Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Thiocyanation of BODIPY dyes and their conversion to thioalkylated derivatives

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Contents

Photophysical properties

Table S1 Photophysical properties of the synthesized compounds

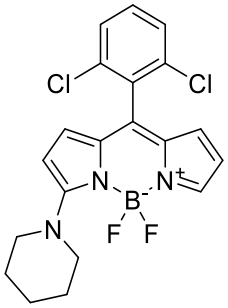
Comp./ Solv	λ (nm)		Stokes Shift (cm^{-1})	FWHM (cm^{-1})		QY
	abs	em		abs	em	
10						
MeOH	476	551	2860	3326	2228	0.02
MeCN	471	555	3212	3280	2382	0.005
THF	488	555	2474	3167	2143	0.09
Tol	507	561	1899	2818	2115	0.27
11						
MeOH	495	509	556	1220	1463	0.87
MeCN	495	508	517	1253	1482	0.90
THF	499	515	623	1252	1478	0.98
Tol	506	525	715	1009	1423	0.94
12						
MeOH	493	507	560	1539	1312	0.96
MeCN	492	507	601	1555	1317	0.94
THF	497	513	628	1326	1309	0.99
Tol	505	518	497	1133	1277	0.91
13						
MeOH	485	505	817	1270	1619	0.93
MeCN	484	503	780	1339	1706	0.98
THF	489	510	842	1198	1683	0.93
Tol	495	516	822	1081	1615	0.99
14						
MeOH	490	508	723	1231	1253	0.04
MeCN	490	509	762	1326	1184	0.04
THF	493	512	753	1215	1214	0.06
Tol	498	512	549	865	1182	0.27
15						
MeOH	502	520	690	1139	1277	0.06
MeCN	502	518	615	1238	1224	0.06
THF	506	521	569	1055	1206	0.07
Tol	511	530	702	945	1210	0.01
16						
MeOH	494	510	635	1171	1284	0.06
MeCN	494	513	750	1140	1553	0.01
THF	498	519	812	1109	1562	0.37
Tol	503	524	797	1006	1531	0.46
17						
MeOH	496	513	668	1227	1333	0.20
MeCN	494	511	673	1230	1275	0.10
THF	498	515	663	1021	1274	0.05
Tol	503	520	650	975	1207	0.06
18						

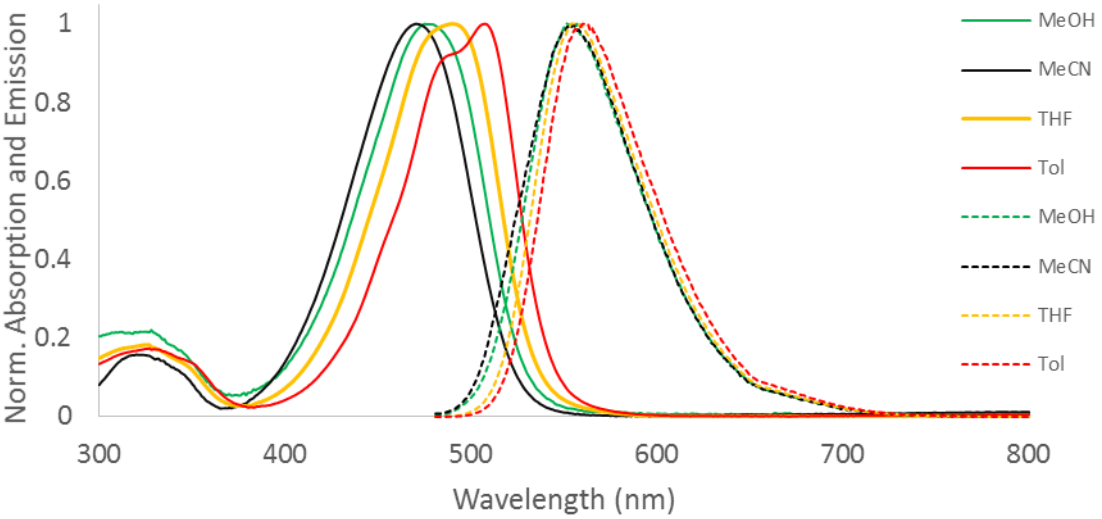
MeOH	459	562	3993	3591	2278	0.004
MeCN	451	567	4536	3645	2571	0.002
THF	467	569	3839	3624	2109	0.01
Tol	483	561	1899	3481	1988	0.09
19						
MeOH	490	507	684	1174	1841	0.62
MeCN	490	507	684	1532	2100	0.46
THF	494	513	750	1214	1848	0.71
Tol	501	518	655	1046	1641	0.97
20						
MeOH	499	570	2496	1002	4032	0.05
MeCN	498	581	2869	1074	4073	0.05
THF	502	568	2315	1022	3387	0.11
Tol	507	561	1899	956	3065	0.23
21						
MeOH	499	547	1759	1029	1759	0.09
MeCN	498	549	1865	106	1865	0.08
THF	502	556	1934	984	1935	0.21
Tol	507	544	1342	926	1342	0.38
22						
MeOH	500	538	1413	1023	1413	0.1
MeCN	499	556	2054	1055	2054	0.09
THF	503	540	1362	995	1362	0.19
Tol	508	542	1235	940	1235	0.37
23						
MeOH	509	583	2494	1179	3047	0.04
MeCN	507	591	2803	1227	2930	0.03
THF	512	580	2290	1167	2677	0.10
Tol	517	576	1981	1089	2519	0.22

Figure S1. From left to right: Fluorescence emission observed under UV light (368 nm) of compounds **3**, **13**, **19**, **20**, **21**, **22**, **23**.

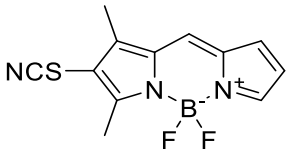
Absorption and emission spectra

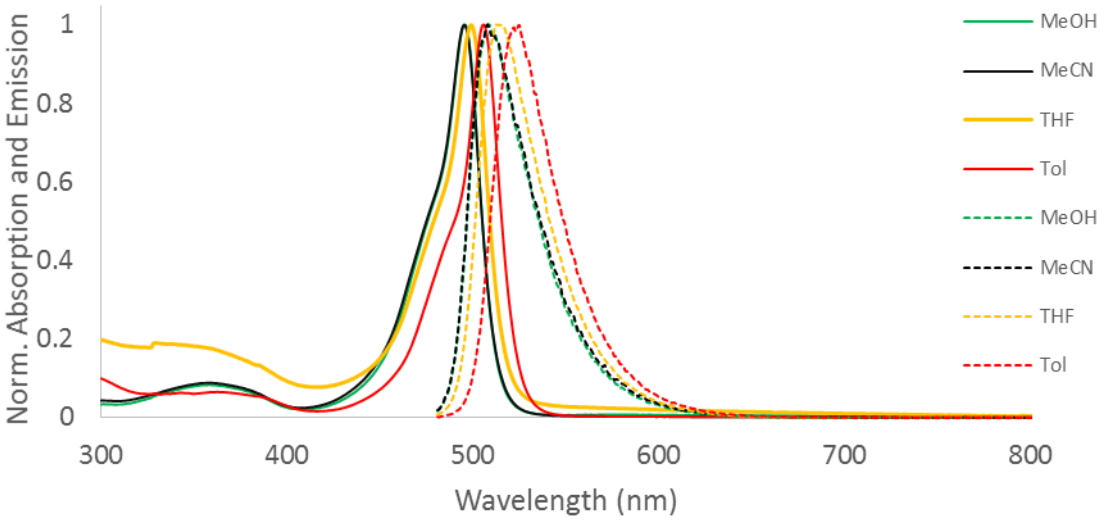
Absorption and Emission of **10**



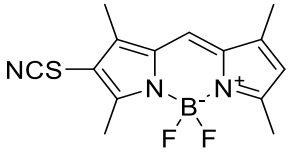


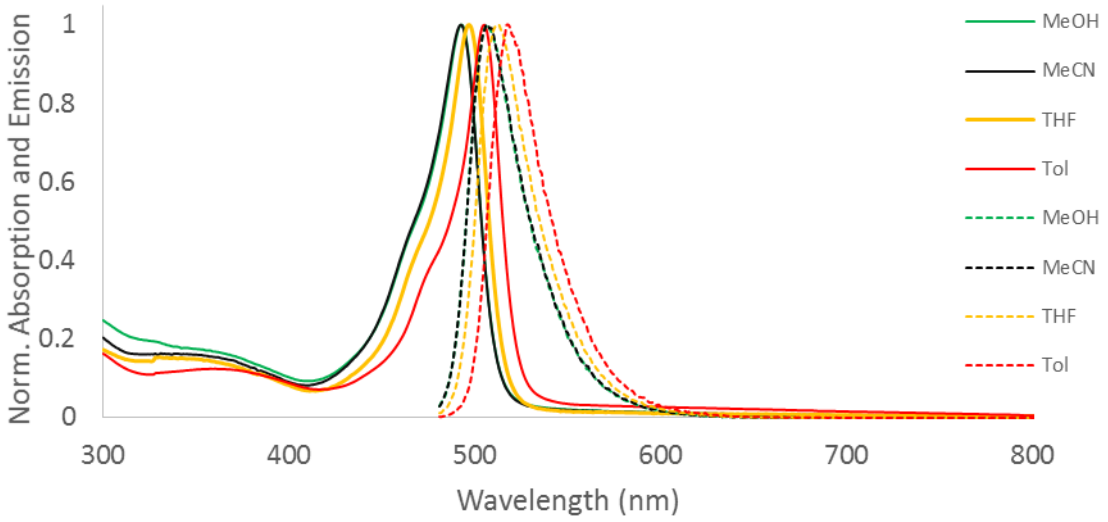
Absorption and emission of **11**



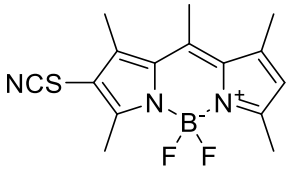


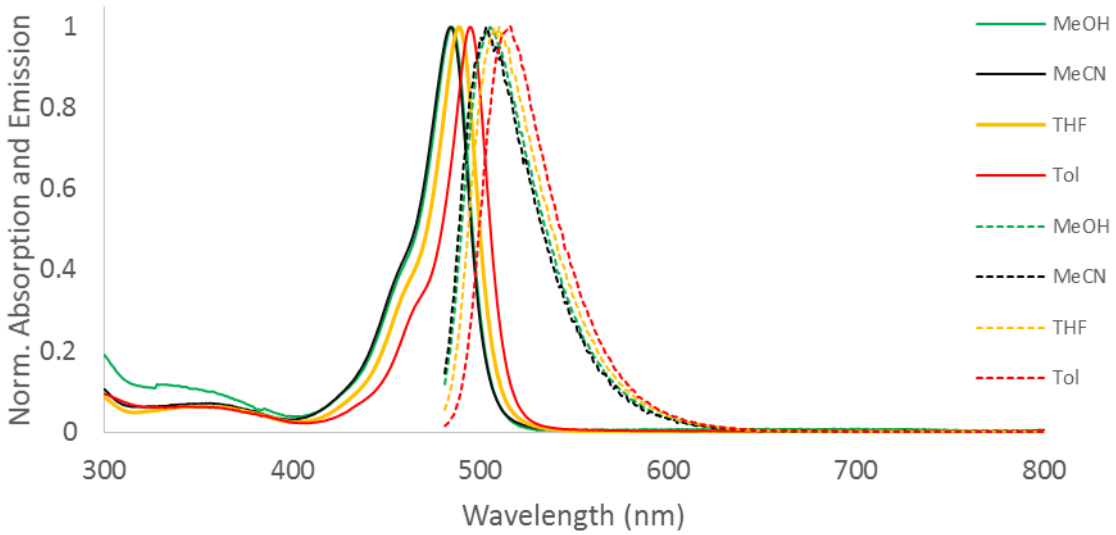
Absorption and emission of **12**



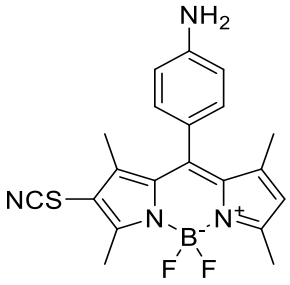


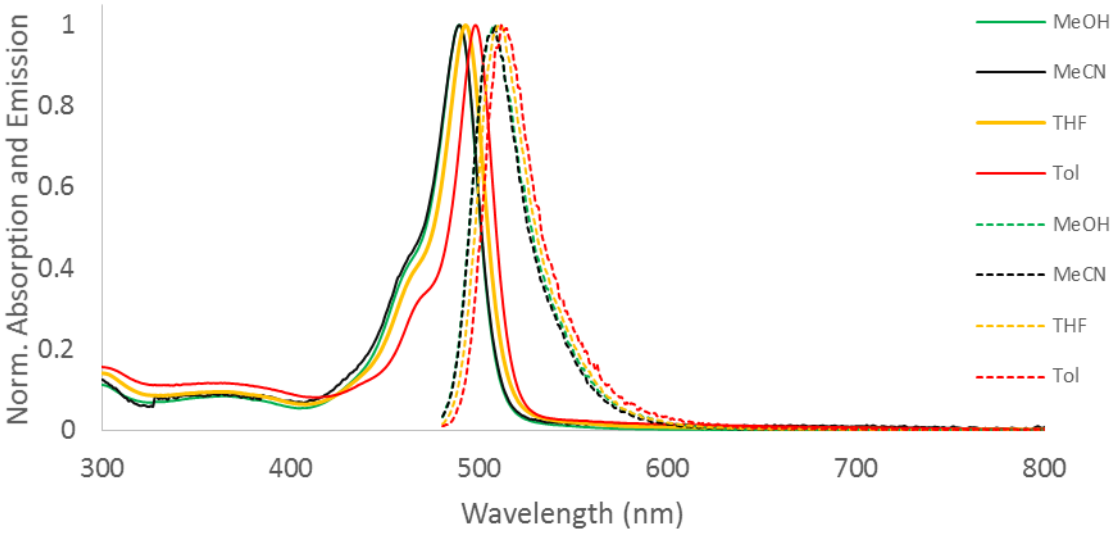
Absorption and emission of **13**



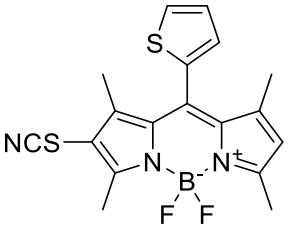


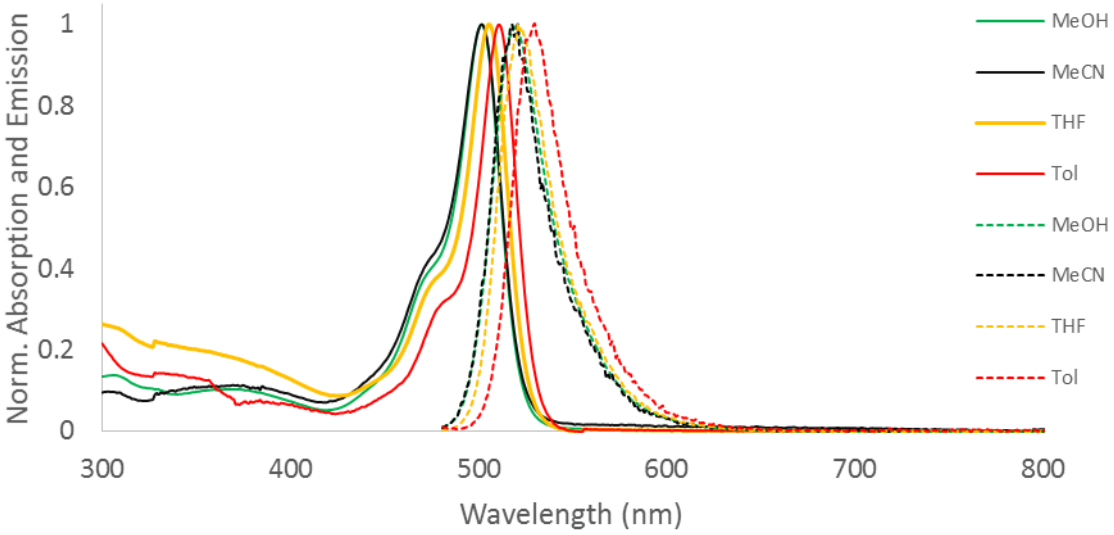
Absorption and emission of **14**



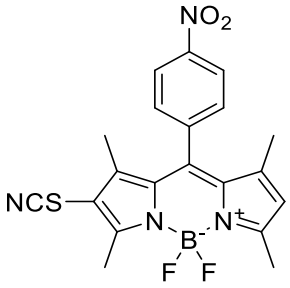


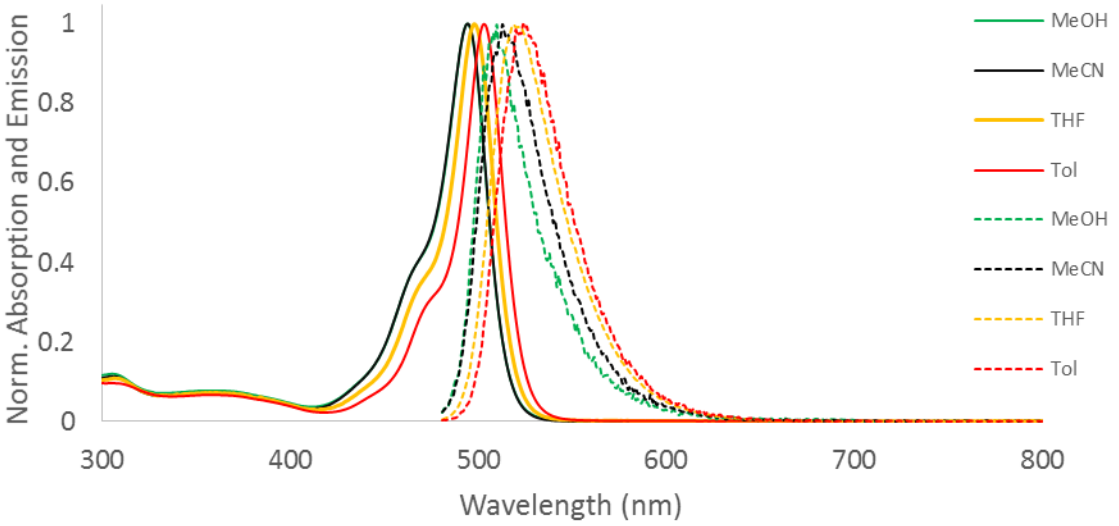
Absorption and emission of **15**



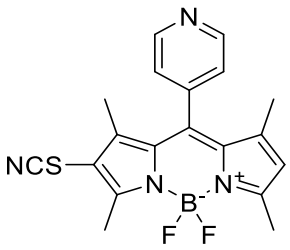


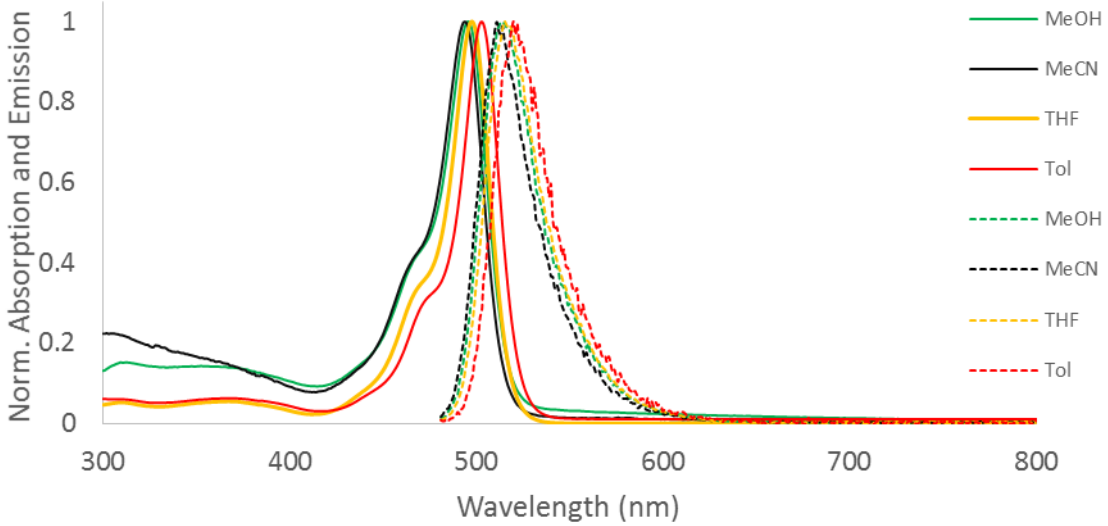
Absorption and emission of **16**



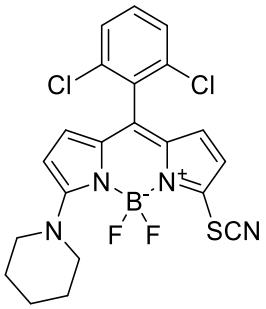


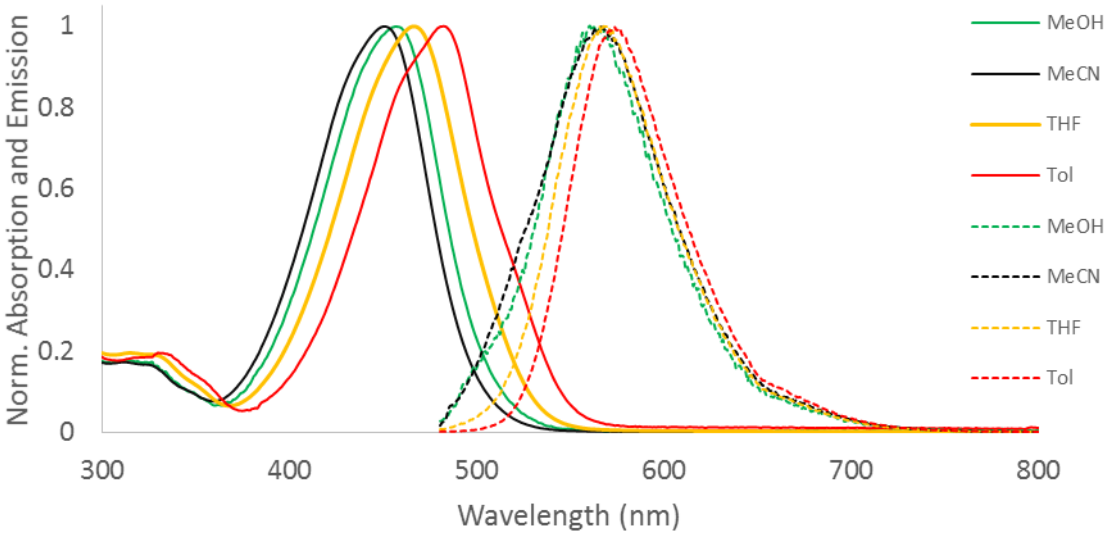
Absorption and emission of **17**



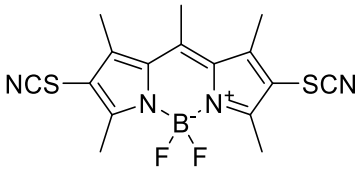


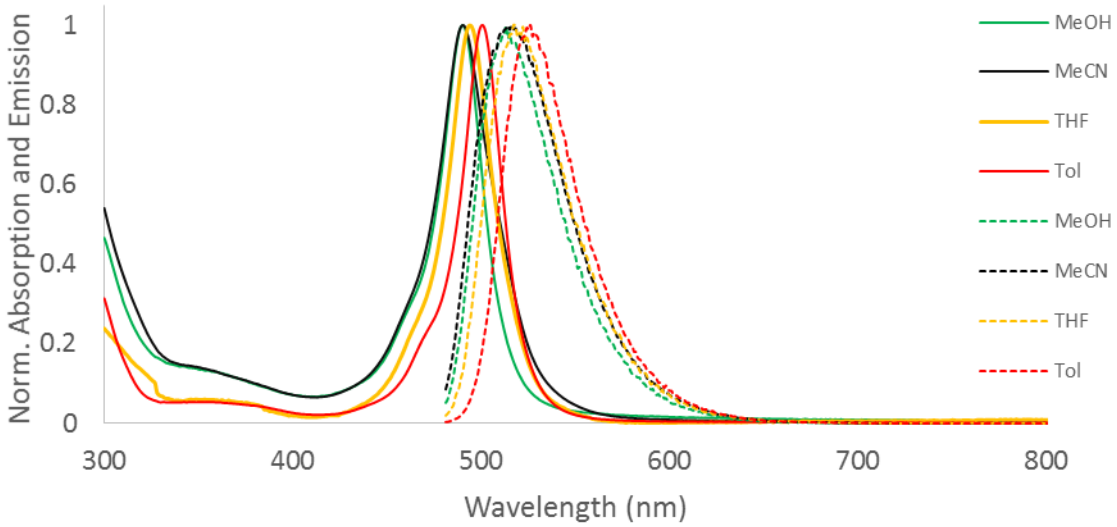
Absorption and emission of **18**



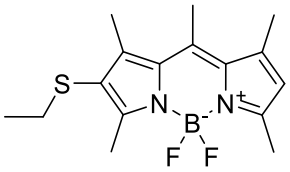


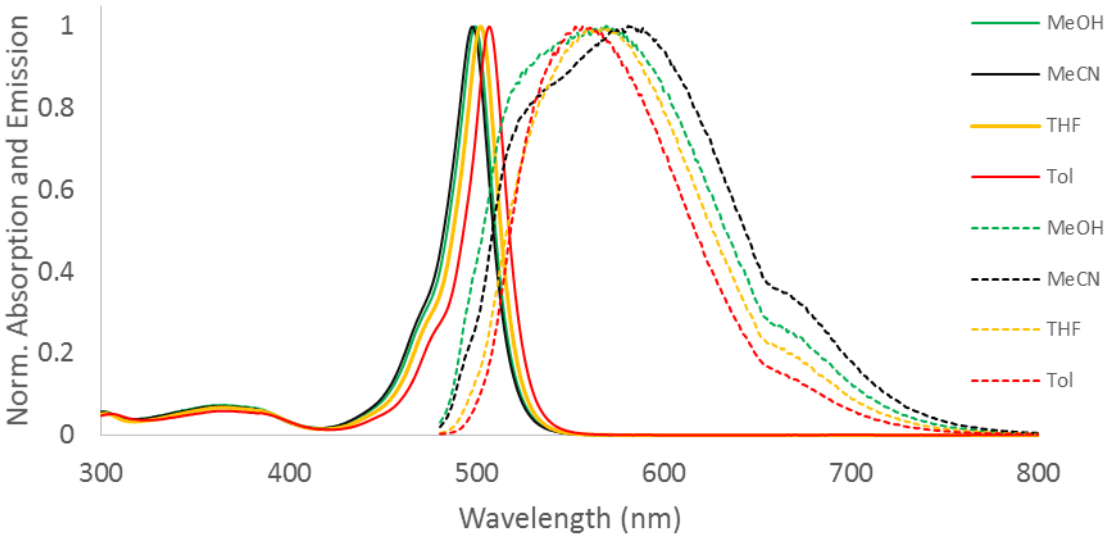
Absorption and emission of **19**



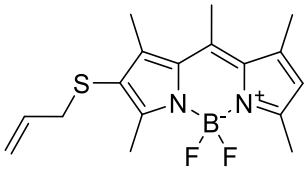


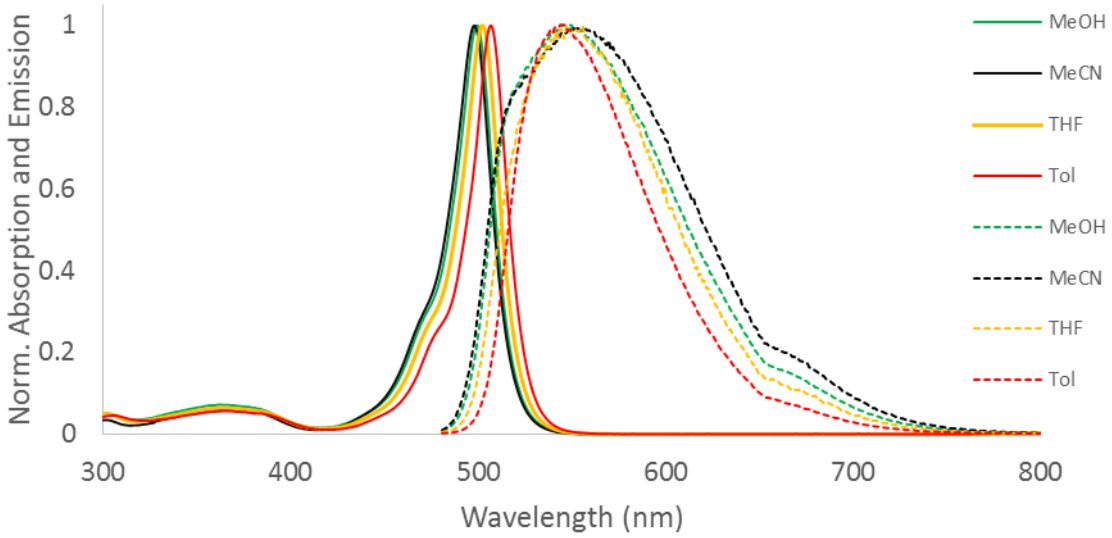
Absorption and emission of **20**



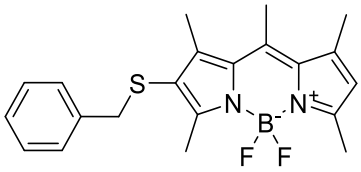


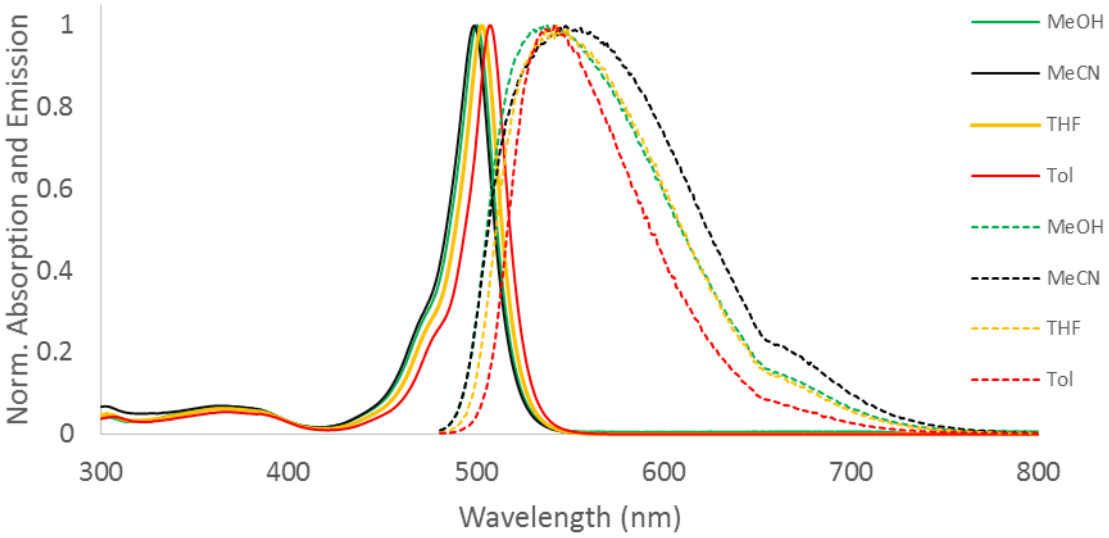
Absorption and emission of **21**



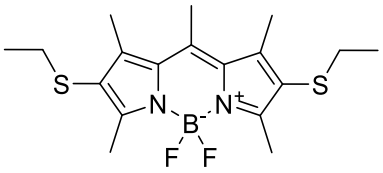


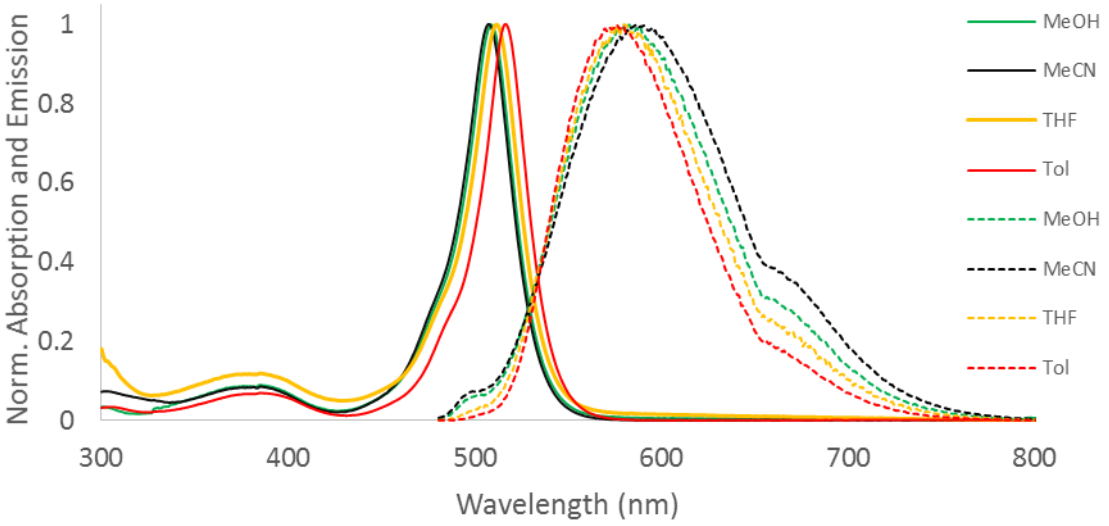
Absorption and emission of **22**



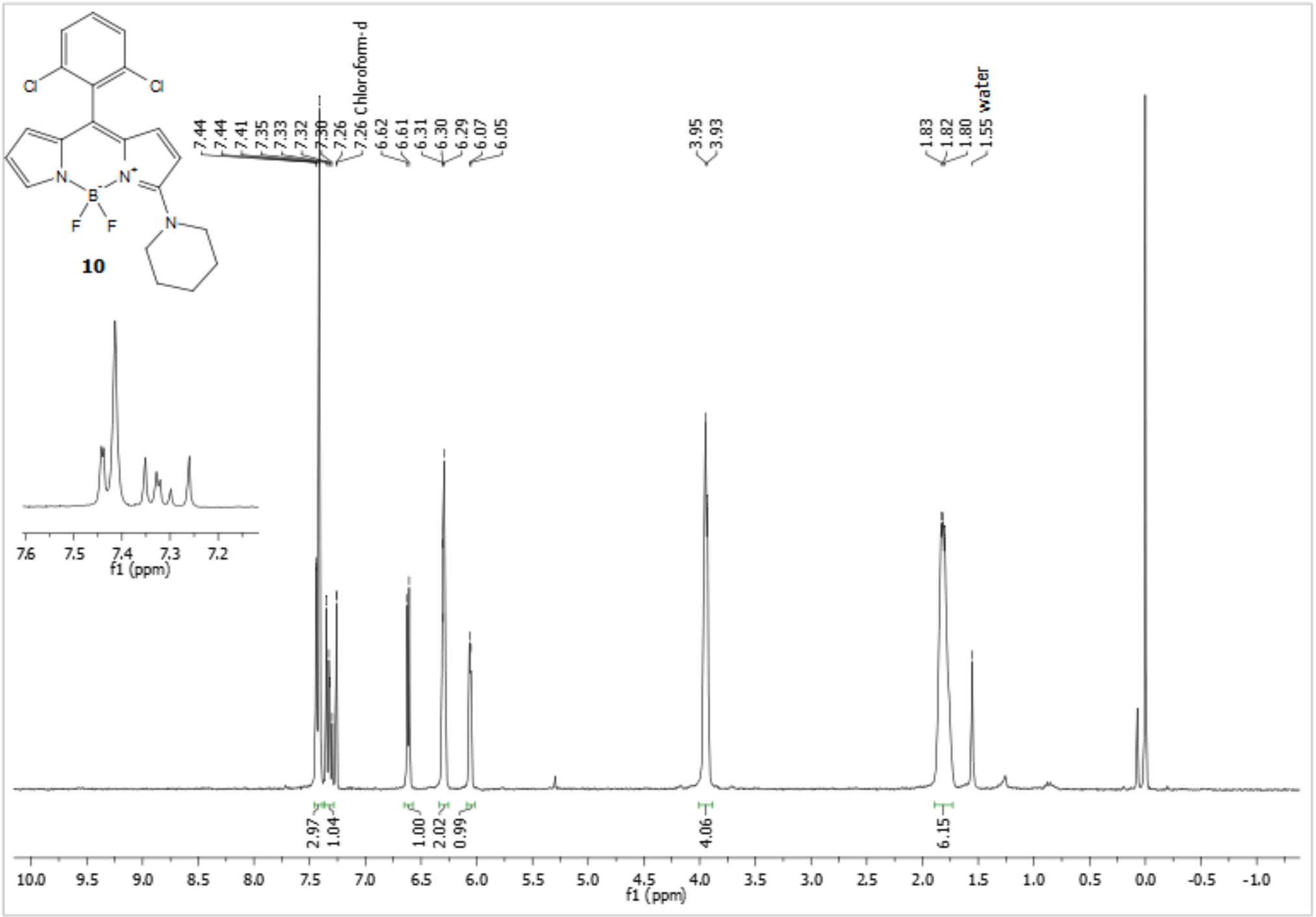


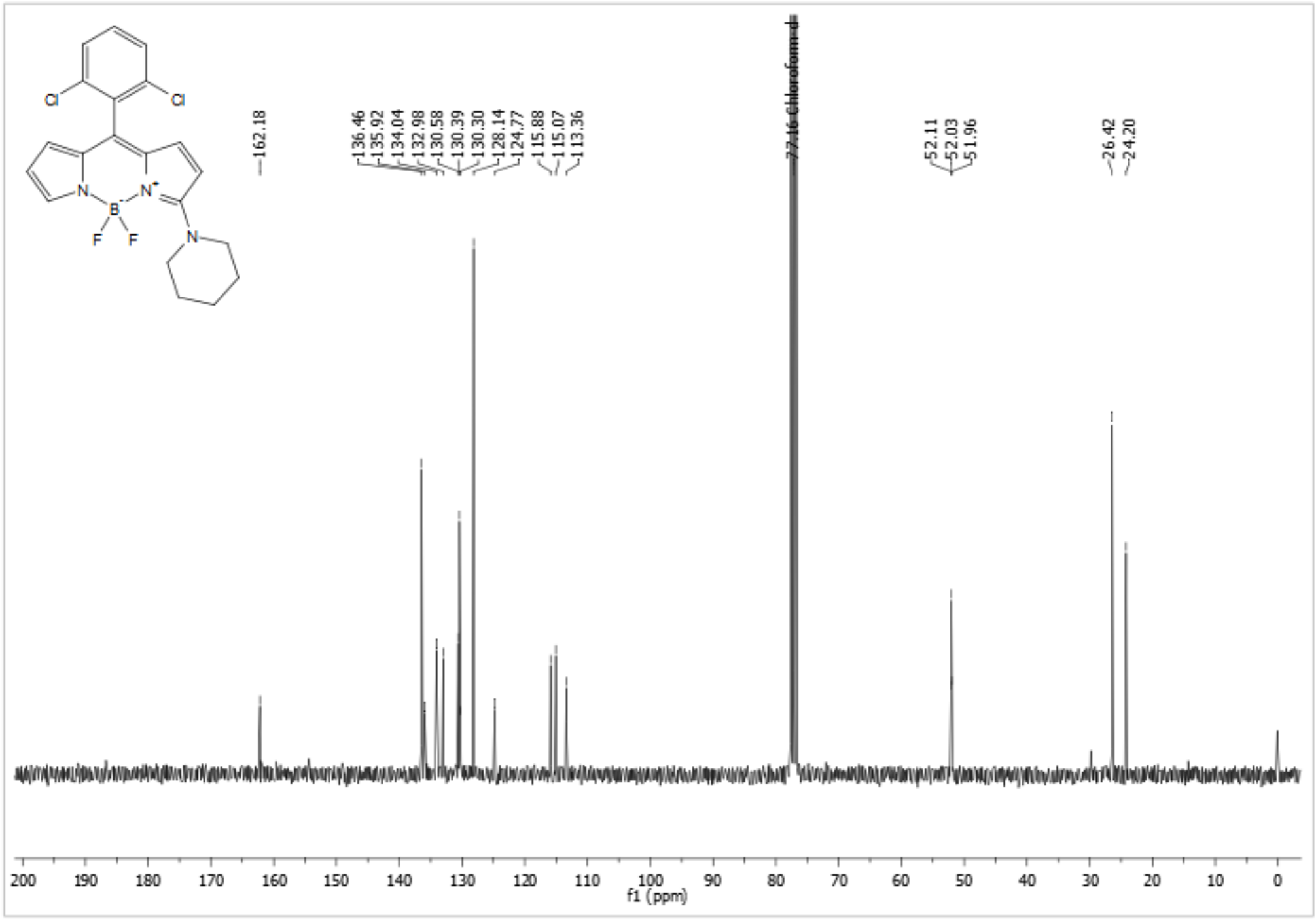
Absorption and emission of **23**

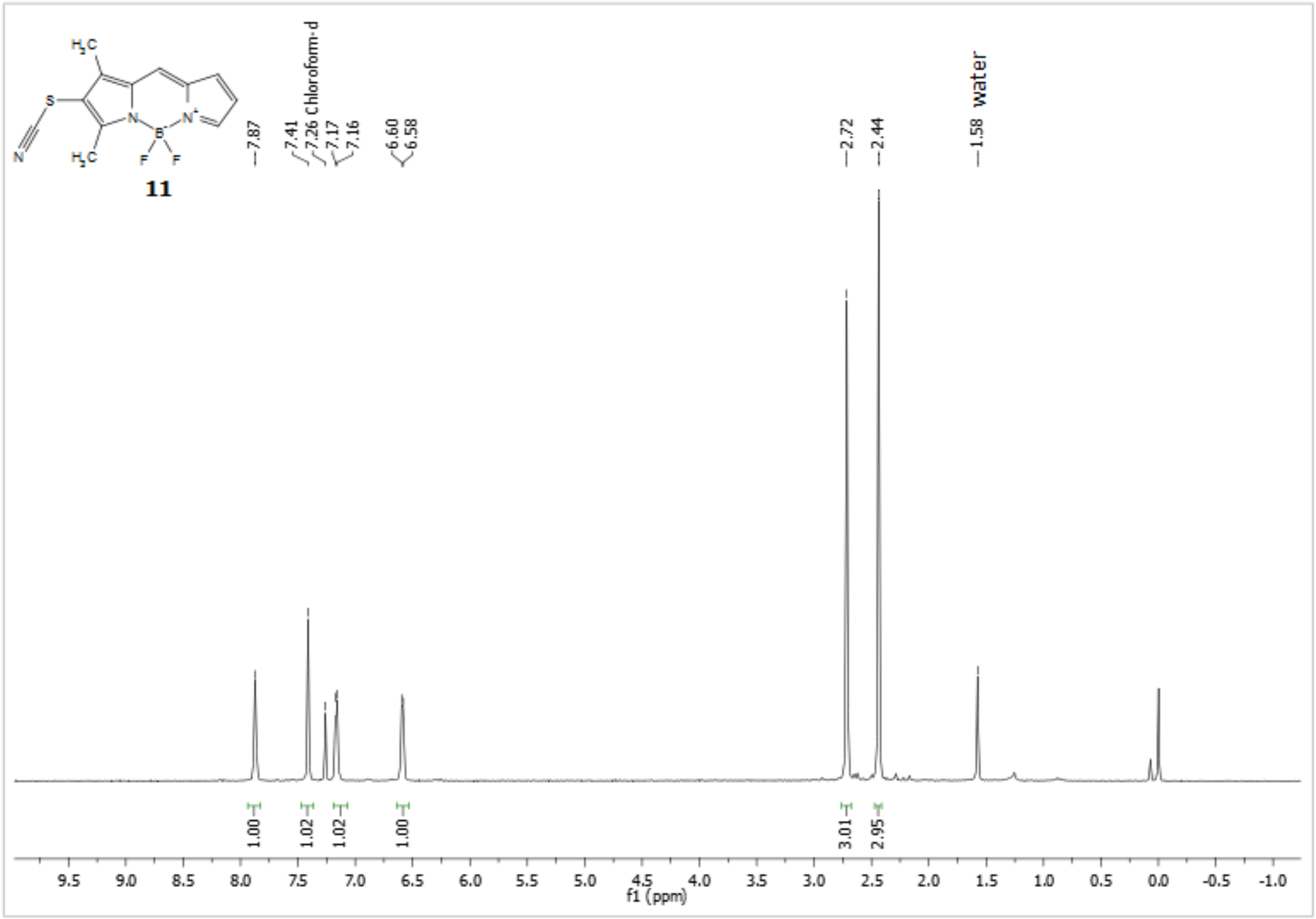


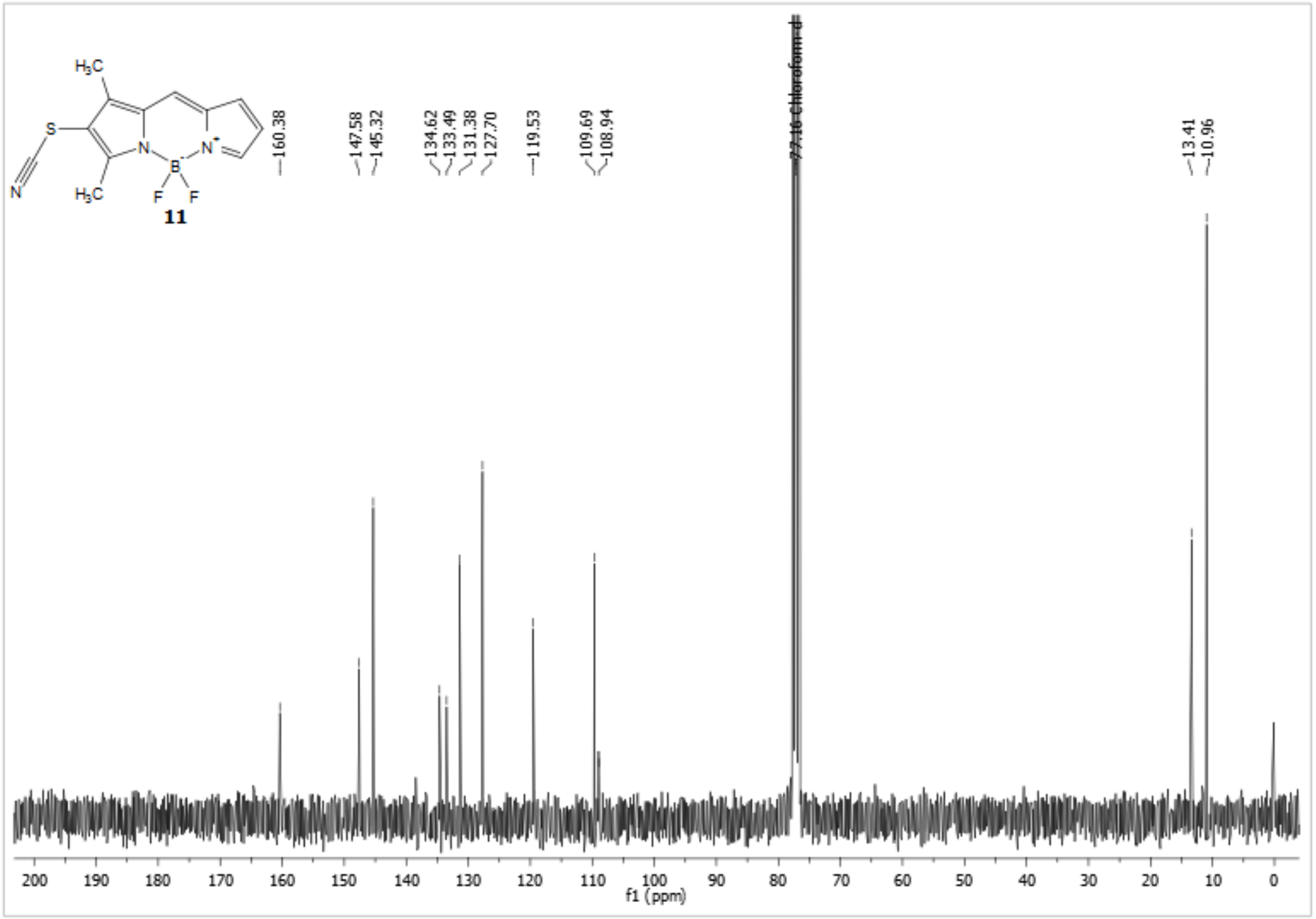


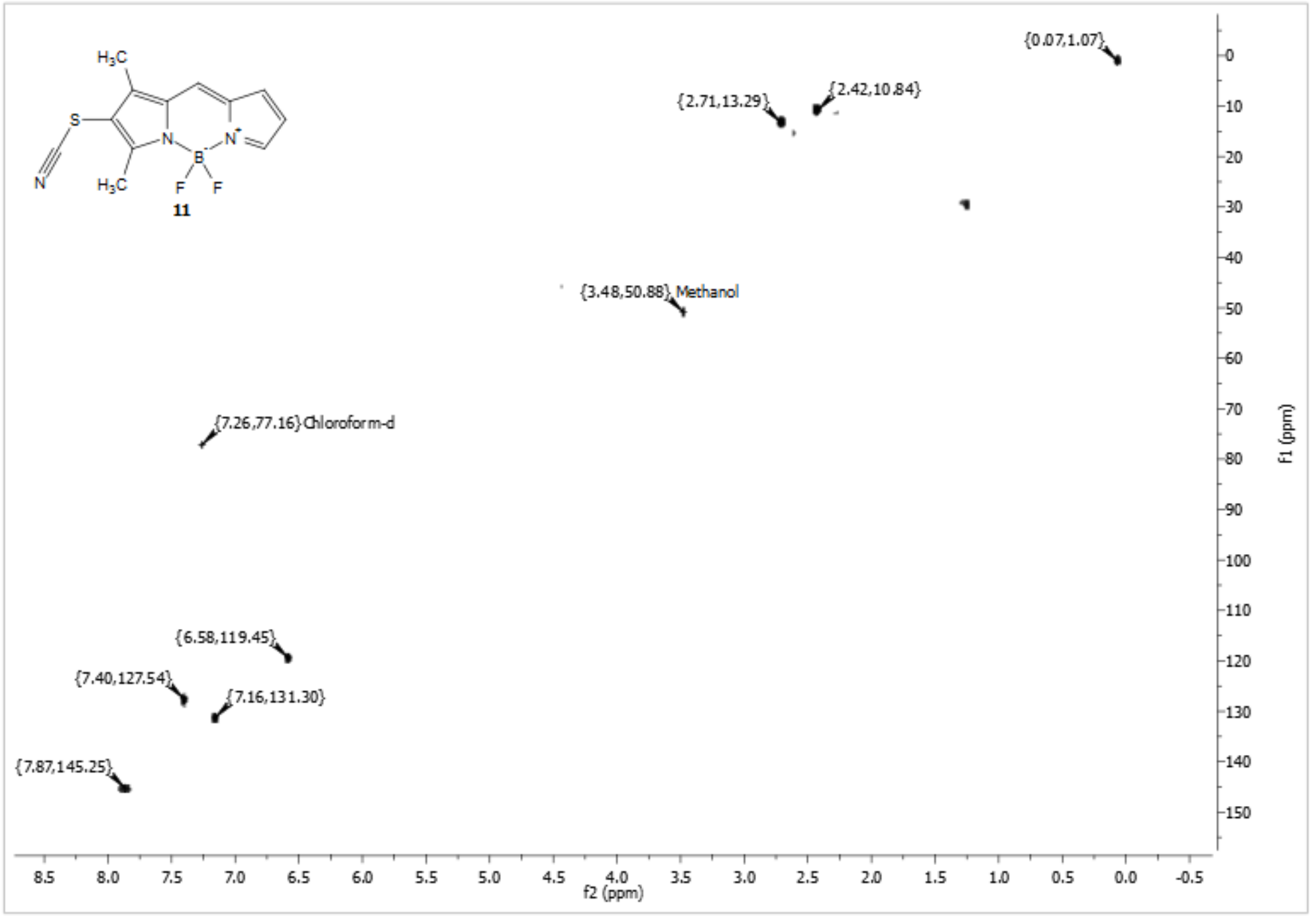
NMR spectra

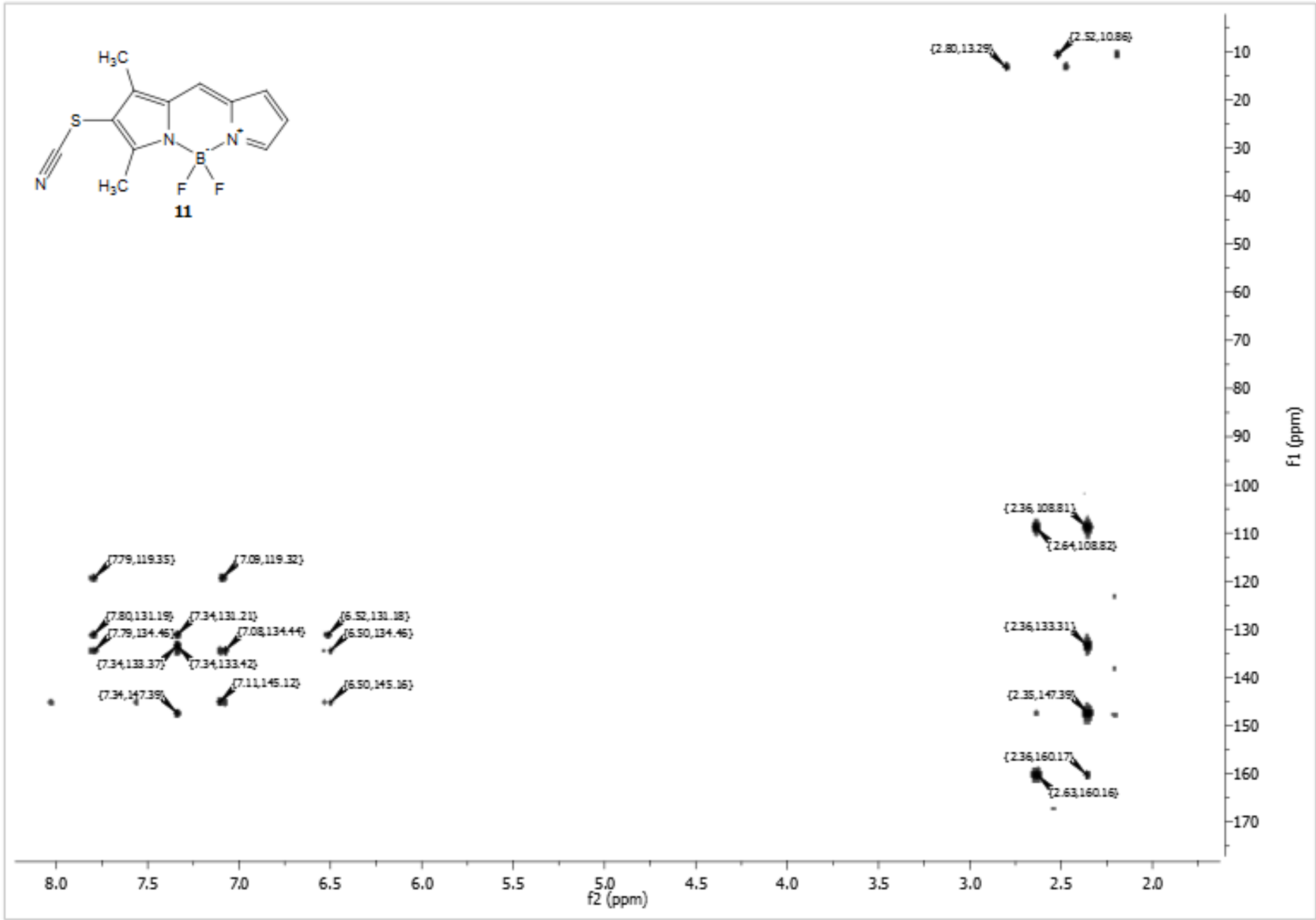

Cl
Cl
N
B
N+
F
F
N
10
7.44
7.44
7.41
7.35
7.33
7.32
7.30
7.26 Chloroform-d
6.62
6.61
6.31
6.30
6.29
6.07
6.05
3.95
3.93
1.83
1.82
1.80
1.55 water
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
2.97
1.04
1.00
2.02
0.99
4.06
6.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

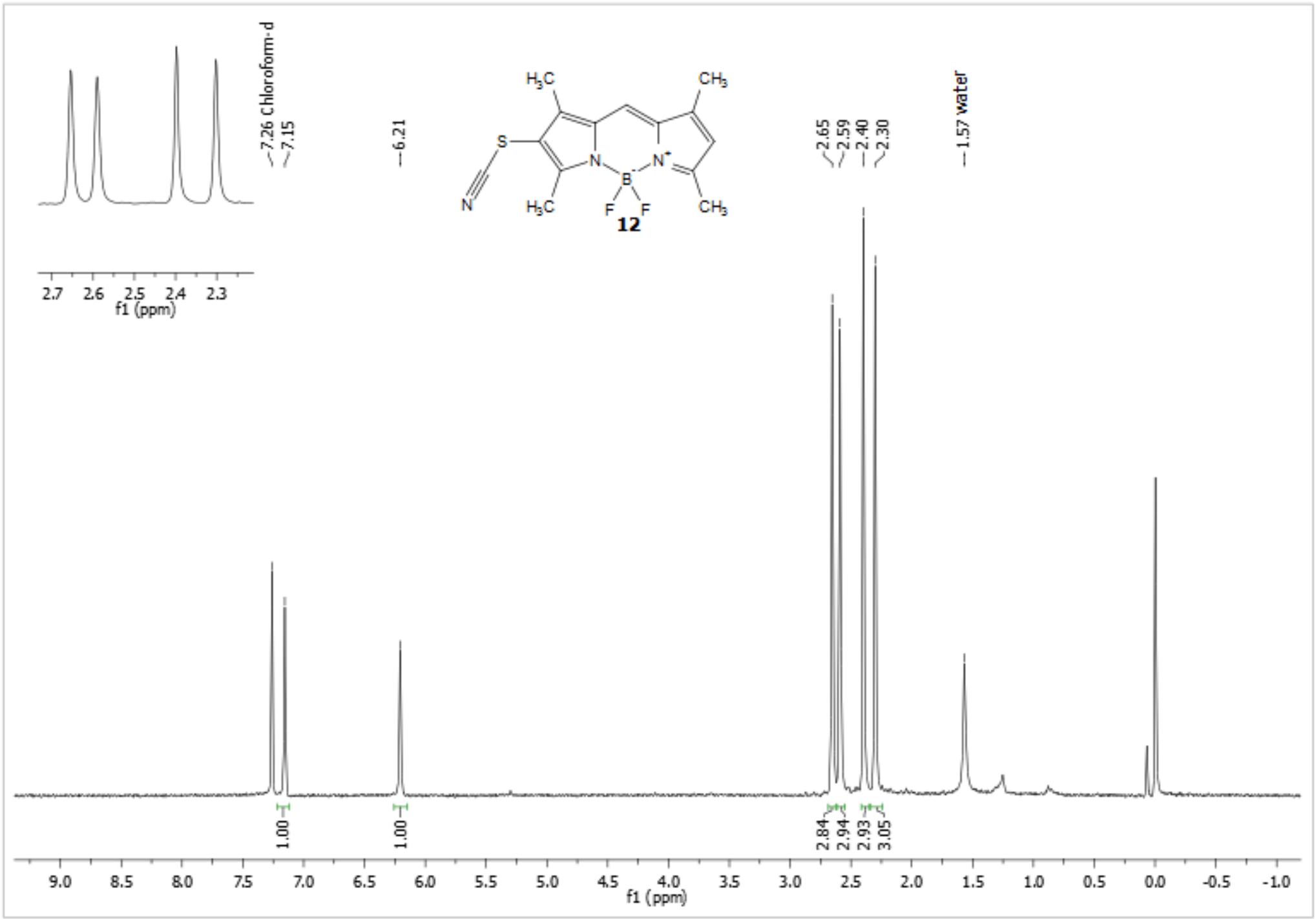

Cl
Cl
N
B
N+
F
F
N
162.18
136.46
135.92
134.04
132.98
130.58
130.39
130.30
128.14
124.77
115.88
115.07
113.36
77.16 Chloroform-d
52.11
52.03
51.96
26.42
24.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

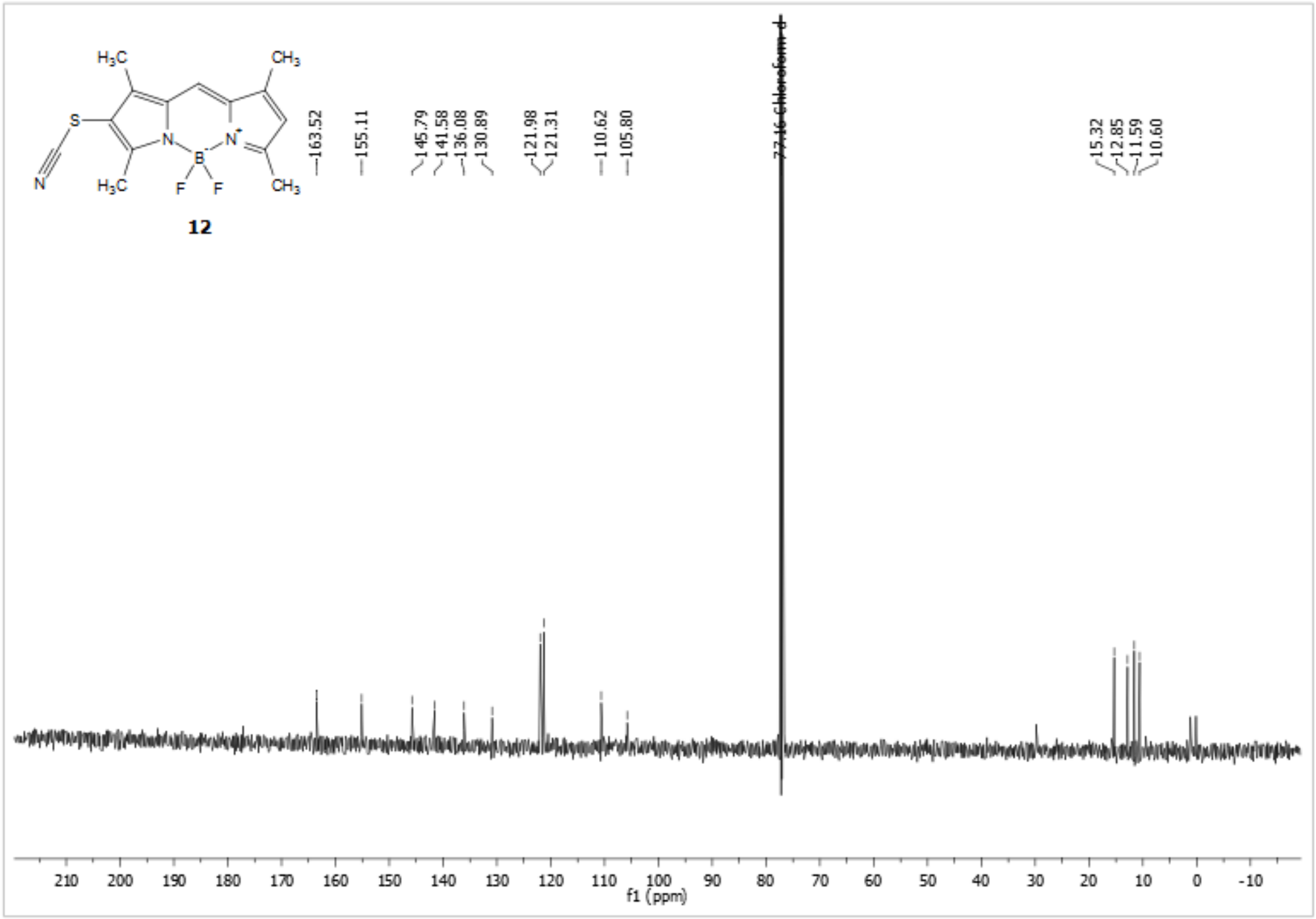

11
7.87
7.41
7.26 Chloroform-d
7.17
7.16
6.60
6.58
2.72
2.44
1.58 water
1.00
1.02
1.02
1.00
3.01
2.95
f1 (ppm)

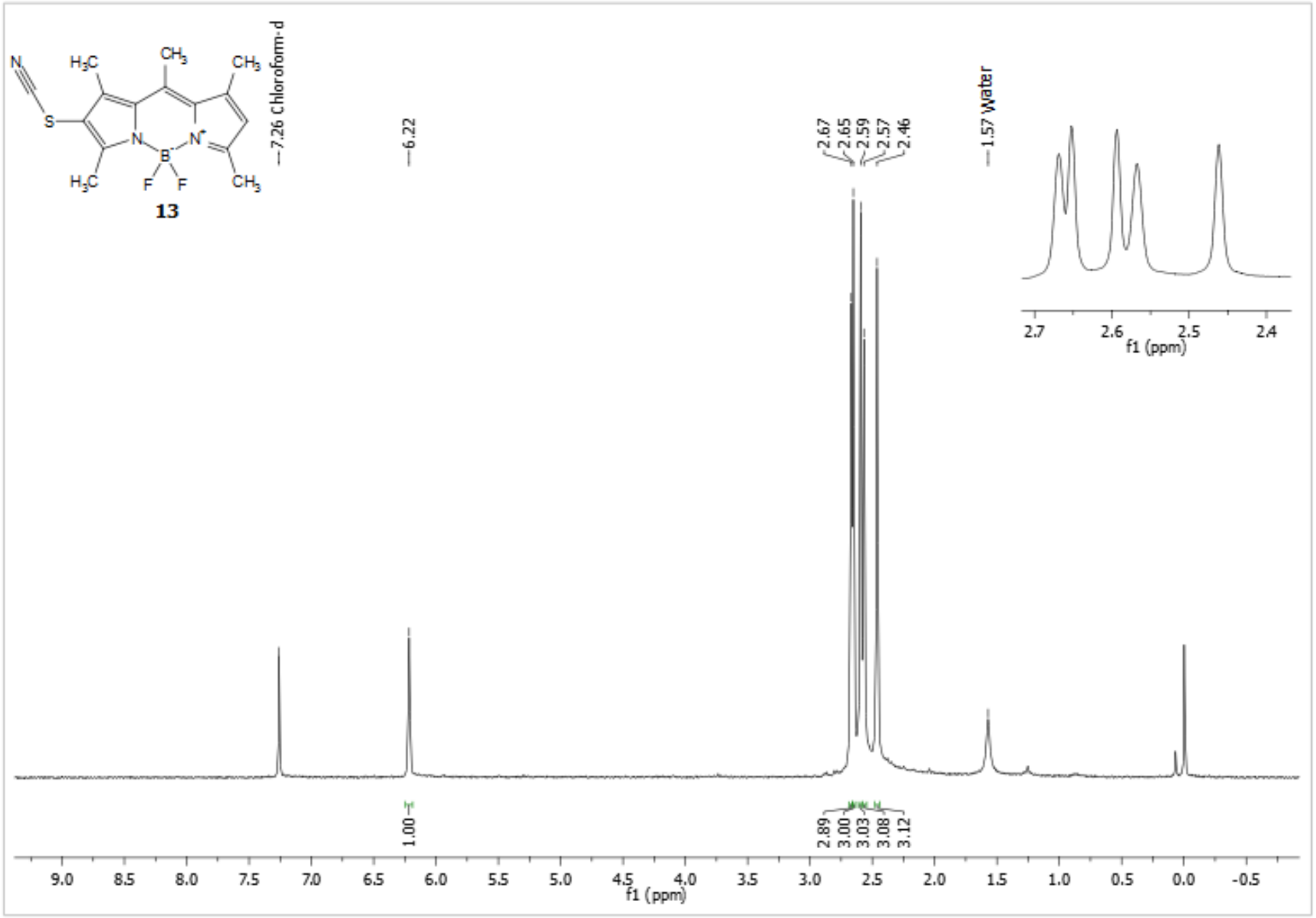

H3C
S
N
N+
B-
F
F
H3C
N
11
160.38
147.58
145.32
134.62
133.49
131.38
127.70
119.53
109.69
108.94
77.16 Chloroform-d
13.41
10.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

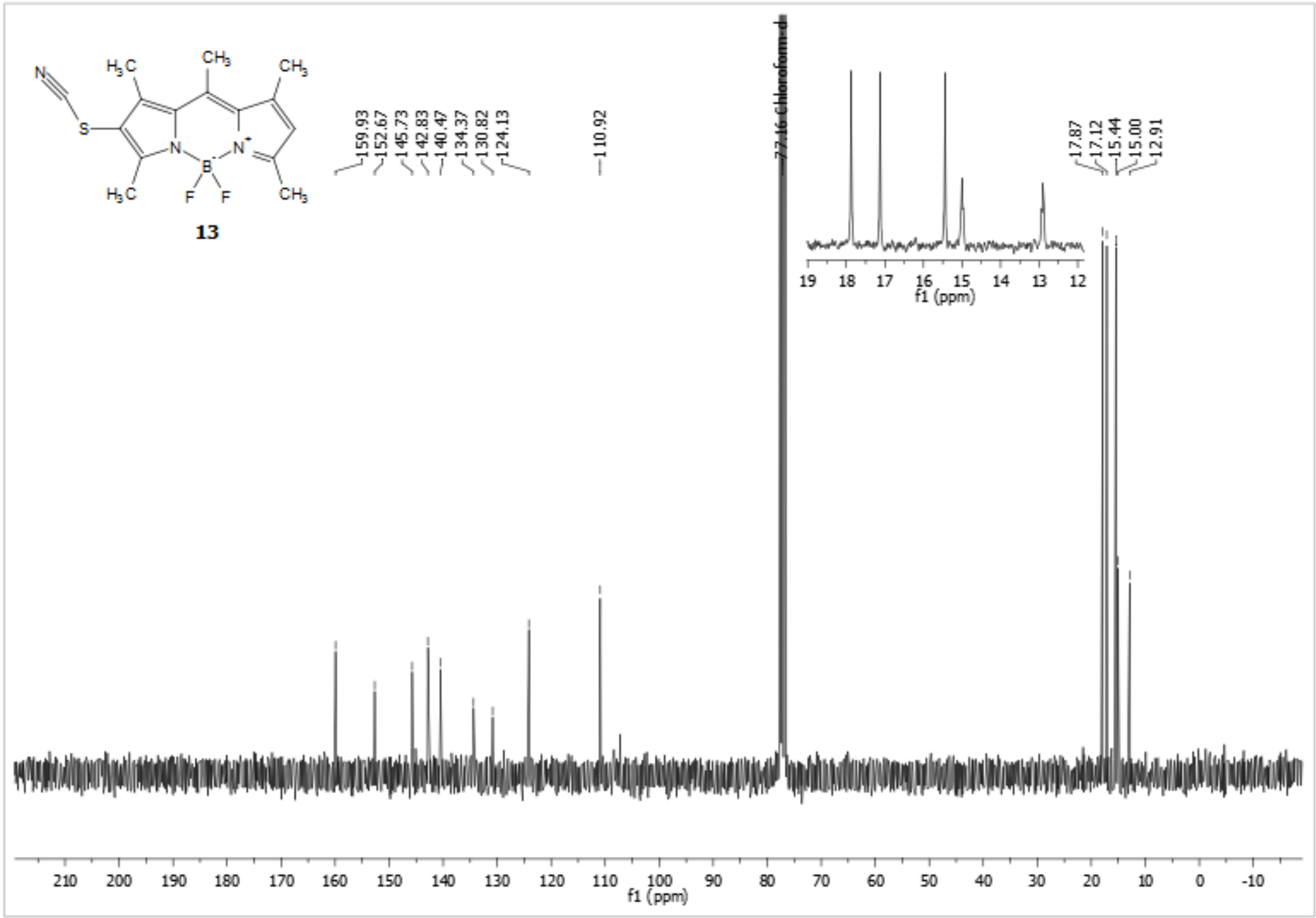

H3C
S
N
B
N+
F
F
H3C
N
11
{0.07,1.07}
{2.71,13.29}
{2.42,10.84}
{3.48,50.88} Methanol
{7.26,77.16} Chloroform-d
{6.58,119.45}
{7.40,127.54}
{7.16,131.30}
{7.87,145.25}
f1 (ppm)
f2 (ppm)

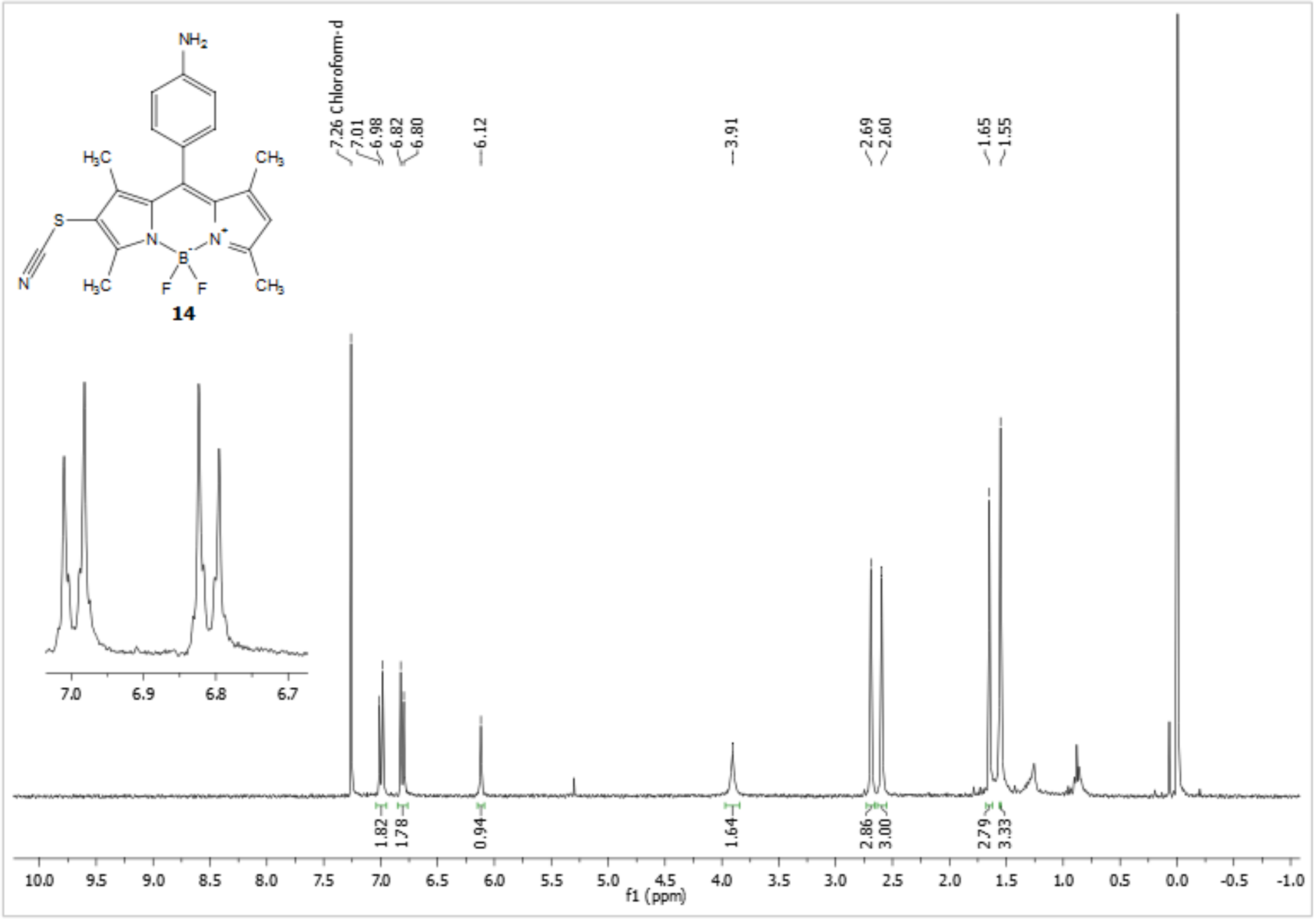

H3C
S
N
B
N+
N
H3C
F
F
11
{2.80,13.29}
{2.52,10.86}
{7.79,119.35}
{7.09,119.32}
{7.80,131.19}
{7.34,131.21}
{6.52,131.18}
{7.79,134.46}
{7.08,134.44}
{6.50,134.46}
{7.34,133.37}
{7.34,133.42}
{7.34,147.39}
{7.11,145.12}
{6.50,145.16}
{2.36,108.81}
{2.64,108.82}
{2.36,133.31}
{2.35,147.39}
{2.36,160.17}
{2.63,160.16}
f1 (ppm)
f2 (ppm)

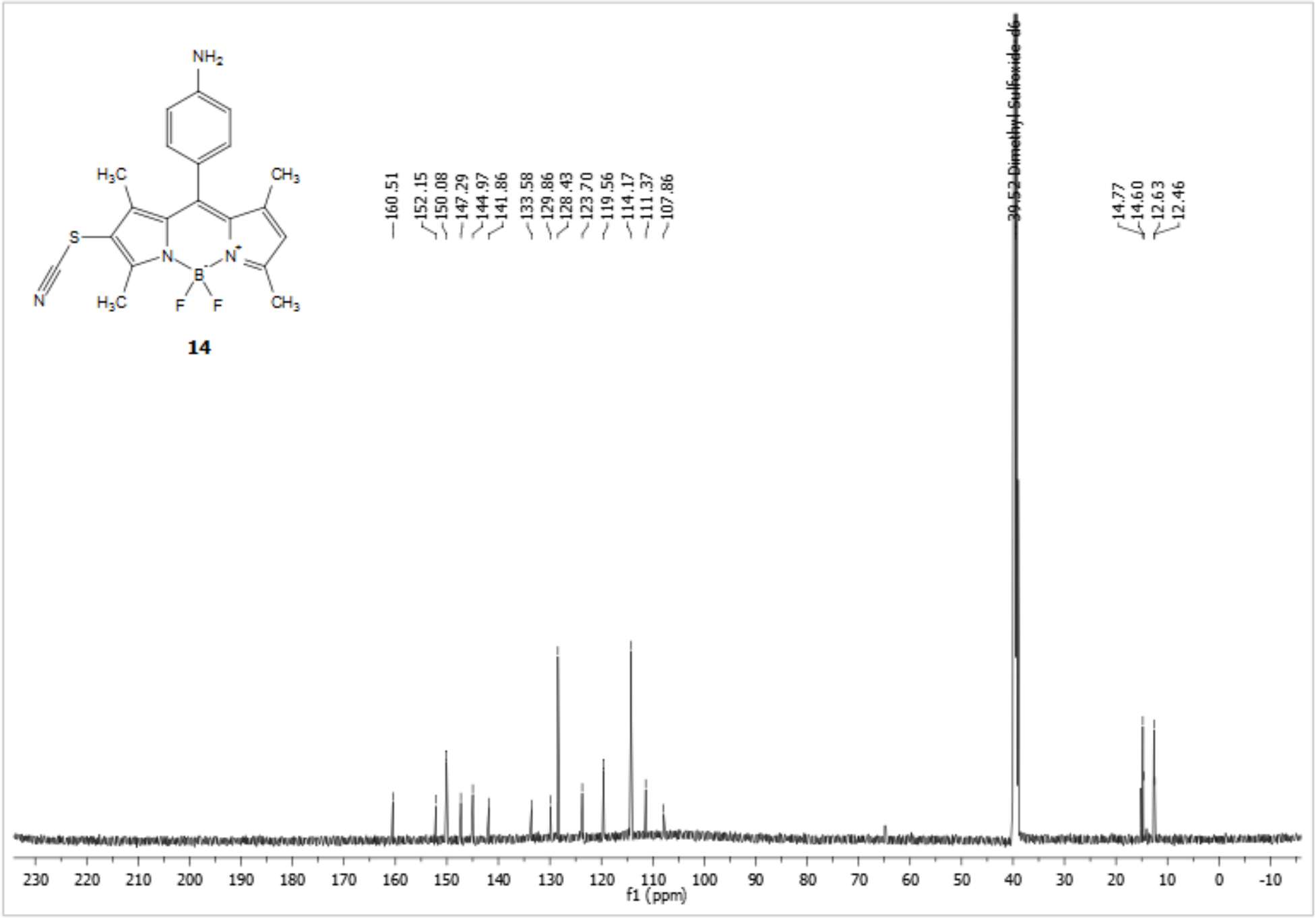

7.26 Chloroform-d
7.15
6.21
2.65
2.59
2.40
2.30
1.57 water
12
1.00
1.00
2.84
2.94
2.93
3.05
f1 (ppm)


H3C
CH3
S
N
N
B
N+
F
F
H3C
CH3
N
12
163.52
155.11
145.79
141.58
136.08
130.89
121.98
121.31
110.62
105.80
77.16 chloroform-d
15.32
12.85
11.59
10.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

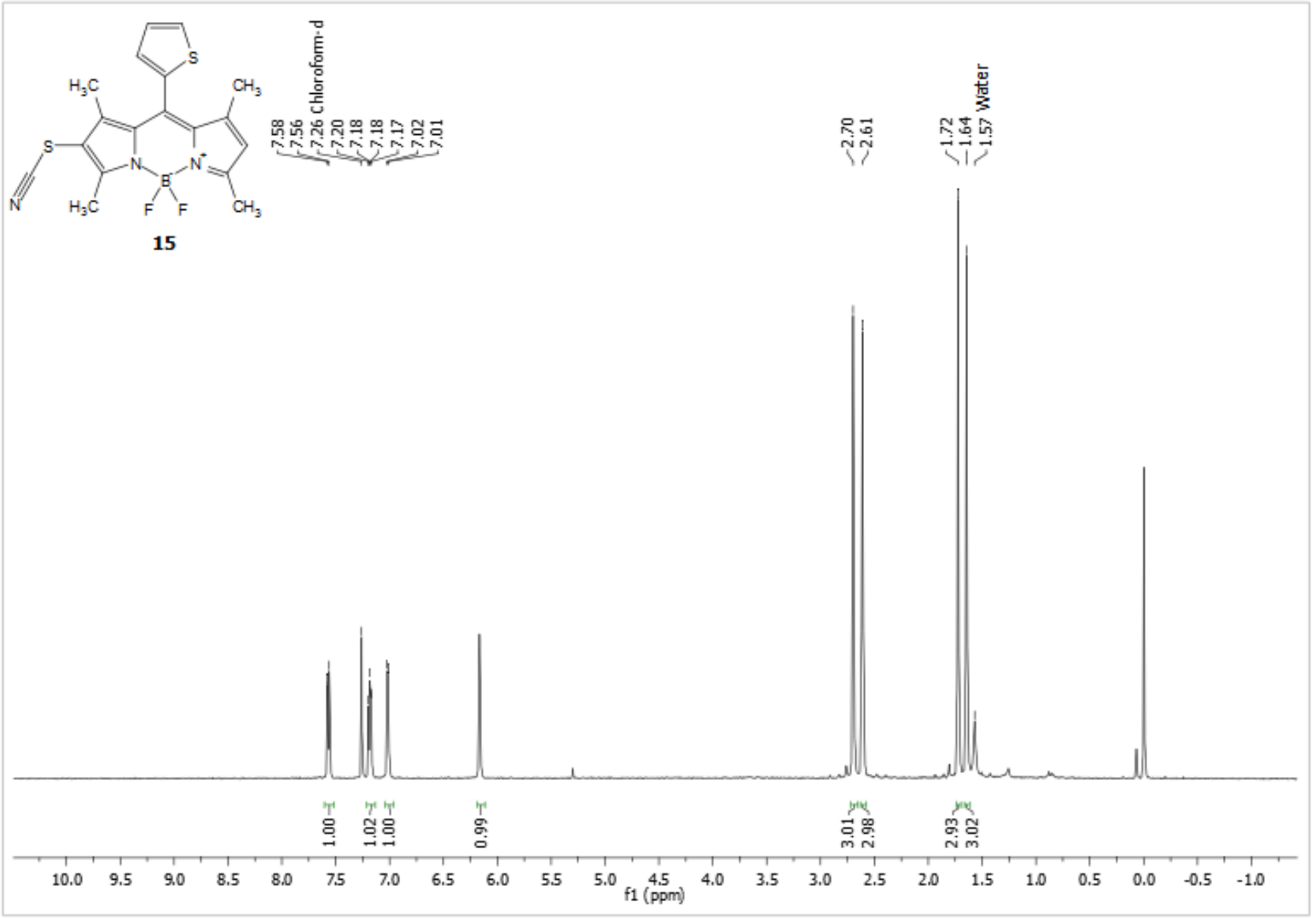

13
7.26 Chloroform-d
6.22
2.67
2.65
2.59
2.57
2.46
1.57 water
1.00
2.89
3.00
3.03
3.08
3.12
f1 (ppm)

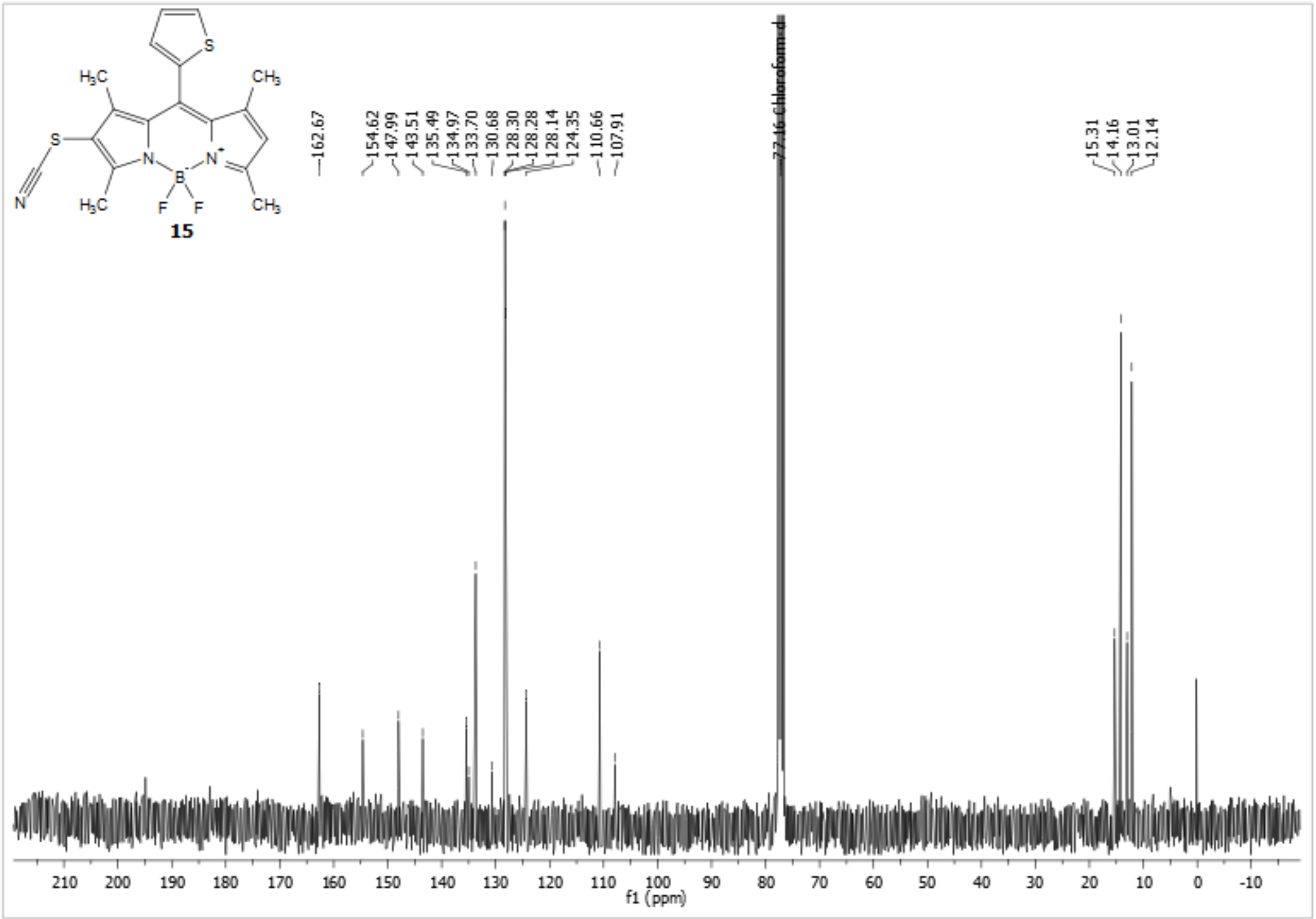

13
159.93
152.67
145.73
142.83
140.47
134.37
130.82
124.13
110.92
77.16 Chloroform-d
17.87
17.12
15.44
15.00
12.91
f1 (ppm)
f1 (ppm)

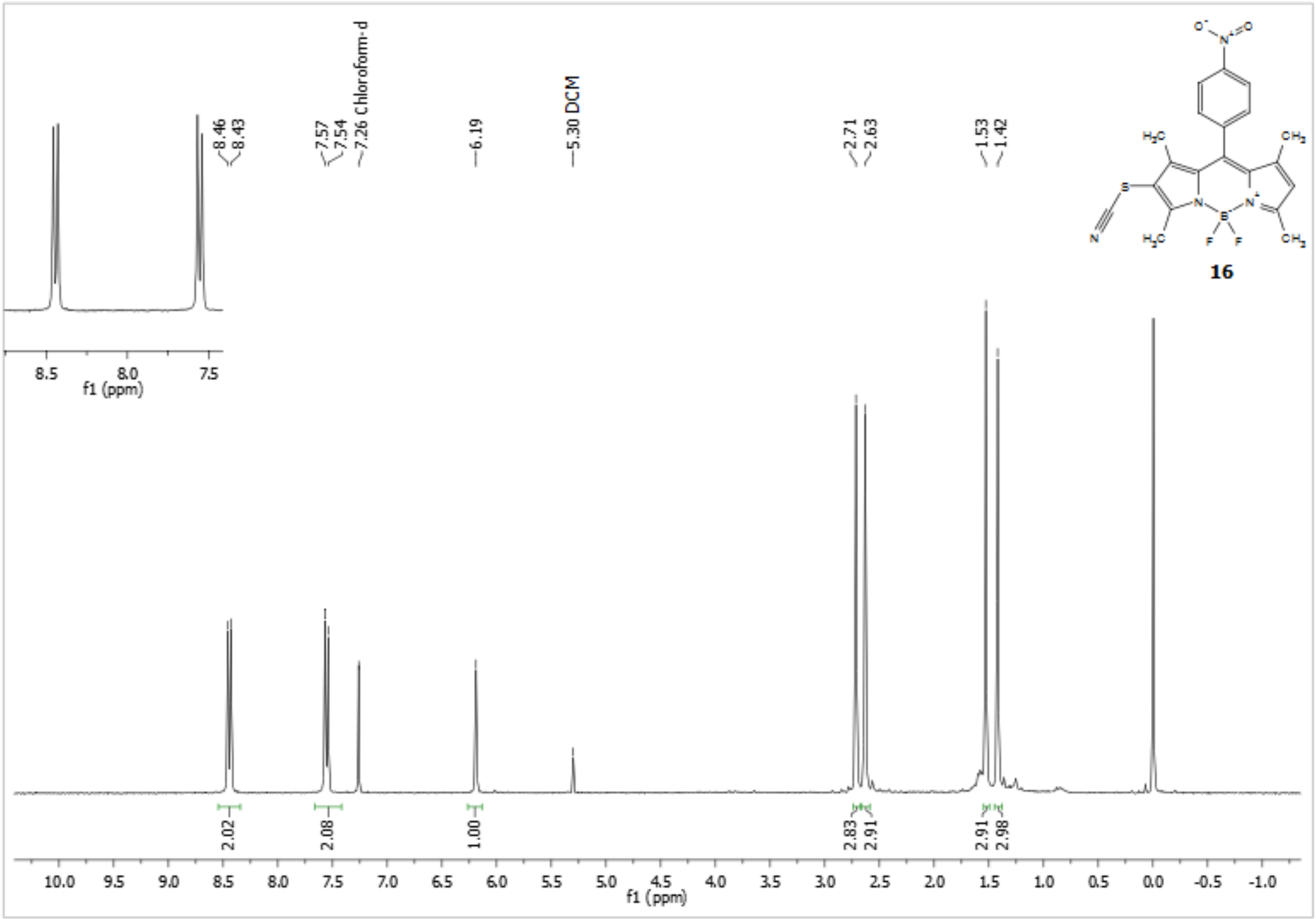

NH2
H3C
CH3
S
N
B
N+
F
F
H3C
CH3
N
14
7.26 Chloroform-d
7.01
6.98
6.82
6.80
6.12
3.91
2.69
2.60
1.65
1.55
1.82
1.78
0.94
1.64
2.86
3.00
2.79
3.33
f1 (ppm)


NH2
H3C
CH3
S
N
N
B
N+
F
F
H3C
CH3
N
160.51
152.15
150.08
147.29
144.97
141.86
133.58
129.86
128.43
123.70
119.56
114.17
111.37
107.86
39.52 Dimethyl Sulfoxide-d6
14.77
14.60
12.63
12.46
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

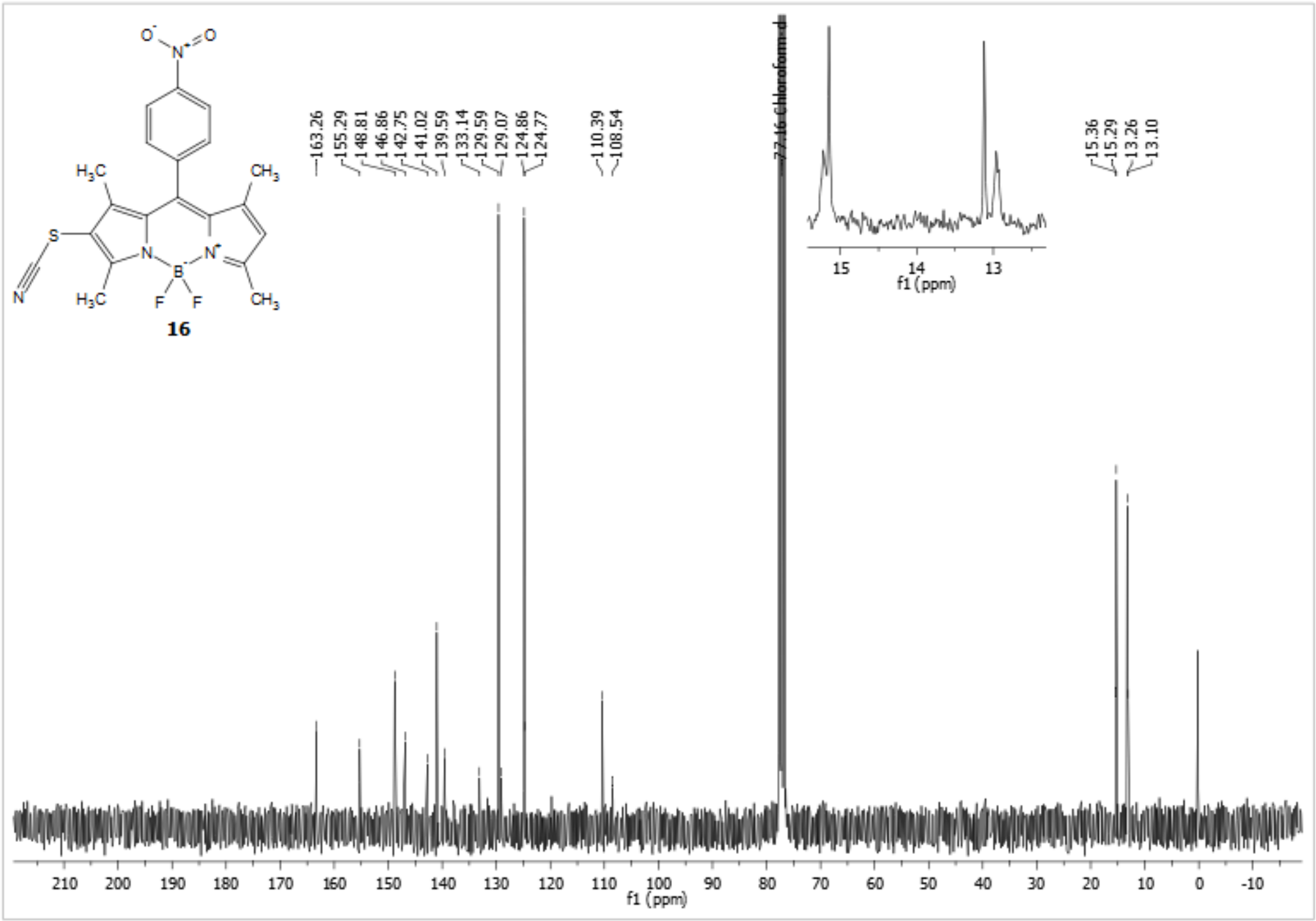
14

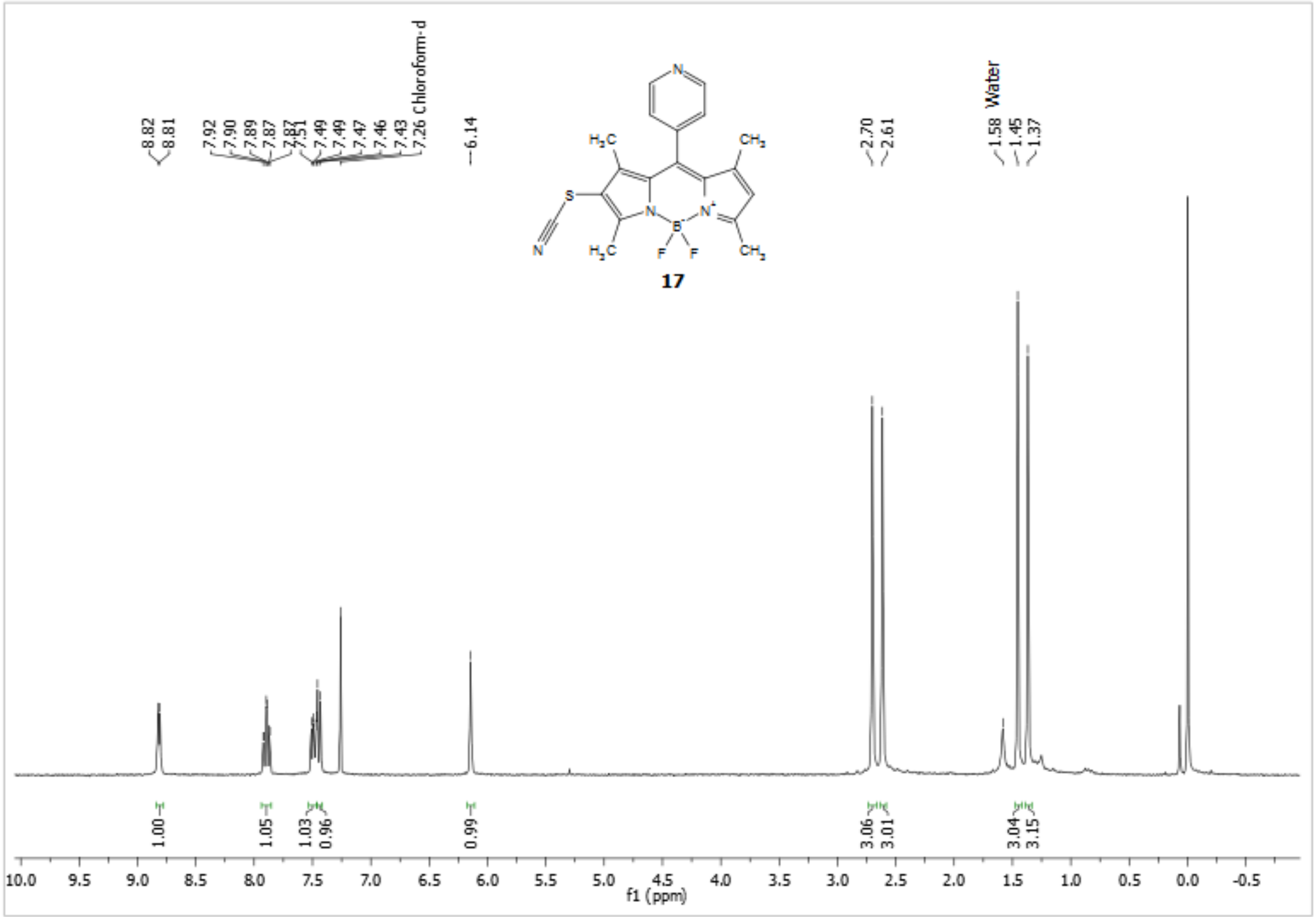

15
7.58
7.56
Chloroform-d
7.26
7.20
7.18
7.18
7.17
7.02
7.01
2.70
2.61
1.72
1.64
Water
1.57
1.00
1.02
1.00
0.99
3.01
2.98
2.93
3.02
f1 (ppm)


S
H3C
CH3
S
N
B
N+
N
H3C
F
F
CH3
15
162.67
154.62
147.99
143.51
135.49
134.97
133.70
130.68
128.30
128.28
128.14
124.35
110.66
107.91
77.16 Chloroform-d
15.31
14.16
13.01
12.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

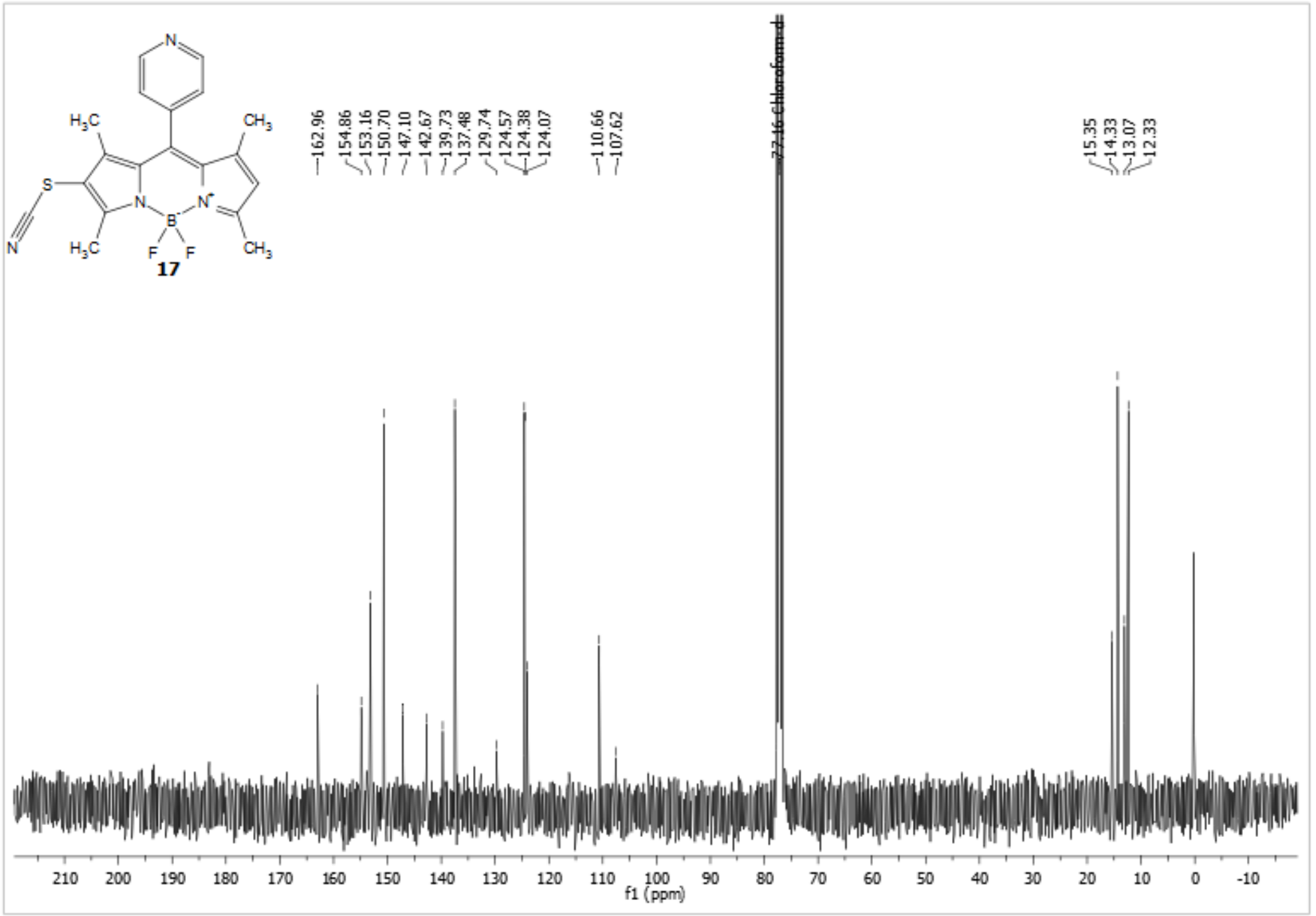

8.46
8.43
7.57
7.54
7.26 Chloroform-d
6.19
5.30 DCM
2.71
2.63
1.53
1.42
8.5
8.0
7.5
f1 (ppm)
2.02
2.08
1.00
2.83
2.91
2.91
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

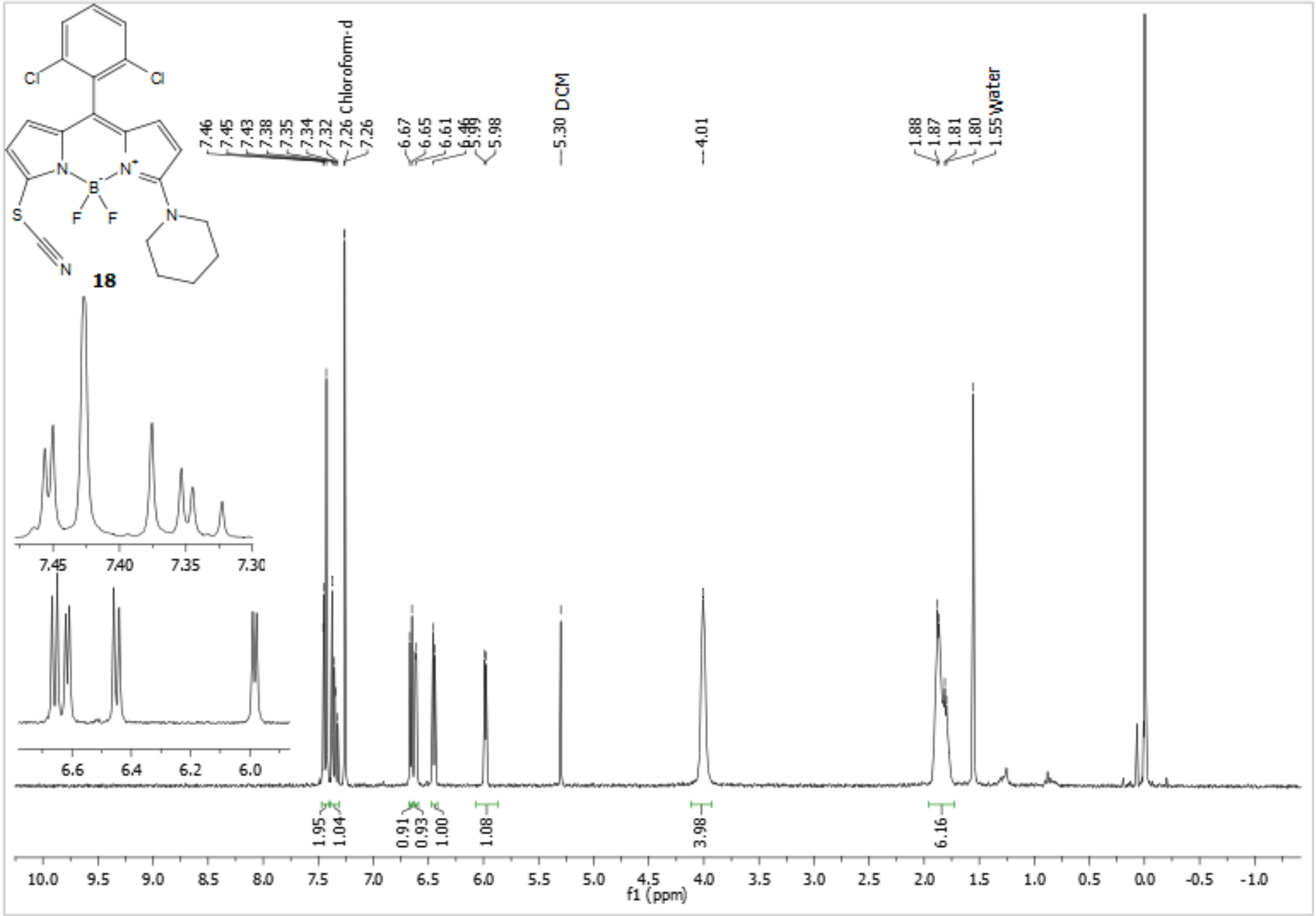
16

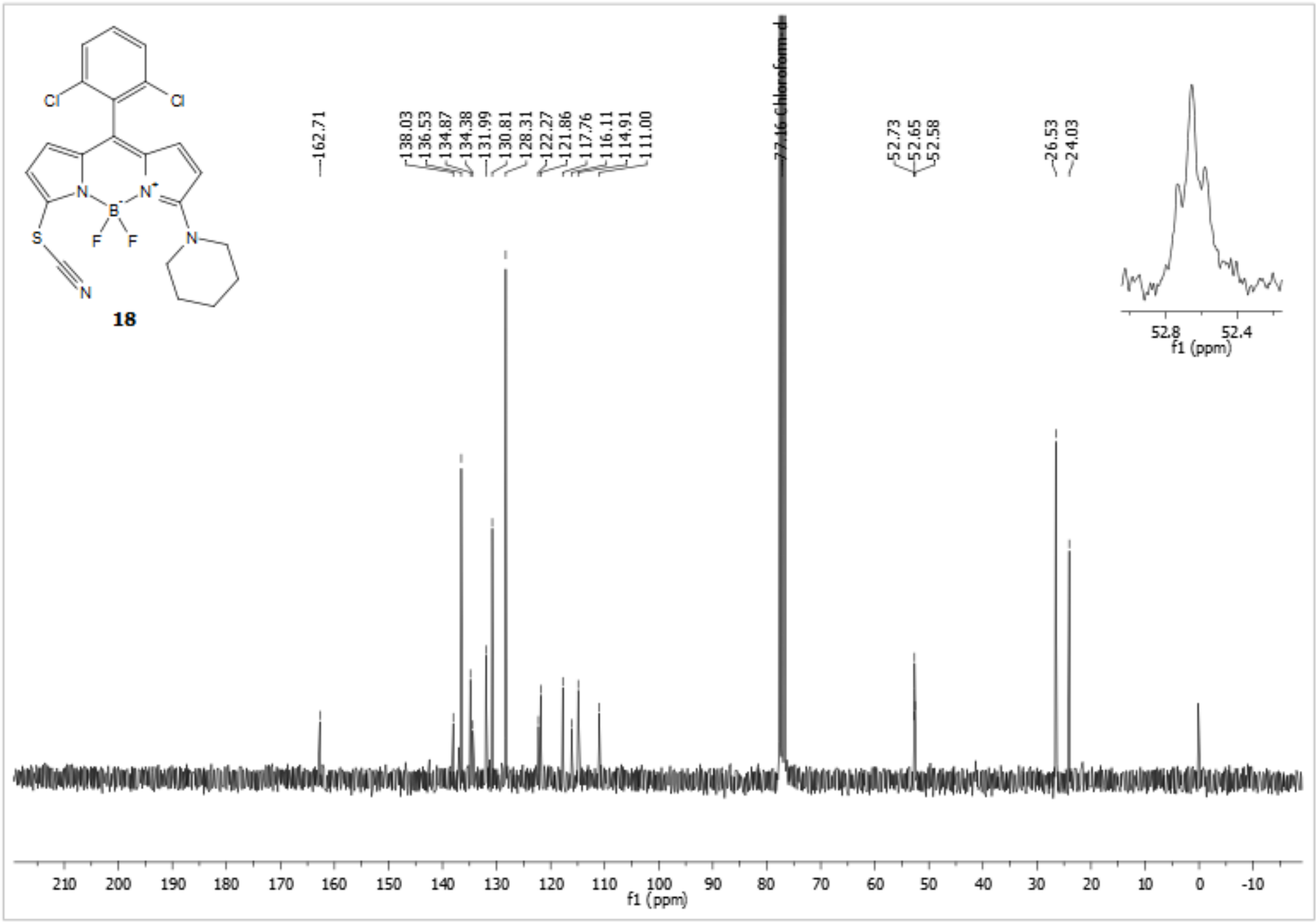

O
N
O
H3C
CH3
S
N
N
B
N
F
F
H3C
CH3
N
16
163.26
155.29
148.81
146.86
142.75
141.02
139.59
133.14
129.59
129.07
124.86
124.77
110.39
108.54
77.16 CHloroform-d
15.36
15.29
13.26
13.10
15
14
13
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

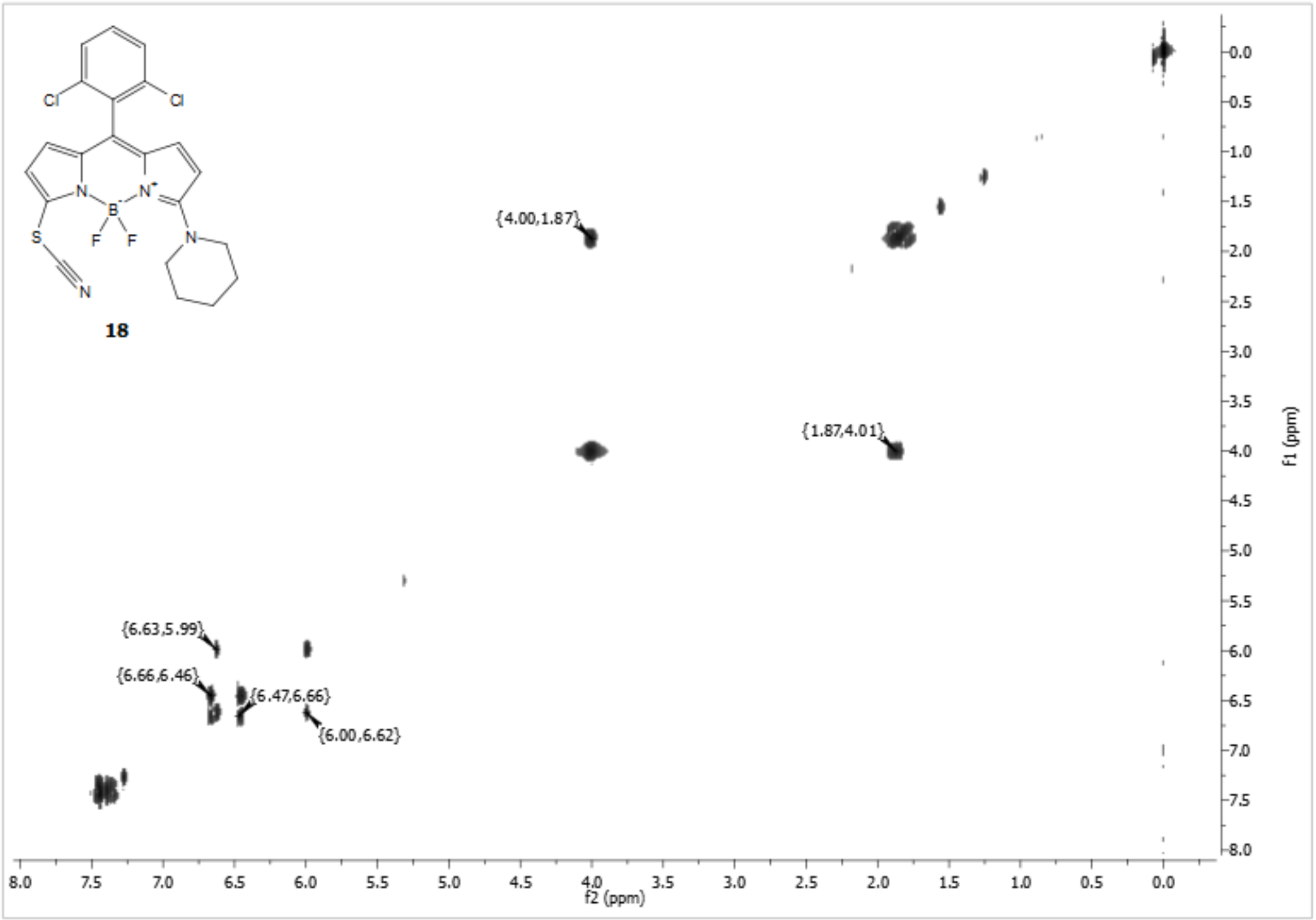

8.82
8.81
7.92
7.90
7.89
7.87
7.87
7.51
7.49
7.49
7.47
7.46
7.43
7.26 Chloroform-d
6.14
2.70
2.61
1.58 Water
1.45
1.37
1.00
1.05
1.03
0.96
0.99
3.06
3.01
3.04
3.15
f1 (ppm)

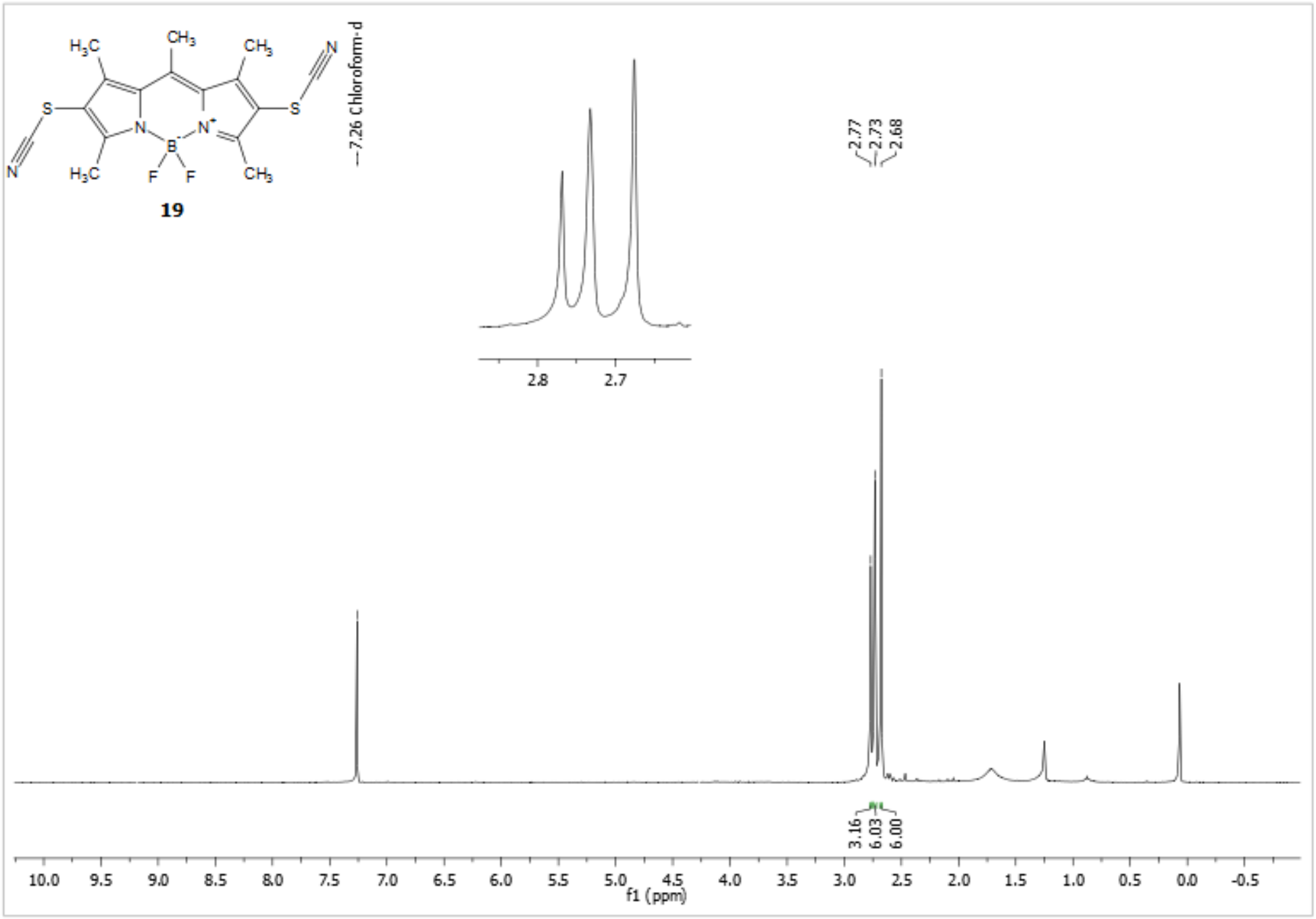
17

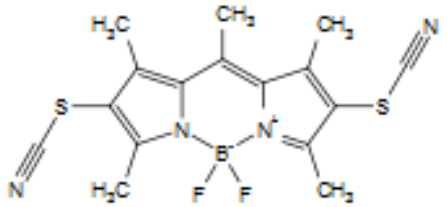

17
162.96
154.86
153.16
150.70
147.10
142.67
139.73
137.48
129.74
124.57
124.38
124.07
110.66
107.62
77.16 Chloroform-d
15.35
14.33
13.07
12.33
f1 (ppm)


Cl
Cl
N
B
N+
F
F
S
N
N
18
7.46
7.45
7.43
7.38
7.35
7.34
7.32
7.26 Chloroform-d
7.26
6.67
6.65
6.61
6.46
5.99
5.98
5.30 DCM
4.01
1.88
1.87
1.81
1.80
1.55 water
7.45
7.40
7.35
7.30
6.6
6.4
6.2
6.0
1.95
1.04
0.91
0.93
1.00
1.08
3.98
6.16
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
-0.5
-1.0
f1 (ppm)


Cl
Cl
N
B
N+
F
F
S
N
N
18
162.71
138.03
136.53
134.87
134.38
131.99
130.81
128.31
122.27
121.86
117.76
116.11
114.91
111.00
77.16 Chloroform-d
52.73
52.65
52.58
26.53
24.03
52.8
52.4
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

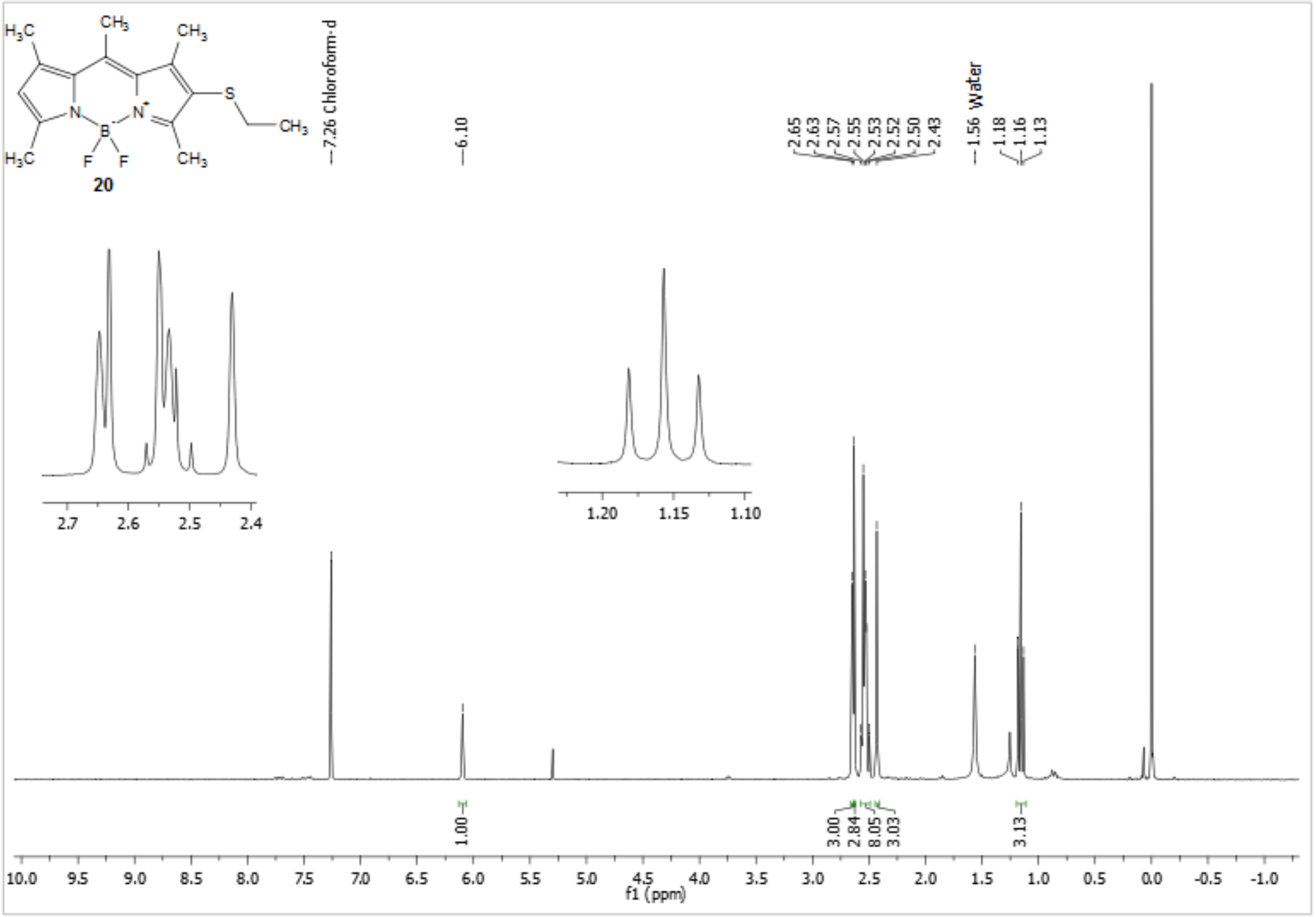

Cl
Cl
N
B
N+
F
F
S
N
N
18
{4.00,1.87}
{1.87,4.01}
{6.63,5.99}
{6.66,6.46}
{6.47,6.66}
{6.00,6.62}
f2 (ppm)
f1 (ppm)

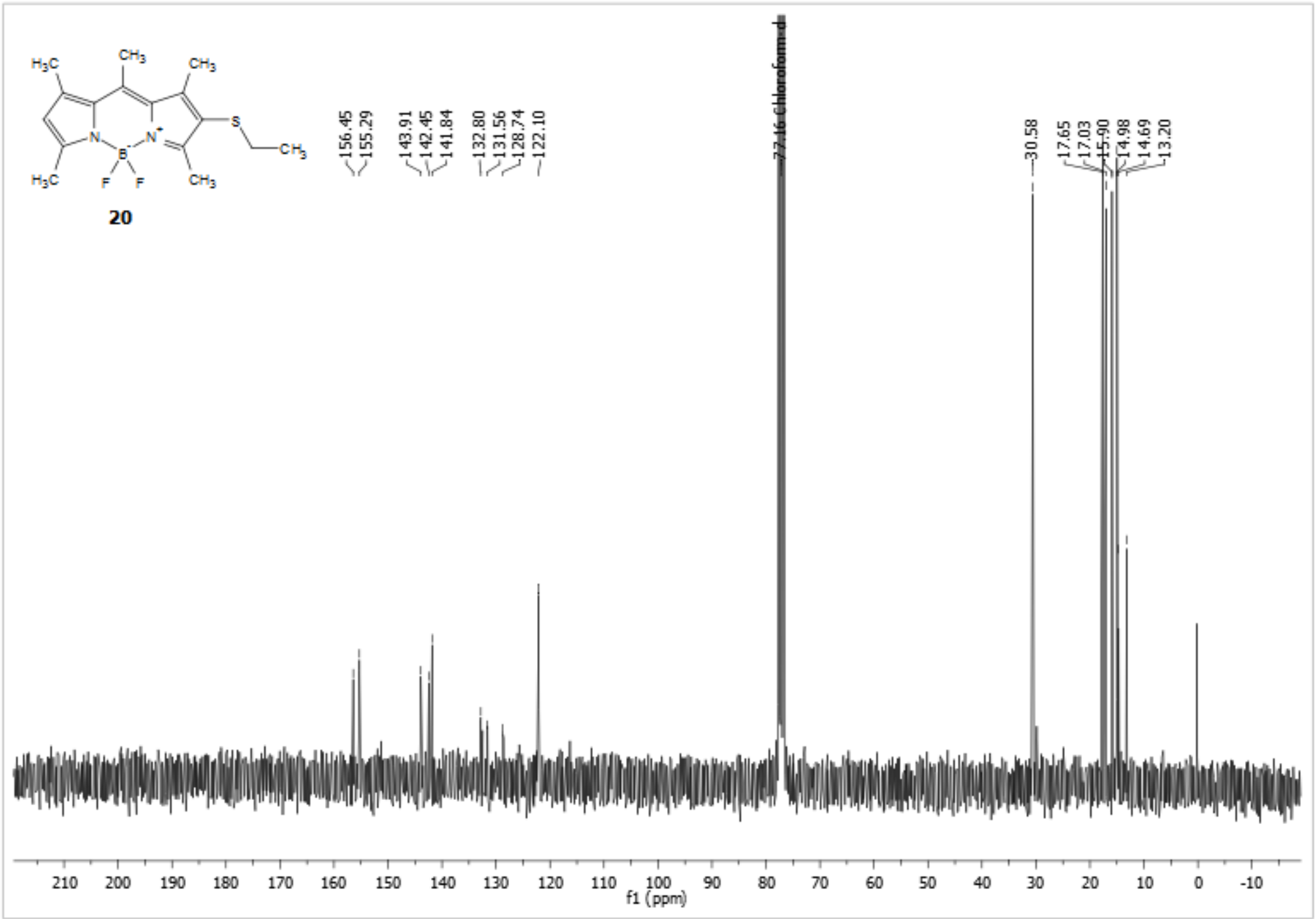

H3C
CH3
CH3
N
S
S
N
N
B
N+
F
F
H3C
CH3
19
7.26 Chloroform-d
2.77
2.73
2.68
2.8
2.7
3.16
6.03
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

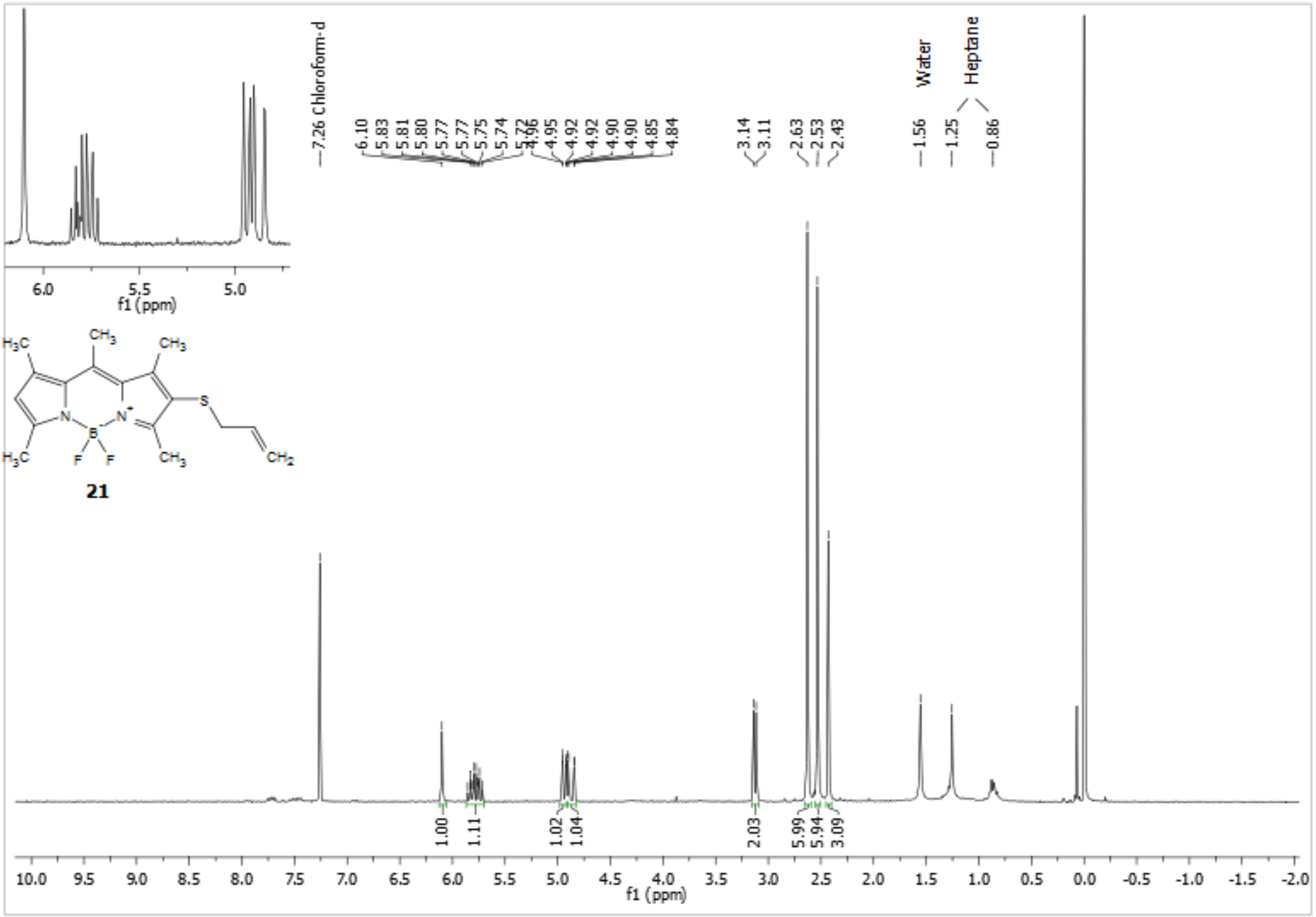

H3C
CH3
CH3
N
S
S
N
N
B
N+
F
F
H3C
CH3

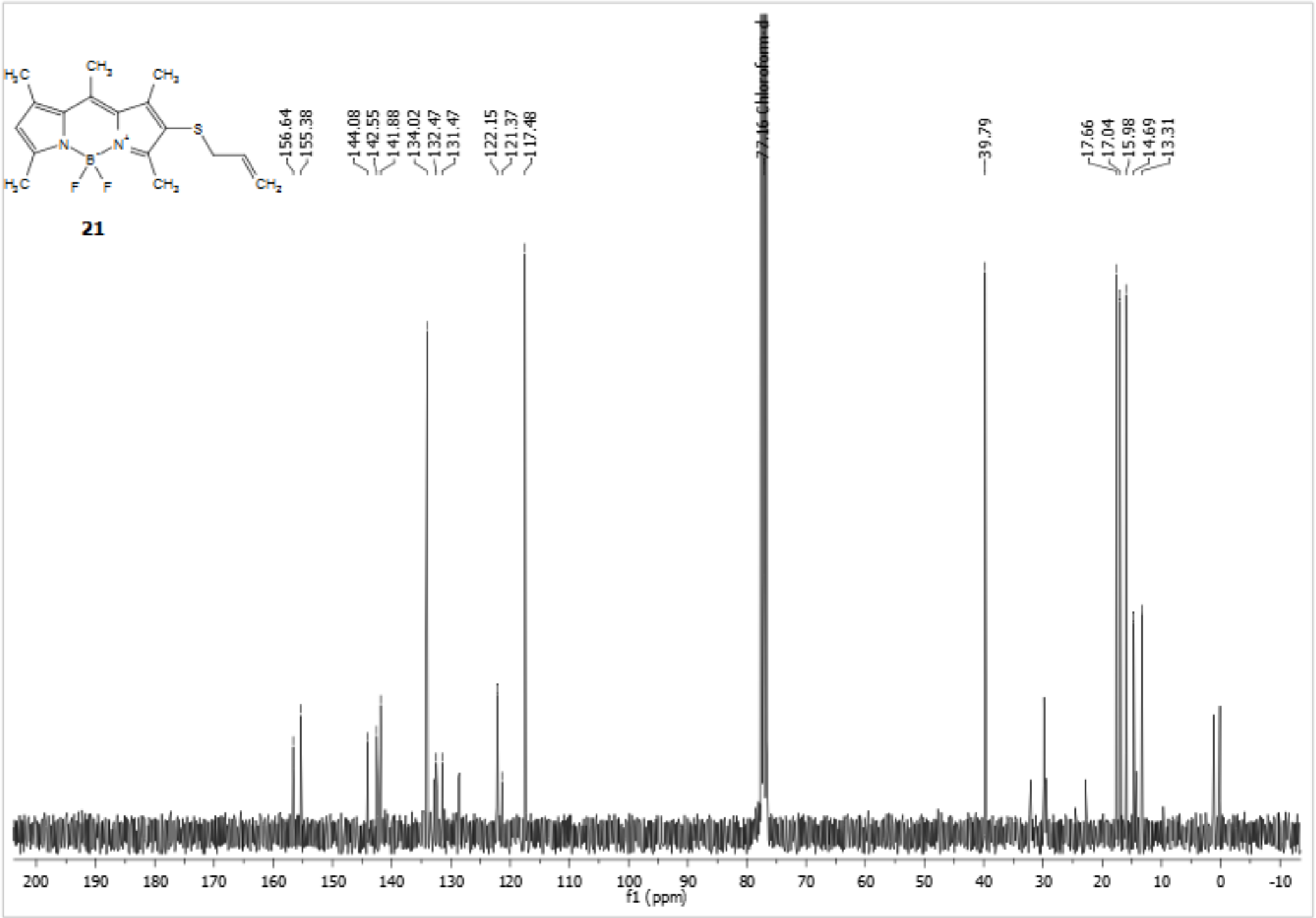
19

157.77
146.42
146.28
132.58
111.31
109.83
77.16 Chloroform-d
18.04
16.38
13.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

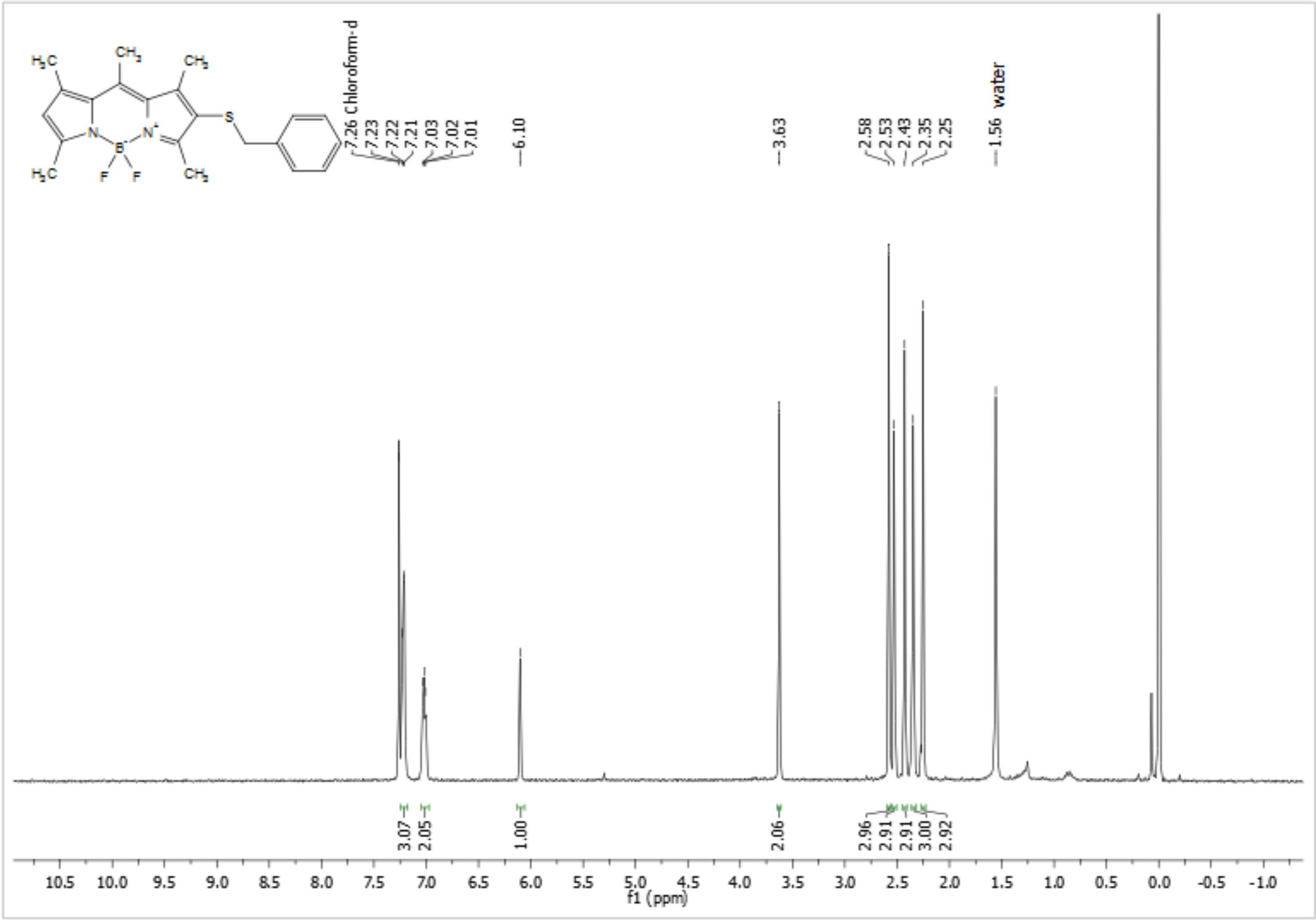

H3C
CH3
CH3
S
CH3
N
B
N
F
F
H3C
CH3
20
7.26 Chloroform-d
6.10
2.65
2.63
2.57
2.55
2.53
2.52
2.50
2.43
1.56 Water
1.18
1.16
1.13
2.7
2.6
2.5
2.4
1.20
1.15
1.10
1.00
3.00
2.84
8.05
3.03
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

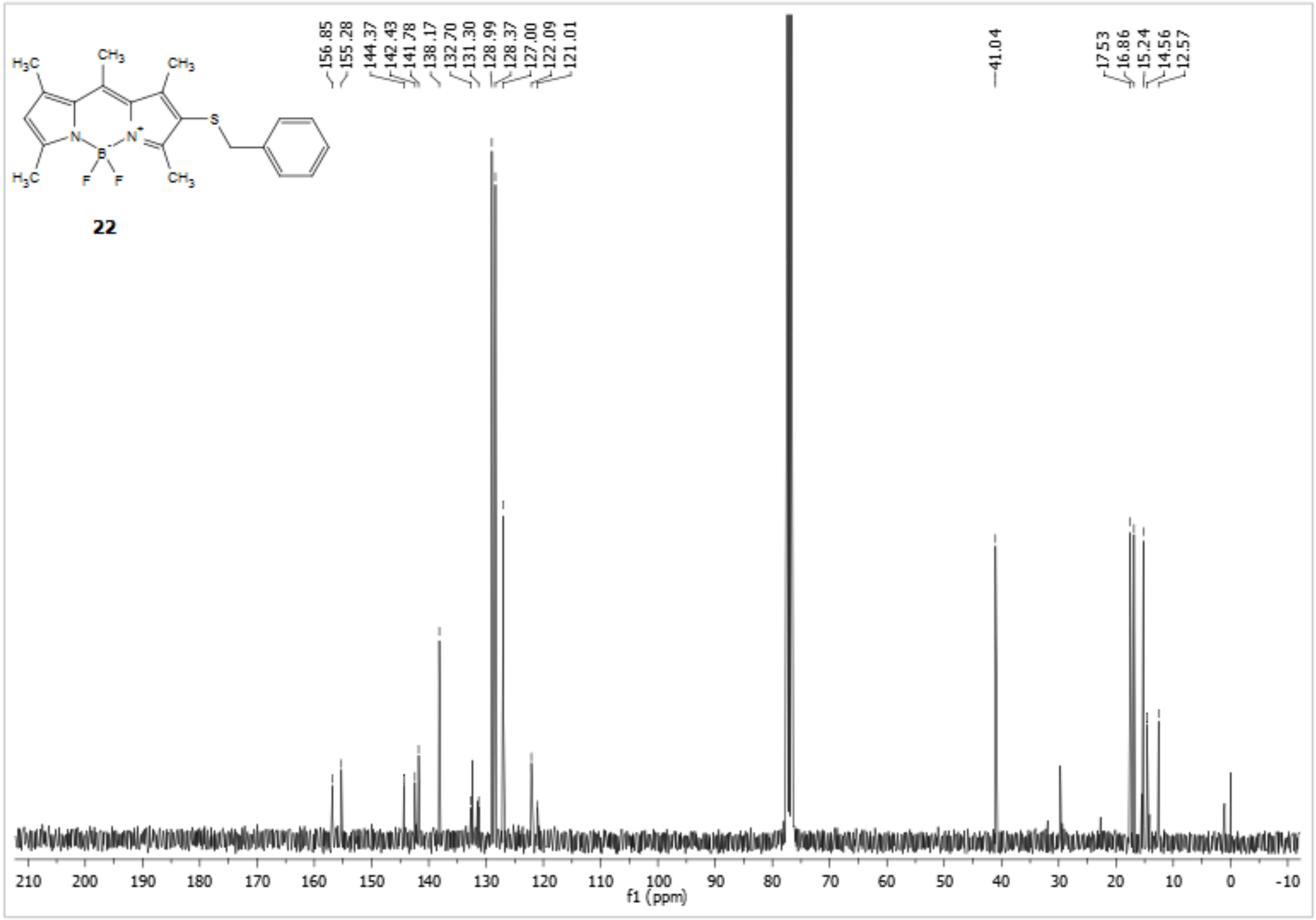

H3C
CH3
CH3
S
CH3
N
B
N+
F
F
H3C
CH3
20
156.45
155.29
143.91
142.45
141.84
132.80
131.56
128.74
122.10
77.16 Chloroform-d
30.58
17.65
17.03
15.90
14.98
14.69
13.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 Chloroform-d
6.10
5.83
5.81
5.80
5.77
5.77
5.75
5.74
5.72
4.96
4.95
4.92
4.92
4.90
4.90
4.85
4.84
3.14
3.11
2.63
2.53
2.43
1.56
Water
1.25
Heptane
0.86
1.00
1.11
1.02
1.04
2.03
5.99
5.94
3.09
f1 (ppm)
6.0
5.5
5.0
f1 (ppm)
H3C
CH3
CH3
N
B
N+
S
F
F
H3C
CH3
CH2
21

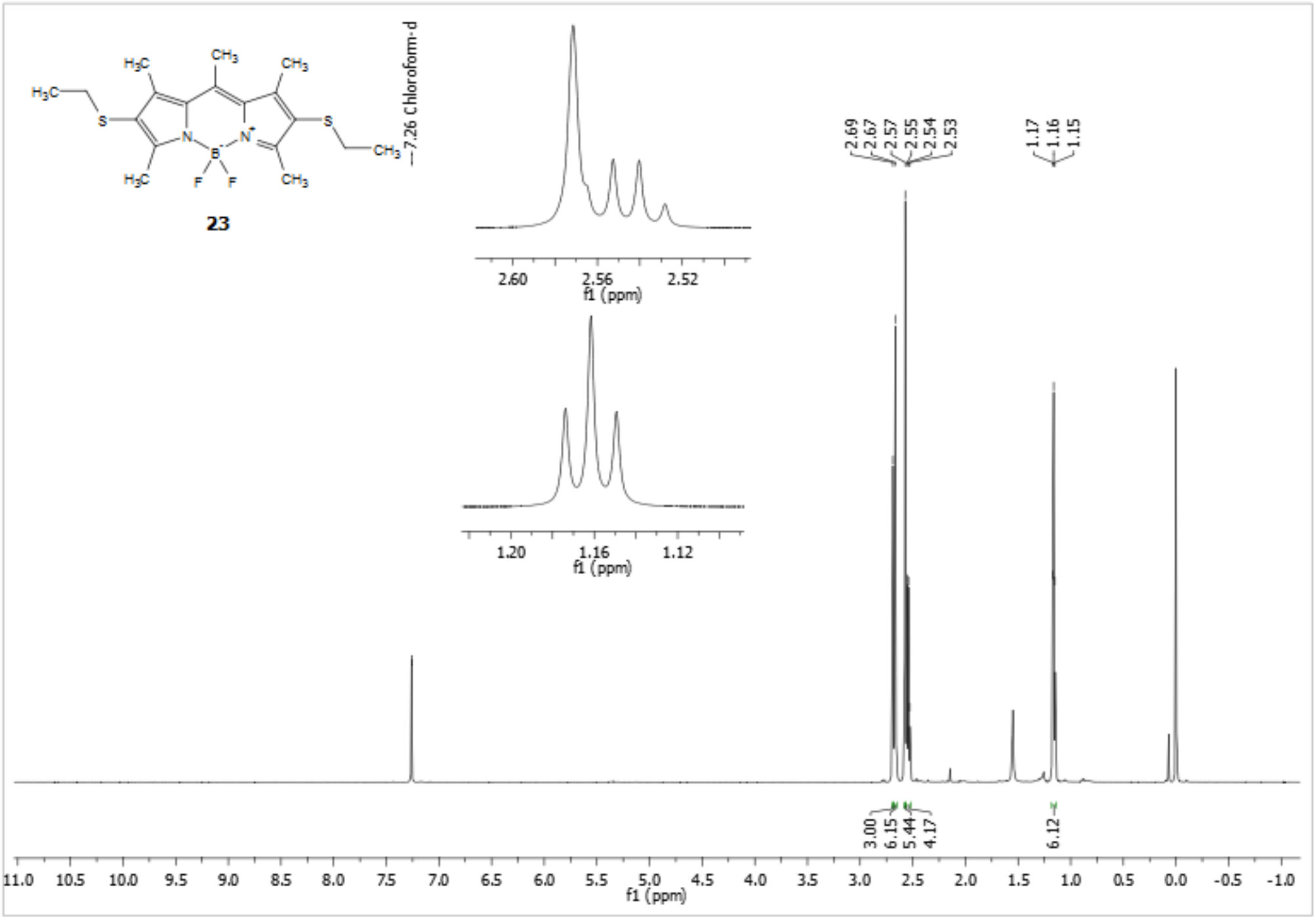

156.64
155.38
144.08
142.55
141.88
134.02
132.47
131.47
122.15
121.37
117.48
77.16 Chloroform-d
39.79
17.66
17.04
15.98
14.69
13.31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

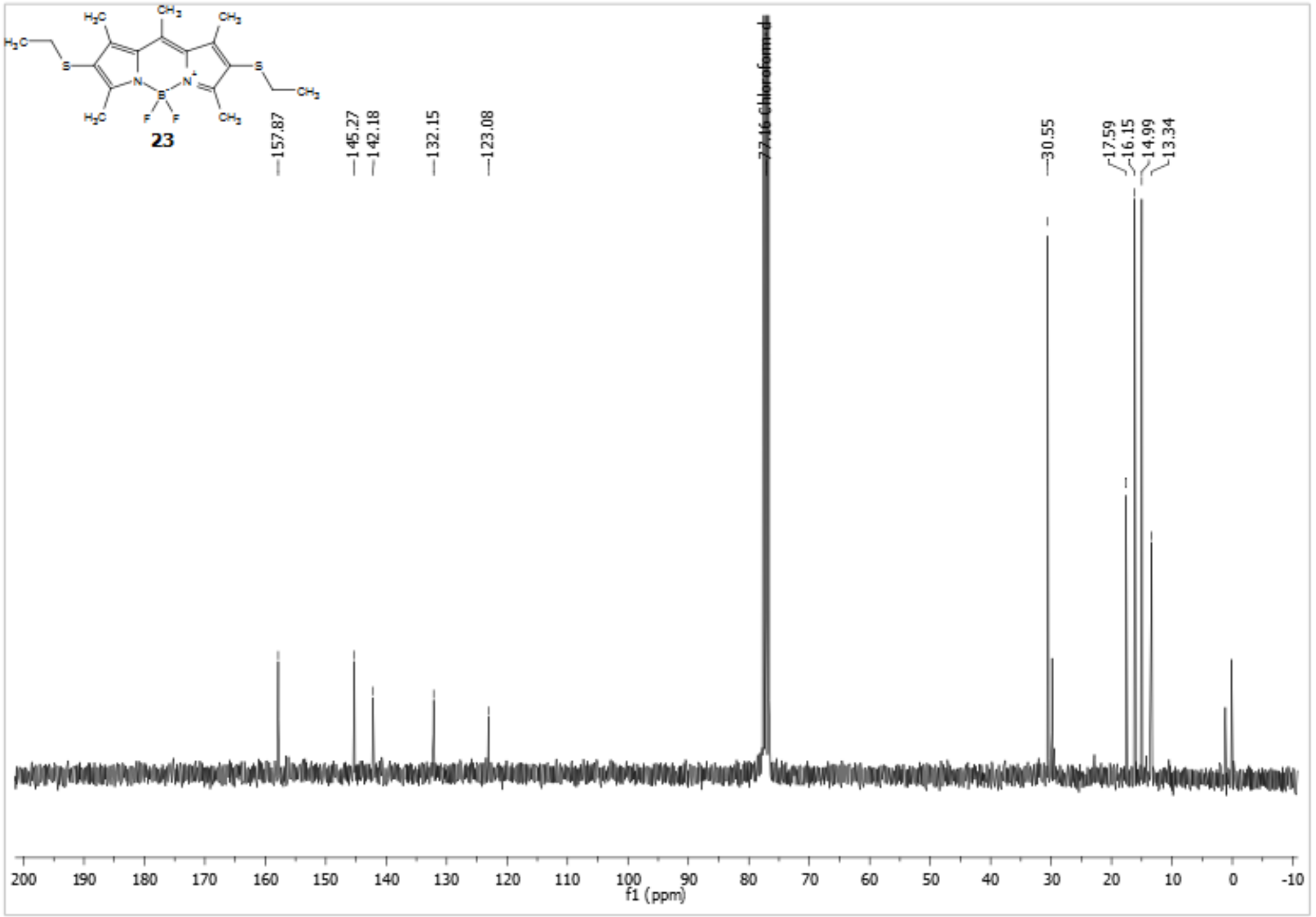
21


H3C
CH3
CH3
H3C
CH3
N
B
N+
F
F
S
7.26 Chloroform-d
7.23
7.22
7.21
7.03
7.02
7.01
6.10
3.63
2.58
2.53
2.43
2.35
2.25
1.56 water
3.07
2.05
1.00
2.06
2.96
2.91
2.91
3.00
2.92
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 -0.5 -1.0
f1 (ppm)


156.85
155.28
144.37
142.43
141.78
138.17
132.70
131.30
128.99
128.37
127.00
122.09
121.01
41.04
17.53
16.86
15.24
14.56
12.57
f1 (ppm)

22


H3C
CH3
CH3
H3C
S
S
N
B
N
F
F
CH3
H3C
CH3
23
7.26 Chloroform-d
2.69
2.67
2.57
2.55
2.54
2.53
1.17
1.16
1.15
2.60
2.56
2.52
f1 (ppm)
1.20
1.16
1.12
f1 (ppm)
3.00
6.15
5.44
4.17
6.12
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
-0.5
-1.0
f1 (ppm)


23
157.87
145.27
142.18
132.15
123.08
77.16 chloroform-d
30.55
17.59
16.15
14.99
13.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)