*Supporting Information for*

# Visible-light Photocatalytic Trifluoromethylthiolation of Aryldiazonium Salts: Conversion of Amino Group into Trifluoromethylthiol Group

Xia Zhao,*[a] Xiancai Zheng,[a,c] Miaomiao Tian,[a,c] Yifan Tong,[a] Bo Yang,[a] Xianfu Wei,[a,b] Di Qiu[a] and Kui Lu[b]

[a] *College of Chemistry, Tianjin College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key laboratory of Inorganic-organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Normal University, Tianjin 300387, China.*

[b] *College of Biotechnology, Tianjin University of Science & Technology Tianjin 300457, China.*

hxxyzhx@mail.tjnu.edu.cn

## 1) General and Materials

**General:**

All solvents were distilled prior to use. Unless otherwise noted, chemicals were used as received without further purification. The solvents for reaction were distilled over Na (for toluene, 1,4-dioxane and THF) or $CaH_2$ (for DCE and MeCN) under a nitrogen atmosphere. All reactions were carried out in oven-dried glassware under an inert atmosphere (nitrogen or argon). For chromatography, 200−300 mesh silica gel was employed. $^1H$, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz respectively. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. HRMS was performed on an FTMS mass instrument. Melting points are reported as uncorrected.

**The spectral data of the trifluoromethylthiolation products**

***Methyl 4-((trifluoromethyl)thio)benzoate (3a):***[1] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3a** was isolated as a yellow oil (41 mg, 70 %); $R_f$ (PE : EA = 50 : 1) = 0.45; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J*

= 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.40 (s, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.5, 135.5, 132.6, 130.4, 129.8 (q, *J* = 2.02 Hz), 129.1 (q, *J* = 306 Hz), 61.4, 14.2; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 42.0 (s, 3F).

***(4-methoxyphenyl)(trifluoromethyl)sulfane (3b)*:**[2] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3b** was isolated as a white solid (25 mg, 48 % ); $R_f$ (PE : EA = 50 : 1) = 0.56; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 161.9, 138.3, 129.6 (q, *J* = 306 Hz), 115.0, 114.9 (q, *J* = 1.96 Hz), 55.4; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 43.3 (s, 3F).

***(4-phenoxyphenyl)(trifluoromethyl)sulfane (3c)*:**[2] After purification by silica gel column chromatography (PE), compound **3c** was isolated as a white solid (41 mg, 61 %); $R_f$ (PE) = 0.59; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.41-7.34 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 160.4, 155.6, 138.3, 129.6 (q, *J* = 306 Hz), 128.0, 124.6, 120.1, 118.6, 117.3 (q, *J* = 1.96 Hz); $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 43.5 (s, 3 F).

***Methyl(4-((trifluoromethyl)thio)phenyl)sulfane (3d)*:**[2] After purification by silica gel column chromatography (PE), compound **3d** was isolated as a yellow oil (30 mg, 53 %); $R_f$ (PE) = 0.58; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 2.50 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 143.3, 136.7, 129.5 (q, *J*= 306.46 Hz), 126.4, 119.7, 15.0; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 43.3 (s, 3F).

***[1,1'-biphenyl]-4-yl(trifluoromethyl)sulfane (3e)*:**[2] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3e** was isolated as a white solid (48 mg, 76 %); $R_f$ (PE : EA = 50 : 1) = 0.45; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.66-7.60 (m, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 143.9, 139.7, 136.7, 129.7 (q, *J* = 306 Hz), 129.0, 128.2, 127.2, 123.1 (q, *J* = 1.88 Hz); $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 42.7 (s, 3F).

***(4-(tert-butyl)phenyl)(trifluoromethyl)sulfane (3f)*:** [1] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3f** was isolated as a colorless solid (28 mg, 47 %); $R_f$ (PE : EA = 50 : 1) = 0.45; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 1.14 (s, 9H); $^{13}$C NMR (100 MHz, CDCl3): δ 154.4, 136.1, 129.7 (q, *J* = 306 Hz), 126.6, 120.9 (q, *J* =1.67 Hz), 34.9, 31.1; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 43.0 (s, 3F).

***(4-bromophenyl)(trifluoromethyl)sulfane (3g)***:[2] After purification by silica gel column chromatography (PE), compound **3g** was isolated as a colorless oil (27 mg, 44 %); $R_f$ (PE) = 0.82; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 137.7 132.8 128.4 (q, *J* = 306 Hz), 124.6, 123.5 (q, *J* = 2.04 Hz); $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 42.7(s, 3F).

***4-((trifluoromethyl)thio)benzonitrile (3h):***[2] After purification by silica gel column chromatography (PE : EA = 100 : 1), compound **3h** was isolated as a white solid (21 mg, 41 %); $R_f$ (PE : EA = 50 : 1) = 0.41; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 135.9, 132.9, 130.6 (q, *J* = 2.07 Hz), 128.9 (q, *J* = 307 Hz), 117.6, 114.7; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 41.5 (s, 3F).

***(4-nitrophenyl)(trifluoromethyl)sulfane (3i):*** After purification by silica gel column chromatography (PE : EA = 100 : 1), compound **3i** was isolated as a yellow solid (31 mg, 56 %); $R_f$ (PE : EA = 50 : 1) = 0.52; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl3): δ 149.2, 136.1, 132.6 (q, *J* = 2.10 Hz), 128.9 (q, *J* = 306.97 Hz), 124.3; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 41.3 (s, 3F)

***1-(4-((trifluoromethyl)thio)phenyl)ethanone (3j):***[2] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3j** was isolated as a yellow soil (26 mg, 50 %); $R_f$ (PE : EA = 50 : 1) = 0.22; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 2.64 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.0, 138.5, 135.7, 130.1 (q, *J* = 1.99 Hz), 129.3 (q, *J* = 306 Hz), 129.1, 26.8; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 41.8 (s, 3F).

***Phenyl(4-((trifluoromethyl)thio)phenyl)methanone (3k)***:[2] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3k** was isolated as a white solid (46 mg, 65 %); $R_f$ (PE : EA = 50 : 1) = 0.48; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.84-7.76 (m, 6H), 7.65-7.61 (m, 1H), 7.51 (s, *J* = 7.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 195.5, 139.4, 136.8, 135.5, 132.9, 130.6, 130.0, 129.3 (q, *J* = 307 Hz), 129.1 (q, *J* = 2.00 Hz), 128.46; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 41.8 (s, 3F).

***5-((trifluoromethyl)thio)isoindoline-1,3-dione (3l)***: [2] After purification by silica gel column chromatography (PE : EA = 5 : 1), compound **3l** was isolated as a white solid (32 mg, 52 %); $R_f$ (PE : EA = 3 : 1) = 0.52; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.14(s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.8 Hz 1H), 7.82 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.0, 166.8, 141.3, 134.2, 133.6, 132.3 (q, *J* = 1.96 Hz), 130.4, 128.9 (q, *J* = 307 Hz), 124.5; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 41.5 (s, 3F).

***2-phenyl-7-((trifluoromethyl)thio)-4H-chromen-4-one (3m):*** After purification by silica gel column chromatography (PE : EA = 10 : 1), compound **3m** was isolated as a white solid (22 mg, 28 %); $R_f$ (PE : EA = 5 : 1) = 0.45; m.p.= 126-127℃; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.95-7.92 (m, 3H), 7.67-7.65 (m, 1H), 7.60-7.53 (m, 3H), 6.87 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 177.4, 163.9, 155.8, 132.0, 131.4, 131.3, 130.8 (q, *J* = 2.05 Hz), 129.2 (q, *J* = 307 Hz), 129.2, 126.9, 126.4, 125.2, 125.1, 108.0; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 41.4 (s, 3F); HRMS (ESI) m/z calcd for $C_{16}H_{10}F_3O_2S^+$ $(M+H)^+$ 323.0348, found 323.0349.

***(4-ethoxyphenyl)(trifluoromethyl)sulfane (3n):***[1] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound **3n** was isolated as a colorless oil (26 mg, 46 %); $R_f$ (PE : EA = 50 : 1) = 0.60; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 161.3, 138.3, 129.6 (q, *J* = 306 Hz), 115.4, 114.5 (q, *J* = 1.82 Hz), 63.7, 14.6; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 44.0 (s, 3F).

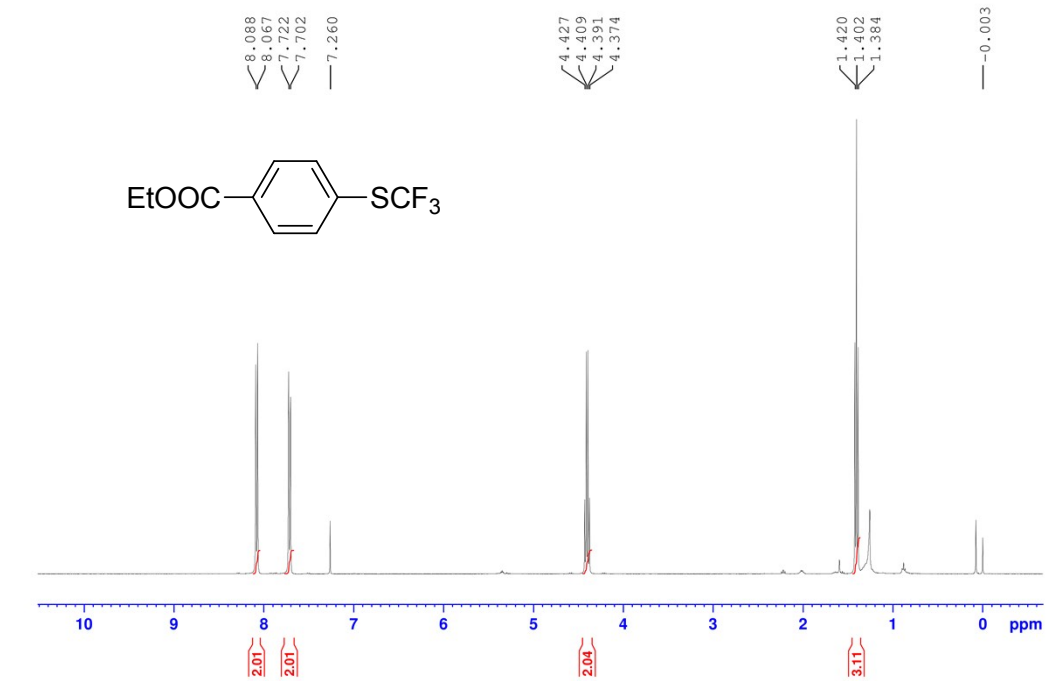
***2-phenyl-6-((trifluoromethyl)thio)-4H-chromen-4-one (3o):*** After purification by silica gel column chromatography (PE : EA = 10 : 1), compound **3o** was isolated as a white solid (25 mg, 31 %); $R_f$ (PE : EA = 5 : 1) = 0.49; m. p.= 139-141℃; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 2.4 Hz, 1H), 7.96-7.92 (m, 3H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.60-7.53 (m, 3 H), 6.87 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 177.0, 163.8, 157.4, 140.8, 134.6, 132.0, 131.2, 129.3 (q, *J* = 307 Hz), 129.2, 126.4, 124.5, 121.6 (q, *J* = 2.21 Hz), 119.7, 108.0; $^{19}$F NMR (375 MHz, $CDCl_3$): δ = – 42.6 (s, 3F); HRMS (ESI) m/z calcd for $C_{16}H_{10}F_3O_2S^+$ $(M+H)^+$ 323.0348, found 323.0350.

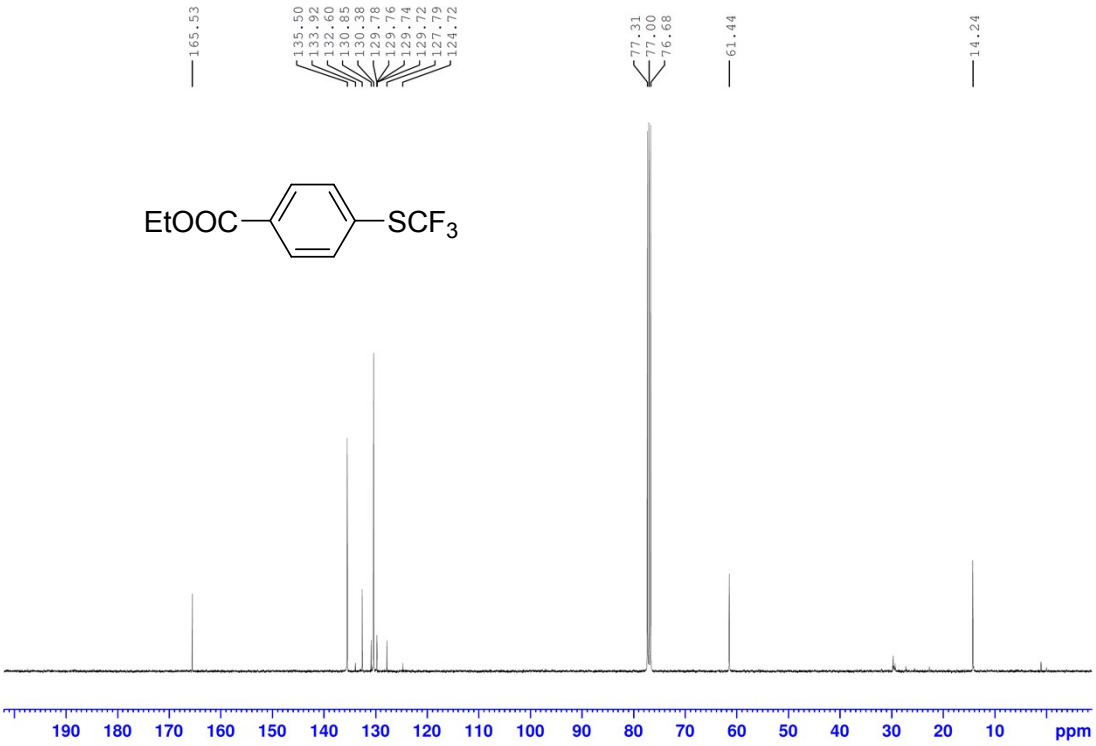
**Reference**

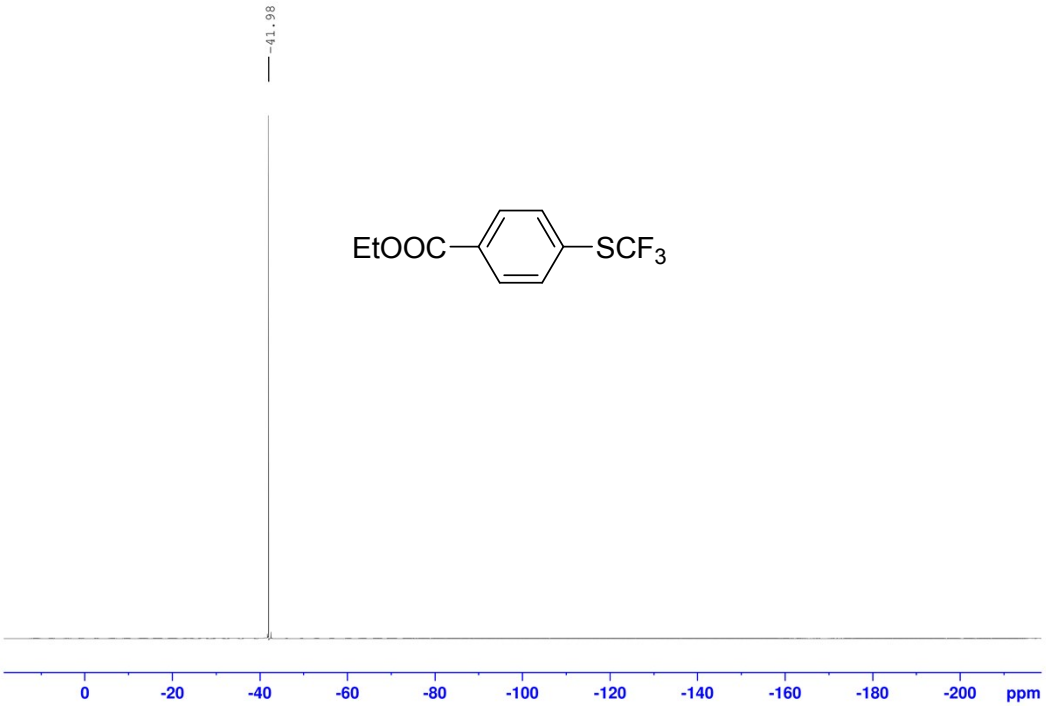
[1] K. Kang, C. Xu and Q. Shen, *Org. Chem. Front.*, 2014, **1**, 294.

[2] C. Matheis, V. Wagner and L. J. Goossen, *Chem. Eur. J.* 2016, **22**, 79.

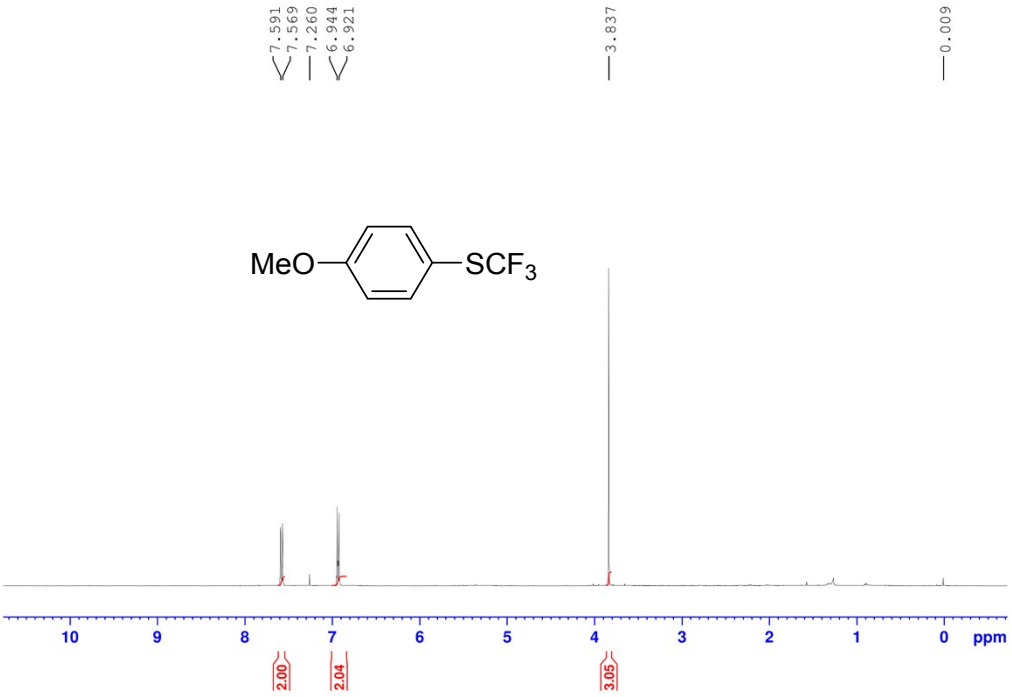
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***Methyl 4-((trifluoromethyl)thio)benzoate (3a)*** in $CDCl_3$

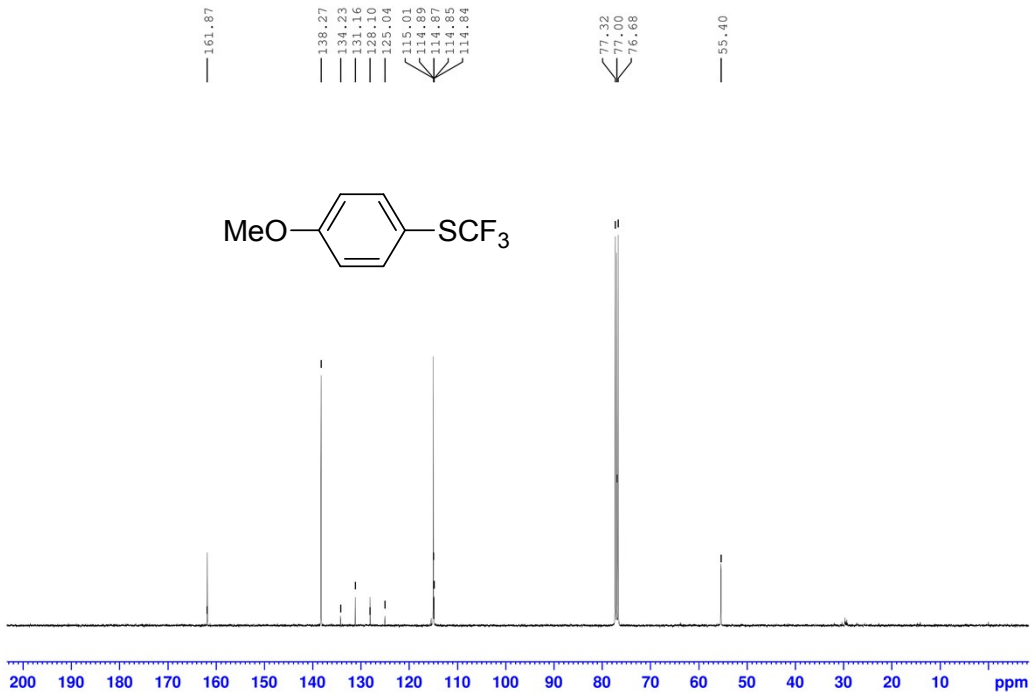


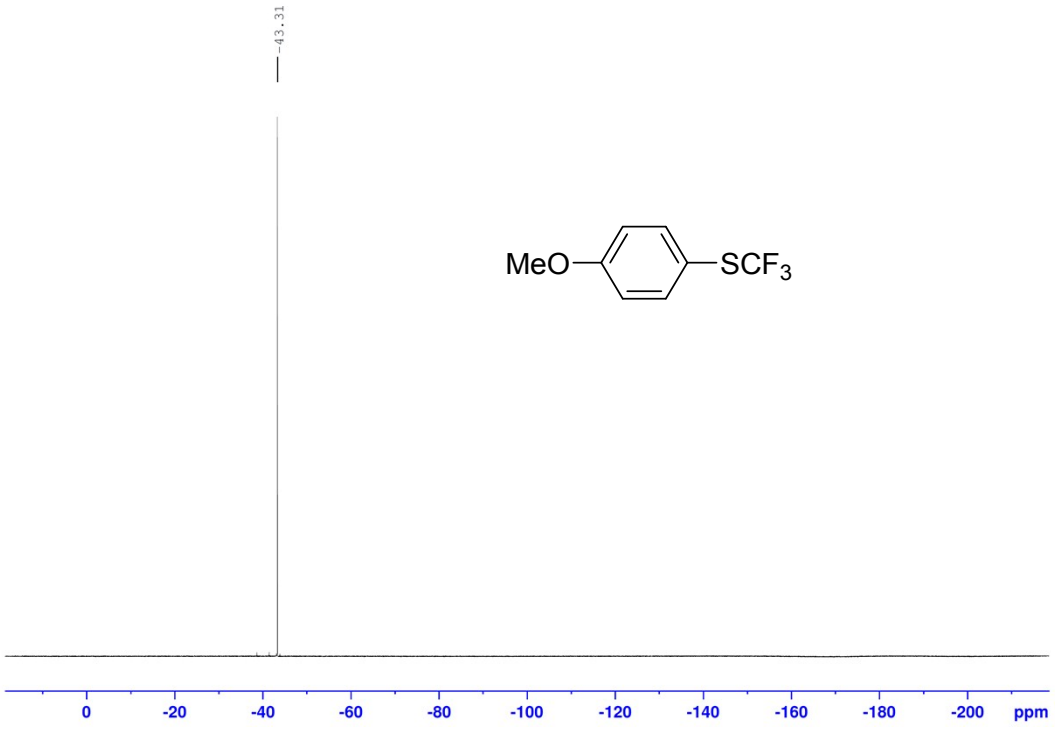





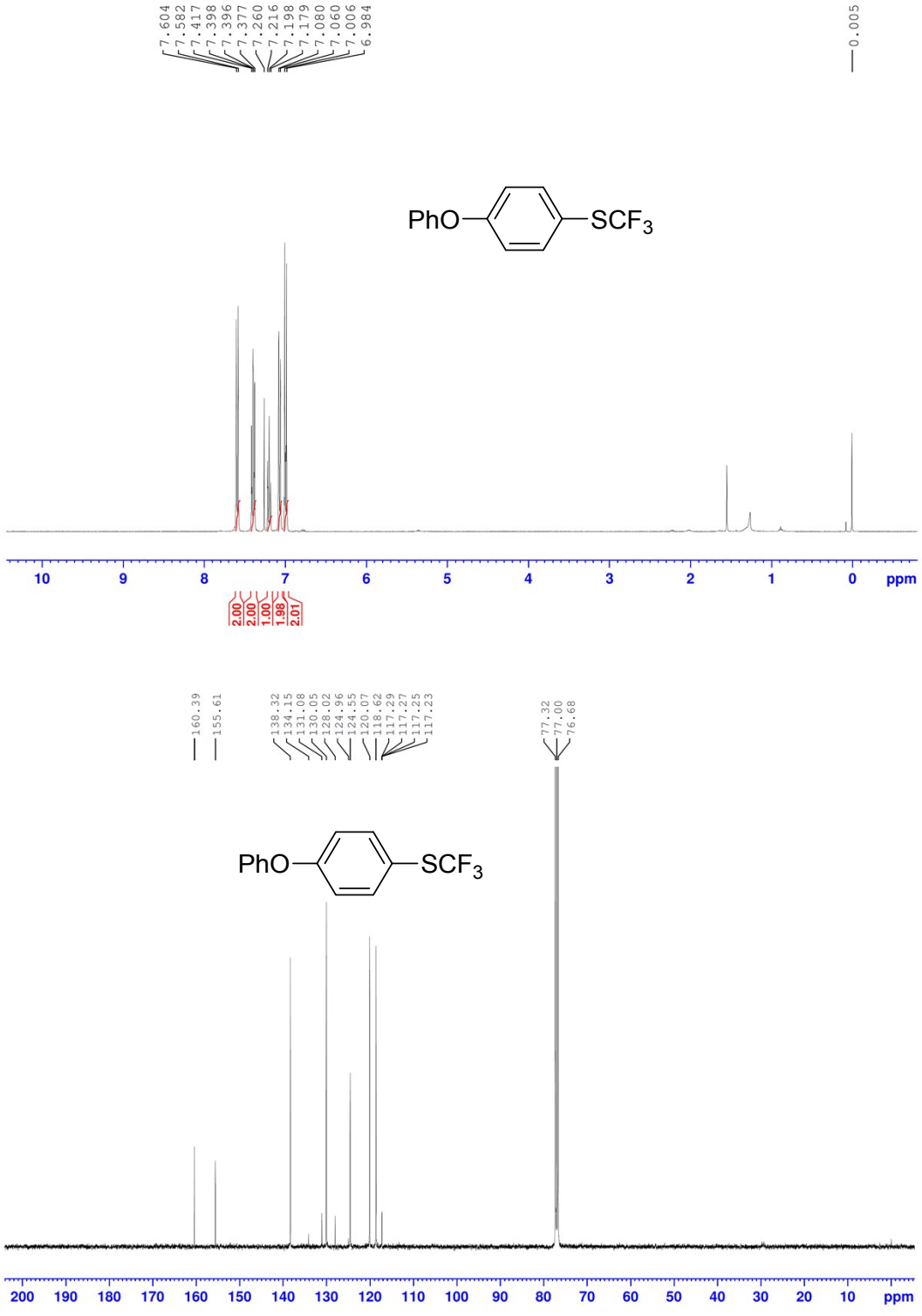

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***(4-methoxyphenyl)(trifluoromethyl)sulfane (3b)*** in $CDCl_3$

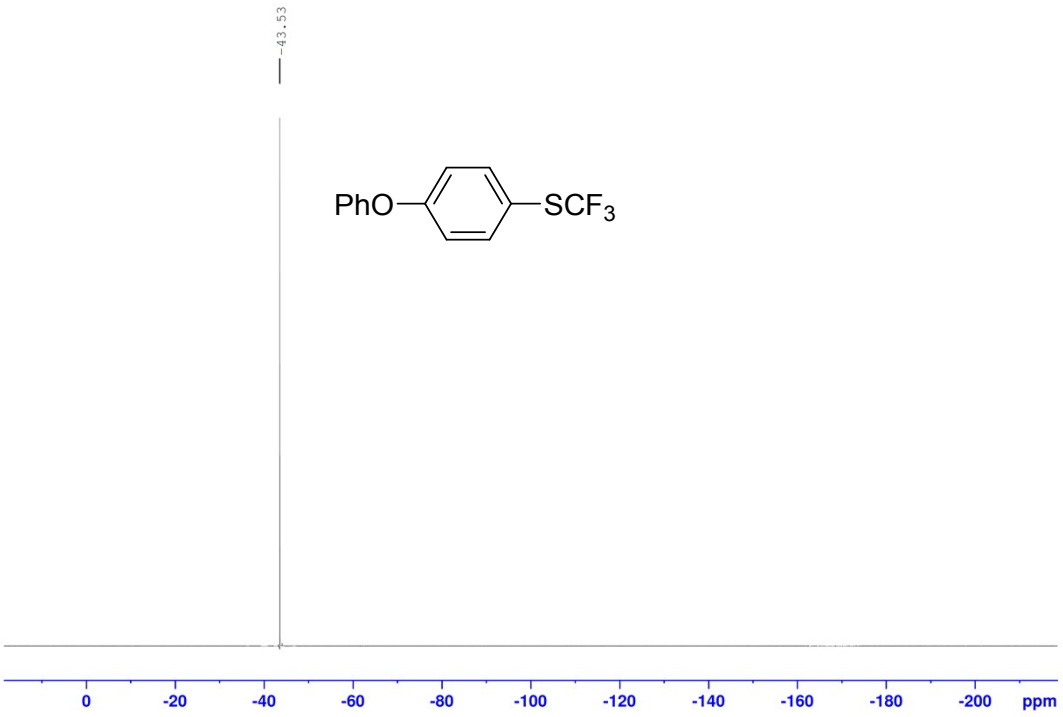



161.87
138.27
134.23
131.16
128.10
125.04
115.01
114.89
114.87
114.85
114.84
77.32
77.00
76.68
55.40
MeO
SCF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

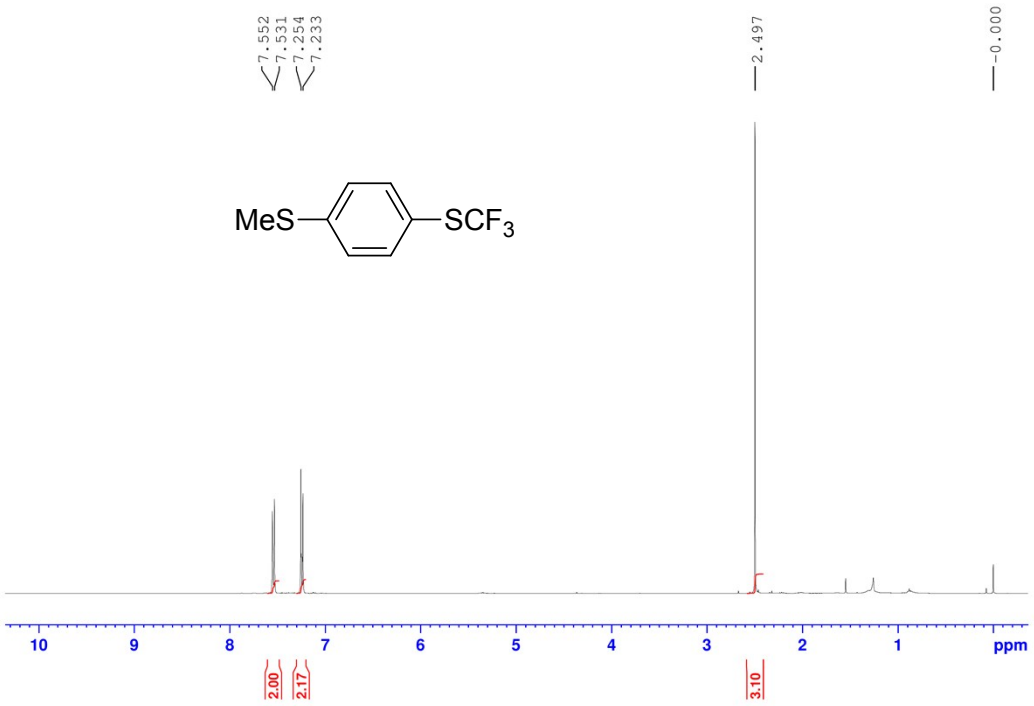

-43.31
MeO
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

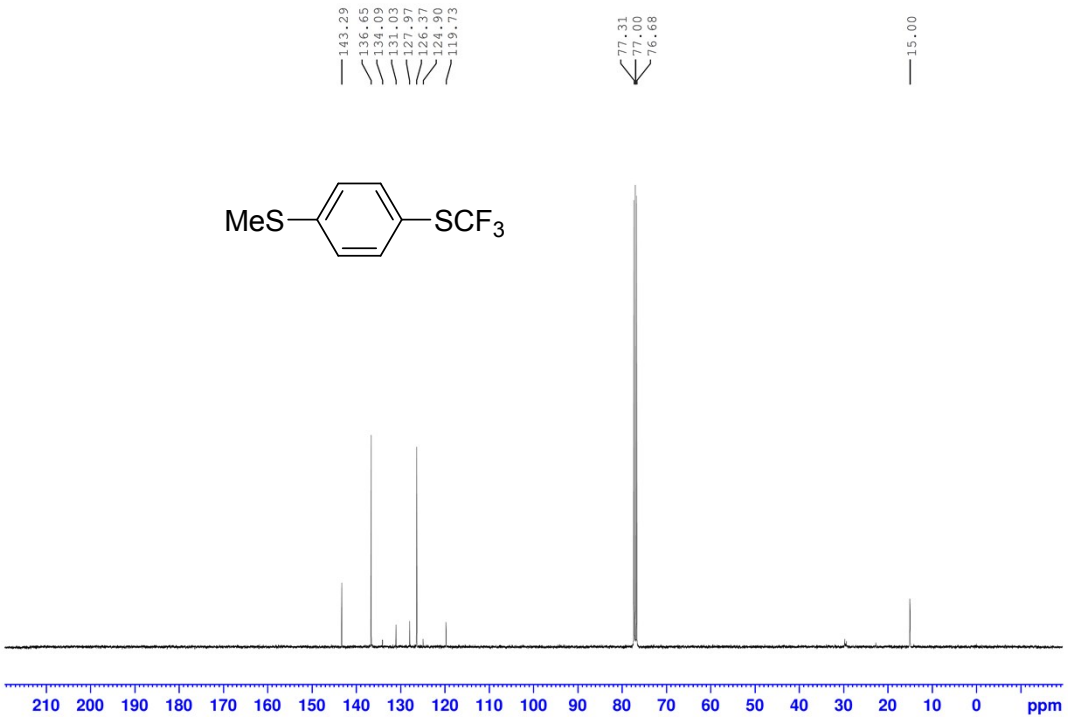
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***(4-phenoxyphenyl)(trifluoromethyl)sulfane (3c)*** in $CDCl_3$

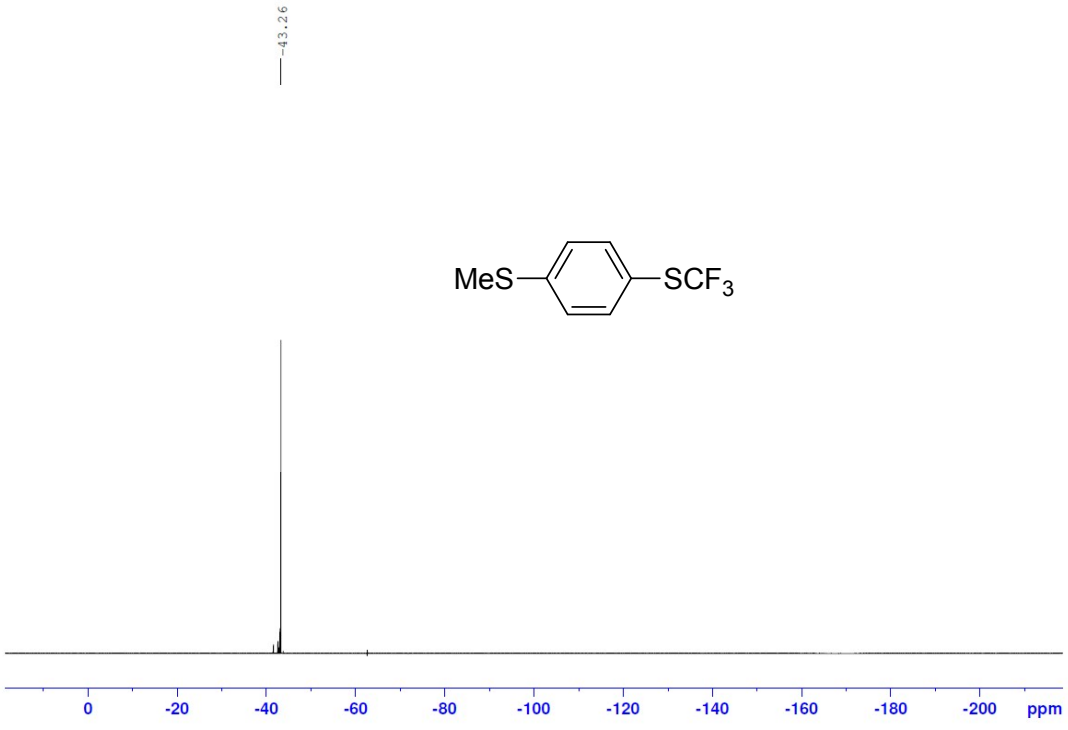




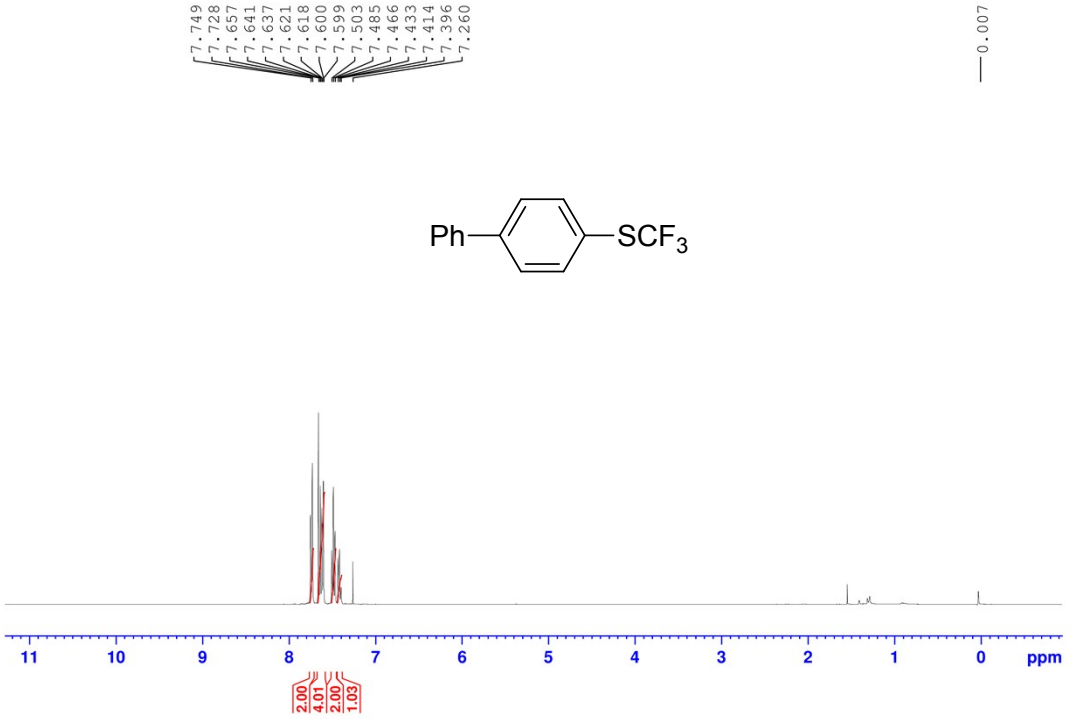

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***Methyl(4-((trifluoromethyl)thio)phenyl)sulfane (3d)*** in $CDCl_3$

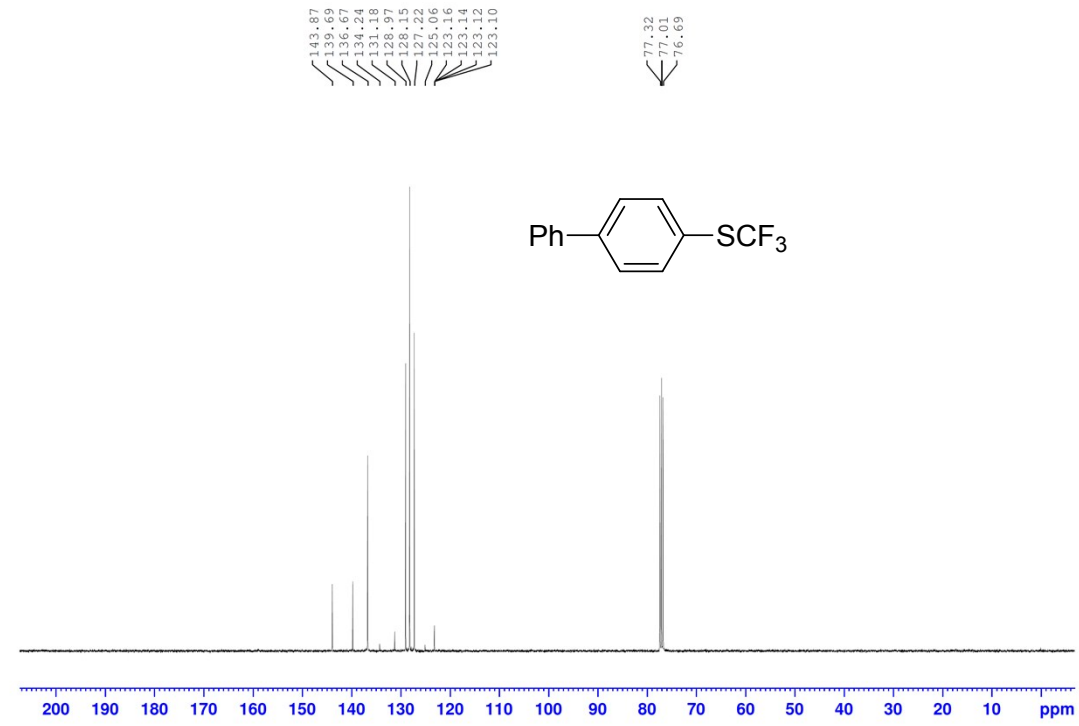


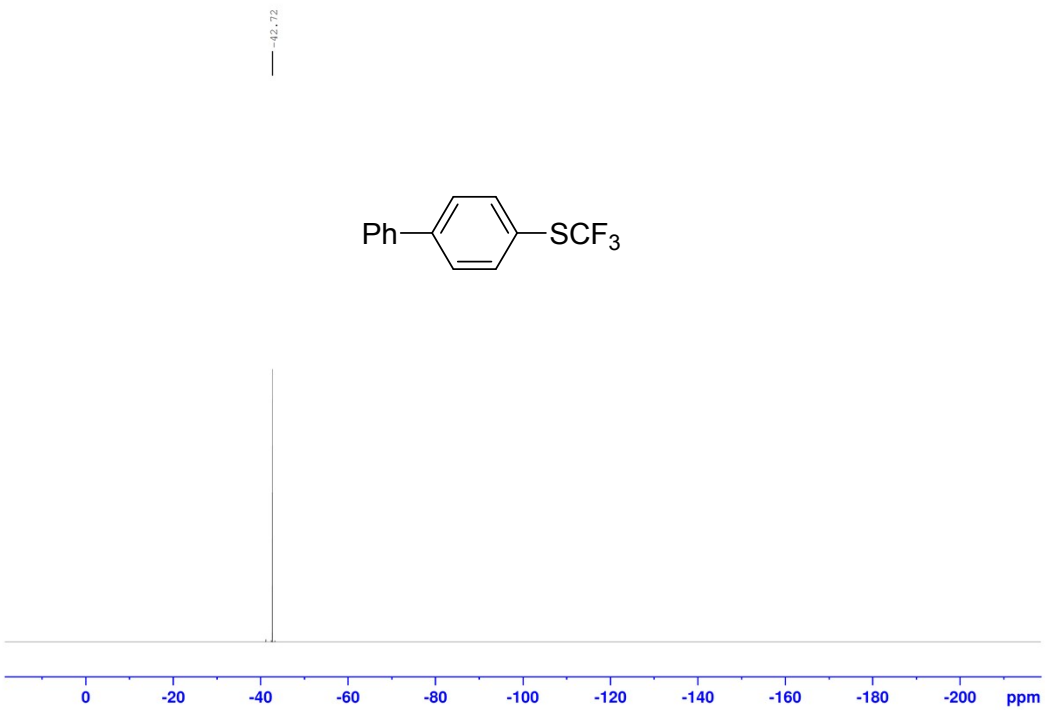

143.29
136.65
134.09
131.03
127.97
126.37
124.90
119.73
77.31
77.00
76.68
15.00
MeS
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-43.26
MeS
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

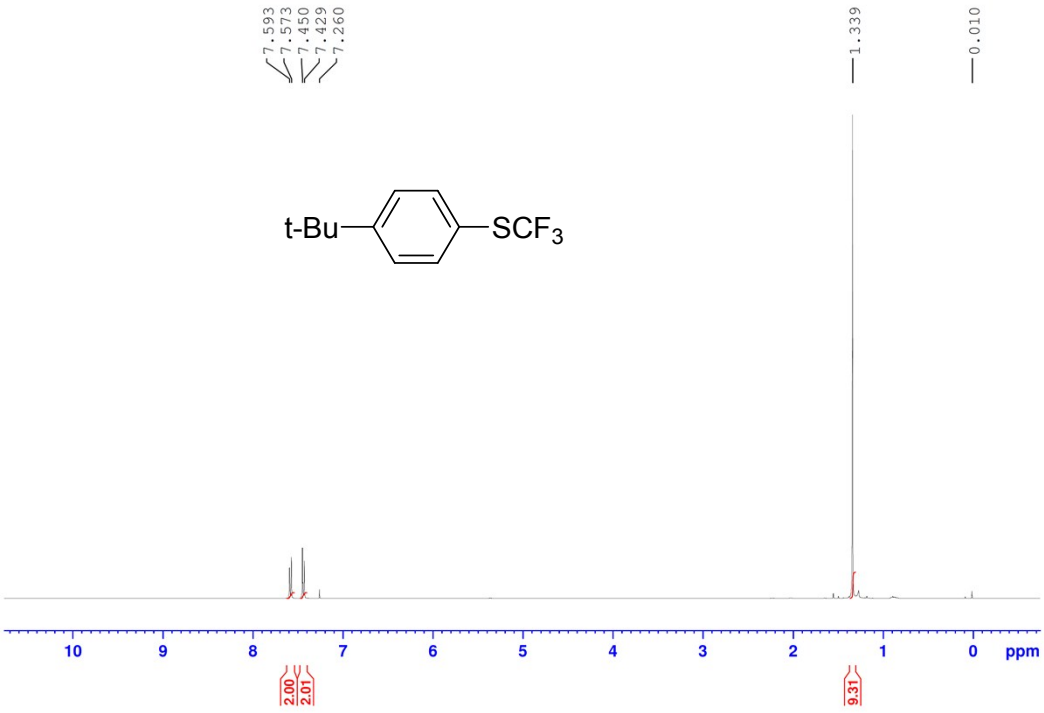
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***[1,1'-biphenyl]-4-yl(trifluoromethyl)sulfane (3e)*** in $CDCl_3$

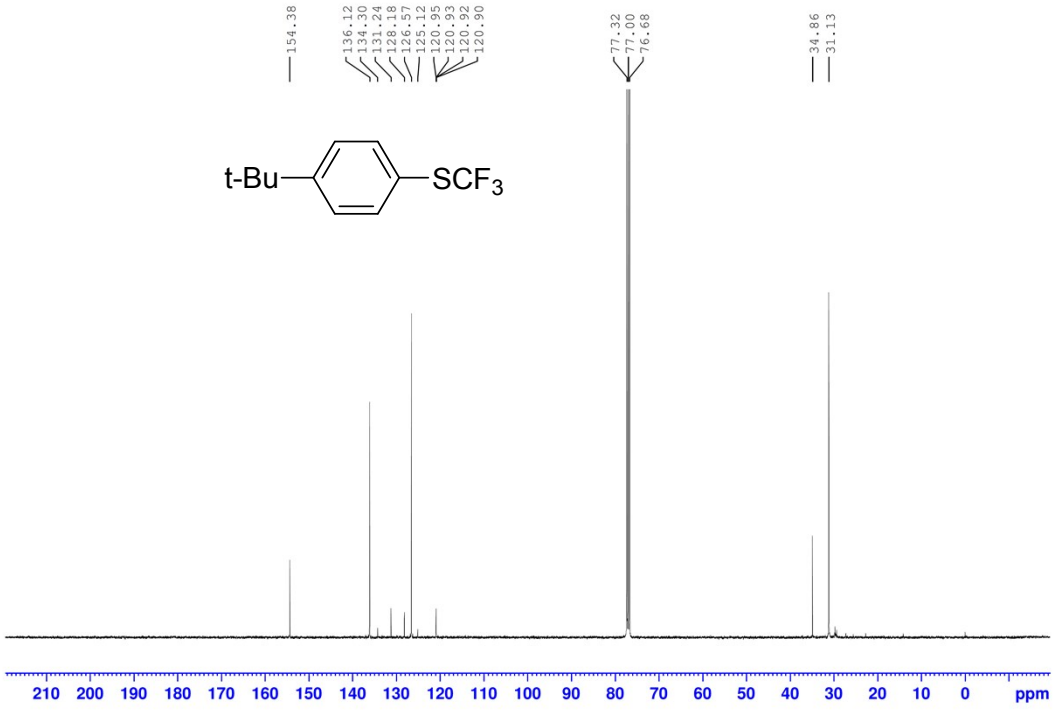


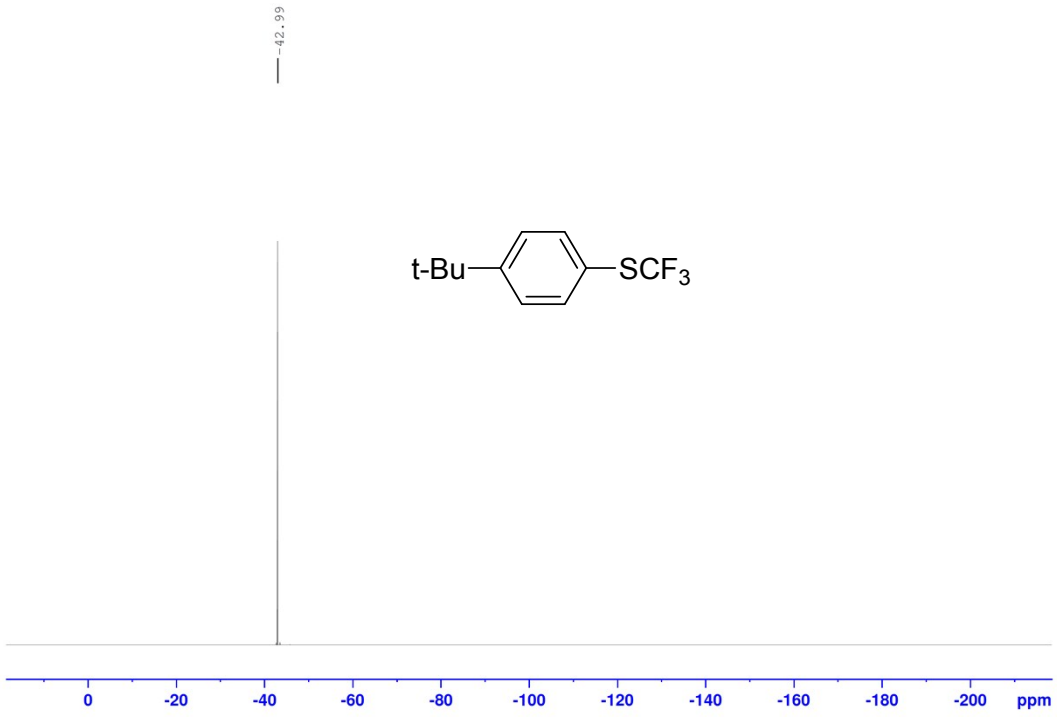





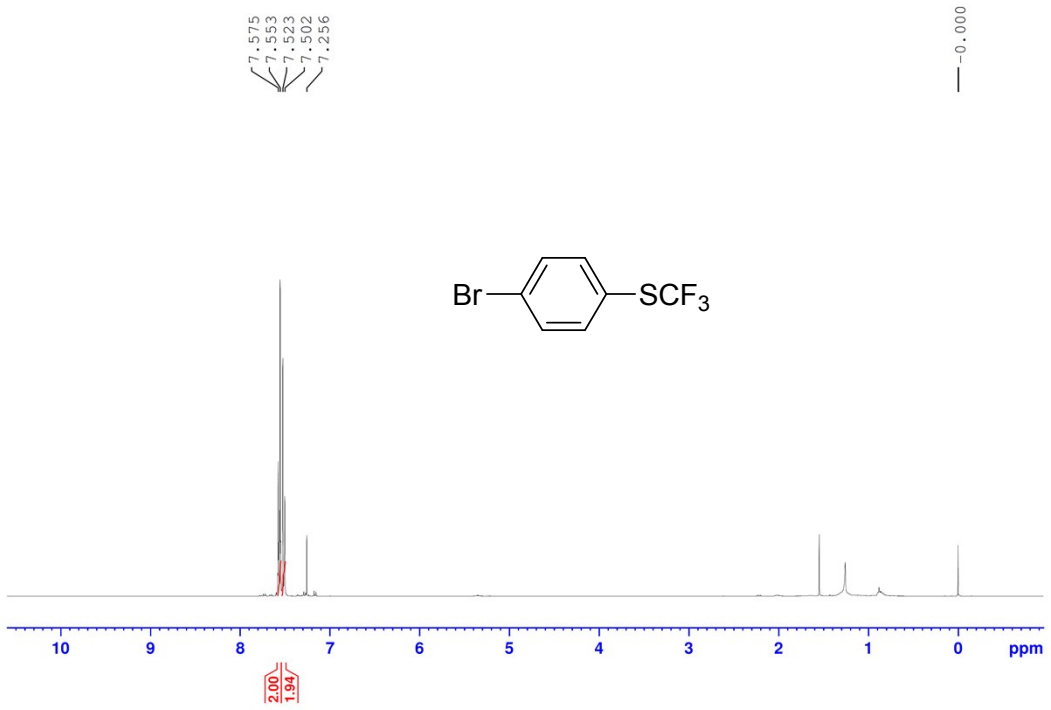

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***(4-(tert-butyl)phenyl)(trifluoromethyl)sulfane (3f)*** in $CDCl_3$

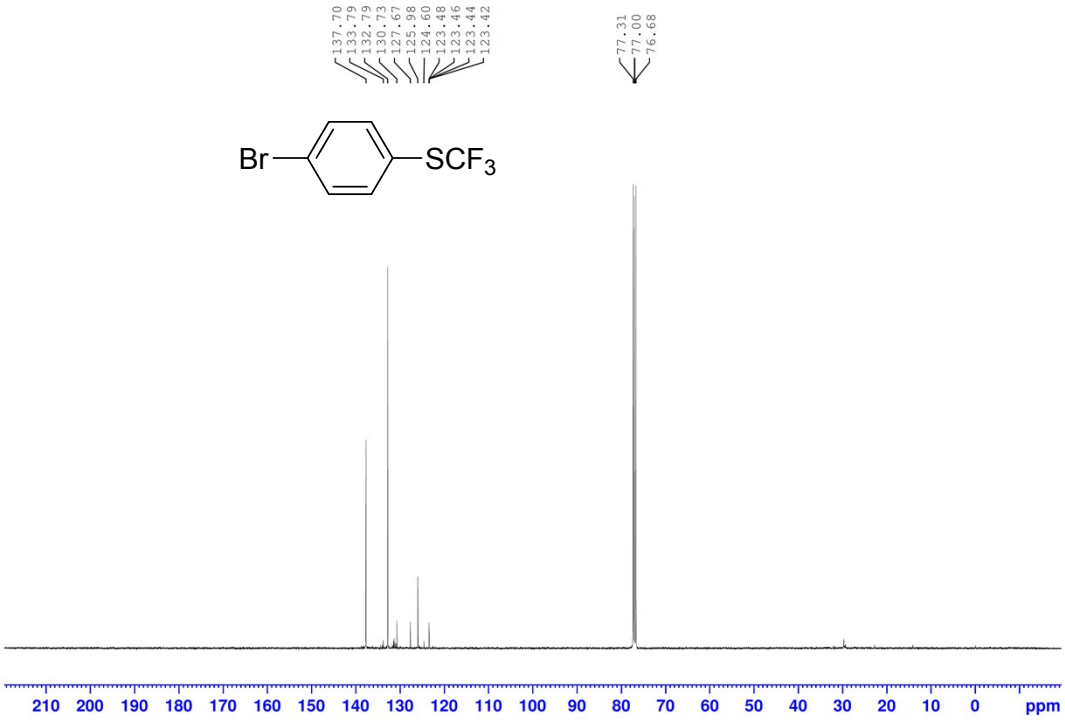


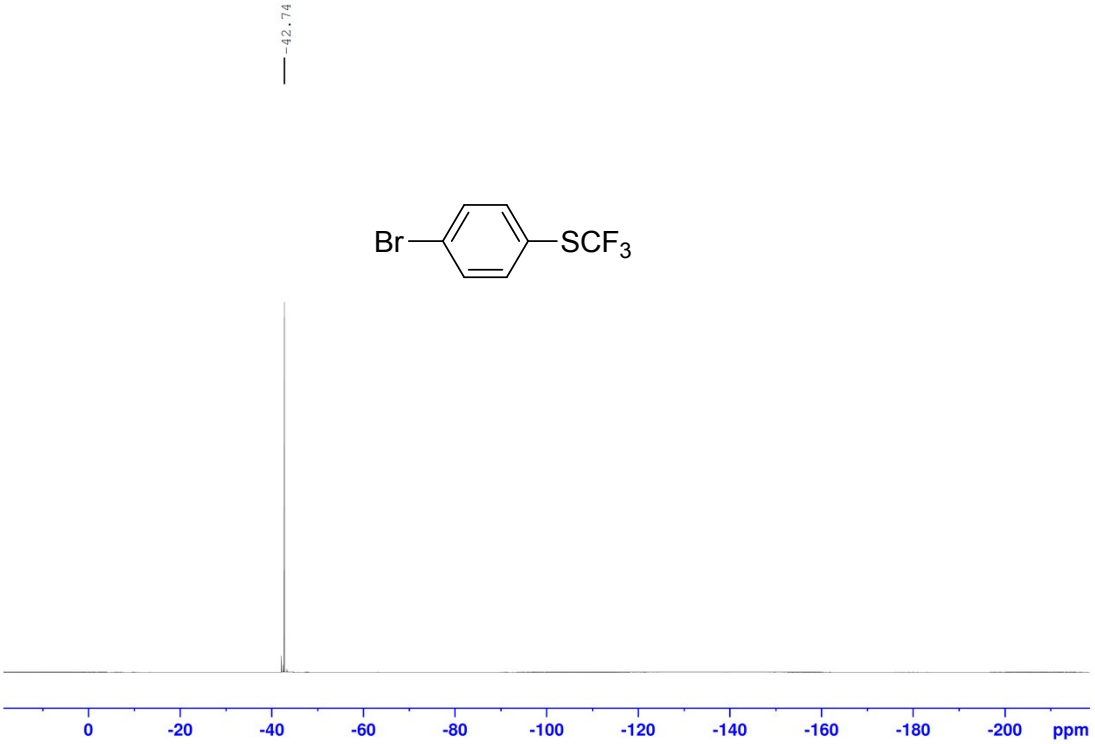

154.38
136.12
134.30
131.24
128.18
126.57
125.12
120.95
120.93
120.92
120.90
77.32
77.00
76.68
34.86
31.13
t-Bu
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-42.99
t-Bu
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

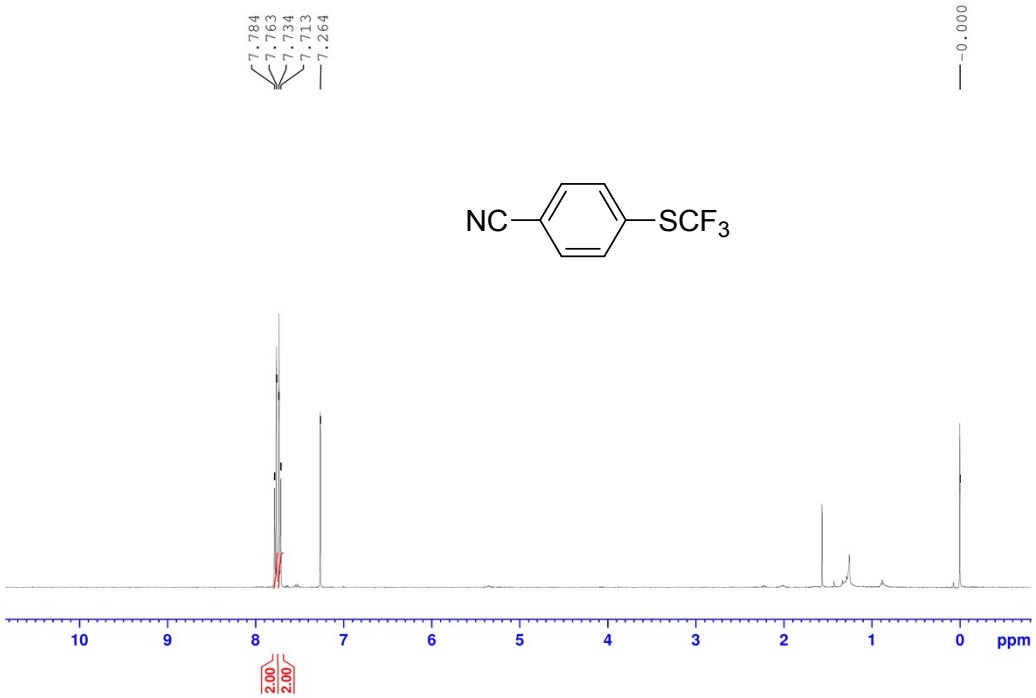
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***(4-bromophenyl)(trifluoromethyl)sulfane (3g)*** in $CDCl_3$

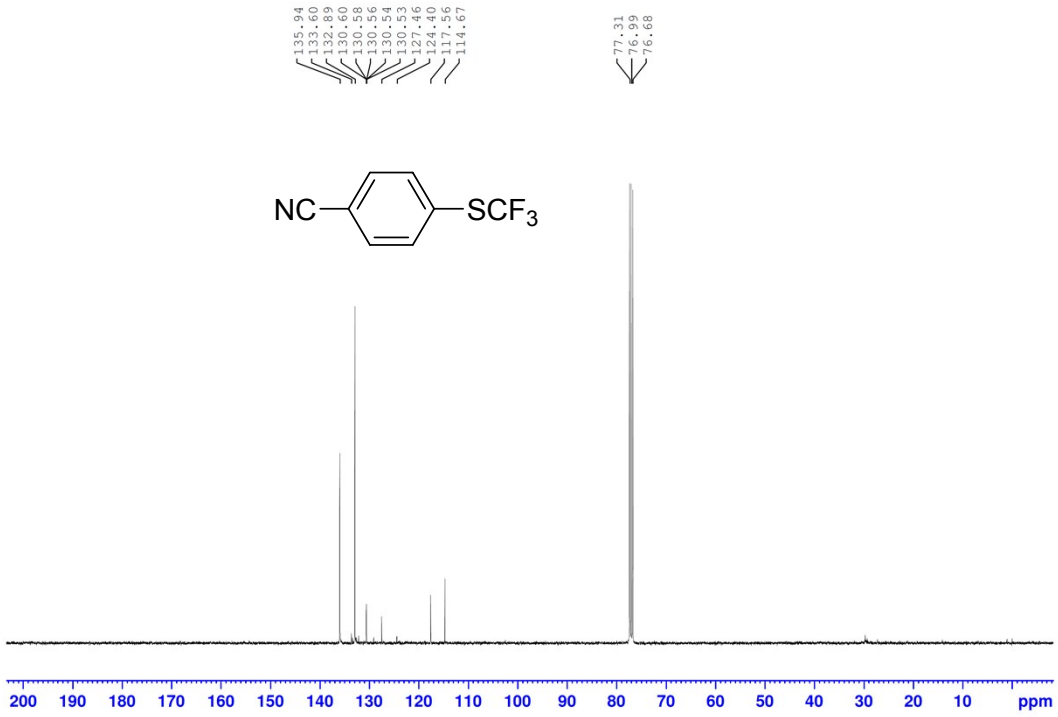


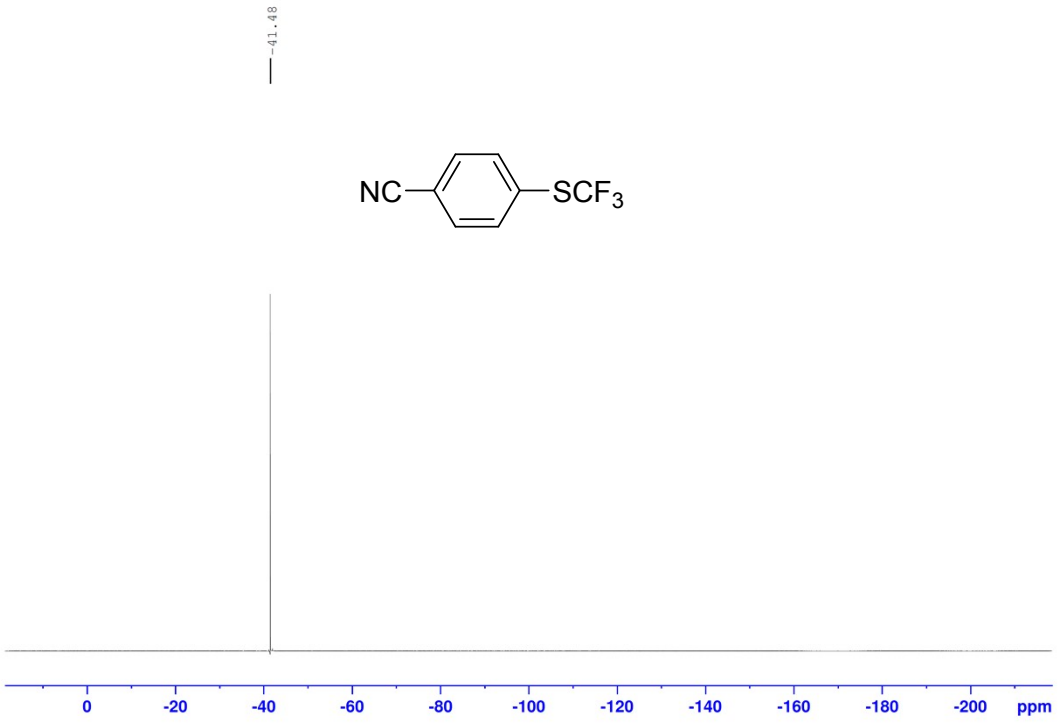





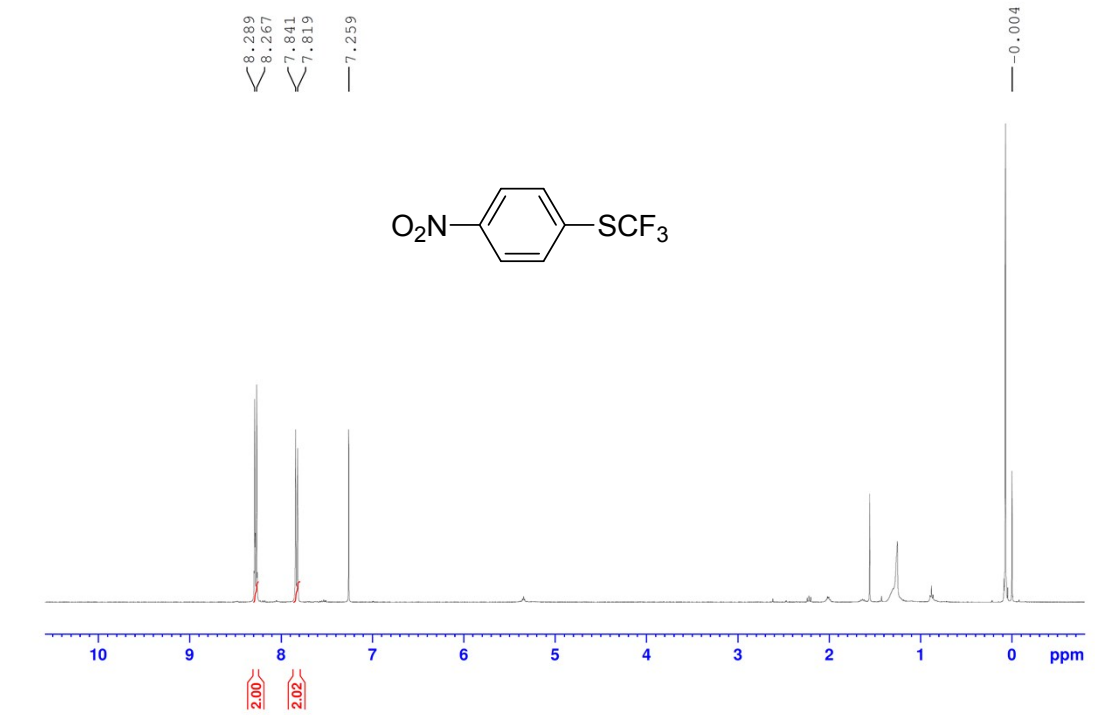

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***4-((trifluoromethyl)thio)benzonitrile (3h)*** in $CDCl_3$

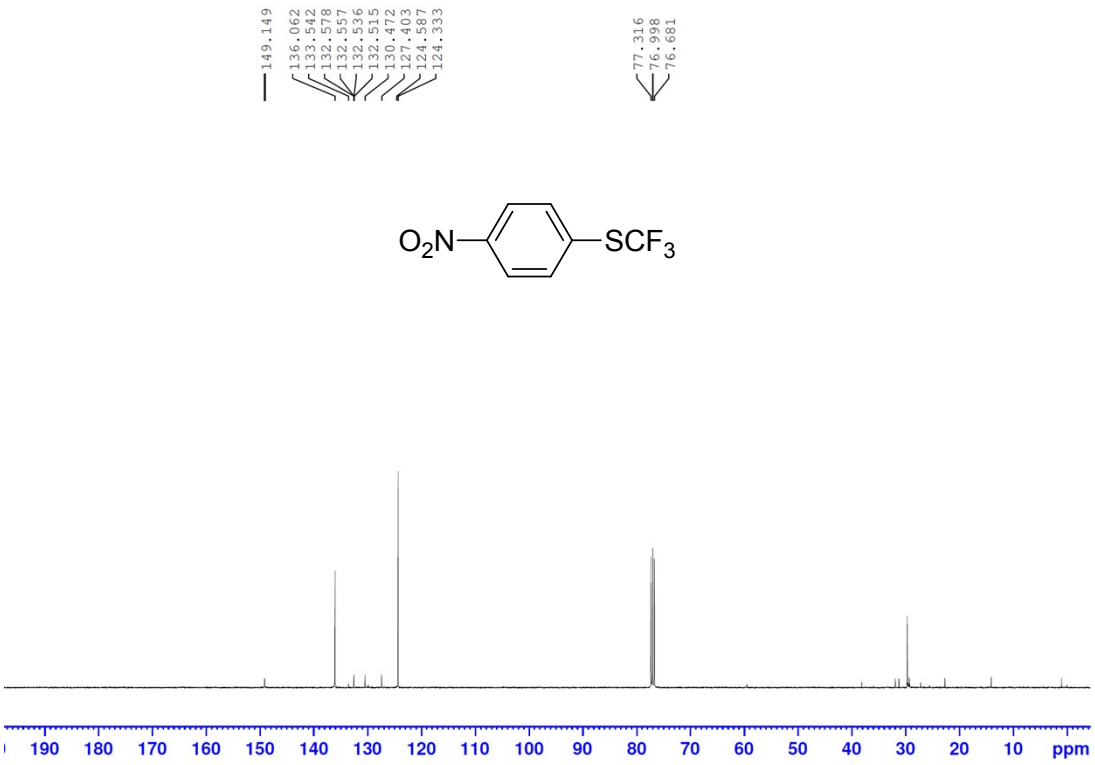


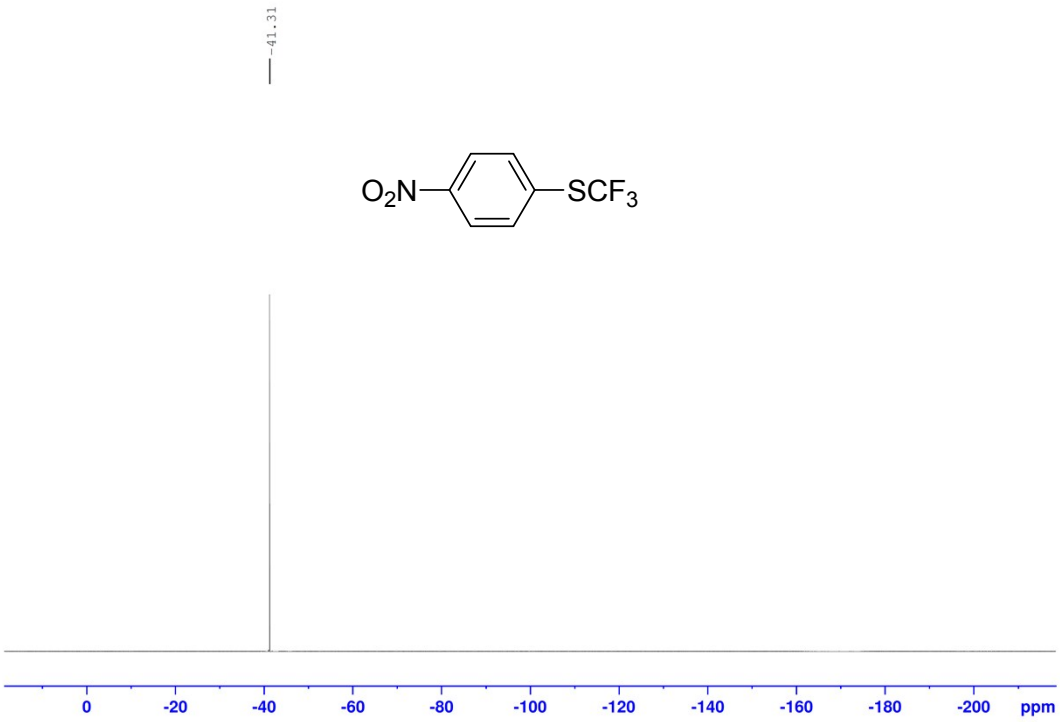

135.94
133.60
132.89
130.60
130.58
130.56
130.54
130.53
127.46
124.40
117.56
114.67
77.31
76.99
76.68
NC
SCF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-41.48
NC
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

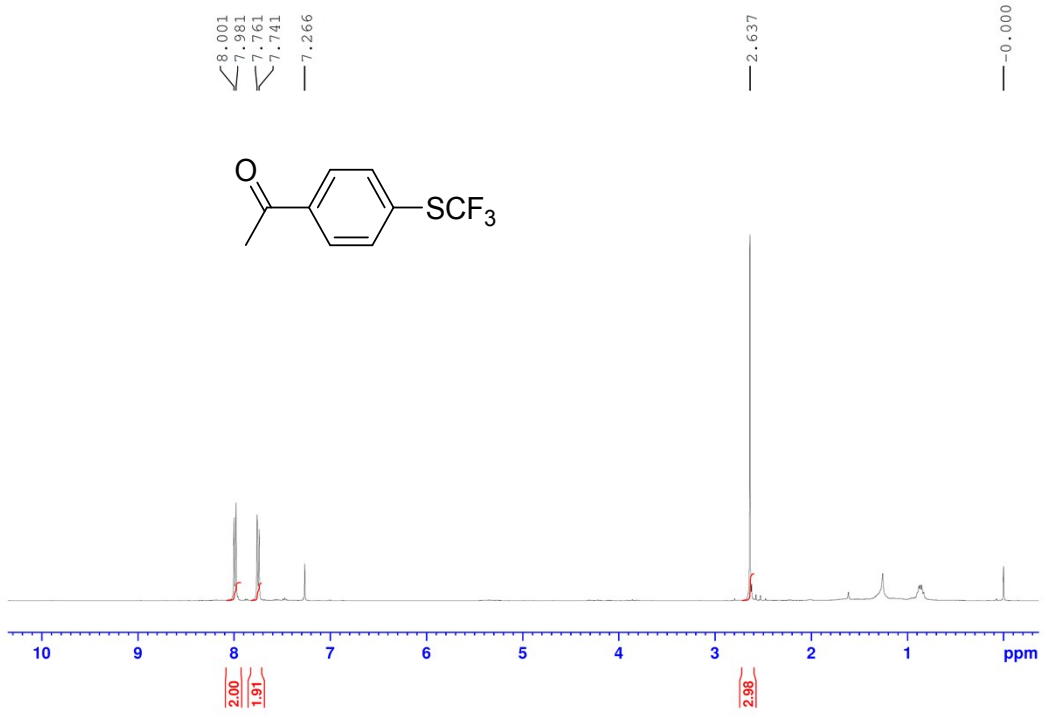
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***(4-nitrophenyl)(trifluoromethyl)sulfane (3i)*** in $CDCl_3$

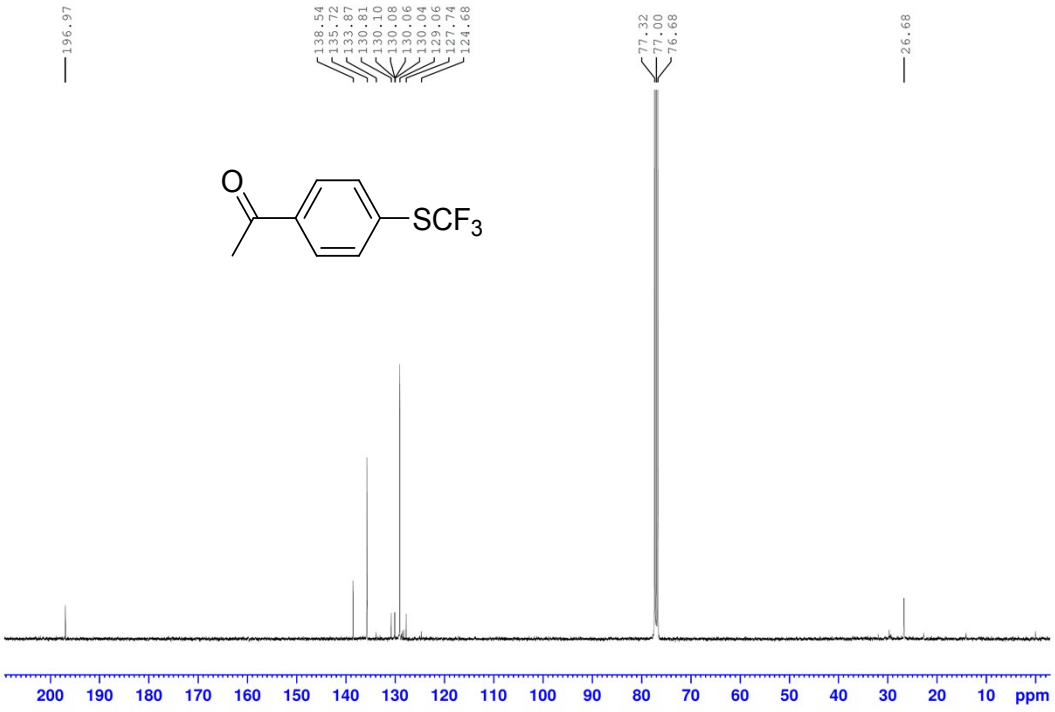


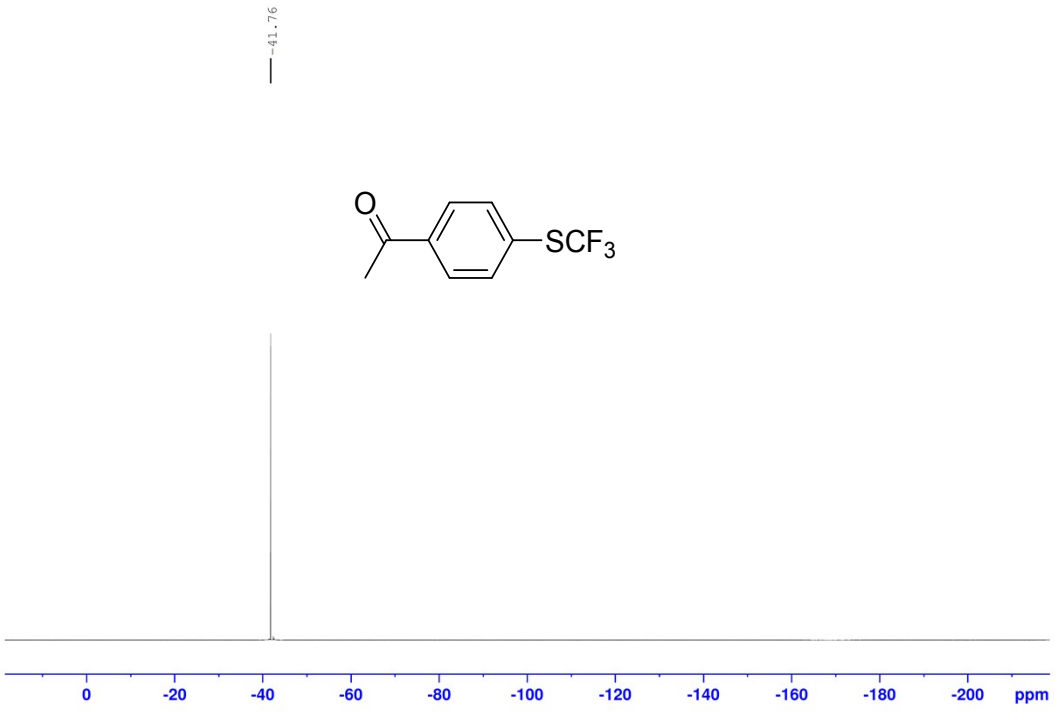





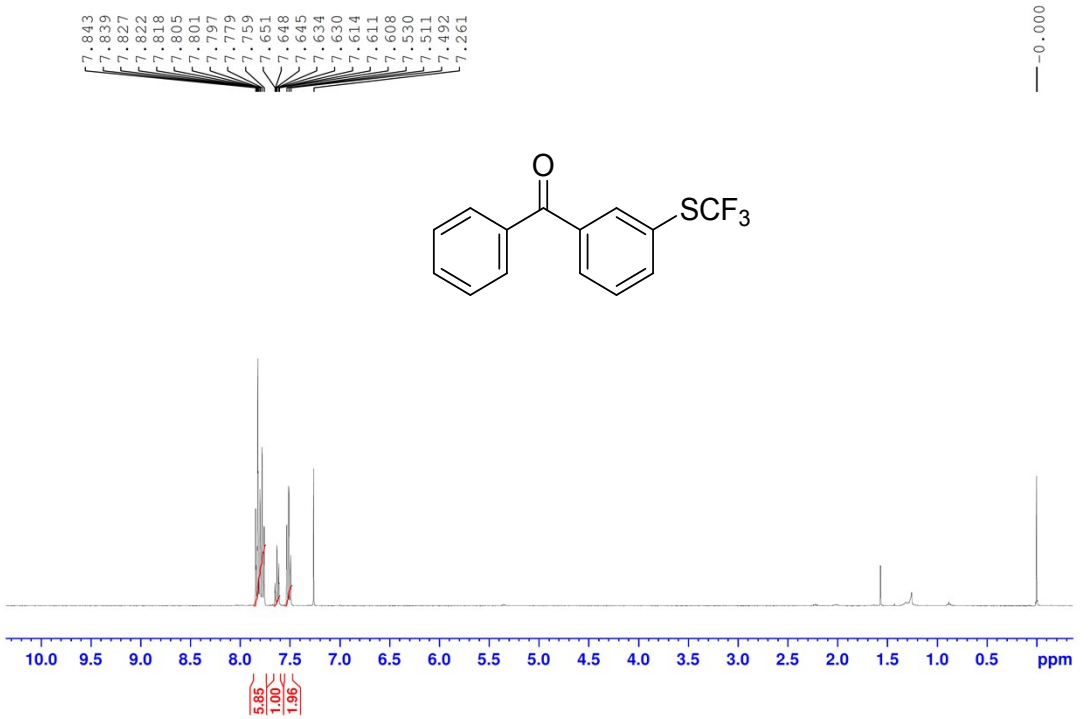

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***1-(4-((trifluoromethyl)thio)phenyl)ethanone (3J)*** in $CDCl_3$

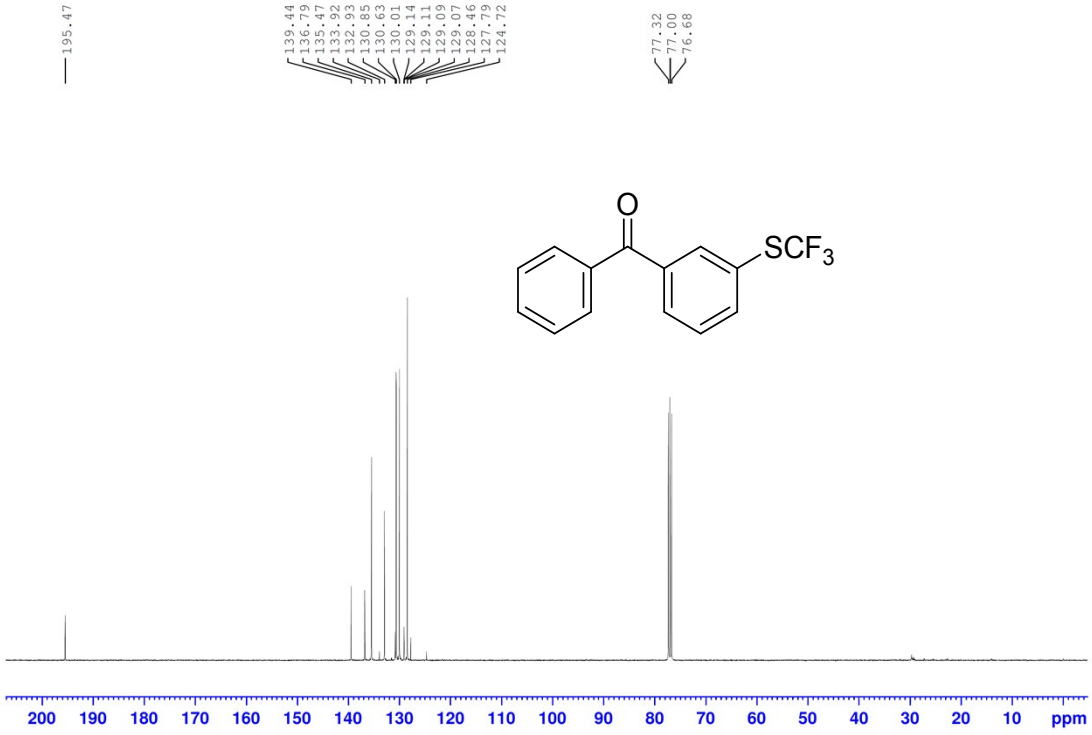


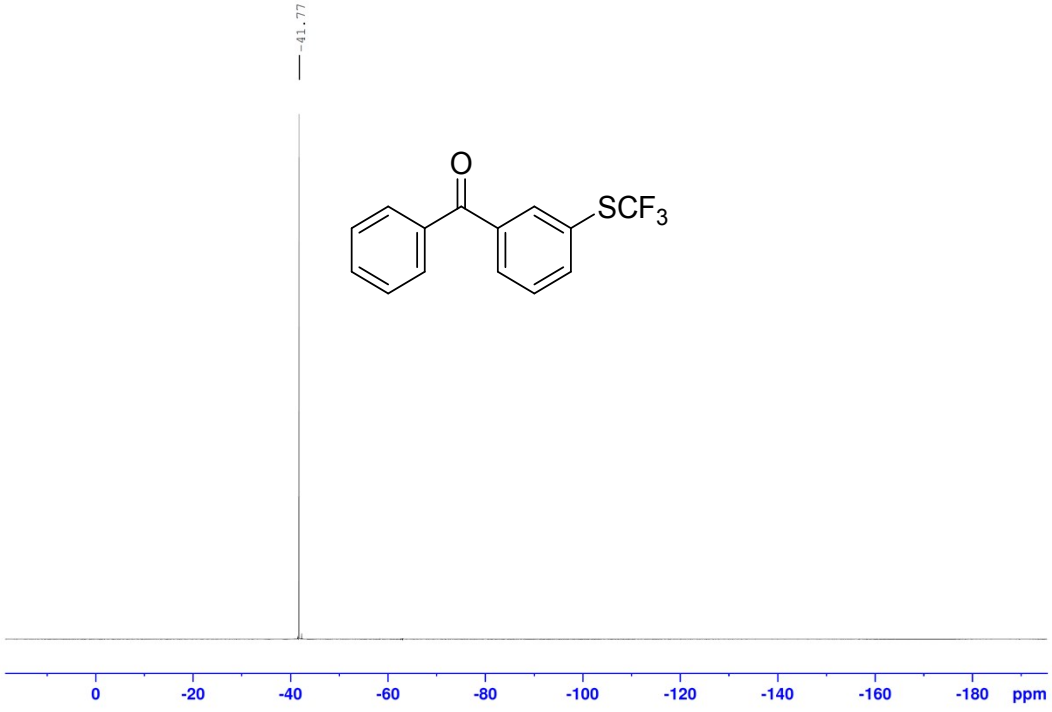

196.97
138.54
135.72
133.87
130.81
130.10
130.08
130.06
130.04
129.06
127.74
124.68
77.32
77.00
76.68
26.68
O
SCF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-41.76
O
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

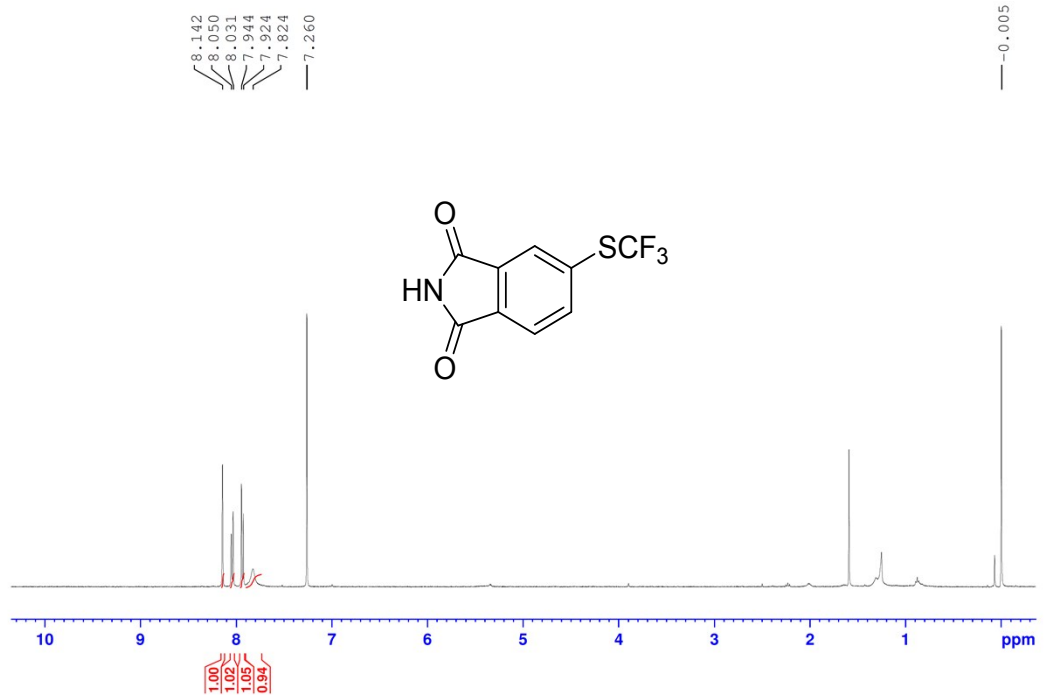
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***Phenyl(4-((trifluoromethyl)thio)phenyl)methanone (3k)*** in $CDCl_3$

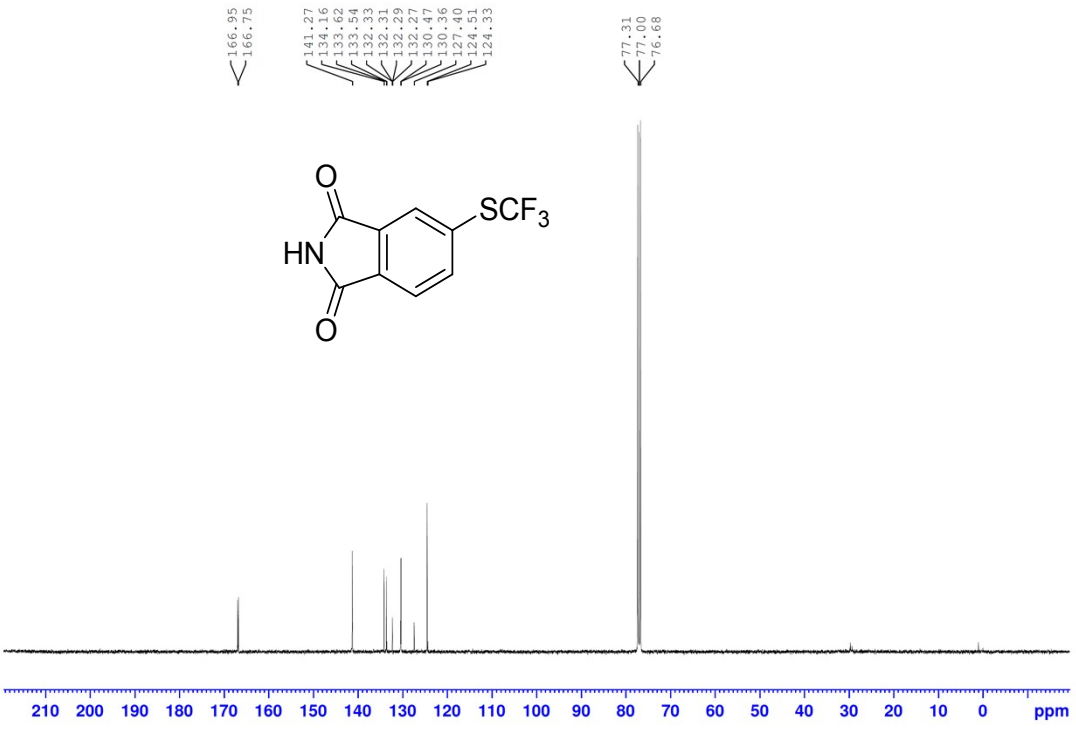


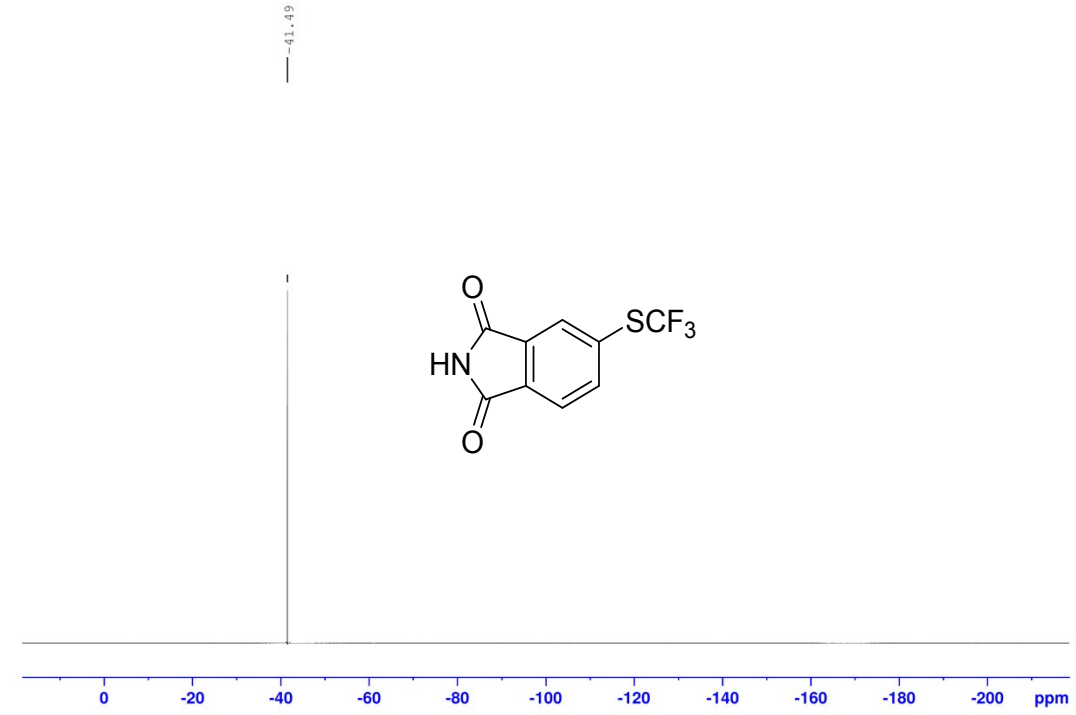





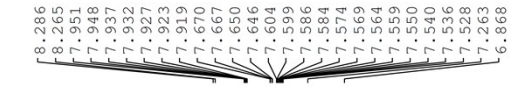

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***5-((trifluoromethyl)thio)isoindoline-1,3-dione (3l)*** in $CDCl_3$

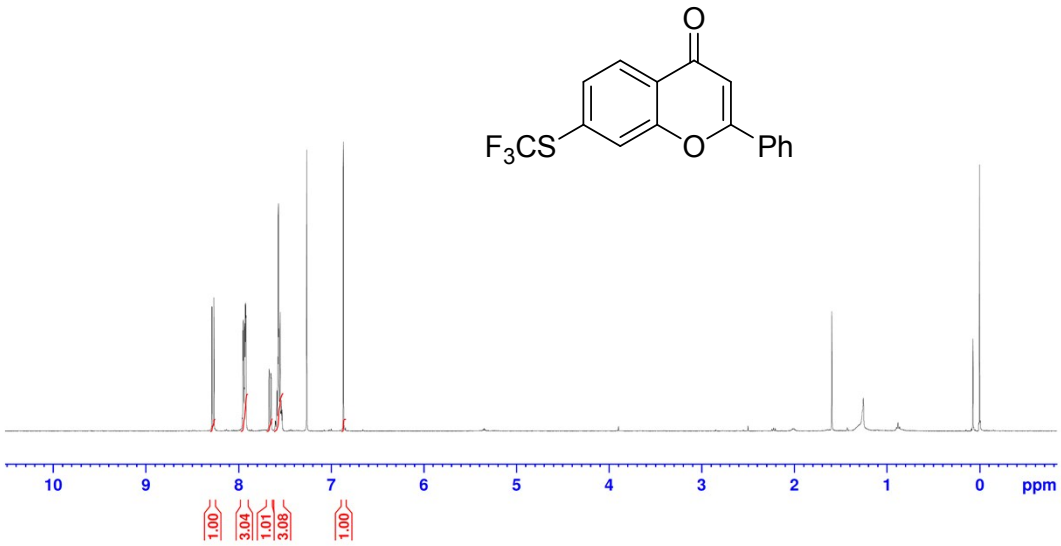


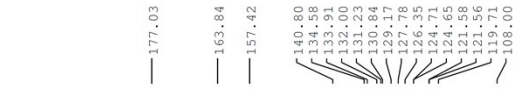

166.95
166.75
141.27
134.16
133.62
133.54
132.33
132.31
132.29
132.27
130.47
130.36
127.40
124.51
124.33
77.31
77.00
76.68
O
HN
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

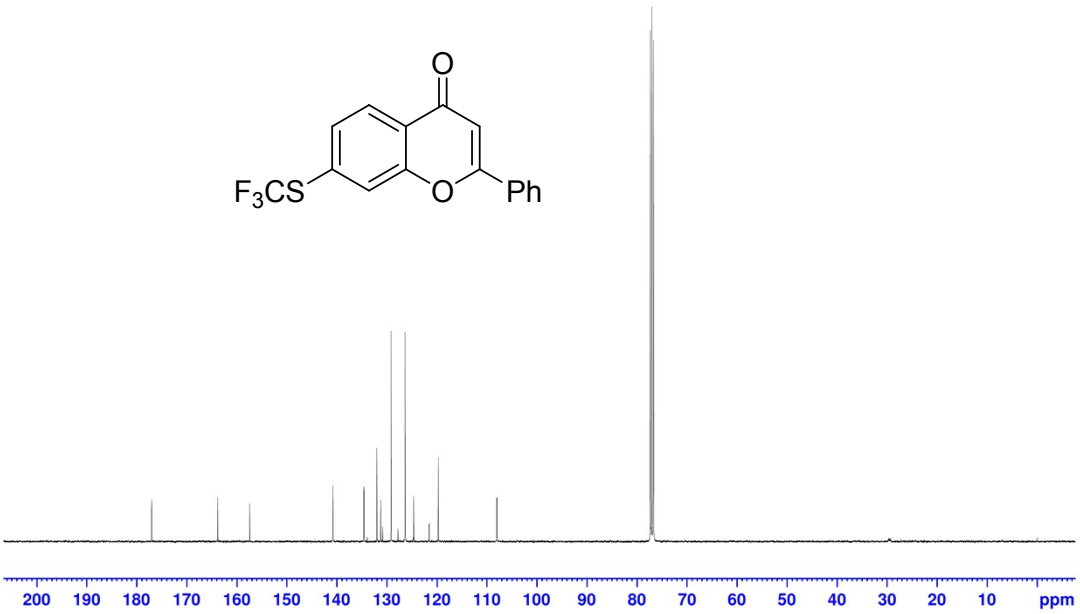

-41.49
O
HN
O
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

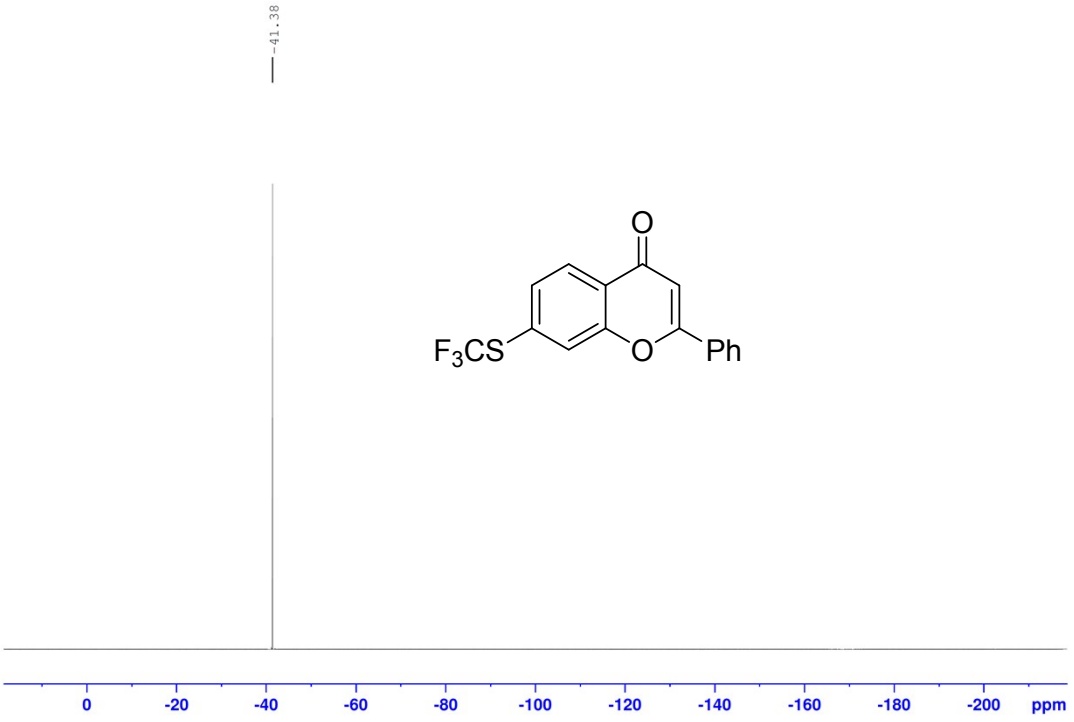
$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***2-phenyl-7-((trifluoromethyl)thio)-4H-chromen-4-one (3m)*** in $CDCl_3$



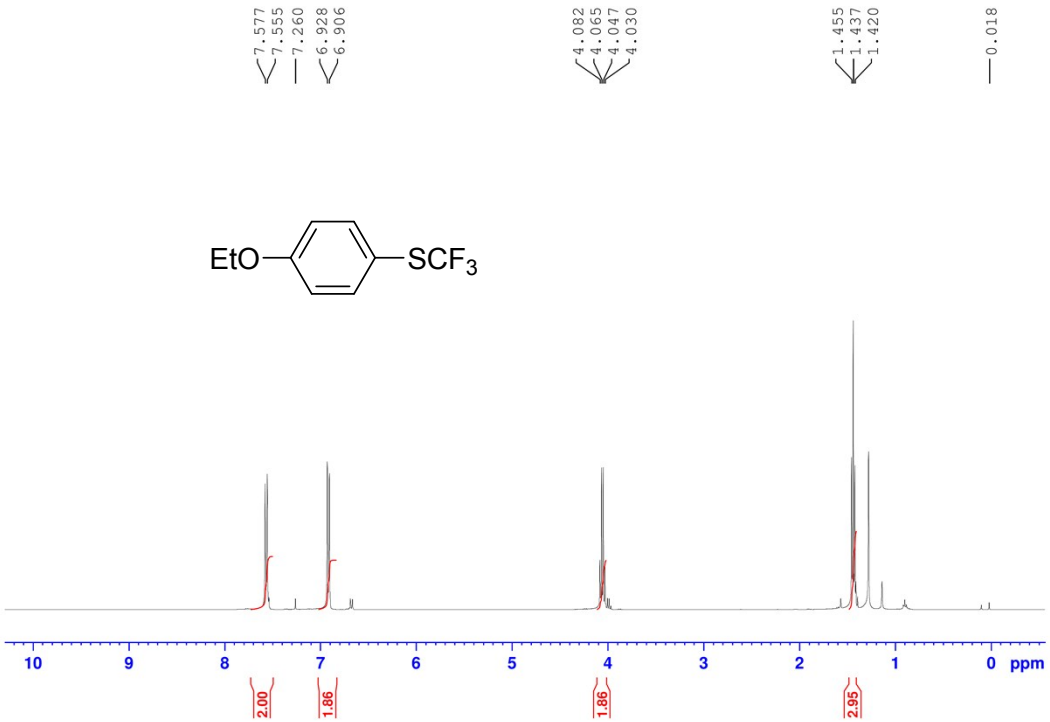



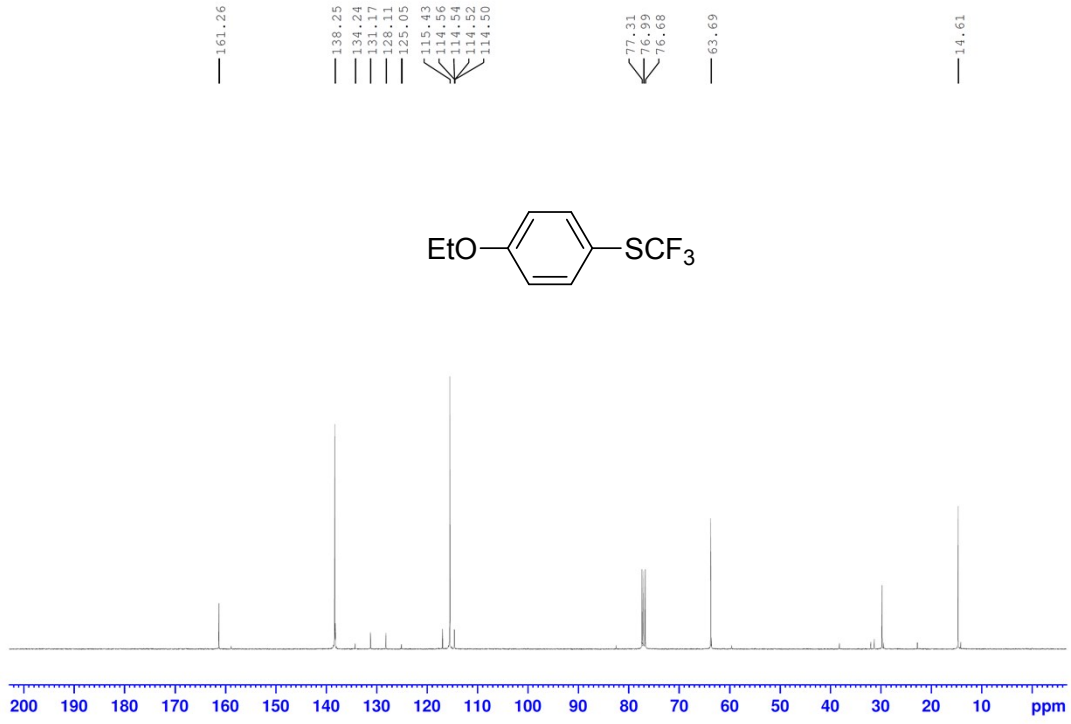



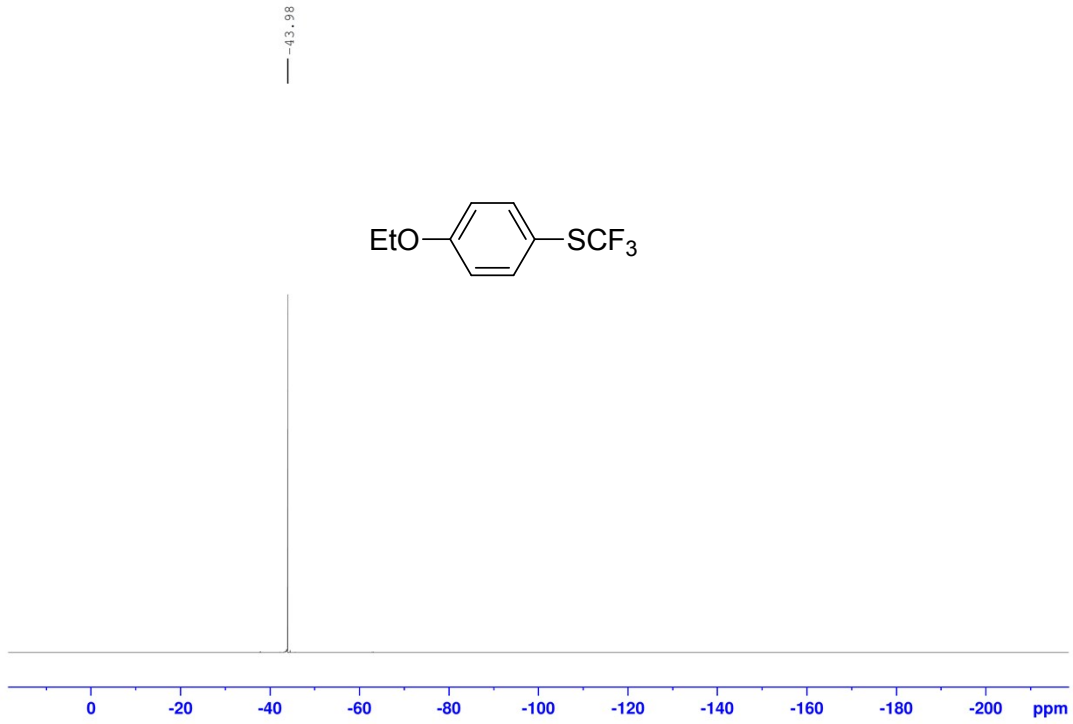





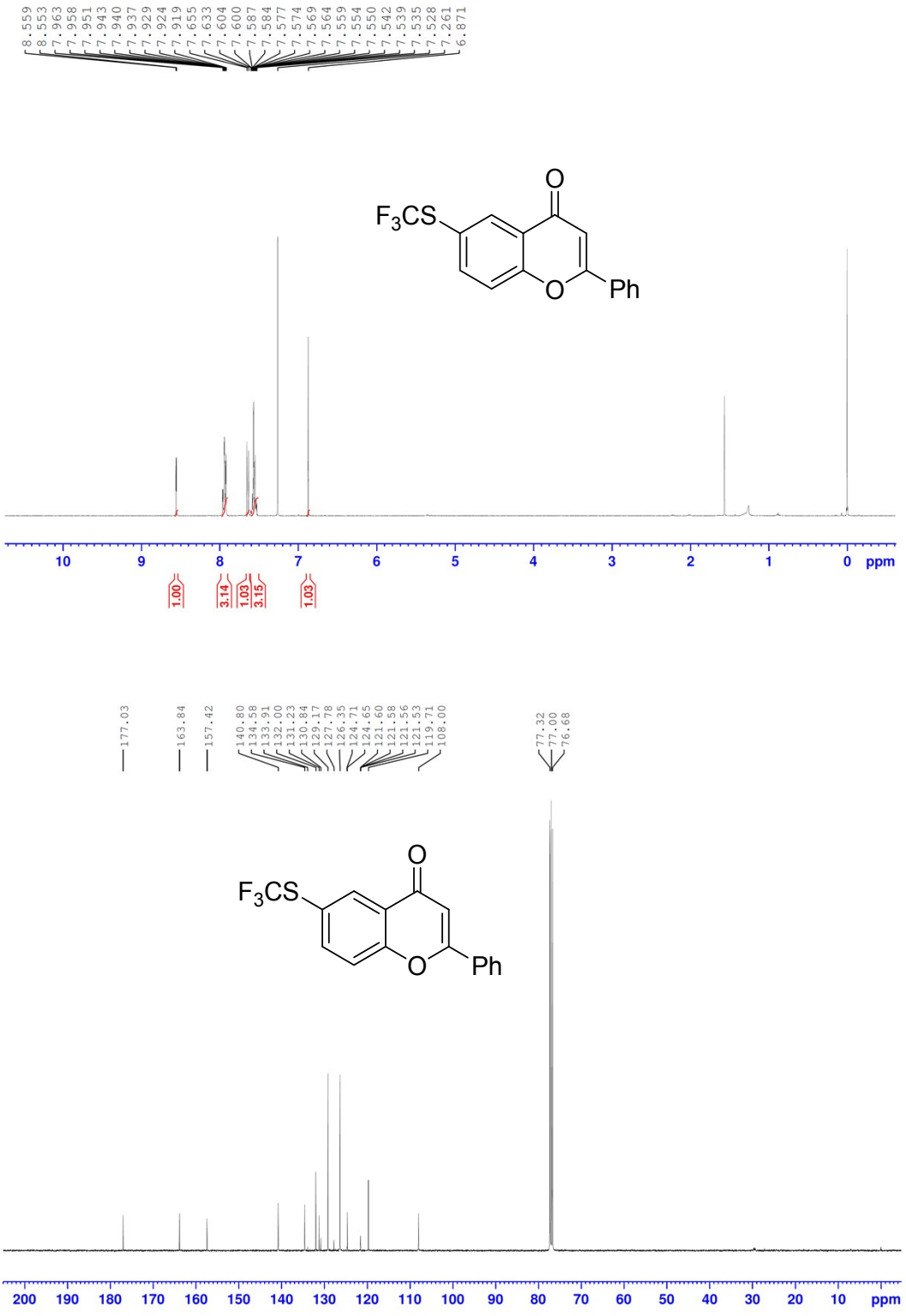

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of **(4-ethoxyphenyl)(trifluoromethyl)sulfane (3n)** in $CDCl_3$

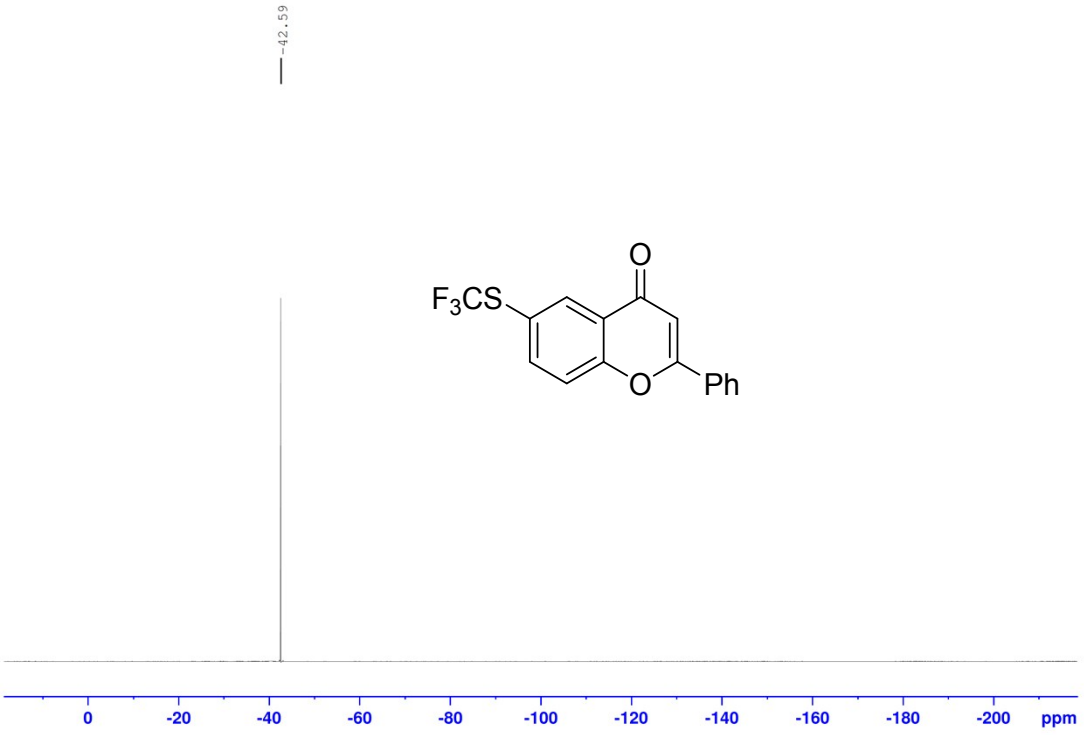



161.26
138.25
134.24
131.17
128.11
125.05
115.43
114.56
114.54
114.52
114.50
77.31
76.99
76.68
63.69
14.61
EtO
SCF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-43.98
EtO
SCF3
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

$^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra of ***2-phenyl-6-((trifluoromethyl)thio)-4H-chromen-4-one (3o)*** in $CDCl_3$




-42.59
O
F3CS
O
Ph
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm