Supporting Information

Nickel-Catalyzed Direct C–H Bond Sulfenylation of Acylhydrazines

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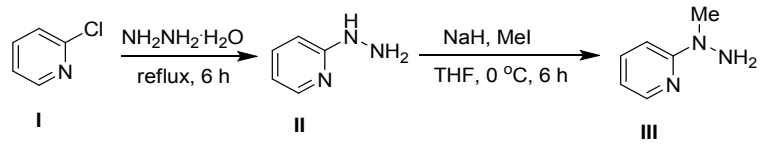
1 Experimental Section

1.1 Synthesis of Starting Materials

Compounds **1a-1j** and **1l** were prepared following typical method A, compounds **1k** and **1m-1p** were prepared following typical method B.

Preparation of 1-methyl-1-(pyridin-2-yl)-hydrazine (III)

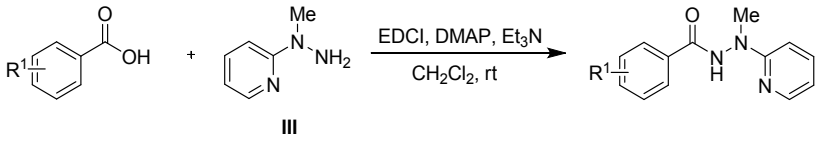


I **II** **III**

Synthesis of 2-hydrazinopyridine (II) Hydrazine monohydrate (85% solution, 9.7 mL, 0.2 mol) was added to 2-chloropyridine (**I**, 2.26 g, 20 mmol), the resulting mixture was refluxed for 6 h under argon atmosphere. Then the solution was cooled to room temperature and extracted with Et_2O for three times. The organic phase was combined and dried over anhydrous Na_2SO_4, crude **II** was obtained as brown liquid after condensation under reduced pressure. The crude **II** was used directly for the next step.

Synthesis of 1-methyl-1-(pyridin-2-yl)-hydrazine (III) NaH (960 mg, 40 mmol) was introduced into a flask containing absolute tetrahydrofuran. Crude **II** was added dropwise to the slurry at 0 °C and stirred for 30 minutes. Then MeI (3.41 g, 24 mmol) was added dropwise to the mixture and stirred for 6 h at 0 °C. The reaction solution was quenched with ice water, and extracted with Et_2O for three times. The organic phase was combined and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to give product **III** as deep red oil (2.15 g, 87.5% yield from **I**).

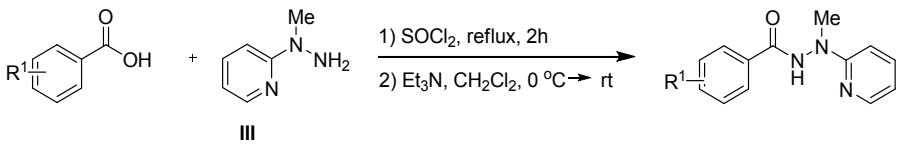
General procedure for the preparation of benzamide substrates (Method A)



III

A mixture of **III** (123 mg, 1 mmol), substituted aryl acid (1 mmol), EDCI (2.29 g, 1.2 mmol), DMAP (24.4 mg, 0.2 mmol) and Et_3N (202 mg, 2 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. Water was added and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

General Procedure for the preparation of benzamide substrates (Method B)

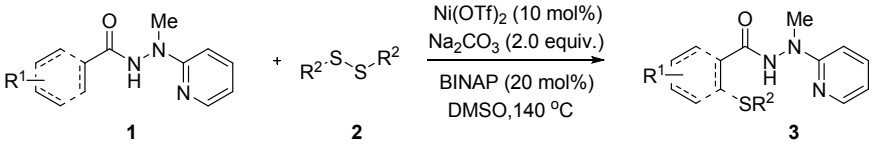


III

Aryl acid (5 mmol) was refluxed in $SOCl_2$ (5 mL) for 2 h, then cooled to rt. The excess $SOCl_2$ was

removed under vacuum to give the corresponding acyl chloride. The acyl chloride was dissolved in 5 mL CH_2Cl_2, and added dropwise at 0 °C to a dry CH_2Cl_2 solution (20 mL) containing **III** (615 mg, 5 mmol) and Et_3N (2.02 g, 10 mmol). Then the mixture was warmed to rt and stirred for 3 h, the resulting mixture was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

1.2 General Procedure for the Thiolation

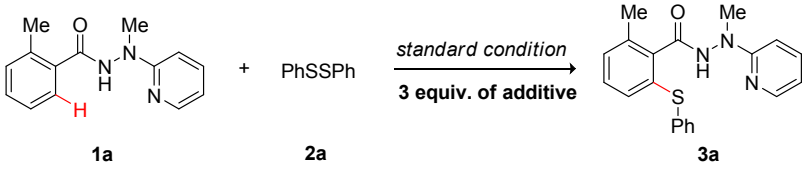


1 **2** **3**

An oven-dried pressure tube was charged with benzamide **1** (0.2 mmol), disulfide **2** (0.24 mmol), $Ni(OTf)_2$ (7.14 mg, 0.02mmol), Na_2CO_3 (42 mg, 0.4 mmol), BINAP (24.88 mg, 0.04 mmol), and DMSO (1.0 mL). The tube was then sealed and stirred vigorously at 140 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted water, extracted with CH_2Cl_2 (3×10 mL). The combined phase was then washed with brine and dried over anhydrous sodium sulfate. After concentration, the resulting residue was purified by preparative TLC using CH_2Cl_2/EtOAc as the eluent to afford product **3**.

1.3 Mechanistic Investigation

General procedures for the radical trapping

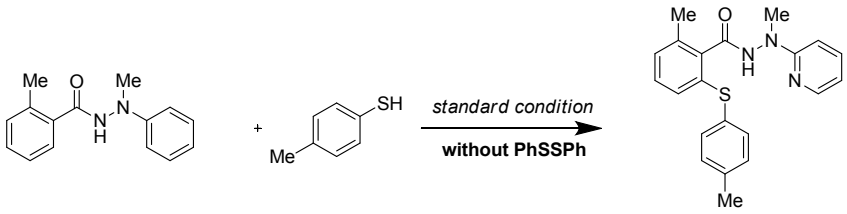


1a **2a** **3a**

additive (3.0 equiv.)	yield (%)
TEMPO	63
BHT	71

An oven-dried pressure tube was charged with benzamide **1a** (48.2 mg, 0.2 mmol), disulfide **2a** (52.32 mg, 0.24 mmol), $Ni(OTf)_2$ (7.14 mg, 0.02 mmol), Na_2CO_3 (42 mg, 0.4 mmol), BINAP (24.88 mg, 0.04 mmol), TEMPO (93.6 mg, 0.6 mmol) and DMSO (1.0 mL). The tube was then sealed and stirred vigorously at 140 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with water, extracted with CH_2Cl_2 (3×10 mL). The combined phase was then washed with brine and dried over anhydrous sodium sulfate. After concentration, the resulting residue was purified by preparative TLC using CH_2Cl_2/EtOAc as the eluent to afford product **3a**.

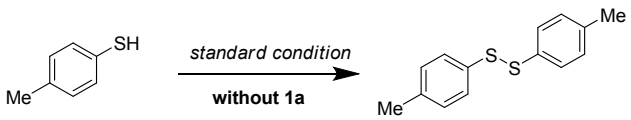
Ni-catalyzed thiolation with 4



1a **4** **3q** 51%

To a Schlenk tube was added benzamide **1a** (48.2 mg, 0.2 mmol), 4-methylbenzenethiol **4** (52.32 mg, 0.24 mmol), $Ni(OTf)_2$ (7.14 mg, 0.02 mmol), Na_2CO_3 (42 mg, 0.4 mmol), BINAP (24.88 mg, 0.04 mmol) and DMSO (1.0 mL). The mixture was stirred at 140 °C for 12 h. The mixture was then cooled to room temperature, diluted with water, extracted with CH_2Cl_2 (3×10 mL). The combined phase was then washed with brine and dried over anhydrous sodium sulfate. After concentration, the resulting residue was purified by preparative TLC using CH_2Cl_2/EtOAc as the eluent to afford product **3q**.

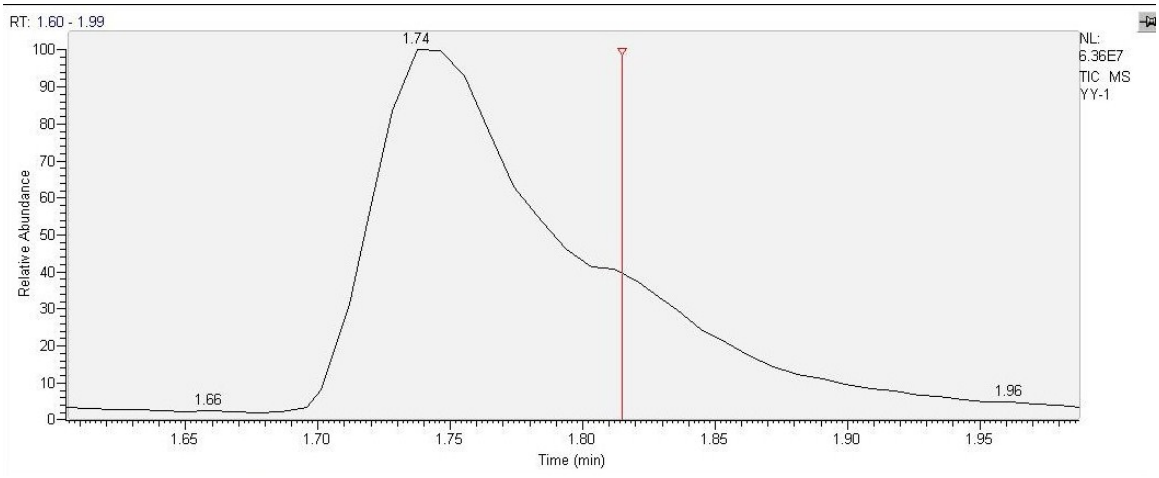
Oxidation of thiol 4 to form disulfide

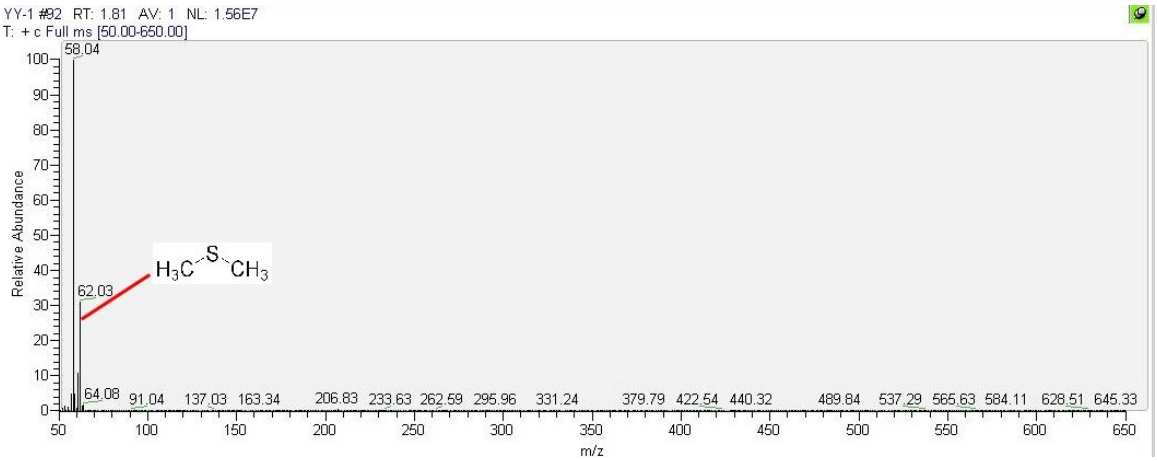


4 **2b**, determined by ^{1}H NMR

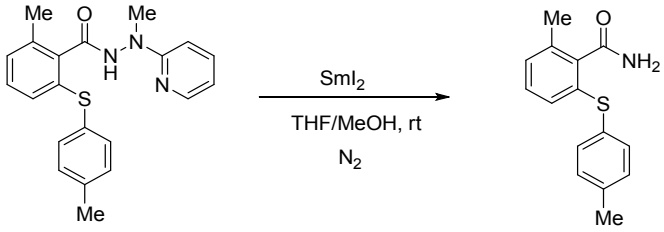
To a Schlenk tube was added 4-methylbenzenethiol **4** (0.2 mmol), $Ni(OTf)_2$ (7.14 mg, 0.02 mmol), Na_2CO_3 (42 mg, 0.4 mmol), BINAP (24.88 mg, 0.04 mmol) and DMSO (1.0 mL). The mixture was stirred at 140 °C for 8 h. Then the mixture was cooled to room temperature, diluted with water, extracted with CH_2Cl_2 (3×10 mL). The combined phase was then washed with brine and dried with anhydrous sodium sulfate. After concentration, the resulting residue was purified by preparative TLC using petroleum ether as the eluent to afford product **2b**, which was confirmed by ^{1}H NMR spectrum. Dimethyl sulfide, a byproduct of DMSO, can be detected by GC-MS, which provided an evidence for the DMSO oxidant (**Figure S1**).

Figure S1





1.4 Hydrolysis of Hydrazine to Amide

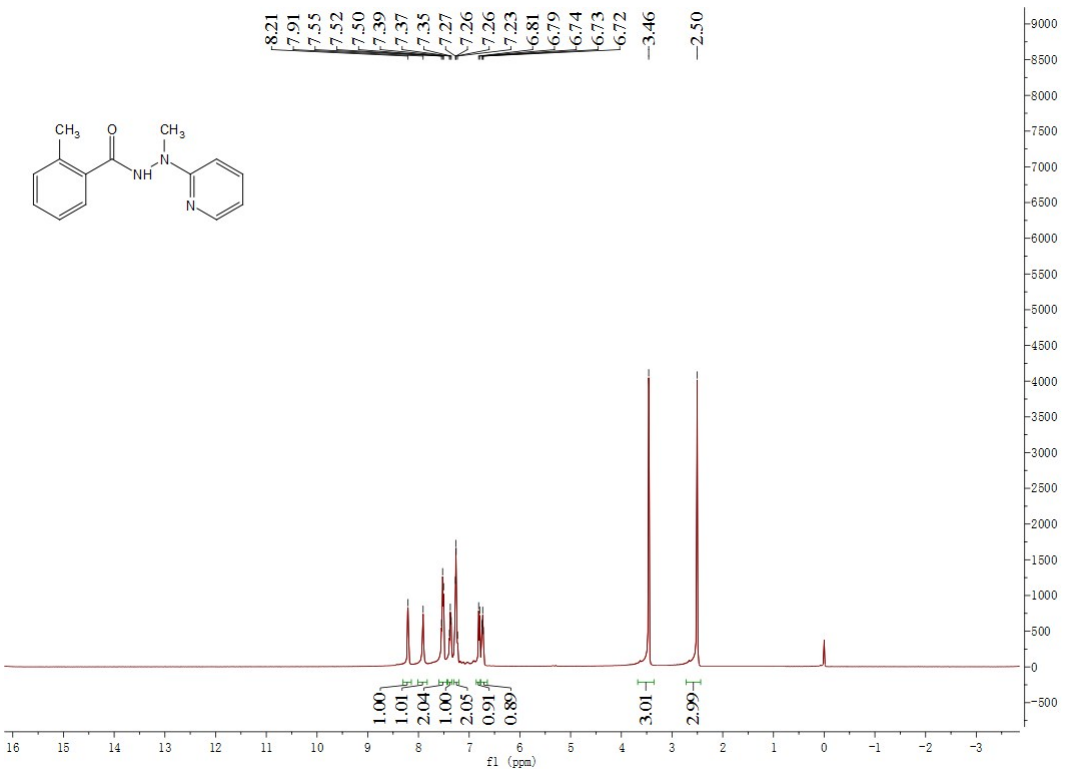


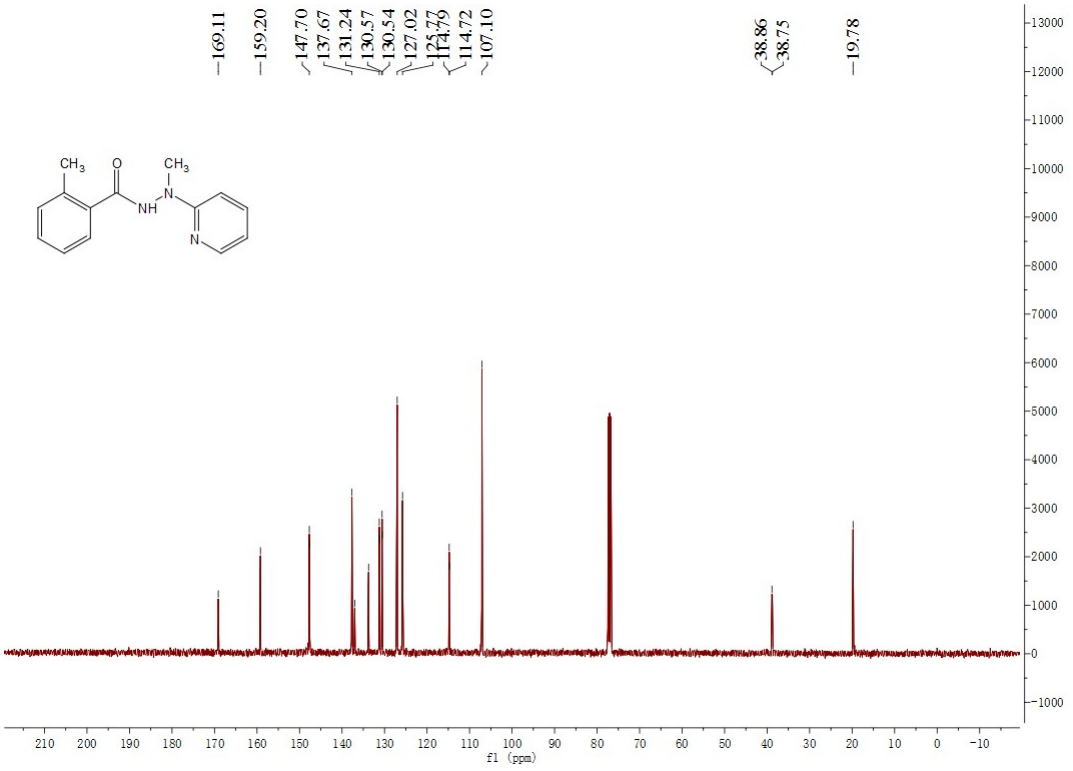
3q **5**, 63%

To a solution of **3q** (72 mg, 0.2 mmol) in THF/MeOH (20 mL, 4:1 V/V) under N_2 was added SmI_2 (5 mL, 0.1 M in THF) dropwise. Upon addition, the blue color of the SmI_2 solution was decolorized. After complete addition, the reaction was allowed to stir for 30 min. The reaction was then concentrated on a Rotovap, and the resulting residue was purified by preparative TLC using CH_2Cl_2/EtOAc as the eluent to afford product **5**. White solid, yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (s, 1H), 7.13 (dt, J = 17.8, 8.4 Hz, 4H), 7.05 (d, J = 7.7 Hz, 1H), 5.95 (s, 1H), 5.67 (s, 1H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.50, 137.21, 136.61, 134.64, 131.90, 130.74, 130.49, 129.13, 128.47, 128.30, 128.01, 20.08, 18.38.

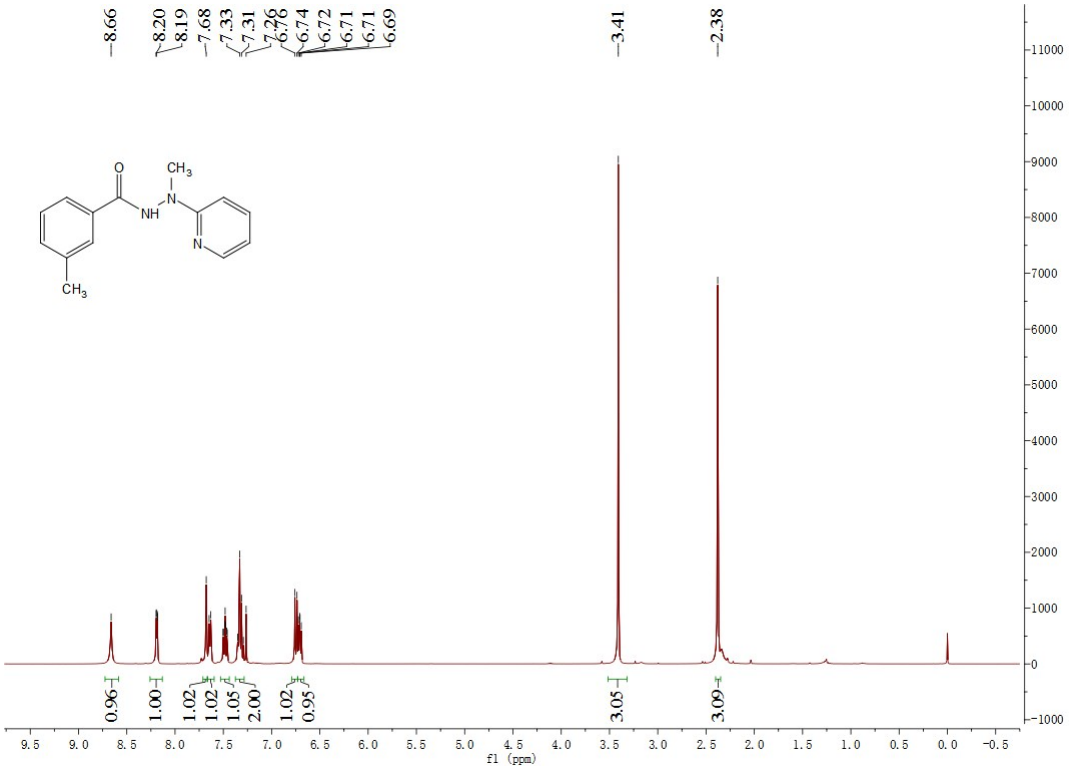
2 NMR Spectra

Compound **1a**





Compound **1b**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7.68
7.33
7.31
7.26
6.78
6.74
6.72
6.71
6.71
6.69
3.41
2.38
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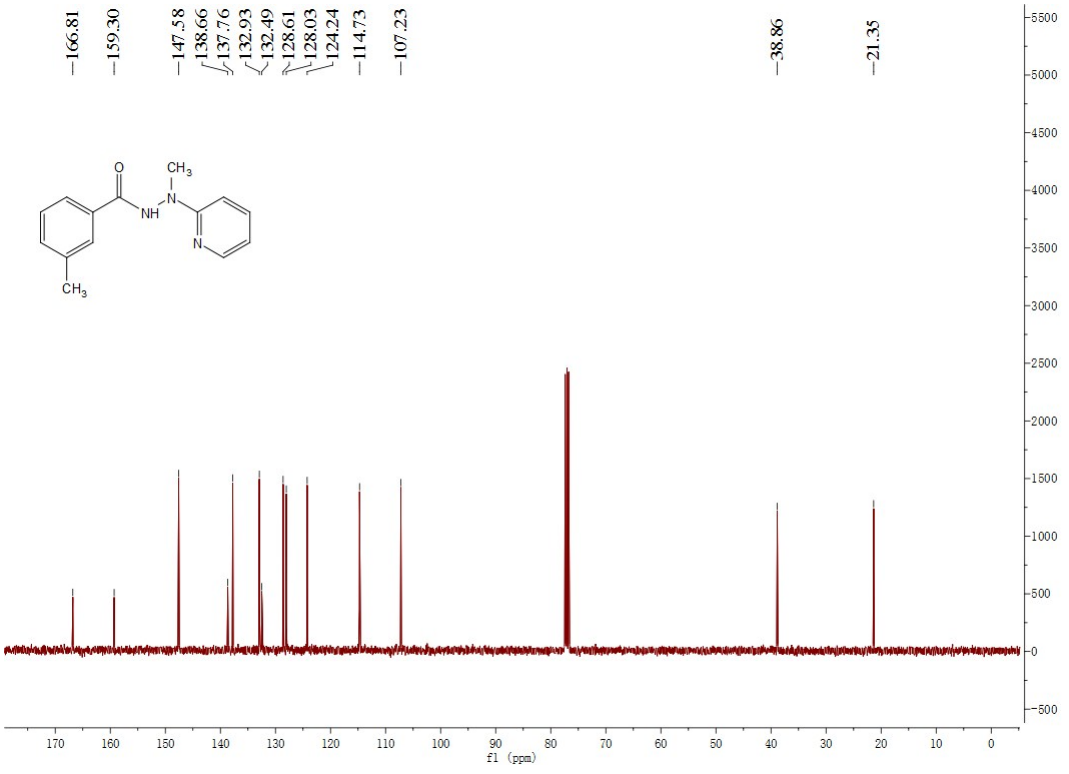
1.02
1.02
1.05
2.00
1.02
0.95
3.05
3.09
f1 (ppm)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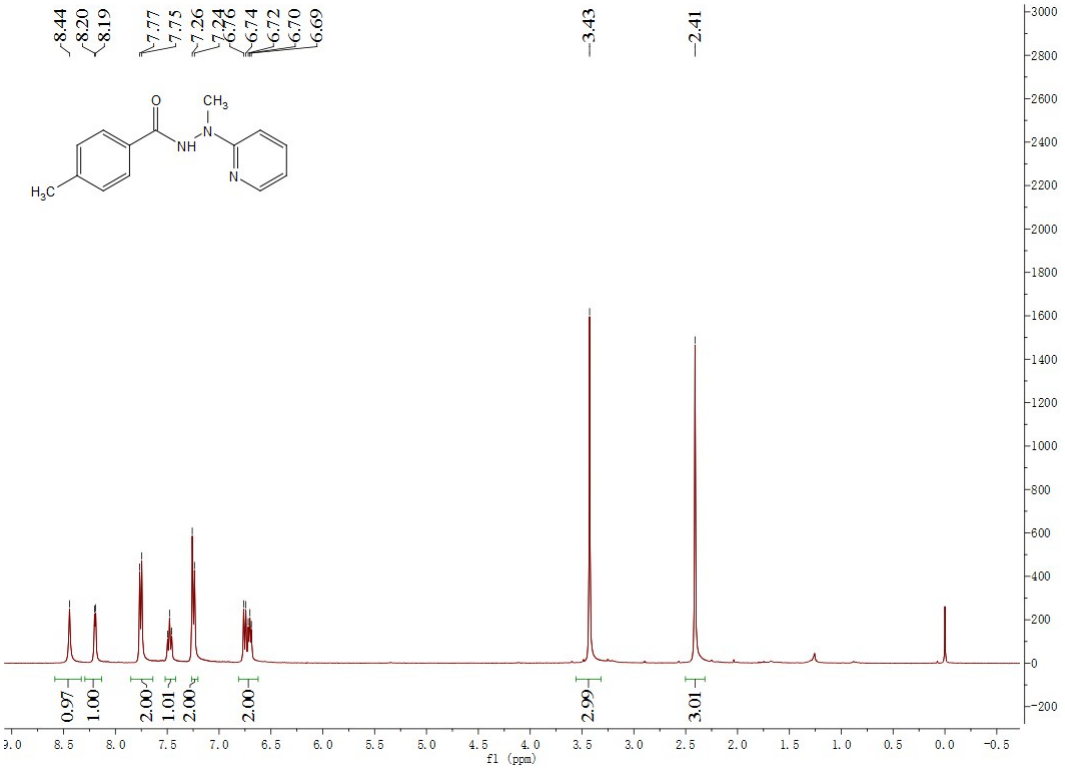
38.86
21.35
f1 (ppm)

Compound **1c**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2.41
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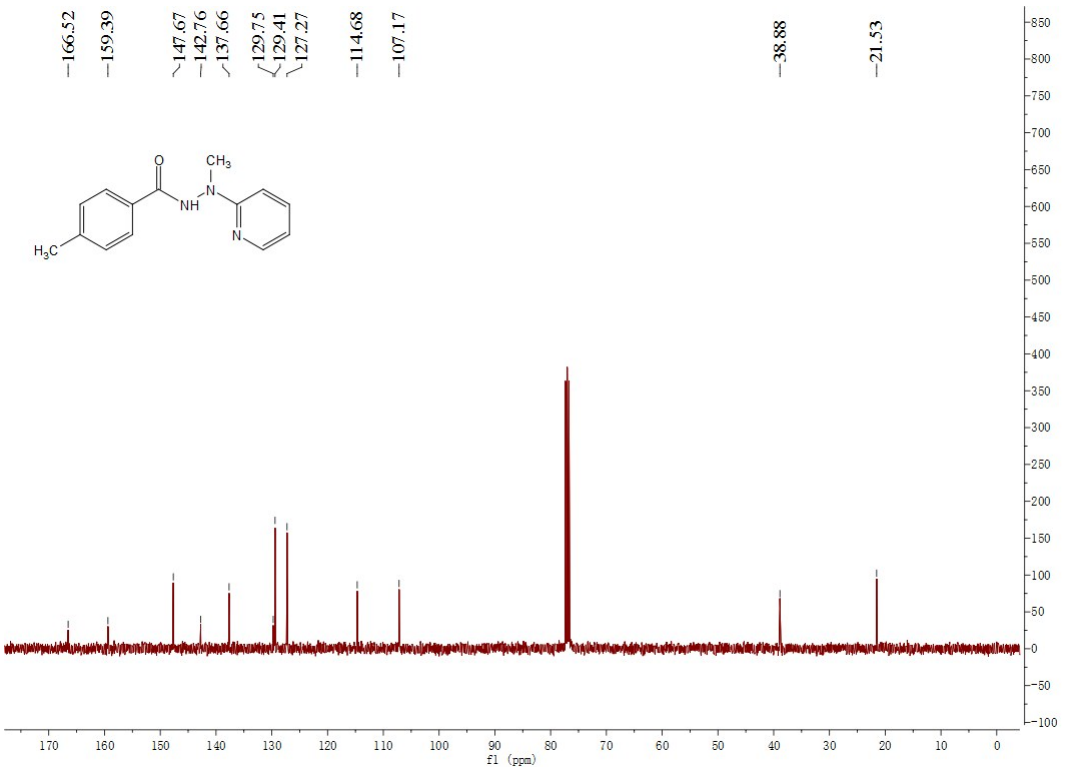
f1 (ppm)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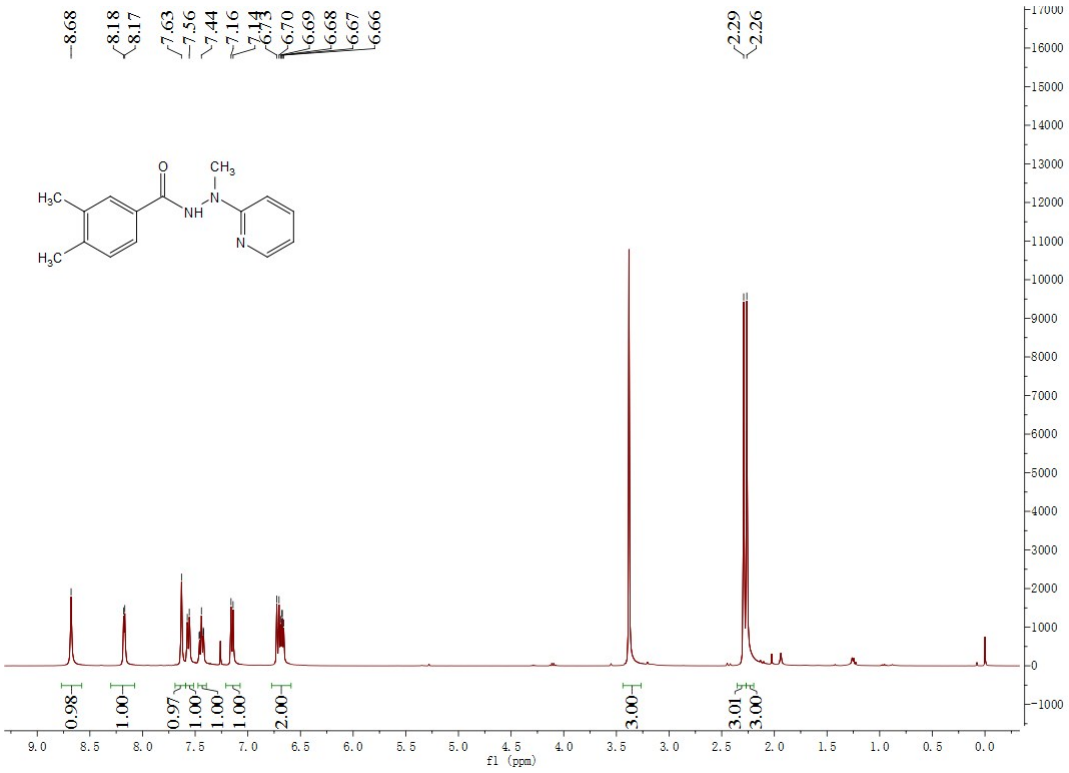
N
NH
N
H3C
f1 (ppm)

Compound **1d**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7.44
7.16
7.14
6.70
6.69
6.68
6.67
6.66
2.29
2.26
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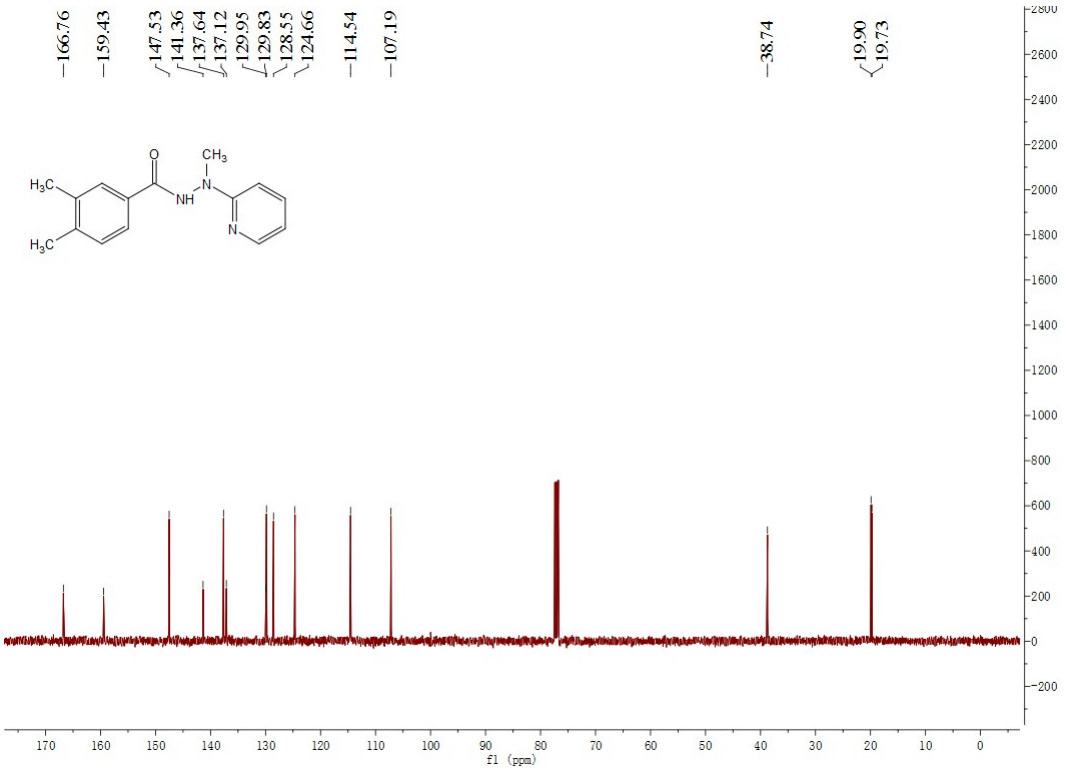
0.97
1.00
1.00
1.00
2.00
3.00
3.01
3.00
f1 (ppm)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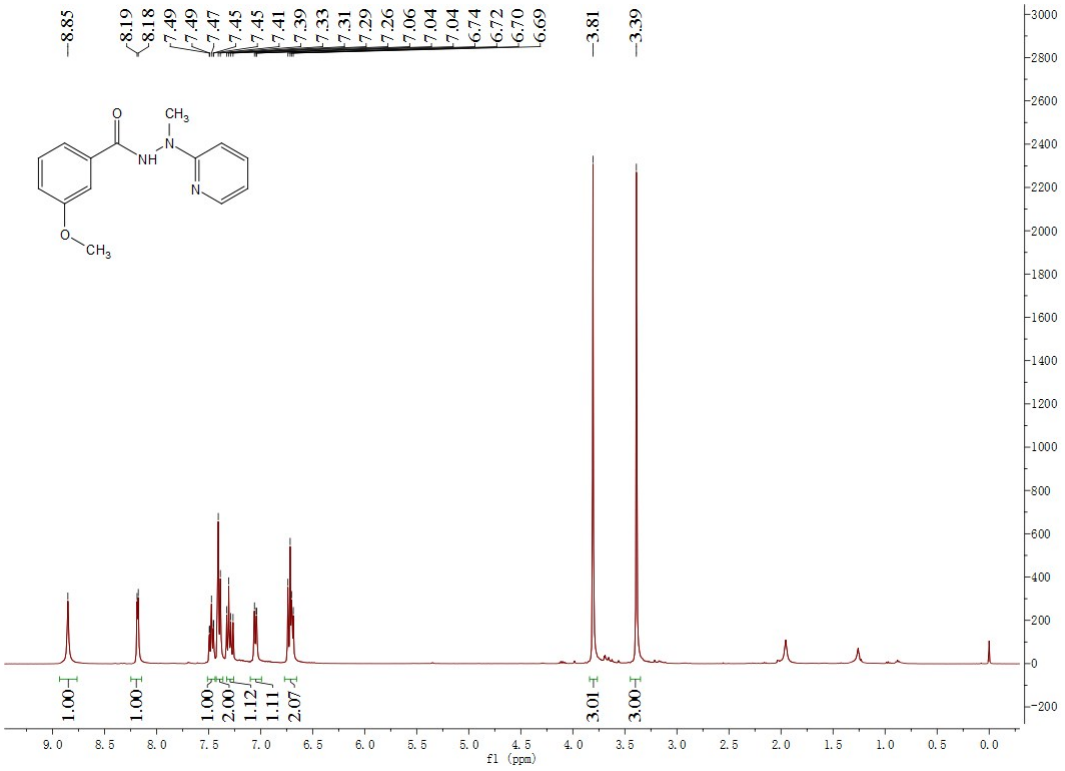
19.90
19.73
f1 (ppm)

Compound **1e**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7.29
7.26
7.06
7.04
7.04
6.74
6.72
6.70
6.69
3.81
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CH3
NH
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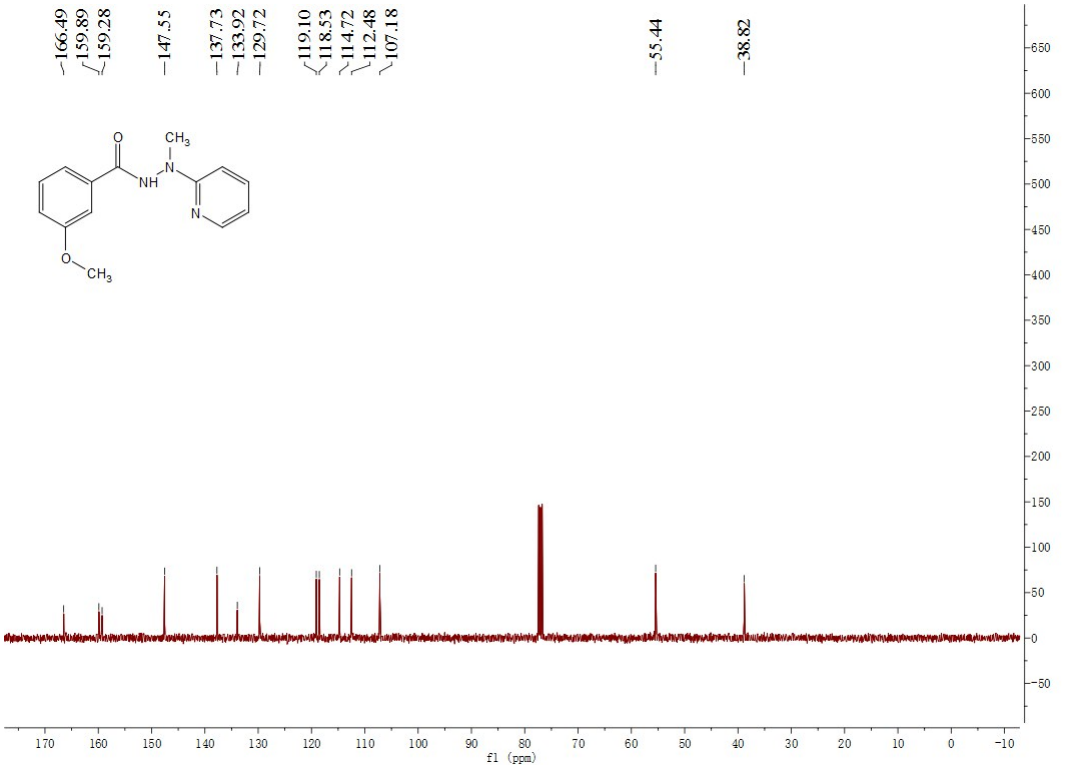
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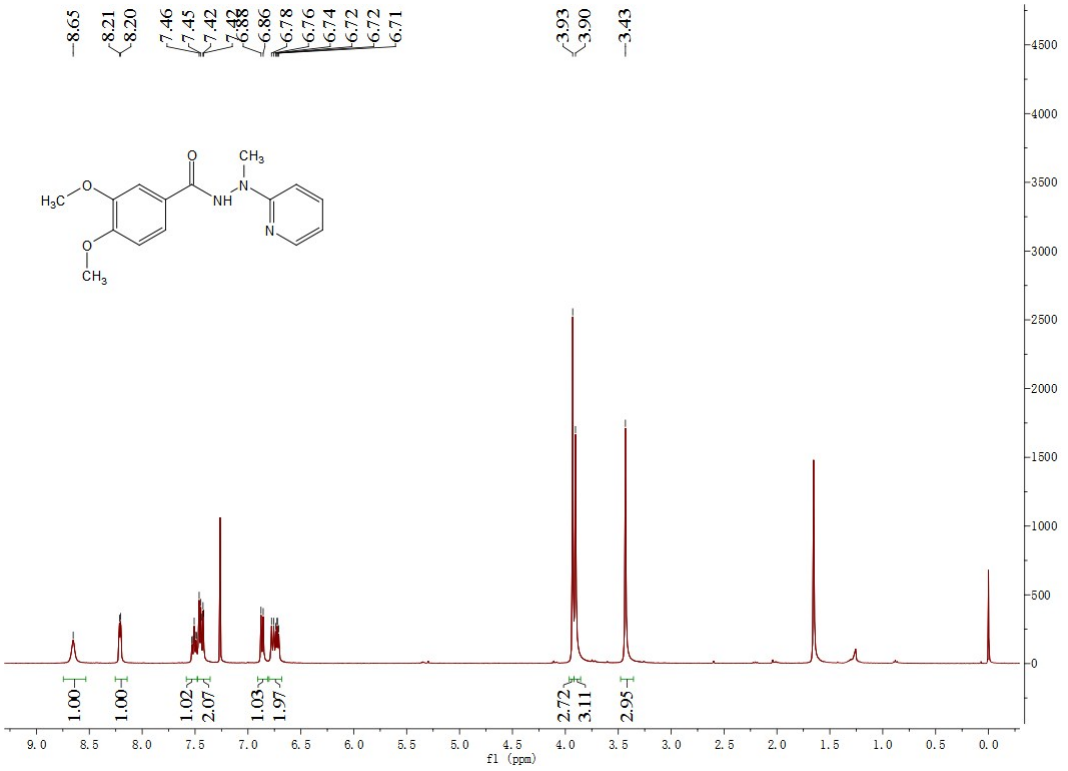
N
O
CH3
f1 (ppm)

Compound **1f**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6.71
3.93
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1.97
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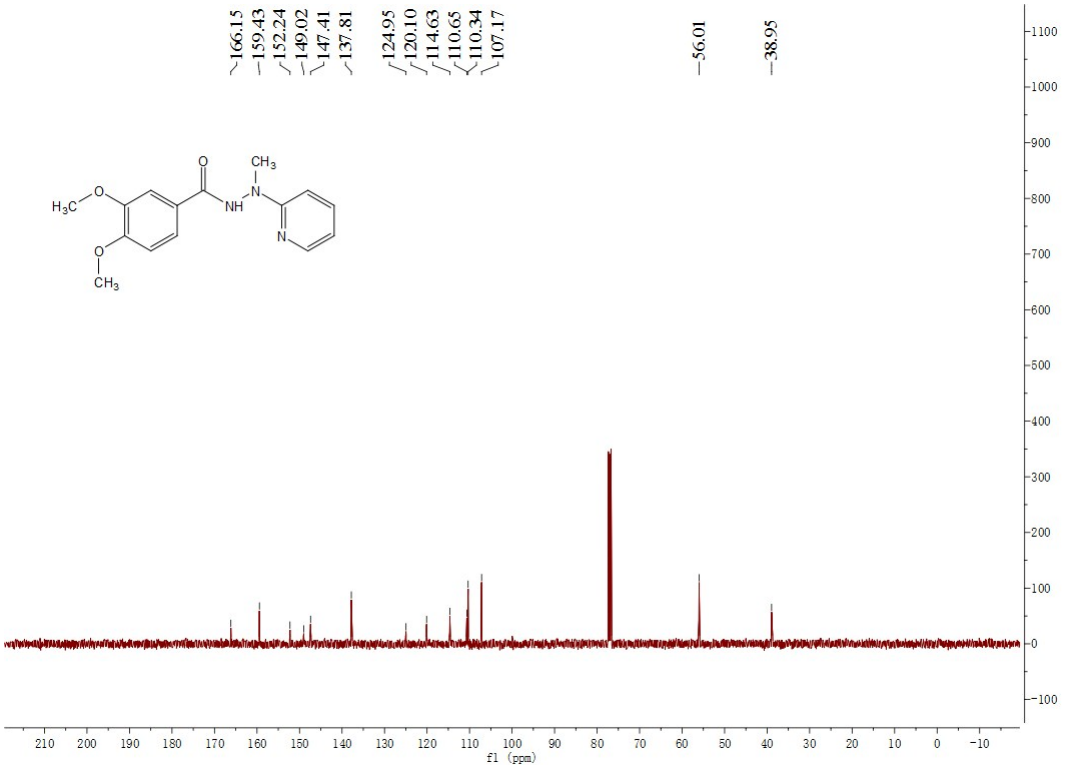
2.95
f1 (ppm)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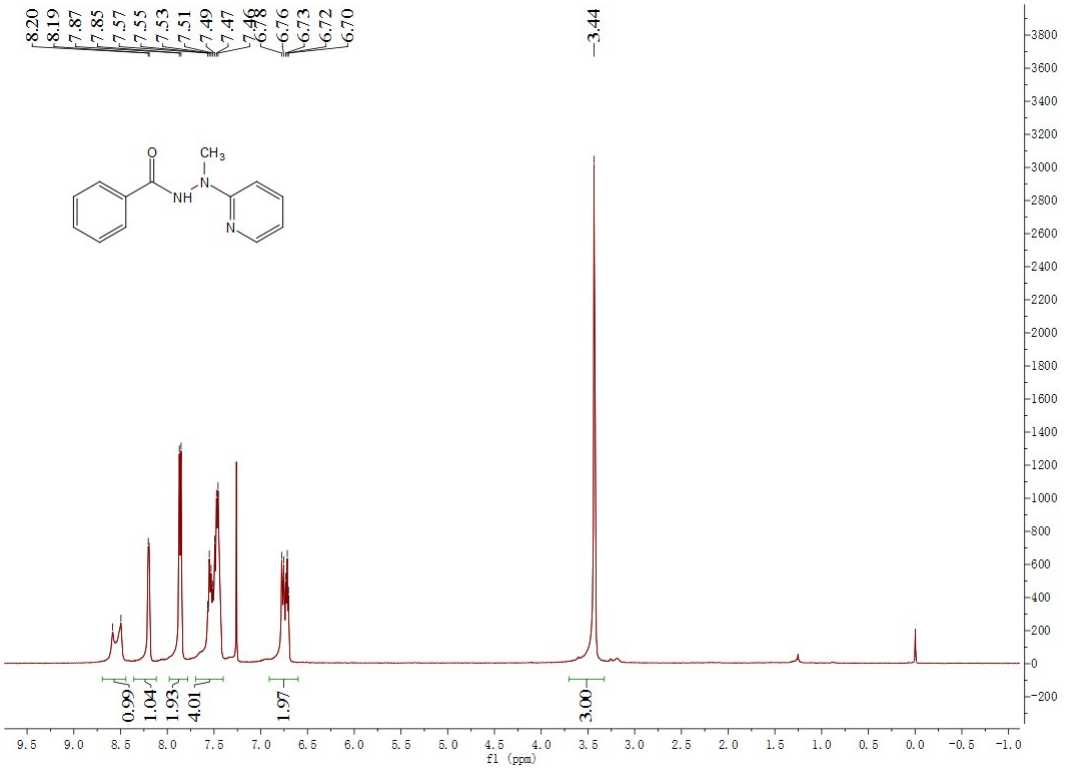
f1 (ppm)

Compound **1g**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7.53
7.51
7.49
7.47
7.46
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6.76
6.73
6.72
6.70
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4.01
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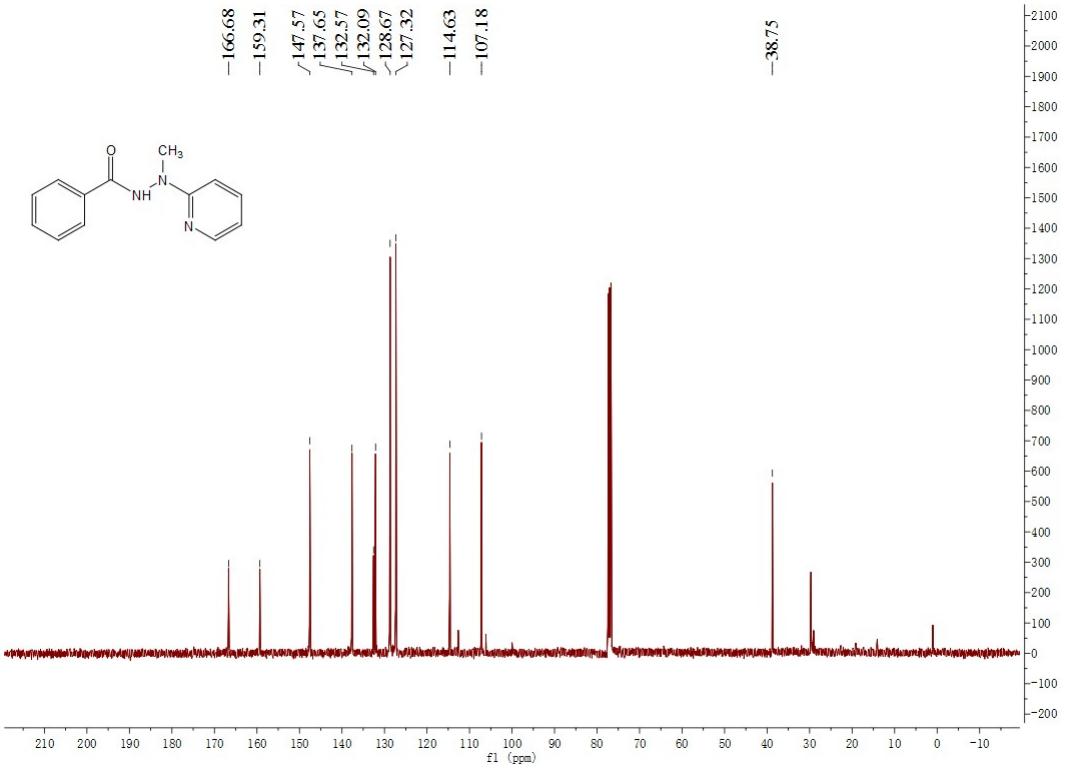
3.00
f1 (ppm)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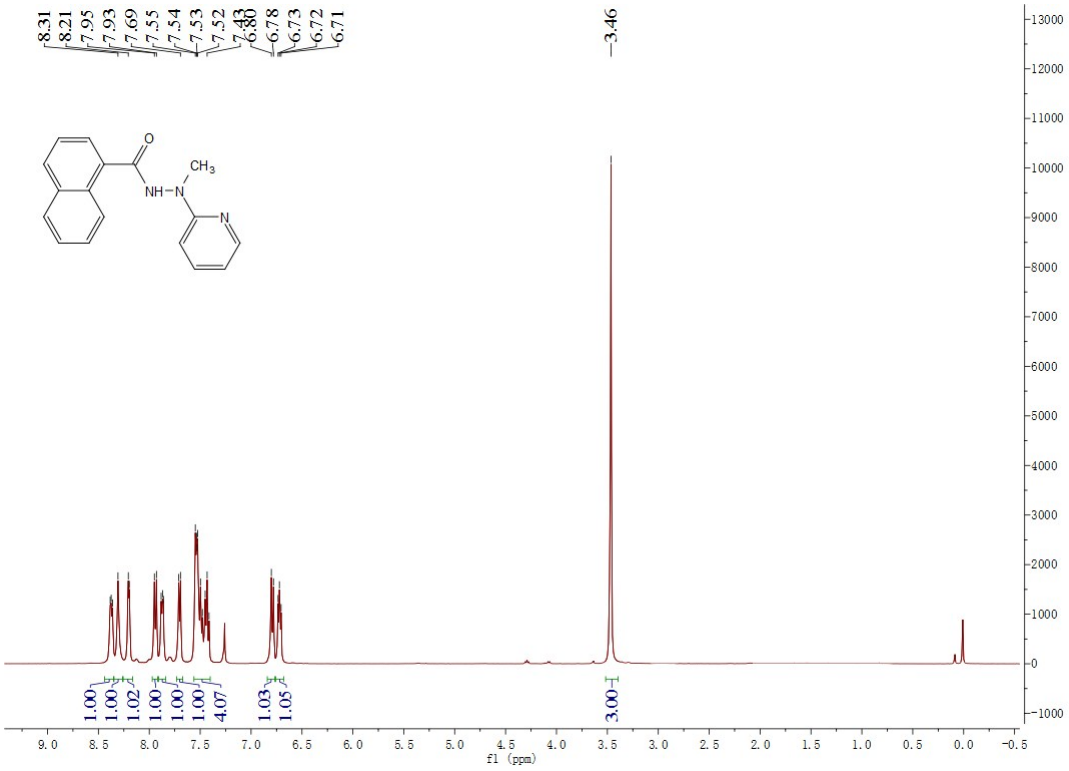
NH
N
N
f1 (ppm)

Compound **1h**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6.72
6.71
3.46
O
CH3
NH-N
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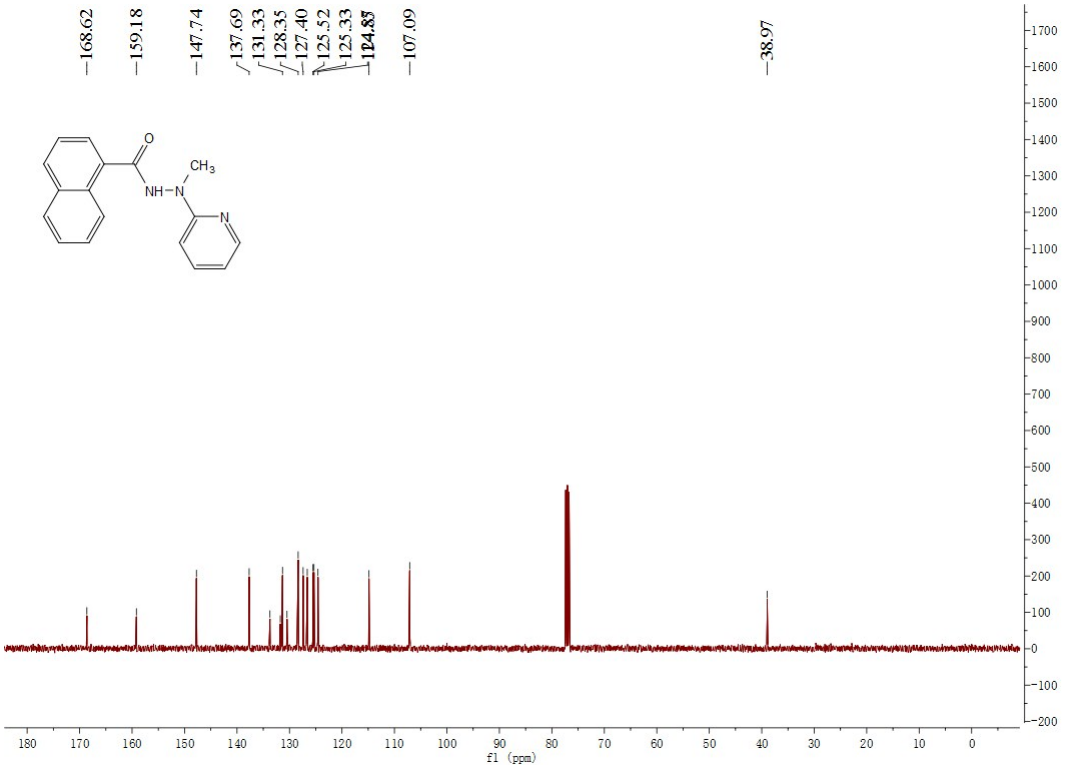
f1 (ppm)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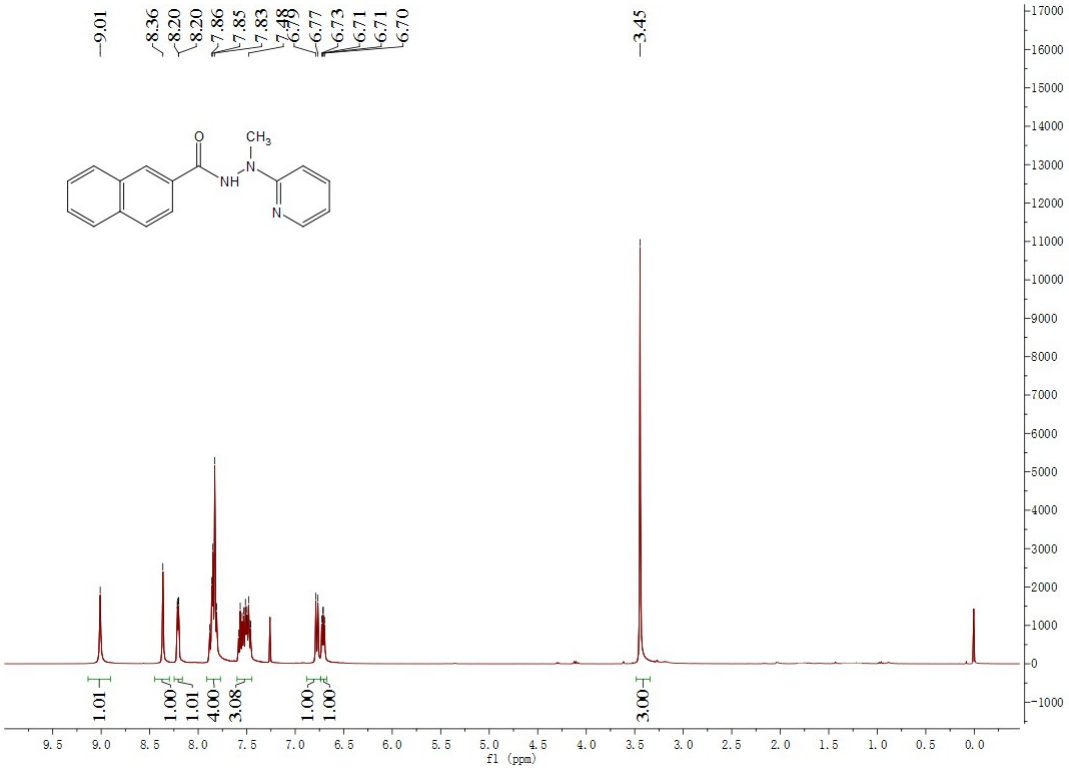
f1 (ppm)

Compound **1i**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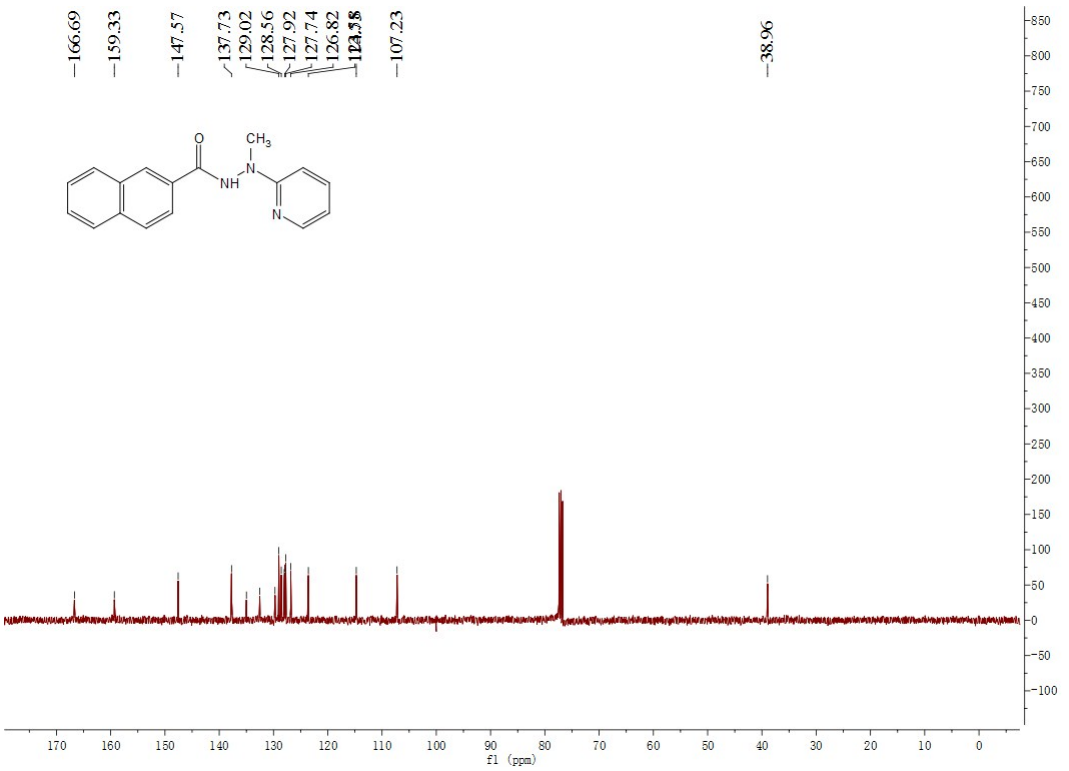
3.00
f1 (ppm)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127.92
127.74
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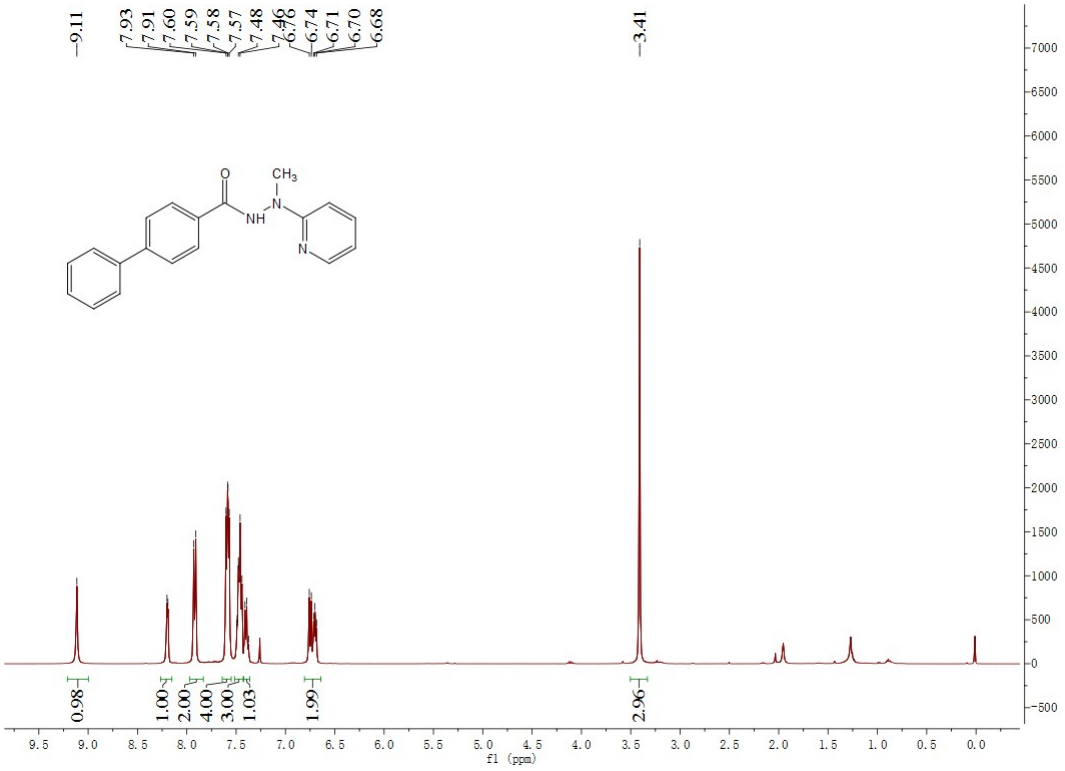
107.23
38.96
f1 (ppm)

Compound **1j**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NH
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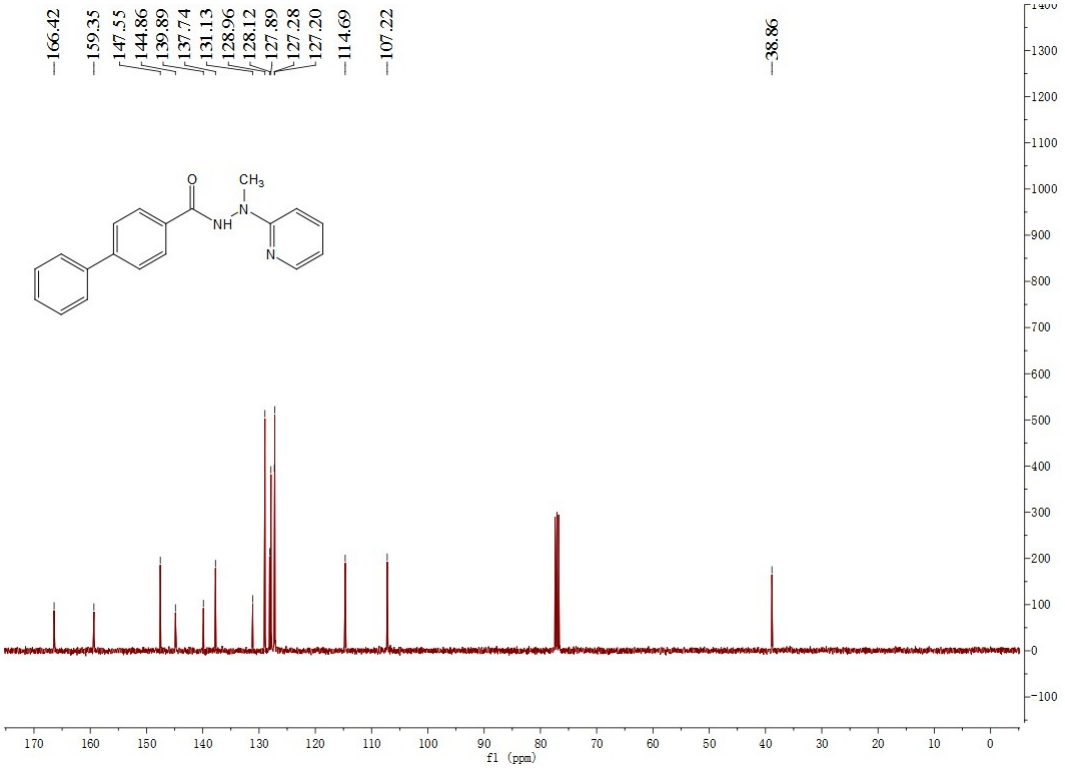
2.00
4.00
3.00
1.03
1.99
2.96
f1 (ppm)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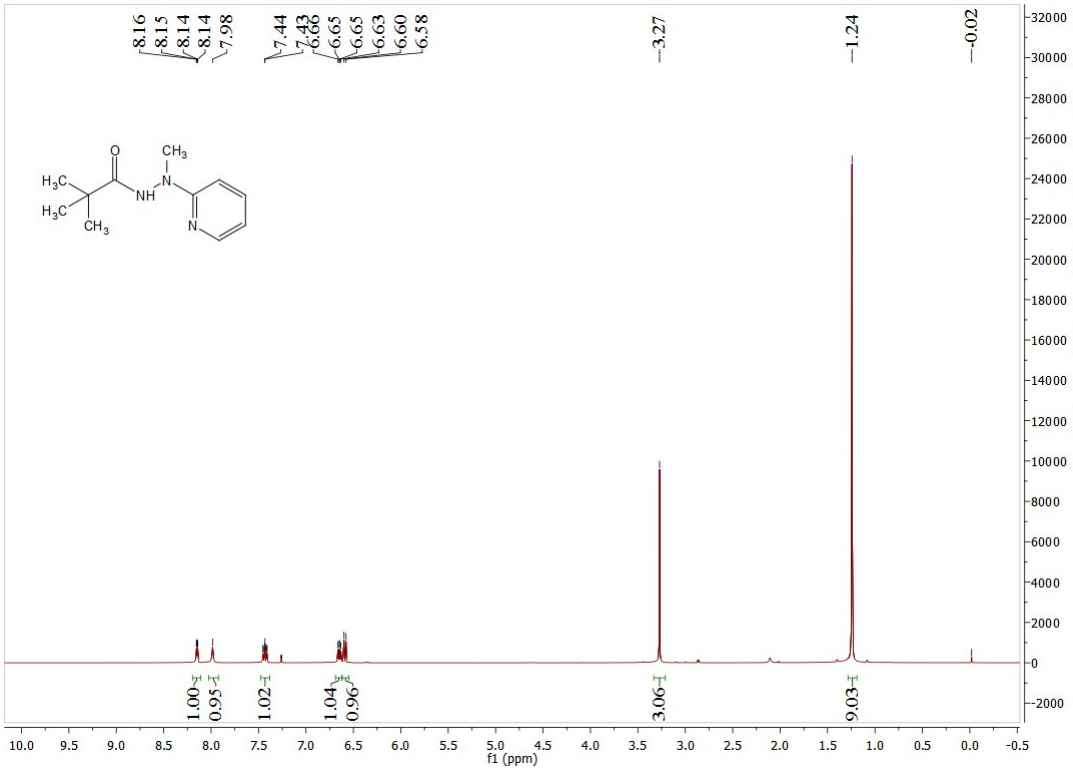
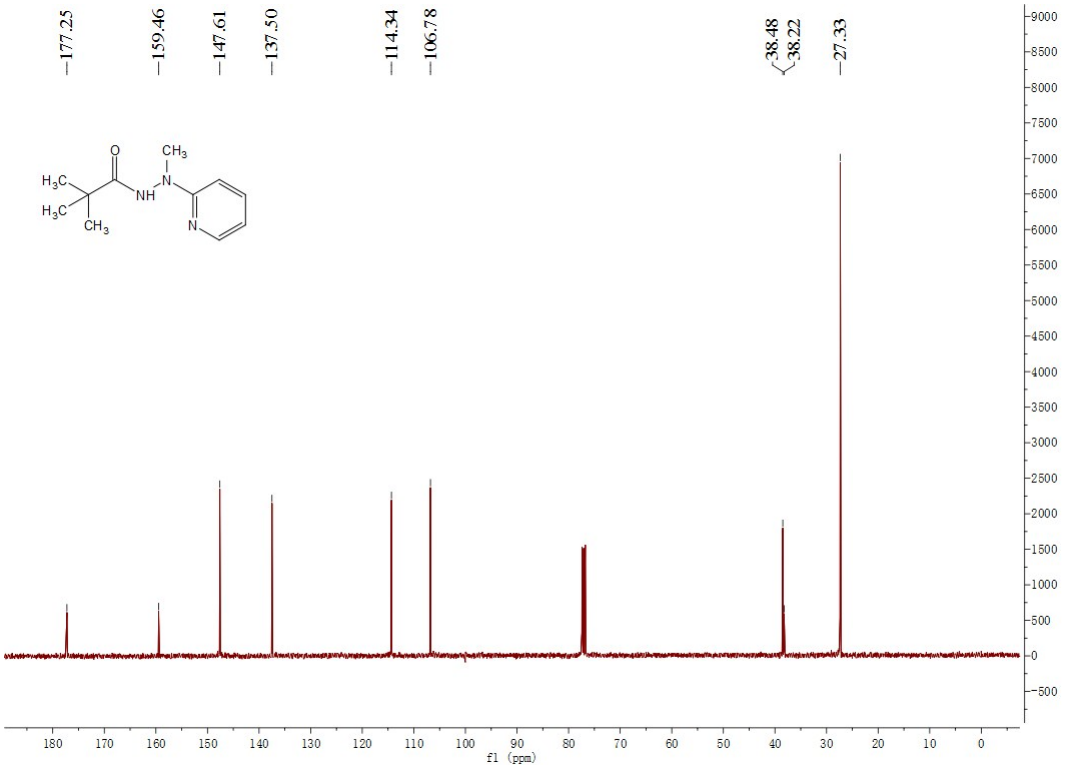
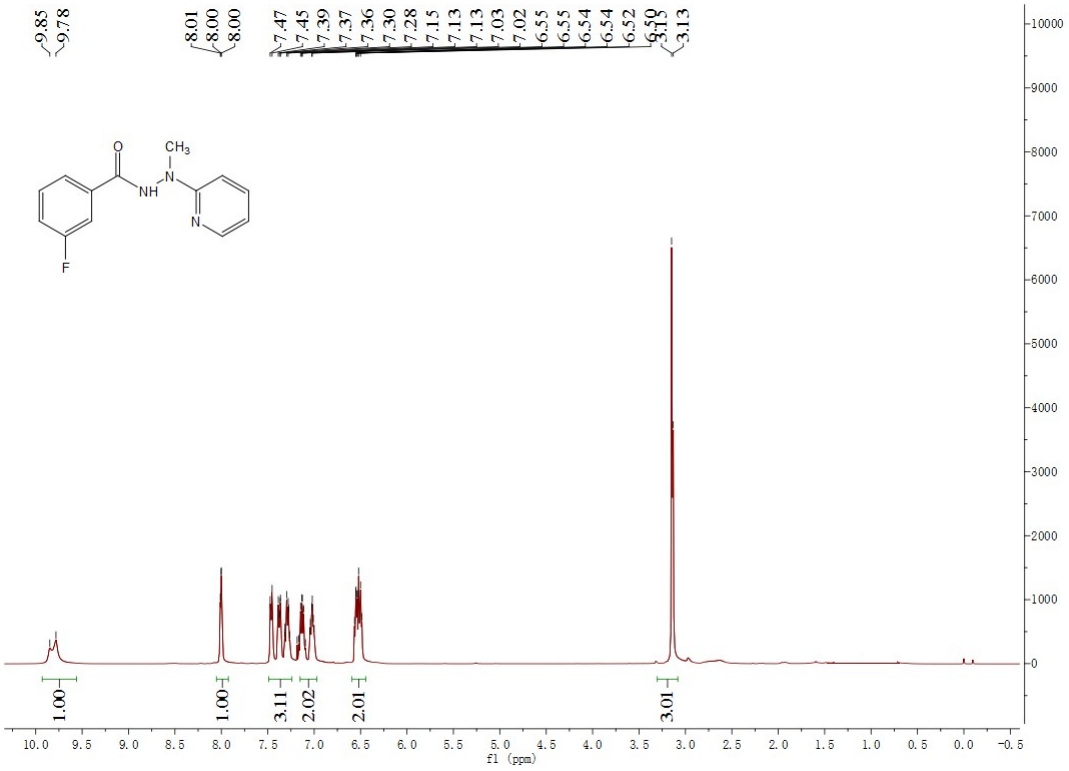
137.74
131.13
128.96
128.12
127.89
127.28
127.20
114.69
107.22
38.86
O
CH3
NH
N
N
f1 (ppm)

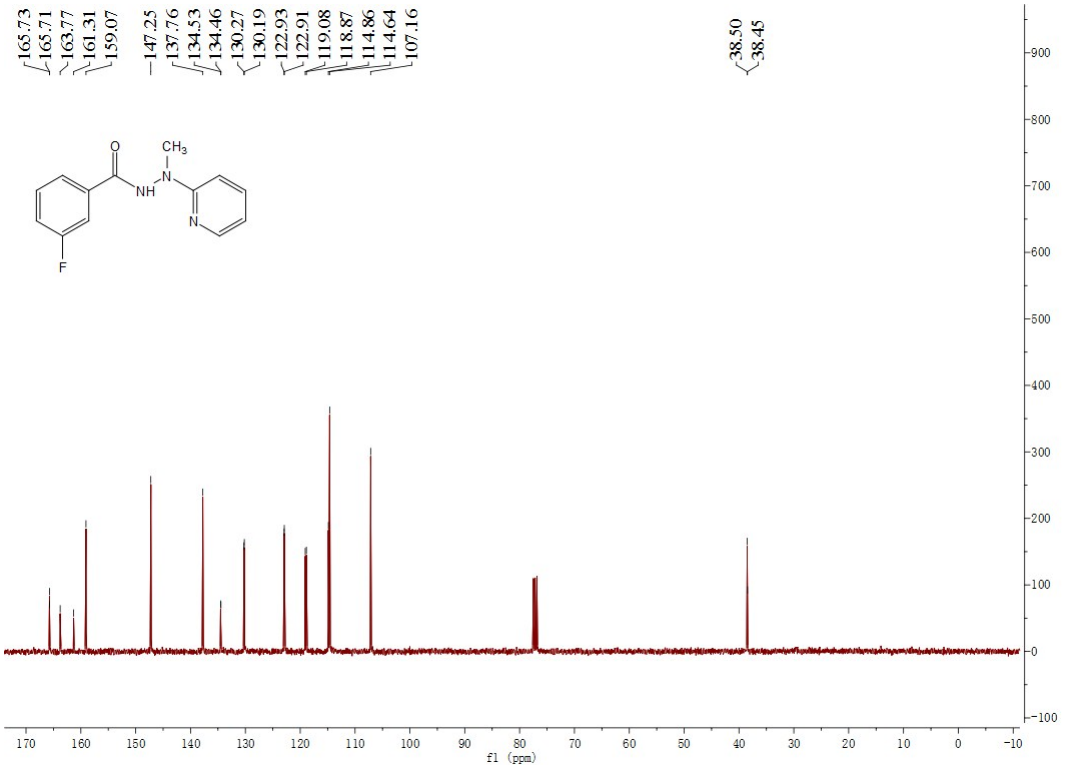
Compound **1k**

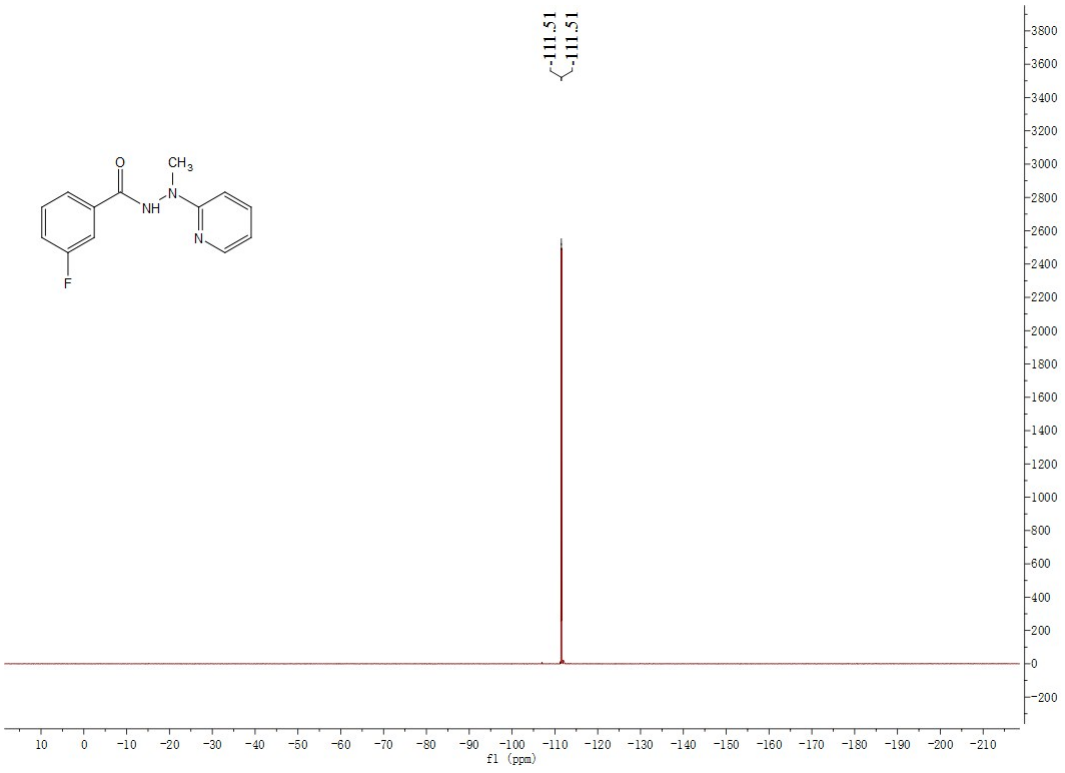

8.16
8.15
8.14
8.14
7.98
7.44
7.43
6.66
6.65
6.65
6.63
6.60
6.58
3.27
1.24
0.02
1.00
0.95
1.02
1.04
0.96
3.06
9.03
f1 (ppm)


177.25
159.46
147.61
137.50
114.34
106.78
38.48
38.22
27.33
f1 (ppm)

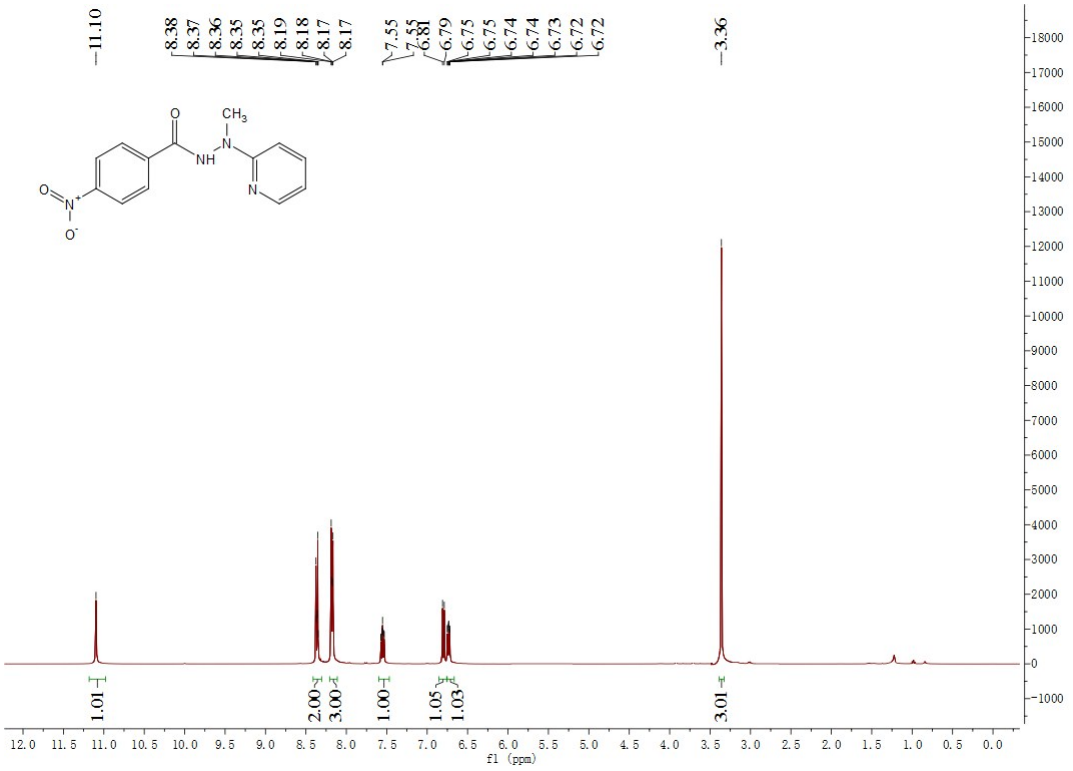
Compound **1l**

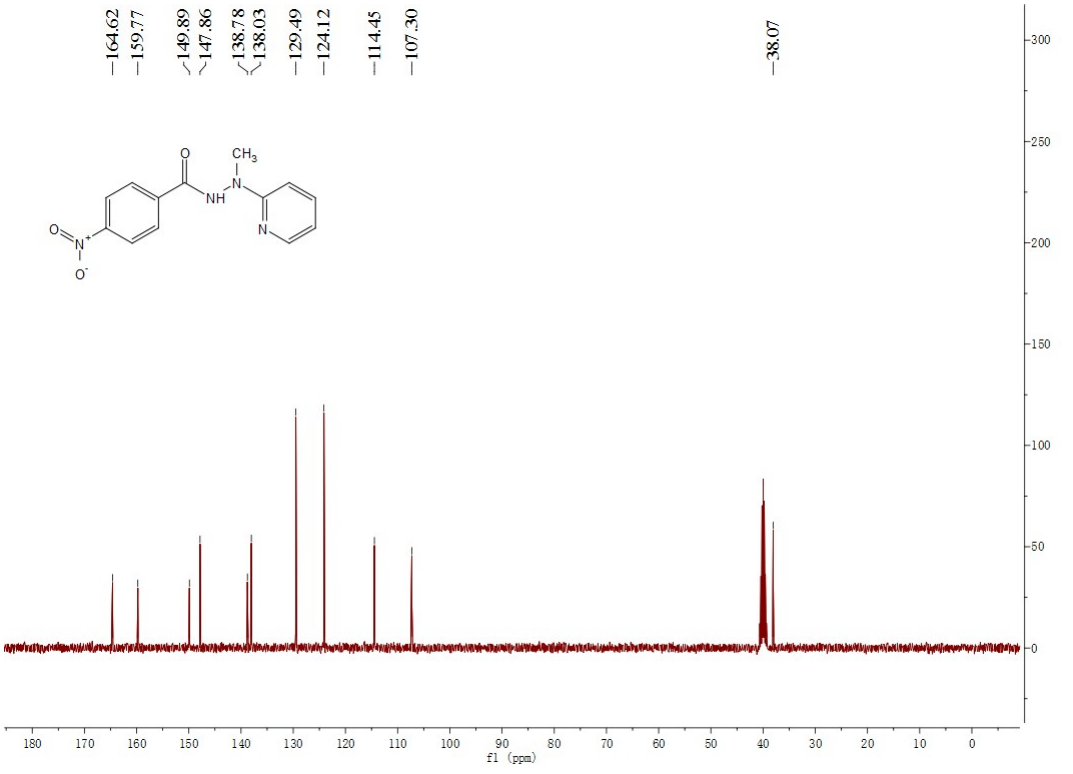

9.85
9.78
8.01
8.00
8.00
7.47
7.45
7.39
7.37
7.36
7.30
7.28
7.15
7.13
7.13
7.03
7.02
6.55
6.55
6.54
6.54
6.52
3.15
3.13
O
CH3
NH
N
N
F
1.00
1.00
3.11
2.02
2.01
3.01
f1 (ppm)


165.73
165.71
163.77
161.31
159.07
147.25
137.76
134.53
134.46
130.27
130.19
122.93
122.91
119.08
118.87
114.86
114.64
107.16
38.50
38.45
O
CH3
NH
N
N
F
f1 (ppm)

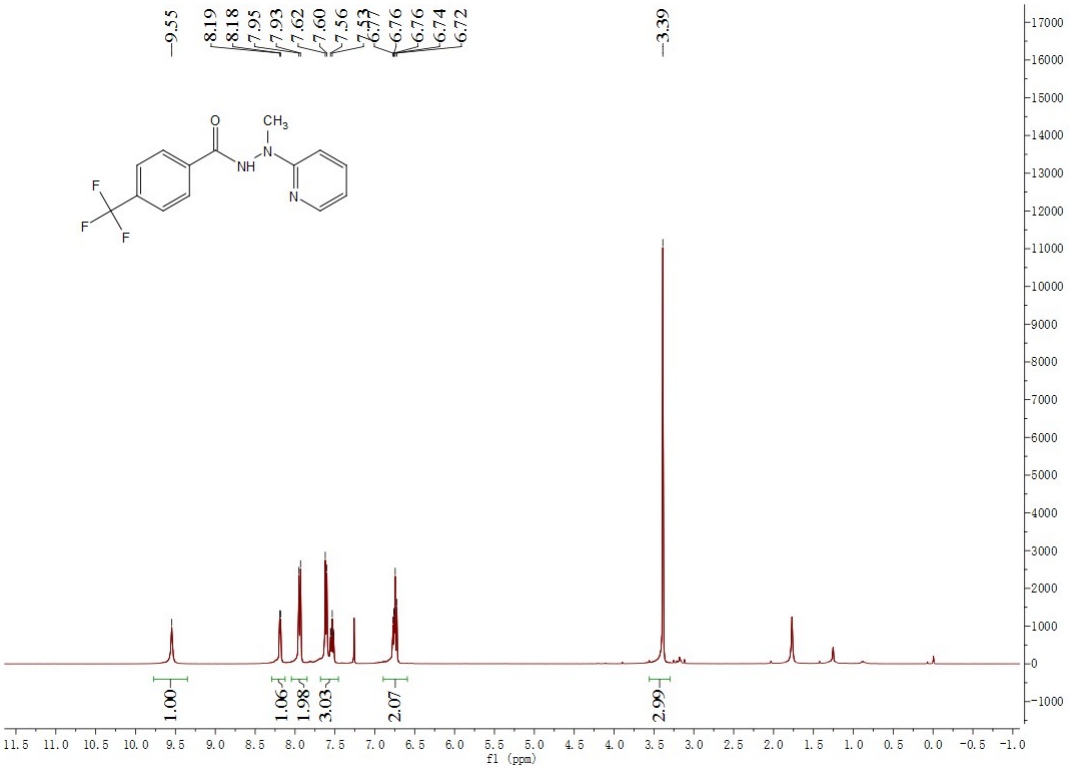

-111.51
-111.51
O
CH3
NH
N
N
F
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

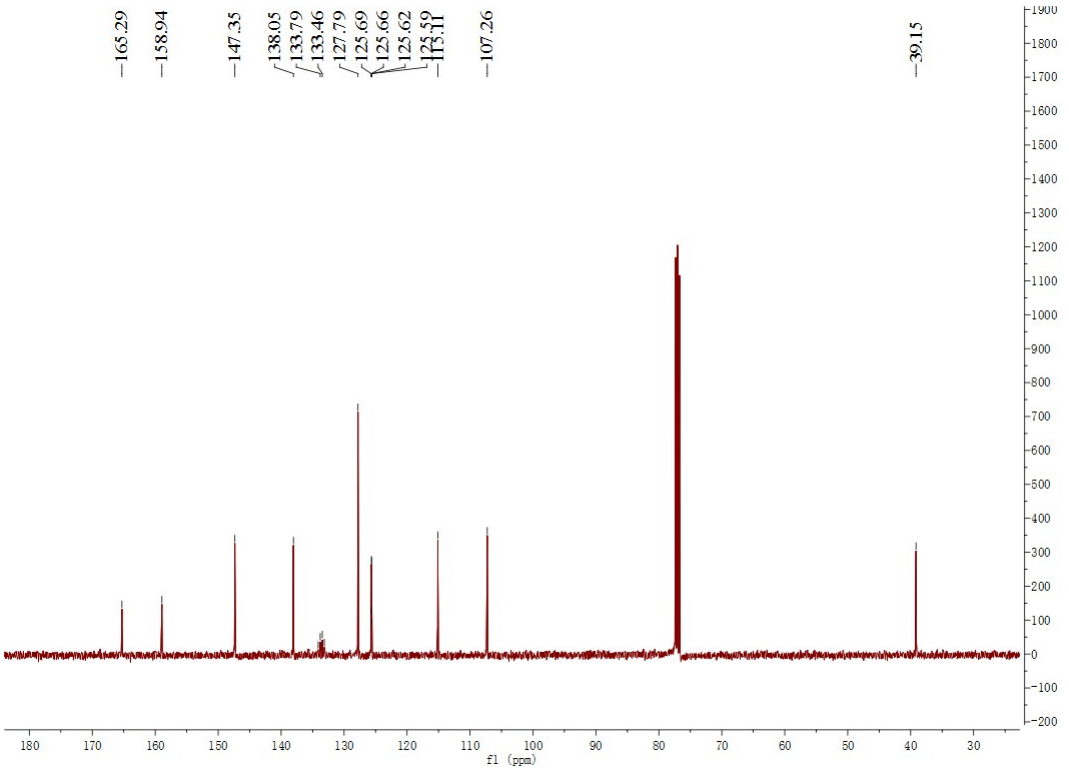
Compound **1m**

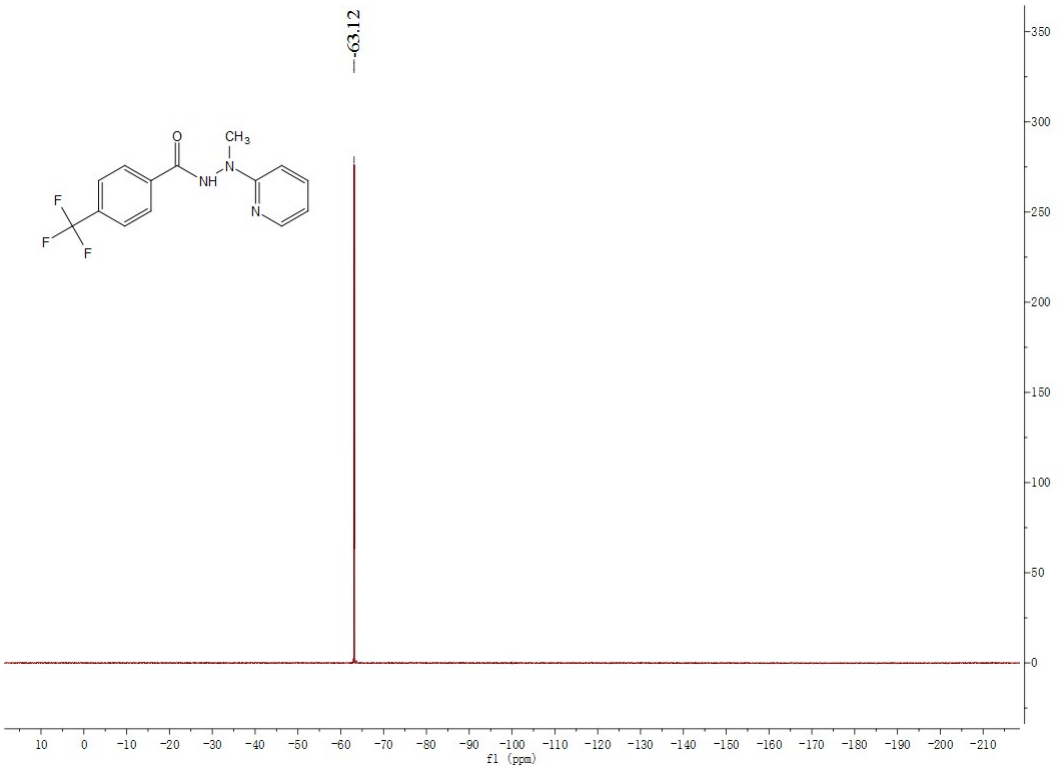

11.10
8.38
8.37
8.36
8.35
8.35
8.19
8.18
8.17
8.17
7.55
7.55
6.81
6.79
6.75
6.75
6.74
6.74
6.73
6.72
6.72
3.36
1.01
2.00
3.00
1.00
1.05
1.03
3.01
f1 (ppm)


164.62
159.77
149.89
147.86
138.78
138.03
129.49
124.12
114.45
107.30
38.07
f1 (ppm)

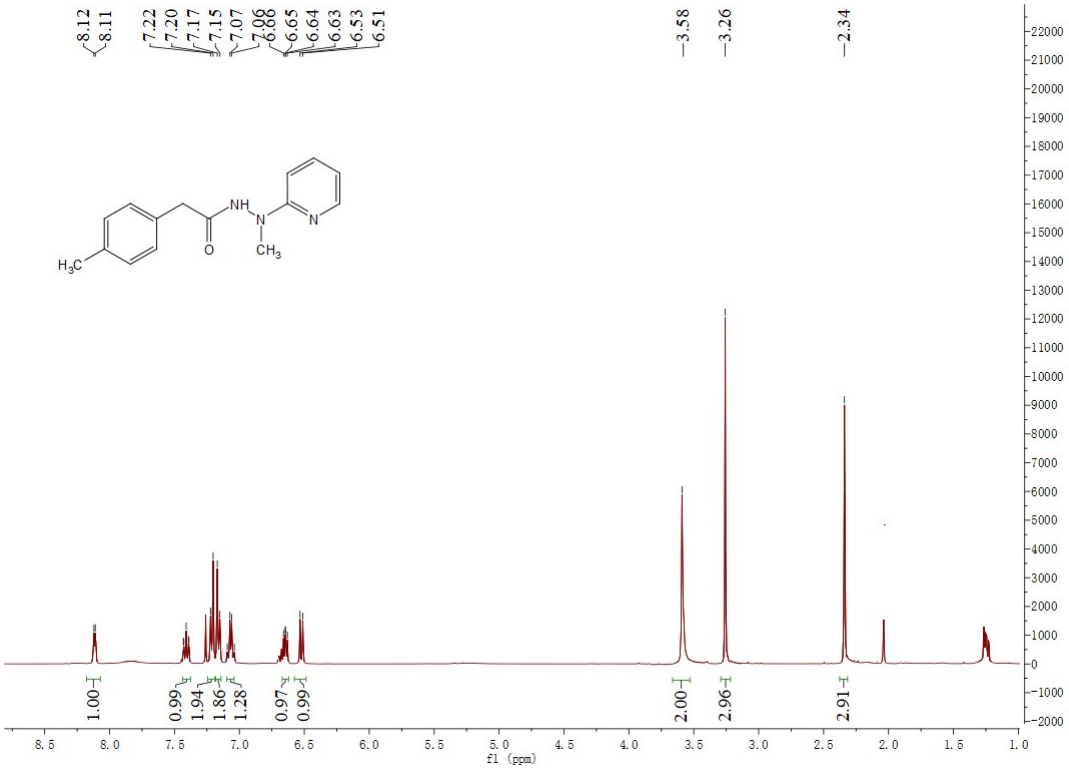
Compound **1n**

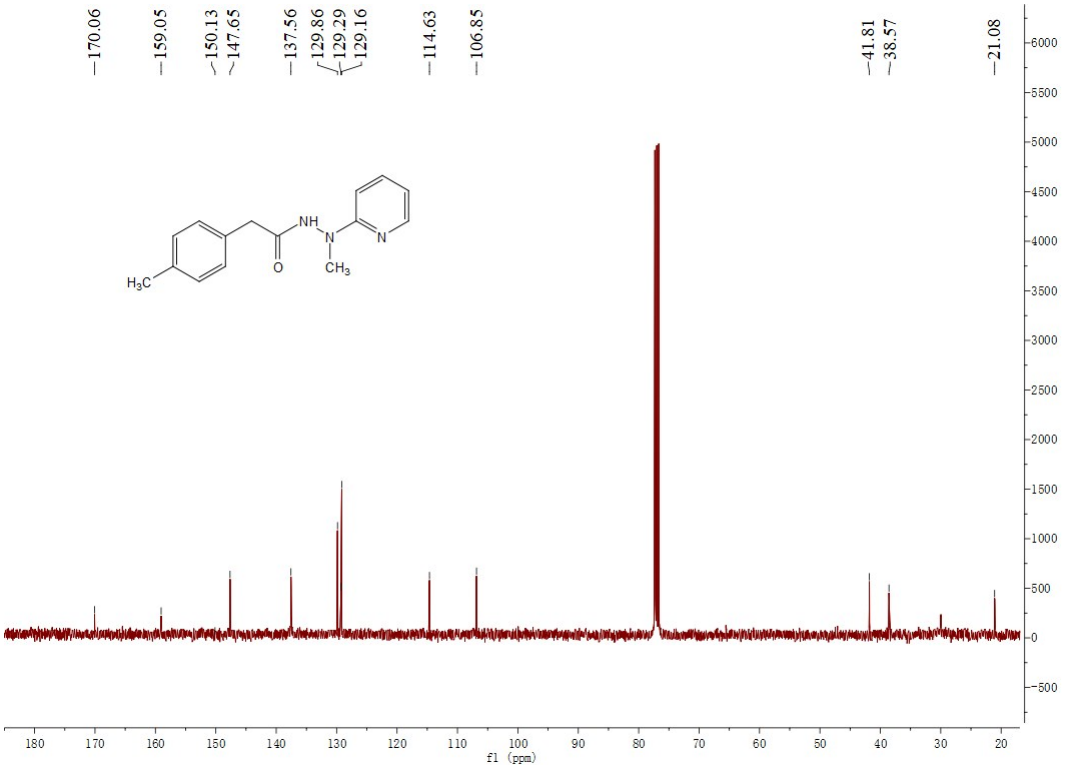

9.55
8.19
8.18
7.95
7.93
7.62
7.60
7.56
7.53
6.77
6.76
6.76
6.74
6.72
3.39
O
CH3
NH
N
N
F
F
F
1.00
1.06
1.98
3.03
2.07
2.99
f1 (ppm)


165.29
158.94
147.35
138.05
133.79
133.46
127.79
125.69
125.66
125.62
123.59
115.11
107.26
39.15
f1 (ppm)

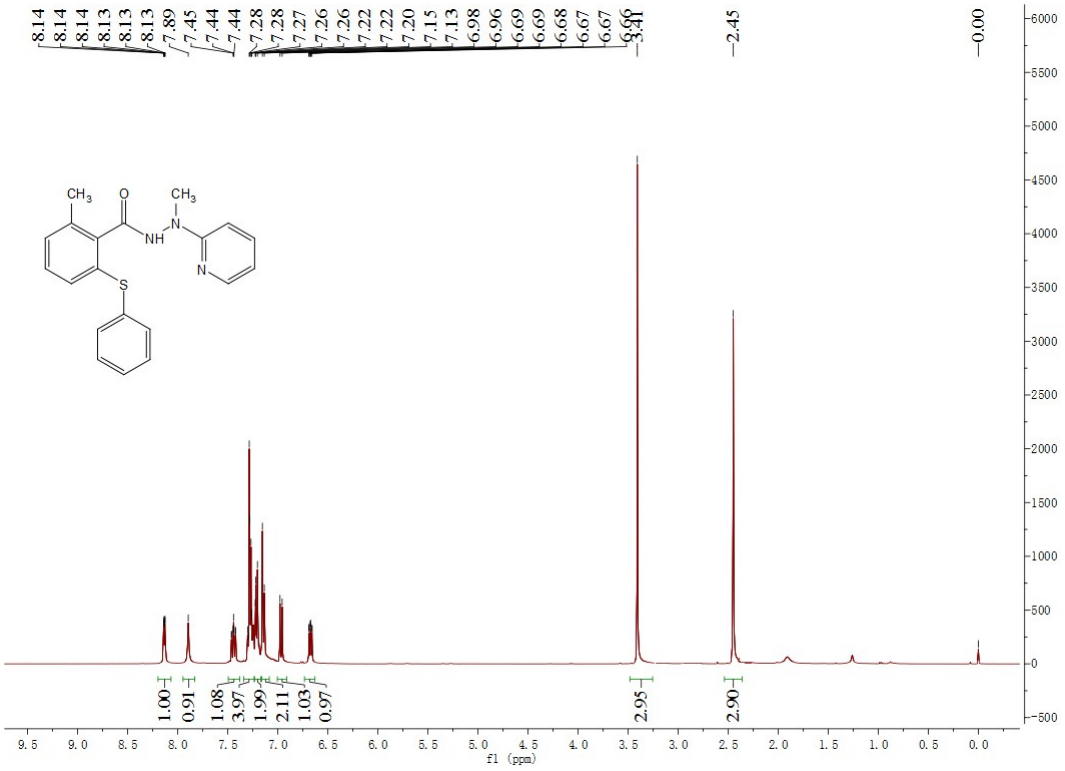

-63.12
O
CH3
NH
N
N
F
F
F
350
300
250
200
150
100
50
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

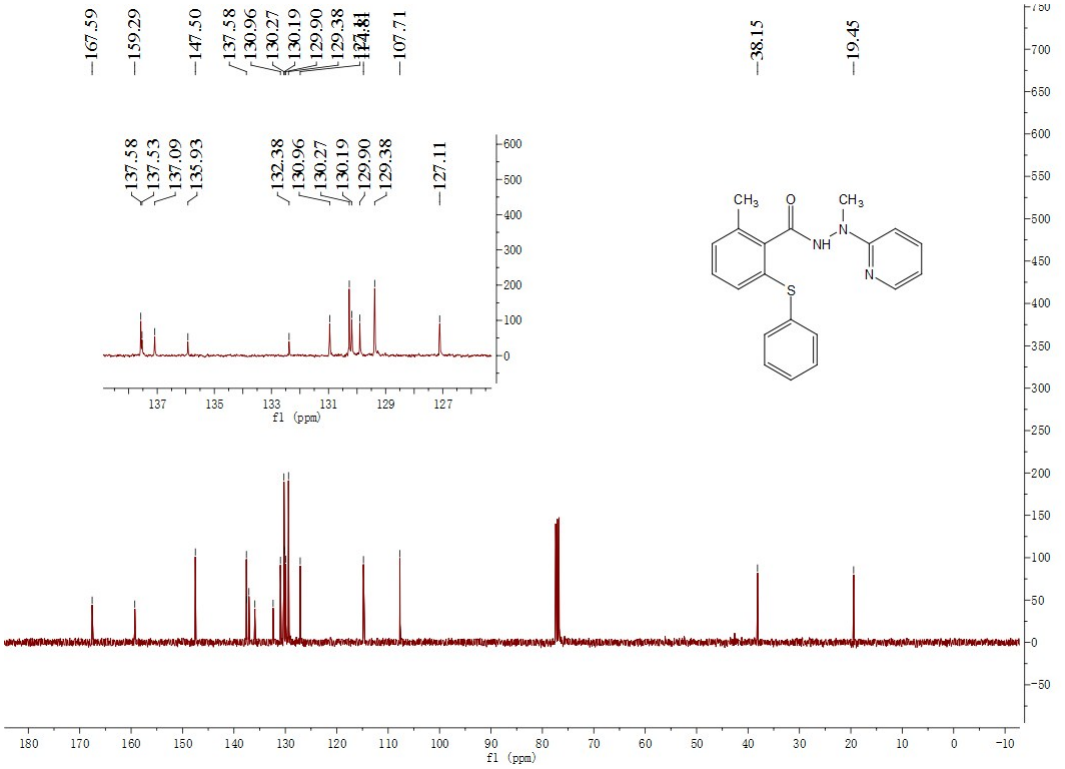
Compound **1p**


8.12
8.11
7.22
7.20
7.17
7.15
7.07
7.06
6.66
6.65
6.64
6.63
6.53
6.51
3.58
3.26
2.34
NH
N
N
O
CH3
H3C
1.00
0.99
1.94
1.86
1.28
0.97
0.99
2.00
2.96
2.91
f1 (ppm)

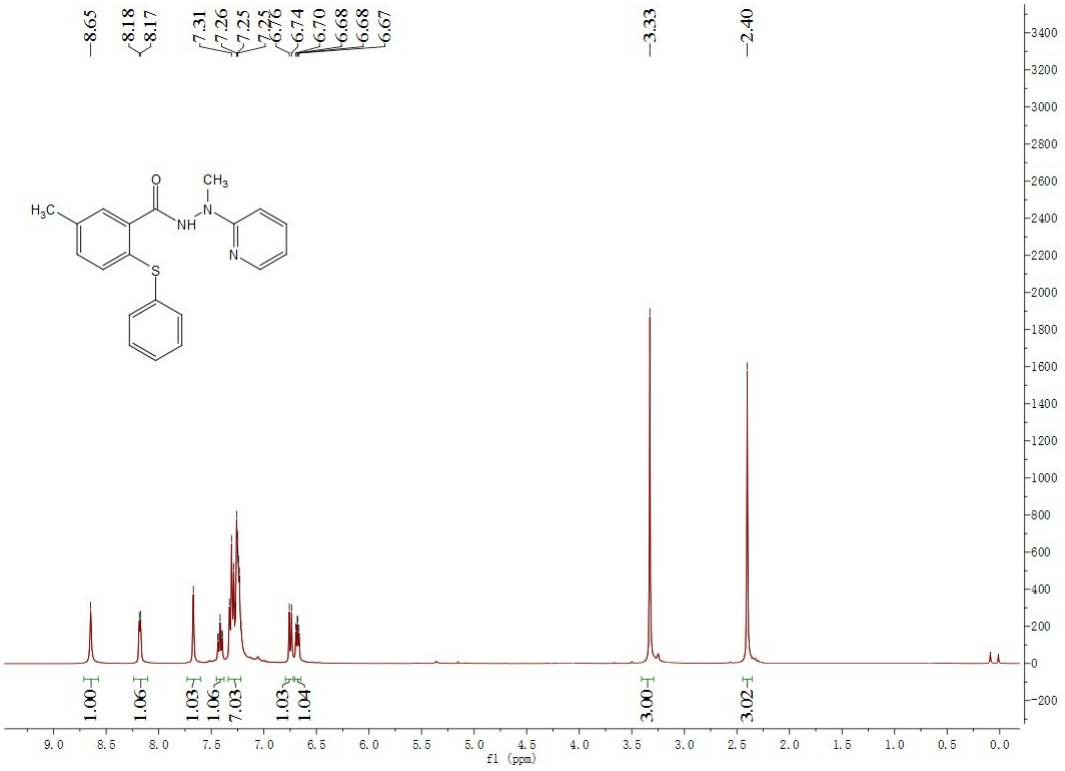

170.06
159.05
150.13
147.65
137.56
129.86
129.29
129.16
114.63
106.85
41.81
38.57
21.08
NH
N
N
O
CH3
H3C
f1 (ppm)

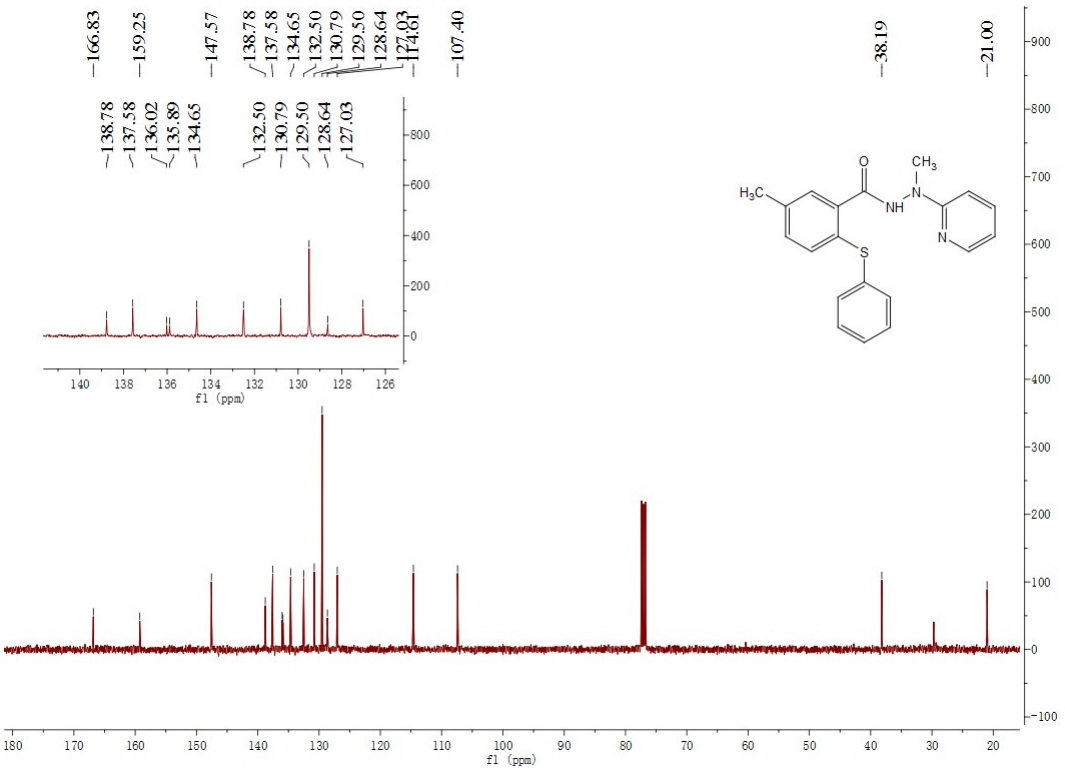
Compound **3a**


8.14
8.14
8.14
8.13
8.13
8.13
7.89
7.45
7.44
7.44
7.28
7.28
7.27
7.26
7.26
7.22
7.22
7.20
7.15
7.13
6.98
6.96
6.69
6.69
6.68
6.67
6.67
6.66
3.41
2.45
0.00
CH3
O
CH3
NH
N
N
S
1.00
0.91
1.08
3.97
1.99
2.11
1.03
0.97
2.95
2.90
f1 (ppm)

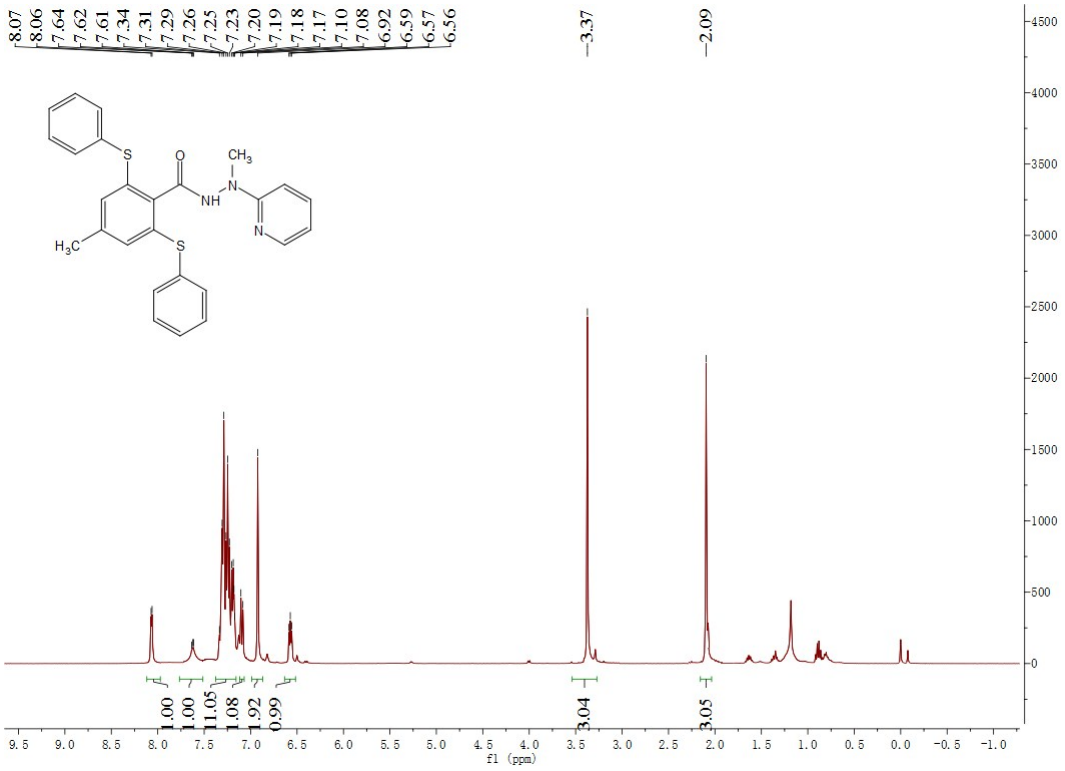

167.59
159.29
147.50
137.58
130.96
130.27
130.19
129.90
129.38
124.81
124.81
107.71
38.15
19.45
137.58
137.53
137.09
135.93
132.38
130.96
130.27
130.19
129.90
129.38
127.11
CH3
O
CH3
NH
N
N
S
f1 (ppm)
f1 (ppm)

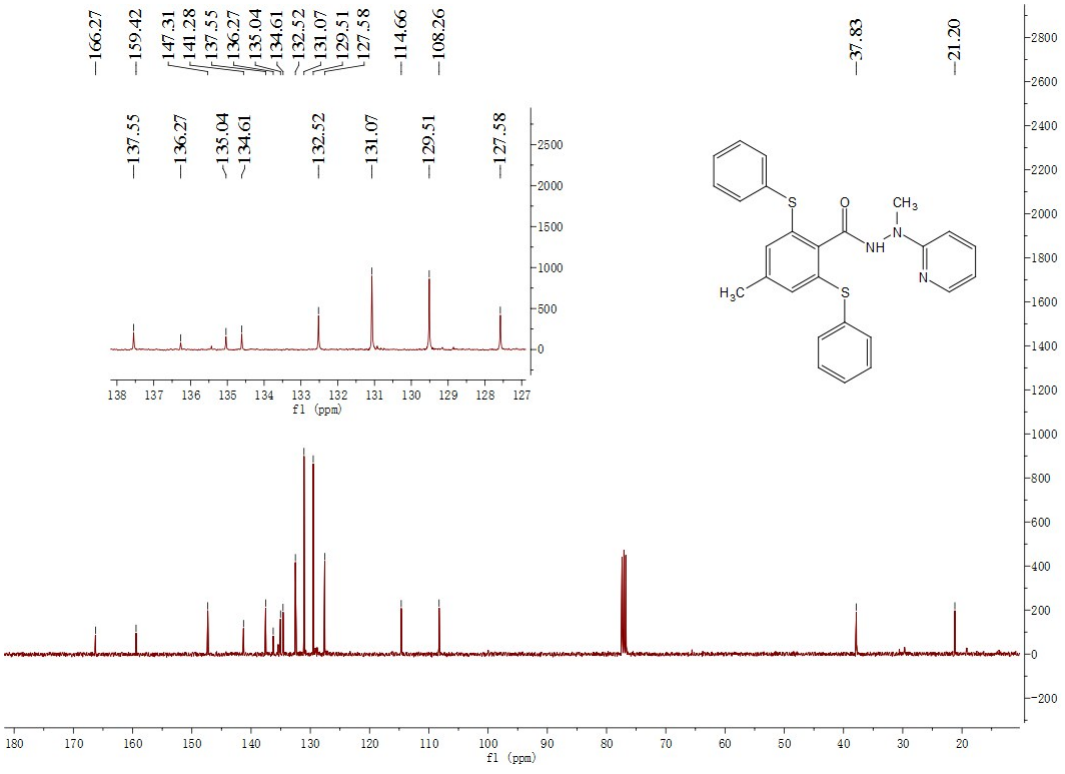
Compound **3b**


8.65
8.18
8.17
7.31
7.26
7.25
7.25
6.76
6.74
6.70
6.68
6.68
6.67
3.33
2.40
1.00
1.06
1.03
1.06
7.03
1.03
1.04
3.00
3.02
f1 (ppm)

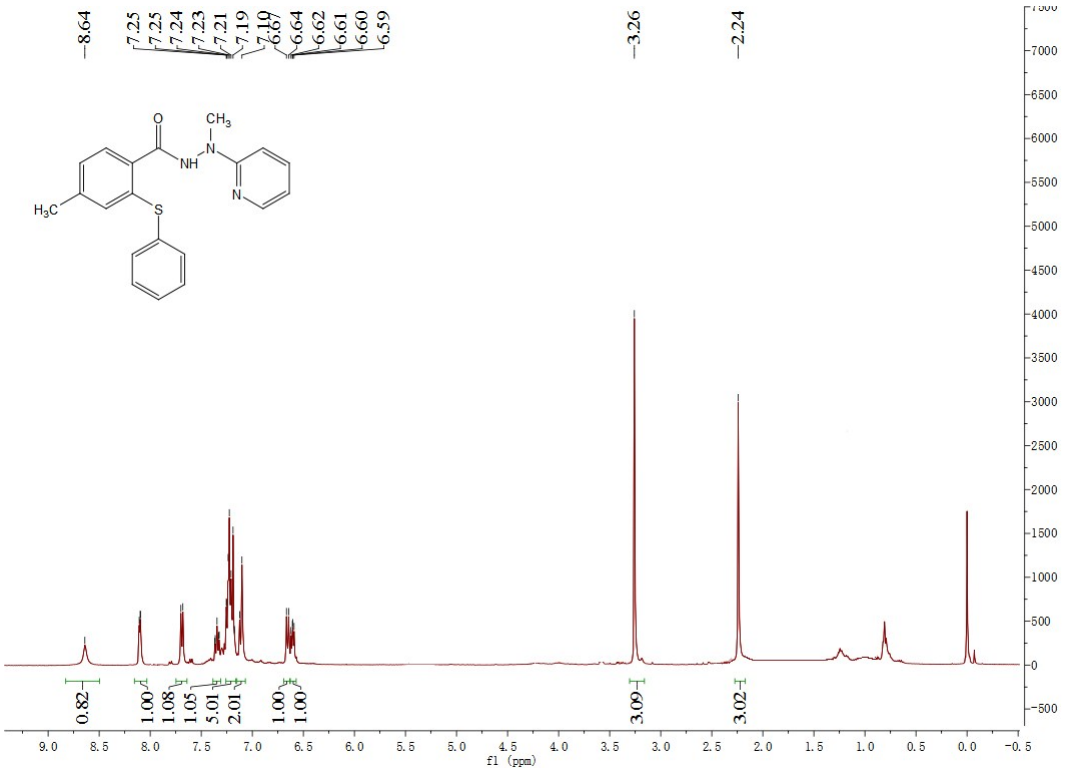

166.83
159.25
147.57
138.78
137.58
134.65
132.50
130.79
129.50
128.64
127.03
114.61
107.40
38.19
21.00
f1 (ppm)

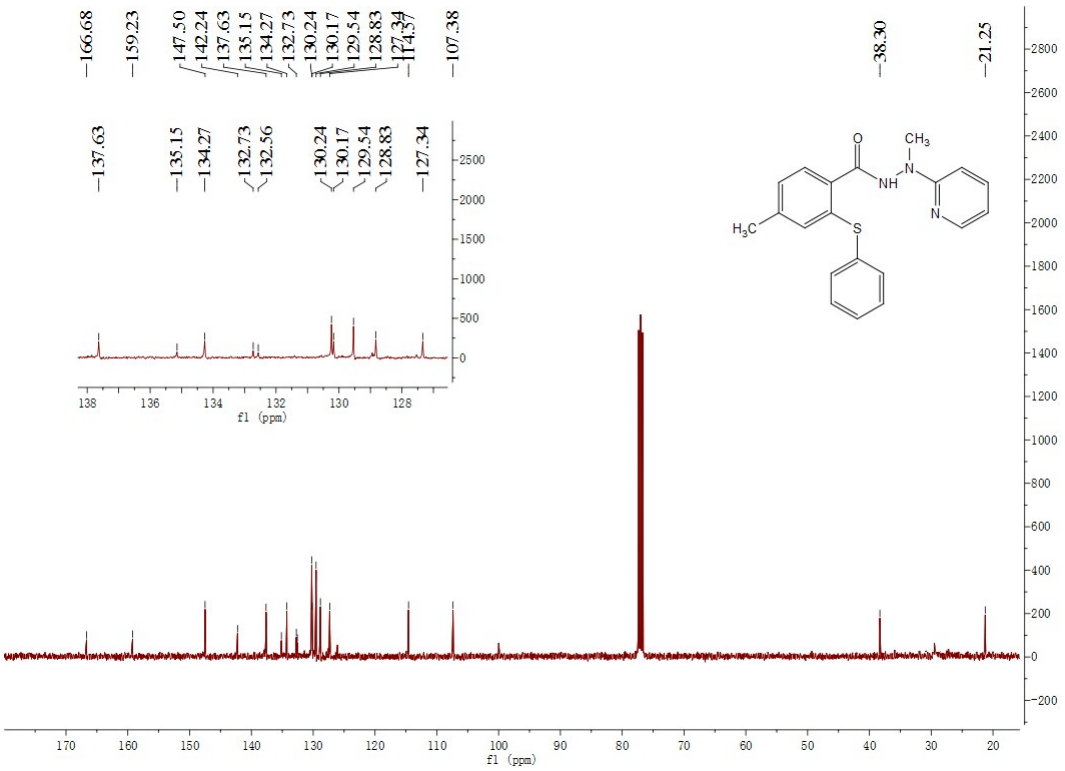
Compound **3c'**


8.07
8.06
7.64
7.62
7.61
7.34
7.31
7.29
7.26
7.25
7.23
7.20
7.19
7.18
7.17
7.10
7.08
6.92
6.59
6.57
6.56
3.37
2.09
1.00
1.00
11.05
1.08
1.92
0.99
3.04
3.05
f1 (ppm)

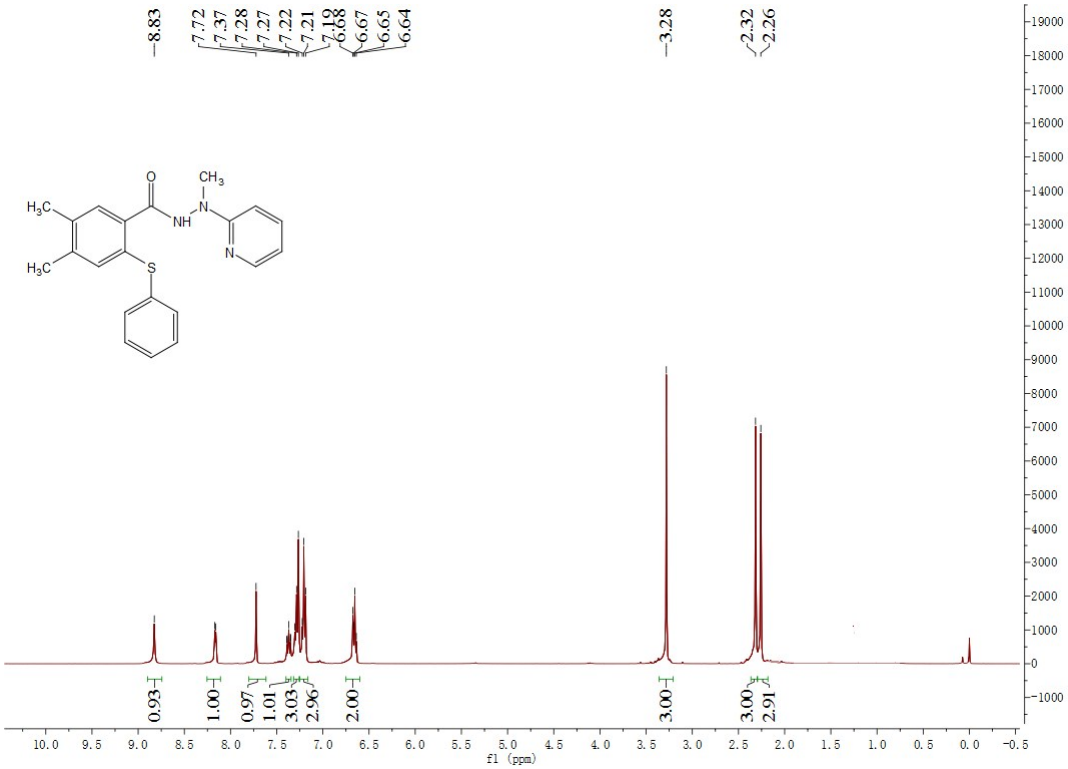

166.27
159.42
147.31
141.28
137.55
136.27
135.04
134.61
132.52
131.07
129.51
127.58
114.66
108.26
37.83
21.20
f1 (ppm)

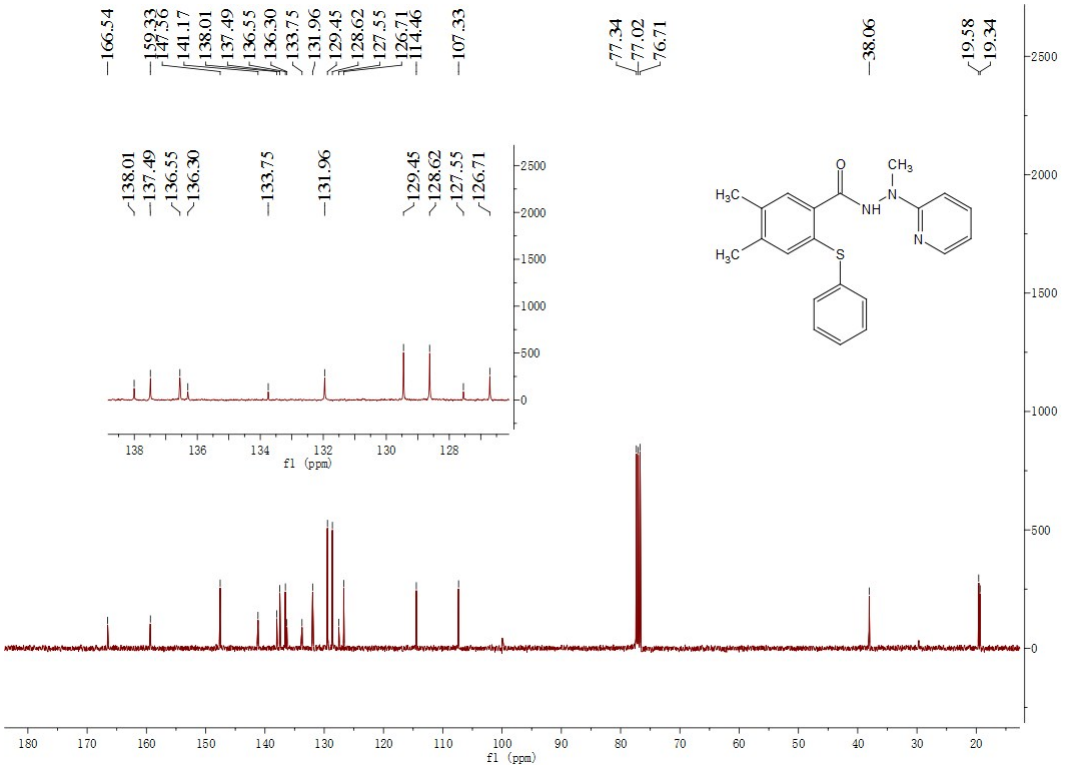
Compound **3c**


8.64
7.25
7.25
7.24
7.23
7.21
7.19
7.10
6.67
6.64
6.62
6.61
6.60
6.59
3.26
2.24
0.82
1.00
1.08
1.05
5.01
2.01
1.00
1.00
3.09
3.02
f1 (ppm)

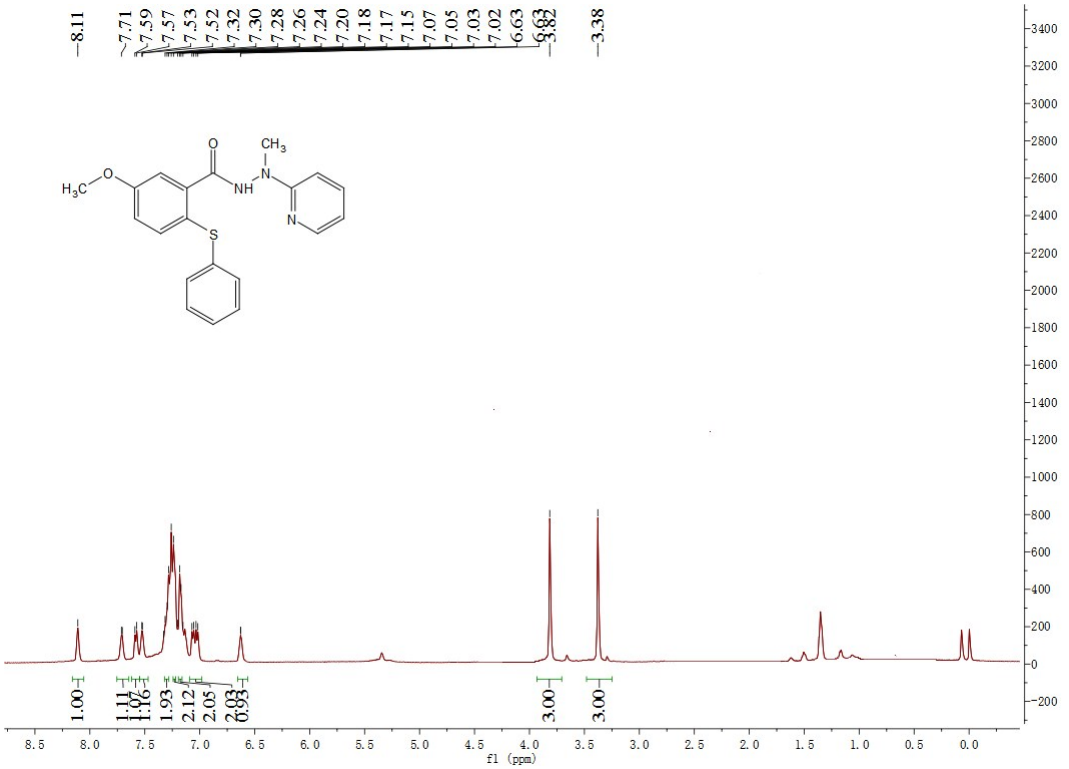

166.68
159.23
147.50
142.24
137.63
135.15
134.27
132.73
130.24
130.17
129.54
128.83
127.34
114.57
107.38
38.30
21.25
137.63
135.15
134.27
132.73
132.56
130.24
130.17
129.54
128.83
127.34
f1 (ppm)

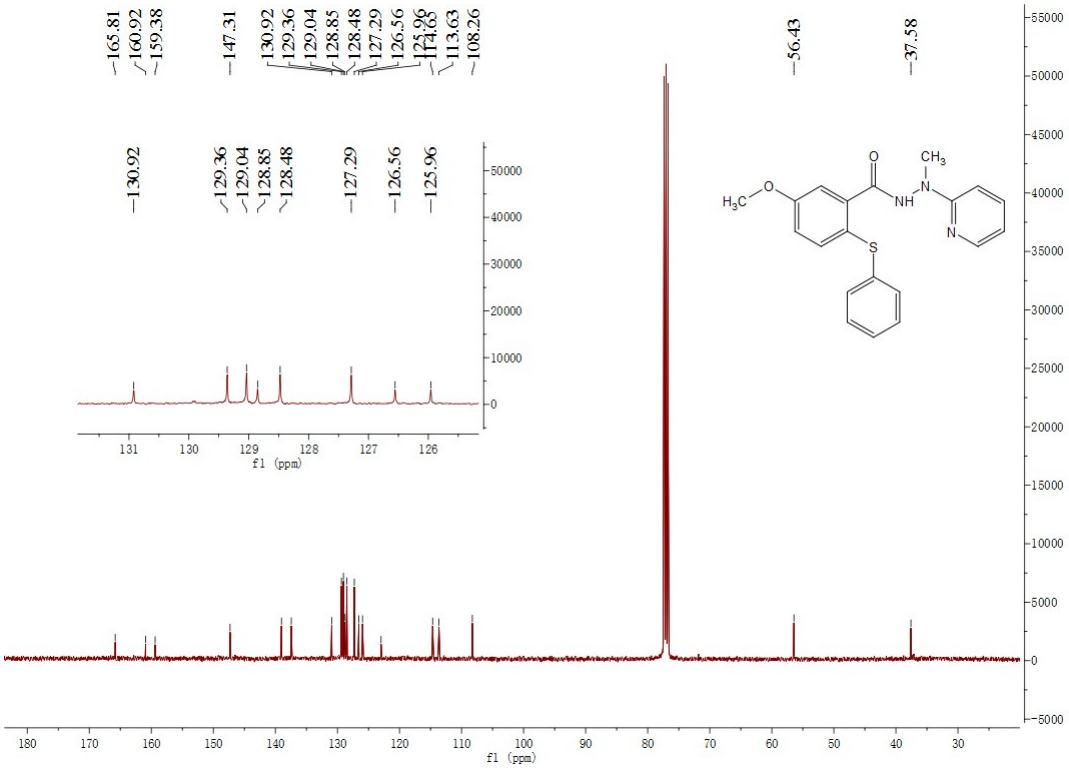
Compound **3d**


8.83
7.72
7.37
7.28
7.27
7.22
7.21
7.18
6.68
6.67
6.65
6.64
3.28
2.32
2.26
0.93
1.00
0.97
1.01
3.03
2.96
2.00
3.00
3.00
2.91
f1 (ppm)

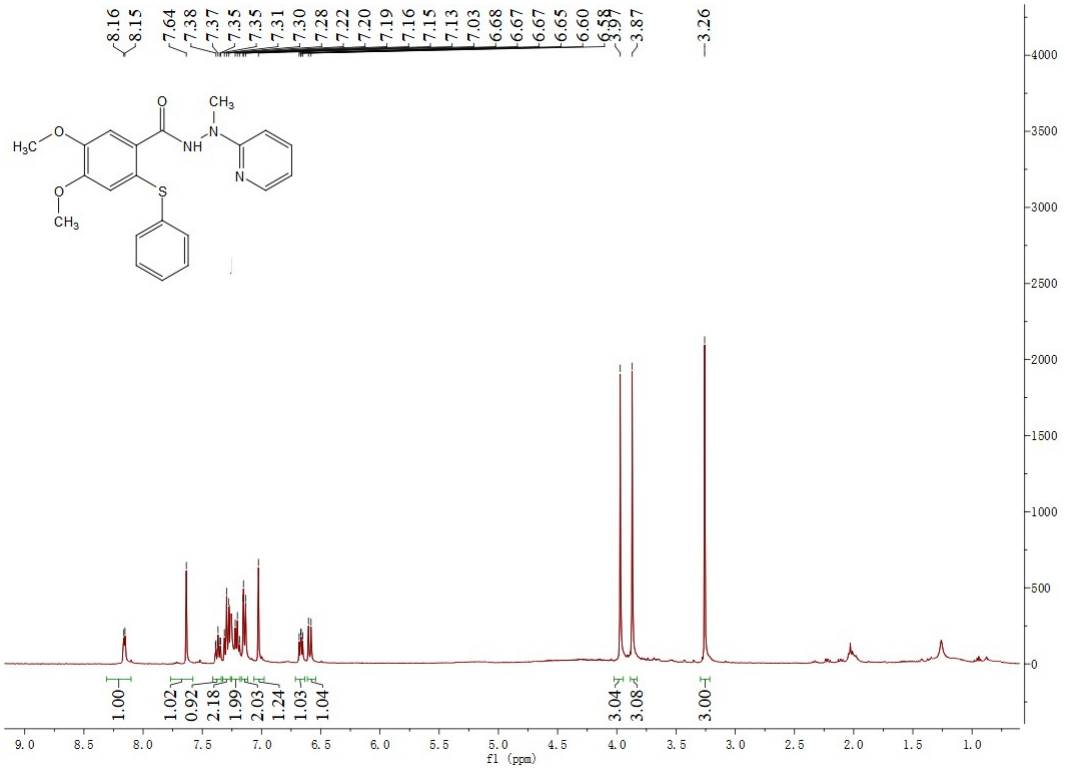

166.54
159.33
147.36
141.17
138.01
137.49
136.55
136.30
133.75
131.96
129.45
128.62
127.55
126.71
114.46
107.33
77.34
77.02
76.71
38.06
19.58
19.34
f1 (ppm)

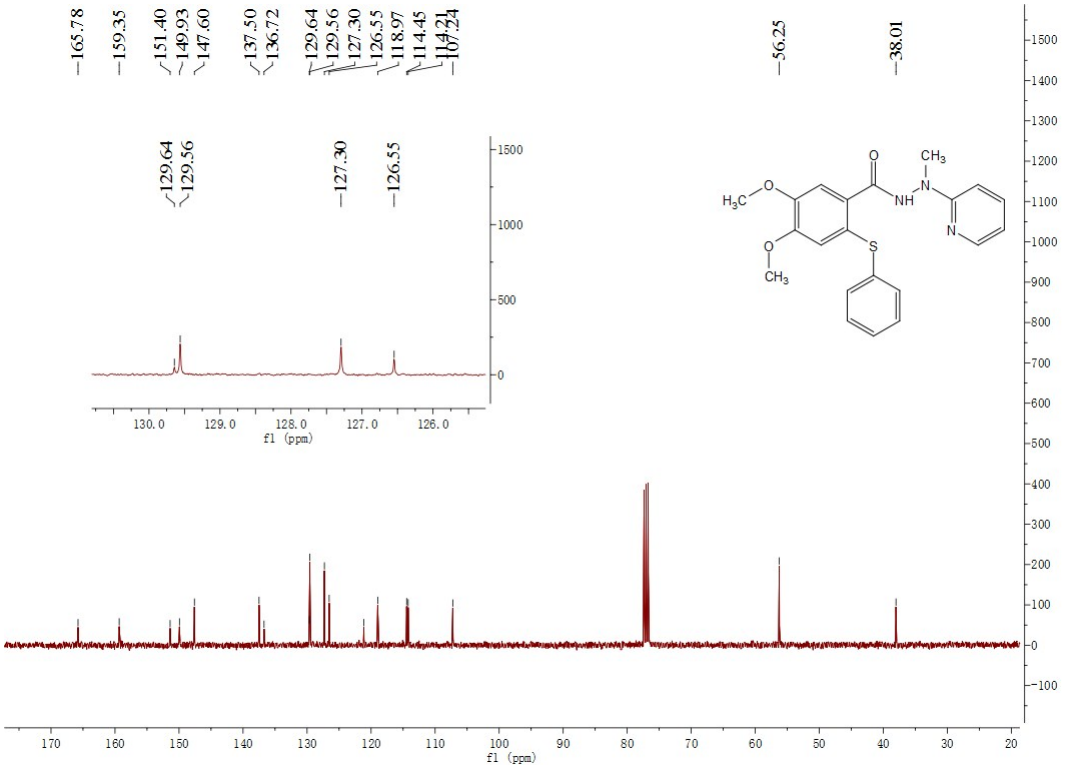
Compound **3e**


8.11
7.71
7.59
7.57
7.53
7.52
7.32
7.30
7.28
7.26
7.24
7.20
7.18
7.17
7.15
7.07
7.05
7.03
7.02
6.63
3.82
3.38
1.00
1.11
1.07
1.16
1.93
2.12
2.05
2.03
0.93
3.00
3.00
f1 (ppm)

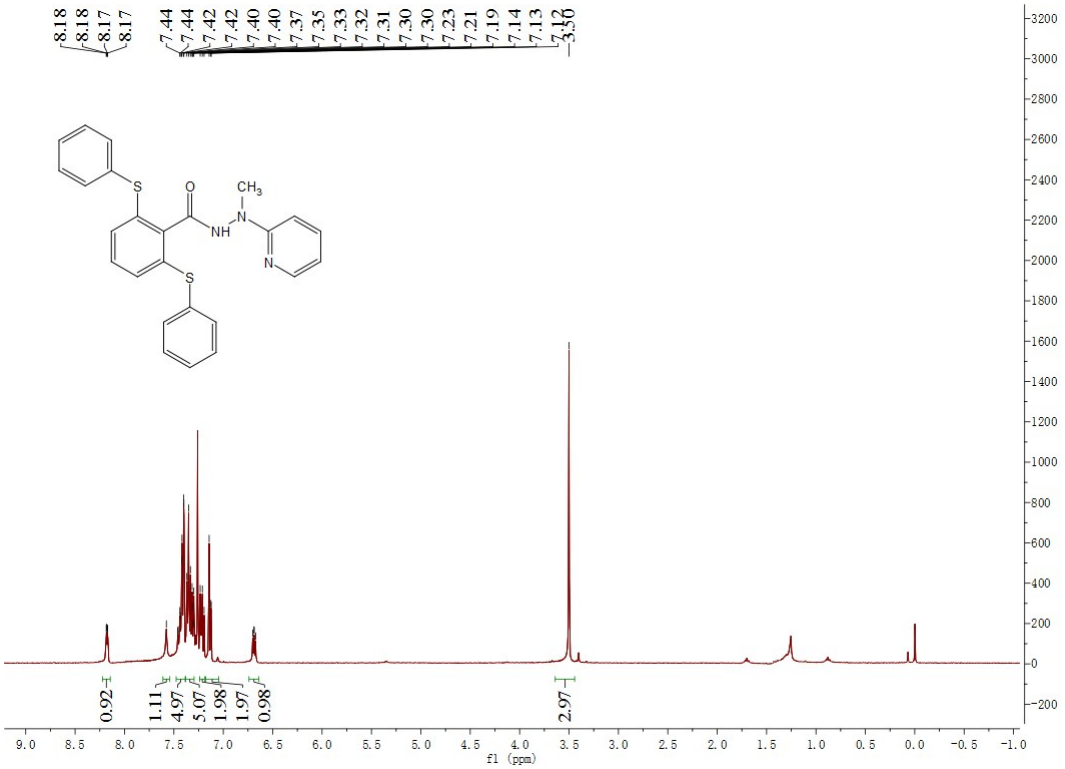

165.81
160.92
159.38
147.31
130.92
129.36
129.04
128.85
128.48
127.29
126.56
125.96
114.65
113.63
108.26
56.43
37.58
f1 (ppm)

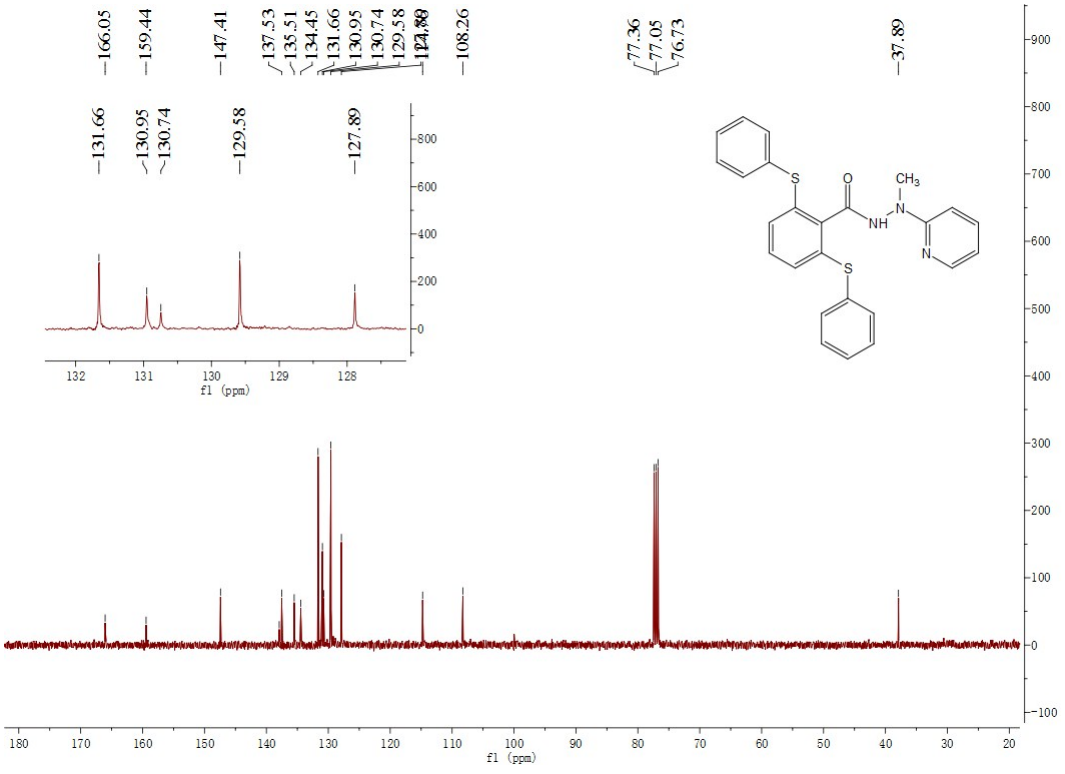
Compound **3f**


8.16
8.15
7.64
7.38
7.37
7.35
7.35
7.31
7.30
7.28
7.22
7.20
7.19
7.16
7.15
7.13
7.03
6.68
6.67
6.67
6.65
6.60
6.58
3.97
3.87
3.26
1.00
1.02
0.92
2.18
1.99
2.03
1.24
1.03
1.04
3.04
3.08
3.00
f1 (ppm)

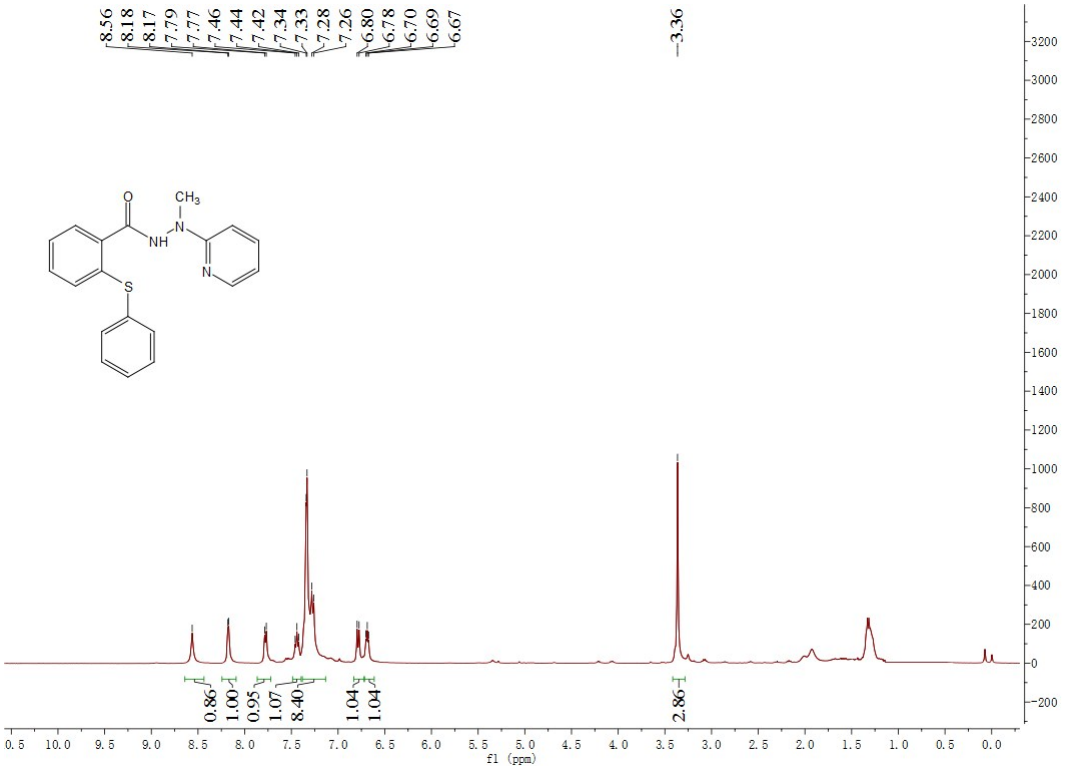

165.78
159.35
151.40
149.93
147.60
137.50
136.72
129.64
129.56
127.30
126.55
118.97
114.45
114.21
107.24
56.25
38.01
129.64
129.56
127.30
126.55
f1 (ppm)

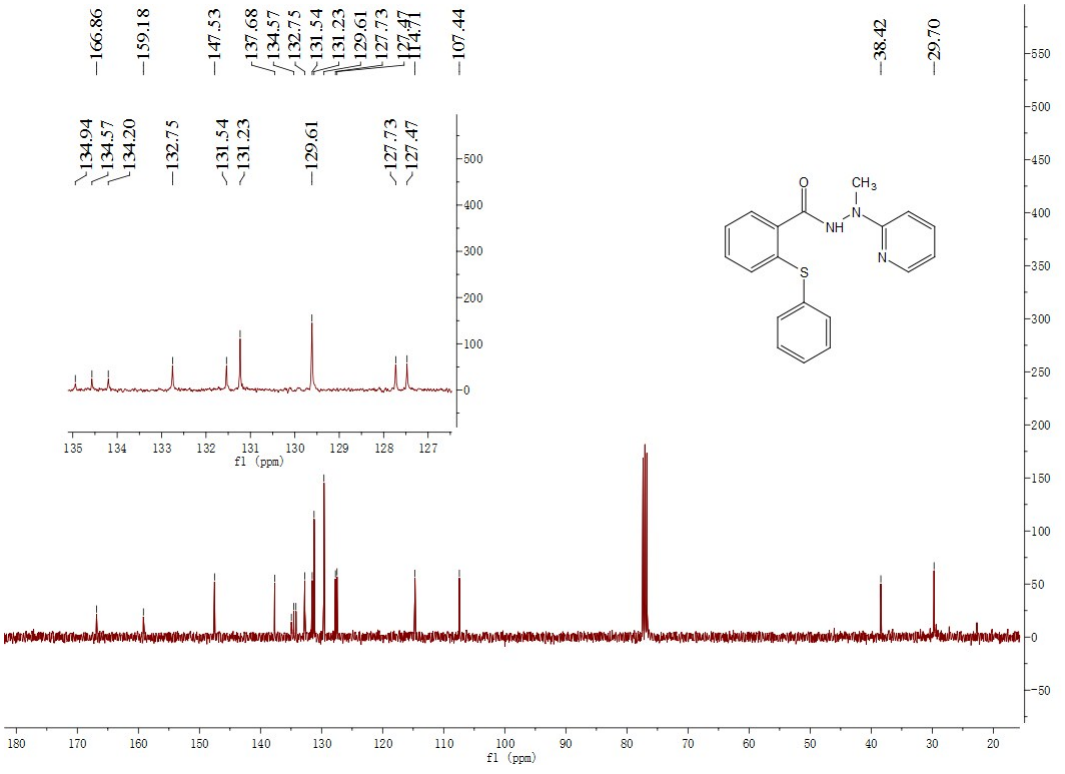
Compound **3g'**


8.18
8.18
8.17
8.17
7.44
7.44
7.42
7.42
7.40
7.40
7.37
7.35
7.33
7.32
7.31
7.30
7.30
7.23
7.21
7.19
7.14
7.13
7.12
3.56
0.92
1.11
4.97
5.07
1.98
1.97
0.98
2.97
f1 (ppm)

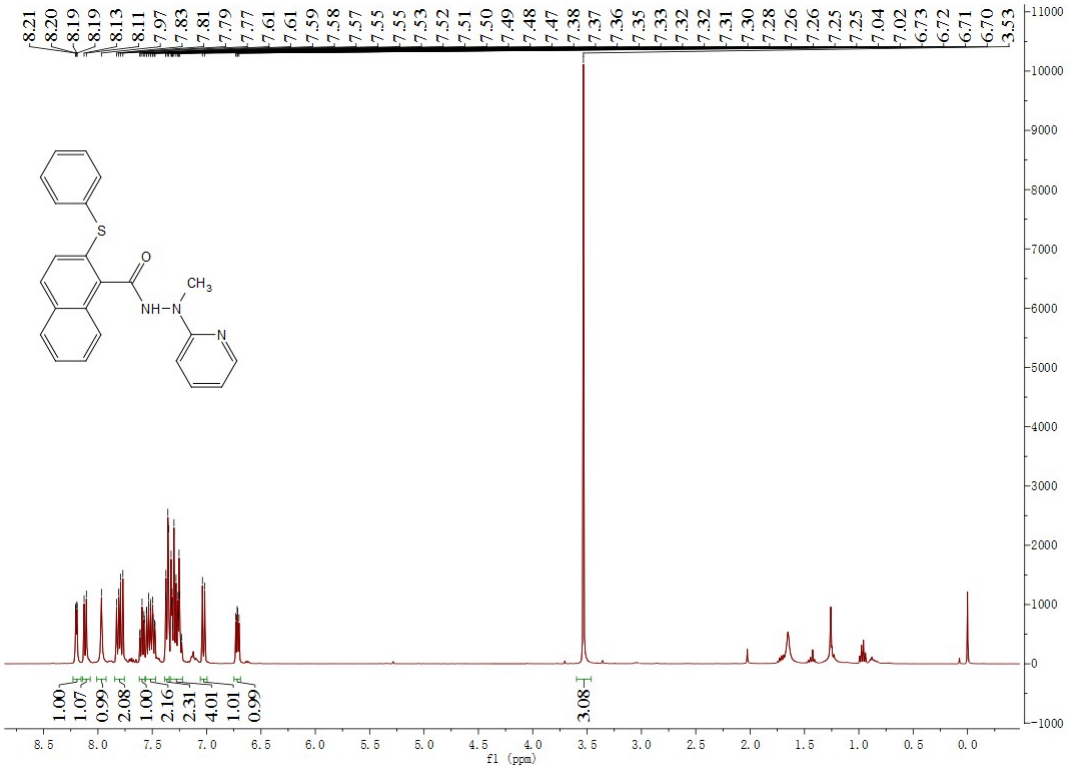

166.05
159.44
147.41
137.53
135.51
134.45
131.66
130.95
130.74
129.58
108.26
77.36
77.05
76.73
37.89
131.66
130.95
130.74
129.58
127.89
f1 (ppm)

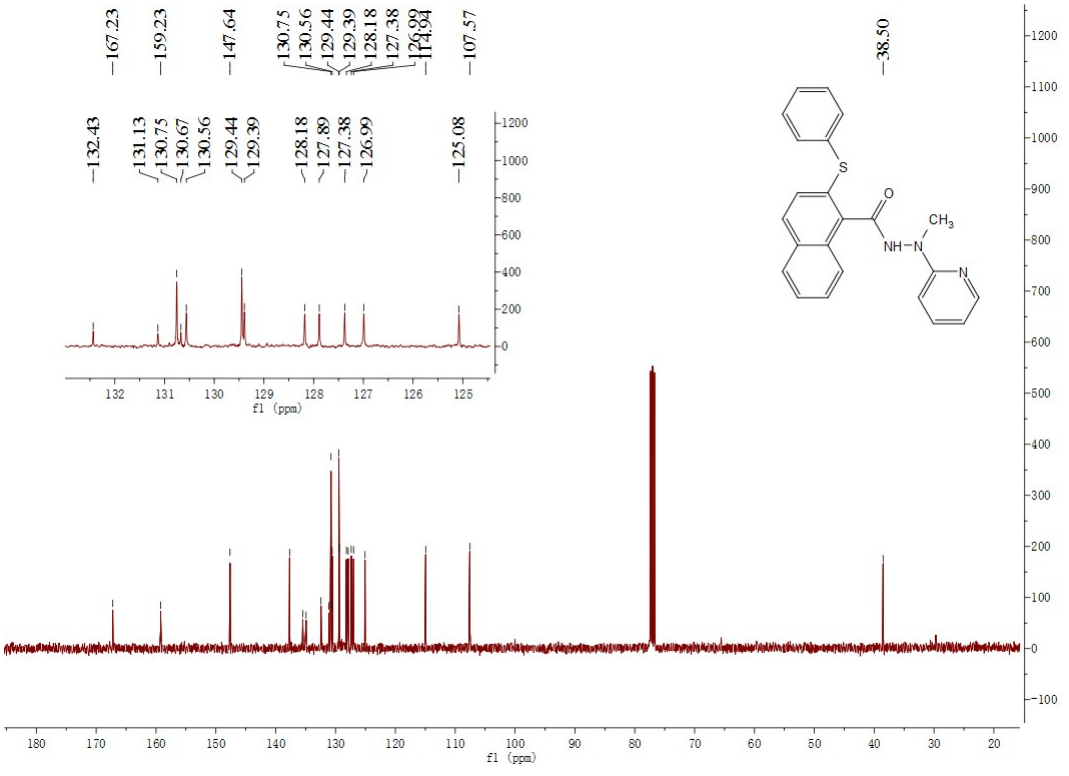
Compound **3g**


8.56
8.18
8.17
7.79
7.77
7.46
7.44
7.42
7.34
7.33
7.28
7.26
6.80
6.78
6.70
6.69
6.67
3.36
O
CH3
N
NH
N
S
0.86
1.00
0.95
1.07
8.40
1.04
1.04
2.86
f1 (ppm)

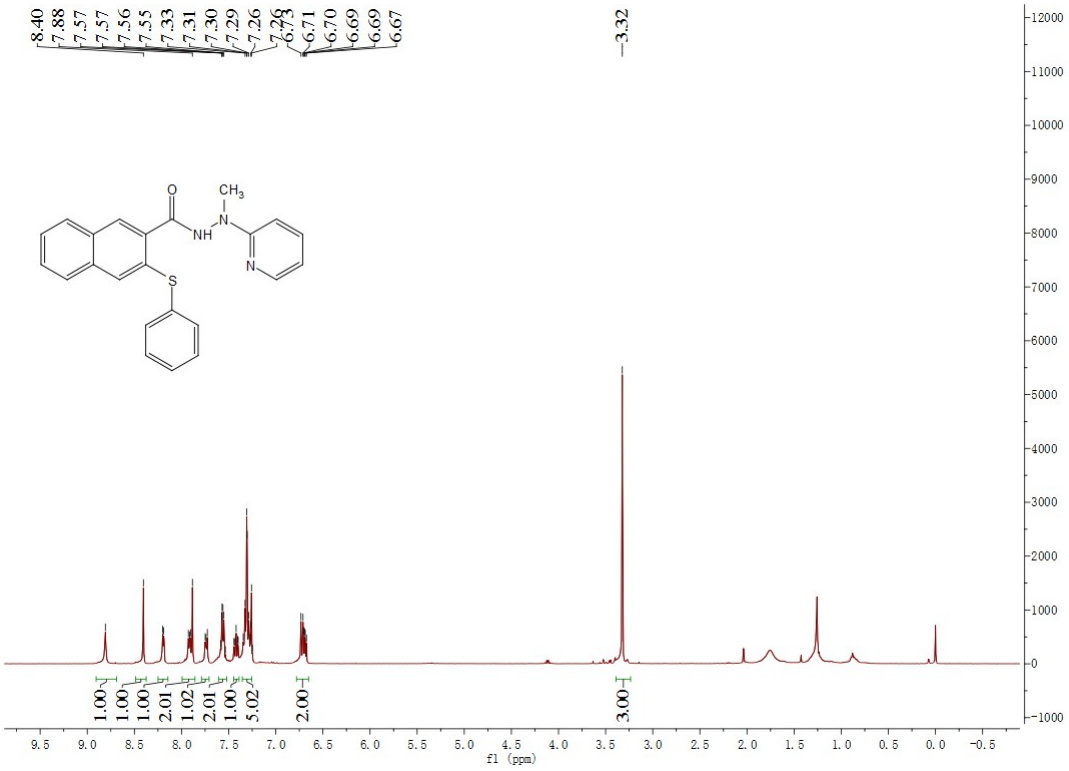

166.86
159.18
147.53
137.68
134.57
132.75
131.54
131.23
129.61
127.73
127.47
114.71
107.44
38.42
29.70
134.94
134.57
134.20
132.75
131.54
131.23
129.61
127.73
127.47
O
CH3
N
NH
N
S
f1 (ppm)

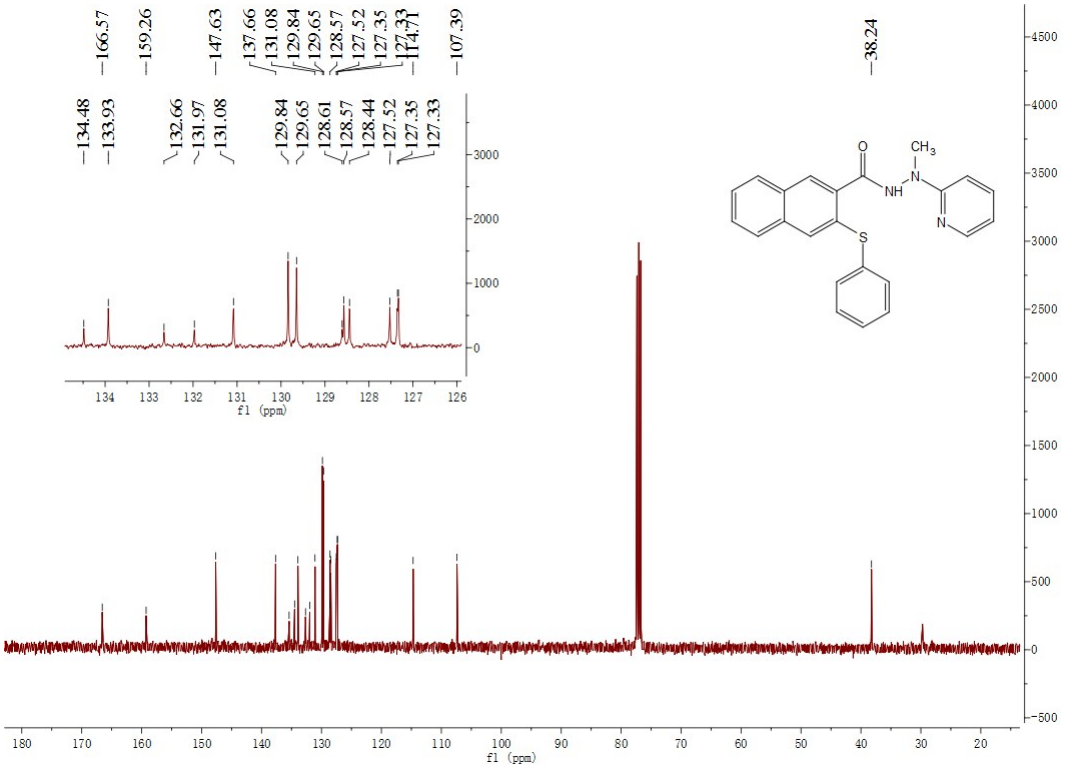
Compound **3h**


8.21 8.20 8.19 8.19 8.13 8.11 7.97 7.83 7.81 7.79 7.77 7.61 7.61 7.59 7.58 7.57 7.55 7.55 7.53 7.52 7.51 7.50 7.49 7.48 7.47 7.38 7.37 7.36 7.35 7.33 7.32 7.32 7.31 7.30 7.28 7.26 7.26 7.25 7.25 7.04 7.02 6.73 6.72 6.71 6.70 3.53
1.00 1.07 0.99 2.08 1.00 2.16 2.31 4.01 1.01 0.99 3.08
f1 (ppm)

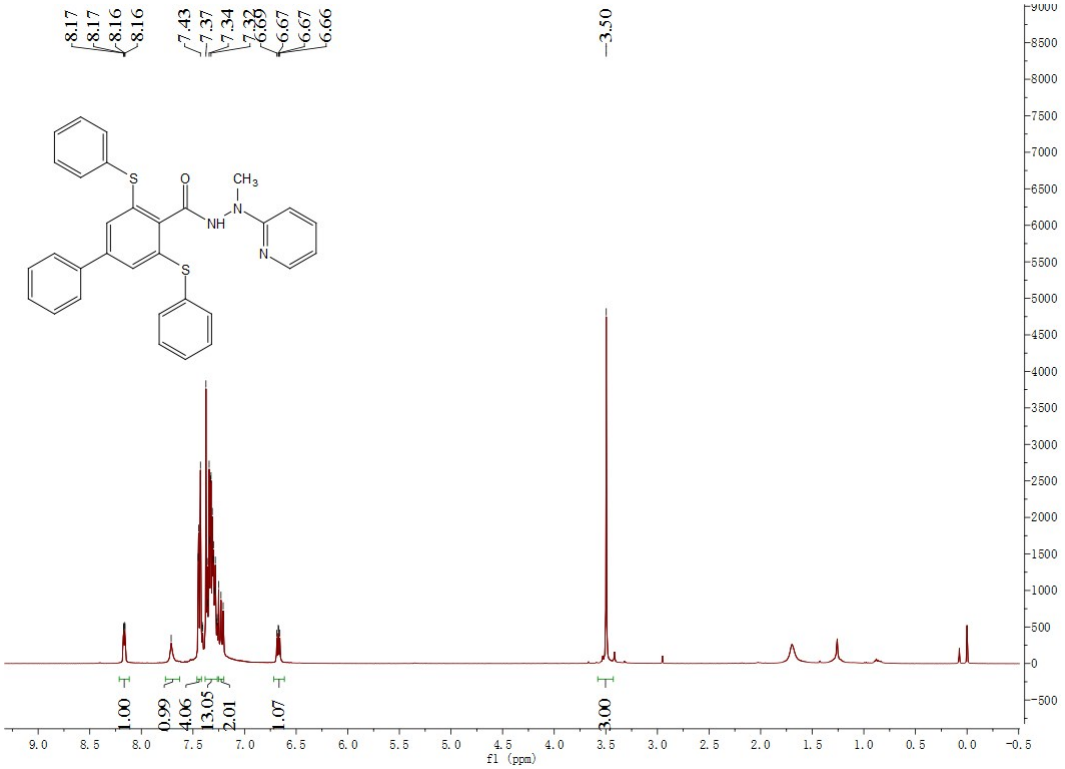

167.23 159.23 147.64 130.75 130.56 129.44 129.39 128.18 127.38 126.99 114.94 107.57 38.50
132.43 131.13 130.75 130.67 130.56 129.44 129.39 128.18 127.89 127.38 126.99 125.08
f1 (ppm)

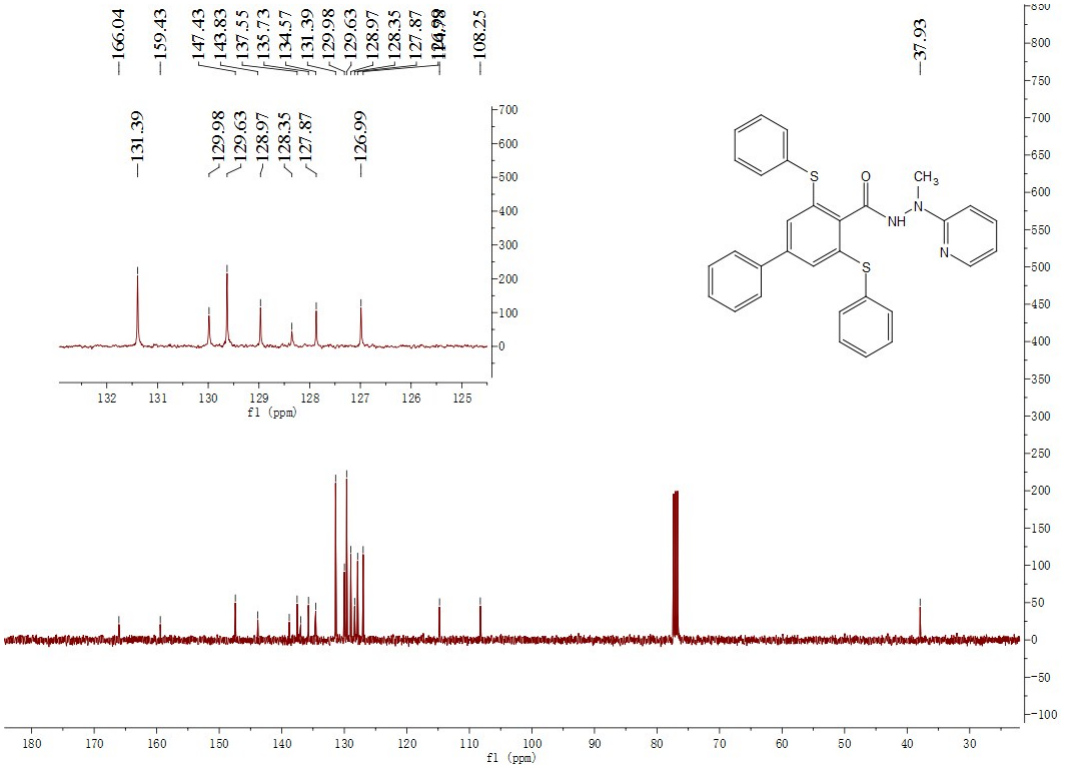
Compound **3i**


8.40
7.88
7.57
7.57
7.56
7.55
7.33
7.31
7.30
7.29
7.26
7.26
6.73
6.71
6.70
6.69
6.69
6.67
3.32
O
CH3
N
NH
N
S
1.00
1.00
1.00
2.01
1.02
2.01
1.00
5.02
2.00
3.00
f1 (ppm)

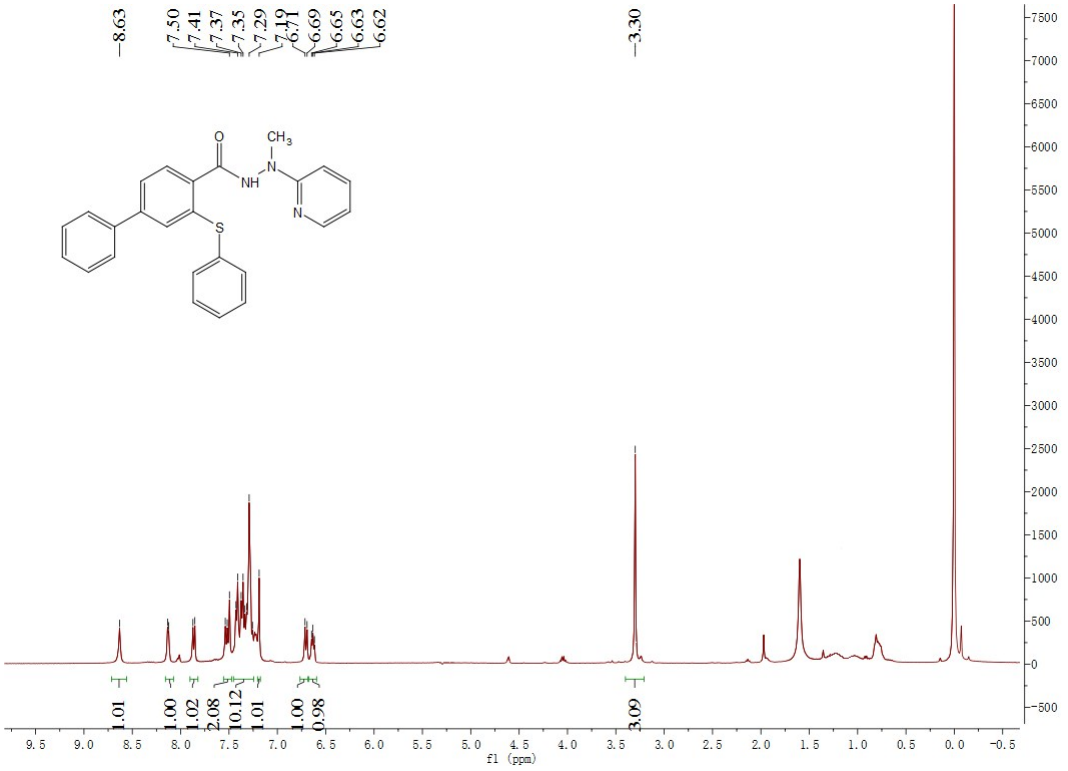

166.57
159.26
147.63
137.66
131.08
129.84
129.65
128.57
127.52
127.35
127.33
114.71
107.39
38.24
134.48
133.93
132.66
131.97
131.08
129.84
129.65
128.61
128.57
128.44
127.52
127.35
127.33
O
CH3
N
NH
N
S
f1 (ppm)

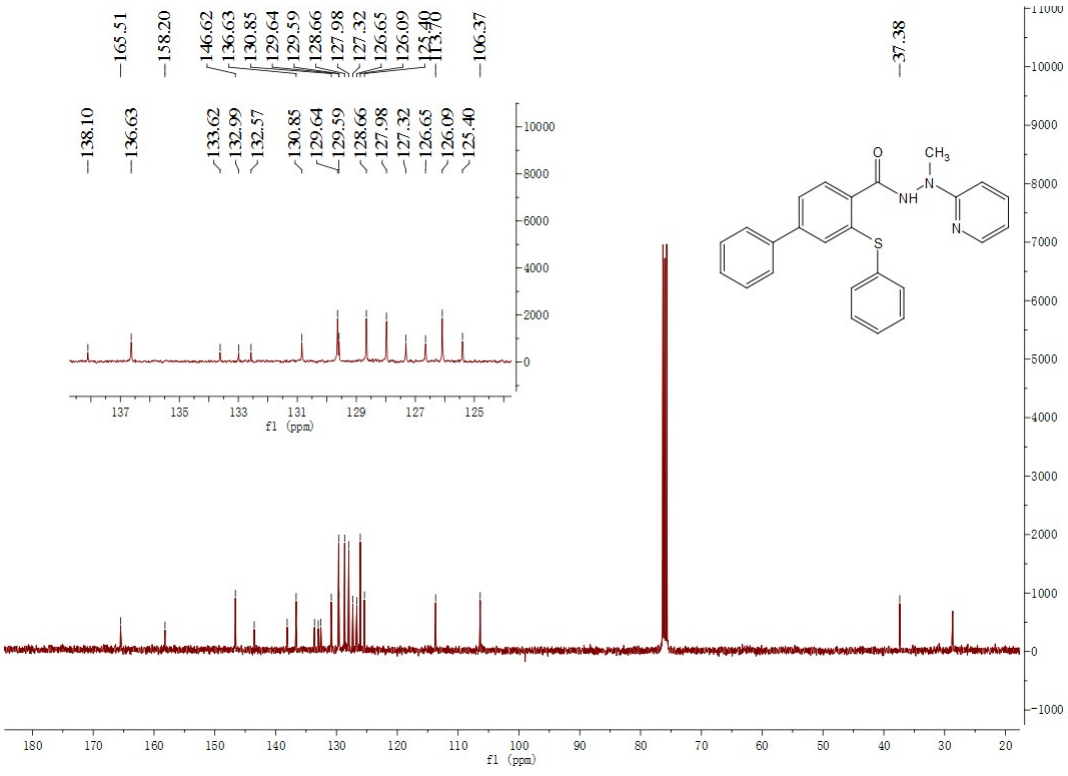
Compound **3j'**


8.17
8.17
8.16
8.16
7.43
7.37
7.34
7.32
6.68
6.67
6.67
6.66
3.50
S
O
CH3
NH
N
N
S
1.00
0.99
4.06
13.05
2.01
1.07
3.00
f1 (ppm)

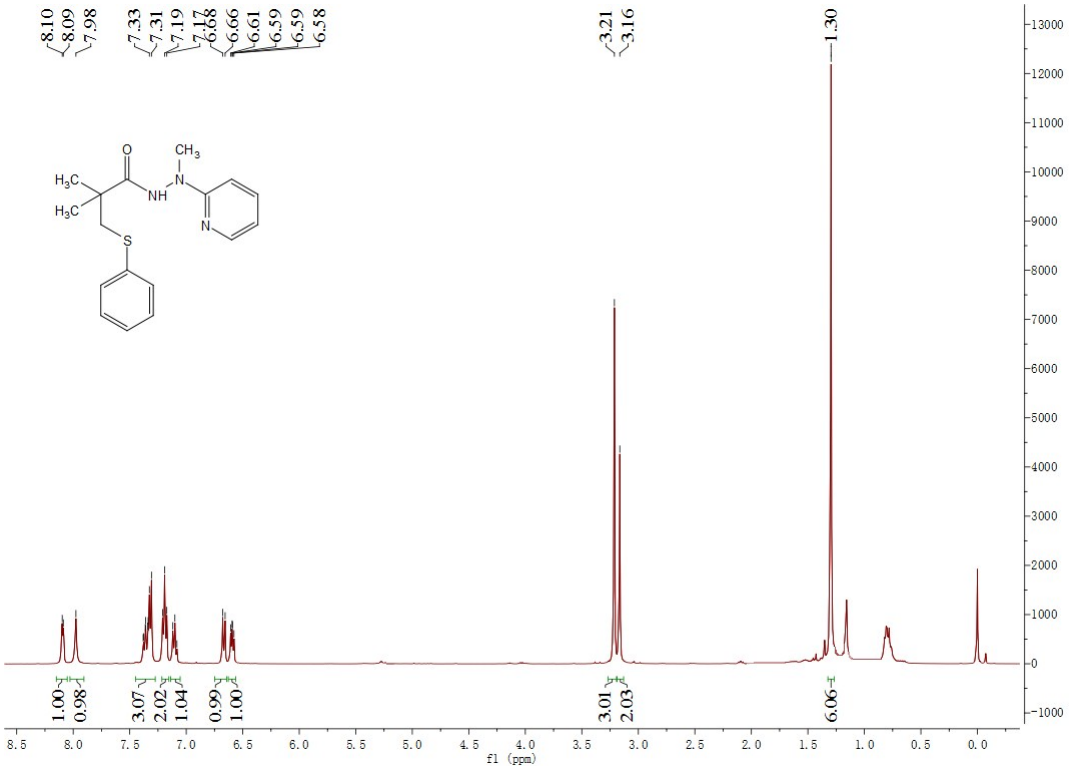

166.04
159.43
147.43
143.83
137.55
135.73
134.57
131.39
129.98
129.63
128.97
128.35
127.87
108.25
37.93
131.39
129.98
129.63
128.97
128.35
127.87
126.99
S
O
CH3
NH
N
N
S
f1 (ppm)
f1 (ppm)

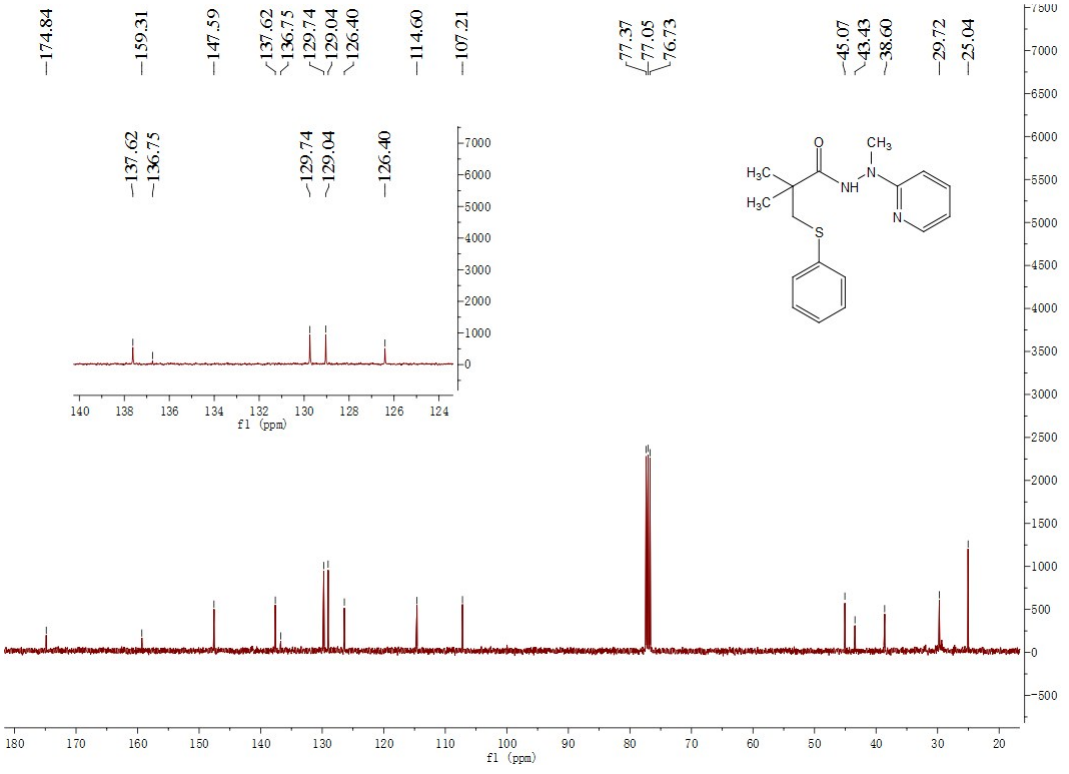
Compound **3j**


8.63
7.50
7.41
7.37
7.35
7.29
7.19
6.71
6.69
6.65
6.63
6.62
3.30
1.01
1.00
1.02
2.08
10.12
1.01
1.00
0.98
3.09
f1 (ppm)

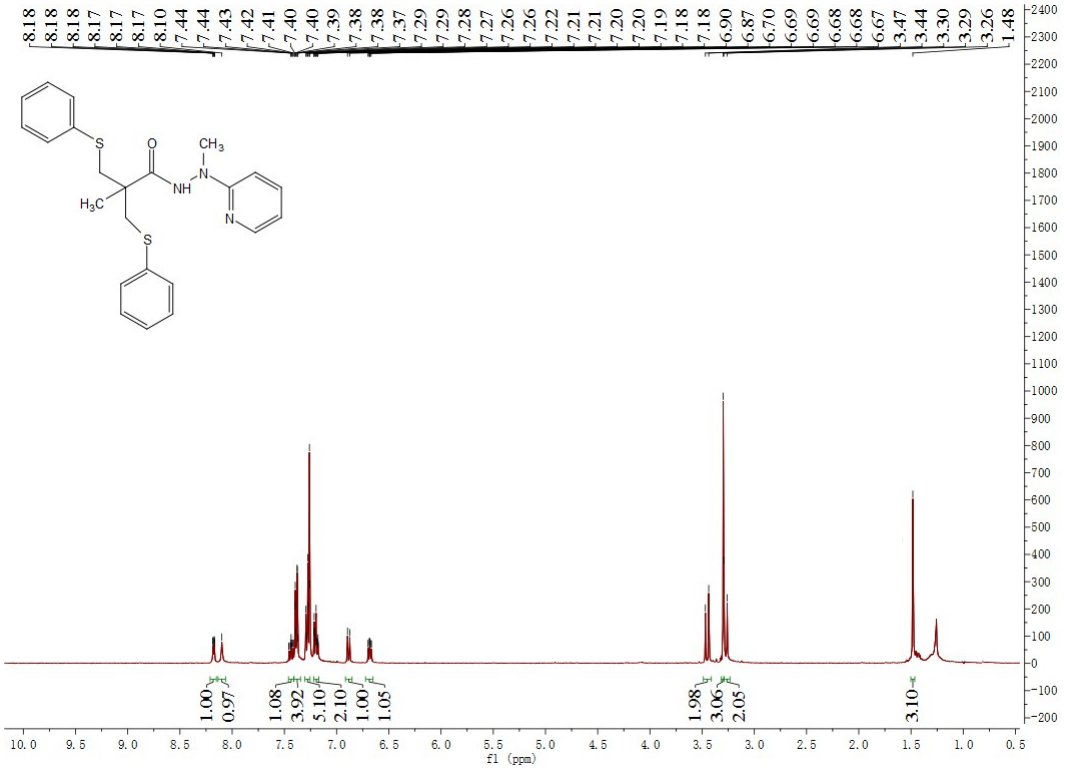

165.51
158.20
146.62
136.63
130.85
129.64
129.59
128.66
127.98
127.32
126.65
126.09
125.40
113.70
106.37
37.38
138.10
136.63
133.62
132.99
132.57
130.85
129.64
129.59
128.66
127.98
127.32
126.65
126.09
125.40
f1 (ppm)
f1 (ppm)

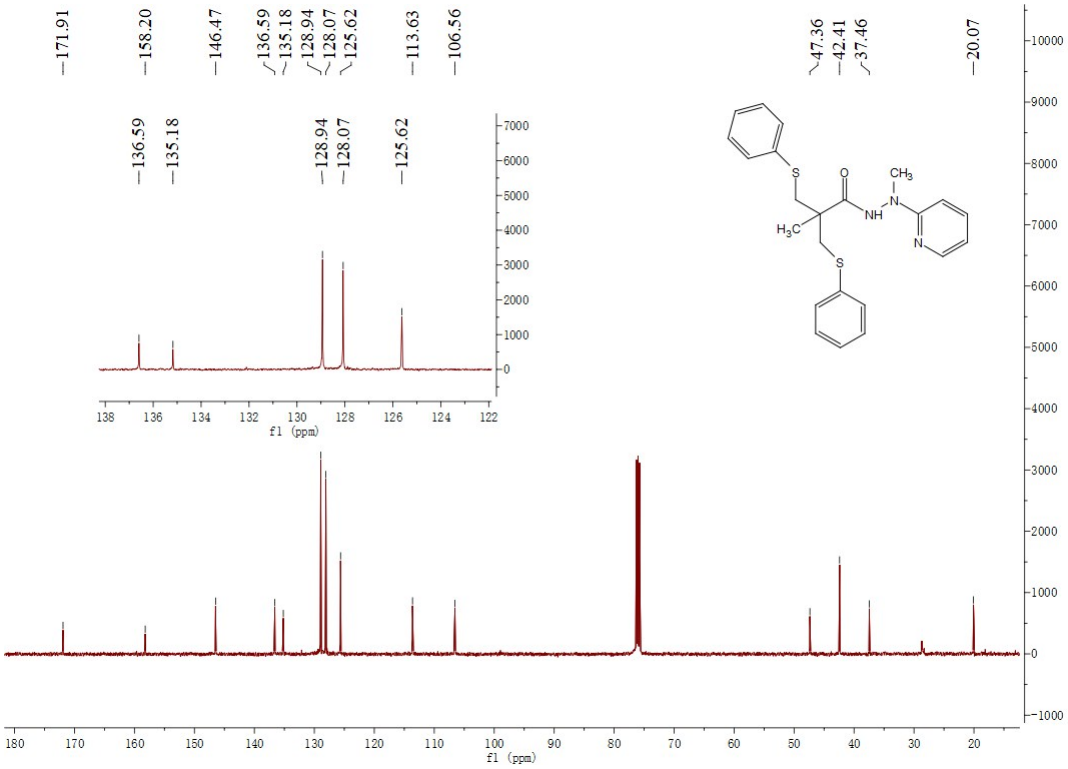
Compound **3k**


8.10
8.09
7.98
7.33
7.31
7.19
7.17
6.68
6.66
6.61
6.59
6.58
3.21
3.16
1.30
1.00
0.98
3.07
2.02
1.04
0.99
1.00
3.01
2.03
6.06
f1 (ppm)

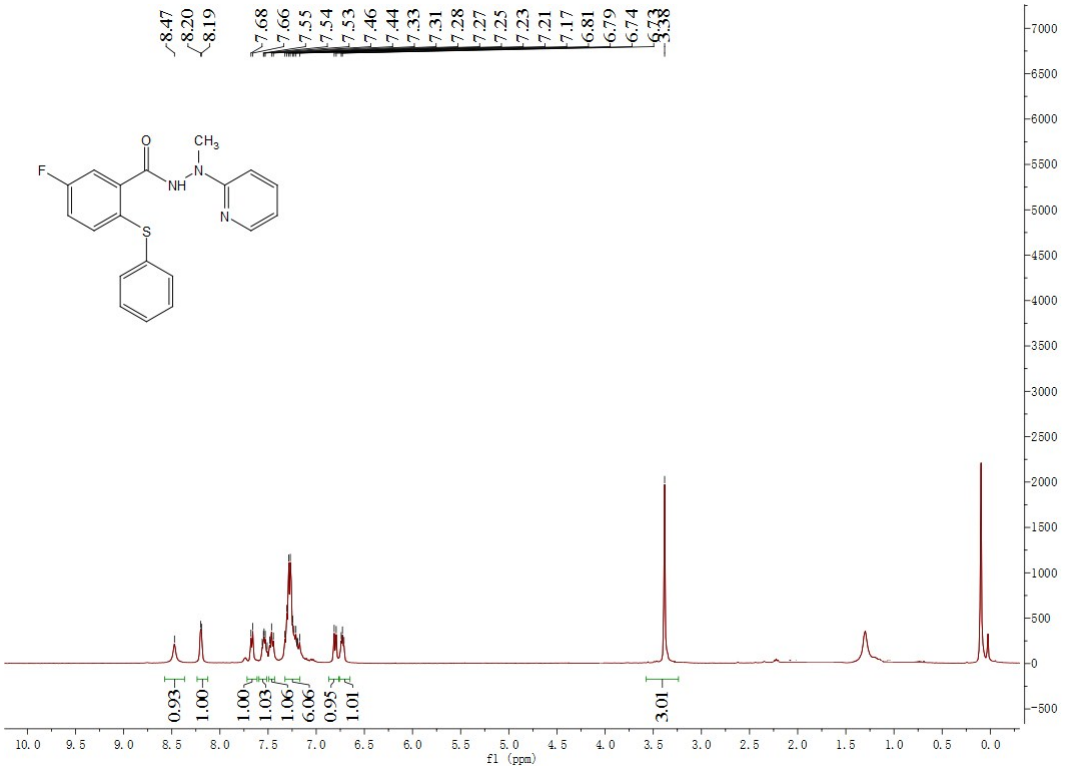

174.84
159.31
147.59
137.62
136.75
129.74
129.04
126.40
114.60
107.21
77.37
77.05
76.73
45.07
43.43
38.60
29.72
25.04
f1 (ppm)

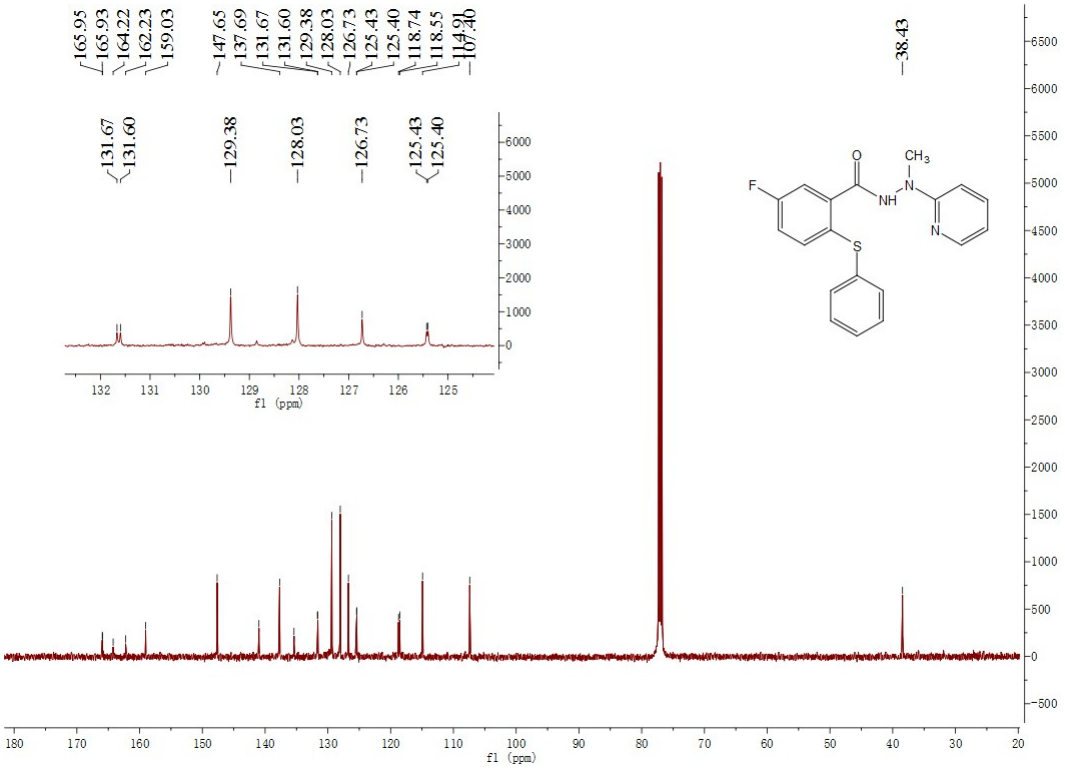
Compound **3k'**

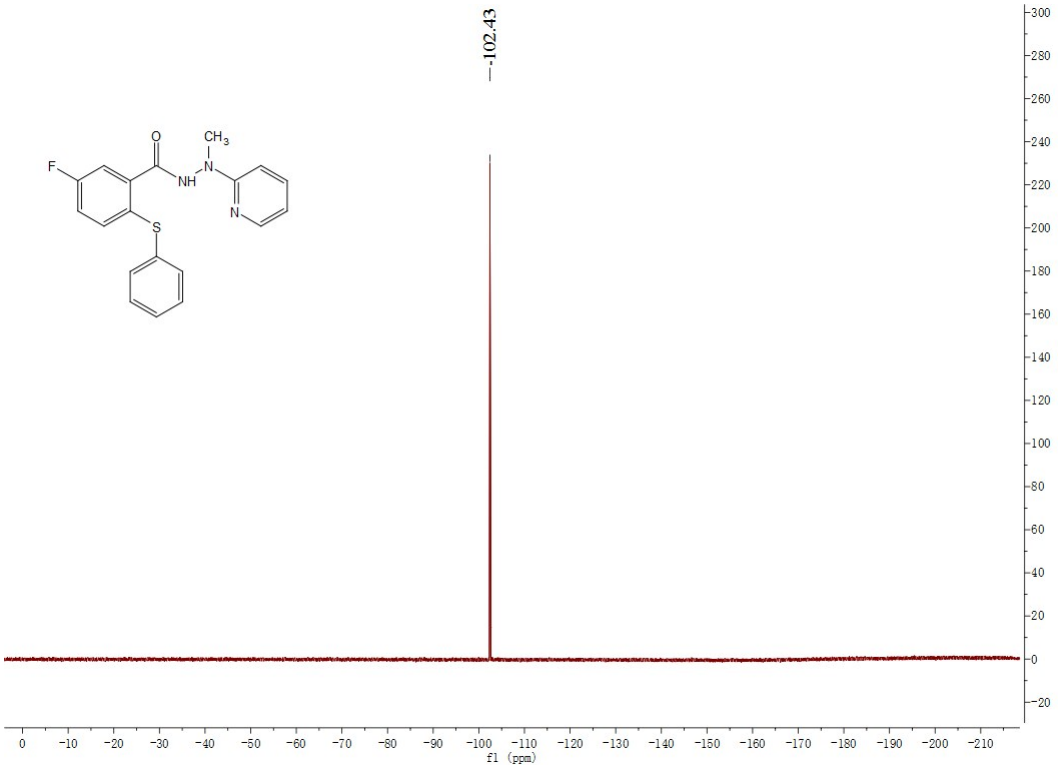




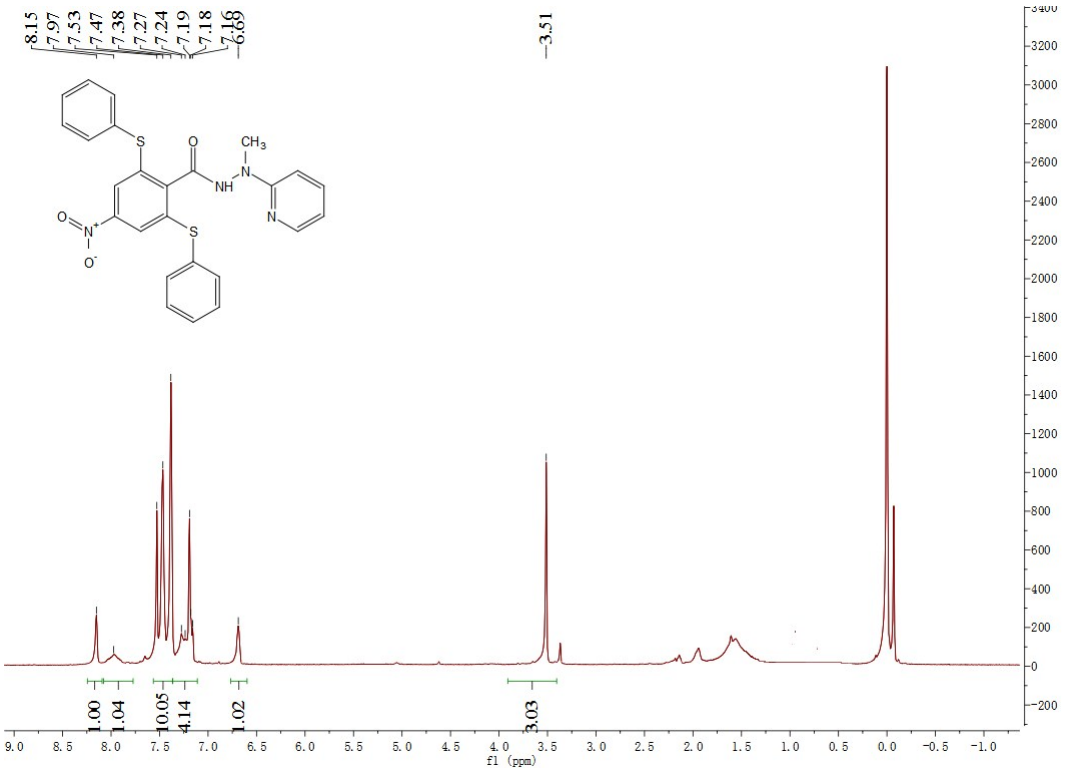
Compound **3l**

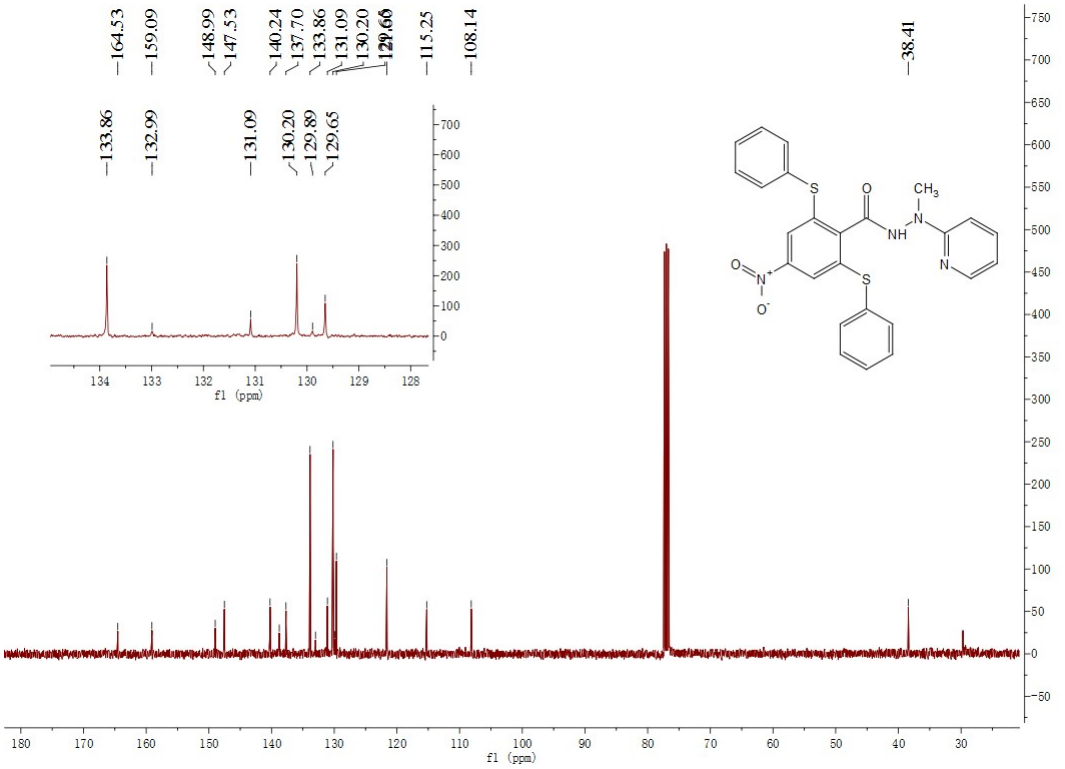

8.47
8.20
8.19
7.68
7.66
7.55
7.54
7.53
7.46
7.44
7.33
7.31
7.28
7.27
7.25
7.23
7.21
7.17
6.81
6.79
6.74
6.73
3.38
0.93
1.00
1.00
1.03
1.06
6.06
0.95
1.01
3.01
f1 (ppm)


165.95
165.93
164.22
162.23
159.03
147.65
137.69
131.67
131.60
129.38
128.03
126.73
125.43
125.40
118.74
118.55
114.91
107.40
38.43
f1 (ppm)

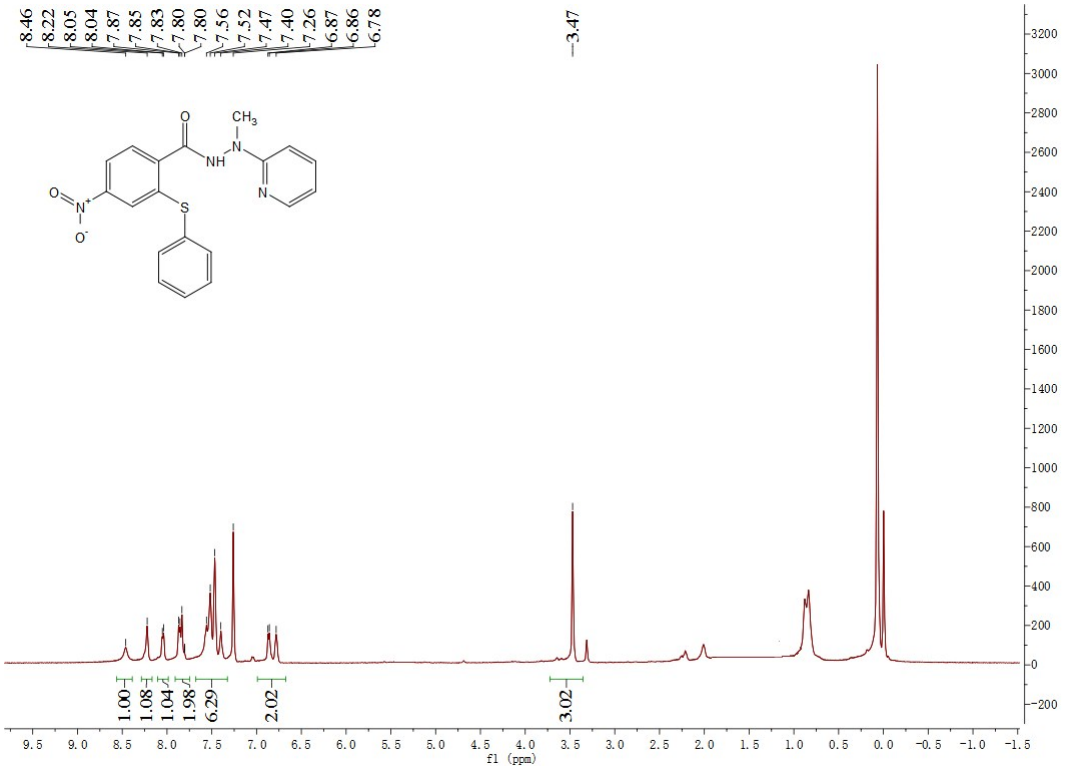

-102.43
F
O
NH
N
CH3
N
S
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

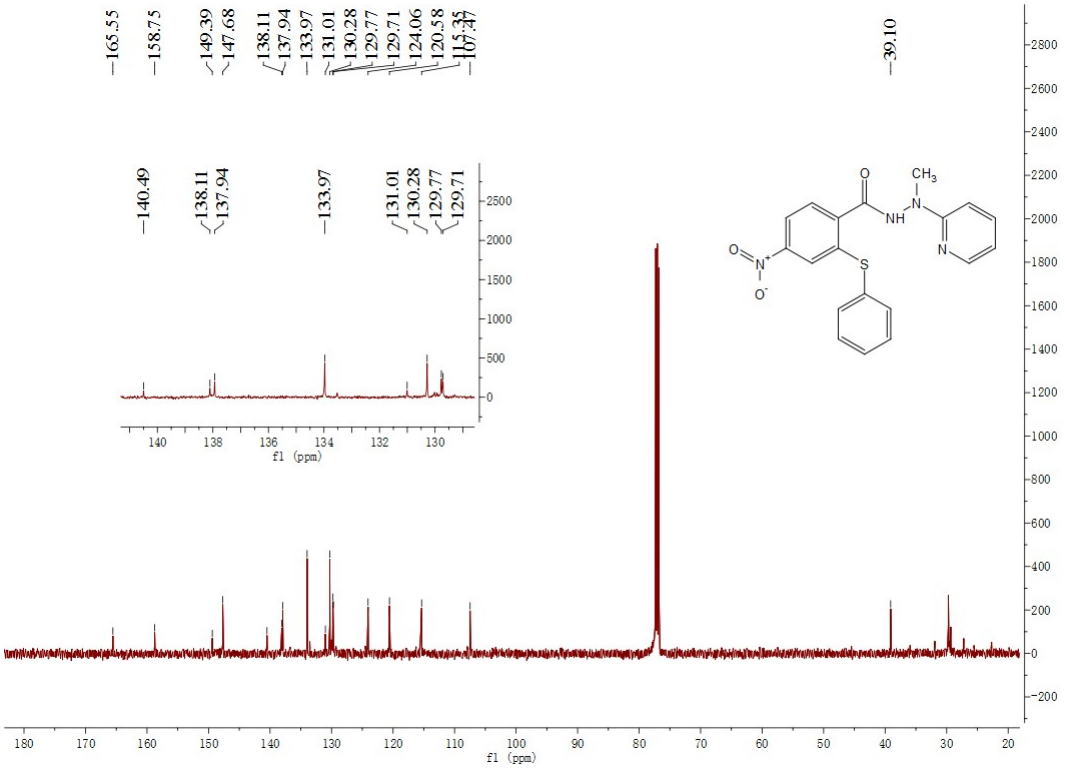
Compound **3m'**


8.15
7.97
7.53
7.47
7.38
7.27
7.24
7.19
7.18
7.16
6.69
3.51
1.00
1.04
10.05
4.14
1.02
3.03
f1 (ppm)

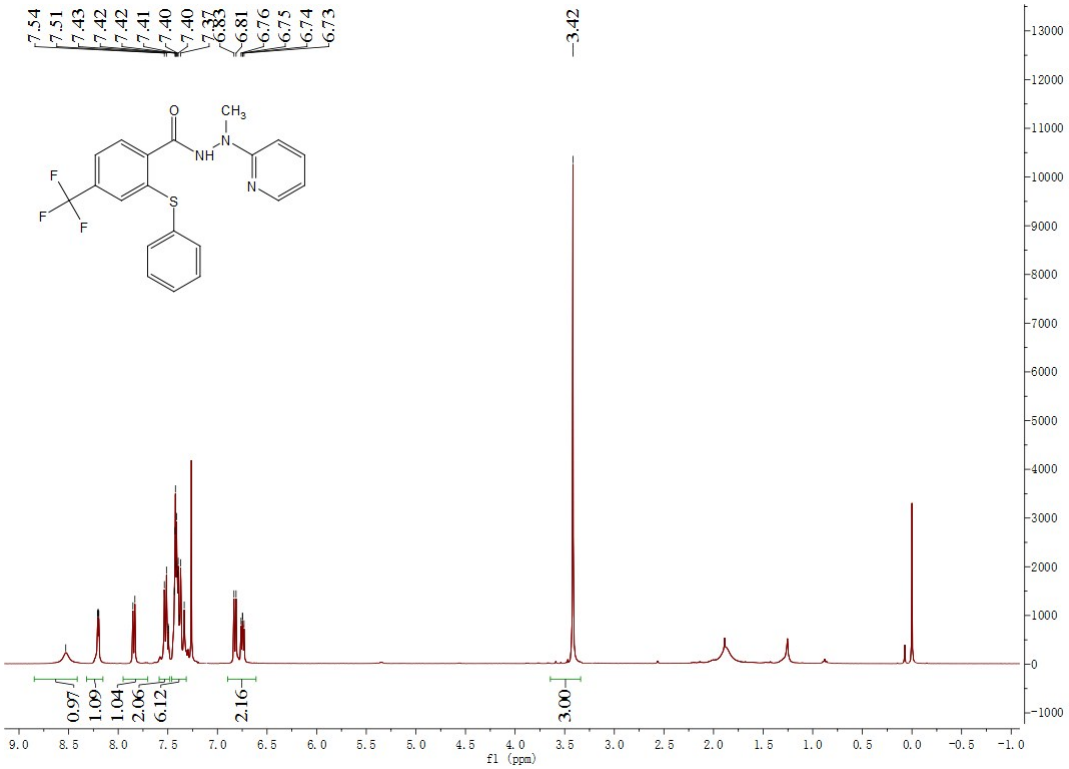

164.53
159.09
148.99
147.53
140.24
137.70
133.86
131.09
130.20
115.25
108.14
38.41
133.86
132.99
131.09
130.20
129.89
129.65
f1 (ppm)

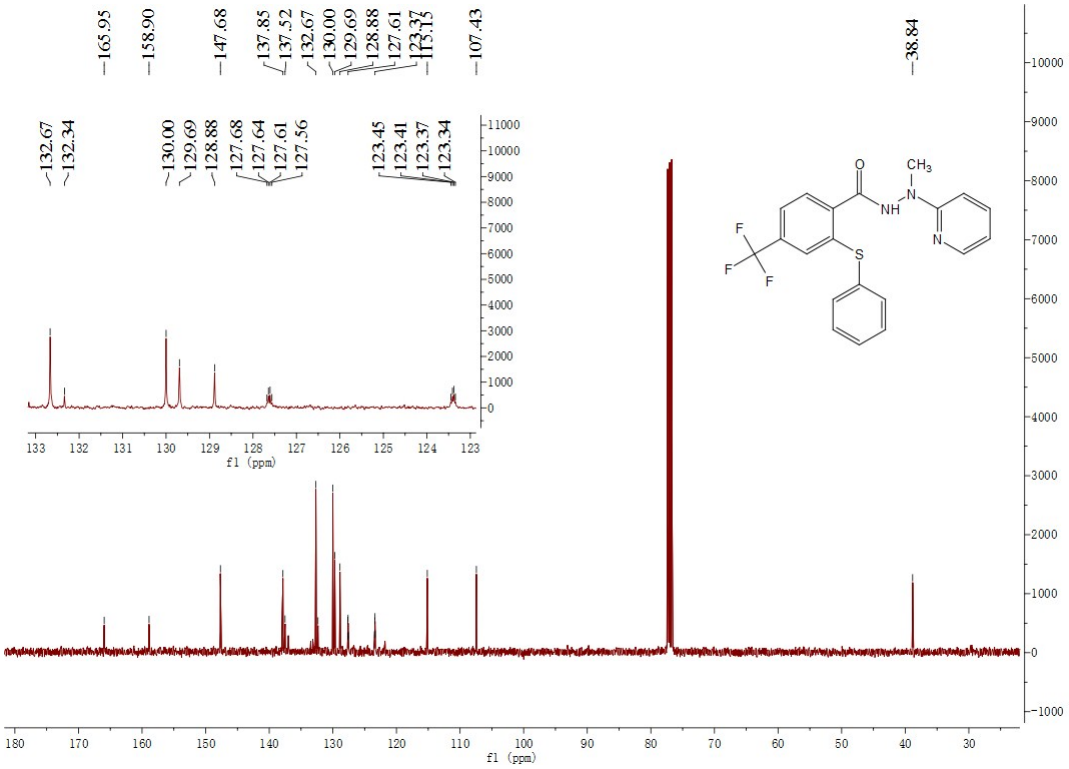
Compound **3m**

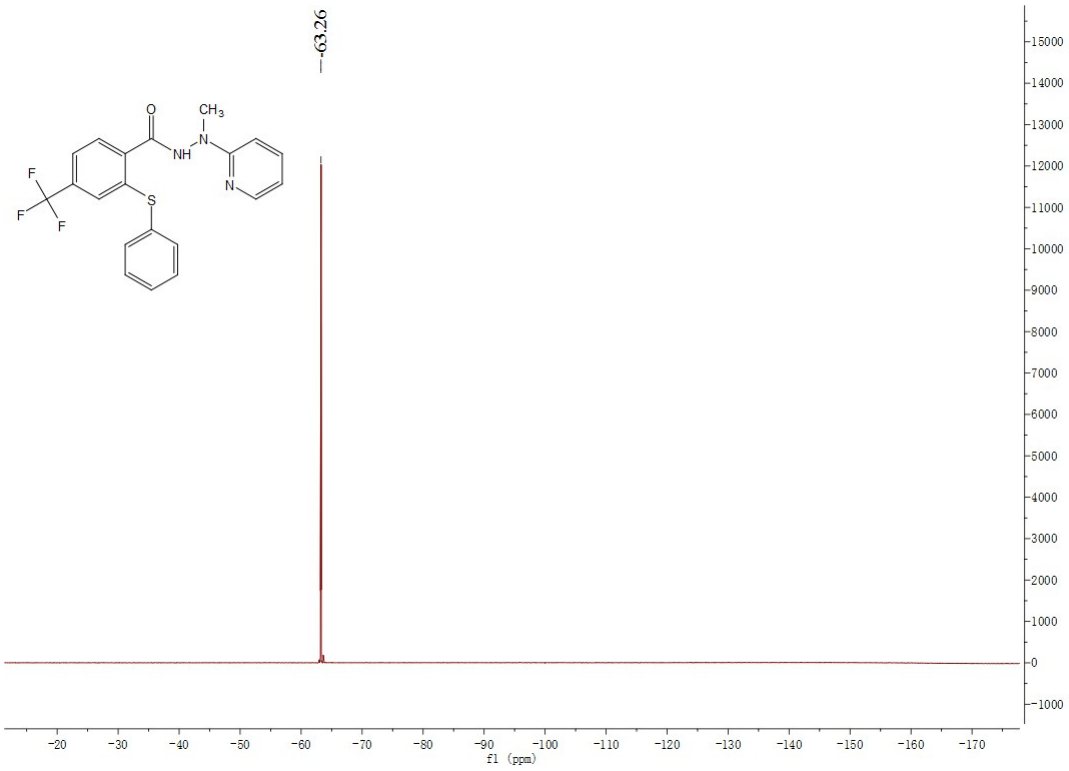

8.46
8.22
8.05
8.04
7.87
7.85
7.83
7.80
7.80
7.56
7.52
7.47
7.40
7.26
6.87
6.86
6.78
3.47
1.00
1.08
1.04
1.98
6.29
2.02
3.02
f1 (ppm)


165.55
158.75
149.39
147.68
138.11
137.94
133.97
131.01
130.28
129.77
129.71
124.06
120.58
115.35
107.47
39.10
140.49
138.11
137.94
133.97
131.01
130.28
129.77
129.71
f1 (ppm)
f1 (ppm)

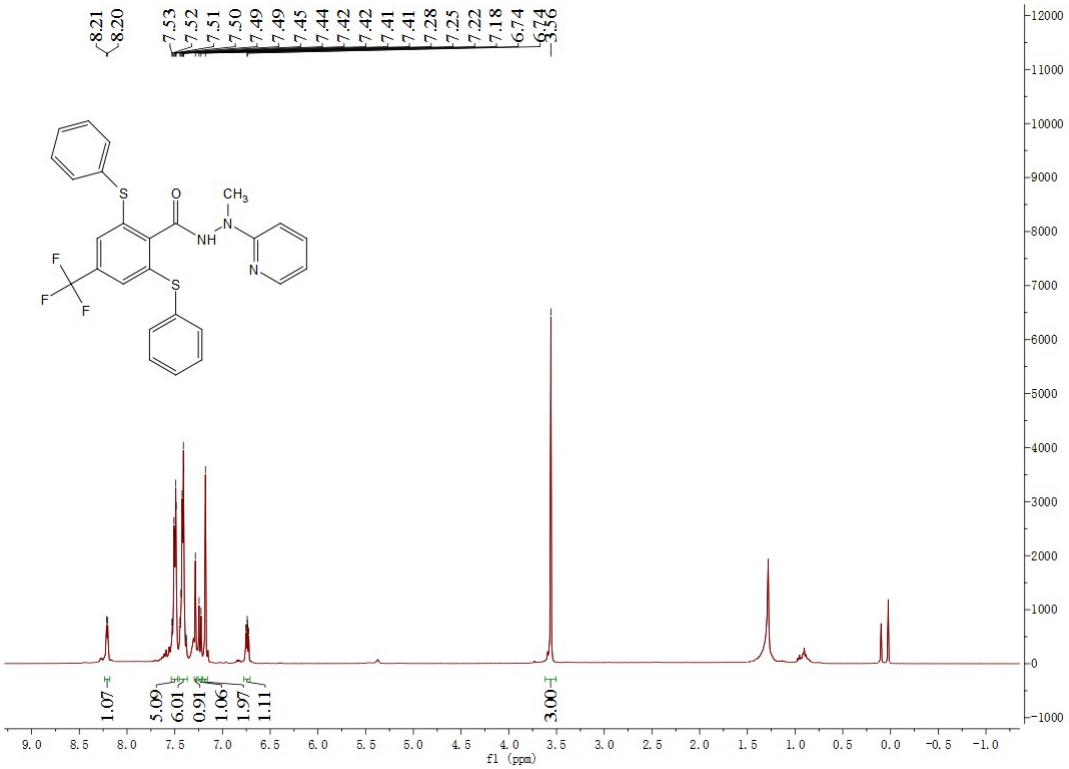
Compound **3n**

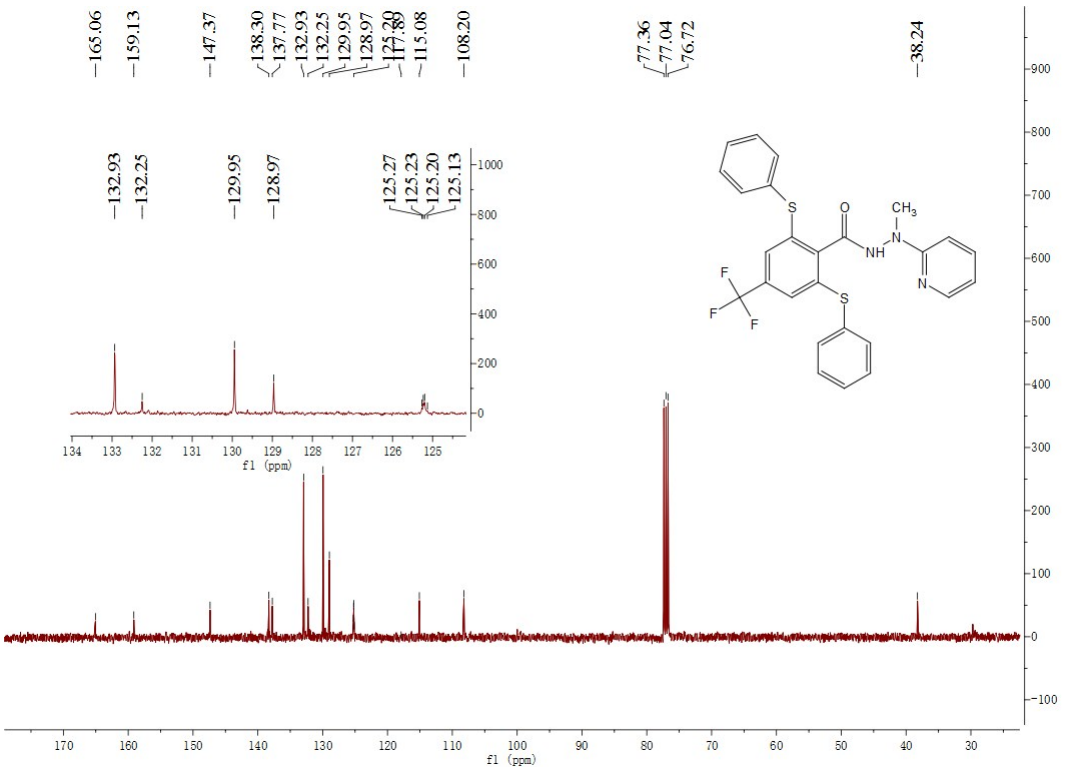

7.54
7.51
7.43
7.42
7.42
7.41
7.40
7.40
7.37
6.83
6.81
6.76
6.75
6.74
6.73
3.42
0.97
1.09
1.04
2.06
6.12
2.16
3.00
f1 (ppm)


165.95
158.90
147.68
137.85
137.52
132.67
130.00
129.69
128.88
127.61
123.37
123.15
107.43
38.84
132.67
132.34
130.00
129.69
128.88
127.68
127.64
127.61
127.56
123.45
123.41
123.37
123.34
f1 (ppm)

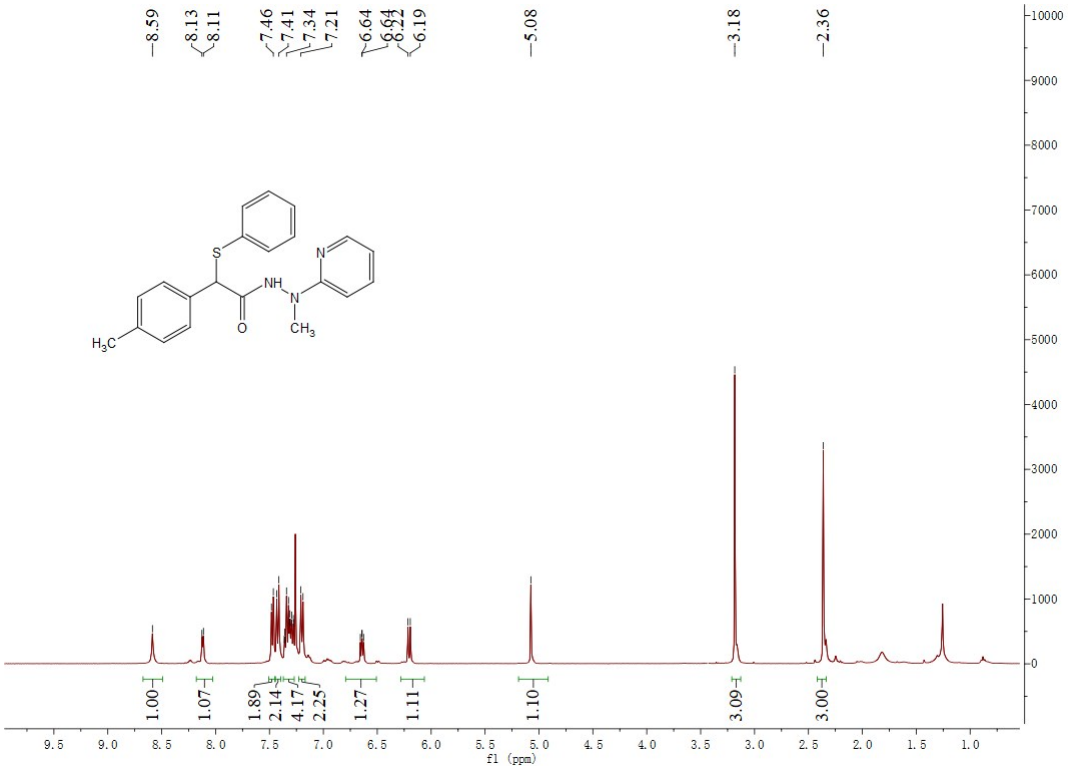

-63.26
O
CH3
NH
N
N
F
F
F
S
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

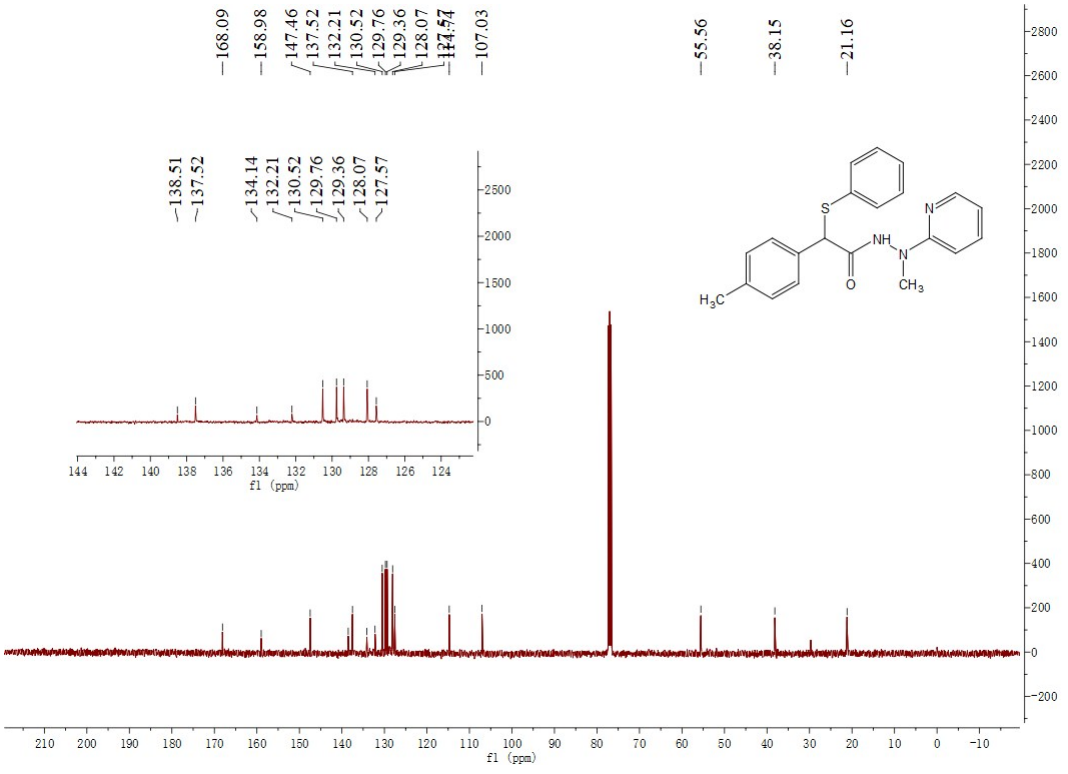
Compound **3n'**


8.21
8.20
7.53
7.52
7.51
7.50
7.49
7.49
7.45
7.44
7.42
7.42
7.41
7.41
7.28
7.25
7.22
7.18
6.74
6.74
3.56
1.07
5.09
6.01
0.91
1.06
1.97
1.11
3.00
f1 (ppm)

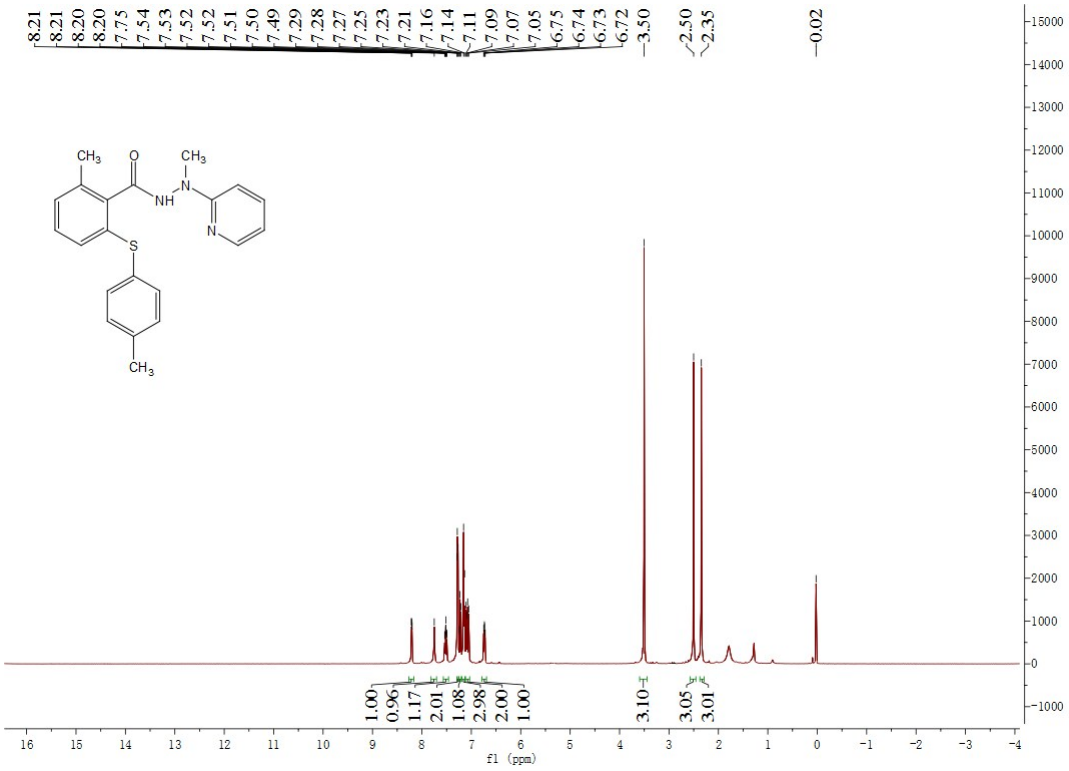

165.06
159.13
147.37
138.30
137.77
132.93
132.25
129.95
128.97
125.27
125.23
125.20
125.13
115.08
108.20
77.36
77.04
76.72
38.24
f1 (ppm)

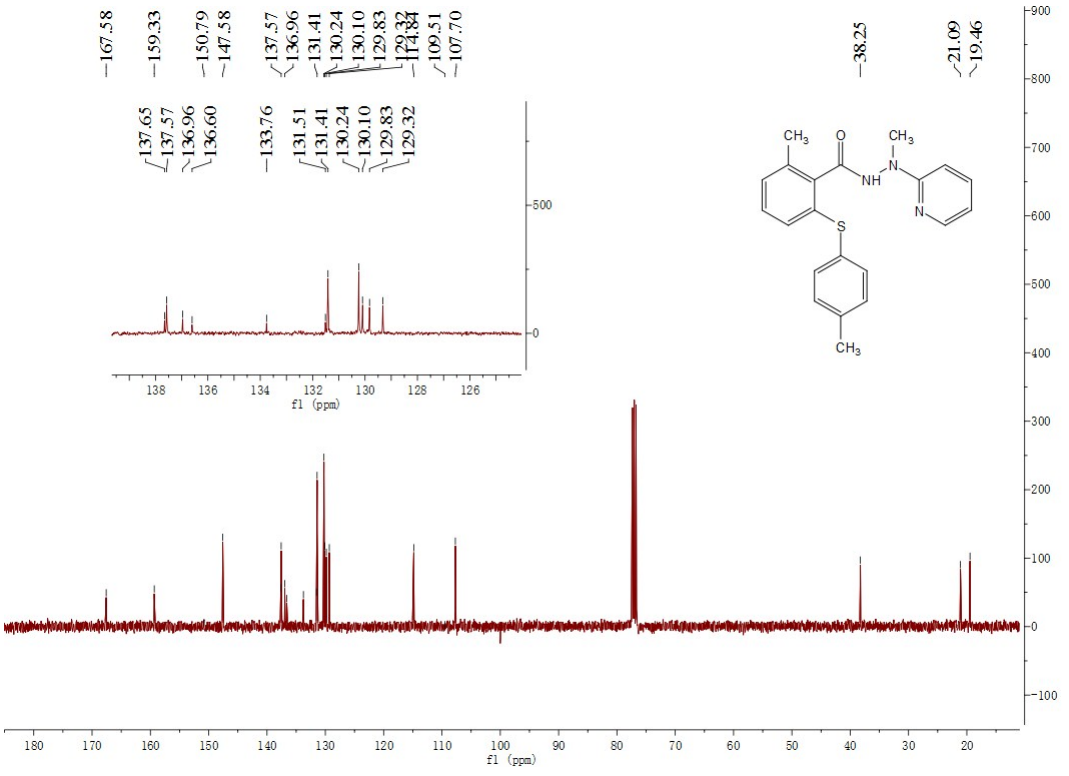
Compound **3p**


8.59
8.13
8.11
7.46
7.41
7.34
7.21
6.64
6.22
6.19
5.08
3.18
2.36
1.00
1.07
1.89
2.14
4.17
2.25
1.27
1.11
1.10
3.09
3.00
f1 (ppm)

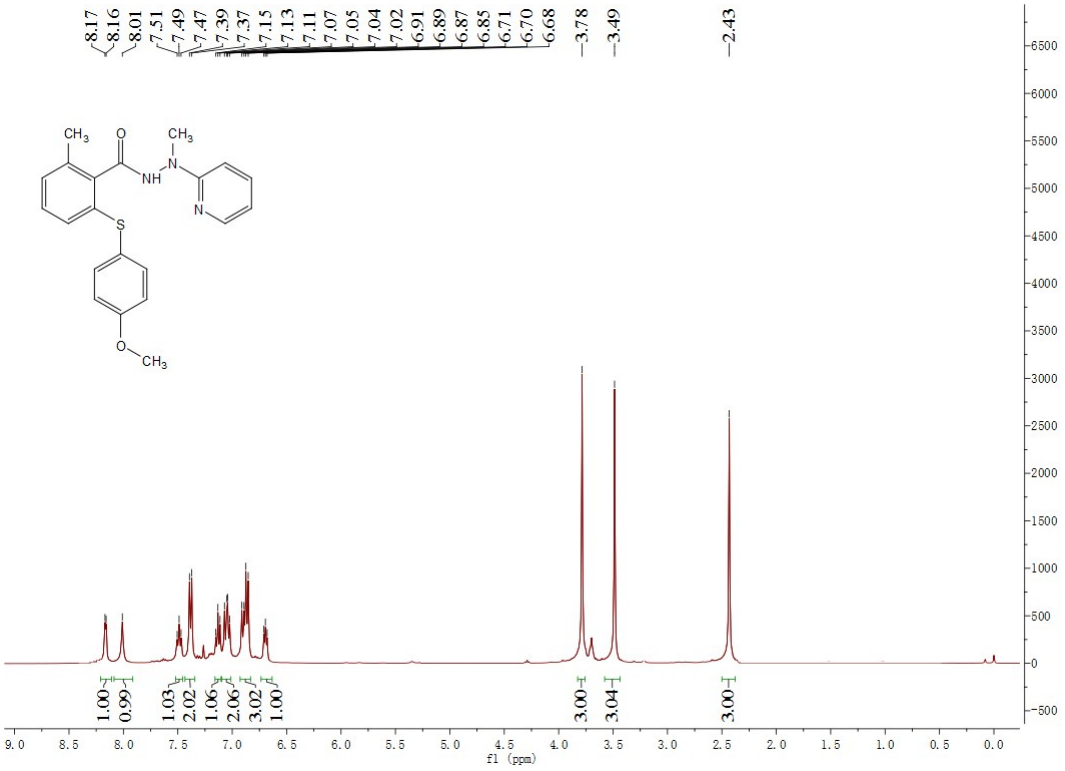

168.09
158.98
147.46
137.52
132.21
130.52
129.76
129.36
128.07
107.03
55.56
38.15
21.16
138.51
137.52
134.14
132.21
130.52
129.76
129.36
128.07
127.57
f1 (ppm)

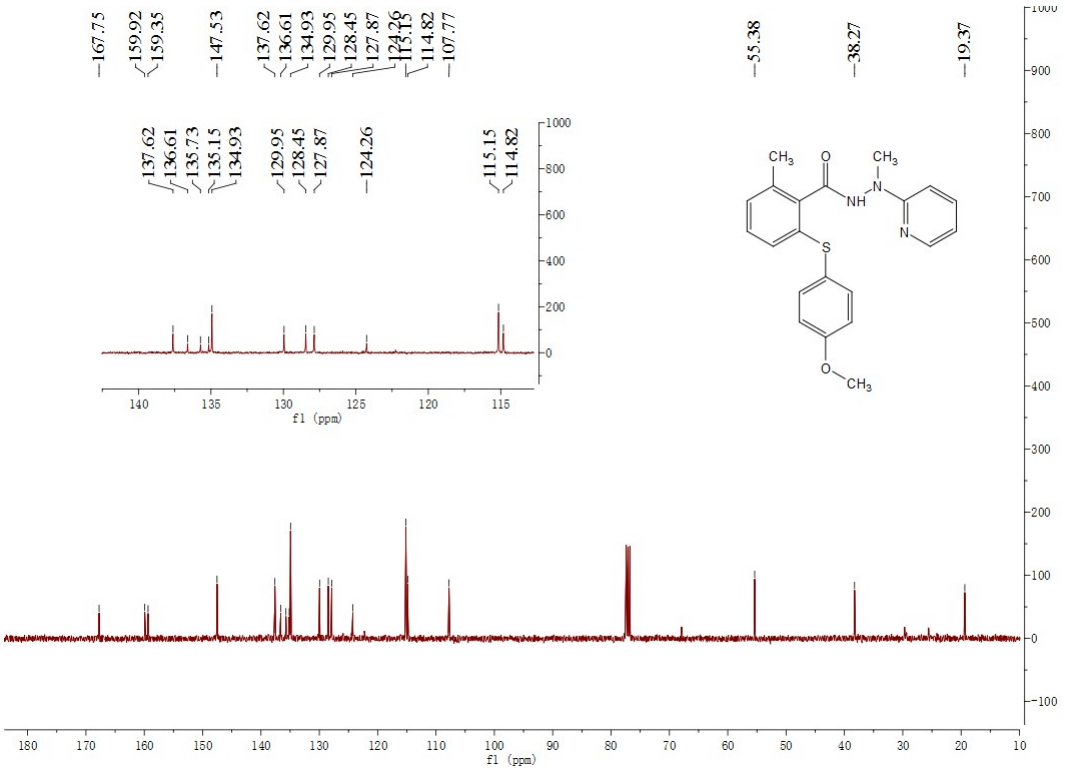
Compound **3q**


8.21
8.21
8.20
8.20
7.75
7.54
7.53
7.52
7.52
7.51
7.50
7.49
7.29
7.28
7.27
7.25
7.23
7.21
7.16
7.14
7.11
7.09
7.07
7.05
6.75
6.74
6.73
6.72
3.50
2.50
2.35
0.02
CH3
O
CH3
NH
N
N
S
CH3
1.00
0.96
1.17
2.01
1.08
2.98
2.00
1.00
3.10
3.05
3.01
f1 (ppm)

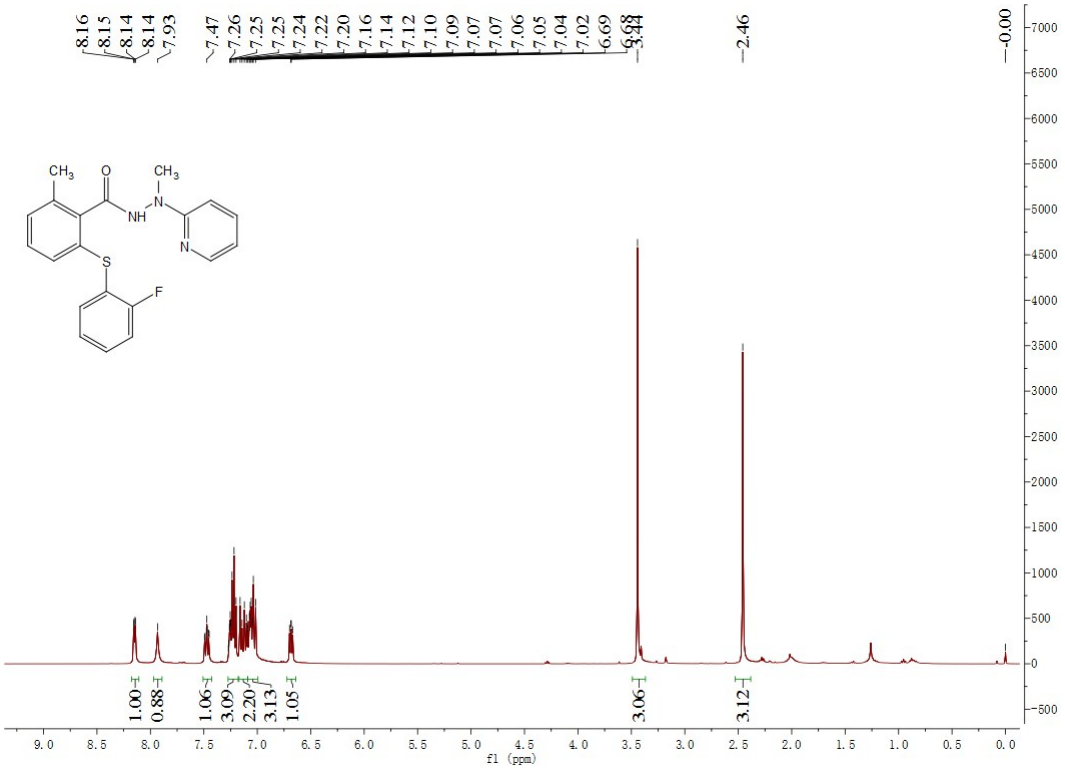

167.58
159.33
150.79
147.58
137.57
136.96
131.41
130.24
130.10
129.83
129.32
114.84
109.51
107.70
38.25
21.09
19.46
137.65
137.57
136.96
136.60
133.76
131.51
131.41
130.24
130.10
129.83
129.32
CH3
O
CH3
NH
N
N
S
CH3
f1 (ppm)
f1 (ppm)

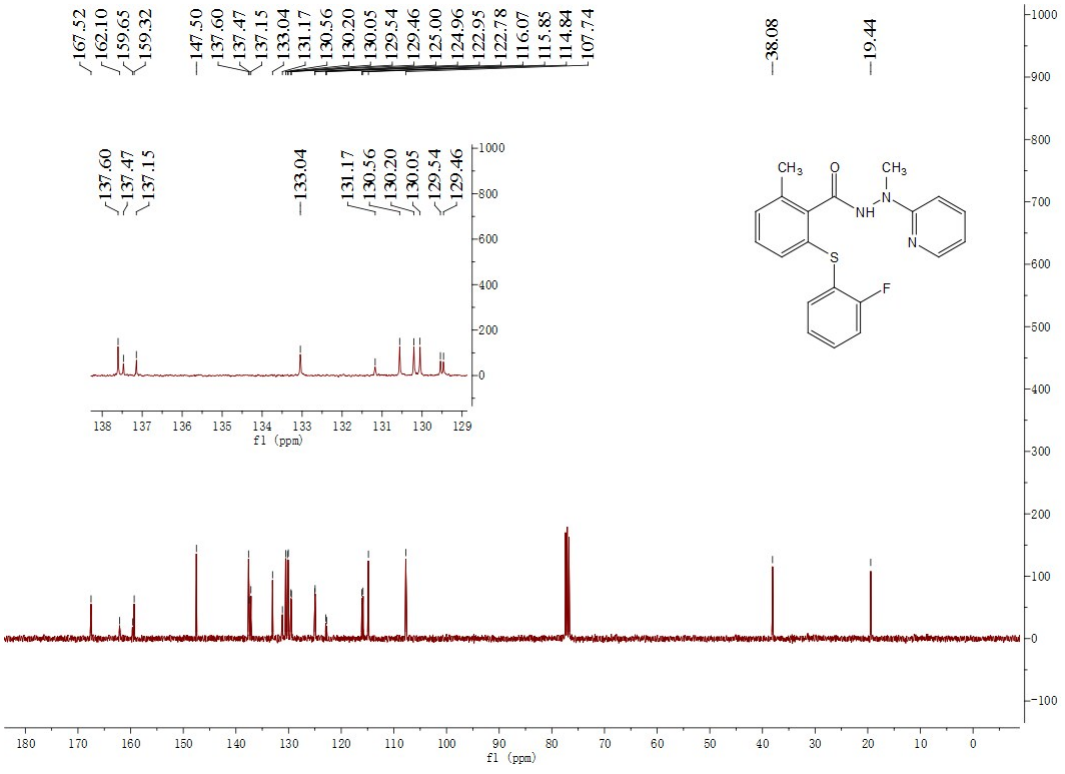
Compound **3r**

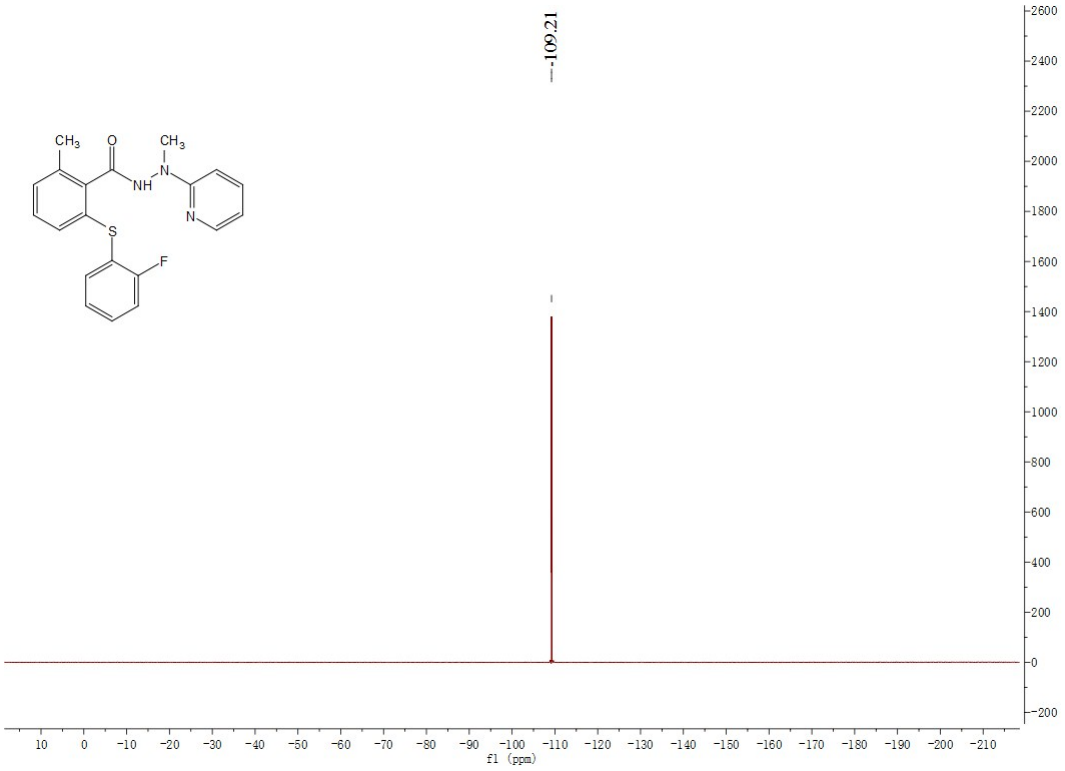

8.17
8.16
8.01
7.51
7.49
7.47
7.39
7.37
7.15
7.13
7.11
7.07
7.05
7.04
7.02
6.91
6.89
6.87
6.85
6.71
6.70
6.68
3.78
3.49
2.43
1.00
0.99
1.03
2.02
1.06
2.06
3.02
1.00
3.00
3.04
3.00
f1 (ppm)


167.75
159.92
159.35
147.53
137.62
136.61
134.93
129.95
128.45
127.87
124.26
115.15
114.82
107.77
55.38
38.27
19.37
f1 (ppm)

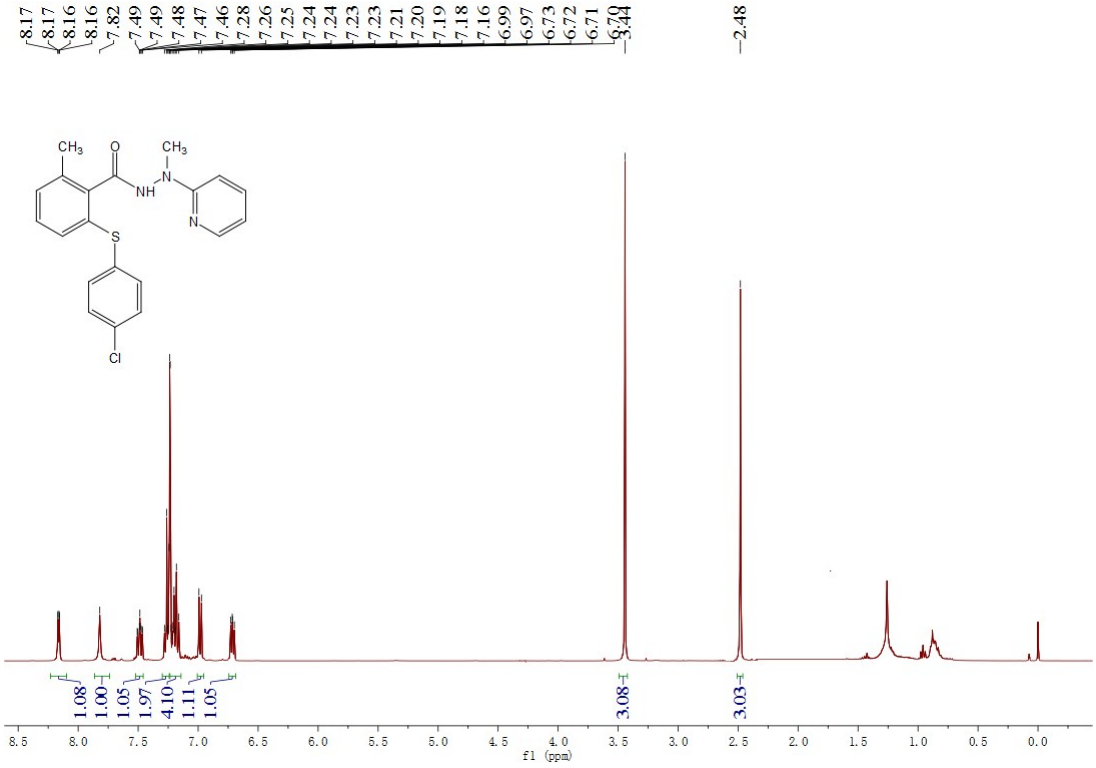
Compound **3s**

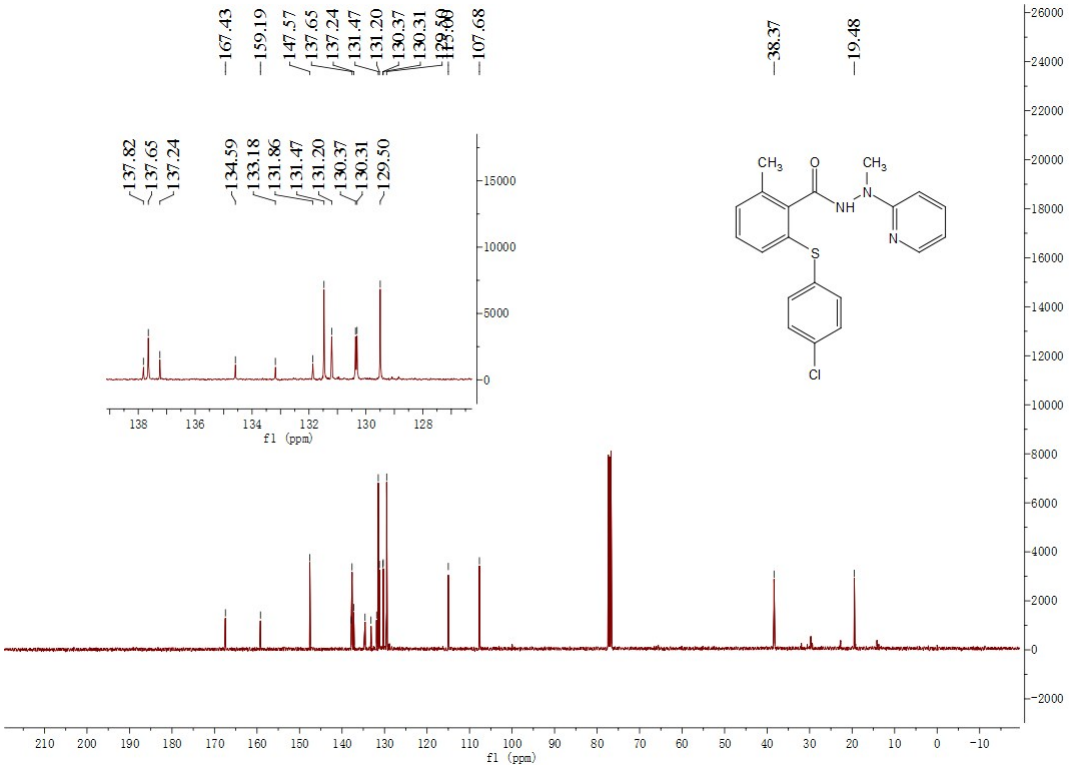

8.16
8.15
8.14
8.14
7.93
7.47
7.26
7.25
7.25
7.24
7.22
7.20
7.16
7.14
7.12
7.10
7.09
7.07
7.07
7.06
7.05
7.04
7.02
6.69
6.68
3.44
2.46
0.00
1.00
0.88
1.06
3.09
2.20
3.13
1.05
3.06
3.12
f1 (ppm)


167.52
162.10
159.65
159.32
147.50
137.60
137.47
137.15
133.04
131.17
130.56
130.20
130.05
129.54
129.46
125.00
124.96
122.95
122.78
116.07
115.85
114.84
107.74
38.08
19.44
f1 (ppm)

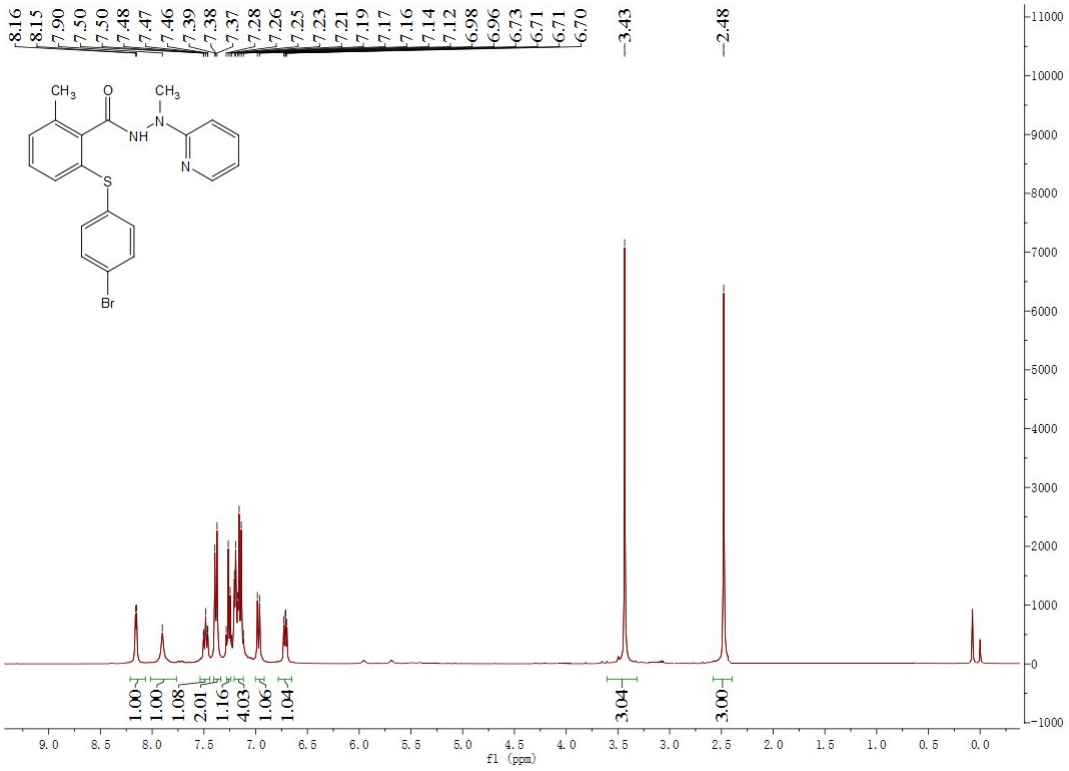

-109.21
CH3
O
CH3
NH
N
N
S
F
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

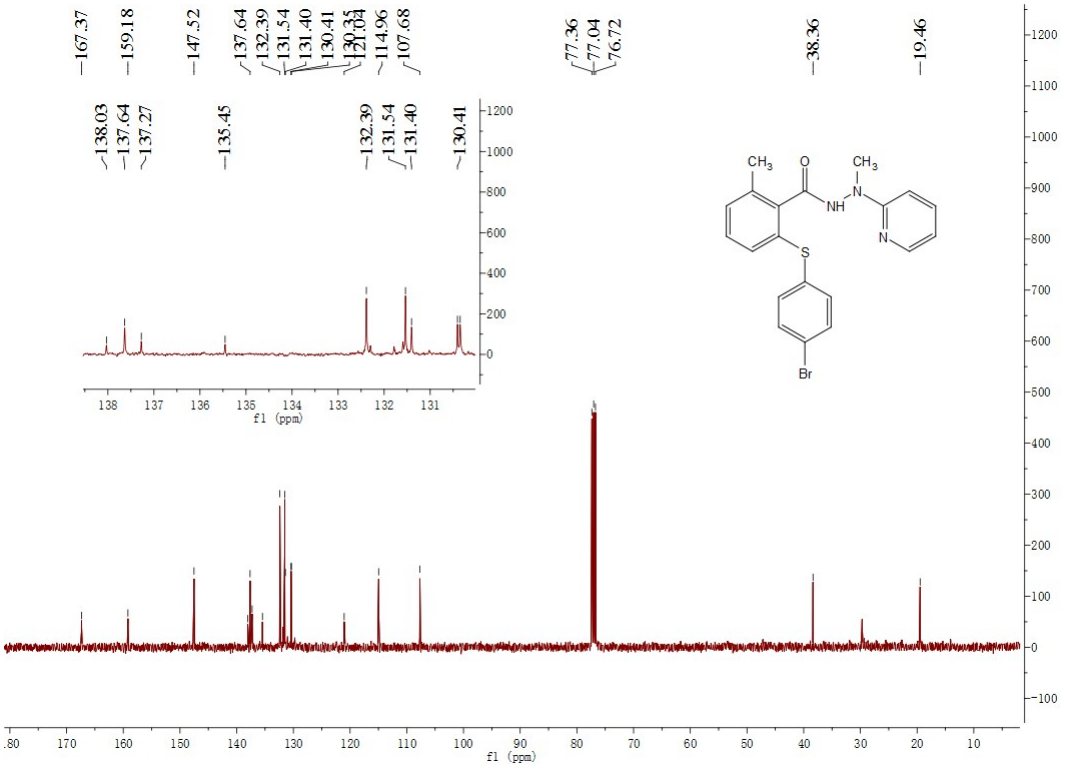
Compound **3t**


8.17
8.17
8.16
8.16
7.82
7.49
7.49
7.48
7.47
7.46
7.28
7.26
7.25
7.24
7.24
7.23
7.23
7.21
7.20
7.19
7.18
7.16
6.99
6.97
6.73
6.72
6.71
6.70
3.44
2.48
CH3
O
CH3
NH
N
N
S
Cl
1.08
1.00
1.05
1.97
4.10
1.11
1.05
3.08
3.03
f1 (ppm)

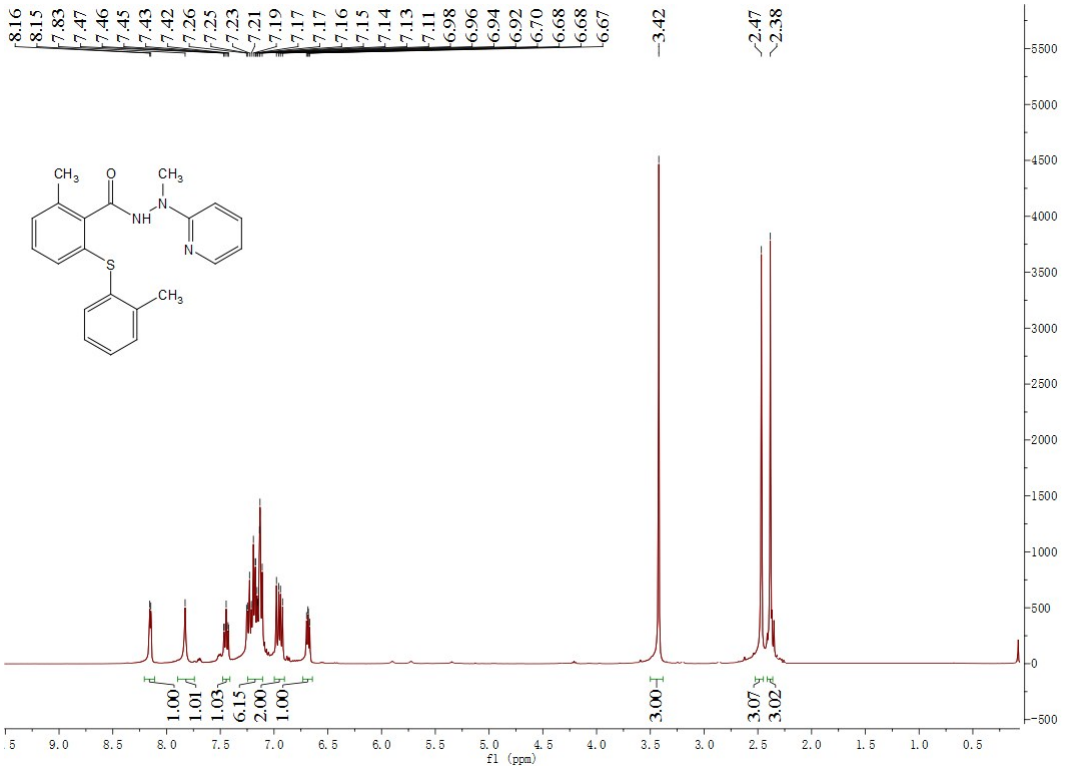

167.43
159.19
147.57
137.65
137.24
131.47
131.20
130.37
130.31
129.50
107.68
38.37
19.48
137.82
137.65
137.24
134.59
133.18
131.86
131.47
131.20
130.37
130.31
129.50
CH3
O
CH3
NH
N
N
S
Cl
f1 (ppm)
f1 (ppm)

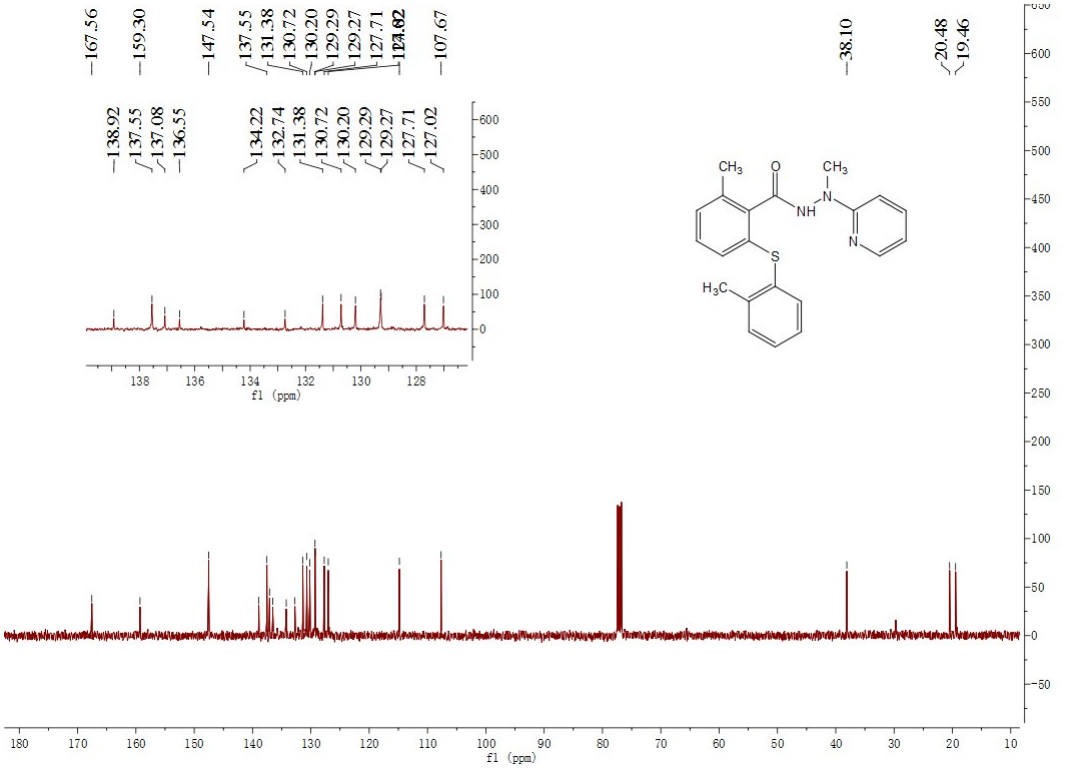
Compound **3u**


8.16
8.15
7.90
7.50
7.50
7.48
7.47
7.46
7.39
7.38
7.37
7.28
7.26
7.25
7.23
7.21
7.19
7.17
7.16
7.14
7.12
6.98
6.96
6.73
6.71
6.71
6.70
3.43
2.48
CH3
O
CH3
NH
N
N
S
Br
1.00
1.00
1.08
2.01
1.16
4.03
1.06
1.04
3.04
3.00
f1 (ppm)

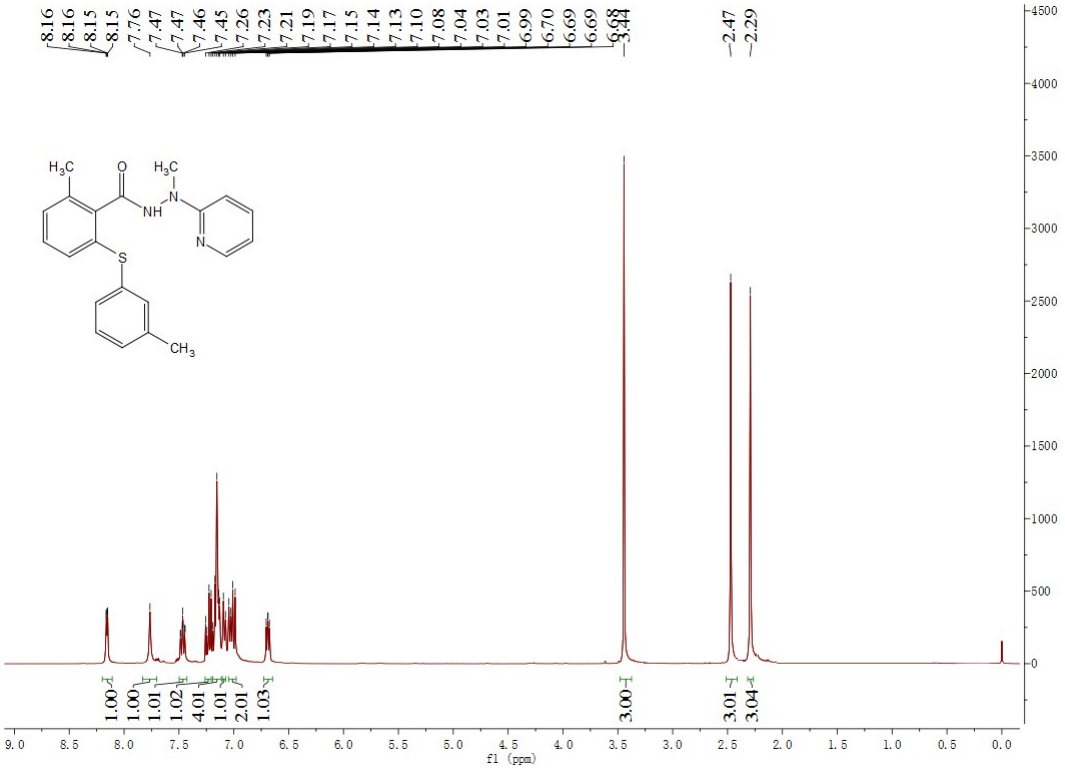

167.37
159.18
147.52
137.64
132.39
131.54
131.40
130.41
114.96
107.68
77.36
77.04
76.72
38.36
19.46
138.03
137.64
137.27
135.45
132.39
131.54
131.40
130.41
CH3
O
CH3
NH
N
N
S
Br
f1 (ppm)

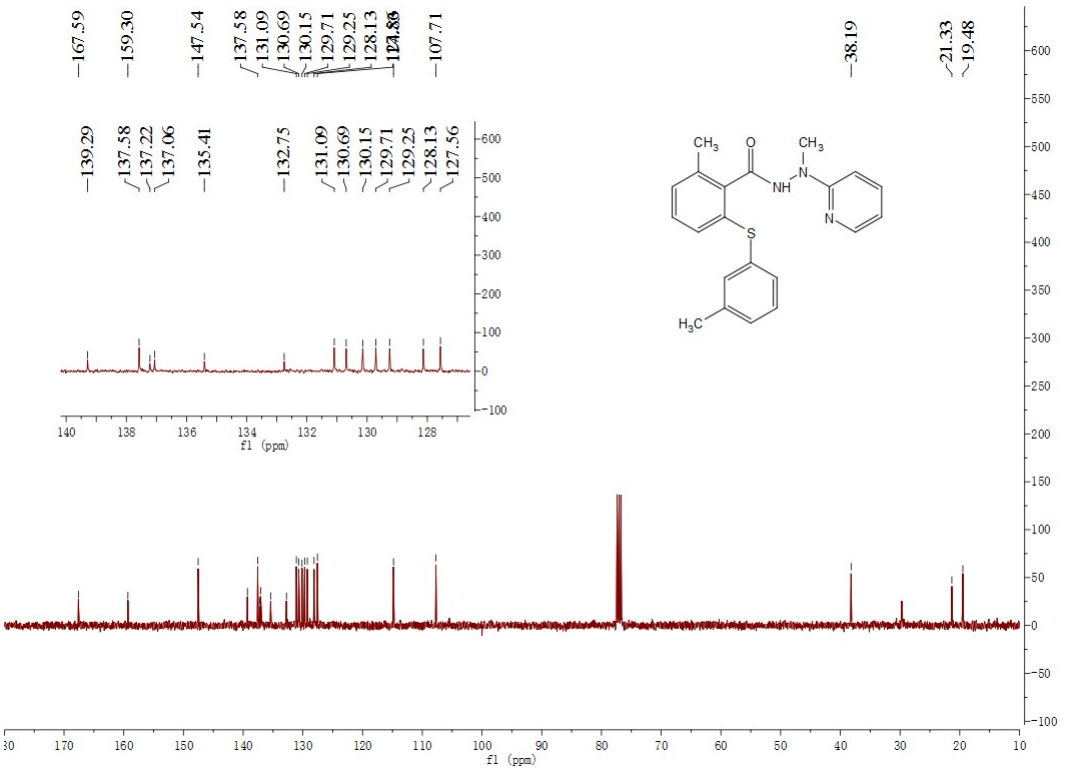
Compound **3v**


8.16
8.15
7.83
7.47
7.46
7.45
7.43
7.42
7.26
7.25
7.23
7.21
7.19
7.17
7.17
7.16
7.15
7.14
7.13
7.11
6.98
6.96
6.94
6.92
6.70
6.68
6.67
3.42
2.47
2.38
1.00
1.01
1.03
6.15
2.00
1.00
3.00
3.07
3.02
f1 (ppm)

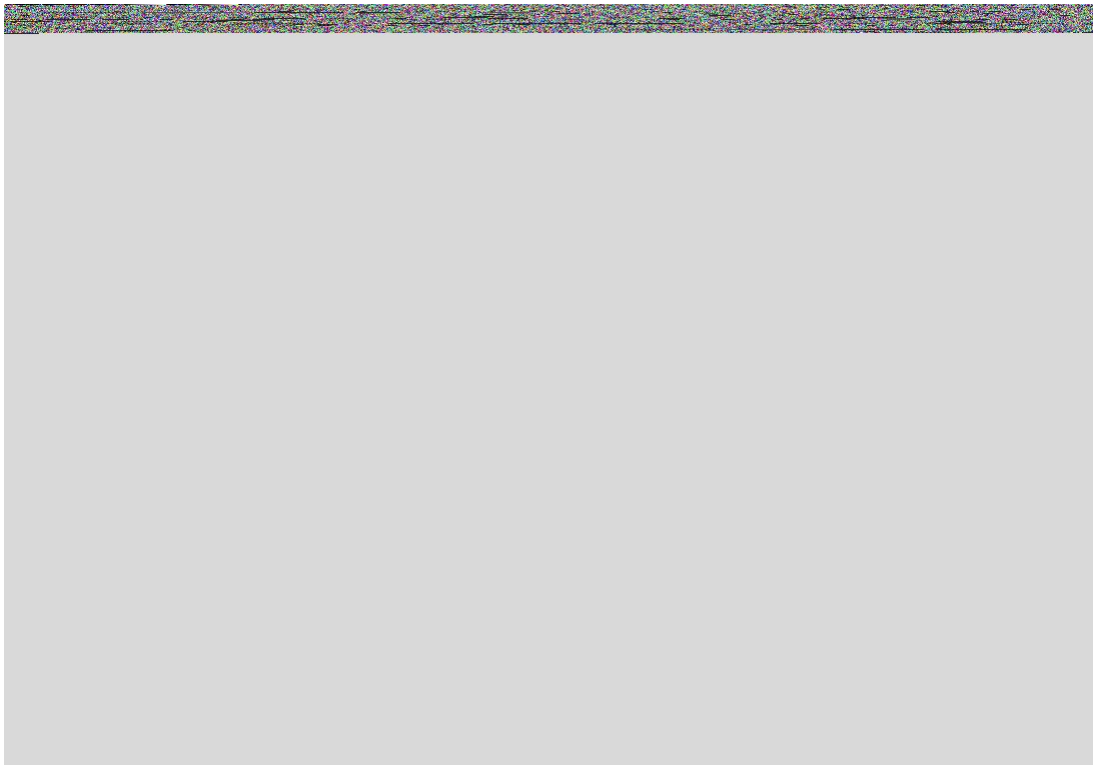

167.56
159.30
147.54
137.55
131.38
130.72
130.20
129.29
129.27
127.71
124.82
107.67
38.10
20.48
19.46
138.92
137.55
137.08
136.55
134.22
132.74
131.38
130.72
130.20
129.29
129.27
127.71
127.02
f1 (ppm)

Compound **3w**

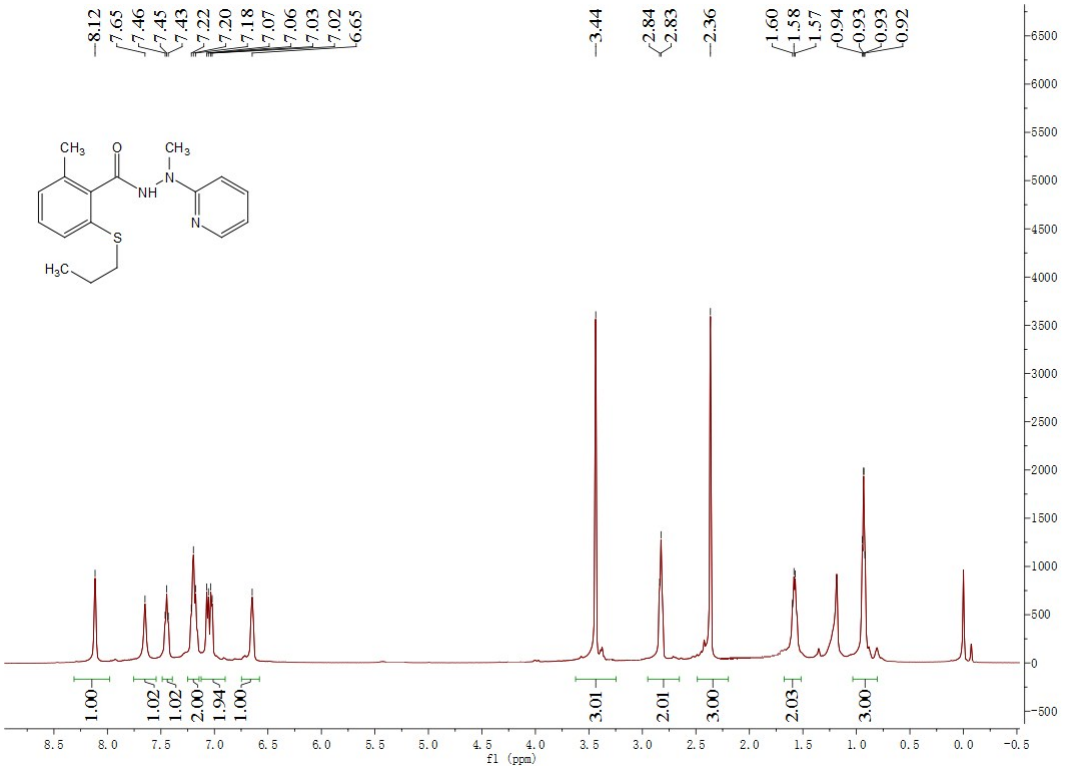

8.16
8.16
8.15
8.15
7.76
7.47
7.47
7.46
7.45
7.26
7.23
7.21
7.19
7.17
7.15
7.14
7.13
7.10
7.08
7.04
7.03
7.01
6.99
6.70
6.69
6.69
6.68
3.44
2.47
2.29
H3C
O
H3C
N
NH
N
S
CH3
1.00
1.00
1.01
1.02
4.01
1.01
2.01
1.03
3.00
3.01
3.04
f1 (ppm)

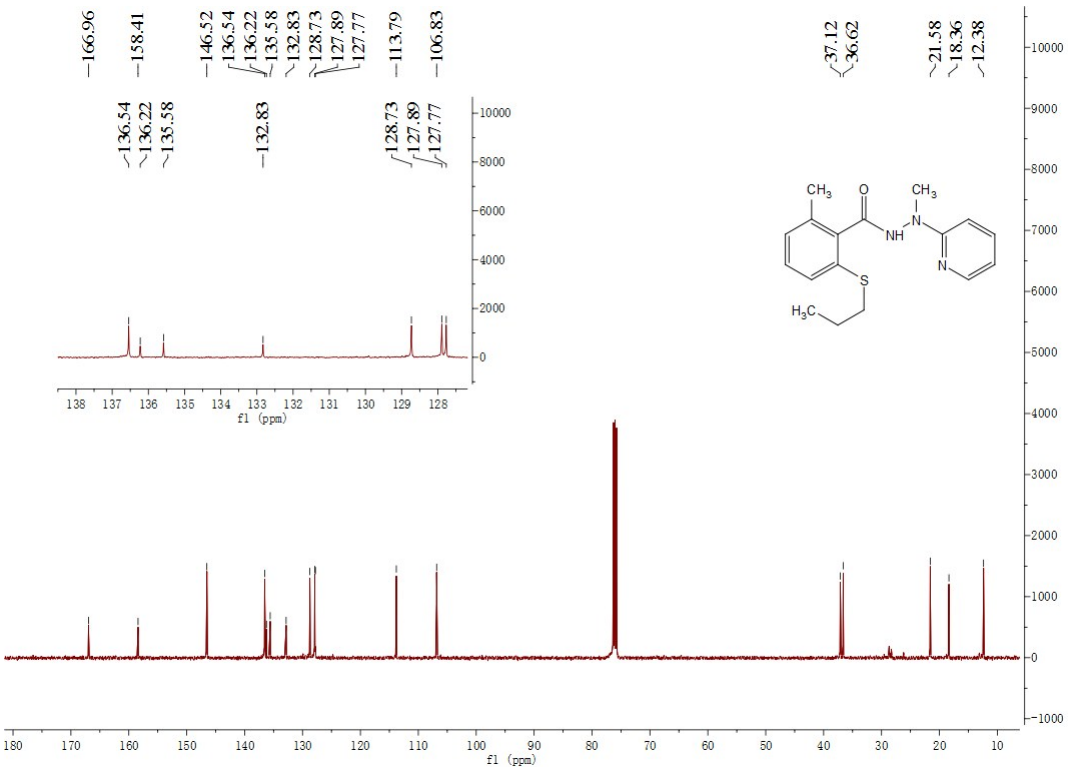

167.59
159.30
147.54
137.58
131.09
130.69
130.15
129.71
129.25
128.13
107.71
38.19
21.33
19.48
139.29
137.58
137.22
137.06
135.41
132.75
131.09
130.69
130.15
129.71
129.25
128.13
127.56
CH3
O
CH3
N
NH
N
S
H3C
f1 (ppm)
f1 (ppm)

Compound **3x**

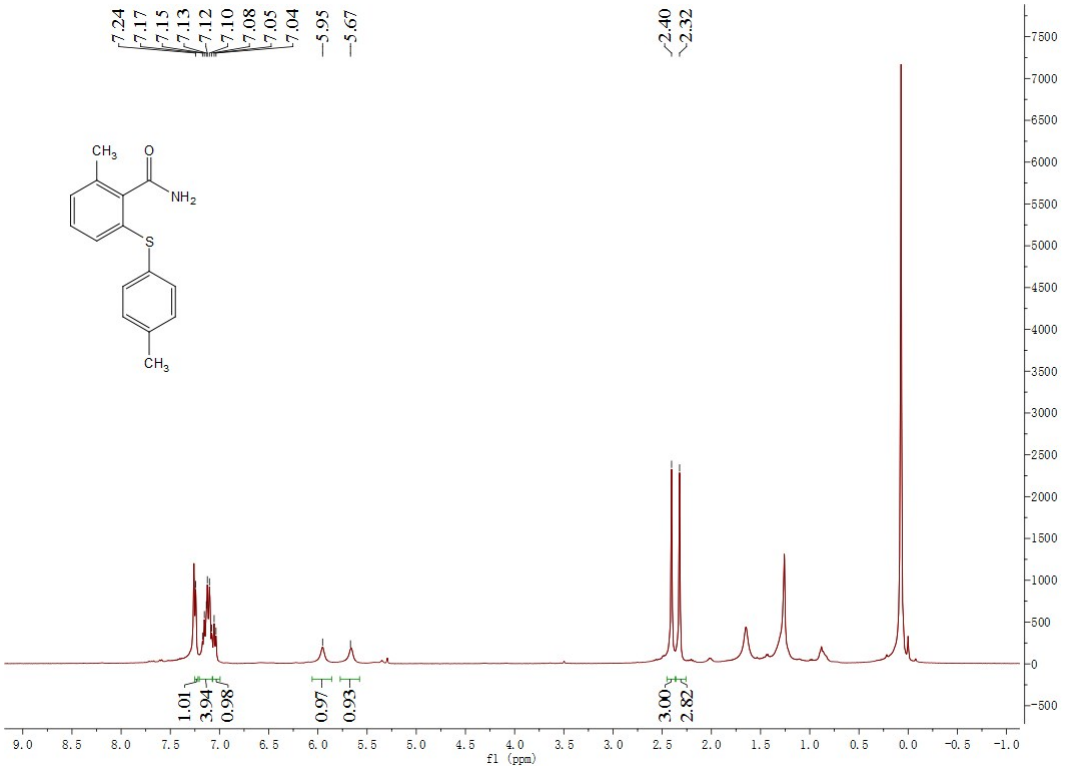


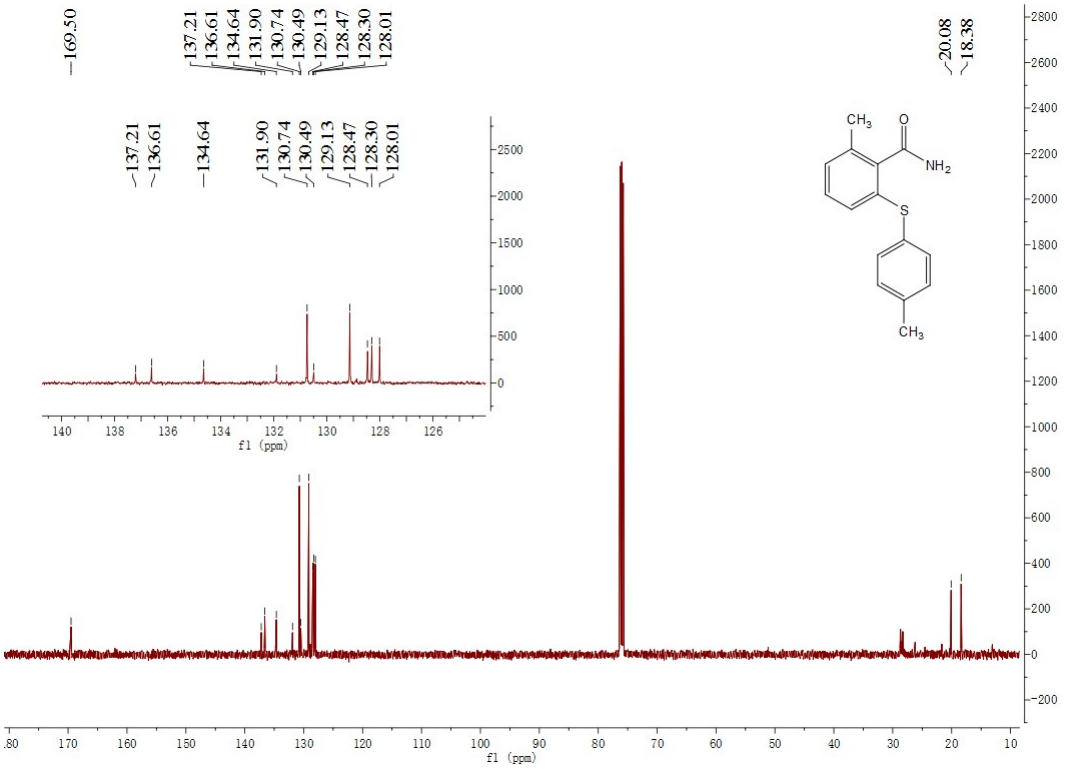
Compound **3y**


8.12
7.65
7.46
7.45
7.43
7.22
7.20
7.18
7.07
7.06
7.03
7.02
6.65
3.44
2.84
2.83
2.36
1.60
1.58
1.57
0.94
0.93
0.93
0.92
1.00
1.02
1.02
2.00
1.94
1.00
3.01
2.01
3.00
2.03
3.00
f1 (ppm)


166.96
158.41
146.52
136.54
136.22
135.58
132.83
128.73
127.89
127.77
113.79
106.83
37.12
36.62
21.58
18.36
12.38
f1 (ppm)

Compound **5**


7.24
7.17
7.15
7.13
7.12
7.10
7.08
7.05
7.04
5.95
5.67
2.40
2.32
CH3
O
NH2
S
CH3
1.01
3.94
0.98
0.97
0.93
3.00
2.82
f1 (ppm)


169.50
137.21
136.61
134.64
131.90
130.74
130.49
129.13
128.47
128.30
128.01
20.08
18.38
CH3
O
NH2
S
CH3
f1 (ppm)