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Nucleophilic substitution in azasydnone-modified dinitroanisoles

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Experimental section

General Experimental.

IR spectra were recorded on a BrukerALPHA instrument in KBr pellets. ^{13}C и ^{14}N spectra of benzotriazoles **3a,b** were obtained on a Bruker DRX-500 (125.76 and 36.14 MHz), the rest spectra were obtained on a Bruker AM-300 (300.13 and 282.40 MHz) in DMSO-d$_6$ at 299 K. The chemical shifts of ^1H and ^{13}C nuclei were reported relative to TMS, for ^{14}N nuclei – relative to $MeNO_2$, high-filed chemical shifts are given with a minus sign. High-resolution mass spectra with electrospray ionization were recorded on a Bruker MicroOTOF II instrument. Melting points were determined by Kofler method on a Boetius bench (heating rate 4 K min^{-1}) and were not corrected. The reaction progress and purity of the obtained compounds were controlled by TLC on Merck Silicagel 60 F254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Silica gel (Kieselgel) 60 (0.04–0.063 mm) was used for column chromatography.

All the reagents were of analytical grade, purchased from commercial sources, and used as received. The starting (4-methoxy-3,5-dinitrophenyl)azasydnone **1** was synthesized following a literature method.[S1]

The synthesis of 3-(4-amino-3,5-dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate 2a and 2b. A solution of azasydnone-containing dinitroanisole **1** (0.1 g, 0.35 mmol) in MeOH (10 ml) was cooled to 0 °C, methanolic ammonia (7N, 0.2 ml) was added to this solution drop by drop in the case of **2a**, or methylamine (40% aq., 0.2 ml) in the case of **2b**. The reaction mixture was stirred at room temperature for 20 minutes, cooled to –20 ° C for 1 h. The obtained precipitate was filtered off and air-dried.

3-(4-Amino-3,5-dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate (2a). The yield was 80%, yellow cubical crystals, mp 198–200 ºC (MeOH). IR (ν/cм$^{-1}$): 3443 (m), 3323 (m), 3105 (w), 1793 (vs), 1638 (s), 1578 (m), 1536 (m), 1439 (w), 1315 (m), 1263 (s), 1189 (w), 899 (w), 746 (w). ^{1}H NMR, δ: 8.94 (s, 2 H, NH_2); 8.89 (s, 2 H). ^{13}C NMR, δ: 164.82 (C-O); 142.70; 134.93; 126.04 (CH); 119.27. ^{14}N, NMR δ: –15.69 (NO_2); –77.47 (N^+). Found, *m/z*: 269.0266 $[M+H]^+$. $C_7H_5N_6O_6$. Calculated, *m/z*: 269.0265.

3-(4-Methylamino-3,5-dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate (2b). The yield was 63%, yellow powder, mp 159–161 ºC (MeOH). IR (ν/cм$^{-1}$): 3343 (m), 1789 (vs), 1626 (s), 1540 (s), 1385 (w), 1336 (m), 1276 (m), 1190 (w), 1163 (w), 929 (w), 742 (w). ^{1}H NMR, δ: 9.09 (s, 1 H, NH); 8.82 (s, 2 H); 2.84 (s, 3 H, NMe). ^{13}C NMR, δ: 164.82 (C-O); 142.30; 136.80; 124.70 (CH); 118.94; 33.00 (Me). ^{14}N NMR, δ: –18.08 (NO_2); –80.06 (N^+). Found, *m/z*: 283.0416 $[M+H]^+$. $C_8H_7N_6O_6$. Calculated, *m/z*: 283.0422.

3-[3,5-Dinitro-4-(pyrrolidin-1-yl)phenyl]-1,2,3,4-oxatriazolium-5-olate (2c). Pyrrolidine (0.088 ml, 1.06 mmol) was added to a solution of compound **1** (0.2 g, 0.7 mmol) in MeCN (8 ml), the mixture was stirred at room temperature for 1 h. The solvent was removed by evaporation at reduced pressure to give a dark yellow solid, which was purified by silica gel column chromatography using CH_2Cl_2–MeOH (50:1). The yield was 0.174 g, 77%, yellow crystals, mp 151–152 °C ($CHCl_3$), R_f 0.7 (CH_2Cl_2–MeOH (20 : 1). IR (ν/cм$^{-1}$): 1580 (m), 1509 (s), 1337 (s), 1087 (w), 1068 (w), 1009 (m), 848 (w), 813 (m), 743 (w), 475 (w). ^{1}H NMR, δ: 8.70 (s, 2 H), 3.25 (t, 4 H, *J* = 6.4 Hz,), 1.95 (t, 4 H, *J* = 6.4 Hz,). ^{13}C NMR, δ: 164.90 (C–O), 140.29, 137.20 (C+C), 123.22 (2CH), 117.24, 54.25 (2CH_2), 24.63 (2CH_2). ^{14}N NMR, δ: –12.05 (NO_2), –79.96 (N^+). Found, 345.0550 $[M+Na]^+$. $C_{11}H_{10}N_6NaO_6$. Calculated, *m/z*: 345.0554.

Reaction of 3-(4-methoxy-3,5-dinitrophenyl]-1,2,3,4-oxatriazolium-5-olate 1 with hydrazines – the synthesis of 3a,b and 5a,b (general procedure). A solution of azasydnone-containing dinitroanisole **1** (0.28 g, 1 mmol) in MeOH (20 ml) was cooled to 5 – 10 °C, an alkylhydrazine (0.2 mmol) was added to this solution in the case of **3a,b** or carbazate (0.3 mmol) in the case of **5a,b**. After that, the reaction mixture was stirred at room temperature for 0.5 h (for **3a,b**) or 24 h (for **5a,b**) and cooled to –10 ° C for 1 h. The obtained precipitate was filtered off, washed with MeOH and air-dried.

1-Methyl-7-nitro-5-(5-oxido-1,2,3,4-oxatriazolium-3-yl)-1*H*-benzo[*d*][1,2,3]triazole 3-oxide (3a). The yield was 0.22 g, 79%, dark beige powder, mp 233–235 ºC (dec.). IR (ν/cм$^{-1}$): 3077 (w), 3033 (w), 1817 (vs), 1628 (w), 1531 (w), 1441 (w), 1347 (m), 1314 (m), 1240 (m), 1189 (w), 742 (m). ^{1}H NMR, δ: 8.99 (s, 1 H, Ar); 8.88 (s, 1 H, Ar); 4.37 (s, 3 H, NMe). ^{13}C NMR, δ: 166.00 (C-O); 138.83; 133.54; 130.01; 128.56; 121.09 (CH); 118.45 (CH); 38.41 (NCH_3). ^{14}N NMR, δ: –19.49 (NO_2); –76.19 (N^+). Found, *m/z*: 302.0243 $[M+Na]^+$. $C_8H_5N_7NaO_5$. Calculated, *m/z*: 302.0244.

1-Ethyl-7-nitro-5-(5-oxido-1,2,3,4-oxatriazolium-3-yl)-1*H*-benzo[*d*][1,2,3]triazole 3-oxide (3b). The yield was 0.22 g, 76%, dark yellow powder, mp 194–196 ºC (dec.). IR (ν/cм$^{-1}$): 3031 (w), 1808 (vs), 1626 (w), 1531 (m), 1407 (w), 1309 (m), 1185 (m), 735 (w). ^{1}H NMR, δ: 9.02 (s, 1 H, Ar); 8.90 (s, 1 H, Ar); 4.80 (q, 2 H, CH_2, *J* = 7.2 Hz); 1.58 (t, 3 H, CH_3, *J* = 7.2 Hz). ^{13}C NMR, δ: 164.86 (C-O), 137.84; 132.51; 128.93; 127.69; 119.91 (CH); 116.70 (CH); 45.66 (NCH_2); 12.22 (CH_3). ^{14}N NMR, δ: –16.17 (NO_2); –75.45 (N^+). Found, *m/z*: 294.0580 $[M+H]^+$. $C_9H_8N_7O_5$. Calculated, *m/z*: 294.0581.

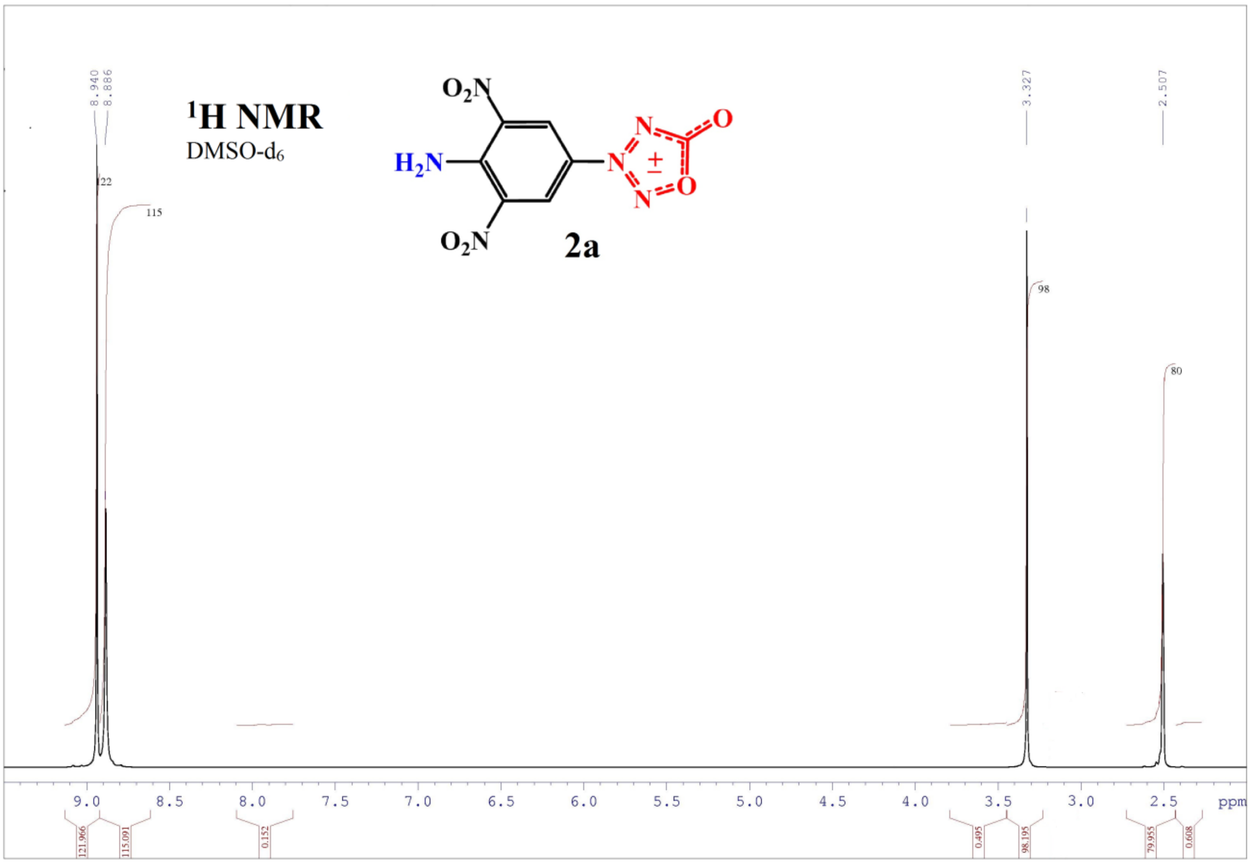
3-{4-[2-(Ethoxycarbonyl)hydrazinyl]-3,5-dinitrophenyl}-1,2,3,4-oxatriazolium-5-olate (5a). The yield was 0.29 g, 83%, yellow needle-like crystals, mp 170–172 ºC (MeOH). IR (ν/cм$^{-1}$): 3280 (s), 1798 (s), 1709 (s), 1629 (m), 1543 (m), 1330 (w), 1266 (w). ^{1}H NMR, δ: 10.04 (br.s, 1 H, NH); 9.76 (br.s, 1 H, NH); 8.81 (s, 2 H, Ph); 4.06 (q, 2 H, CH_2, *J* =6.7 Hz); 1.32 (br.s, 3 H, CH_3). ^{13}C NMR, δ: 164.78 (C-O); 156.34 (CO); 141.34; 136.95; 123.10 (CH); 122.11; 61.36 (CH_2); 14.37 (CH_3). ^{14}N NMR, δ: –14.74 (NO_2); –79.86 (N^+). Found, *m/z*: 356.0574 $[M+H]^+$. $C_{10}H_{10}N_7O_8$. Calculated, *m/z*: 356.0585.

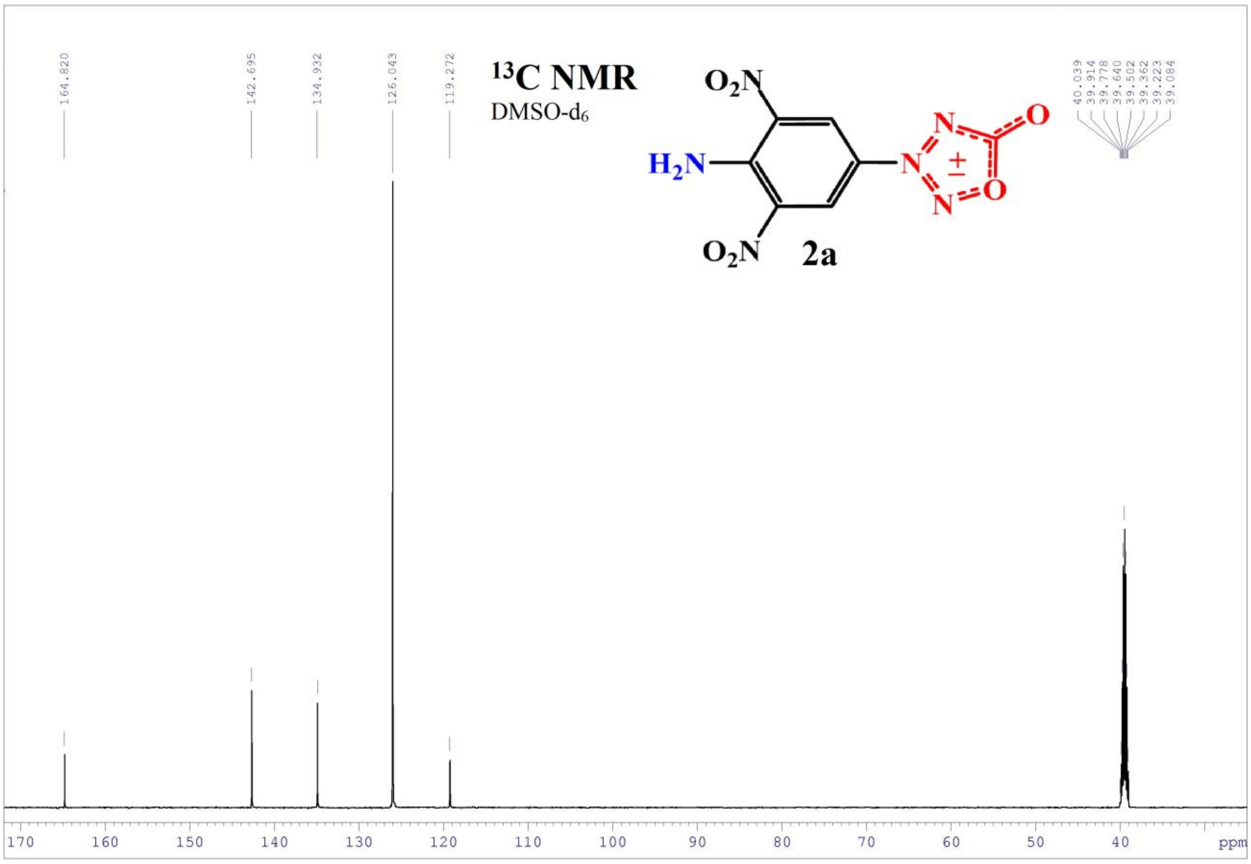
3-{4-[2-(*tert*-Butoxycarbonyl)hydrazinyl]-3,5-dinitrophenyl}-1,2,3,4-oxatriazolium-5-olate (5b). The yield was 0.30 g, 80%, yellow needle-like crystals, mp 190–192 ºC (MeOH, dec.). IR (ν/cм$^{-1}$): 3284 (m), 1779 (s), 1718 (m), 1629 (w), 1543 (m), 1330 (m), 1157 (w). ^{1}H NMR, δ: 9.99 (br.s, 1 H, NH); 9.53 (br.s, 1 H, NH); 8.80 (s, 2 H, Ar); 1.40 (br.s, 9 H, CH_3). ^{13}C NMR, δ: 164.81 (C-O); 155.19 (CO); 141.68; 137.02; 123.01 (CH); 121.96; 80.56 ($\underline{C}(CH_2)_3$); 27.87 (CH_3). ^{14}N NMR, δ: –12.85 (NO_2); –78.67 (N^+). Found, *m/z*: 401.1165 $[M+NH_4]^+$. $C_{12}H_{17}N_8O_8$. Calculated, *m/z*: 401.1164.

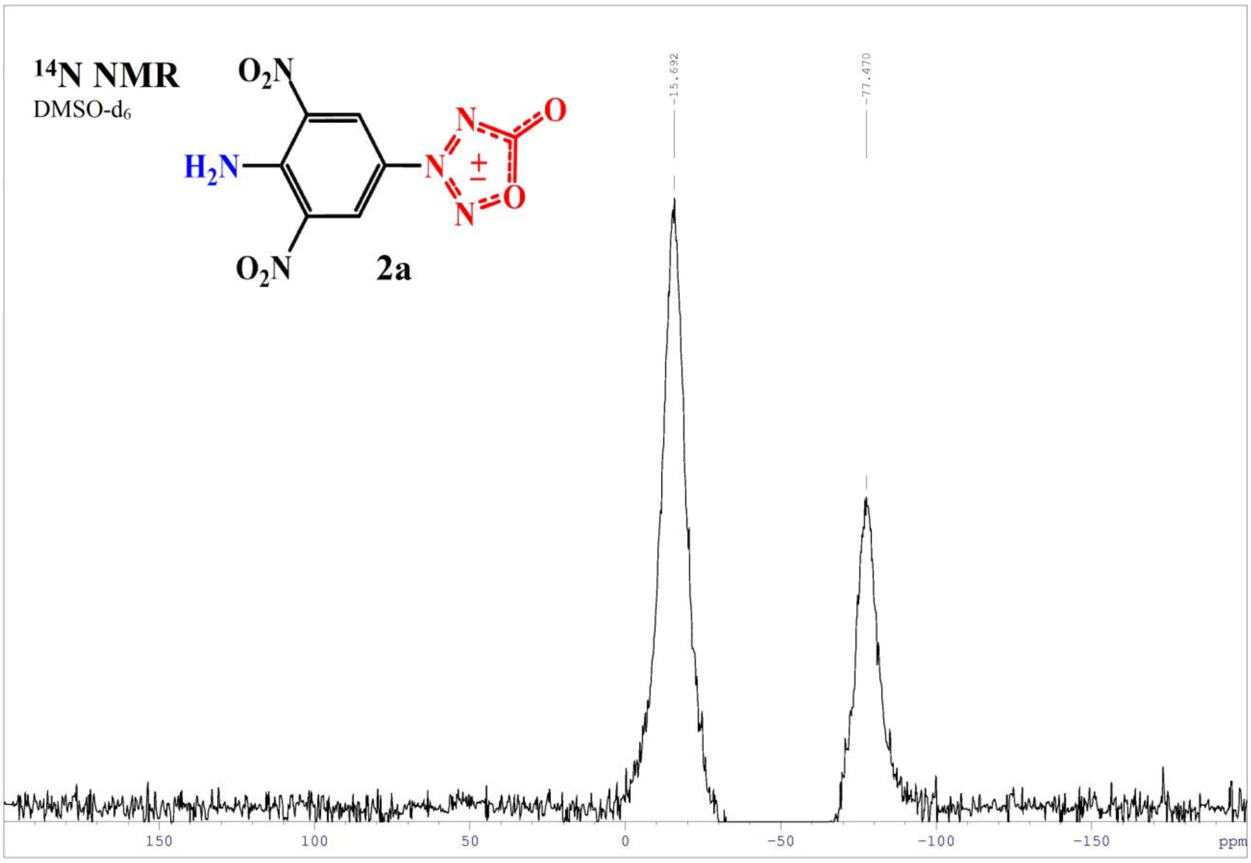
References

[S1] I. L. Dalinger, O. V. Serushkina, D. L. Lipilin, A. A. Anisimov, K. Yu. Suponitsky and A. B. Sheremetev, *ChemPlusChem*, 2019, **84**, 802, https://doi.org/10.1002/cplu.201900243.

NMR Spectra of synthesized compounds







14N NMR
DMSO-d6
O2N
H2N
O2N
N
N
N
O
O
±
2a
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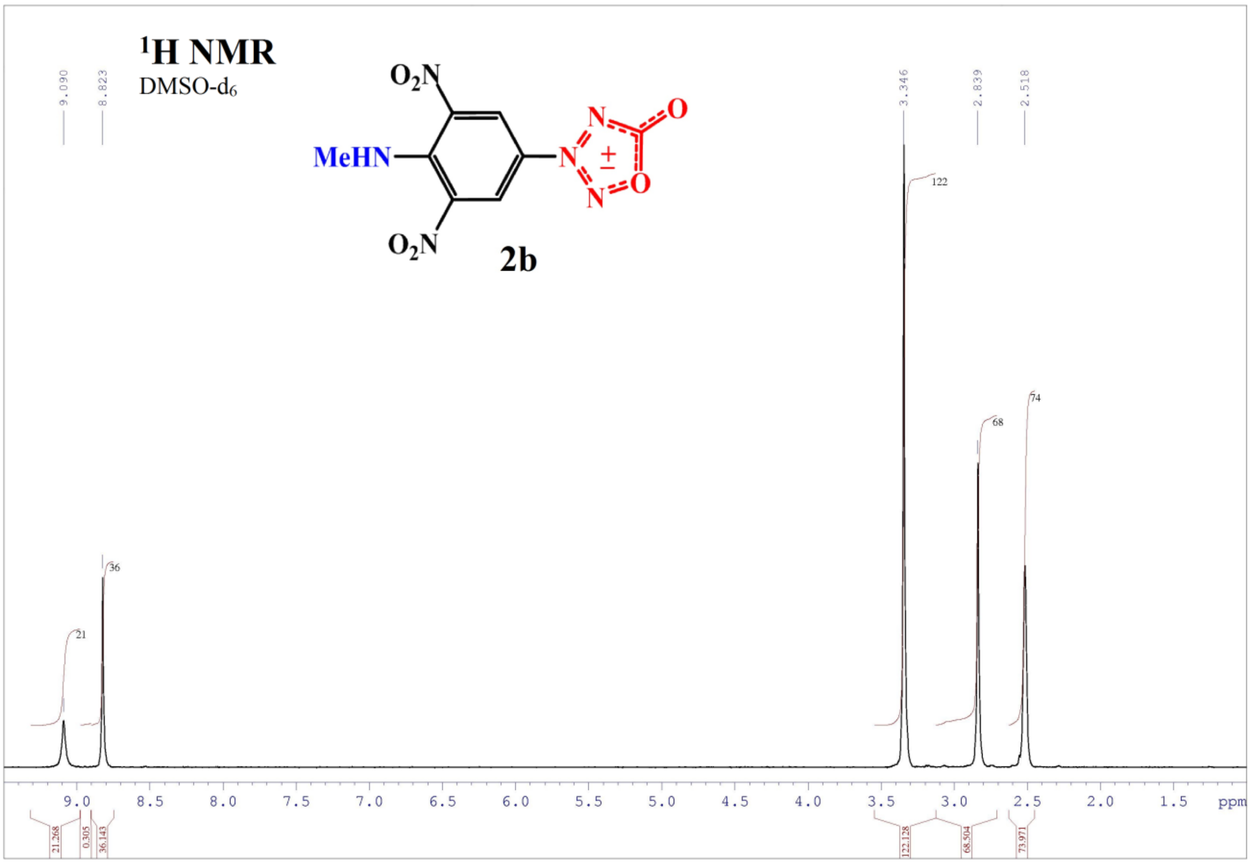
-77.470
150
100
50
0
-50
-100
-150
ppm



1H NMR
DMSO-d6
O2N
MeHN
O2N
N
N
N
O
O
±
2b
9.090
8.823
3.346
2.839
2.518
21
36
122
68
74
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
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21.268
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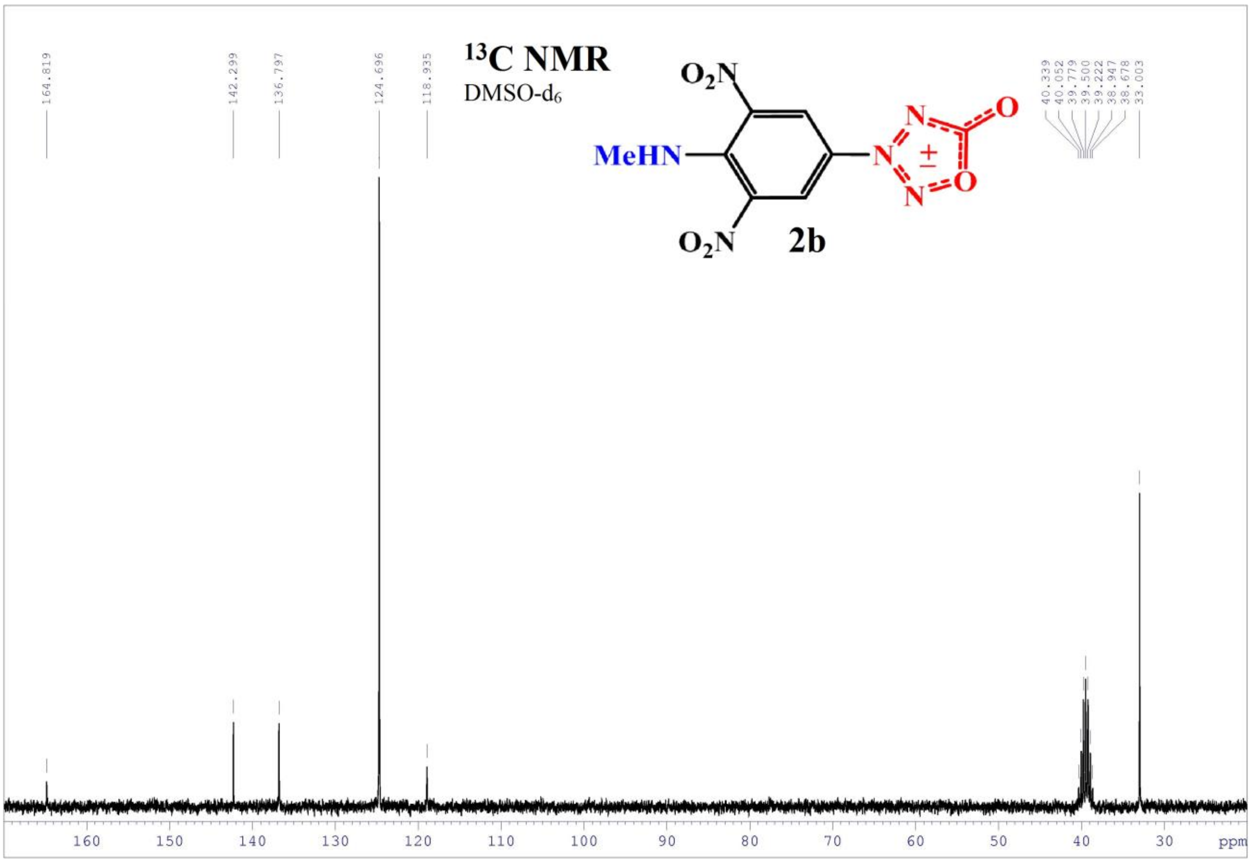
122.128
68.504
73.971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136.797
124.696
118.935
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40.052
39.779
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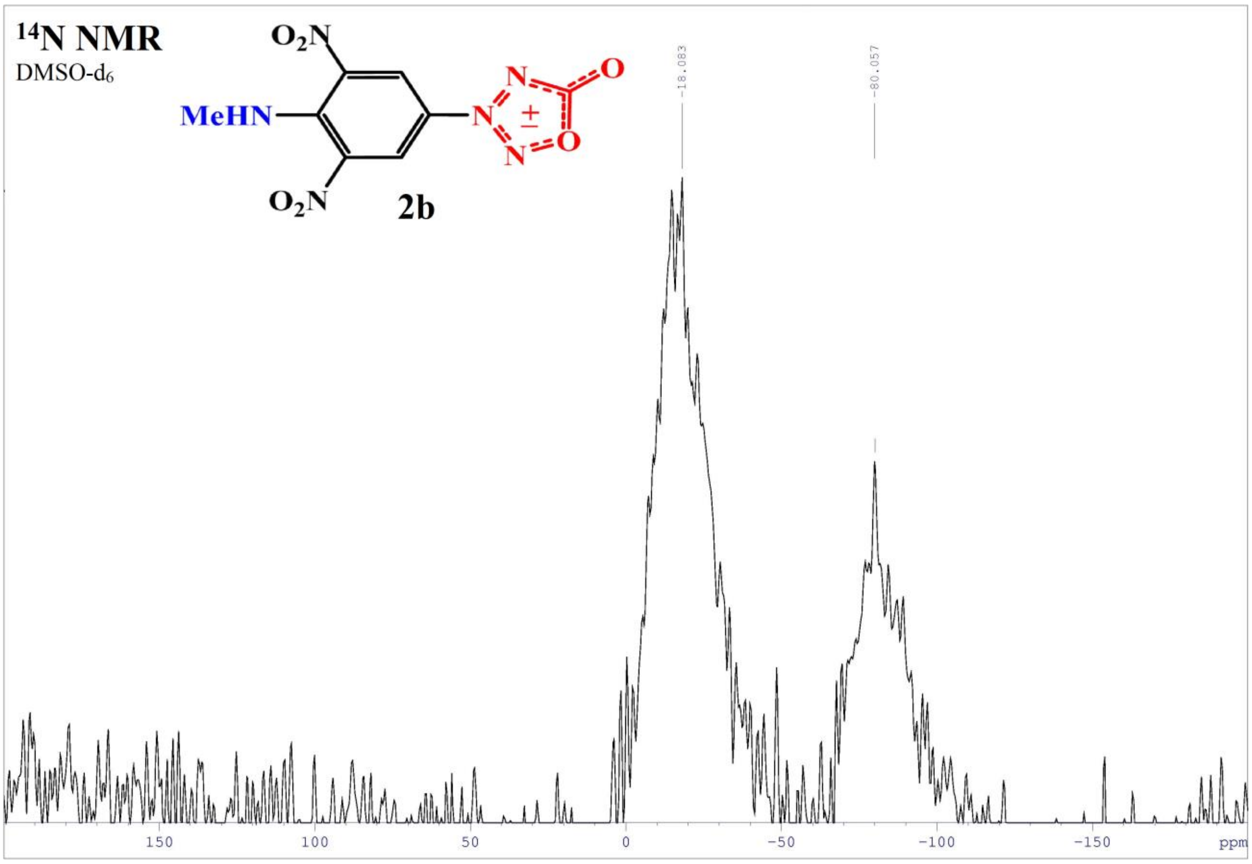
39.222
38.947
38.678
33.003
O2N
MeHN
O2N
N
N
N
O
O
±
2b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


14N NMR
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-18.083
-80.057
O2N
MeHN
O2N
N
N
N
O
O
±
2b
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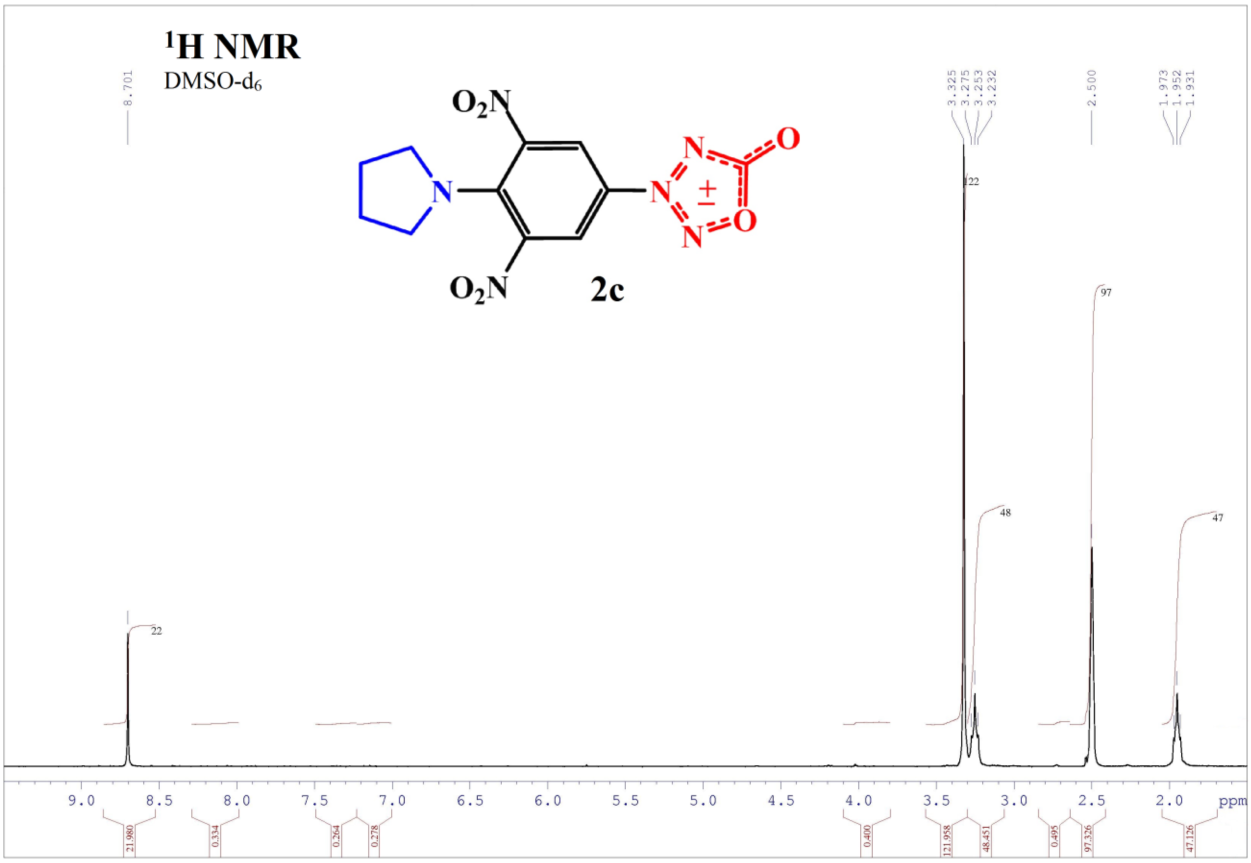
100
50
0
-50
-100
-150
ppm


¹H NMR
DMSO-d₆
8.701
3.325
3.275
3.253
3.232
2.500
1.973
1.952
1.931
O₂N
N
N
N
N
O
O
±
O₂N
2c
22
122
48
97
47
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
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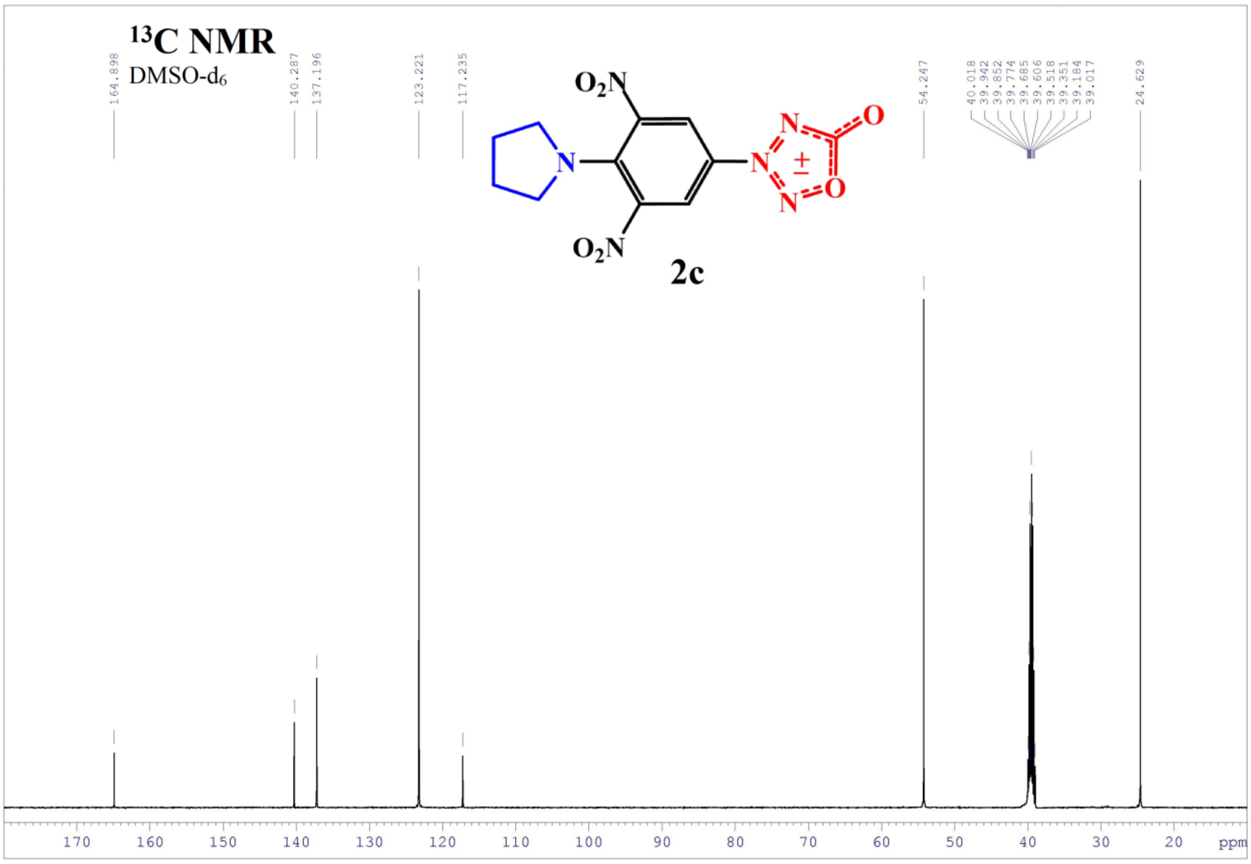
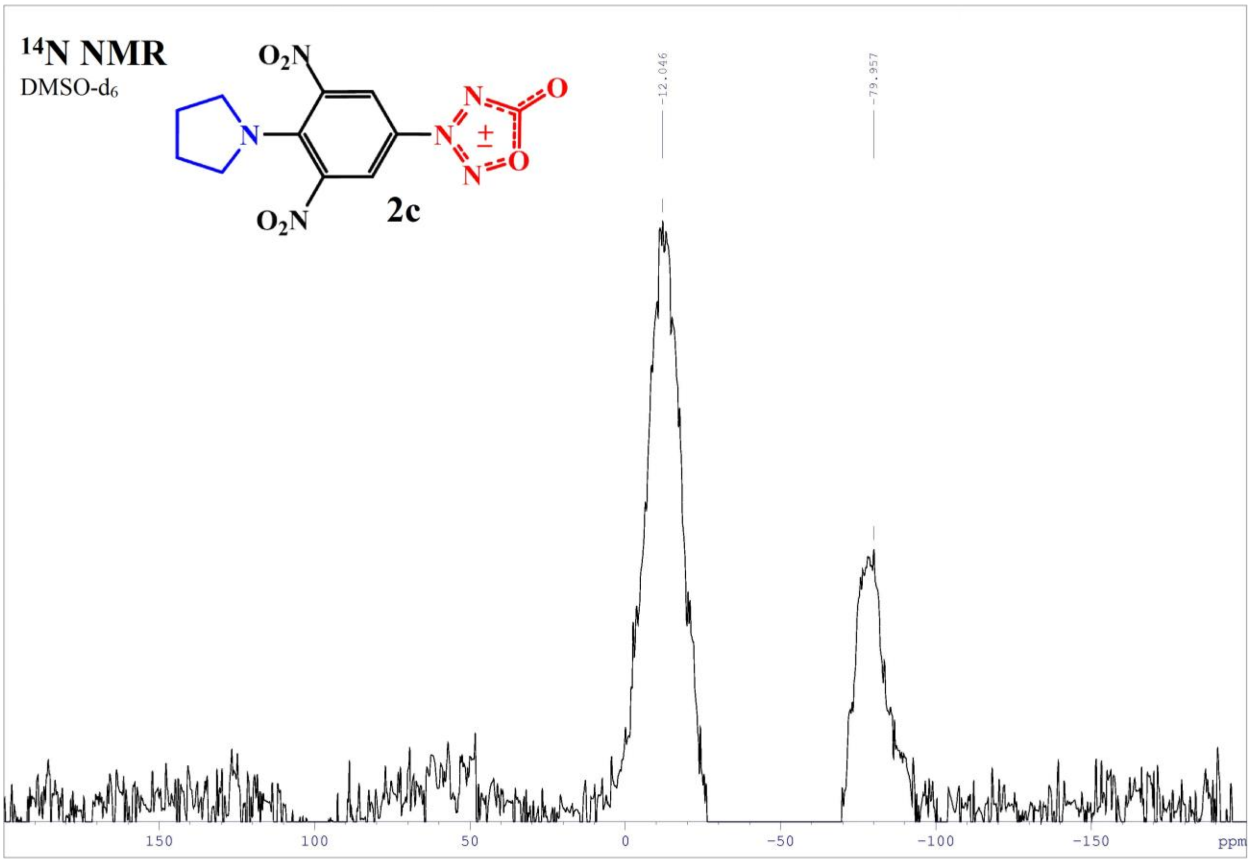
0.278
0.400
121.958
48.451
0.495
97.326
47.126


¹³C NMR
DMSO-d₆
164.898
140.287
137.196
123.221
117.235
54.247
40.018
39.942
39.852
39.774
39.685
39.606
39.518
39.351
39.184
39.017
24.629
O₂N
N
N
N
N
O
O
±
O₂N
2c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



^{14}N NMR
DMSO-d$_6$
O_2N
N
N
N
N
±
O
O
O_2N
2c
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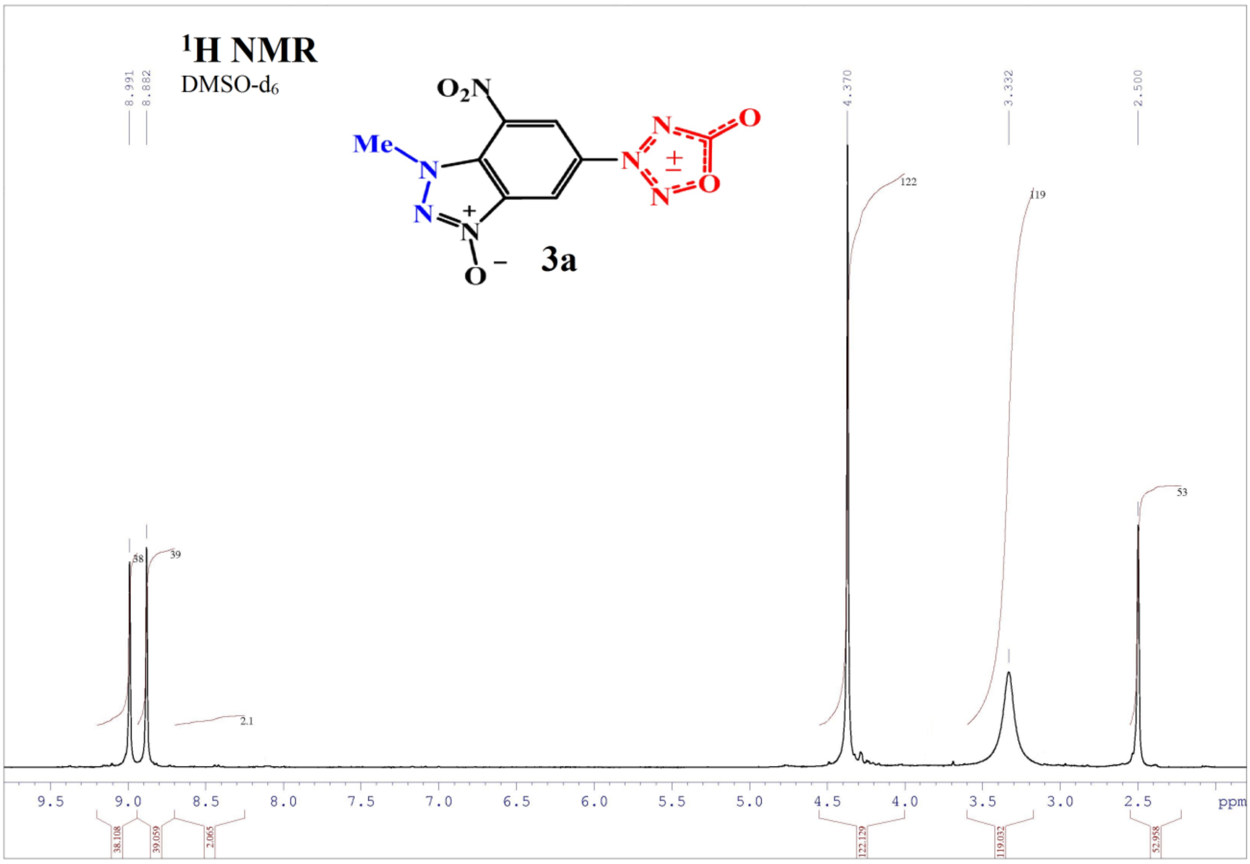
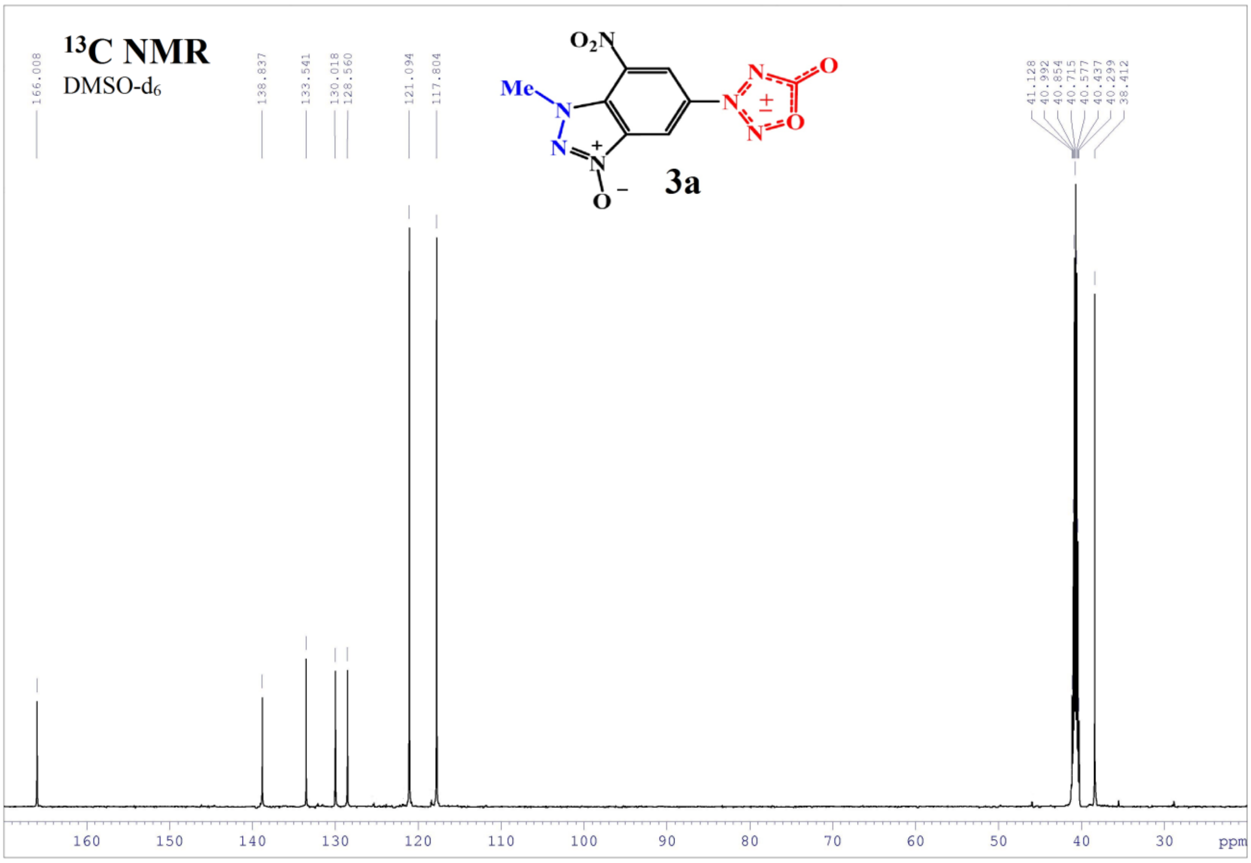
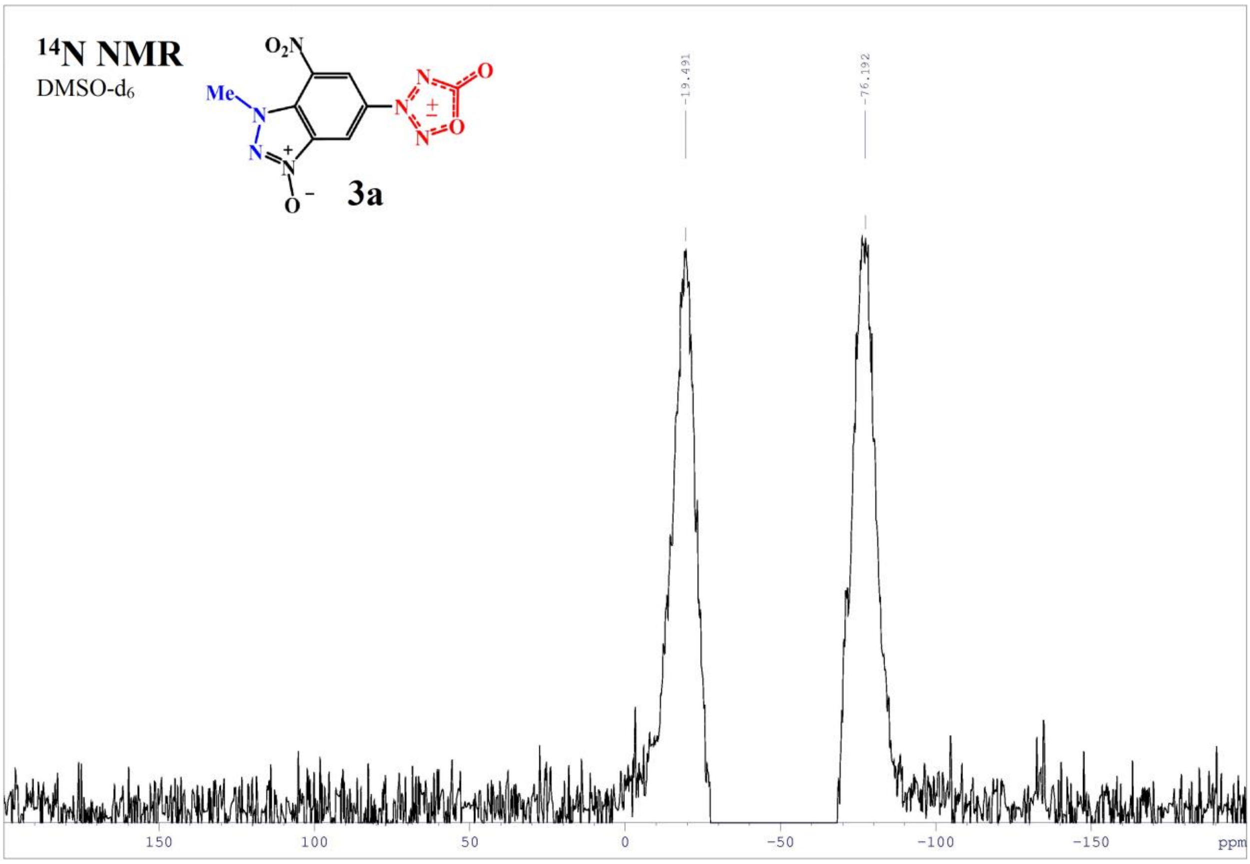
-79.957
150
100
50
0
-50
-100
-150
ppm



^{1}H NMR
DMSO-d$_6$
8.991
8.882
4.370
3.332
2.500
O_2N
Me
N
N
N
+
O
−
N
N
N
±
O
O
3a
58
39
2.1
122
119
53
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
ppm
38.108
39.059
2.065
122.129
119.032
52.958


13C NMR
DMSO-d6
166.008
138.837
133.541
130.018
128.560
121.094
117.804
41.128
40.992
40.854
40.715
40.577
40.437
40.299
38.412
O2N
Me
N
N
N
O
N
N
N
O
O
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


14N NMR
DMSO-d6
O2N
Me
N
N
N
O
N
N
N
O
O
3a
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-76.192
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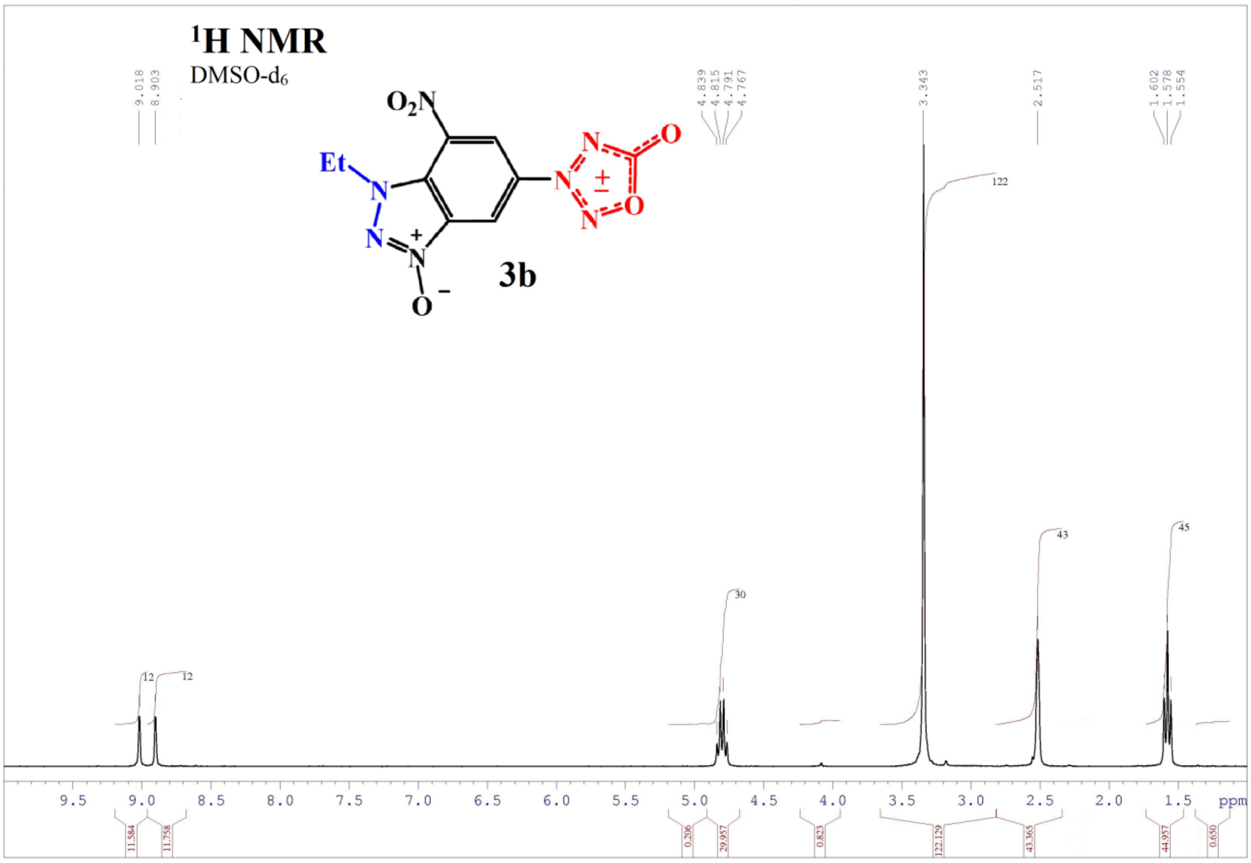
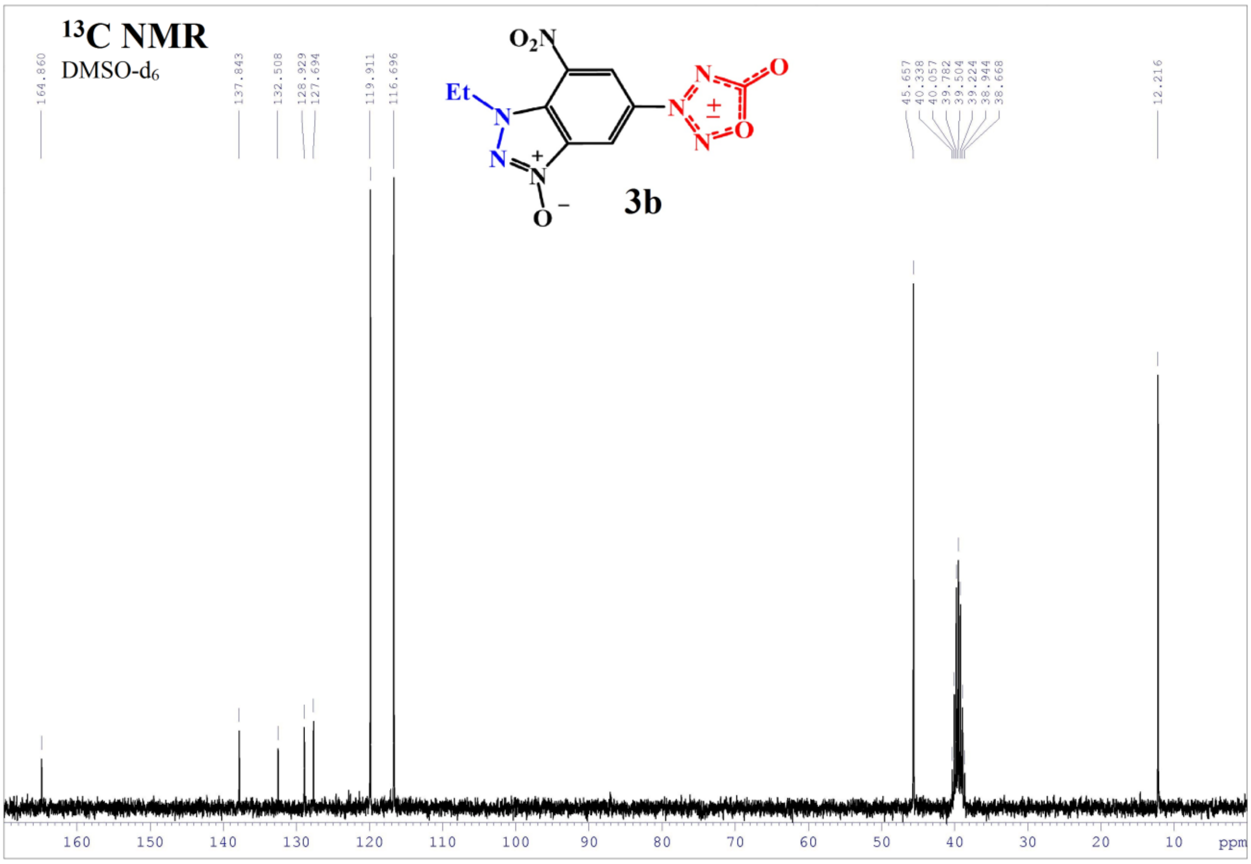
100
50
0
-50
-100
-150
ppm



^{1}H NMR
DMSO-d$_6$
9.018
8.903
4.839
4.815
4.791
4.767
3.343
2.517
1.602
1.578
1.554
O$_2$N
Et
N
N
N
O
+
−
N
N
N
O
O
±
3b
12
12
30
122
43
45
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
ppm
11.584
11.758
0.206
29.957
0.823
122.129
43.365
44.957
0.650



^{13}C NMR
DMSO-d$_6$
164.860
137.843
132.508
128.929
127.694
119.911
116.696
45.657
40.338
40.057
39.782
39.504
39.224
38.944
38.668
12.216
O$_2$N
Et
N
N
N
O
+
−
N
N
N
O
O
±
3b
160
150
140
130
120
110
100
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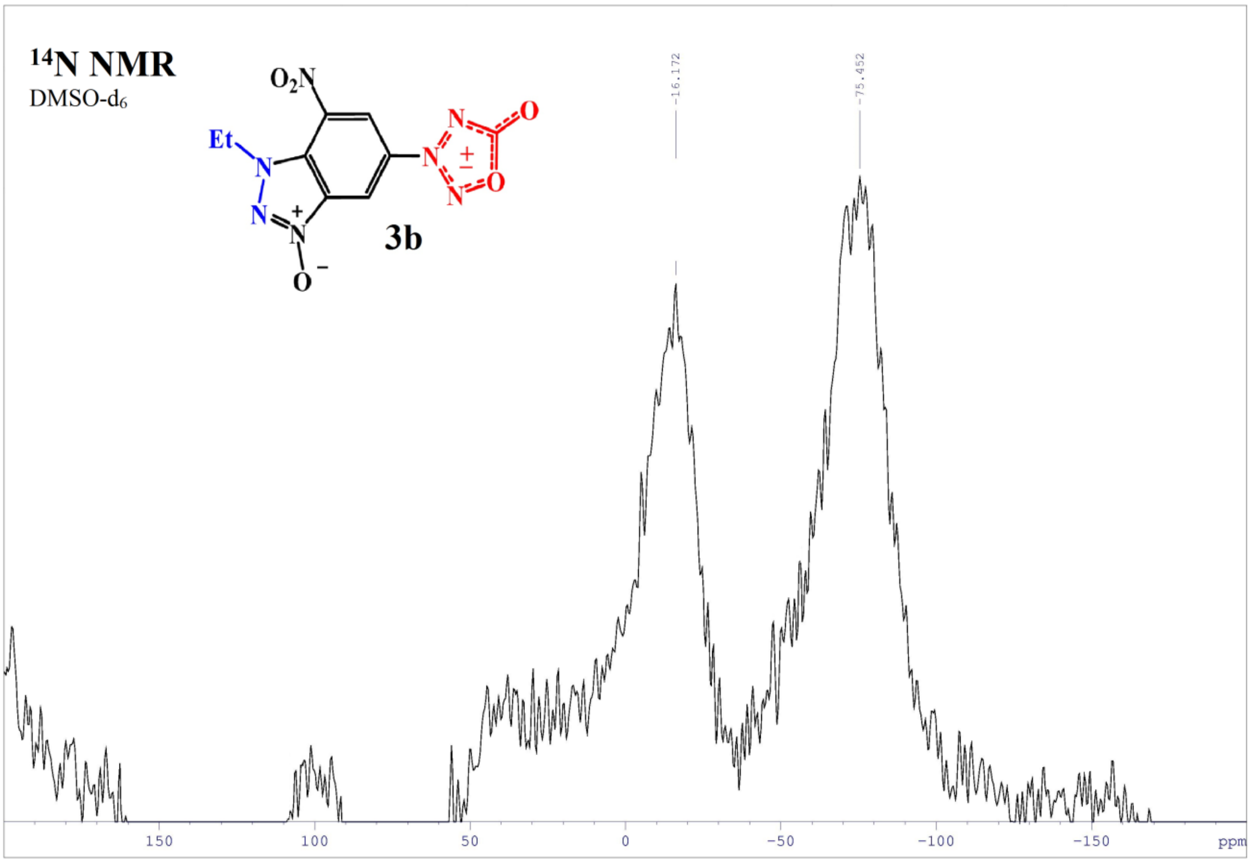
50
40
30
20
10
ppm



^{14}N NMR
DMSO-d$_6$
3b
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-75.452
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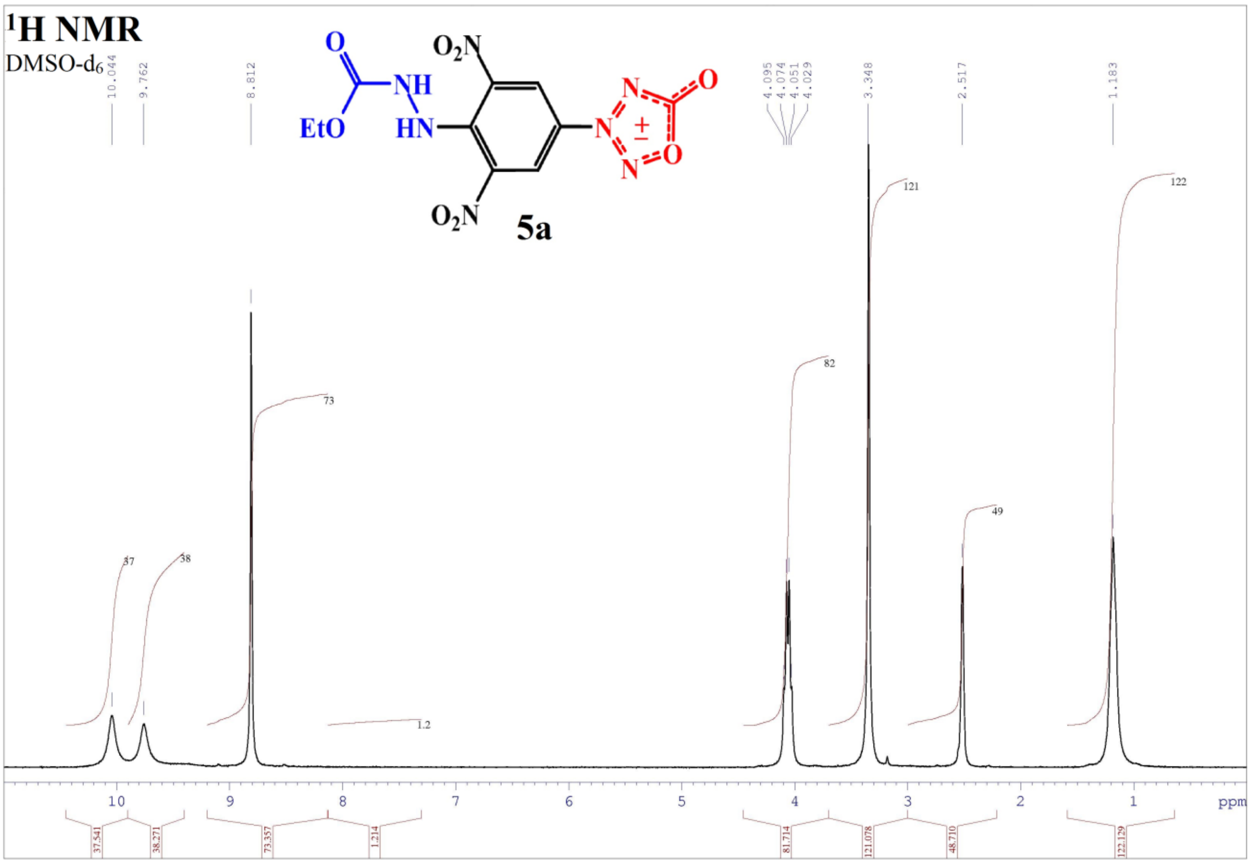
100
50
0
-50
-100
-150
ppm



^{1}H NMR
DMSO-d$_6$
5a
10.044
9.762
8.812
4.095
4.074
4.051
4.029
3.348
2.517
1.183
37
38
73
1.2
82
121
49
122
10
9
8
7
6
5
4
3
2
1
ppm
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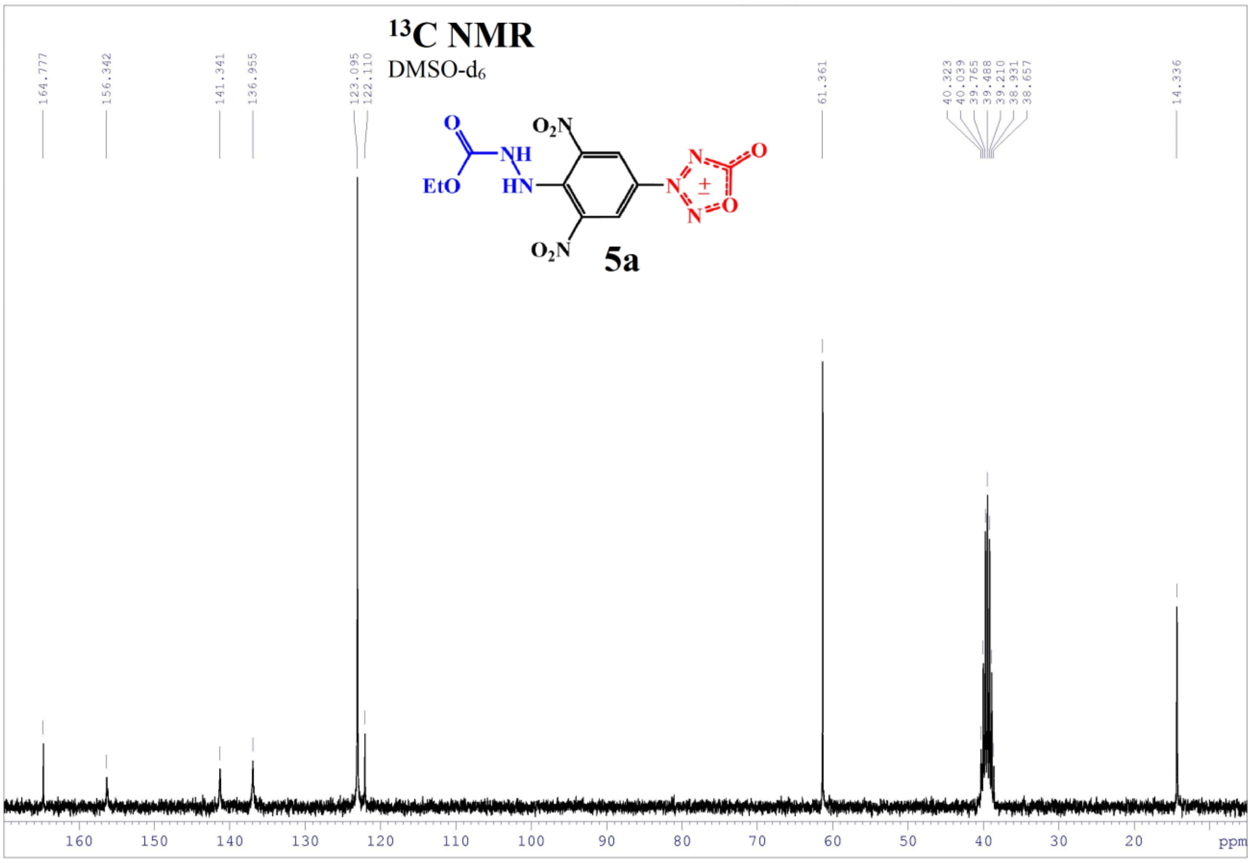
38.271
73.357
1.214
81.714
121.078
48.710
122.129



^{13}C NMR
DMSO-d$_6$
164.777
156.342
141.341
136.955
123.095
122.110
61.361
40.323
40.039
39.765
39.488
39.210
38.931
38.657
14.336
O
EtO
NH
HN
O$_2$N
O$_2$N
N
N
N
O
O
±
5a
160
150
140
130
120
110
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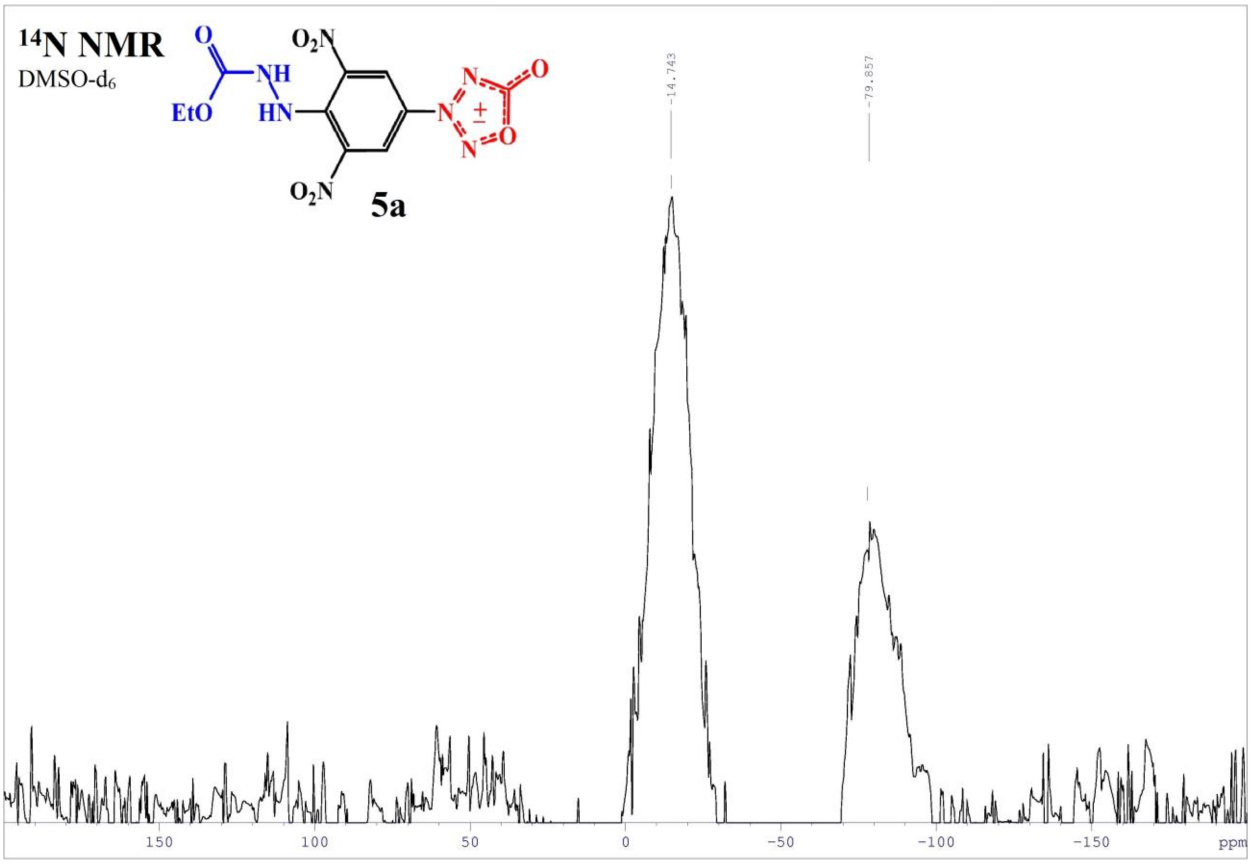
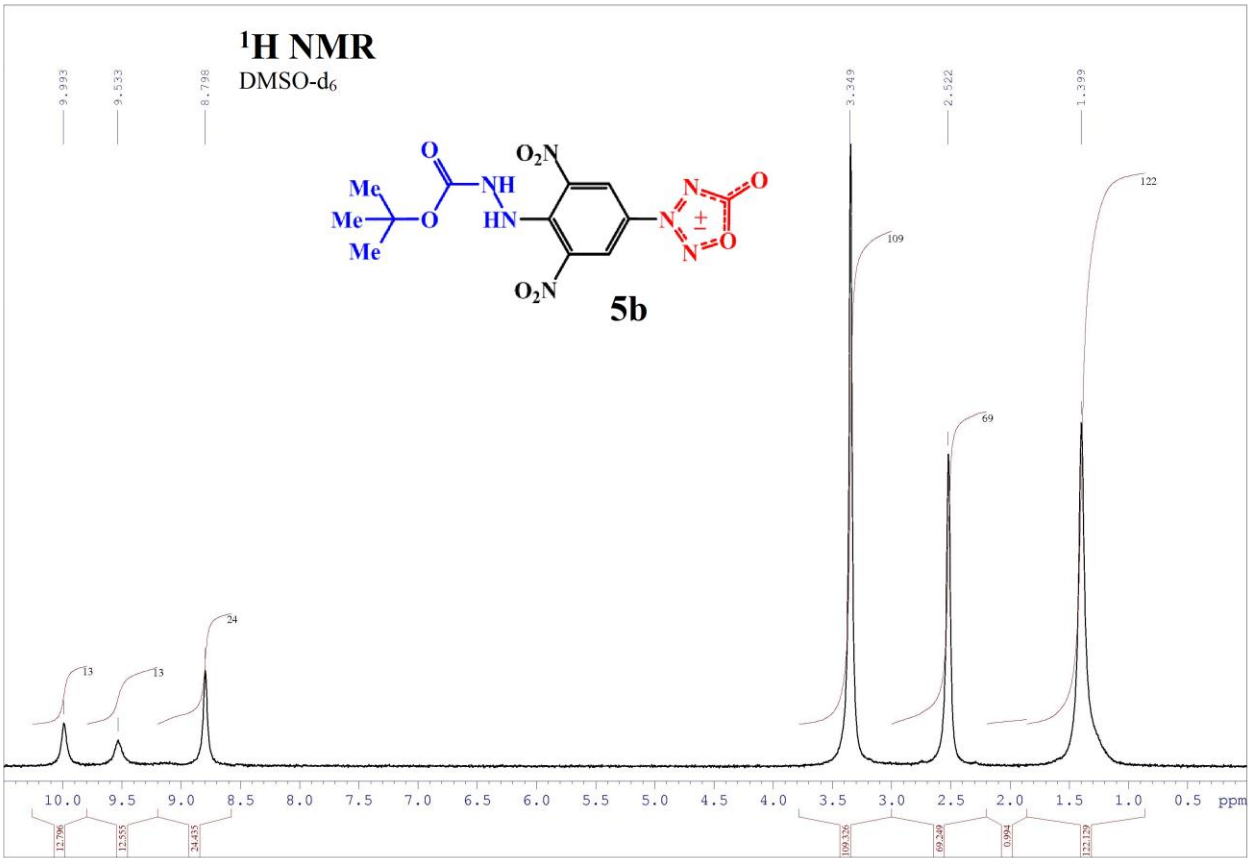
60
50
40
30
20
ppm



^{14}N NMR
DMSO-d$_6$
O
EtO
NH
HN
O$_2$N
O$_2$N
N
N
N
O
O
±
5a
-14.743
-79.857
150
100
50
0
-50
-100
-150
ppm


^{1}H NMR
DMSO-d$_6$
9.993
9.533
8.798
3.349
2.522
1.399
13
13
24
109
69
122
Me
Me
Me
O
O
NH
HN
O_2N
O_2N
N
N
N
O
O
±
5b
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
ppm
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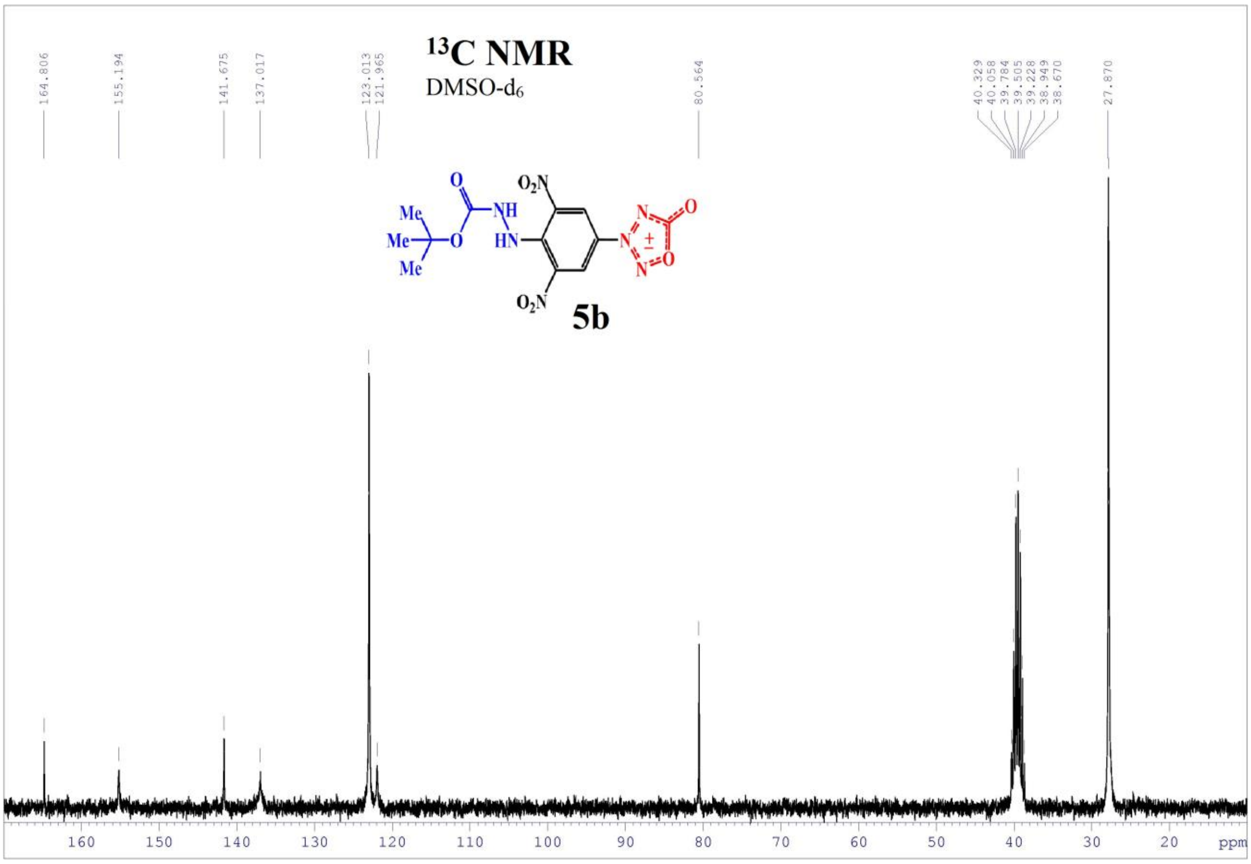
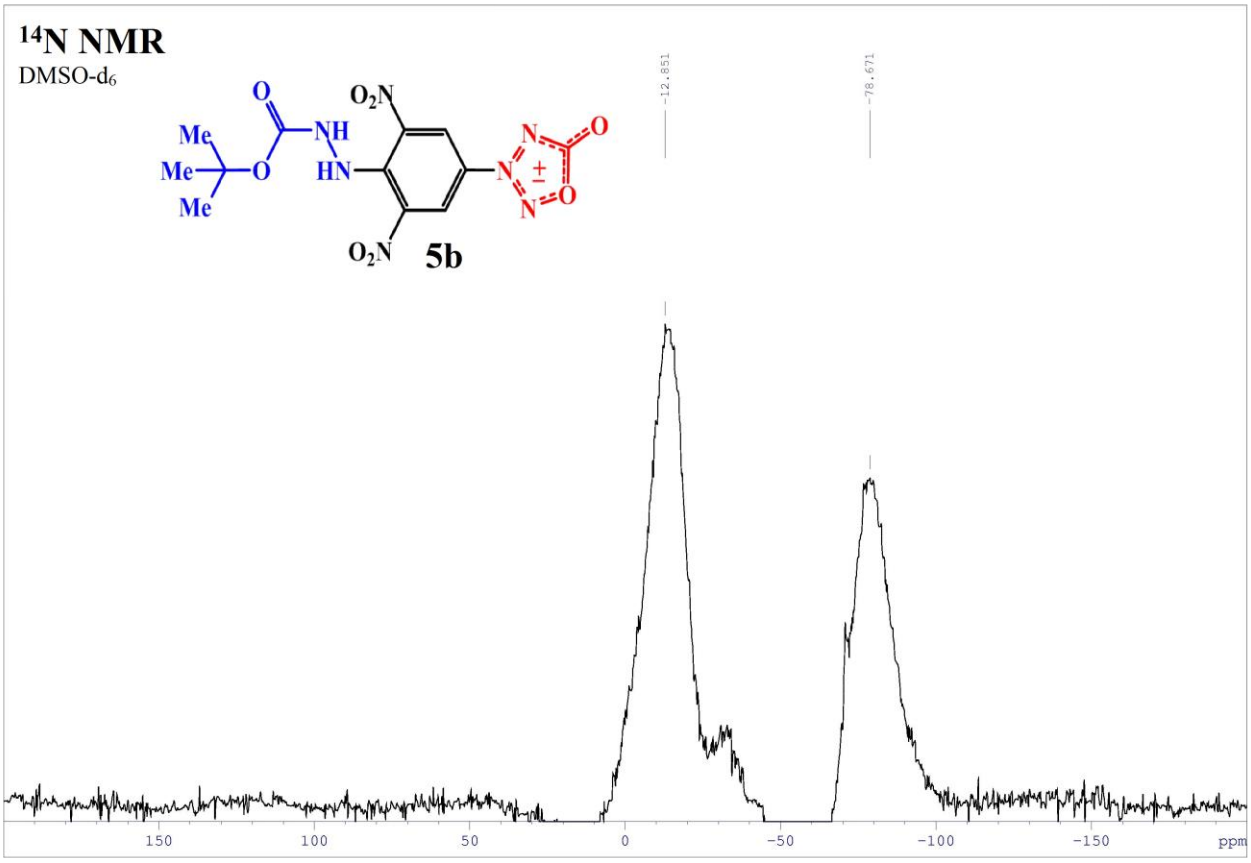
12.555
24.435
109.326
69.249
0.994
122.129


^{13}C NMR
DMSO-d$_6$
164.806
155.194
141.675
137.017
123.013
121.965
80.564
40.329
40.058
39.784
39.505
39.228
38.949
38.670
27.870
Me
Me
Me
O
O
NH
HN
O_2N
O_2N
N
N
N
O
O
±
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


^{14}N NMR
DMSO-d$_6$
Me
Me
Me
O
O
NH
HN
O$_2$N
O$_2$N
N
N
N
O
O
±
5b
-12.851
-78.671
150
100
50
0
−50
−100
−150
ppm