Supporting Information

NNB-Type Tridentate Boryl Ligands Enabling a Highly Active Iridium-catalyst for C–H Borylation

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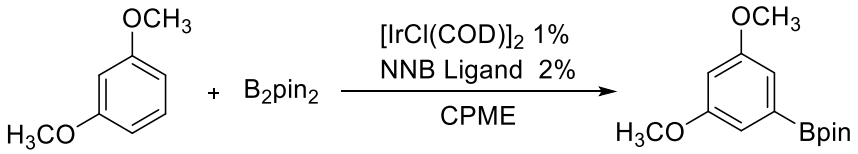
1. NNB-Type Tridentate Boryl Ligands Enabling a Highly Active Iridium-catalyst for C–H Borylation

1.1 Optimization Reactions

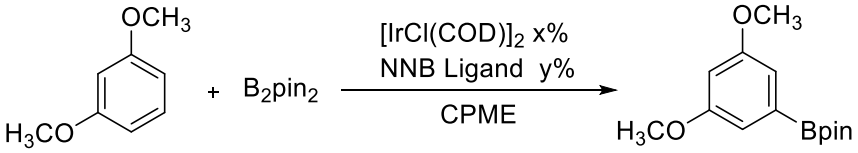
Table S1. Ir-NNB ligand catalytic system for aryl borylation *via* C–H bond cleavage



NNB ligand	B_2pin_2(eq.)	Reaction temperature	Reaction time	Yield (NMR)[b]
1 (L1)	1.0	100	3h	94%(90%[c])
2 (L1)	0.5	100	3h	64%
3 (L1)	0.6	100	3h	68%
4 (L1)	0.7	100	3h	71%
5 (L1)	0.8	100	3h	82%
6 (L1)	1.1	100	3h	86%
7 (L1)	1.0	100	0.5h	25%
8 (L1)	1.0	100	1h	82%
9 (L1)	1.0	100	2h	89%
10 (L1)	1.0	80	3h	66%
11 (L2)	1.0	100	3h	90%
12 (L3)	1.0	100	3h	82%

[a] Reaction conditions：1,3-dimethoxylbenzene (0.2 mmol), NNB ligand (4 μmol, 2.0 mmol%), $[Ir(Cl)(COD)]_2$ (2 μmol, 1.0 mmol%) and $(Bpin)_2$ (x mmol), solvent 0.5 mL, 2 hours; [b] NMR yield using tridecane as internal standard.

Table 4-2 Screening for the optimal reaction conditions via the Ir-NNB ligand catalytic system

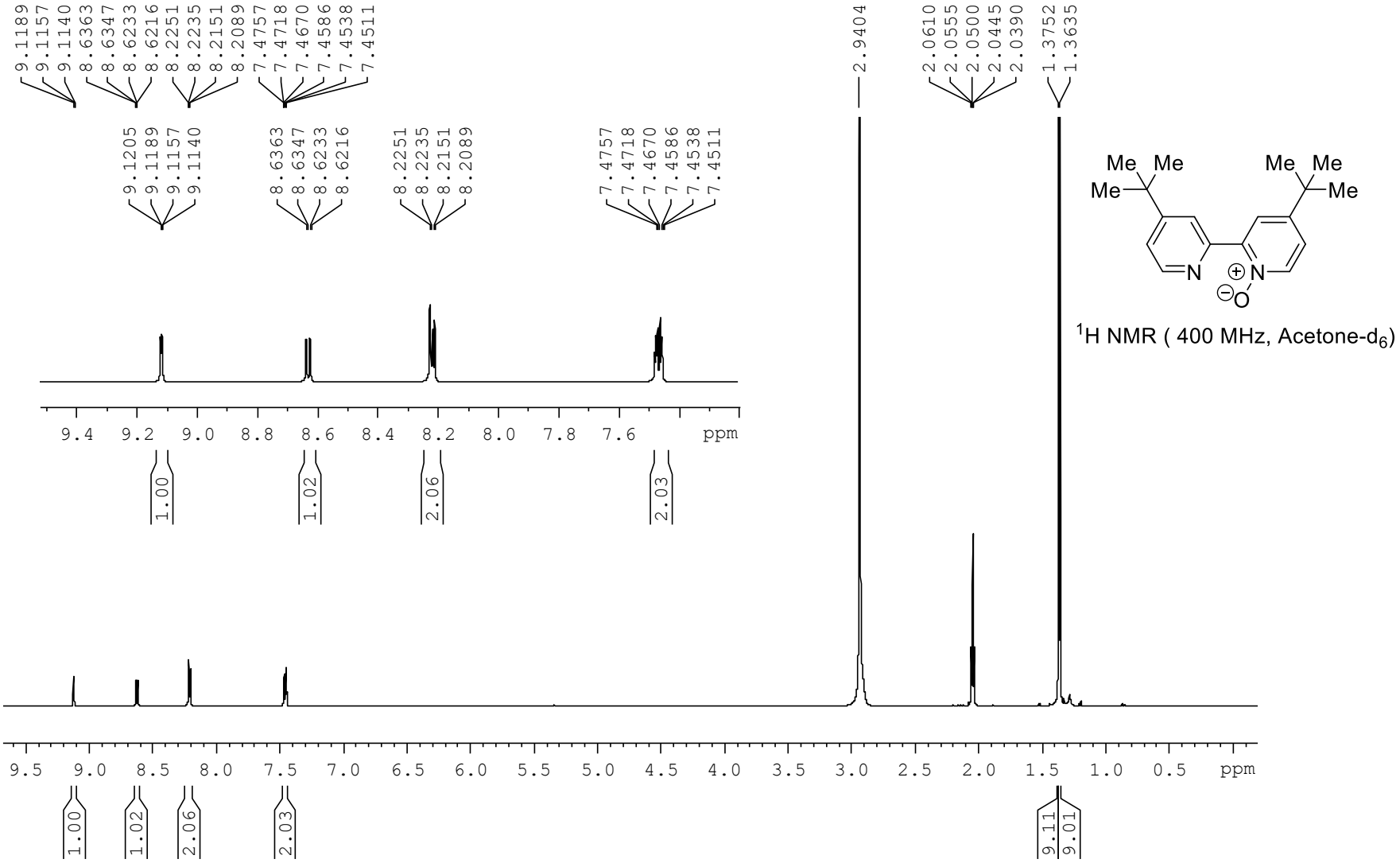


Entry	[Ir] x %	NNB ligand y %	Reaction time	Yield (NMR)[b]
1	0.1	0.2	3	60
2	0.1	0.2	6	70
3	0.1	0.2	18	90
4	0.2	0.4	3	80
5	0.2	0.4	6	95
6	0.2	0.4(dtbpy)	3	72

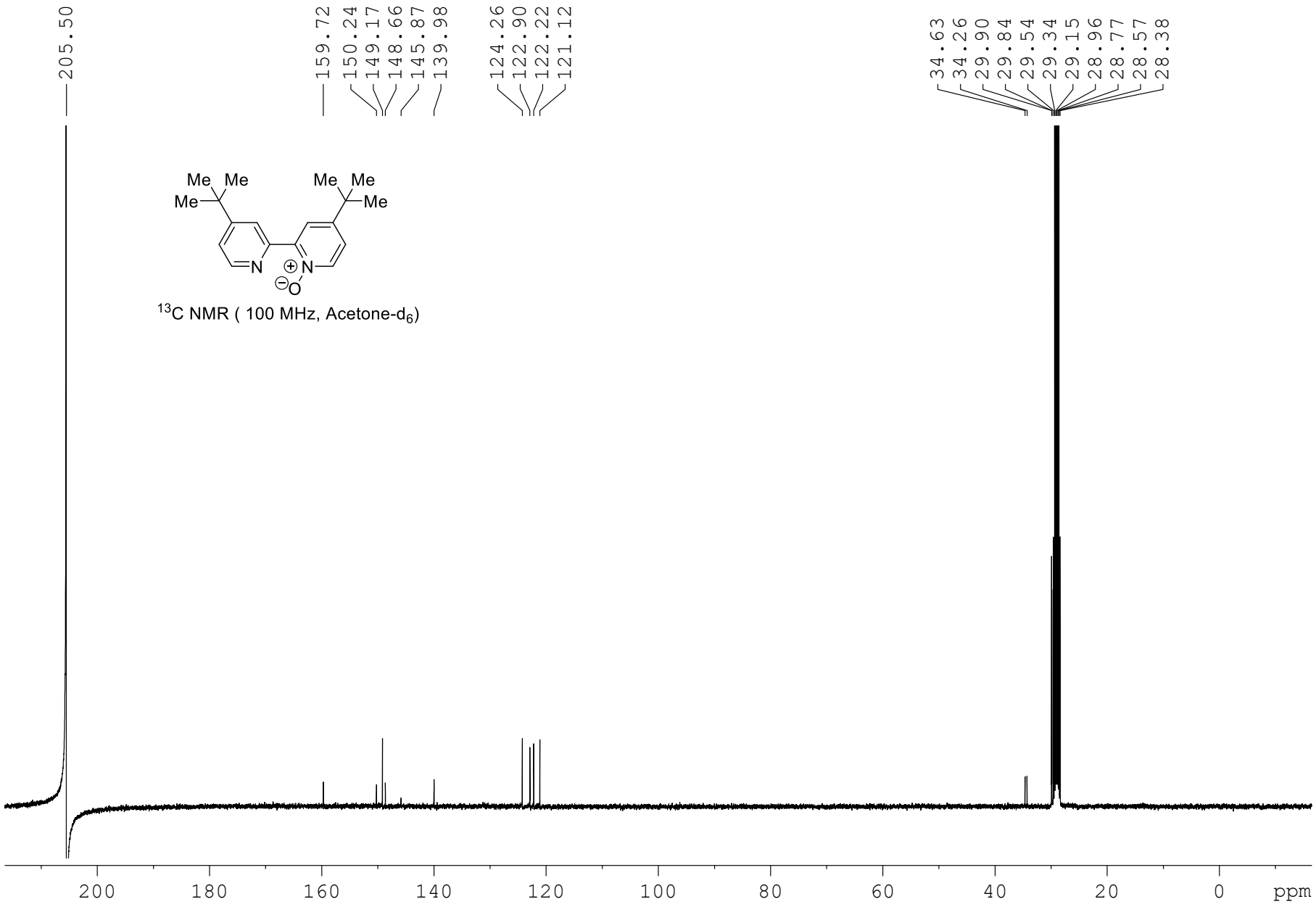
Entry	[Ir] x %	NNB ligand y %	Reaction time	Yield (NMR)[b]
7	0.2	0.4(phen)	3	90
8	0.2	0.4(me-phen)	3	94

[a] Reaction conditions：1,3-dimethoxylbenzene (2 mmol), NNB ligand (y mmol%), $[Ir(Cl)(COD)]_2$ (x mmol%) and $(Bpin)_2$ (2 mmol), solvent 0.5 mL, 2 hours; [b]NMR yield using tridecane as internal standard; dtbpy: 4,4'-di^{t}butyl-2,2'-bipyridine; Phen: 1,10-phenanthroline; me-phen: 3,4,7,8-tetramethyl-1,10-phenanthroline.

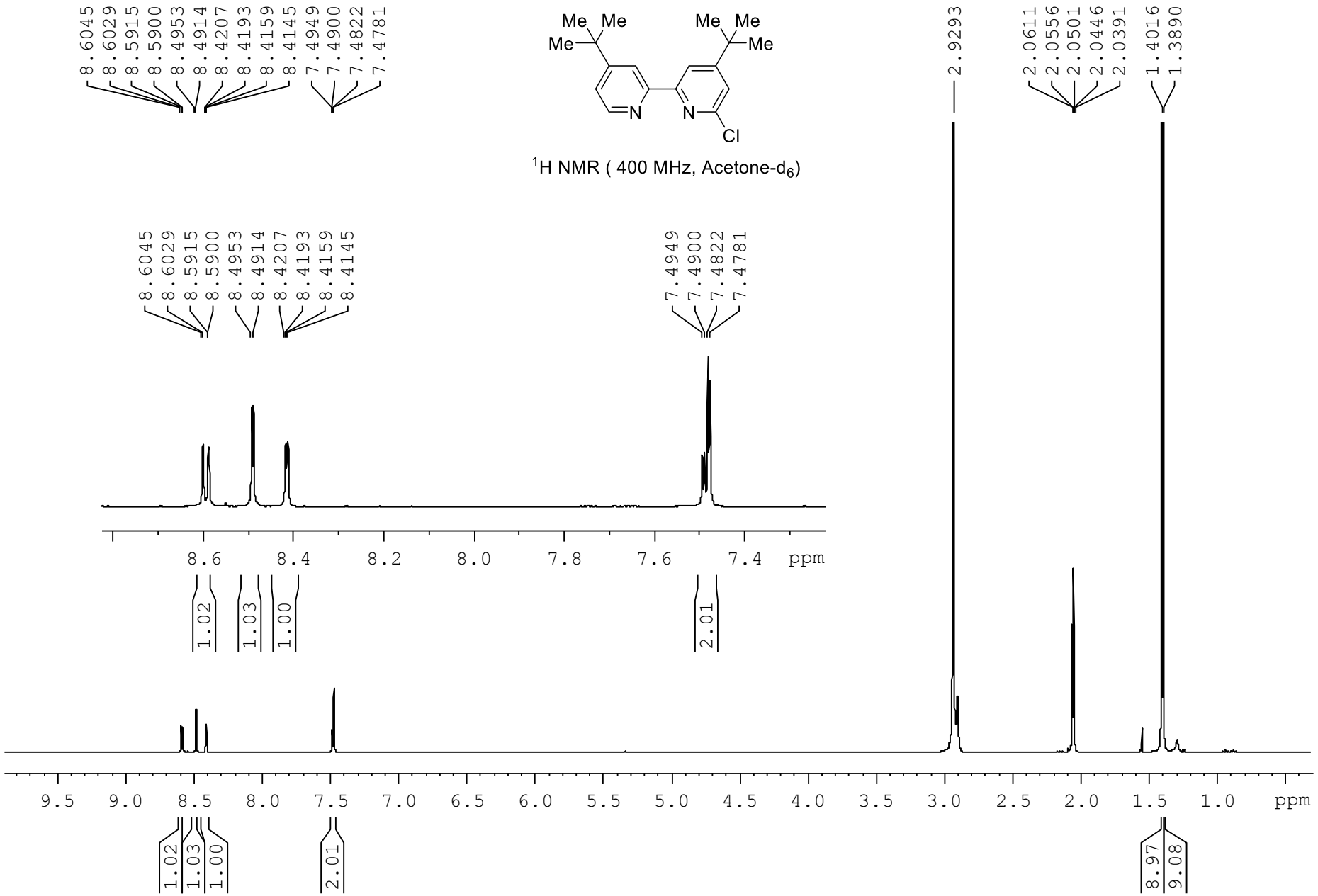
2. Copy of NMR spectra



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



^{13}C NMR (100 MHz, Acetone-d_6)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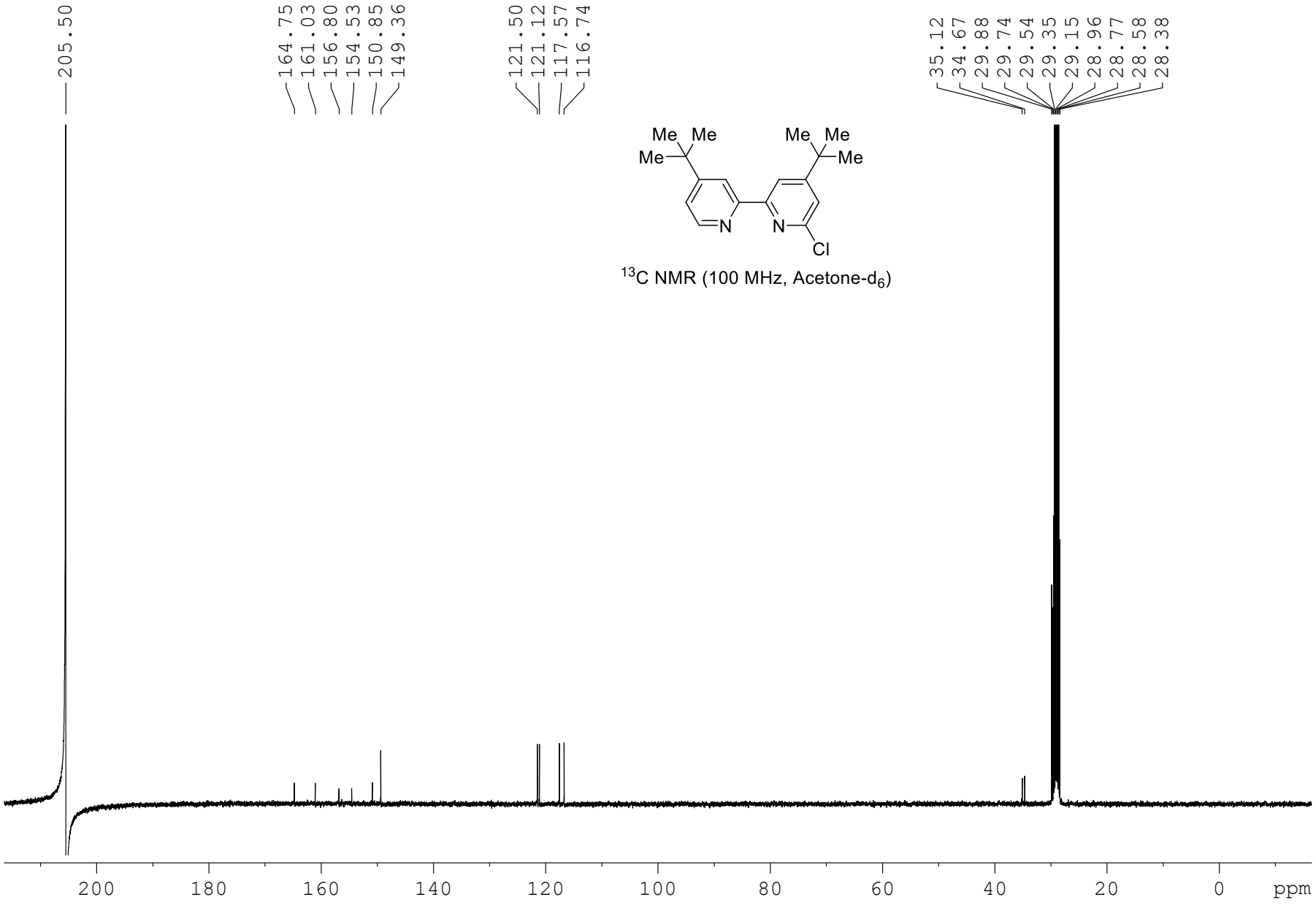
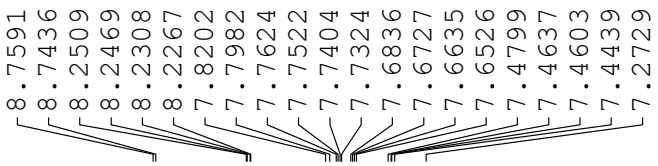
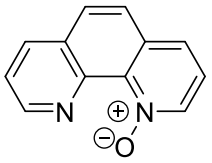
8.5915
8.5900
8.4953
8.4914
8.4207
8.4193
8.4159
8.4145
7.4949
7.4900
7.4822
7.4781
2.9293
2.0611
2.0556
2.0501
2.0446
2.0391
1.4016
1.3890
Me
Me
Me
Me
Me
Me
N
N
Cl
1H NMR (400 MHz, Acetone-d6)
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
1.02
1.03
1.00
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.02
1.03
1.00
2.01
8.97
9.08

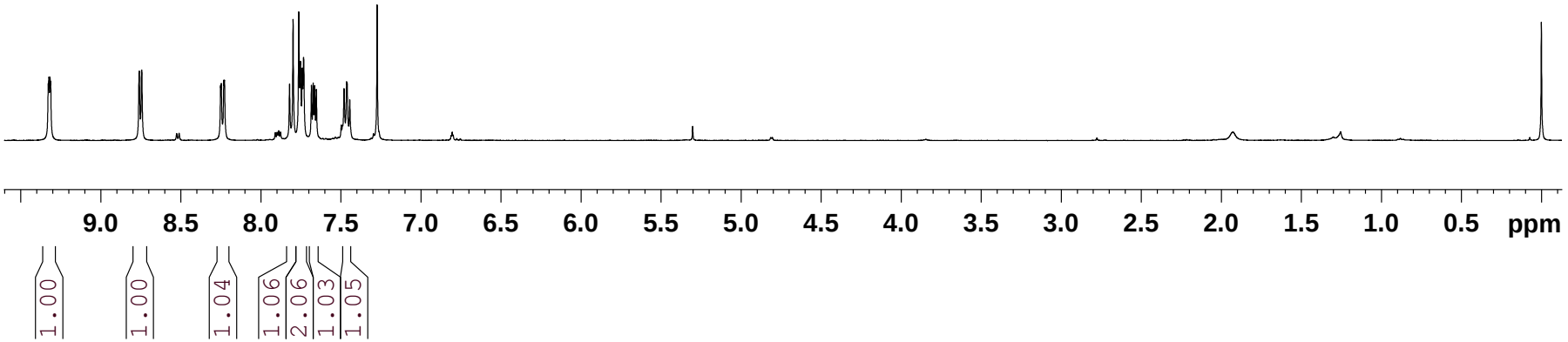


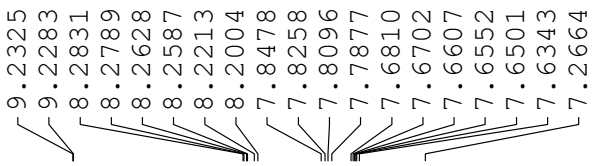
^{13}C NMR (100 MHz, Acetone-d_6)

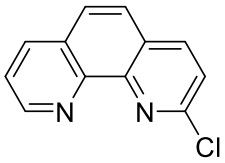




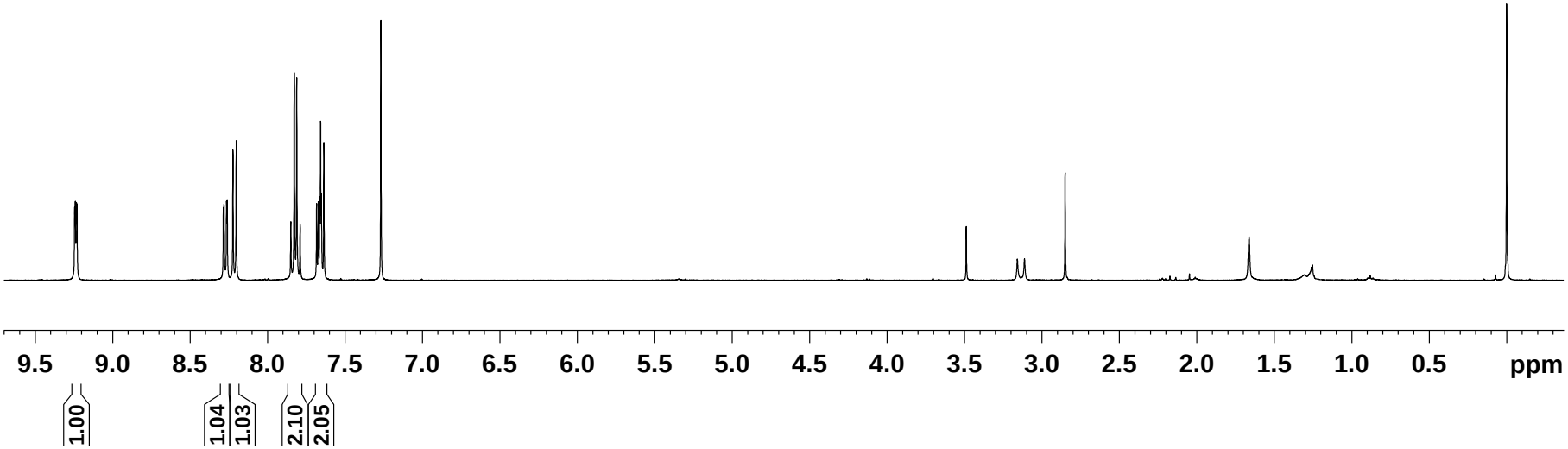
^{1}H NMR (400 MHz, $CDCl_3$)

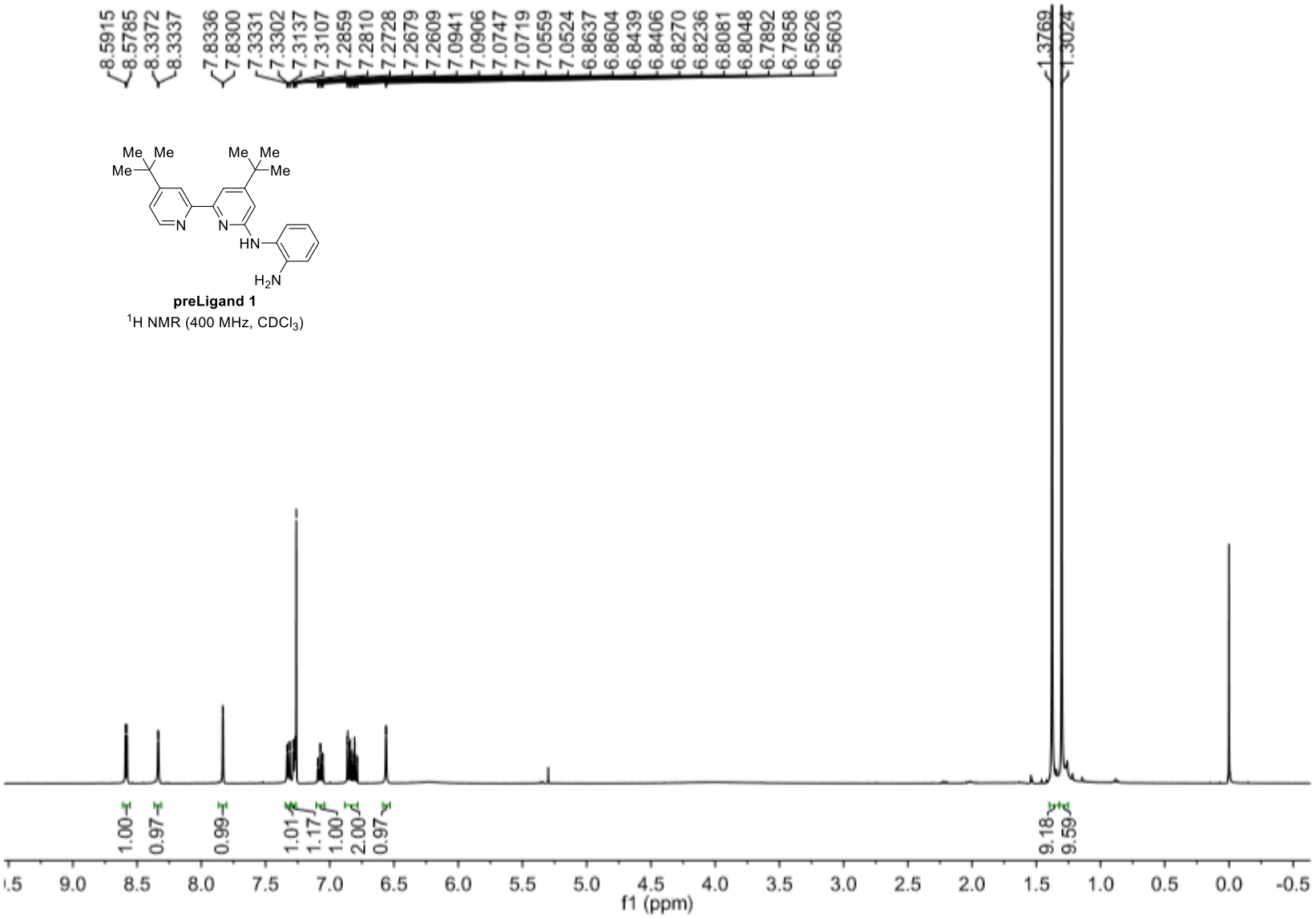






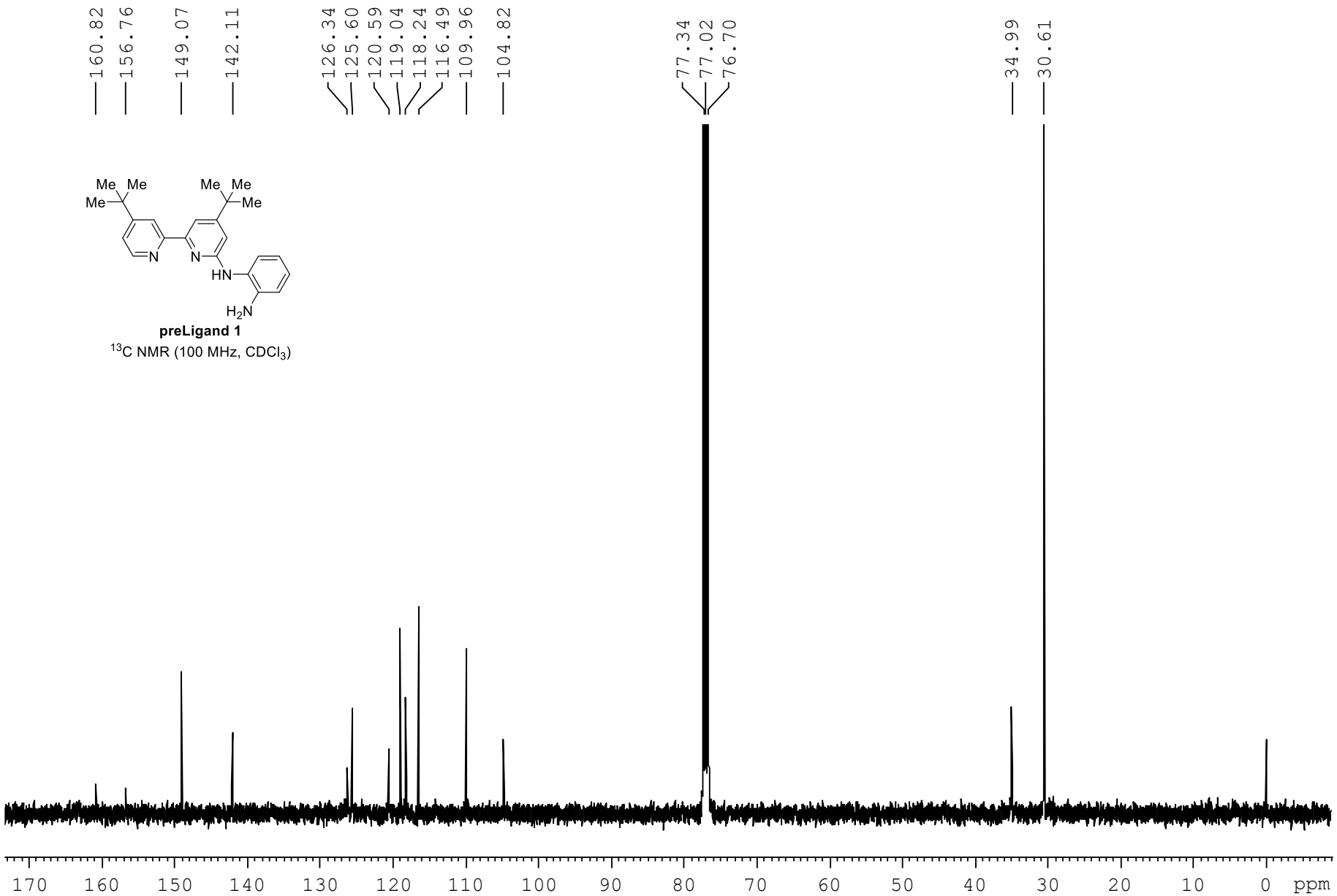
^{1}H NMR (400 MHz, $CDCl_3$)





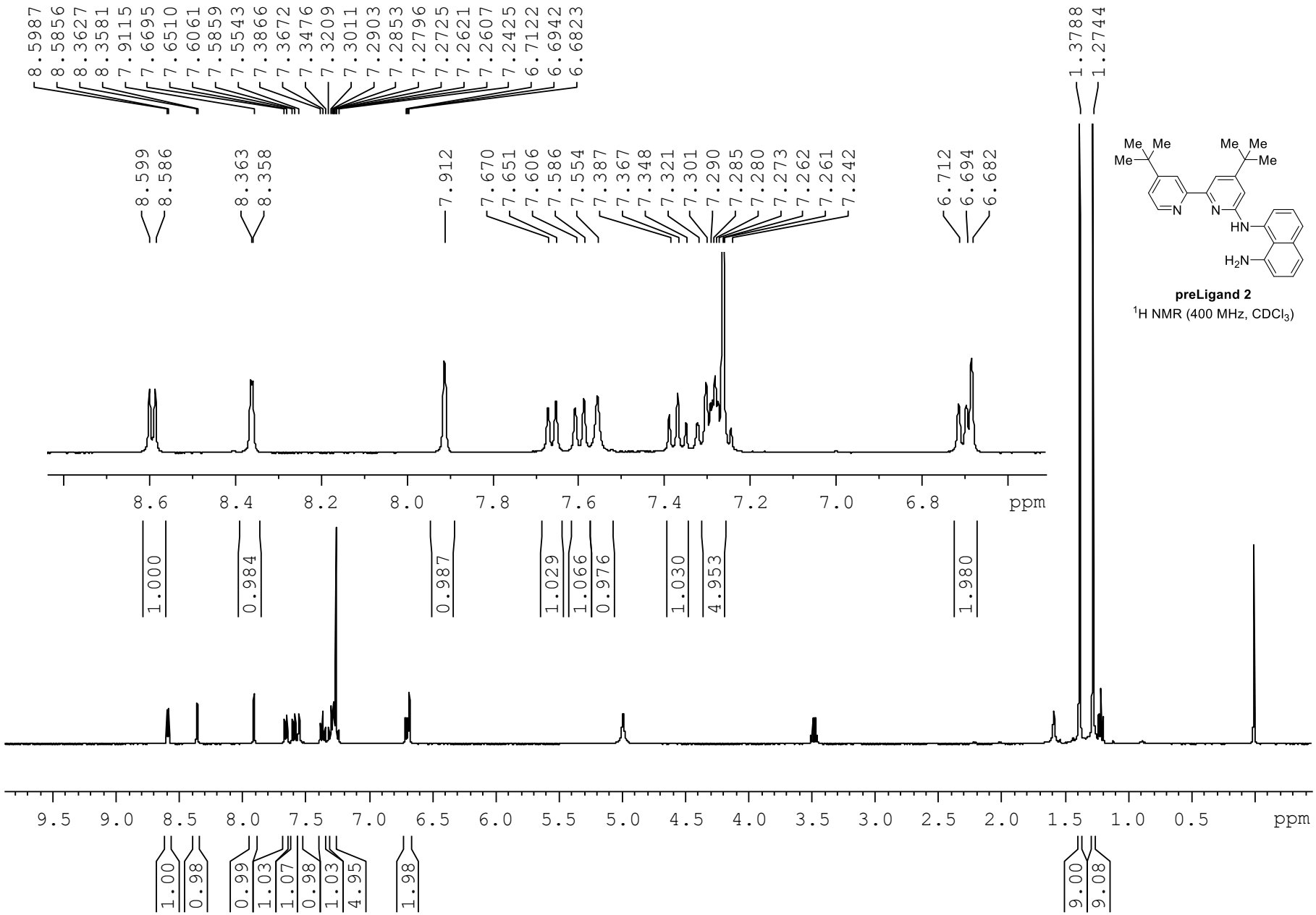
preLigand 1

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



preLigand 1

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



preLigand 2

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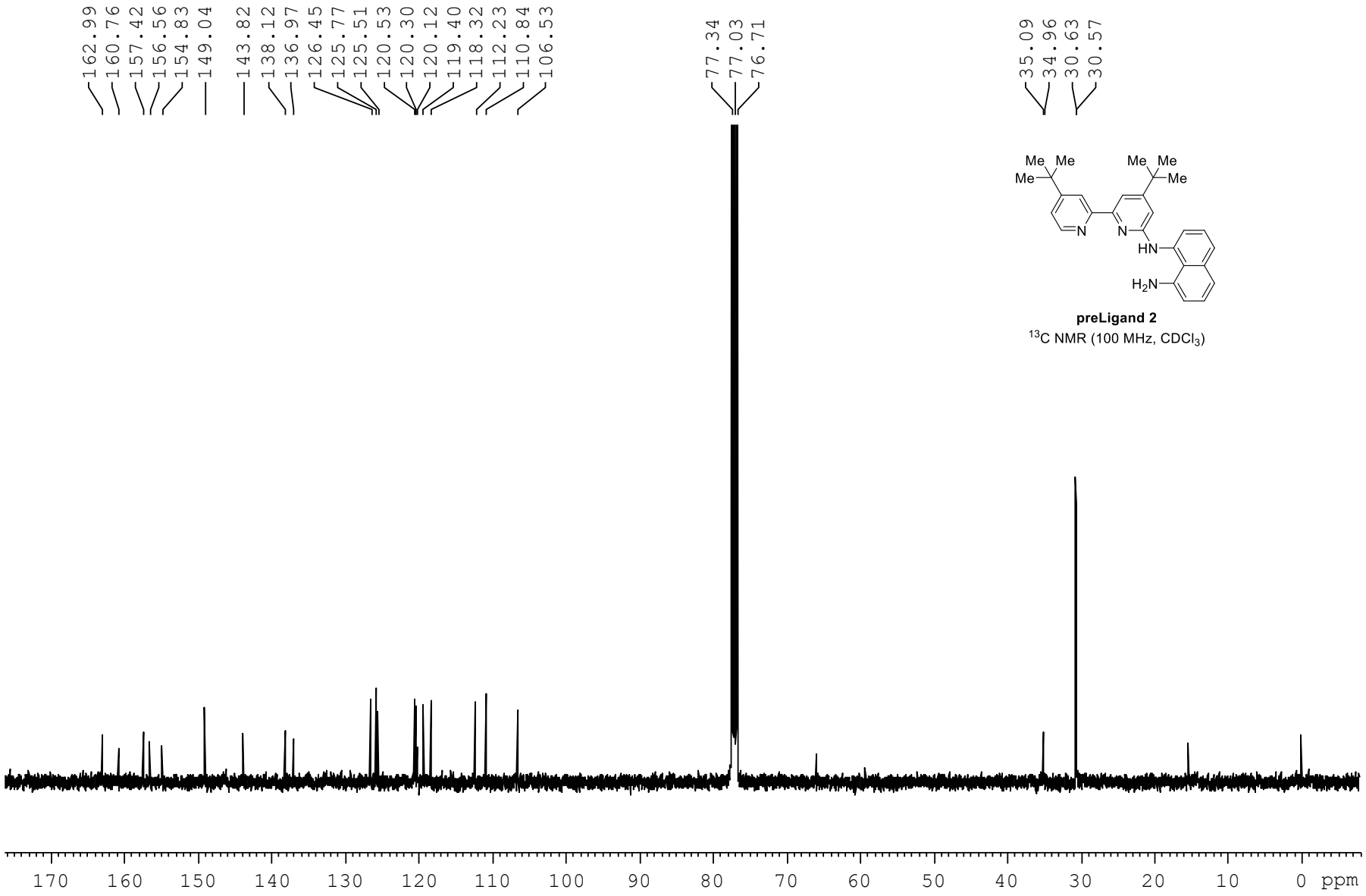
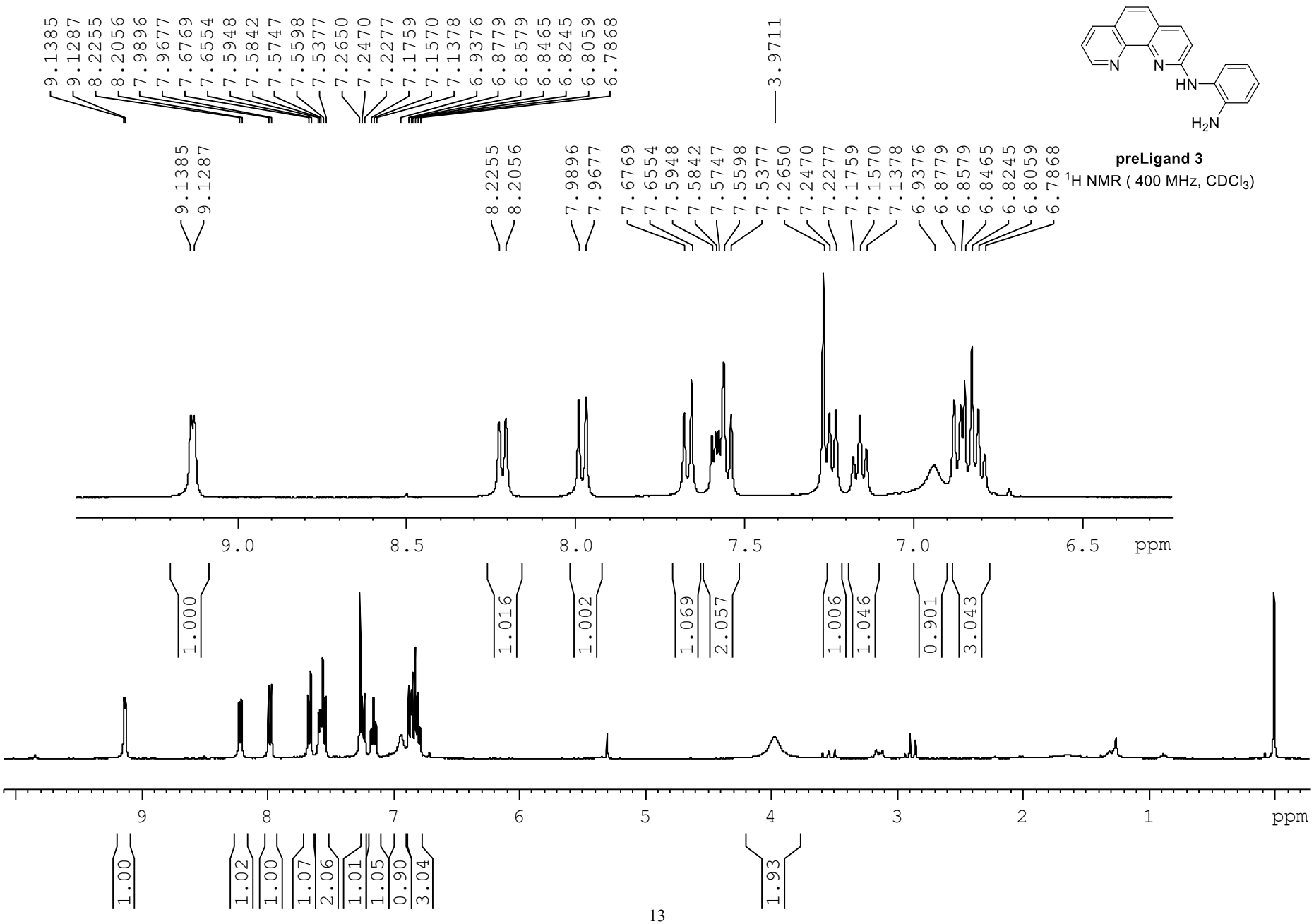
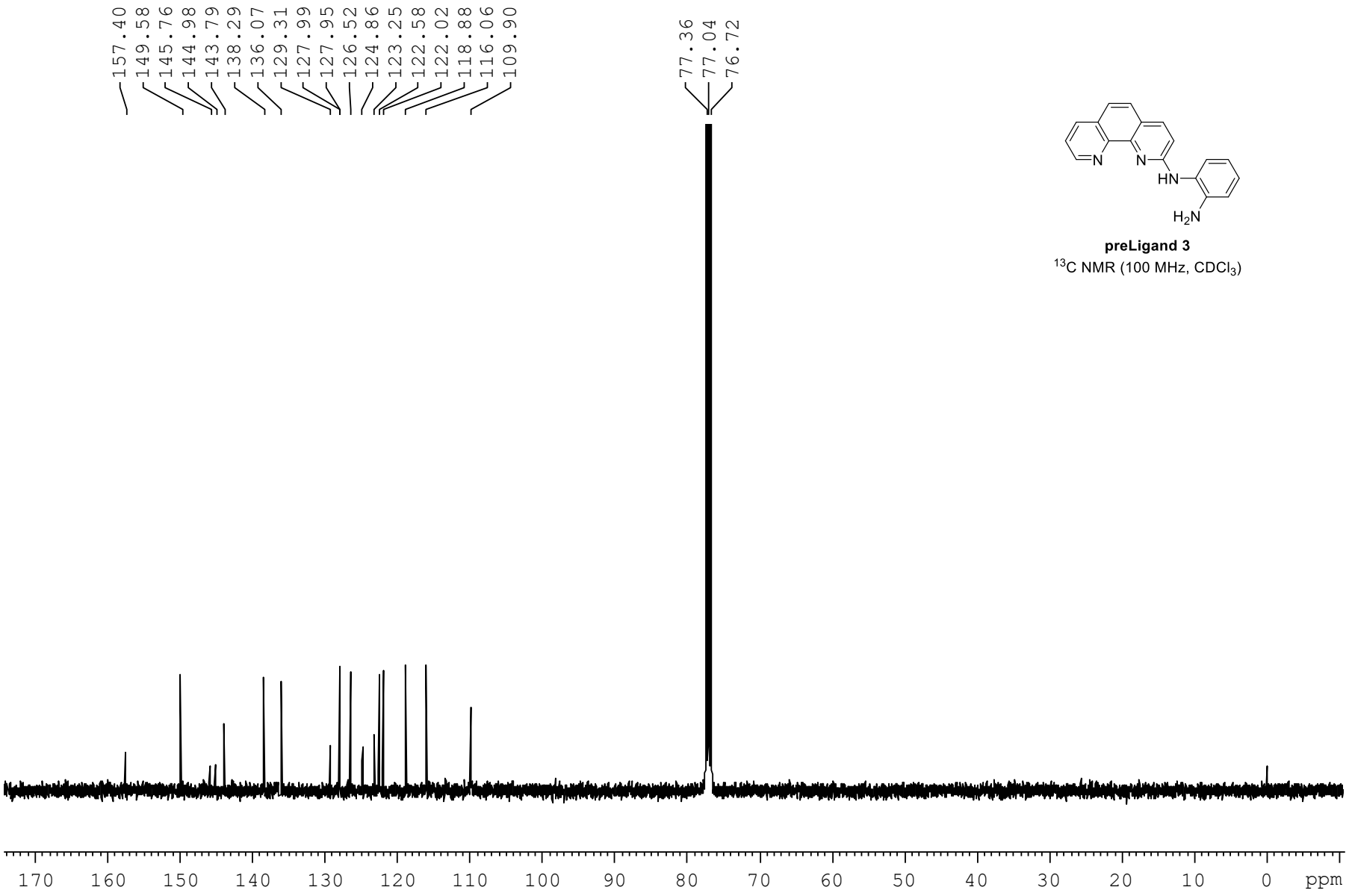


preLigand 2

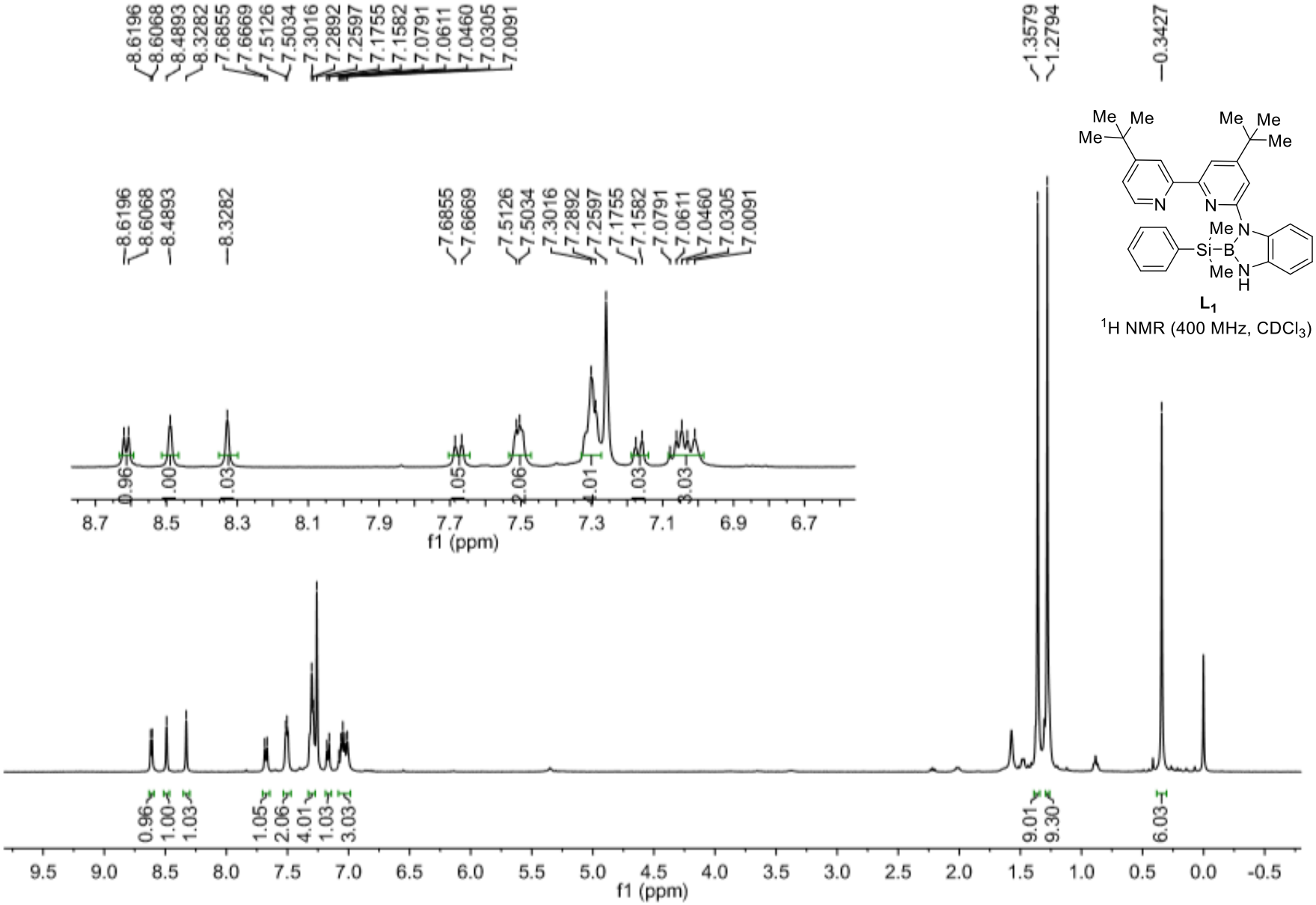
^{13}C NMR (100 MHz, $CDCl_3$)

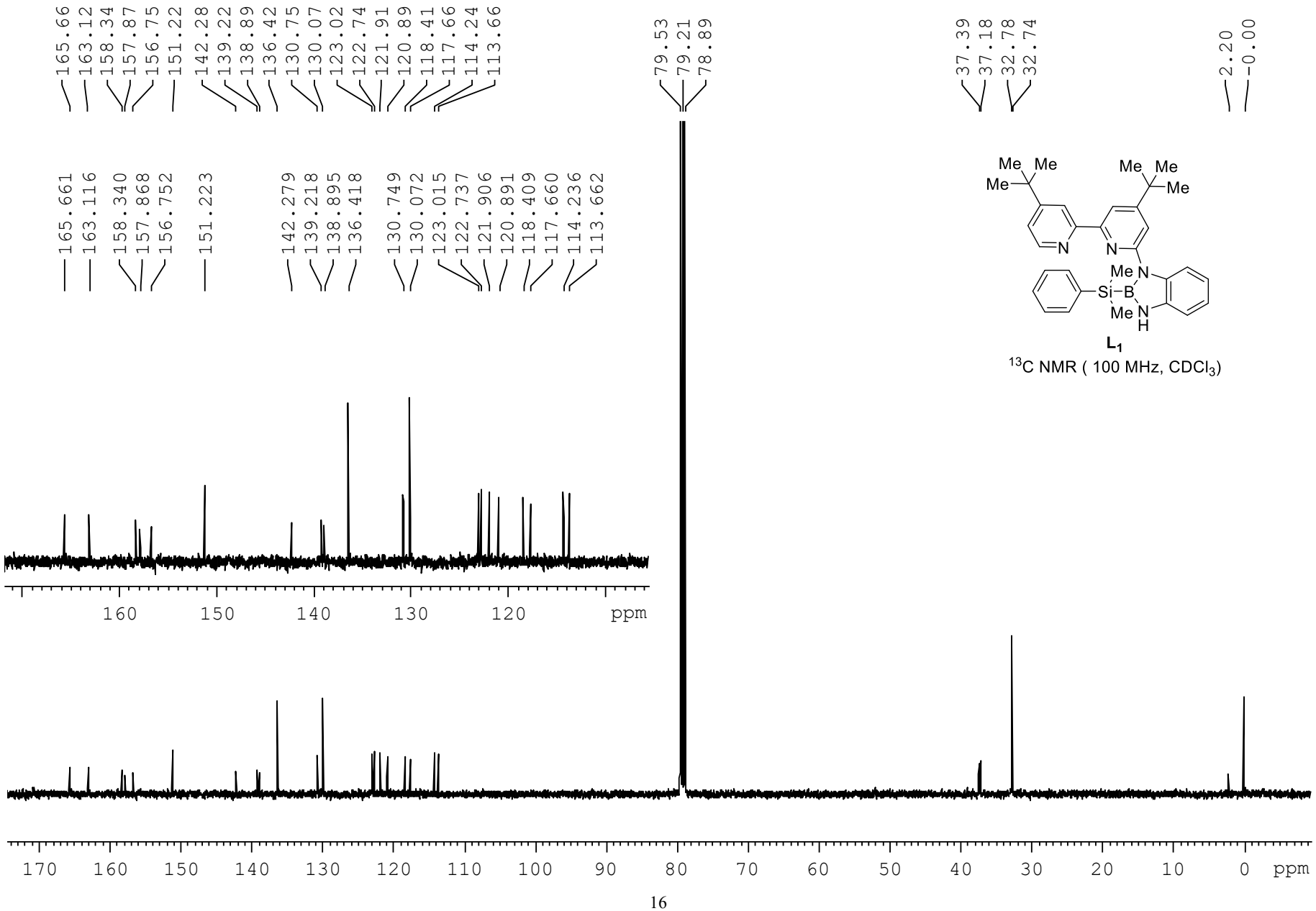

9.1385
9.1287
8.2255
8.2056
7.9896
7.9677
7.6769
7.6554
7.5948
7.5842
7.5747
7.5598
7.5377
7.2650
7.2470
7.2277
7.1759
7.1570
7.1378
6.9376
6.8779
6.8579
6.8465
6.8245
6.8059
6.7868
3.9711
N
N
HN
H2N
preLigand 3
1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
ppm
1.000
1.016
1.002
1.069
2.057
1.006
1.046
0.901
3.043
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.00
1.07
2.06
1.01
1.05
0.90
3.04
1.93

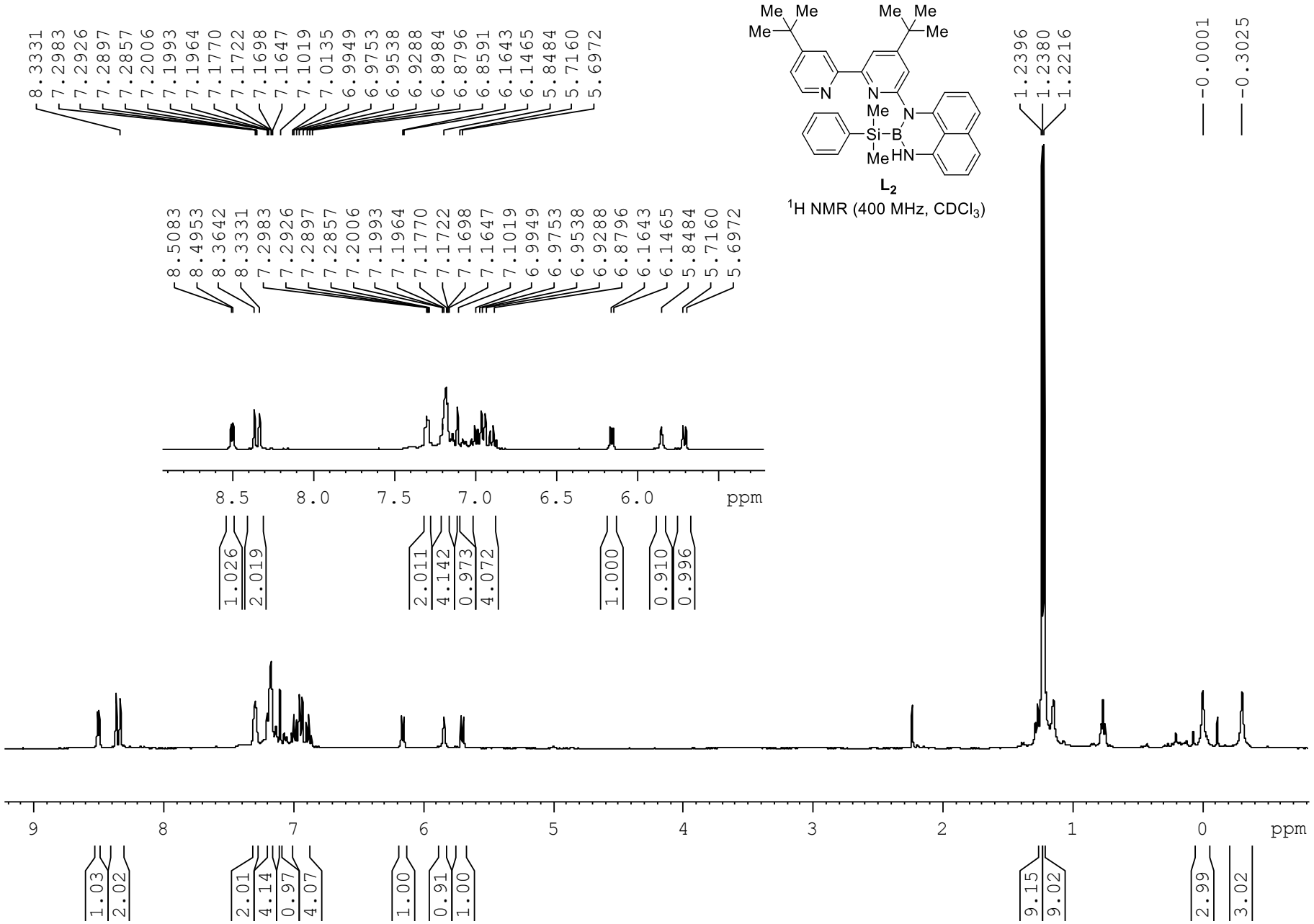


preLigand 3

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


8.6196
8.6068
8.4893
8.3282
7.6855
7.6669
7.5126
7.5034
7.3016
7.2892
7.2597
7.1755
7.1582
7.0791
7.0611
7.0460
7.0305
7.0091
1.3579
1.2794
0.3427
0.96
1.00
1.03
1.05
2.06
4.01
1.03
3.03
9.01
9.30
6.03
f1 (ppm)
Me
Me
Me
Me
Me
Me
N
N
Si
B
N
H
L1
1H NMR (400 MHz, CDCl3)


165.66
163.12
158.34
157.87
156.75
151.22
142.28
139.22
138.89
136.42
130.75
130.07
123.02
122.74
121.91
120.89
118.41
117.66
114.24
113.66
79.53
79.21
78.89
37.39
37.18
32.78
32.74
2.20
0.00
165.661
163.116
158.340
157.868
156.752
151.223
142.279
139.218
138.895
136.418
130.749
130.072
123.015
122.737
121.906
120.891
118.409
117.660
114.236
113.662
Me Me
Me
Me Me
Me
N
N
Me N
Si B
Me N
H
L1
13C NMR (100 MHz, CDCl3)
160
150
140
130
120
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.3331
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7.2897
7.2857
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7.1993
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7.1770
7.1722
7.1698
7.1647
7.1019
7.0135
6.9949
6.9753
6.9538
6.9288
6.8984
6.8796
6.8591
6.1643
6.1465
5.8484
5.7160
5.6972
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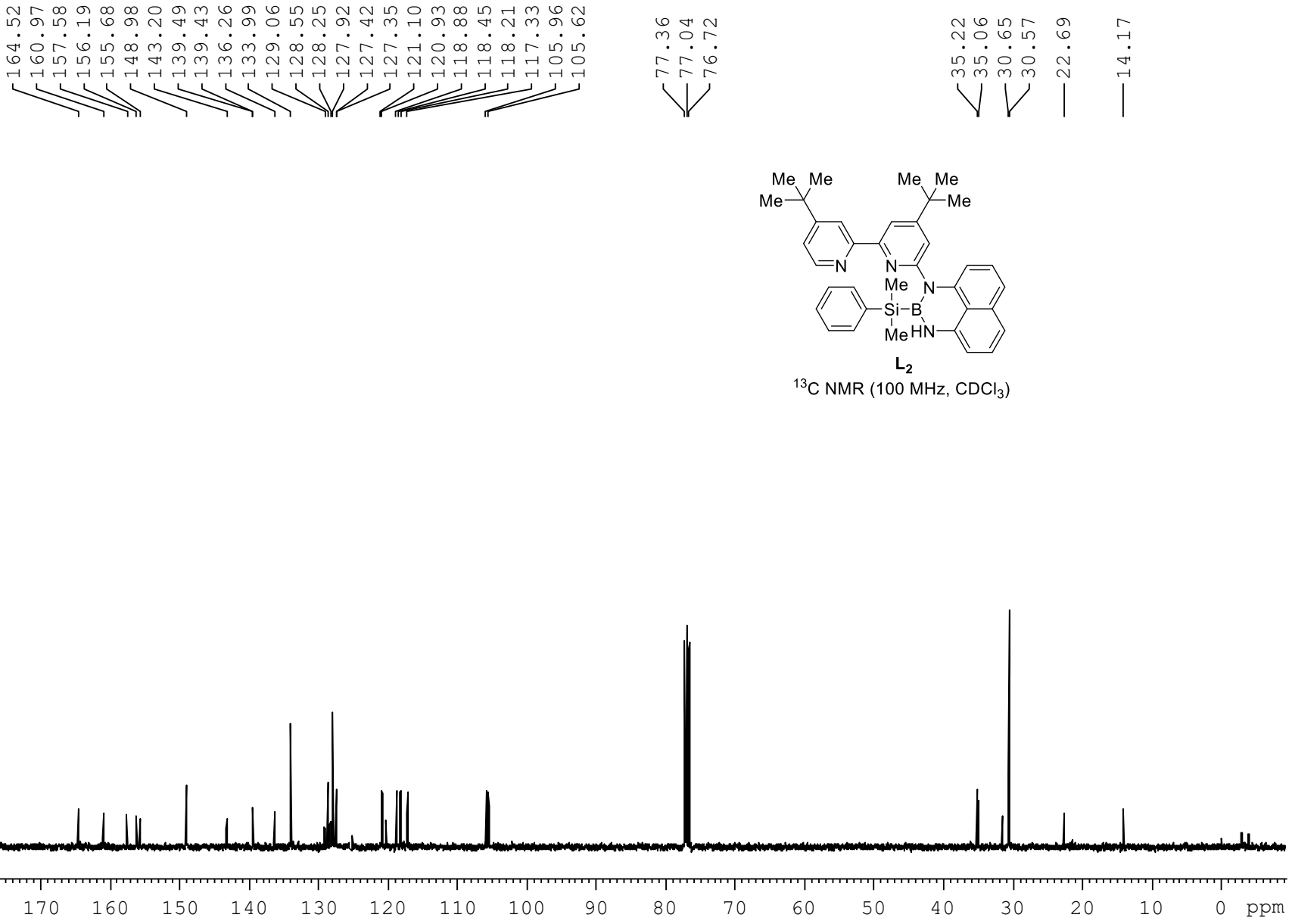
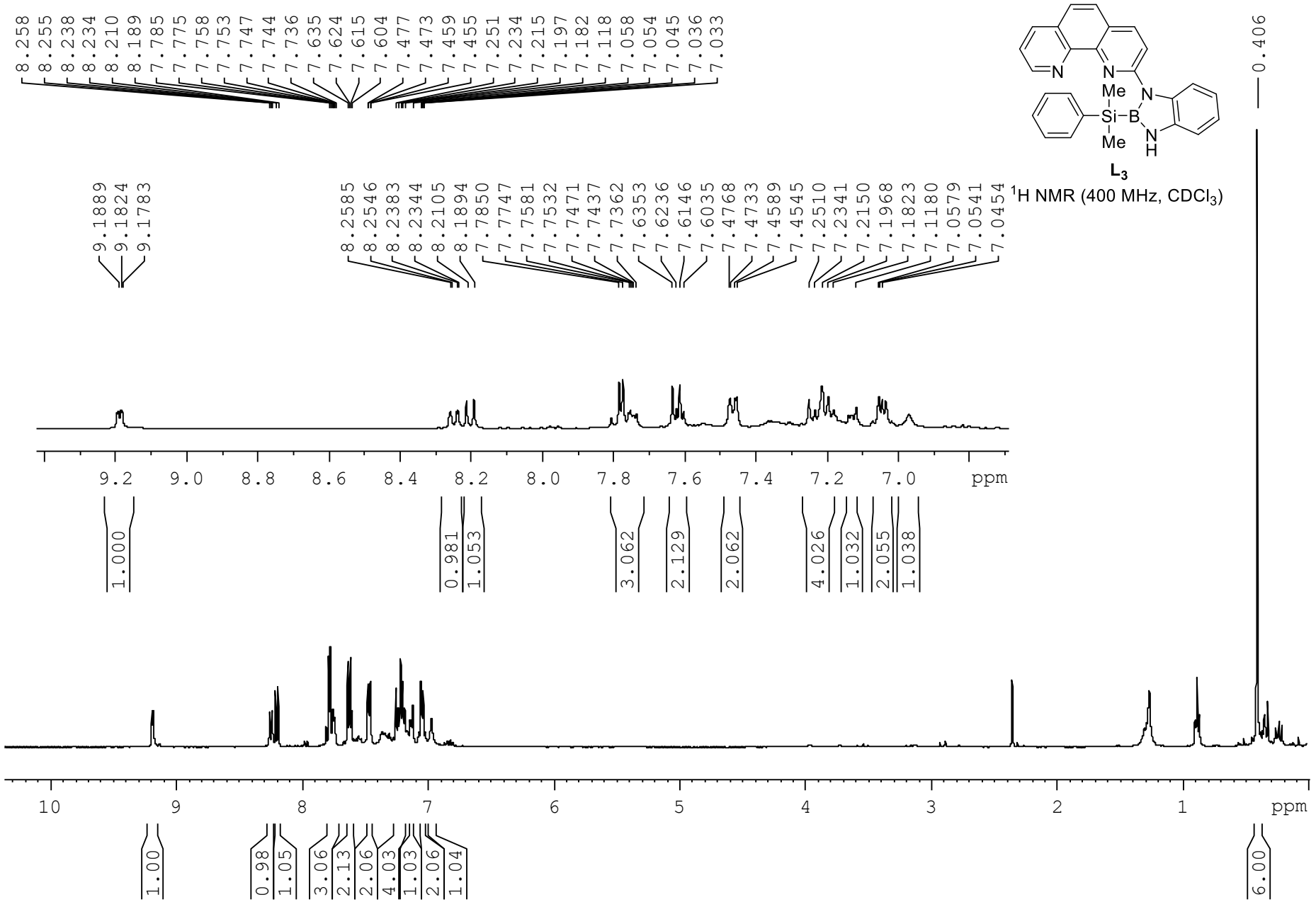
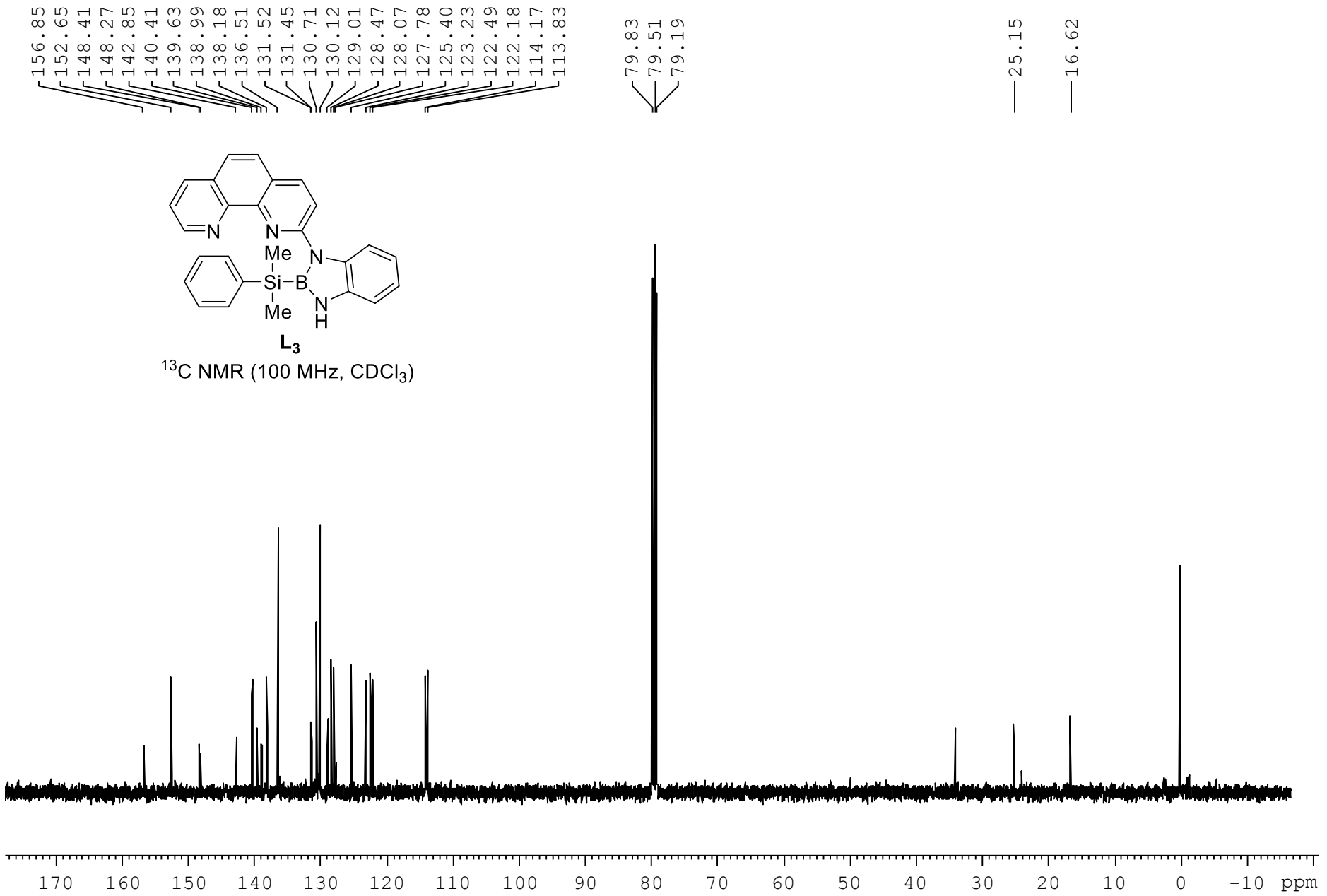
8.4953
8.3642
8.3331
7.2983
7.2926
7.2897
7.2857
7.2006
7.1993
7.1964
7.1770
7.1722
7.1698
7.1647
7.1019
6.9949
6.9753
6.9538
6.9288
6.8796
6.1643
6.1465
5.8484
5.7160
5.6972
1.2396
1.2380
1.2216
-0.0001
-0.3025
Me
Me
Me
Me
Me
Me
N
N
N
Me
Si
B
Me
HN
L2
1H NMR (400 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
ppm
1.026
2.019
2.011
4.142
0.973
4.072
1.000
0.910
0.996
9
8
7
6
5
4
3
2
1
0
ppm
1.03
2.02
2.01
4.14
0.97
4.07
1.00
0.91
1.00
9.15
9.02
2.99
3.02

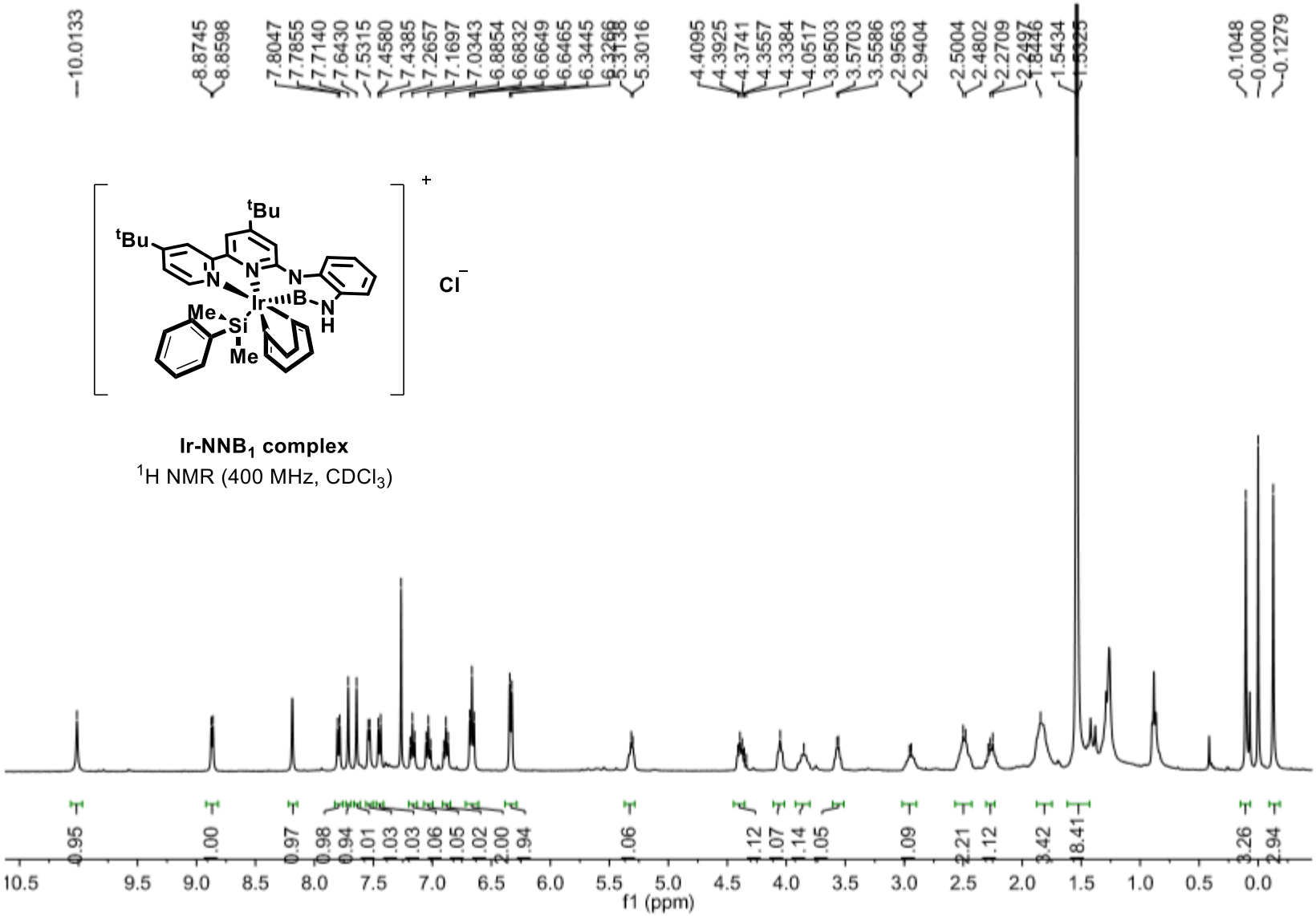

164.52
160.97
157.58
156.19
155.68
148.98
143.20
139.49
139.43
136.26
133.99
129.06
128.55
128.25
127.92
127.42
127.35
121.10
120.93
118.88
118.45
118.21
117.33
105.96
105.62
77.36
77.04
76.72
35.22
35.06
30.65
30.57
22.69
14.17
Me Me
Me
Me Me
Me
N
N
Me
N
Si
B
Me
HN
L2
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.258
8.255
8.238
8.234
8.210
8.189
7.785
7.775
7.758
7.753
7.747
7.744
7.736
7.635
7.624
7.615
7.604
7.477
7.473
7.459
7.455
7.251
7.234
7.215
7.197
7.182
7.118
7.058
7.054
7.045
7.036
7.033
0.406
N
N
Me
Si
B
N
Me
N
H
L3
1H NMR (400 MHz, CDCl3)
9.1889
9.1824
9.1783
8.2585
8.2546
8.2383
8.2344
8.2105
8.1894
7.7850
7.7747
7.7581
7.7532
7.7471
7.7437
7.7362
7.6353
7.6236
7.6146
7.6035
7.4768
7.4733
7.4589
7.4545
7.2510
7.2341
7.2150
7.1968
7.1823
7.1180
7.0579
7.0541
7.0454
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.000
0.981
1.053
3.062
2.129
2.062
4.026
1.032
2.055
1.038
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
1.05
3.06
2.13
2.06
4.03
1.03
2.06
1.04
6.00



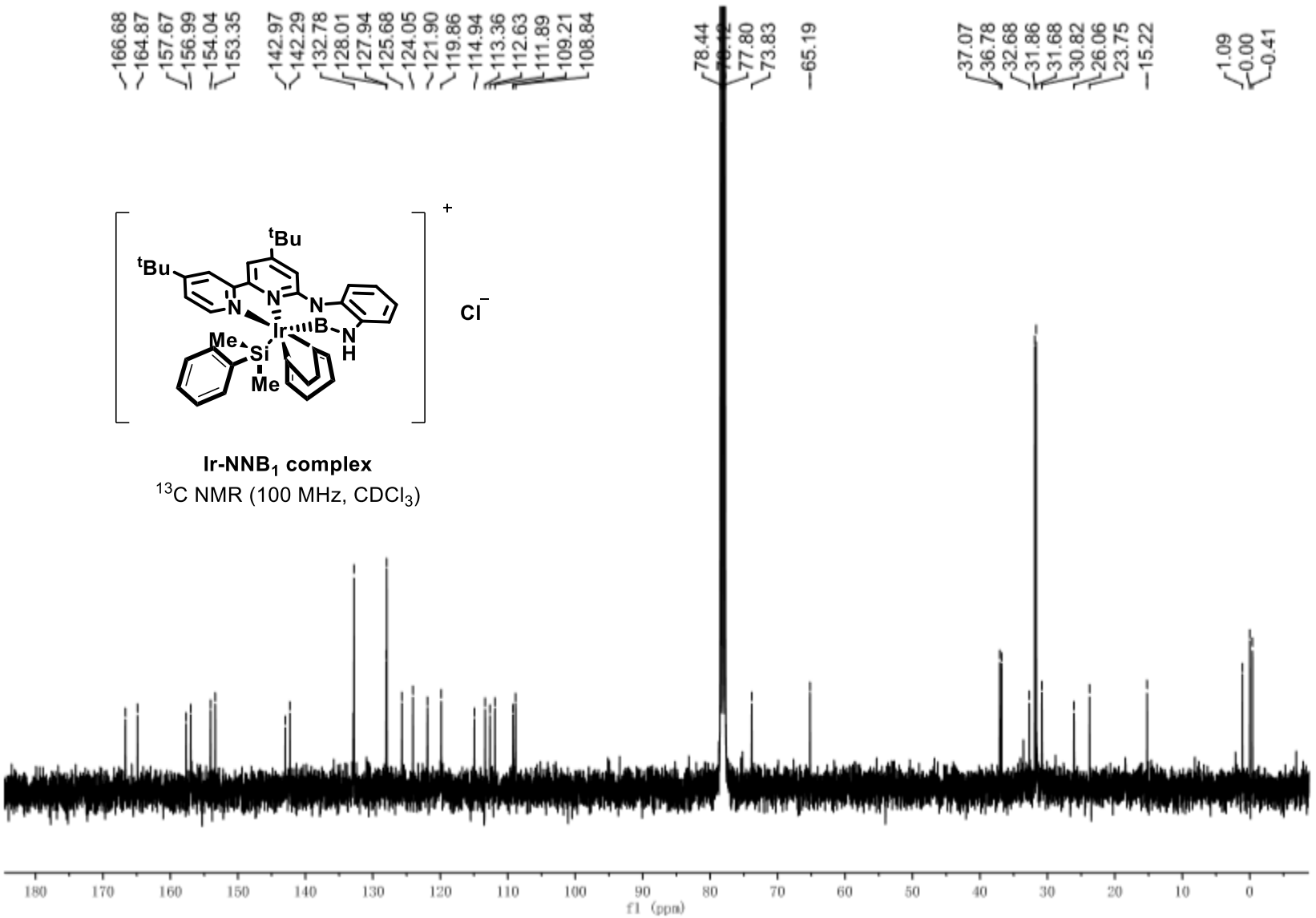
L_3

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



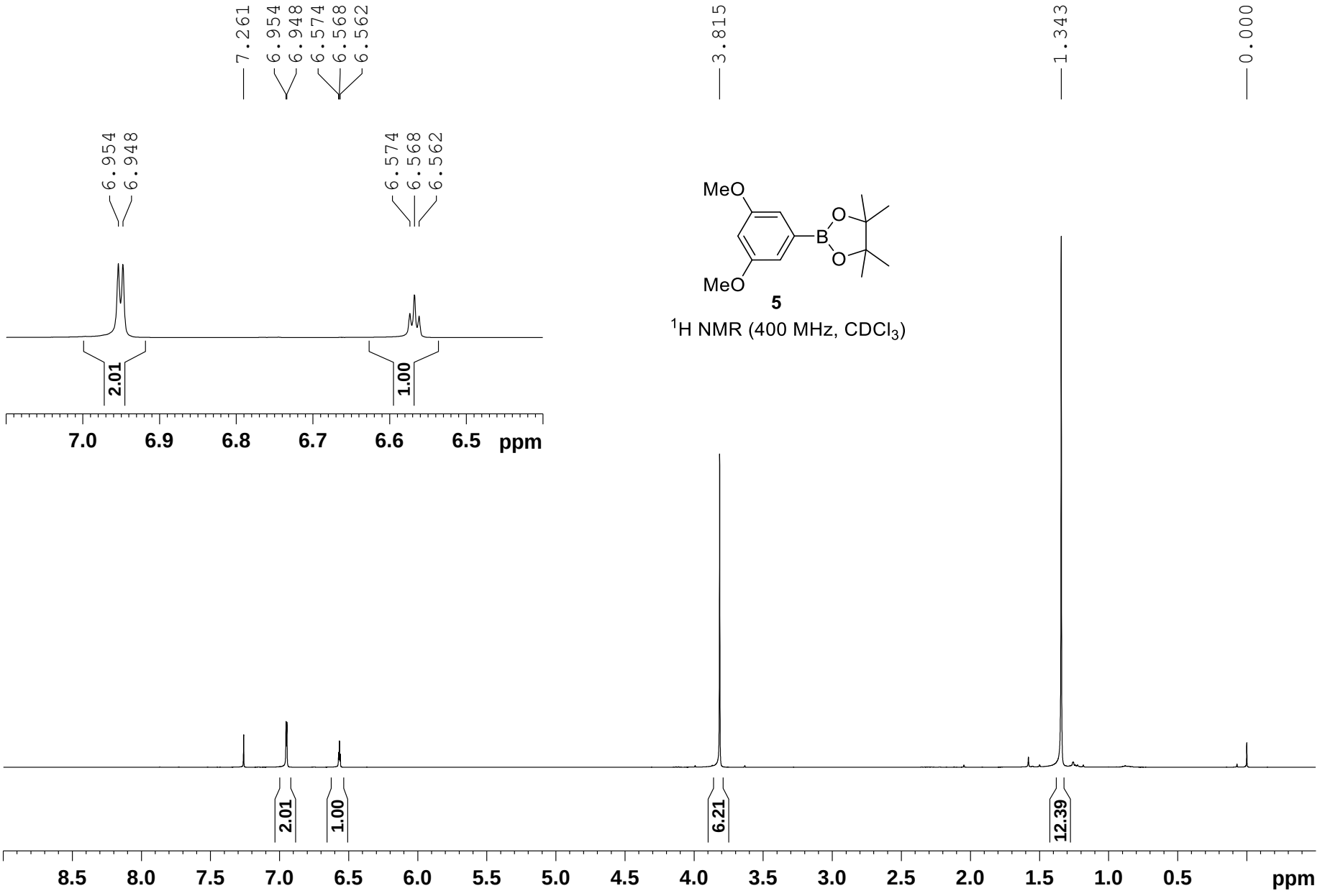
Ir-NNB$_1$ complex

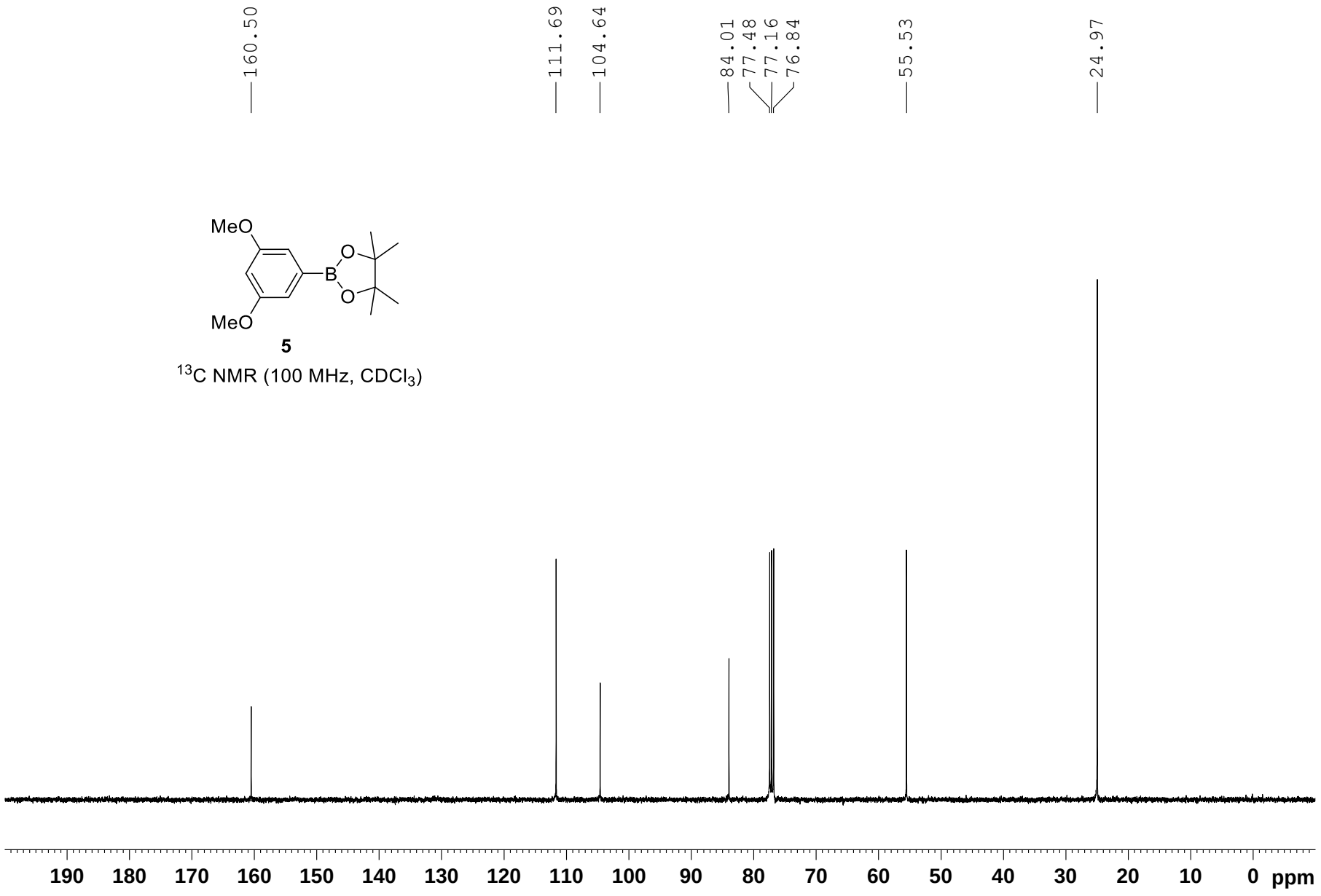
^{1}H NMR (400 MHz, $CDCl_3$)



Ir-NNB$_1$ complex

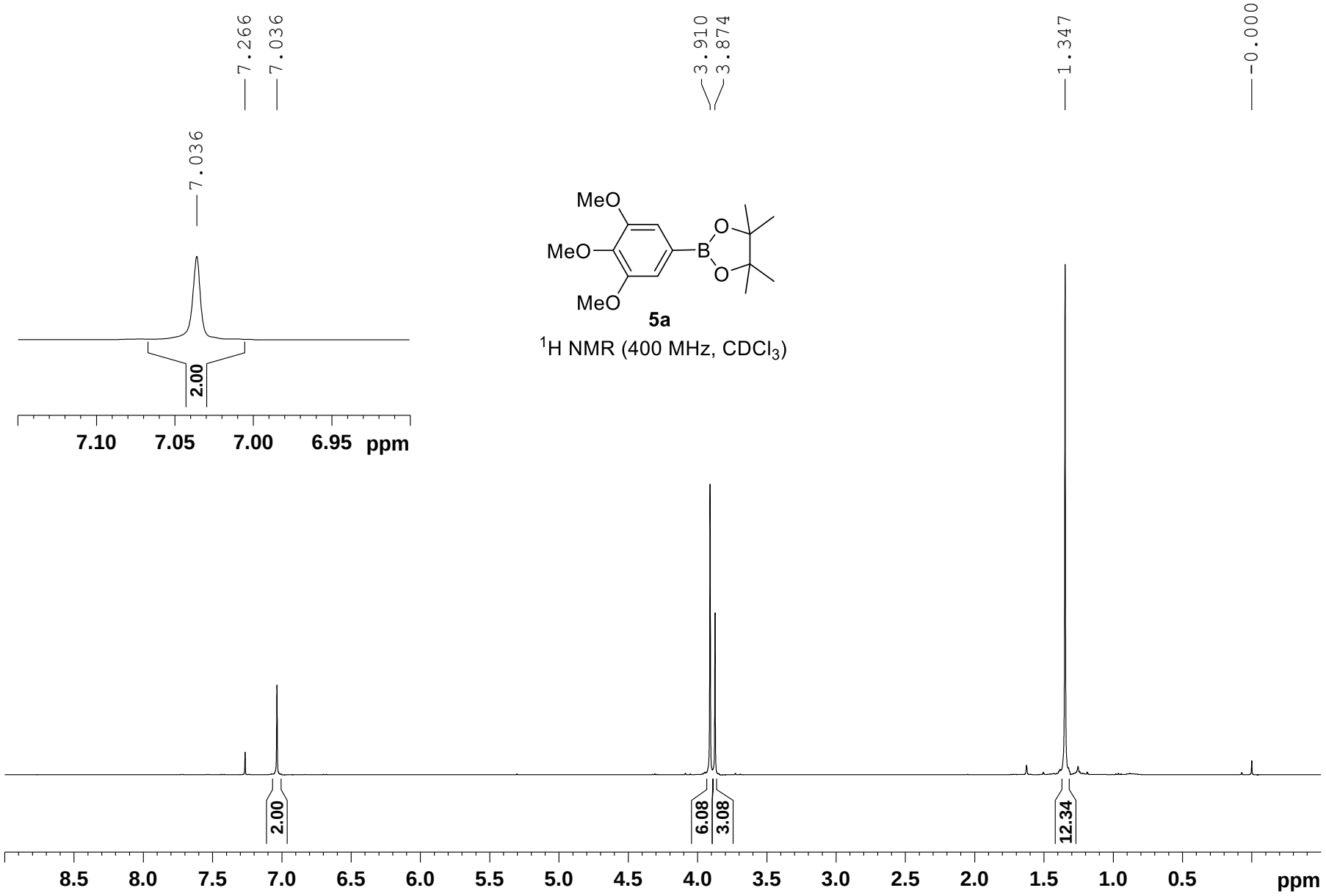
^{13}C NMR (100 MHz, $CDCl_3$)

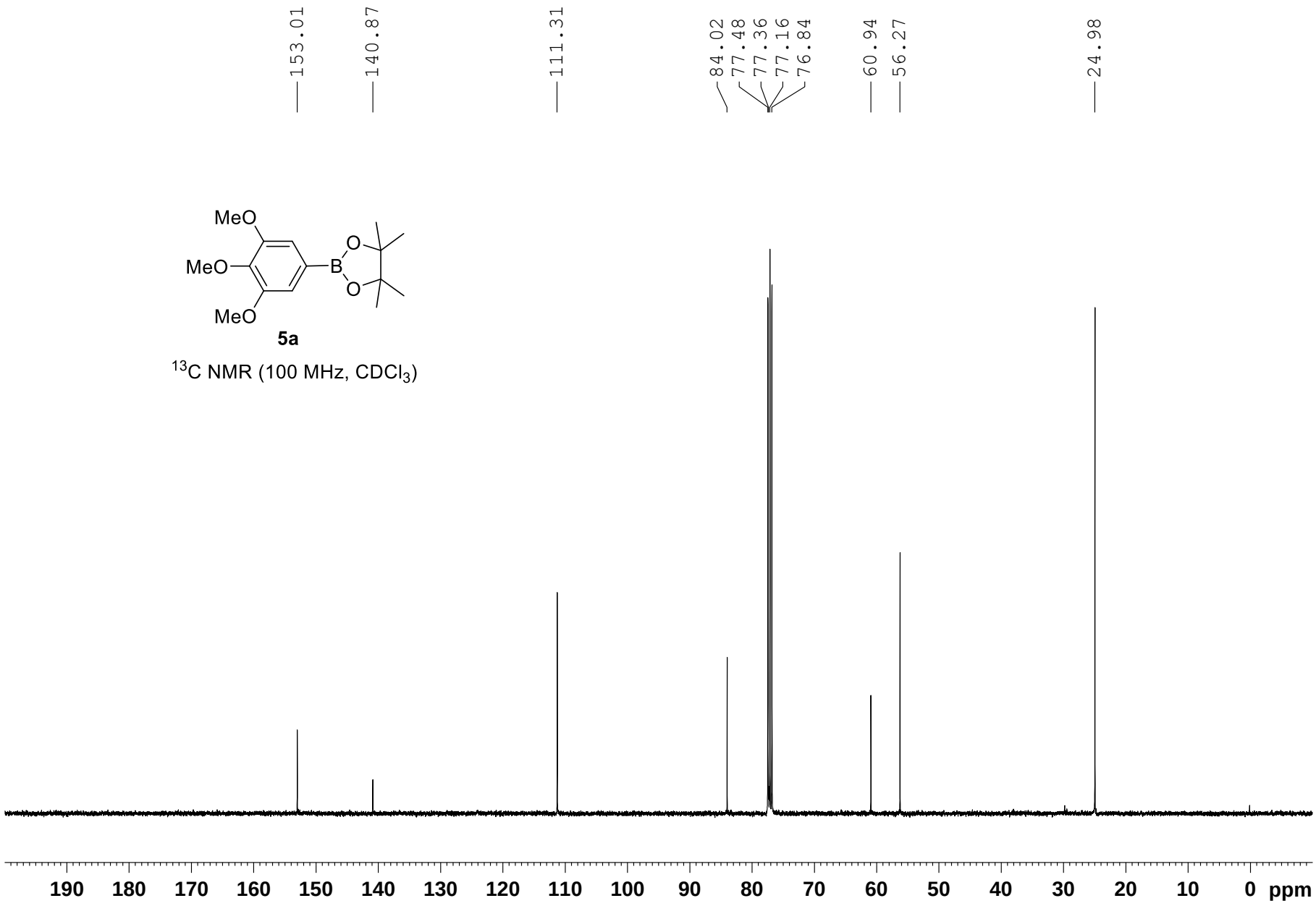

7.261
6.954
6.948
6.574
6.568
6.562
3.815
1.343
0.000
MeO
MeO
B
O
O
5
1H NMR (400 MHz, CDCl3)
2.01
1.00
6.21
12.39
ppm



5

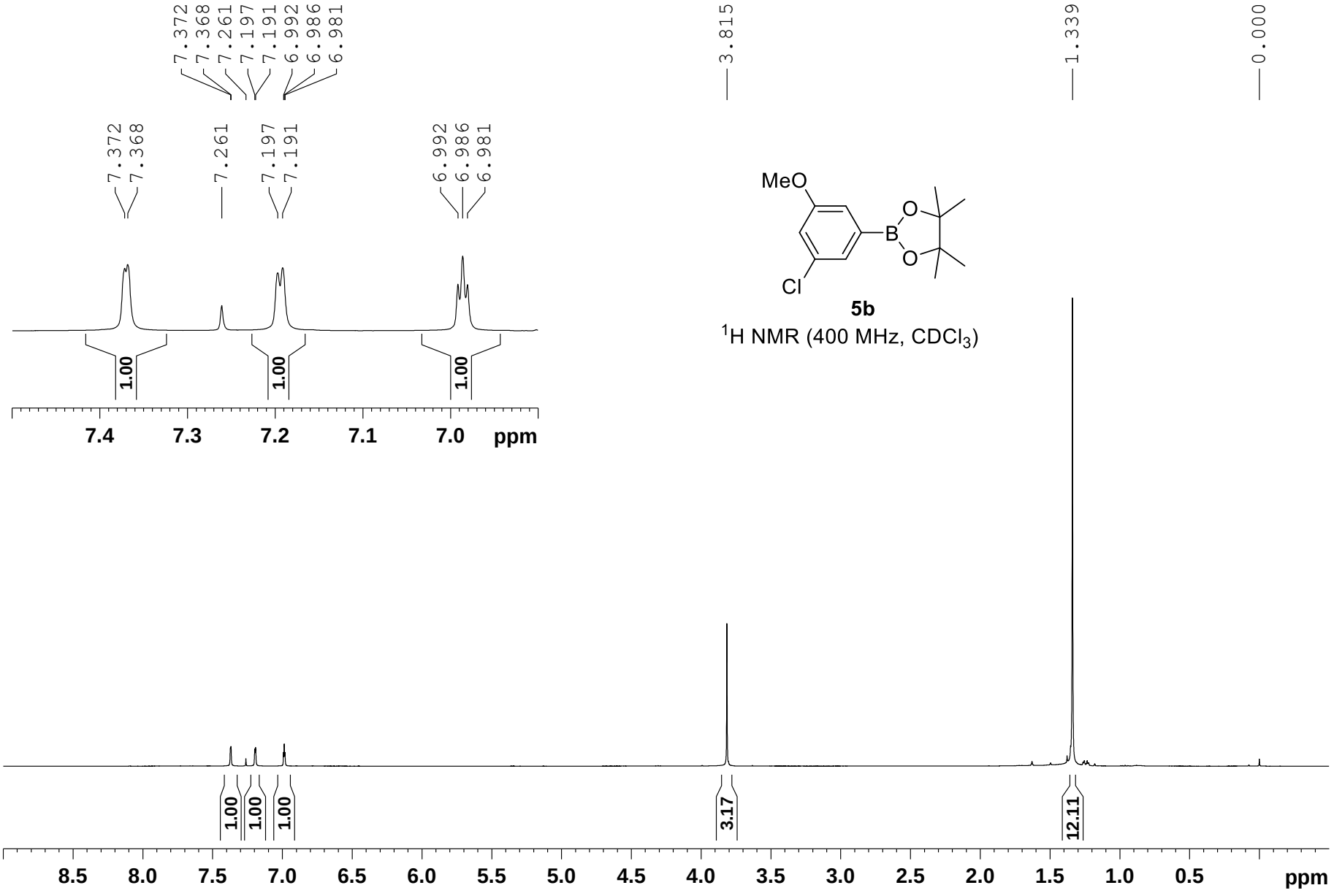
^{13}C NMR (100 MHz, $CDCl_3$)

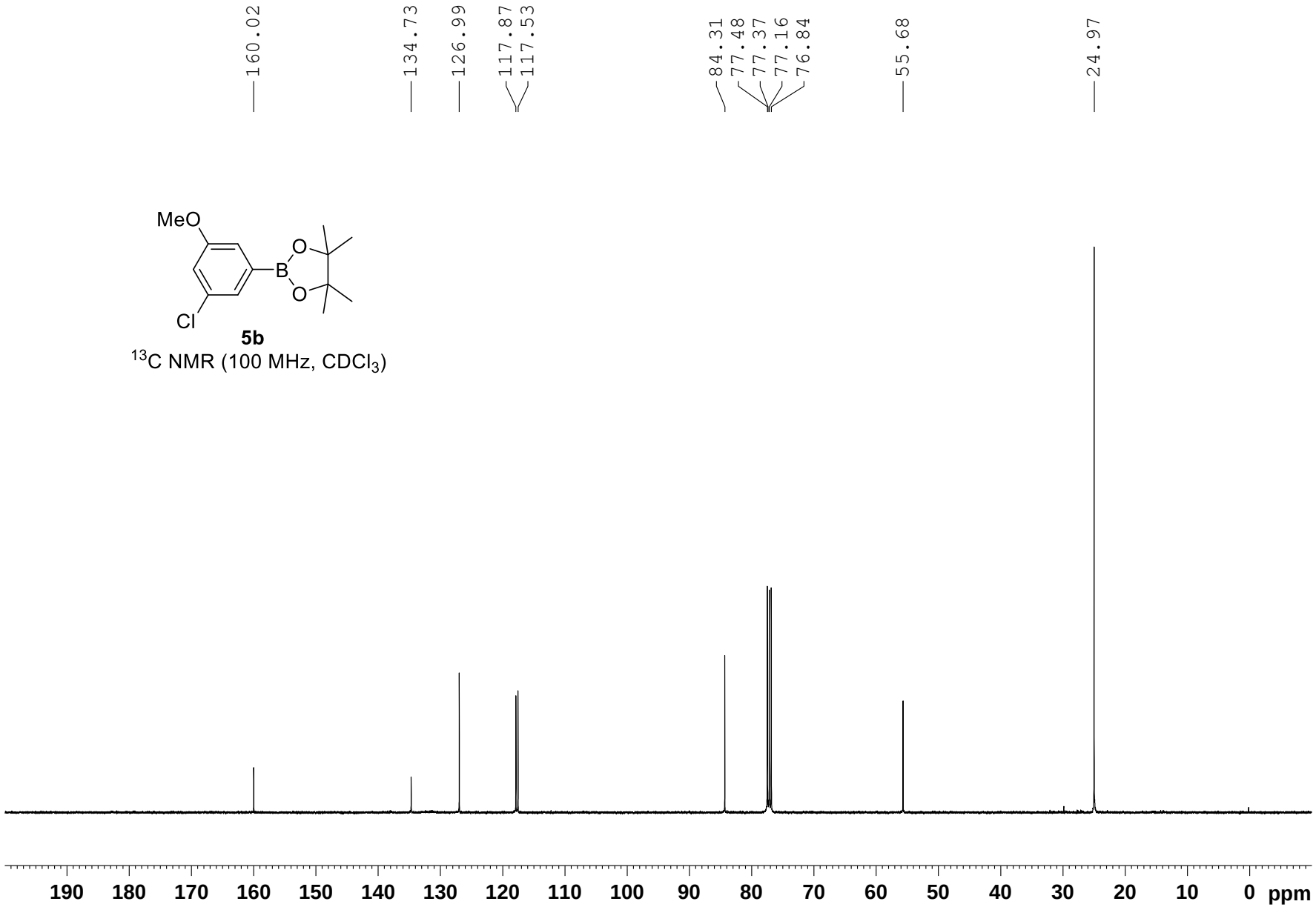

7.266
7.036
3.910
3.874
1.347
0.000
7.036
MeO
MeO
MeO
B
O
O
5a
1H NMR (400 MHz, CDCl3)
2.00
7.10
7.05
7.00
6.95
ppm
2.00
6.08
3.08
12.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

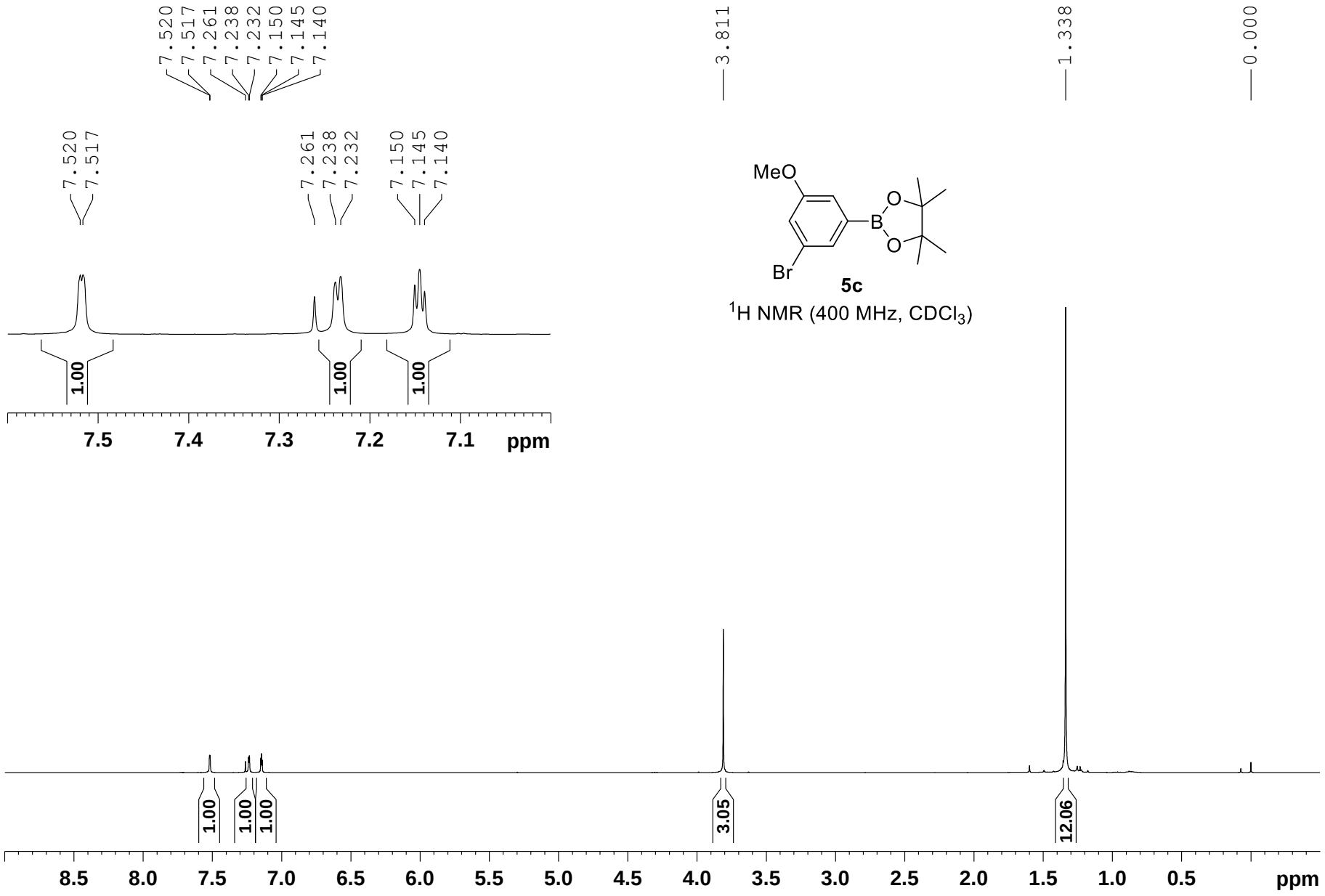


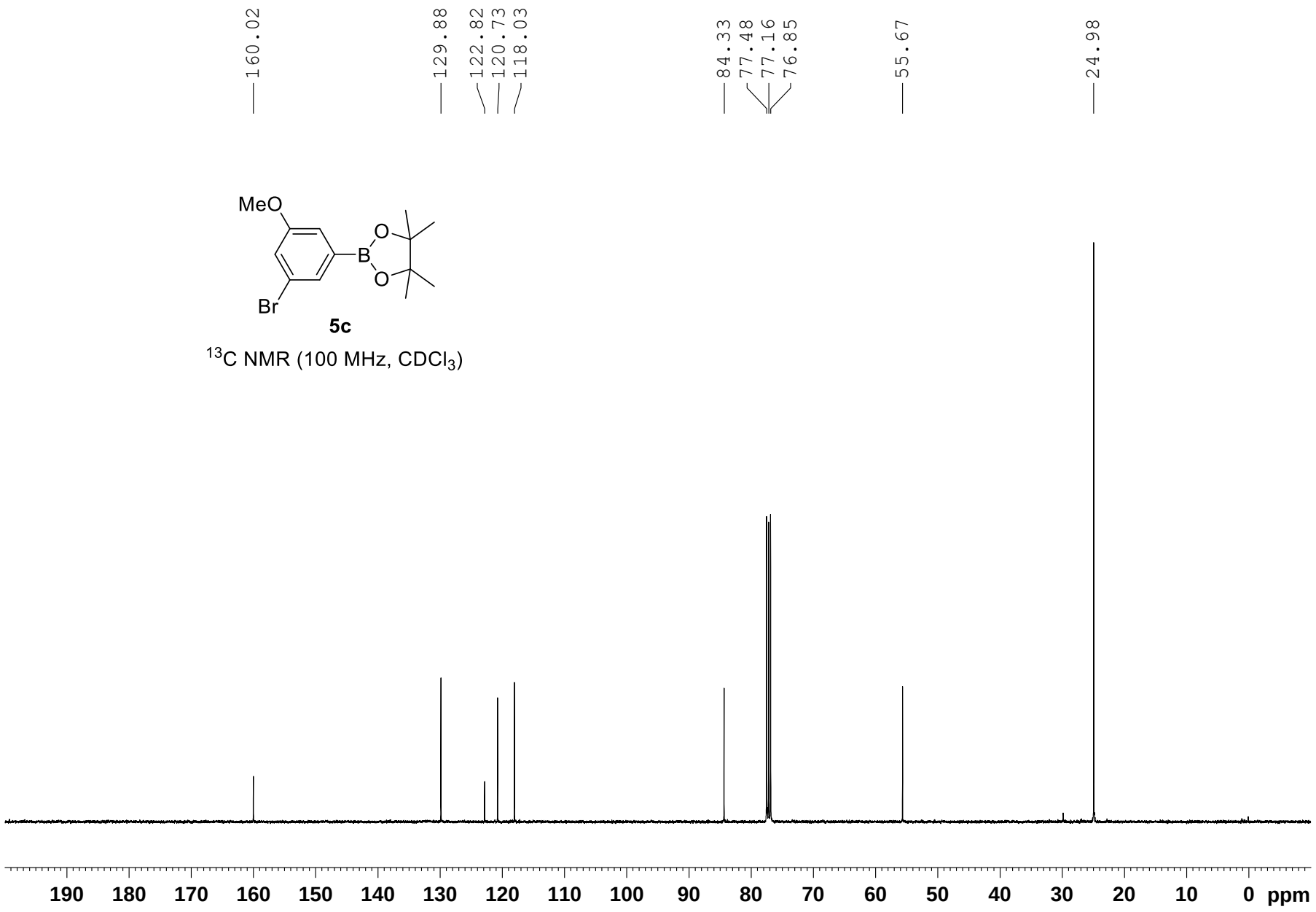
5a

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


7.372
7.368
7.261
7.197
7.191
6.992
6.986
6.981
3.815
1.339
0.000
MeO
Cl
B
O
O
5b
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
3.17
12.11
7.4
7.3
7.2
7.1
7.0
ppm
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
ppm

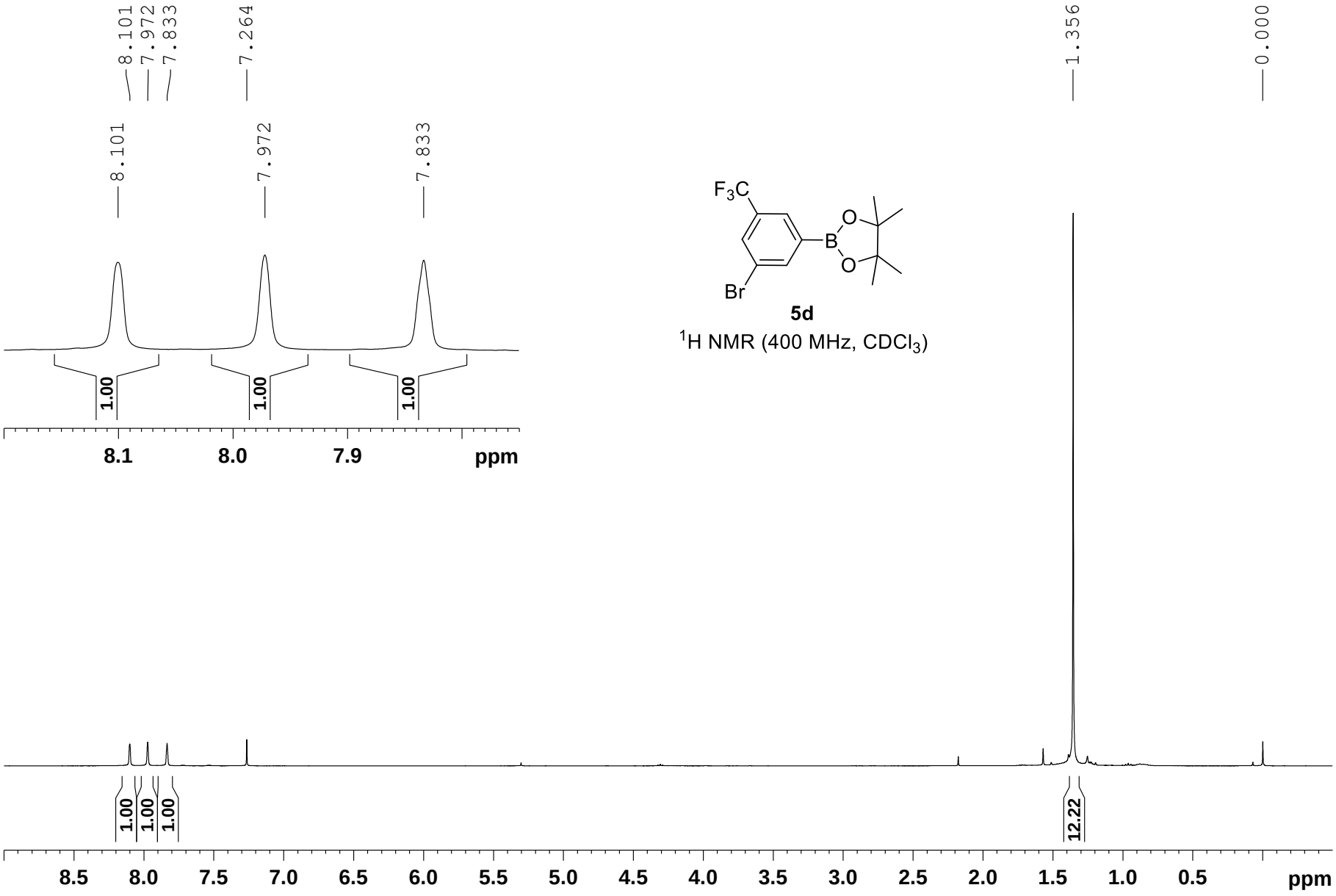

160.02
134.73
126.99
117.87
117.53
84.31
77.48
77.37
77.16
76.84
55.68
24.97
MeO
O
B
O
Cl
5b
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

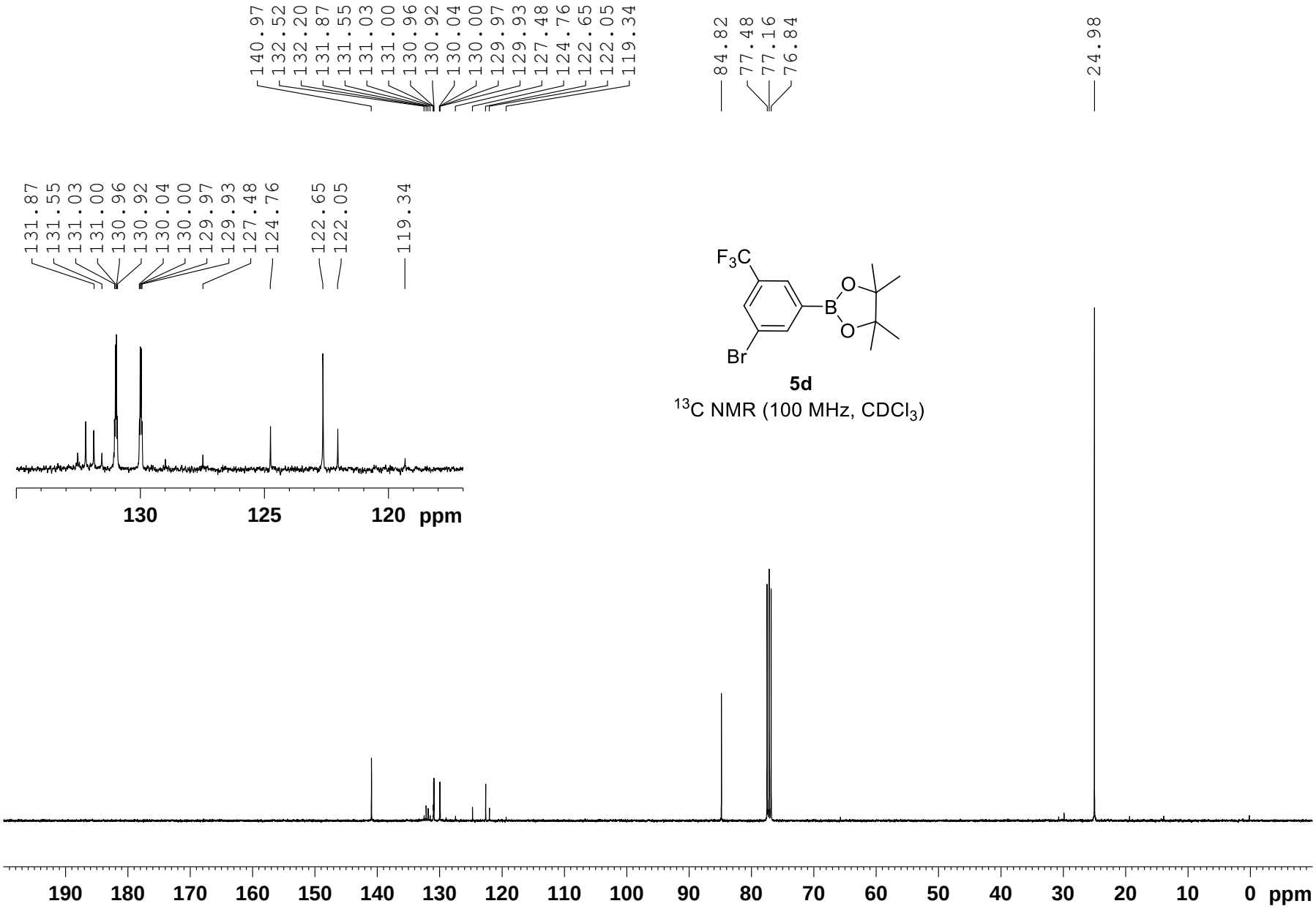

7.520
7.517
7.261
7.238
7.232
7.150
7.145
7.140
3.811
1.338
0.000
MeO
B
O
O
Br
5c
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.00
1.00
1.00
1.00
1.00
3.05
12.06
7.5
7.4
7.3
7.2
7.1
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

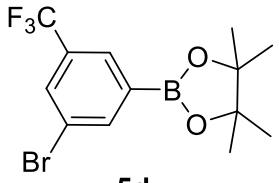


5c

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

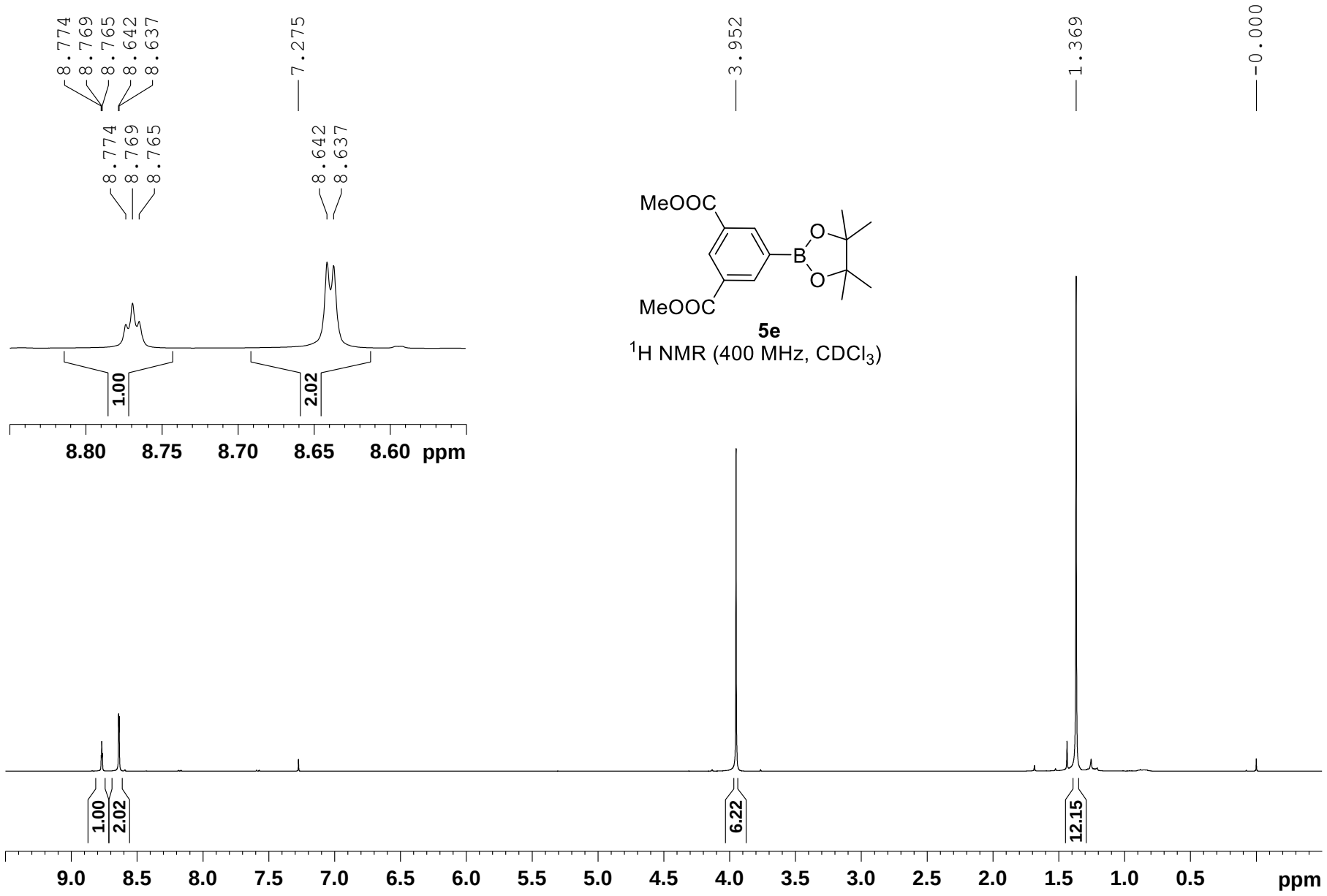

8.101
7.972
7.833
7.264
1.356
0.000
F3C
B
O
O
Br
5d
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
12.22
8.1
8.0
7.9
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

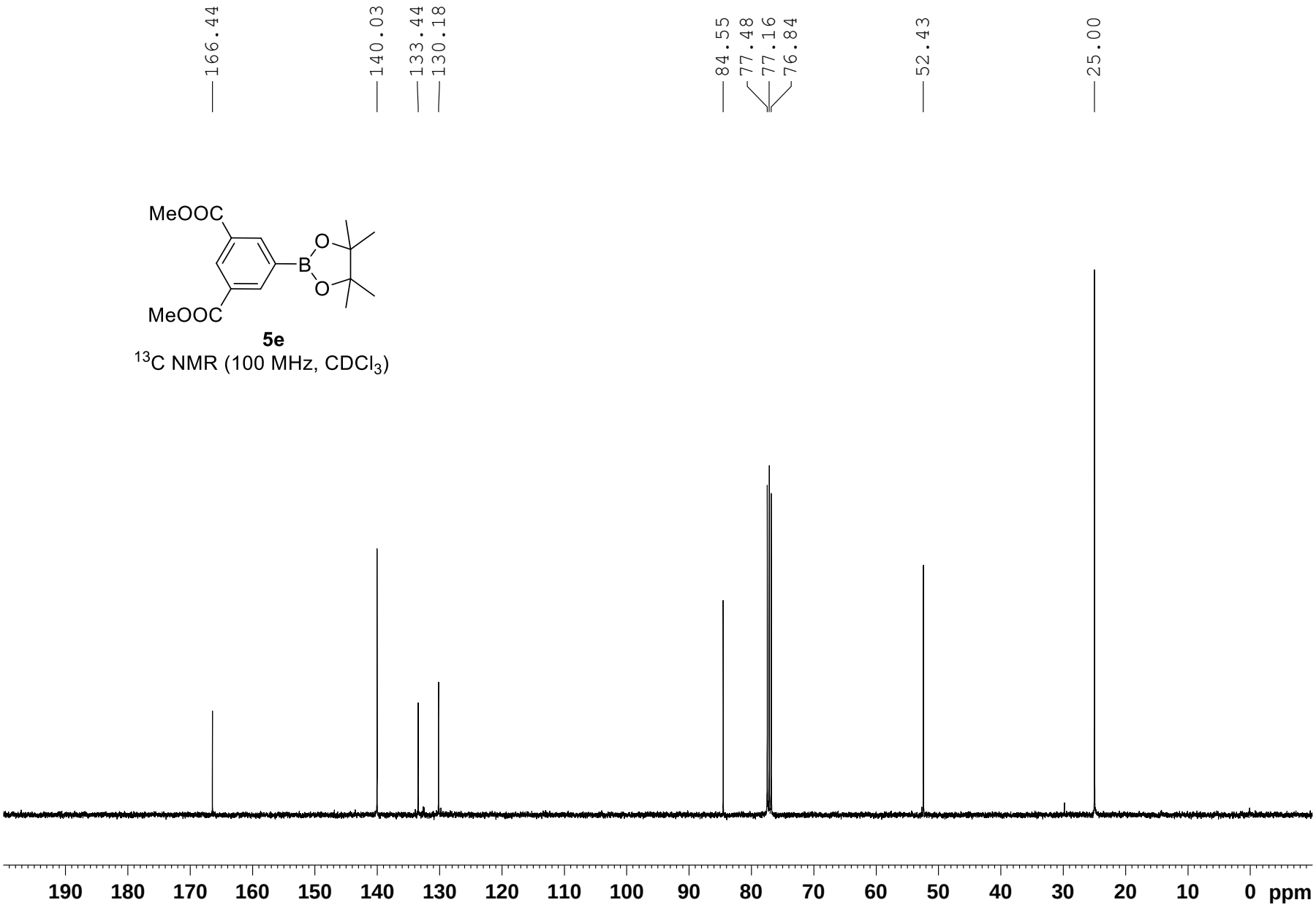

140.97
132.52
132.20
131.87
131.55
131.03
131.00
130.96
130.92
130.04
130.00
129.97
129.93
127.48
124.76
122.65
122.05
119.34
84.82
77.48
77.16
76.84
24.98
131.87
131.55
131.03
131.00
130.96
130.92
130.04
130.00
129.97
129.93
127.48
124.76
122.65
122.05
119.34
130
125
120 ppm
F3C
B
O
O
Br
5d
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



5d

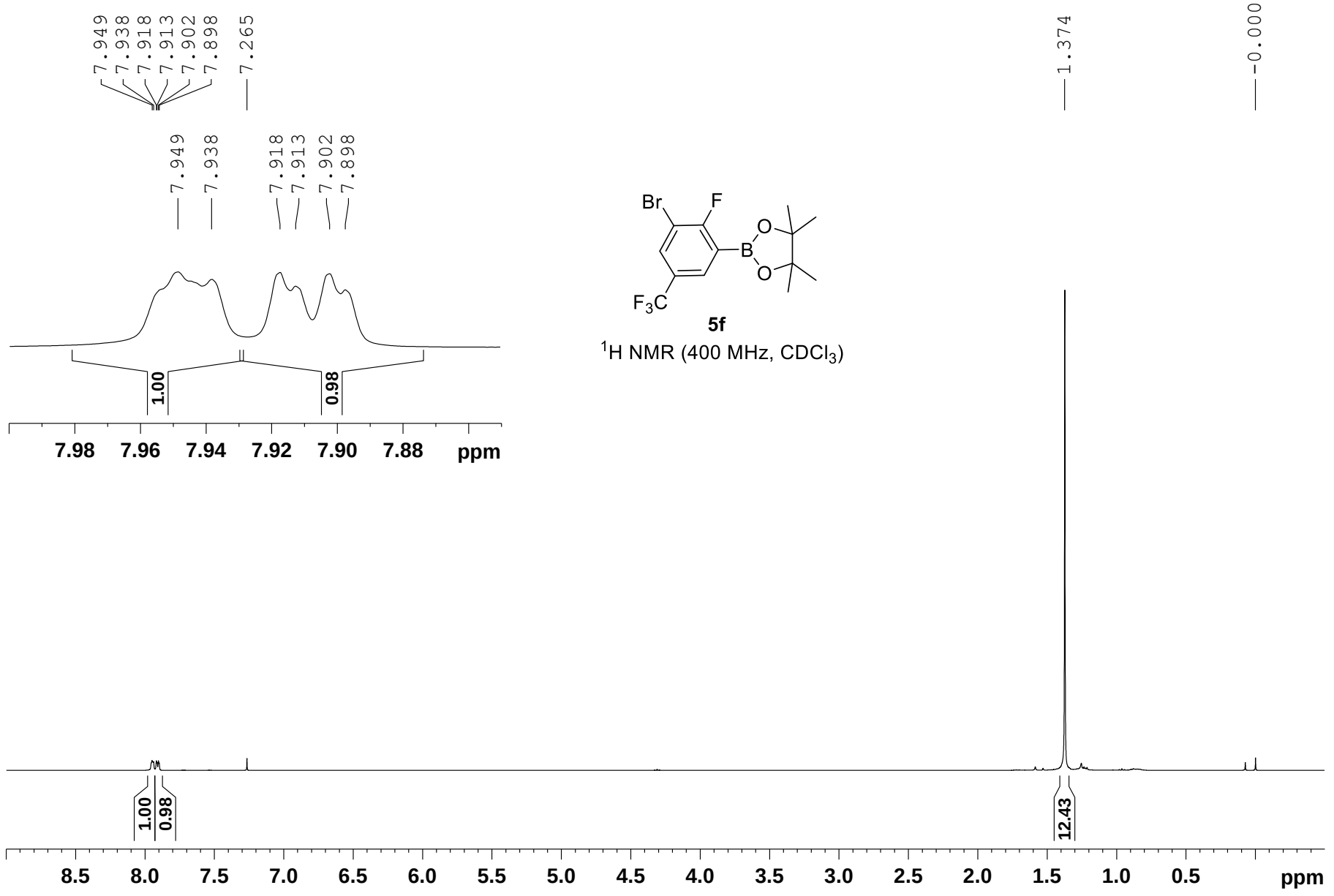
^{19}F NMR (376.5 MHz, $CDCl_3$)

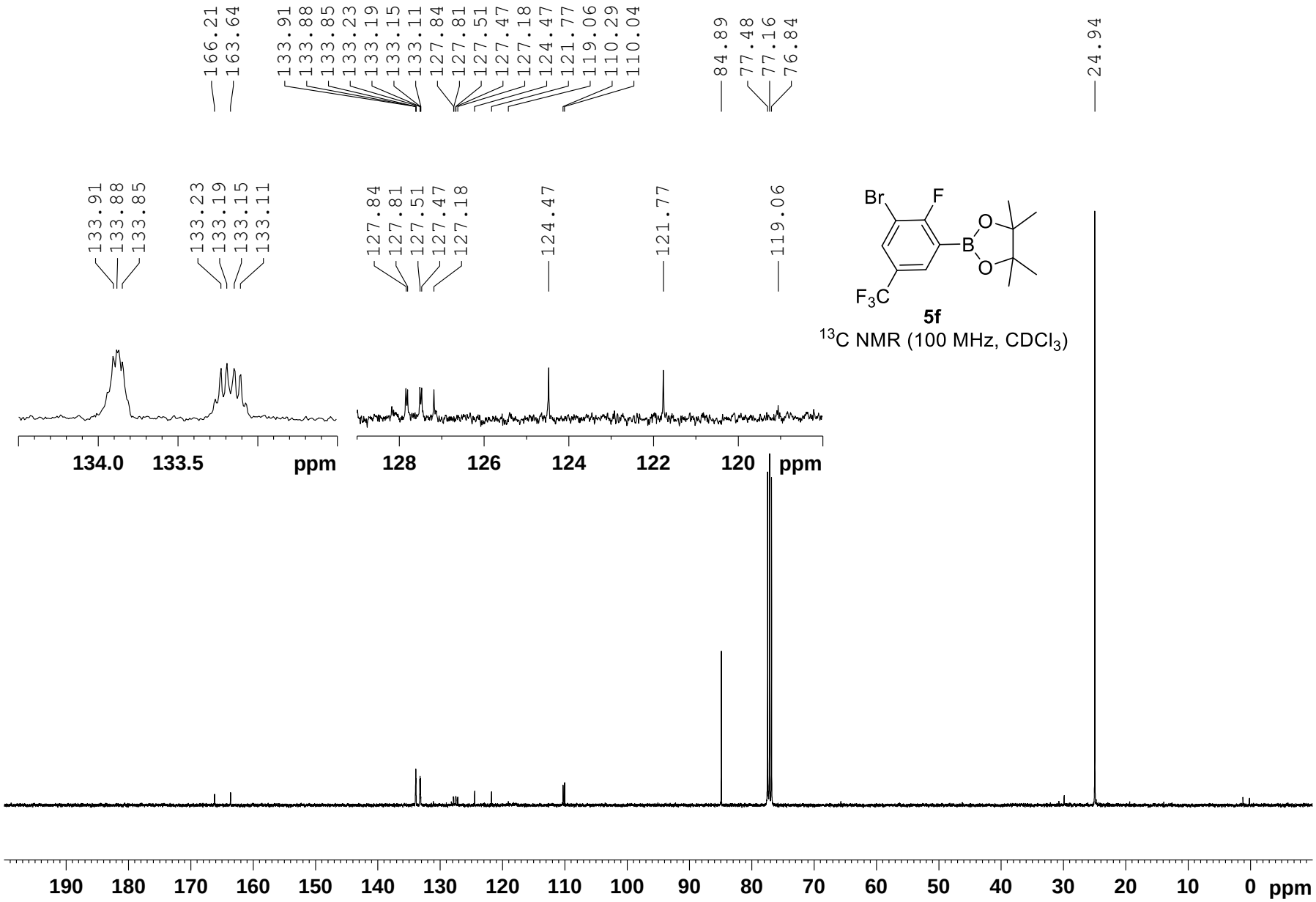

8.774
8.769
8.765
8.642
8.637
7.275
3.952
1.369
0.000
MeOOC
MeOOC
O
B
O
5e
1H NMR (400 MHz, CDCl3)
1.00
2.02
6.22
12.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.80
8.75
8.70
8.65
8.60
ppm

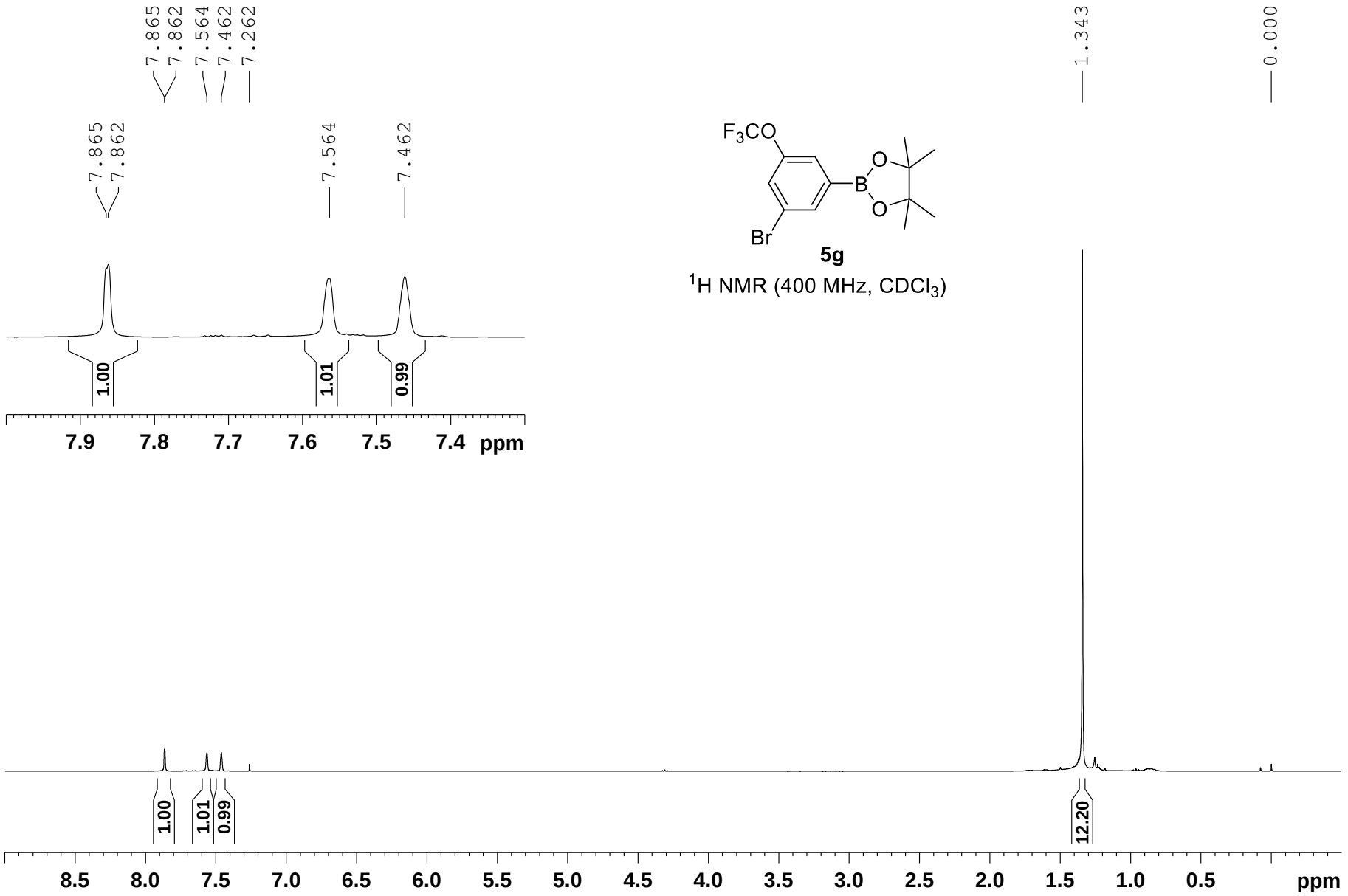


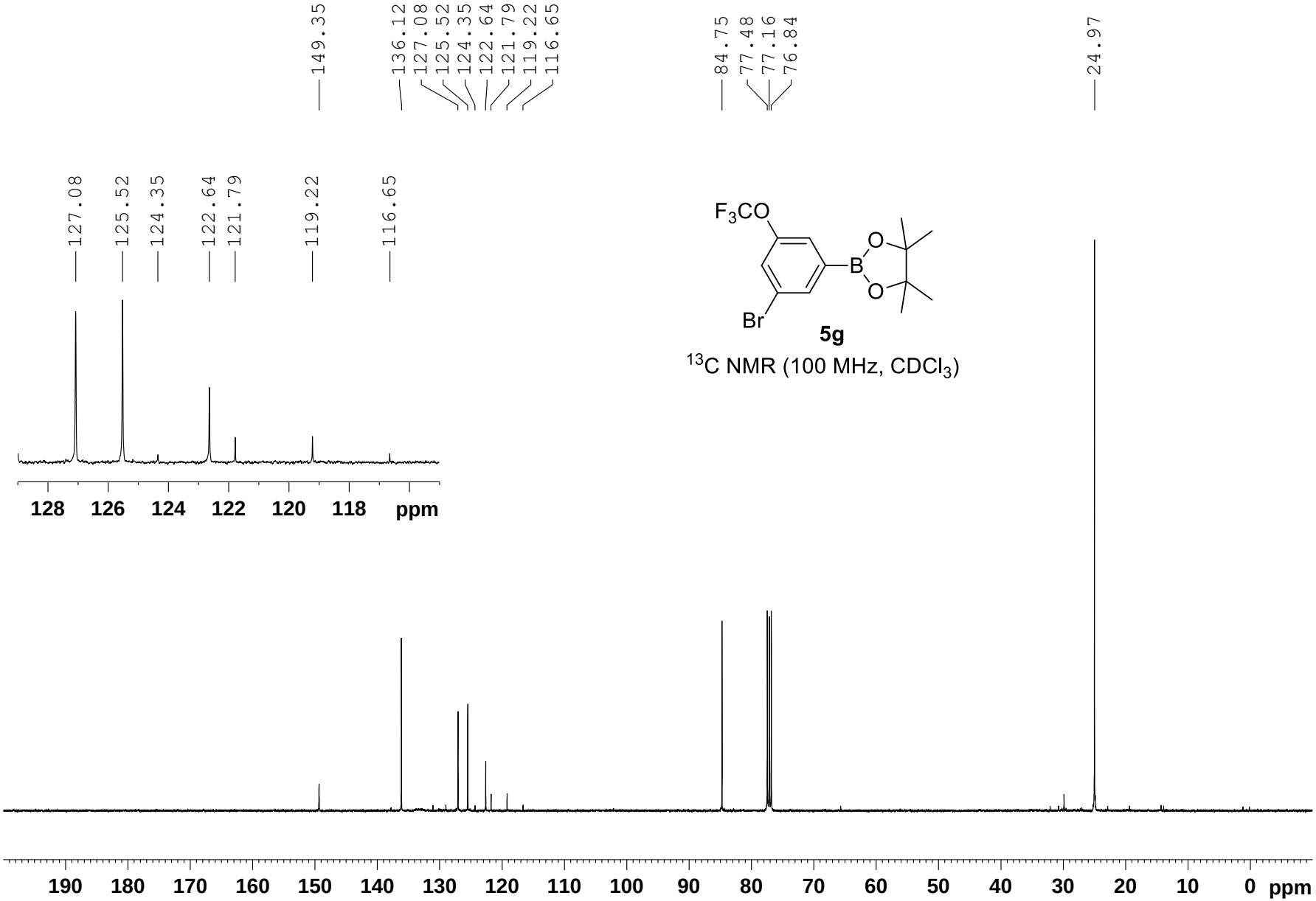
5e

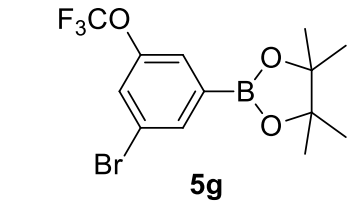
^{13}C NMR (100 MHz, $CDCl_3$)


7.949
7.938
7.918
7.913
7.902
7.898
7.265
1.374
-0.000
Br
F
B
O
O
F3C
5f
1H NMR (400 MHz, CDCl3)
1.00
0.98
12.43
7.98 7.96 7.94 7.92 7.90 7.88 ppm
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 ppm


166.21
163.64
133.91
133.88
133.85
133.23
133.19
133.15
133.11
127.84
127.81
127.51
127.47
127.18
124.47
121.77
119.06
110.29
110.04
84.89
77.48
77.16
76.84
24.94
Br
F
O
B
O
F3C
5f
13C NMR (100 MHz, CDCl3)
134.0
133.5
ppm
128
126
124
122
120
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

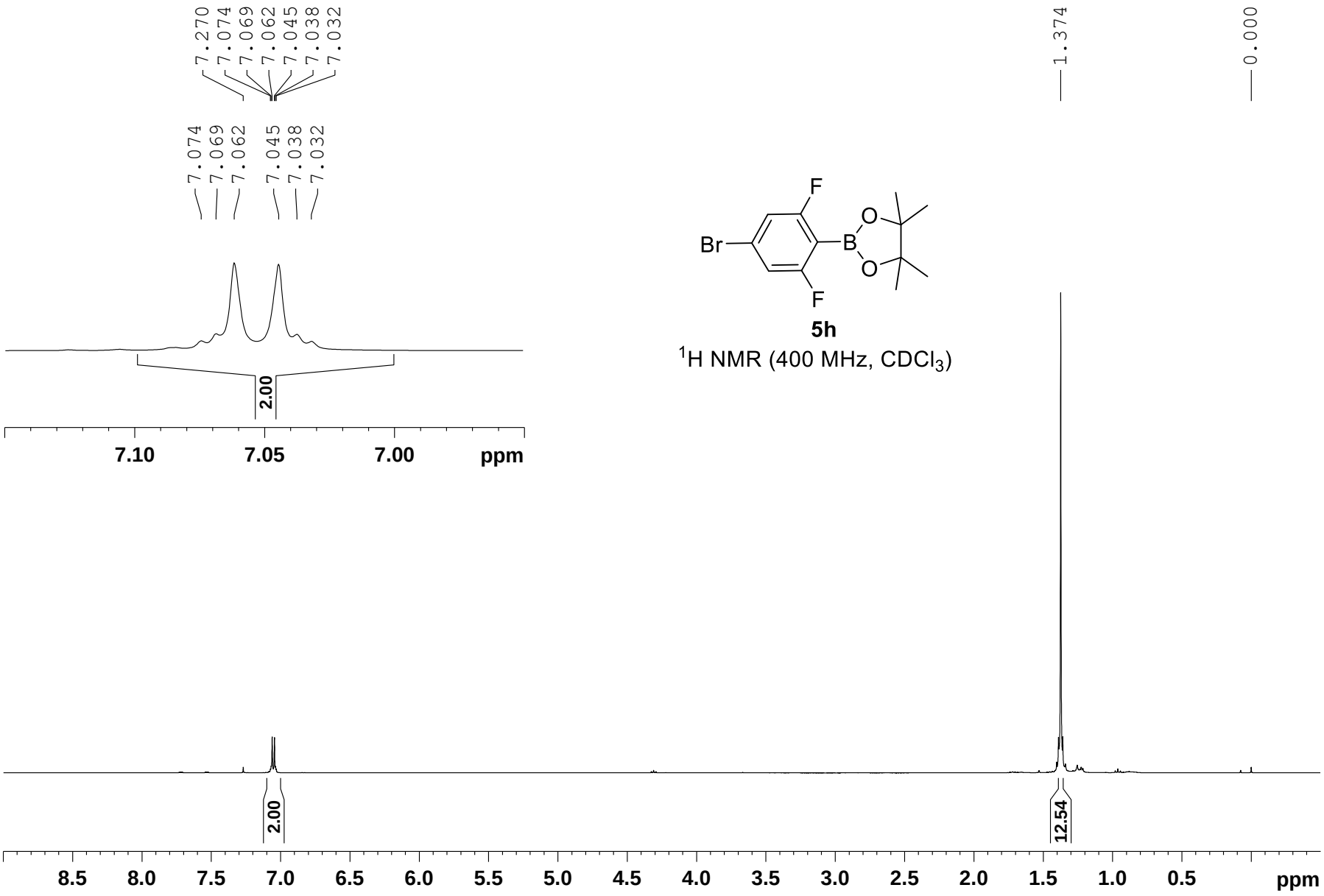

7.865
7.862
7.564
7.462
7.262
1.343
0.000
F3CO
B
O
O
Br
5g
1H NMR (400 MHz, CDCl3)
1.00
1.01
0.99
12.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.9
7.8
7.7
7.6
7.5
7.4
ppm

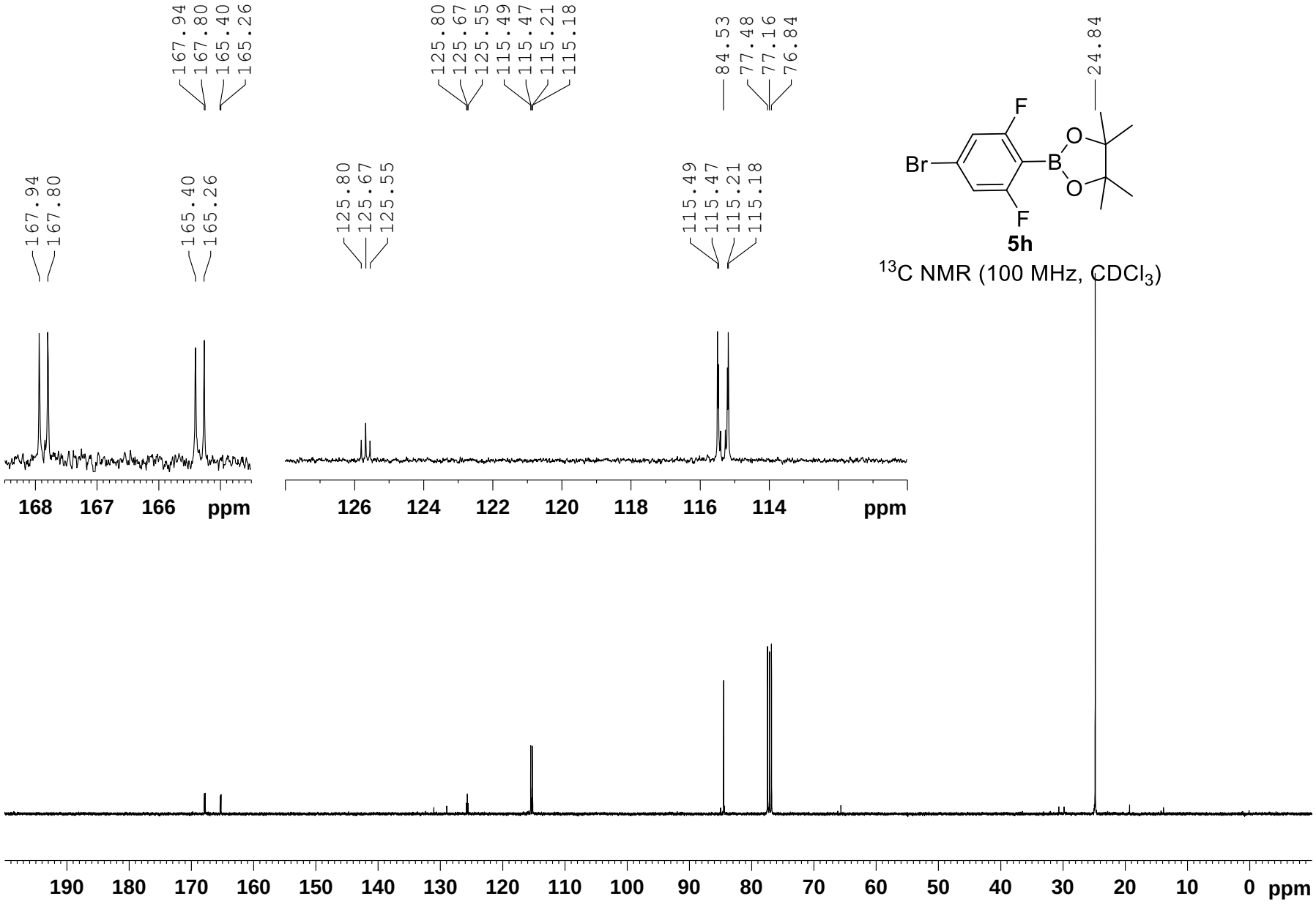

149.35
136.12
127.08
125.52
124.35
122.64
121.79
119.22
116.65
84.75
77.48
77.16
76.84
24.97
F3CO
B
O
O
Br
5g
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
128 126 124 122 120 118 ppm

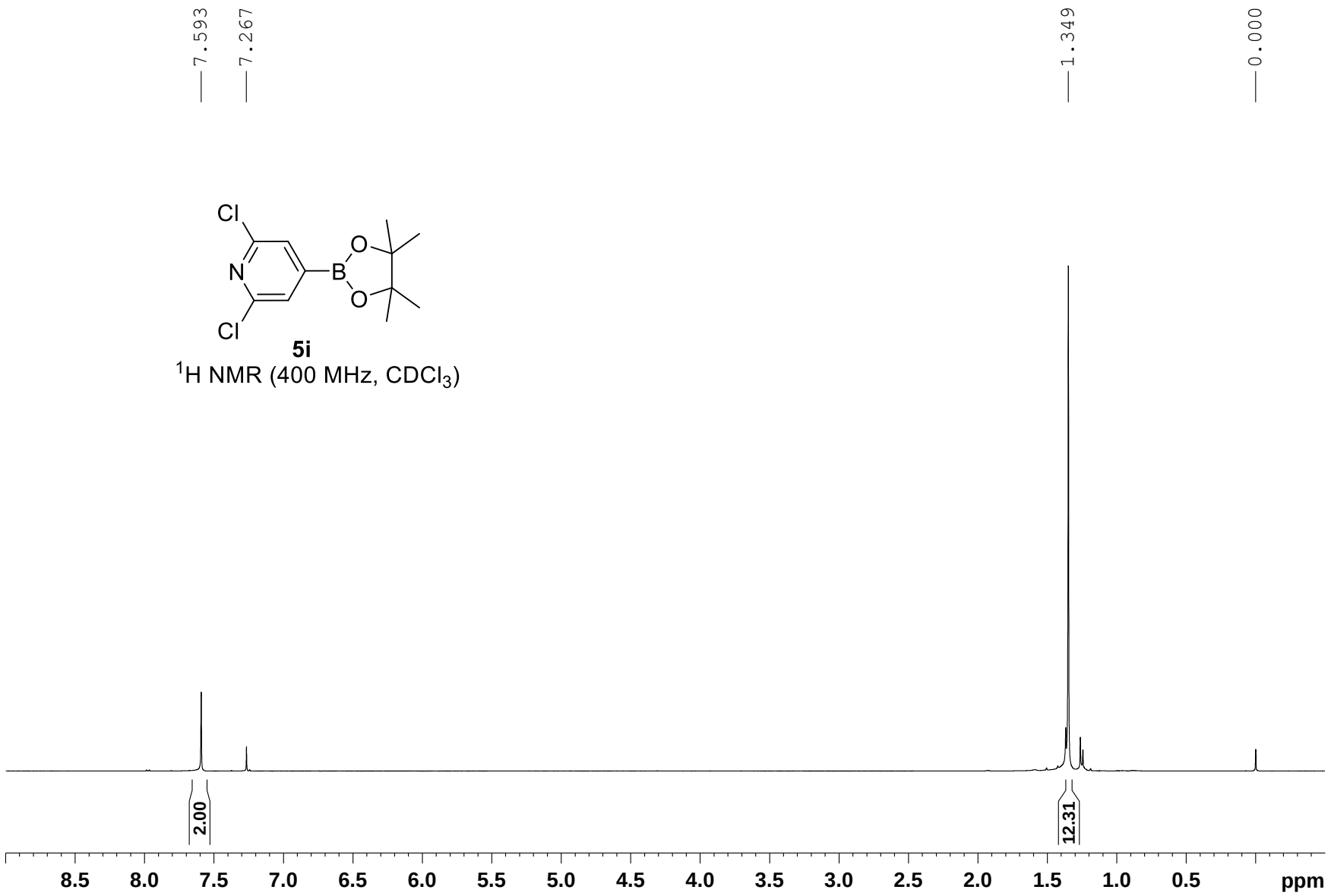


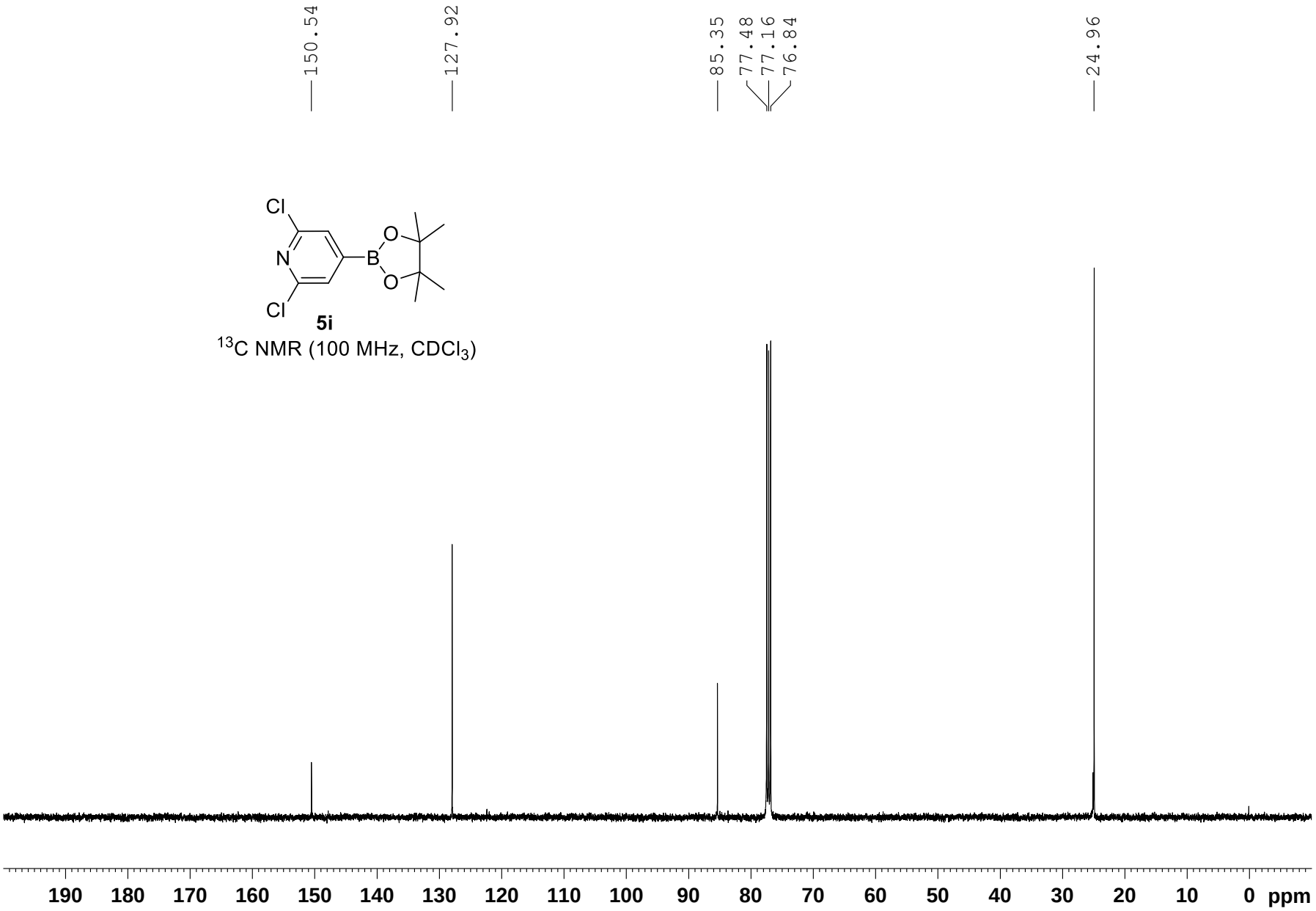
5g

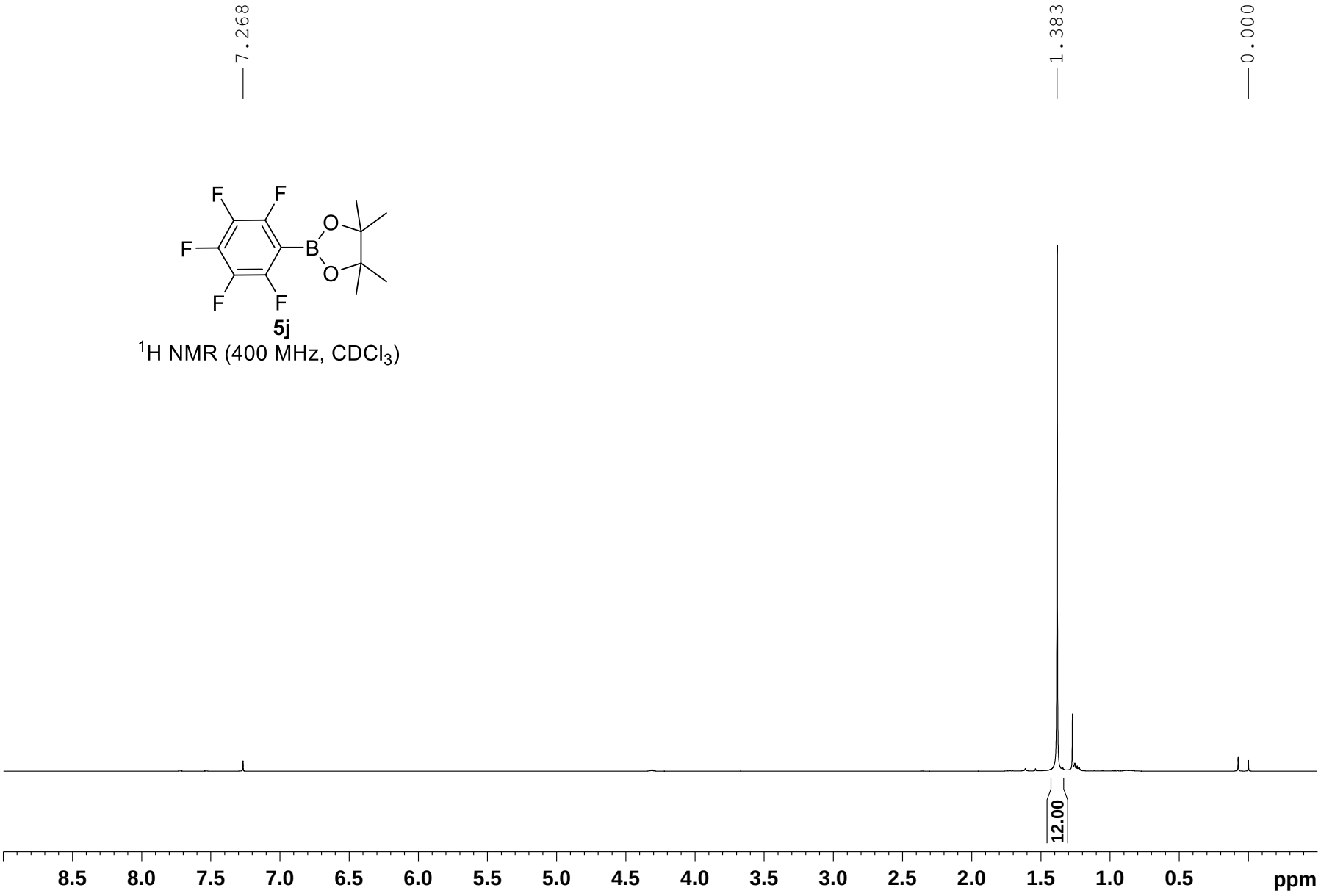
^{19}F NMR (376.5 MHz, $CDCl_3$)

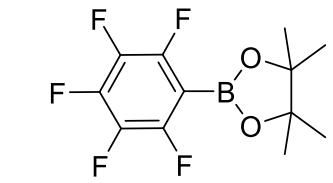

7.270
7.074
7.069
7.062
7.045
7.038
7.032
1.374
0.000
F
Br
B
O
O
F
5h
1H NMR (400 MHz, CDCl3)
2.00
7.10
7.05
7.00
ppm
2.00
12.54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


167.94
167.80
165.40
165.26
125.80
125.67
125.55
115.49
115.47
115.21
115.18
84.53
77.48
77.16
76.84
24.84
F
Br
B
O
O
F
5h
13C NMR (100 MHz, CDCl3)
168
167
166
ppm
126
124
122
120
118
116
114
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.593
7.267
1.349
0.000
Cl
N
Cl
B
O
O
5i
1H NMR (400 MHz, CDCl3)
2.00
12.31
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
ppm

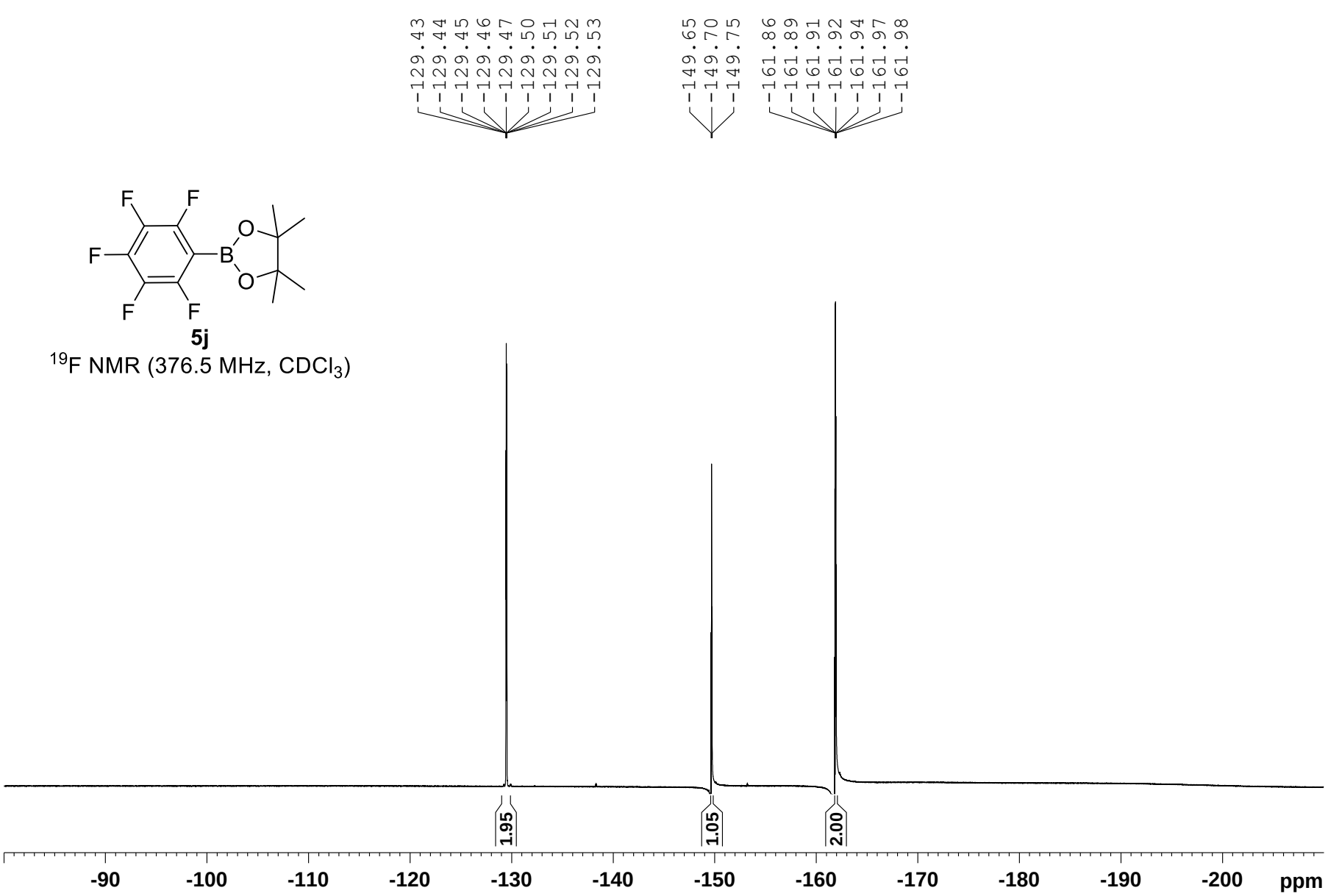

150.54
127.92
85.35
77.48
77.16
76.84
24.96
Cl
N
B
O
O
Cl
5i
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.268
1.383
0.000
F
F
F
F
F
B
O
O
5j
1H NMR (400 MHz, CDCl3)
12.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



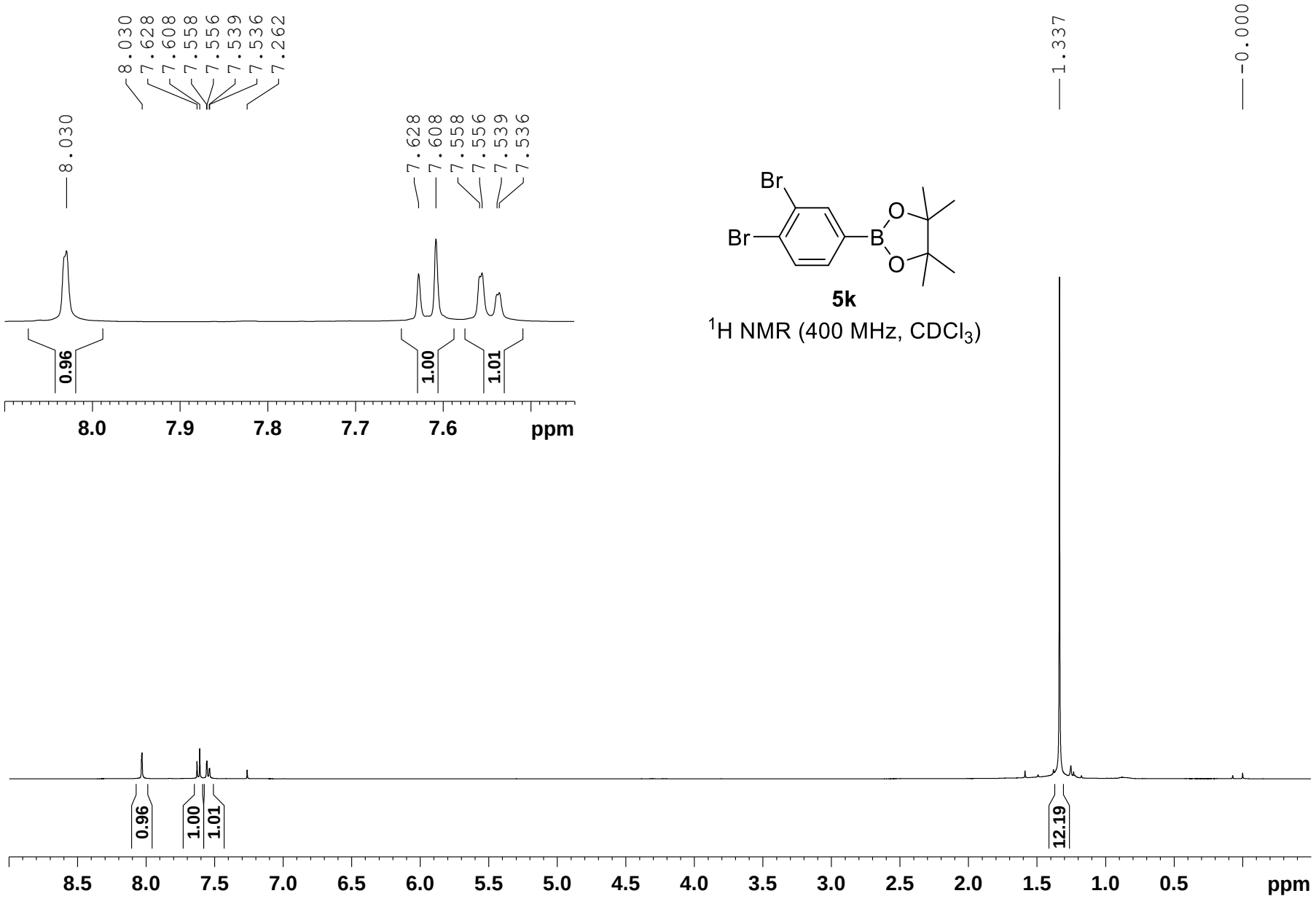
5j

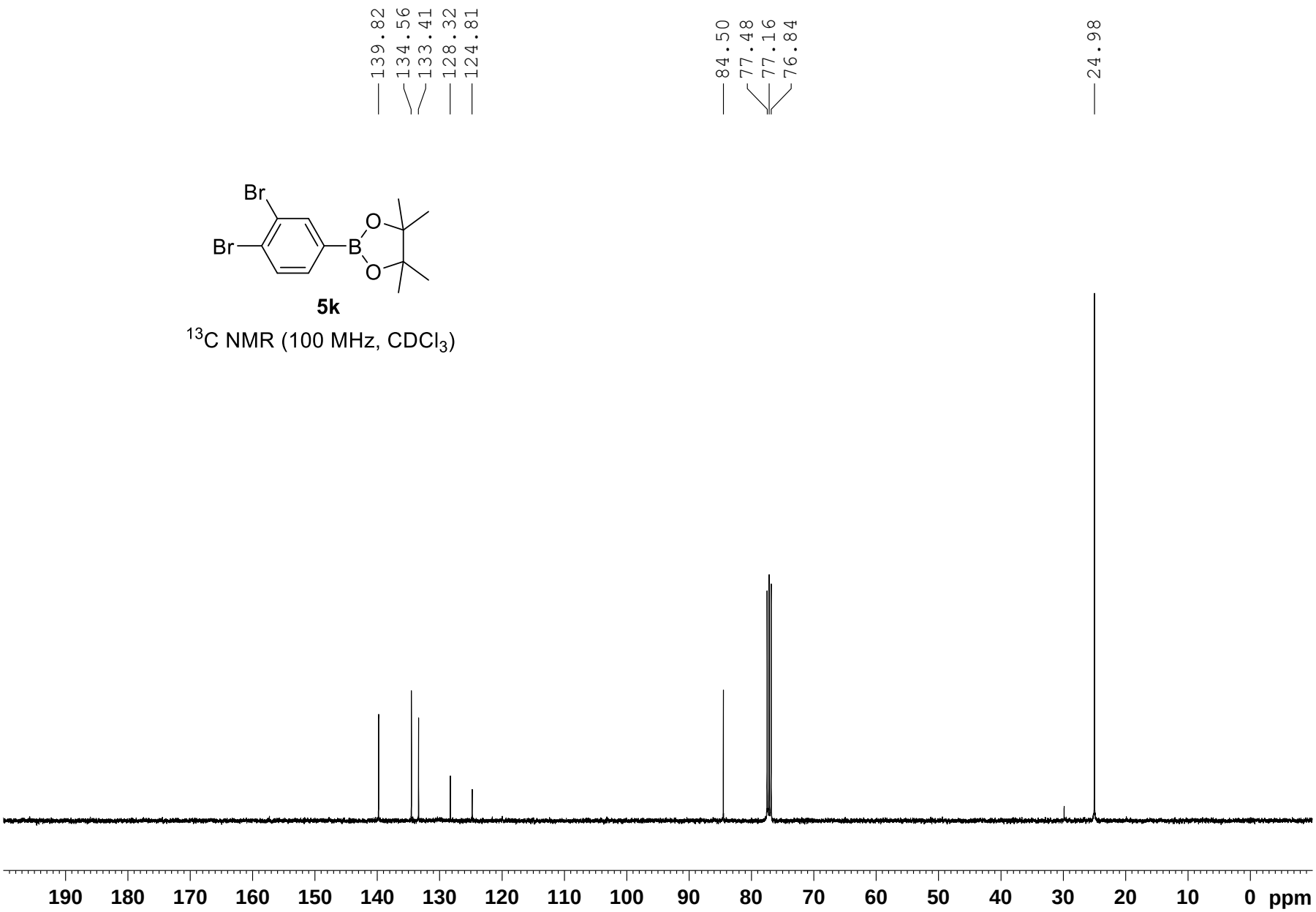
^{13}C NMR (100 MHz, $CDCl_3$)



5j

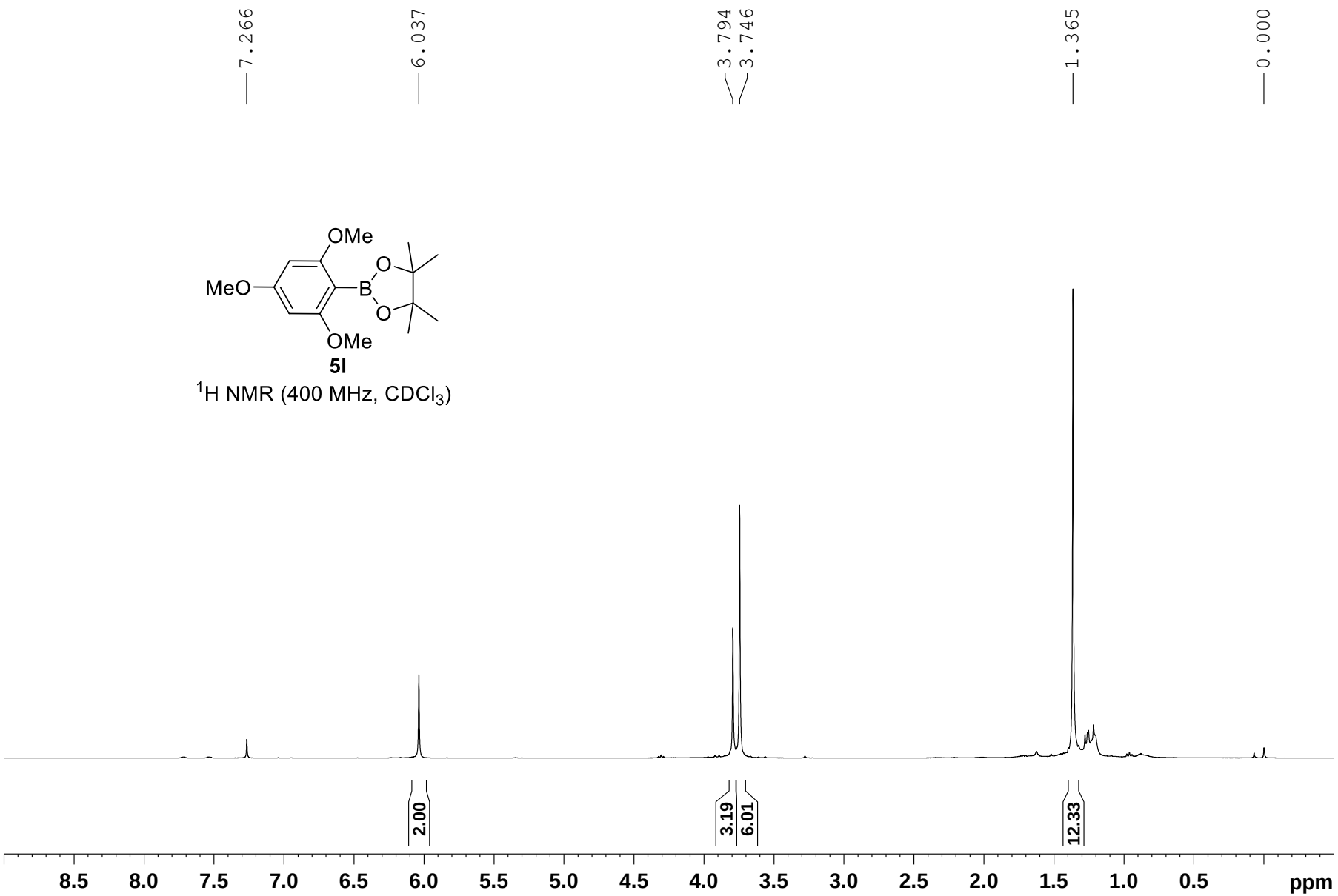
^{19}F NMR (376.5 MHz, $CDCl_3$)

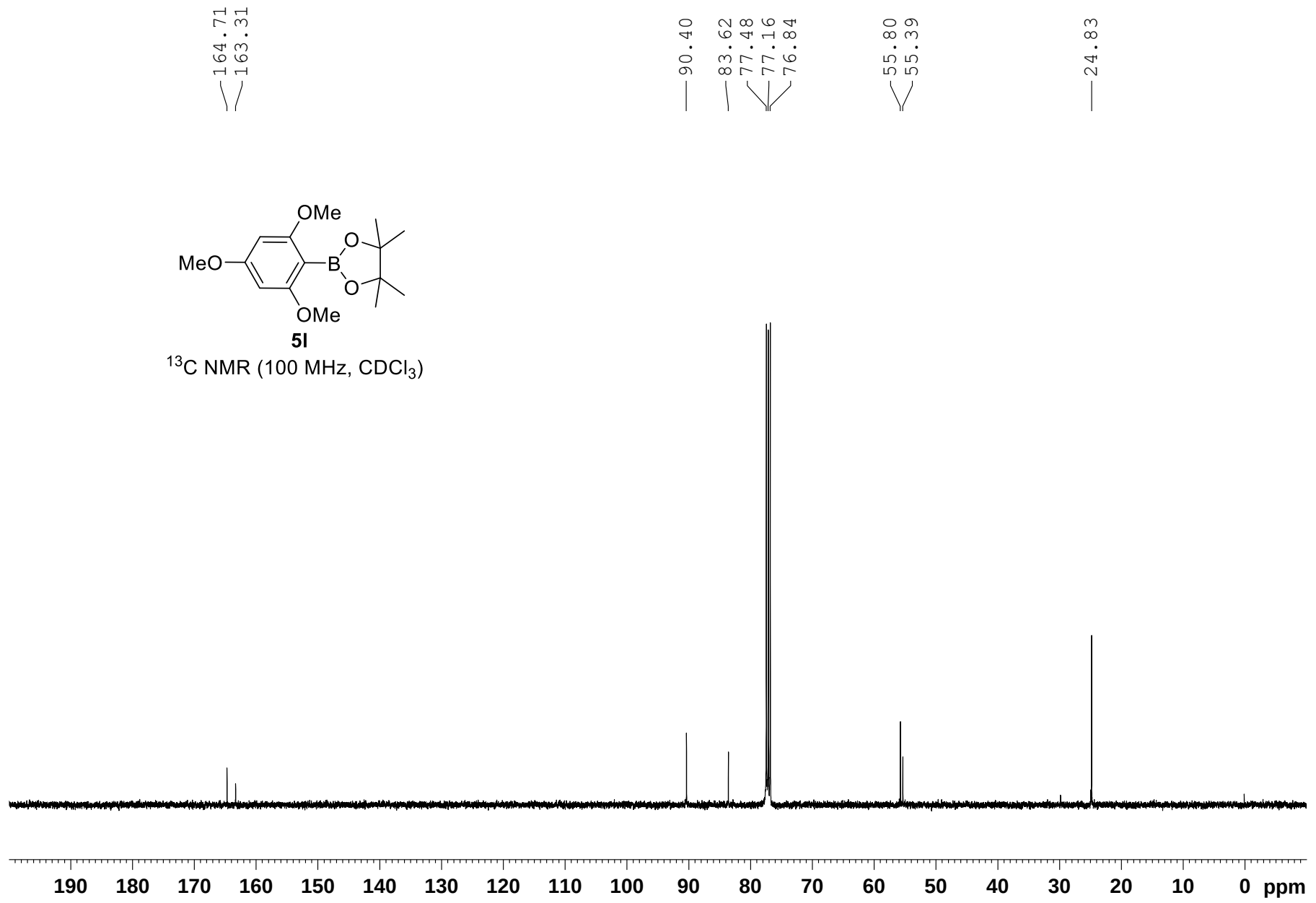

8.030
7.628
7.608
7.558
7.556
7.539
7.536
7.262
1.337
-0.000
Br
Br
B
O
O
5k
1H NMR (400 MHz, CDCl3)
0.96
1.00
1.01
12.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



5k

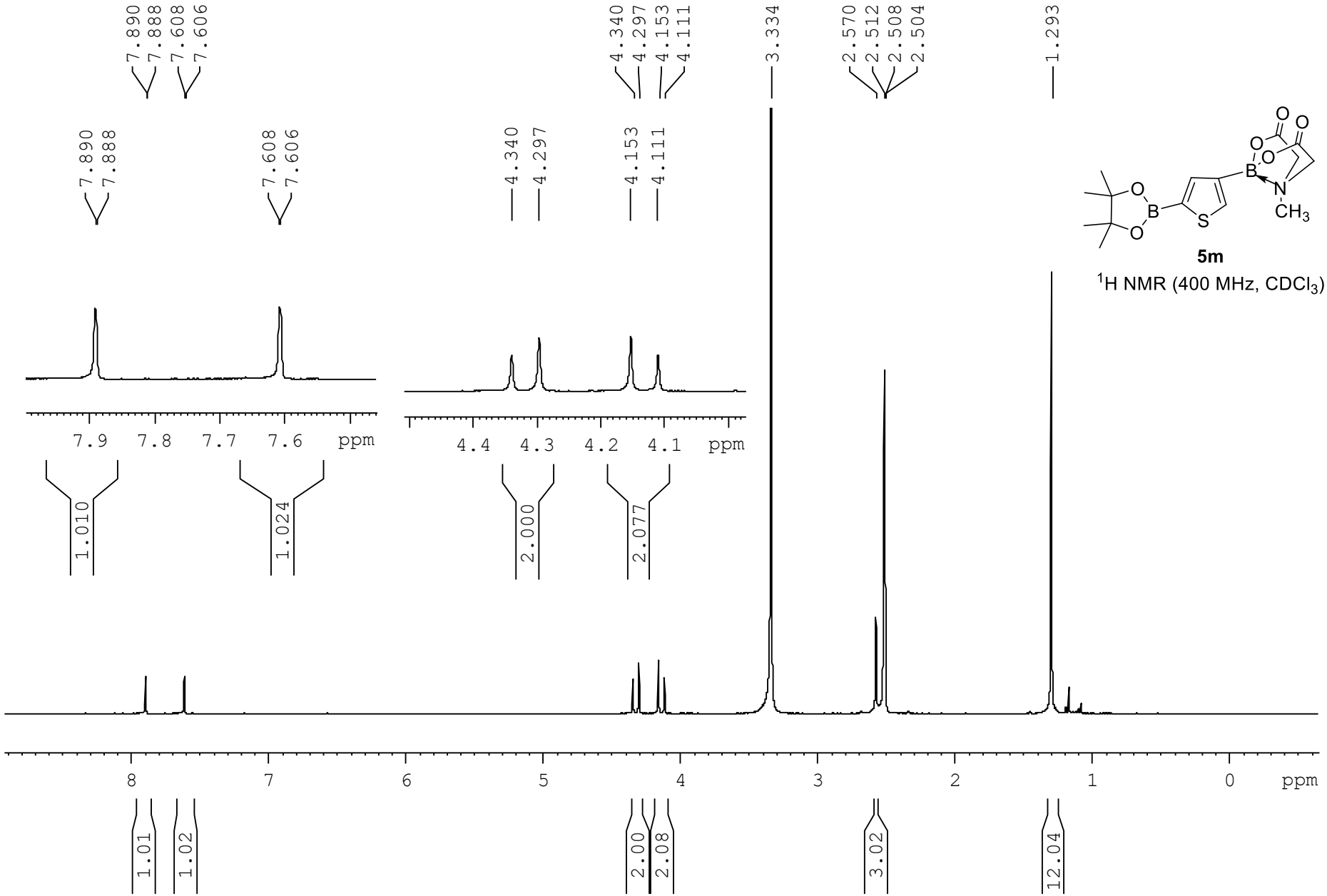
^{13}C NMR (100 MHz, $CDCl_3$)

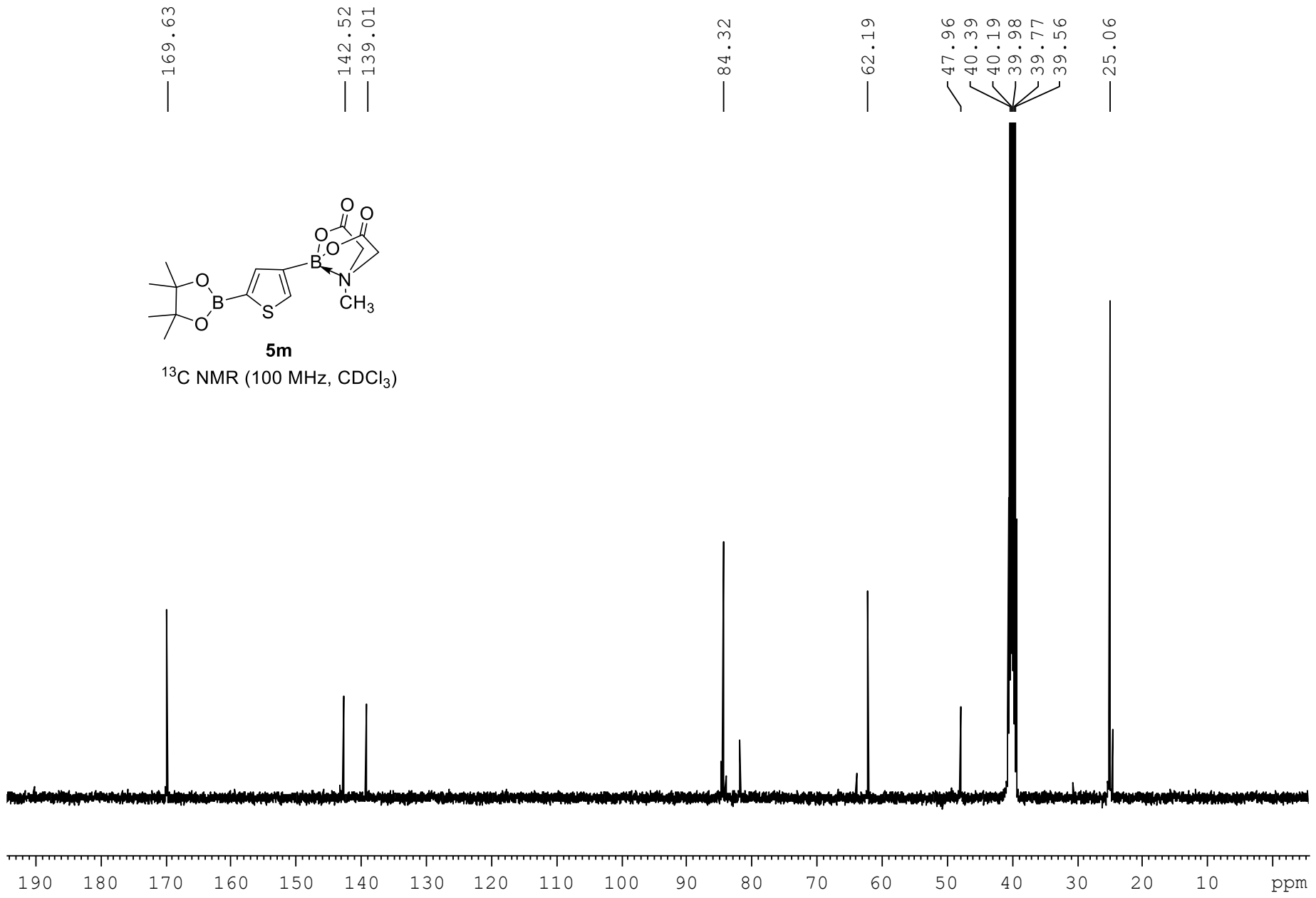

7.266
6.037
3.794
3.746
1.365
0.000
OMe
MeO
B
O
O
OMe
5l
1H NMR (400 MHz, CDCl3)
2.00
3.19
6.01
12.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



5l

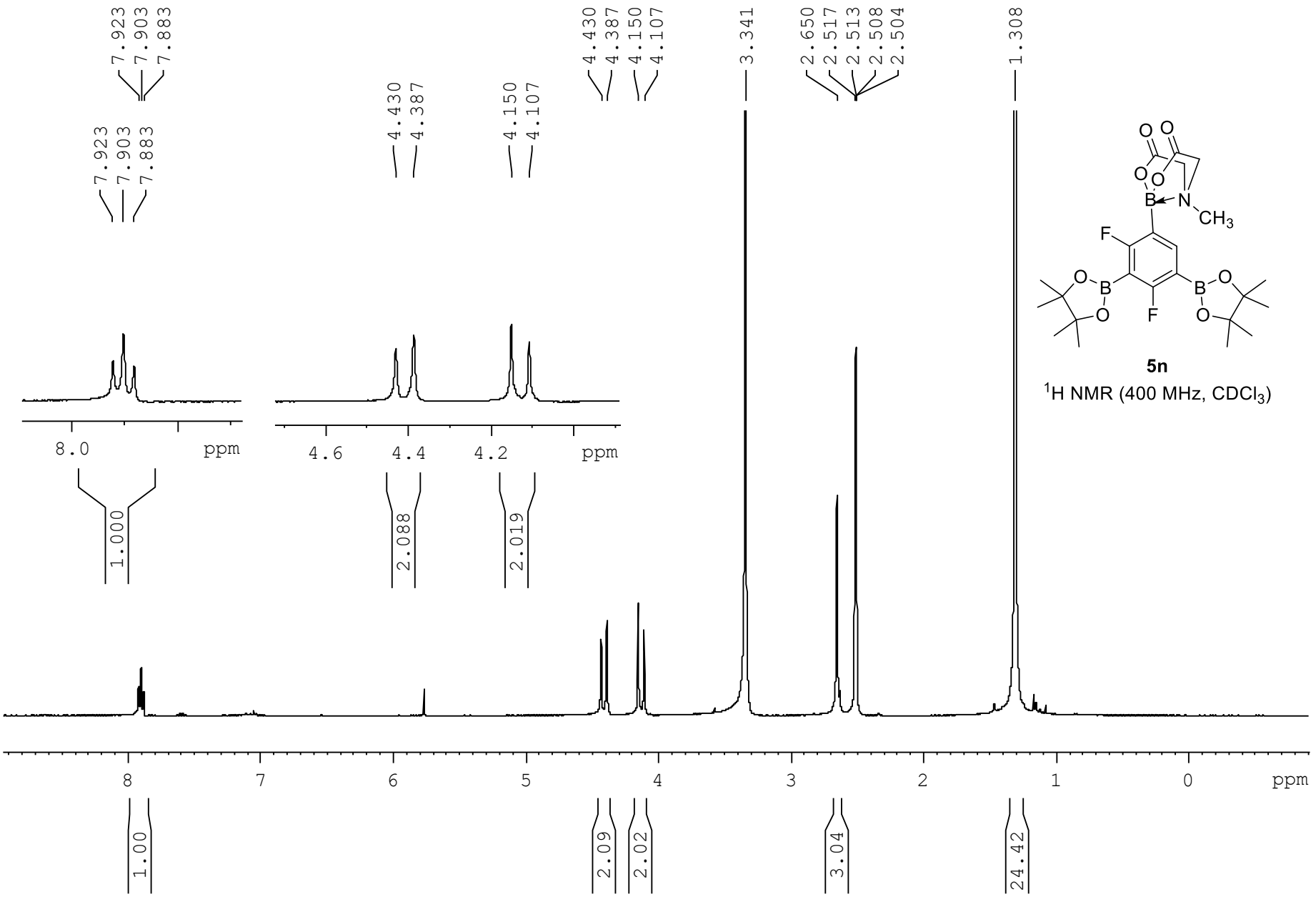
^{13}C NMR (100 MHz, $CDCl_3$)

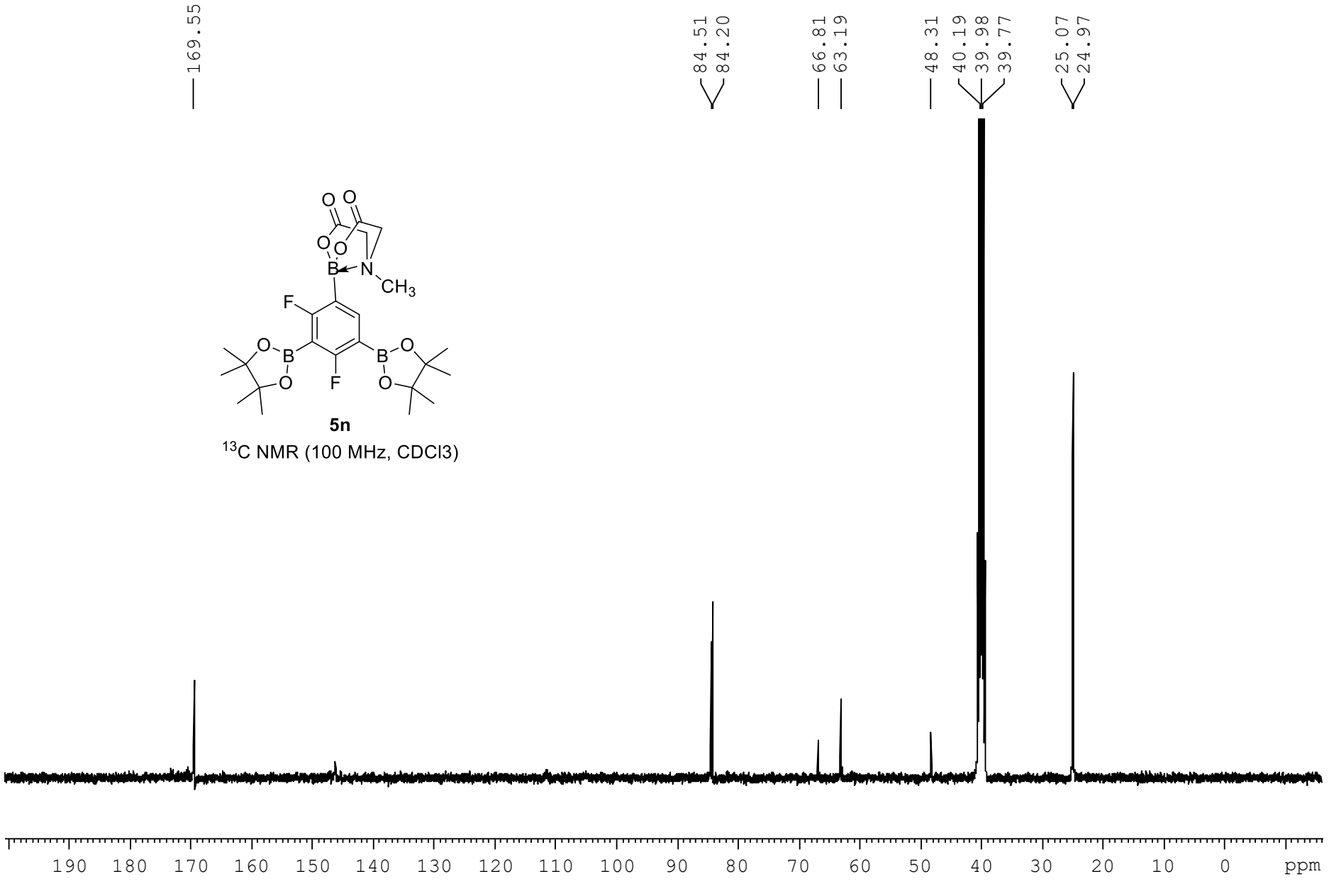

7.890
7.888
7.608
7.606
4.340
4.297
4.153
4.111
3.334
2.570
2.512
2.508
2.504
1.293
7.9
7.8
7.7
7.6
ppm
4.4
4.3
4.2
4.1
ppm
1.010
1.024
2.000
2.077
8
7
6
5
4
3
2
1
0
ppm
1.01
1.02
2.00
2.08
3.02
12.04
O
O
O
O
B
N
CH3
O
B
O
S
5m
1H NMR (400 MHz, CDCl3)



5m

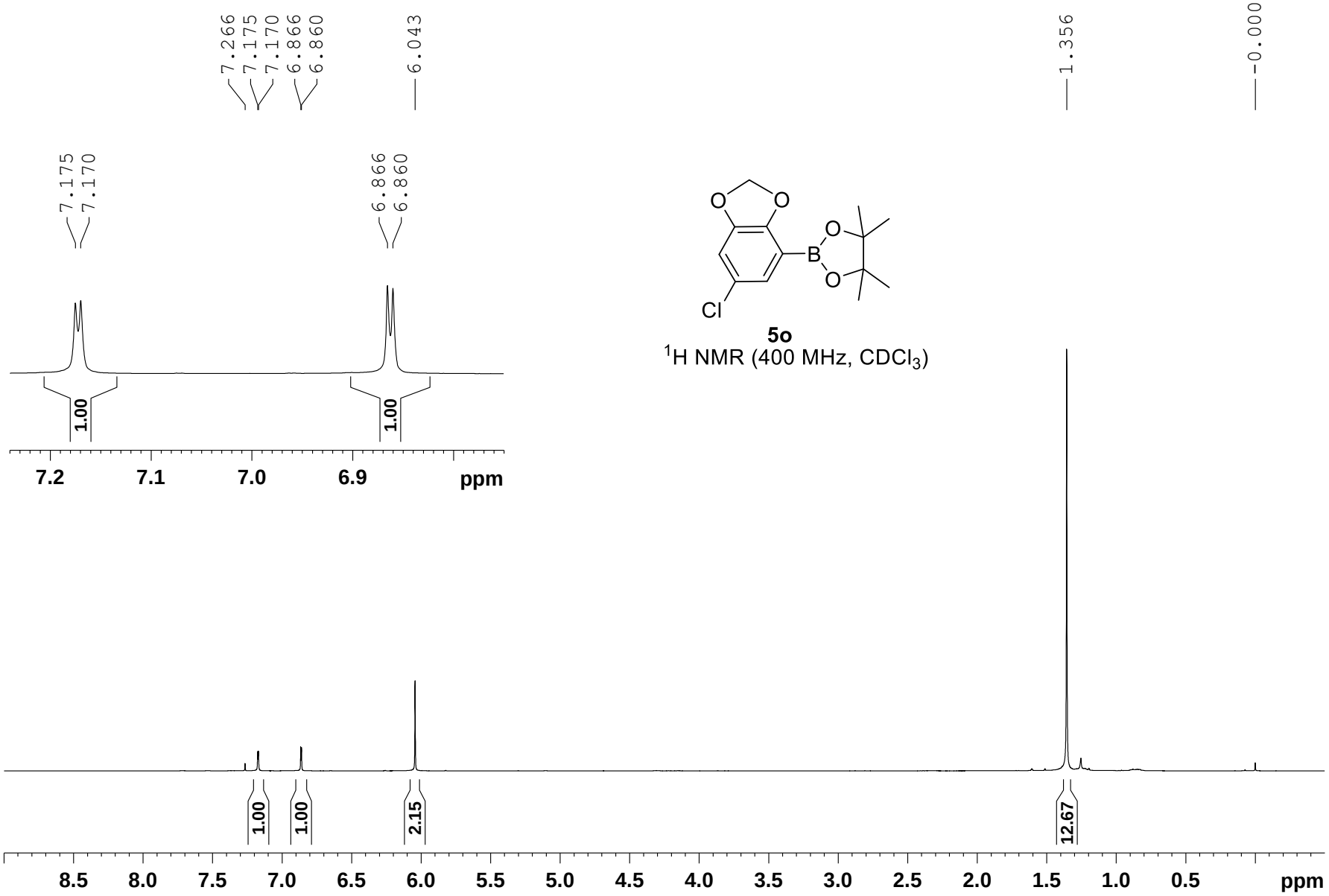
^{13}C NMR (100 MHz, $CDCl_3$)

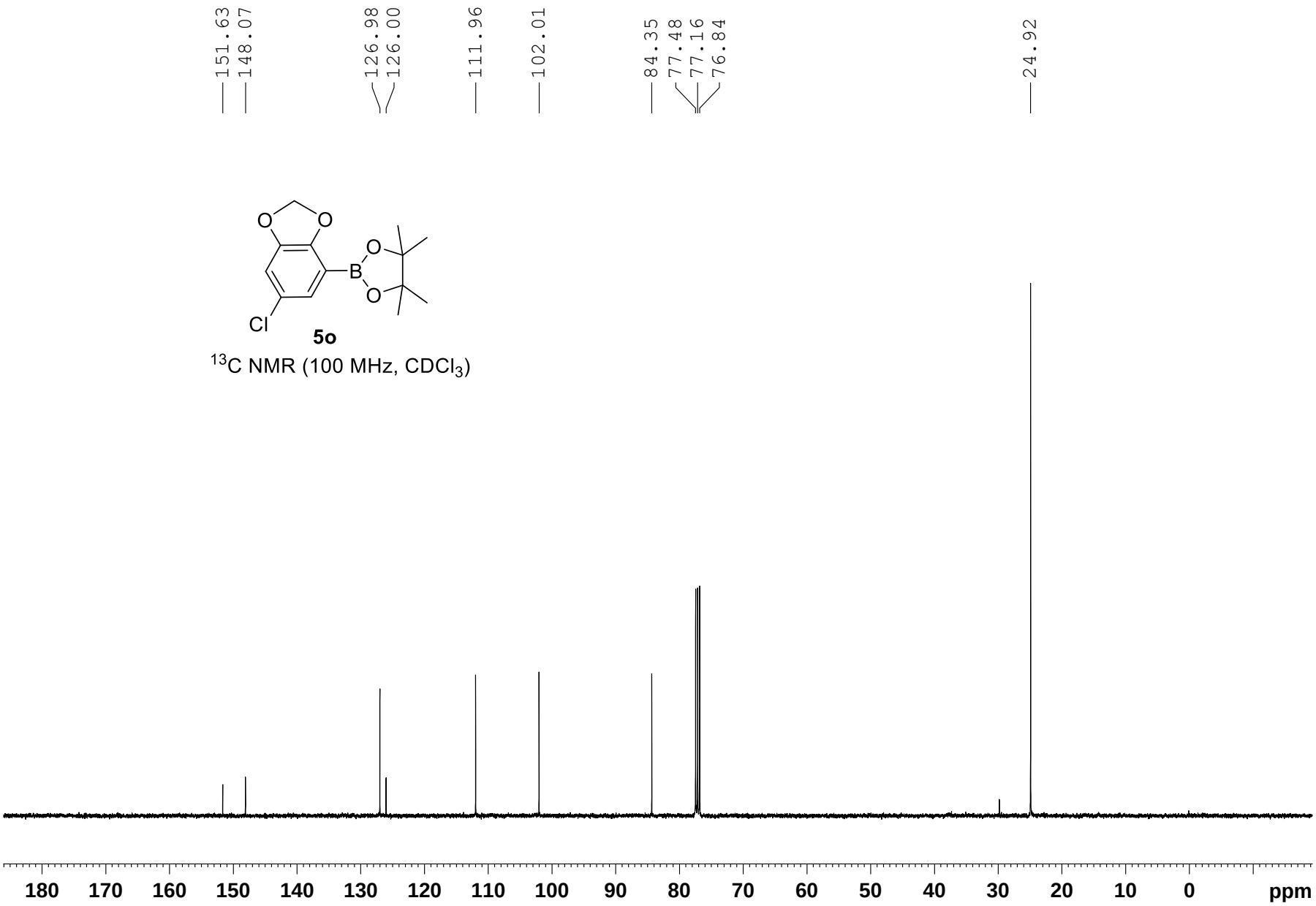

7.923
7.903
7.883
4.430
4.387
4.150
4.107
3.341
2.650
2.517
2.513
2.508
2.504
1.308
8.0
ppm
4.6
4.4
4.2
ppm
1.000
2.088
2.019
8
7
6
5
4
3
2
1
0
ppm
1.00
2.09
2.02
3.04
24.42
5n
1H NMR (400 MHz, CDCl3)



5n

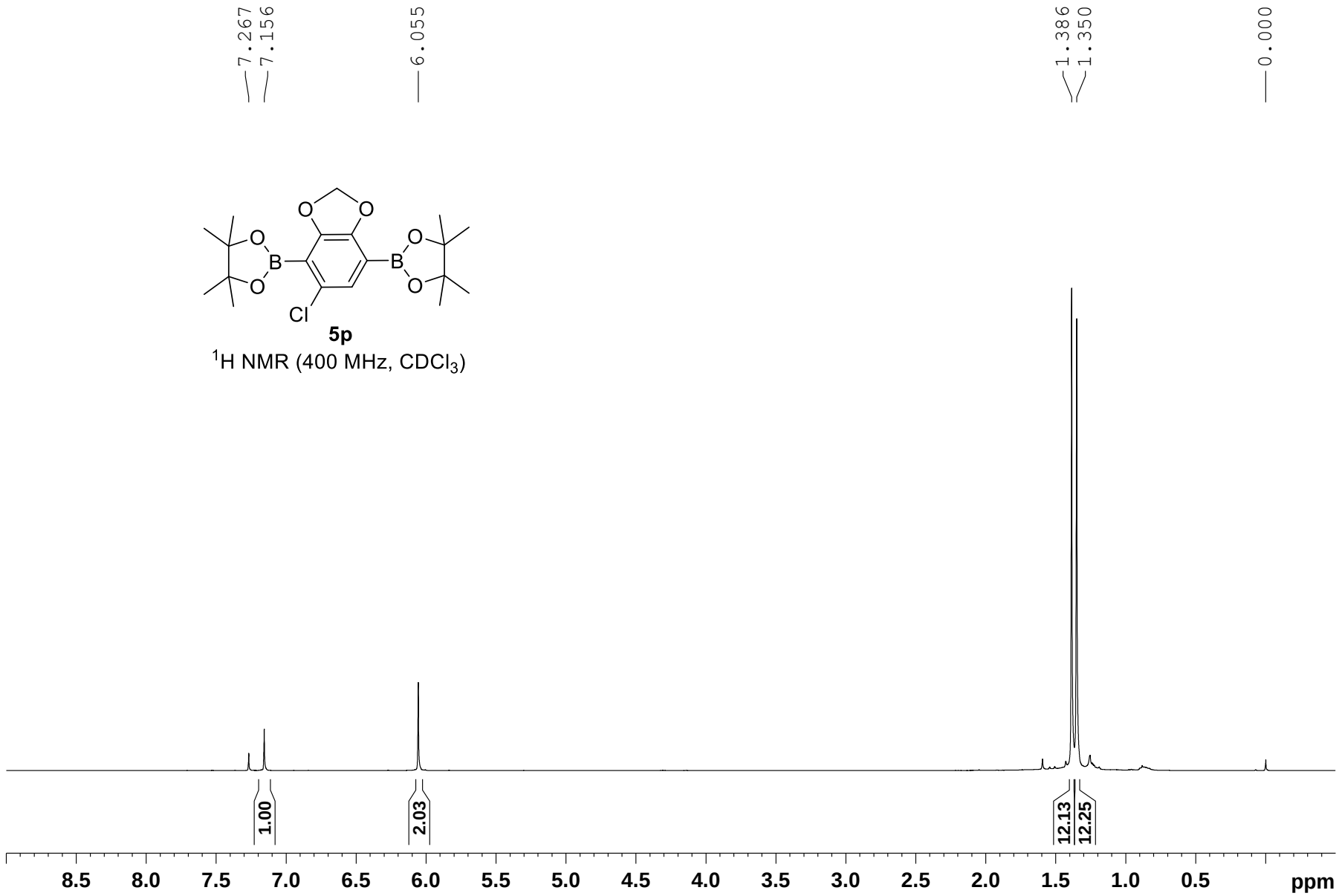
^{13}C NMR (100 MHz, CDCl3)

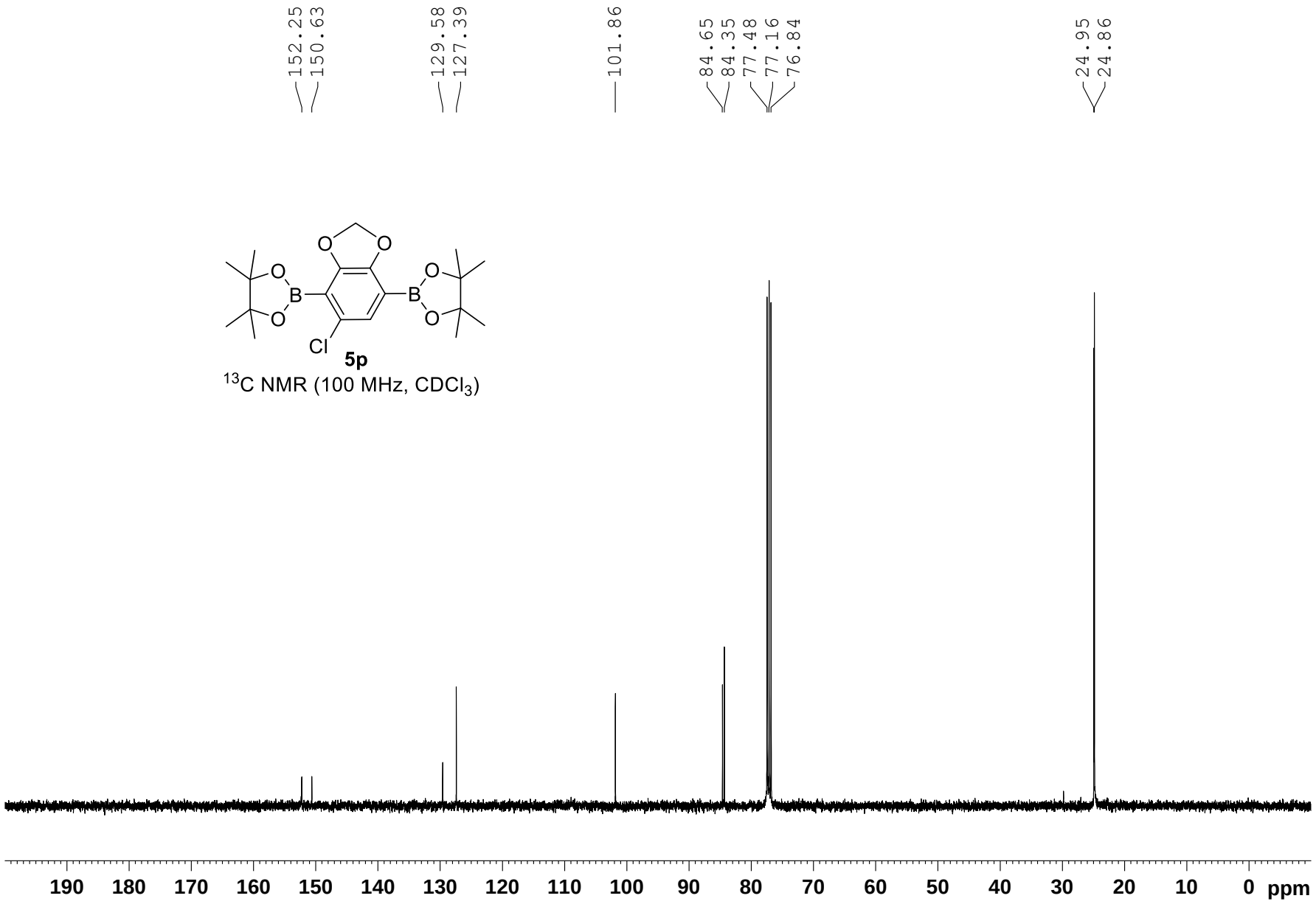

7.266
7.175
7.170
6.866
6.860
6.043
1.356
-0.000
7.175
7.170
6.866
6.860
1.00
1.00
7.2
7.1
7.0
6.9
ppm
O
O
O
B
O
Cl
5o
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.15
12.67
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



5o

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


7.267
7.156
6.055
1.386
1.350
0.000
O
O
O
B
O
B
O
O
Cl
5p
1H NMR (400 MHz, CDCl3)
1.00
2.03
12.13
12.25
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
ppm


152.25
150.63
129.58
127.39
101.86
84.65
84.35
77.48
77.16
76.84
24.95
24.86
O
O
O
B
O
B
O
O
Cl
5p
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm