Electronic Supplementary Information

Energetic salts based on 1-methoxy-5-nitroiminotetrazole

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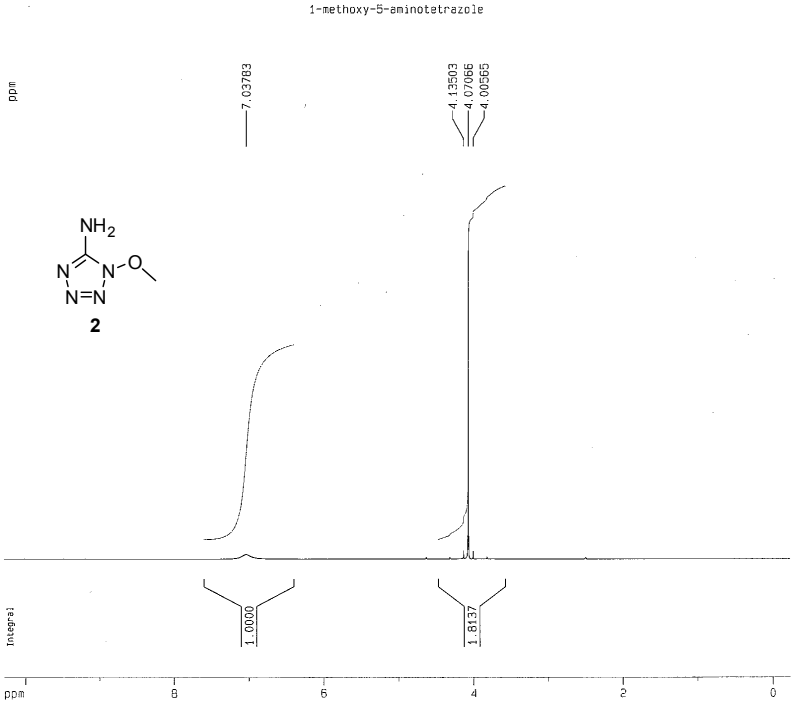
DSC, IR, ^{1}H NMR, ^{13}C NMR ^{15}N NMR Spectra

^{1}H NMR

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FIDRES            0.094190 Hz
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TE                 302.0 K
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PL1                  3.00 dB
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1D NMR plot parameters
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CY                    8.00 cm
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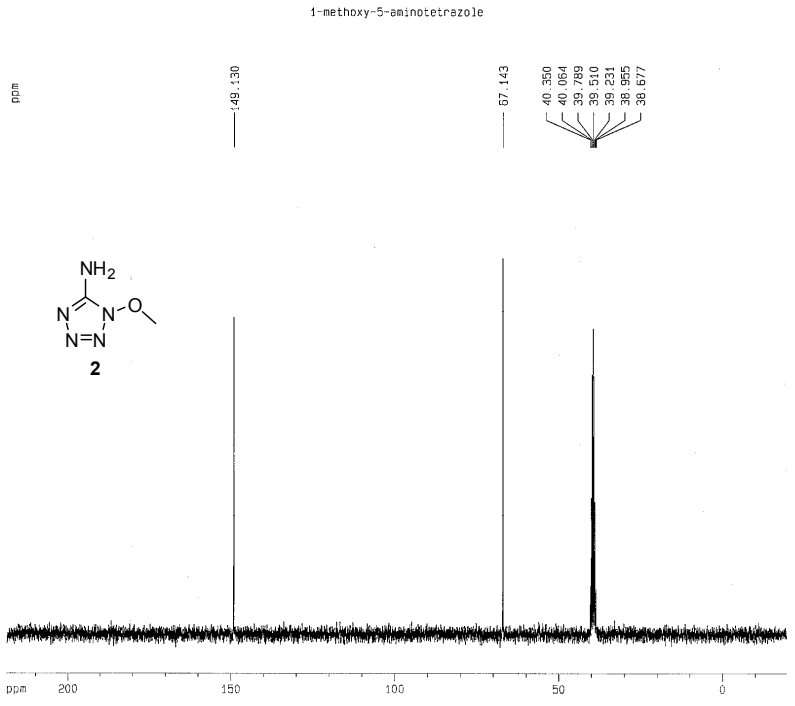
^{13}C NMR

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RG                   812.7
DW                27.800 usec
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TE                 303.4 K
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d11             0.03000000 sec
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MCREST          0.00000000 sec
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P1                  8.70 usec
PL1                  8.00 dB
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======== CHANNEL f2 ========
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PL12                22.17 dB
PL13                24.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
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1D NMR plot parameters
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F1               16512.11 Hz
F2P                -19.525 ppm
F2               -1473.50 Hz
PPMCM            11.91609 ppm/cm
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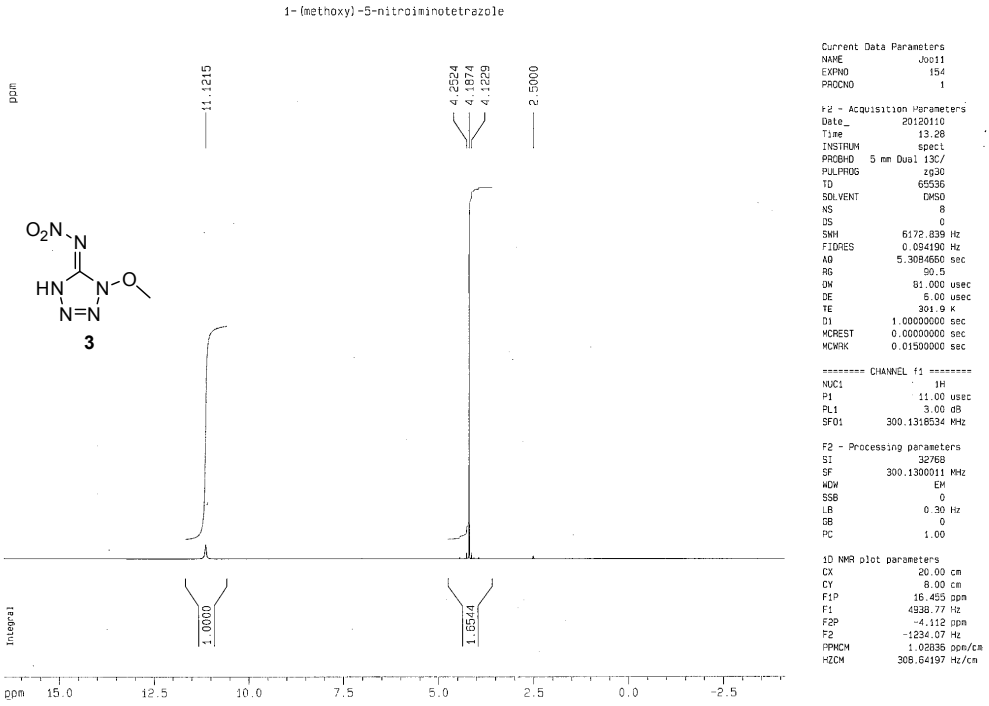
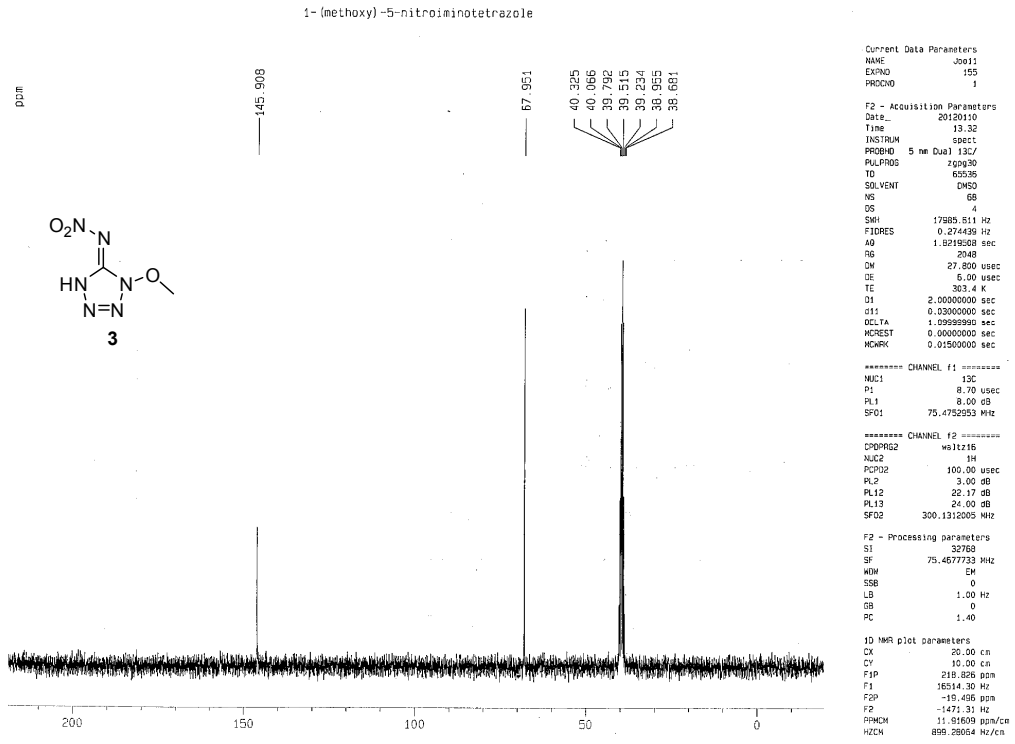
^{1}H NMR



^{13}C NMR



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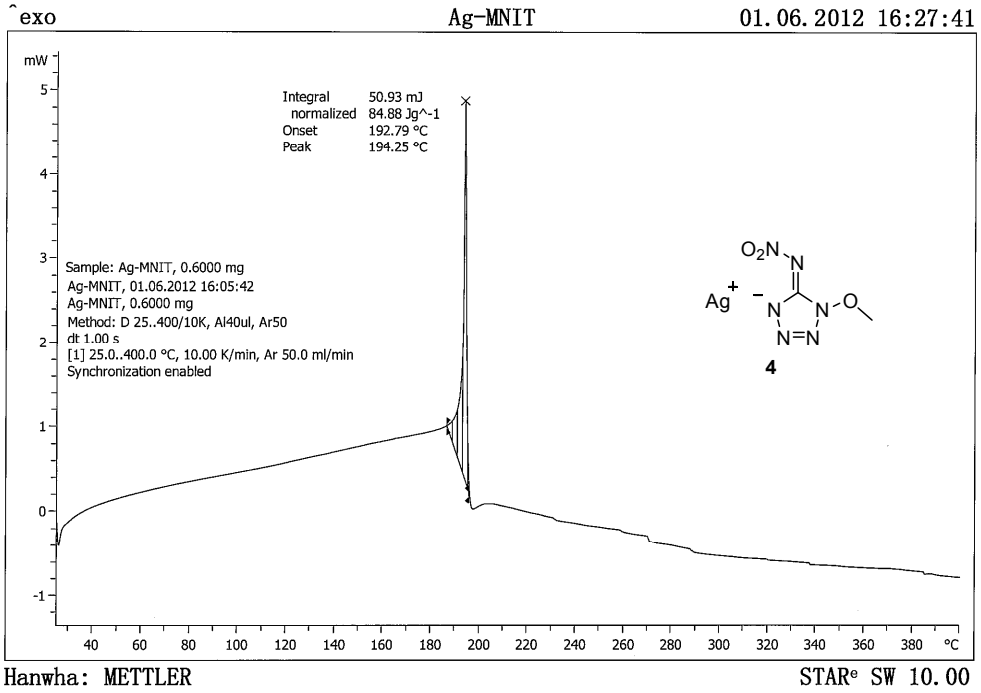

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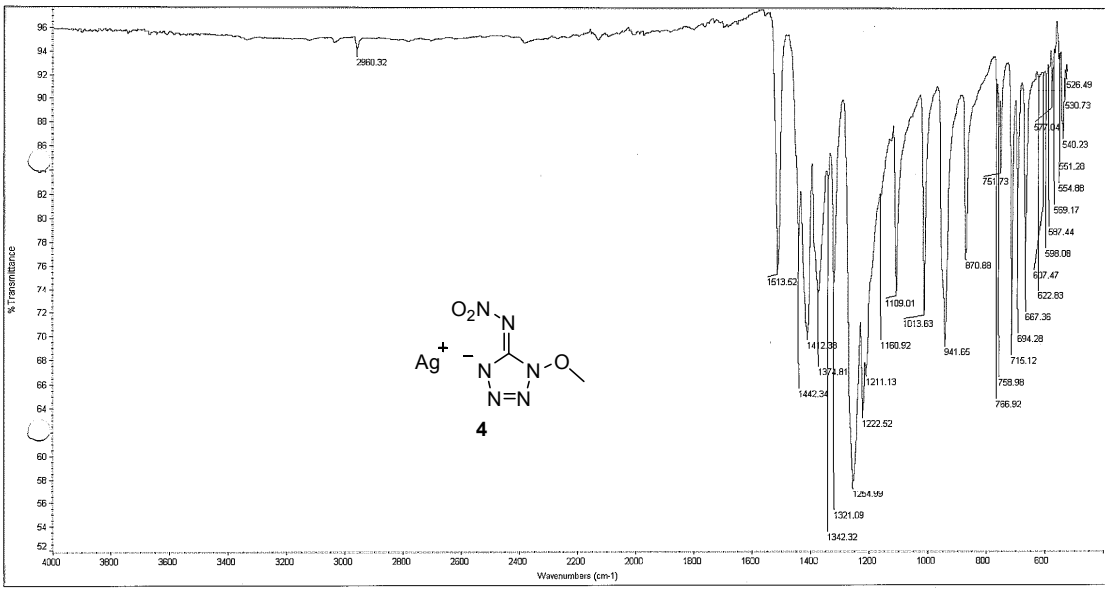

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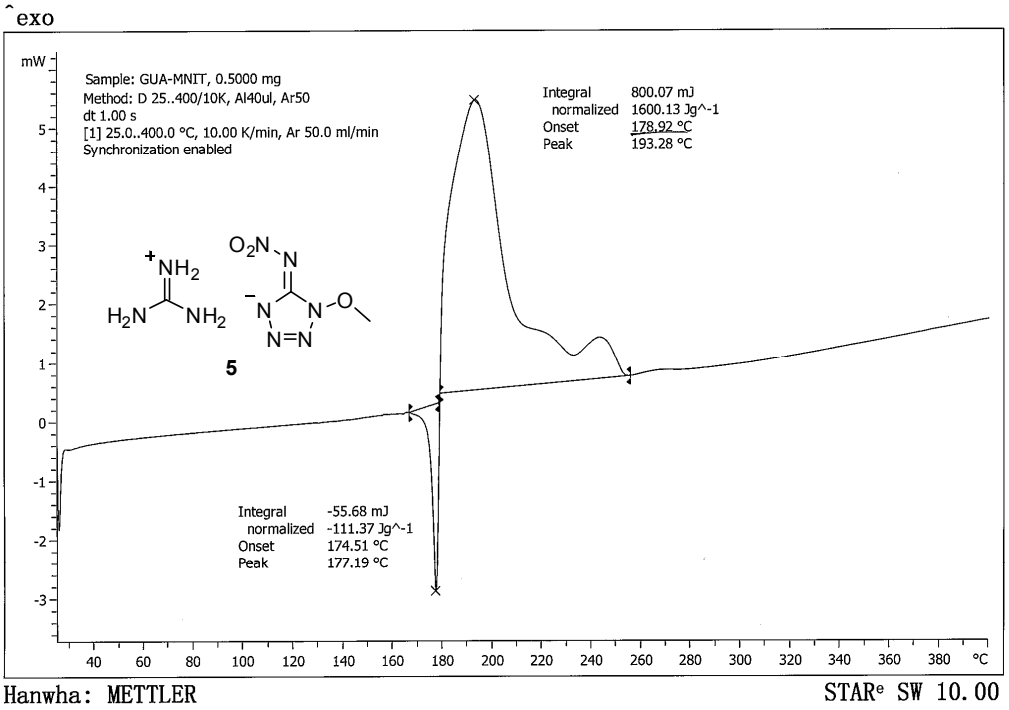

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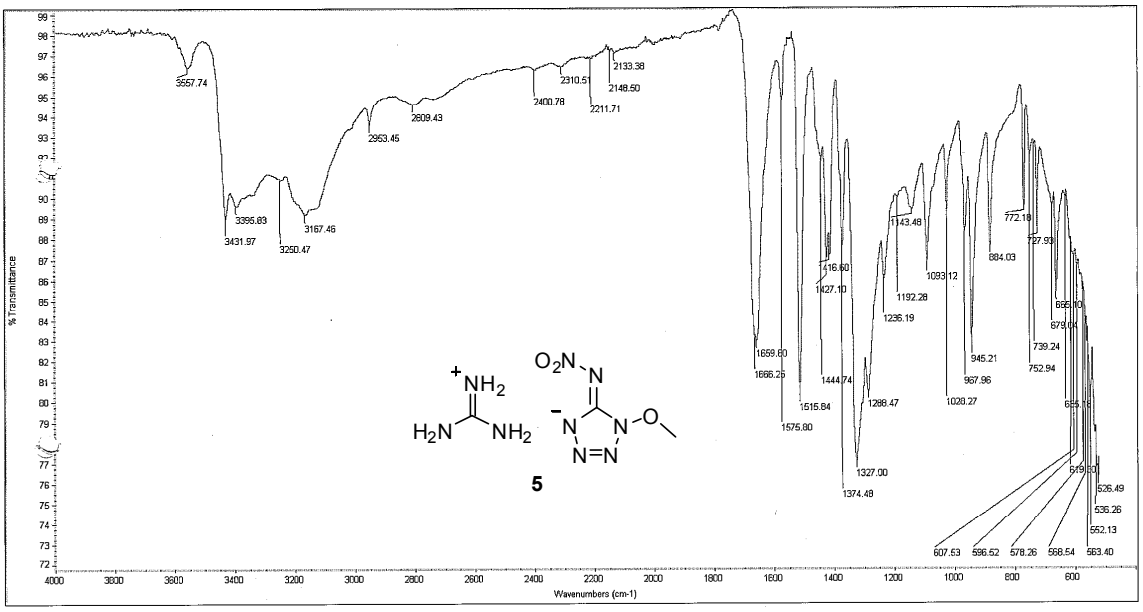
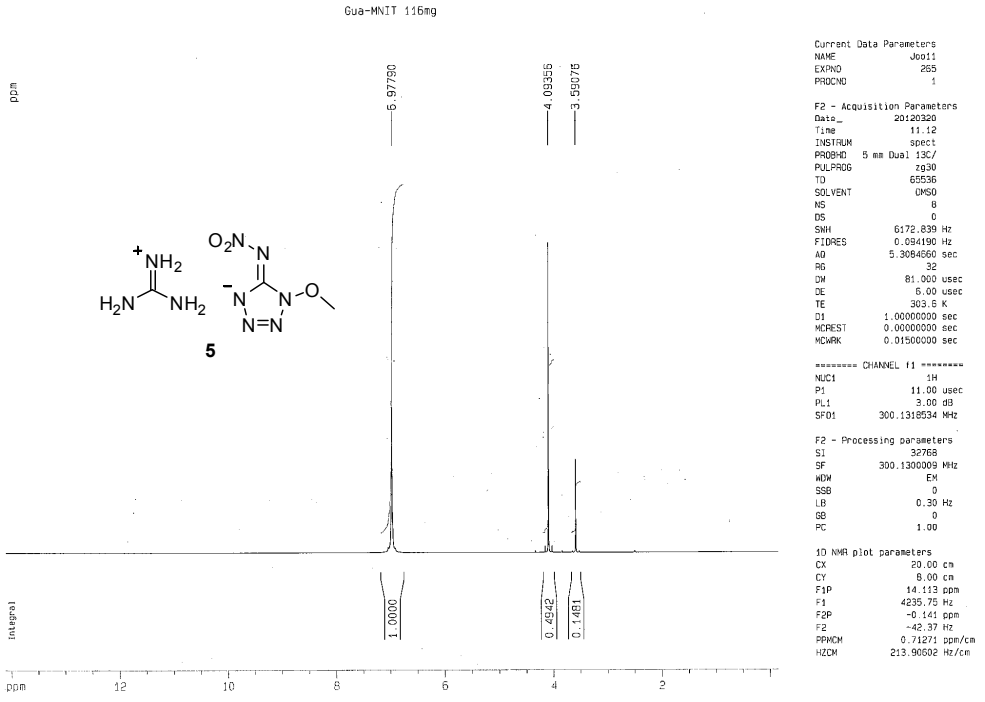


^{1}H NMR



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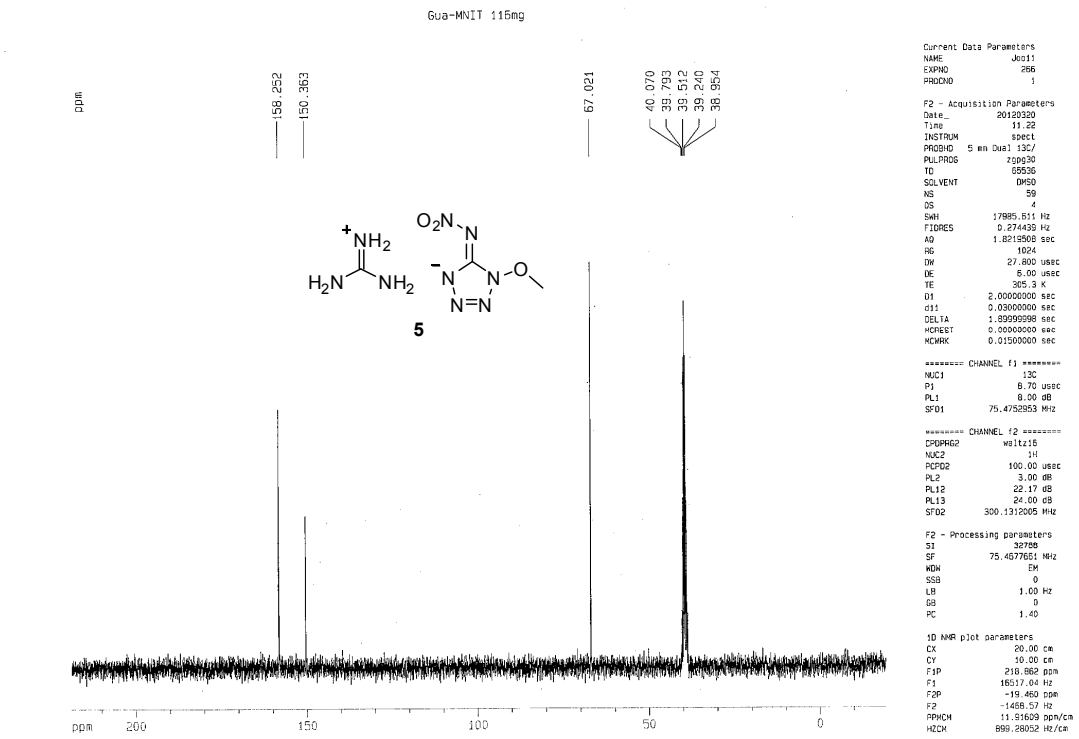
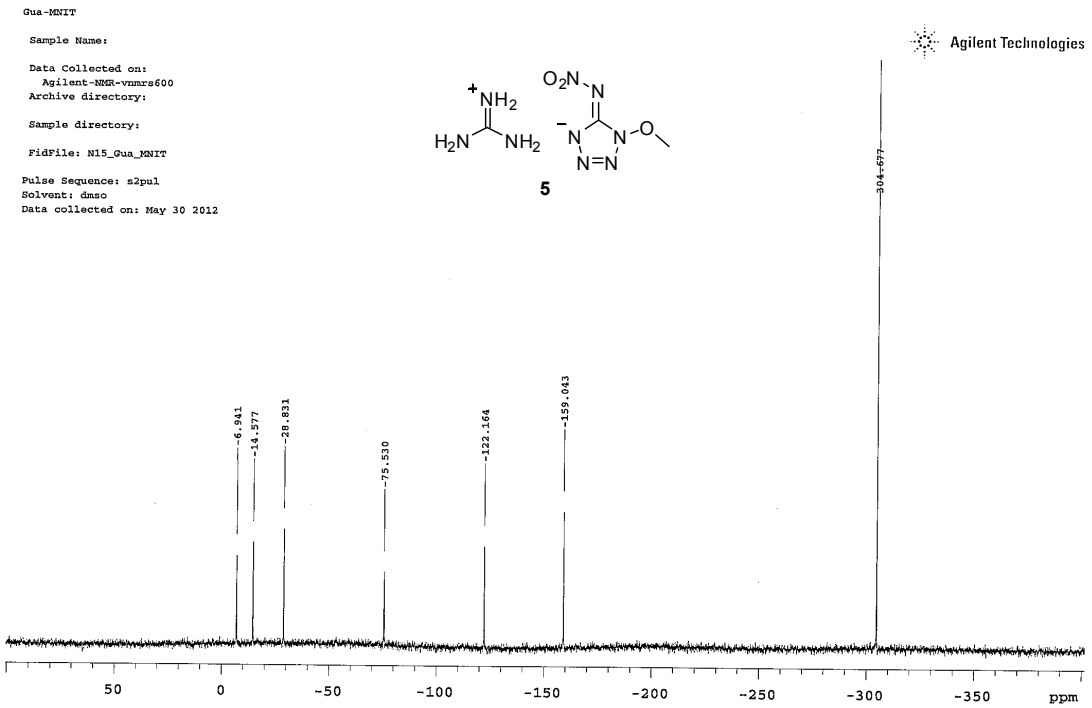


^{15}N NMR



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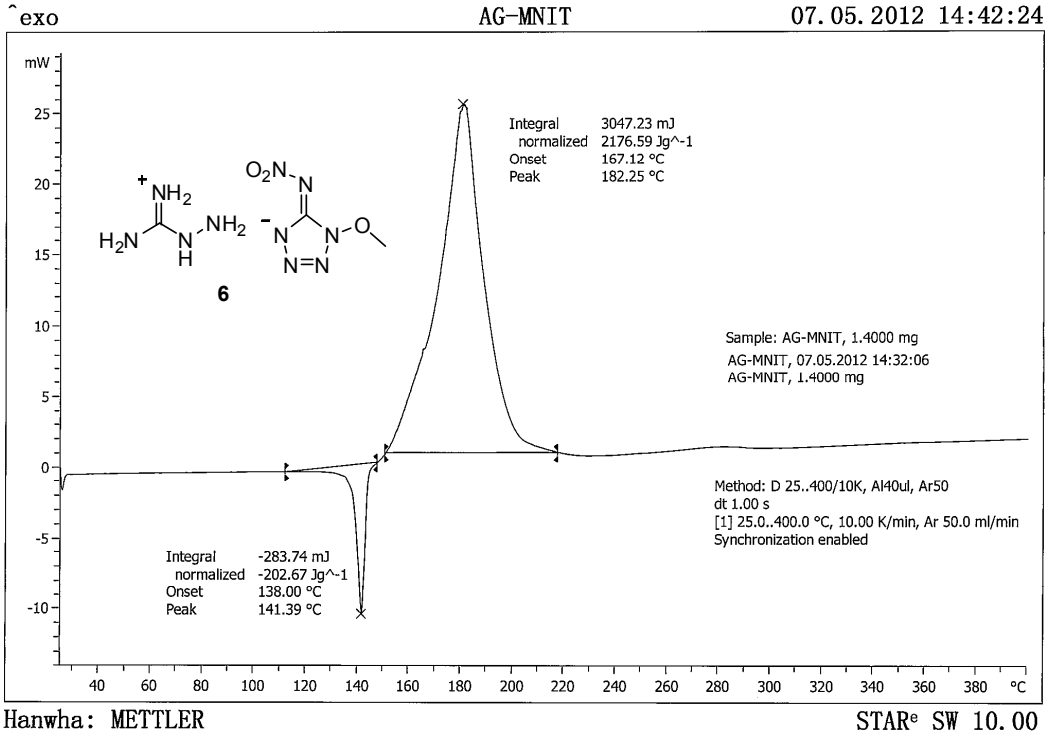

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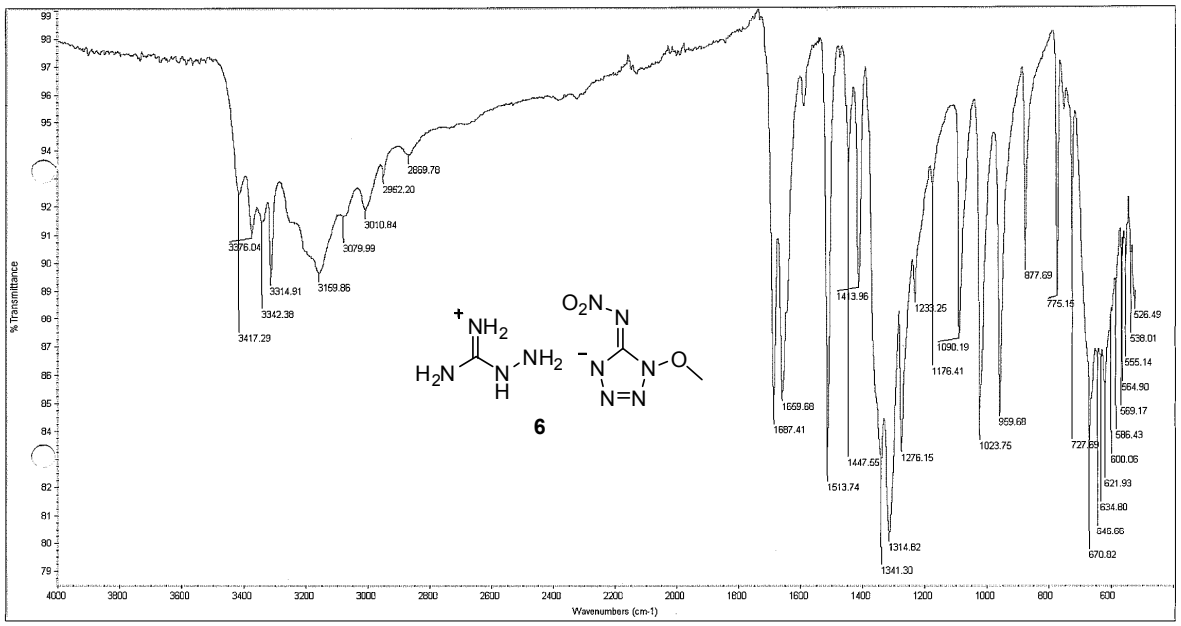

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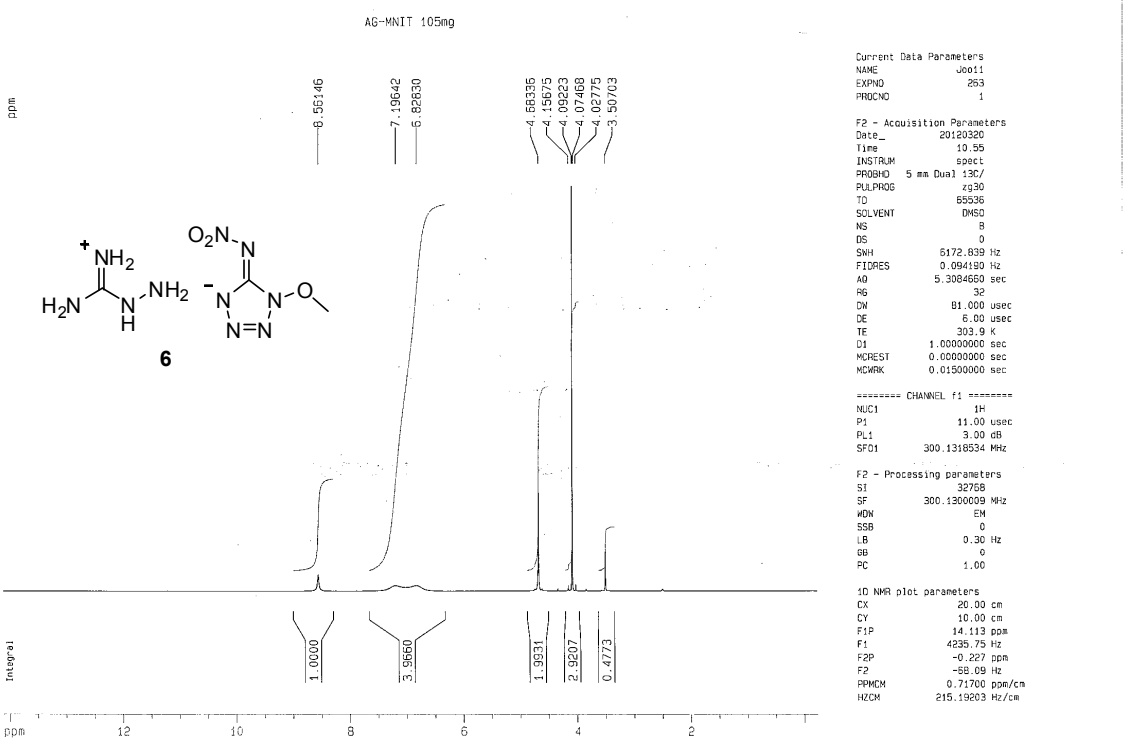

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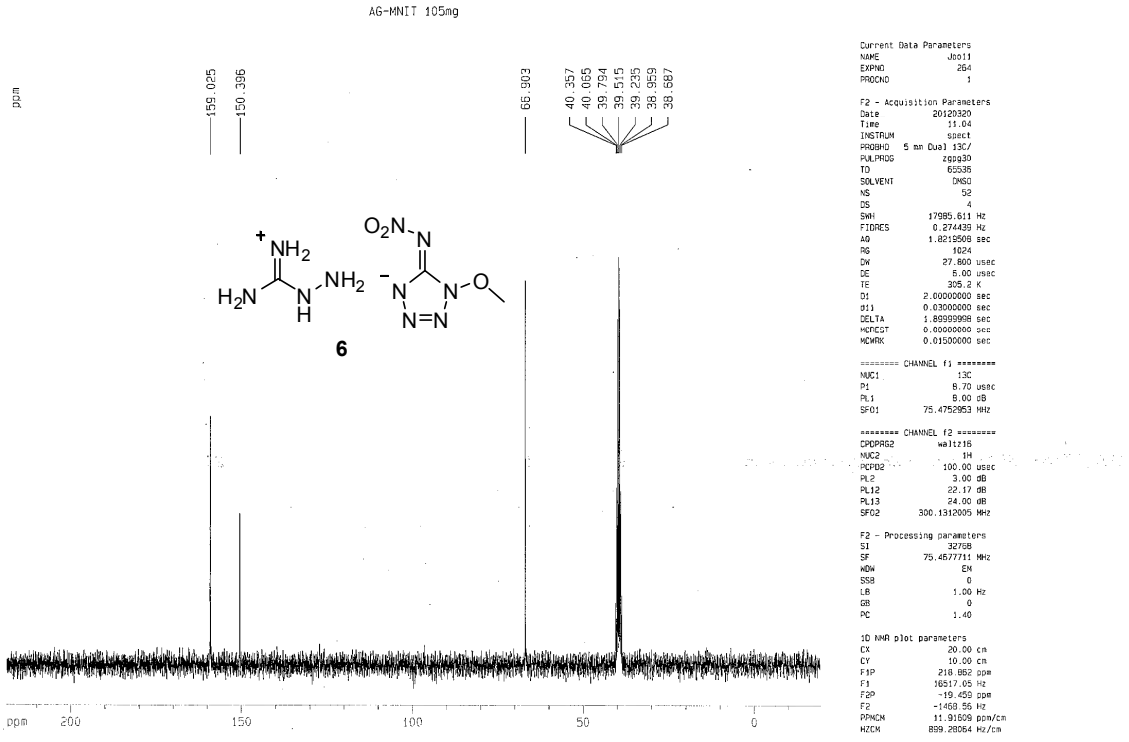

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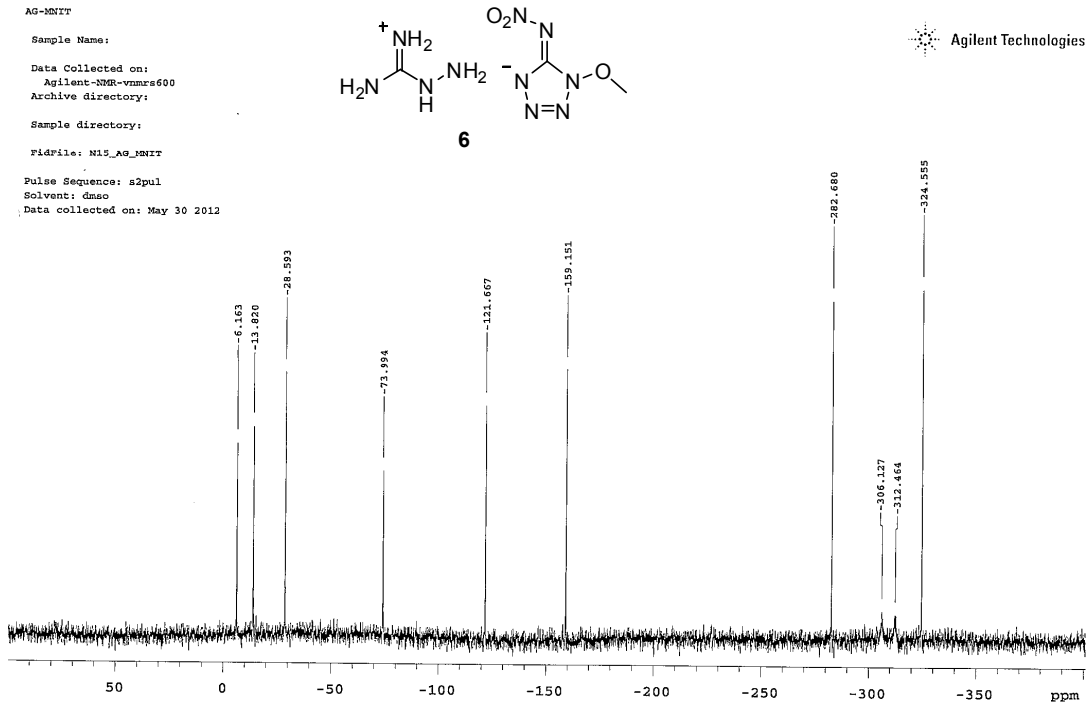

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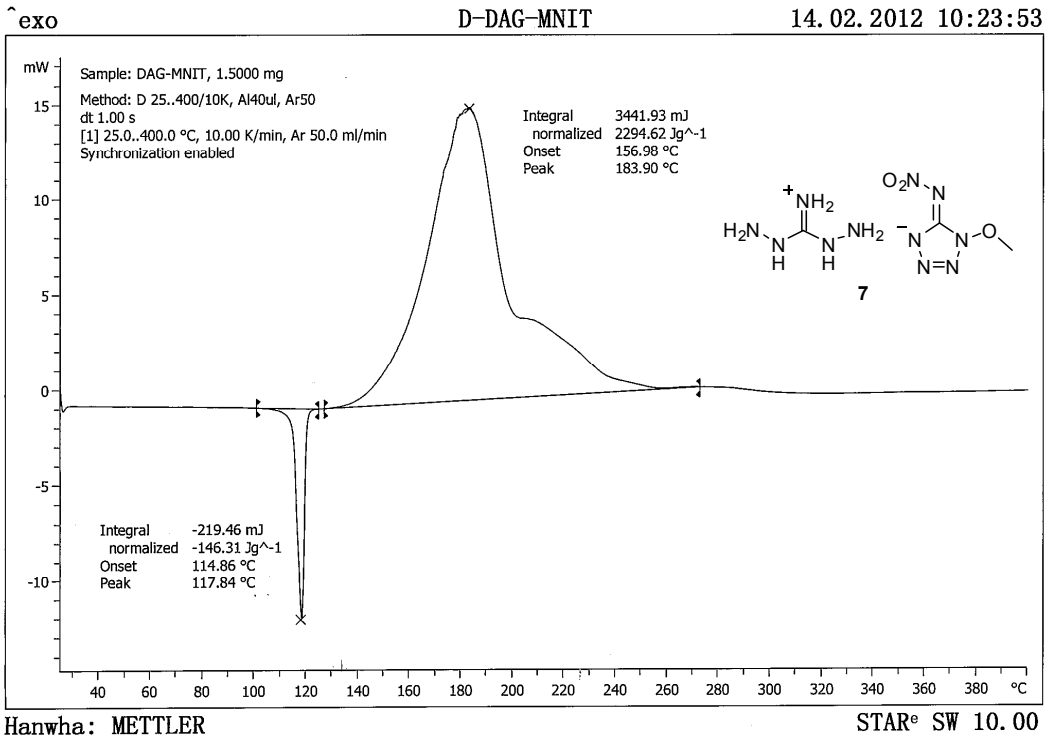

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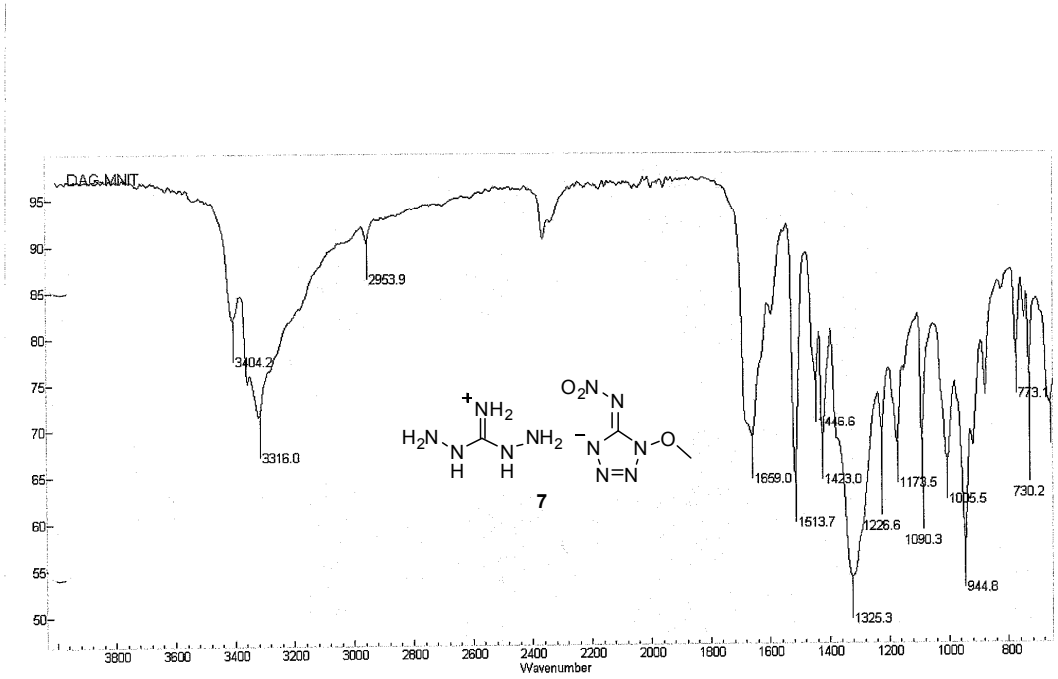

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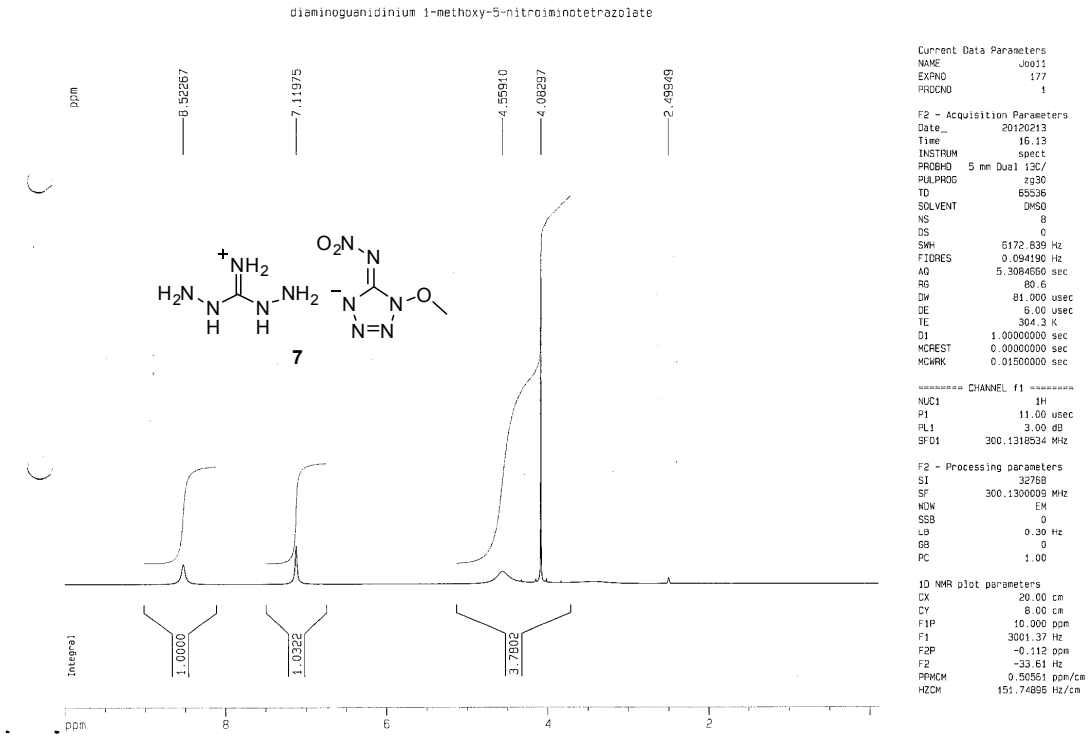


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SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084660 sec
RG                     80.6
DW                81.000 usec
DE                 6.00 usec
TE                 304.3 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 11.00 usec
PL1                 3.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF          300.1300009 MHz
WDW                     EM
SSB                      0
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GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                    8.00 cm
F1P                 10.000 ppm
F1                3001.37 Hz
F2P                -0.112 ppm
F2                 -33.61 Hz
PPMCM             0.50561 ppm/cm
HZCM            151.74896 Hz/cm
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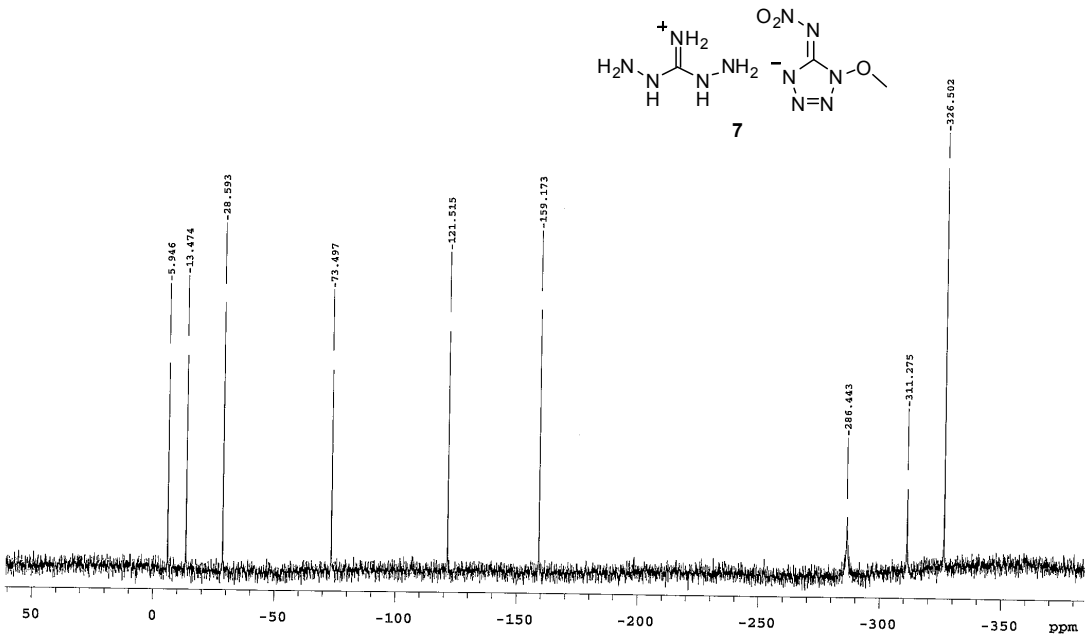
^{15}N NMR



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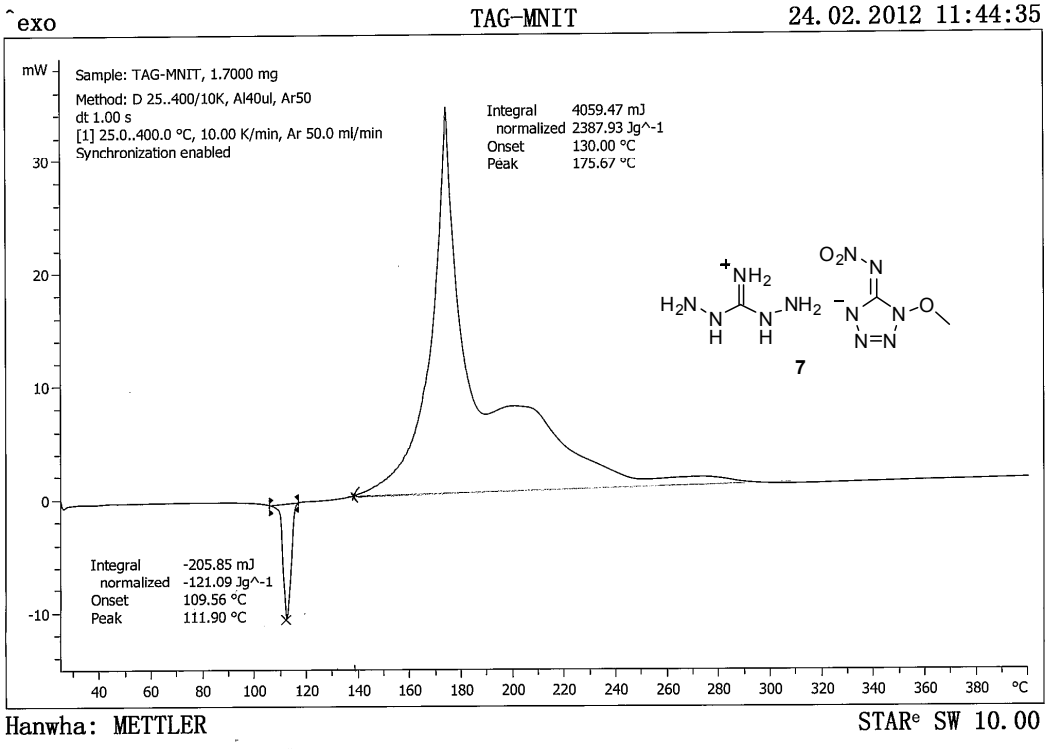

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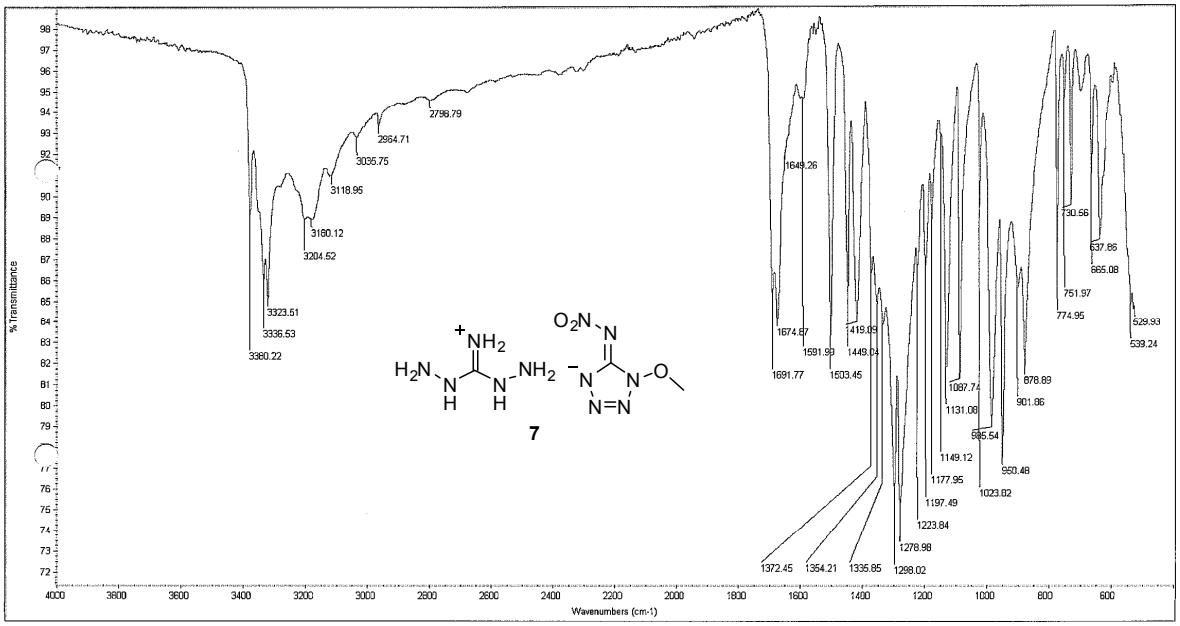
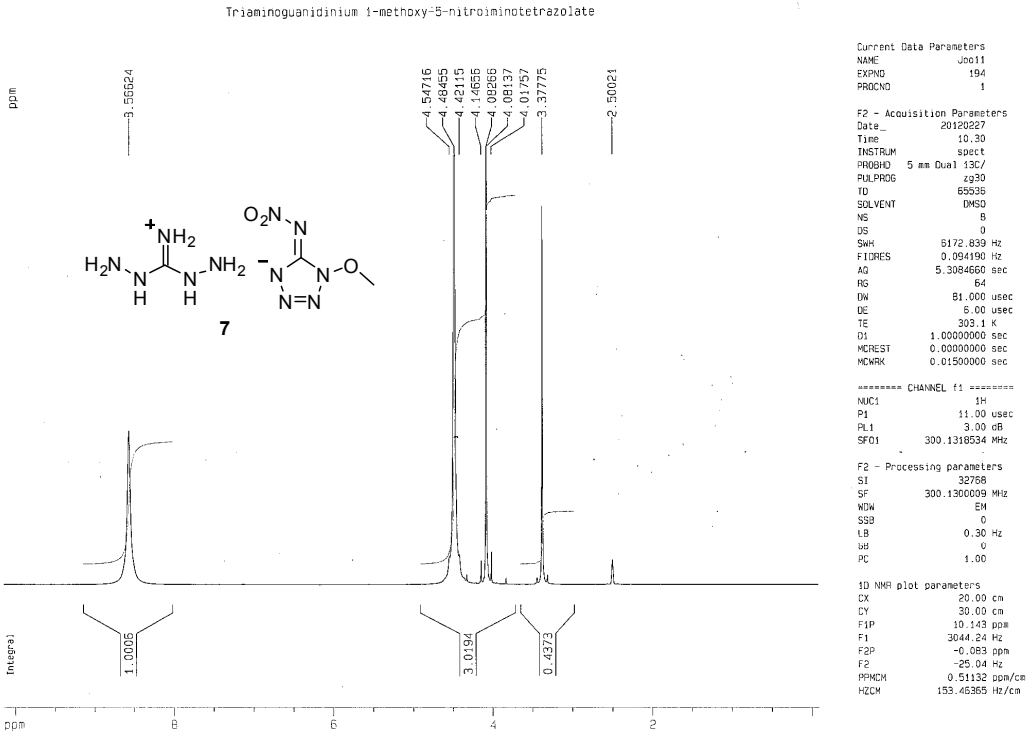
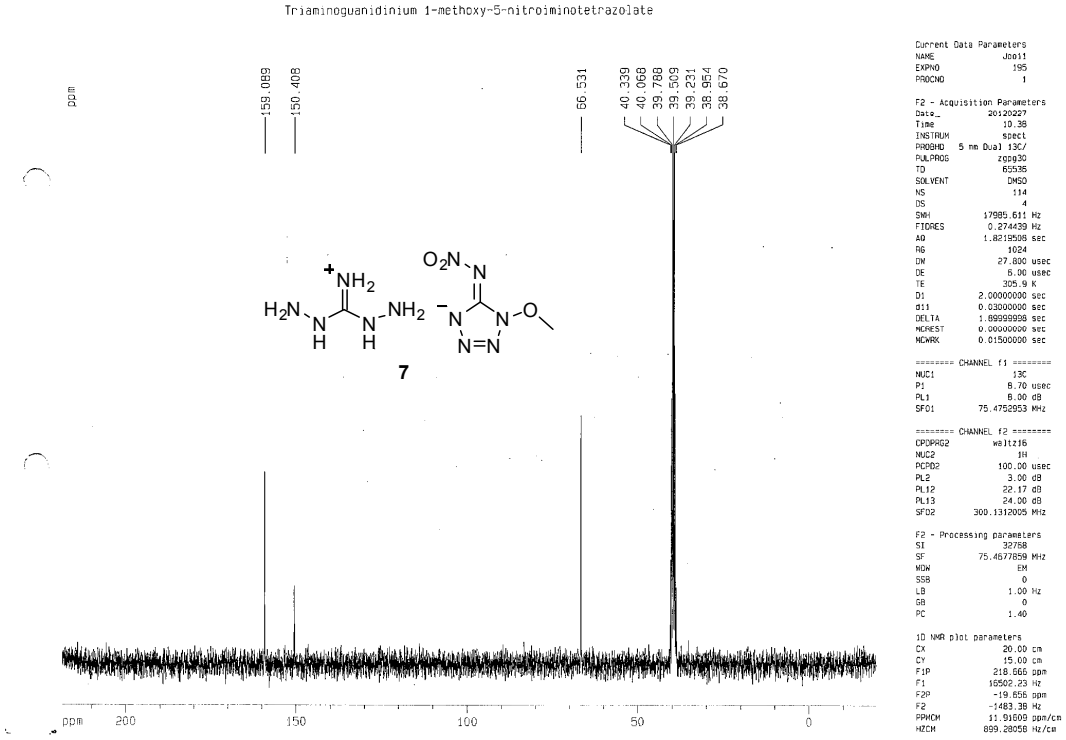


^{1}H NMR



^{13}C NMR



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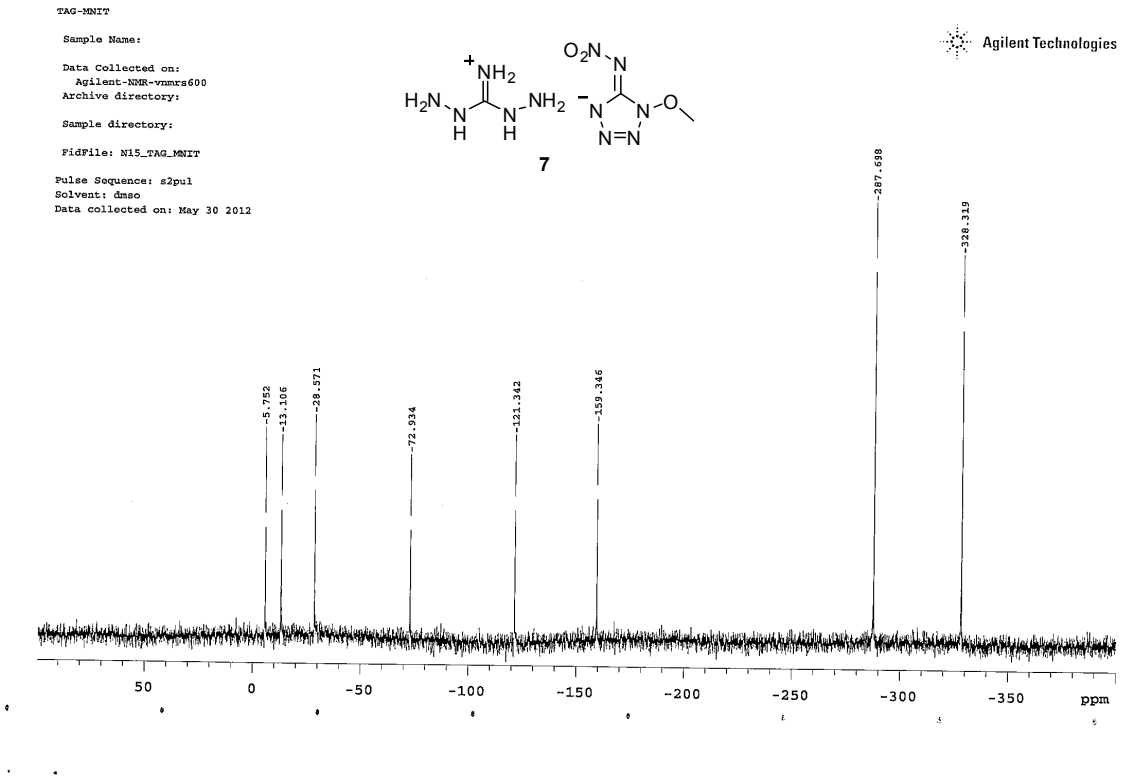

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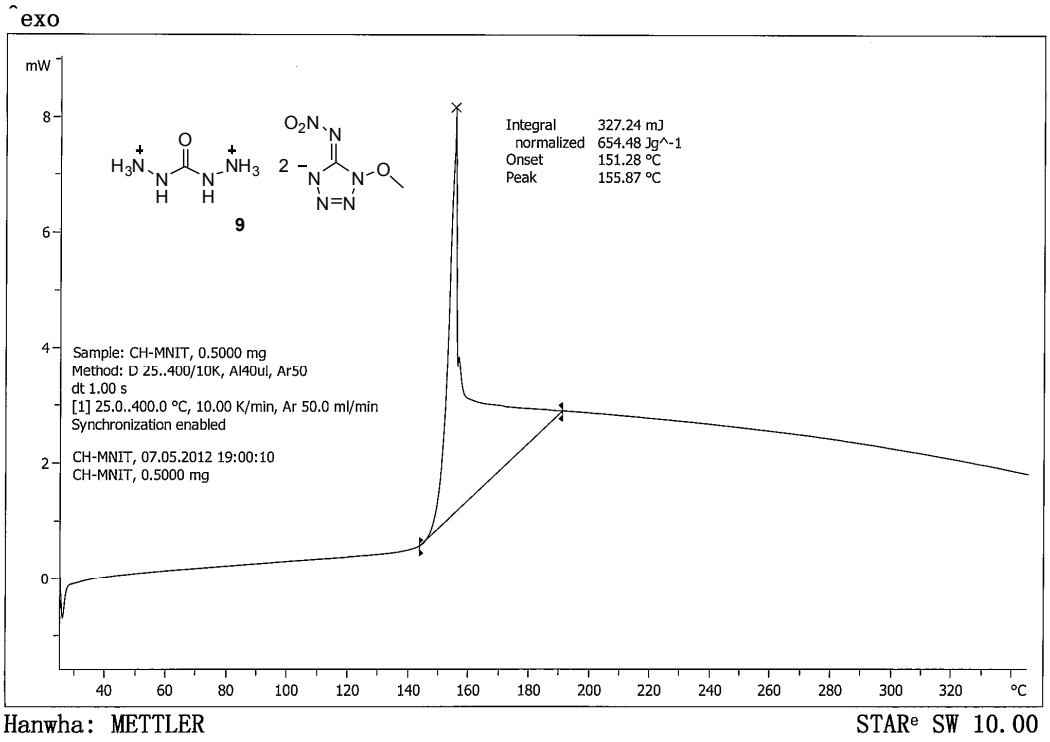

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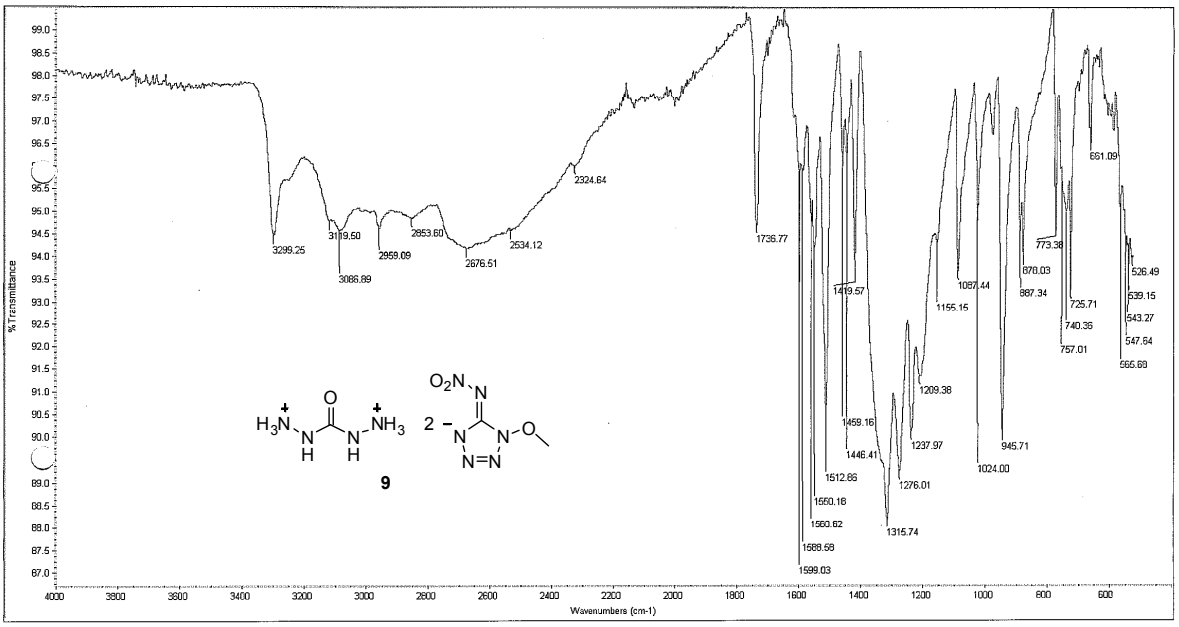

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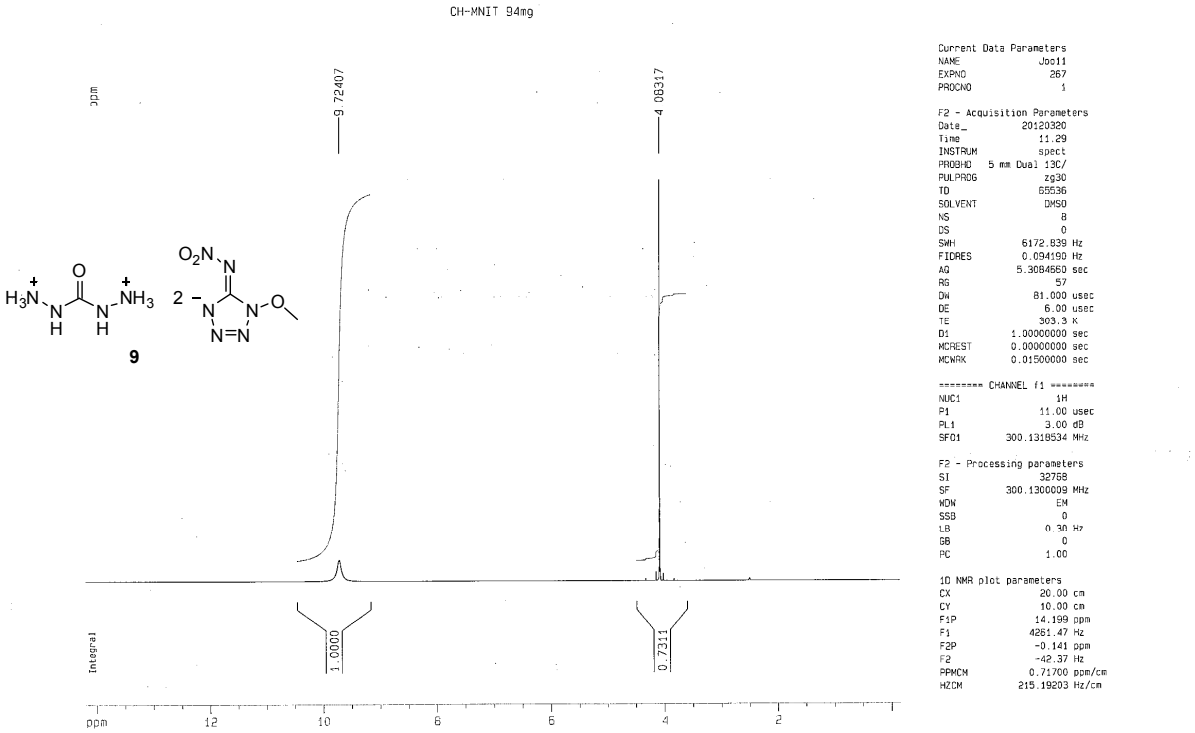

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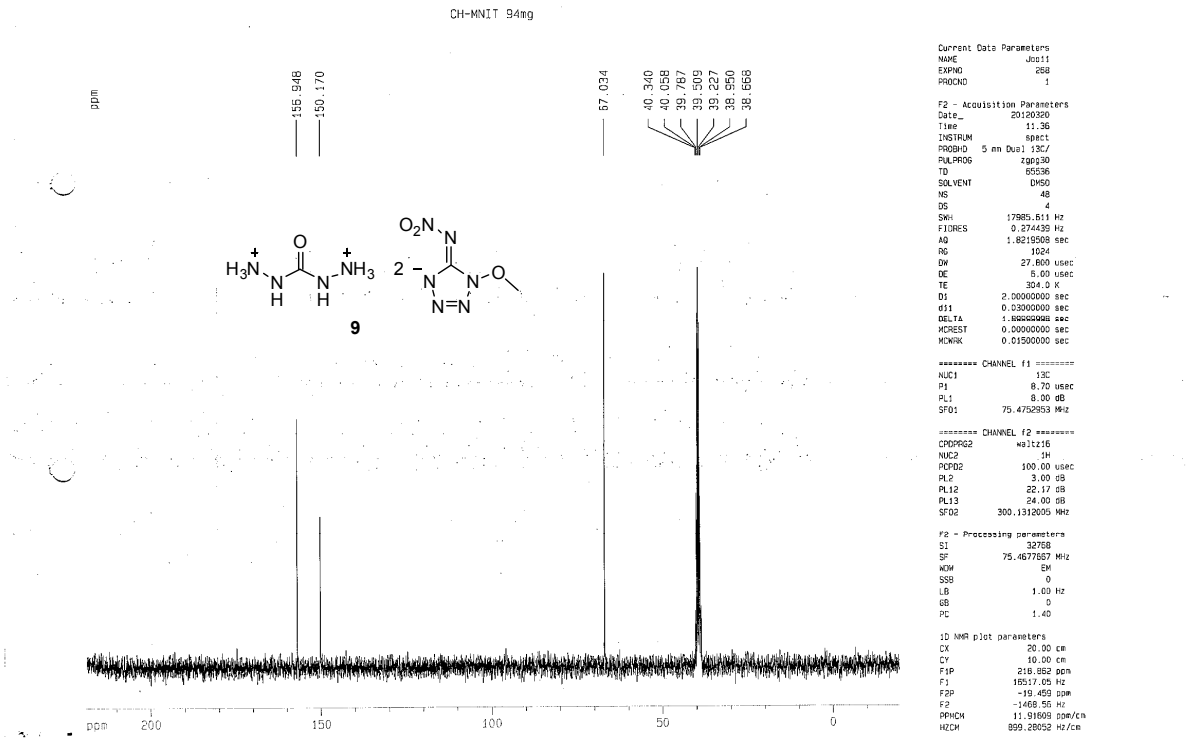

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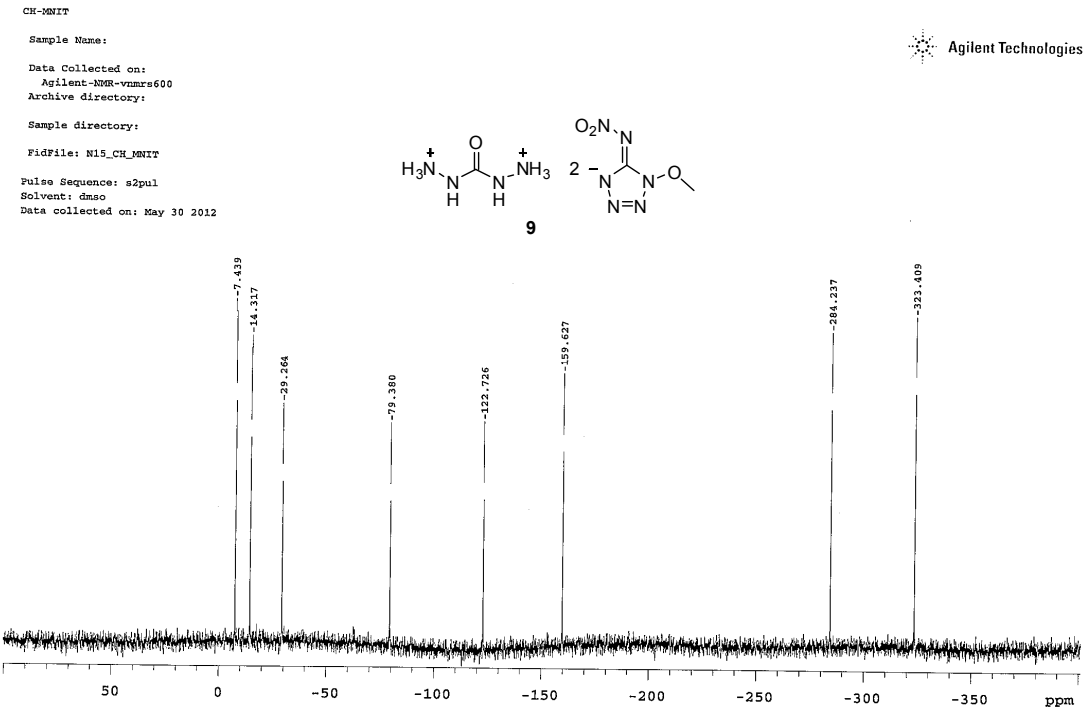

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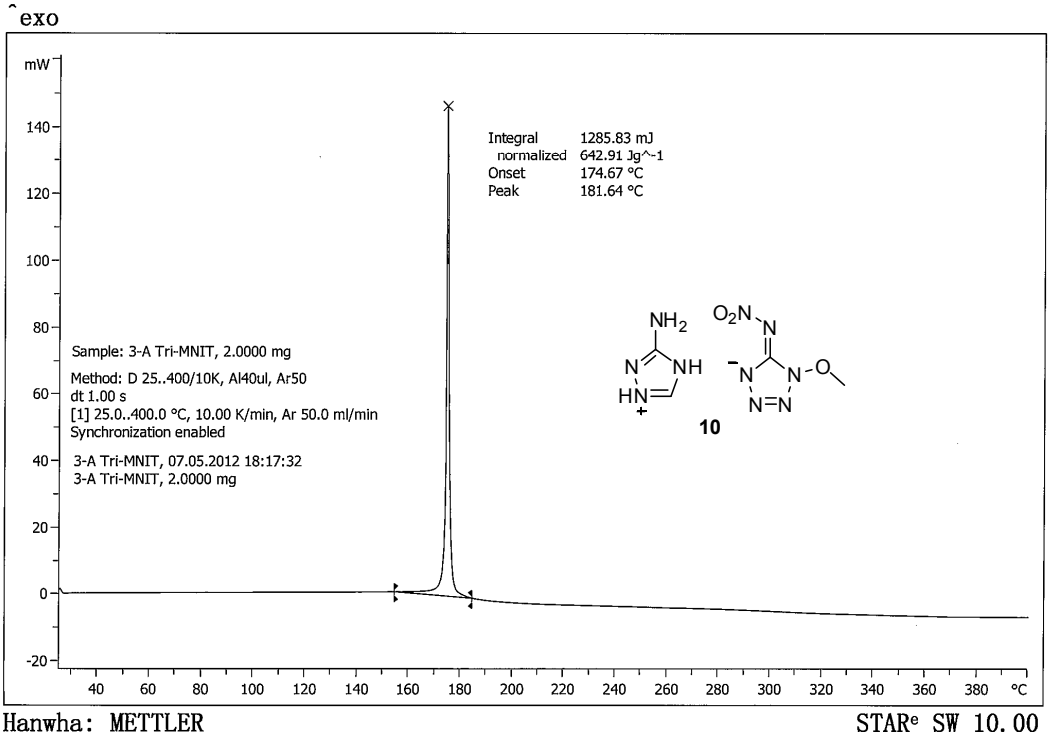

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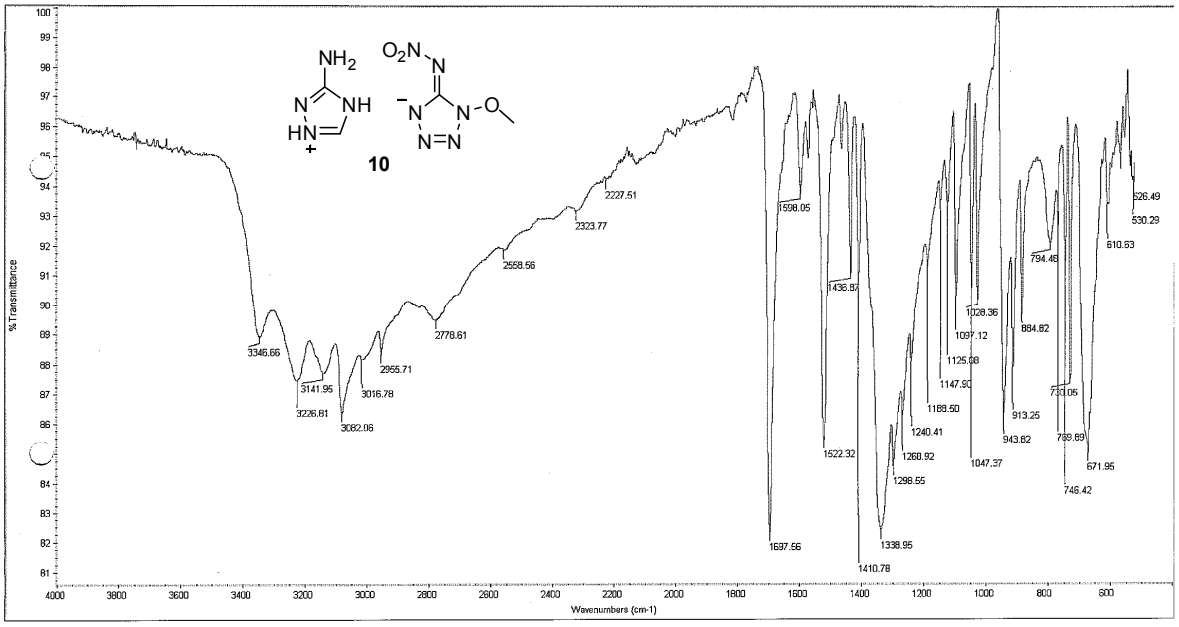

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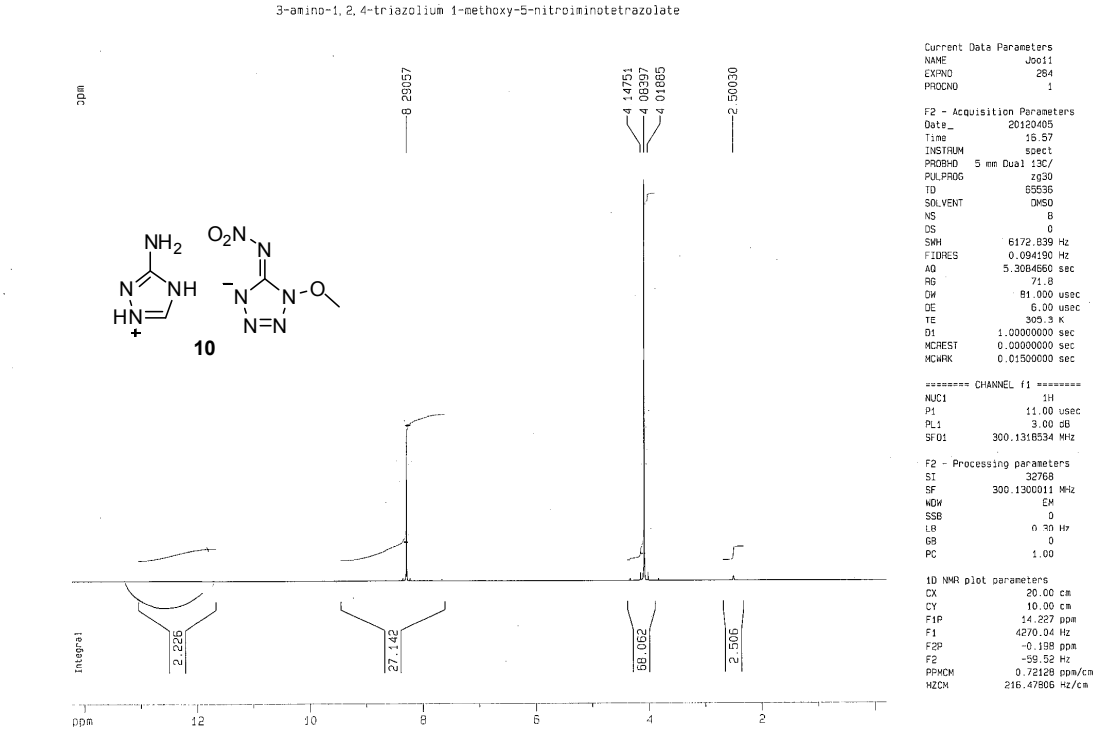

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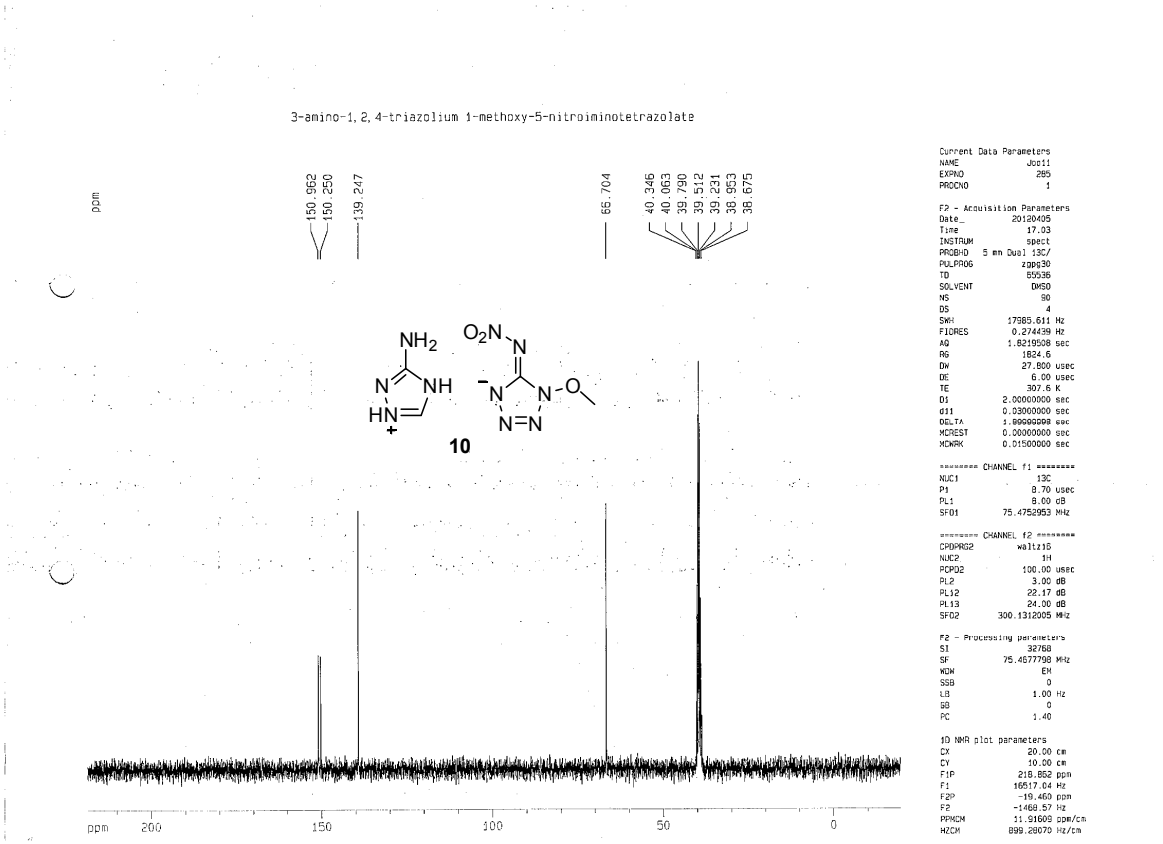

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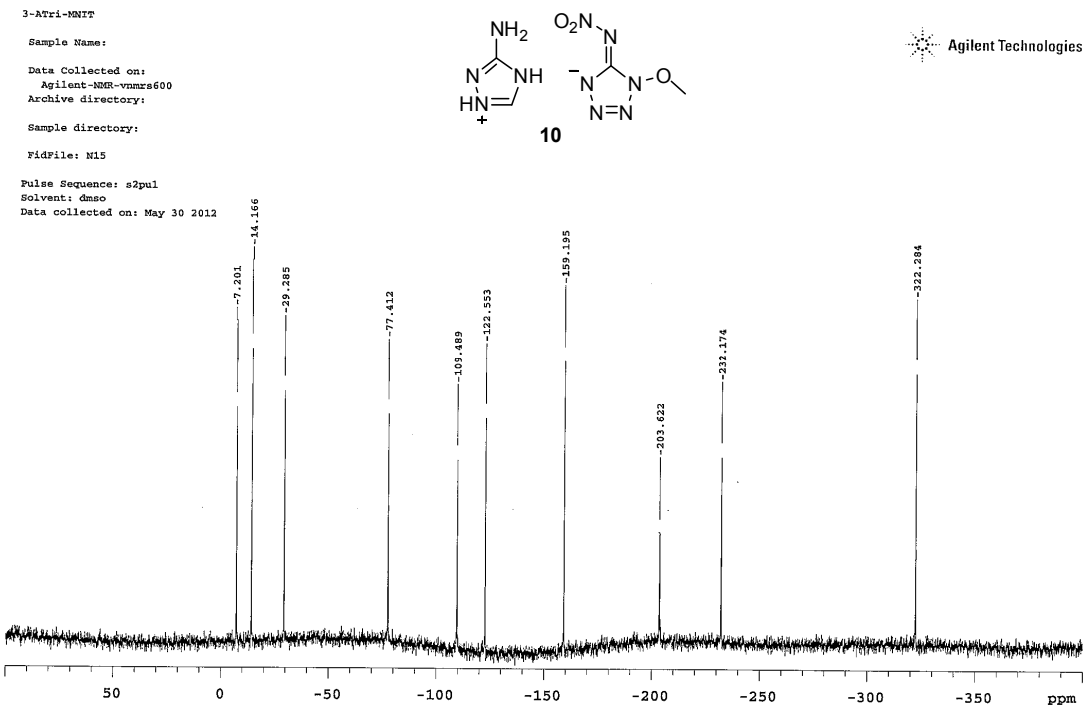

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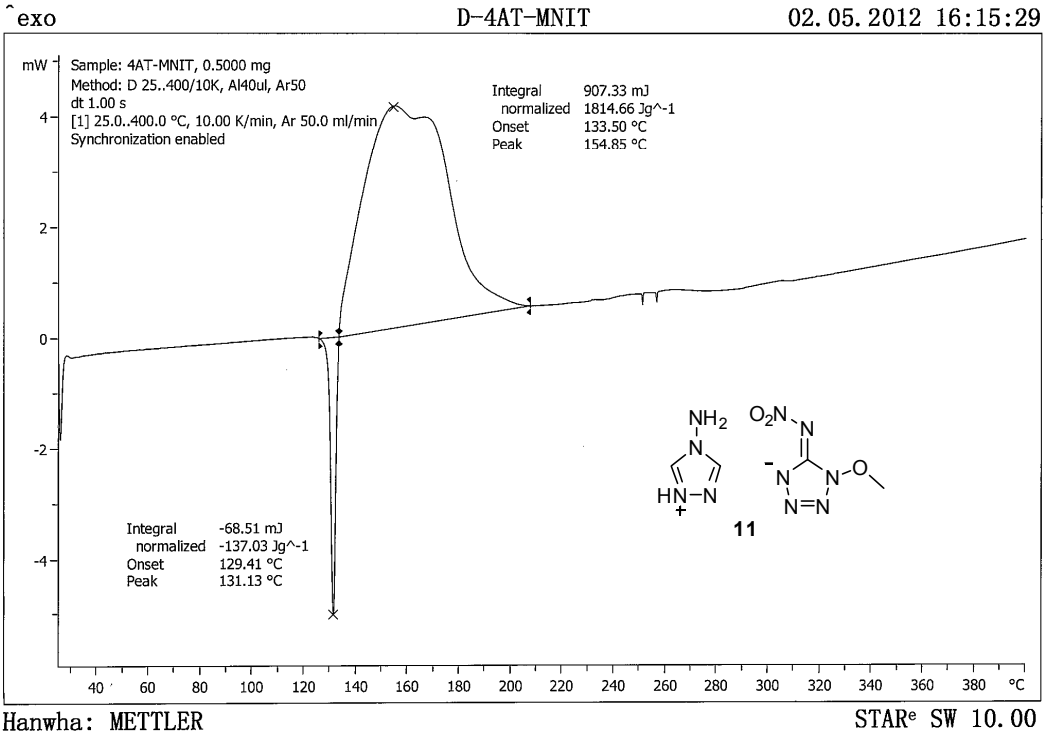

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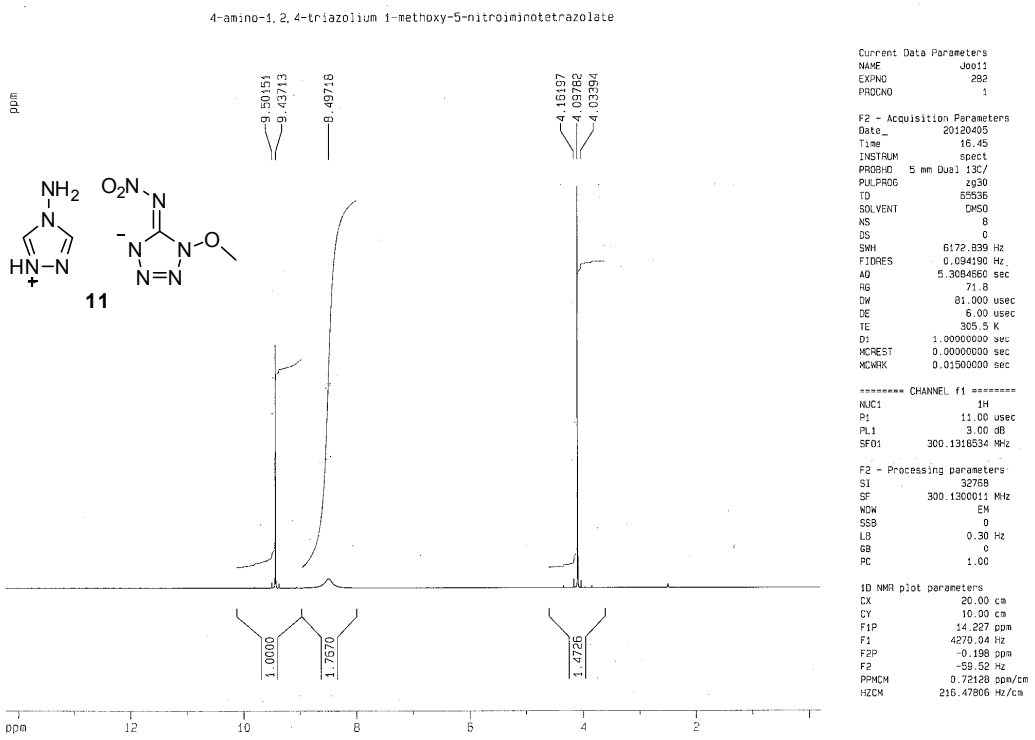

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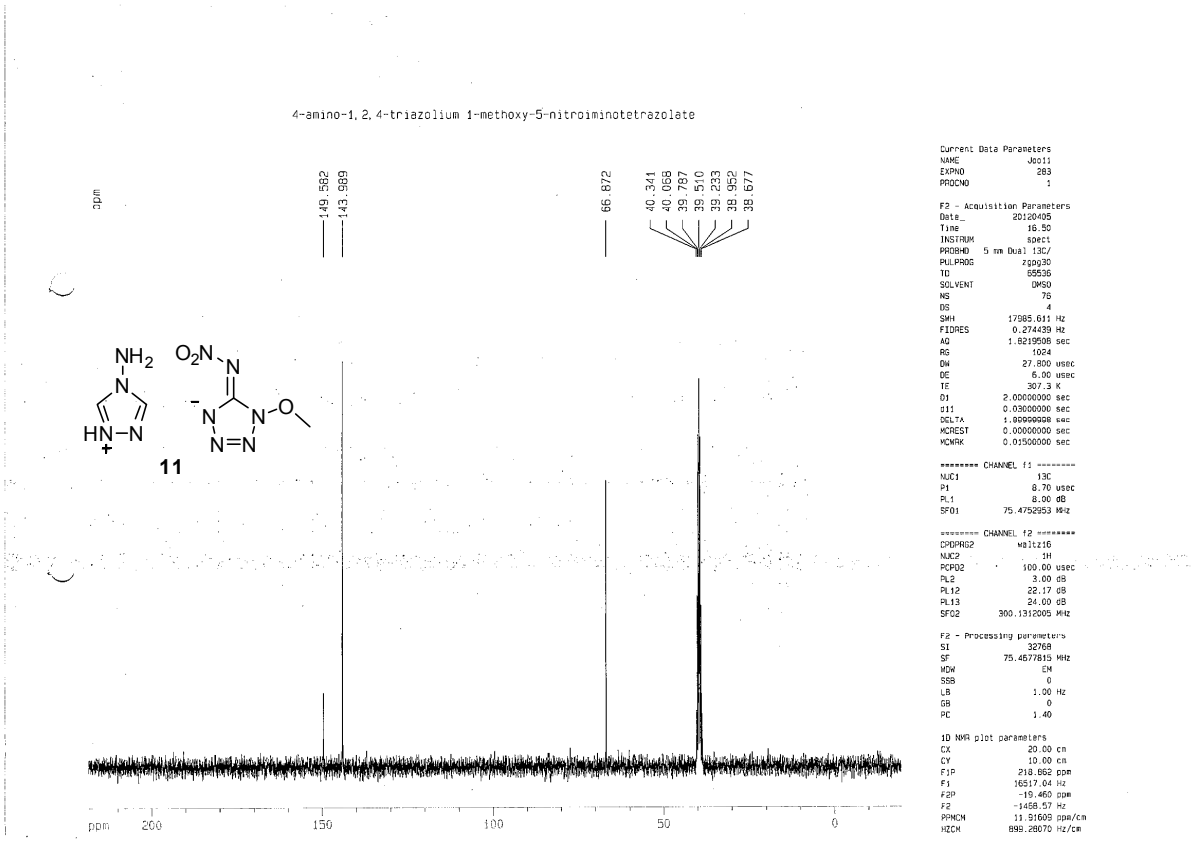

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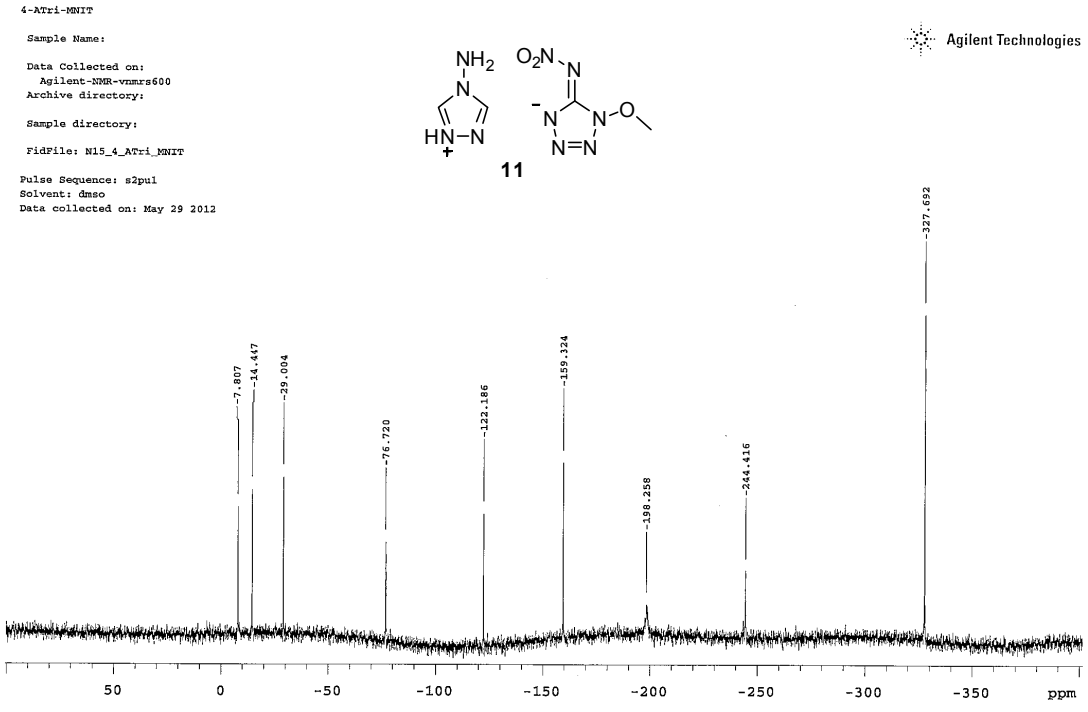

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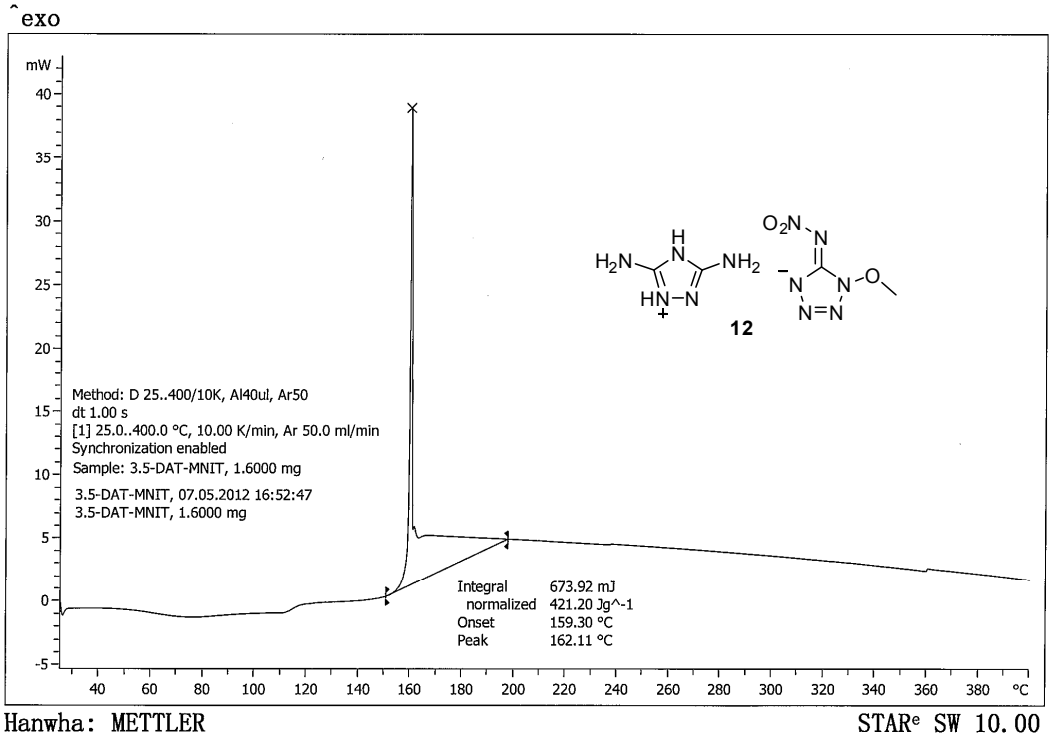

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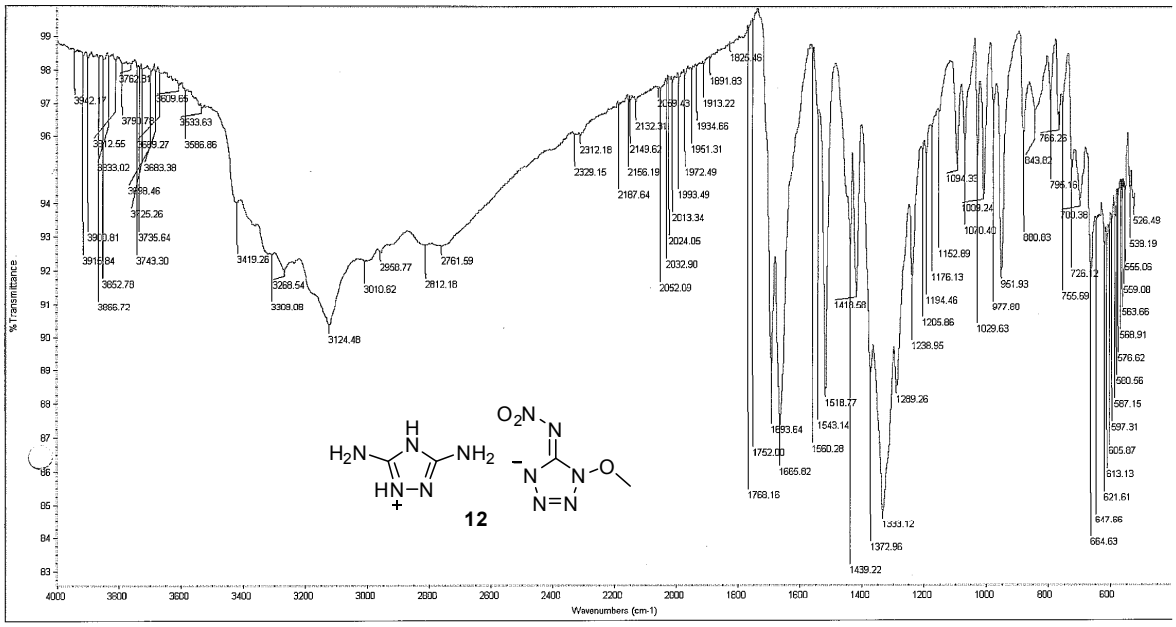
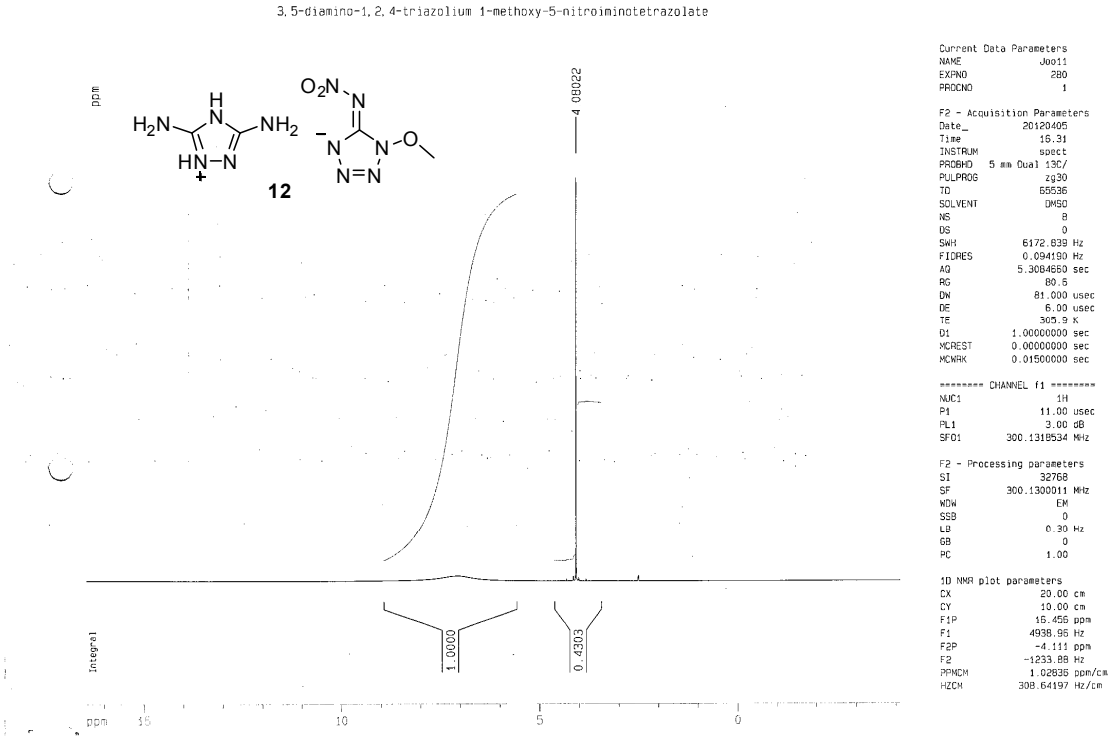


^{1}H NMR



Current Data Parameters
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EXPNO 280
PROCNO 1

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SOLVENT DMSO
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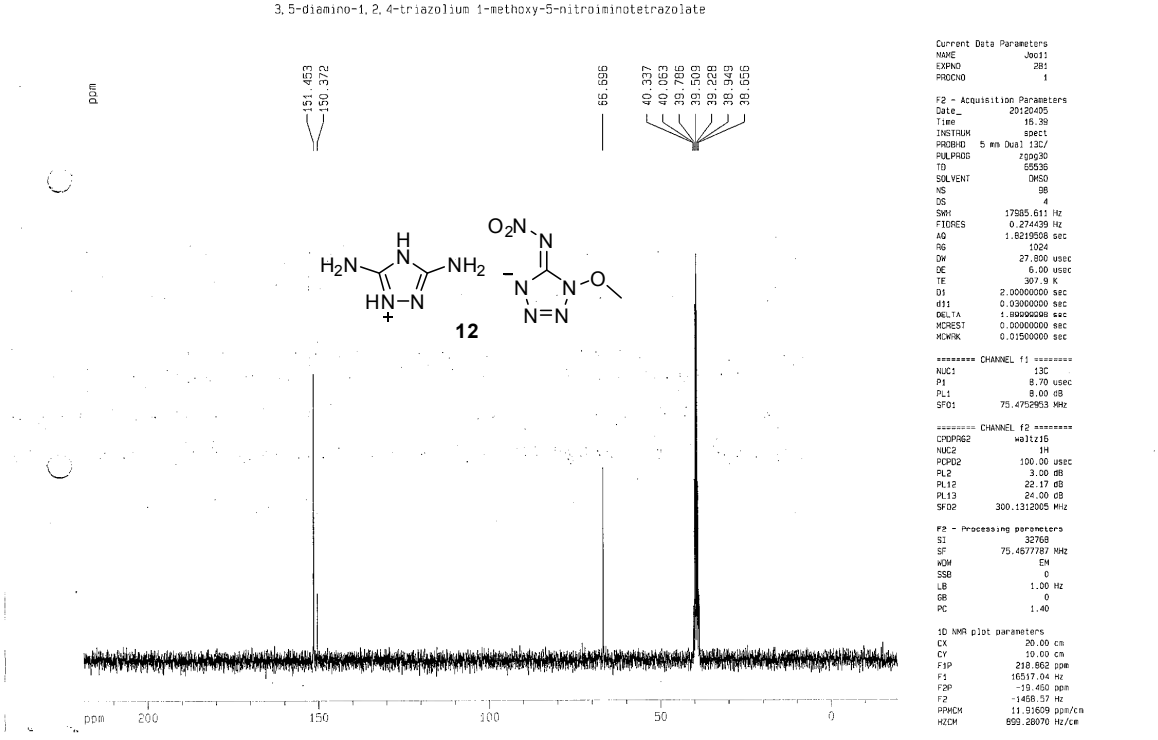
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 80.6
DW 81.000 usec
DE 6.00 usec
TE 305.9 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300011 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 16.456 ppm
F1 4938.95 Hz
F2P -4.111 ppm
F2 -1233.88 Hz
PPMCM 1.02635 ppm/cm
HZCM 308.64197 Hz/cm

^{13}C NMR



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TD 65536
SOLVENT DMSO
NS 98
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1024
DW 27.800 usec
DE 6.00 usec
TE 307.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
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PL1 8.00 dB
SFO1 75.4758953 MHz

======== CHANNEL f2 ========
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NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.17 dB
PL13 24.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
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SF 75.4677787 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 218.862 ppm
F1 16517.04 Hz
F2P -19.460 ppm
F2 -1468.57 Hz
PPMCM 11.91609 ppm/cm
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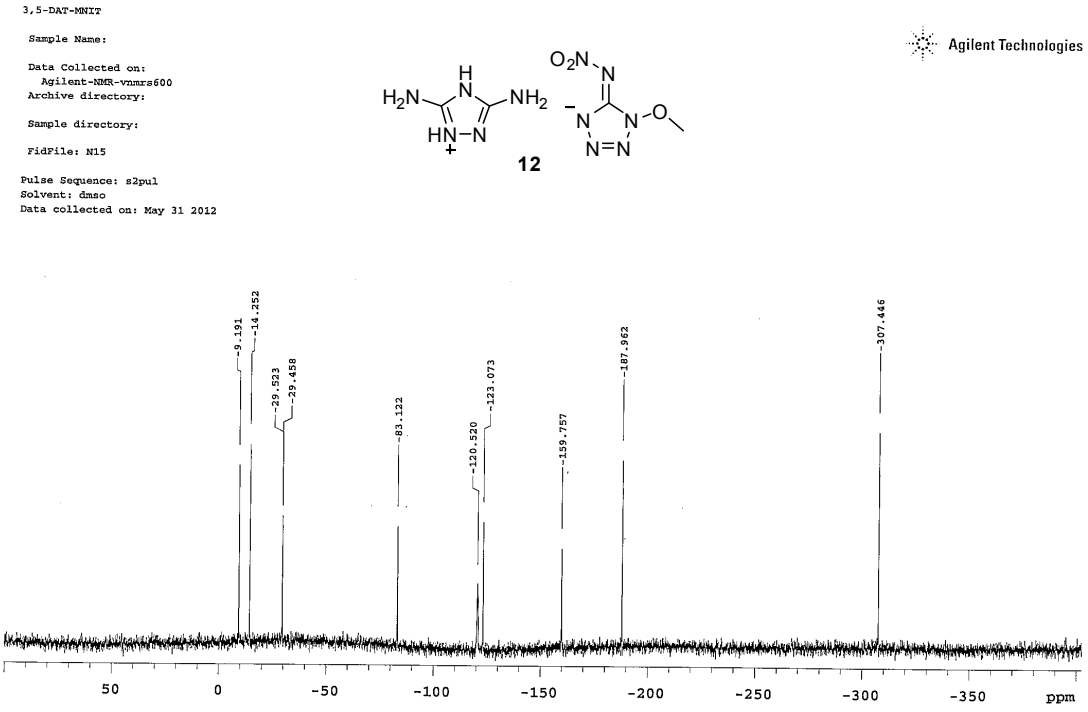
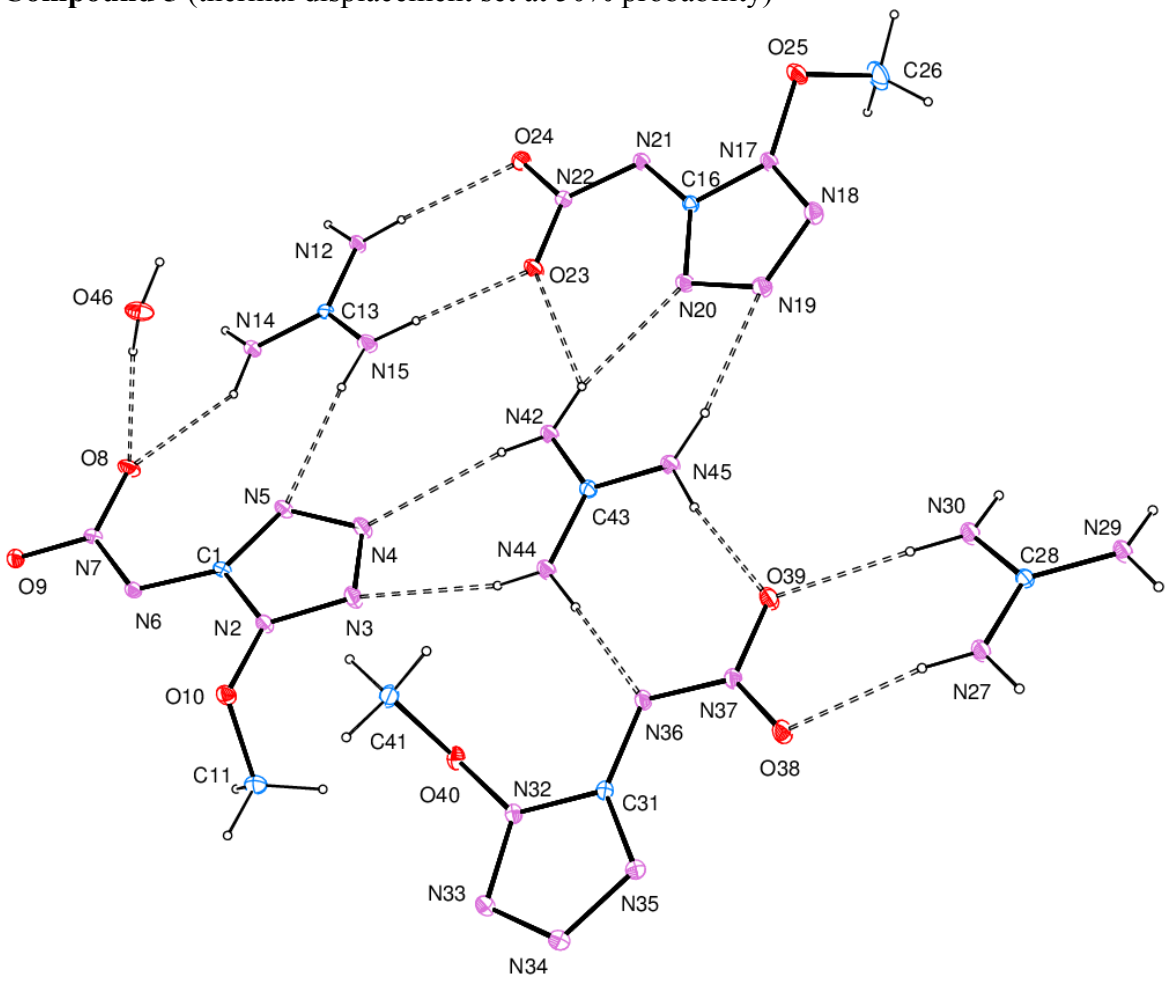
^{15}N NMR

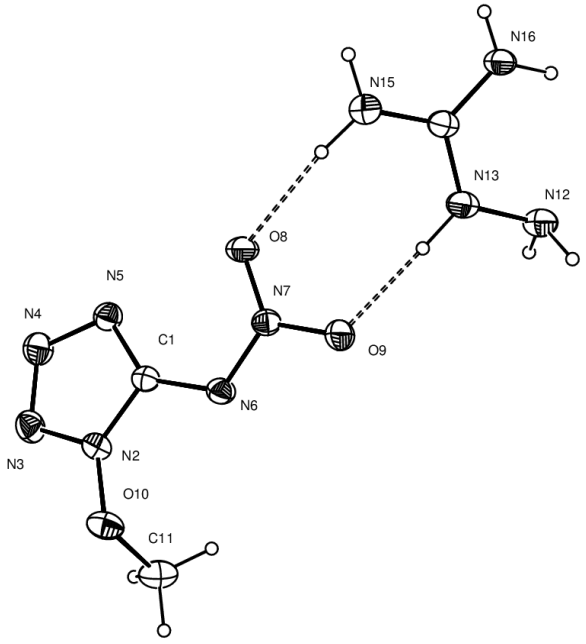


X-ray information

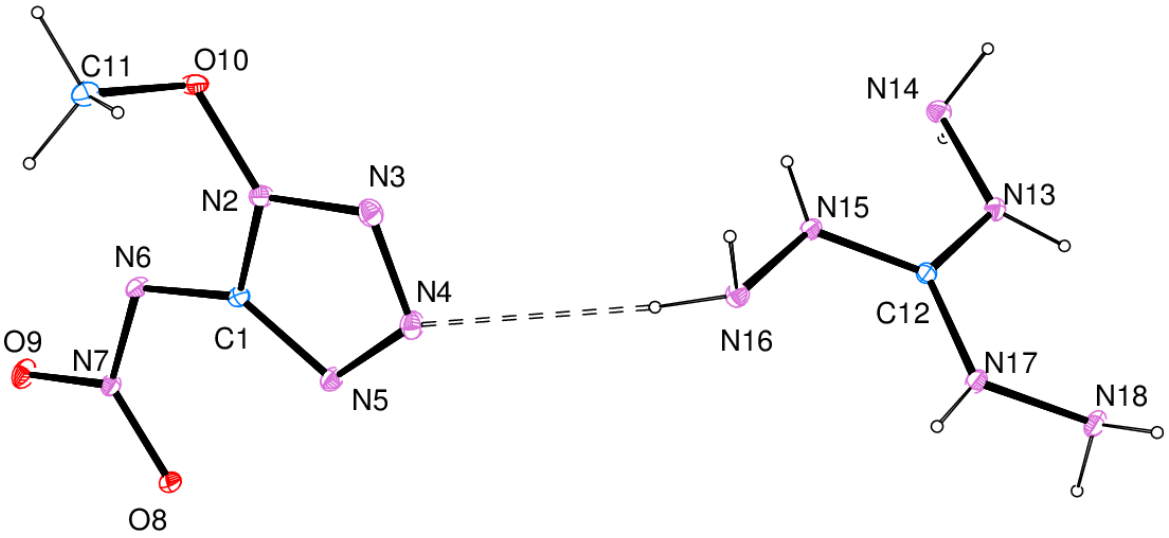
Compound 5 (thermal displacement set at 50% probability)



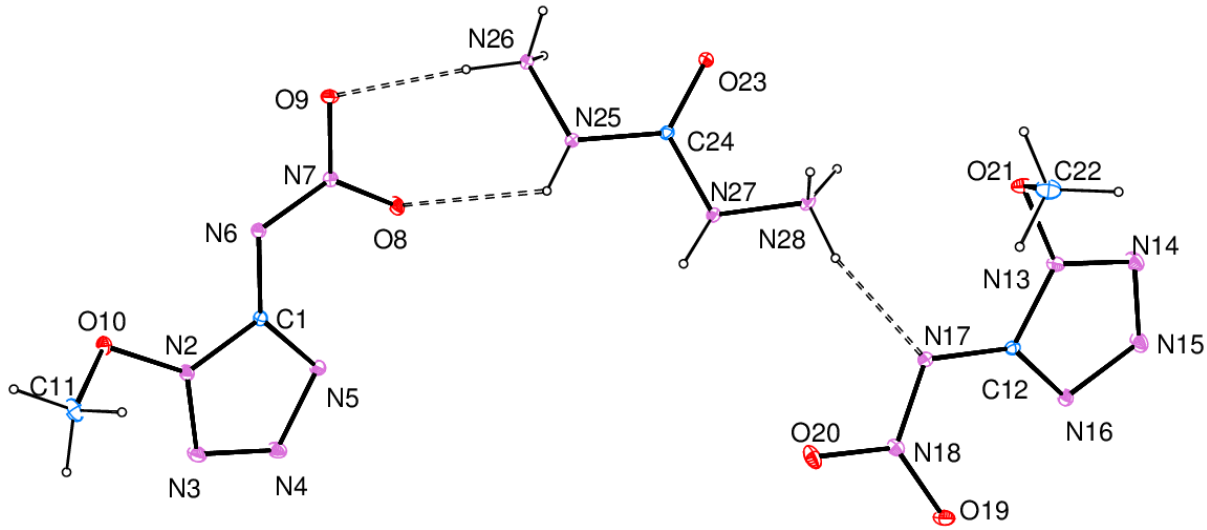
Compound 6 (thermal displacement set at 50% probability)



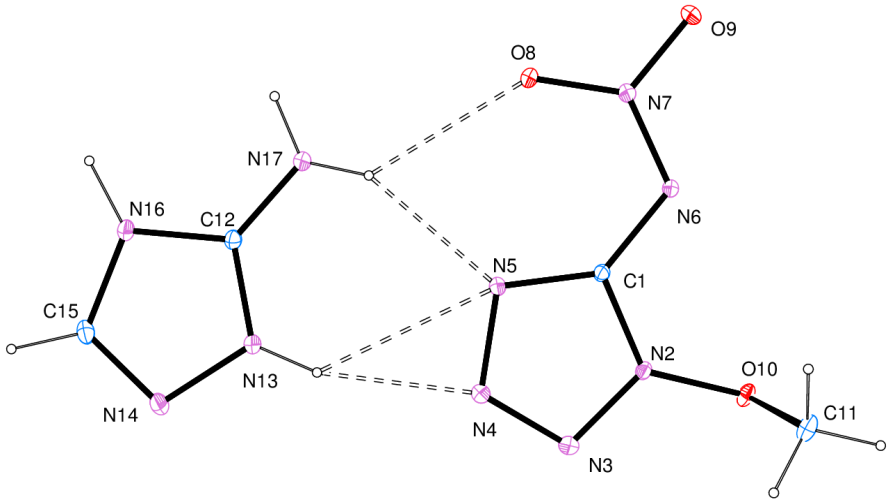
Compound (thermal displacement set at 50% probability)



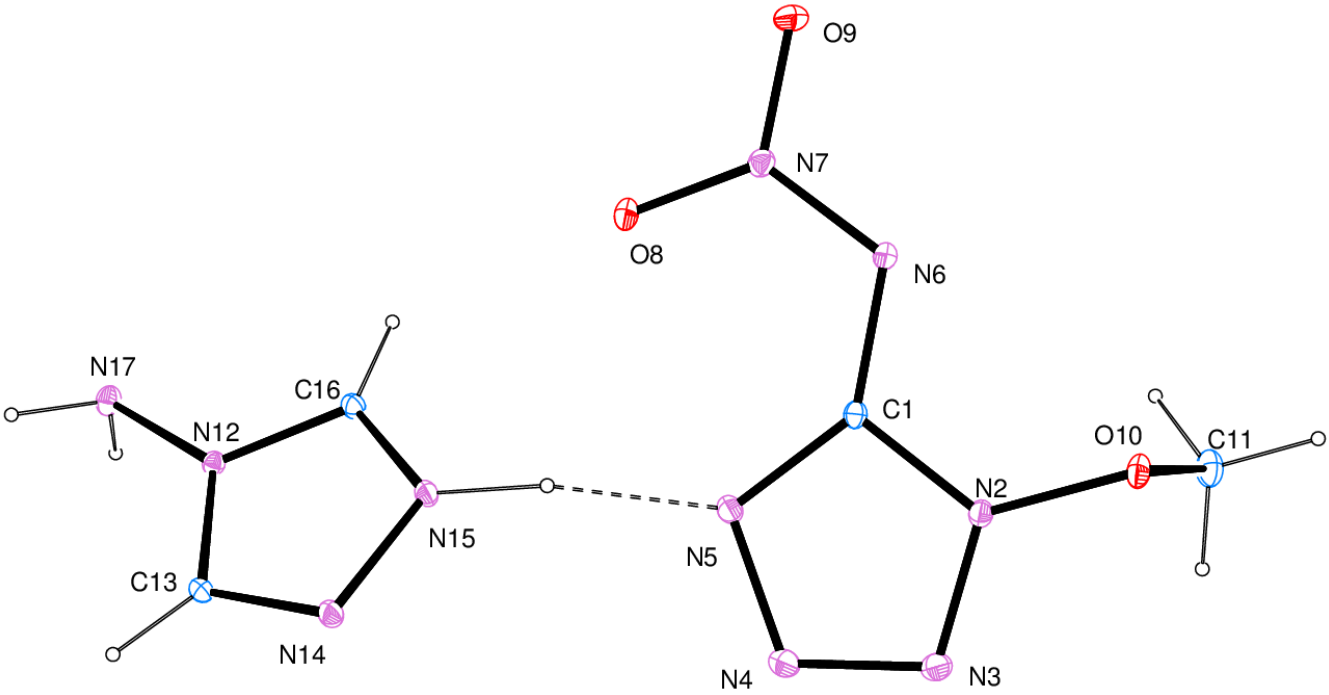
Compound 9 (thermal displacement set at 50% probability)



Compound 10 (thermal displacement set at 50% probability)



Compound 11 (thermal displacement set at 50% probability)



Computation information

Theoretical study. Calculations were carried out by using the Gaussian 03 (Revision D.01) suite of programs. The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set,[1] and single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without having imaginary frequencies.

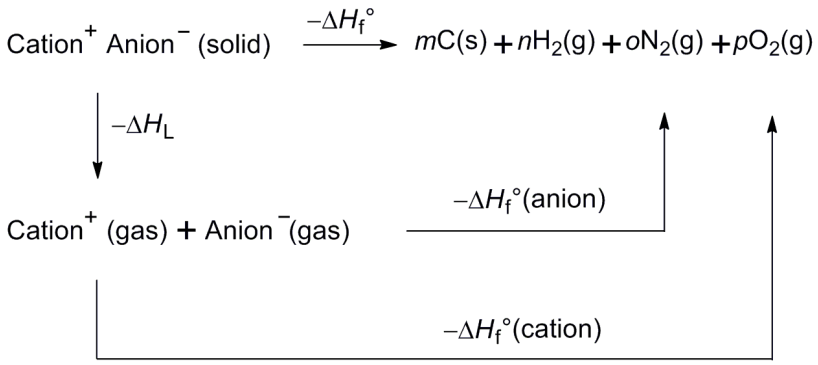


Figure S1. Born-Haber cycle for the formation of 1-methoxy-5-nitroiminotetrazole salts.

Based on Born-Haber energy cycles, heats of formation of ionic salts can be simplified by the formula [Eq. (1)]:

$\Delta H_f°$ (ionic salt, 298 K) = $\Delta H_f°$ (cation, 298 K) + $\Delta H_f°$ (anion, 298 K) – ΔH_L (1)

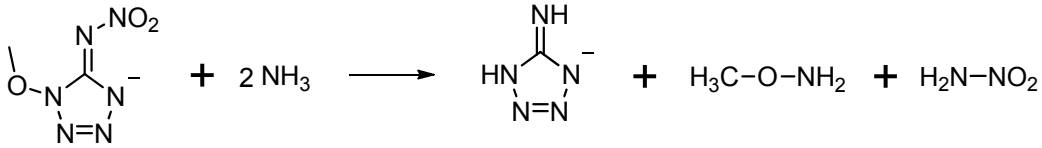
where ΔH_L is the lattice energy of the ionic salt. The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [Equation (2)],[2] where U_{POT} is the lattice potential energy and n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_L = U_{POT} + [p(n_M / 2 - 2) + q(n_X / 2 - 2)]RT \qquad (2)$$

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3),

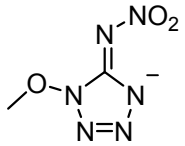
$$U_{POT}\ (\text{kJ mol}^{-1}) = \gamma\ (\rho_m/M_m)^{1/3} + \delta \qquad (3)$$

where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[15]

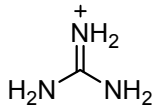


Scheme S1. Isodesmic reation of 1-methoxy-nitroiminotetrazolate anion

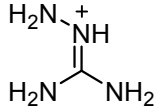
Calculated (B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E_0), Zero Point Energy (ZPE), Values of Thermal correction (H_T), and Heats of Formation (HoF) [kJ/mol] of the compounds.



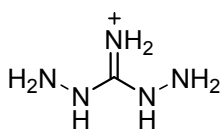
E_0	ZPE	H_T	HoF
-630.6396716	0.01035	0.01260	315.92



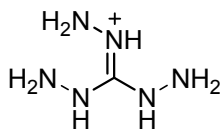
E_0	ZPE	H_T	HoF
-204.8735031	0.075945	0.005496	26.0



E_0	ZPE	H_T	HoF
-260.5457263	0.114876	0.006227	566.7



E_0	ZPE	H_T	HoF
-315.7583524	0.13361	0.007123	769.0176204



E_0	ZPE	H_T	HoF
-370.9707208	0.152308	0.008131	871.4723014

References

[1] Parr, R. G.; Yang, W. Density *Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[2] Jenkins, H. D. B.;Tudela, D.;Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364-2367.