Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting Information

A Domino Decarboxylative Alkylation/Annulation for the Synthesis of Pyrrolo-benzimidazolones

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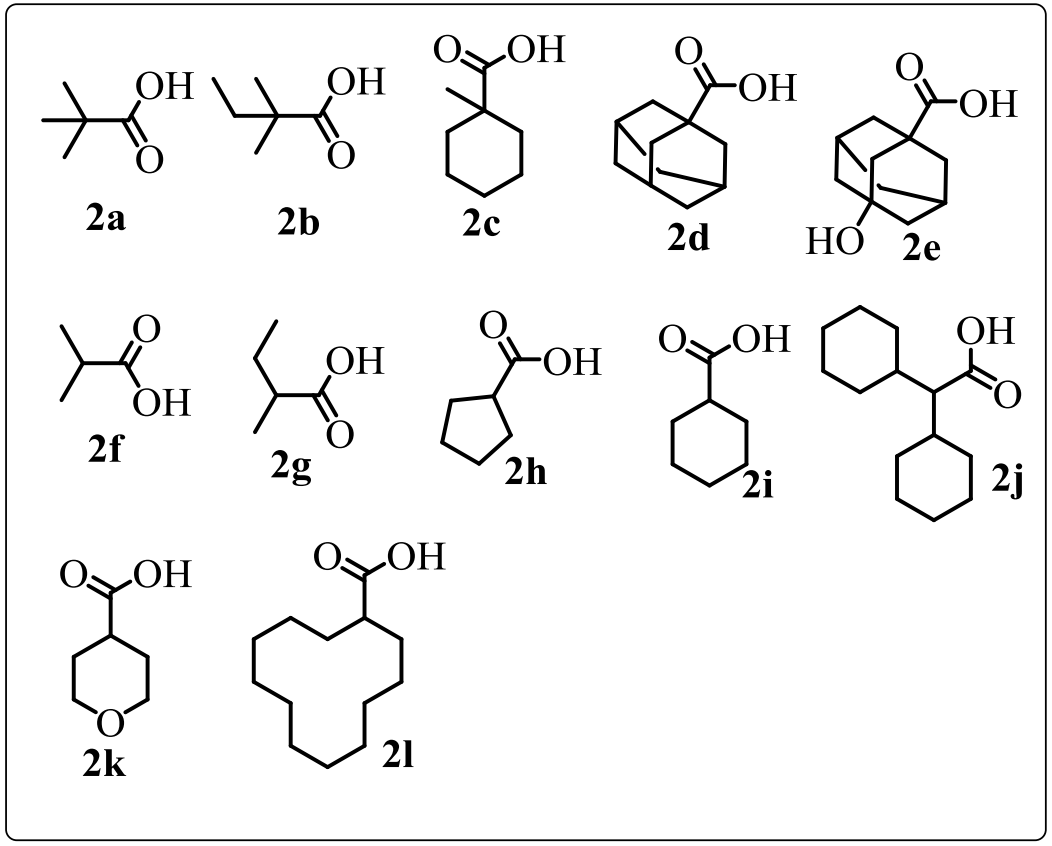
Table of Contents

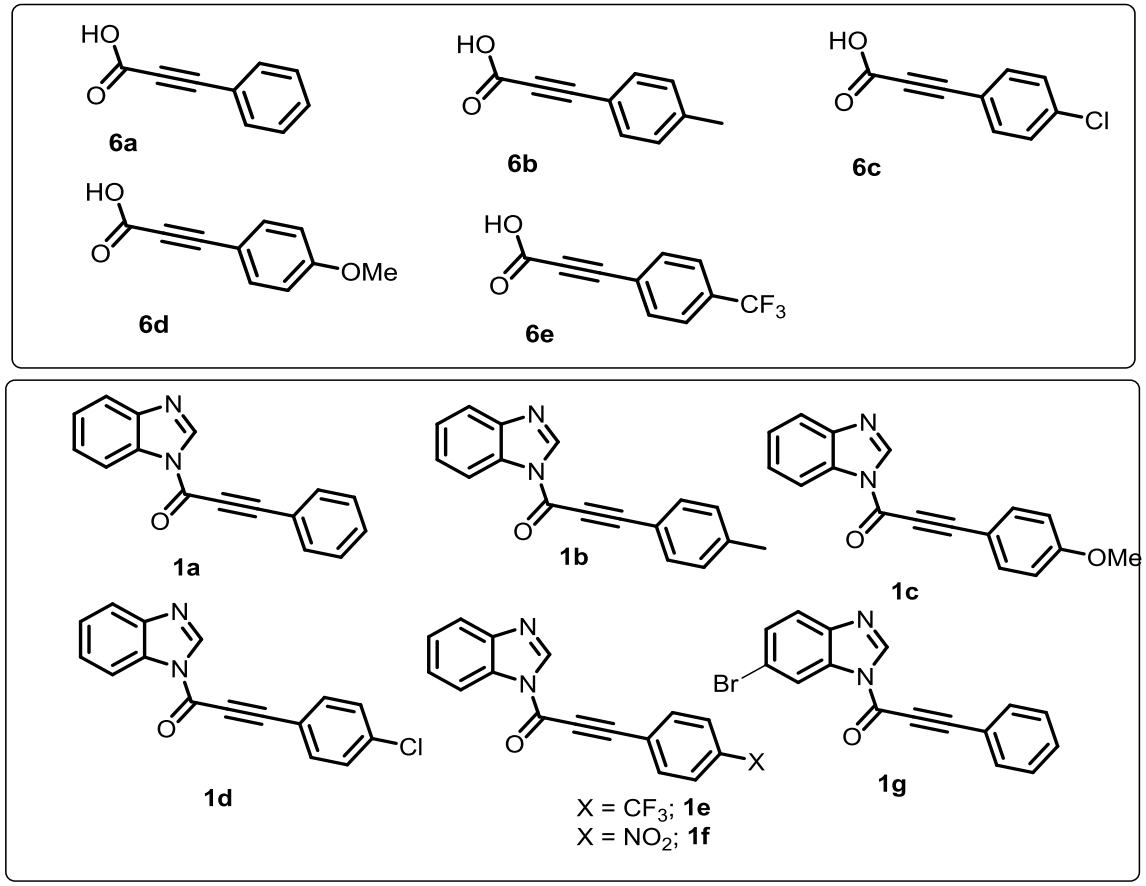
1. Structures of Aliphatic Carboxylic acids

Commercially accessible aliphatic acids (**2**) were utilized in the synthesis of pyrrolo-benzimidazolone.



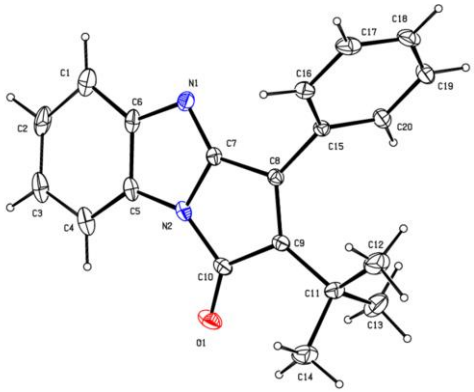
2. Structures of Pyrrolo[1,2-*a*]benzimidazol-1-ones:

Commercially accessible substituted phenyl propiolic acids (**6**) were utilized in the synthesis of substituted N-Propiolyl Phenyl benzimidazole (1).



Crystal structure determination of 3a

Crystal Data for $C_{20}H_{18}N_2O$ (M =302.36 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 12.363(3) Å, b = 9.134(2) Å, c = 14.586(3) Å, β = 91.078(10)°, V = 1646.9(7) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.076 mm^{-1}, *Dcalc* = 1.220 g/cm^3, 10590 reflections measured (6.592° ≤ 2Θ ≤ 49.986°), 2838 unique (R_{int} = 0.0622, R_{sigma} = 0.0753) which were used in all calculations. The final R_1 was 0.0576 (I > 2σ(I)) and wR_2 was 0.1491 (all data). **CCDC 2418004** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/



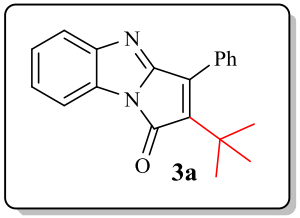
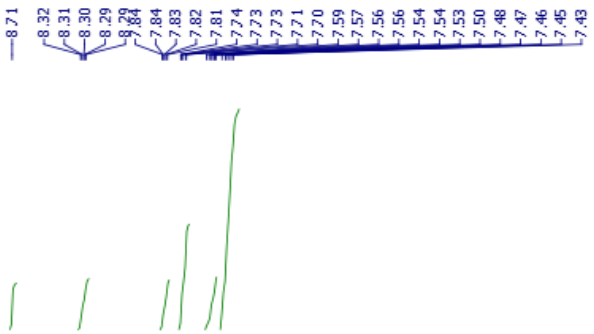
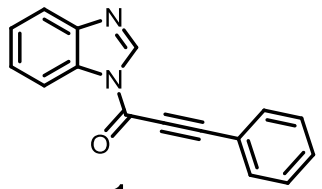


Figure caption: ORTEP diagram of **3a** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Atoms C2/C3 were disordered over two positions and their site occupational factors were refined to 0.57(9) and 0.43(9) respectively. The minor disordered atoms were omitted for clarity.

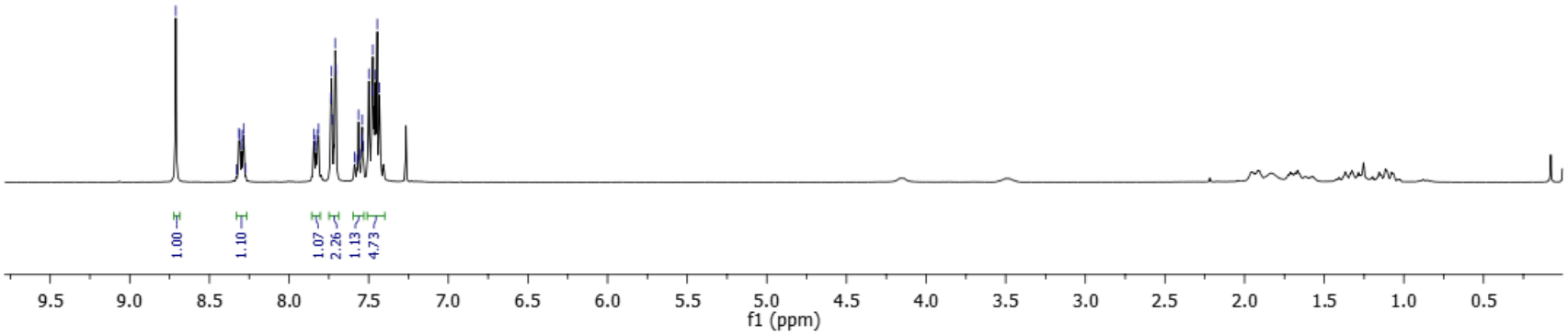
1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.

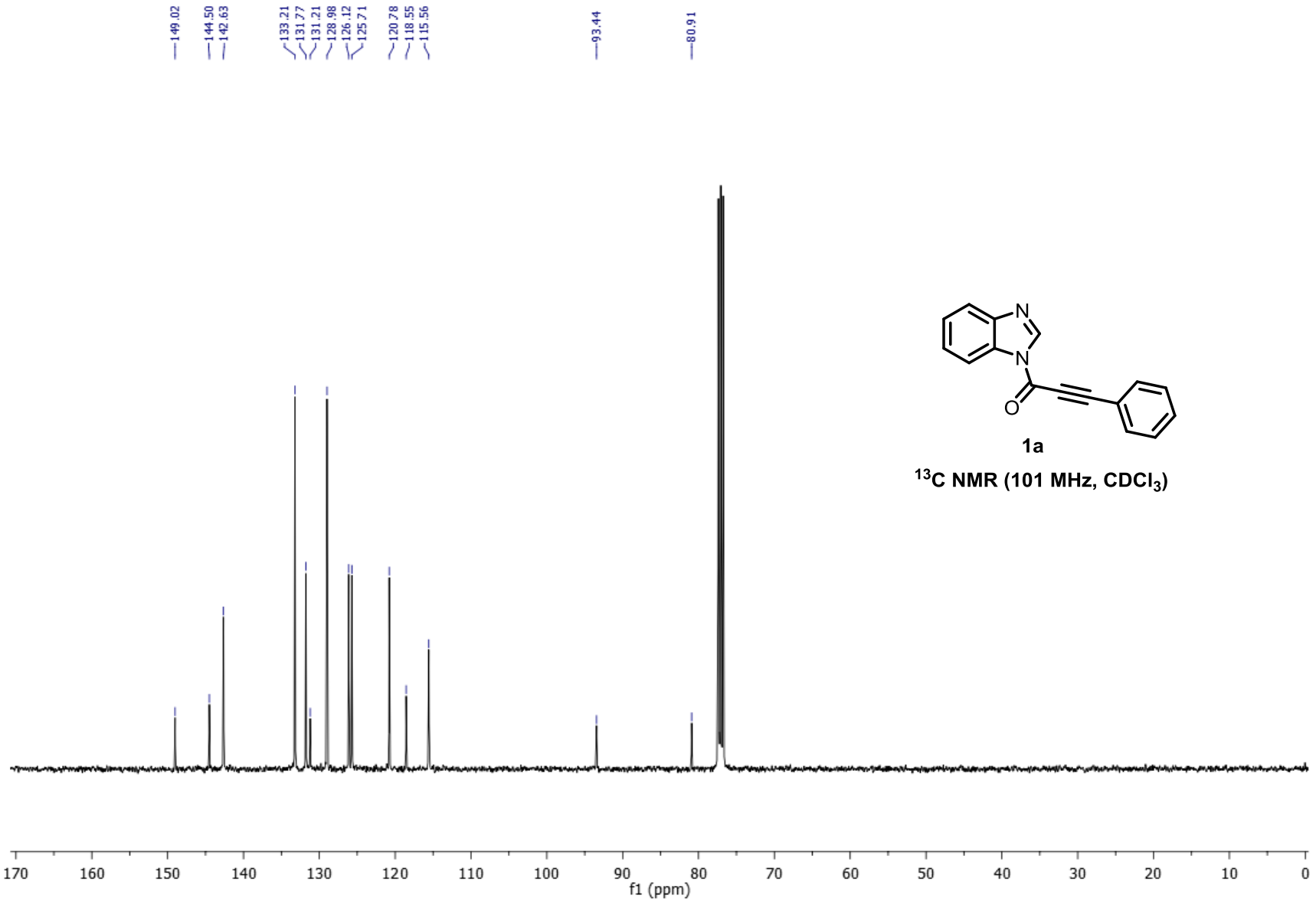




1a

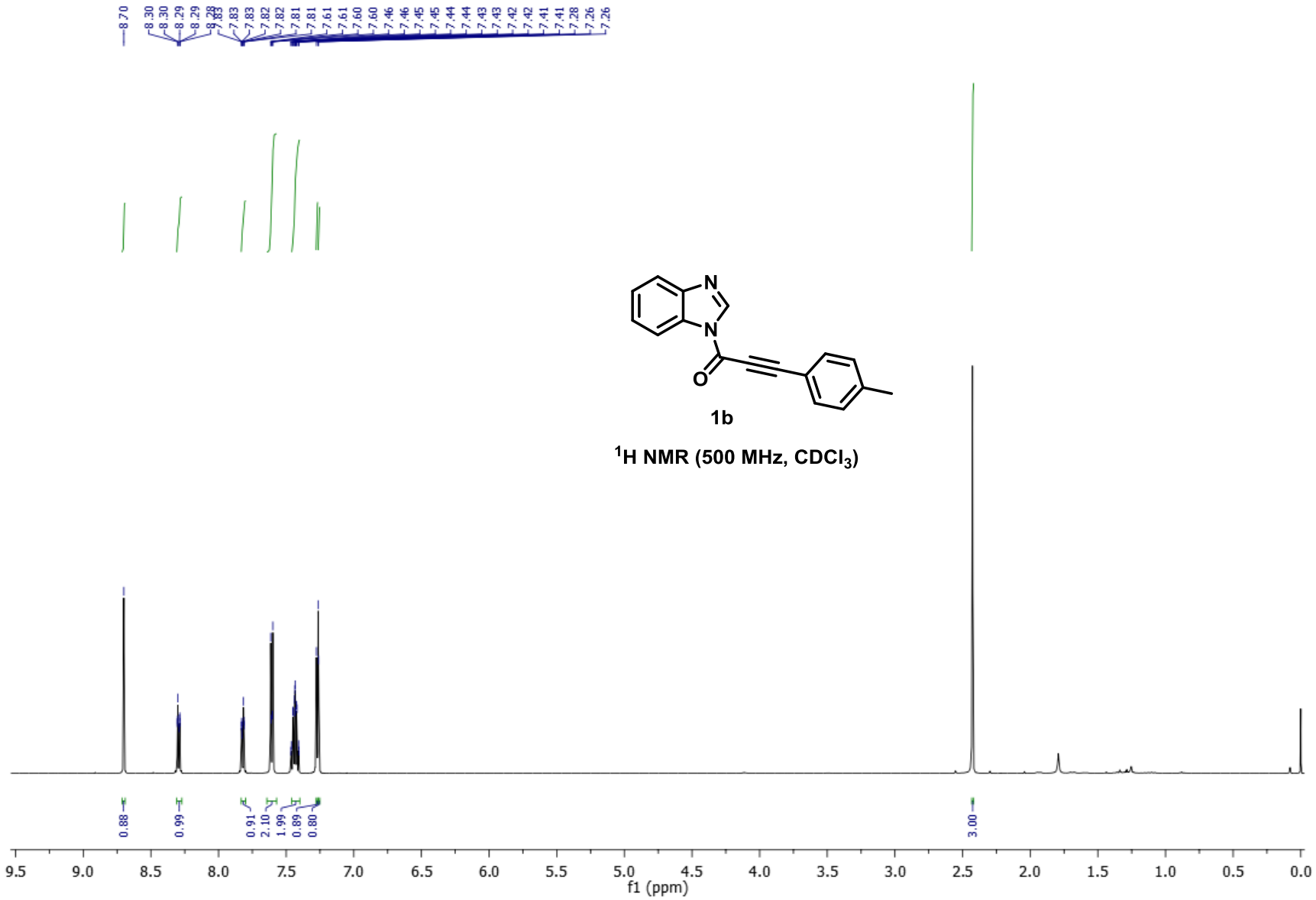
^{1}H NMR (300 MHz, $CDCl_3$)





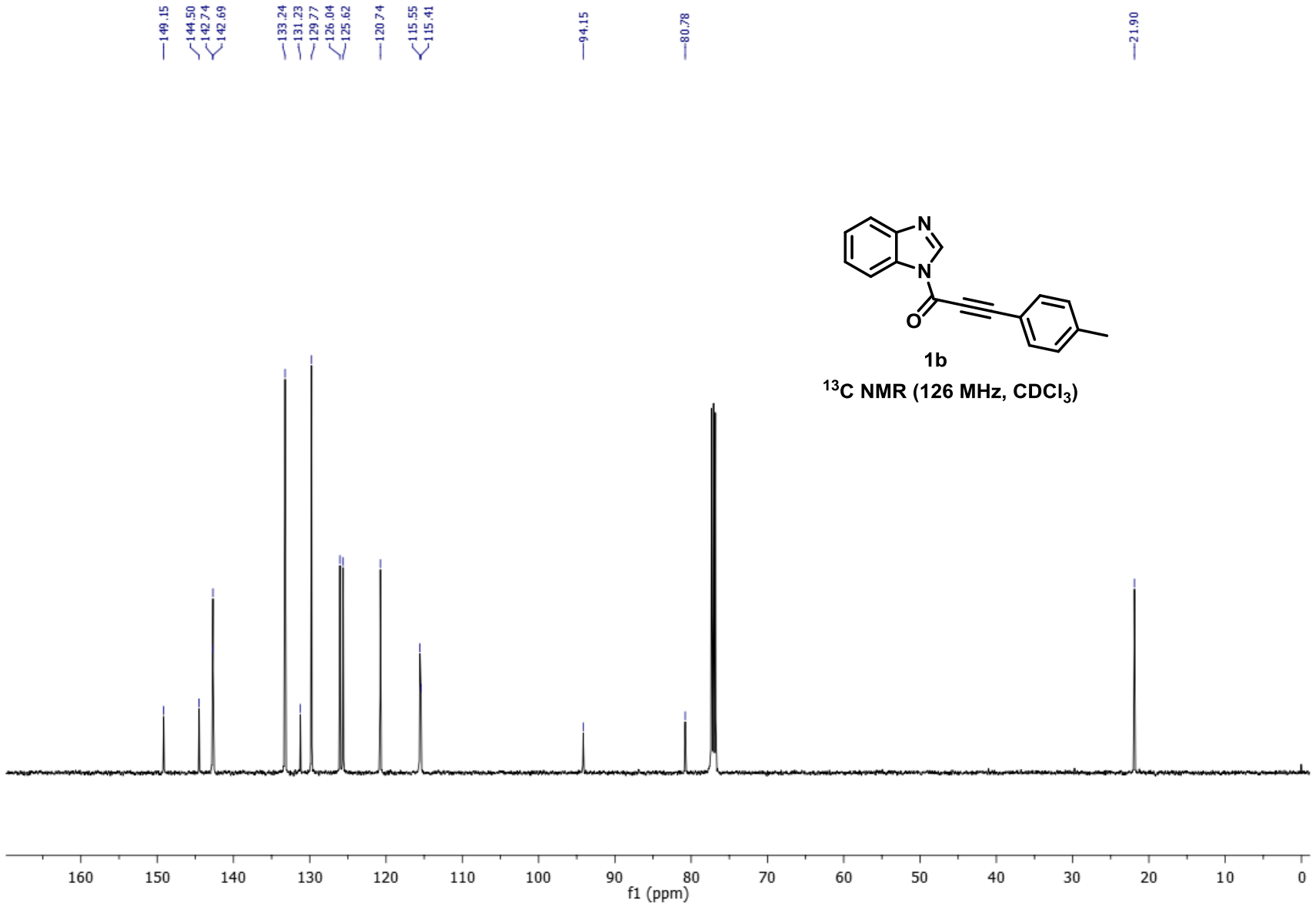
1a

^{13}C NMR (101 MHz, $CDCl_3$)



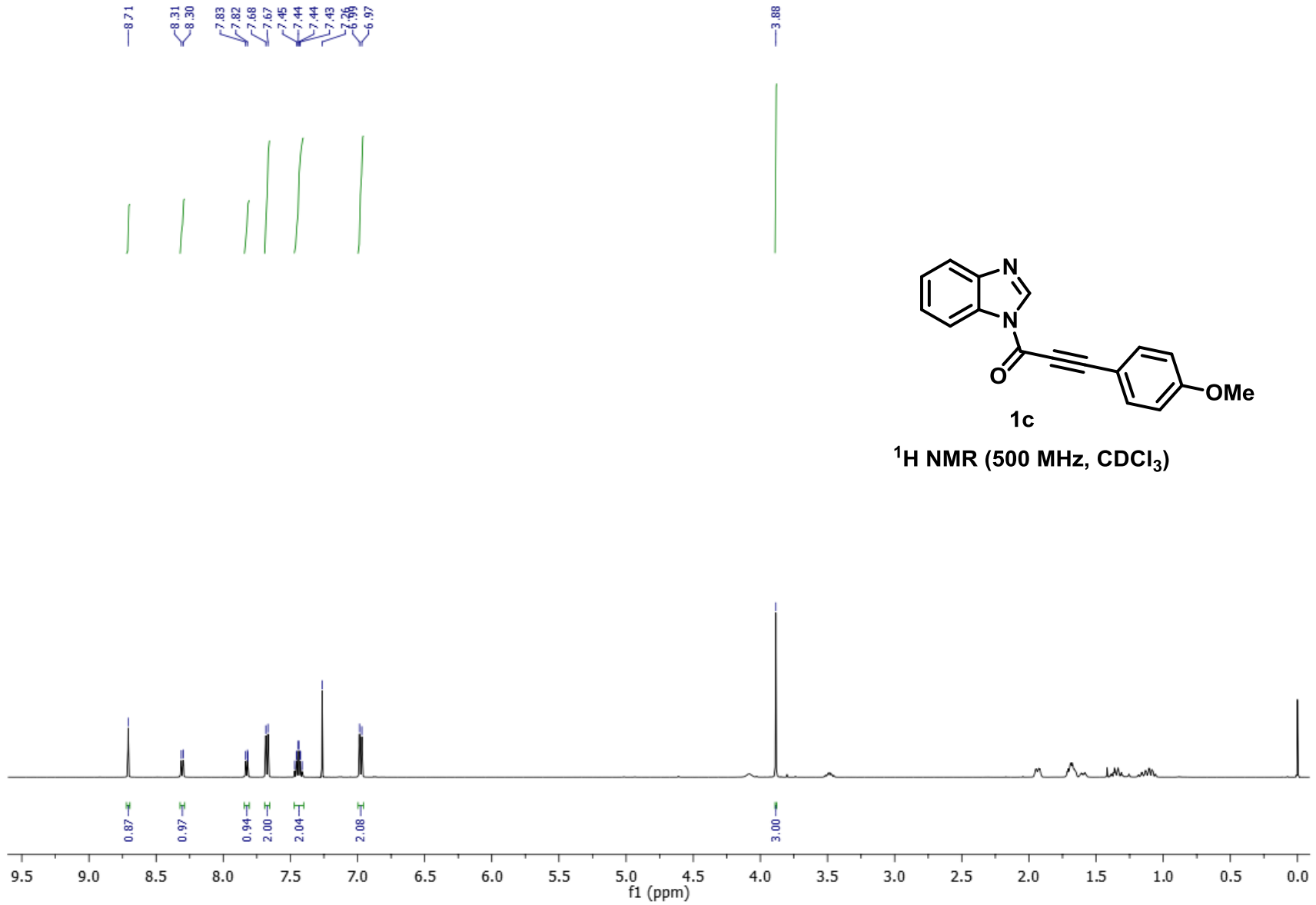
1b

^{1}H NMR (500 MHz, $CDCl_3$)



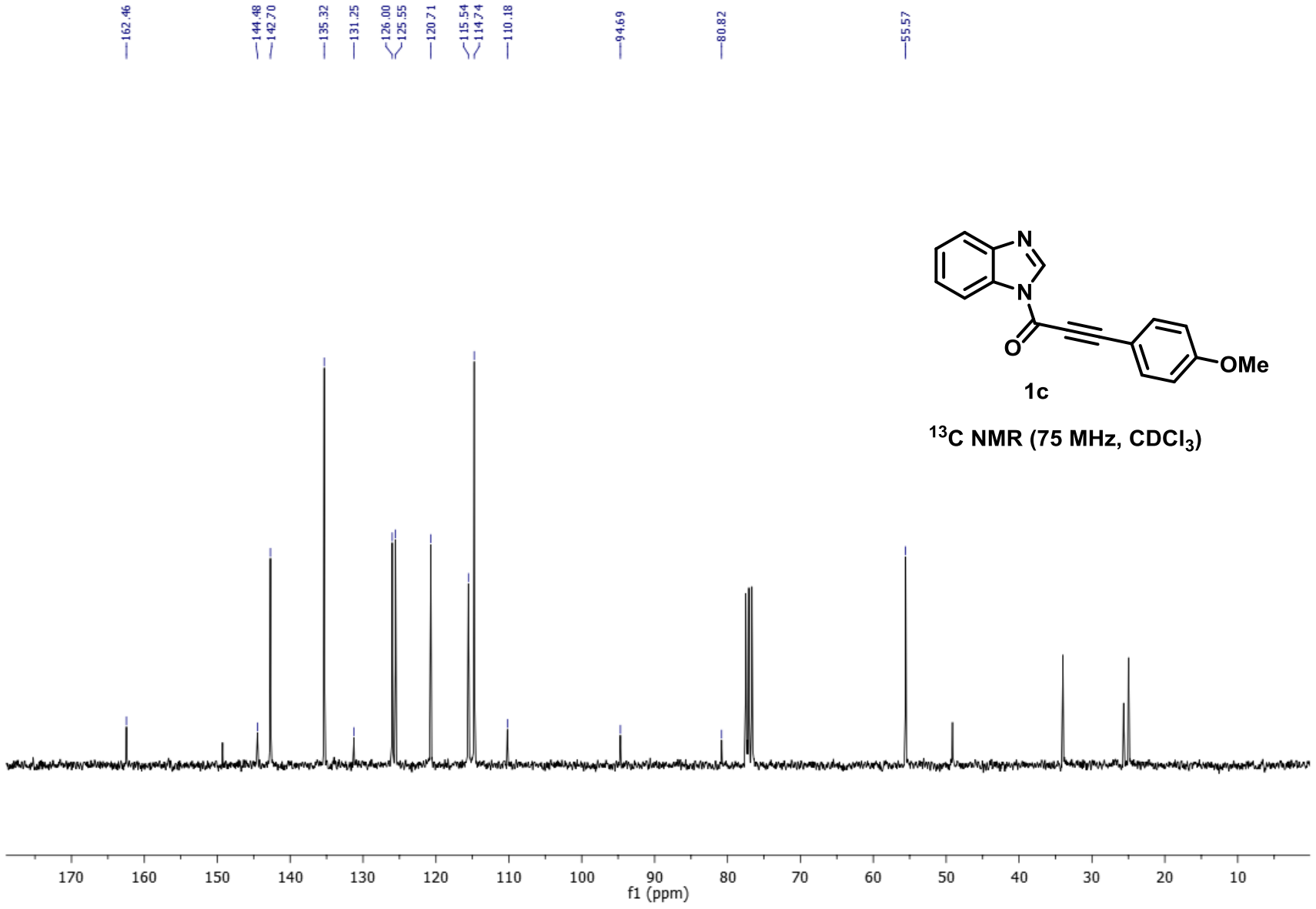
1b

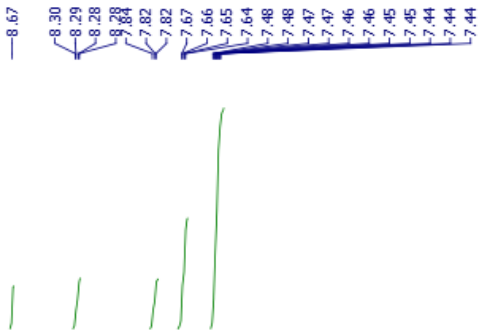
^{13}C NMR (126 MHz, $CDCl_3$)

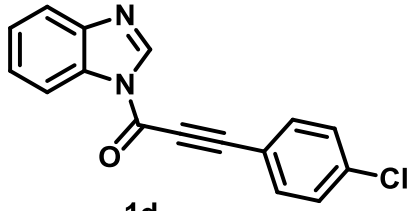


1c

^{1}H NMR (500 MHz, $CDCl_3$)

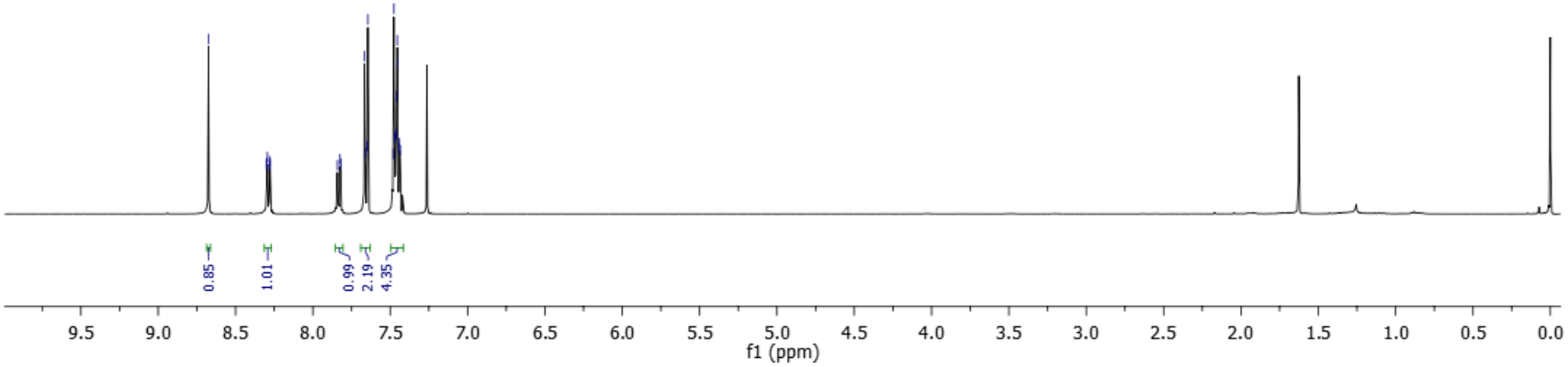

162.46
144.48
142.70
135.32
131.25
126.00
125.55
120.71
115.54
114.74
110.18
94.69
80.82
55.57
N
N
O
OMe
1c
^{13}C NMR (75 MHz, CDCl$_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

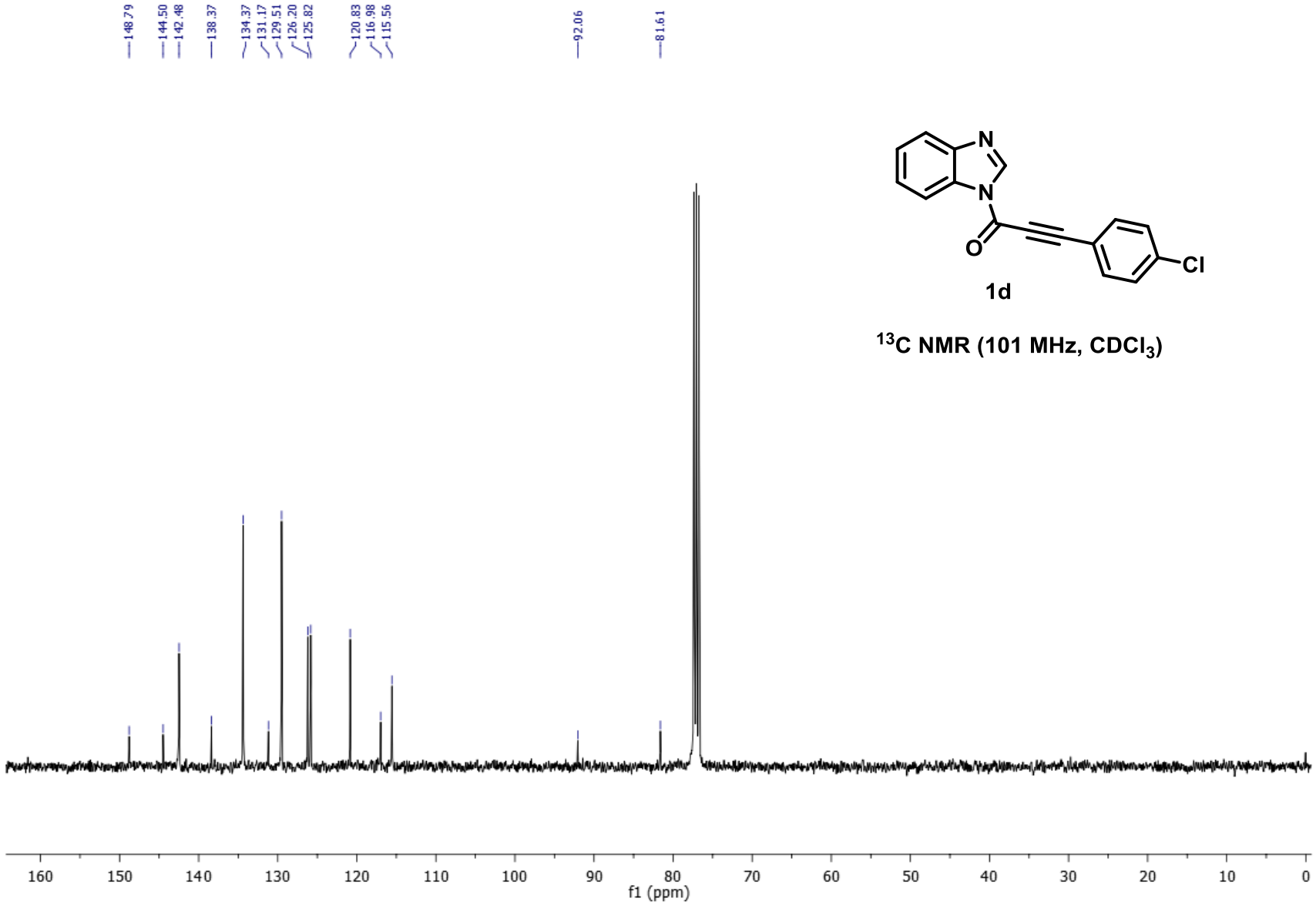




1d

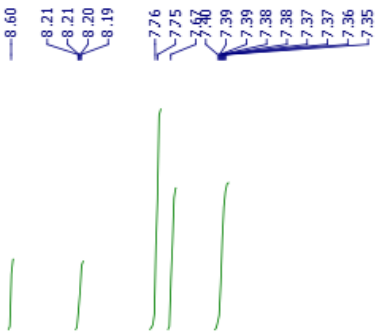
^{1}H NMR (400 MHz, $CDCl_3$)

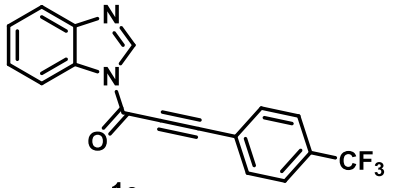




1d

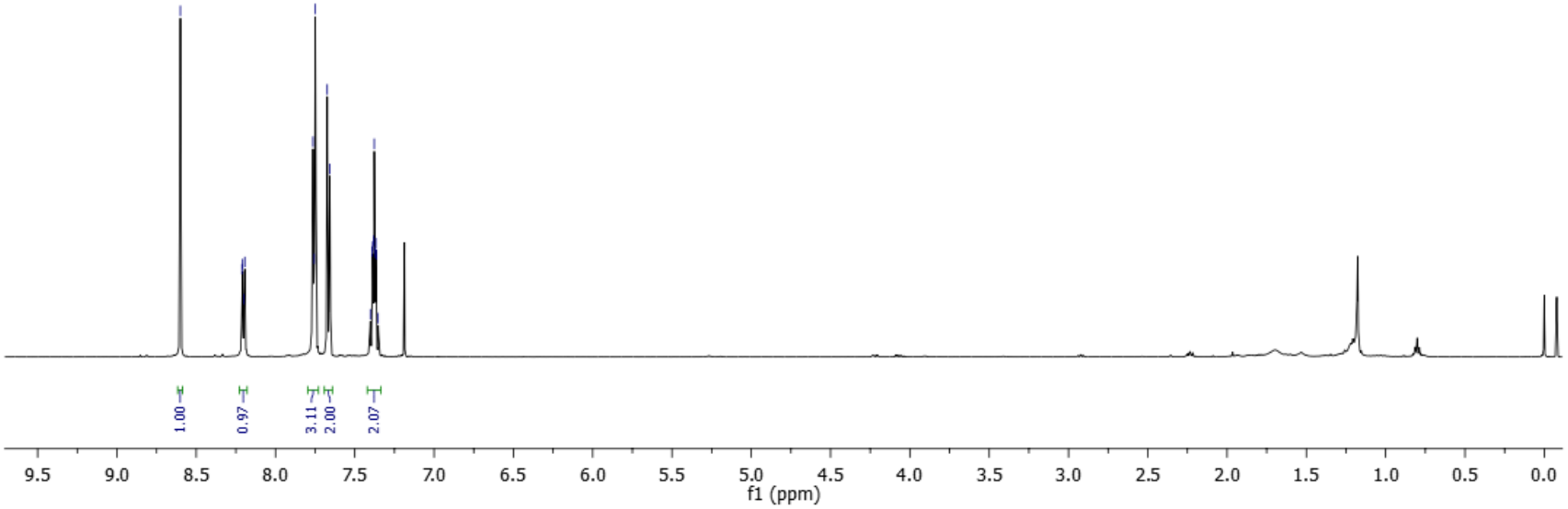
^{13}C NMR (101 MHz, $CDCl_3$)

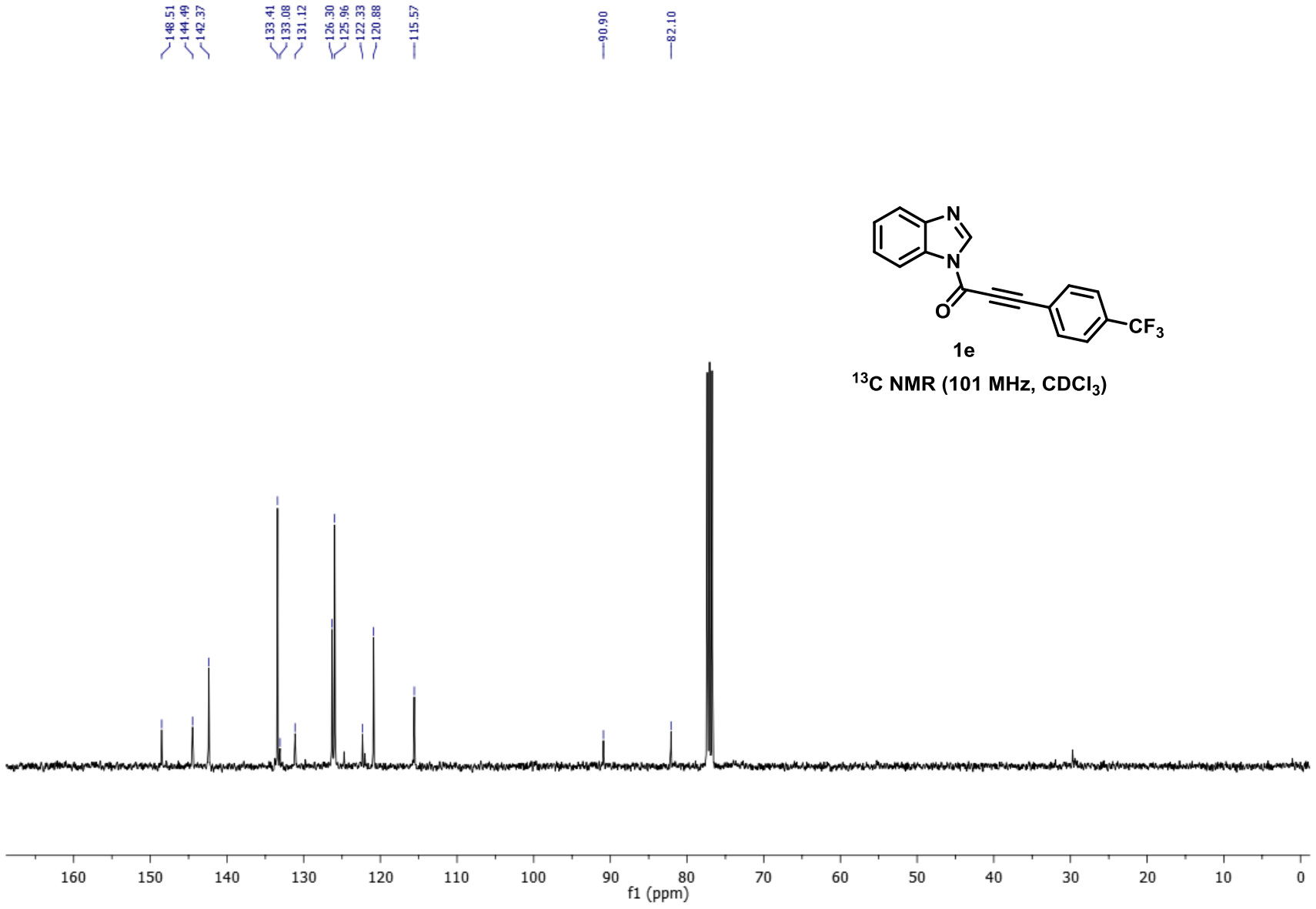




1e

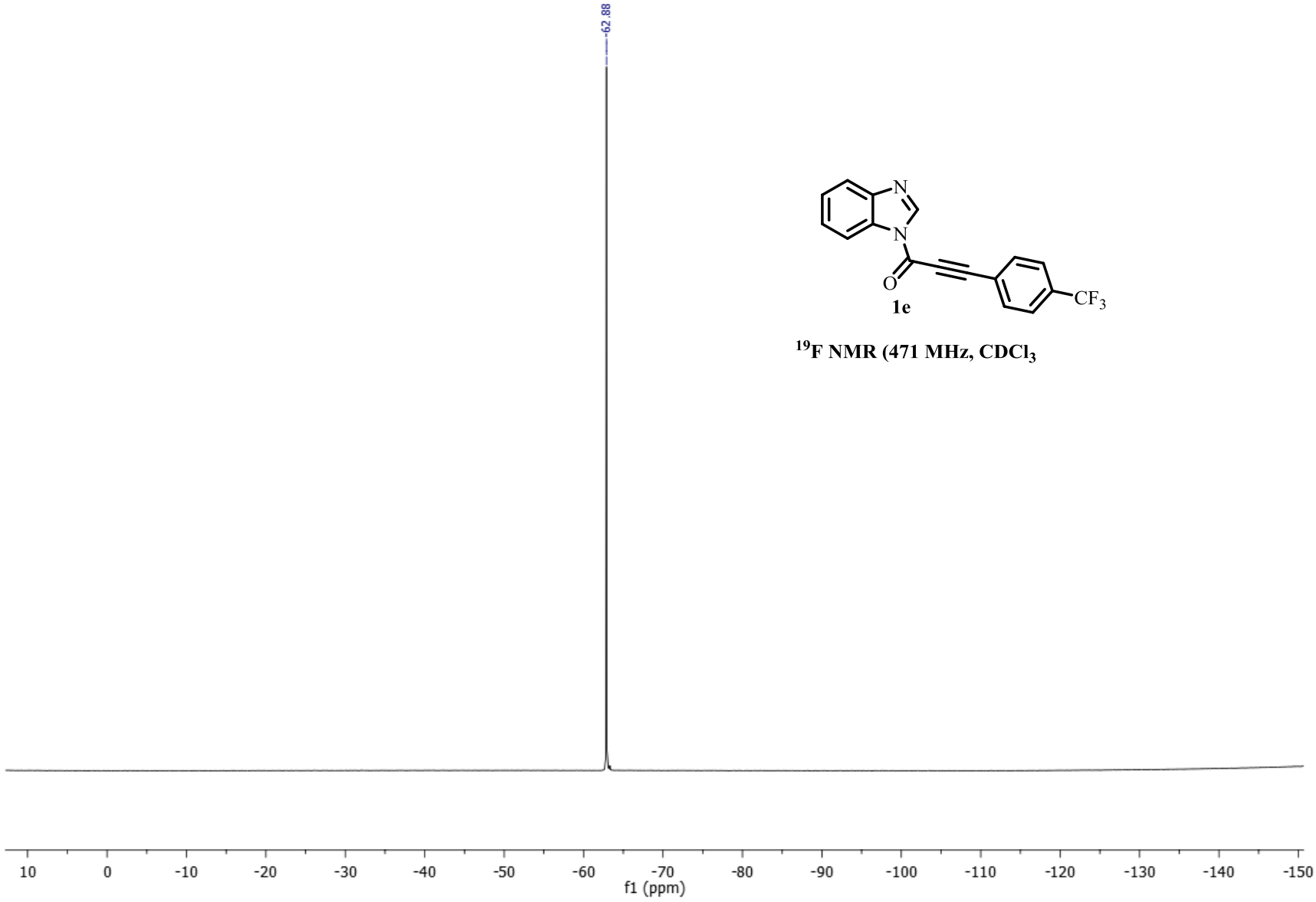
^{1}H NMR (500 MHz, $CDCl_3$)





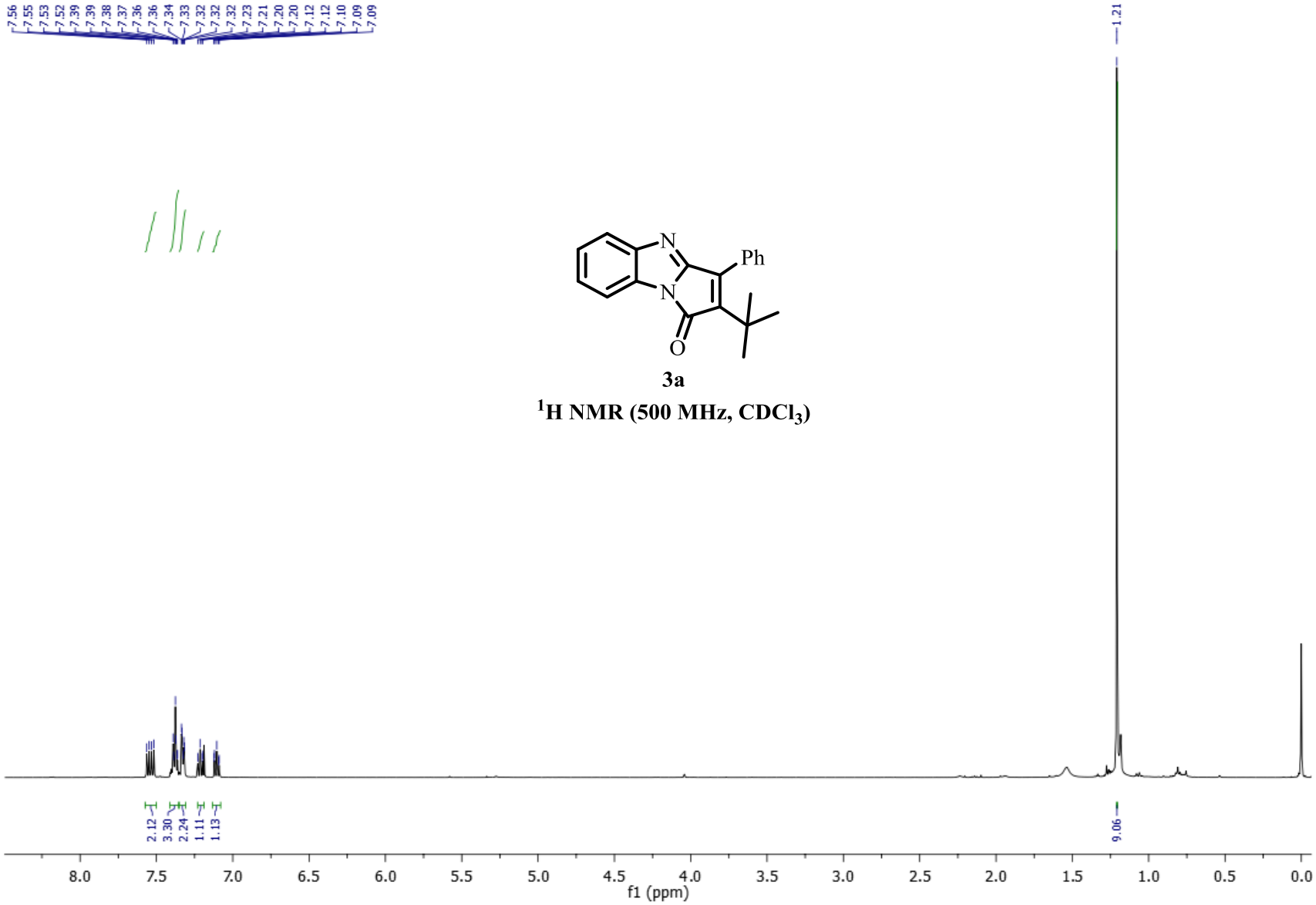
1e

^{13}C NMR (101 MHz, $CDCl_3$)



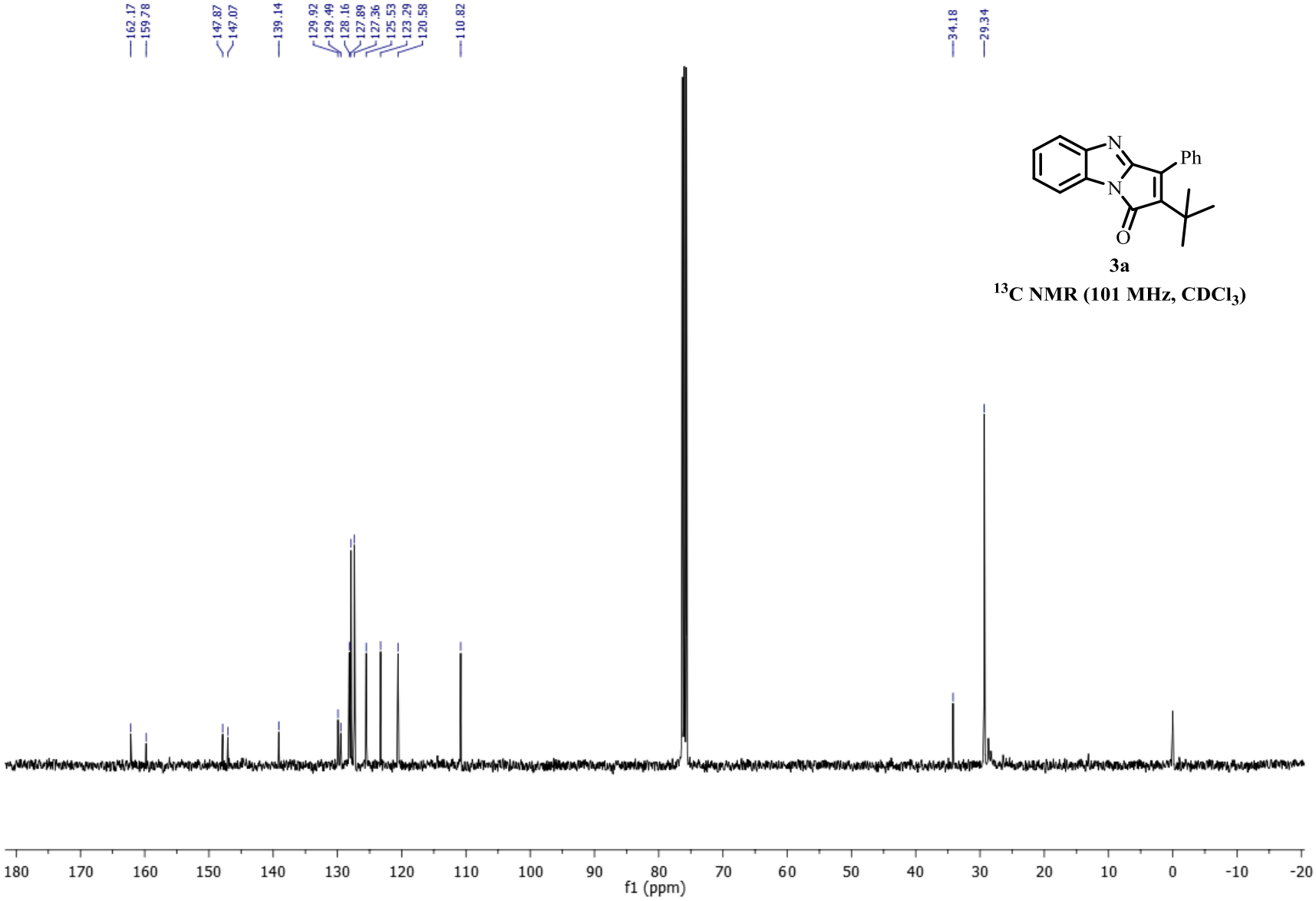
1e

^{19}F NMR (471 MHz, $CDCl_3$



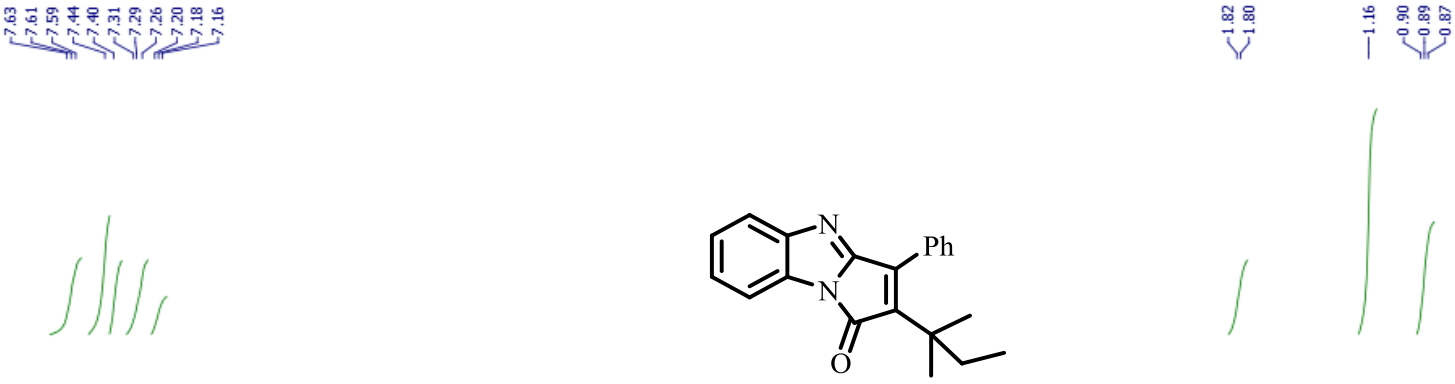
3a

^{1}H NMR (500 MHz, $CDCl_3$)



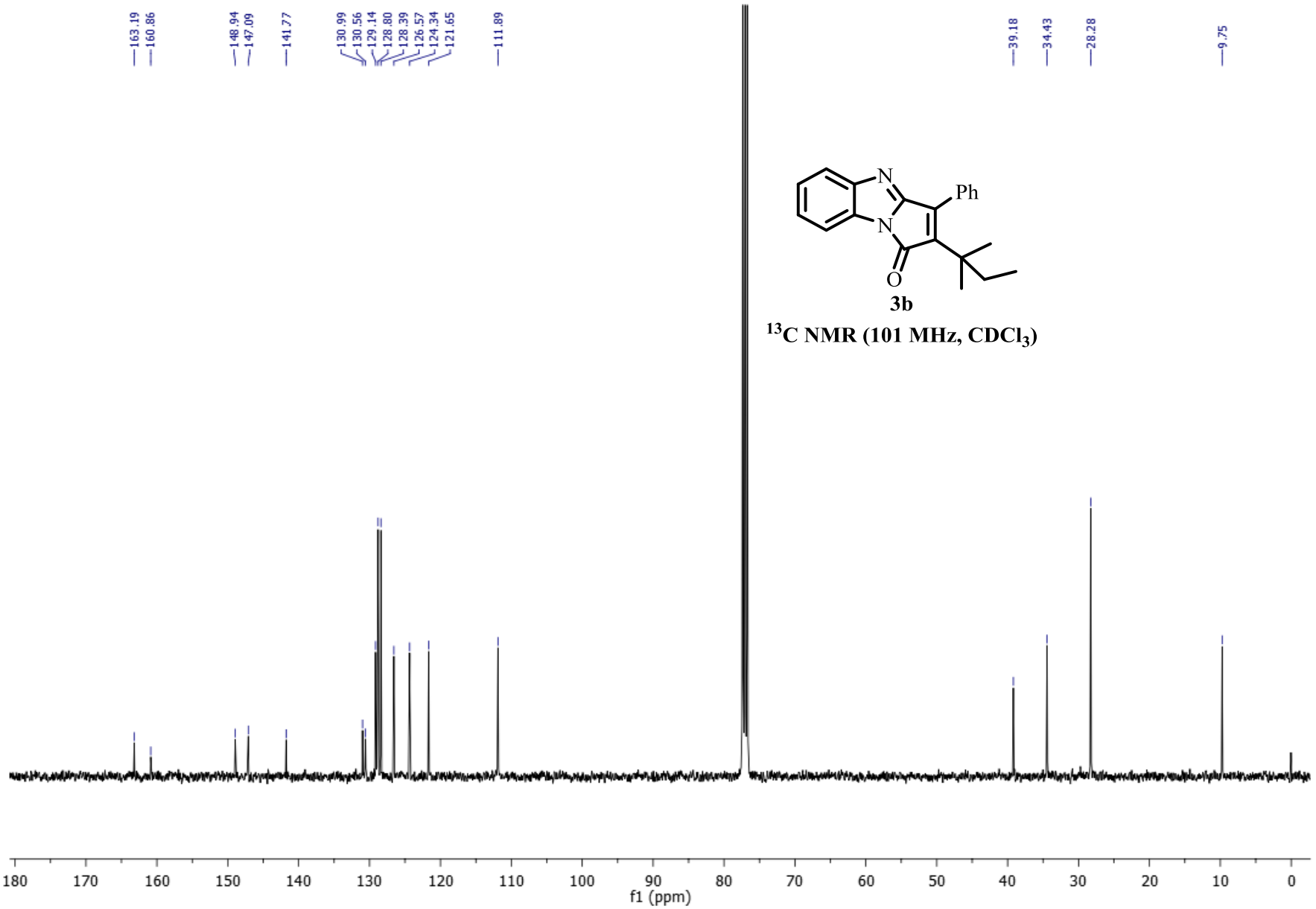
3a

^{13}C NMR (101 MHz, $CDCl_3$)



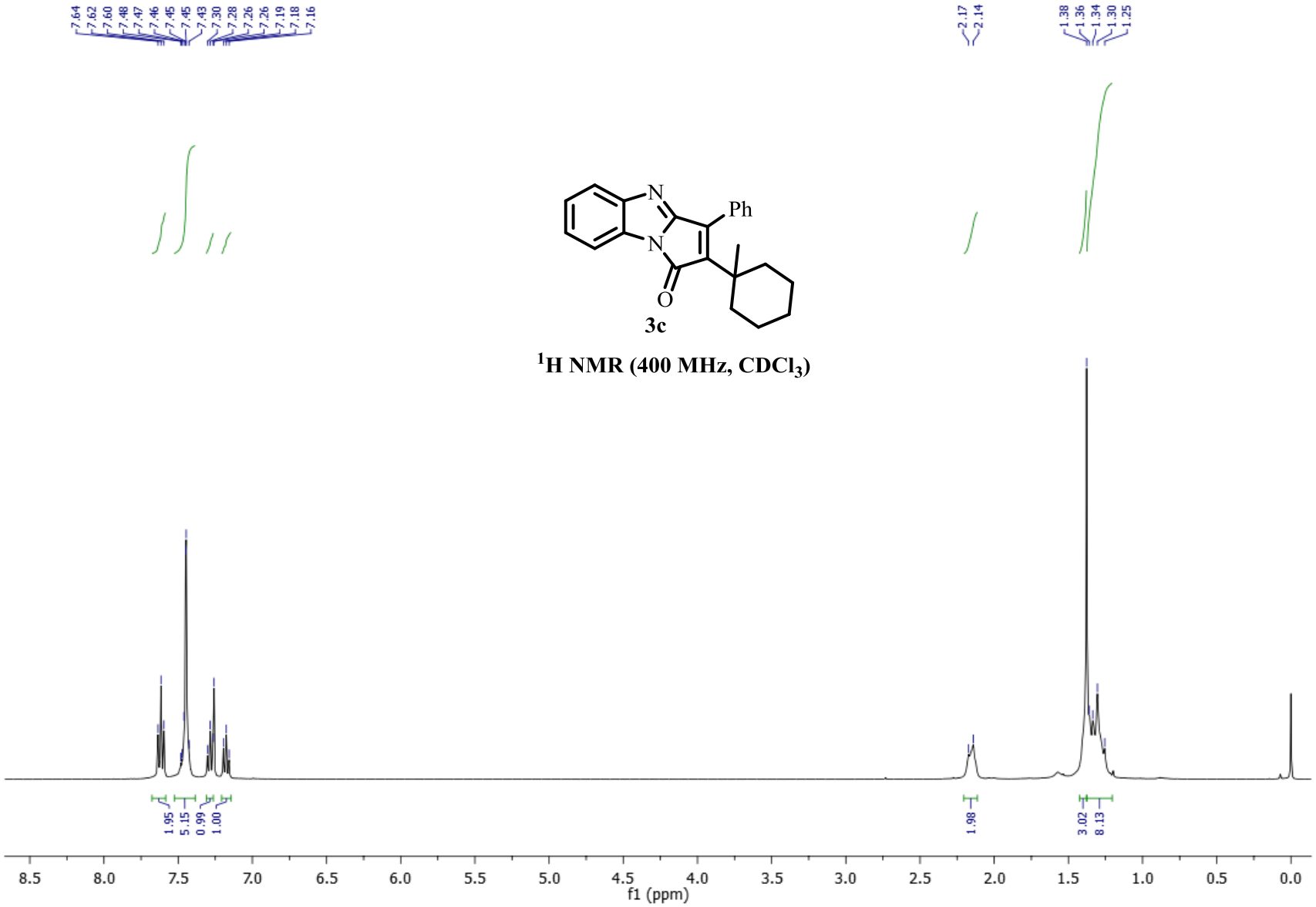
3b

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



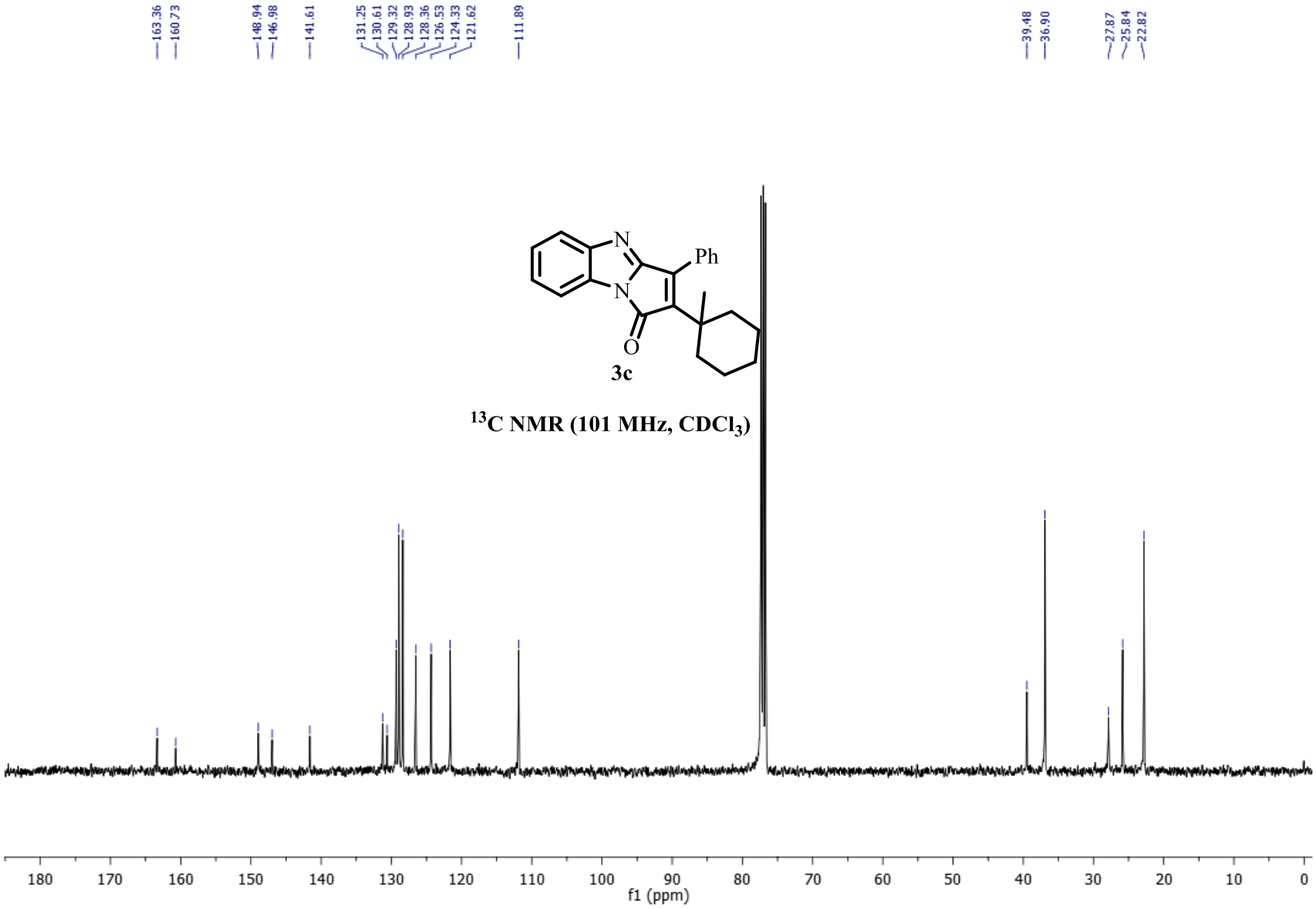
3b

^{13}C NMR (101 MHz, $CDCl_3$)

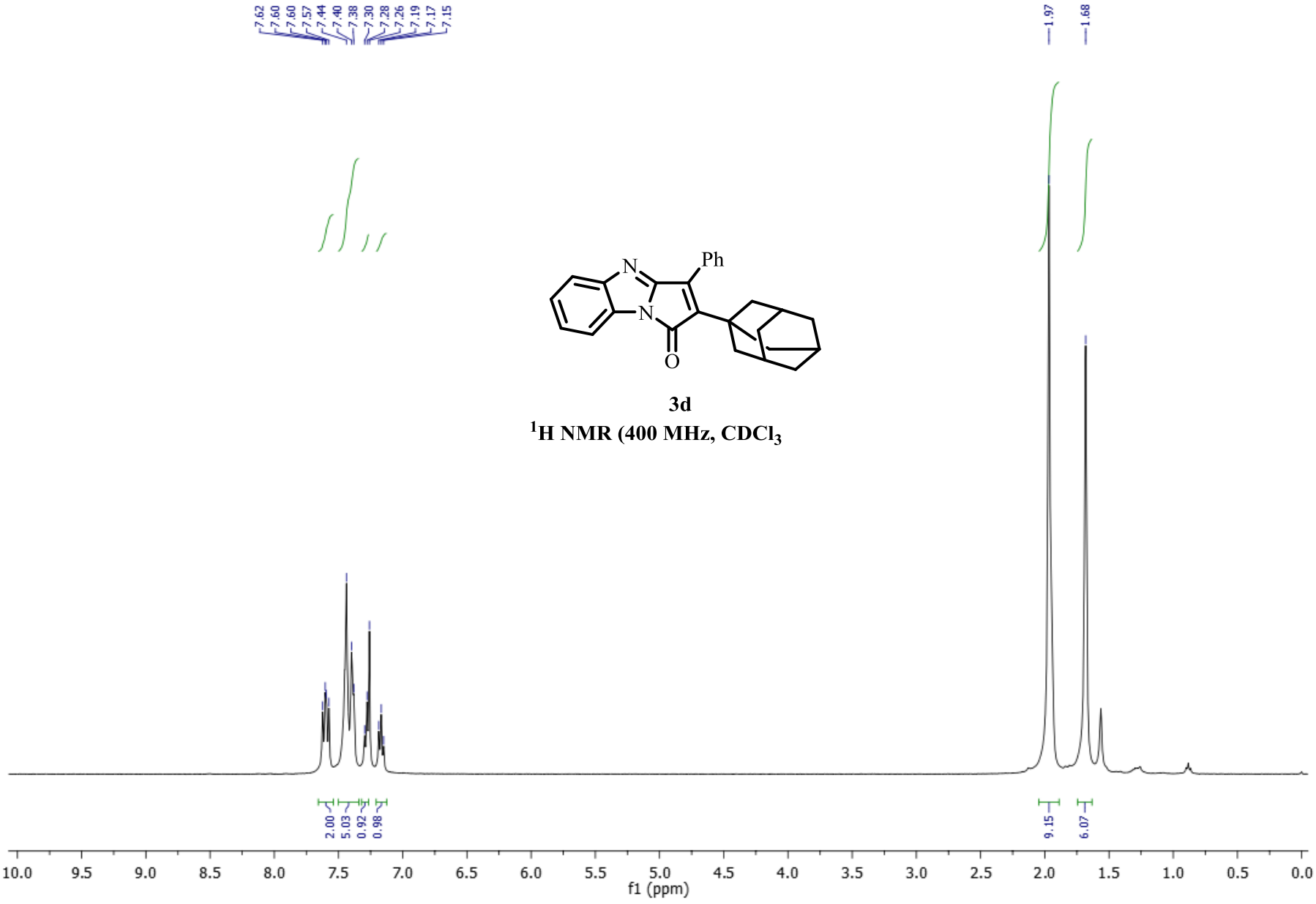


3c

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

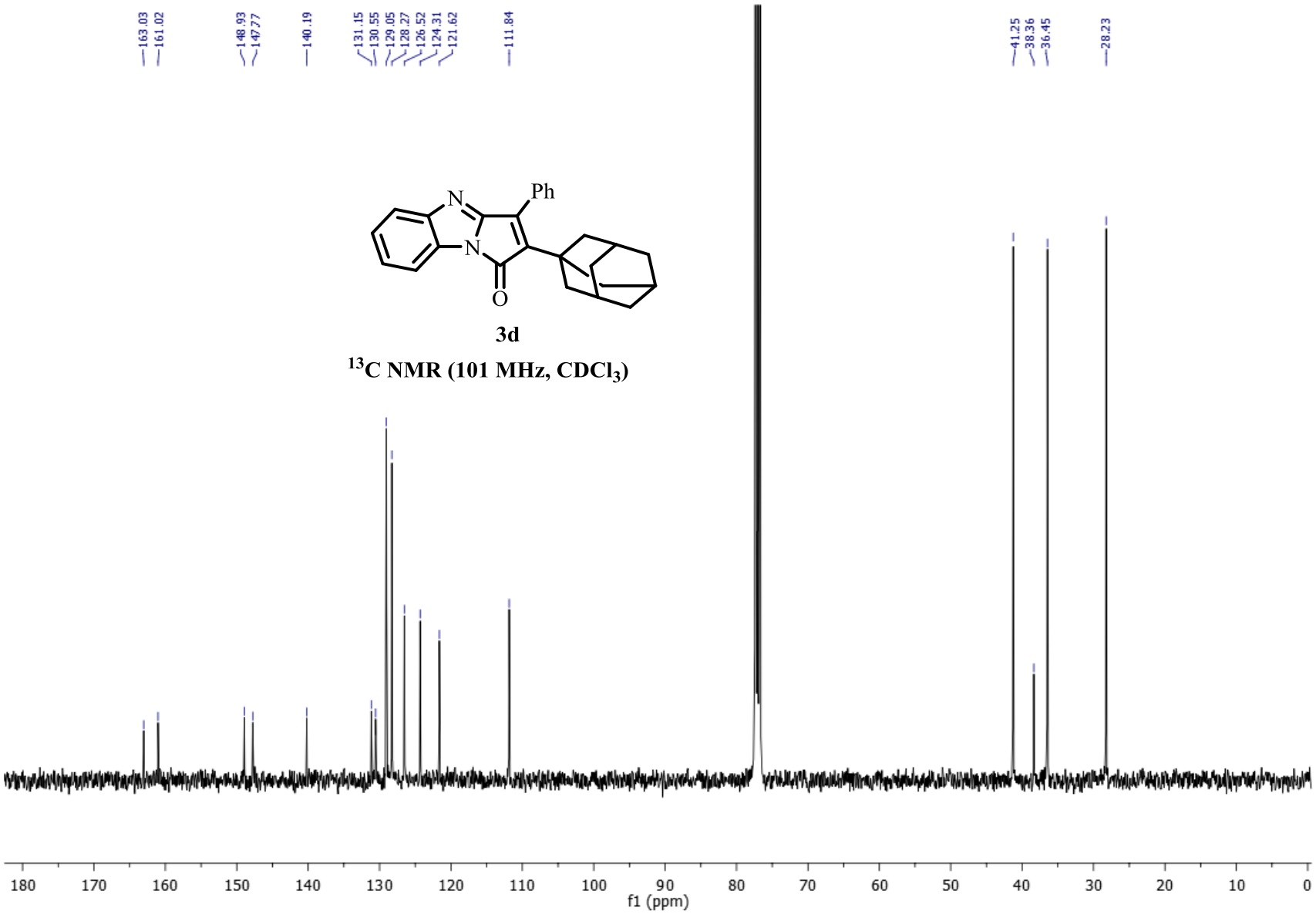


^{13}C NMR (101 MHz, $CDCl_3$)



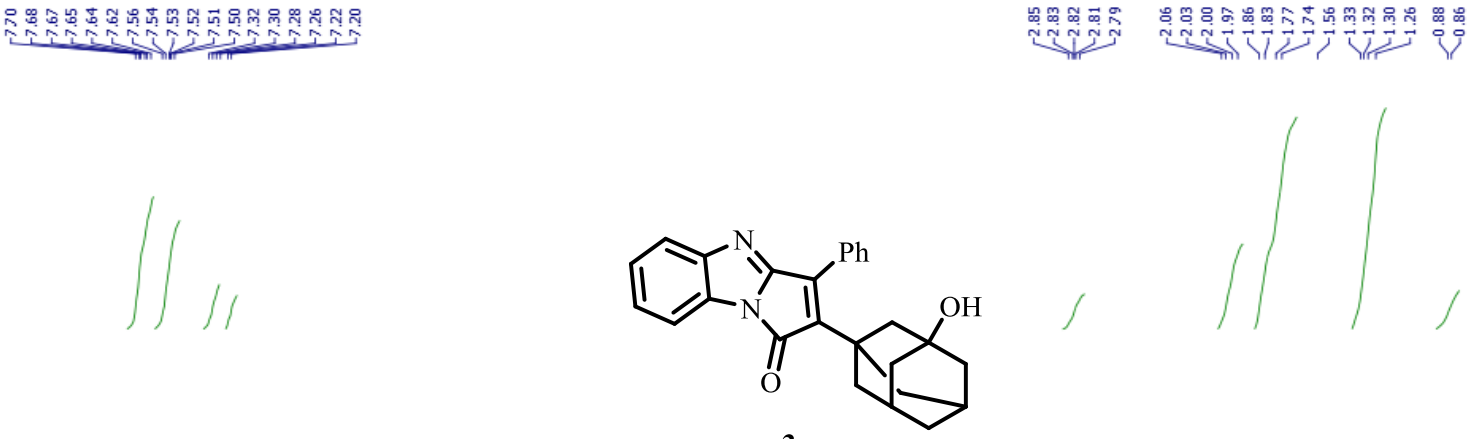
3d

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



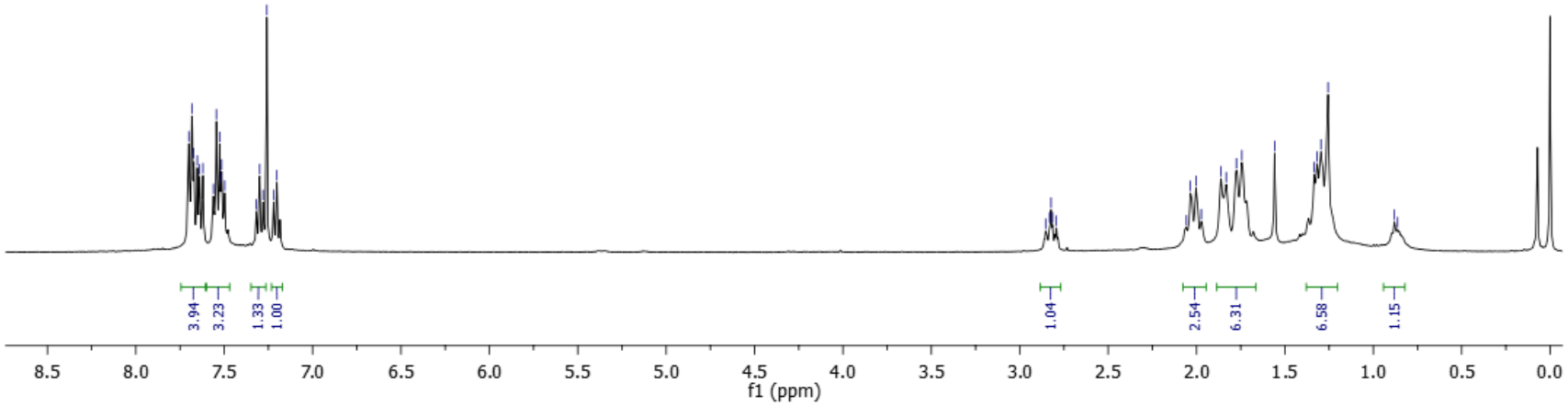
3d

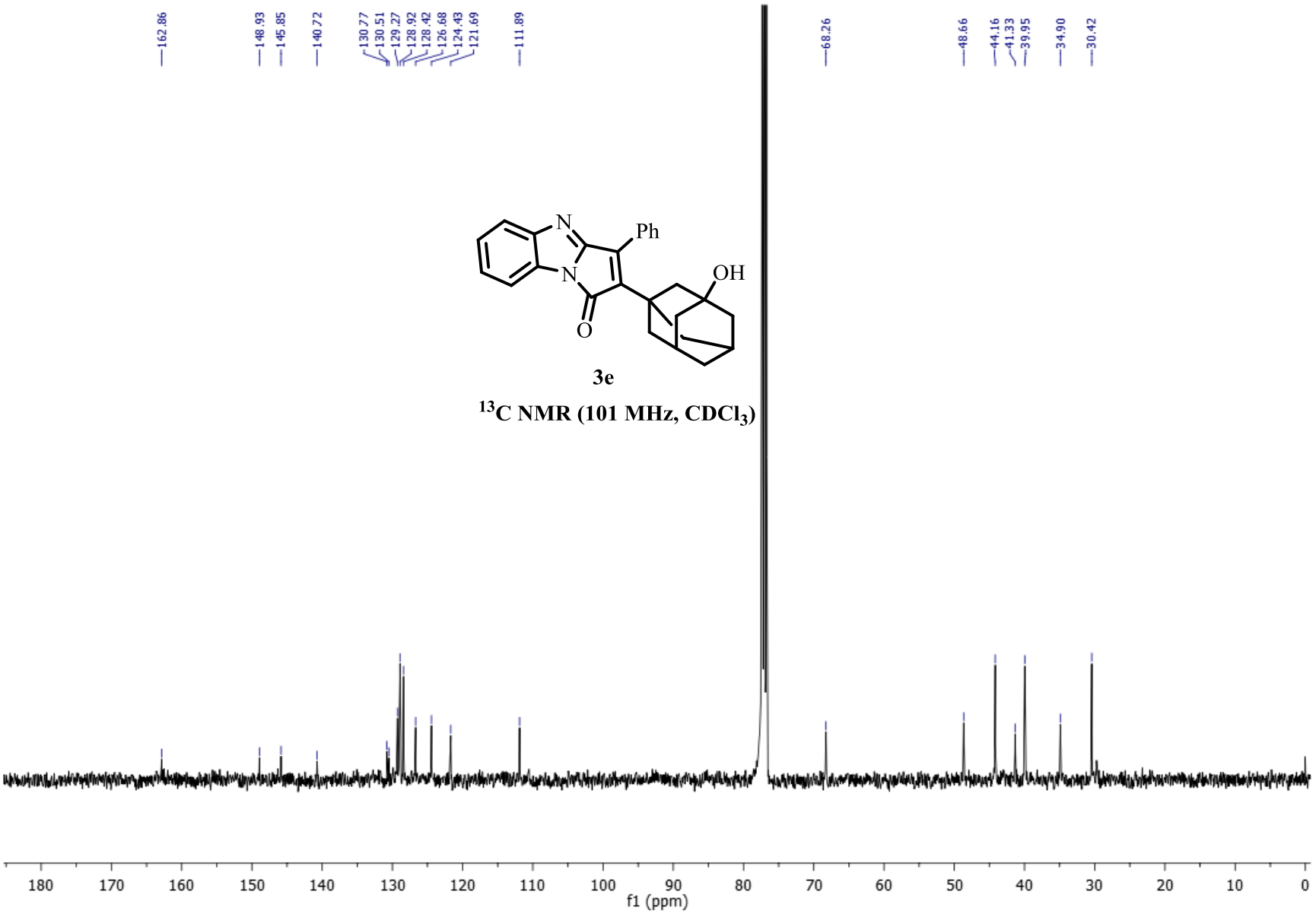
^{13}C NMR (101 MHz, $CDCl_3$)



3e

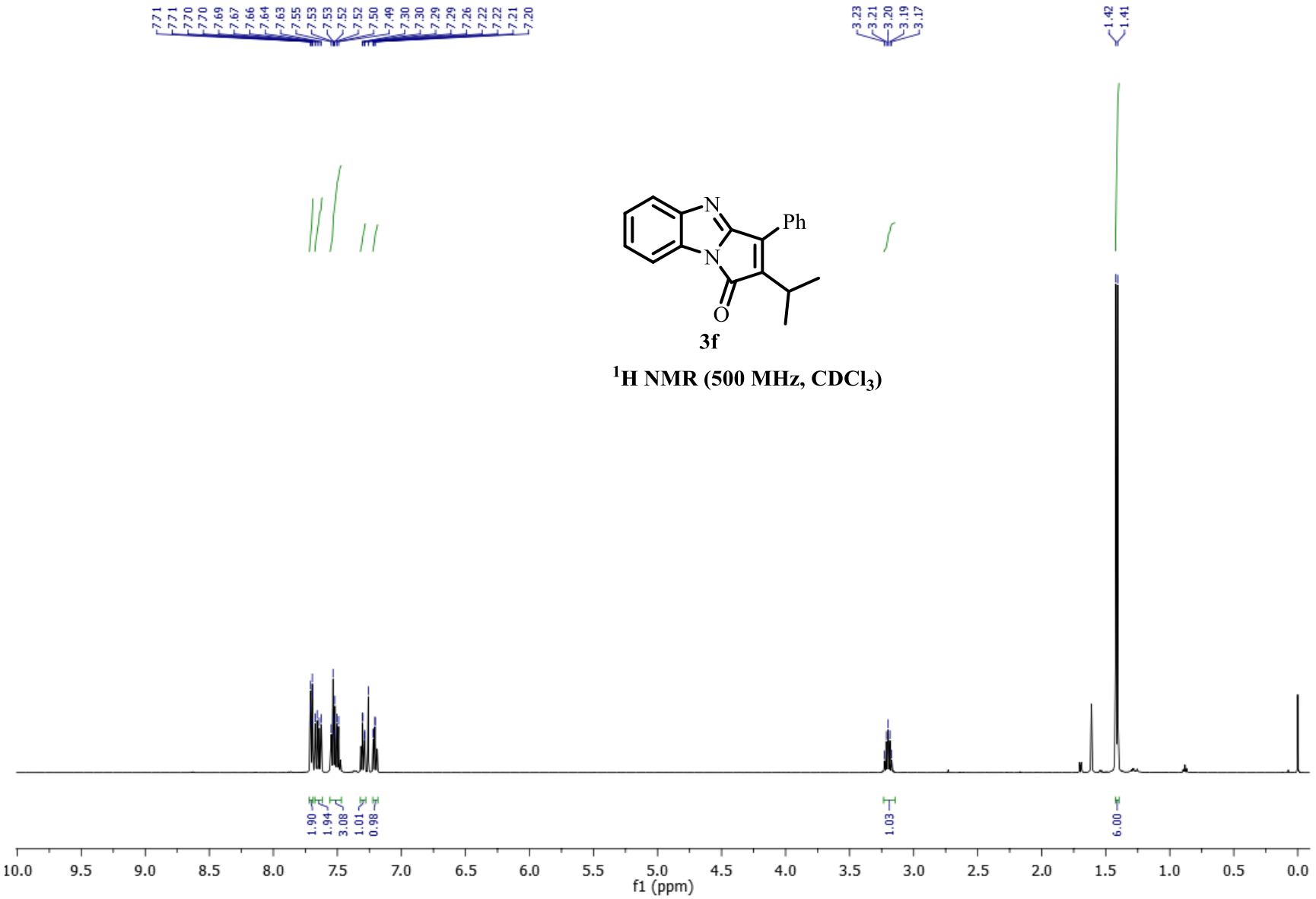
^{1}H NMR (400 MHz, $CDCl_3$)





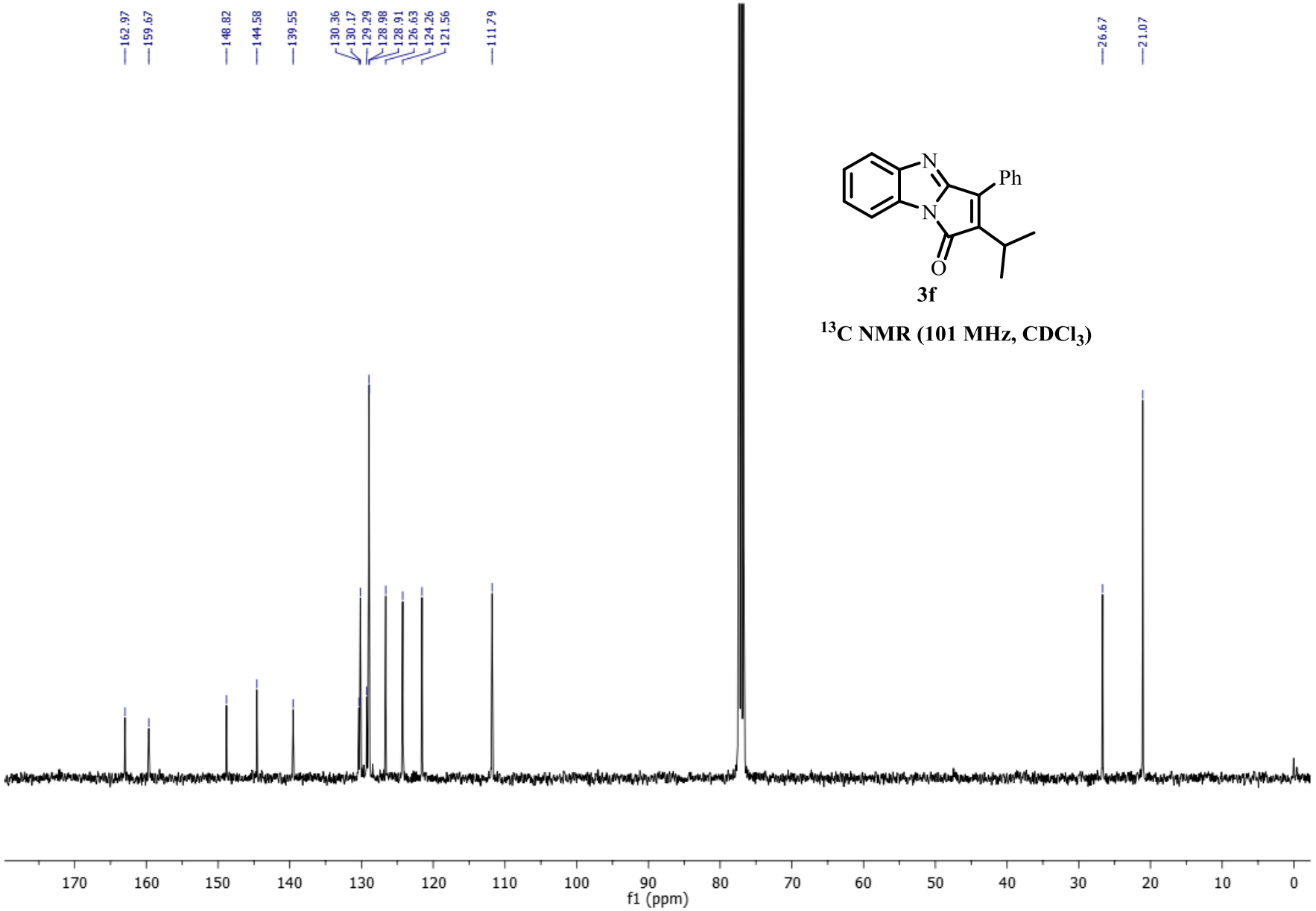
3e

^{13}C NMR (101 MHz, $CDCl_3$)



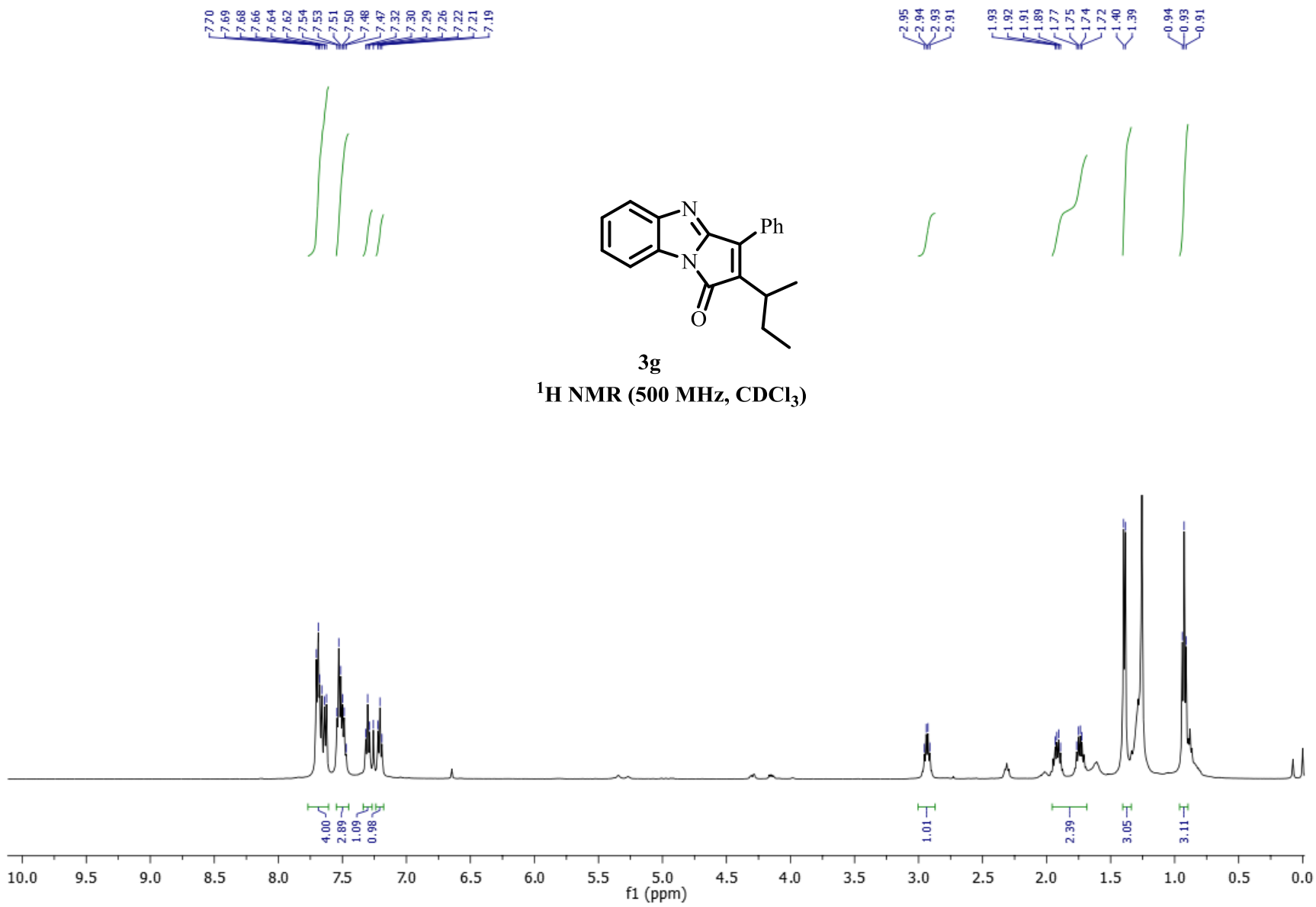
3f

^{1}H NMR (500 MHz, $CDCl_3$)



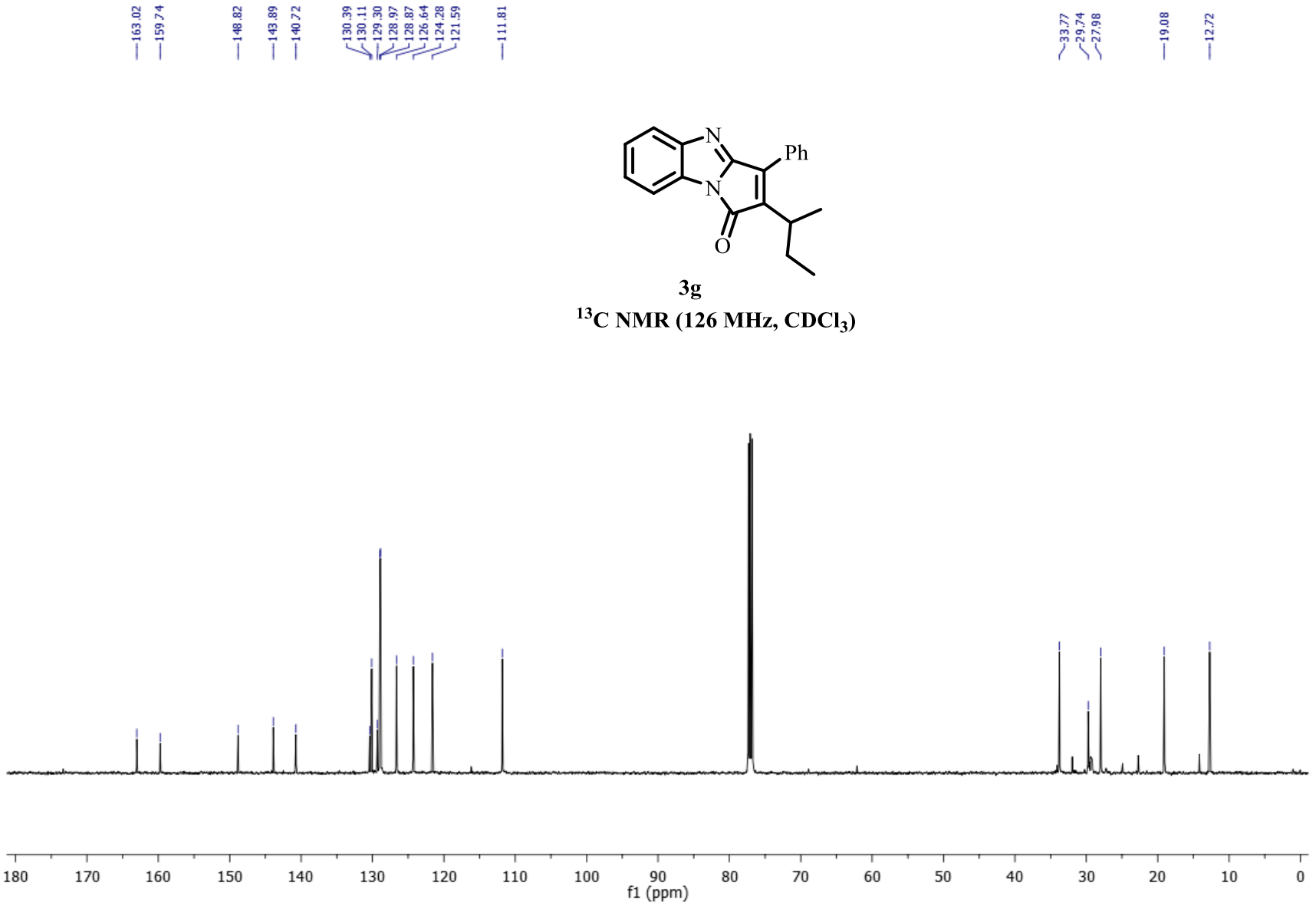
3f

^{13}C NMR (101 MHz, $CDCl_3$)



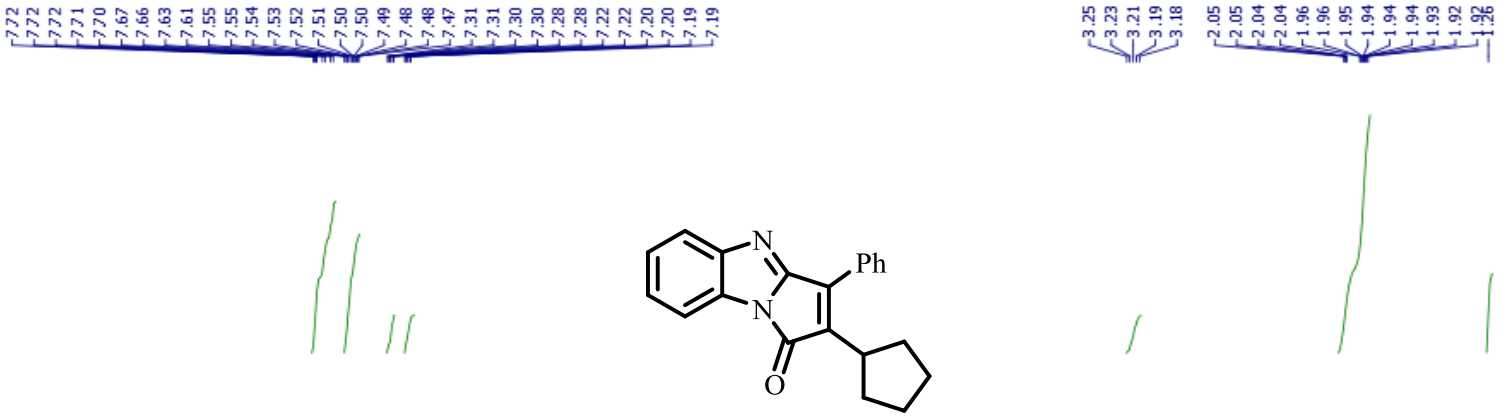
3g

^{1}H NMR (500 MHz, $CDCl_3$)



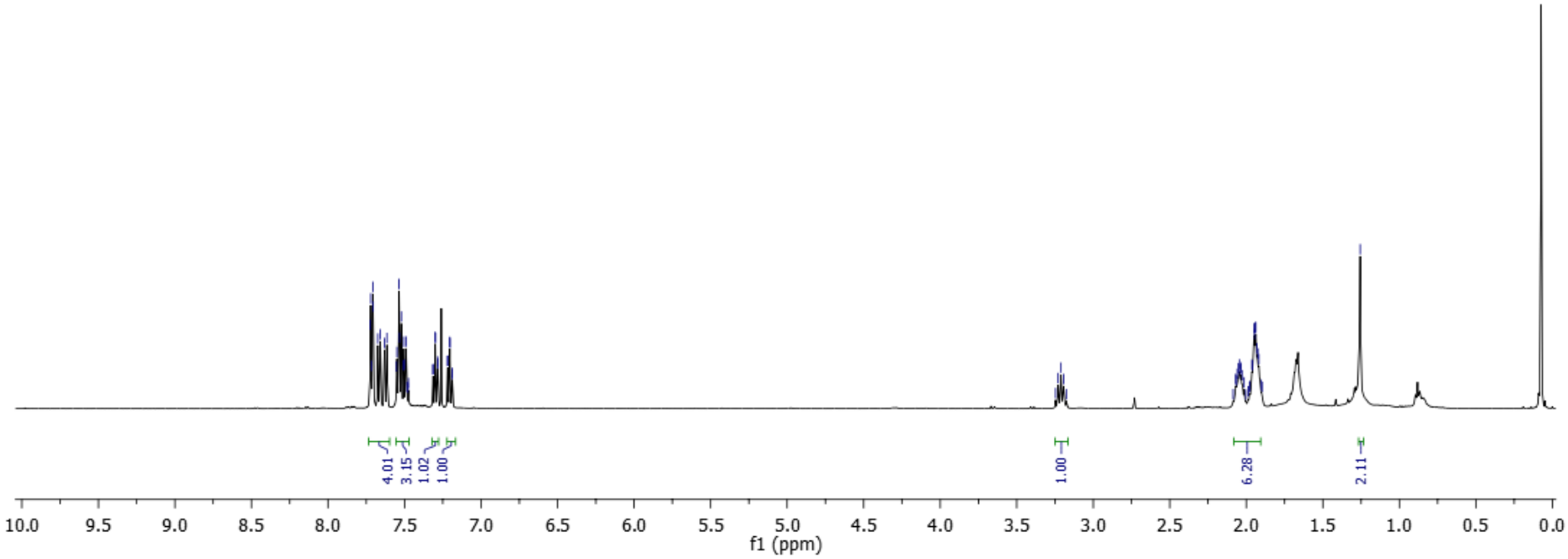
3g

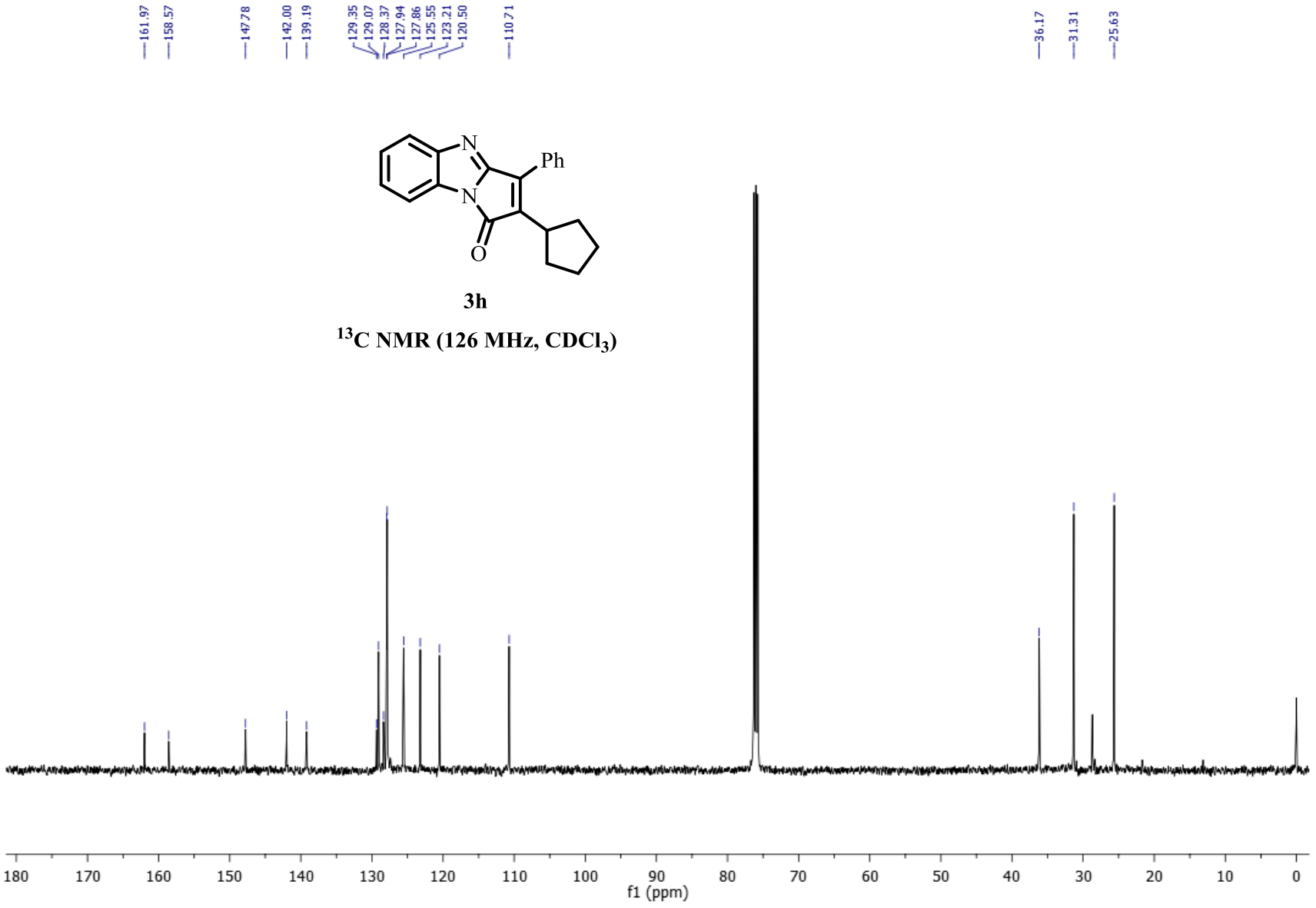
^{13}C NMR (126 MHz, $CDCl_3$)



3h

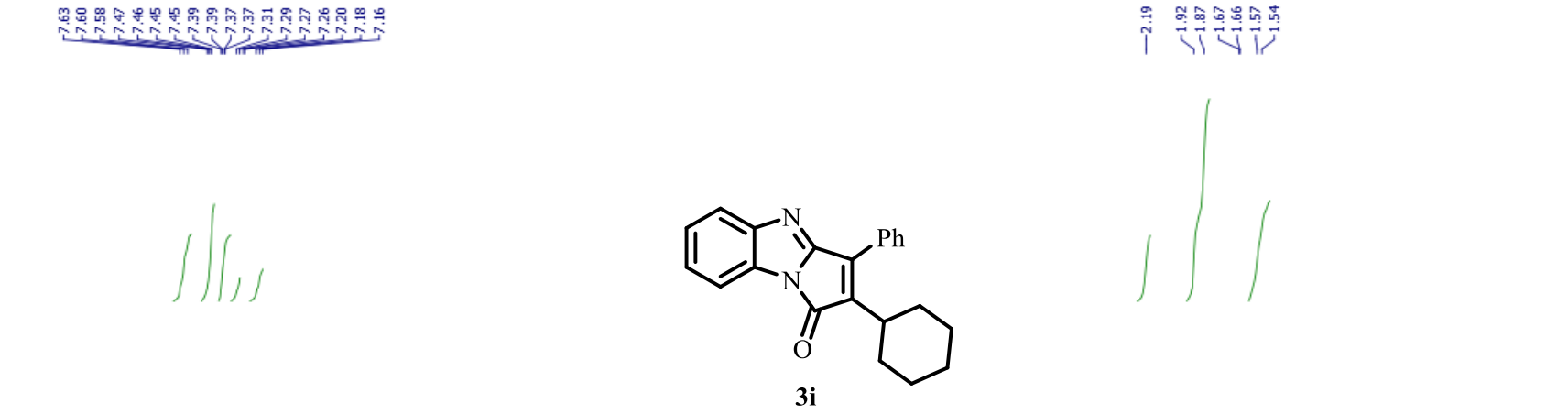
^{1}H NMR (500 MHz, $CDCl_3$)





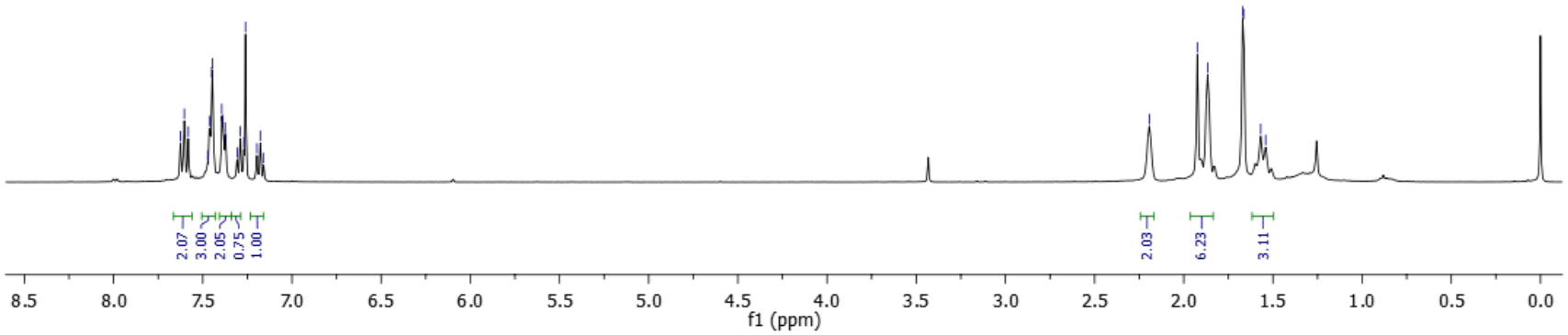
3h

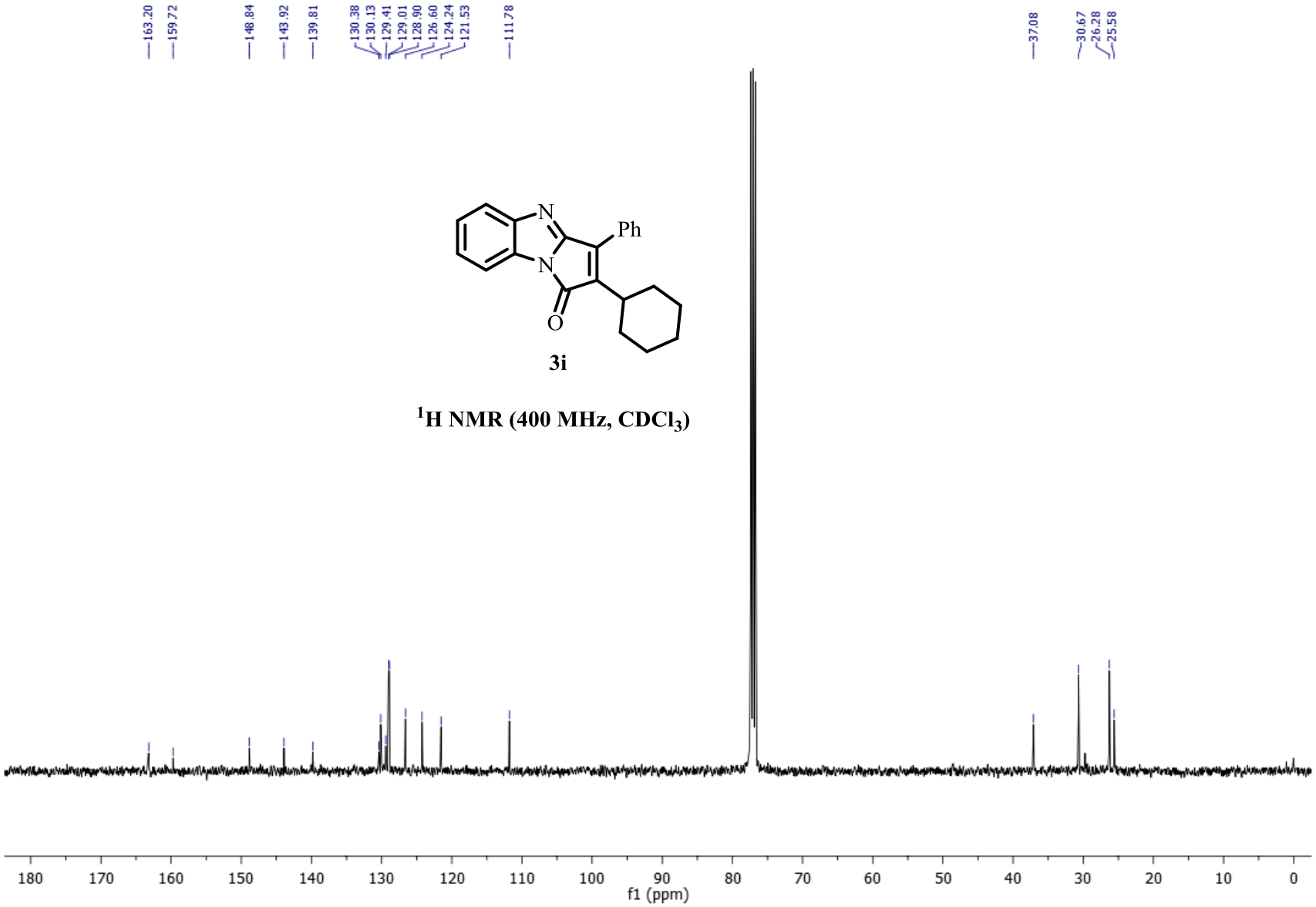
^{13}C NMR (126 MHz, $CDCl_3$)



3i

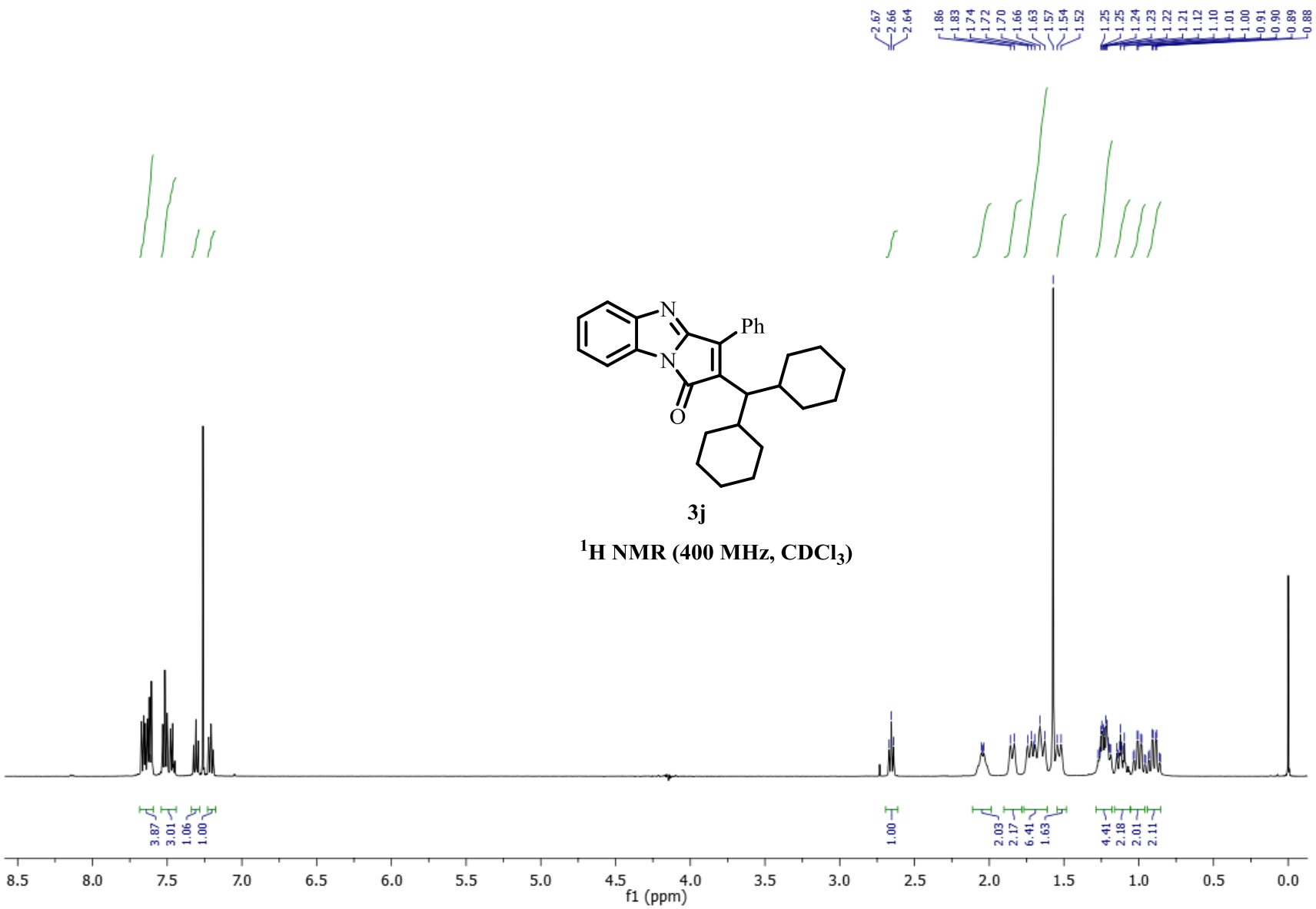
^{1}H NMR (400 MHz, $CDCl_3$)





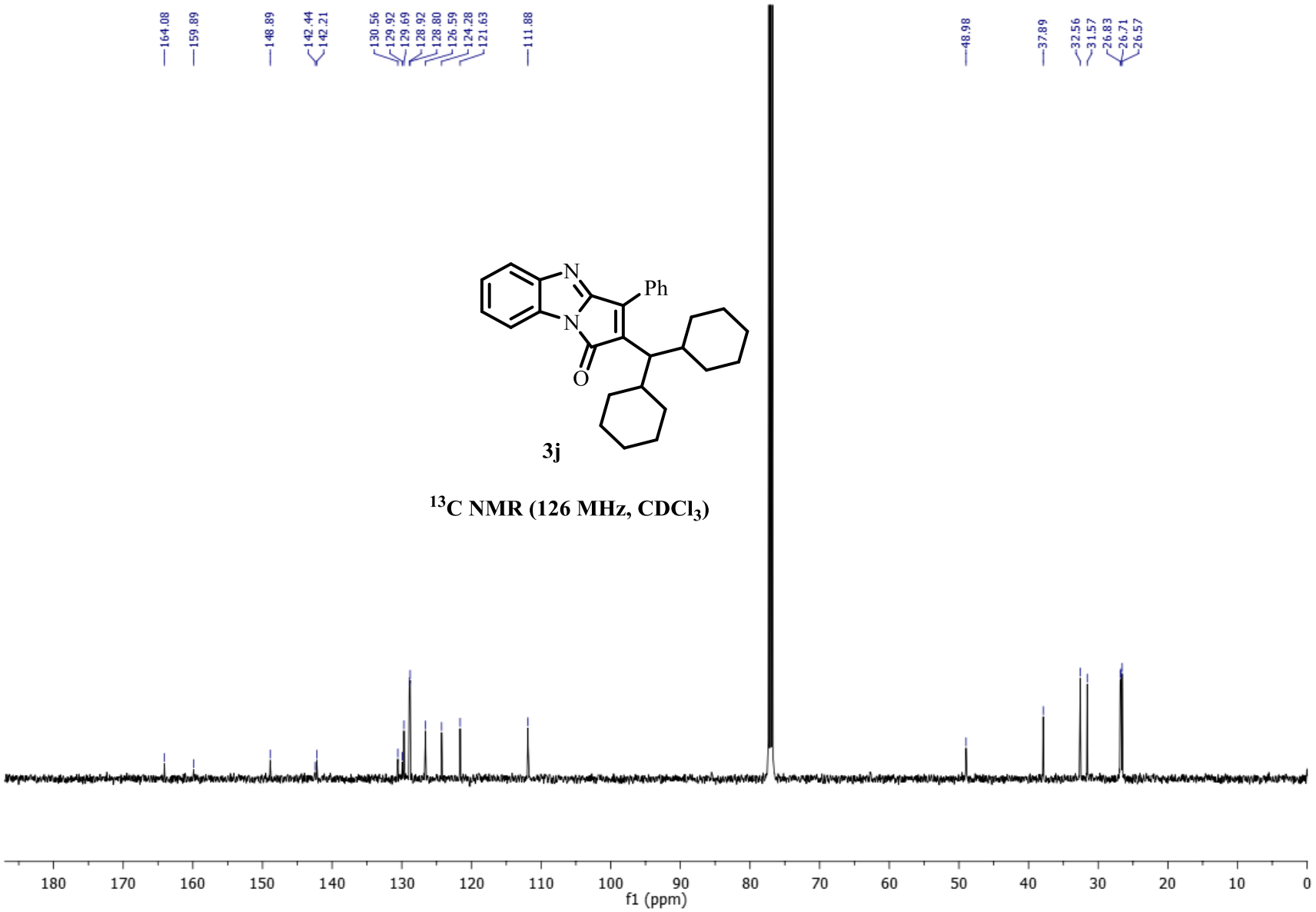
3i

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



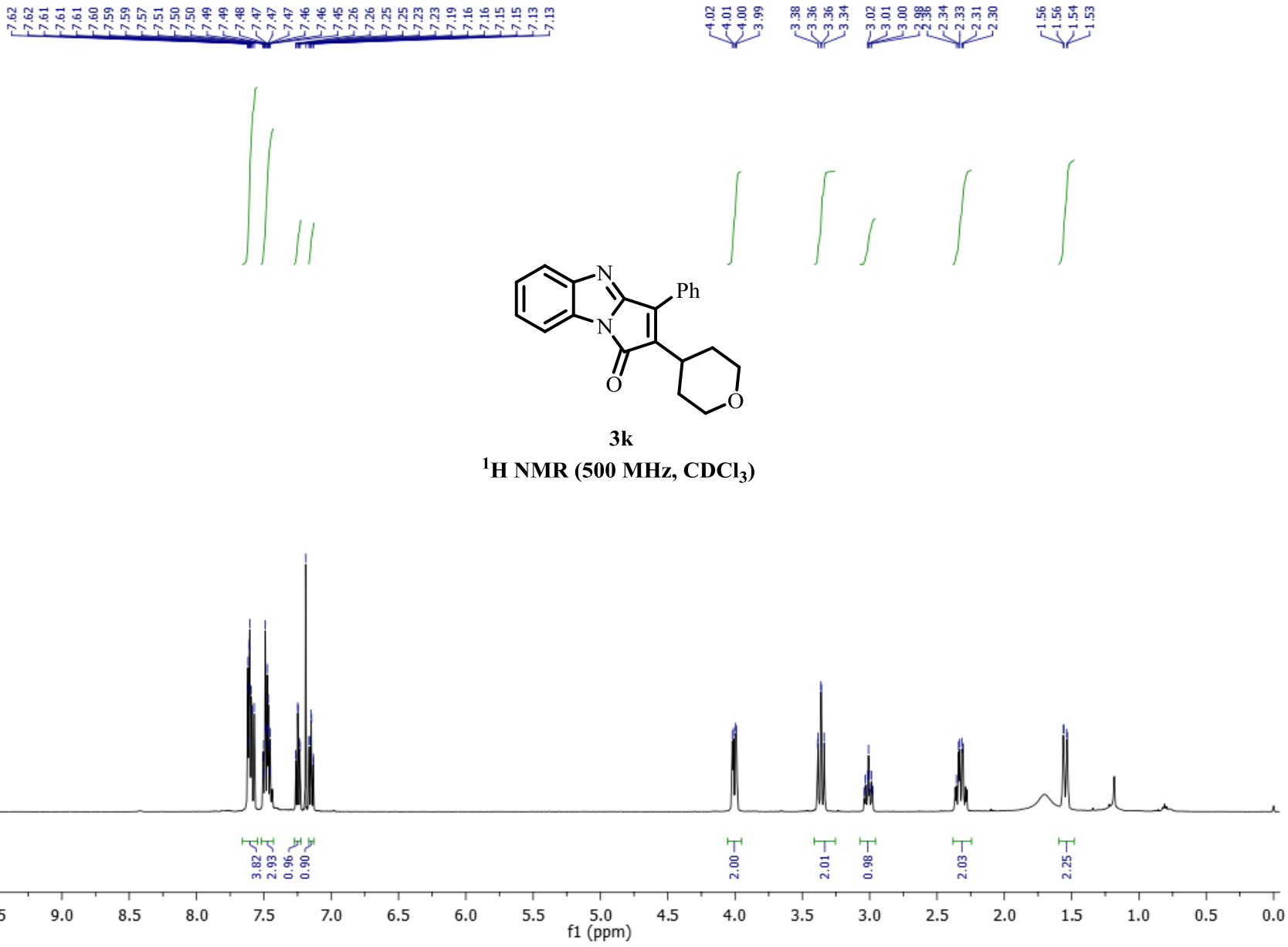
3j

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



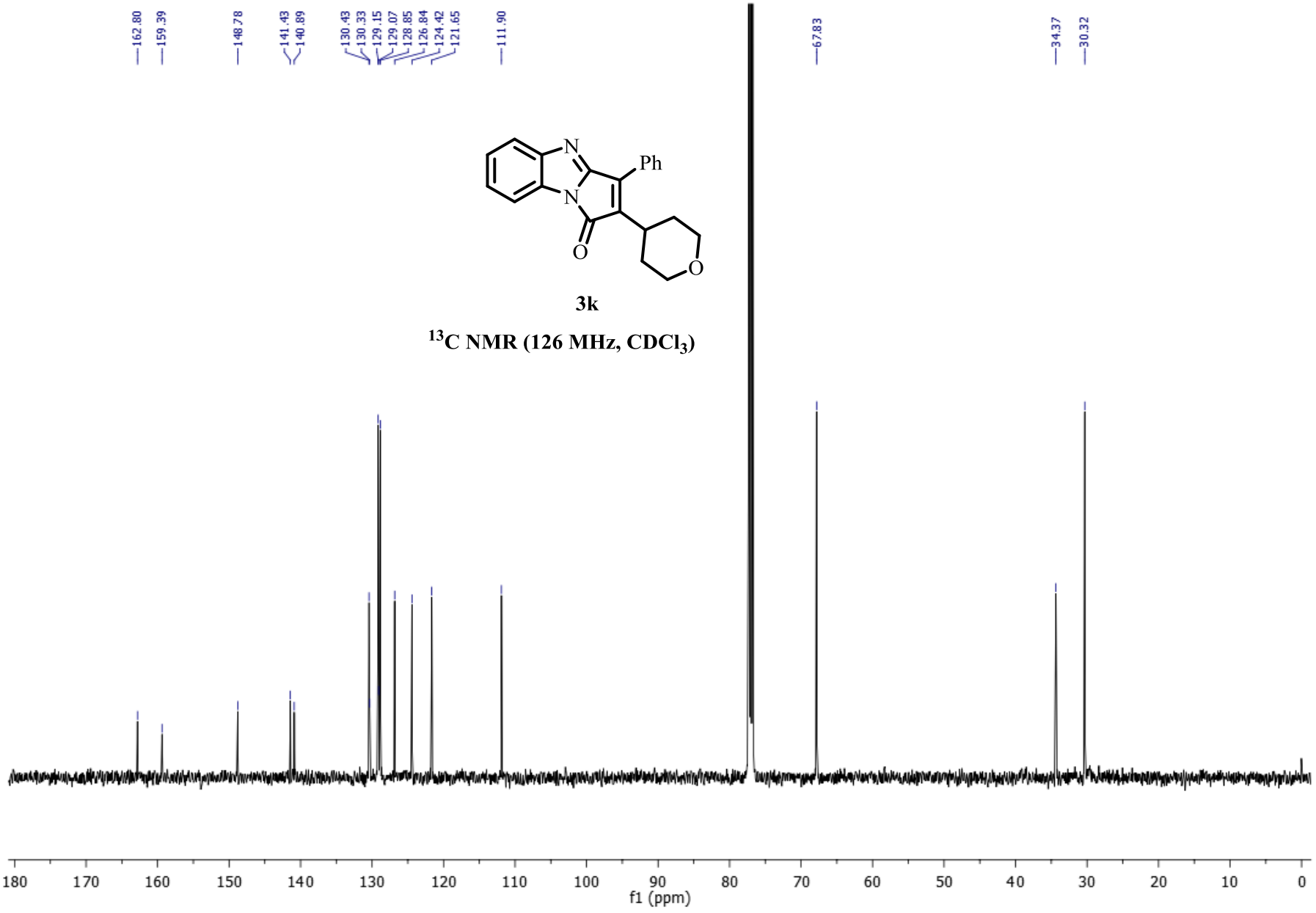
3j

^{13}C NMR (126 MHz, $CDCl_3$)



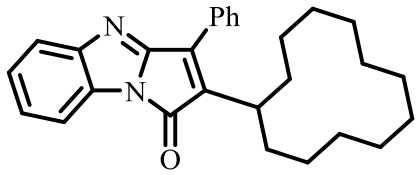
3k

^{1}H NMR (500 MHz, $CDCl_3$)



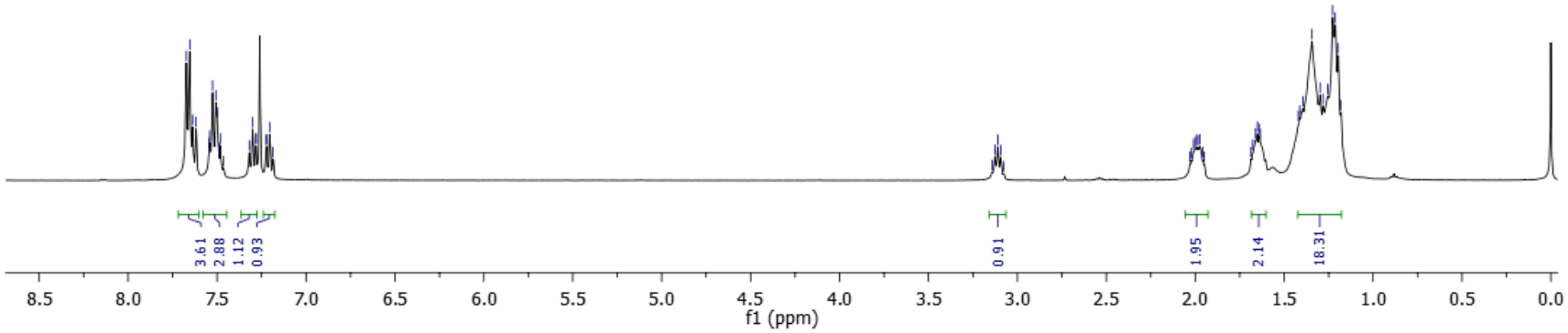
3k

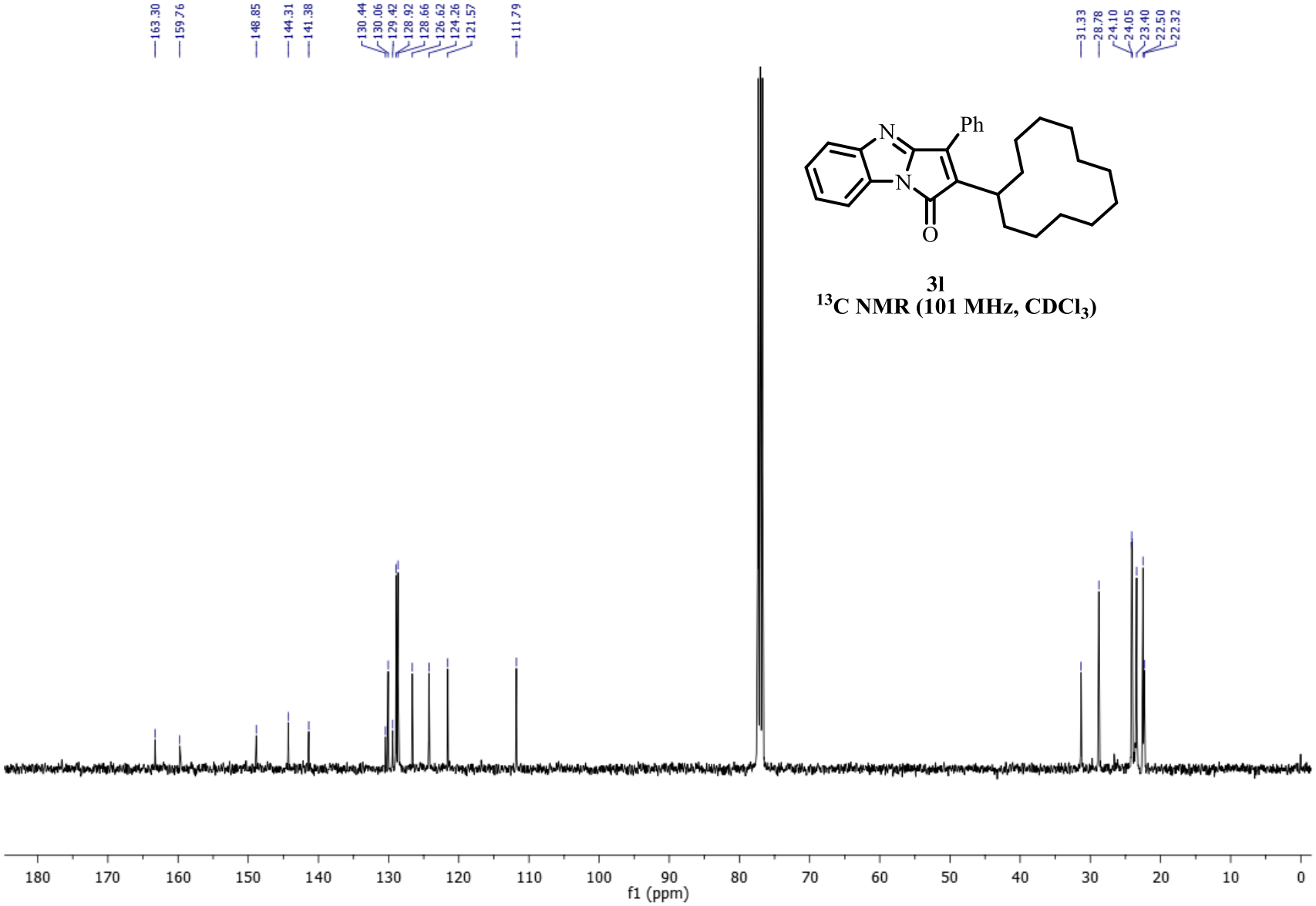
^{13}C NMR (126 MHz, $CDCl_3$)



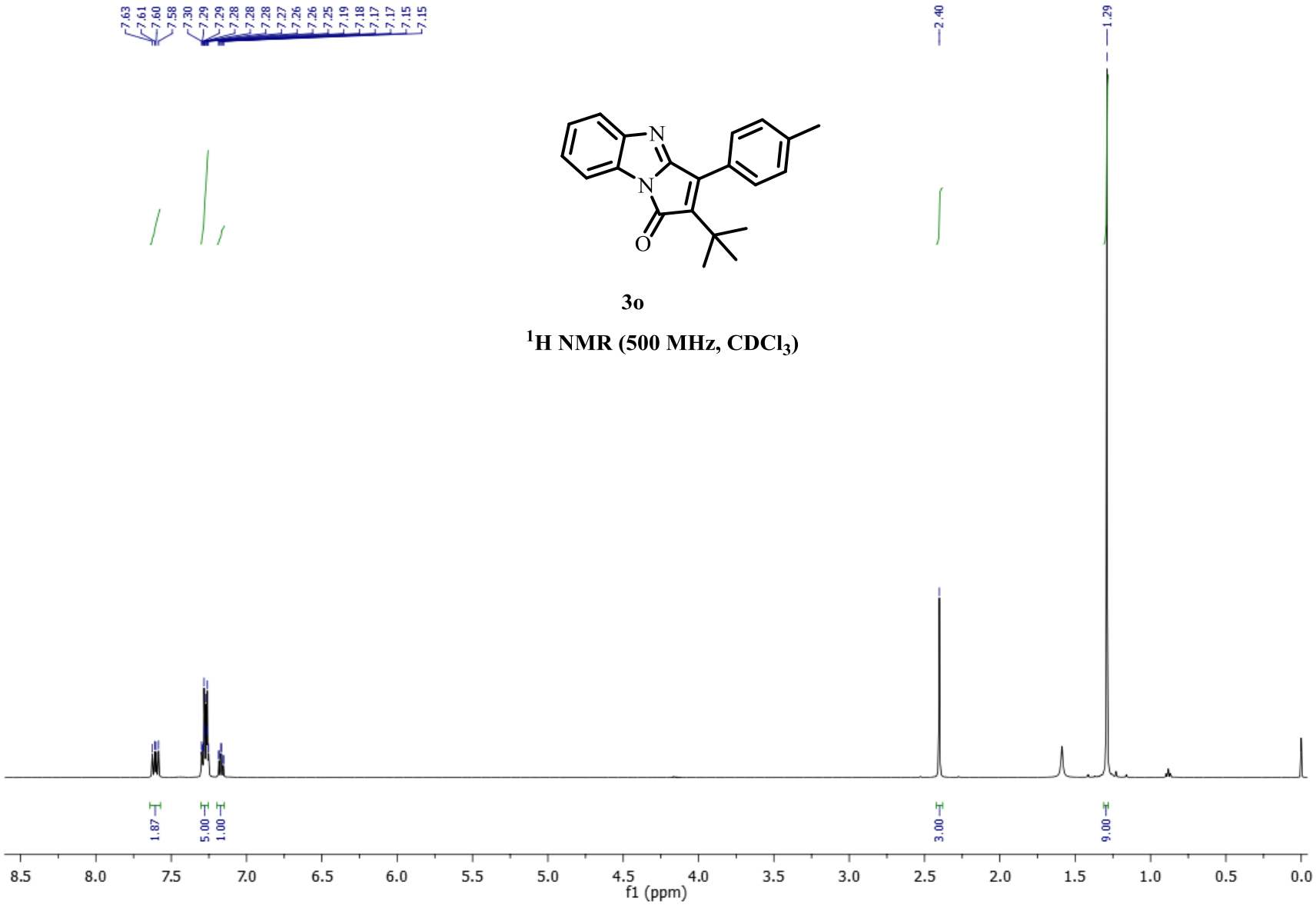
3l

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



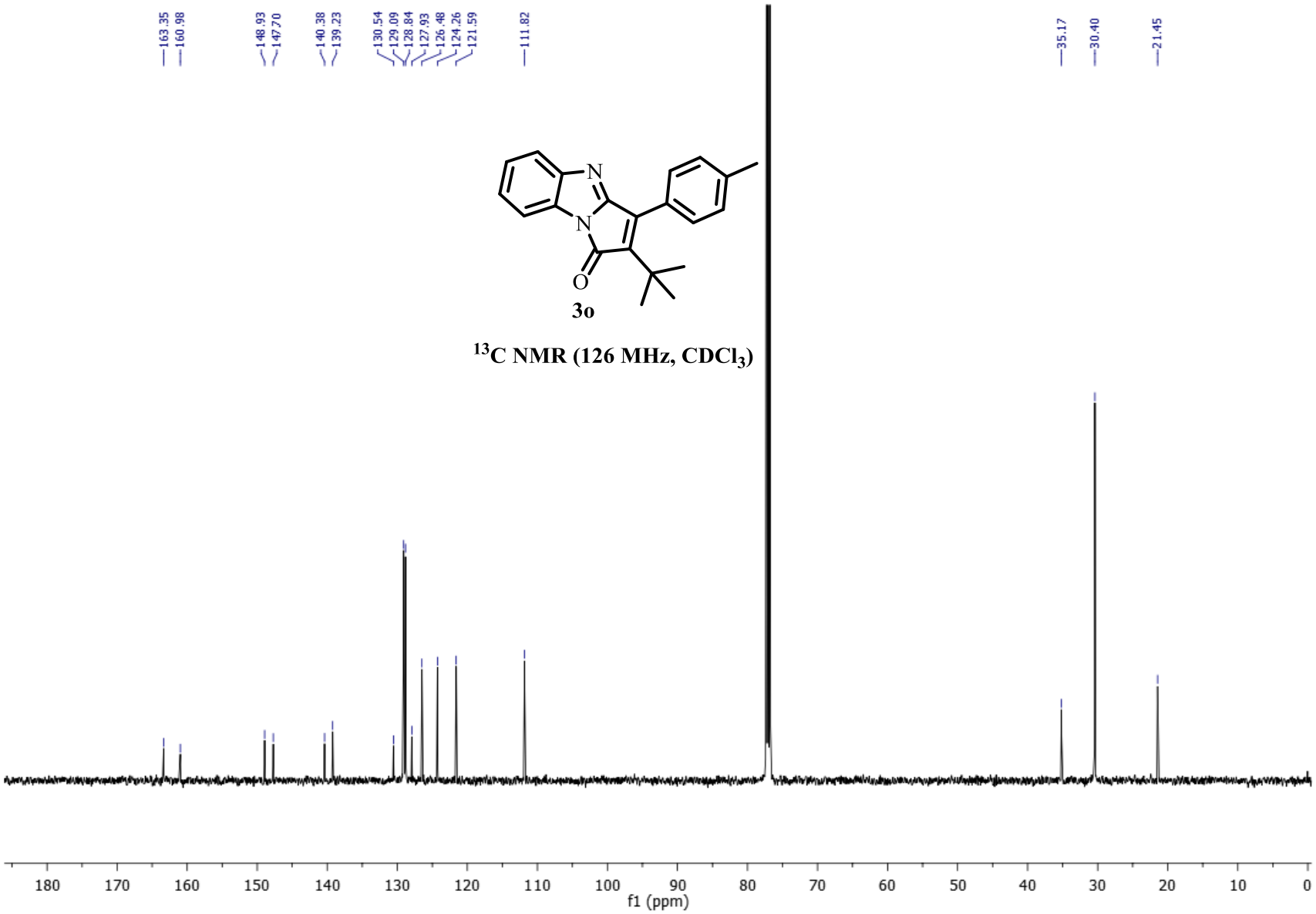


3l
^{13}C NMR (101 MHz, $CDCl_3$)



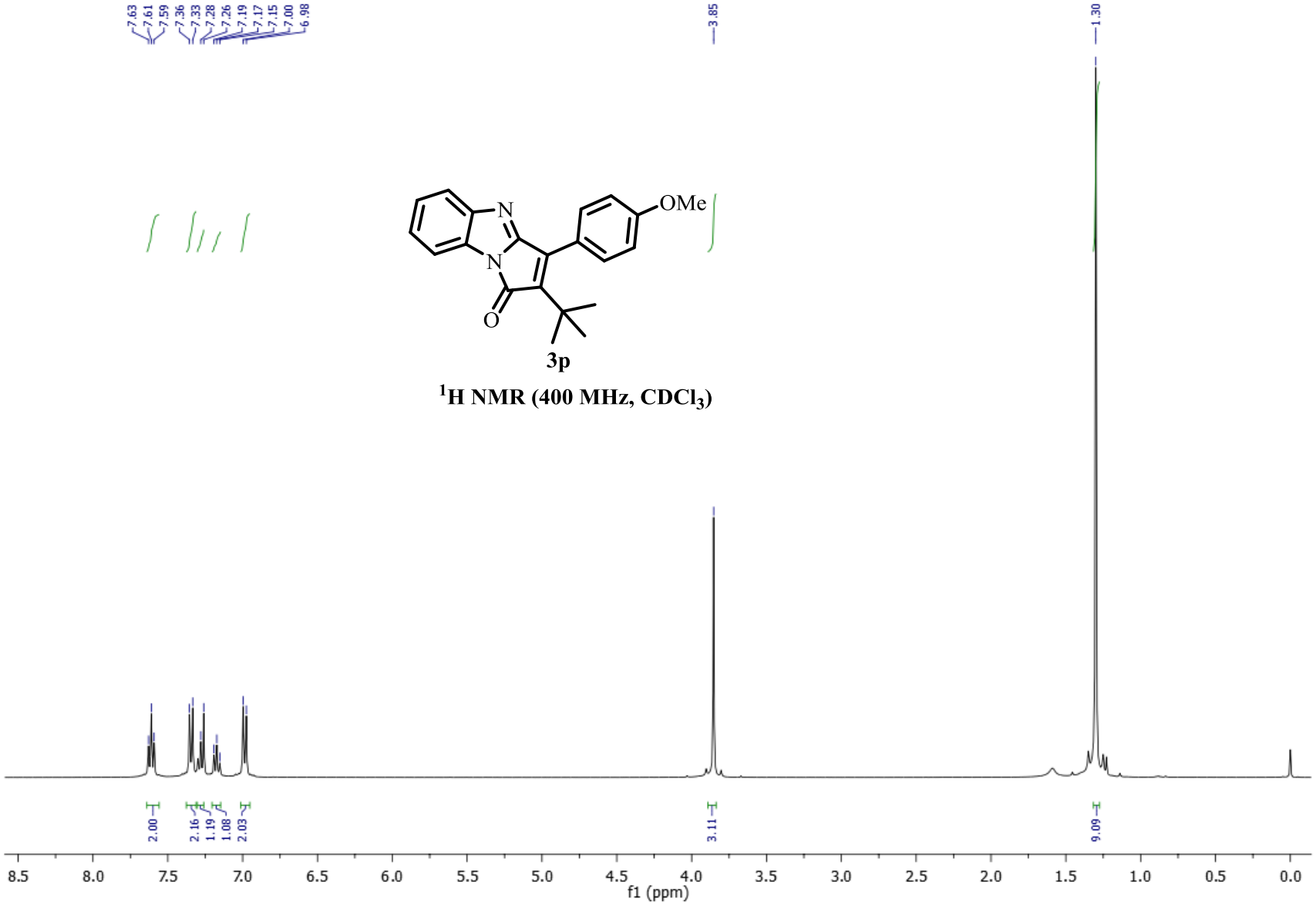
3o

^{1}H NMR (500 MHz, $CDCl_3$)



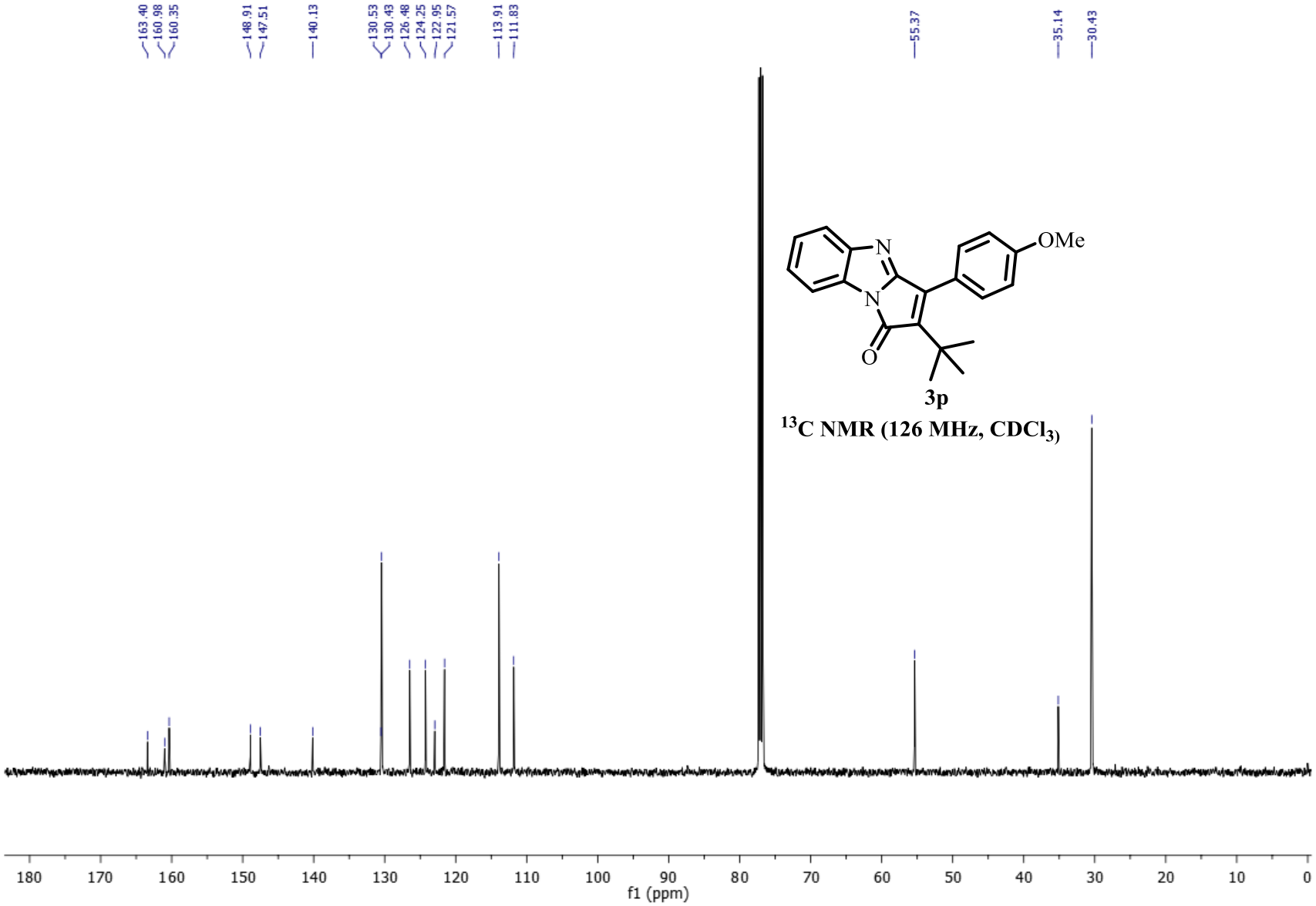
3o

^{13}C NMR (126 MHz, $CDCl_3$)



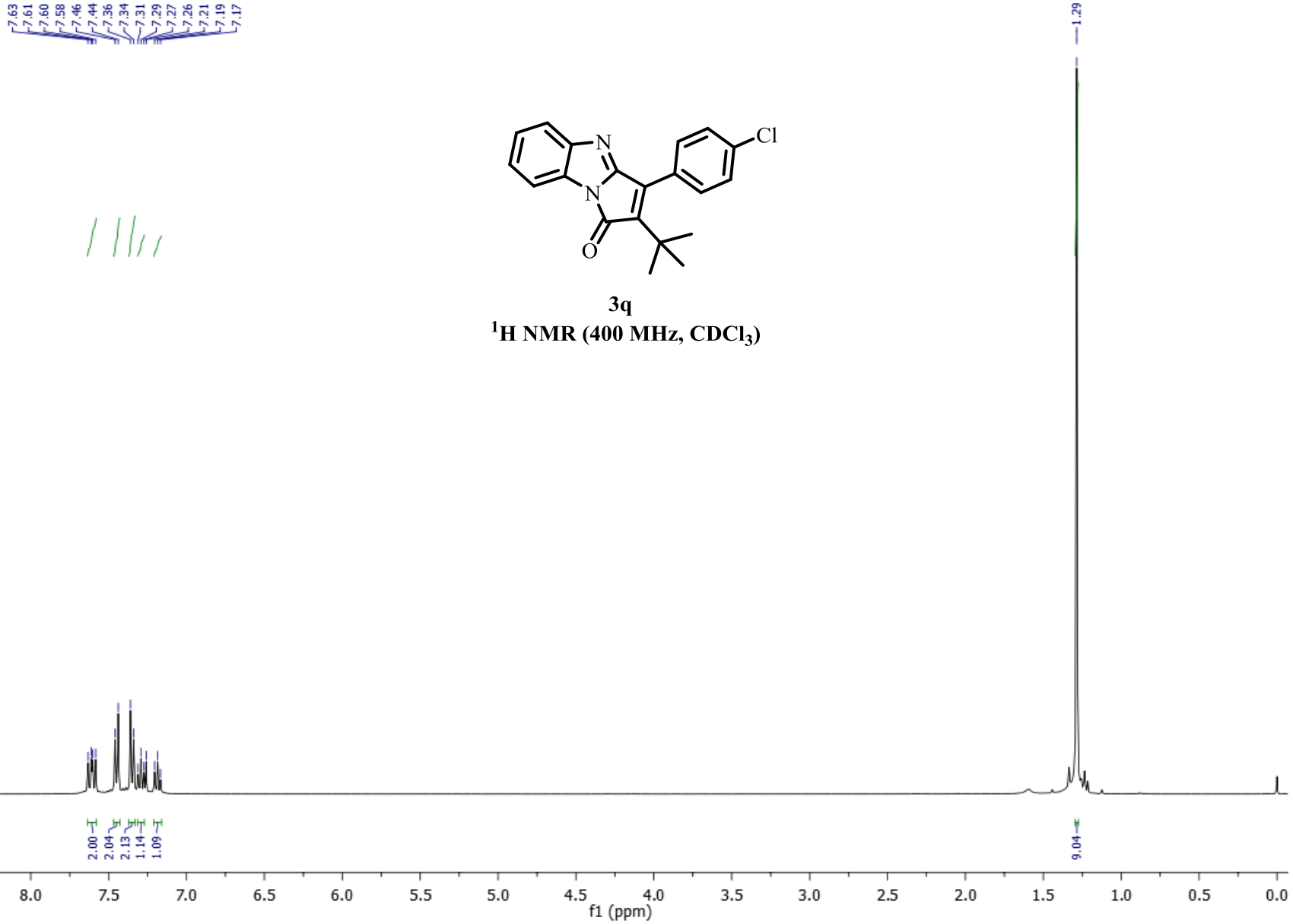
3p

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



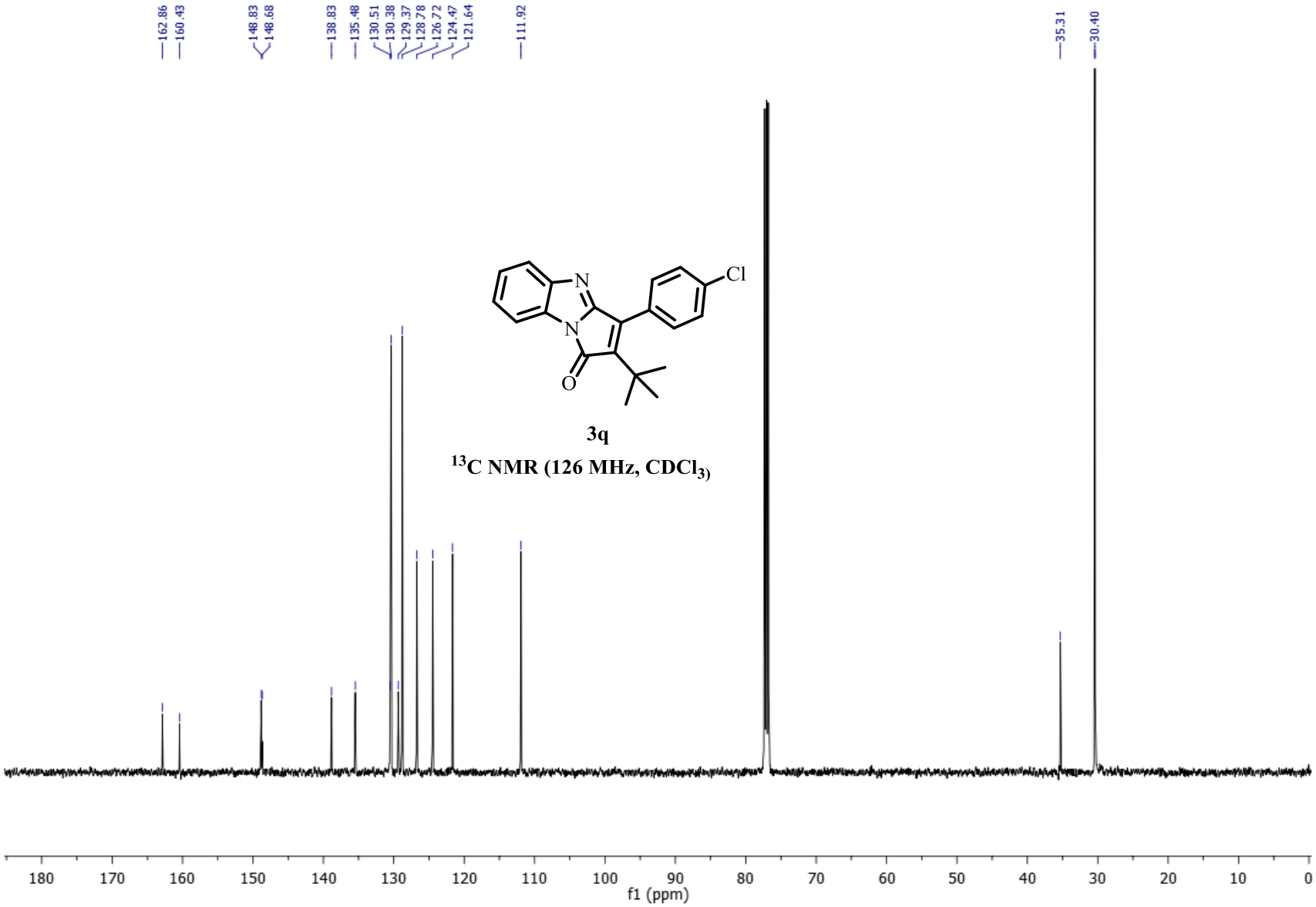
3p

^{13}C NMR (126 MHz, $CDCl_3$)



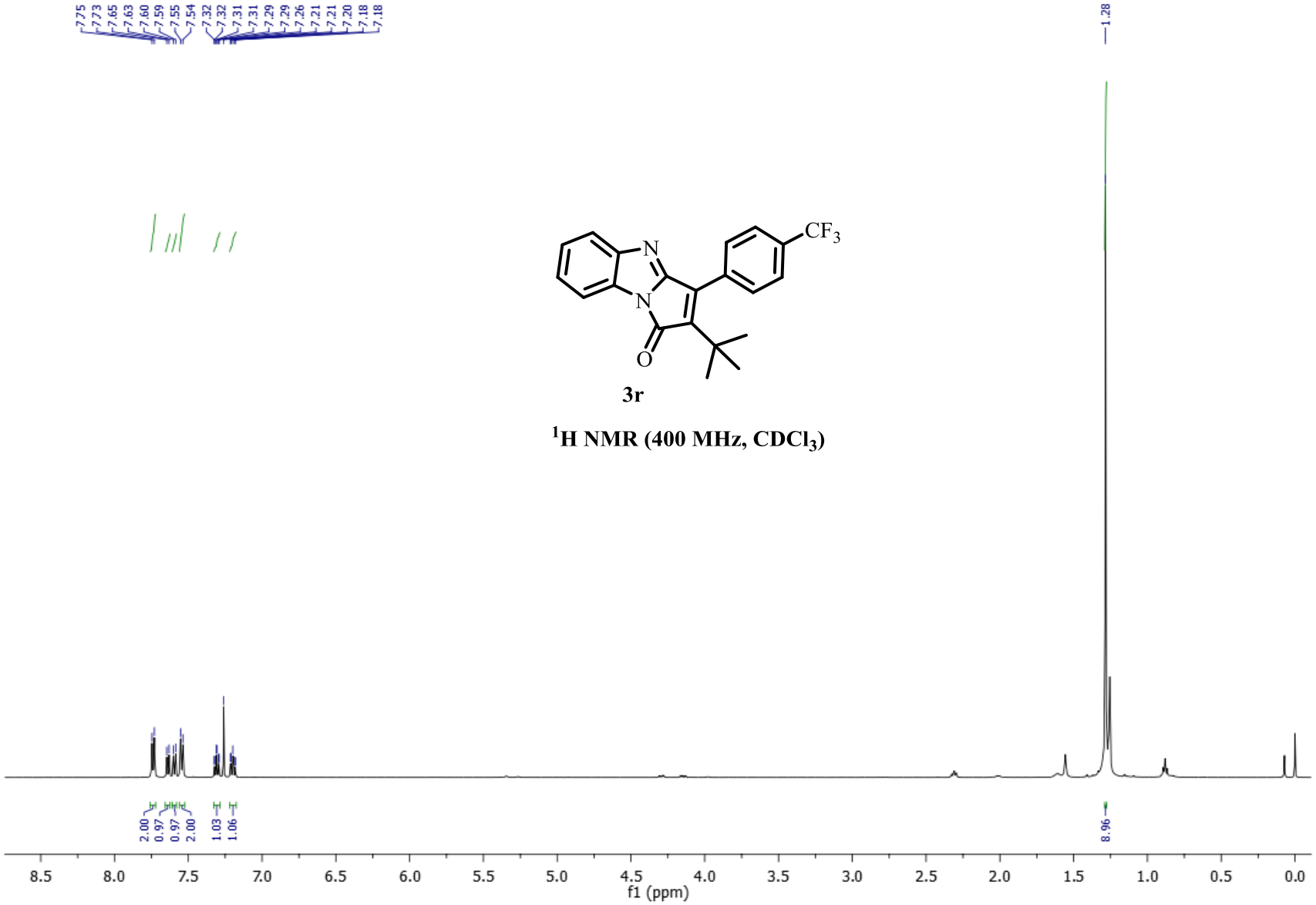
3q

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



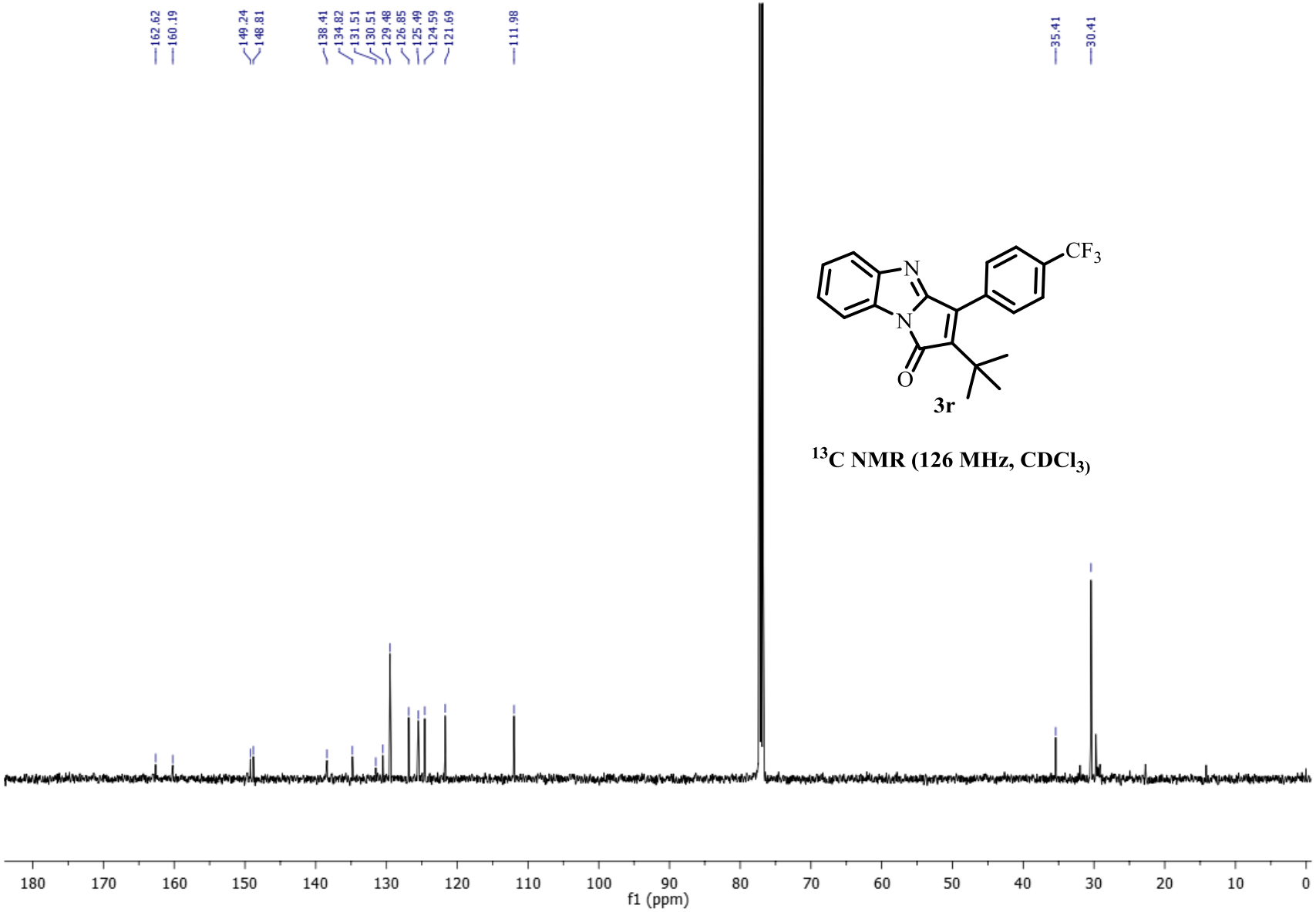
3q

^{13}C NMR (126 MHz, $CDCl_3$)



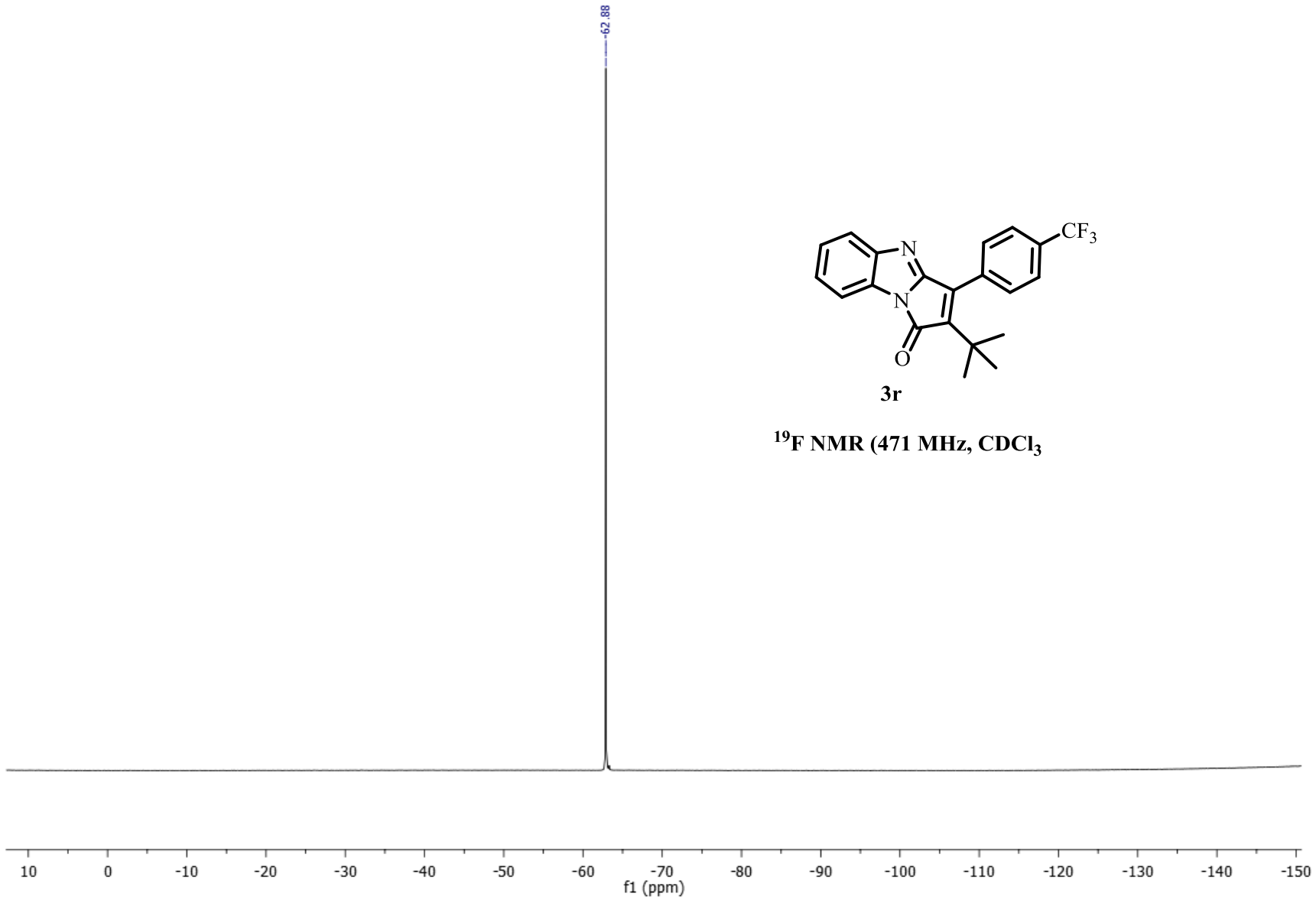
3r

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



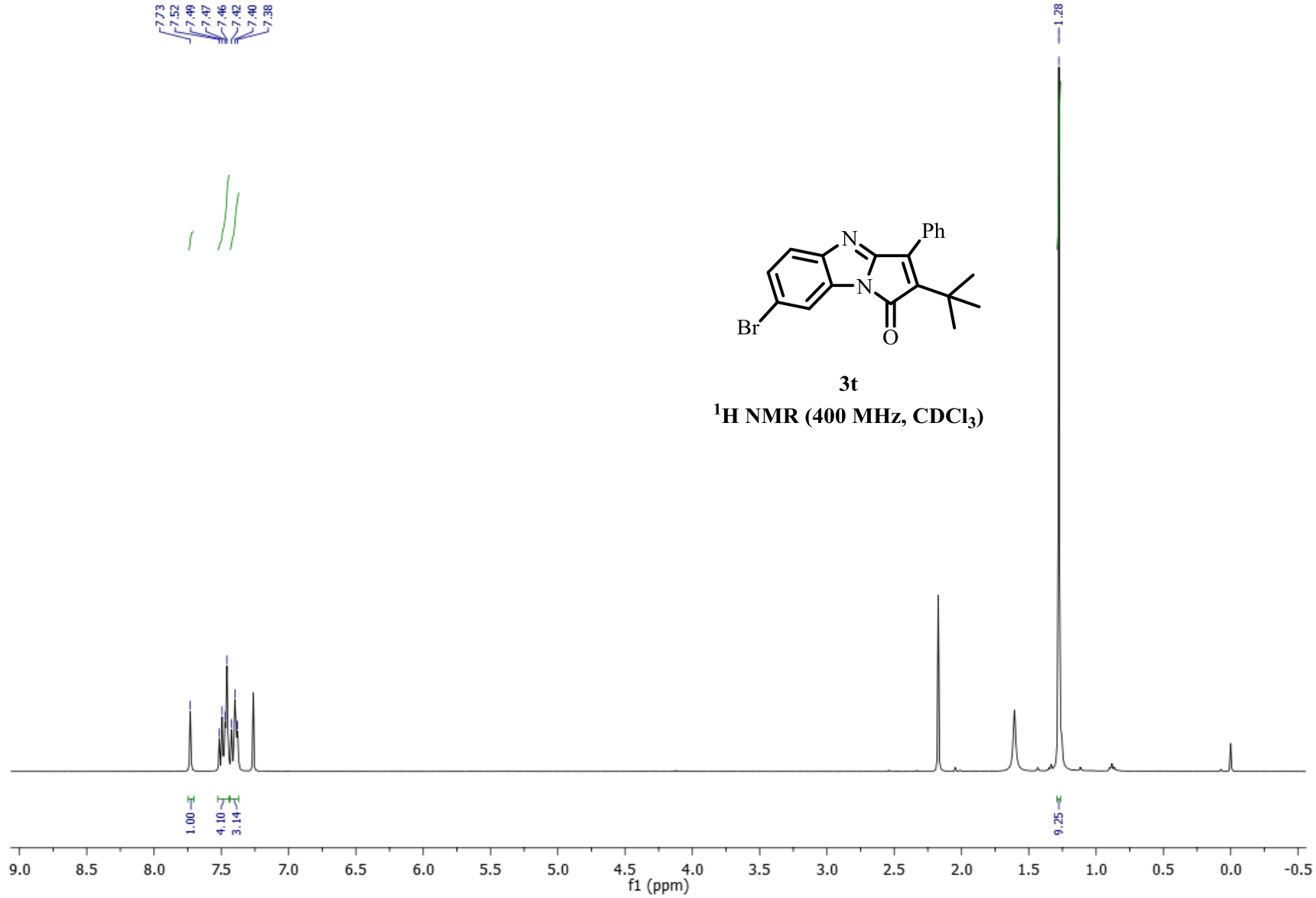
3r

^{13}C NMR (126 MHz, $CDCl_3$)



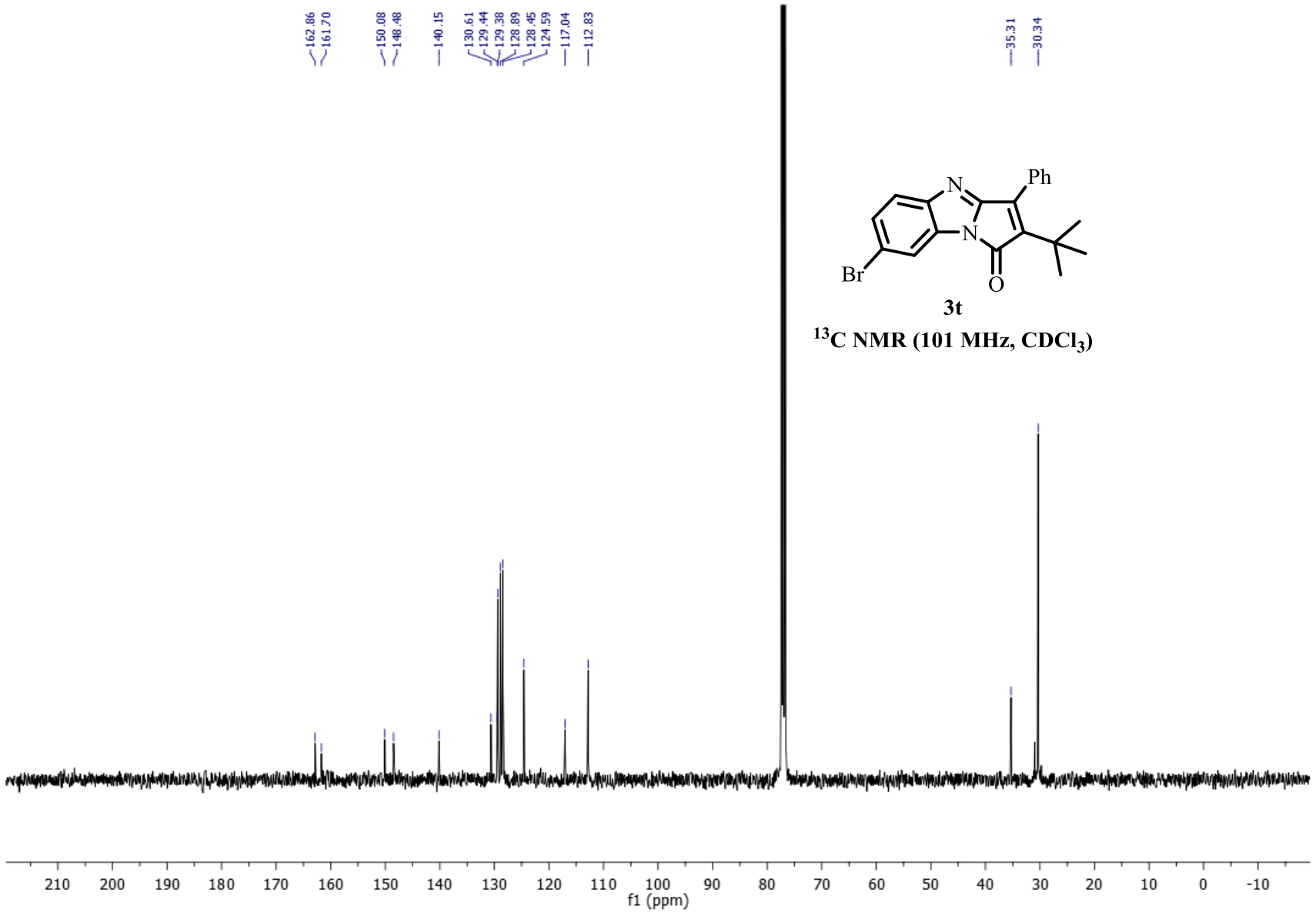
3r

^{19}F NMR (471 MHz, $CDCl_3$



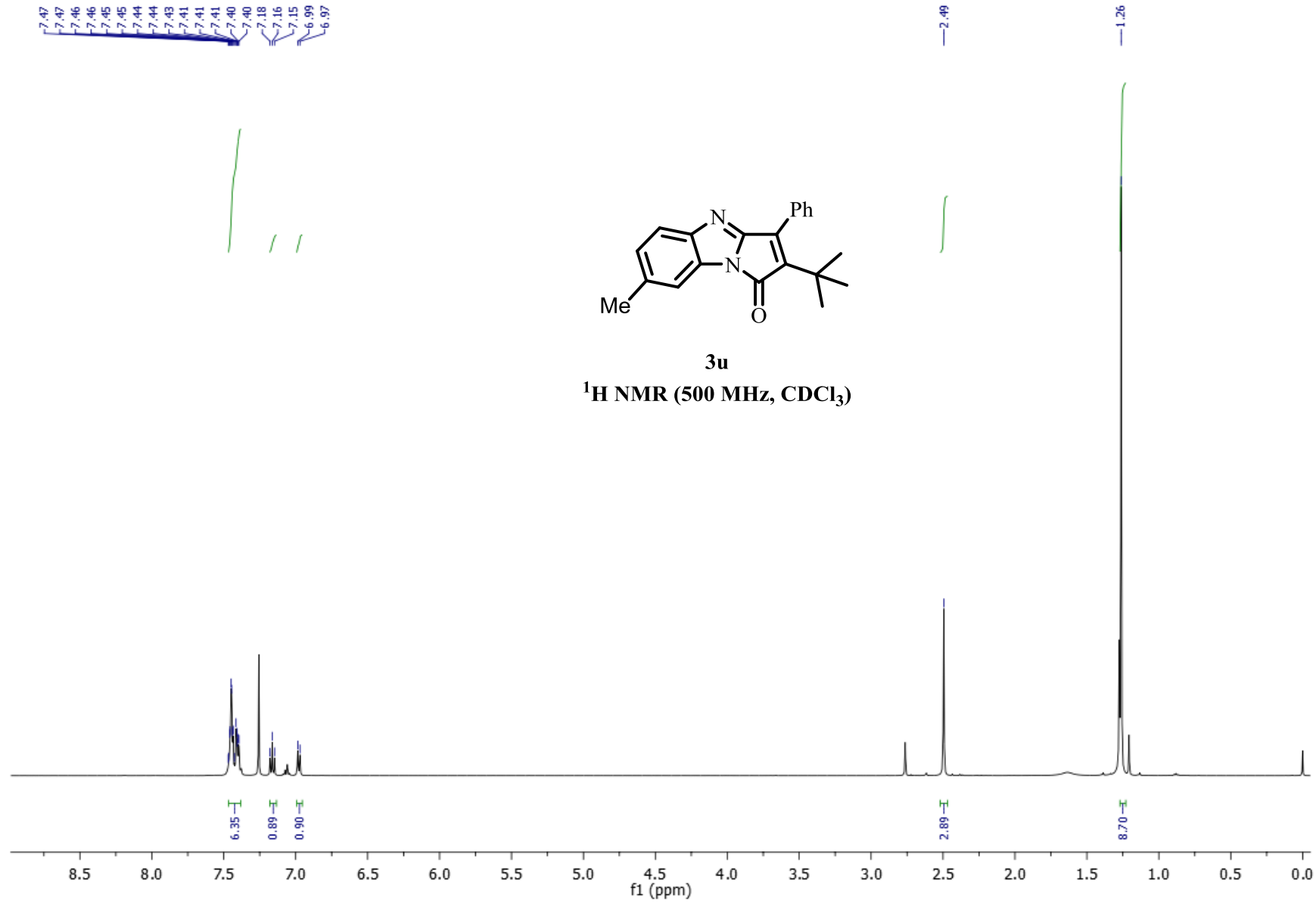
3t

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



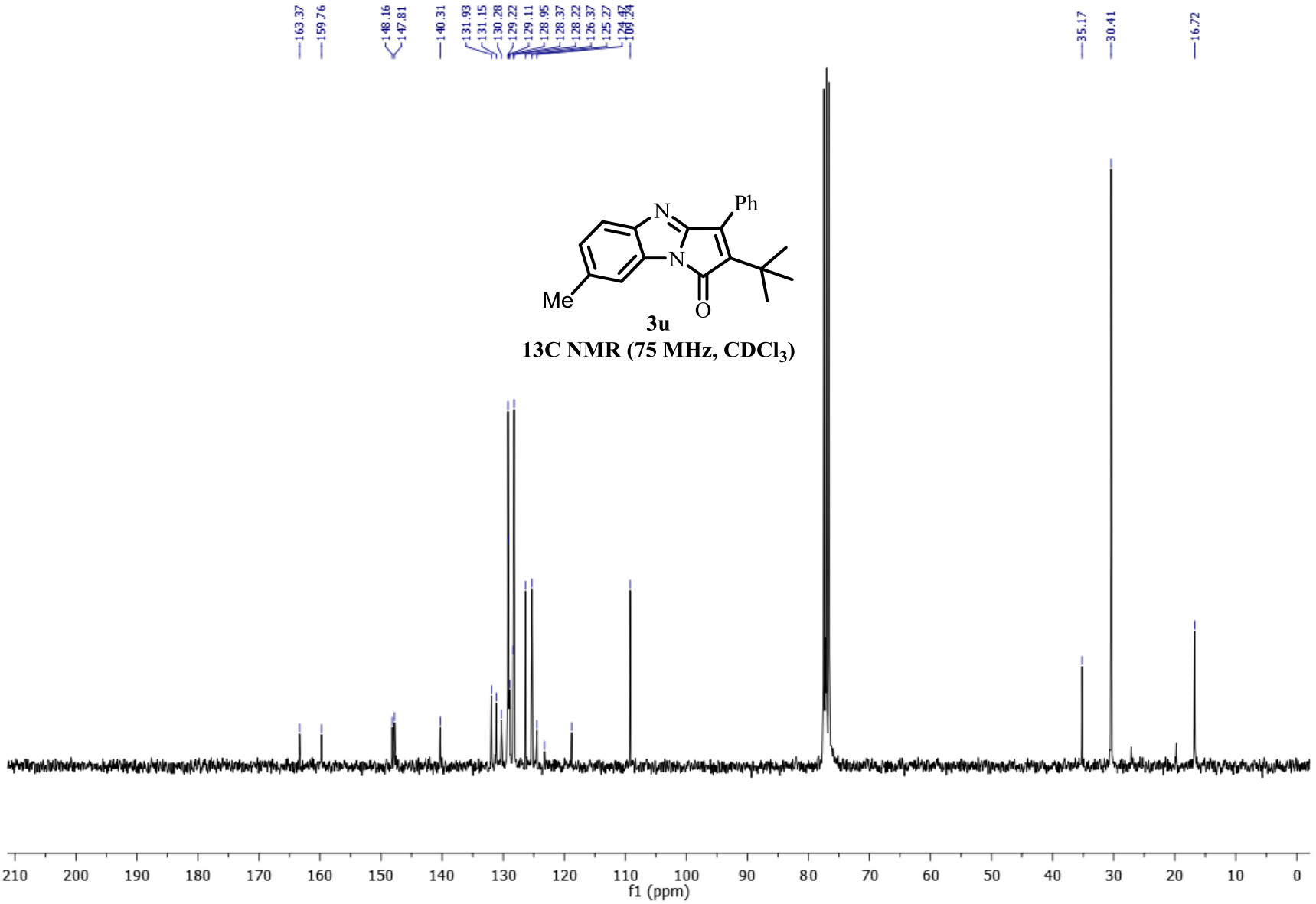
3t

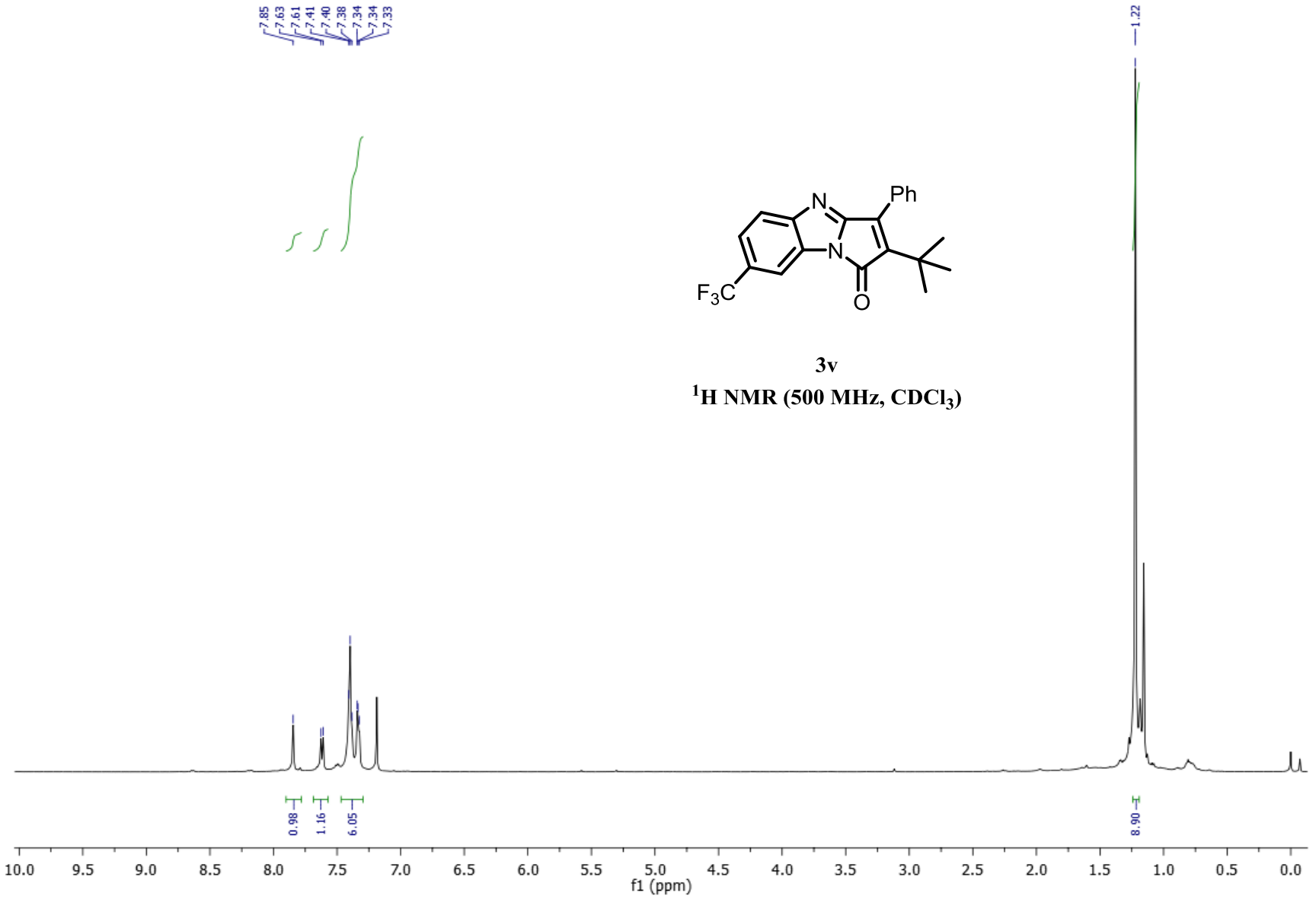
^{13}C NMR (101 MHz, $CDCl_3$)



3u

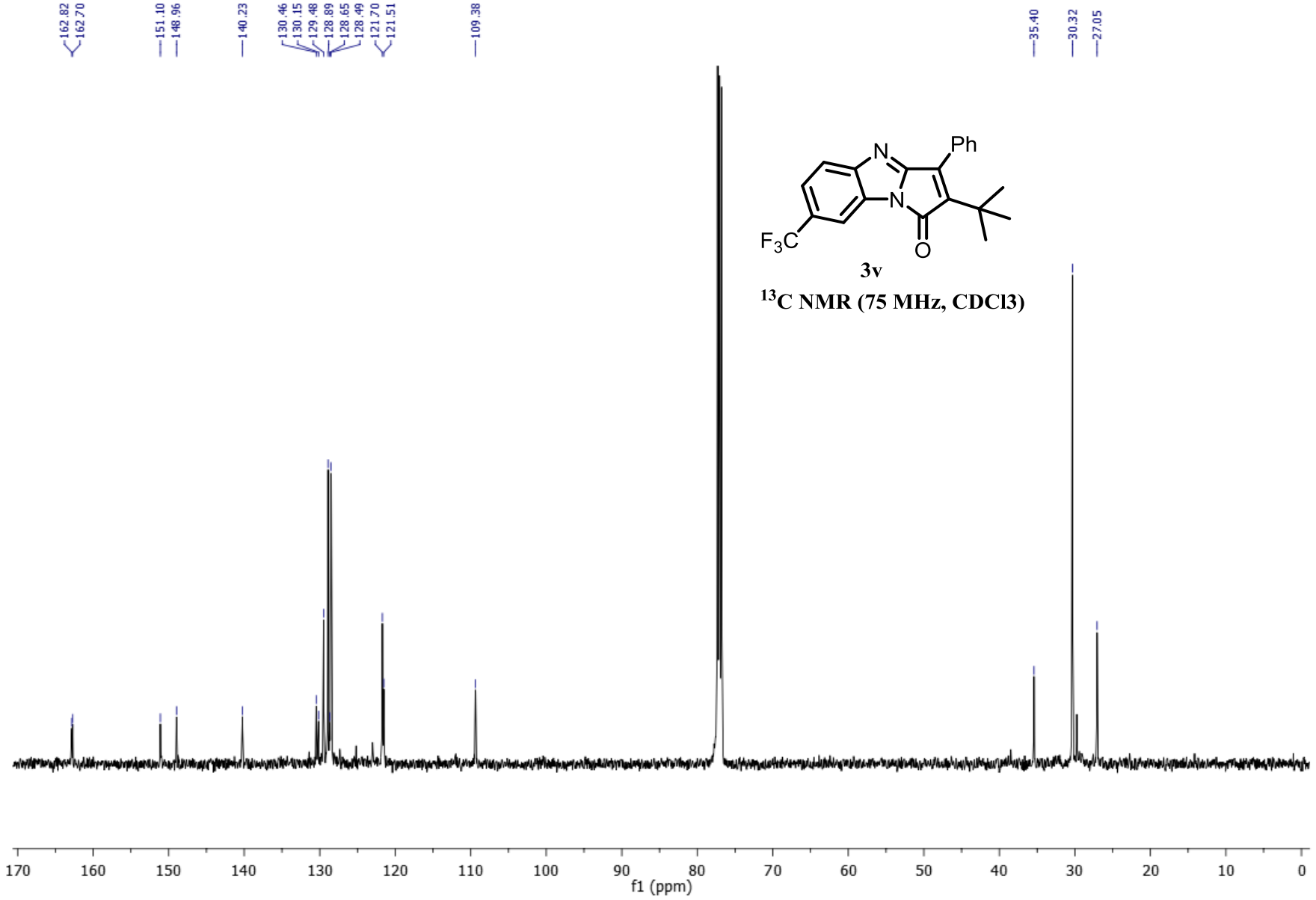
^{1}H NMR (500 MHz, $CDCl_3$)

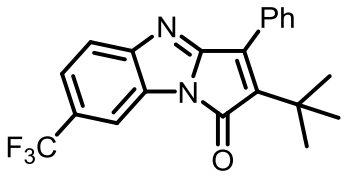

163.37
159.76
148.16
147.81
140.31
131.93
131.15
130.28
129.22
129.11
128.95
128.37
128.22
126.37
125.27
35.17
30.41
16.72
N
N
Ph
Me
O
3u
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3v

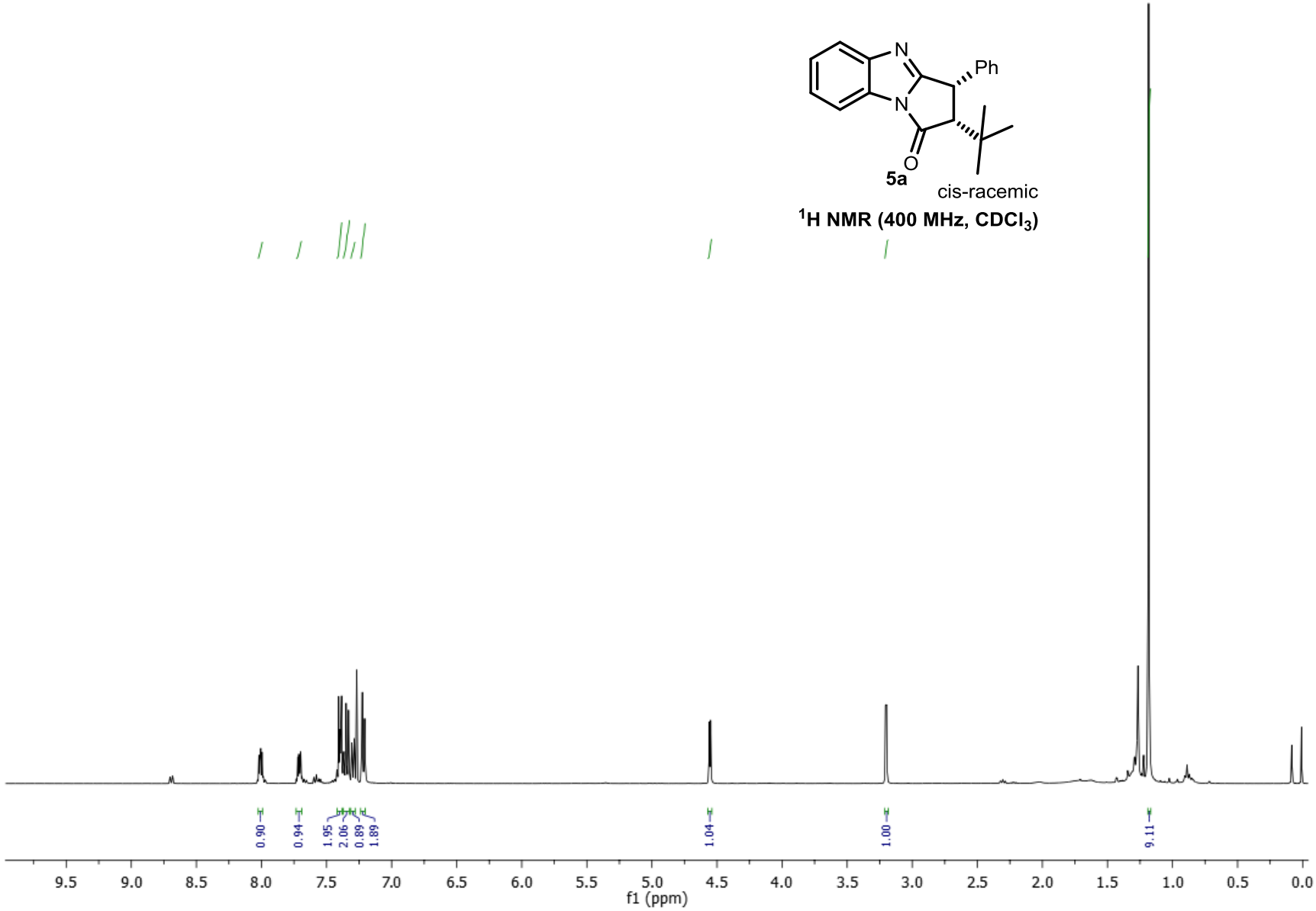
^{1}H NMR (500 MHz, $CDCl_3$)

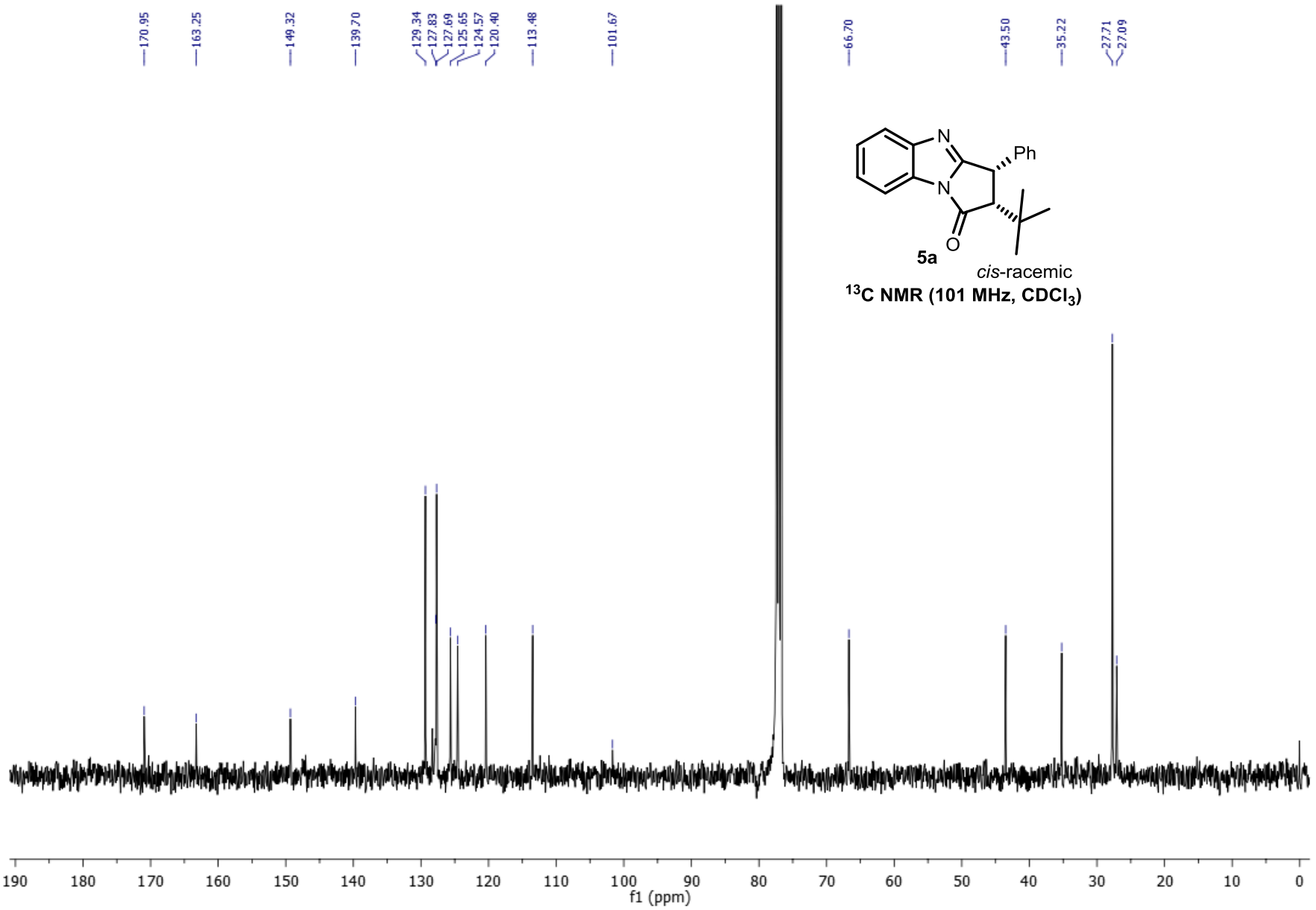

162.82
162.70
151.10
148.96
140.23
130.46
130.15
129.48
128.89
128.65
128.49
121.70
121.51
109.38
35.40
30.32
27.05
N
Ph
N
F3C
O
3v
13C NMR (75 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

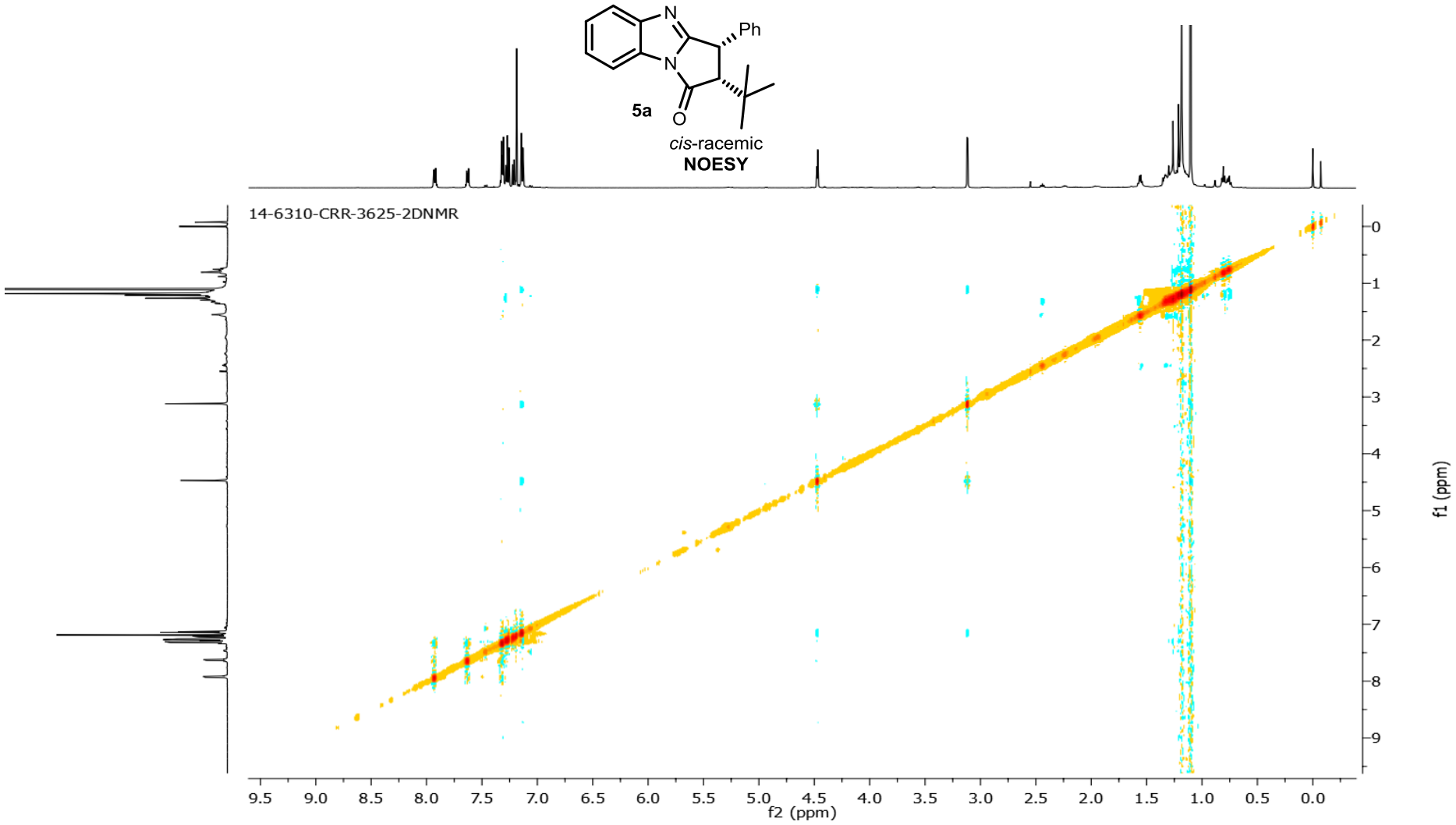


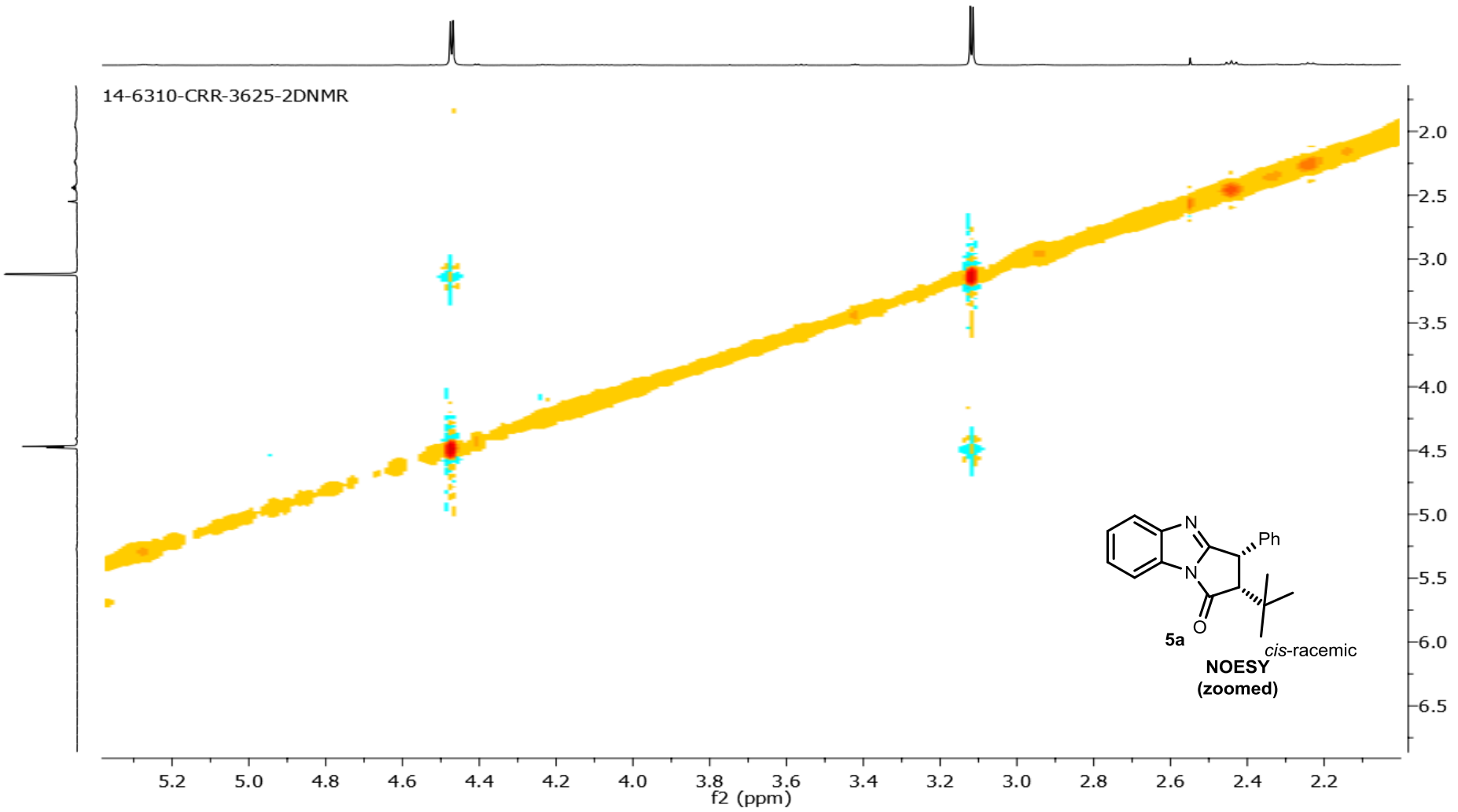
3v

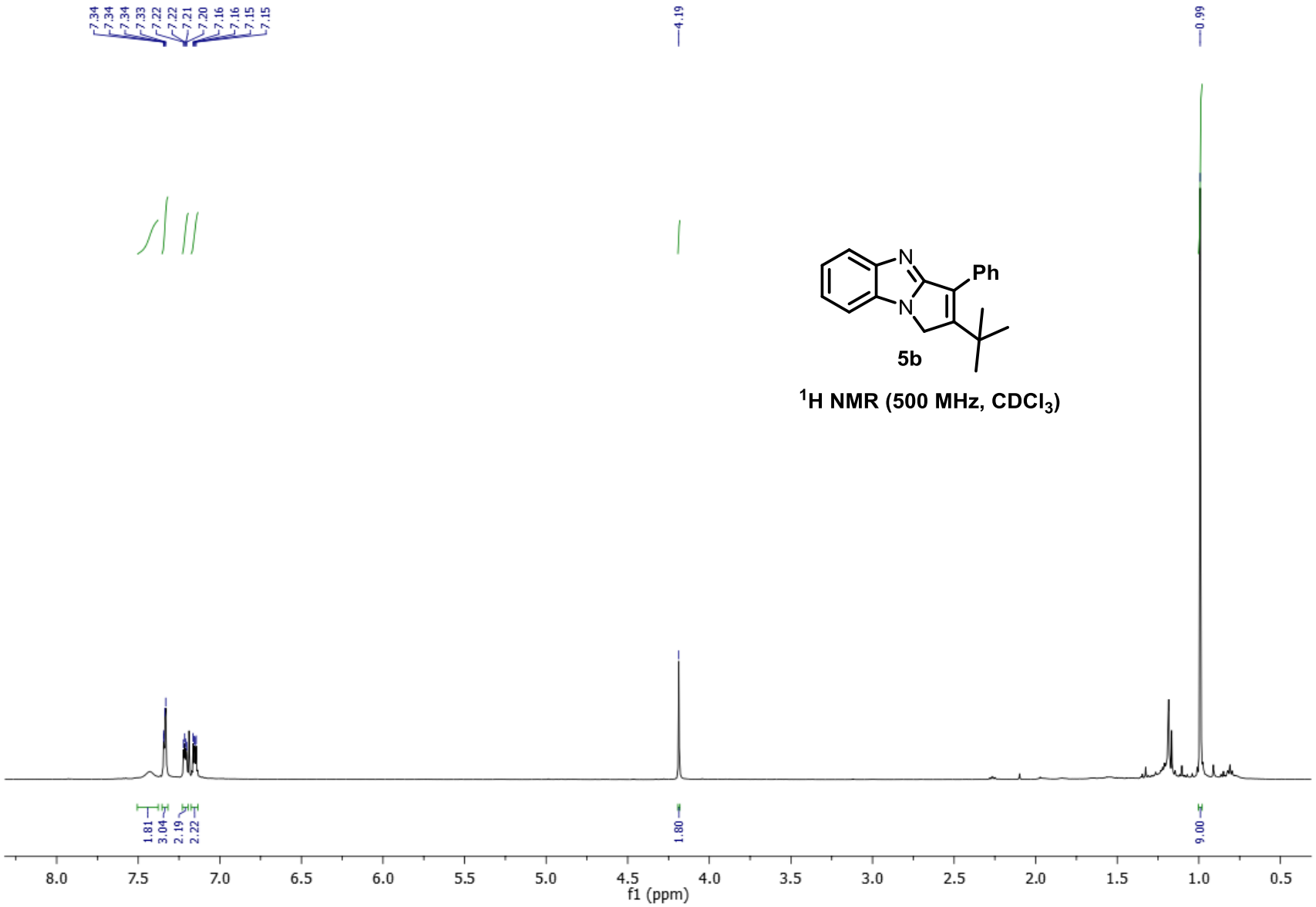
^{19}F NMR (471 MHz, CDCl3)

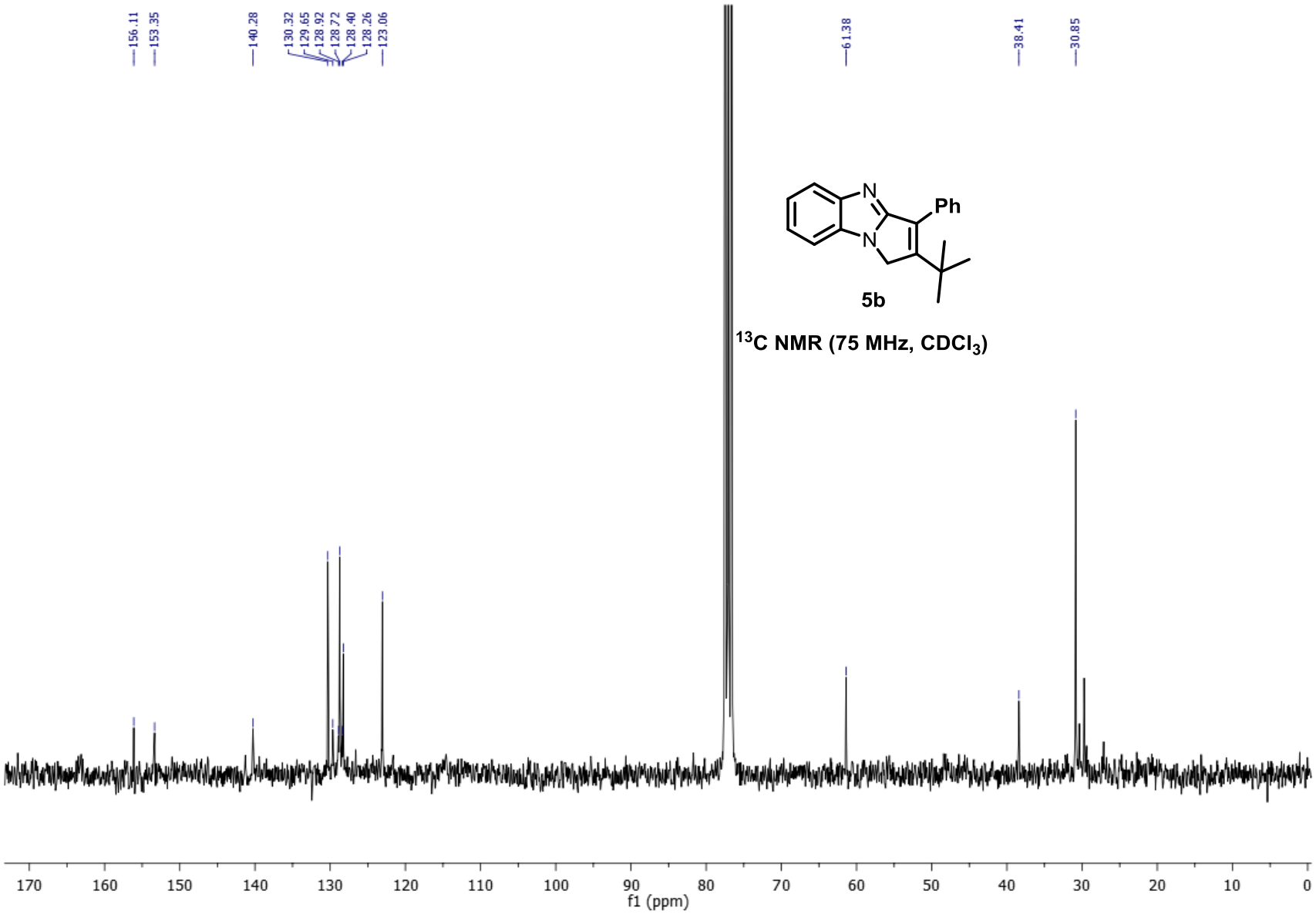

N
Ph
N
O
5a
cis-racemic
^{1}H NMR (400 MHz, CDCl$_3$)
0.90
0.94
1.95
2.06
0.89
1.89
1.04
1.00
9.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.95
163.25
149.32
139.70
129.34
127.83
127.69
125.65
124.57
120.40
113.48
101.67
66.70
43.50
35.22
27.71
27.09
N
N
Ph
O
5a
cis-racemic
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
N
Ph
O
5a
cis-racemic
NOESY
14-6310-CRR-3625-2DNMR
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
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)


14-6310-CRR-3625-2DNMR
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
N
N
Ph
O
5a
cis-racemic
NOESY
(zoomed)


7.34
7.34
7.34
7.33
7.22
7.22
7.21
7.20
7.16
7.16
7.15
7.15
4.19
0.99
N
N
Ph
5b
1H NMR (500 MHz, CDCl3)
1.81
3.04
2.19
2.22
1.80
9.00
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
f1 (ppm)


156.11
153.35
140.28
130.32
129.65
128.92
128.72
128.40
128.26
123.06
61.38
38.41
30.85
N
N
Ph
5b
^{13}C NMR (75 MHz, CDCl$_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)