Supporting information

Catalyst-Free Synthesis of Phenanthridines *via* Electrochemical Coupling of 2-Isocyanobiphenyls and Amines

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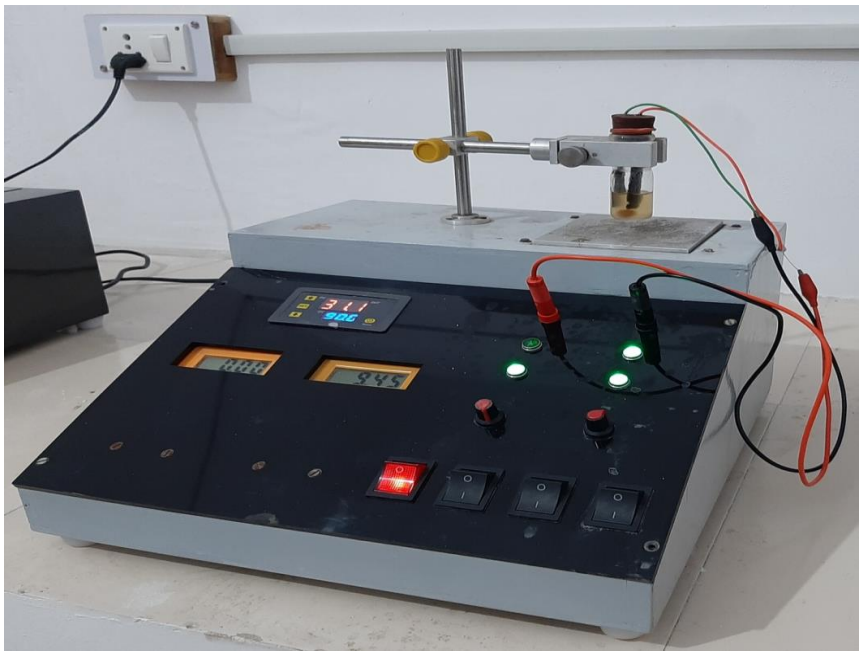
1. Experimental Setup



2. Cyclic Voltammetry studies of 3 and 5

General Procedure for Cyclic Voltammetry (CV): Cyclic Voltammetry studies were carried out using IKA ElectraSyn 2.0 Pro with three electrode cell connected to a nitrogen balloon at room temperature. The working electrode was glassy carbon electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous 3M KCl solution, and separated from reaction by a salt bridge. The scan rate is 0.1 V/s, ranging from -2.36 V to 1.6 V and the peak potential were measured vs. Ag/AgCl. The cyclic voltammetry (CV) experiments were carried out to study the redox potential of the substrate. All the experiment data taken 10 min after stirring. According to the CV data, we have confirmed the*in-situ* generation of diazonium salt see in details Fig S1 and S2.In Figure S1 and Figure S2 curve had cathodic reduction of **1a**, in fig S1 peak was observed at -0.26 V in nBu_4NBF_4 (0.05M) as an electrolyte in CH_3CN/H_2O (10:1), and in fig S2 two peaks was observed at -0.34 V and -1.92 V in nBu_4NBF_4 (0.05M) as a electrolyte in CH_3CN. In fig. S2 curve of **1a** gave two reduction peaks, corresponded to the reduction of aryl diazonium to aryl radicals and possibly further to aryl anion, respectively. Infig.S3, the anodic oxidation peak of nBu_4NBF_4 (0.05M) was observed at 0.77 V in CH_3CN (curve **a)**. In fig. S4, the CV of the mixture of **1a** and **2a** substrate with nBu_4NBF_4, **1a** and **2a** had two oxidation peaks at 0.83 and 1.08 V (curve **b**). Interestingly, we found that the same voltage peaks but promoted oxidation was observed (curve **c**) when HFIP was used as co-solvent with CH_3CN.

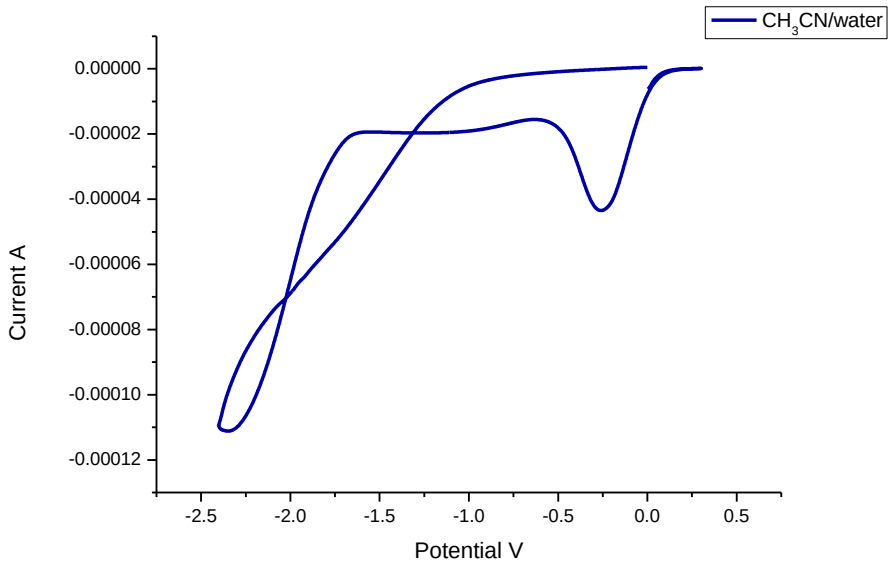


Figure S1. Cyclic voltammograms of CH_3CN/H_2O (10:1) as solution, using glassy carbon electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl as a reference electrode, scan rate of 0.1 V/s: (a)**1a**(0.01M)+ *i*-AmONO (0.01M) + nBu_4NBF_4 (0.05M).

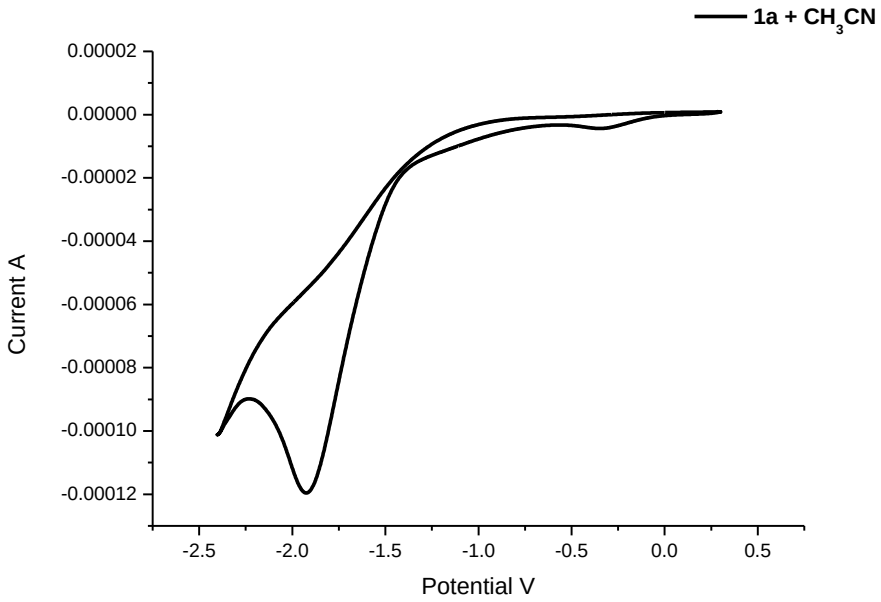


Figure S2. Cyclic voltammograms of CH_3CN as solution, using glassy carbon electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl as a reference electrode, scan rate of 0.1 V/s: (a) **1a**(0.01M) + *i*-AmONO(0.01M) + nBu_4NBF_4 (0.05M).

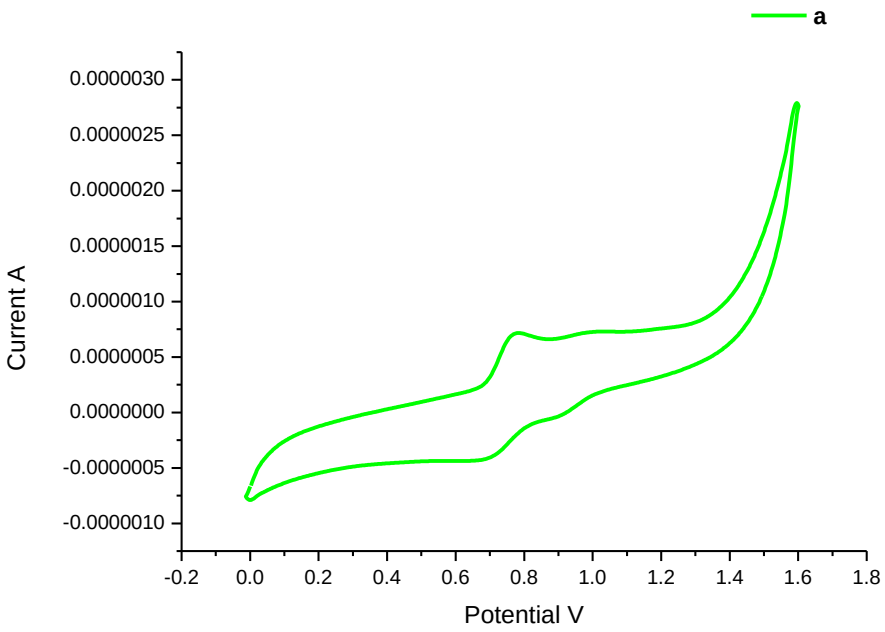


Figure S3. Cyclic voltammograms of CH_3CN as solution, using glassy carbon electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl as a reference electrode, scan rate of 0.1 V/s: (**a**) nBu_4NBF_4 (0.05M).

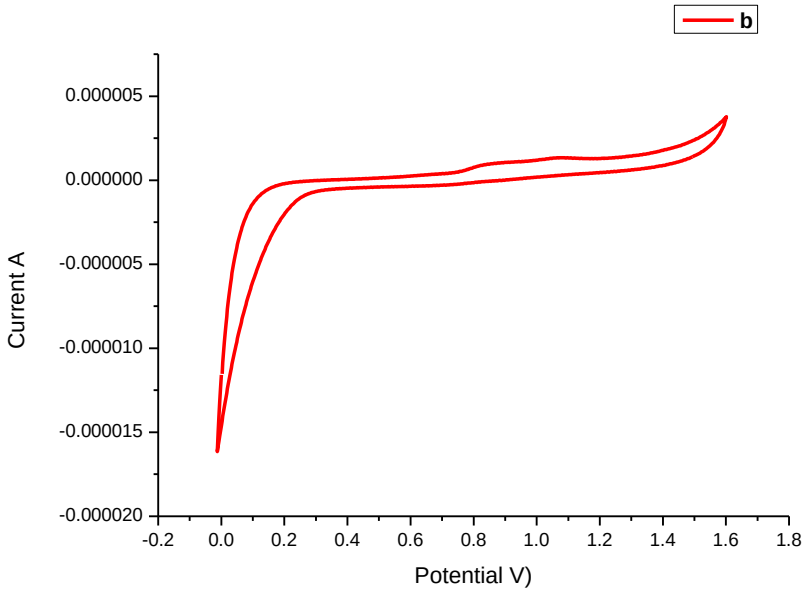


Figure S4. Cyclic voltammograms of CH_3CN as solution, using glassy carbon electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl as a reference electrode, scan rate of 0.1 V/s: (**b**)**1a** (0.01M) + *i*-AmONO(0.01M) + **2b**(0.01M) +nBu_4NBF_4 (0.05M).

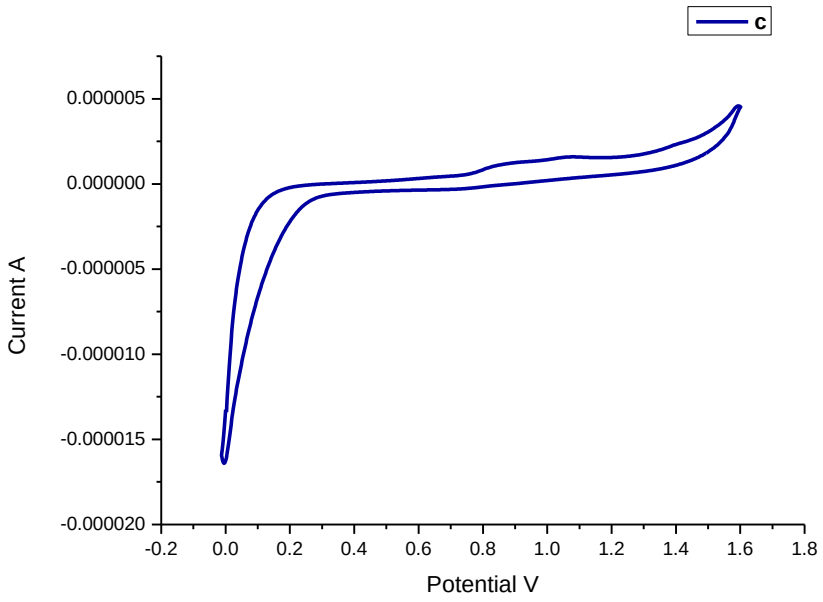
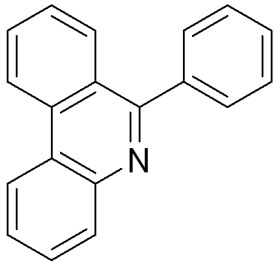


Figure S5. Cyclic voltammograms of CH_3CN as solution, using glassy carbon electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl as a reference electrode, scan rate of 0.1 V/s: (**c**) **1a** (0.01 M) + *i*-AmONO(0.01M) + **2a** (0.01 M) + nBu_4NBF_4 (0.05M) + HFIP (0.005 M)

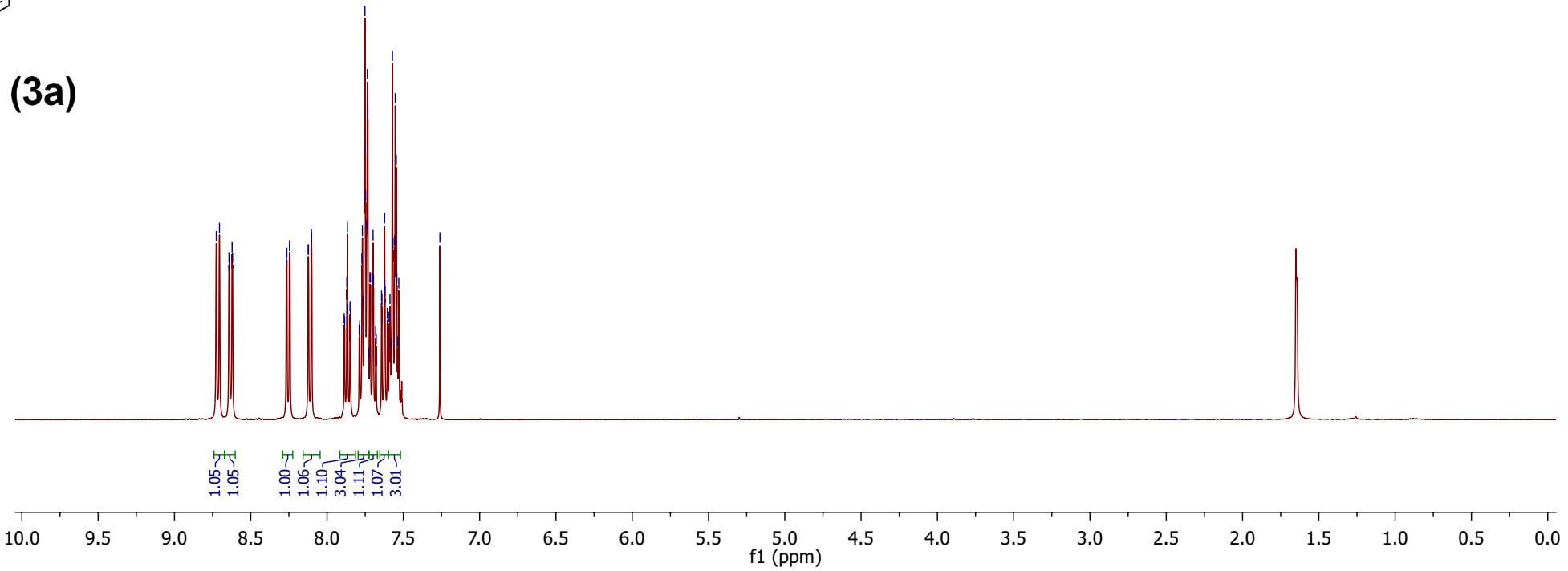
Feb11-2021
sb-101

8.726
8.705
8.643
8.640
8.622
8.619
7.756
7.752
7.748
7.736
7.732
7.622
7.571
7.553
7.546
7.260

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



(3a)



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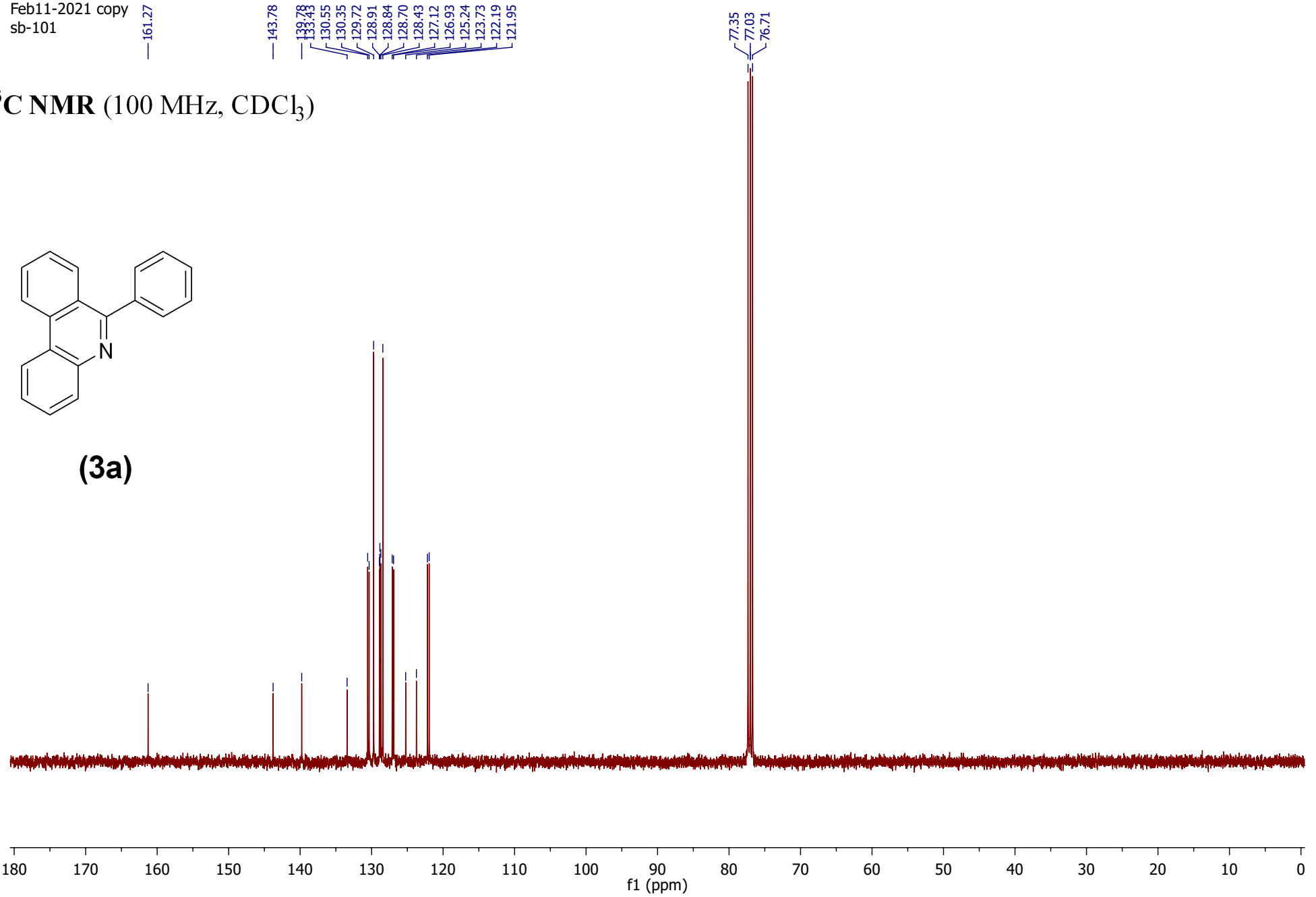
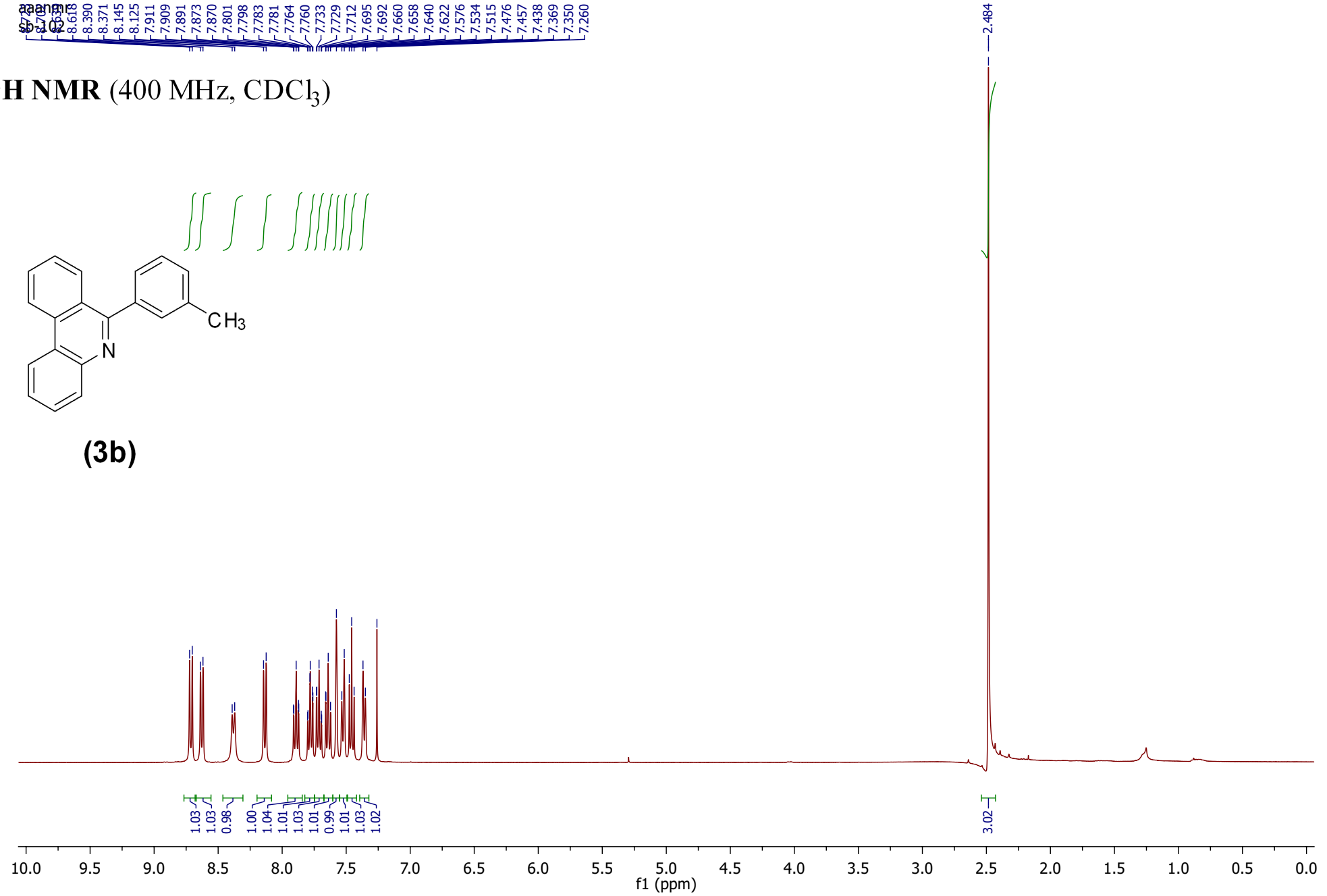
sb-101



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

(3a)



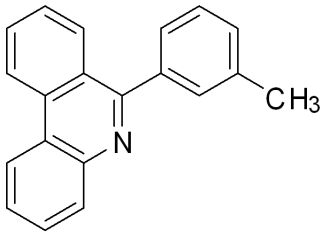
^{1}H NMR (400 MHz, $CDCl_3$)

(3b)

aaanmr
sb-102

161.38
138.30
133.60
131.09
130.39
129.84
129.67
129.34
129.10
128.25
127.32
127.19
126.98
125.12
123.77
122.22
121.97
77.35
77.03
76.71
21.55

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



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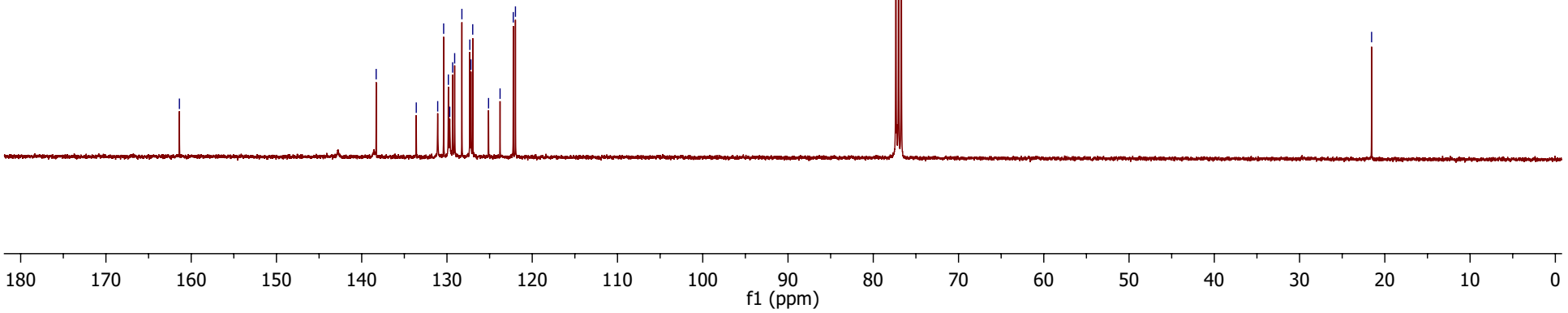
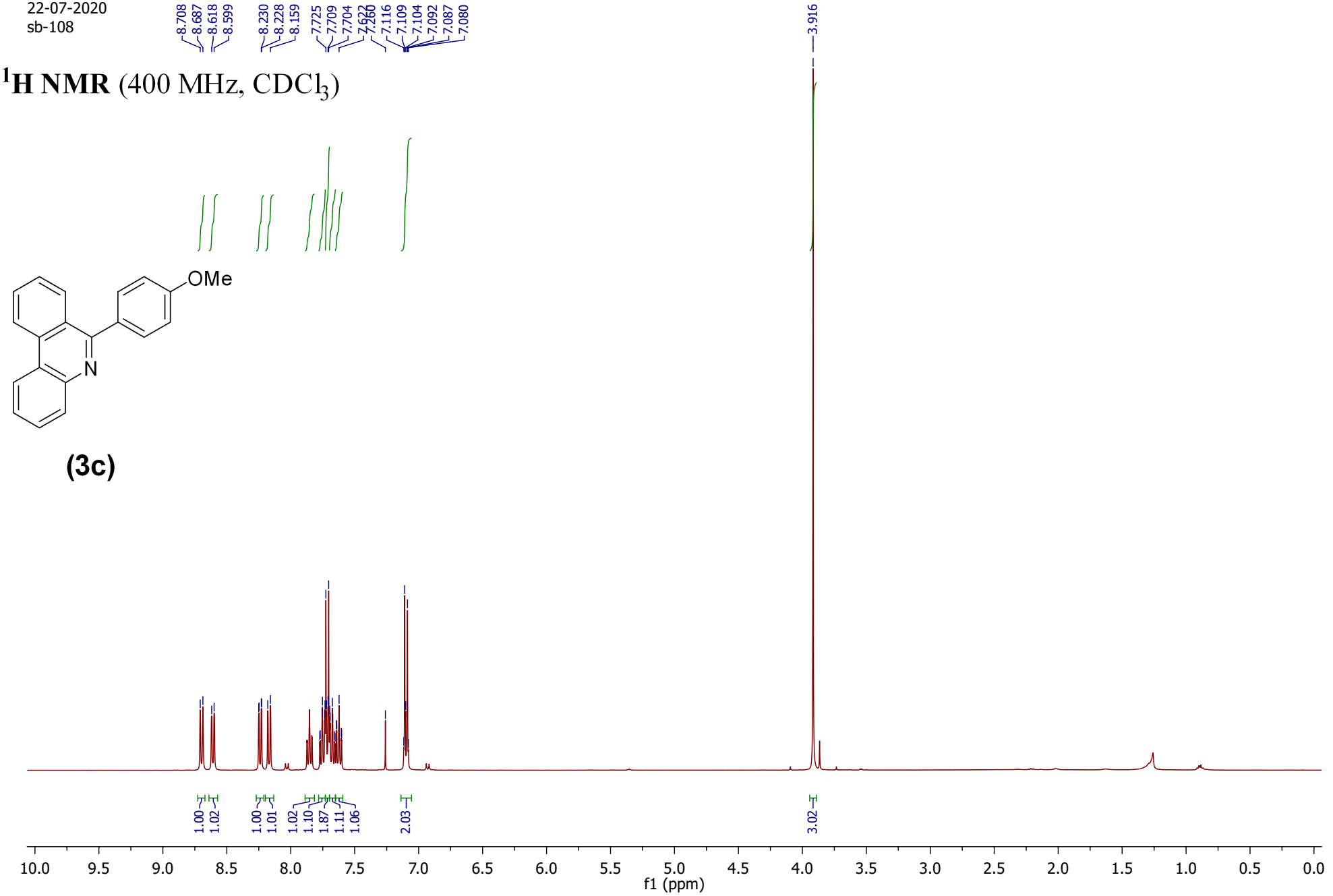


22-07-2020
sb-108

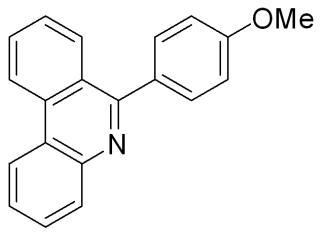
^{1}H NMR (400 MHz, $CDCl_3$)



(3c)

22-07-2020
sb-108

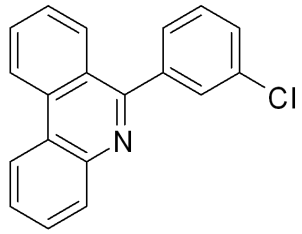
^{13}C NMR (100 MHz, $CDCl_3$)



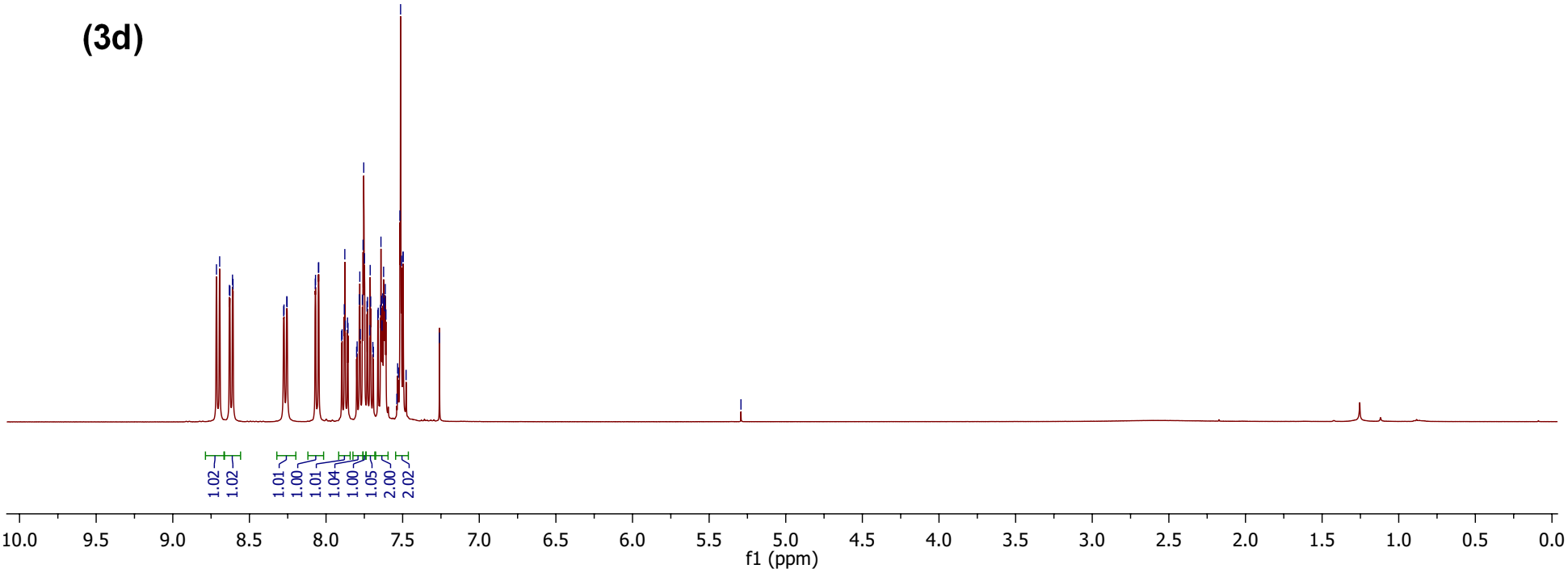
(3c)

aa
sb-107

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



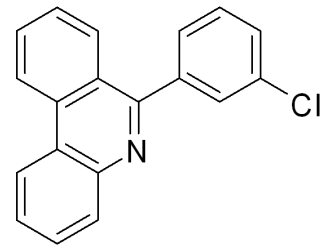
(3d)



aa
sb-107

159.63
143.39
141.23
134.48
133.47
130.88
130.20
129.82
129.70
129.04
128.94
128.52
127.98
127.38
127.30
124.86
123.80
122.32
121.99
77.35
77.03
76.71

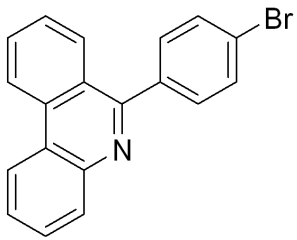
^{13}C NMR (100 MHz, $CDCl_3$)



(3d)

22-07-2020
sb-103

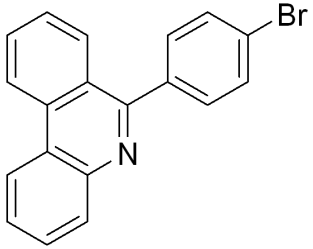
^{1}H NMR (400 MHz, $CDCl_3$)



(3e)

22-07-2020
sb-103

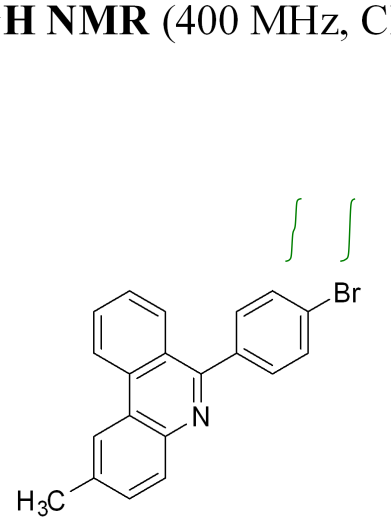
^{13}**C NMR** (100 MHz, $CDCl_3$)



(3e)

Oct26-2020 (1)
sb-83

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

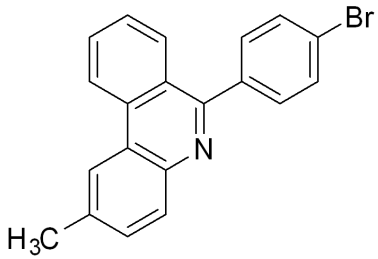


(3f)

Oct26-2020 (1)
sb-83

158.98
142.03
138.77
137.08
133.19
131.58
131.45
130.68
130.45
130.04
128.36
127.09
124.96
123.56
122.99
122.28
121.57
77.35
77.03
76.71
22.04

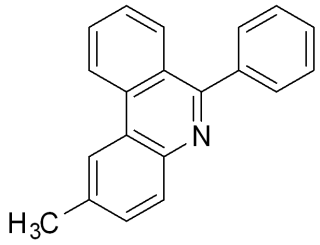
^{13}C NMR (100 MHz, $CDCl_3$)



(3f)

Phenenthridine NMR file
sb-77

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

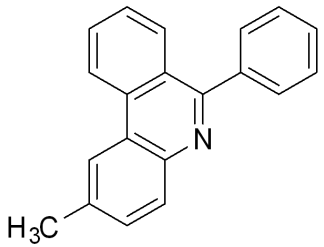


(3g)

Phenenthridine NMR file
sb-77

160.22
141.99
139.77
136.75
133.09
130.51
130.27
129.95
129.70
128.75
128.55
128.34
126.89
125.20
123.50
122.08
121.50
77.35
77.03
76.71
21.97

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



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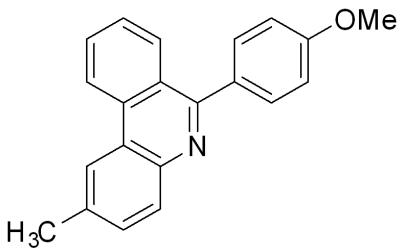
Feb11-2021
sb-79

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



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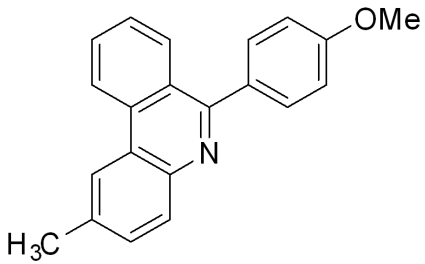
Feb11-2021
sb-79

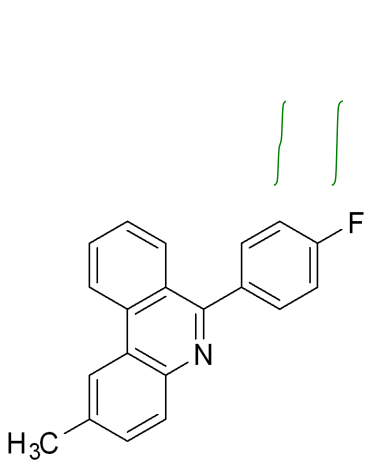
^{13}C NMR (100 MHz, $CDCl_3$)



(3h)

22-07-2020
sb-85

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



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sb-85

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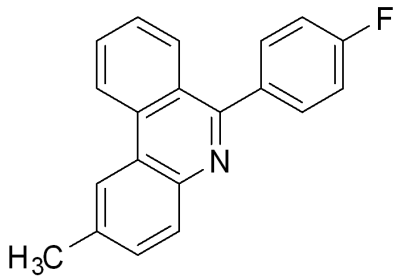

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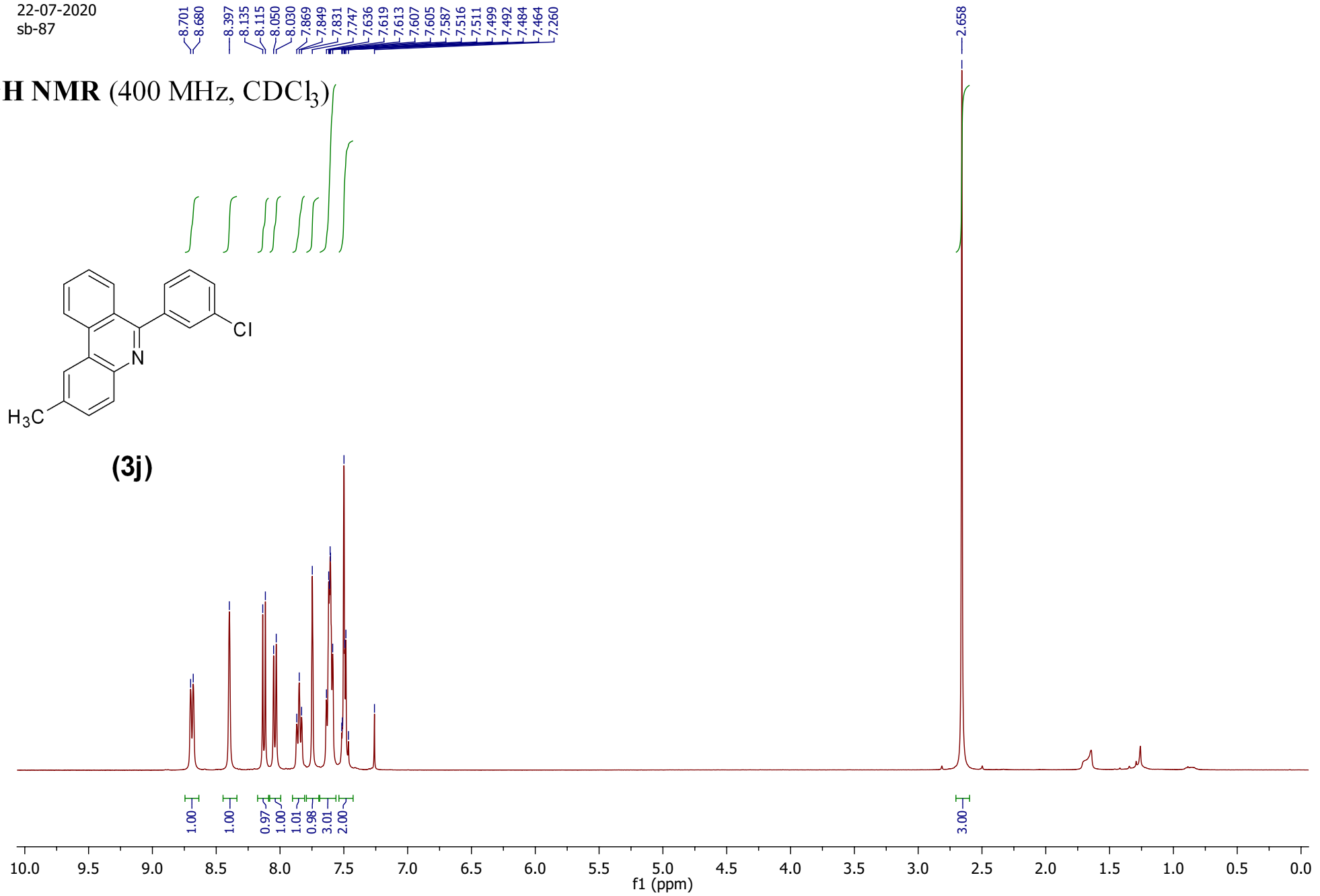
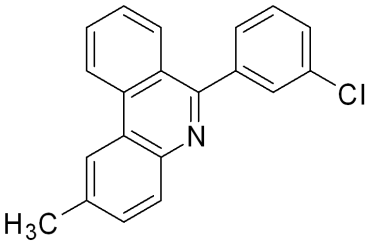

22-07-2020
sb-87
8.701
8.680
8.397
8.135
8.115
8.050
8.030
7.869
7.849
7.831
7.747
7.636
7.619
7.613
7.607
7.605
7.587
7.516
7.511
7.499
7.492
7.484
7.464
7.260
2.658
1H NMR (400 MHz, CDCl3)
Cl
N
H3C
(3j)
1.00
1.00
0.97
1.00
1.01
0.98
3.01
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

22-07-2020
sb-87

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

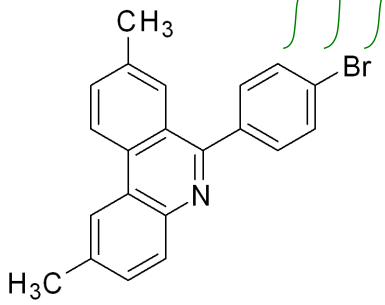


(3j)

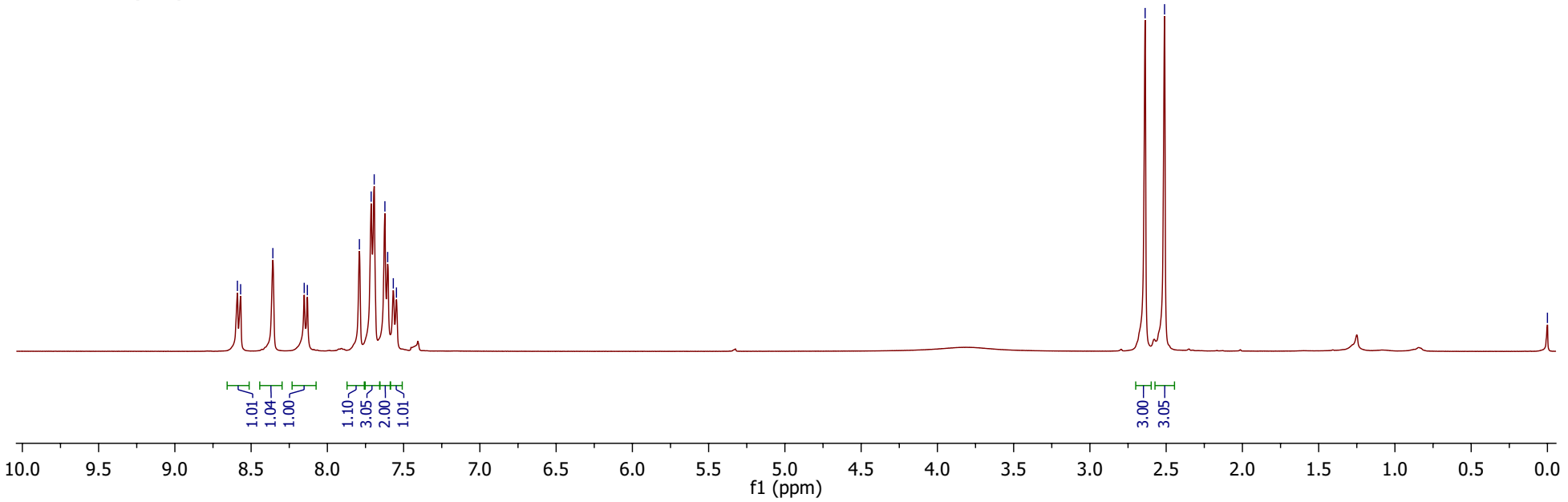
Phenenthridine NMR file
sb-84

8.590 8.569 8.357 8.152 8.131 7.790 7.713 7.693 7.623 7.604 7.568 7.547 2.638 2.511 0.000

^{1}H NMR (400 MHz, $CDCl_3$ + DMSO d_6)



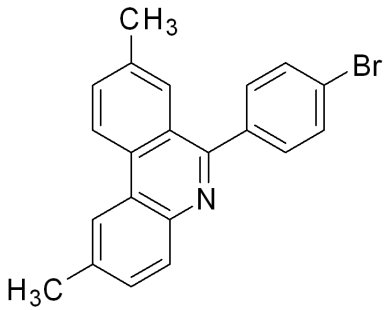
(3k)



Phenenthridine NMR file
sb-84

158.18
137.09
136.98
132.45
131.23
131.16
130.82
130.08
128.93
127.45
124.52
123.36
122.82
122.00
121.17
77.35
77.03
76.71
40.14
39.93
39.72
39.52
39.31
21.69
21.40

^{13}C NMR (100 MHz, $CDCl_3$ + DMSO d_6)



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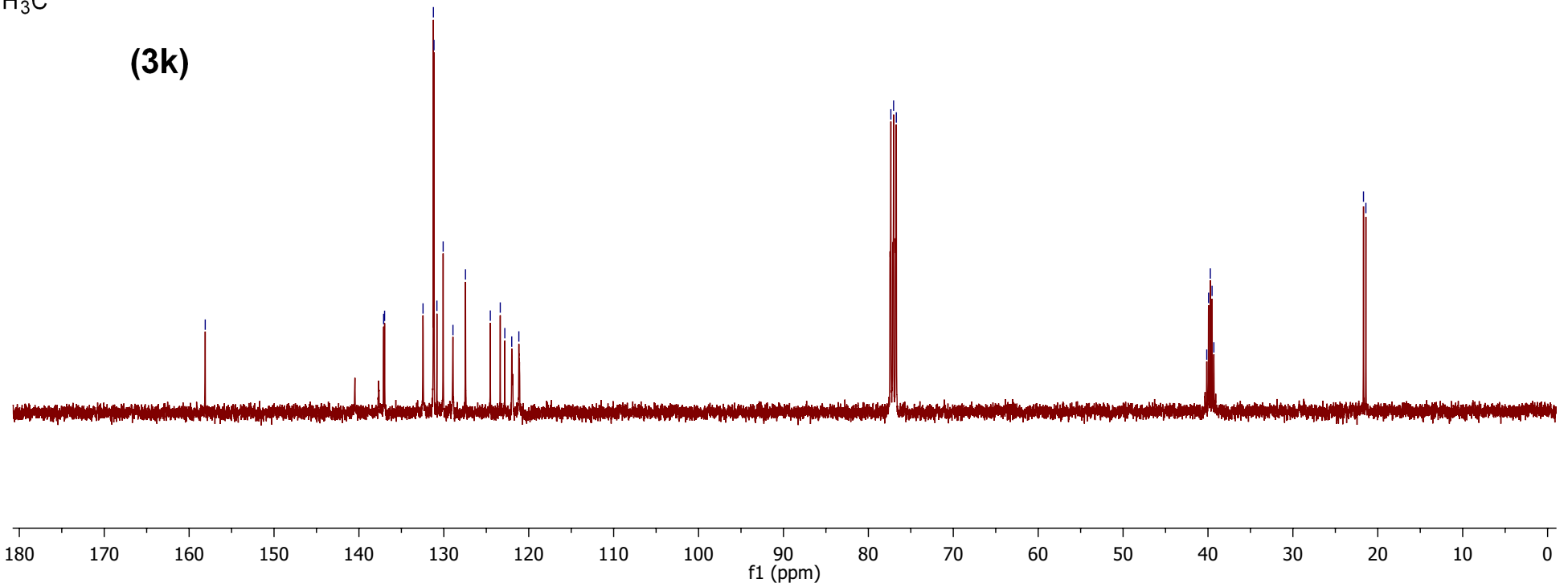
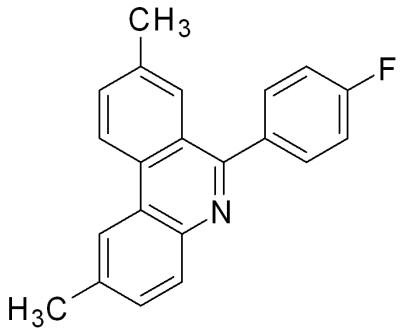


22-07-2020
sb-86

8.945 8.923 8.752 8.277 8.256 8.009 7.988 7.909 7.895 7.888 7.874 7.821 7.759 7.738 7.556 7.534 7.512 2.626 2.500

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



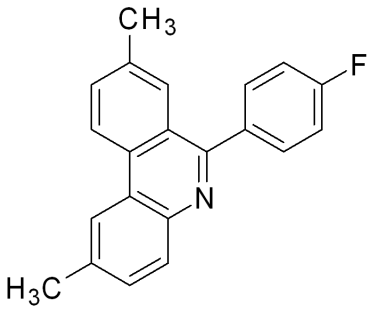
(3l)

1.00 1.00 1.01 1.04 2.00 1.01 1.01 2.00 3.04 3.93

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)

22-07-2020
sb-86

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



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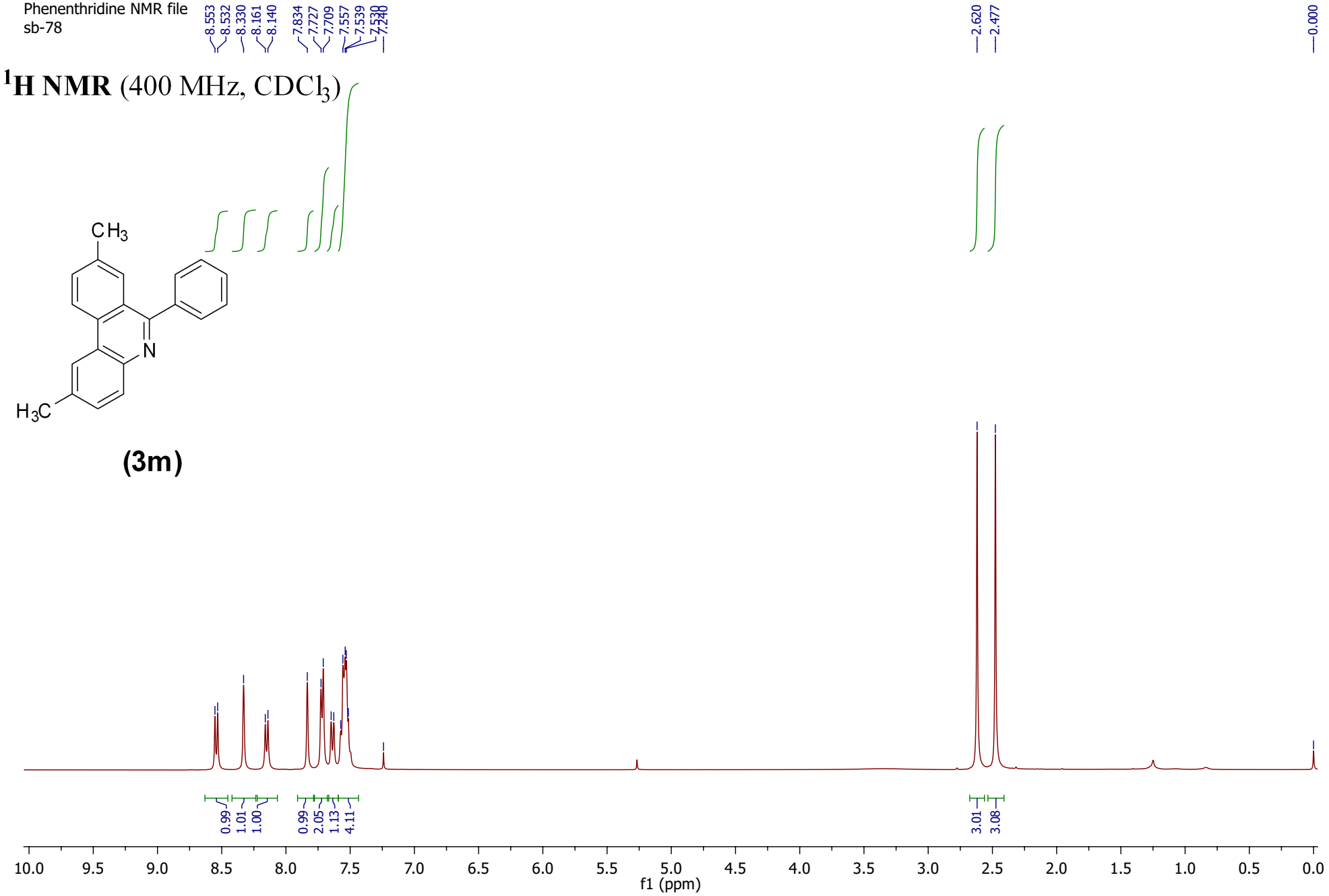
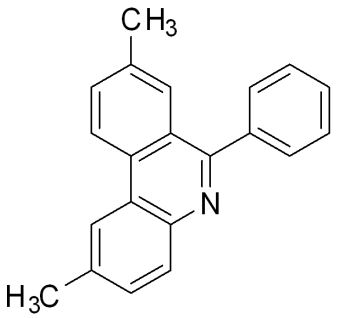
Phenenthridine NMR file
sb-78



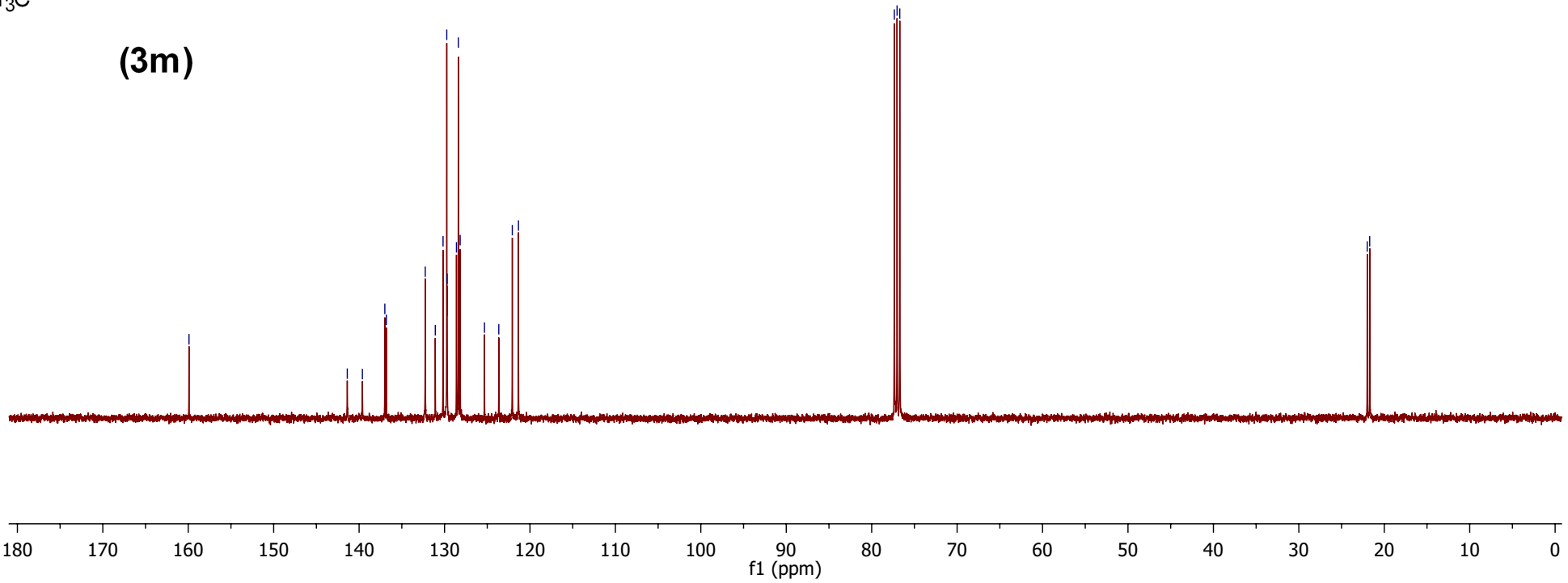
Phenenthridine NMR file
sb-78

159.90 141.38 139.62 136.99 136.81 132.26 131.08 130.17 129.74 129.69 128.60 128.39 128.17 125.32 123.65 122.07 121.35 77.35 77.03 76.71 21.99 21.71

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

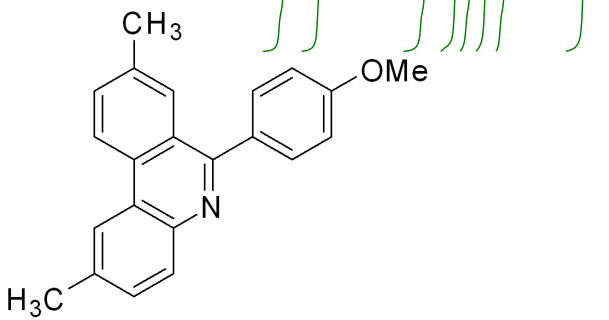


(3m)

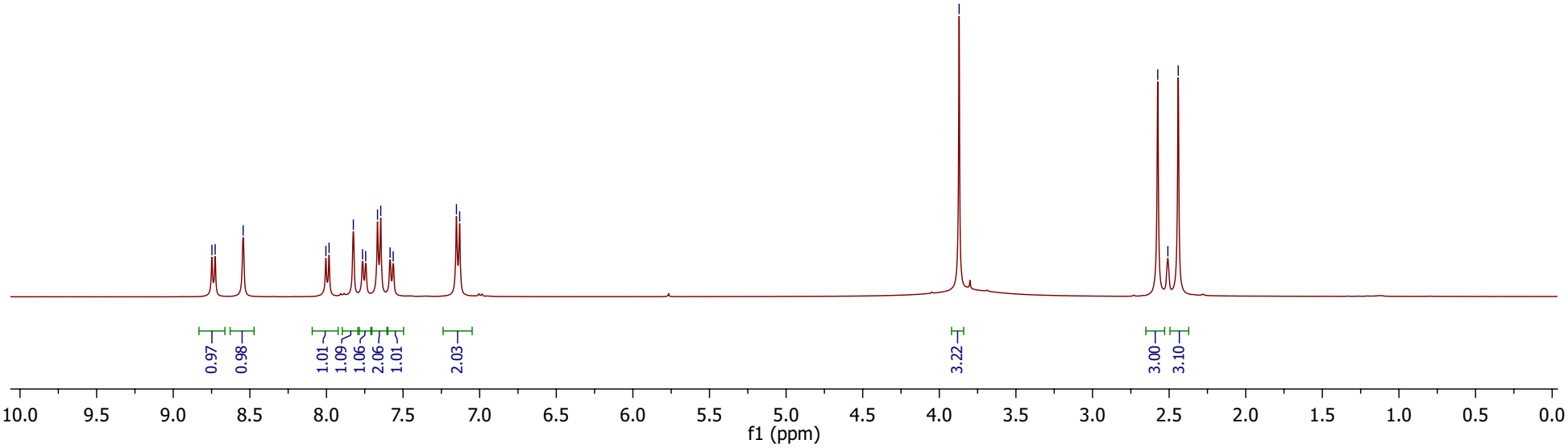


EXTRA SB-80
sb-80

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



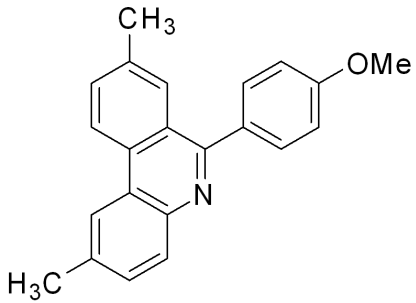
(3n)



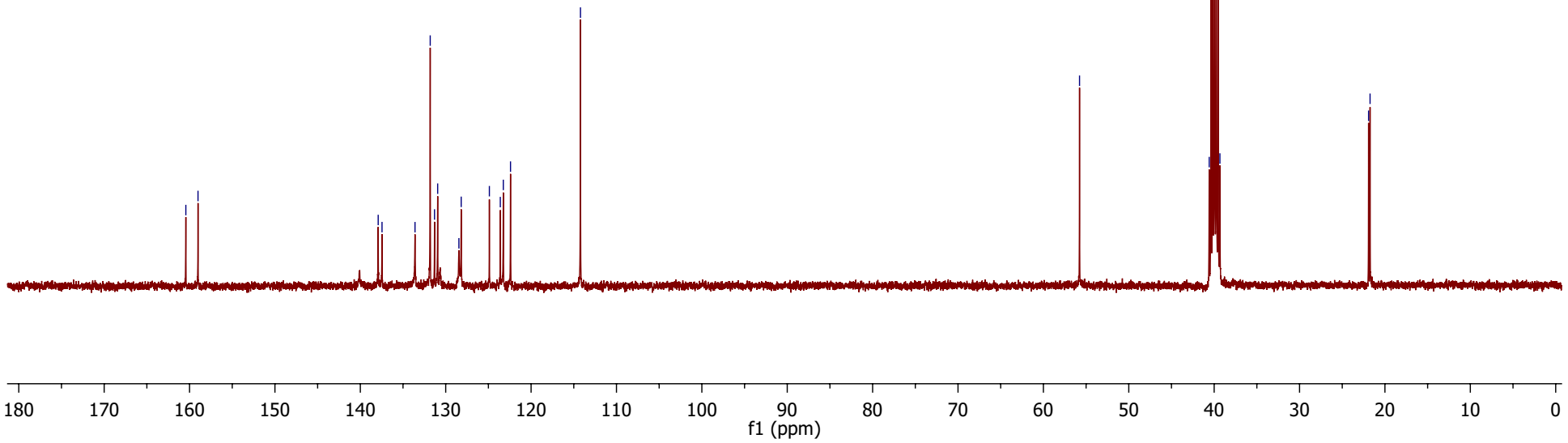
EXTRA SB-80
sb-80

160.43
159.01
137.91
137.46
133.59
131.81
131.31
130.94
128.45
128.19
124.88
123.61
123.25
122.41
114.22
55.77
40.58
40.37
40.16
39.95
39.74
39.54
39.33
21.92
21.74

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

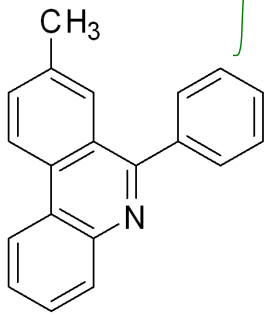


(3n)



Phenenthridine NMR file
sb-94

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

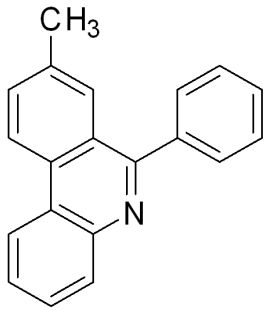


(3o)

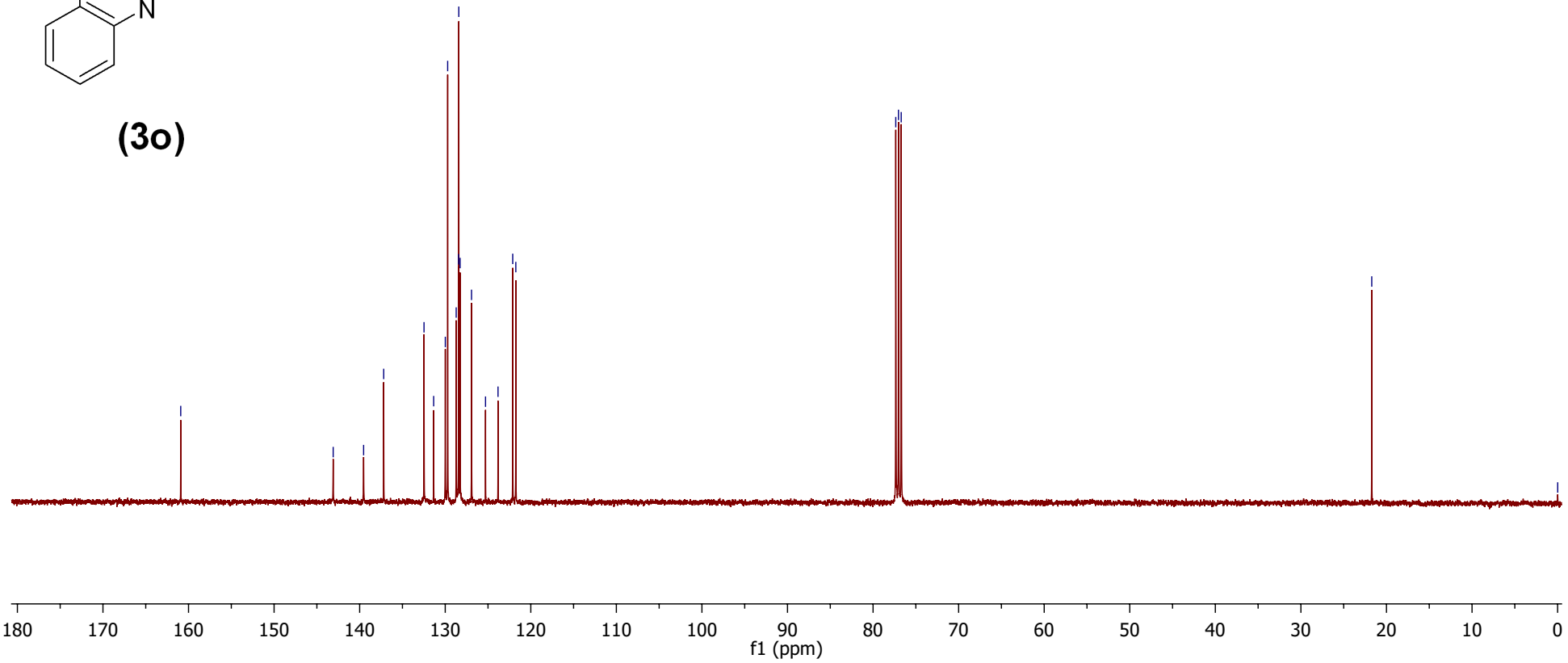
Phenenthridine NMR file
sb-94

160.91
143.09
139.54
137.19
132.48
131.35
129.99
129.71
128.72
128.44
128.41
128.26
126.93
125.29
123.83
122.11
121.75
77.35
77.03
76.71
21.72
-0.01

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

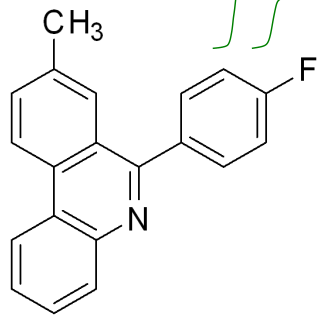


(3o)

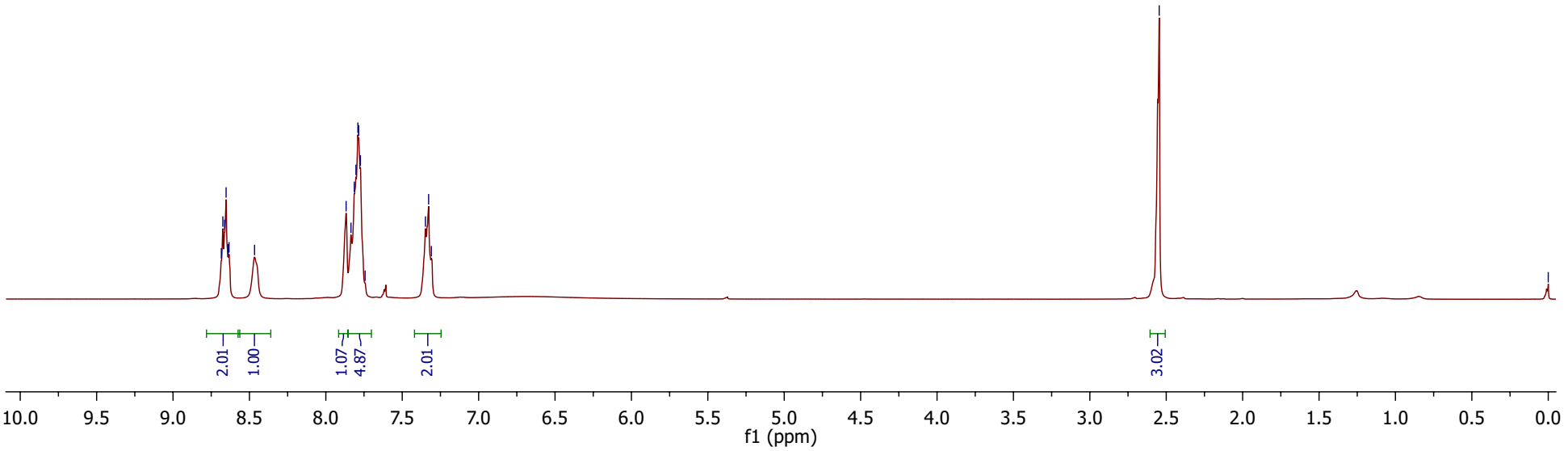


EXTRA SB-95
sb-95

^{1}H NMR (400 MHz, $CDCl_3$ + DMSO d_6)



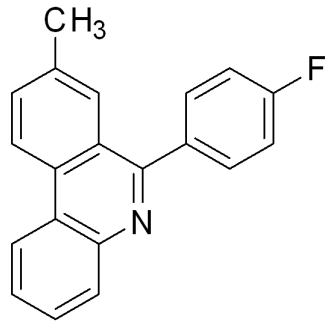
(3p)



EXTRA SB-95
sb-95

164.02 161.54 158.36 139.17 137.62 133.71 131.41 131.32 131.16 128.48 127.83 127.27 126.83 123.72 123.19 121.82 121.40 115.00 114.78 77.35 77.03 76.71 39.86 39.65 39.44 39.23 39.02 38.81 38.61 20.94

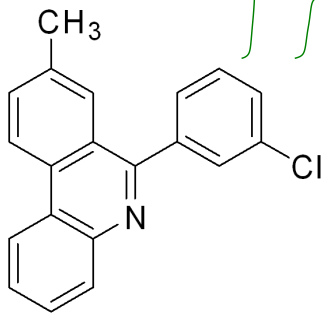
^{13}C NMR (100 MHz, $CDCl_3$ + DMSO d_6)



(3p)

Phenenthridine NMR file
sb-96

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

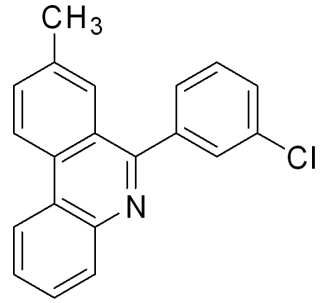


(3q)

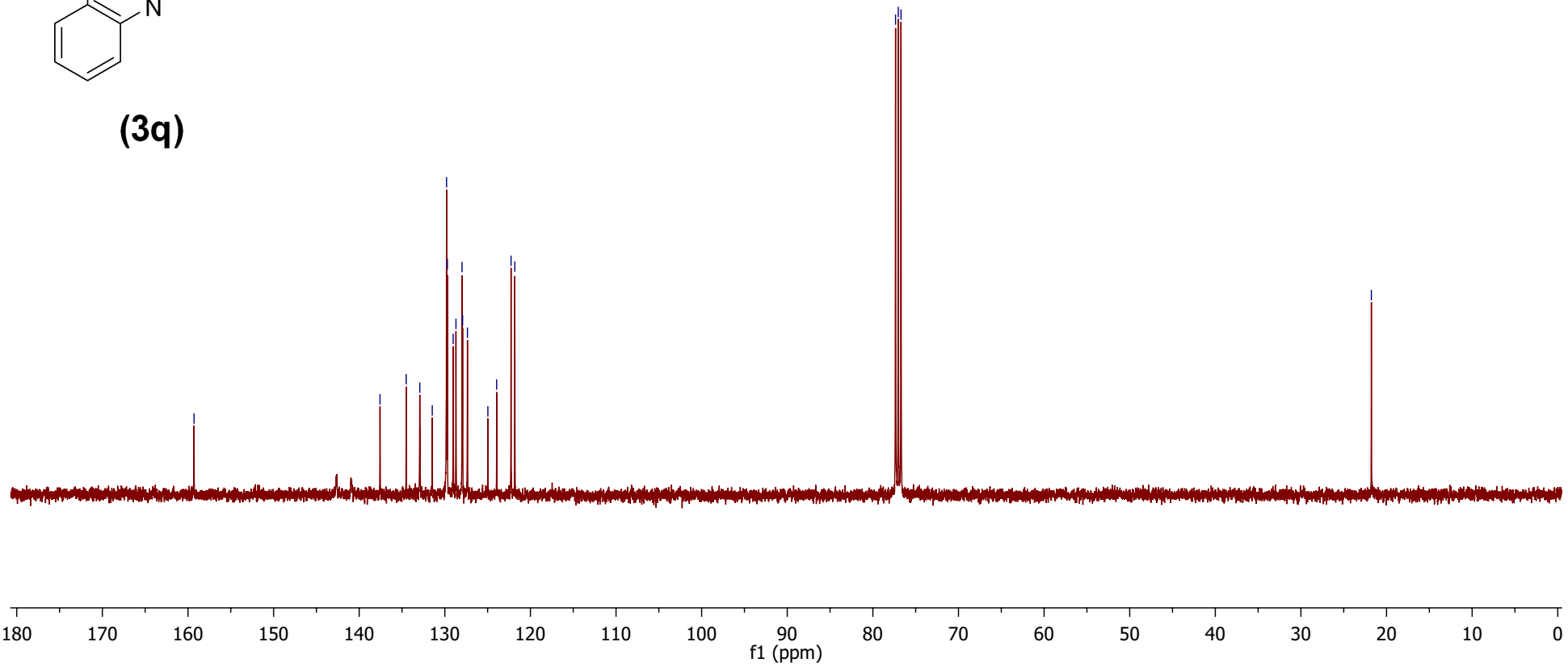
Phenenthridine NMR file
sb-96

159.28
137.57
134.51
132.92
131.47
129.80
129.70
129.02
128.70
127.99
127.92
127.36
124.97
123.94
122.26
121.82
77.35
77.03
76.71
21.77

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

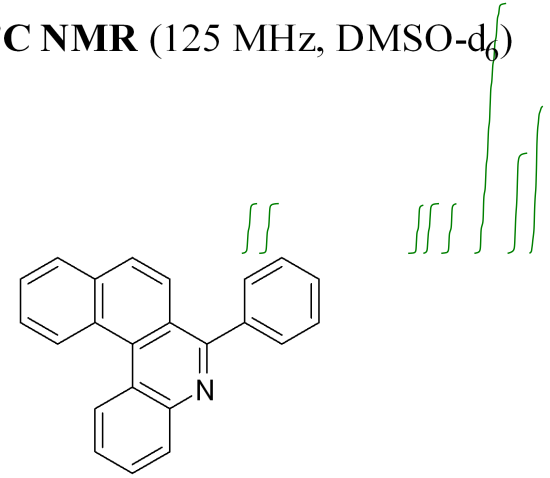


(3q)

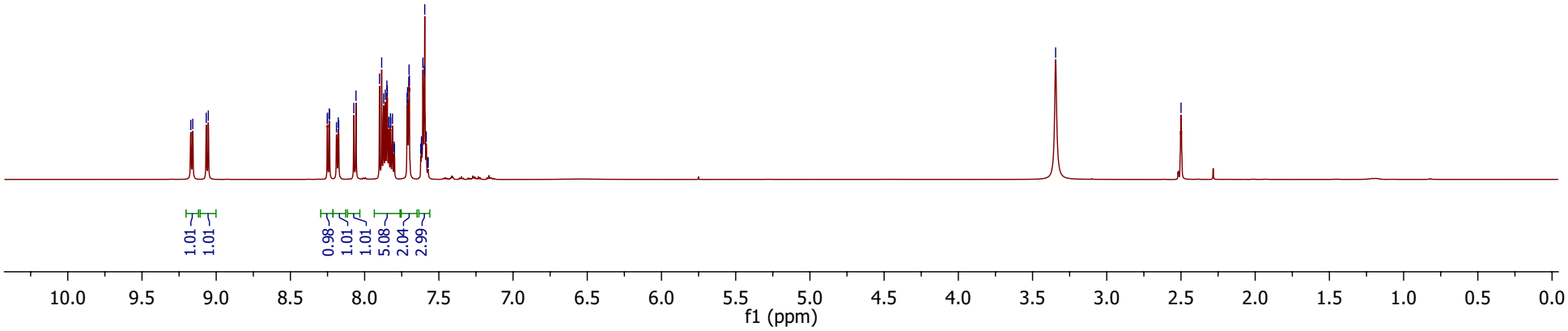


SID105

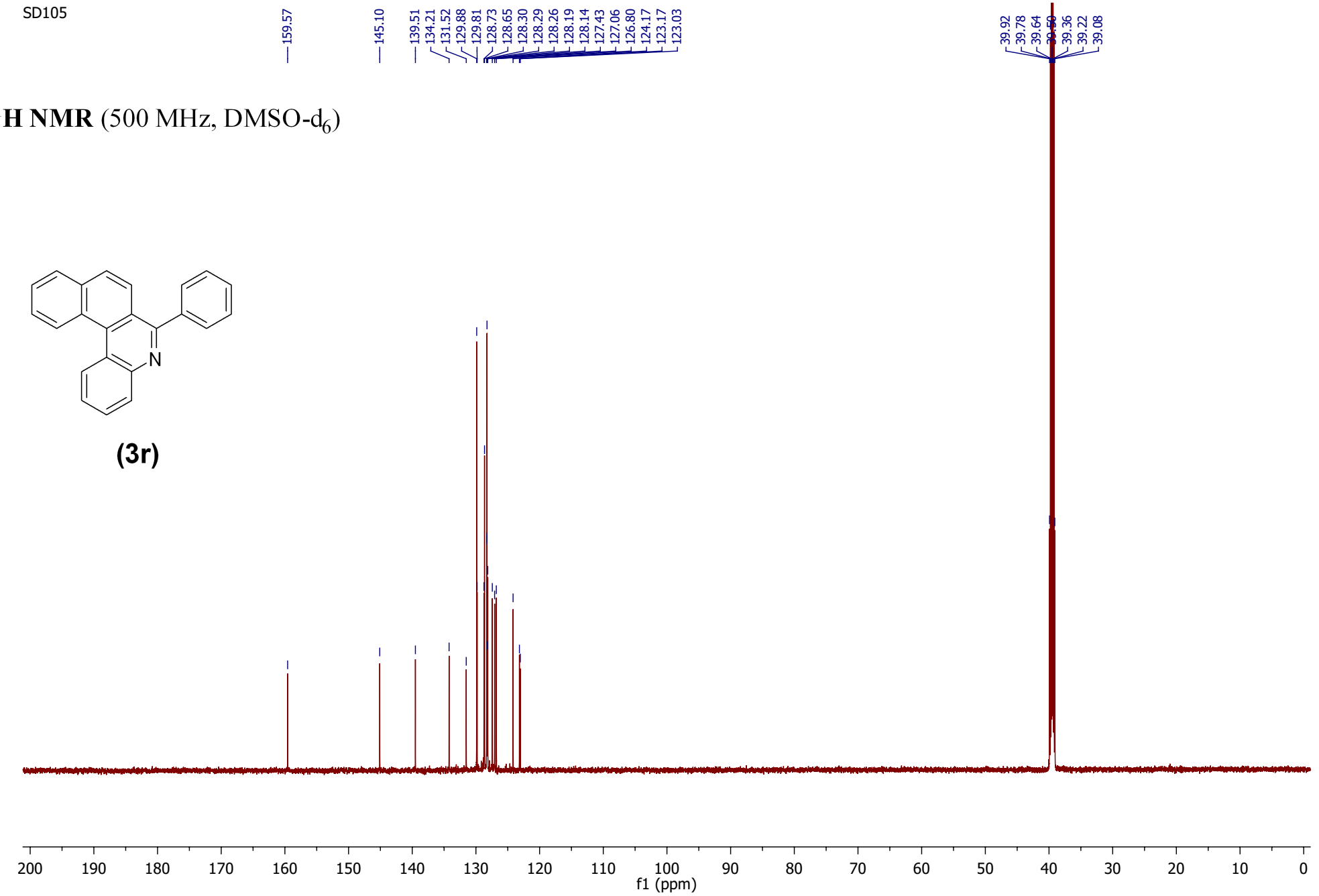
^{13}C NMR (125 MHz, DMSO-d_6)



(3r)



SD105

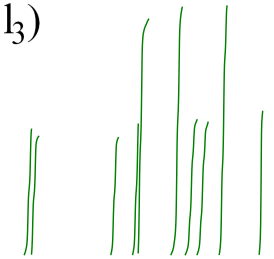


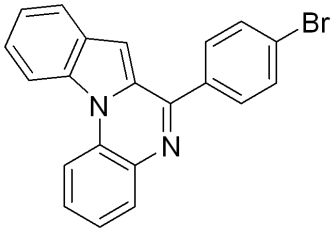
^{1}H NMR (500 MHz, DMSO-d_6)

(3r)

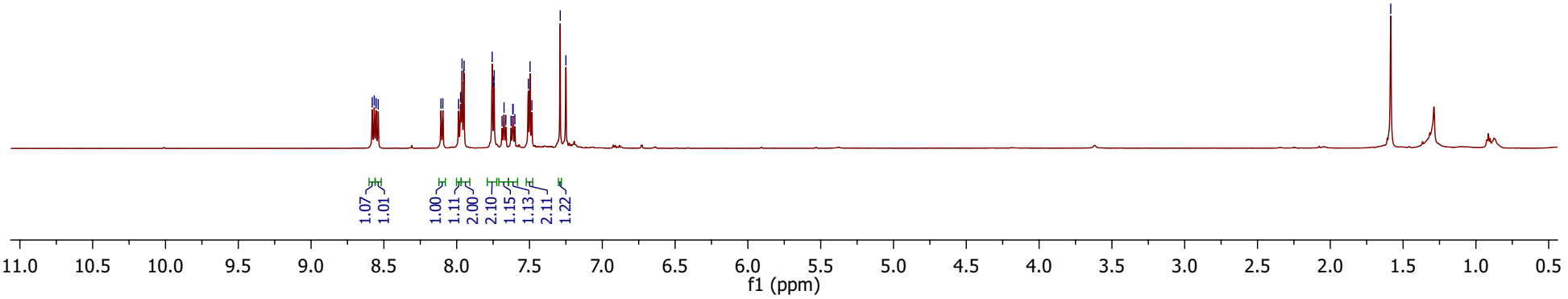
SID-431-021914
SID-431-02192014 1H

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





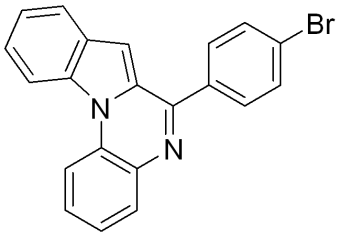
(**3s**)



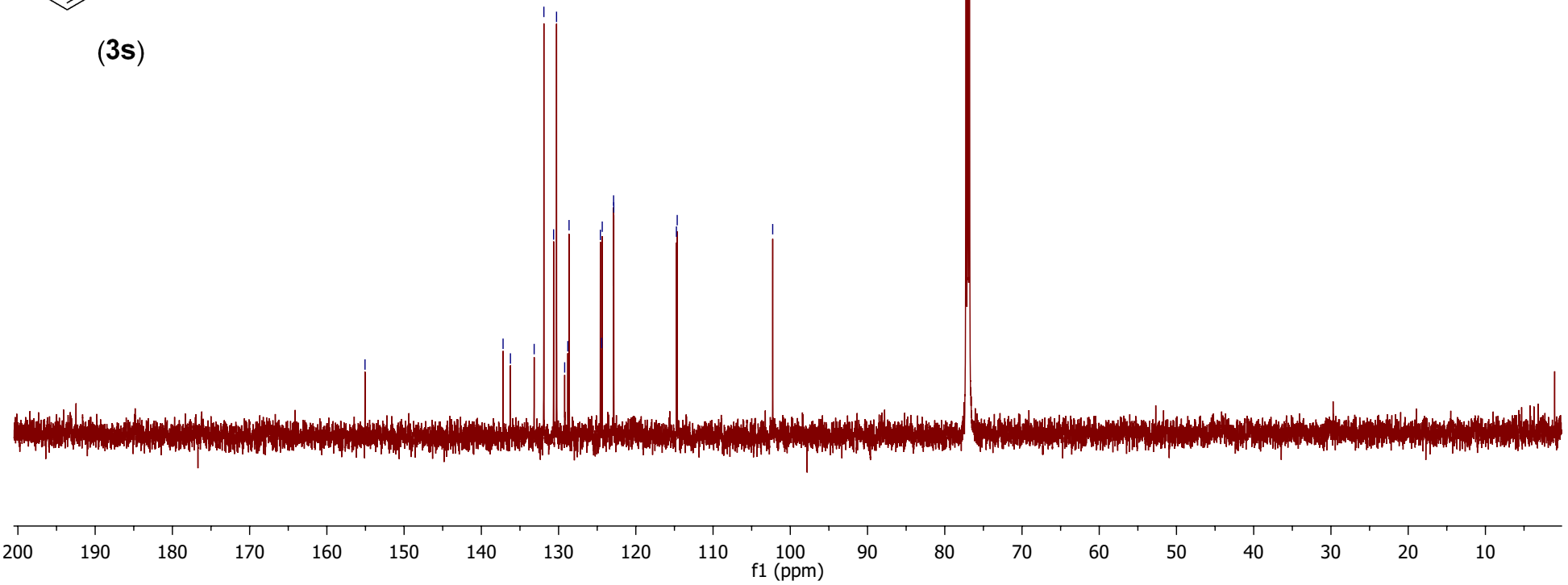
SID-431-021914
SID-431-02192014 1H

155.06
137.19
136.23
133.16
131.90
130.64
130.26
129.21
128.80
128.64
124.59
124.42
124.35
122.88
122.85
114.74
114.64
102.28
77.24
77.03
76.82

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

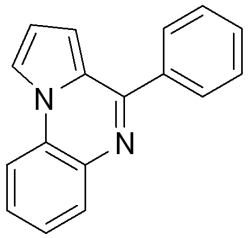


(**3s**)



SID-314-121213
SID-314-121313

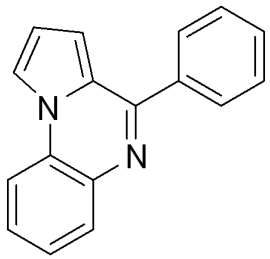
^{1}H NMR (400 MHz, $CDCl_3$)



(3t)

SID-314-121213
SID-314-121313

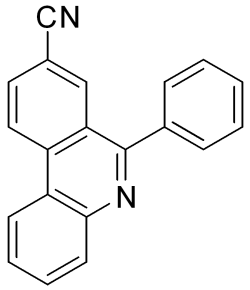
^{13}C NMR (100 MHz, $CDCl_3$)



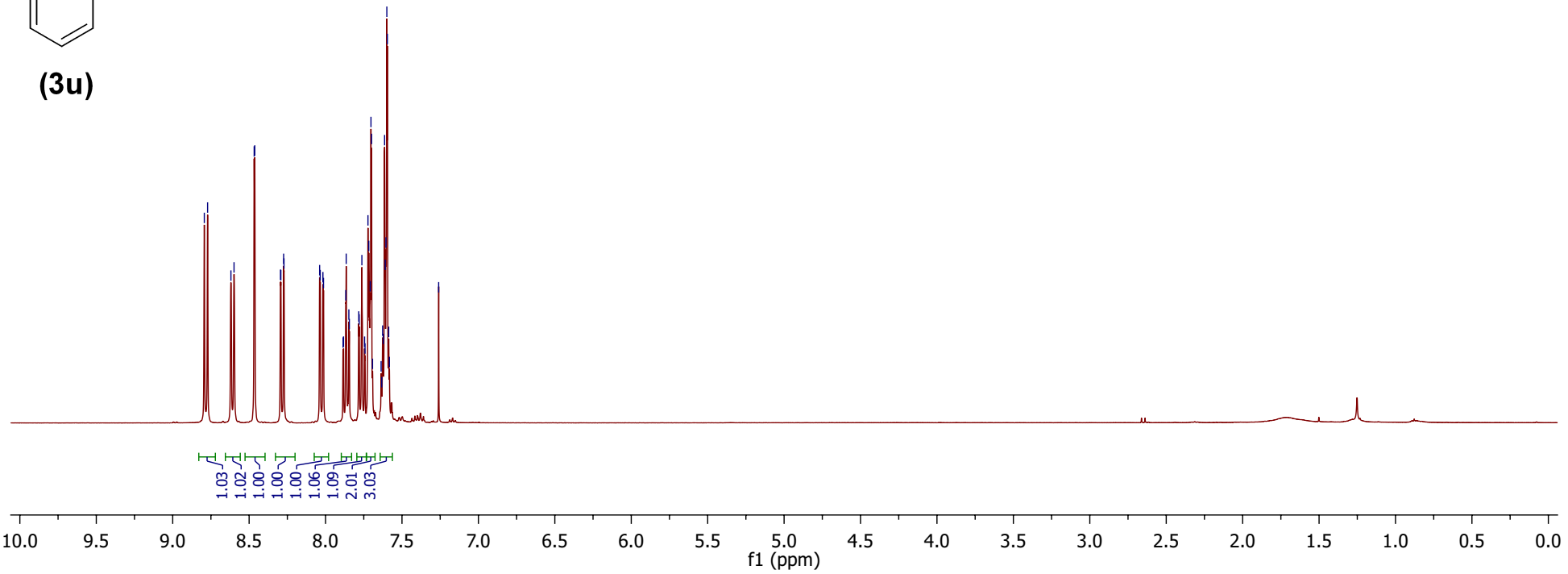
(3t)

22-07-2020
sb-128

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

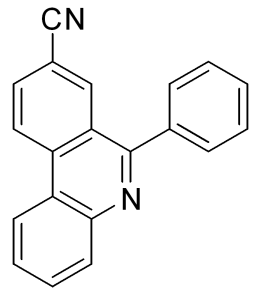


(3u)



22-07-2020
sb-128

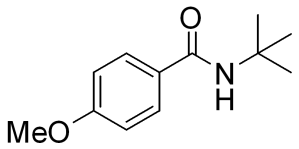
^{13}C NMR (100 MHz, $CDCl_3$)



(3u)

Amide NMR
sid-bk-204

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

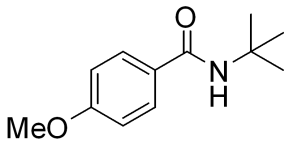


(5a)

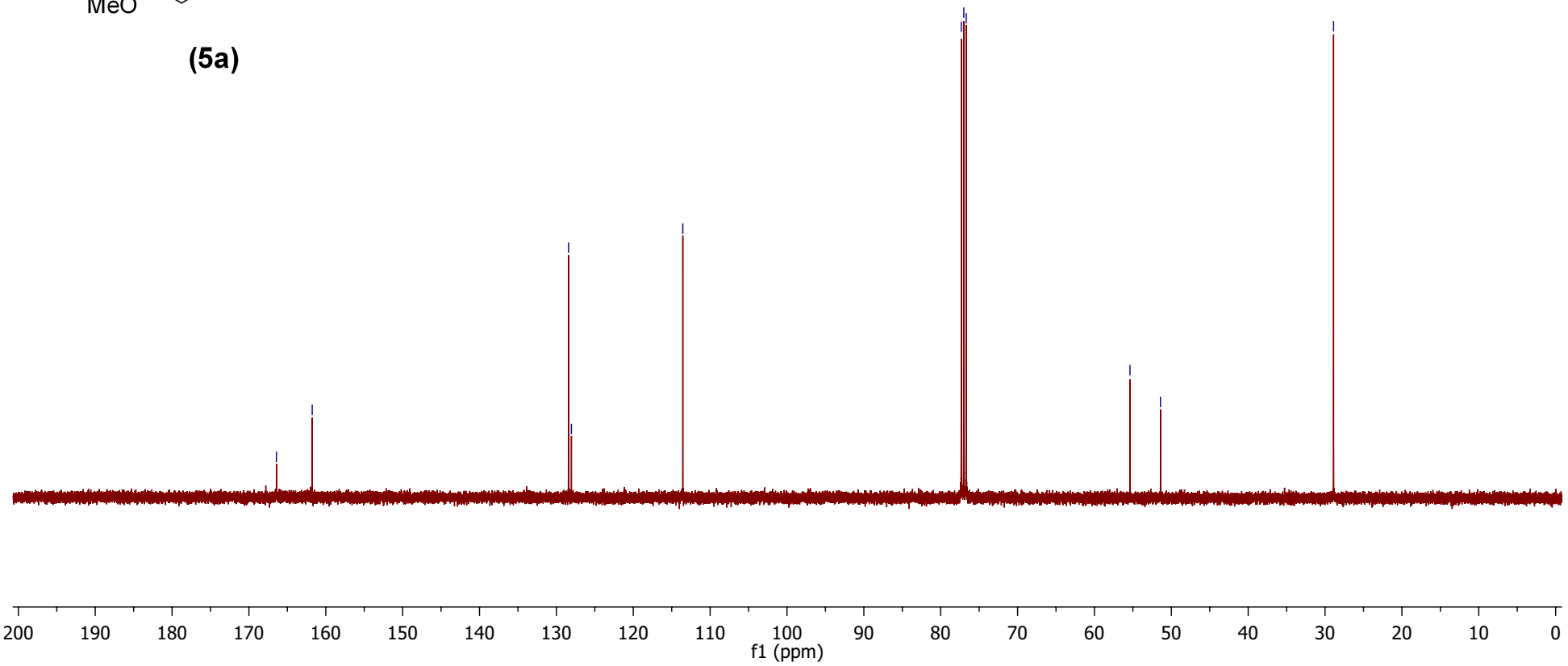
Amide NMR
sid-bk-204

166.42
161.77
128.42
128.05
113.55
77.32
77.00
76.68
55.38
51.41
28.89

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

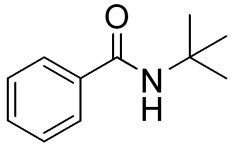


(5a)



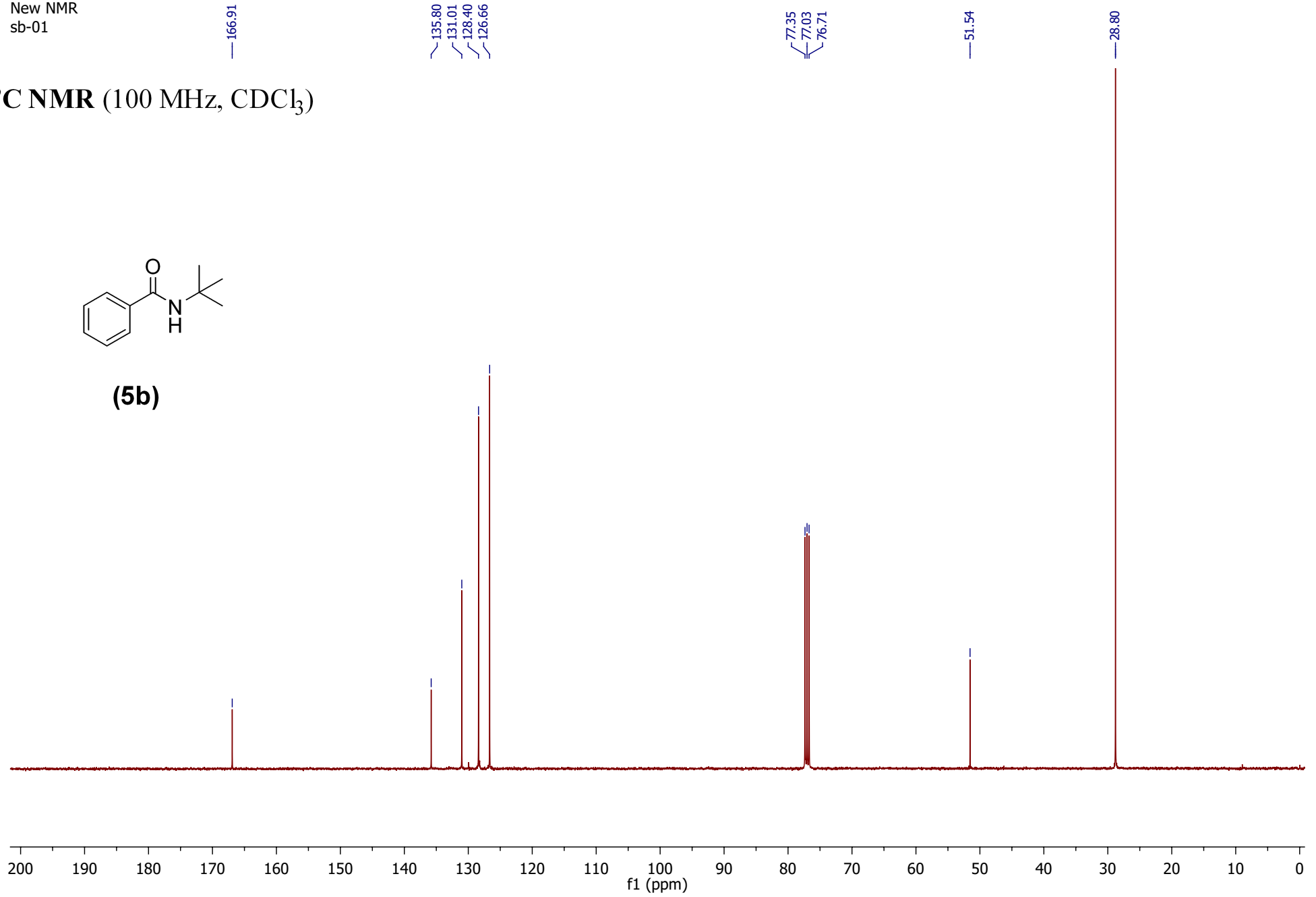
New NMR
sb-01

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



(5b)

New NMR
sb-01

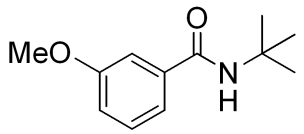


^{13}C NMR (100 MHz, $CDCl_3$)

(5b)

22-07-2020
sb-10

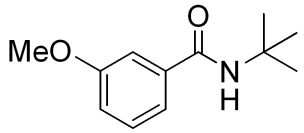
^{1}H NMR (400 MHz, $CDCl_3$)



(5c)

22-07-2020
sb-10

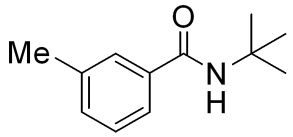
^{13}C NMR (100 MHz, $CDCl_3$)



(5c)

New NMR
sb-15

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

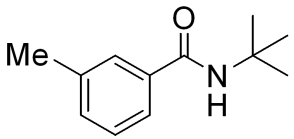


(5d)

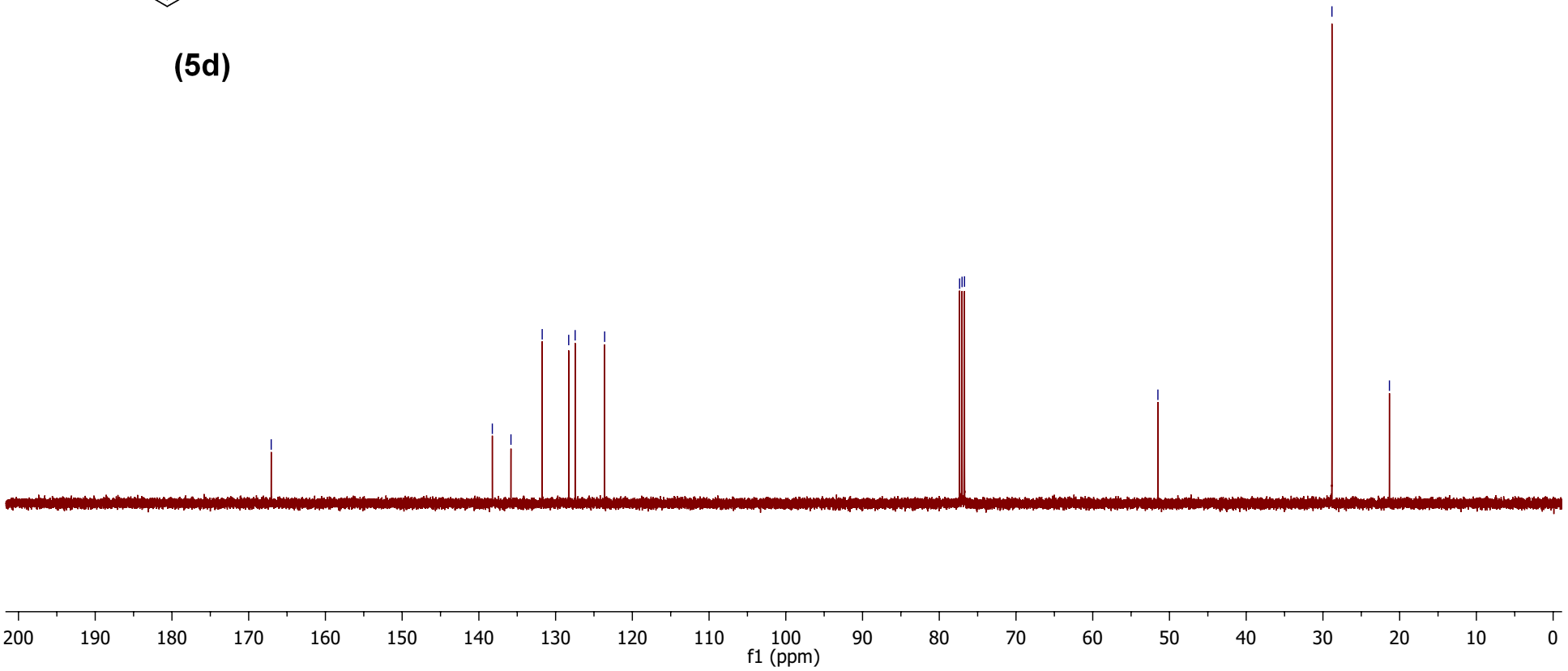
New NMR
sb-15

167.06
138.25
135.82
131.75
128.29
127.45
123.61
77.35
77.03
76.71
51.51
28.82
21.33

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

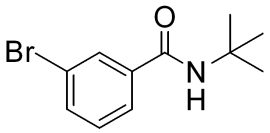


(5d)



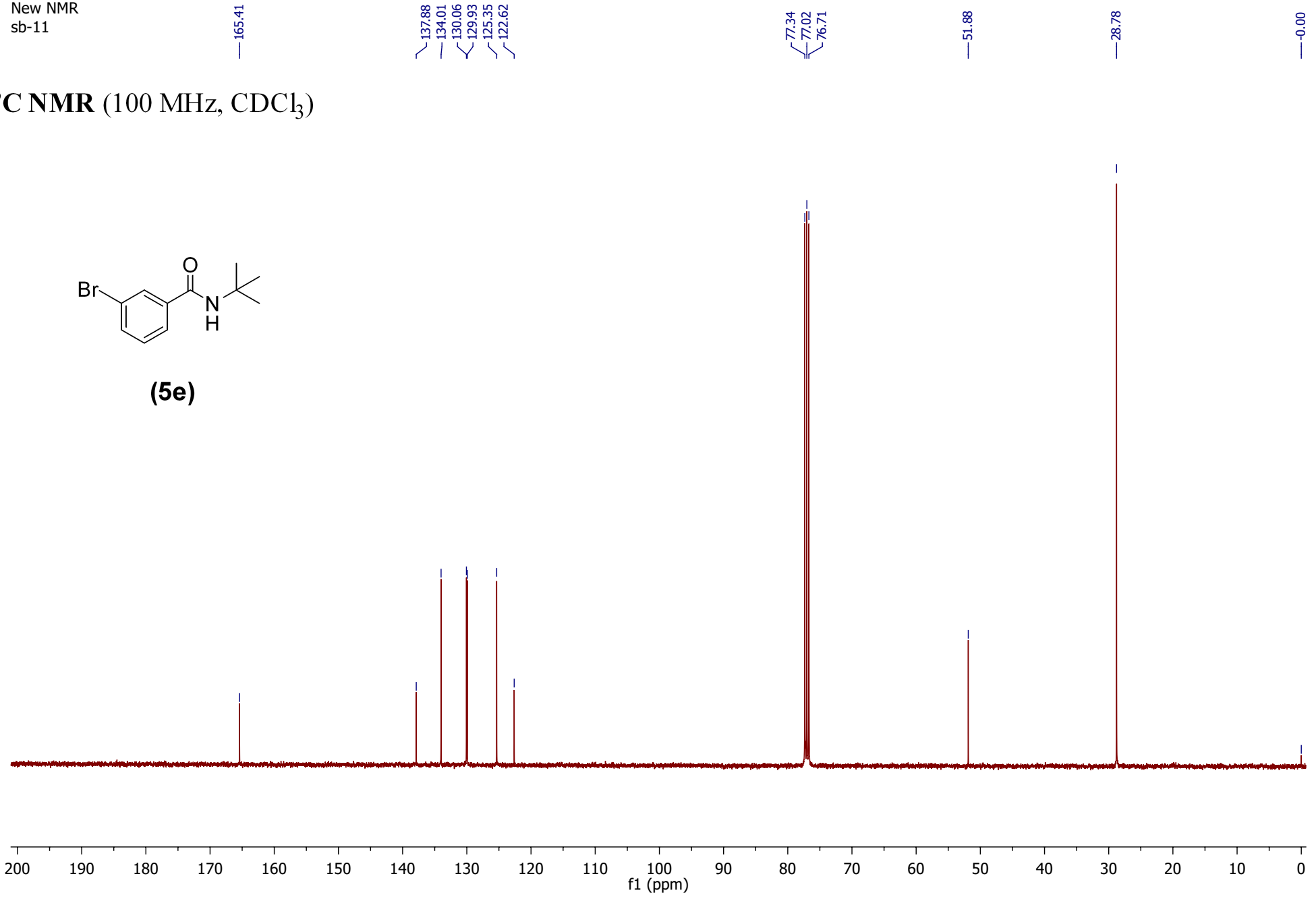
New NMR
sb-11

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



(5e)

New NMR
sb-11

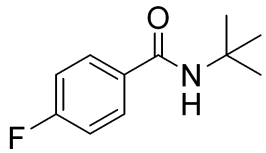


^{13}C NMR (100 MHz, $CDCl_3$)

(5e)

22-07-2020
sb-14

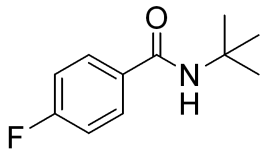
^{1}H NMR (400 MHz, $CDCl_3$)



(5f)

22-07-2020
sb-14

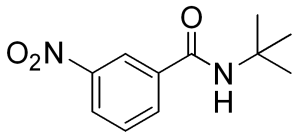
^{13}C NMR (100 MHz, $CDCl_3$)



(5f)

22-07-2020
sb-09

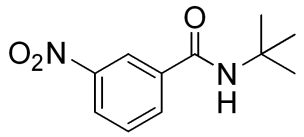
^{1}H NMR (400 MHz, $CDCl_3$)



(5g)

22-07-2020
sb-09

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

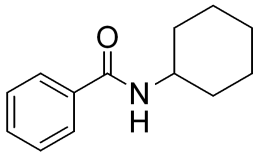


(5g)

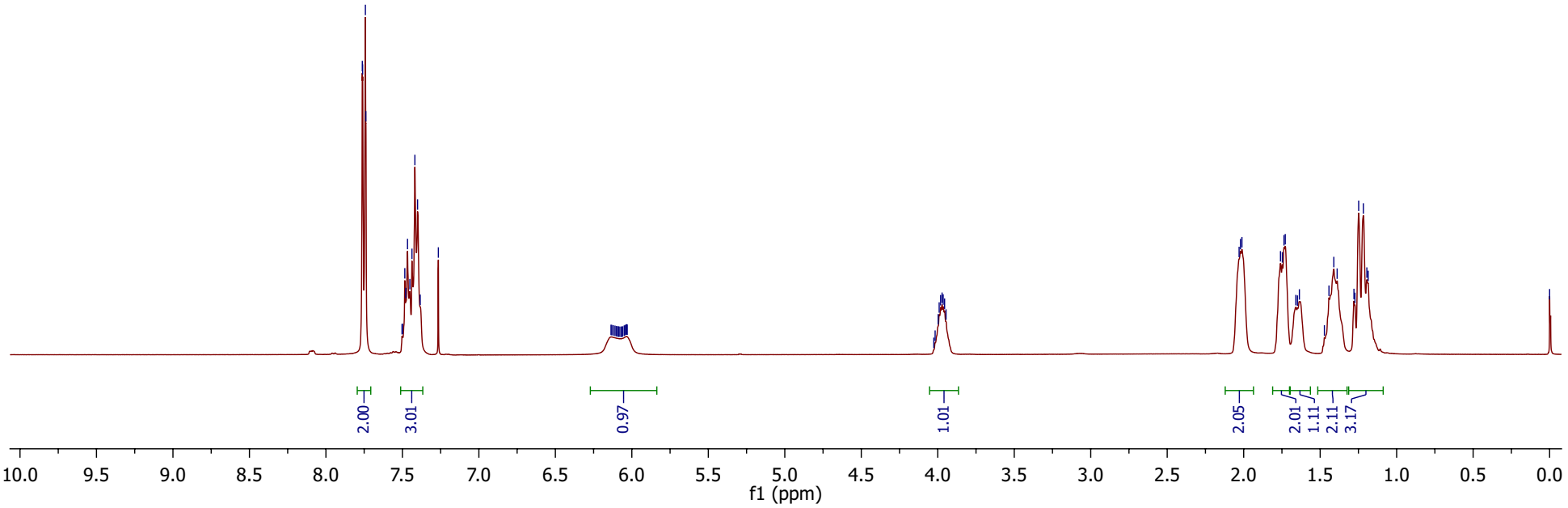
New NMR
sb-03

7.762 7.760 7.742 7.739 7.503 7.499 7.484 7.478 7.467 7.451 7.437 7.418 7.401 7.383 7.265 6.136 6.131 6.121 6.110 6.102 6.093 6.088 6.083 6.072 6.067 6.061 6.050 6.045 6.038 6.033 6.030 4.026 4.017 3.997 3.991 3.981 3.972 3.965 3.955 3.946 2.030 2.021 2.011 1.759 1.747 1.736 1.728 1.636 1.443 1.411 1.389 1.279 1.273 1.248 1.218 1.195 1.186 0.000

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



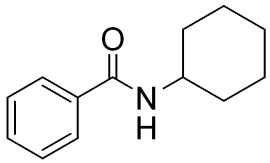
(5h)



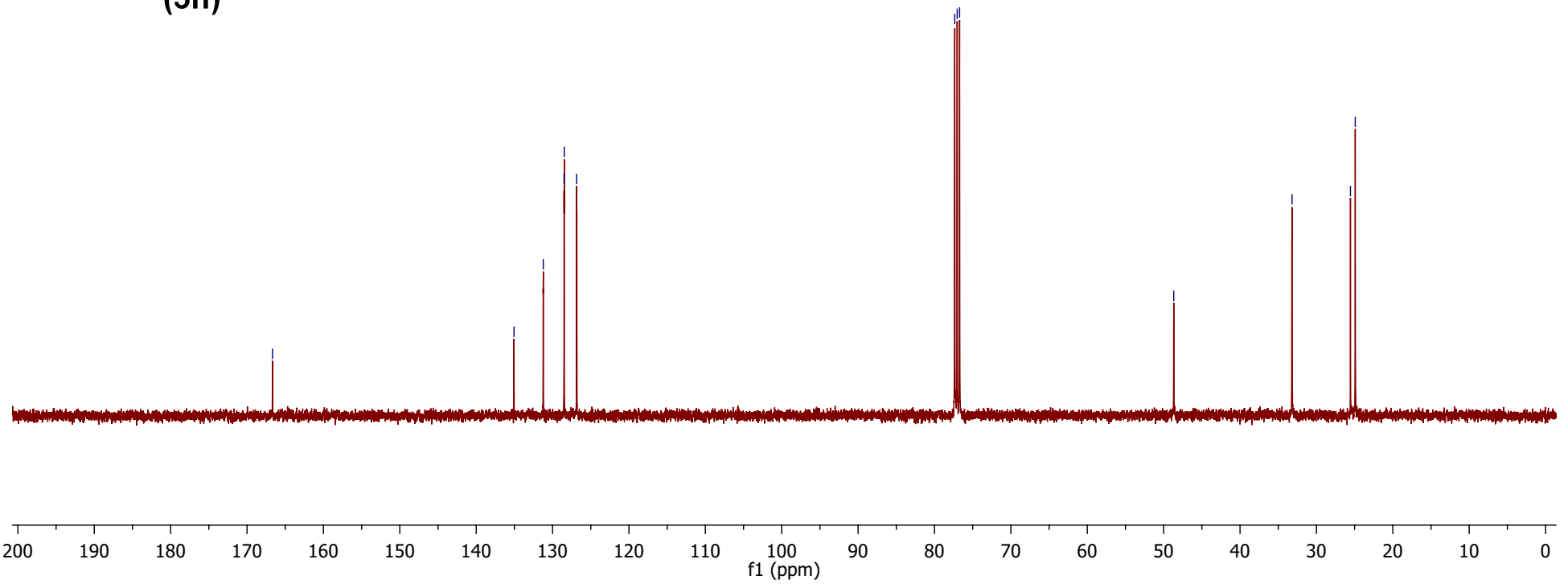
New NMR
sb-03

166.66
135.05
131.21
128.50
128.47
126.85
77.35
77.03
76.71
48.68
33.19
25.54
24.92

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

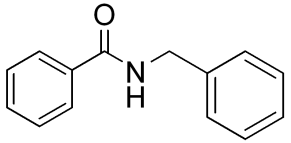


(5h)



New NMR
sb-04

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

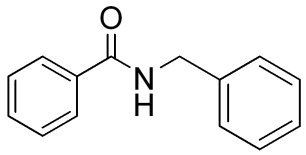


(5i)

New NMR
sb-04

167.38
138.17
134.33
131.53
128.76
128.57
127.89
127.58
126.96
77.35
77.03
76.71
44.08

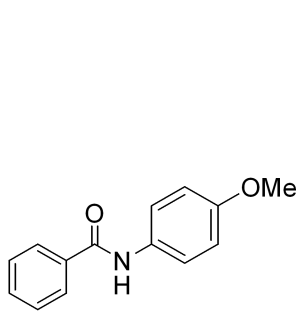
^{13}C NMR (100 MHz, $CDCl_3$)



(5i)

New NMR
sb-05

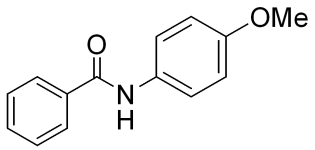
^{1}H NMR (400 MHz, $CDCl_3$)



(5j)

New NMR
sb-05

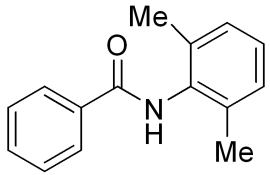
^{13}C NMR (100 MHz, $CDCl_3$)



(5j)

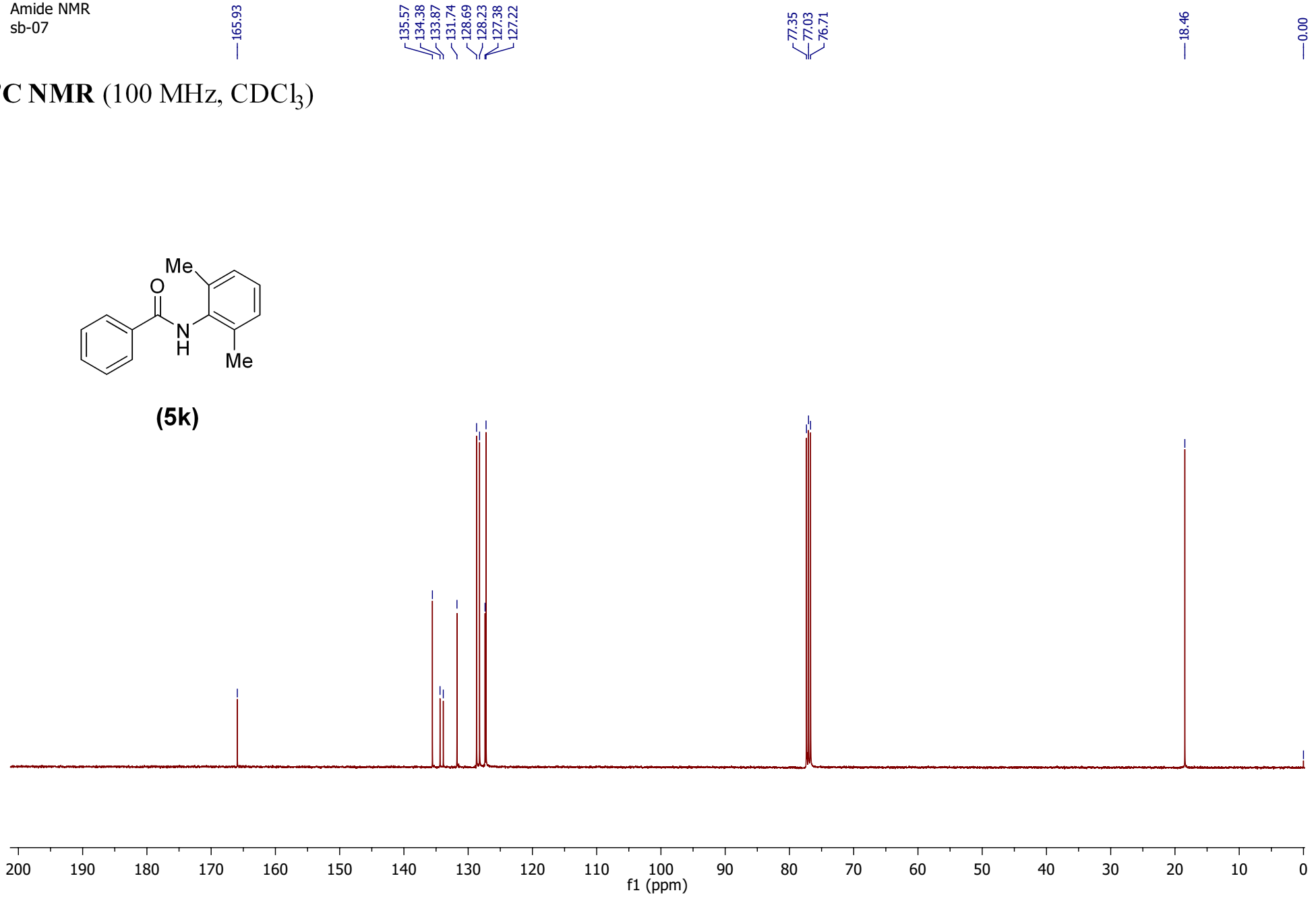
Amide NMR
sb-07

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



(5k)

Amide NMR
sb-07

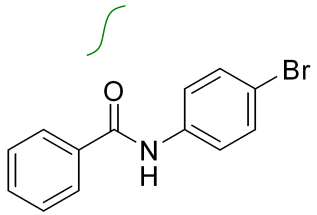


^{13}C NMR (100 MHz, $CDCl_3$)

(5k)

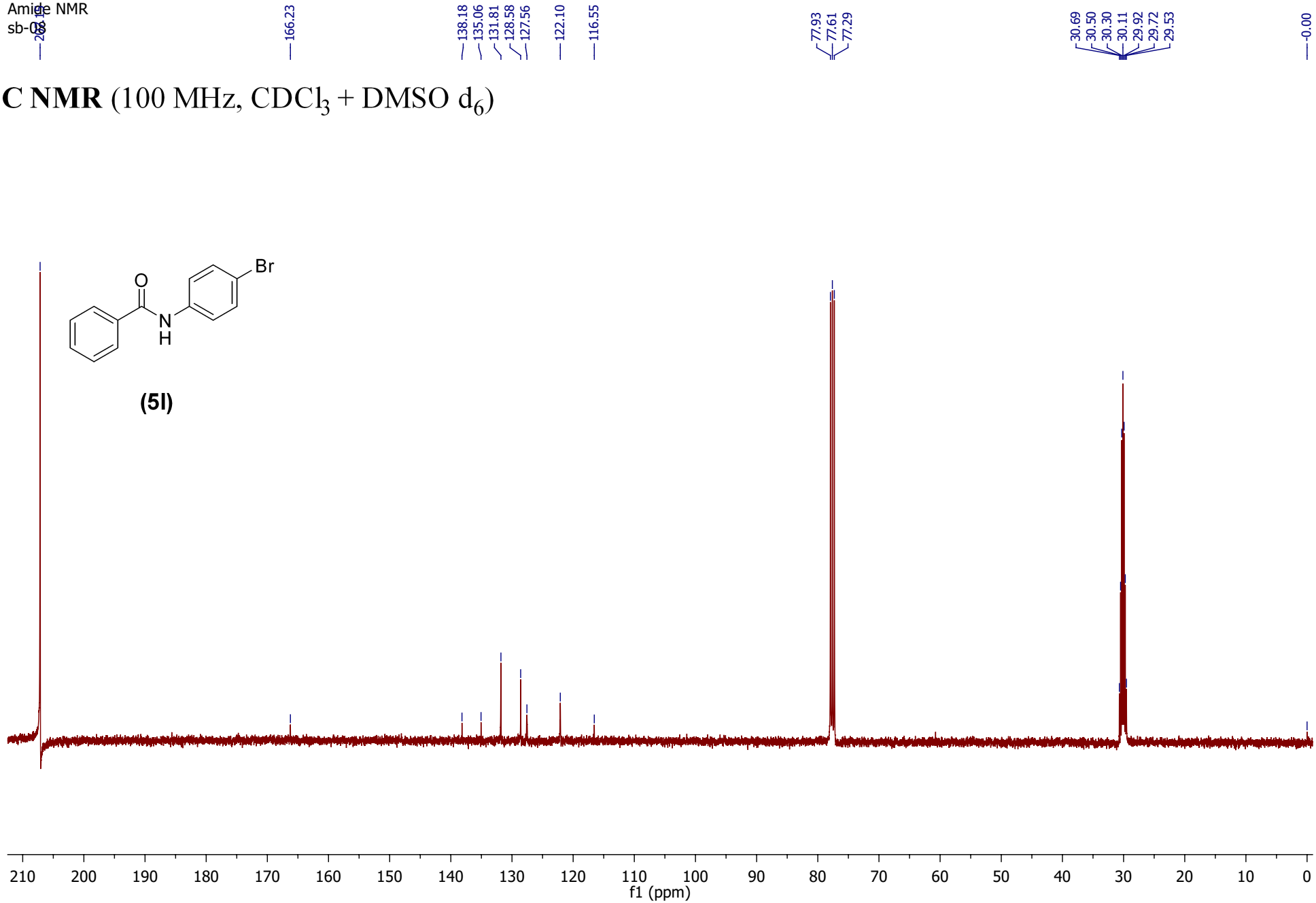
Amide NMR
sb-08

^{1}H NMR (400 MHz, $CDCl_3$ + DMSO d_6)



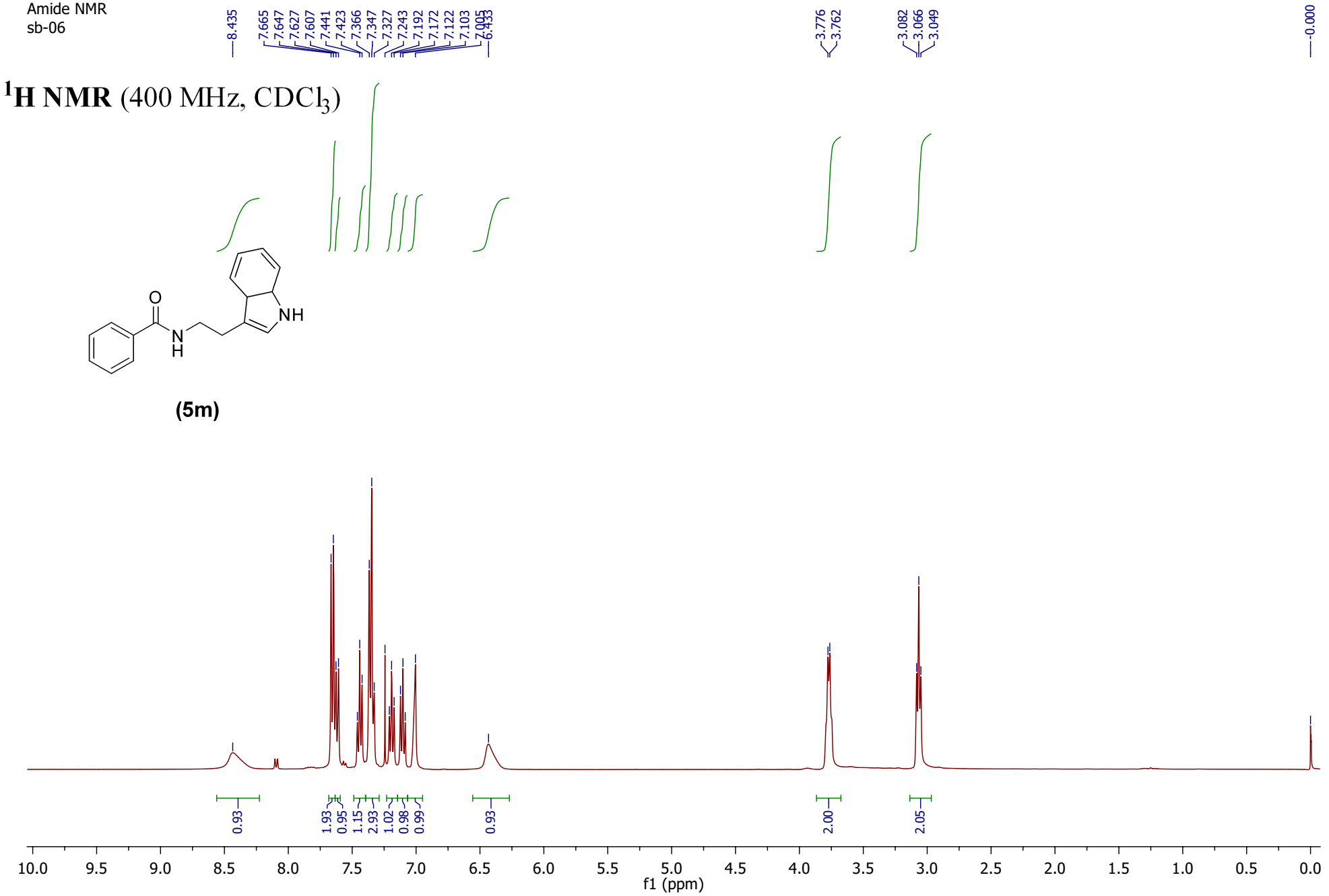
(5l)

Amide NMR
sb-08



^{13}C NMR (100 MHz, $CDCl_3$ + DMSO d_6)

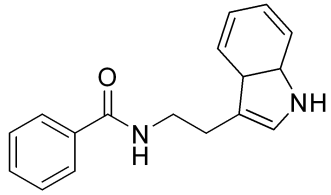
Amide NMR
sb-06



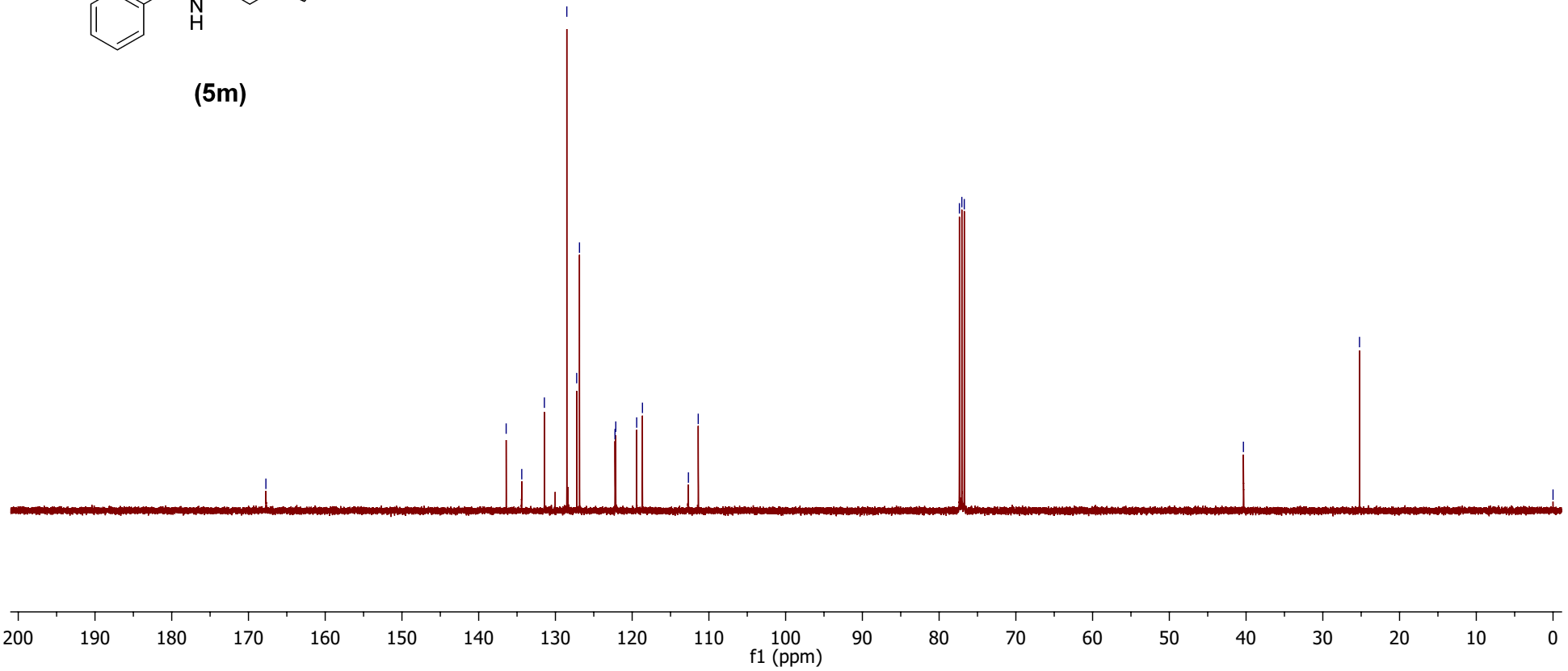
Amide NMR
sb-06

167.73
136.42
134.39
131.44
128.52
127.23
126.87
122.24
122.13
119.41
118.66
112.67
111.39
77.36
77.04
76.72
40.35
25.22
0.00

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

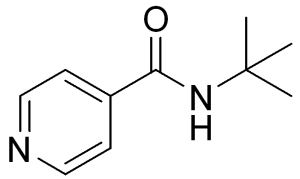


(5m)



NJC
bb-38

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

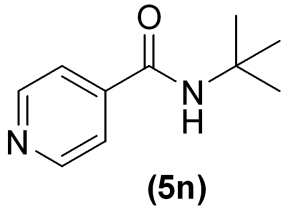


(5n)

NJC
bb-38

164.83
150.29
142.82
120.74
77.32
77.00
76.68
52.03
28.59

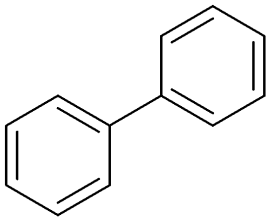
^{13}C NMR (100 MHz, $CDCl_3$)



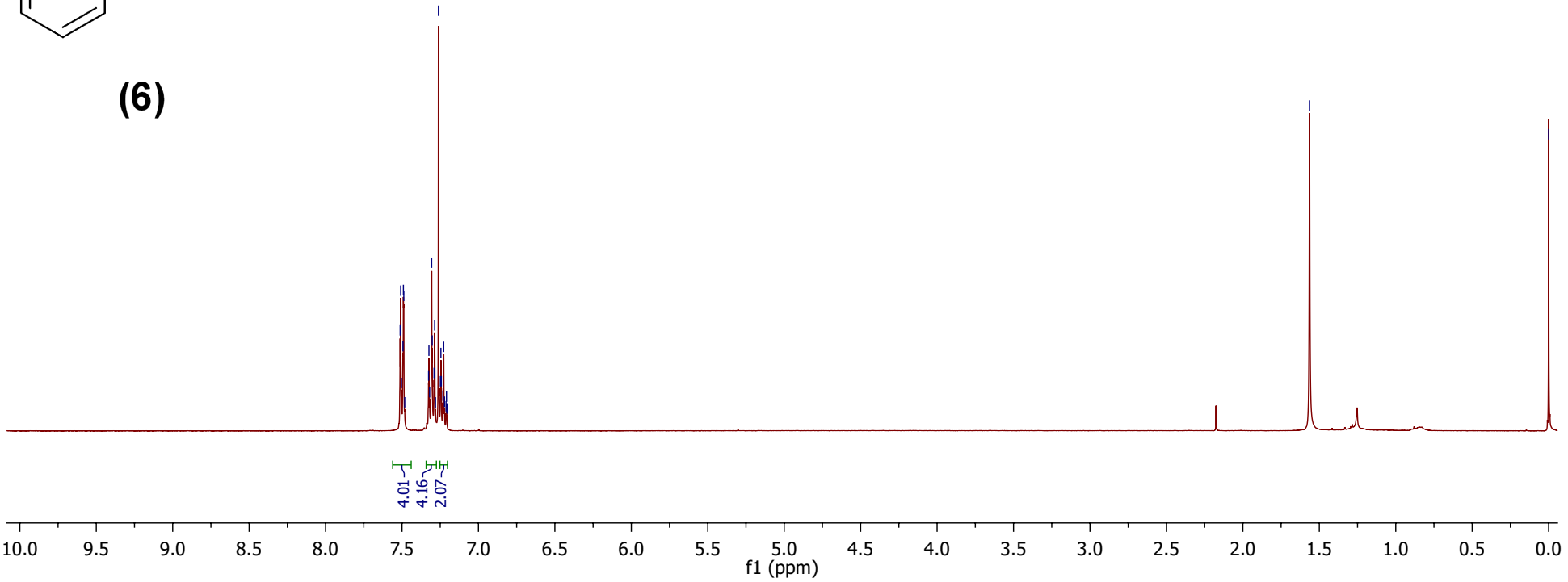
(5n)

NMR july 2019
sb-47

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

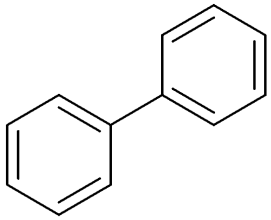


(6)

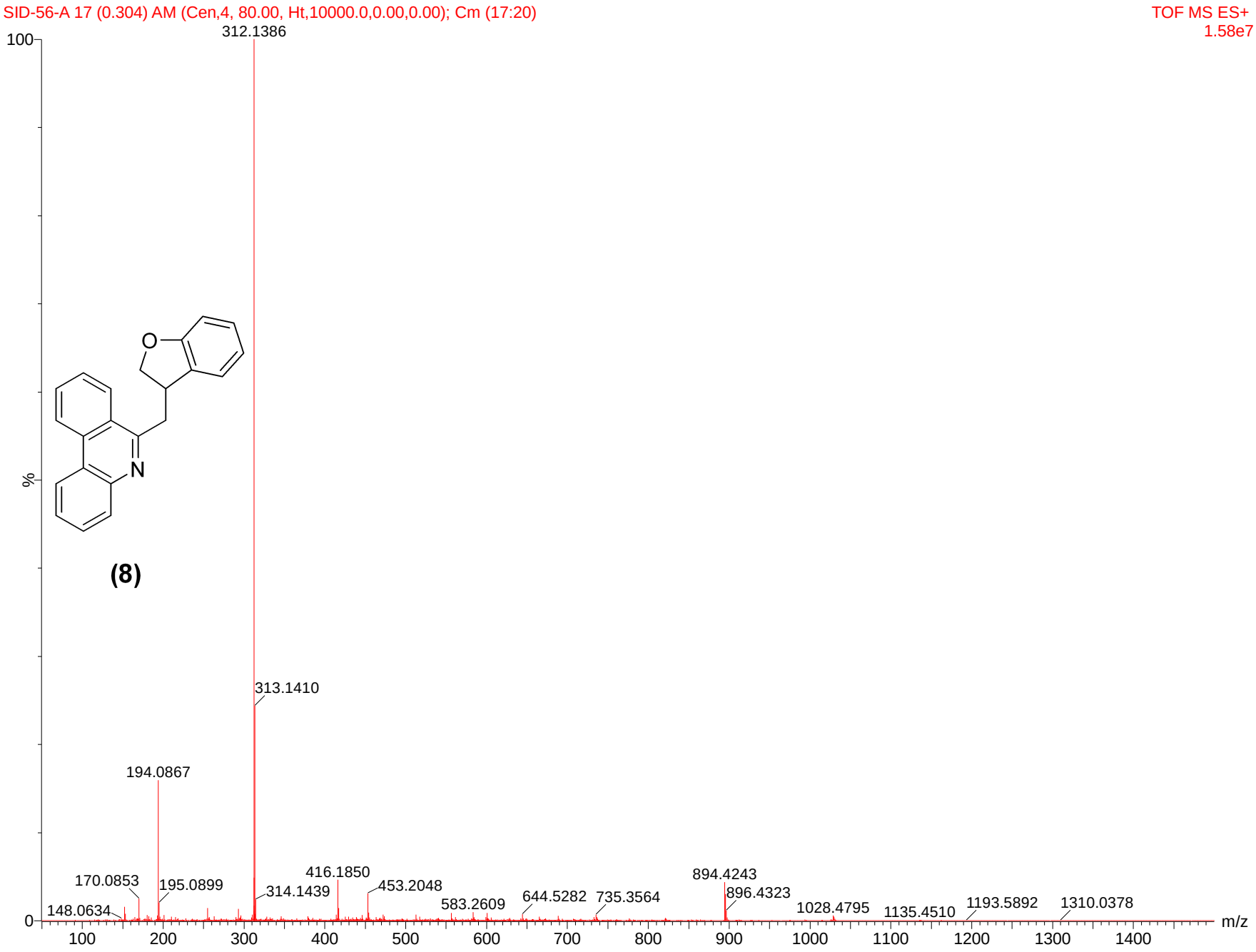


NMR july 2019
sb-47

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



(6)


SID-56-A 17 (0.304) AM (Cen,4, 80.00, Ht,10000.0,0.00,0.00); Cm (17:20)
TOF MS ES+
1.58e7
100
%
0
312.1386
313.1410
194.0867
170.0853
195.0899
148.0634
314.1439
416.1850
453.2048
583.2609
644.5282
735.3564
894.4243
896.4323
1028.4795
1135.4510
1193.5892
1310.0378
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
O
N
(8)