**Electronic Supplementary Information**

# "On water" palladium catalyzed diastereoselective boronic acid addition to structurally diverse cyclopropane nitriles

**Dwaipayan Das, Prasun Mukherjee, Asish R. Das***

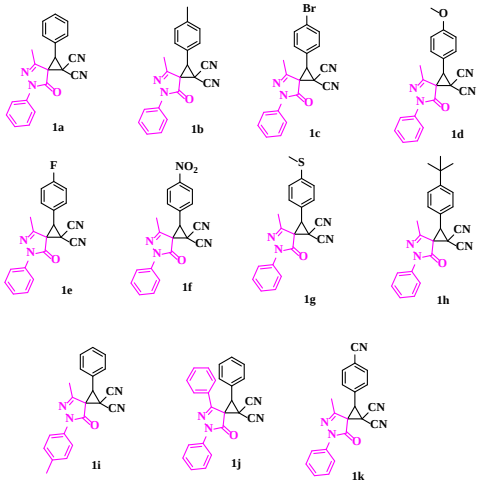
Department of Chemistry, University of Calcutta, Kolkata-700009, India

*Corresponding author: Tel.: +913323501014, +919433120265; fax: +913323519754;

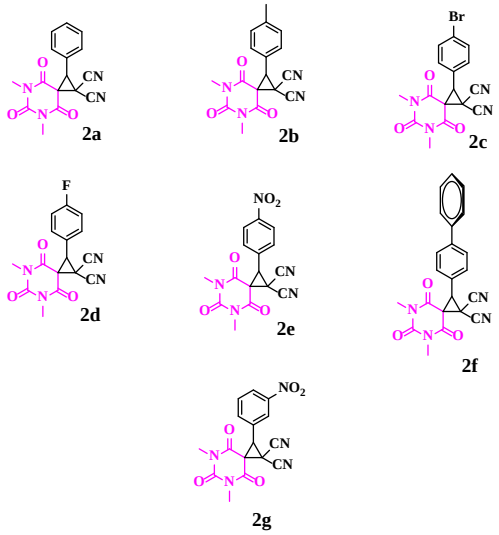
E-mail: ardchem@caluniv.ac.in, ardas66@rediffmail.com

## I. List of starting materials:

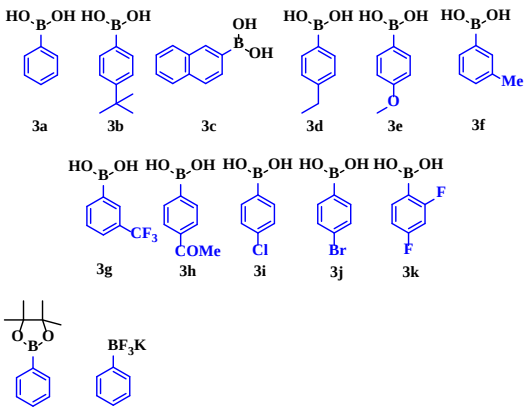
### a. Pyrazolo cyclopropanes:




### b. Barbiturate cyclopropanes:

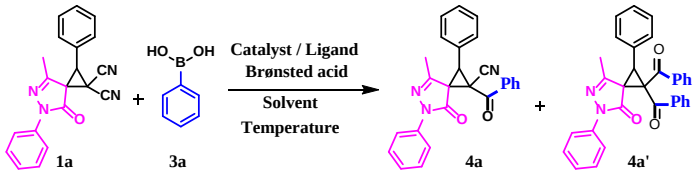



### c. Organo-boron Compounds:



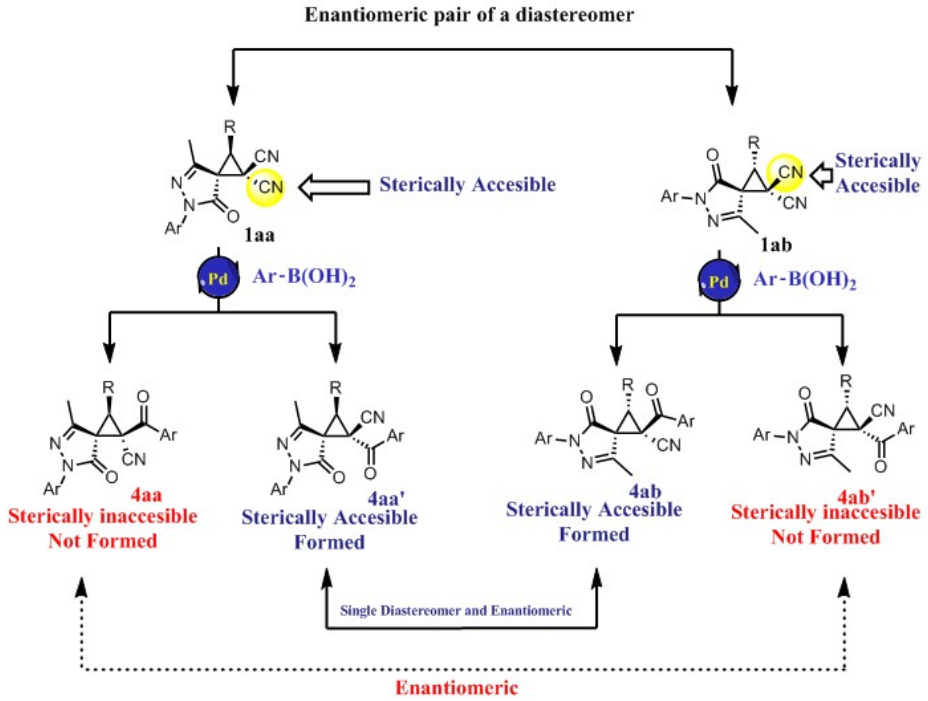
## II. Optimization of the reaction conditions and study of stereoselectivity of compound 4:

**Table S1**. Screening of catalysts, ligands, acids, solvents and optimization of reaction conditions[a]




| Entry | Catalyst (mol%) | Ligand (mol%) | Brønsted acid (equiv.) | Solvent | Temp. (°C) | Time (h) | Yield of 4a[b] (%) |
|---|---|---|---|---|---|---|---|
| 1[c] | $Pd(OAc)_2$(5) | L1(5) | AcOH(2.0) | 1,4-dioxane+$H_2O$ (1:1) | 100 | 3.0 | 10 |
| 2[c] | $Pd(OAc)_2$(5) | L3(5) | AcOH(2.0) | 1,4-dioxane+$H_2O$ (1:1) | 100 | 3.0 | 18 |
| 3 | $Pd(TFA)_2$(3) | L2(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | 84 |
| 4 | $Pd(CH_3CN)_2Cl_2$(3) | L2(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | 61 |
| 5 | $Pd(acac)_2$(3) | L2(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | 88 |
| 6 | $Pd(OAc)_2$(3) | L1(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | 42 |
| 7 | $Pd(OAc)_2$(3) | L3(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | 87 |
| 8 | $Pd(OAc)_2$(3) | L4(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | - |
| 9 | $Pd(OAc)_2$(3) | L5(3) | DBSA(0.2) | $H_2O$ | 90 | 2.0 | - |
| 10 | $Pd(OAc)_2$(3) | L2(3) | (±)CSA(1.1) | THF + $H_2O$ (1:1) | 90 | 2.0 | 50 |
| 11 | $Pd(OAc)_2$(3) | L2(3) | TFA(1.1) | THF + $H_2O$ (1:1) | 90 | 2.0 | 31 |
| 12 | $Pd(OAc)_2$(3) | L2(3) | Phenylacetic Acid(1.1) | THF + $H_2O$ (1:1) | 90 | 2.0 | 12 |
| 13 | $Pd(OAc)_2$(3) | L2(3) | Benzoic Acid(1.1) | THF + $H_2O$ (1:1) | 90 | 2.0 | - |
| 14 | $Pd(OAc)_2$(3) | L2(3) | p-nitro Benzoic Acid(1.1) | THF + $H_2O$ (1:1) | 90 | 2.0 | - |
| 15 | $Pd(OAc)_2$(3) | - | DBSA(0.2) | $H_2O$ | 90 | 2.0 | 42 |
| 16 | $Pd(OAc)_2$(3) | L2(3) | - | $H_2O$ | 90 | 2.0 | 12 |
| 17 | $Pd(OAc)_2$(3) | L2(3) | - | $H_2O$ | 90 | 24.0 | 38 |
| 18 | $Pd(OAc)_2$(3) | L2(3) | - | THF | 90 | 24.0 | 14 |
| 19 | $Pd(OAc)_2$(3) | L2(3) | - | 1, 4-dioxane | 90 | 24.0 | 12 |
| 20 | $Pd(OAc)_2$(3) | L2(3) | - | Toluene | 90 | 24.0 | - |

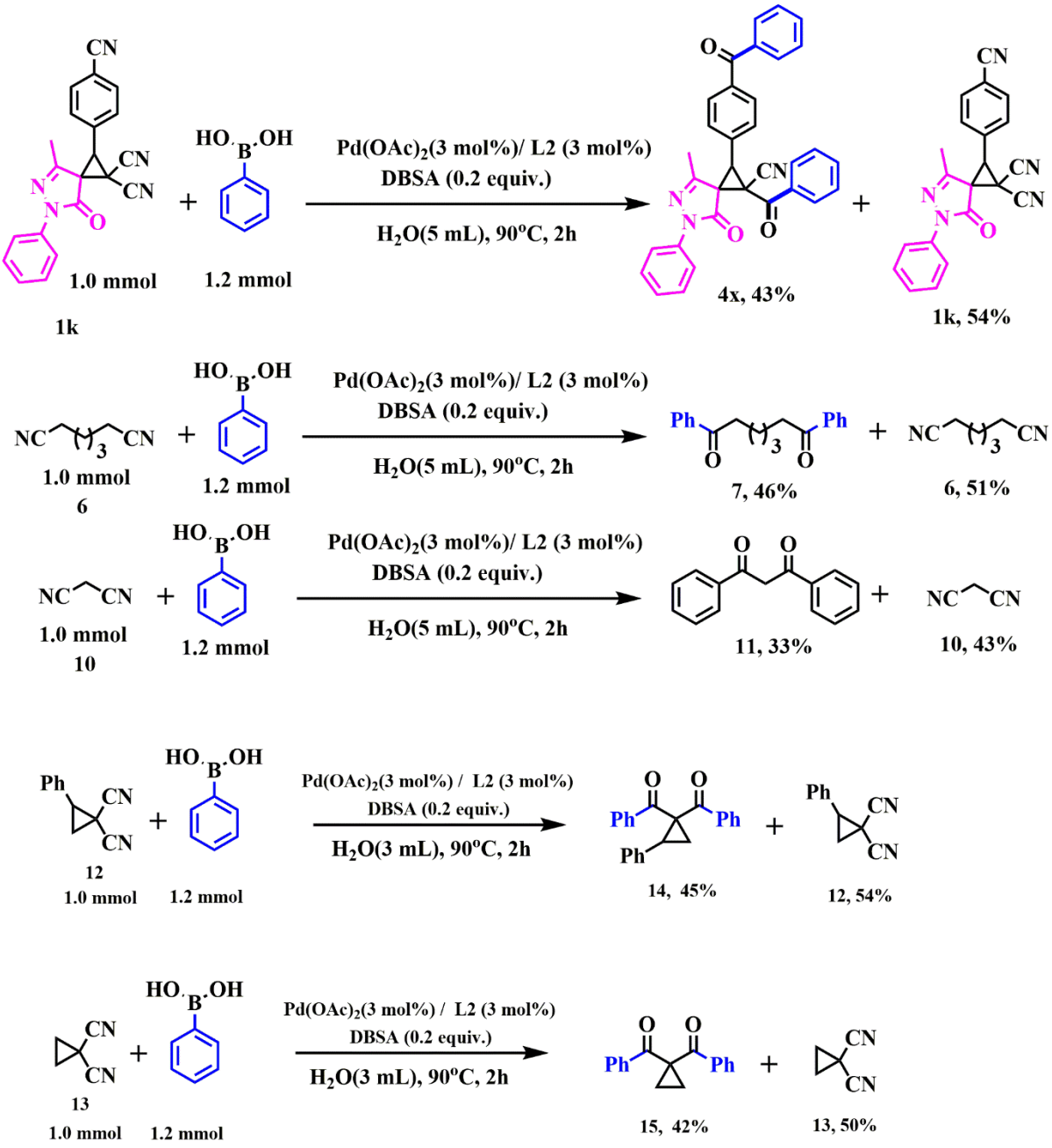
[a] all the reactions were carried out with **1a (0.5 mmol)** and **2a (0.6 mmol)** in 3 mL of solvent or solvent mixture; [b] isolated yields of **4a** and **4a´** was not obtained in every case. [c] 2.0 equiv. of phenylboronic acid(**3a**) was used instead of 1.2 equiv.




**Scheme S1**. Diastereoselectivity of compound **4**

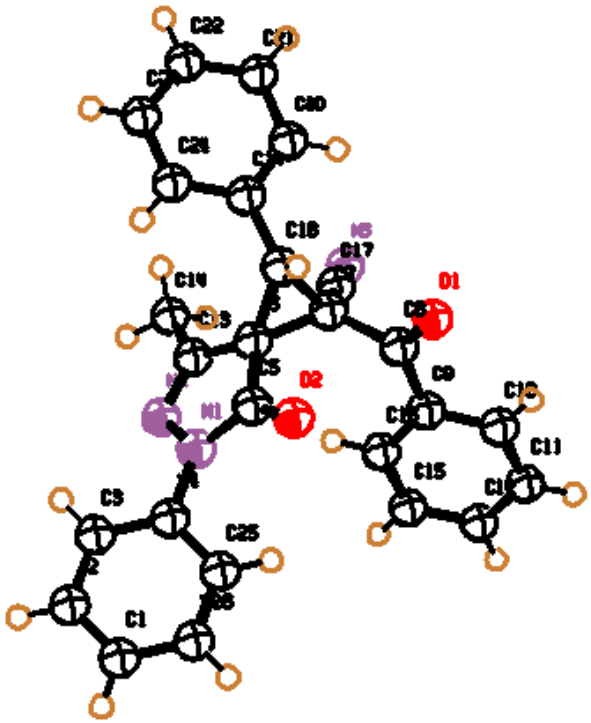
We have started from compound **1** which has been prepared according to our previous work[1] and has two diastereomers of which we have only considered the major one and have only explained the diastereoselectivity of it. Since **1aa and 1ab** are in enantiomeric relationship, during the reaction four stereoisomers can be obtained, at least theoretically. However, since formation of isomer **4aa** and **4ab**' are sterically forbidden they were not obtained during the reaction which is confirmed by NMR and X-ray. Only **4aa'** and **4ab** were found to be as the products which are essentially enantiomers with respect to each other. Interestingly, **4aa** and 4ab', bearing enantiomeric relationship to each other, possess diastereomeric relationship with **4aa'** and **4ab** respectively. Thus, it is quite clear that this reaction is indeed a diastereoselective reaction and affording only one diastereomer as an enantiomeric mixture.

## III. Control Experiments:

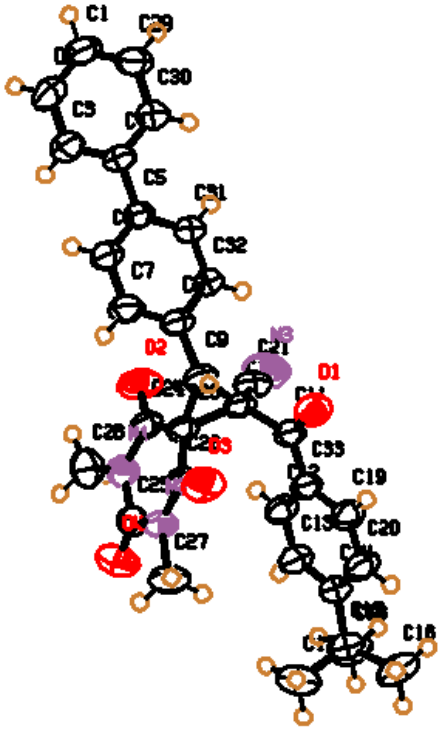



**Scheme S2**: Some control experiments performed varying the amount of boronic acids for different dinitrile compounds

## IV. X-ray Crystallography Data of Compound 4a (CCDC 1952896) and 5g (CCDC 1952797):




The X-ray structure of **4a**. The ellipsoid contour percent probability level is 70%.




The X-ray structure of **5g**. The ellipsoid contour percent probability level is 70%.

**Single crystal X-ray data for compound Compound4a (CCDC 1952896) and 5g (CCDC 1952797):**

Single crystals suitable for X-ray diffraction of **4a** and **5g** were grown from ethyl acetate. The crystals were carefully chosen using a stereo zoom microscope supported by a rotatable polarizing stage. In all the cases the data were collected at 296(2) K on a CCD diffractometer with graphite monochromated Mo-Kα radiation (0.71073 Å). The data were processed using the package SAINT.[1] Structures were solved by direct and Fourier methods and refined by full-matrix least squares based on F2 using SHELXTL[2] and SHELXL-97[3] packages.

**Table 1**. Crystallographic data for the compound **4a** and **5g**

| **Compounds** | **4a** | **5g** |
|---|---|---|
| **Empirical formula** | $C_{26}$ $H_{19}$ $N_3$ $O_2$ | $C_{32}$ $H_{30}$ $N_3$ $O_4$ |
| **Formula weight** | 405.44 | 520.59 |
| **crystal system** | Monoclinic | Monoclinic |
| **space group** | *P 21/c* | *P2(1)/c* |
| ***a* (Å)** | 10.086(2) | 18.0183(7) |
| ***b*(Å)** | 16.995(3) | 7.4454(3) |
| ***c* (Å)** | 12.365(3) | 20.6732(7) |
| **$\alpha$ (°)** | 90.00 | 90.00 |
| **$\beta$ (°)** | 98.074(3) | 104.0510(10) |
| **$\gamma$(°)** | 90.00 | 90.00 |
| ***V* (Å$^3$)** | 2098.5(7) | 2690.40(18) |
| ***Z*** | 4 | 4 |
| ***T*, K** | 296(2) | 296(2) |
| **Wavelength (Å)** | 0.71073 | 0.71073 |
| **$2\theta$ (°)** | 2.37-20.47 | 2.30-35.46 |
| **$\mu$ (mm$^{-1}$)** | 0.083 | 0.086 |
| **$\rho_{calcd}$ (g cm$^{-3}$)** | 1.283 | 1.285 |
| ***F* (000)** | 848 | 1100 |
| **absorption correction** | multi-Scan | multi-Scan |
| **index ranges** | -11 ≤*h*≤12 | -29≤*h*≤29 |
| | -21 ≤*k*≤21 | -10≤*k*≤12 |
| | -15 ≤*l*≤15 | -31≤*l*≤34 |
| **reflections collected** | 15560 | 45612 |

| | | |
|---|---|---|
| **independent reflections ($R_{int}$)** | 2902(0.0405) | 9986(0.0281) |
| **Goodness-of-fit on $F^2$** | 0.900 | 0.927 |
| **$R_1^a$ /w$R_2^b$ ($I > 2\sigma(I)$)** | 0.0439/0.1249 | 0.0616/ 0.1812 |
| **$R_1^a$/w$R_2^b$ (for all data)** | 0.0854/0.1555 | 0.1040/0.2218 |
| **Largest diff. peak/hole / e Å$^{-3}$** | 0.141/-0.163 | 0.393/-0.213 |

$^aR_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$

**References:**

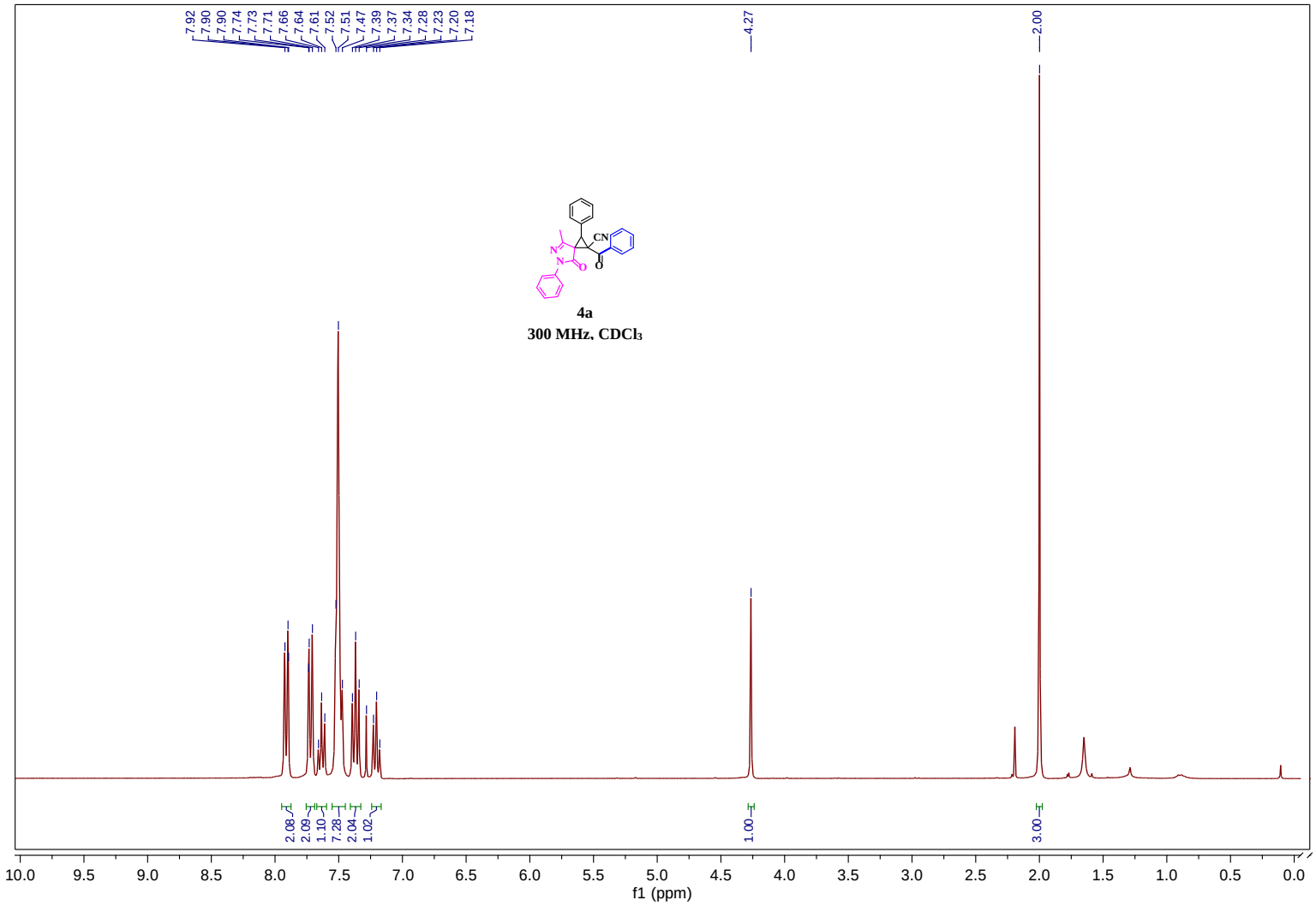

1. P. Mukherjee, A. R. Das. *J. Org. Chem.*, 2017, **82**, 2794

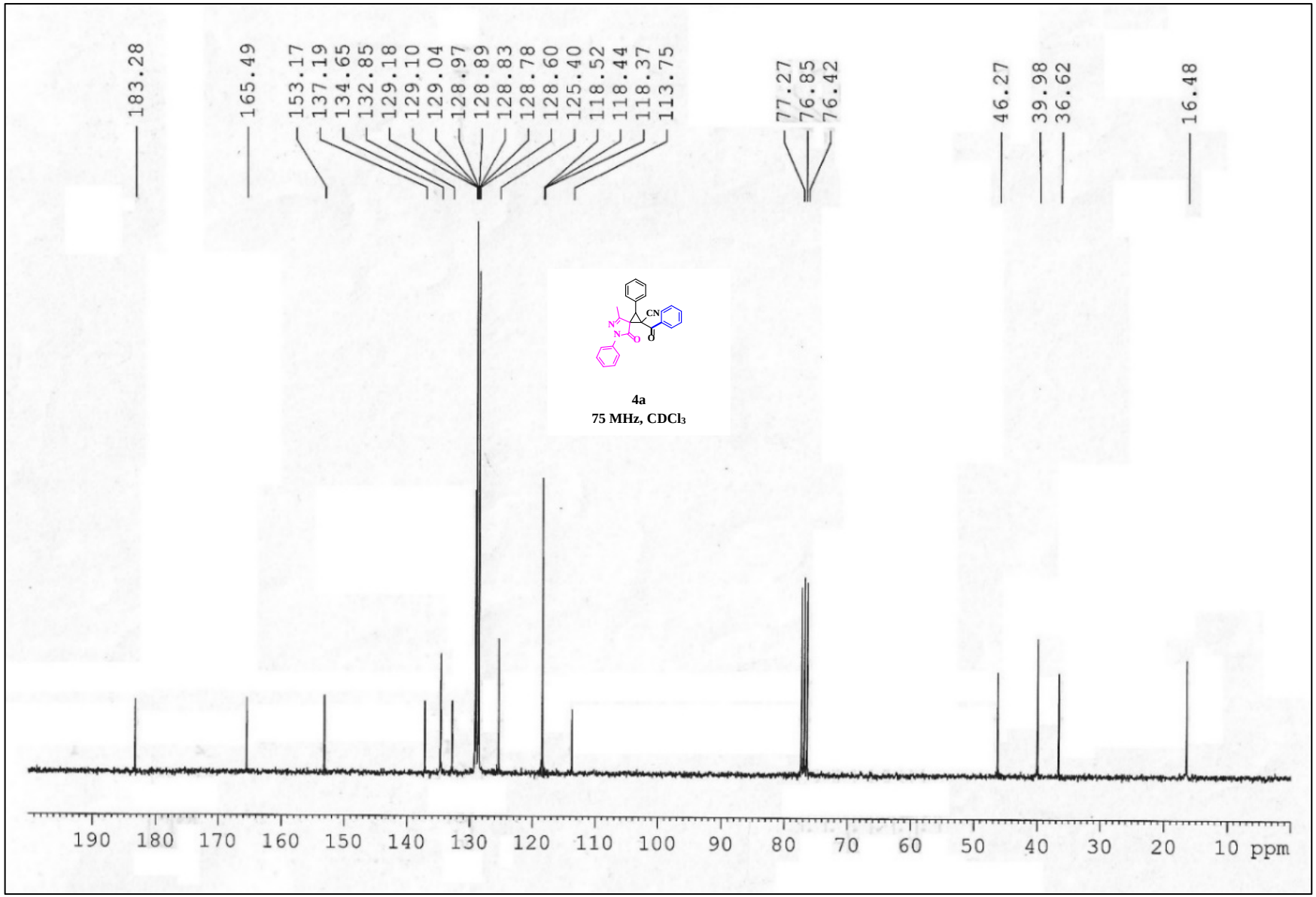
2. *APEX-II*, *SAINT-Plus*, and *TWINABS;* Bruker-Nonius AXS Inc.: Madison, WI, 2004.

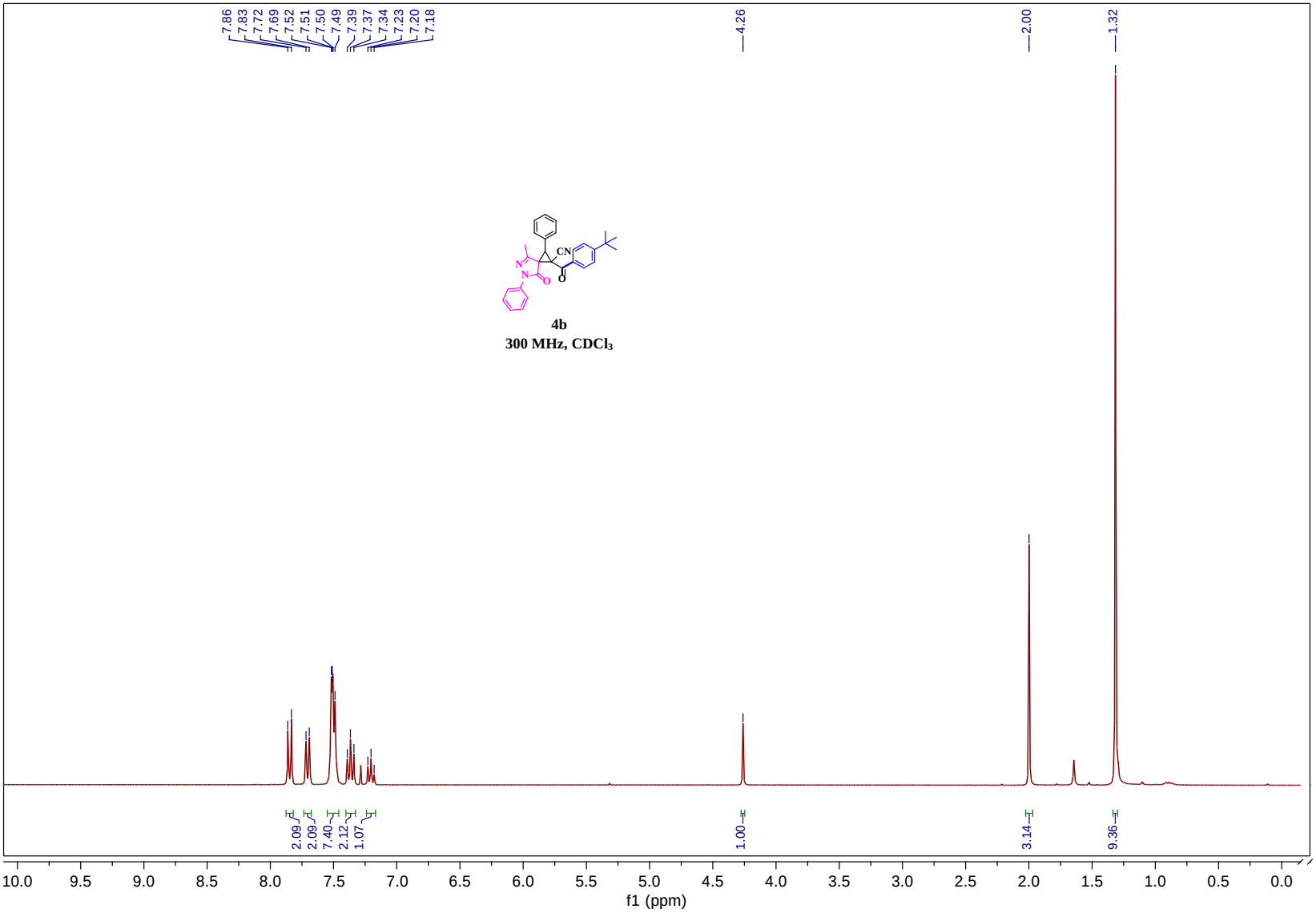
3.*SHELXTL*, version 6.10; Bruker AXS Inc.: Madison, WI, 2002.

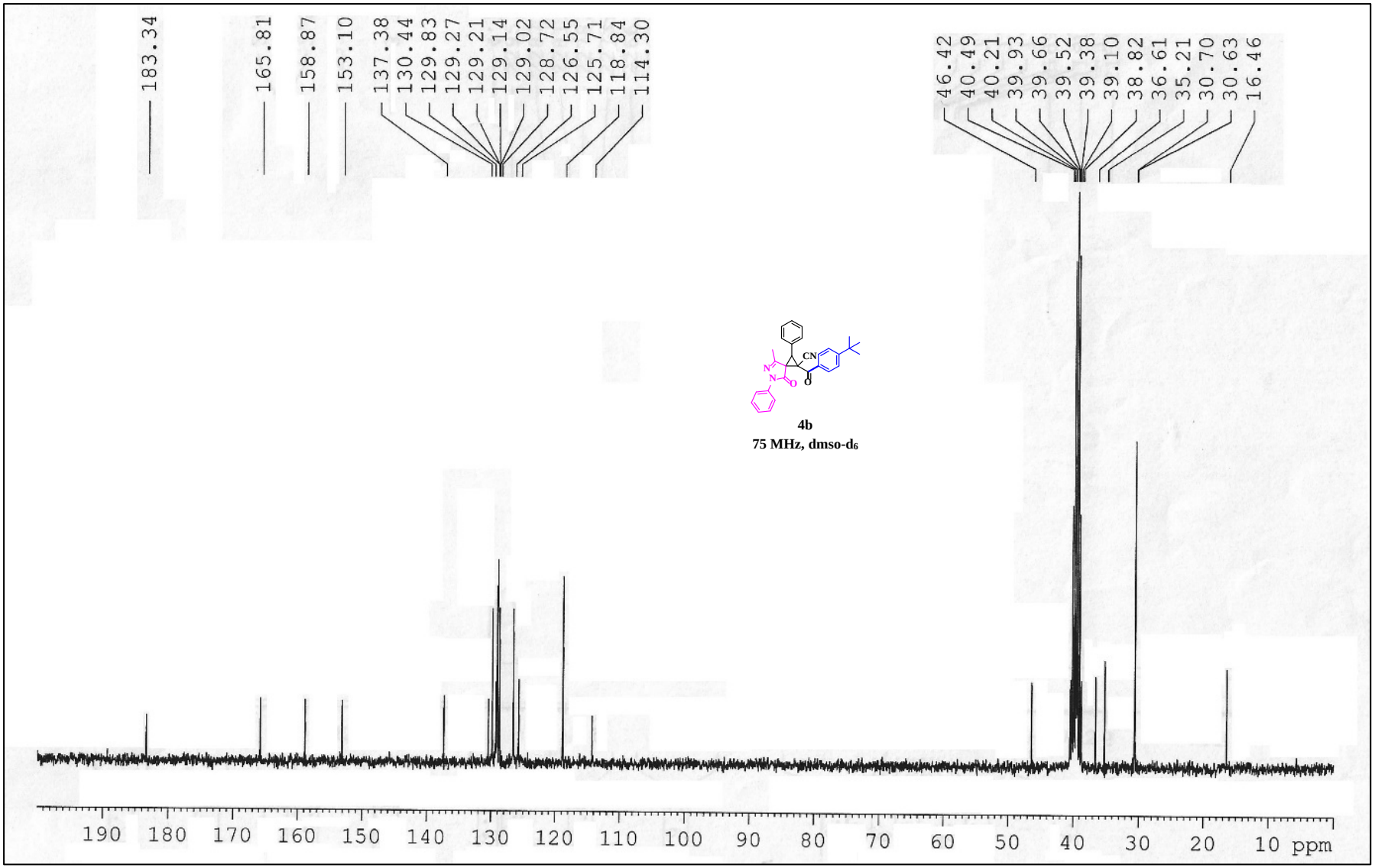
4. Sheldrick, G. M. *SHELXL-97*, *Crystal Structure Refinement Program;* University of Göttingen: Göttingen, Germany, 1997.

## V. $^{1}H$ and $^{13}C$ NMR spectra for the products 4a-4w, 5a-i



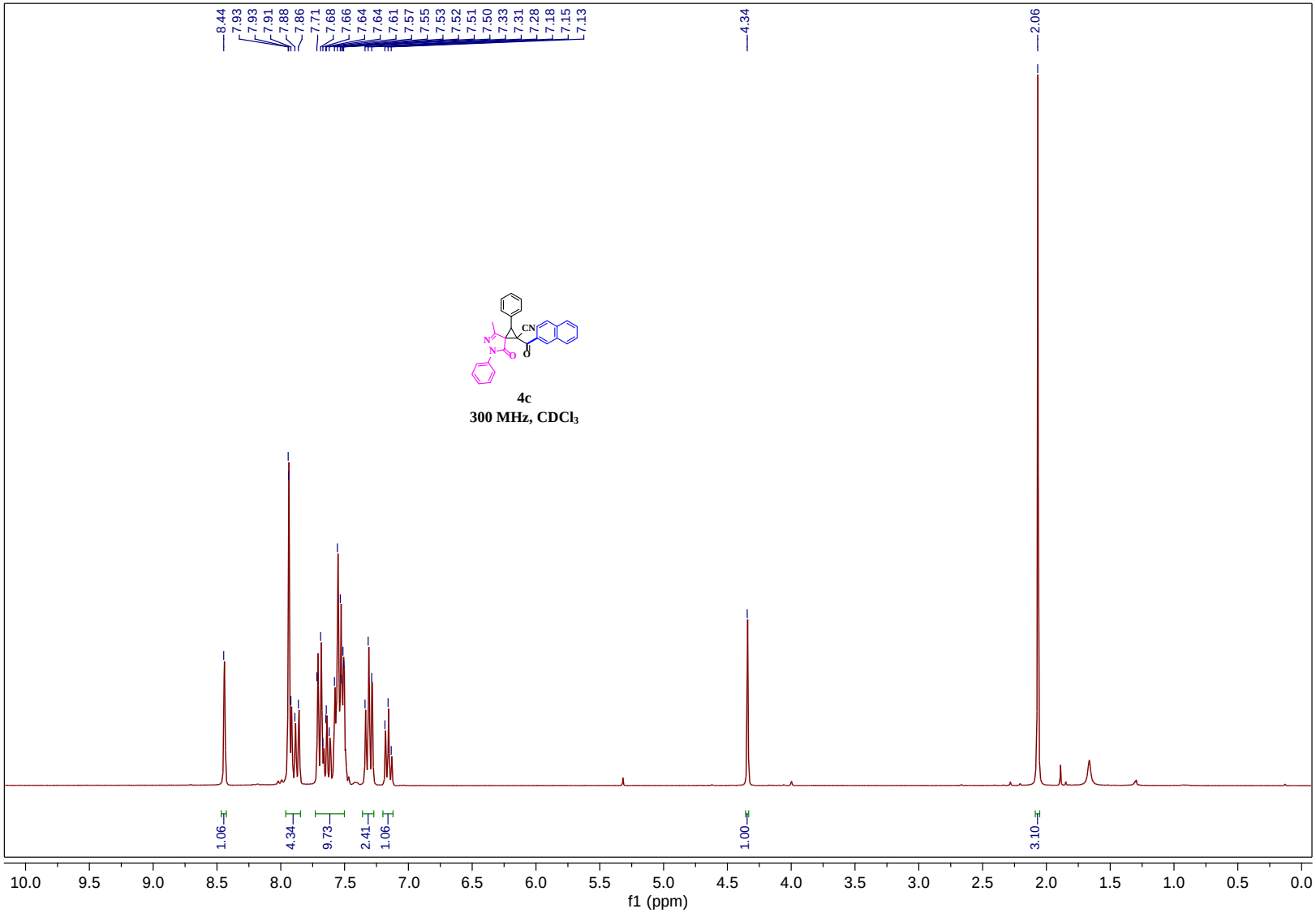

183.28
165.49
153.17
137.19
134.65
132.85
129.18
129.10
129.04
128.97
128.89
128.83
128.78
128.60
125.40
118.52
118.44
118.37
113.75
77.27
76.85
76.42
46.27
39.98
36.62
16.48
CN
O
N
N
O
4a
75 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

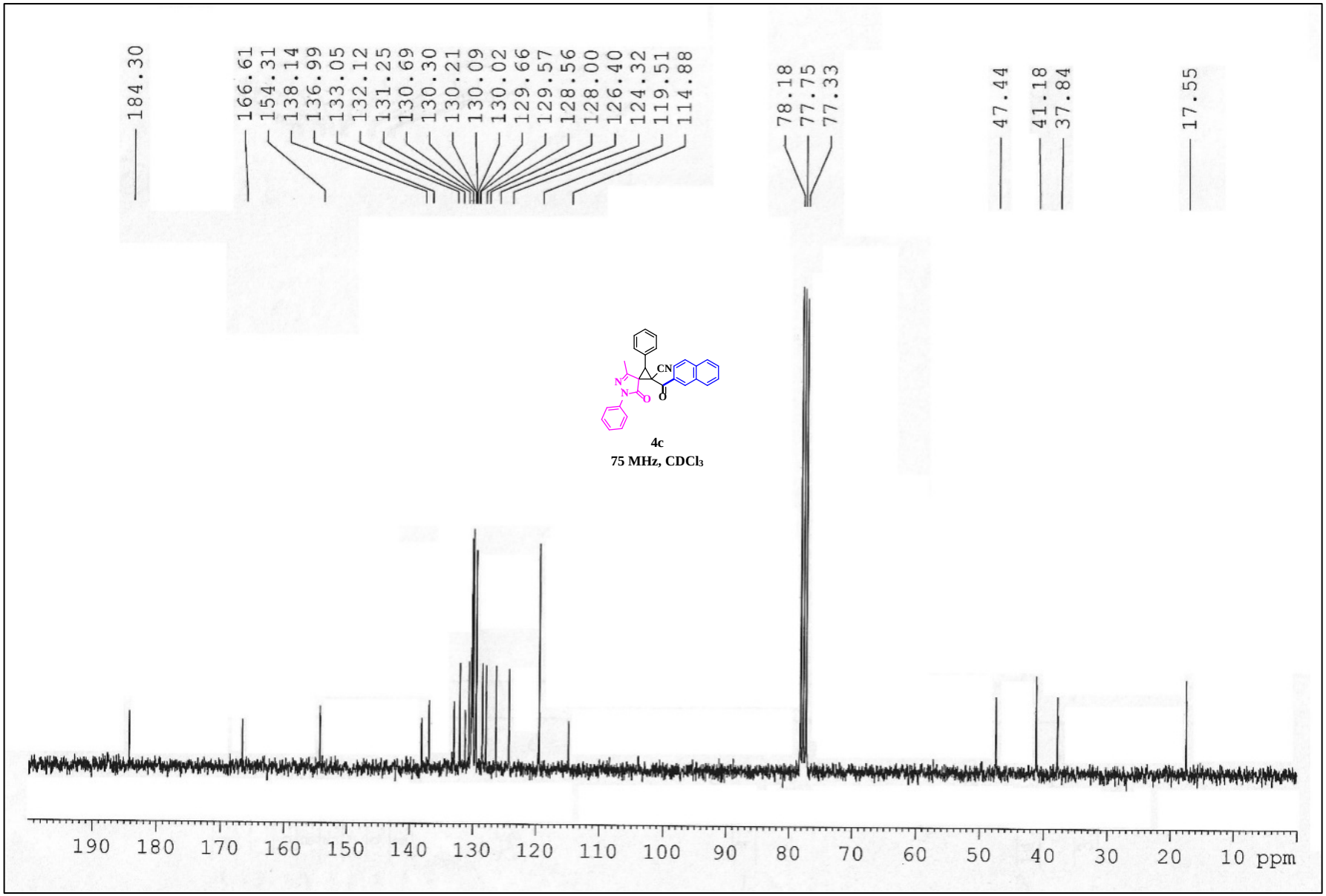

7.86
7.83
7.72
7.69
7.52
7.51
7.50
7.49
7.39
7.37
7.34
7.23
7.20
7.18
4.26
2.00
1.32
CN
O
N
O
4b
300 MHz, CDCl3
2.09
2.09
7.40
2.12
1.07
1.00
3.14
9.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

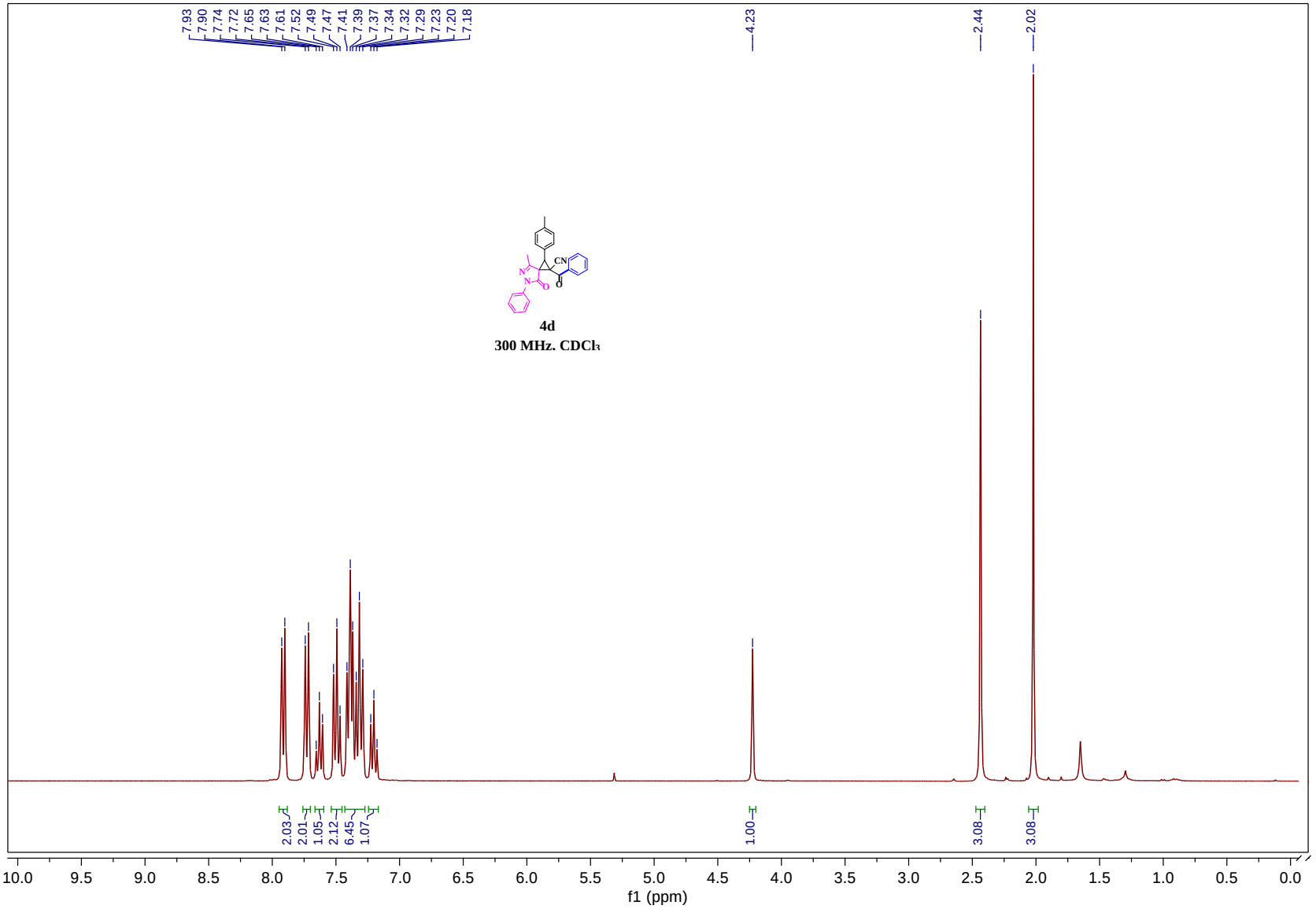


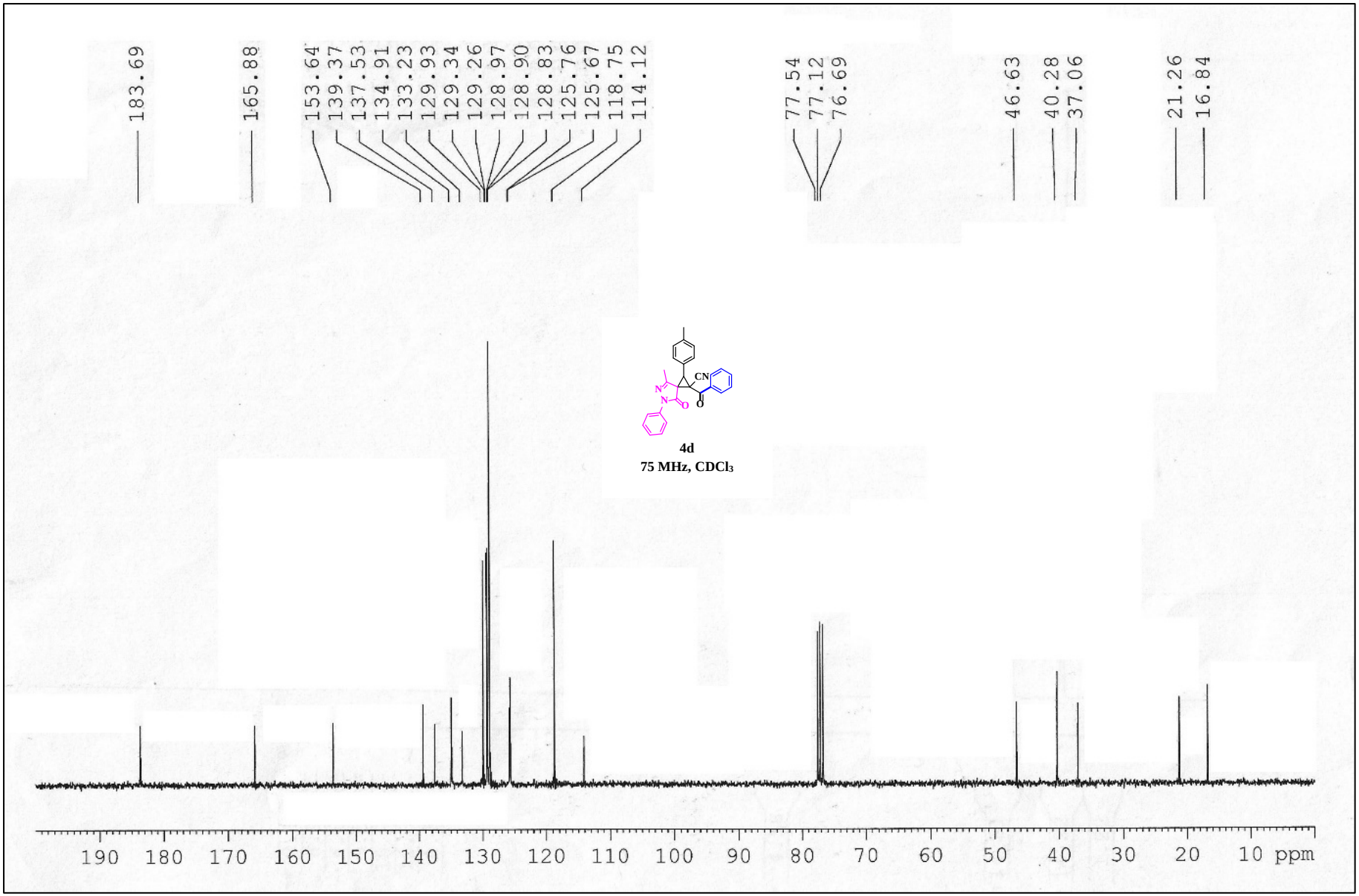

**4b**

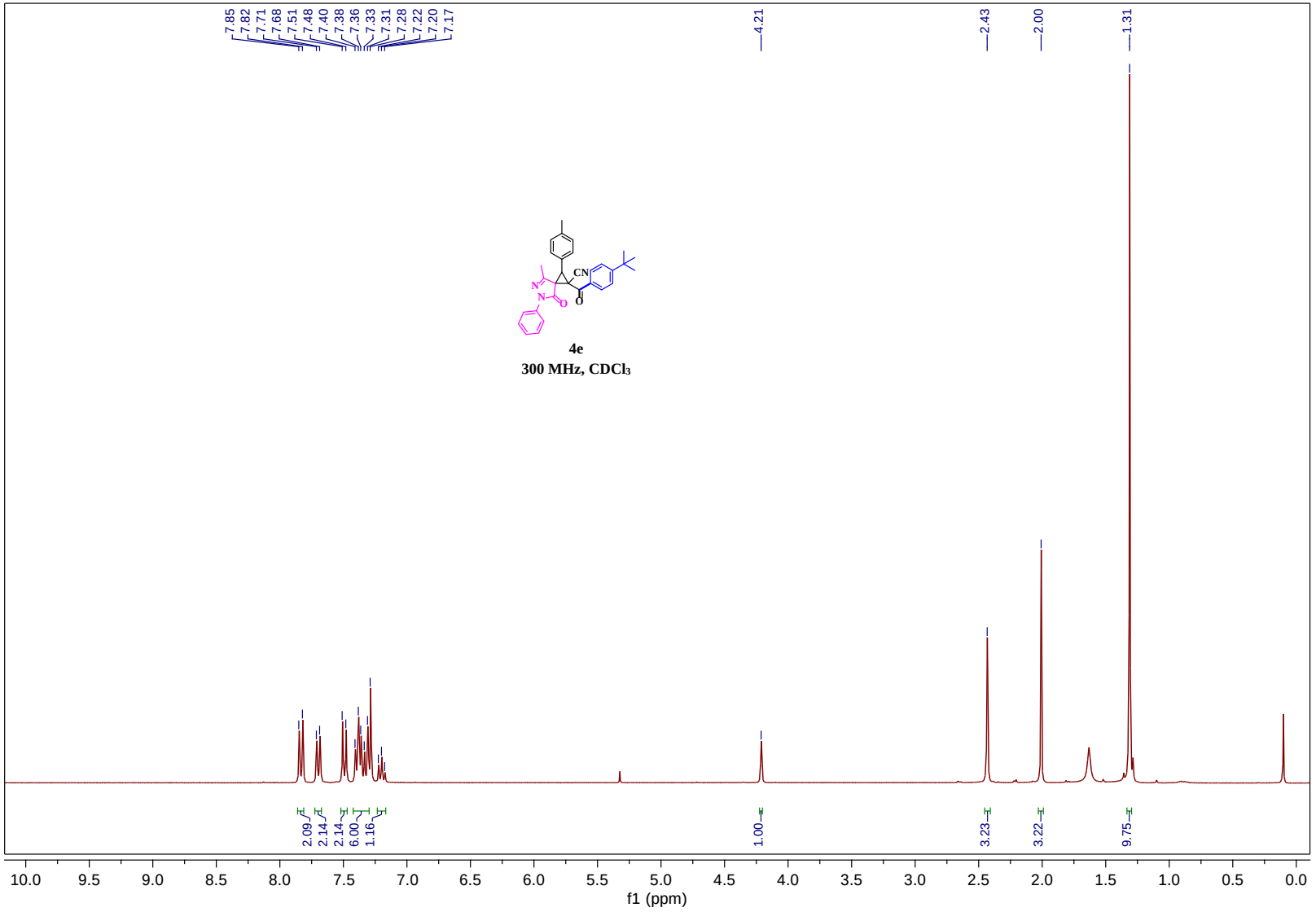
**75 MHz, dmso-$d_6$**

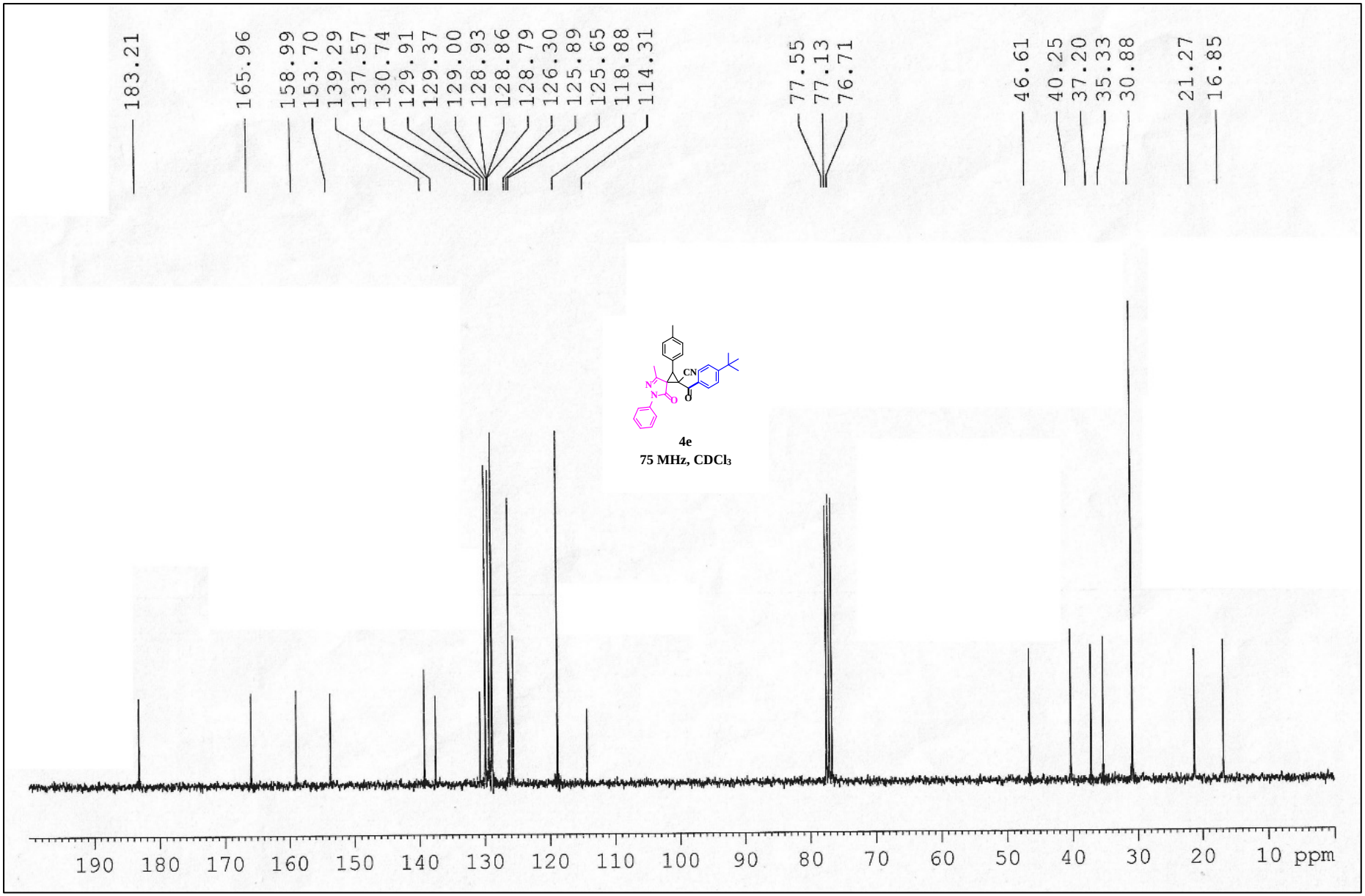

8.44
7.93
7.93
7.91
7.88
7.86
7.71
7.68
7.66
7.64
7.64
7.61
7.57
7.55
7.53
7.52
7.51
7.50
7.33
7.31
7.28
7.18
7.15
7.13
4.34
2.06
CN
O
N
N
O
4c
300 MHz, CDCl3
1.06
4.34
9.73
2.41
1.06
1.00
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


184.30
166.61
154.31
138.14
136.99
133.05
132.12
131.25
130.69
130.30
130.21
130.09
130.02
129.66
129.57
128.56
128.00
126.40
124.32
119.51
114.88
78.18
77.75
77.33
47.44
41.18
37.84
17.55
CN
O
N
N
O
4c
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.93
7.90
7.74
7.72
7.65
7.63
7.61
7.52
7.49
7.47
7.41
7.39
7.37
7.34
7.32
7.29
7.23
7.20
7.18
4.23
2.44
2.02
CN
O
4d
300 MHz. CDCl3
2.03
2.01
1.05
2.12
6.45
1.07
1.00
3.08
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)

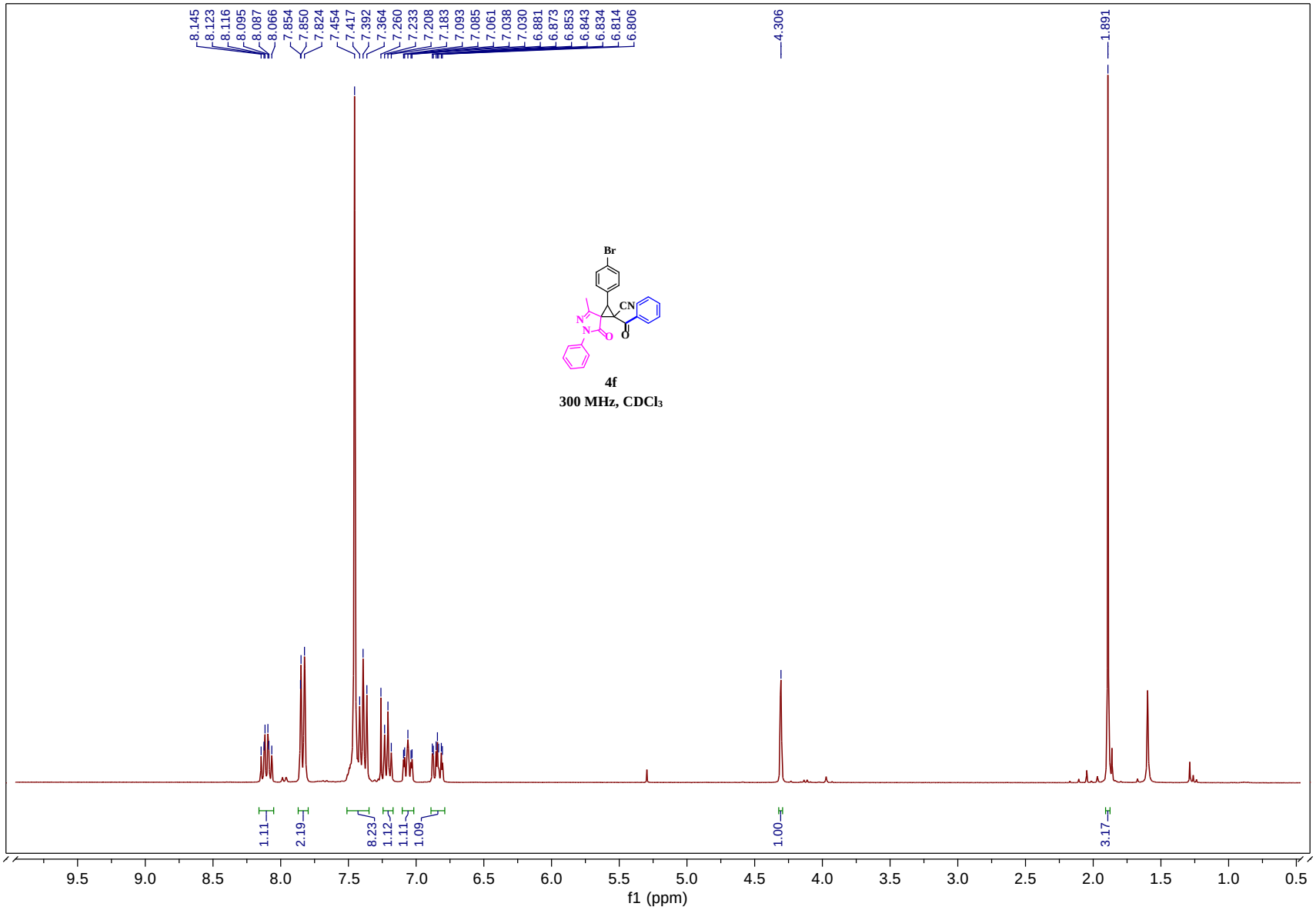

183.69
165.88
153.64
139.37
137.53
134.91
133.23
129.93
129.34
129.26
128.97
128.90
128.83
125.76
125.67
118.75
114.12
77.54
77.12
76.69
46.63
40.28
37.06
21.26
16.84
CN
N
N
O
O
4d
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

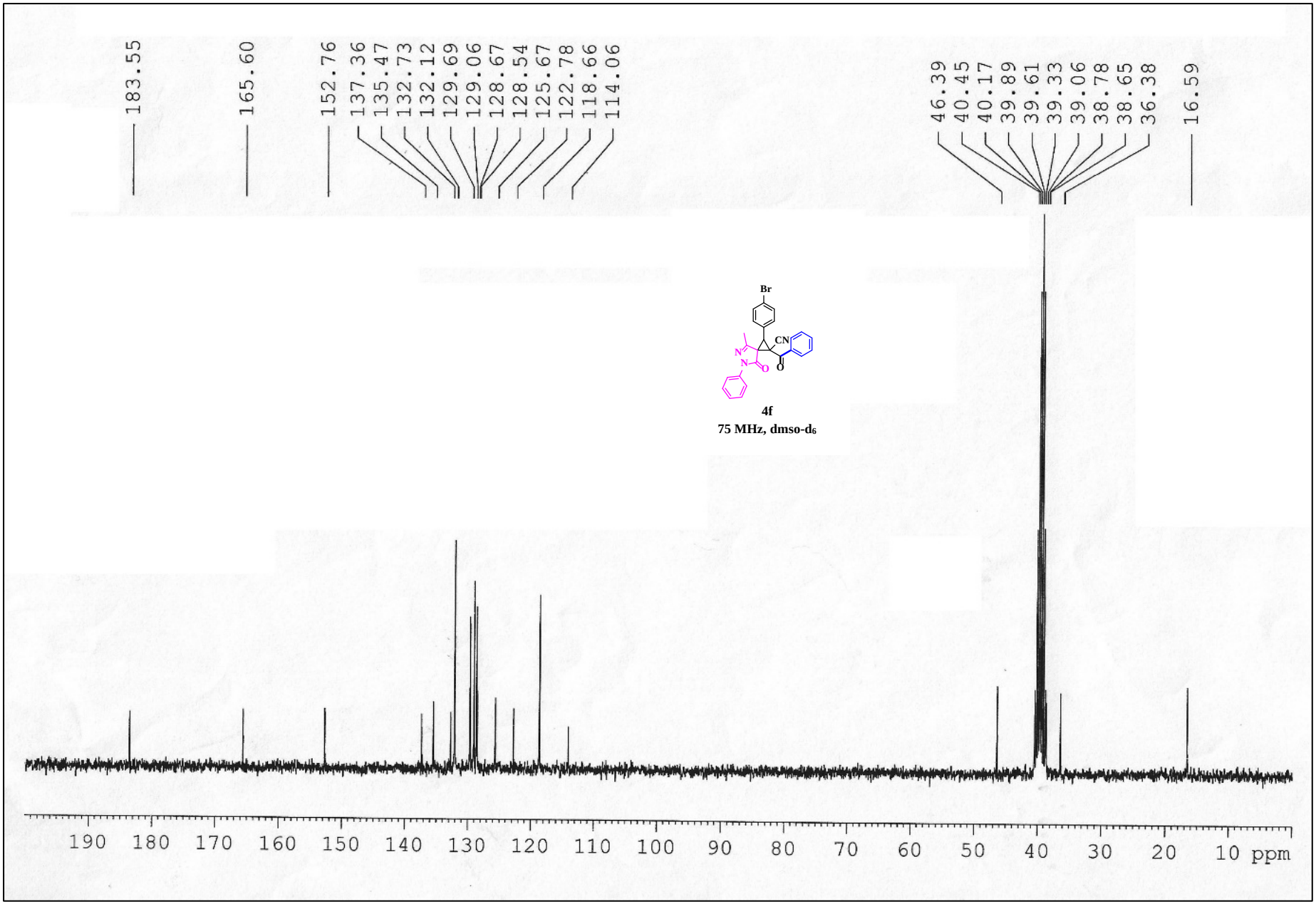

7.85
7.82
7.71
7.68
7.51
7.48
7.40
7.38
7.36
7.33
7.31
7.28
7.22
7.20
7.17
4.21
2.43
2.00
1.31
CN
N
N
O
O
4e
300 MHz, CDCl3
2.09
2.14
2.14
6.00
1.16
1.00
3.23
3.22
9.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

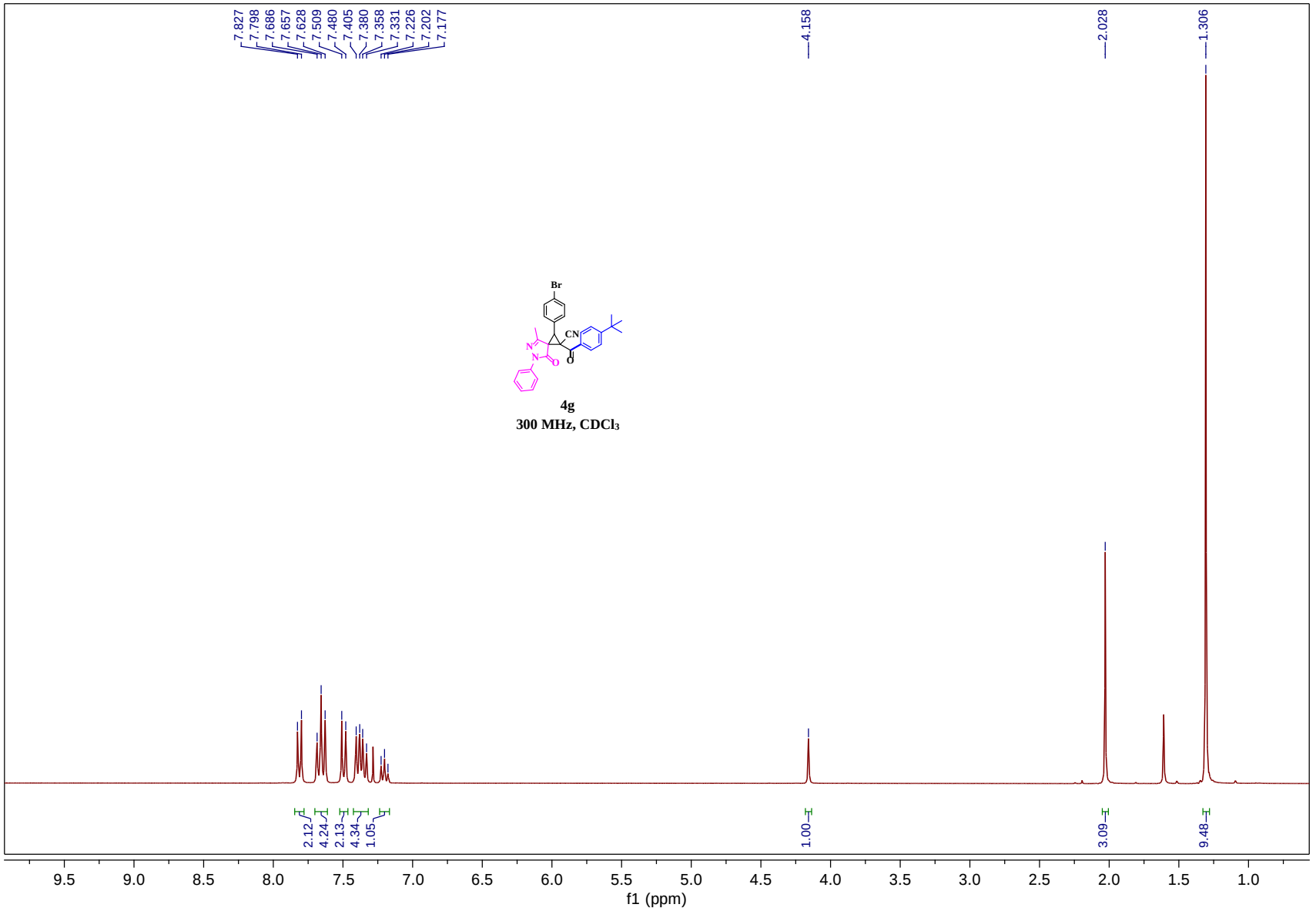


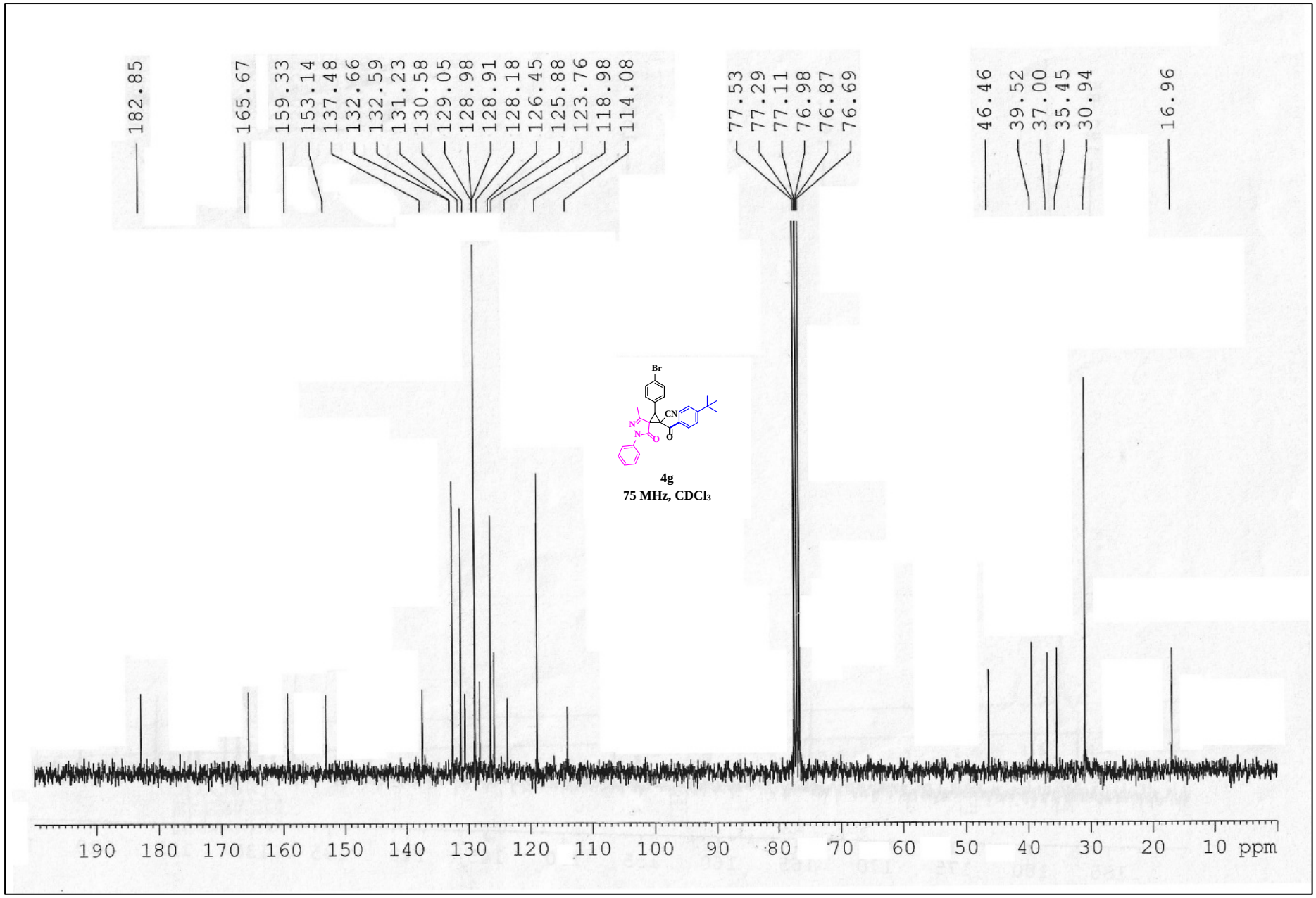

**4e**

**75 MHz, $CDCl_3$**


8.145
8.123
8.116
8.095
8.087
8.066
7.854
7.850
7.824
7.454
7.417
7.392
7.364
7.260
7.233
7.208
7.183
7.093
7.085
7.061
7.038
7.030
6.881
6.873
6.853
6.843
6.834
6.814
6.806
4.306
1.891
Br
CN
N
N
O
O
4f
300 MHz, CDCl3
1.11
2.19
8.23
1.12
1.11
1.09
1.00
3.17
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
f1 (ppm)

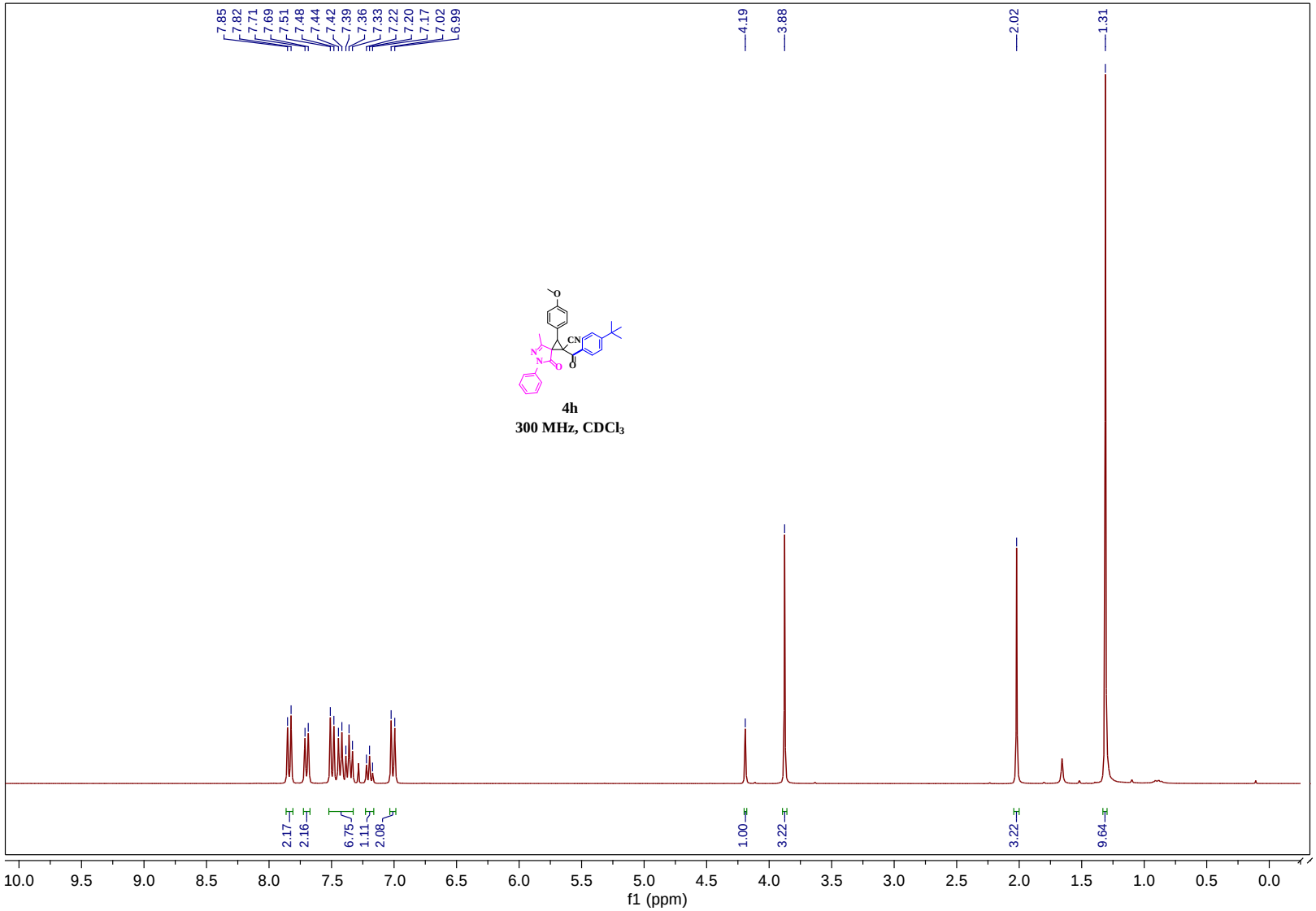

183.55
165.60
152.76
137.36
135.47
132.73
132.12
129.69
129.06
128.67
128.54
125.67
122.78
118.66
114.06
46.39
40.45
40.17
39.89
39.61
39.33
39.06
38.78
38.65
36.38
16.59
Br
CN
O
N
N
O
4f
75 MHz, dmso-d6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

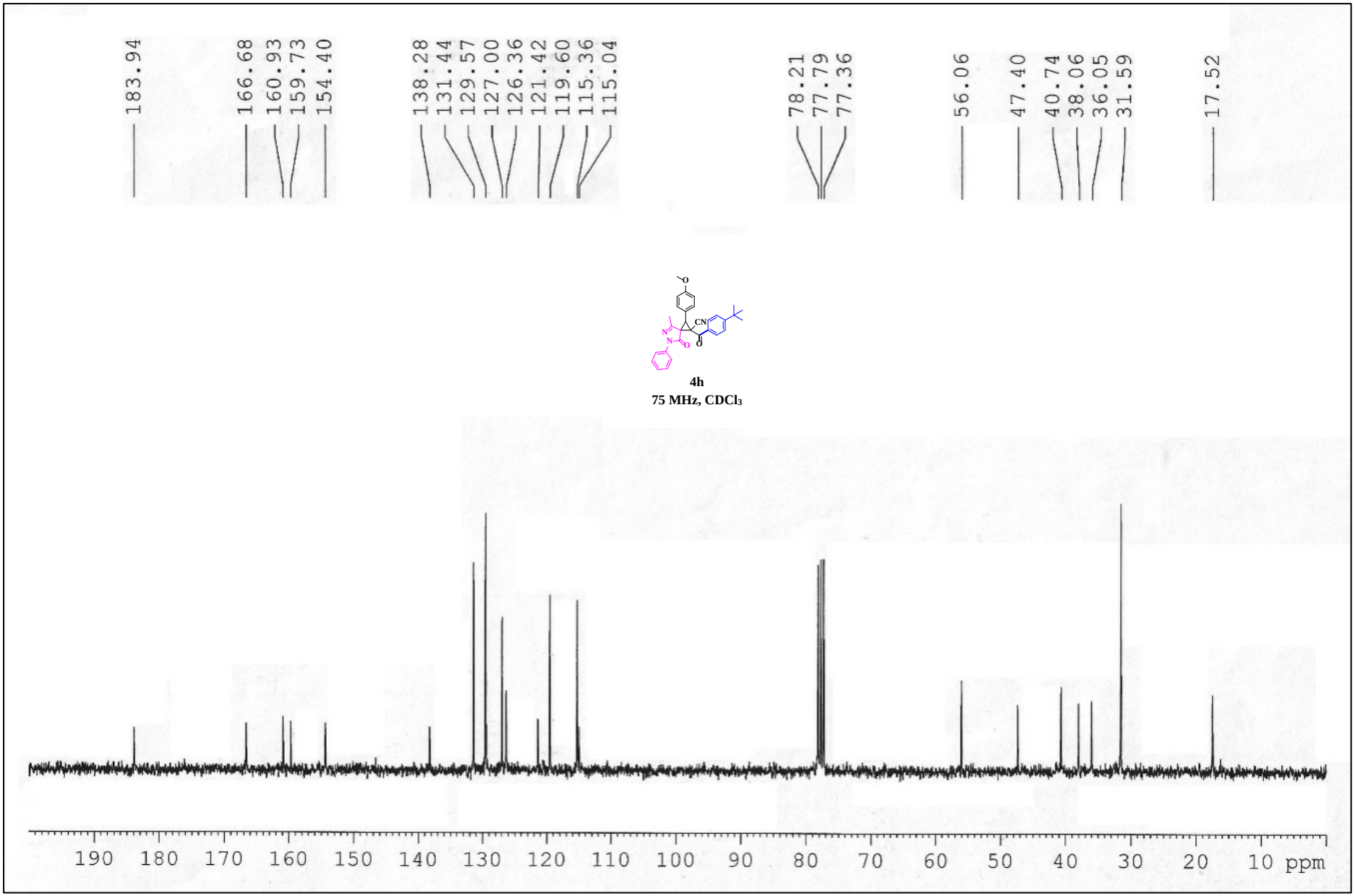

7.827
7.798
7.686
7.657
7.628
7.509
7.480
7.405
7.380
7.358
7.331
7.226
7.202
7.177
4.158
2.028
1.306
Br
CN
O
N
N
O
4g
300 MHz, CDCl3
2.12
4.24
2.13
4.34
1.05
1.00
3.09
9.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)




**4g**

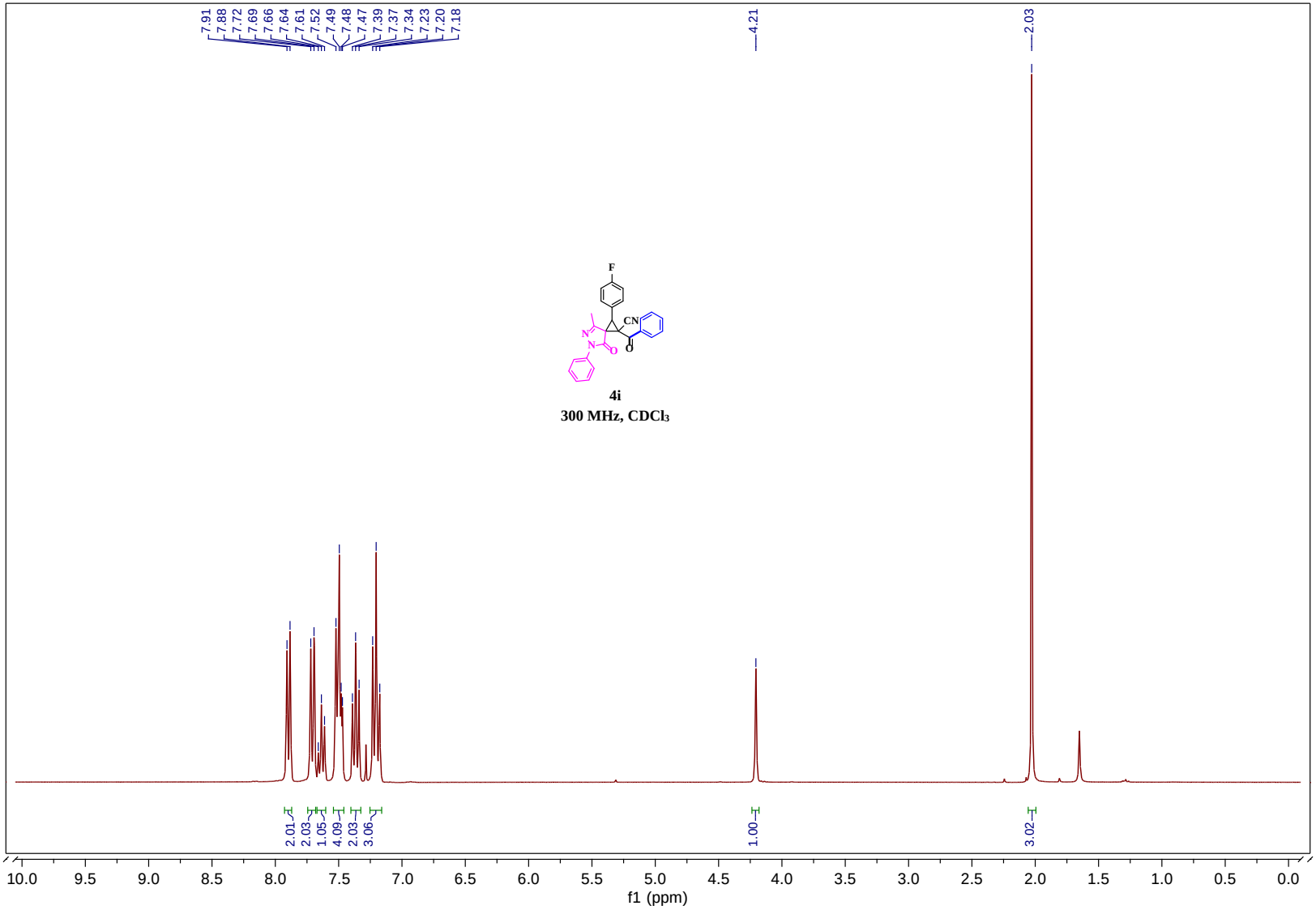
**75 MHz, $CDCl_3$**

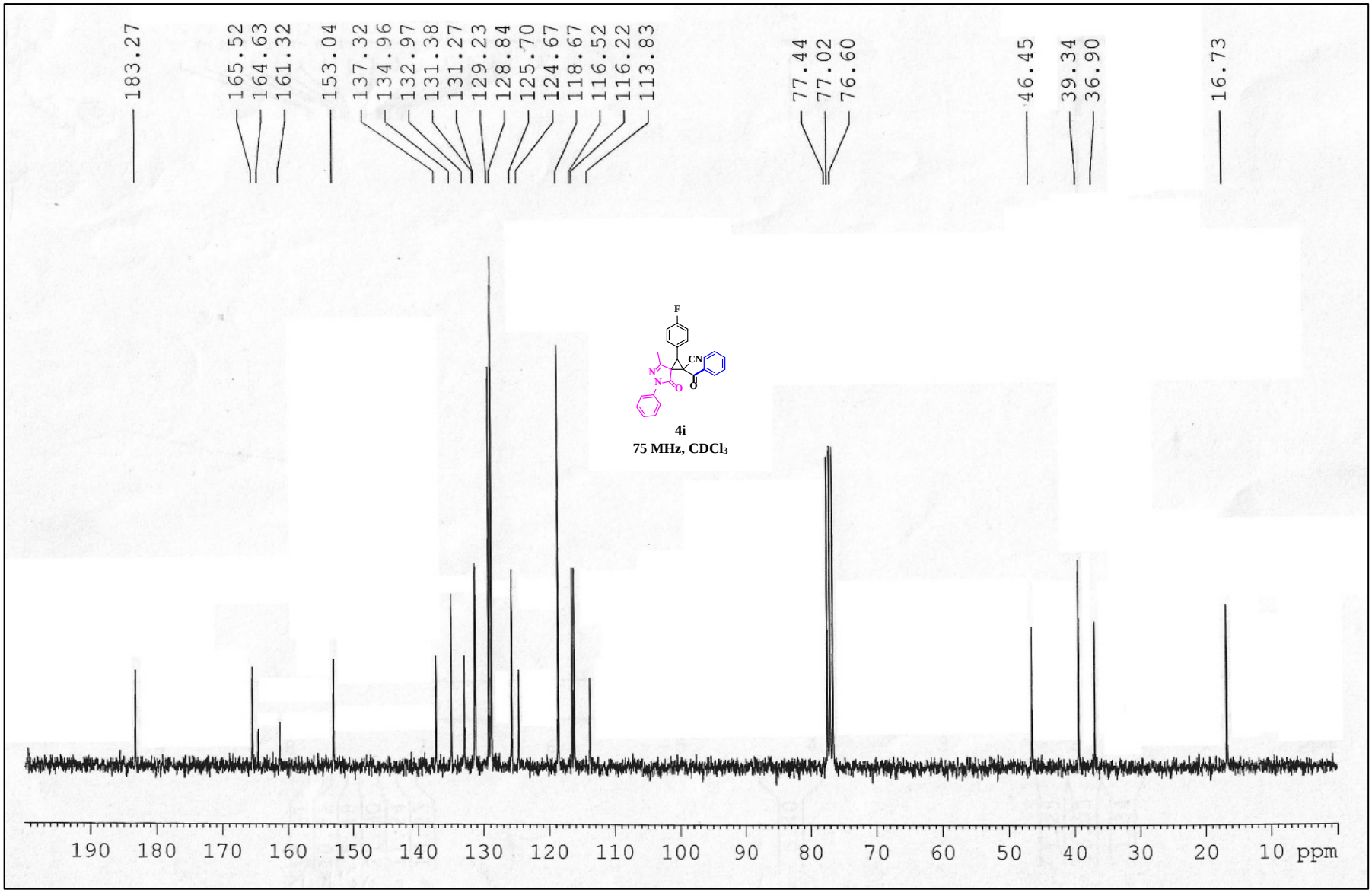

7.85
7.82
7.71
7.69
7.51
7.48
7.44
7.42
7.39
7.36
7.33
7.22
7.20
7.17
7.02
6.99
4.19
3.88
2.02
1.31
4h
300 MHz, CDCl3
2.17
2.16
6.75
1.11
2.08
1.00
3.22
3.22
9.64
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

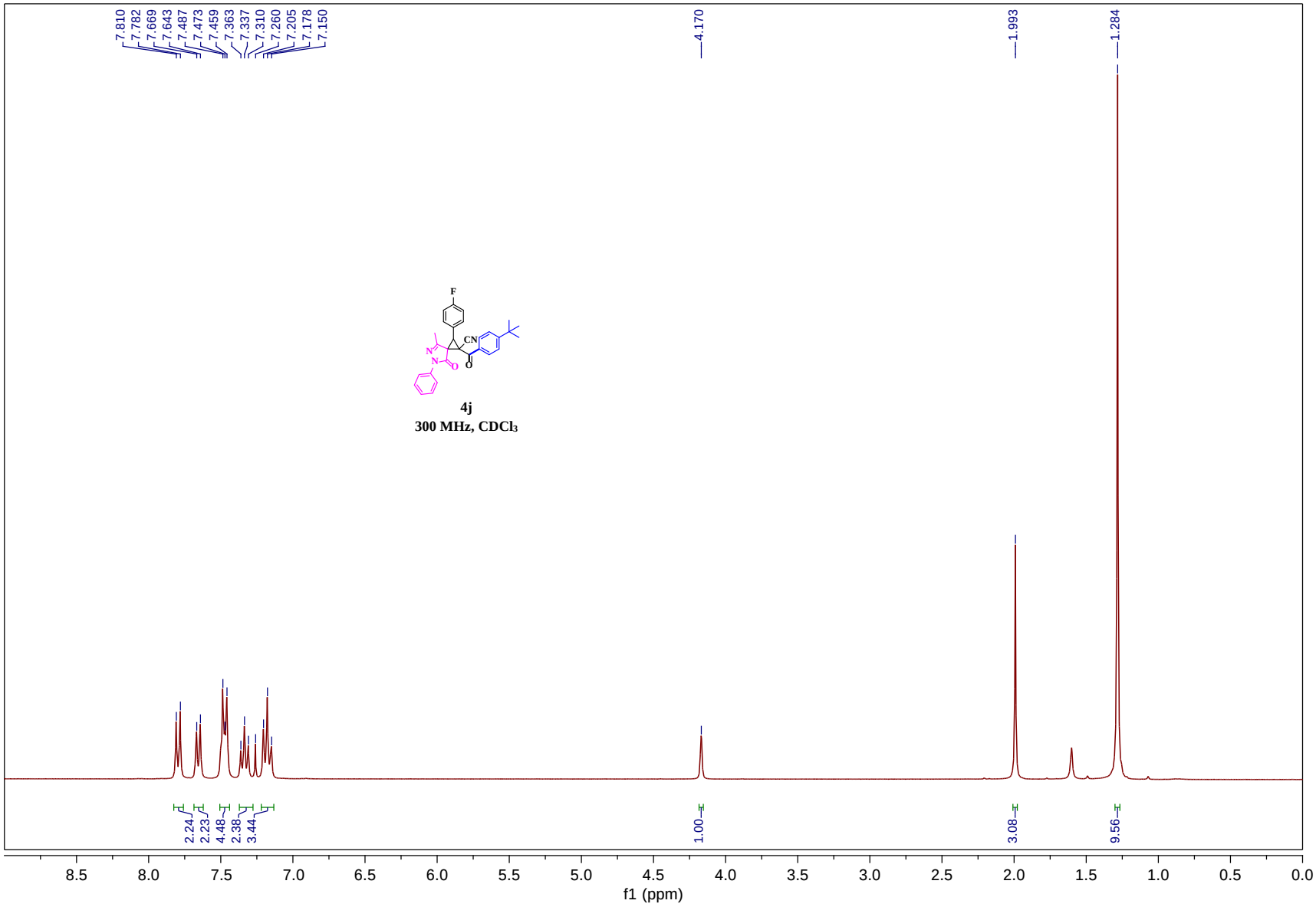


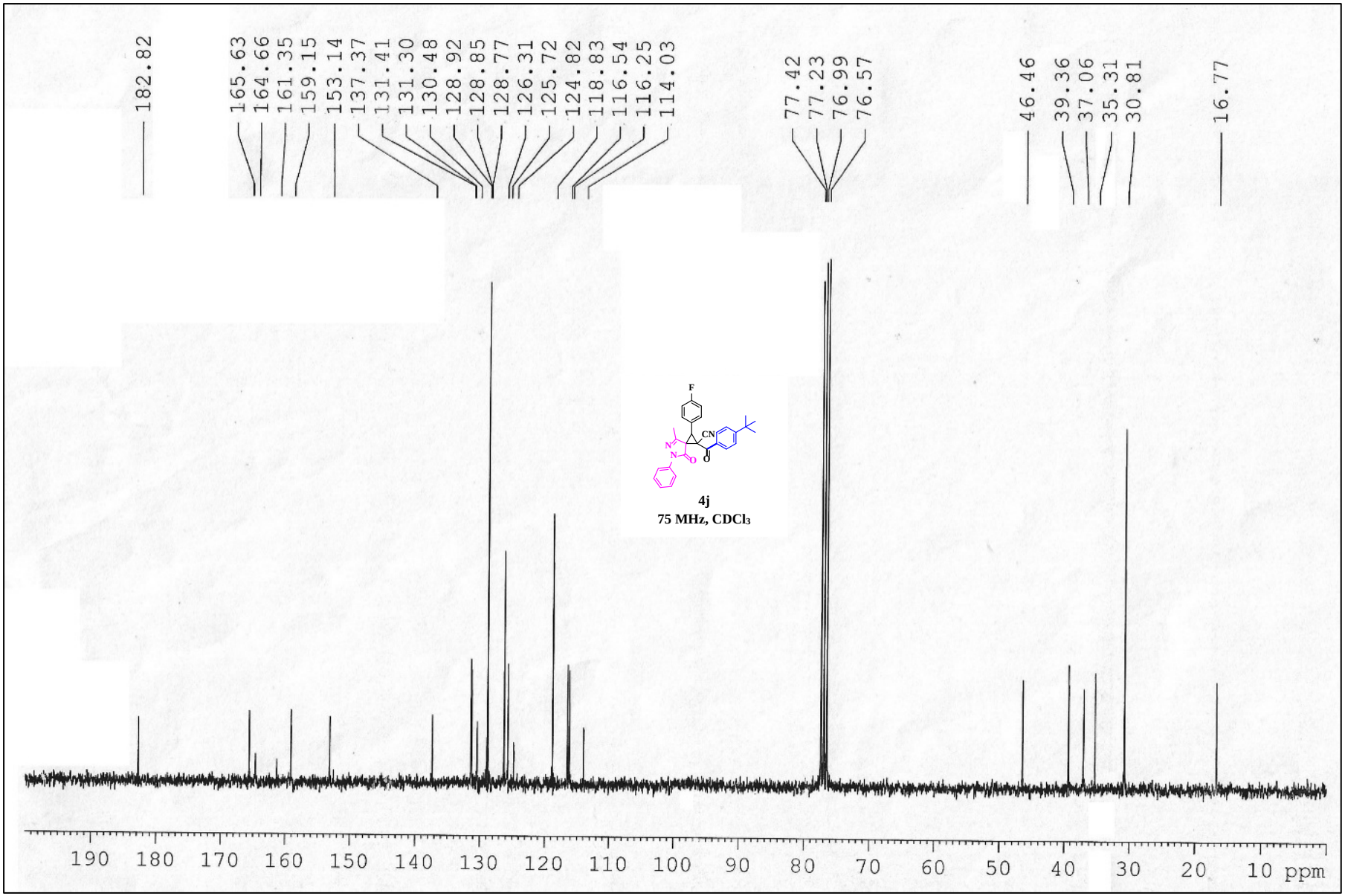

**4h**

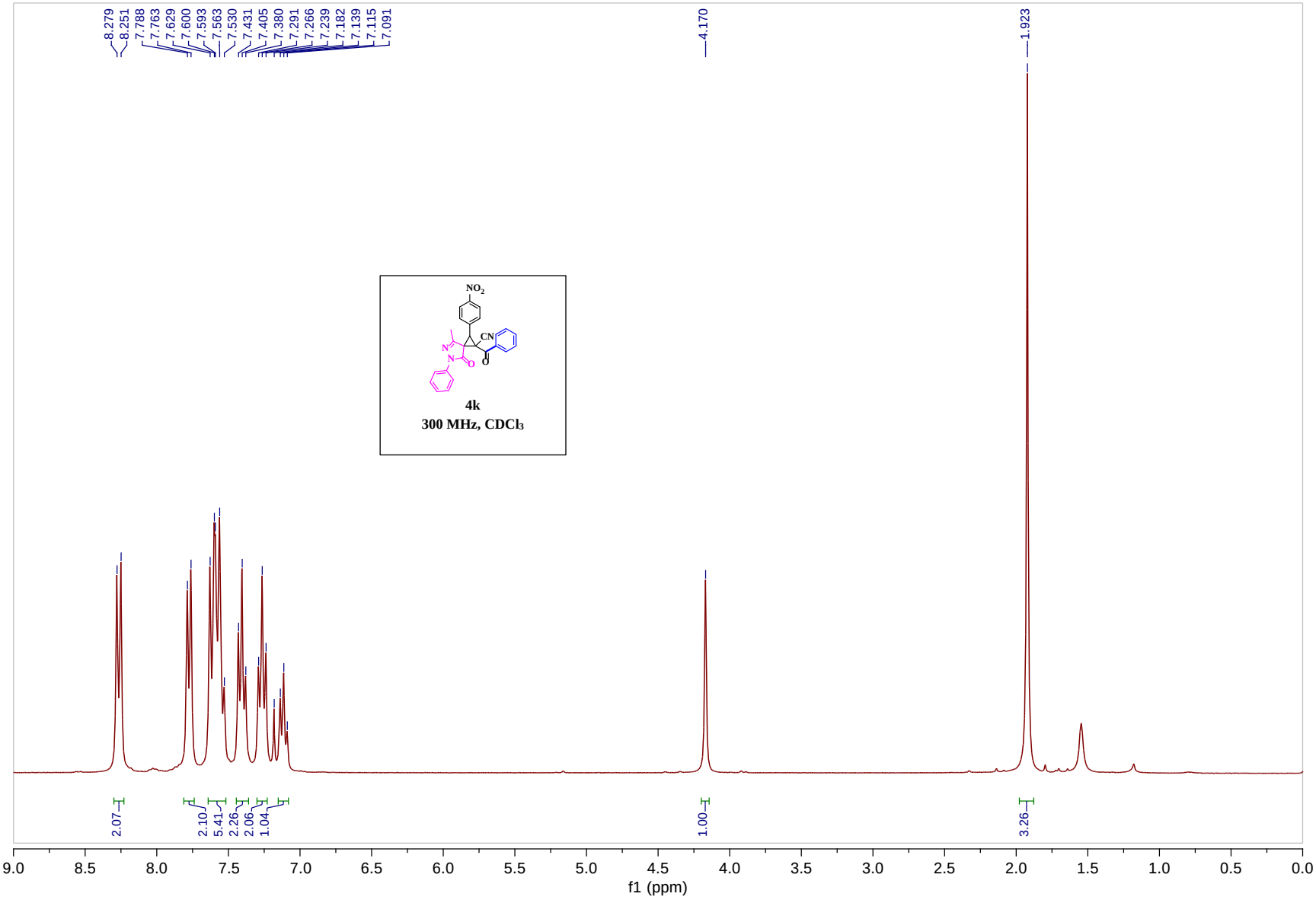
**75 MHz, $CDCl_3$**

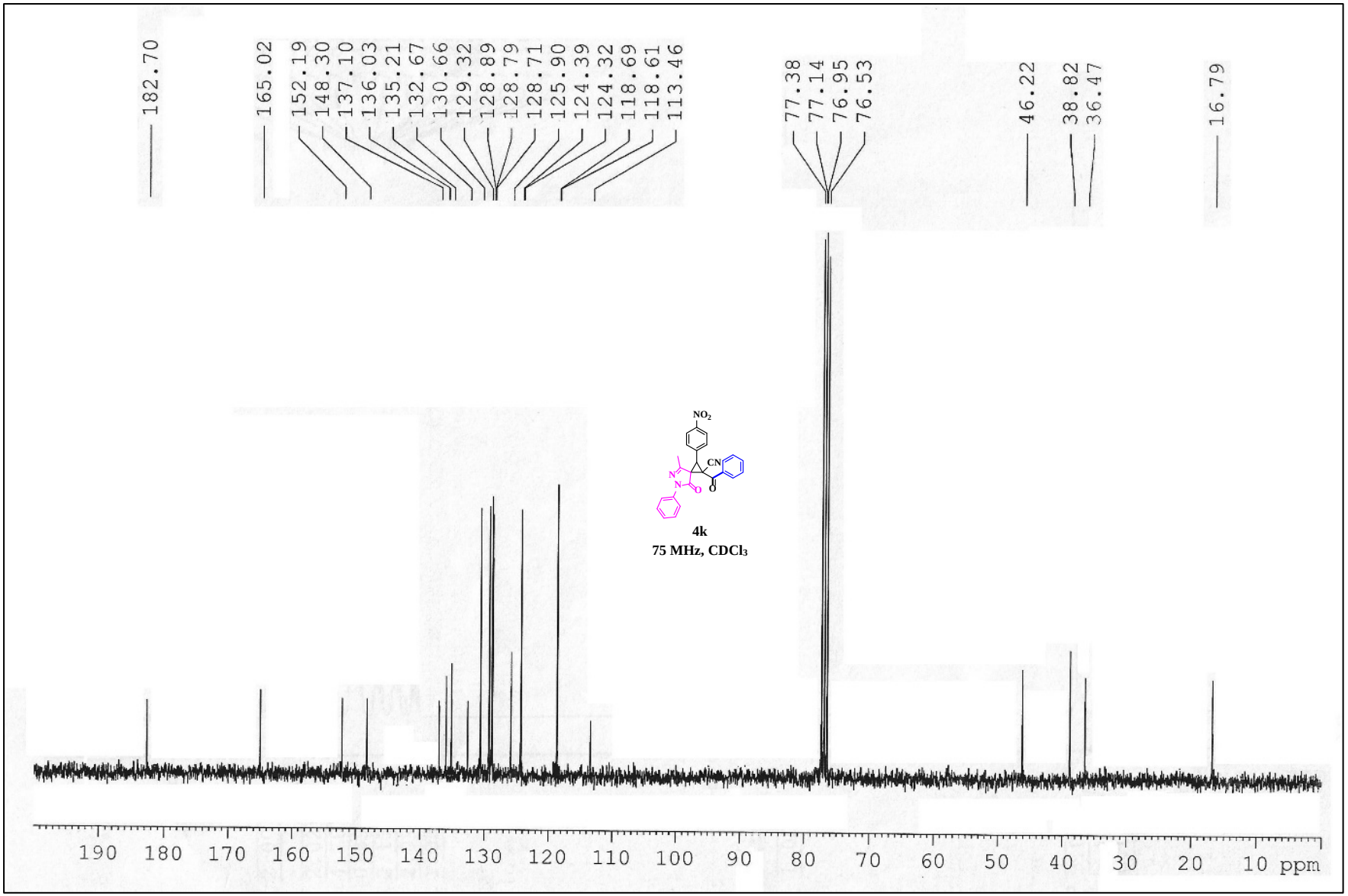

7.91
7.88
7.72
7.69
7.66
7.64
7.61
7.52
7.49
7.48
7.47
7.39
7.37
7.34
7.23
7.20
7.18
4.21
2.03
F
CN
O
N
N
O
4i
300 MHz, CDCl3
2.01
2.03
1.05
4.09
2.03
3.06
1.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

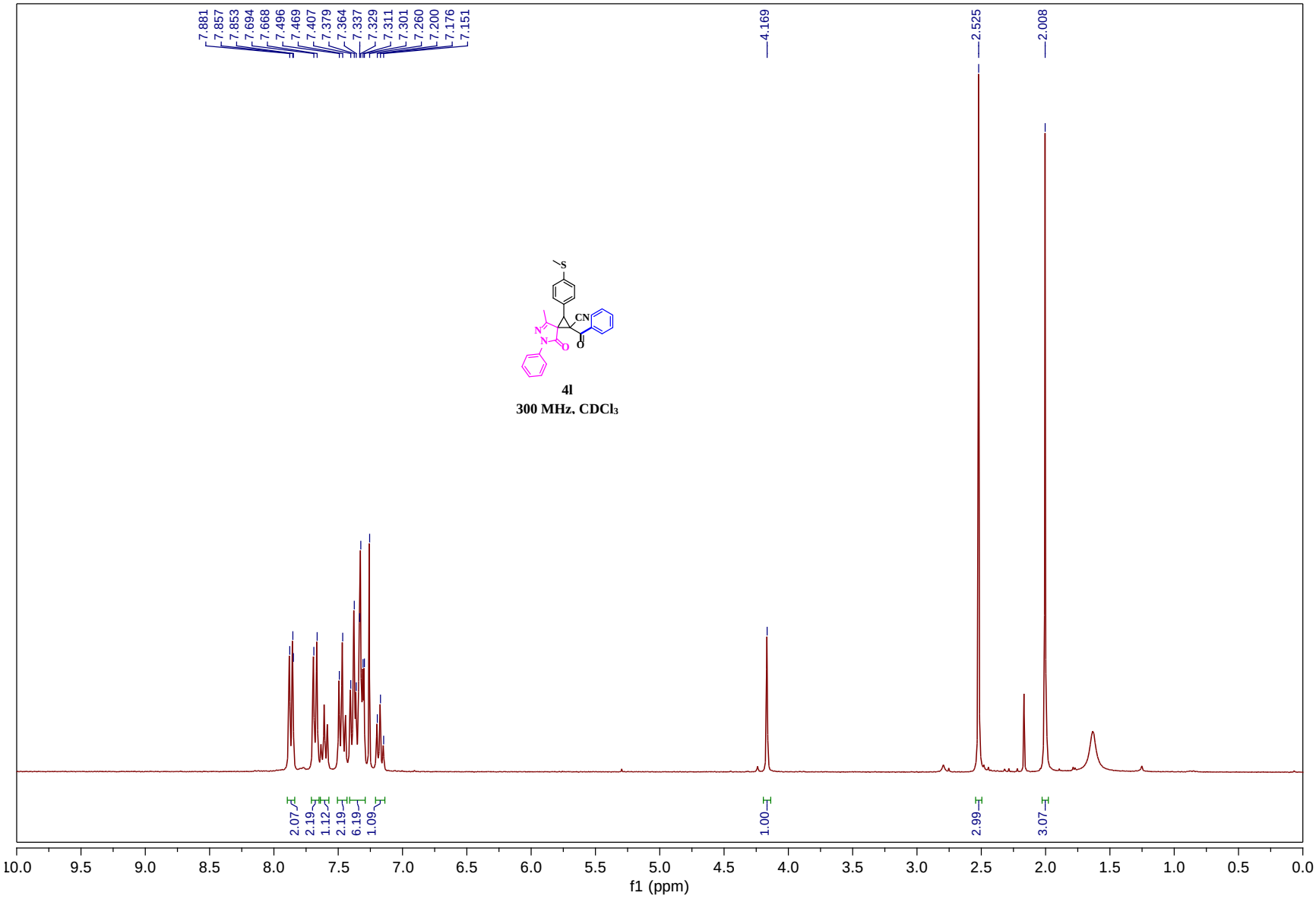

183.27
165.52
164.63
161.32
153.04
137.32
134.96
132.97
131.38
131.27
129.23
128.84
125.70
124.67
118.67
116.52
116.22
113.83
77.44
77.02
76.60
46.45
39.34
36.90
16.73
F
CN
N
N
O
O
4i
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.810
7.782
7.669
7.643
7.487
7.473
7.459
7.363
7.337
7.310
7.260
7.205
7.178
7.150
4.170
1.993
1.284
F
CN
O
O
N
N
4j
300 MHz, CDCl3
2.24
2.23
4.48
2.38
3.44
1.00
3.08
9.56
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)


182.82
165.63
164.66
161.35
159.15
153.14
137.37
131.41
131.30
130.48
128.92
128.85
128.77
126.31
125.72
124.82
118.83
116.54
116.25
114.03
77.42
77.23
76.99
76.57
46.46
39.36
37.06
35.31
30.81
16.77
F
CN
O
N
O
4j
75 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

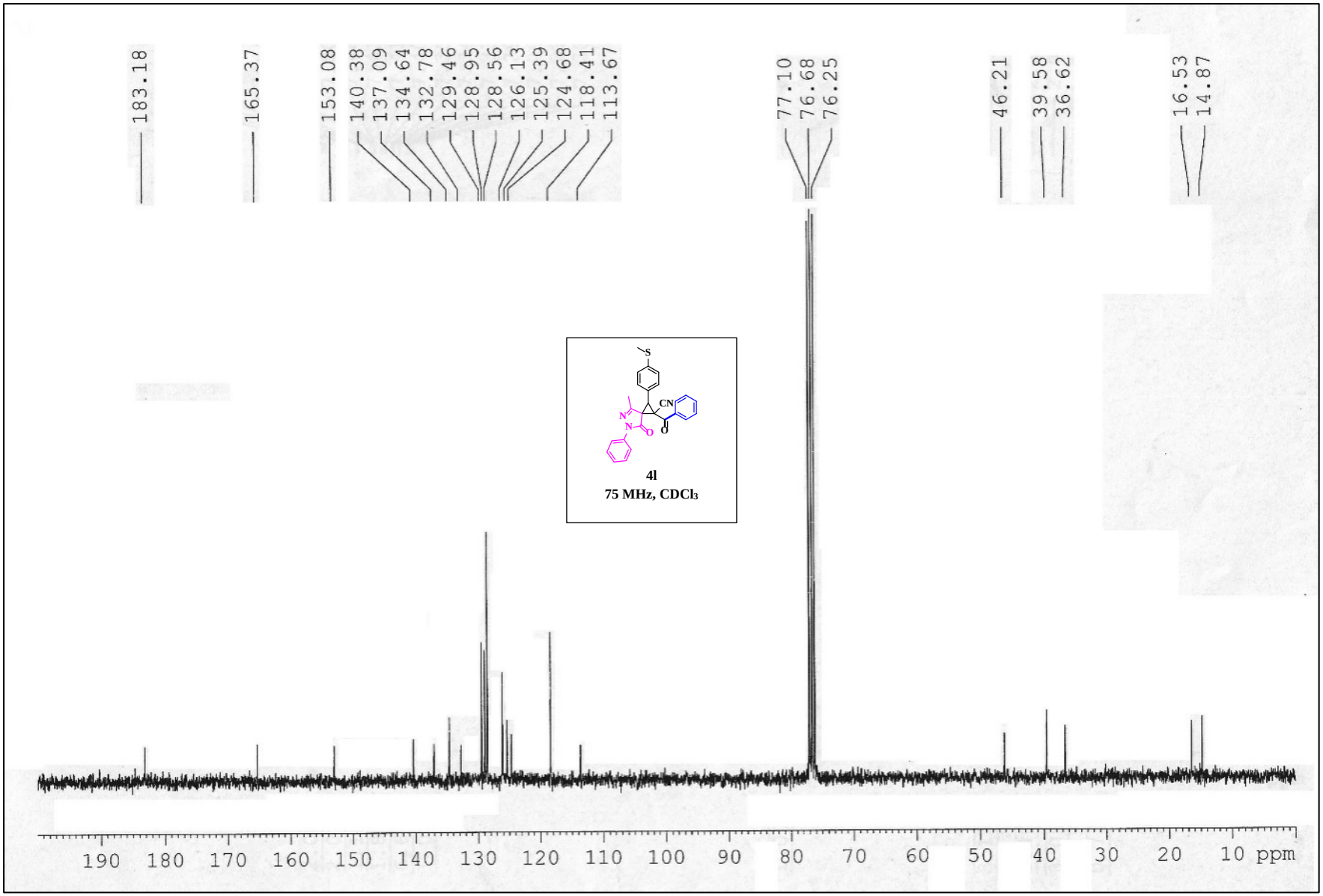

8.279
8.251
7.788
7.763
7.629
7.600
7.593
7.563
7.530
7.431
7.405
7.380
7.291
7.266
7.239
7.182
7.139
7.115
7.091
4.170
1.923
NO2
CN
O
O
4k
300 MHz, CDCl3
2.07
2.10
5.41
2.26
2.06
1.04
1.00
3.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

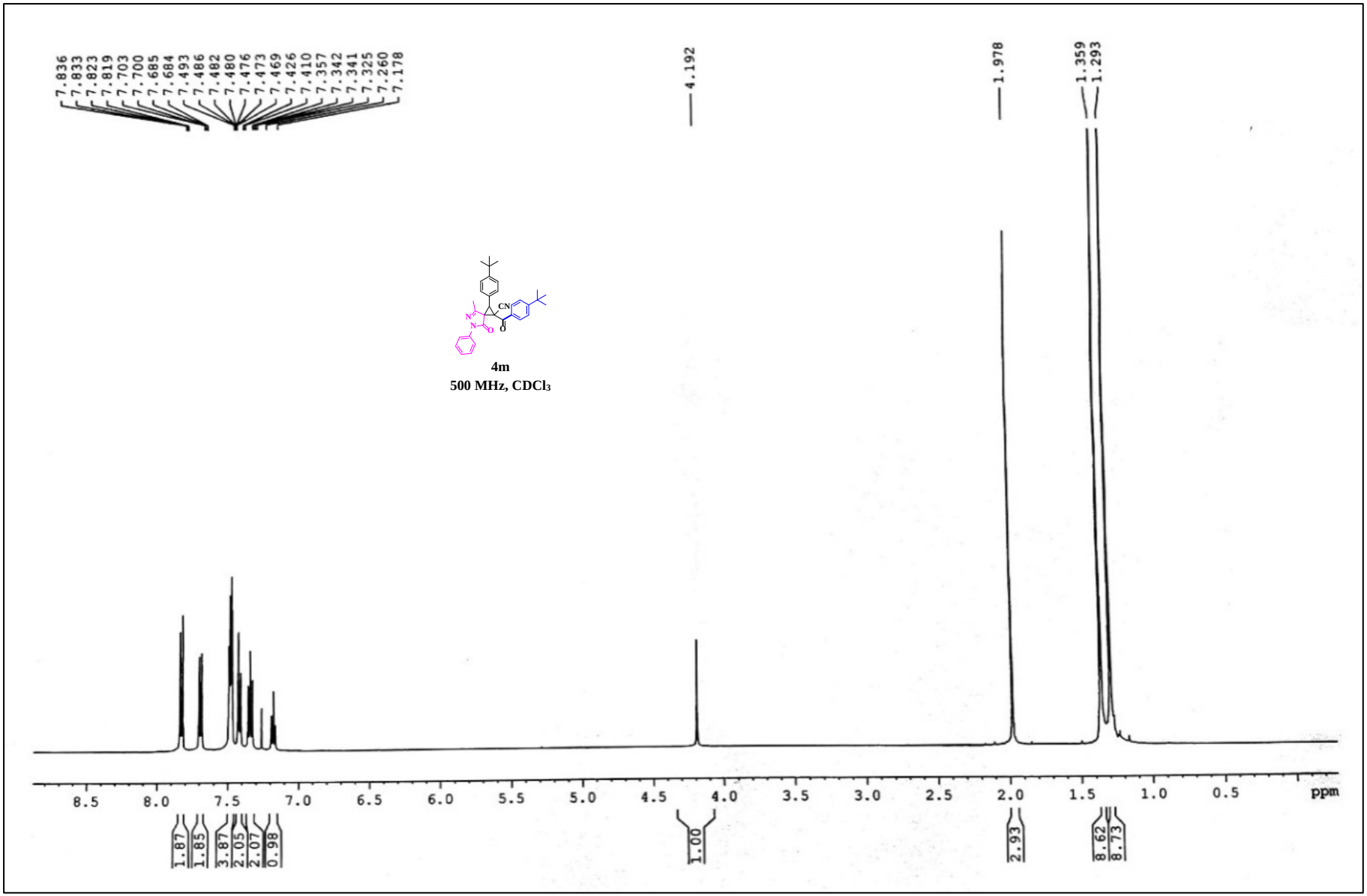

182.70
165.02
152.19
148.30
137.10
136.03
135.21
132.67
130.66
129.32
128.89
128.79
128.71
125.90
124.39
124.32
118.69
118.61
113.46
77.38
77.14
76.95
76.53
46.22
38.82
36.47
16.79
NO2
CN
O
N
4k
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

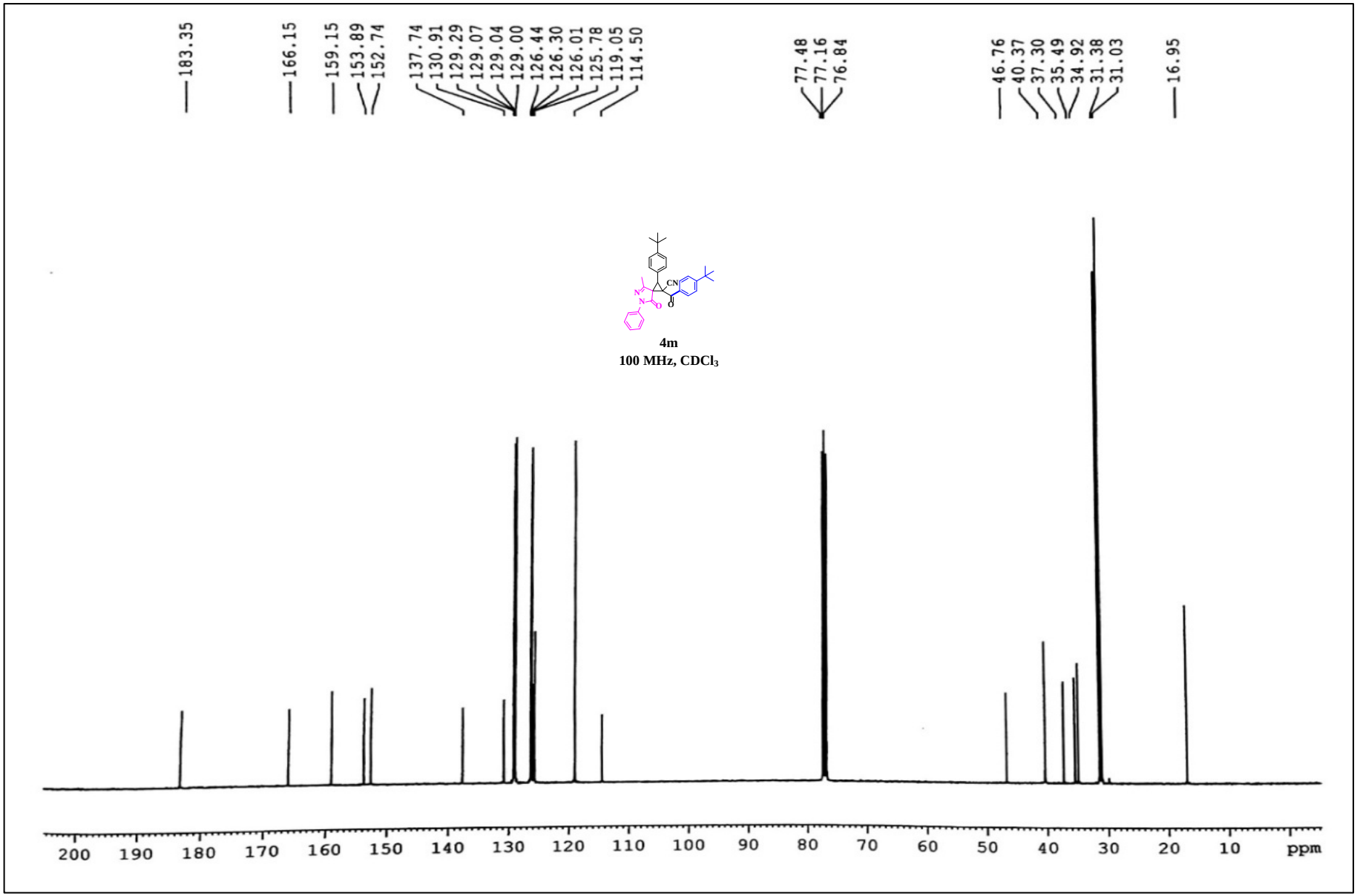


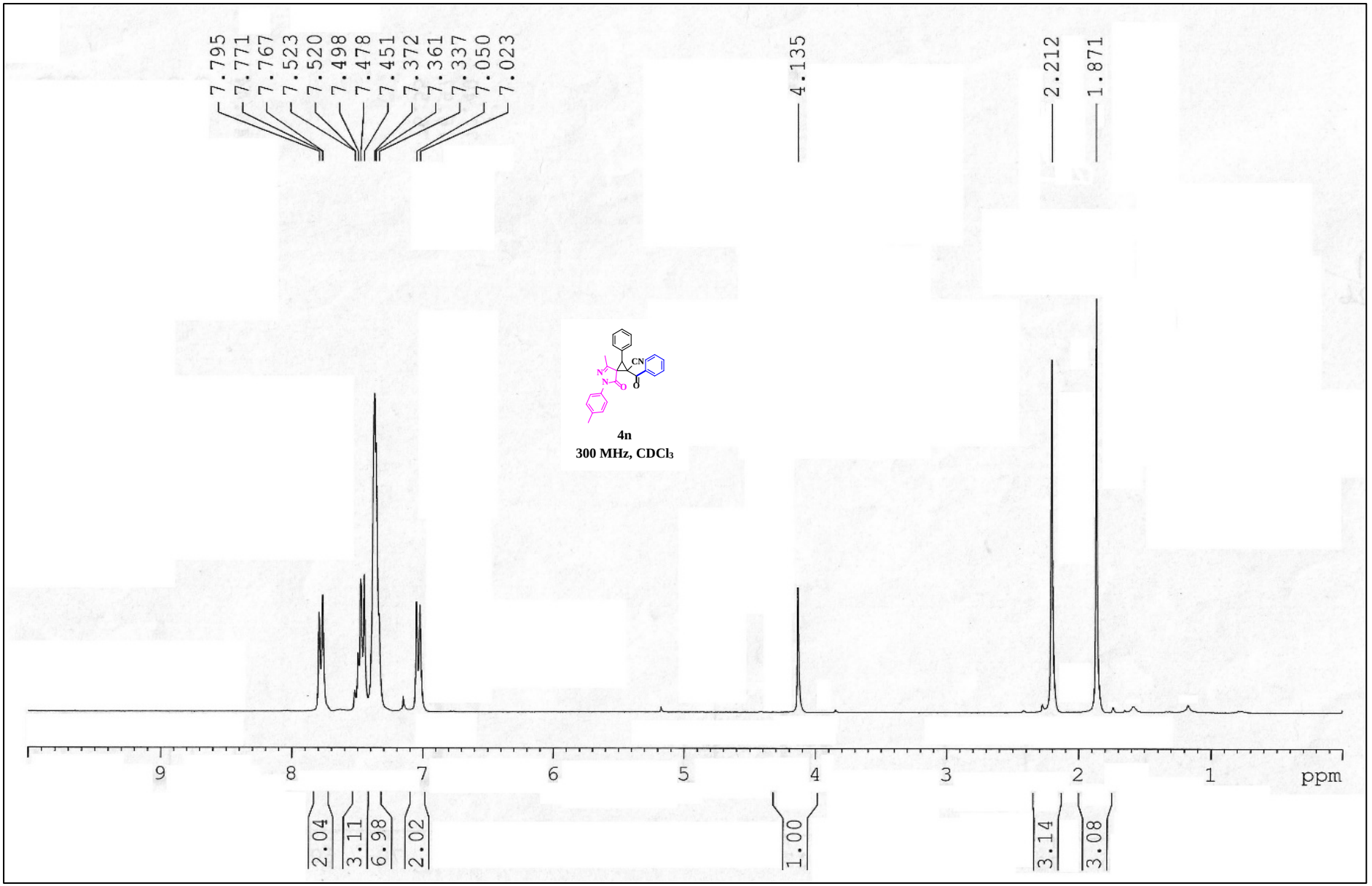

**4l**

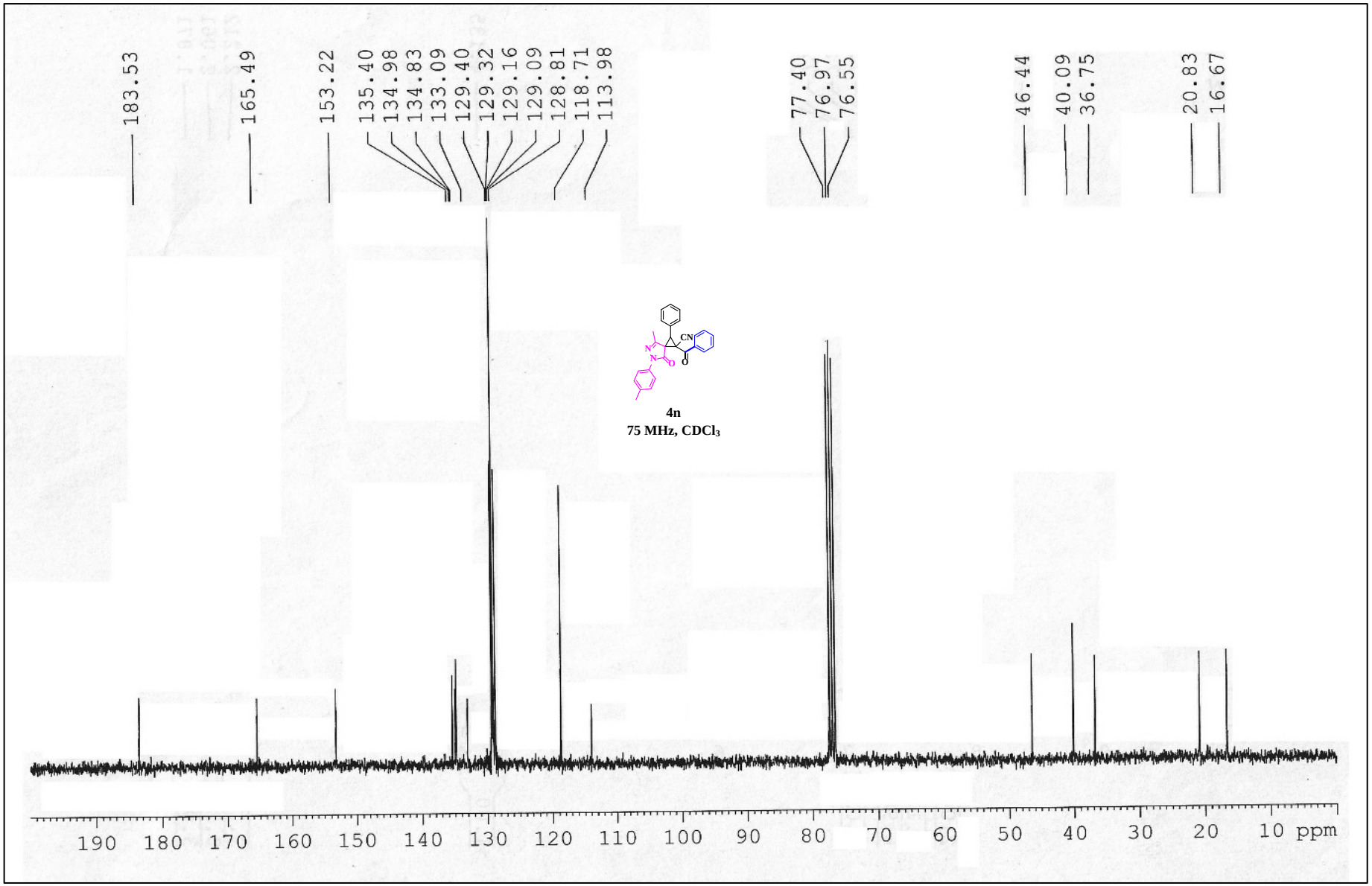
**300 MHz, $CDCl_3$**


183.18
165.37
153.08
140.38
137.09
134.64
132.78
129.46
128.95
128.56
126.13
125.39
124.68
118.41
113.67
77.10
76.68
76.25
46.21
39.58
36.62
16.53
14.87
S
CN
N
O
O
4l
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.836
7.833
7.823
7.819
7.703
7.700
7.685
7.684
7.493
7.486
7.482
7.480
7.476
7.473
7.469
7.426
7.410
7.357
7.342
7.341
7.325
7.260
7.178
4.192
1.978
1.359
1.293
CN
O
4m
500 MHz, CDCl3
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
1.87
1.85
3.87
2.05
2.07
0.98
1.00
2.93
8.62
8.73

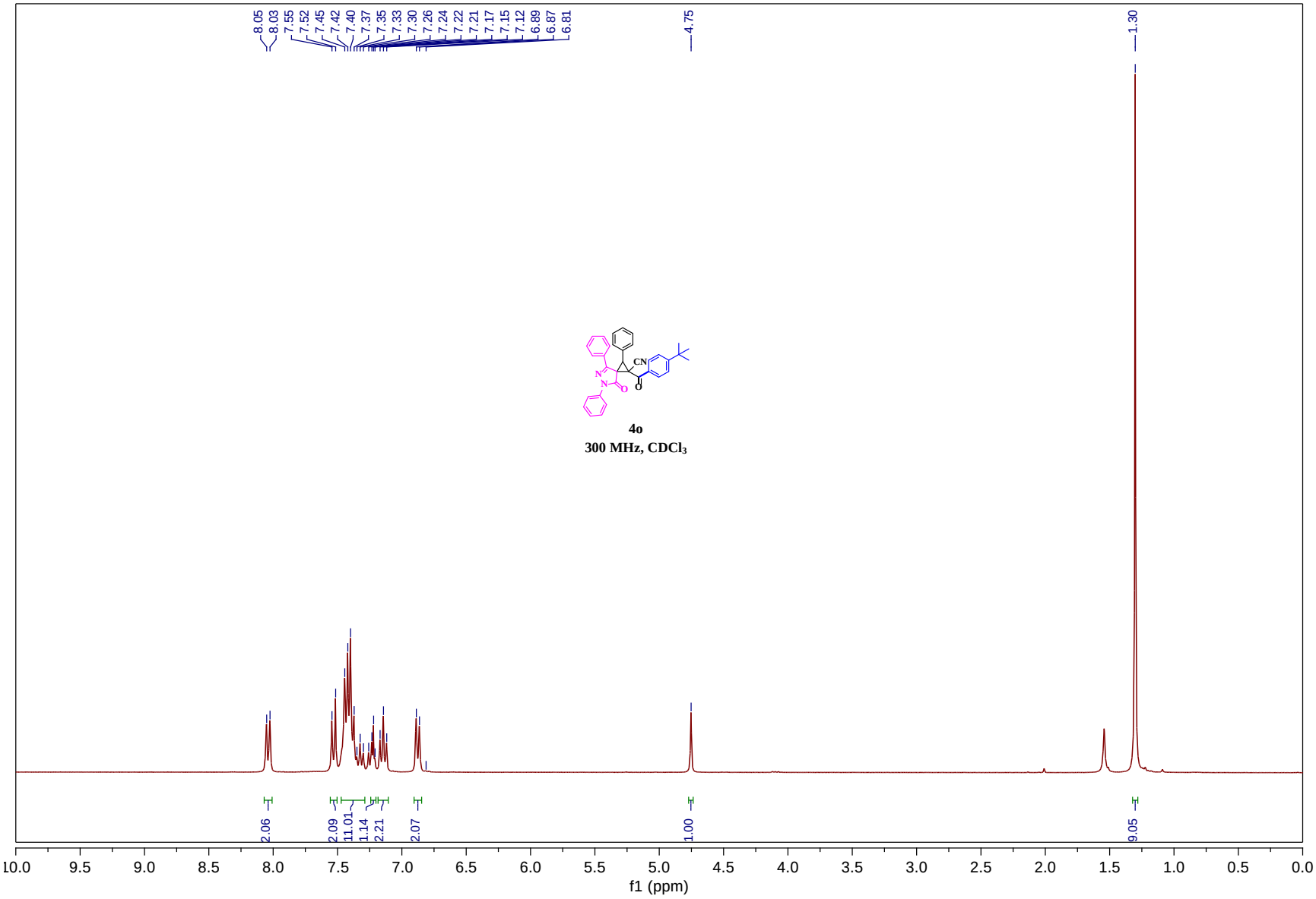

183.35
166.15
159.15
153.89
152.74
137.74
130.91
129.29
129.07
129.04
129.00
126.44
126.30
126.01
125.78
119.05
114.50
77.48
77.16
76.84
46.76
40.37
37.30
35.49
34.92
31.38
31.03
16.95
CN
O
4m
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

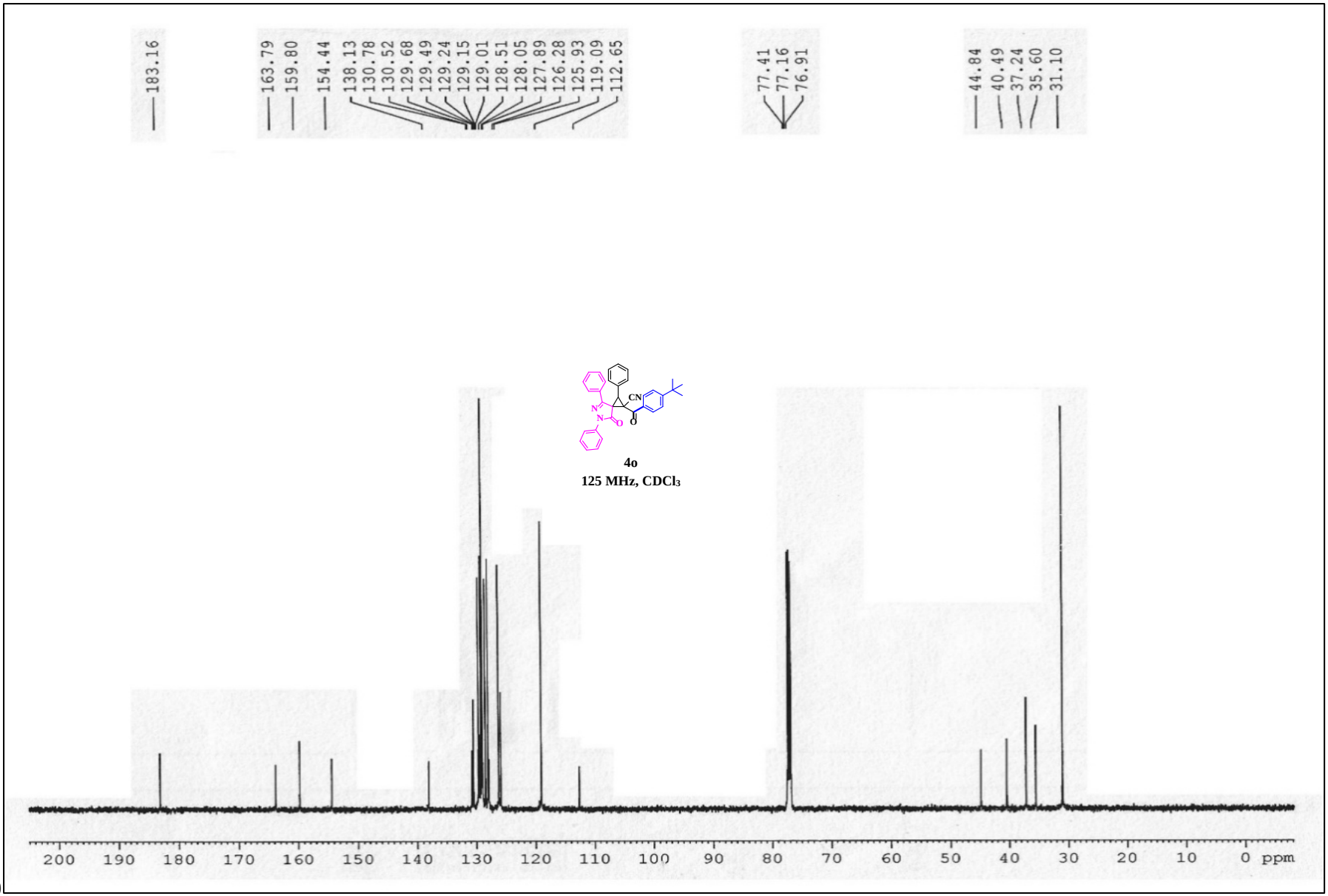

7.795
7.771
7.767
7.523
7.520
7.498
7.478
7.451
7.372
7.361
7.337
7.050
7.023
4.135
2.212
1.871
CN
O
4n
300 MHz, CDCl3
9
8
7
6
5
4
3
2
1
ppm
2.04
3.11
6.98
2.02
1.00
3.14
3.08

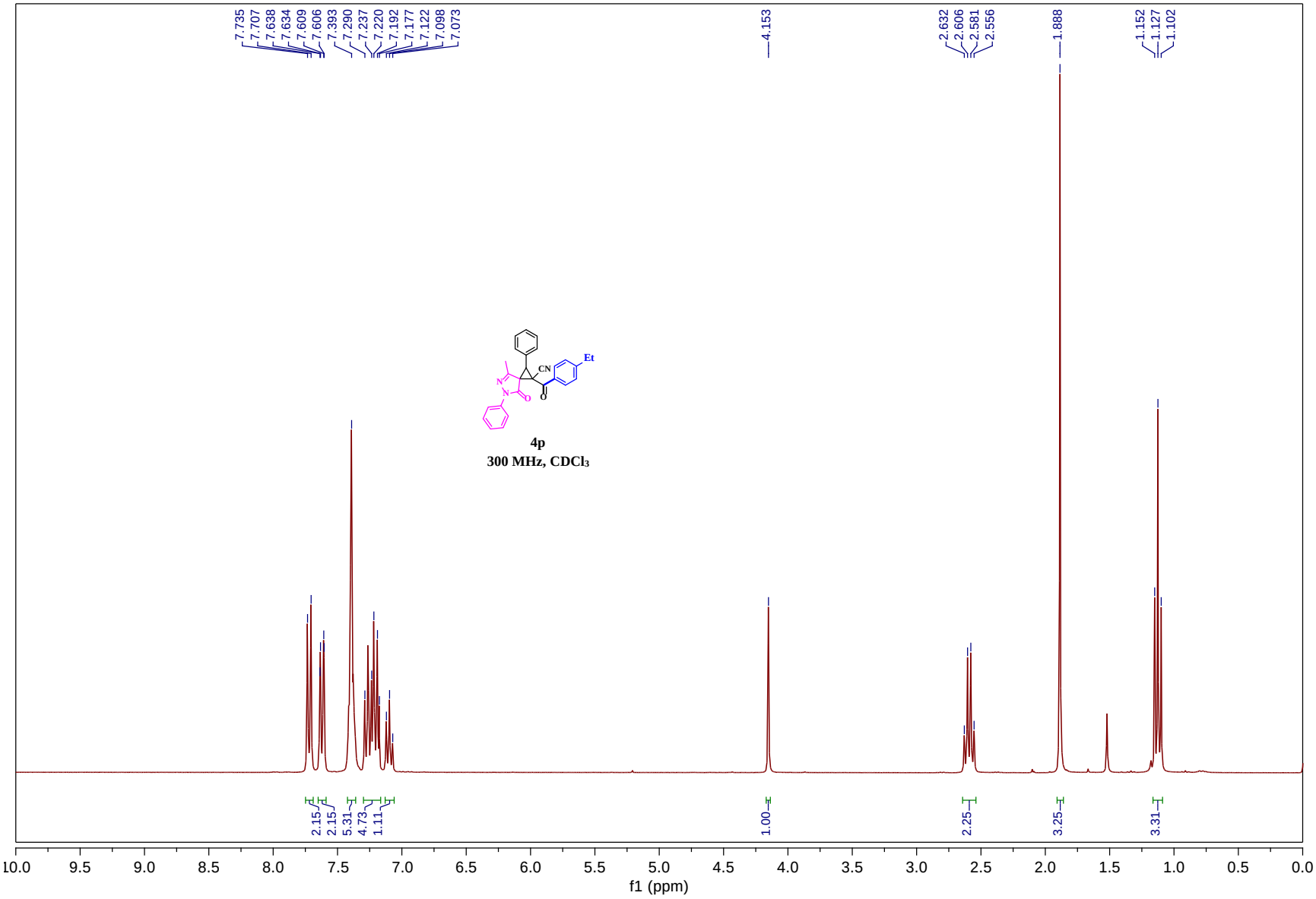


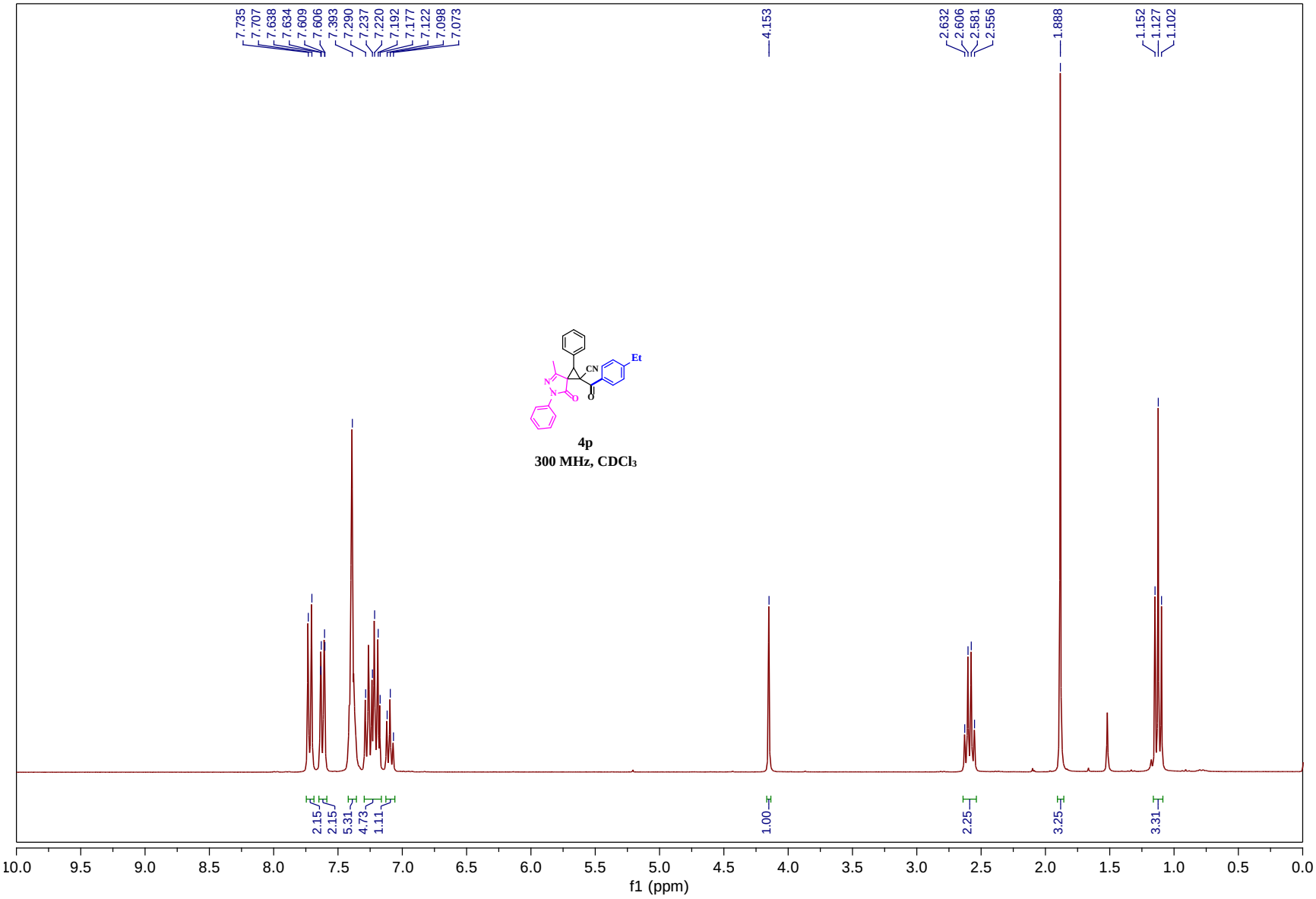

**4n**

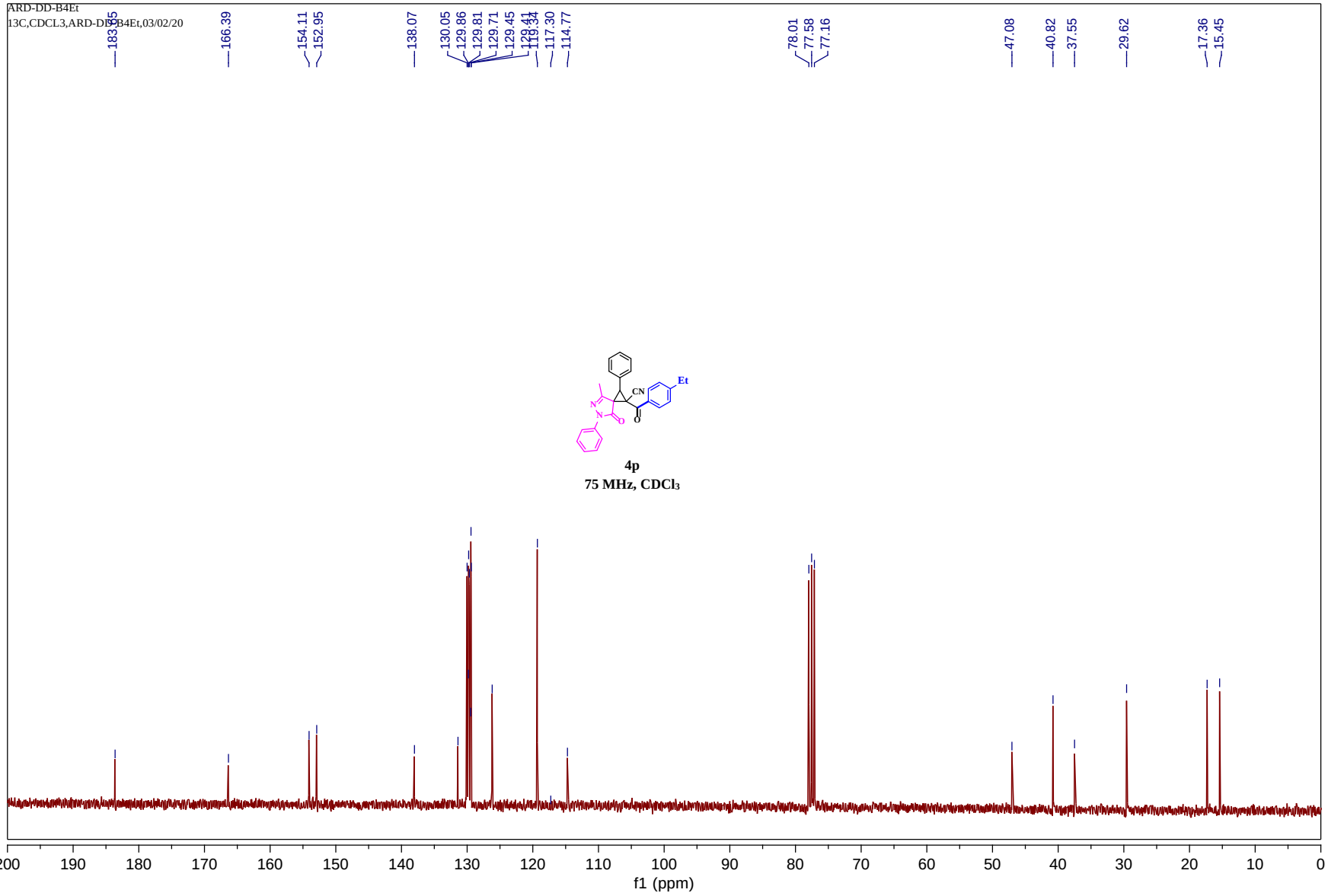
**75 MHz, $CDCl_3$**

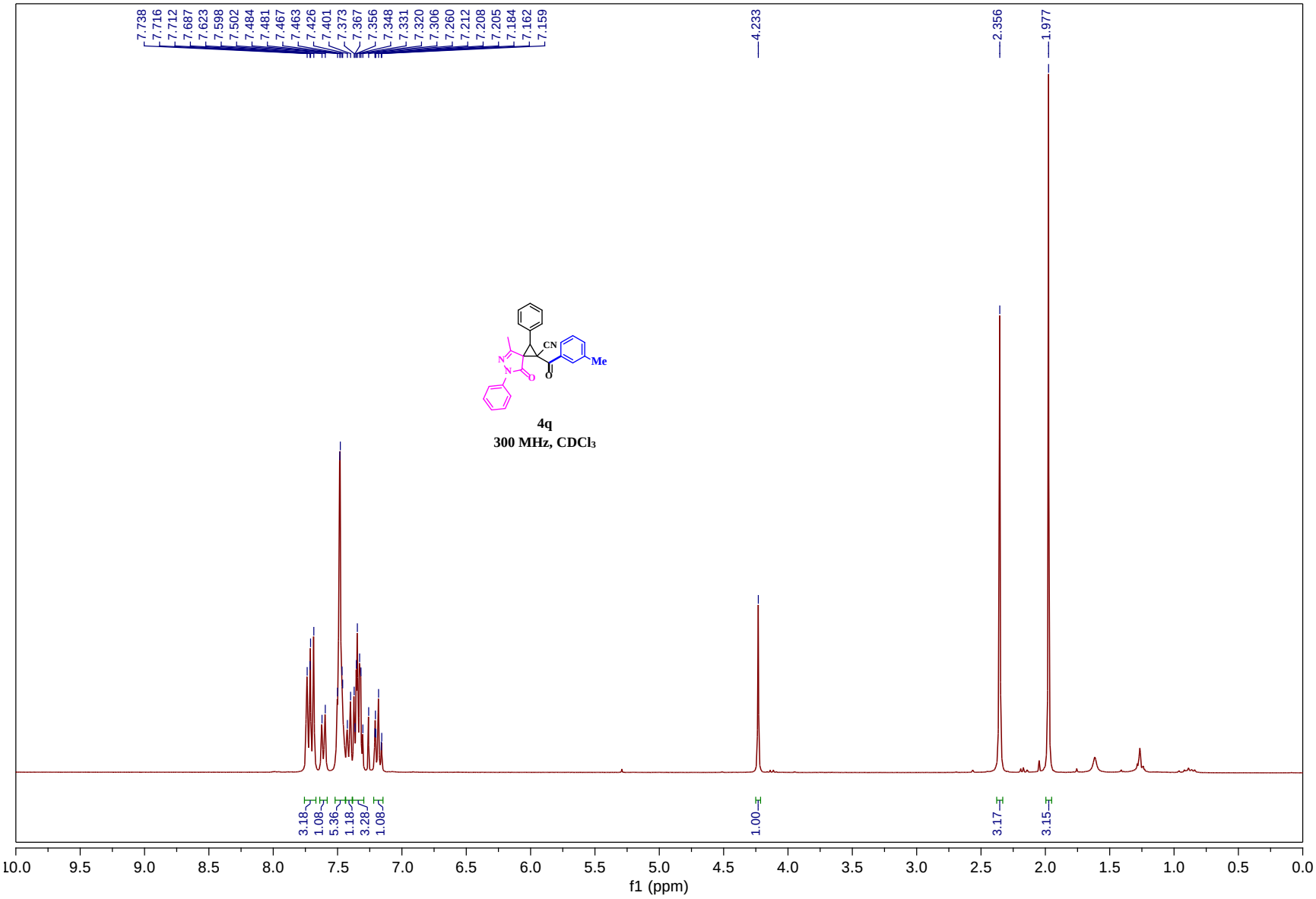

8.05
8.03
7.55
7.52
7.45
7.42
7.40
7.37
7.35
7.33
7.30
7.26
7.24
7.22
7.21
7.17
7.15
7.12
6.89
6.87
6.81
4.75
1.30
CN
O
N
N
O
4o
300 MHz, CDCl3
2.06
2.09
11.01
1.14
2.21
2.07
1.00
9.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


183.16
163.79
159.80
154.44
138.13
130.78
130.52
129.68
129.49
129.24
129.15
129.01
128.51
128.05
127.89
126.28
125.93
119.09
112.65
77.41
77.16
76.91
44.84
40.49
37.24
35.60
31.10
CN
O
N
N
O
4o
125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.735
7.707
7.638
7.634
7.609
7.606
7.393
7.290
7.237
7.220
7.192
7.177
7.122
7.098
7.073
4.153
2.632
2.606
2.581
2.556
1.888
1.152
1.127
1.102
CN
Et
N
N
O
O
4p
300 MHz, CDCl3
2.15
2.15
5.31
4.73
1.11
1.00
2.25
3.25
3.31
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)

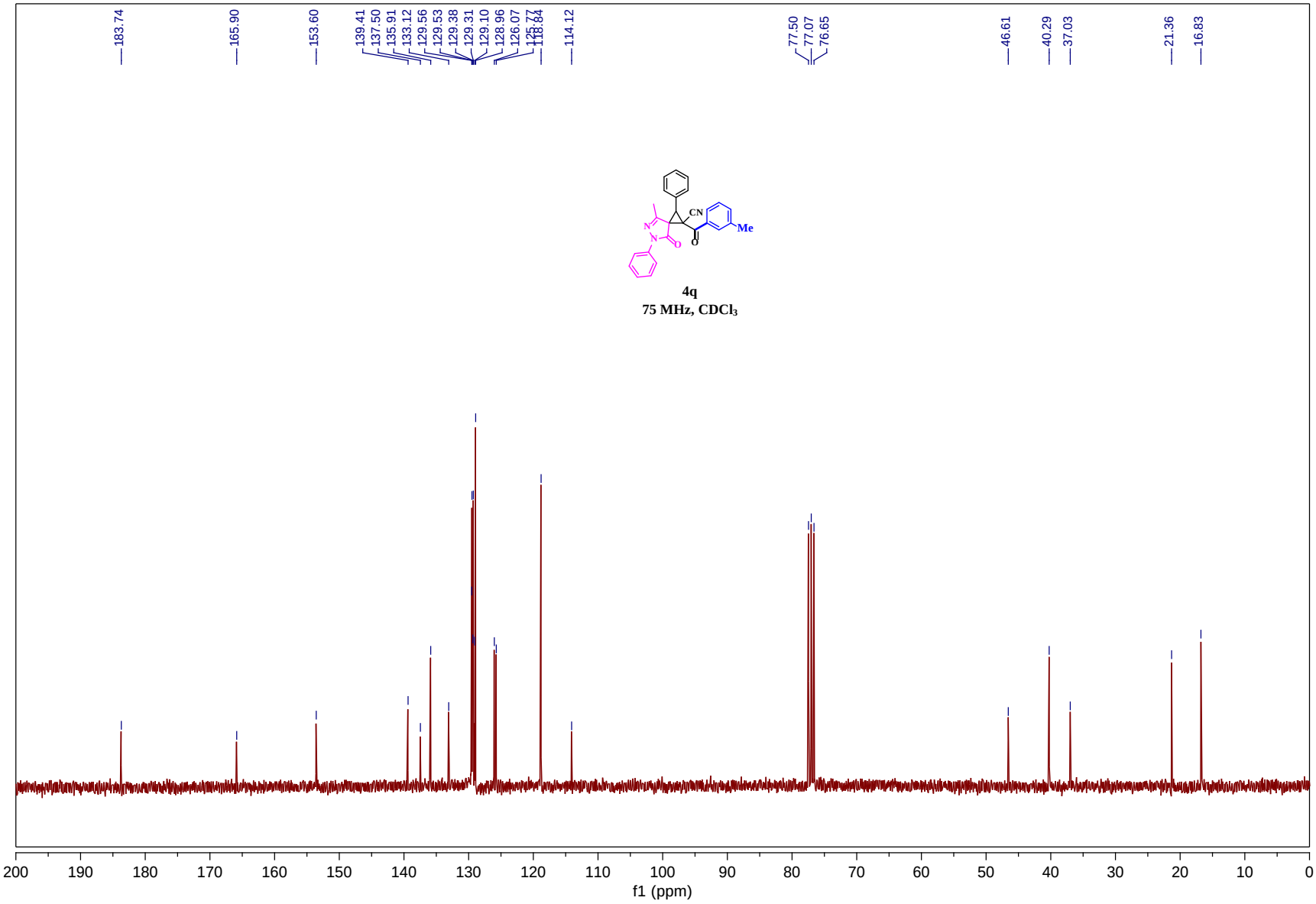

7.735
7.707
7.638
7.634
7.609
7.606
7.393
7.290
7.237
7.220
7.192
7.177
7.122
7.098
7.073
4.153
2.632
2.606
2.581
2.556
1.888
1.152
1.127
1.102
CN
Et
O
N
N
O
4p
300 MHz, CDCl3
2.15
2.15
5.31
4.73
1.11
1.00
2.25
3.25
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

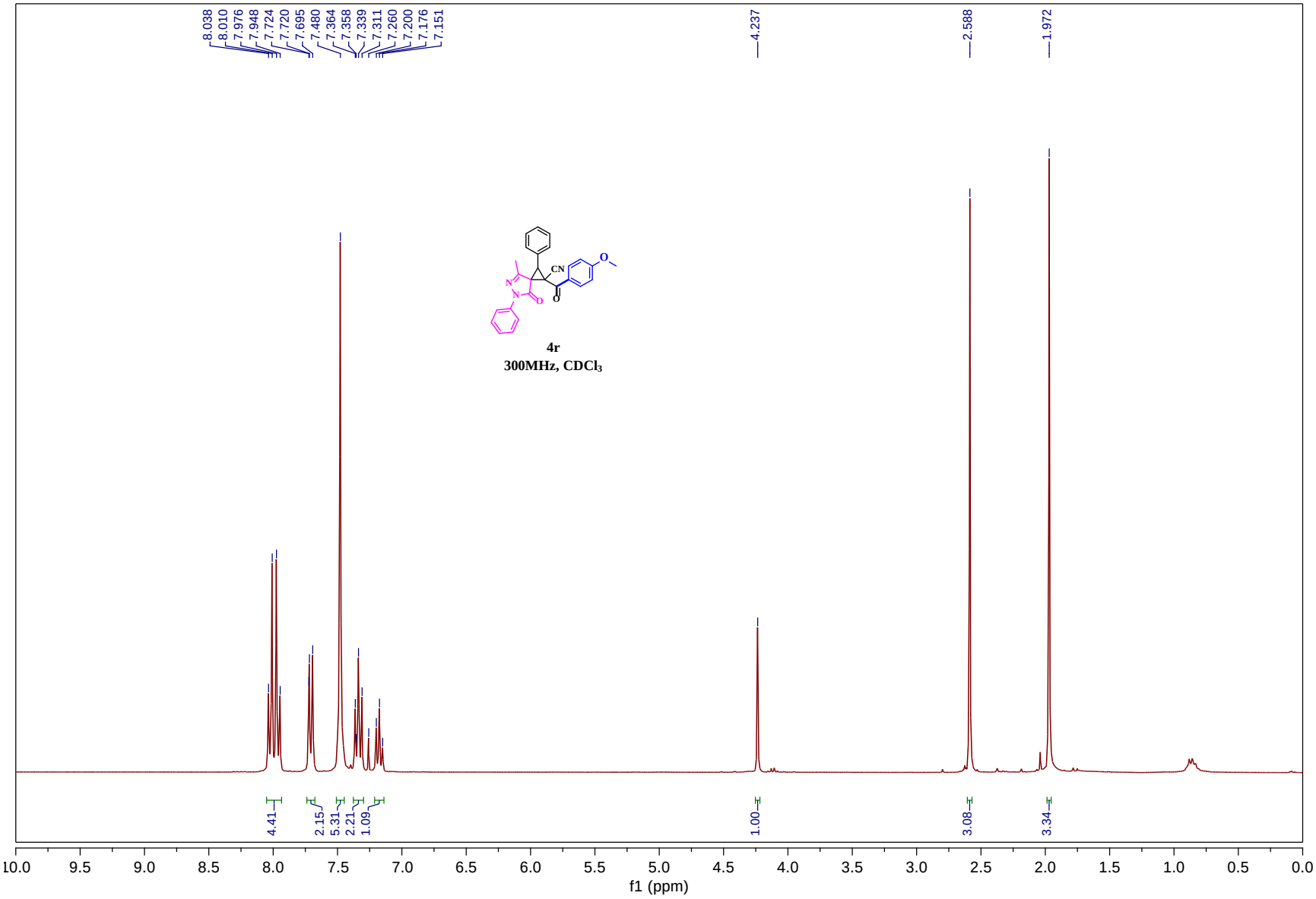

ARD-DD-B4Et
13C,CDCL3,ARD-DD-B4Et,03/02/20
183.95
166.39
154.11
152.95
138.07
130.05
129.86
129.81
129.71
129.45
129.41
119.34
117.30
114.77
78.01
77.58
77.16
47.08
40.82
37.55
29.62
17.36
15.45
CN
Et
N
N
O
O
4p
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

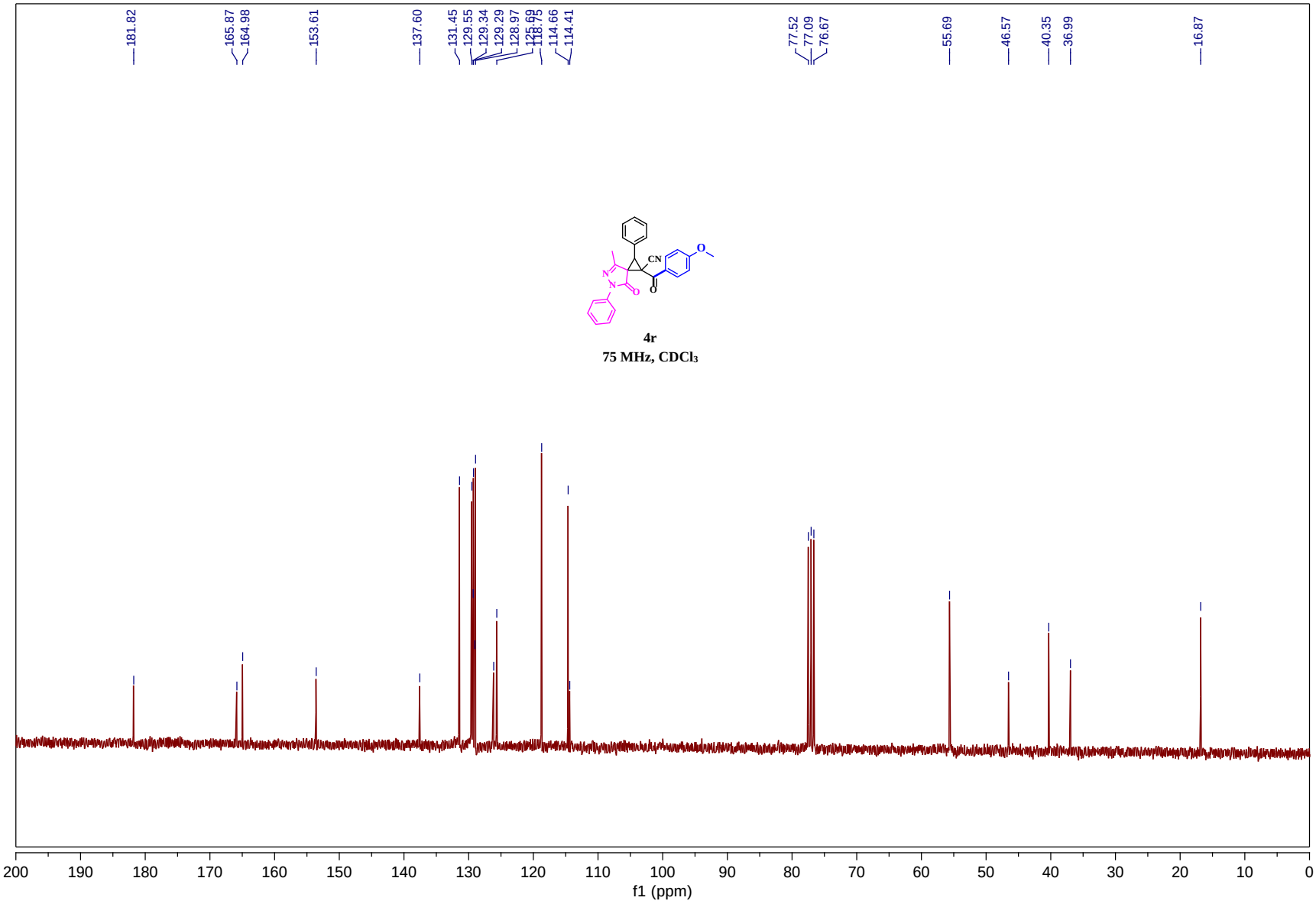


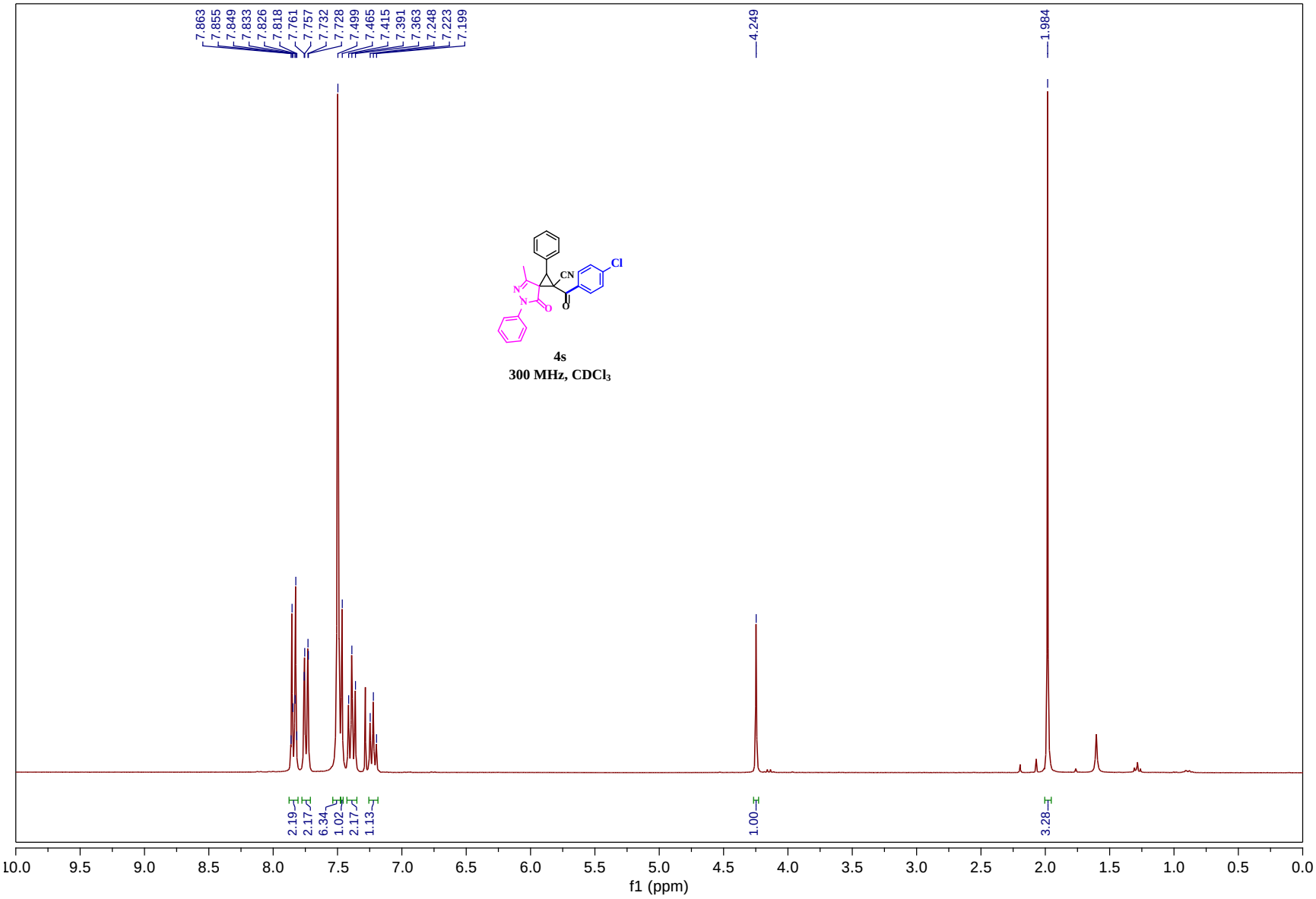

**4q**

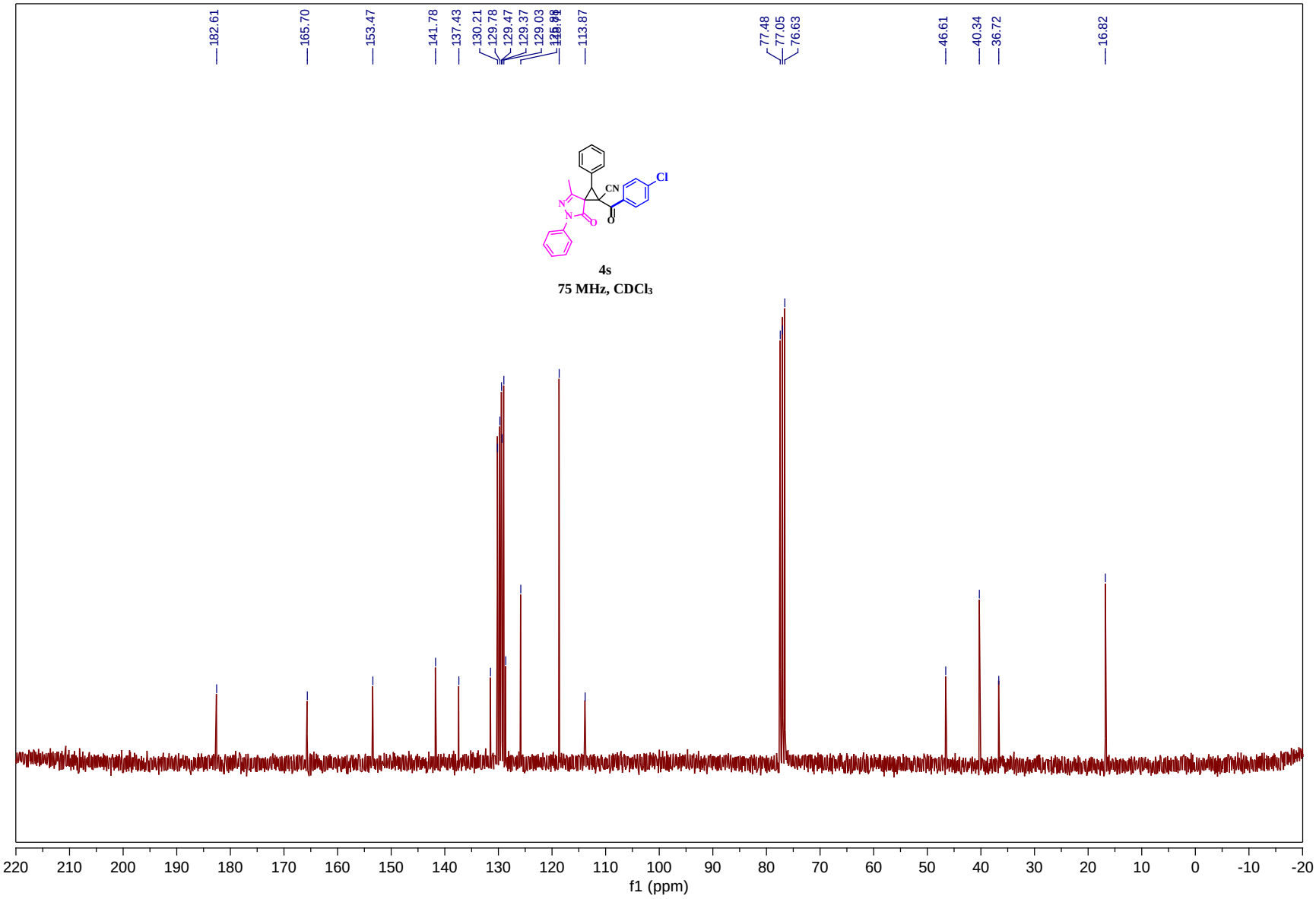
**300 MHz, $CDCl_3$**

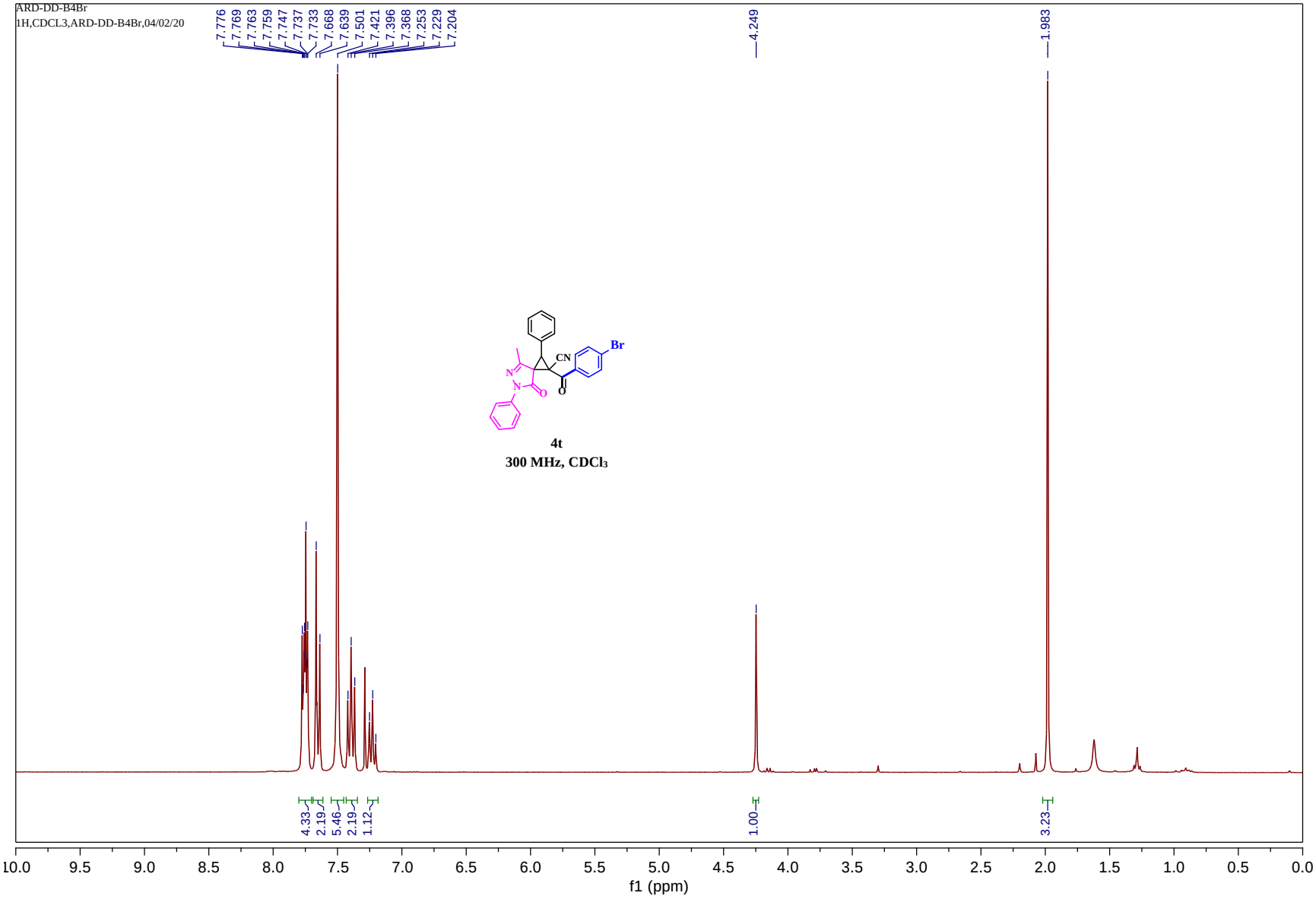

183.74
165.90
153.60
139.41
137.50
135.91
133.12
129.56
129.53
129.38
129.31
129.10
128.96
126.07
125.77
118.84
114.12
77.50
77.07
76.65
46.61
40.29
37.03
21.36
16.83
CN
Me
O
O
N
N
4q
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

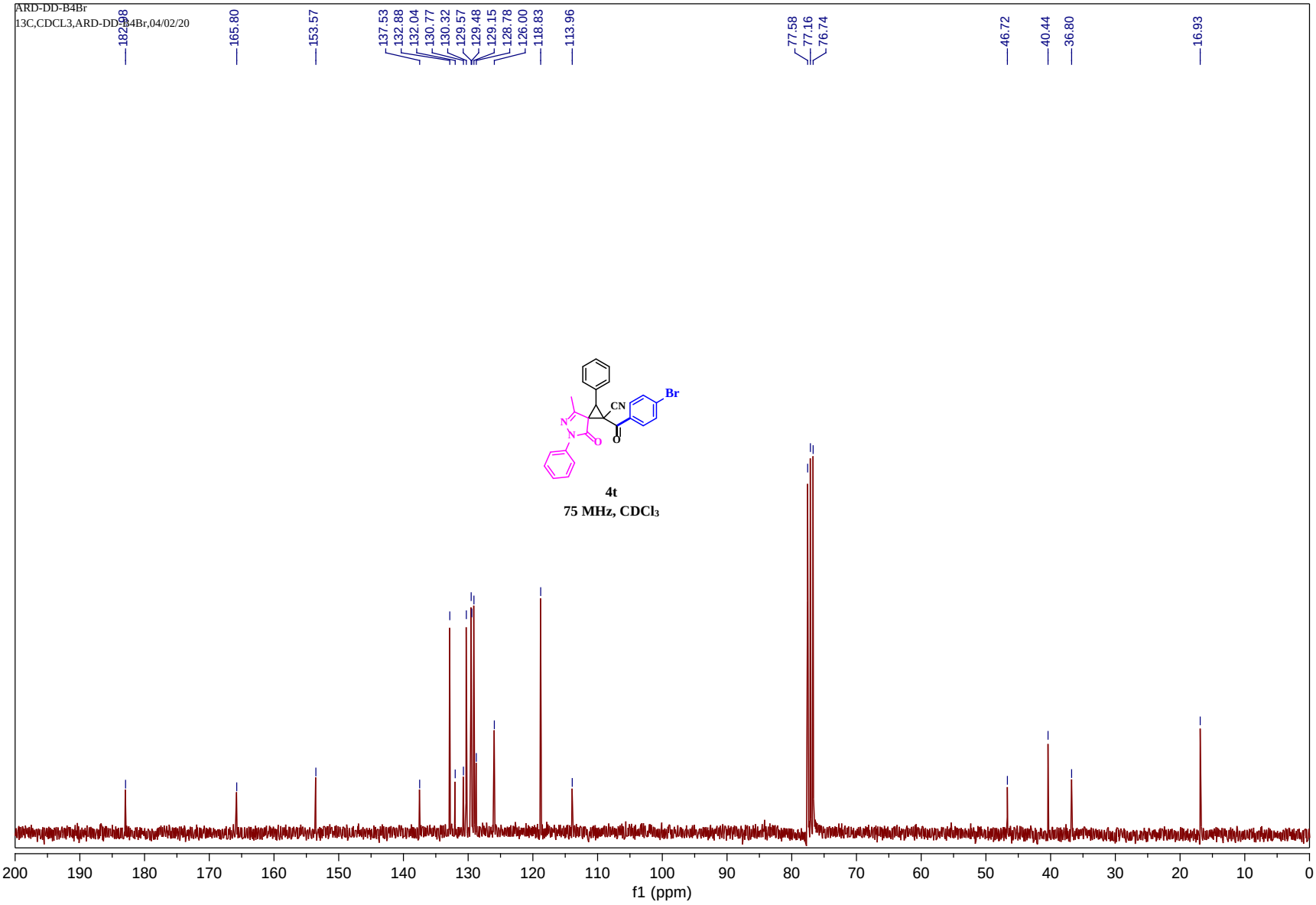

8.038
8.010
7.976
7.948
7.724
7.720
7.695
7.480
7.364
7.358
7.339
7.311
7.260
7.200
7.176
7.151
4.237
2.588
1.972
CN
O
N
N
O
O
4r
300MHz, CDCl3
4.41
2.15
5.31
2.21
1.09
1.00
3.08
3.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

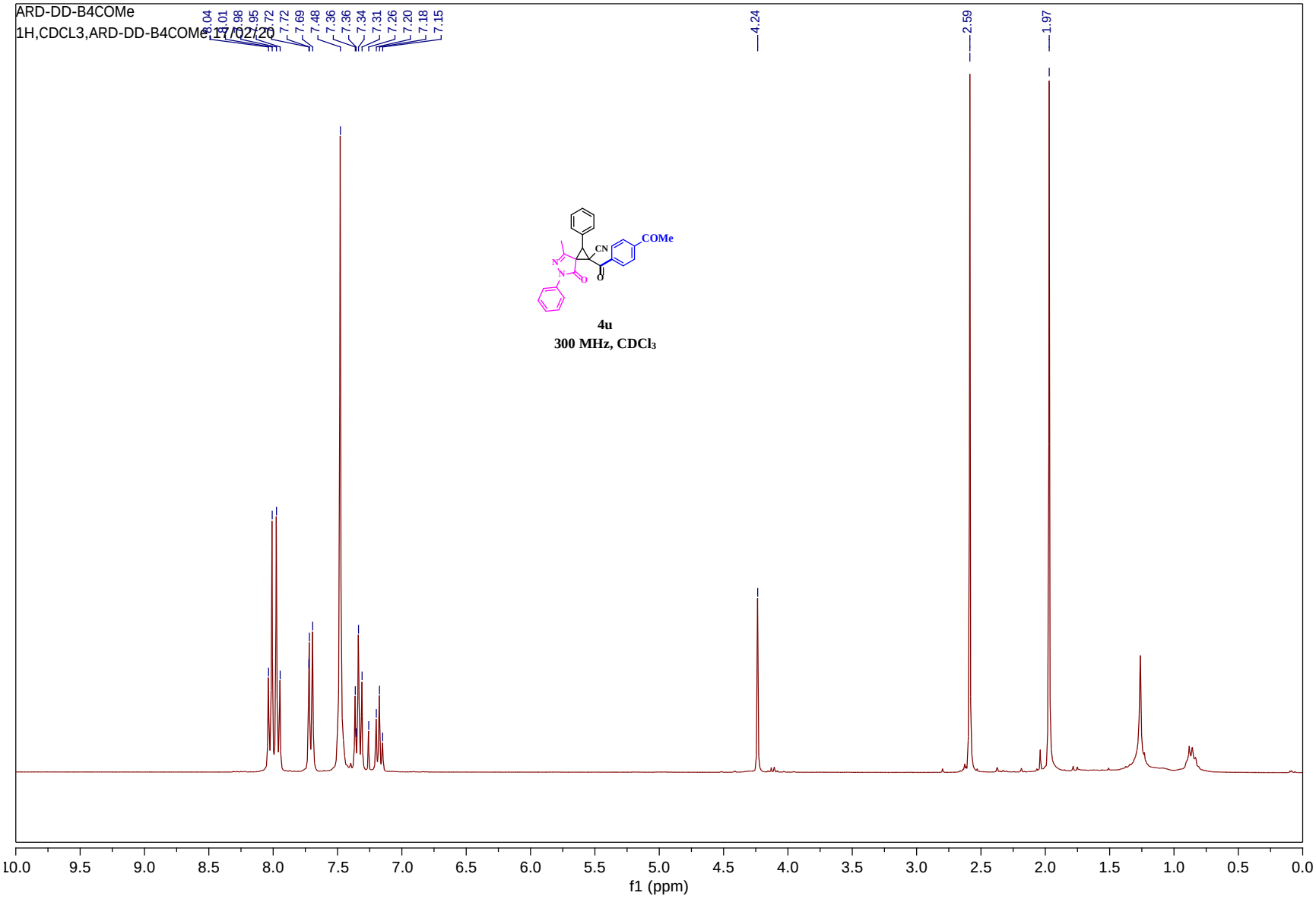

181.82
165.87
164.98
153.61
137.60
131.45
129.55
129.34
129.29
128.97
125.69
114.66
114.41
77.52
77.09
76.67
55.69
46.57
40.35
36.99
16.87
CN
O
N
N
O
O
4r
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

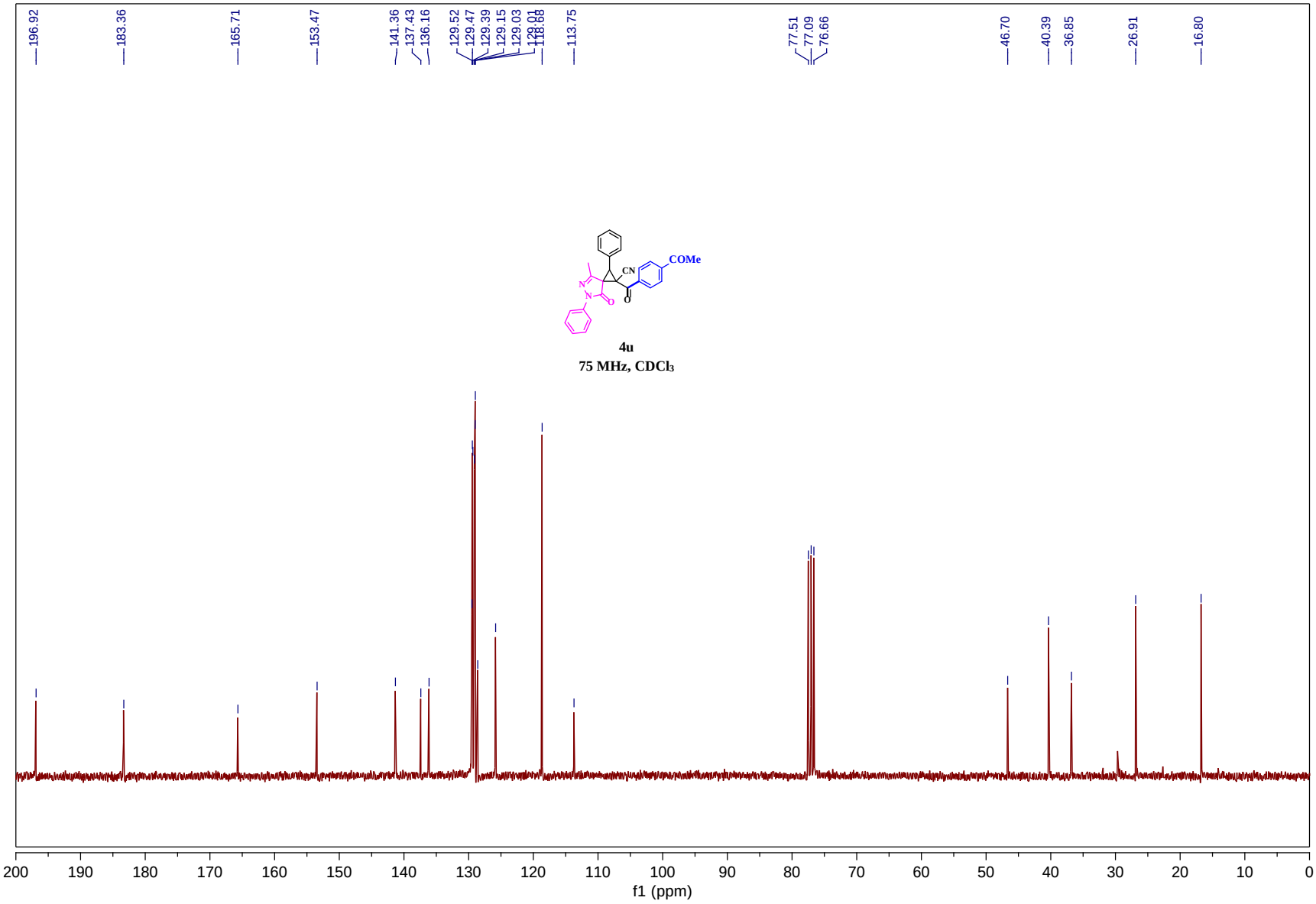

7.863
7.855
7.849
7.833
7.826
7.818
7.761
7.757
7.732
7.728
7.499
7.465
7.415
7.391
7.363
7.248
7.223
7.199
4.249
1.984
CN
Cl
O
N
N
4s
300 MHz, CDCl3
2.19
2.17
6.34
1.02
2.17
1.13
1.00
3.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

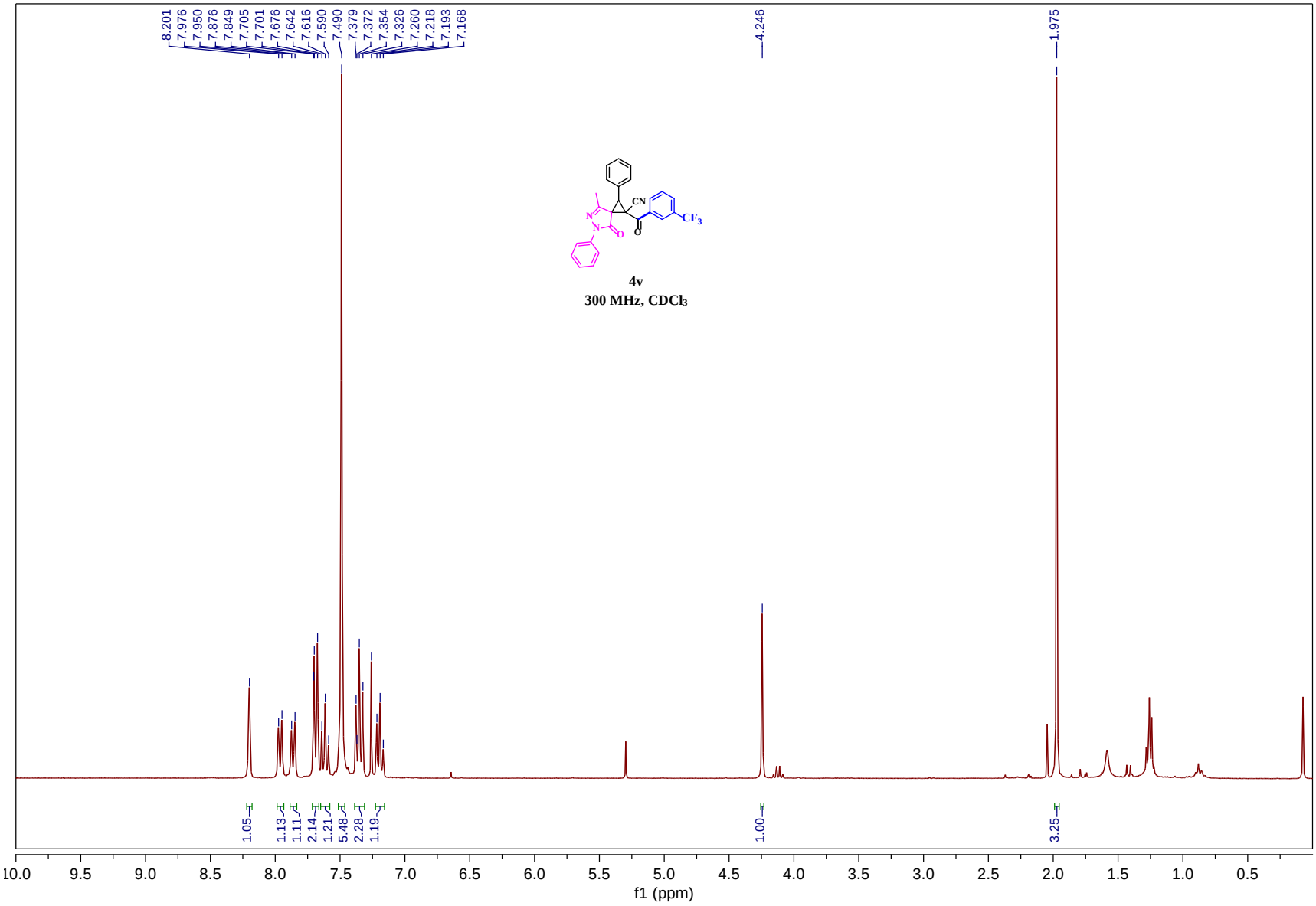

182.61
165.70
153.47
141.78
137.43
130.21
129.78
129.47
129.37
129.03
113.87
77.48
77.05
76.63
46.61
40.34
36.72
16.82
CN
Cl
O
N
N
O
4s
75 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

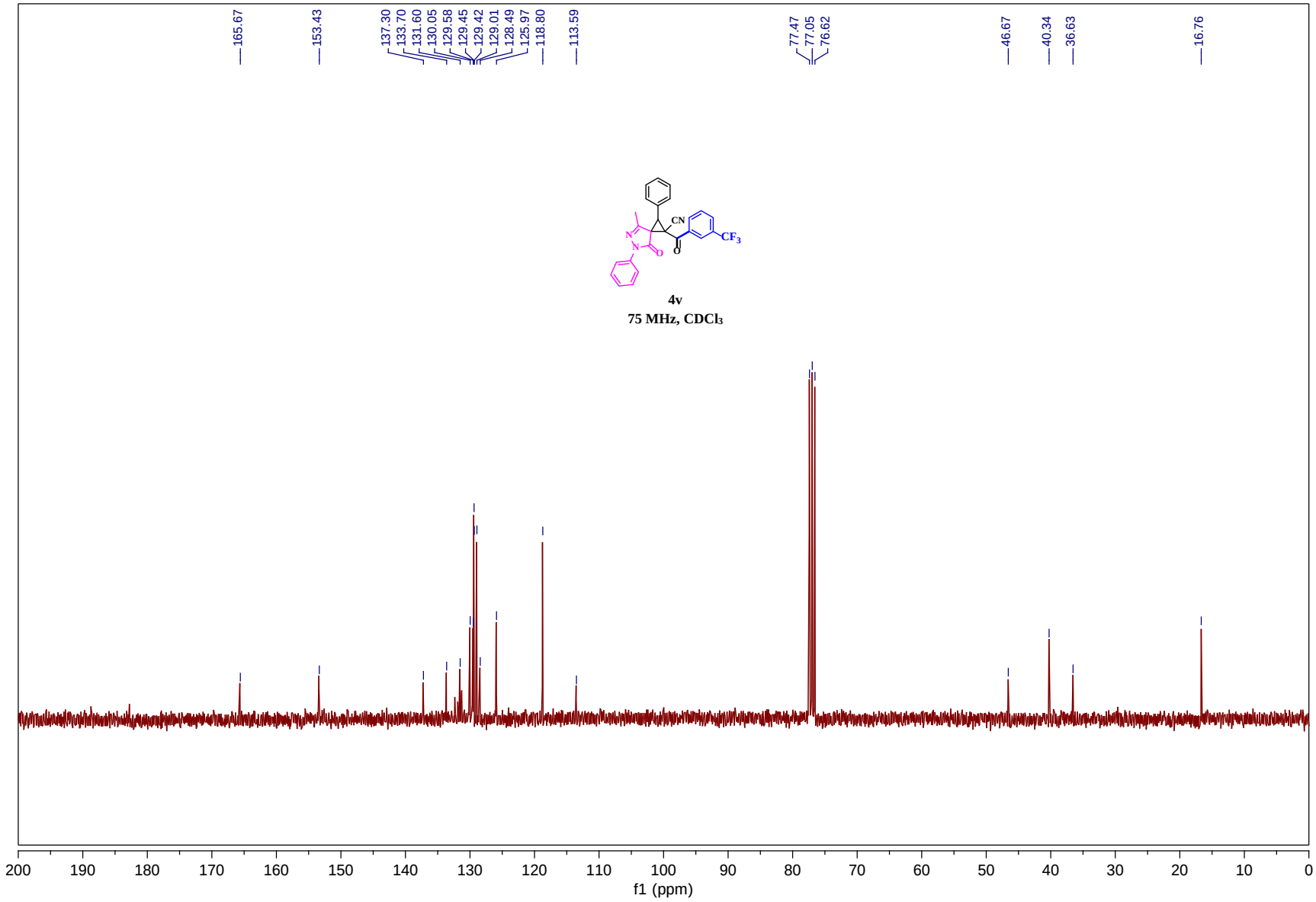

ARD-DD-B4Br
1H,CDCL3,ARD-DD-B4Br,04/02/20
7.776
7.769
7.763
7.759
7.747
7.737
7.733
7.668
7.639
7.501
7.421
7.396
7.368
7.253
7.229
7.204
4.249
1.983
Br
CN
O
N
N
O
4t
300 MHz, CDCl3
4.33
2.19
5.46
2.19
1.12
1.00
3.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

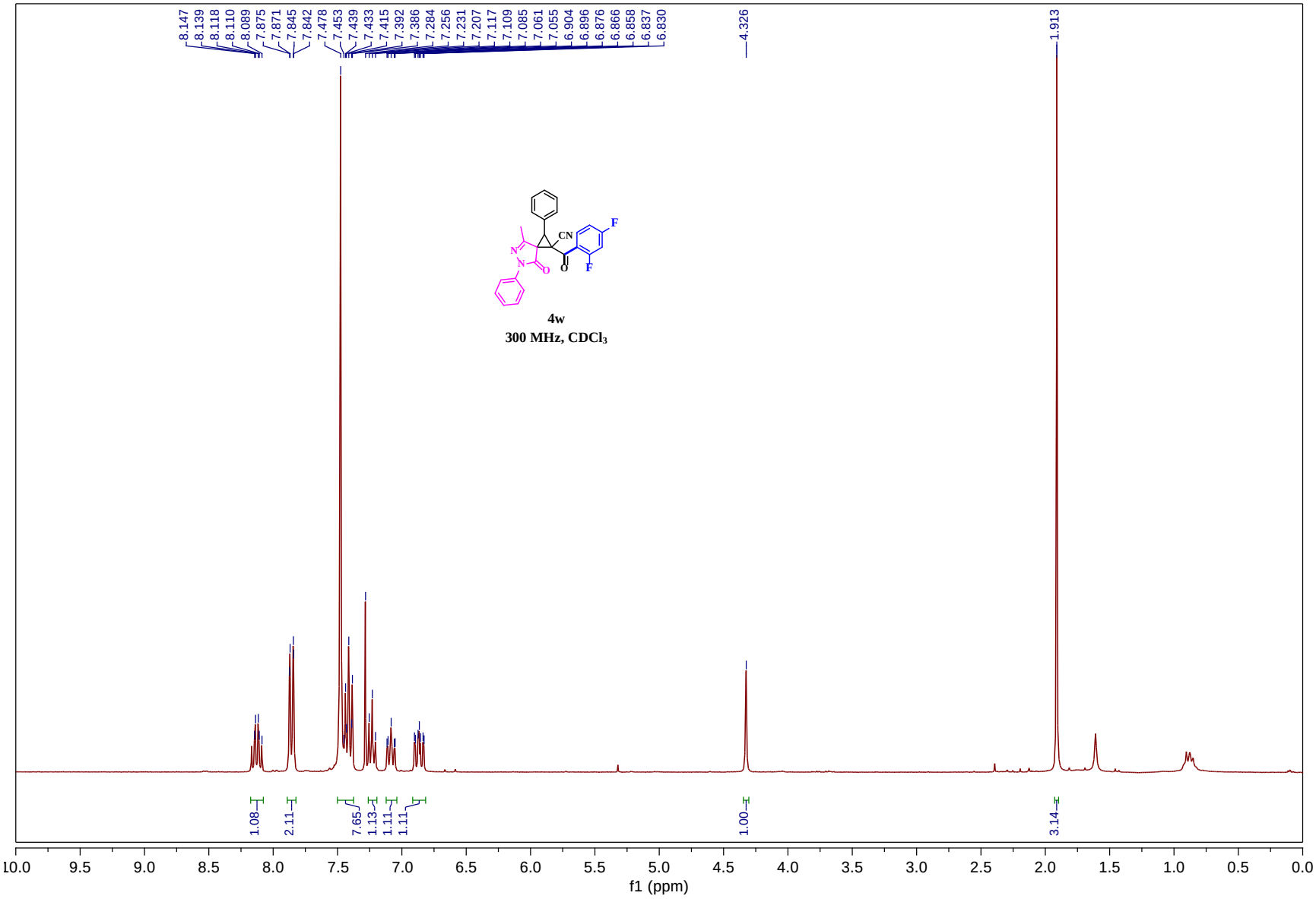

ARD-DD-B4Br
13C,CDCL3,ARD-DD-B4Br,04/02/20
182.98
165.80
153.57
137.53
132.88
132.04
130.77
130.32
129.57
129.48
129.15
128.78
126.00
118.83
113.96
77.58
77.16
76.74
46.72
40.44
36.80
16.93
Br
CN
N
N
O
O
4t
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

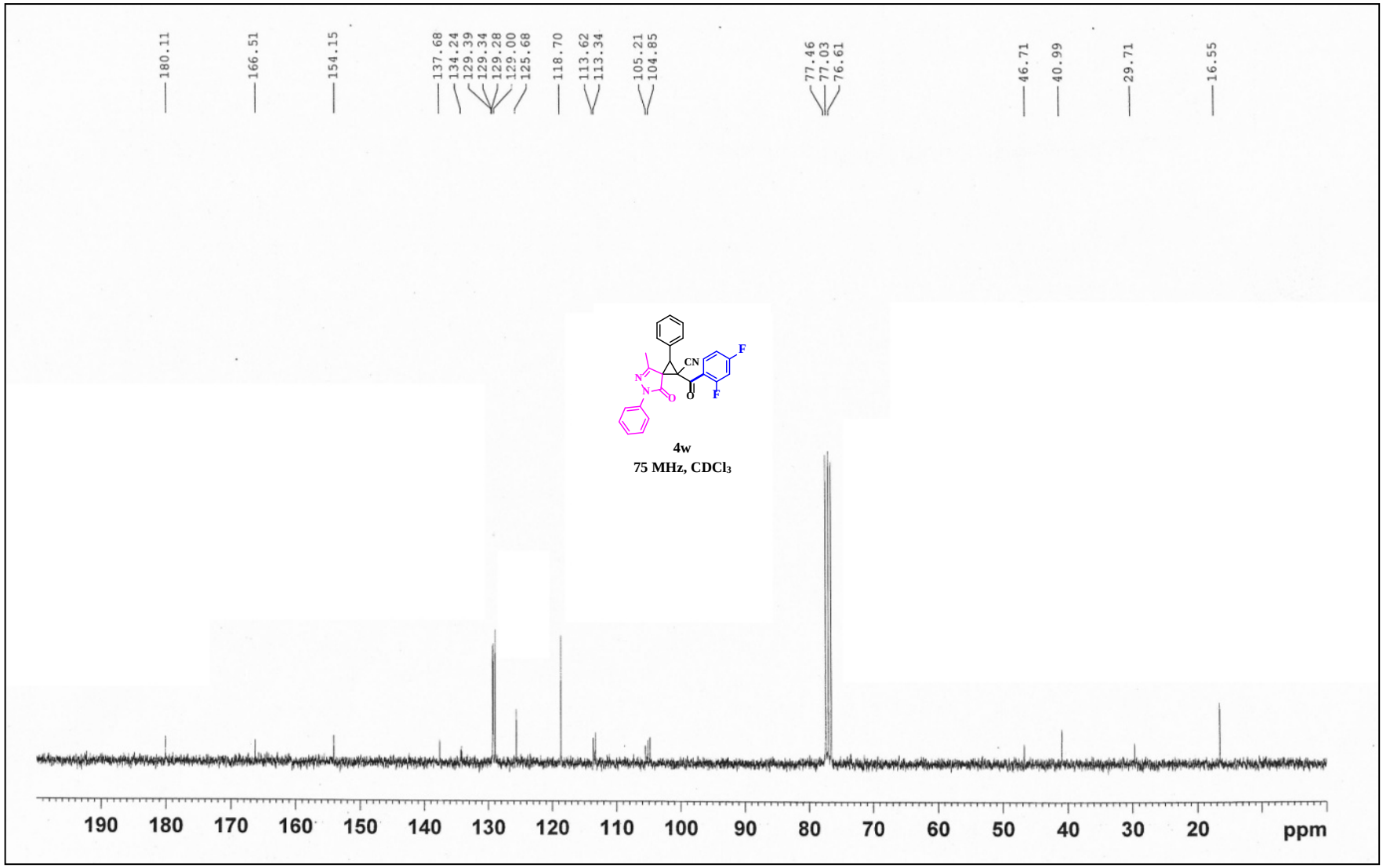

ARD-DD-B4COMe
1H,CDCL3,ARD-DD-B4COMe,17/02/20
8.04
8.01
7.98
7.95
7.72
7.72
7.69
7.48
7.36
7.36
7.34
7.31
7.26
7.20
7.18
7.15
4.24
2.59
1.97
CN
COMe
O
N
N
O
4u
300 MHz, CDCl3
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

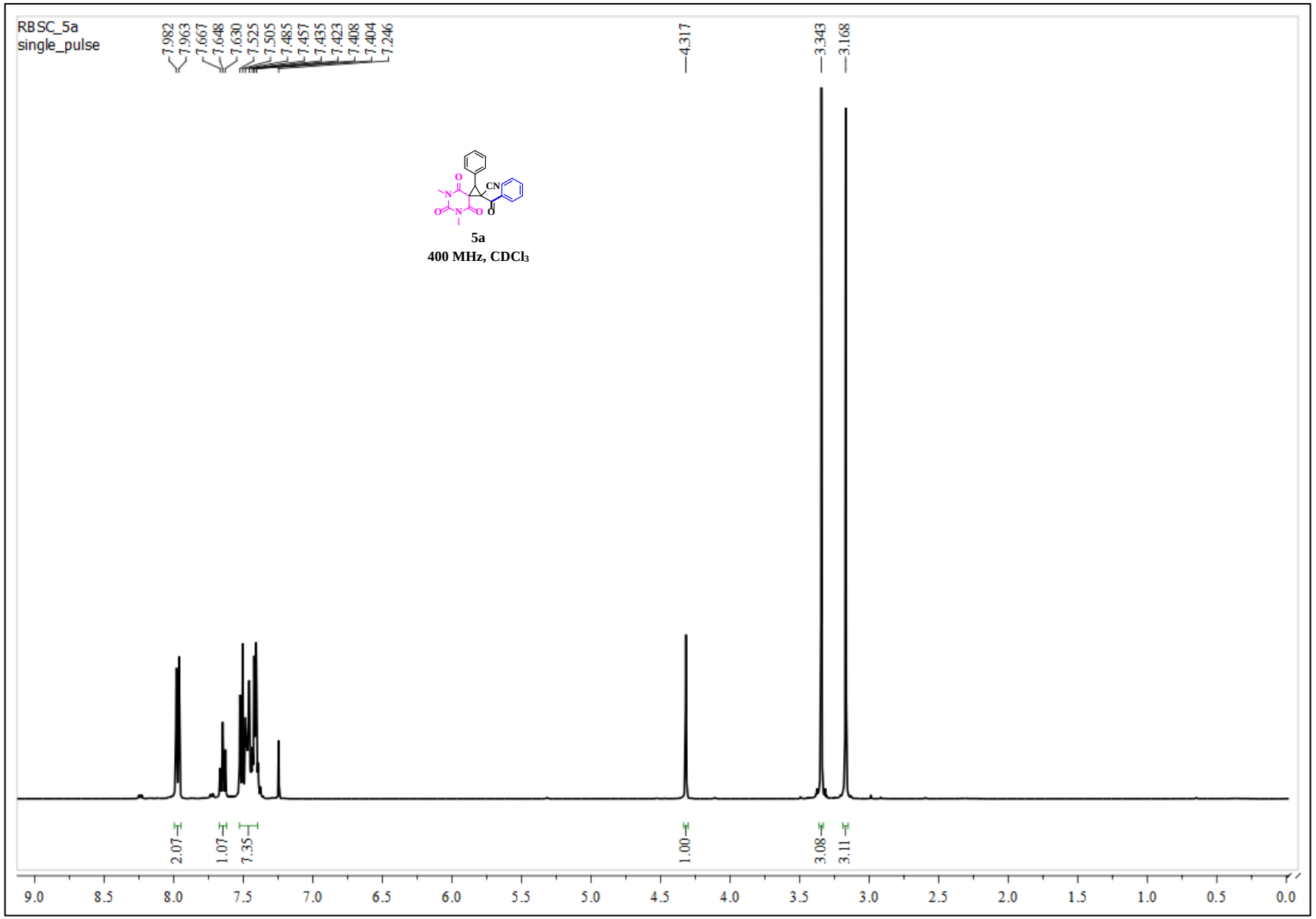

196.92
183.36
165.71
153.47
141.36
137.43
136.16
129.52
129.47
129.39
129.15
129.03
129.01
118.88
113.75
77.51
77.09
76.66
46.70
40.39
36.85
26.91
16.80
CN
COMe
O
N
N
O
4u
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

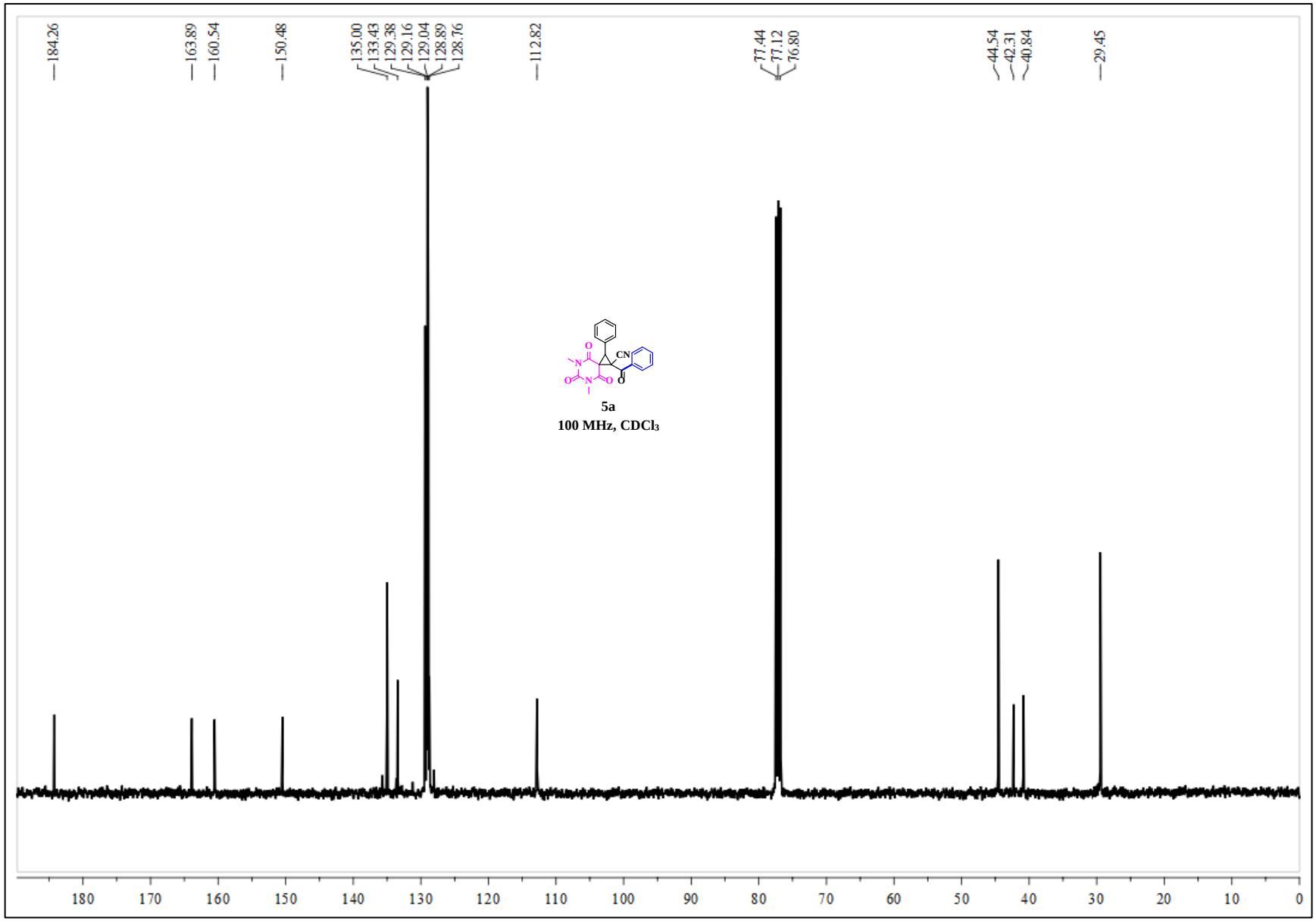

8.201
7.976
7.950
7.876
7.849
7.705
7.701
7.676
7.642
7.616
7.590
7.490
7.379
7.372
7.354
7.326
7.260
7.218
7.193
7.168
4.246
1.975
CN
CF3
O
N
N
O
4v
300 MHz, CDCl3
1.05
1.13
1.11
2.14
1.21
5.48
2.28
1.19
1.00
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


165.67
153.43
137.30
133.70
131.60
130.05
129.58
129.45
129.42
129.01
128.49
125.97
118.80
113.59
77.47
77.05
76.62
46.67
40.34
36.63
16.76
CN
CF3
N
N
O
O
4v
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.147
8.139
8.118
8.110
8.089
7.875
7.871
7.845
7.842
7.478
7.453
7.439
7.433
7.415
7.392
7.386
7.284
7.256
7.231
7.207
7.117
7.109
7.085
7.061
7.055
6.904
6.896
6.876
6.866
6.858
6.837
6.830
4.326
1.913
CN
F
F
O
N
N
4w
300 MHz, CDCl3
1.08
2.11
7.65
1.13
1.11
1.11
1.00
3.14
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)

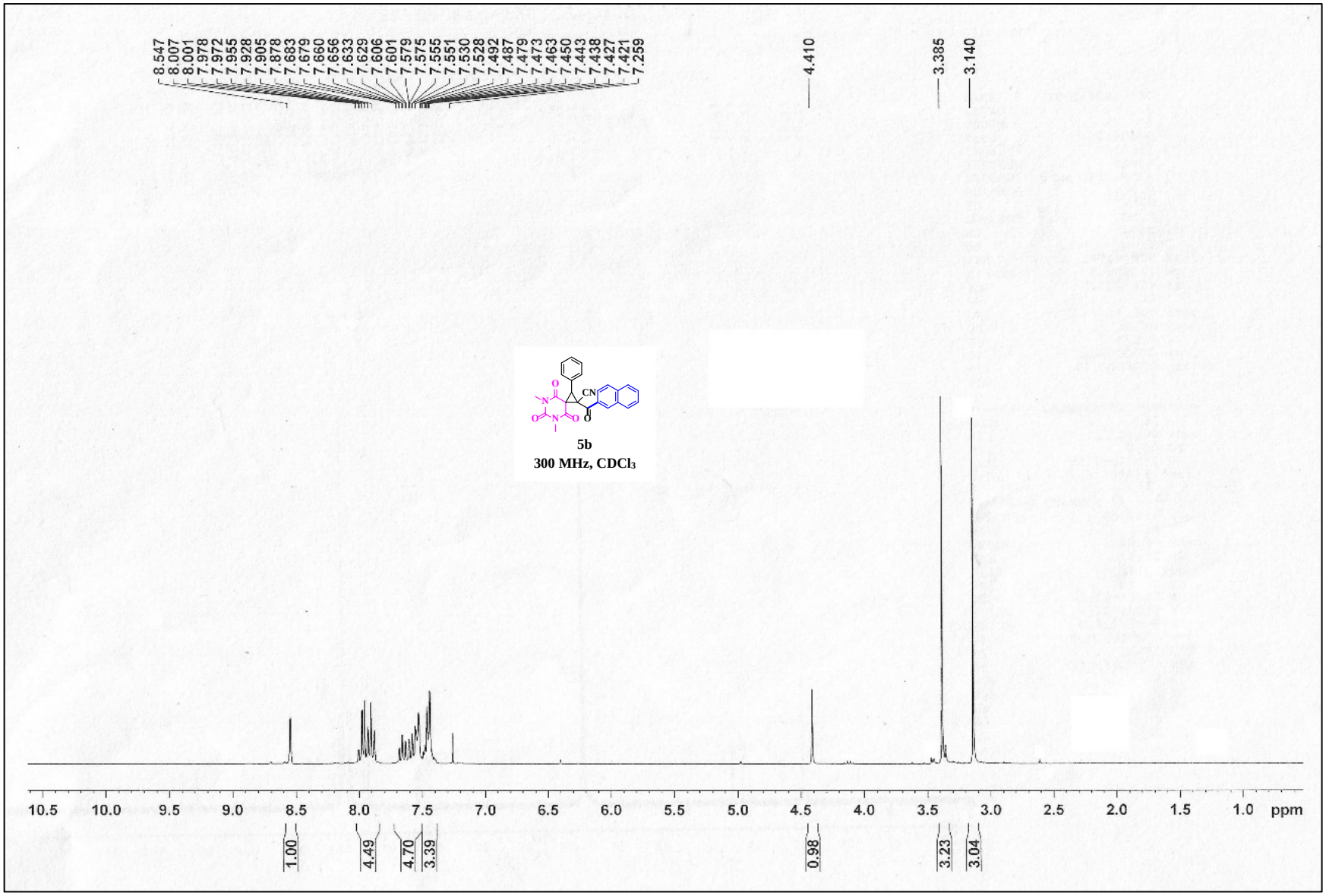

180.11
166.51
154.15
137.68
134.24
129.39
129.34
129.28
129.00
125.68
118.70
113.62
113.34
105.21
104.85
77.46
77.03
76.61
46.71
40.99
29.71
16.55
CN
F
F
O
N
N
4w
75 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

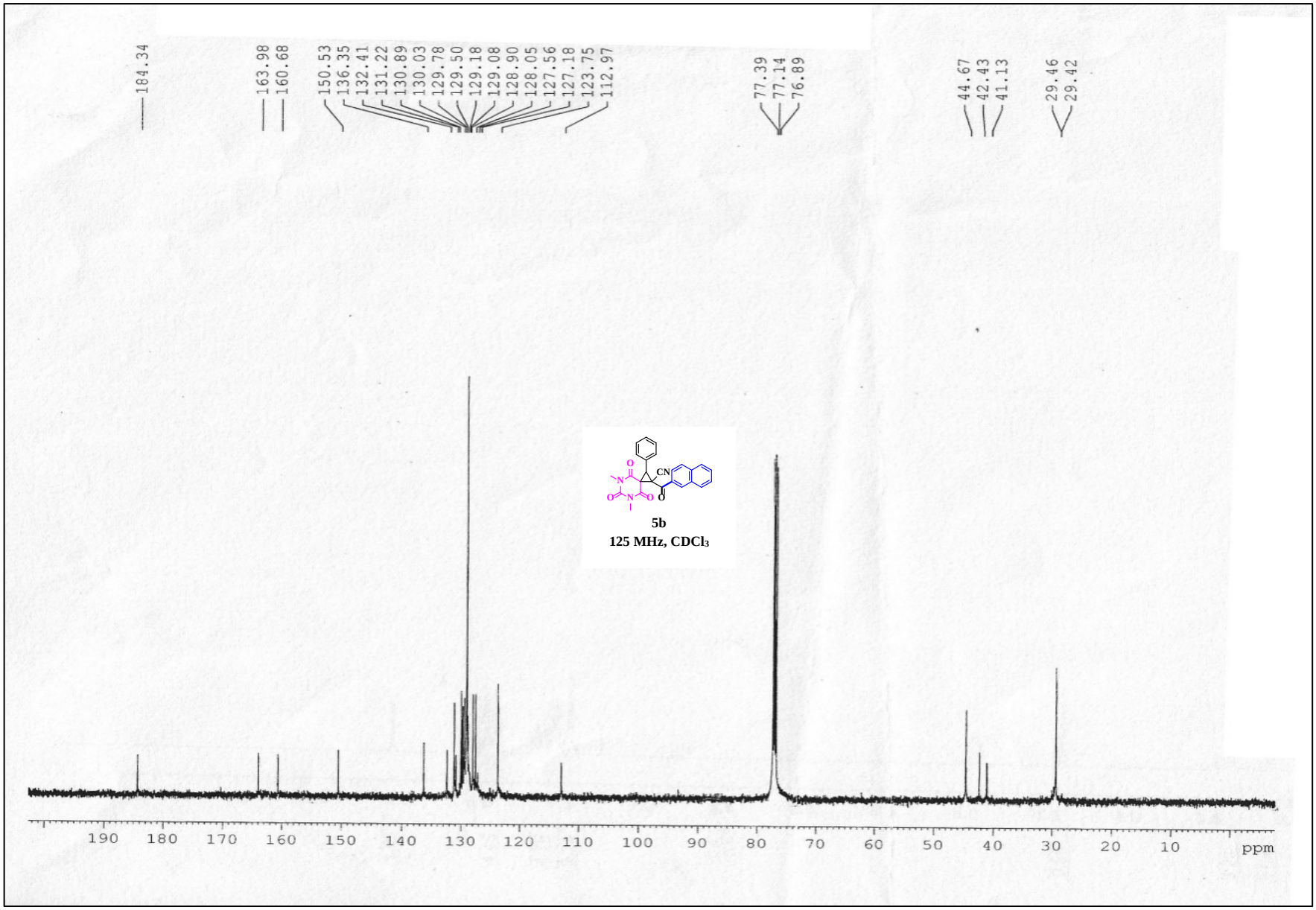

RBSC_5a
single_pulse
7.982
7.963
7.667
7.648
7.630
7.525
7.505
7.485
7.457
7.435
7.423
7.408
7.404
7.246
4.317
3.343
3.168
CN
5a
400 MHz, CDCl3
2.07
1.07
7.35
1.00
3.08
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0




**5a**

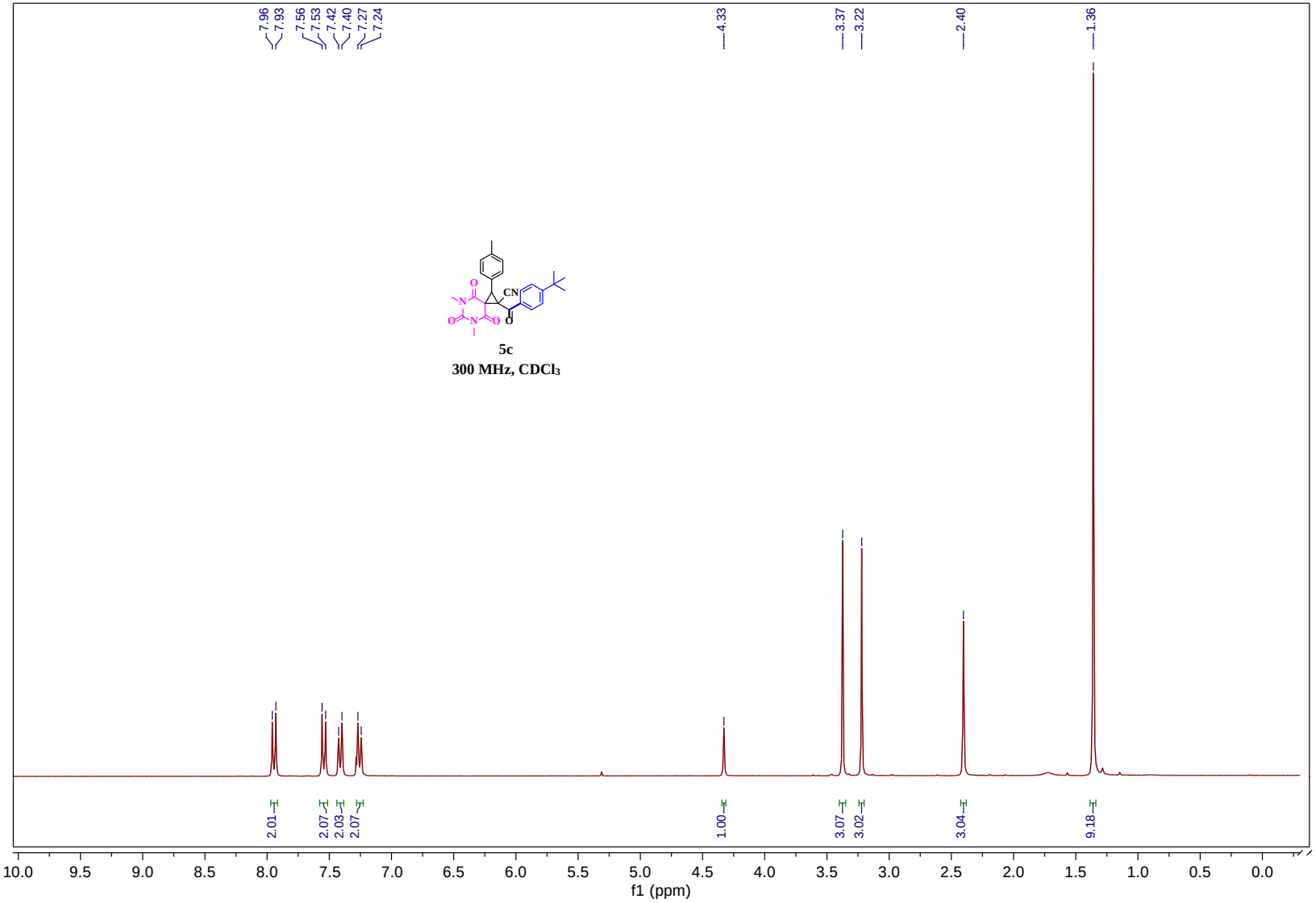
**100 MHz, $CDCl_3$**

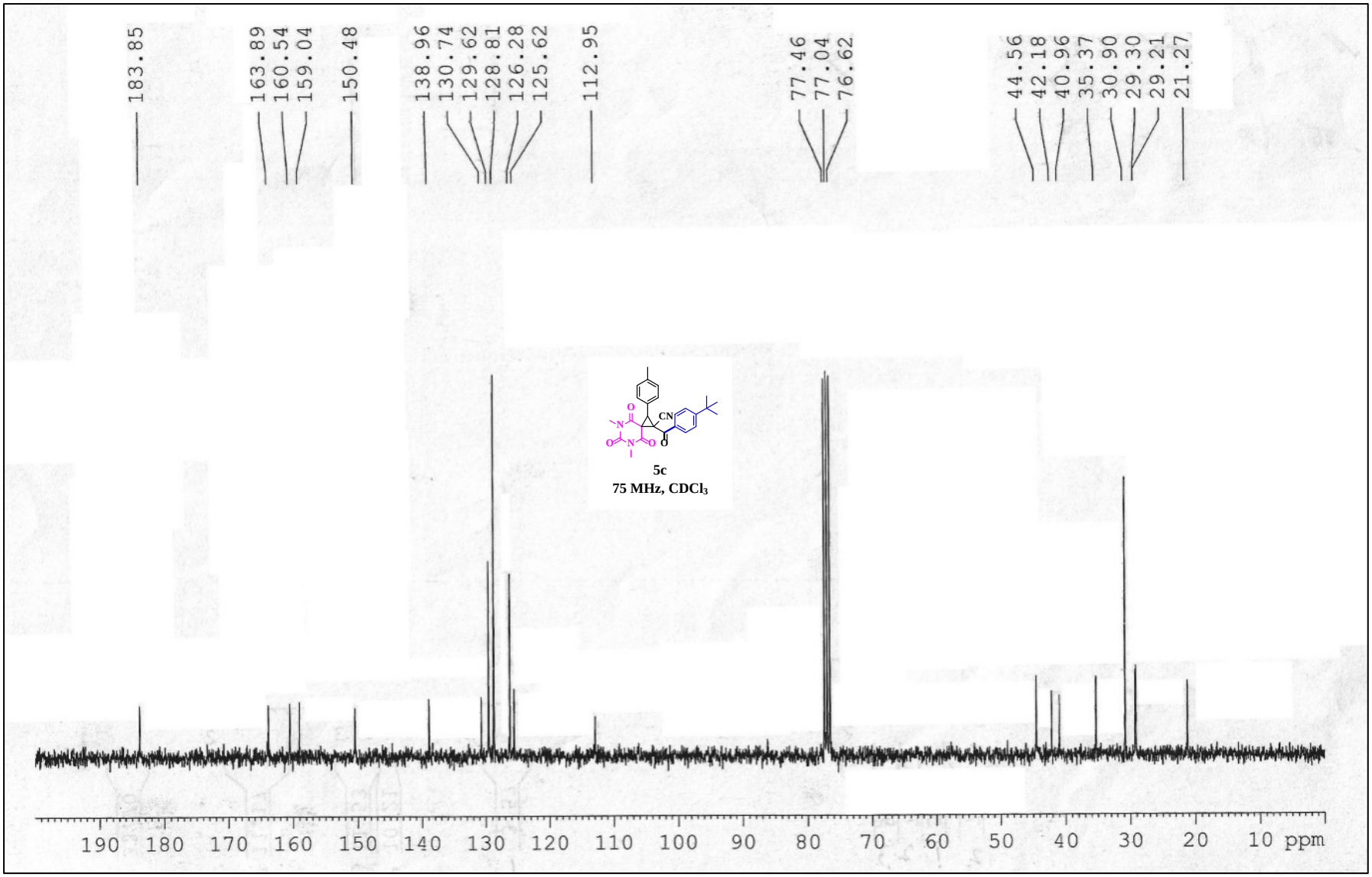

8.547
8.007
8.001
7.978
7.972
7.955
7.928
7.905
7.878
7.683
7.679
7.660
7.656
7.633
7.629
7.606
7.601
7.579
7.575
7.555
7.551
7.530
7.528
7.492
7.487
7.479
7.473
7.463
7.450
7.443
7.438
7.427
7.421
7.259
4.410
3.385
3.140
CN
O
O
O
O
5b
300 MHz, CDCl3
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
4.49
4.70
3.39
0.98
3.23
3.04

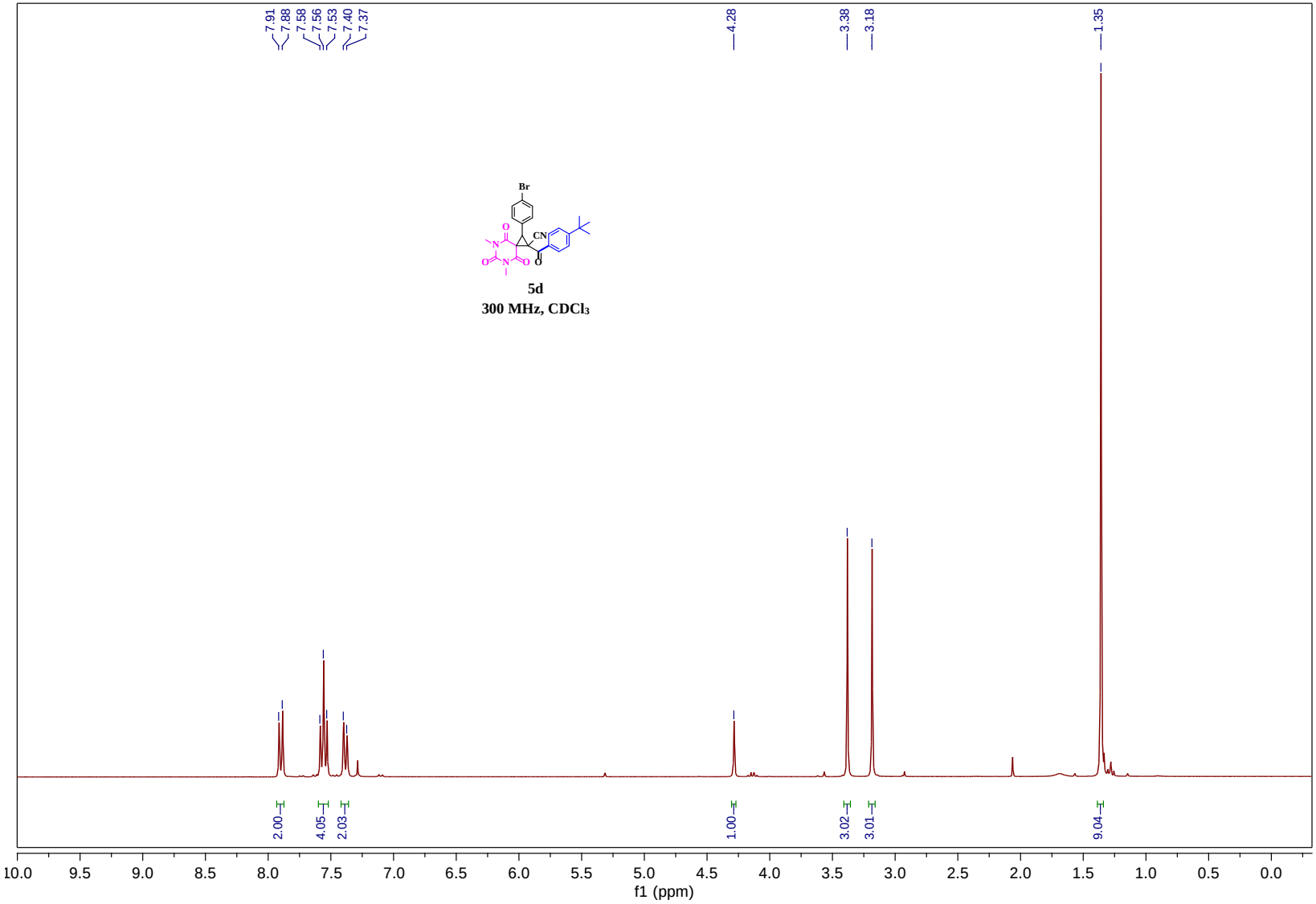


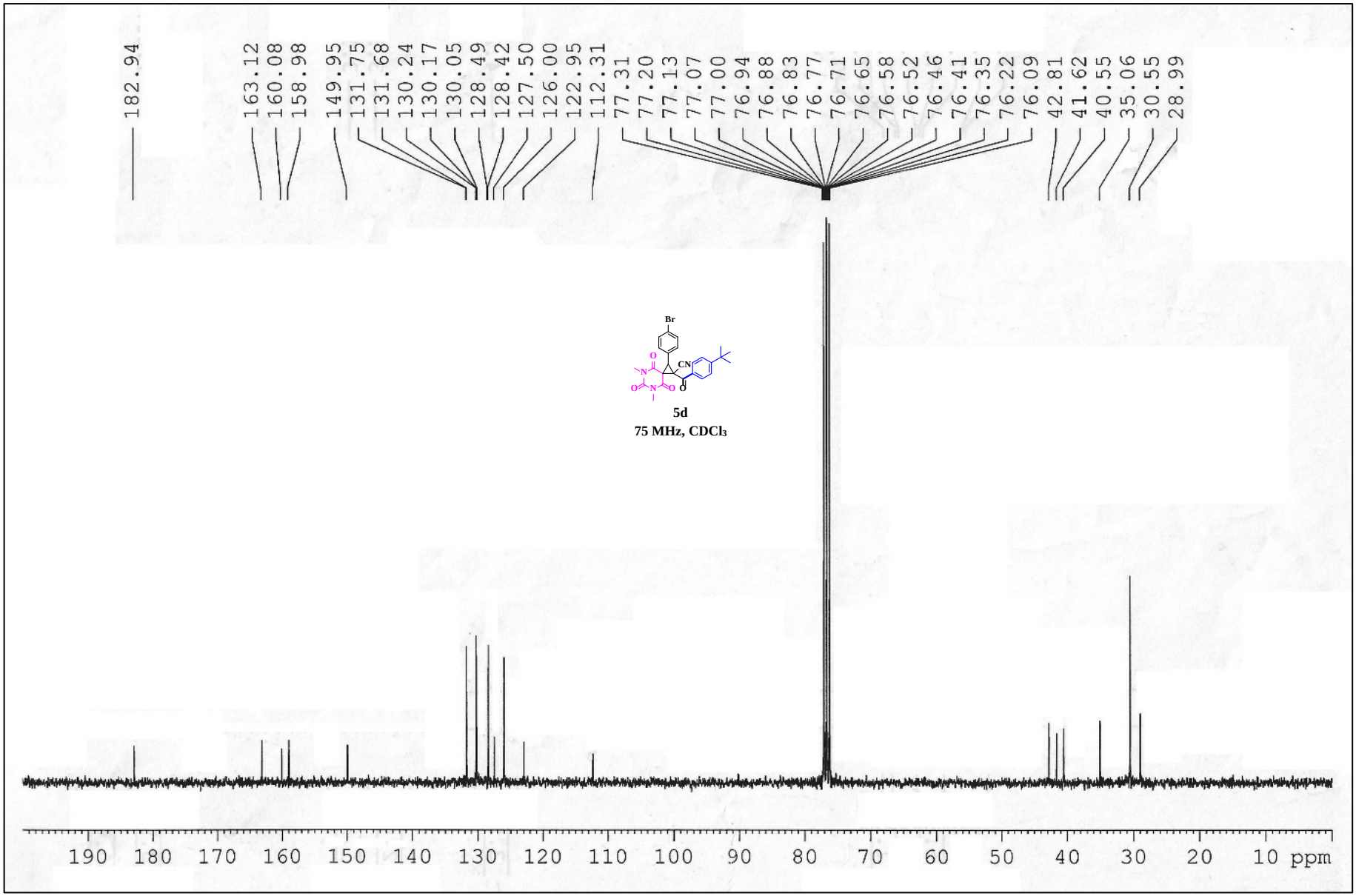

**5b**

**125 MHz, $CDCl_3$**


7.96
7.93
7.56
7.53
7.42
7.40
7.27
7.24
4.33
3.37
3.22
2.40
1.36
CN
O
N
O
N
O
O
5c
300 MHz, CDCl3
2.01
2.07
2.03
2.07
1.00
3.07
3.02
3.04
9.18
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)

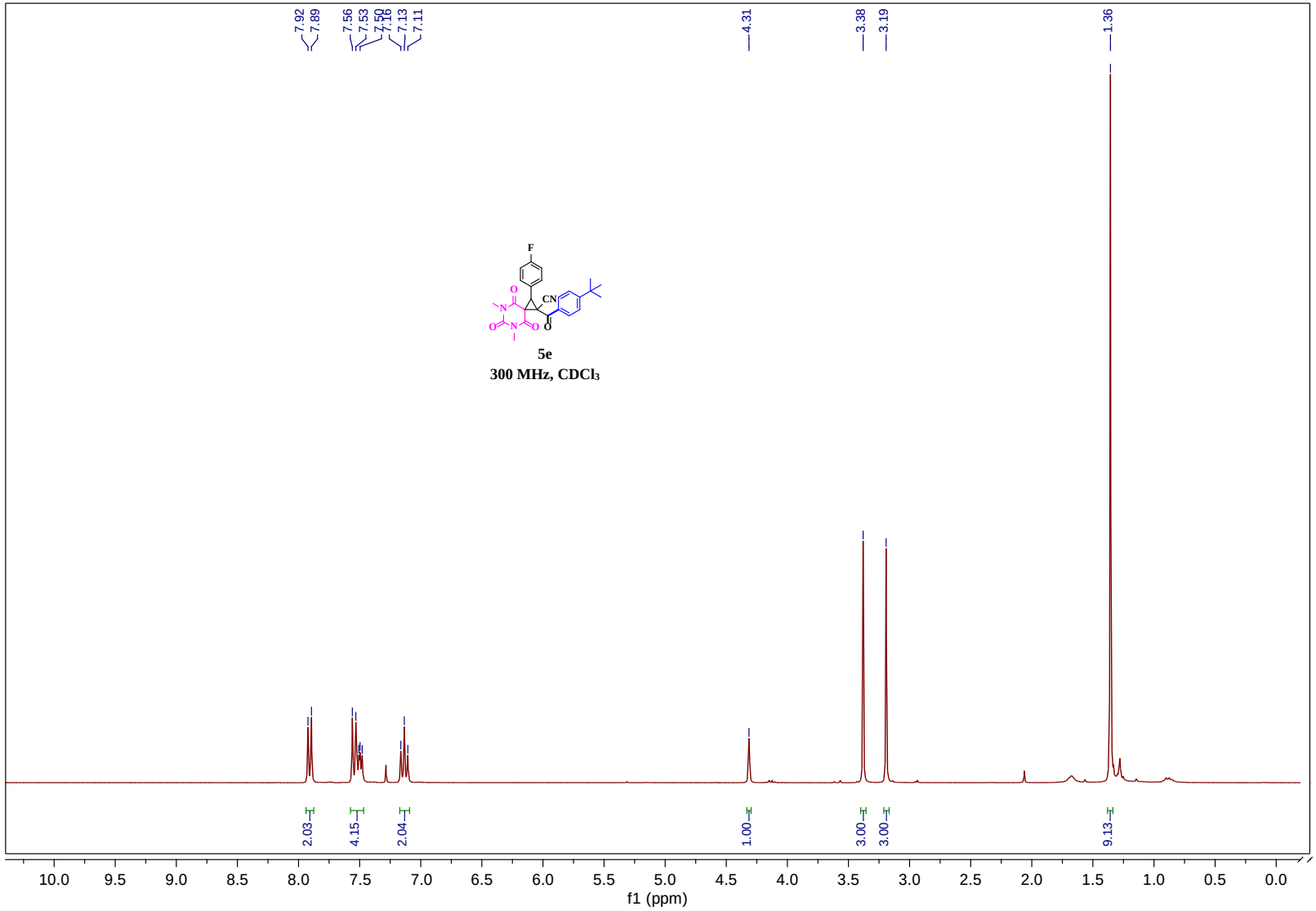

183.85
163.89
160.54
159.04
150.48
138.96
130.74
129.62
128.81
126.28
125.62
112.95
77.46
77.04
76.62
44.56
42.18
40.96
35.37
30.90
29.30
29.21
21.27
CN
O
O
O
N
N
5c
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

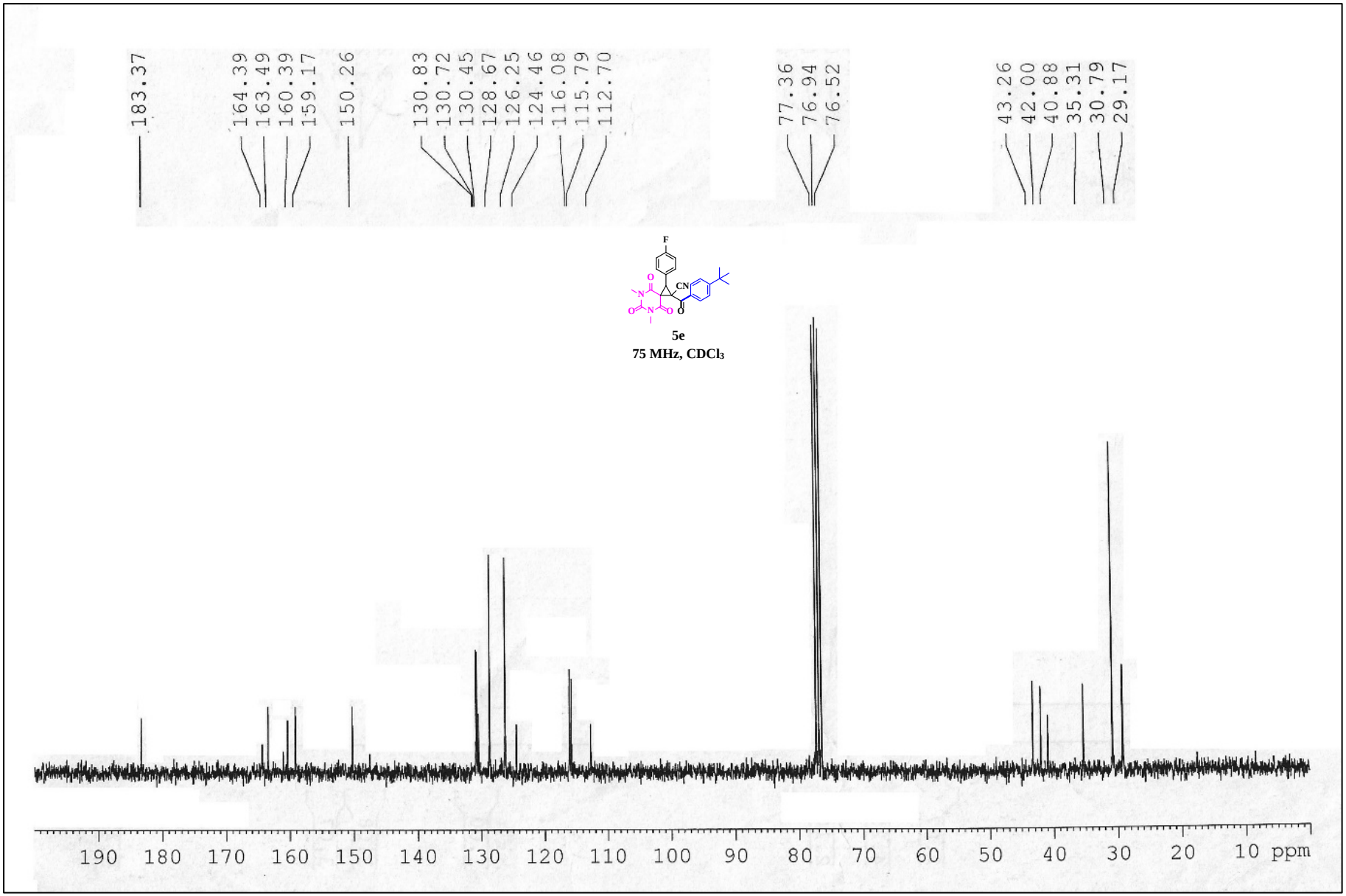

7.91
7.88
7.58
7.56
7.53
7.40
7.37
4.28
3.38
3.18
1.35
Br
CN
O
N
O
N
O
O
5d
300 MHz, CDCl3
2.00
4.05
2.03
1.00
3.02
3.01
9.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)




**5d**

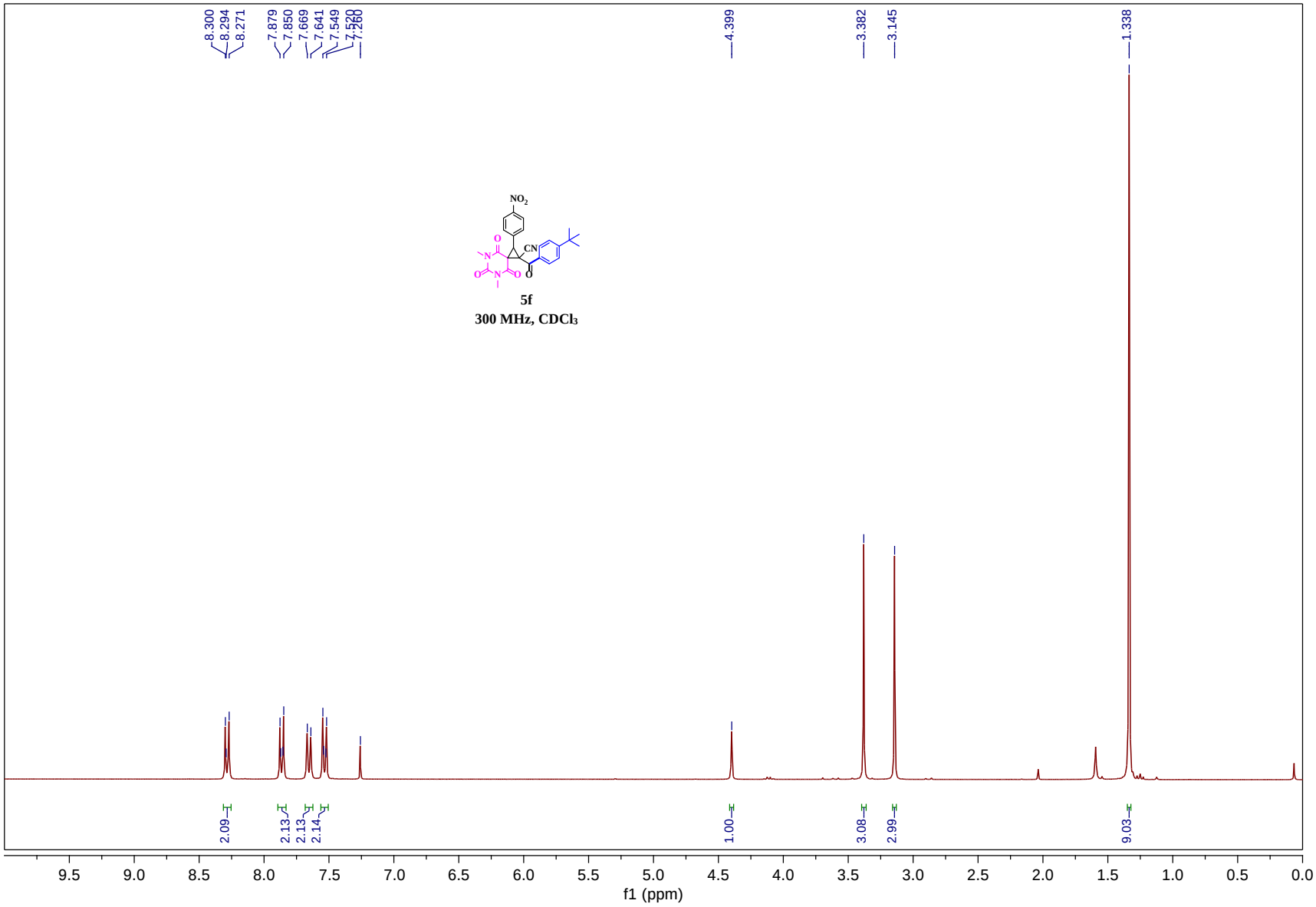
**75 MHz, $CDCl_3$**

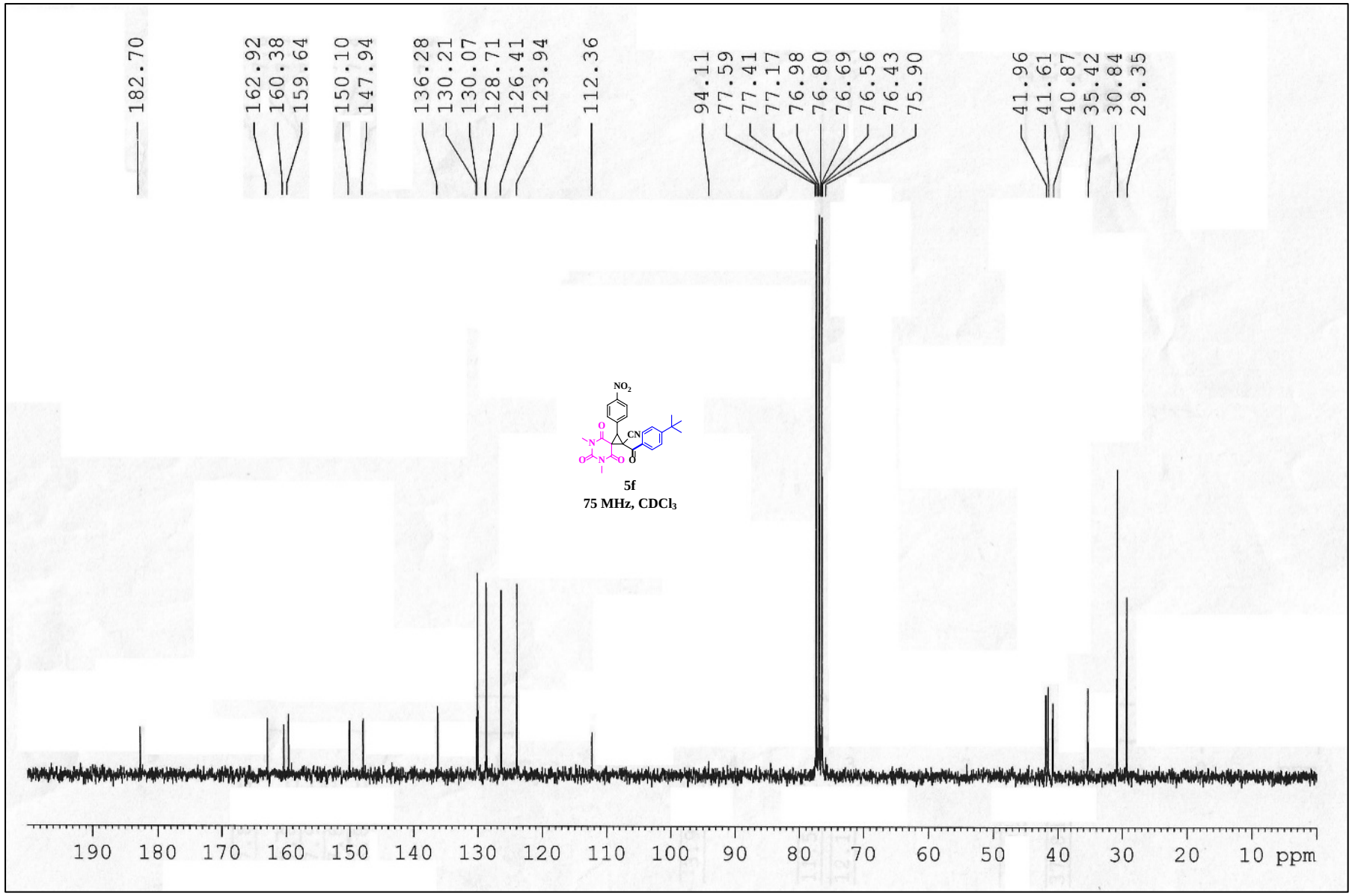

7.92
7.89
7.56
7.53
7.50
7.16
7.13
7.11
4.31
3.38
3.19
1.36
F
CN
O
N
O
O
N
O
5e
300 MHz, CDCl3
2.03
4.15
2.04
1.00
3.00
3.00
9.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)




**5e**

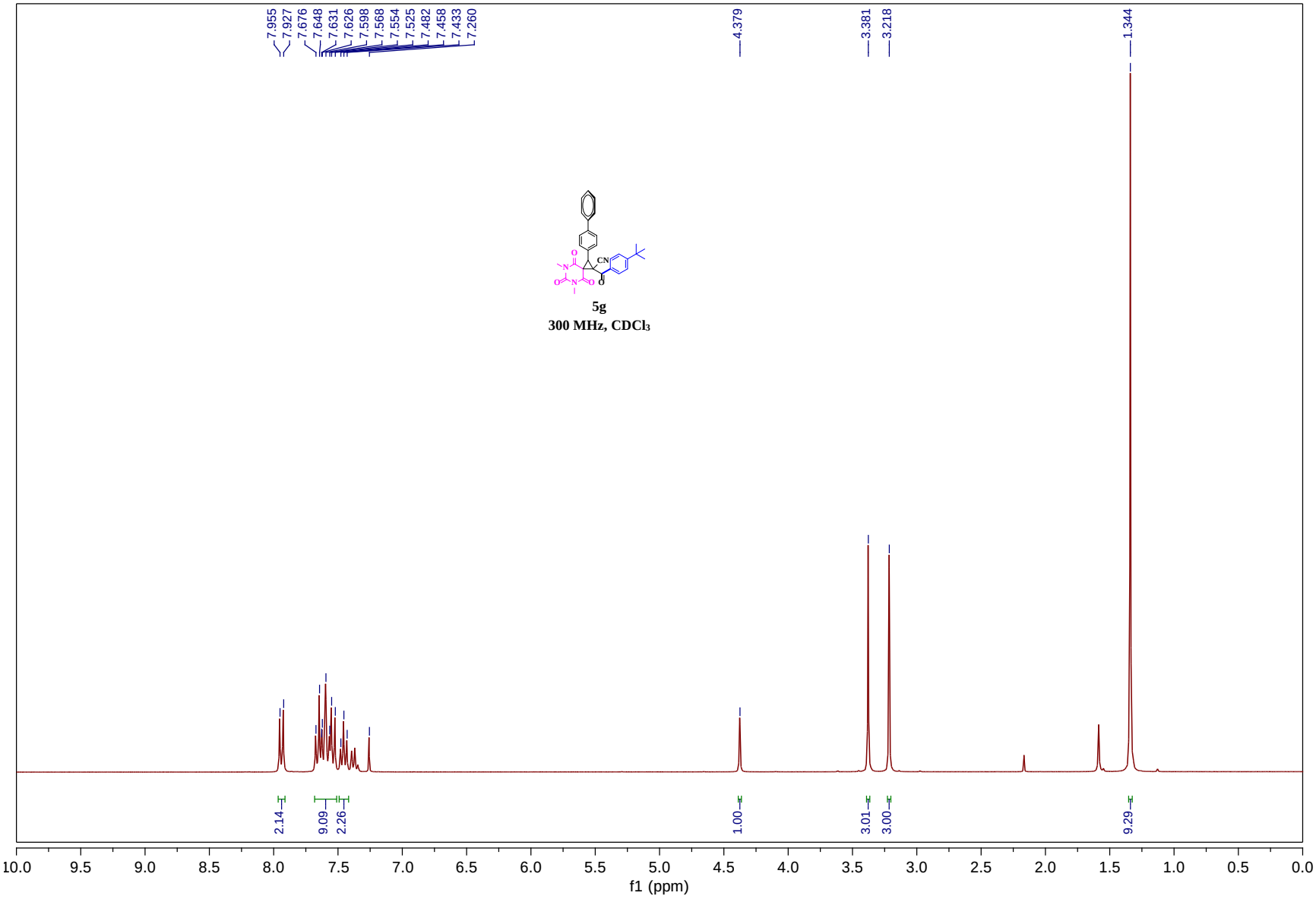
**75 MHz, $CDCl_3$**

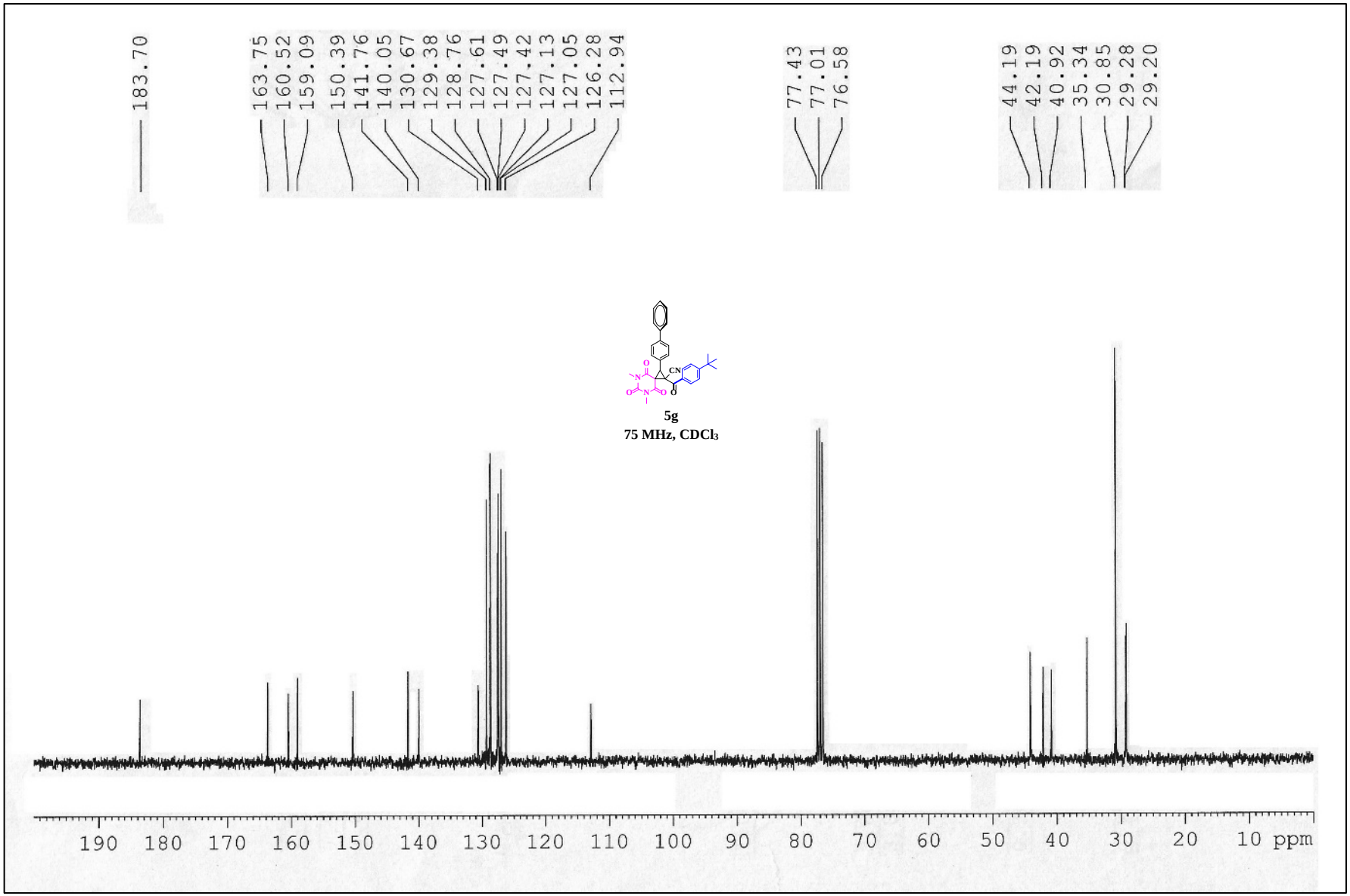

8.300
8.294
8.271
7.879
7.850
7.669
7.641
7.549
7.520
7.260
4.399
3.382
3.145
1.338
NO2
CN
O
N
O
N
O
O
5f
300 MHz, CDCl3
2.09
2.13
2.13
2.14
1.00
3.08
2.99
9.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

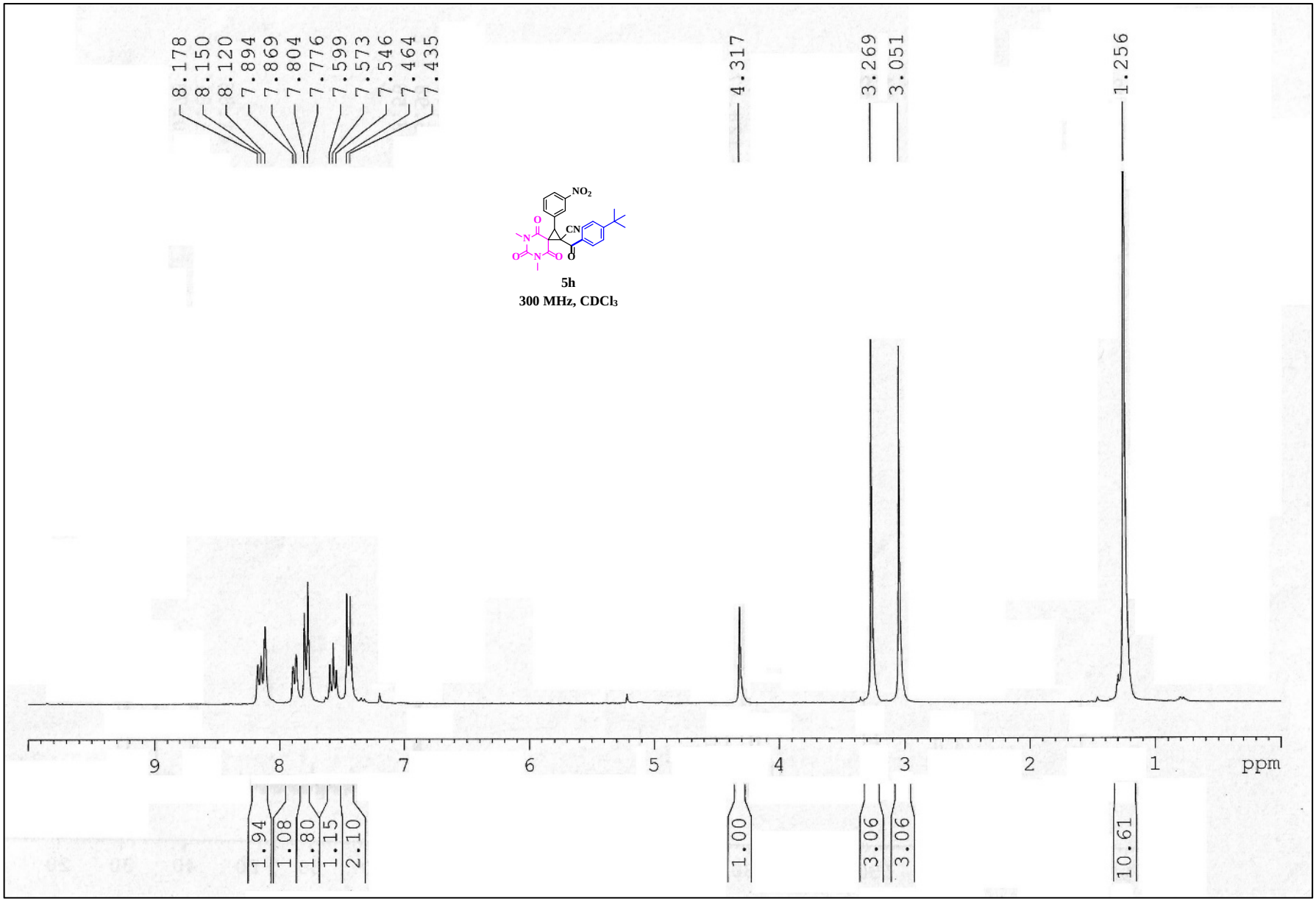


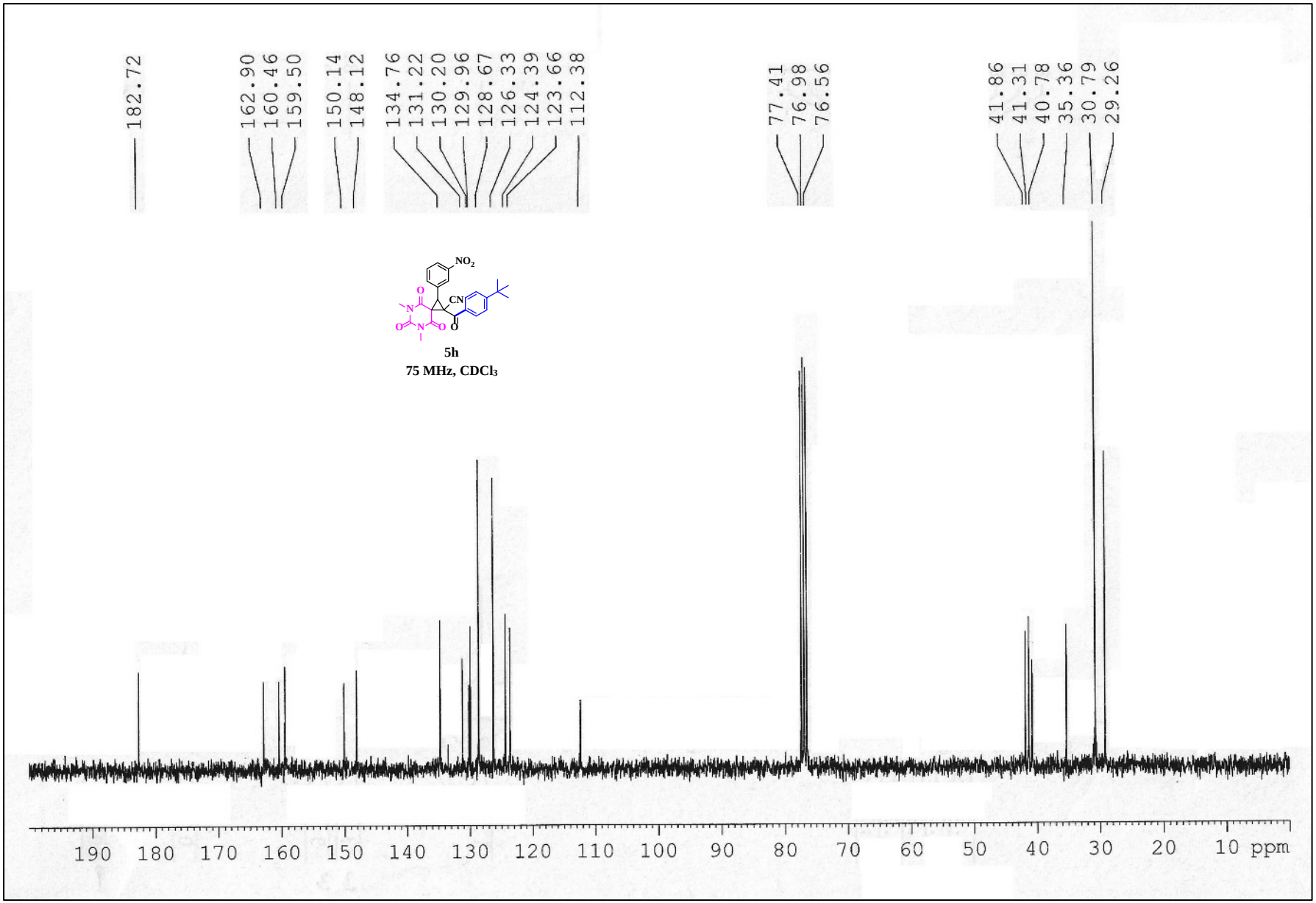

**5f**

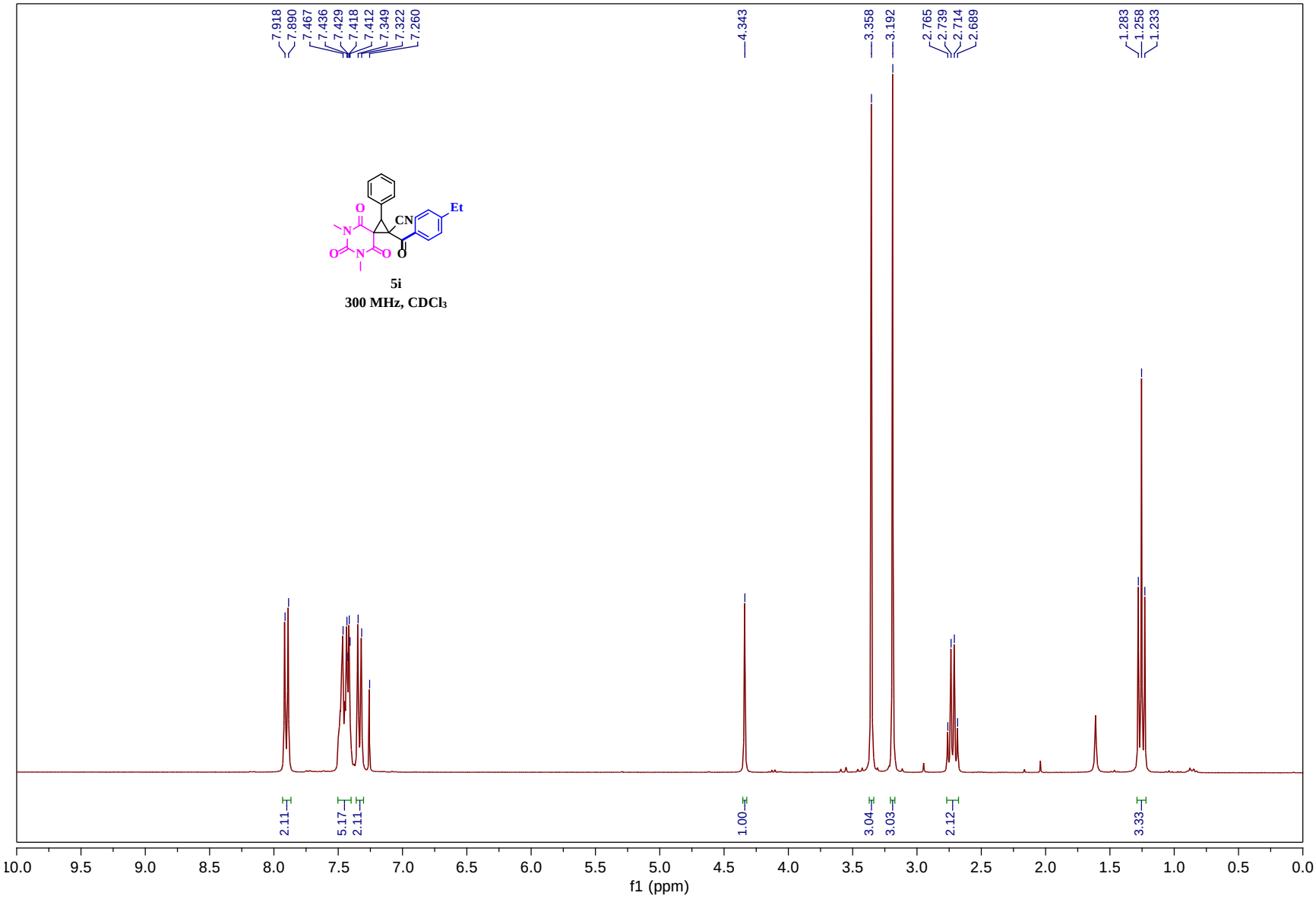
**75 MHz, $CDCl_3$**

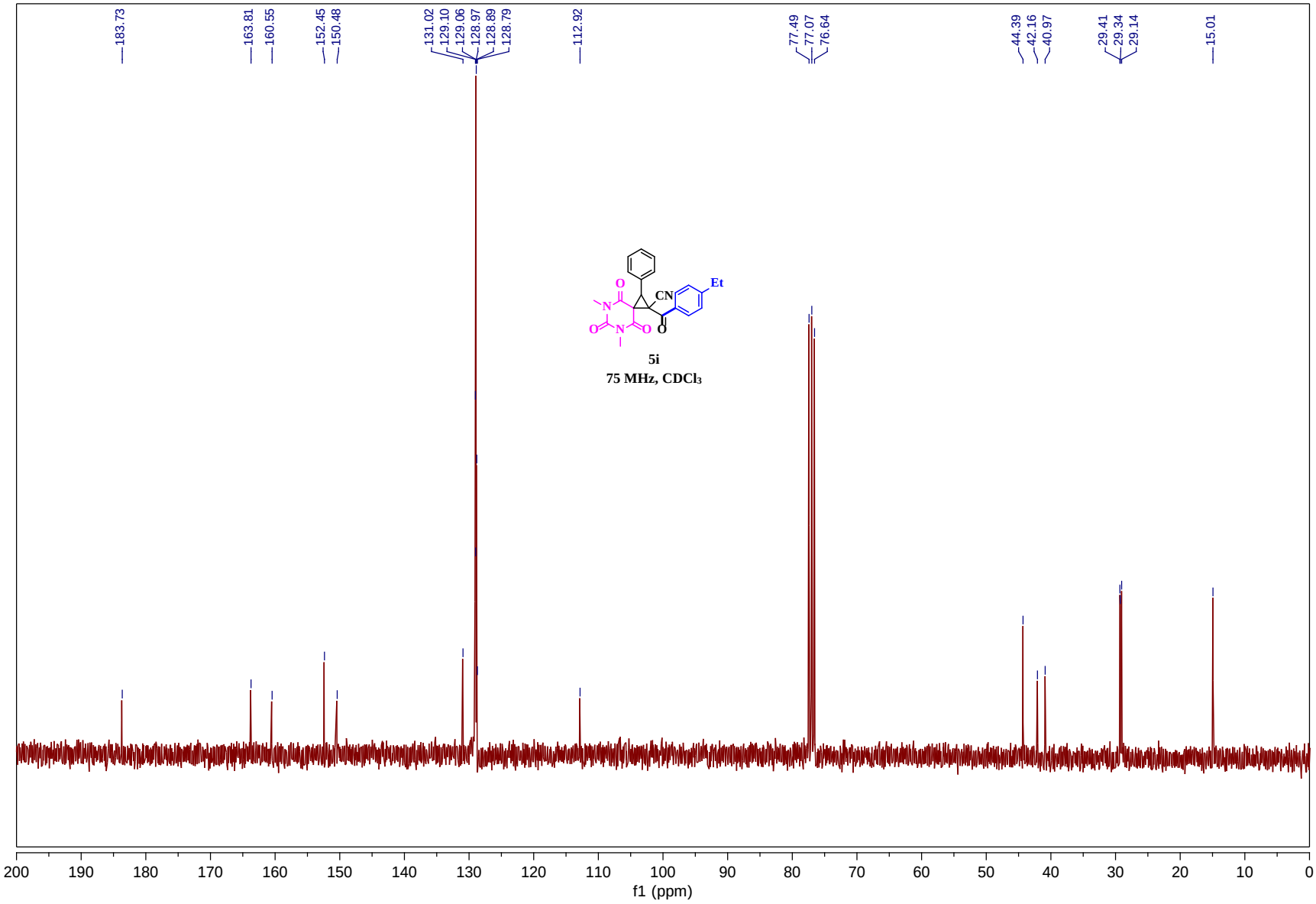

7.955
7.927
7.676
7.648
7.631
7.626
7.598
7.568
7.554
7.525
7.482
7.458
7.433
7.260
4.379
3.381
3.218
1.344
CN
O
O
O
O
O
N
N
I
5g
300 MHz, CDCl3
2.14
9.09
2.26
1.00
3.01
3.00
9.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


183.70
163.75
160.52
159.09
150.39
141.76
140.05
130.67
129.38
128.76
127.61
127.49
127.42
127.13
127.05
126.28
112.94
77.43
77.01
76.58
44.19
42.19
40.92
35.34
30.85
29.28
29.20
CN
5g
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

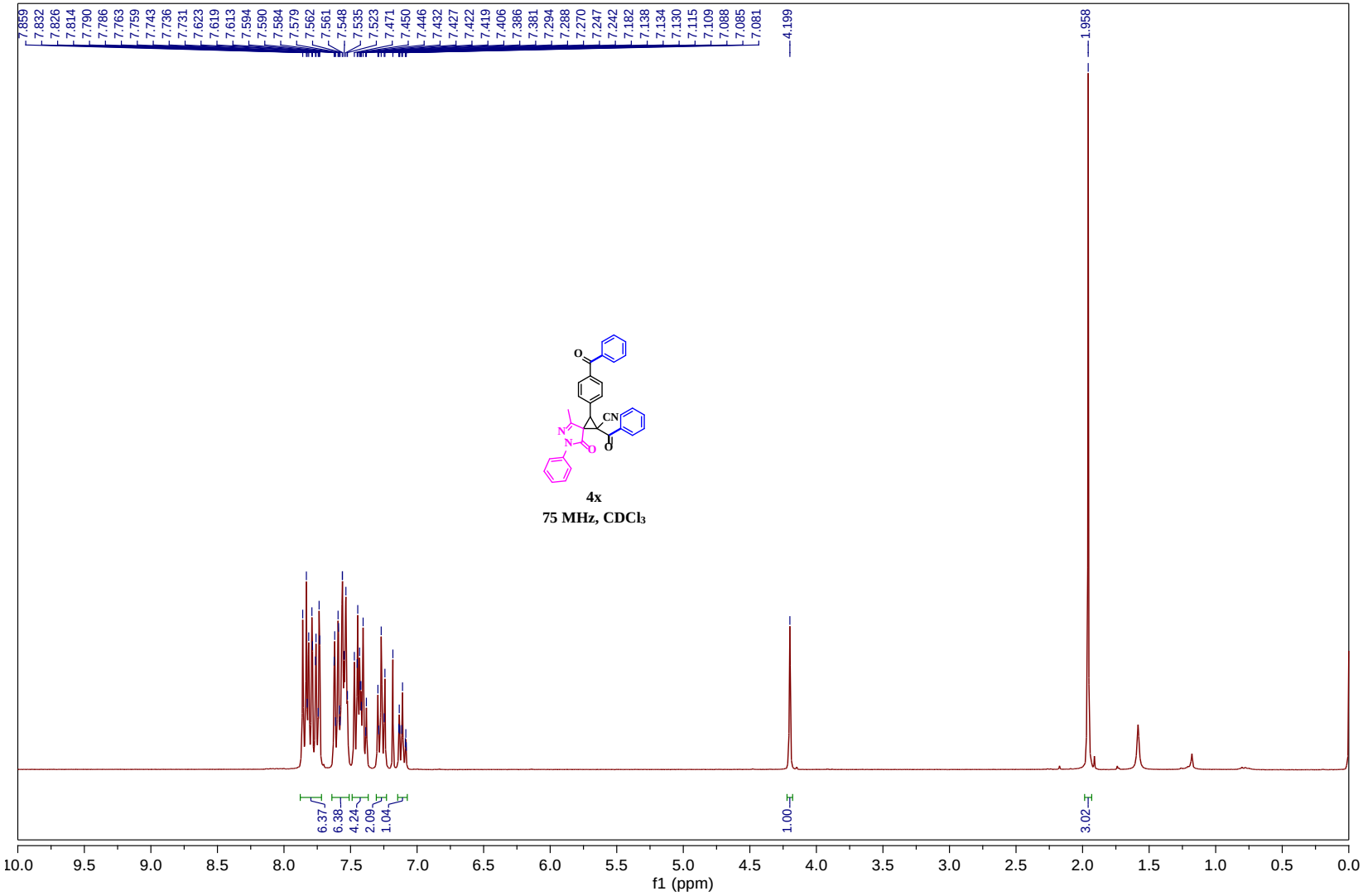

8.178
8.150
8.120
7.894
7.869
7.804
7.776
7.599
7.573
7.546
7.464
7.435
4.317
3.269
3.051
1.256
NO2
CN
O
N
O
N
O
O
5h
300 MHz, CDCl3
9
8
7
6
5
4
3
2
1
ppm
1.94
1.08
1.80
1.15
2.10
1.00
3.06
3.06
10.61

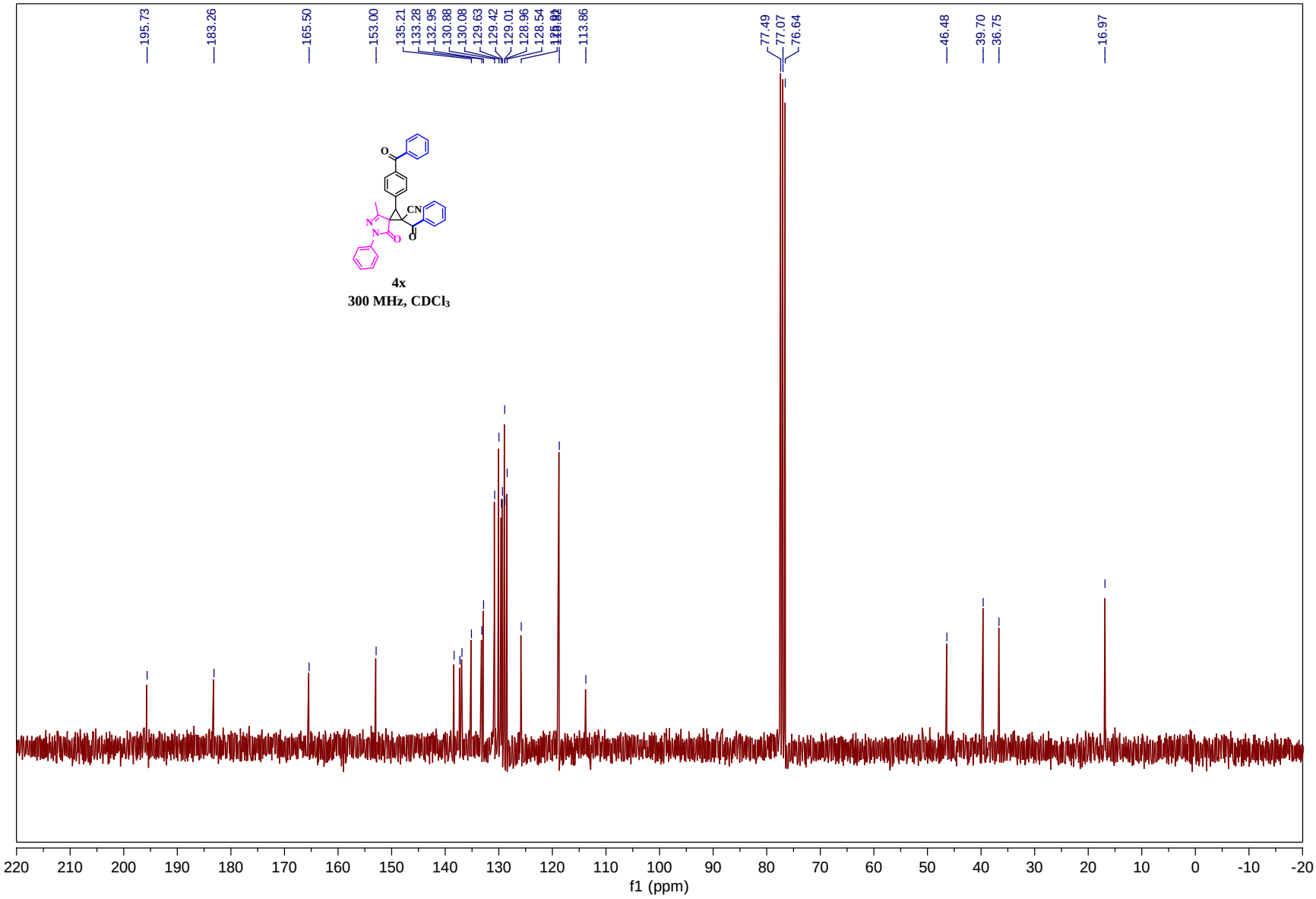

182.72
162.90
160.46
159.50
150.14
148.12
134.76
131.22
130.20
129.96
128.67
126.33
124.39
123.66
112.38
77.41
76.98
76.56
41.86
41.31
40.78
35.36
30.79
29.26
NO2
CN
O
O
O
O
N
N
5h
75 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

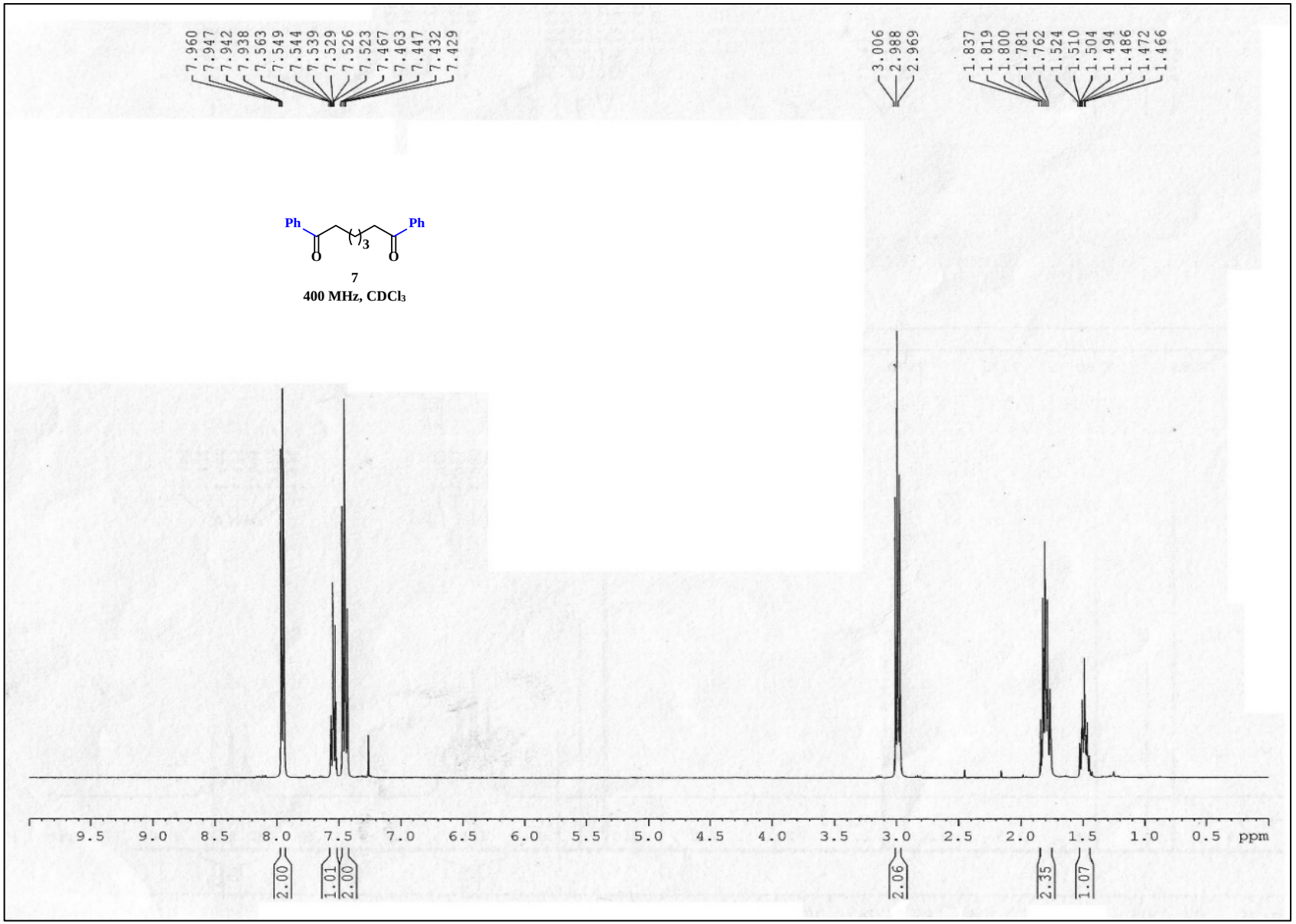

7.918
7.890
7.467
7.436
7.429
7.418
7.412
7.349
7.322
7.260
4.343
3.358
3.192
2.765
2.739
2.714
2.689
1.283
1.258
1.233
O
N
CN
Et
O
N
O
O
5i
300 MHz, CDCl3
2.11
5.17
2.11
1.00
3.04
3.03
2.12
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


183.73
163.81
160.55
152.45
150.48
131.02
129.10
129.06
128.97
128.89
128.79
112.92
77.49
77.07
76.64
44.39
42.16
40.97
29.41
29.34
29.14
15.01
O
N
O
N
O
O
CN
Et
5i
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

## VI. $^{1}H$ and $^{13}C$ NMR spectra for the products 4x, 7, 9, 11, 14 and 15

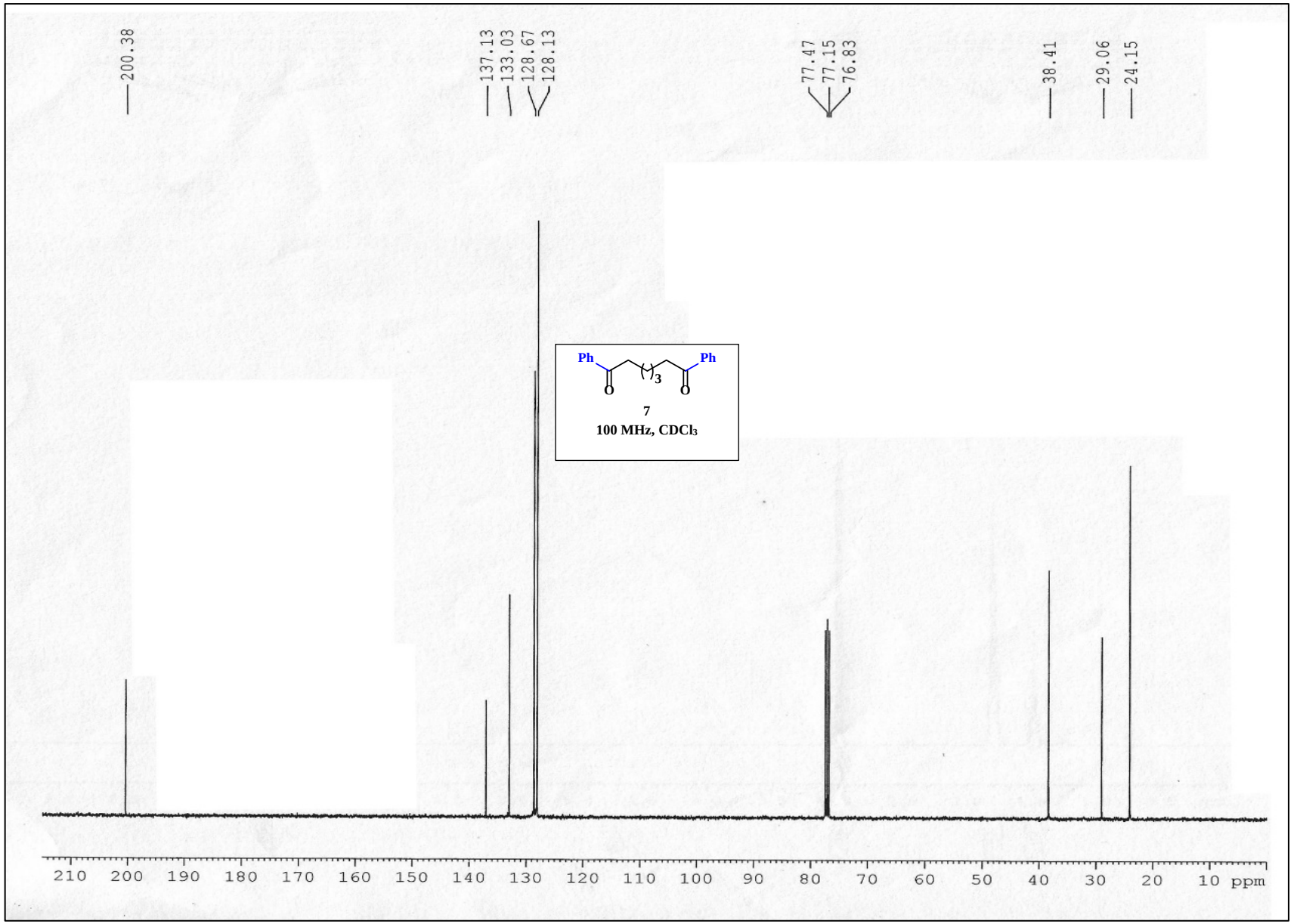


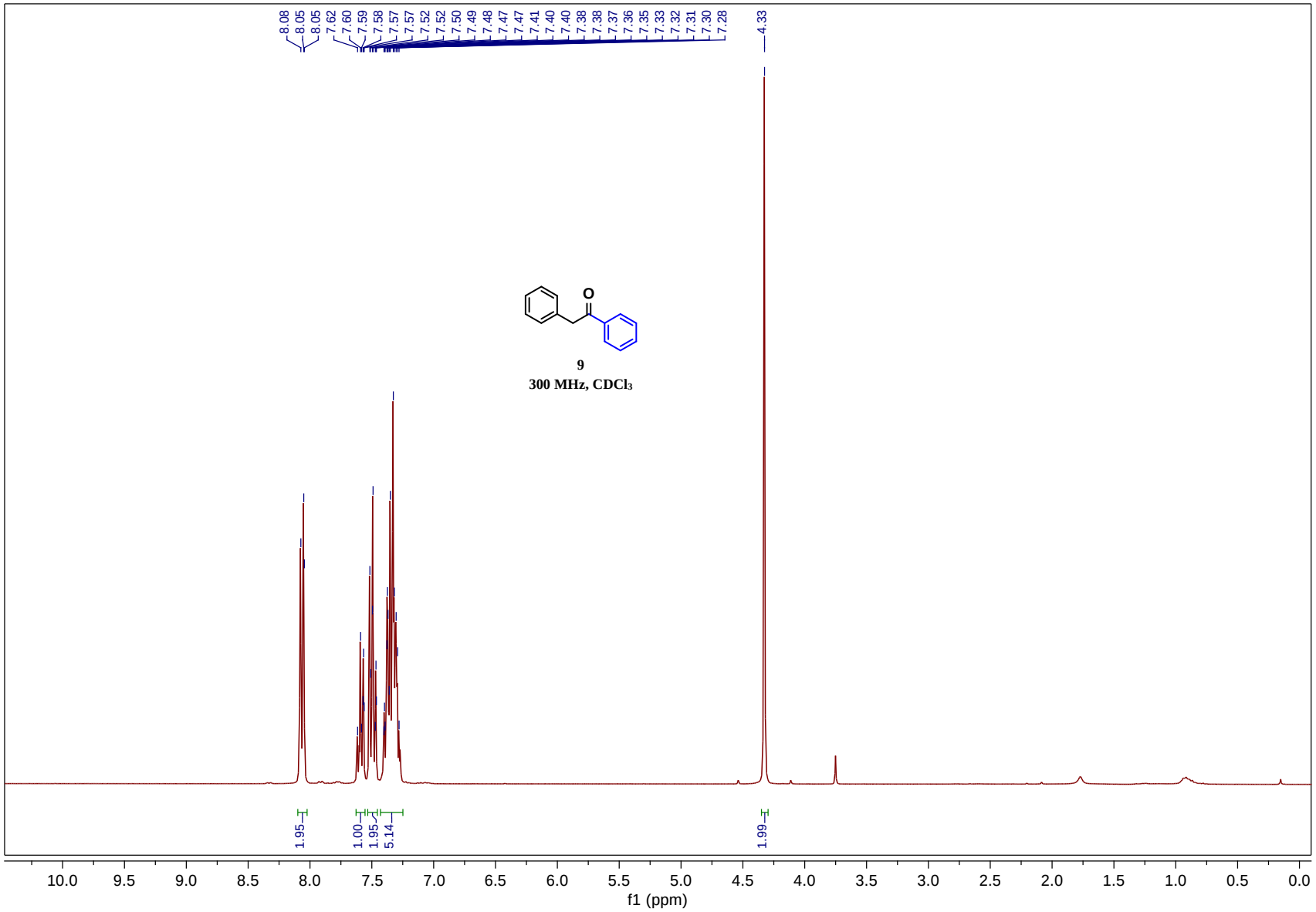

195.73
183.26
165.50
153.00
135.21
133.28
132.95
130.88
130.08
129.63
129.42
129.01
128.96
128.54
113.86
77.49
77.07
76.64
46.48
39.70
36.75
16.97
O
CN
N
N
O
O
4x
300 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

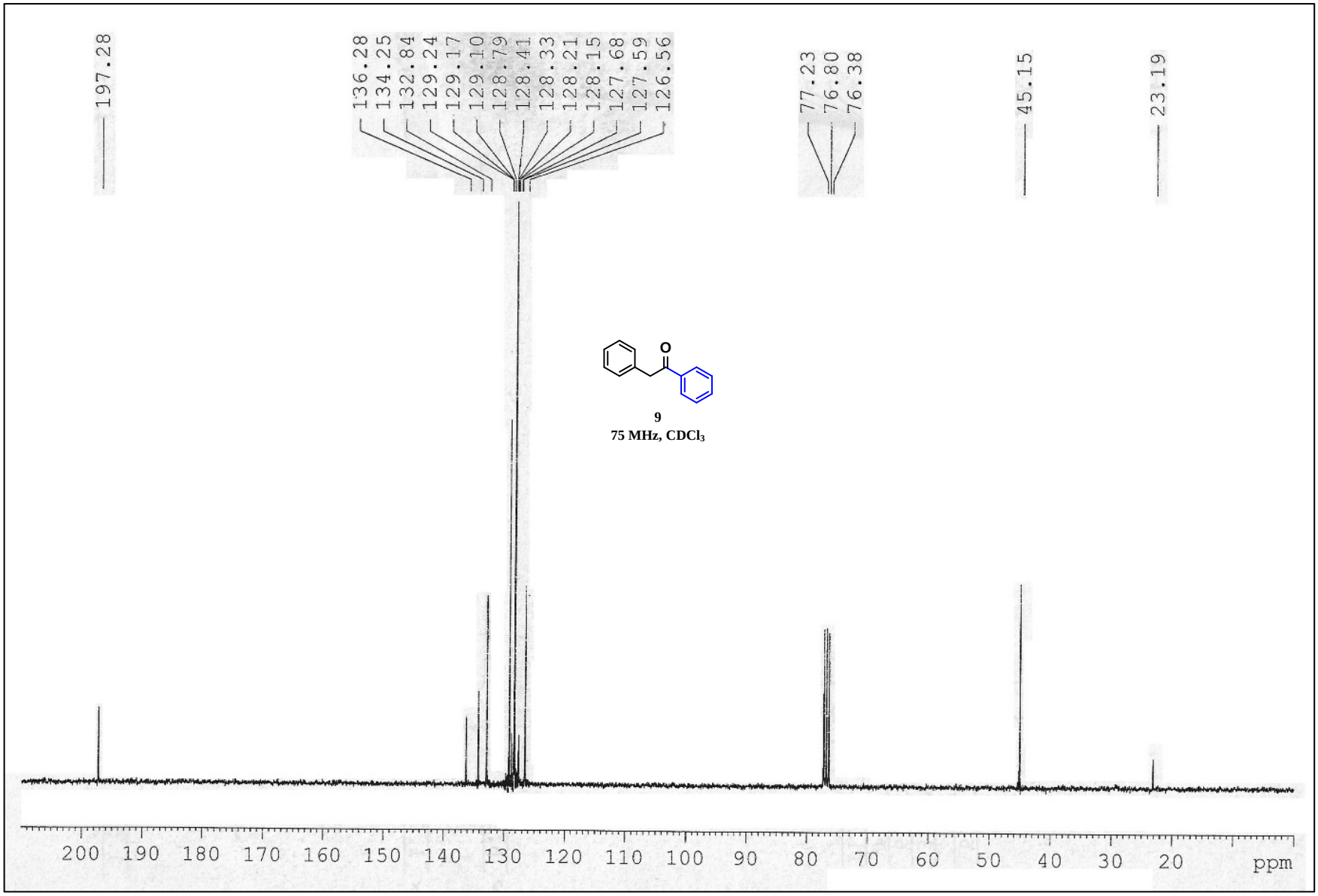


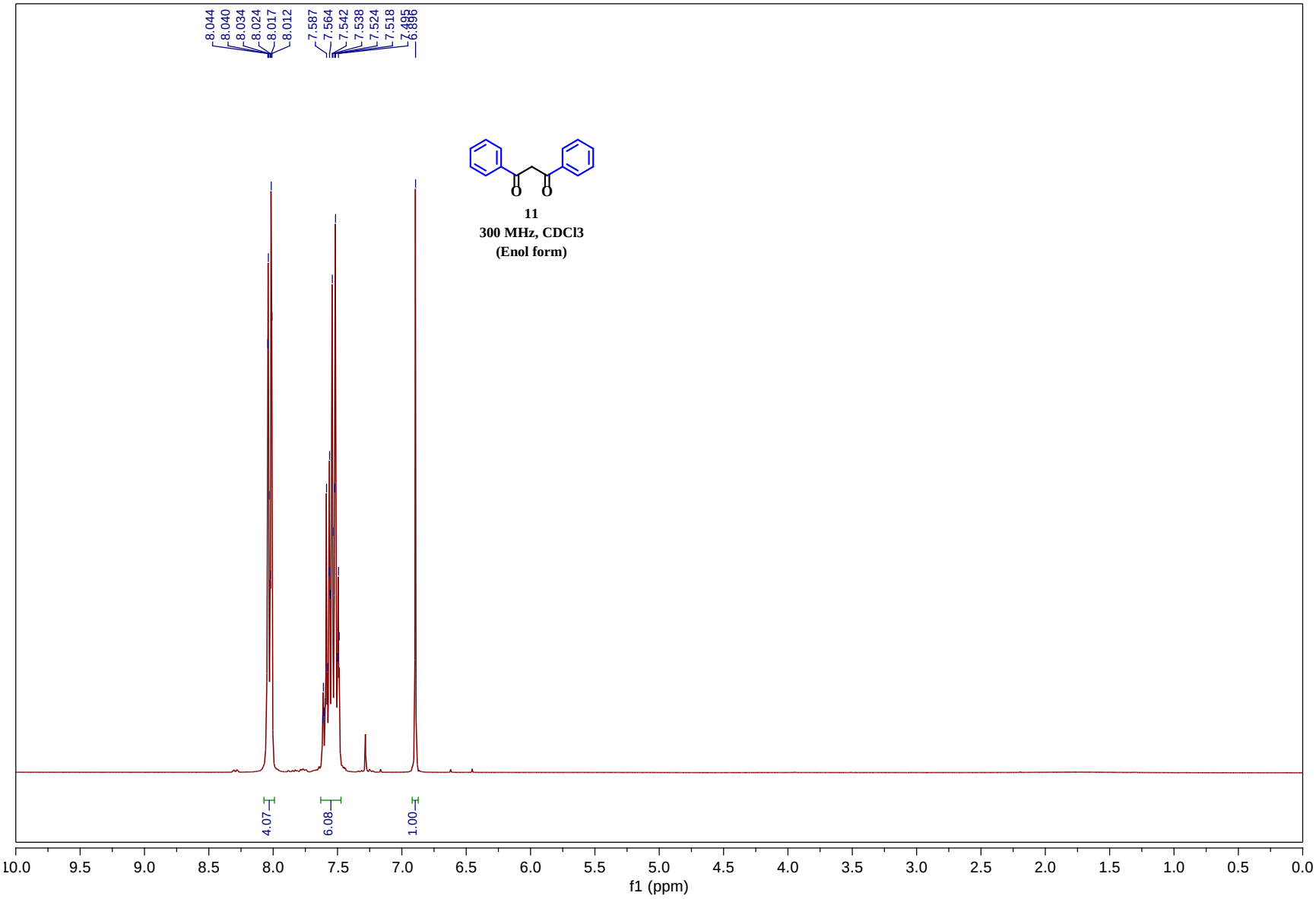

**7**

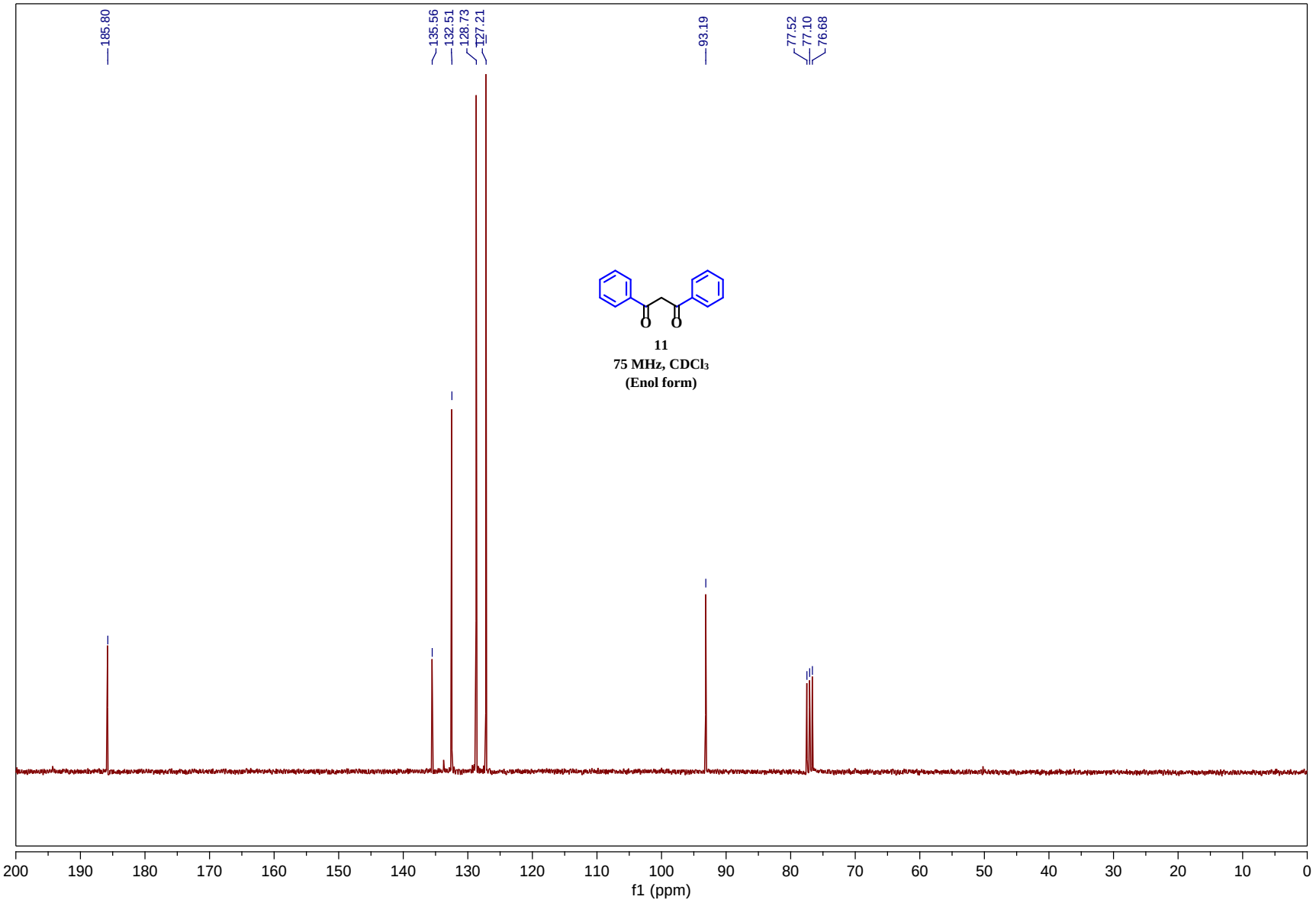
**400 MHz, $CDCl_3$**

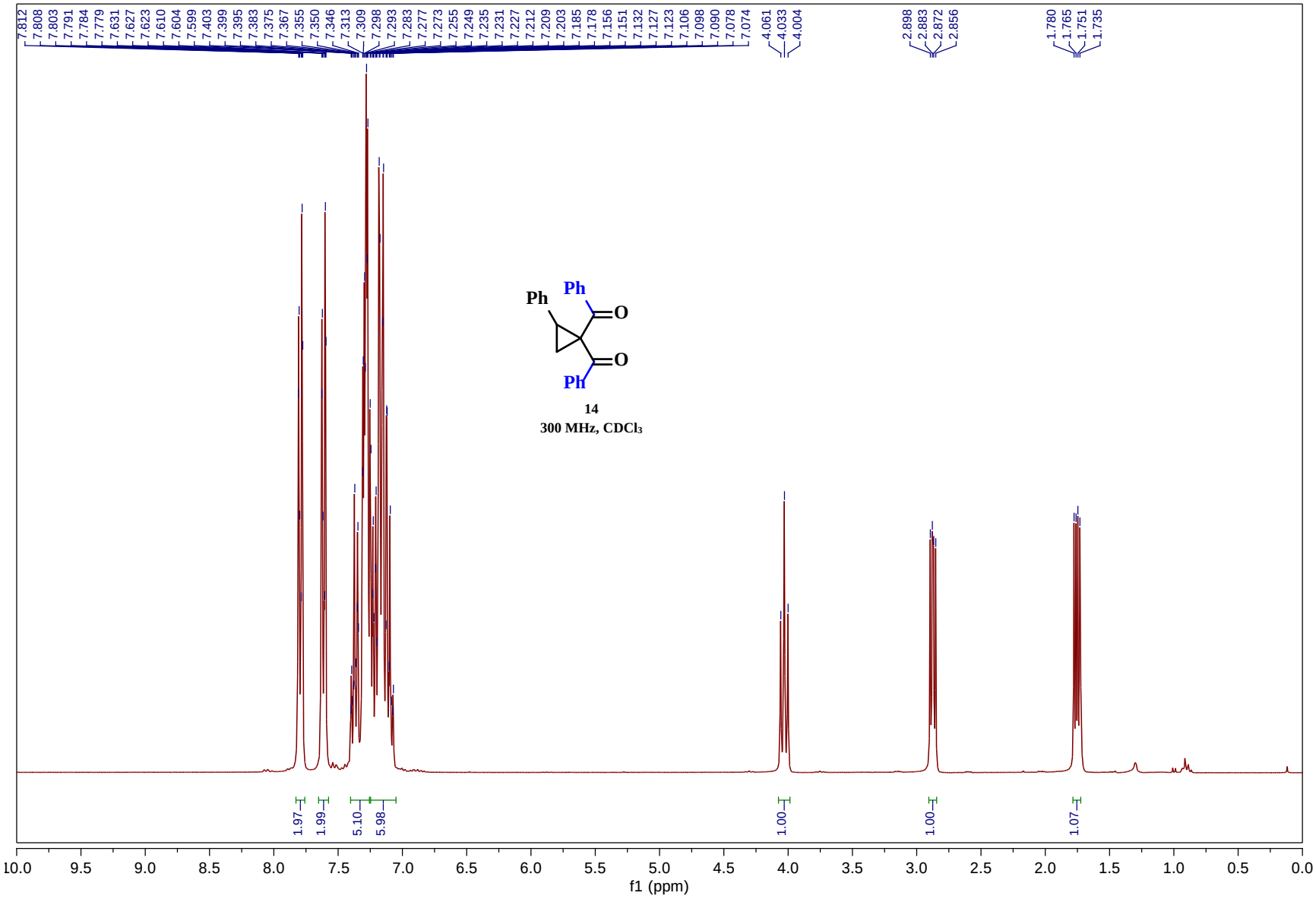

200.38
137.13
133.03
128.67
128.13
77.47
77.15
76.83
38.41
29.06
24.15
Ph
Ph
3
O
O
7
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

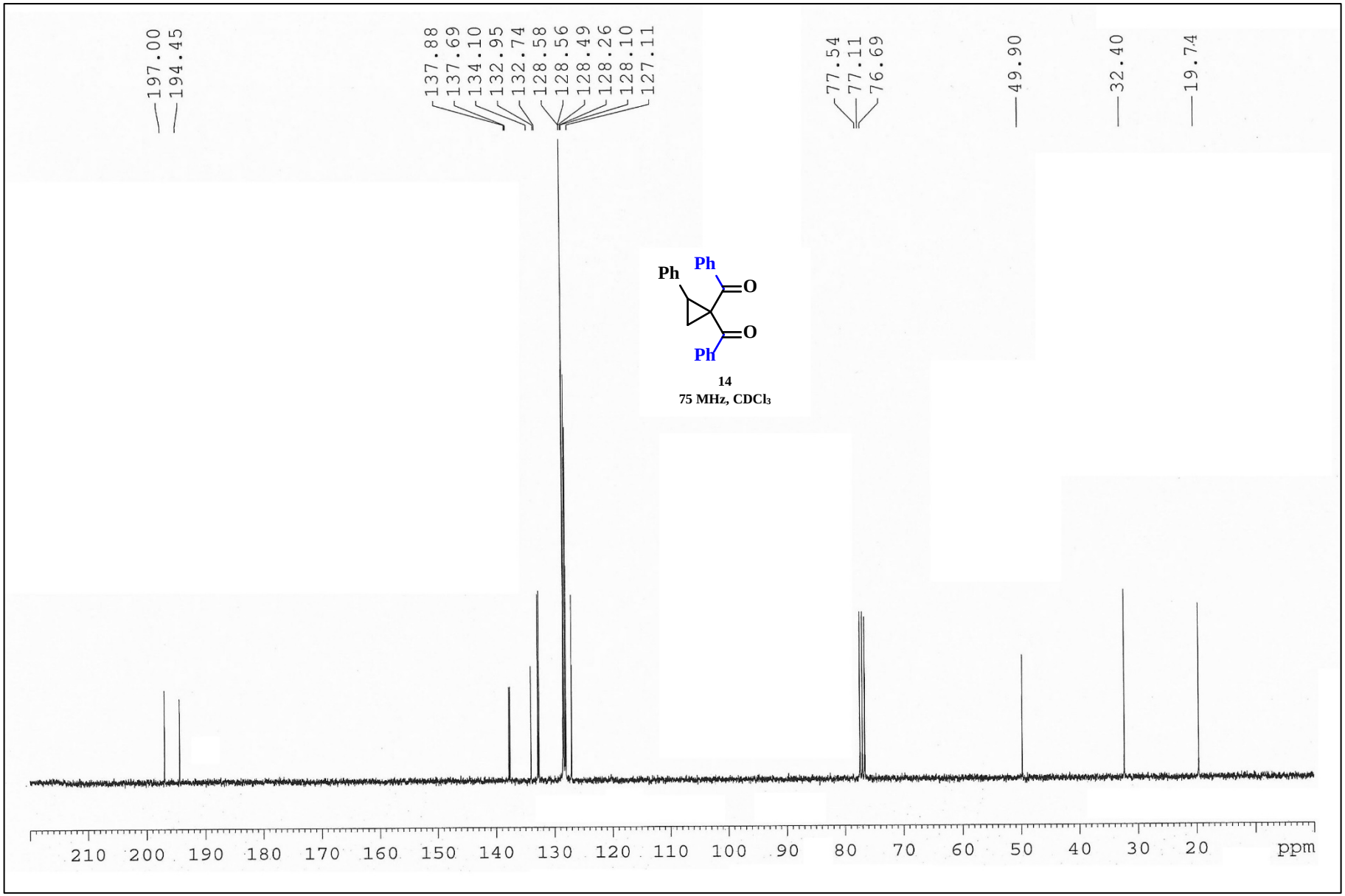

8.08
8.05
8.05
7.62
7.60
7.59
7.58
7.57
7.57
7.52
7.52
7.50
7.49
7.48
7.47
7.47
7.41
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.33
7.32
7.31
7.30
7.28
4.33
O
9
300 MHz, CDCl3
1.95
1.00
1.95
5.14
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

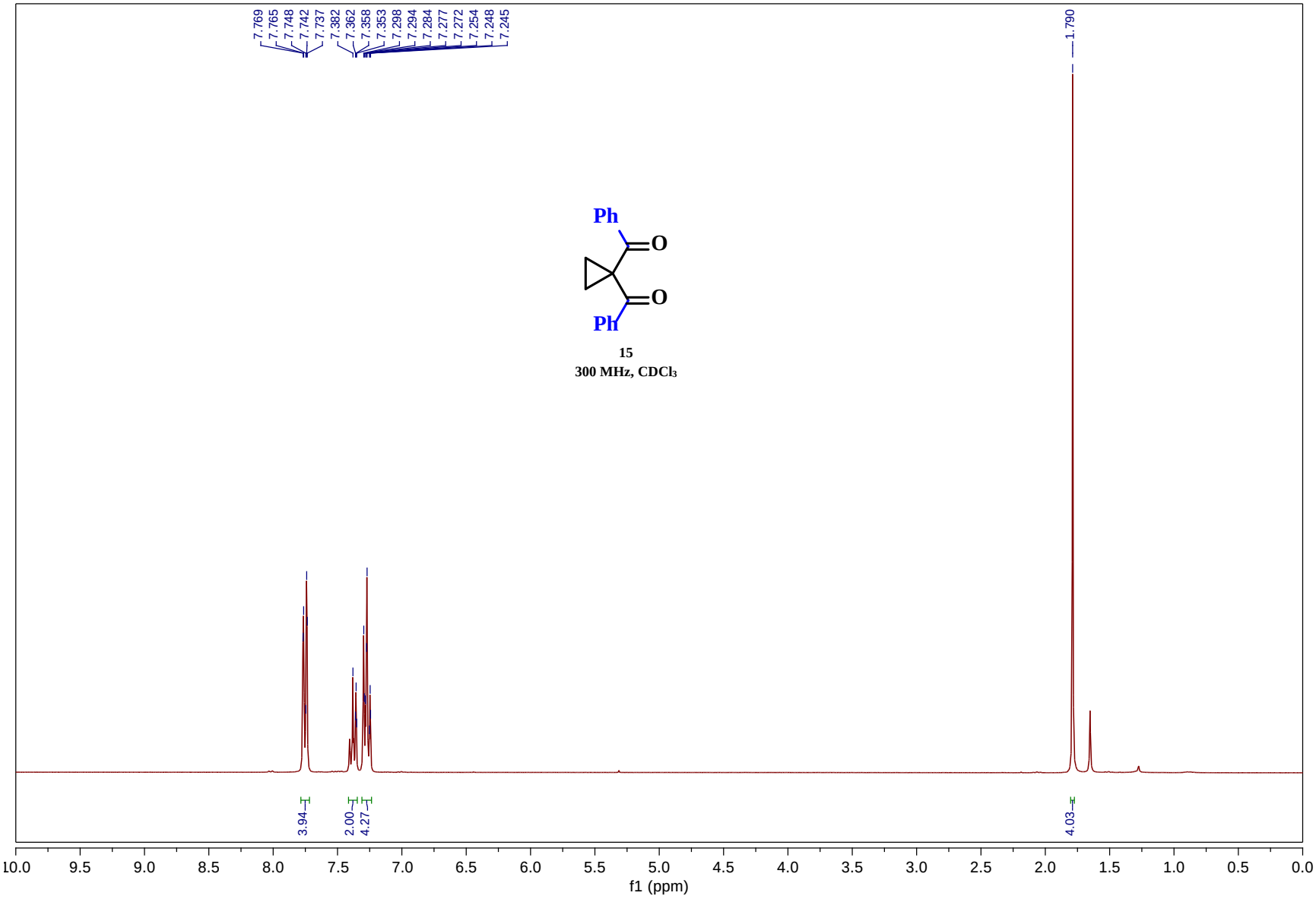

197.28
136.28
134.25
132.84
129.24
129.17
129.10
128.79
128.41
128.33
128.21
128.15
127.68
127.59
126.56
77.23
76.80
76.38
45.15
23.19
O
9
75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

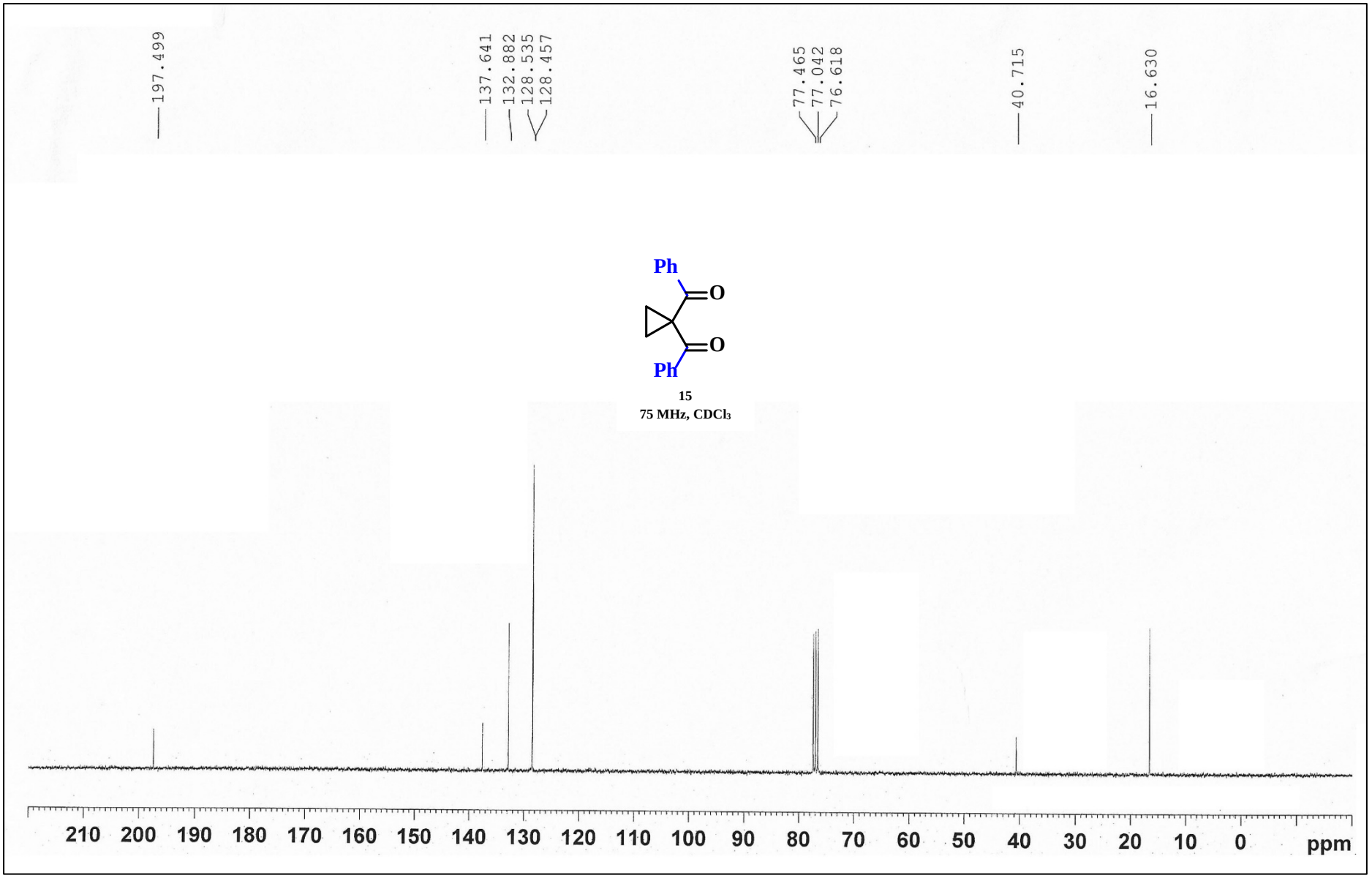

8.044
8.040
8.034
8.024
8.017
8.012
7.587
7.564
7.542
7.538
7.524
7.518
7.495
7.486
O
O
11
300 MHz, CDCl3
(Enol form)
4.07
6.08
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


185.80
135.56
132.51
128.73
127.21
93.19
77.52
77.10
76.68
O
O
11
75 MHz, CDCl3
(Enol form)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.812
7.808
7.803
7.791
7.784
7.779
7.631
7.627
7.623
7.610
7.604
7.599
7.403
7.399
7.395
7.383
7.375
7.367
7.355
7.350
7.346
7.313
7.309
7.298
7.293
7.283
7.277
7.273
7.255
7.249
7.235
7.231
7.227
7.212
7.209
7.203
7.185
7.178
7.156
7.151
7.132
7.127
7.123
7.106
7.098
7.090
7.078
7.074
4.061
4.033
4.004
2.898
2.883
2.872
2.856
1.780
1.765
1.751
1.735
Ph
Ph
O
O
Ph
14
300 MHz, CDCl3
1.97
1.99
5.10
5.98
1.00
1.00
1.07
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)


197.00
194.45
137.88
137.69
134.10
132.95
132.74
128.58
128.56
128.49
128.26
128.10
127.11
77.54
77.11
76.69
49.90
32.40
19.74
Ph
Ph
O
O
Ph
14
75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.769
7.765
7.748
7.742
7.737
7.382
7.362
7.358
7.353
7.298
7.294
7.284
7.277
7.272
7.254
7.248
7.245
1.790
Ph
O
O
Ph
15
300 MHz, CDCl3
3.94
2.00
4.27
4.03
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)


197.499
137.641
132.882
128.535
128.457
77.465
77.042
76.618
40.715
16.630
Ph
O
O
Ph
15
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 ppm