Supporting Information for

Renaissance of Dinitroazetidine: Novel Hybrid Energetic Boosters and Oxidizers

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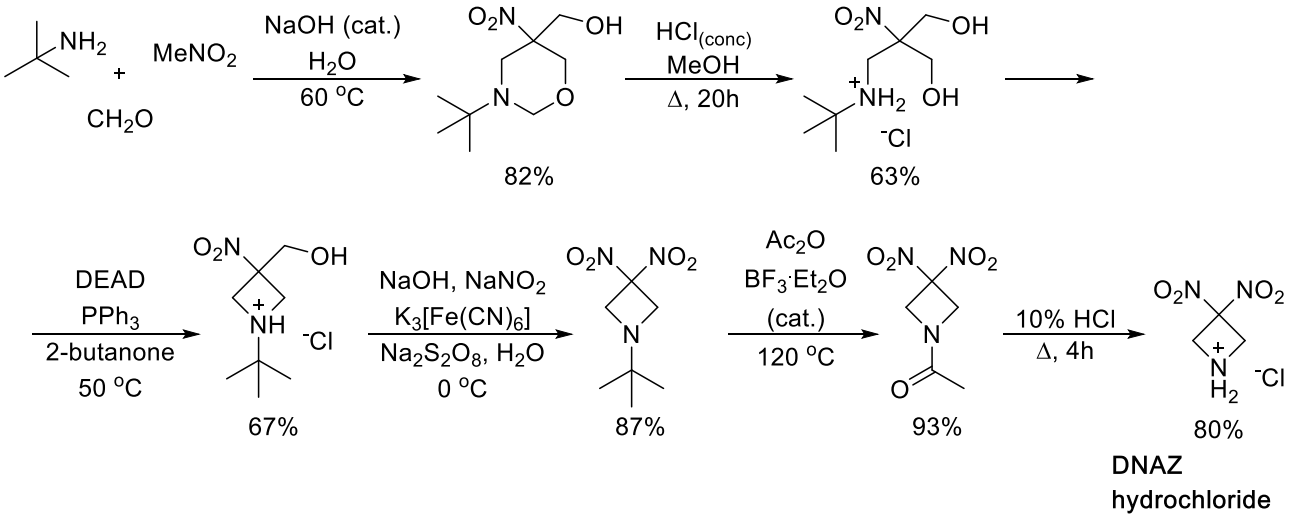
S1. Synthesis of 3,3-dinitroazetidine (**DNAZ**)



Scheme S1. Synthesis of **DNAZ** hydrochloride.

The synthesis of **DNAZ** hydrochloride was accomplished via a previously described procedure starting from *t*-butylamine, paraform and nitromethane. The details of the synthetic procedures can be found in corresponding references:

1. Y.-H. Kown, J.-S. Kim, H.-S. Kim, 1-Glycidyl-3,3-dinitroazetidine containing explosive moiety and preparation method thereof. US Patent 20090299079A1, publication date Dec. 3, 2009.
2. M. A. Hiskey, M. D. Coburn, M. A. Mitchell, B. C. Benicewicz, Synthesis of 3,3-dinitroazetidine from 1-*t*-butyl-3,3-dinitroazetidine. *J. Heterocycl. Chem.*, 1992, **29**, 1855-1856.

S2. Crystallographic data

Table S1. The main crystallography data and refinement details for **3** and **4**.

	3	**4**
Formula	$C_6H_4N_6O_9$	$C_5H_6N_6O_{10}$
Molecular Mass	304.15	310.16
T, K	100	140
Crystal system	Monoclinic	Monoclinic
Space group	C_2/c	Pn
Z (Z')	8 (1)	2 (1)
a, Å	35.7181(13)	8.5418(5)
b, Å	5.4680(2)	7.1633(4)
c, Å	11.2106(4)	9.5501(5)
a, °	90	90
b, °	92.986(2)	101.7793(16)
g, °	90	90
V, $Å^3$	2186.53(14)	572.04(6)
d_{calc}, g cm^{-3}	1.848	1.801
F(000)	1232	316
$2q_{max}$, °	50	50
Number of reflections measured	36666	9582
Independent reflections	3208	3312
Reflections with I>2s(I)	2610	2632
Number of parameters	206	190
R_1	0.0389	0.0352
wR_2	0.0950	0.0799
GOF	1.030	0.986
Residual electron density, e Ч$Å^{-3}$(d_{max}/d_{min})	0.363/-0.245	0.203/-0.235

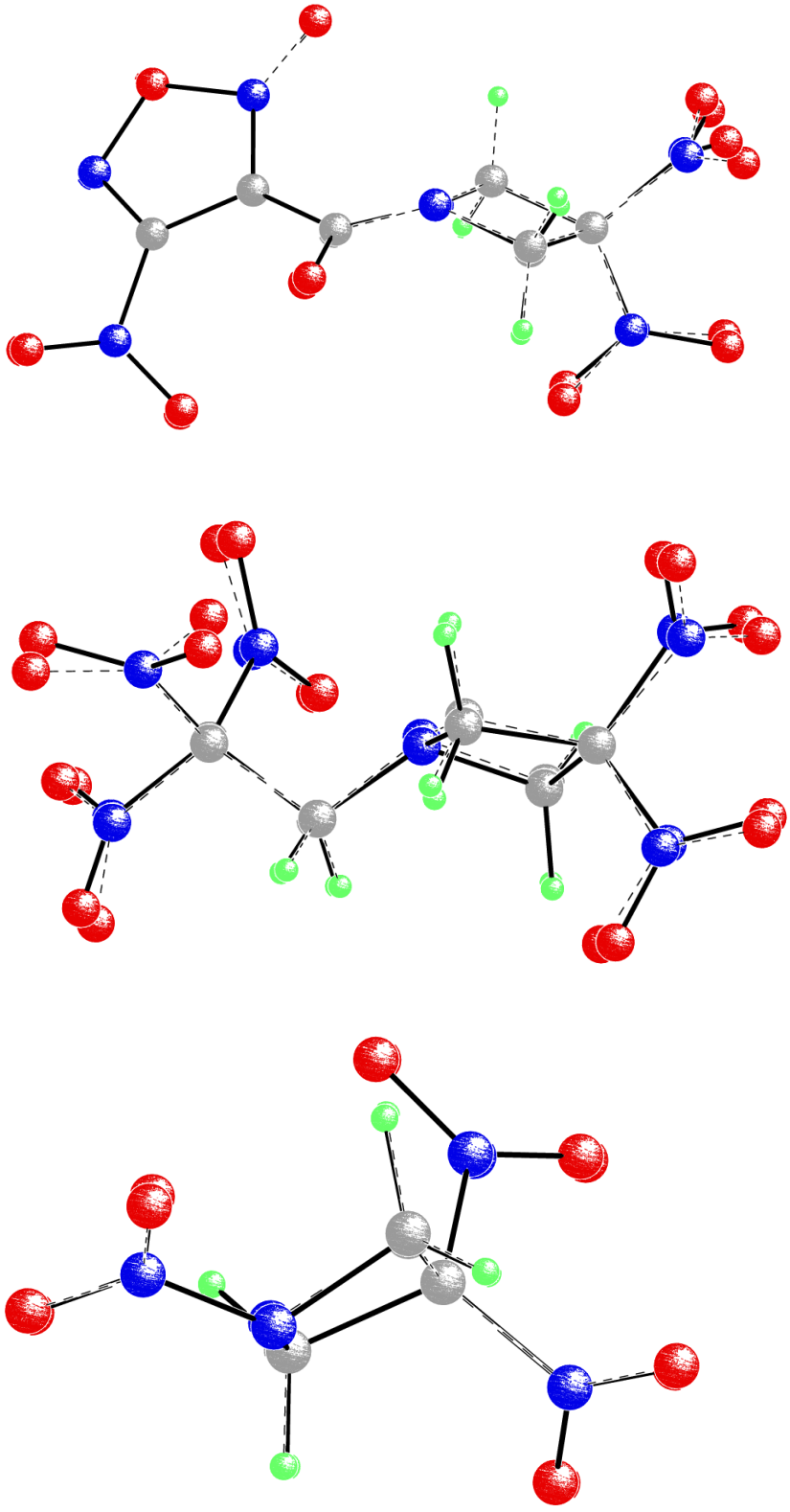


Figure S1. The best mean square overlap for crystal (dashed lines) and isolated (solid lines) structures of **3** (top), **4** (middle) and **TNAZ** (bottom). Position of hydrogen atoms were optimized in all cases at the PBE0-D3/def2tzvp level.

S3. Thermal analysis

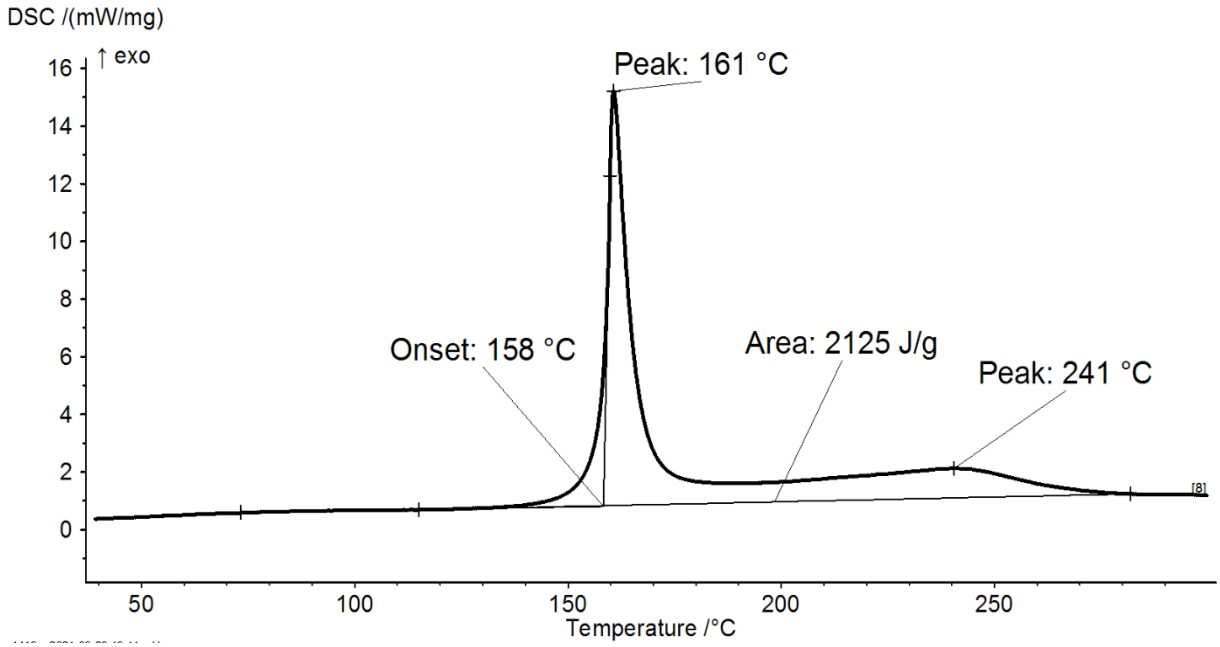


Figure S2. Differential scanning calorimetry of **2**. Heating rate is 5 K min^{-1}.

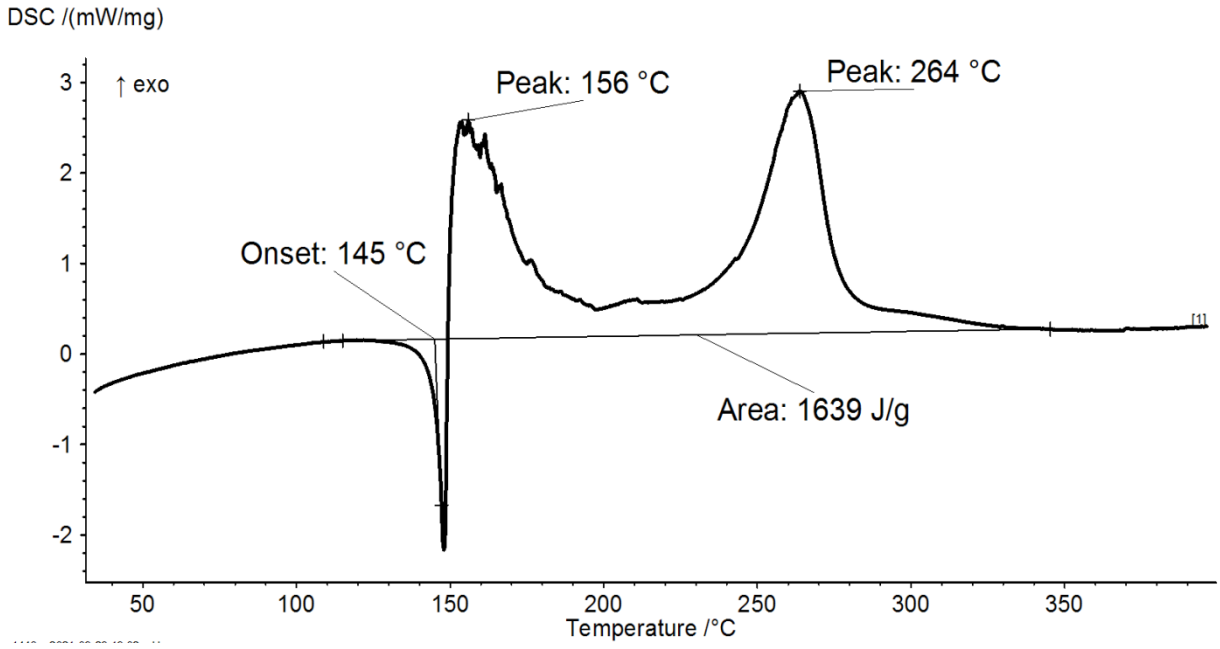
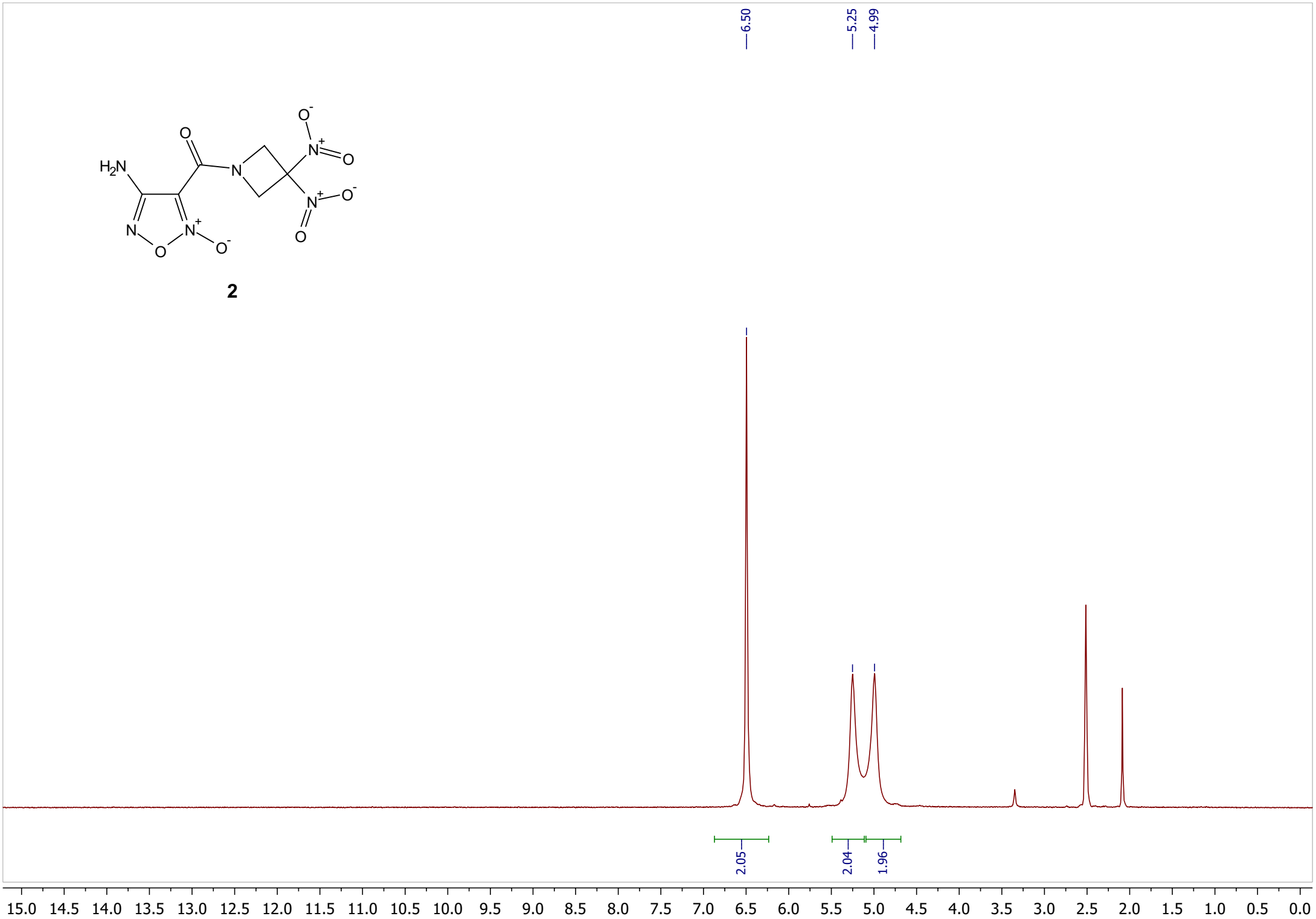


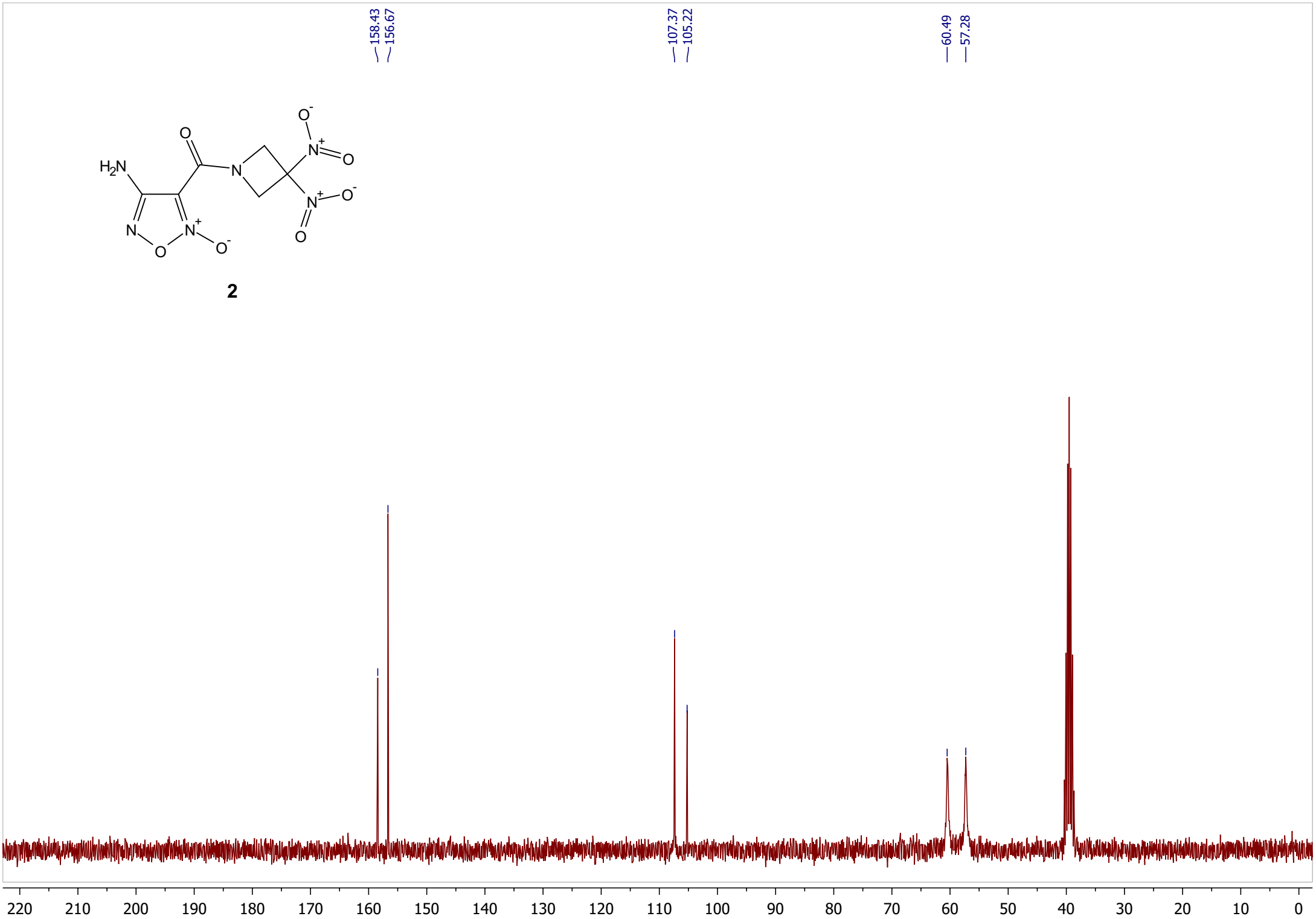
Figure S3. Differential scanning calorimetry of **3**. Heating rate is 5 K min^{-1}.

S4. Copies of NMR spectra

2


6.50
5.25
4.99
2.05
2.04
1.96
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 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 0.5 0.0

2


158.43
156.67
107.37
105.22
60.49
57.28
220
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
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H2N
O
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N+
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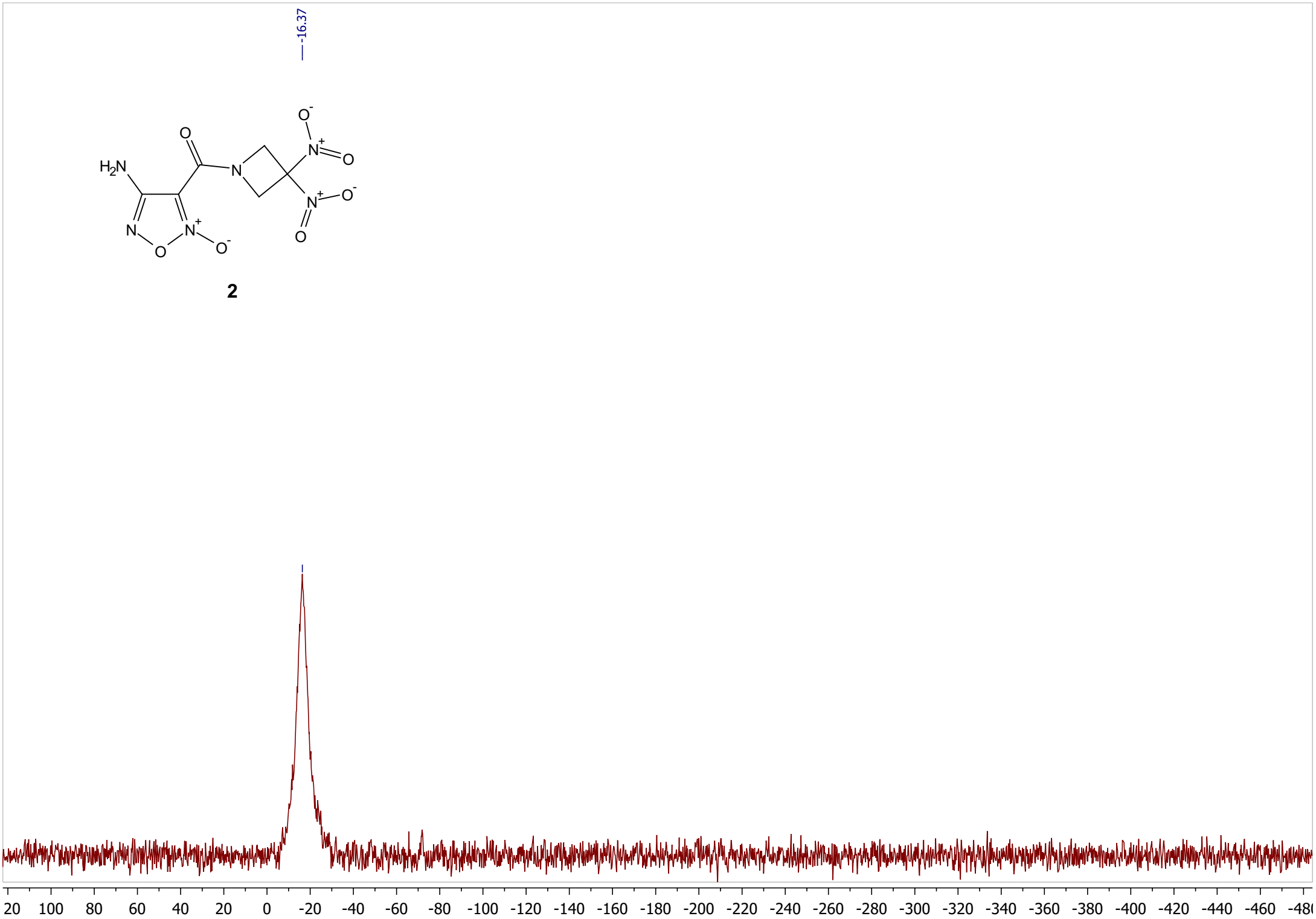
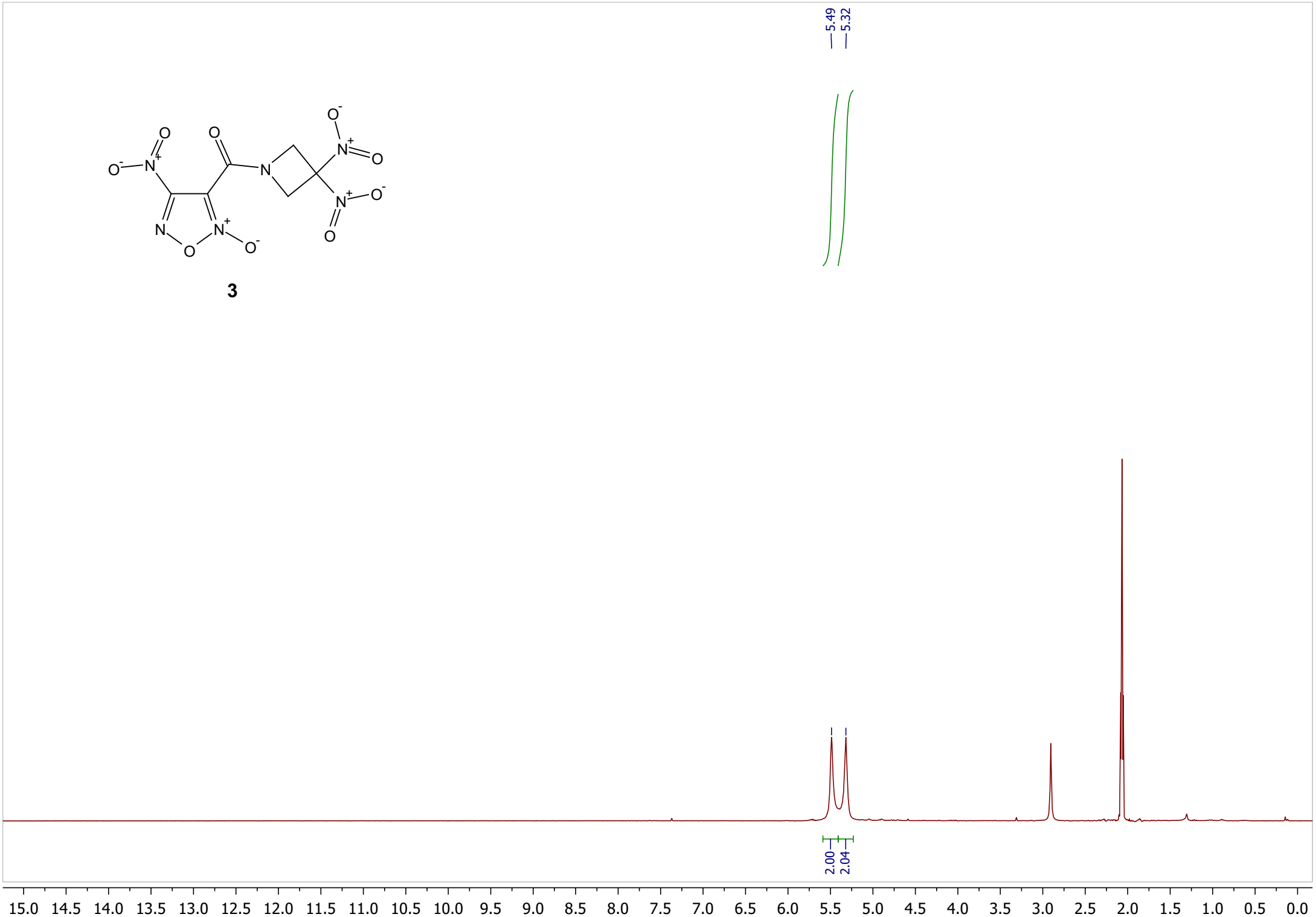
N+
O-
O
N
O
N+
O-

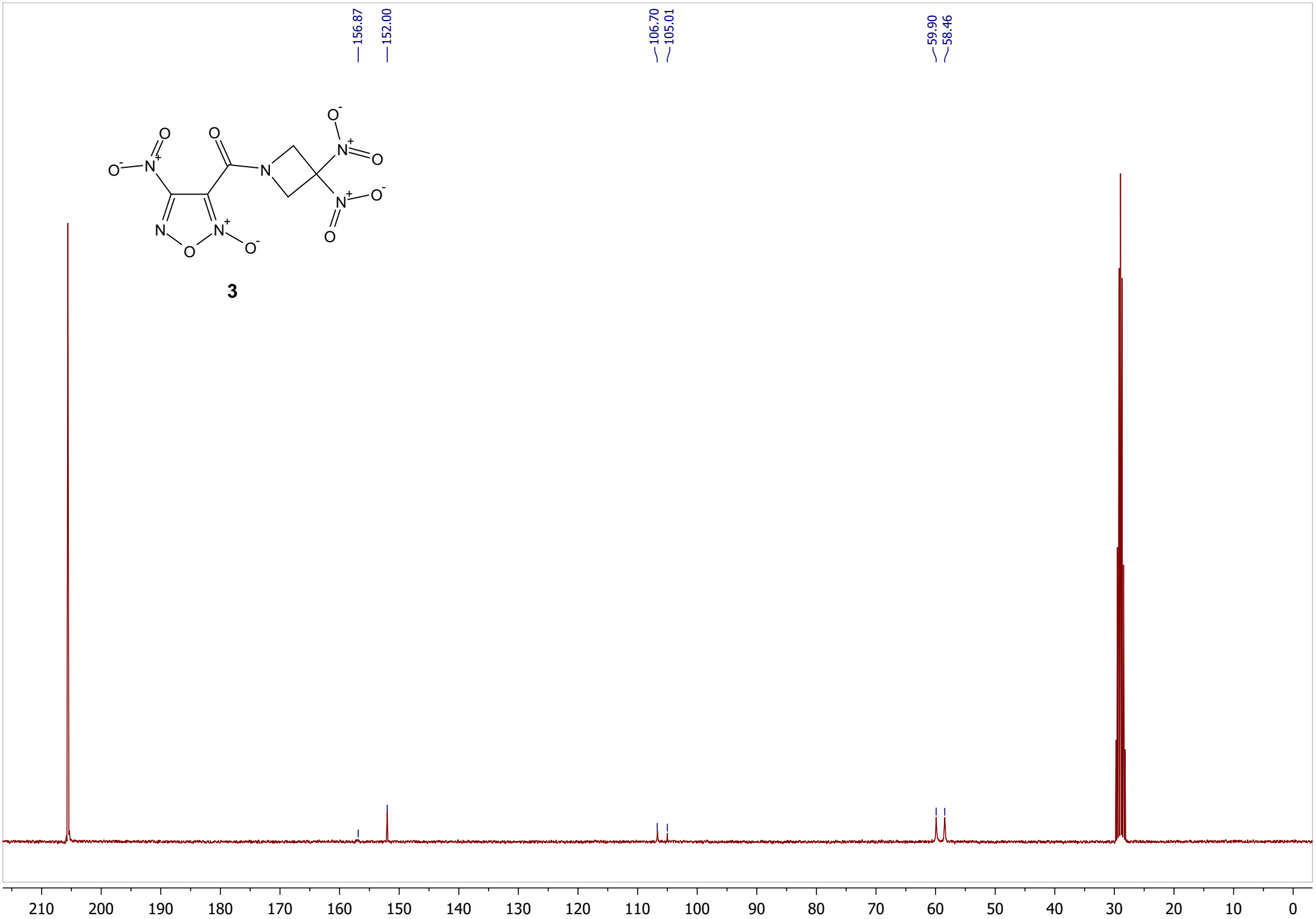
2


-16.37
20 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -340 -360 -380 -400 -420 -440 -460 -48

3


5.49
5.32
2.00
2.04
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 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 0.5 0.0

3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105.01
59.90
58.46
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200
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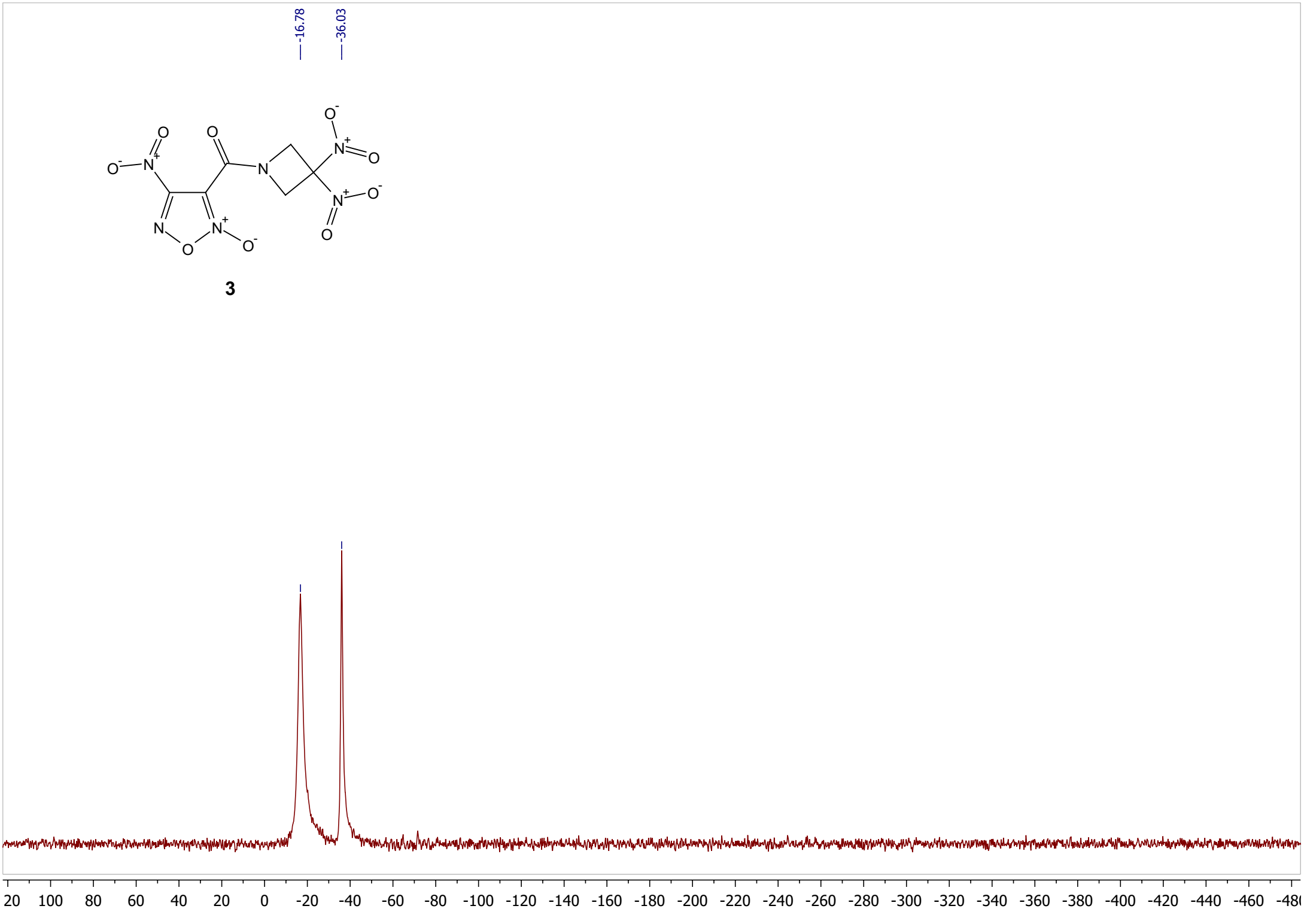
80
70
60
50
40
30
20
10
0

3


-16.78
-36.03
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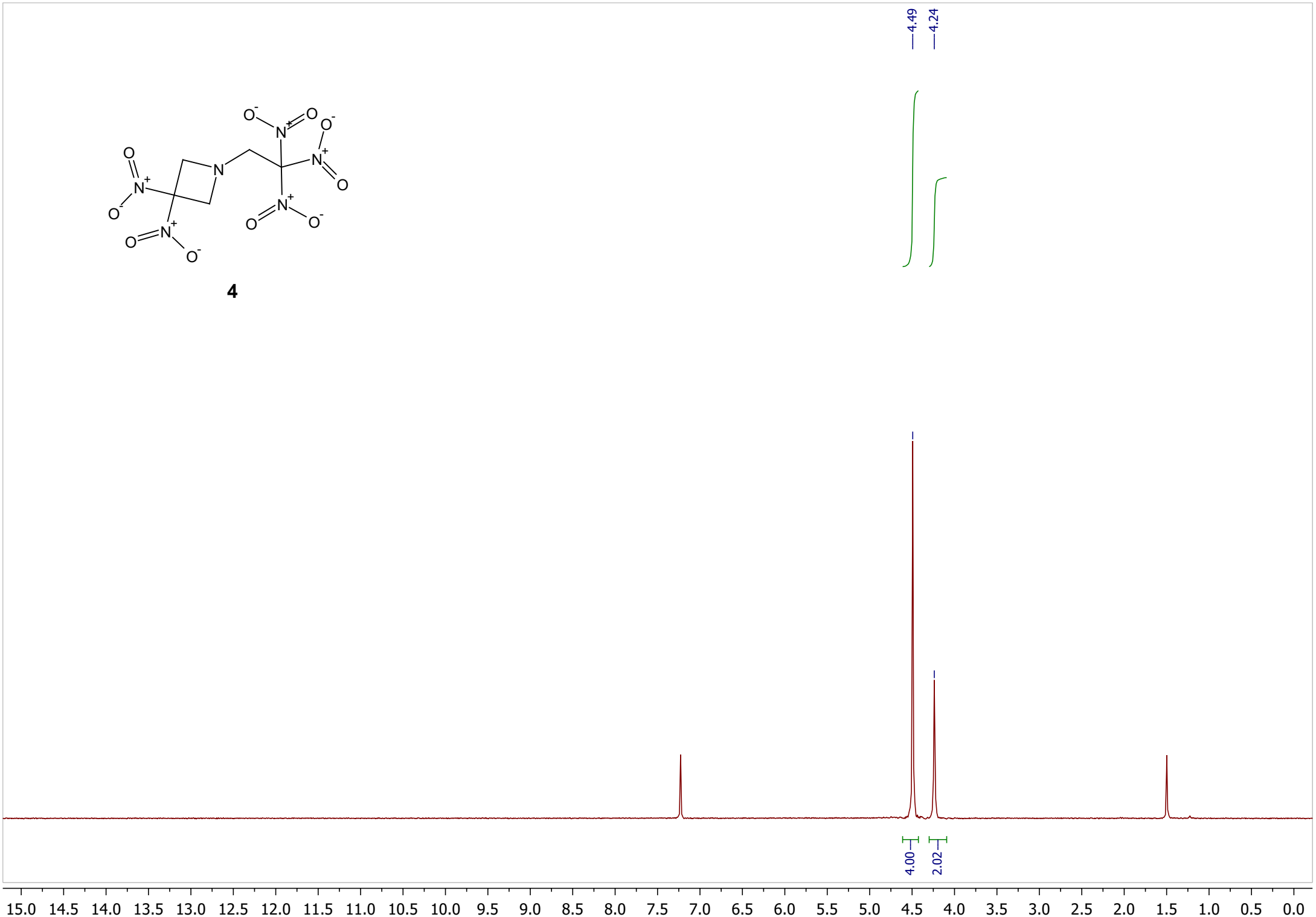
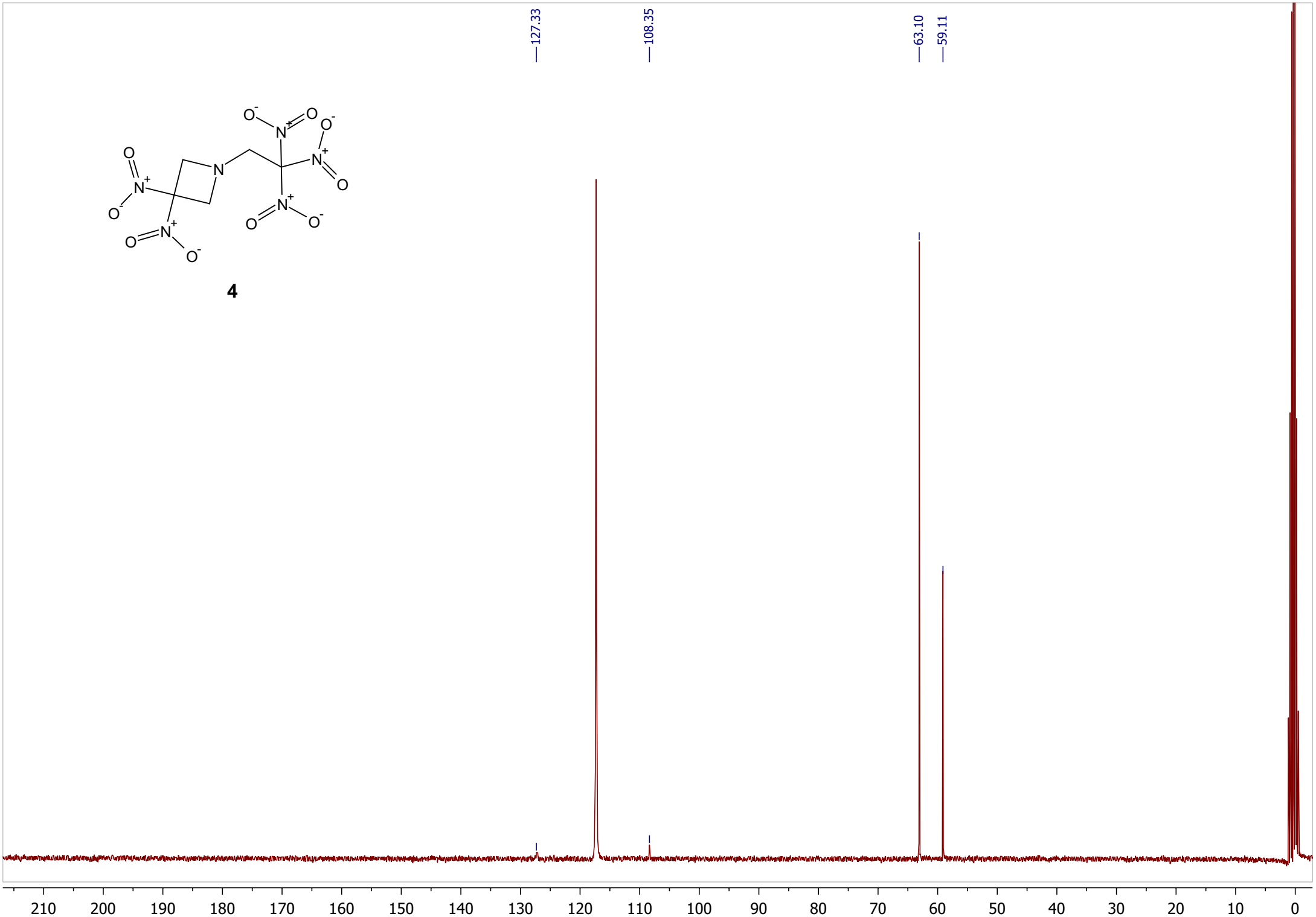
4


4.49
4.24
4.00
2.02
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 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 0.5 0.0

4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108.35
63.10
59.11
210
200
190
180
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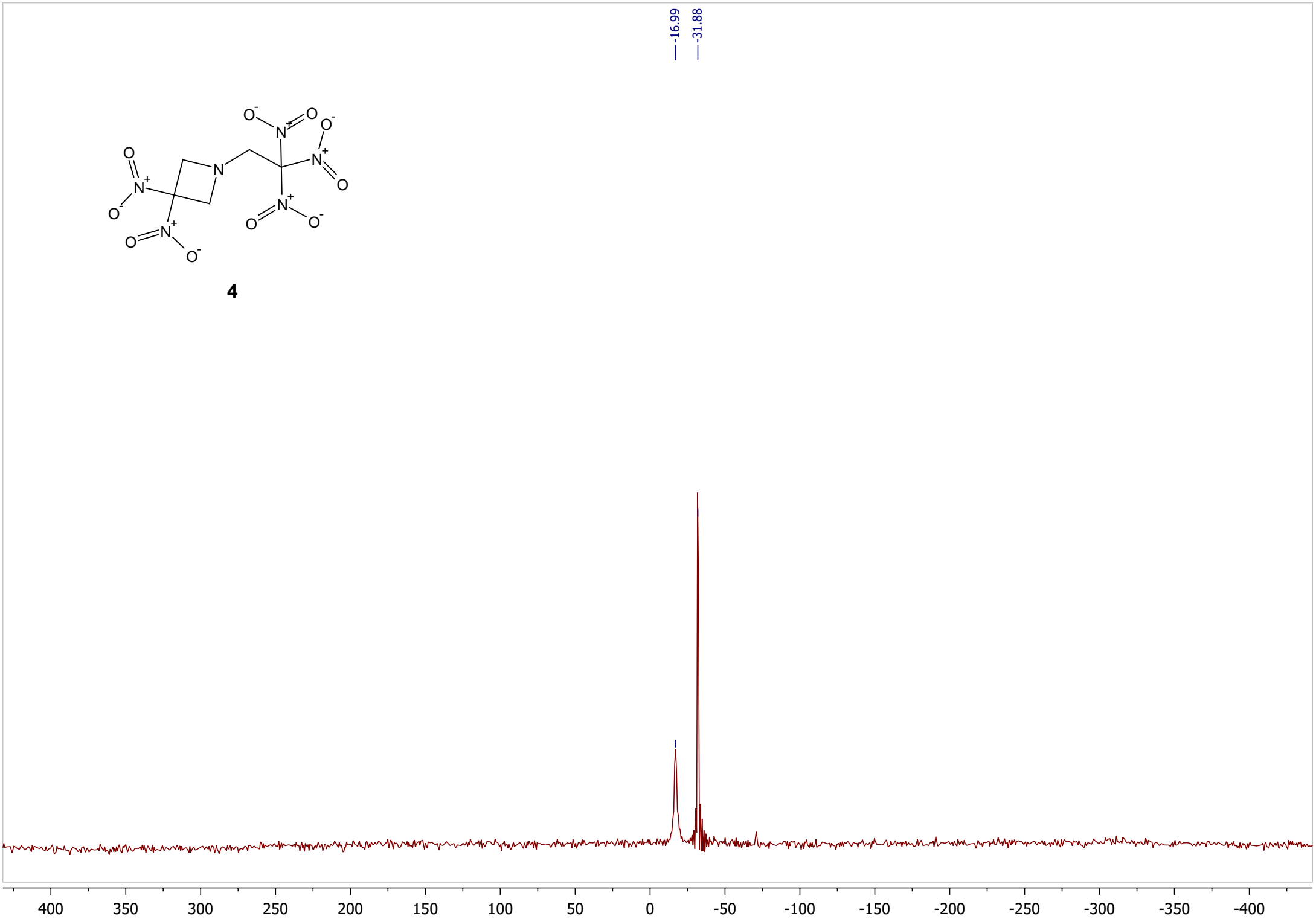
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4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-31.88
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400