Carbonylative Cyclization of Biaryl Enones with Aldehydes and Oxamic Acids

Chada Raji Reddy,[*,a,b] Dattahari H. kolgave,[a,b,‡] Sana Fatima[a,b,‡] and Remya Ramesh[a,b]

[a]Department of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India.
[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India
‡Both these authors contributed equally

Table of Contents

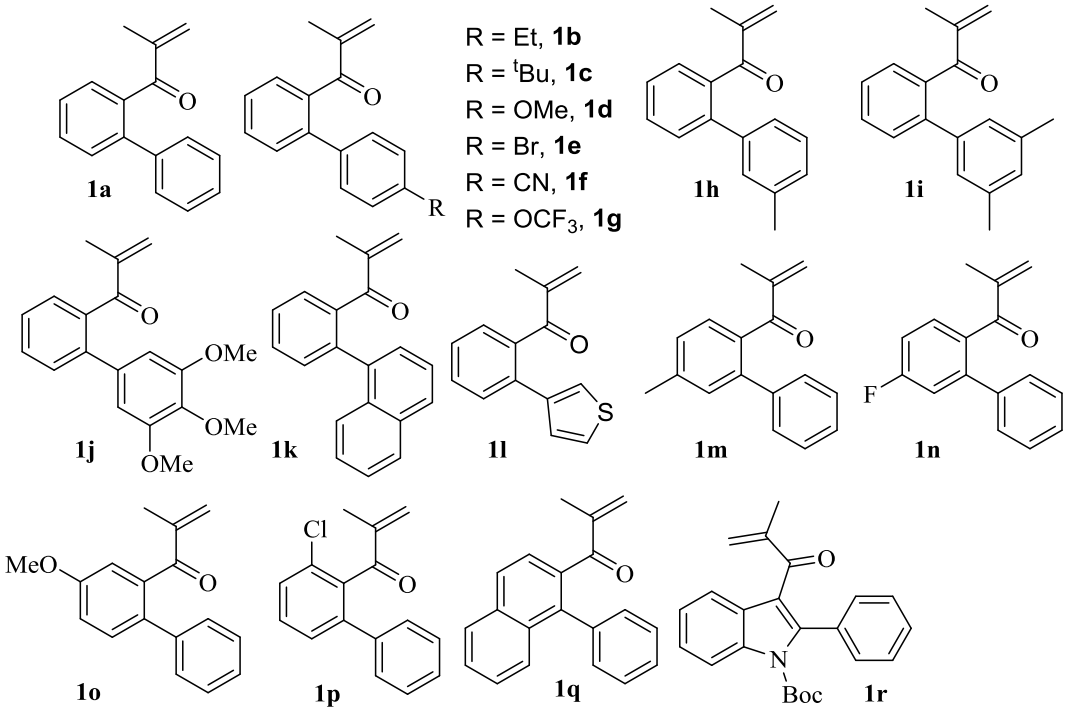
1. General information

All the reactions were performed in oven-dried glass apparatus, the air and moisture sensitive reactions were carried out under inert atmosphere (nitrogen) using freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde for visualization. Column chromatography was performed on silica gel (100-200 mesh) using hexanes and ethyl acetate as eluent. ^{1}H NMR was recorded in $CDCl_3$, DMSO on 500 MHz and 400 MHz and ^{13}C NMR was recorded on 151 MHz, 126 MHz and 101 MHz. δ7.26 and δ77 and δ 2.5, δ 39.5 are corresponding to $CDCl_3$ and DMSO-d_6 in ^{1}H NMR and ^{13}C NMR respectively. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and *J* values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. FTIR spectra were recorded on Alpha (Bruker) Infrared Spectrophotometer. High resolution mass spectra (HRMS) [ESI+] were obtain using either a TOF or a double focusing spectrometer.

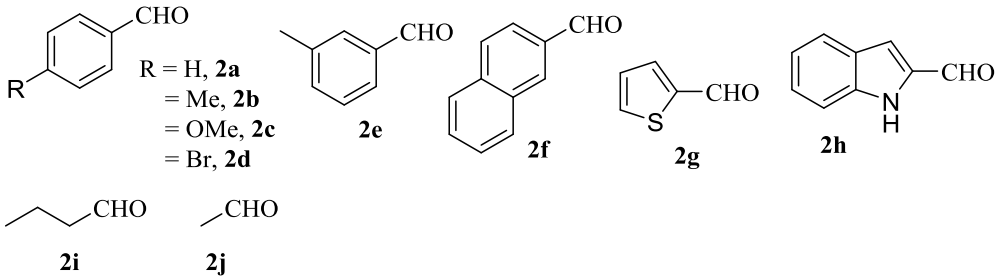
Structures of Bialy Enones:

All the biaryl enones were prepared following the literature procedures.[1-3]

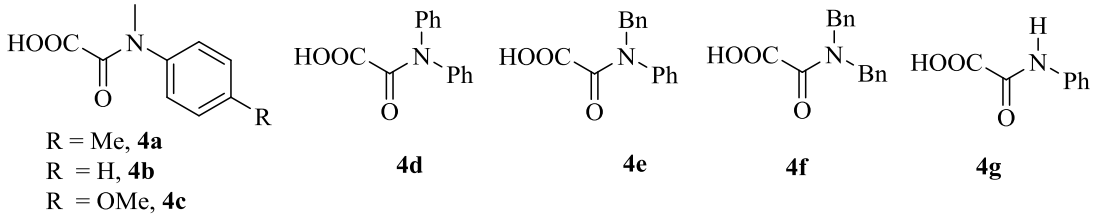
Strcutures of Biaryl Enones 1a to 1q:



Strcutures of Aldehydes 2a to 2j:



Strcutures of Oxamic Acids 4a to 4f:

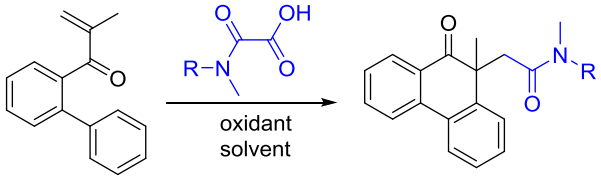


2. Optimization table, Control experiments and Plausible mechanism:

A. Optimization of reaction conditions:

Optimization of the reaction conditions, the cyclic reaction of 1-([1,1'-biphenyl]-2-yl)-2-methylprop-2-en-1-one (1a) with 2 equiv. of oxoacetic acid as the carbamoylating agent was chosen as a model reaction**.**

Table S1: Optimization of carbamoyl radical-promoted cyclization of biaryl enones:

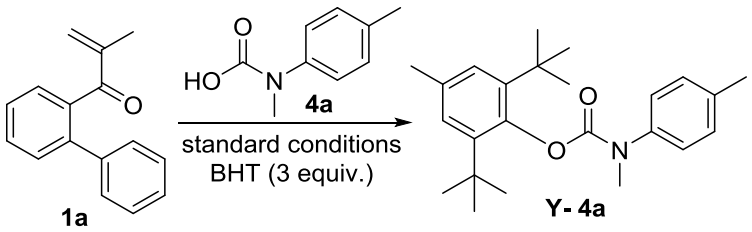


Entry	Oxidant	Catalyst	Solvent	Temp (°C)	Yield (%)[b]
1	$K_2S_2O_8$	AgOAc	CH_3CN	80	33
2	$K_2S_2O_8$	AgOTf	CH_3CN	80	28
3	$K_2S_2O_8$	$AgNO_3$	CH_3CN	80	60
4	**$K_2S_2O_8$**	**Ag_2CO_3**	**CH_3CN**	**80**	**86**
5	$Na_2S_2O_8$	Ag_2CO_3	CH_3CN	80	12
6	$(NH_4)_2S_2O_8$	Ag_2CO_3	CH_3CN	80	43
7	TBHP	Ag_2CO_3	CH_3CN	80	18
8	$K_2S_2O_8$	Ag_2CO_3	DMF	80	48
9	$K_2S_2O_8$	Ag_2CO_3	toluene	80	-
10	$K_2S_2O_8$	Ag_2CO_3	DMSO	80	42
11	$K_2S_2O_8$	Ag_2CO_3	1,4-dioxane	80	50
12	$K_2S_2O_8$	Ag_2CO_3	THF	60	30
13	$K_2S_2O_8$	Ag_2CO_3	CH_3CN	rt	-
14	$K_2S_2O_8$	-	CH_3CN	80	-
15	-	Ag_2CO_3	CH_3CN	80	-

Unless otherwise stated all the reactions were performed using **1a** (0.3 mmol) with **4a** (0.6 mmol), Ag_2CO_3 (20mol%) oxidant (1.2 mmol) in 3 mL of solvent, [b]Isolated yield

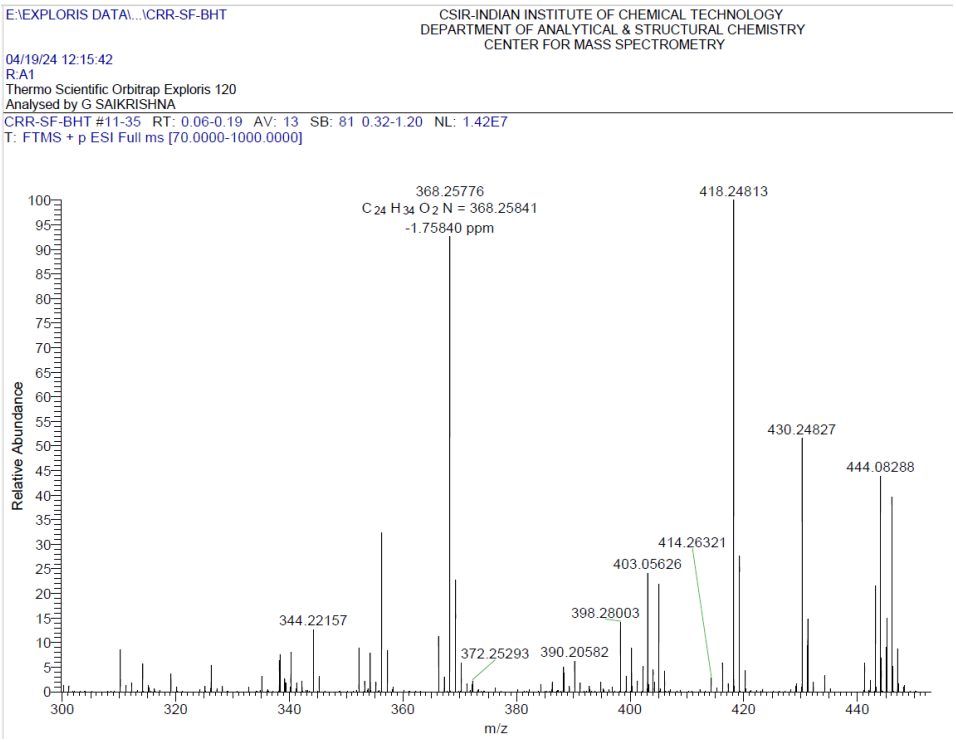
B. Radical trapping experiment:

Control experiment was conducted by adding methyl(p-tolyl) carbamic acid to biaryl enone in presence of 3.0 equiv of butylated hydroxytoluene (BHT; radical scavenger), and was found that the reaction was completely inhibited and no product (**5a**) formation, instead BHT-adduct **Y-4a** was isolated (confirmed by the reaction mass HRMS).



BHT-carbamoyl adduct
confirmed by HRMS found for
C24H34NO2: 368.2577; Calculated : 368.2511

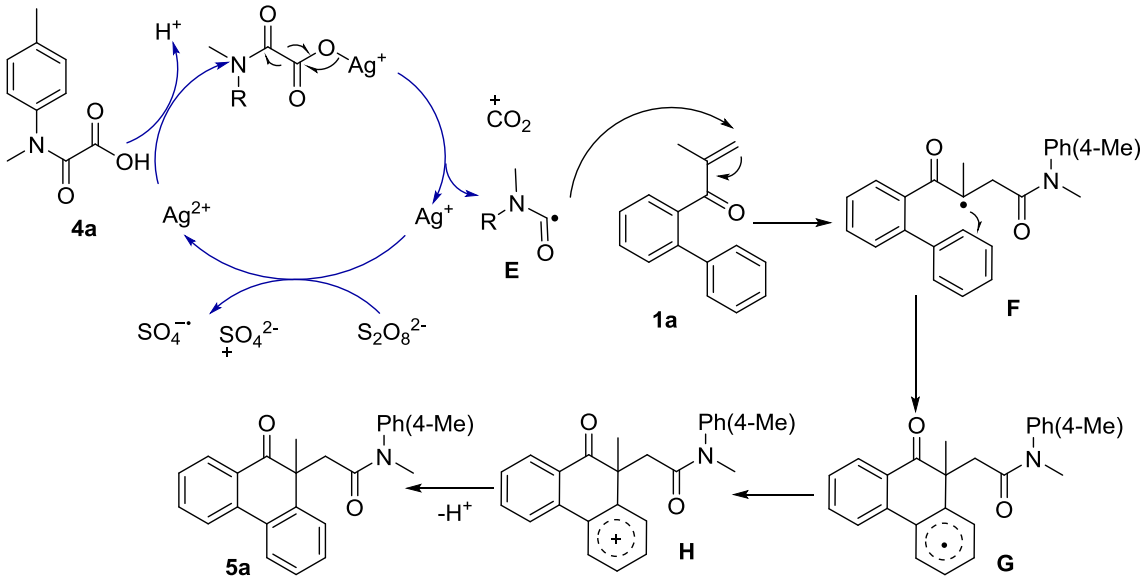
Scheme S1



HRMS for BHT-carbamoyl adduct Y-4a

Plausible mechanism:

A plausible mechanism is proposed based on the result of control experiment and literature survey (scheme 5). First, Ag(I) is oxidized to an Ag (II) species by $S2O8^{2-}$. Then, the Ag (II) species oxidizes oxamic acid to form carbamoyl radical **E** *via* decarboxylation. Regioselective addition of **E** on to olefin produces the tertiary radical **F**, which undergoes an intramolecular cyclization with the adjacent phenyl ring to give radical intermediate **G**. Then, a single electron transfer (SET) from **G** to oxidant, generates the cation **H**, which then rearomatizes through the loss of a proton producing the phenanthrenone **5a**.



Scheme S2

3. X-ray Crystallography:

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector.[4] The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques.[5] Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

A. Crystal structure determination of 3a:

Crystal Data for $C_{23}H_{18}O_2$ (*M* =326.37 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.843(8) Å, *b* = 13.341(7) Å, *c* = 16.884(7) Å, *β* = 116.018(17)°, *V* = 3409(3) Å^3, *Z* = 8, *T* = 294.15 K, μ(MoKα) = 0.080 mm^{-1}, *Dcalc* = 1.272 g/cm^3, 29333 reflections measured (2.69° ≤ 2Θ ≤ 50°), 5915 unique (R_{int} = 0.1299, R_{sigma} = 0.1005) which were used in all calculations. The final R_1 was 0.0599 (I > 2σ(I)) and wR_2 was 0.1517 (all data). **CCDC 2344358** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

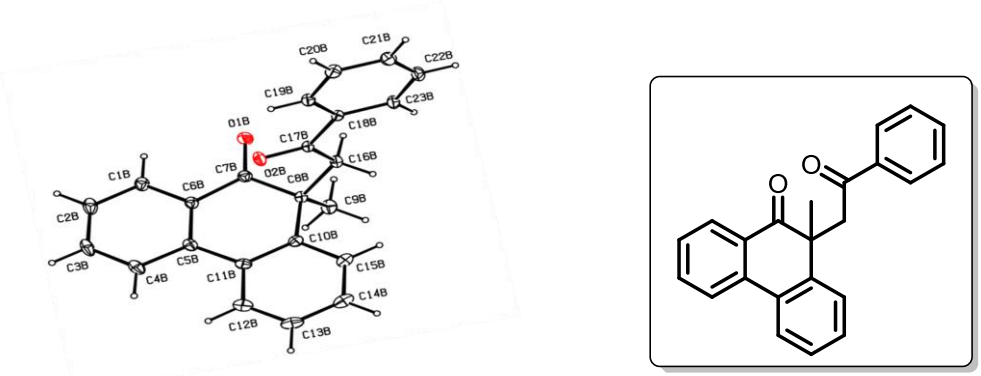


Figure S1: ORTEP diagram of **3a** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

B. Crystal structure determination of 7:

Crystal Data for $C_{17}H_{14}O_2$ (M =250.28 g/mol): orthorhombic, space group Pbca (no. 61), a = 18.905(6) Å, b = 7.073(2) Å, c = 18.994(7) Å, V = 2539.8(14) Å^3, Z = 8, T = 294.15 K, μ(MoKα) = 0.085 mm^{-1}, *Dcalc* = 1.309 g/cm^3, 14223 reflections measured (4.288° ≤ 2Θ ≤ 57.834°), 3225 unique (R_{int} = 0.0342, R_{sigma} = 0.0372) which were used in all calculations. The final R_1 was 0.0471 (I > 2σ(I)) and wR_2 was 0.1500 (all data). **CCDC 2344359** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

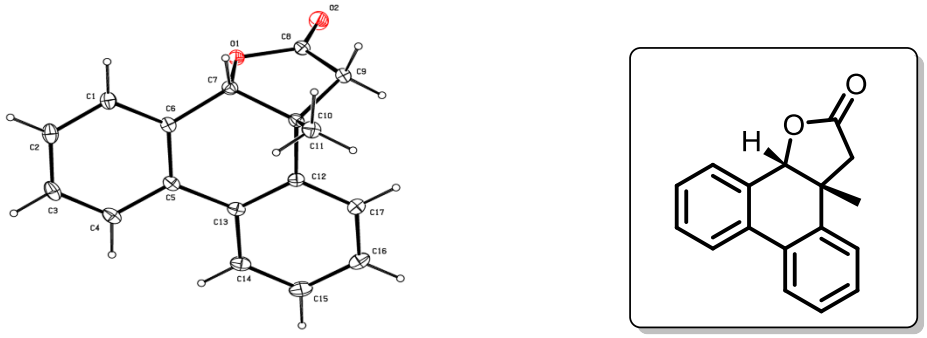
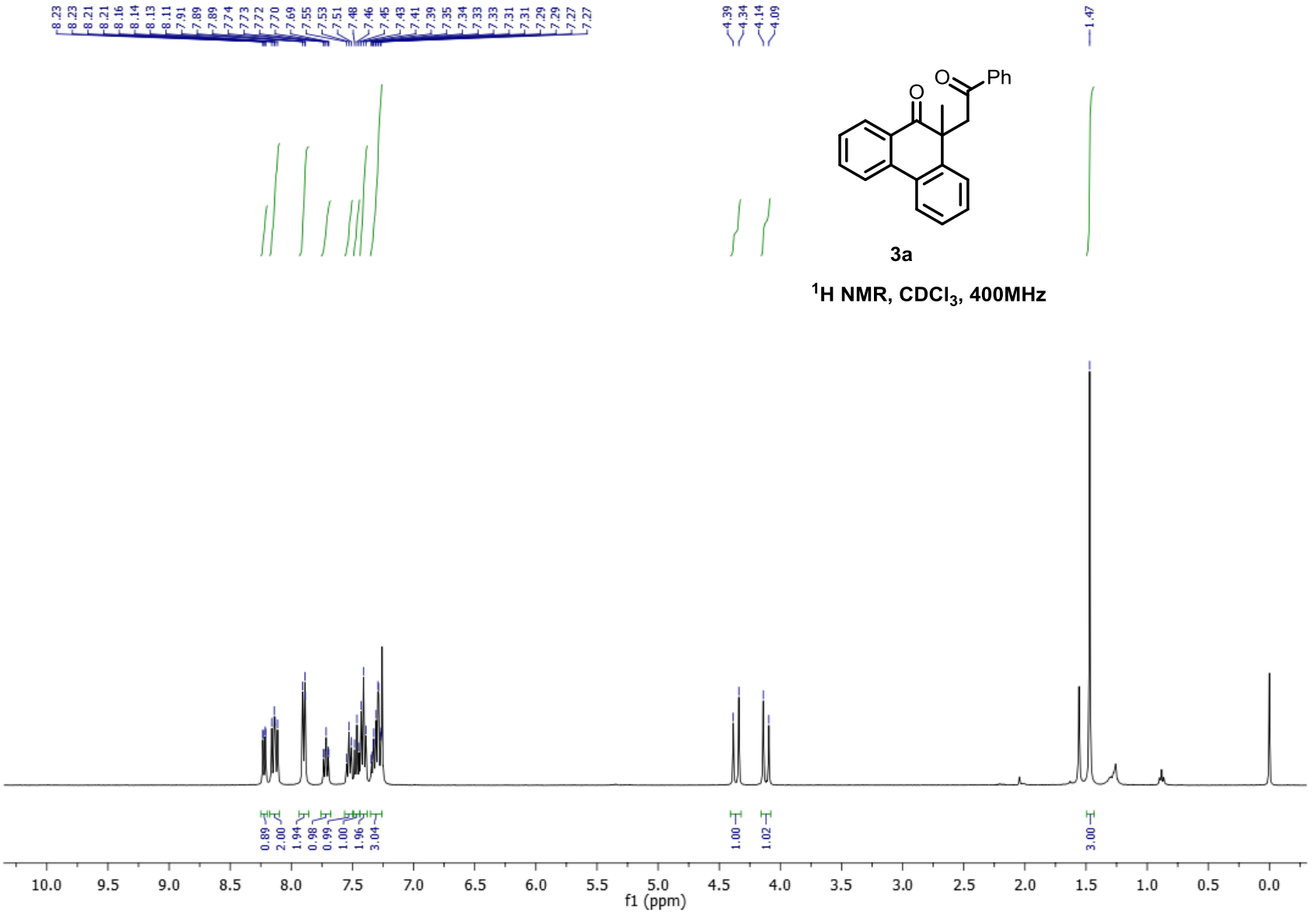


Figure S2: ORTEP diagram of **7** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

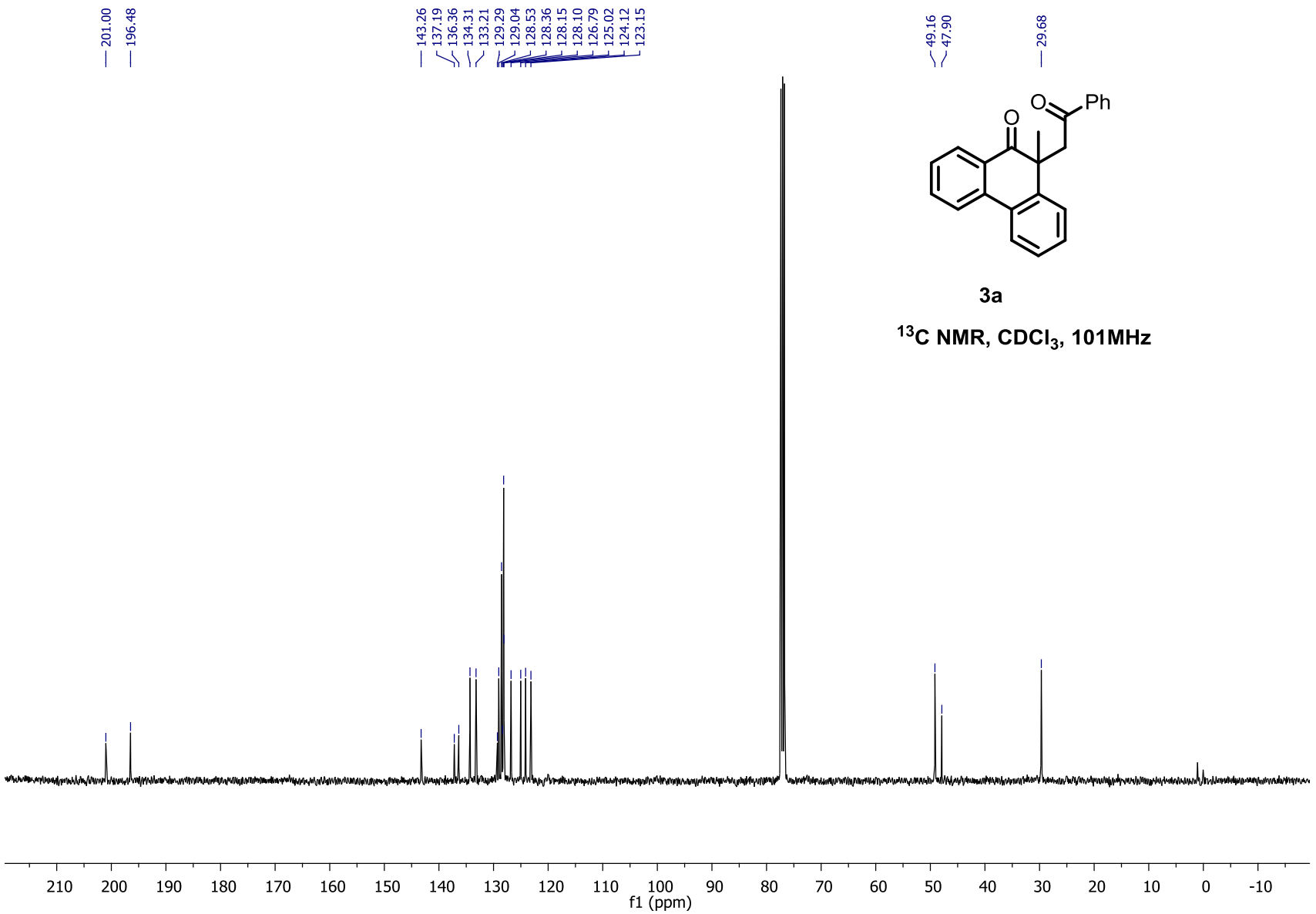
4. References:

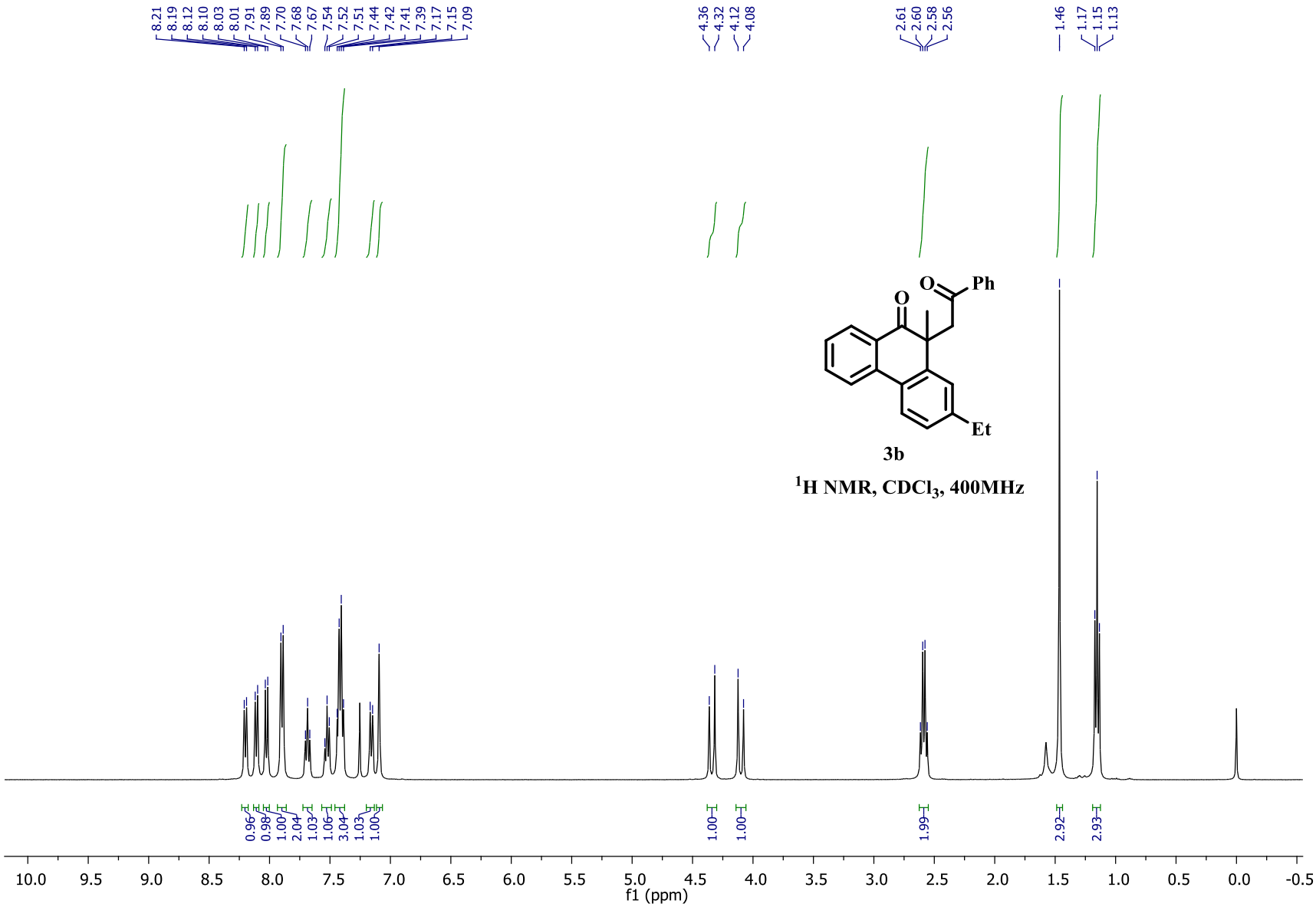
1. C. R. Reddy, S. Fatima, D. H. Kolgave and B. Sridhar, *Org. Biomol. Chem*., 2023, ***21***, 7327–7338.
2. X. Yang, J. Liu, Y. Gao, L. Wang, Y. Zhang, and P. Li, *Asian J. Org. Chem.*, 2022, **11**, e202200269.
3. X. Yang, G. Zhang, J. Zhou, C. Zhou, L. Wang and P. Li, *Org. Biomol. Chem.*, 2023, **21,** 4018-4021.
4. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
5. Sheldrick G. M. (2015). ActaCrystallogr C71: 3-8.



3a

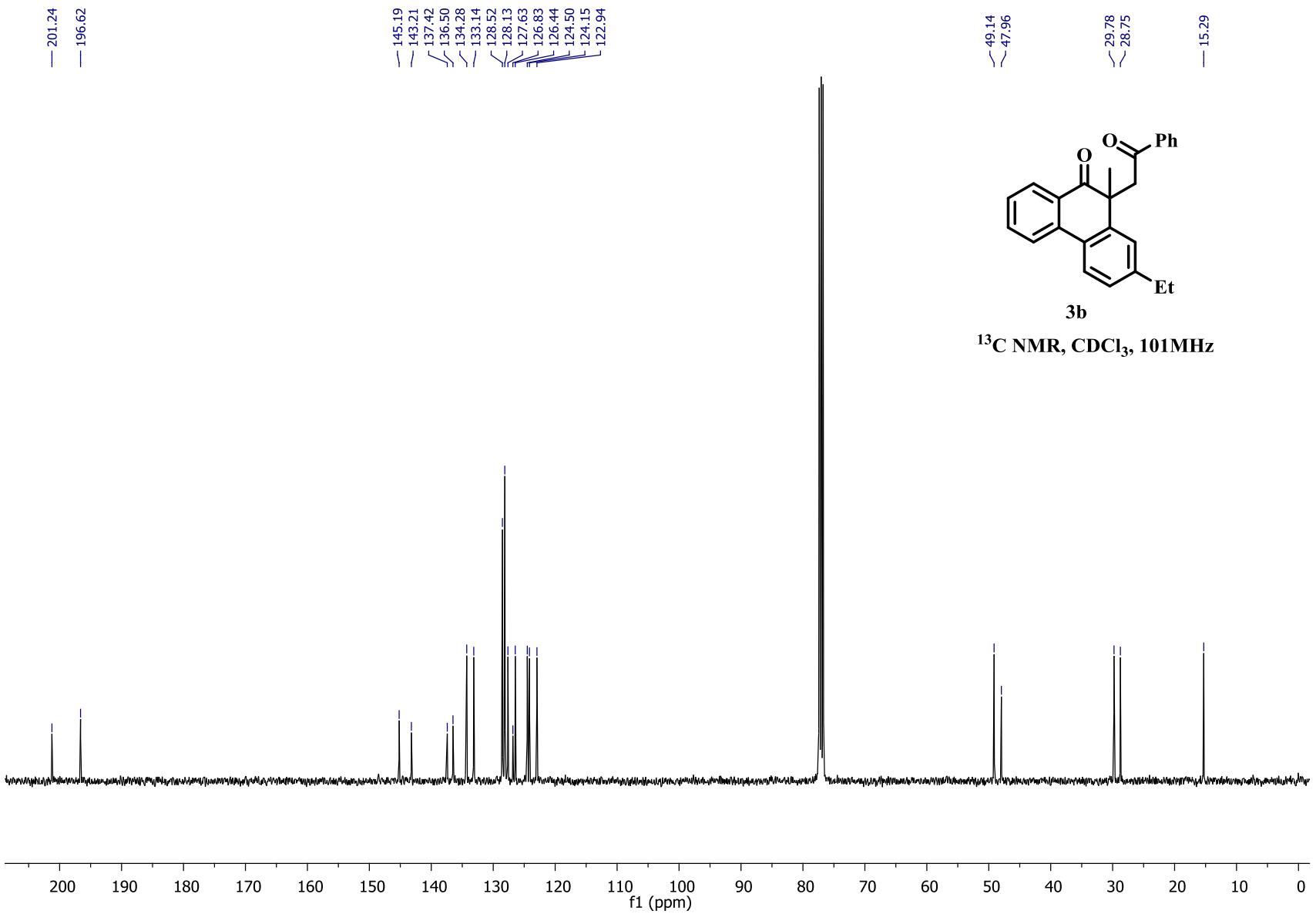
^{1}H NMR, $CDCl_3$, 400MHz

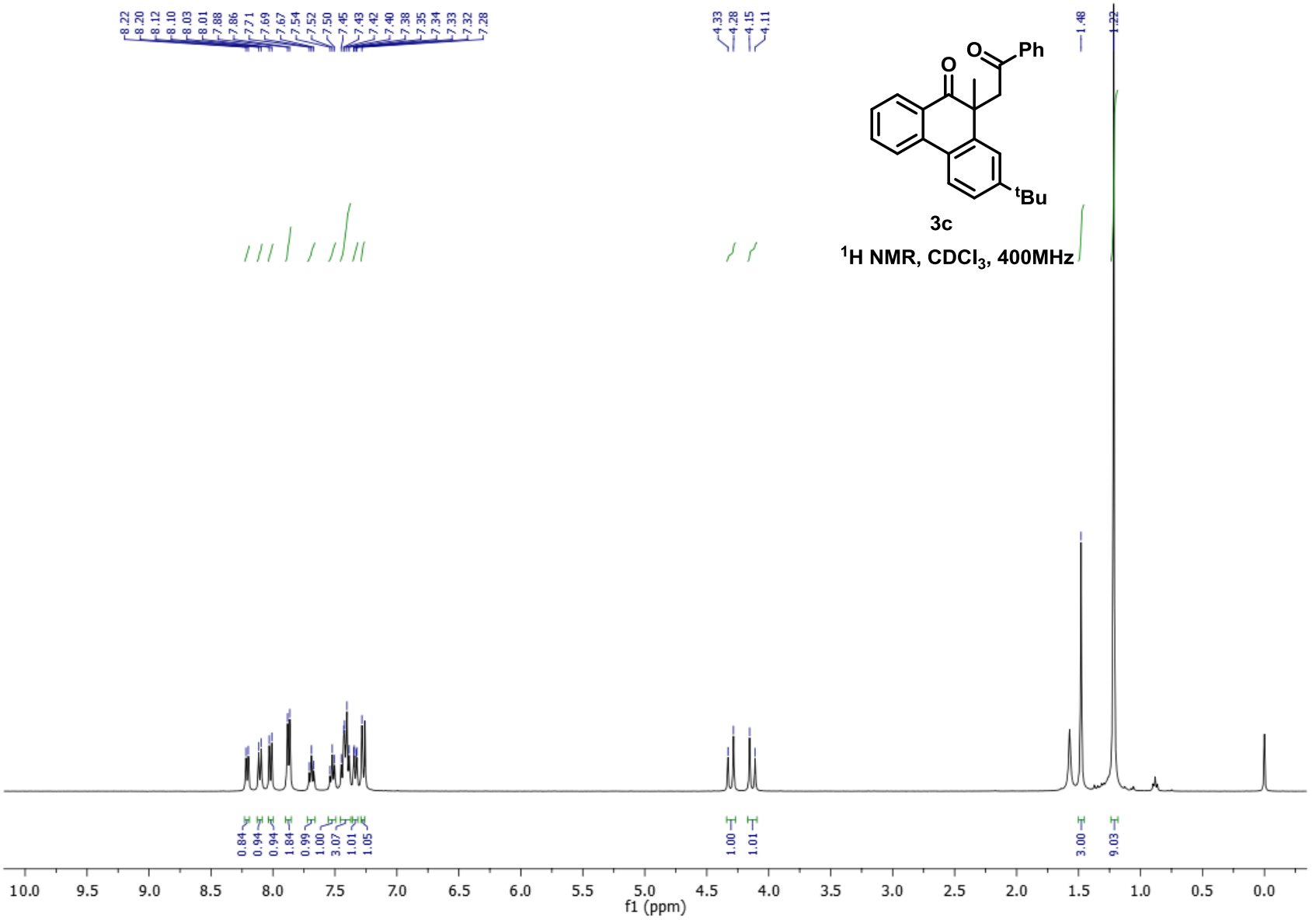

201.00
196.48
143.26
137.19
136.36
134.31
133.21
129.29
129.04
128.53
128.36
128.15
128.10
126.79
125.02
124.12
123.15
49.16
47.90
29.68
O
O
Ph
3a
13C NMR, CDCl3, 101MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

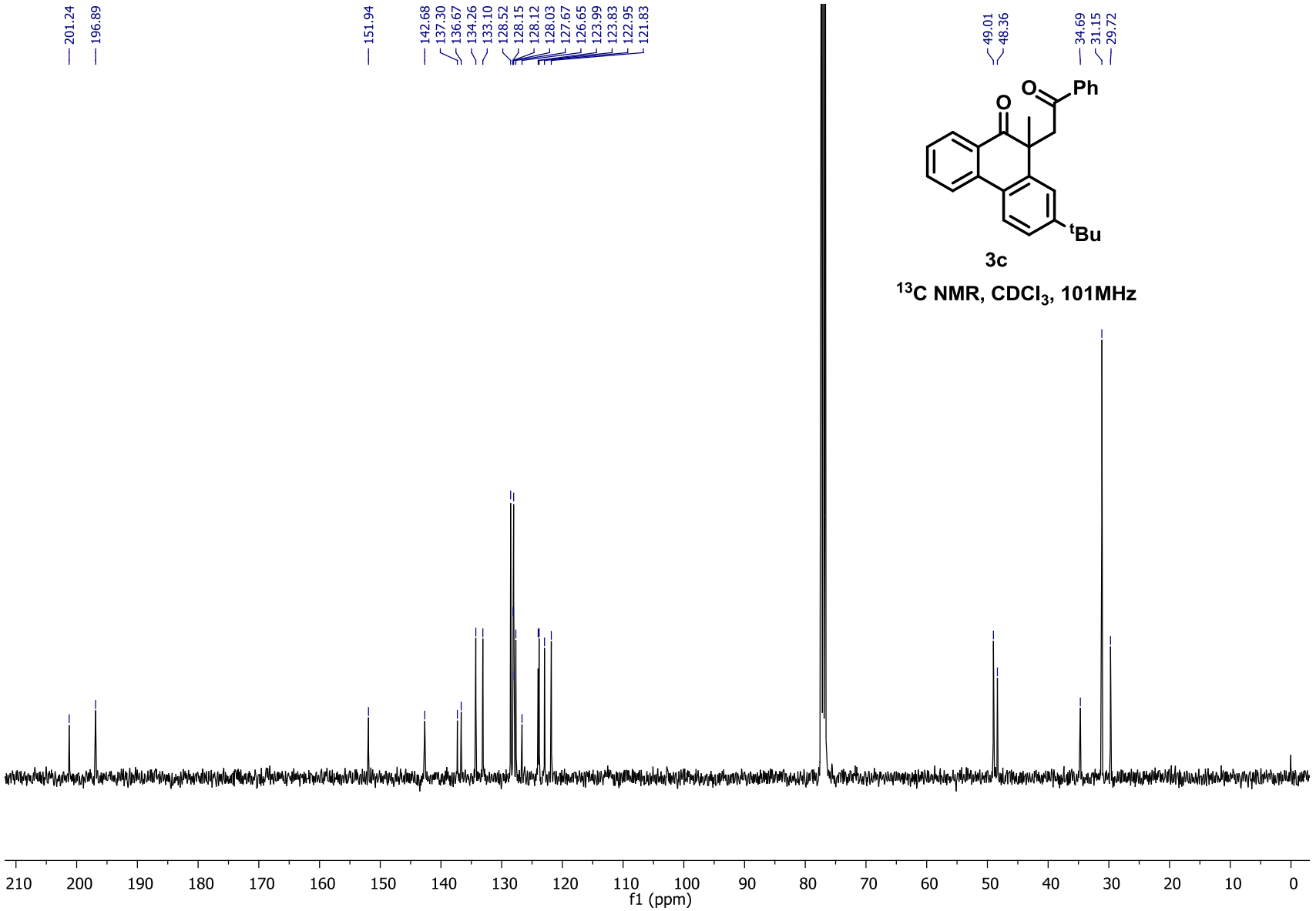


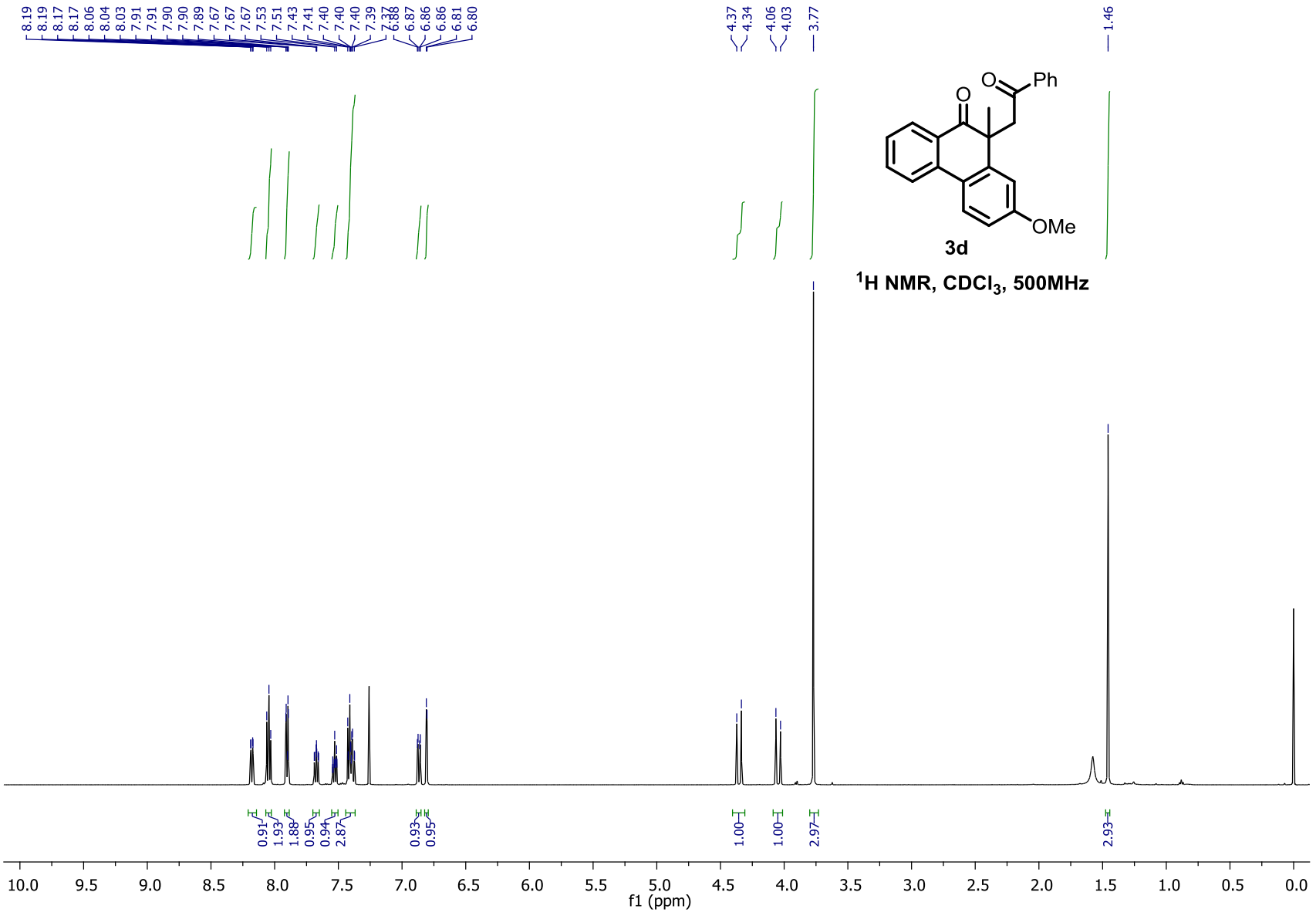
3b

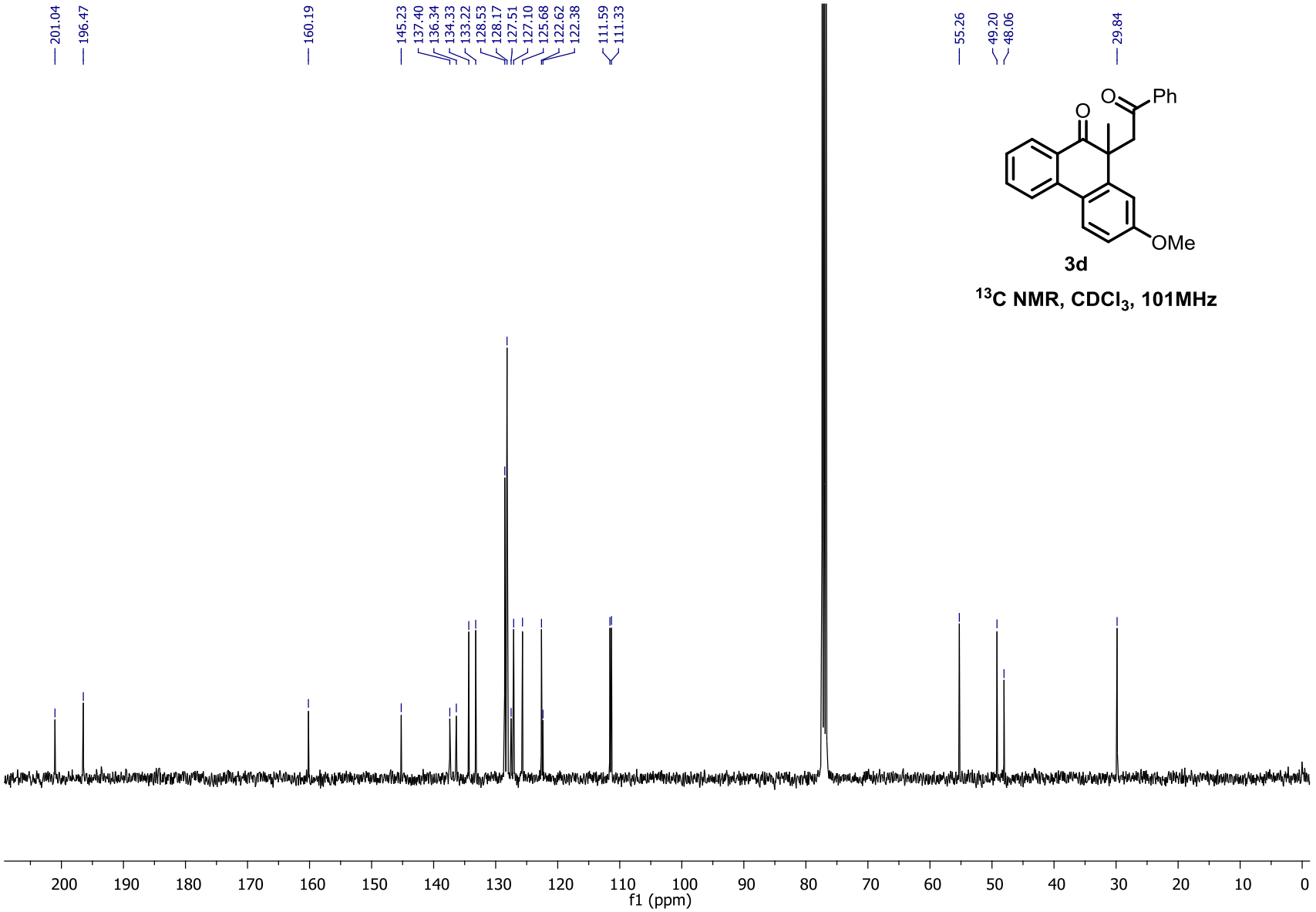
^{1}H NMR, $CDCl_3$, 400MHz

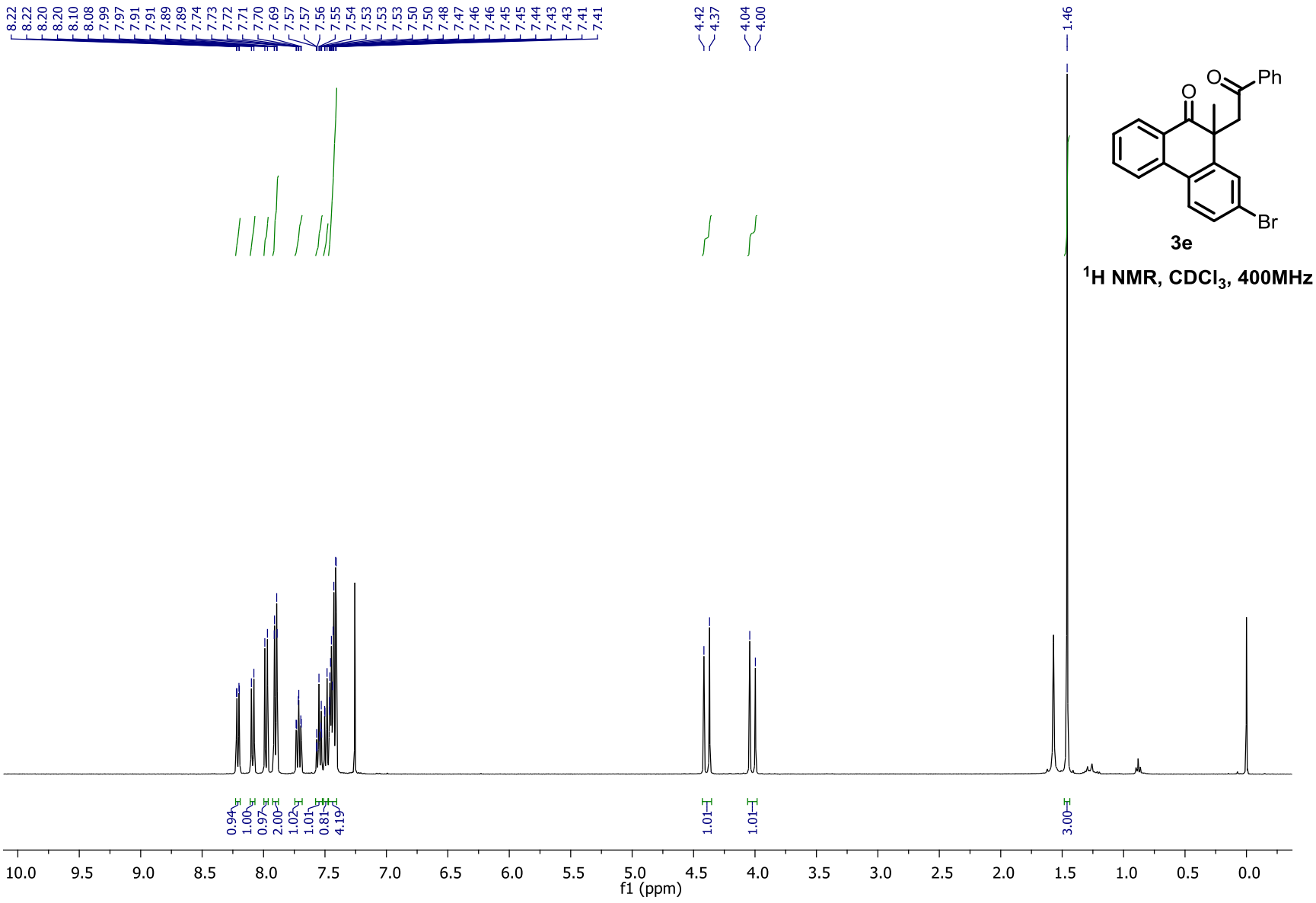

201.24
196.62
145.19
143.21
137.42
136.50
134.28
133.14
128.52
128.13
127.63
126.83
126.44
124.50
124.15
122.94
49.14
47.96
29.78
28.75
15.29
O
O
Ph
Et
3b
^{13}C NMR, CDCl$_3$, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

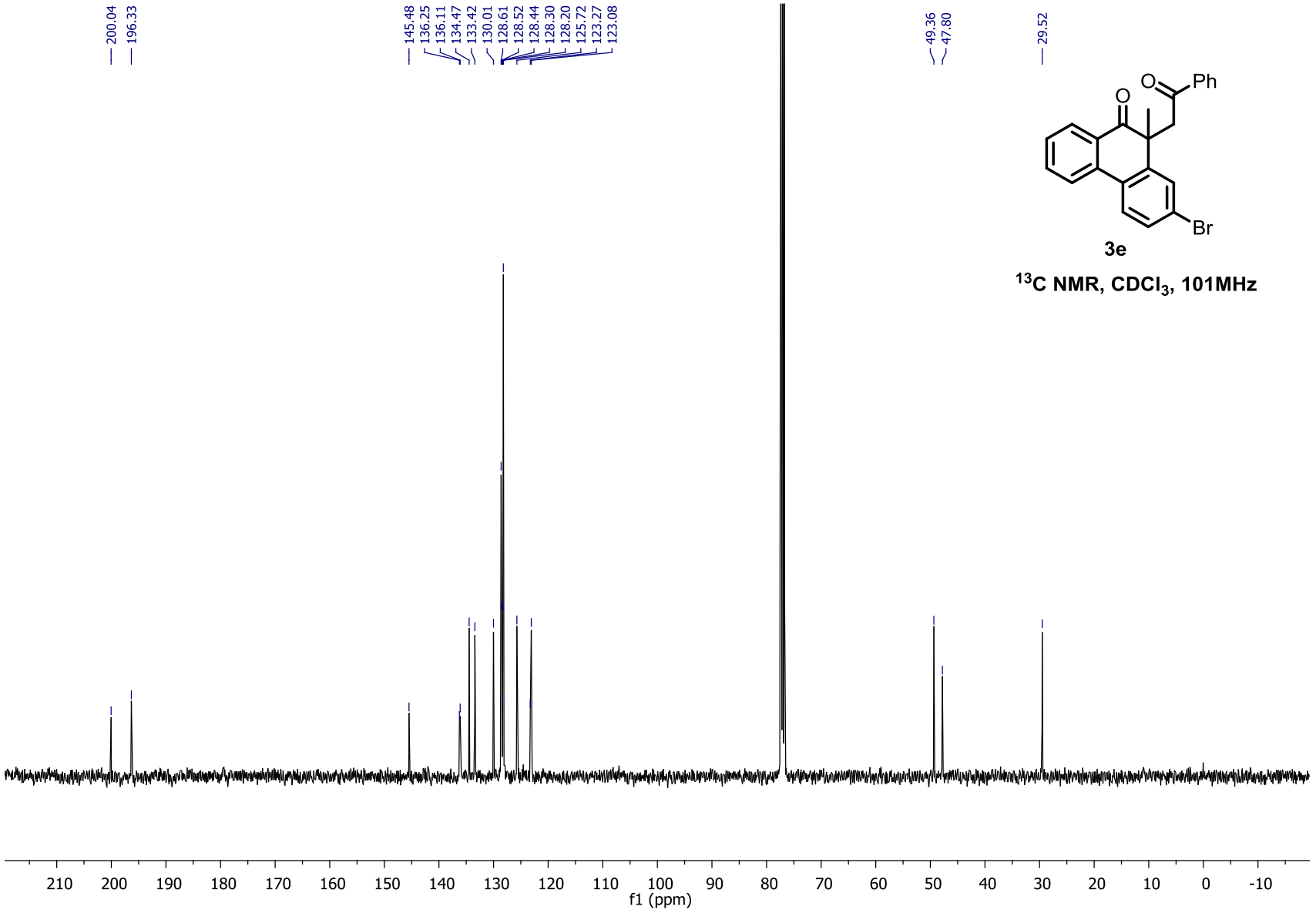

8.22
8.20
8.12
8.10
8.03
8.01
7.88
7.86
7.71
7.69
7.67
7.54
7.52
7.50
7.45
7.43
7.42
7.40
7.38
7.35
7.34
7.33
7.32
7.28
4.33
4.28
4.15
4.11
1.48
1.22
O
O
Ph
tBu
3c
1H NMR, CDCl3, 400MHz
0.84
0.94
0.94
1.84
0.99
1.00
3.07
1.01
1.05
1.00
1.01
3.00
9.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

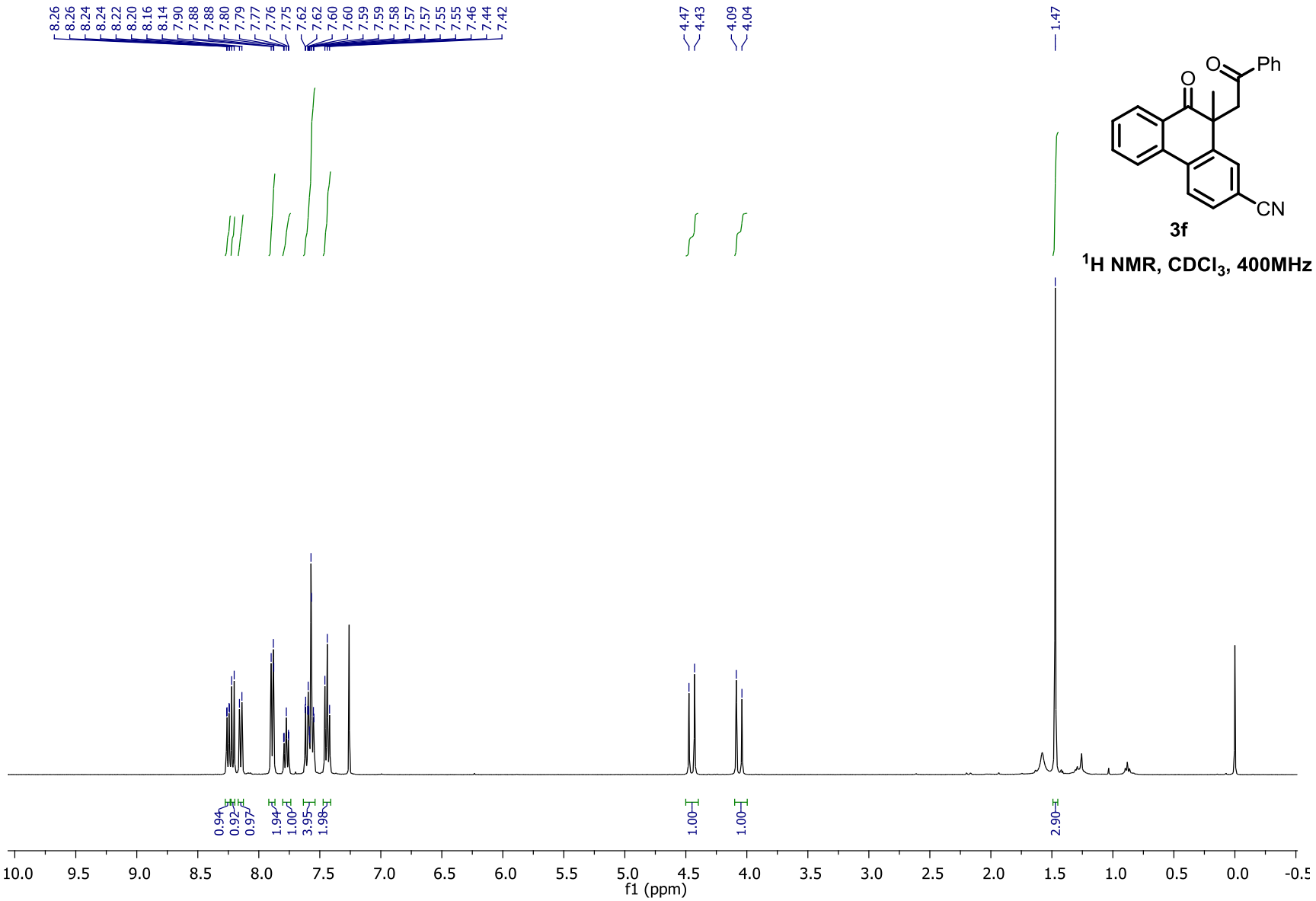

201.24
196.89
151.94
142.68
137.30
136.67
134.26
133.10
128.52
128.15
128.12
128.03
127.67
126.65
123.99
123.83
122.95
121.83
49.01
48.36
34.69
31.15
29.72
O
O
Ph
tBu
3c
13C NMR, CDCl3, 101MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

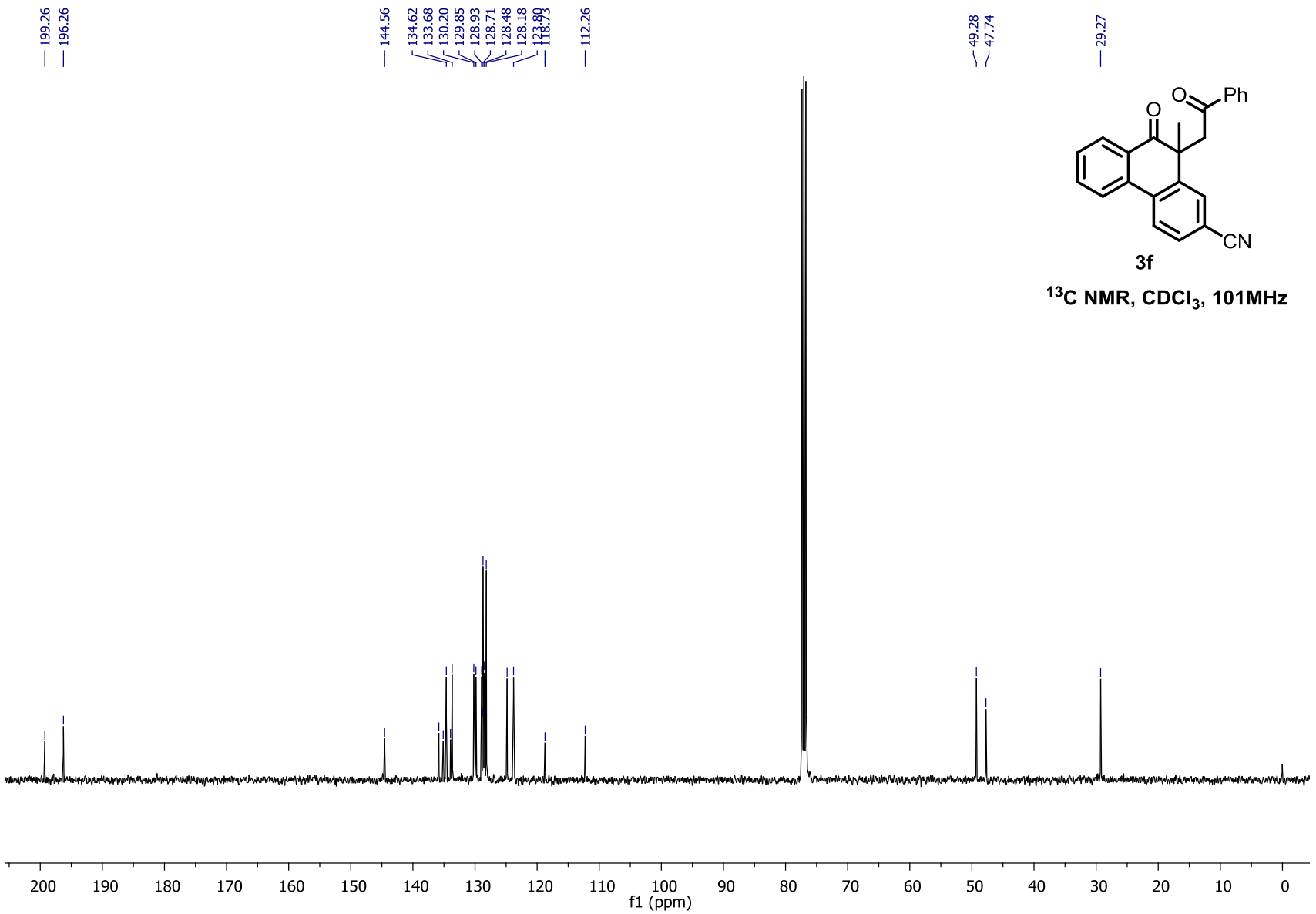

8.19
8.19
8.17
8.17
8.06
8.04
8.03
7.91
7.91
7.90
7.90
7.89
7.67
7.67
7.67
7.53
7.51
7.43
7.41
7.40
7.40
7.40
7.39
6.88
6.87
6.86
6.86
6.81
6.80
4.37
4.34
4.06
4.03
3.77
1.46
O
O
Ph
OMe
3d
^{1}H NMR, CDCl$_3$, 500MHz
0.91
1.93
1.88
0.95
0.94
2.87
0.93
0.95
1.00
1.00
2.97
2.93
10.0
9.5
9.0
8.5
8.0
7.5
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)

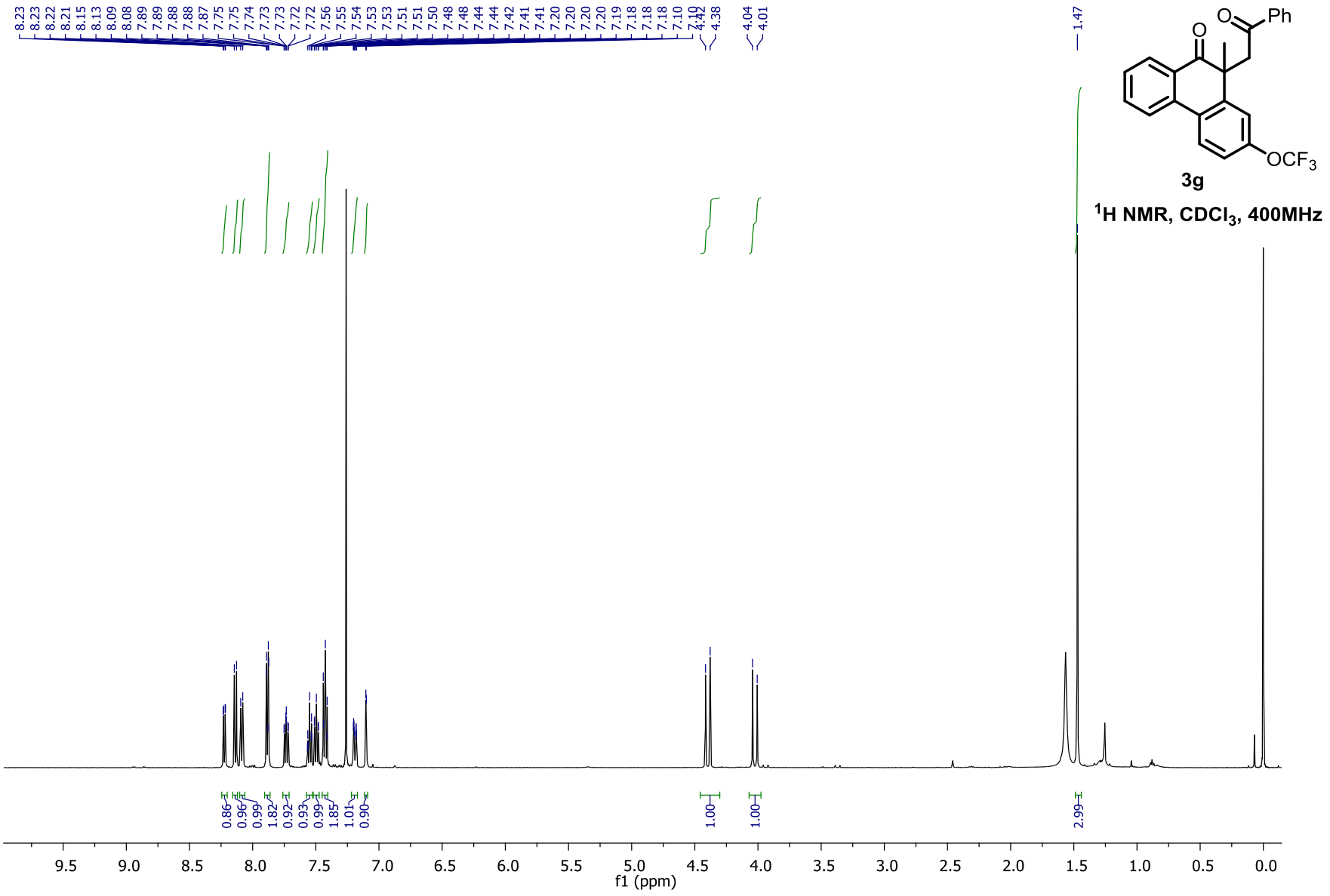

201.04
196.47
160.19
145.23
137.40
136.34
134.33
133.22
128.53
128.17
127.51
127.10
125.68
122.62
122.38
111.59
111.33
55.26
49.20
48.06
29.84
O
O
Ph
OMe
3d
13C NMR, CDCl3, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

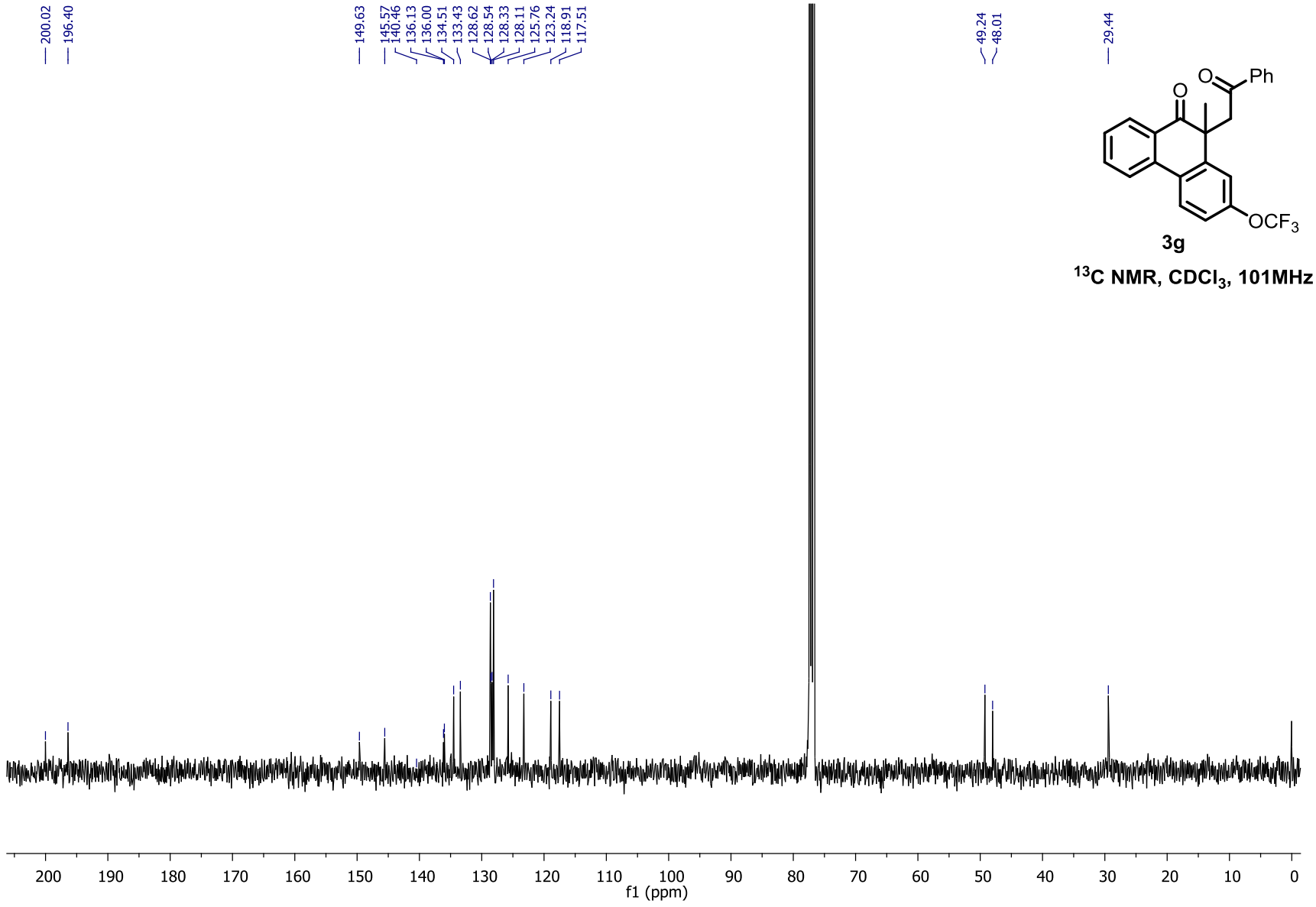

8.22
8.22
8.20
8.20
8.10
8.08
7.99
7.97
7.91
7.91
7.89
7.89
7.74
7.73
7.72
7.71
7.70
7.69
7.57
7.57
7.56
7.55
7.54
7.53
7.53
7.53
7.50
7.50
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.41
7.41
4.42
4.37
4.04
4.00
1.46
O
O
Ph
Br
3e
^{1}H NMR, CDCl$_3$, 400MHz
0.94
1.00
0.97
2.00
1.02
1.01
0.81
4.19
1.01
1.01
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)


200.04
196.33
145.48
136.25
136.11
134.47
133.42
130.01
128.61
128.52
128.44
128.30
128.20
125.72
123.27
123.08
49.36
47.80
29.52
O
O
Ph
Br
3e
^{13}C NMR, CDCl$_3$, 101MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.26
8.26
8.24
8.24
8.22
8.20
8.16
8.14
7.90
7.88
7.88
7.80
7.79
7.77
7.76
7.75
7.62
7.62
7.60
7.60
7.59
7.59
7.58
7.57
7.57
7.55
7.55
7.46
7.44
7.42
4.47
4.43
4.09
4.04
1.47
O
O
Ph
CN
3f
^{1}H NMR, CDCl$_3$, 400MHz
0.94
0.92
0.97
1.94
1.00
3.95
1.98
1.00
1.00
2.90
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)

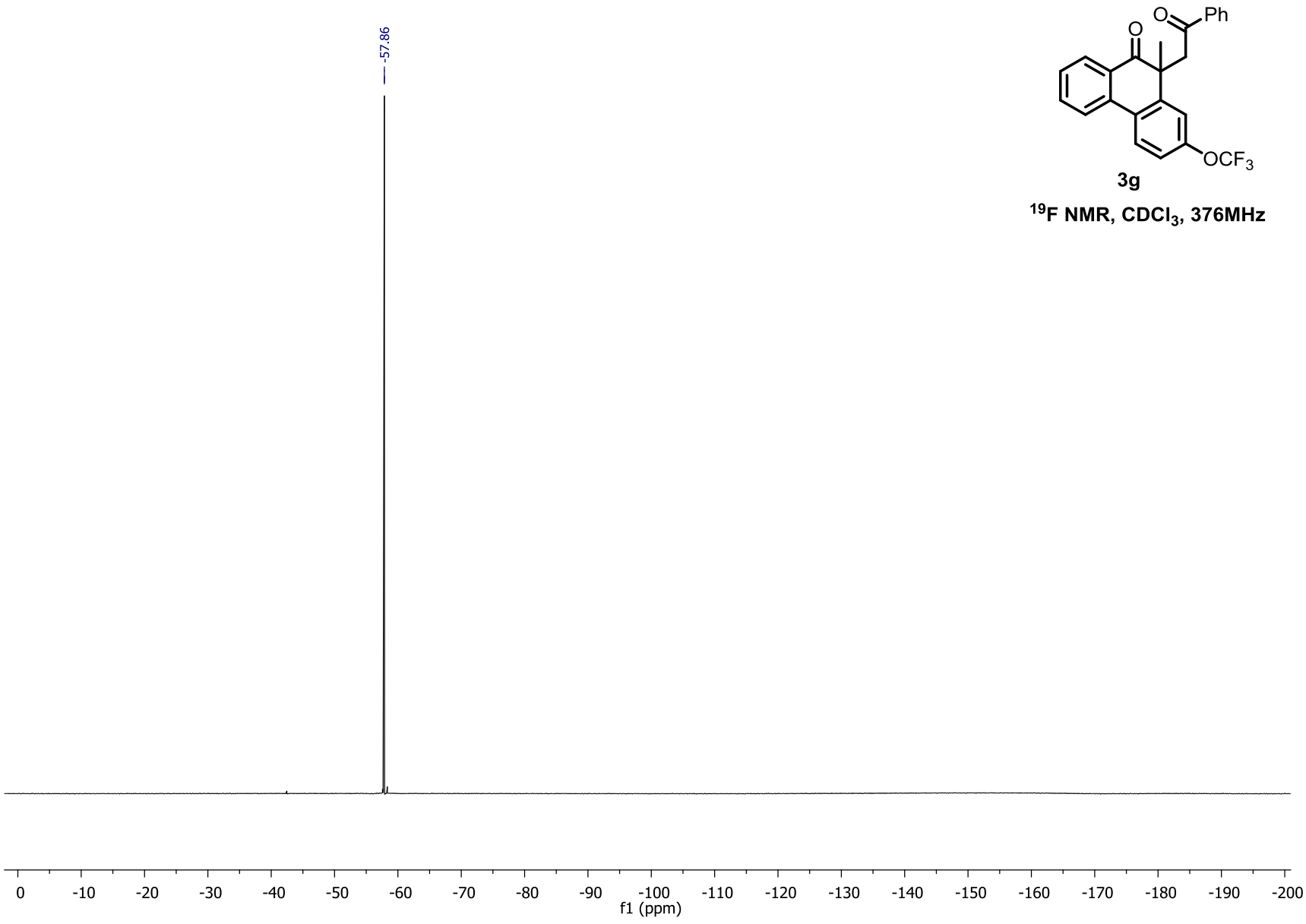

199.26
196.26
144.56
134.62
133.68
130.20
129.85
128.93
128.71
128.48
128.18
123.80
118.73
112.26
49.28
47.74
29.27
O
O
Ph
CN
3f
^{13}C NMR, CDCl$_3$, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.23 8.23 8.22 8.21 8.15 8.13 8.09 8.08 7.89 7.89 7.88 7.88 7.87 7.75 7.75 7.74 7.73 7.73 7.72 7.72 7.56 7.55 7.54 7.53 7.53 7.51 7.51 7.50 7.48 7.48 7.44 7.44 7.42 7.41 7.41 7.20 7.20 7.20 7.19 7.18 7.18 7.18 7.10 7.10 4.42 4.38 4.04 4.01 1.47
O
O
Ph
OCF3
3g
1H NMR, CDCl3, 400MHz
0.86 0.96 0.99 1.82 0.92 0.93 0.99 1.85 1.01 0.90 1.00 1.00 2.99
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)



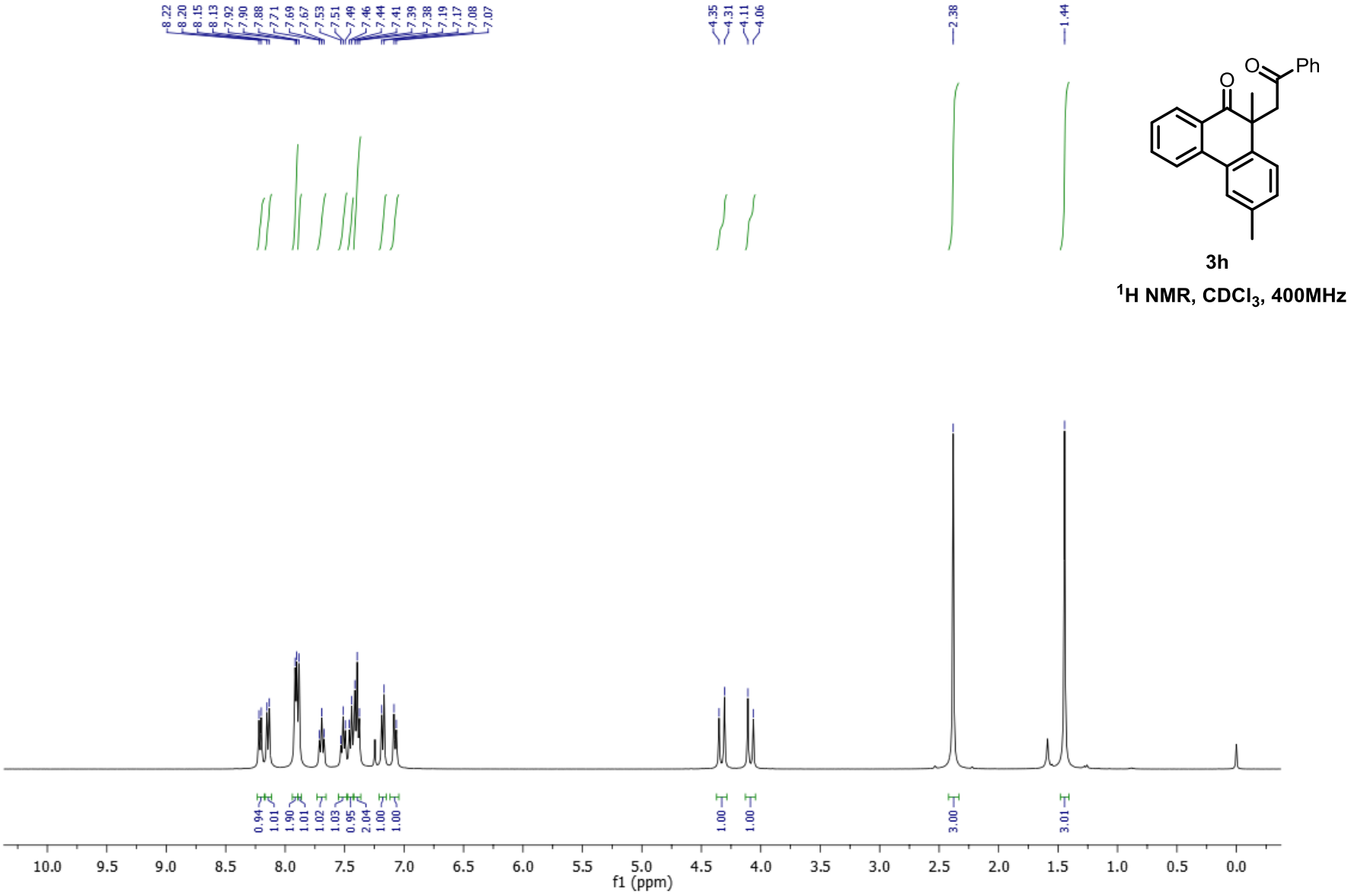
3g

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



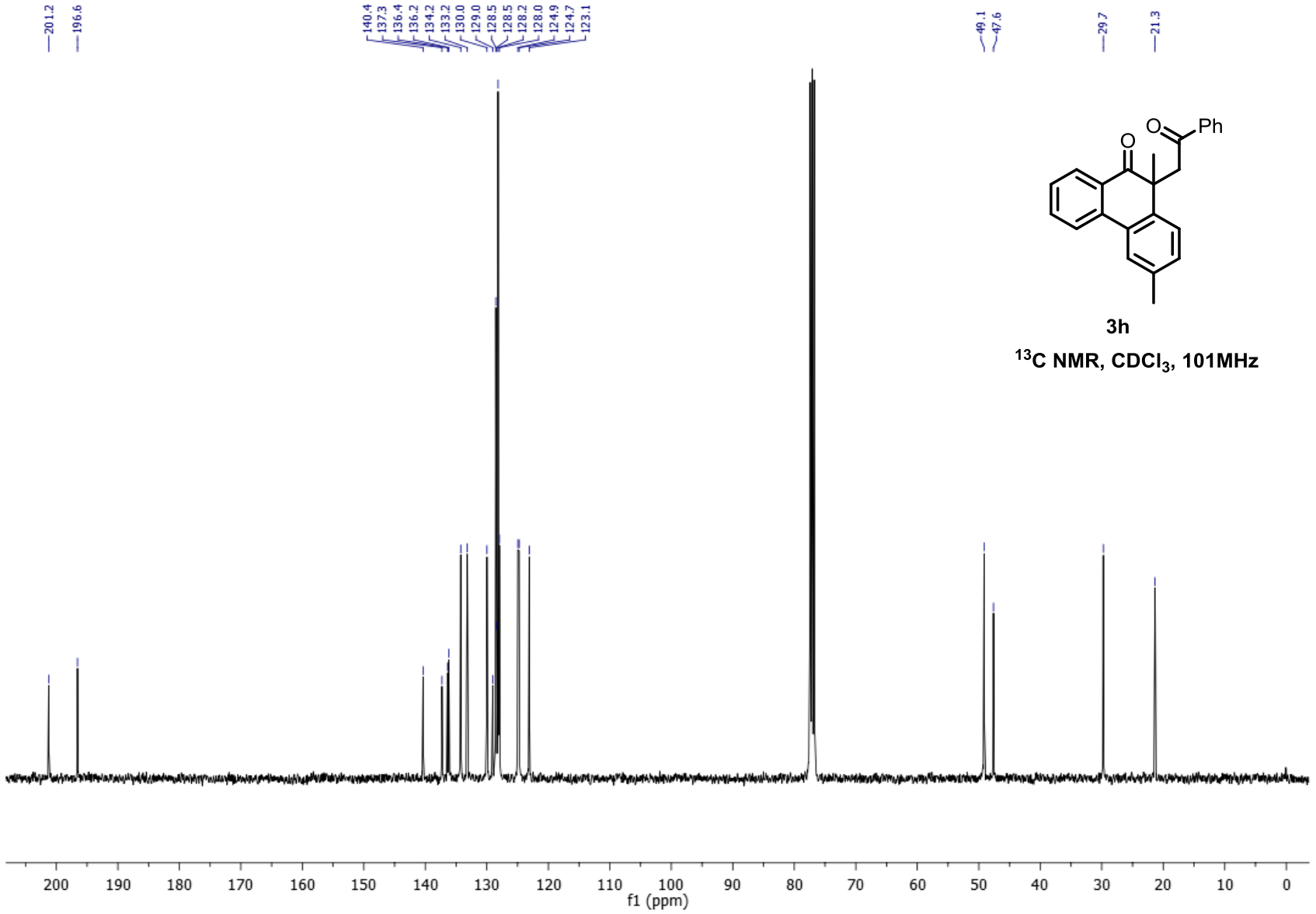
3g

^{19}F NMR, $CDCl_3$, 376MHz



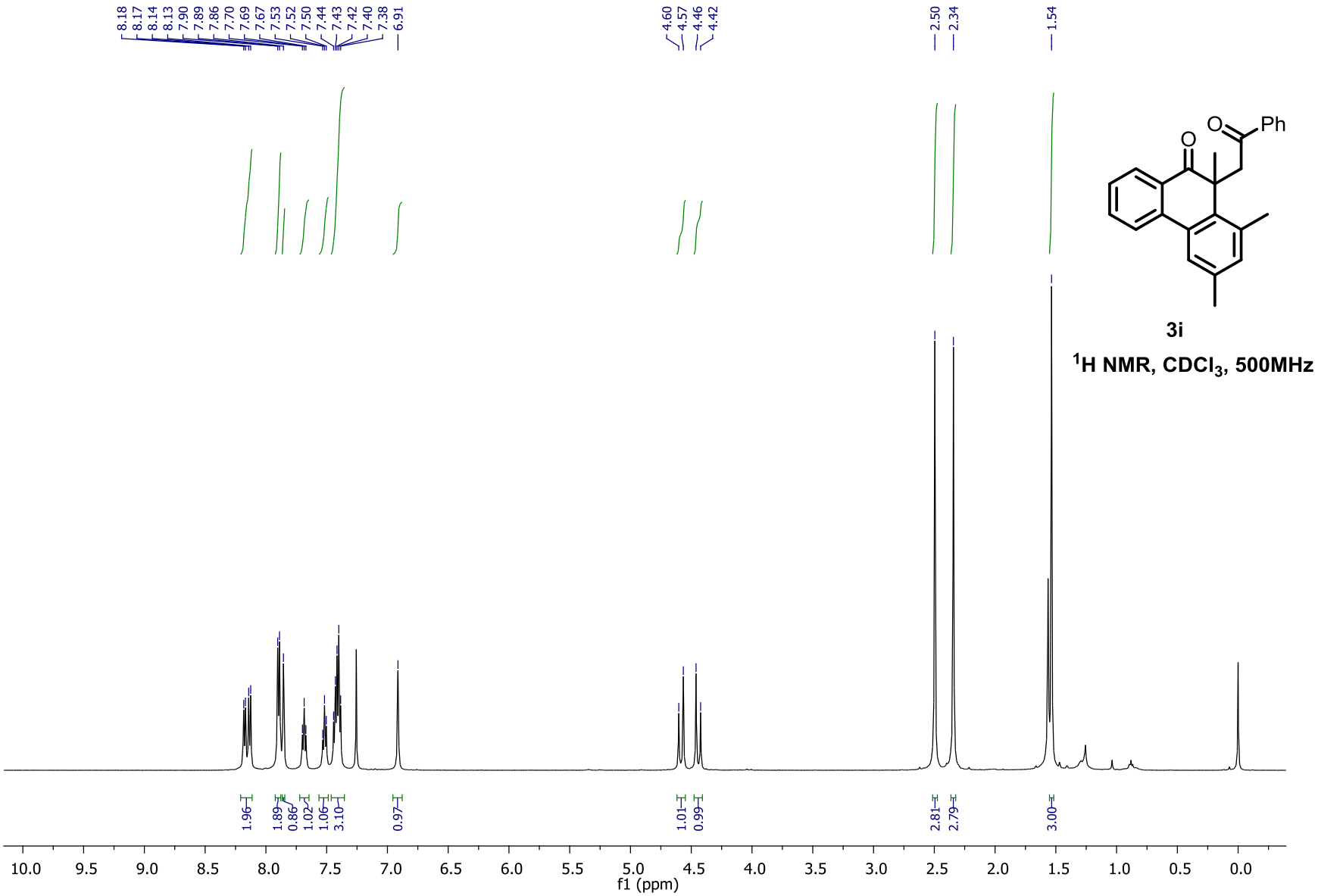
3h

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



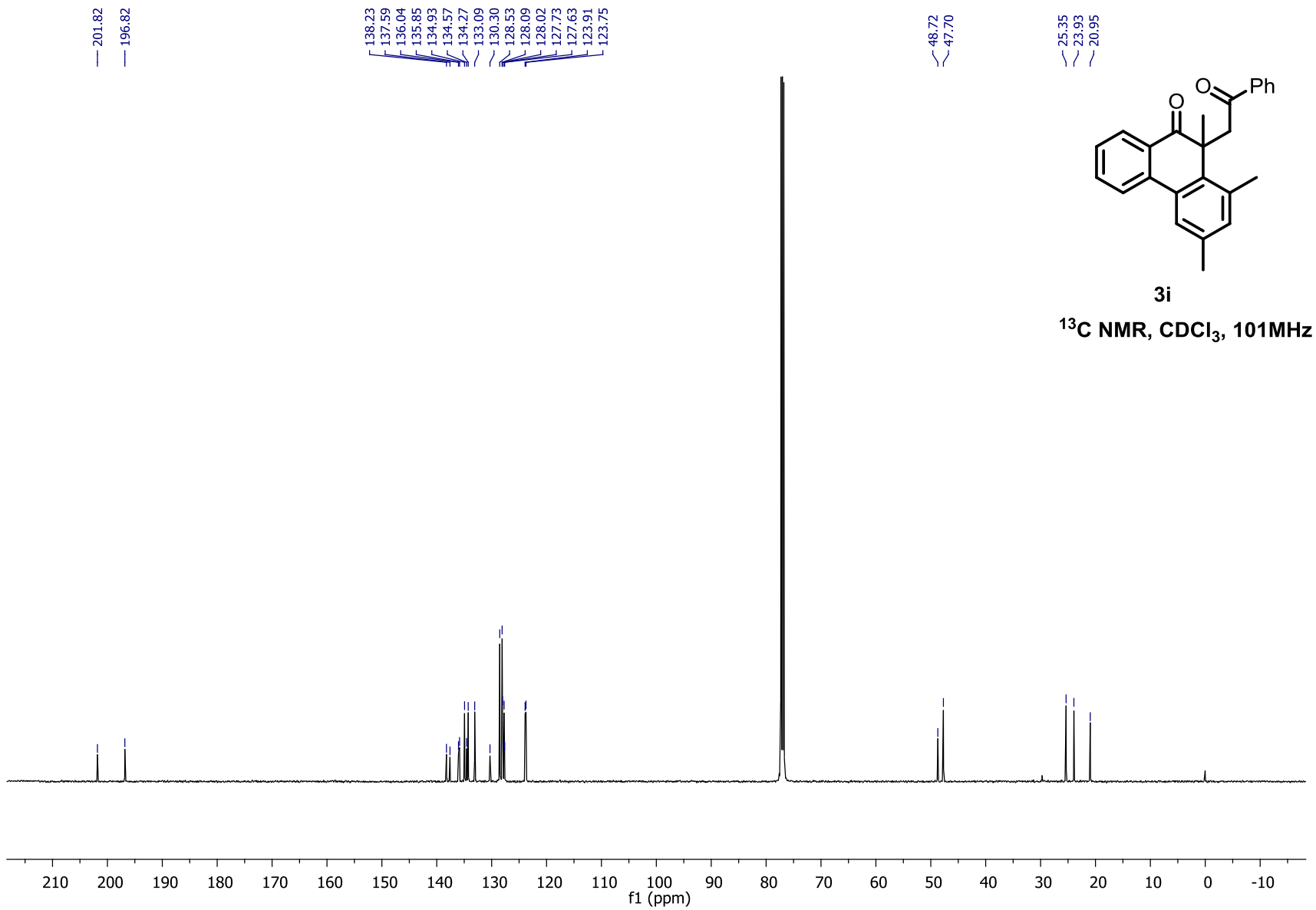
3h

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



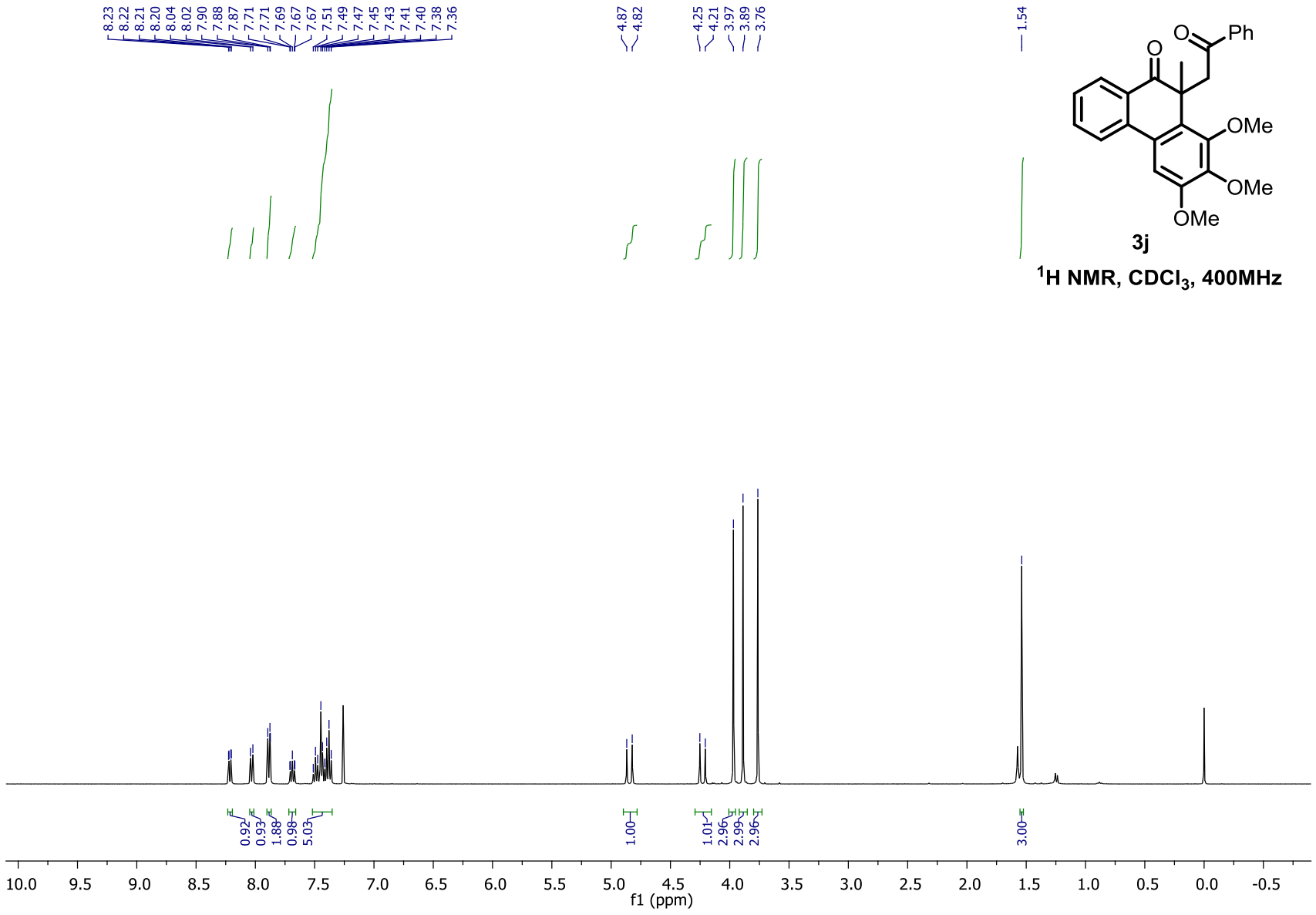
3i

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



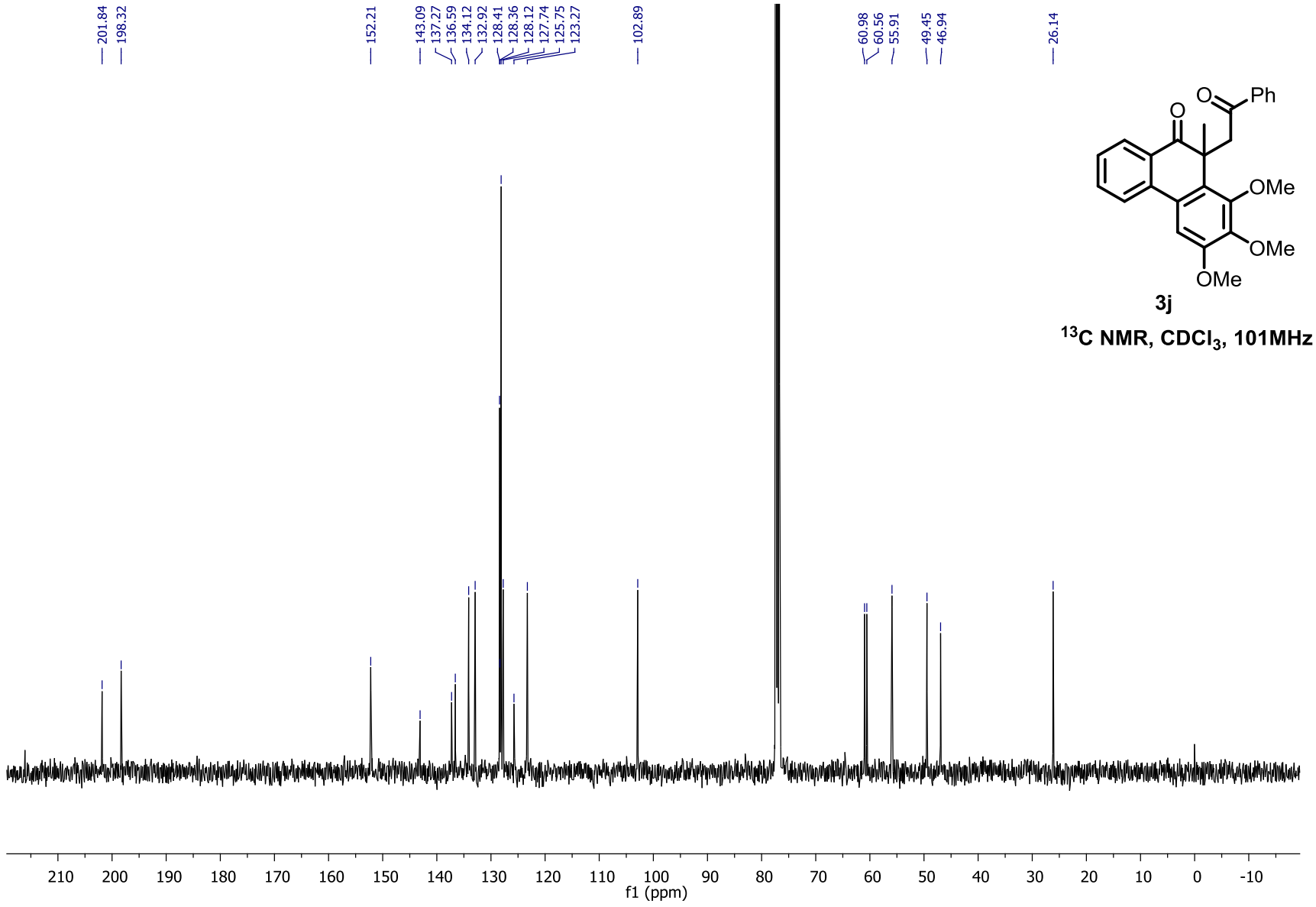
3i

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



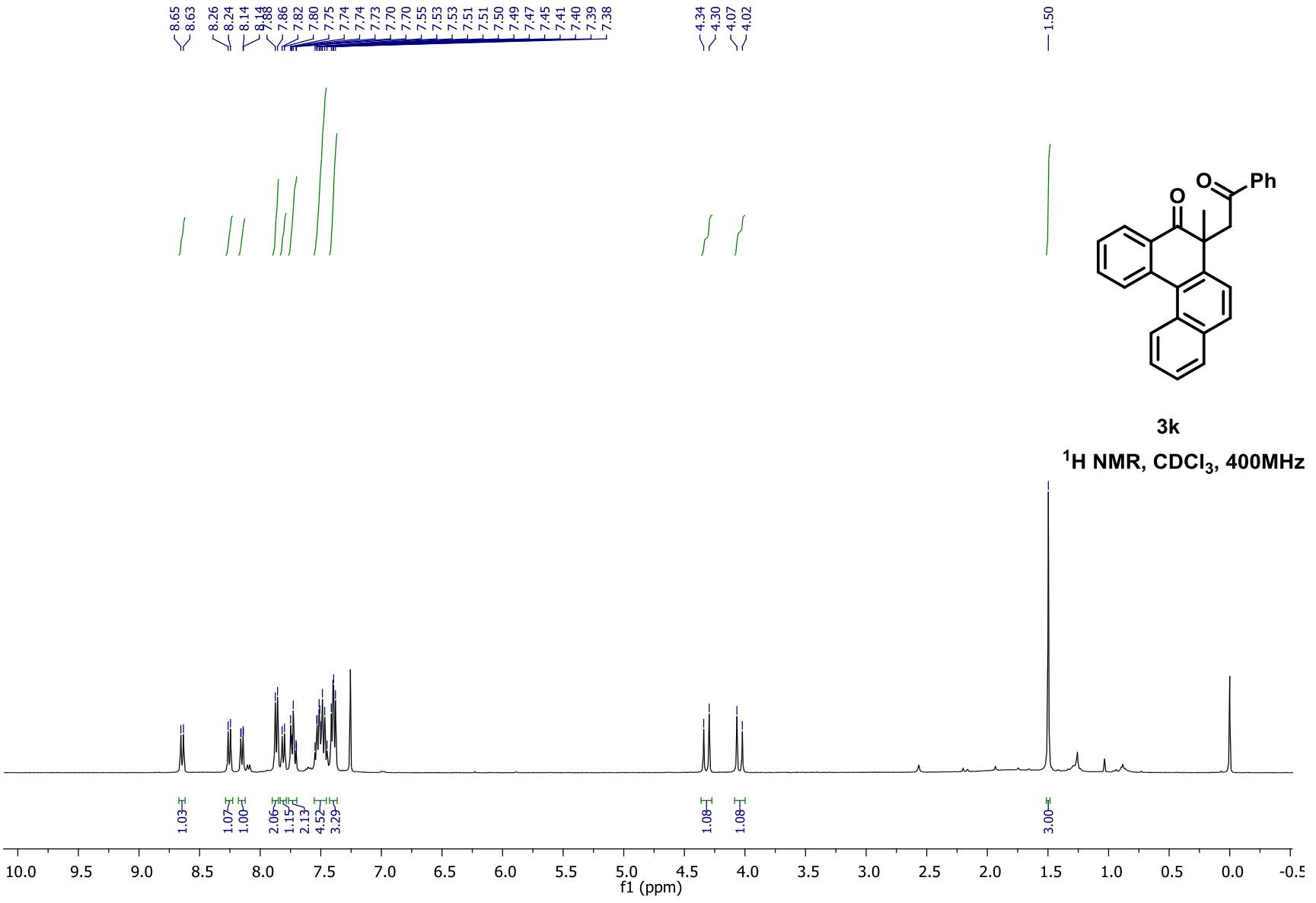
3j

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



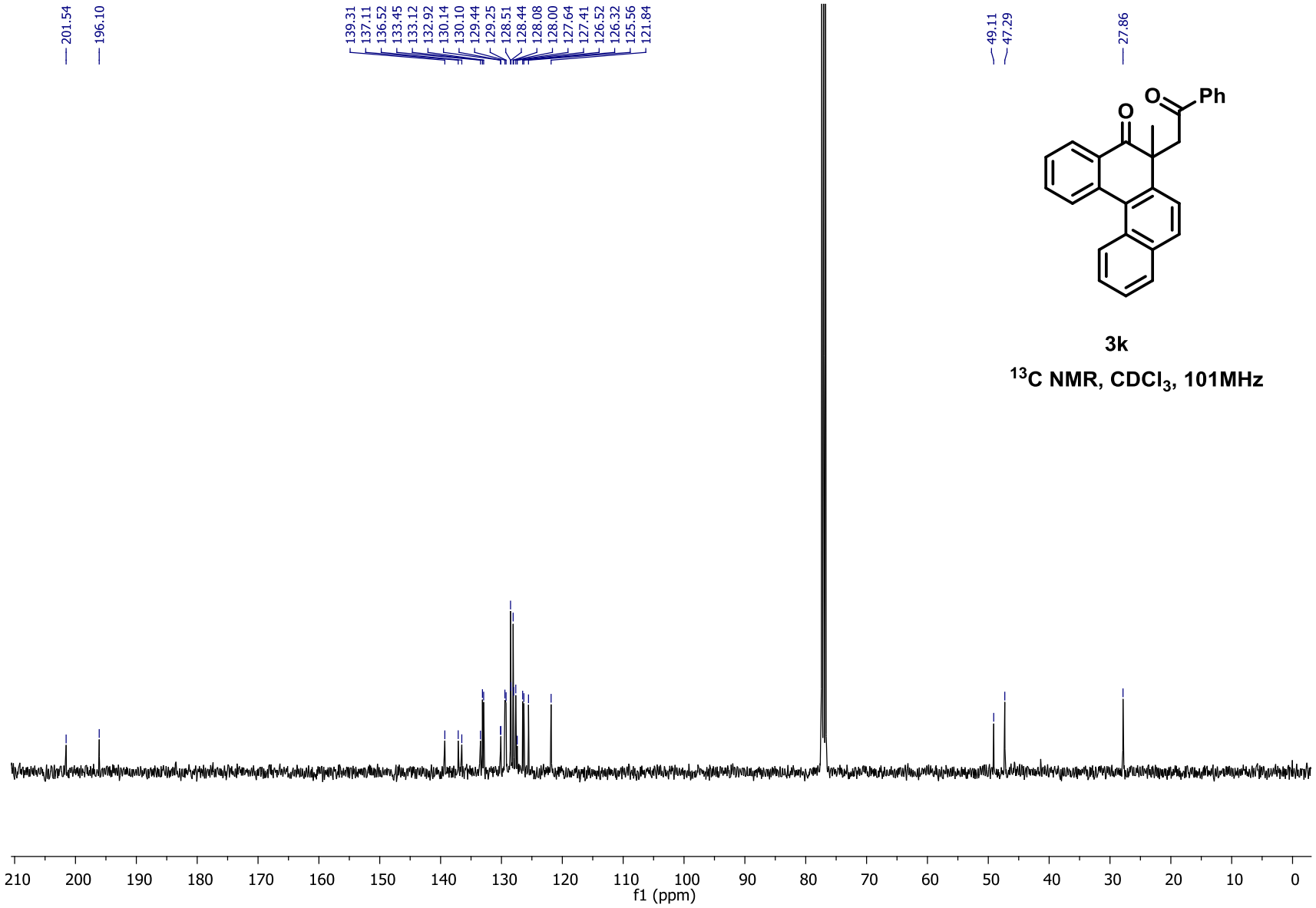
3j

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



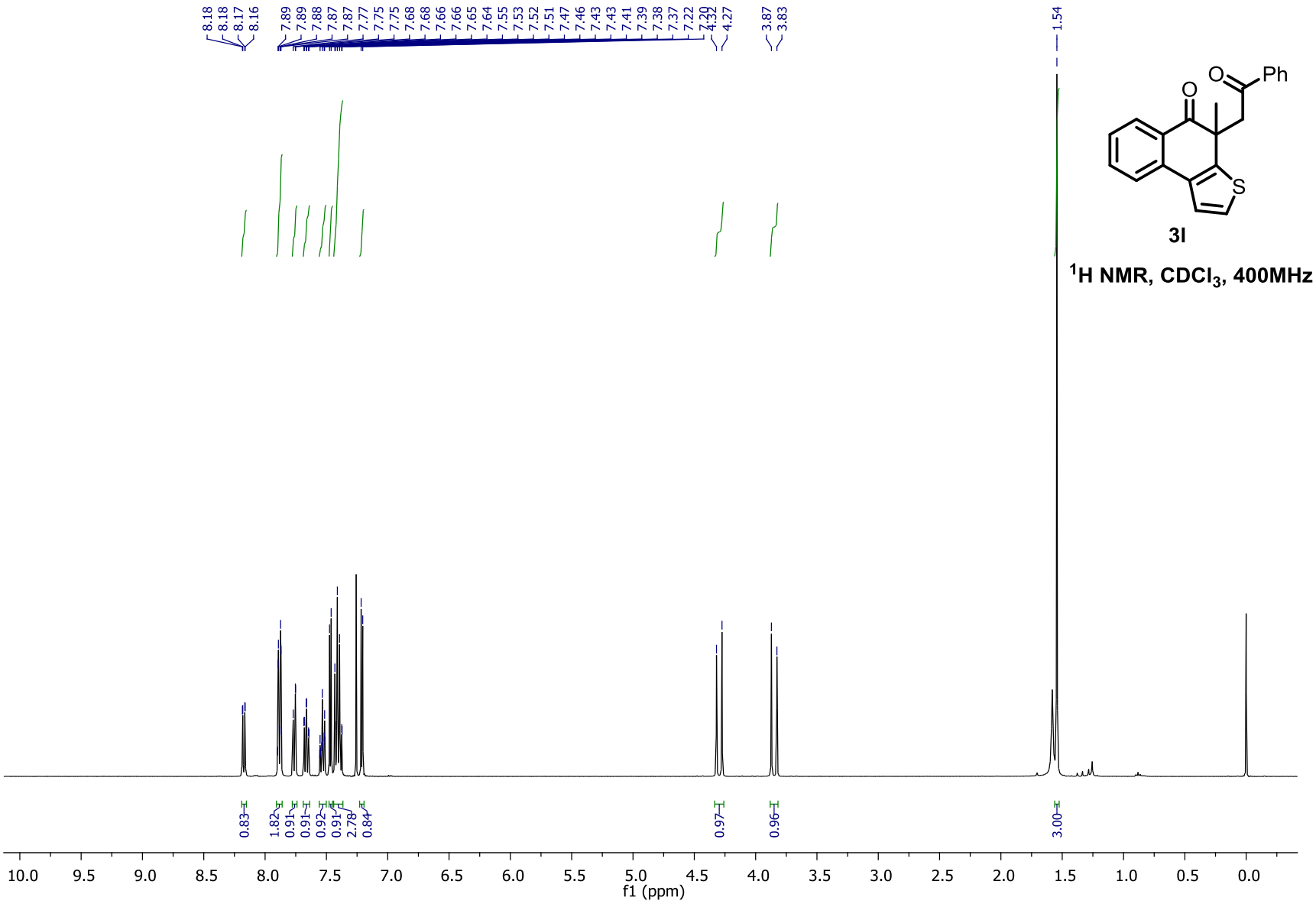
3k

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



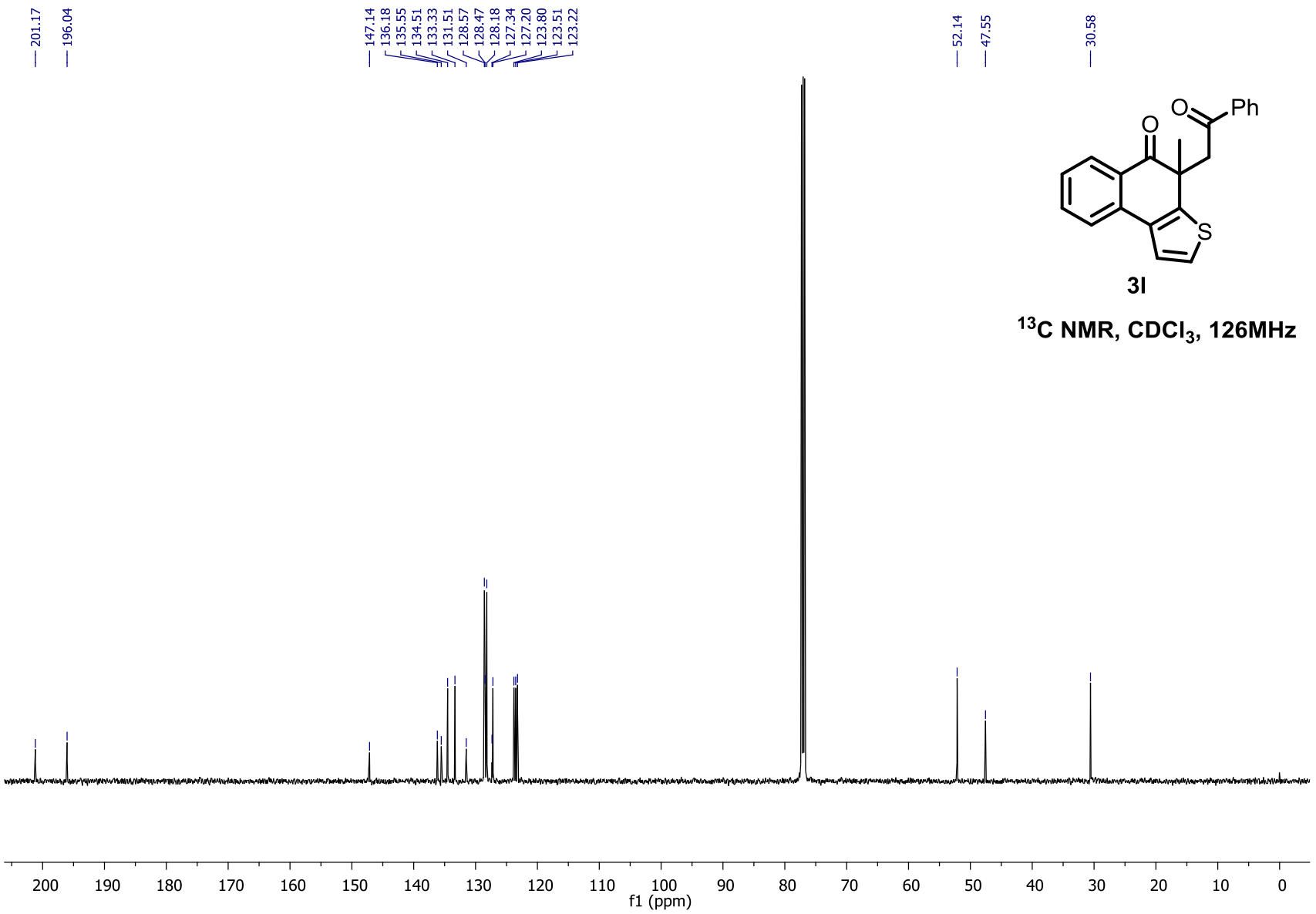
3k

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



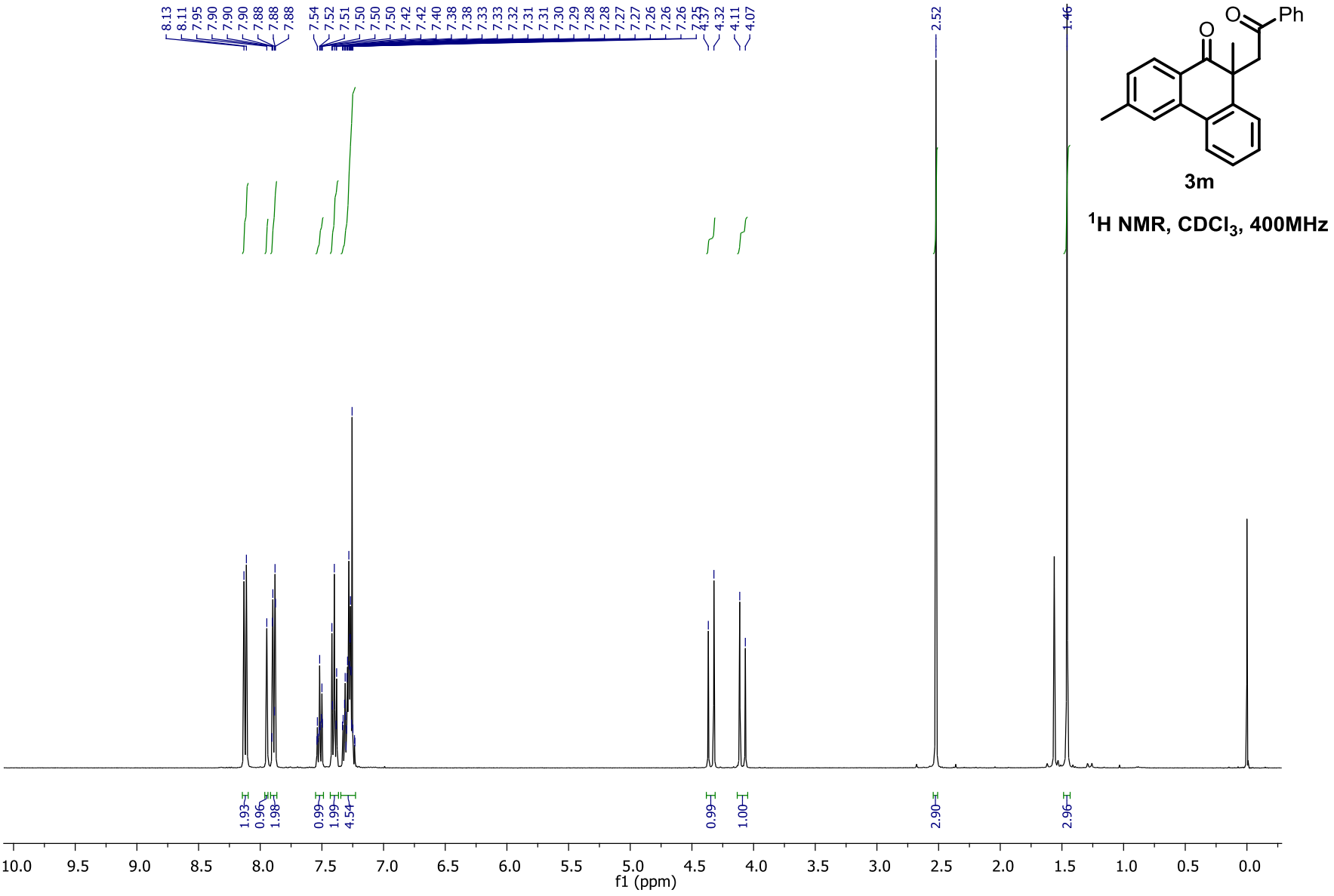
3l

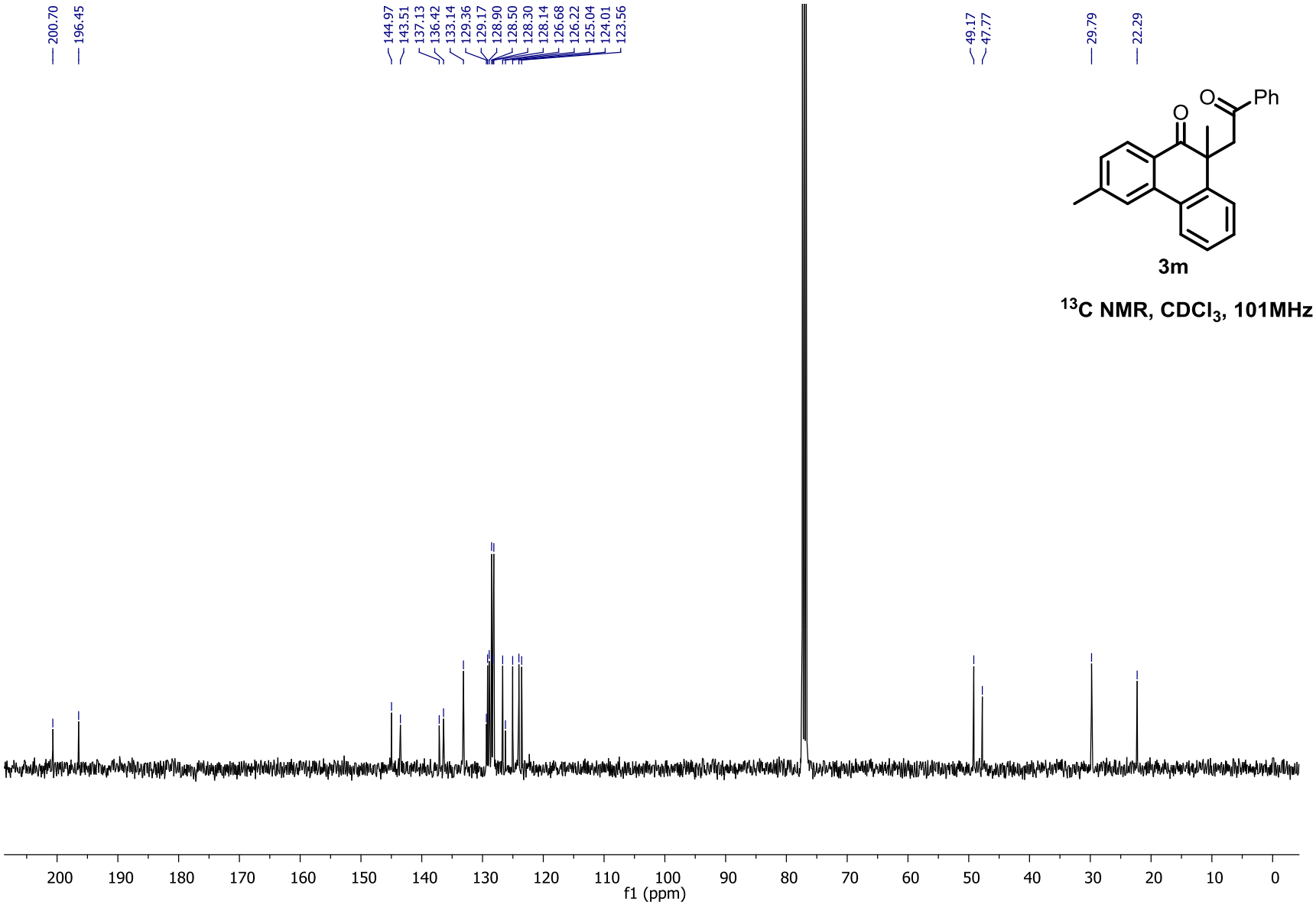
^{1}H NMR, $CDCl_3$, 400MHz

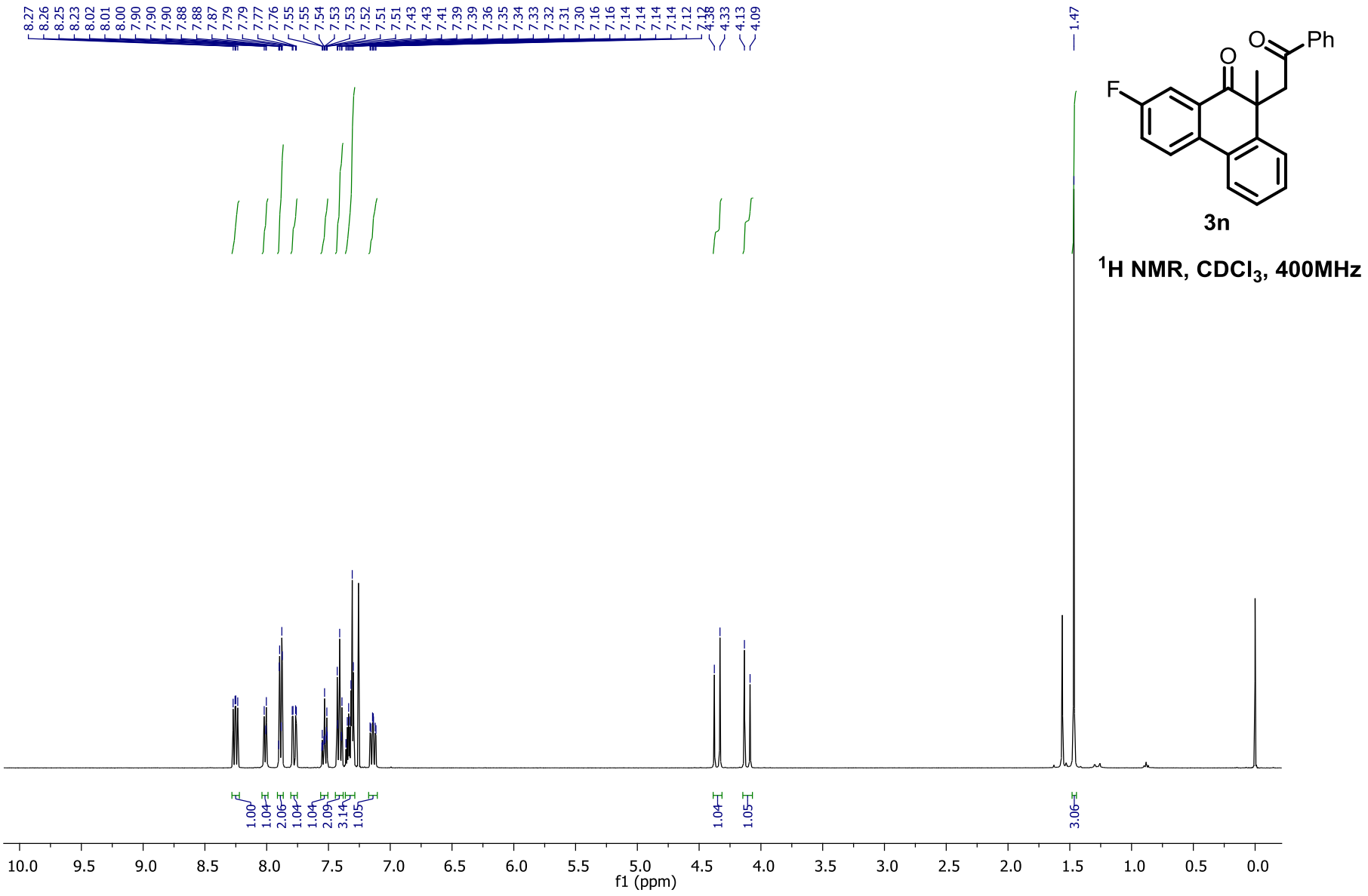


3l

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

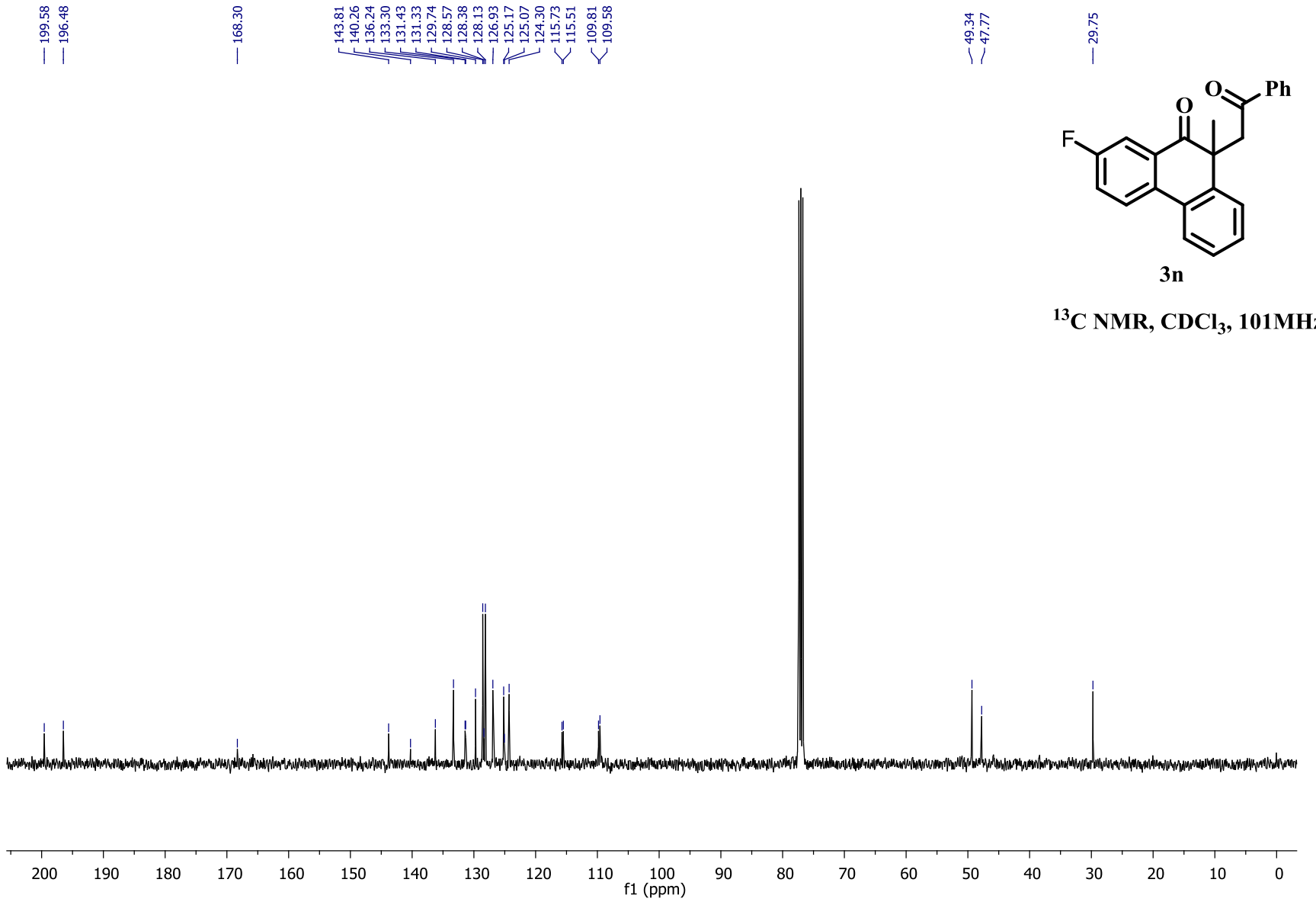

8.13
8.11
7.95
7.90
7.90
7.90
7.88
7.88
7.88
7.54
7.52
7.51
7.50
7.50
7.50
7.42
7.42
7.40
7.38
7.38
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26
4.37
4.32
4.11
4.07
2.52
1.46
1.93
0.96
1.98
0.99
1.99
4.54
0.99
1.00
2.90
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
Ph
3m
^{1}H NMR, CDCl$_3$, 400MHz

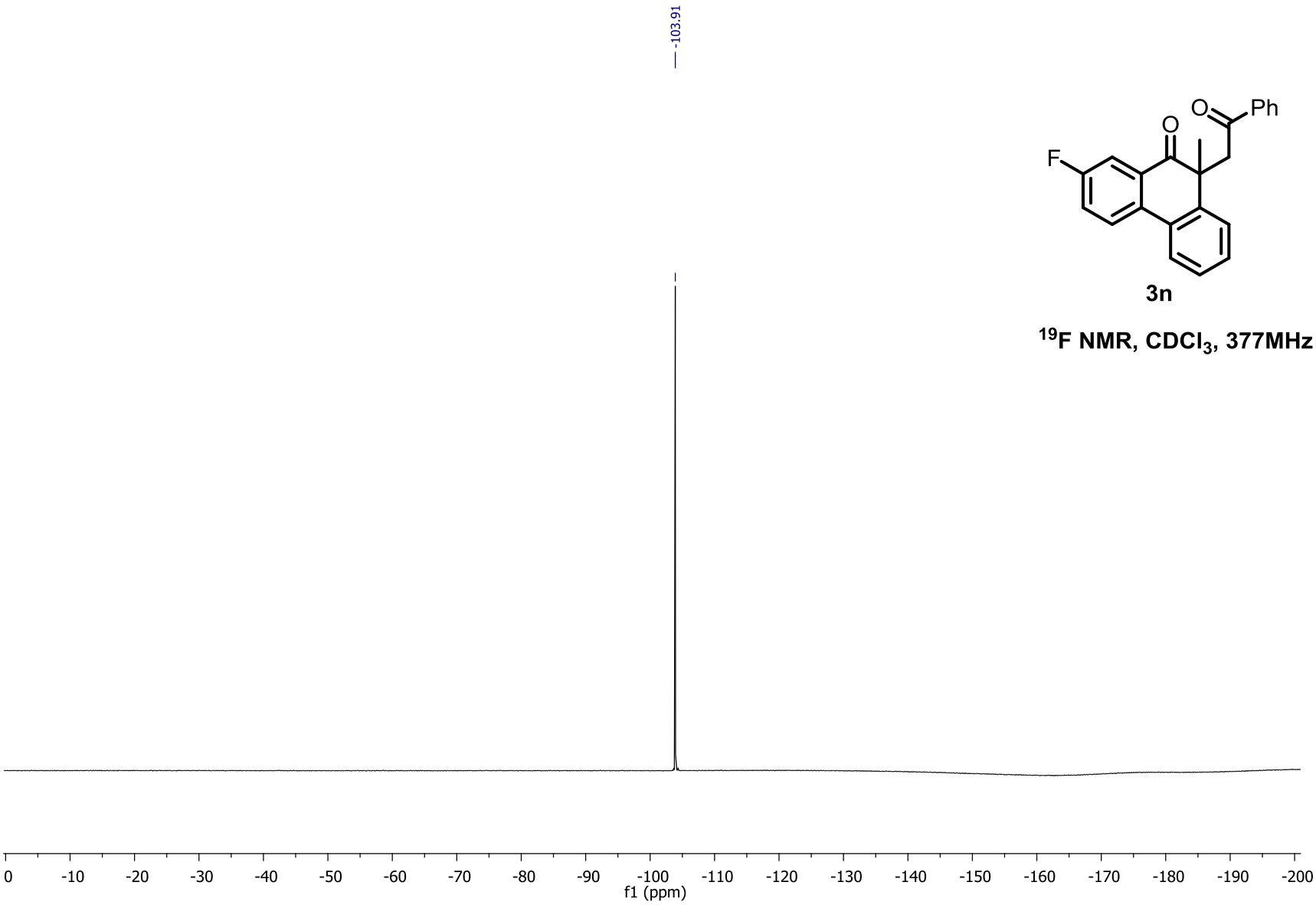

200.70
196.45
144.97
143.51
137.13
136.42
133.14
129.36
129.17
128.90
128.50
128.30
128.14
126.68
126.22
125.04
124.01
123.56
49.17
47.77
29.79
22.29
O
O
Ph
3m
^{13}C NMR, CDCl$_3$, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3n

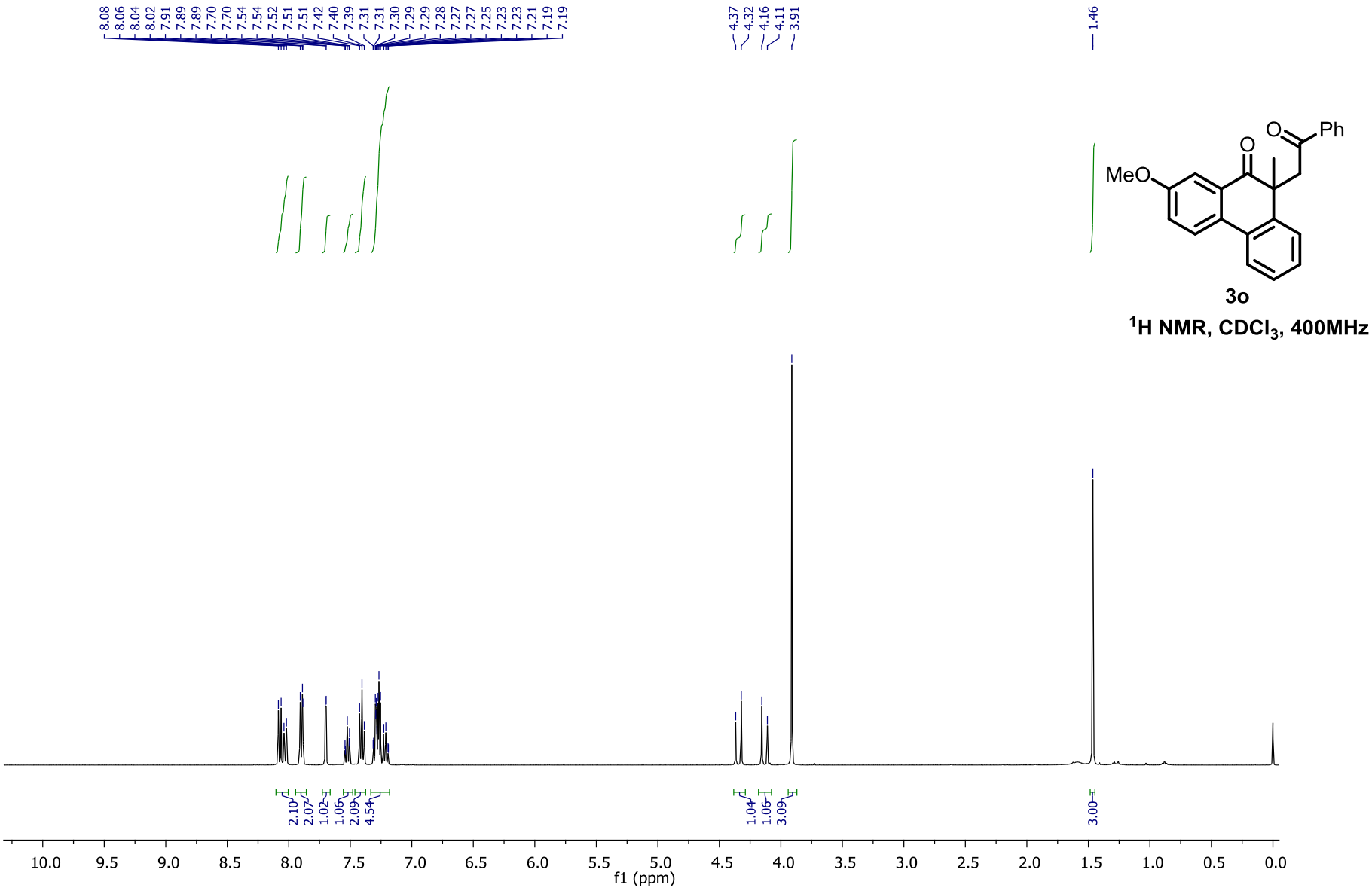
^{1}H NMR, $CDCl_3$, 400MHz


199.58
196.48
168.30
143.81
140.26
136.24
133.30
131.43
131.33
129.74
128.57
128.38
128.13
126.93
125.17
125.07
124.30
115.73
115.51
109.81
109.58
49.34
47.77
29.75
O
O
Ph
F
3n
^{13}C NMR, CDCl$_3$, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



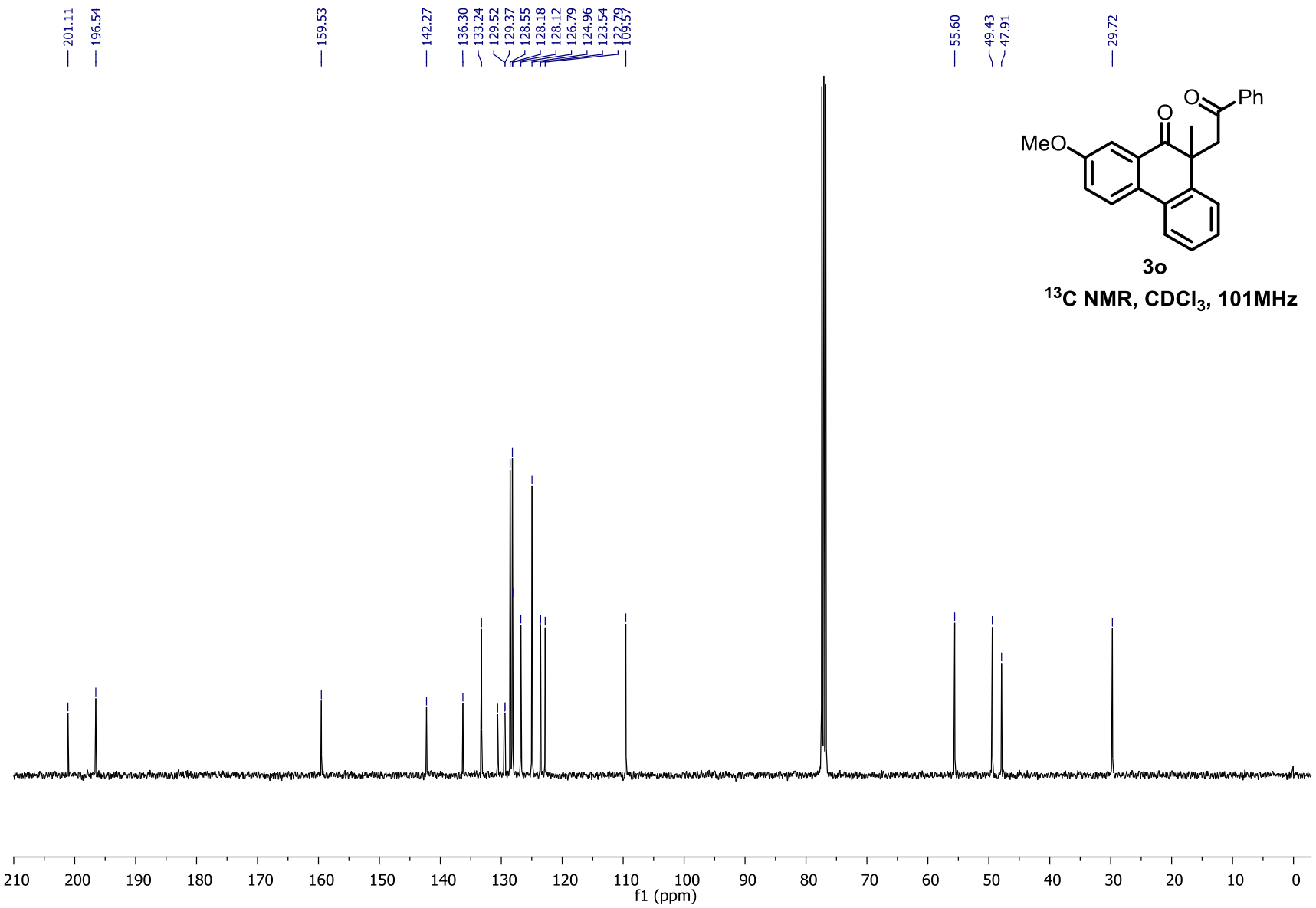
3n

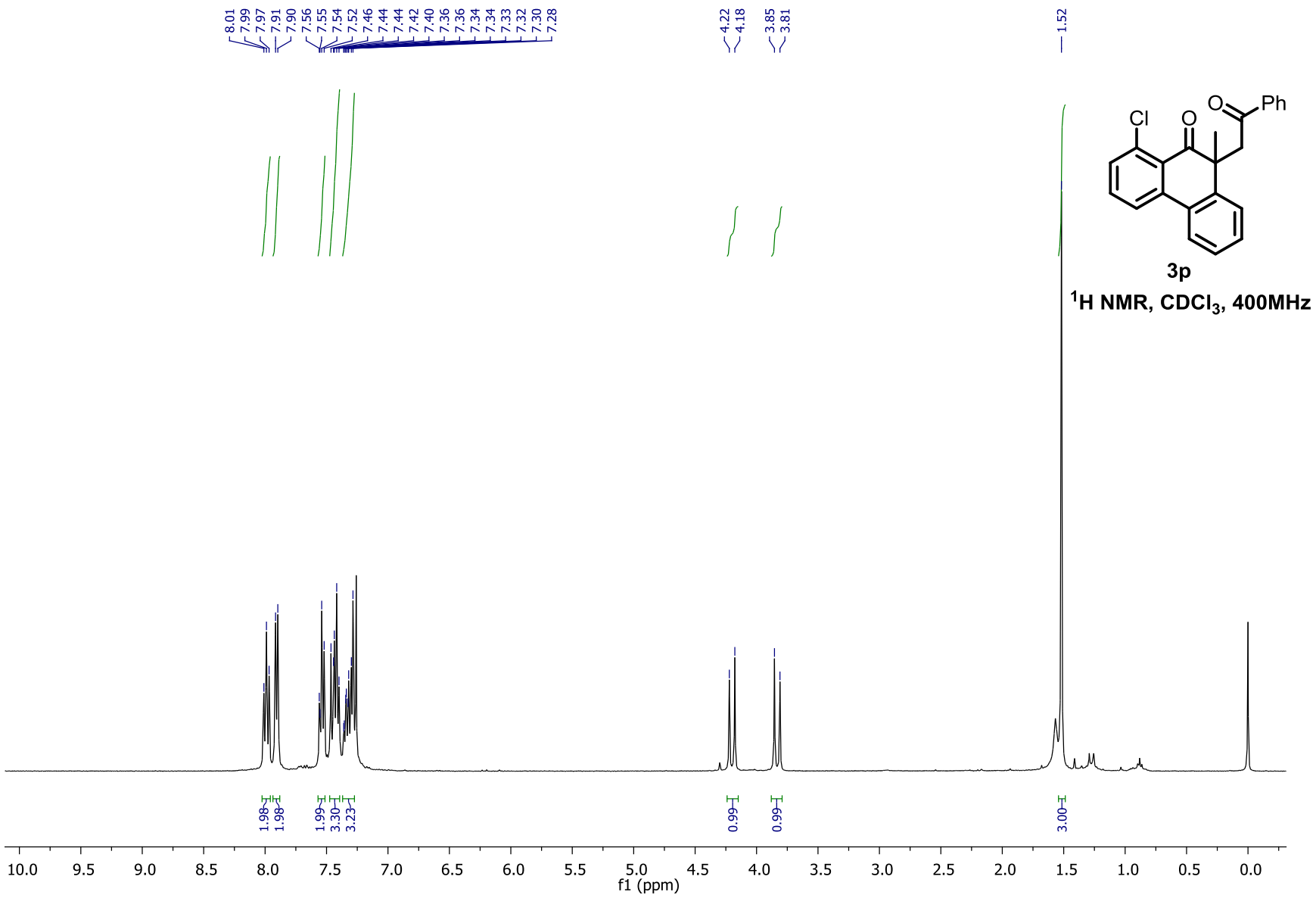
^{19}F NMR, $CDCl_3$, 377MHz

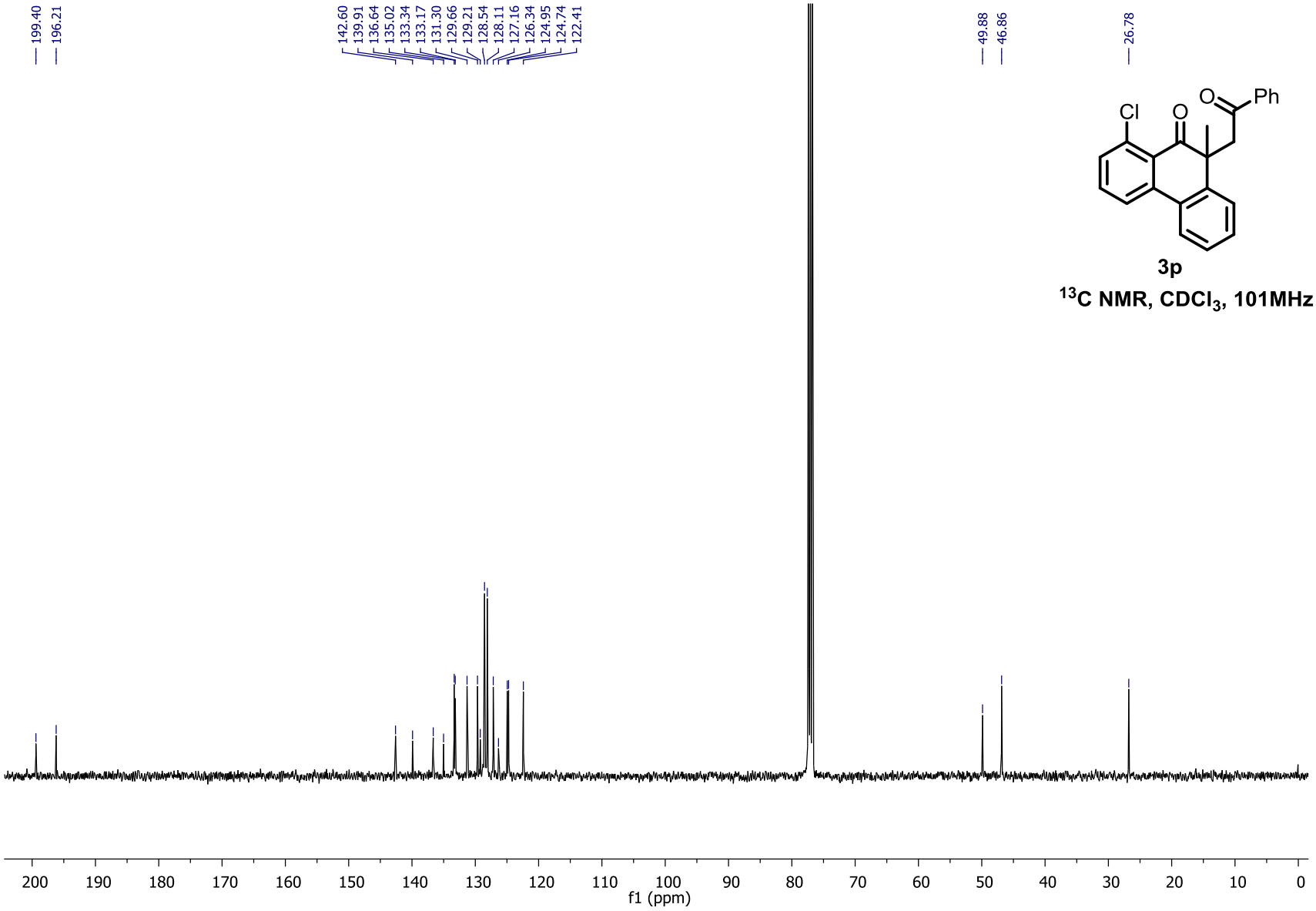


3o

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

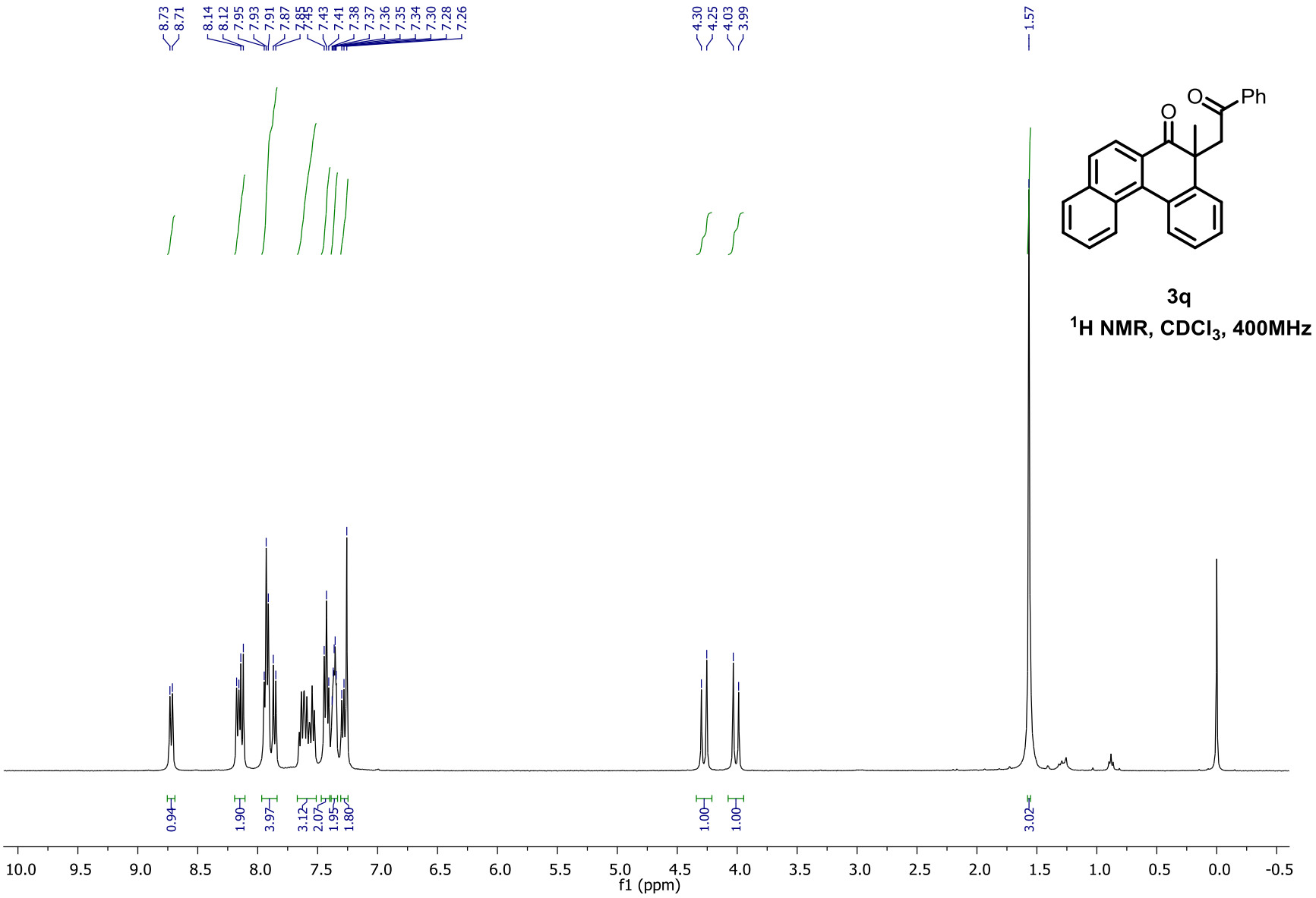

201.11
196.54
159.53
142.27
136.30
133.24
129.52
129.37
128.55
128.18
128.12
126.79
124.96
123.54
55.60
49.43
47.91
29.72
MeO
O
O
Ph
3o
^{13}C NMR, CDCl$_3$, 101MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.01
7.99
7.97
7.91
7.90
7.56
7.55
7.54
7.52
7.46
7.44
7.44
7.42
7.40
7.36
7.36
7.34
7.34
7.33
7.32
7.30
7.28
4.22
4.18
3.85
3.81
1.52
Cl
O
O
Ph
3p
1H NMR, CDCl3, 400MHz
1.98
1.98
1.99
3.30
3.23
0.99
0.99
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)



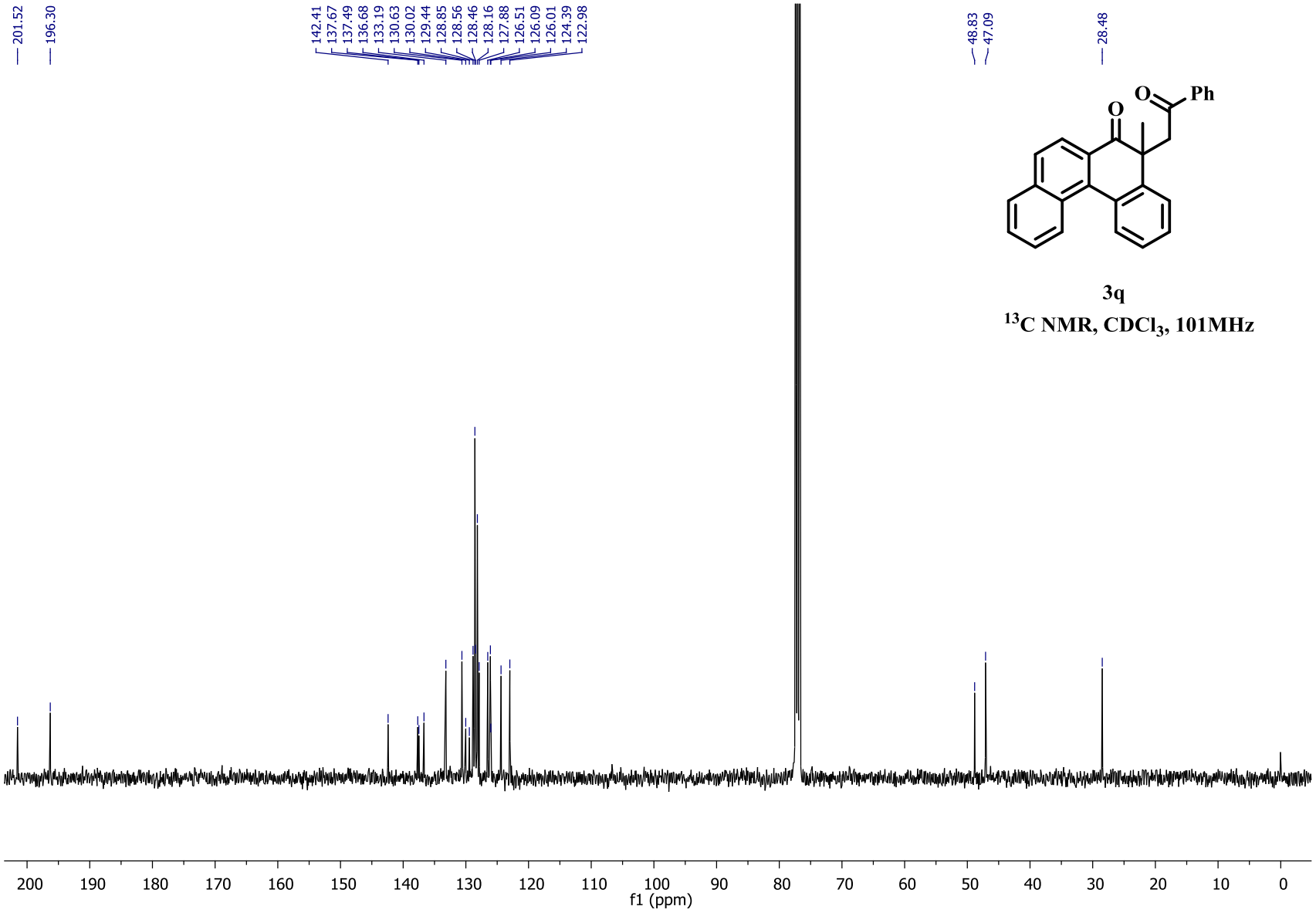
3p

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



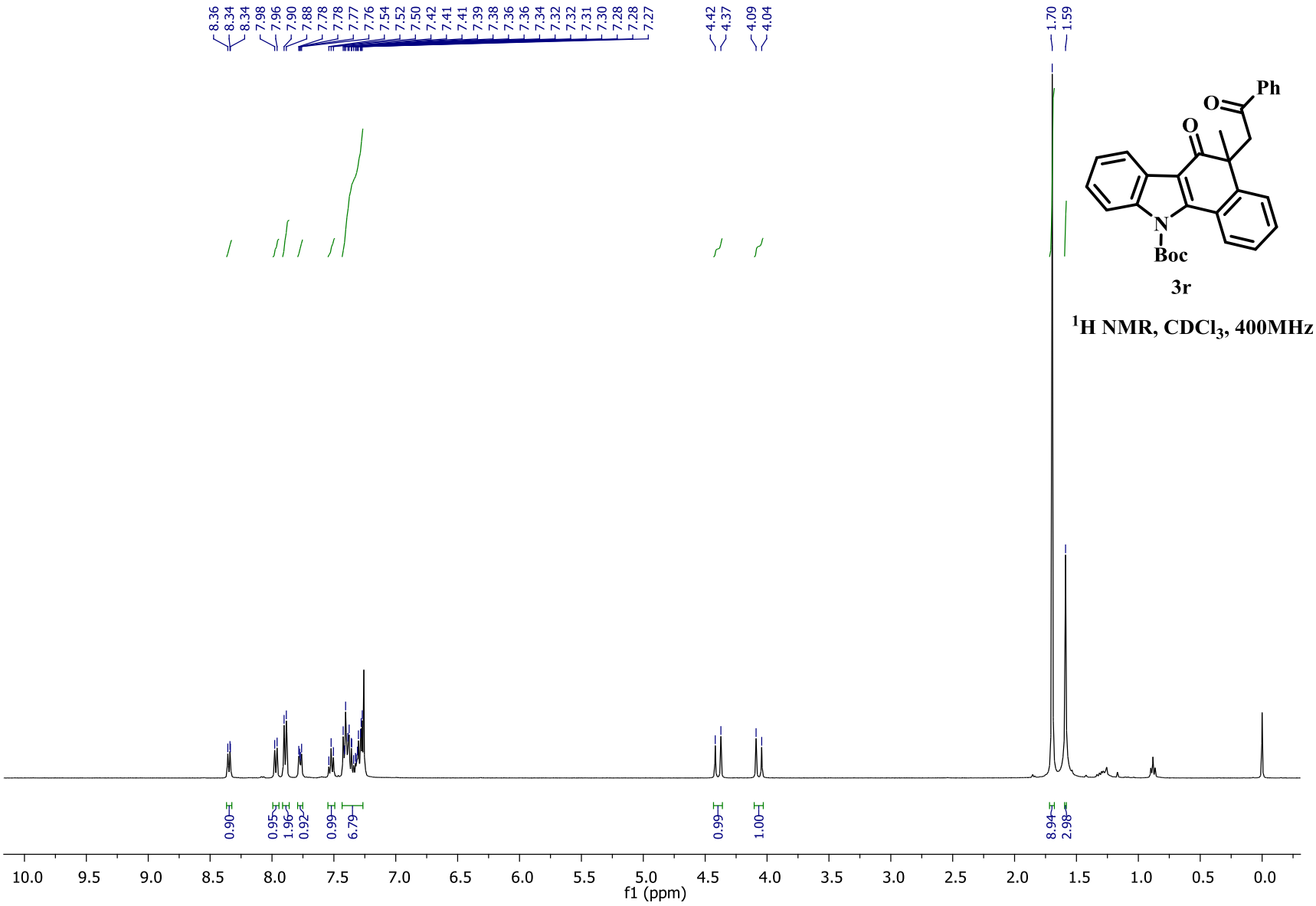
3q

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



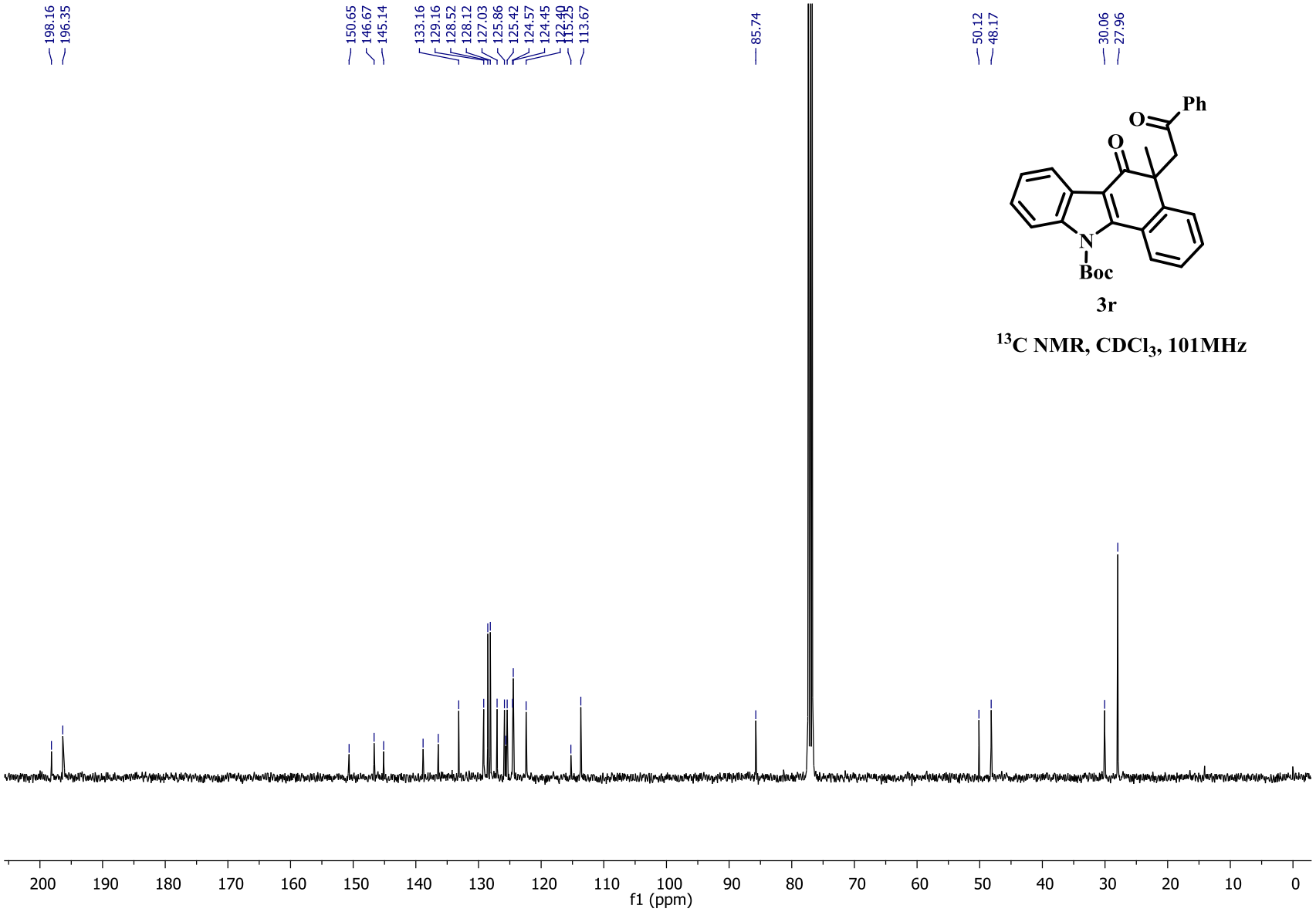
3q

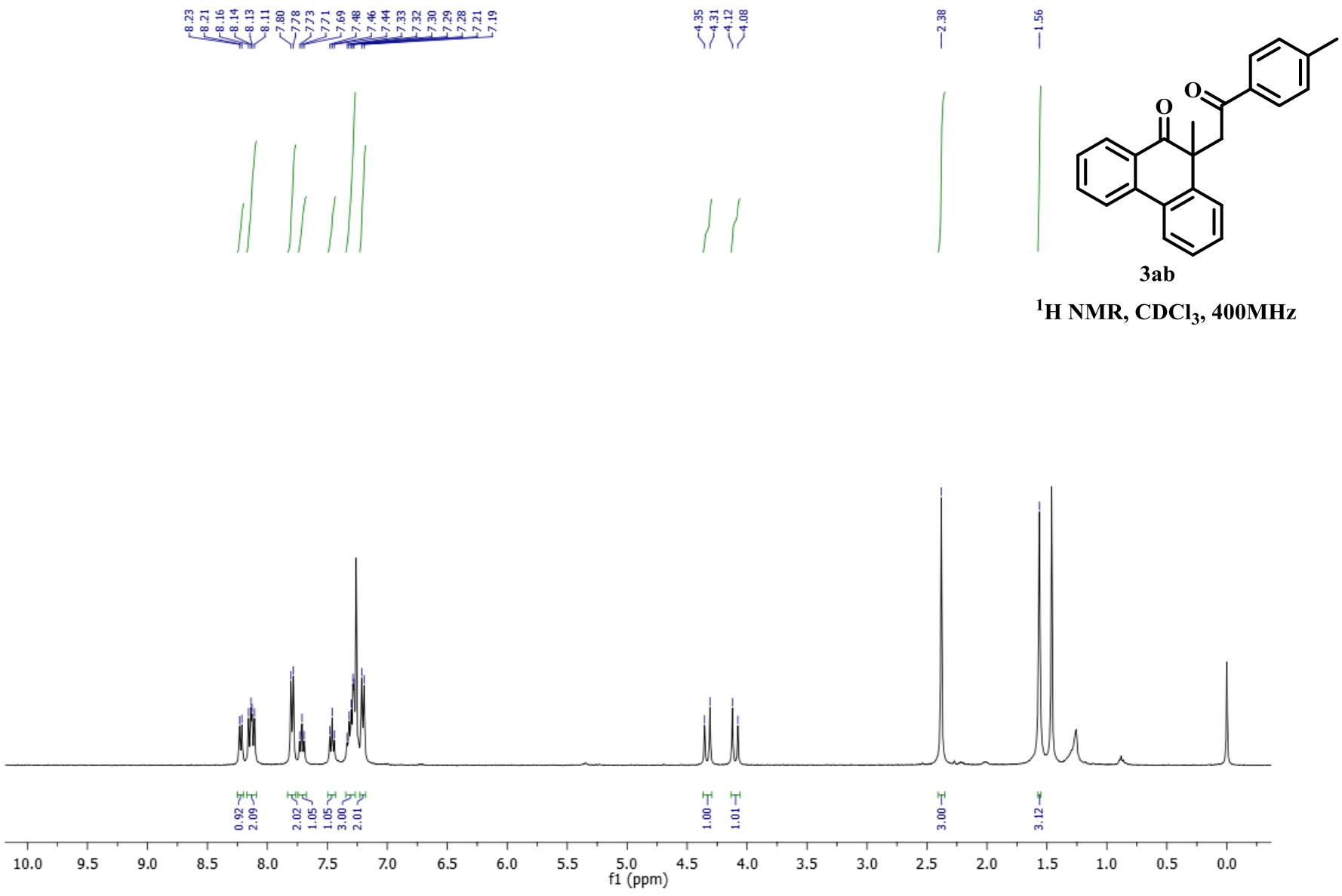
^{13}C NMR, $CDCl_3$, 101MHz



3r

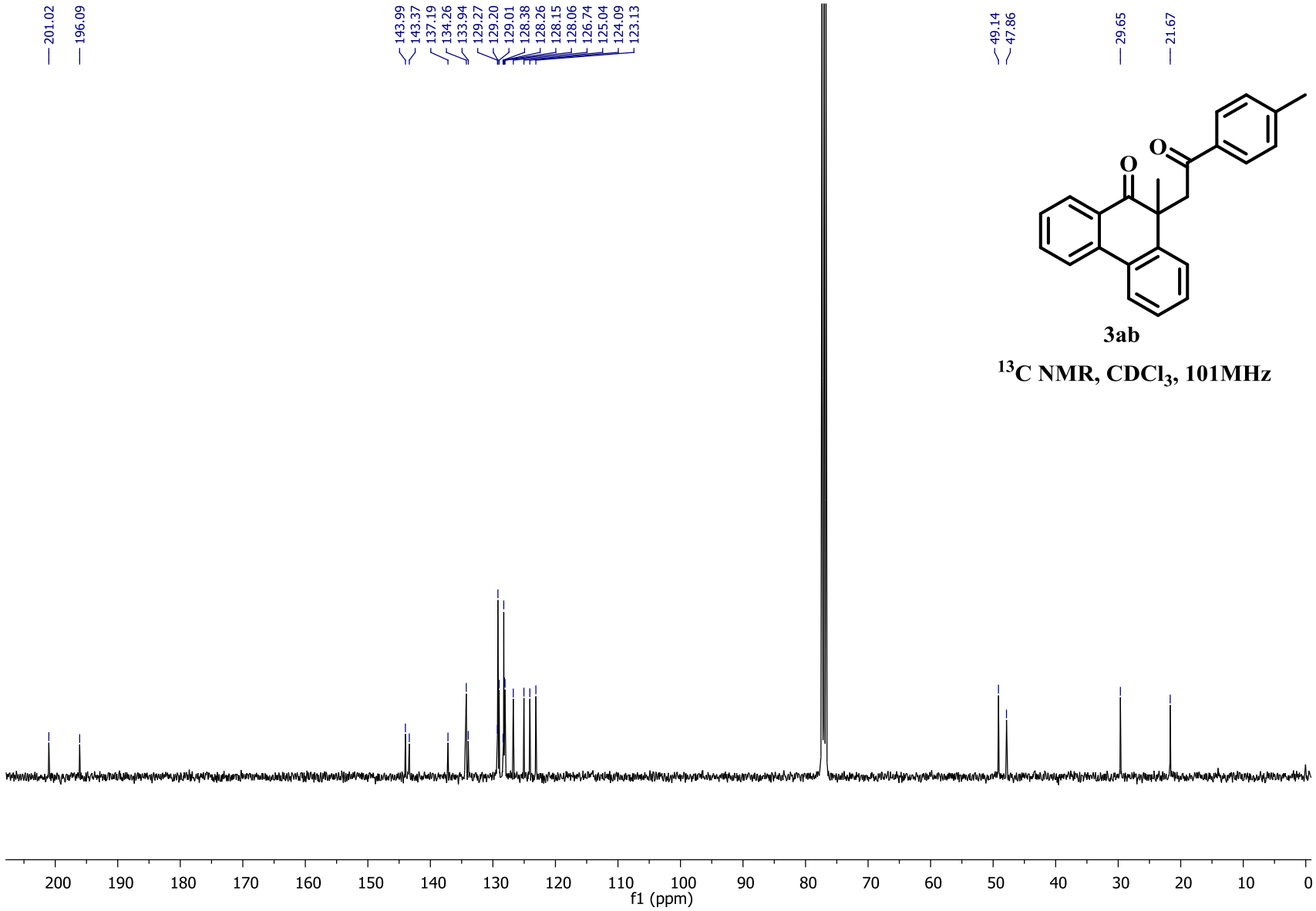
^{1}H NMR, $CDCl_3$, 400MHz

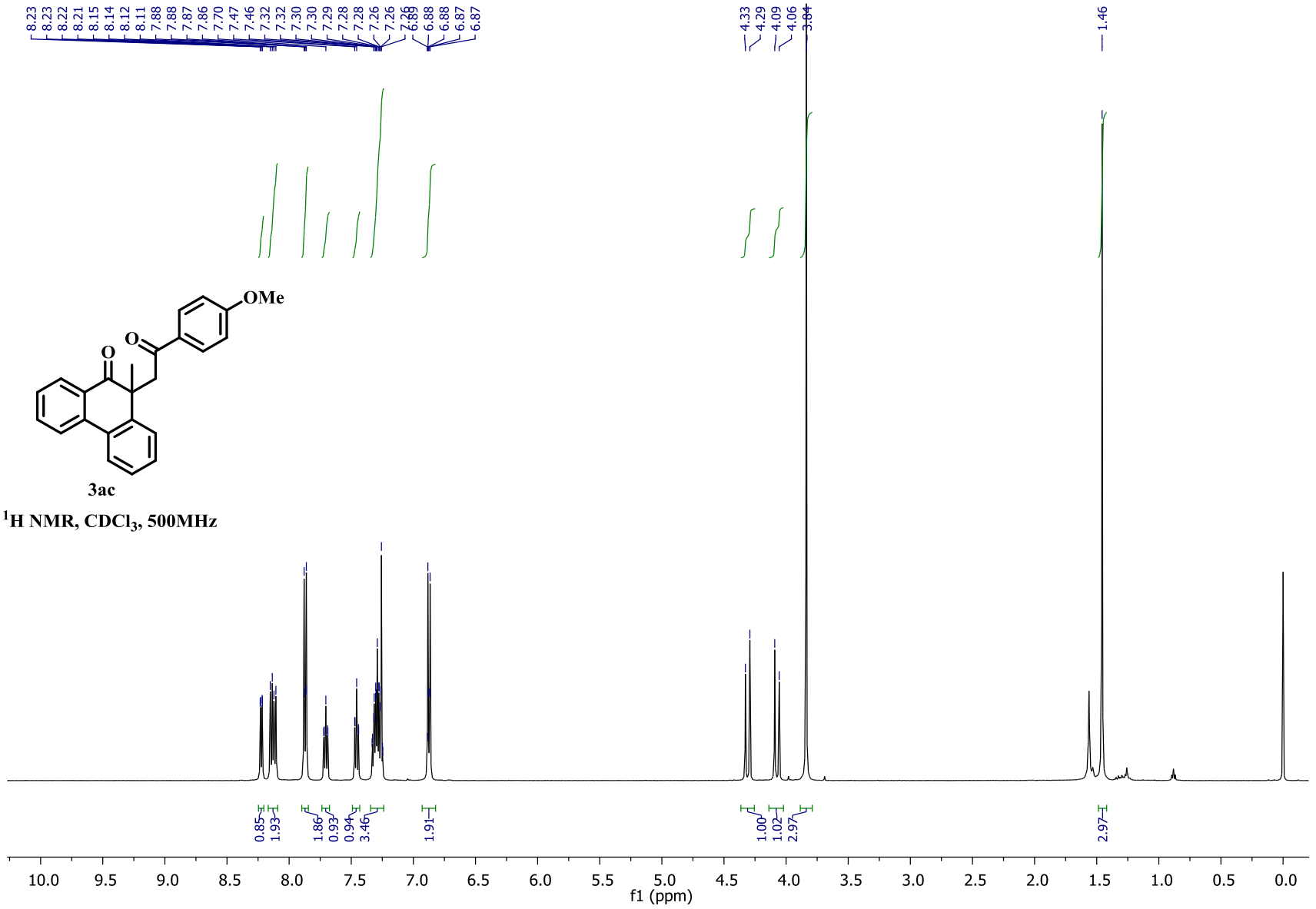

198.16
196.35
150.65
146.67
145.14
133.16
129.16
128.52
128.12
127.03
125.86
125.42
124.57
124.45
113.67
85.74
50.12
48.17
30.06
27.96
Ph
O
O
N
Boc
3r
^{13}C NMR, CDCl$_3$, 101MHz
f1 (ppm)

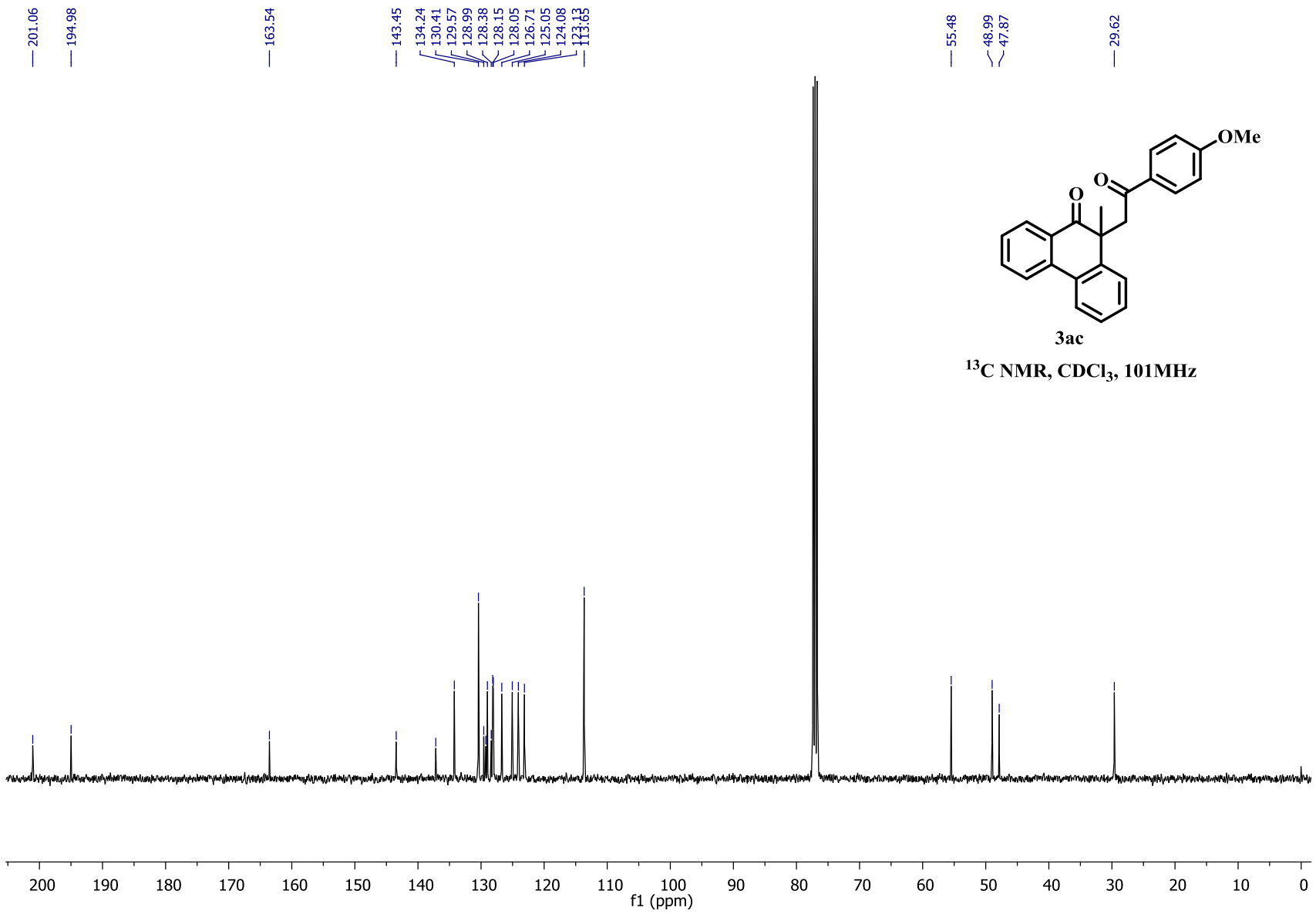


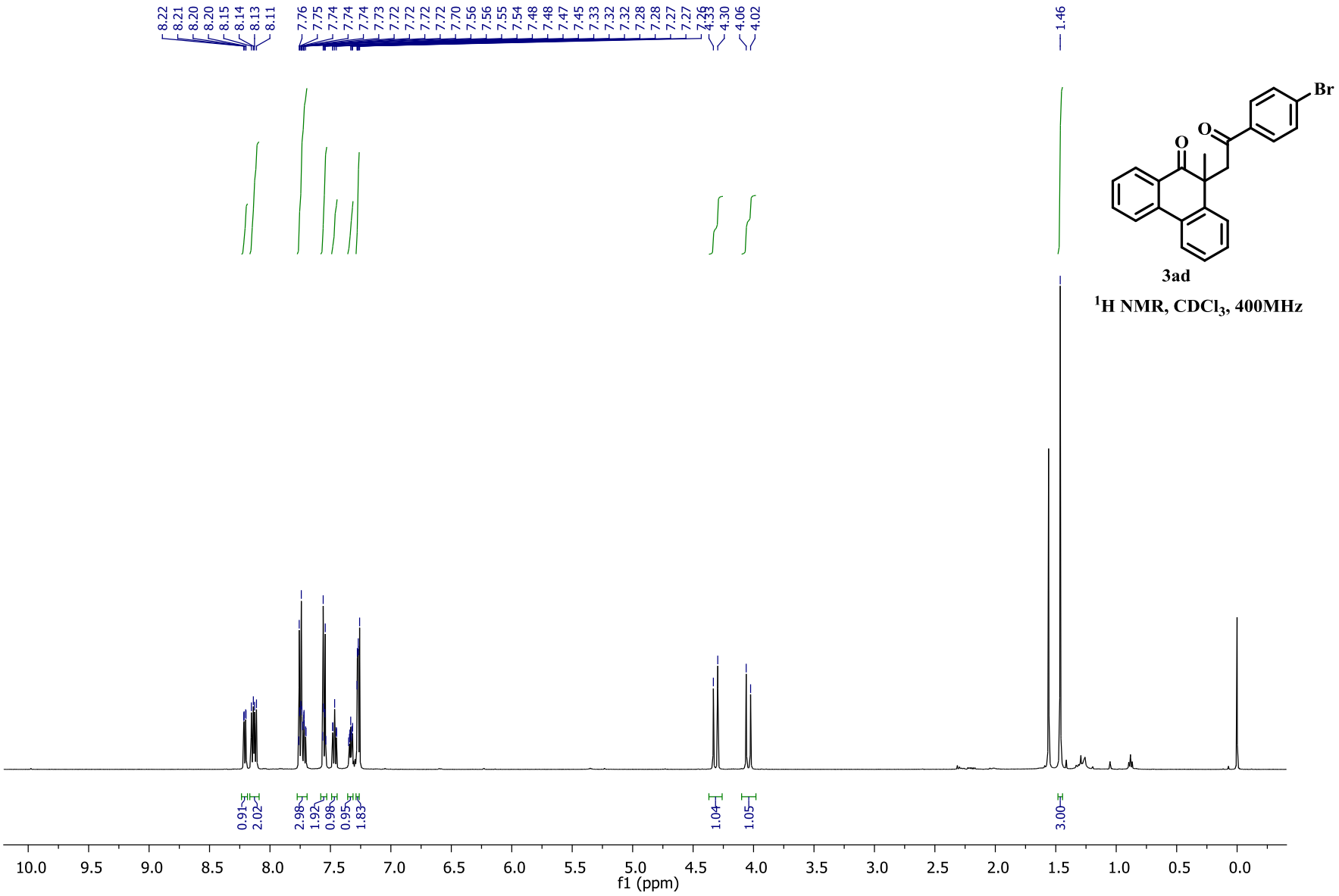
3ab

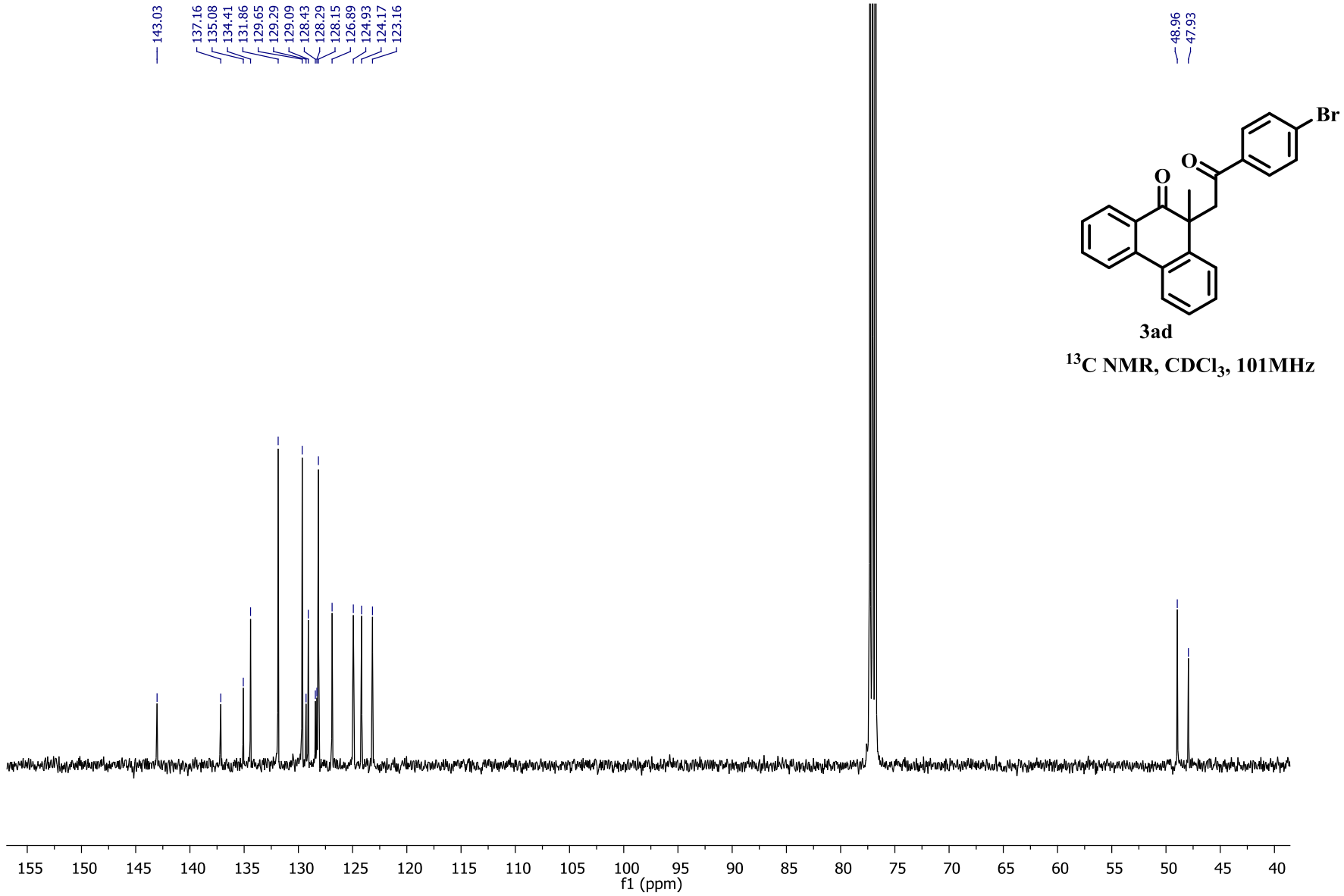
^{1}H NMR, $CDCl_3$, 400MHz


201.02
196.09
143.99
143.37
137.19
134.26
133.94
129.27
129.20
129.01
128.38
128.26
128.15
128.06
126.74
125.04
124.09
123.13
49.14
47.86
29.65
21.67
O
O
3ab
13C NMR, CDCl3, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.23
8.23
8.22
8.21
8.15
8.14
8.12
8.11
7.88
7.88
7.87
7.86
7.70
7.47
7.46
7.32
7.32
7.30
7.30
7.29
7.28
7.28
7.26
7.26
6.89
6.88
6.88
6.87
6.87
4.33
4.29
4.09
4.06
3.84
1.46
OMe
O
O
3ac
^{1}H NMR, CDCl$_3$, 500MHz
0.85
1.93
1.86
0.93
0.94
3.46
1.91
1.00
1.02
2.97
2.97
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)

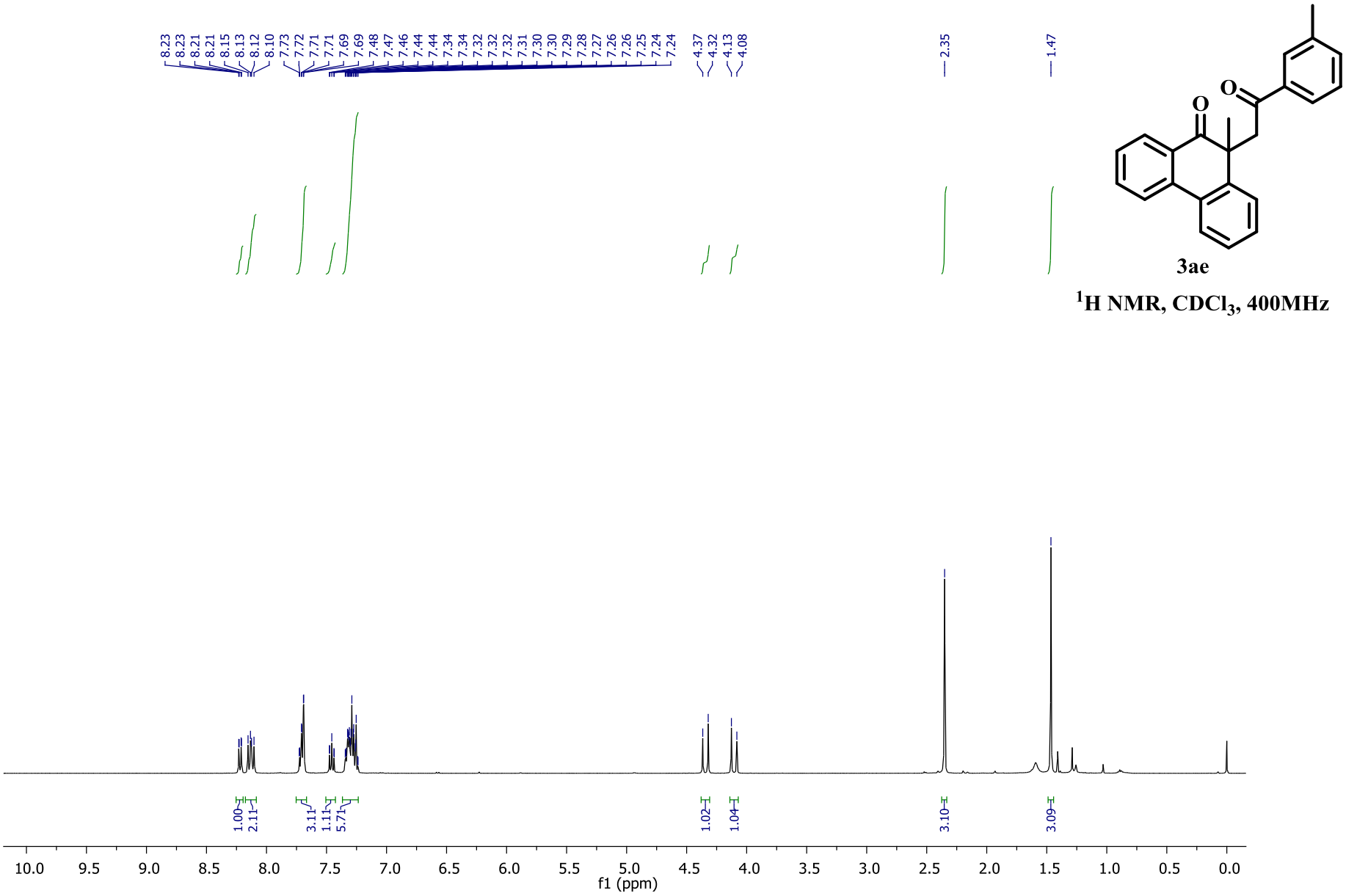

201.06
194.98
163.54
143.45
134.24
130.41
129.57
128.99
128.38
128.15
128.05
126.71
125.05
124.08
123.13
113.65
55.48
48.99
47.87
29.62
OMe
O
O
3ac
^{13}C NMR, CDCl$_3$, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.22
8.21
8.20
8.20
8.15
8.14
8.13
8.11
7.76
7.75
7.74
7.74
7.74
7.73
7.72
7.72
7.72
7.72
7.70
7.56
7.56
7.55
7.54
7.48
7.48
7.47
7.45
7.33
7.32
7.32
7.28
7.28
7.27
7.27
7.26
4.33
4.30
4.06
4.02
1.46
Br
O
O
3ad
^{1}H NMR, $CDCl_3$, 400MHz
0.91
2.02
2.98
1.92
0.98
0.95
1.83
1.04
1.05
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)



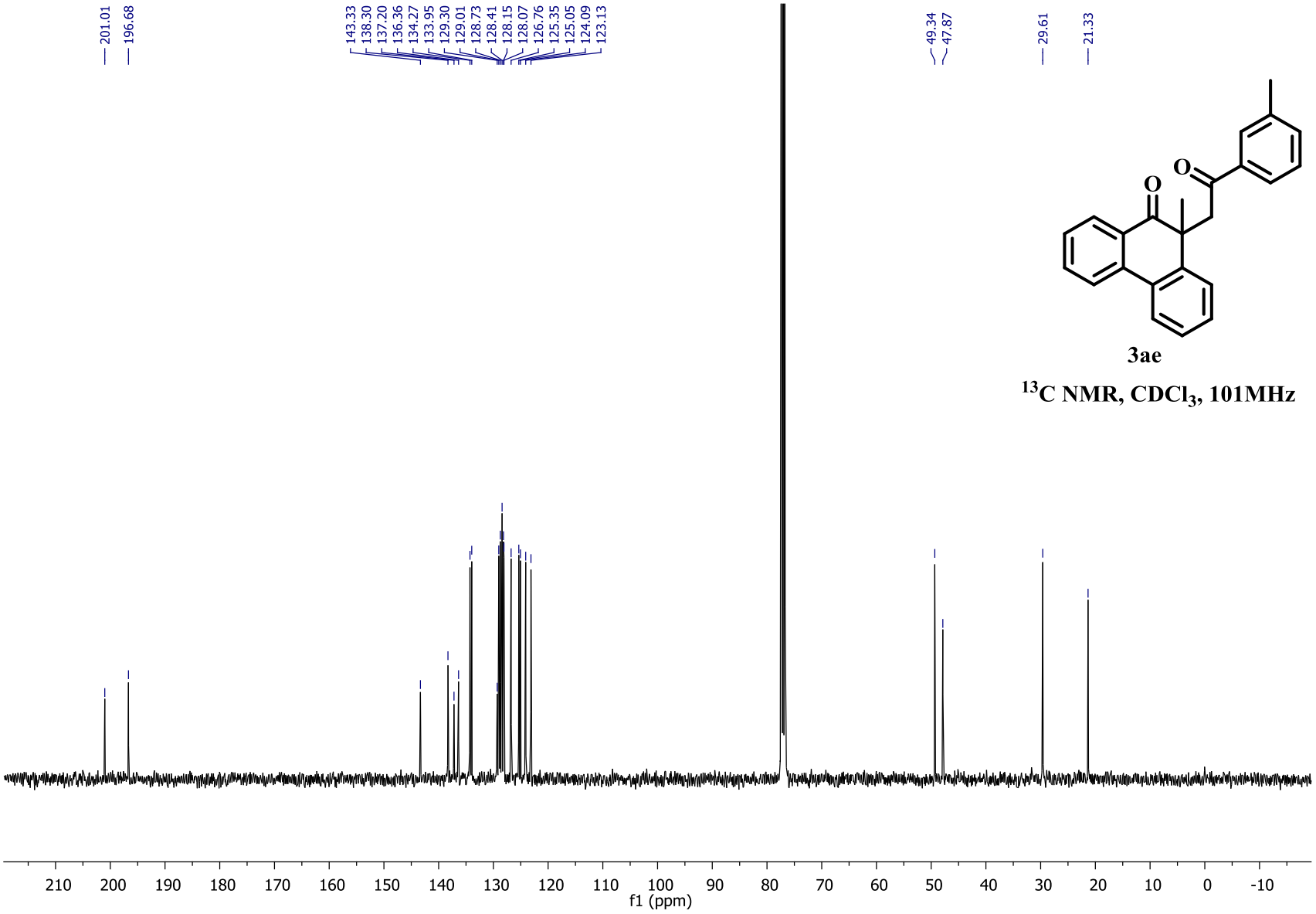
3ad

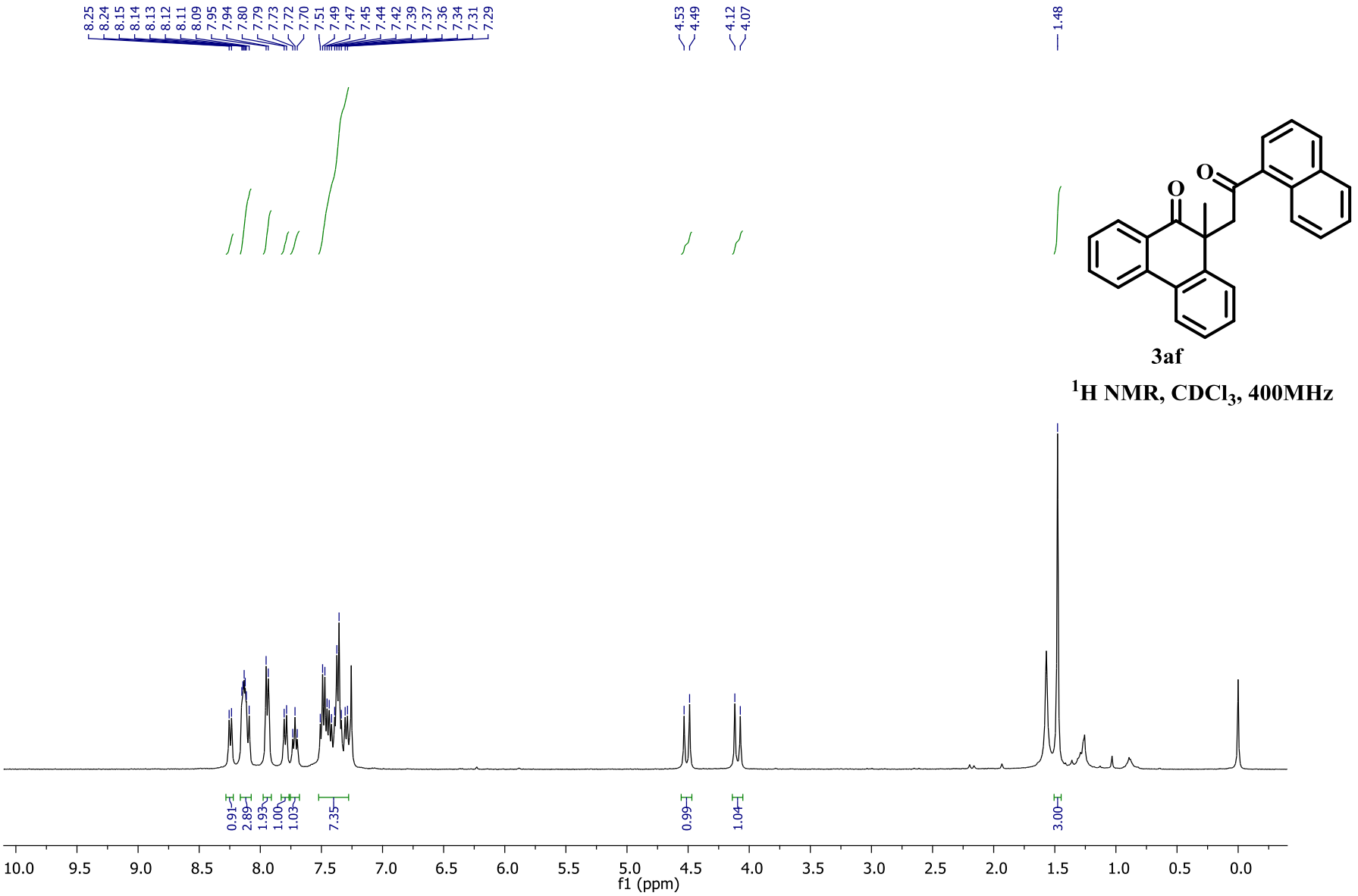
^{13}C NMR, $CDCl_3$, 101MHz



3ae

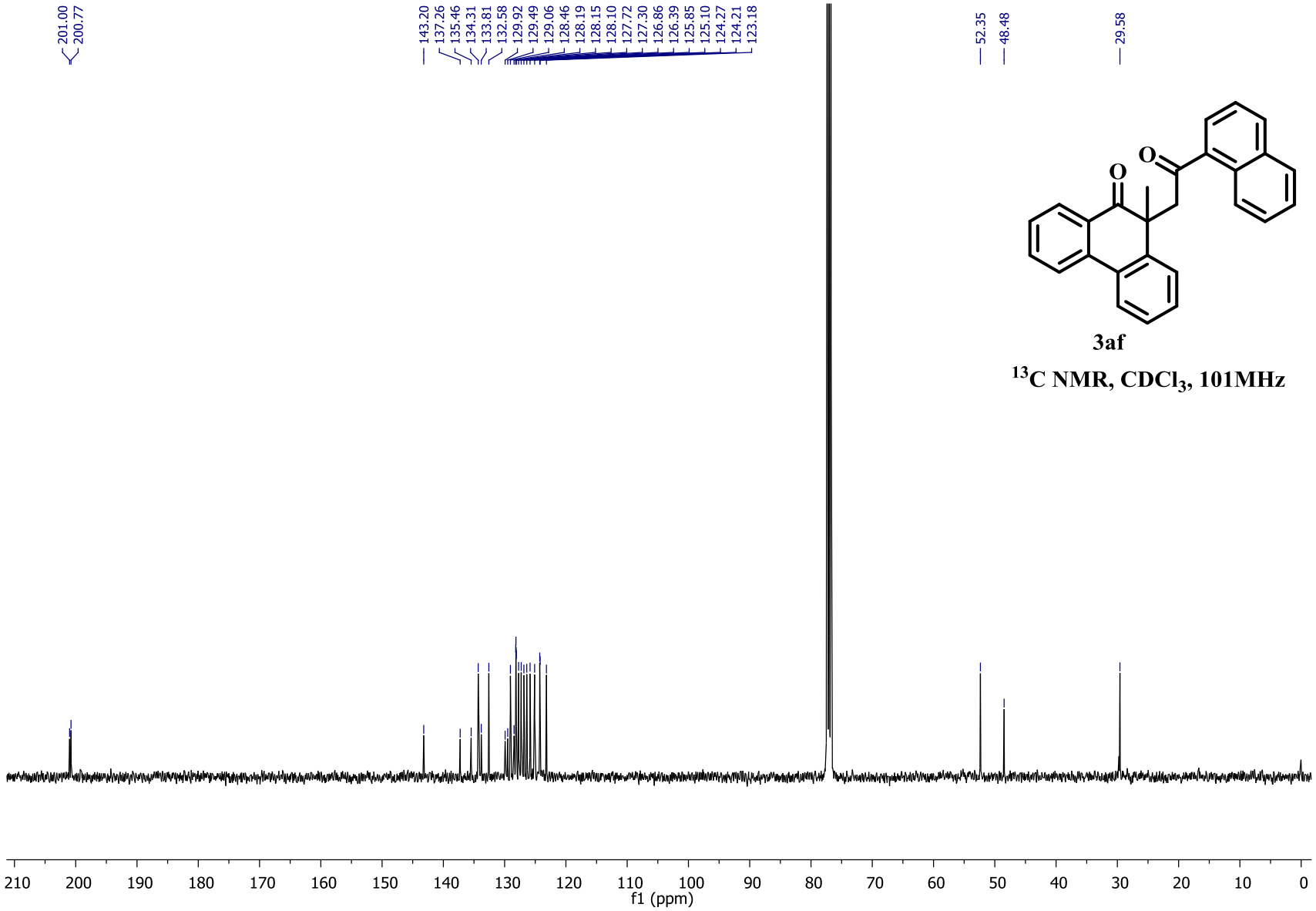
^{1}H NMR, $CDCl_3$, 400MHz


201.01
196.68
143.33
138.30
137.20
136.36
134.27
133.95
129.30
129.01
128.73
128.41
128.15
128.07
126.76
125.35
125.05
124.09
123.13
49.34
47.87
29.61
21.33
O
O
3ae
13C NMR, CDCl3, 101MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



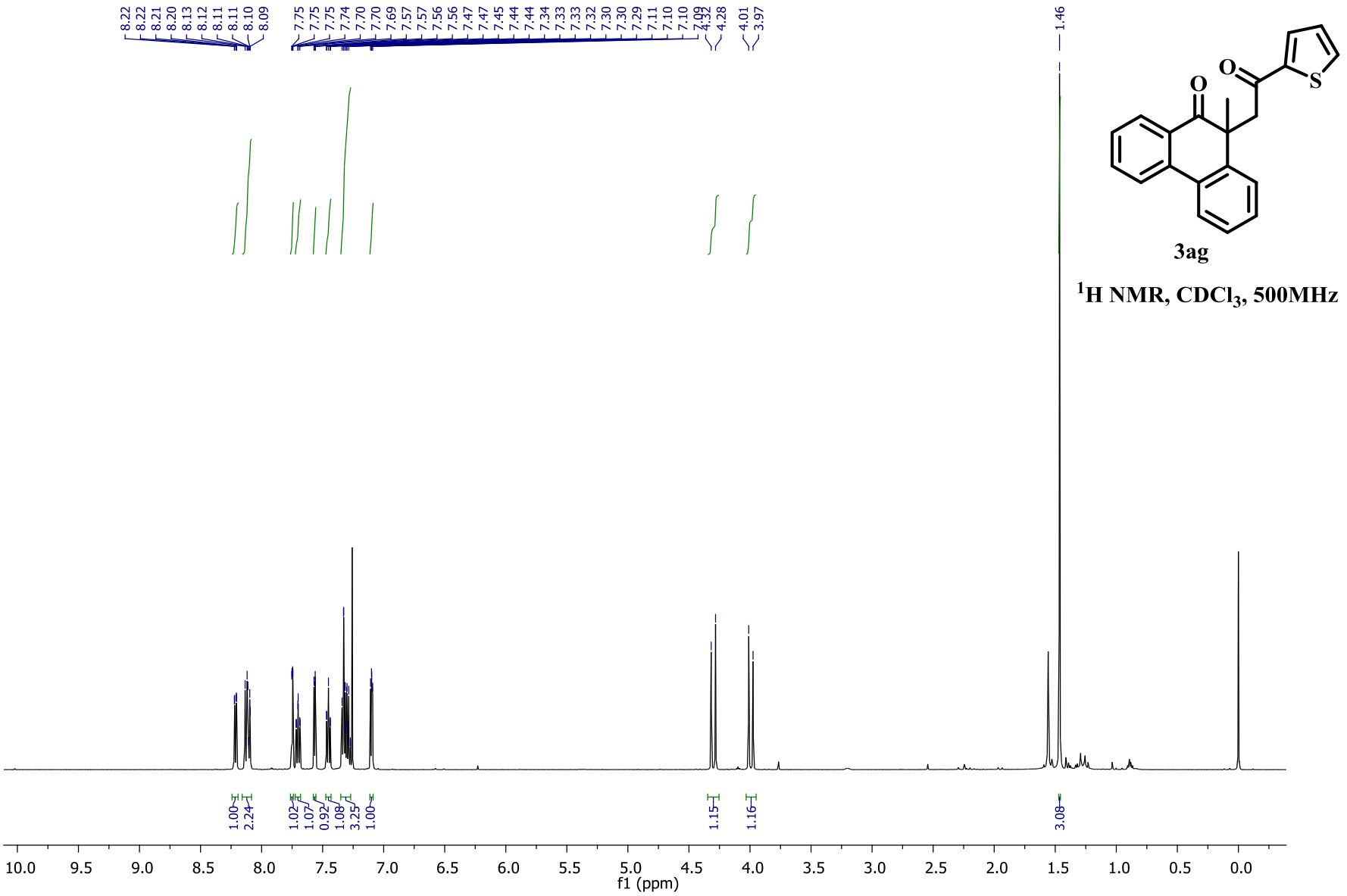
3af

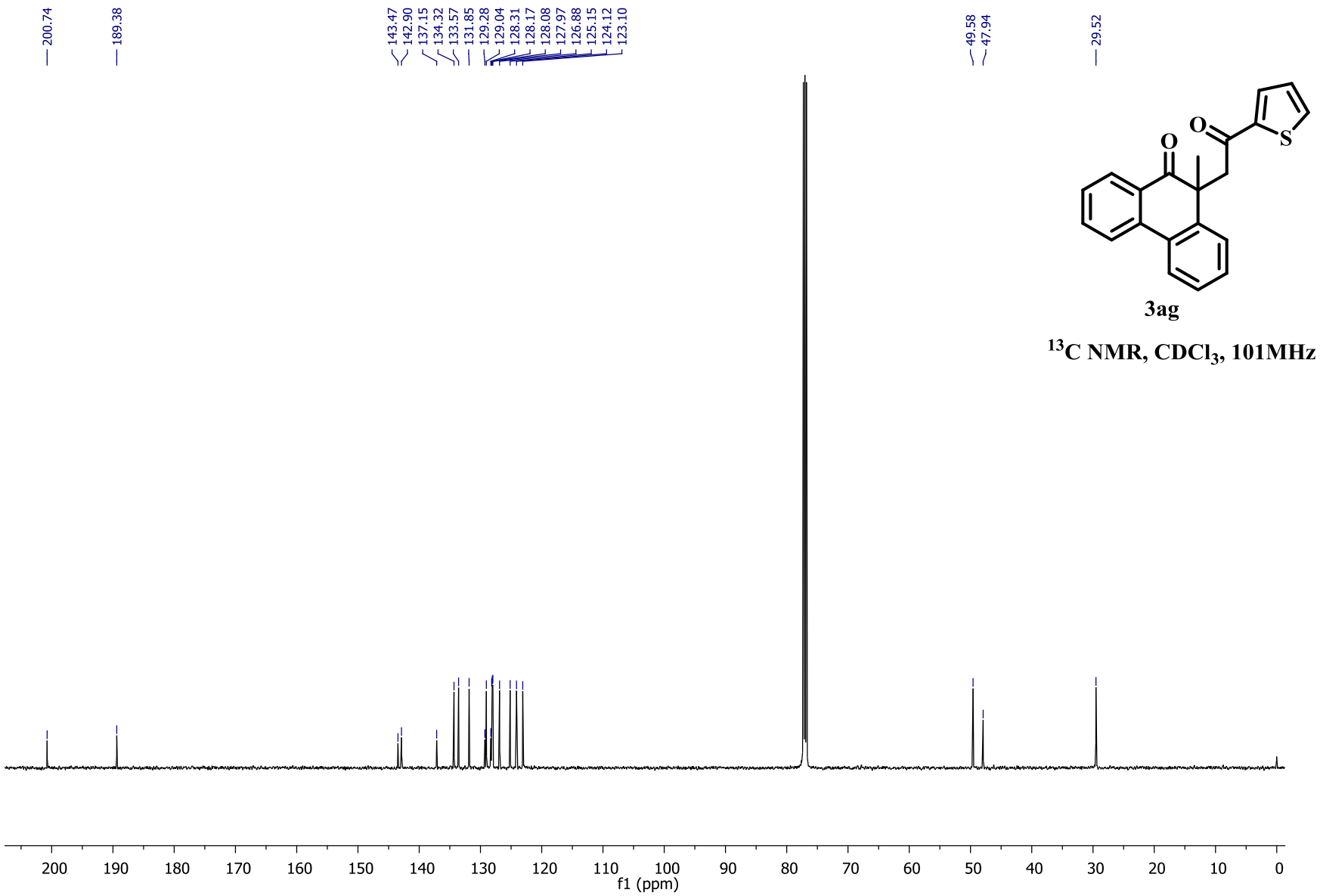
^{1}H NMR, $CDCl_3$, 400MHz



3af

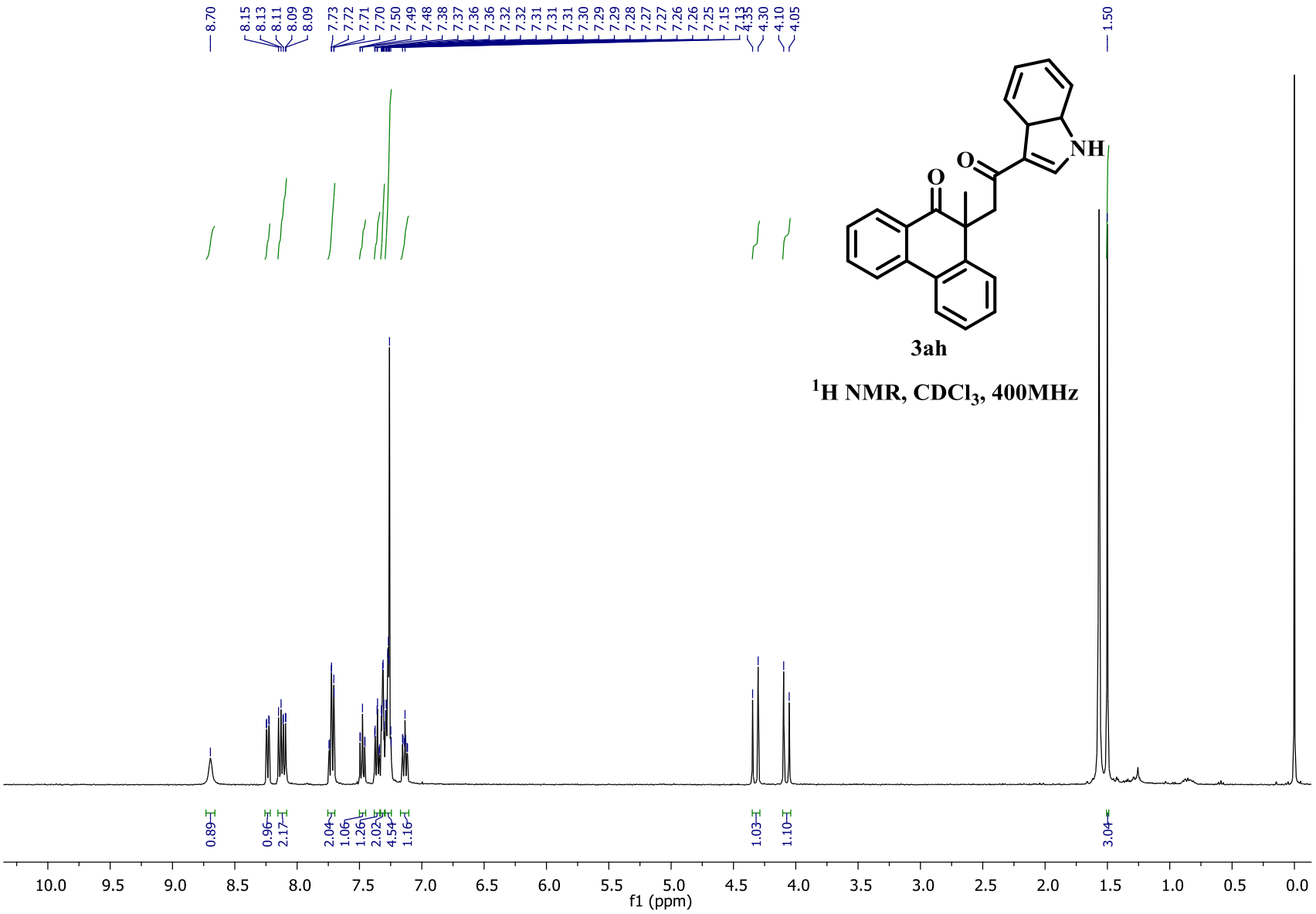
^{13}C NMR, $CDCl_3$, 101MHz

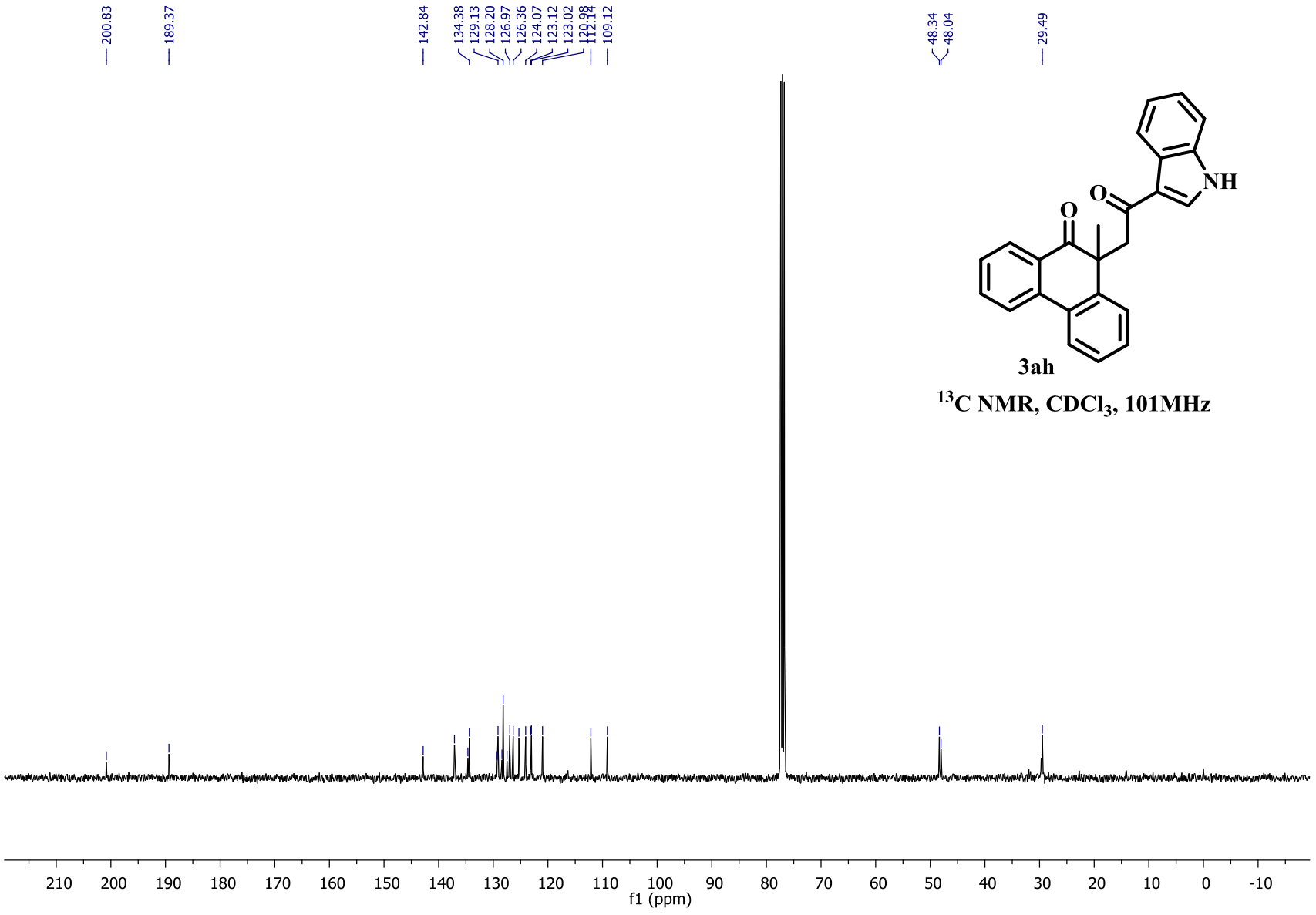

8.22
8.22
8.21
8.20
8.13
8.12
8.11
8.11
8.10
8.09
7.75
7.75
7.75
7.74
7.70
7.70
7.69
7.57
7.57
7.56
7.56
7.47
7.47
7.45
7.44
7.44
7.34
7.33
7.33
7.32
7.30
7.30
7.29
7.11
7.10
7.10
4.32
4.28
4.01
3.97
1.46
O
O
S
3ag
1H NMR, CDCl3, 500MHz
1.00
2.24
1.02
1.07
0.92
1.08
3.25
1.00
1.15
1.16
3.08
10.0
9.5
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)



3ag

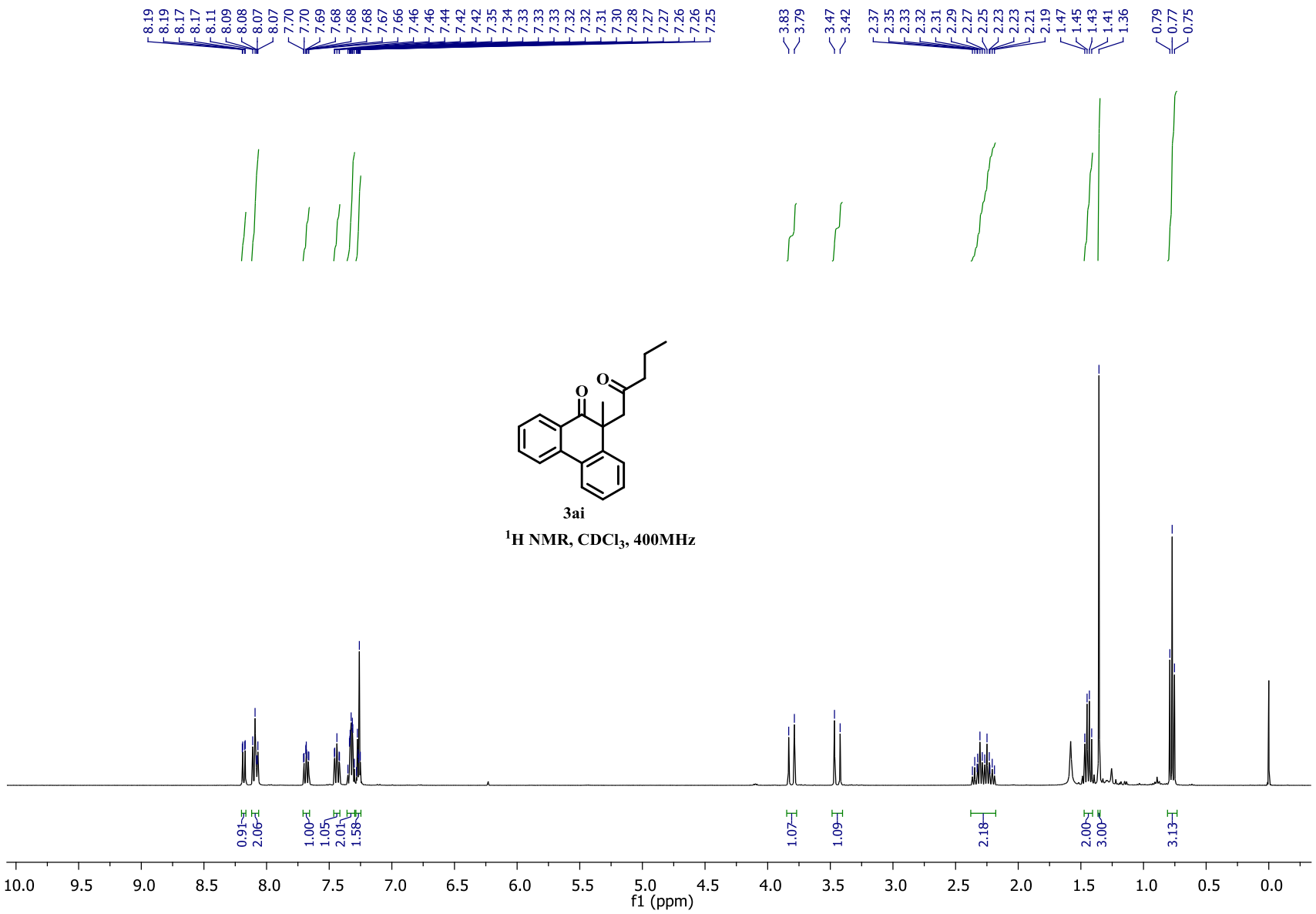
^{13}C NMR, $CDCl_3$, 101MHz


8.70
8.15
8.13
8.11
8.09
8.09
7.73
7.72
7.71
7.70
7.50
7.49
7.48
7.38
7.37
7.36
7.36
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.15
7.13
4.35
4.30
4.10
4.05
1.50
NH
O
O
3ah
^{1}H NMR, CDCl$_3$, 400MHz
0.89
0.96
2.17
2.04
1.06
1.26
2.02
4.54
1.16
1.03
1.10
3.04
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)



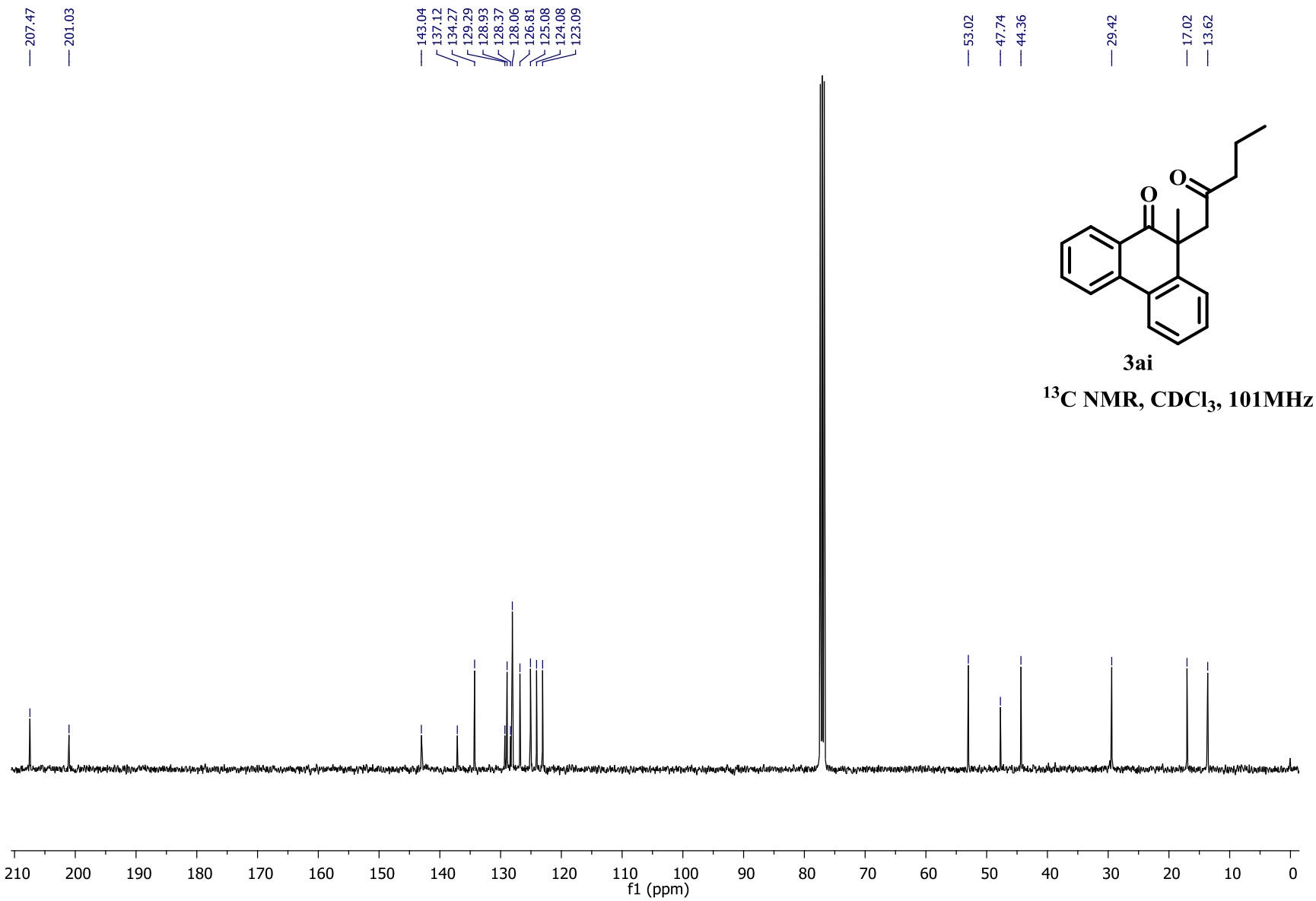
3ah

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



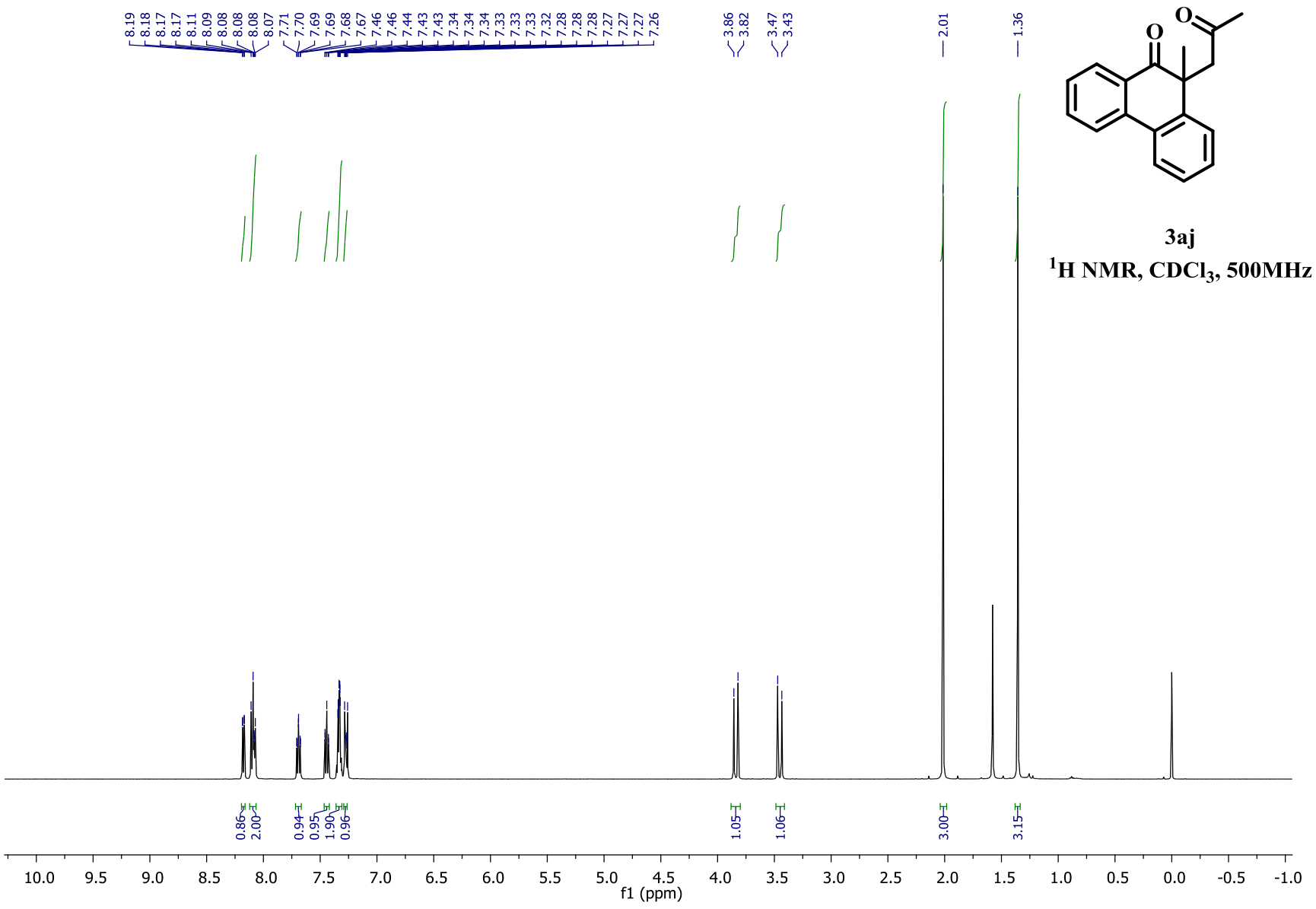
3ai

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



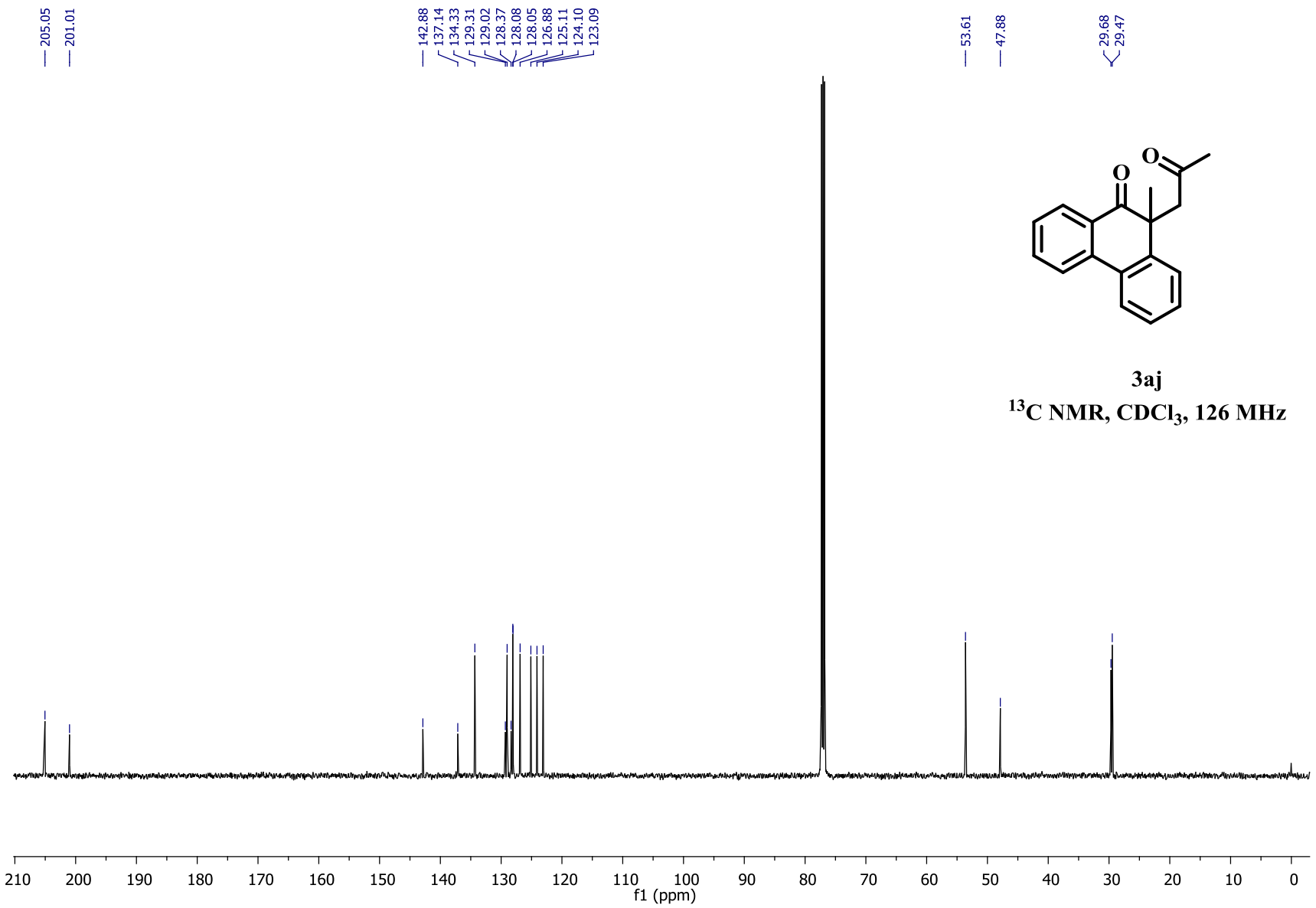
3ai

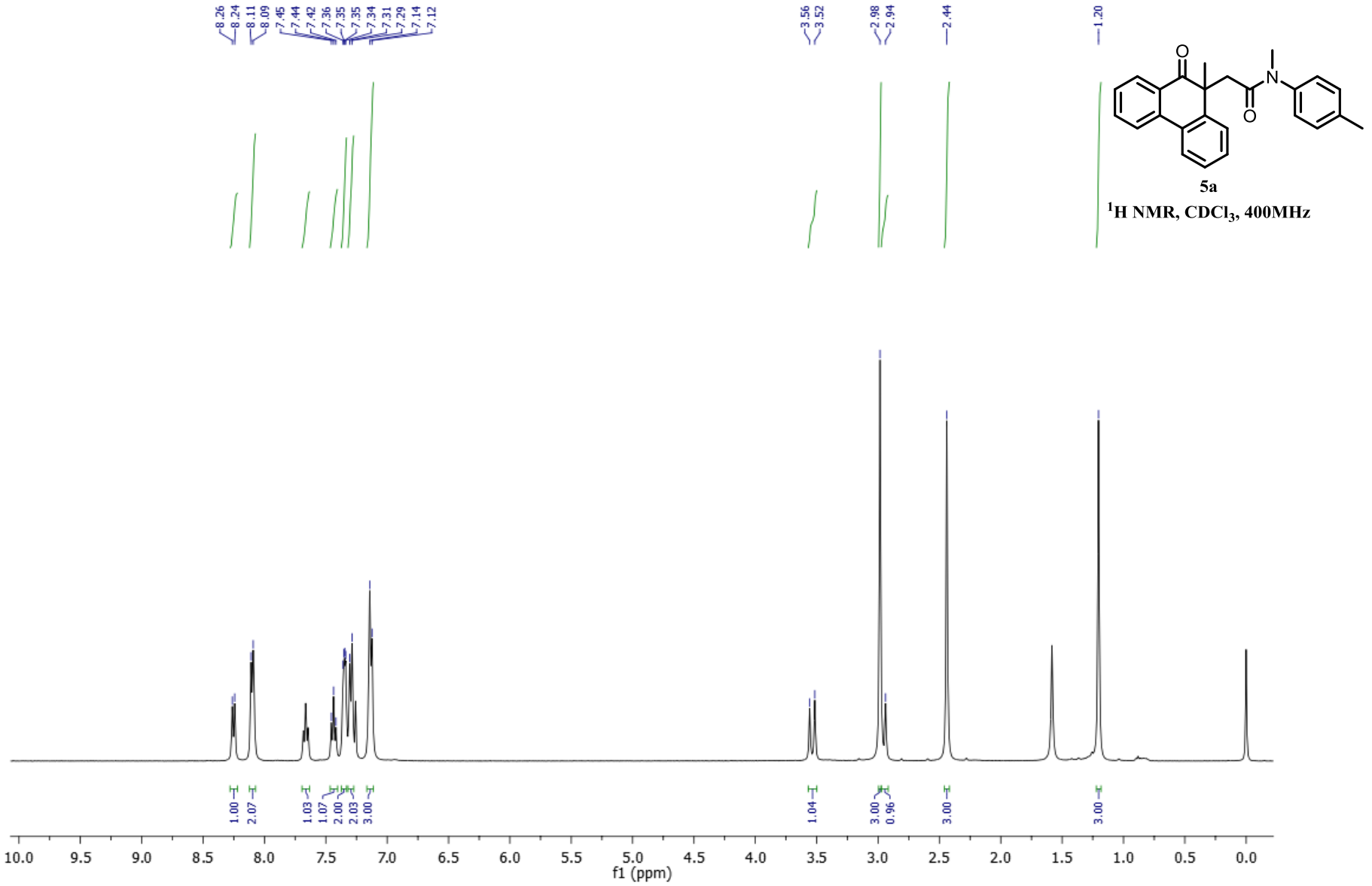
^{13}C NMR, $CDCl_3$, 101MHz



3aj

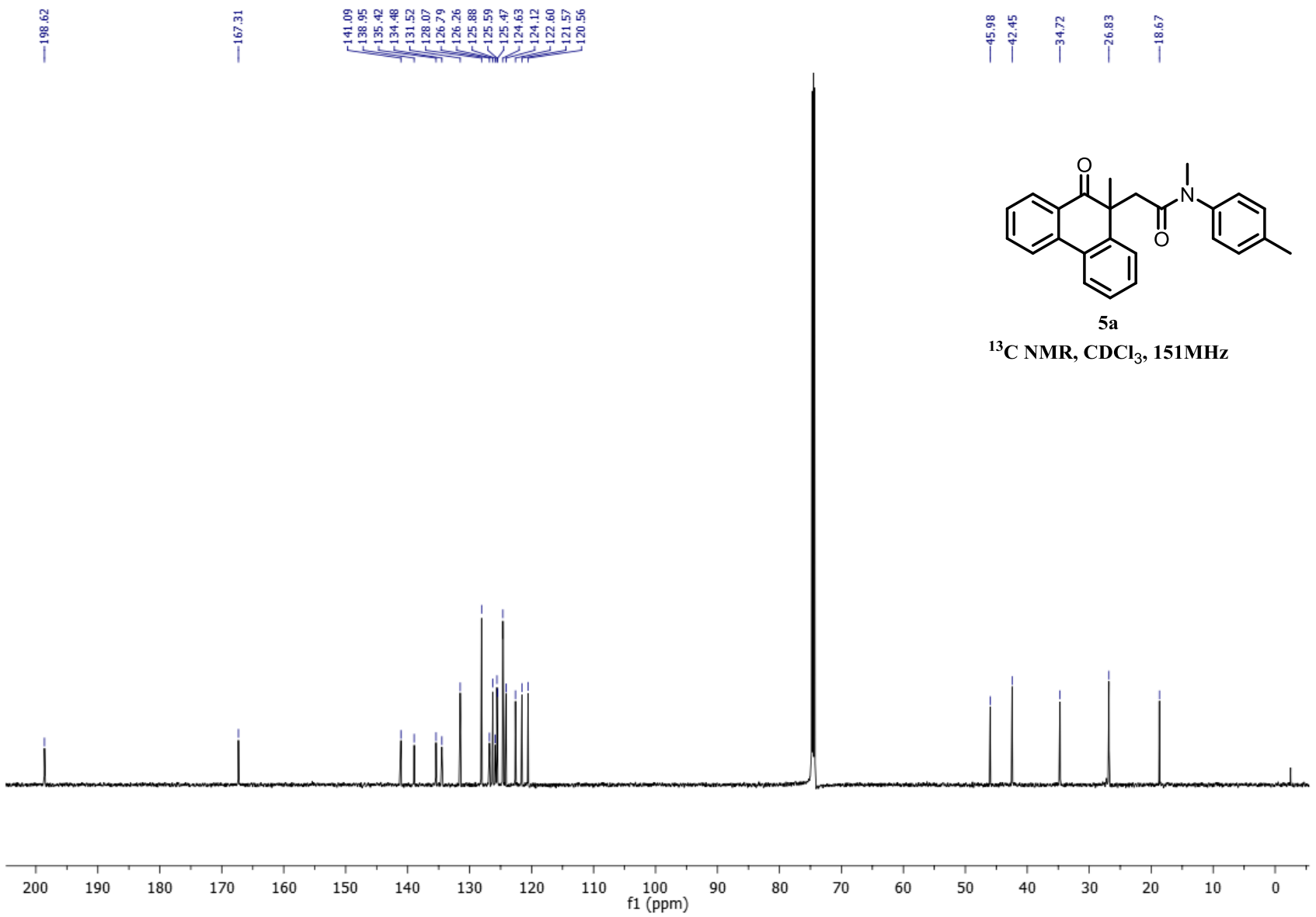
^{1}H NMR, $CDCl_3$, 500MHz


205.05
201.01
142.88
137.14
134.33
129.31
129.02
128.37
128.08
128.05
126.88
125.11
124.10
123.09
53.61
47.88
29.68
29.47
O
O
3aj
13C NMR, CDCl3, 126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



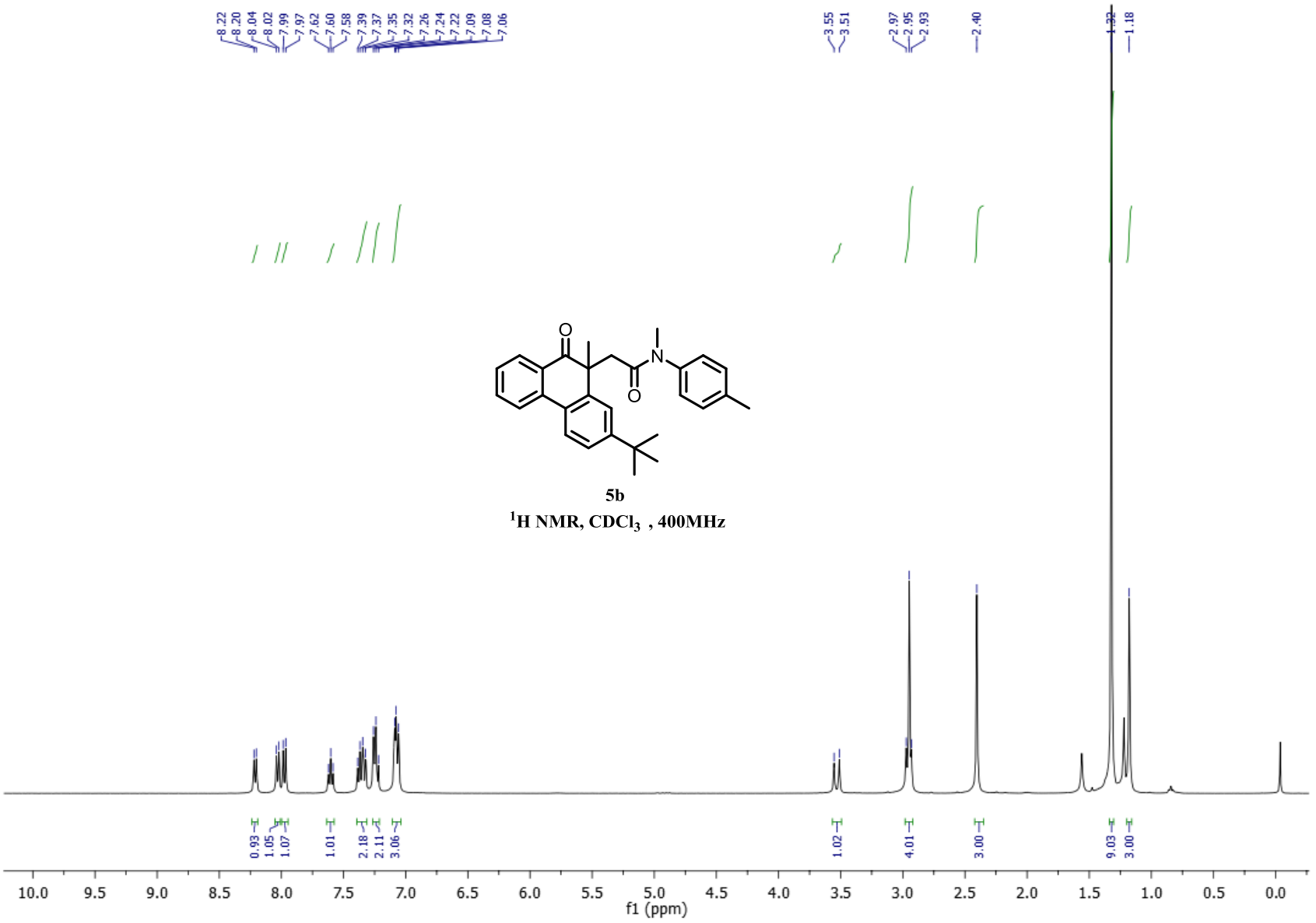
5a

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



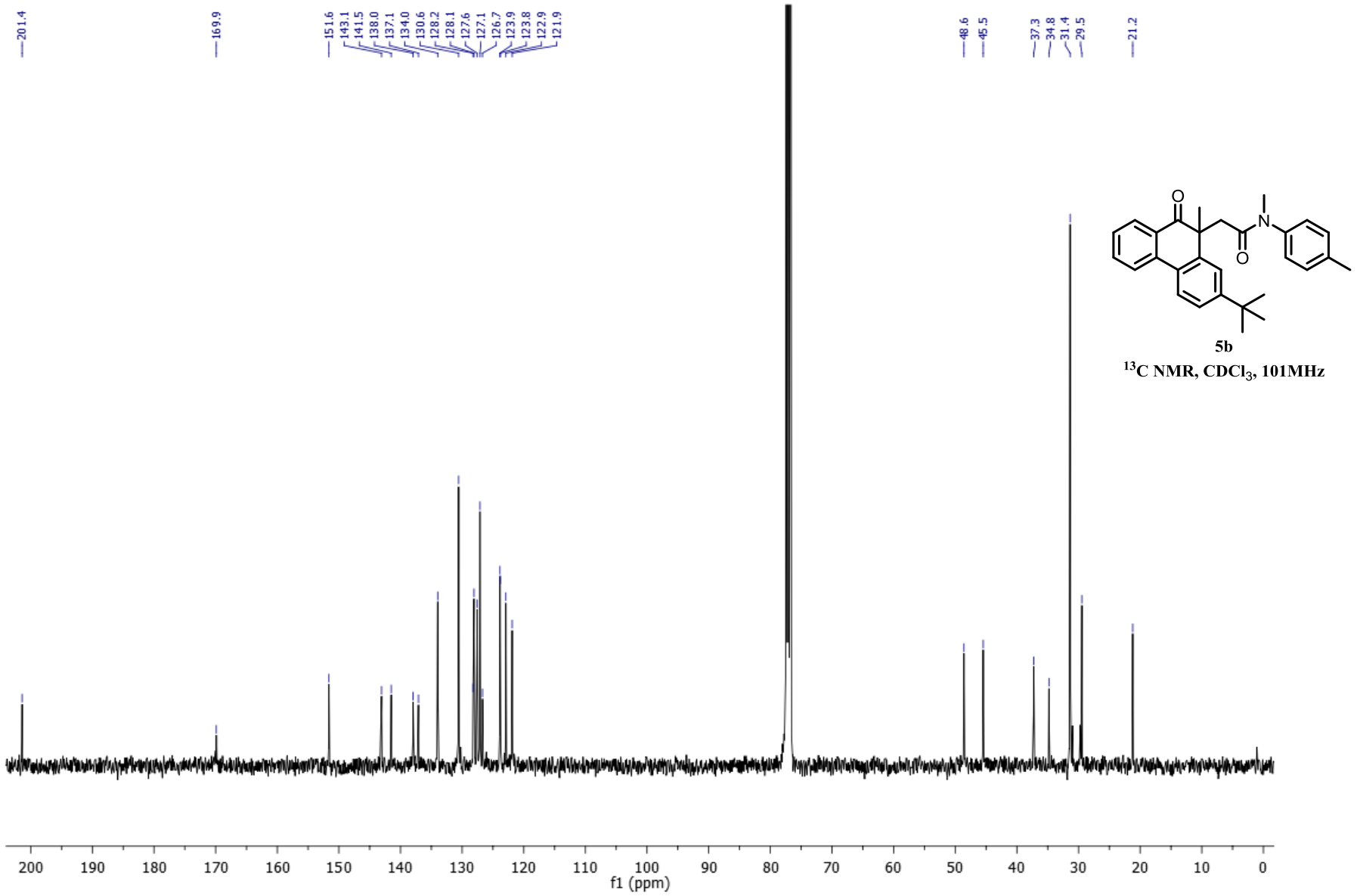
5a

^{13}C NMR, $CDCl_3$, 151MHz



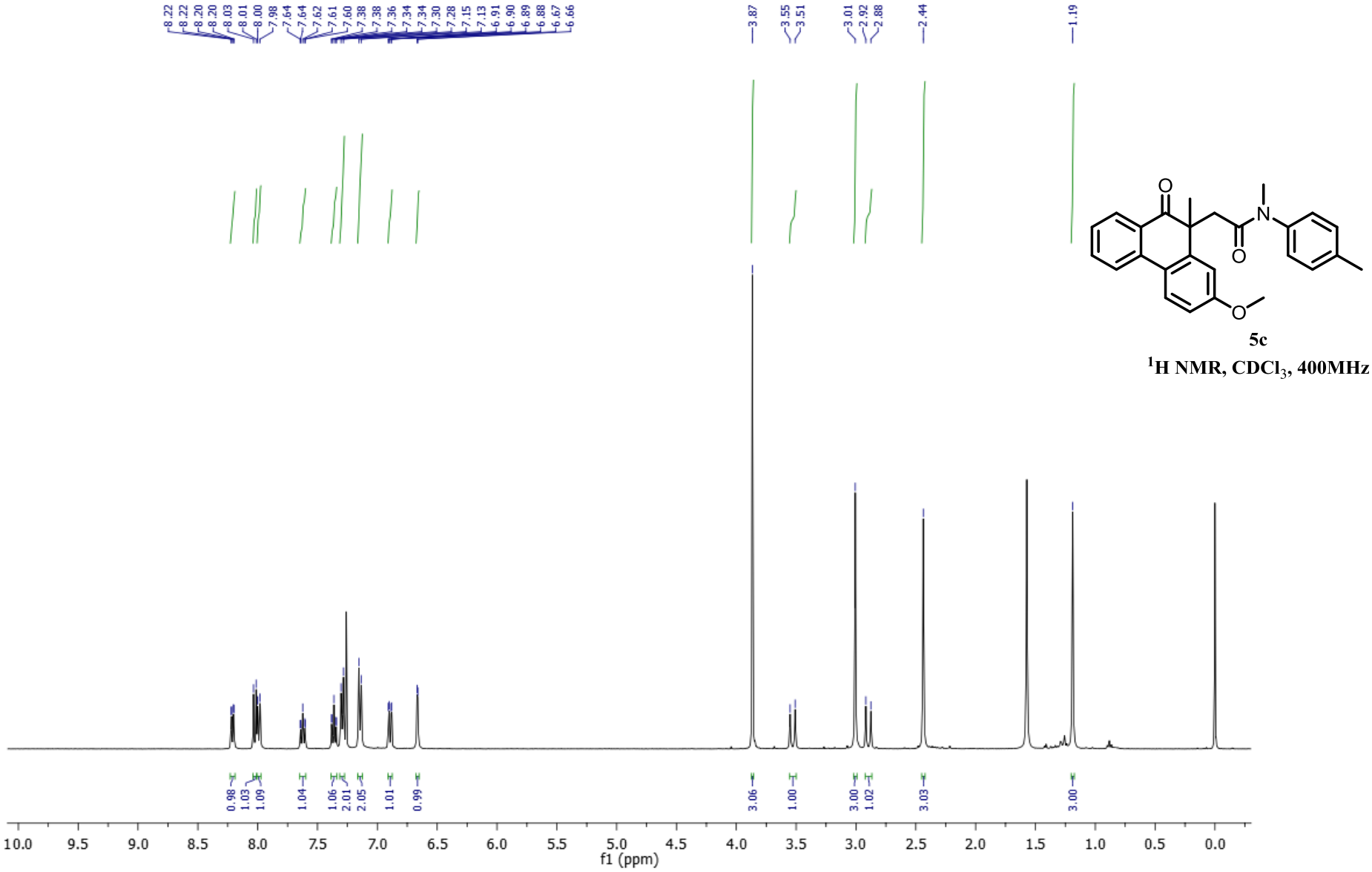
5b

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



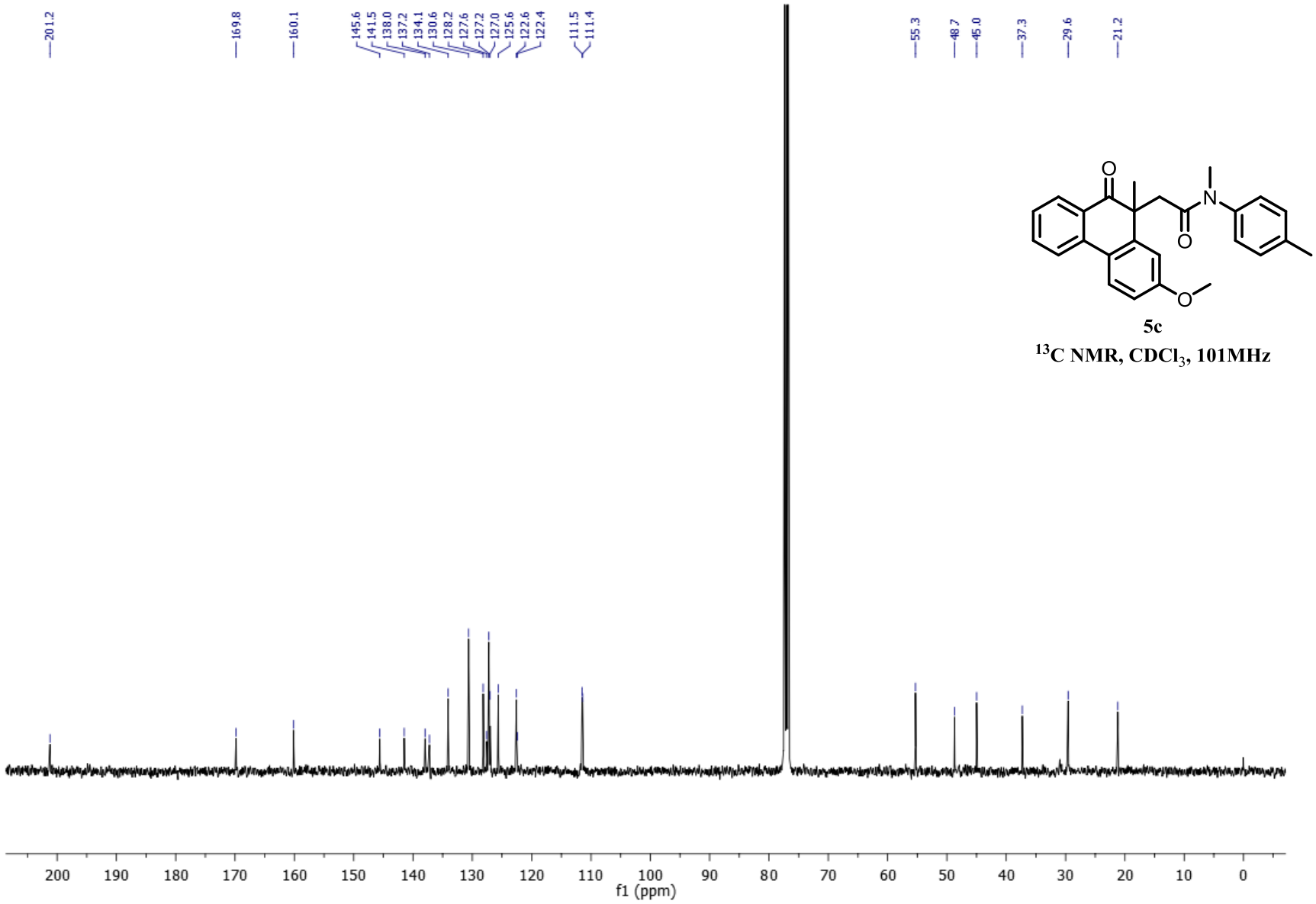
5b

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



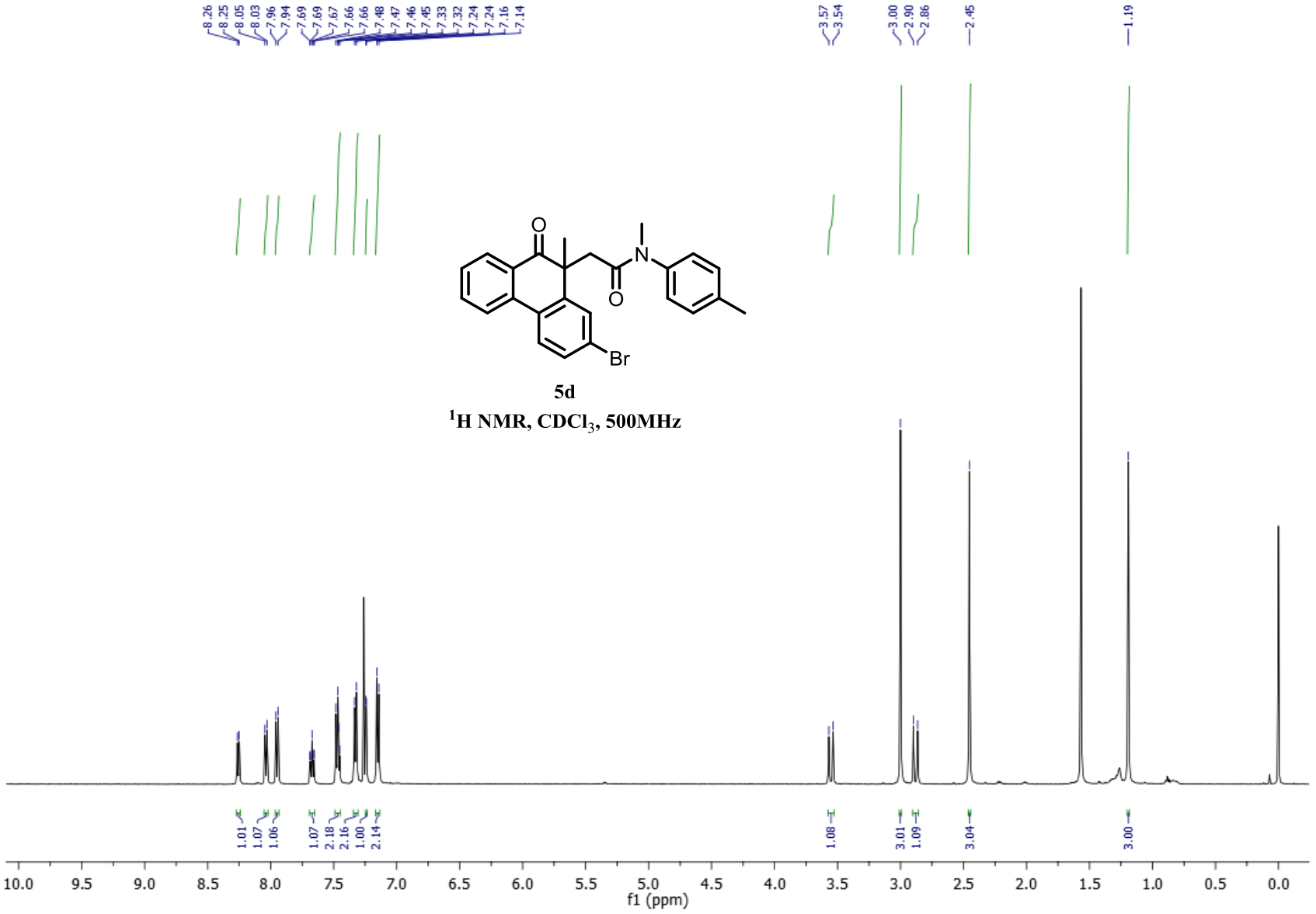
5c

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



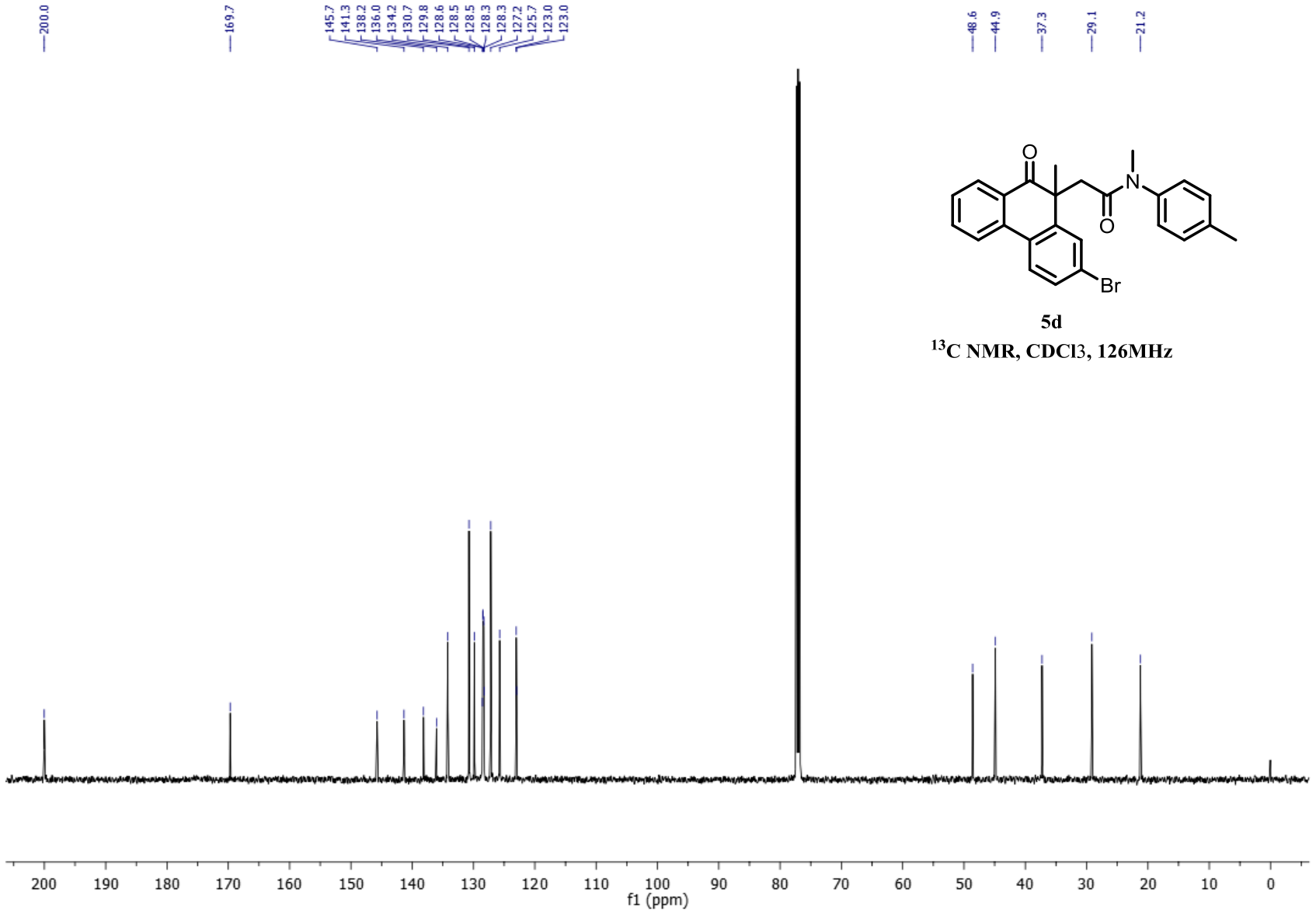
5c

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



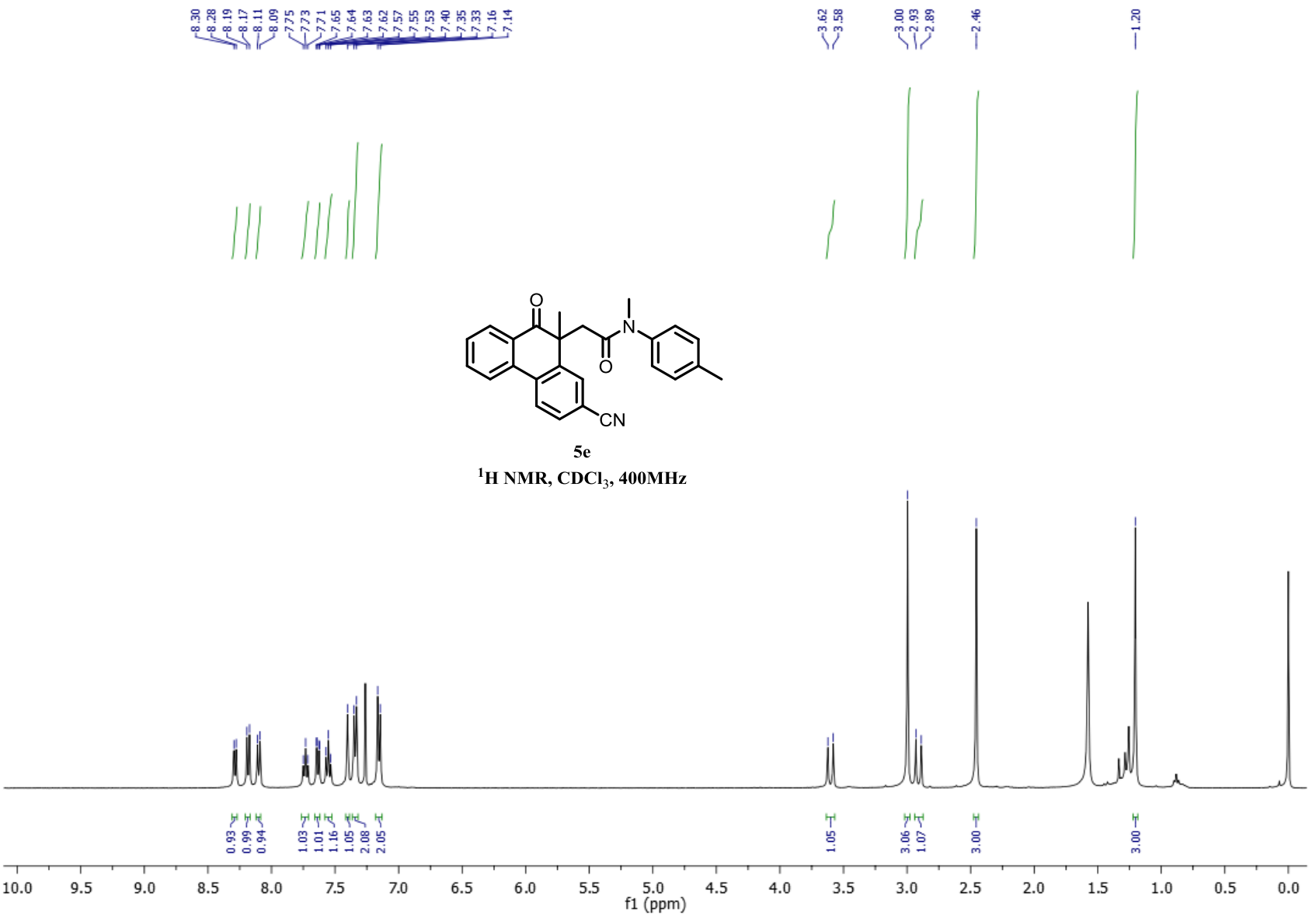
5d

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



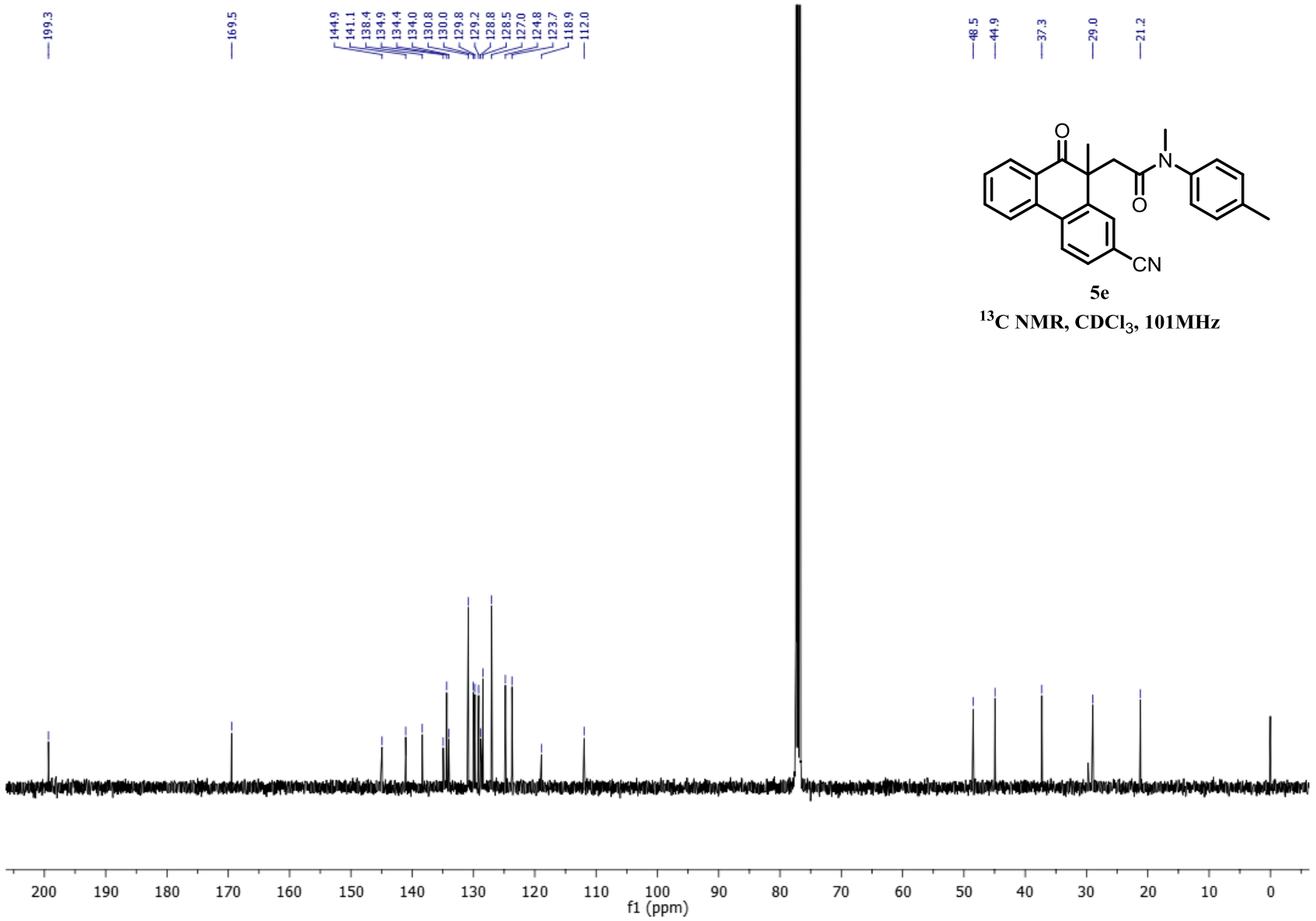
5d

^{13}C NMR, CDCl3, 126MHz



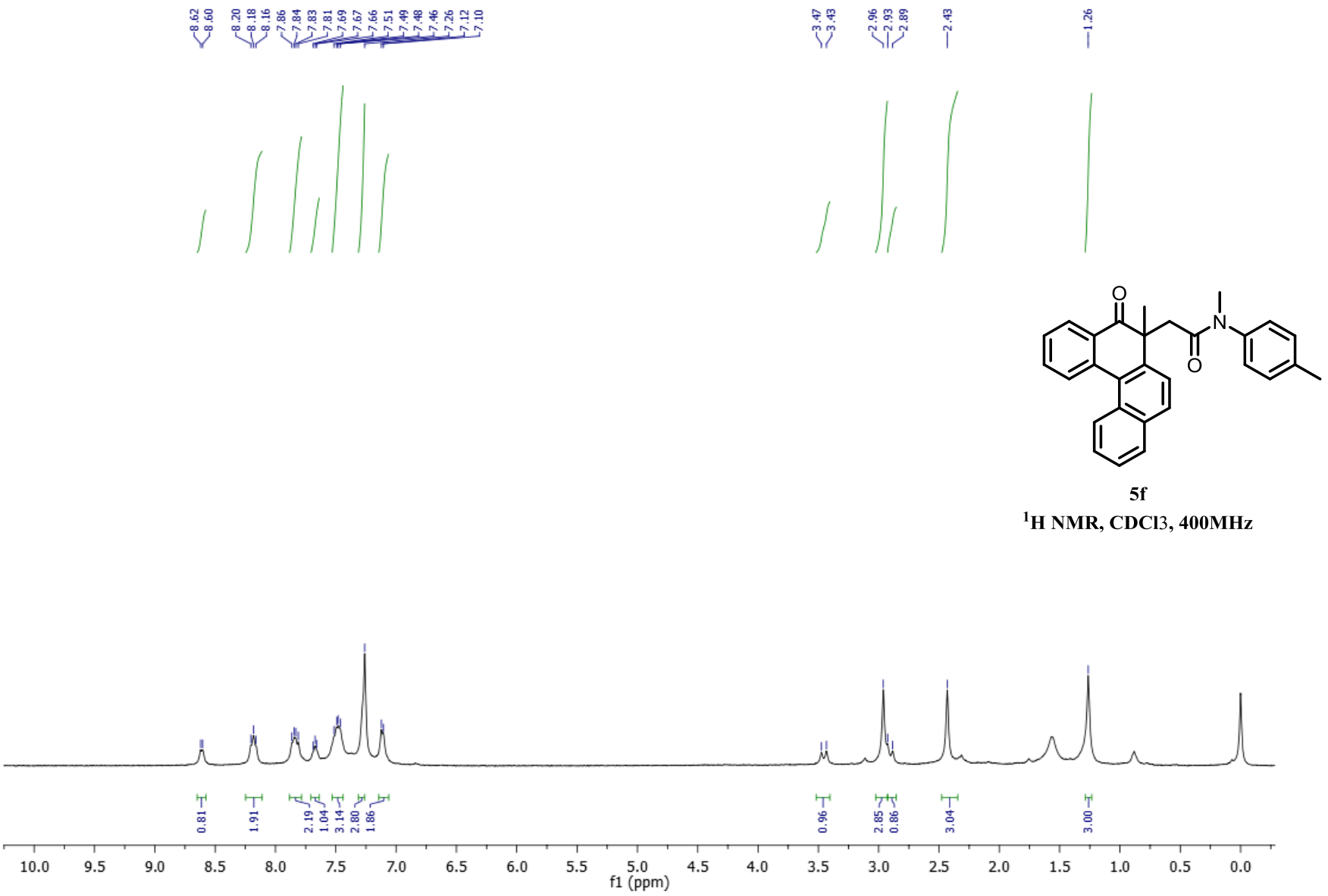
5e

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



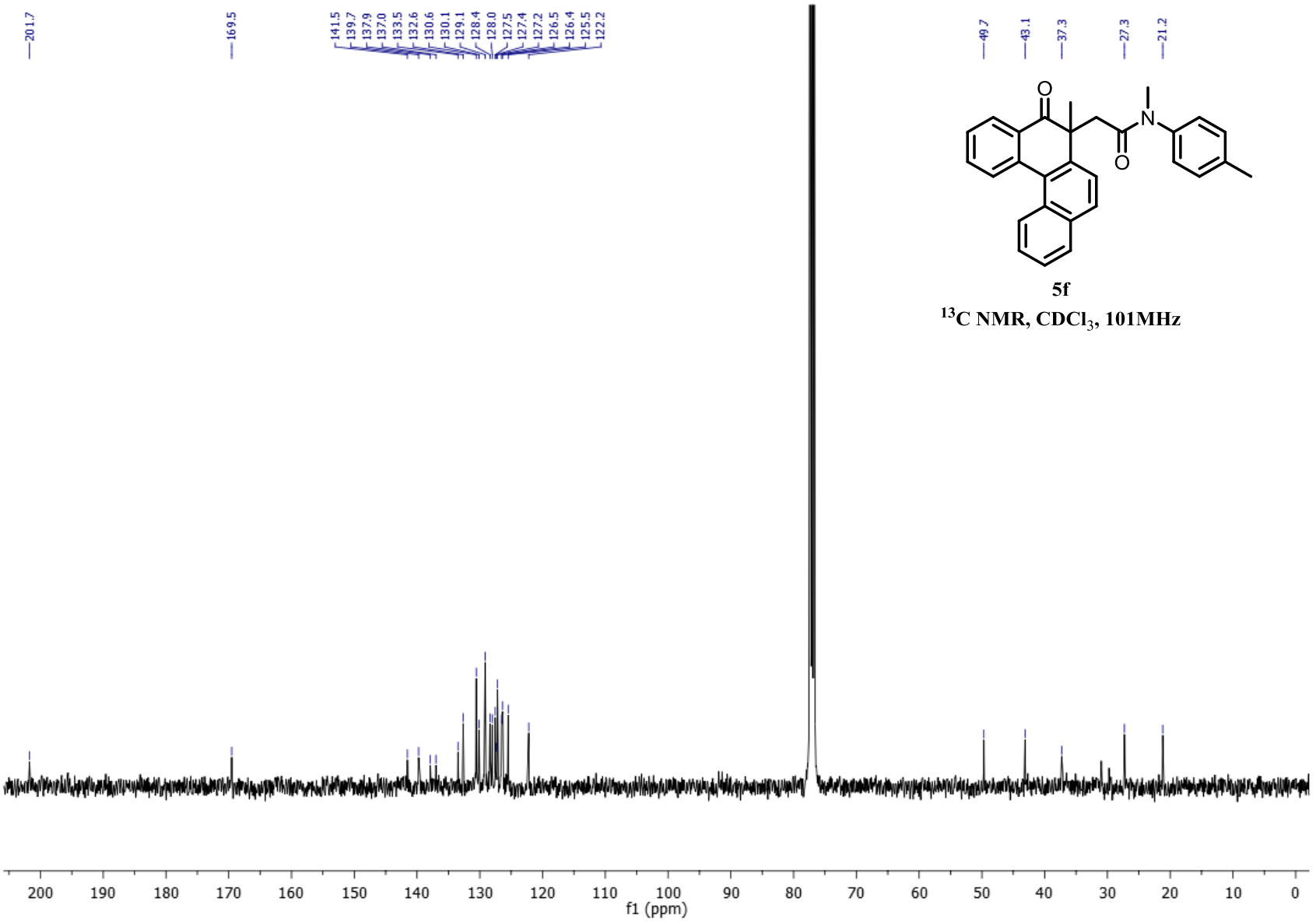
5e

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



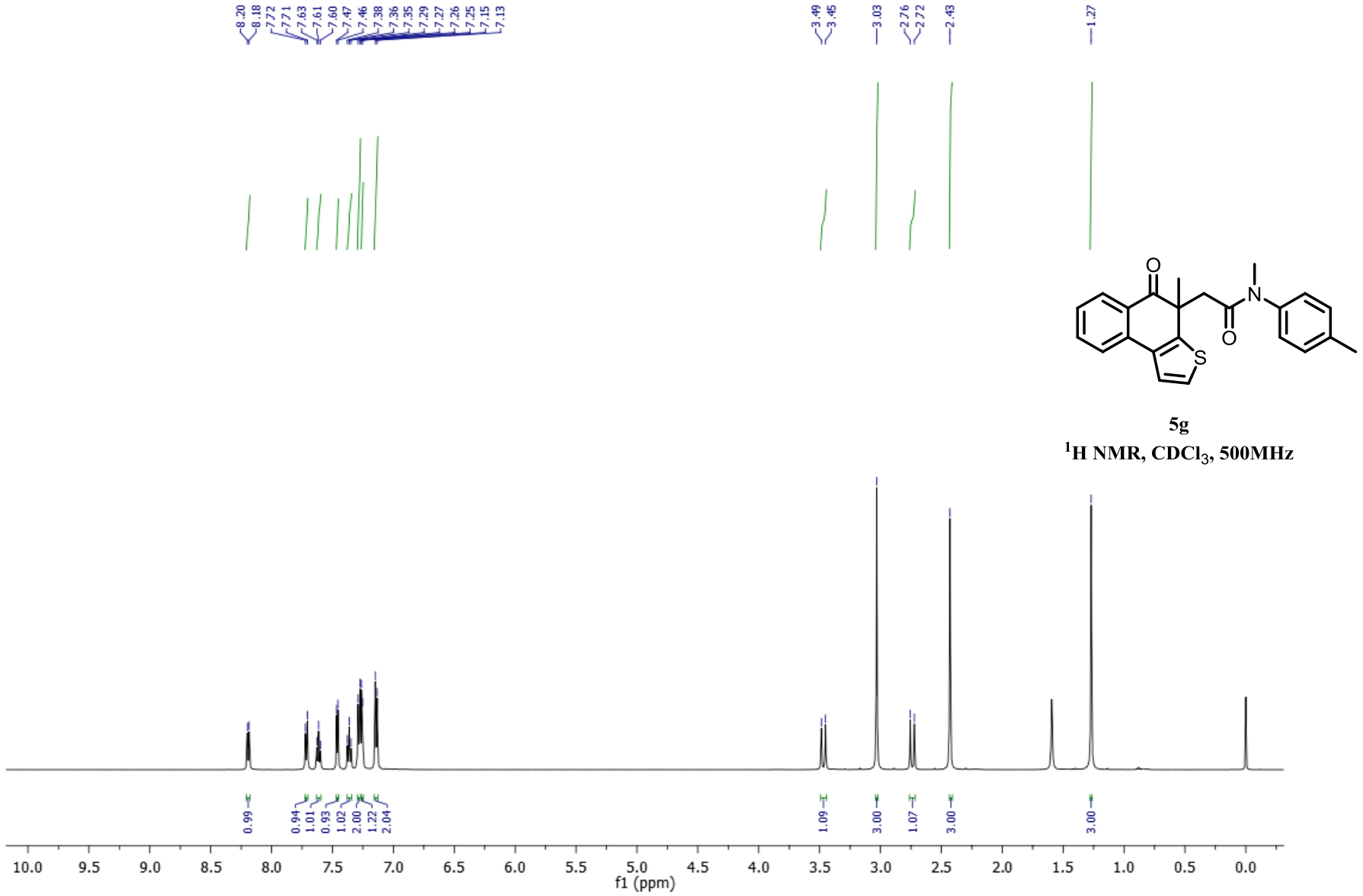
5f

^{1}H NMR, CDCl3, 400MHz



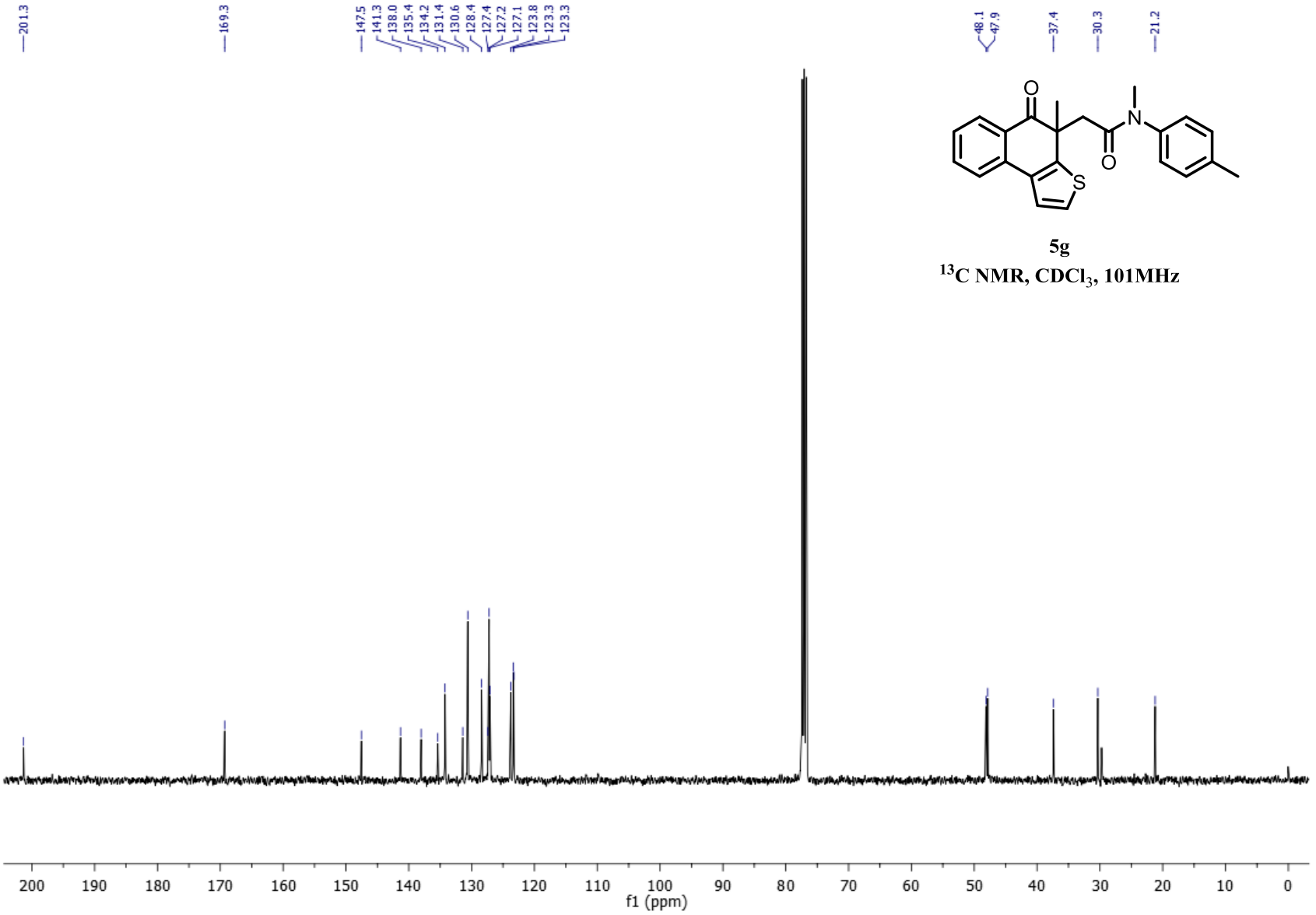
5f

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



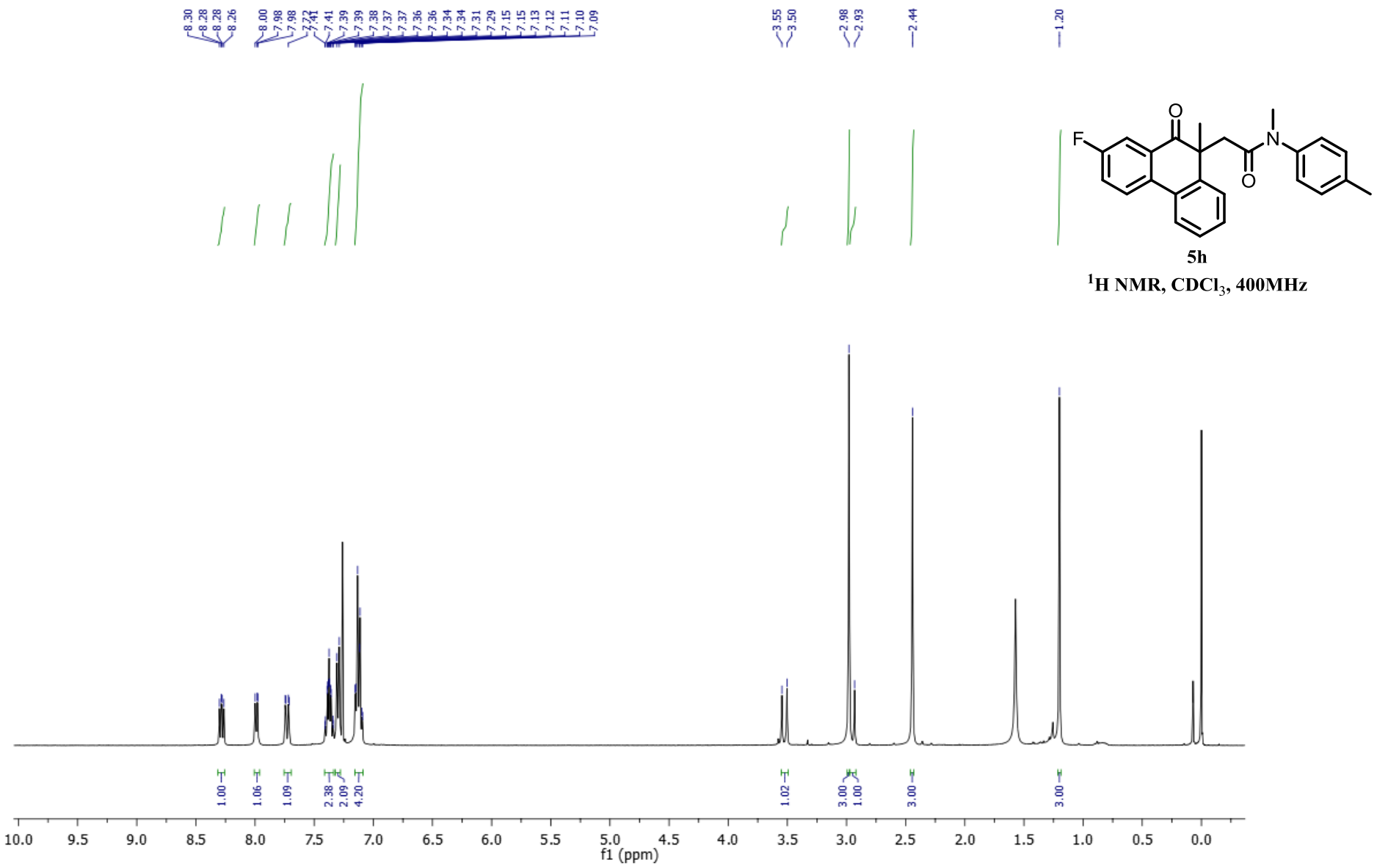
5g

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



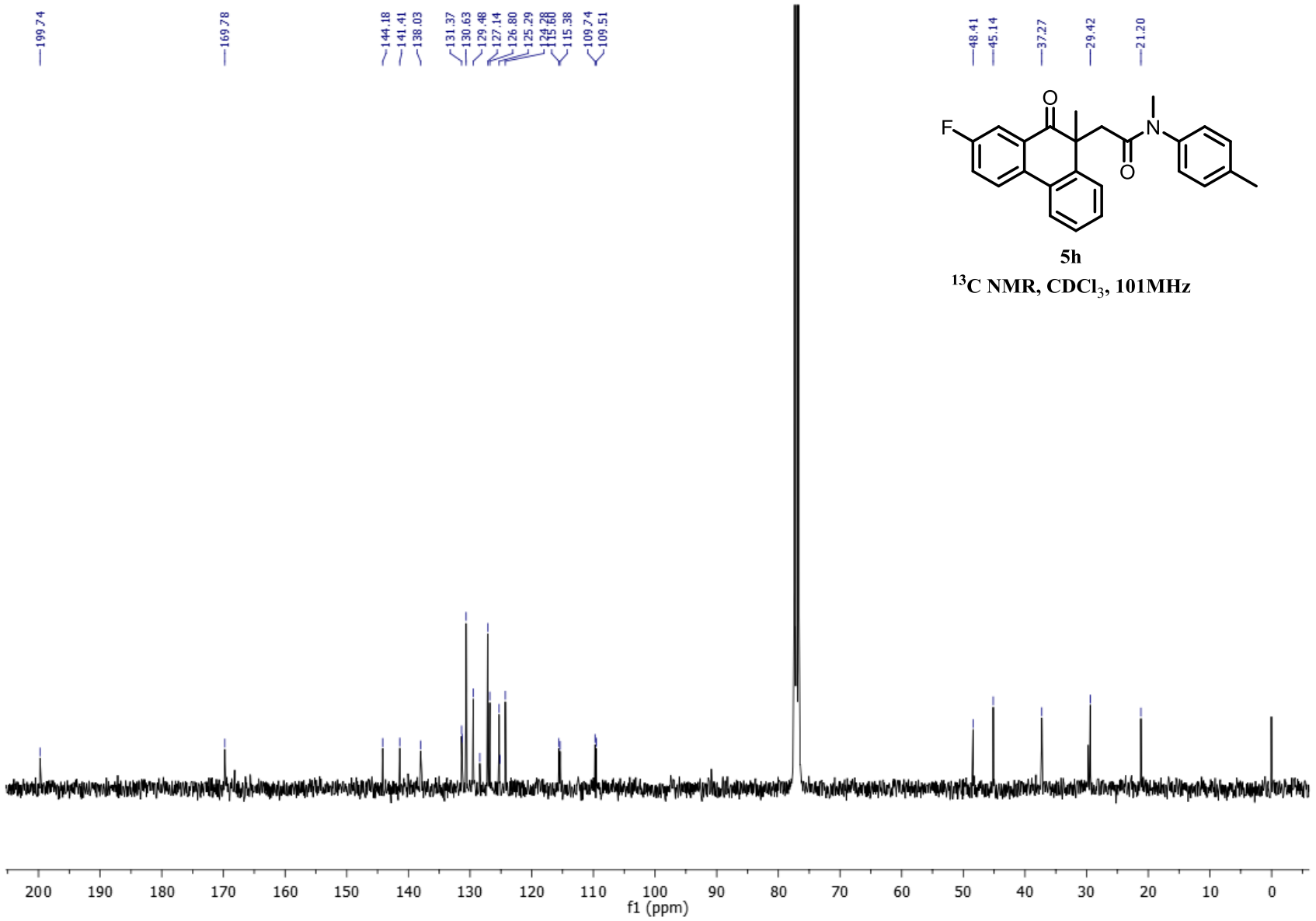
5g

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



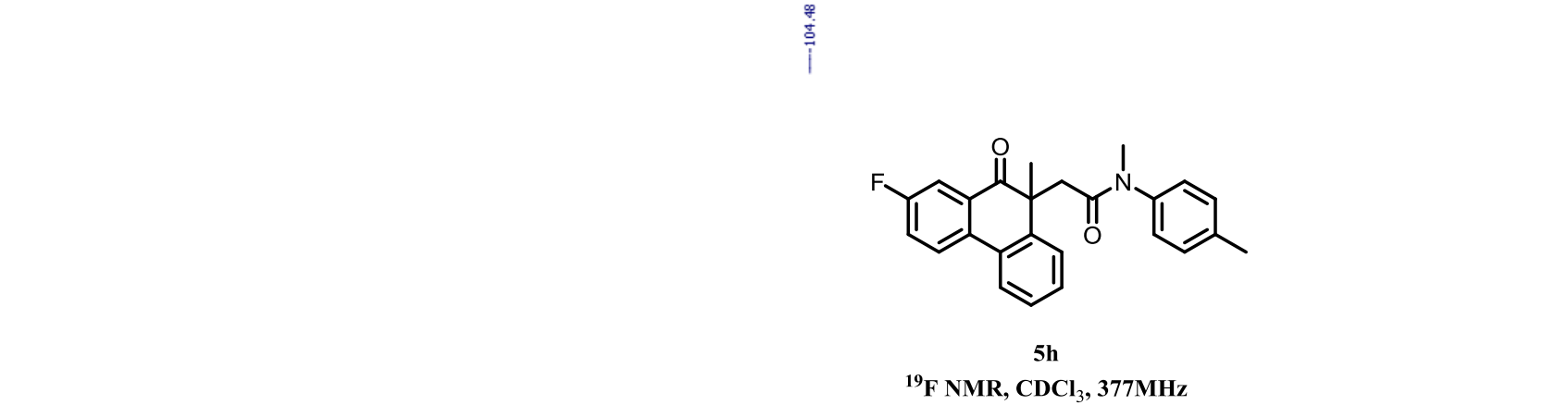
5h

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



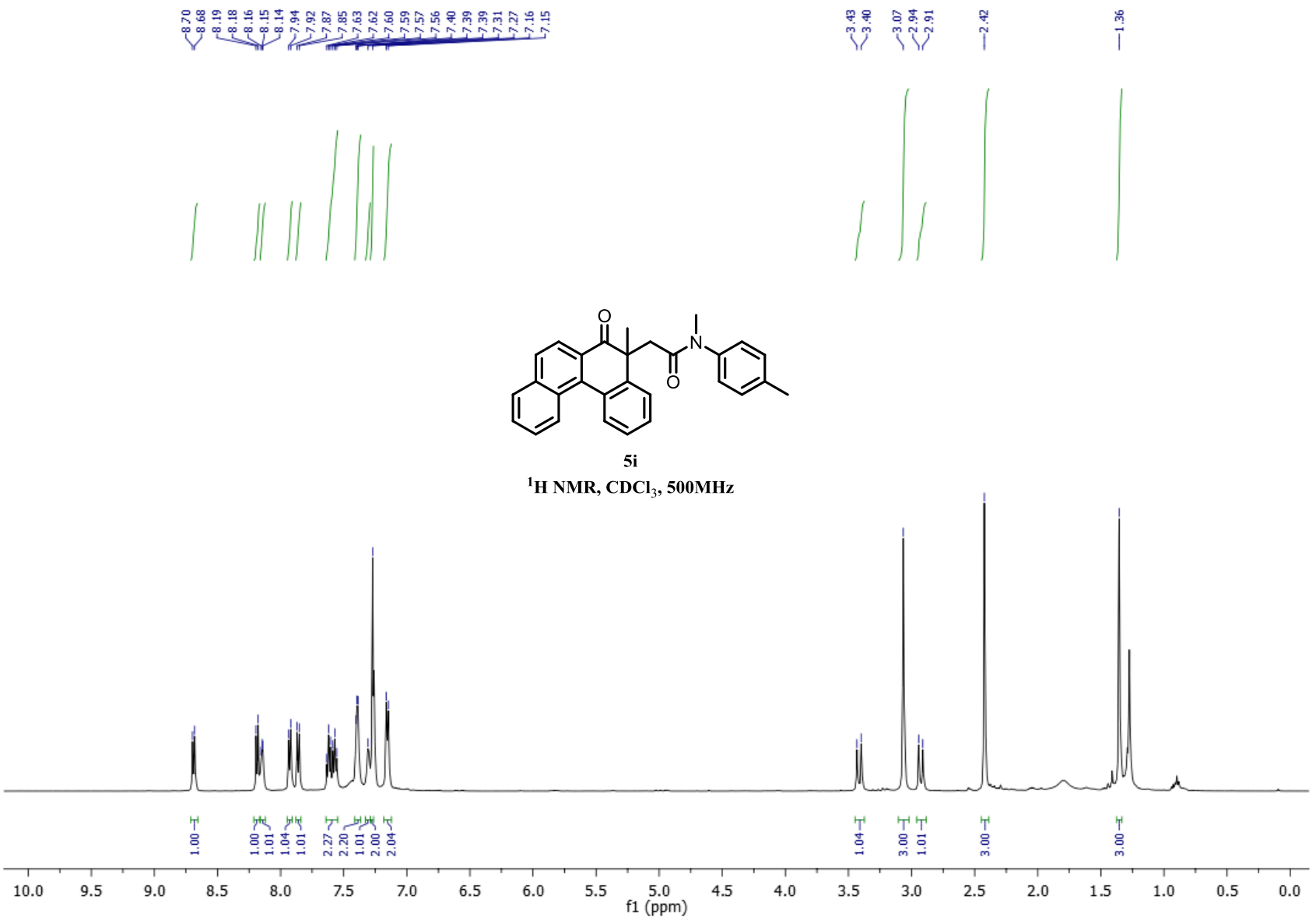
5h

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



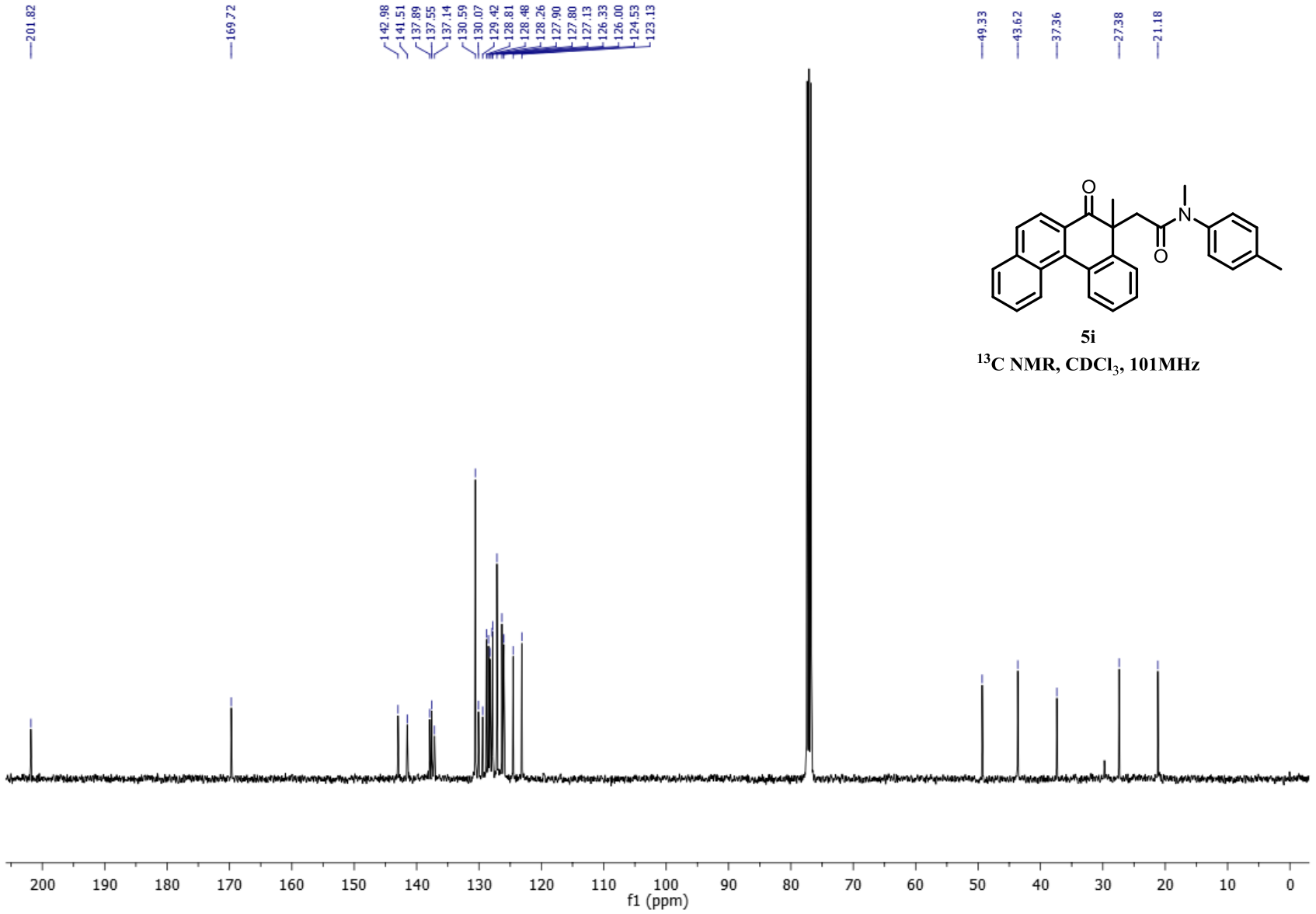
5h

^{19}F NMR, $CDCl_3$, 377MHz



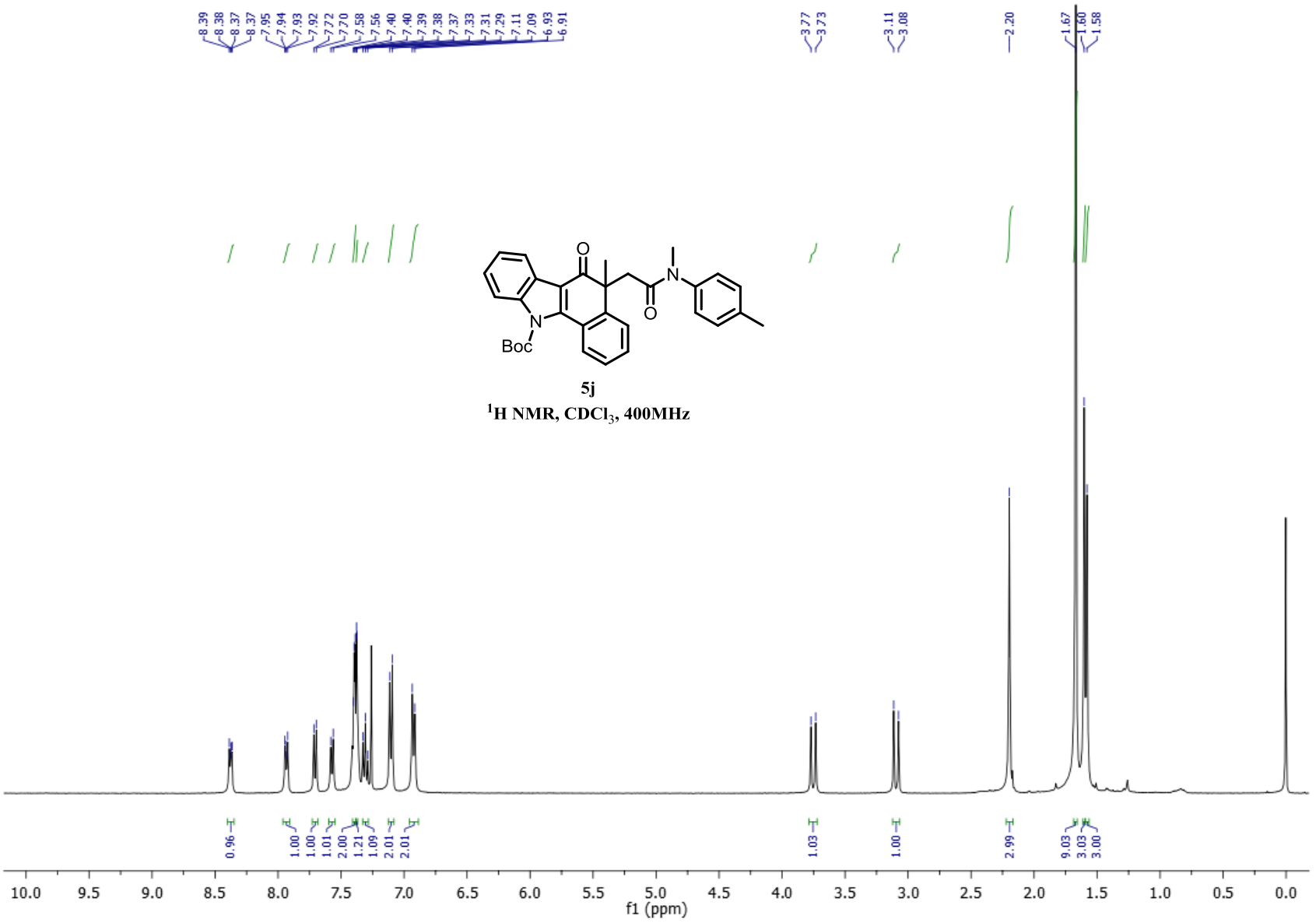
5i

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



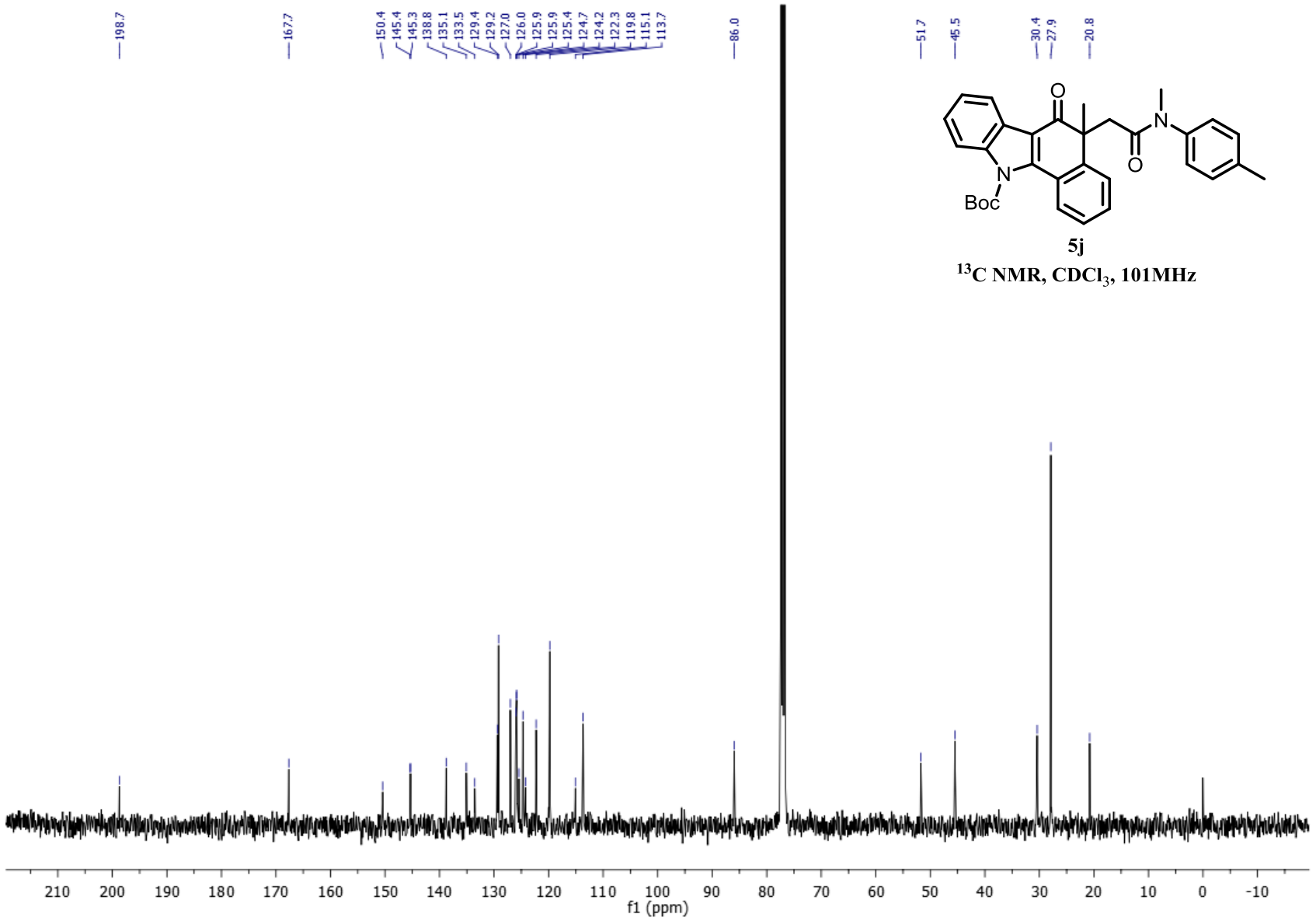
5i

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



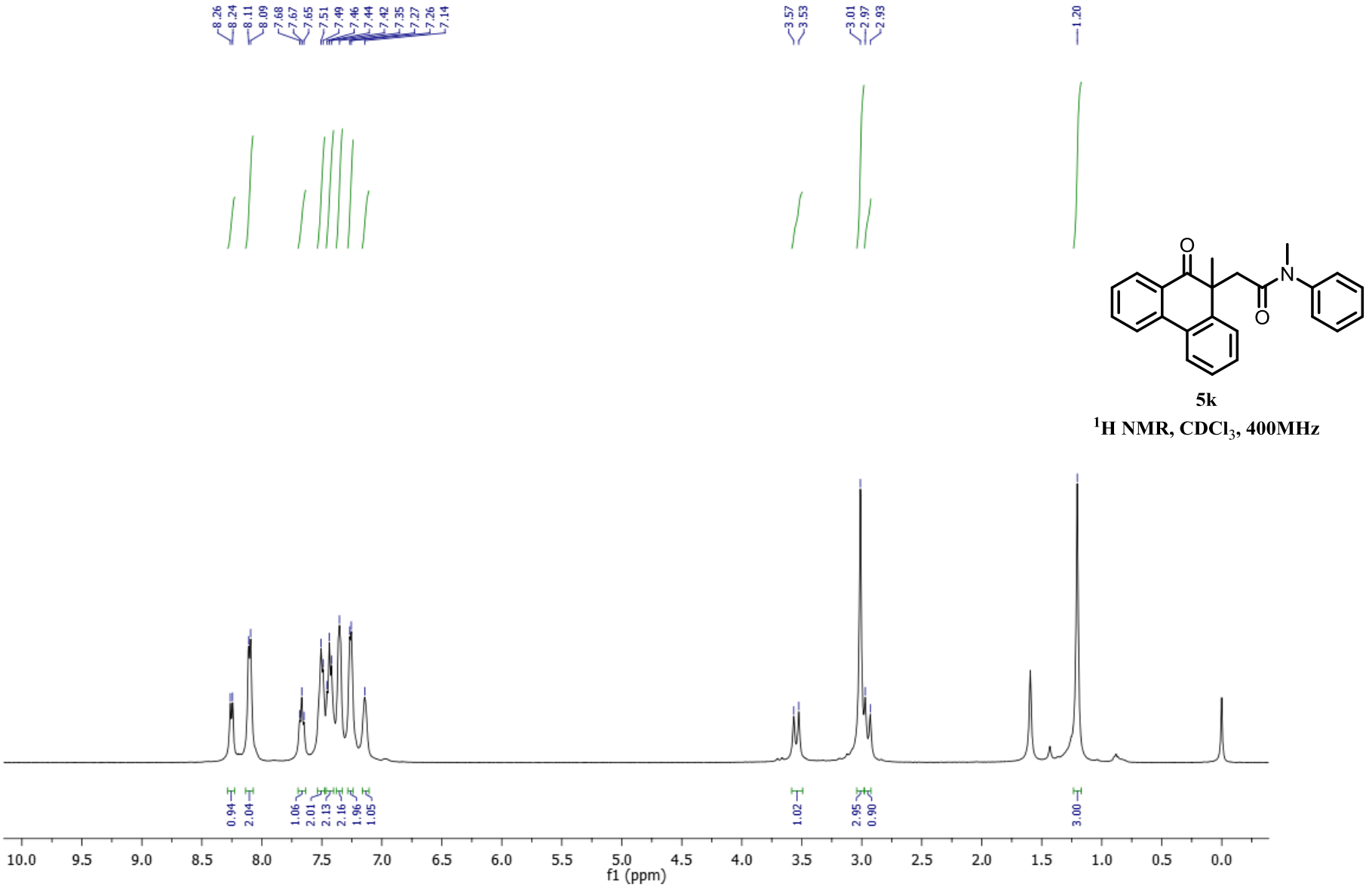
5j

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



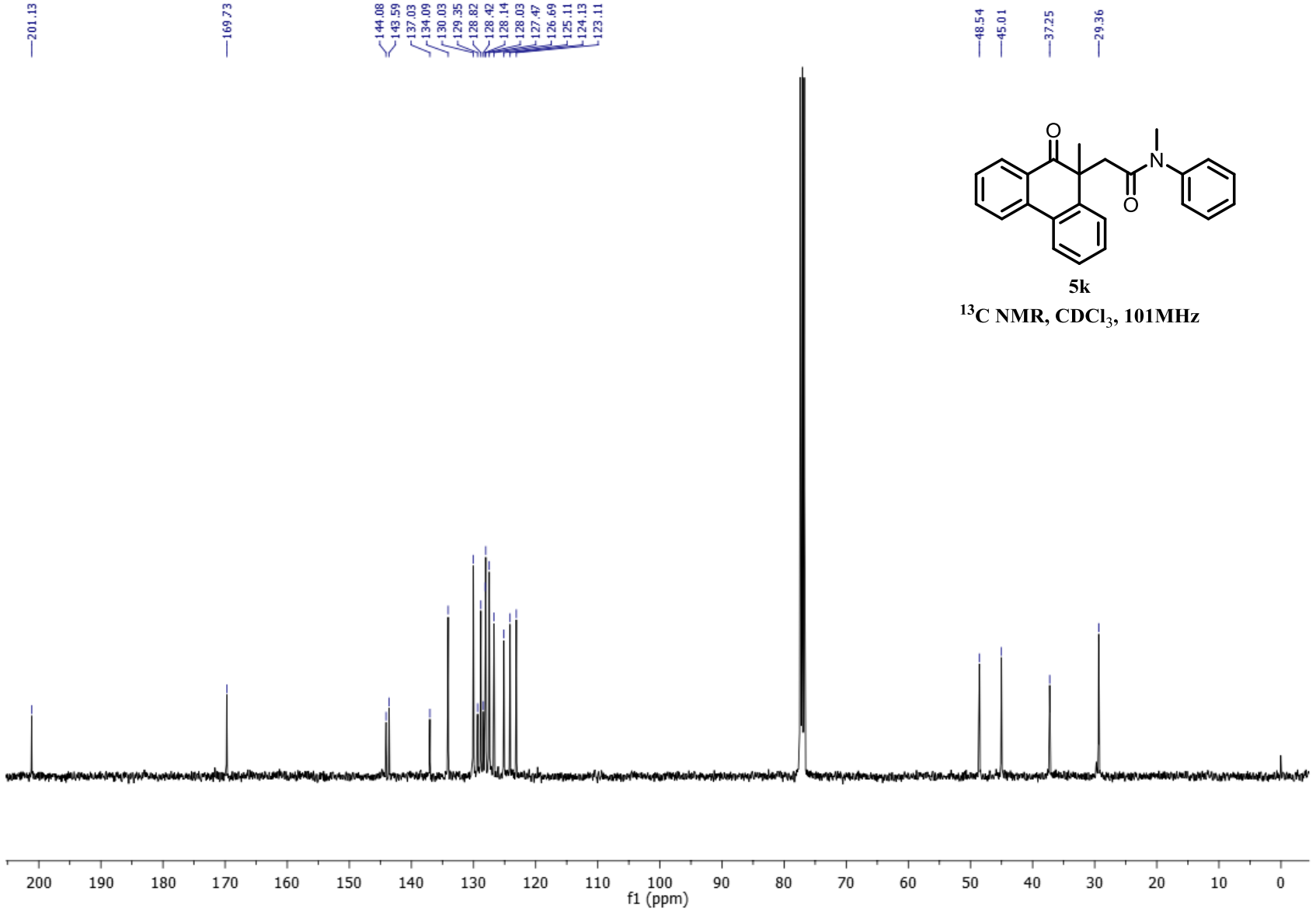
5j

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



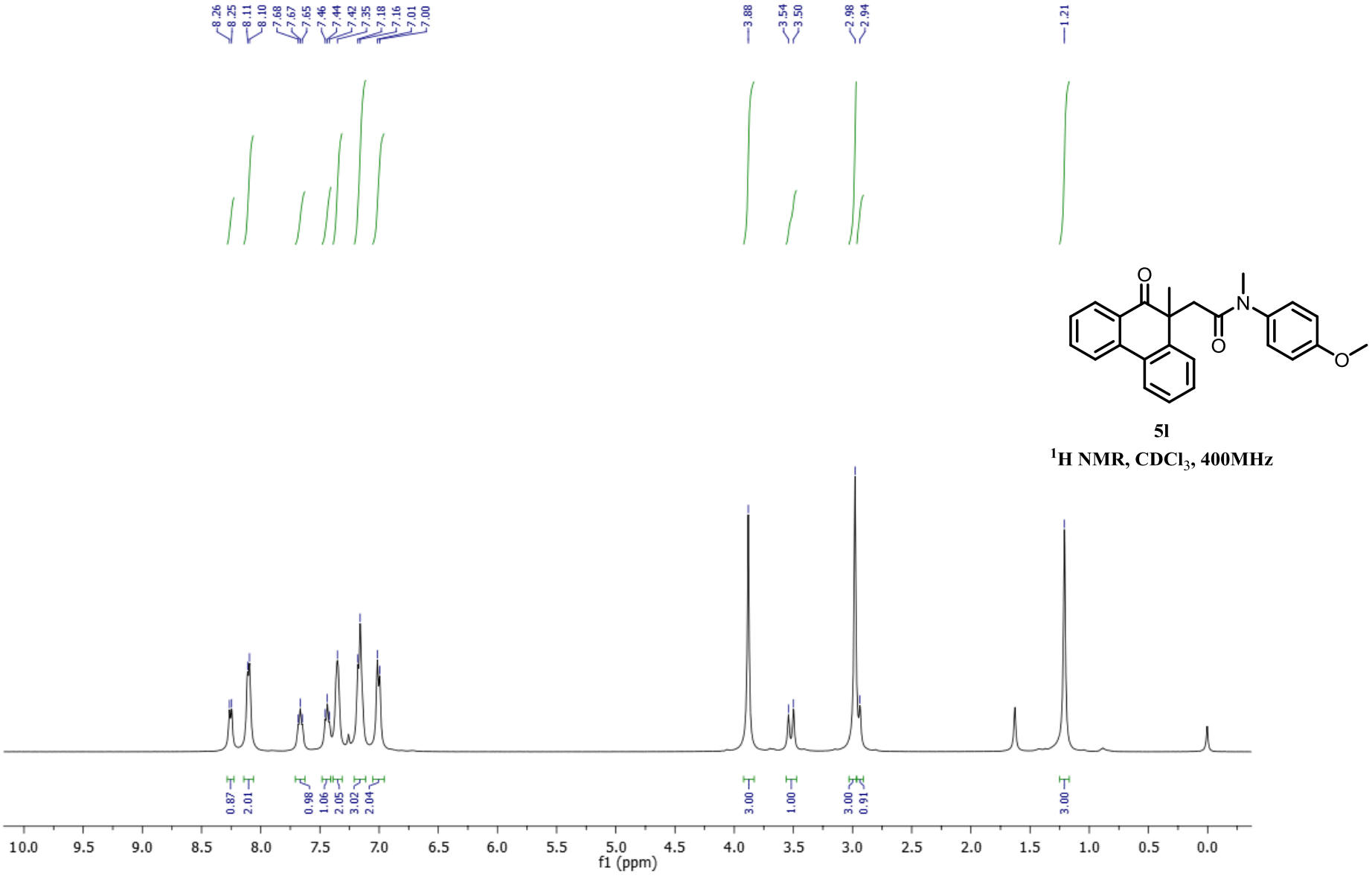
5k

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



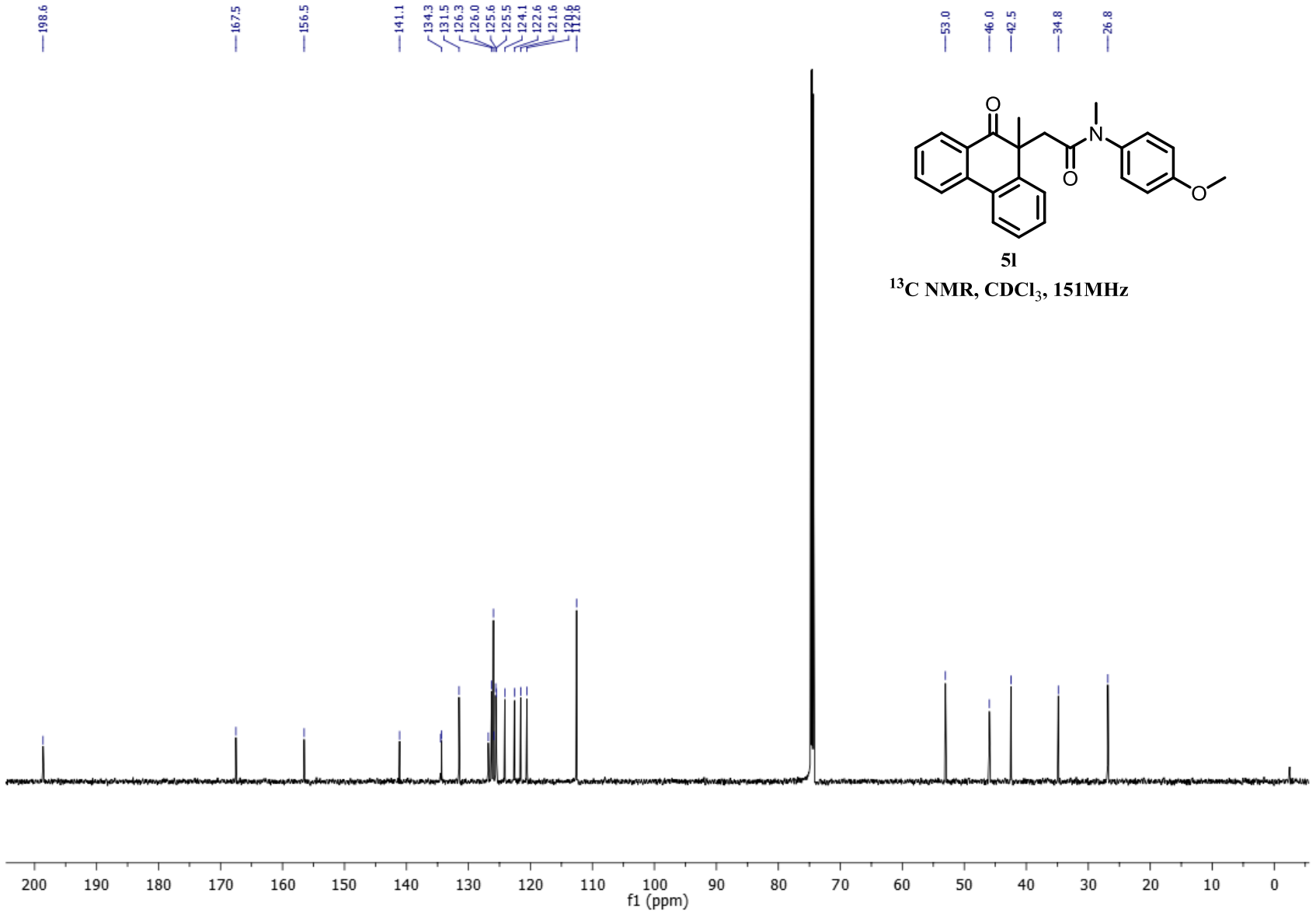
5k

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



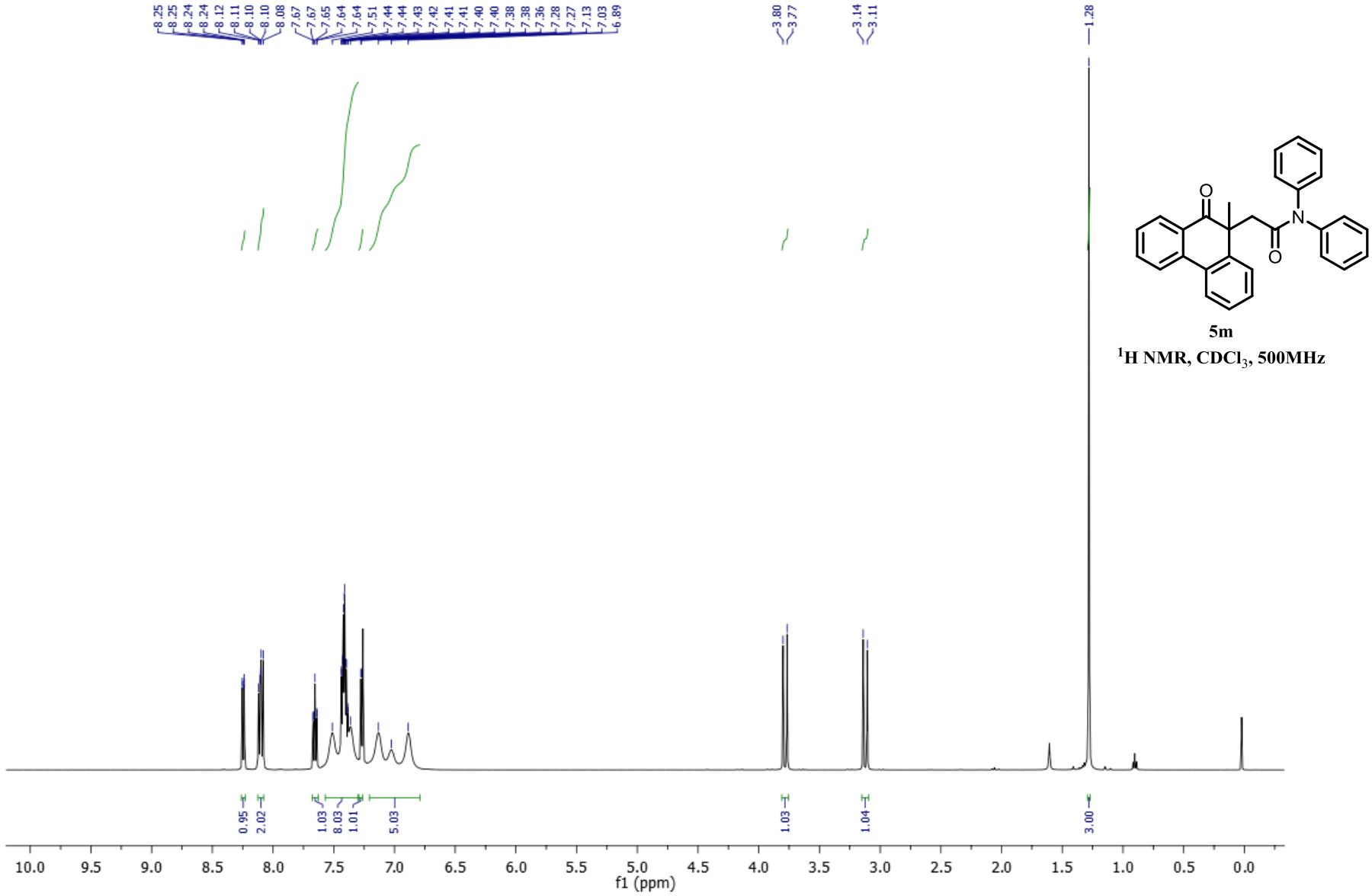
5l

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



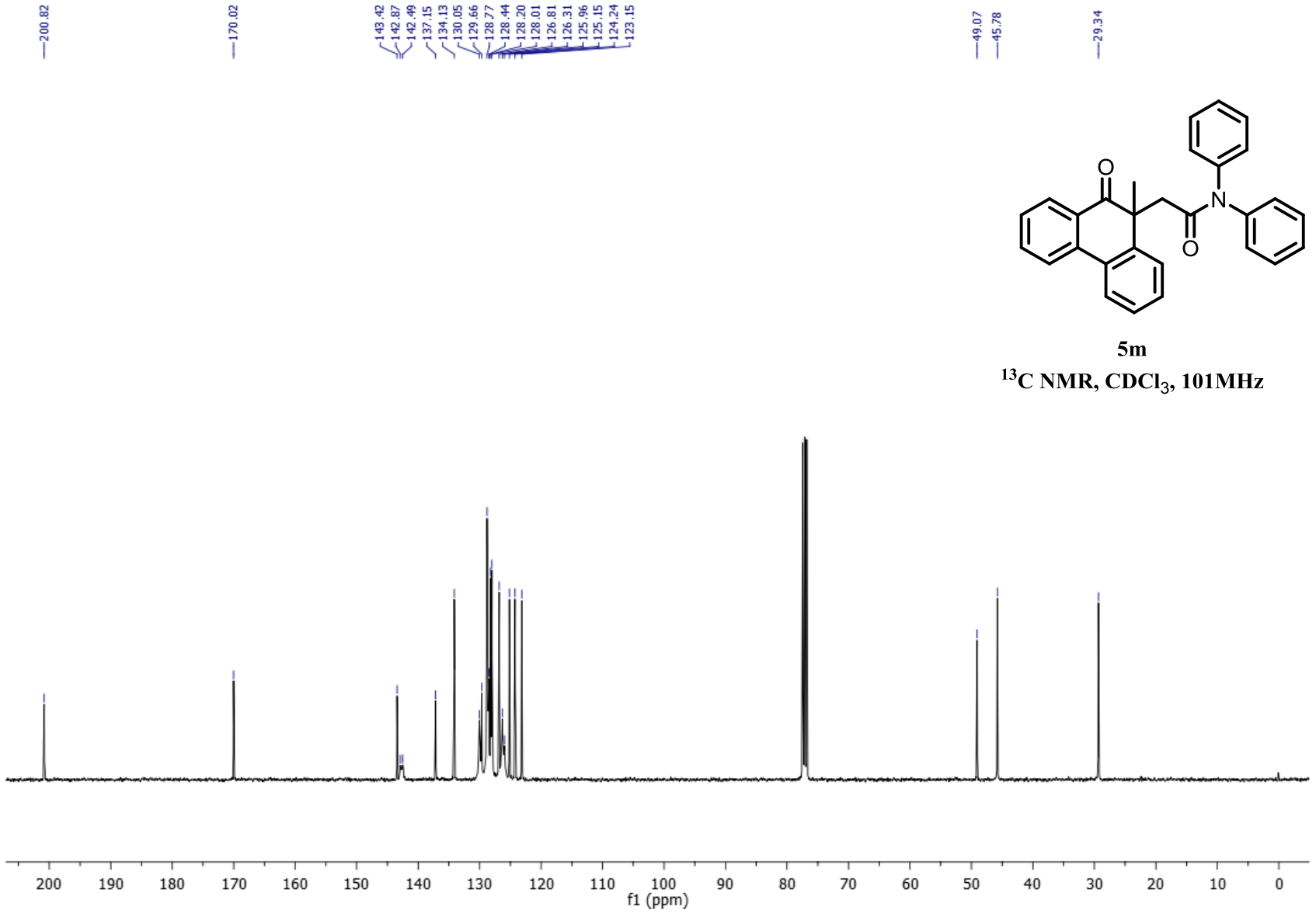
5l

^{13}C NMR, $CDCl_3$, 151MHz



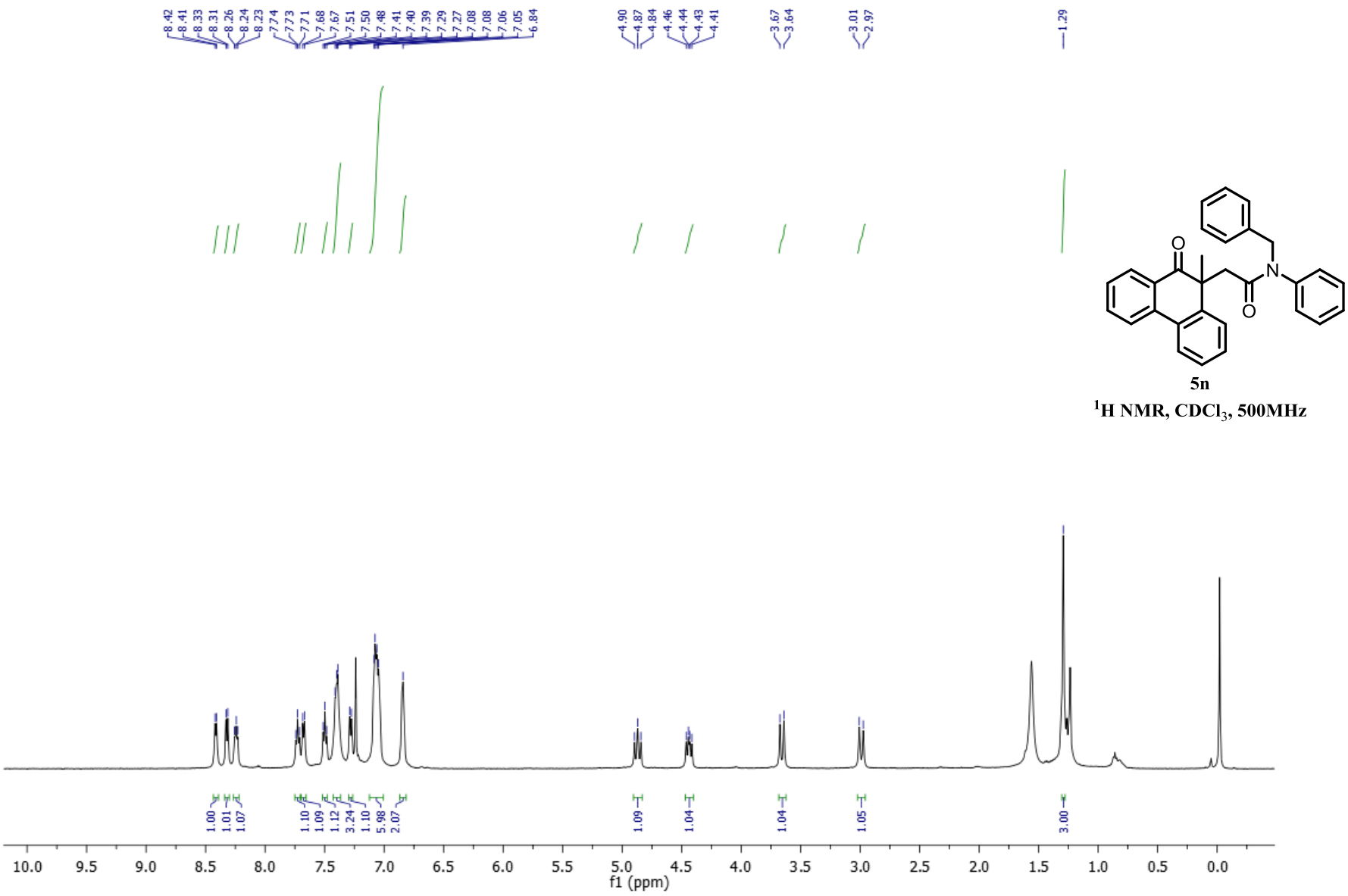
5m

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



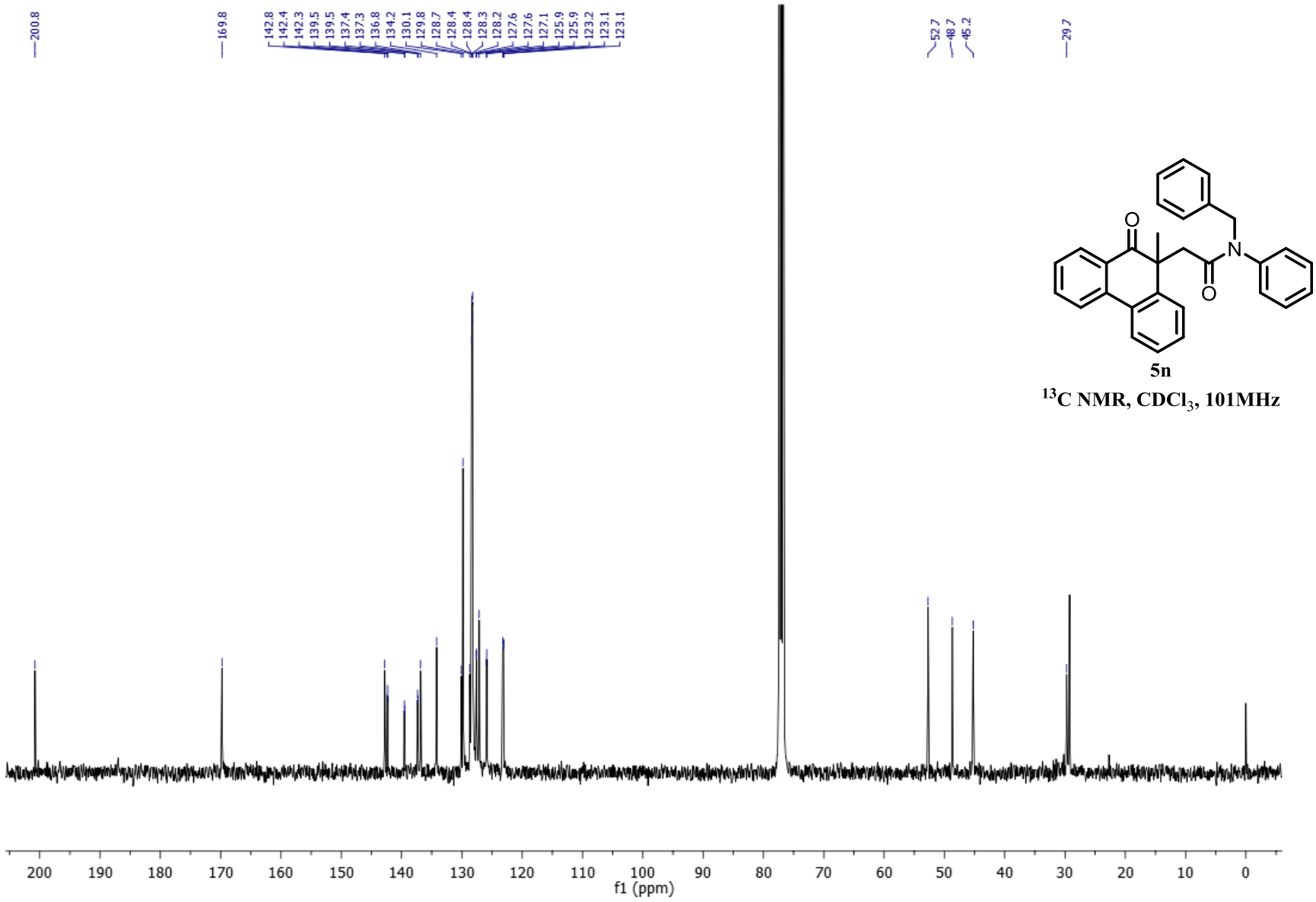
5m

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



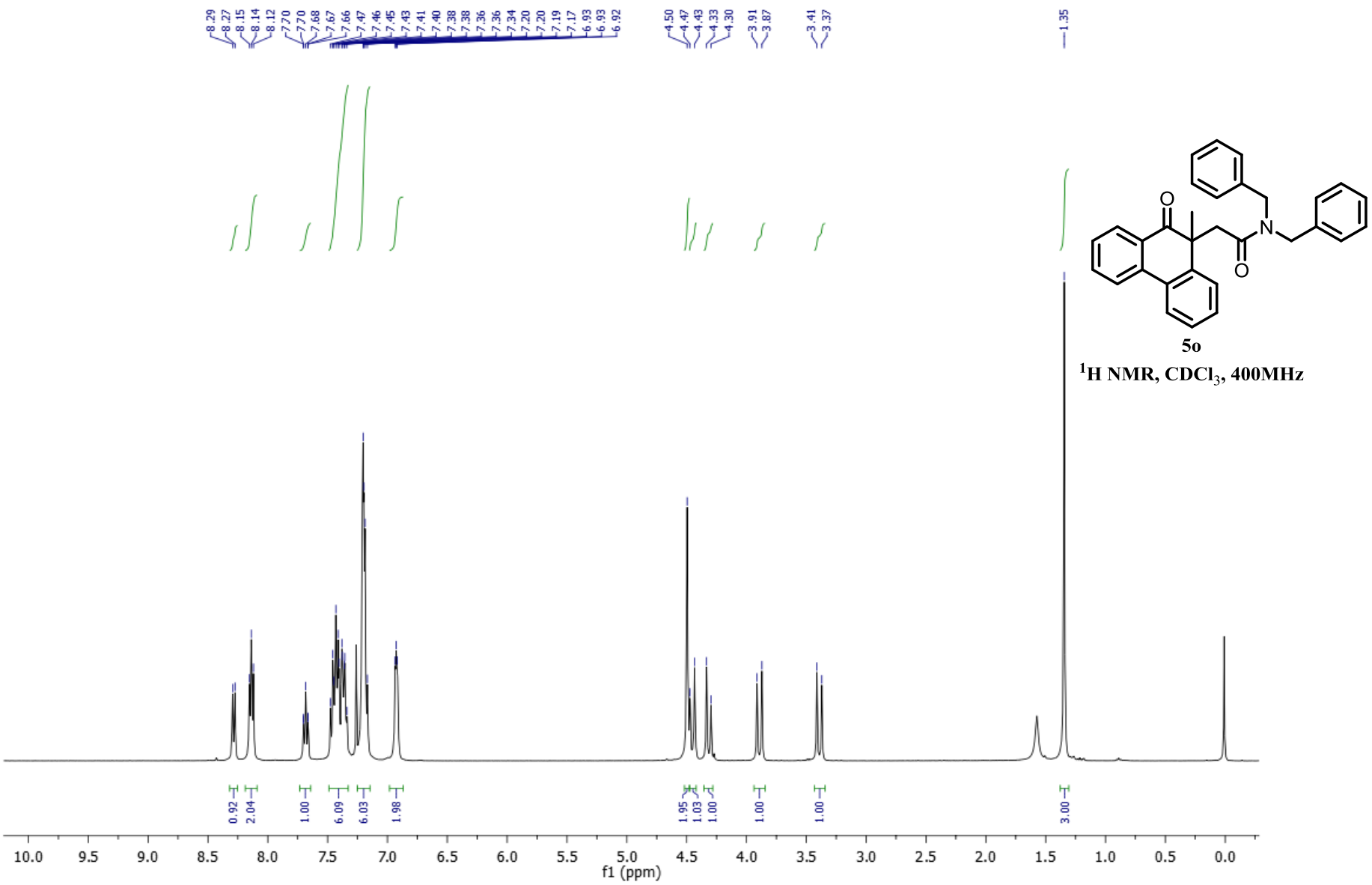
5n

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



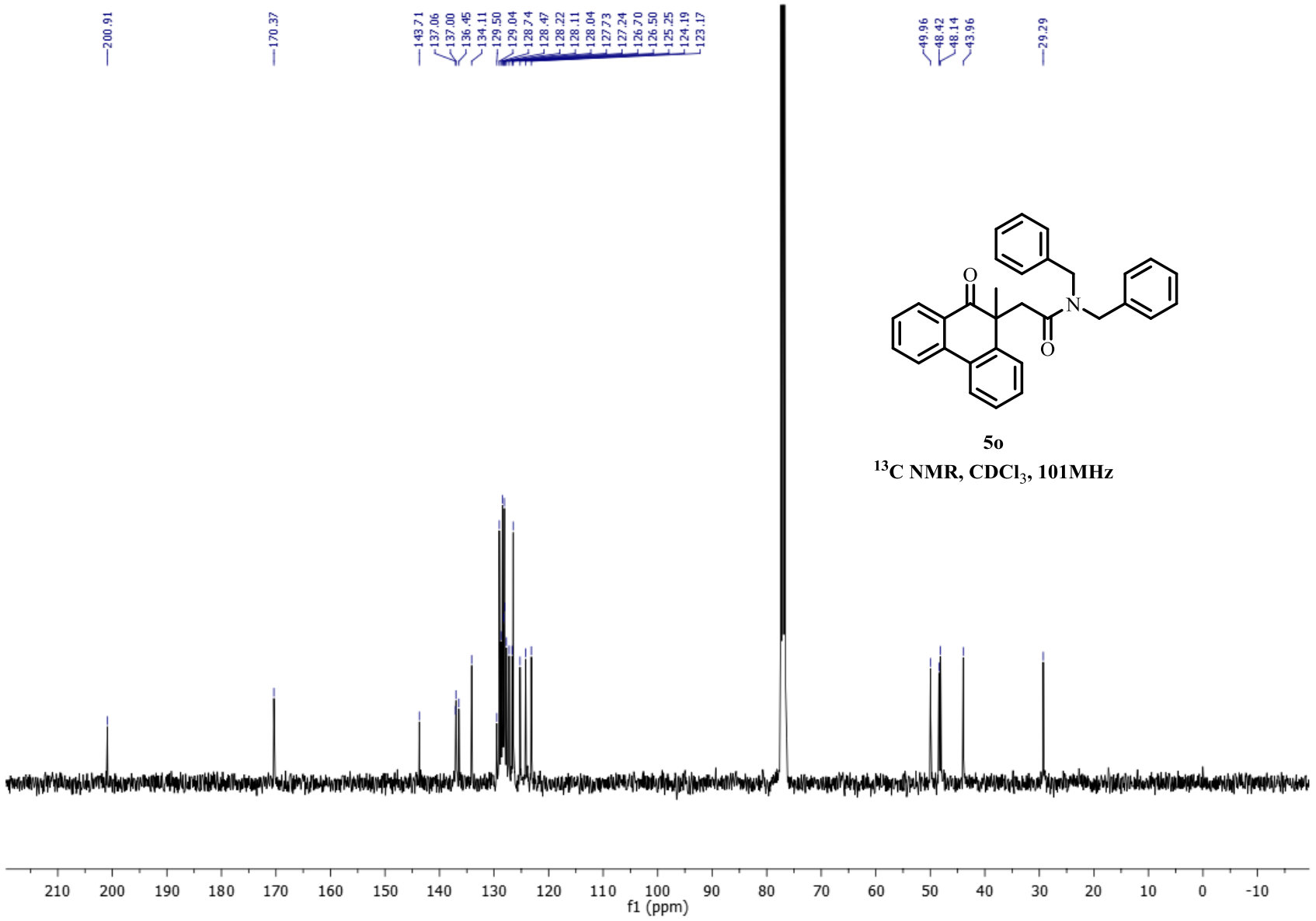
5n

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



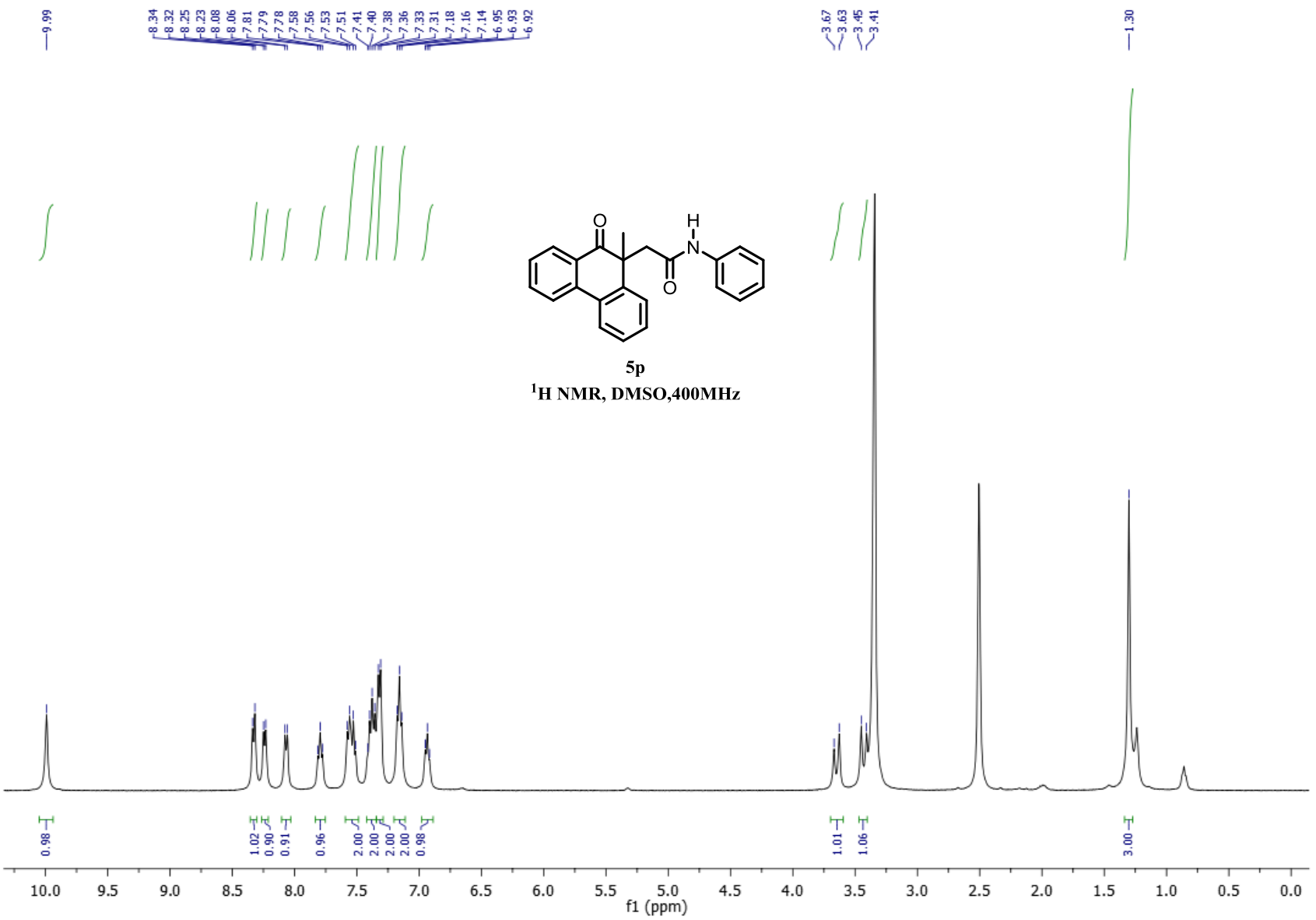
5o

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



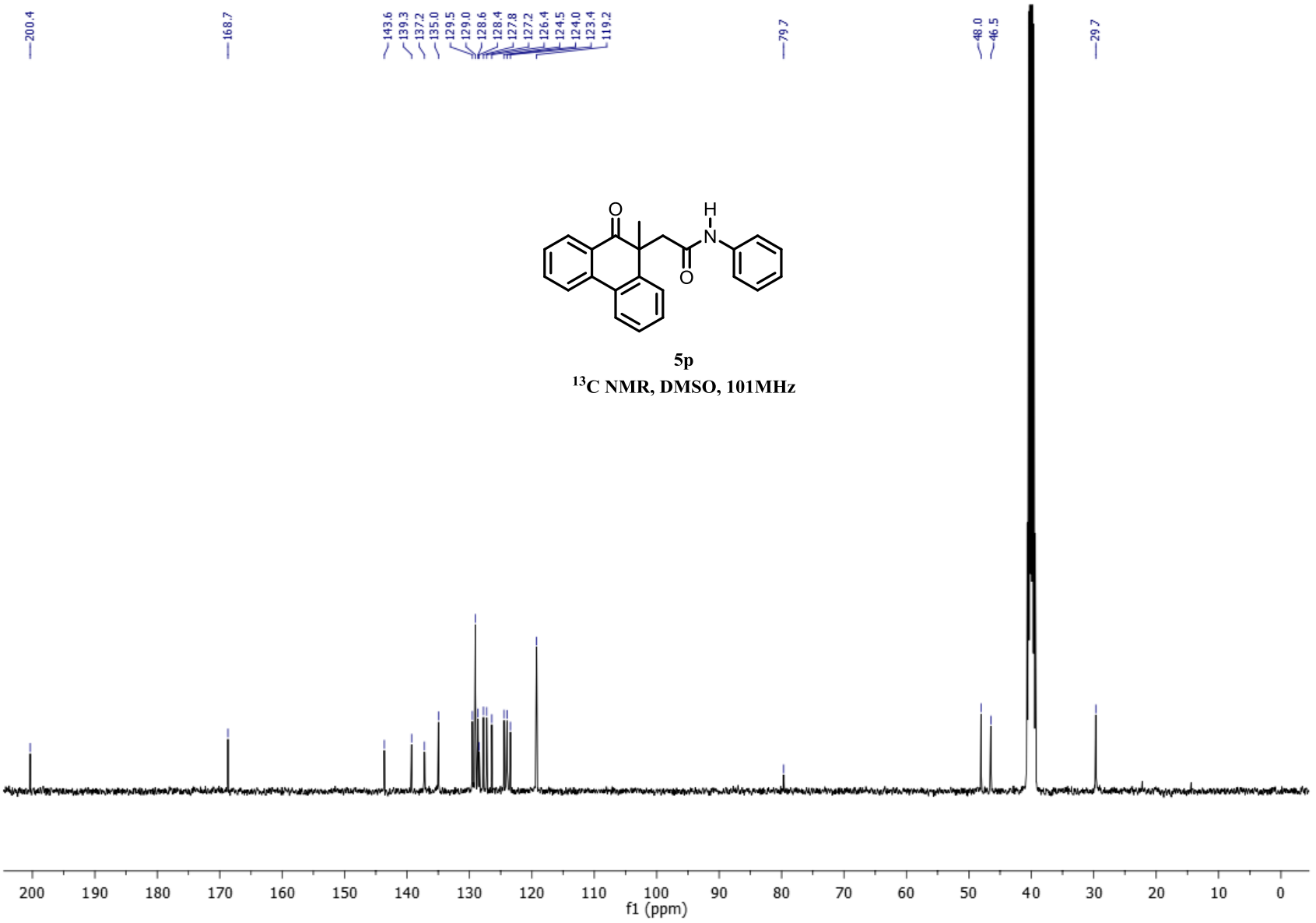
5o

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



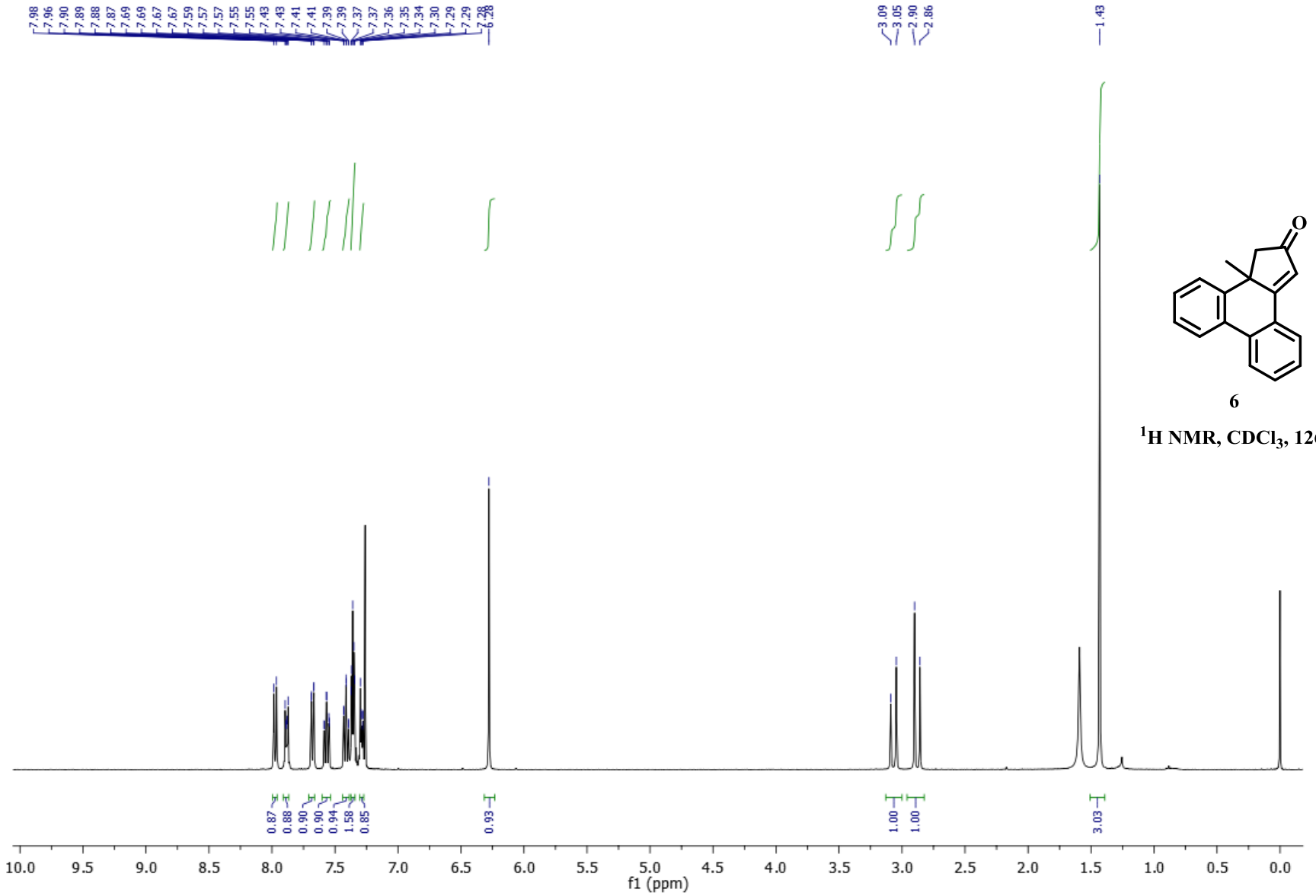
5p

^{1}H NMR, DMSO,400MHz



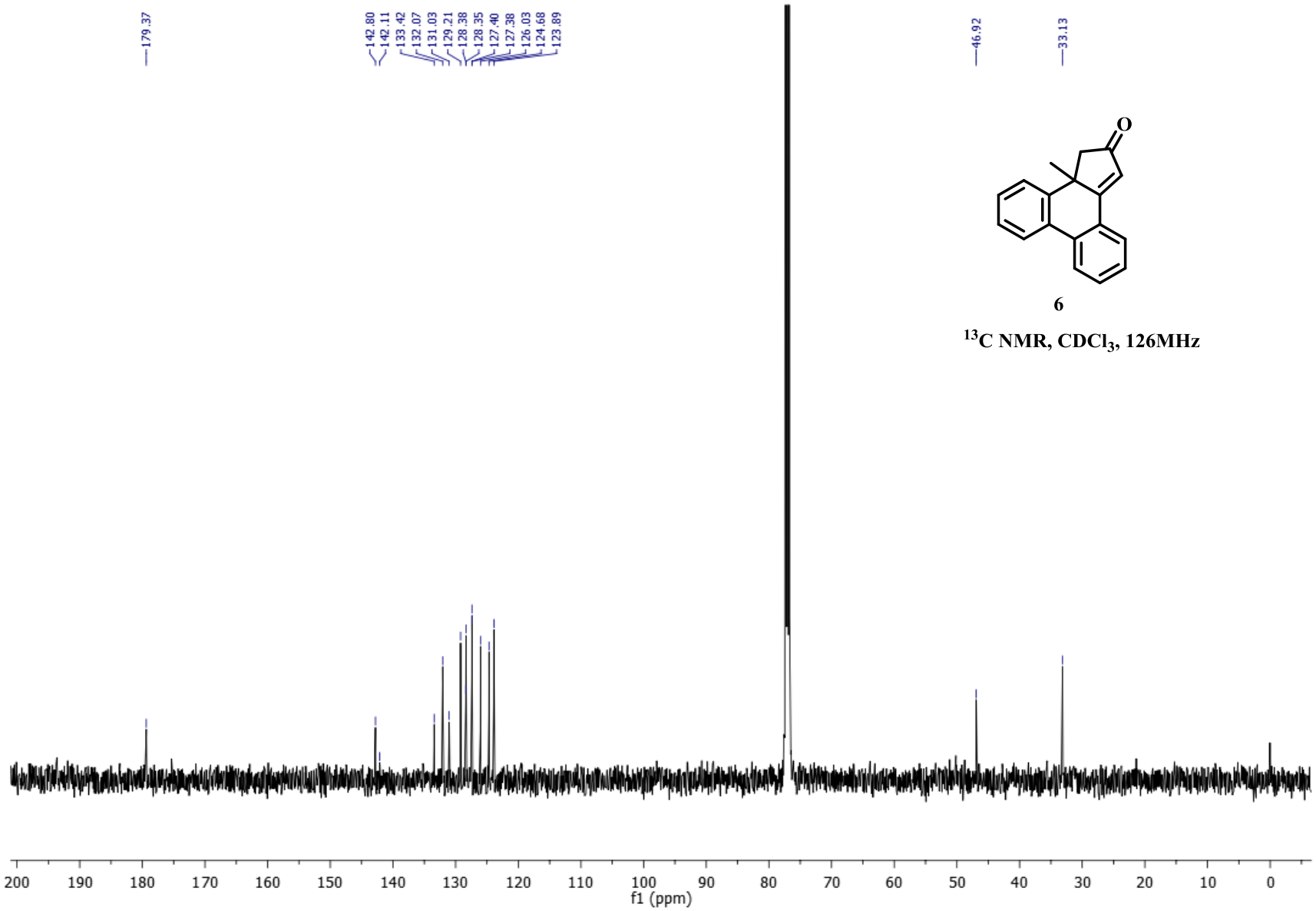
5p

^{13}C NMR, DMSO, 101MHz



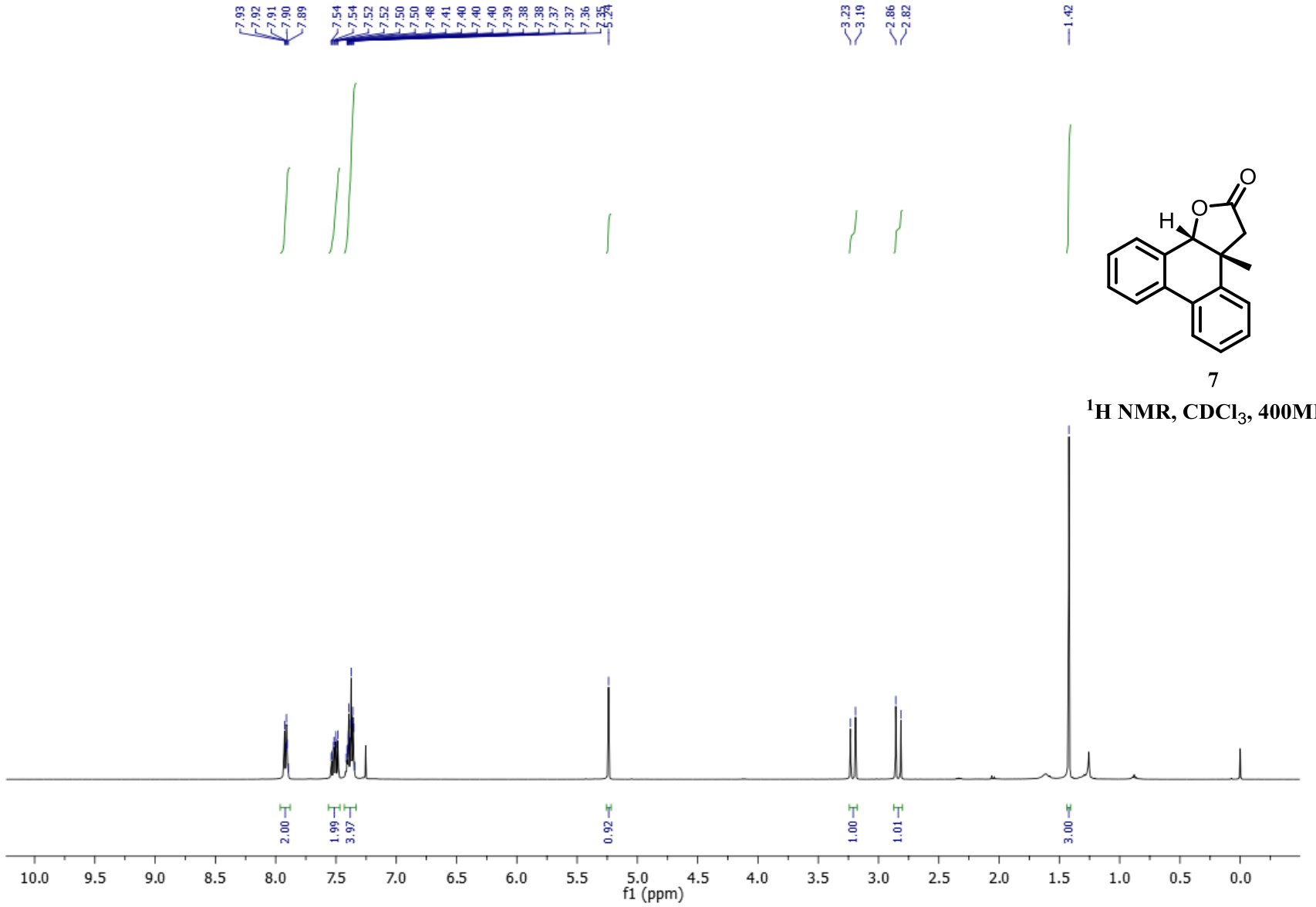
6

^{1}H NMR, $CDCl_3$, 126MHz



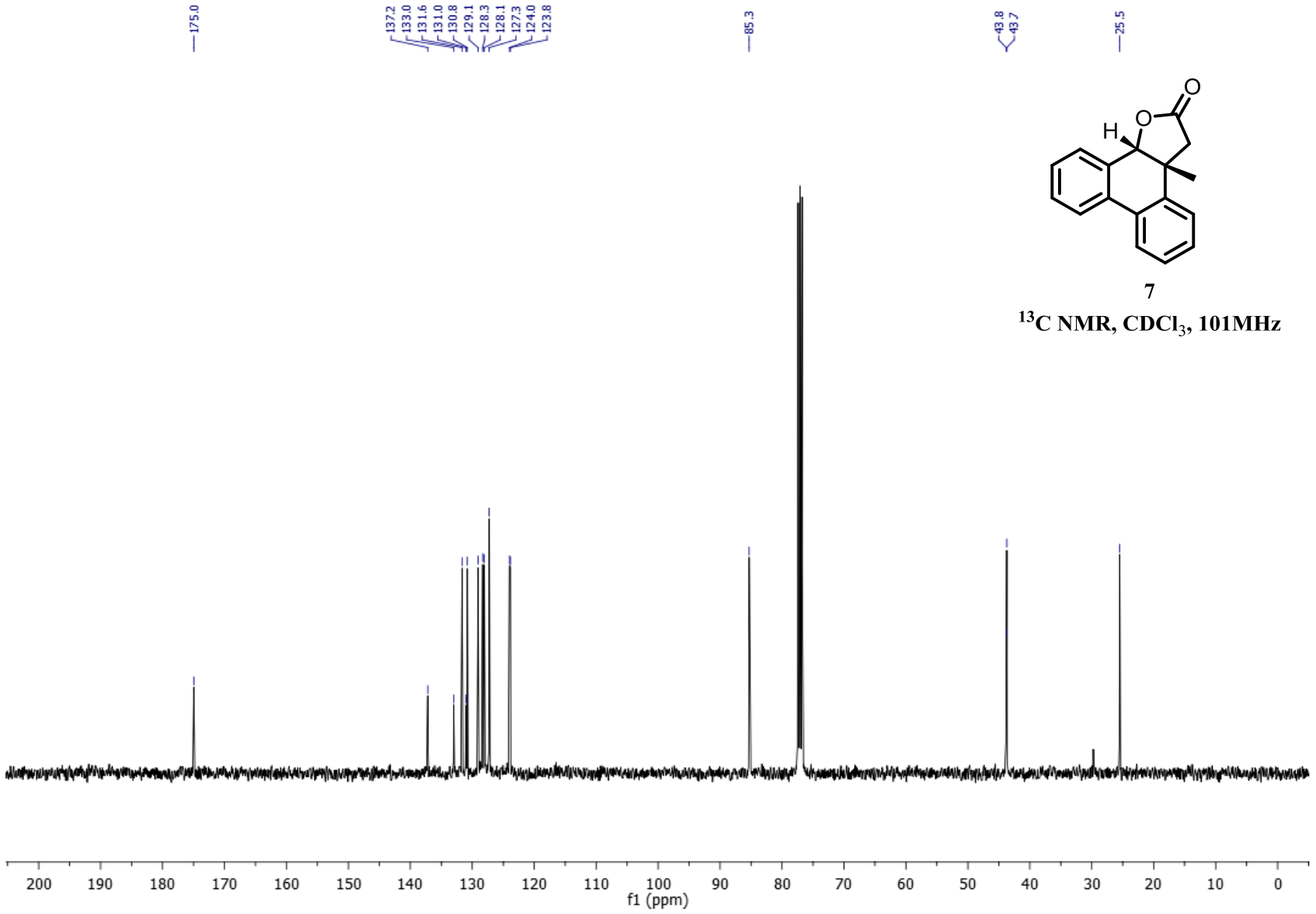
6

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



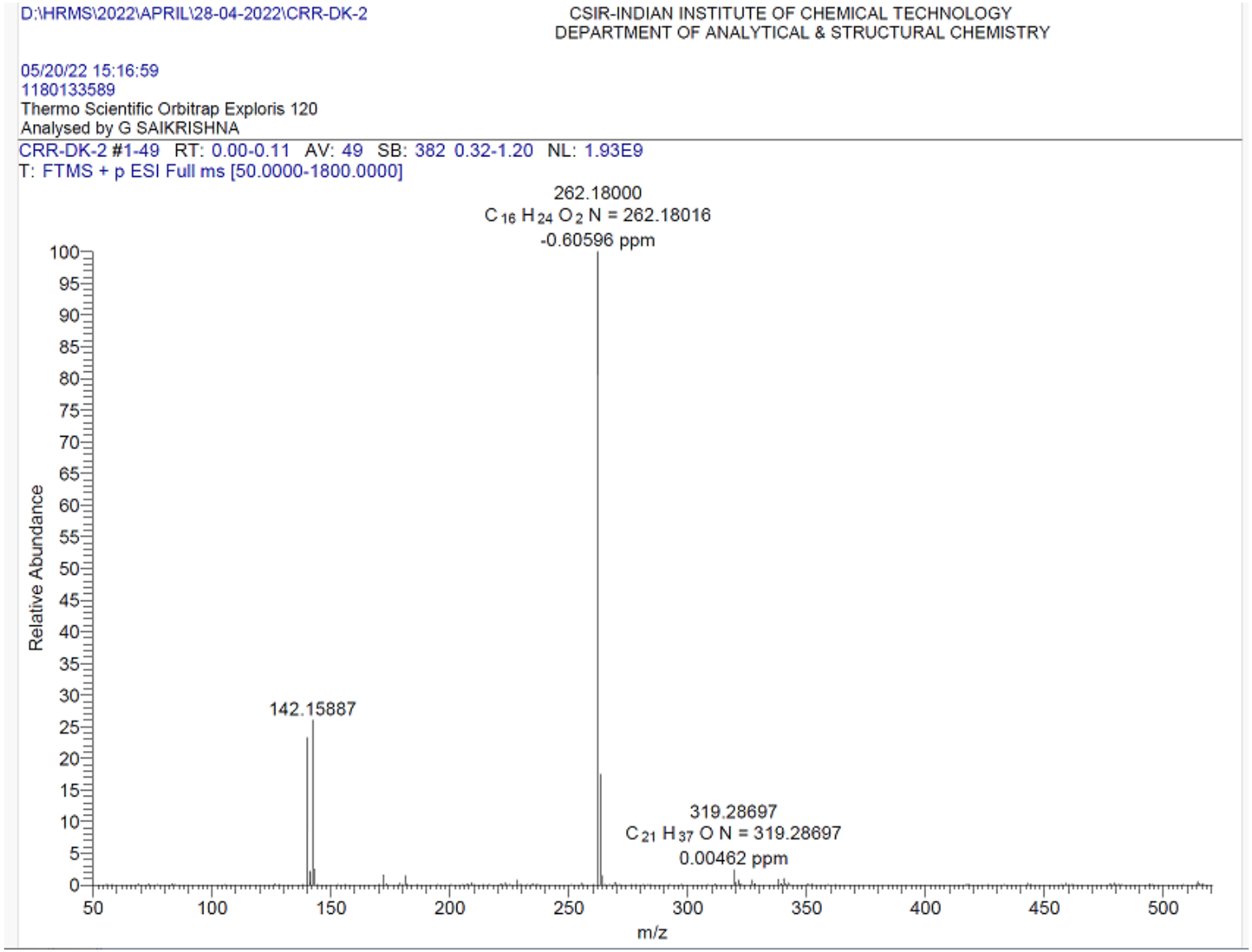
7

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



7

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



HRMS spectrum of TEMPO-benzoyl adduct **X-2a**