Supplementary Information

An efficient and mild oxidant for the synthesis of *s*-tetrazines

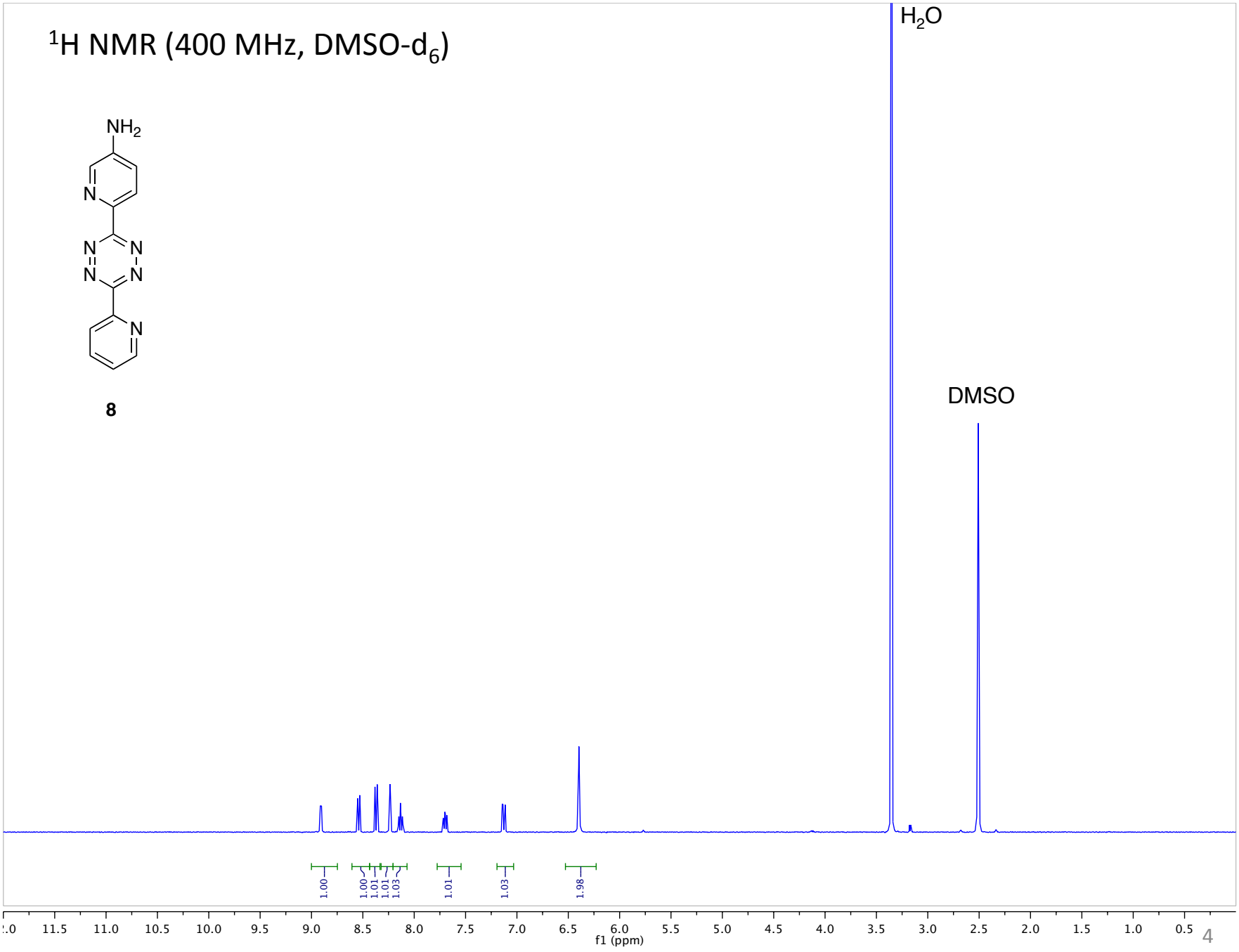
Ramajeyam Selvaraj[a] , Joseph M. Fox[a]*

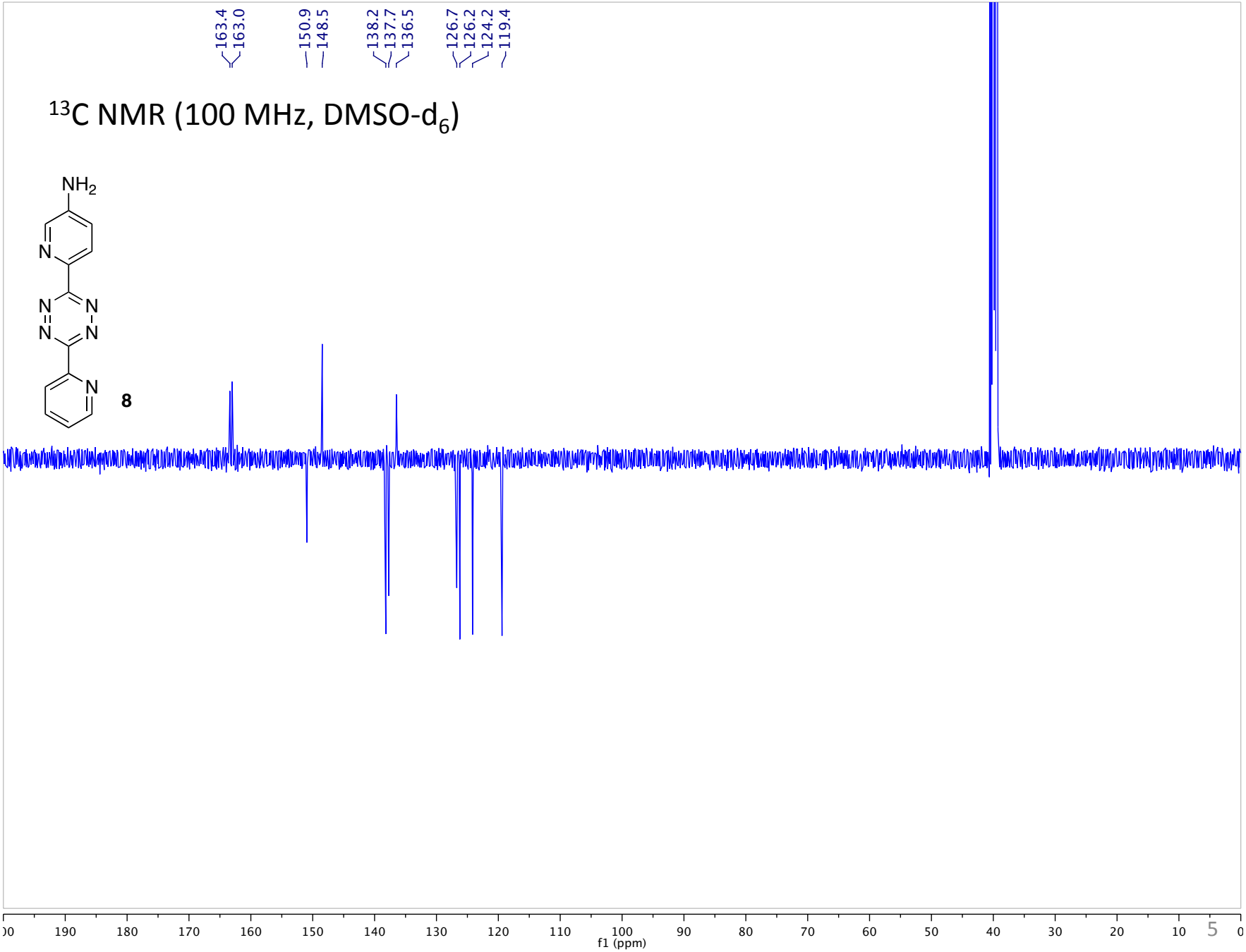
[a]*Department of Chemistry and Biochemistry, University of Delaware, Newark DE 19716*

E-mail: jmfox@udel.edu

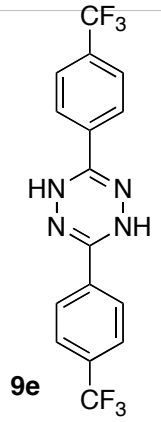
^{1}H NMR (400 MHz, DMSO-d_6)

8




163.4
163.0
150.9
148.5
138.2
137.7
136.5
126.7
126.2
124.2
119.4
13C NMR (100 MHz, DMSO-d6)
NH2
N
N
N
N
N
N
8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

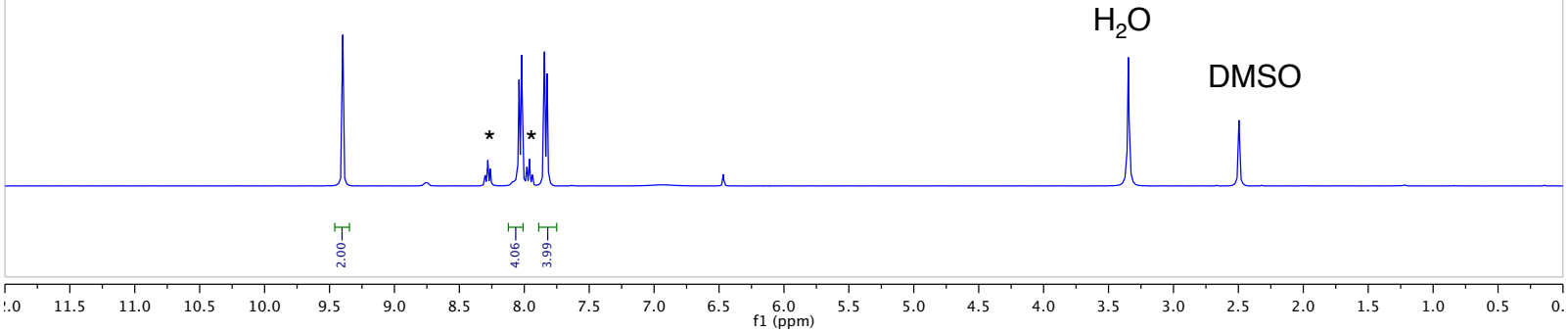
^{1}H NMR (400 MHz, DMSO-d_6)

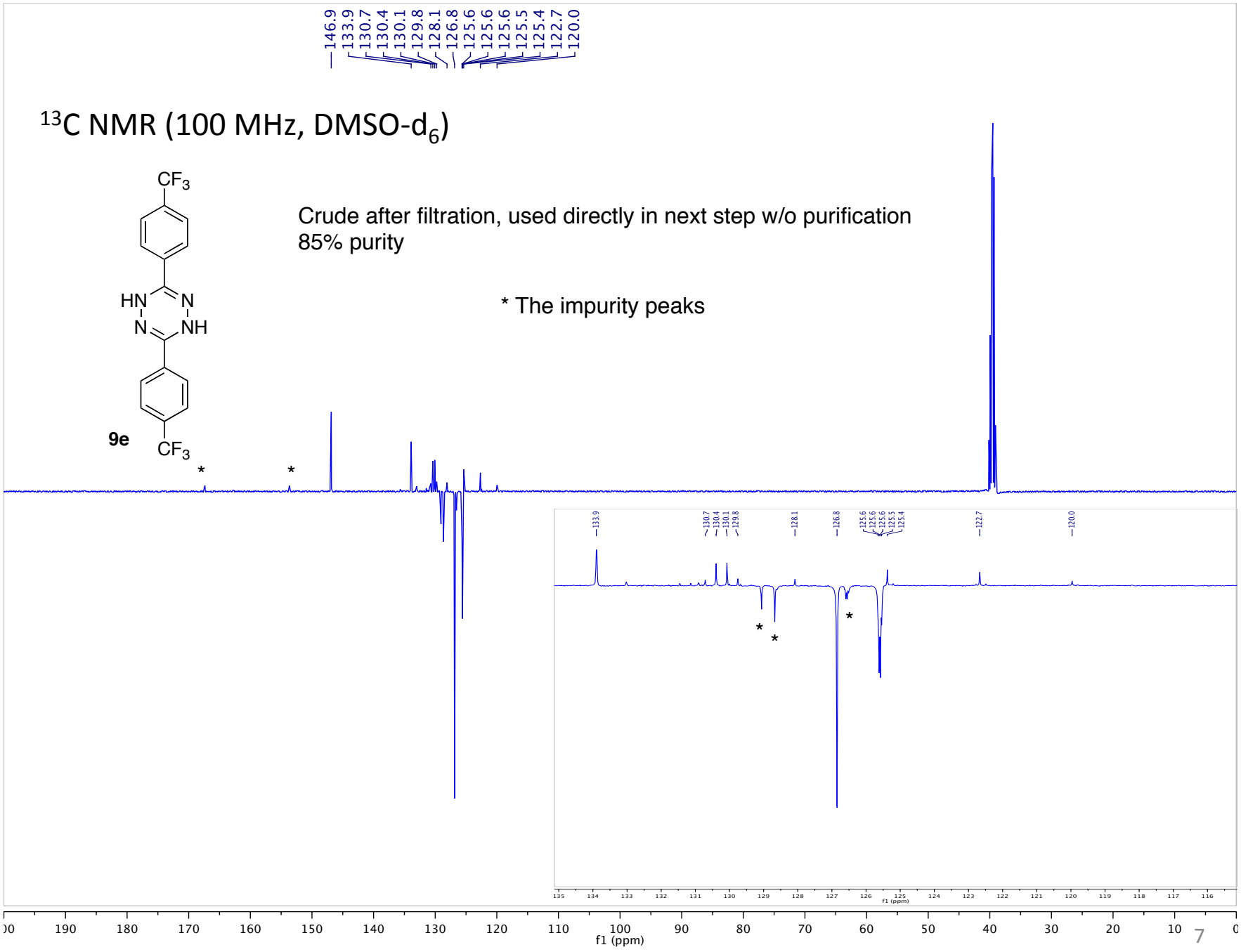


9e

Crude after filtration, used directly in next step w/o purification
85% purity

* Impurity peaks



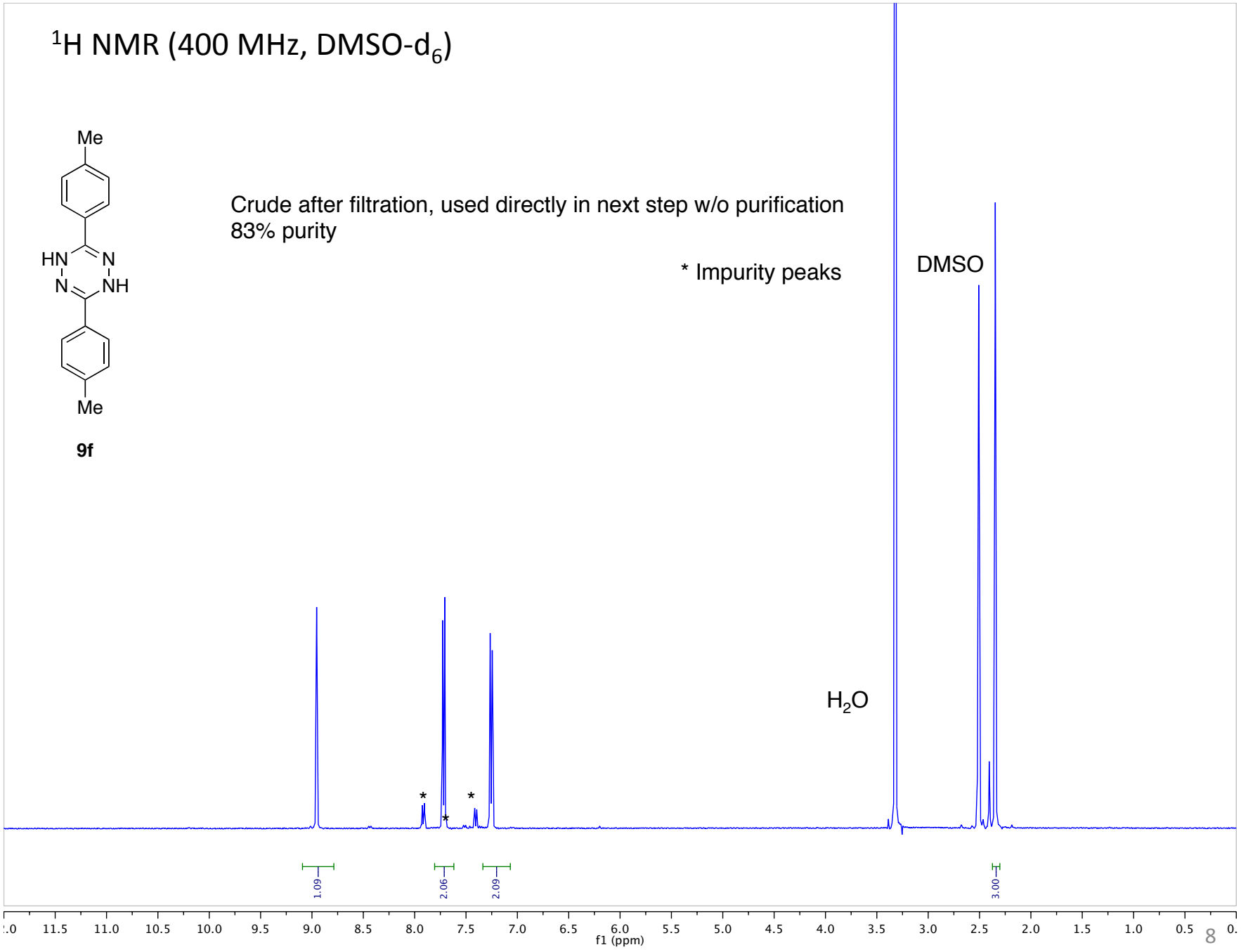

146.9
133.9
130.7
130.4
130.1
129.8
128.1
126.8
125.6
125.6
125.6
125.5
125.4
122.7
120.0
13C NMR (100 MHz, DMSO-d6)
CF3
HN
N
N
NH
CF3
9e
Crude after filtration, used directly in next step w/o purification
85% purity
* The impurity peaks
*
*
*
*
*
f1 (ppm)

^{1}H NMR (400 MHz, DMSO-d_6)

9f

Crude after filtration, used directly in next step w/o purification
83% purity

* Impurity peaks

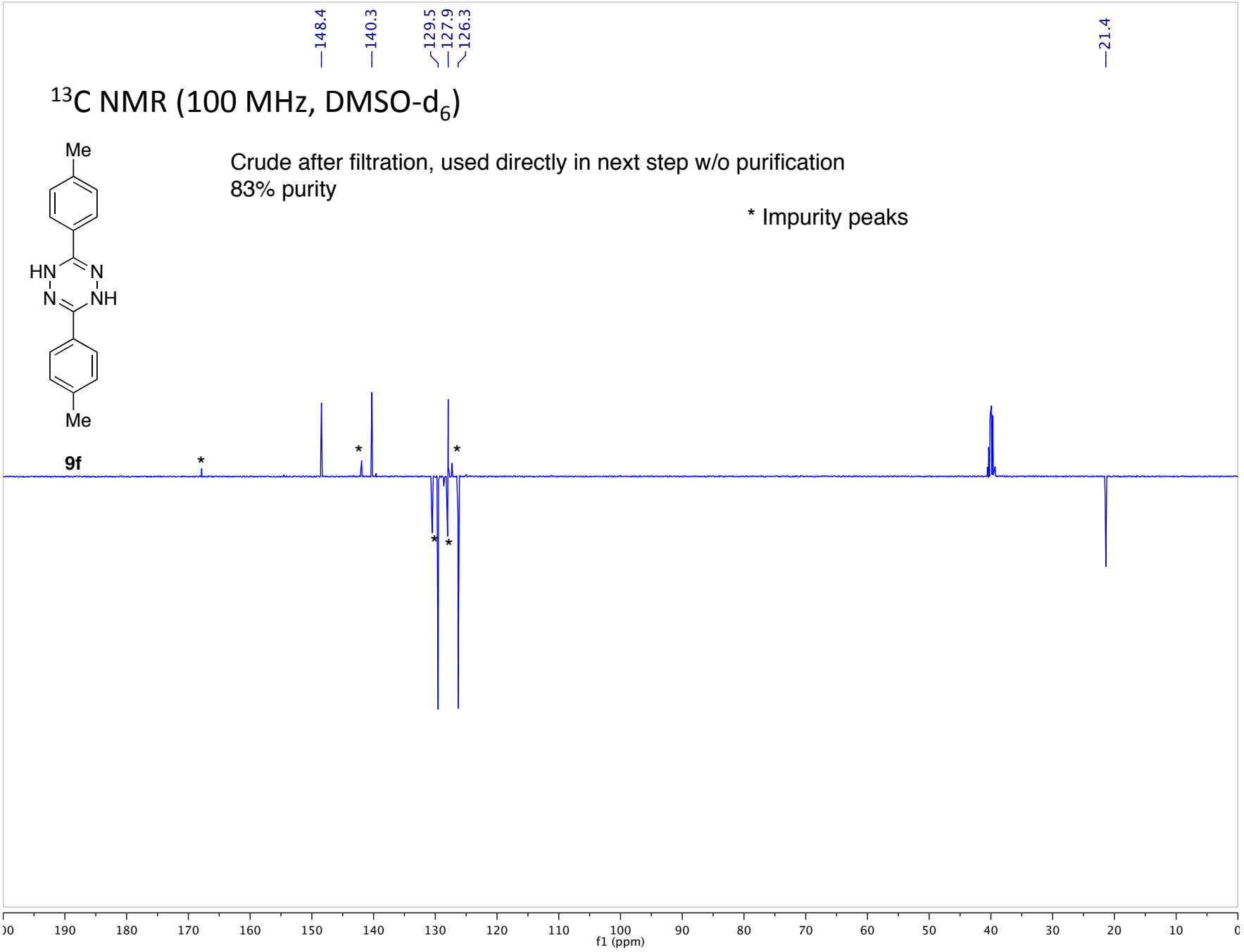


^{13}C NMR (100 MHz, DMSO-d_6)

9f

Crude after filtration, used directly in next step w/o purification
83% purity

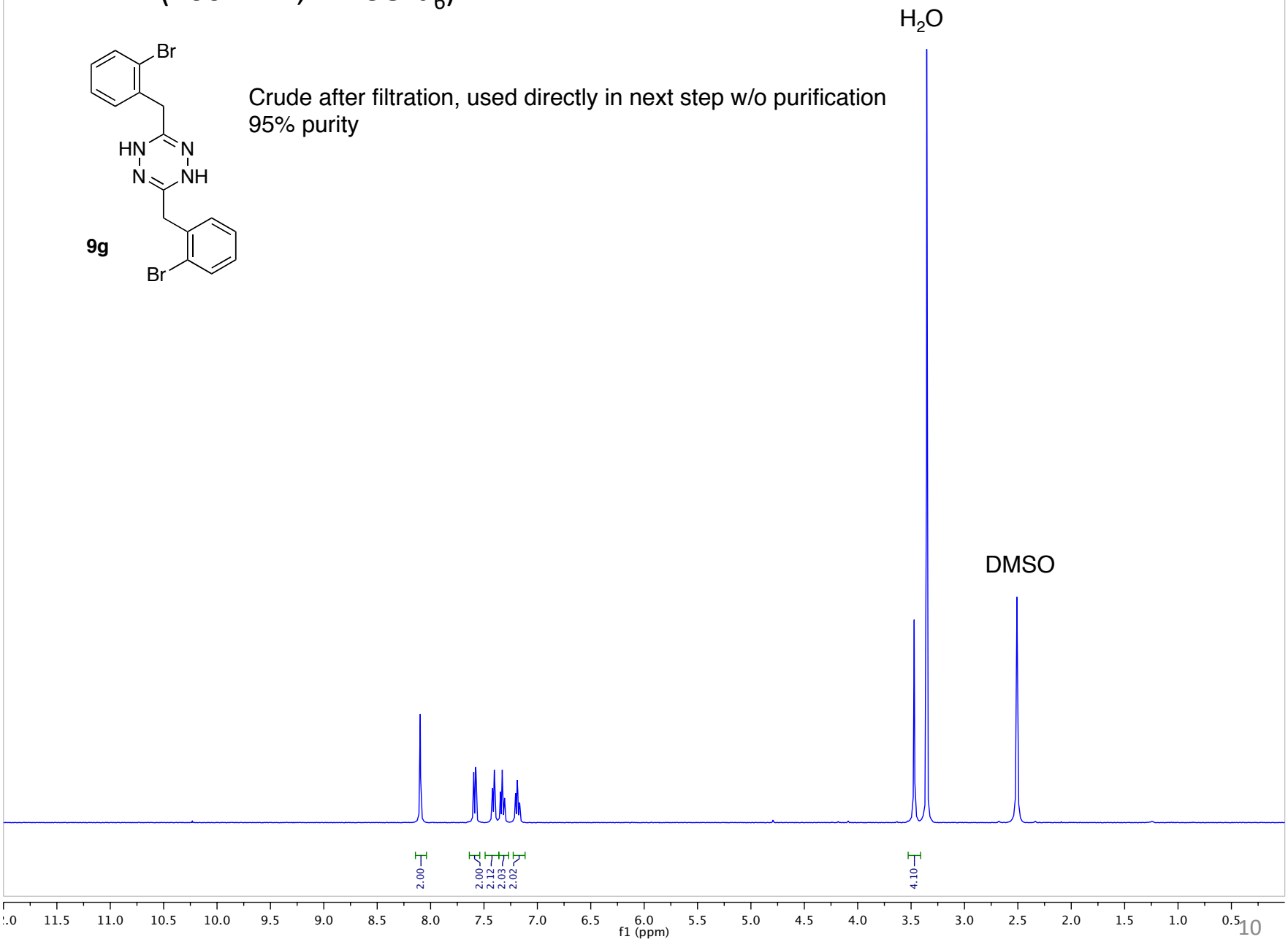
* Impurity peaks



^{1}H NMR (400 MHz, DMSO-d_6)

9g

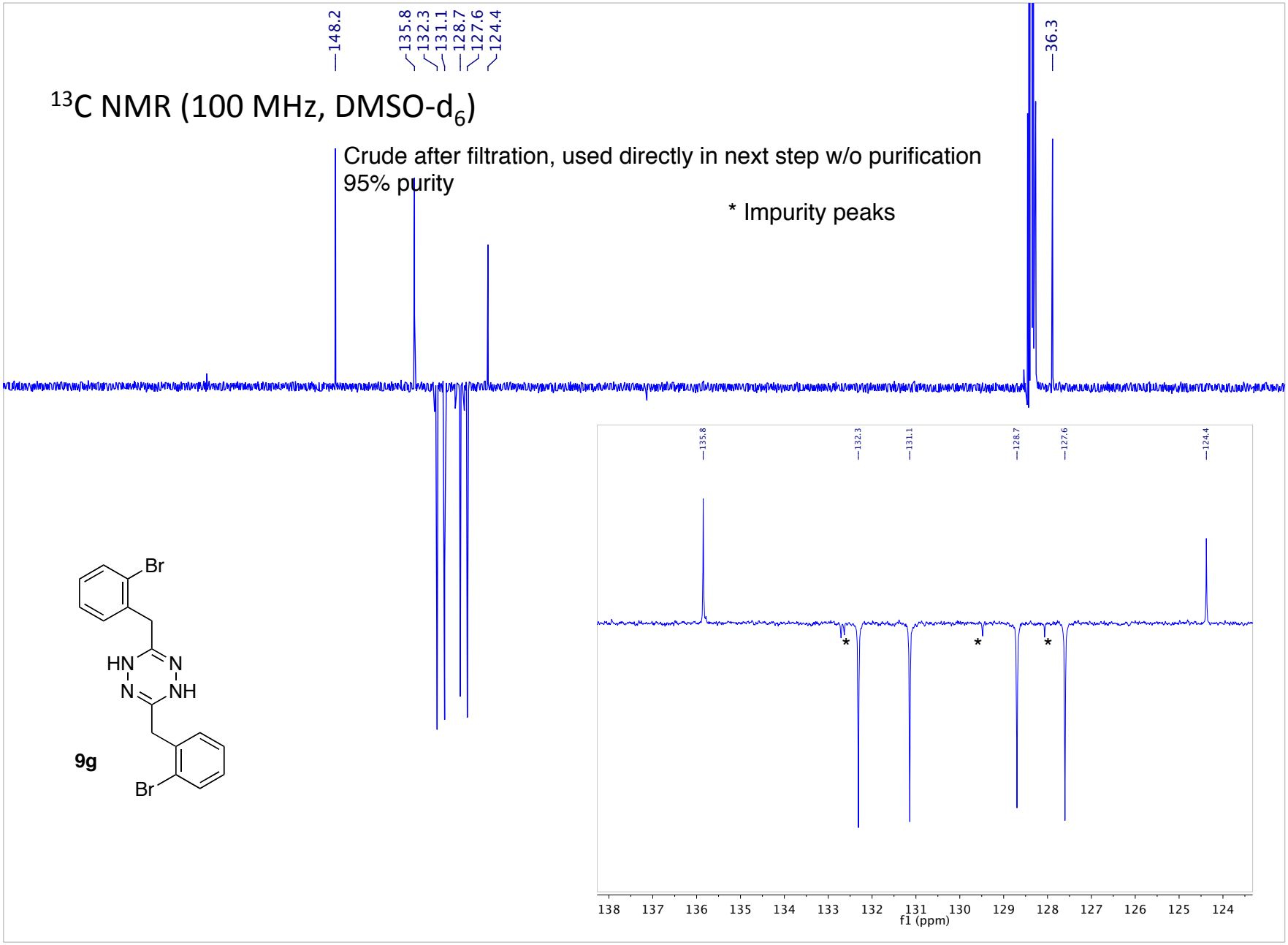
Crude after filtration, used directly in next step w/o purification
95% purity



^{13}C NMR (100 MHz, DMSO-d_6)

Crude after filtration, used directly in next step w/o purification
95% purity

* Impurity peaks

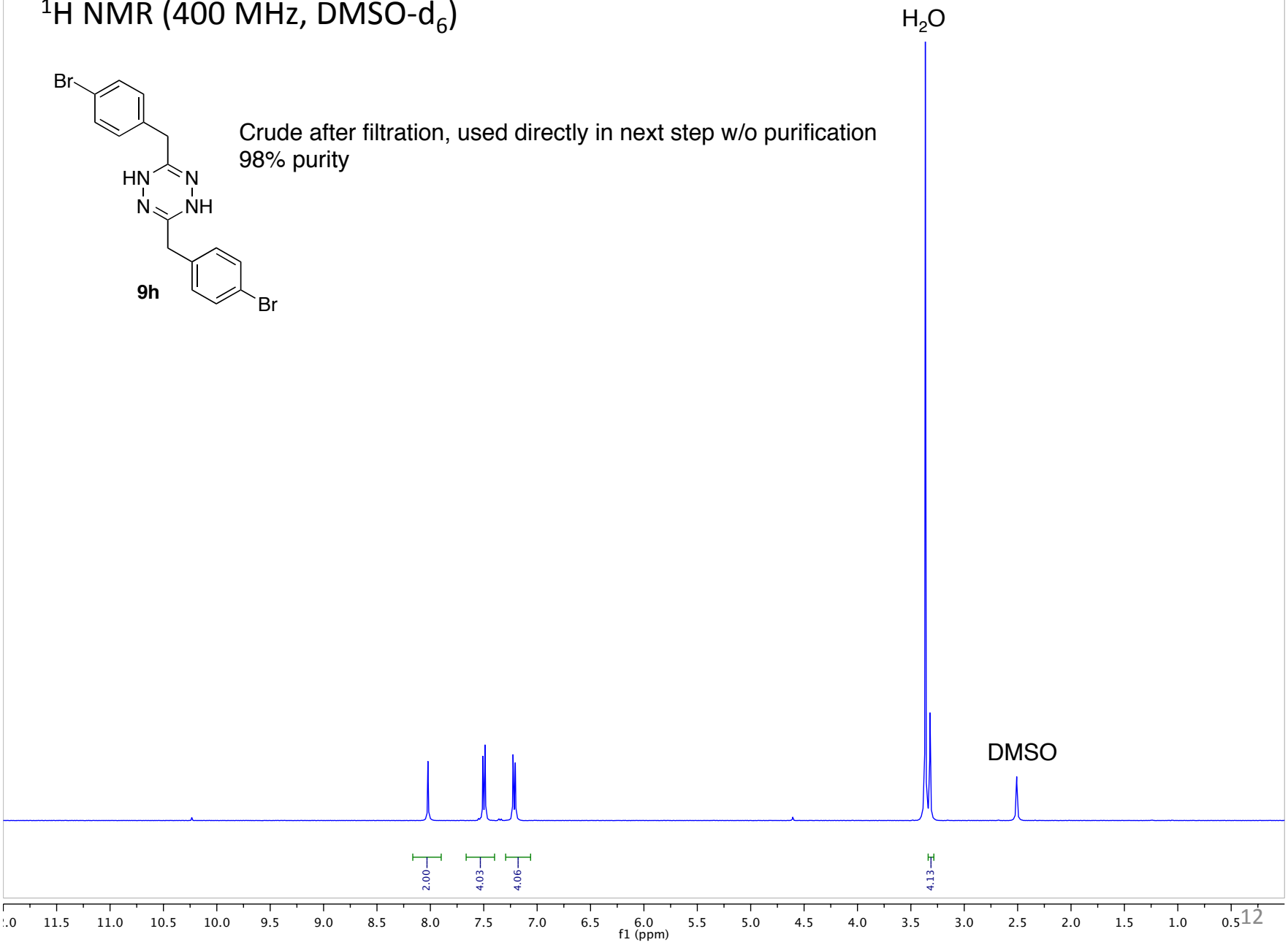


9g

^{1}H NMR (400 MHz, DMSO-d_6)

9h

Crude after filtration, used directly in next step w/o purification
98% purity

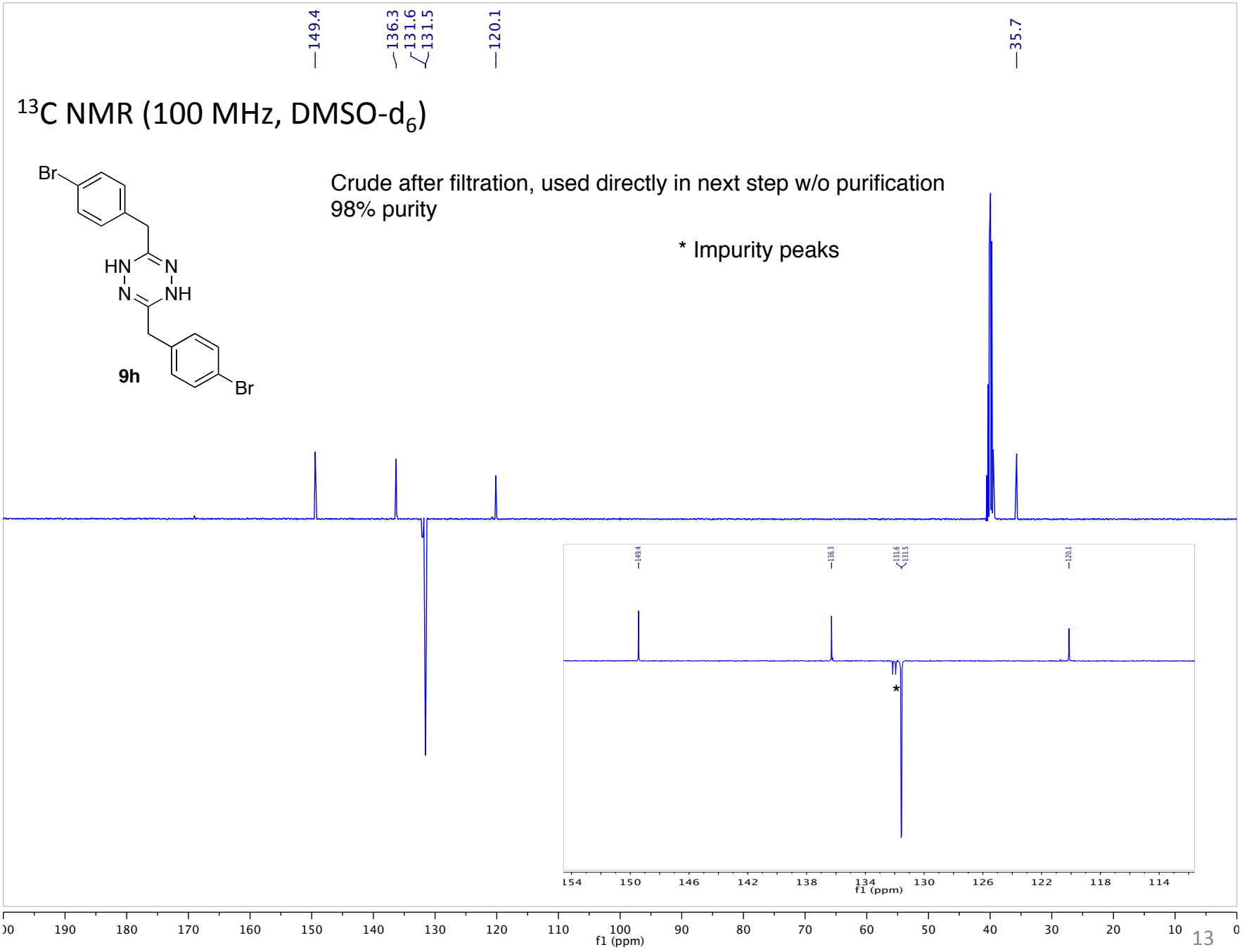


^{13}C NMR (100 MHz, DMSO-d_6)

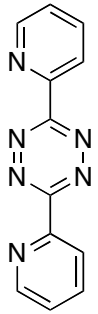
9h

Crude after filtration, used directly in next step w/o purification
98% purity

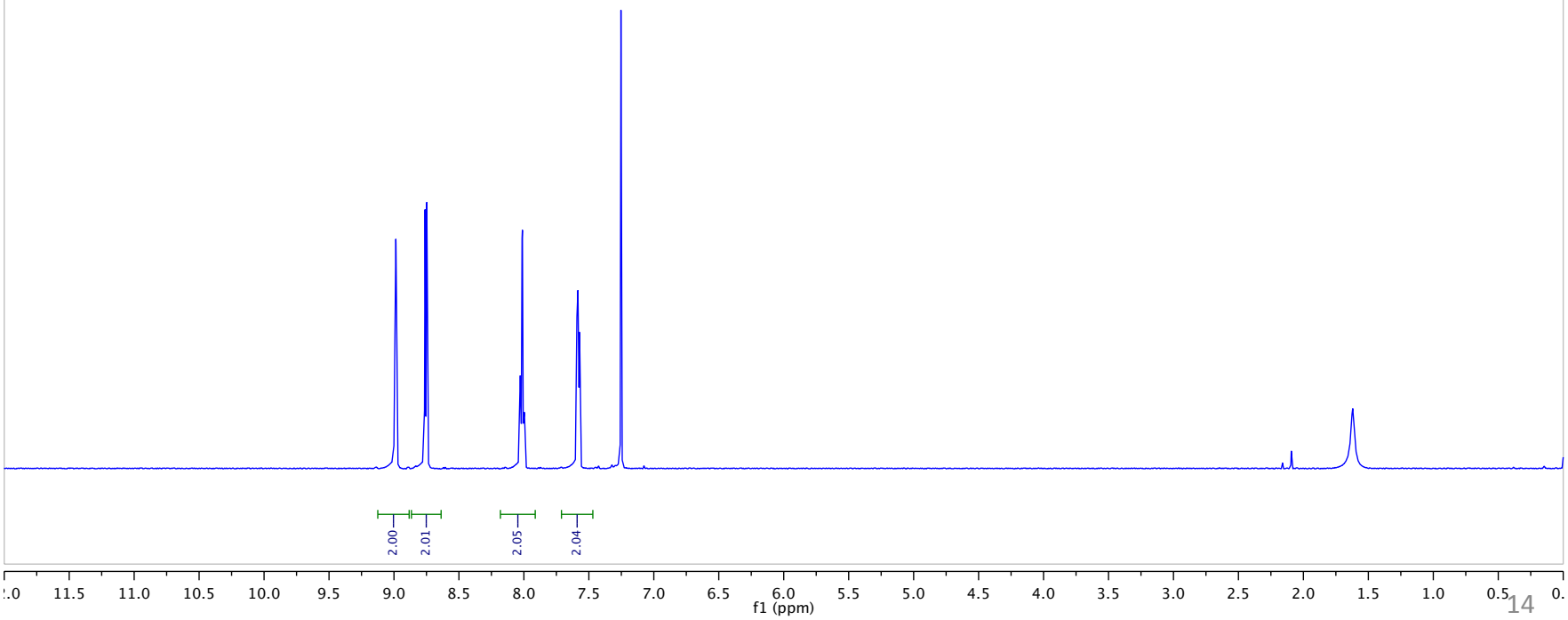
* Impurity peaks



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

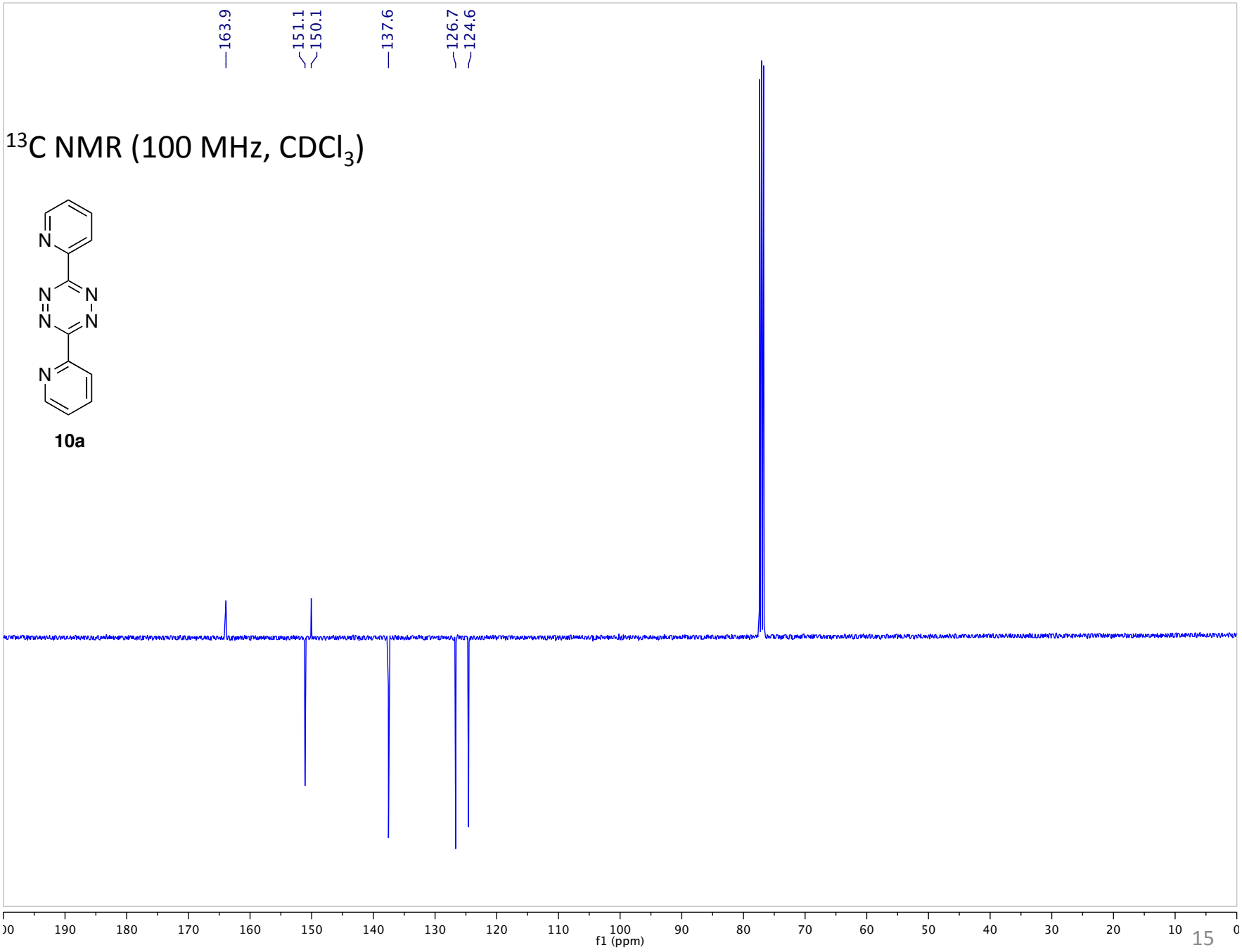


10a



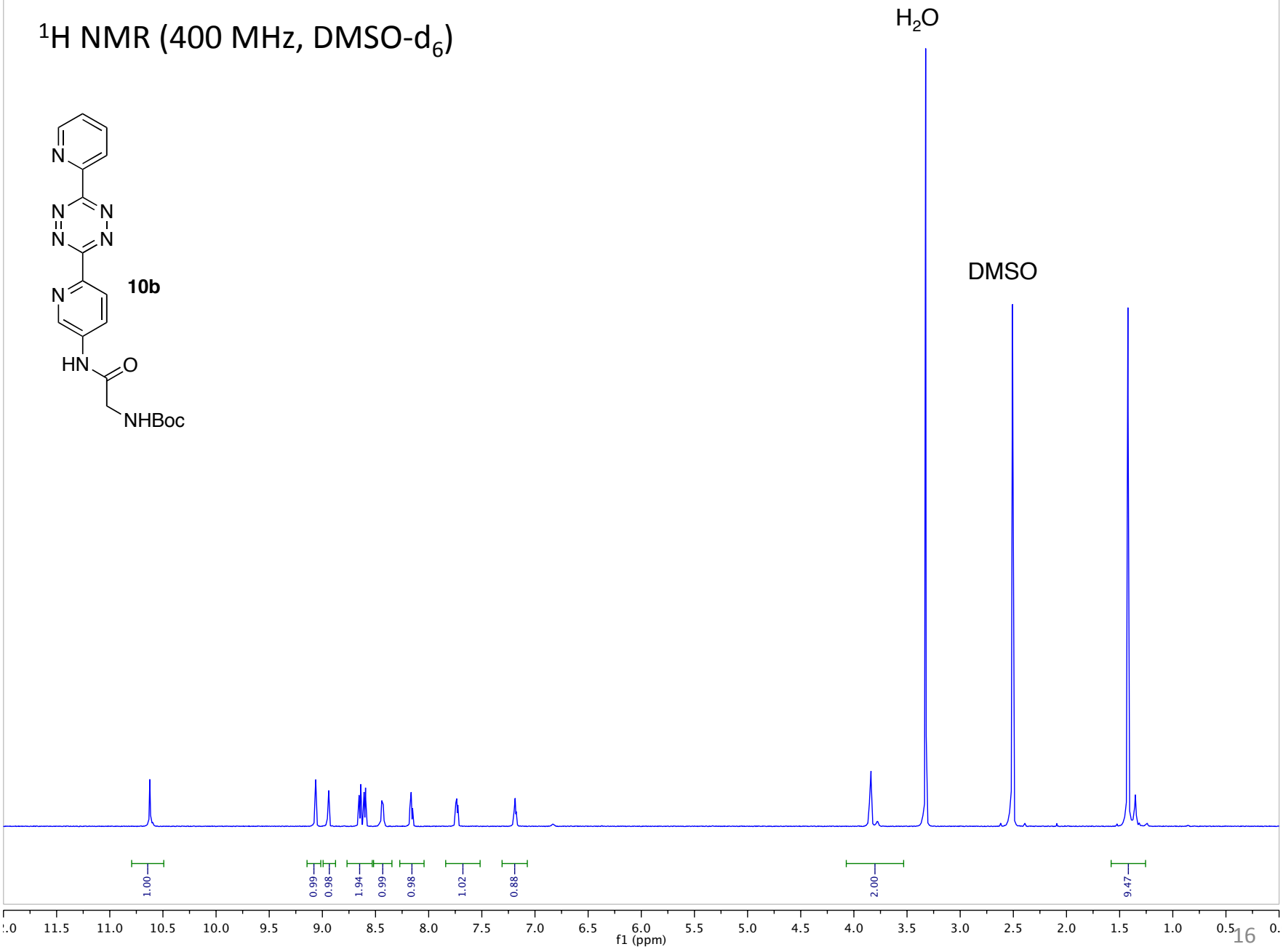
^{13}C NMR (100 MHz, $CDCl_3$)

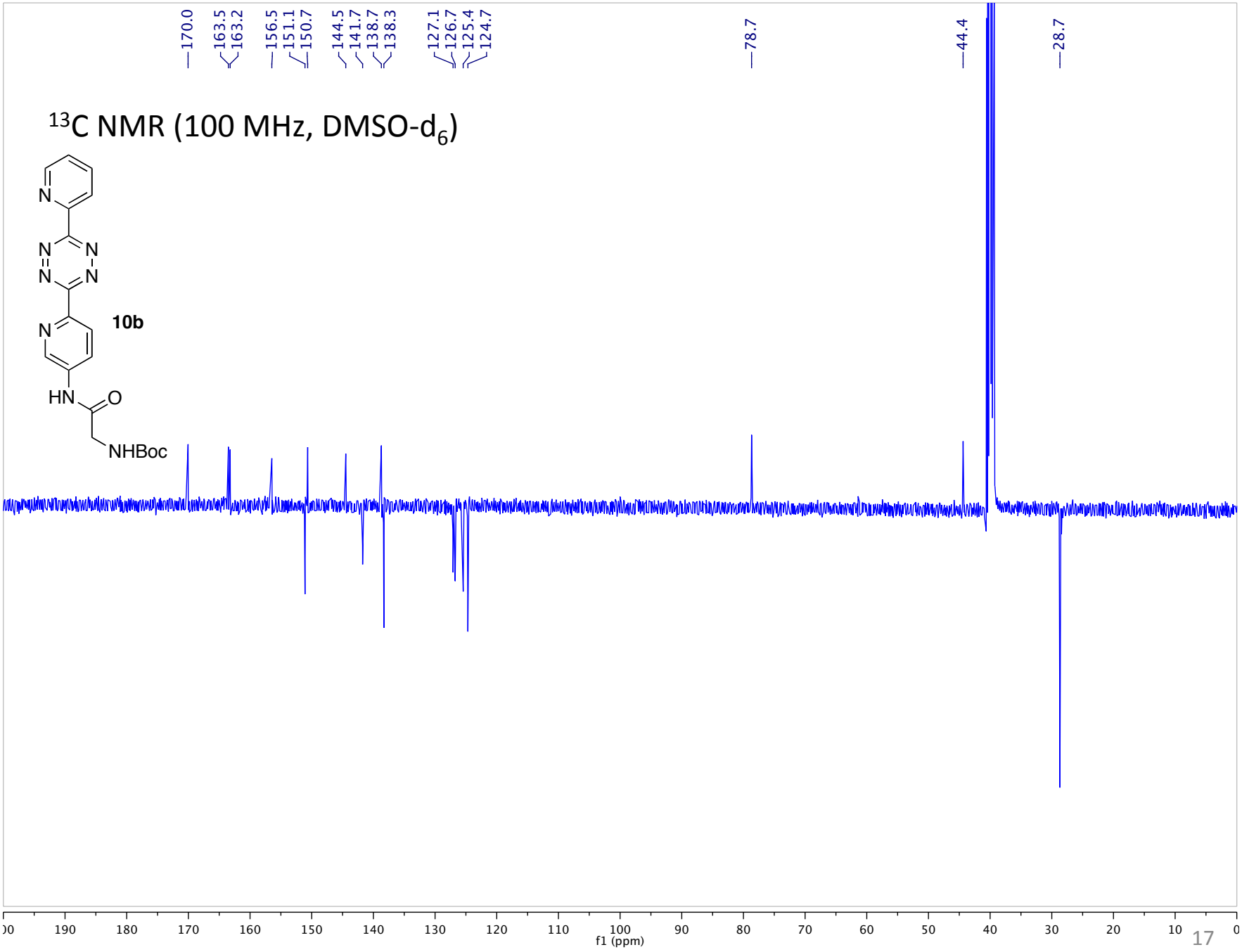
10a



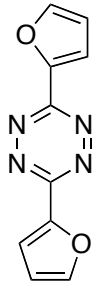
^{1}H NMR (400 MHz, DMSO-d_6)

10b

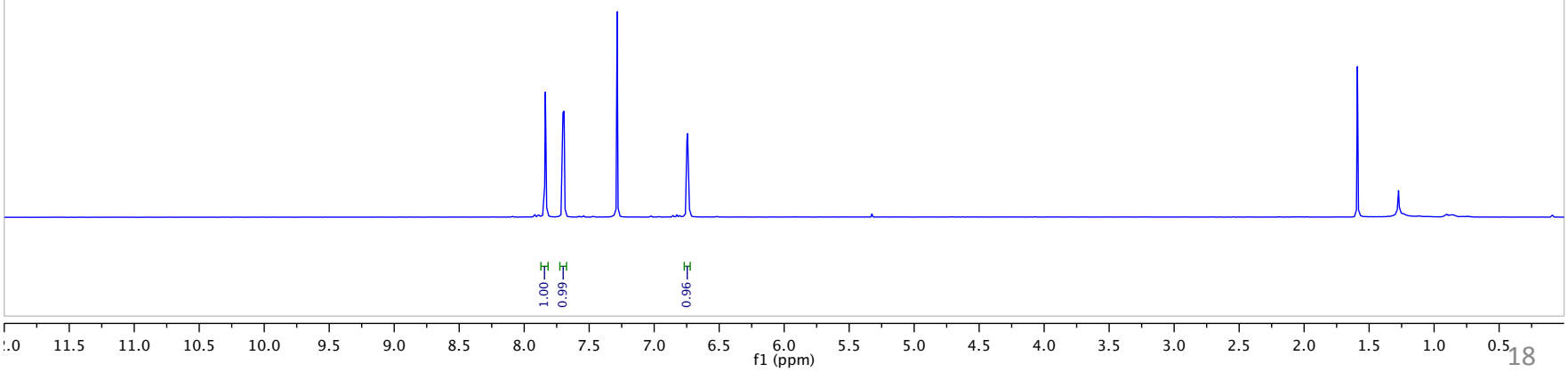


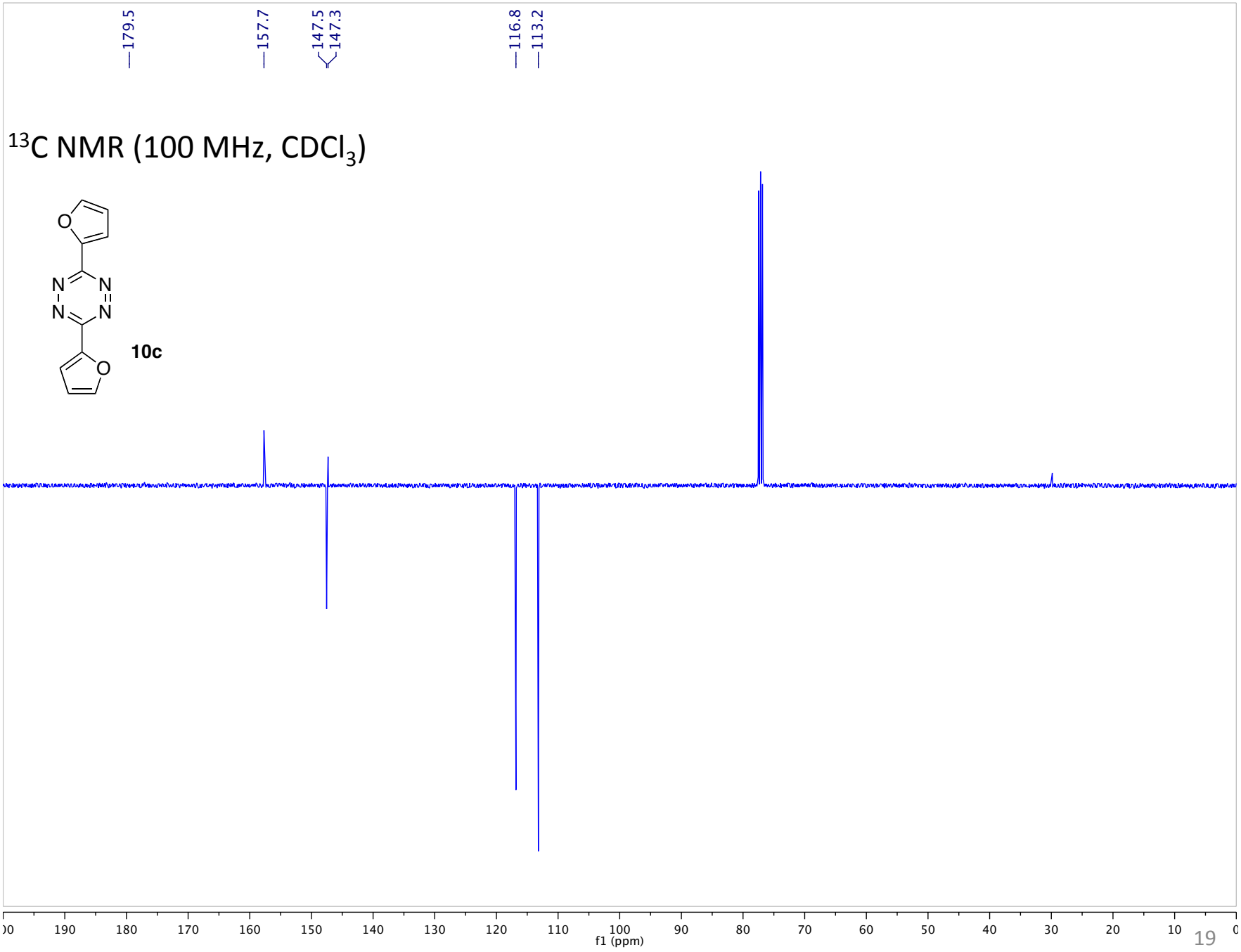

170.0
163.5
163.2
156.5
151.1
150.7
144.5
141.7
138.7
138.3
127.1
126.7
125.4
124.7
78.7
44.4
28.7
13C NMR (100 MHz, DMSO-d6)
10b
HN
O
NHBoc
f1 (ppm)

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



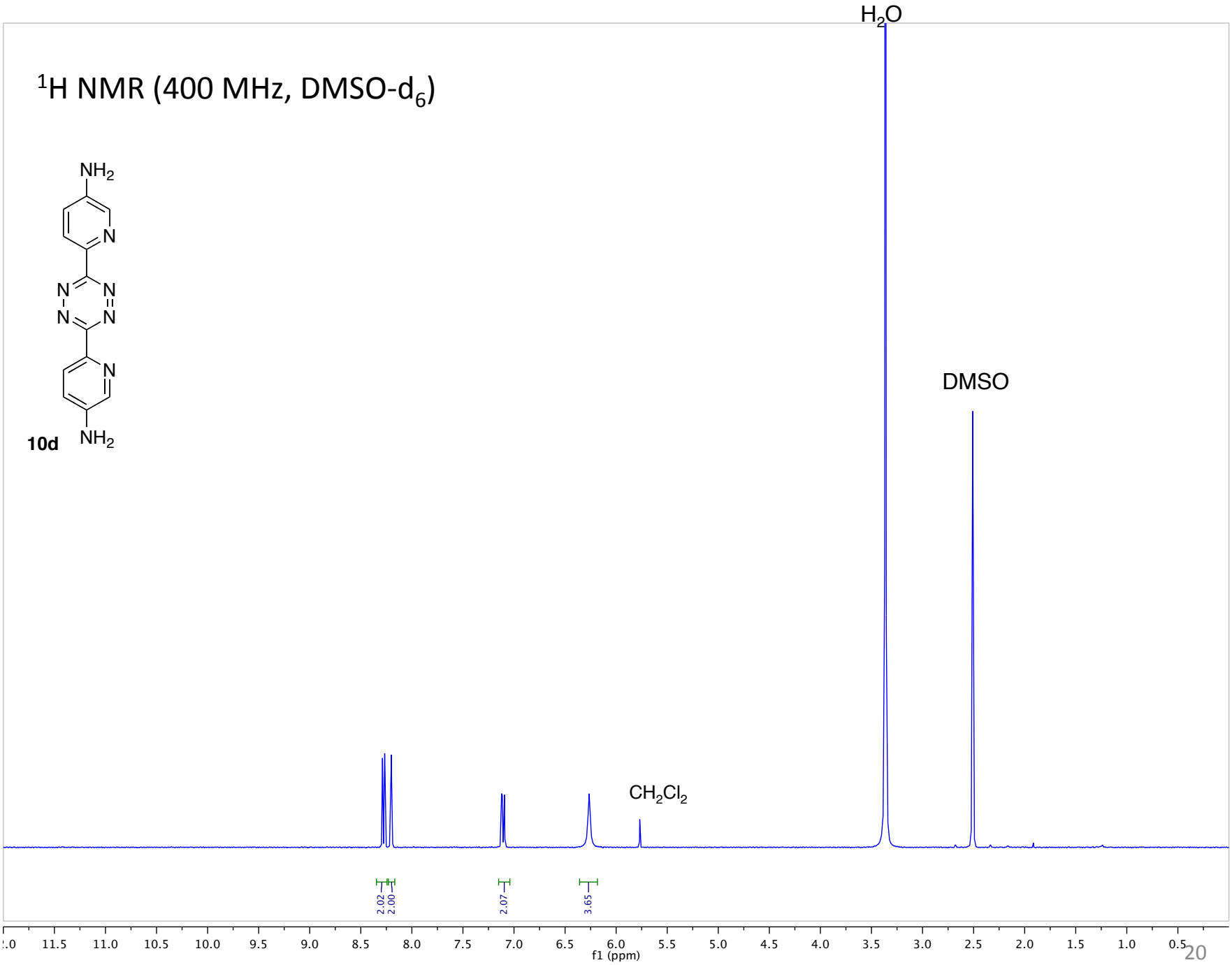
10c

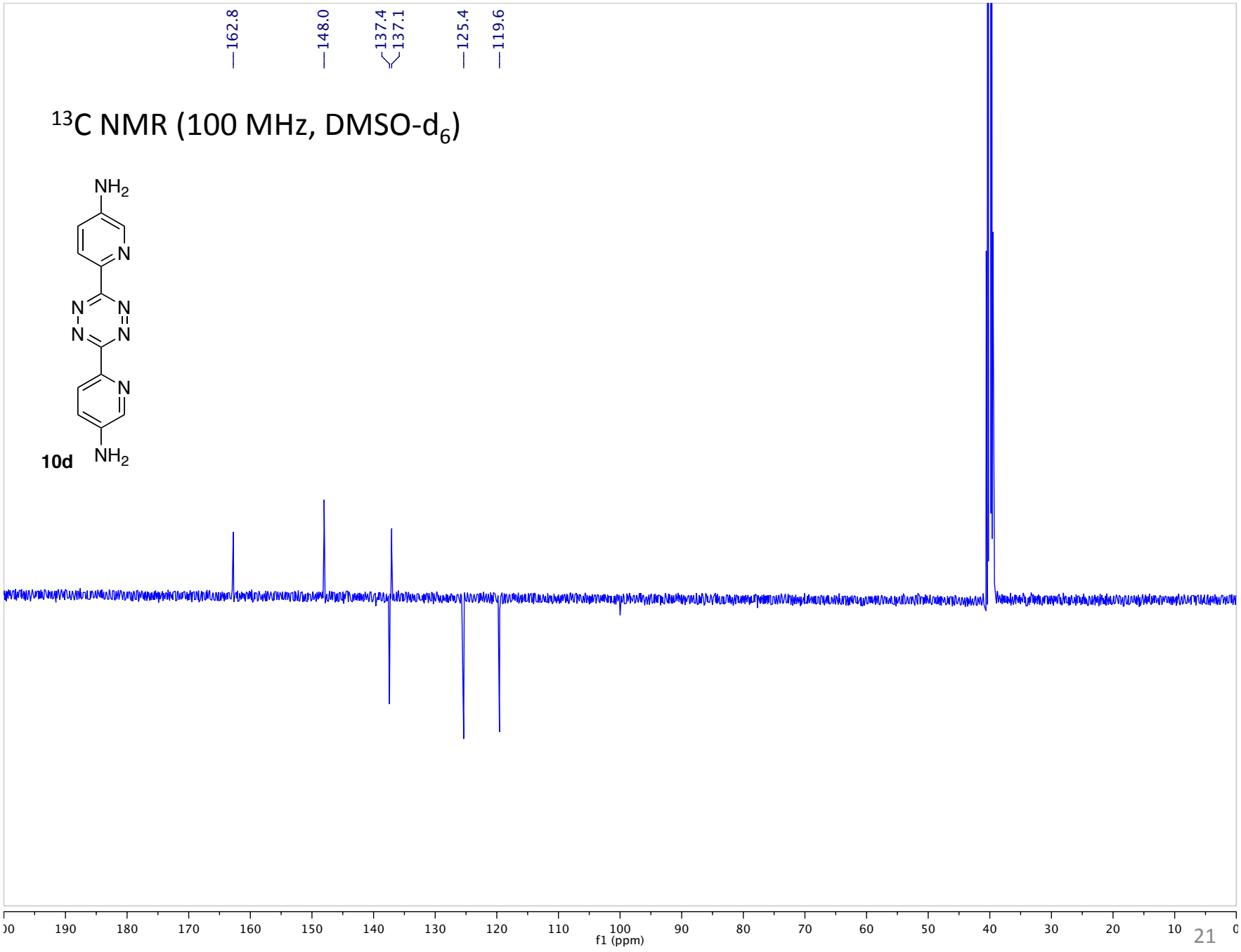



179.5
157.7
147.5
147.3
116.8
113.2
13C NMR (100 MHz, CDCl3)
10c
f1 (ppm)

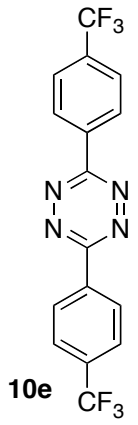
^{1}H NMR (400 MHz, DMSO-d_6)

10d

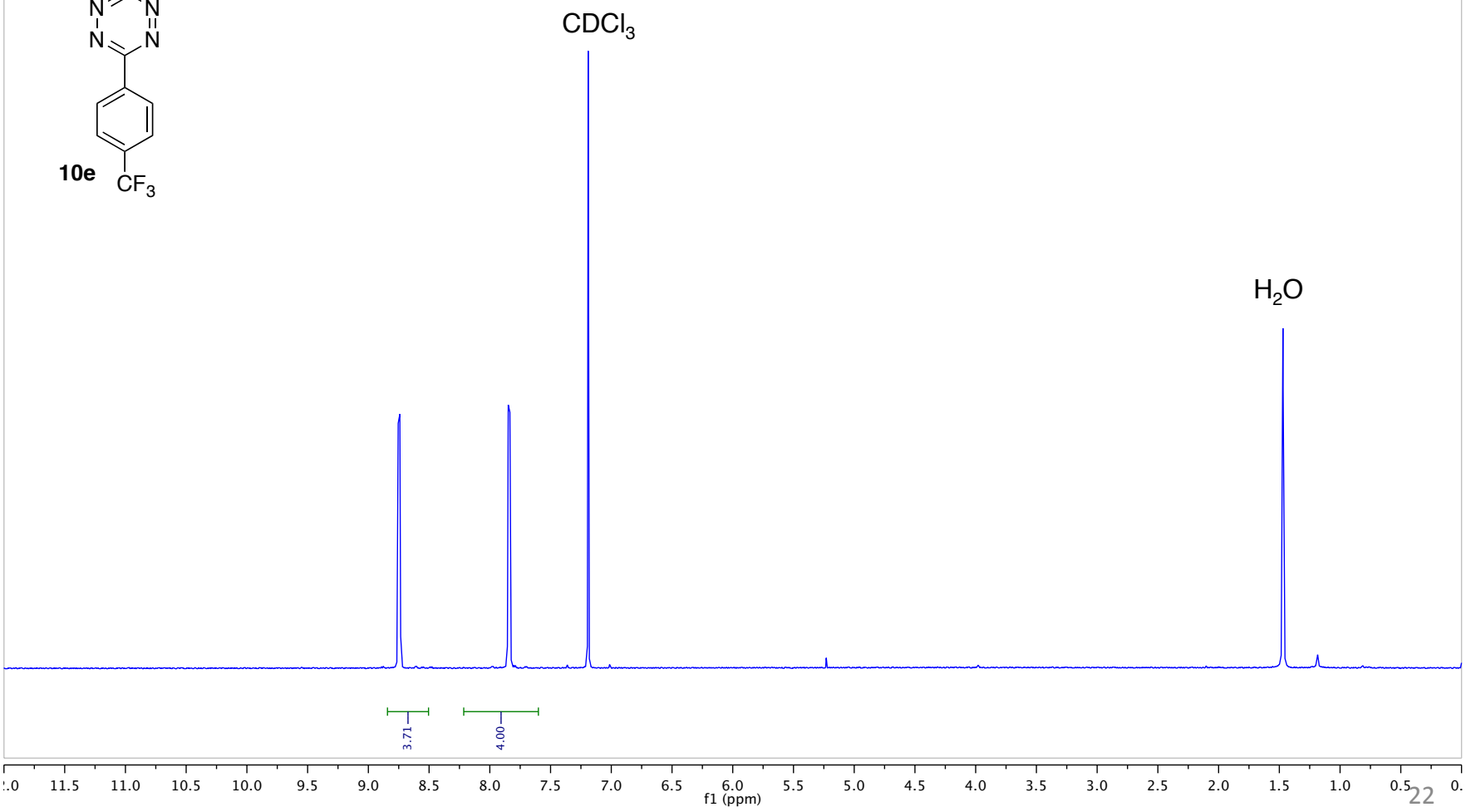


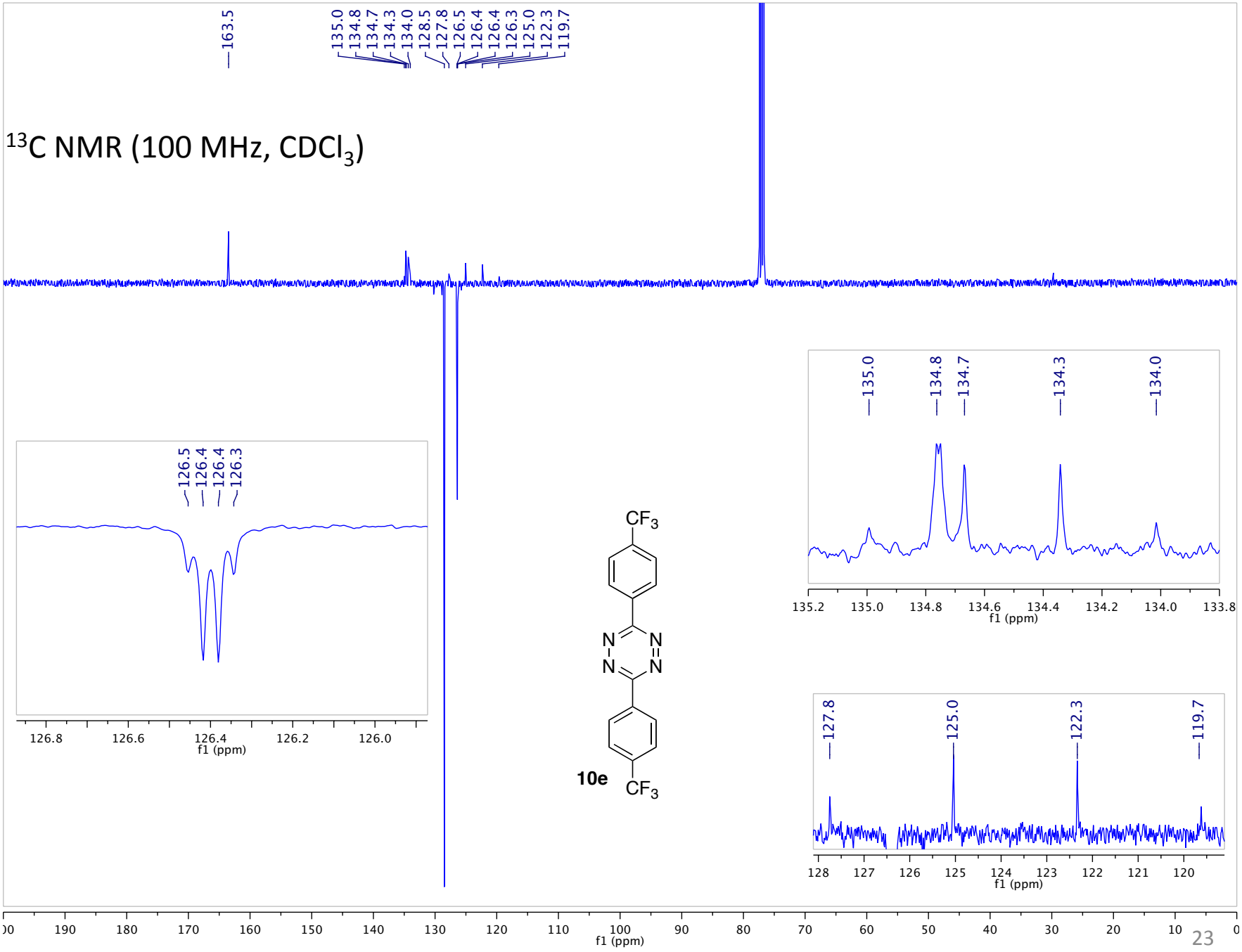

162.8
148.0
137.4
137.1
125.4
119.6
13C NMR (100 MHz, DMSO-d6)
NH2
N
N
N
N
N
N
NH2
10d
f1 (ppm)

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



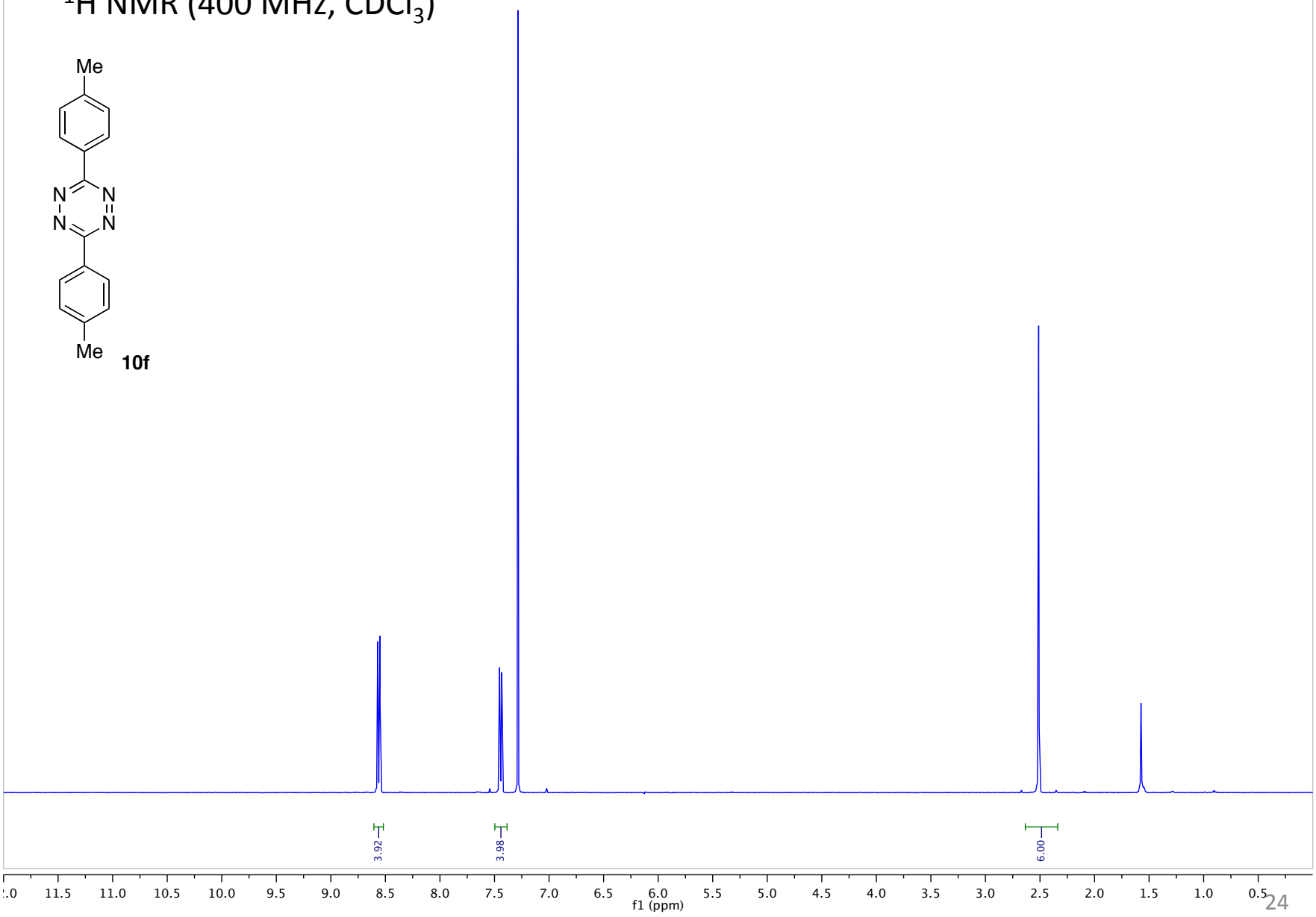
10e

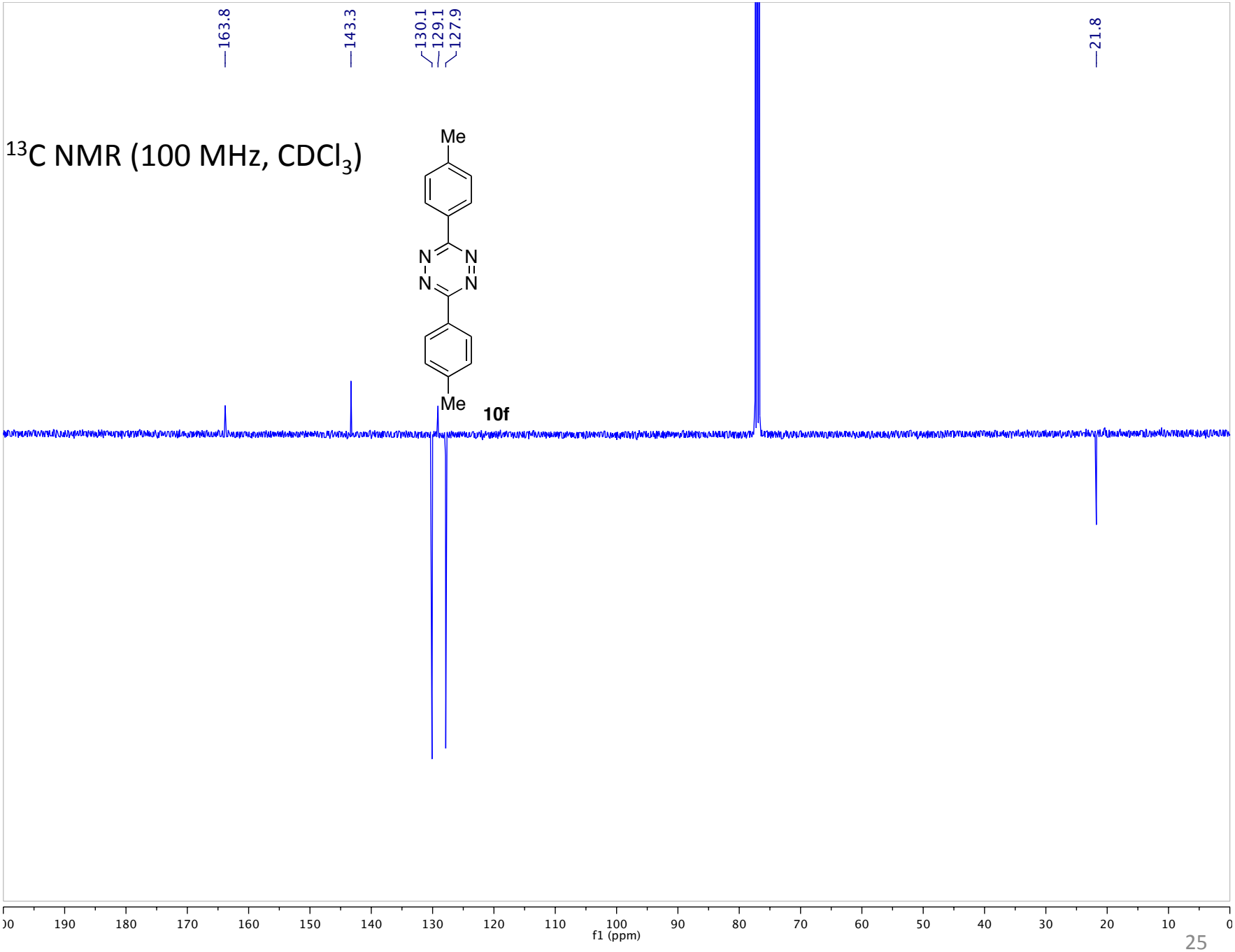



163.5
135.0
134.8
134.7
134.3
134.0
128.5
127.8
126.5
126.4
126.4
126.3
125.0
122.3
119.7
13C NMR (100 MHz, CDCl3)
126.5
126.4
126.4
126.3
126.8
126.6
126.4
126.2
126.0
f1 (ppm)
CF3
N
N
N
N
CF3
10e
135.0
134.8
134.7
134.3
134.0
135.2
135.0
134.8
134.6
134.4
134.2
134.0
133.8
f1 (ppm)
127.8
125.0
122.3
119.7
128
127
126
125
124
123
122
121
120
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

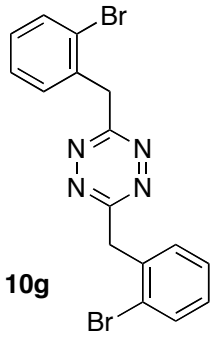
^{1}H NMR (400 MHz, $CDCl_3$)

10f

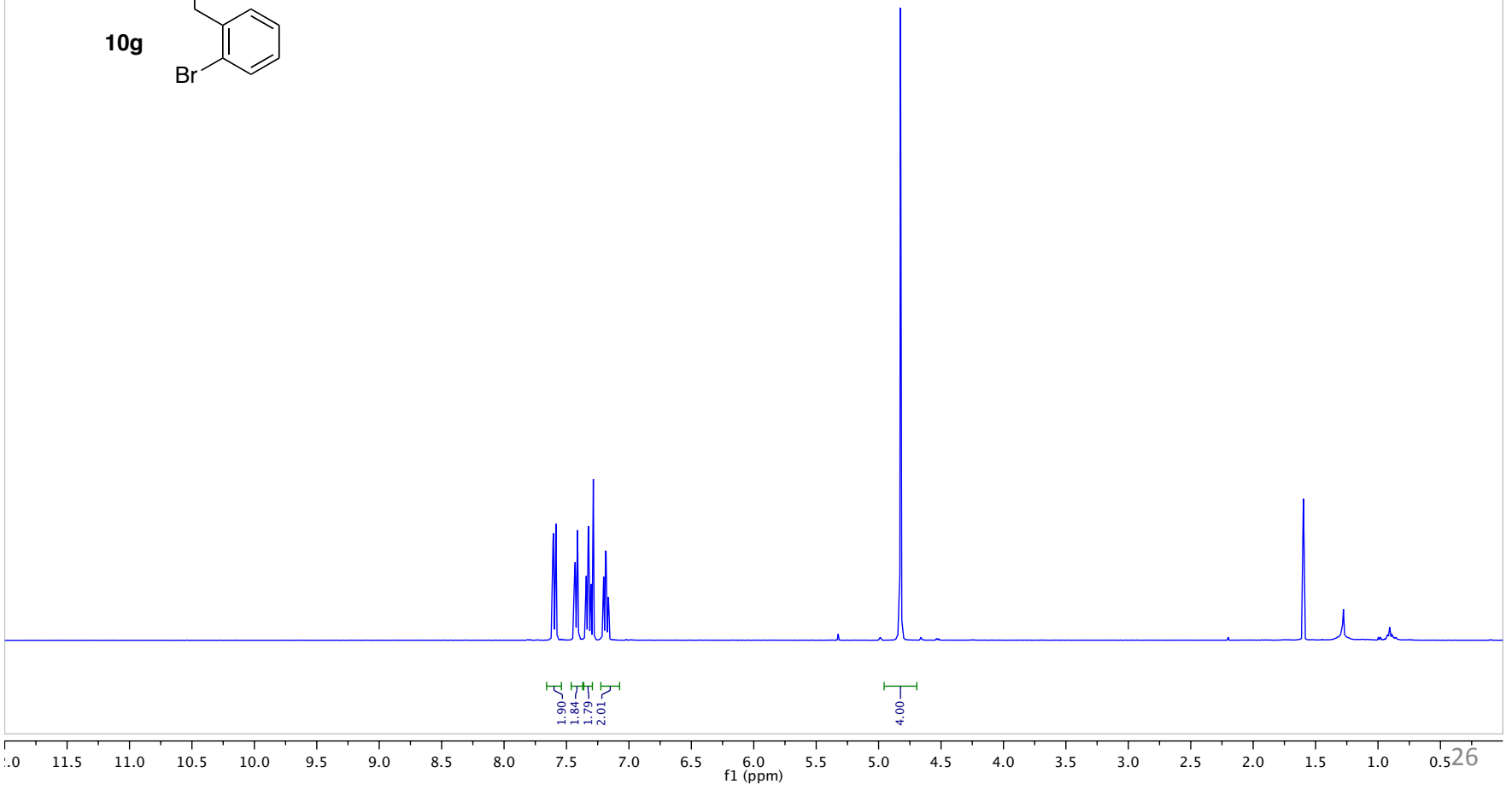


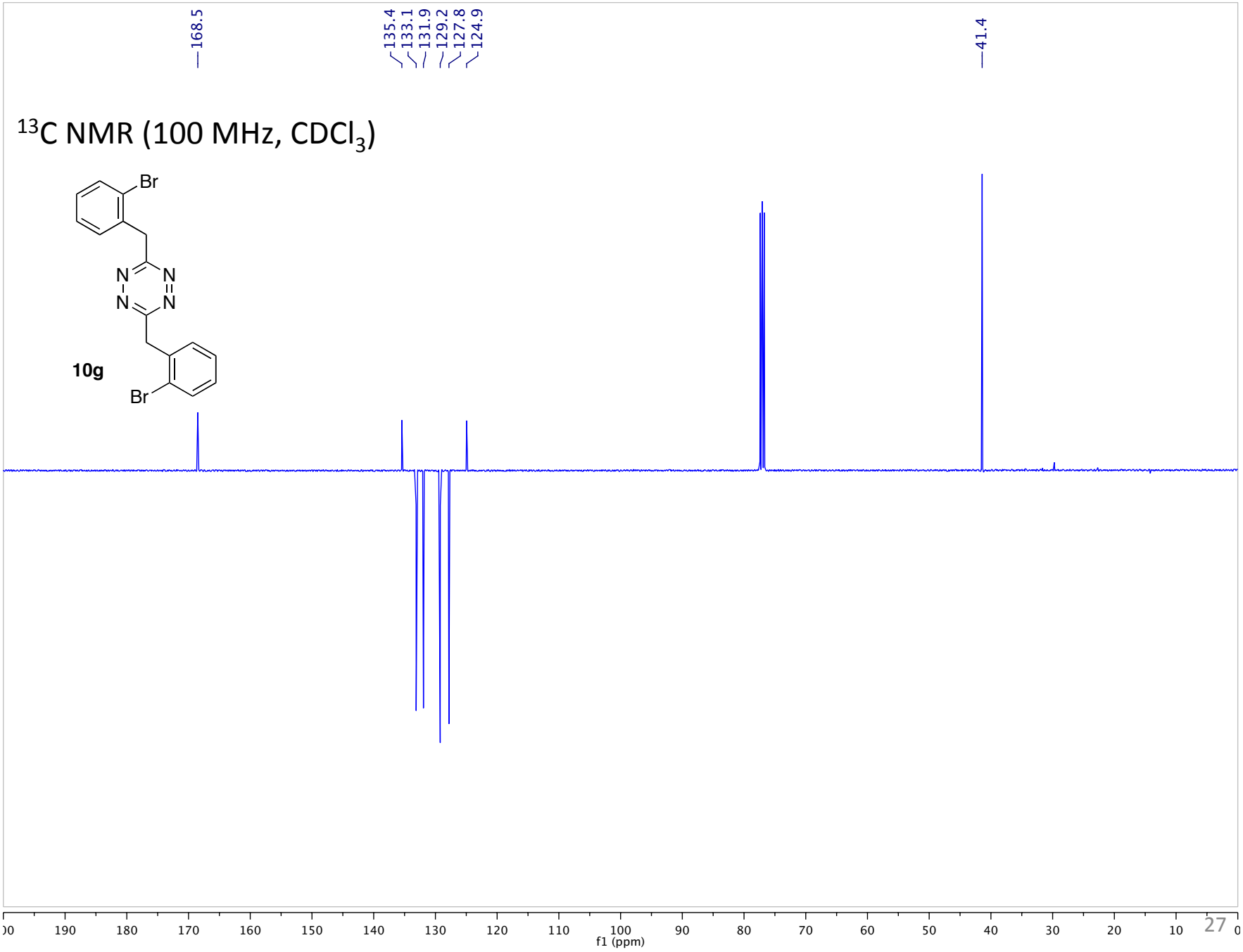

163.8
143.3
130.1
129.1
127.9
21.8
^{13}C NMR (100 MHz, $CDCl_3$)
Me
N
N
N
N
Me
10f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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



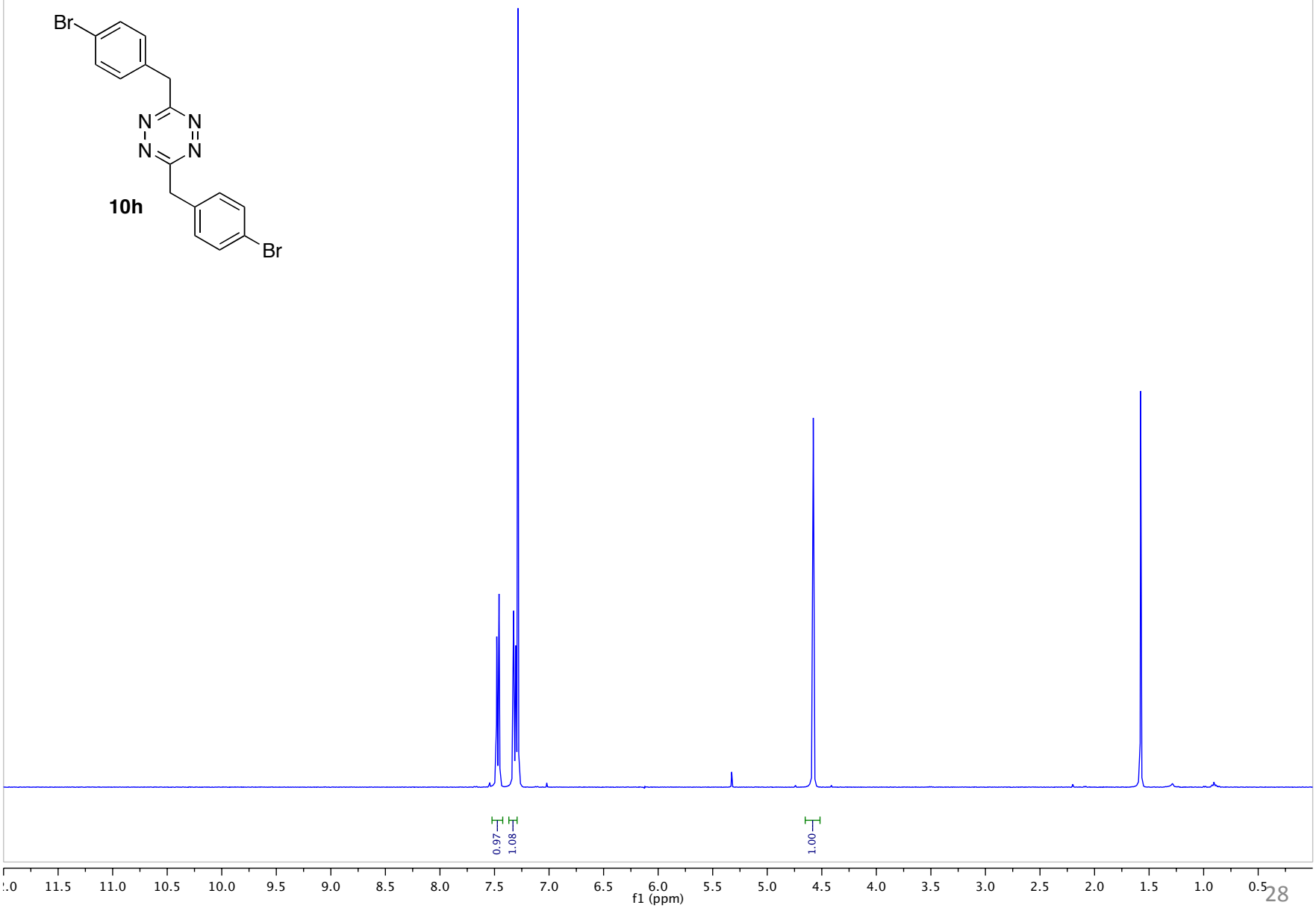
10g

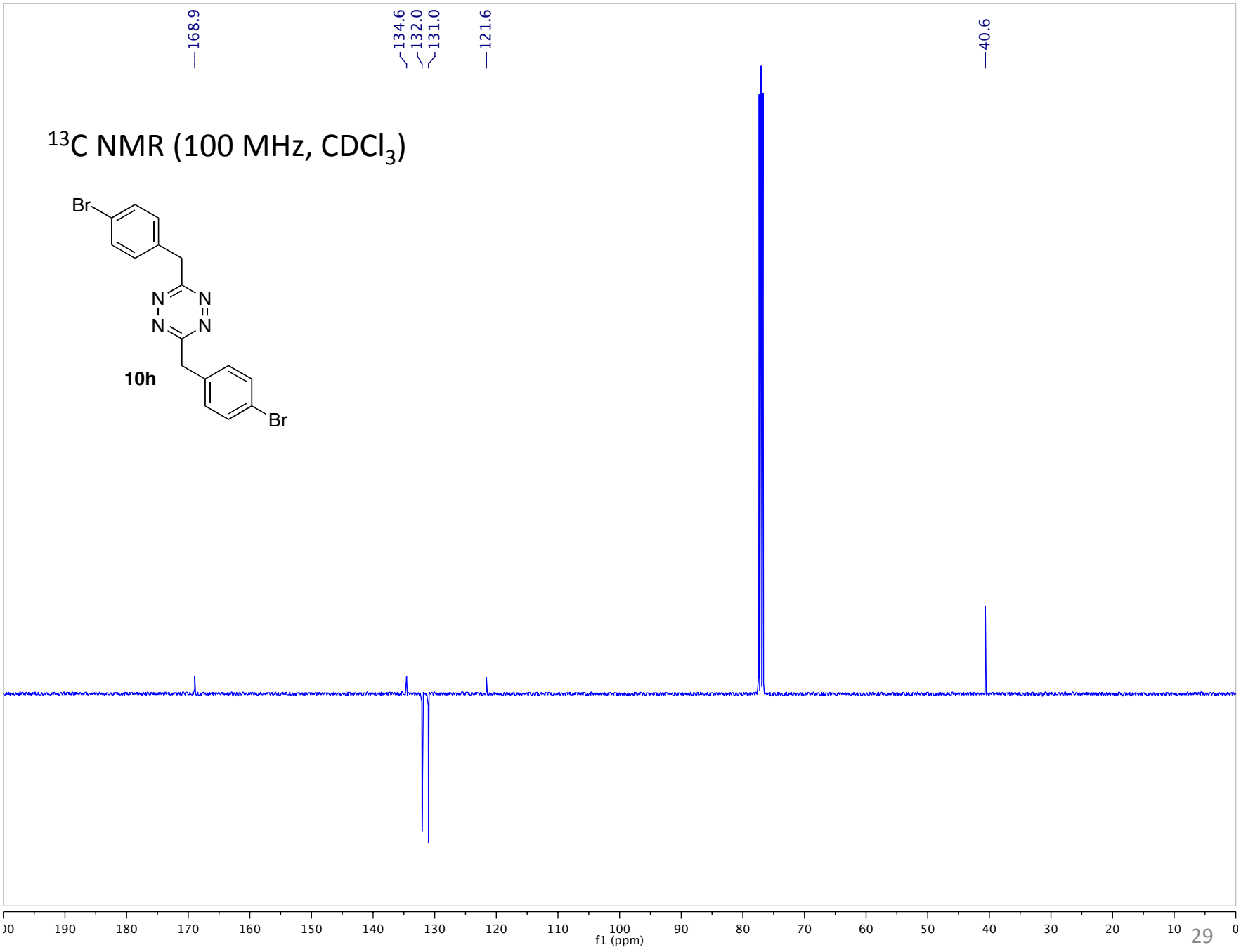



168.5
135.4
133.1
131.9
129.2
127.8
124.9
41.4
13C NMR (100 MHz, CDCl3)
Br
N
N
N
N
10g
Br
f1 (ppm)

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

10h




168.9
134.6
132.0
131.0
121.6
40.6
13C NMR (100 MHz, CDCl3)
Br
N
N
N
N
10h
Br
f1 (ppm)