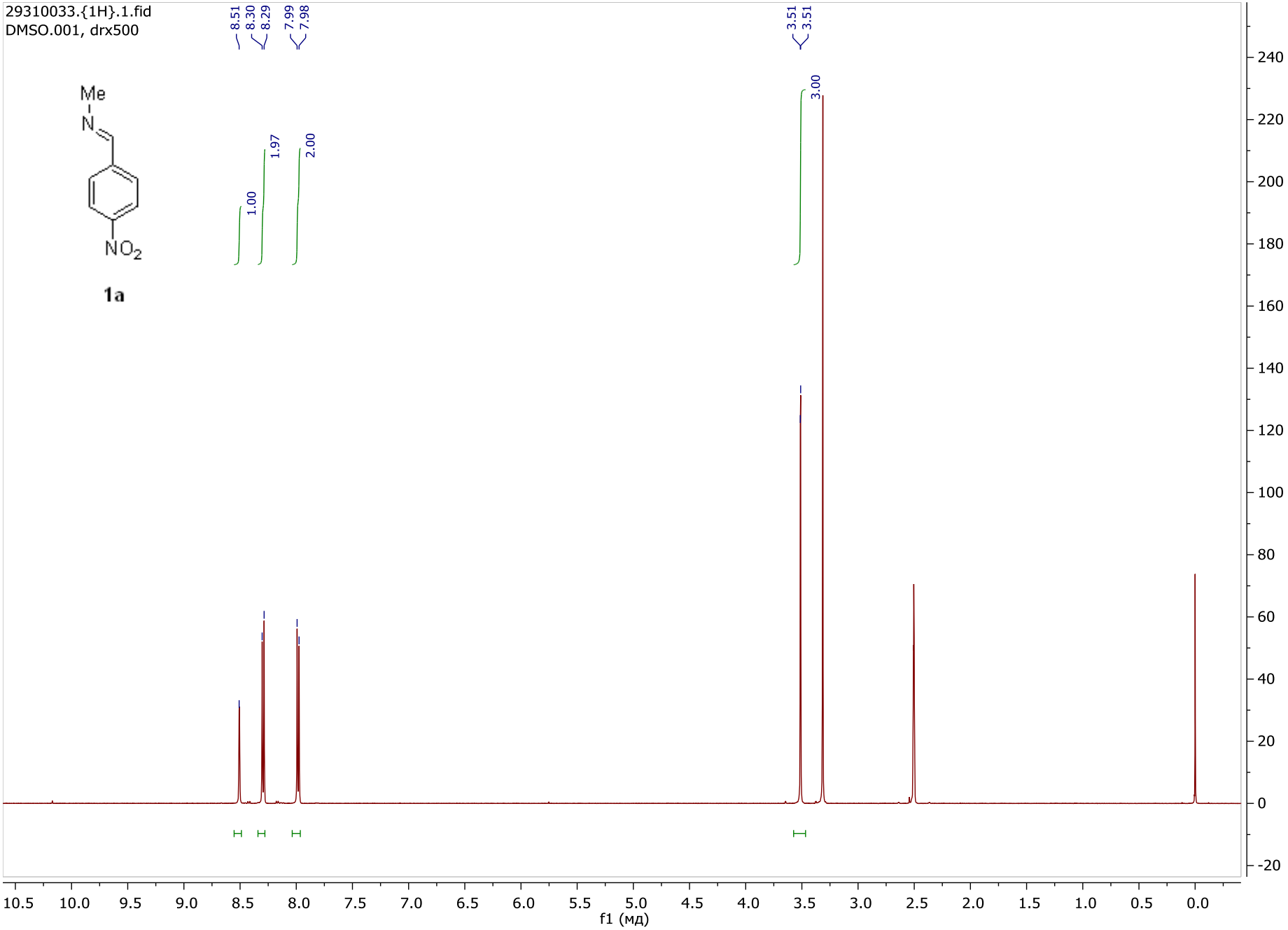
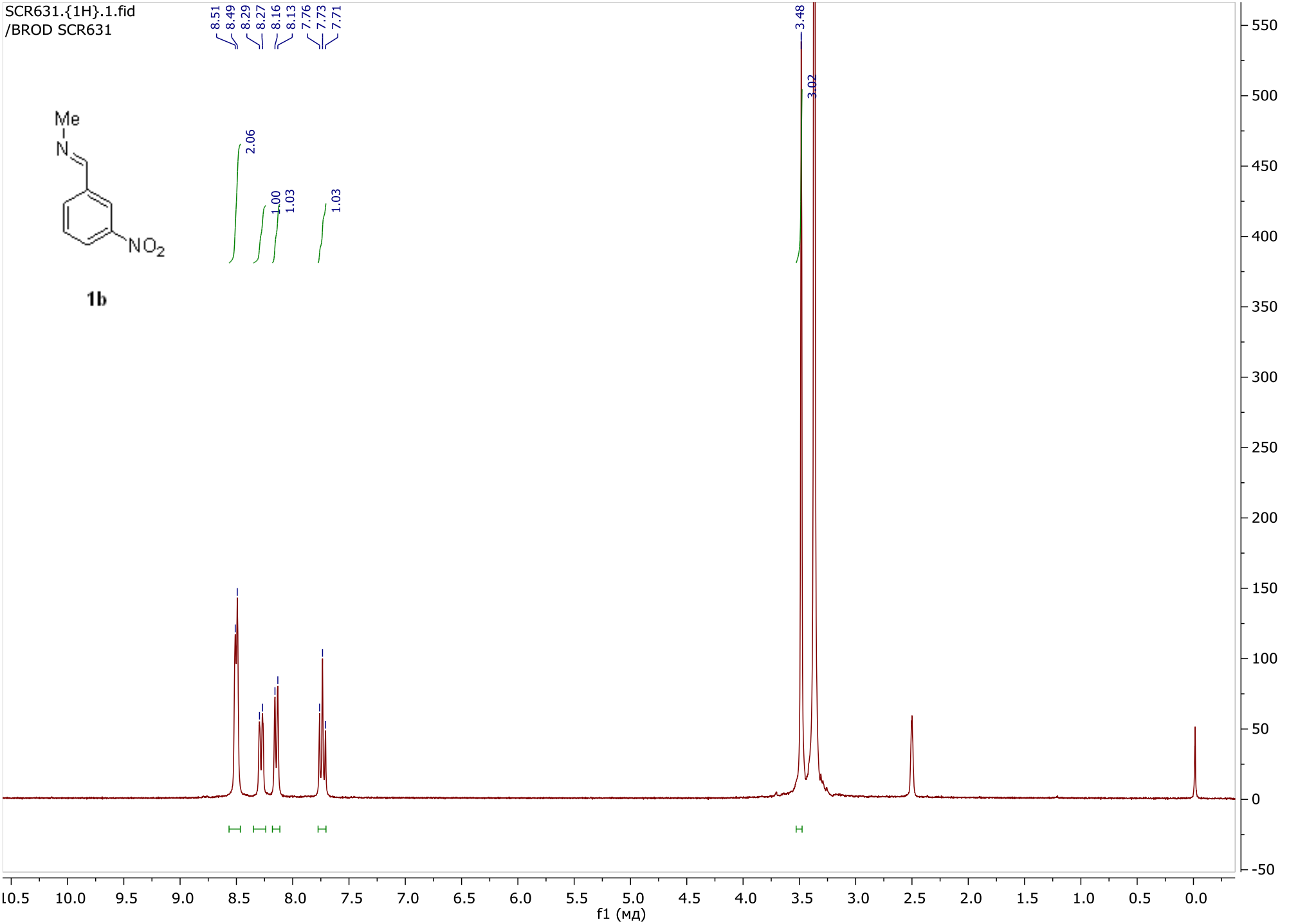
Supporting Information

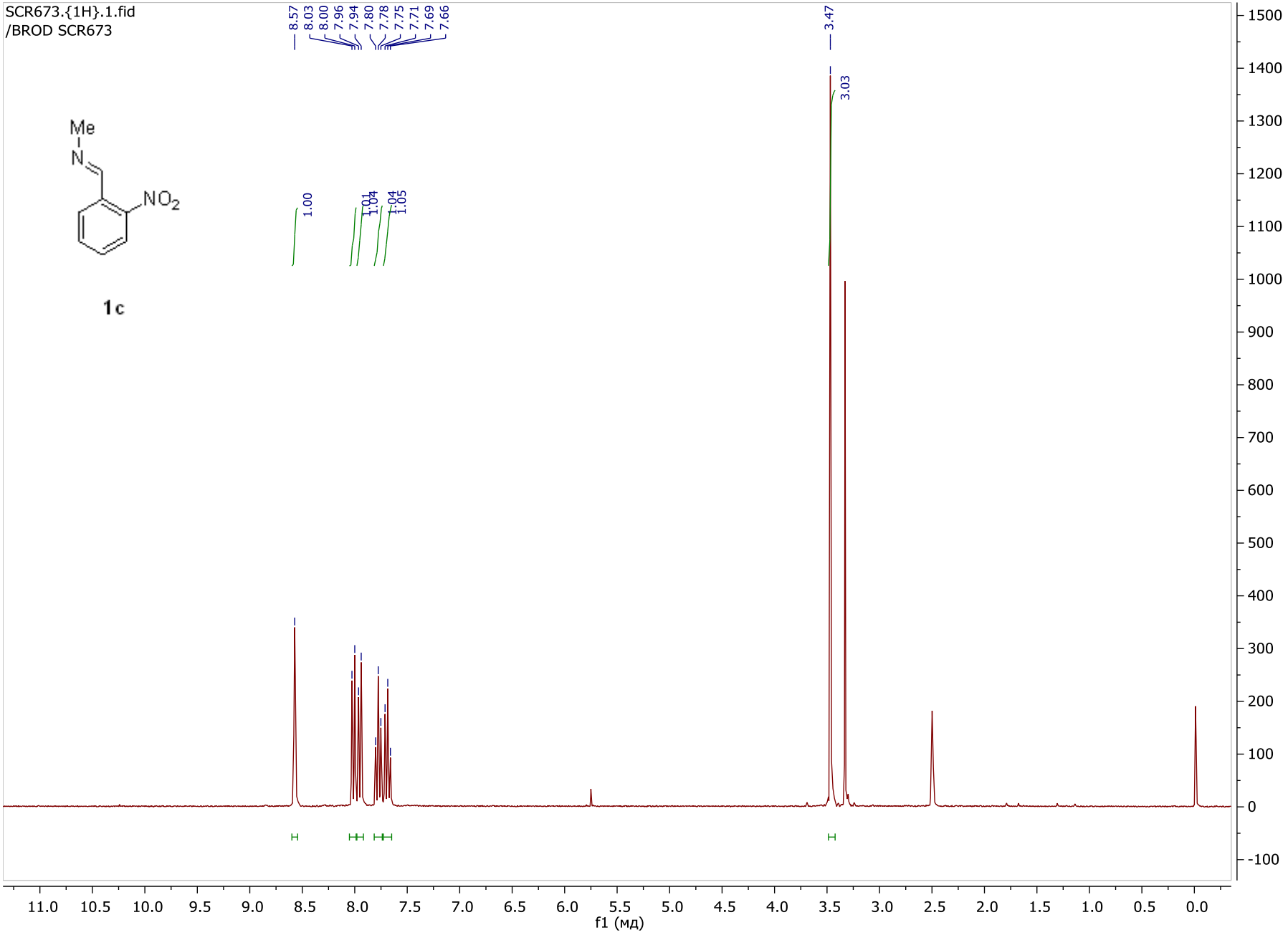
Straightforward approach to vicinal diaryl-1,2,3-triazoles from α-nitrostilbenes and sodium azide

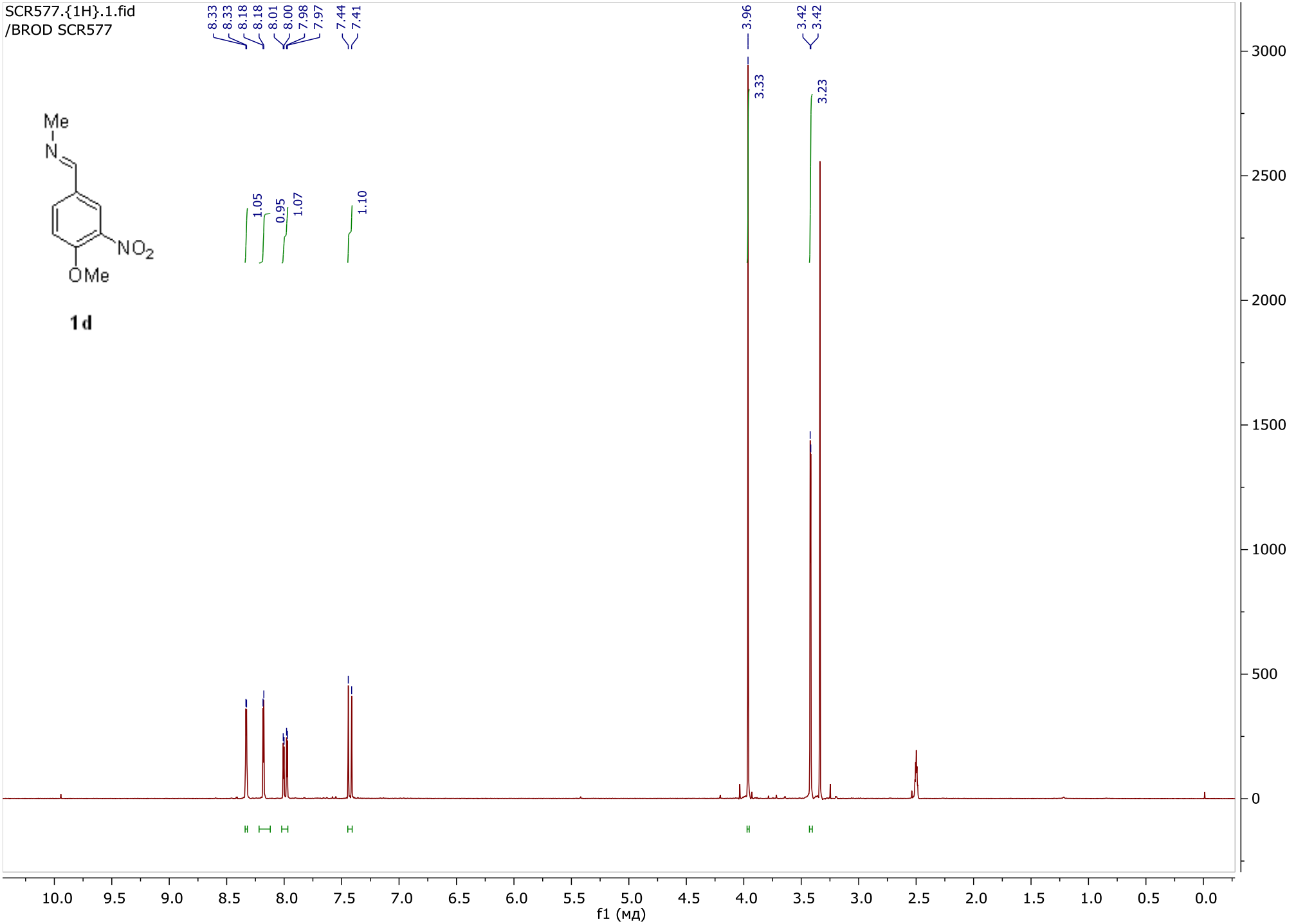
I. A. Koblov, K. A. Semenov, E. D. Daeva, M. E. Minyaev, and V. P. Kislyi

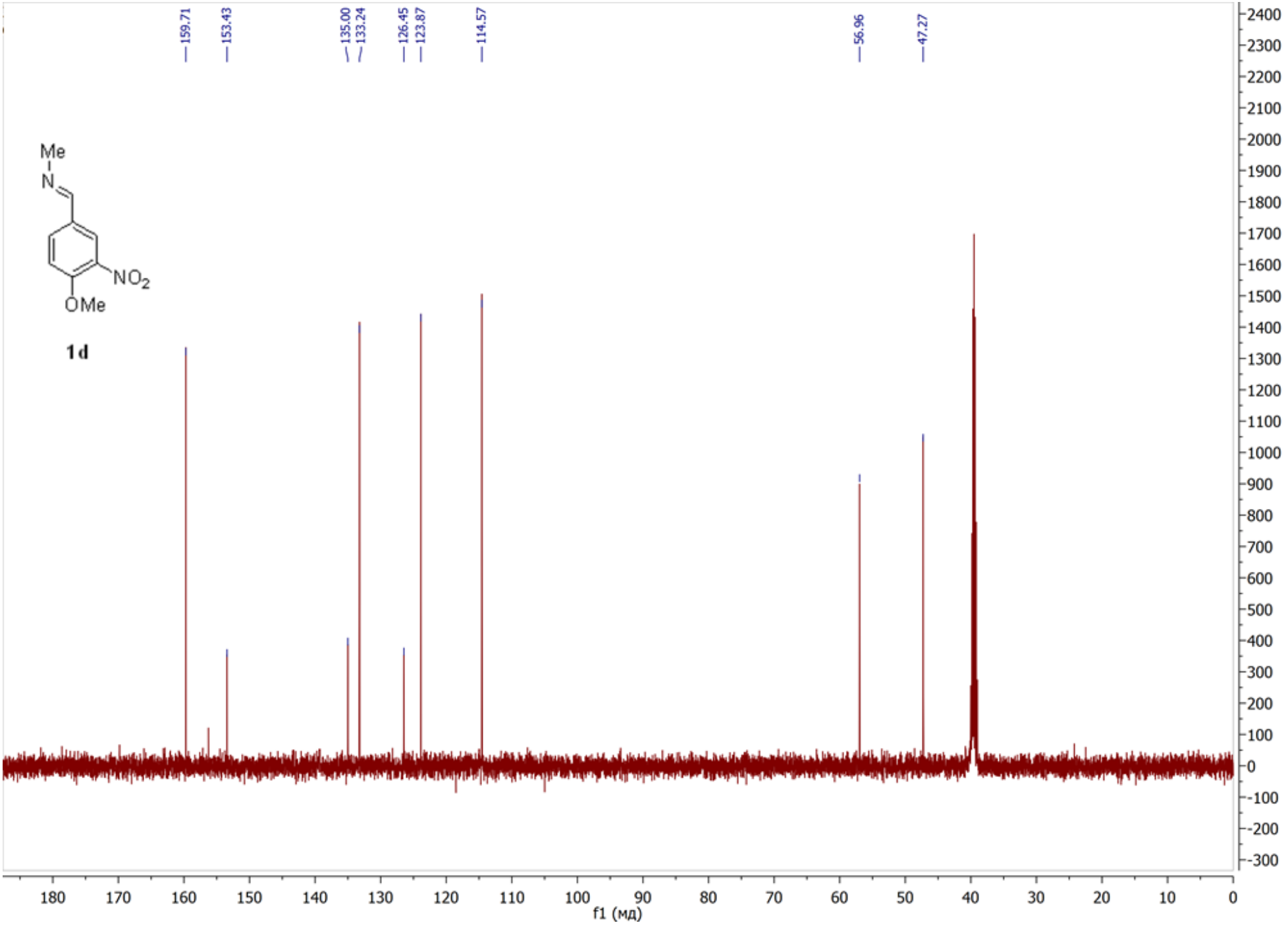
Table of Contents

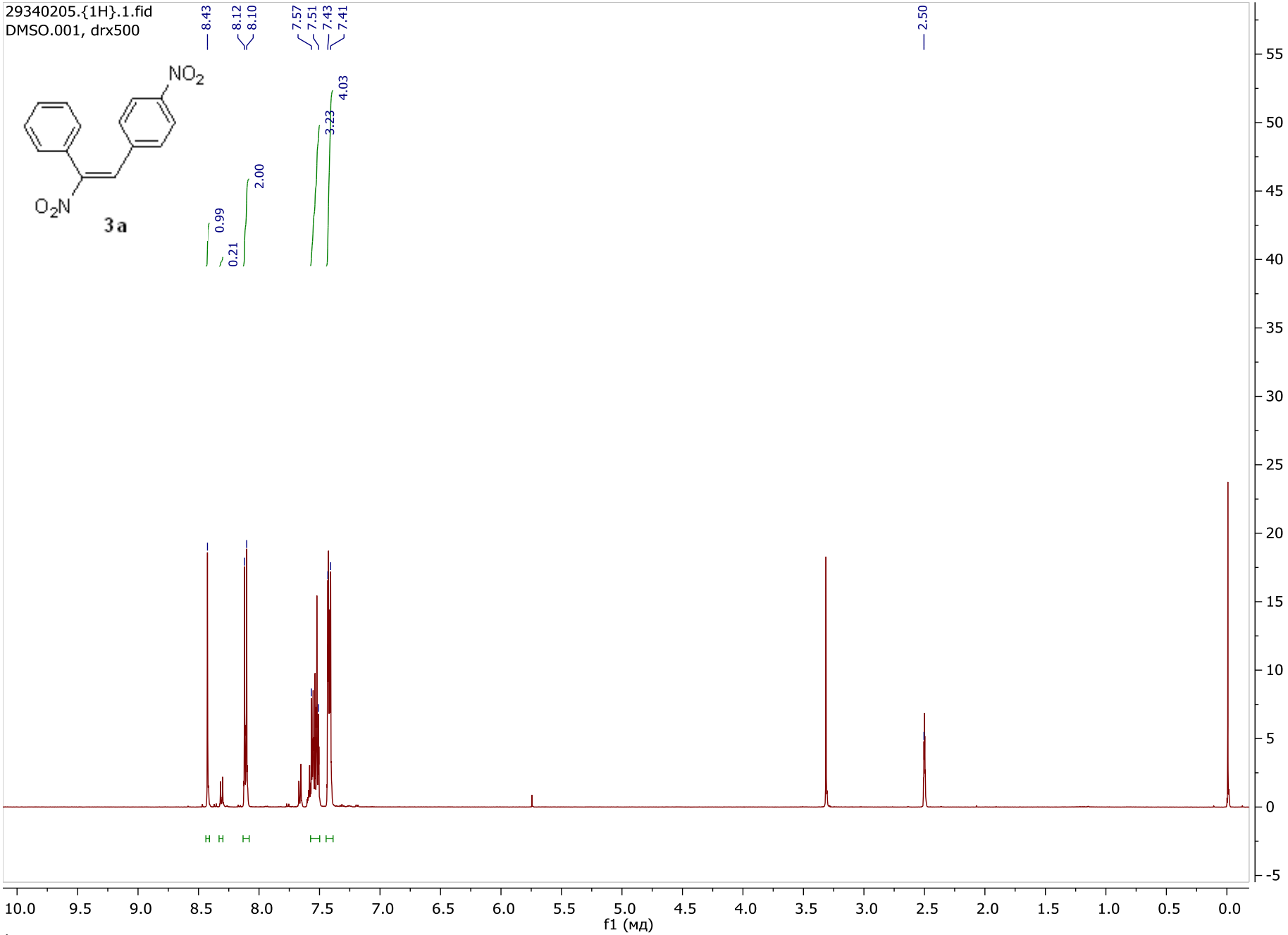

29310033.{1H}.1.fid
DMSO.001, drx500
8.51
8.30
8.29
7.99
7.98
3.51
3.51
3.00
1.97
2.00
1.00
Me
N
NO2
1a
f1 (мд)


SCR631.{1H}.1.fid
/BROD SCR631
8.51
8.49
8.29
8.27
8.16
8.13
7.76
7.73
7.71
3.48
3.02
2.06
1.00
1.03
1.03
Me
N
NO2
1b
f1 (мд)

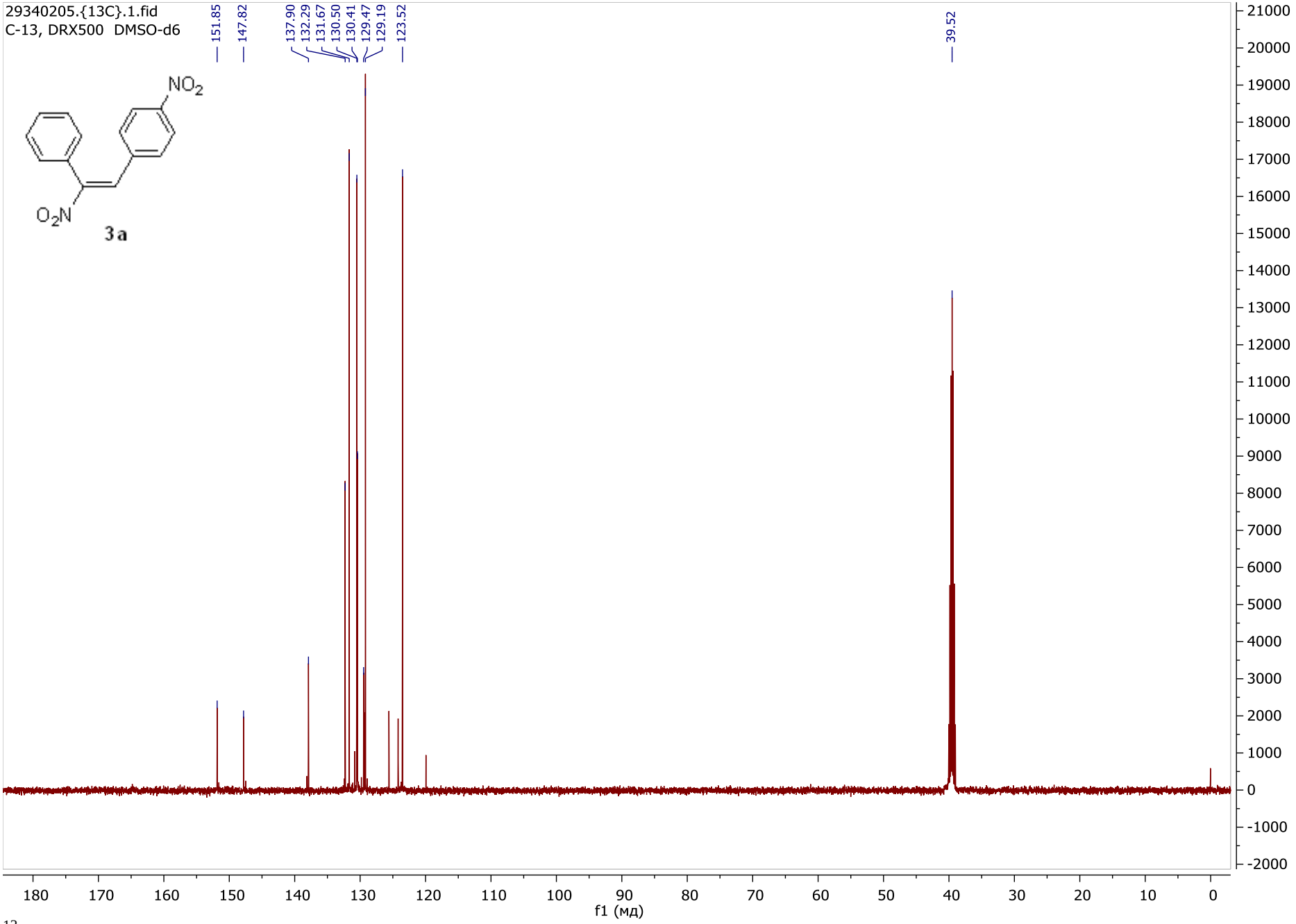

SCR673.{1H}.1.fid
/BROD SCR673
8.57
8.03
8.00
7.96
7.94
7.80
7.78
7.75
7.71
7.69
7.66
3.47
3.03
1.00
1.01
1.04
1.04
1.05
Me
N
NO2
1c
f1 (мд)


SCR577.{1H}.1.fid
/BROD SCR577
8.33
8.33
8.18
8.18
8.01
8.00
7.98
7.97
7.44
7.41
3.96
3.42
3.42
3.33
3.23
1.05
0.95
1.07
1.10
Me
N
NO2
OMe
1d
3000
2500
2000
1500
1000
500
0
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 (мд)

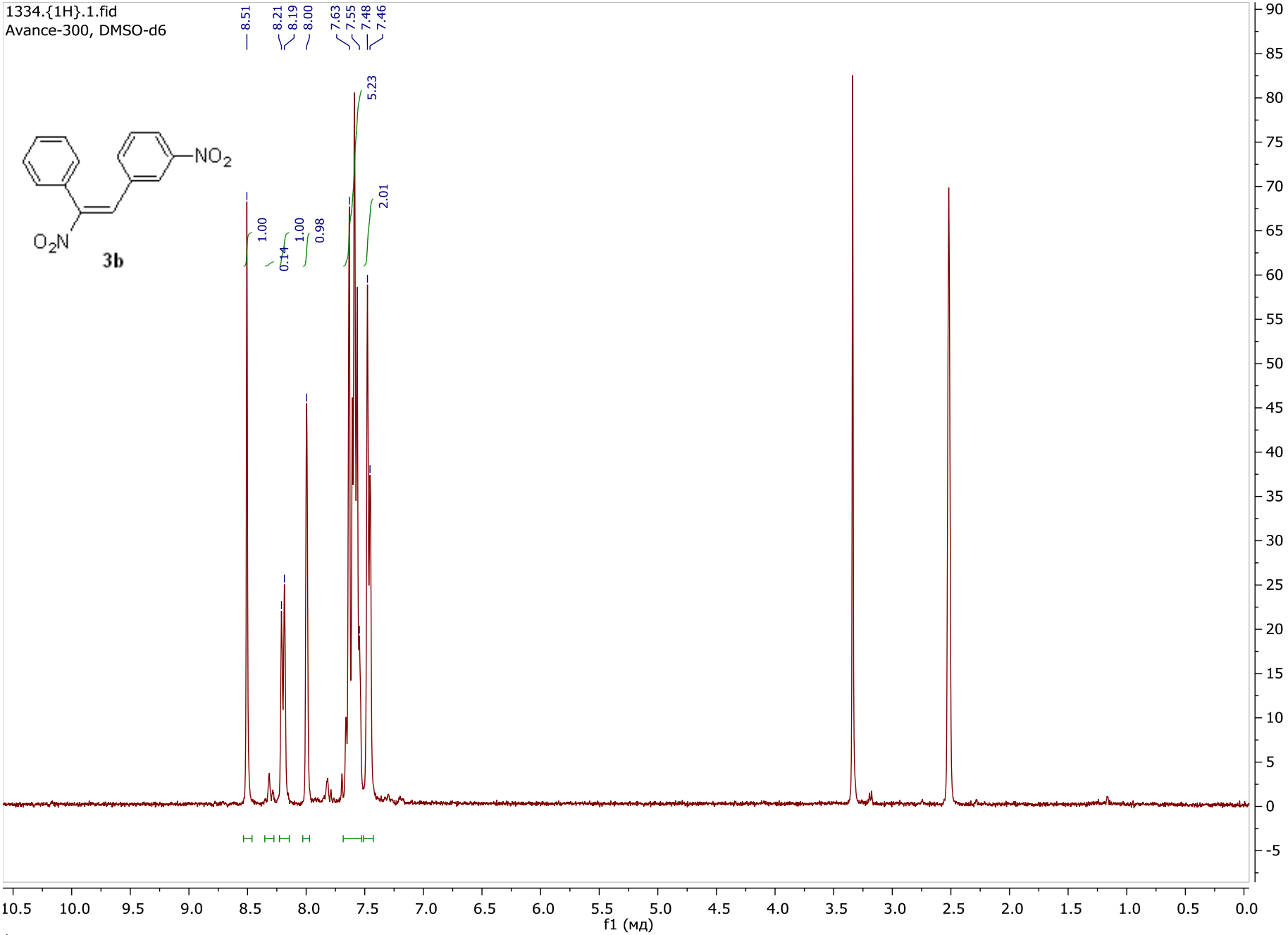

159.71
153.43
135.00
133.24
126.45
123.87
114.57
56.96
47.27
Me
N
NO2
OMe
1d
f1 (мд)



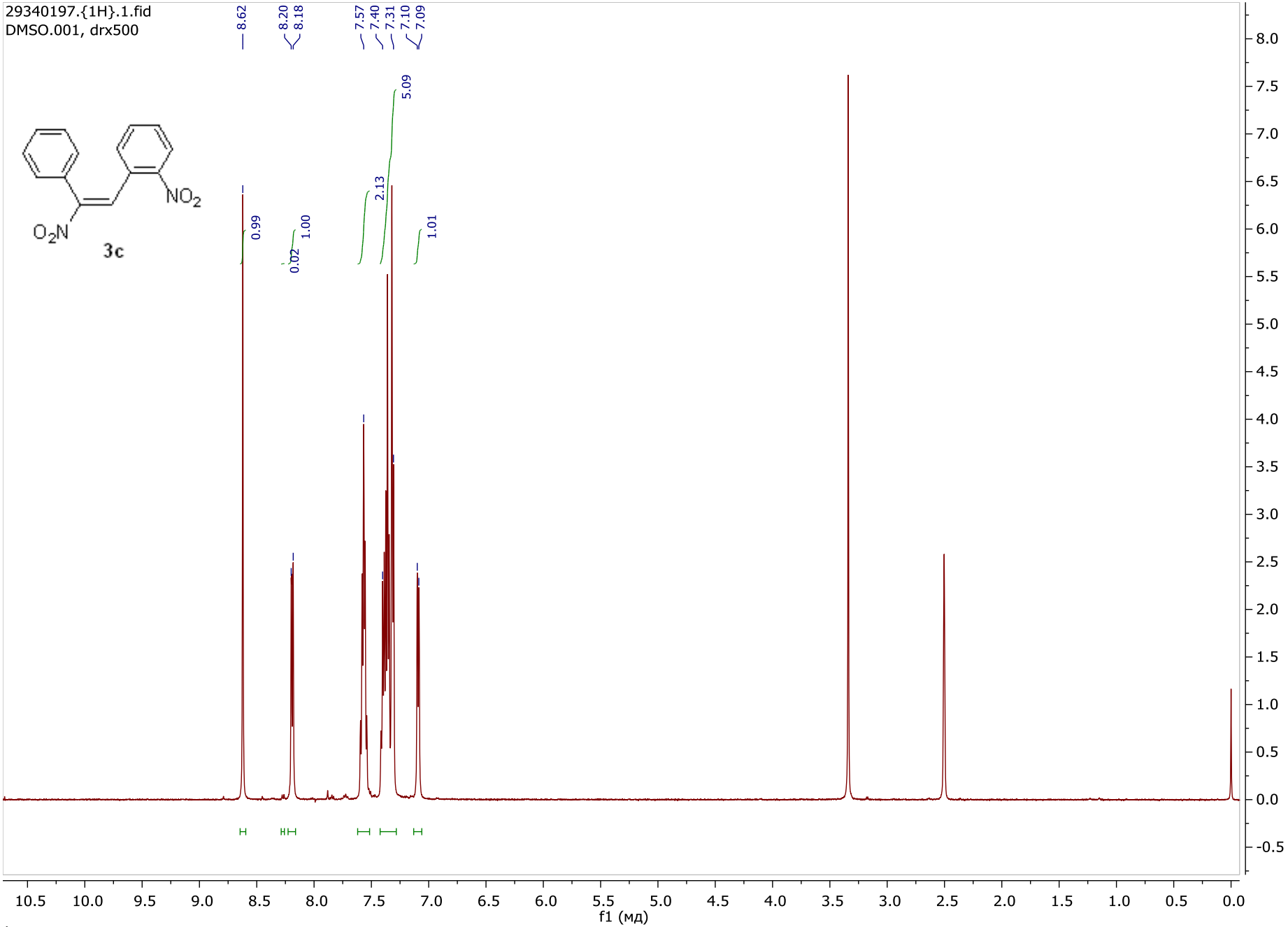
[1]H NMR spectrum of (E)-2-(4-Nitrophenyl)-1-phenyl-1-nitroethylene (**3a**) with admixture of 9% (Z)-isomer.



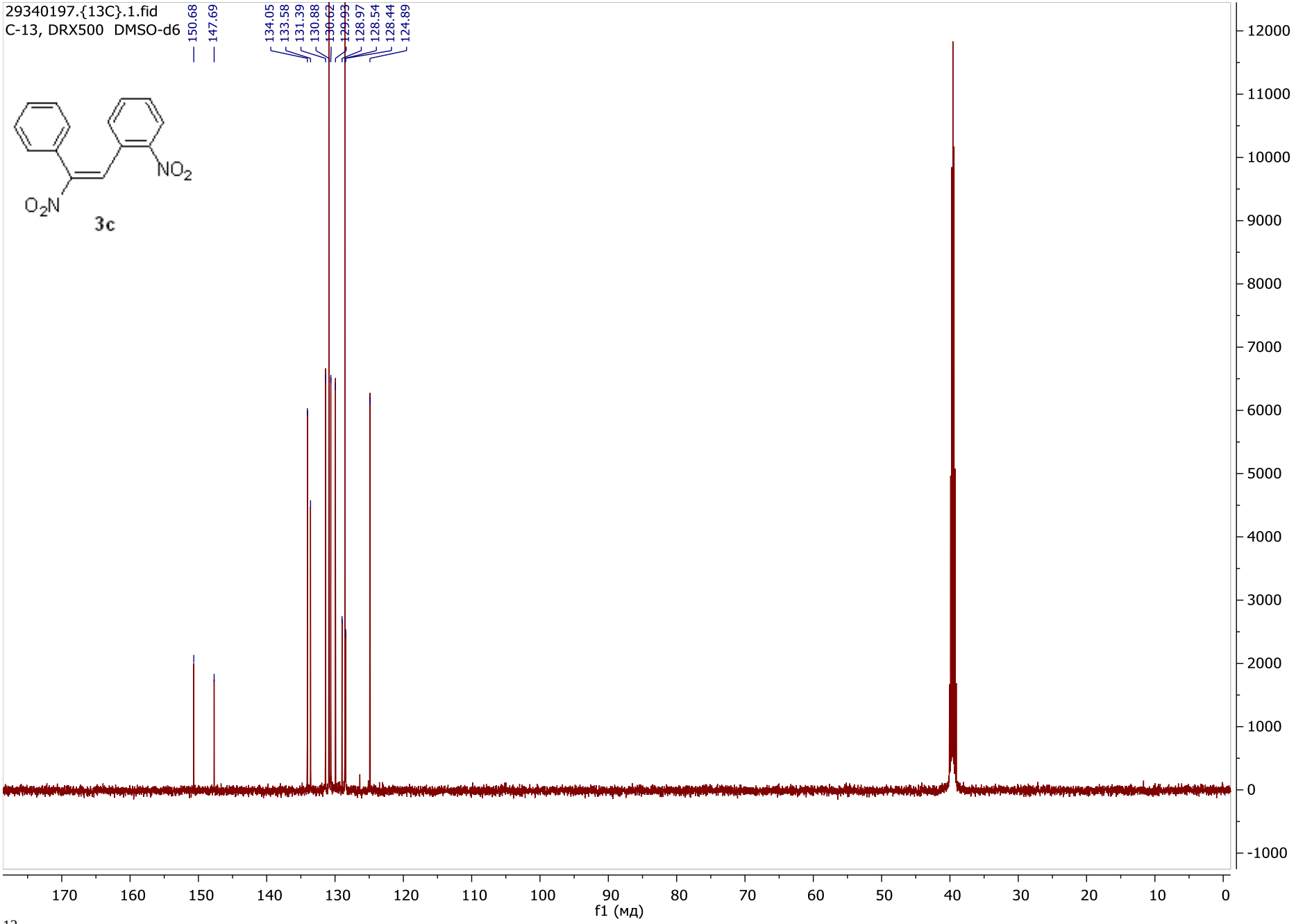
^{13}C NMR spectrum of (E)-2-(4-Nitrophenyl)-1-phenyl-1-nitroethylene (**3a**) with admixture of (Z)-isomer.



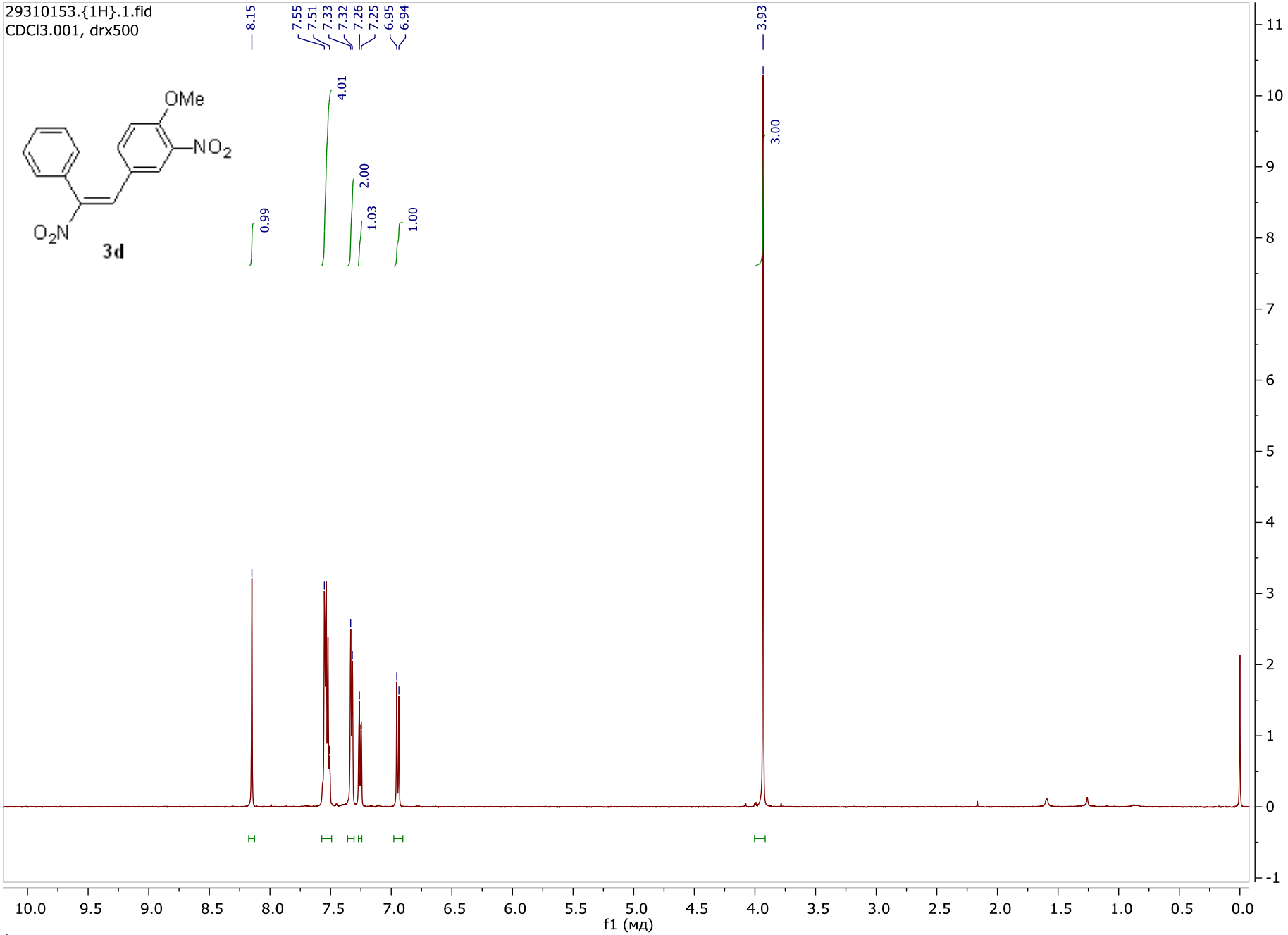
^{1}H NMR spectrum of (E)-2-(3-nitrophenyl)-1-phenyl-1-nitroethylene (**3b**) with admixture of 12% (Z)-isomer.



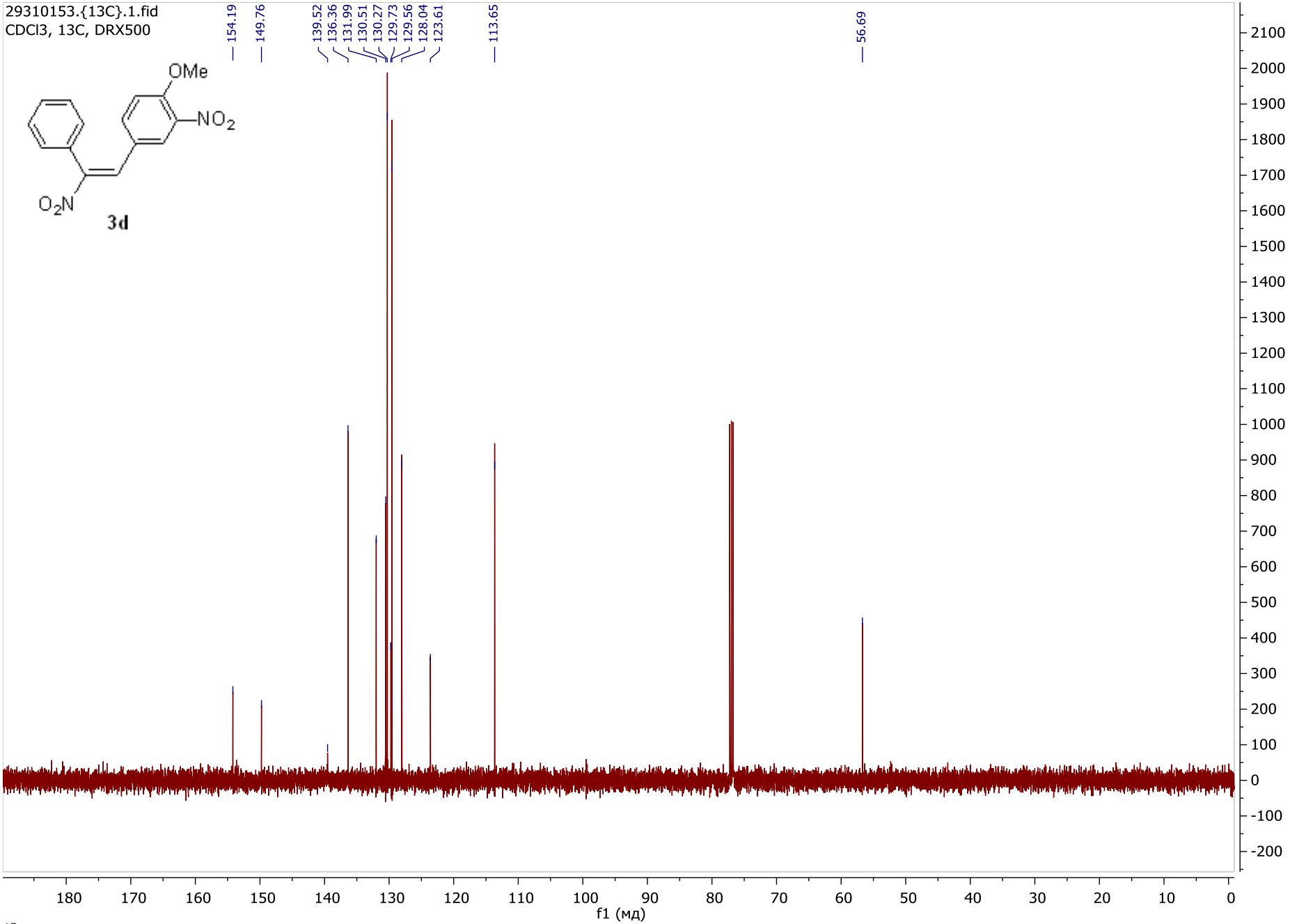
^{1}H NMR spectrum of (E)-2-(2-nitrophenyl)-1-phenyl-1-nitroethylene (**3c**) with admixture of 1% (Z)-isomer.



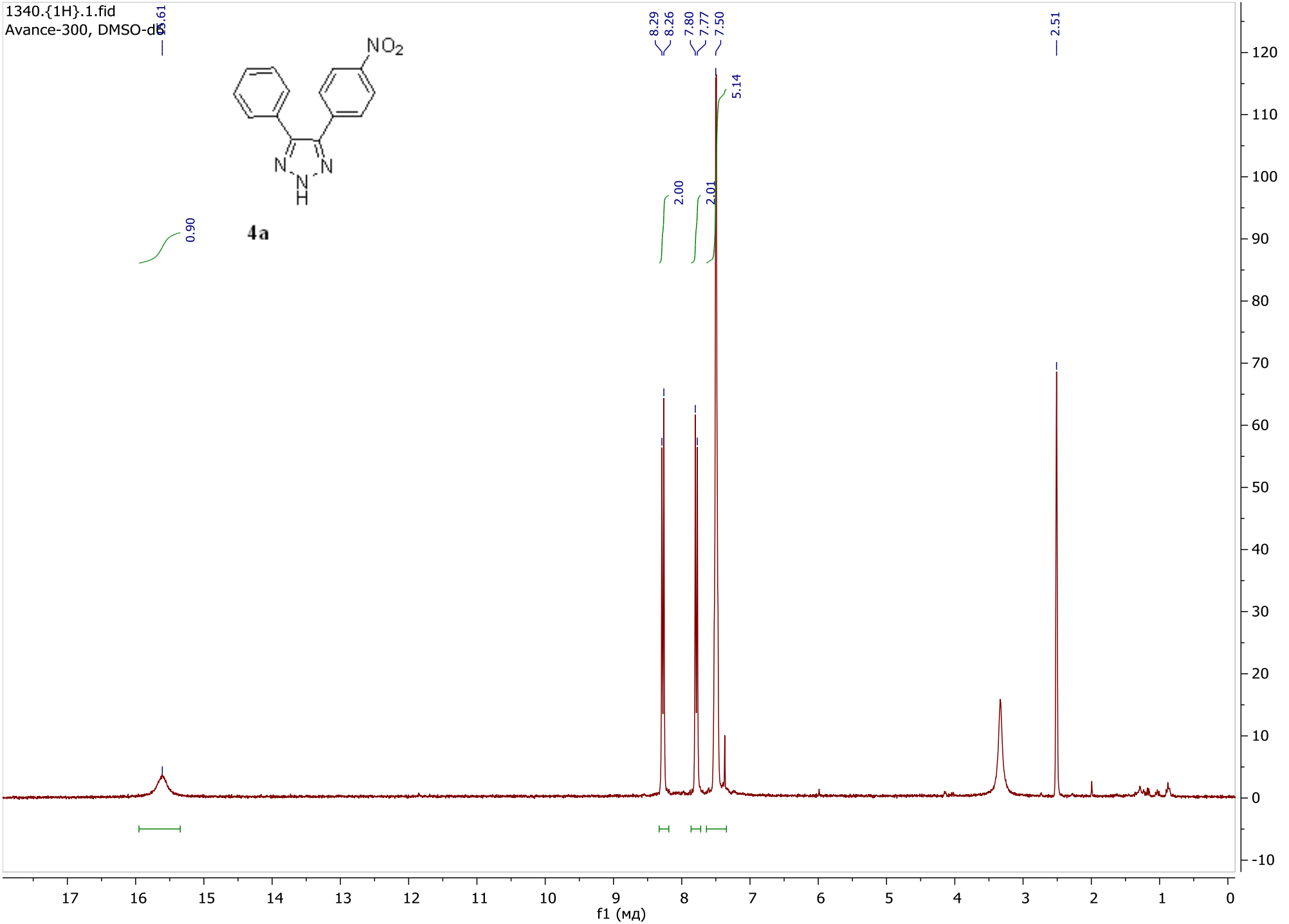
^{13}C NMR spectrum of (E)-2-(2-nitrophenyl)-1-phenyl-1-nitroethylene (**3c**) with admixture of (Z)-isomer.

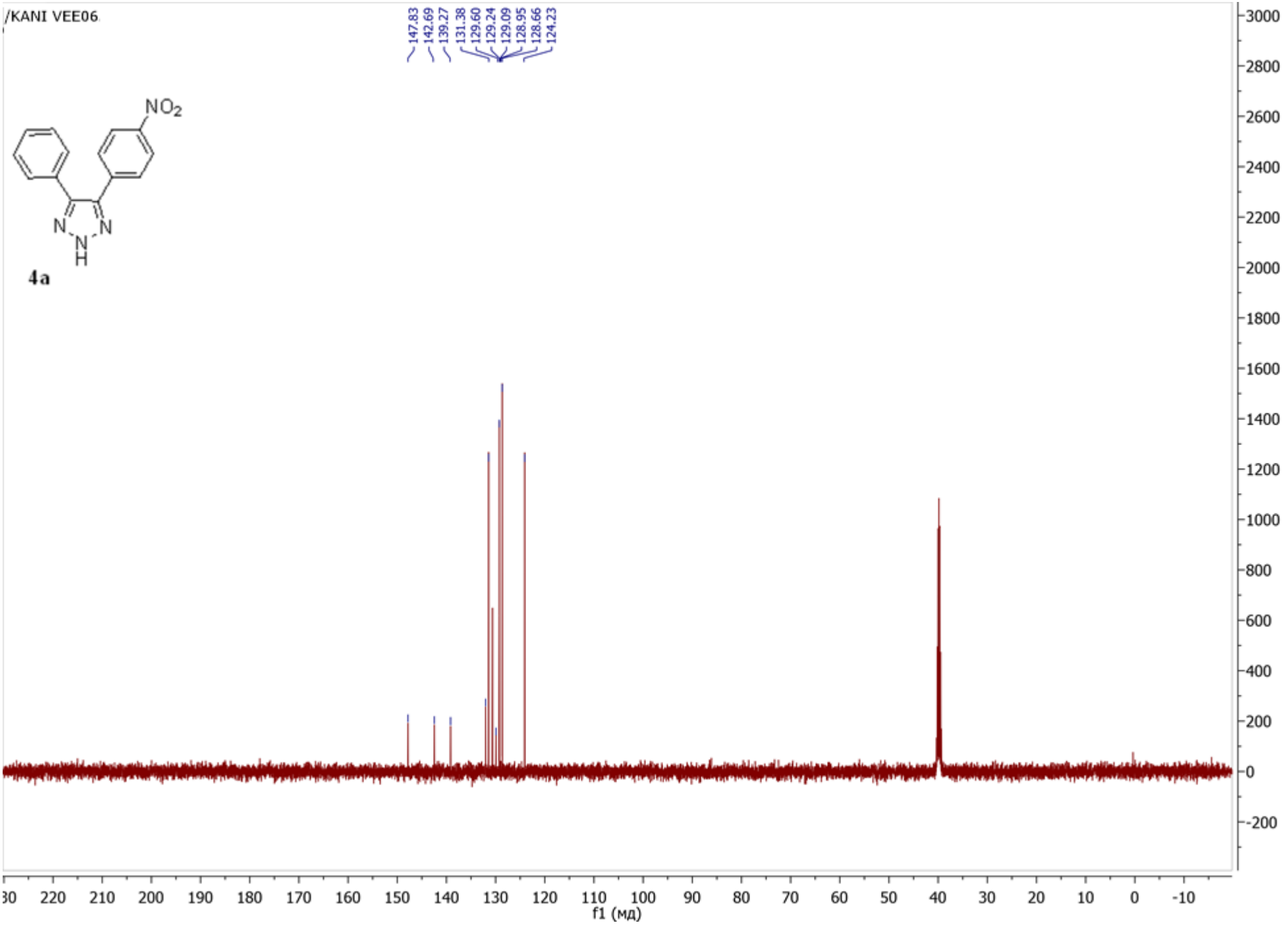


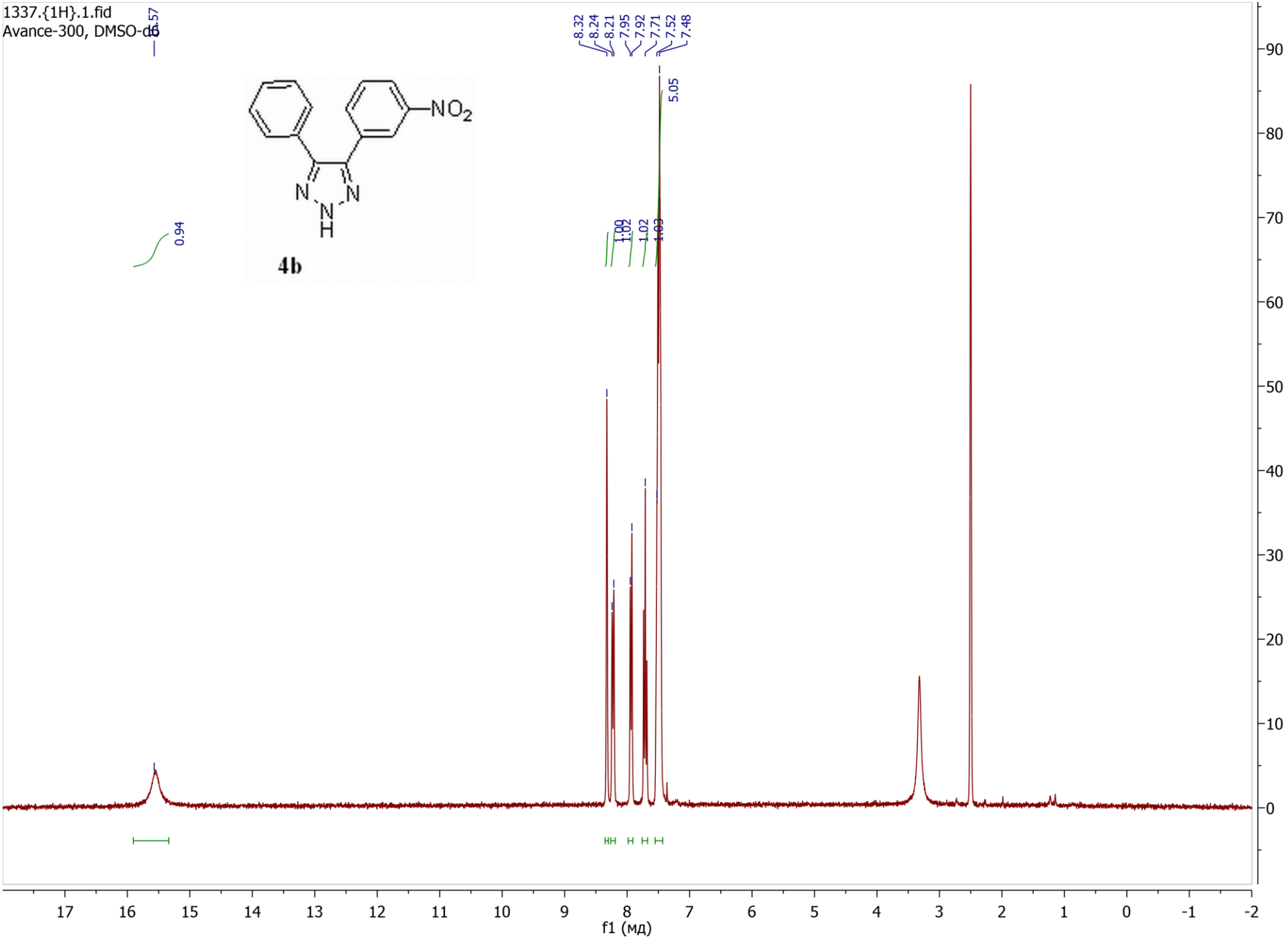
[1]H NMR spectrum of (E)-2-(4-methoxy-3-nitrophenyl)-1-phenyl-1-nitroethylene (**3d**).

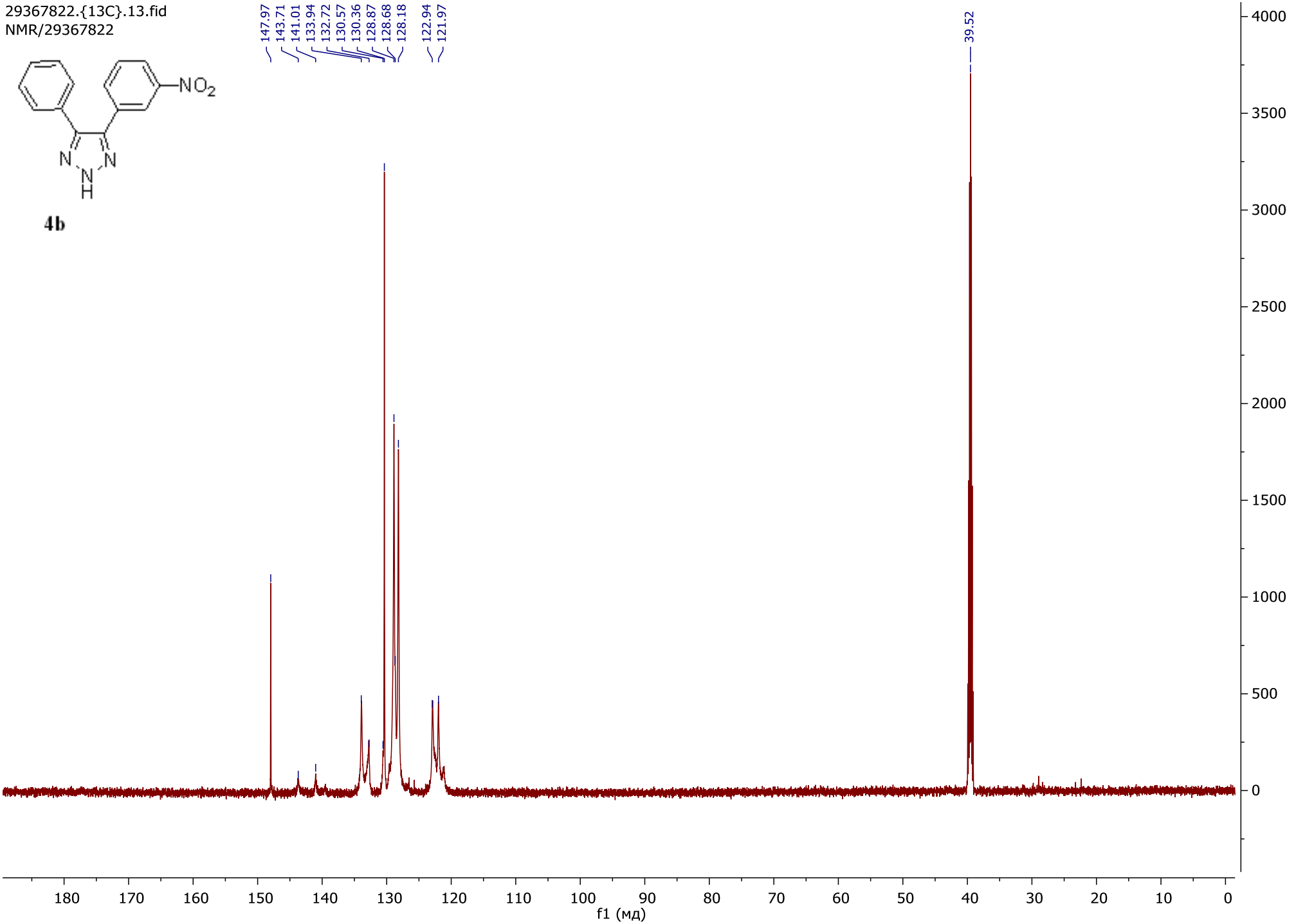


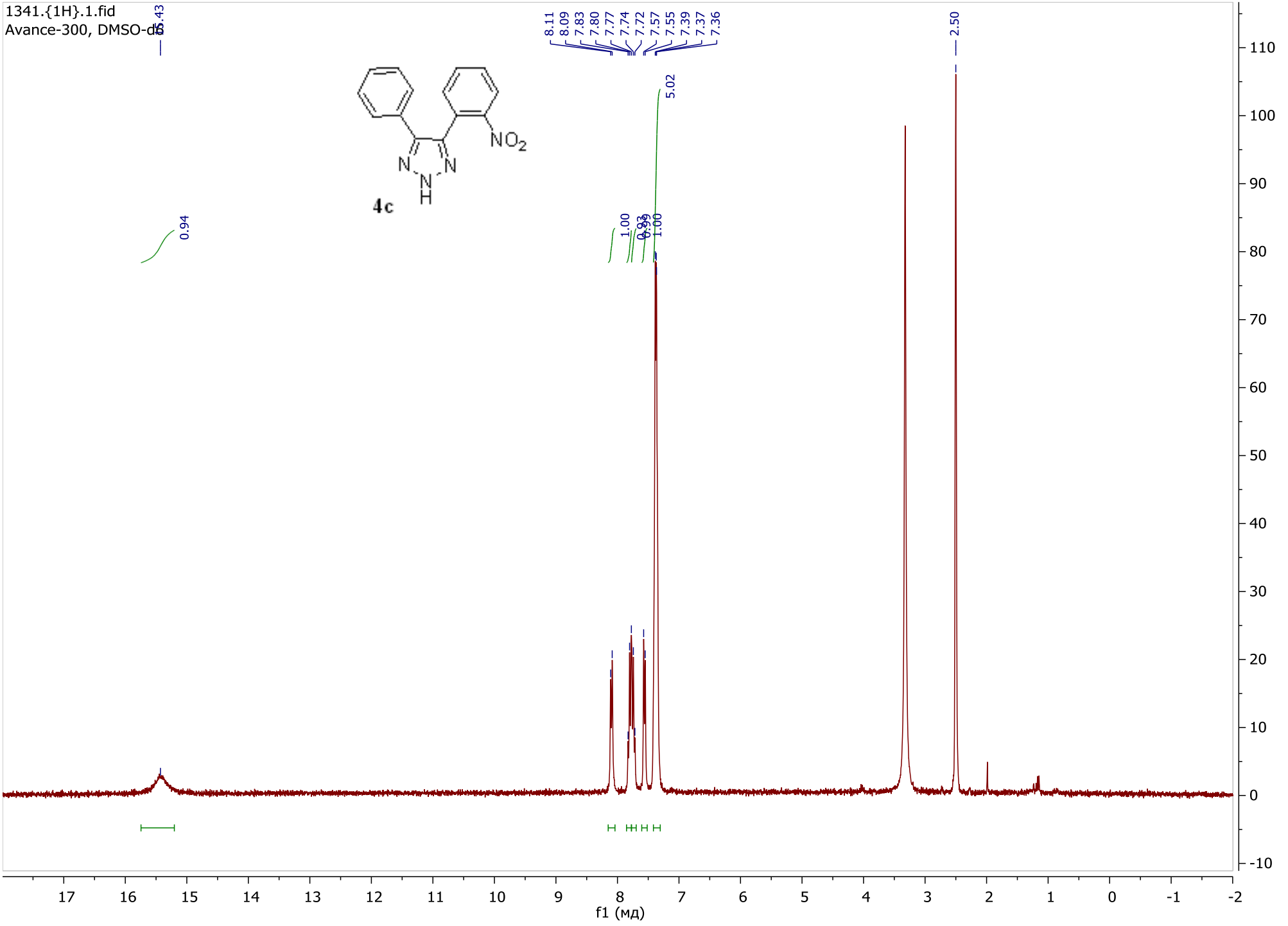
^{13}C NMR spectrum of (E)-2-(4-methoxy-3-nitrophenyl)-1-phenyl-1-nitroethylene (**3d**).

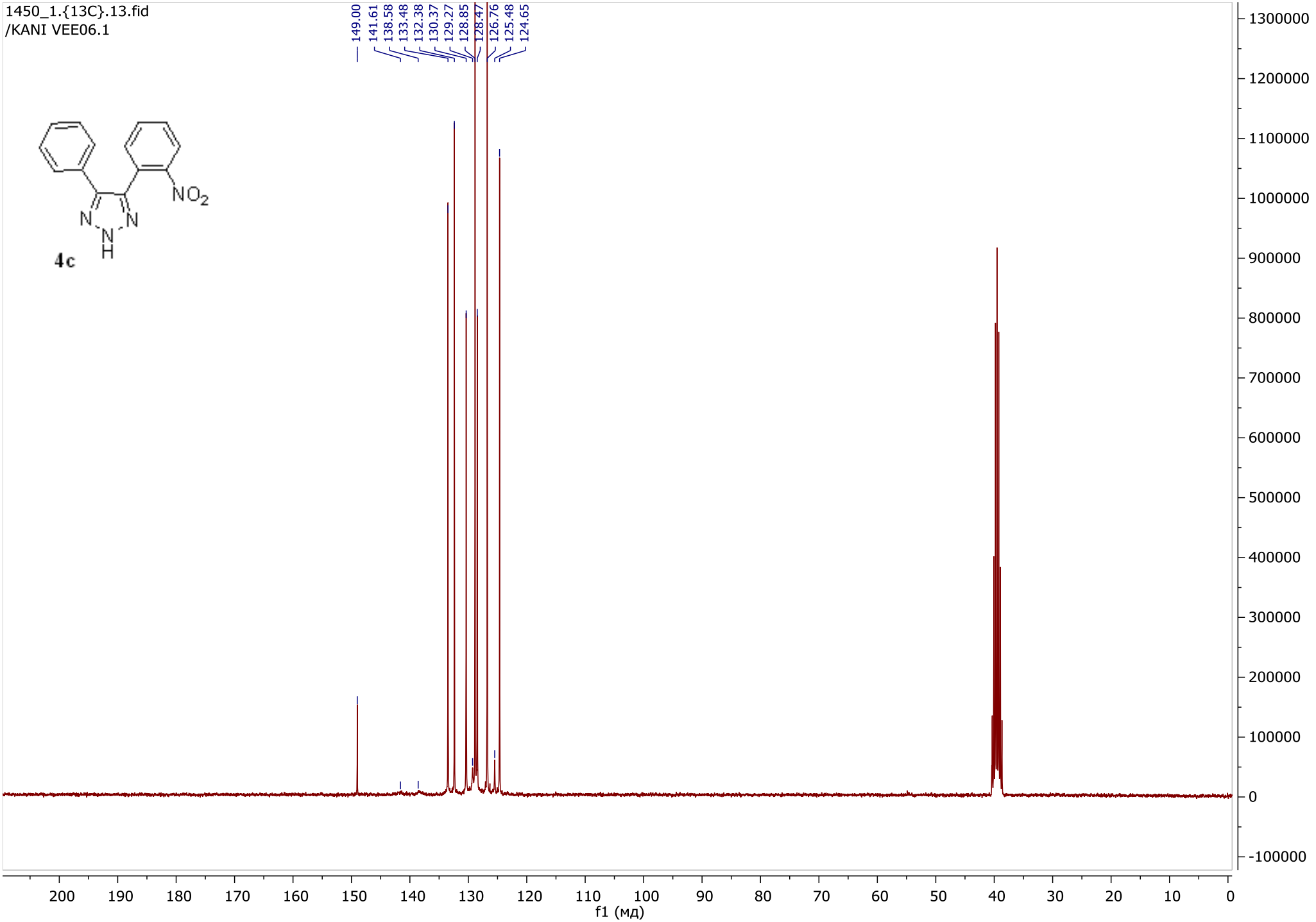

1340.{1H}.1.fid
Avance-300, DMSO-d6
13.61
8.29
8.26
7.80
7.77
7.50
5.14
2.51
2.00
2.01
0.90
NO2
N
N
H
4a
f1 (мд)

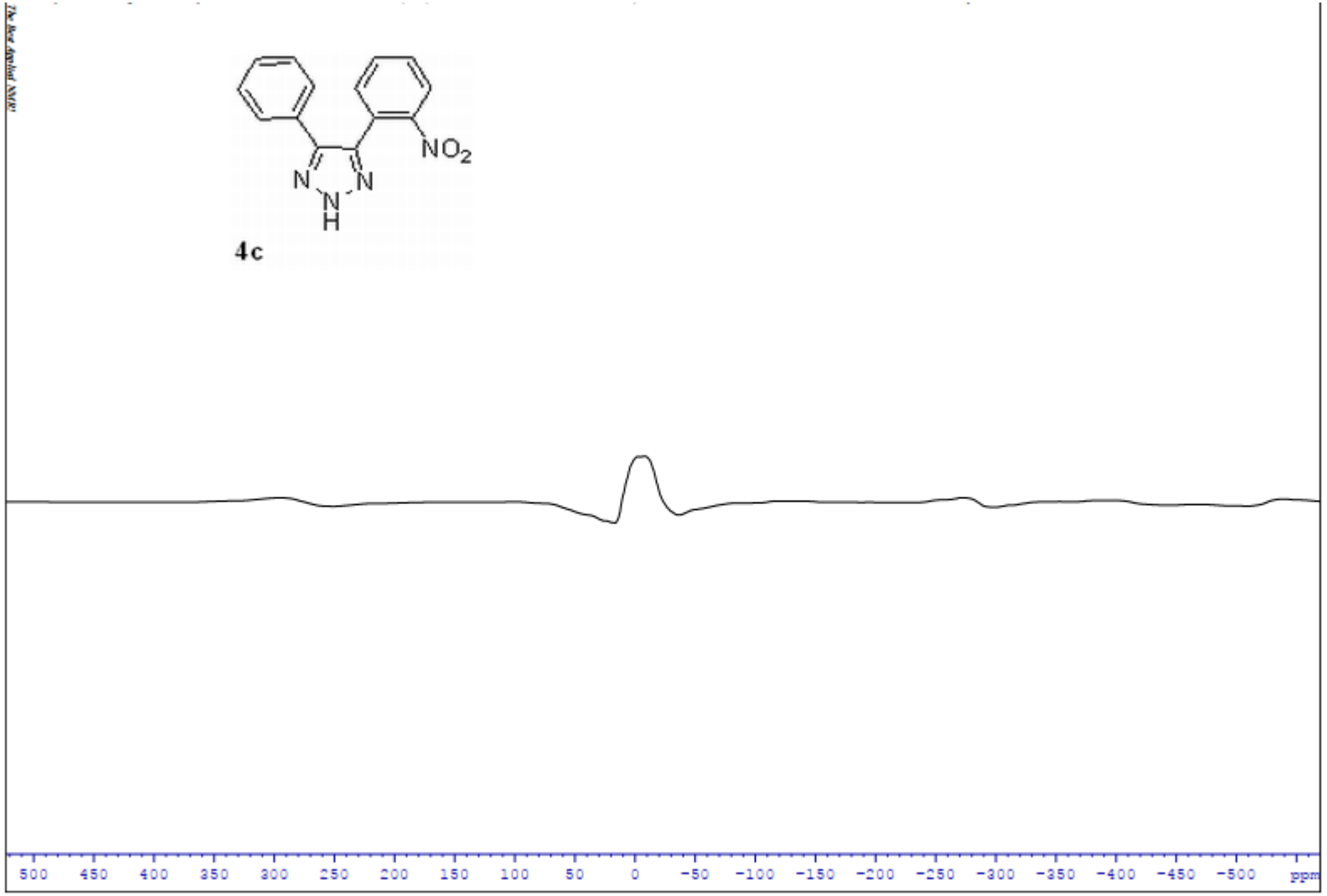

/KANI VEE06
147.83
142.69
139.27
131.38
129.60
129.24
129.09
128.95
128.66
124.23
NO2
N
N
N
H
4a
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (мд)


1337.{1H}.1.fid
Avance-300, DMSO-d6
8.57
8.32
8.24
8.21
7.95
7.92
7.71
7.52
7.48
5.05
1.09
1.02
1.03
0.94
NO2
N
N
H
4b
90
80
70
60
50
40
30
20
10
0
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (мд)

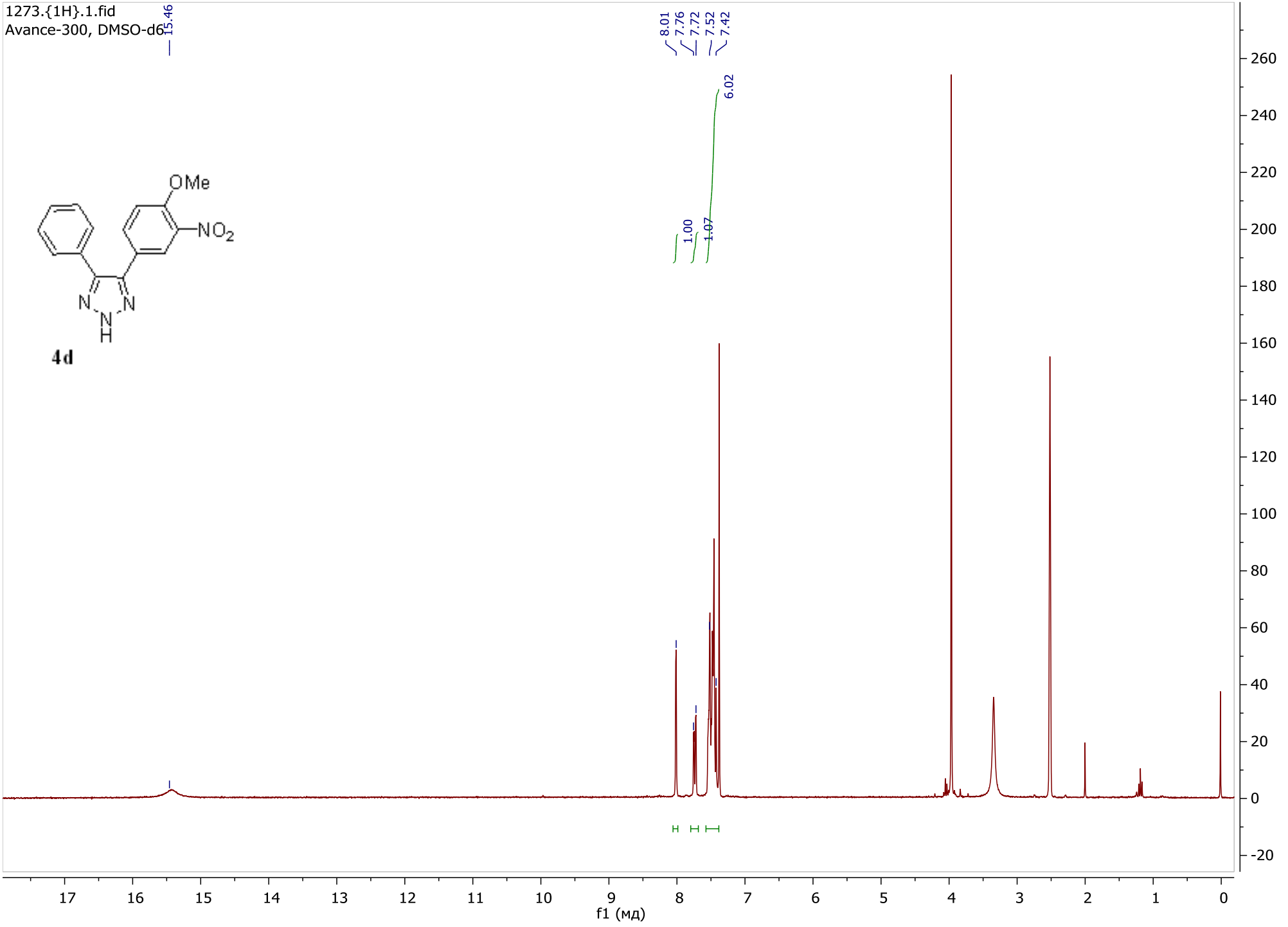

29367822.{13C}.13.fid
NMR/29367822
147.97
143.71
141.01
133.94
132.72
130.57
130.36
128.87
128.68
128.18
122.94
121.97
39.52
NO2
N
N
N
H
4b
4000
3500
3000
2500
2000
1500
1000
500
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

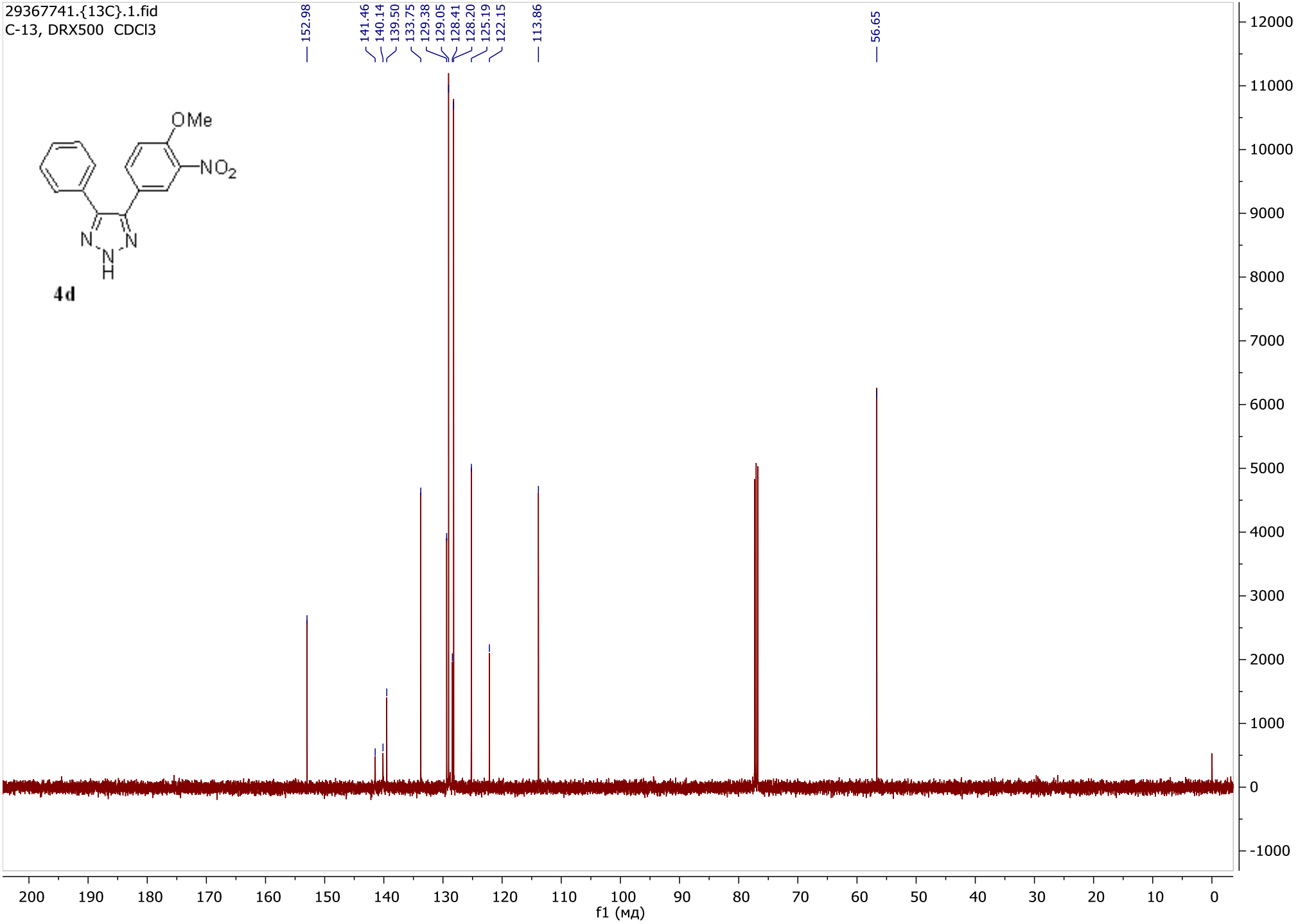

1341.{1H}.1.fid
Avance-300, DMSO-d6
16.43
8.11
8.09
7.83
7.80
7.77
7.74
7.72
7.57
7.55
7.39
7.37
7.36
2.50
5.02
0.94
1.00
0.93
0.99
1.00
NO2
N
N
N
H
4c
f1 (мд)

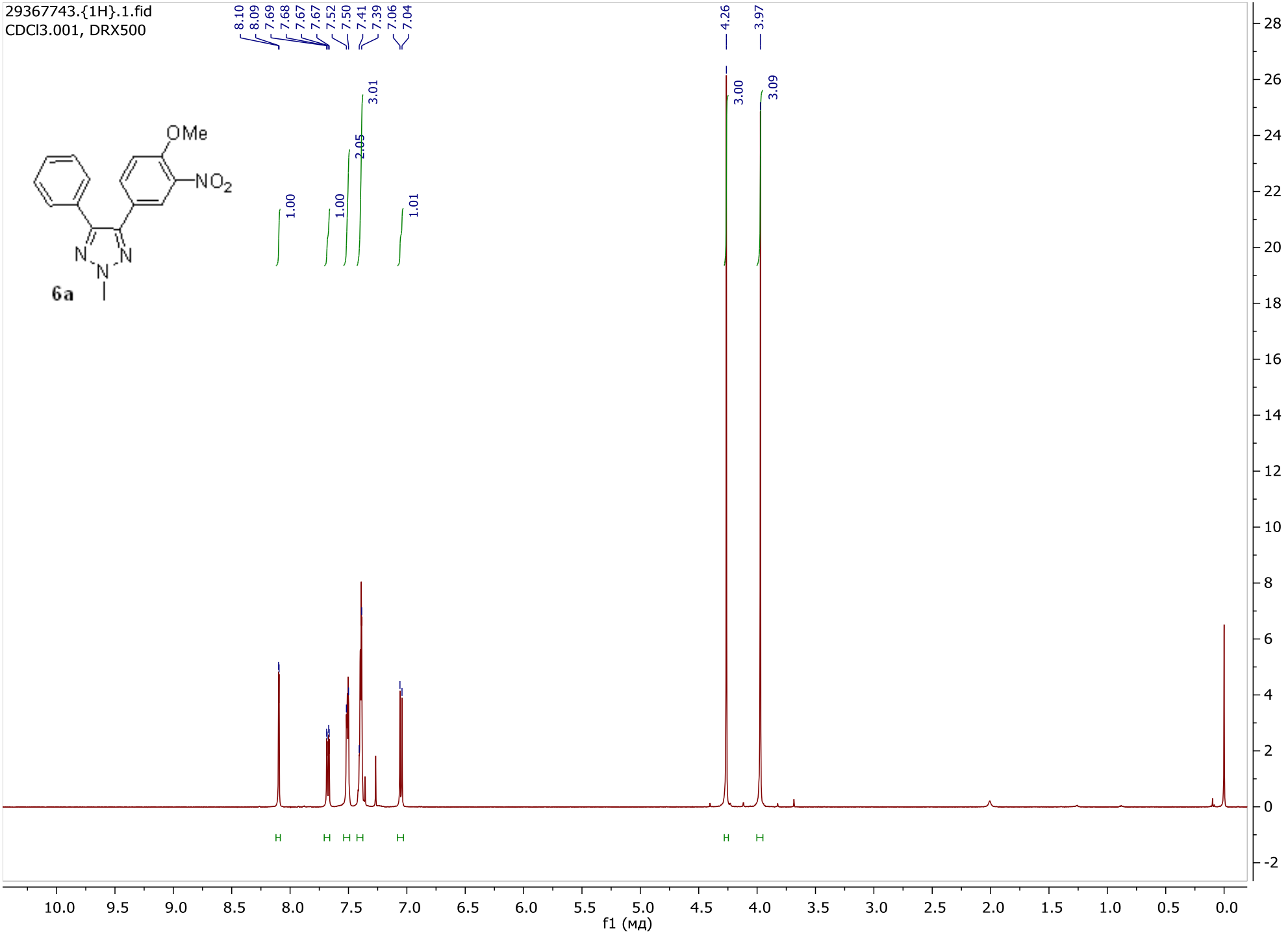

1450_1.{13C}.13.fid
/KANI VEE06.1
149.00
141.61
138.58
133.48
132.38
130.37
129.27
128.85
128.47
126.76
125.48
124.65
NO2
N
N
N
H
4c
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

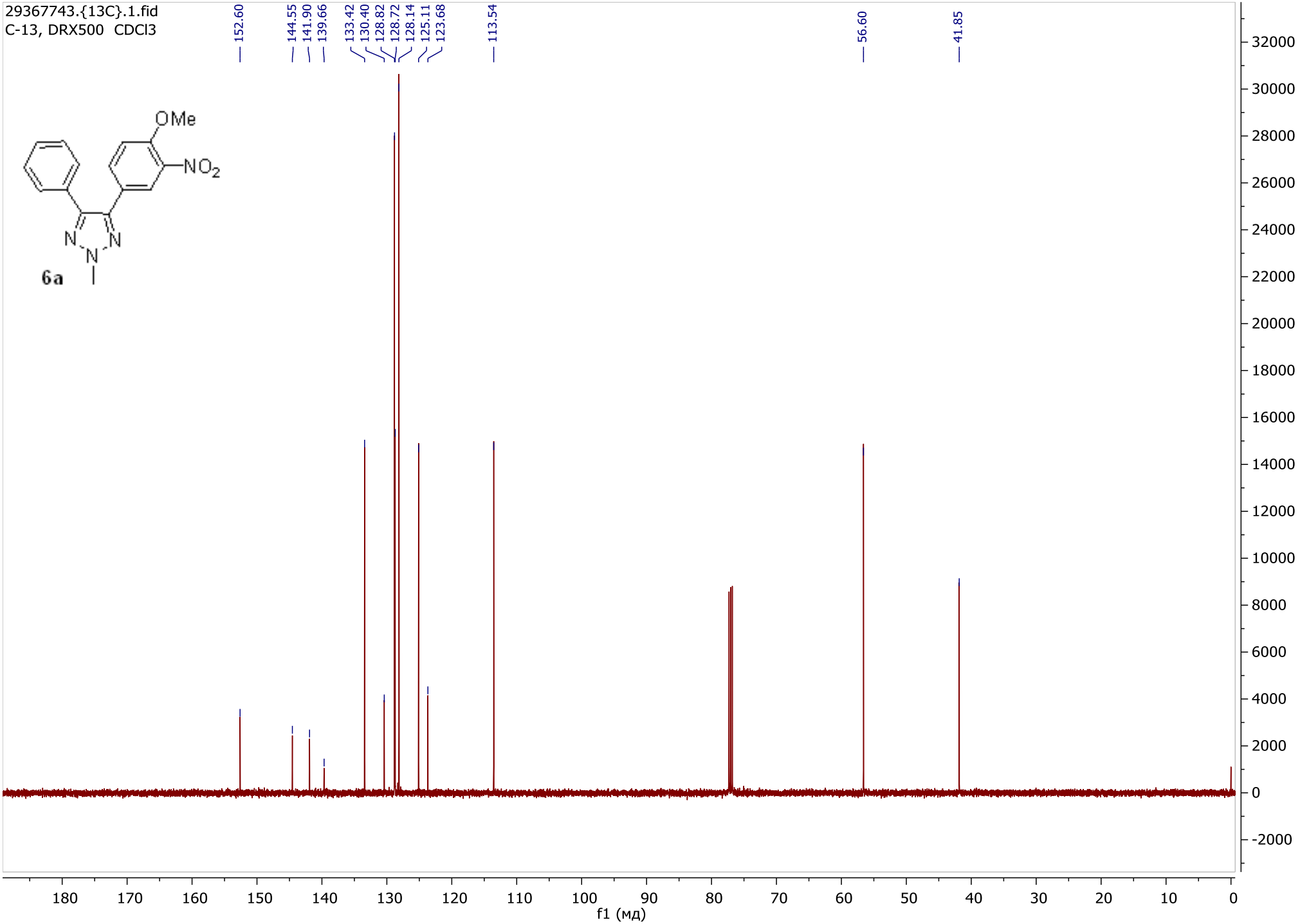


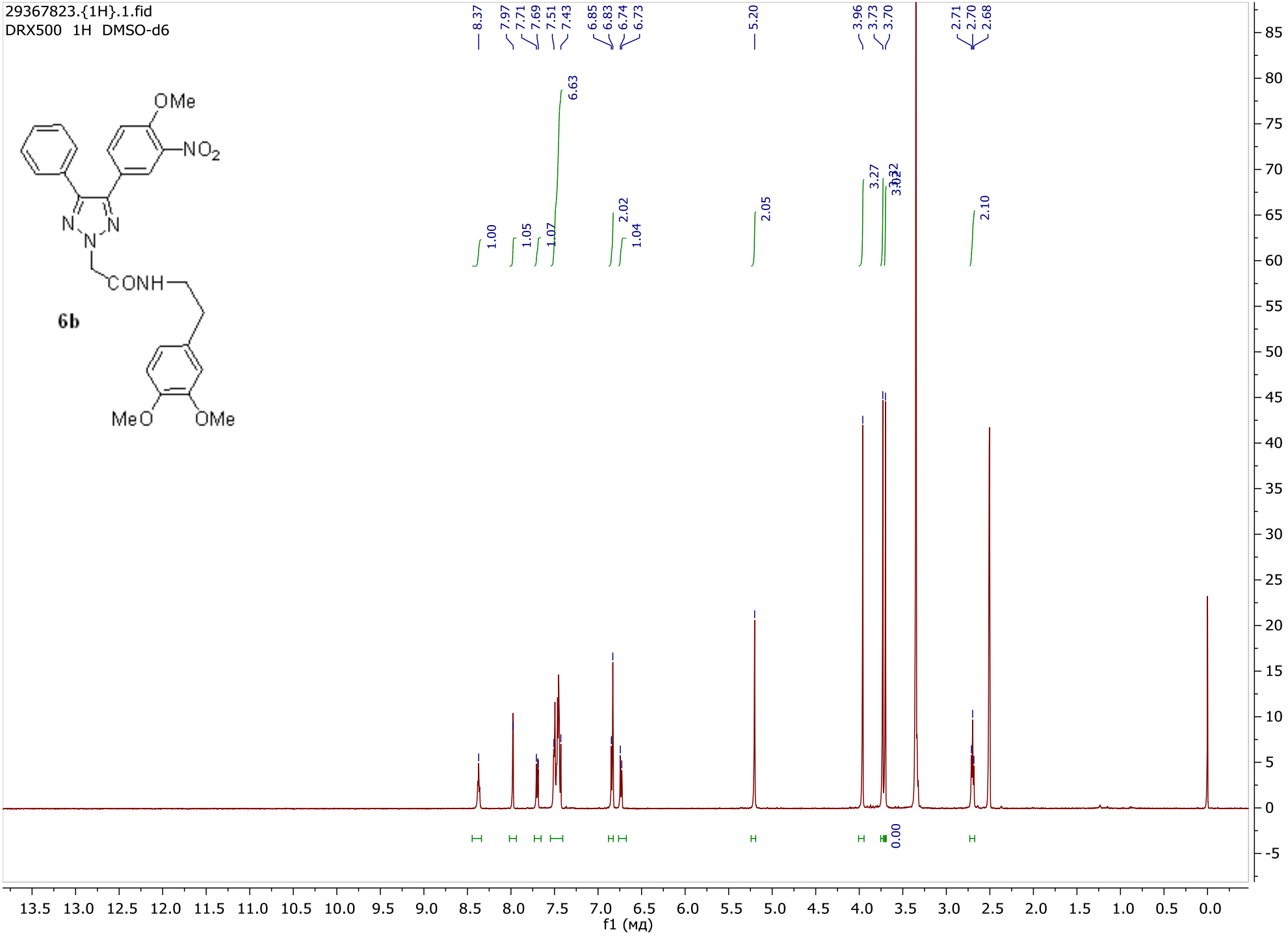
^{14}N NMR spectrum of 4-(2-nitrophenyl)-5-phenyl-1H-1,2,3-triazole (**4c**).)

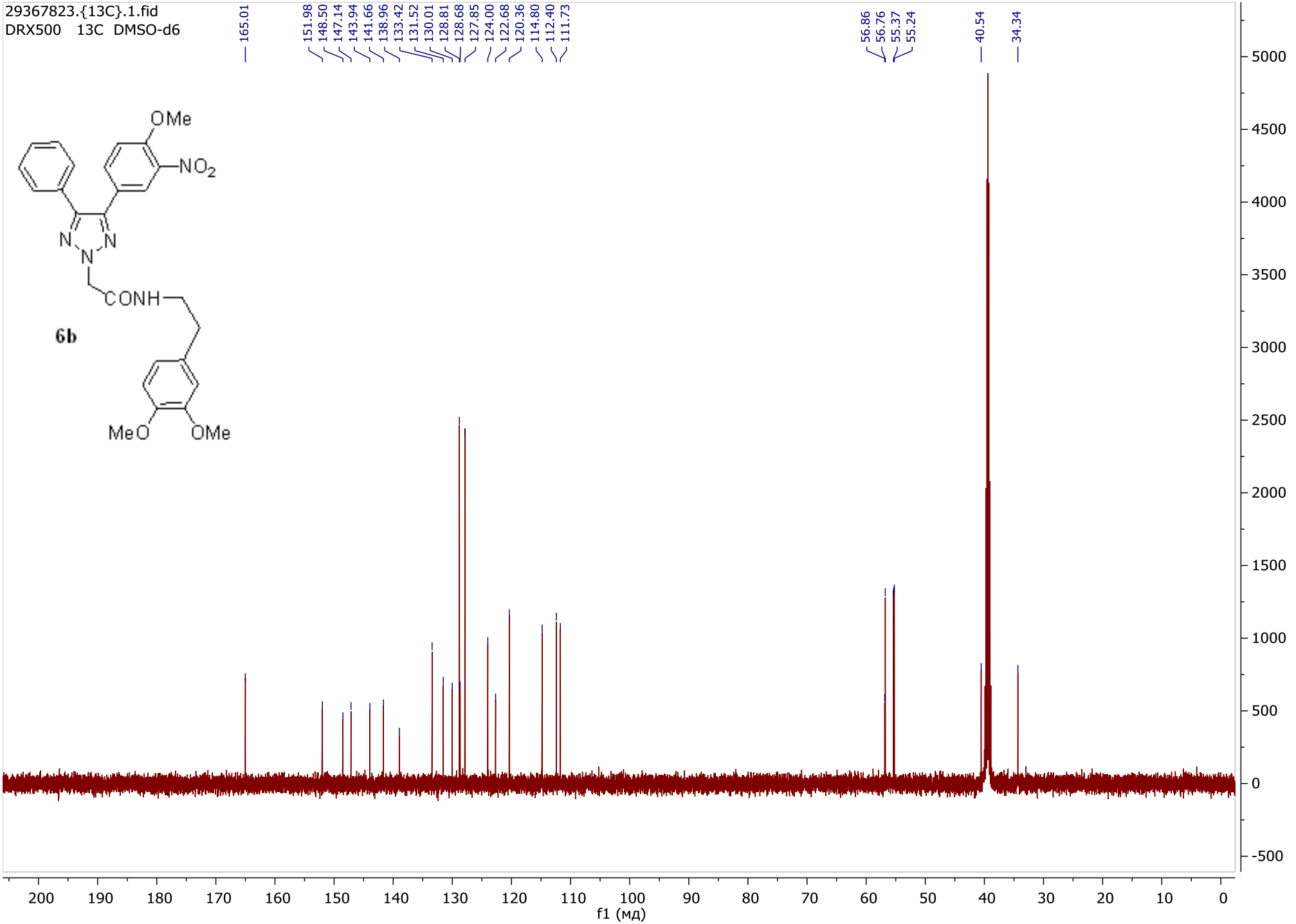

1273.{1H}.1.fid
Avance-300, DMSO-d6
15.46
8.01
7.76
7.72
7.52
7.42
6.02
1.00
1.07
OMe
NO2
N
N
N
H
4d
f1 (мд)

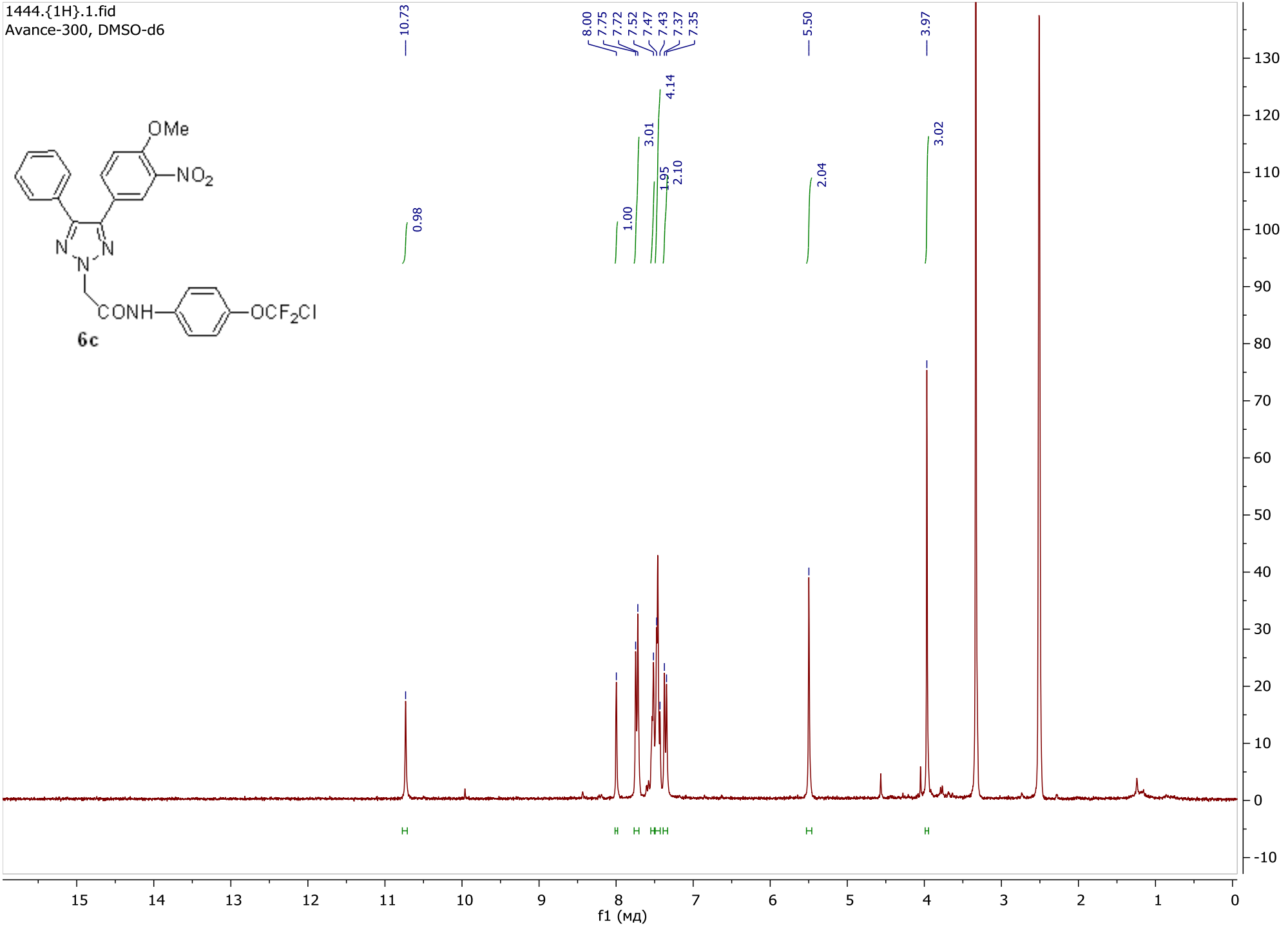

29367741.{13C}.1.fid
C-13, DRX500 CDCl3
152.98
141.46
140.14
139.50
133.75
129.38
129.05
128.41
128.20
125.19
122.15
113.86
56.65
OMe
NO2
N
N
N
H
4d
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

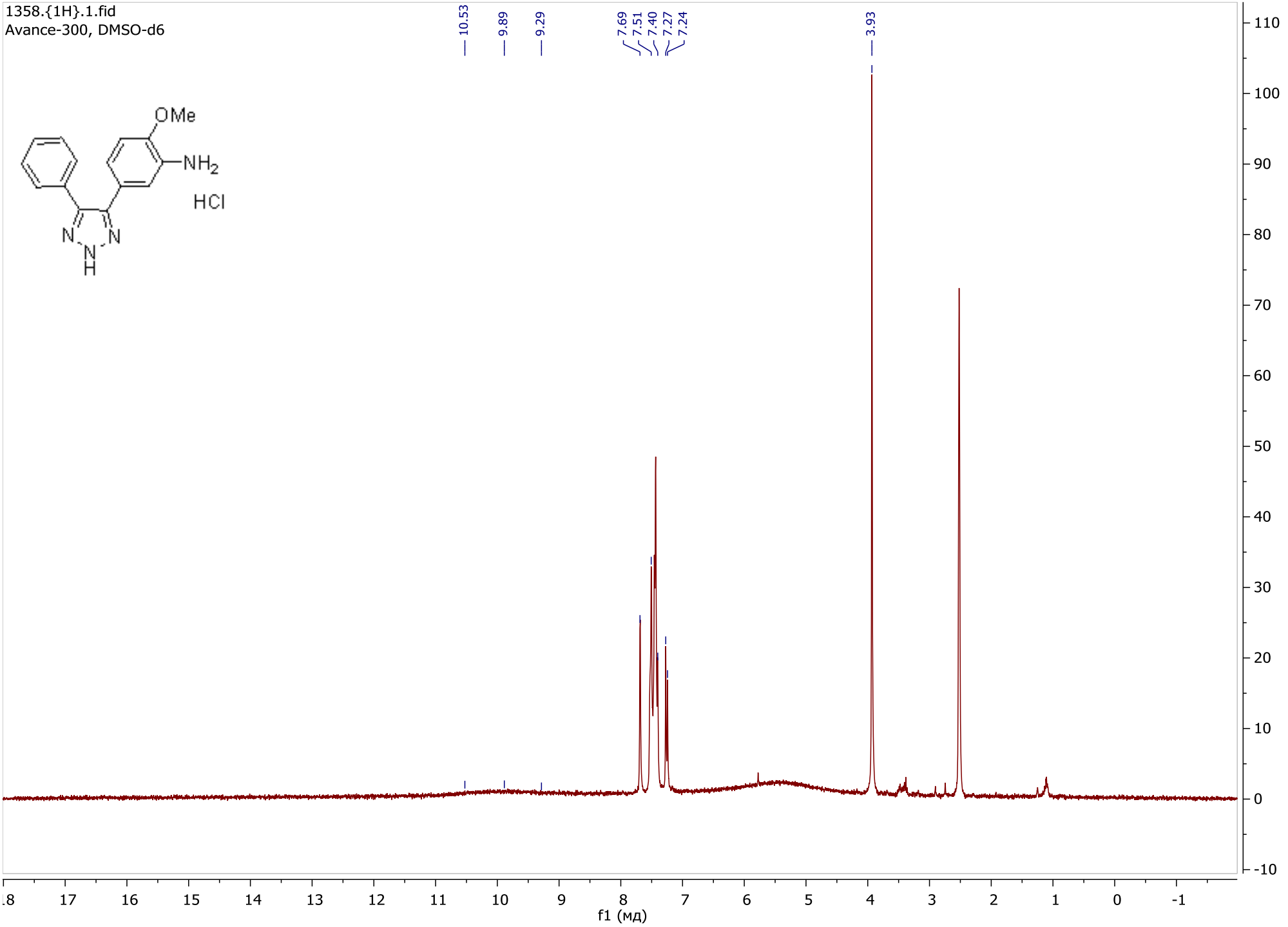

29367743.{1H}.1.fid
CDCl3.001, DRX500
8.10
8.09
7.69
7.68
7.67
7.67
7.52
7.50
7.41
7.39
7.06
7.04
4.26
3.97
3.01
2.05
1.00
1.00
1.01
3.00
3.09
OMe
NO2
N
N
N
6a
f1 (мд)

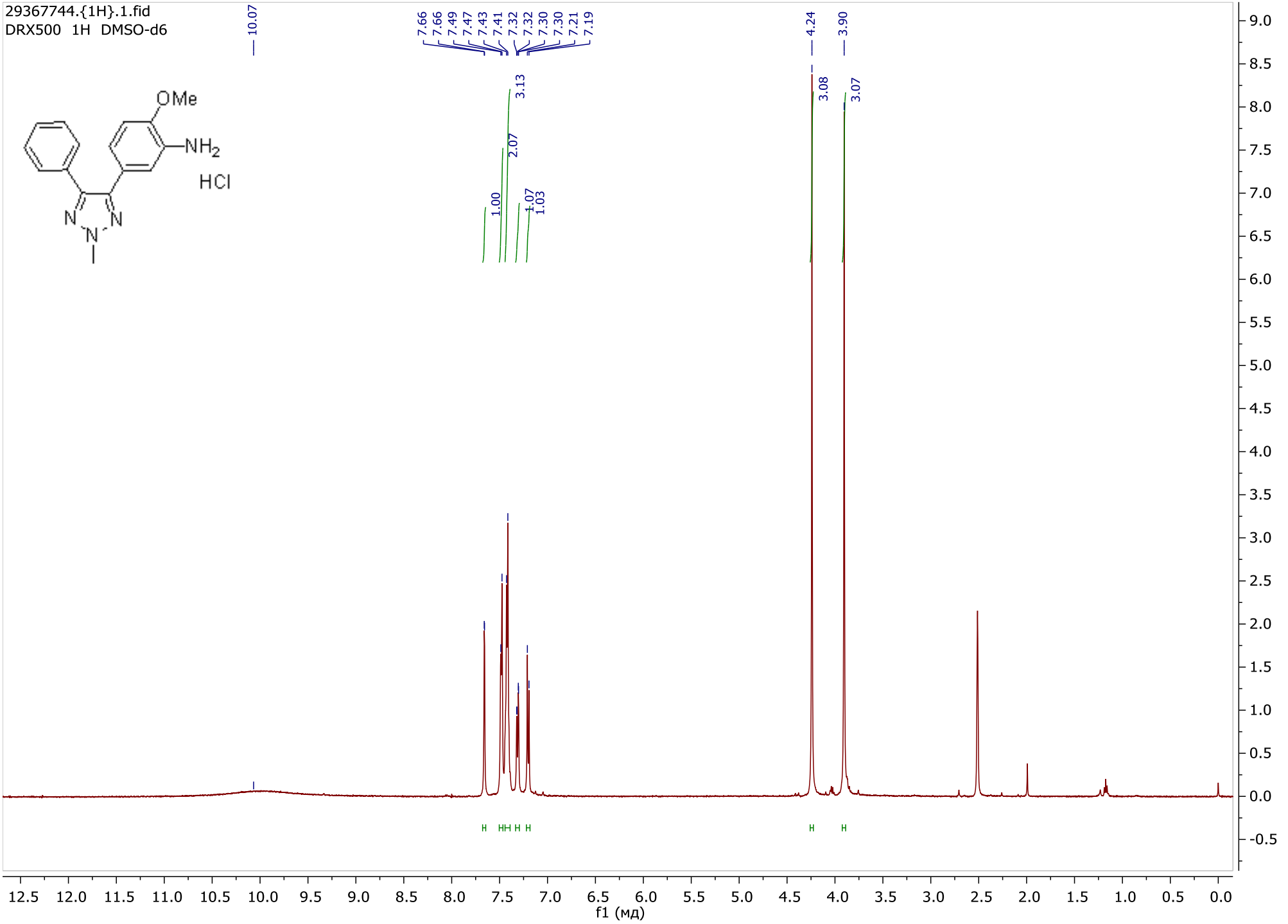

29367743.{13C}.1.fid
C-13, DRX500 CDCl3
152.60
144.55
141.90
139.66
133.42
130.40
128.82
128.72
128.14
125.11
123.68
113.54
56.60
41.85
OMe
NO2
N
N
N
6a
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

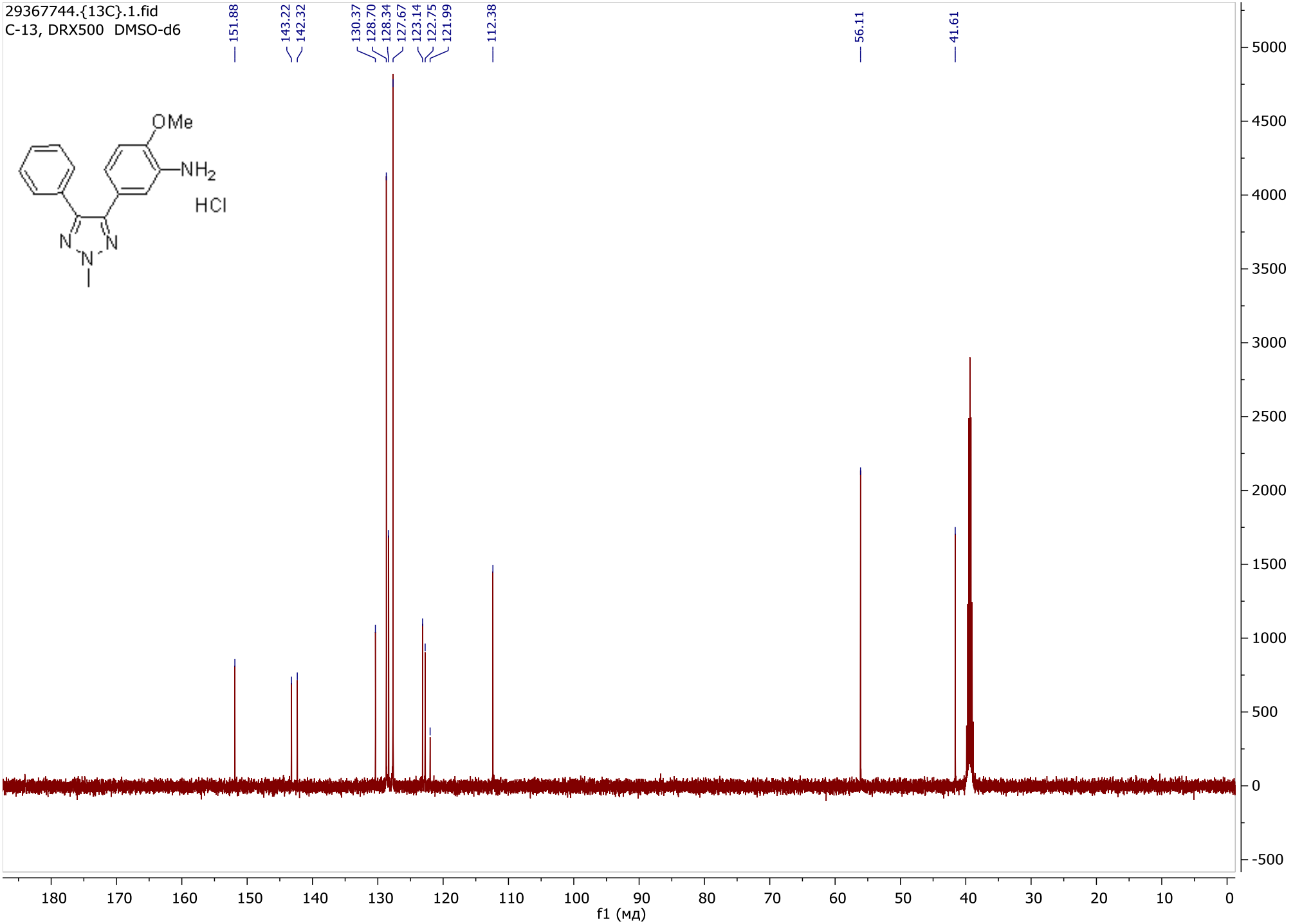

29367823.{1H}.1.fid
DRX500 1H DMSO-d6
8.37
7.97
7.71
7.69
7.51
7.43
6.85
6.83
6.74
6.73
5.20
3.96
3.73
3.70
2.71
2.70
2.68
6.63
3.27
2.05
2.10
2.02
1.00
1.05
1.07
1.04
0.00
OMe
NO2
N
N
N
CONH
6b
MeO
OMe
f1 (мд)


29367823.{13C}.1.fid
DRX500 13C DMSO-d6
165.01
151.98
148.50
147.14
143.94
141.66
138.96
133.42
131.52
130.01
128.81
128.68
127.85
124.00
122.68
120.36
114.80
112.40
111.73
56.86
56.76
55.37
55.24
40.54
34.34
OMe
NO2
N
N
N
CONH
6b
MeO
OMe
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)


1444.{1H}.1.fid
Avance-300, DMSO-d6
10.73
8.00
7.75
7.72
7.52
7.47
7.43
7.37
7.35
5.50
3.97
4.14
3.01
3.02
2.10
1.95
2.04
1.00
0.98
OMe
NO2
N
N
N
CONH
OCF2Cl
6c
f1 (мд)


1358.{1H}.1.fid
Avance-300, DMSO-d6
10.53
9.89
9.29
7.69
7.51
7.40
7.27
7.24
3.93
OMe
NH2
HCl
N
N
N
H
110
100
90
80
70
60
50
40
30
20
10
0
-10
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (мд)


29367744.{1H}.1.fid
DRX500 1H DMSO-d6
10.07
7.66
7.66
7.49
7.47
7.43
7.41
7.32
7.32
7.30
7.30
7.21
7.19
4.24
3.90
3.13
2.07
1.00
1.07
1.03
3.08
3.07
OMe
NH2
HCl
N
N
N
f1 (мд)


29367744.{13C}.1.fid
C-13, DRX500 DMSO-d6
151.88
143.22
142.32
130.37
128.70
128.34
127.67
123.14
122.75
121.99
112.38
56.11
41.61
OMe
NH2
HCl
N
N
N
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

X-ray diffraction studies.

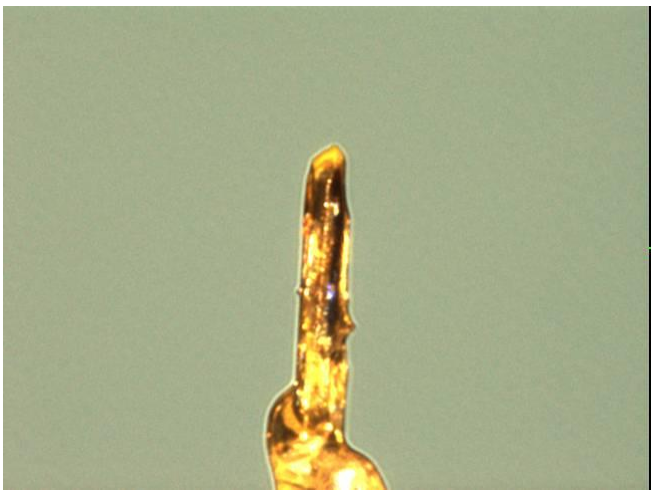
X-ray diffraction data for two polymorph modifications **6a-I** and **6a-II** were collected at temperature of 100K on a Rigaku XtaLAB Synergy-S four-circle diffractometer equipped with a HyPix-6000HE area-detector, using shutterless ω-scan technique and monochromatized Cu K_α-radiation. The intensity data of collected reflections were integrated and analytically corrected for absorption and decay by the CrysAlisPro program.[1] Both structures were solved by direct methods using SHELXT-2014/5[2] and refined by the full-matrix least-squares minimization method on F^2 using SHELXL-2018/3[3] in the OLEX2 program.[4] Crystals of **6a-II** always exhibited the presence of several crystal domains usually without surly identified twin laws. Therefore, the best model of **6a-II** was processed as a non-merohedral twin, in which the 2nd component was rotated by 180° around the axis [0.00 0.00 1.00] (direct space); minor unidentified crystals domains were ignored. Although positions of all hydrogen atoms in **6a-I** and most hydrogen atoms in **6a-II** were found from the electron density-difference map, all hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}(H)=1.5U_{eq}(C)$ for methyl groups and $U_{iso}(H)=1.2U_{eq}(C)$ for aromatic hydrogen atoms. A rotating group model was applied for methyl groups. In model **6a-I**, the C-H distances were refined.

The structures **6a-I** and **6a-II** have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2484340 and 2484341, correspondingly; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/structures/

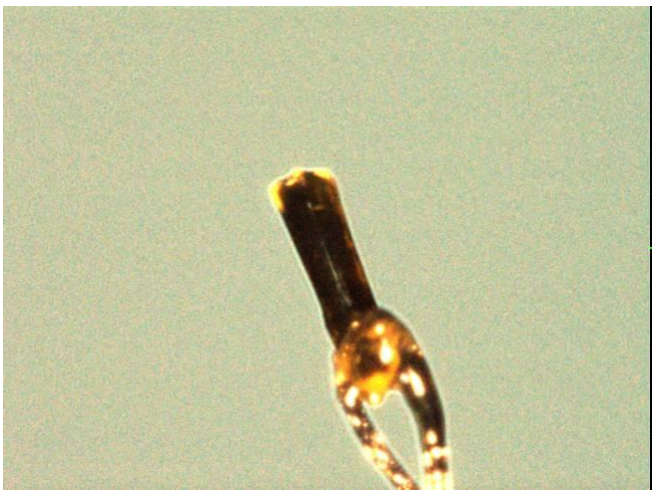
Table 1. Crystal data, data collection and structure refinement details.

Identification code	**6a-I**	**6a-II**
Empirical formula	$C_{16}H_{14}N_4O_3$	$C_{16}H_{14}N_4O_3$
Formula weight	310.31	310.31
Temperature, K	99.94(18)	99.95(18)
Wavelength, Å	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a, Å	7.57260(9)	22.4980(6)
b, Å	13.19846(16)	17.1518(4)
c, Å	14.67806(16)	7.6134(2)
β, °	100.8144(11)	96.353(2)
Volume, Å3	1440.97(3)	2919.83(13)
Z	4	8
Density (calculated), g•cm^{-3}	1.430	1.412

Absorption coefficient (μ), mm^{-1}	0.847	0.836
F(000)	648	1296
Crystal size, mm	0.515×0.097×0.084	0.455×0.112×0.069
θ range for data collection, °	4.542 to 79.838	3.247 to 81.935
Index ranges	$-9 \le h \le 9$,	$-28 \le h \le 28$,
	$-16 \le k \le 15$,	$-21 \le k \le 21$,
	$-18 \le l \le 18$	$-9 \le l \le 9$
Reflections		
collected	19806	108004
independent [R_{int}]	3146 [0.0381]	11570 [0.1077]
observed with I>2σ(I)	3018	11509
Completeness to θ_{full} / θ_{max}	1.000 / 0.998	0.999 / 0.986
Max. / min. transmission	1.000 / 0.613	0.954 / 0.794
Data / restraints / parameters	3146 / 0 / 220	11570 / 0 / 421
Goodness-of-fit on F^2	1.050	1.194
R_1 / wR_2 (I>2σ(I))	0.0379 / 0.1061	0.1359 / 0.3110
R_1 / wR_2 (all data)	0.0390 / 0.1074	0.1363 / 0.3112
Largest diff. peak / hole, $\bar{e}$•$Å^{-3}$	0.308 / -0.335	0.695 / -0.573
CCDC deposition number	2484340	2484341



6a-I



6a-II

Figure 1. Photographs of crystals mounted on a loop.

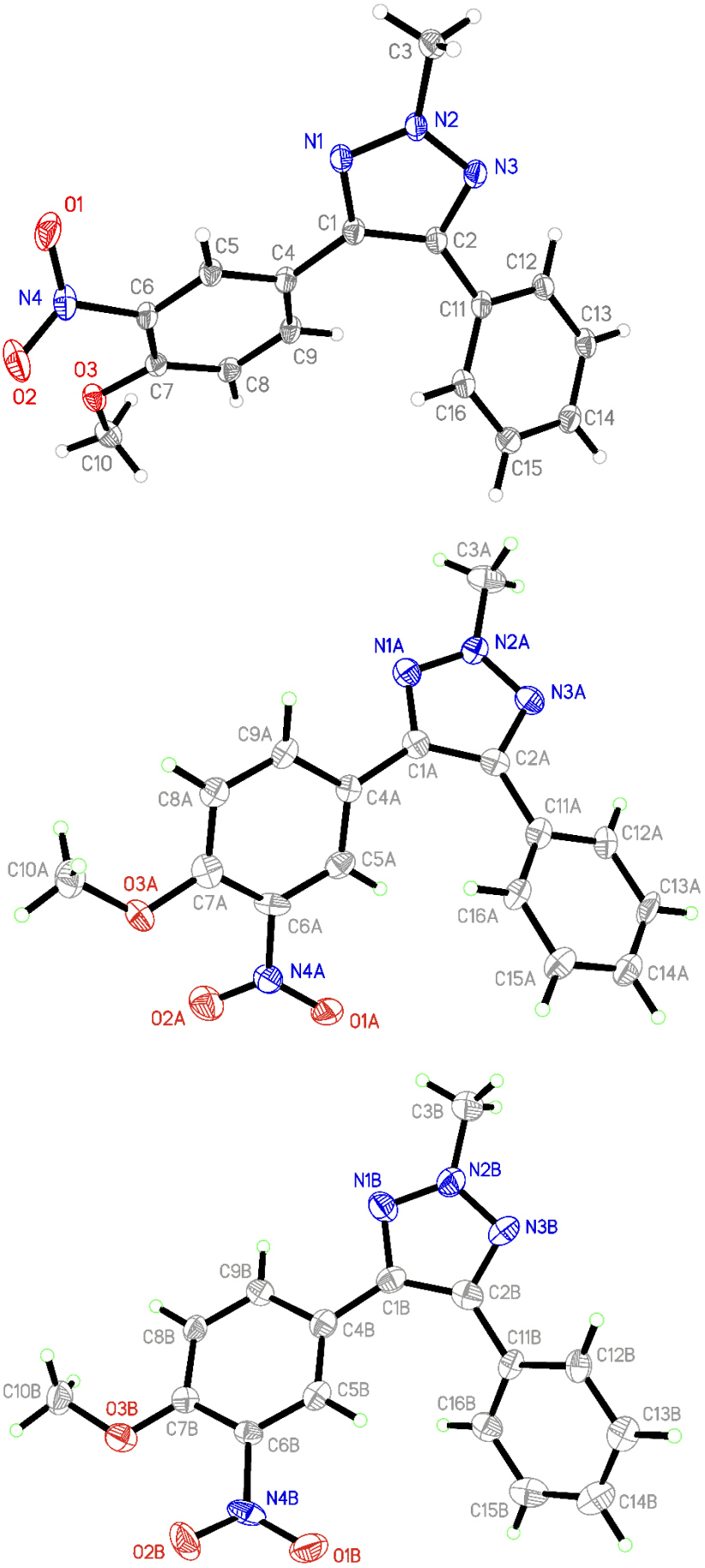


Figure 2. Molecular structure of **6a** in **6a-I** (top) and two symmetrically unique molecules of **6a** in **6a-II** (middle and bottom).

Selected bond distances, Å

Bond	**6a-I**	**6a-II**, molecule A	**6a-II**, molecule B
O1-N4	1.2334(14)	1.217(8)	1.242(8)
O2-N4	1.2251(14)	1.243(8)	1.191(8)
O3-C7	1.3509(13)	1.359(8)	1.353(8)
O3-C10	1.4359(13)	1.411(9)	1.440(9)
N1-N2	1.3282(13)	1.326(8)	1.320(8)
N1-C1	1.3455(14)	1.333(8)	1.358(9)
N2-N3	1.3289(13)	1.335(8)	1.325(8)
N2-C3	1.4543(14)	1.439(8)	1.459(9)
N3-C2	1.3472(14)	1.355(8)	1.342(9)
N4-C6	1.4658(14)	1.455(8)	1.482(8)
C1-C2	1.4122(15)	1.429(9)	1.408(10)
C1-C4	1.4708(15)	1.456(8)	1.474(10)
C2-C11	1.4772(15)	1.474(9)	1.481(10)
C4-C5	1.3947(15)	1.393(9)	1.388(10)
C4-C9	1.3976(15)	1.402(9)	1.422(10)
C5-C6	1.3846(15)	1.385(10)	1.389(9)
C6-C7	1.4053(15)	1.400(10)	1.413(9)
C7-C8	1.3999(15)	1.390(10)	1.395(9)
C8-C9	1.3862(15)	1.365(9)	1.380(9)
C11-C12	1.3996(15)	1.413(9)	1.366(9)
C11-C16	1.3989(16)	1.391(9)	1.379(10)
C12-C13	1.3886(16)	1.384(10)	1.390(10)
C13-C14	1.3898(17)	1.384(11)	1.390(11)
C14-C15	1.3902(17)	1.393(10)	1.371(12)
C15-C16	1.3920(16)	1.367(9)	1.409(11)

References

1. CrysAlisPro. Version 1.171.44. *Rigaku Oxford Diffraction*, **2025**.
2. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71(1), 3-8. http://doi.org/10.1107/S2053273314026370
3. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71(1), 3-8. http://doi.org/10.1107/S2053229614024218
4. Dolomanov O.V.; Bourhis L.J.; Gildea R.J.; Howard J.A.K.; Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42(2), 339-341. http://doi.org/10.1107/S0021889808042726