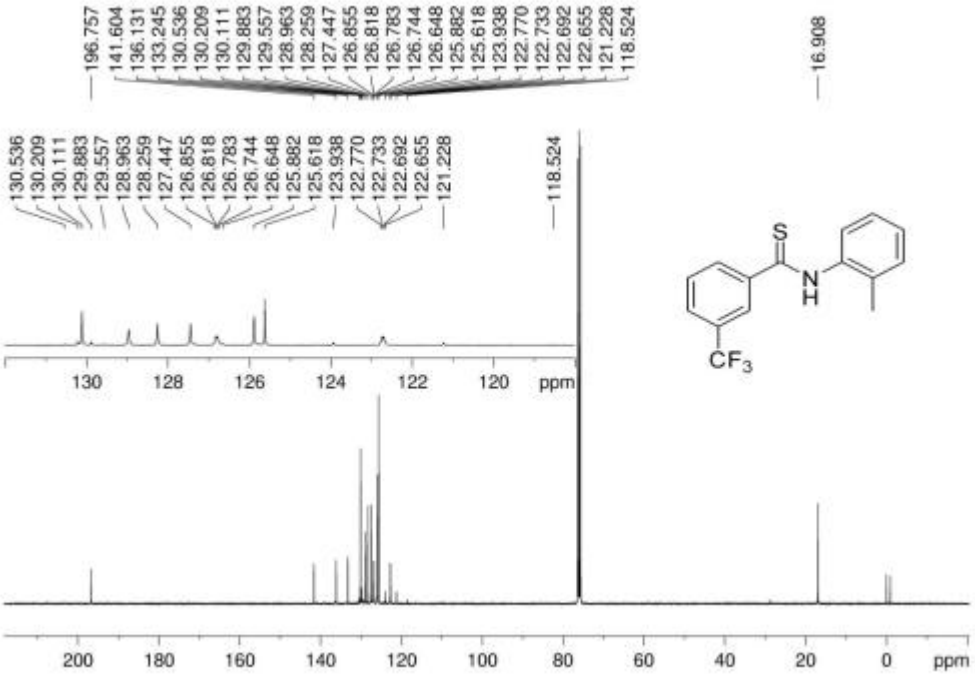

8.945
7.869
7.851
7.713
7.694
7.636
7.618
7.412
7.395
7.377
7.277
7.259
7.242
S
N
H
F3C
7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
2.035
2.005
2.048
2.026
1.030
9 8 7 6 5 4 3 2 1 ppm
1.000
2.035
2.005
2.048
2.026
1.030

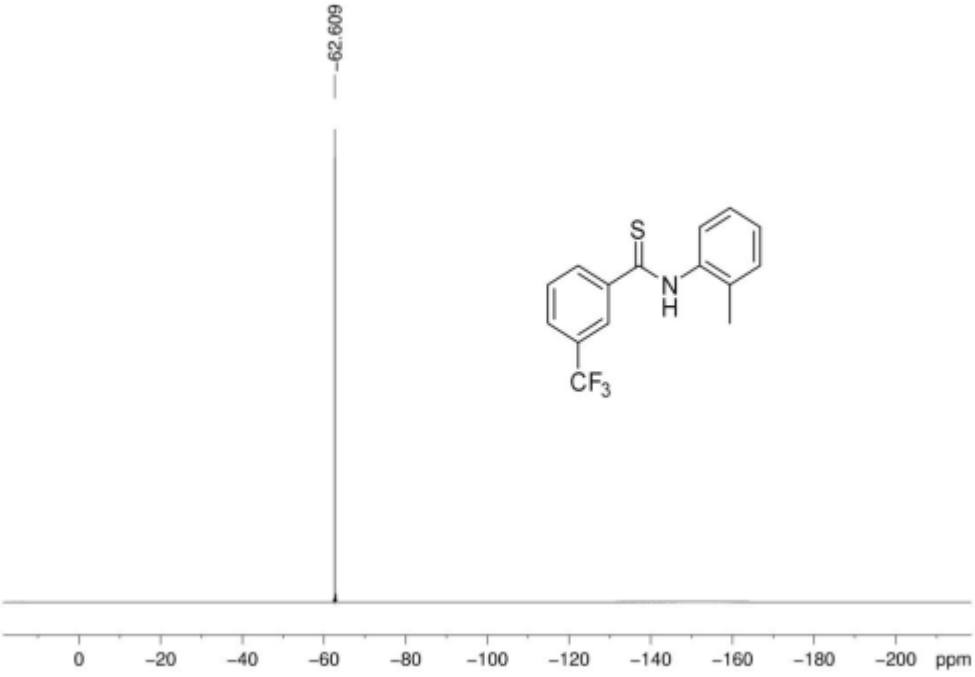

195.700
145.196
137.615
132.208
131.886
131.563
131.166
128.171
126.685
126.331
126.033
124.767
124.726
124.689
124.652
123.979
122.567
121.269
118.567
S
N
H
F3C
132 130 128 126 124 122 120 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm



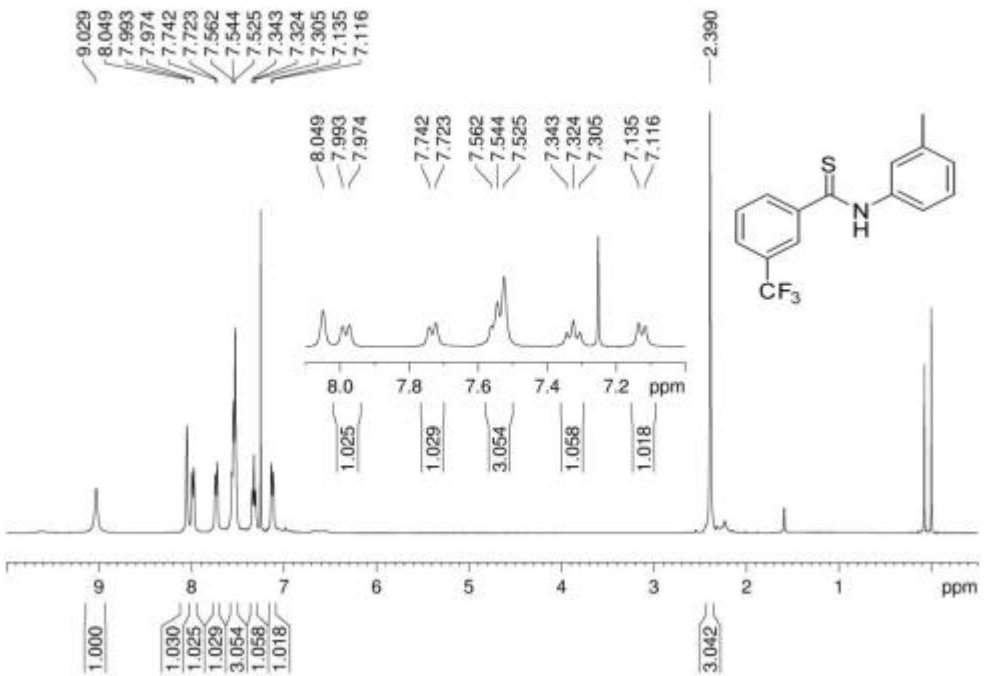
Compound 3eb

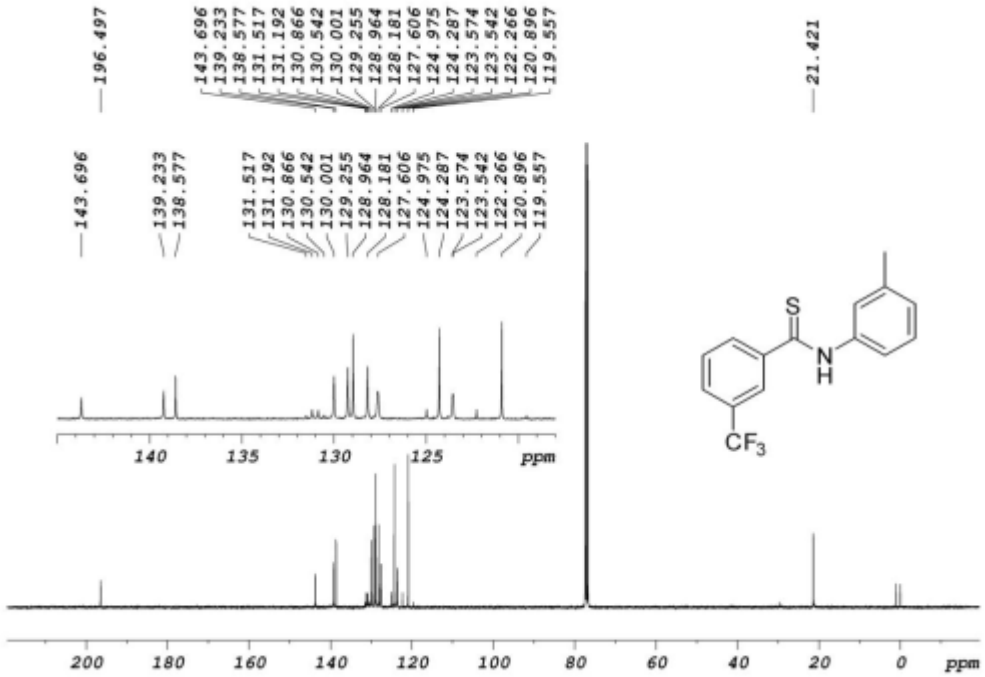


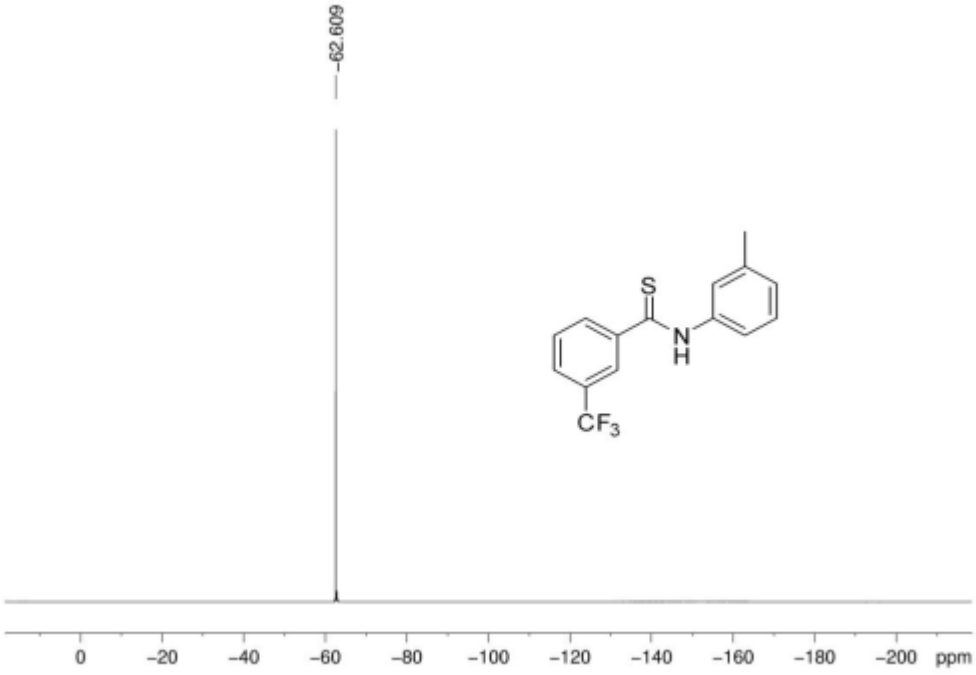




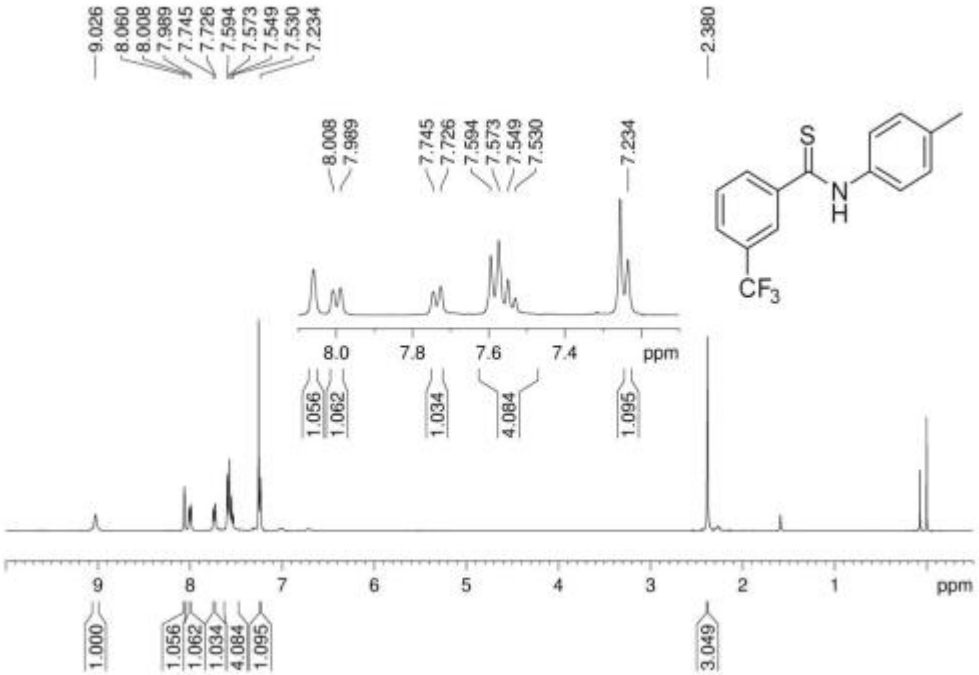
Compound 3ec

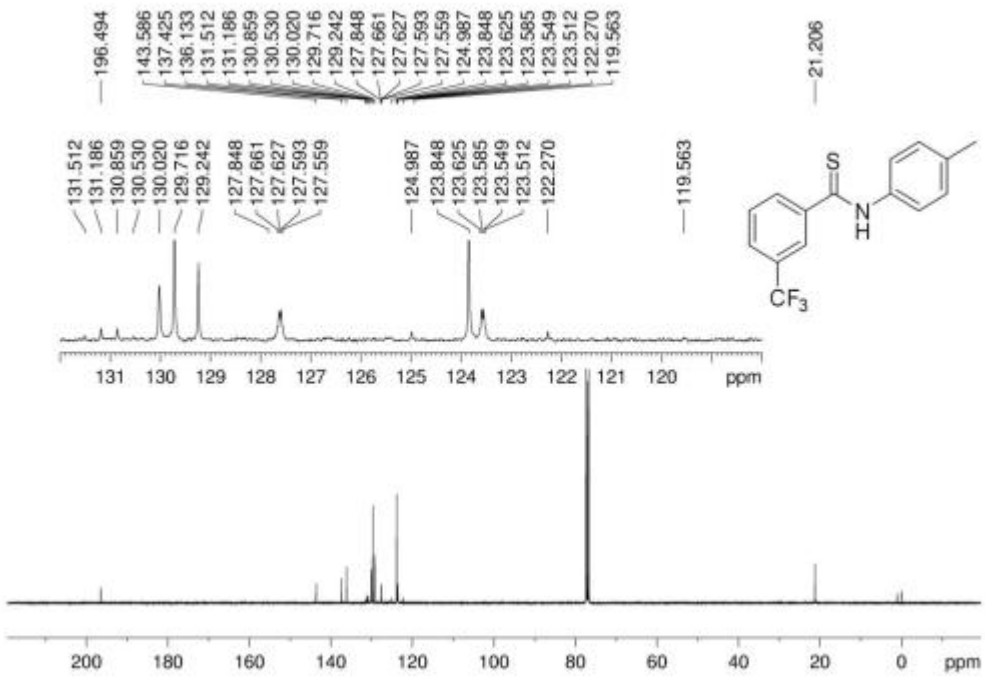

9.029
8.049
7.993
7.974
7.742
7.723
7.562
7.544
7.525
7.343
7.324
7.305
7.135
7.116
2.390
S
N
H
CF3
8.0
7.8
7.6
7.4
7.2
ppm
1.025
1.029
3.054
1.058
1.018
9
8
7
6
5
4
3
2
1
ppm
1.000
1.030
1.025
1.029
3.054
1.058
1.018
3.042

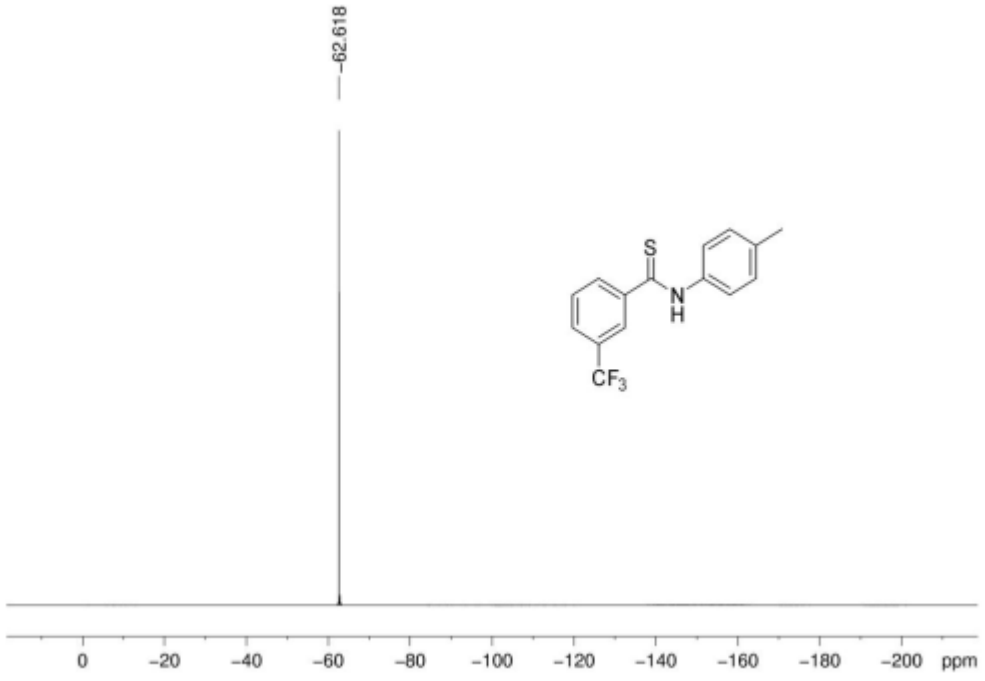

196.497
143.696
139.233
138.577
131.517
131.192
130.866
130.542
130.001
129.255
128.964
128.181
127.606
124.975
124.287
123.574
123.542
122.266
120.896
119.557
21.421
S
N
H
CF3
140
135
130
125
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



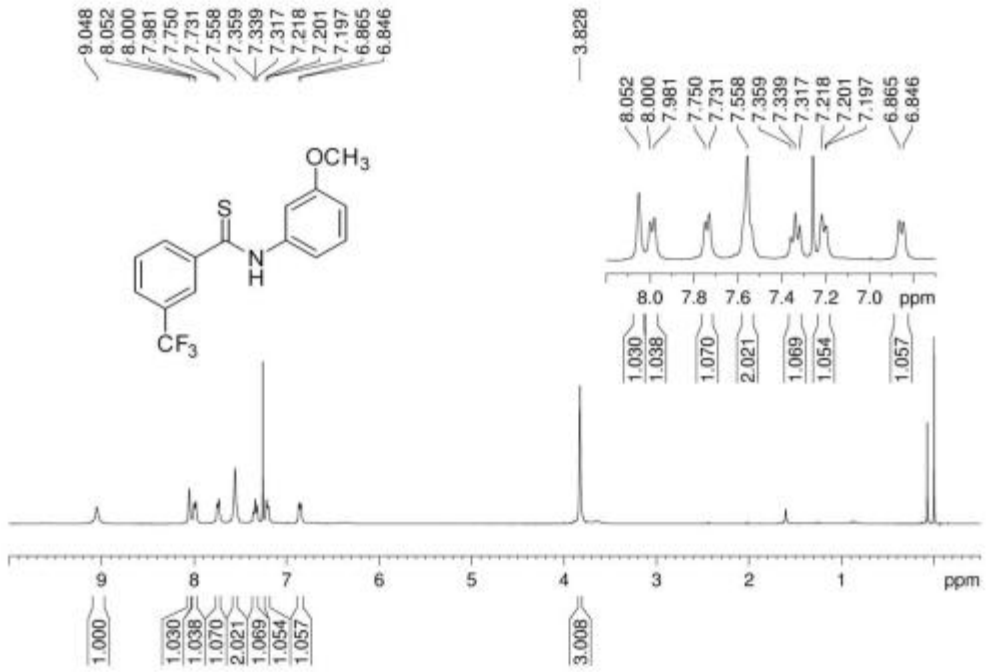
Compound 3ed

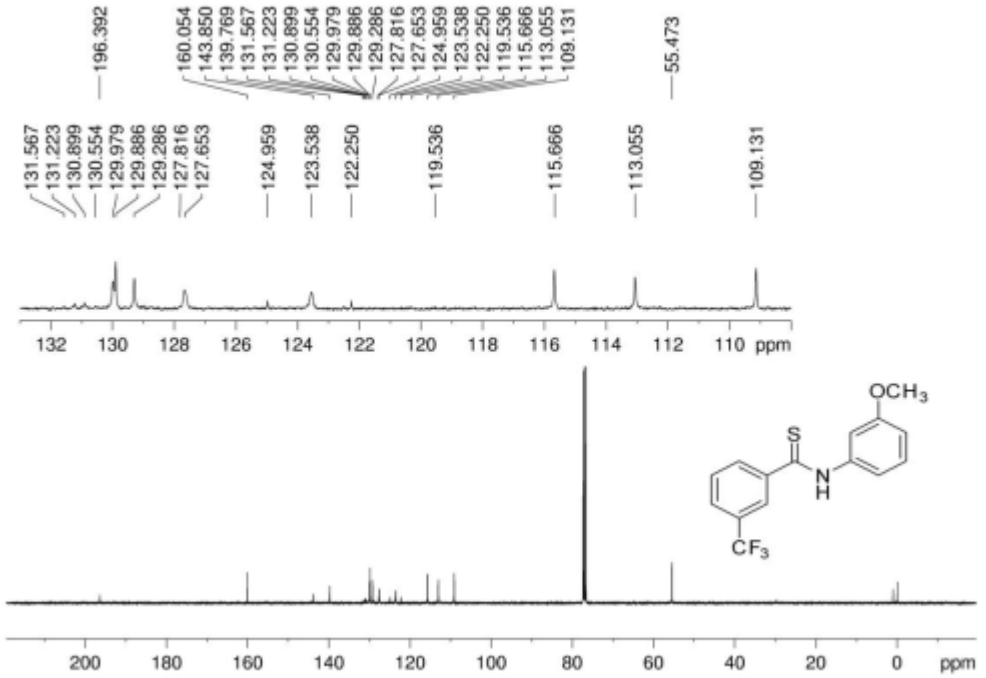


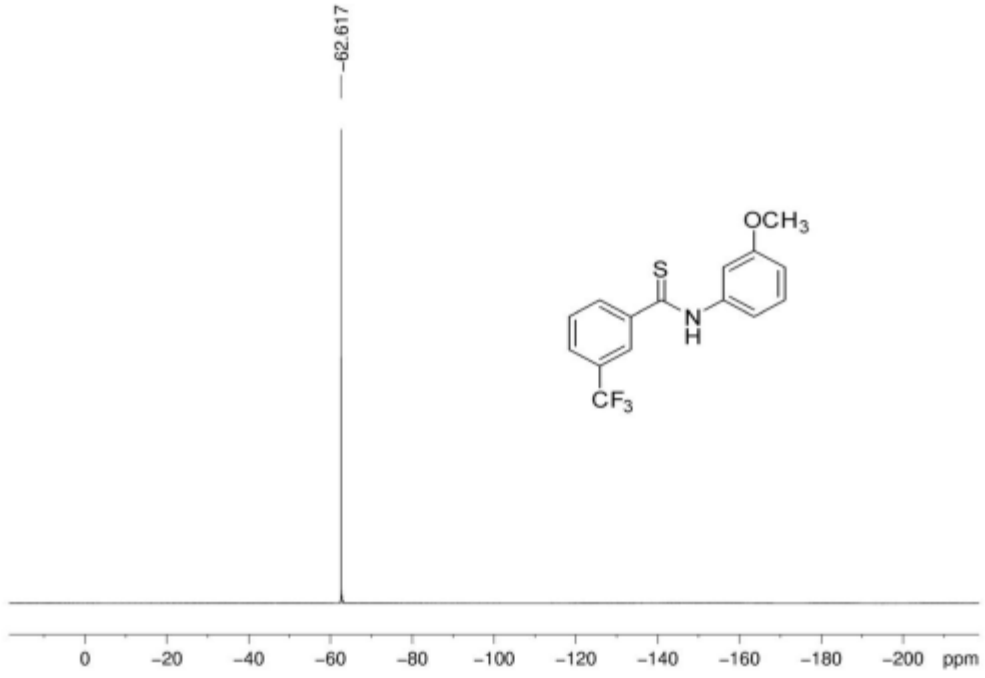




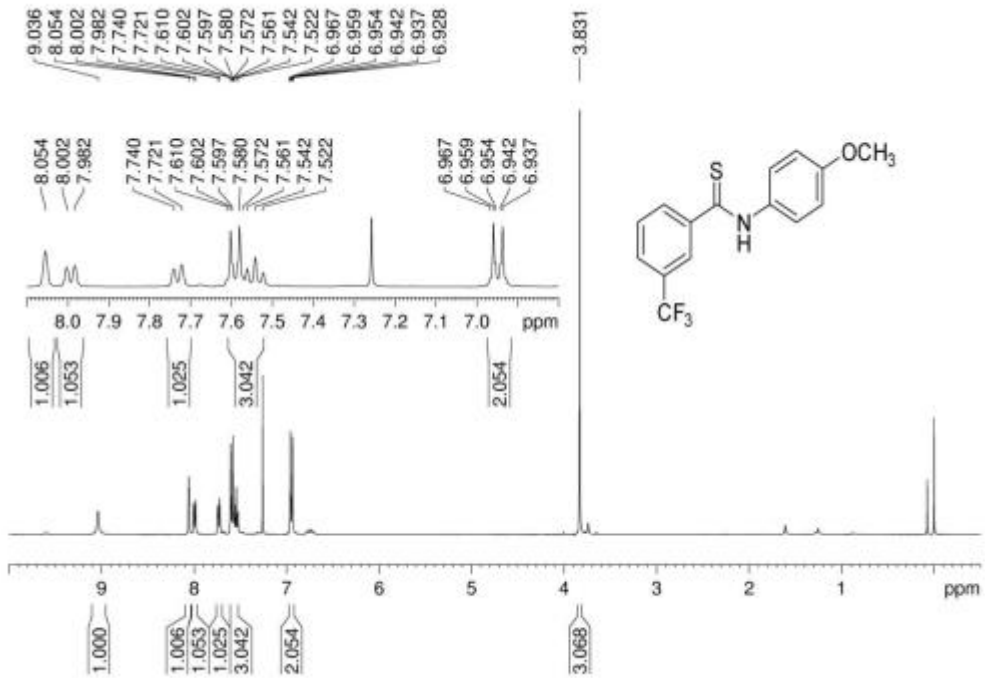
Compound 3ee

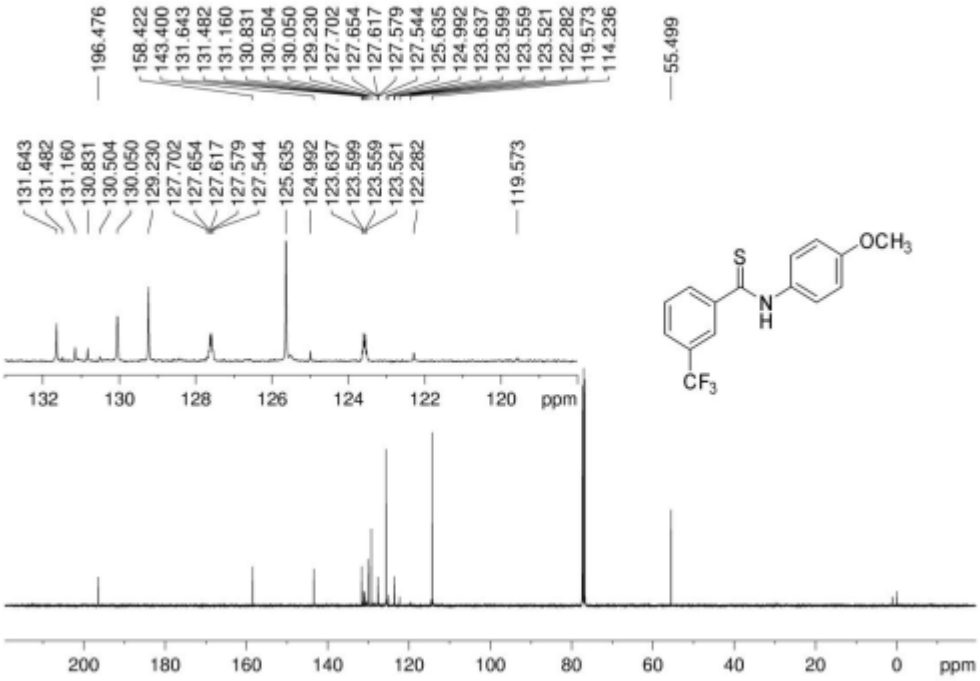

9.048
8.052
8.000
7.981
7.750
7.731
7.558
7.359
7.339
7.317
7.218
7.201
7.197
6.865
6.846
3.828
OCH3
S
N
H
CF3
8.0 7.8 7.6 7.4 7.2 7.0 ppm
1.030
1.038
1.070
2.021
1.069
1.054
1.057
1.000
3.008
9 8 7 6 5 4 3 2 1 ppm

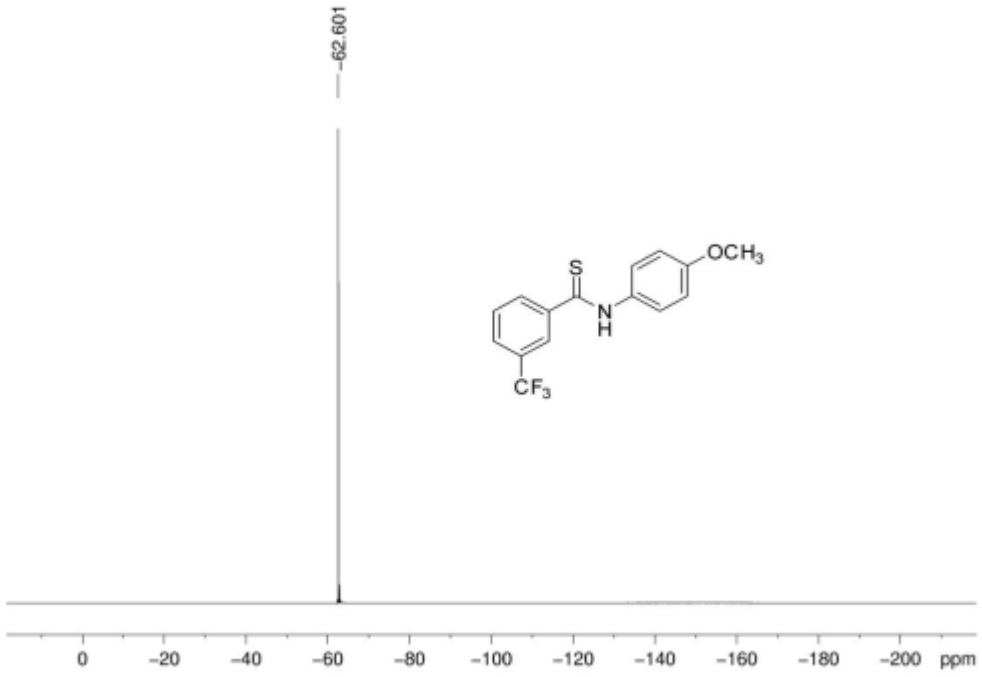

196.392
160.054
143.850
139.769
131.567
131.223
130.899
130.554
129.979
129.886
129.286
127.816
127.653
124.959
123.538
122.250
119.536
115.666
113.055
109.131
55.473
132 130 128 126 124 122 120 118 116 114 112 110 ppm
OCH3
S
N
H
CF3
200 180 160 140 120 100 80 60 40 20 0 ppm



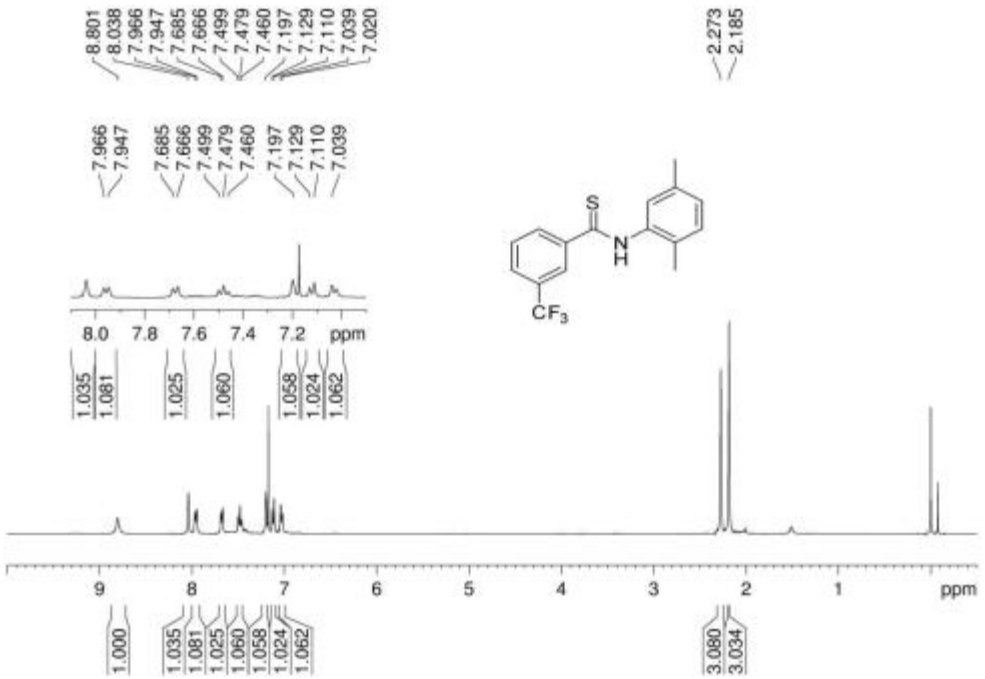
Compound 3ef

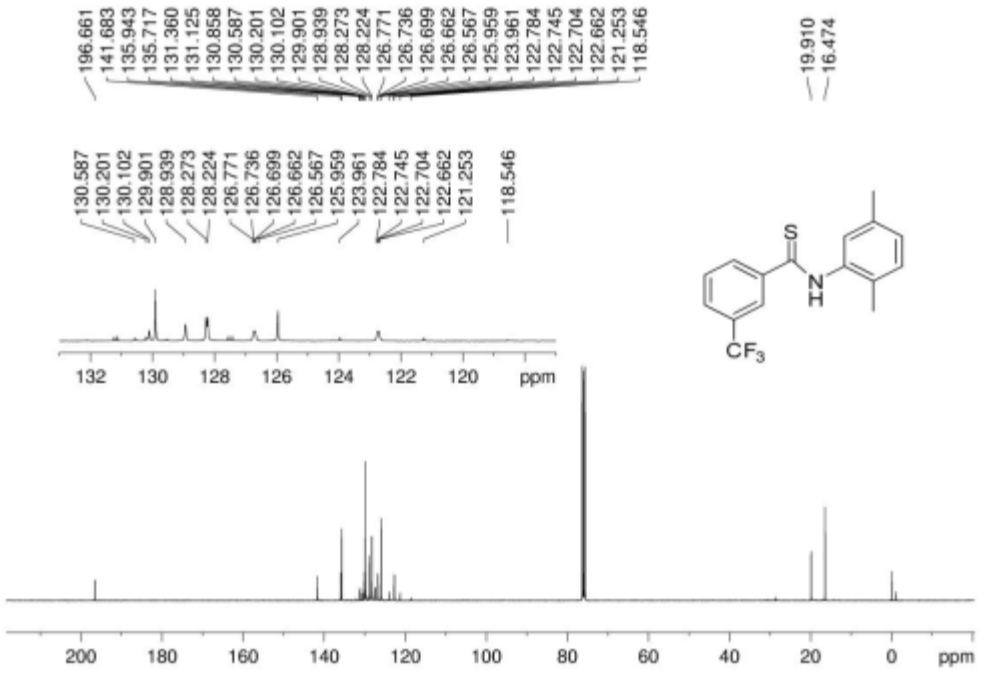


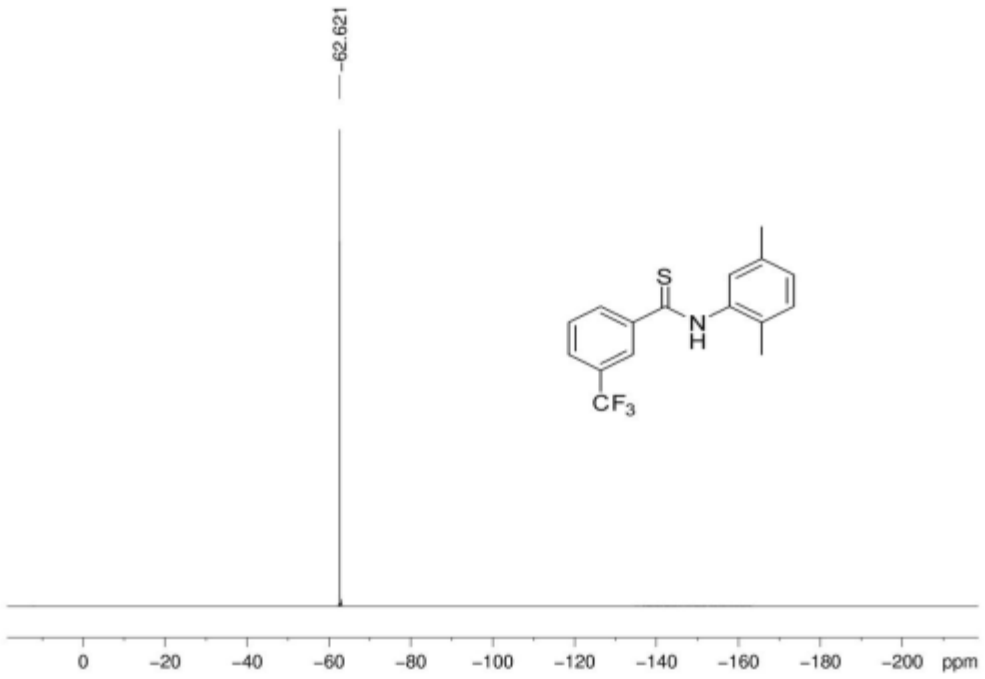




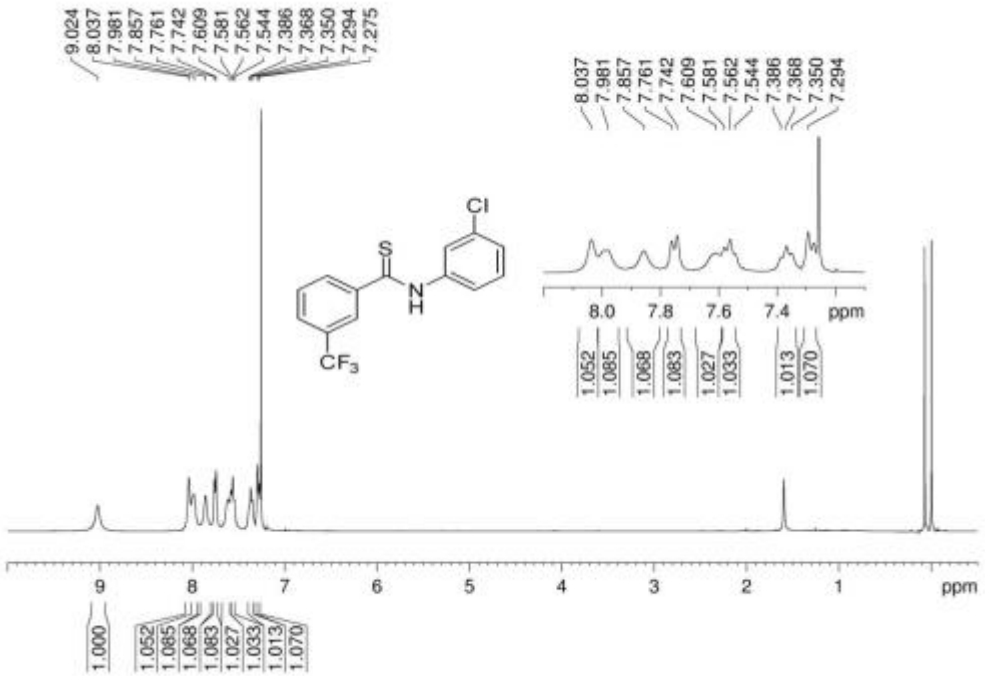
Compound 3eg

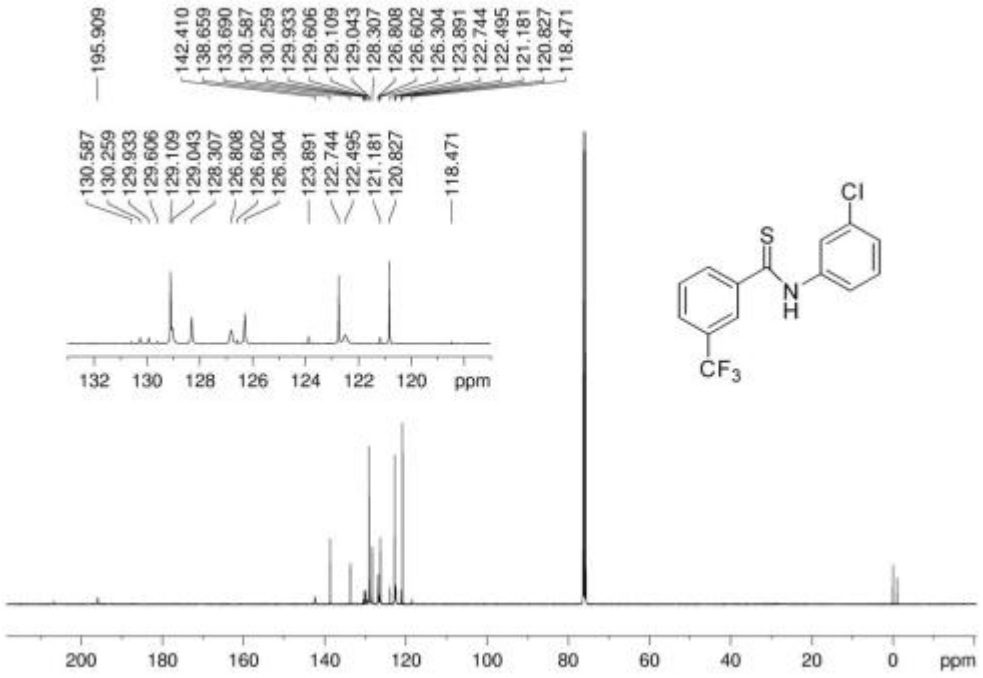

8.801
8.038
7.966
7.947
7.685
7.666
7.499
7.479
7.460
7.197
7.129
7.110
7.039
7.020
2.273
2.185
S
N
H
CF3
8.0
7.8
7.6
7.4
7.2
ppm
1.035
1.081
1.025
1.060
1.058
1.024
1.062
9
8
7
6
5
4
3
2
1
ppm
1.000
3.080
3.034

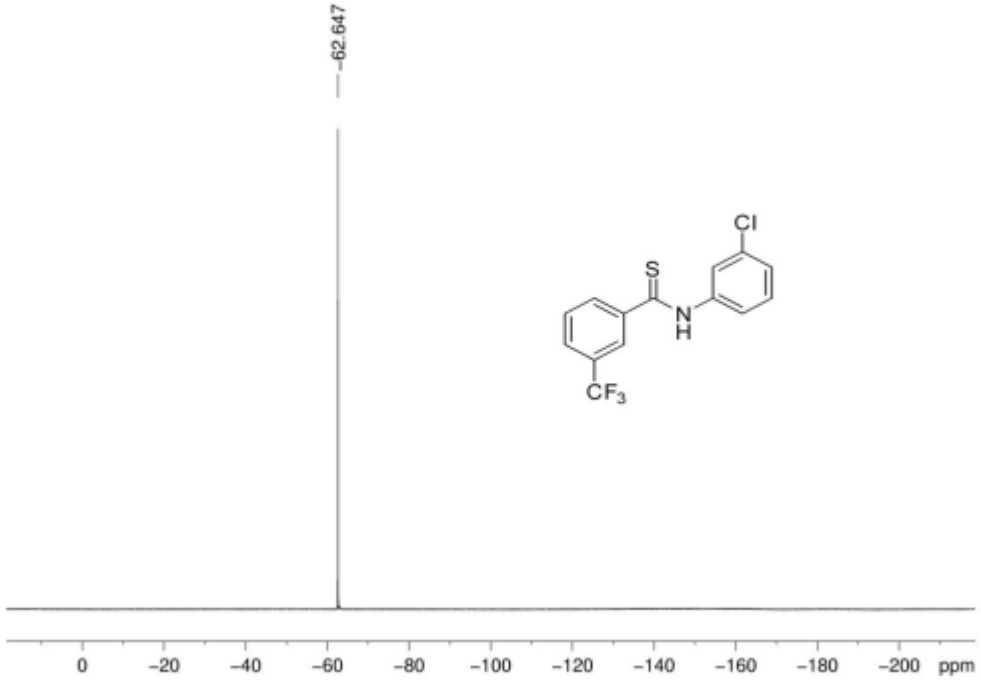

196.661
141.683
135.943
135.717
131.360
131.125
130.858
130.587
130.201
130.102
129.901
128.939
128.273
128.224
126.771
126.736
126.699
126.662
126.567
125.959
123.961
122.784
122.745
122.704
122.662
121.253
118.546
19.910
16.474
S
N
H
CF3
132
130
128
126
124
122
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



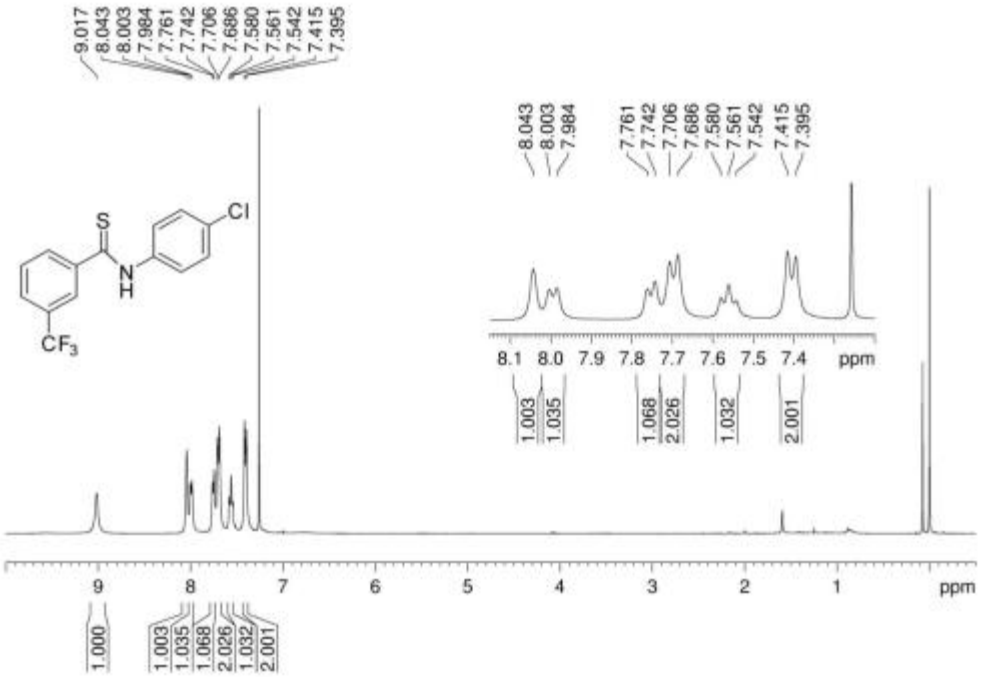
Compound 3ei

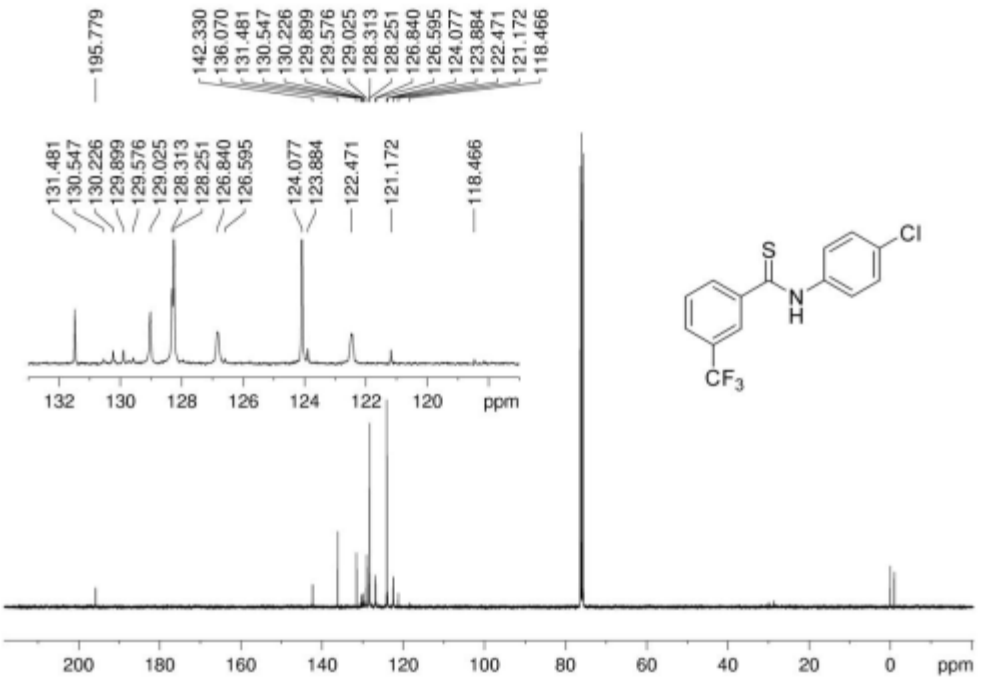


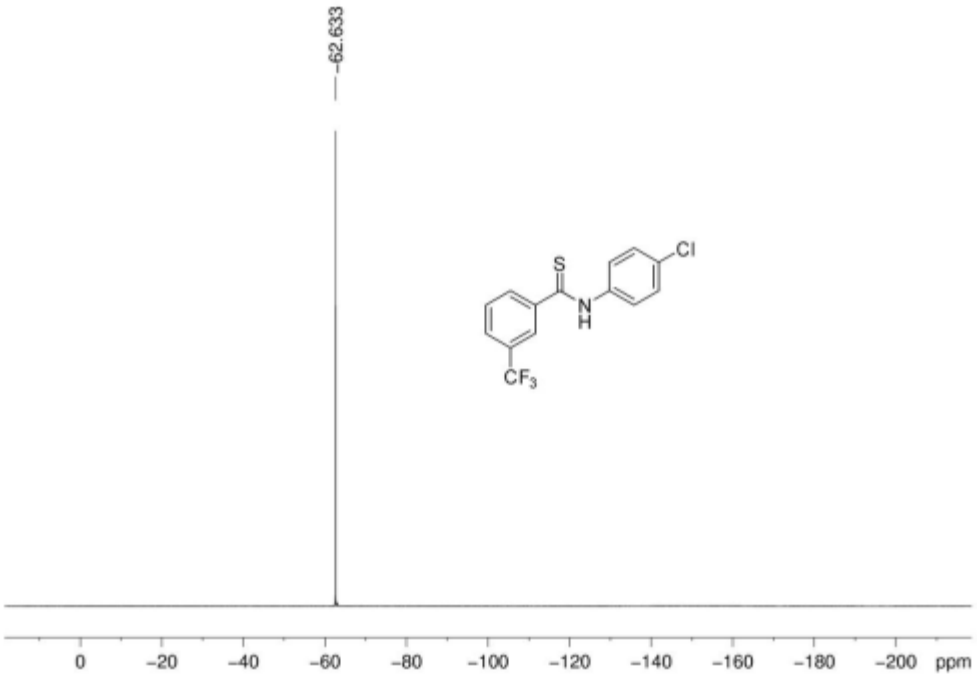




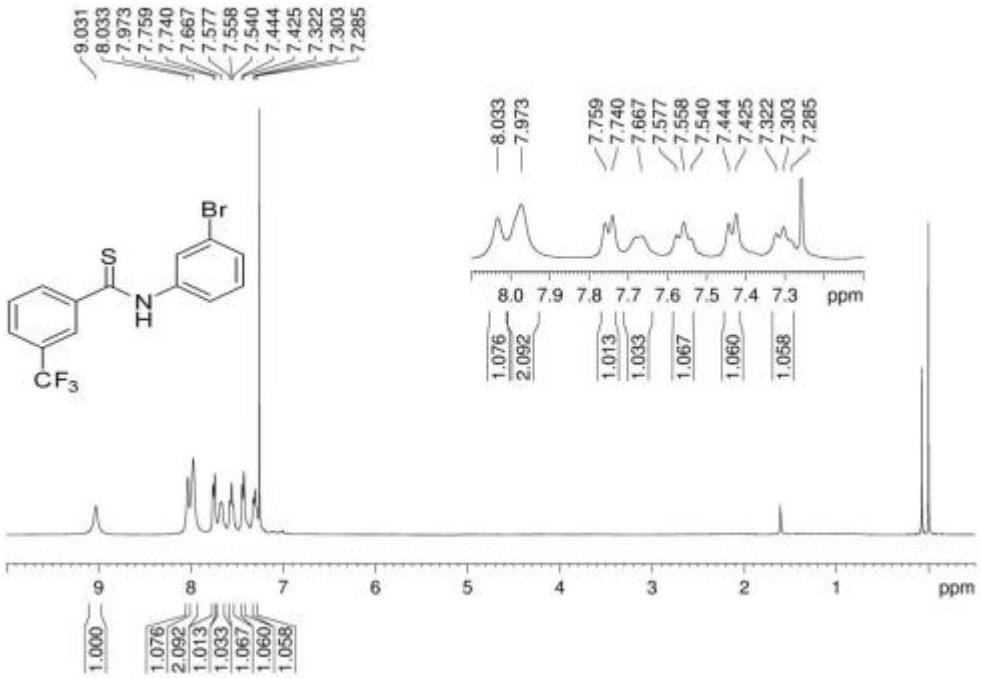
Compound 3ej

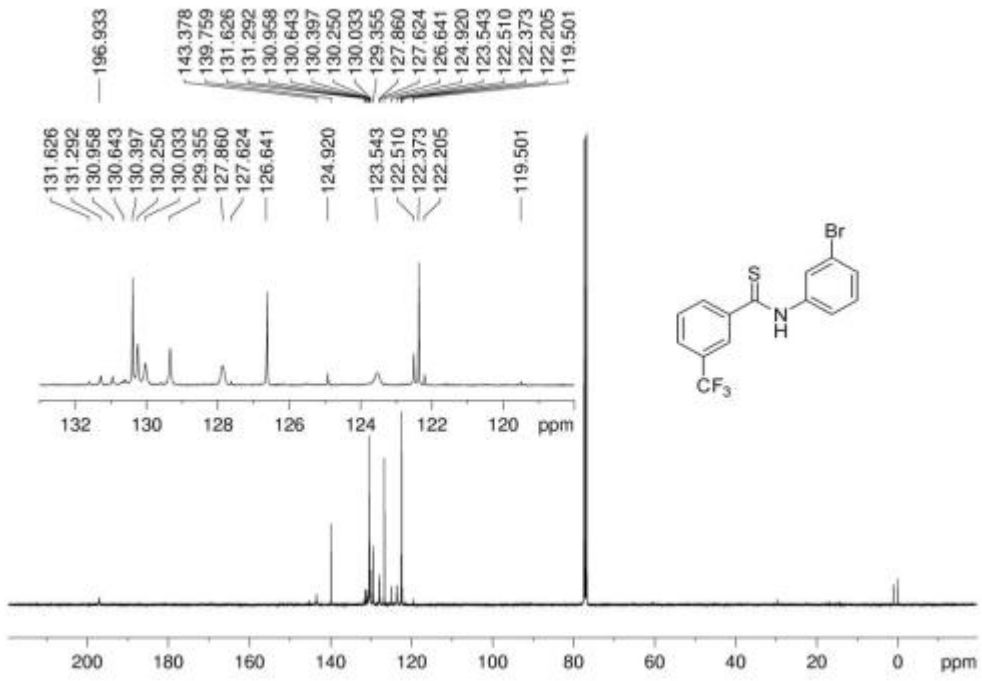

9.017
8.043
8.003
7.984
7.761
7.742
7.706
7.686
7.580
7.561
7.542
7.415
7.395
S
N
H
Cl
CF3
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
1.003
1.035
1.068
2.026
1.032
2.001
9 8 7 6 5 4 3 2 1 ppm
1.000

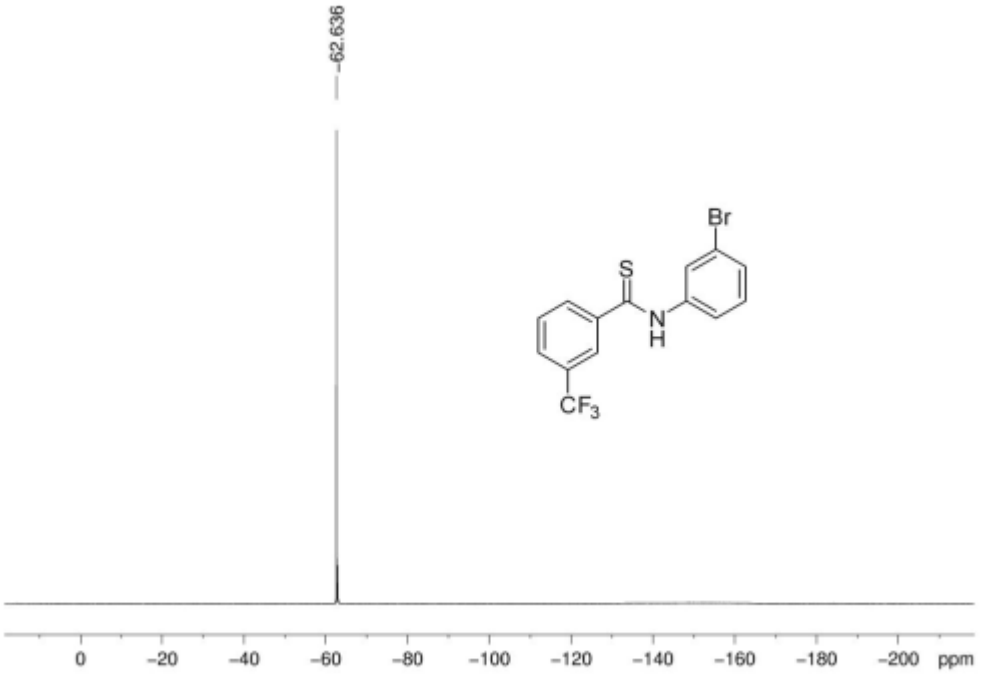

195.779
142.330
136.070
131.481
130.547
130.226
129.899
129.576
129.025
128.313
128.251
126.840
126.595
124.077
123.884
122.471
121.172
118.466
132 130 128 126 124 122 120 ppm
S
N
H
Cl
CF3
200 180 160 140 120 100 80 60 40 20 0 ppm



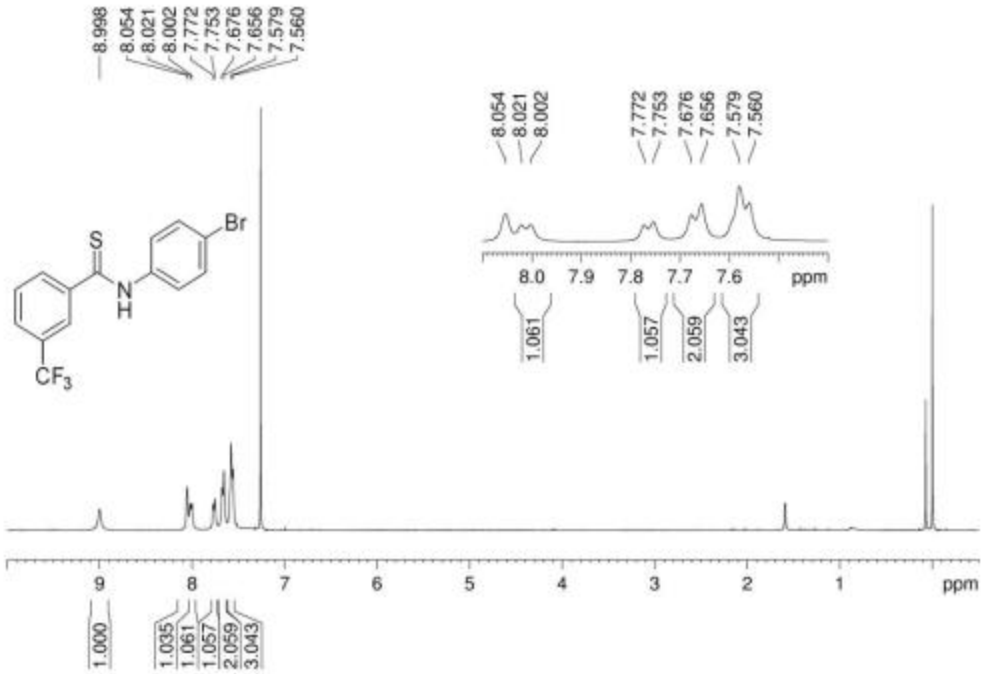
Compound 3ek

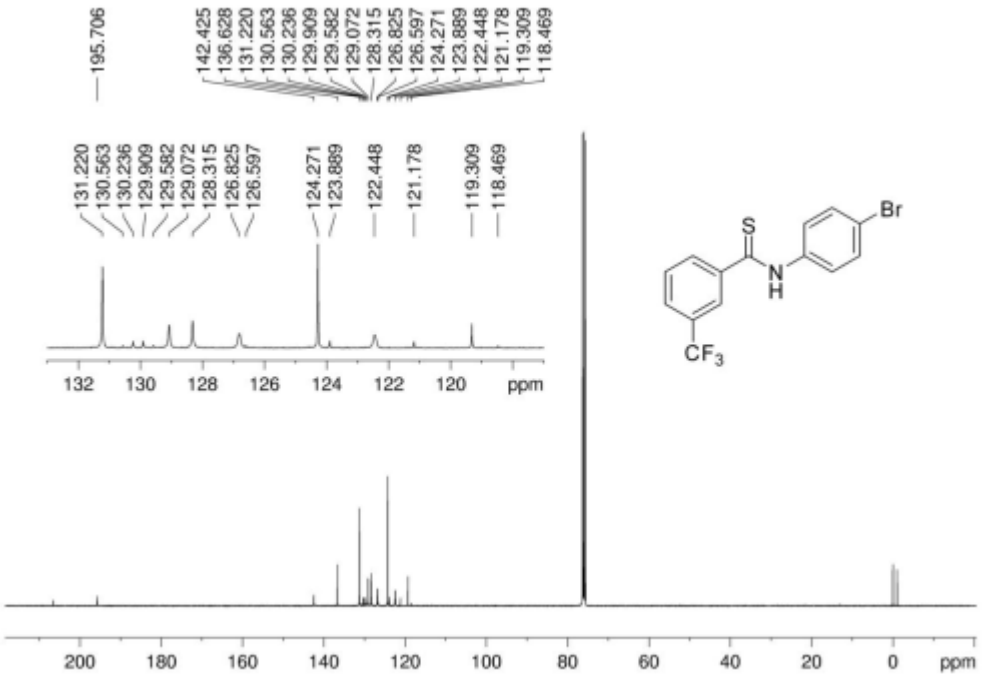


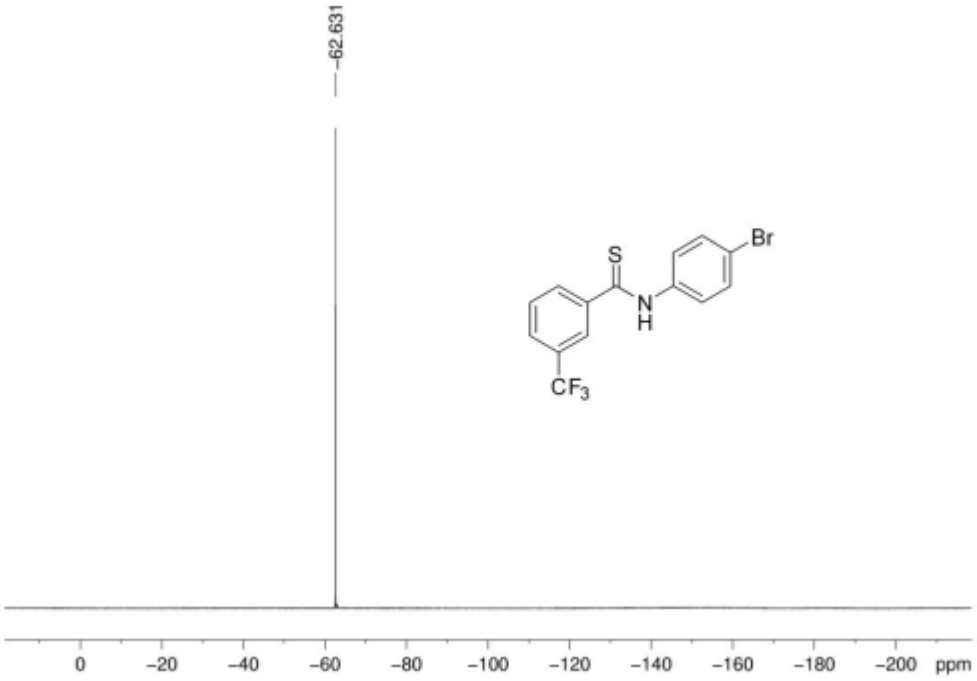




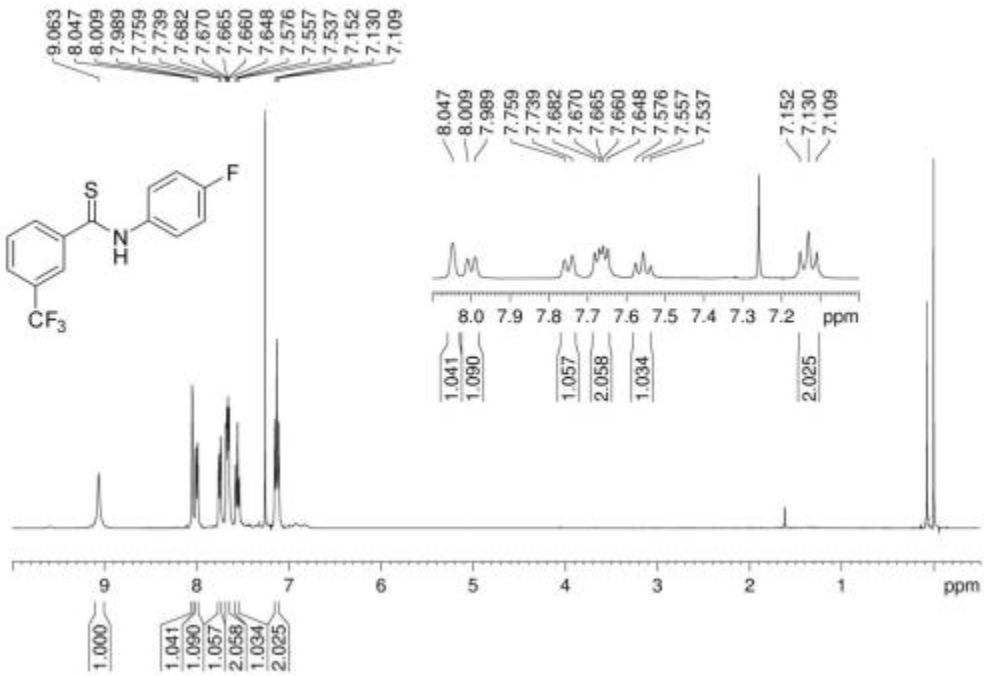
Compound 3el

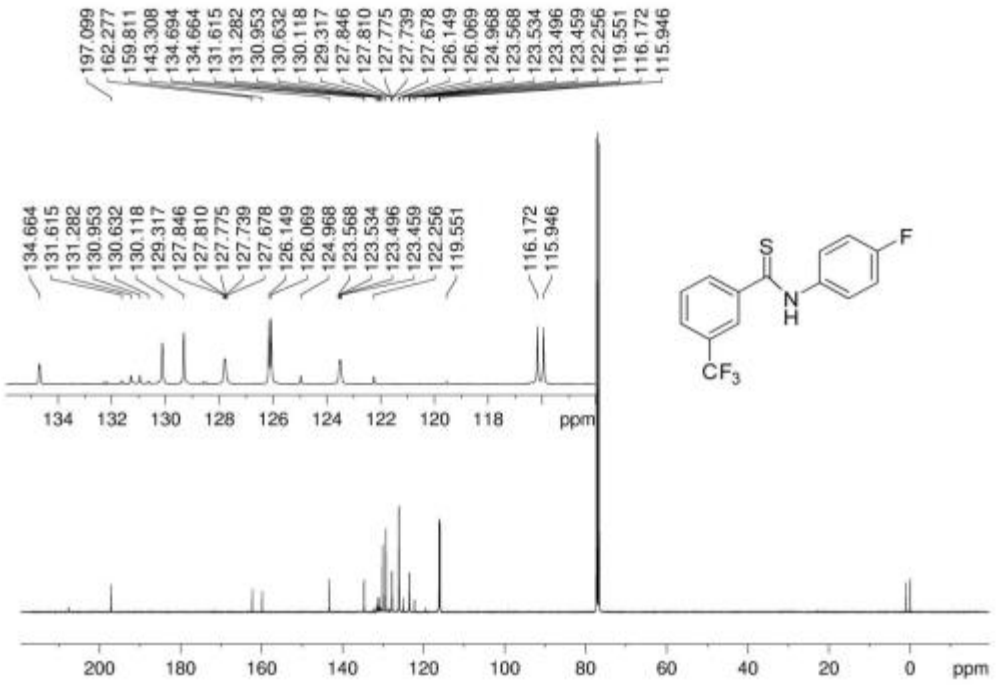

8.998
8.054
8.021
8.002
7.772
7.753
7.676
7.656
7.579
7.560
S
N
H
Br
CF3
8.0
7.9
7.8
7.7
7.6
ppm
1.061
1.057
2.059
3.043
9
8
7
6
5
4
3
2
1
ppm
1.000
1.035
1.061
1.057
2.059
3.043

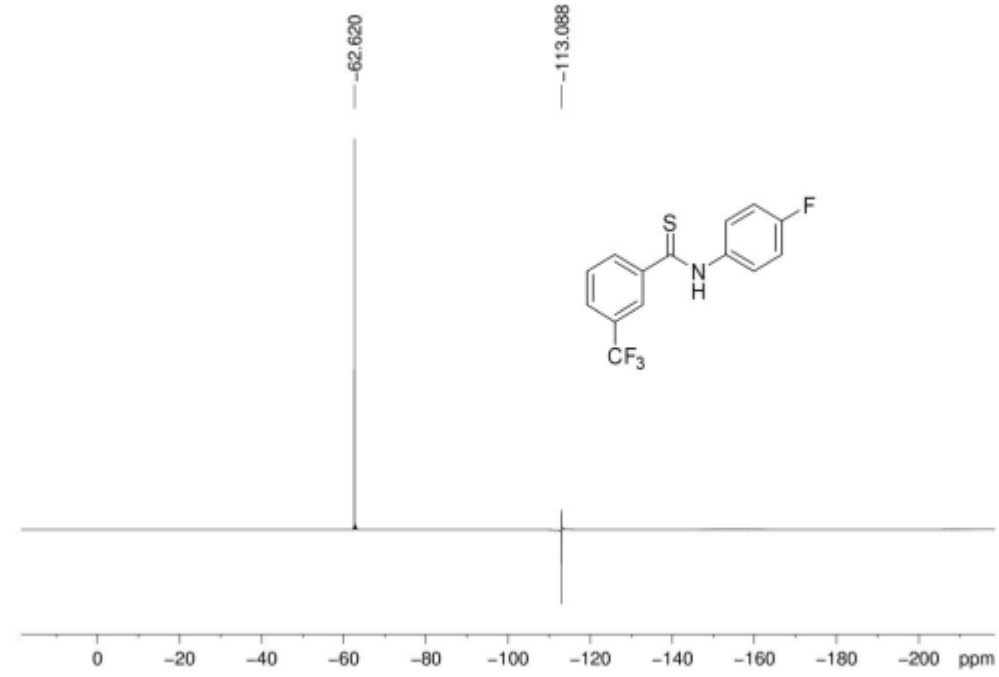

195.706
142.425
136.628
131.220
130.563
130.236
129.909
129.582
129.072
128.315
126.825
126.597
124.271
123.889
122.448
121.178
119.309
118.469
S
N
H
Br
CF3
132
130
128
126
124
122
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



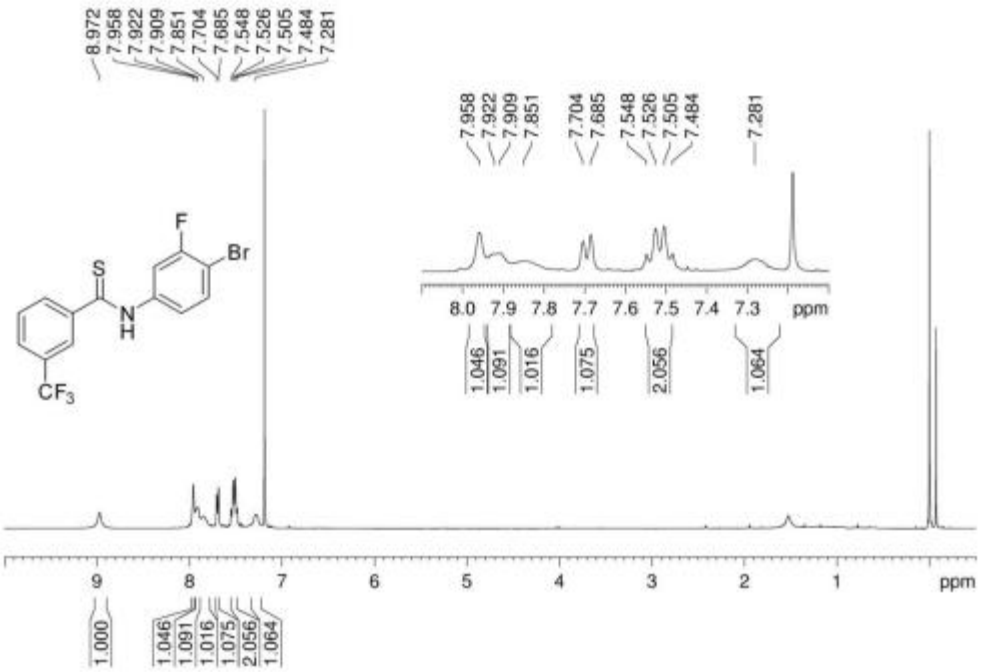
Compound 3em

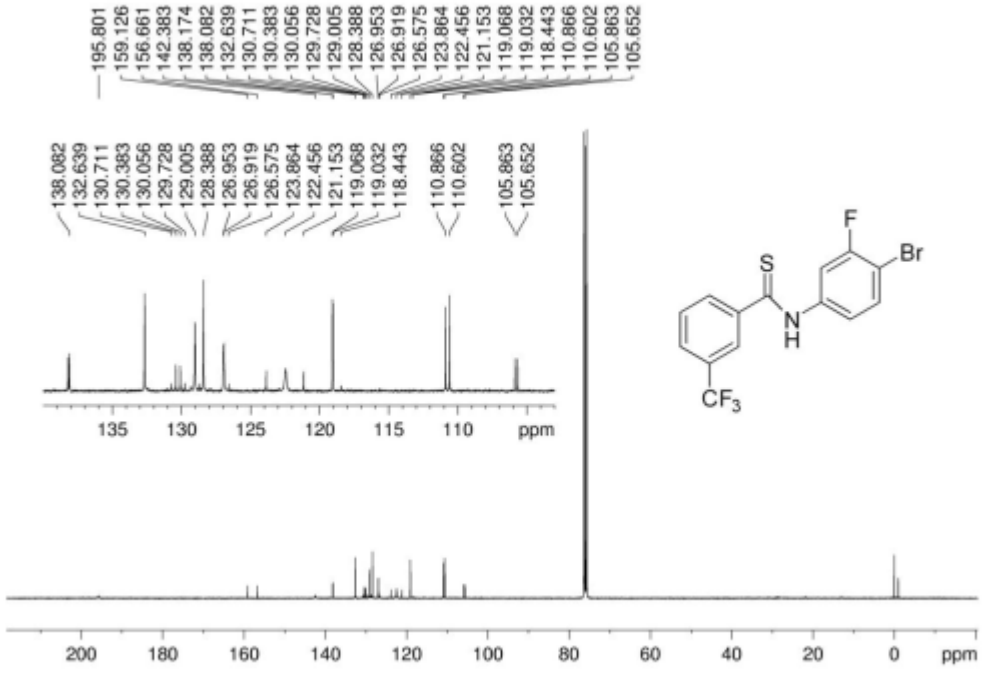


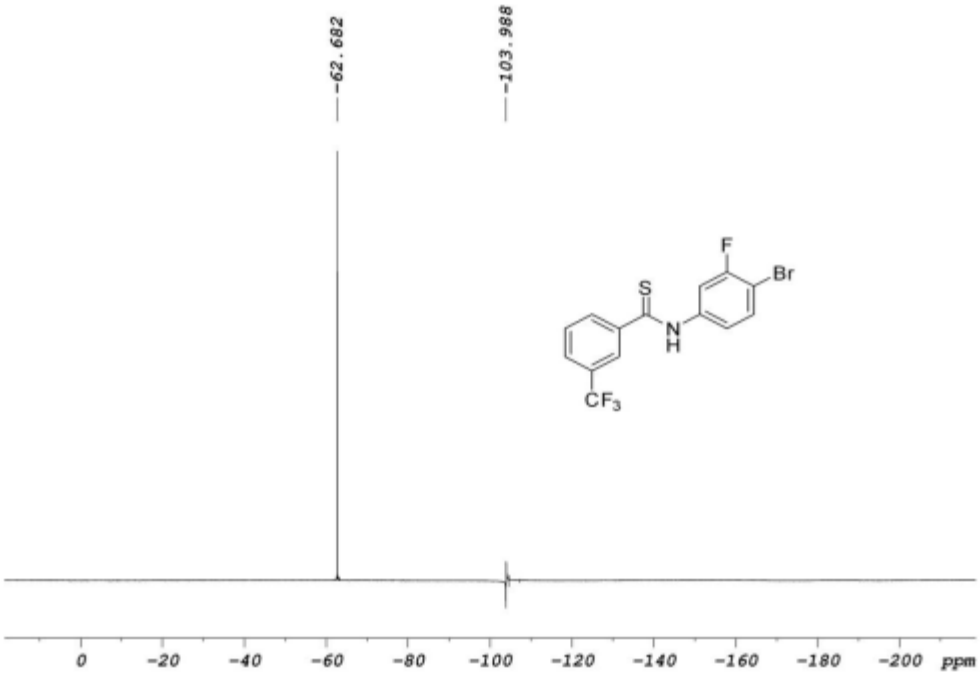




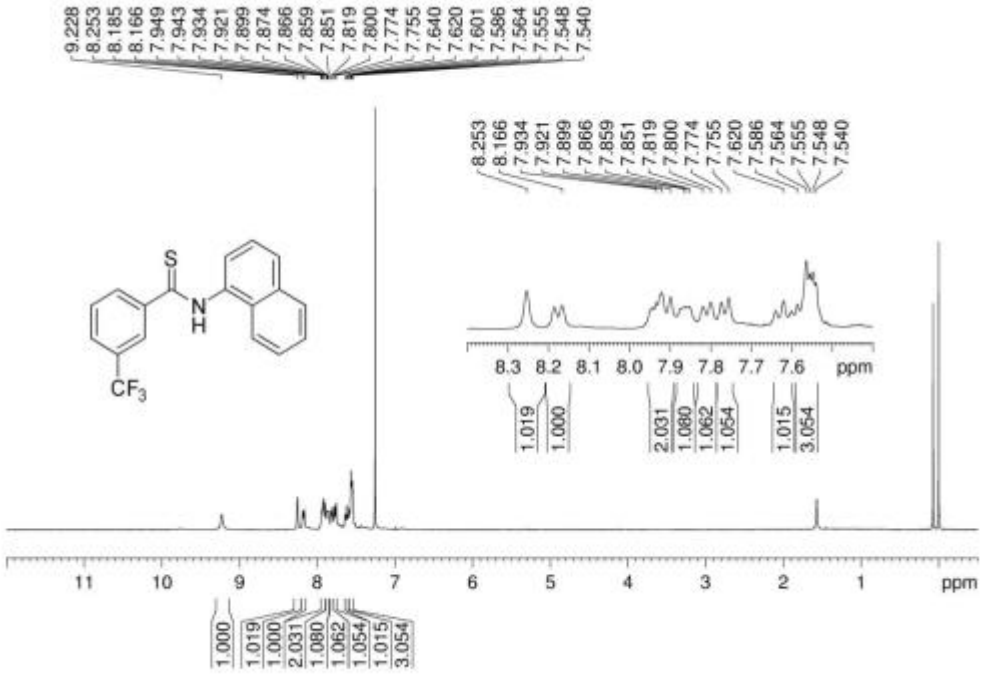
Compound 3en

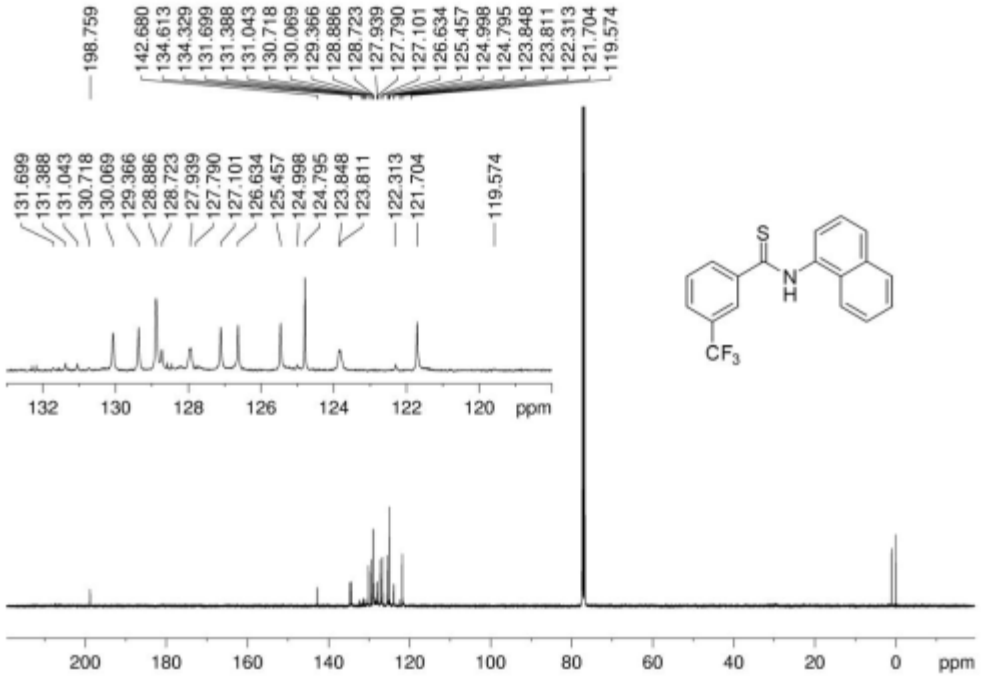

8.972
7.958
7.922
7.909
7.851
7.704
7.685
7.548
7.526
7.505
7.484
7.281
F
Br
S
N
H
CF3
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
1.046
1.091
1.016
1.075
2.056
1.064
9 8 7 6 5 4 3 2 1 ppm
1.000

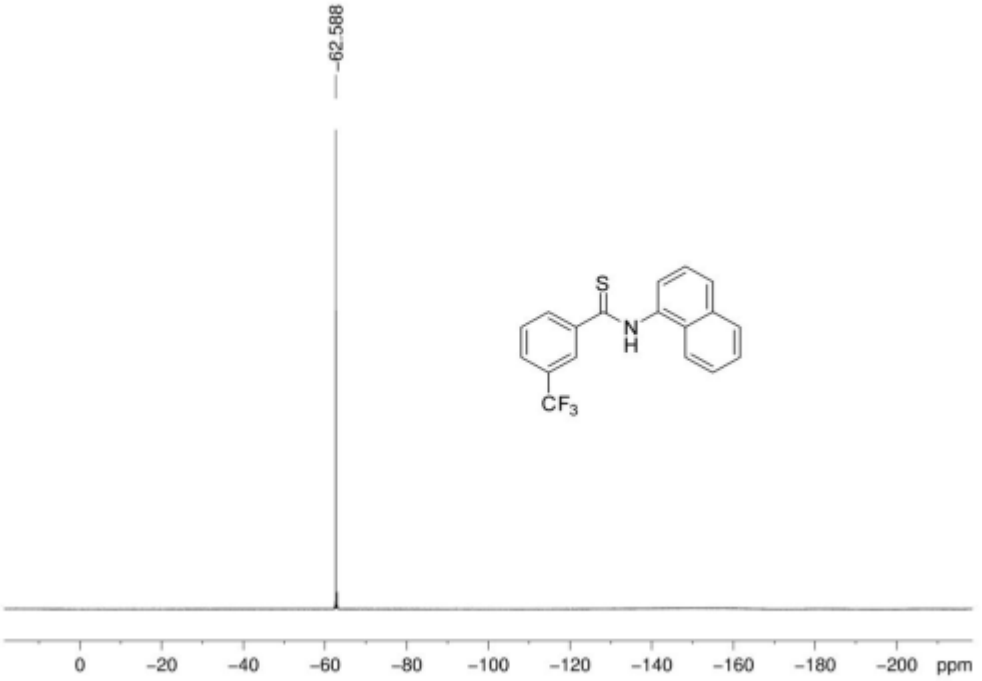

195.801
159.126
156.661
142.383
138.174
138.082
132.639
130.711
130.383
130.056
129.728
129.005
128.388
126.953
126.919
126.575
123.864
122.456
121.153
119.068
119.032
118.443
110.866
110.602
105.863
105.652
F
Br
S
N
H
CF3
135 130 125 120 115 110 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm



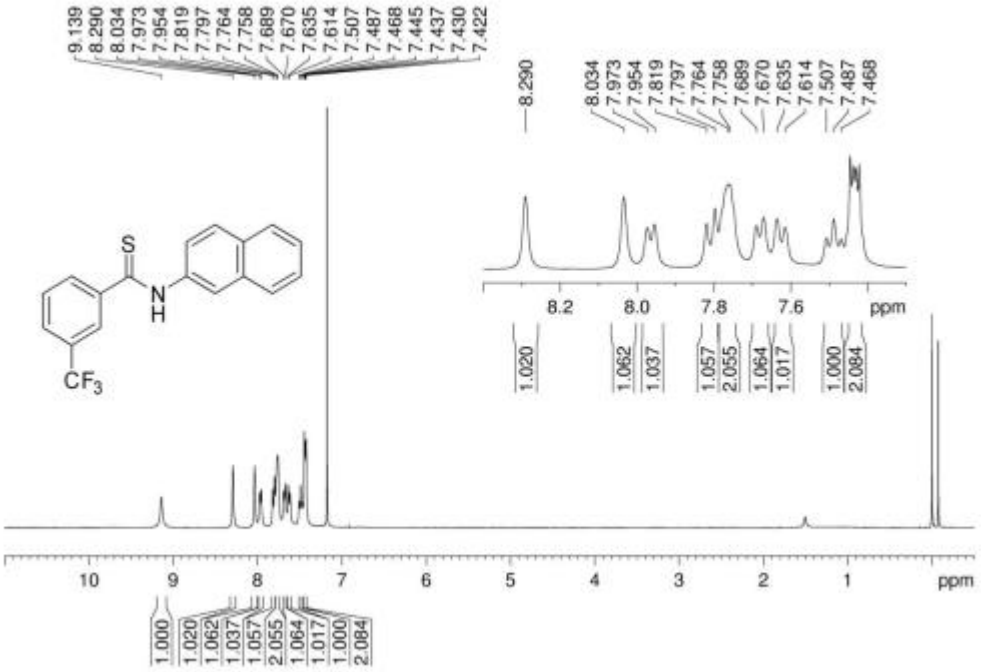
Compound 3eo

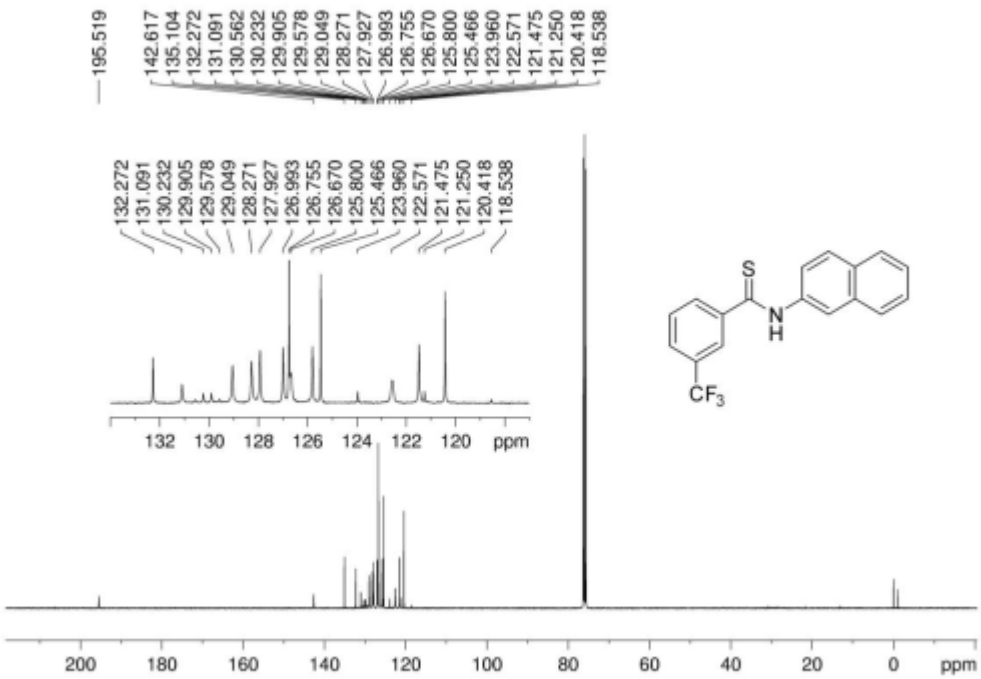


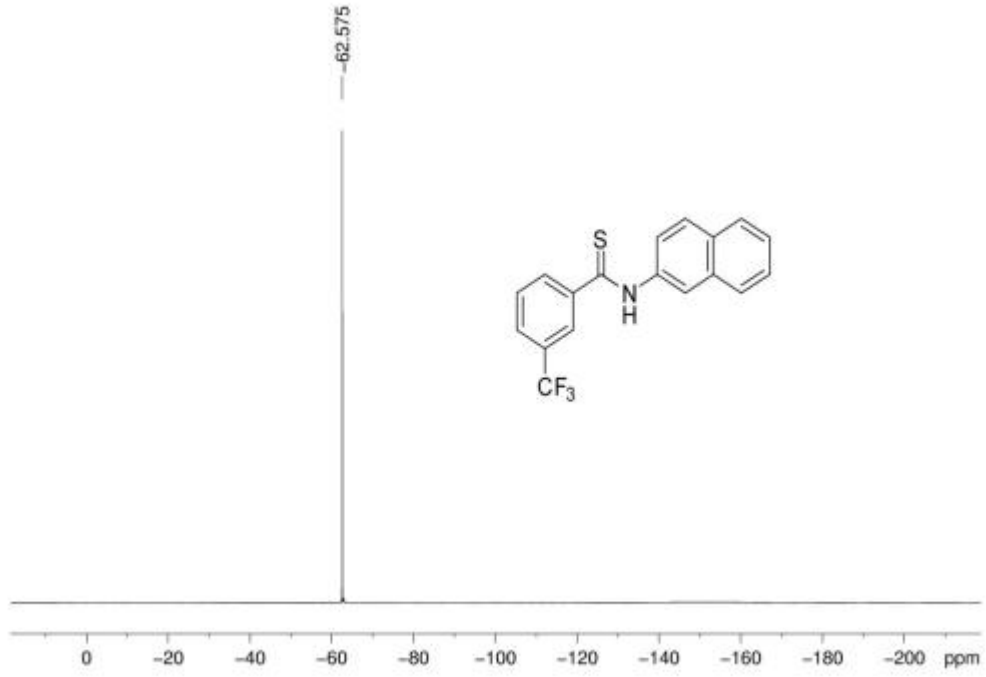




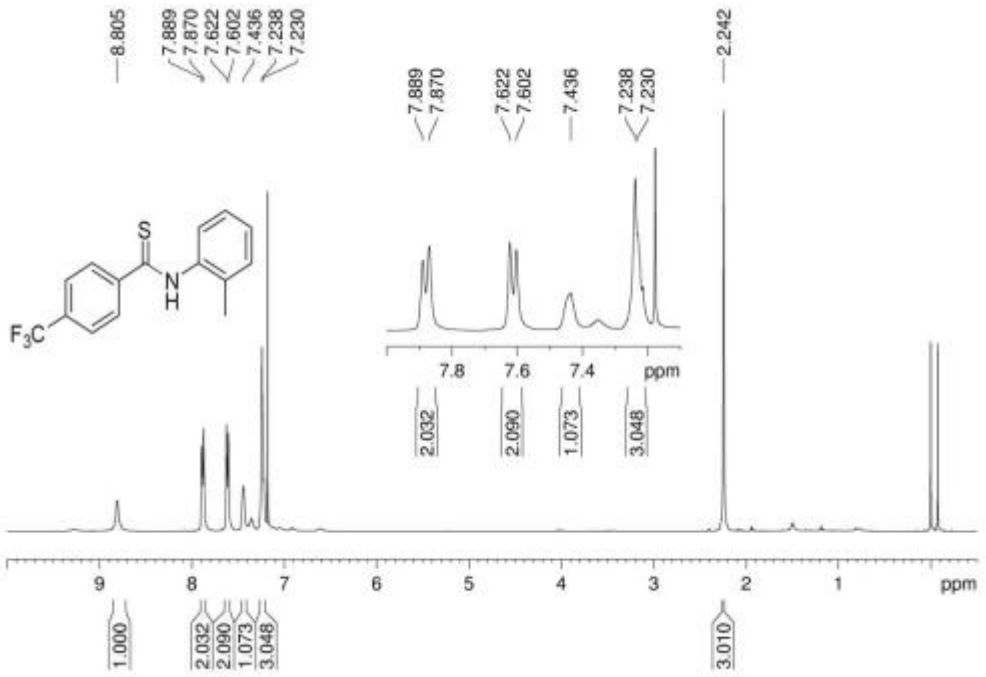
Compound 3ep

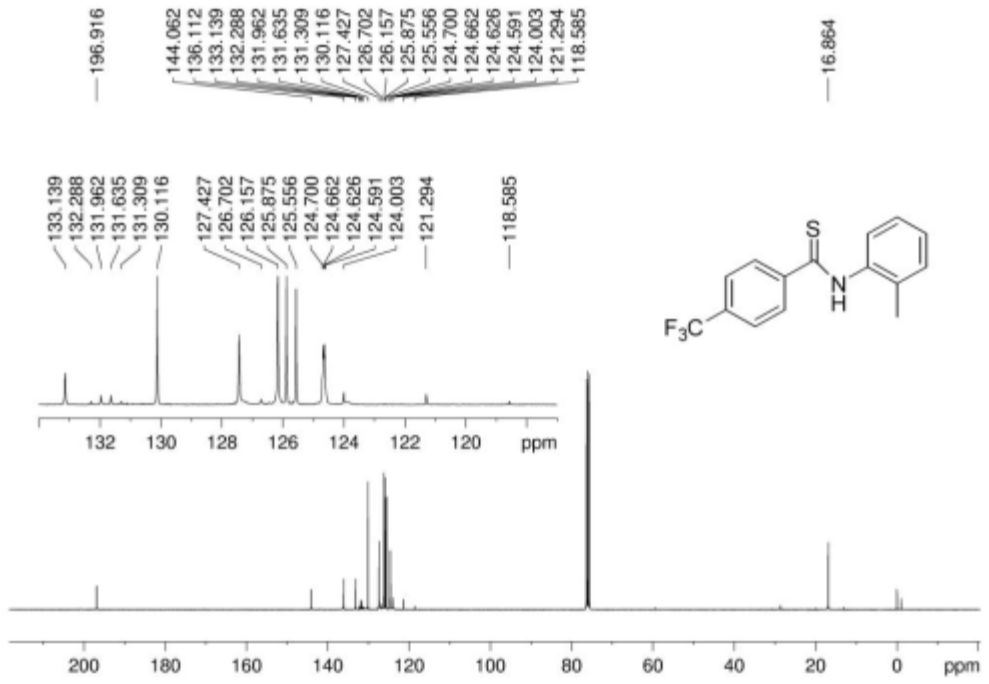

9.139
8.290
8.034
7.973
7.954
7.819
7.797
7.764
7.758
7.689
7.670
7.635
7.614
7.507
7.487
7.468
7.445
7.437
7.430
7.422
S
N
H
CF3
8.2
8.0
7.8
7.6
ppm
1.020
1.062
1.037
1.057
2.055
1.064
1.017
1.000
2.084
10
9
8
7
6
5
4
3
2
1
ppm

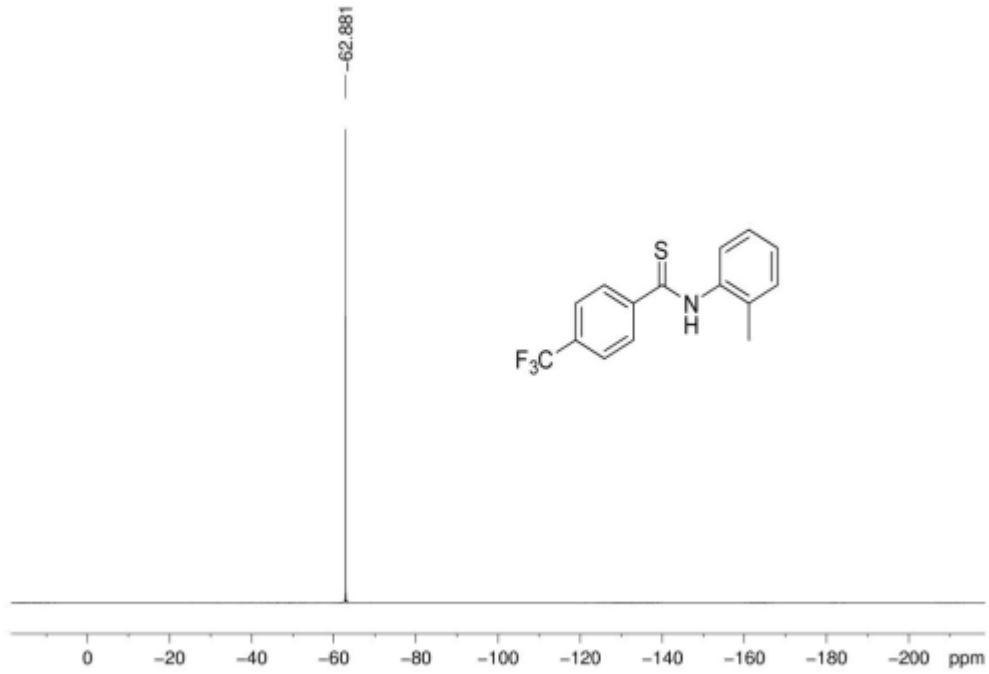

195.519
142.617
135.104
132.272
131.091
130.562
130.232
129.905
129.578
129.049
128.271
127.927
126.993
126.755
126.670
125.800
125.466
123.960
122.571
121.475
121.250
120.418
118.538
S
N
H
CF3
132
130
128
126
124
122
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



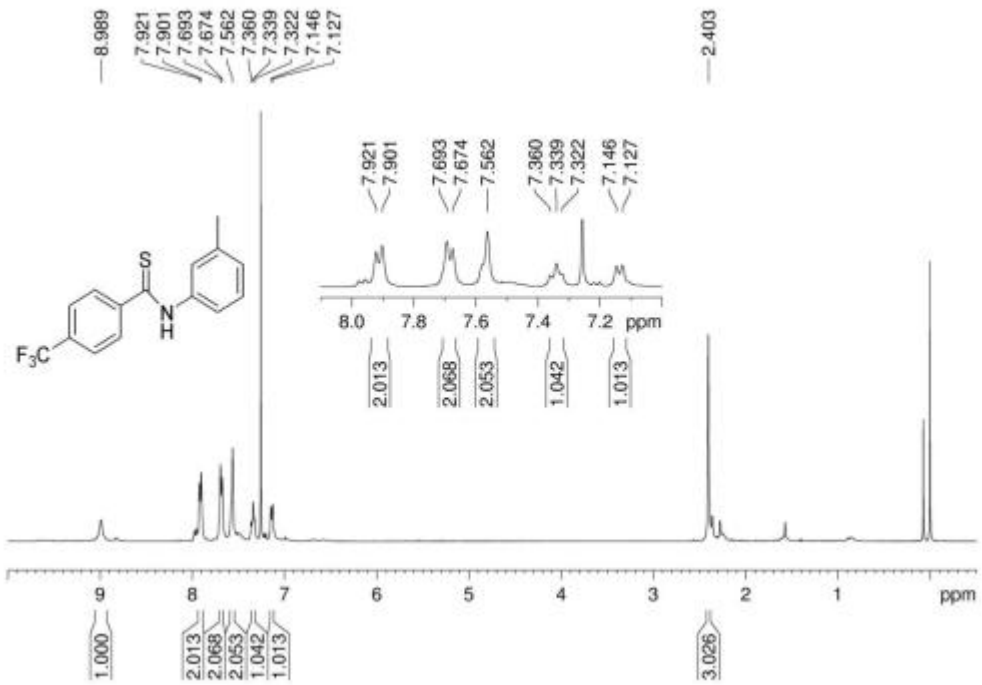
Compound 3hb

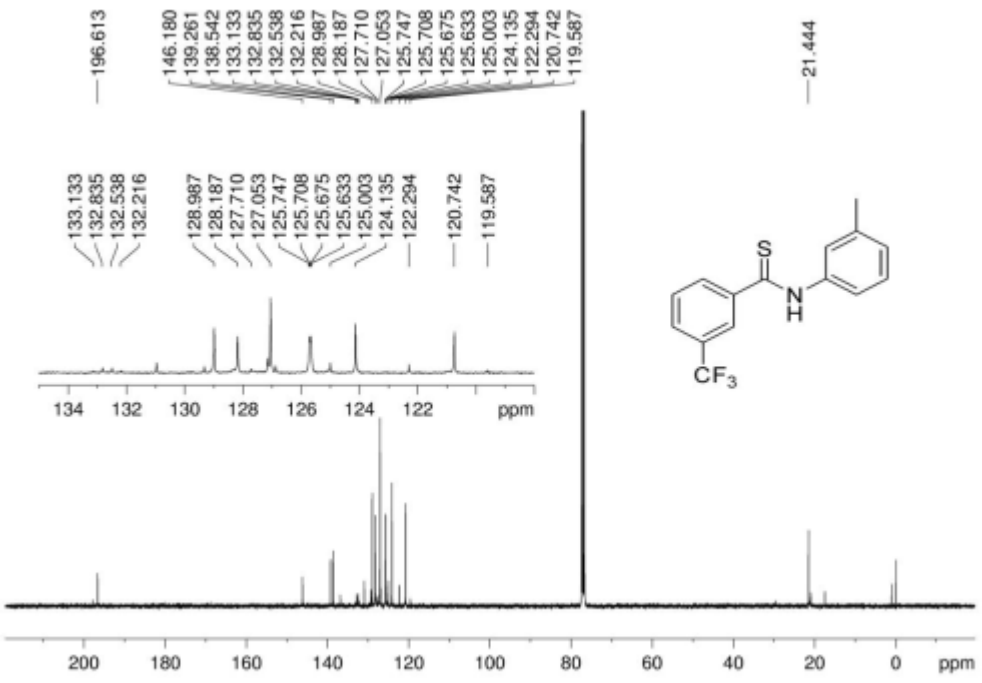


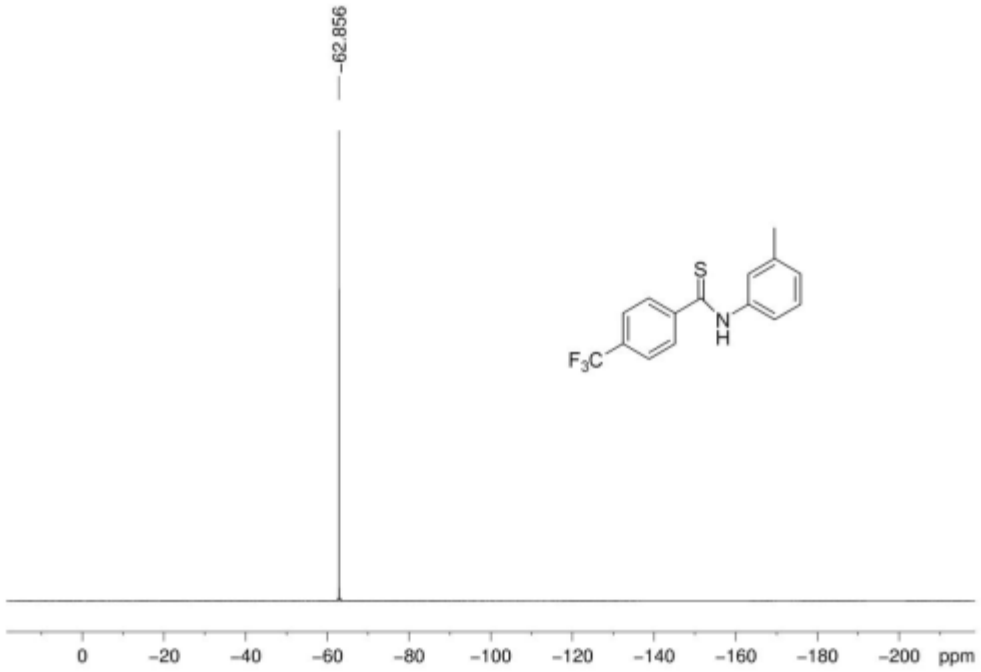




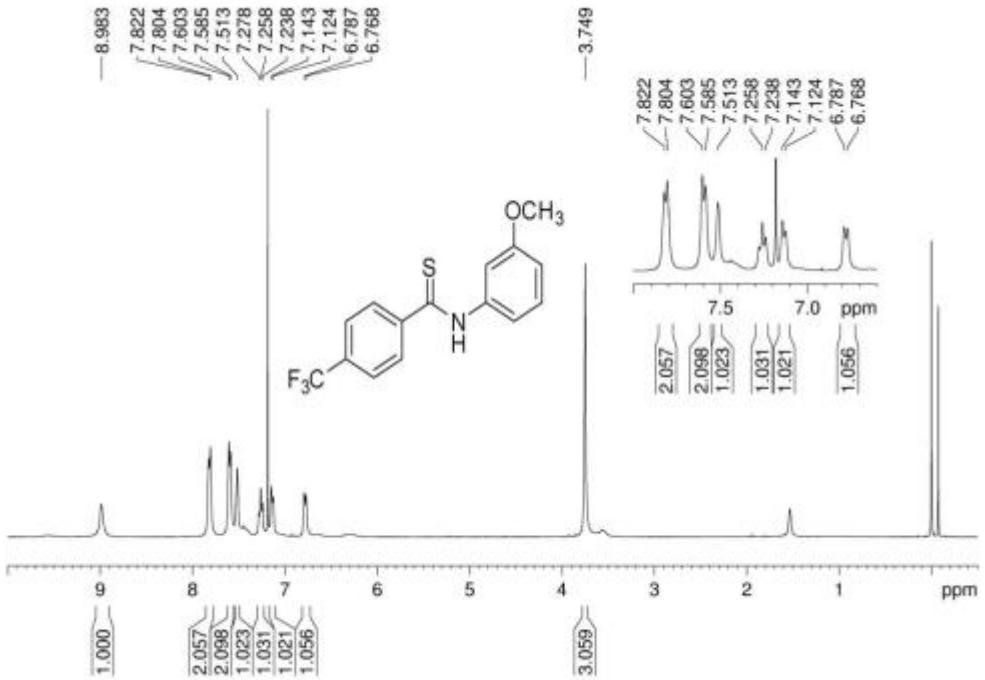
Compound 3hc

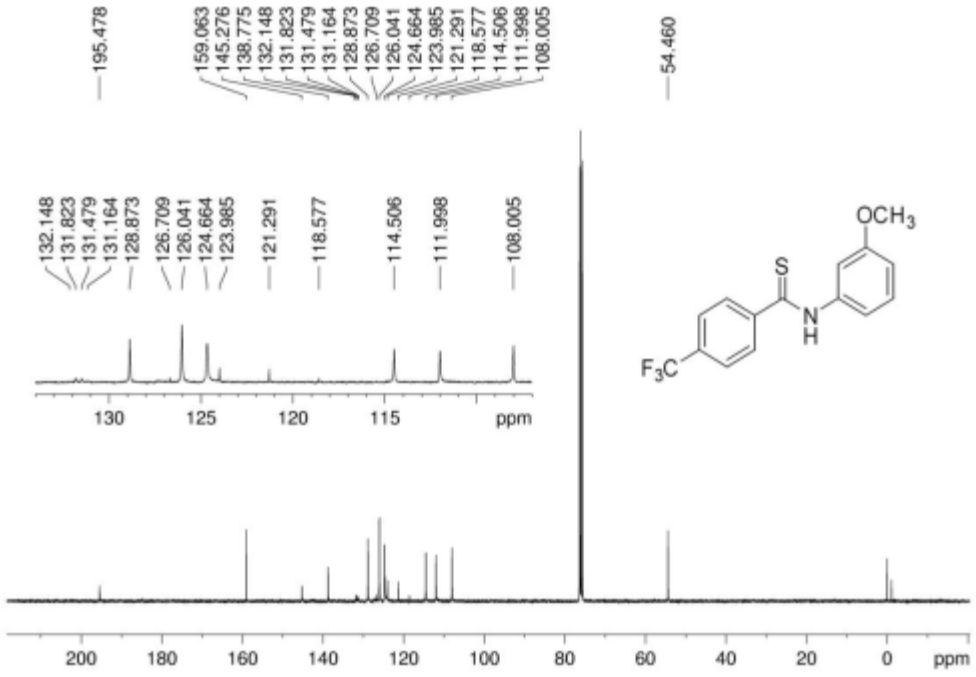

8.989
7.921
7.901
7.693
7.674
7.562
7.360
7.339
7.322
7.146
7.127
2.403
S
N
H
F3C
8.0
7.8
7.6
7.4
7.2
ppm
2.013
2.068
2.053
1.042
1.013
9
8
7
6
5
4
3
2
1
ppm
1.000
2.013
2.068
2.053
1.042
1.013
3.026

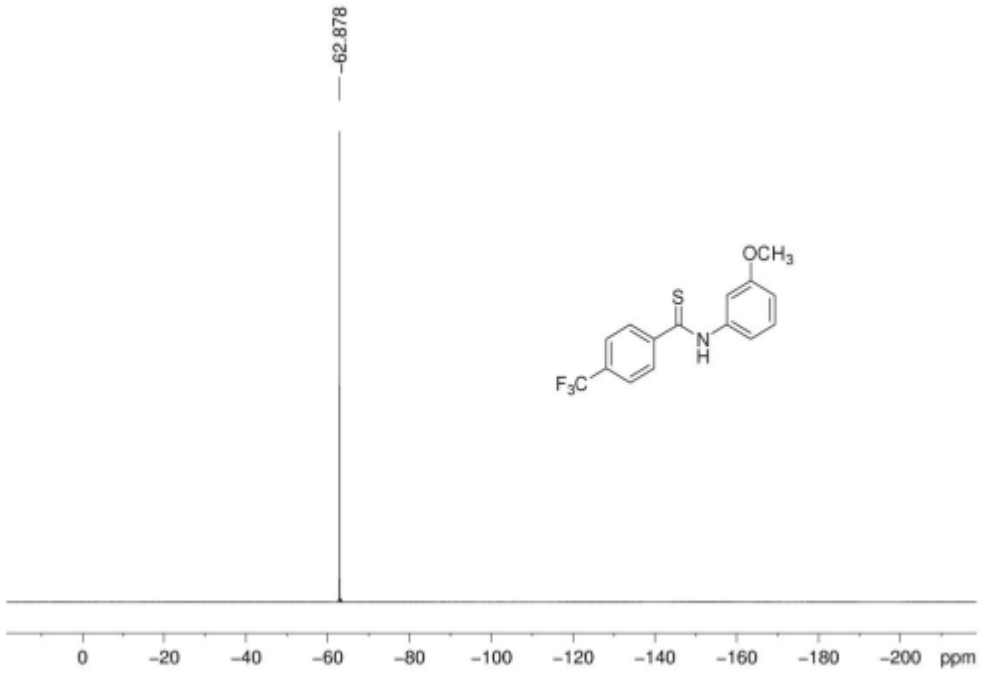

196.613
146.180
139.261
138.542
133.133
132.835
132.538
132.216
128.987
128.187
127.710
127.053
125.747
125.708
125.675
125.633
125.003
124.135
122.294
120.742
119.587
21.444
S
N
H
CF3
134
132
130
128
126
124
122
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



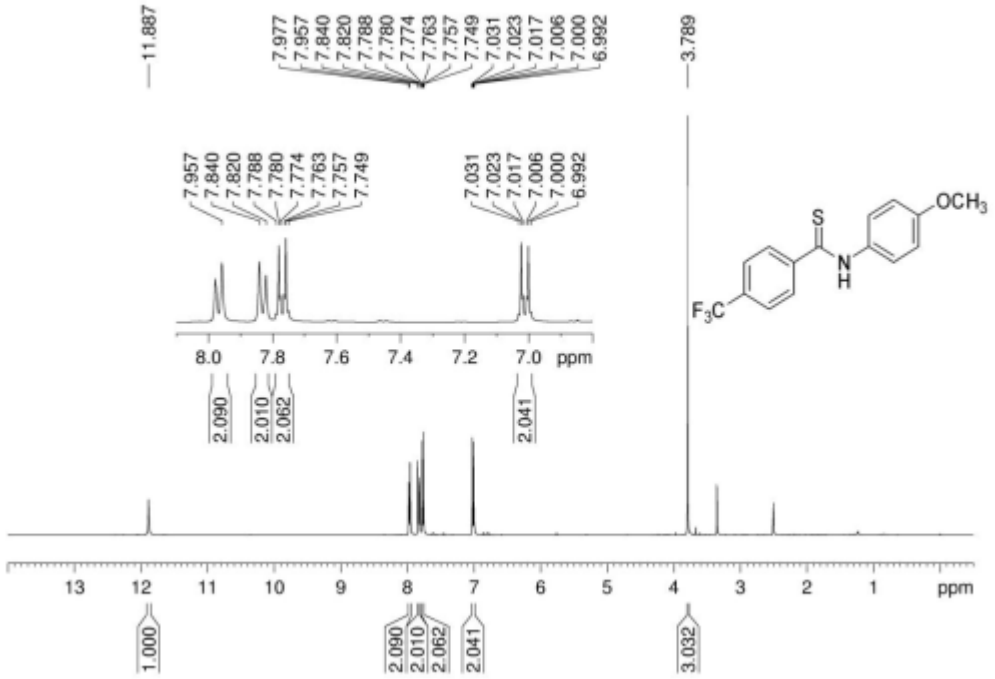
Compound 3hd

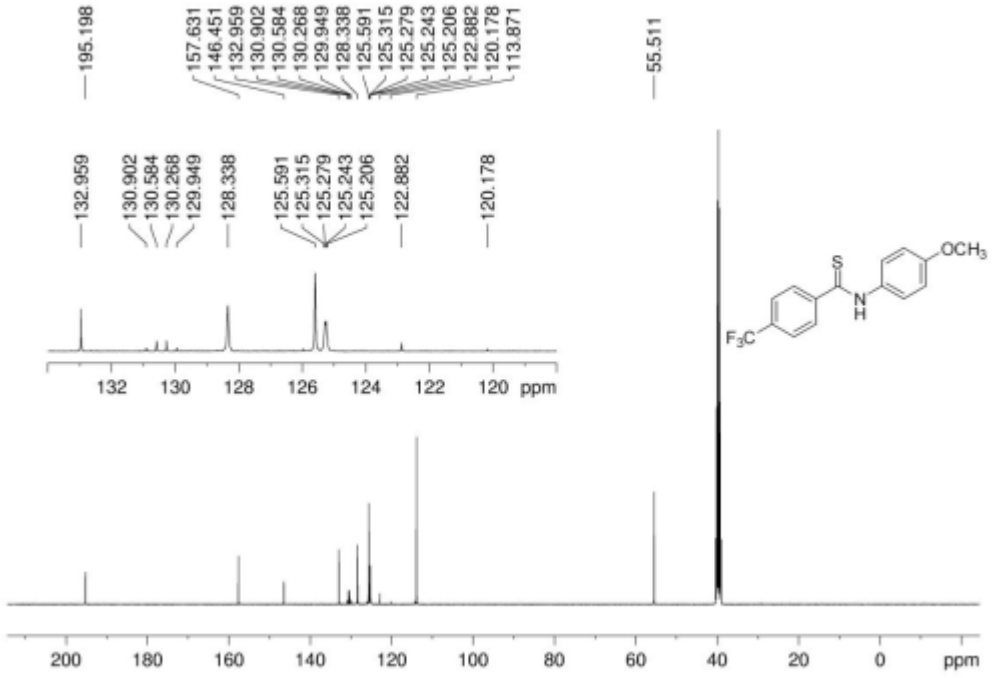


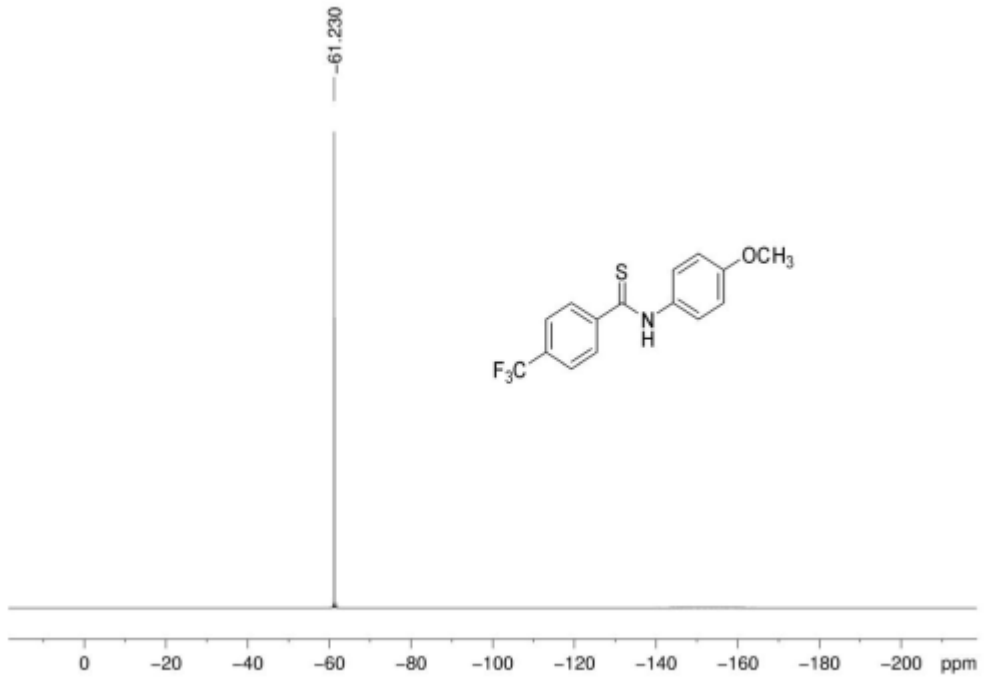




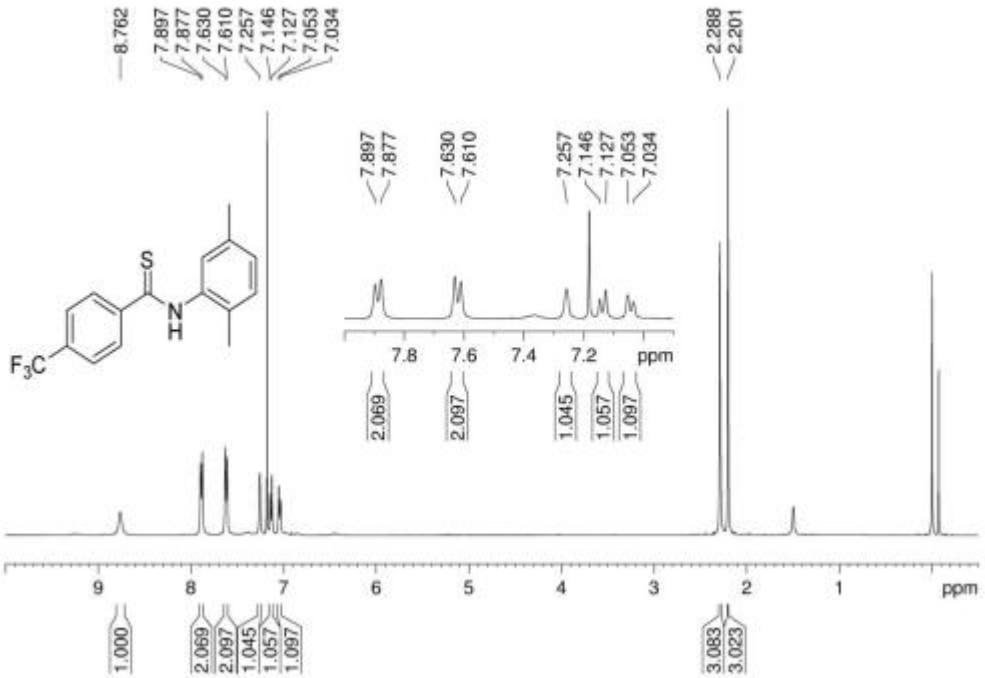
Compound 3he

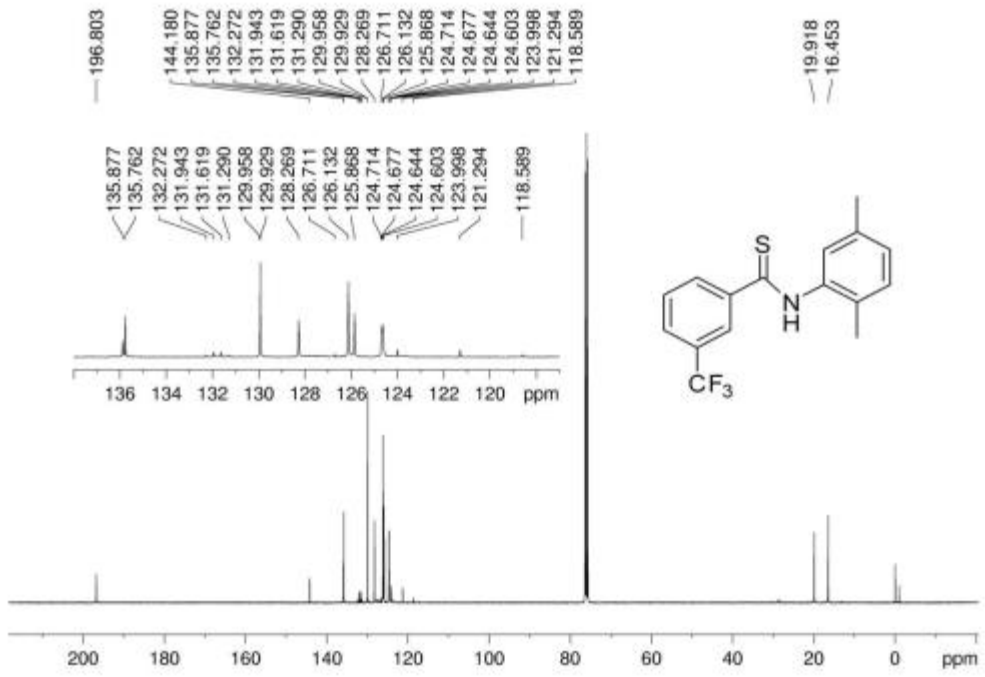

11.887
7.977
7.957
7.840
7.820
7.788
7.780
7.774
7.763
7.757
7.749
7.031
7.023
7.017
7.006
7.000
6.992
3.789
OCH3
S
N
H
F3C
8.0
7.8
7.6
7.4
7.2
7.0
ppm
2.090
2.010
2.062
2.041
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
2.090
2.010
2.062
2.041
3.032

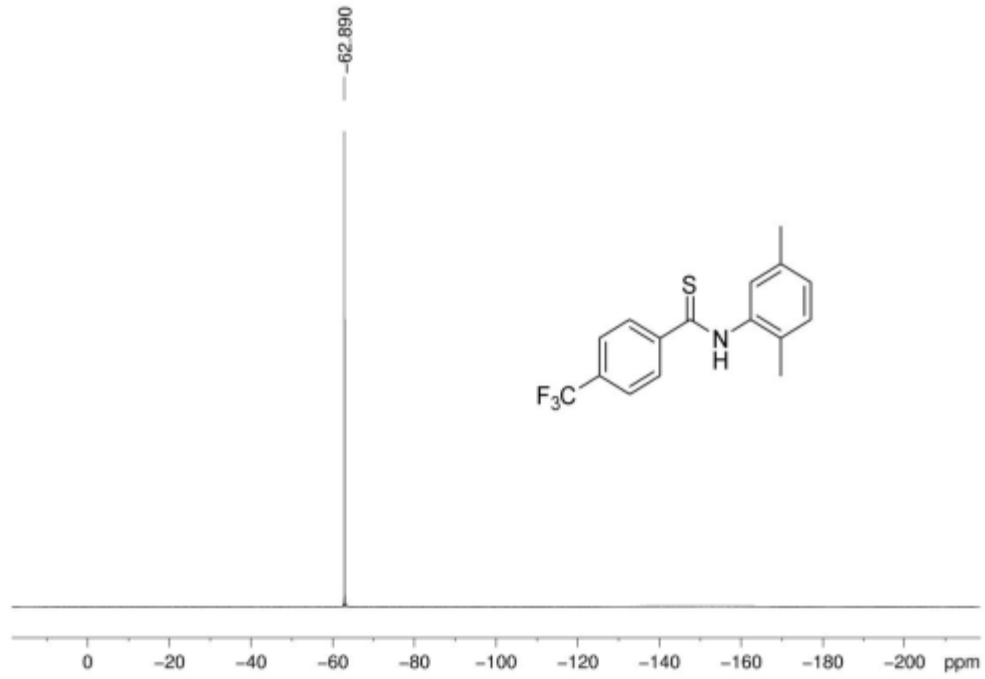

195.198
157.631
146.451
132.959
130.902
130.584
130.268
129.949
128.338
125.591
125.315
125.279
125.243
125.206
122.882
120.178
113.871
55.511
OCH3
S
N
H
F3C
132
130
128
126
124
122
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



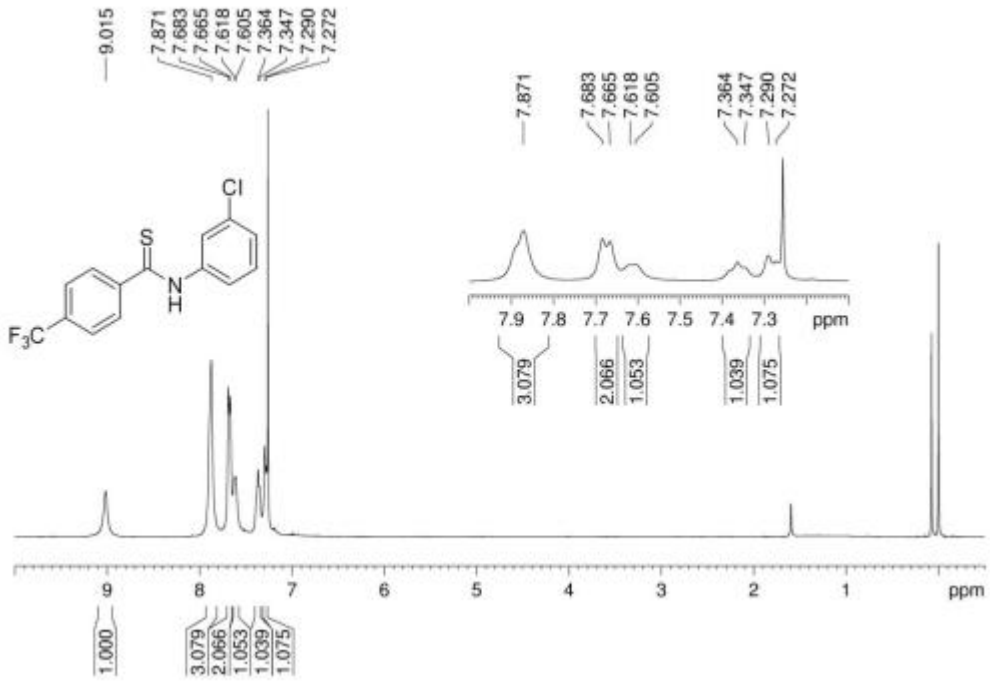
Compound 3hg

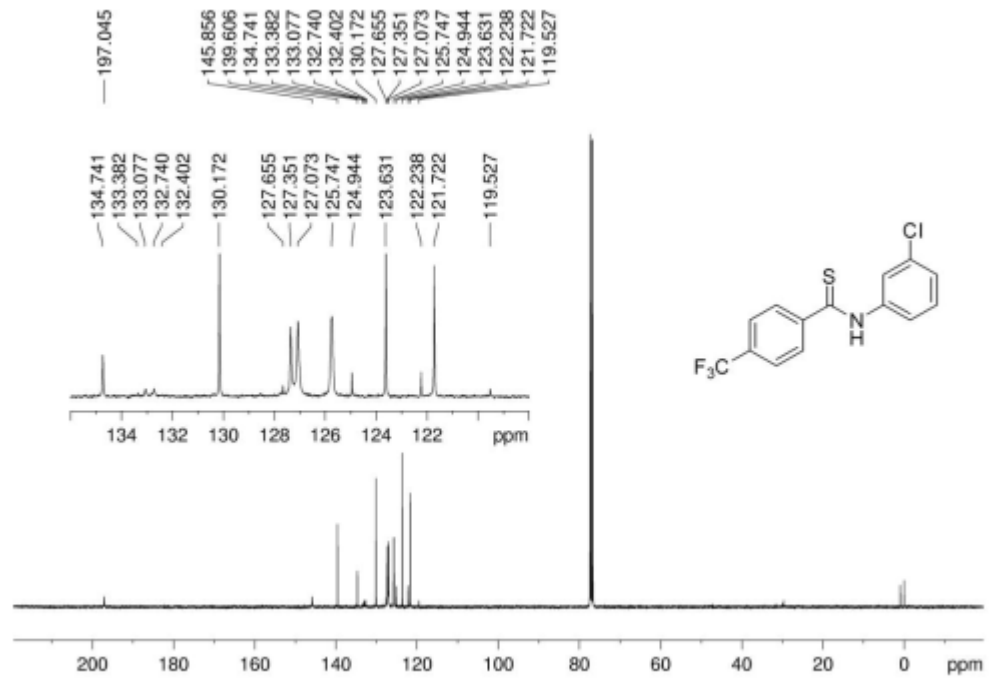


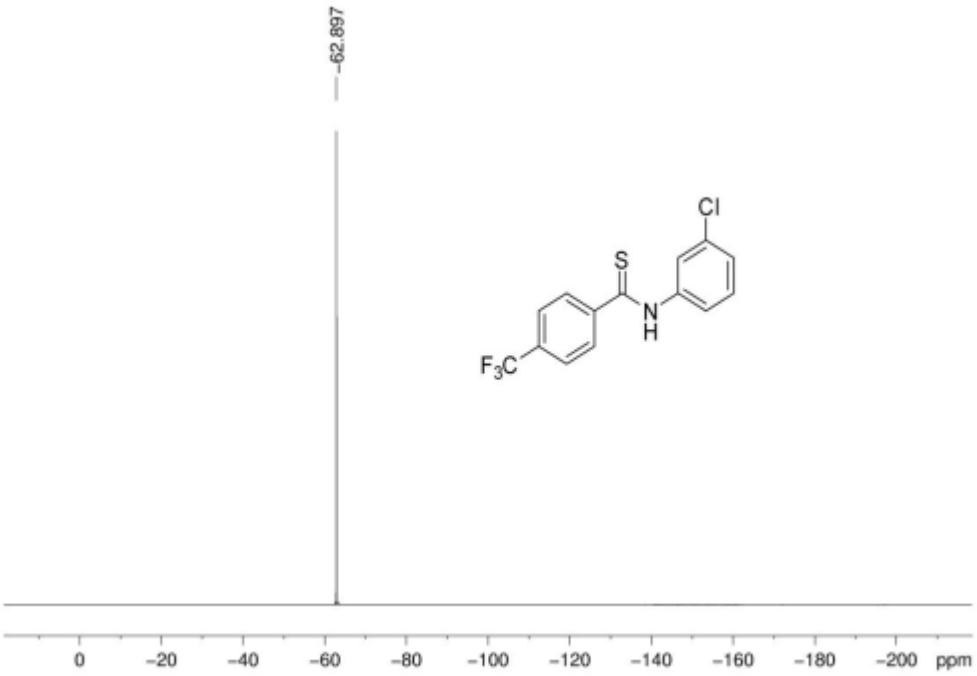




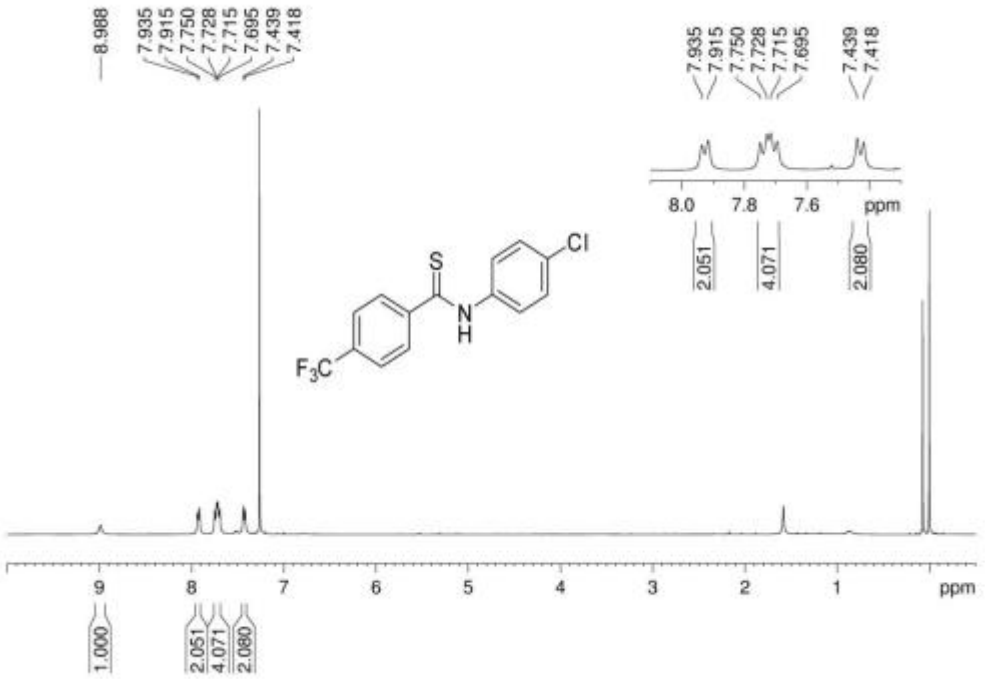
Compound 3hi

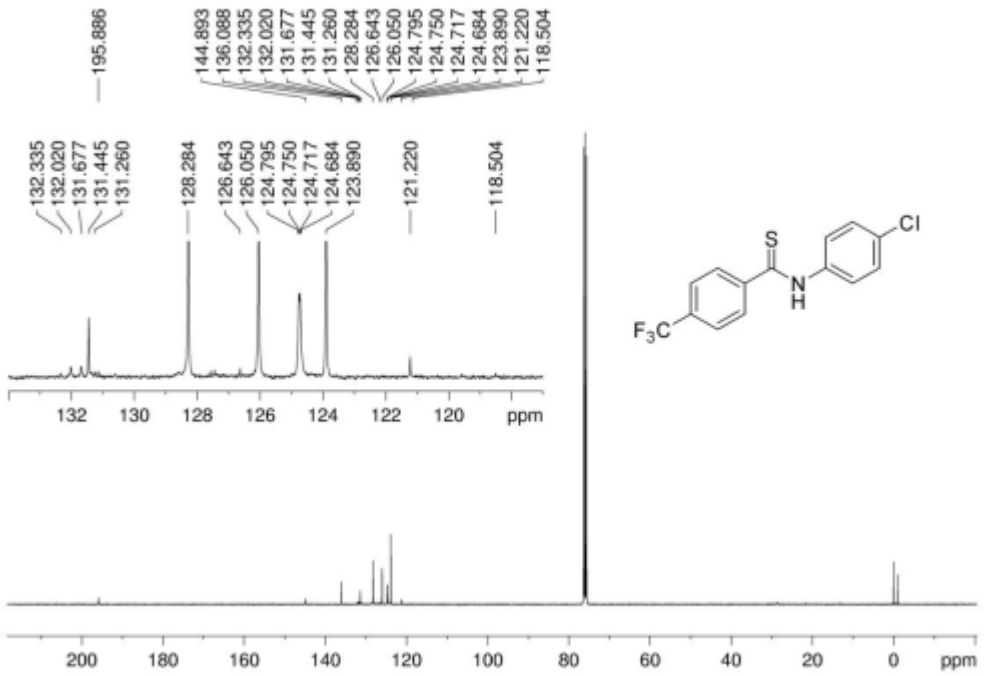

9.015
7.871
7.683
7.665
7.618
7.605
7.364
7.347
7.290
7.272
Cl
S
N
H
F3C
7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
3.079
2.066
1.053
1.039
1.075
9 8 7 6 5 4 3 2 1 ppm
1.000
3.079
2.066
1.053
1.039
1.075

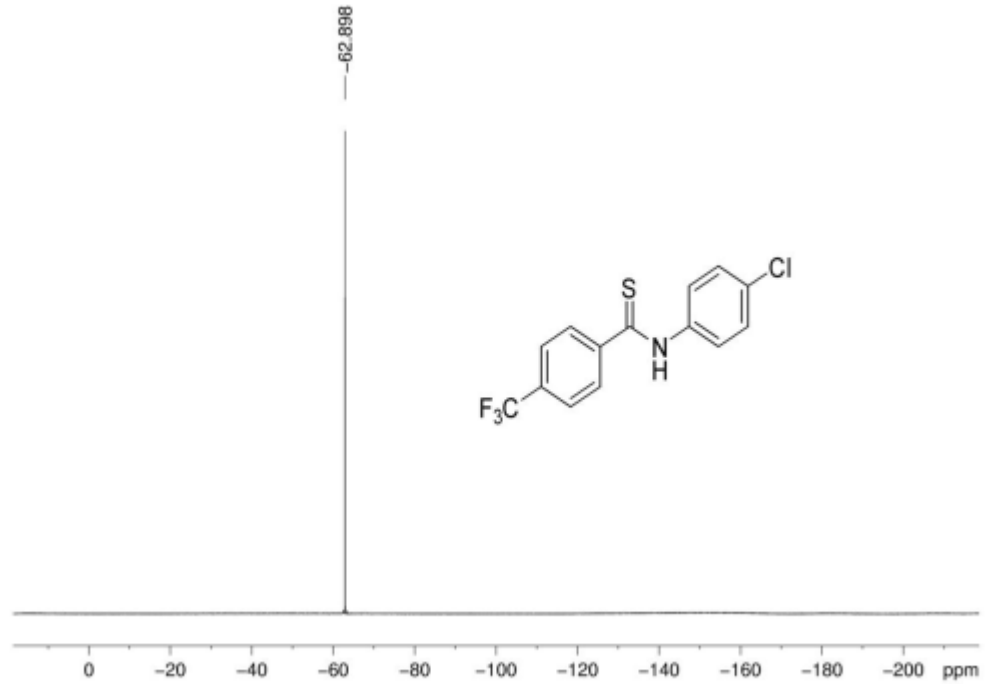

197.045
145.856
139.606
134.741
133.382
133.077
132.740
132.402
130.172
127.655
127.351
127.073
125.747
124.944
123.631
122.238
121.722
119.527
Cl
S
N
H
F3C
134 132 130 128 126 124 122 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm



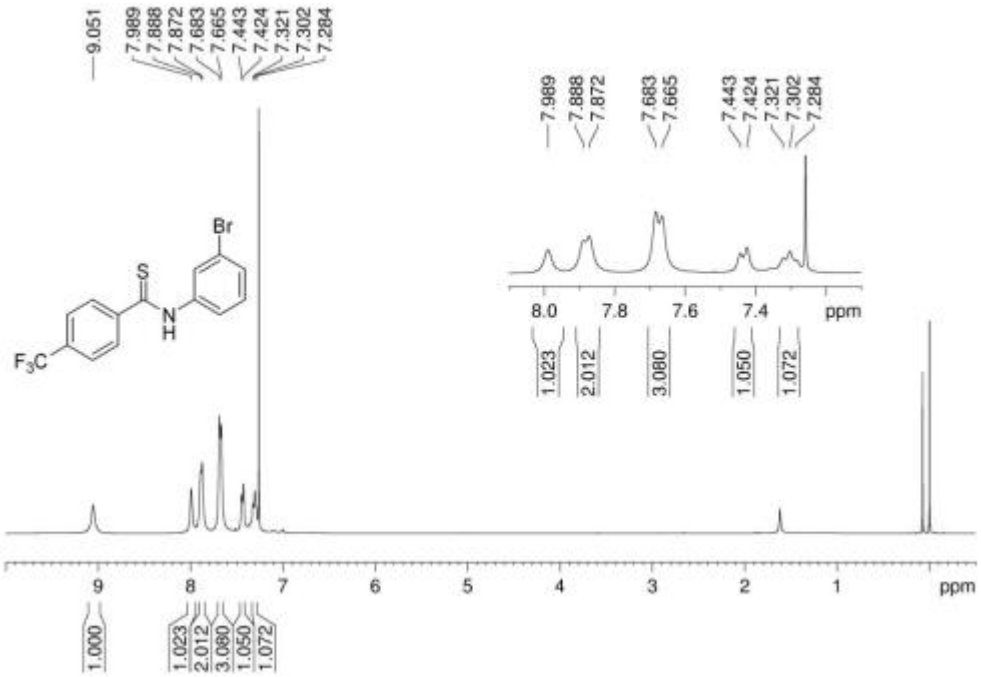
Compound 3hj

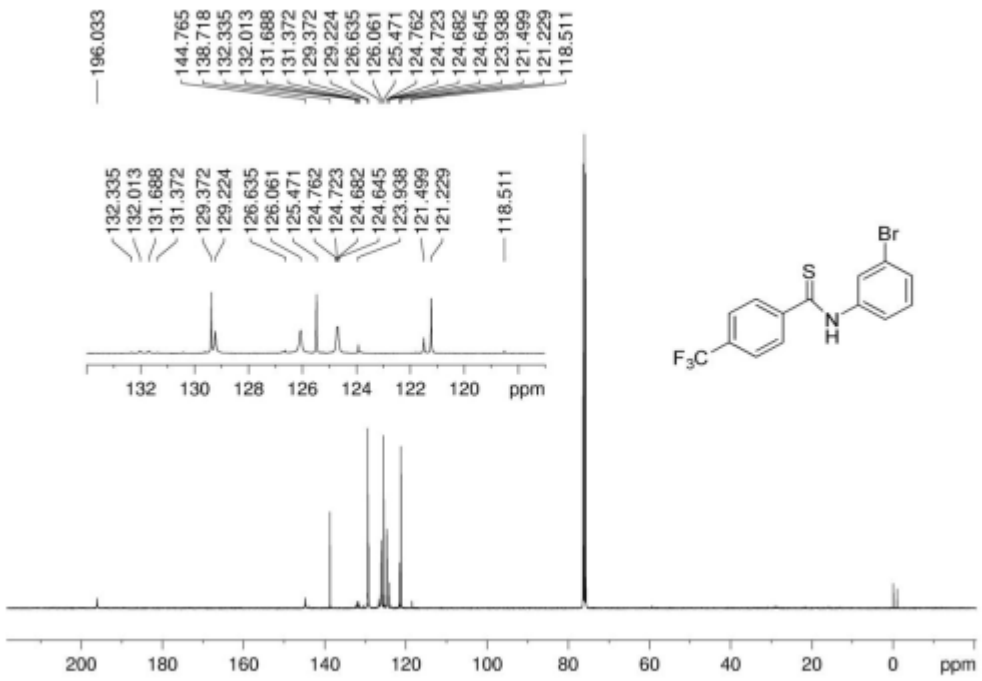


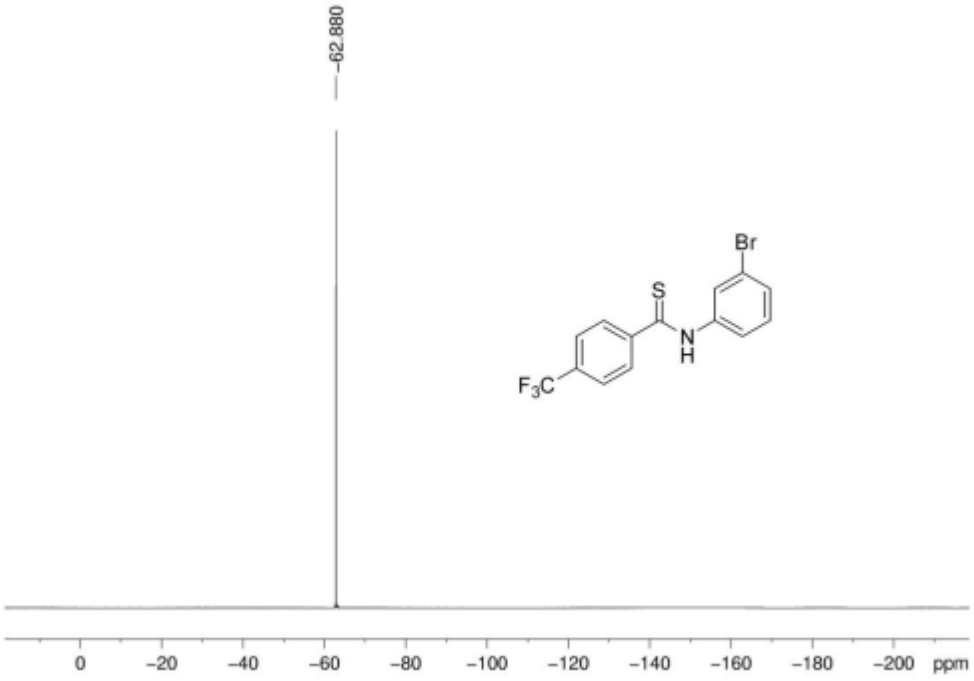




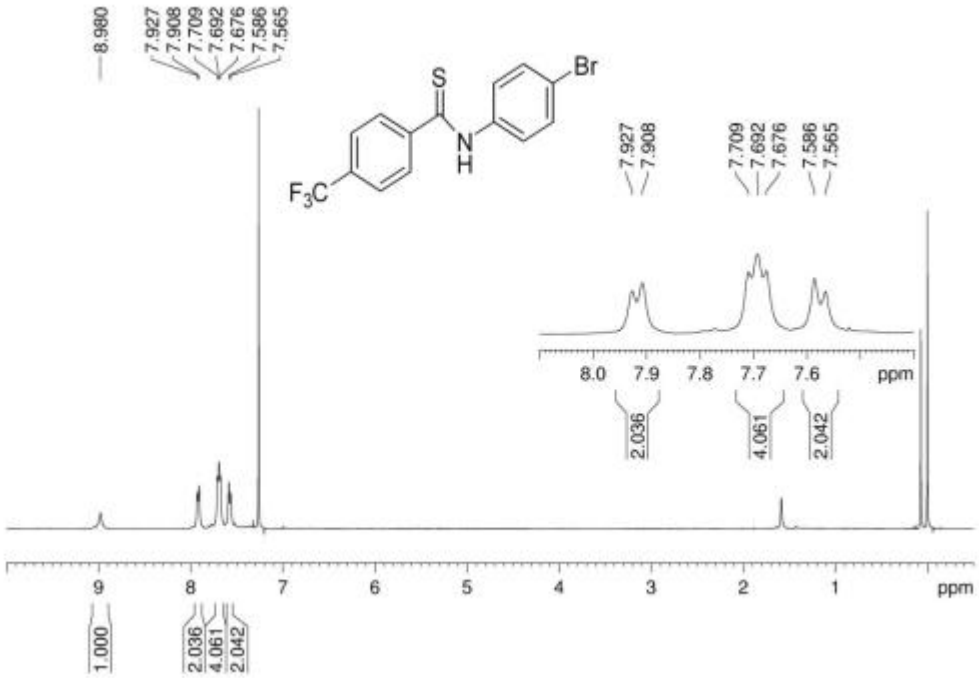
Compound 3hk

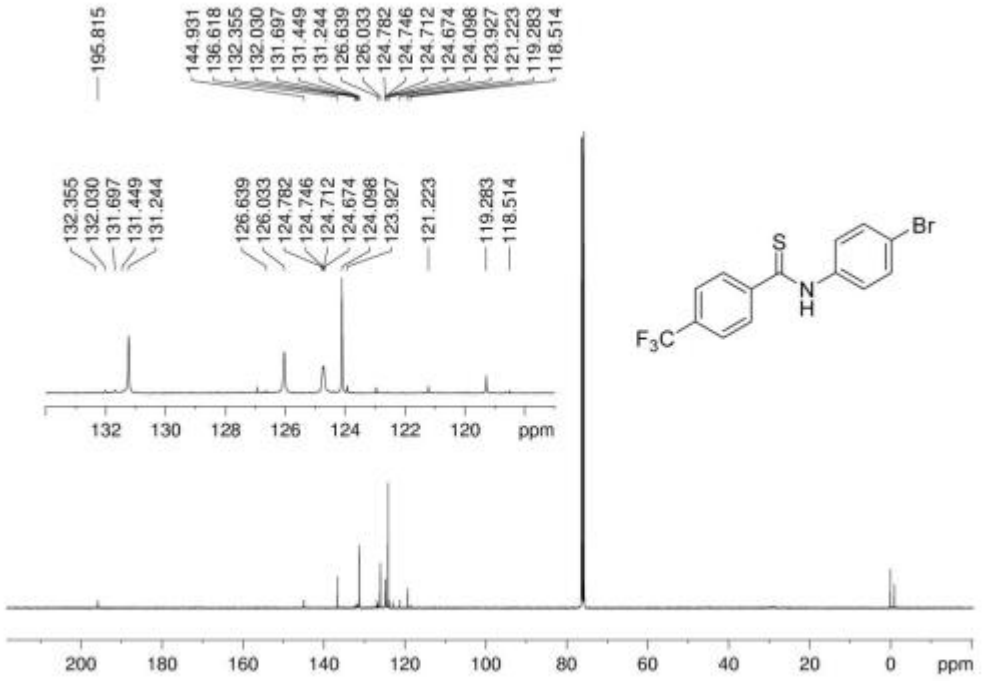

9.051
7.989
7.888
7.872
7.683
7.665
7.443
7.424
7.321
7.302
7.284
Br
S
N
H
F3C
8.0
7.8
7.6
7.4
ppm
1.023
2.012
3.080
1.050
1.072
9
8
7
6
5
4
3
2
1
ppm
1.000
1.023
2.012
3.080
1.050
1.072

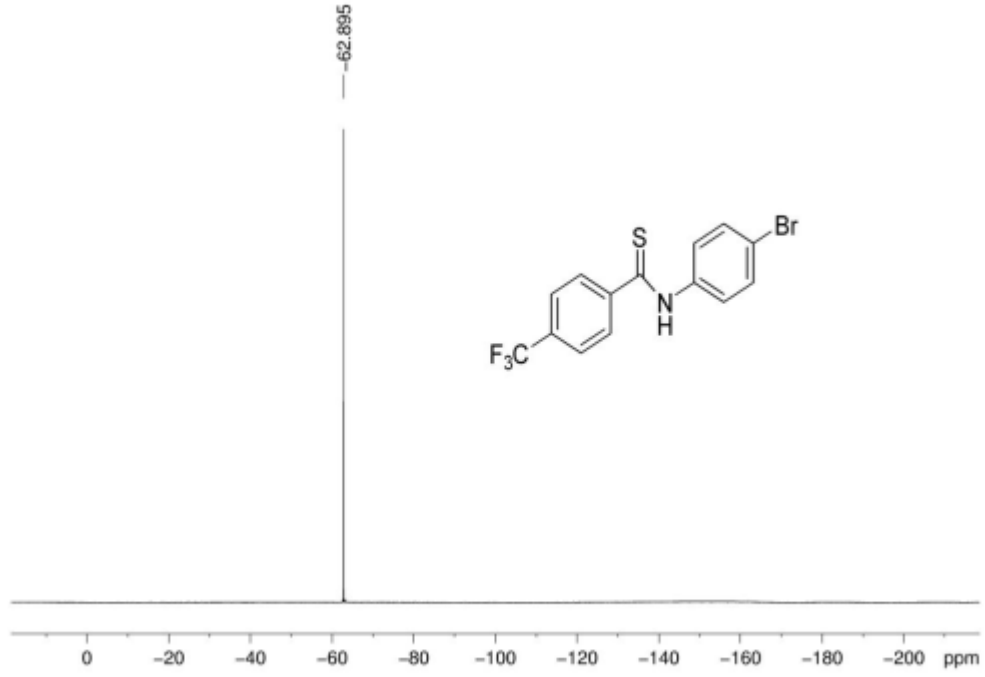

196.033
144.765
138.718
132.335
132.013
131.688
131.372
129.372
129.224
126.635
126.061
125.471
124.762
124.723
124.682
124.645
123.938
121.499
121.229
118.511
Br
S
N
H
F3C
132
130
128
126
124
122
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



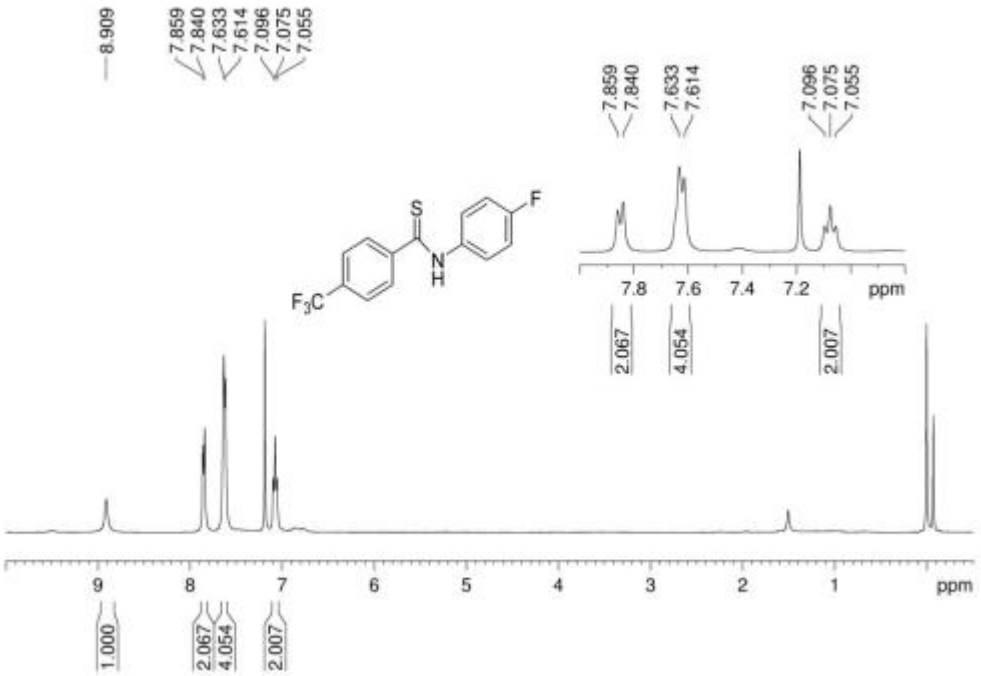
Compound 3hl

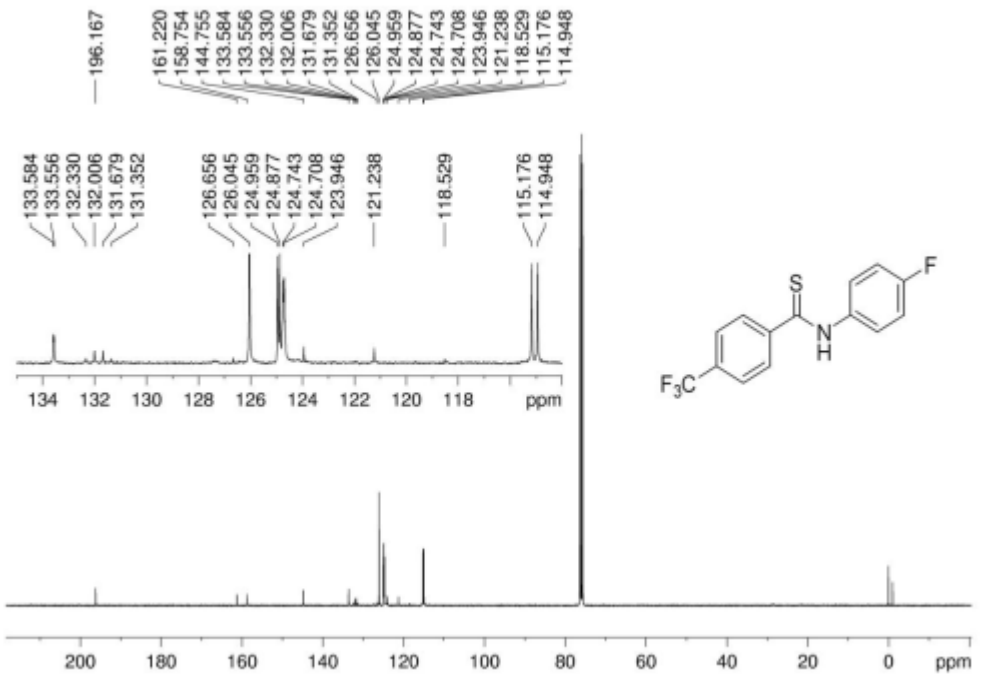


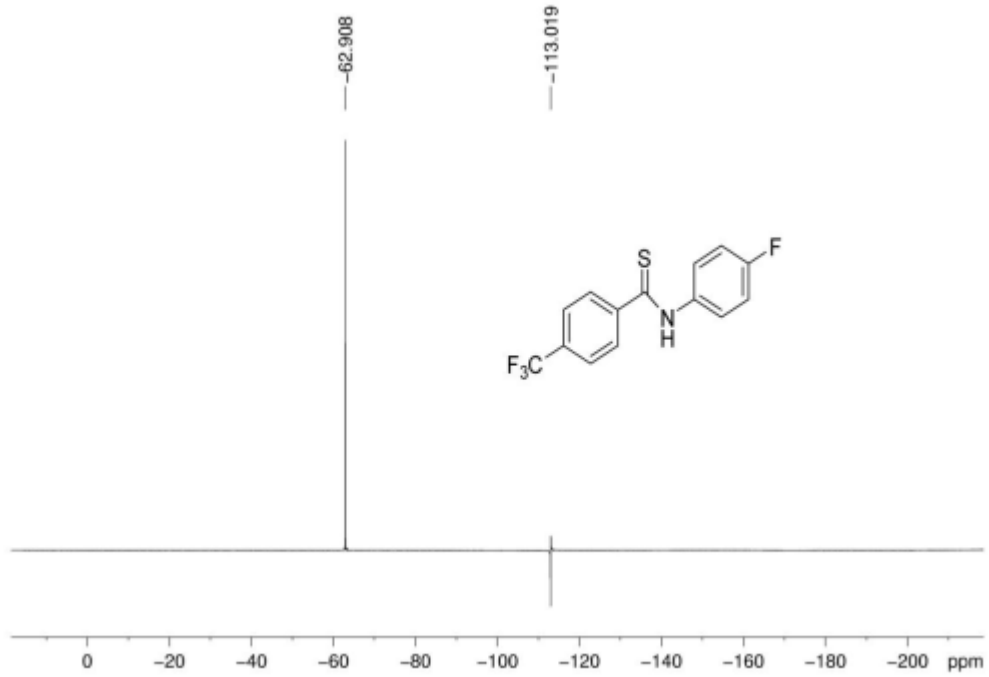




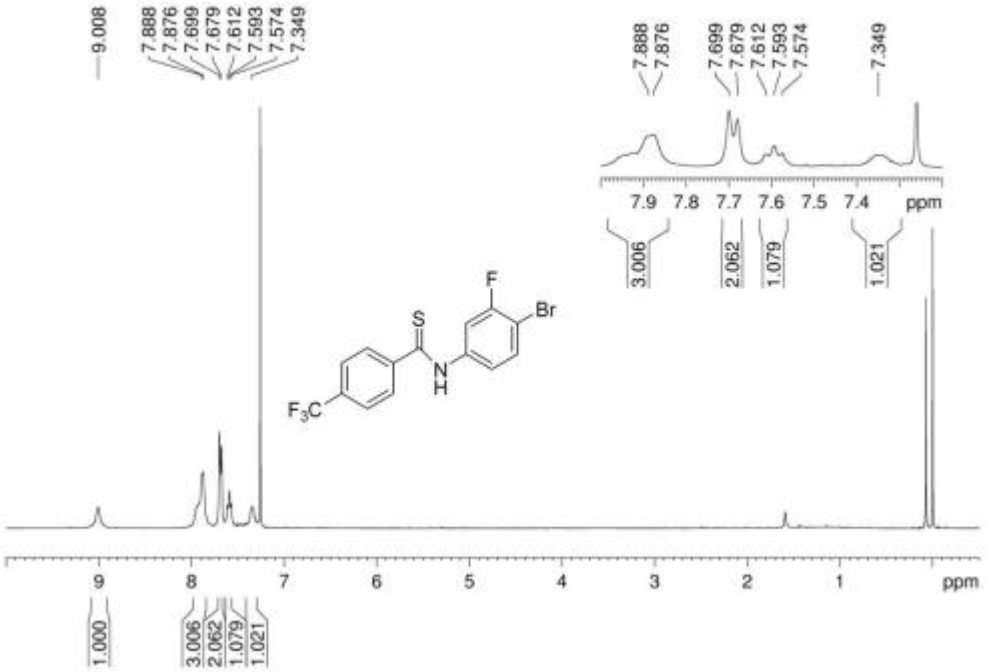
Compound 3hm

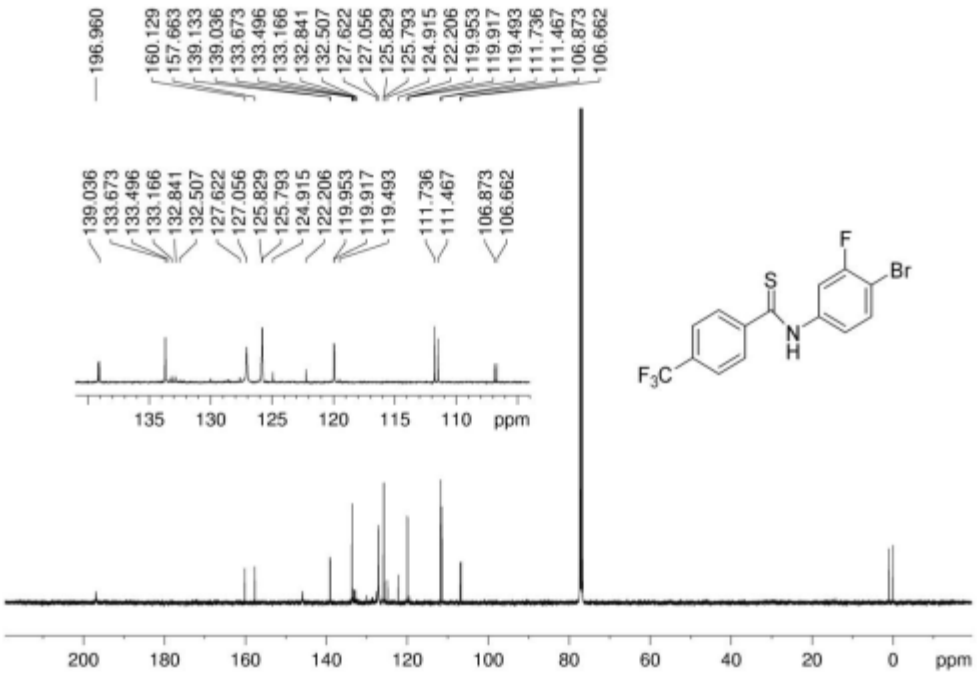

8.909
7.859
7.840
7.633
7.614
7.096
7.075
7.055
S
N
H
F
F3C
7.8
7.6
7.4
7.2
ppm
2.067
4.054
2.007
9
8
7
6
5
4
3
2
1
ppm
1.000
2.067
4.054
2.007

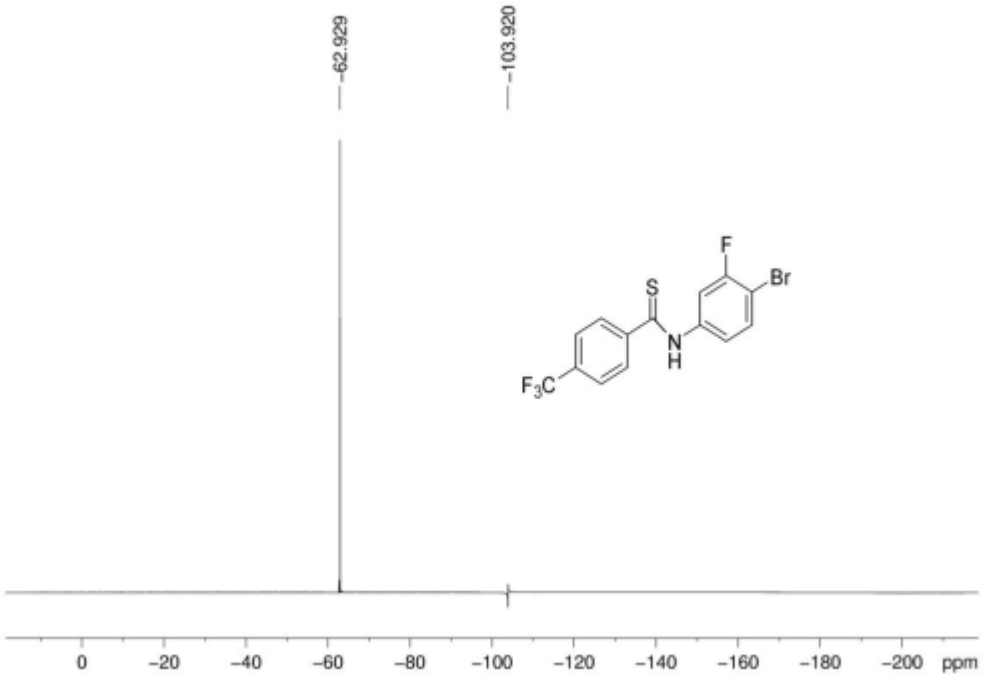

196.167
161.220
158.754
144.755
133.584
133.556
132.330
132.006
131.679
131.352
126.656
126.045
124.959
124.877
124.743
124.708
123.946
121.238
118.529
115.176
114.948
134
132
130
128
126
124
122
120
118
ppm
S
N
H
F
F3C
200
180
160
140
120
100
80
60
40
20
0
ppm



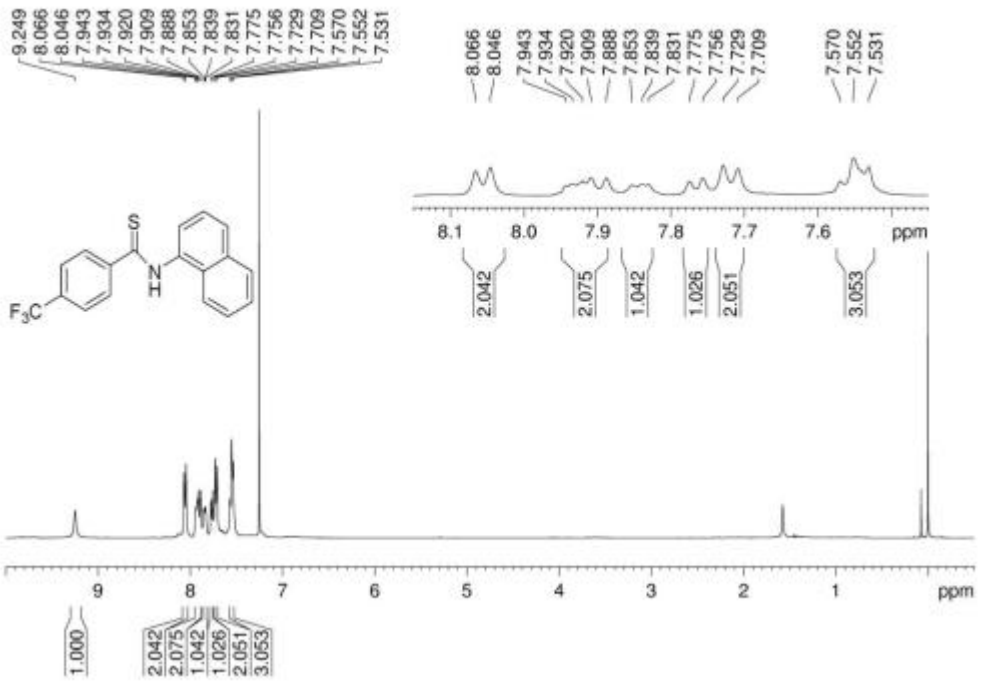
Compound 3hn

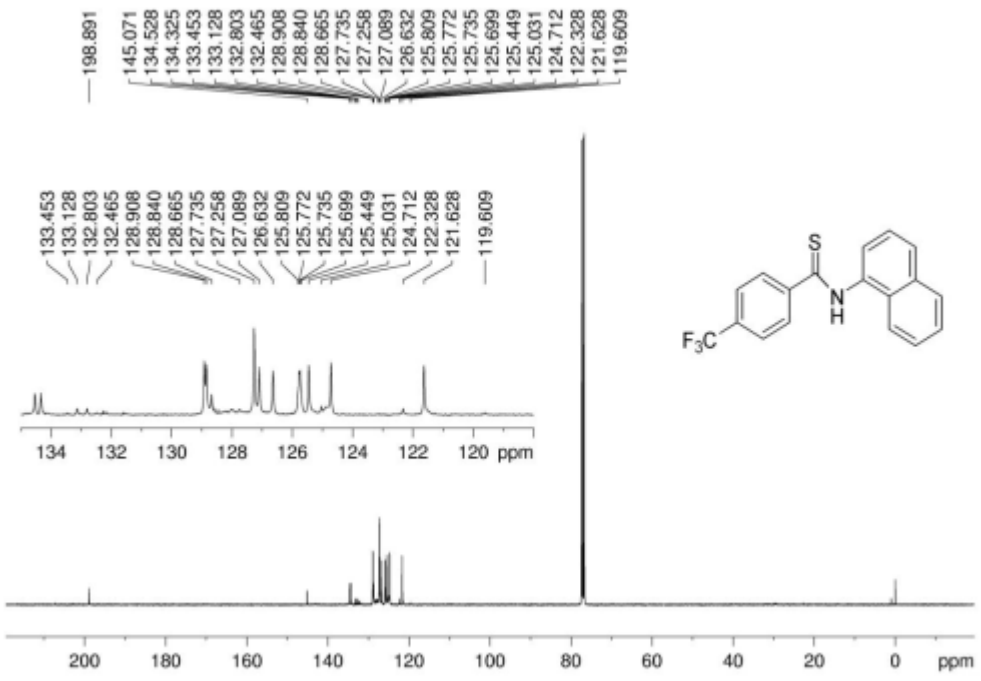


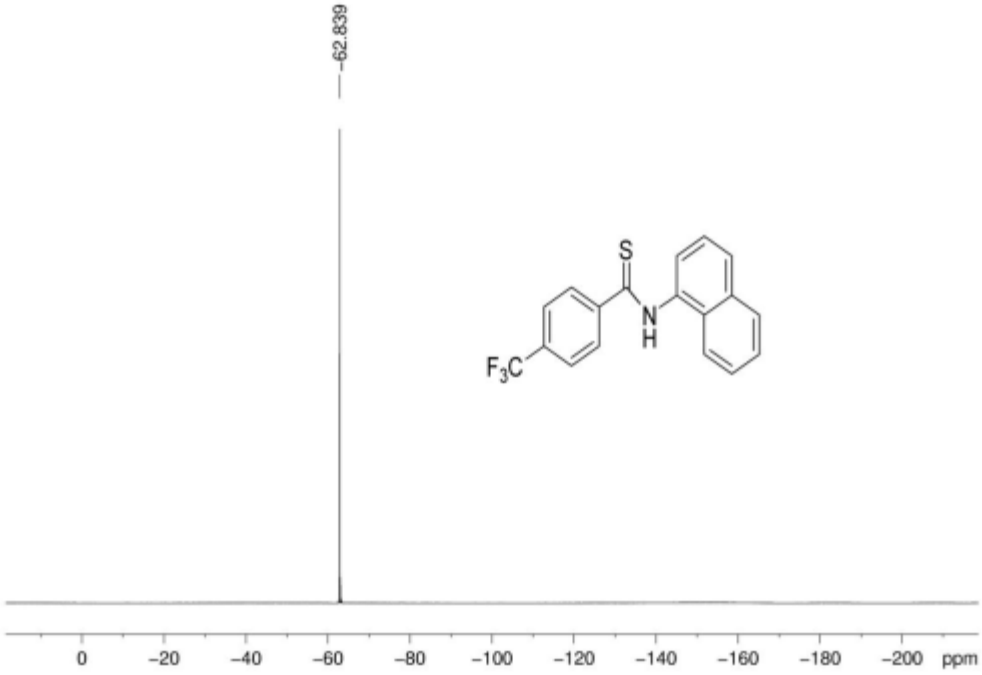




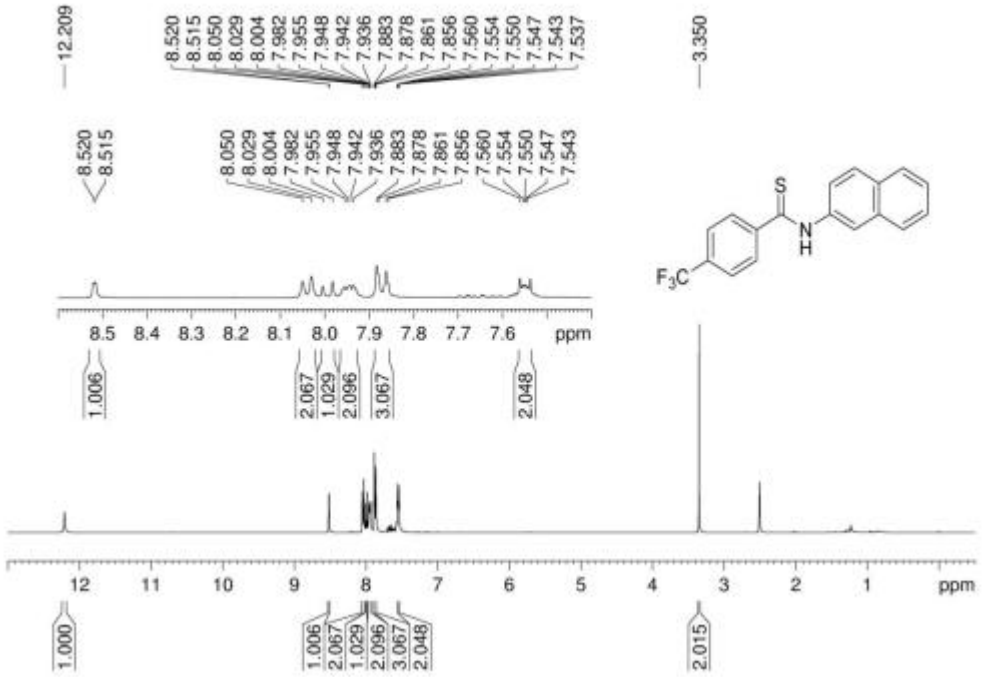
Compound 3ho

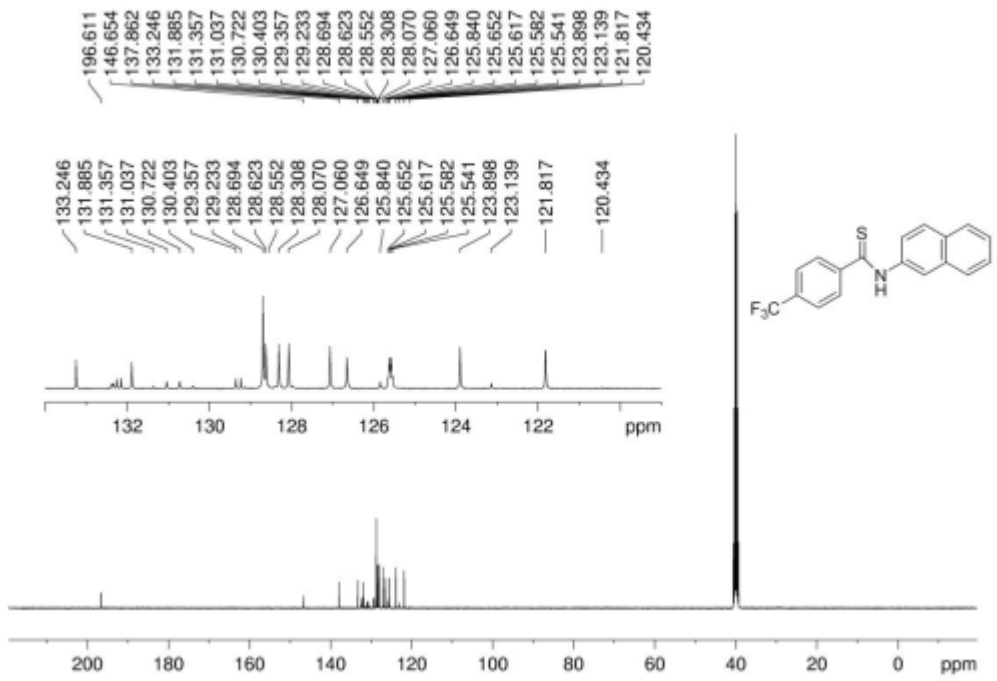

9.249
8.066
8.046
7.943
7.934
7.920
7.909
7.888
7.853
7.839
7.831
7.775
7.756
7.729
7.709
7.570
7.552
7.531
S
N
H
F3C
8.1
8.0
7.9
7.8
7.7
7.6
ppm
2.042
2.075
1.042
1.026
2.051
3.053
9
8
7
6
5
4
3
2
1
ppm
1.000
2.042
2.075
1.042
1.026
2.051
3.053

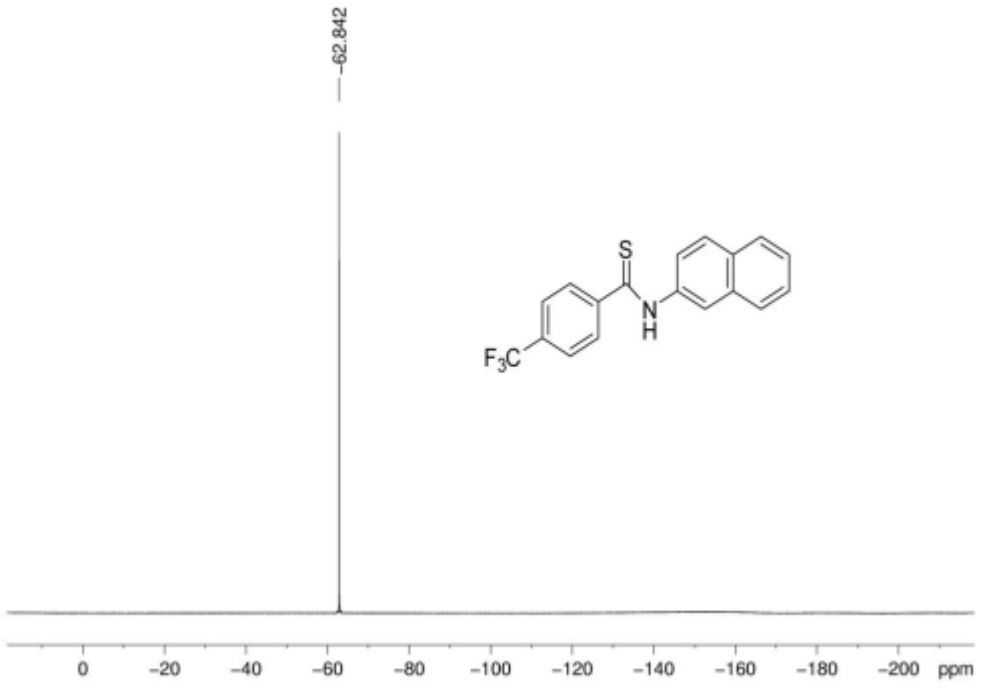

198.891
145.071
134.528
134.325
133.453
133.128
132.803
132.465
128.908
128.840
128.665
127.735
127.258
127.089
126.632
125.809
125.772
125.735
125.699
125.449
125.031
124.712
122.328
121.628
119.609
S
N
H
F3C
134
132
130
128
126
124
122
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm



Compound 3hp




196.611
146.654
137.862
133.246
131.885
131.357
131.037
130.722
130.403
129.357
129.233
128.694
128.623
128.552
128.308
128.070
127.060
126.649
125.840
125.652
125.617
125.582
125.541
123.898
123.139
121.817
120.434
S
N
H
F3C
132
130
128
126
124
122
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm


-62.842
S
N
H
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

9. References

[1] A. J. McKnight, B. J. Classon, *Immunology*. **1992**, 75, 286-292.

[2] X. T. Li, Q. Pan, R. H. Hu, X. Wang, Z.Yang, S. Q. Han, Asian J. Org. Chem. **2016**, 5, 1353 - 1358.

[3] K. Inamoto, K. Nozawa, Y.Kondo, *Synlett*. **2012**, 23, 1678 - 1682.

[4] Downer-Riley,K. Nadale, Jackson, A. Yvette, *Tetrahedron*, **2008**, 64(33), 7741-7744.

[5] Davidson, S. John, *Synthesis*. **1979**, 5, 359 - 361.

[6] Pace, Vittorio, et al, *Chem. Eur. J.* **2015**, 21(52), 18966 -18970.

[7] Folgueiras-Amador, A. Ana, et al, *Chem. Eur. J. 2018*. 24(2), 487 - 491.

[8] D. Liu, et al, *RSC Advances*. **2016**, 6(41), 34198-34203.

[9] G. T. Zhang, et al, *J. Am. Chem. Soc.* **2015**, 137(29), 9273-9280.

[10] K. Waisser, J. Kunes, L. Kubicova, M. Budesinsky, O. Exner, *Magnetic Resonance in Chemistry*. **1997**, 35(8), 543 - 548.