Supplementary Materials

Reactions of Trifluorotriacetic Acid Lactone and Hexafluorodehydroacetic Acid with Amines: Synthesis of Trifluoromethylated 4-Pyridones and Aminoenones

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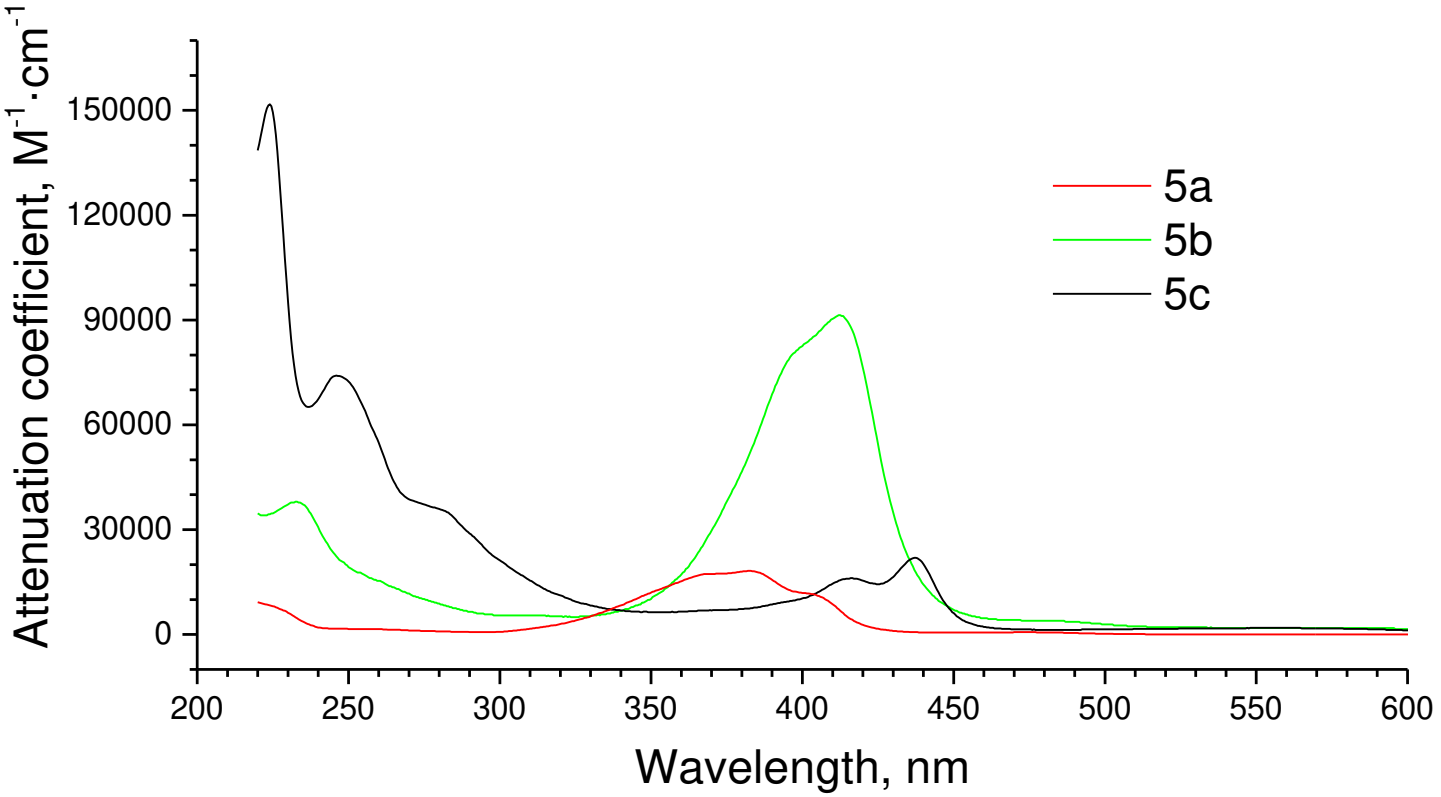
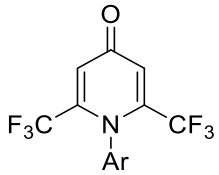


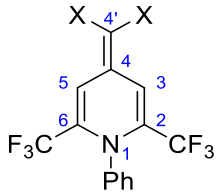
Figure S1. UV/Vis spectra of compounds **5** in EtOH (10^{-5}–10^{-6} M)

Table S1. Characteristic chemical shifts in the ^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds **3** in $CDCl_3$, δ, ppm (J, Hz)



3	Ar	C***F***$_3$	3-C***H***,5-C***H***	***C***F$_3$	2-***C***CF$_3$,6-***C***CF$_3$	3-***C***H,5-***C***H	4-***C***O
a	Ph	100.7	6.97	119.4 (275.7)	141.2 (33.3)	119.4 (4.7)	177.4
b	4-MeOC$_6$H$_4$	100.5	6.95				
c	3,4-F$_2$C$_6$H$_3$	100.7	6.96	119.3 (275.7)	140.9 (33.3)	119.4 (4.7)	177.1
d	4-BrC$_6$H$_4$	100.7	6.97	119.3 (275.8)	141.0 (32.8)	119.3 (4.5)	177.3
e	2,5-F$_2$C$_6$H$_3$	98.5	6.99	119.3 (275.5)	140.8 (34.1)	119.5 (4.6)	177.2
f	3-AcC$_6$H$_4$	100.8	6.99	119.2 (276.1)	141.6 (unresolved)	119.0 (unresolved)	177.2
g	3-F$_3$CC$_6$H$_4$	98.7	6.99	119.3 (275.5)	140.9 (33.4)	119.4 (4.7)	177.2
h	2-MeC$_6$H$_4$	99.0	7.01	119.3 (275.8)	141.3 (32.2)	119.6 (4.2)	177.9
i	2-ClC$_6$H$_4$	98.7	7.02	119.3 (275.8)	140.9 (33.9)	119.6 (4.5)	177.6
j	2,5-Me$_2$C$_6$H$_3$	99.0	7.01				
k	4-O$_2$NC$_6$H$_4$	101.0	7.01				

Table S2. Characteristic chemical shifts in the ^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds **5** in DMSO-d_6, δ, ppm (J, Hz)



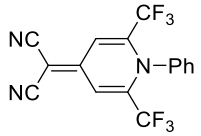
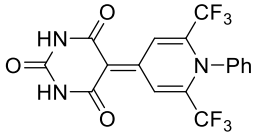
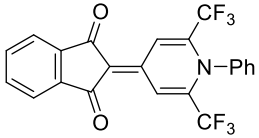
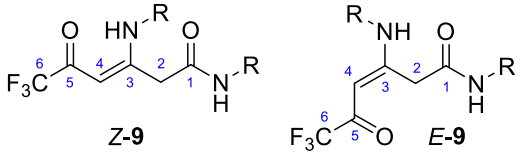
5	Structure	C***F***$_3$	***H***-3,5	***C***F$_3$	***C***-2, ***C***-6	***C***-3, ***C***-5	***C***-4	***C***-4'	2C Ph	2C Ph	C Ph	C Ph
a		102.5	7.26	118.7 (275.9)	138.2 (33.0)	112.7 (5.3)	154.2	57.1	130.0	130.4	132.1	135.6
b		103.2	9.77	119.8 (275.5)	138.3 (32.3)	116.8 (5.7)	153.0	95.0	128.7	130.1	131.7	134.6
c		102.8	9.10	119.2 (275.2)	138.9 (32.7)	113.4 (5.7)	146.0	107.2	128.5	130.0	131.6	135.1

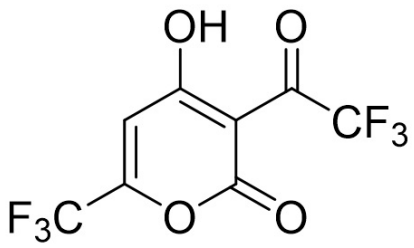
Table S3. Characteristic chemical shifts in the ^{1}H, ^{13}C, and ^{19}F NMR spectra of *E*- and *Z*-isomers of enaminones **9** used for analysis of equilibrium mixtures, δ, ppm (J, Hz)



Z-**9** *E*-**9**

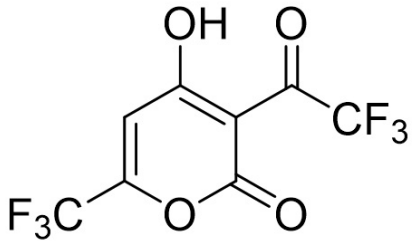
R	Solvent	Enaminone	C***F***$_3$	2-C***H***$_2$	4-C***H***	1-N***H***	3-N***H***	1-***C***O	2-***C***H$_2$	***C***-3	4-***C***H	5-***C***O	***C***F$_3$
Ph	DMSO-d$_6$	***Z*-9a**	87.1	3.65	5.79	10.08	12.56						
		***E*-9a**	86.6	4.06	5.59	10.23 and 10.31							
Ph	$CDCl_3$	***Z*-9a**	85.1	3.49	5.72	7.77	12.58	163.4	41.5	164.0	91.3	177.8 (33.7)	117.2 (288.3)
		***E*-9a**	84.8	4.04	5.82	8.71	9.70	162.5	42.3	166.3	88.7	177.6 (32.1)	117.6 (290.2)
4-BrC$_6$H$_4$	$CDCl_3$	***Z*-9b**	85.0	3.41	5.70	7.43	12.42						
		***E*-9b**	84.8	3.98	5.78	8.32	9.62						
4-MeOC$_6$H$_4$	$CDCl_3$	***Z*-9c**	85.1	3.38	5.68	7.12	12.39	164.0 or 164.2	41.4	164.0 or 164.2	90.9	177.5 (33.6)	117.3 (288.6)
		***E*-9c**	84.9	4.00	5.68	8.74	9.63	163.2	42.0	165.9	88.25	177.9 (31.3)	117.7 (290.2)
Bn	DMSO-d$_6$	***Z*-9d**		3.55	5.50	8.76	11.29						
		***E*-9d**		3.84	5.27	8.45	9.08						
Bn	$CDCl_3$	***Z*-9d**	85.1	3.31	5.44	6.04	11.32	164.9	41.1	165.3	90.2	177.0 (33.5)	117.3 (288.4)
		***E*-9d**	84.9	3.79	5.41	7.90	7.90	163.5	40.5	168.0	86.3	176.9 (32.1)	117.7 (290.5)
Bu	$CDCl_3$	***Z*-9e**	85.0	3.27	5.36	5.65	11.08						
		***E*-9e**	84.9	3.75	5.32	7.10	7.36						

^{1}H NMR (500 MHz, DMSO)



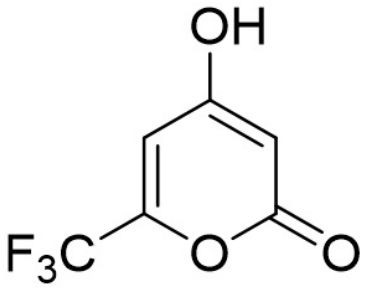
1

^{19}F NMR (471 MHz, DMSO)



1

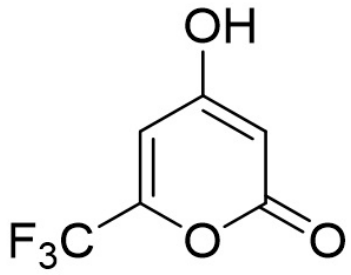
^{1}H NMR (500 MHz, DMSO)



2

92.02

^{19}F NMR (471 MHz, DMSO) δ 92.02.



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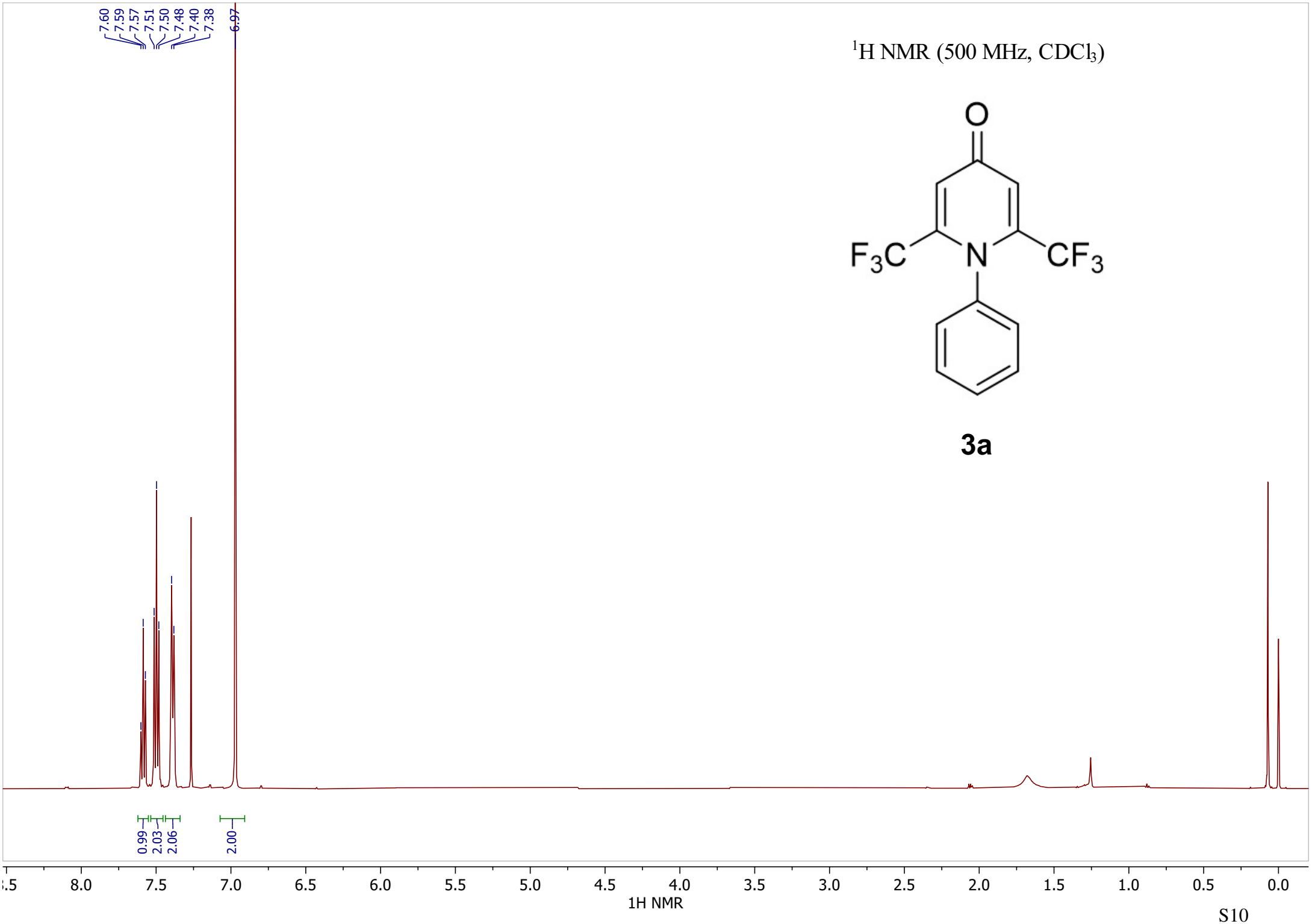
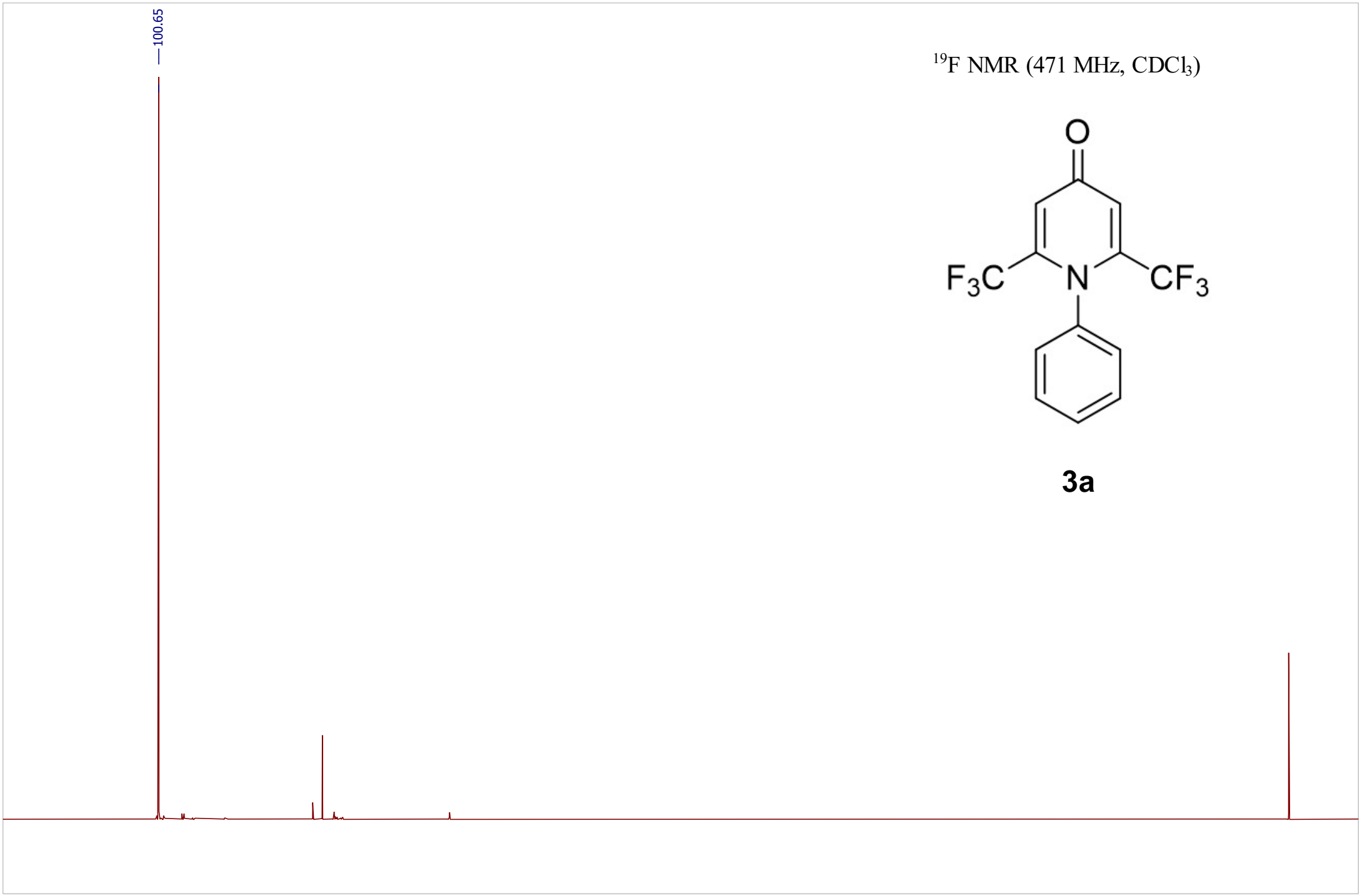
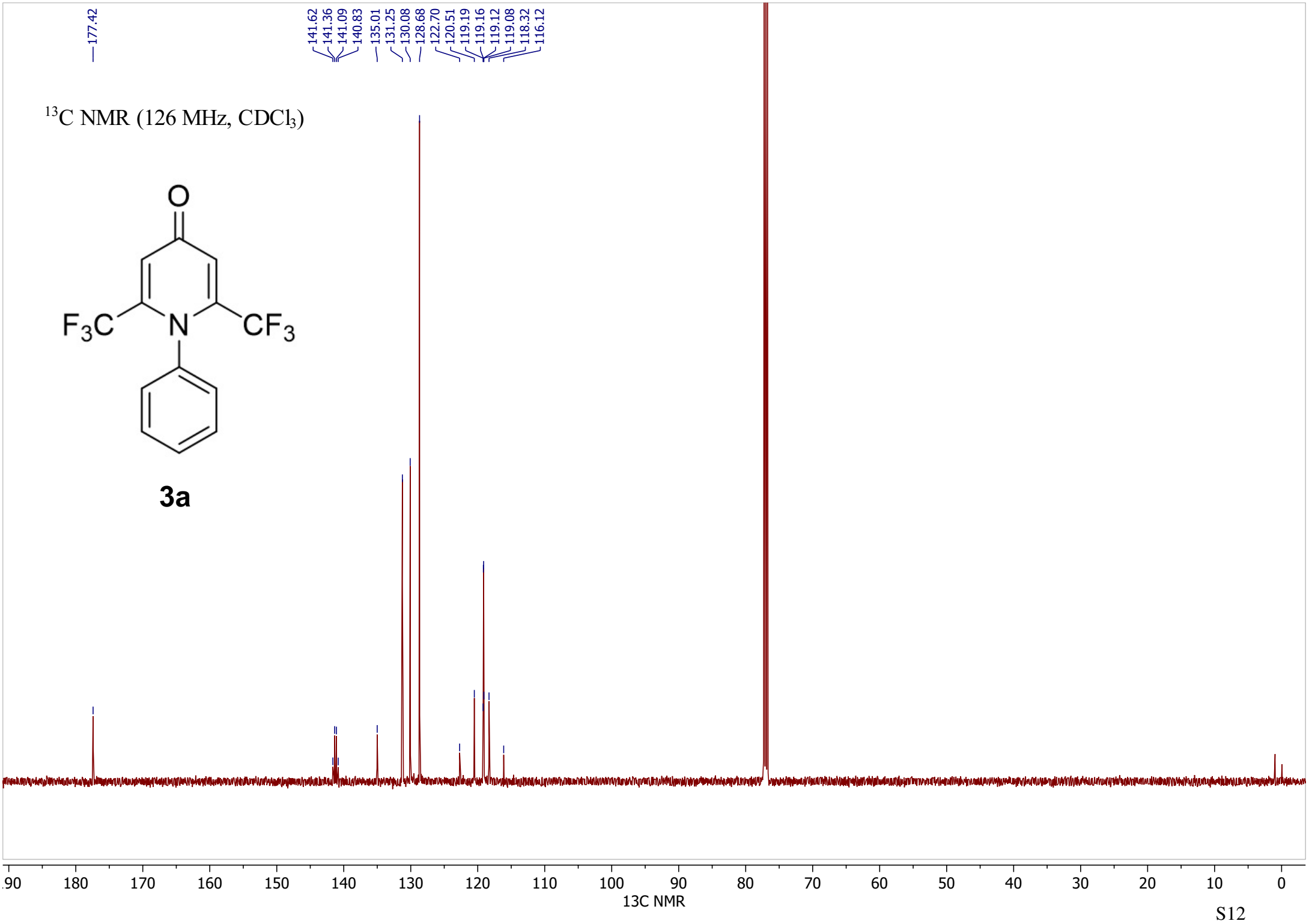


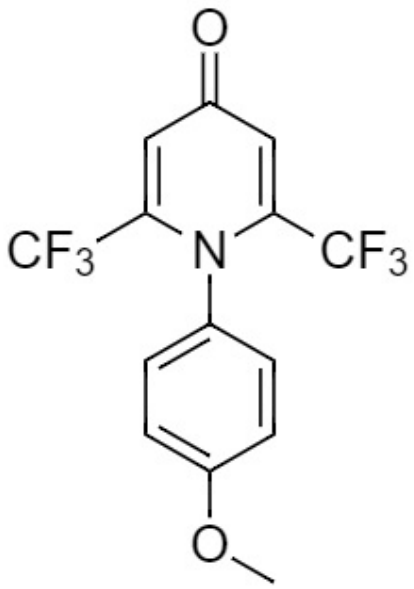
^{1}H NMR (500 MHz, $CDCl_3$)

3a

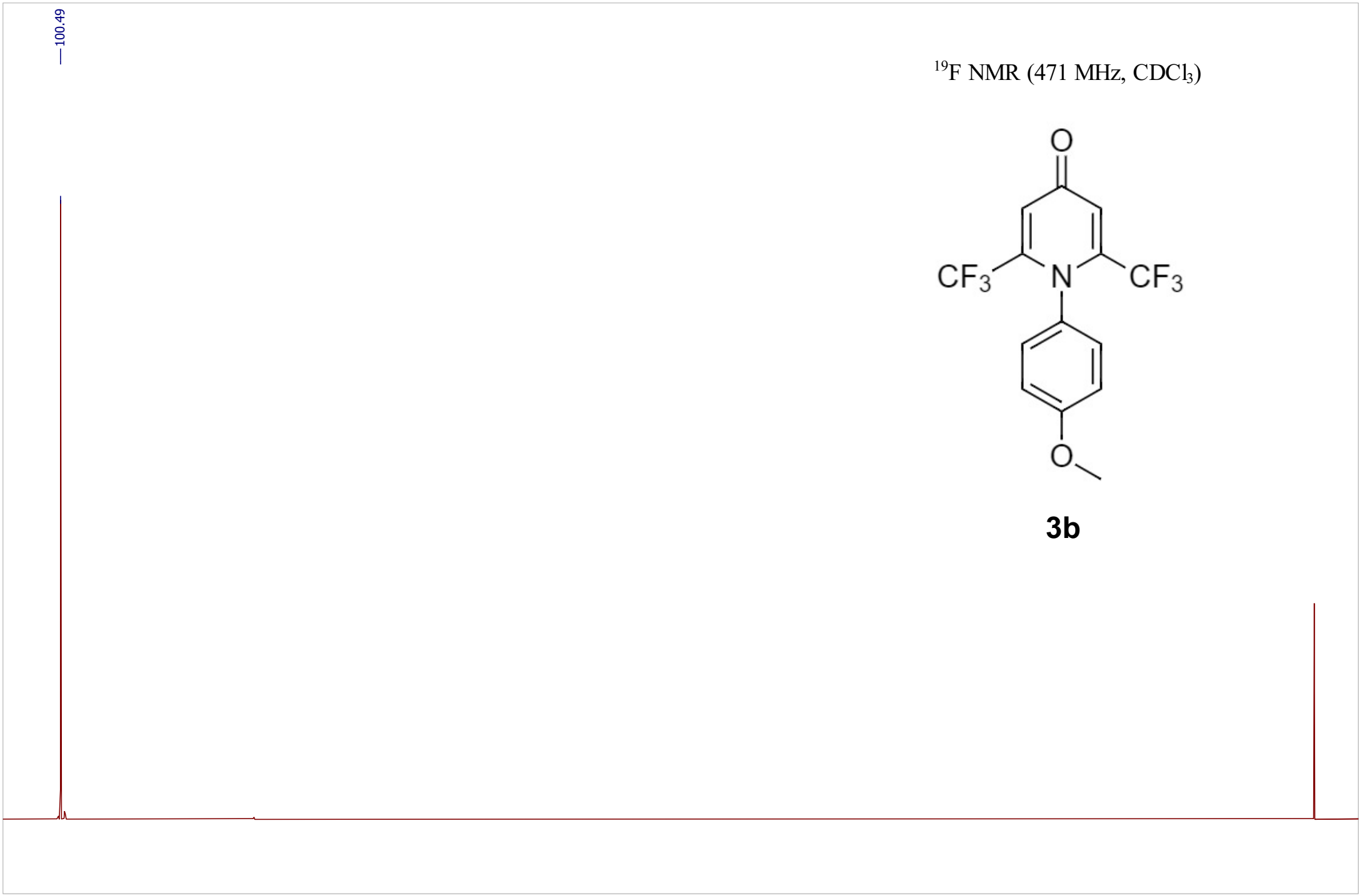

100.65
19F NMR (471 MHz, CDCl3)
O
F3C
N
CF3
3a
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
19F NMR


177.42
141.62
141.36
141.09
140.83
135.01
131.25
130.08
128.68
122.70
120.51
119.19
119.16
119.12
119.08
118.32
116.12
13C NMR (126 MHz, CDCl3)
O
F3C
N
CF3
3a
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR

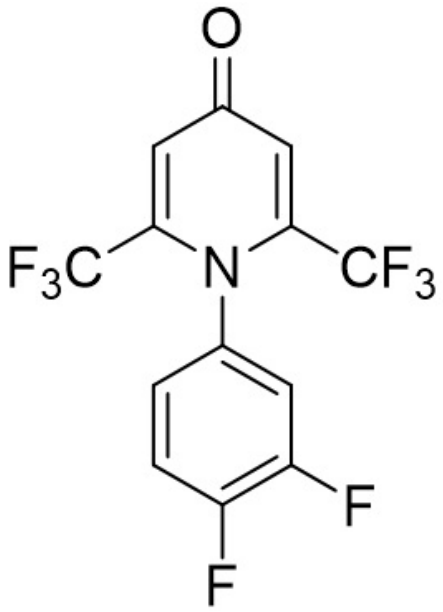
^{1}H NMR (500 MHz, $CDCl_3$)



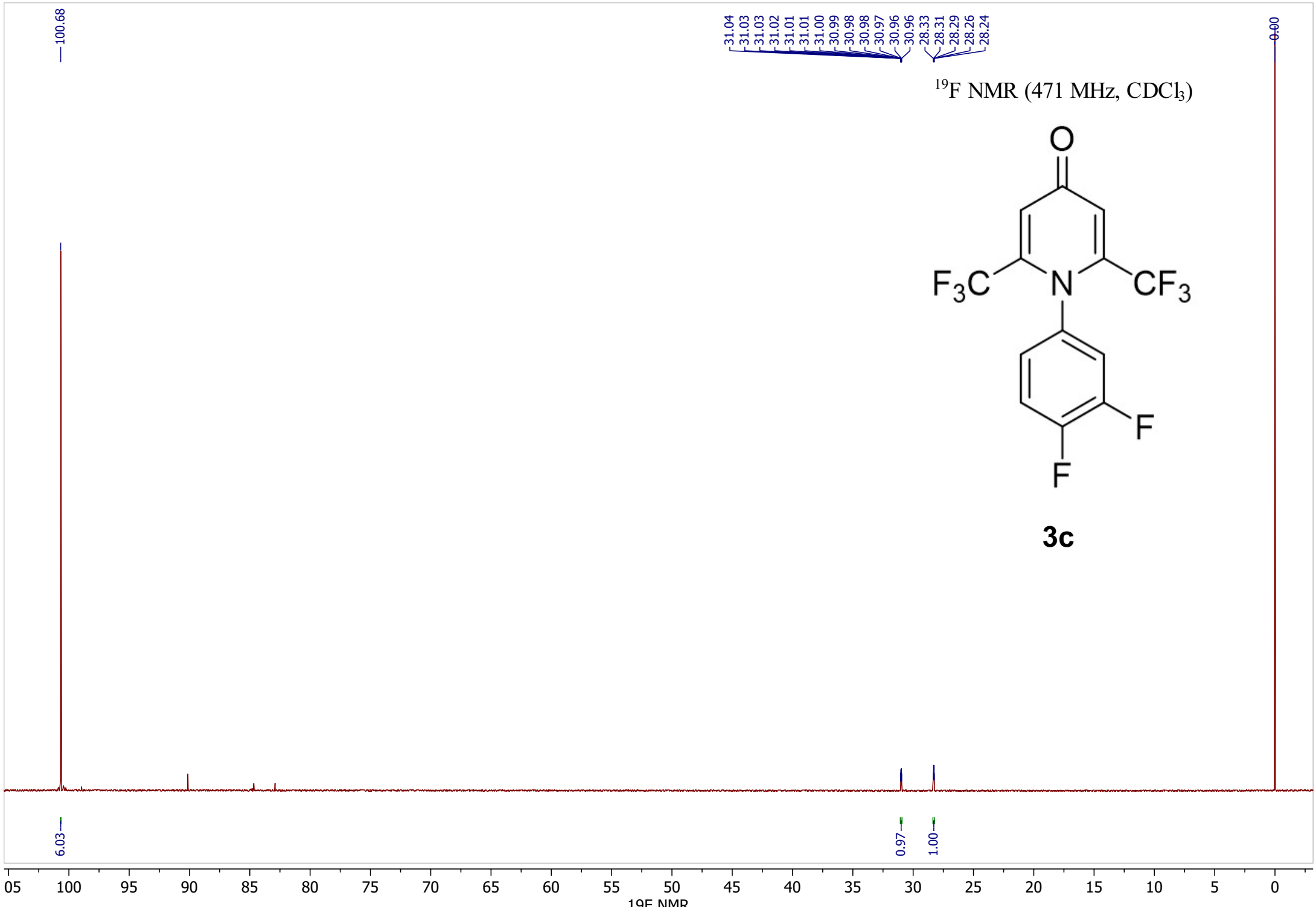
3b

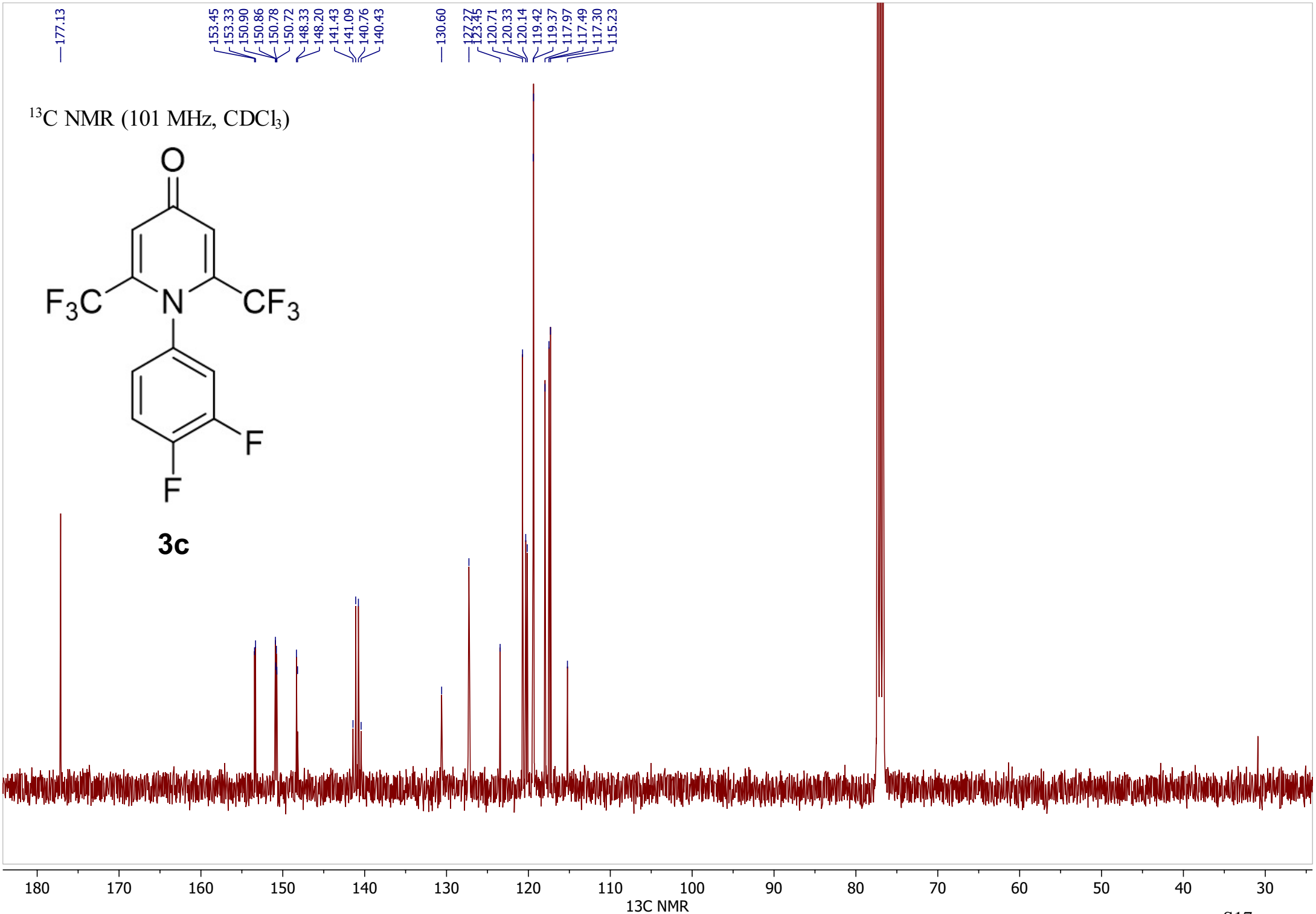

100.49
^{19}F NMR (471 MHz, $CDCl_3$)
O
CF_3
N
CF_3
O
3b
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
19F NMR

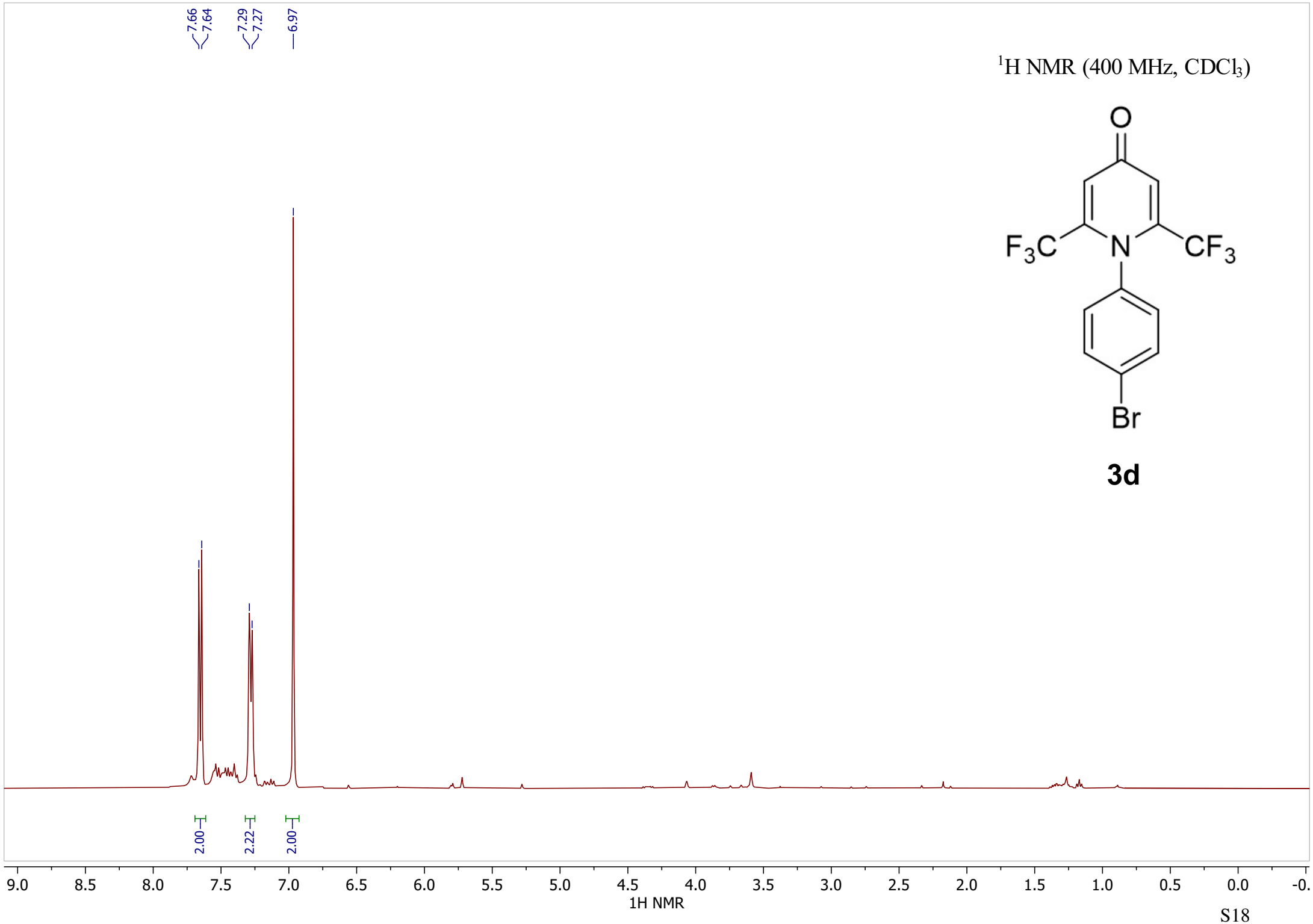
^{1}H NMR (500 MHz, $CDCl_3$)



3c

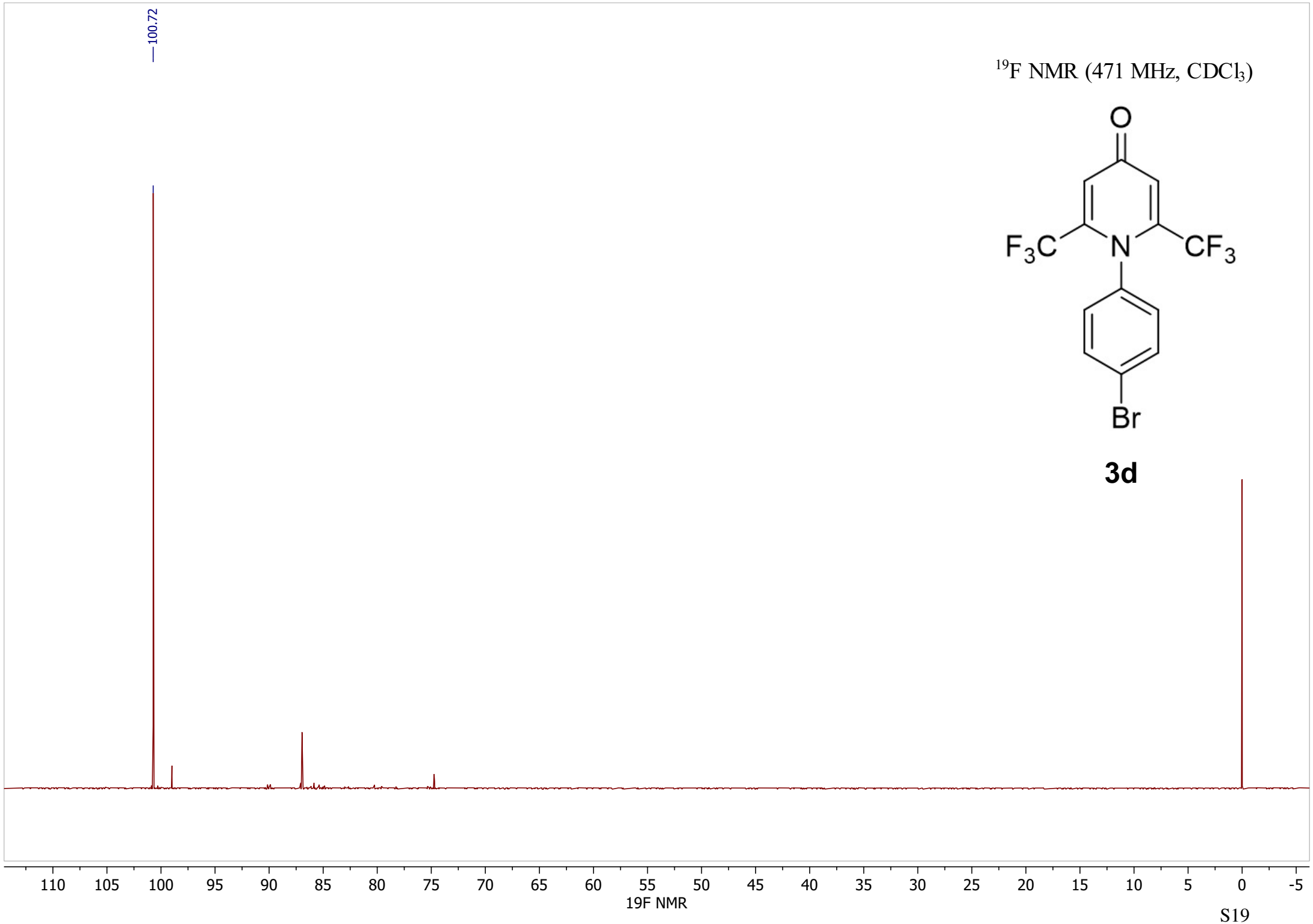

100.68
31.04
31.03
31.03
31.02
31.01
31.01
31.00
30.99
30.98
30.98
30.97
30.96
30.96
28.33
28.31
28.29
28.26
28.24
0.00
19F NMR (471 MHz, CDCl3)
O
F3C
N
CF3
F
F
3c
6.03
0.97
1.00
05
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
19F NMR

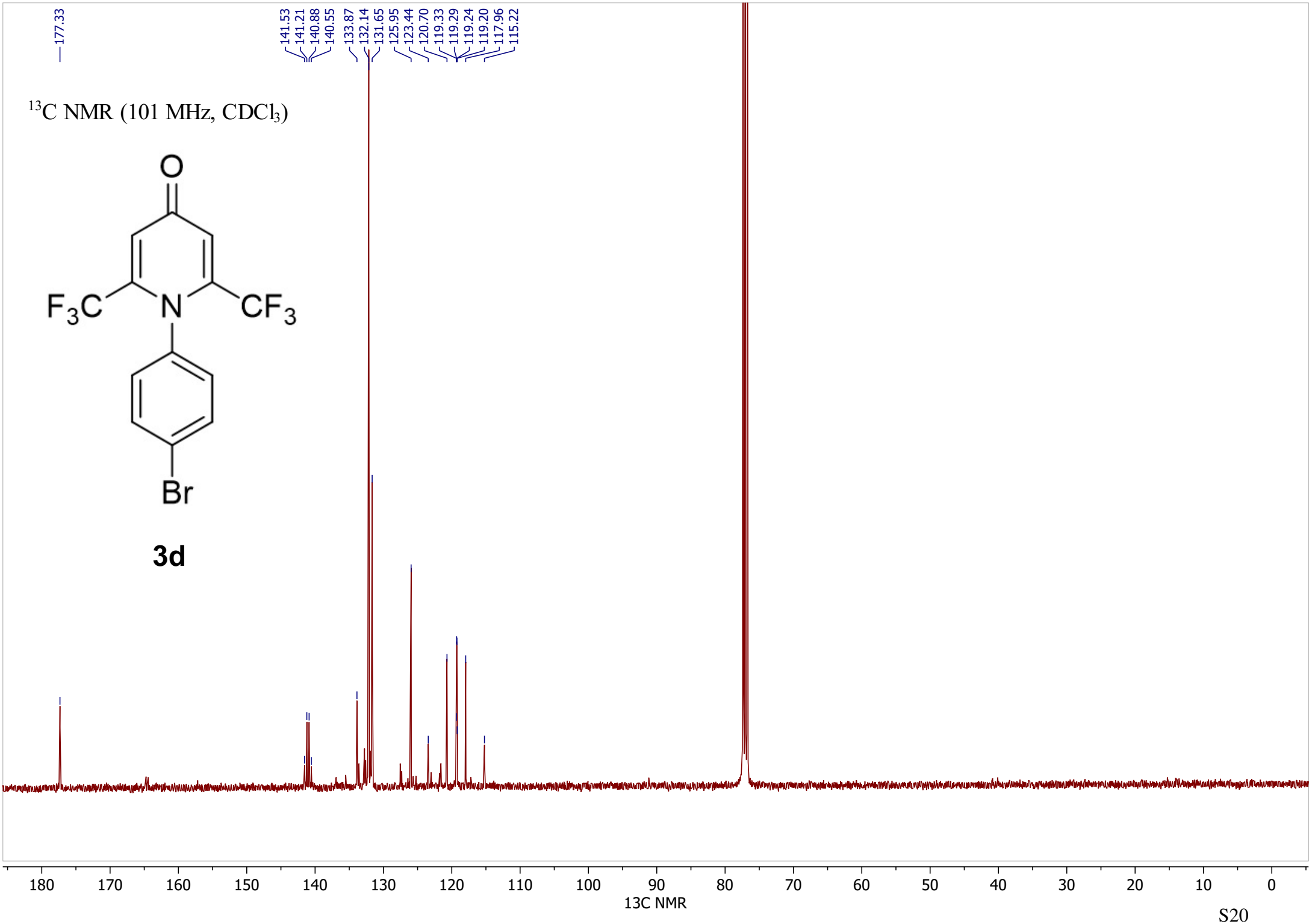

177.13
153.45
153.33
150.90
150.86
150.78
150.72
148.33
148.20
141.43
141.09
140.76
140.43
130.60
127.27
123.45
120.71
120.33
120.14
119.42
119.37
117.97
117.49
117.30
115.23
13C NMR (101 MHz, CDCl3)
O
F3C
N
CF3
F
F
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
13C NMR

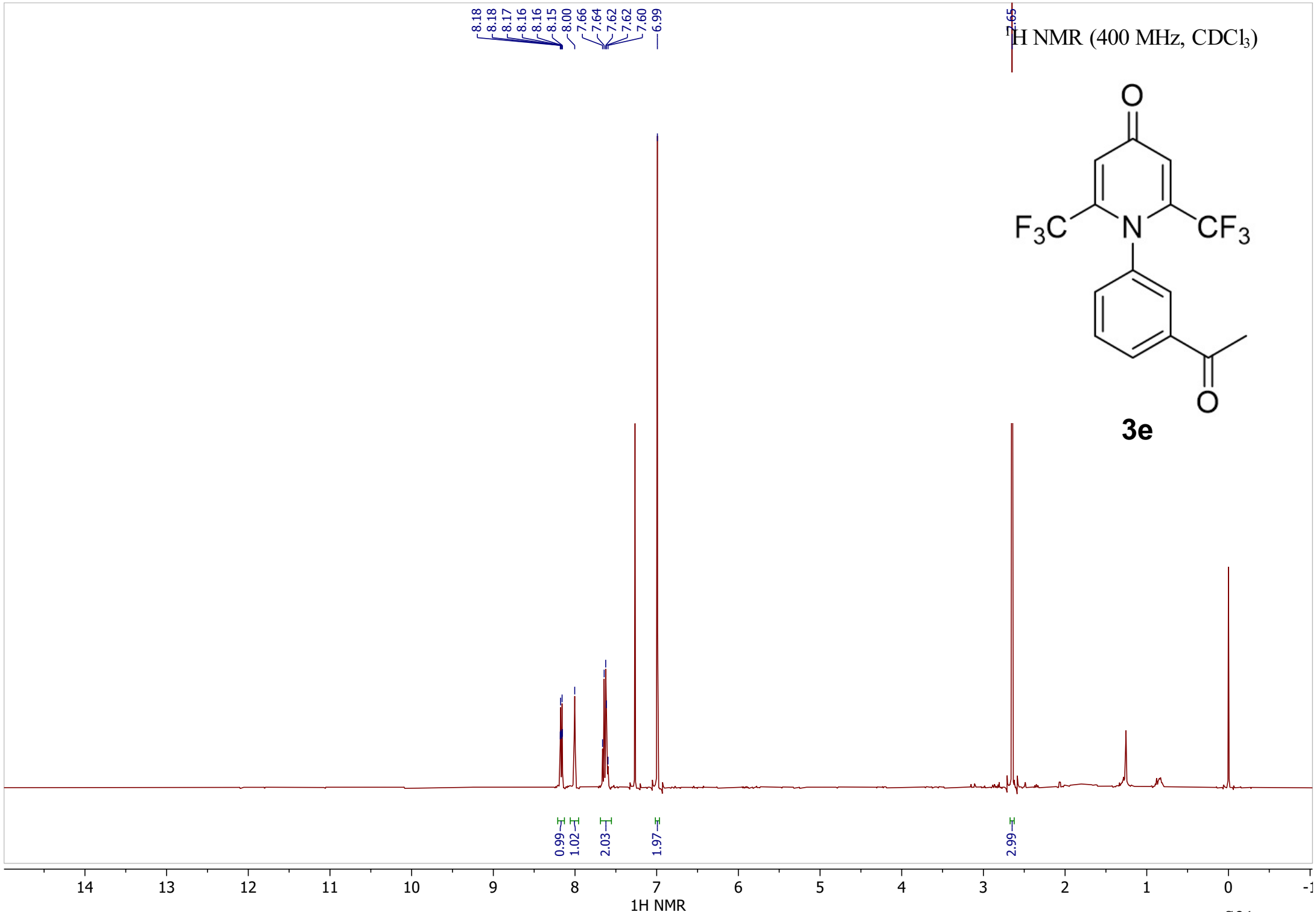


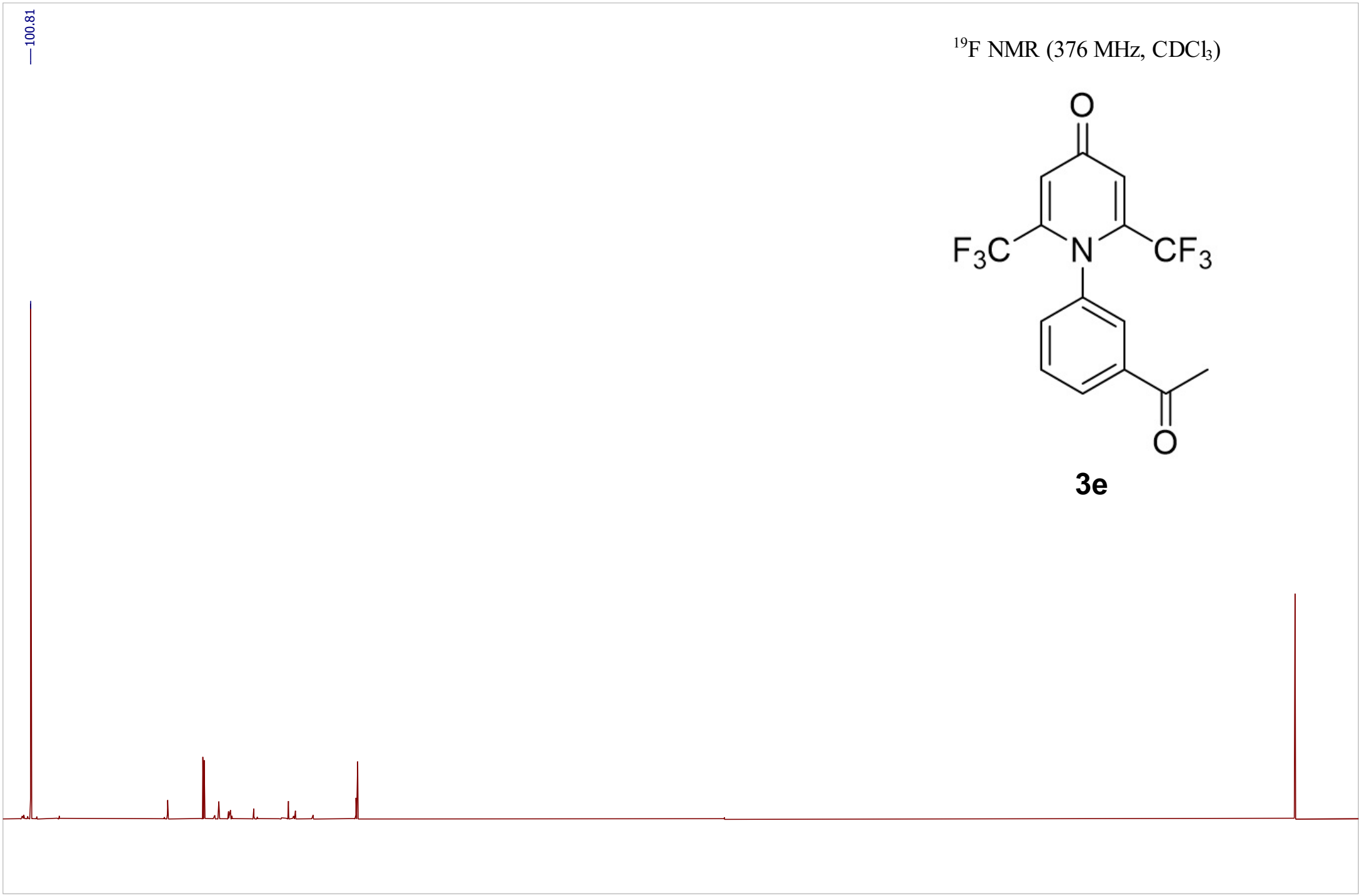
^{1}H NMR (400 MHz, $CDCl_3$)

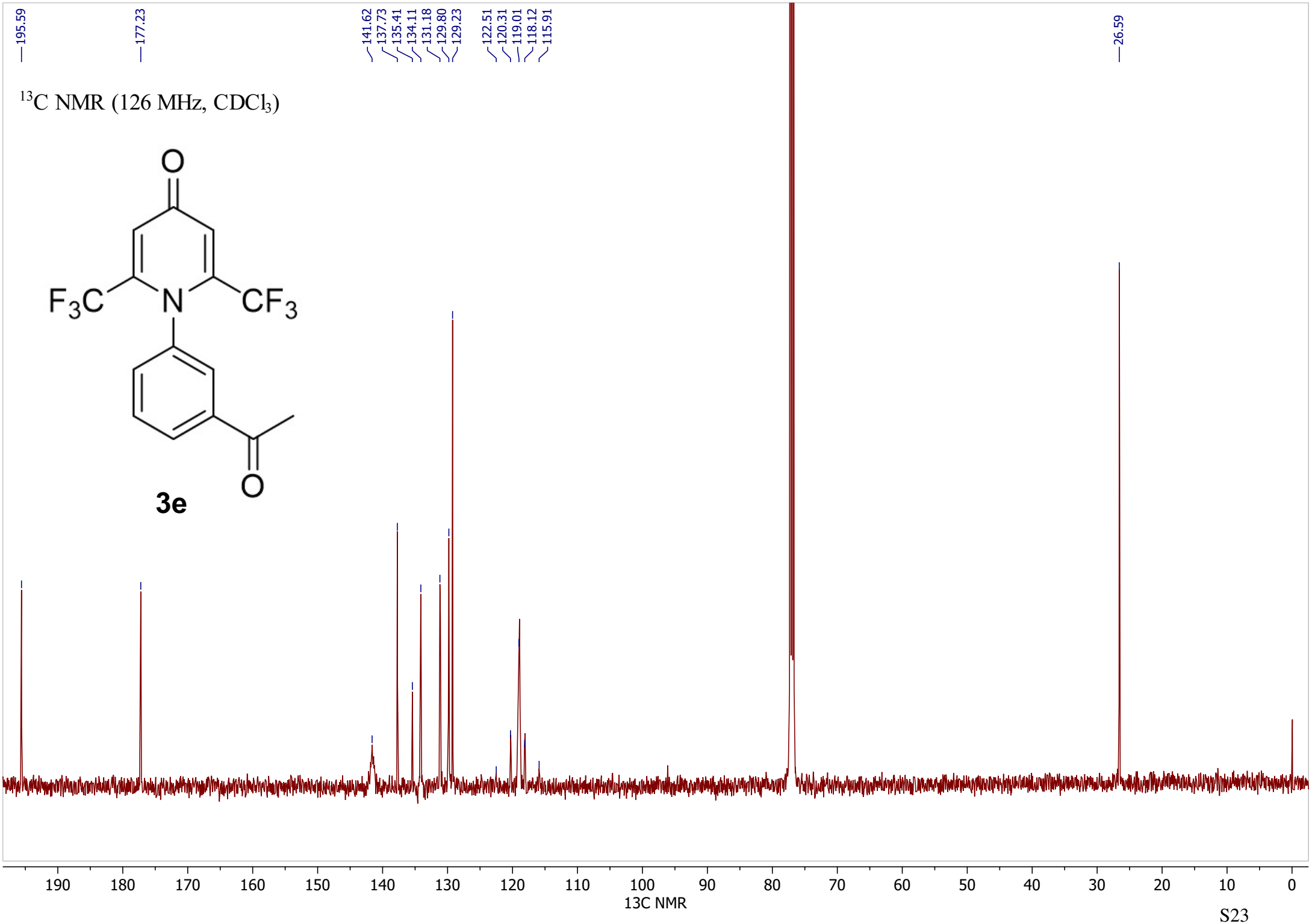
3d


100.72
^{19}F NMR (471 MHz, $CDCl_3$)
O
F_3C
N
CF_3
Br
3d
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
19F NMR

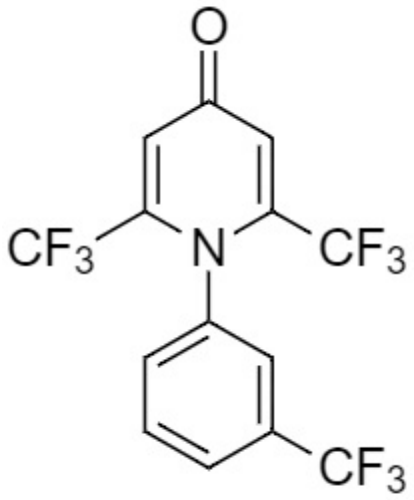

177.33
141.53
141.21
140.88
140.55
133.87
132.14
131.65
125.95
123.44
120.70
119.33
119.29
119.24
119.20
117.96
115.22
^{13}C NMR (101 MHz, $CDCl_3$)
O
F_3C
N
CF_3
Br
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR


8.18
8.18
8.17
8.16
8.16
8.15
8.00
7.66
7.64
7.62
7.62
7.60
6.99
2.65
^{1}H NMR (400 MHz, $CDCl_3$)
O
F_3C
N
CF_3
O
3e
0.99
1.02
2.03
1.97
2.99
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1H NMR

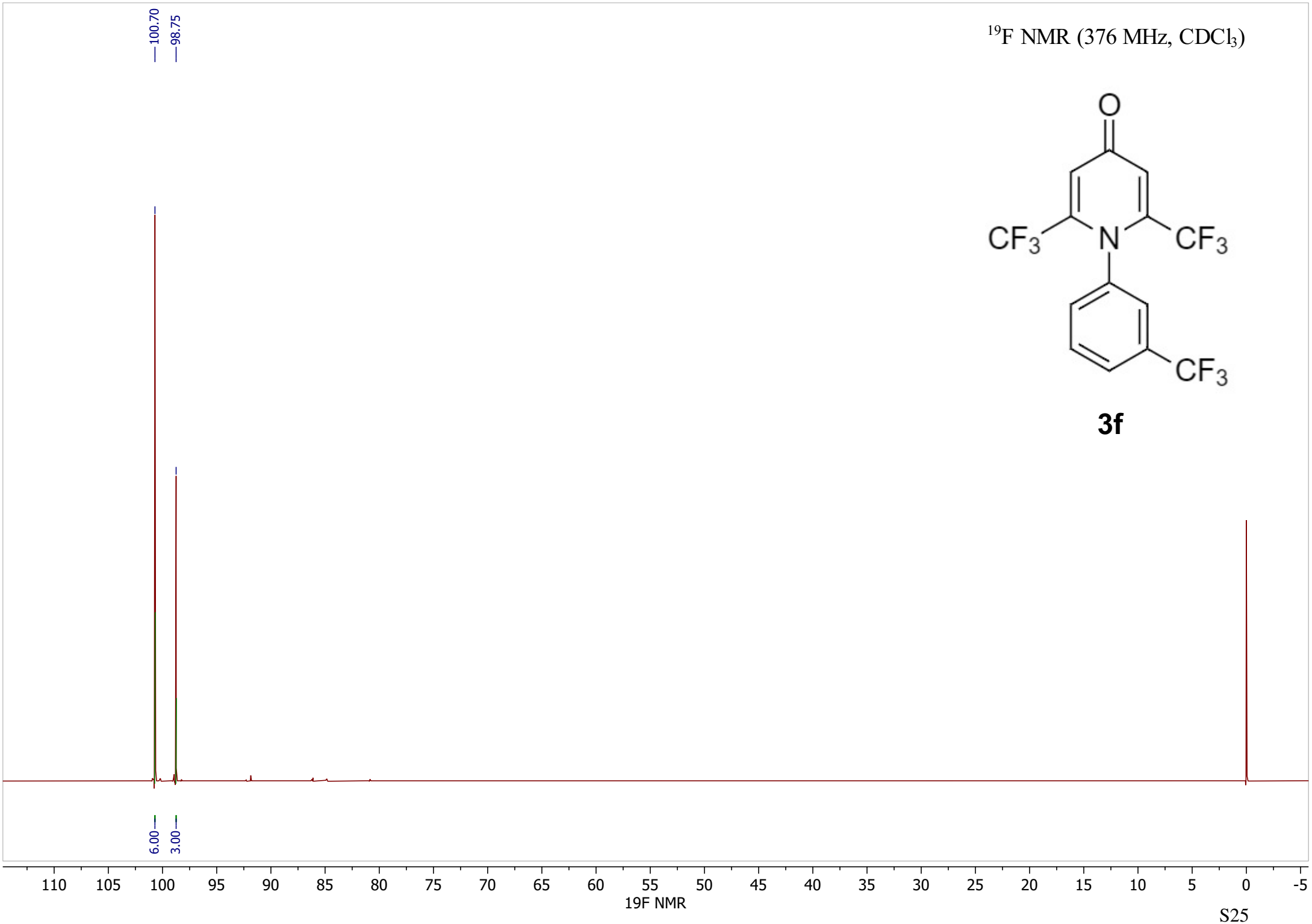

100.81
19F NMR (376 MHz, CDCl3)
O
F3C
N
CF3
O
3e
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
19F NMR

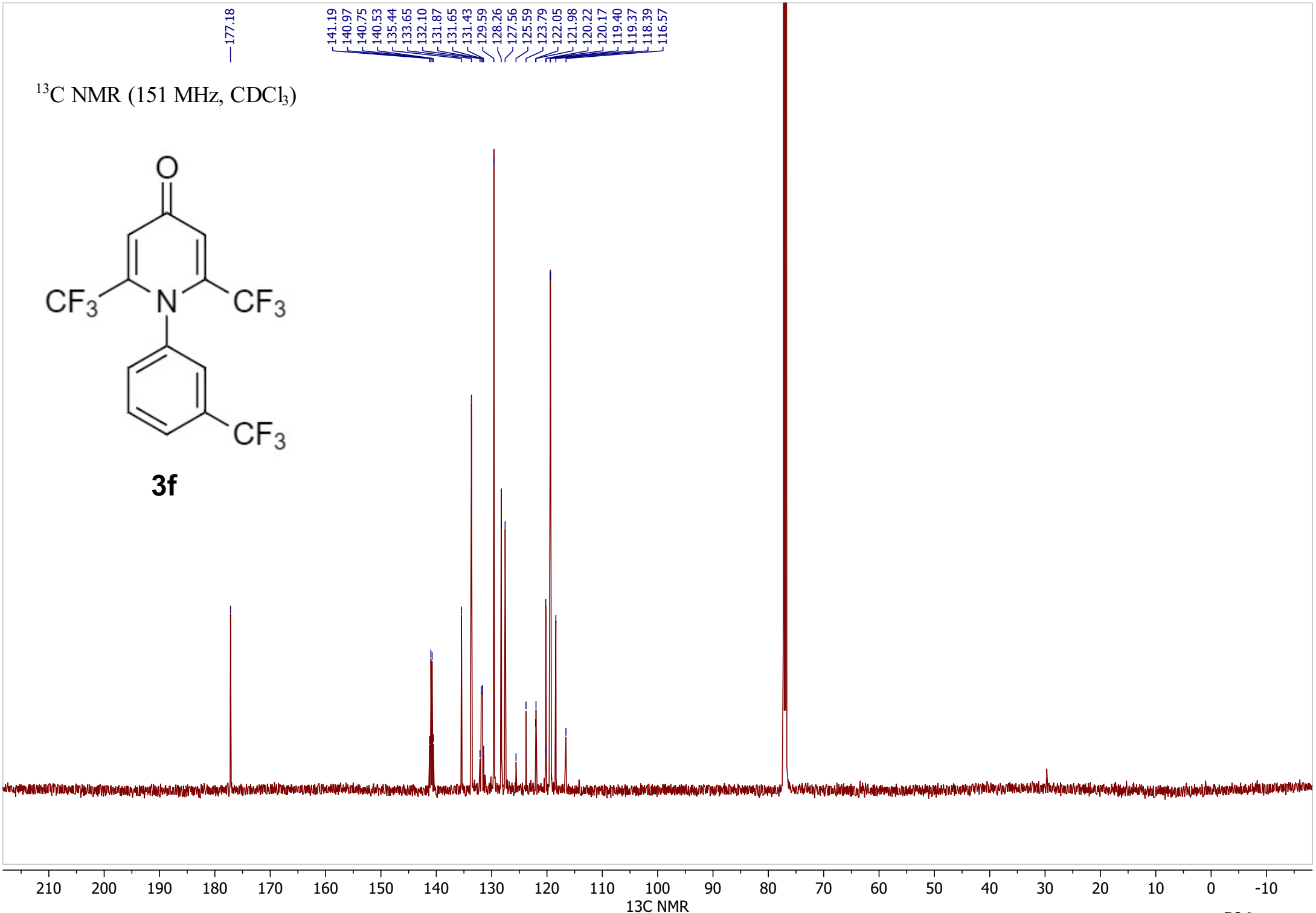

195.59
177.23
141.62
137.73
135.41
134.11
131.18
129.80
129.23
122.51
120.31
119.01
118.12
115.91
26.59
13C NMR (126 MHz, CDCl3)
O
F3C
N
CF3
O
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR

^{1}H NMR (600 MHz, $CDCl_3$)

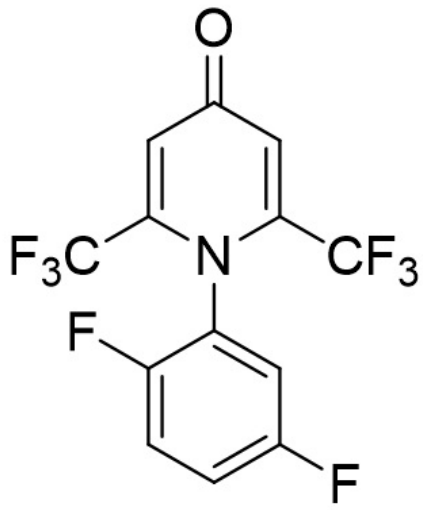


3f


100.70
98.75
^{19}F NMR (376 MHz, $CDCl_3$)
O
CF_3
N
CF_3
CF_3
3f
6.00
3.00
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
19F NMR

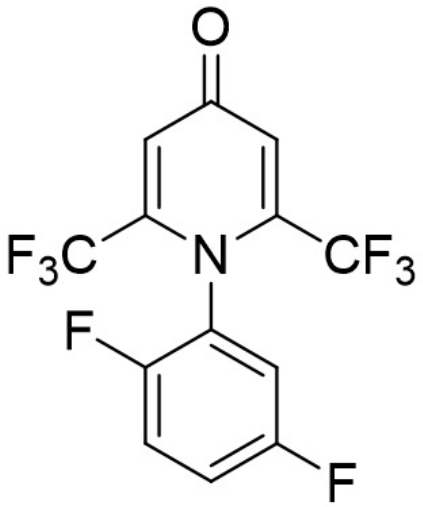

177.18
141.19
140.97
140.75
140.53
135.44
133.65
132.10
131.87
131.65
131.43
129.59
128.26
127.56
125.59
123.79
122.05
121.98
120.22
120.17
119.40
119.37
118.39
116.57
^{13}C NMR (151 MHz, $CDCl_3$)
O
CF_3
N
CF_3
CF_3
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C NMR

^{1}H NMR (500 MHz, $CDCl_3$)

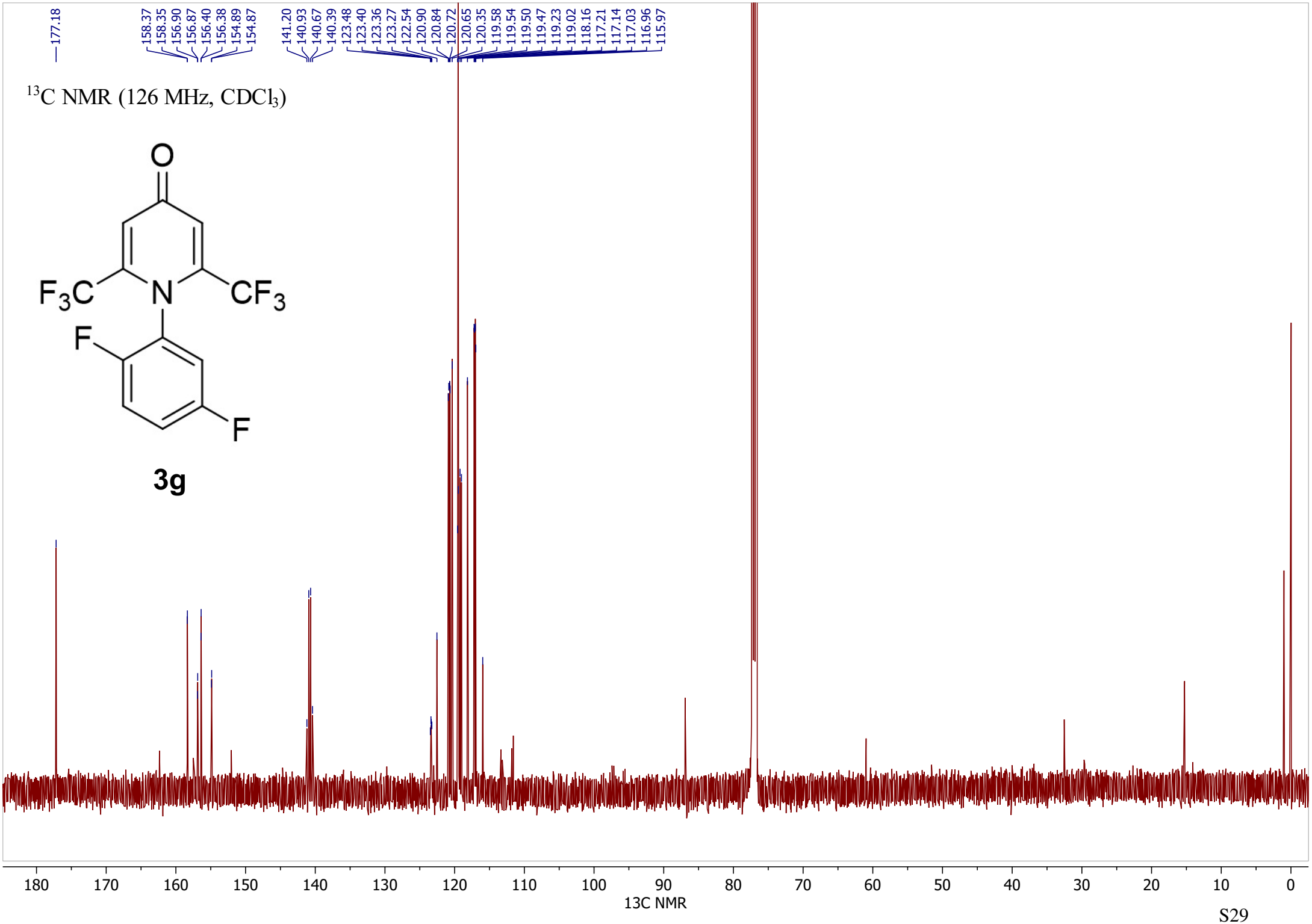


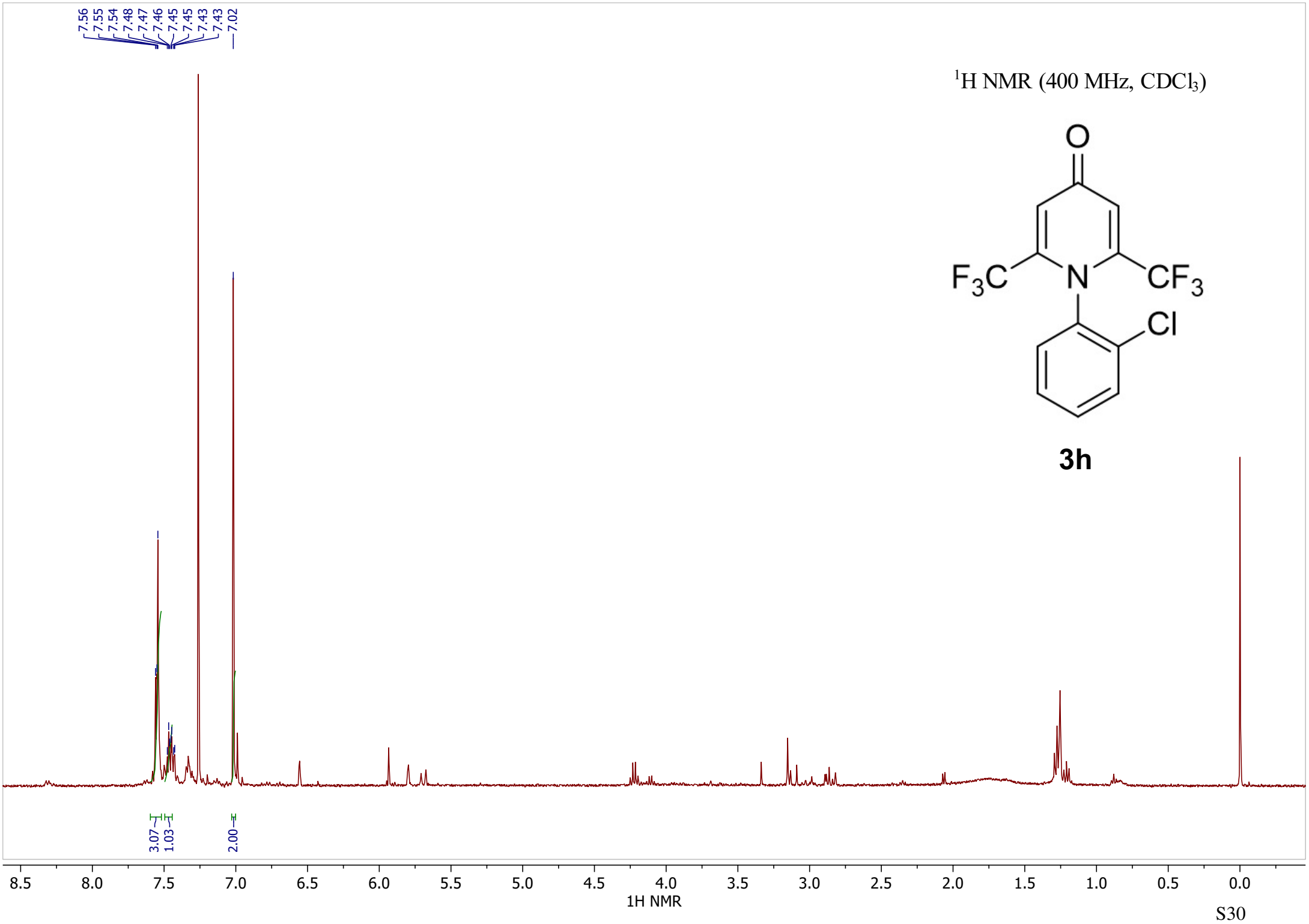
3g

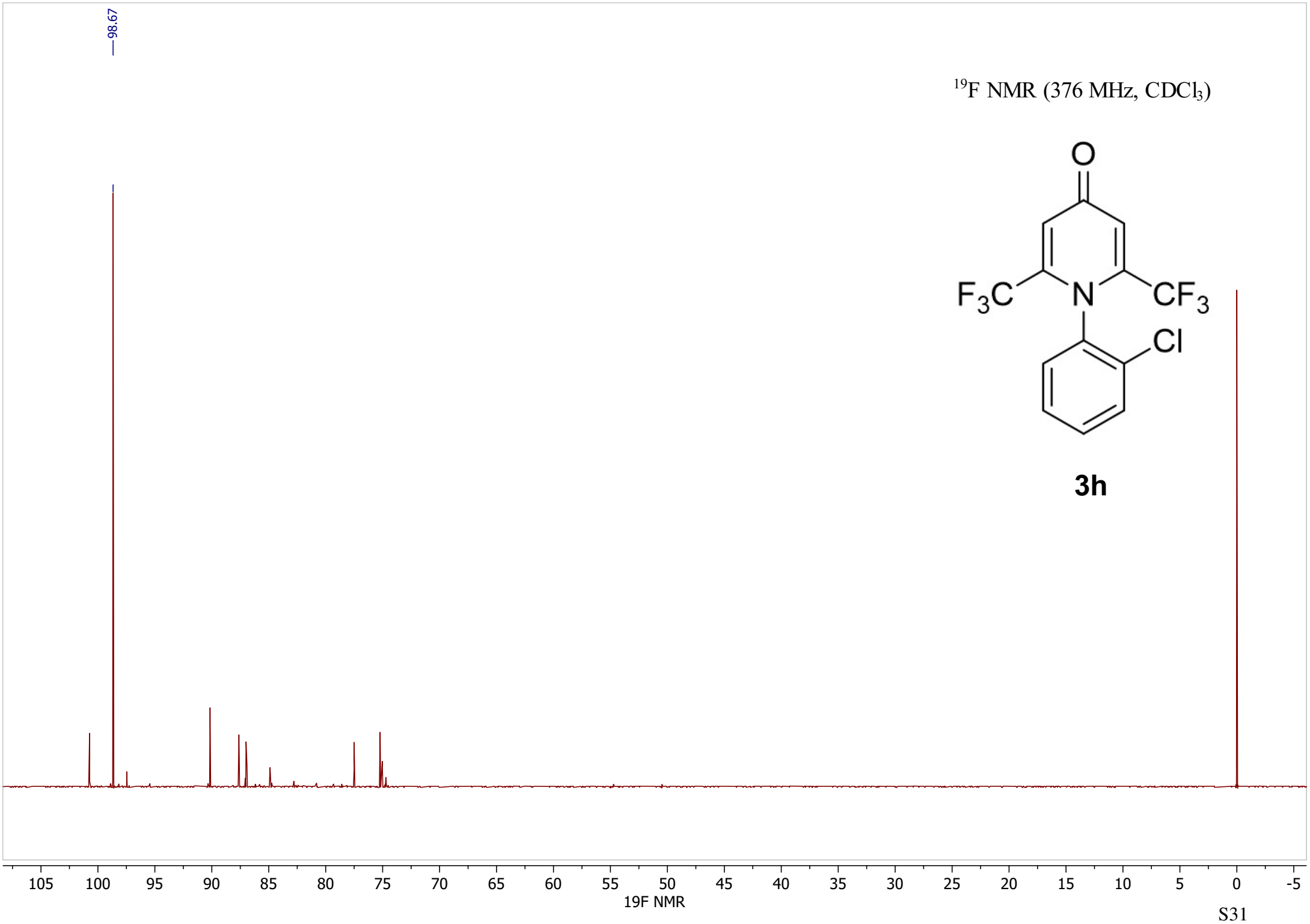
^{19}F NMR (376 MHz, $CDCl_3$)



3g

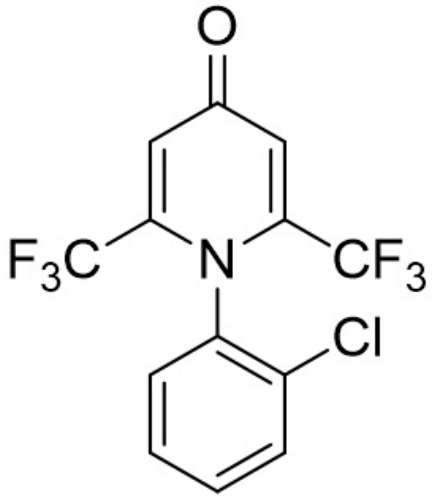

177.18
158.37
158.35
156.90
156.87
156.40
156.38
154.89
154.87
141.20
140.93
140.67
140.39
123.48
123.40
123.36
123.27
122.54
120.90
120.84
120.72
120.65
120.35
119.58
119.54
119.50
119.47
119.23
119.02
118.16
117.21
117.14
117.03
116.96
115.97
13C NMR (126 MHz, CDCl3)
O
F3C
N
CF3
F
F
3g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR


7.56
7.55
7.54
7.48
7.47
7.46
7.45
7.45
7.43
7.43
7.02
^{1}H NMR (400 MHz, $CDCl_3$)
O
F_3C
N
CF_3
Cl
3h
3.07
1.03
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR

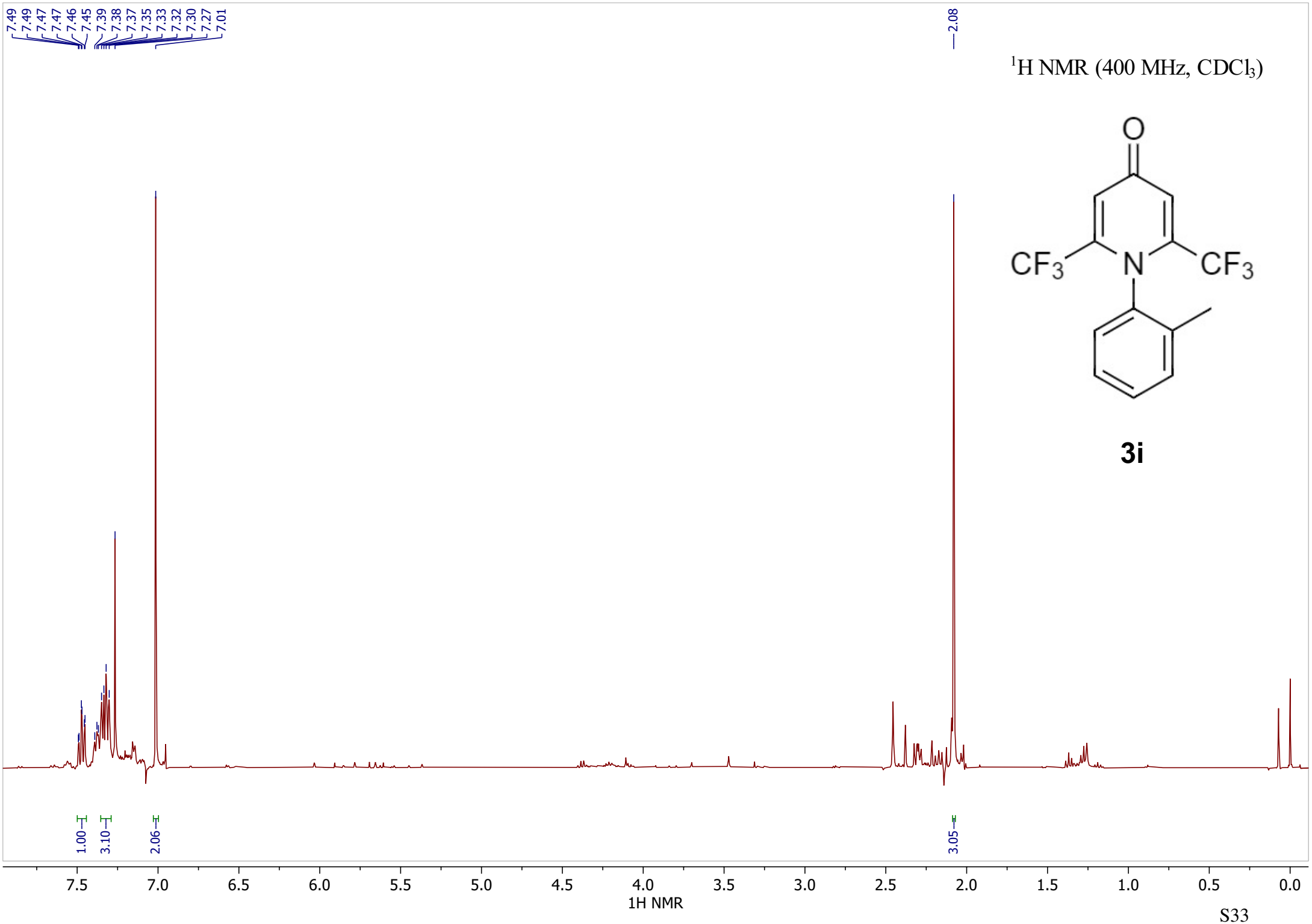

98.67
19F NMR (376 MHz, CDCl3)
O
F3C
N
CF3
Cl
3h
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
19F NMR

177.57
141.34
141.07
140.80
140.53
135.92
132.89
132.74
131.86
130.05
127.15
122.55
120.36
119.66
119.63
119.59
119.55
118.17
115.97

^{13}C NMR (126 MHz, $CDCl_3$)



3h

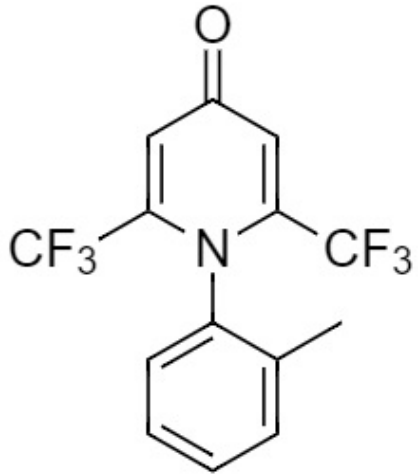


^{1}H NMR (400 MHz, $CDCl_3$)

3i

98.95

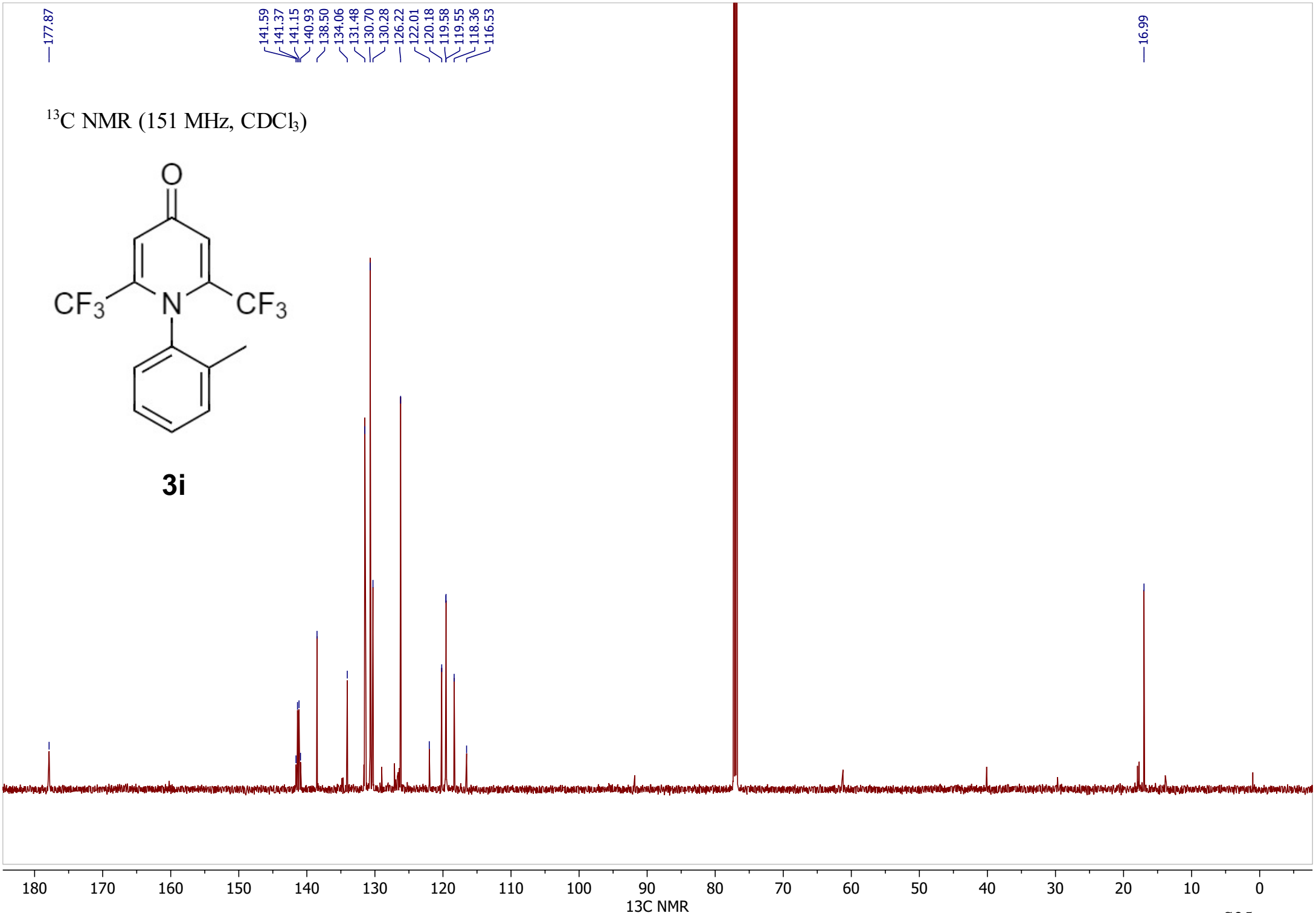
^{19}F NMR (376 MHz, $CDCl_3$)

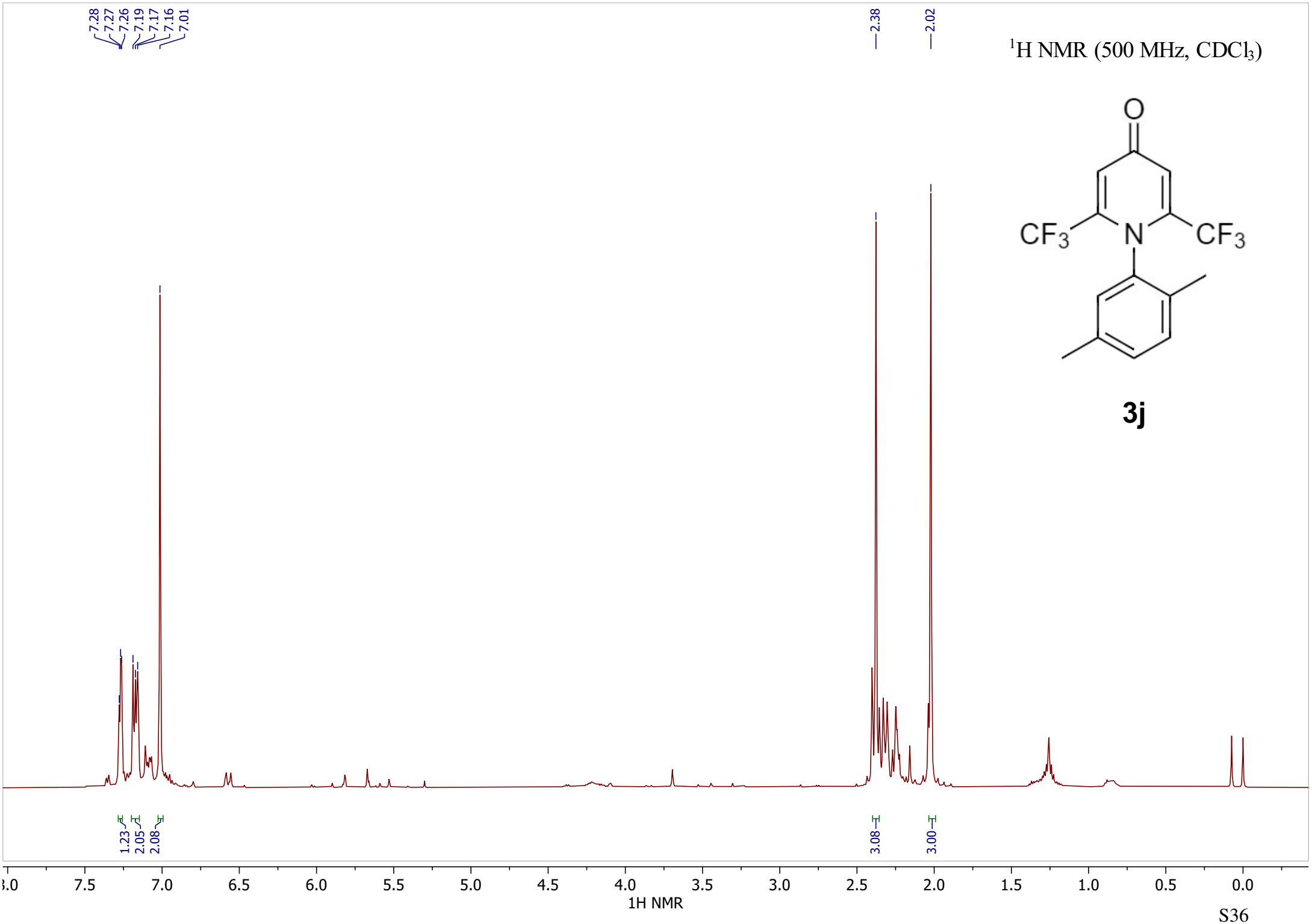


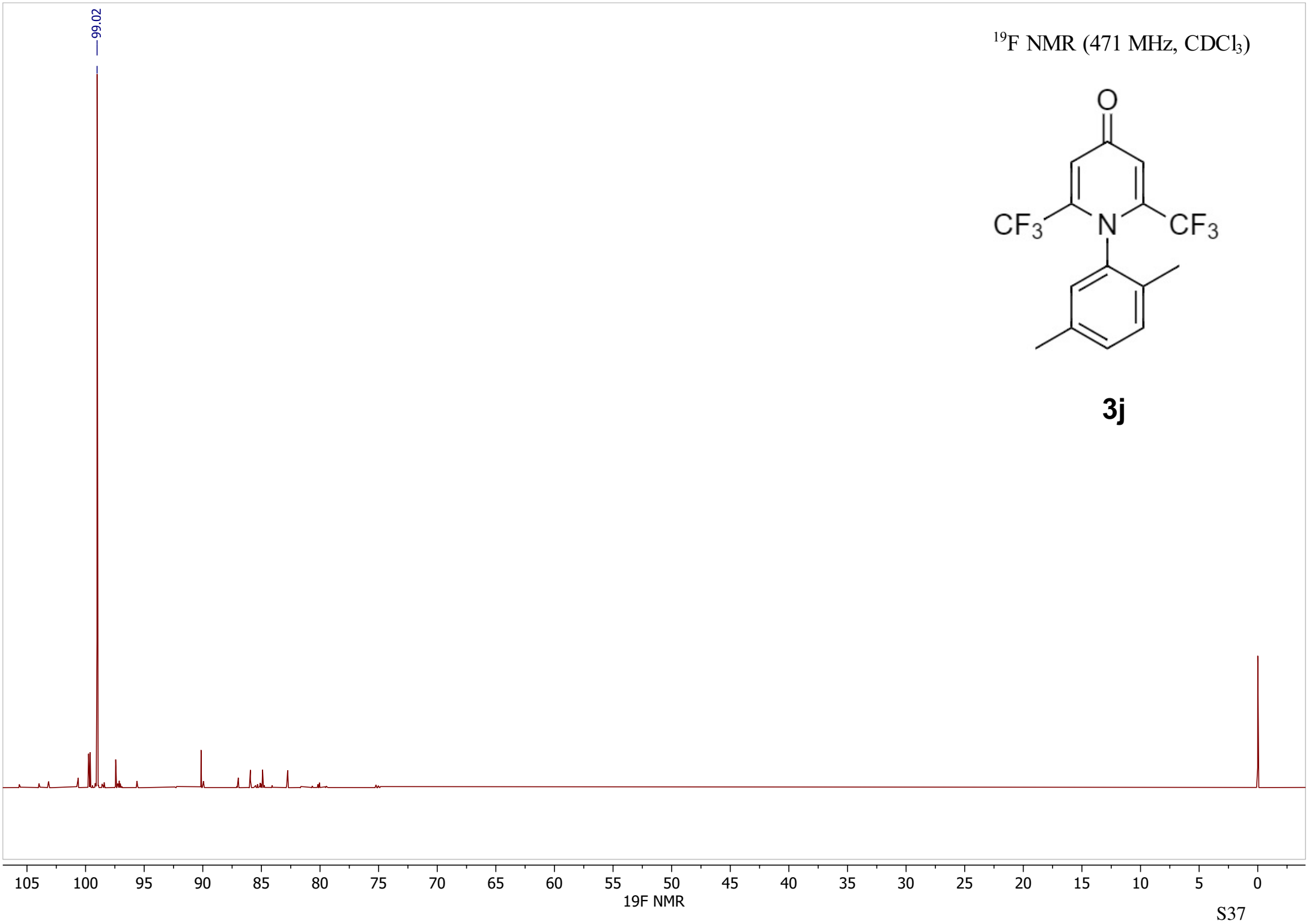
3i

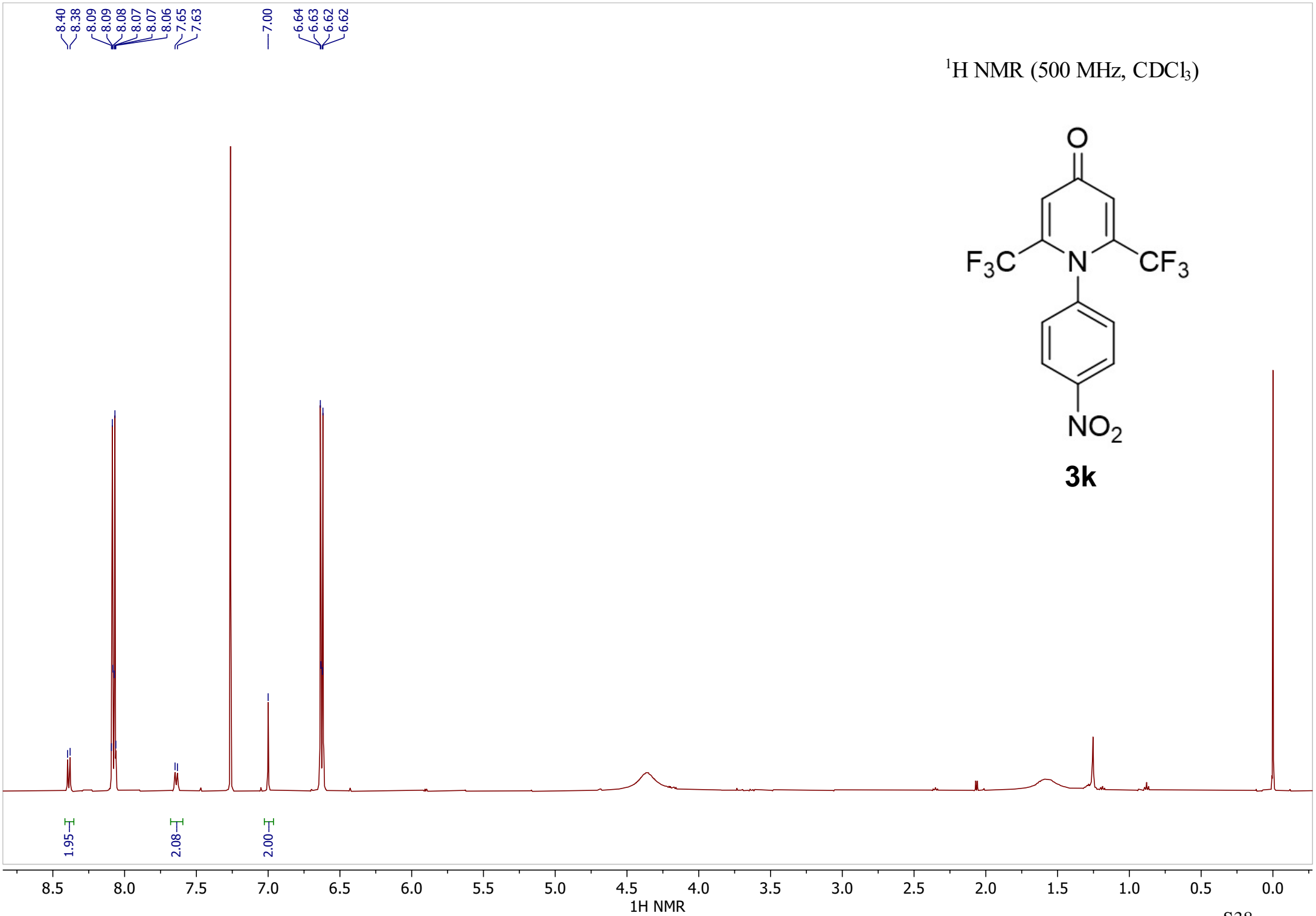
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5

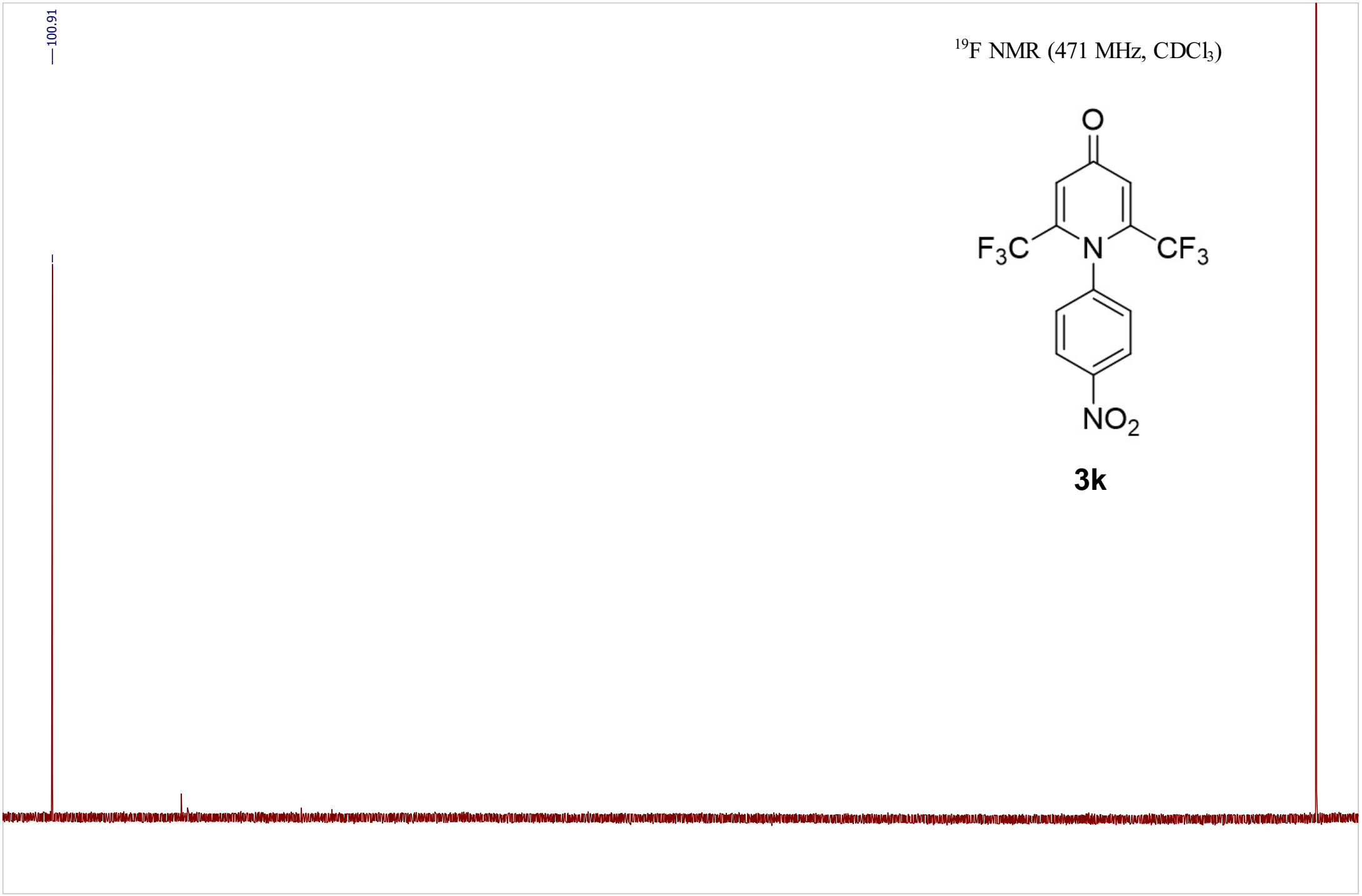
19F NMR


177.87
141.59
141.37
141.15
140.93
138.50
134.06
131.48
130.70
130.28
126.22
122.01
120.18
119.58
119.55
118.36
116.53
16.99
13C NMR (151 MHz, CDCl3)
O
CF3
N
CF3
3i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR

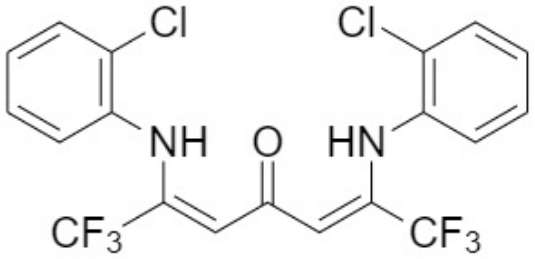

7.28
7.27
7.26
7.19
7.17
7.16
7.01
2.38
2.02
^{1}H NMR (500 MHz, $CDCl_3$)
O
CF_3
N
CF_3
3j
1.23
2.05
2.08
3.08
3.00
1H NMR


99.02
19F NMR (471 MHz, CDCl3)
O
CF3
N
CF3
3j
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
19F NMR

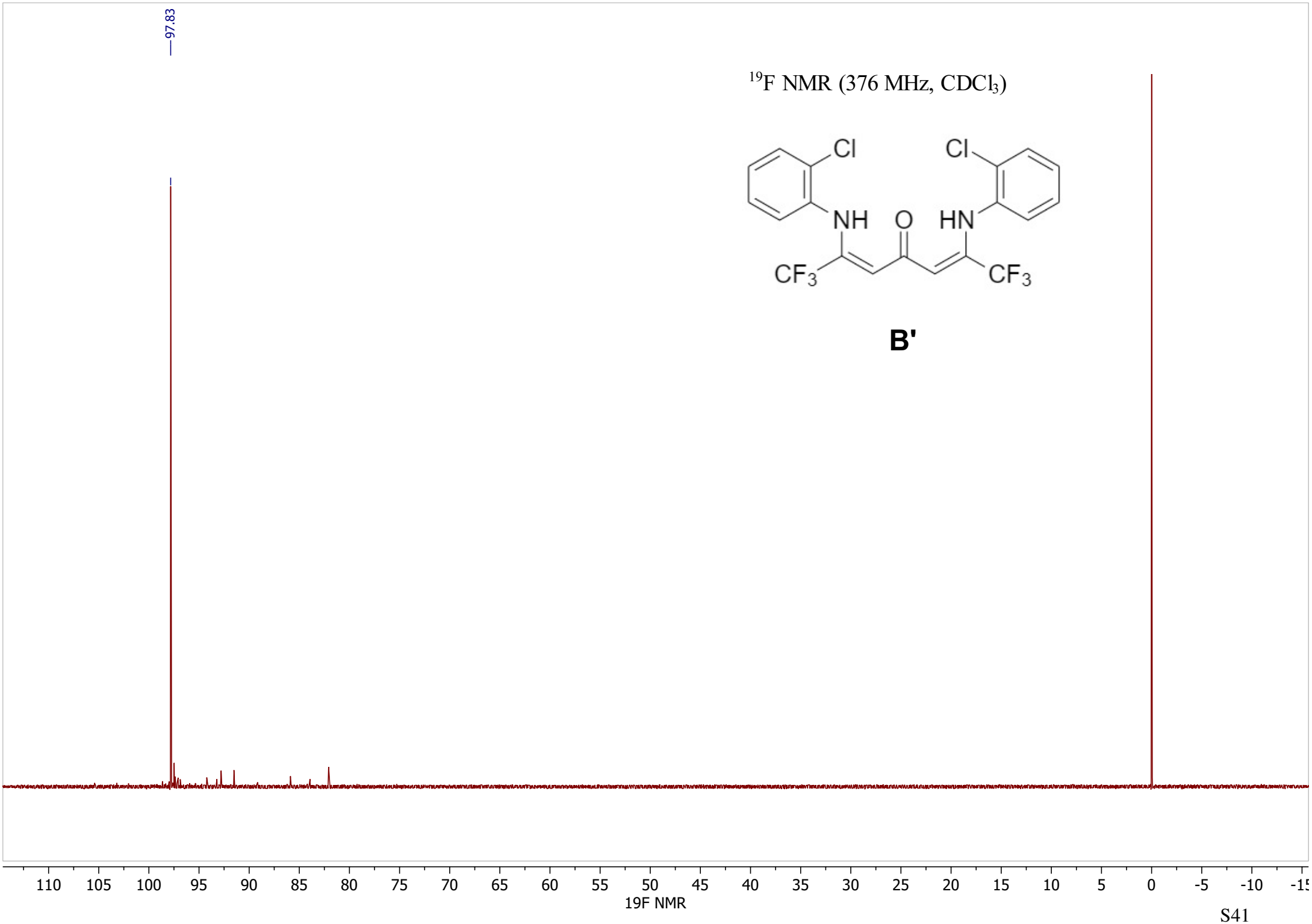

8.40
8.38
8.09
8.09
8.08
8.07
8.07
8.06
7.65
7.63
7.00
6.64
6.63
6.62
6.62
1H NMR (500 MHz, CDCl3)
O
F3C
N
CF3
NO2
3k
1.95
2.08
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR


100.91
19F NMR (471 MHz, CDCl3)
O
F3C
N
CF3
NO2
3k
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
19F NMR

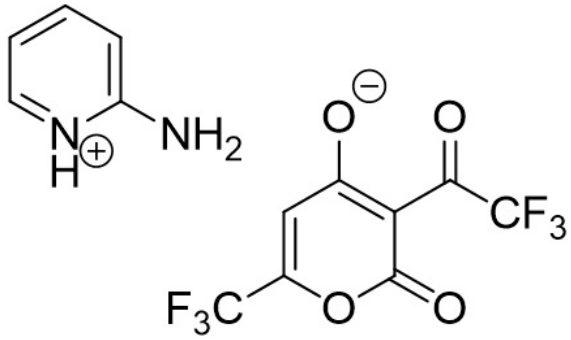
^{1}H NMR (400 MHz, $CDCl_3$)



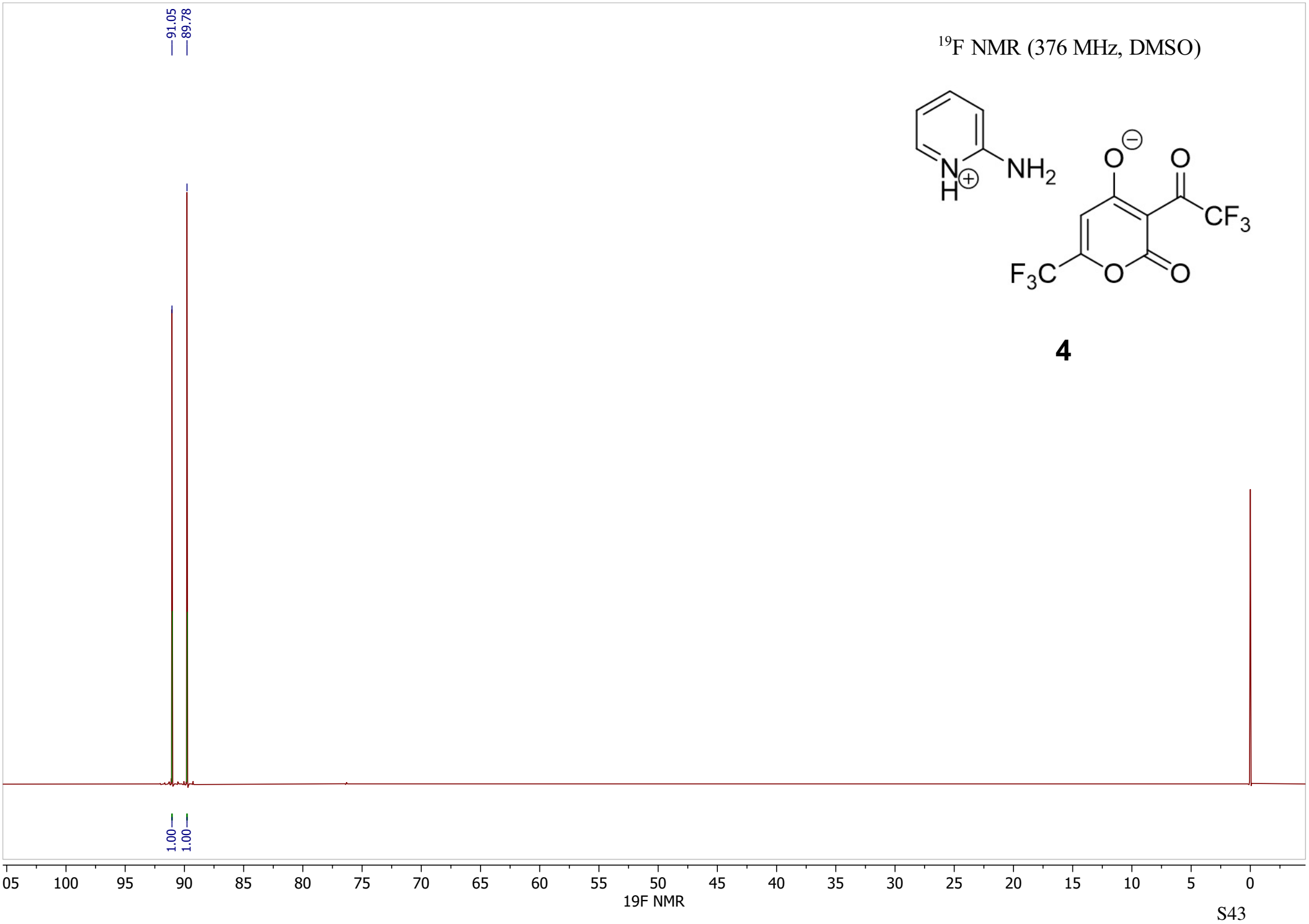
B'


97.83
19F NMR (376 MHz, CDCl3)
Cl
Cl
NH
O
HN
CF3
CF3
B'
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
19F NMR

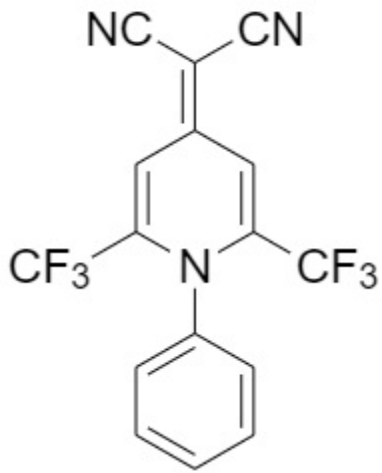
^{1}H NMR (400 MHz, DMSO)



4

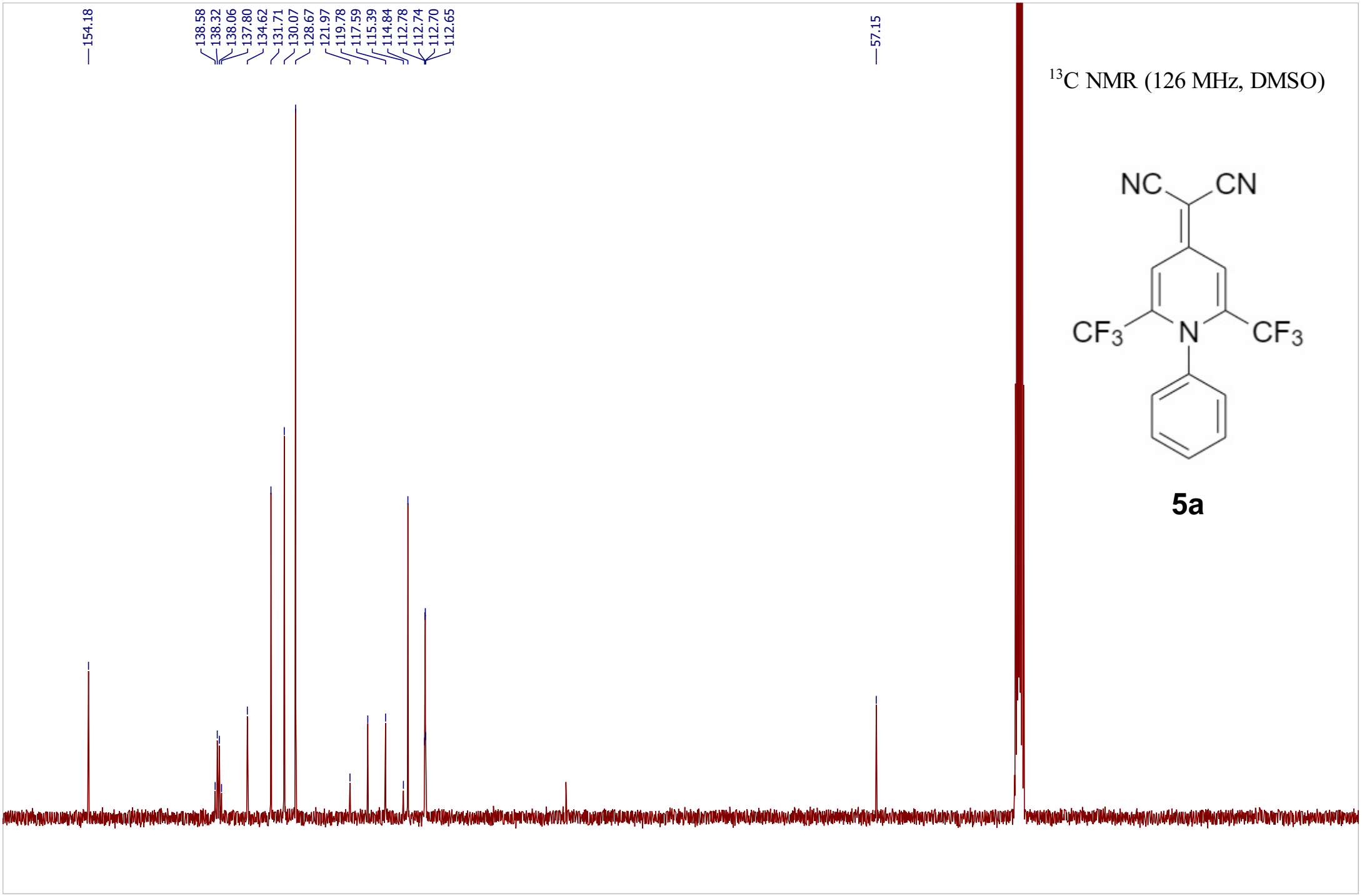

91.05
89.78
19F NMR (376 MHz, DMSO)
NH2
CF3
F3C
O
O
O
O
O
4
1.00
1.00
05
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
19F NMR

^{1}H NMR (500 MHz, DMSO)

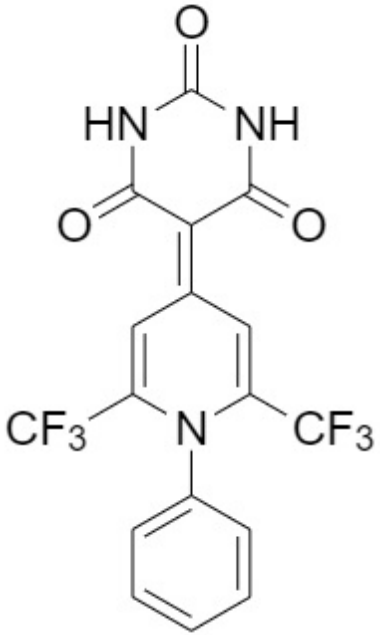


5a


102.54
19F NMR (471 MHz, DMSO)
NC
CN
CF3
N
CF3
5a
15 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
19F NMR

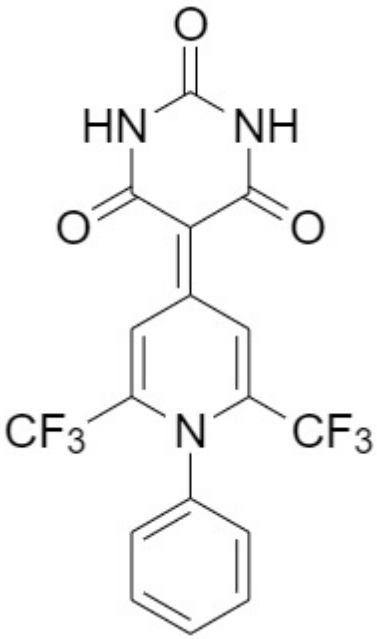

154.18
138.58
138.32
138.06
137.80
134.62
131.71
130.07
128.67
121.97
119.78
117.59
115.39
114.84
112.78
112.74
112.70
112.65
57.15
^{13}C NMR (126 MHz, DMSO)
NC
CN
CF3
N
CF3
5a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR

^{1}H NMR (500 MHz, DMSO)

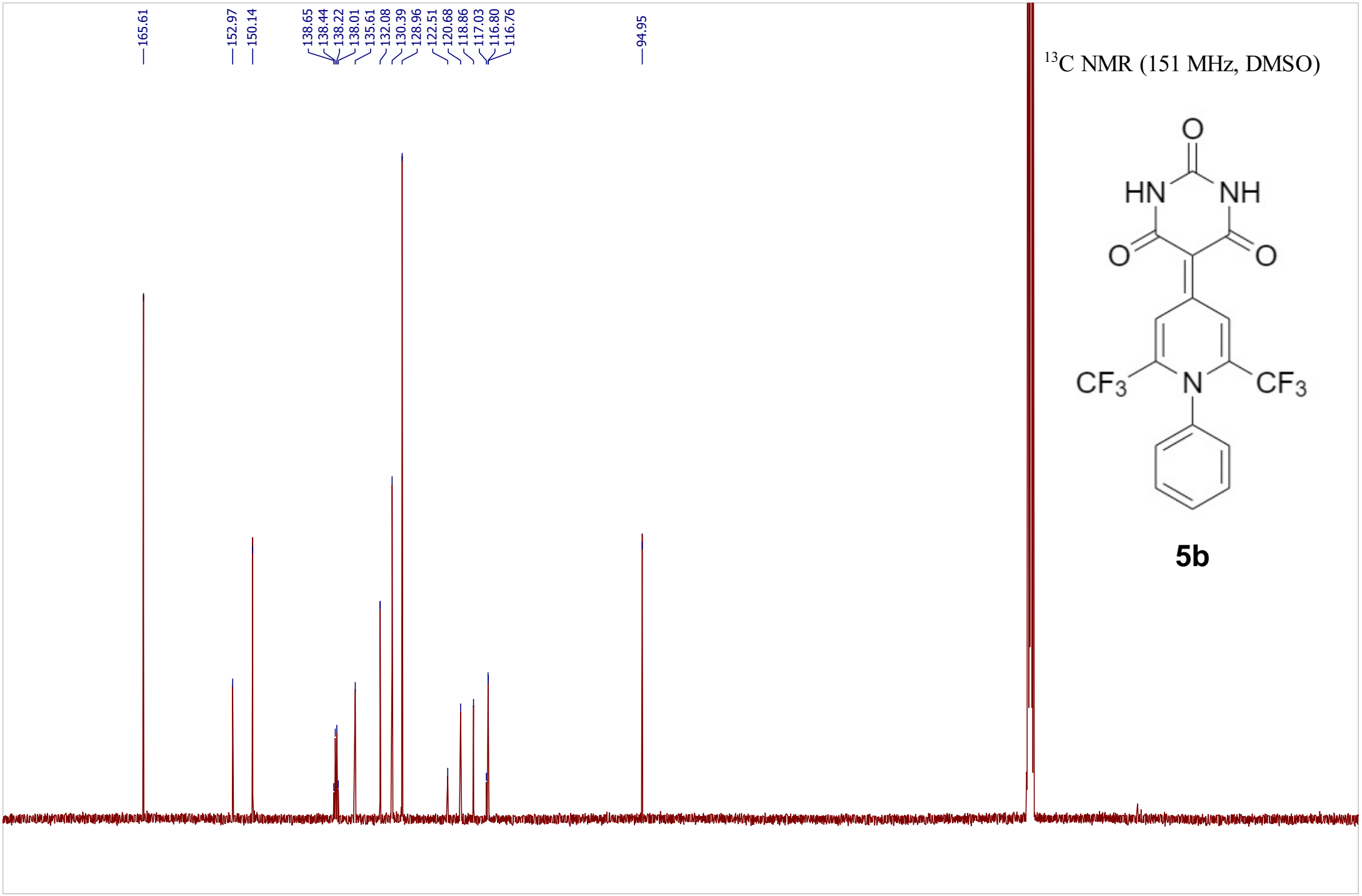


5b

^{19}F NMR (471 MHz, DMSO)

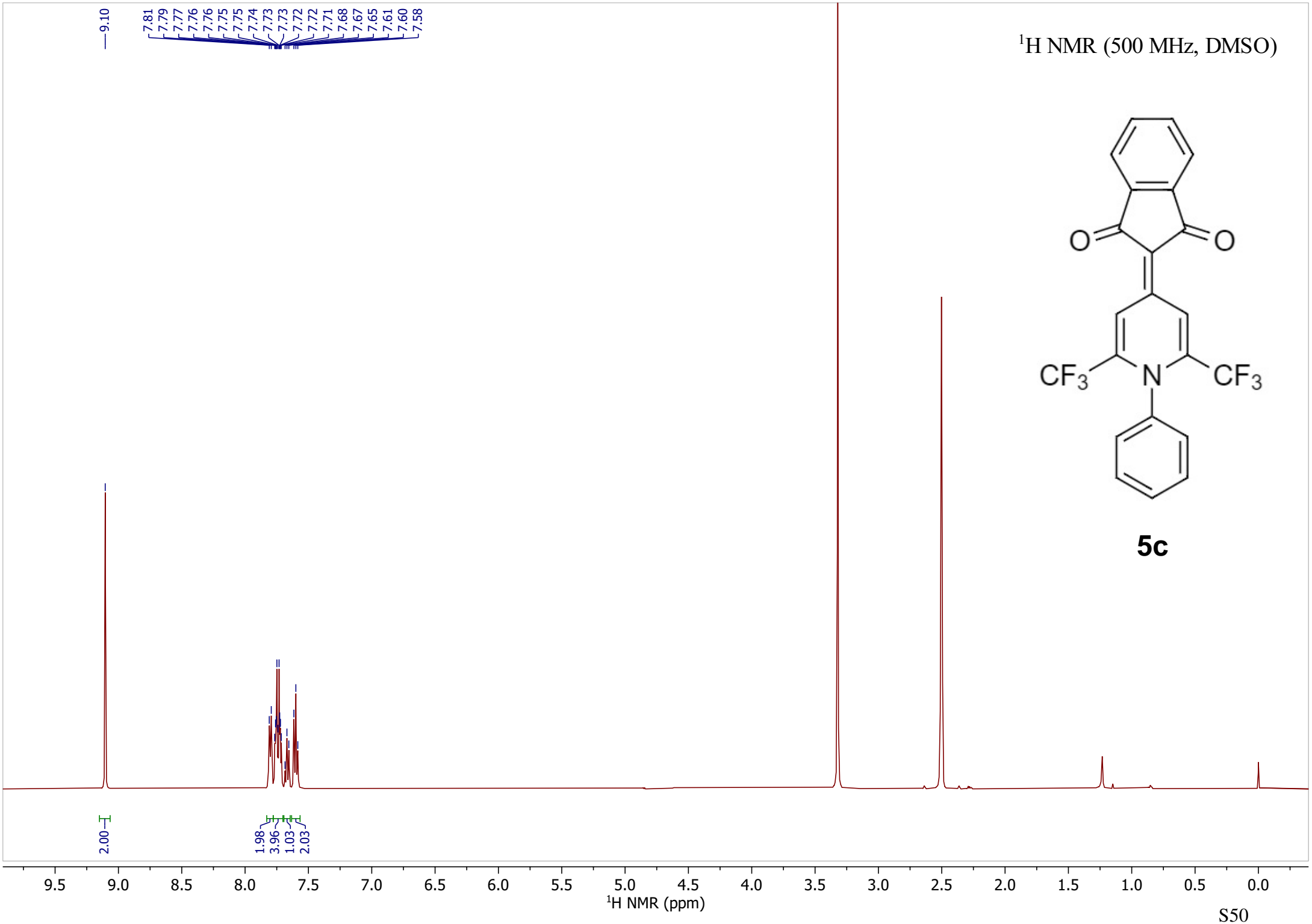


5b

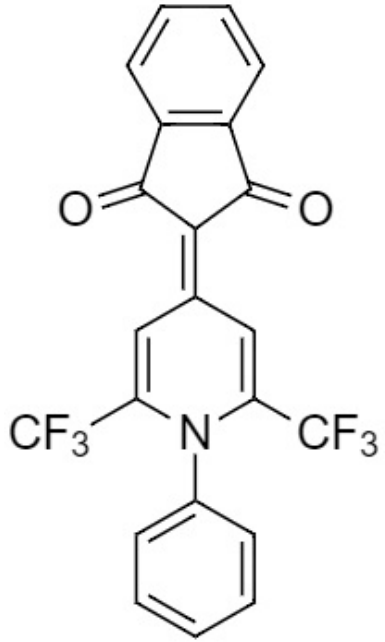


^{13}C NMR (151 MHz, DMSO)

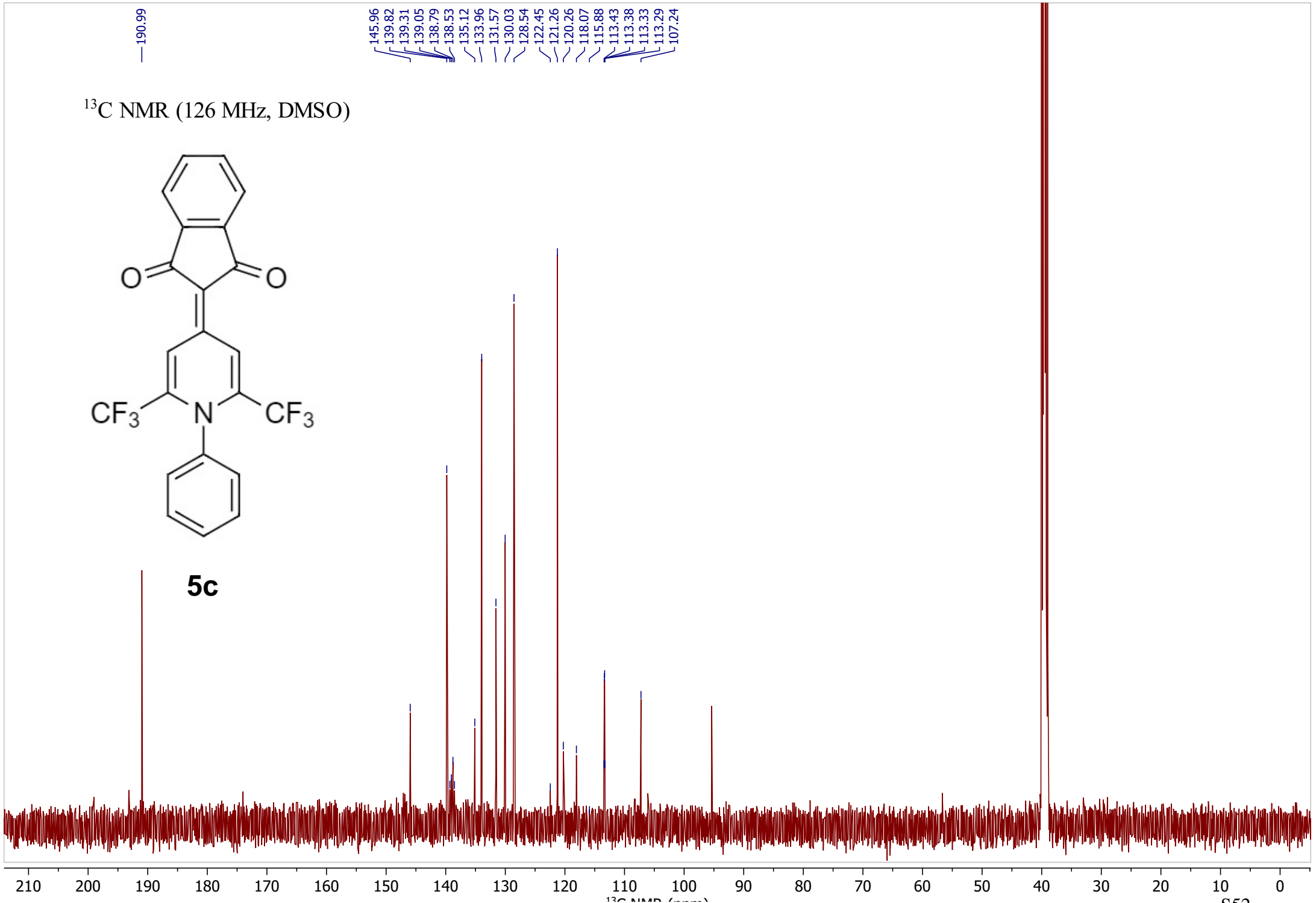
5b


9.10
7.81
7.79
7.77
7.76
7.76
7.75
7.75
7.74
7.73
7.73
7.72
7.72
7.71
7.68
7.67
7.65
7.61
7.60
7.58
^{1}H NMR (500 MHz, DMSO)
O
O
CF_3
N
CF_3
5c
2.00
1.98
3.96
1.03
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
^{1}H NMR (ppm)

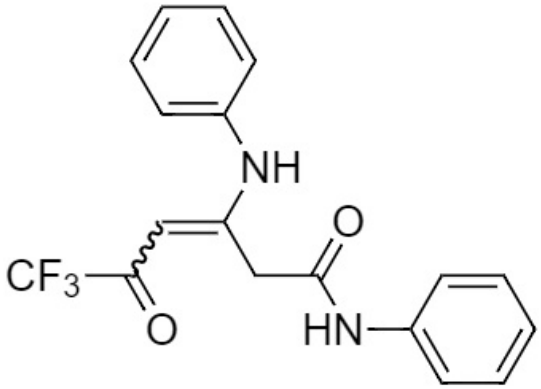
^{19}F NMR (471 MHz, DMSO)



5c

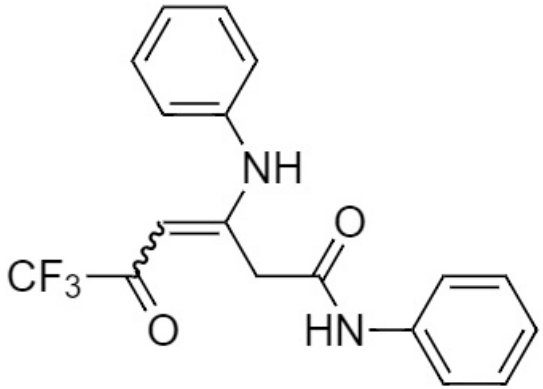

190.99
145.96
139.82
139.31
139.05
138.79
138.53
135.12
133.96
131.57
130.03
128.54
122.45
121.26
120.26
118.07
115.88
113.43
113.38
113.33
113.29
107.24
^{13}C NMR (126 MHz, DMSO)
O
O
CF3
N
CF3
5c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR (500 MHz, DMSO)



9a

^{19}F NMR (376 MHz, DMSO)

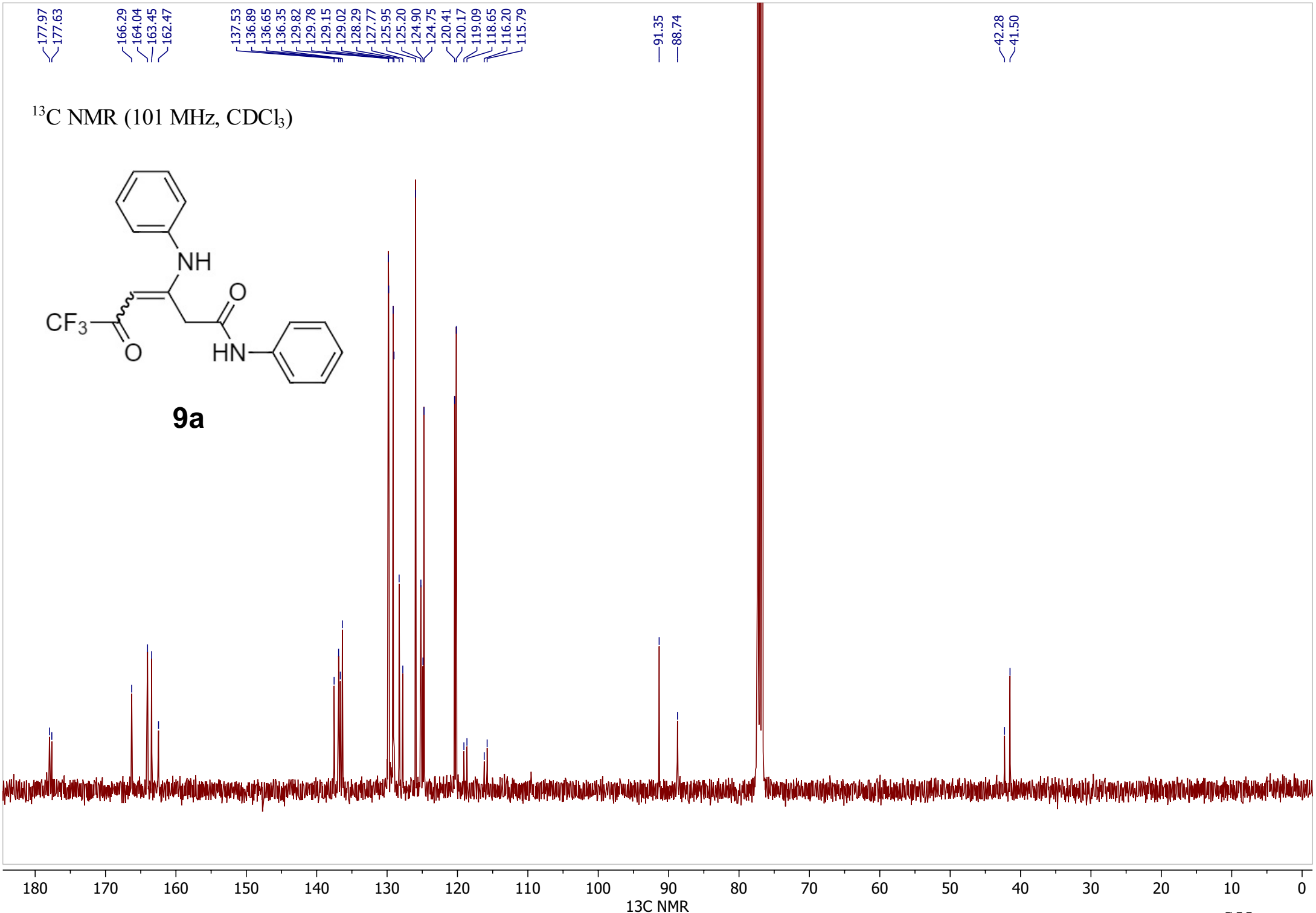


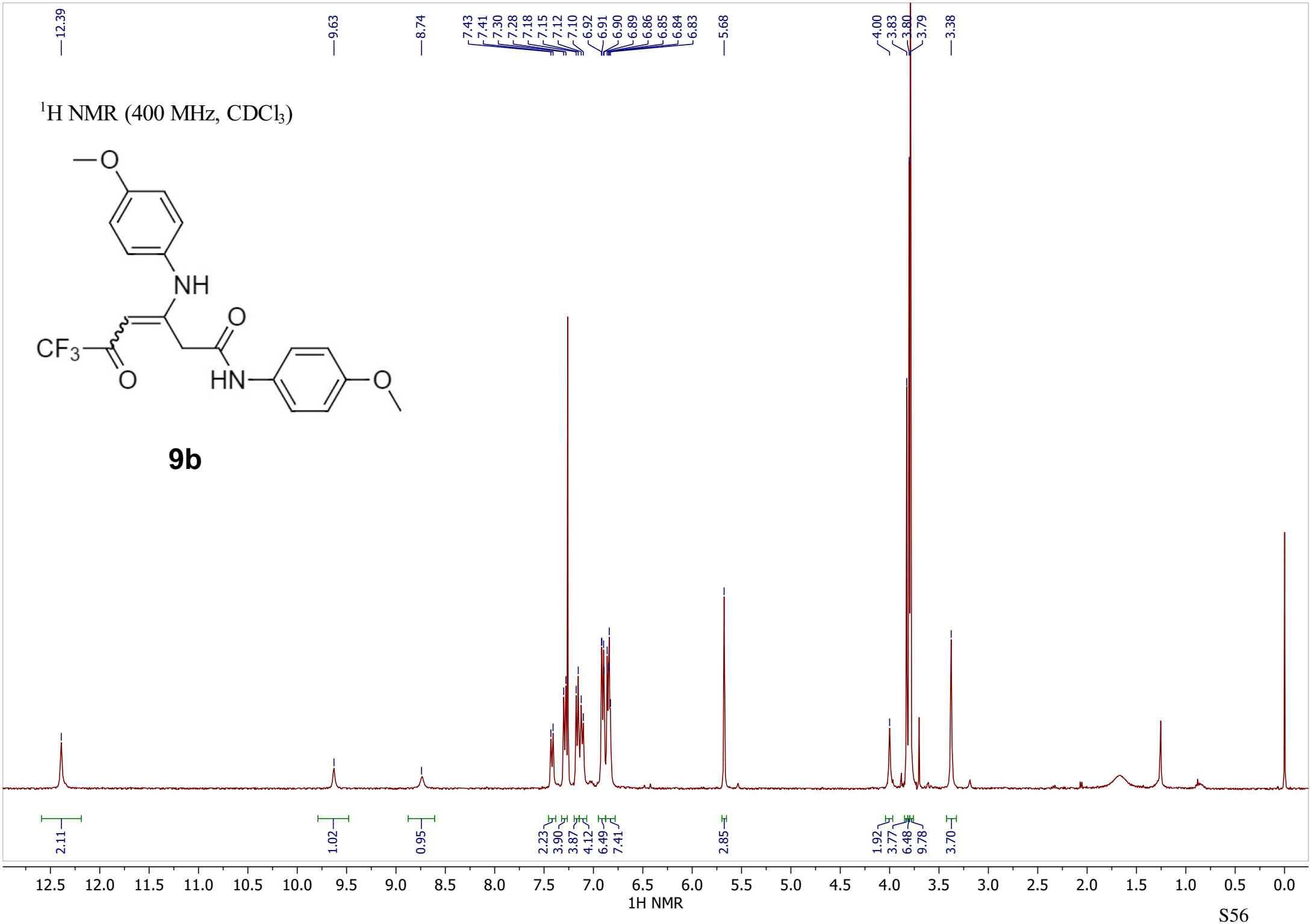
9a

87.14
86.57
43.59
56.41

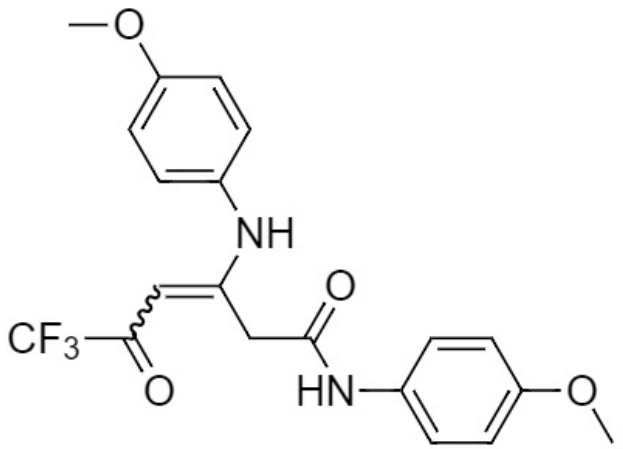
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

^{19}F NMR (ppm)

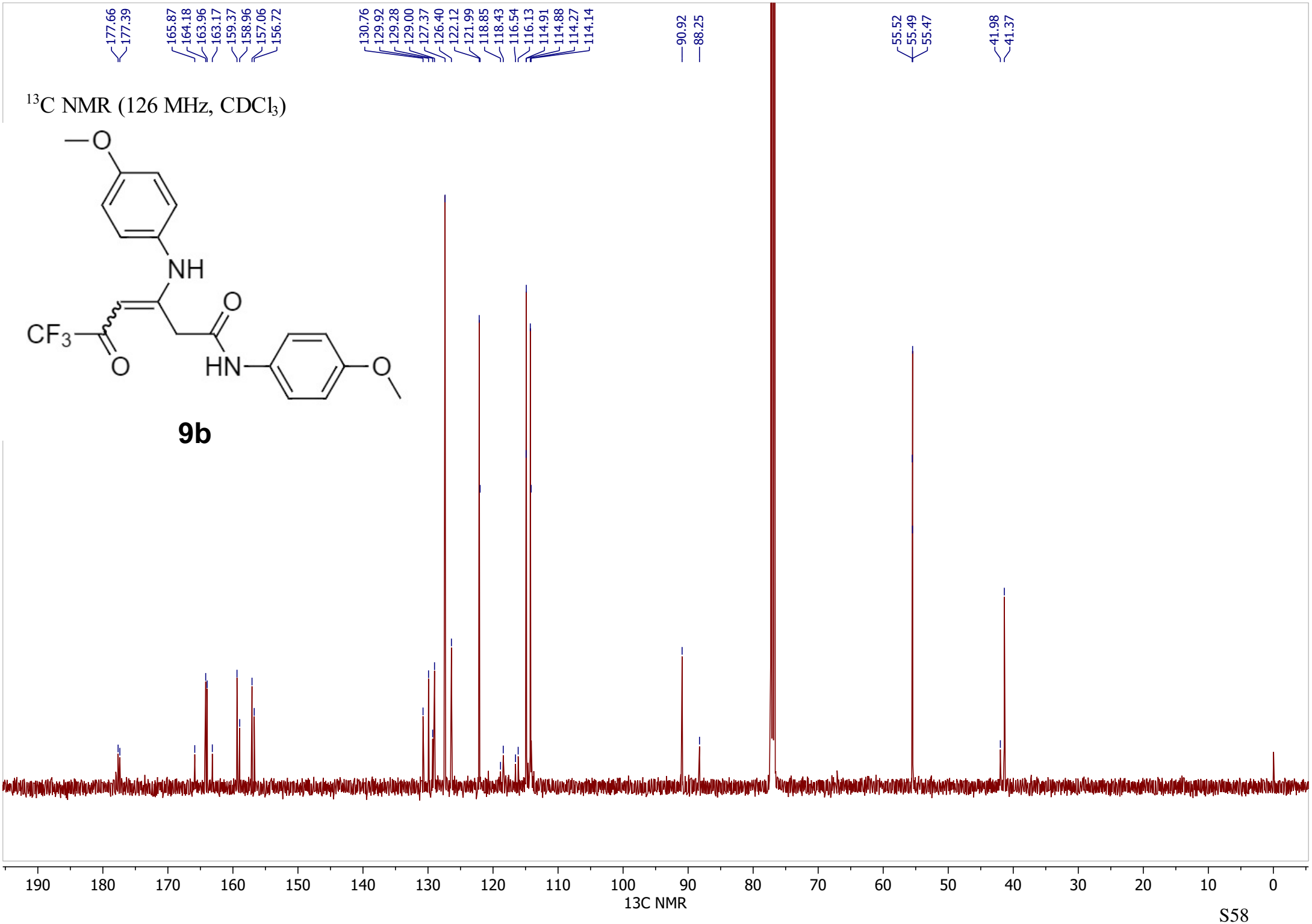

177.97
177.63
166.29
164.04
163.45
162.47
137.53
136.89
136.65
136.35
129.82
129.78
129.15
129.02
128.29
127.77
125.95
125.20
124.90
124.75
120.41
120.17
119.09
118.65
116.20
115.79
91.35
88.74
42.28
41.50
13C NMR (101 MHz, CDCl3)
NH
O
CF3
O
HN
9a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR

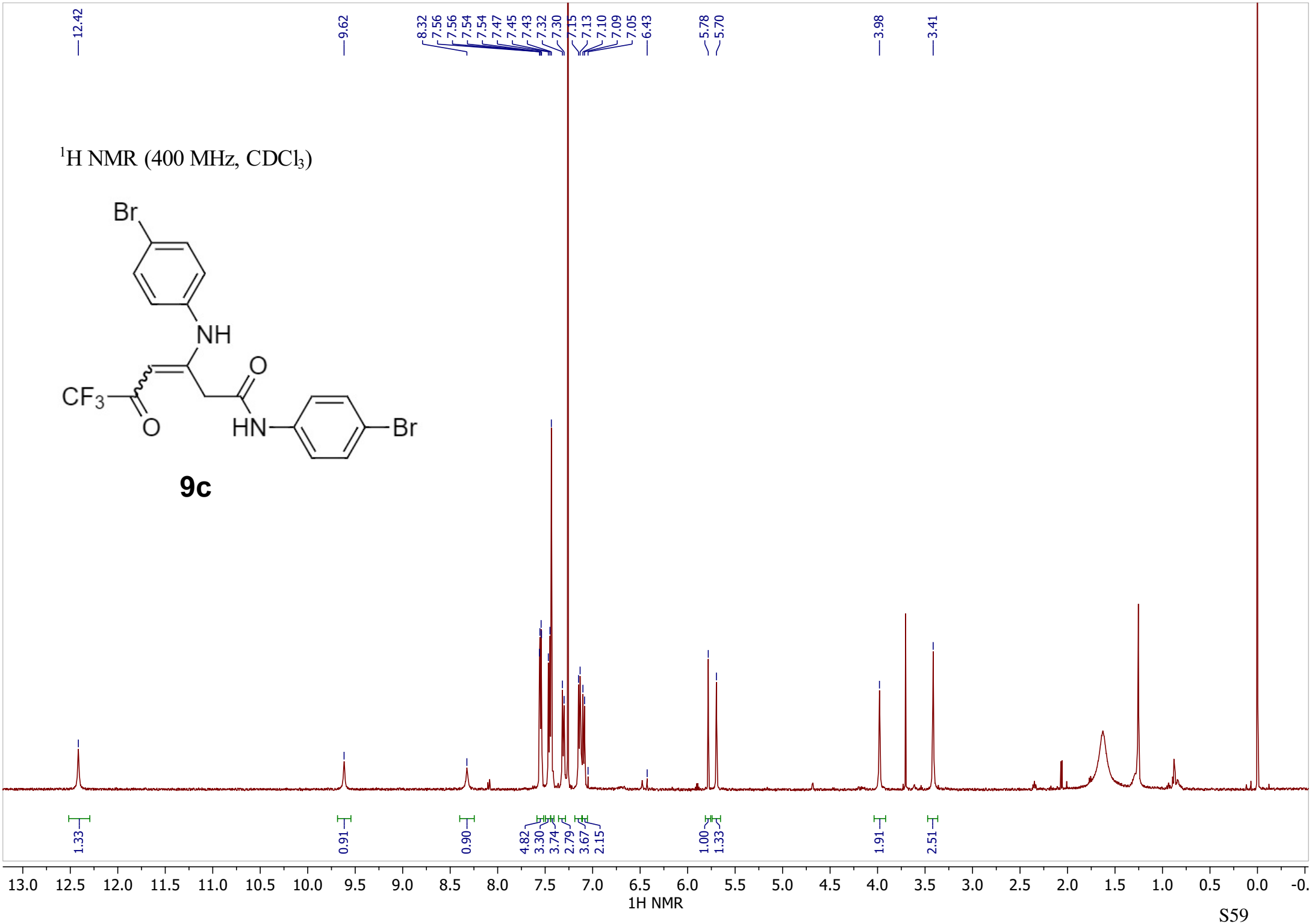

12.39
9.63
8.74
7.43
7.41
7.30
7.28
7.18
7.15
7.12
7.10
6.92
6.91
6.90
6.89
6.86
6.85
6.84
6.83
5.68
4.00
3.83
3.80
3.79
3.38
^{1}H NMR (400 MHz, $CDCl_3$)
NH
O
CF_3
O
HN
O
9b
2.11
1.02
0.95
2.23
3.90
3.87
4.12
6.49
7.41
2.85
1.92
3.77
6.48
9.78
3.70
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1H NMR

^{19}F NMR (376 MHz, $CDCl_3$)



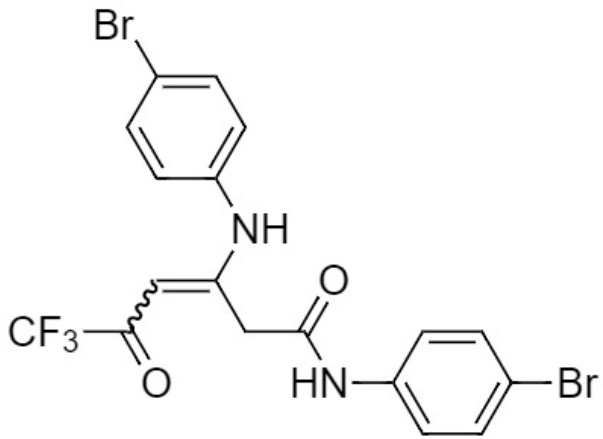
9b


177.66
177.39
165.87
164.18
163.96
163.17
159.37
158.96
157.06
156.72
130.76
129.92
129.28
129.00
127.37
126.40
122.12
121.99
118.85
118.43
116.54
116.13
114.91
114.88
114.27
114.14
90.92
88.25
55.52
55.49
55.47
41.98
41.37
13C NMR (126 MHz, CDCl3)
NH
O
CF3
O
HN
O
9b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR


12.42
9.62
8.32
7.56
7.56
7.54
7.54
7.47
7.45
7.43
7.32
7.30
7.15
7.13
7.10
7.09
7.05
6.43
5.78
5.70
3.98
3.41
1H NMR (400 MHz, CDCl3)
Br
NH
O
CF3
O
HN
Br
9c
1.33
0.91
0.90
4.82
3.30
3.74
2.79
3.67
2.15
1.00
1.33
1.91
2.51
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
1H NMR

84.95
84.76

^{19}F NMR (471 MHz, $CDCl_3$)



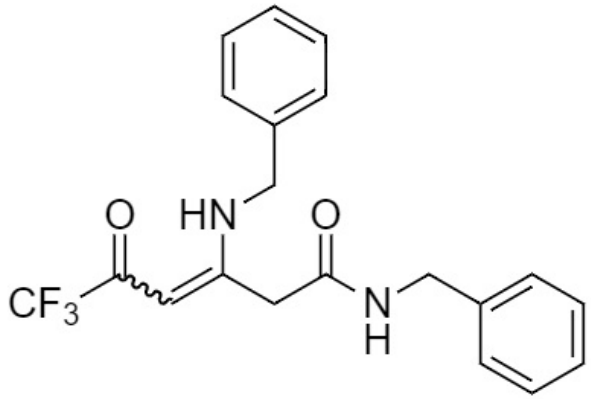
9c

1.41
1.00

85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

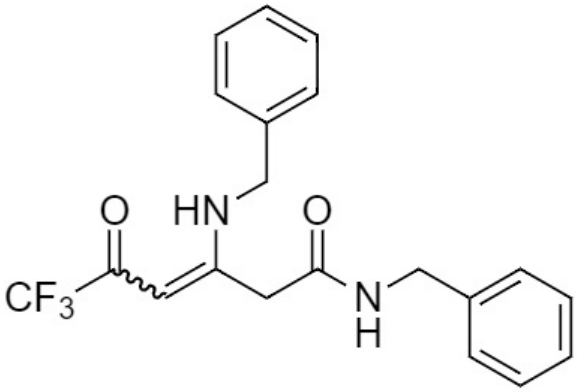
19F NMR

^{1}H NMR (500 MHz, DMSO)



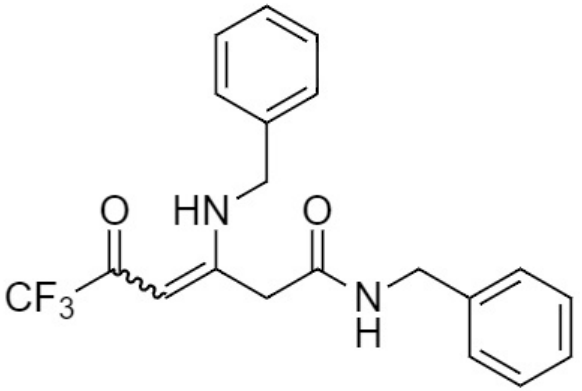
9d

^{1}H NMR (500 MHz, $CDCl_3$)

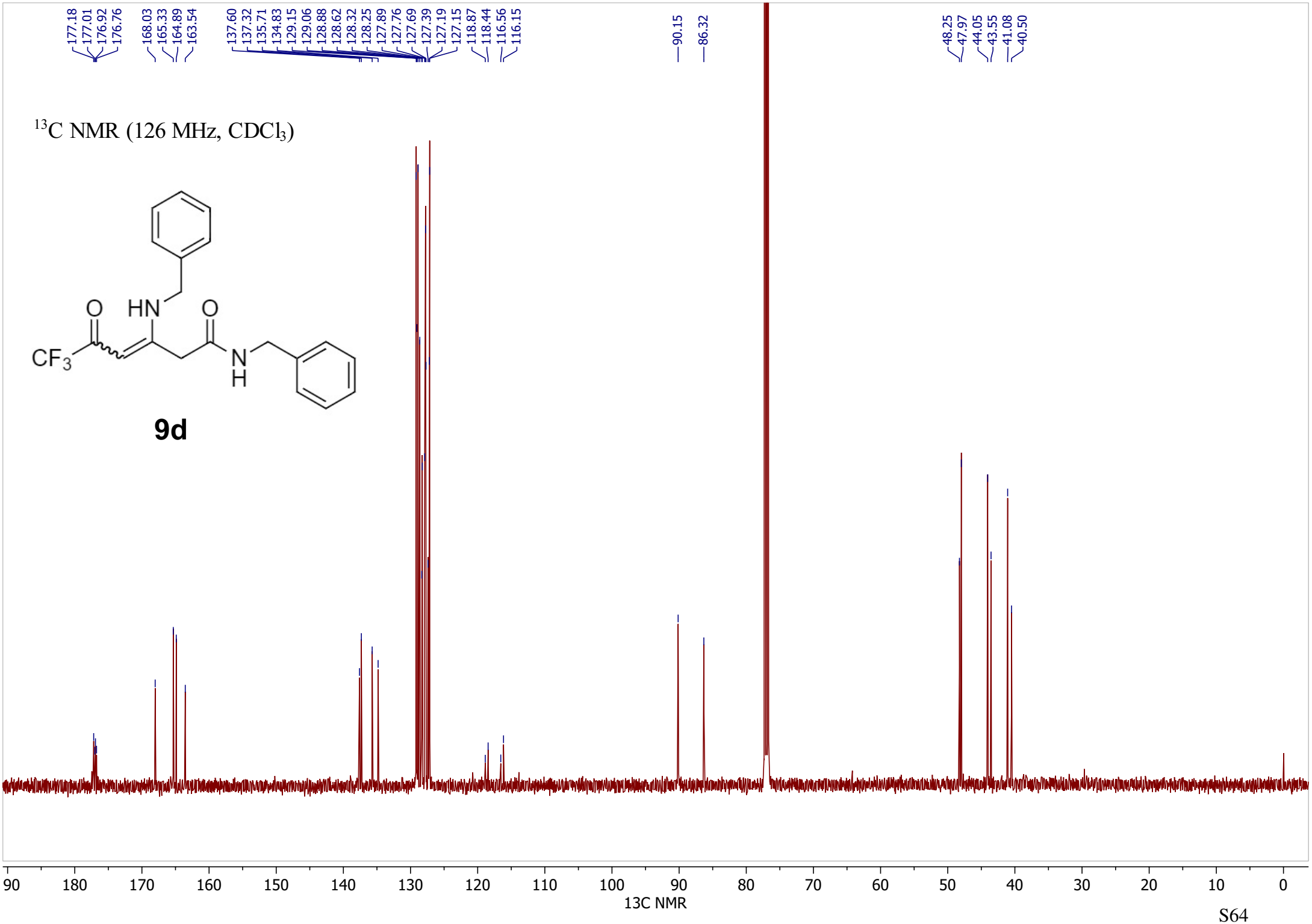


9d

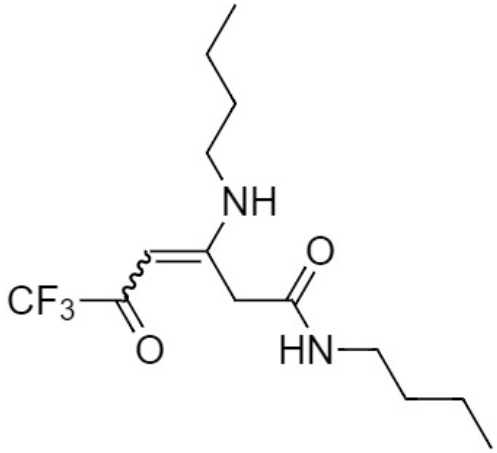
^{19}F NMR (471 MHz, $CDCl_3$)



9d

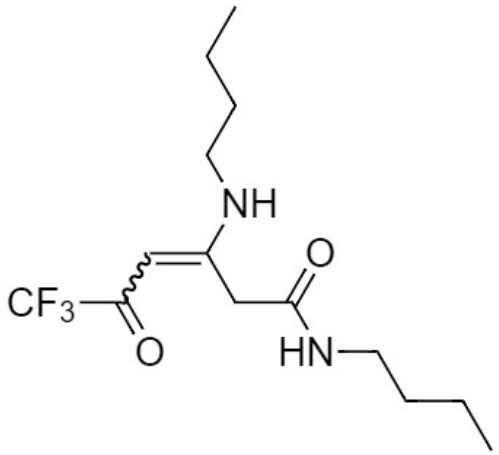

177.18
177.01
176.92
176.76
168.03
165.33
164.89
163.54
137.60
137.32
135.71
134.83
129.15
129.06
128.88
128.62
128.32
128.25
127.89
127.76
127.69
127.39
127.19
127.15
118.87
118.44
116.56
116.15
90.15
86.32
48.25
47.97
44.05
43.55
41.08
40.50
13C NMR (126 MHz, CDCl3)
O
HN
O
CF3
N
H
9d
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C NMR

^{1}H NMR (500 MHz, $CDCl_3$)



9e

^{19}F NMR (471 MHz, $CDCl_3$)



9e

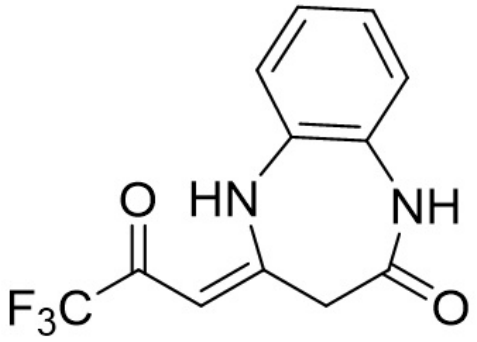
85.04
84.90

62.88
33.37

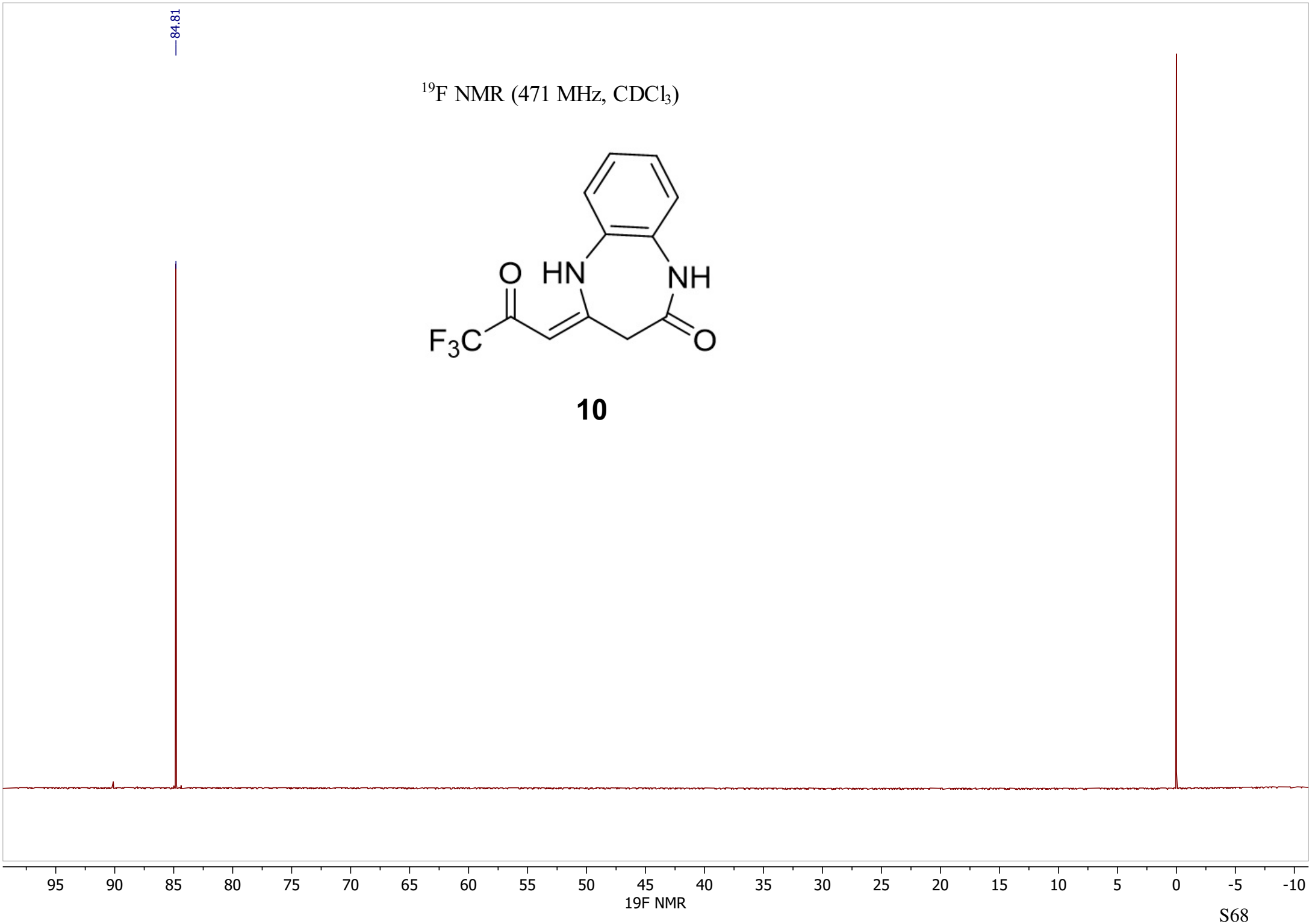
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

19F NMR

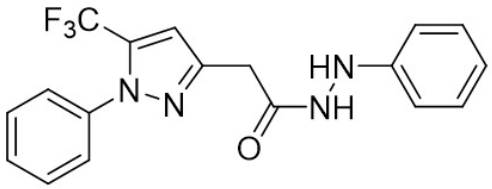
^{1}H NMR (500 MHz, $CDCl_3$)



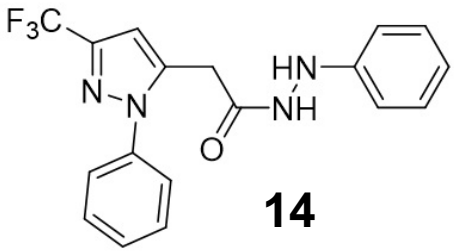
10


84.81
19F NMR (471 MHz, CDCl3)
O
HN
NH
F3C
O
10
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
19F NMR

^{1}H NMR (500 MHz, DMSO)



13



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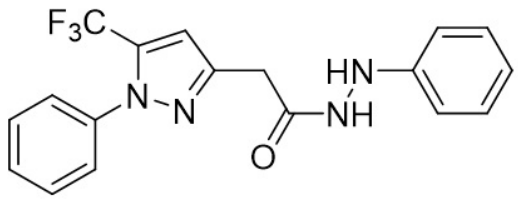
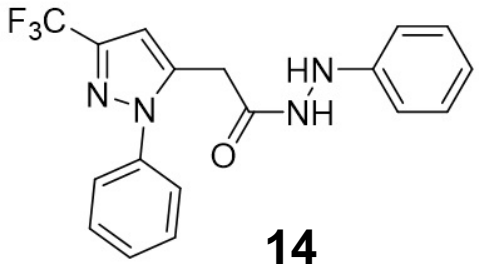
^{19}F NMR (471 MHz, DMSO)



13



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