

Supporting Information for:

Thioarylation of Anilines using Dual Catalysis: Two-Step Synthesis of Phenothiazines

Amy C. Dodds, Sabrina Puddu and Andrew Sutherland*

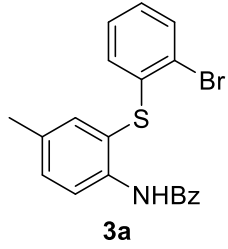
*School of Chemistry, The Joseph Black Building, University of Glasgow, Glasgow G12 8QQ,
UK. Email: Andrew.Sutherland@glasgow.ac.uk.*

Table of Contents

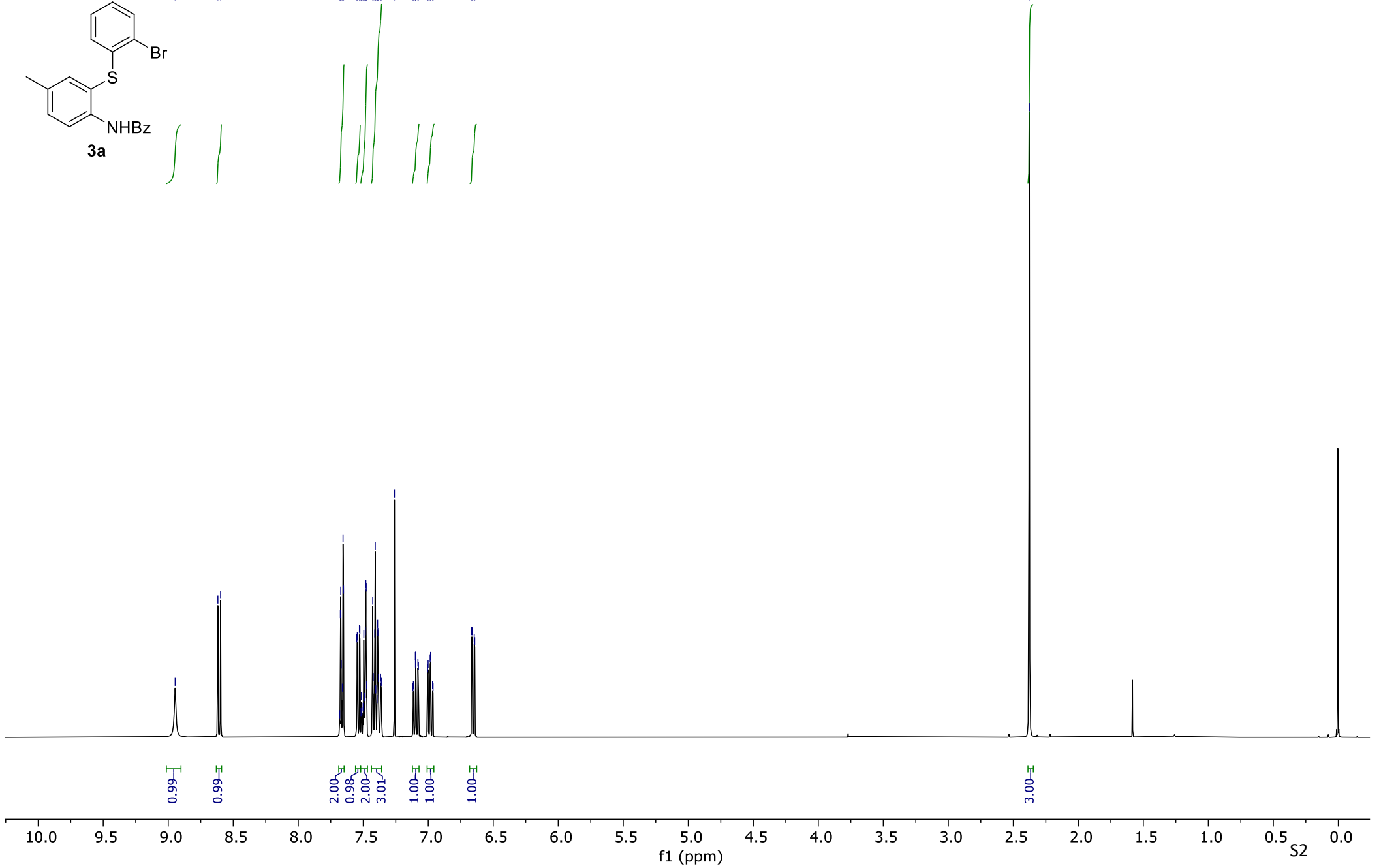
1. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra for all Compounds	S2–S69
---	--------

400 MHz, CDCl₃

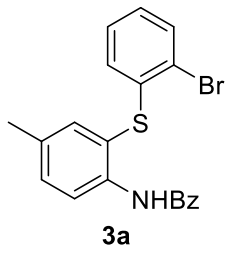
¹H and ¹³C{¹H} NMR Spectra for all Compounds



8.95
8.62
8.60
7.68
7.67
7.67
7.66
7.66
7.65
7.55
7.55
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.36
7.26 CDCl₃
7.12
7.11
7.10
7.10
7.10
7.08
7.08
7.01
7.00
6.99
6.98
6.97
6.96
6.67
6.66
6.64
2.38



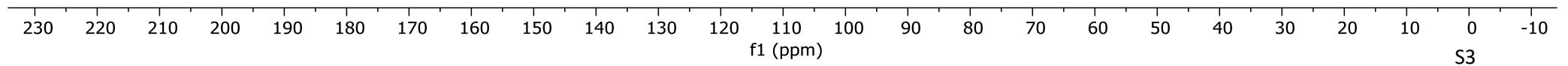
101 MHz, CDCl₃



165.17
137.99
137.53
137.25
134.74
134.71
133.10
132.64
132.03
128.89
128.40
127.35
127.32
127.06
121.23
120.86
119.08

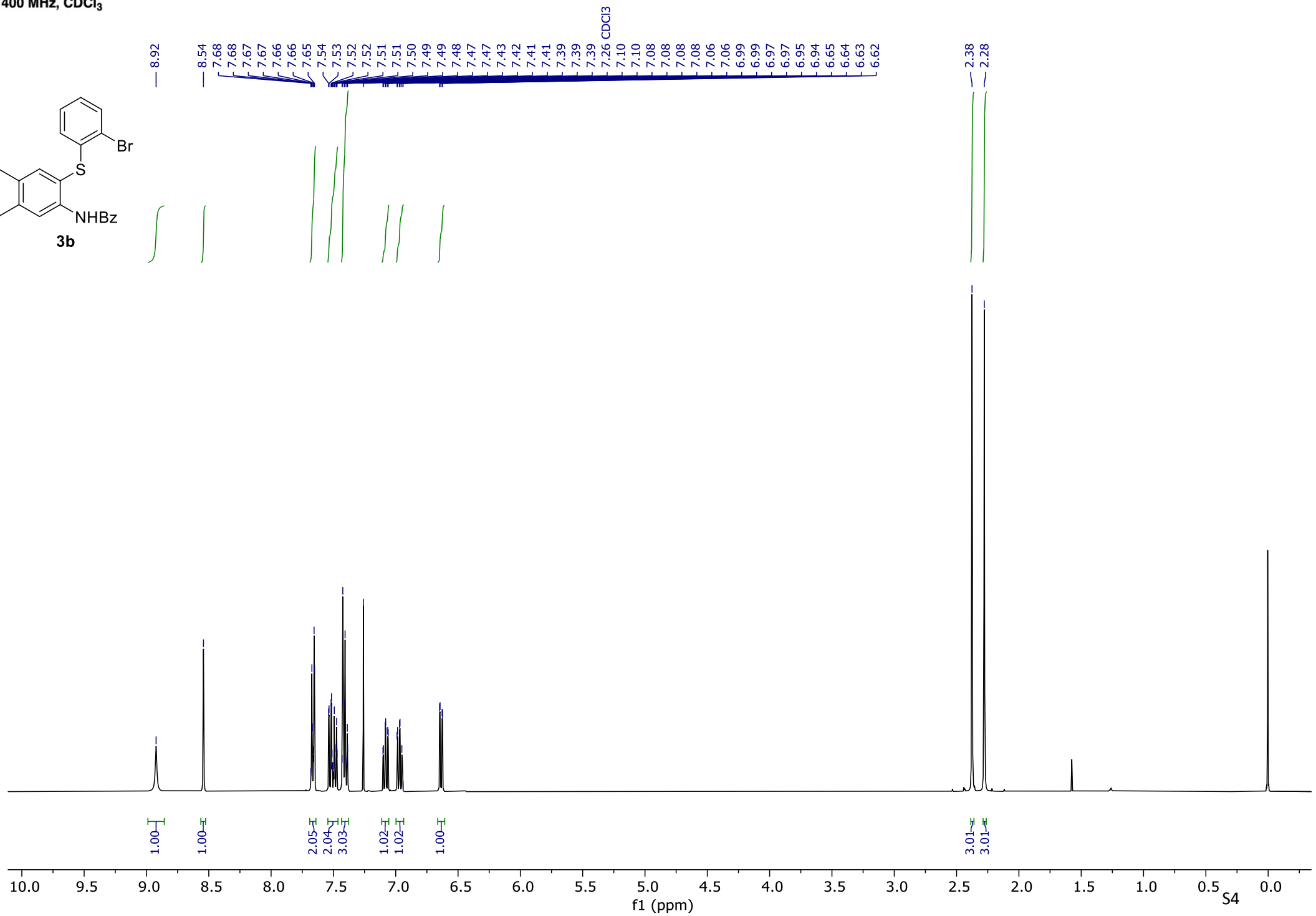
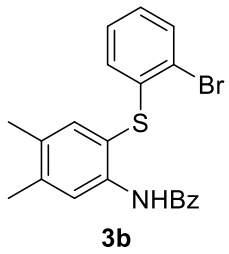
77.16 CDCl₃

20.84

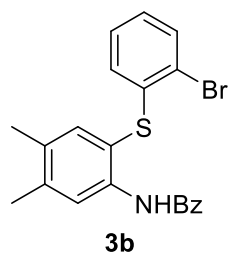


S3

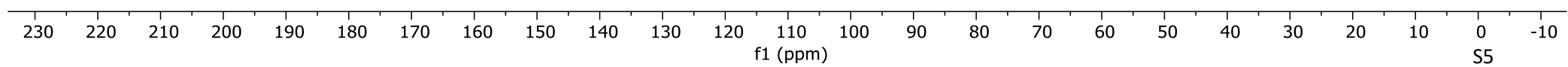
400 MHz, CDCl₃



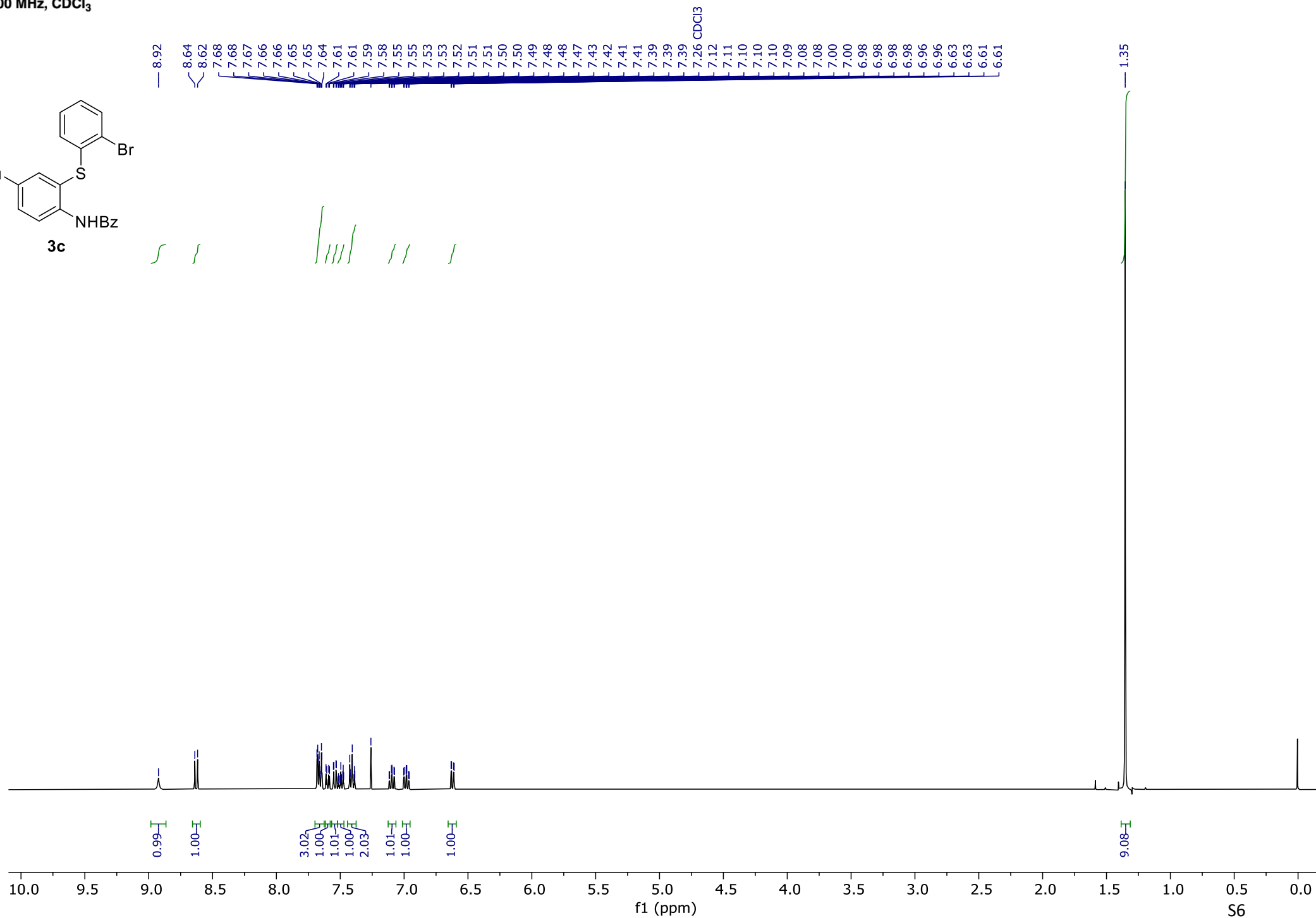
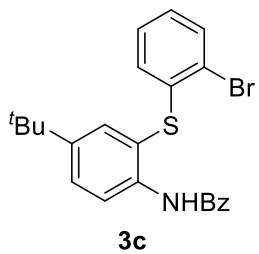
101 MHz, CDCl₃



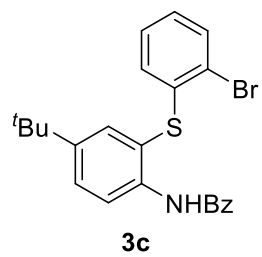
165.12
141.25
138.22
137.89
137.65
134.79
133.58
133.04
131.99
128.89
128.33
127.13
127.05
127.05
122.07
120.98
115.84
77.16 CDCl₃
20.42
19.31



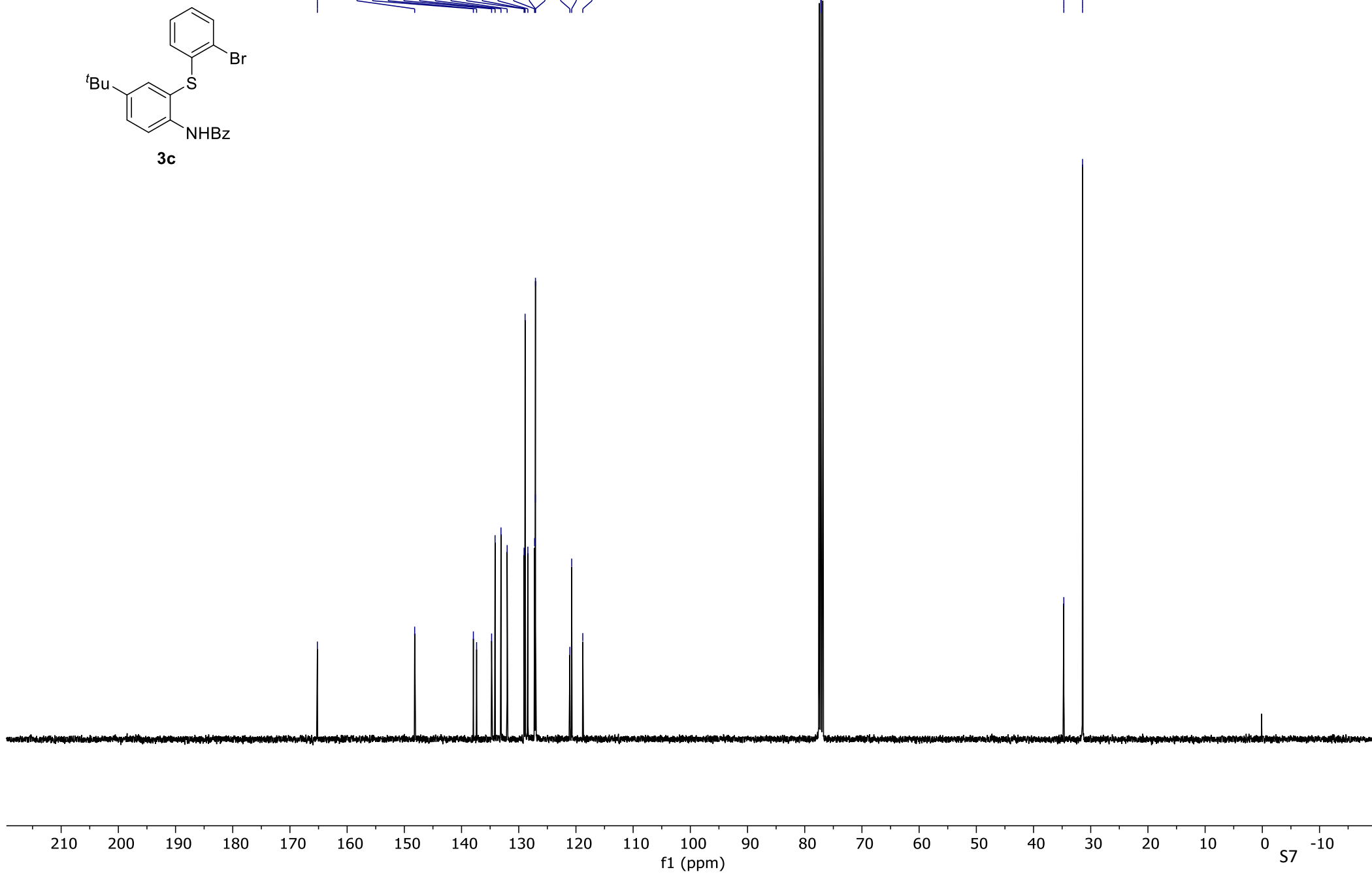
400 MHz, CDCl₃



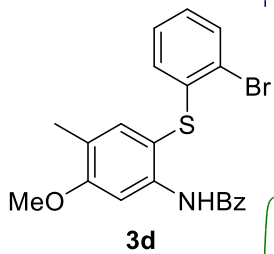
101 MHz, CDCl₃



165.21
148.19
137.93
137.37
134.75
134.14
133.10
132.03
129.07
128.89
128.41
127.23
127.09
127.07
121.06
120.74
118.80
77.16 CDCl₃
34.71
31.43



400 MHz, CDCl₃



9.09

8.44

7.71

7.70

7.70

7.68

7.68

7.54

7.54

7.53

7.52

7.52

7.51

7.51

7.50

7.49

7.48

7.44

7.44

7.42

7.42

7.40

7.40

7.26 CDCl₃

7.11

7.11

7.09

7.09

7.09

7.07

7.07

6.99

6.99

6.97

6.97

6.97

6.95

6.95

6.62

6.62

6.60

6.60

3.97

2.22

1.01

1.01

2.02

2.02

3.01

1.01

1.01

1.00

3.00

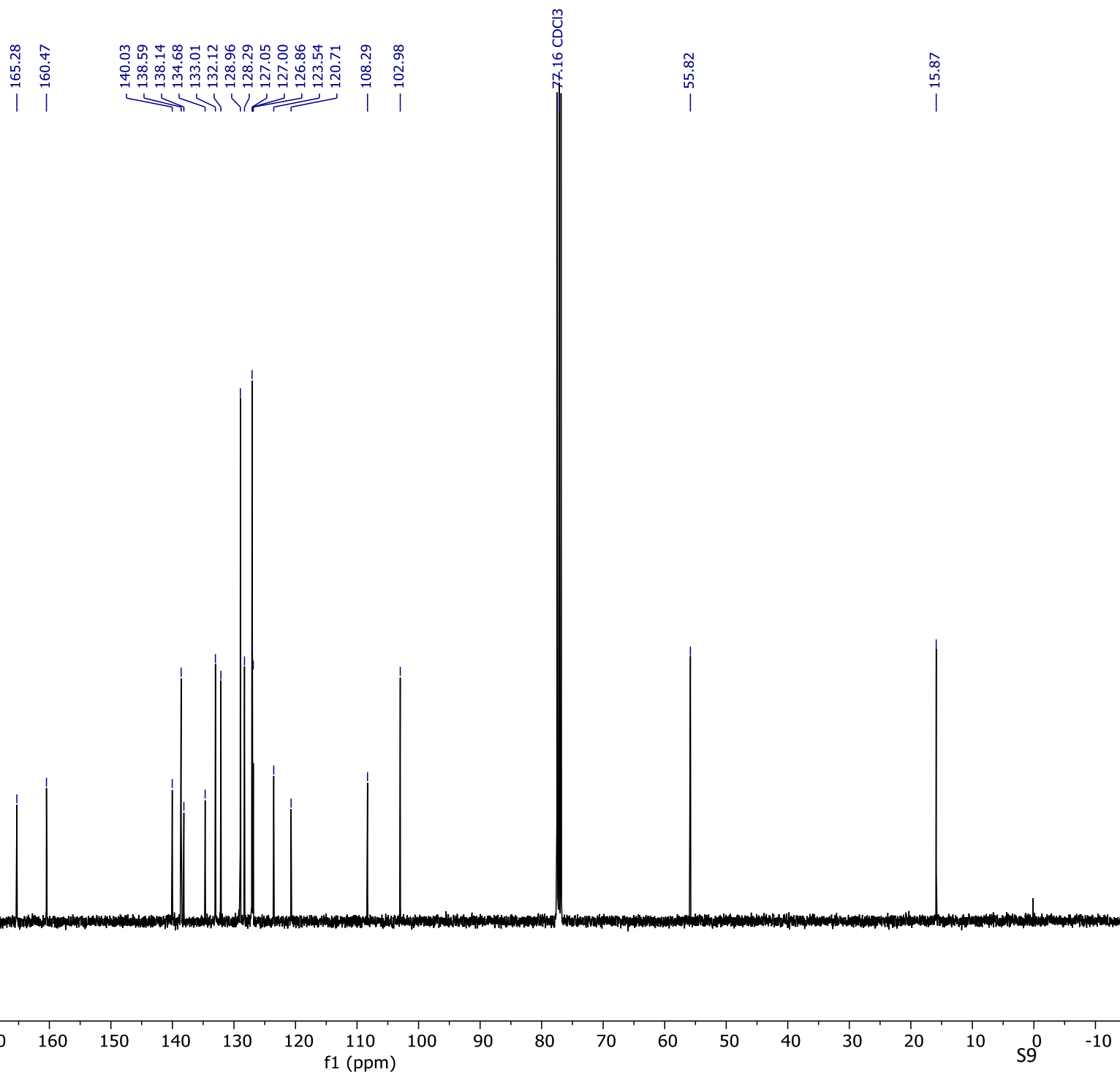
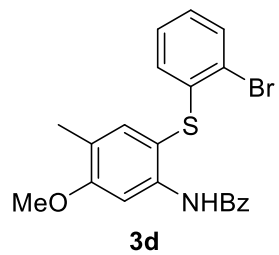
3.01

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

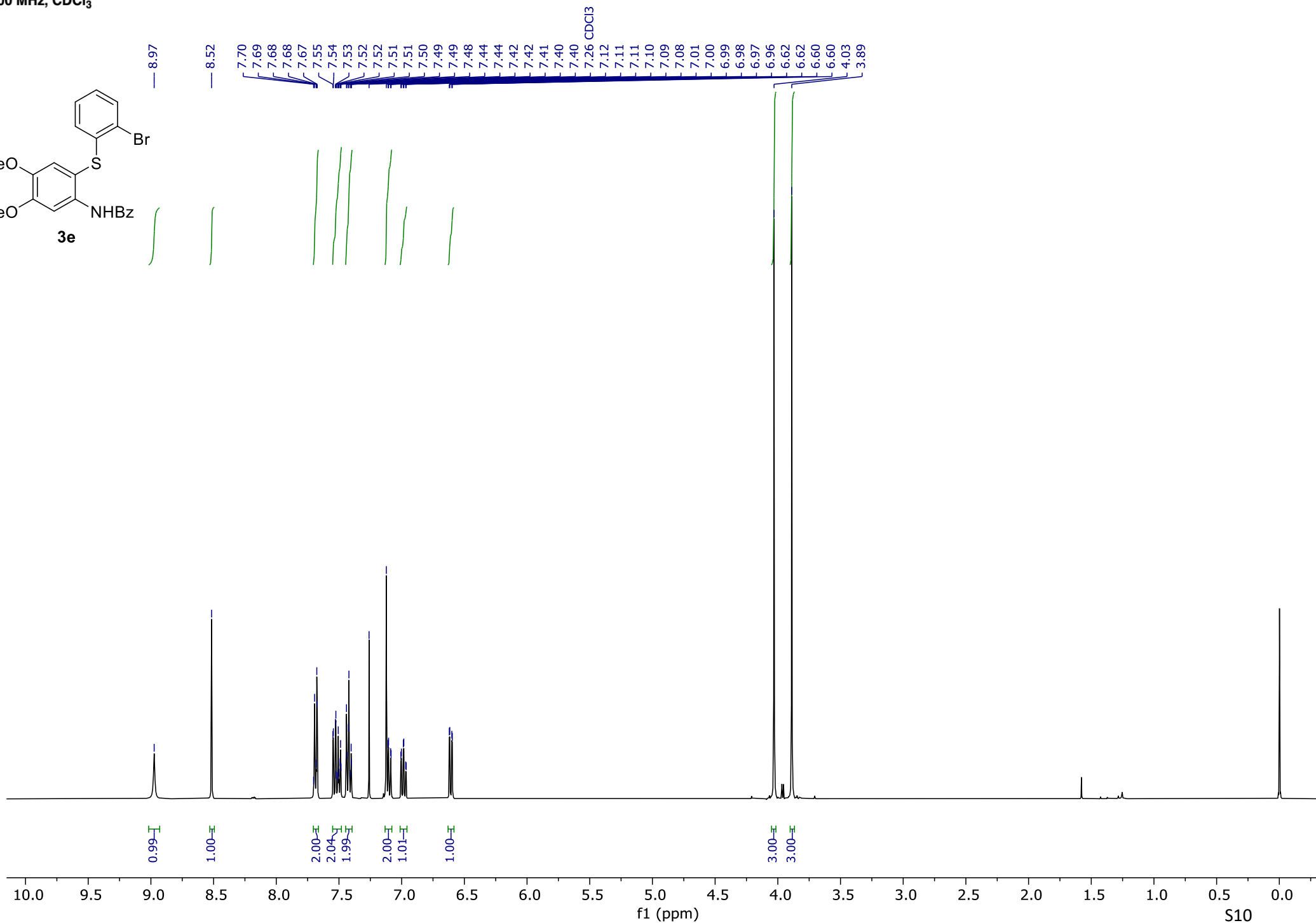
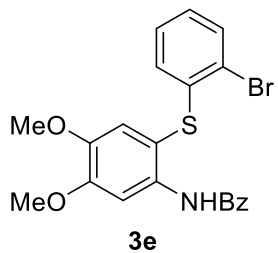
f1 (ppm)

S8

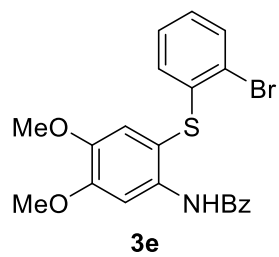
101 MHz, CDCl₃



400 MHz, CDCl₃



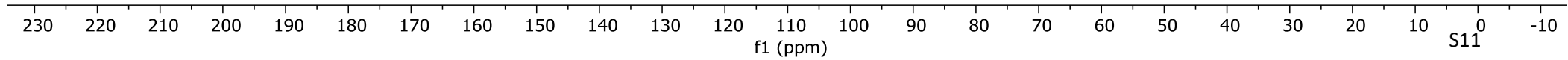
101 MHz, CDCl₃



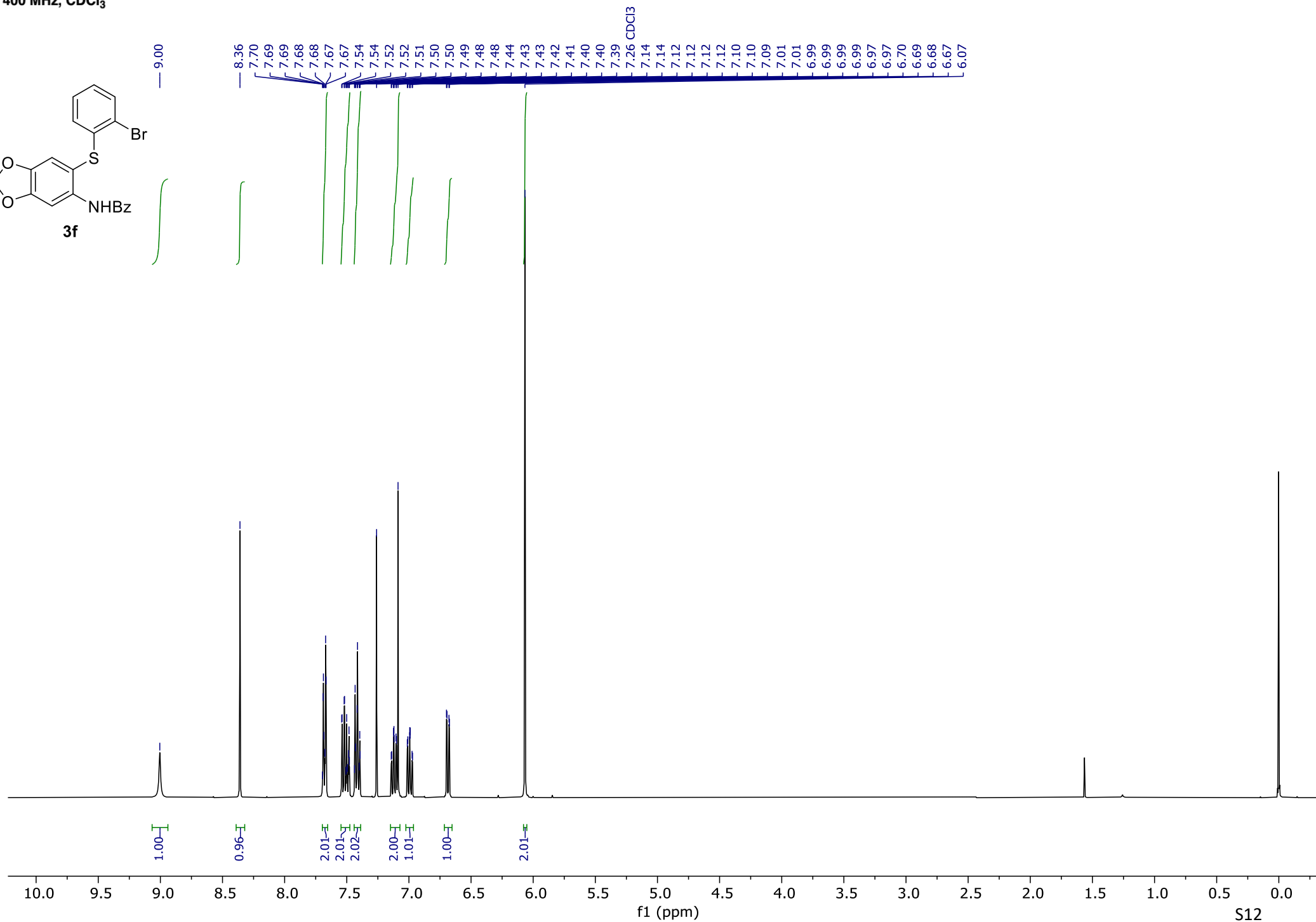
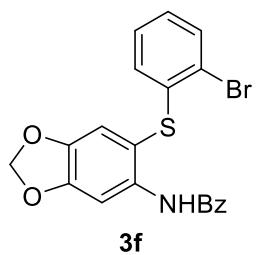
165.18
151.65
145.78
137.78
135.55
134.66
133.09
132.12
128.97
128.39
127.16
127.01
126.76
120.70
118.93
108.58
104.66

77.16 CDCl₃

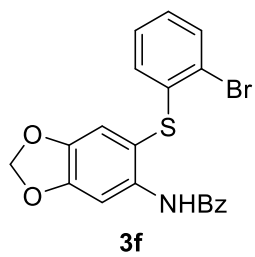
56.43
56.33



400 MHz, CDCl₃

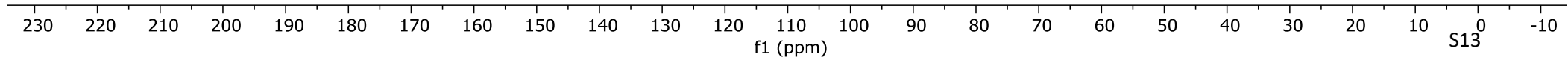


101 MHz, CDCl₃

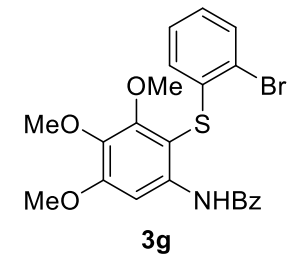
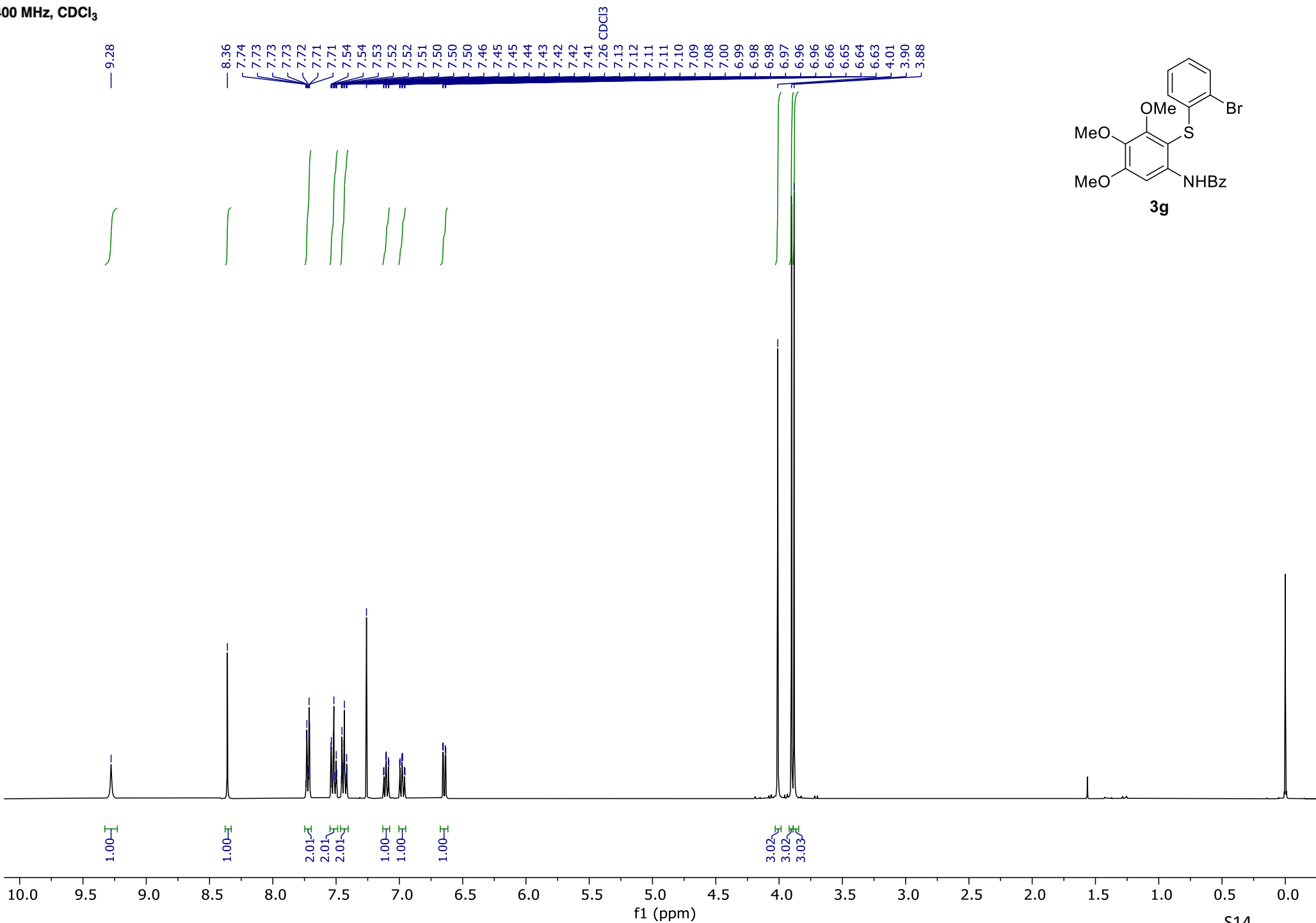


— 165.04
— 150.56
— 144.32
— 137.52
— 136.28
— 134.62
— 133.14
— 132.11
— 128.93
— 128.40
— 127.34
— 127.06
— 127.01
— 120.96
— 115.75
— 110.20
— 102.94
— 102.15

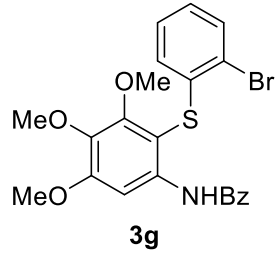
77.16 CDCl₃



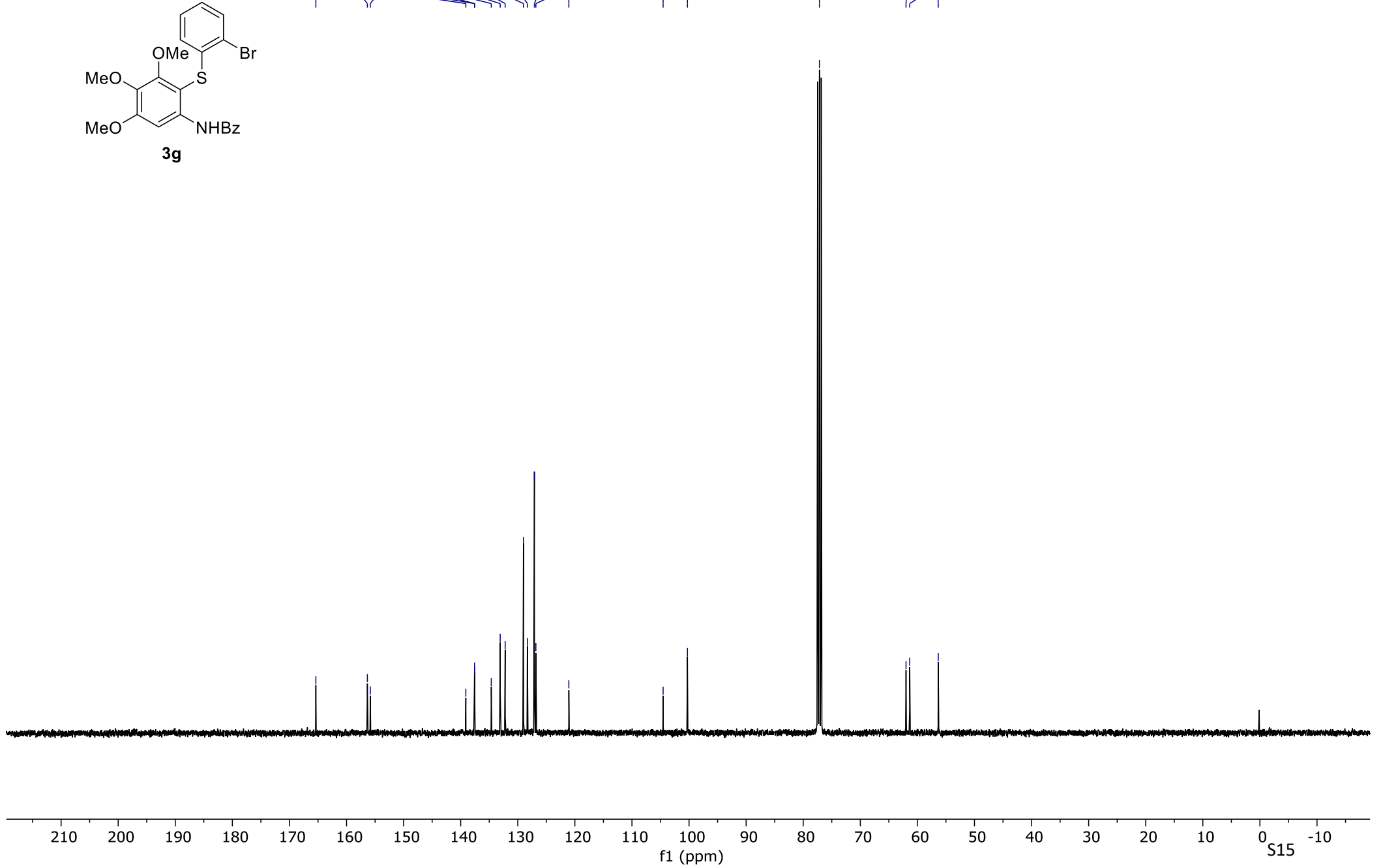
400 MHz, CDCl₃



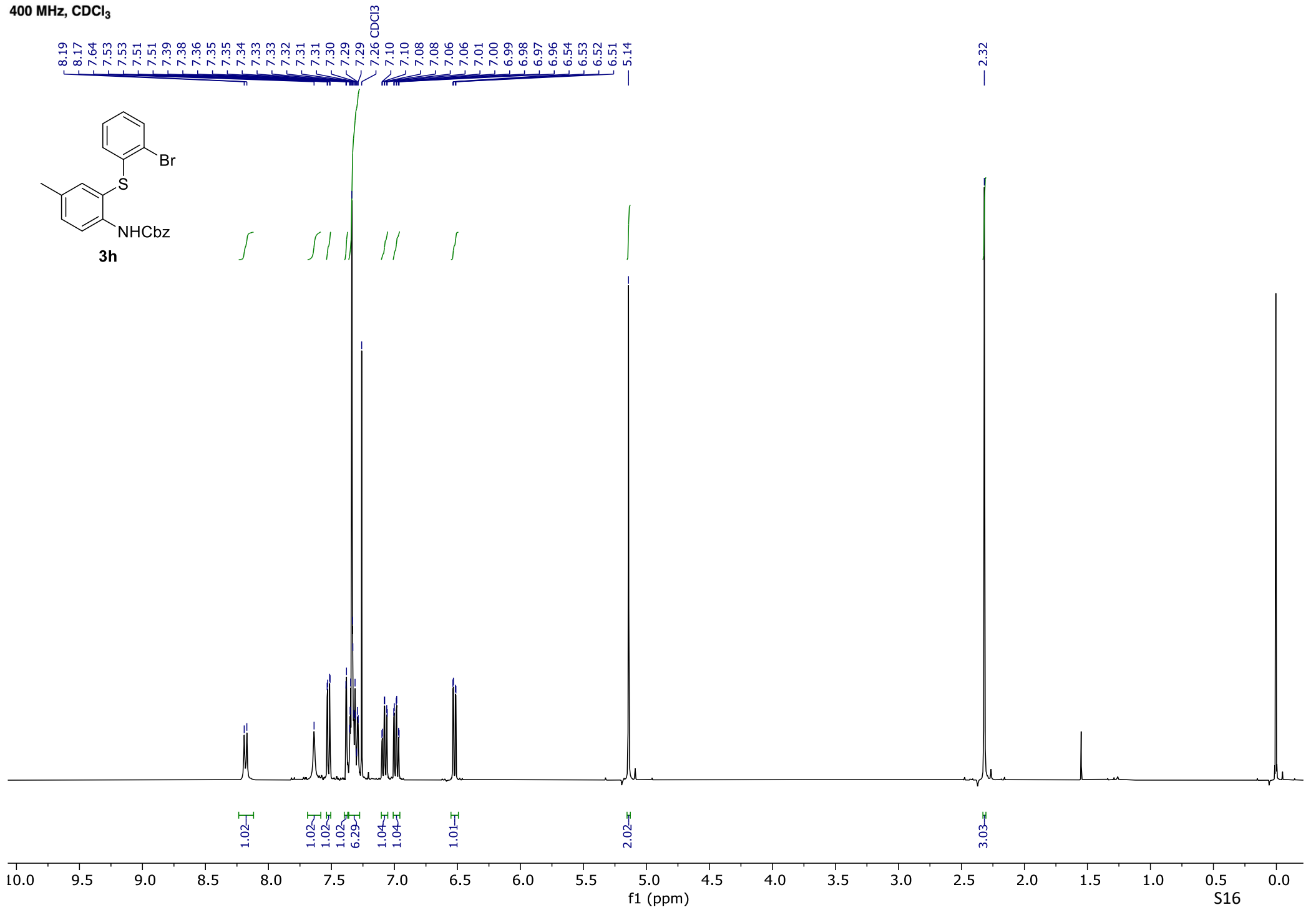
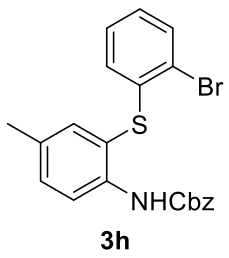
101 MHz, CDCl₃



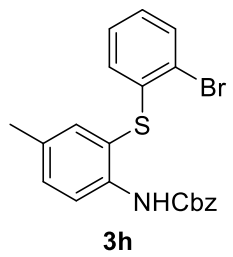
165.37
156.35
155.83
139.10
137.57
137.56
134.64
133.08
132.21
129.00
128.32
127.09
126.83
121.05
104.54
100.28
77.16 CDCl₃
61.99
61.34
56.34



400 MHz, CDCl₃



101 MHz, CDCl₃

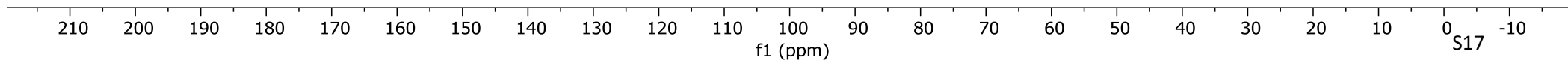


153.37
138.33
137.78
137.60
136.09
133.86
133.07
132.54
128.70
128.41
128.33
128.15
127.02
126.92
121.20
119.61
118.10

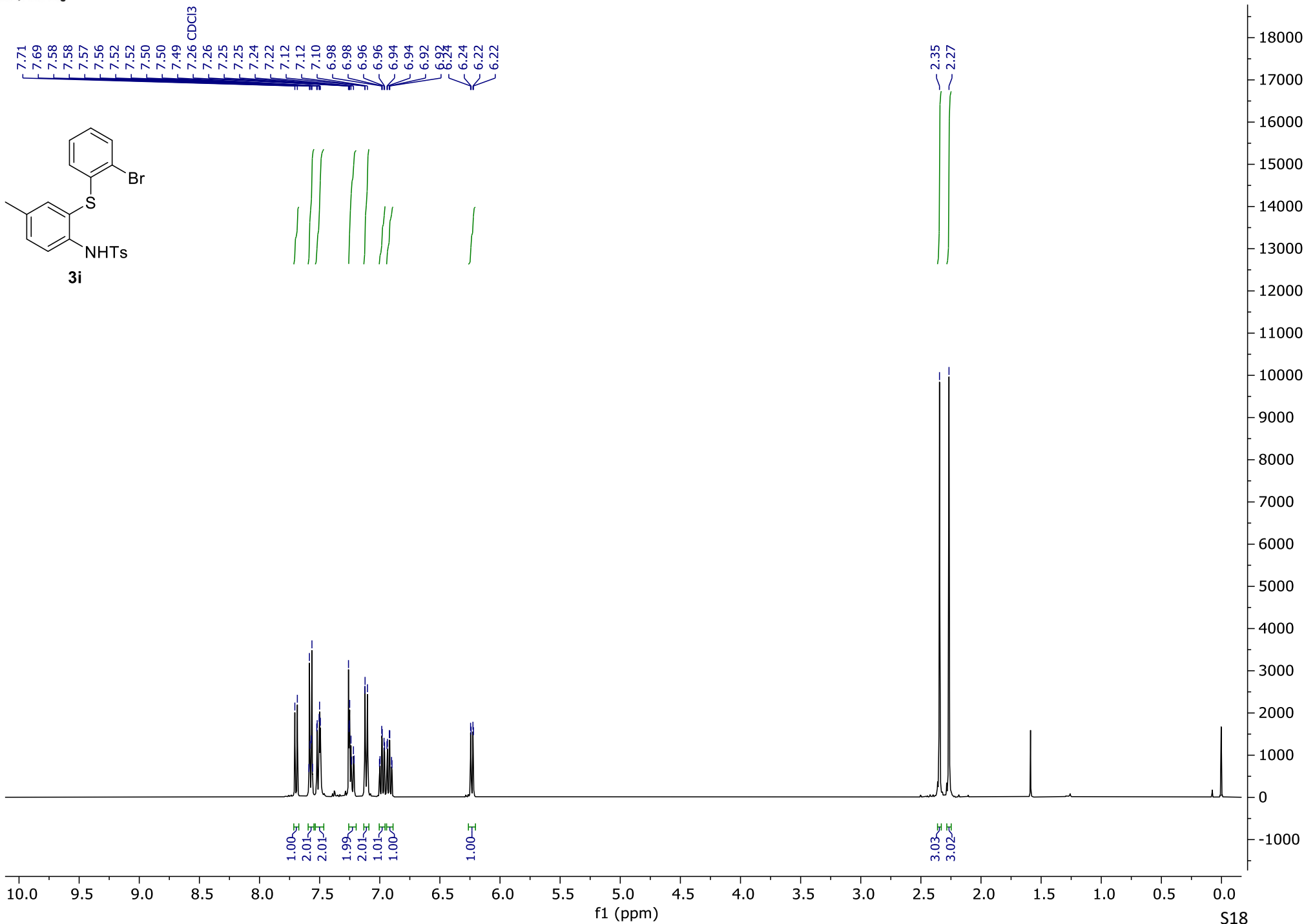
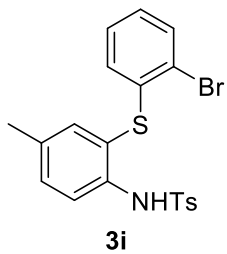
77.16 CDCl₃

67.13

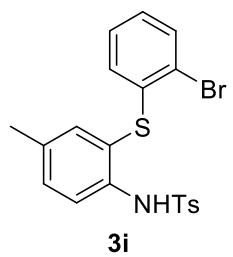
20.64



400 MHz, CDCl₃



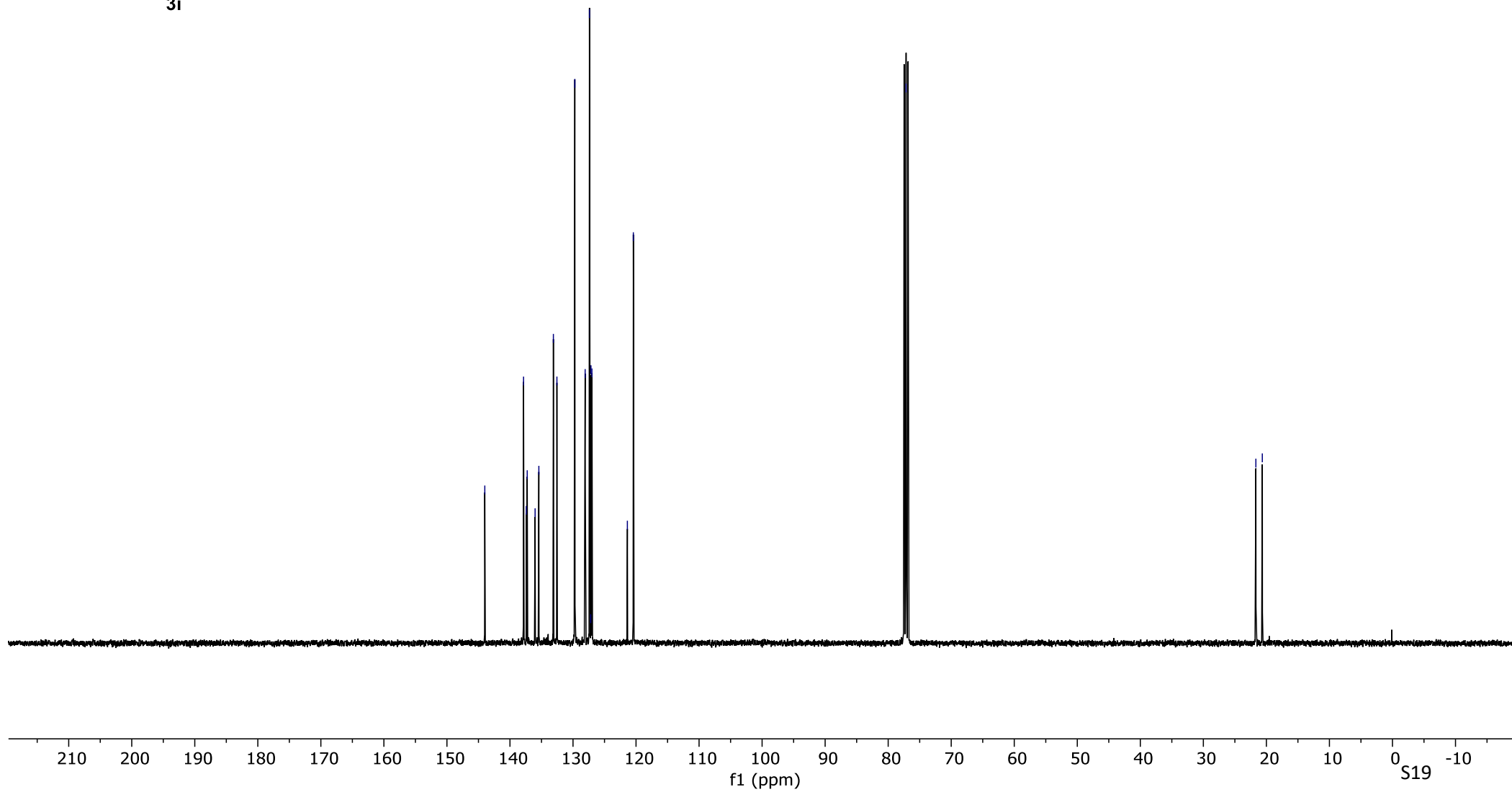
101 MHz, CDCl₃



143.99
137.84
137.41
137.26
136.01
135.42
133.11
132.55
129.71
128.07
127.39
127.19
127.15
127.00
121.37
120.43

77.16 CDCl₃

21.67
20.65



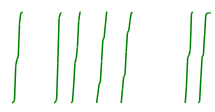
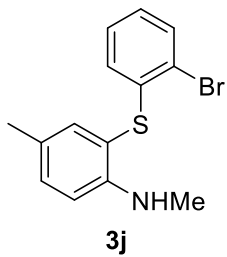
400 MHz, CDCl₃

7.52
7.52
7.50
7.30
7.30
7.26 CDCl₃
7.22
7.20
7.20
7.19
7.10
7.09
7.08
7.08
7.07
7.06
7.06
6.97
6.97
6.95
6.95
6.95
6.93
6.84
6.62
6.57
6.57
6.55
6.55

4.74
4.74
4.72
4.71

2.81
2.80

2.26



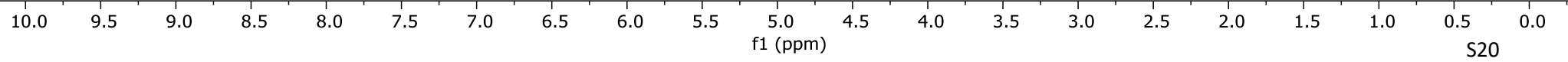
1.00
1.00
1.01
1.00
1.00

1.01
1.00

1.00

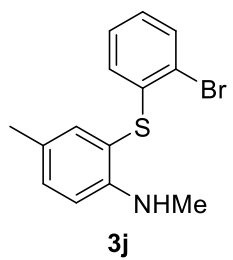
3.01

3.00

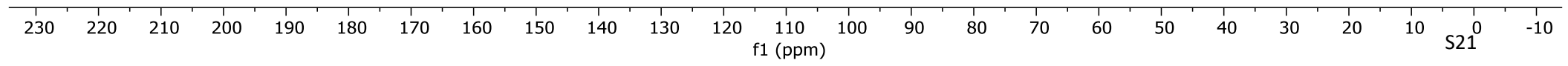


S20

101 MHz, CDCl₃



148.92
138.46
138.32
132.92
132.84
127.86
126.40
126.22
126.16
120.69
112.36
110.46
77.16 CDCl₃
30.79
20.23



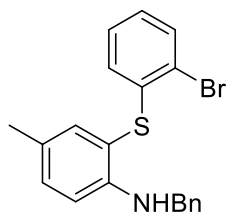
400 MHz, CDCl₃

7.53
7.52
7.51
7.50
7.33
7.32
7.26
7.26 CDCl₃
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.18
7.18
7.16
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.00
7.00
6.98
6.98
6.65
6.63
6.63
6.57
6.55

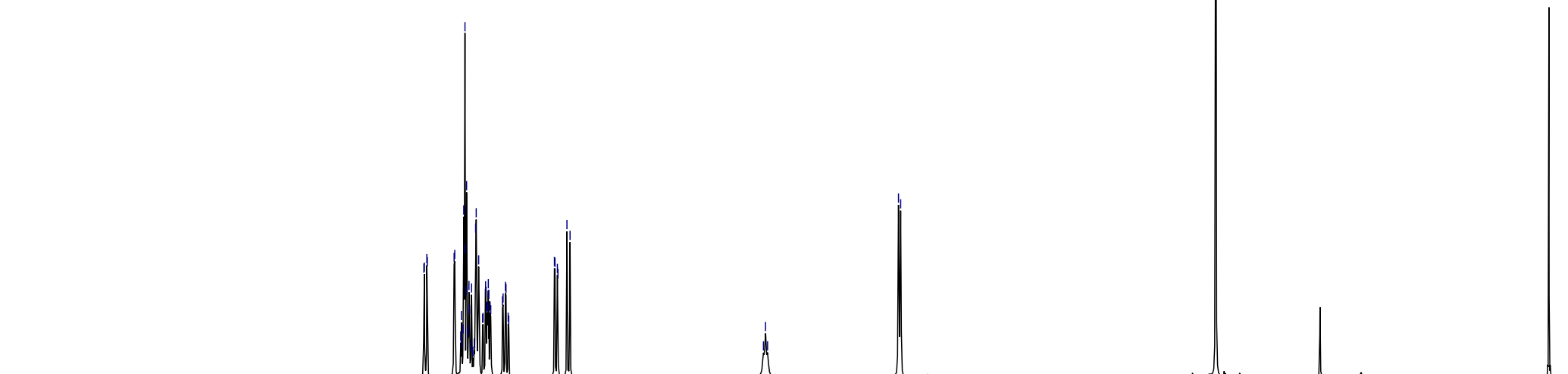
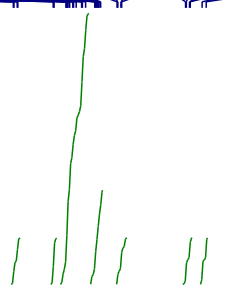
5.26
5.24
5.23

4.35
4.34

2.23



3k



1.01
1.01
5.89
2.05
1.02

1.02
1.01

1.01

2.02

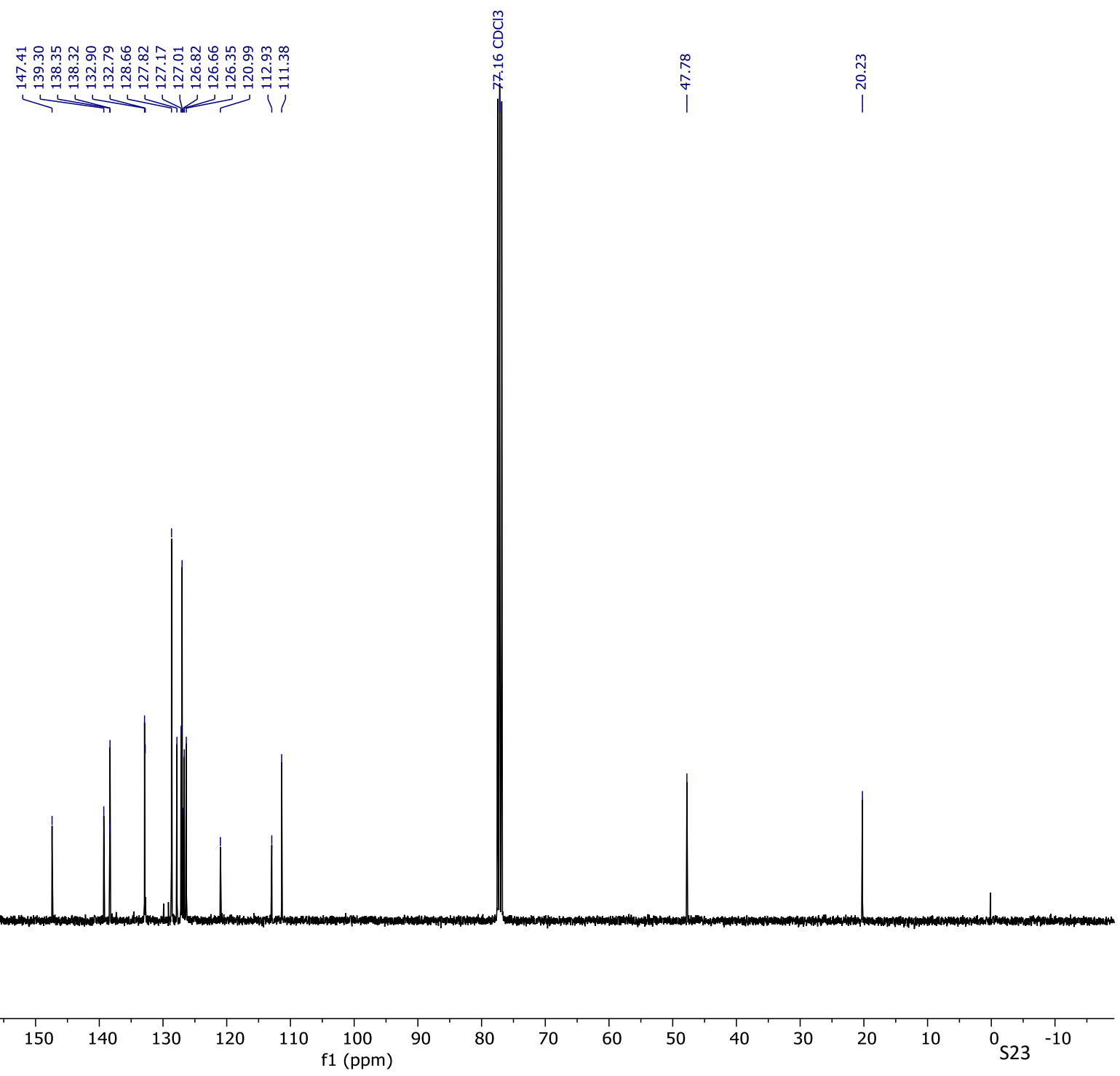
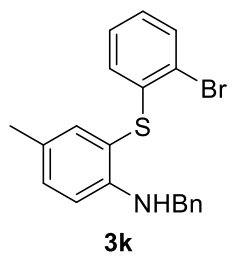
3.03

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

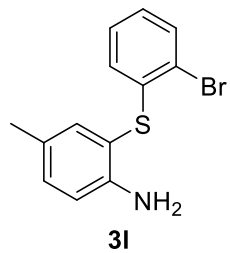
f1 (ppm)

S22

101 MHz, CDCl₃



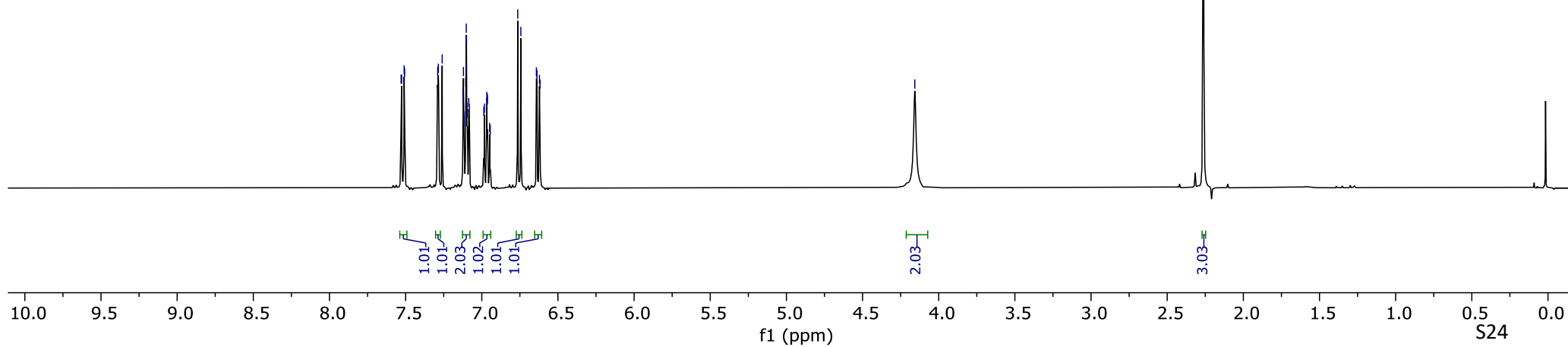
400 MHz, CDCl₃



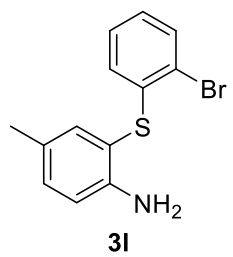
7.53
7.53
7.51
7.51
7.29
7.26 CDCl₃
7.12
7.12
7.12
7.12
7.11
7.10
7.10
7.10
7.10
7.10
7.09
7.08
6.99
6.98
6.97
6.96
6.96
6.95
6.94
6.76
6.74
6.64
6.64
6.62
6.62

4.16

2.26



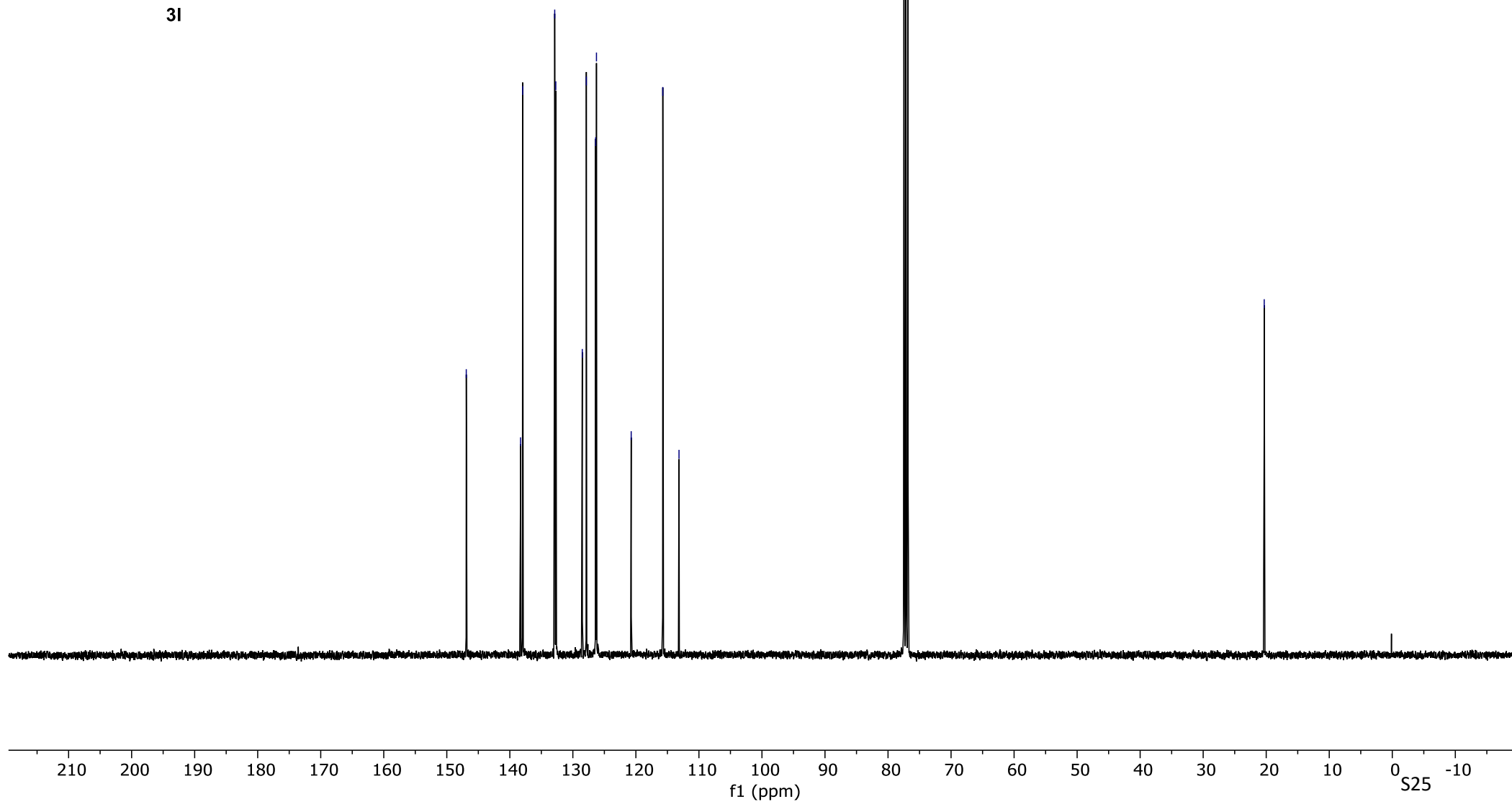
101 MHz, CDCl₃



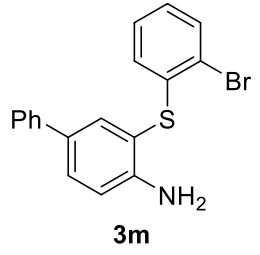
146.91
138.30
137.96
132.88
132.70
128.51
127.86
126.39
126.25
120.75
115.73
113.16

77.16 CDCl₃

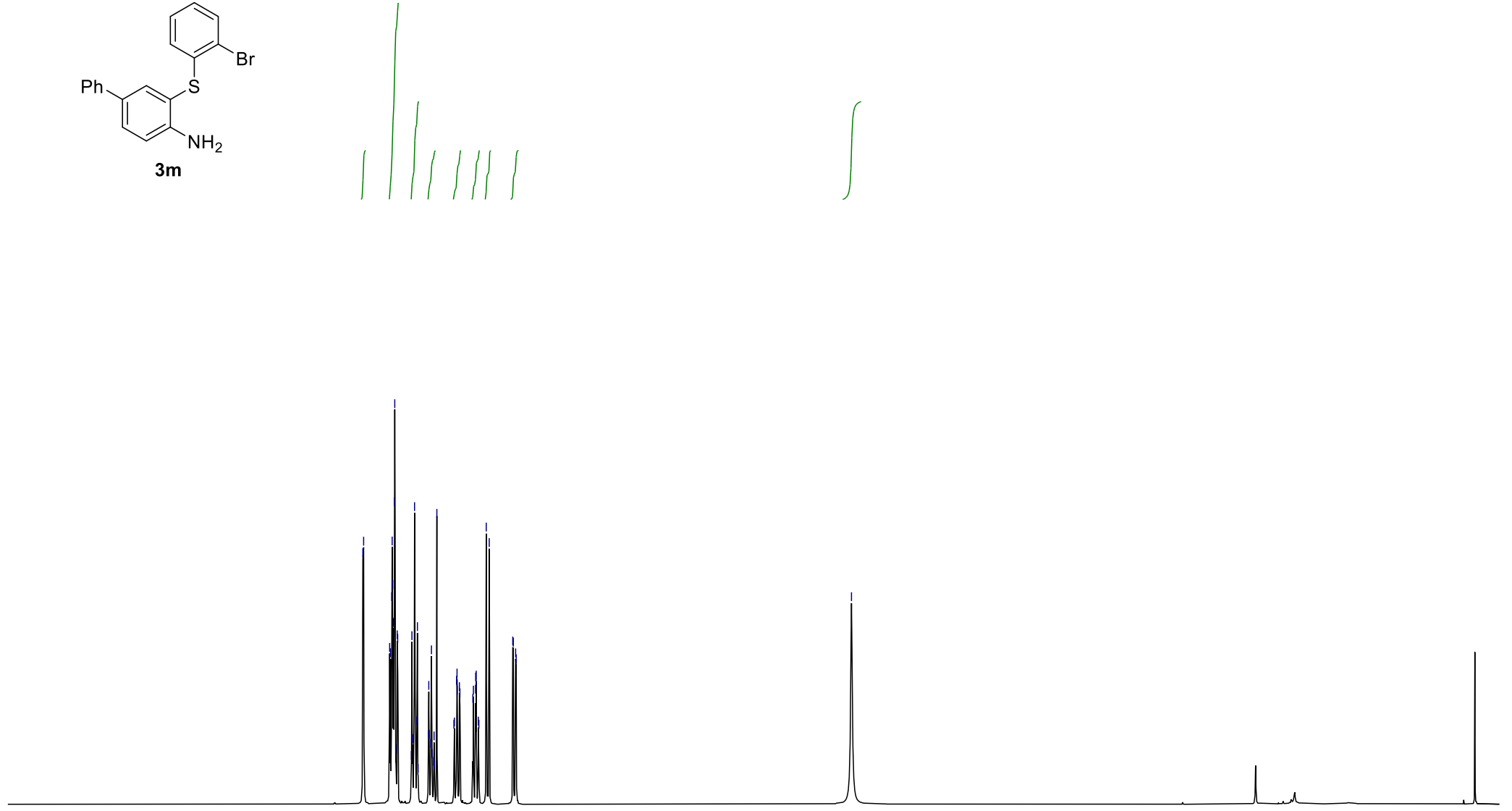
20.32



400 MHz, CDCl₃



7.78
7.77
7.59
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.44
7.43
7.43
7.42
7.40
7.40
7.39
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.26 CDCl₃
7.14
7.14
7.12
7.12
7.12
7.12
7.10
7.01
7.01
6.99
6.99
6.99
6.97
6.97
6.92
6.89
6.73
6.71
6.71
4.37



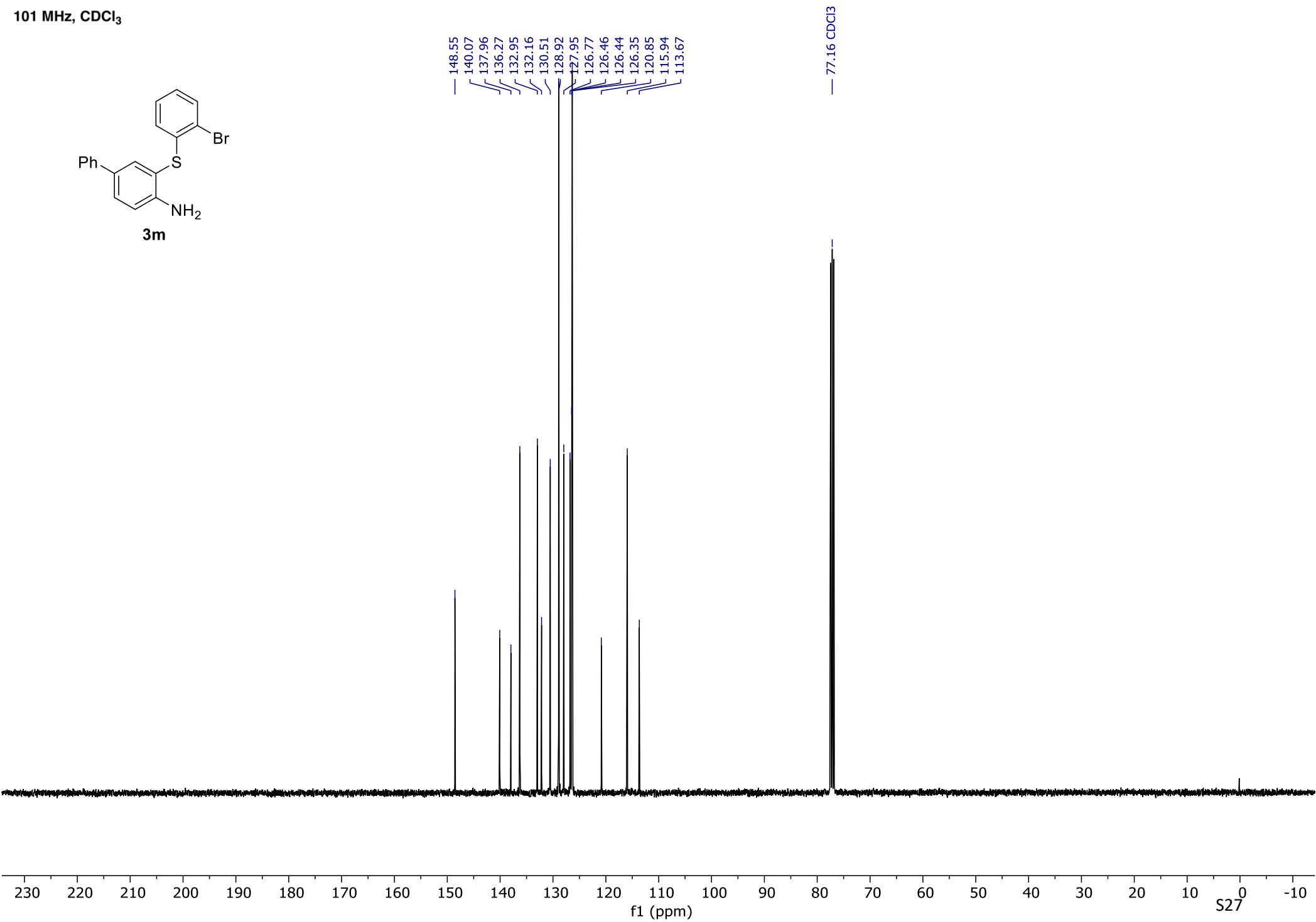
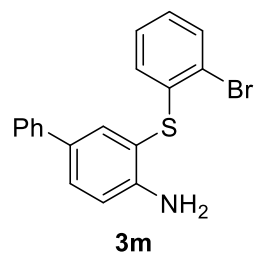
1.00
4.02
2.01
1.00
1.01
1.00
1.00
1.00
2.00

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

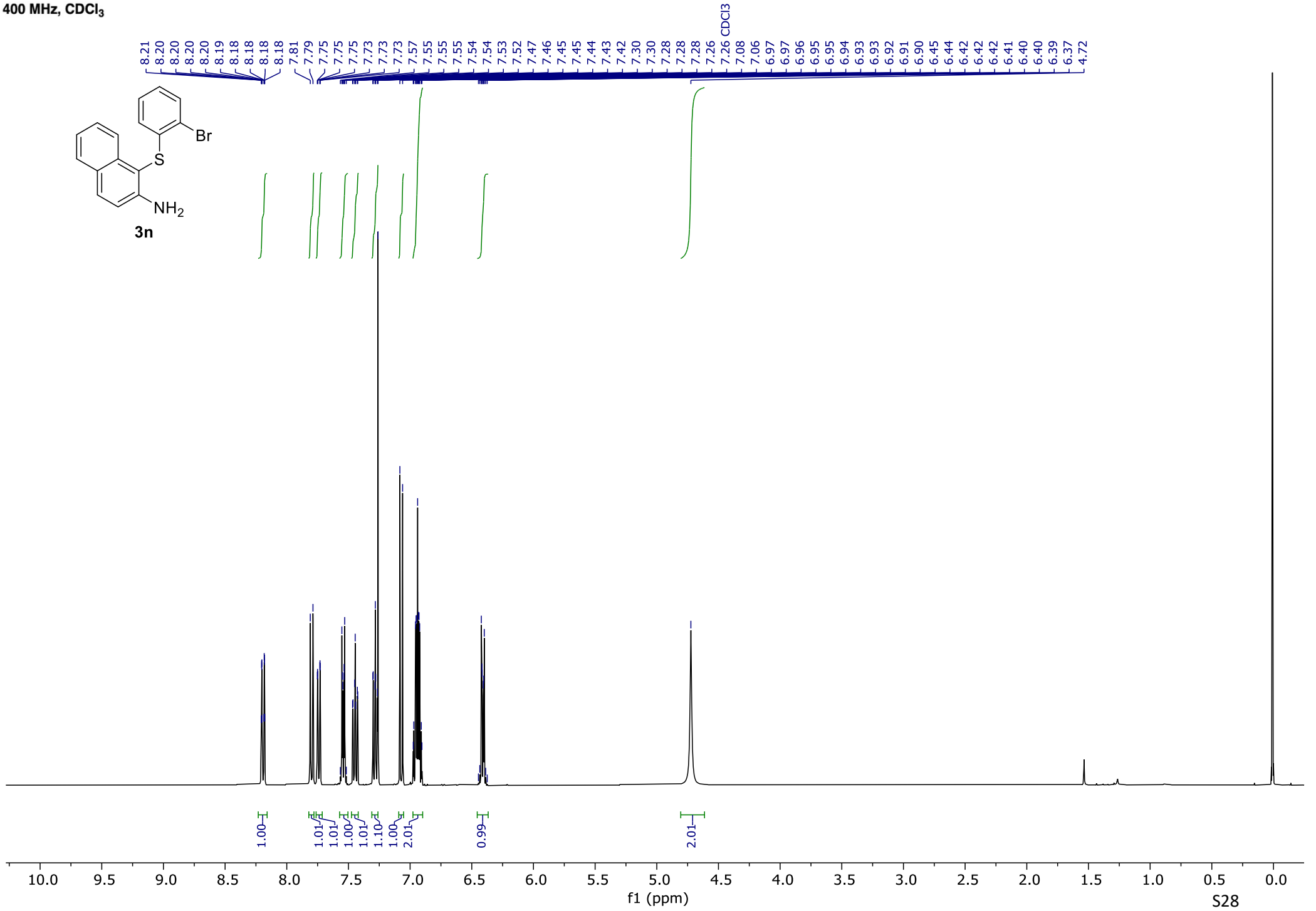
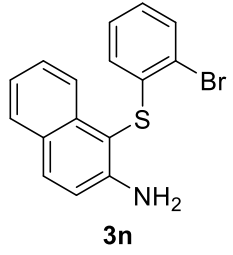
f1 (ppm)

S26

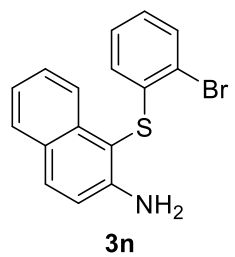
101 MHz, CDCl₃



400 MHz, CDCl₃

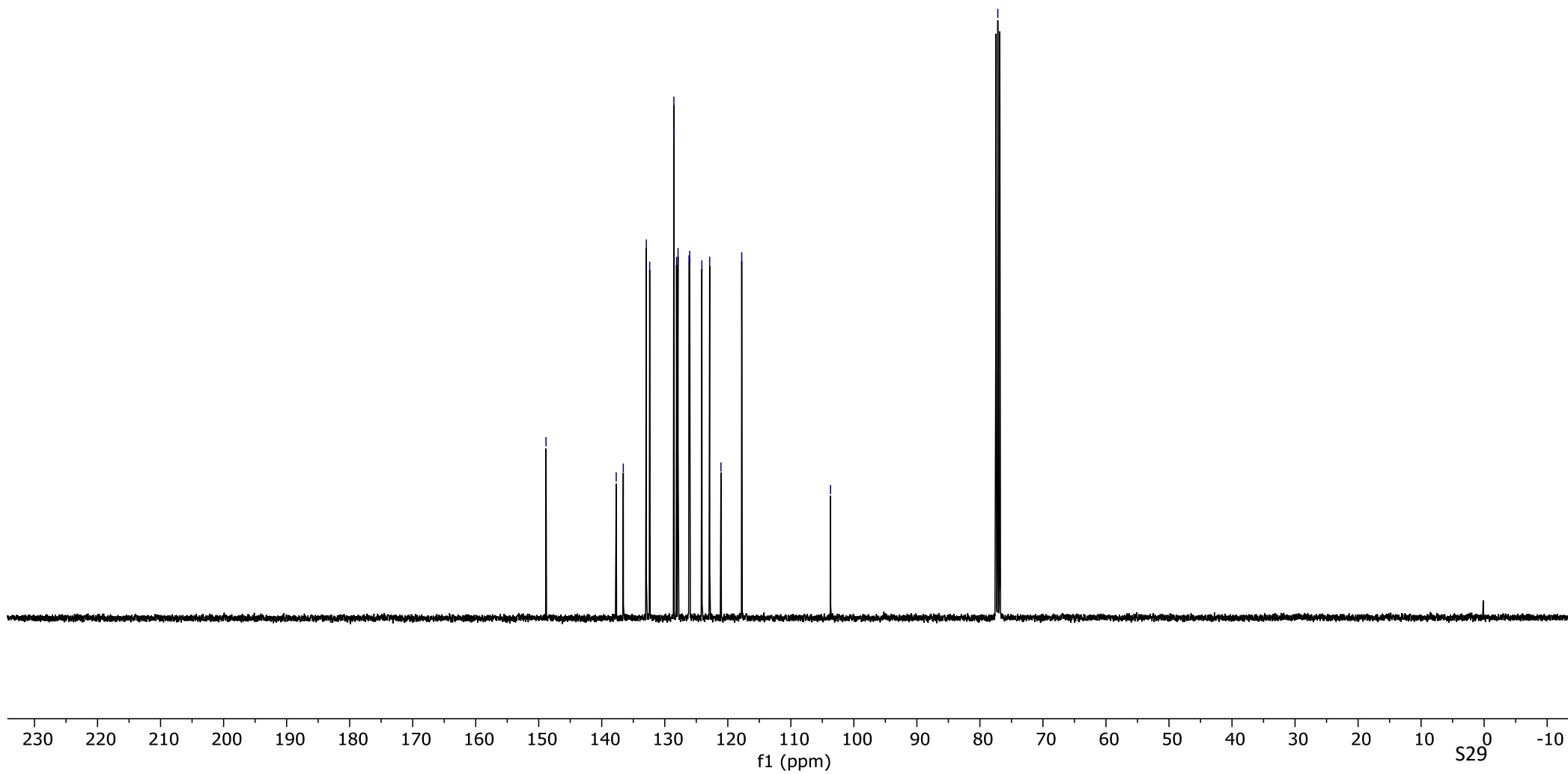


101 MHz, CDCl₃

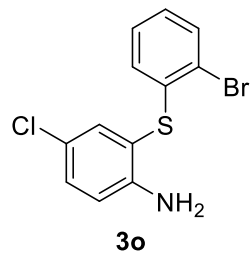


148.84
137.70
136.58
132.93
132.39
128.56
128.55
128.13
127.89
126.15
126.05
124.11
122.88
121.09
117.79
103.70

77.16 CDCl₃

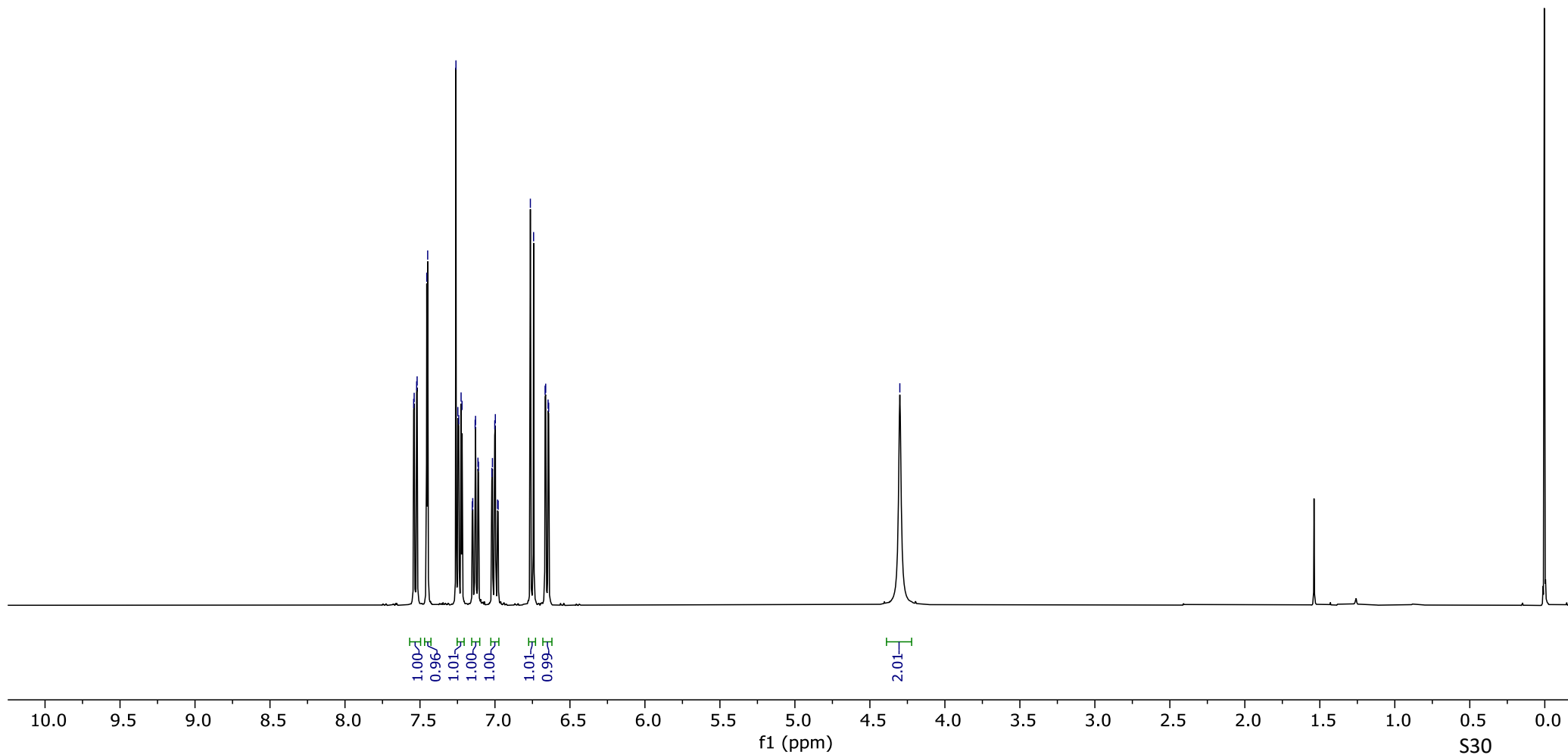


400 MHz, CDCl₃

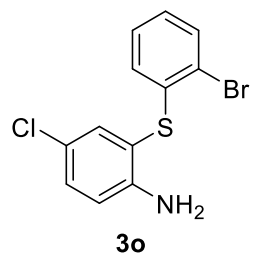


7.54
7.54
7.52
7.52
7.45
7.45
7.26 CDCl₃
7.25
7.24
7.23
7.22
7.15
7.15
7.13
7.13
7.11
7.11
7.02
7.02
7.00
7.00
6.98
6.98
6.76
6.74
6.67
6.66
6.65
6.64

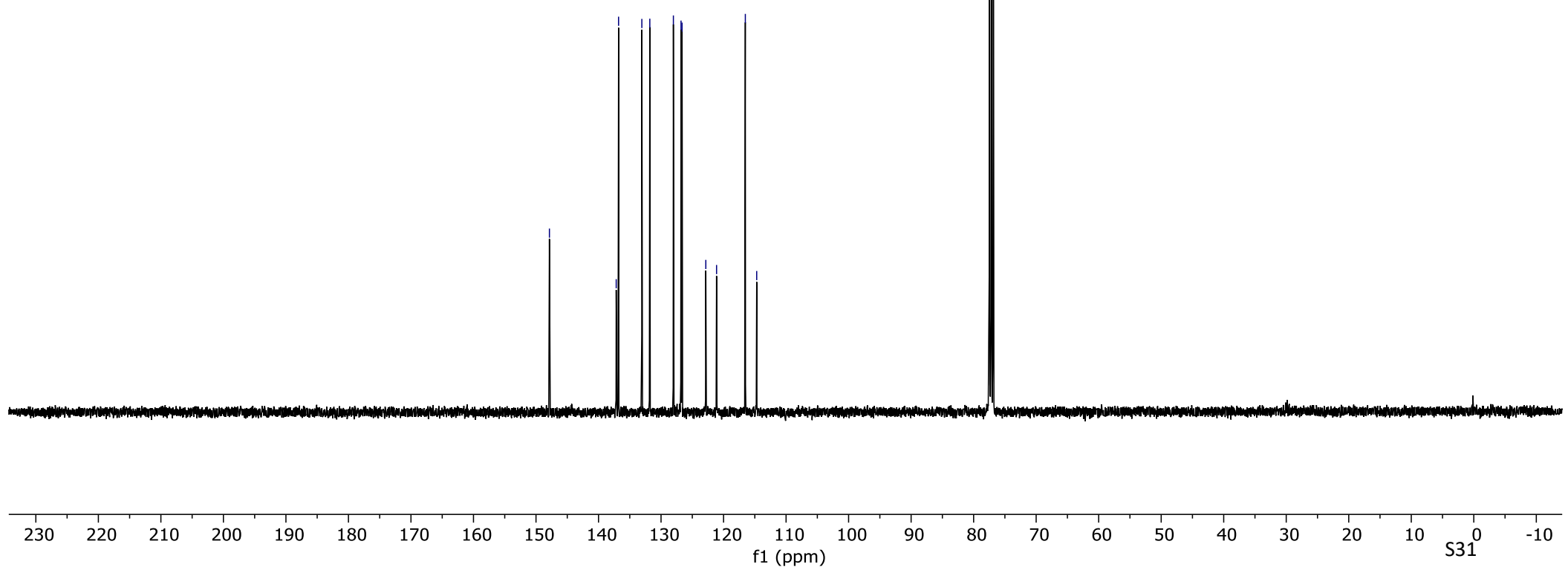
4.30



101 MHz, CDCl₃

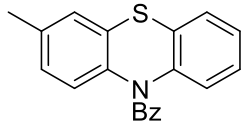


— 147.85
— 137.17
— 136.79
— 133.07
— 131.80
— 128.02
— 126.80
— 126.64
— 122.84
— 121.12
— 116.52
— 114.70
— 77.16 CDCl₃

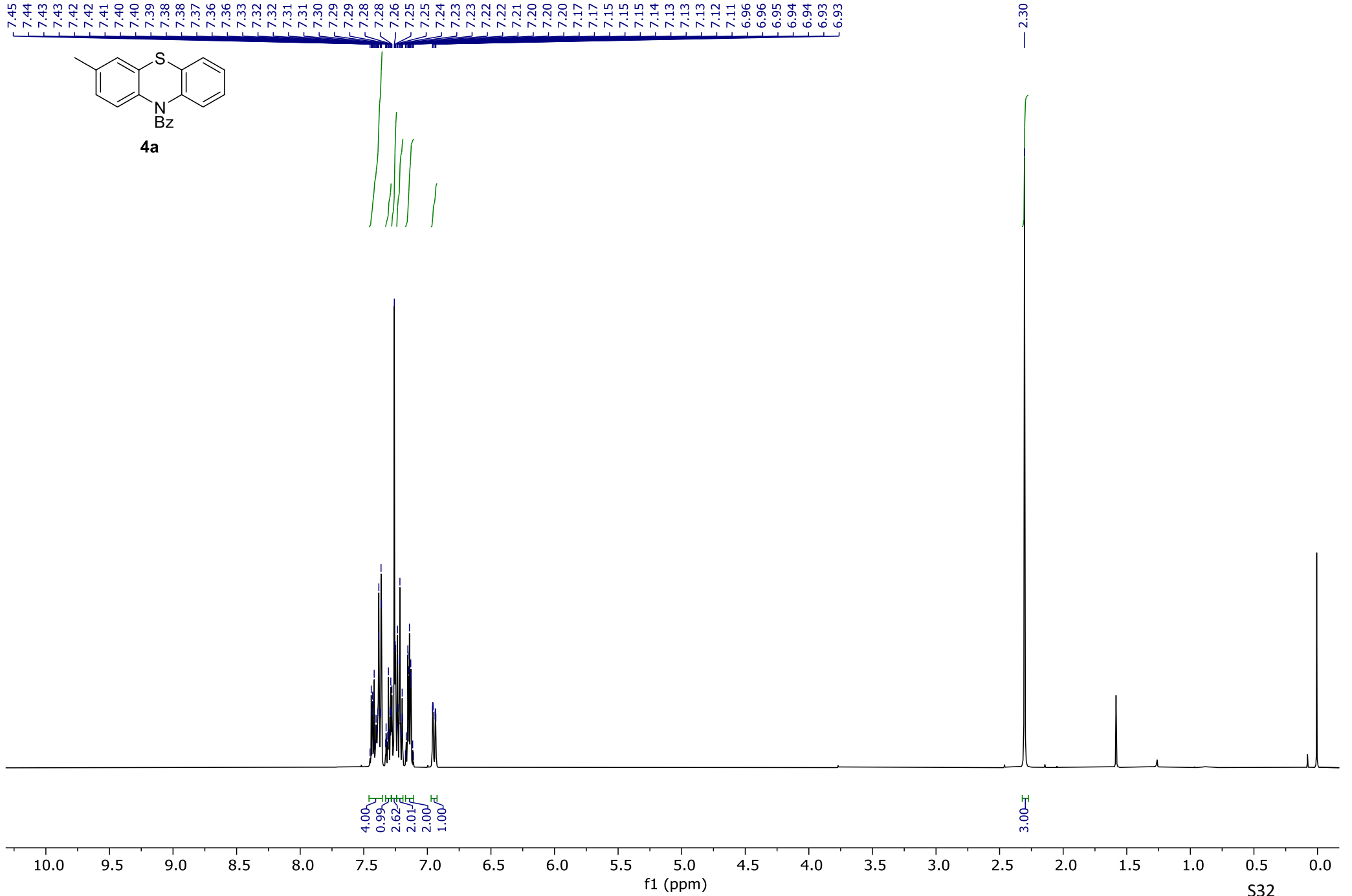


400 MHz, CDCl₃

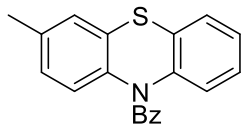
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.26 CDCl₃
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.20
7.20
7.17
7.17
7.15
7.15
7.15
7.15
7.14
7.13
7.13
7.13
7.12
7.11
7.11
6.96
6.96
6.95
6.95
6.94
6.94
6.93
6.93



4a



101 MHz, CDCl₃



4a

168.99

139.77

137.05

136.60

135.46

132.43

132.03

130.38

128.96

128.16

128.07

127.81

127.79

127.19

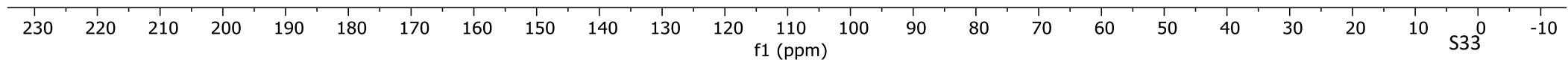
126.90

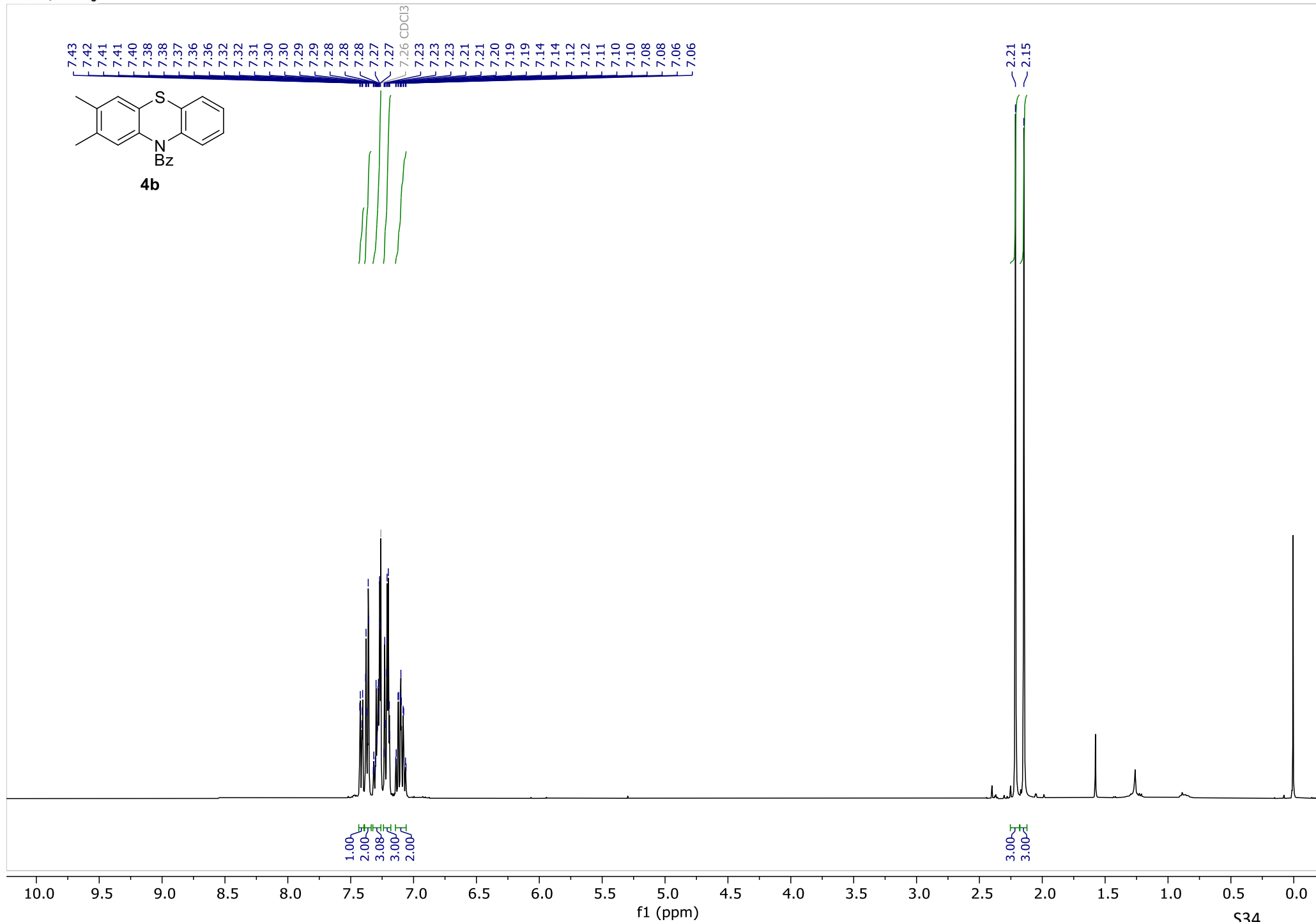
126.83

126.46

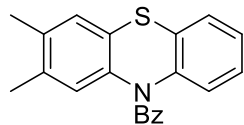
77.16 CDCl₃

21.00





101 MHz, CDCl₃



4b

168.98

140.00
137.12
135.76
135.57
135.33
132.89
130.31
128.90
128.77
128.44
128.08
128.02
127.79
127.19
126.77
126.36

77.16 CDCl₃

19.62
19.46

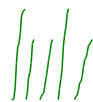
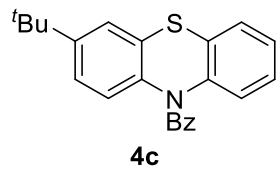
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

S35

400 MHz, CDCl₃

7.45
7.45
7.44
7.43
7.42
7.39
7.38
7.37
7.37
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26 CDCl₃
7.23
7.22
7.22
7.21
7.20
7.20
7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.11
7.09
7.09
7.07
7.07



3.02
2.01
2.00
3.03
2.01

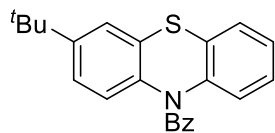
9.08
1.30

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

f1 (ppm)

S36

101 MHz, CDCl₃



4c

168.99

149.96

139.90

136.80

135.45

132.57

131.61

130.39

128.98

128.02

127.80

127.22

126.86

126.56

126.42

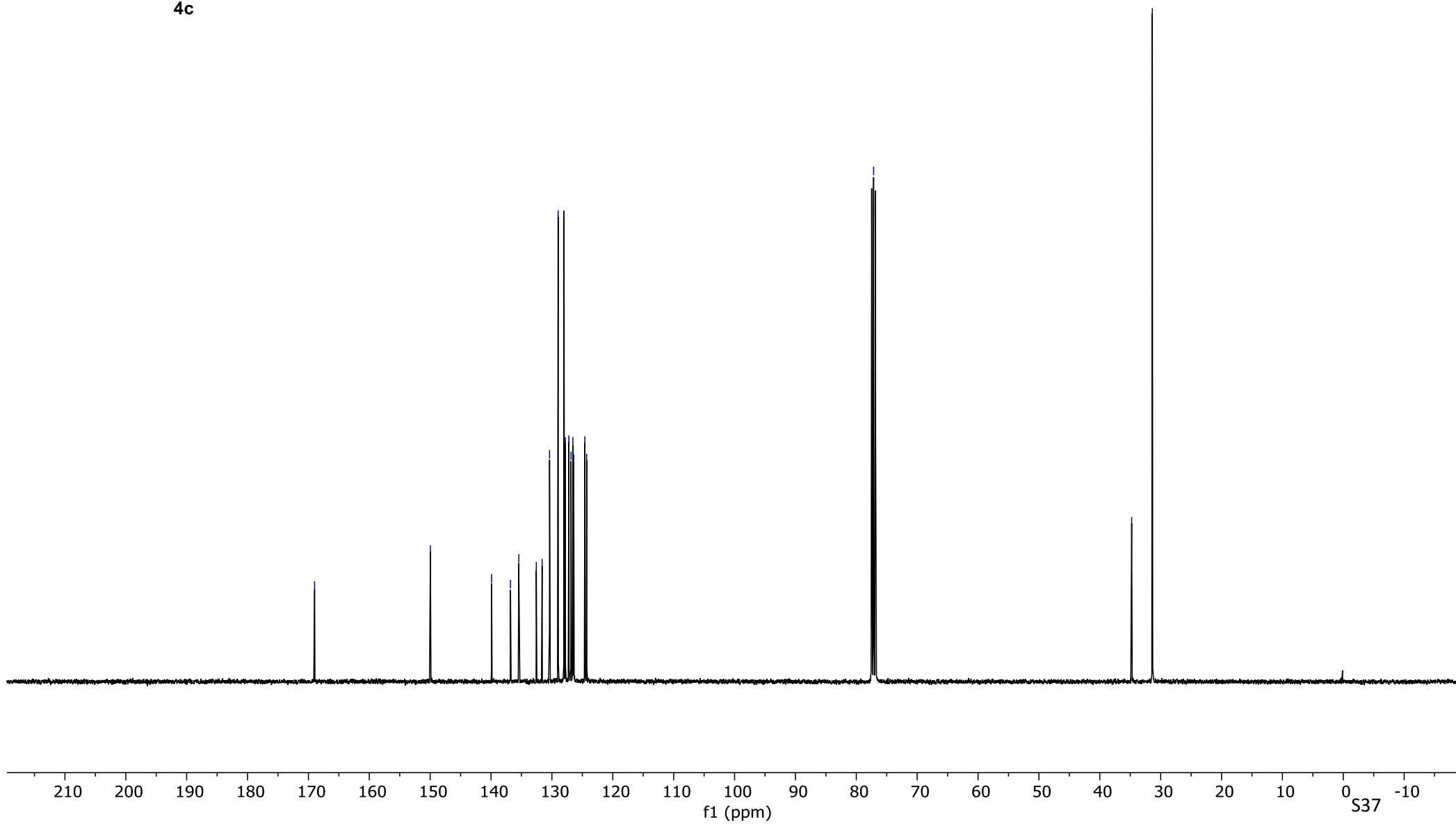
124.59

124.29

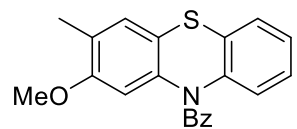
77.16 CDCl₃

34.76

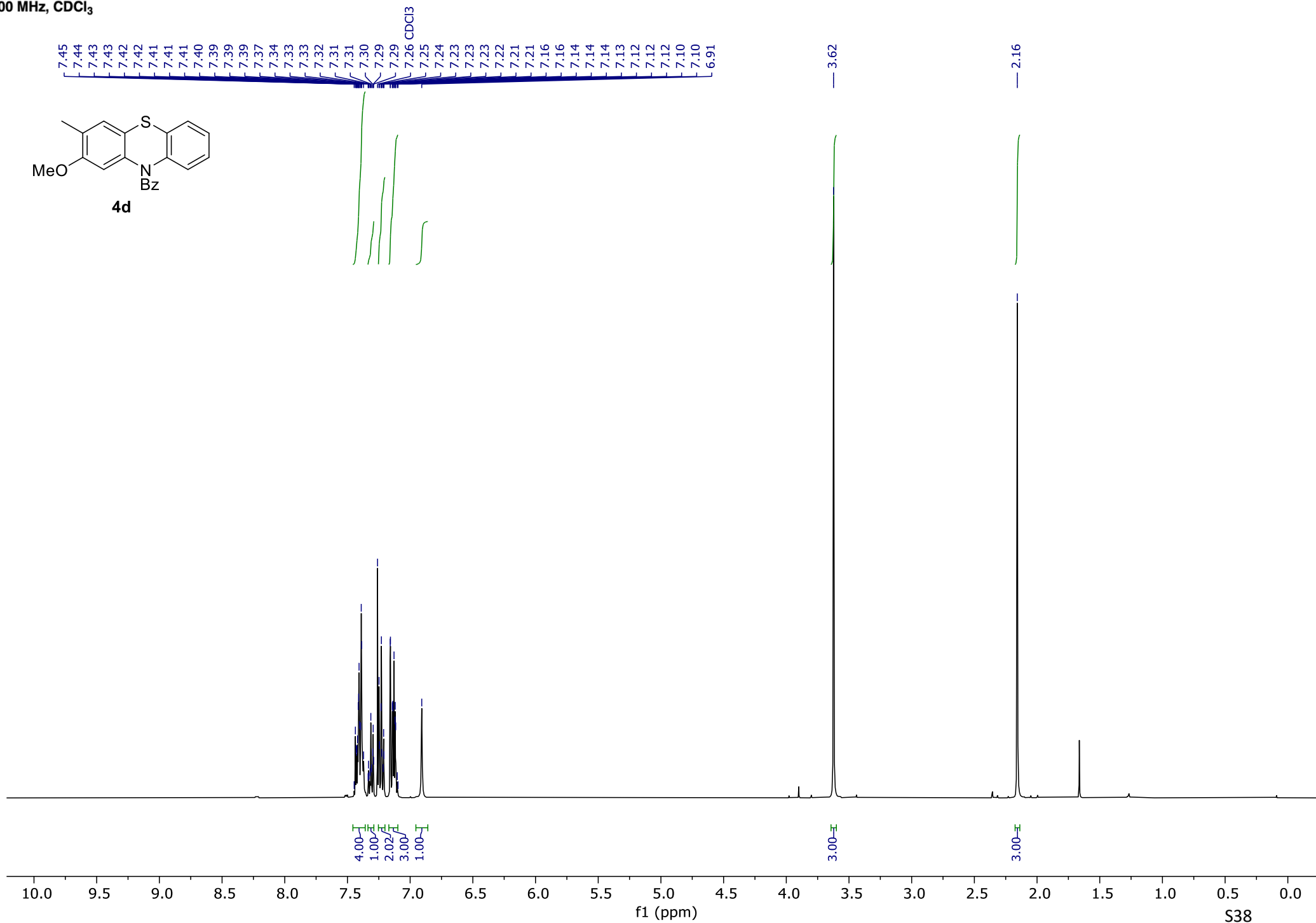
31.37



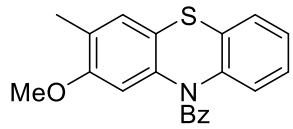
400 MHz, CDCl₃



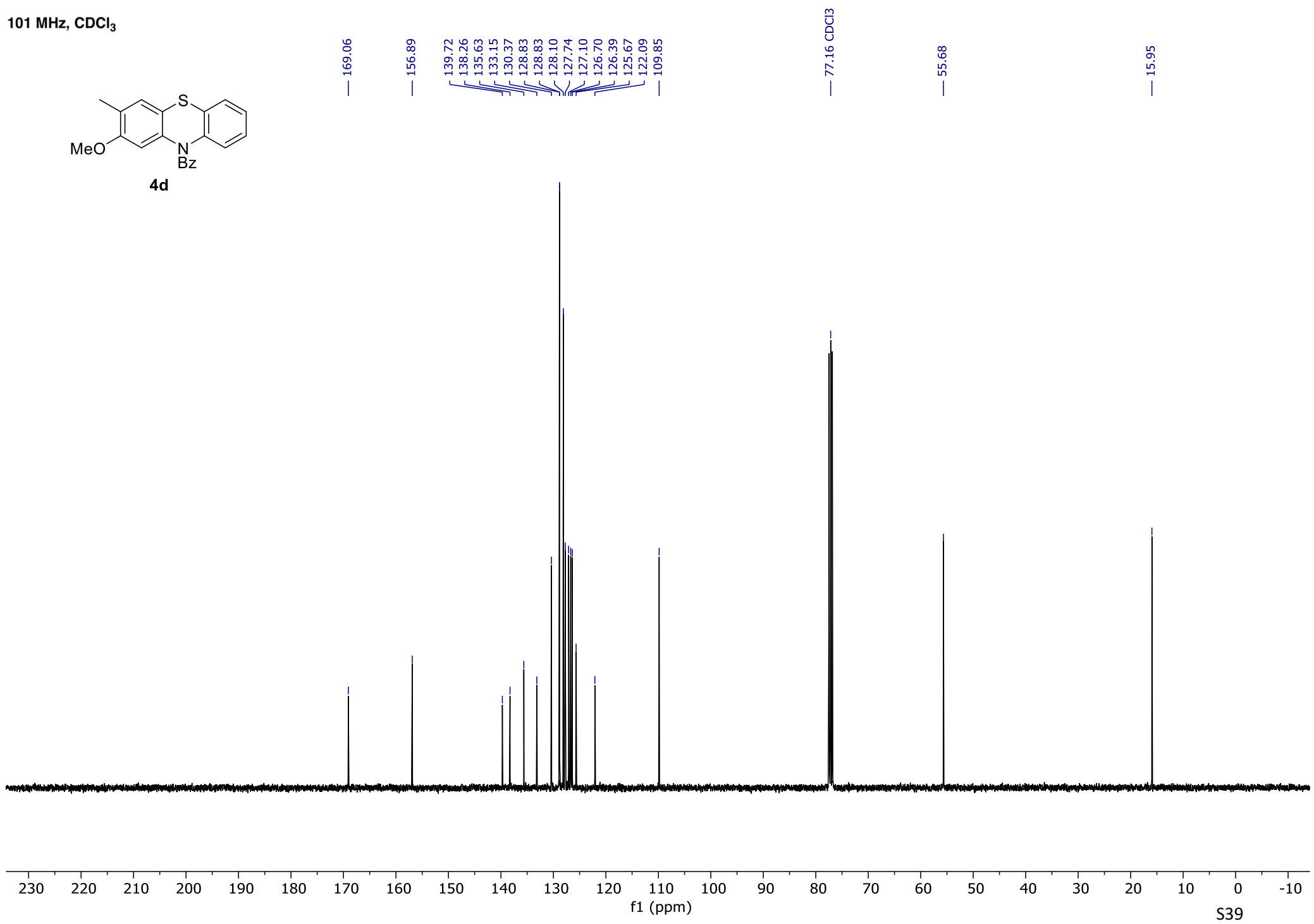
4d



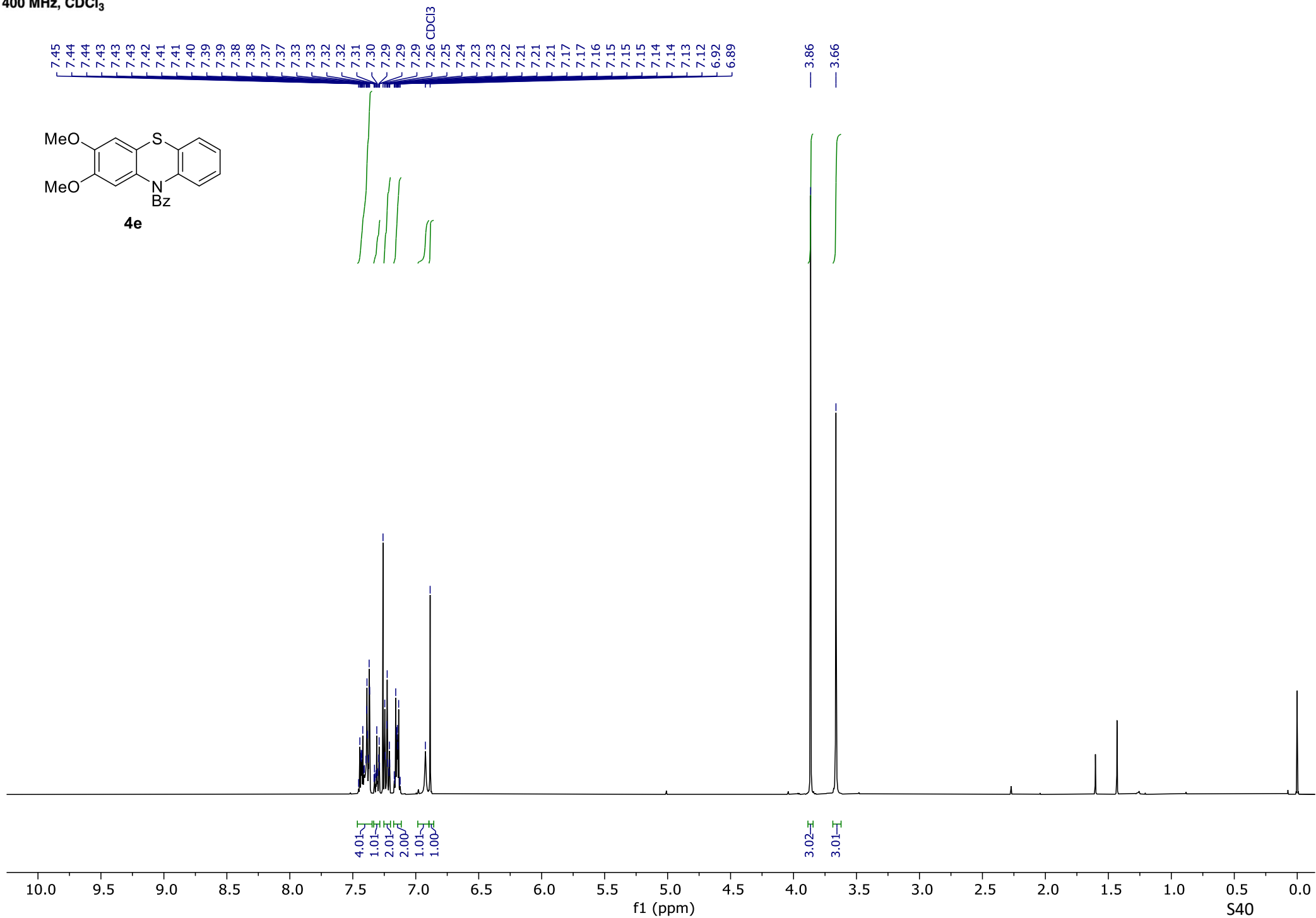
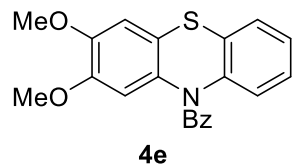
101 MHz, CDCl₃



4d

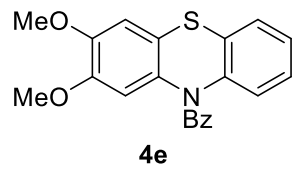


400 MHz, CDCl₃



S40

101 MHz, CDCl₃

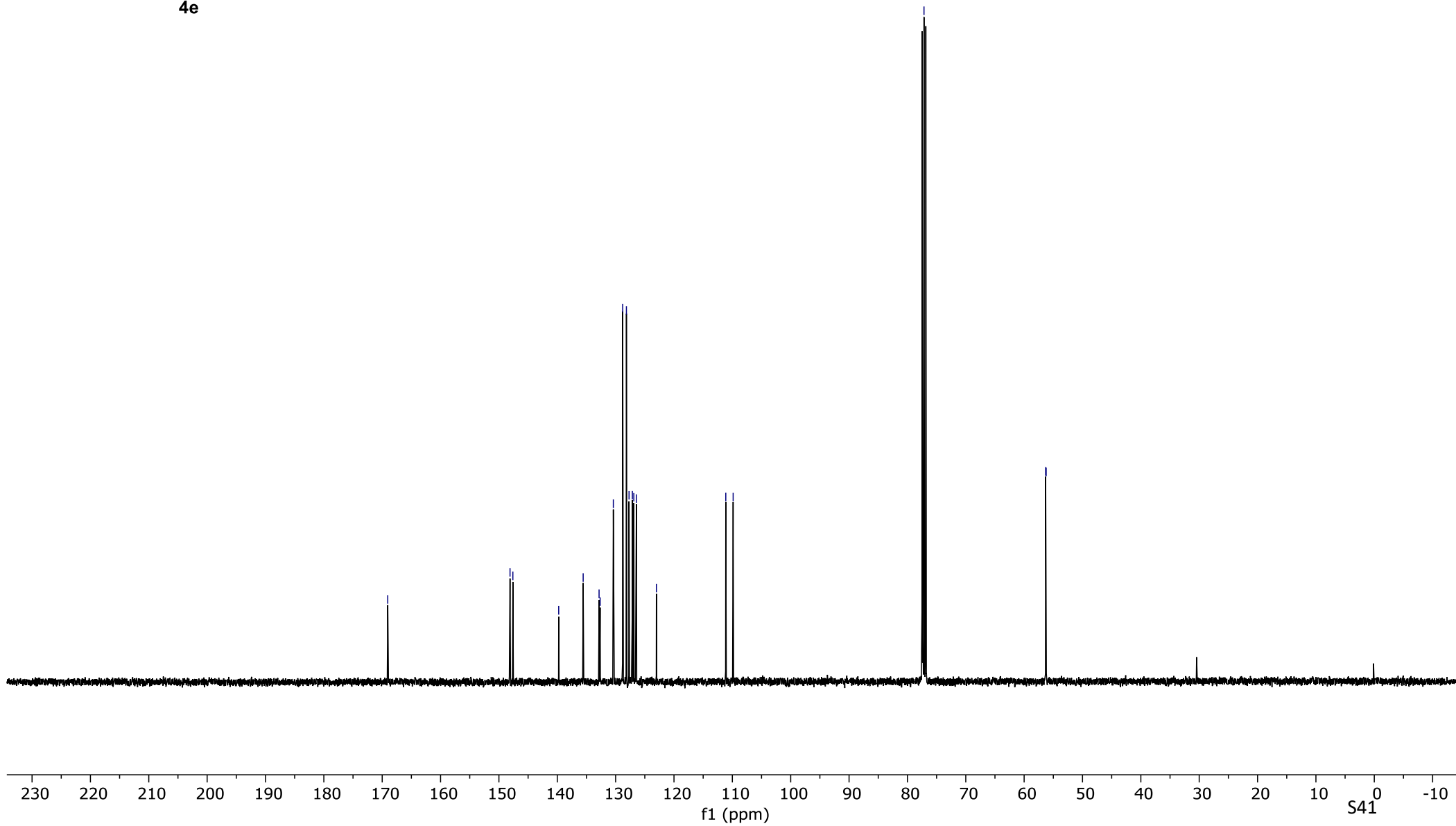


169.05

148.10
147.61
139.75
135.56
132.84
132.66
130.39
128.79
128.15
127.70
127.14
126.88
126.44
123.01
111.13
109.86

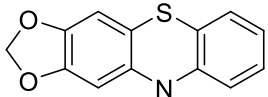
77.16 CDCl₃

56.32
56.23

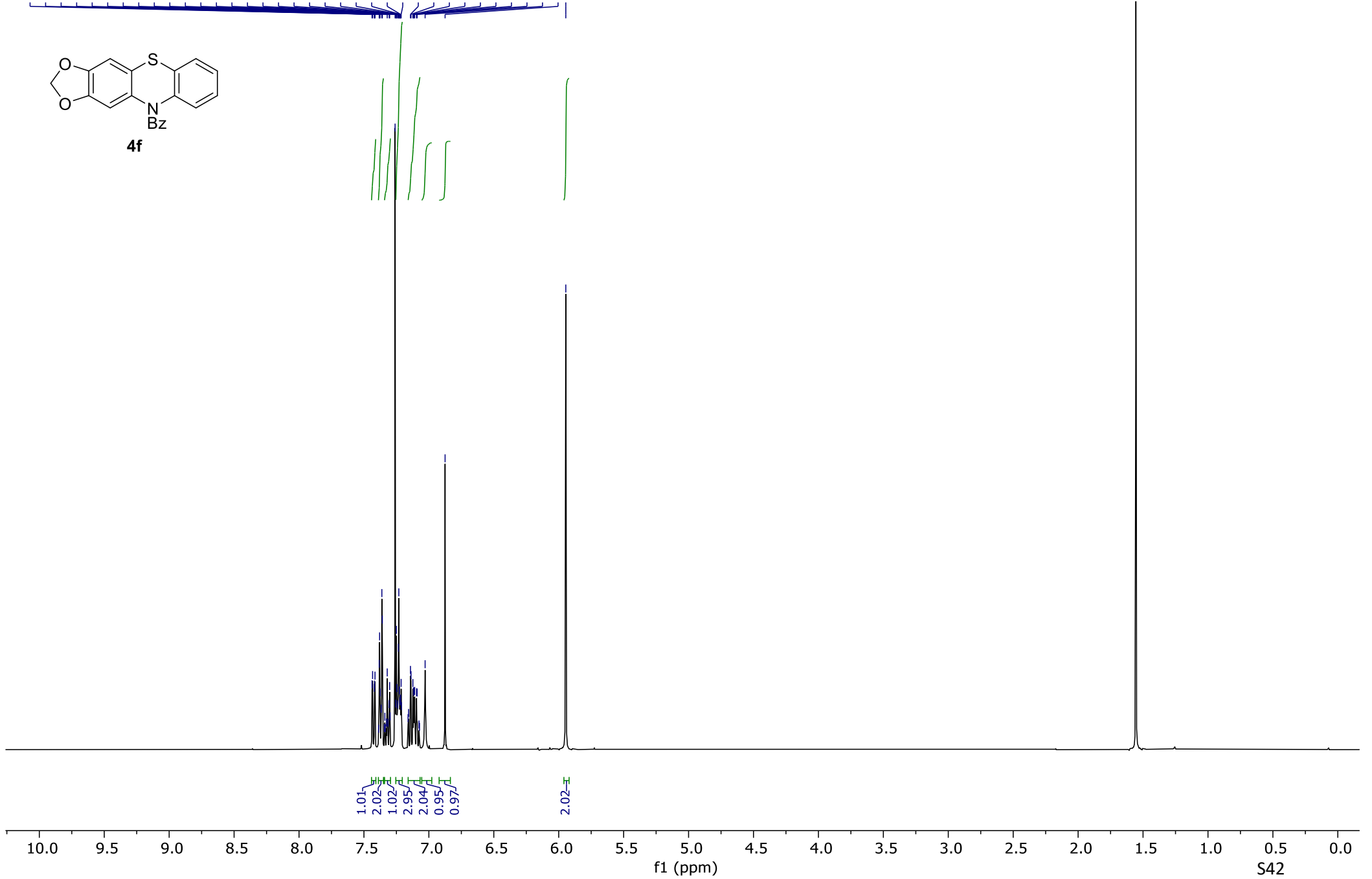


400 MHz, CDCl₃

7.44
7.43
7.42
7.42
7.41
7.38
7.38
7.36
7.36
7.32
7.31
7.30
7.26 CDCl₃
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.14
7.14
7.12
7.12
7.11
7.11
7.09
7.09
7.03
6.88



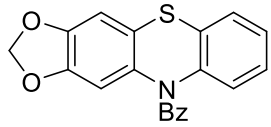
4f



1.01
2.02
1.02
2.95
2.04
0.95
0.97
2.02

S42

101 MHz, CDCl₃



4f

168.96

147.32
146.32
140.10
135.30
133.55
133.22
130.53
128.92
128.17
127.67
127.18
127.00
126.51
124.76
108.62
107.39
102.08

77.46 CDCl₃

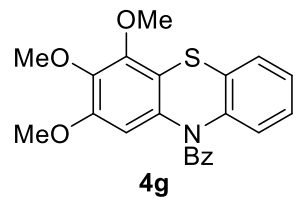


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

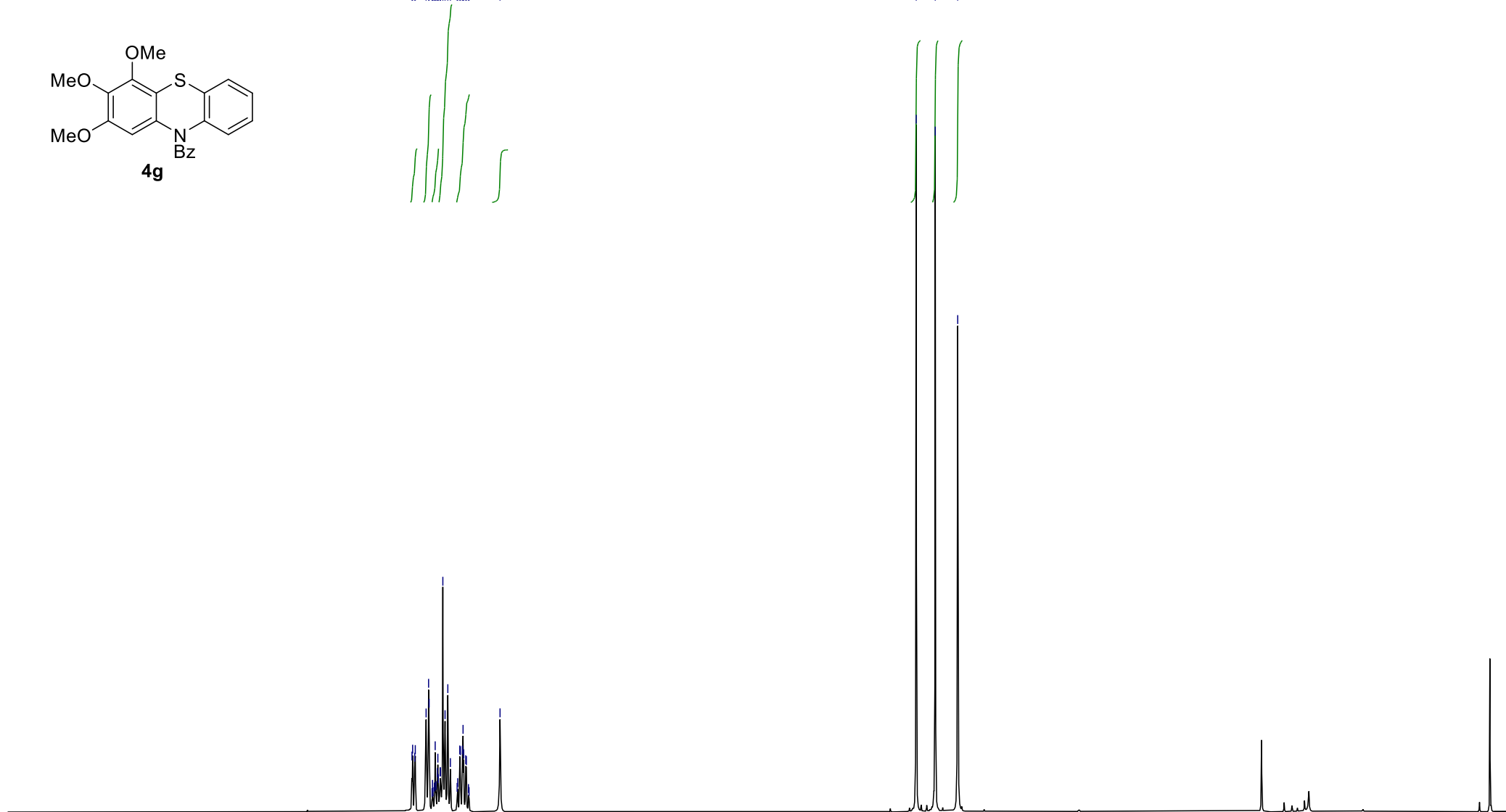
S43

400 MHz, CDCl₃



7.47
7.47
7.45
7.45
7.38
7.36
7.36
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.26 CDCl₃
7.24
7.23
7.21
7.16
7.16
7.14
7.14
7.12
7.12
7.12
7.10
7.10
7.08
7.08
6.86

3.98
3.85
3.69

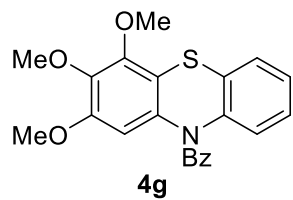


1.00
2.00
1.00
3.66
2.00
0.97

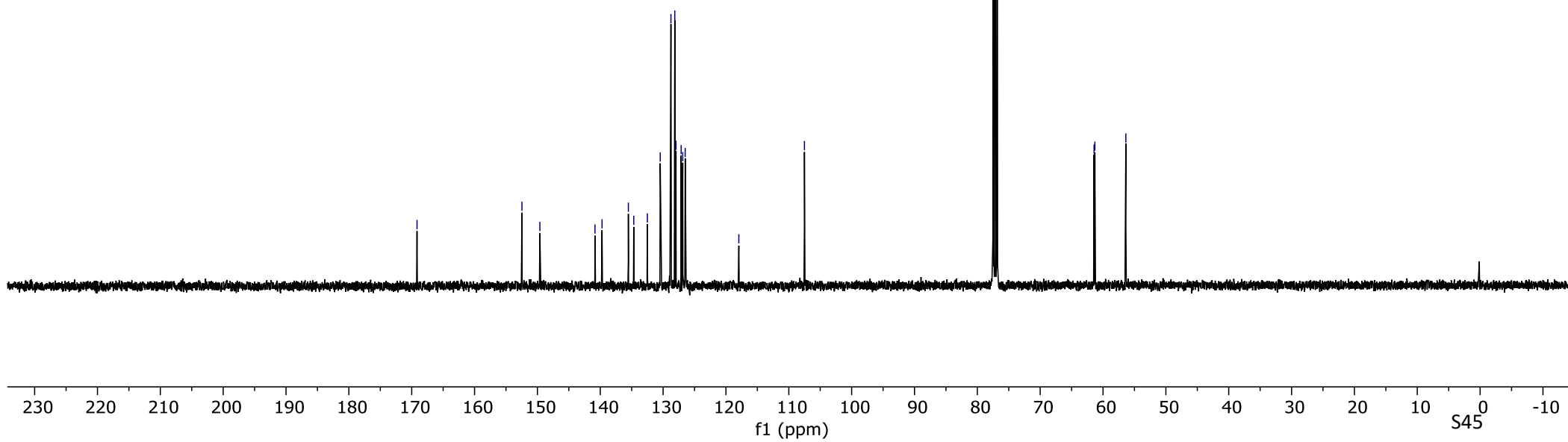
3.00
3.00
3.00

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

101 MHz, CDCl₃

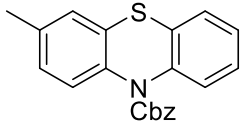


169.15
152.46
149.61
140.84
139.72
135.53
134.67
132.50
130.45
128.75
128.14
127.95
127.13
126.88
126.48
117.95
107.51
77.16 CDCl₃
61.43
61.30
56.37

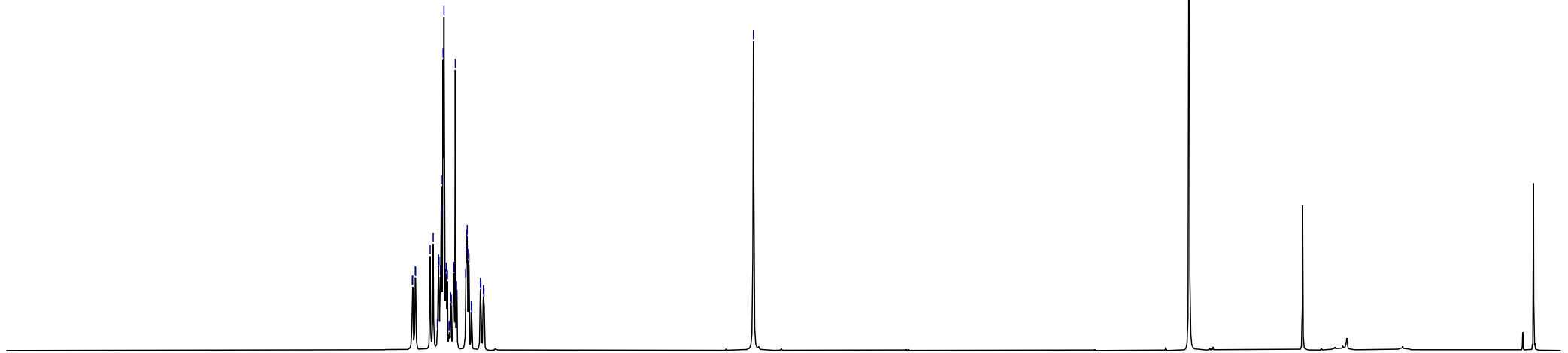


400 MHz, CDCl₃

7.55
7.55
7.53
7.53
7.43
7.41
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.27
7.27
7.26 CDCl₃
7.25
7.25
7.19
7.19
7.18
7.18
7.17
7.17
7.15
7.15
7.09
7.09
7.07
7.07
5.26



4h



1.01
1.01
6.03
1.79
2.04
1.00

2.01

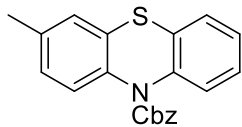
3.01

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

f1 (ppm)

S46

101 MHz, CDCl₃



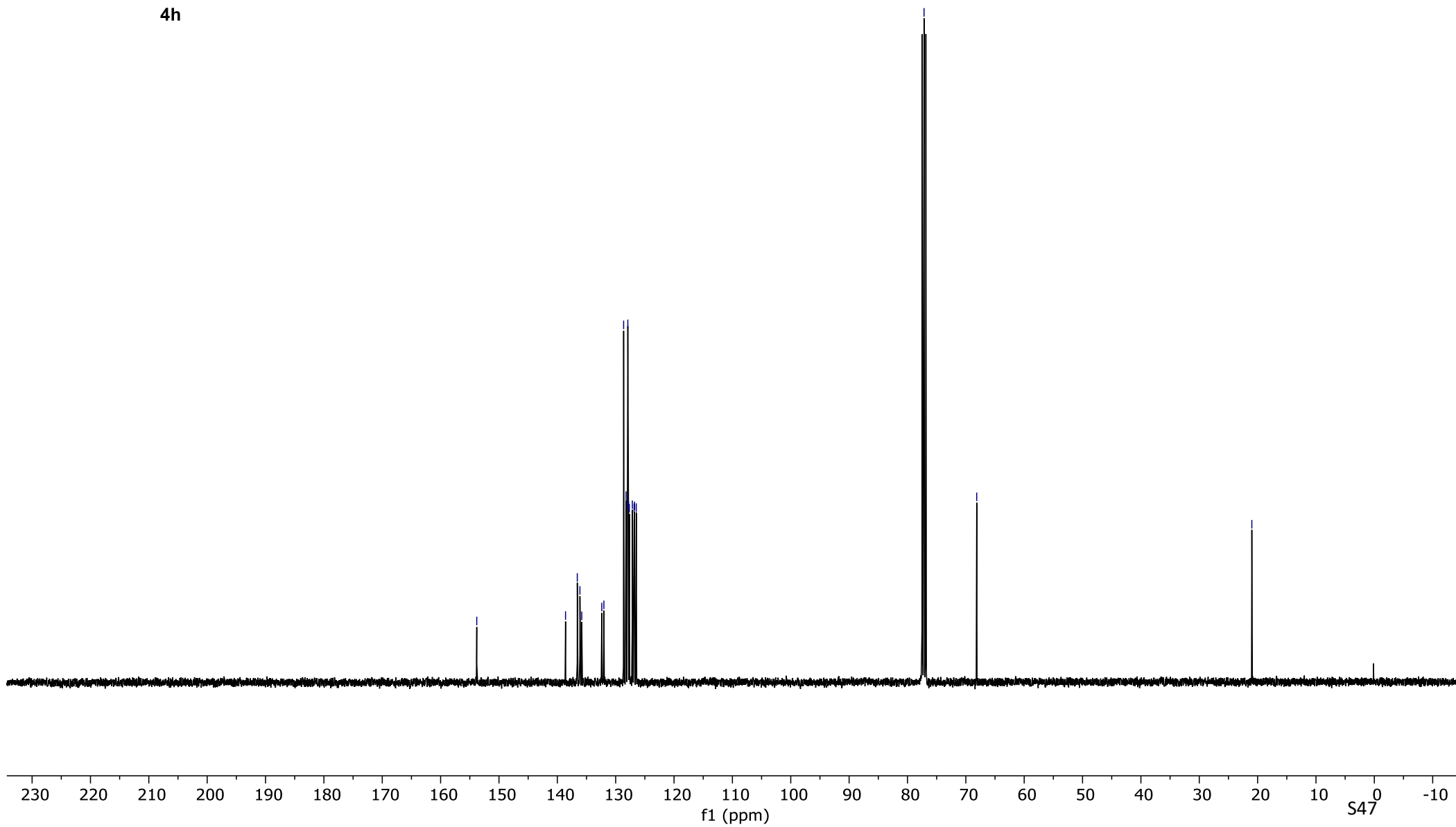
4h

153.81
138.59
136.58
136.13
135.81
132.38
132.02
128.64
128.22
127.97
127.92
127.80
127.66
127.14
126.85
126.76
126.47

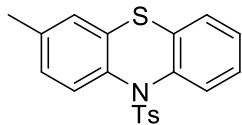
77.16 CDCl₃

68.13

20.99



400 MHz, CDCl₃



4i

7.75
7.74
7.73
7.72
7.62
7.60
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26 CDCl₃
7.22
7.22
7.20
7.20
7.19
7.18
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.09
7.09
7.06
7.05
7.03
7.03
6.92
6.92

2.37
2.32

1.01
1.00
1.03
1.03
4.04
2.04
1.00

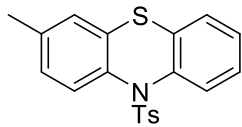
3.04
3.03

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

f1 (ppm)

S48

101 MHz, CDCl₃

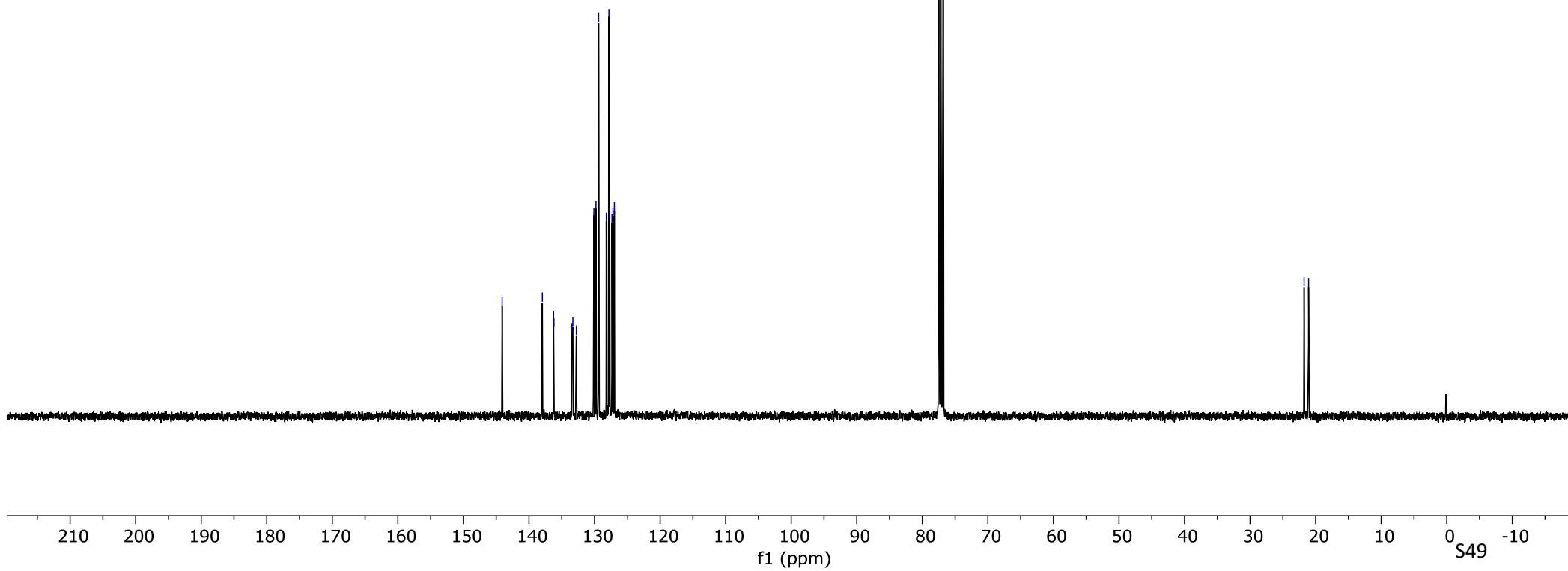


4i

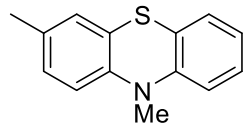
144.10
137.96
136.25
136.20
133.45
133.31
132.78
130.10
129.78
129.38
128.21
127.81
127.69
127.34
127.20
126.98

77.16 CDCl₃

21.77
21.08

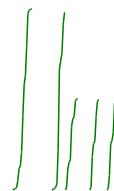


400 MHz, CDCl₃



4j

7.26 CDCl₃
7.19
7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.14
6.98
6.98
6.96
6.96
6.96
6.94
6.93
6.92
6.92
6.90
6.90
6.81
6.81
6.79
6.72
6.70



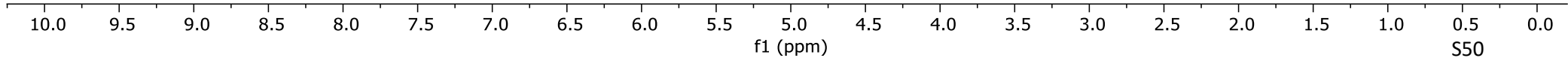
1.99
1.96
1.01
1.00
1.00

3.00

3.01

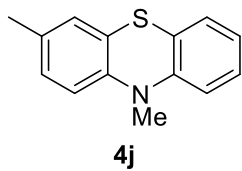
3.35

2.26



S50

101 MHz, CDCl₃

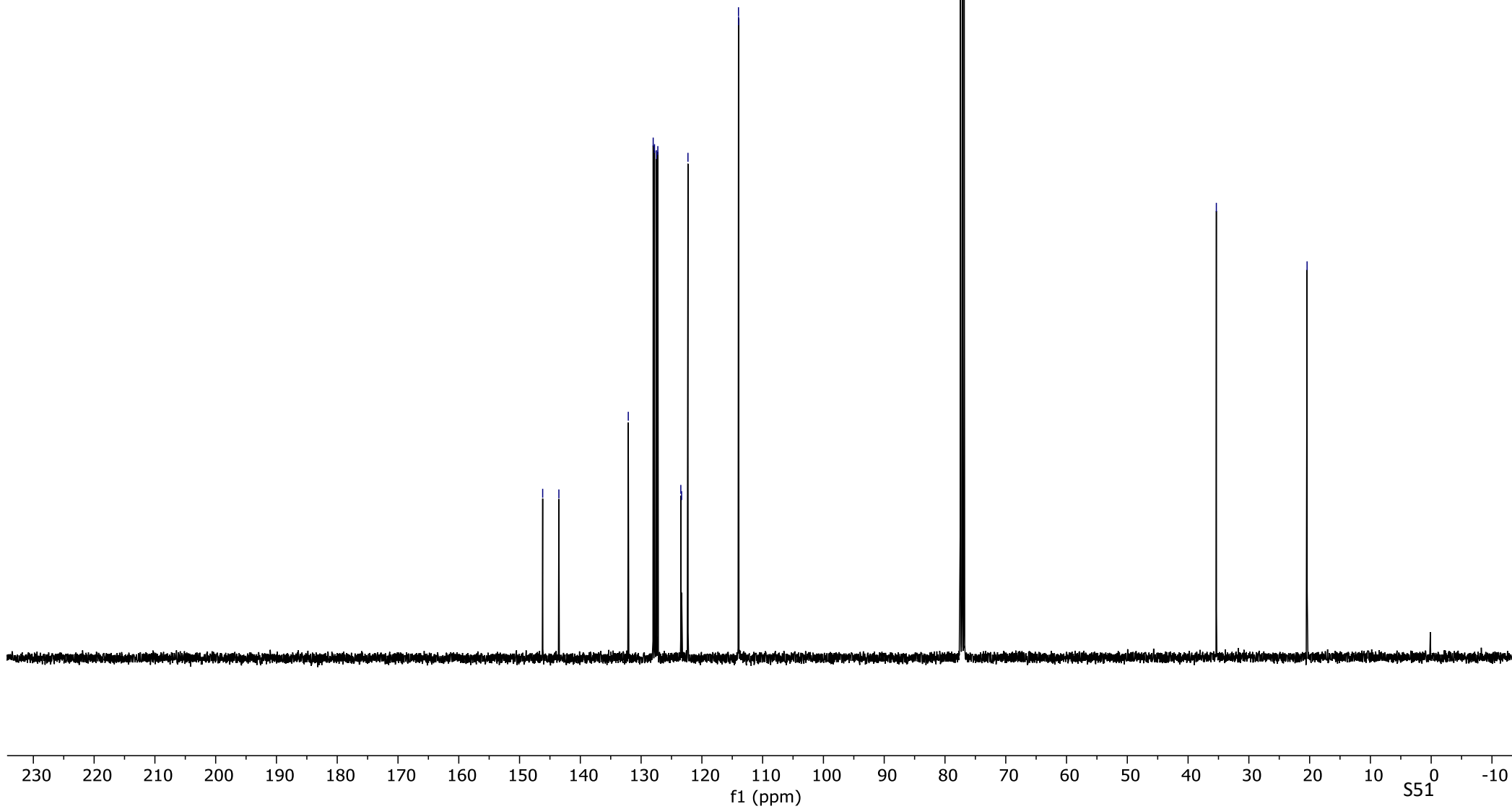


146.20
143.53
132.11
128.01
127.80
127.47
127.25
123.47
123.34
122.29
113.98
113.97

77.16 CDCl₃

35.35

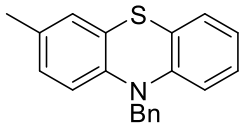
20.42



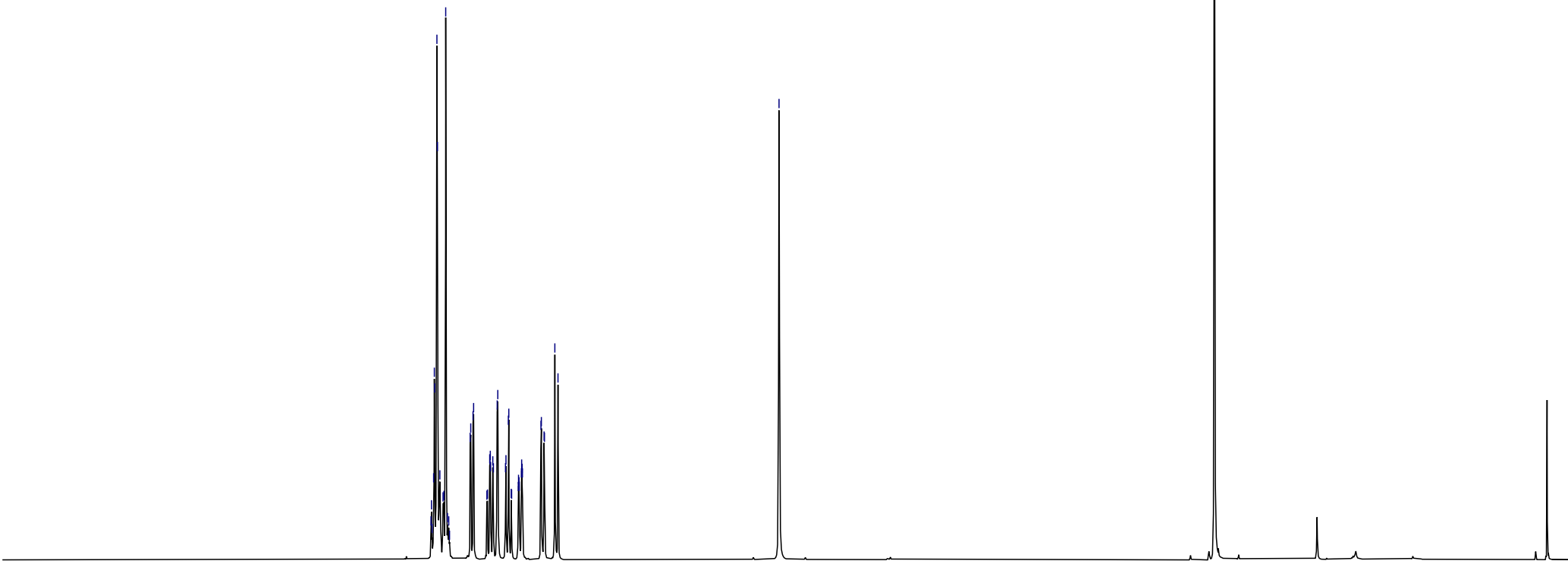
400 MHz, CDCl₃

CDCl₃

7.34
7.33
7.33
7.32
7.31
7.30
7.27
7.26
7.10
7.10
7.08
7.08
6.99
6.99
6.97
6.97
6.97
6.95
6.95
6.92
6.92
6.87
6.86
6.85
6.85
6.83
6.83
6.83
6.78
6.78
6.78
6.78
6.76
6.76
6.76
6.76
6.63
6.61
6.61
6.54
6.52



4k



4.00
1.72
1.00
1.00
0.99
1.00
1.00
1.00
1.00

1.99

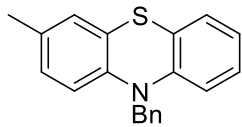
3.00

2.21

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
f1 (ppm)

S52

101 MHz, CDCl₃



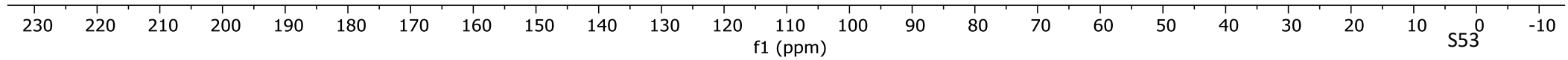
4k

144.80
142.10
136.95
132.17
128.82
127.82
127.44
127.28
127.06
126.92
126.75
123.13
123.04
122.33
115.36
115.34

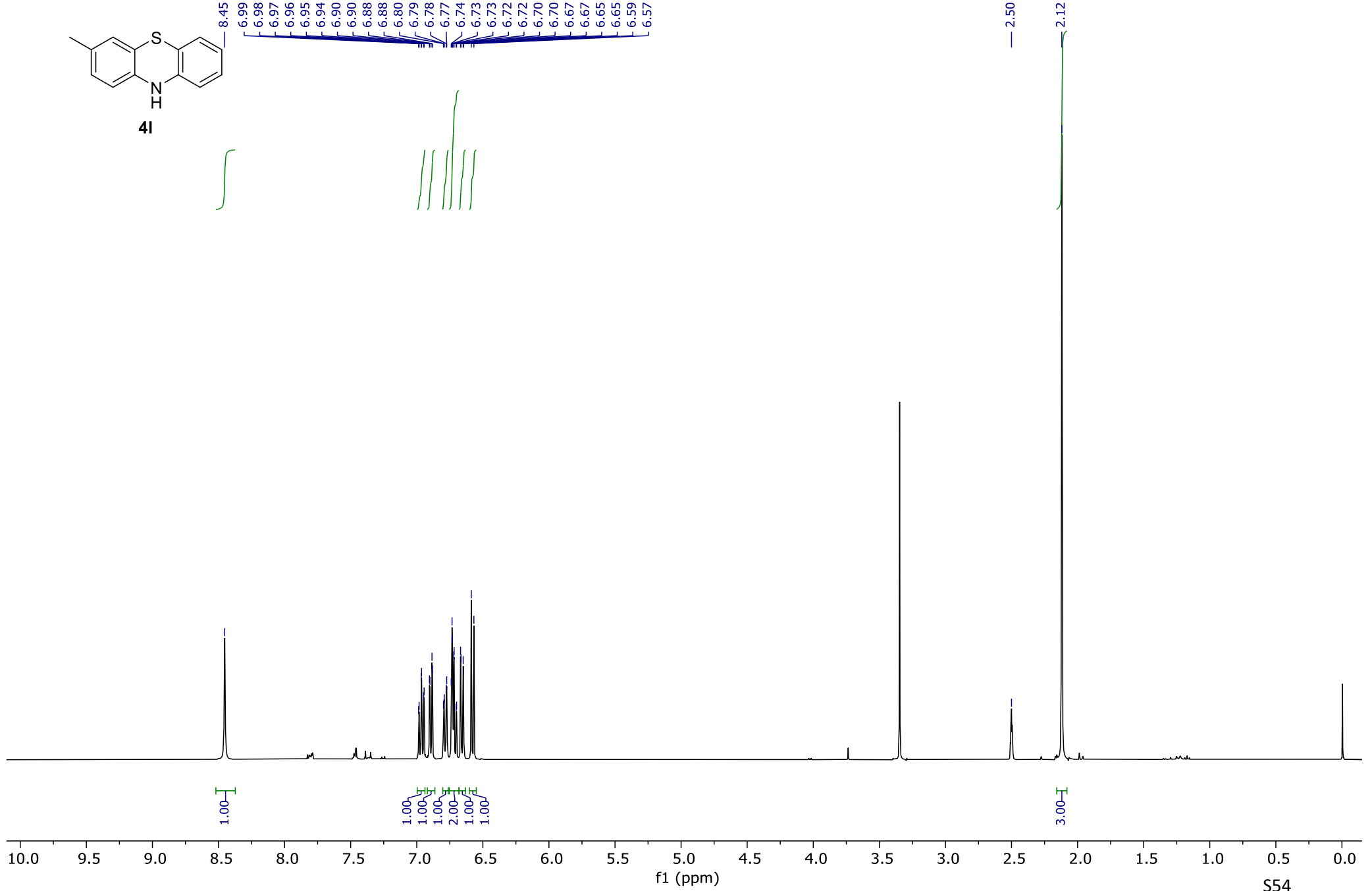
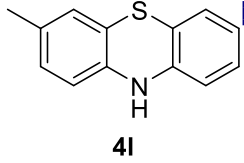
77.16 CDCl₃

52.72

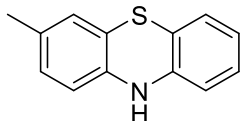
20.37



400 MHz, DMSO-d₆



101 MHz, DMSO-d₆

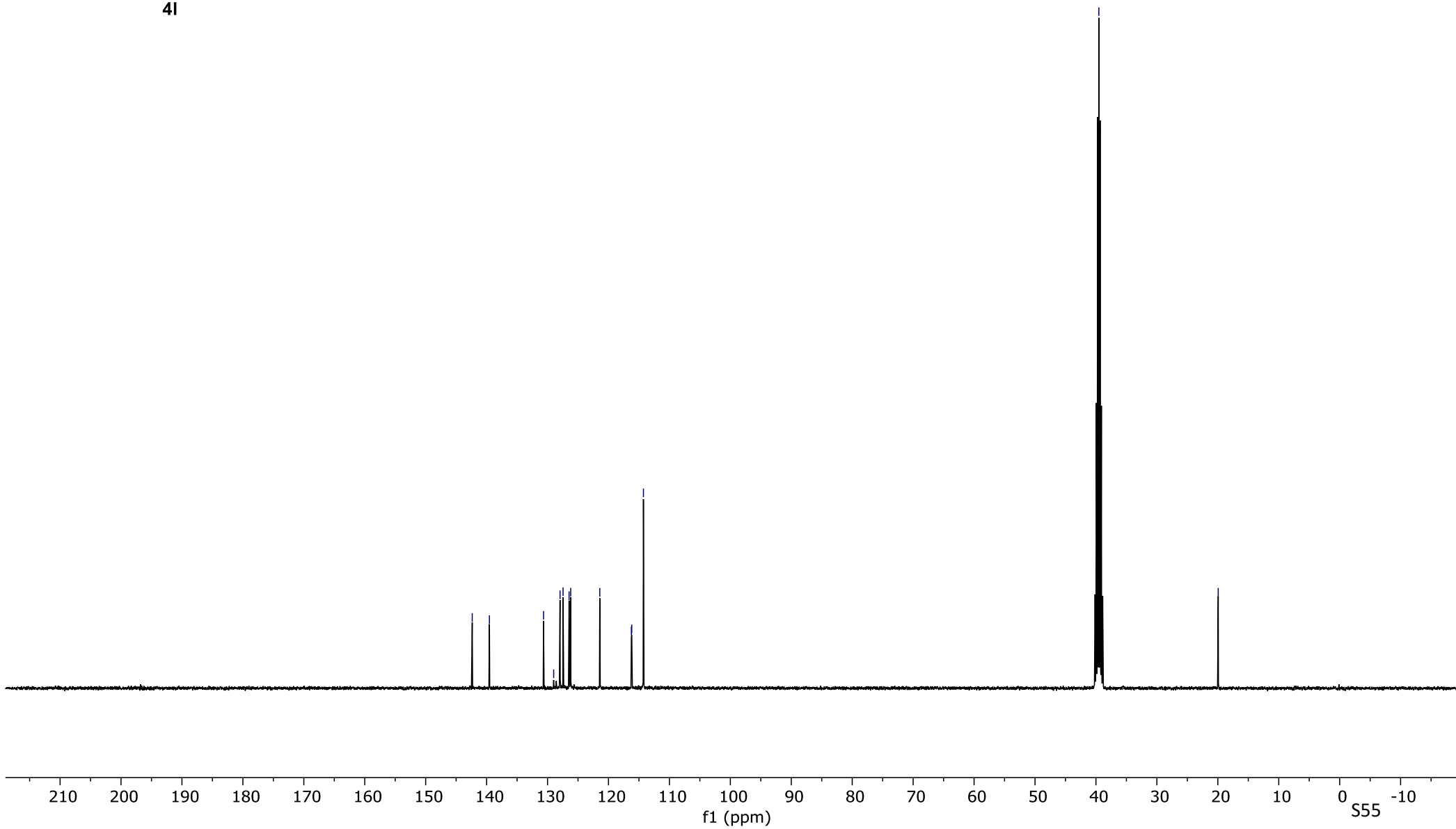


4I

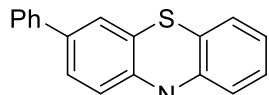
142.36
139.54
130.66
128.99
127.95
127.46
126.46
126.20
121.43
116.24
116.18
114.26

39.52 DMSO-d₆

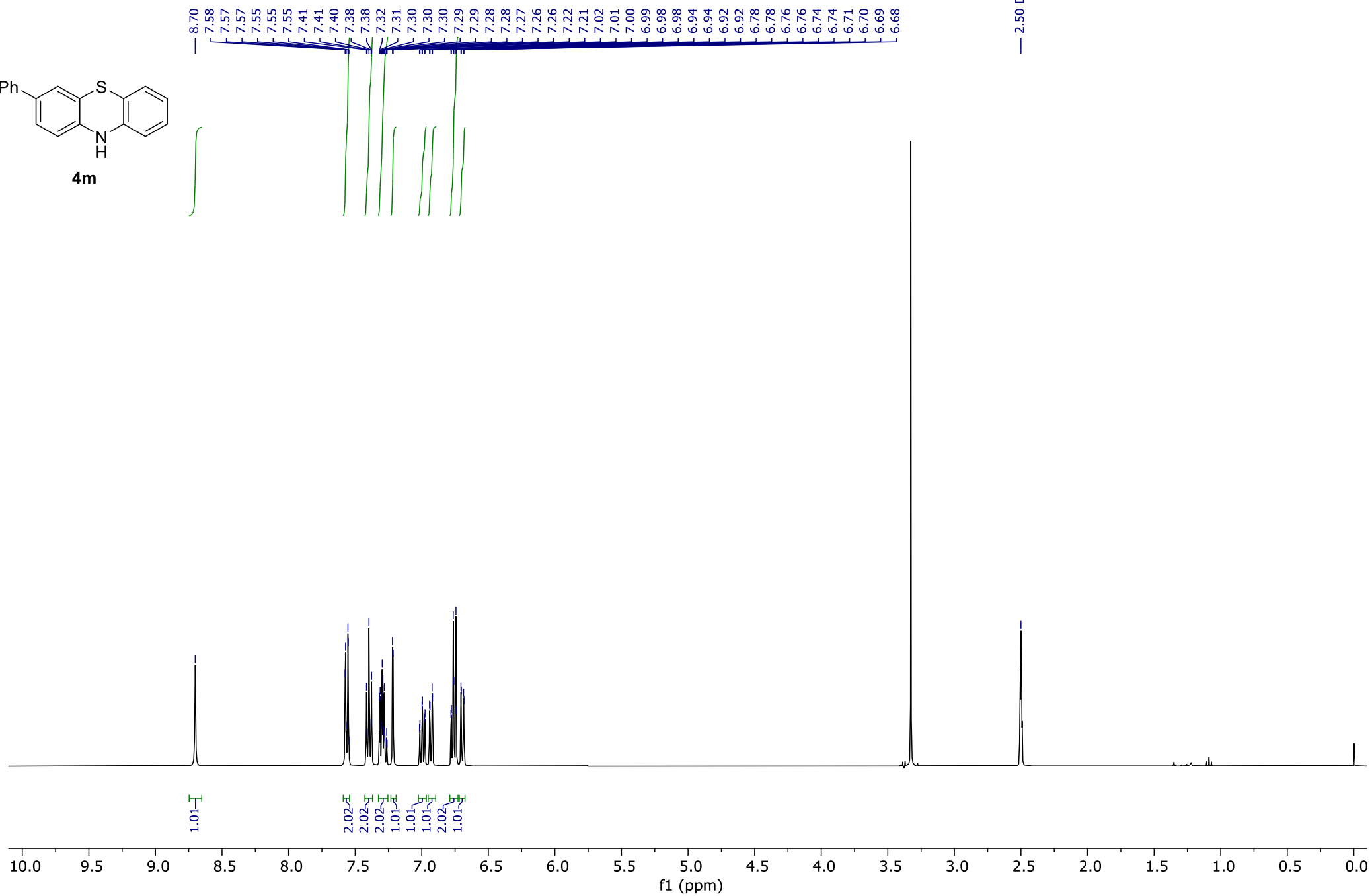
19.93



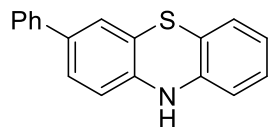
400 MHz, DMSO-d₆



4m

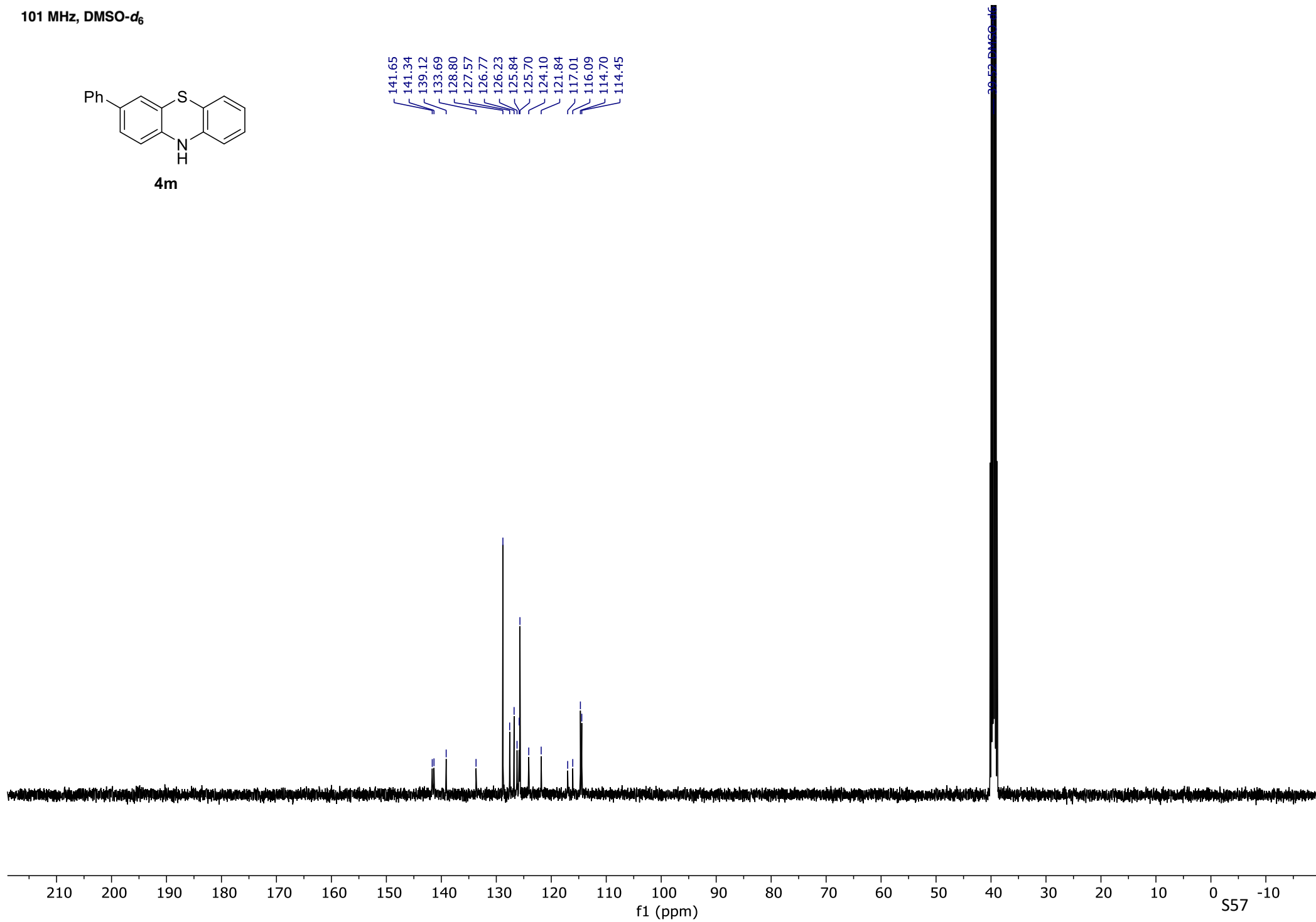


101 MHz, DMSO- d_6

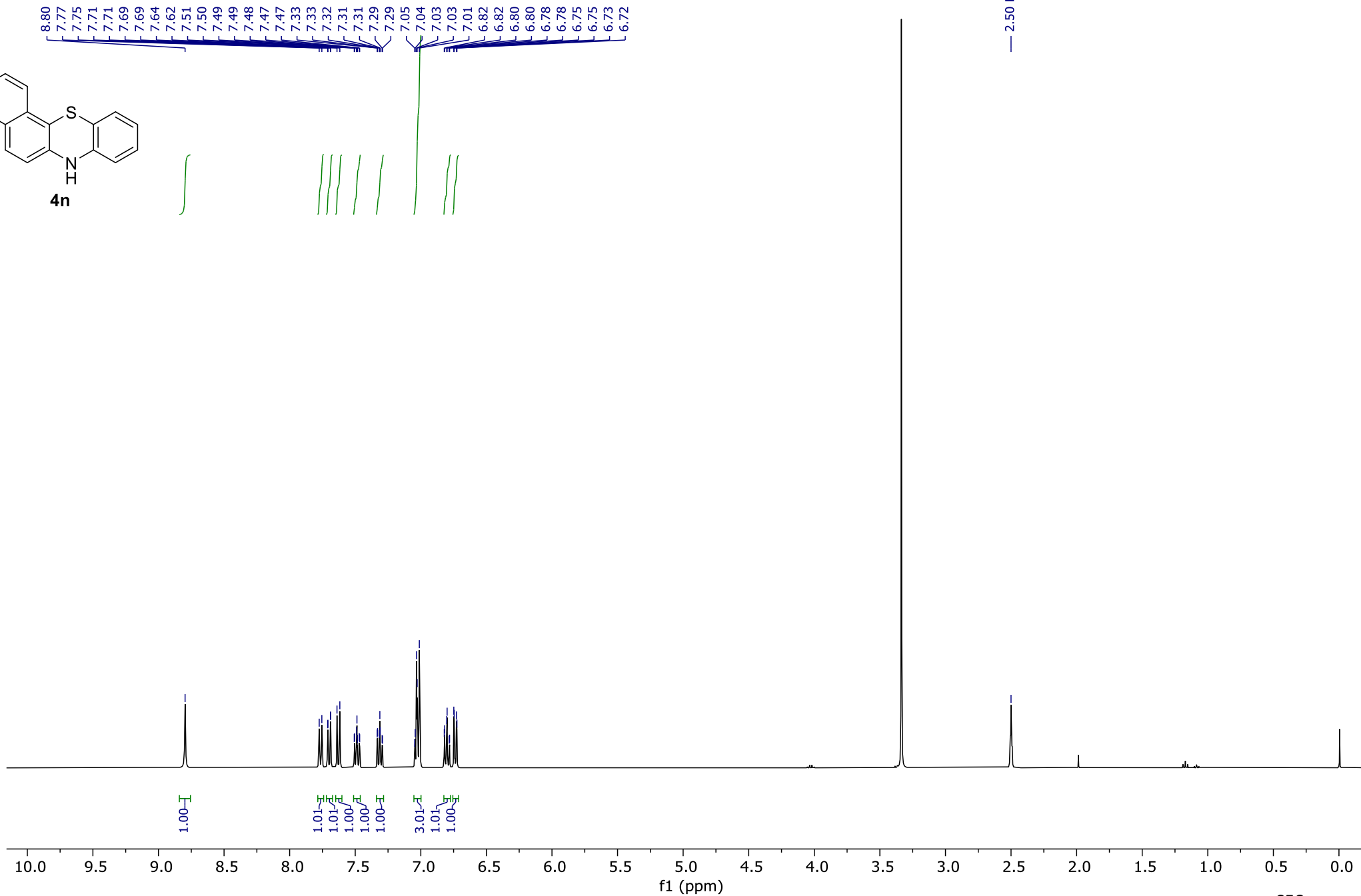
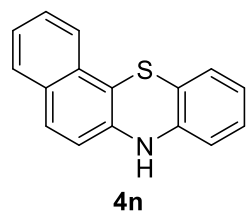


4m

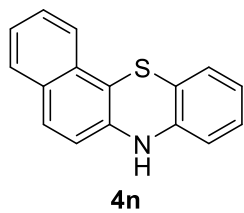
141.65
141.34
139.12
133.69
128.80
127.57
126.77
126.23
125.84
125.70
124.10
121.84
117.01
116.09
114.70
114.45



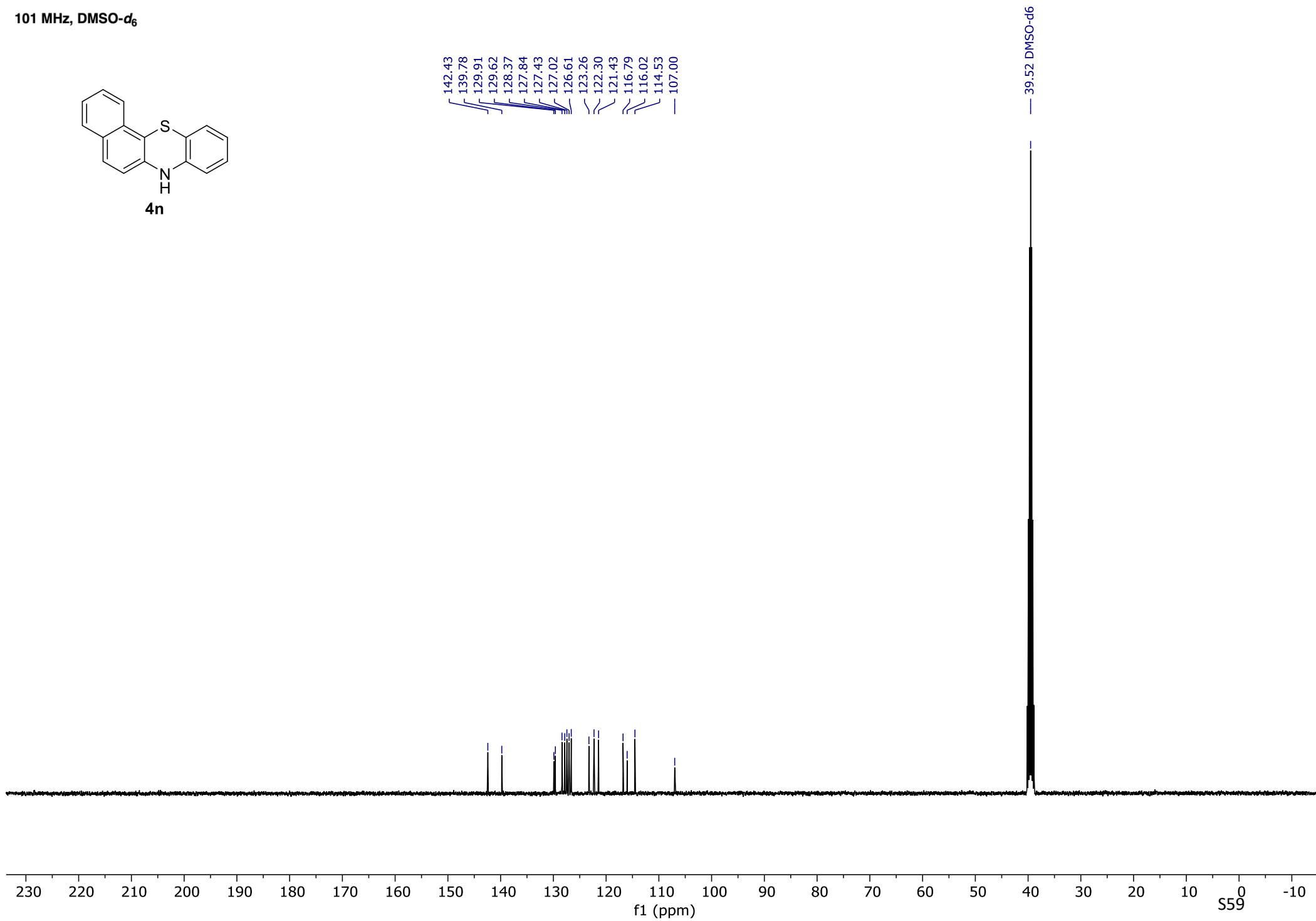
400 MHz, DMSO-d₆



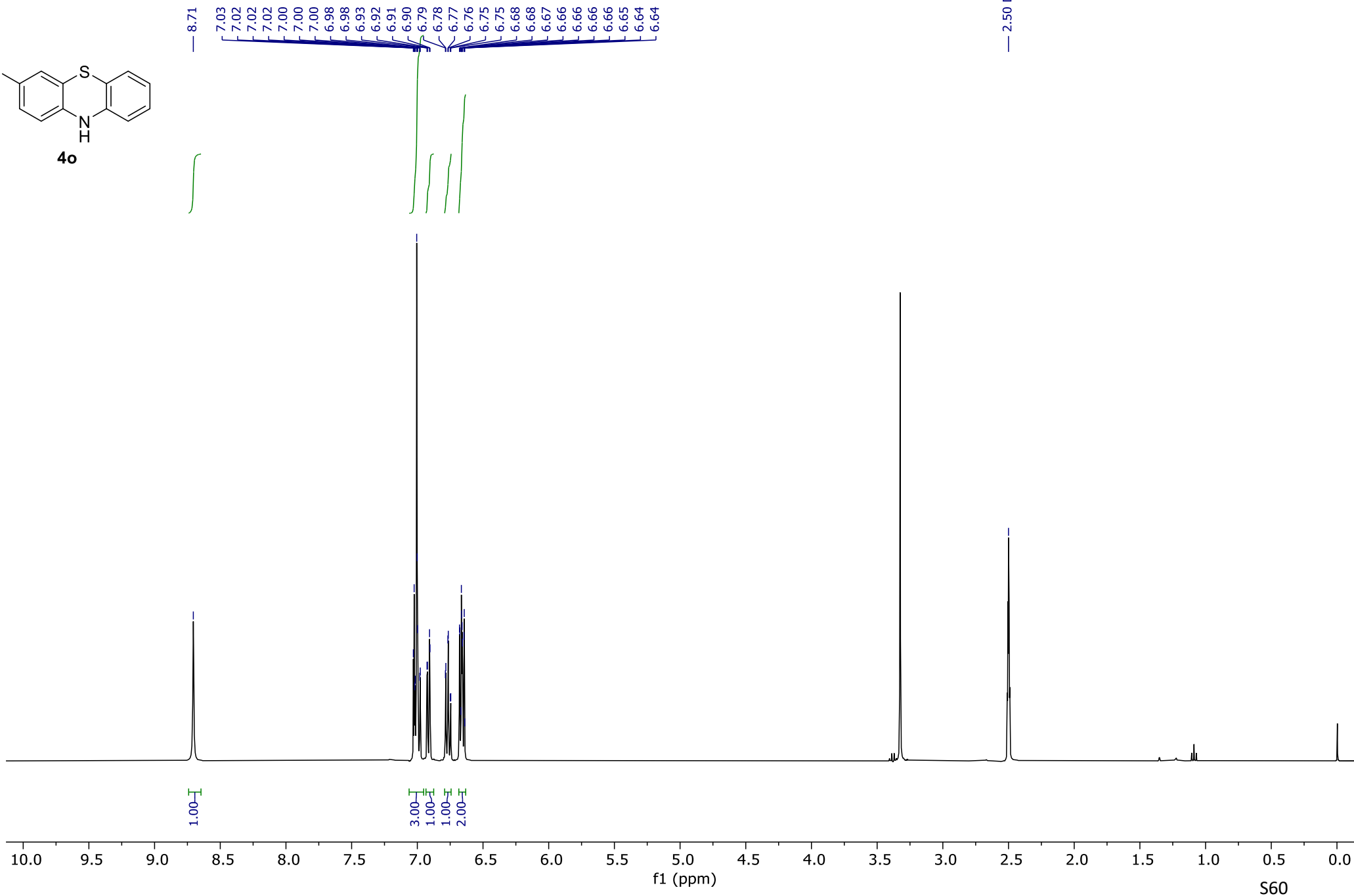
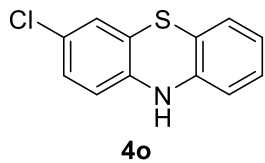
101 MHz, DMSO-d₆



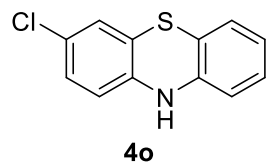
142.43
139.78
129.91
129.62
128.37
127.84
127.43
127.02
126.61
123.26
122.30
121.43
116.79
116.02
114.53
— 107.00



400 MHz, DMSO-d₆

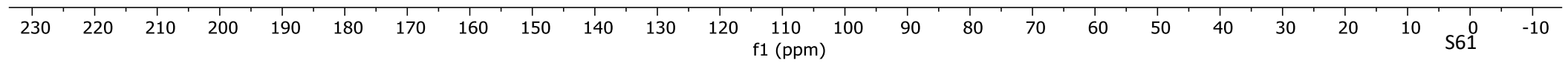


101 MHz, DMSO-d₆

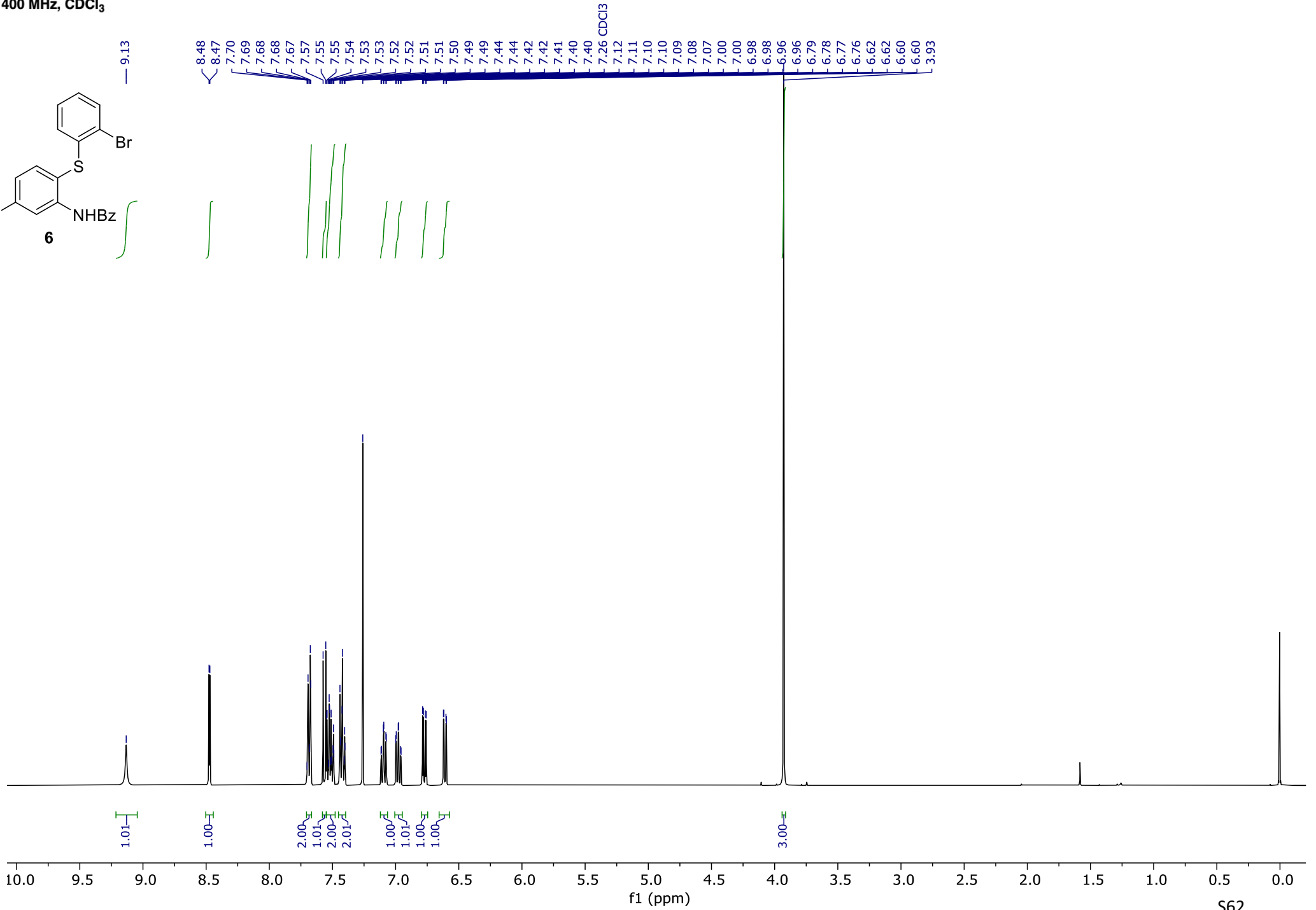
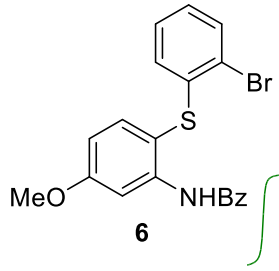


141.58
141.09
127.82
127.21
126.28
125.39
124.94
122.08
118.56
115.49
115.38
114.56

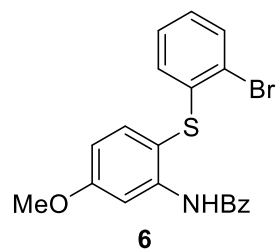
39.52-DMSO-d6



400 MHz, CDCl₃



101 MHz, CDCl₃



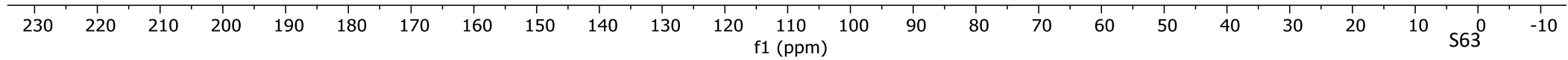
165.37
162.70

141.93
138.41
137.90
134.59
133.07
132.22
128.98
128.34
127.13
127.10
126.84
120.79

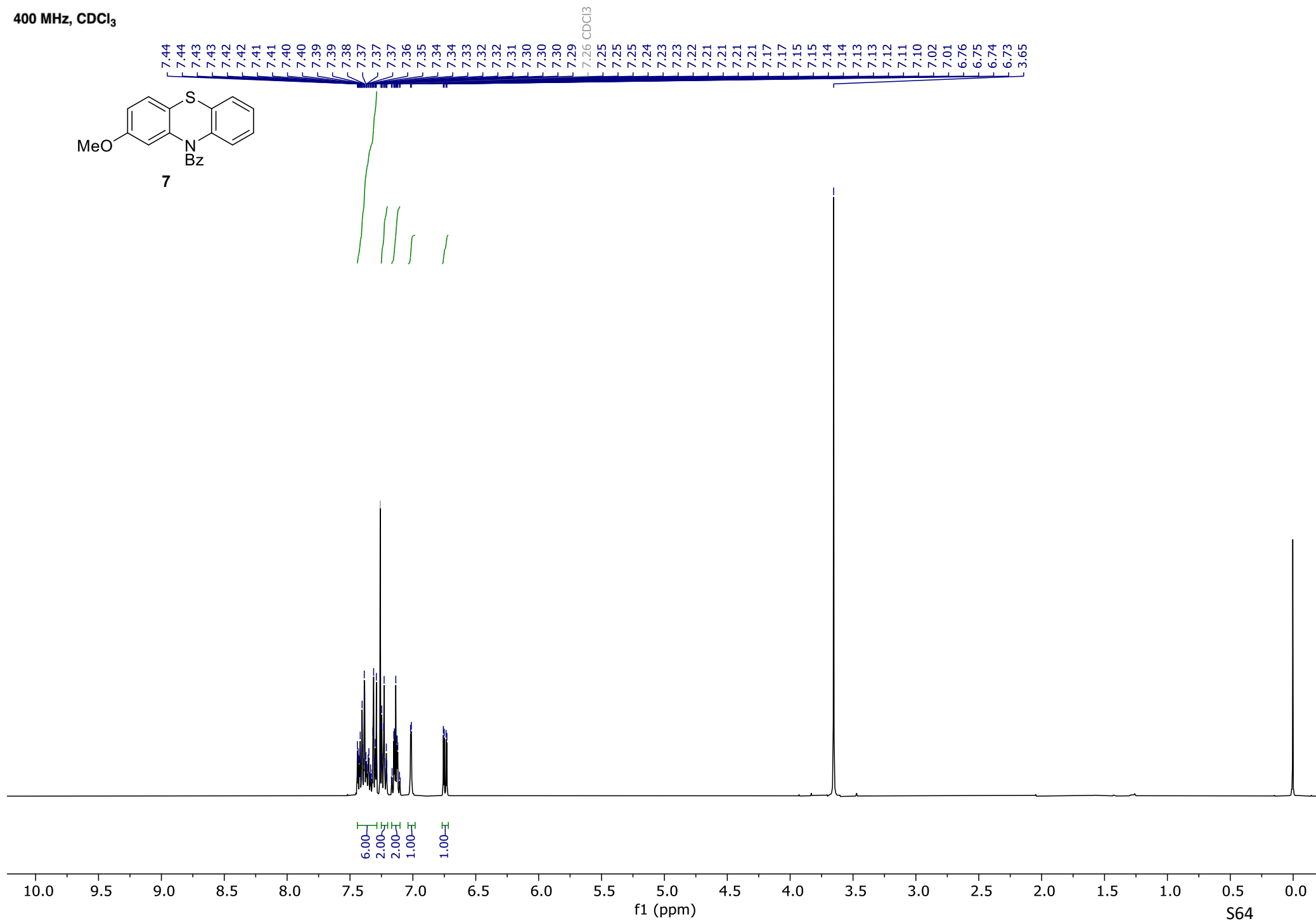
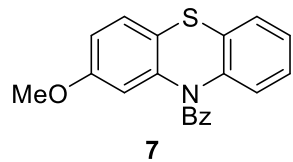
111.70
109.36
105.61

77.16 CDCl₃

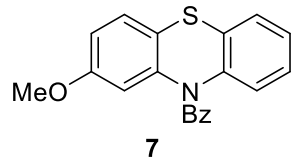
55.77



400 MHz, CDCl₃



101 MHz, CDCl₃



— 169.05

— 159.10

— 140.80

— 139.66

— 135.43

— 133.01

— 130.53

— 128.91

— 128.15

— 128.15

— 127.77

— 127.21

— 126.85

— 126.53

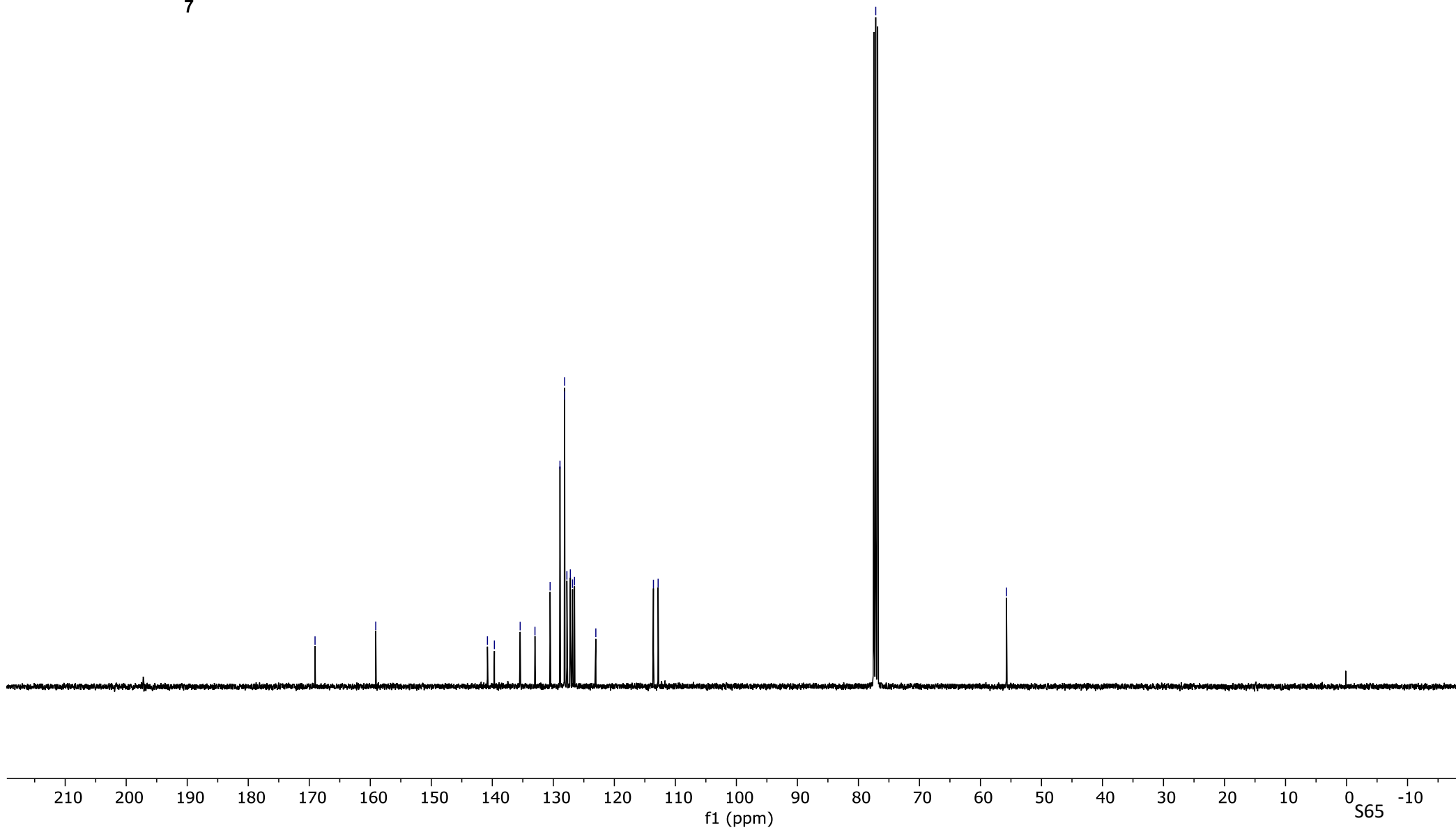
— 123.03

— 113.60

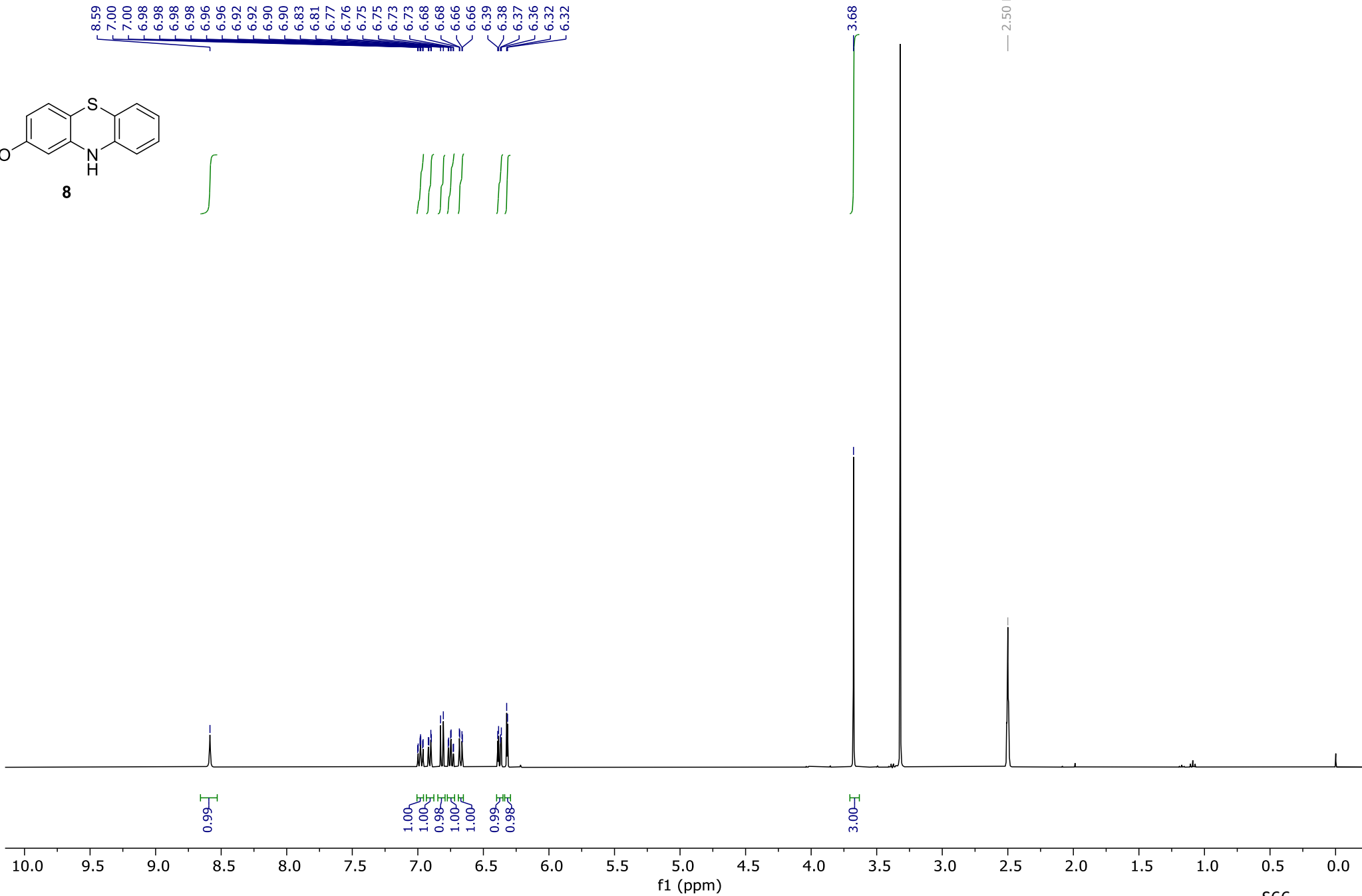
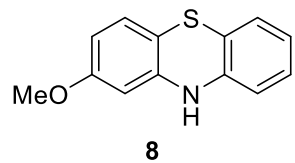
— 112.82

— 77.16 CDCl₃

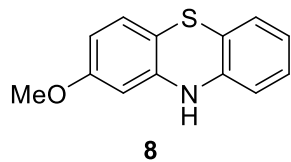
— 55.74



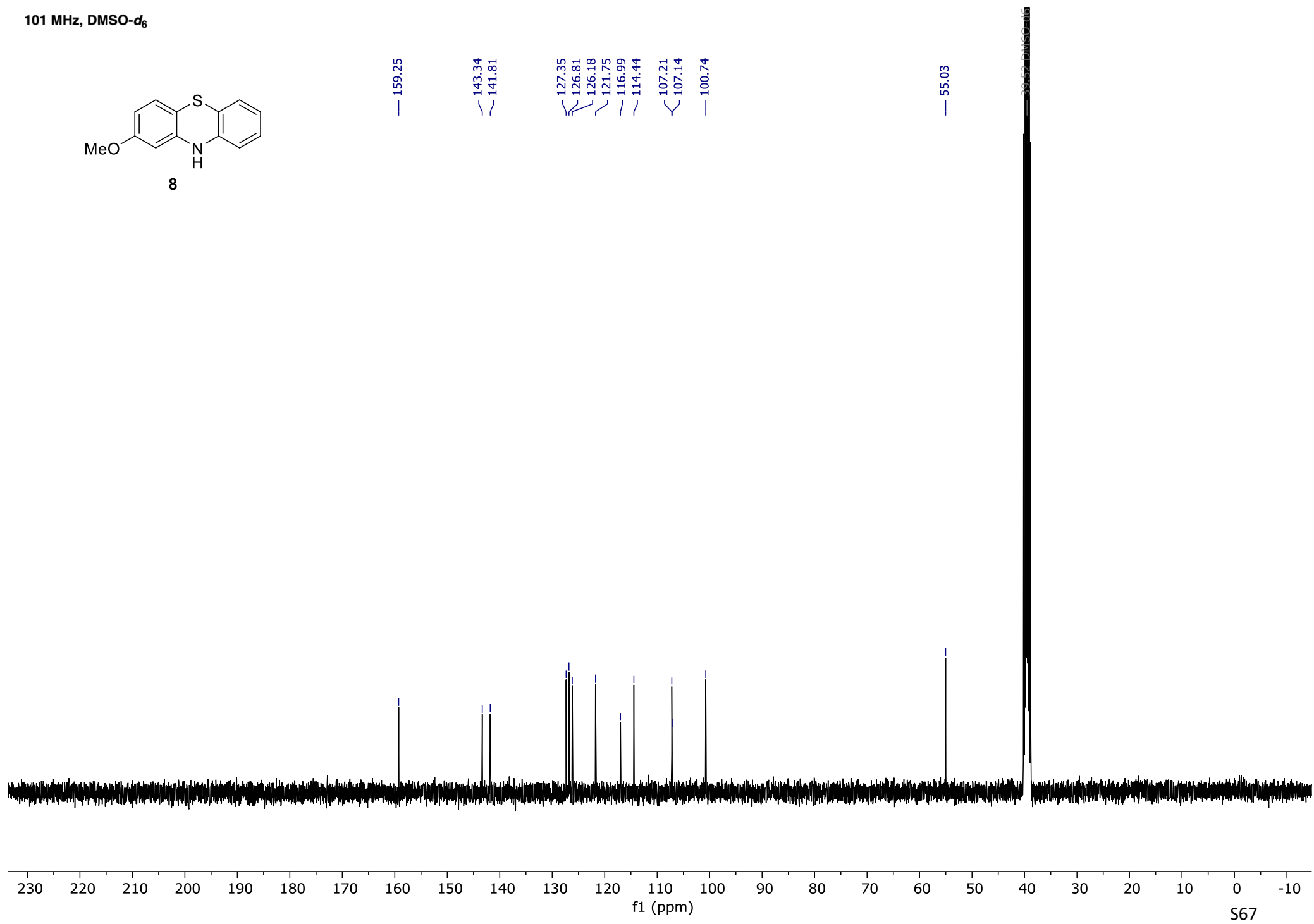
400 MHz, DMSO-d₆



101 MHz, DMSO-*d*₆

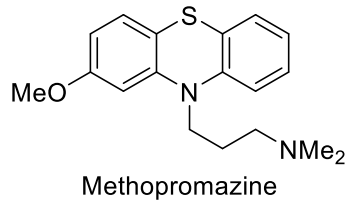


- 159.25
- 143.34
- 141.81
- 127.35
- 126.81
- 126.18
- 121.75
- 116.99
- 114.44
- 107.21
- 107.14
- 100.74
- 55.03

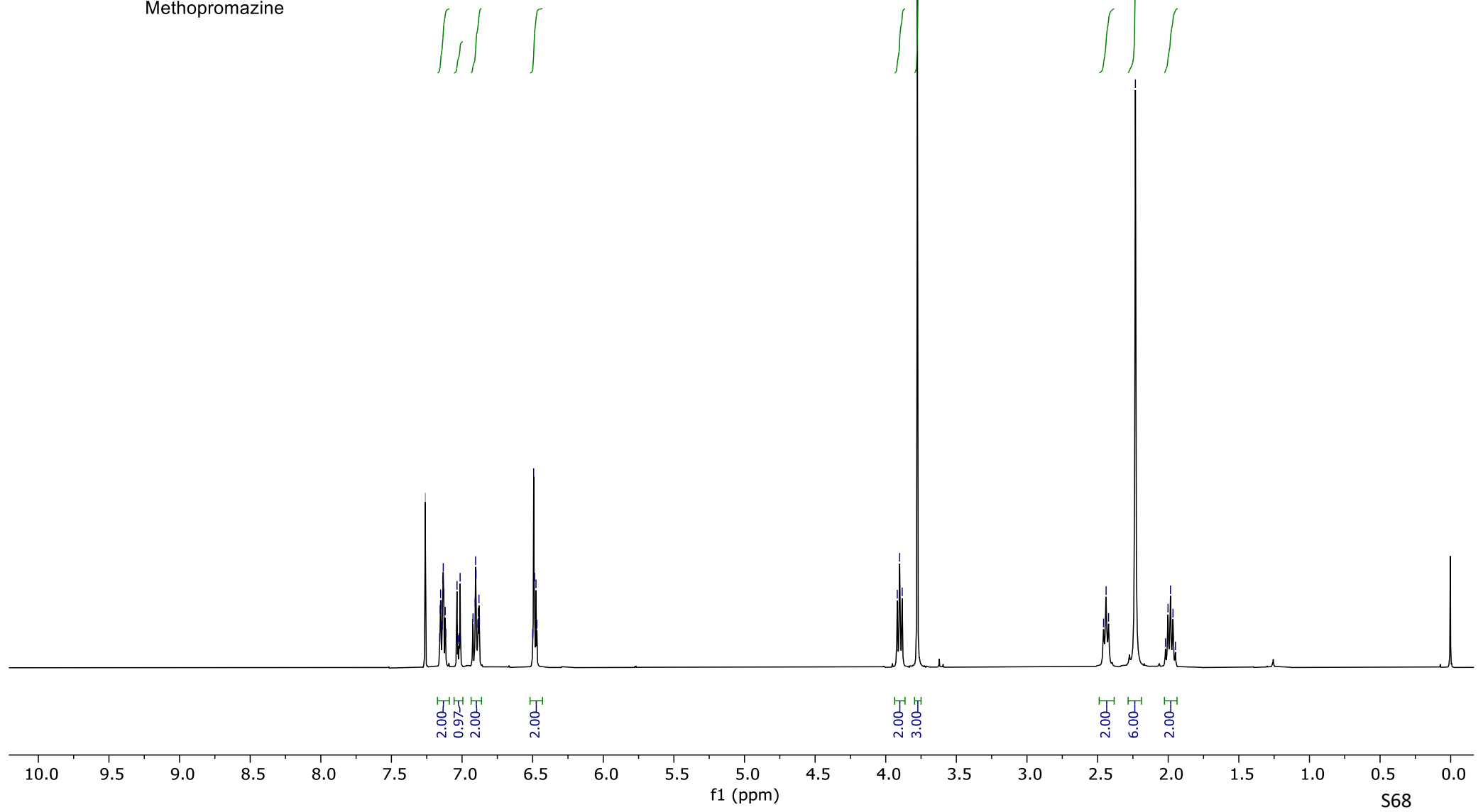


400 MHz, CDCl₃

7.26 CDCl₃
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.04
7.03
7.02
7.01
6.93
6.92
6.91
6.90
6.89
6.88
6.88
6.88
6.50
6.49
6.49
6.48
6.47



3.92
3.90
3.88
3.78
2.46
2.44
2.42
2.23
2.02
2.00
1.98
1.97
1.95



101 MHz, CDCl₃

